Synthesis of the Privileged 8-Arylmenthol Class by Radical Arylation of Isopulegol

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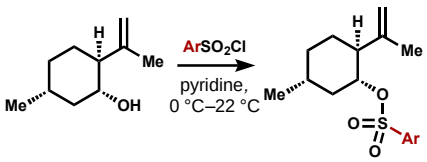
1. Materials and Methods

All reactions were carried out under positive pressure of argon unless otherwise noted. Phenylsilane was purchased from Oakwood Chemicals or Acros and used without further purification. Pentane, hexanes, dichloromethane (DCM), toluene, ethyl acetate (EtOAc), and diethyl ether were purchased from Fisher Chemicals and used without further purification. Benzene, dimethylsulfoxide (DMSO), methanol (MeOH), *N*-dimethylformamide (DMF), dichloroethane (DCE), α, α, α –trifluorotoluene and triethylamine were purchased from Sigma Aldrich, EMD Chemicals, Fisher Chemicals or Acros Organics and used without further purification. All anhydrous solvents were purchased from Fisher Chemicals, Sigma Aldrich or Acros Organics and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) with precoated silica gel plates from EMD Chemicals (TLC Silica gel 60 F254, 250 μm thickness) using UV light as the visualizing agent and an acidic mixture of anisaldehyde, phosphomolybdic acid (PMA), chromic acid, iodine vapor, Seebach's stain, or basic aqueous potassium permanganate ($KMnO_4$), and heat as developing agents. Preparatory thin layer chromatography (PTLC) was performed using the aforementioned silica gel plates. Flash column chromatography was performed over silica gel 60 (particle size 0.035- 0.07 mm) from Acros Organics. NMR spectra were recorded on Bruker DRX-600 (equipped with a 5mm DCH Cryoprobe), AV-600, DRX-500 or DPX-400 and calibrated using residual non-deuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; C_6D_6 @ 7.16 ^{1}H NMR, 128.06 ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sep = septet m = multiplet, br = broad. LC/MS analysis was performed on an Agilent 1200 series HPLC/MS equipped with an Agilent SB-C18 2.1 mm x 50 mm column, with mass spectra recorded on a 6120 Quadrupole mass spectrometer (API-ES), using ACN and H_2O as the mobile phase (0.1% formic acid). LC/MS runs used the following method unless otherwise specified: flow rate of 0.5 mL / min is used, initial equilibration of 5% ACN / H_2O with a linear gradient to 95% ACN / H_2O over 5 minutes, then a hold at 95% ACN / H_2O for an additional 3 minutes. GC/MS analysis was performed on Agilent 7820A/5975 GC/MSD system with helium as a carrier gas. Unless otherwise specified, GC/MS runs were performed with the following method: GC/MSD; HP-5MS (30m x 0.25mm ID, part # 19091S-433); 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then held for 2 min. GC/FID analysis was conducted on an Agilent 7820A GC/FID system with nitrogen as a carrier gas and with air and hydrogen as combustion gasses. Unless otherwise specified, GC/FID runs were prepared with the following method: GC/FID; HP-5MS UI (20m x 0.180mm ID, part # 190915-577UI); inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then held for 2 min. Chiral HPLC analysis was performed on Agilent 1100 series equipped with a DAD detector. Chiralcel OZ-3, 3 µm particle size, 250 mm x 6 mm column; flow rate 1 mL/min with solvent mixture of 98% hexanes and 2% isopropanol; detection wavelength 210 nm. Optical rotations of arylated menthol derivatives were measured digitally on an Autopol III polarimeter from Rudolph Research Analytic, using a flow cell with a 0.5 decimeter pathlength and the sodium lamp D-line wavelength (λ=589.3 nm).

2. General Procedures

<u>2.1 General procedure for the synthesis of aryl sulfonate esters</u>



General Procedure 2.1A - For cases where the aryl sulfonyl chloride reagent was a liquid:

A flame-dried round bottom flask was charged with a stir bar, the alcohol reagent (1.0 eq.) and anhydrous pyridine [0.8 M] under an Argon atmosphere. The solution was cooled to 0 °C in an ice bath. The aryl sulfonyl chloride (1.2 eq.) was then added slowly with stirring and the reaction was allowed to warm to ambient temperature. The reaction was stirred until completion, as monitored by TLC through the disappearance of the starting alcohol, or for 24 hours, whichever occurred first.

General Procedure 2.1B - For cases where the aryl sulfonyl chloride reagent was a solid:

The above procedure was used, but the sulfonyl chloride was added in one portion. Following this addition, the reaction was placed under positive pressure of argon for 5-10 minutes with a balloon of argon gas to flush most of the air out.

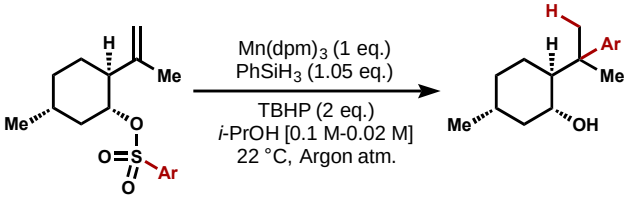
In cases of sluggish reactions (i.e. with highly electron-rich or sterically encumbered aryl moieties), 4-dimethylaminopyridine (DMAP) may optionally be added in catalytic quantities (~10-20 mol%) to accelerate reaction. In these cases, washing of the crude reaction mixture with portions of HCl followed by half-saturated sodium bicarbonate may be effective in removing residual DMAP and/or sulfonate byproducts.

Work-up: In cases where the aryl group was a carboaromatic group, addition of a small amount of cold water (0 – 4 °C) usually resulted in the precipitation of the desired product as a white or pink/white crystalline solid. In these cases, the precipitate was filtered off and rinsed with excess cold water and dried in a vial under high vacuum (<1 torr) to remove water. The desired products were used without further purification in the title HAT hydroarylation reaction.

In cases where the aryl group was a heteroaromatic group, a precipitate typically does not form upon addition of cold water; so two different work-up procedures were followed. In the first case, the reaction was concentrated directly (without addition of water) *in vacuo* and loaded onto a silica column for purification by flash column chromatography with an appropriate eluent system (typically mixtures of Et_2O/hexanes, EtOAc/hexanes, or toluene). Alternatively, the reaction may be quenched by the addition of cold water, extracted with methylene chloride or Et_2O (3x), washed with brine and dried over $MgSO_4$. The drying agent was then filtered off and the organic solvent was removed *in vacuo* to obtain a residue suitable for purification by flash column chromatography in an appropriate solvent system.

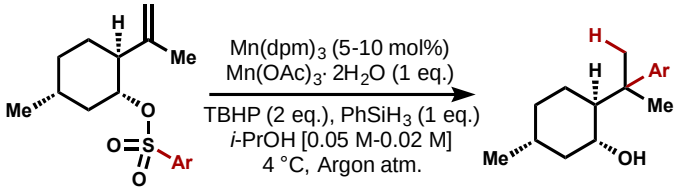
2.2 General procedure for the intramolecular hydroarylation

General Procedure 2.2A - Small Scale (Generally used for < 50 mg. of substrate. Pros: involves fewer reagents, is simpler to set up, and is completed more quickly. Cons: The reaction uses 1 eq. of $Mn(dpm)_3$.)



A flame-dried round bottom flask (of ~2x the volume of solvent to be used for the reaction) was charged with a stir bar, substrate (1.0 eq.) and $Mn(dpm)_3$ (1.0 eq.). The reaction vessel was evacuated on a vacuum gas manifold and refilled with nitrogen gas successively three times. The flask was removed from the manifold and swiftly placed under positive pressure of argon. (Argon was allowed to flow over the surface of the reaction using a 22 gauge needles for the inlet and outlet needles). Degassed *i*-PrOH (0.1M – 0.02 M; *0.025 M is recommended* for difficult substrates, but 0.1 M is usually fine for most substrates) was then added via a syringe. The reaction was stirred and TBHP (2.0 eq. as a solution in n-decane or hexanes) was added (TBHP addition is optional – TBHP accelerates the reaction). Finally, $PhSiH_3$ (1.05 eq.) was added in one portion to the reaction. The outlet needle for the Argon was removed after $PhSiH_3$ addition. The reaction was monitored by TLC and stirred at ambient temperature. After the starting material was consumed, after the reaction turned pale yellow,[1] *or* after 24hrs, the reaction was worked-up. *Work-up*: The reaction was concentrated directly *in vacuo* and purified by FCC on silica gel using an appropriate solvent system. (Typically mixtures of Et_2O/hex, EtOAc/hex, or pure toluene.) Alternatively, the reaction may be quenched with water, extracted with an appropriate solvent (CH_2Cl_2, Et_2O, EtOAc and hexanes are all fine); the organics washed with $NaHCO_3$ (a saturated aqueous solution), brine (saturated aqueous solution), dried over Na_2SO_4 or $MgSO_4$, filtered, concentrated *in vacuo* and purified by FCC over silica gel with an appropriate solvent system.

General Procedure 2.2B - Large Scale (Generally used for > 50 mg. of substrate. Pros: The reaction is cleaner and uses a cheaper Mn(III) source. Cons: The reaction may be slow, taking ~1 week to complete at 5 mol% $Mn(dpm)_3$ loading. The reaction is faster at higher $Mn(dpm)_3$ loading.)



A flame-dried round bottom flask was charged with a stir bar, substrate (1.0 eq.), $Mn(OAc)_3$•$2H_2O$ (1.0 eq.) and $Mn(dpm)_3$ (5-10 mol%). The reaction vessel was evacuated SLOWLY [to minimize $Mn(OAc)_3$•$2H_2O$ powder from being pulled up into the manifold] and refilled with nitrogen gas successively three times. The reaction was removed from the manifold and swiftly placed under positive pressure of argon. Degassed *i*-PrOH (0.025 M) was then added via a syringe or cannula. Next, TBHP (2.0 eq., as a solution in hexanes or *n*-decane) was added. The reaction was cooled to 4 °C in a cold room while stirring. After ~20 minutes, $PhSiH_3$ (1.0 eq.) was added slowly. The reaction was stirred until complete. *Work-up*: The reaction was concentrated *in vacuo* to remove *i*-PrOH. The remaining oily solid was suspended in hexanes and filtered over a medium glass frit to remove most of the [Mn] salts. The filtrate was then concentrated *in vacuo* and purified by FCC on silica using an appropriate solvent system.

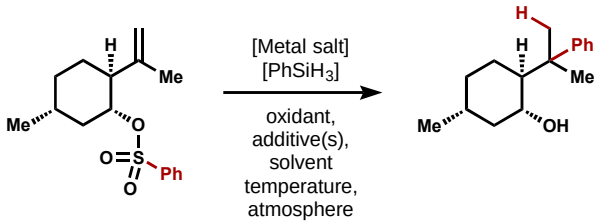
Note: *i*-PrOH was degassed by bubbling argon gas through the solution for >30 minutes while sonicating, longer for larger volumes of solvent. Non-anhydrous *i*-PrOH was used in most cases. No noticeable differences were observed between use of anhydrous and non-anhydrous *i*-PrOH. TBHP solutions were prepared according to by extraction of a commercial 70% aq. w/w solution with hexanes according to this procedure and

[1] The color of the reaction is initially black and gradually becomes clearer as Mn^{3+} (black) is reduced to Mn^{2+} (yellow). Complete disappearance of the black color indicates complete consumption of Mn^{3+}.

stored at -30 °C over 4Å molecular sieves.[2] $Mn(dpm)_3$ was prepared from $MnSO_4$ following a previously reported procedure.[3]

2.3 Comments regarding the title HAT Hydroarylation method

The title reaction was optimized around the conversion of sulfonate **3** to (–)-**1**, shown here:

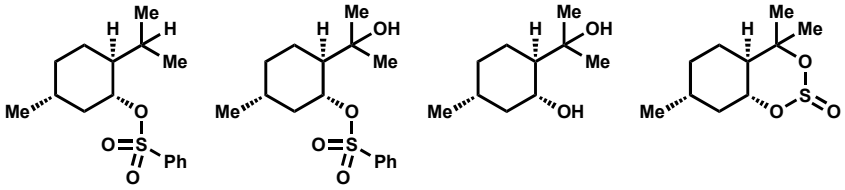


3 **(–)-1**

Analysis of variations in reaction conditions was conducted using thin layer chromatography (primarily) and NMR (secondarily). The reaction conditions were modified in order to maximize consumption of starting material (**3**) and formation of the desired product **(–)-1**, and to minimize side products. TLC analysis provided qualitative information that guided our optimization efforts. *The following comments are intended to provide further insight into this reaction based on conclusions drawn from TLC data*.

Regarding reaction byproducts:

In addition to the desired compound (**–)-1**, a number of other side products were identified. These include:

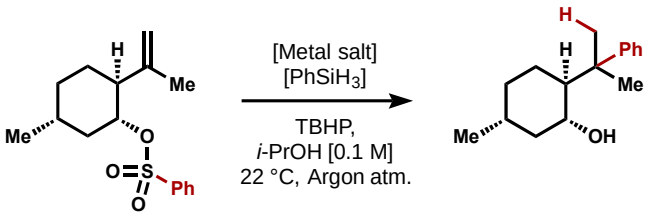


X1 **X2** **X3** **X4**

The reduced compound **X1** was generally the major byproduct in this reaction. Hydrate **X2** and diol **X3** appeared if oxygen (O_2) was permitted to enter the reaction vessel, and sulfite ester **X4** was observed in certain cases when $Mn(OAc)_3 \bullet 2H_2O$ was present. The appearance of **X2** and **X3** when oxygen was present led us to exclude oxygen from the system, and so the reactions were conducted under an Argon atmosphere.

Regarding selection of the metal complex:

[2] Iwasaki, K.; Wan, K.; Oppedisano, A.; Crossley, S.W.M.; Shenvi, R.A. *J. Am. Chem. Soc.*, **2014**, *136* (4), pp 1300–1303. See SI-pg. 4.
[3] Ibid. See SI-pg. 2-3.



3 **(–)-1**

Exploration of metal complexes for the title reaction focused on Mn, Fe, and Co complexes bearing 1,3-diketonate ligands, which to generate carbon-centered radicals in the presence of *i*-PrOH and $PhSiH_3$.[4] In particular, we considered $Mn(acac)_3$, $Mn(dibm)_3$, $Mn(dpm)_3$, $Fe(acac)_3$, $Fe(dibm)_3$, $Fe(dpm)_3$, $Co(acac)_3$, $Co(acac)_2$ and $Co(dpm)_3$ (acac = acetylacetonato; dibm = diisobutyrylmethanato; dpm = dipivaloylmethanato). Mn^{3+} and Fe^{3+} complexes were all able to effect the desired transformation but Co^{3+} complexes were completely inactive under the reaction conditions and only starting material **3** was observed. $Co(acac)_2$ could only effect the desired transformation when oxygen was present, which also led to significant formation of Mukaiyama hydration side products **X1** and **X2**. The behavior of Mn^{3+} salts and Fe^{3+} salts for the conversion of **3** to **(–)-1** was qualitatively similar, but Mn^{3+} complexes effected the transformation more quickly at room temperature, gave better yields, and were much easier to remove from reactions since they could be removed by filtration over a silica pad, while Fe salts required a work-up involving an aqueous solution of KHF_2. Between ligands, dibm and dpm behaved similarly and were superior to acac. Specifically, 2 eq. of $Mn(acac)_3$ were required to consume starting material **3** while only 1 eq. of $Mn(dibm)_3$ and $Mn(dpm)_3$ were required. $Mn(dpm)_3$ was preferred over $Mn(dibm)_3$ because the Hdpm ligand is commercially available, as is $Mn(dpm)_3$ itself.

Regarding reaction concentration:

Effect of concentration

entry	$Mn(dpm)_3$	$Mn(OAc)_3$	$PhSiH_3$	TBHP	Temp.	**[*i*-PrOH]**	**3**		**X1**		**(–)-1**
1	0.05 equiv.	1 equiv.	1.05 equiv.	2 equiv.	4 °C	**0.02 M**	0	:	1	:	20
2	0.05 equiv.	1 equiv.	1.05 equiv.	2 equiv.	4 °C	**0.025 M**	0	:	1	:	15
3	0.05 equiv.	1 equiv.	1.05 equiv.	2 equiv.	4 °C	**0.05 M**	0	:	1	:	7
4	0.05 equiv.	1 equiv.	1.05 equiv.	2 equiv.	4 °C	**0.1 M**	0	:	1	:	3

Entries are based on NMR spectra of crude reaction mixtures.

Higher dilution results in a cleaner reaction (less hydrogenation side product in particular) but also in longer reaction times. At concentrations less than [0.02 M], the reaction stalls. At concentrations above [0.1 M], hydrogenation dominates and conversion is lower because hydrogenation consumes twice as much $PhSiH_3$ and $Mn(dpm)_3$. Longer reaction times are significant only when stoichiometric $Mn(OAc)_3 \bullet 2H_2O$ (alongside catalytic $Mn(dpm)_3$) is used. Higher dilution has minimal effects on lengthening reaction times when stoichiometric $Mn(dpm)_3$ is used.

Regarding temperature:

[4] See citations by Mukaiyama, Boger, Baran, Shenvi, Herzon and Norton in main paper.

At 4 °C, the reactions are slower than at 22 °C but appear moderately cleaner by TLC analysis and results in better consumption of starting material. Conversion is better at 4 °C than at 22 °C when $Mn(OAc)_3 \bullet 2H_2O$ is used. Consumption of the sulfonyl ester starting material **3** is markedly worse at elevated temperatures.

Regarding $PhSiH_3$ loading:

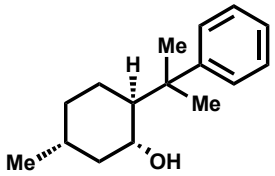
Based on TLC analysis, increasing $PhSiH_3$ loading increased the formation of hydrogenated byproducts **X2** and **X3**. At a loading of less than 1 eq. however, substrate was not fully consumed.

Regarding TBHP loading:

Two equivalents of TBHP seemed to have the optimal effect on rate acceleration based on TLC analysis. Although beneficial, TBHP is not necessary for the reaction to work.

3. Experimental Procedures and Characterization Data

3.01 **(–)-1**: **(–)**-8-phenylmenthol



Large scale: Compound **(–)-1** was obtained following procedure 2.2B of the intramolecular HAT hydroarylation method. Specifically, 15 g. of compound **3** (1.0 eq., 50.9 mmol), $Mn(dpm)_3$ (0.05 eq., 1.54 g.), $Mn(OAc)_3 \bullet 2H_2O$ (1.0 eq., 13.7 g.), $PhSiH_3$ (1.05 eq., 6.59 mL); TBHP (2.0 eq., 10.2 mL of a 10.0 M solution in hexanes), and *i*-PrOH ([0.025 M], 2.036 L) were used. However, the reaction still showed indication of starting material after one week and so was allowed to stir for one more week, but no noticeable change was observed by TLC during that time period. Consequently, the reaction was worked-up as per the standard procedure and the resultant ~21 g. of crude material purified in three batches over silica gel using a solvent gradient of 10% Et_2O/hex to 15% Et_2O/hex to obtain 9.2 g. (39.6 mmol, 78% yield) of 8-phenyl menthol **(–)-1** as a viscous clear pale yellow oil. Approximately 500 mg. of starting material was recovered.

Characterization data of 8-phenylmenthol **(–)-1:**

R_f 0.45 (25% Et_2O in hexanes, stains purple in anisaldehyde)

Opt. Rot. -24.8° (c = 2.04 in EtOH, 22 °C)

^{1}H NMR (600 MHz, $CDCl_3$)
δ 7.43 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.21 – 7.17 (m, 1H), 3.54 (ddd, *J* = 10.8, 9.5, 4.3 Hz, 1H), 1.85 (dtd, *J* = 12.4, 4.0, 2.4 Hz, 1H), 1.77 – 1.68 (m, 2H), 1.68 – 1.60 (m, 1H), 1.43 (s, 3H), 1.43 – 1.35 (m, 1H), 1.30 (s, 3H), 1.11 – 0.91 (m, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.91 – 0.82 (m, 1H)

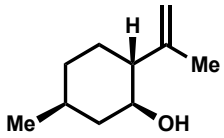
^{13}C NMR (151 MHz, $CDCl_3$)
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 128.6, 125.9, 125.9, 73.1, 54.3, 45.5, 39.9, 35.0, 31.6, 28.9, 26.6, 24.4, 22.1

GC-MS (EI) Retention time: 8.42 min.

m/z	% Max

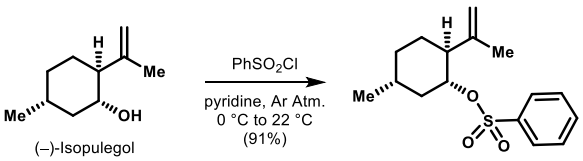
232.1	0.10
143.1	5.52
132.1	4.65
131.1	4.83
129.0	4.70
120.1	15.6
119.1	100
118.1	24.6
117.1	6.71
115.0	5.19
105.1	12.3
95.1	4.57
91.1	31.8
79.1	5.46
77.0	6.03

3.02 **(+)-2:** (+)-isopulegol



(+)-Isopulegol was prepared following a modification[5] of a reported procedure[6] in decagram scale with a 68% yield. Silica gel chromatography was employed with 18% Et_2O/hexanes as the solvent system. Characterization data corresponds to that previously reported.

3.03 **3**: sulfonate precursor to **(–)**-8-Phenylmenthol



A magnetically stirred 250 mL round-bottom flask was charged with anhydrous pyridine ([0.8M], 81 mL) and (–)-isopulegol (64.8 mmol, 11 mL, 1.0 eq.) at 0 °C under an atmosphere of argon gas. To this solution was added benzenesulfonyl chloride (77.8 mmol, 10 mL, 1.2 eq.) in a slow but steady stream at 0 °C. The ice bath was then removed to allow the reaction to warm to ambient temperature. The reaction was stirred for 18 hours, at which point TLC indicated high conversion to the desired product. Cold water (150 mL) was added to the reaction and stirred at 0 °C for 1 hour. A pink/white solid (the desired product) precipitated from this solution. This precipitate was filtered off over a ground glass frit and rinsed several times with cold water. After air-drying, the desired product was dried under high vacuum for >24 hrs. to remove excess water and pyridine.

[5] J. Peng; H. Zhanao; C. Zhaogang; C. Wenchang; Z. Jinbao; Z. Changzheng (Faming Zhuanli Shenqing Gongkai Shuomingshu), CN101602651, **2009**.
[6] Y. Nakatani, K. Kawashima, *Synthesis* **1978**, *1978*, 147-148.

The pink color gradually faded over time. The title compound was obtained in 91% yield (17.3 g.) without need for further purification.

Characterization data of sulfonate ester **3:**

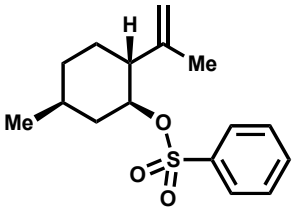
R_f 0.51 (25% Et_2O in hexanes, stains blue in anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.90 – 7.83 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.45 (m, 2H), 4.66 (dt, *J* = 1.7, 0.8 Hz, 1H), 4.59 (p, *J* = 1.6 Hz, 1H), 4.47 (td, *J* = 10.8, 4.5 Hz, 1H), 2.24 (dddd, *J* = 12.4, 4.9, 3.3, 1.8 Hz, 1H), 2.13 (ddd, *J* = 12.6, 10.6, 3.8 Hz, 1H), 1.72 – 1.58 (m, 2H), 1.51 (m, 1H), 1.41 (s, 3H), 1.39 – 1.18 (m, 2H), 0.92 (t, *J* = 6.5 Hz, 3H), 0.98 – 0.84 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$)
δ 145.0, 137.8, 133.4, 128.9, 128.0, 113.1, 83.6, 50.9, 41.9, 33.8, 31.7, 30.5, 22.0, 19.4

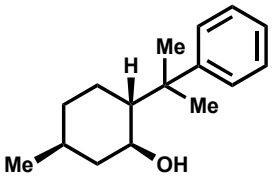
ESI-LCMS *m/z* = 317.2 $(M + Na)^+$

3.04 *ent*-**3:** sulfonate precursor to **(+)**-8-phenylmenthol



A magnetically stirred 50 mL round-bottom flask was charged with (+)-isopulegol (9.59 mmol, 1.48g, 1.0 eq.) and anhydrous pyridine ([0.8 M], 12 mL) at 0 ºC under a positive atmosphere of argon. To this solution, benzenesulfonyl chloride (12.47 mmol, 1.59 mL, 1.3 eq.) was added dropwise at 0 ºC. The ice bath was removed and the reaction was stirred for 12 hours. Water (20 mL) was added to the reaction to precipitate the desired product from solution, which was filtrated with a Büchner funnel and rinsed with water. After air-drying for one hour, the pink/white solid was dried under high vacuum overnight to remove traces of water and pyridine. The pink color gradually faded over time. The title compound was obtained in 88% yield (2.48 g) without need for further purification. Characterization data matches that of **3**.

3.05 **(+)-1: (+)**-8-phenylmenthol



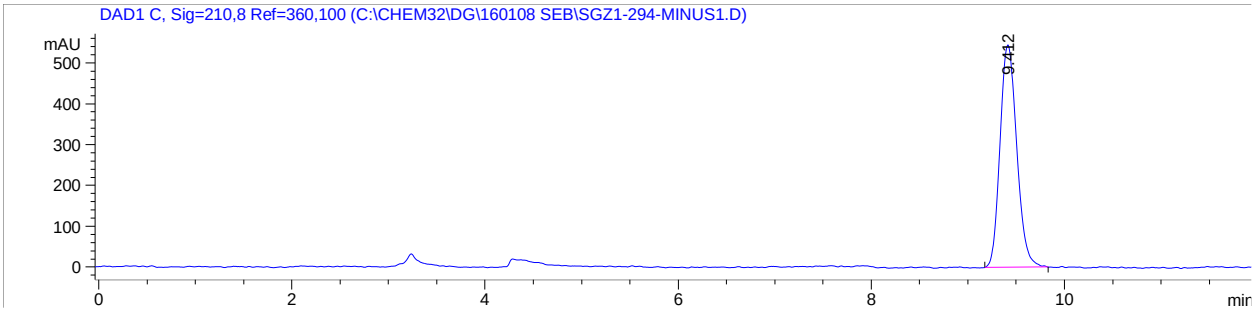
Following General Procedure 2.2B, sulfonate ester *ent*-**3** (2.45g, 8.39 mmol, 1.0 eq.), $Mn(OAc)_3$ (2.25g, 8.39 mmol, 1 eq.) and $Mn(dpm)_3$ (381 mg, 0.629 mmol, 7.5 mol%) were added to a flame-dried 1 L round-bottom flask under a positive argon atmosphere. After three high-vacuum/argon cycles, degassed isopropanol was added via cannula (336 mL, [0.025 M], degassed by bubbling argon for one hour under sonication). The flask was transferred to a cold room at 4 ºC and left to equilibrate for one hour. Cold TBHP (1.79 mL, [9.4 M] in hexanes, 2 eq.) was added to the stirring solution via the wall of the flask, followed by the slow addition of cold phenylsilane (1.09 mL, 8.84 mmol, 1.05 eq.). After 2 weeks, the reaction was removed from the cold room and concentrated *in vacuo*. The remaining material was washed and filtered with excess hexanes, to obtain a yellow/copper oil. This crude material was purified by silica gel chromatography with 13% diethyl

ether in hexanes to yield 1.32 g (68% yield) of (+)-8-phenylmenthol as a clear, pale yellow oil. Characterization data matches that of **(–)-1**.

Opt. Rot. $[\alpha]_D^{22}$ +23.5° (c = 2.0 in EtOH, 22 °C)

The optical purity for 8-phenylmenthol **(+)-1** and **(–)-1** was established by chiral HPLC analysis.

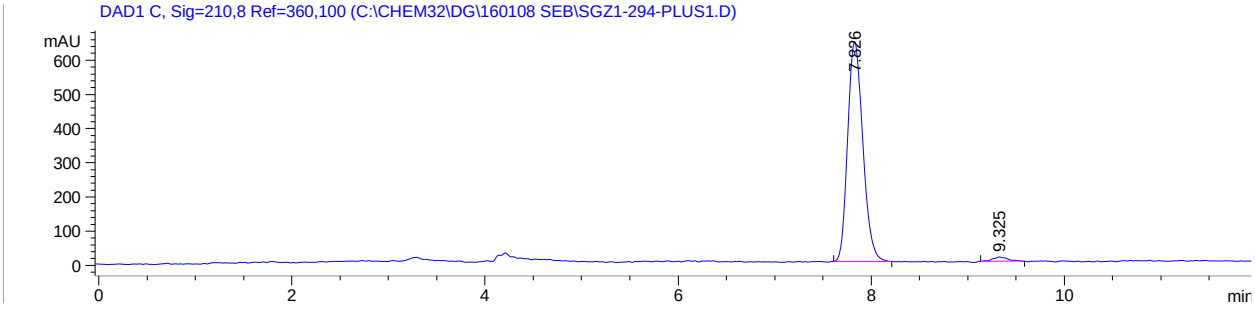
(–)-1 (–)-8-phenylmenthol – 100% *ee*



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.412	BB	0.1908	6578.77148	545.24707	100.0000
Totals :				6578.77148	545.24707	

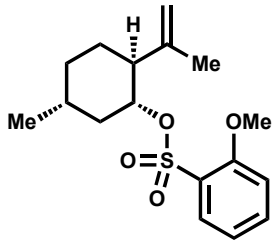
(+)-1 (+)-8-phenylmenthol – 96% *ee*.



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.826	BB	0.1718	7050.32764	643.54315	97.8921
2	9.325	BB	0.1502	151.81441	12.99945	2.1079
Totals :				7202.14204	656.54260	

3.06 **SI-01**: sulfonate precursor to **4a**



General Procedure 2.1B was followed, treating (–)-isopulegol (2.42 mmol, 0.41 mL, 1.0 eq.) with sulfonyl chloride[7] (3.15 mmol, 651 mg, 1.3 eq.) in pyridine [0.8 M]. Sulfone ester **SI-01** was obtained as a pale yellow viscous oil (675 mg, 86% yield).

Characterization data of sulfonate ester **SI-01:**

R_f 0.22 (35% EtO_2/Hex, anisaldehyde, stains dark blue)

^{1}H NMR (500 MHz, $CDCl_3$)

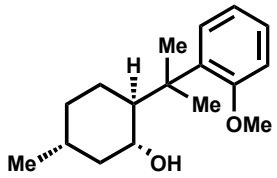
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.55 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.00 (td, *J* = 7.7, 1.0 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.61 (dt, *J* = 1.7, 0.8 Hz, 1H), 4.52 (p, *J* = 1.6 Hz, 1H), 4.47 (td, *J* = 10.8, 4.5 Hz, 1H), 3.91 (s, 3H), 2.26 (dtd, *J* = 12.4, 4.8, 4.1, 1.8 Hz, 1H), 2.15 (ddd, *J* = 12.6, 10.6, 3.8 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.54 – 1.42 (m, 1H), 1.42 (s, 3H), 1.37 – 1.21 (m, 2H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.98 – 0.84 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (126 MHz, DMSO) δ 157.8, 145.2, 135.3, 130.9, 125.6, 119.9, 112.4, 112.2, 84.0, 56.0, 50.9, 42.1, 33.8, 31.7, 30.8, 22.0, 19.4

ESI-LCMS 347.1 $[M+Na]^+$

3.07 **4a:** 8-(*o*-anisole)menthol



Compound **4a** was obtained following procedure **2.1B**. Specifically, compound **SI-01** (0.13 mmol, 43 mg.), $Mn(dpm)_3$ (1.01 eq, 80 mg.), TBHP (2.0 eq, 28.2 μL of a 9.4 M solution in hexanes), $PhSiH_3$ (1.05 eq., 17.2 μL) and degassed *i*-PrOH ([0.025 M], 5.3 mL) were used. The reaction was stirred at room temperature for 4 hours, during which time the solution turned color from black to clear and yellow. The solution was concentrated directly *in vacuo*, and the resulting residue was purified by FCC on silica with a gradient of

[7] R. R. Milburn, V. Snieckus, *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 892-894.

hexanes to 10% Et_2O/hex to 20% Et_2O/hex. The desired compound was obtained as a pale yellow oil in 80% yield (28 mg.).

Characterization data of 8-arylmenthol **4a:**

R_f 0.30 (20% Et_2O in hexanes, stains blue in anisaldehyde)

Opt. Rot. -26.6° (c = 1.00 in CH_2Cl_2, 21 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.21 (td, *J* = 7.7, 1.7 Hz, 1H), 6.94 – 6.88 (m, 2H), 3.85 (s, 3H), 3.57 (td, *J* = 10.4, 4.3 Hz, 1H), 2.35 (ddd, *J* = 12.1, 10.0, 3.4 Hz, 1H), 1.84 (dtd, *J* = 12.3, 3.8, 2.1 Hz, 1H), 1.68 – 1.60 (m, 2H), 1.45 (s, 3H), 1.44 – 1.35 (m, 1H), 1.37 (s, 3H), 1.24 – 1.18 (m, 1H), 1.01 (qd, *J* = 13.9, 13.3, 3.8 Hz, 1H), 0.97 – 0.90 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.90 – 0.82 (m, 1H)

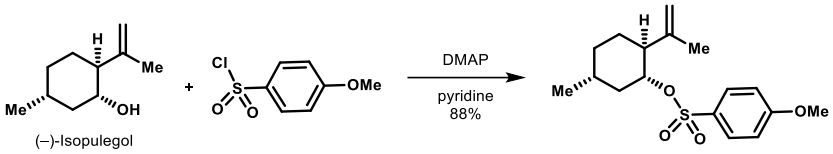
^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 139.0, 127.7, 126.3, 121.0, 112.4, 73.2, 55.3, 49.3, 45.3, 40.2, 35.3, 31.7, 26.7, 26.3, 24.7, 22.2

GC-MS (EI) Retention time: 9.19 minutes

m/z	% Max
262.2	1.68
244.2	2.54
161.1	1.96
150.1	11.27
149.1	100
148.1	3.11
135.1	5.03
134.1	1.61
133.1	3.03
131.1	1.58
122.1	1.98
121.1	22.16
119.1	1.95
115.1	5.16
109.1	1.64
105.1	3.74
103	1.80
79.1	2.24
77.1	3.68
55.1	2.31

3.08 **SI-02**: sulfonate precursor to **4b**



A magnetically stirred 50 mL round-bottom flask was charged with a solution of (-)-isopulegol (10.0 mmol, 1.69 mL, 1.0 eq.) in anhydrous pyridine (20 mL) at 22 °C under an atmosphere of air. To this solution was added 4-methoxybenzenesulfonyl chloride (18.0 mmol, 3.72 g, 1.8 eq.) and DMAP (1.0 mmol, 122 mg). The reaction vessel was capped and allowed to stir for 12 hours, at which point TLC indicated incomplete conversion. An additional portion of 4-methoxybenzenesulfonyl chloride (6.0 mmol, 1.24 g, 0.6 eq.) was added at this point, the reaction vessel was capped and allowed to stir another 12 hours. The reaction mixture was then quenched with water (50 mL) and precipitated solids were collected on a fritted filter funnel. Collected solids were then slurried with half-saturated sodium bicarbonate solution (50 mL, to remove residual sulfonate and pyridine), collected via filtration, and washed with water (2x 50 mL). After air-drying, resulting solids were dried 24 hours under high vacuum to remove residual water. Sulfonate ester **SI-02** was obtained as a white solid (2.87 g, 88%). NMR analysis indicated no further purification was necessary, but if desired, resulting sulfonate ester may be chromatographed on silica gel using toluene as the eluant.

Characterization data of sulfonate ester **SI-02:**

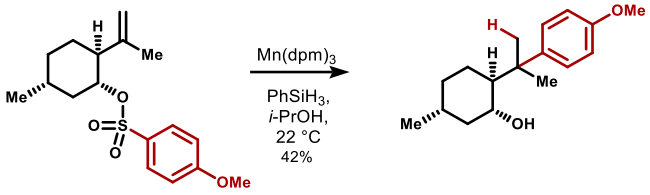
R_f 0.45 (100% toluene, anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.79 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.74 – 4.54 (m, 2H), 4.43 (td, *J* = 10.8, 4.5 Hz, 1H), 3.87 (s, 3H), 2.29 – 2.19 (m, 1H), 2.17 – 2.06 (m, 1H), 1.70 – 1.59 (m, 2H), 1.55 – 1.42 (m, 4H), 1.38 – 1.17 (m, 2H), 0.97 – 0.84 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$)
δ 163.5, 145.1, 130.1, 129.4, 114.1, 113.0, 83.0, 55.8, 50.9, 41.9, 33.8, 31.7, 30.5, 22.0, 19.4.

ESI-LCMS *m/z* = 325.1 $(M + 1)^+$

3.09 **4b**: 8-(*p*-anisole)menthol



Compound **4b** (36.7 mg, 42.4%) was prepared according to General Procedure 2.2A with the following adjustments: 1.0 equiv. substrate **SI-02** (0.33 mmol, 107 mg) was treated with 1.1 equv. $Mn(dpm)_3$ (.363 mmol, 220 mg) and 1.22 equiv phenylsilane (0.406 mmol, 50 µL) in *i*-PrOH (3.33 mL), reaction time = 36 hours.

Characterization data of 8-aryl-menthol **4b:**

R_f 0.15 (100% toluene, blue spot with anisaldehyde stain)

Opt. Rot. $[\alpha]_D^{21}$ = -13.5° (c = 0.915, EtOH)

^{1}H NMR (600 MHz, $CDCl_3$)

δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.52 (td, *J* = 10.3, 4.2 Hz, 1H), 1.84 (ddd, *J* = 12.2, 5.9, 3.7 Hz, 1H), 1.74 (dq, *J* = 13.2, 3.3 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.44 – 1.33 (m, 4H), 1.27 (s, 3H), 1.08 – 0.99 (m, 2H), 0.95 – 0.82 (m, 5H).

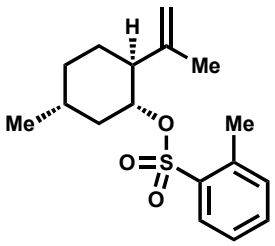
^{13}C NMR (151 MHz, $CDCl_3$)

δ 157.7, 143.3, 126.9, 114.0, 73.1, 55.4, 54.3, 45.4, 39.2, 35.1, 31.6, 29.5, 26.6, 24.0, 22.2.

GC-MS (EI) Retention time: 9.73 Minutes.

m/z	**% Max**
262.1	0.56%
244.1	2.35%
229.1	3.00%
187.1	0.76%
173.1	3.00%
161.1	8.64%
149.1	100.00%
121.1	12.13%
91.0	6.99%

3.10 **SI-03:** Sulfonate precursor to **5a**



Following General Procedure 2.1A, the sulfonyl chloride (0.75 mmol, 144 µL, 1.5 eq.) was added to a cold solution of (–)-isopulegol (0.50 mmol, 84.6 µL, 1.0 eq.) in pyridine [0.8 M]. Extraction with H_2O and CH_2Cl_2, followed by silica gel FCC afforded sulfone ester **SI-03** as a clear, viscous oil (123 mg, 80%).

Characterization data of sulfonate ester **SI-03:**

R_f 0.41 (10% Et_2O in hexanes, stains blue in anisaldehyde)

^{1}H NMR (500 MHz, $CDCl_3$)

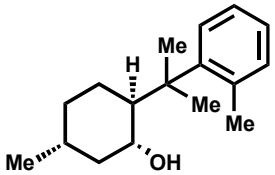
δ 7.94 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.46 (td, *J* = 7.5, 1.2 Hz, 1H), 7.28 (dq, *J* = 7.3, 3.5 Hz, 2H), 4.64 (s, 1H), 4.56 – 4.52 (m, 1H), 4.43 (td, *J* = 10.8, 4.5 Hz, 1H), 2.60 (s, 3H), 2.23 (ddt, *J* = 12.3, 4.8, 1.8 Hz, 1H), 2.15 (ddd, *J* = 12.6, 10.8, 3.8 Hz, 1H), 1.63 (ddt, *J* = 12.8, 8.6, 3.2 Hz, 2H), 1.46 (ttd, *J* = 14.7, 8.3, 7.5, 4.2 Hz, 1H), 1.35 – 1.32 (m, 3H), 1.32 – 1.17 (m, 2H), 1.05 – 0.92 (m, 4H)

^{13}C NMR (126 MHz, $CDCl_3$)
δ 144.77, 138.81, 136.34, 133.37, 132.42, 129.26, 125.88, 113.10, 83.46, 51.18, 41.92, 33.72, 31.66, 30.66, 21.94, 20.77, 18.68.

GC-MS (EI) Retention time: 10.18 min

m/z	% Max
55	24.0
65	26.0
67	26.0
69	28.0
79	49.0
80	39.0
81	100
90	54.9
91	13.8
92	39.2
93	44.5
94	38.0
107	54.0
108	22.0
109	23.0
121	74.0
136	78.0
308	0.25

3.11 **5a:** 8-(*o*-tolyl)menthol



Compound **5a** was prepared according to procedure **2.2a**. Specifically, substrate **SI-03** (1.0 eq., 0.213 mmol., 66.0 mg.), $Mn(dpm)_3$ (1.0 eq., 130.4 mg.), TBHP (2.0 eq., 45.5 μL, 0.428 mmol), degassed *i*-PrOH ([0.025 M], 8.6 mL, and $PhSiH_3$ (1.05 eq., 27.6 μL) were used. The reaction was stirred for 5 hours during which time the reaction changed color from black to light yellow. The reaction was concentrated *in vacuo*, suspended in hexanes, filtered through a plug of celite (rinsing with hexanes) and the filtrate was concentrated. The resulting residue was purified by FCC on silica with 25% Et_2O/hexanes. The compound was still partially impure and so was purified further by prep plate with 100% toluene as the eluent. The desired compound **5a** was obtained as a clear, pale yellow oil in 29% yield (15.8 mg.).

Characterization data of 8-arylmenthol **5a:**

R_f 0.24 (100% toluene, stains purple in anisaldehyde)

Opt. Rot. -13.3 ° (c = 0.54 in CH_2Cl_2, 20 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 1H), 7.17 – 7.08 (m, 3H), 3.63 (td, *J* = 10.2, 4.3 Hz, 1H), 2.55 (s, 3H), 2.10 (ddd, *J* = 12.5, 9.7, 3.3 Hz, 1H), 1.86 (dtd, *J* = 12.4, 4.0, 2.2 Hz, 1H), 1.68 – 1.58 (m, 2H), 1.52 (s, 3H), 1.45 – 1.35 (m, 1H), 1.40 (s, 3H), 1.12 (br s, 1H), 1.06 (qd, *J* = 13.7, 3.8 Hz, 1H), 0.98 – 0.81 (m, 2H), 0.89 (d, *J* = 6.5 Hz, 3H)

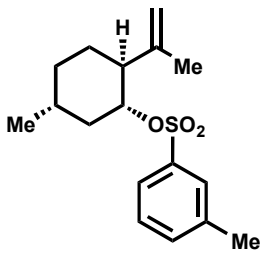
^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8, 136.6, 133.5, 126.4, 126.3, 126.0, 73.0, 50.5, 45.3, 41.3, 35.2, 31.6, 27.1, 26.8, 26.3, 23.9, 22.2

GC-MS (EI) Retention time: 9.05 minutes

m/z	% Max
246.2	0.76
228.2	4.47
145.1	2.71
134.1	13.35
133.2	100
132.1	25.18
131.1	2.70
129.1	2.70
128.1	2.83
119.1	7.46
117.1	6.79
115.1	6.08
106.1	3.26
105.1	36.1
93.1	4.64
91.1	9.25
77.1	3.24

3.12 **SI-04:** sulfonate precursor to **5b**



General Procedure 2.1A was followed, using 2.0 eq. of sulfonyl chloride (1.0 mmol, 145 µL) to yield sulfone ester **SI-04** as a clear oil which solidified to a white crystalline solid (134 mg, 87%) upon freezing temperatures.

Characterization data of sulfonate ester **SI-04:**

R_f 0.28 (10% EtOAc/hex, anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

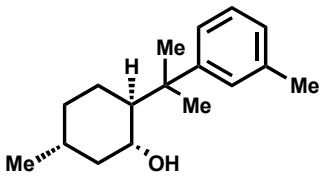
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.75 (m, 2H), 7.42 – 7.35 (m, 2H), 4.67 (s, 1H), 4.61 (p, *J* = 1.6 Hz, 1H), 4.46 (td, *J* = 10.8, 4.5 Hz, 1H), 2.42 (d, *J* = 0.7 Hz, 3H), 2.26 (dddd, *J* = 12.4, 4.8, 3.5, 1.8 Hz, 1H), 2.13 (ddd, *J* = 12.6, 10.5, 3.8 Hz, 1H), 1.70 – 1.60 (m, 2H), 1.55 – 1.45 (m, 1H), 1.41 (s, 3H), 1.38 – 1.29 (m, 1H), 1.25 (td, *J* = 12.4, 11.0 Hz, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.98 – 0.86 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 139.1, 137.6, 134.1, 128.8, 128.4, 125.1, 113.0, 83.4, 50.9, 42.0, 33.8, 31.7, 30.5, 22.0, 21.4, 19.4

ESI-LCMS 331.1 $(M+Na)^+$

3.13 **5b:** 8-(*m*-tolyl)menthol



Compound **5b** was prepared according to procedure **2.2A**. Specifically, substrate **SI-04** (1.0 eq., 0.162 mmol., 50 mg.), $Mn(dpm)_3$ (1.0 eq., 130.4 mg.), degassed *i*-PrOH ([0.1 M], 1.6 mL, and $PhSiH_3$ (1.0 eq., 20 µL) were used. The reaction was stirred for 24 hours, then the reaction was concentrated *in vacuo*, and the resulting residue was purified by FCC on silica with 10% EtOAc/hexanes. The desired compound **5b** was obtained as a clear, pale yellow oil in 41% yield (16.3 mg.).

Characterization data of 8-arylmenthol **5b:**

R_f 0.36 (25% Et_2O/hex, stains purple in anisaldehyde)

Opt. Rot. -29.8° (c = 0.95 in CH_2Cl_2, 24 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 3H), 7.03 – 6.98 (m, 1H), 3.54 (ddt, *J* = 14.2, 10.1, 3.8 Hz, 1H), 2.35 (s, 3H), 1.84 (dtd, *J* = 12.4, 4.0, 2.4 Hz, 1H), 1.79 – 1.69 (m, 2H), 1.65 (ddd, *J* = 12.9, 6.0, 3.5 Hz, 1H), 1.44 – 1.35 (m, 1H), 1.40 (s, 3H), 1.27 (s, 3H), 1.12 – 0.97 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.97 – 0.80 (m, 2H).

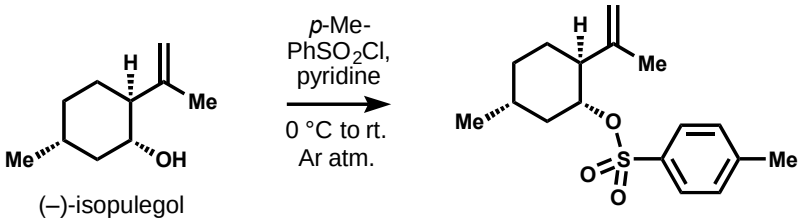
^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 138.1, 128.5, 126.8, 126.7, 122.9, 73.1, 54.3, 45.3, 39.7, 35.1, 31.6, 29.3, 26.6, 23.9, 22.2, 21.9

GC-MS (EI) Retention time: 8.78 minutes

m/z	% Max
246.1	0.15
157.1	2.61
145.1	3.06
135.1	3.72
134.1	22.0
133.1	100
132.1	17
131.1	2.54
119.1	9.15
117	4.86
115.1	4.42
105.1	20.0
93.1	5.25
91.1	7.29
77.1	3.23

3.14 **SI-05:** sulfonate precursor to **5c**



(–)-isopulegol

A magnetically stirred 10 mL round-bottom flask was charged with a solution of (-)-isopulegol (2,0 mmol, 340 µL, 1.0 eq.) in anhydrous pyridine ([0.8M], 2.5 mL) at 0 °C under an atmosphere of argon. To this solution 4-toluenesulfonyl chloride (2.4 mmol, 460 mg, 1.2 eq.) was added in one portion at 0 °C. The ice bath was then removed and the reaction was stirred for 18 hours, at which point TLC indicated high conversion to the desired product. Cold water (~2 mL) was added to the reaction and stirred at 0 °C for 1 hour. A pink/white solid (the desired product) precipitated from this solution. This precipitate was filtered off over a ground glass frit and rinsed several times with cold water. After air-drying, the desired product was dried under high vacuum for >24 hrs to remove excess water and pyridine. The title compound **SI-05** was obtained in 80% yield (491 mg.) without need for further purification.

Characterization data of sulfonate ester **SI-05:**

R_f 0.58 (25% Et_2O in hexanes, stains blue in anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$)

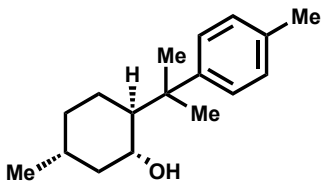
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.67 (s, 1H), 4.61 (m, 1H), 4.45 (td, *J* = 10.8, 4.5 Hz, 1H), 2.43 (s, 3H), 2.29 – 2.19 (m, 1H), 2.18 – 2.07 (m, 1H), 1.65 (m, 2H), 1.50 (m, 1H), 1.43 (s, 3H), 1.40 – 1.17 (m, 2H), 0.92 (d, *J* = 5.6 Hz), 0.98 – 0.84 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.3, 134.8, 129.5, 128.0, 113.1, 83.2, 51.0, 41.9, 33.8, 31.7, 30.5, 22.0, 21.8, 19.4

ESI-LCMS *m/z* = 331.2 $(M+Na)^+$

3.15 **5c:** 8-(*p*-tolyl)menthol



Compound **5c** was prepared from **SI-05** following method 2.2A. Specifically, compound **SI-07** (50.0 mg, 1.0 eq., 0.162 mmol), $Mn(dpm)_3$ (1.0 eq, 98 mg.), $PhSiH_3$ (1.0 eq., 20 μL) and *i*-PrOH ([0.1 M], 1.62 mL) were used. The starting material **SI-07** was not completely consumed after 24 hours, so 1.0 eq. more $PhSiH_3$ was added. After another 24 hours, the desired compound **5c** (20.5 mg., 51% yield) was isolated as a slightly opaque pale yellow oil after FCC on silica with 100% toluene as the eluent system.

Characterization data of 8-arylmenthol **5c:**

R_f 0.26 (100% toluene, stains dark blue/purple with anisaldehyde)

Opt. Rot. -16.2° (c = 0.408 in CH_2Cl_2, 23 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (dt, *J* = 8.3, 2.3 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 3.57 – 3.48 (m, 1H), 2.31 (s, 3H), 1.84 (dtd, *J* = 12.4, 3.9, 2.4 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.65 (dqd, *J* = 12.9, 3.5, 2.3 Hz, 1H), 1.40 (s, 3H), 1.44-1.33 (m, 1H), 1.27 (s, 3H), 1.11 – 0.96 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.97 – 0.79 (m, 2H)

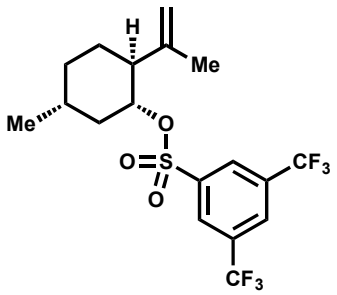
^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 135.5, 129.4, 125.8, 73.1, 54.3, 45.3, 39.5, 35.1, 31.6, 29.4, 26.6, 23.9, 22.2, 21.0

GC-MS (EI) Retention time: 8.93 minutes.

m/z	% Max
246.2	0.57
145.1	3.44
134.1	11.9
133.1	100
132.1	12.7
119.1	4.63
117.1	4.07
105.1	16.3
93.1	4.07
91.1	5.76
77.0	2.69

3.16 **SI-06:** sulfonate precursor to **6a**



Employing General Procedure 2.1B, 2.0 eq. of sulfonyl chloride (156 mg, 2.0 eq.) were used to give, after silica gel FCC, sulfone ester **SI-06** as white crystalline needles (59 mg, 55%).

Characterization data of sulfonate ester **SI-06:**

R_f 0.24 (4% Et_2O/hex, anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.31 (s, 2H), 8.10 (s, 1H), 4.62 (s, 1H), 4.60 (td, *J* = 10.9, 4.6 Hz, 1H), 4.53 (s, 1H), 2.39 – 2.30 (m, 1H), 2.15 (ddd, *J* = 12.4, 10.6, 3.8 Hz, 1H), 1.74 – 1.64 (m, 2H), 1.62 – 1.53 (m, 1H), 1.41 (s, 3H), 1.40 – 1.27 (m, 2H), 0.97 (d, *J* = 6.5 Hz, 3H), 1.01 – 0.90 (m, 1H)

^{13}C NMR (126 MHz, $CDCl_3$)

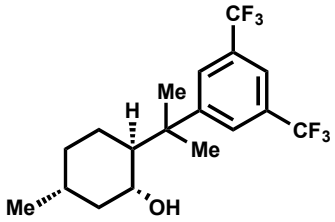
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 140.5, 132.9 (q, *J* = 34.7 Hz), 128.3 (q, *J* = 3.2 Hz), 126.8 (sep, *J* = 3.3 Hz), 122.53 (q, *J* = 273.6 Hz), 113.2, 85.9, 50.7, 42.3, 33.6, 31.8, 30.5, 21.9, 19.7

^{19}F NMR (376 MHz, $CDCl_3$). Not calibrated.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3

MALDI-TOF 431.11 $[M+H]^+$, 453.09 $[M+Na]^+$

3.17 **6a:** 8-[3,5-bis(trifluoromethyl)phenyl]menthol



Compound **6a** was prepared following procedure **2.2A** with some modifications. Specifically, compound **SI-06** (0.023 mmol, 10 mg.), $Mn(dpm)_3$ (1.2 eq, 16.5 mg.), $PhSiH_3$ (1.0 eq., 3.4 μL) and degassed *i*-PrOH ([0.04 M], 550 μL) were used. The reaction was stirred at room temperature for 24 hours, concentrated directly *in vacuo*, and the resulting residue was purified by FCC on silica with a 15% Et_2O/hexanes. The desired compound **6a** was obtained as a pale yellow oil in 84% yield (7 mg.).

Characterization data of 8-arylmenthol **6a:**

R_f 0.4 (25% Et_2O/hex, stains pale purple/pink in anisaldehyde)

Opt. Rot. -18.3° (c = 0.342 in CH_2Cl_2, 24 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (s, 2H), 7.67 (s, 1H), 3.47 (td, *J* = 10.4, 4.1 Hz, 1H), 1.86 (dtd, *J* = 12.3, 3.9, 2.2 Hz, 1H), 1.66 – 1.59 (m, 2H), 1.55 – 1.47 (m, 1H), 1.49 (s, 3H), 1.45 – 1.37 (1H), 1.37 (s, 3H), 1.02 – 0.91 (m, 2H), 0.91 – 0.80 (m, 1H), 0.88 (d, *J* = 6.5, 3H), 0.68 (s, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 131.1 (q, *J* = 32.6), 126.3 (q, *J* = 2.7), 123.8 (q, *J* = 272.7 Hz), 119.4 (sep, *J* = 4.0 Hz), 73.1, 54.2, 46.4, 40.9, 34.7, 31.7, 27.3, 26.8, 26.3, 22.0

^{19}F NMR (376 MHz, $CDCl_3$). Not calibrated.

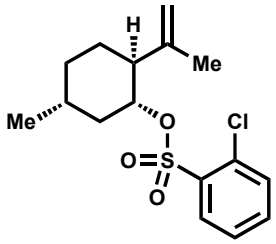
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s)

GC-MS (EI) Retention time: 7.46 minutes

m/z	% Max
368.4	-
255.1	10.3
254.1	12.5
237.1	13.3
227.1	22.9
113.1	30.0
112.1	3.50
96.1	13.0
95.1	100
93.1	3.52
81.1	5.41

71.1	3.17
69.1	7.67
67.1	9.98
57.1	5.93
55.1	7.93

3.18 **SI-07:** sulfonate precursor to **6b**



Compound **6b** was prepared according to procedure **2.1A** with the some modifications. Specifically, (–)-isopulegol (1.0 eq., 1.0 mmol, 169 μL), 2-chlorobenzene sulfonyl chloride (2.0 eq, 272 μL), and anhydrous pyridine ([0.5 M], 2 mL) were used, and the reaction was conducted at room temperature. The reaction was complete within 7 hours, at which point the reaction was quenched with H_2O (2 mL), extracted with Et_2O (3x 5 mL), and the organic layer was dried over $MgSO_4$. After filtration and concentration *in vacuo*, the resulting residue was purified by FCC in 5% EtOAc/hex. The desired compound **SI-07** was initially obtained as a slightly opaque, pale yellow viscous oil, which upon sitting crystallized as a white crystalline solid in 85% yield (281 mg.).

Characterization data of sulfonate ester **SI-07:**

R_f 0.4 (10% EtOAc/hex, stains purple in anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

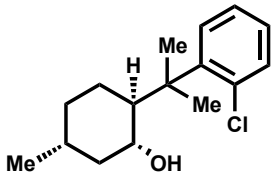
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 8.01 (m, 1H), 7.55 – 7.48 (m, 2H), 7.38 (ddd, *J* = 7.9, 5.2, 3.4 Hz, 1H), 4.64 (s, 1H), 4.57 (td, *J* = 10.9, 4.6 Hz, 1H), 4.53 (p, *J* = 1.6 Hz, 1H), 2.22 – 2.15 (m, 2H), 1.69 (dq, *J* = 13.6, 3.5 Hz, 1H), 1.63 (dqd, *J* = 12.3, 3.5, 2.0 Hz, 1H), 1.53 – 1.44 (m, 1H), 1.48 (s, 3H), 1.35 – 1.24 (m, 2H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.97 – 0.87 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 136.1, 134.2, 133.5, 132.0, 131.0, 126.8, 113.0, 85.3, 50.8, 41.8, 33.7, 31.8, 30.8, 22.0, 19.6

ESI-LCMS 351.2 $(M+Na)^+$

3.19 **6b:** 8-(2-chlorophenyl)menthol



A 5 mL round bottom flask was charged with a stir bar, substrate **SI-07** (1.0 eq., 0.12 mmol, 40.0 mg.), and $Mn(dpm)_3$ (1.0 eq., 73.6 mg.). The reaction vessel was evacuated and refilled with nitrogen gas 3x successively, and then placed under an Argon atmosphere. Anhydrous and degassed *i*-PrOH ([0.1 M], 1.2 mL) was next added, followed by $PhSiH_3$ (1.0 eq., 15 μL). The reaction was stirred for 24 hours, then the reaction was concentrated to dryness and purified by FCC on silica with 100% toluene as eluent. The desired compound **6b** was obtained as a clear yellow oil in 80% yield (26 mg.).

Characterization data of 8-arylmenthol **6b:**

R_f (25% Et_2O/hex, stains pale purple/pink in anisaldehyde)

Opt. Rot. -29.9° (c = 1.00 in CH_2Cl_2, 22 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 7.12 (ddd, *J* = 7.8, 7.3, 1.7 Hz, 1H), 3.59 (td, *J* = 10.4, 4.2 Hz, 1H), 2.60 (ddd, *J* = 12.0, 9.9, 3.4 Hz, 1H), 1.87 (dtd, *J* = 12.3, 3.9, 2.3 Hz, 1H), 1.67 – 1.49 (m, 2H), 1.58 (s, 3H), 1.45 (s, 3H), 1.44 – 1.35 (m, 1H), 1.03 – 0.92 (m, 2H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.92 – 0.76 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$)

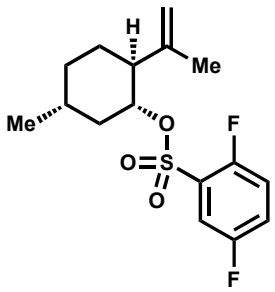
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 133.6, 132.4, 128.0, 127.3, 127.0, 73.4, 48.7, 45.9, 41.7, 35.1, 31.8, 27.0, 25.9, 25.5, 22.1

GC-MS (EI) Retention time: 9.32 minutes

m/z	% Max
266.1	-
248.2	2.74
230.2	25.0
155.1	36.0
154.1	33.0
153.0	98.0
152.0	62.0
139.0	16.0
128.1	11.0
127.0	36.0
125.0	100
119.1	24.0
117.1	13.0

115.1	25.0
103.1	10.0
95.1	42.0
91.1	20.0
77.1	12.0
55.1	12.7

3.20 **SI-08:** sulfonate precursor to **6c**



Compound **SI-08** was obtained following the standard procedure 2.1A. Specifically, (–)-isopulegol (0.2 mmol, 1.0 eq., 34 µL), 2,5-difluorobenzene sulfonyl chloride (1.5 eq., 0.3 mmol, 40.4 µL) and anhydrous pyridine ([0.8 M], 250 µL) were used. The reaction was stirred for 24 hours, quenched by the addition of cold water and the desired compound precipitated as a yellow-tinged white powder, which was isolated by filtration in 85% yield (56 mg.)

Characterization data of sulfonate ester **SI-08:**

R_f 0.5 (25% Et_2O/hex, stains blue/purple in anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (ddd, *J* = 7.5, 5.2, 3.2 Hz, 1H), 7.29 (ddt, *J* = 9.0, 7.0, 3.4 Hz, 1H), 7.17 (td, *J* = 8.9, 4.0 Hz, 1H), 4.65 (s, 1H), 4.59 (dt, *J* = 10.9, 5.5 Hz, 1H), 4.56 (p, *J* = 1.6 Hz, 1H), 2.25 (dddd, *J* = 12.3, 4.7, 3.5, 1.9 Hz, 1H), 2.17 (ddd, *J* = 12.5, 10.6, 3.9 Hz, 1H), 1.71 (dq, *J* = 13.7, 3.5 Hz, 1H), 1.65 (dddd, *J* = 13.0, 6.6, 3.3, 1.9 Hz, 1H), 1.51 (s, 3H), 1.59 – 1.45 (m, 1H), 1.39 – 1.27 (m, 2H), 0.94 (d, *J* = 6.5, 3H), 1.01 – 0.88 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

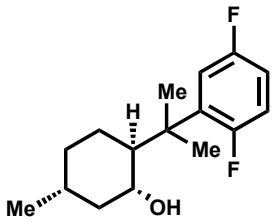
^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.7 (d, *J* = 247.9 Hz), 155.6 (d, *J* = 255.3), 144.7, 127.1 (dd, *J* = 16.7, 6.9 Hz), 122.3 (dd, *J* = 23.8, 8.2 Hz), 118.7 (dd, *J* = 23.9, 7.6 Hz), 117.3 (d, *J* = 27.2 Hz), 113.1, 86.0, 50.7, 42.0, 33.7, 31.8, 30.7, 21.9, 19.7

^{19}F NMR (376 MHz, $CDCl_3$). Not calibrated.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.7 (d, *J* = 17.8 Hz), -116.4 (d, *J* = 17.8 Hz)

ESI-LCMS 331.12 $[M+H]^+$, 353.10 $[M+Na]^+$

3.21 **6c:** 8-(2,5-difluorophenyl)menthol



Compound **6c** was obtained following general procedure **2.2A** with some modification. Specifically, compound **SI-08** (0.151 mmol, 50 mg.), $Mn(dpm)_3$ (1.0 eq, 91.5 mg.), TBHP (2.0 eq, 28.2 μL of a 9.4 M solution in hexanes), $PhSiH_3$ (1.05 eq., 19.5 μL) and degassed *i*-PrOH ([0.025 M], 6.04 mL) were used. The reaction was stirred at room temperature for 4 hours, during which time the solution turned color from black to clear and yellow. The solution was concentrated directly *in vacuo*, and the resulting residue was purified by FCC on silica with a gradient of hexanes to 5% Et_2O/hex to 10% Et_2O/hex. The desired compound was obtained as a pale yellow oil in 91% yield (37 mg.).

Characterization data of 8-arylmenthol **6c:**

R_f 0.46 (25% Et_2O/hex, stains grey/green in anisaldehyde)

Opt. Rot. -31.1° (c = 1.61 in CH_2Cl_2, 23 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.98 (ddd, *J* = 10.4, 6.3, 3.2 Hz, 1H), 6.93 (ddd, *J* = 11.7, 8.9, 4.9 Hz, 1H), 6.83 (ddt, *J* = 8.9, 6.9, 3.3 Hz, 1H), 3.55 (tdd, *J* = 10.4, 4.3, 2.4 Hz, 1H), 2.01 (dddd, *J* = 11.9, 10.0, 3.5, 1.6 Hz, 1H), 1.87 (dtd, *J* = 12.3, 3.8, 2.2 Hz, 1H), 1.64 – 1.57 (m, 1H), 1.53 (dq, *J* = 13.2, 3.4 Hz, 1H), 1.46 (s, 3H), 1.45 – 1.36 (m, 1H), 1.33 (s, 3H), 1.31 – 1.14 (m, 1H), 1.03 – 0.91 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.91 – 0.80 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.7 (dd, *J* = 240.7, 2.2 Hz), 157.4 (dd, *J* = 243.0, 2.2 Hz), 140.5 (dd, *J* = 14.2, 6.5 Hz), 117.3 (dd, *J* = 28.3, 8.8 Hz), 114.3 (dd, *J* = 25.2, 6.6 Hz), 113.5 (dd, *J* = 23.9, 9.5 Hz), 73.1, 50.8, 46.0, 40.2, 34.9, 31.8, 26.9, 25.4, 25.3, 22.1 (Peaks at 30.0 and 27.6 are impurities)

^{19}F NMR (376 MHz, $CDCl_3$). Not calibrated.

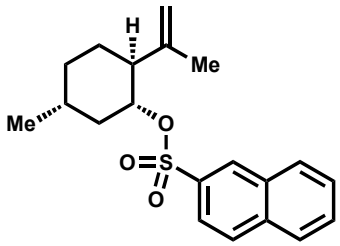
^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.73 (d, *J* = 17.8 Hz), -119.29 (d, *J* = 17.8 Hz)

GC-MS (EI) Retention time: 8.29 minutes.

m/z	% Max
268.1	1.51
168.1	11.7
156.1	39.2
155.1	100
154.1	74.7
153.1	10.6
141.1	28.0

127.0	85.0
113.1	17.2
96.1	10.7
95.1	78.2
69.1	9.59
67.1	12.6
55.1	11.2

3.22 **SI-09:** sulfonate precursor to **7**



General Procedure 2.1B was followed, using 2.0 eq. of sulfonyl chloride (227 mg) in pyridine [1.0 M], which after precipitation with water and filtration produced sulfone ester **SI-09** as an off-white/pink solid (171 mg, 93%).

Characterization data of sulfonate ester **SI-09:**

R_f 0.46 (25% Et_2O/Hexanes, anisaldehyde)

^{1}H NMR (500 MHz, $CDCl_3$)

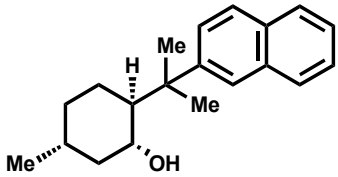
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.01 – 7.88 (m, 3H), 7.83 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.63 (m, 2H), 4.66 (s, 1H), 4.58 – 4.50 (td, *J* = 6.3, 4.5 Hz, 1H), 4.54 (s, 1H), 2.33 – 2.25 (m, 1H), 2.14 (ddd, *J* = 12.3, 10.5, 3.8 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.51 (m, 1H), 1.36 (s, 3H), 1.35 – 1.22 (m, 2H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.97 – 0.85 (m, 1H)

^{13}C NMR (126 MHz, $CDCl_3$)

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 135.2, 134.7, 132.0, 129.4, 129.3, 129.2 (2C), 128.0, 127.7, 123.1, 113.1, 83.6, 50.9, 42.0, 33.7, 31.7, 30.5, 21.9, 19.4 (Overlapping peaks at 129.2)

ESI-LCMS 367.1 $(M+Na)^+$

3.23 **7:** 8-(2-naphthyl)menthol



Compound **7** was prepared from compound **SI-09** via method 2.2A. Specifically, compound **SI-09** (50.0 mg, 1.0 eq., 0.1645 mmol), $Mn(dpm)_3$ (1.0 eq, 88 mg.), $PhSiH_3$ (1.0 eq., 18 µL) and isopropanol ([0.1 M], 1.45 mL) were used. After 24 hours, precipitates that had formed in the reaction were filtered off and the reaction was concentrated *in vacuo*. The resulting residue was purified by FCC in 10% Et_2O/hex. The desired compound **7** (27 mg.**)** was obtained as a viscous pale yellow oil in 66% yield.

Characterization data of 8-arylmenthol **7:**

R_f 0.33 (25% Et_2O in hexanes, stains green in anisaldehyde); 0.21 (10% Et_2O in hexanes, stains green in anisaldehyde)

Opt. Rot. -26.0° (c = 1.01 in CH_2Cl_2, 24 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 – 7.77 (m, 3H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.58 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.48 – 7.40 (m, 2H), 3.60 (td, *J* = 10.3, 4.2 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.71 (dq, *J* = 13.4, 3.5 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.46 – 1.33 (m, 1H), 1.08 (tdd, *J* = 13.3, 12.1, 3.5 Hz, 1H), 1.01 (s, 1H), 0.95 (td, *J* = 12.3, 10.8 Hz, 1H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.91 – 0.82 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

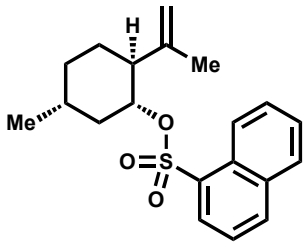
^{13}C NMR (151 MHz, $CDCl_3$) δ 149.1, 133.5, 131.9, 128.2, 128.1, 127.5, 126.1, 125.6, 125.3, 123.3, 73.2, 53.9, 45.5, 40.2, 35.0, 31.7, 28.5, 26.7, 24.8, 22.1

GC-MS (EI) Retention time: 11.21 minutes.

m/z	% Max
282.2	1.41
264.2	6.79
249.1	6.88
193.1	9.07
179.1	7.86
178.1	7.30
170.1	29.8
169.1	100
168.1	14.4
167.1	7.05
165.1	13.3
155.1	10.7
154.1	7.44

153.1	13.5
152.1	13.2
141.1	25.8
128.0	14.2

3.24 **SI-10:** sulfonate precursor to **8**



Same modifications to General Procedure 2.1B as for **SI-09**, obtaining a white solid (158mg, 92%).

Characterization data of sulfonate ester **SI-12:**

R_f 0.51 (25% Et_2O/hex, anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

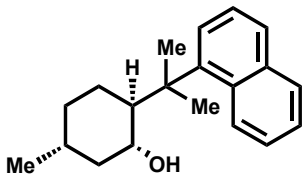
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.60 (dq, *J* = 8.7, 1.0 Hz, 1H), 8.24 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.61 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 4.49 (td, *J* = 10.9, 4.5 Hz, 1H), 4.43 (s, 1H), 4.11 (p, *J* = 1.6 Hz, 1H), 2.25 (dddd, *J* = 12.4, 4.8, 3.4, 1.7 Hz, 1H), 2.09 (ddd, *J* = 12.6, 10.5, 3.7 Hz, 1H), 1.63 – 1.56 (m, 2H), 1.47 (ttd, *J* = 12.1, 6.6, 3.4 Hz, 1H), 1.30 – 1.17 (m, 2H), 1.14 (s, 3H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.92 – 0.83 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 134.9, 134.1, 133.4, 129.4, 128.9, 128.5, 128.2, 127.1, 126.2, 123.9, 113.0, 84.2, 50.9, 41.9, 33.7, 31.7, 30.7, 22.0, 19.1

ESI-LCMS 367.1 $(M+Na)^+$

3.25 **8:** 8-(1-naphthyl)menthol



Compound **8** was prepared from compound **SI-10** according to procedure 2.2A. Specifically, compound **SI-10** (50.0 mg, 1.0 eq., 0.145 mmol), $Mn(dpm)_3$ (1.0 eq, 88 mg.), $PhSiH_3$ (1.0 eq., 19 μL), TBHP (2.0 eq. of a 10.0

M solution in hexanes) and isopropanol ([0.05 M], 2.9 mL) were used. TLC analysis indicated that the reaction was complete within 2 hours of the $PhSiH_3$ addition. The reaction was concentrated *in vacuo* and purified by FCC on silica in a 25% Et_2O/hexanes solvent system to obtain 32.4 mg (78% yield) of the desired compound **8** as a pale yellow oil. The compound exists as a mixture of rotamers.

Characterization data of 8-aryl menthol **8:**

R_f 0.29 (25% Et_2O in hexanes, stains blue in anisaldehyde)

Opt. Rot. -29.0° (c = 1.00 in CH_2Cl_2, 21 °C)

^{1}H NMR (600 MHz, $CDCl_3$). T = 323 K

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.53 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 3.73 (td, *J* = 10.2, 4.3 Hz, 1H), 2.57 (ddd, *J* = 12.8, 9.5, 3.4 Hz, 1H), 1.86 (dtd, *J* = 12.4, 3.9, 2.2 Hz, 1H), 1.73 (s, 3H), 1.60 (s, 3H), 1.69 – 1.54 (m, 1H), 1.48 – 1.37 (m, 2H), 1.21 – 1.07 (m, 1H), 0.97 – 0.88 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.89 – 0.79 (m, 1H).

(600 MHz, $CDCl_3$). T = 298 K

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.39 (dd, *J* = 8.1, 7.4 Hz, 1H), 3.72 (td, *J* = 10.1, 4.2 Hz, 1H), 2.57 (ddd, *J* = 12.7, 9.6, 3.5 Hz, 1H), 1.90 – 1.79 (m, 1H), 1.71 (s, 3H), 1.59 (s, 3H), 1.65 – 1.55 (m, 1H), 1.48 – 1.36 (m, 1H), 1.28 (d, *J* = 24.7 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 1H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.99 – 0.79 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$). T = 323 K

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 135.6, 131.8, 130.0, 128.0, 127.0, 125.4, 125.0, 124.8, 123.7, 73.5, 51.4, 45.7, 42.1, 35.3, 31.7, 28.0, 27.7, 27.2, 22.1

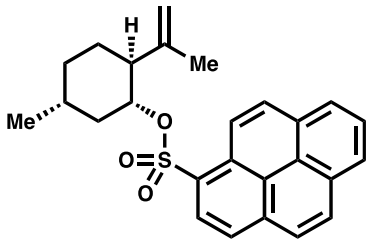
(151 MHz, $CDCl_3$). T = 298 K

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 135.5, 131.6, 130.0, 128.0, 126.9, 125.4, 125.0, 124.9, 123.6, 73.4, 51.2, 45.4, 41.9, 35.1, 31.6, 28.0, 27.5, 26.9, 22.1

GC-MS (EI) Retention time: 11.05 minutes.

m/z	% Max
282.2	4.18
170.1	16.2
169.1	100
168.1	5.30
167.1	4.58
165.1	7.87
155.1	6.37
154.1	4.81
153.1	10.4
152.1	7.04
141.1	24.2
129.1	9.16
128.0	9.00

3.26 **SI-11**: sulfonate precursor to **9**



Compound **SI-11** was prepared via procedure **2.2A** by coupling (–)-isopulegol with pyrene-1-sulfonyl chloride. Pyrene-1-sulfonyl chloride was prepared from pyrene-1sulfonic acid according to a reported procedure.[8]

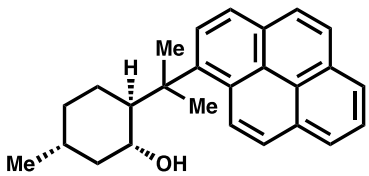
A 10 mL round bottom flask was charged with a stir bar, pyrene-1-sulfonyl chloride (1.8 eq., 1.43 mmol, 430 mg.; slightly impure), DMAP (0.1 eq.; 9.7 mg.), anhydrous pyridine ([0.16 M], 5 mL) and (–)-isopulegol (1.0 eq., 0.79 mmol, 134 μL) under an argon atmosphere. The reaction was stirred at room temperature for 24 hours, at which point H_2O (5 mL) was added, causing a yellow precipitate to form. The reaction was cooled to 0 °C, stirred for 1 hour, then the sticky yellow precipitate was filtered off. This sticky residue proved unmanageable, so it was dissolved in CH_2Cl_2 (100 mL) and combined with the filtrate. Water (30 mL) was added to the aqueous layer and extracted with CH_2Cl_2 (2x 25 mL). The organic layer was washed with $CuSO_4$ (sat'd. aqu. 1x20 mL), 2M HCl (1x 20 mL), $NaHCO_3$ (sat'd aqu. 1x 20 mL) and brine (1x 20 mL) and dried over $MgSO_4$. This was filtered, concentrated *in vacuo* and the resulting residue was purified by FCC on silica with 15% Et_2O/hex and then a second time with 75% toluene/hex to obtain the desired product **SI-11** as a bright yellow viscous oil in 45% yield (149 mg.).

Characterization data of sulfonate ester **SI-11:**

R_f	0.31 (25% Et_2O/hex, anisaldehyde)
^{1}H NMR	(500 MHz, $CDCl_3$)
	^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.91 (d, *J* = 9.3 Hz, 1H), 8.66 (d, *J* = 8.1 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.29 dd, *J* = 8.4, 1.6 Hz, 1H), 8.26 (dd, *J* = 9.3, 1.6 Hz, 1H), 8.22 – 8.15 (m, 2H), 8.12 – 8.05 (m, 2H), 4.60 (td, *J* = 10.8, 4.5 Hz, 1H), 4.48 (s, 1H), 4.07 (p, *J* = 1.6 Hz, 1H), 2.30 – 2.23 (m, 1H), 2.13 (ddd, *J* = 12.5, 10.5, 3.7 Hz, 1H), 1.63 – 1.54 (m, 2H), 1.52 – 1.42 (m, 1H), 1.32 – 1.20 (m, 2H), 1.12 (s, 3H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.78 (m, 1H)
^{13}C NMR	(151 MHz, $CDCl_3$)
	^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 135.3, 131.0, 130.6, 130.3, 129.8, 129.7, 129.1, 127.1 (2C), 127.0 (2C), 126.9, 125.1, 124.7, 123.8, 123.6, 113.1, 84.0, 51.0, 41.9, 33.7, 31.7, 30.7, 22.0, 19.0
GCMS-TOF	419.17 $(M+H)^+$

[8] Yan, N.; Xu, Z.; Diehn, K.K.; Raghavan, S.R.; Fang, Y.; Weiss, R.G. *J. Am. Chem. Soc.*, **2013**, *135* (24), pp 8989–8999.

3.27 **9**: 8-(1-pyrenyl)menthol

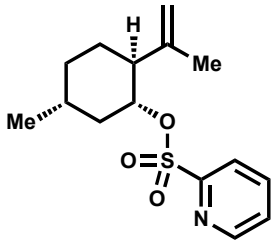


Compound **9** was prepared according to procedure 2.2A with some modification. Specifically, compound **SI-11** (0.35 mmol, 148 mg.), $Mn(dpm)_3$ (1.01 eq, 214 mg.), TBHP (2.0 eq, 75.2 μL of a 9.4 M solution in hexanes), $PhSiH_3$ (1.05 eq., 45.8 μL), degassed *i*-PrOH ([0.025 M], 14 mL) and degassed benzene (1 mL; as cosolvent to help solubilize compound **SI-11**) were used. The reaction was stirred at room temperature for 12 hours, during which time the solution turned color from black to opaque and yellow. The solution was concentrated directly *in vacuo*, and the resulting residue was purified by FCC on silica with a gradient of hexanes to 15% Et_2O/hex to toluene. A yellow foam was obtained which contained a fluorescent impurity. This material was further purified by prep plate with toluene as the eluent to obtain the desired compound **9** in 25% yield as a yellow foam/semi-solid.

Characterization data for 8-aryl-menthol **9:**

R_f	0.19 (100% toluene, stains purple in anisaldehyde)
Opt. Rot.	-9.6° (c = 1.00 in CH_2Cl_2, 22 °C)
^{1}H NMR	(500 MHz, $CDCl_3$)
	^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 9.5 Hz, 1H), 8.28 – 8.16 (m, 5H), 8.11 – 8.05 (m, 3H), 3.86 (ddd, *J* = 13.2, 9.1, 3.4 Hz, 1H), 2.81 (ddd, *J* = 12.7, 9.6, 3.4 Hz, 1H), 2.03 – 1.90 (m, 1H), 1.97 (s, 3H), 1.83 (s, 3H), 1.75 – 1.65 (s, 1H), 1.57 – 1.45 (m, 1H), 1.27 (q, *J* = 12.3, 11.8 Hz, 1H), 0.95 (d, *J* = 6.6 Hz, 3H), 1.10 – 0.87 (m, 4H)
^{13}C NMR	(151 MHz, $CDCl_3$)
	^{13}C NMR (126 MHz, DMSO) δ 145.7, 131.7, 130.4, 130.2, 128.8, 127.6, 127.1, 126.5, 126.2, 126.1, 126.0, 125.5, 125.1 (2C), 124.9, 124.2, 73.5, 52.3, 45.7, 42.3, 35.1, 31.7, 28.4, 27.2, 27.0, 22.1
GC/MS	Retention time = 23.38 minutes, *m/*z = 356.21 $[M]^+$

3.28 **SI-12:** sulfonate precursor to **10**



Compound **SI-12** was obtained by sulfonylation of (–)-isopulegol with pyridine-2-sulfonyl chloride following a known procedure.[9]

A 5 mL round bottom flask was charged with a stir bar, anhydrous NEt_3 (0.5 mL, [2.3 M]) and (–)-isopulegol (1.15 mmol, 195 μL) under an Argon atmosphere. The solution was cooled to ~0 °C, then freshly prepared pyridine-2-sulfonyl chloride[9] (1.1 eq., 225 mg.) was added in one portion. The solution was stirred at 0 °C under an Argon atmosphere. After 3.25 hours, cold water (~2 mL) was added and the aqueous solution was extracted with cold Et_2O (3x 5 mL). The organic layer was washed with $NaHCO_3$ (3 mL of a 10% aqueous solution of a saturated $NaHCO_3$ solution, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting residue was purified by FCC on silica with a gradient elution of 25% Et_2O/hex to 60% Et_2O/hex. The desired compound **SI-12** was obtained in 48% yield (163 mg.; 54% brsm) as a yellow/white fluffy solid.

Characterization data of sulfonate ester **SI-12:**

R_f 0.13 (25% EtO_2/hex, anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

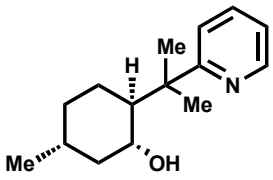
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.69 (m, 1H), 8.02 – 7.95 (m, 1H), 7.91 (td, *J* = 7.8, 1.7 Hz, 1H), 7.57 – 7.49 (m, 1H), 4.74 (td, *J* = 10.9, 4.6 Hz, 1H), 4.62 (s, 1H), 4.52 (s, 1H), 2.33 – 2.22 (m, 1H), 2.15 (ddd, *J* = 12.4, 10.5, 3.8 Hz, 1H), 1.74 – 1.60 (m, 2H), 1.60 – 1.46 (m, 1H), 1.52 (s, 3H), 1.44 – 1.18 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.98 – 0.85 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$). DEPT-Q

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 150.1, 145.0, 138.0, 127.3, 123.2, 112.9, 85.6, 50.9, 41.9, 33.8, 31.7, 30.5, 22.0, 19.9

ESI-LCMS 613.3 $(2M+Na)^+$; 318.1 $(M+Na)^+$

3.29 **10:** 8-(2-pyridyl)menthol



A 10 mL round bottom flask was charged with a stir bar, substrate **SI-12** (1.0 eq., 41.3 mg., 0.14 mmol.) and $Mn(dpm)_3$ (1.0 eq., 86 mg.). The reaction vessel was evacuated and refilled with nitrogen gas 3x on a vacuum manifold and then placed under positive pressure of Argon. Degassed anhydrous *i*-PrOH ([0.1 M, 1.4 mL) was

[9] Corey, E.J.; Posner, G.H.; Atkinson, R.F.; Wingard, A.K.; Halloran, D.J.; Radzik, D.M.; Nash, J.J. *J. Org. Chem.* **1989**, *54*(2), 389-393.

added, followed by $PhSiH_3$ (1.0 eq., 17.3 μL). The reaction was stirred for 24 hours, during the course of which the solution turned from clear and black to opaque and light yellow-brown in color. The precipitate that had formed in the reaction was filtered off and the filtrated was concentrated *in vacuo*. The resulting residue was purified by FCC on silica with a gradient from 100% CH_2Cl_2 to 50% Et_2O/hex. The desired compound **10** was obtained as a clear yellow oil in 89% yield (30 mg.)

Characterization data for 8-aryl menthol **10:**

R_f 0.23 (50% Et_2O/hex, stains pink in anisaldehyde)

Opt. Rot. -13.7° (c = 1.38 in CH_2Cl_2, 23 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.50 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.62 (td, *J* = 7.8, 1.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.09 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H), 3.24 (ddd, *J* = 10.6, 4.0 Hz, 1H), 1.92 – 1.76 (m, 3H), 1.69 – 1.59 (m, 1H), 1.40 (s, 3H), 1.39 (s, 3H), 1.46 – 1.31 (m, 1H), 1.04 – 0.92 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.92 – 0.79 (m, 2H)

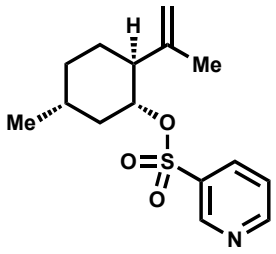
^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 148.1, 136.8, 120.9, 120.6, 73.3, 53.2, 45.0, 42.7, 35.1, 31.8, 29.8, 26.5, 24.0, 22.2 (Impurity at 30.4 ppm)

GC-MS (EI) Retention time: 8.42 minutes

m/z	% Max
233.1	0.24
201.2	9.25
200.1	59.0
134.1	37.0
122.1	9.66
121.1	100
120.1	52.0
118.1	9.34
117.1	7.67
106.1	24.0
93.1	11.0
92.0	6.68
79.0	6.47
78.1	6.88

3.30 **SI-13:** sulfonate precursor to **11**



A 5 mL round bottom flask was charged with a stir bar, (–)-isopulegol (1.0 eq., 1.02 mmol, 173 μL) and anhydrous NEt_3 ([2.3 M], 435 μL). The reaction was placed under positive pressure of Argon and then cooled to 0 °C in an ice bath. Next, pyridine 3-sulfonyl chloride (1.13 mmol, 200 mg., 134 μL) was added and the reaction was stirred for four hours, at which point TLC indicated consumption of isopulegol. The reaction was quenched by addition of water (1 mL) and extracted with Et_2O (3x 2 mL). The organic layer was washed with $NaHCO_3$ (sat'd. aq., 1x 1 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by FCC on silica with 30% Et_2O/hex as eluent. The desired product **SI-13** was obtained as a yellow-tinged white waxy solid in 84% yield (248 mg.)

Characterization data of sulfonate ester **SI-13:**

R_f 0.28 (40% EtO_2/hex, stains purple in anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

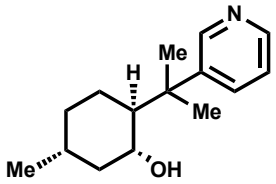
^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 2.4 Hz, 1H), 8.83 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.13 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.44 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H), 4.64 (s, 1H), 4.58 (p, *J* = 1.6 Hz, 1H), 4.54 (td, *J* = 10.9, 4.6 Hz, 1H), 2.31 – 2.23 (m, 1H), 2.13 (ddd, *J* = 12.6, 10.6, 3.9 Hz, 1H), 1.73 – 1.58 (m, 2H), 1.53 (m, 1H), 1.43, (s, 3H), 1.31 (m, 2H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.97 – 0.88 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 148.7, 144.9, 135.5, 134.6, 123.5, 113.3, 84.8, 50.7, 42.1, 33.7, 31.8, 30.5, 21.9, 19.6

ESI-LCMS 296.2 $(M+H)^+$

3.31 **11:** 8-(3-pyridyl)menthol



Compound **11** was obtained via the standard procedure **2.2A** with some modification. Specifically, substrate **SI-13** (1.0 eq., 49.1 mg., 0.166 mmol), $Mn(dpm)_3$ (0.1 eq, 10 mg.), $Mn(OAc)_3$•$2H_2O$ (1.0 eq., 45 mg.), $PhSiH_3$ (1.05 eq., 21.5 μL), TBHP (2.0 eq.) and degassed *i*-PrOH ([0.05 M], 3.3 mL) were used. The reaction was stirred at 4 °C for 48 hours, at which point TLC indicated full consumption of starting material. The reaction was then concentrated *in vacuo*. Water (5 mL) was added to the residue, which was then extracted with Et_2O (3x 5mL). The organic layer was washed with 2M NaOH (3x 3mL) and brine (1x 3mL), then dried over Na_2SO_4. The reaction was filtered and concentrated *in vacuo* to obtain a residue which was purified by FCC over silica with 100% EtOAc as eluent. The desired compound **11** was obtained as viscous yellow oil in 82% yield (32 mg.)

Characterization data for 8-arylmenthol **11:**

R_f 0.26 (100% EtOAc, stains purple in anisaldehyde)

Opt. Rot. -34.0° (c = 2.08 in CH_2Cl_2, 22 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 2.5 Hz, 1H), 8.38 (d, *J* = 3.3 Hz, 1H), 7.66 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.20 (dd, *J* = 8.1, 4.7 Hz, 1H), 3.46 (td, *J* = 10.4, 4.2 Hz, 1H), 1.85 (dtd, *J* = 12.3, 3.9, 2.1 Hz, 1H), 1.68 – 1.52 (m, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.42 – 1.31 (m, 1H), 1.31 – 1.12 (m, 1H), 1.02 – 0.91 (m, 2H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.90 – 0.75 (m, 1H)

(600 MHz, C_6D_6)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.43 (d, *J* = 4.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.82 (dd, *J* = 8.4, 4.6 Hz, 1H), 3.23 (td, *J* = 10.3, 4.1 Hz, 1H), 1.91 (s, 1H), 1.74 – 1.63 (m, 1H), 1.46 (td, *J* = 9.7, 9.3, 4.9 Hz, 1H), 1.43 – 1.32 (m, 2H), 1.39 (s, 3H), 1.29 (s, 3H), 1.06 (m, 1H), 0.86 (q, *J* = 11.7 Hz, 1H), 0.78 (d, *J* = 6.5 Hz, 3H), 0.65 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$). DEPT-Q.

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 146.6, 133.7, 123.0, 73.0, 54.1, 46.3, 39.3, 34.8, 31.7, 27.3, 26.8, 26.1, 22.1 (The quaternary aromatic carbon resonance overlaps with one of the other carbon resonances. Cf. with the spectrum in C_6D_6)

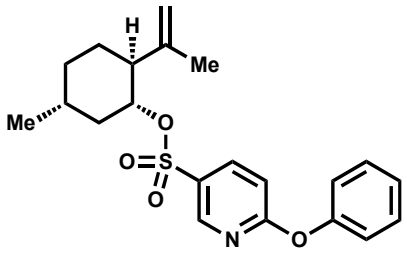
(151 MHz, C_6D_6)

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8, 146.8, 146.3, 133.6, 122.8, 72.7, 53.9, 46.8, 39.5, 35.0, 31.8, 27.5, 27.1, 26.8, 22.

GC-MS (EI) Retention time: 9.08 minutes

m/z	% Max
233.2	2.61
138.1	8.91
122.1	9.12
121.1	63.0
120.1	100
119.1	28.0
118.0	5.44
117.0	5.27
106.1	16.0
93.0	4.93
92.1	19.0
78.0	18.0

3.32 **SI-14:** sulfonate precursor to **12**



A 5 mL round bottom flask was charged with a stir bar, (–)-isopulegol (1.0 eq., 0.32 mmol., 55 µL), 6-phenoxypyridine-3-sulfonyl chloride (2.0 eq., 173 mg.) and DMAP (0.1 eq., 3.9 mg.). The reaction vessel was evacuated and filled with nitrogen 3x on a vacuum manifold and then placed under an Argon atmosphere. Anhydrous pyridine ([0.5 M], 640 µL) was added and the reaction was stirred for 24 hours. The reaction was concentrated *in vacuo*, diluted with CH_2Cl_2 (4 mL), washed with H_2O (1 mL), 2M HCl (aq., 1 mL), and brine (1 mL). The organic layer was dried over Na_2SO_4. The organic residue was concentrated and purified by FCC over silica (25 g.) with a gradient of hexanes (100 mL), 10% Et_2O/hex (100 mL), 20% Et_2O/hex (230 mL), 100% Et_2O (80 mL). The desired product **SI-14** was obtained as a clear, slightly white oil in 47% yield (58 mg.; 66% brsm).

Characterization data of sulfonate ester **SI-14:**

R_f 0.52 (25% EtO_2/hex, stains blue in anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$)

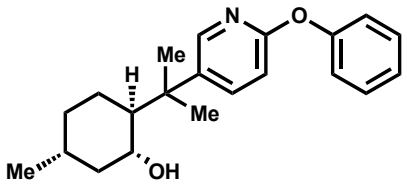
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.28 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 1H), 4.67 (s, 1H), 4.63 (s, 1H), 4.49 (td, *J* = 10.9, 4.6 Hz, 1H), 2.34 – 2.20 (m, 1H), 2.13 (td, *J* = 11.6, 3.6 Hz, 1H), 1.76 – 1.61 (m, 2H), 1.57 – 1.42 (m, 1H), 1.48 (s, 3H), 1.40 – 1.19 (m, 2H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.99 – 0.86 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 153.0, 148.3, 144.9, 139.1, 130.0, 128.8, 125.9, 121.5, 113.2, 111.3, 84.1, 50.8, 42.0, 33.7, 31.7, 30.5, 21.9, 19.7

ESI-LCMS 388.2 $(M+H)^+$

3.33 **12**: 8-(6-phenoxy-pyrid-3-yl)menthol



A 5 mL round bottom flask was charged with a stir bar, compound **SI-14** (1.0 eq., 23 mg., 0.06 mmol.), and $Mn(dpm)_3$ (1 eq., 36 mg.). The reaction vessel was evacuated and refilled with nitrogen gas 3x successively and then placed under positive pressure of Argon. Degassed *i*-PrOH ([0.1 M], 590 µL) was then added. The reaction was sonicated for ~20 min. to help dissolve the substrate. $PhSiH_3$ (1.0 eq., 7.3 µL) was added in one

portion and the reaction was stirred at ambient temperature. The solution turned opaque and a greyish-yellow color over the course of two hours, and TLC indicated nearly full consumption of starting material **SI-14**. The reaction was stirred for another hour, then concentrated directly *in vacuo* and purified by FCC over silica gel with a gradient of 50% Et_2O/hex to 100% Et_2O. The desired product **12** was obtained as a clear colorless oil in 75% yield (15 mg.).

Characterization data for 8-arylmenthol **12:**

R_f 0.21 (25% Et_2O/hex, stains pink in anisaldehyde)

Opt. Rot. -12.8° (c = 0.258 in CH_2Cl_2, 21 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

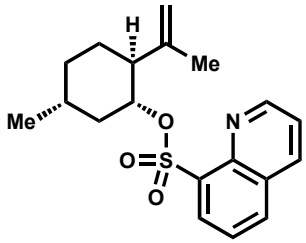
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 2.7, 0.7 Hz, 1H), 7.69 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.18 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.84 (dd, *J* = 8.6, 0.7 Hz, 1H), 3.48 (td, *J* = 10.3, 4.2 Hz, 1H), 1.86 (dtd, *J* = 12.3, 3.8, 2.1 Hz, 1H), 1.75 – 1.52 (m, 4H), 1.43 (s, 3H), 1.42 – 1.35 (m, 1H), 1.33 (s, 3H), 1.01 – 0.92 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.90 – 0.75 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8, 154.5, 145.2, 141.2, 137.9, 129.8, 124.6, 121.3, 110.8, 73.2, 54.1, 46.3, 38.8, 34.9, 31.7, 27.6, 26.8, 26.3, 22.1. (Impurity at 29.9 ppm)

ESI-LCMS 326.2 $(M+H)^+$

3.34 **SI-15:** sulfonate precursor to **13**



Same modifications to General Procedure 2.1B as for **SI-09**, obtaining an off-white powder (162mg, 88%).

Characterization data of sulfonate ester **SI-15:**

R_f 0.31 (40% EtOAc/hex, anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$)

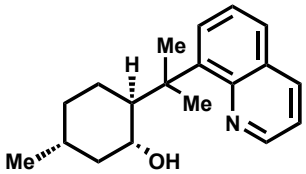
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (dd, *J* = 4.2, 2.0 Hz, 1H), 8.44 (d, *J* = 7.4 Hz, 1H), 8.22 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 8.5, 4.3 Hz, 1H), 4.68 (td, *J* = 10.9, 4.5 Hz, 1H), 4.35 (s, 1H), 3.92 (s, 1H), 2.27 (dt, *J* = 12.9, 3.8 Hz, 1H), 2.13 (td, *J* = 12.5, 11.7, 3.6 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.56 – 1.42 (m, 1H), 1.38 – 1.18 (m, 2H), 1.17 (s, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.96 – 0.77 (m, 1 H)

^{13}C NMR (101 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 144.8, 144.4, 136.3, 135.4, 134.3, 132.2, 129.0, 125.1, 122.3, 112.2, 85.1, 50.6, 42.2, 33.8, 31.8, 30.8, 22.0, 19.5

ESI-LCMS 346.1 $(M+H)^+$

3.35 **13:** 8-(8-quinolyl)menthol



A 10 mL round bottom flask was charged with a stir bar, substrate **SI-17** (1.0 eq., 40.0 mg., 0.113 mmol.) and $Mn(dpm)_3$ (1.0 eq. 68.2 mg.). The reaction vessel was evacuated and refilled with nitrogen gas 3x successively and then placed under positive pressure of Argon. Degassed and anhydrous *i*-PrOH ([0.1 M], 1.13 mL) was then added, followed by $PhSiH_3$ (1.0 eq., 13.9 μL). The reaction was stirred for 24 hours. A precipitate formed during the course of the reaction, and this precipitate was filtered off. The filtrate was concentrated *in vacuo* and then purified by FCC on silica with a gradient of 10% EtOAc/hex to 20% EtOAc/hex. The desired product **13** was obtained as a clear pale yellow oil in 78% yield (25 mg.).

Characterization data of 8-aryl menthol **13:**

R_f 0.55 (20% EtOAc/hex, stains pink in anisaldehyde)

Opt. Rot. -19.8° (c=1.00 in CH_2Cl_2, 24 °C)

^{1}H NMR (600 MHz, $CDCl_3$)

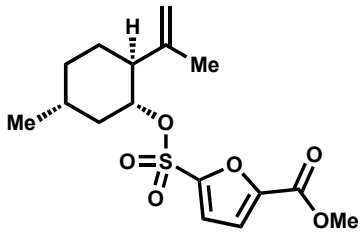
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.90 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.12 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.68 (td, *J* = 7.8, 1.4 Hz, 2H), 7.46 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.36 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.54 (td, *J* = 10.5, 4.1 Hz, 1H), 2.97 (ddd, *J* = 13.1, 10.3, 3.4 Hz, 1H), 2.39 (s, 1H), 1.82 (dtd, *J* = 12.4, 3.9, 2.3 Hz, 1H), 1.72 (s, 3H), 1.68 (s, 3H), 1.62 (s, 1H), 1.60 – 1.52 (m, 1H), 1.34 (m, 1H), 1.02 – 0.90 (m, 2H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.90 – 0.79 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 147.5, 147.3, 137.0, 129.5, 127.2, 127.1, 126.2, 120.5, 73.6, 51.4, 45.3, 42.4, 35.2, 31.9, 28.1, 27.8, 27.1, 22.2

ESI-LCMS 284.1 $(M+H)^+$

3.36 **SI-16**: sulfonate precursor to **14**



A 5 mL round bottom flask was charged with a stir bar, (–)-isopulegol (0.2 mmol, 34 μL) and anhydrous pyridine ([0.67 M], 300 μL) and the yellow black oil methyl 5-(chlorosulfonyl)furan-2-carboxylate (2.0 eq., 0.4 mmol, 90 mg.) under an Argon atmosphere at room temperature. The reaction was stirred for 24 hours and the reaction was concentrated directly *in vacuo*, azeotropically removing the pyridine with toluene. The reaction was purified by FCC on silica with toluene as the eluent. The resultant white/yellow gelatinous mass was still impure and so was purified by a second time by FCC with a gradient of 10% Et_2O/hex to 15% Et_2O/hex to obtain **SI-16** a viscous oil/white crystalline solid (18% yield, 12.3 mg.), which contained a small aromatic impurity but was taken on into the next reaction (towards **14**).

This reaction was repeated and a pure sample was obtained by prep plate purification with 100% benzene as eluent for the purposes of characterization.

Characterization data of sulfonate ester **SI-16:**

R_f 0.32 (100% benzene; stains purple in anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

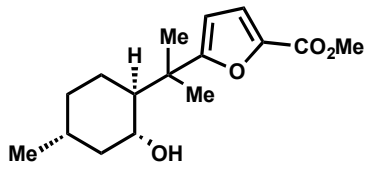
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 3.6 Hz, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 4.72 – 4.57 (m, 3H), 3.94 (s, 3H), 2.26 (dddd, *J* = 12.3, 5.0, 3.4, 1.8 Hz, 1H), 2.16 (ddd, *J* = 12.6, 10.6, 4.0 Hz, 1H), 1.73 (dq, *J* = 13.7, 3.5 Hz, 1H), 1.70 – 1.63 (m, 1H), 1.59 (dd, *J* = 1.5, 0.9 Hz, 3H), 1.60 – 1.50 (m, 1H), 1.40 – 1.26 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 3H), 1.01 – 0.87 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 149.0, 147.2, 144.7, 117.9, 117.7, 112.8, 87.1, 52.7, 50.5, 41.9, 33.7, 31.8, 30.6, 22.0, 20.2

ESI-LCMS 365.1 $[M+Na]^+$

3.37 **14:** 8-(methyl 2-furan-5-carboxylate)menthol



A 5 mL round bottom flask was charged with a stir bar, partially impure aryl sulfonyl **SI-16** (1.0 eq., 12.3 mg, 0.036 mmol) and $Mn(dpm)_3$ (1.05 eq., 22.8 mg). The reaction vessel was evacuated and refilled with nitrogen

gas 3x on a vacuum manifold and placed under positive pressure of argon. Degassed *i*-PrOH ([0.03 M], 720 μL) was then added. Finally, $PhSiH_3$ (1.05 eq., 4.7 μL) was added while stirring. The reaction was stirred for 22 hours, at which point TLC indicated consumption of starting material **SI-16**. The reaction was concentrated directly *in vacuo* and purified by FCC on silica with 25% Et_2O/hexanes. The resultant compound still contained impurities and so was further purified by prep plate with the same eluent system. The desired compound **14** was obtained as a clear viscous oil in 30% yield (3 mg).

Characterization data of 8-arylmenthol **14:**

R_f 0.34 (50% Et_2O/hex, stains purple in anisaldehyde)

Opt. Rot. Due to lack of material, a reliable measurement could not be obtained. (The methyl 5-(chlorosulfonyl)furan-2-carboxylate compound used to make the precursor **SI-16** is very expensive ($2.50/mg) and limits preparation of **SI-16**.)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 3.5 Hz, 1H), 6.12 (d, *J* = 3.5 Hz, 1H), 3.86 (s, 3H), 3.45 (td, *J* = 10.5, 4.2 Hz, 1H), 1.88 (dtd, *J* = 12.2, 3.8, 2.1 Hz, 1H), 1.81 (ddd, *J* = 12.0, 10.0, 3.4 Hz, 1H), 1.68 – 1.57 (m, 2H), 1.44 – 1.35 (m, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 1.21 – 1.30 (m, 1H), 1.10 – 0.90 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.93 – 0.76 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 159.5, 142.7, 119.3, 105.5, 72.7, 52.0, 51.8, 45.7, 38.5, 34.7, 31.7, 26.4, 26.3, 23.4, 22.1

GC-MS (ESI) Retention time: 9.47 minutes

m/z	% Max
280.2	3.0
221.2	7.16
168.1	18.0
167.1	100
166.1	6.13
153.1	14.0
135.0	4.13
95.1	2.62
79.1	5.30
77.0	3.38
55.1	2.70
153.1	14.0
135.0	4.13
95.1	2.62

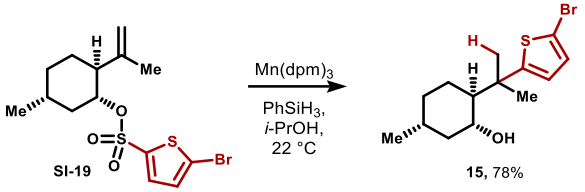
3.38 **SI-17**: sulfonate precursor to **15**

A magnetically stirred vial was charged with a solution of (-)-isopulegol (1.0 mmol, 0.169 mL, 1.0 eq.) in anhydrous pyridine (1 mL) at 22 °C under an atmosphere of air. To this solution was added 5-bromothiophene-2-sulfonyl chloride (1.5 mmol, 392 mg, 1.5 eq., Aldrich) and DMAP (0.2 mmol, 24.4 mg, 0.2 eq). The reaction vessel was capped and allowed to stir for 36 hours. The reaction mixture was then quenched with water (3 mL) and extracted with with DCM (10 mL). Collected organics were sequentially washed with 1N HCl (10 mL) followed by water (10 mL), Saturated sodium bicarbonate solution (10 mL), water (10 mL), and finally brine (10 mL). Organics were then dried over Na_2SO_4 and concentrated *en vacuo*. Residue was then subjected to silica gel chromatography with toluene as eluant and sulfonate ester **SI-17** was obtained as a white solid (228 mg, 60.1%). It should be noted that this compound decomposes into a brown tar upon prolonged storage on the laboratory bench, likely due to instability under light exposure, thus should be stored in the freezer and protected from light.

Characterization data of sulfonate ester **SI-17:**

R_f	0.68 (100% toluene, anisaldehyde)
^{1}H NMR	(400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 4.0, 0.7 Hz, 1H), 7.06 (dd, *J* = 4.0, 0.7 Hz, 1H), 4.70 (s, 2H), 4.51 (td, *J* = 10.9, 4.6 Hz, 1H), 2.29 – 2.19 (m, 1H), 2.14 (ddd, *J* = 12.7, 10.7, 3.7 Hz, 1H), 1.76 – 1.59 (m, 2H), 1.58 – 1.45 (m, 4H), 1.42 – 1.20 (m, 2H), 1.02 – 0.85 (m, 4H).
^{13}C NMR	(101 MHz, $CDCl_3$) δ 144.9, 138.6, 133.8, 130.2, 121.3, 113.2, 85.2, 50.8, 41.8, 33.7, 31.8, 30.5, 22.0, 19.8.
ESI-LCMS	*m/z* = 401.0, 403.2 $(M+Na)^+$

3.39 **15**: 8-(5-bromothiophen-2-yl)menthol



15 (37 mg, 78%) was prepared according to General Procedure 2.2A with the following adjustments: 1.0 equiv. substrate **SI-17** (0.15 mmol, 57 mg) was treated with 1.0 equv. $Mn(dpm)_3$ (0.15 mmol, 91 mg) and 1.08 equiv. phenylsilane (0.162 mmol, 20 µL) in *i*-PrOH (2 mL), reaction time = 23 hours.

Characterization data of 8-aryl-menthol **15:**

R_f 0.35 (20% Et_2O / Hexanes, bright yellow spot with anisaldehyde stain)

Opt. Rot. $[\alpha]_D^{22}$ = -0.411° (c = 1.540, EtOH)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 6.85 (d, *J* = 3.8 Hz, 1H), 6.59 (d, *J* = 3.8 Hz, 1H), 3.63 – 3.36 (m, 1H), 1.88 (ddd, *J* = 12.3, 6.1, 3.9 Hz, 1H), 1.73 – 1.58 (m, 2H), 1.51 (ddd, *J* = 13.3, 9.9, 3.4 Hz, 1H), 1.46 – 1.32 (m, 7H), 1.31 – 1.18 (m, 1H), 1.07 – 0.92 (m, 2H), 0.91 – 0.79 (m, 4H).

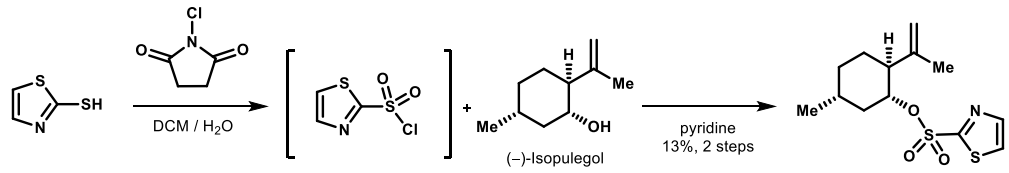
^{13}C NMR (101 MHz, $CDCl_3$)

δ 159.4, 129.2, 122.5, 109.7, 73.1, 55.2, 45.8, 40.6, 34.8, 31.6, 29.7, 27.3, 26.7, 22.1.

GC-MS (EI) Retention time: 9.78 minutes.

m/z	% Max
204.9	100.00
202.9	96.28
190.9	3.55
188.8	3.59
148.9	3.29
136.0	8.81
124.0	18.17
91.0	10.60
81.9	9.74
67.0	7.72
55.0	8.36

3.40 **SI-18**: sulfonate precursor to **16**



Sulfonyl chloride precursor to **SI-18** was prepared by adapting a reported patent procedure (unoptimized).[10] A 100 mL round bottom flask equipped with a magnetic stir bar was charged with a suspension of 2-mercaptothiazole (5.0 mmol, 586 mg, 1.0 eq.) in a biphasic mixture of water (15 mL) and DCM (15 mL). This flask was submerged in a room temperature water bath and rapidly stirred, and N-chlorosuccinimide (20.0 mmol, 2.67 g, 4.0 eq.) was added in a portion-wise fashion, so as to minimize the rise in temperature. After addition, biphasic mixture was allowed to continue stirring for 30 minutes and then diluted with an additional portion of DCM (25 mL) and partitioned in a reparatory funnel. The organic layer was then washed

[10] Portola Pharmaceuticals, Inc., *Preparation Of Heteroarylsulfonylureas And Related Compounds As Platelet ADP Receptor Antagonists*, 2002, US 20020077486.

sequentially with saturated bicarbonate solution, water, and brine before being dried over a minimal amound of sodium sulfate. Following drying, this solution of crude sulfonyl chloride was concentrated to a minimal volume of DCM and a solution of (-)-isopulegol (2 mmol, 0.338 mL, 0.4 eq. with respect to theoretical maximum of sulfonyl chloride) in anhydrous pyridine (4 mL) was added directly. Resulting solution was allowed to stir 24 hours, then quenched with water (10 mL) and extracted with diethyl ether (3x 15 mL). Combined organics were then washed sequentially with 1M H_2SO_4, water, saturated sodium bicarbonate solution, water and brine before being dried over magnesium sulfate. Organics were then removed by rotary evaporation and resulting crude product was chromatographed on silica gel using toluene as the eluting solvent to give the desired sulfonate ester **SI-18** as a beige solid (79 mg, 13% with respect to (-)-isopulegol).

Characterization data of sulfonate ester **SI-18:**

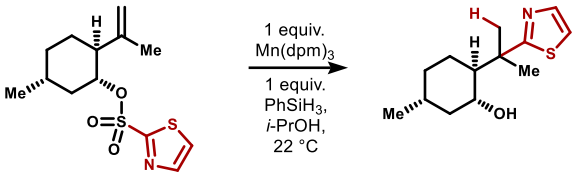
R_f 0.33 (100% toluene, anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)
δ 7.98 (d, *J* = 3.1 Hz, 1H), 7.70 (d, *J* = 3.1 Hz, 1H), 4.77 (td, *J* = 10.9, 4.6 Hz, 1H), 4.62 (s, 1H), 4.57 (s, 1H), 2.34 – 2.23 (m, 1H), 2.16 (ddd, *J* = 12.5, 10.8, 3.9 Hz, 1H), 1.71 (dq, *J* = 13.6, 3.5 Hz, 1H), 1.68 – 1.62 (m, 1H), 1.58 – 1.47 (m, 4H), 1.35 (qd, *J* = 13.2, 3.6 Hz, 1H), 1.28 (q, *J* = 12.1 Hz, 1H), 0.98 – 0.86 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$)
δ 162.4, 144.6, 144.4, 125.8, 113.0, 87.1, 50.7, 41.7, 33.7, 31.7, 30.4, 22.0, 20.0.

ESI-LCMS *m/z* = 301.8 $(M + 1)^+$

3.41 **16**: 8-(2-thiazolyl)menthol



16 (26.5 mg, 71%) was prepared according to General Procedure 2.2A with the following adjustments: 1.0 equiv. substrate **SI-18** (0.156 mmol, 47 mg) was treated with 1.1 equiv. $Mn(dpm)_3$ (0.172 mmol, 104 mg) and 2.0 equiv phenylsilane (0.162 mmol, 20 μL) in *i*-PrOH (2 mL), reaction time = 23 hours.

Characterization data of 8-aryl-menthol **16:**

R_f 0.36 (30% Et_2O / toluene, anisaldehyde stain)

Opt. Rot. $[\alpha]_D^{25}$ = -31.7° (c = 0.835, EtOH)

^{1}H NMR (600 MHz, C_6D_6) δ 7.42 (d, *J* = 3.3 Hz, 1H), 6.56 (d, *J* = 3.3 Hz, 1H), 3.22 (t, *J* = 10.1 Hz, 1H), 2.79 (s, 1H), 1.92 – 1.76 (m, 2H), 1.55 (dq, *J* = 13.1, 3.4 Hz, 1H), 1.48 (s, 3H), 1.46 –

1.41 (m, 4H), 1.11 (ddqt, *J* = 16.5, 13.4, 6.5, 3.6 Hz, 1H), 1.04 – 0.94 (m, 1H), 0.84 (qd, *J* = 13.0, 3.5 Hz, 1H), 0.78 (d, *J* = 6.5 Hz, 3H), 0.69 (qd, *J* = 13.0, 3.6 Hz, 1H).

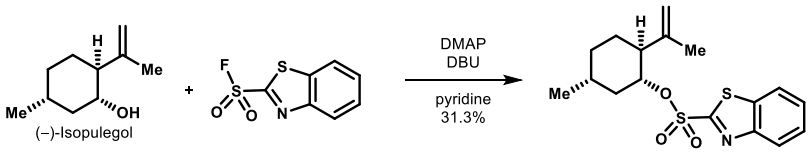
^{13}C NMR (151 MHz, C_6D_6)

δ 182.4, 141.9, 117.6, 73.1, 54.0, 45.7, 43.1, 35.1, 31.8, 30.0, 26.8, 26.7, 22.2.

GC-MS (EI) Retention time: 8.30 minutes.

m/z	% Max
239.1	1.77
211.2	7.13
154.1	6.99
140.1	49.87
127.1	100.00
112.0	32.41
95.1	8.79
85.9	8.36
58.9	11.77

3.42 **SI-19**: sulfonate precursor to **17**



A vial equipped with a magnetic stir bar and a rubber septum was charged with benzothiazole-2-sulfonyl fluoride (1.5 mmol, 326 mg, 1.5 eq., Synthonix) and DMAP (0.2 mmol, 24.4 mg, 0.2 eq), and put under a nitrogen atmosphere. Anhydrous pyridine (1 mL) was then introduced via syringe, followed by (-)-isopulegol (1.0 mmol, 0.169 mL, 1.0 eq.) and the suspension was allowed to stir at 22 °C for 1 hr and 45 mins. At this point, only a small amount of conversion was noted by TLC, so DBU was added (0.151 mL, 1.0 eq.), and the reaction mixture was noted to undergo a mild exotherm and a color change from milky-white to orange-brown. Reaction was allowed to continue stirring at ambient temperature for another 1 hour 10 minutes, at which point it was quenched by pouring into saturated sodium bicarbonate solution (10 mL). Resulting suspension was then extracted twice with DCM (10 mL), and dried over $MgSO_4$. Following concentration *en vacuo*, residue was subjected to silica gel chromatography with an 80:20:1 toluene:hexanes:Et_2O as eluant. Desired product solidified upon removal of eluant volatiles from product-containing fractions, but a minor benzimidazole-type impurity was observed in ^{1}H NMR spectra. This was easily removed via trituration of product with 5% Et_2O / Hexanes (2 mL). **SI-19** was thus obtained as a white powder (110 mg, 31.3%).

Characterization data of sulfonate ester **SI-19:**

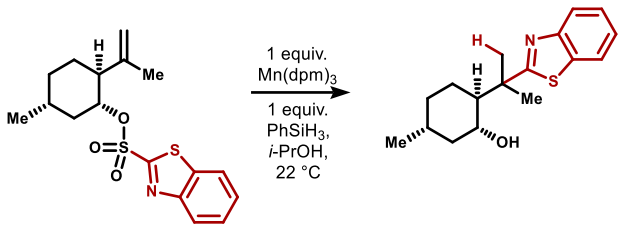
R_f 0.41 (80:20:1 toluene:hexane:Et_2O, anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (ddd, *J* = 8.2, 1.3, 0.7 Hz, 1H), 7.99 (ddd, *J* = 8.0, 1.3, 0.7 Hz, 1H), 7.64 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.61 – 7.58 (m, 1H), 4.87 (td, *J* = 10.9, 4.6 Hz, 1H), 4.62 – 4.58 (m, 1H), 4.39 (p, *J* = 1.5 Hz, 1H), 2.35 (dddd, *J* = 12.2, 4.9, 3.4, 1.9 Hz, 1H), 2.18 (ddd, *J* = 12.6, 10.7, 3.9 Hz, 1H), 1.71 (dq, *J* = 13.6, 3.5 Hz, 1H), 1.69 – 1.62 (m, 1H), 1.62 – 1.52 (m, 1H), 1.48 (dd, *J* = 1.4, 0.9 Hz, 3H), 1.40 – 1.29 (m, 2H), 0.97 – 0.89 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6, 152.1, 144.5, 136.9, 128.1, 127.7, 125.6, 122.2, 113.2, 87.7, 50.7, 41.8, 33.7, 31.8, 30.5, 22.0, 20.1.

ESI-LCMS *m/z* = 374.1 $(M+Na)^+$

3.43 **17:** 8-(2-benzothiazolyl)menthol



17 (3.9 mg, 57.1%) was prepared according to General Procedure 2.2A with the following adjustments: 1.0 equiv. substrate **SI-19** (0.024 mmol, 8.3 mg) was treated with 1.0 equv. $Mn(dpm)_3$ (14.3 mg) and 1.0 equiv phenylsilane (2.9 µL) in *i*-PrOH (1.0 mL), reaction time = 3 hours.

Characterization data of 8-Aryl-menthol **17:**

R_f 0.34 (15% Et_2O / Toluene, UV visualization)

Opt. Rot. $[\alpha]_D^{22}$ = -9.8° (c = 0.195, EtOH)

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.39 (m, 1H), 7.37 – 7.29 (m, 1H), 3.46 – 3.36 (m, 1H), 2.51 (d, *J* = 6.3 Hz, 1H), 2.01 (ddd, *J* = 13.1, 10.1, 3.4 Hz, 1H), 1.94 – 1.81 (m, 2H), 1.74 – 1.63 (m, 1H), 1.57 (s, 3H), 1.52 (s, 3H), 1.41 (dddd, *J* = 14.8, 12.9, 6.7, 3.3 Hz, 1H), 1.11 (qd, *J* = 13.0, 3.5 Hz, 1H), 1.04 (q, *J* = 12.0 Hz, 1H), 0.98 – 0.87 (m, 4H)

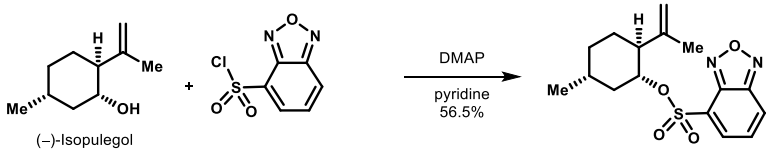
^{13}C NMR (151 MHz, $CDCl_3$) δ 184.2, 152.7, 134.8, 125.9, 124.7, 122.7, 121.6, 73.1, 53.6, 45.3, 43.6, 34.9, 31.8, 29.9, 26.4, 24.9, 22.1

GC-MS (EI) Retention time: 10.90 minutes.

m/z	% Max
289.1	1.34
256.0	2.74
190.0	24.07
177.0	100.00
162.0	24.21
149.0	5.76

136.0	10.75
109.0	12.46
95.0	7.81
69.0	5.84
55.1	6.78

3.44 **SI-20**: sulfonate precursor to **18**



A vial equipped with a magnetic stir bar was charged with 2,1,3-benzoxadiazole-4-sulfonyl chloride (2.0 mmol, 437 mg, 2 eq., Maybridge) and DMAP (0.2 mmol, 24.4 mg, 0.2 eq). (-)-Isopulegol (1.0 mmol, 0.169 mL, 1.0 eq.) in anhydrous pyridine (1 mL) was then added to the vial, and it was capped. The resulting solution was allowed to stir at room temperature for 48 hours. At this point the reaction mixture was diluted in DCM (10 mL) and washed sequentially with water (10 mL) followed by 1M H_2SO_4 (30 mL), then saturated sodium bicarbonate solution (10 mL), and finally brine (10 mL). Organics were then dried over $MgSO_4$ and concentrated *in vacuo*. Residue was then subjected to silica gel chromatography with toluene as eluant and sulfonate ester **SI-20** was obtained as a white solid (190 mg, 56.5%).

Characterization data of sulfonate ester **SI-20:**

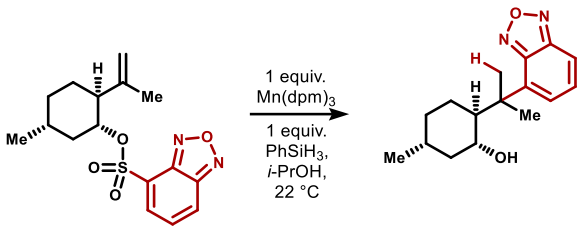
R_f 0.32 (100% toluene, anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.1 Hz, 1H), 8.05 (d, *J* = 6.8 Hz, 1H), 7.54 (dd, *J* = 9.1, 6.8 Hz, 1H), 4.69 (td, *J* = 10.8, 4.6 Hz, 1H), 4.36 (s, 1H), 4.19 – 4.02 (m, 1H), 2.41 – 2.21 (m, 1H), 2.21 – 2.02 (m, 1H), 1.71 – 1.59 (m, 2H), 1.59 – 1.47 (m, 1H), 1.40 – 1.21 (m, 5H), 0.98 – 0.84 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 145.0, 144.7, 133.8, 130.0, 127.2, 122.4, 112.5, 86.9, 50.4, 42.2, 33.6, 31.8, 30.7, 21.9, 20.2

ESI-LCMS *m/z* = 359.1 $(M+Na)^+$

3.45 **18**: 8-(4-benzofurazanyl)menthol



18 (6 mg, 15%) was prepared according to General Procedure 2.2A with the following adjustments: 1.0 equiv. substrate **SI-20** (0.150 mmol, 50.5 mg) was treated with 1.0 equv. $Mn(dpm)_3$ (0.150 mmol, 91 mg) and 1.0 equiv phenylsilane (0.150 mmol, 18.5 µL) in *i*-PrOH (1.5 mL), reaction time = 24 hours, purified by silica gel chromatography with first a short column of 40% Et_2O / Hexanes followed by preparative TLC with 20% Et_2O / Toluene.

Characterization data of 8-Aryl-menthol **18:**

R_f 0.44 (40% Et_2O / Hexanes, Seebach's stain)

Opt. Rot. $[\alpha]_D^{24} = +9.7°$ (c = 0.30, EtOH)

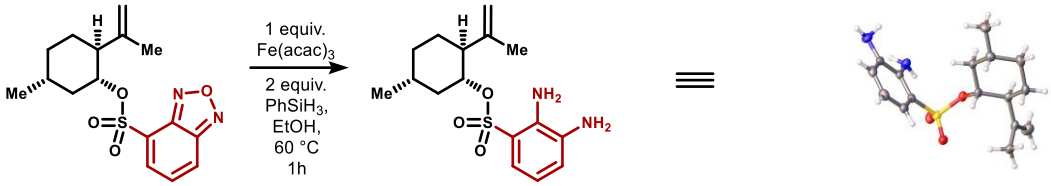
^{1}H NMR δ 7.63 (dd, *J* = 9.0, 0.7 Hz, 1H), 7.31 (dd, *J* = 9.0, 6.8 Hz, 1H), 7.16 – 7.12 (m, 1H), 3.58 (td, *J* = 10.5, 4.2 Hz, 1H), 2.53 (ddd, *J* = 12.1, 10.1, 3.4 Hz, 1H), 1.86 (dtd, *J* = 12.2, 3.9, 2.3 Hz, 1H), 1.61 – 1.50 (m, 6H), 1.48 – 1.37 (m, 4H), 1.05 (qd, *J* = 13.1, 3.5 Hz, 1H), 0.99 – 0.92 (m, 1H), 0.91 – 0.83 (m, 4H).

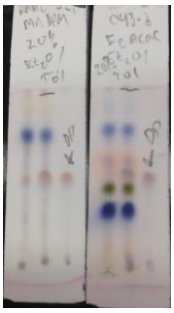
^{13}C NMR δ 150.2, 148.6, 142.8, 131.9, 124.9, 113.7, 73.2, 51.0, 46.0, 41.6, 34.7, 31.9, 26.8, 25.9, 25.1, 22.0.

GC-MS (EI) Retention time: 10.9 minutes.

m/z	% Max
274.0	3.19
259.0	4.29
185.0	2.61
175.0	3.33
162.0	68.13
143.1	44.27
130.0	60.80
119.0	100.00
95.1	59.51
67.0	22.27
55.0	33.74

3.46 **SI-21**: diamine product of benzofurazano double-NO bond reduction





When **SI-20** (39.3mg, 0.117 mmol, 1.0 equiv.) is instead treated with $Fe(acac)_3$ (41.3 mg, 0.117 mmol, 1.0 equiv.), and phenylsilane (0.234 mmol, 29 µL, 2.0 equiv) in EtOH (1.17 mL) under an argon atmosphere for 1 hour at 60 °C, product profile is notably different than above manganese conditions, with the major product isolated being **SI-21** (16 mg, 42%) as a clear solid which quickly turns orange on exposure to air. This product was confirmed by X-ray diffraction following crystallization from DCM. Different iterations (controlling for solvent and temperature differences) of this reaction were performed to confirm this was due to the metal selection. See TLC picture (anisaldehyde stain) – left is $Mn(dpm)_3$ promoted reaction, right is $Fe(acac)_3$ promoted reaction. Both are cospotted (left-most lane) with sample of 8-aryl menthol **18**.

Characterization data of diamino-sulfonate **SI-21:**

R_f 0.32 (20% Et_2O / Toluene, blue spot with anisaldehyde stain)

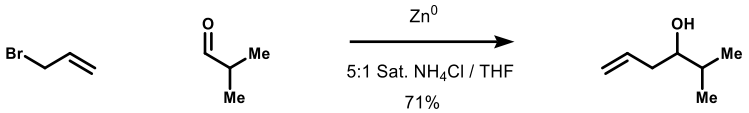
^{1}H NMR (600 MHz, $CDCl_3$)
δ 7.28 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.88 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.68 (t, *J* = 7.9 Hz, 1H), 4.91 – 4.43 (m, 4H), 4.38 (td, *J* = 10.8, 4.5 Hz, 1H), 3.45 (bs, 1H), 2.27 – 2.19 (m, 1H), 2.16 – 2.08 (m, 1H), 1.68 – 1.60 (m, 3H), 1.47 (dddd, *J* = 15.4, 12.2, 6.8, 3.4 Hz, 1H), 1.41 (s, 3H), 1.37 – 1.18 (m, 2H), 0.96 – 0.86 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$)
δ = 145.0, 136.4, 135.3, 121.5, 121.3, 120.4, 117.7, 112.9, 83.0, 51.1, 41.8, 33.8, 31.7, 30.6, 22.0, 19.1.

ESI-LCMS *m/z* = 324.9 $(M+H)^+$

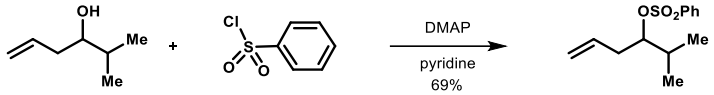
X-RAY See CCDC 1450888 at the Cambridge Crystallographic Data Center for supplementary crystallographic data.

3.47 **SI-22**: 2-methylhex-5-en-3-ol



SI-22 was synthesized by adapting a reported procedure.[11] To a open round-bottom flask eqipped with a magnetic stir bar and immersed in a room-temperature water bath was added zinc powder (10.0 mmol, 654 mg, 1 eq.). THF (2 mL) and saturated ammonium chloride solution (10 mL) were then added, followed by freshly-distilled isobutyraldehyde (10 mmol, 0.913 mL, 1.0 eq.) and allyl bromide (20 mmol, 1.73 mL, 2.0 eq.) in quick succession. Upon addition, vigorous stirring was commenced, and heat and gas evolution from the reaction mixture was noted. After 45 minutes of vigorous stirring, all zinc had been consumed and gas and heat evolution have ceased. Reaction mixture is extracted with diethyl ether (3x 25 mL), and dried over $MnSO_4$. Organics were carefully removed by rotary evaporator (caution: product is volatile and allyl bromide remains), and product was purified by silica gel chromatography (20% Et_2O / Pentane). Homoallylic alcohol **SI-22** was thus obtained as a yellow oil (815 mg, 71.4%). All NMR spectra match with previously reported values.[12]

3.48 **20a**: 2-methylhex-5-en-3-yl benzenesulfonate



Desired benzene sulfonate **20a** was synthesized according to General Procedure 2.1A with the following modifications: reaction is run at room temperature under air in a tightly capped vial. Substrate **SI-22** (0.5 mmol, 57 mg, 1.0 eq.) was treated with benzenesulfonyl chloride (1 mmol, 129 uL, 2.0 eq.) and catalytic DMAP (8 mg, 13 mol %) in anhydrous pyridine (0.5 mL, 1.0 M) to give homoallylic benzene sulfonate **20a** as a pale yellow oil (88 mg, 69%).

Characterization data of homoallylic benzene sulfonate **20a:**

R_f 0.37 (10% Et_2O / hexanes, anisaldehyde stain)

^{1}H NMR (600 MHz, $CDCl_3$)
δ 7.94 – 7.89 (m, 2H), 7.66 – 7.59 (m, 1H), 7.56 – 7.50 (m, 2H), 5.60 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.04 – 4.95 (m, 2H), 4.50 – 4.44 (m, 1H), 2.42 – 2.30 (m, 2H), 1.94 (heptd, *J* = 6.8, 5.2 Hz, 1H), 0.86 (t, *J* = 6.7 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.8, 133.6, 132.7, 129.2, 127.9, 118.5, 88.1, 35.9, 31.04, 18.2, 17.5.

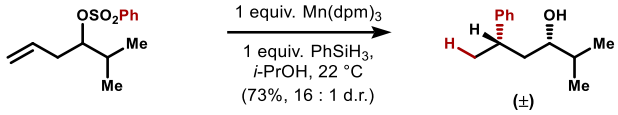
GC-MS (EI) Retention time: 8.18 minutes.

m/z	% Max
213.1	27.70
141.0	100.00
96.0	11.84
81.1	47.54
79.1	27.20
77.0	87.16
67.0	13.23

[11] C. Petrier, J. Luche, *The Journal of Organic Chemistry* 1985, *50*, 910-912.
[12] P. Cleary, K. Woerpel, *Org. Lett.* 2005, *7*, 5531-5533.

63.9	21.67
55.1	23.90

3.49 **20b**: 2-methyl-5-phenylhexan-3-ol



20b (29 mg, 73%) was prepared according to General Procedure 2.2A with the following adjustments: 1.0 equiv. substrate **20a** (0.204 mmol, 25.4 mg) was treated with 1.0 equv. $Mn(dpm)_3$ (0.204 mmol, 124 mg) and 1.0 equiv phenylsilane (0.204 mmol, 25 µL) in *i*-PrOH (2.0 mL), reaction time = 5 hours. Diastereomeric ratio was observed to be 16:1 by GC-FID, and product was isolated as a diastereomeric mixture. NMR Spectra were found to be identical to those previously reported,[13] and diastereomeric configuration was assigned accordingly.

Characterization data of alcohol **20b:**

R_f 0.32 (50:40:10 Hexanes : Toluene : Et_2O, Seebach's stain)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.17 (m, 3H), 3.55 – 3.41 (m, 1H), 2.93 (h, *J* = 7.0 Hz, 1H), 1.74 – 1.63 (m, 3H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 4.9 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 6H).

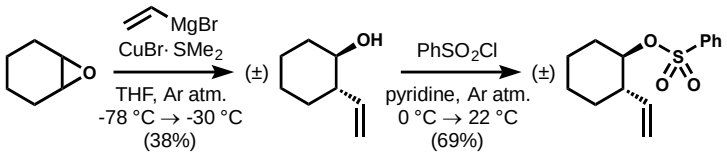
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 128.7, 127.0, 126.2, 74.9, 43.2, 36.9, 33.9, 21.6, 18.9, 17.1.

GC-MS (EI) Retention time: 6.35 minutes.

m/z	% Max
192.1	0.13
190.0	0.66
174.1	8.60
159.1	8.77
131.1	21.38
118.1	25.50
105.1	100.00
91.1	19.47
79.1	10.45
77.1	14.44
51.0	4.81

[13] M. Bossart, R. Fässler, J. Schoenberger, A. Studer, *Eur. J. Org. Chem.* **2002**, *2002*, 2742-2757.

3.50 **21a:** 2-vinylcyclohexyl benzenesulfonate



Compound **21a** was prepared in two steps from cyclohexene oxide following a modified literature procedure.[14] A 25 mL round bottom flask was charged with a stir bar, $CuBr•SMe_2$ (506 µL, 0.5 mmol, 0.1 eq.), and anhydrous THF (5.0 mL, [0.1 M] wrt to cyclohexene oxide) under an Argon atmosphere. This suspension was then cooled to ca. -78 °C using a CryoCool cooler and vinyl MgBr (6.5 mL, 1.3 eq. of a 1.0 M solution in THF) was added to the stirring solution. This mixture was allowed to stir at -78 °C for 30 minutes, at which time cyclohexene oxide was added slowly, but not dropwise. The reaction was warmed to -30 °C during the course of the next 1.5 hrs. TLC analysis indicated consumption of cyclohexene oxide after 1.25 hrs, so the reaction was quenched with NH_4Cl (saturated, aq., ~5 mL) and warmed to room temperature. This mixture was extracted with Et_2O (3x ~5 mL). The organics were combined, dried over Na_2SO_4, filtered off and concentrated *in vacuo*. The resulting crude residue was purified on silica gel in a 10% EtOAc/hexanes solvent system to obtain 242 mg. (38% yield) of the desired trans vinyl cyclohexanol (shown above) as a clear pale yellow oil. NMR data matched reported.[15]

Next, a 10 mL round bottom flask was charged with a stir bar, trans vinyl cyclohexanol (from above) (100 mg, 1.0 eq., 0.78 mmol.) and anhydrous pyridine. The reaction was cooled to 0 °C in ice bath. $PhSO_2Cl$ (152 µL, 1.19 mmol, 1.5 eq.) was added and the reaction was warmed to ambient temperature (22 °C). The reaction was stirred for 20 hours, at which point the reaction was quenched with NH_4Cl (~1 mL, aq., sat'd) and extracted with Et_2O (3x ~2 mL). The organic layer was washed with brine (~1 mL) and then dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified on silica gel with a 7.5% EtOAc/hexanes solvent system to obtain 146 mg. (69% yield) of the desired compound **21a** as a flaky white/yellow tinged solid.

Characterization data of sulfonate ester **21a:**

R_f 0.30 (10% EtOAc/hex, anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.87 (m, 2H), 7.65 – 7.60 (m, 1H), 7.56 – 7.48 (m, 2H), 5.40 (ddd, *J* = 17.2, 10.3, 7.8 Hz, 1H), 4.96 (dt, *J* = 17.2, 1.4 Hz, 1H), 4.84 (ddd, *J* = 10.3, 1.6, 0.7 Hz, 1H), 4.28 (td, *J* = 10.2, 4.4 Hz, 1H), 2.22 – 2.13 (m, 1H), 2.13 – 2.05 (m, 1H), 1.81 – 1.72 (m, 2H), 1.67 – 1.50 (m, 1H), 1.51 (tdd, *J* = 12.6, 10.6, 3.9 Hz, 1H), 1.32 – 1.24 (m, 1H), 1.21 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$)

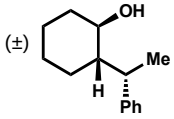
^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 137.7, 133.5, 129.1, 128.0, 116.2, 85.4, 47.2, 32.7, 31.2, 24.4 (2xC)

GC-MS (EI) Retention time: 9.44 minutes

[14] Yang, X.; Toste, D.F. *J. Am. Chem. Soc.* **2015**, *137*(9), 3205-3208.
[15] Jacolot, M.; Jean, M.; Levoin, N.; van Weghe, P. *Org. Lett.* **2012**, *14*(1), 58-61, SI pg 7 and references therein.

m/z	% Max
266.4	-
108.1	58.4
93.1	64.1
91.1	19.4
91	21.0
81.1	14.6
80.1	38.2
79.1	100
78	24.1
77	65.0
67.1	29.4
66.1	10.2
65.1	14.3
55.1	16.7
54.1	11.8
53.1	10.4
51	16.9

3.51 **21b**: (1*R*,2*S*)-2-((*S*)-1-phenylethyl)cyclohexan-1-ol



A 5 mL round bottom flask was charged with a stir bar, **21a** (20.0 mg., 0.075 mmol, 1.0 eq.), and $Mn(dpm)_3$ (1.01 eq., 46 mg.). The reaction vessel was evacuated and refilled with nitrogen gas 3x on a vacuum manifold, then placed under positive pressure of Argon. Degassed *i*-PrOH [0.1 M, 750 μM] was added, followed by $PhSiH_3$ (1.01 eq., 9.3 μL) and the reaction was stirred at room temperature. The reaction was complete after 1.25 hrs (via TLC and GCMS), so the reaction was quenched by addition of ~1 mL of aq. NH_4OH (aq., sat'd.), extracted with EtOAc (3x 1mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by FCC on silica with 8% EtOAc/hex to obtain the desired product **21b** as a clear, pale yellow oil in 75% yield (11.5 mg.). The other possible diastereomer was not observed in the ^1H spectrum or by GC/MS, therefore we consider the diastereoselectivity for this reaction to be ≥20:1.

Characterization data of alcohol **21b:**

R_f 0.26 (25% Et_2O/hex, stains purple in anisaldehyde)

^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 2H), 7.19 – 7.17 (m, 1H), 3.47 (td, *J* = 9.6, 4.5 Hz, 1H), 3.33 (qd, *J* = 7.2, 4.1 Hz, 1H), 2.03 – 1.94 (m, 1H), 1.73 – 1.67 (m, 1H), 1.62 – 1.54 (m, 1H), 1.54 – 1.44 (m, 2H), 1.25 (d, *J* = 7.2 Hz, 3H), 1.30 – 1.20 (m, 3H), 1.12 – 0.99 (m, 2H)

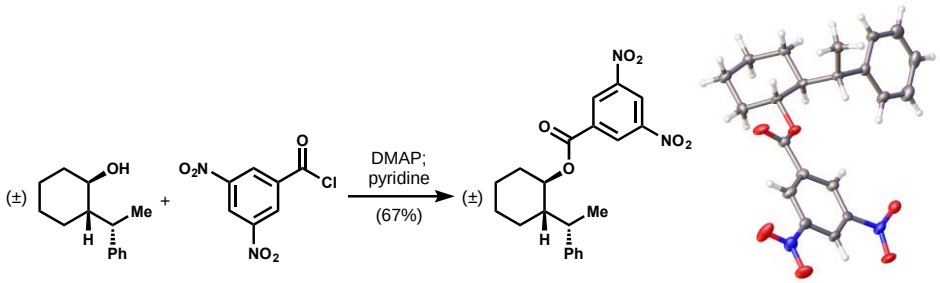
^{13}C NMR (151 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 128.3, 128.0, 125.9, 72.4, 51.6, 38.5, 36.1, 25.6, 25.0, 24.7, 14.0

GC-MS (EI) Retention time: 7.32 minutes

m/z	% Max
204.2	0.11
186.1	26.03
171.1	11.62
143.1	14.03
129.1	22.06
128.1	13.42
118.1	20.2
117.1	12.23
115.1	15.73
106.1	34.26
104	16.36
103	14.66
91.1	38.49
81.1	16.43
80.1	10.09
79.1	20.07
78	12.33
77	23.26

3.52 **SI-23:** (±)-(1*R*,2*S*)-2-((*S*)-1-phenylethyl)cyclohexyl 3,5-dinitrobenzoate



Crystalline compound **SI-23** was prepared from **21b** via the following procedure.[16] A 5 mL round bottom flask was charged with a stir bar, alcohol **21b** (1.0 eq., 10 mg., 0.049 mmol), CH_2Cl_2 ([0.075 M], 650 µL), DMAP (5.0 eq., 30 mg.) and 3,5-dinitrobenzoyl chloride (3 eq., 34 mg.) at room temperature. The stirring solution immediately turned red and a white precipitate formed upon addition of 3,5-dinitrobenzoyl chloride. After 15 minutes, the reaction was quenched by addition of $CuSO_4$ (~1 mL) and the aqueous layer was extracted with CH_2Cl_2 (4x 1mL). The organic layer was dried over Na_2SO_4, filtered and concentrated. The resulting residue was flushed through a silica plug with 10% Et_2O/hexanes (20 mL) and concentrated *in vacuo* to obtain the desired product **SI-23** as a pale yellow oil (13 mg., 69% yield). X-ray quality crystals were grown from hot hexanes by slow evaporation.

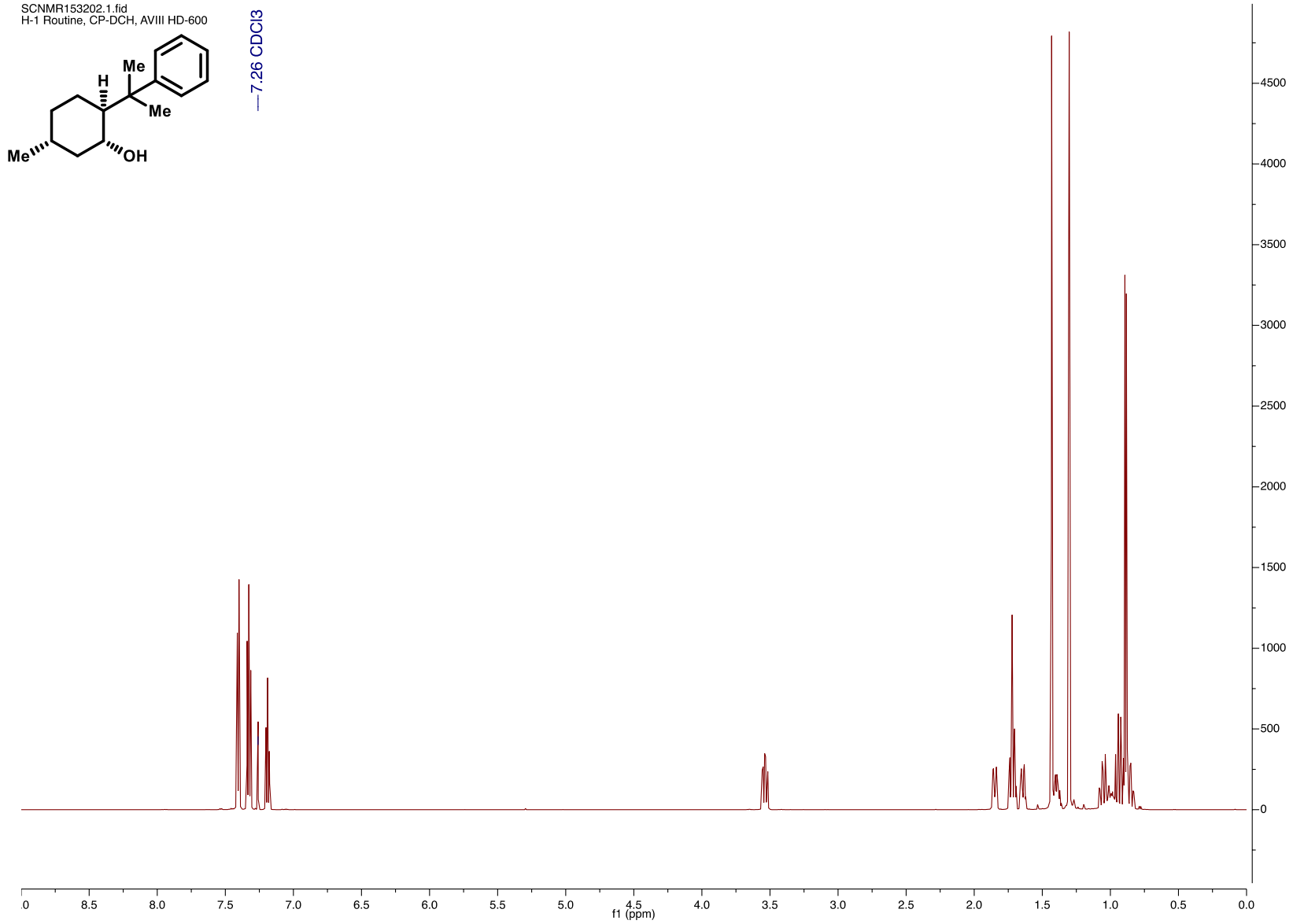
Characterization data of sulfonate ester **SI-23:**

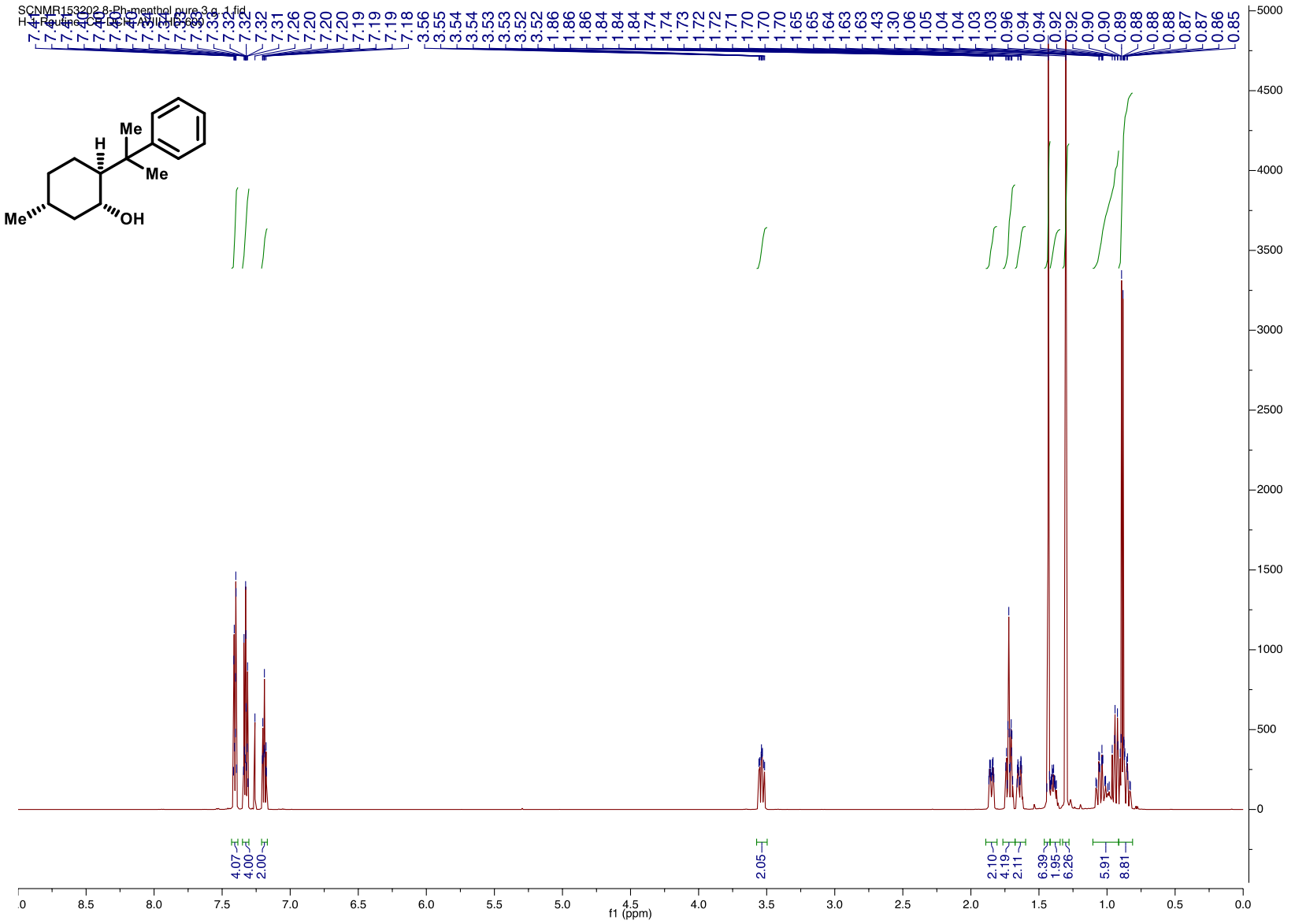
R_f	0.21 (5% Et_2O/hex, stains purple in anisaldehyde)
^{1}H NMR	(600 MHz, $CDCl_3$)
	^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.16 (q, *J* = 1.9 Hz, 1H), 8.90 (t, *J* = 1.7 Hz, 2H), 7.18 – 7.10 (m, 4H), 6.89 (td, *J* = 7.1, 1.6 Hz, 1H), 5.07 (td, *J* = 10.0, 4.4 Hz, 1H), 2.87 (p, *J* = 7.0 Hz, 1H), 2.10 – 2.02 (m, 2H), 1.91 – 1.85 (m, 1H), 1.85 – 1.79 (m, 1H), 1.75 (q, *J* = 4.2 Hz, 1H), 1.54 – 1.38 (m, 2H), 1.30 – 1.23 (m, 2H), 1.21 (dd, *J* = 7.1, 1.2 Hz, 3H)
^{13}C NMR	(151 MHz, $CDCl_3$)
	^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 148.5, 146.9, 134.2, 129.4, 128.4, 127.4, 125.6, 122.2, 78.9, 47.5, 41.2, 32.2, 26.5, 25.1, 24.5, 17.2
ESI-LCMS	399.2 $[M+H]^+$
X-RAY	See CCDC 1451757 at the Cambridge Crystallographic Data Center for supplementary crystallographic data.

[16] McKerrall, S. J.; Jorgensen, L.; Kuttruff, C. A.; Ungeheuer, F.; Felding, J.; Baran, P. S. *J. Am. Chem. Soc.*, **2014**, *136*(15), 5799-5810. SI-12

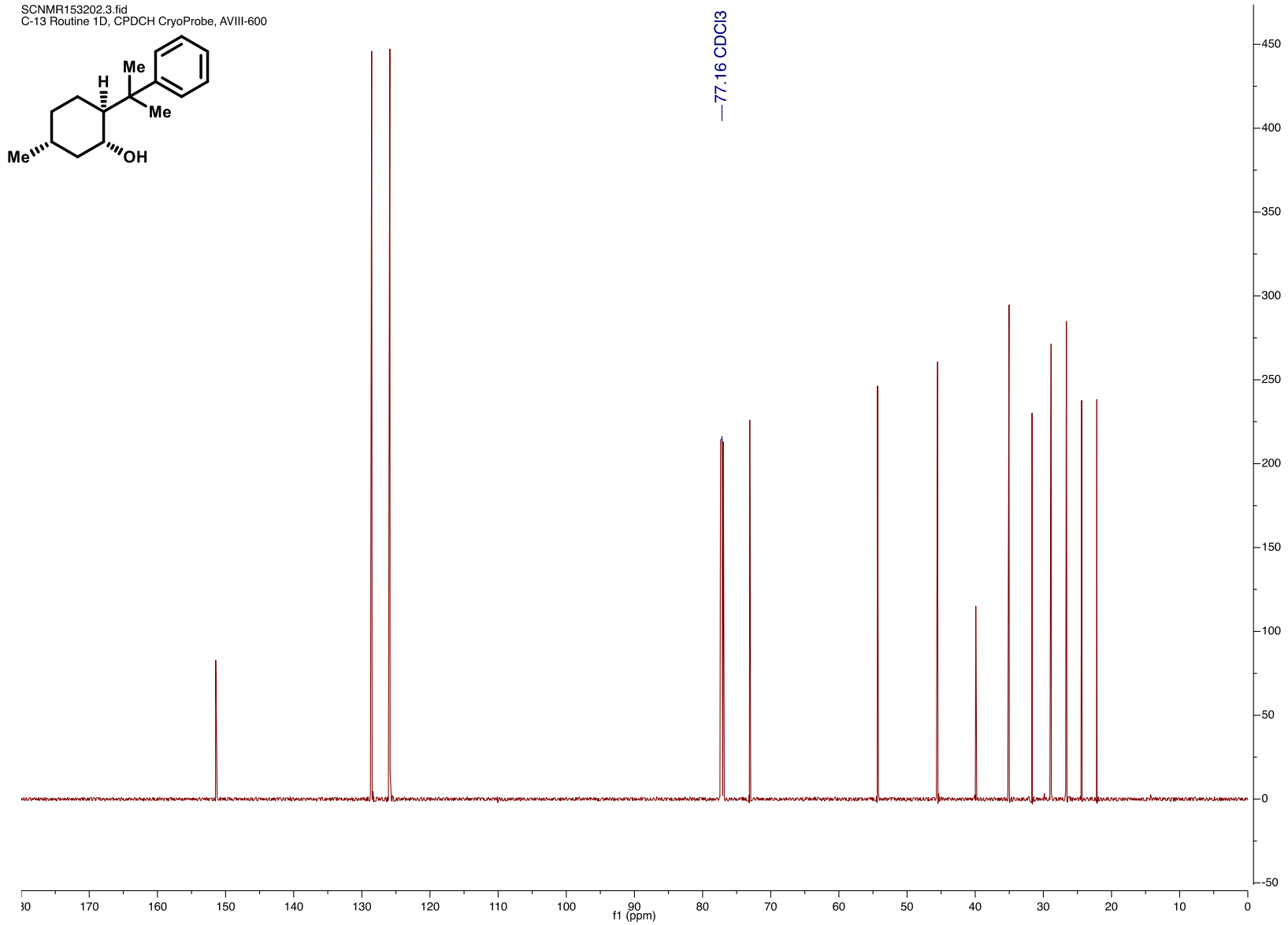
4. NMR Spectra

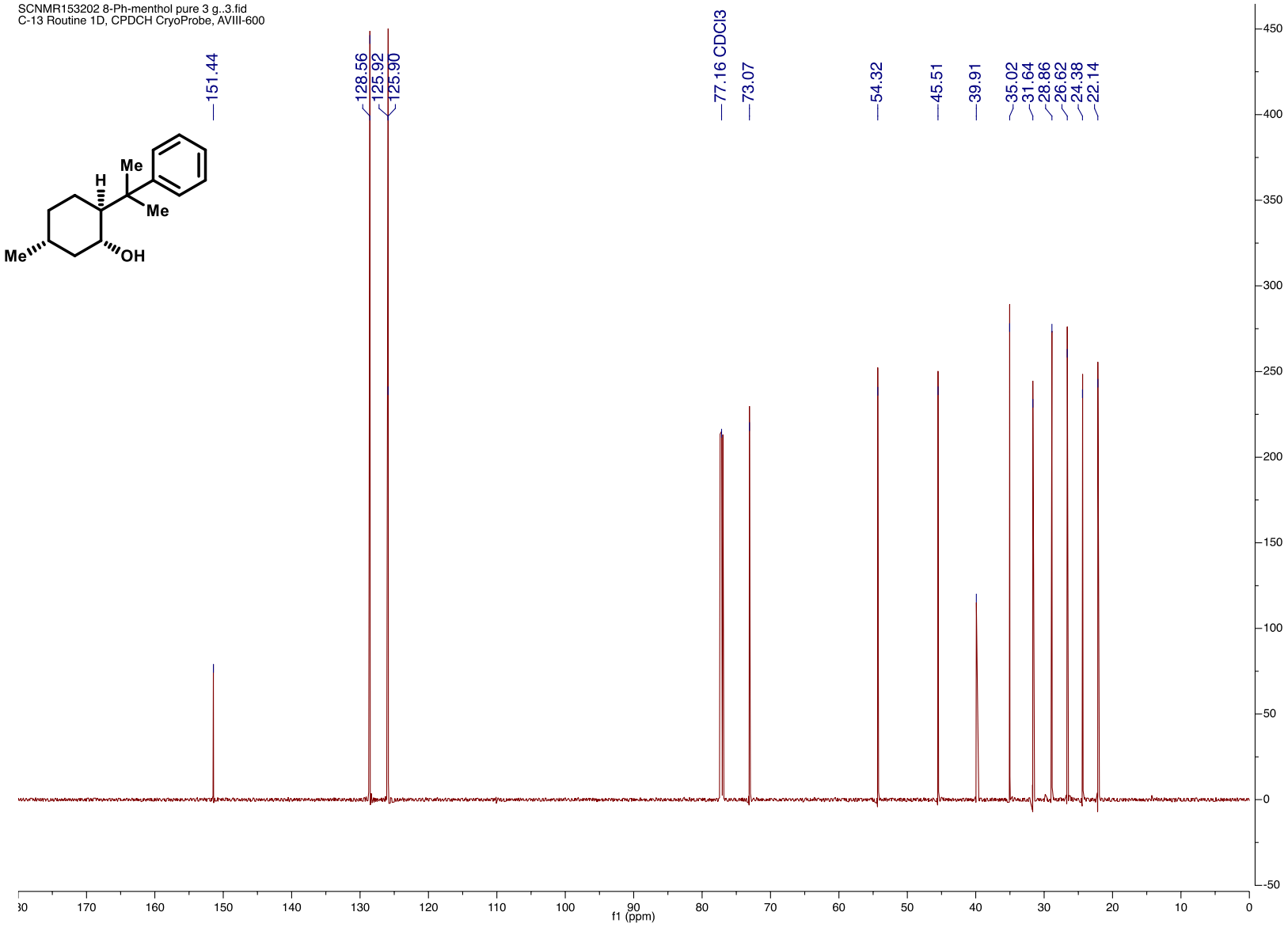
(-)-1: 8-phenylmenthol ^{1}H-NMR



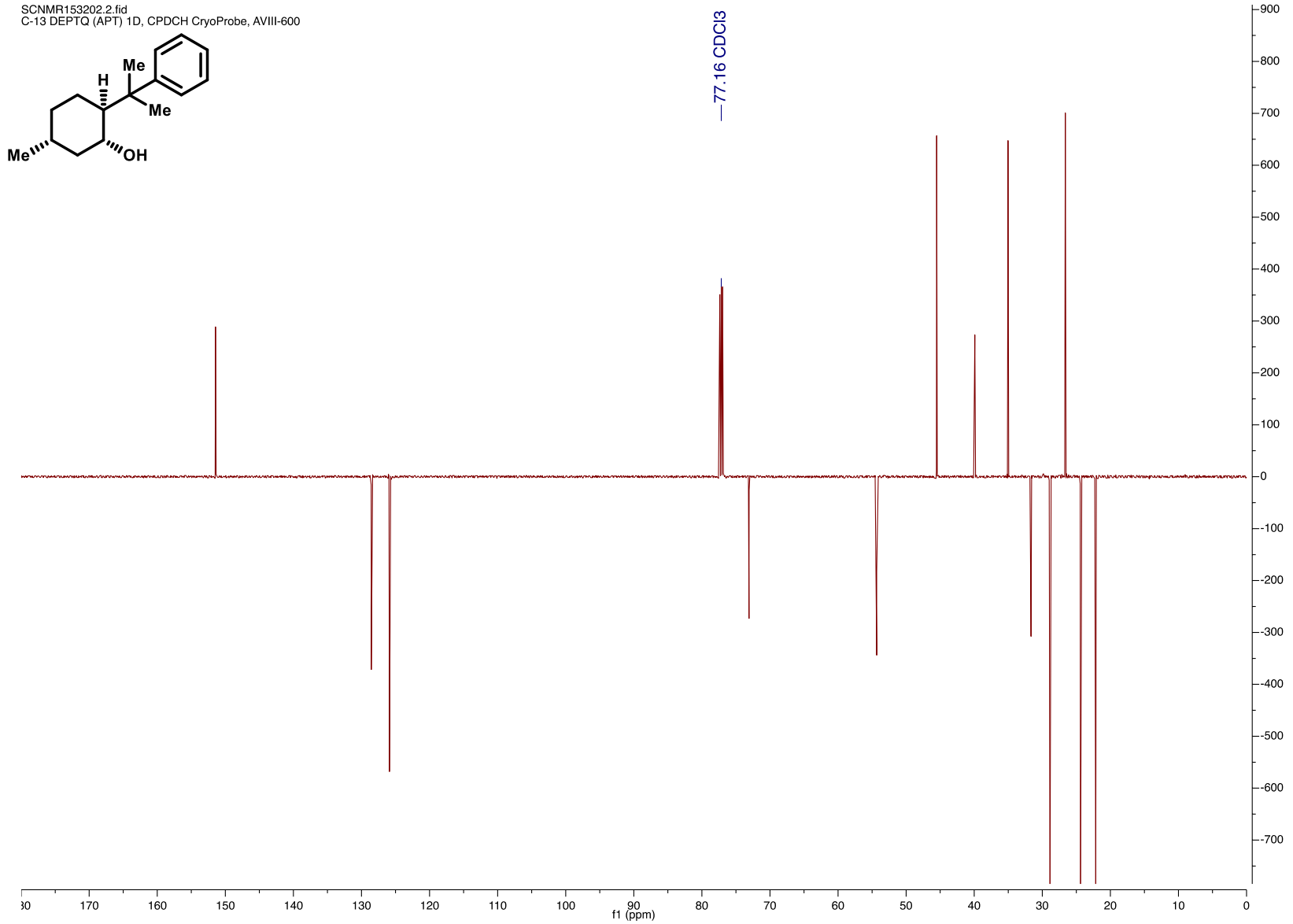

SCNMR153202.8-Ph-menthol pure 3.g.1.fid
H-1-Routine_CDCl3_DEPT-Aviii-ns8-600
Me
H
Me
Me
OH
f1 (ppm)

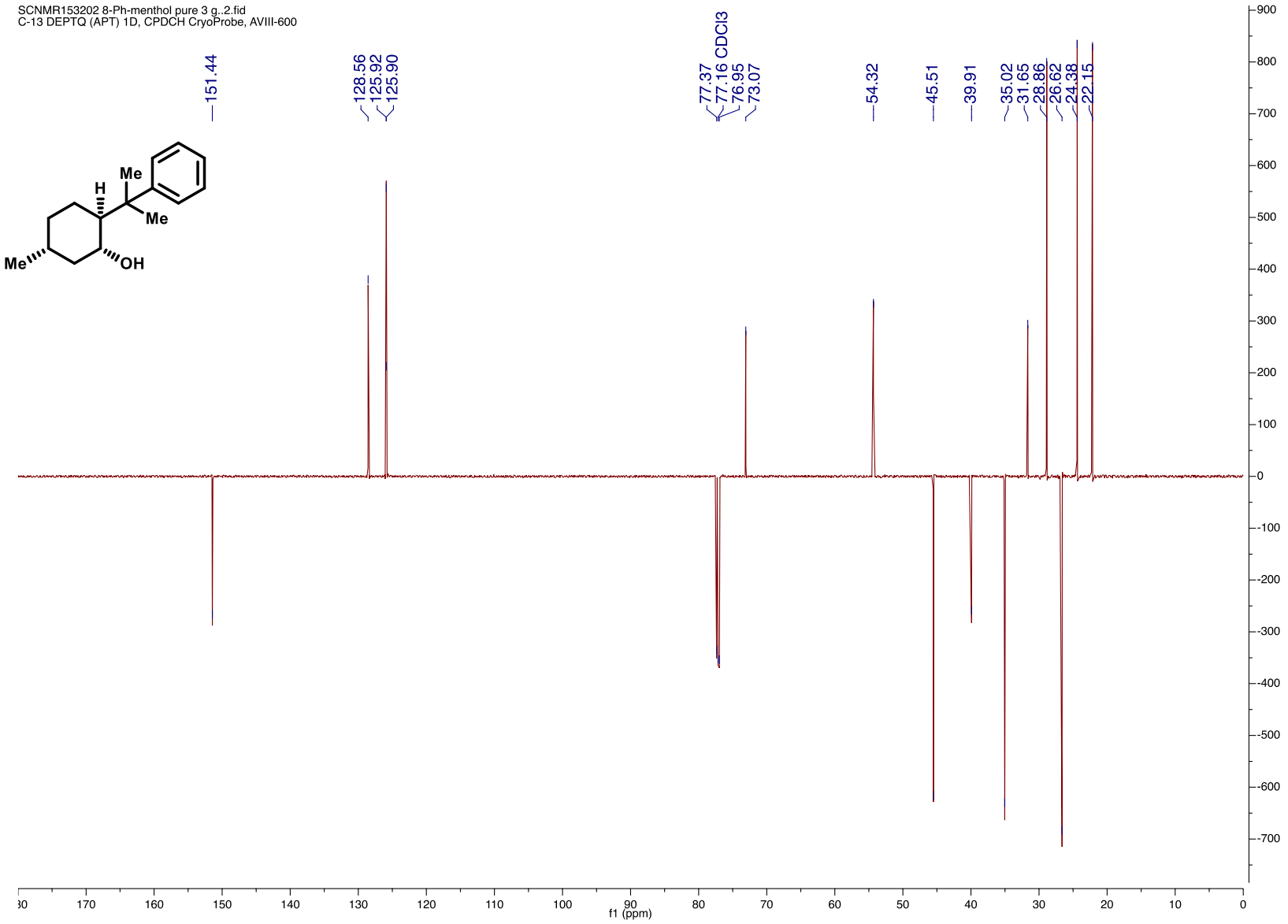
(-)-1: 8-phenylmenthol ^{13}C-NMR



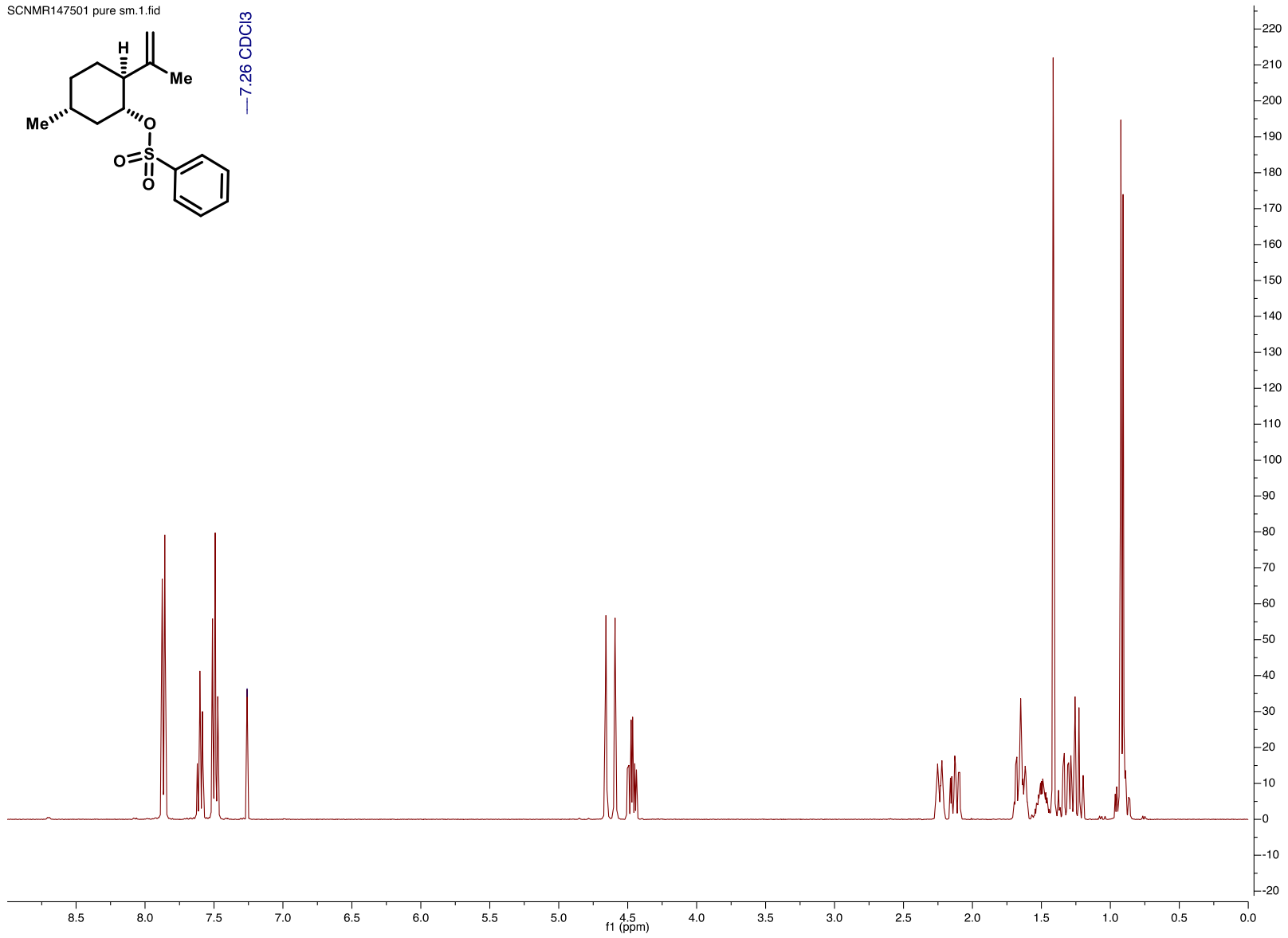

SCNMR153202 8-Ph-menthol pure 3 g..3.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
151.44
128.56
125.92
125.90
77.16 CDCl3
73.07
54.32
45.51
39.91
35.02
31.64
28.86
26.62
24.38
22.14
Me
H
Me
Me
OH
f1 (ppm)

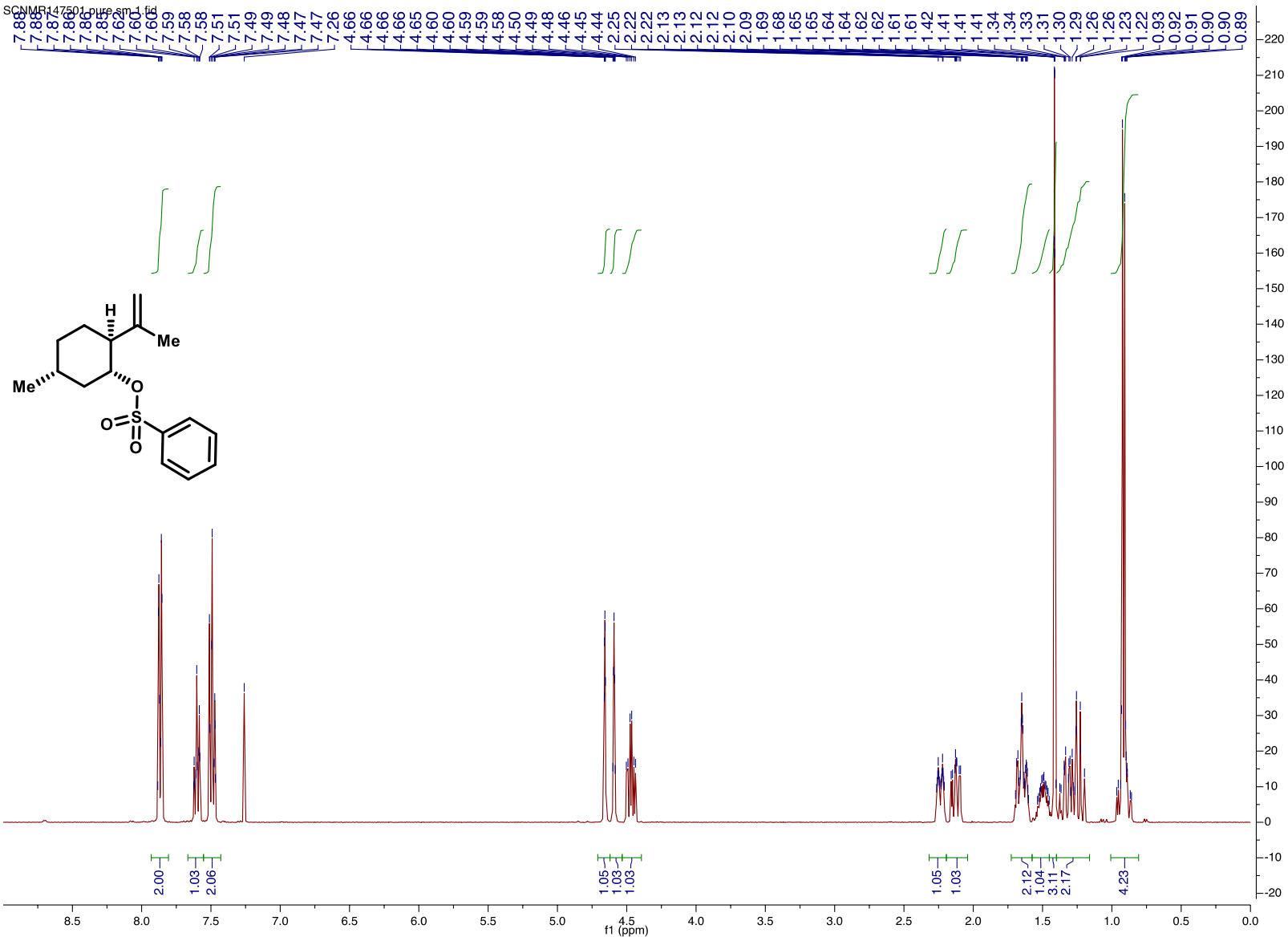
(-)-1: 8-phenylmenthol ^{13}C-DEPT-Q



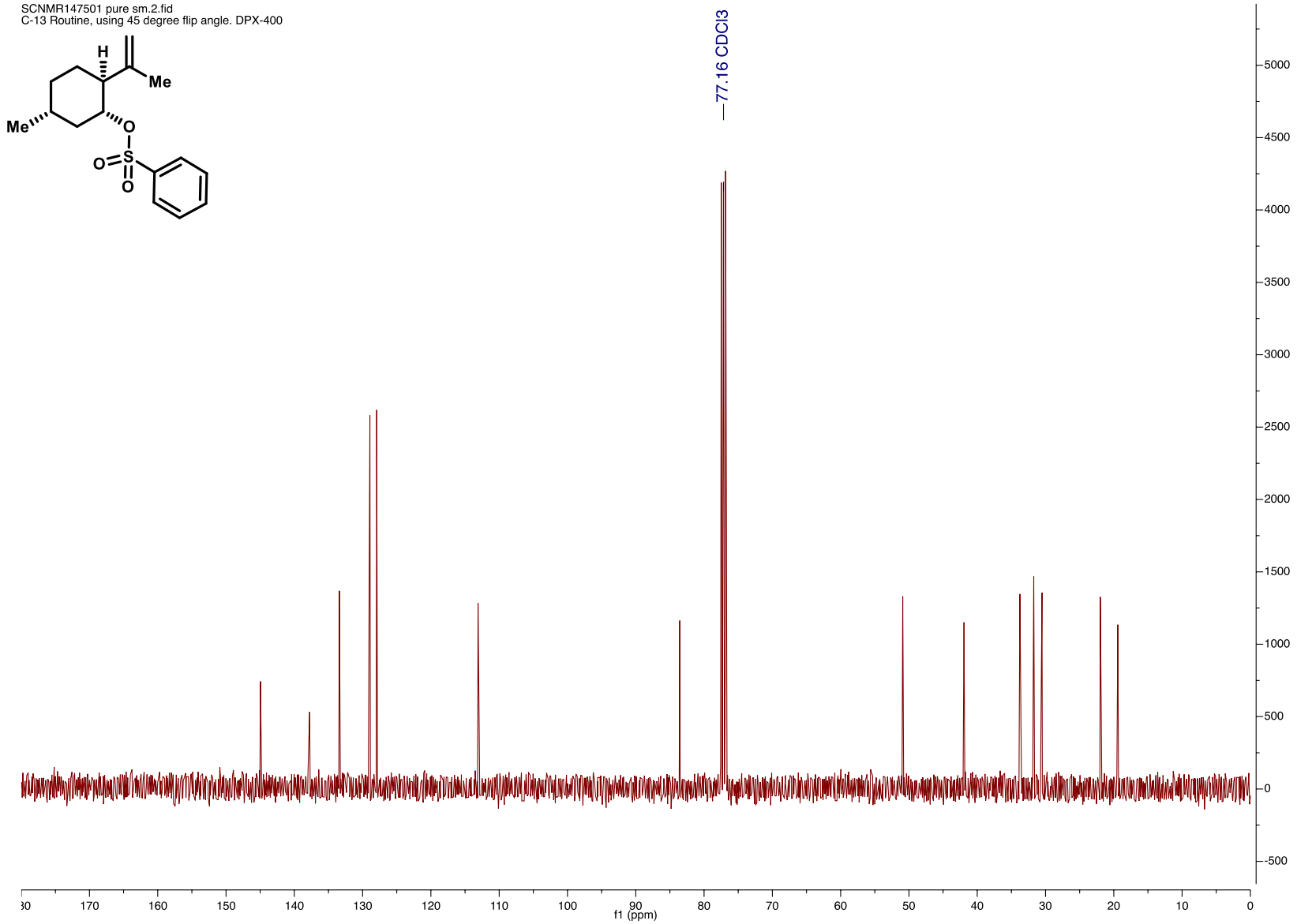

SCNMR153202 8-Ph-menthol pure 3 g..2.fid
C-13 DEPTQ (APT) 1D, CPDCH CryoProbe, AVIII-600
151.44
128.56
125.92
125.90
77.37
77.16 CDCl3
76.95
73.07
54.32
45.51
39.91
35.02
31.65
28.86
26.62
24.38
22.15
Me
H
Me
Me
OH
f1 (ppm)

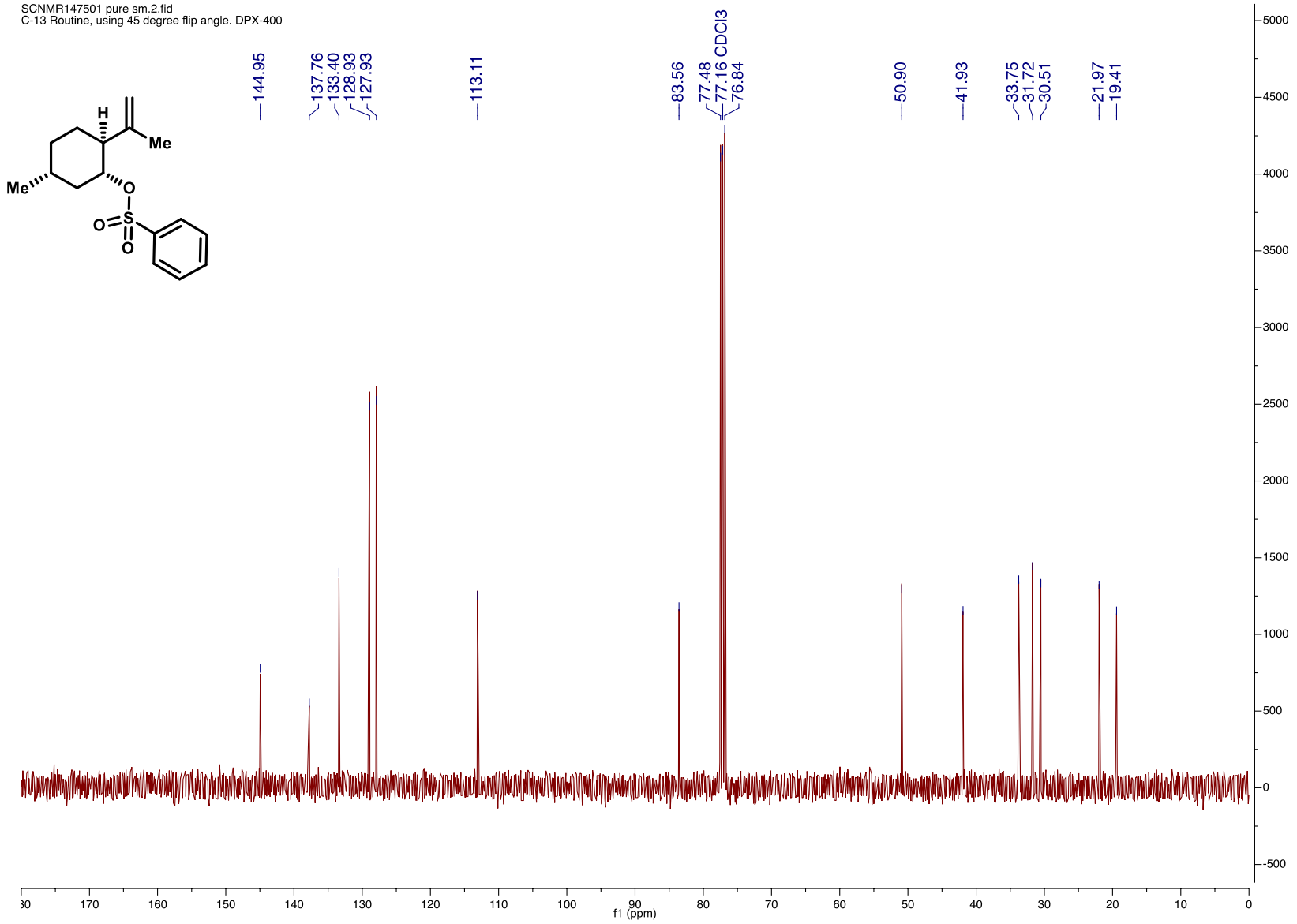
3 ^{1}H-NMR


SCNMR147501 pure sm.1.fid
7.26 CDCl3
H
Me
Me
O
O
S
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
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
f1 (ppm)

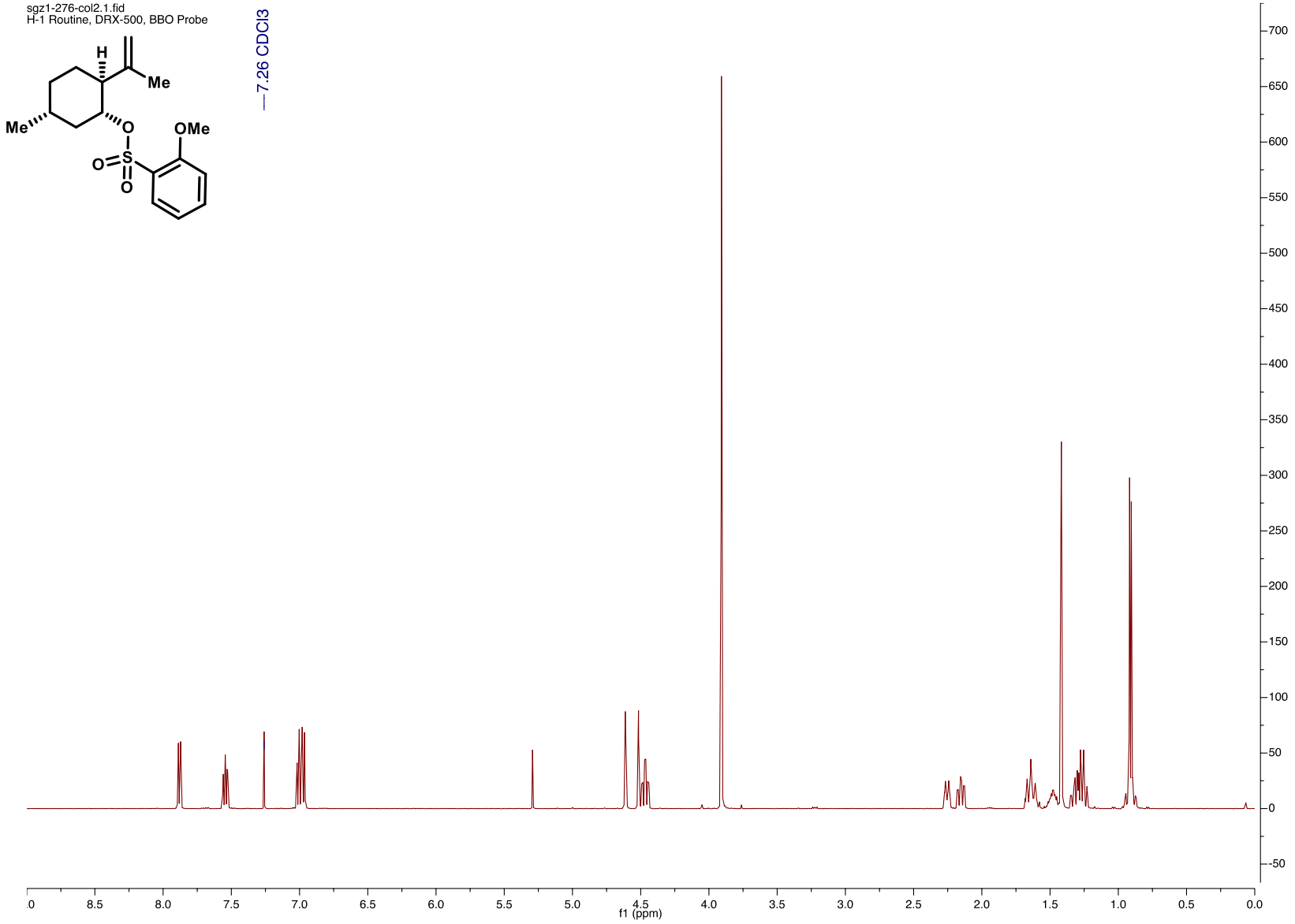

SCNMR147501-pure-sm-1.fid
H
Me
Me
O
O
S
O
O
f1 (ppm)

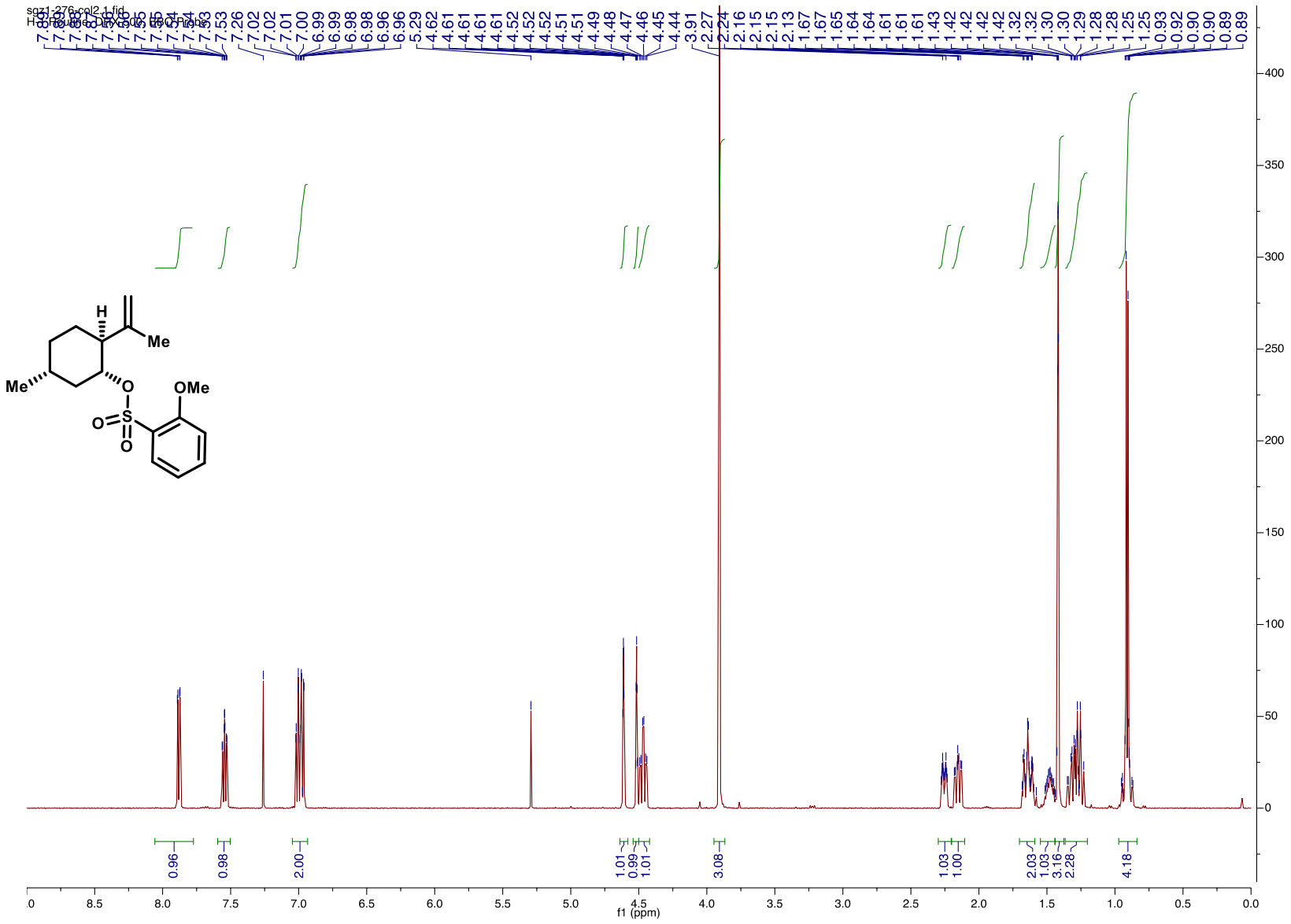
3 ^{13}C-NMR


SCNMR147501 pure sm.2.fid
C-13 Routine, using 45 degree flip angle. DPX-400
H
Me
Me
O
O
S
O
O
77.16 CDCl3
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

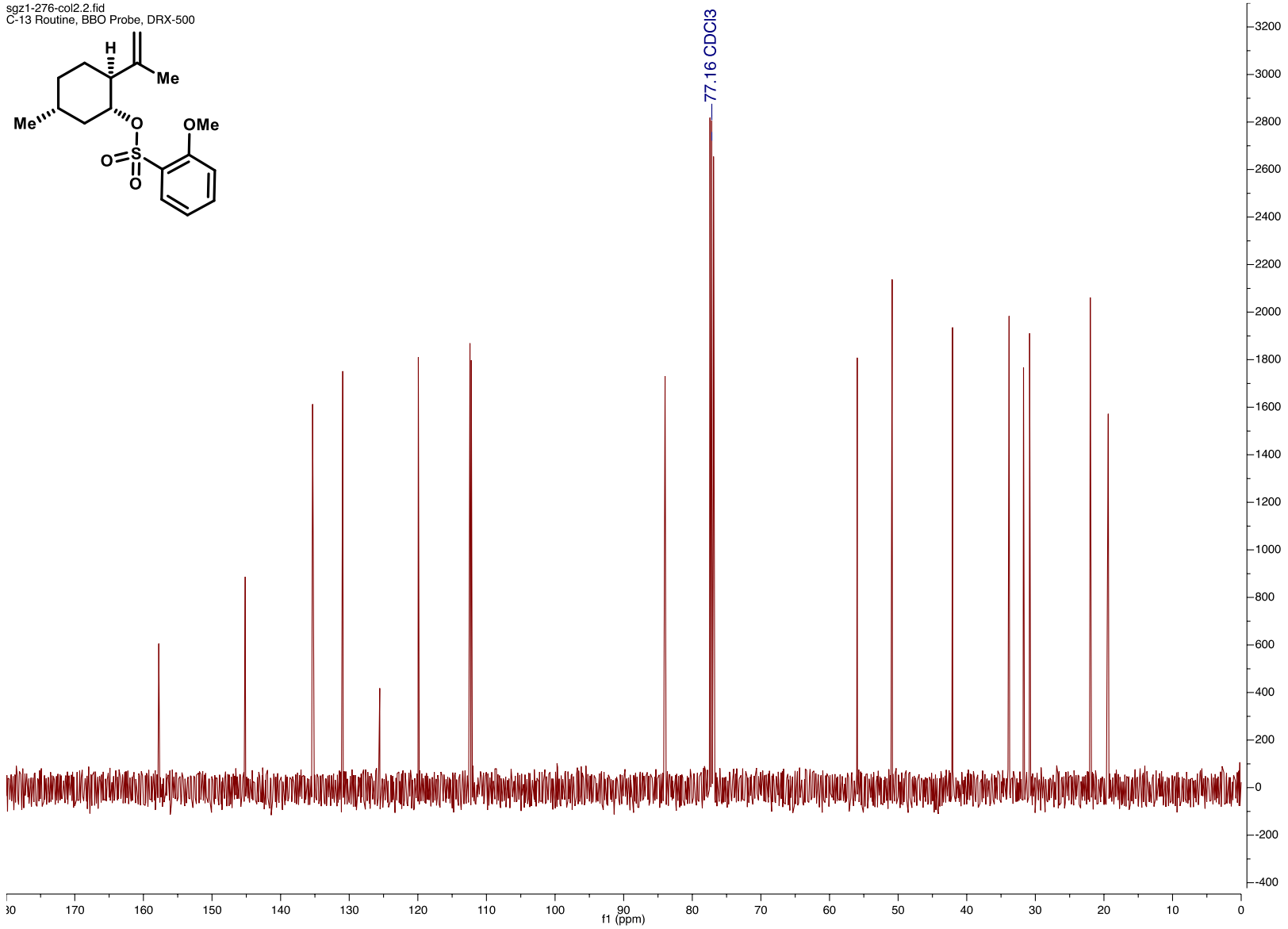

SCNMR147501 pure sm.2.fid
C-13 Routine, using 45 degree flip angle. DPX-400
144.95
137.76
133.40
128.93
127.93
113.11
83.56
77.48
77.16 CDCl3
76.84
50.90
41.93
33.75
31.72
30.51
21.97
19.41
H
Me
Me
O
O
S
O
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

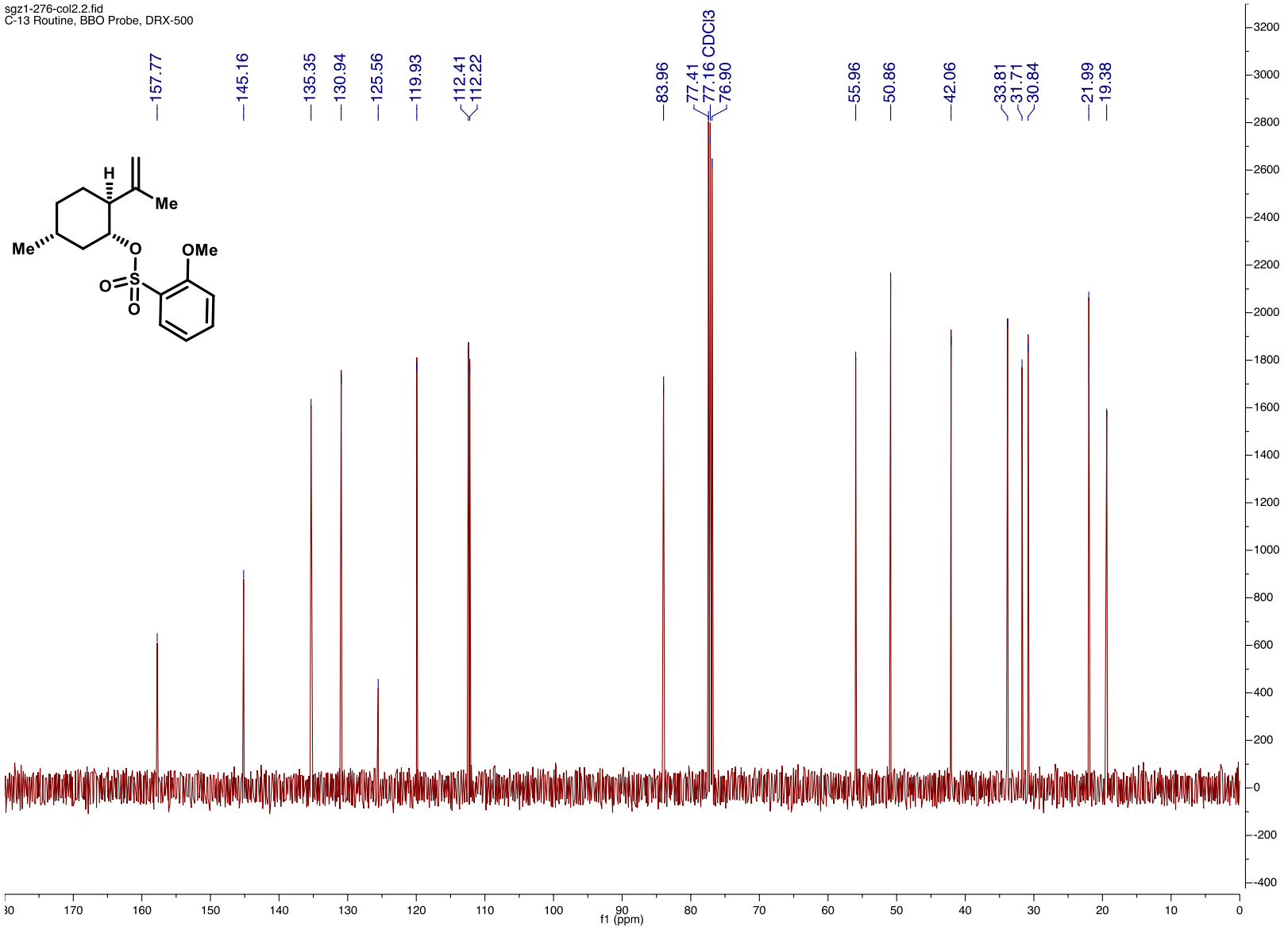
SI-01: ^{1}H-NMR


sgz1-276-col2.1.fid
H-1 Routine, DRX-500, BBO Probe
7.26 CDCl3
H
Me
Me
O
OMe
O
S
O
O
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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
f1 (ppm)

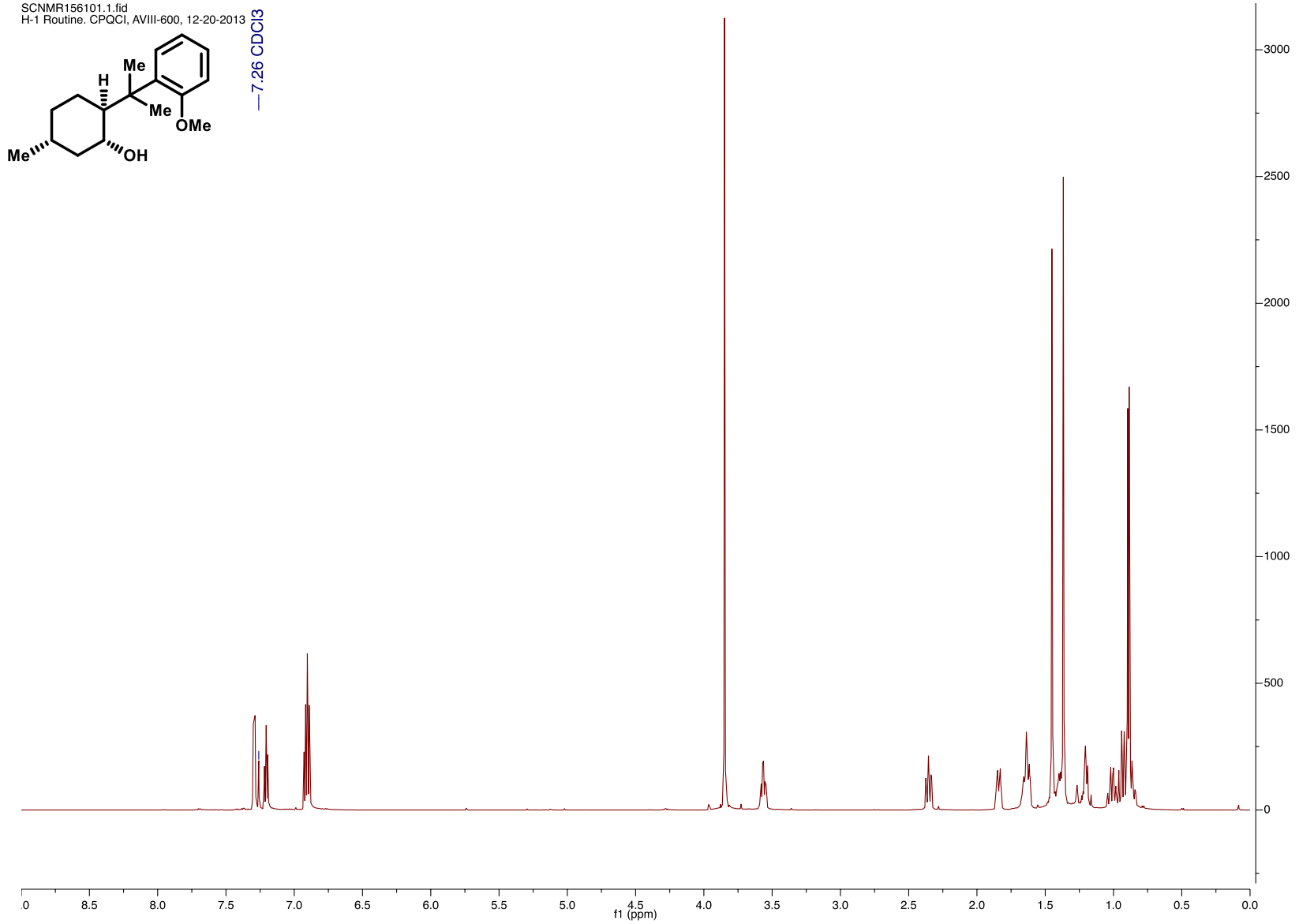

sgz1-276-col2-1.fid
H
Me
Me
O
S
O
O
OMe
f1 (ppm)

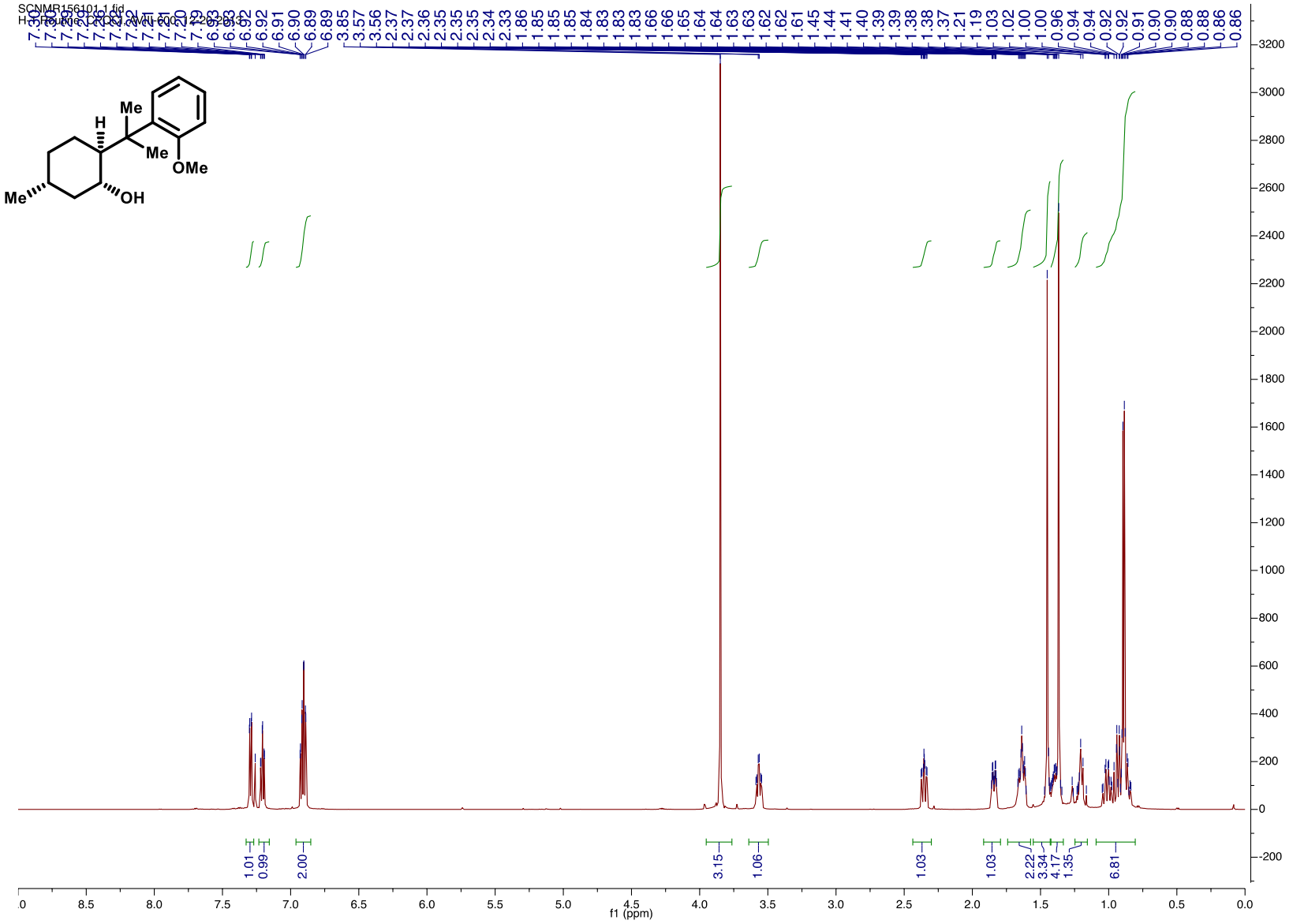
SI-01: ^{13}C-NMR


sgz1-276-col2.2.fid
C-13 Routine, BBO Probe, DRX-500
77.16 CDCl3
f1 (ppm)

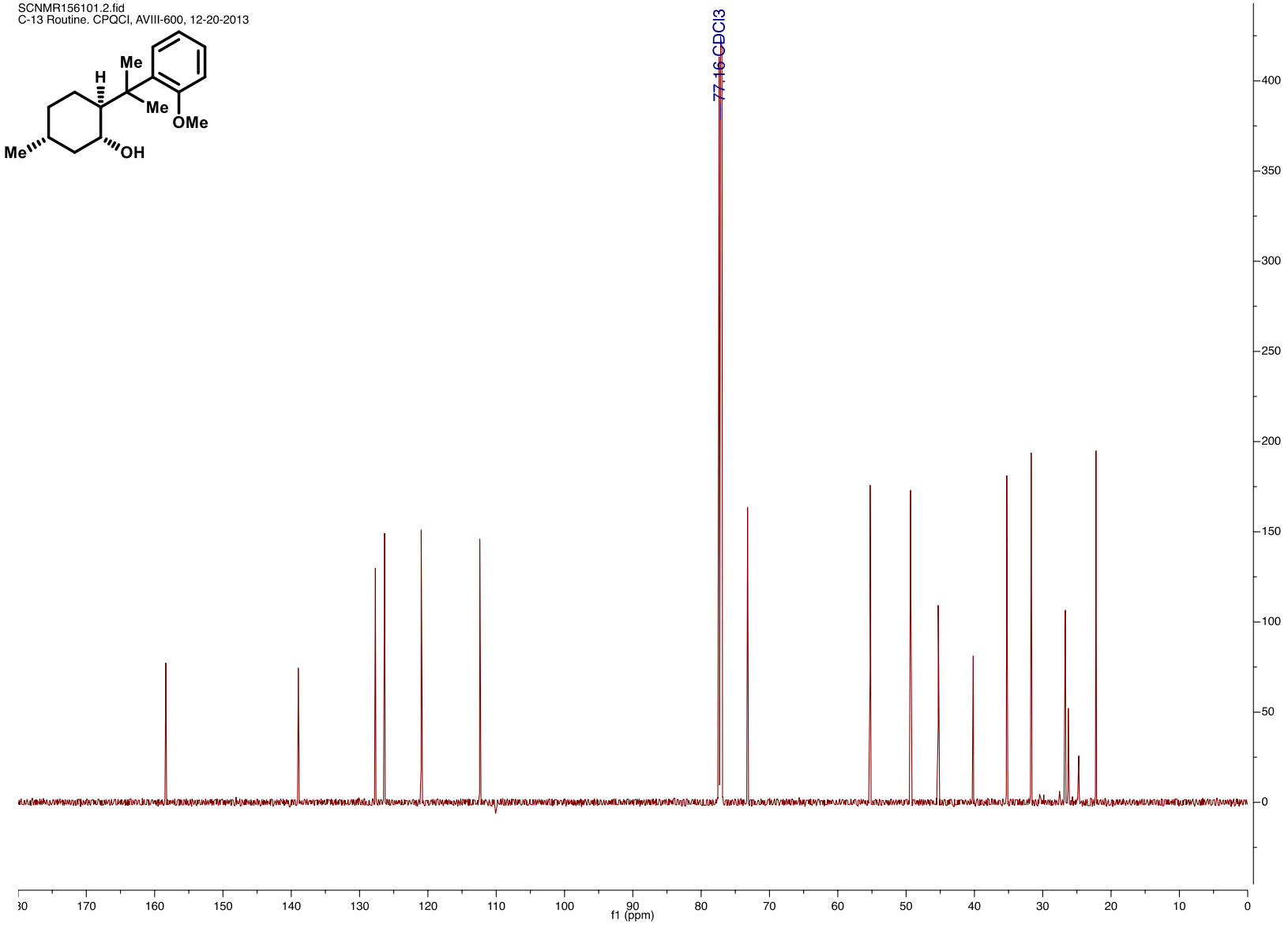

sgz1-276-col2.2.fid
C-13 Routine, BBO Probe, DRX-500
157.77
145.16
135.35
130.94
125.56
119.93
112.41
112.22
83.96
77.41
77.16 CDCl3
76.90
55.96
50.86
42.06
33.81
31.71
30.84
21.99
19.38
H
Me
Me
O
OMe
O
S
O
O
f1 (ppm)

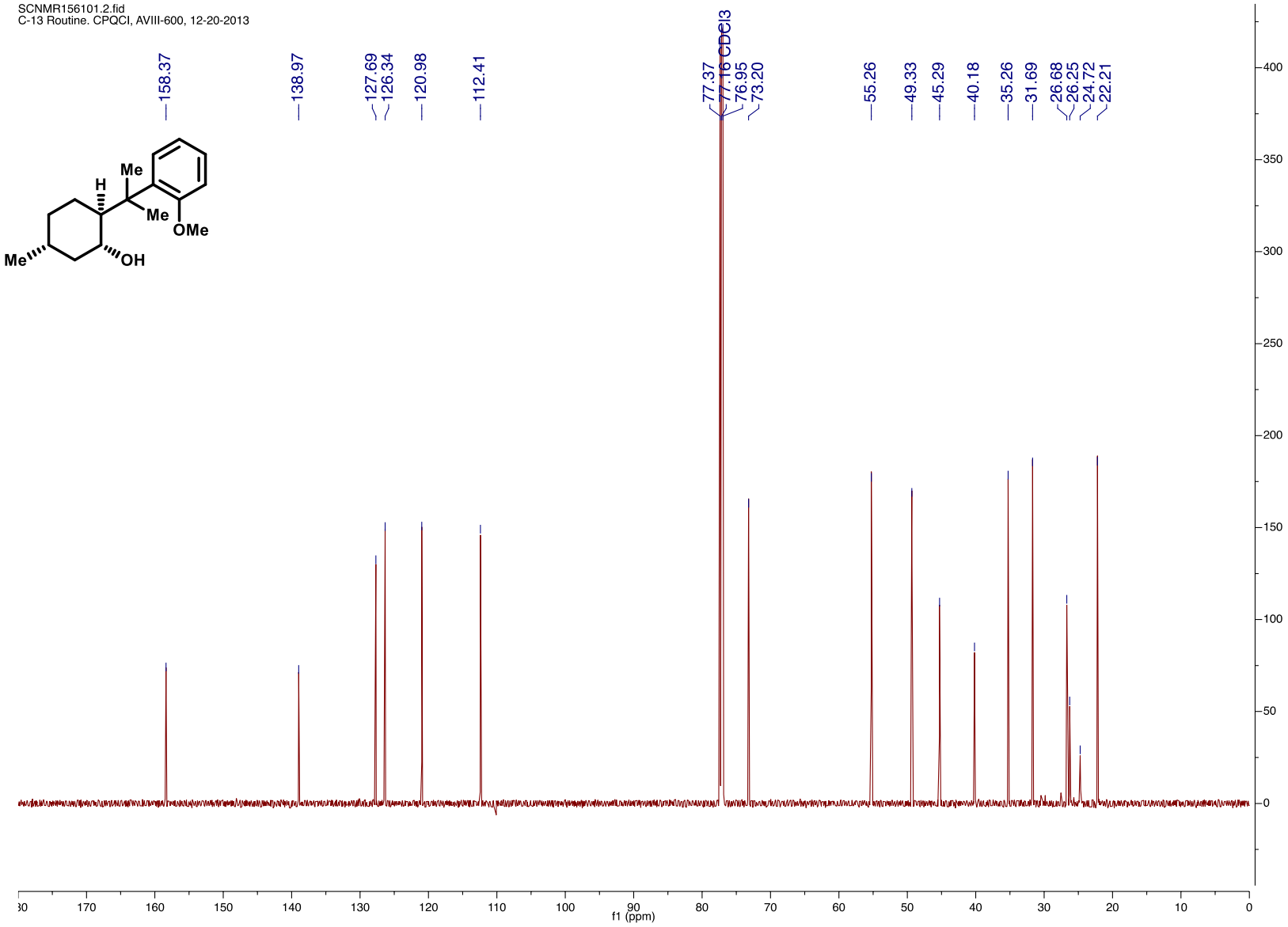
4a: ^{1}H-NMR


SCNMR156101.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
7.26 CDCl3
Me
H
Me
Me
OMe
Me
OH
3000
2500
2000
1500
1000
500
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
f1 (ppm)

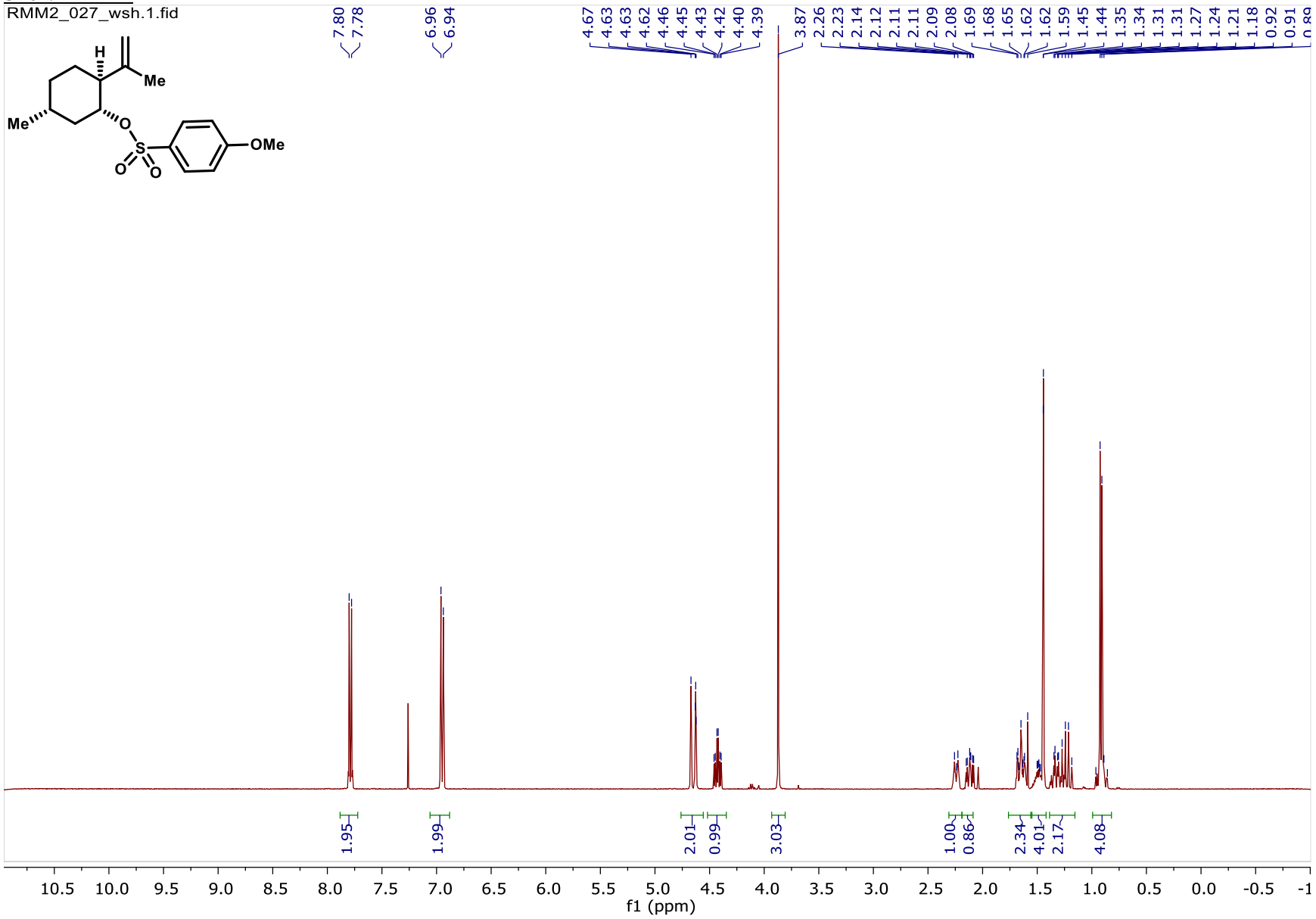

SCNMR156101-1.fid
H-CHLOROFORM-D.cdcl
Me
H
Me
OMe
Me
OH
f1 (ppm)

4a: ^{13}C-NMR

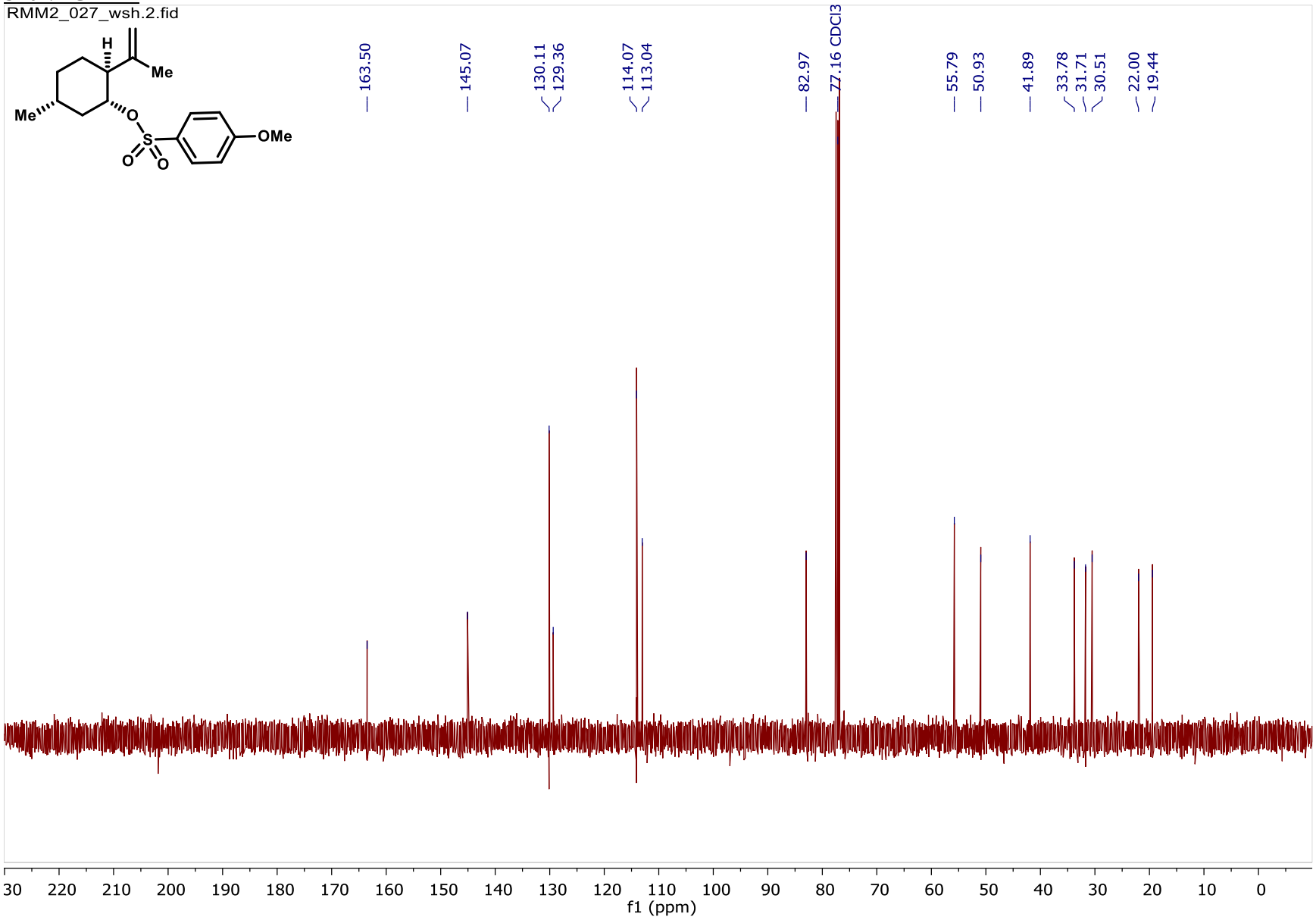

SCNMR156101.2.fid
C-13 Routine. CPQCI, AVIII-600, 12-20-2013
Me
H
Me
OMe
Me
OH
77.16-CDCl3
f1 (ppm)


SCNMR156101.2.fid
C-13 Routine. CPQCI, AVIII-600, 12-20-2013
158.37
138.97
127.69
126.34
120.98
112.41
77.37
77.16 CDCl3
76.95
73.20
55.26
49.33
45.29
40.18
35.26
31.69
26.68
26.25
24.72
22.21
Me
H
Me
Me
OMe
Me
OH
f1 (ppm)

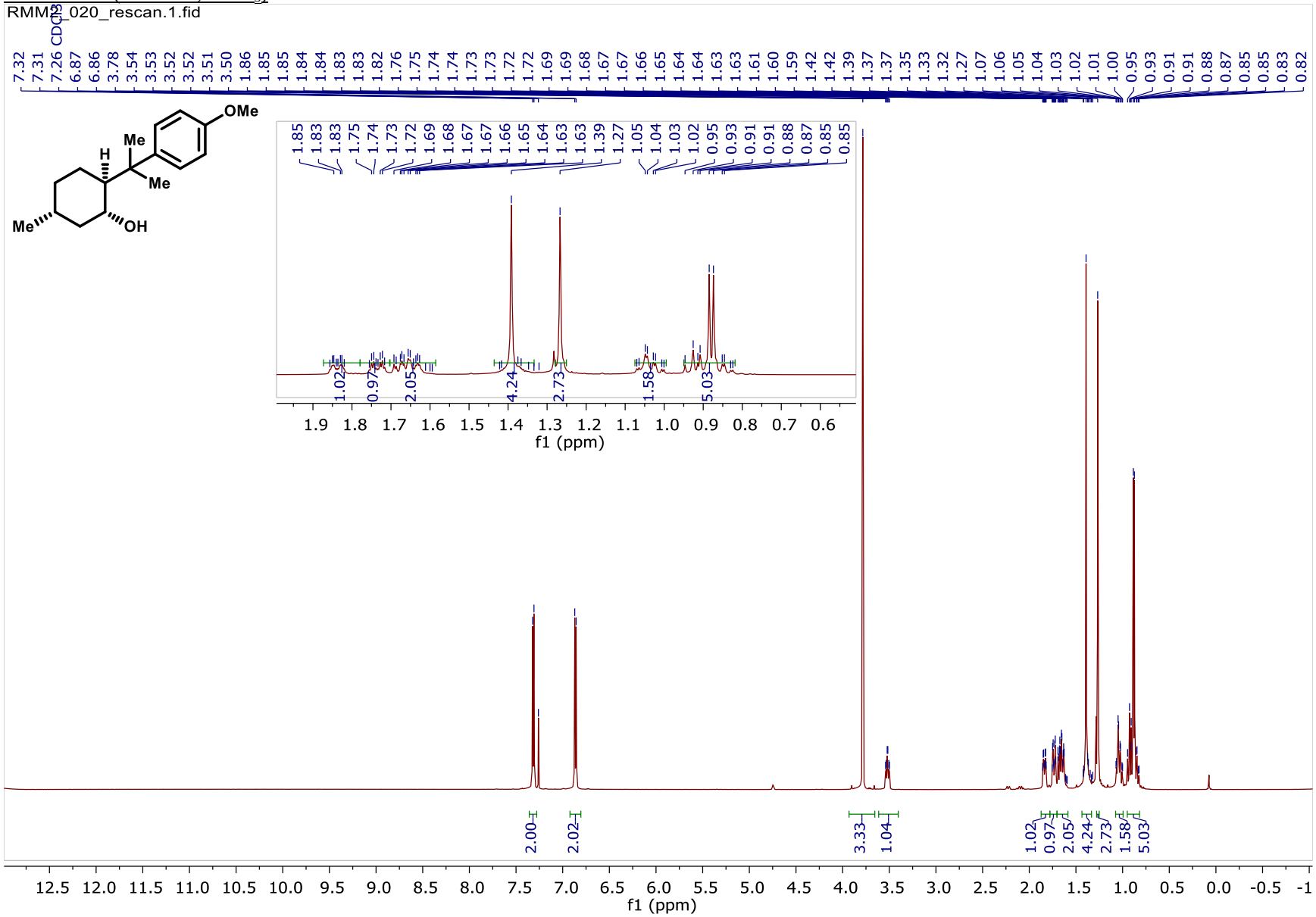
SI-02: ^{1}H-NMR

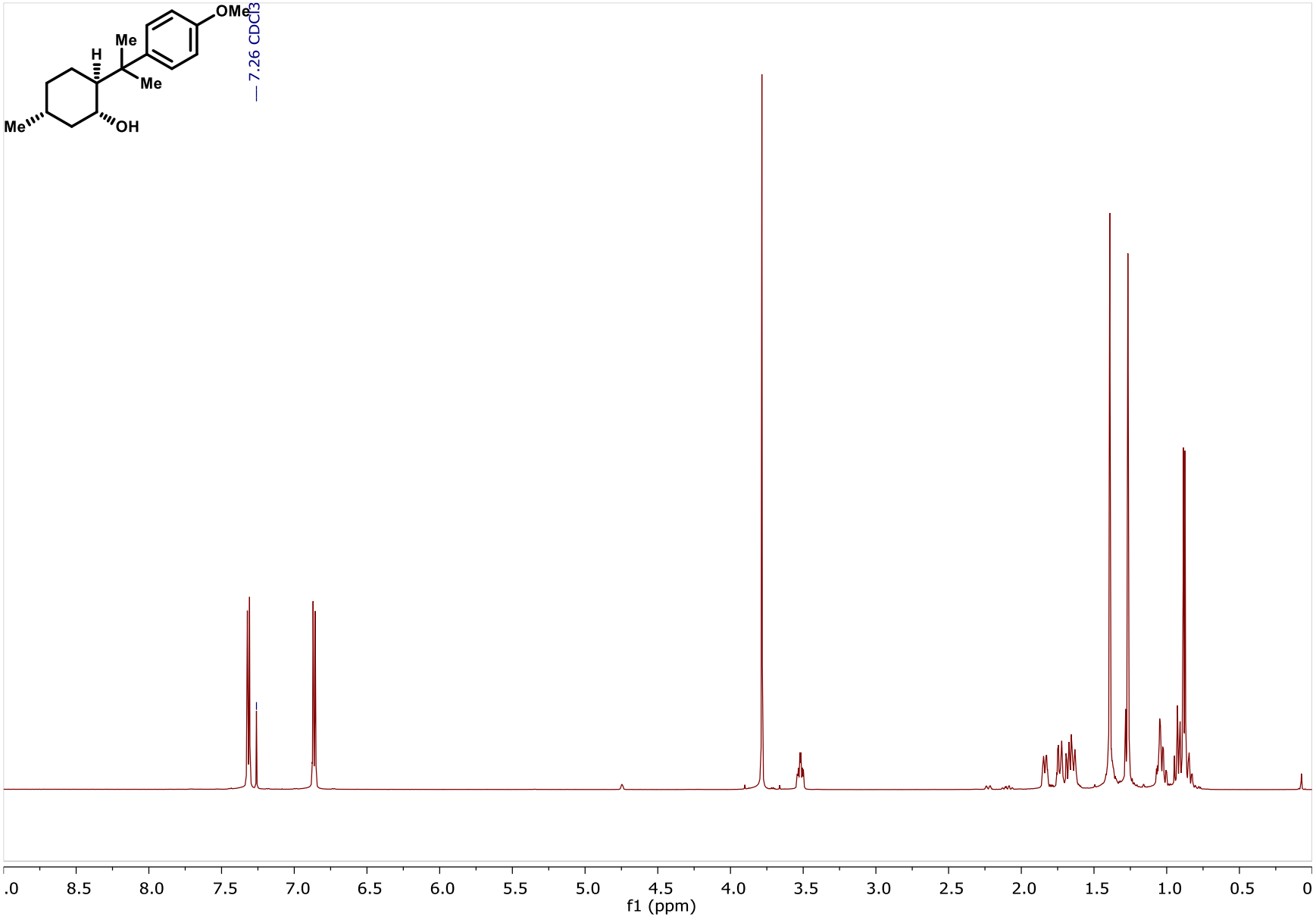

RMM2_027_wsh.1.fid
H
Me
Me
O
S
O
O
OMe
7.80
7.78
6.96
6.94
4.67
4.63
4.63
4.62
4.46
4.45
4.43
4.42
4.40
4.39
3.87
2.26
2.23
2.14
2.12
2.11
2.11
2.09
2.08
1.69
1.68
1.65
1.62
1.62
1.59
1.45
1.44
1.35
1.34
1.31
1.31
1.27
1.24
1.21
1.18
0.92
0.91
1.95
1.99
2.01
0.99
3.03
1.00
0.86
2.34
4.01
2.17
4.08
10.5 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
f1 (ppm)

SI-02: ^{13}C-NMR

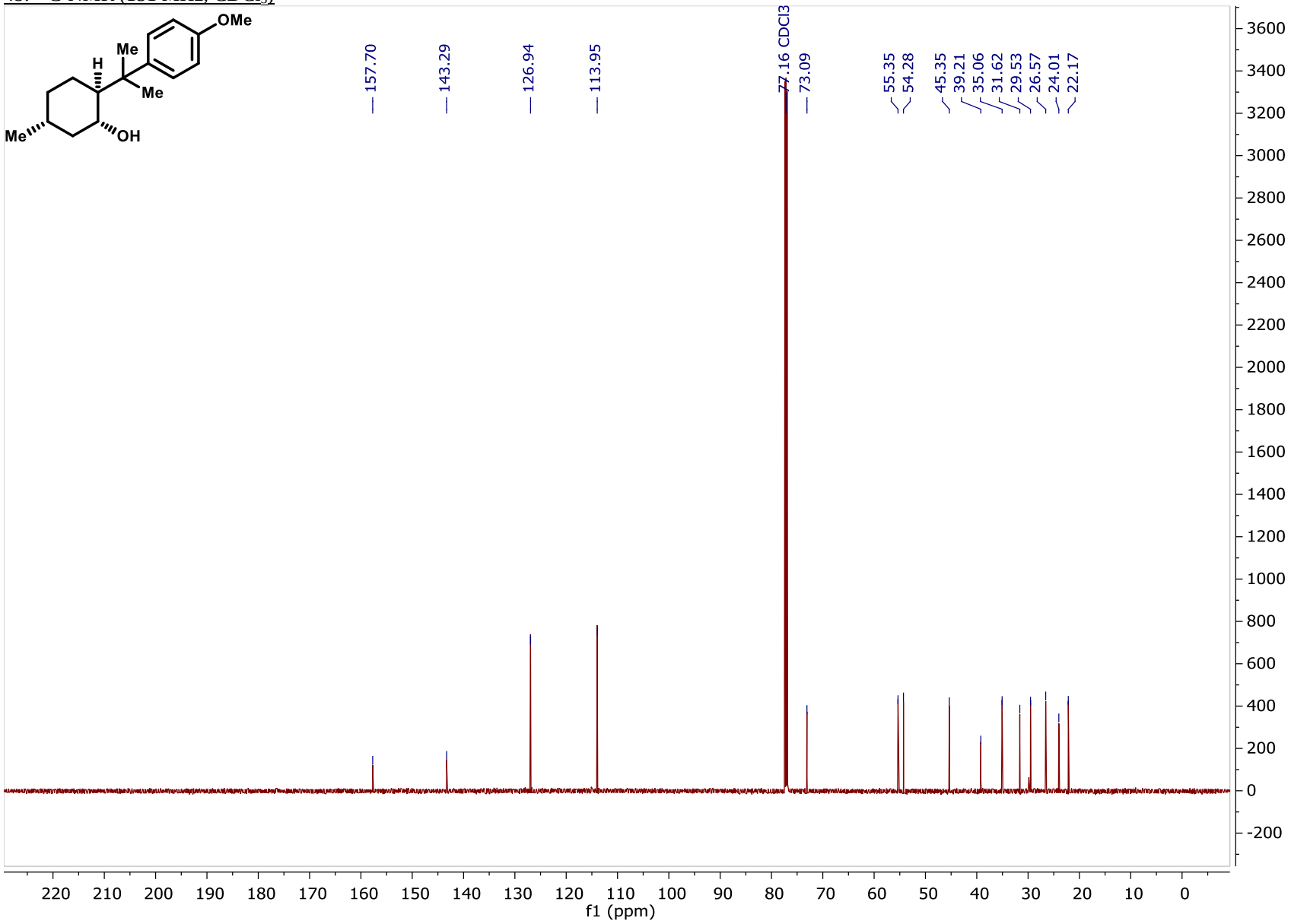

RMM2_027_wsh.2.fid
H
Me
Me
O
S
O
O
OMe
163.50
145.07
130.11
129.36
114.07
113.04
82.97
77.16 CDCl3
55.79
50.93
41.89
33.78
31.71
30.51
22.00
19.44
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4b: ^{1}H-NMR (600 MHz, $CDCl_3$)

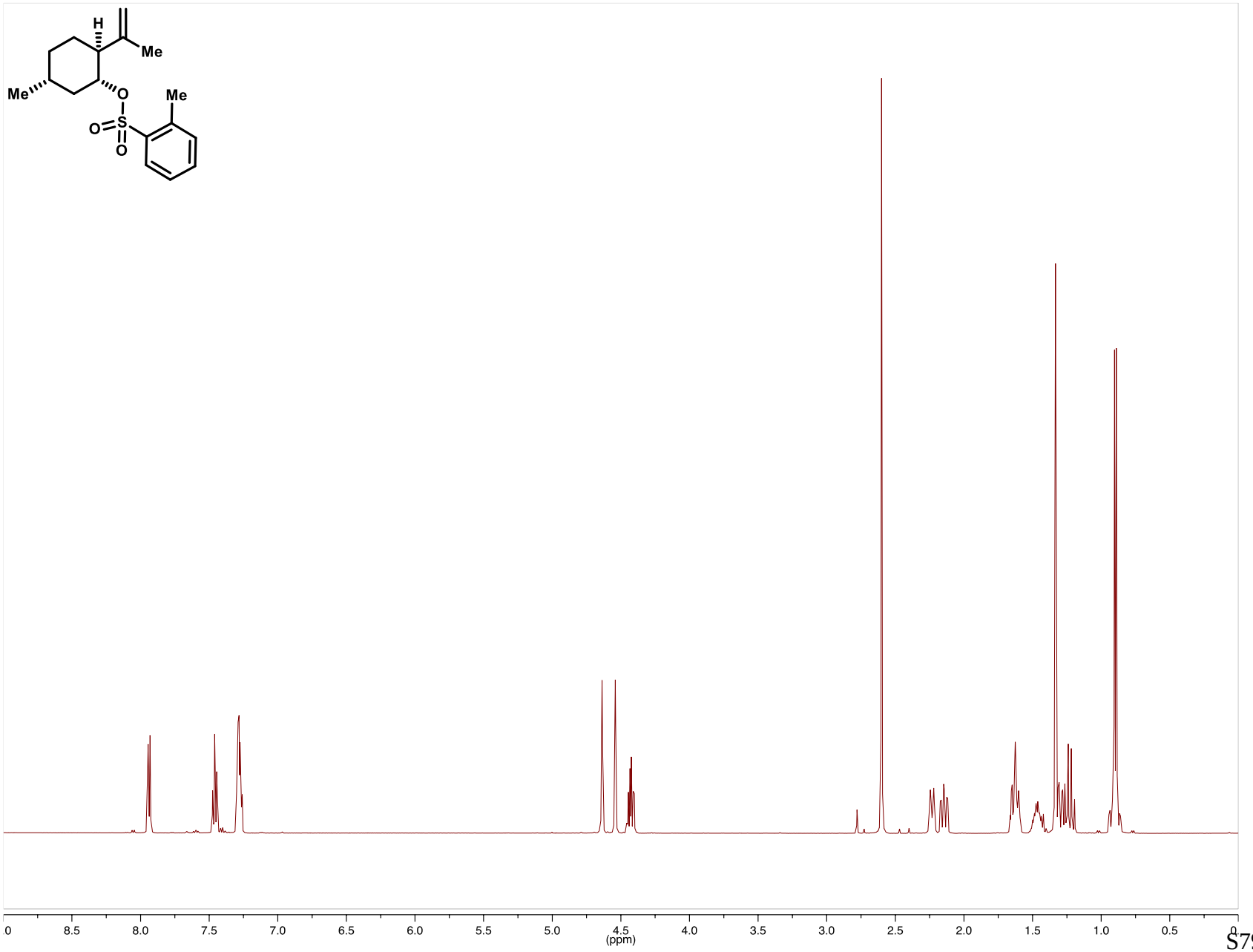



OMe
Me
H
Me
Me
OH
7.26 CDCl3
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

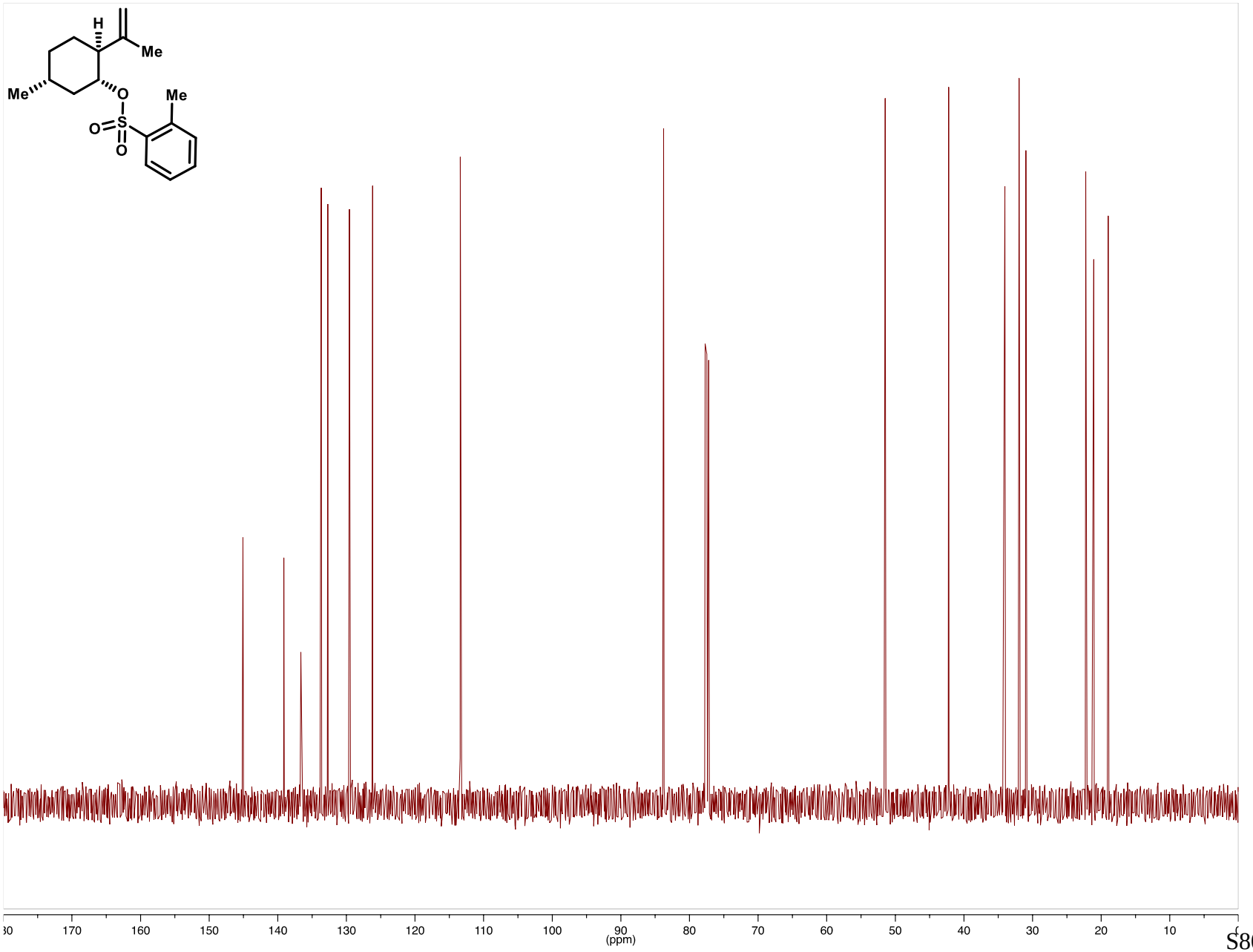
4b: ^{13}C-NMR (151 MHz, $CDCl_3$)



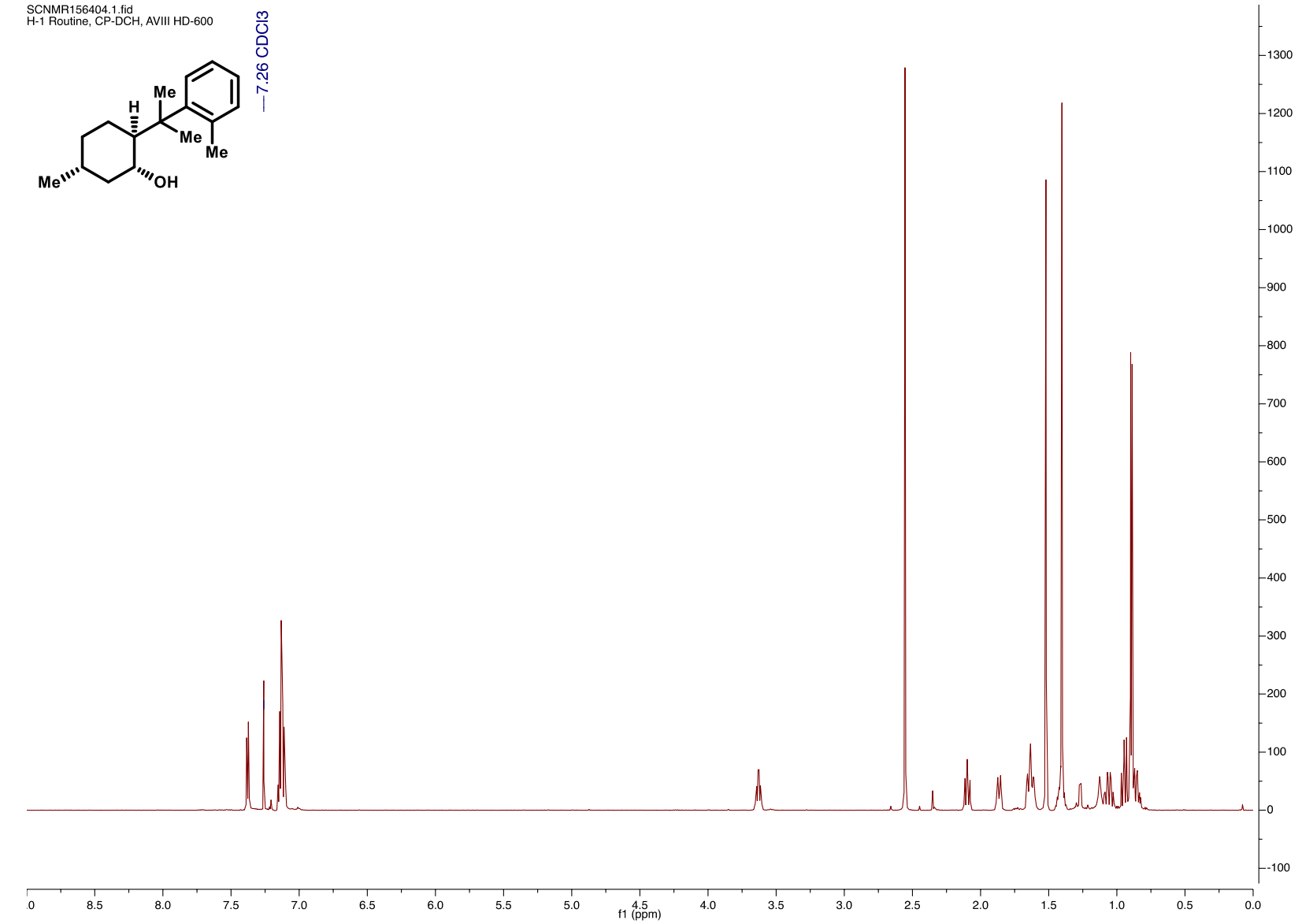
SI-03: ^{1}H-NMR

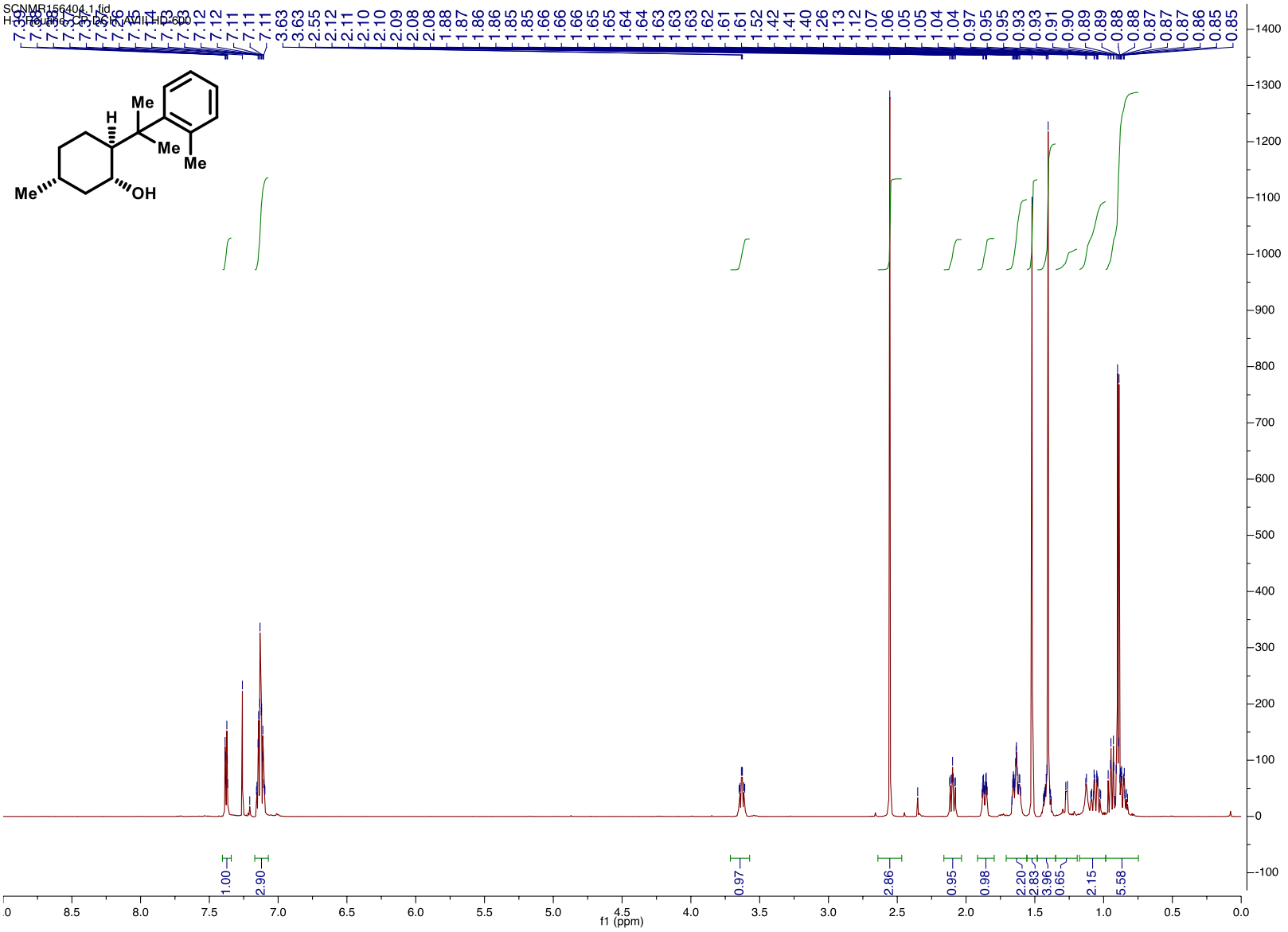


SI-03: ^{13}C-NMR

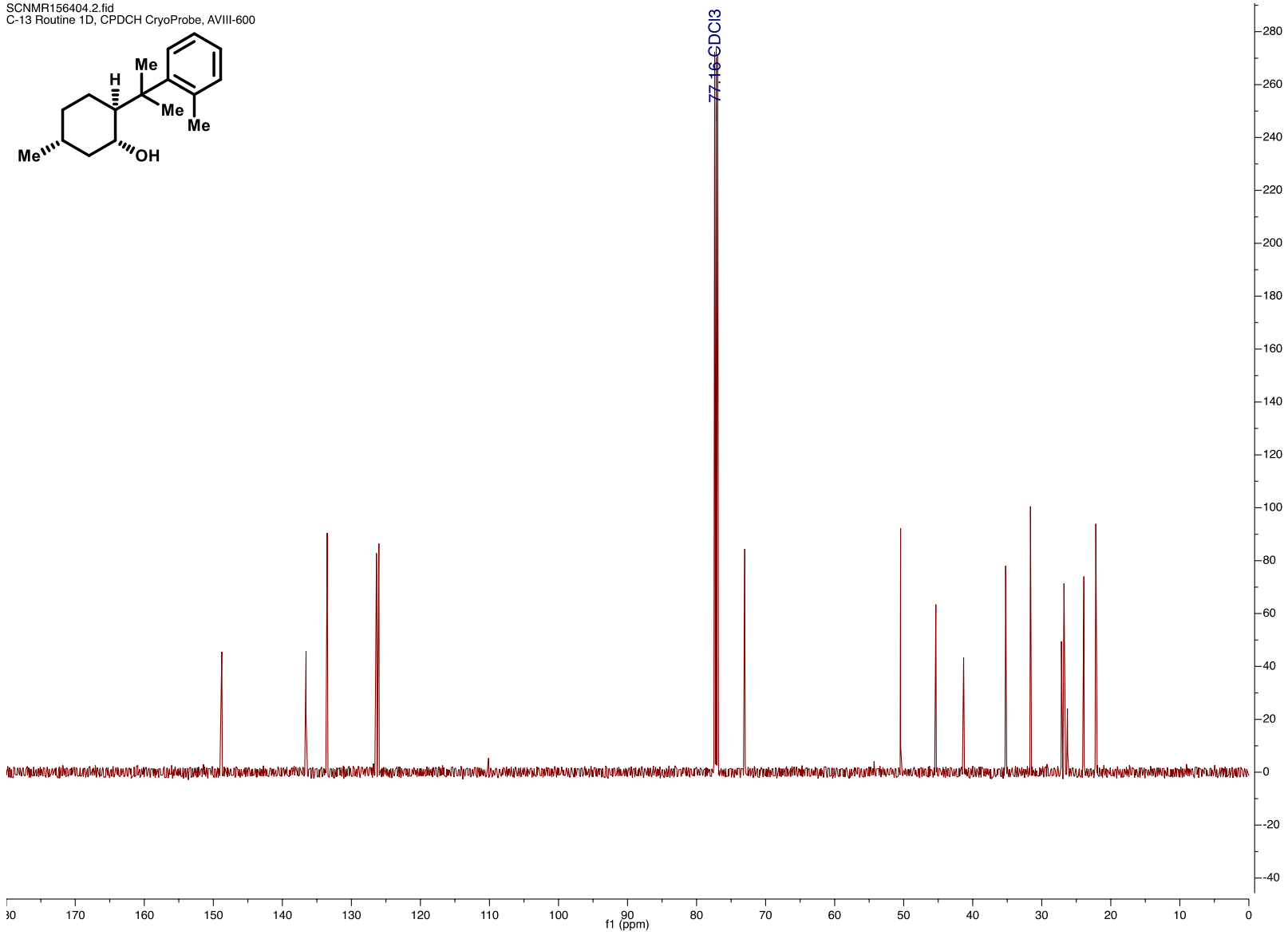

H
Me
Me
O
Me
O
S
O
170
160
150
140
130
120
110
100
90
(ppm)
80
70
60
50
40
30
20
10

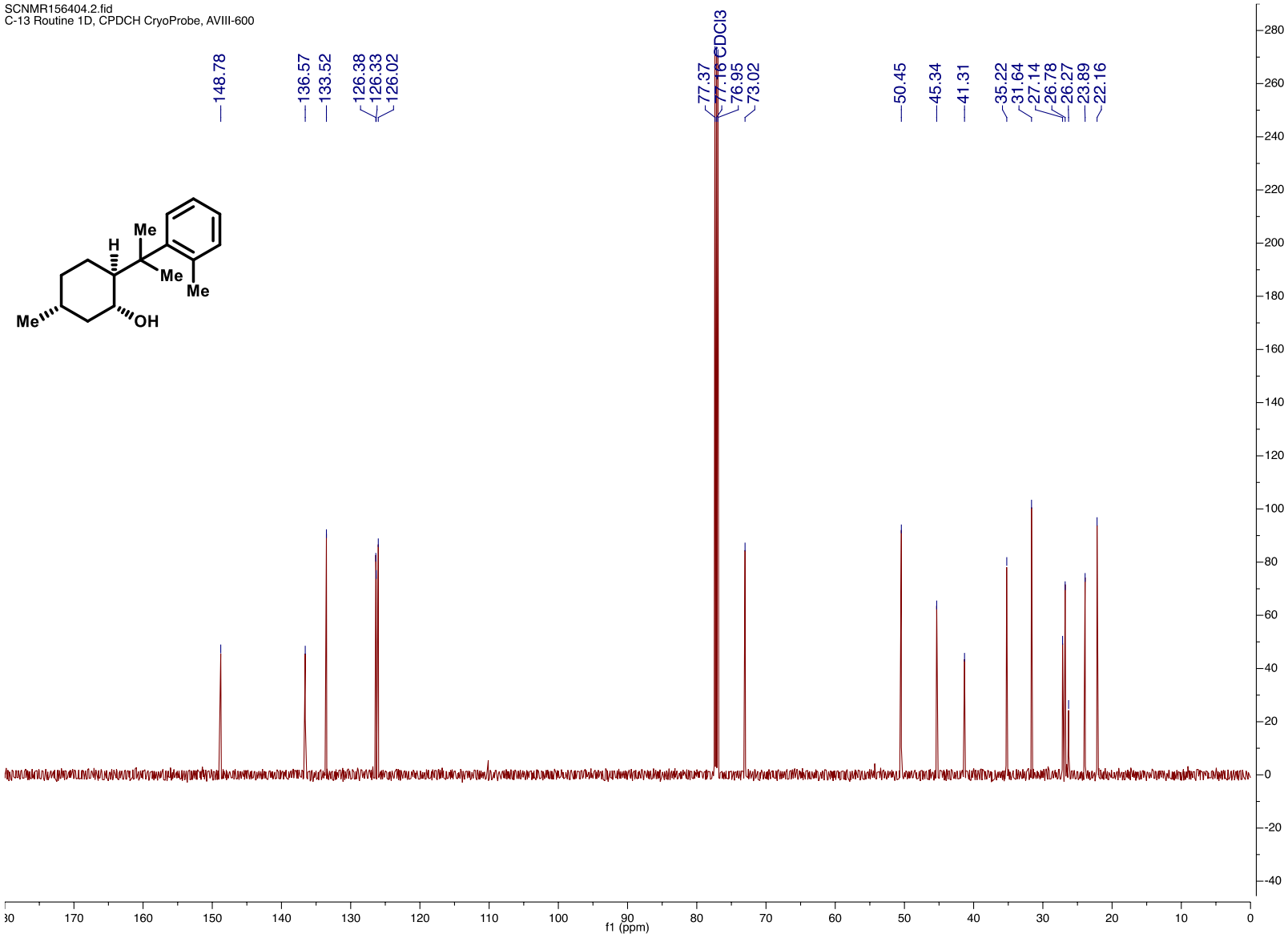
5a: ^{1}H-NMR


SCNMR156404.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
H
Me
Me
Me
OH
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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
f1 (ppm)

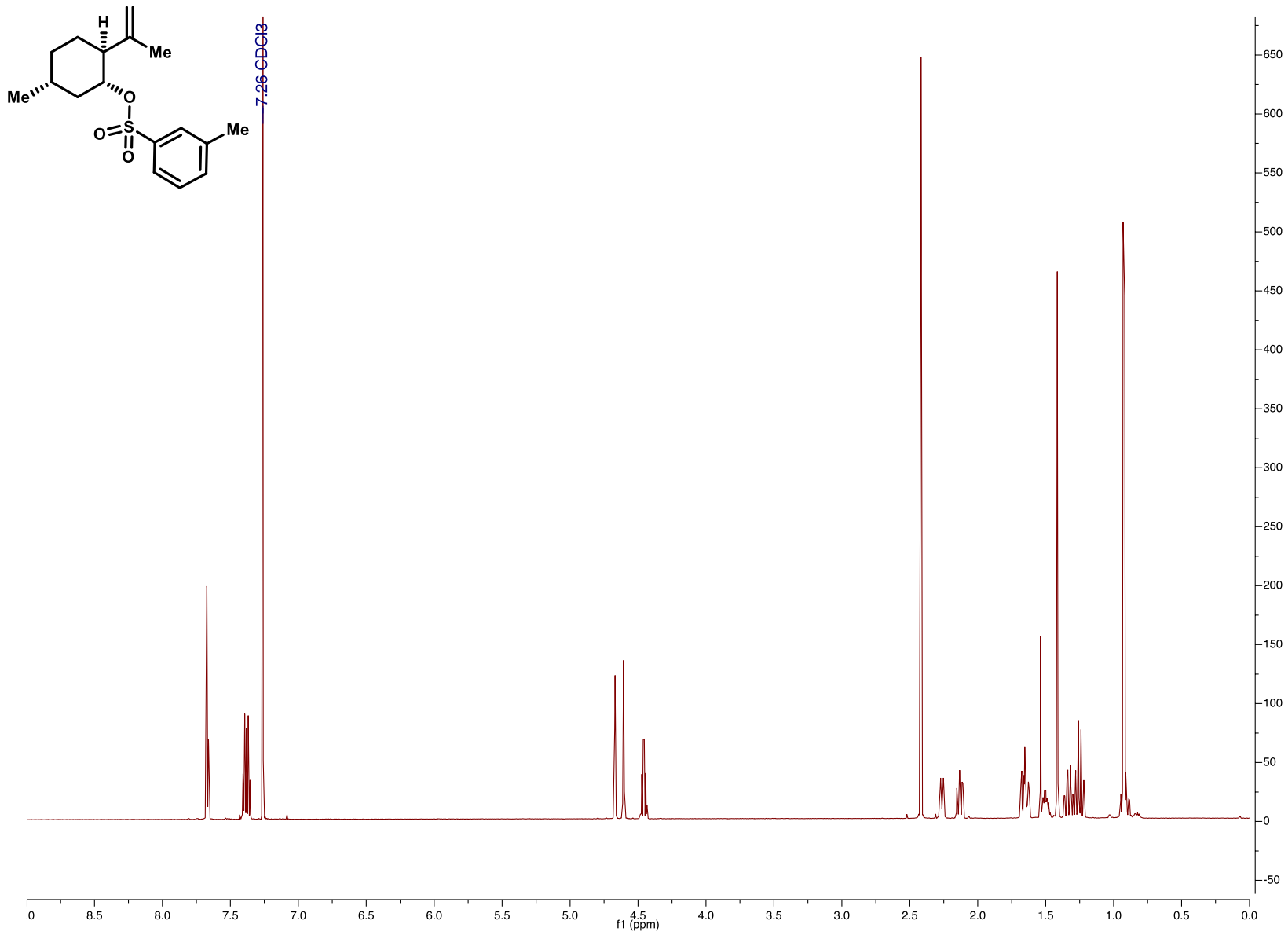

SCNMR156404_1.fid
H-1 PROTON_16_ASIC
Bruker,Cambridge,AVIII_HD-600
Me
H
Me
Me
Me
OH
f1 (ppm)

5a: ^{13}C-NMR

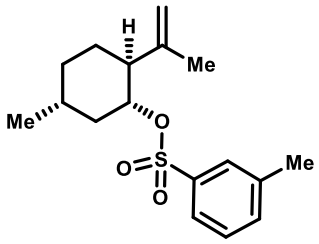

SCNMR156404.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
H
Me
Me
Me
OH
77.16-CDCl3
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


SCNMR156404.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
148.78
136.57
133.52
126.38
126.33
126.02
77.37
77.16 CDCl3
76.95
73.02
50.45
45.34
41.31
35.22
31.64
27.14
26.78
26.27
23.89
22.16
Me
H
Me
Me
Me
OH
f1 (ppm)

SI-04: ^{1}H-NMR

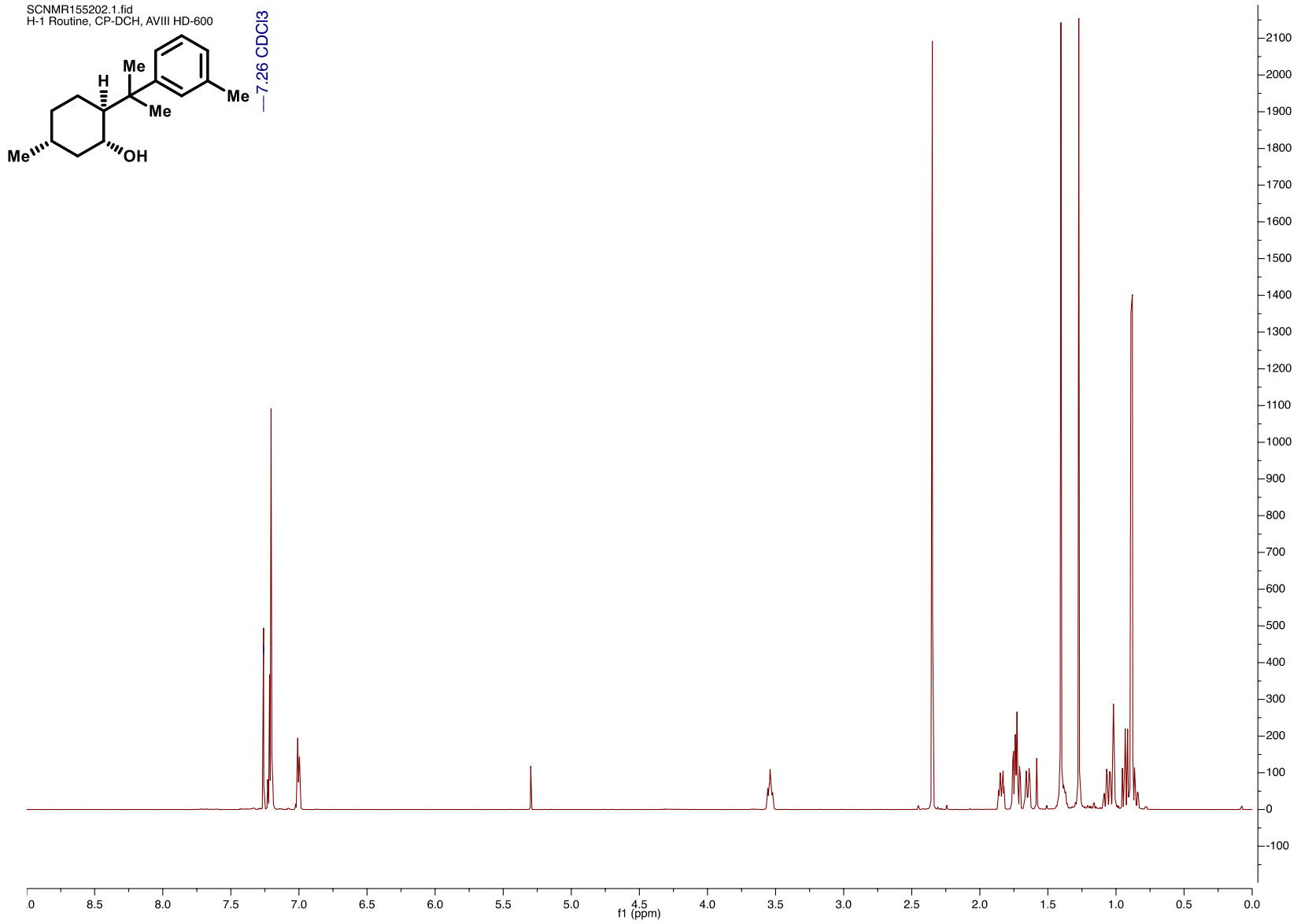

H
Me
Me
O
S
O
O
Me
7.26 CDCl3
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

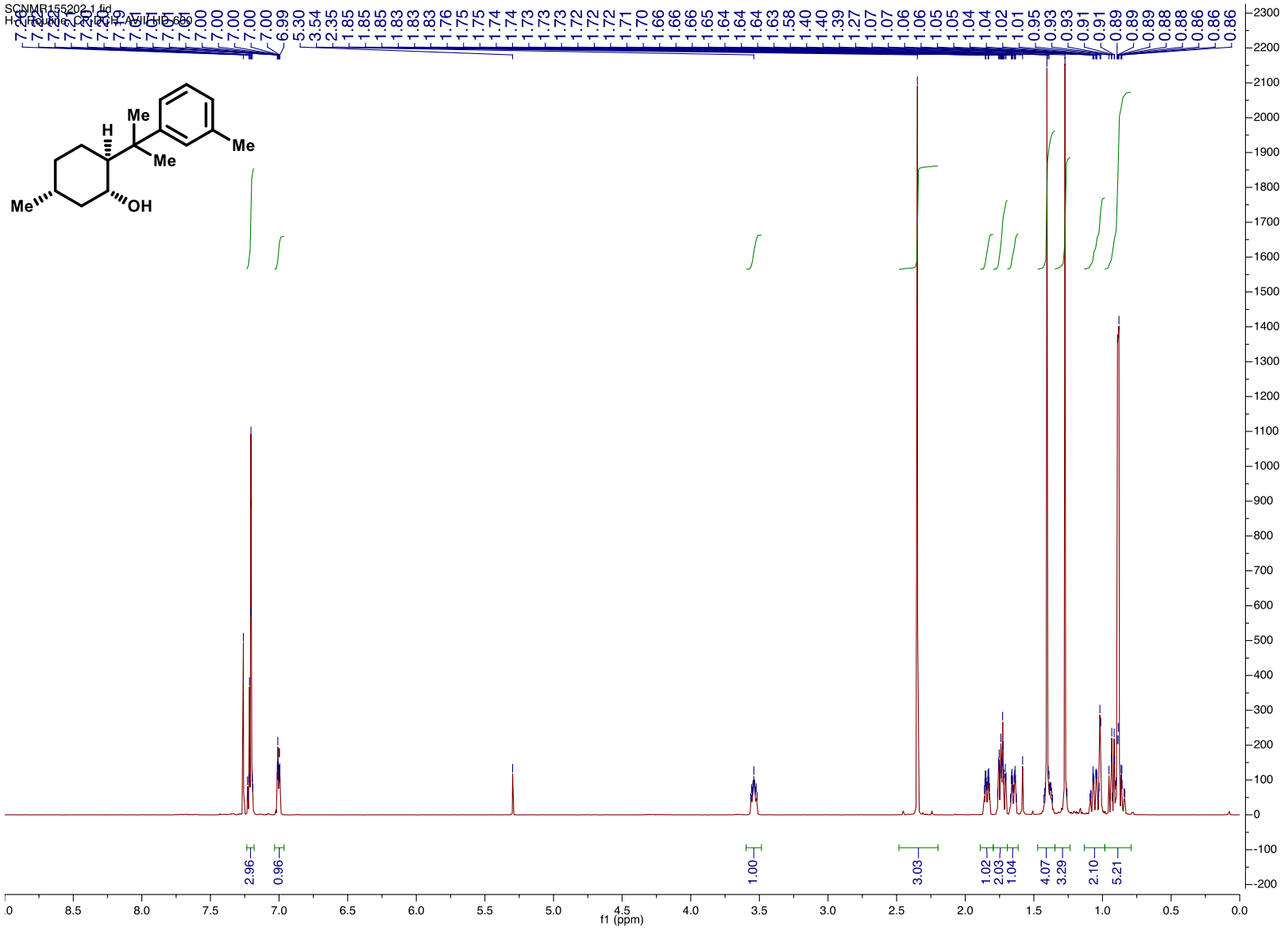
SI-04: ^{13}C-NMR


H
Me
Me
O
S
O
O
Me

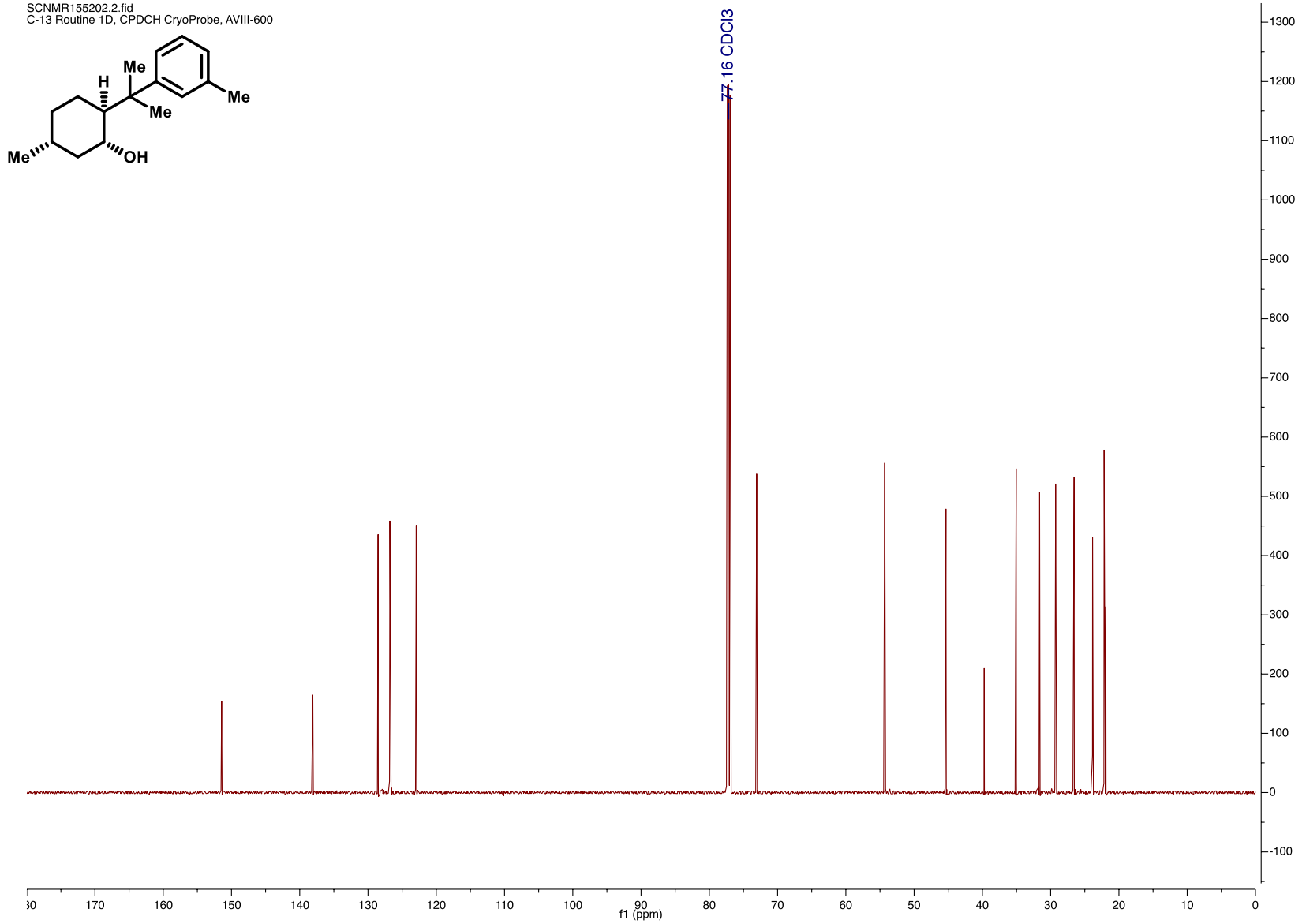
77.16 CDCl3
550
500
450
400
350
300
250
200
150
100
50
0
-50
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

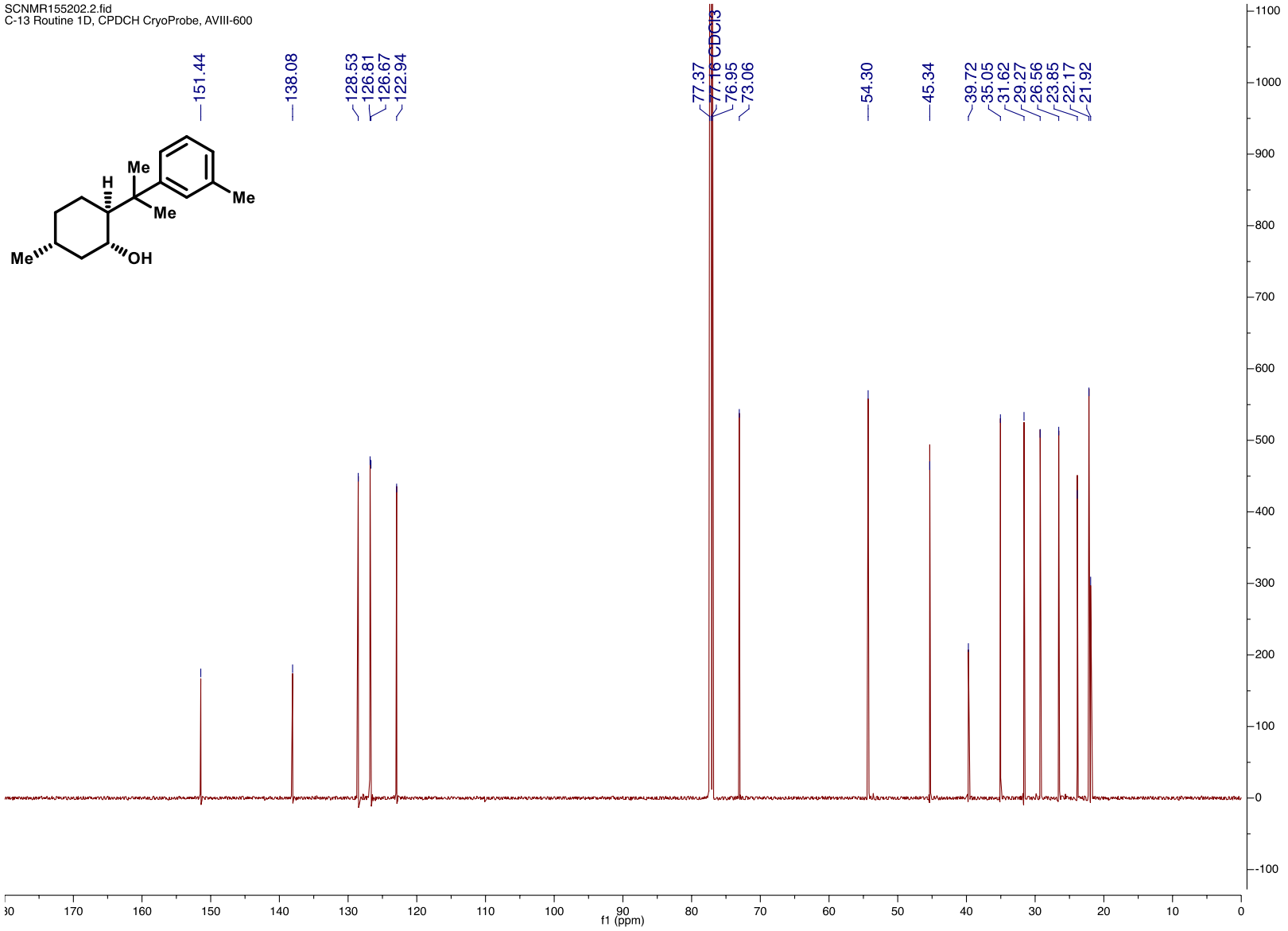
5b: ^{1}H-NMR


SCNMR155202.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
H
Me
Me
Me
OH
f1 (ppm)

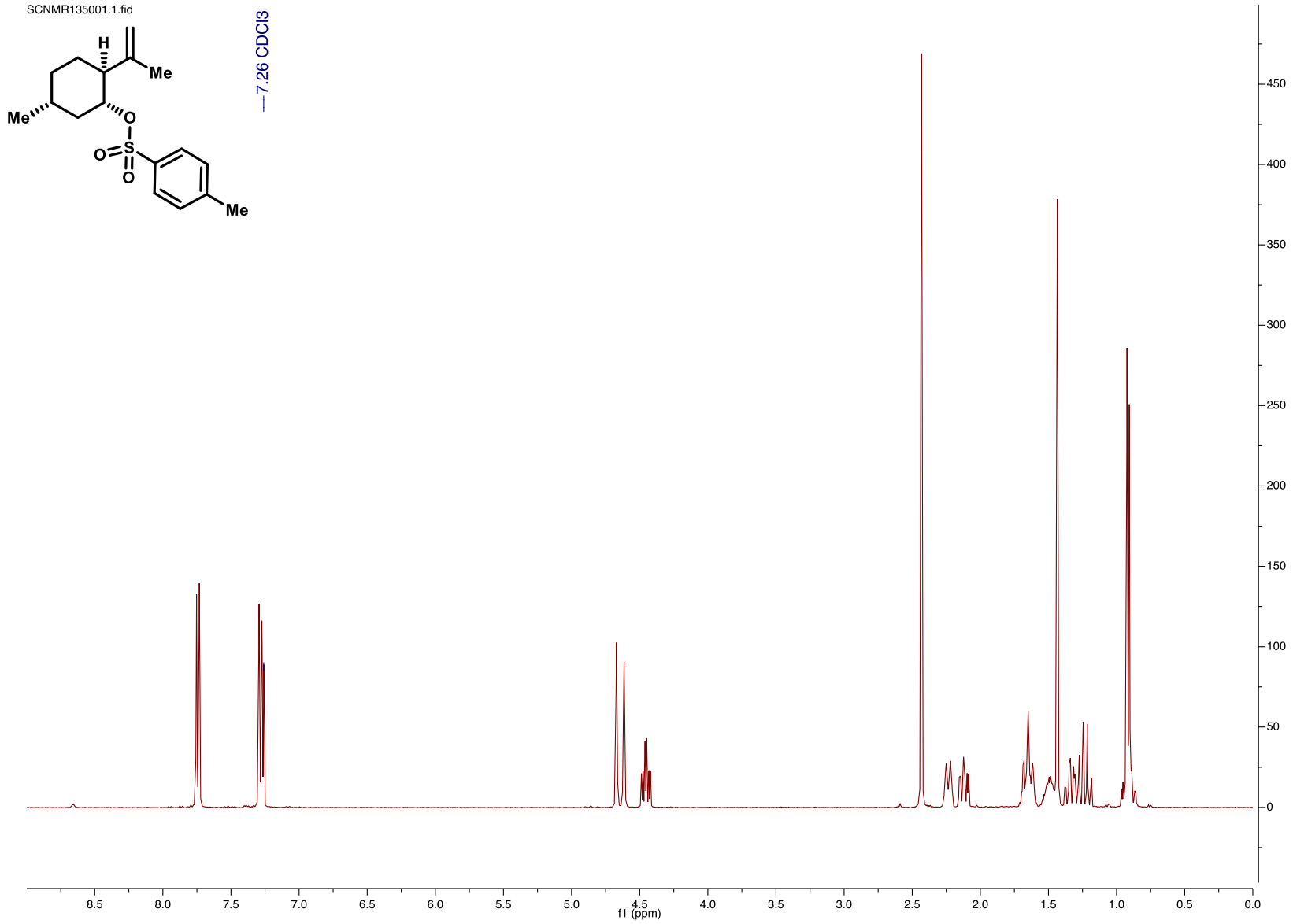

SCNMR155202-1.fid
H-Routine CDCl3 AVIIIHD360
Me
H
Me
Me
Me
OH
f1 (ppm)

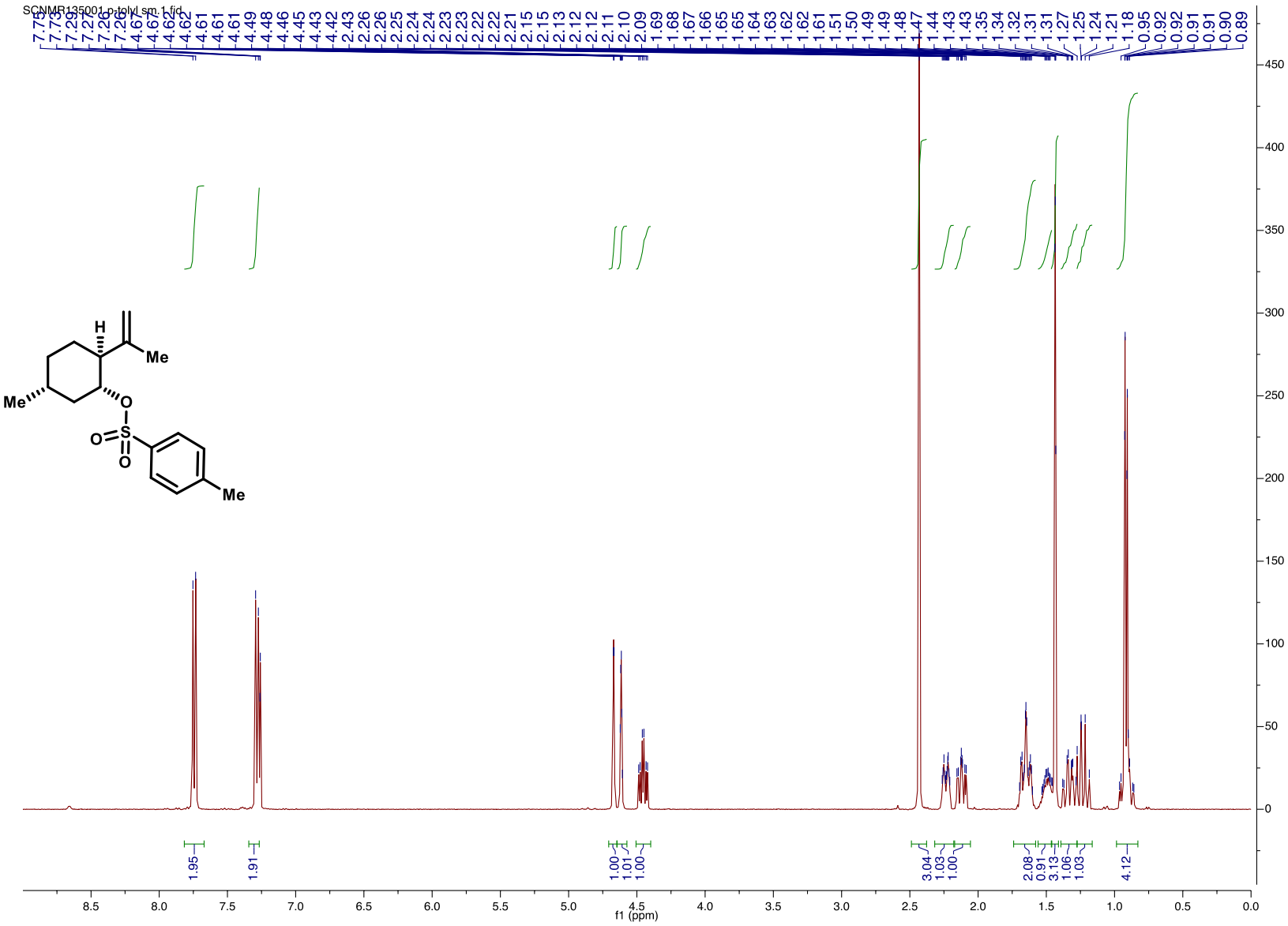
5b: ^{13}C-NMR


SCNMR155202.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
H
Me
Me
Me
Me
OH
77.16 CDCl3
f1 (ppm)

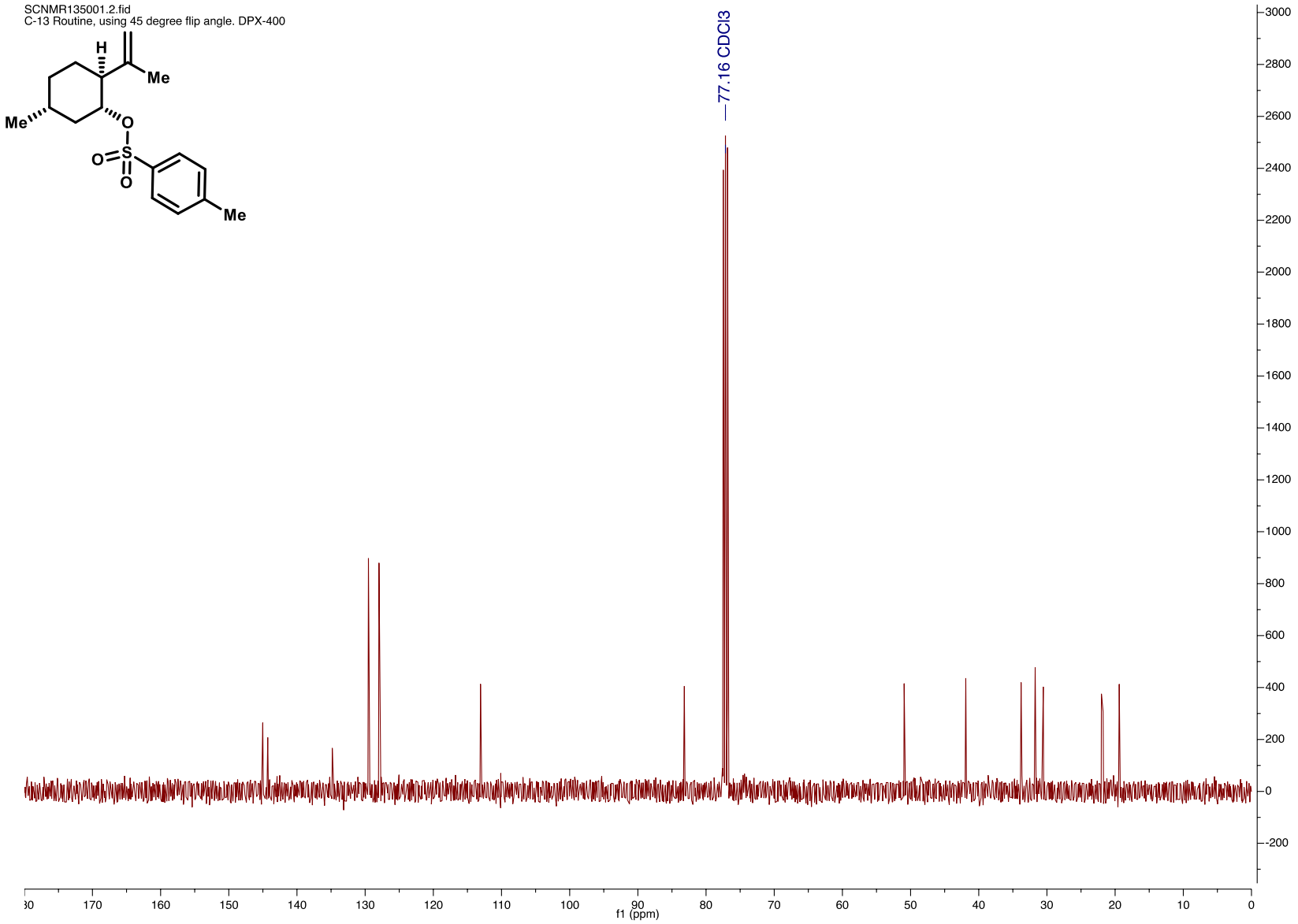

SCNMR155202.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
151.44
138.08
128.53
126.81
126.67
122.94
77.37
77.16 CDCl3
76.95
73.06
54.30
45.34
39.72
35.05
31.62
29.27
26.56
23.85
22.17
21.92
Me
H
Me
Me
Me
OH
f1 (ppm)

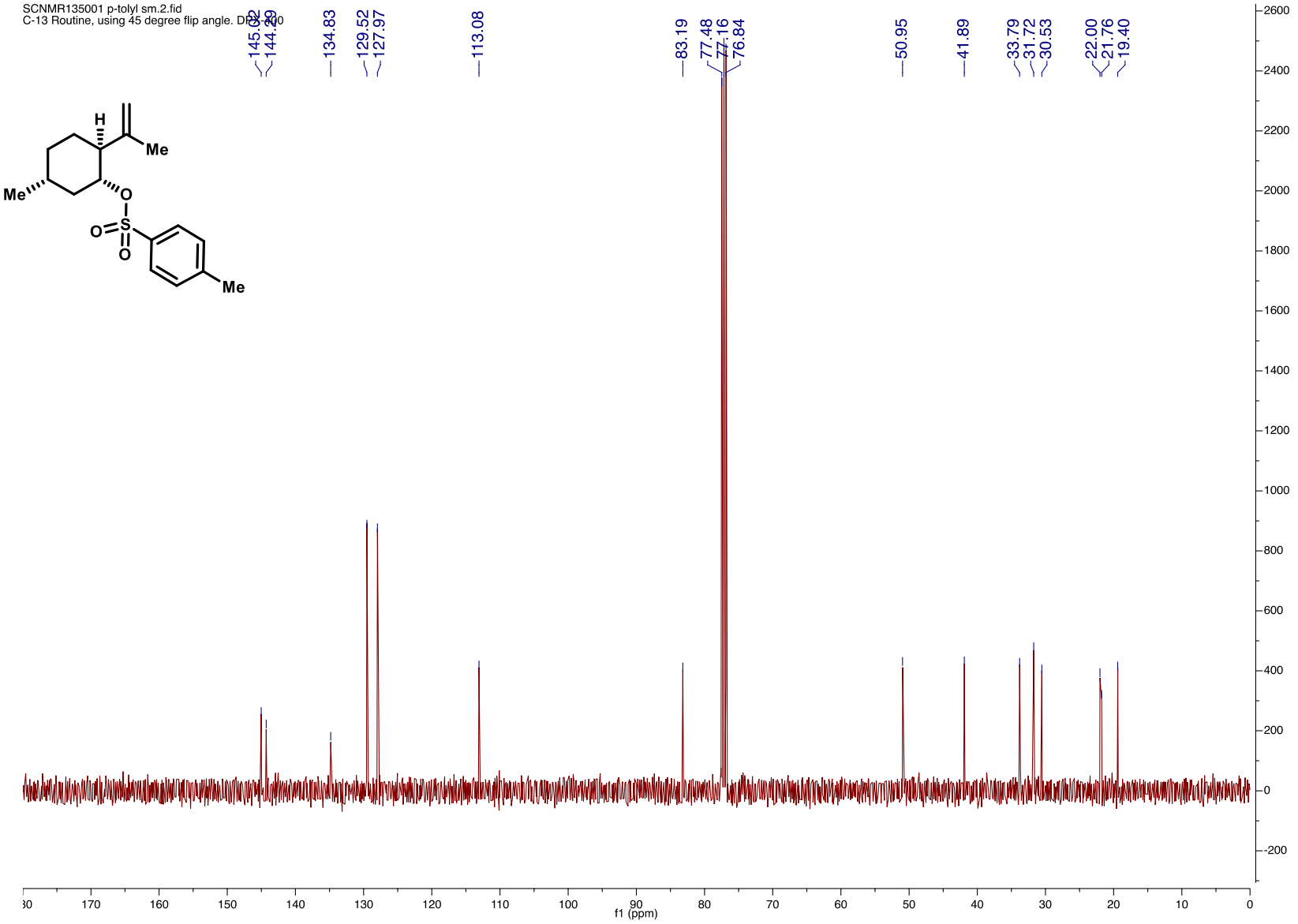
SI-05: ^{1}H-NMR


SCNMR135001.1.fid
7.26 CDCl3
H
Me
Me
O
O
S
O
O
Me
450
400
350
300
250
200
150
100
50
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
f1 (ppm)

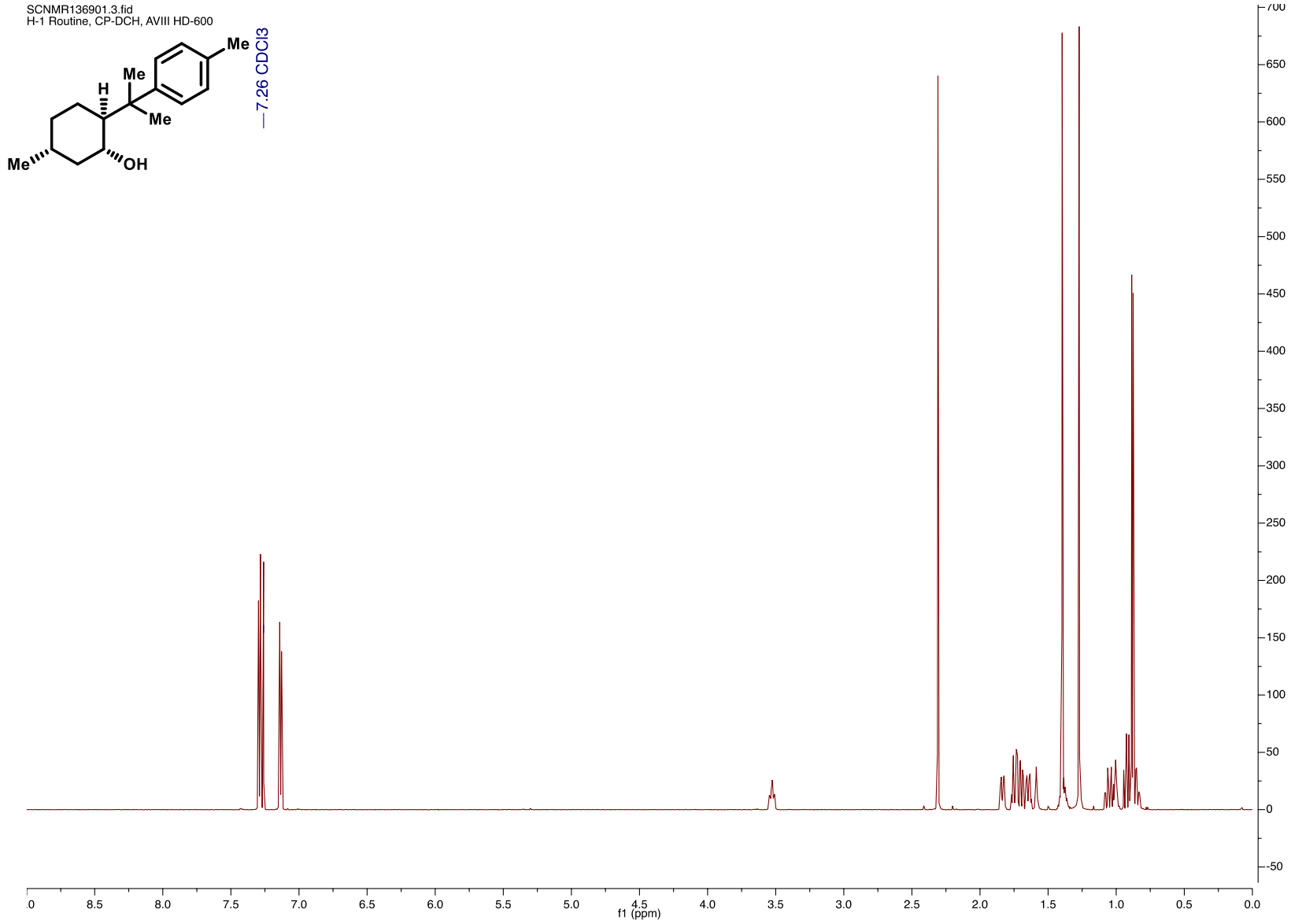

SCNMR135001-p-tolyl-sm-1.fid
7.76 7.75 7.25 7.24 7.24 7.24 4.62 4.61 4.61 4.61 4.61 4.49 4.48 4.46 4.45 4.43 4.42 2.43 2.26 2.25 2.24 2.24 2.23 2.23 2.22 2.22 2.21 2.15 2.15 2.13 2.12 2.12 2.11 2.10 2.09 1.69 1.68 1.67 1.66 1.65 1.65 1.64 1.63 1.62 1.62 1.61 1.51 1.50 1.49 1.49 1.48 1.47 1.44 1.43 1.43 1.35 1.34 1.32 1.31 1.31 1.27 1.25 1.24 1.21 1.18 0.95 0.92 0.92 0.91 0.91 0.90 0.89
H
Me
Me
O
O
S
O
O
Me
1.95
1.91
1.00
1.01
1.00
3.04
1.03
1.00
2.08
0.91
3.13
1.06
1.03
4.12
f1 (ppm)

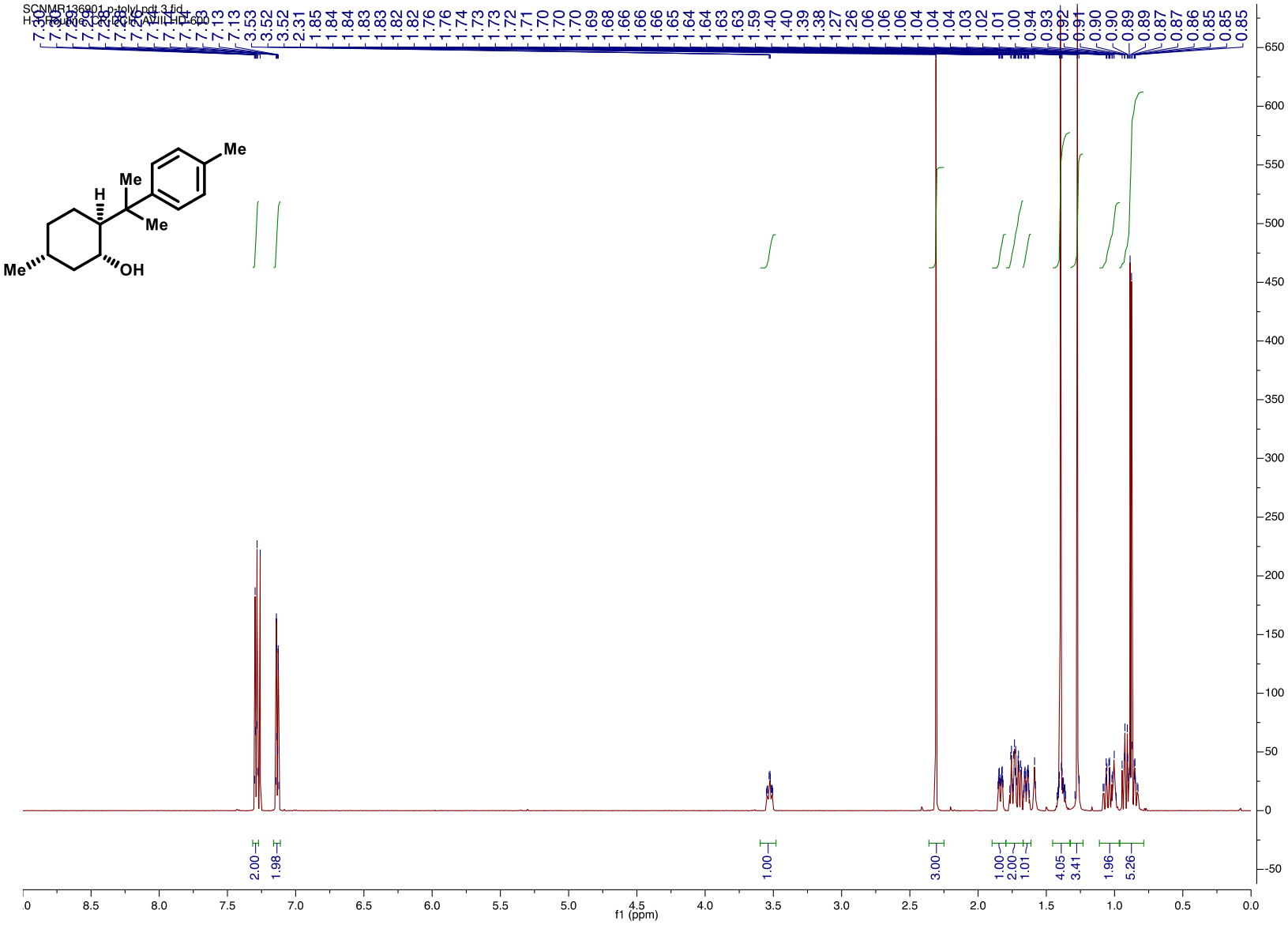
SI-05: ^{13}C-NMR


SCNMR135001.2.fid
C-13 Routine, using 45 degree flip angle. DPX-400
77.16 CDCl3
f1 (ppm)

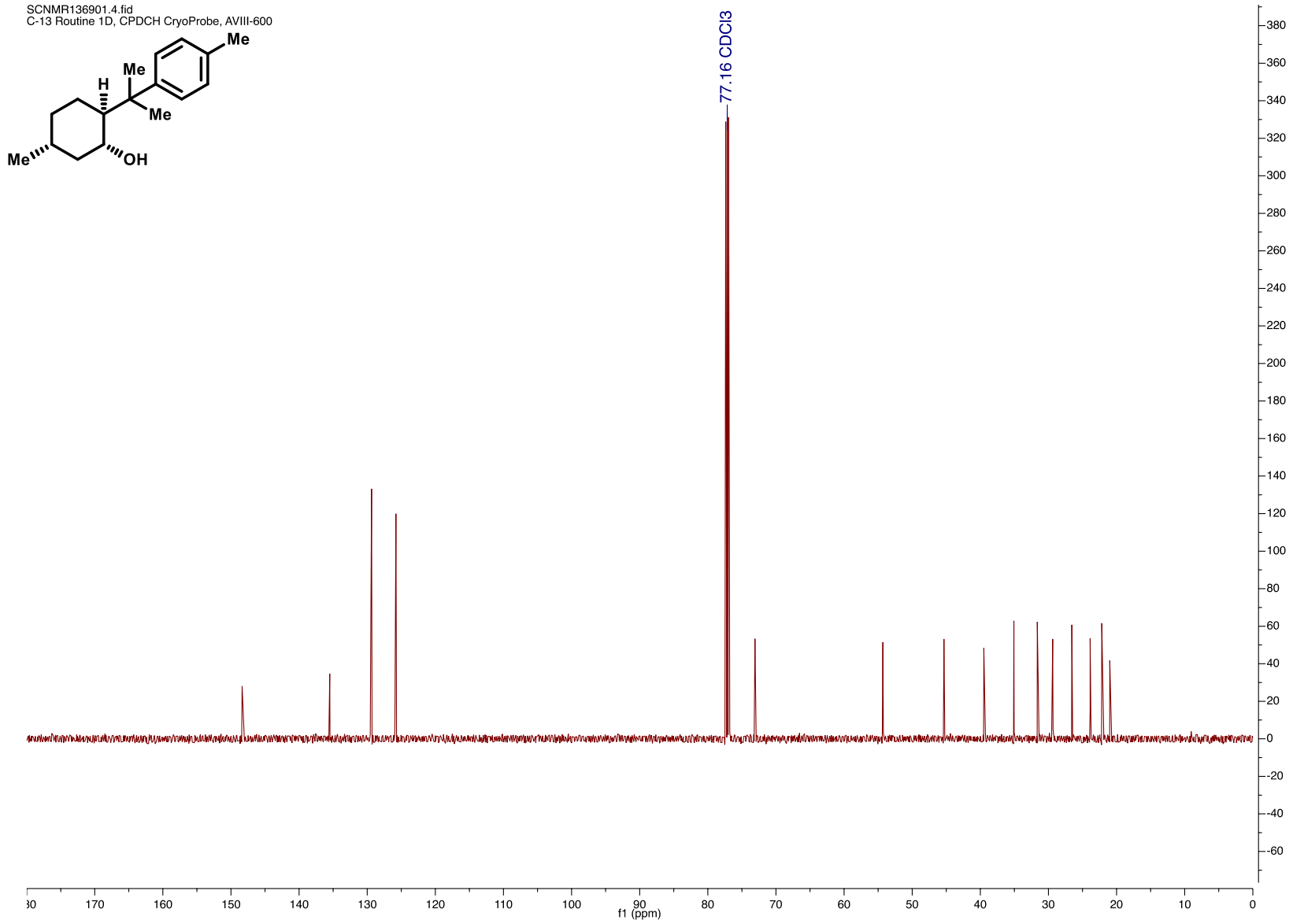

SCNMR135001 p-tolyl sm.2.fid
C-13 Routine, using 45 degree flip angle. DEPT 400
145.32
144.49
134.83
129.52
127.97
113.08
83.19
77.48
77.16
76.84
50.95
41.89
33.79
31.72
30.53
22.00
21.76
19.40
H
Me
Me
O
S
O
O
Me
f1 (ppm)

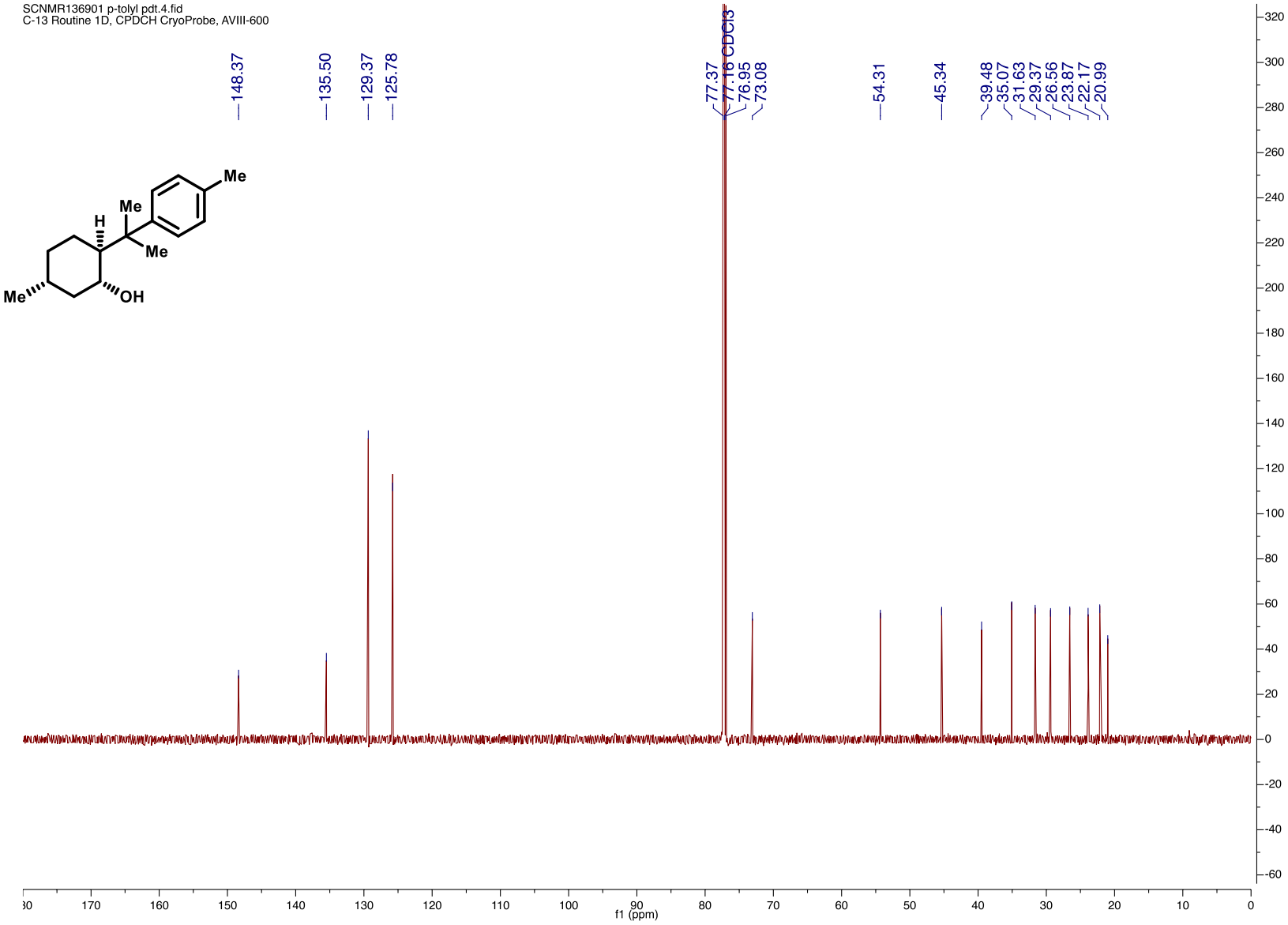
5c: ^{1}H-NMR


SCNMR136901.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
Me
H
Me
Me
OH
f1 (ppm)

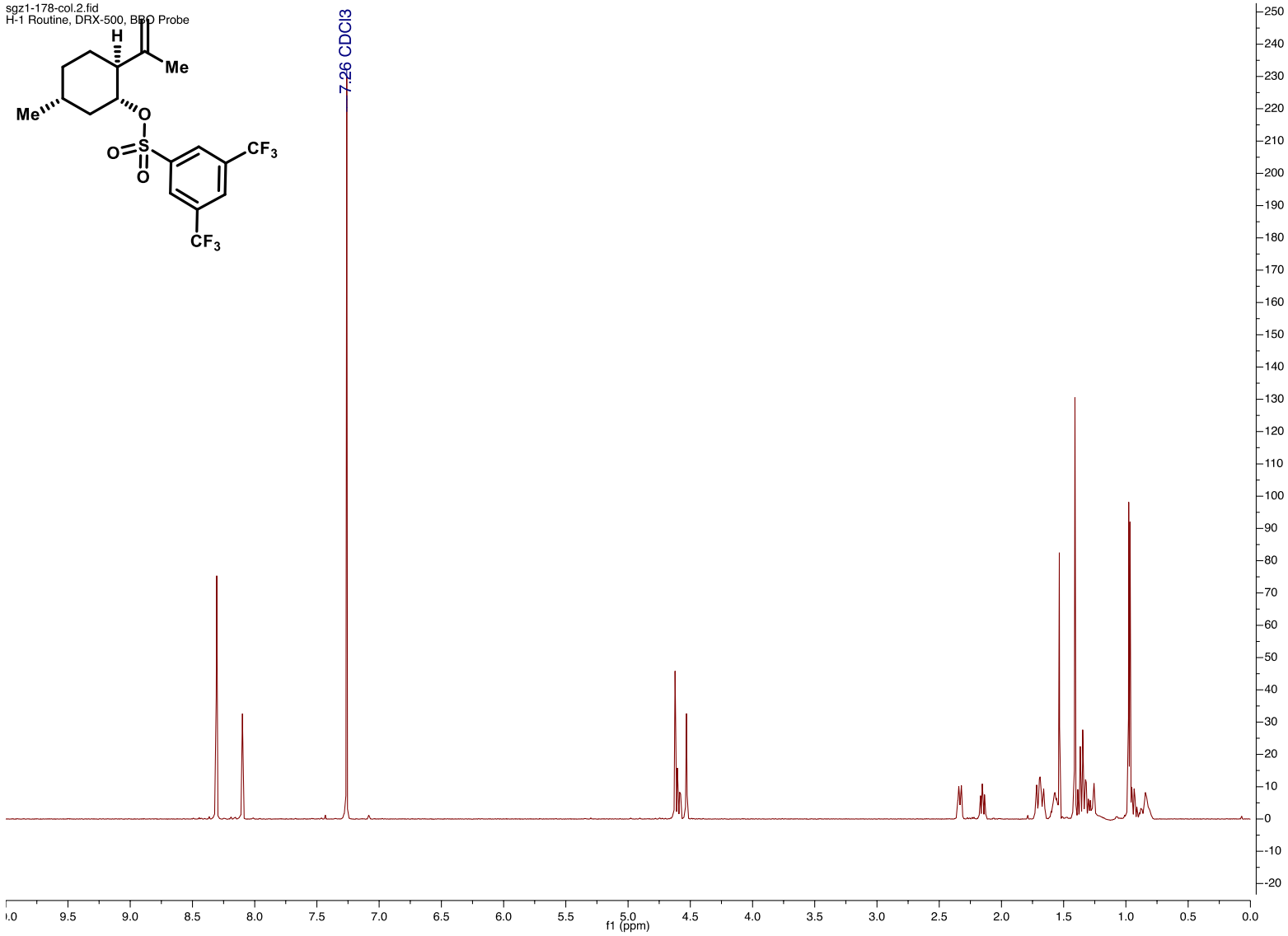

SCNMR136901-p-tolyl.pdt.3.fid
H-CHLOROFORM-D1 (CDCl3)
Bruker Ultra 400 MHz AVIII HD 600
Me
Me
H
Me
Me
OH
f1 (ppm)

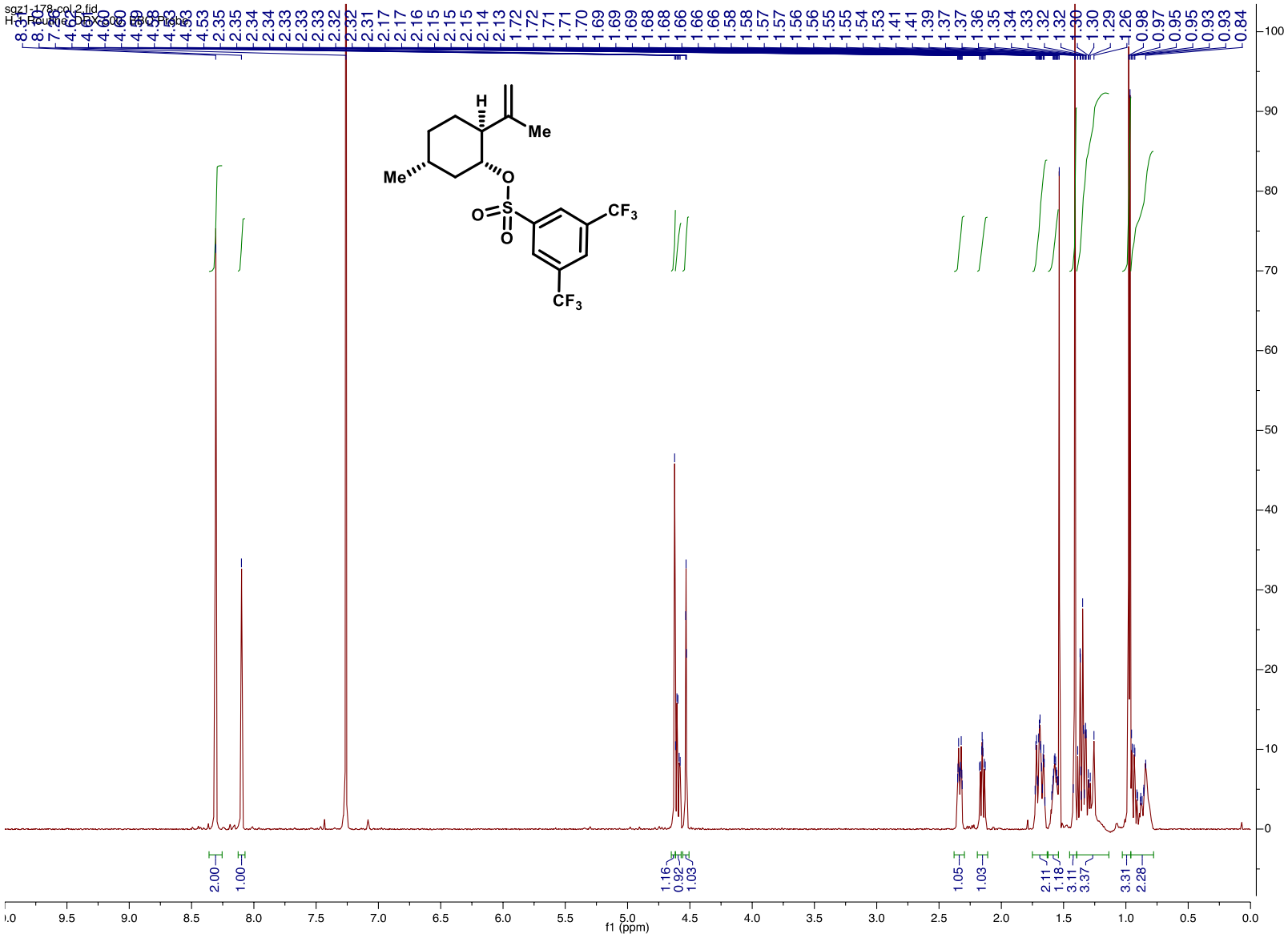
5c: ^{13}C-NMR


SCNMR136901.4.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
Me
H
Me
Me
OH
77.16 CDCl3
f1 (ppm)

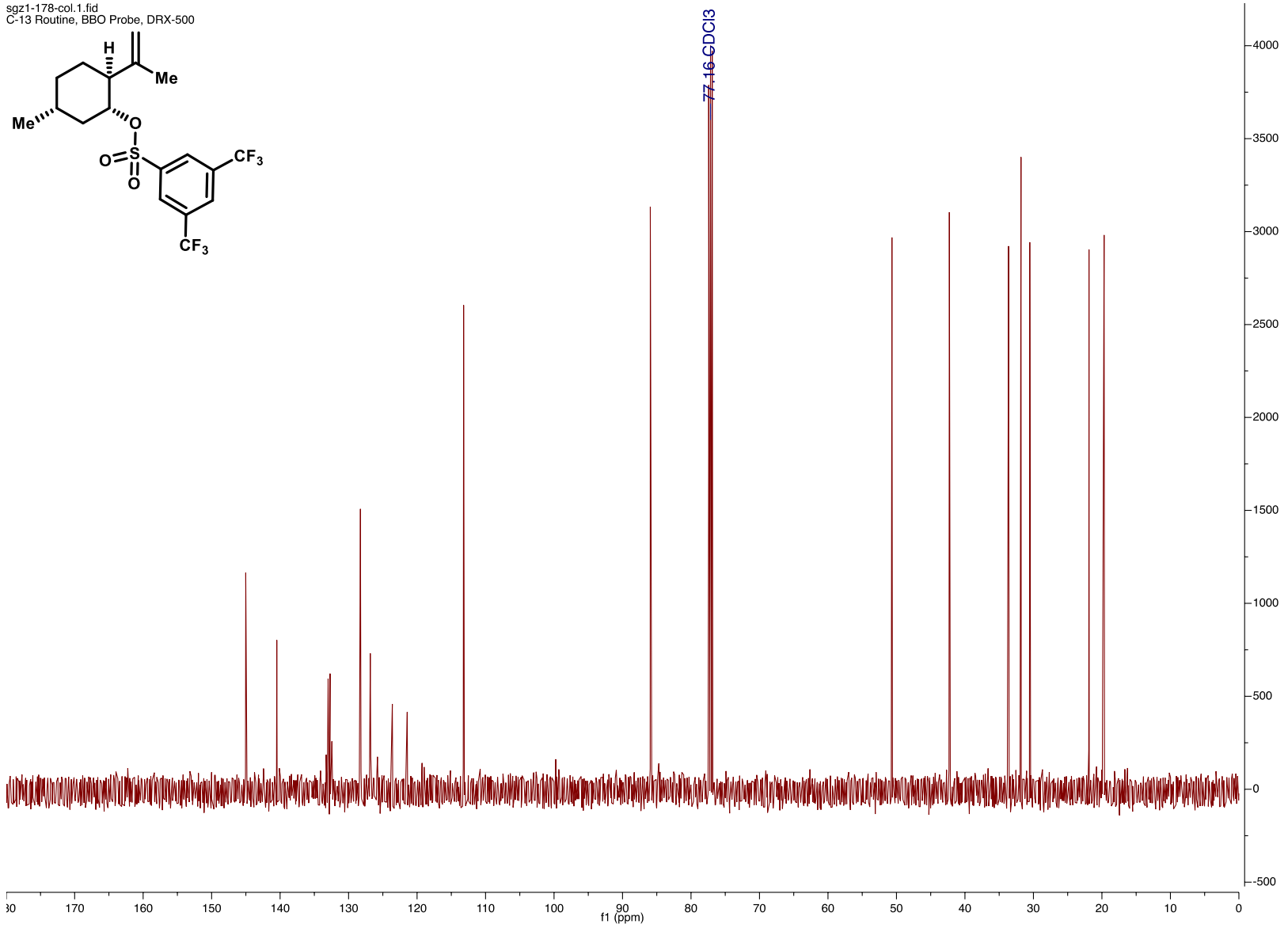

SCNMR136901 p-tolyl pdt.4.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
148.37
135.50
129.37
125.78
77.37
77.16 CDCl3
76.95
73.08
54.31
45.34
39.48
35.07
31.63
29.37
26.56
23.87
22.17
20.99
Me
Me
H
Me
Me
OH
f1 (ppm)

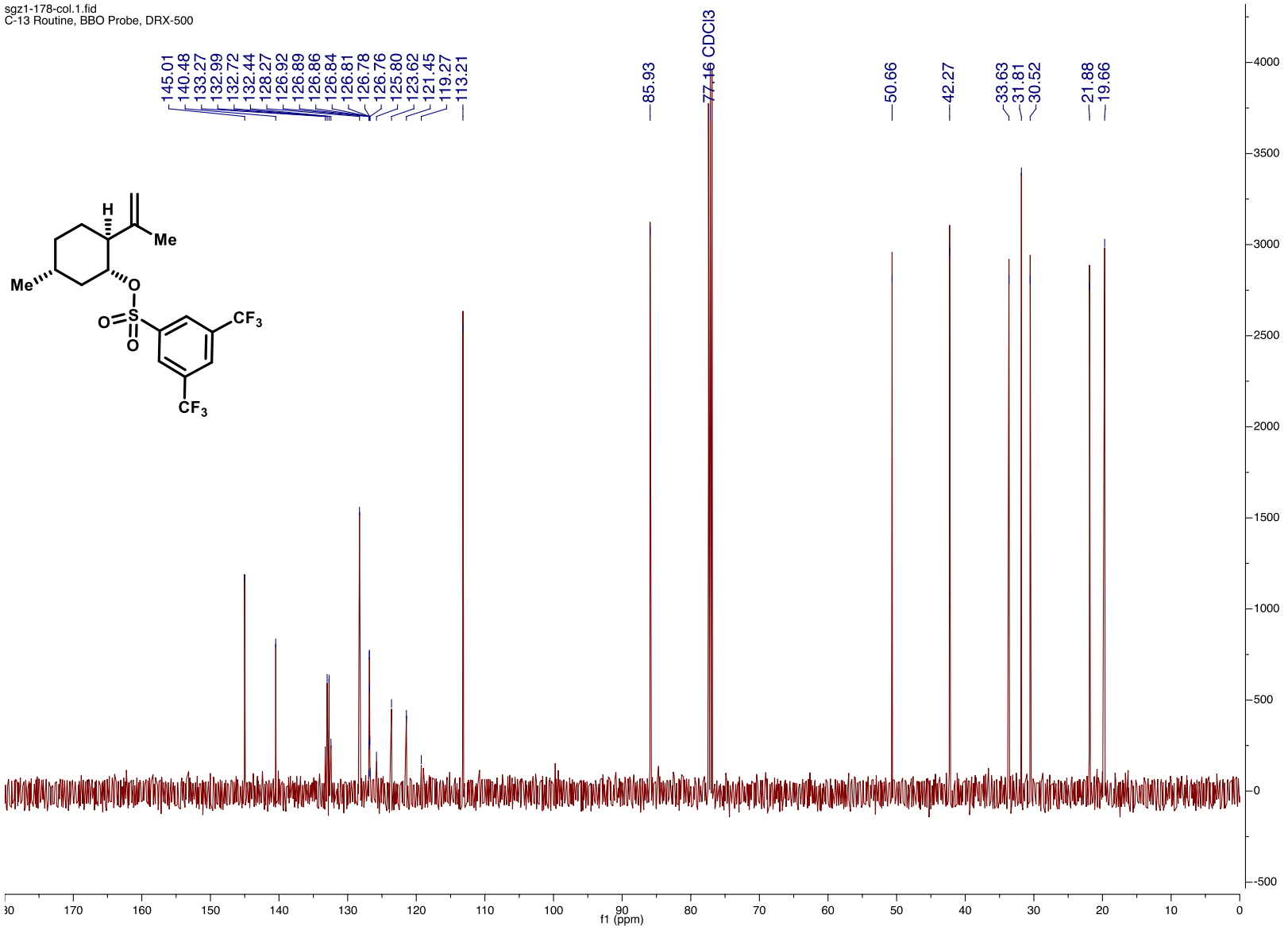
SI-06: ^{1}H-NMR


sgz1-178-col.2.fid
H-1 Routine, DRX-500, BBO Probe
7.26 CDCl3
f1 (ppm)

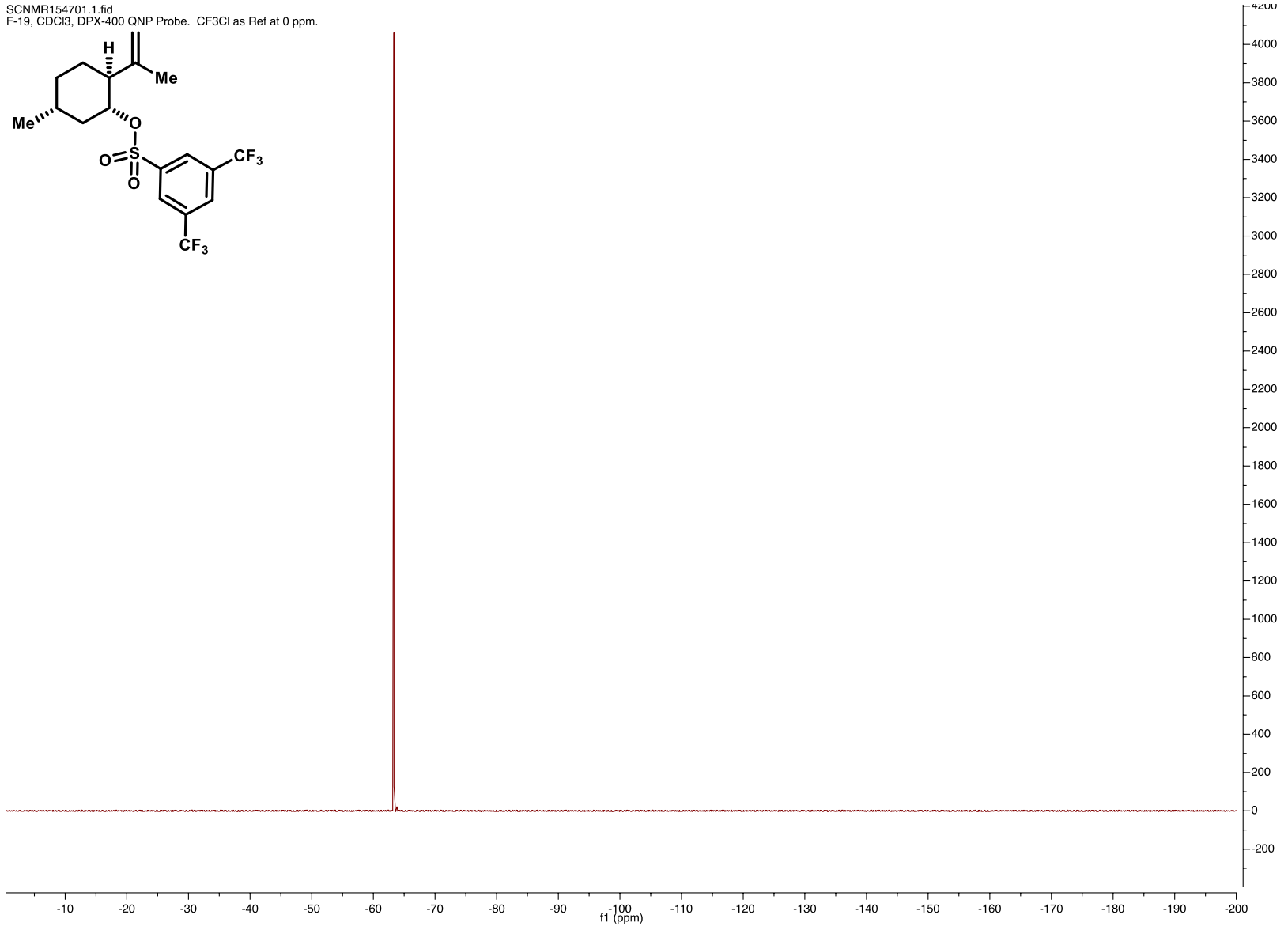

sgzJ-178-col-2.fid
H-1 Room Dmx600 dcz Probe
H
Me
Me
O
O
S
O
O
CF3
CF3
f1 (ppm)

SI-06: ^{13}C-NMR

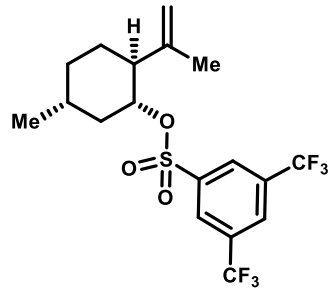

sgz1-178-col.1.fid
C-13 Routine, BBO Probe, DRX-500
77.16-CDCl3
f1 (ppm)


sgz1-178-col.1.fid
C-13 Routine, BBO Probe, DRX-500
145.01
140.48
133.27
132.99
132.72
132.44
128.27
126.92
126.89
126.86
126.84
126.81
126.78
126.76
125.80
123.62
121.45
119.27
113.21
85.93
77.16 CDCl3
50.66
42.27
33.63
31.81
30.52
21.88
19.66
H
Me
Me
O
O
S
O
O
CF3
CF3
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

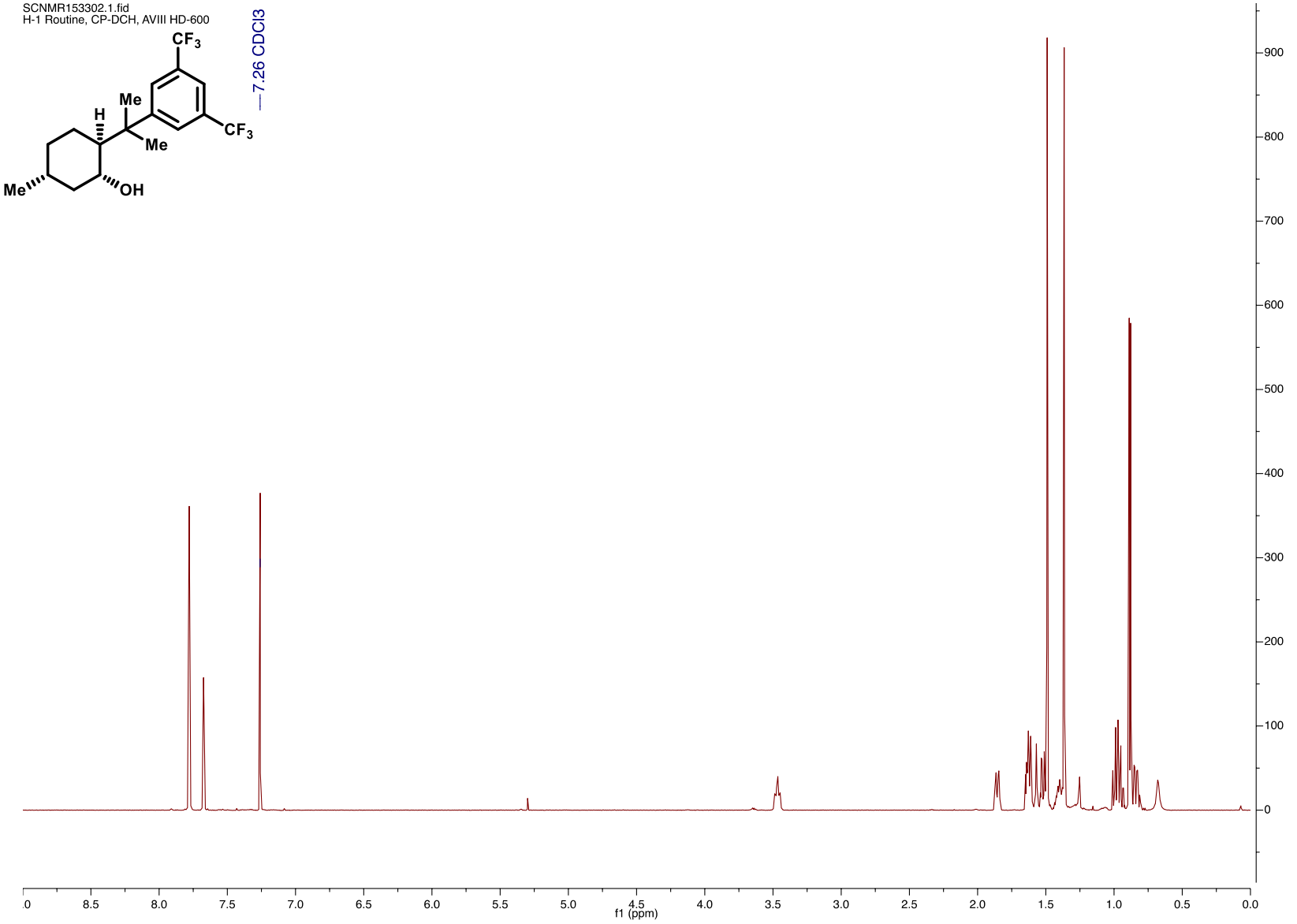
SI-06: ^{19}F-NMR (Uncorrected)

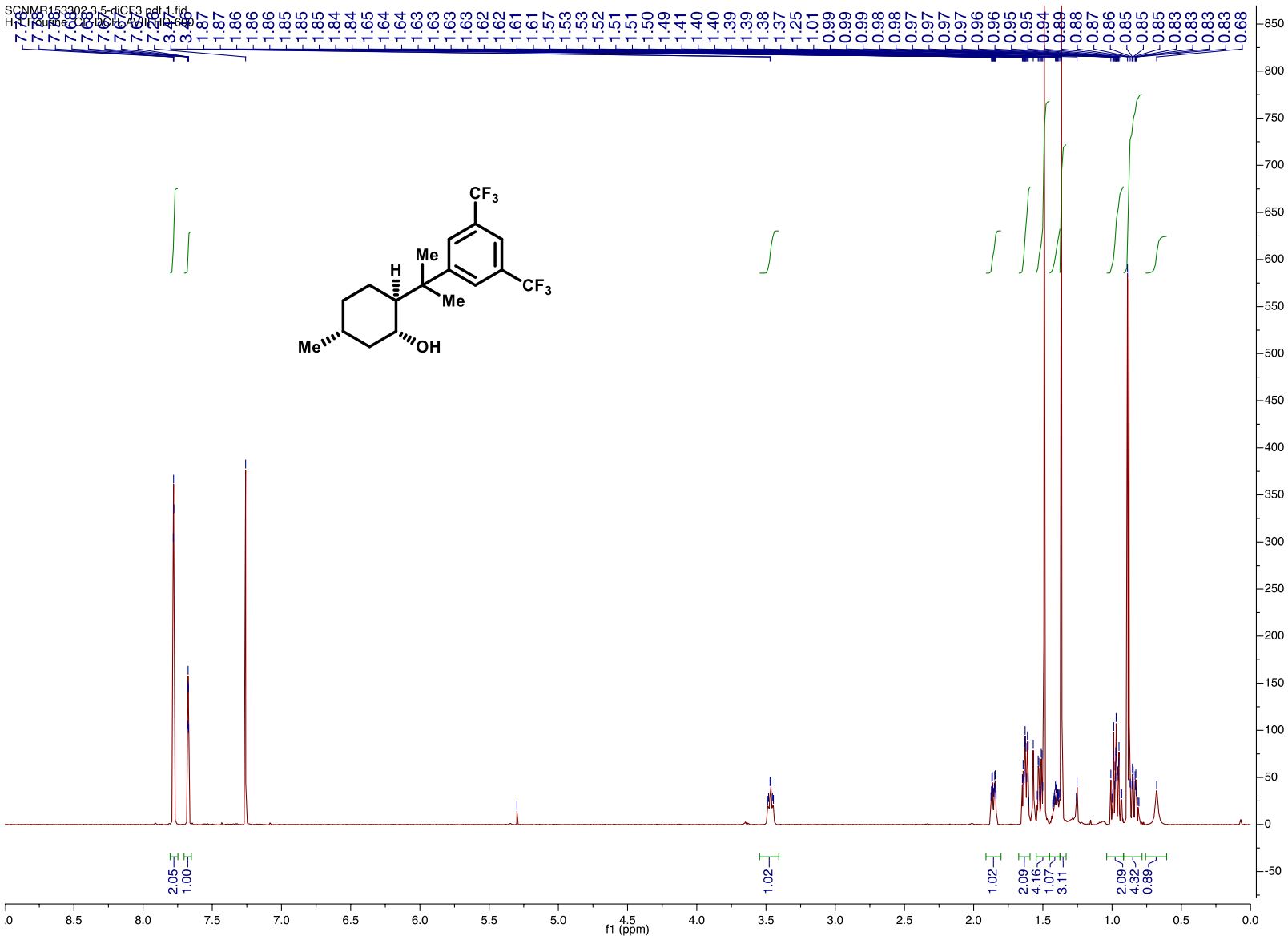


SCNMR154701.1.fid
F-19, CDCl3, DPX-400 QNP Probe. CF3Cl as Ref at 0 ppm.

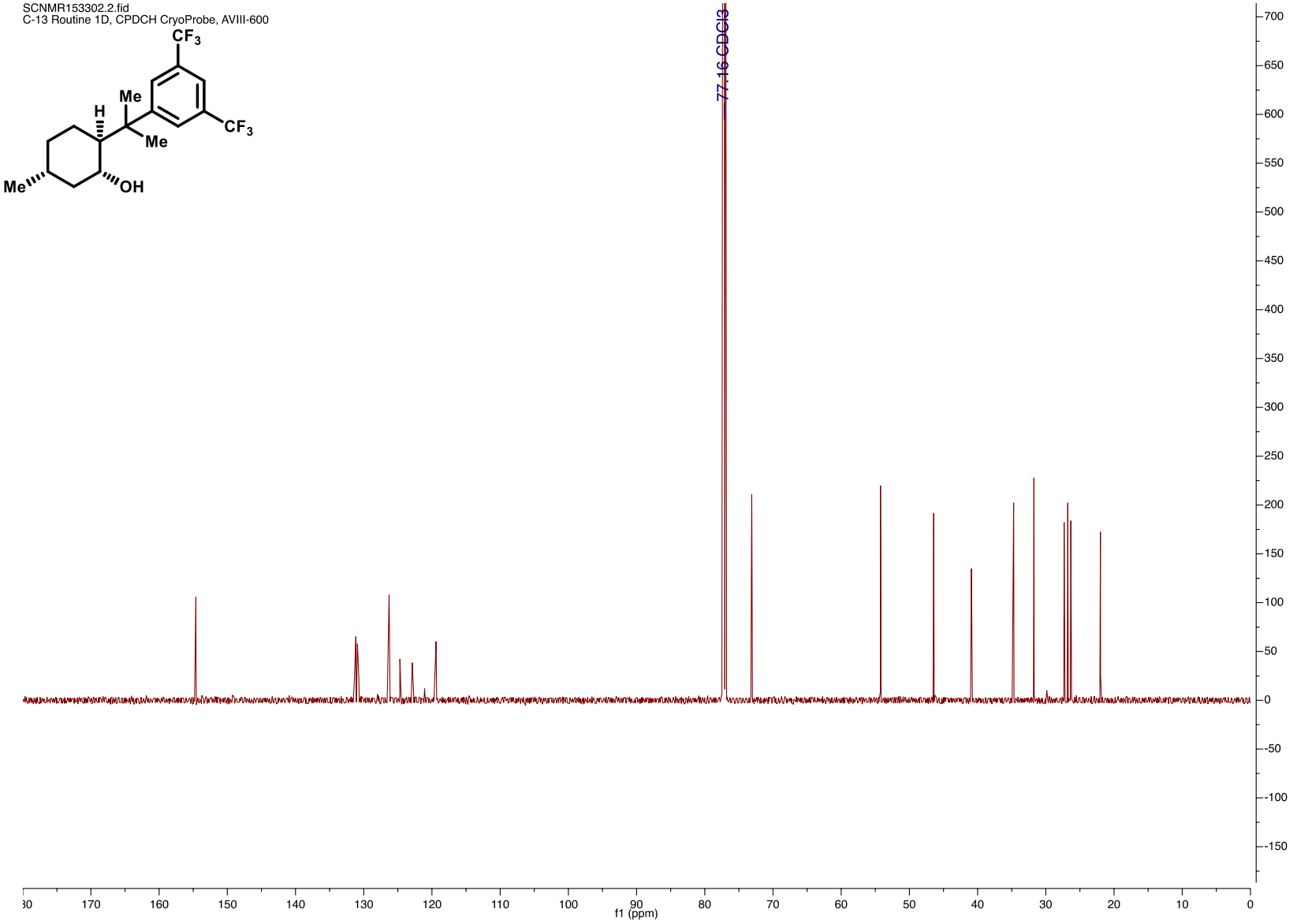


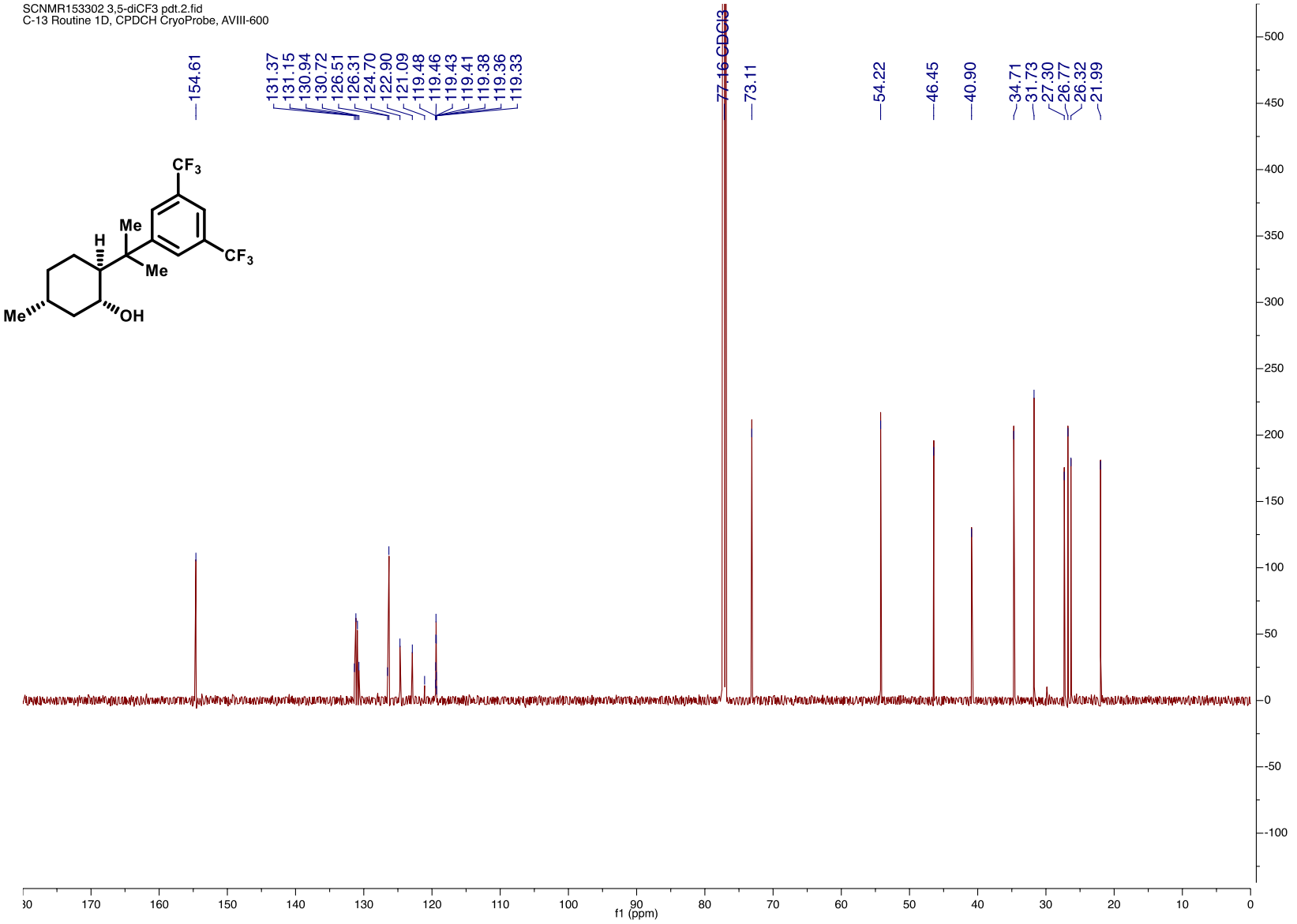
6a: ^{1}H-NMR


SCNMR153302.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
CF3
Me
H
Me
CF3
Me
OH
900
800
700
600
500
400
300
200
100
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
f1 (ppm)

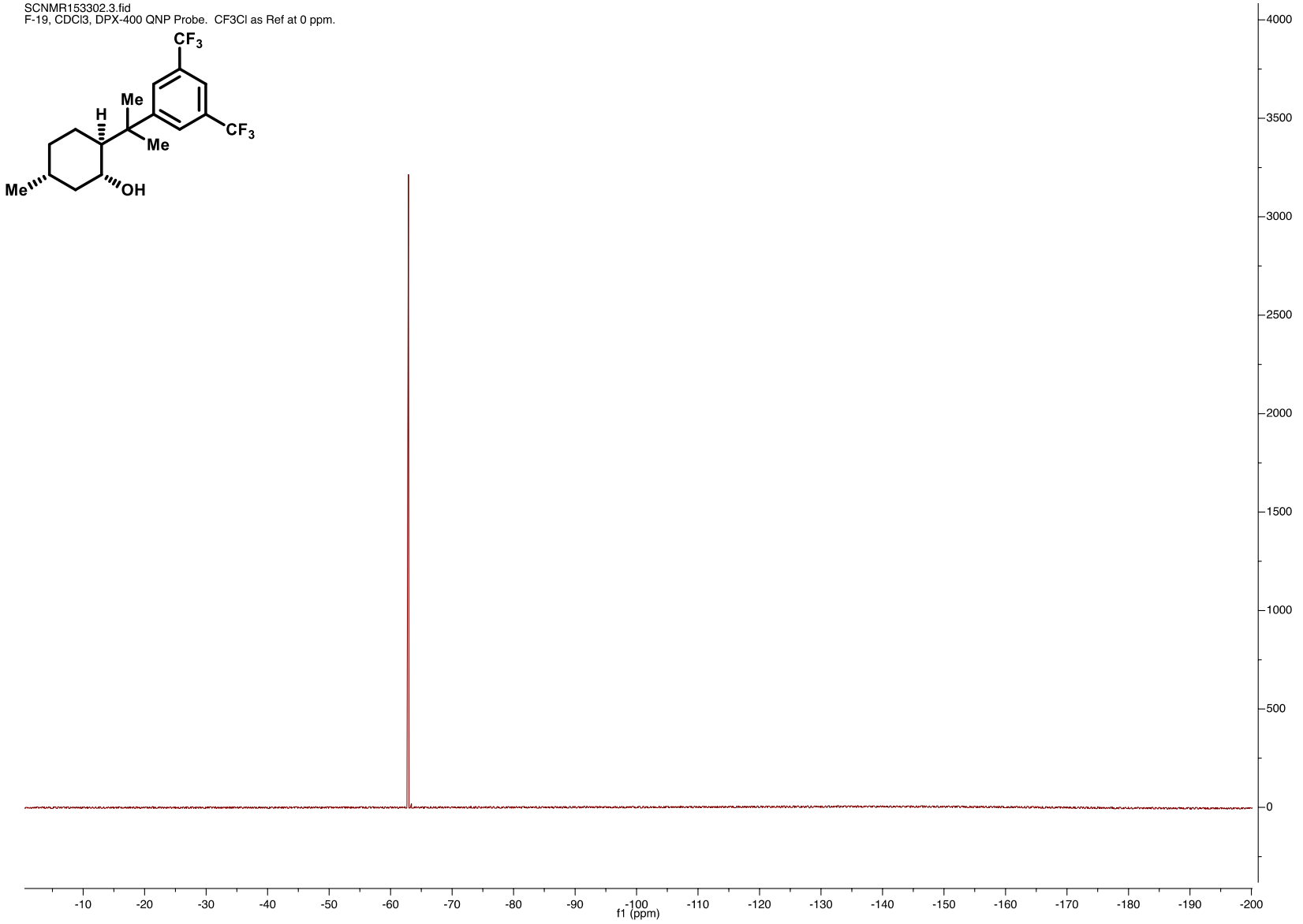

SCNMR153302.3.5-diCF3.pdt.1.fid
CF3
Me
H
Me
CF3
Me
OH
f1 (ppm)

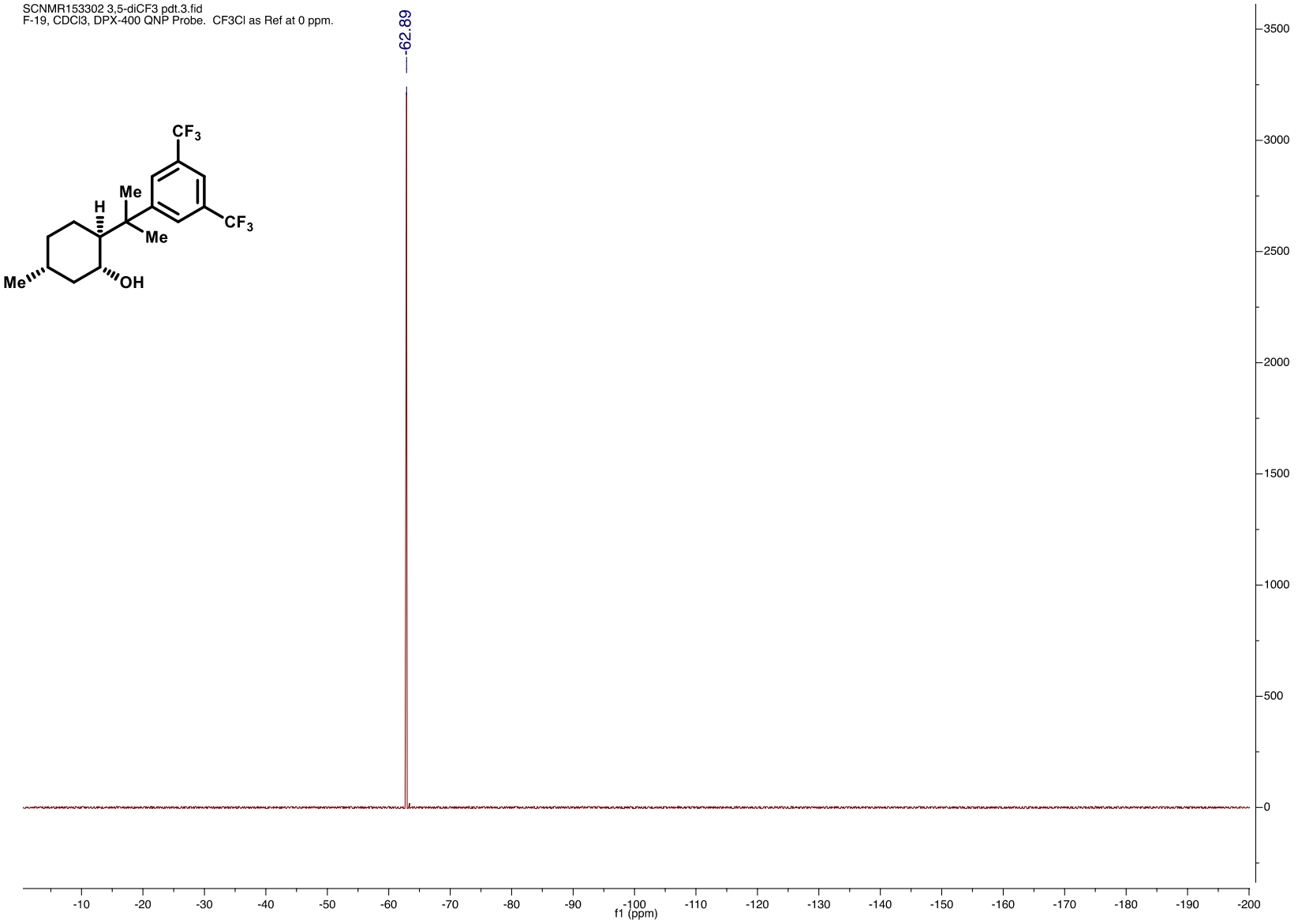
6a: ^{13}C-NMR


SCNMR153302.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
CF3
Me
H
Me
CF3
Me
OH
77.16 CDCl3
f1 (ppm)

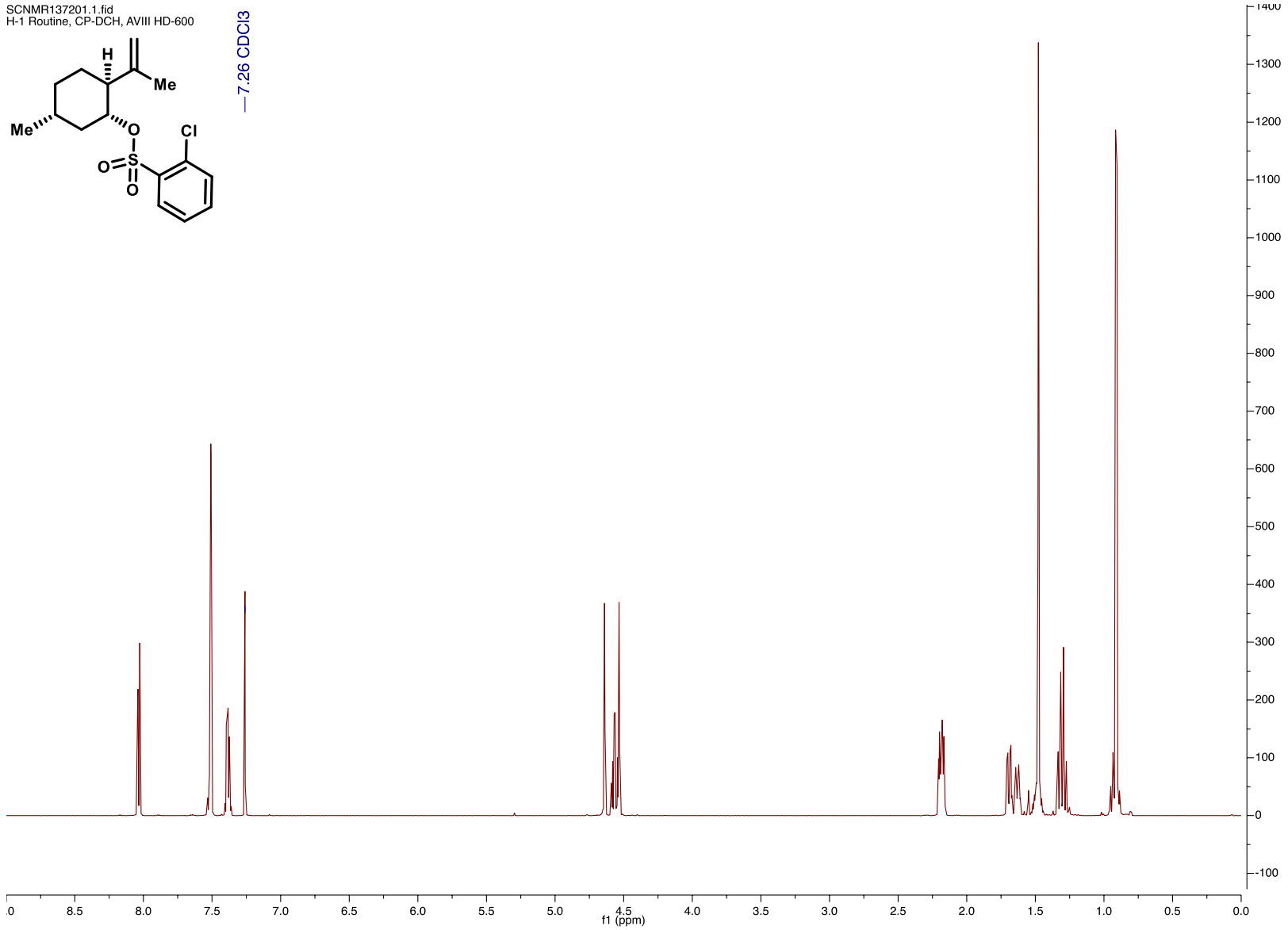

SCNMR153302 3,5-diCF3 pdt.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
154.61
131.37
131.15
130.94
130.72
126.51
126.31
124.70
122.90
121.09
119.48
119.46
119.43
119.41
119.38
119.36
119.33
77.16 CDCl3
73.11
54.22
46.45
40.90
34.71
31.73
27.30
26.77
26.32
21.99
CF3
Me
H
Me
CF3
Me
OH
f1 (ppm)

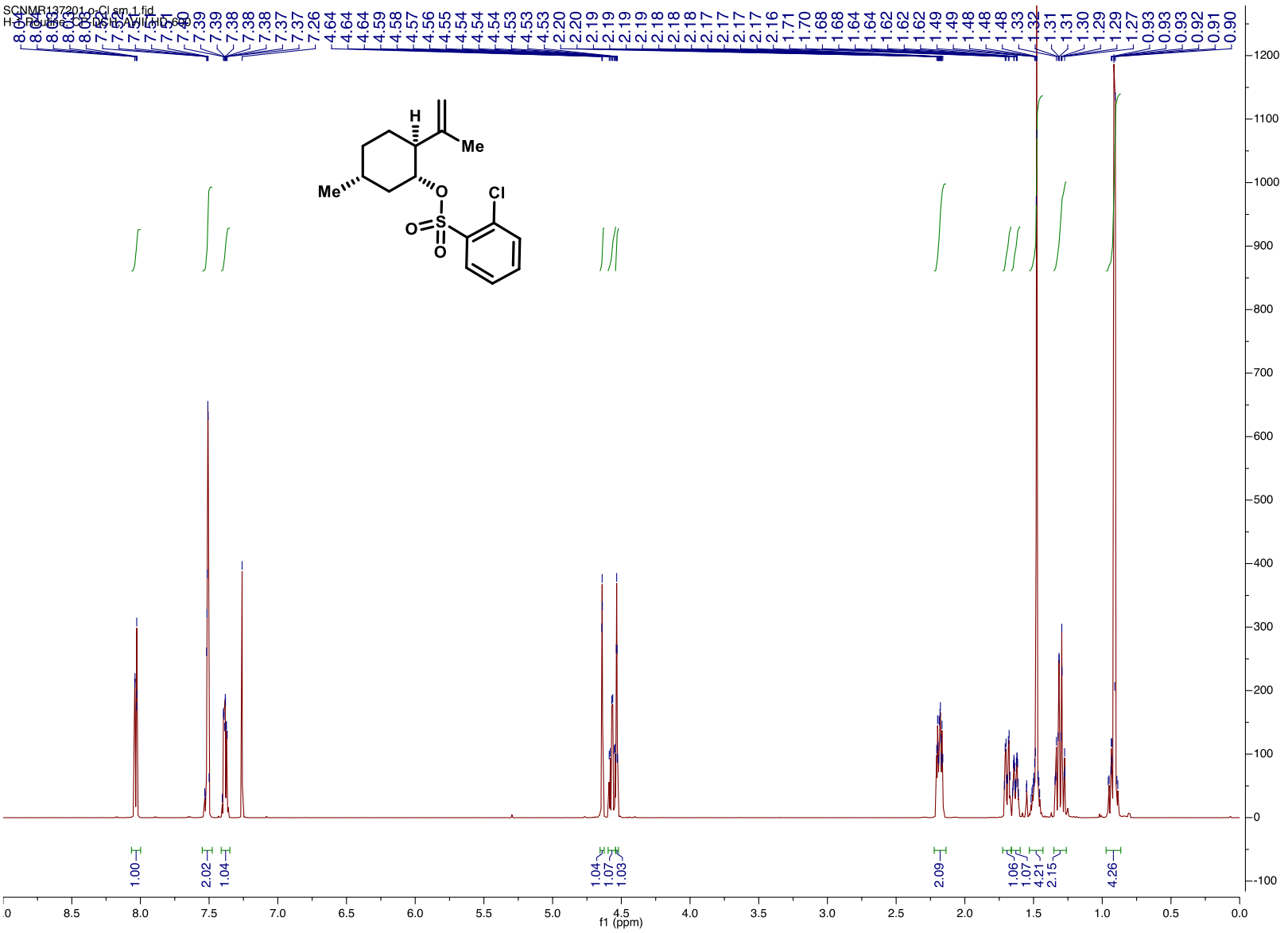
6a: ^{19}F-NMR (Uncorrected)



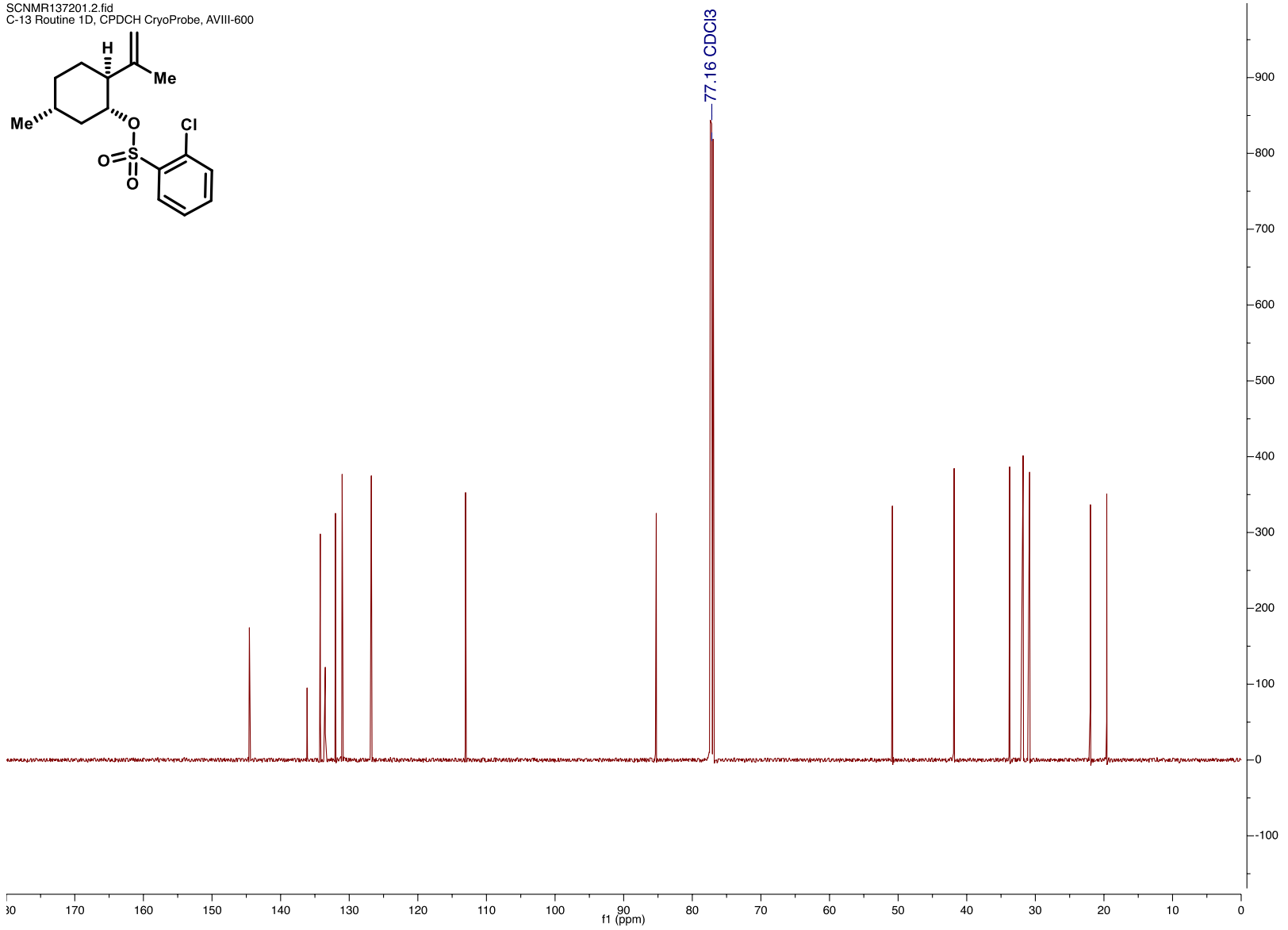

SCNMR153302 3,5-diCF3 pdt.3.fid
F-19, CDCl3, DPX-400 QNP Probe. CF3Cl as Ref at 0 ppm.
-62.89
CF3
Me
H
Me
CF3
Me
OH
3500
3000
2500
2000
1500
1000
500
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

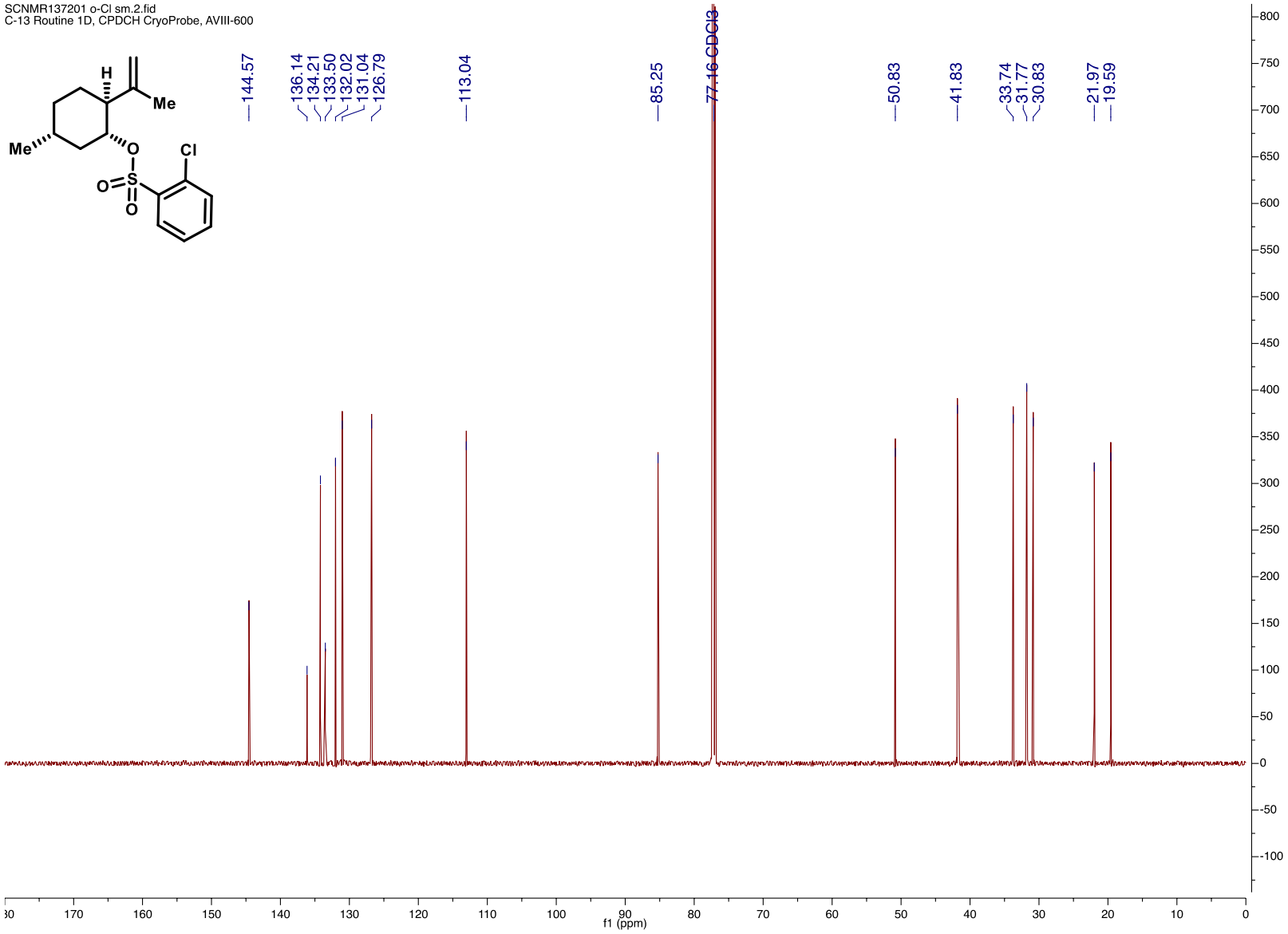
SI-07: ^{1}H-NMR


SCNMR137201.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
H
Me
Me
O
Cl
O
S
O
O
f1 (ppm)

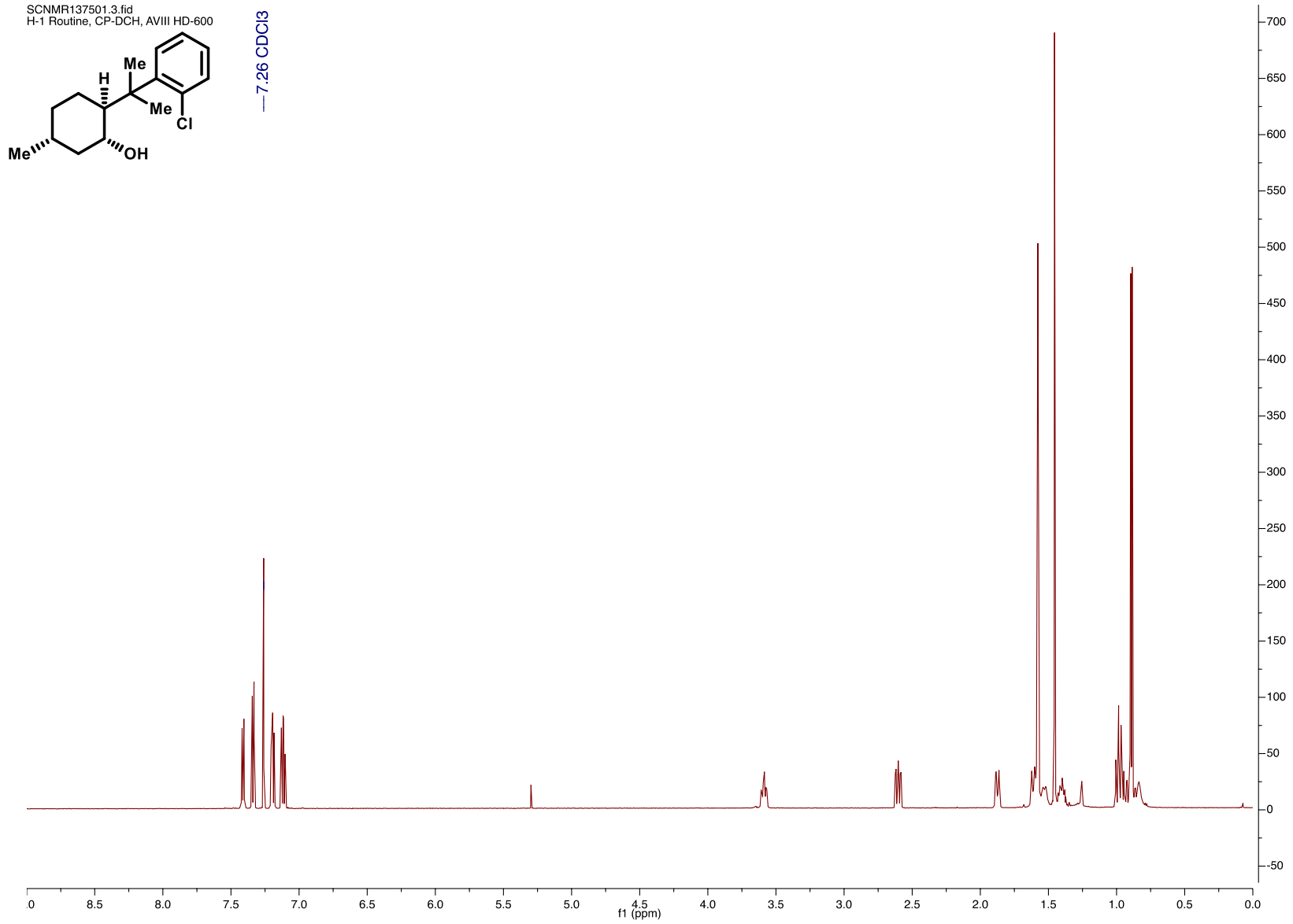

SCNMR137201-o-Cl.sm 1.fid
H-1 PROTON 01 1
H
Me
Me
O
Cl
O
S
O
f1 (ppm)

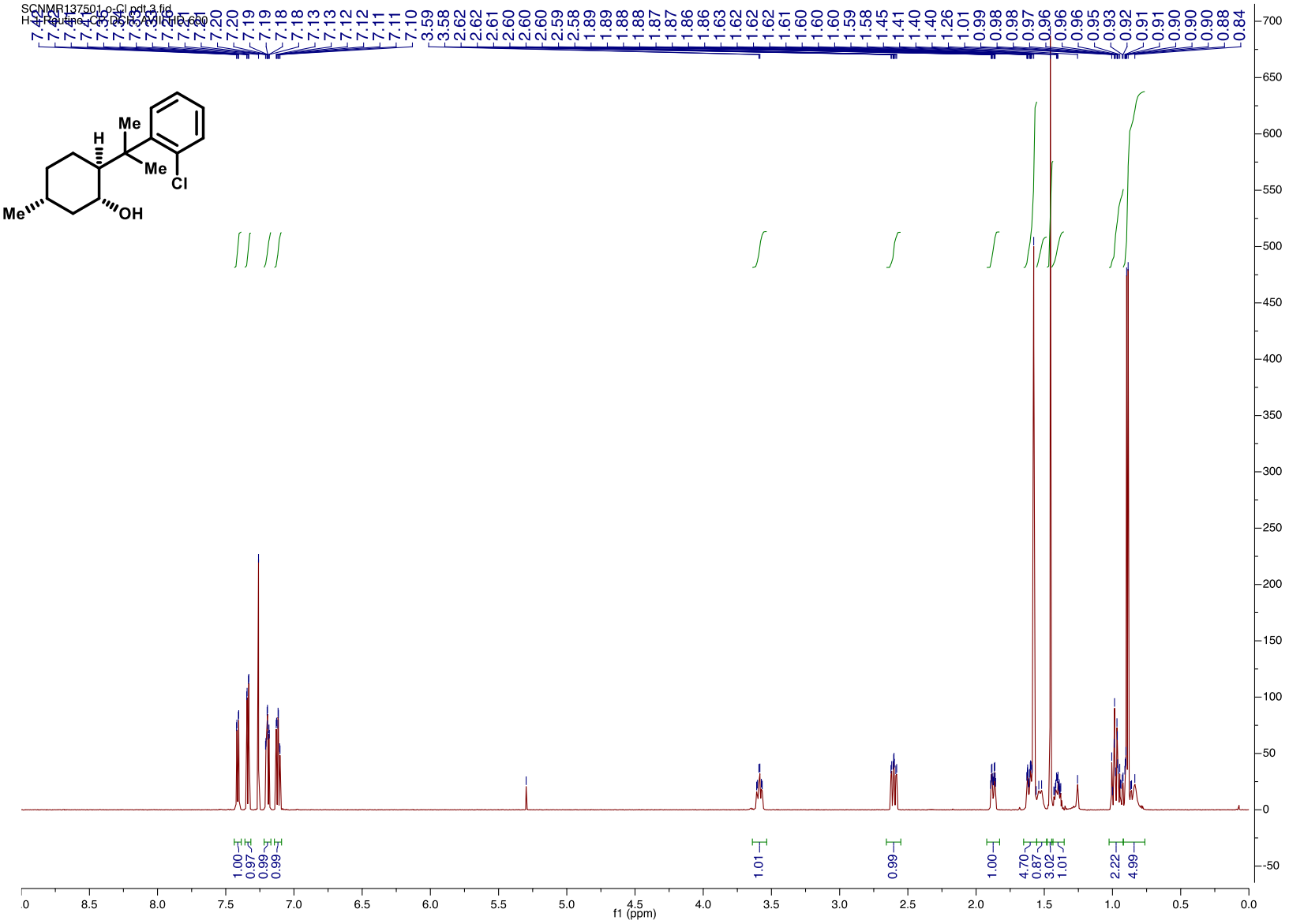
SI-07: ^{13}C-NMR


SCNMR137201.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
77.16 CDCl3
f1 (ppm)

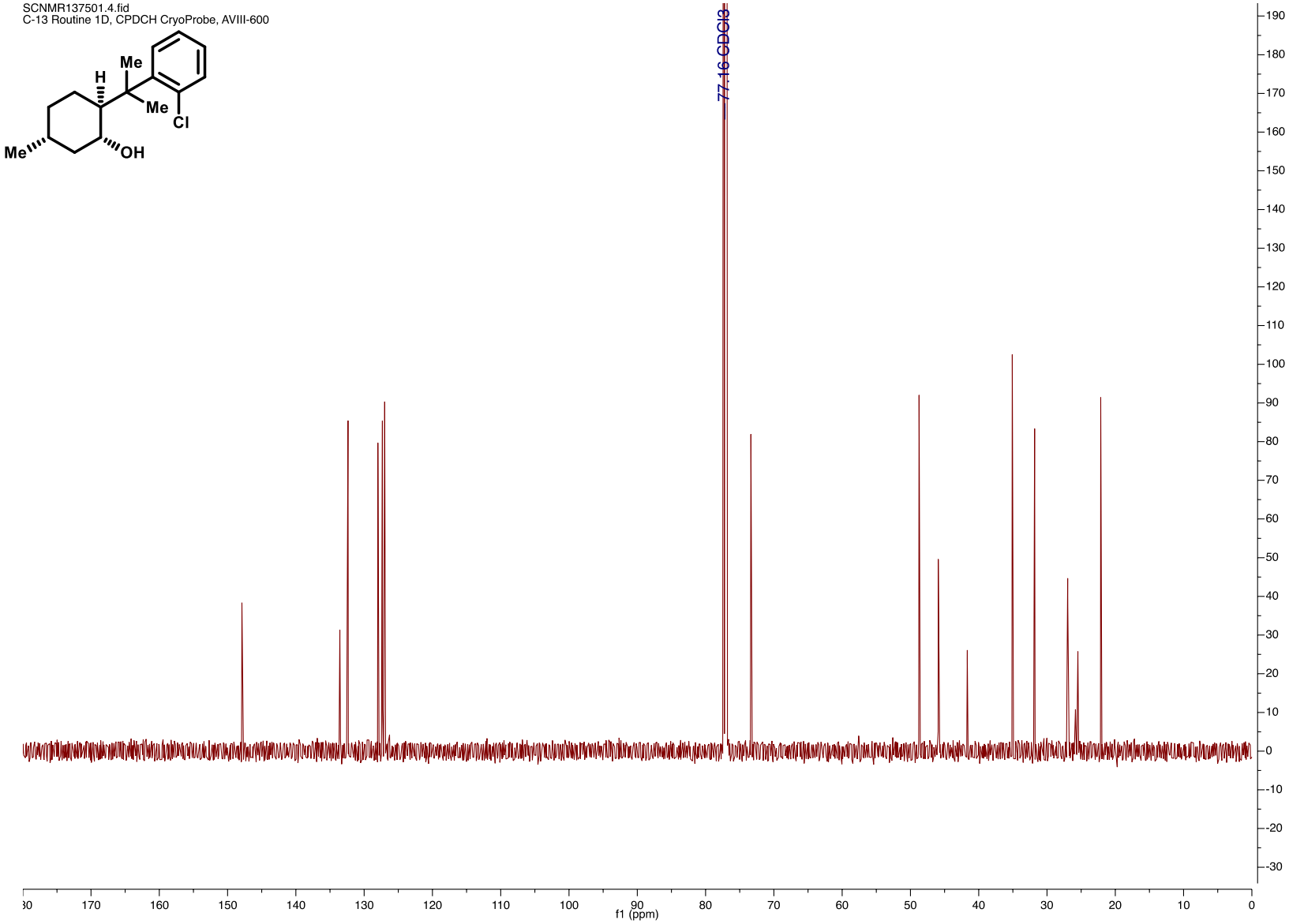

SCNMR137201 o-Cl sm.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
144.57
136.14
134.21
133.50
132.02
131.04
126.79
113.04
85.25
77.16 CDCl3
50.83
41.83
33.74
31.77
30.83
21.97
19.59
H
Me
Me
O
Cl
O
S
O
O
f1 (ppm)

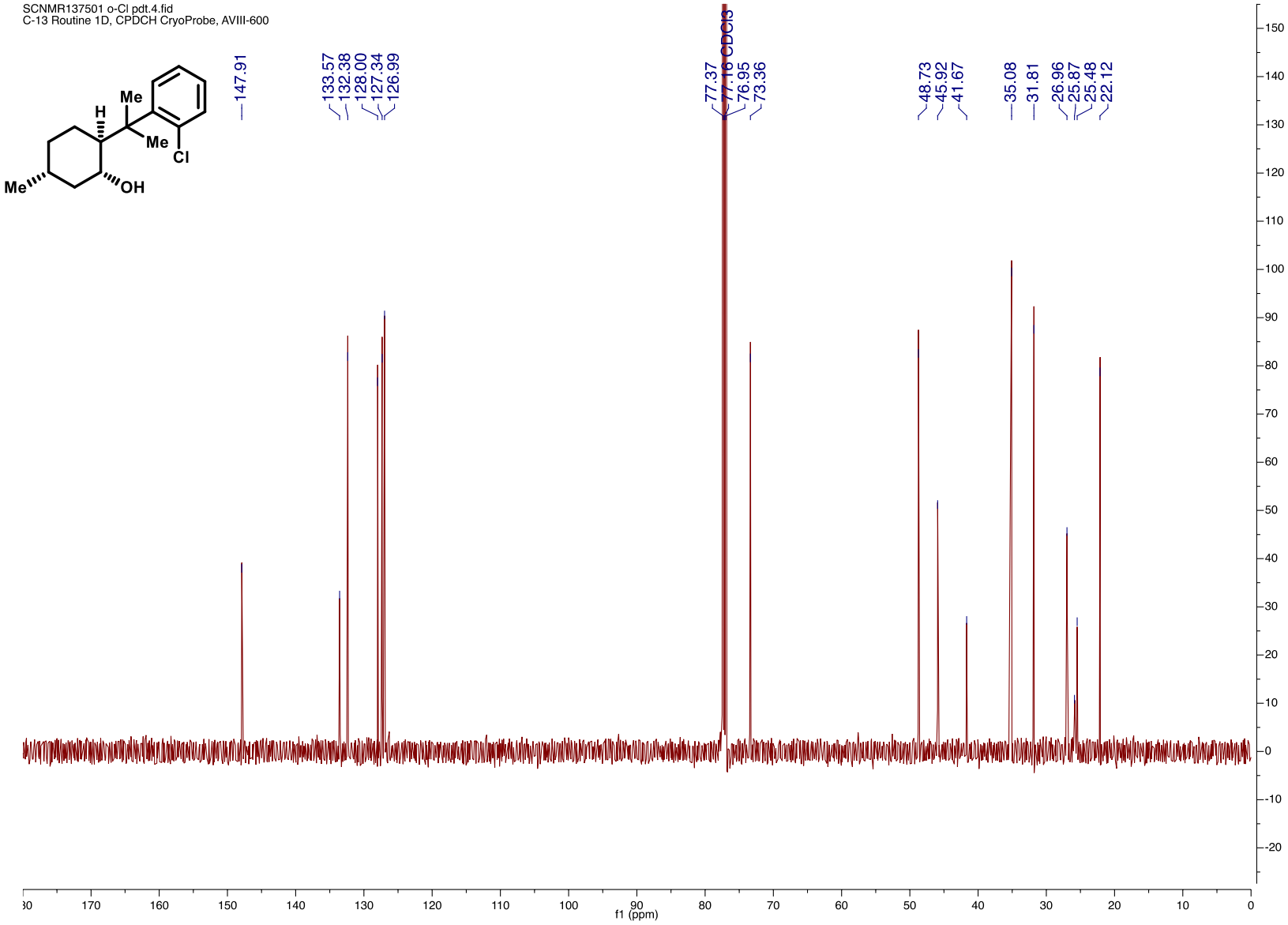
6b: ^{1}H-NMR


SCNMR137501.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
H
Me
Cl
Me
OH
f1 (ppm)

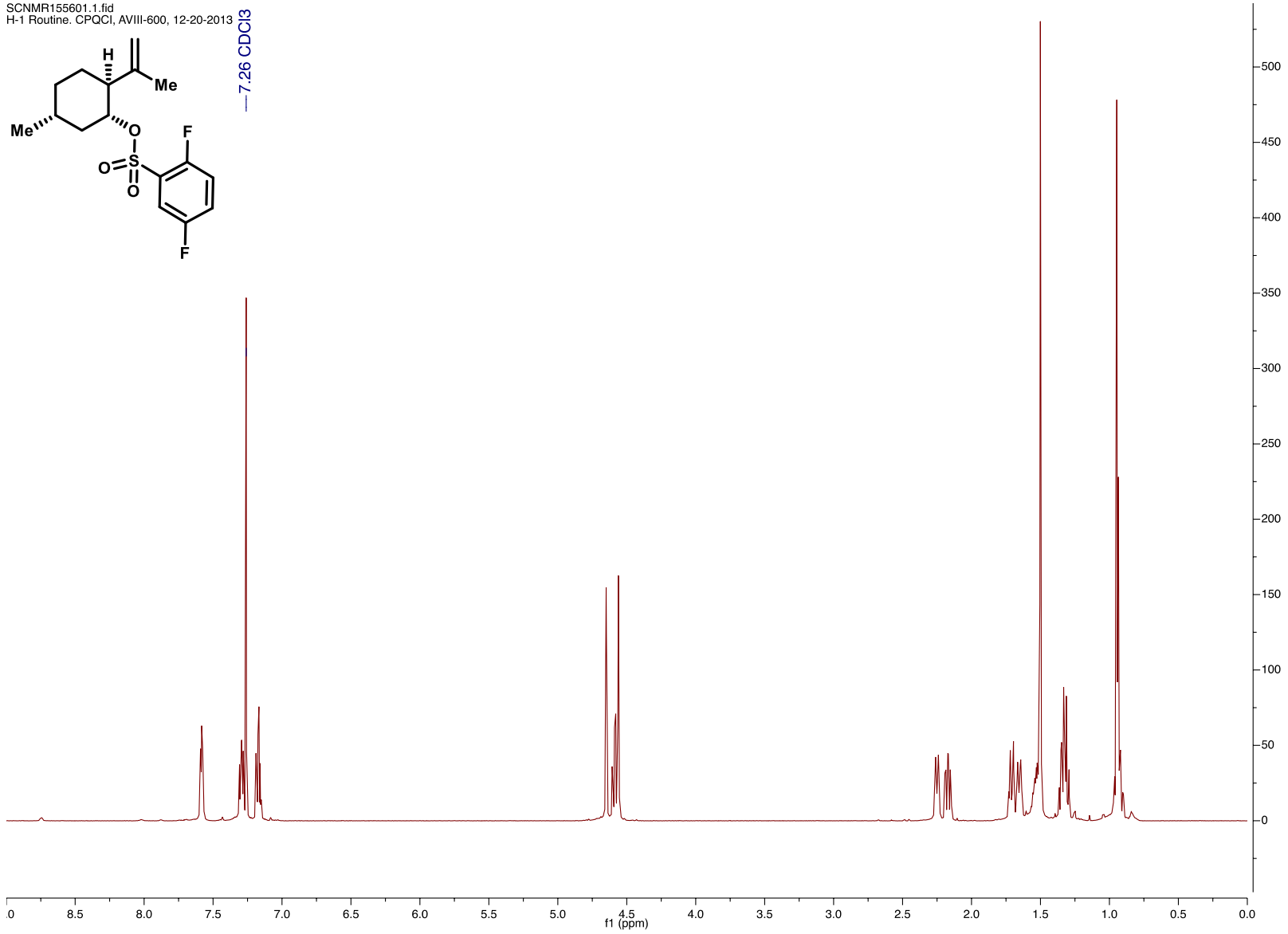

SCNMR137501-o-Cl.pdt.3.fid
H-1 Routine, CHLOROFORM-D, AVIII-500
Me
H
Me
Me
Cl
Me
OH
f1 (ppm)

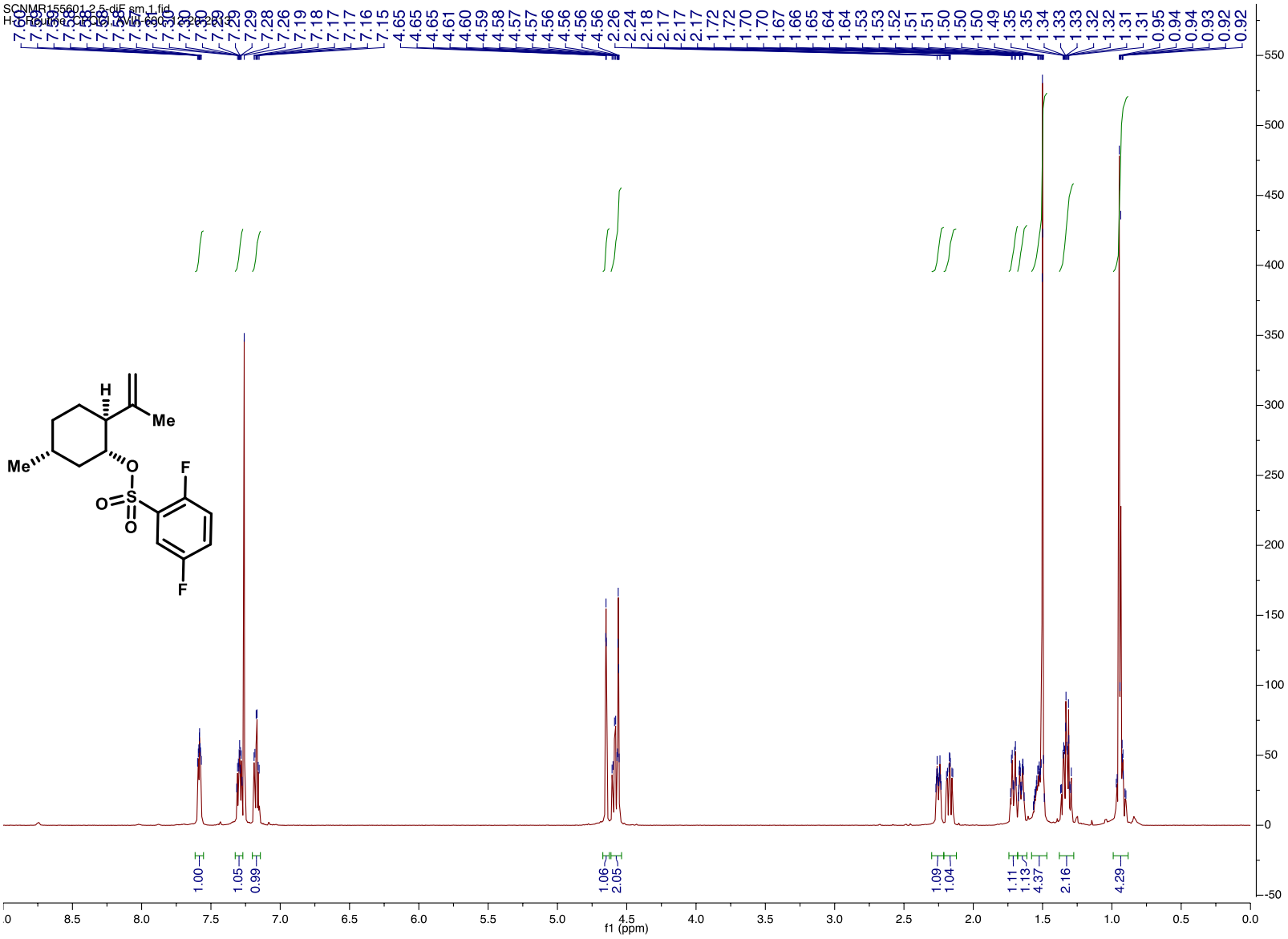
6b: ^{13}C-NMR


SCNMR137501.4.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
H
Me
Me
Cl
Me
OH
77.16 CDCl3
f1 (ppm)

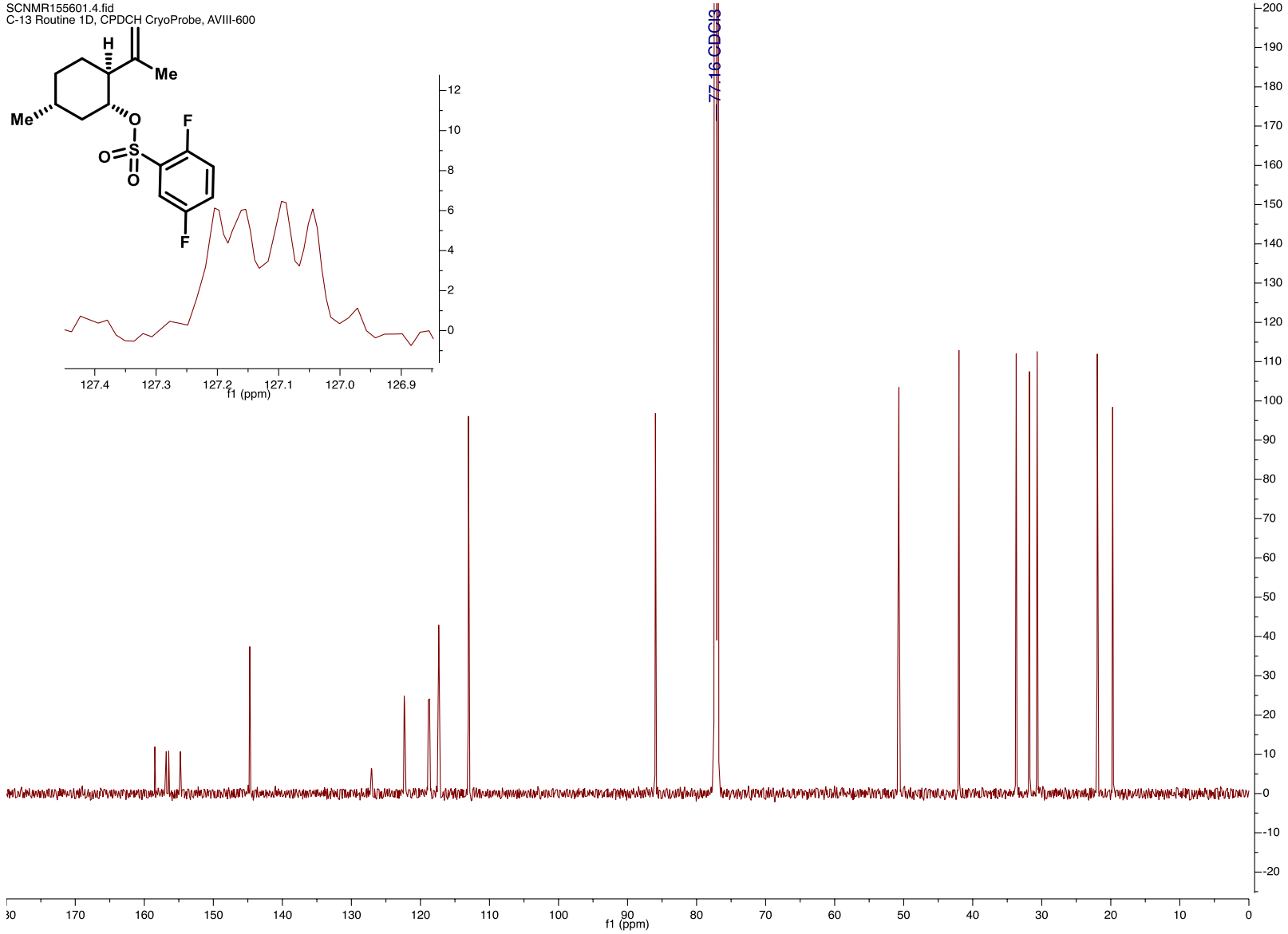

SCNMR137501 o-Cl pdt.4.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
H
Me
Cl
Me
OH
147.91
133.57
132.38
128.00
127.34
126.99
77.37
77.16 CDCl3
76.95
73.36
48.73
45.92
41.67
35.08
31.81
26.96
25.87
25.48
22.12
f1 (ppm)

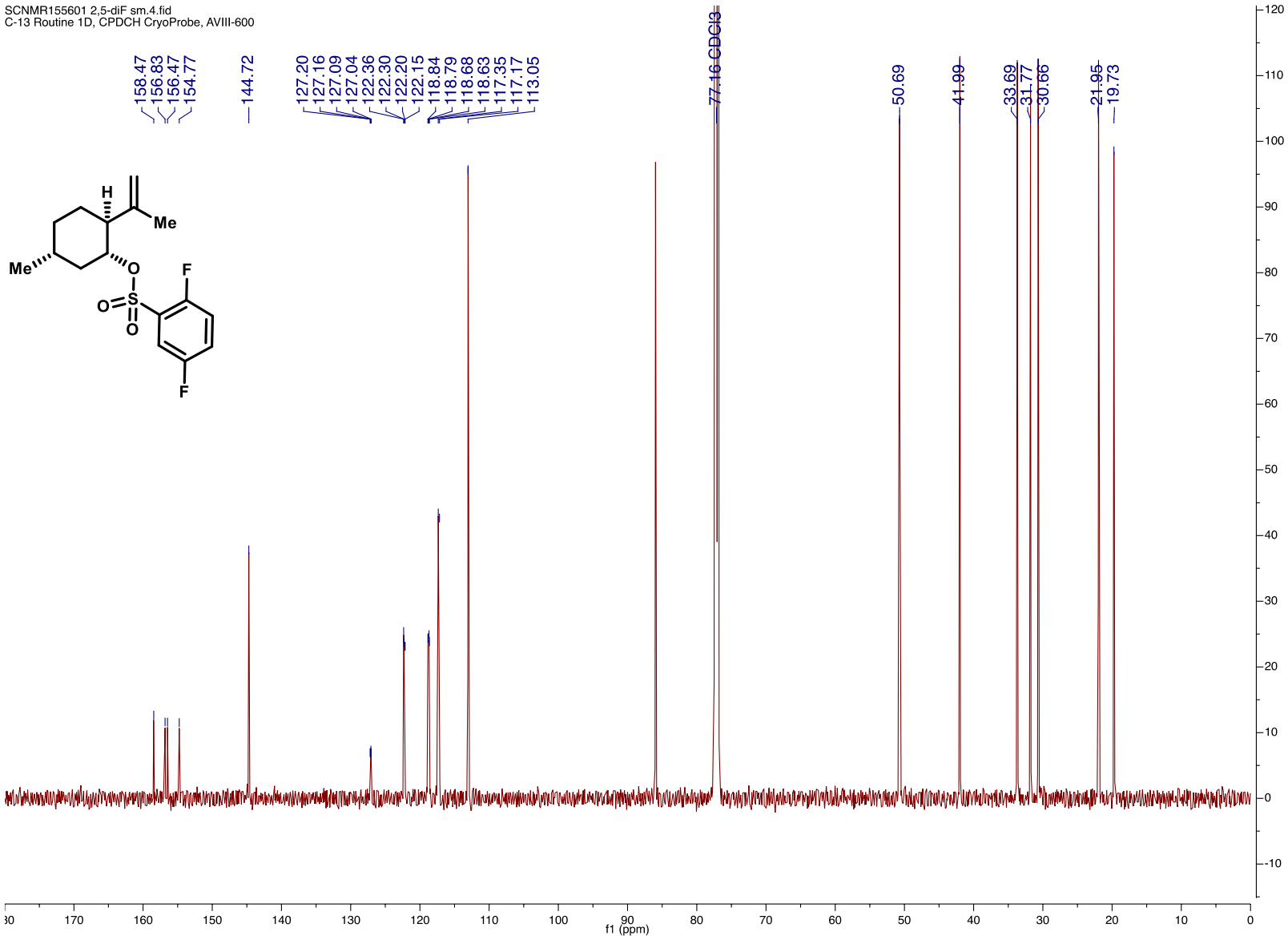
SI-08: ^{1}H-NMR


SCNMR155601.1.fid
H-1 Routine. CPQCl, AVIII-600, 12-20-2013
7.26 CDCl3
H
Me
Me
O
S
O
O
F
F
500
450
400
350
300
250
200
150
100
50
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
f1 (ppm)

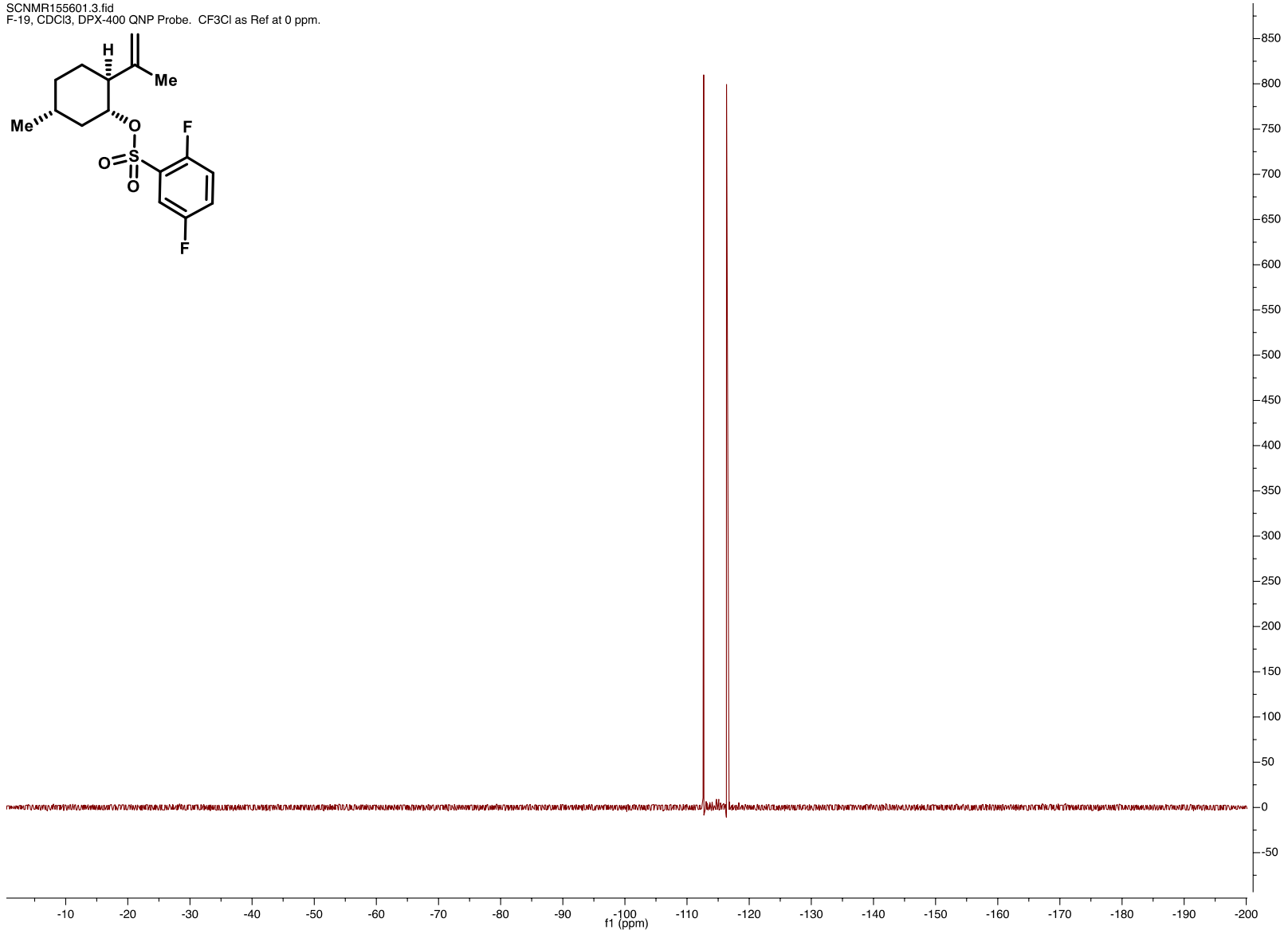

SCNMR155601-2,5-diF sm 1.fid
H-Routine-1-1D-1.xwin-600
H
Me
Me
O
S
O
O
F
F
f1 (ppm)

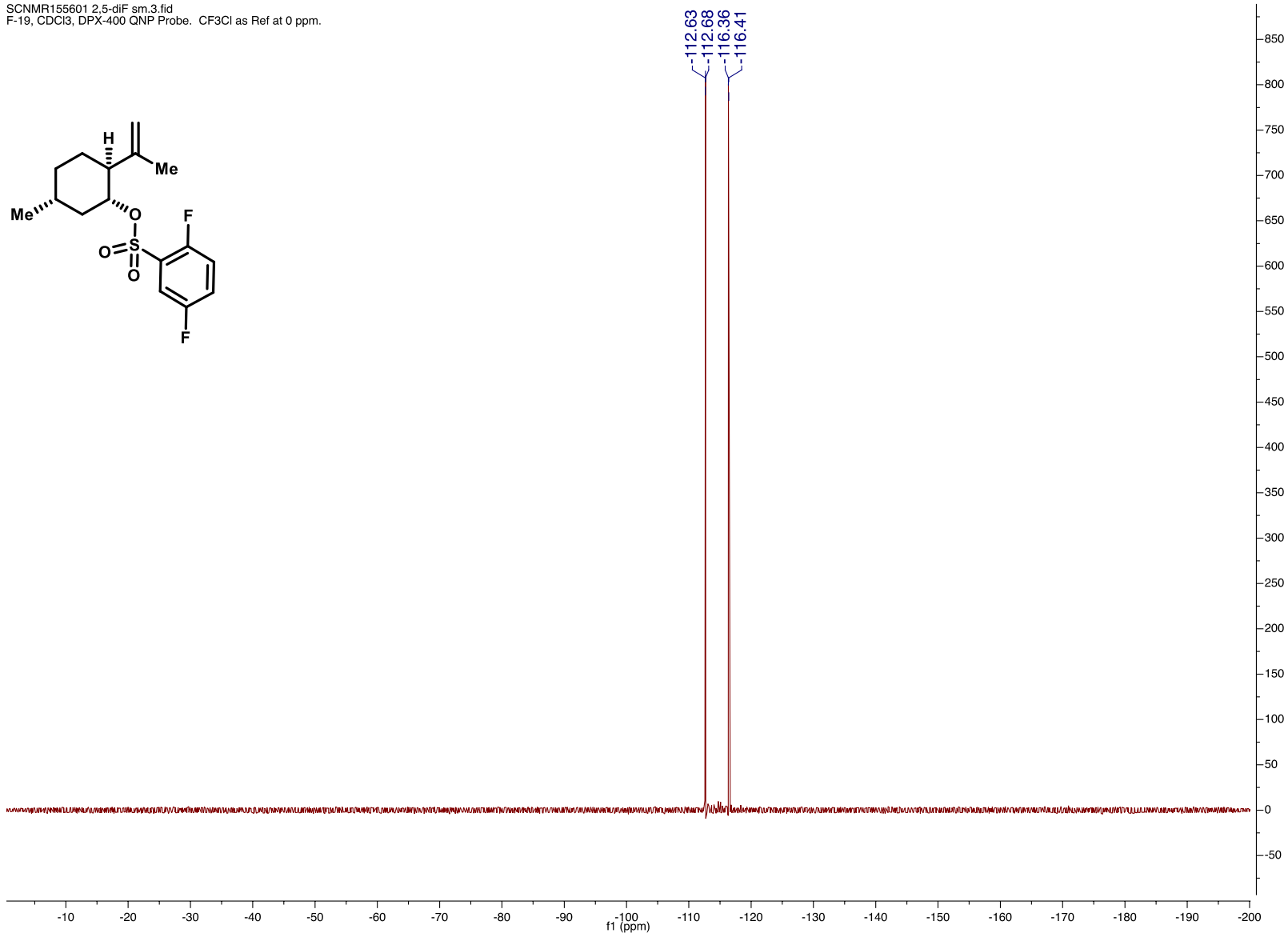
SI-08: ^{13}C-NMR


SCNMR155601.4.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
H
Me
Me
O
S
O
O
F
F
77.16 CDCl3
f1 (ppm)

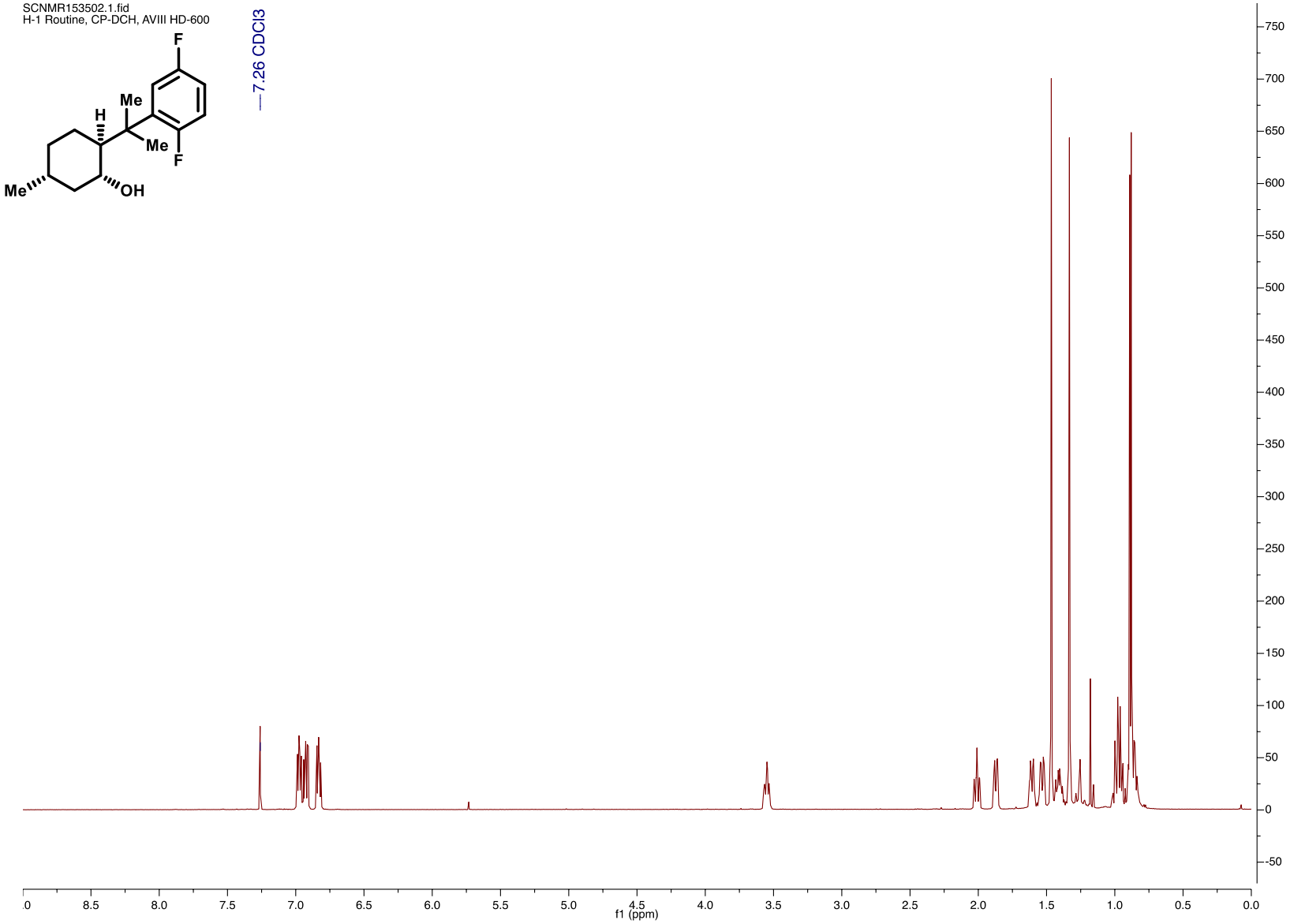

SCNMR155601 2,5-diF sm.4.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
158.47
156.83
156.47
154.77
144.72
127.20
127.16
127.09
127.04
122.36
122.30
122.20
122.15
118.84
118.79
118.68
118.63
117.35
117.17
113.05
77.16 CDCl3
50.69
41.99
33.69
31.77
30.66
21.95
19.73
H
Me
Me
O
S
O
O
F
F
f1 (ppm)

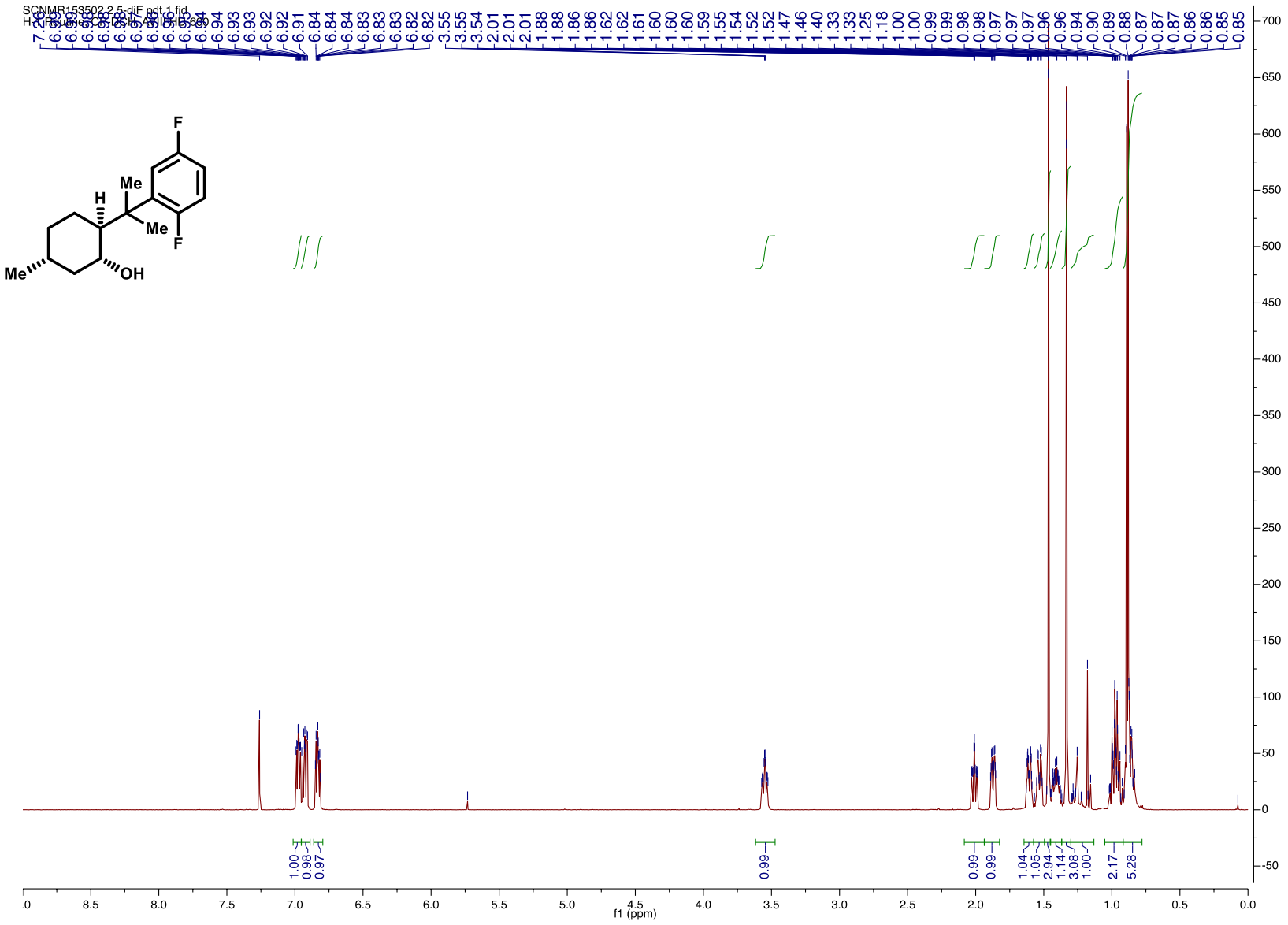
SI-08: ^{19}F-NMR (Uncorrected)



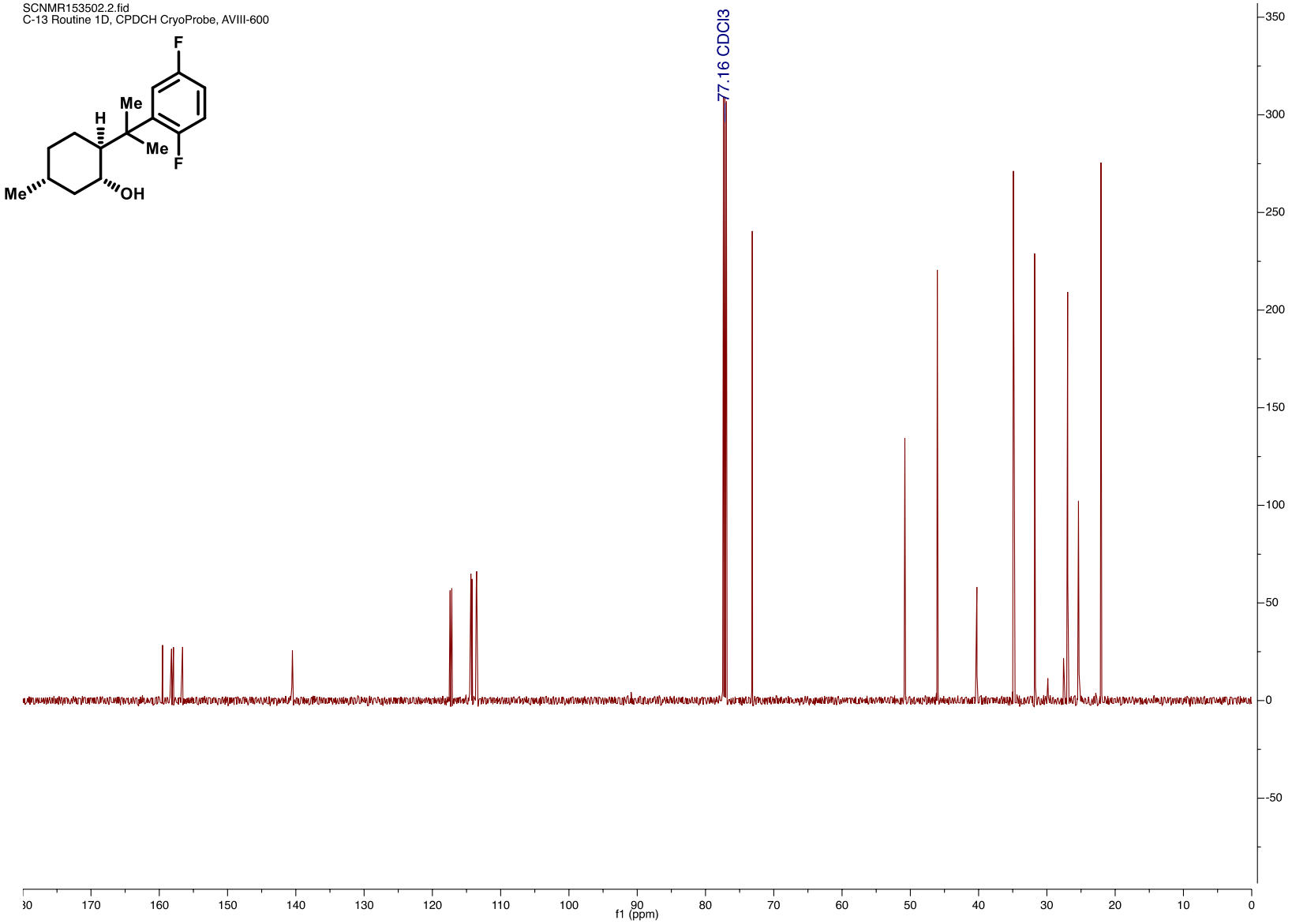

SCNMR155601 2,5-diF sm.3.fid
F-19, CDCl3, DPX-400 QNP Probe. CF3Cl as Ref at 0 ppm.
-112.63
-112.68
-116.36
-116.41
H
Me
Me
O
S
O
O
F
F
f1 (ppm)

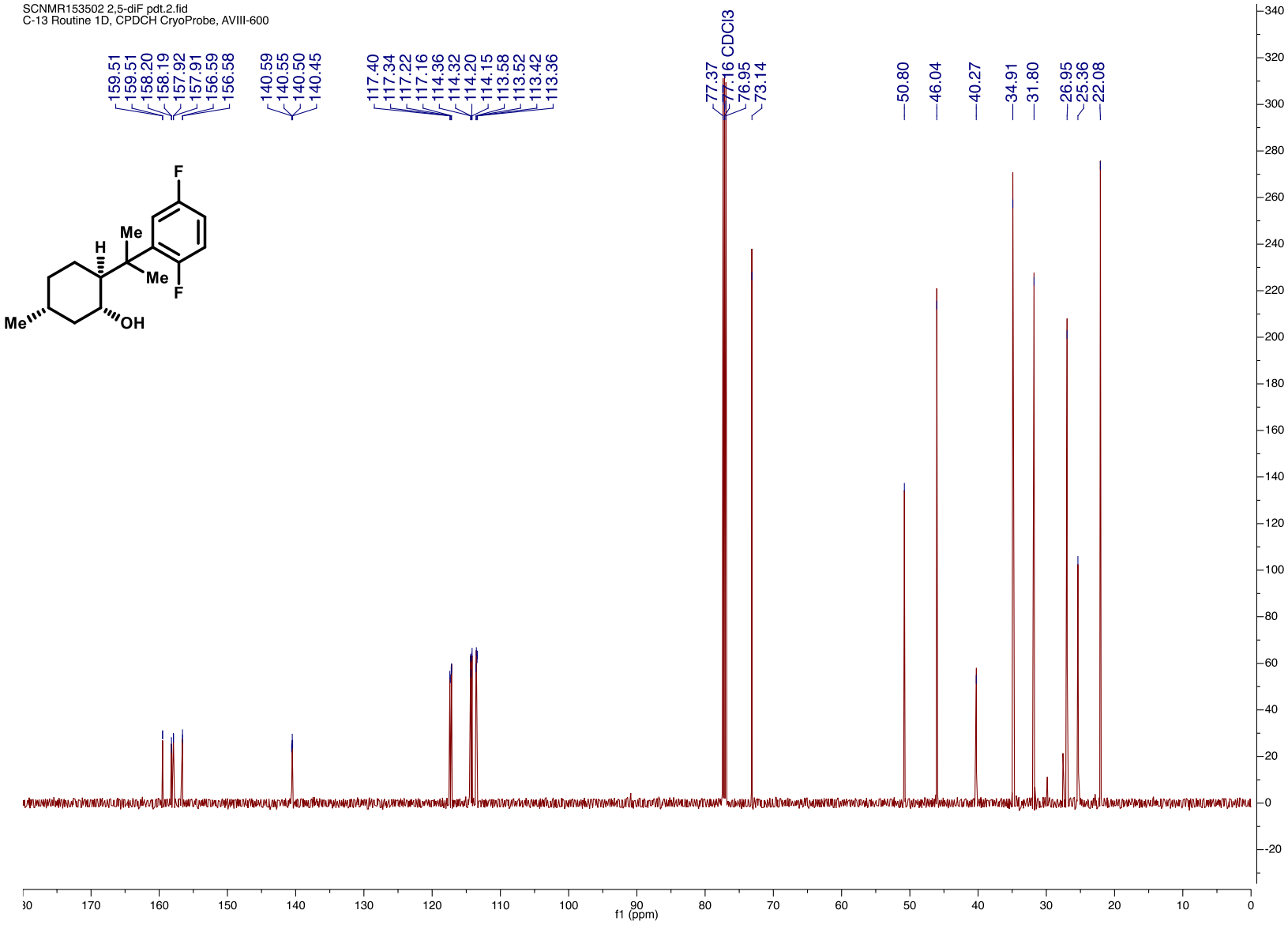
6c: ^{1}H-NMR


SCNMR153502.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
F
Me
H
Me
F
Me
OH
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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
f1 (ppm)

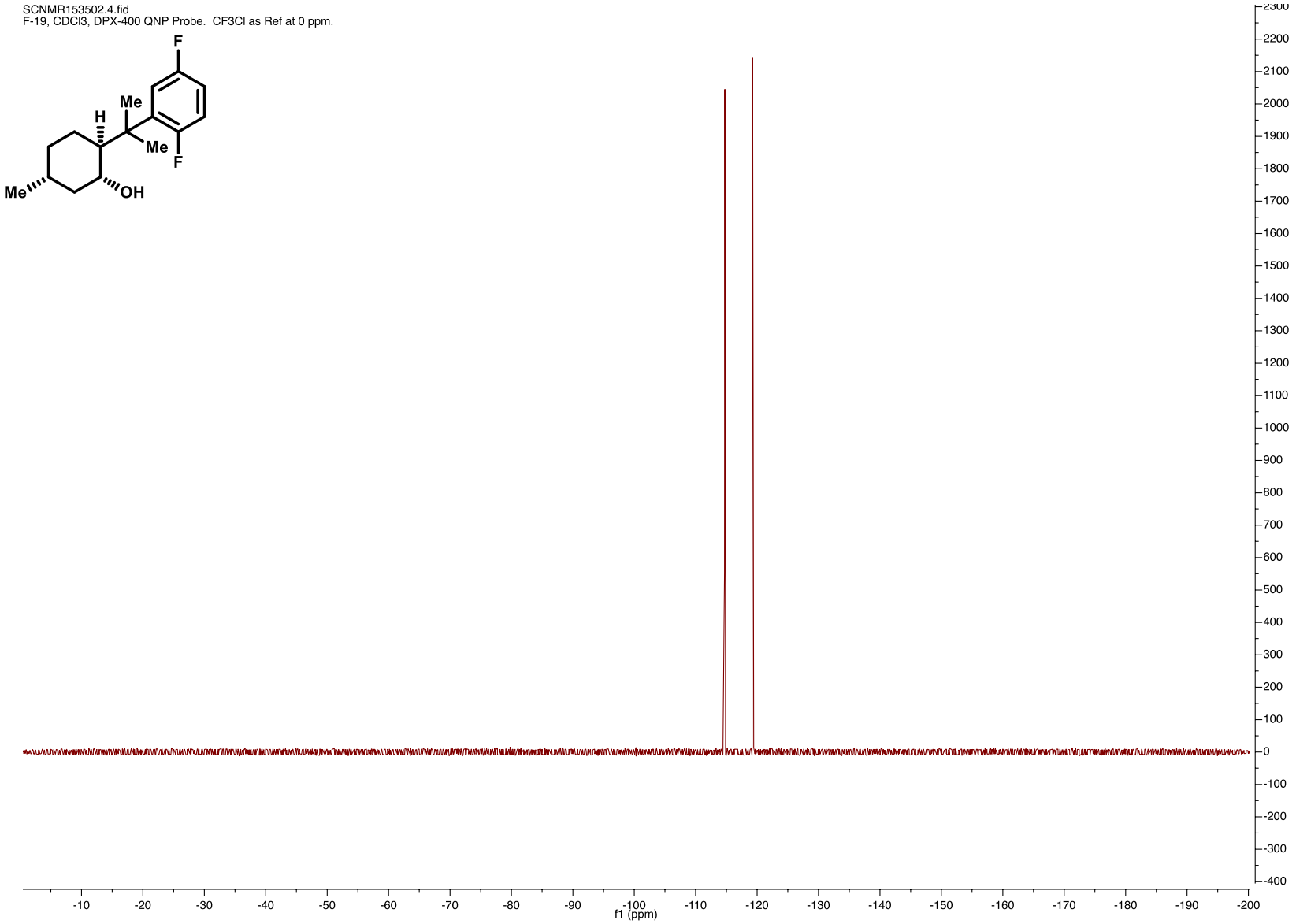

F
Me
H
Me
F
Me
OH
f1 (ppm)

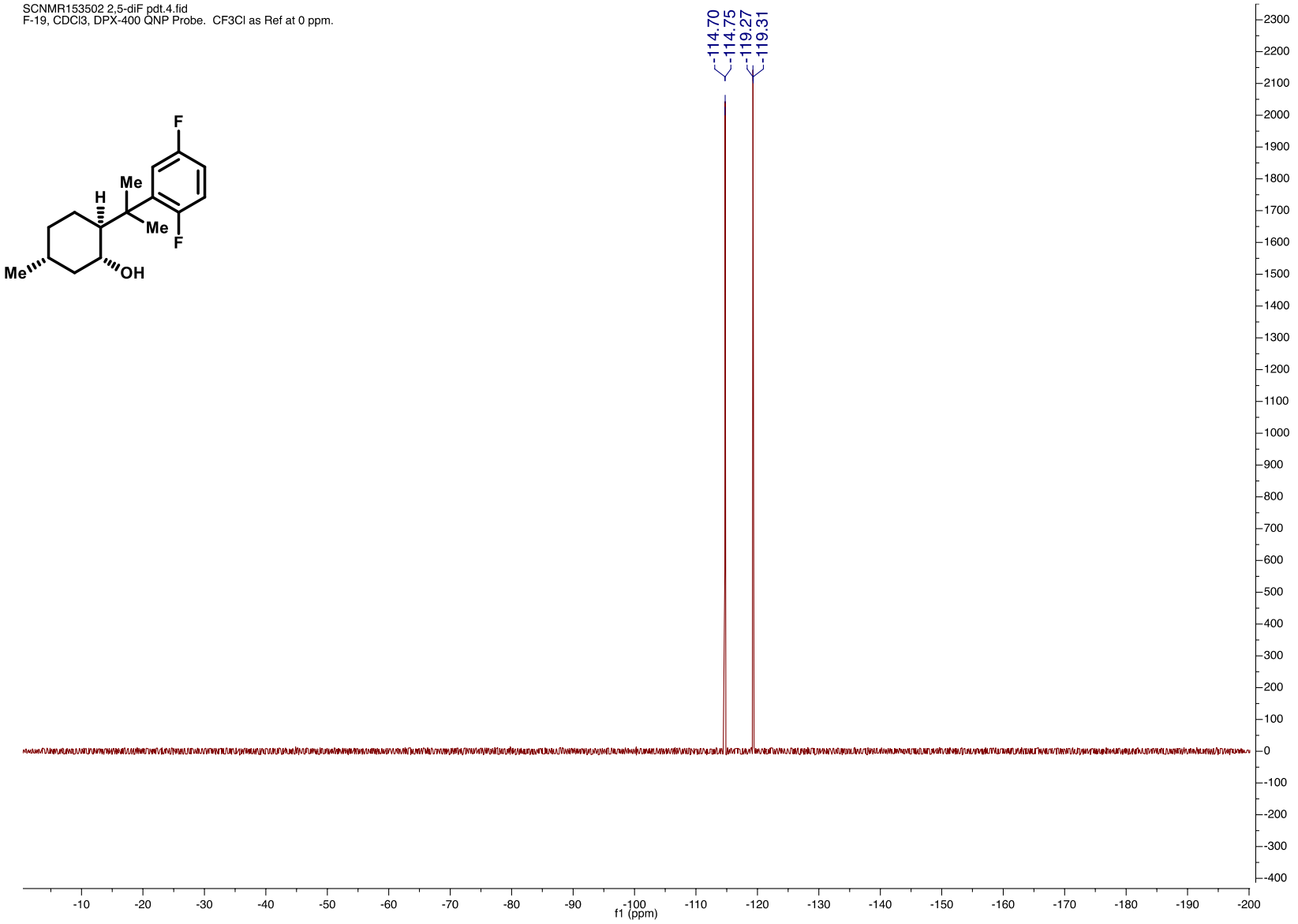
6c: ^{13}C-NMR


SCNMR153502.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
F
Me
H
Me
F
Me
OH
77.16 CDCl3
350
300
250
200
150
100
50
0
-50
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

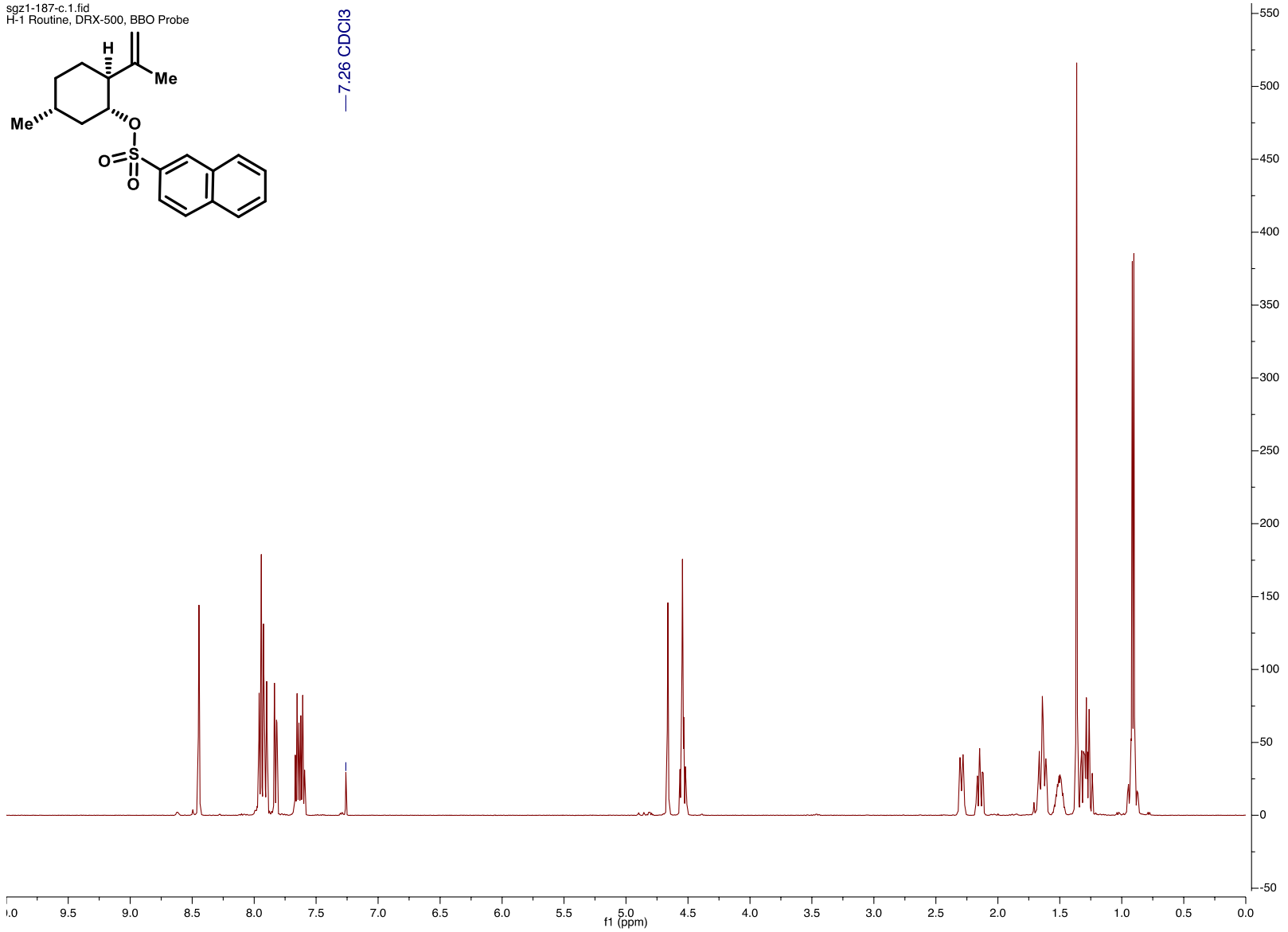

SCNMR153502 2,5-diF pdt.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
159.51
159.51
158.20
158.19
157.92
157.91
156.59
156.58
140.59
140.55
140.50
140.45
117.40
117.34
117.22
117.16
114.36
114.32
114.20
114.15
113.58
113.52
113.42
113.36
77.37
77.16 CDCl3
76.95
73.14
50.80
46.04
40.27
34.91
31.80
26.95
25.36
22.08
F
Me
H
Me
F
Me
OH
f1 (ppm)

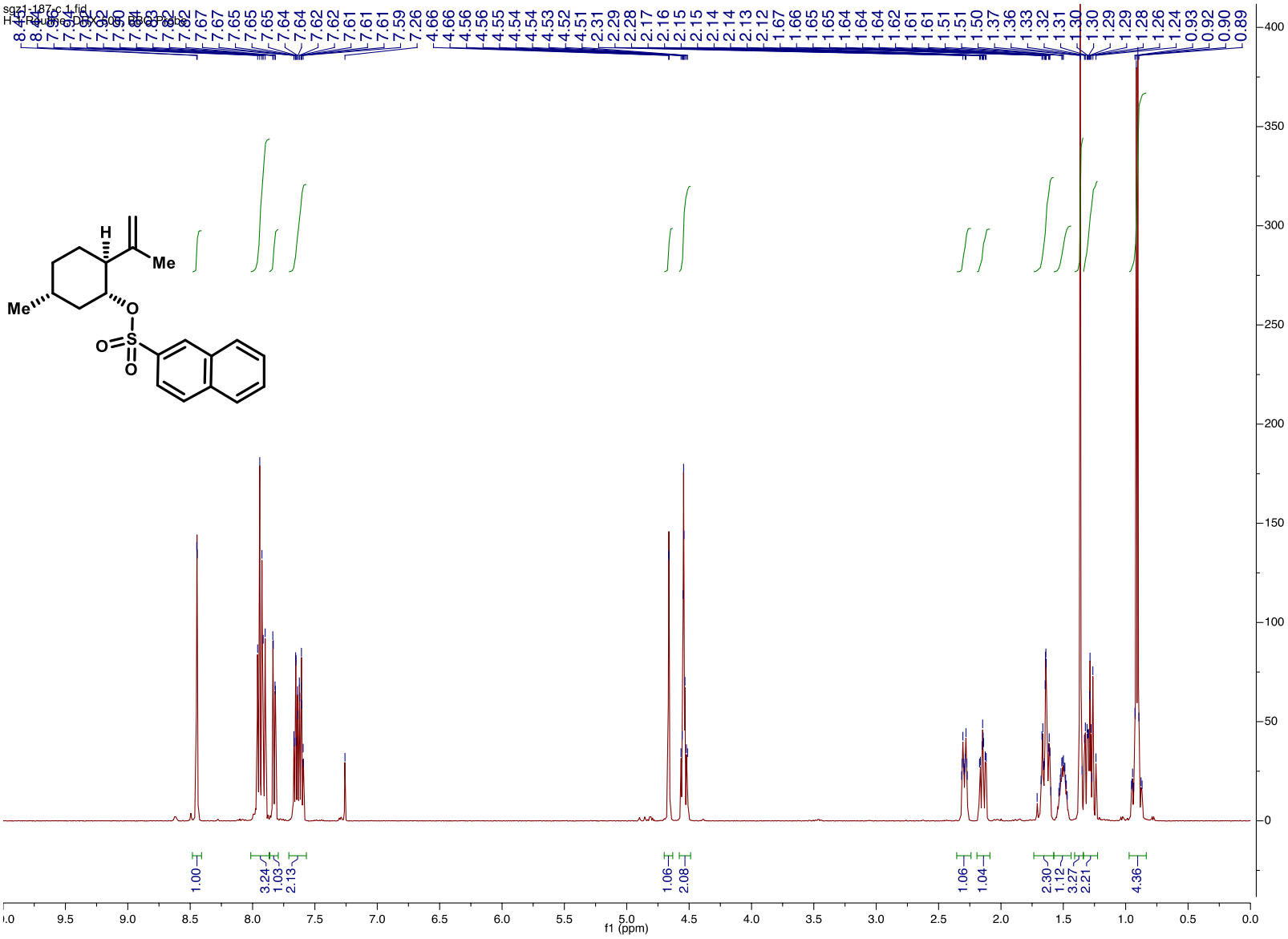
6c: ^{19}F-NMR (Uncorrected)



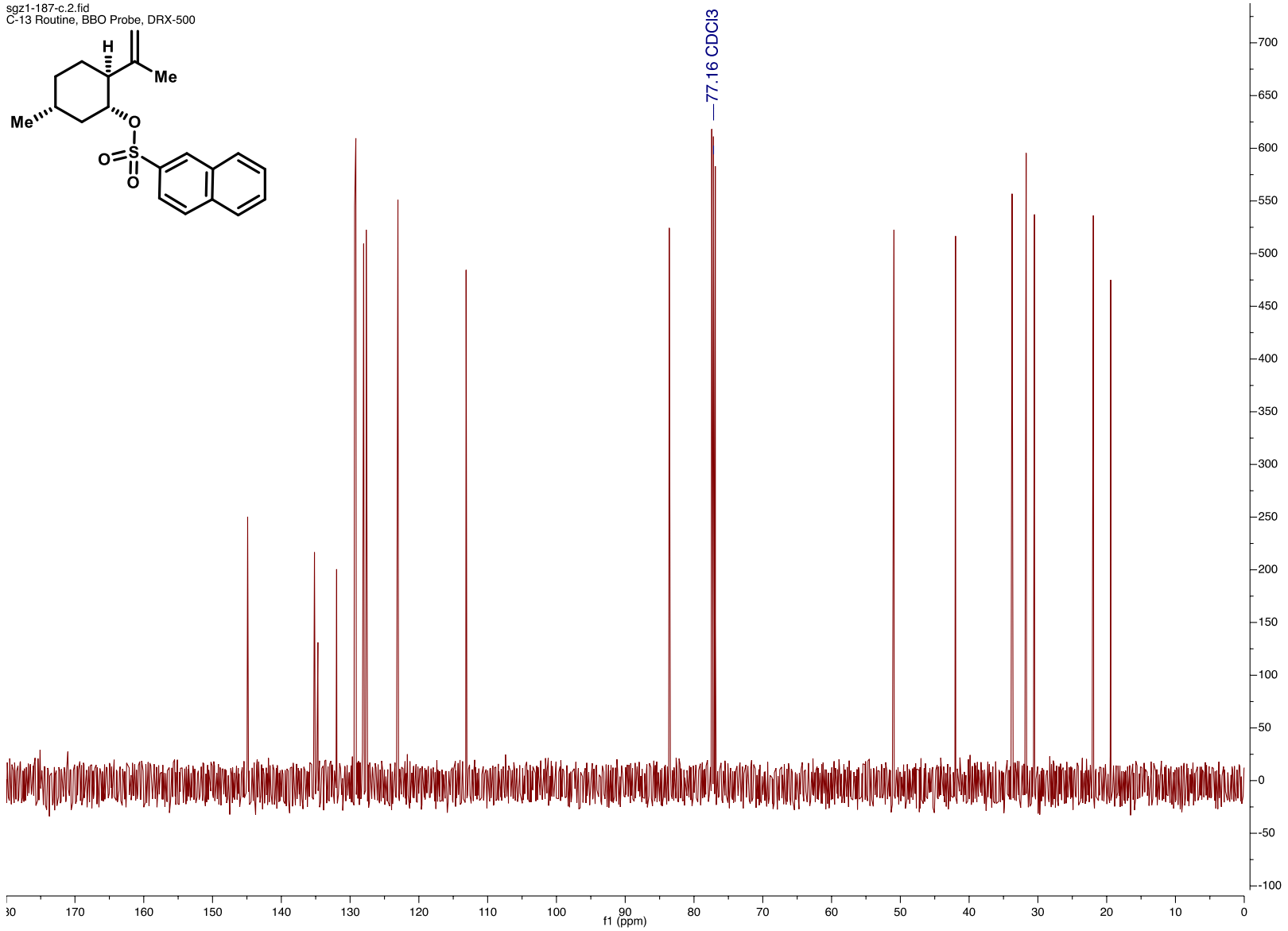

SCNMR153502 2,5-diF pdt.4.fid
F-19, CDCl3, DPX-400 QNP Probe. CF3Cl as Ref at 0 ppm.
-114.70
-114.75
-119.27
-119.31
F
Me
H
Me
F
Me
OH
f1 (ppm)

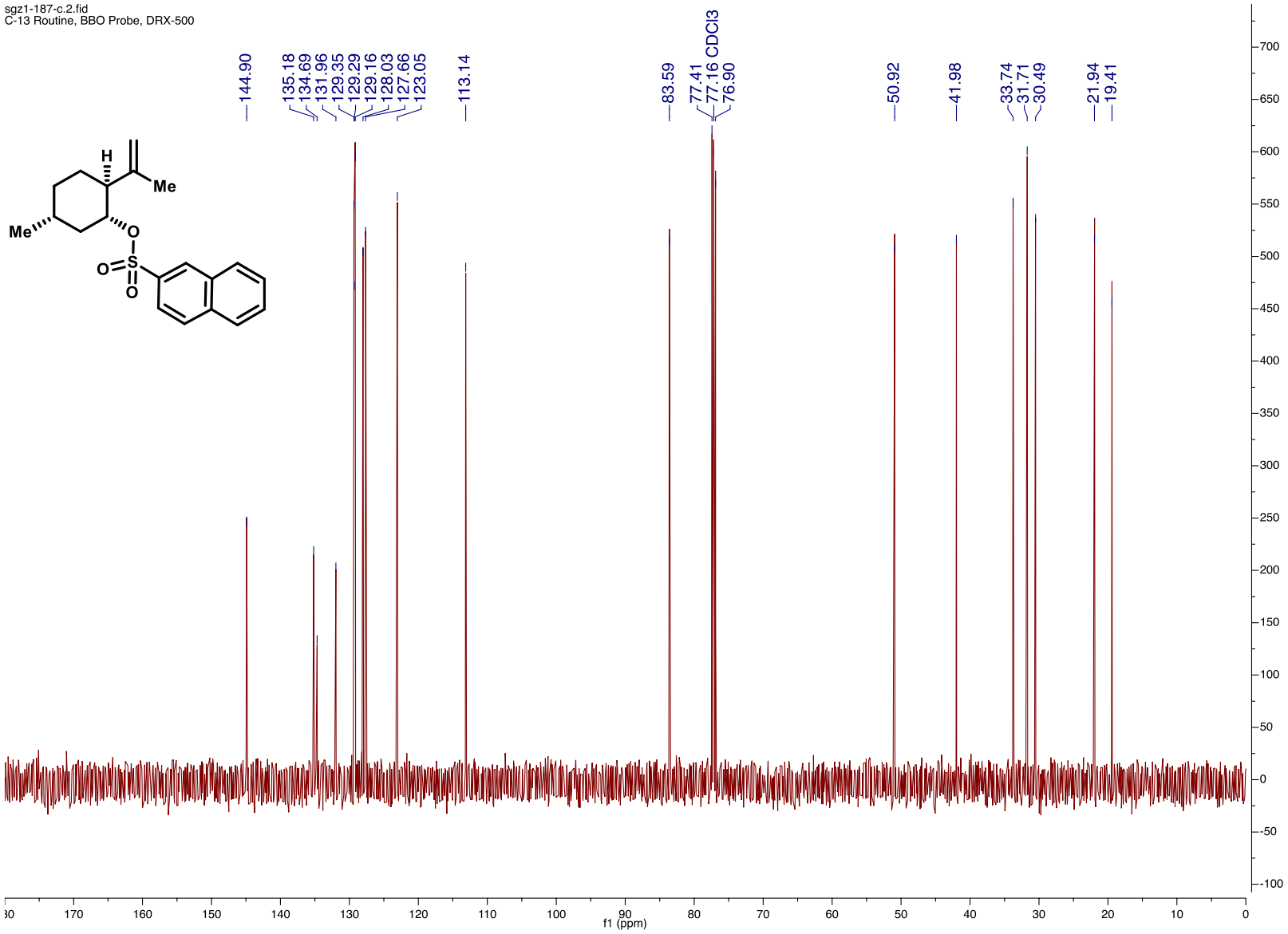
SI-09: ^{1}H-NMR


sgz1-187-c.1.fid
H-1 Routine, DRX-500, BBO Probe
7.26 CDCl3
H
Me
Me
O
S
O
O
f1 (ppm)

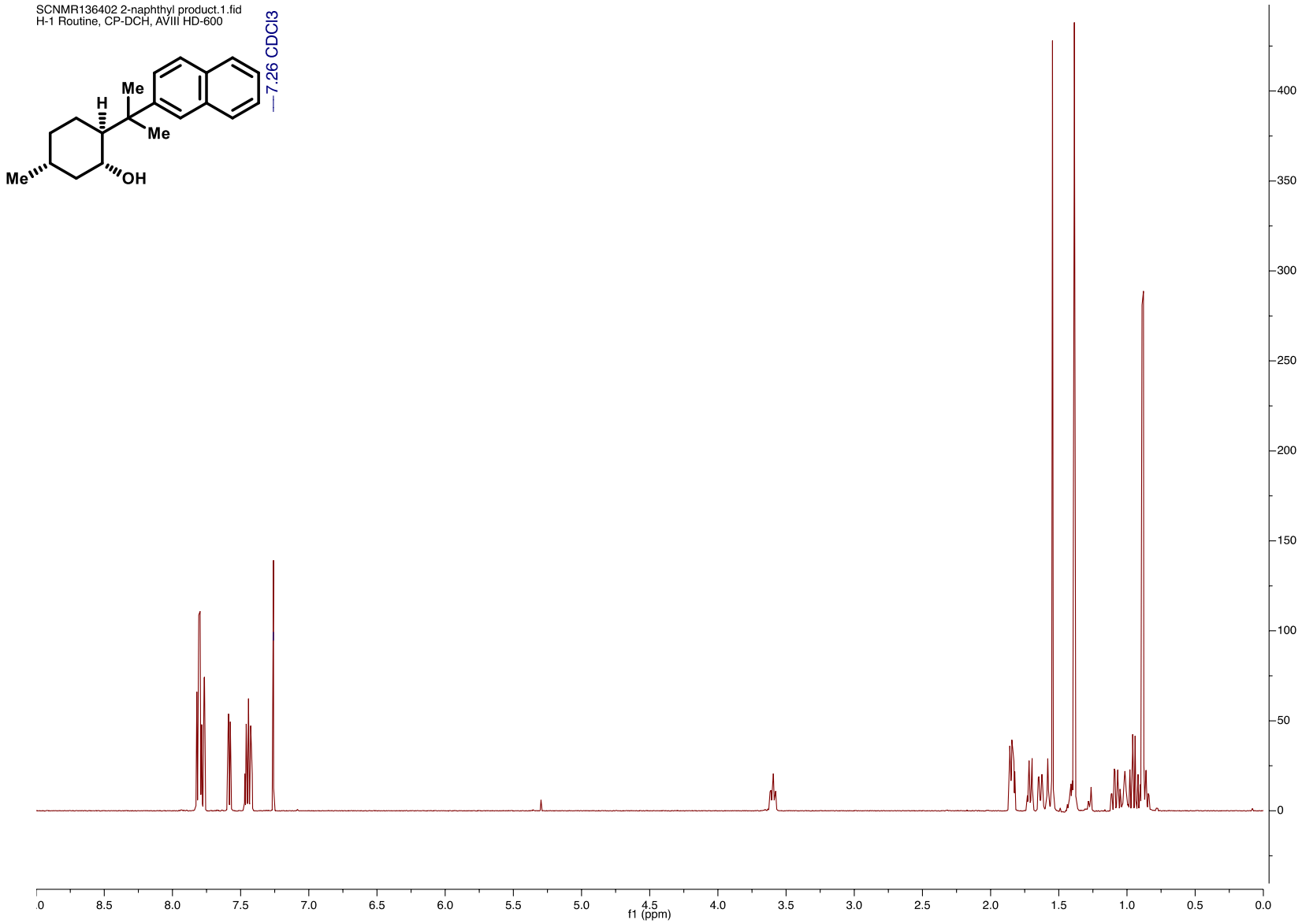

sgz1-187-c-1.fid
H-1 Reuben Dbx 300, 09-07-2016
8.47 8.47 8.47

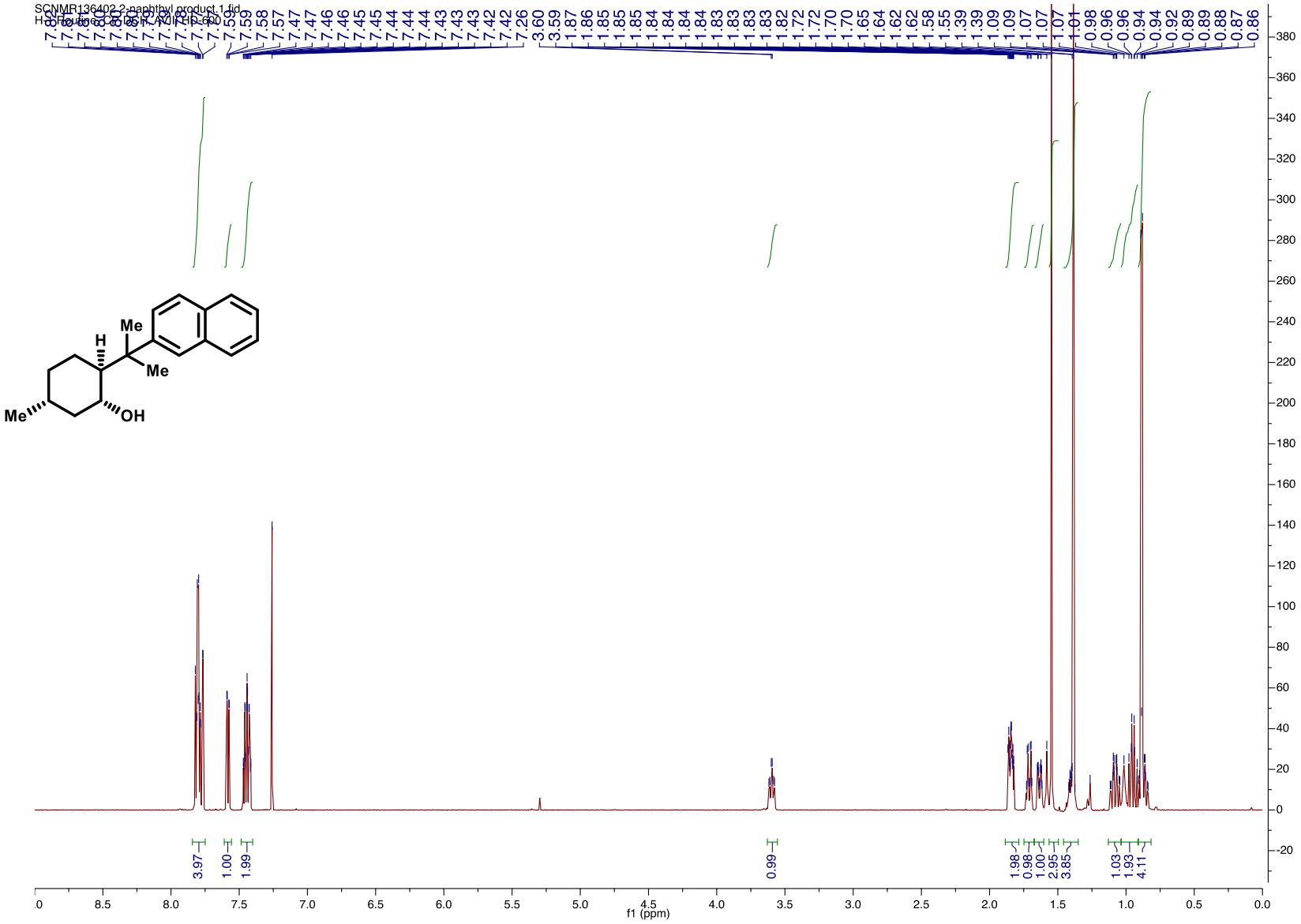
SI-09: ^{13}C-NMR


sgz1-187-c.2.fid
C-13 Routine, BBO Probe, DRX-500
H
Me
Me
O
S
O
O
77.16 CDCl3
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

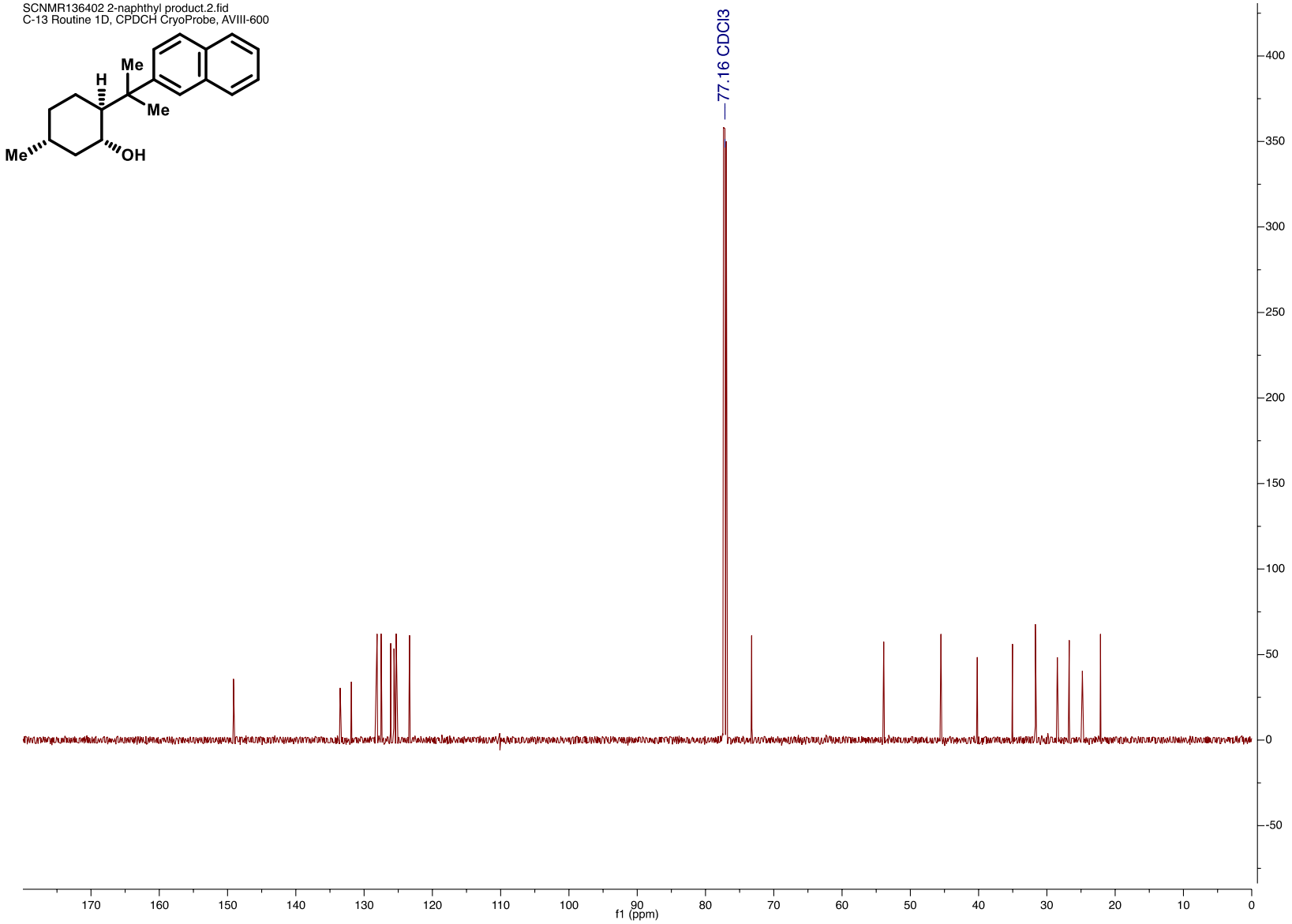

sgz1-187-c.2.fid
C-13 Routine, BBO Probe, DRX-500
144.90
135.18
134.69
131.96
129.35
129.29
129.16
128.03
127.66
123.05
113.14
83.59
77.41
77.16 CDCl3
76.90
50.92
41.98
33.74
31.71
30.49
21.94
19.41
H
Me
Me
O
O
S
O
O
f1 (ppm)

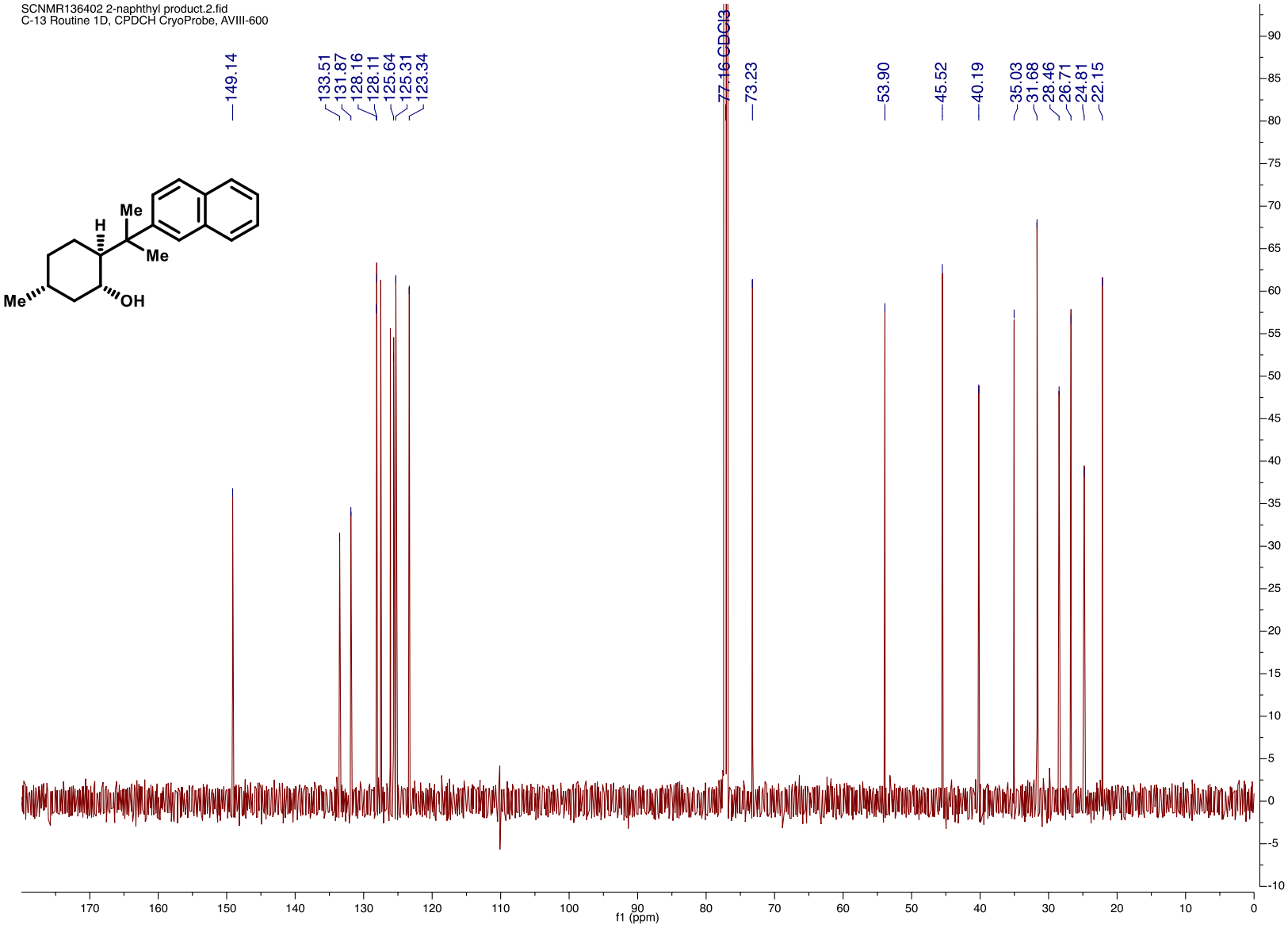
7: ^{1}H-NMR


SCNMR136402 2-naphthyl product.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
H
Me
Me
OH
400
350
300
250
200
150
100
50
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
f1 (ppm)

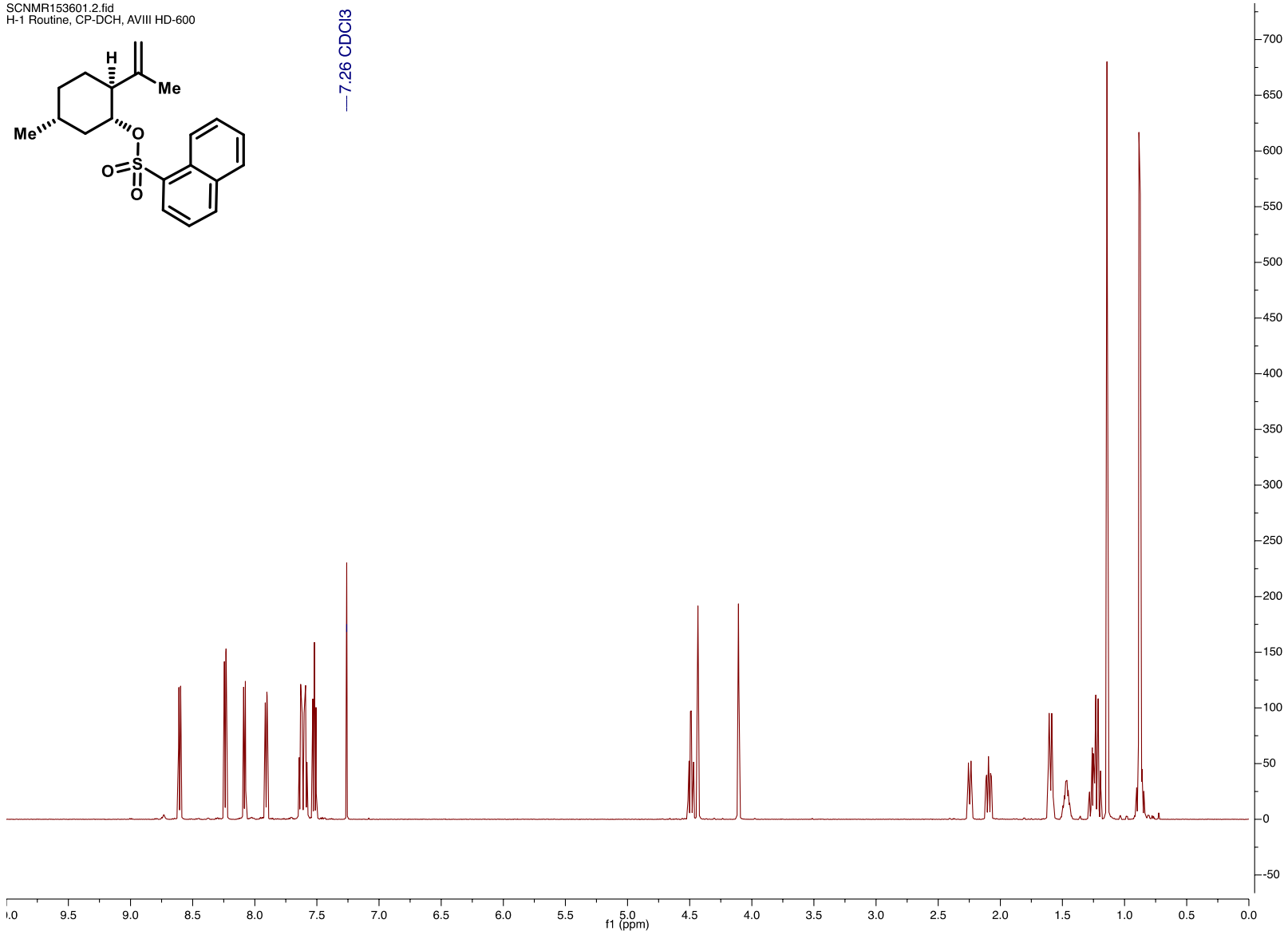

SCNMR136402-2-naphthyl product 1.fid
Me
H
Me
Me
OH
f1 (ppm)

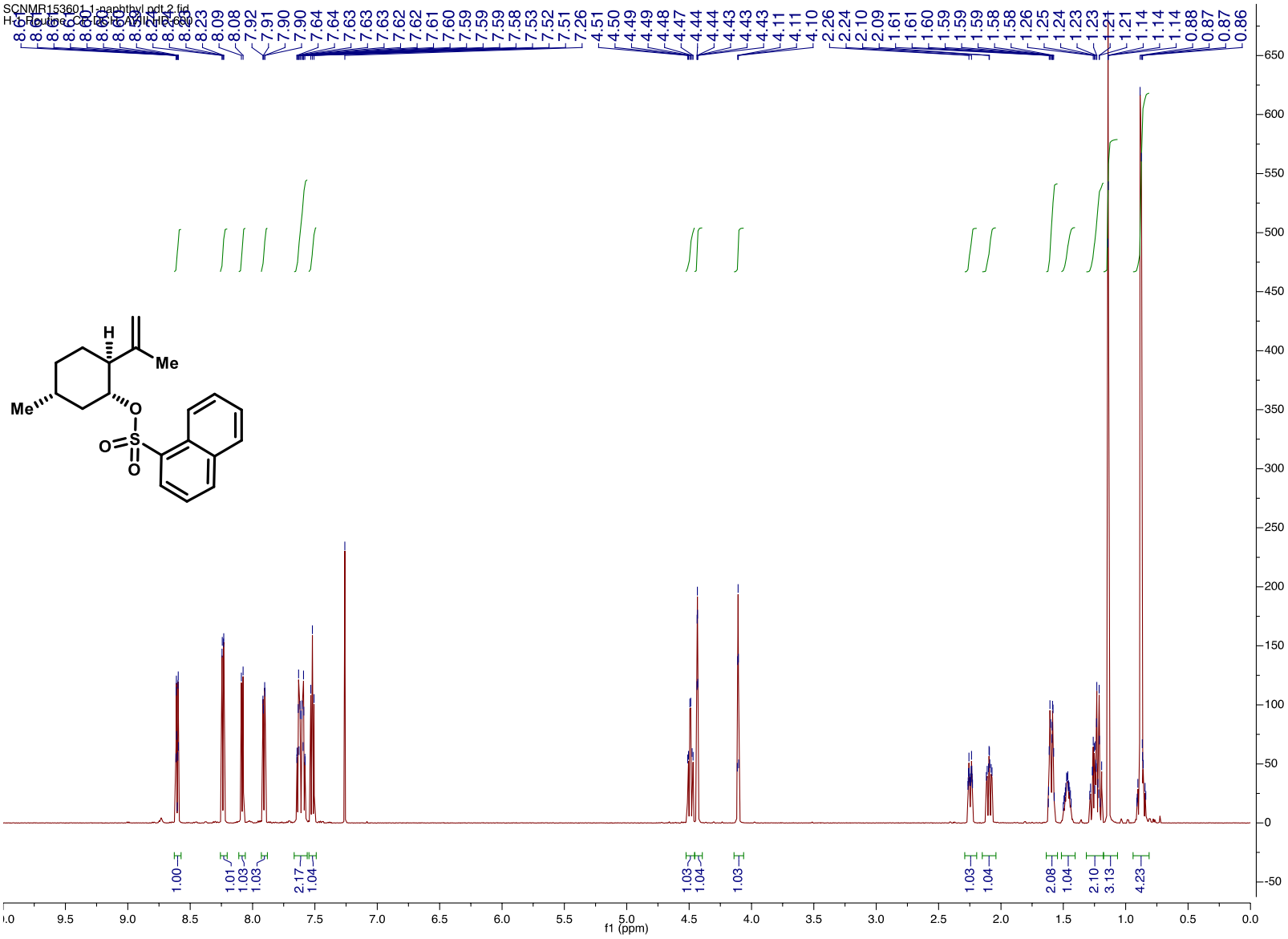
7: ^{13}C-NMR


SCNMR136402 2-naphthyl product.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
H
Me
Me
OH
77.16 CDCl3
400
350
300
250
200
150
100
50
0
-50
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

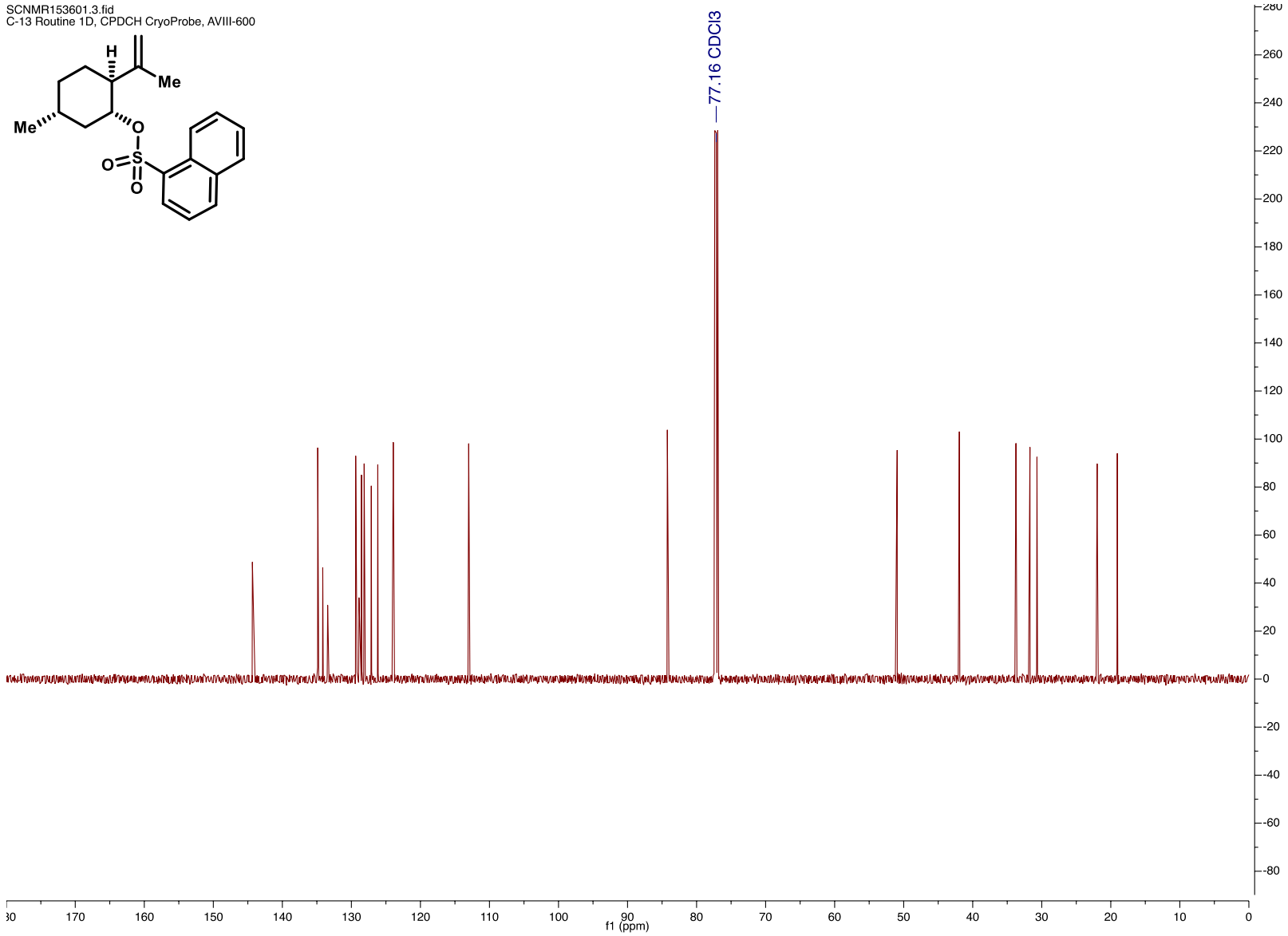

SCNMR136402 2-naphthyl product.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
149.14
133.51
131.87
128.16
128.11
125.64
125.31
123.34
77.16 CDCl3
73.23
53.90
45.52
40.19
35.03
31.68
28.46
26.71
24.81
22.15
Me
H
Me
Me
OH
f1 (ppm)

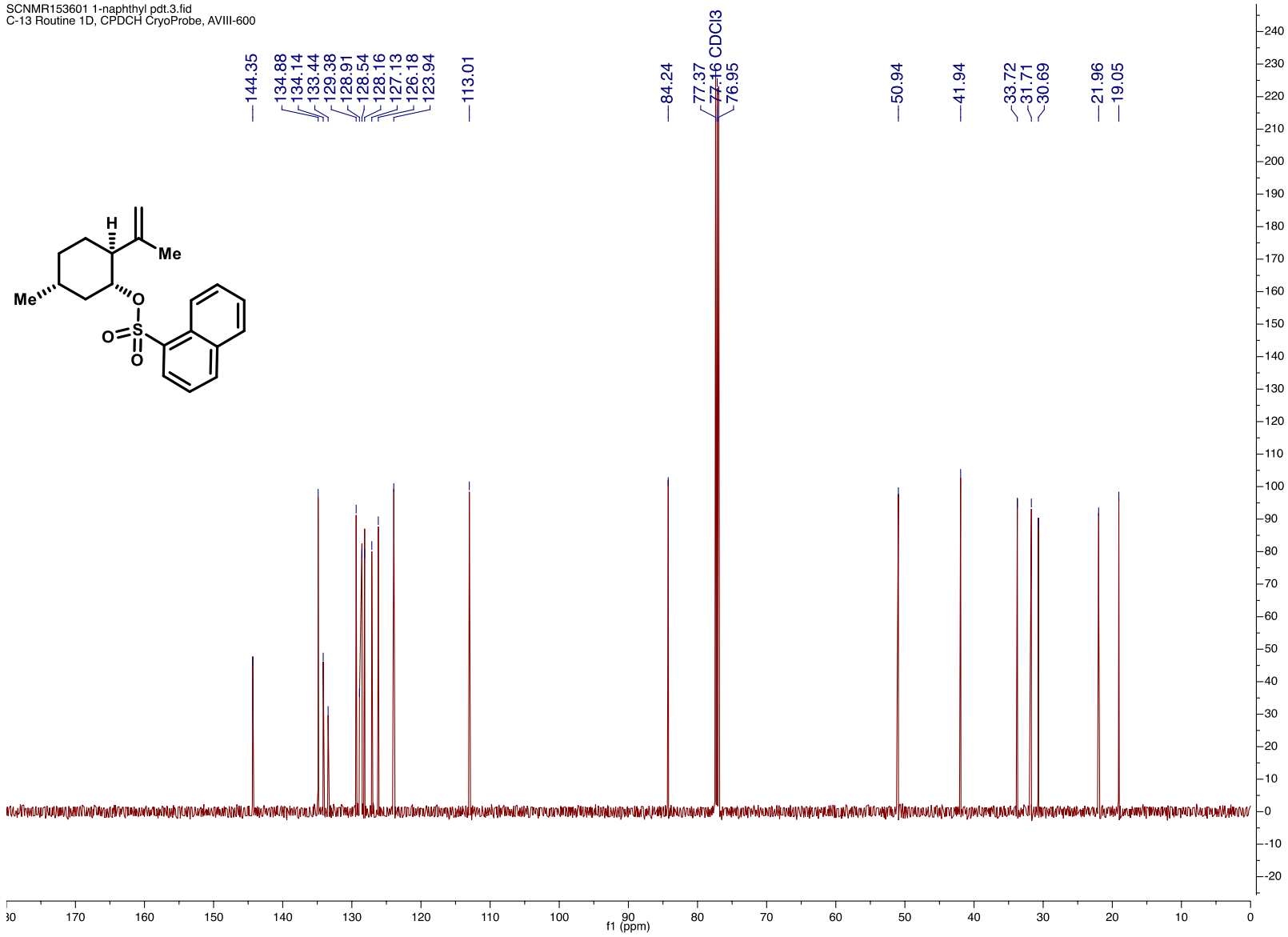
SI-10: ^{1}H-NMR


SCNMR153601.2.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
H
Me
Me
O
S
O
O
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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
f1 (ppm)

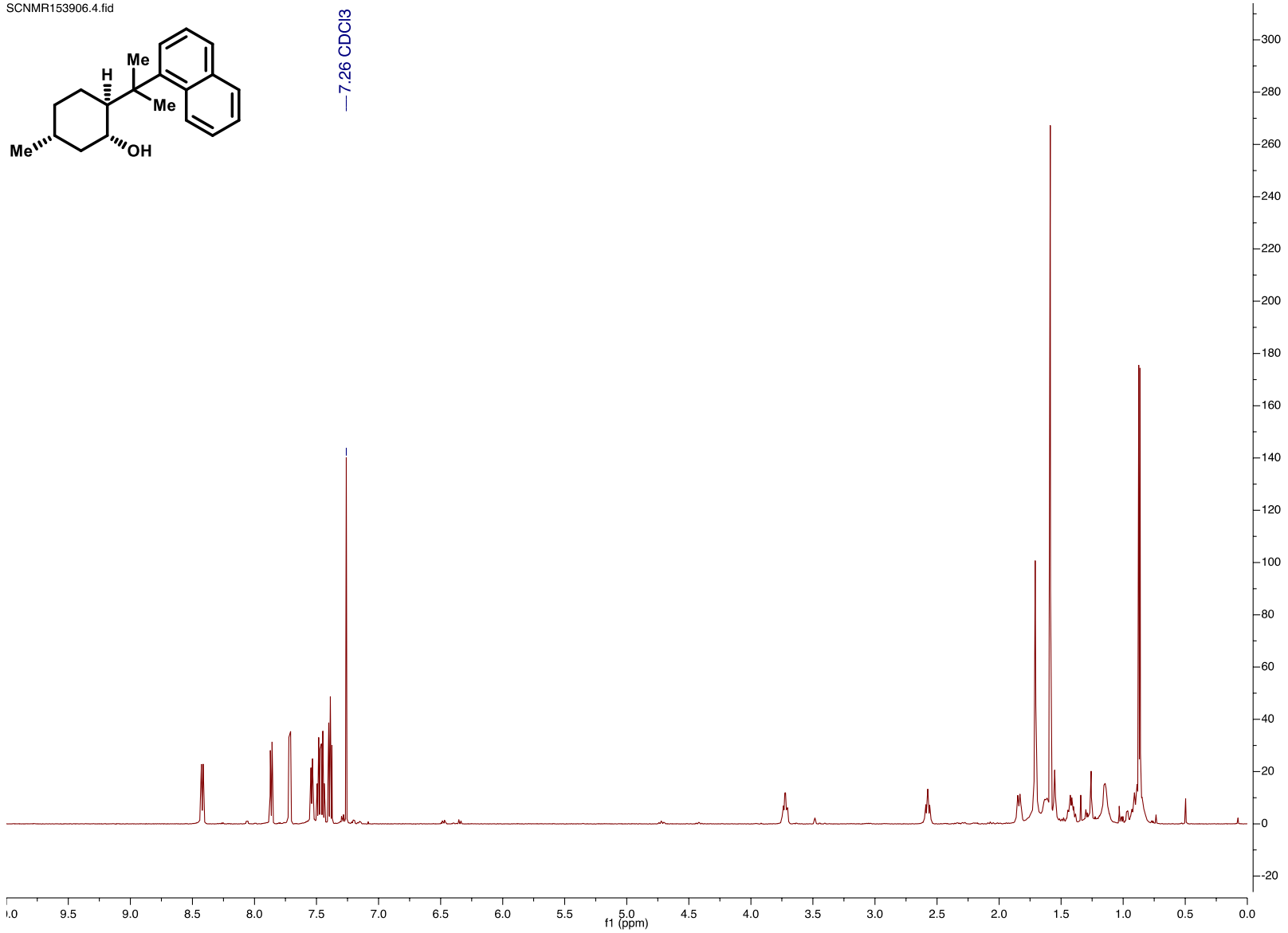

SCNMR153601-1-naphthyl pdt 2.fid
1H Routine CDCl3 (298) AVIIIHD400
8.39 8.38 8.38 8.37 8.37 8.36 8.36 8.35 8.35 8.34 8.34 8.33 8.33 8.32 8.32 8.31 8.31 8.30 8.30 8.29 8.29 8.28 8.28 8.27 8.27 8.26 8.26 8.25 8.25 8.24 8.24 8.23 8.09 8.08 7.92 7.91 7.90 7.90 7.64 7.64 7.63 7.63 7.63 7.62 7.62 7.61 7.60 7.59 7.59 7.59 7.58 7.53 7.52 7.51 7.26 4.51 4.50 4.49 4.49 4.48 4.47 4.44 4.44 4.43 4.43 4.43 4.11 4.10 2.26 2.24 2.10 2.09 1.61 1.61 1.60 1.59 1.59 1.59 1.58 1.58 1.26 1.25 1.24 1.23 1.23 1.21 1.21 1.14 1.14 1.14 0.88 0.87 0.87 0.86
H
Me
Me
O
O
S
O
O
1.00 1.01 1.03 1.03 2.17 1.04 1.03 1.04 1.03 1.03 1.04 2.08 1.04 2.10 3.13 4.23
f1 (ppm)

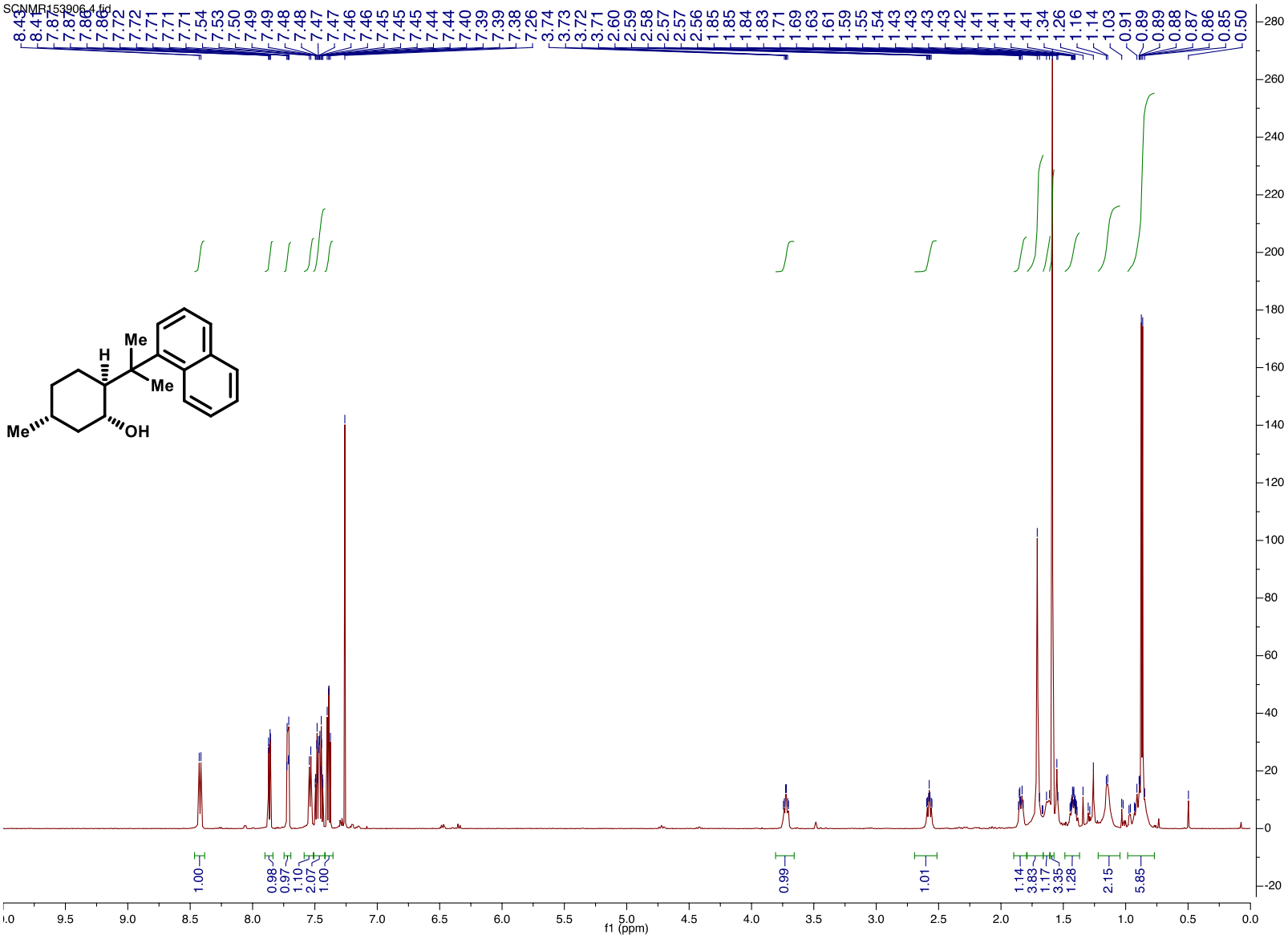
SI-10: ^{13}C-NMR


SCNMR153601.3.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
H
Me
Me
O
O
S
O
O
77.16 CDCl3
f1 (ppm)

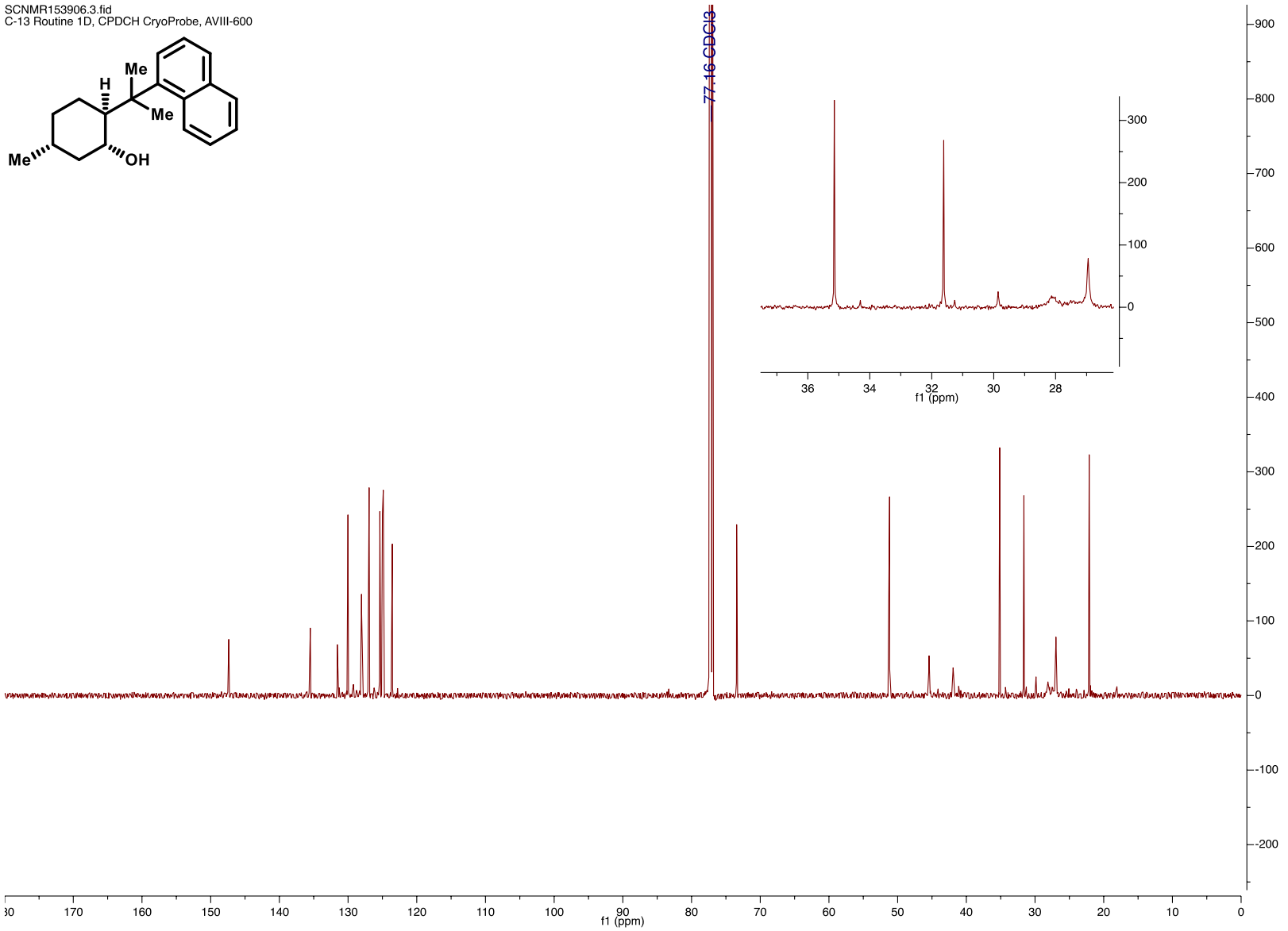

SCNMR153601 1-naphthyl pdt.3.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
144.35
134.88
134.14
133.44
129.38
128.91
128.54
128.16
127.13
126.18
123.94
113.01
84.24
77.37
77.16 CDCl3
76.95
50.94
41.94
33.72
31.71
30.69
21.96
19.05
H
Me
Me
O
O
S
O
O
f1 (ppm)

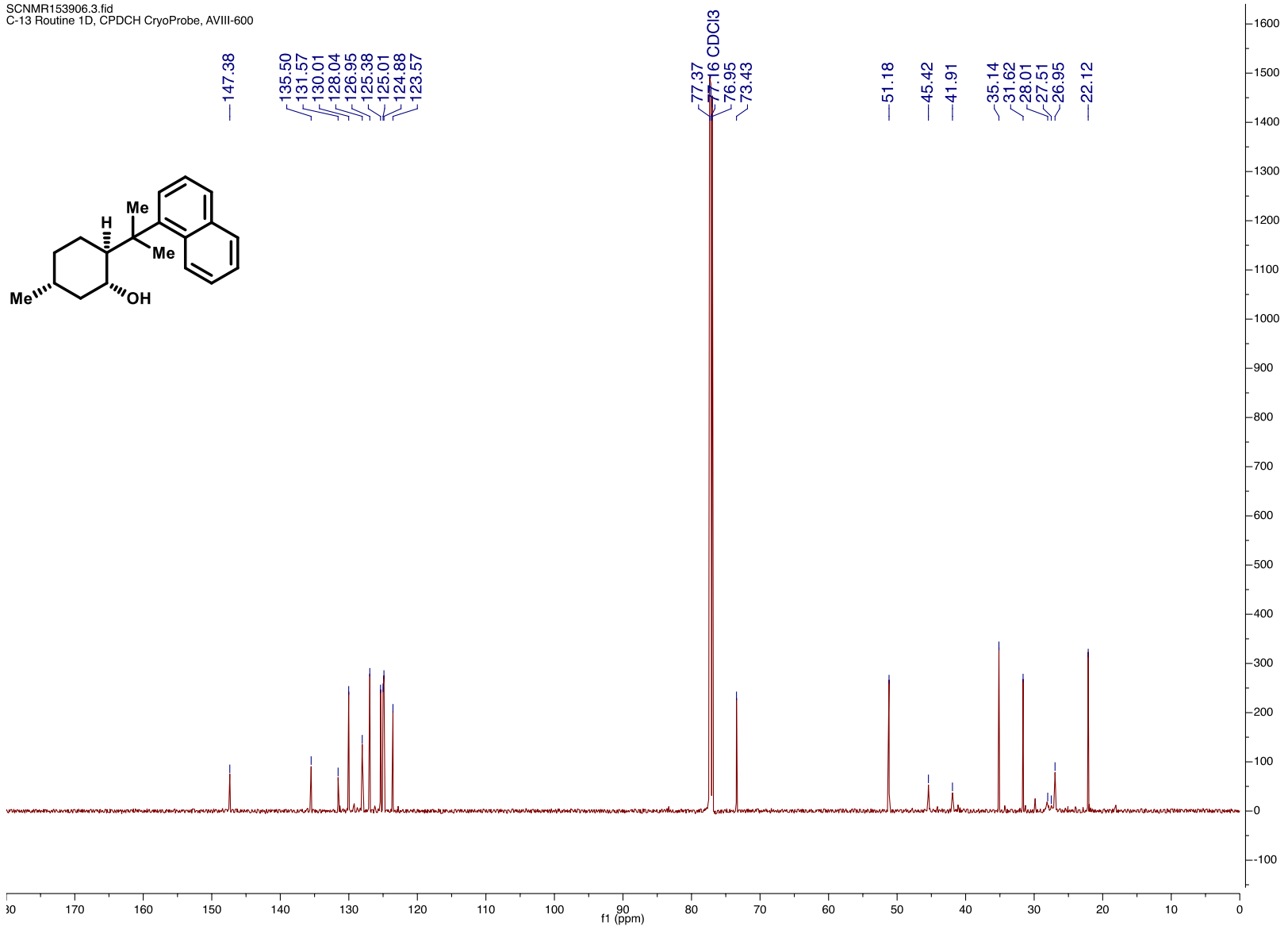
8: ^{1}H-NMR, T=298K



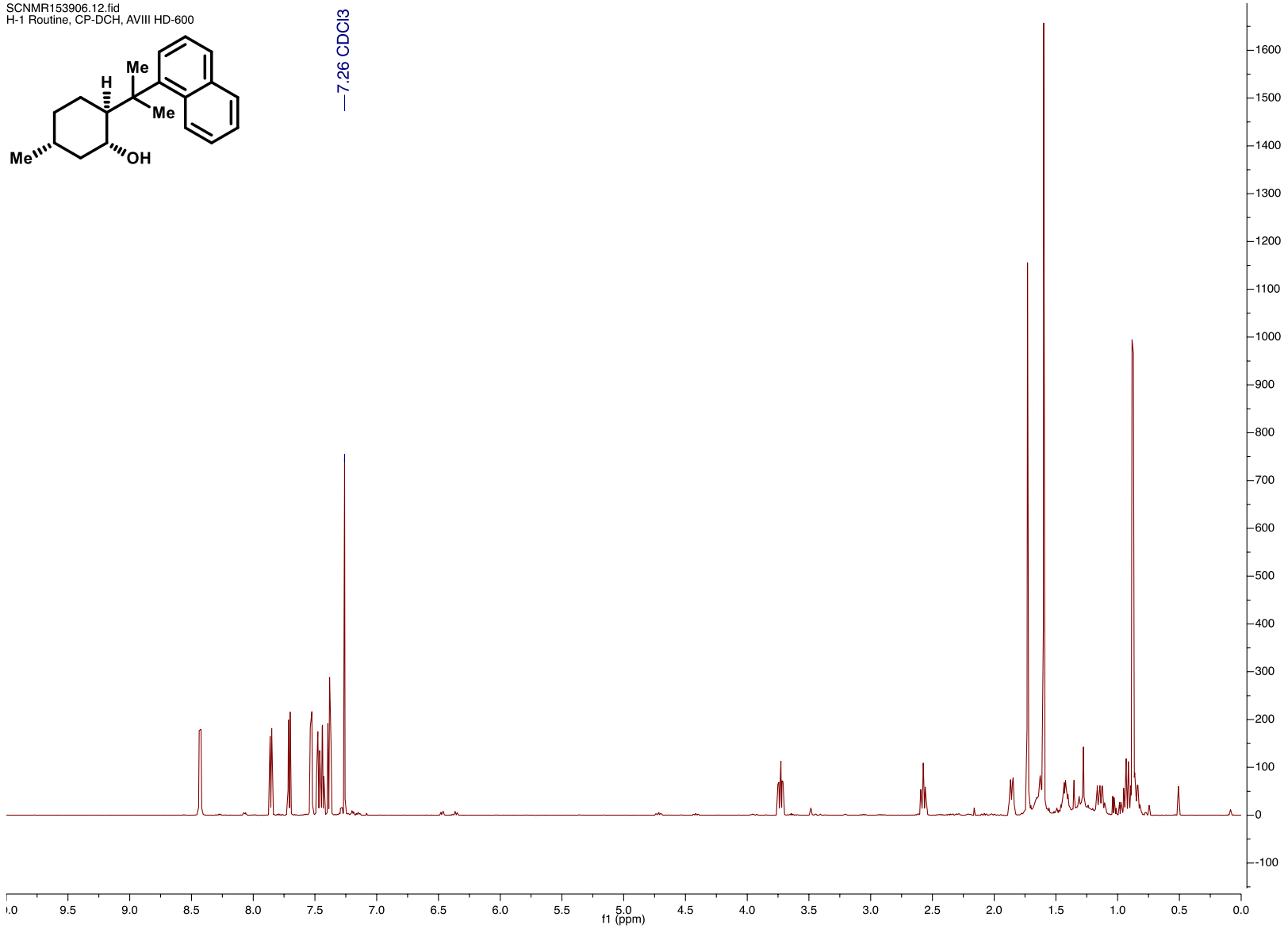

SCNMR153006.4.fid
8.43 8.41 7.87 7.85 7.85 7.80 7.72 7.72 7.71 7.71 7.71 7.54 7.53 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.40 7.39 7.39 7.38 7.26 3.74 3.73 3.72 3.71 2.60 2.59 2.58 2.57 2.57 2.56 1.85 1.85 1.84 1.83 1.71 1.69 1.63 1.61 1.59 1.55 1.54 1.43 1.43 1.43 1.42 1.41 1.41 1.41 1.41 1.34 1.26 1.16 1.14 1.03 0.91 0.89 0.89 0.88 0.87 0.86 0.85 0.50
Me
H
Me
Me
OH
1.00 0.98 0.97 1.10 2.07 1.00 0.99 1.01 1.14 3.83 1.17 3.35 1.28 2.15 5.85
f1 (ppm)

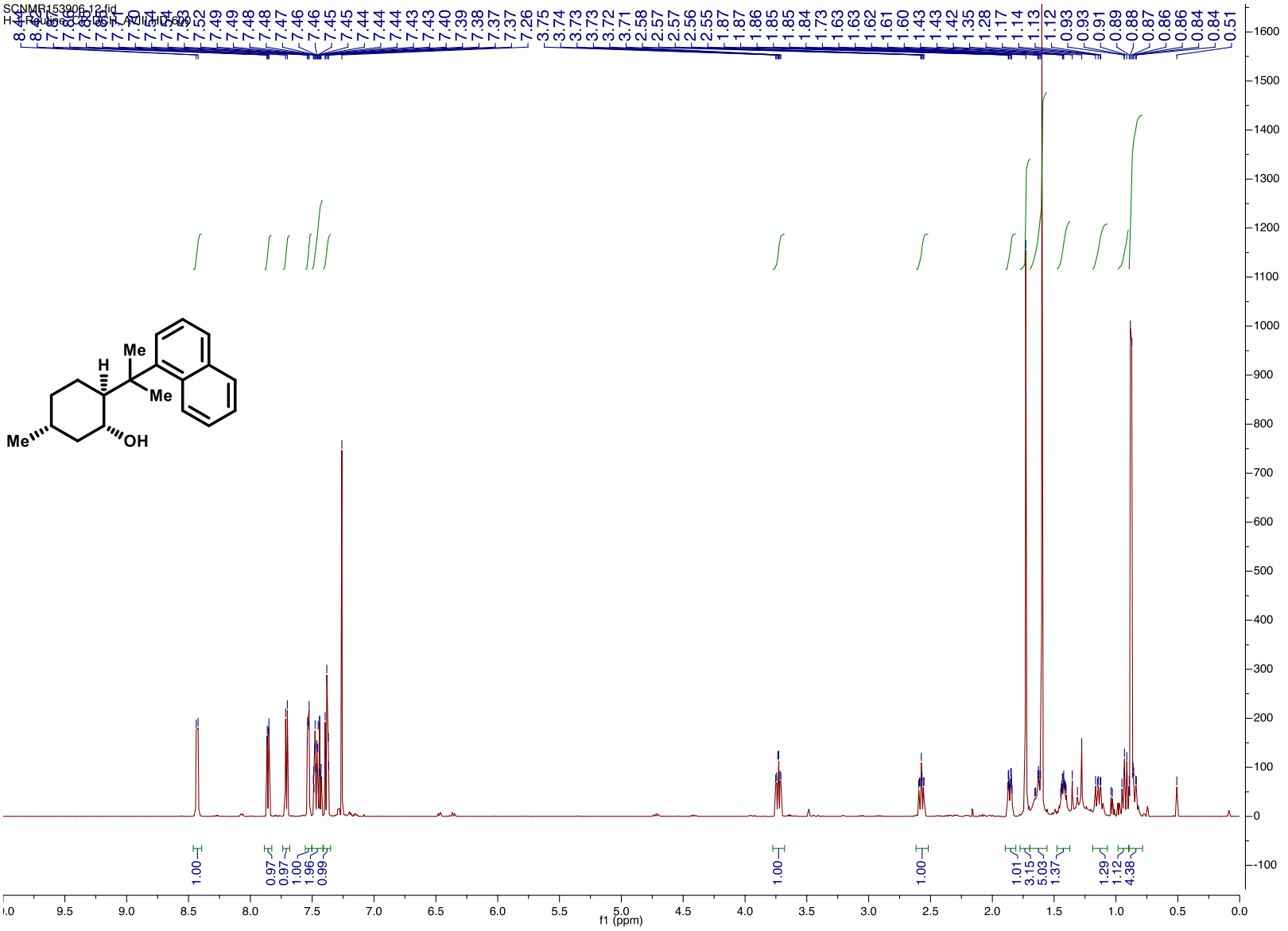
8: ^{13}C-NMR T=298K



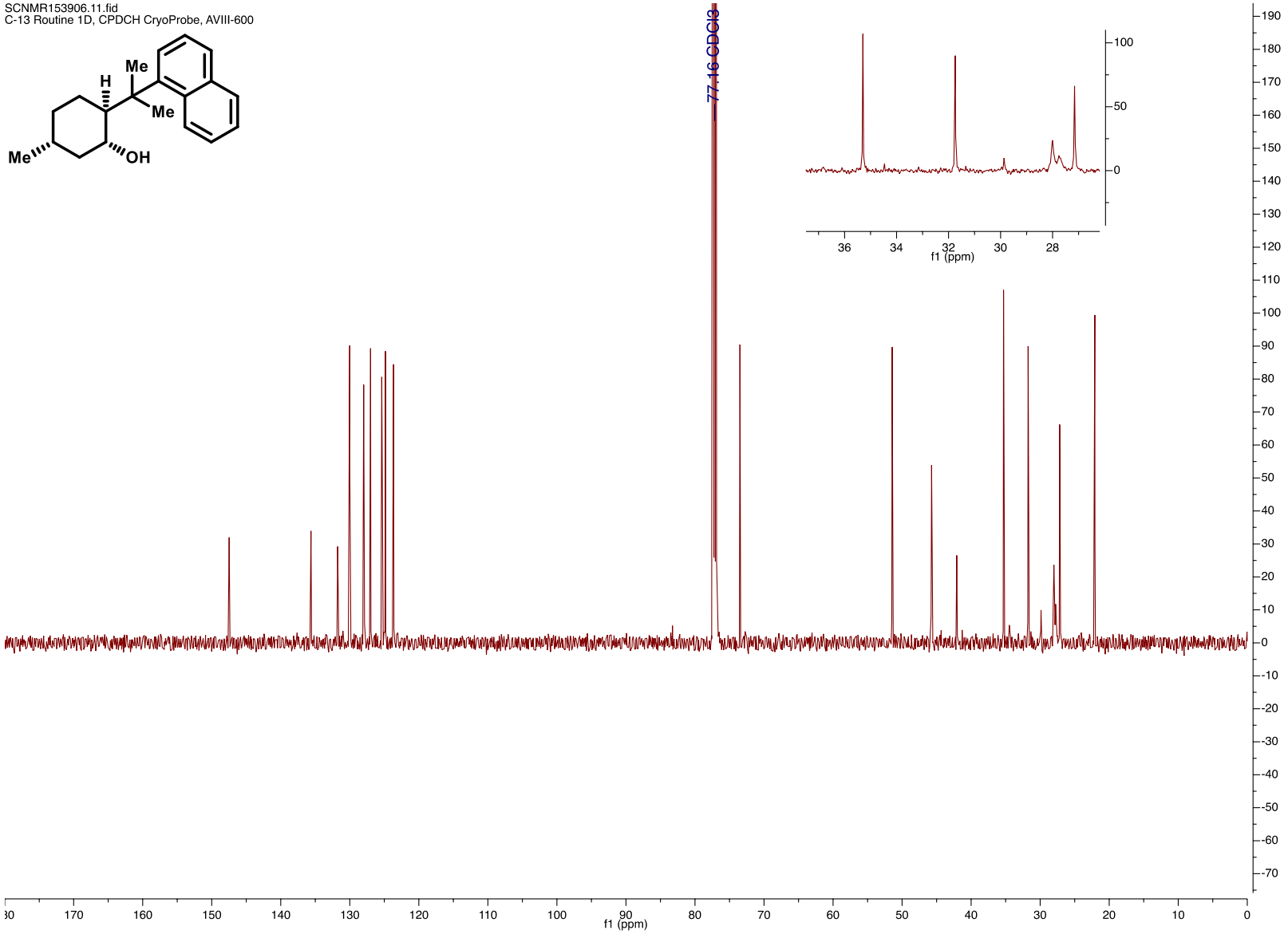

SCNMR153906.3.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
147.38
135.50
131.57
130.01
128.04
126.95
125.38
125.01
124.88
123.57
77.37
77.16 CDCl3
76.95
73.43
51.18
45.42
41.91
35.14
31.62
28.01
27.51
26.95
22.12
Me
H
Me
Me
OH
f1 (ppm)

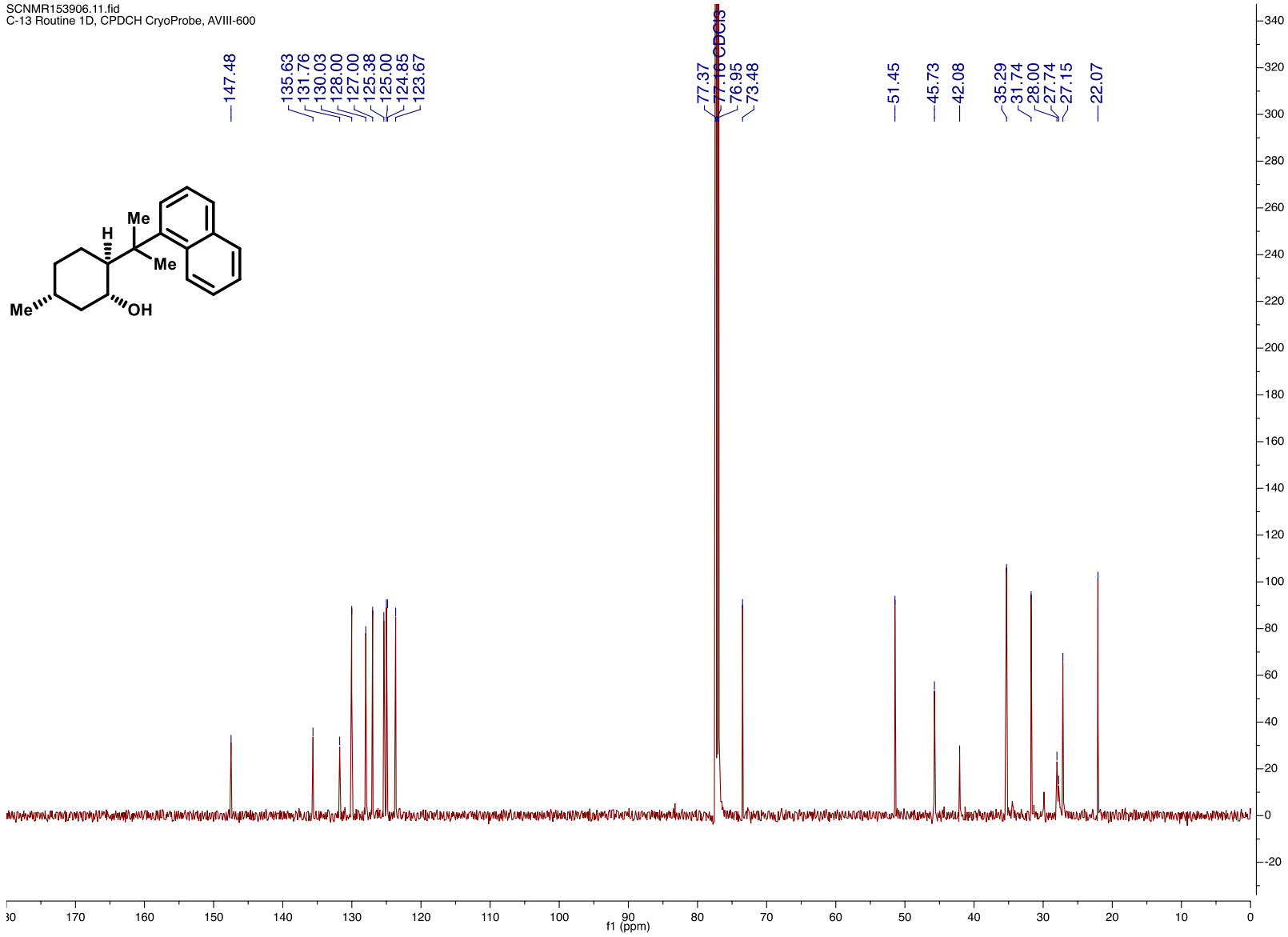
8: ^{1}H-NMR T=323K



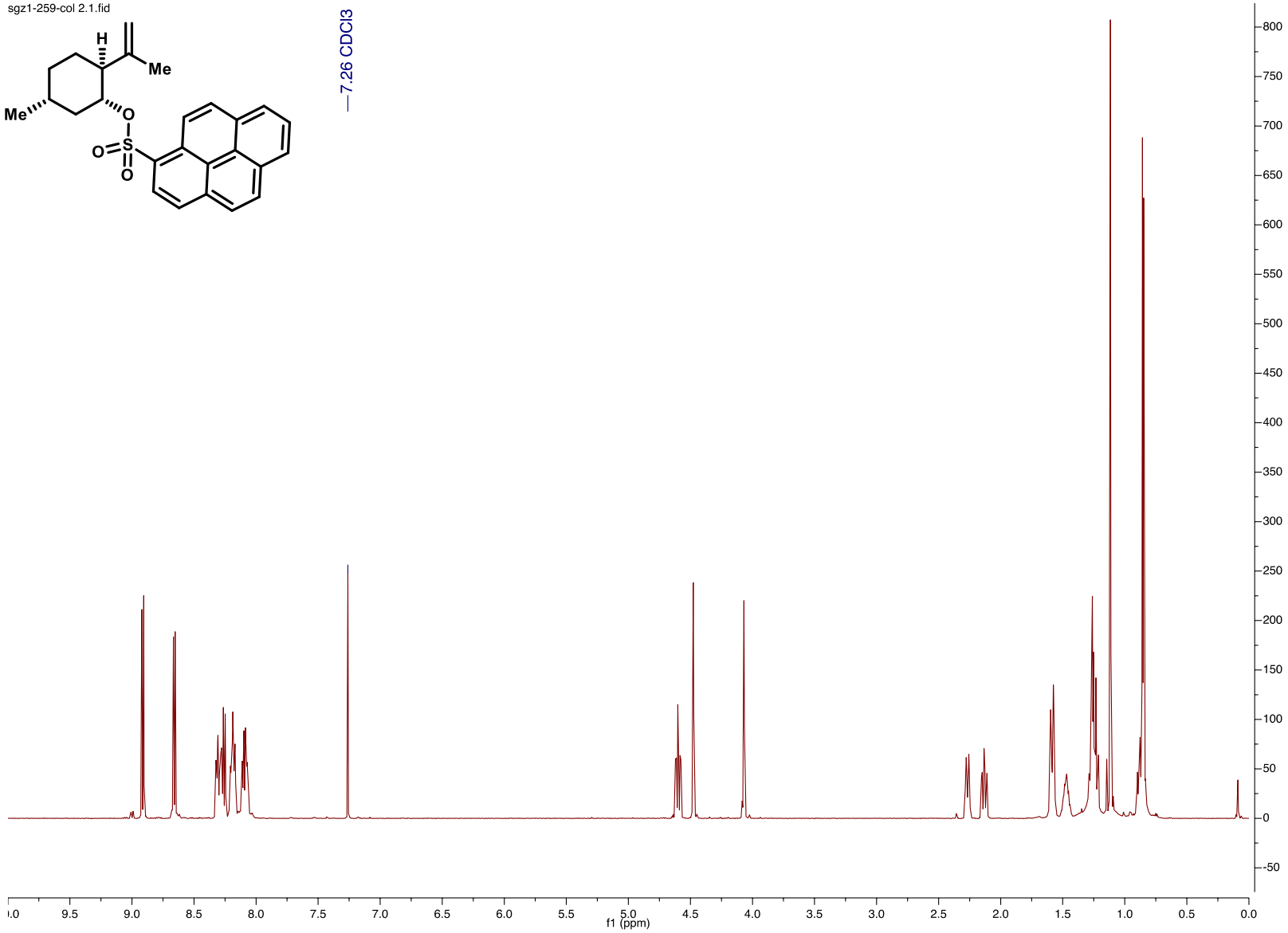

SCNMR153906-12.fid
H-1 Equine Cobalt-1
8.44 8.43 7.80 7.78 7.77 7.70 7.54 7.53 7.52 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.40 7.39 7.38 7.37 7.37 7.26 3.75 3.74 3.73 3.73 3.72 3.71 2.58 2.57 2.57 2.56 2.55 1.87 1.87 1.86 1.85 1.85 1.84 1.73 1.63 1.63 1.62 1.61 1.60 1.43 1.43 1.42 1.35 1.28 1.17 1.14 1.13 1.12 0.93 0.93 0.91 0.89 0.88 0.87 0.86 0.86 0.84 0.84 0.51
Me
H
Me
Me
OH
1.00 0.97 0.97 1.00 1.96 0.99 1.00 1.00 1.01 3.15 5.03 1.37 1.29 1.12 4.38
f1 (ppm)

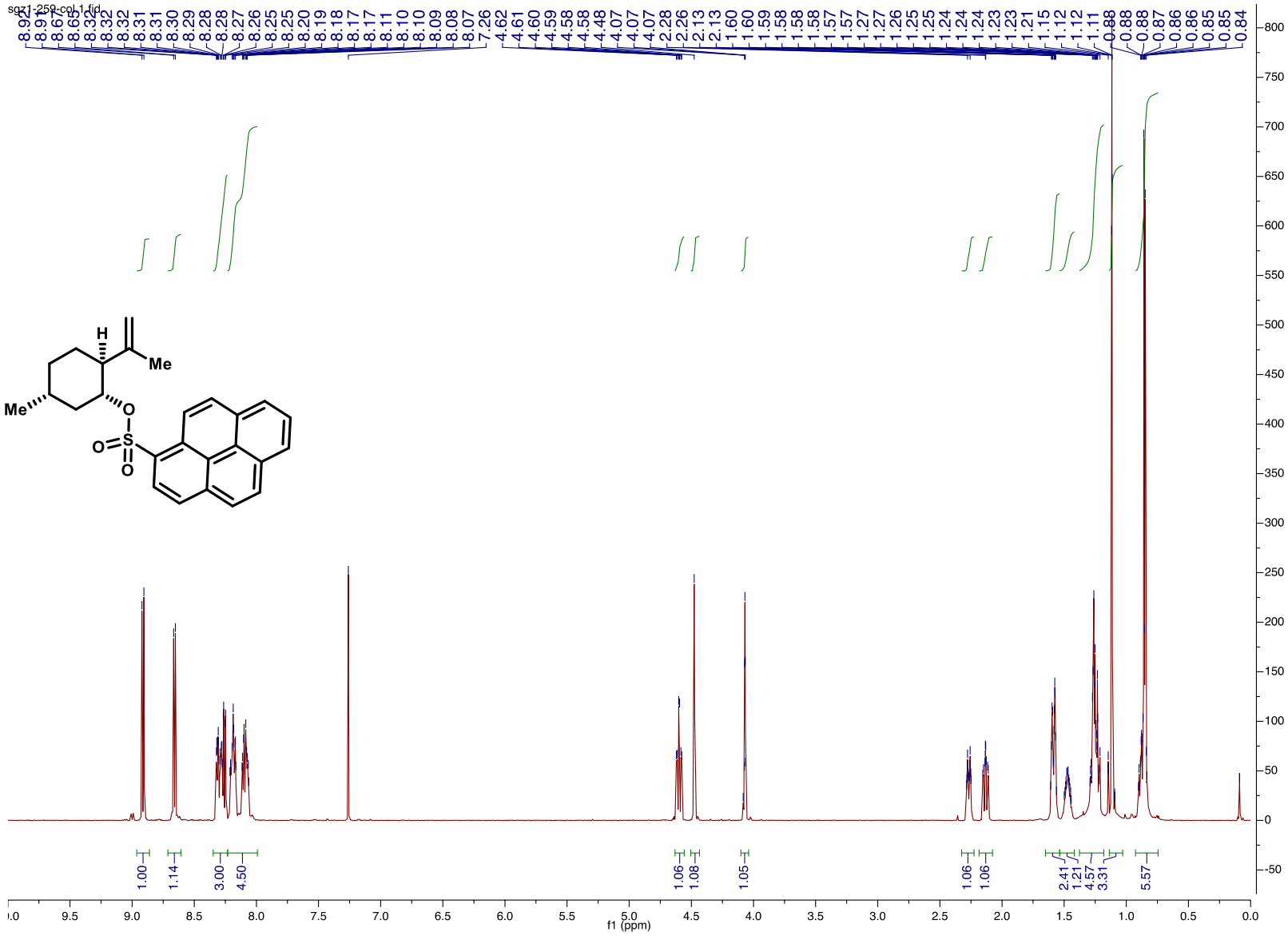
8: ^{13}C-NMR T=323K



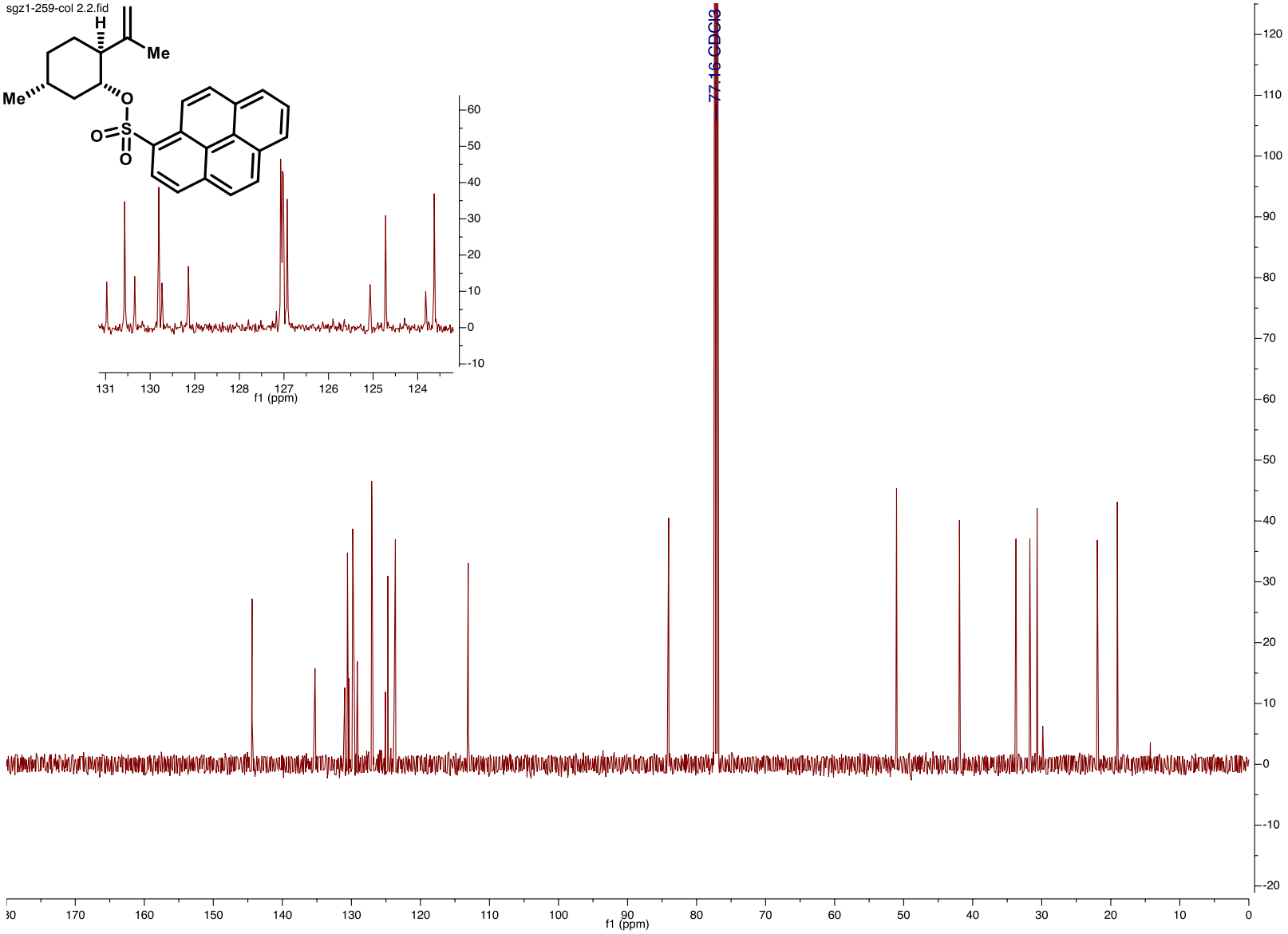

SCNMR153906.11.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
147.48
135.63
131.76
130.03
128.00
127.00
125.38
125.00
124.85
123.67
77.37
77.16 CDCl3
76.95
73.48
51.45
45.73
42.08
35.29
31.74
28.00
27.74
27.15
22.07
Me
H
Me
Me
OH
f1 (ppm)

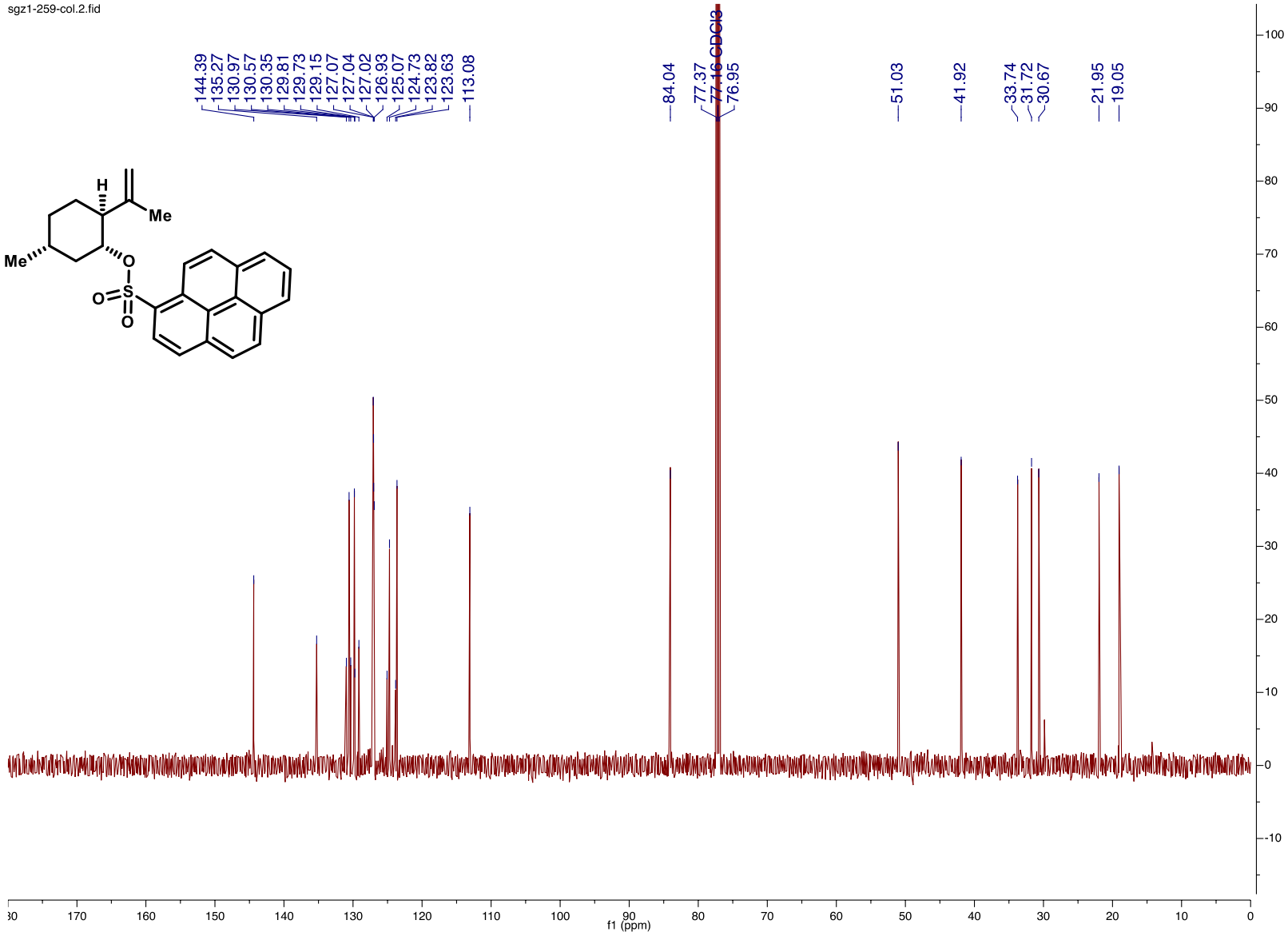
SI-11: ^{1}H-NMR


sgz1-259-col 2.1.fid
7.26 CDCl3
H
Me
Me
O
O
S
O
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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
f1 (ppm)

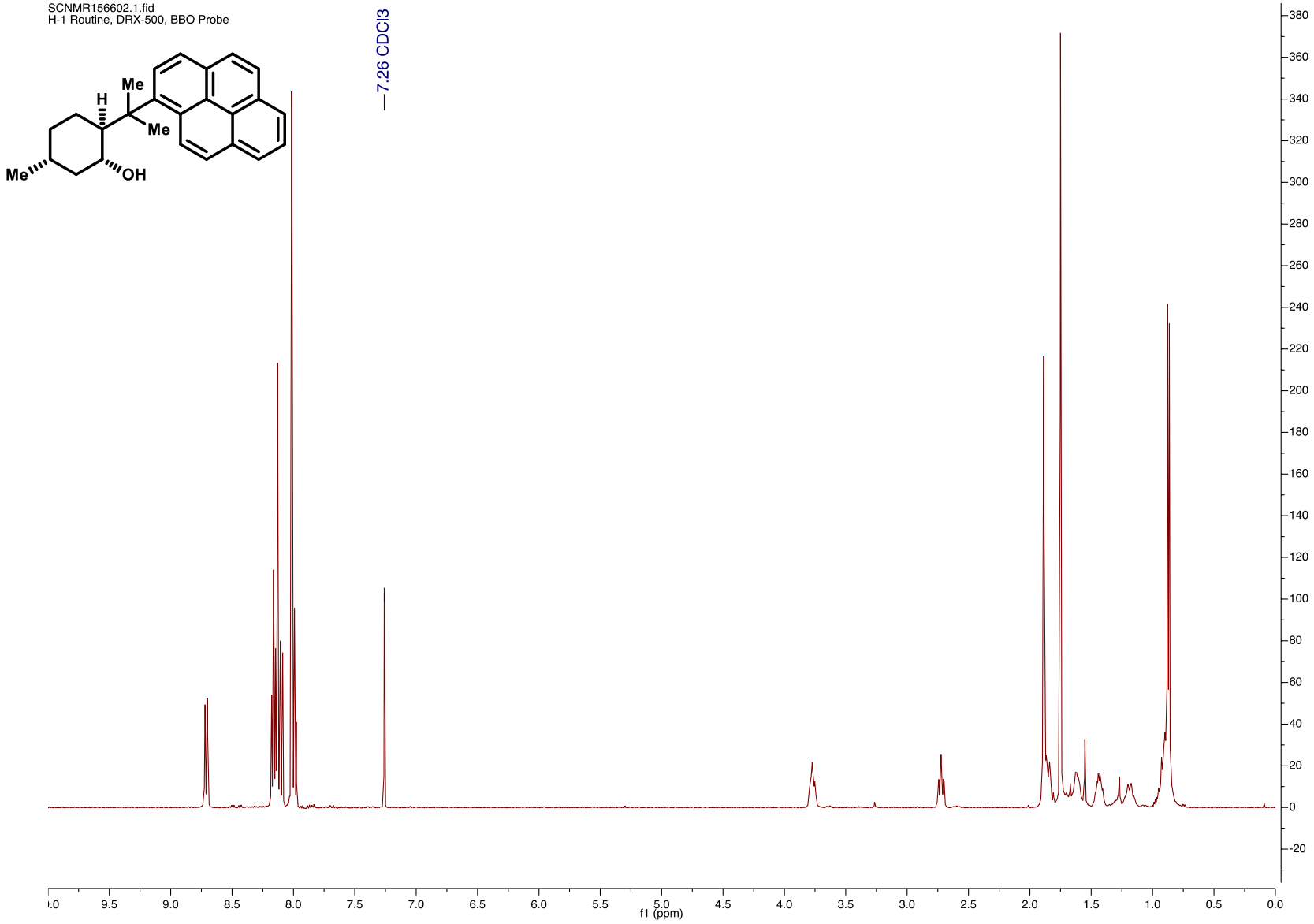

sgz1-259-col-1.fid
f1 (ppm)

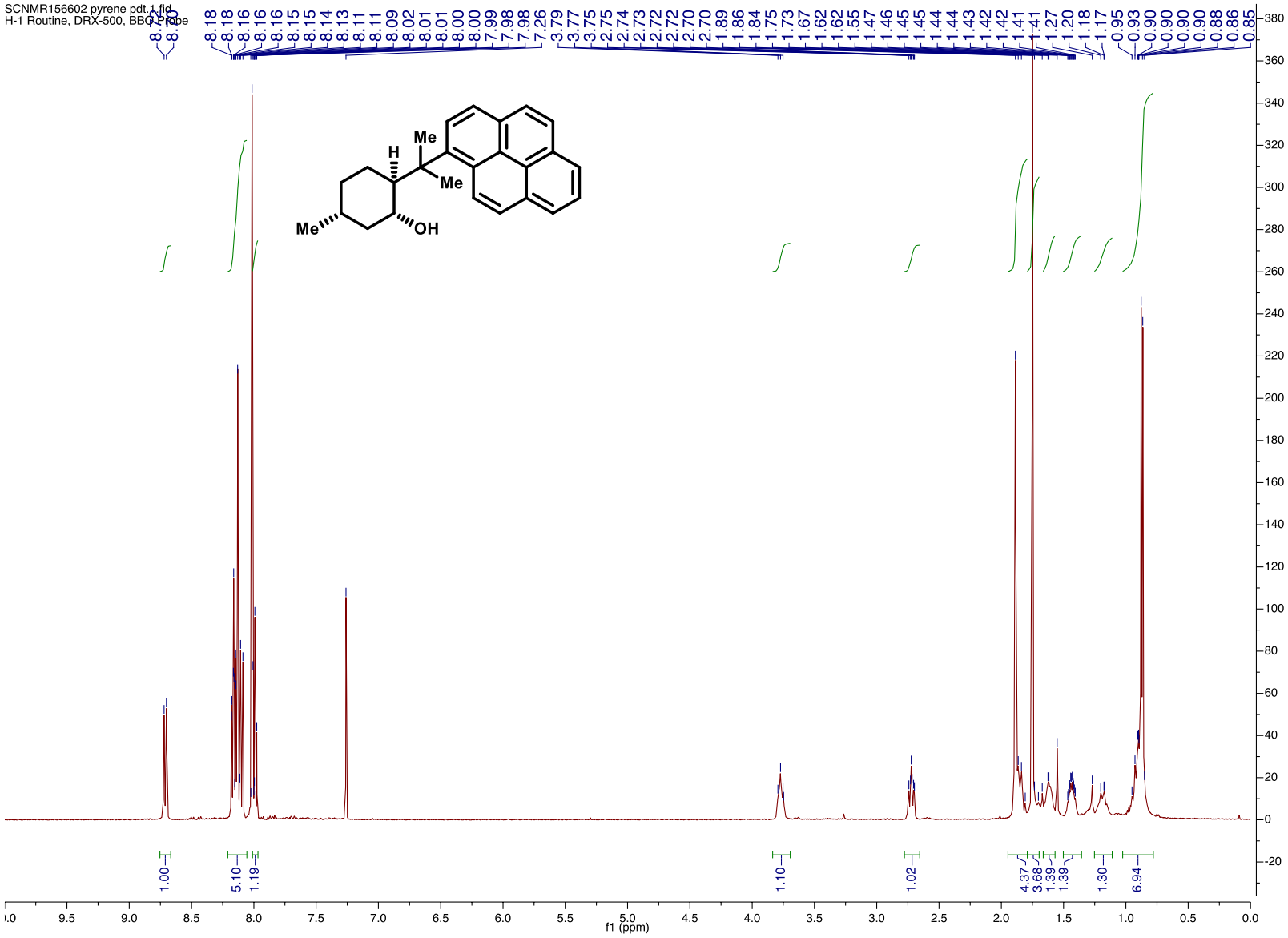
SI-11: ^{13}C-NMR



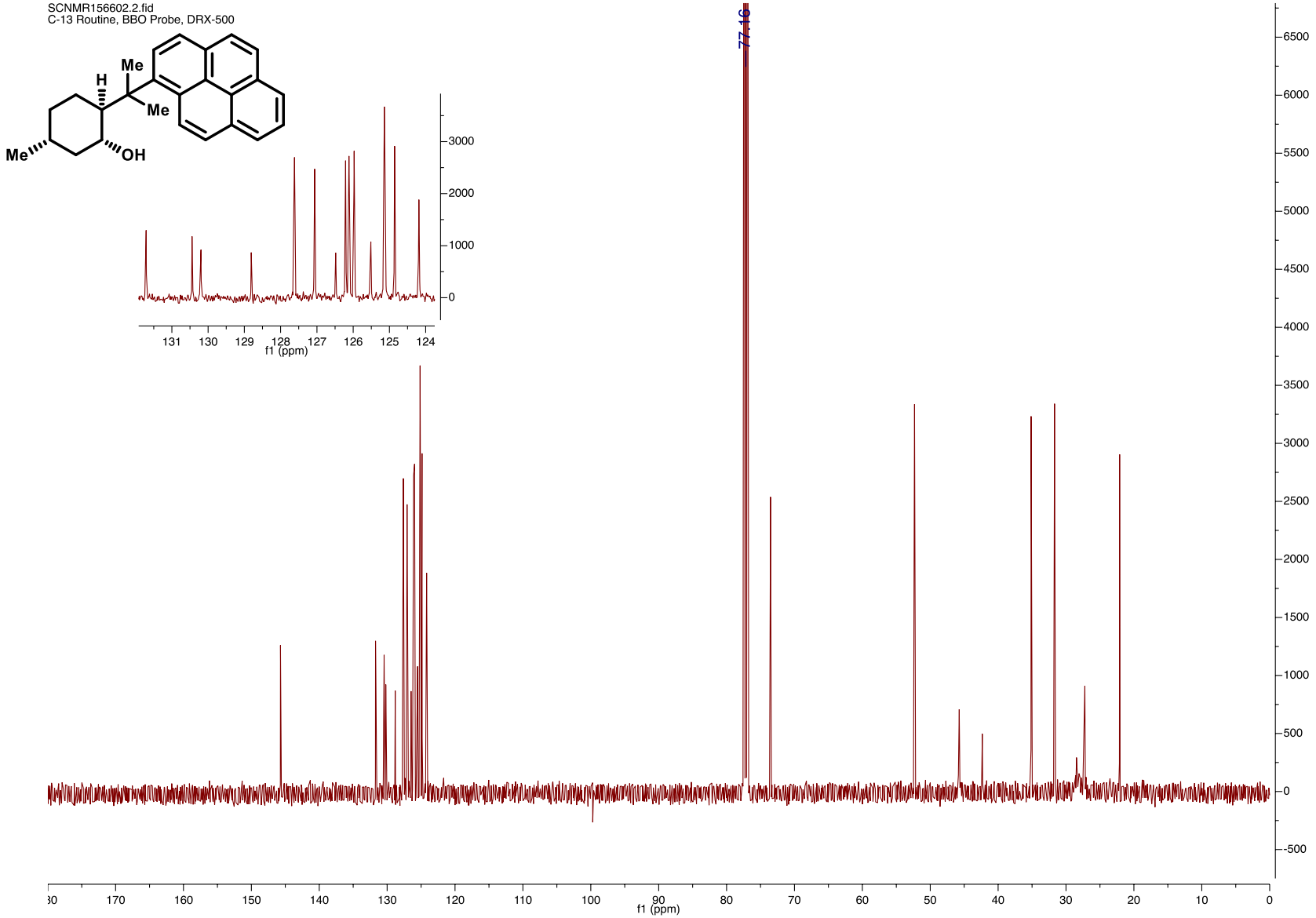

sgz1-259-col.2.fid
144.39
135.27
130.97
130.57
130.35
129.81
129.73
129.15
127.07
127.04
127.02
126.93
125.07
124.73
123.82
123.63
113.08
84.04
77.37
77.16 CDCl3
76.95
51.03
41.92
33.74
31.72
30.67
21.95
19.05
H
Me
Me
O
O
S
O
O
f1 (ppm)

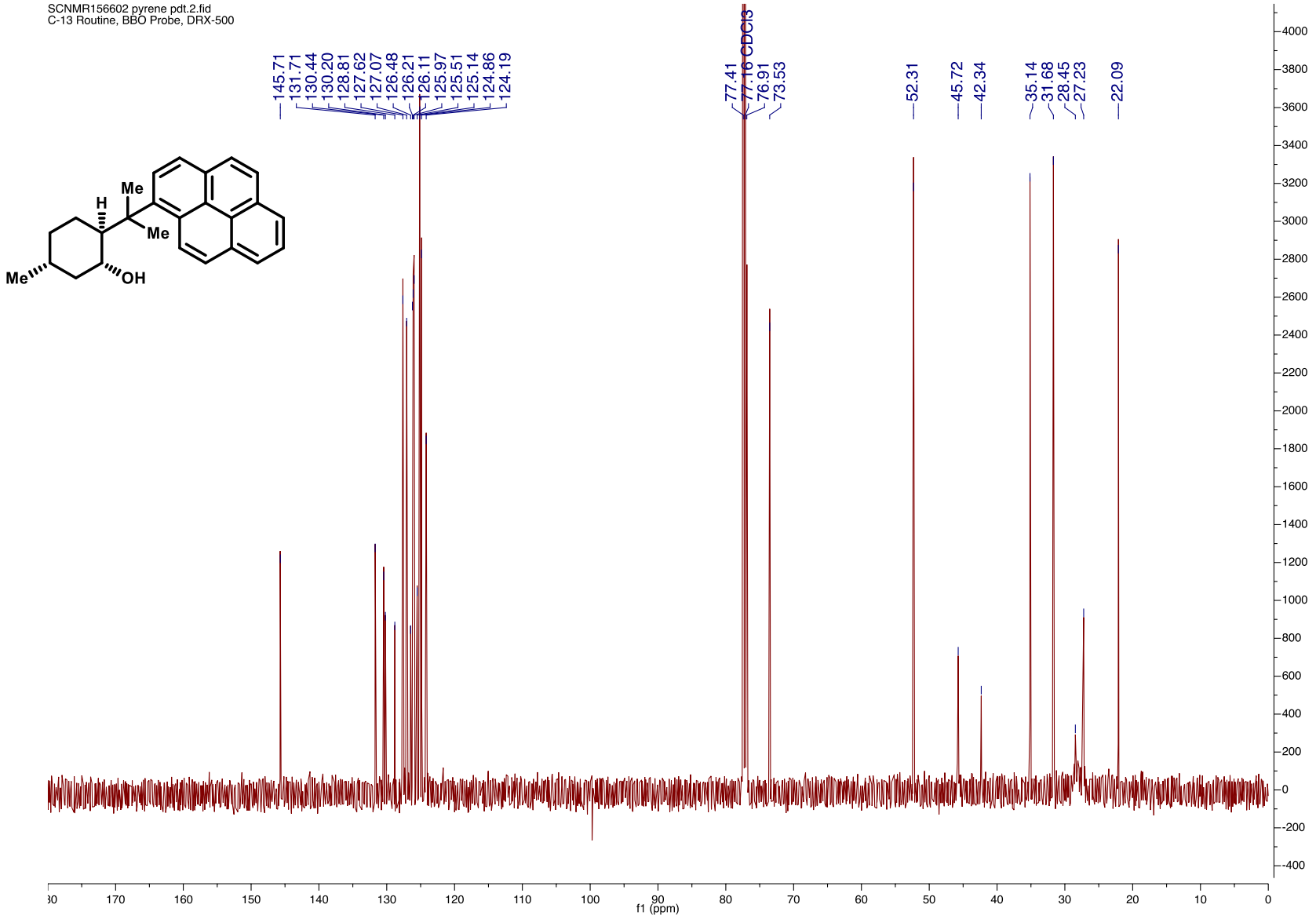
9: ^{1}H-NMR


SCNMR156602.1.fid
H-1 Routine, DRX-500, BBO Probe
7.26 CDCl3
Me
H
Me
Me
OH
f1 (ppm)

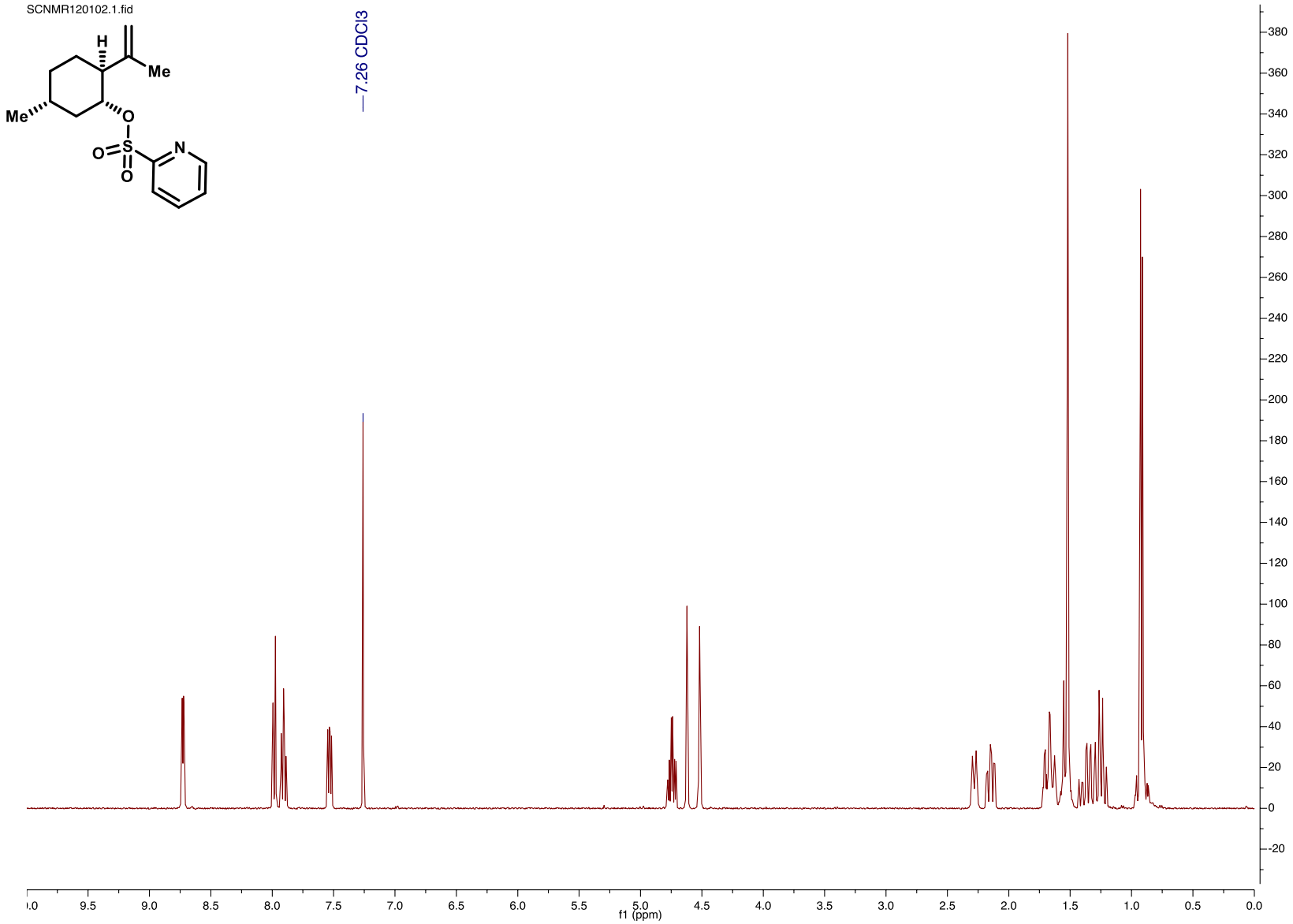

SCNMR156602 pyrene pdt.1.fid
H-1 Routine, DRX-500, BBO Probe
Me
H
Me
Me
OH
f1 (ppm)

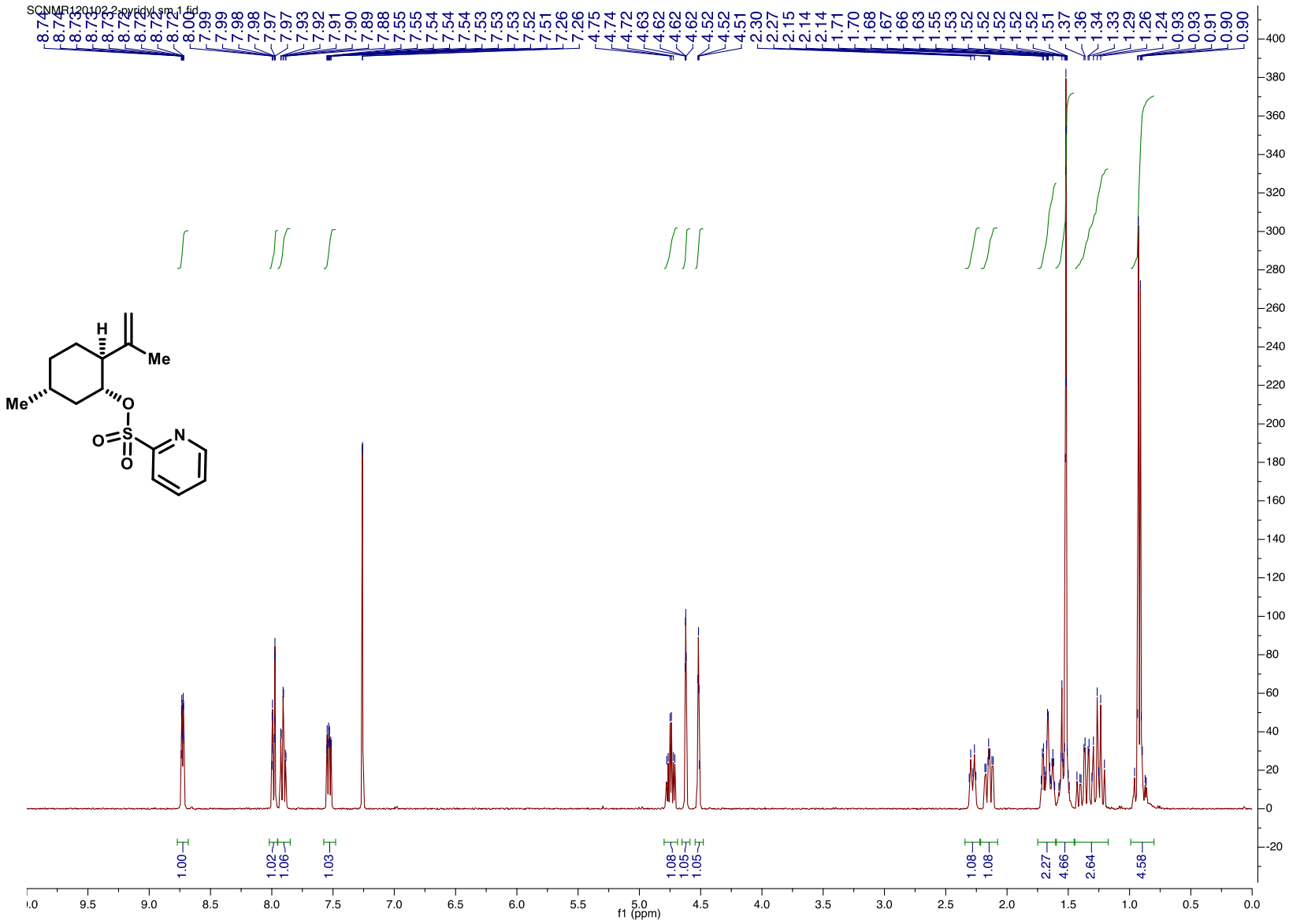
9: ^{13}C-NMR


SCNMR156602.2.fid
C-13 Routine, BBO Probe, DRX-500
Me
H
Me
Me
OH
77.16
f1 (ppm)

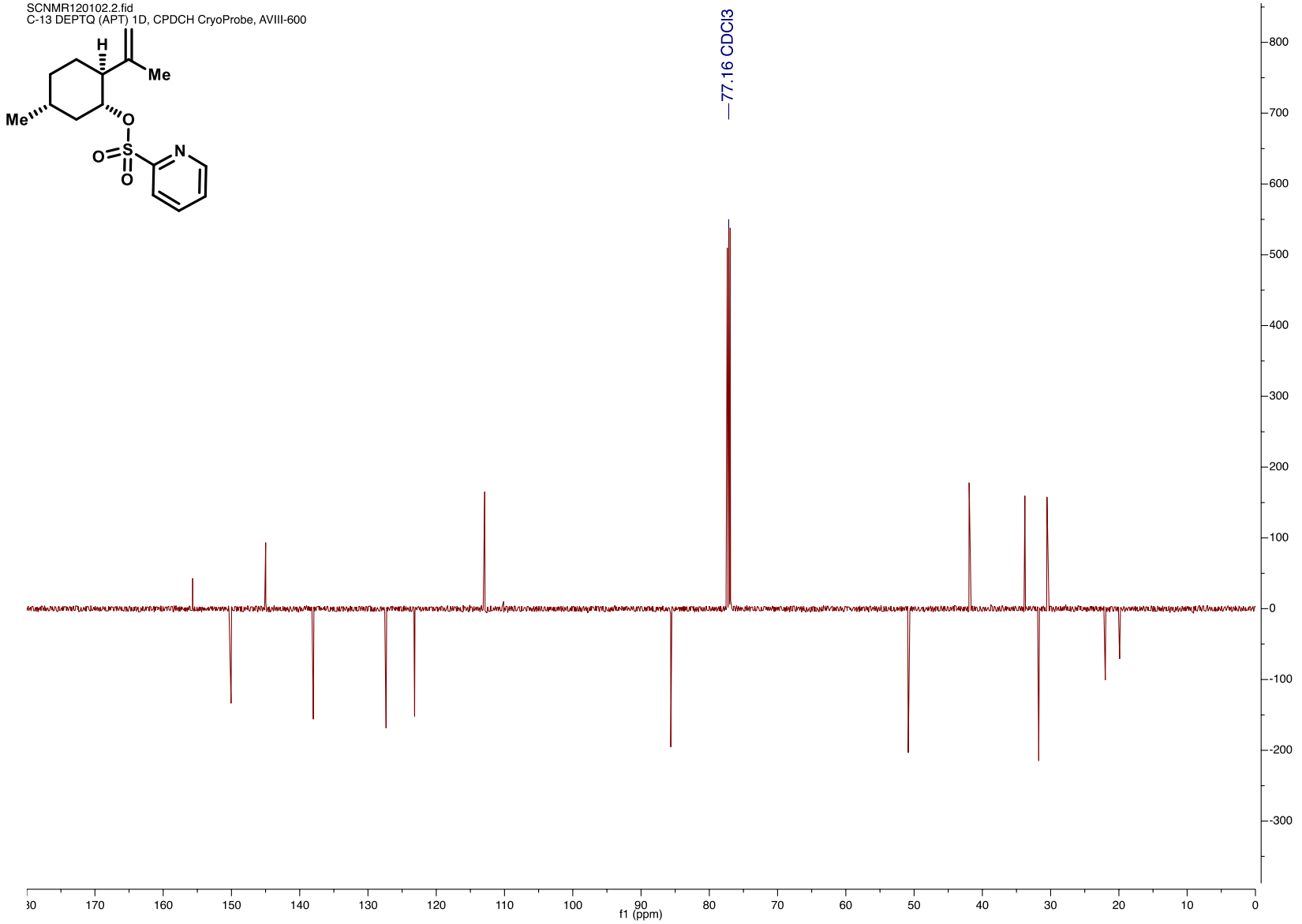

SCNMR156602 pyrene pdt.2.fid
C-13 Routine, BBO Probe, DRX-500
145.71
131.71
130.44
130.20
128.81
127.62
127.07
126.48
126.21
126.11
125.97
125.51
125.14
124.86
124.19
77.41
77.16 CDCl3
76.91
73.53
52.31
45.72
42.34
35.14
31.68
28.45
27.23
22.09
Me
H
Me
Me
OH
f1 (ppm)

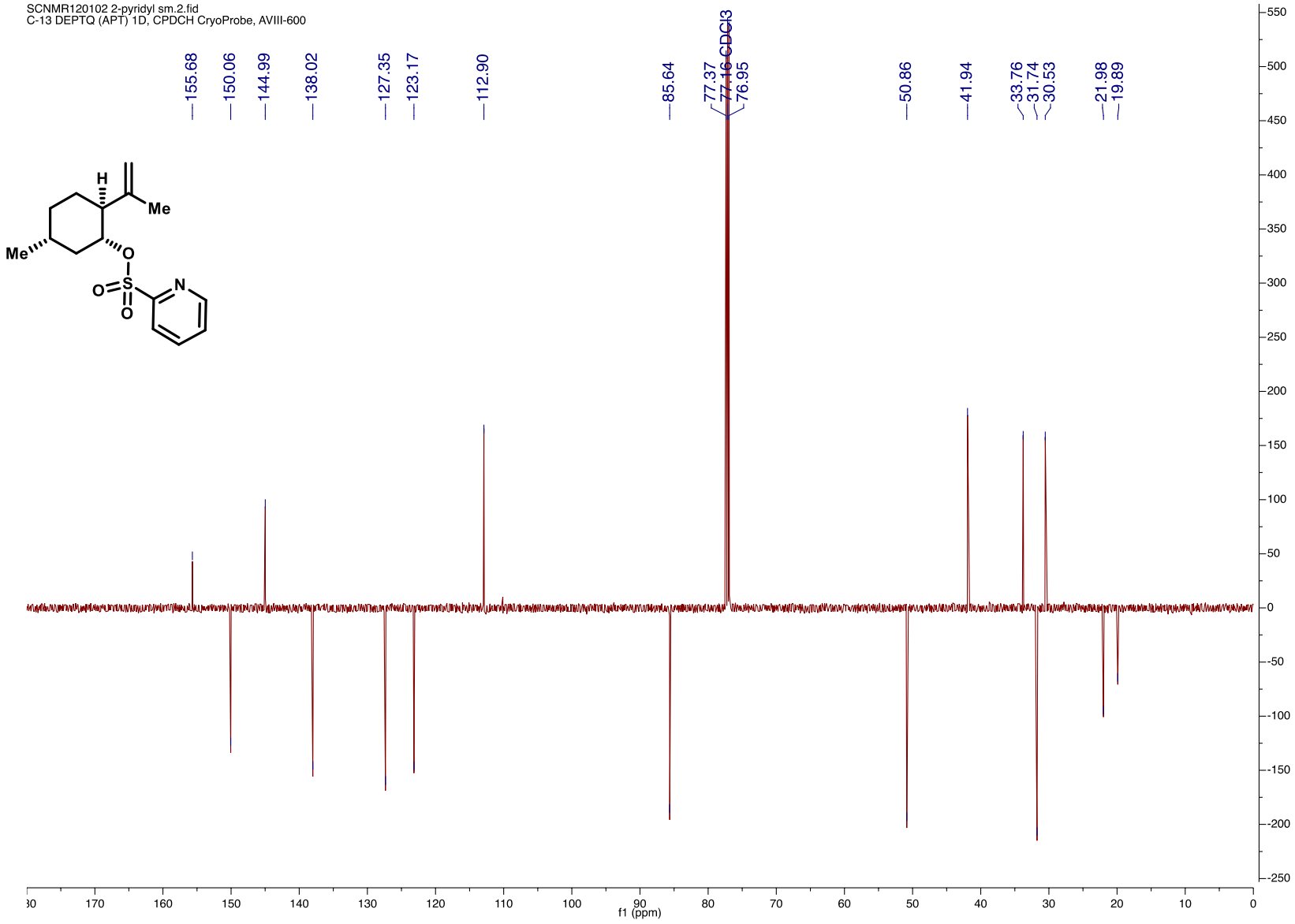
SI-12: ^{1}H-NMR


SCNMR120102.1.fid
7.26 CDCl3
H
Me
Me
O
O
S
O
O
N
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
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
f1 (ppm)

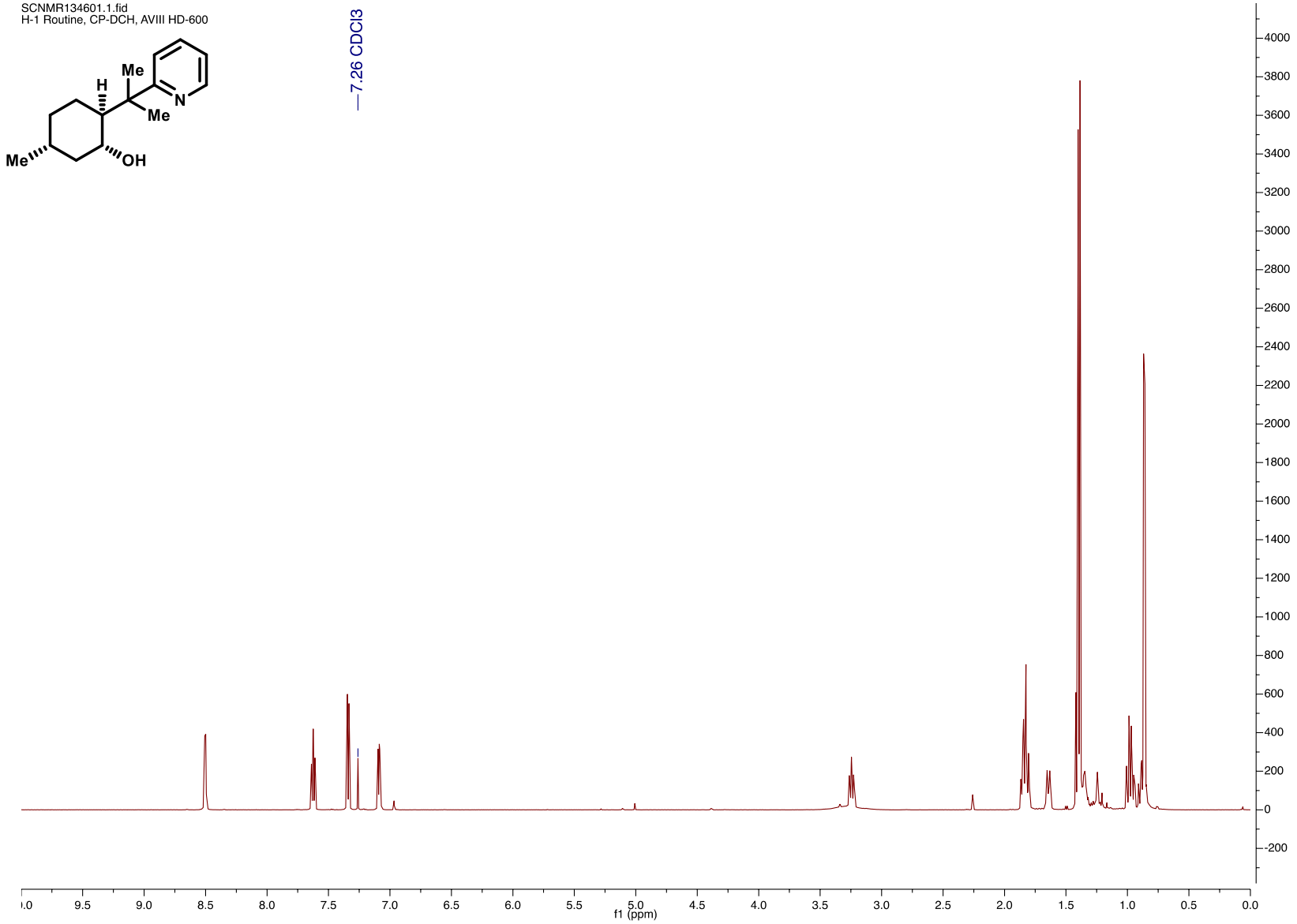

SCNMR120102-2-pyridyl-sm-1.fid
H
Me
Me
O
O
S
O
O
N
f1 (ppm)

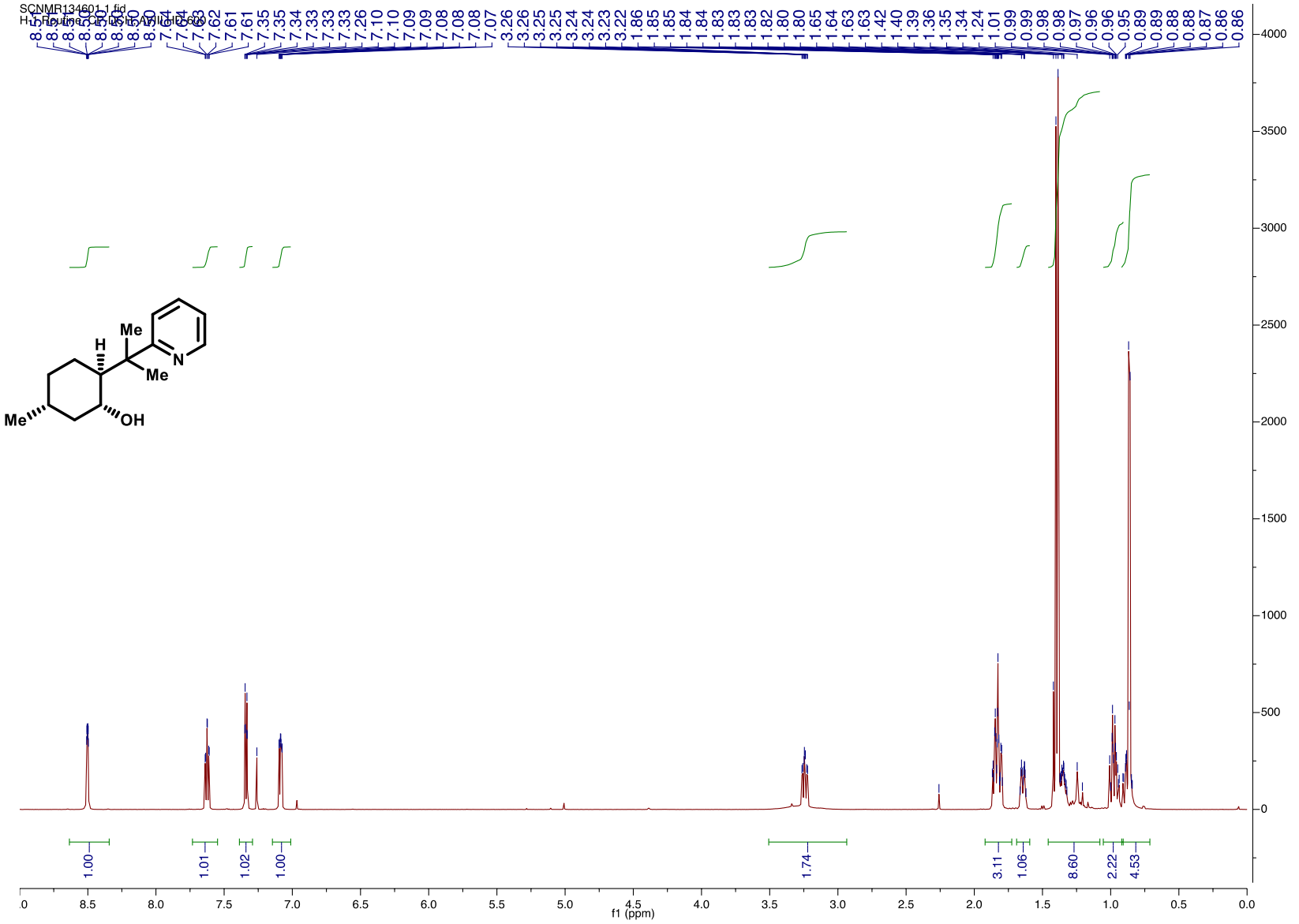
SI-12: ^{13}C-NMR DEPT-Q



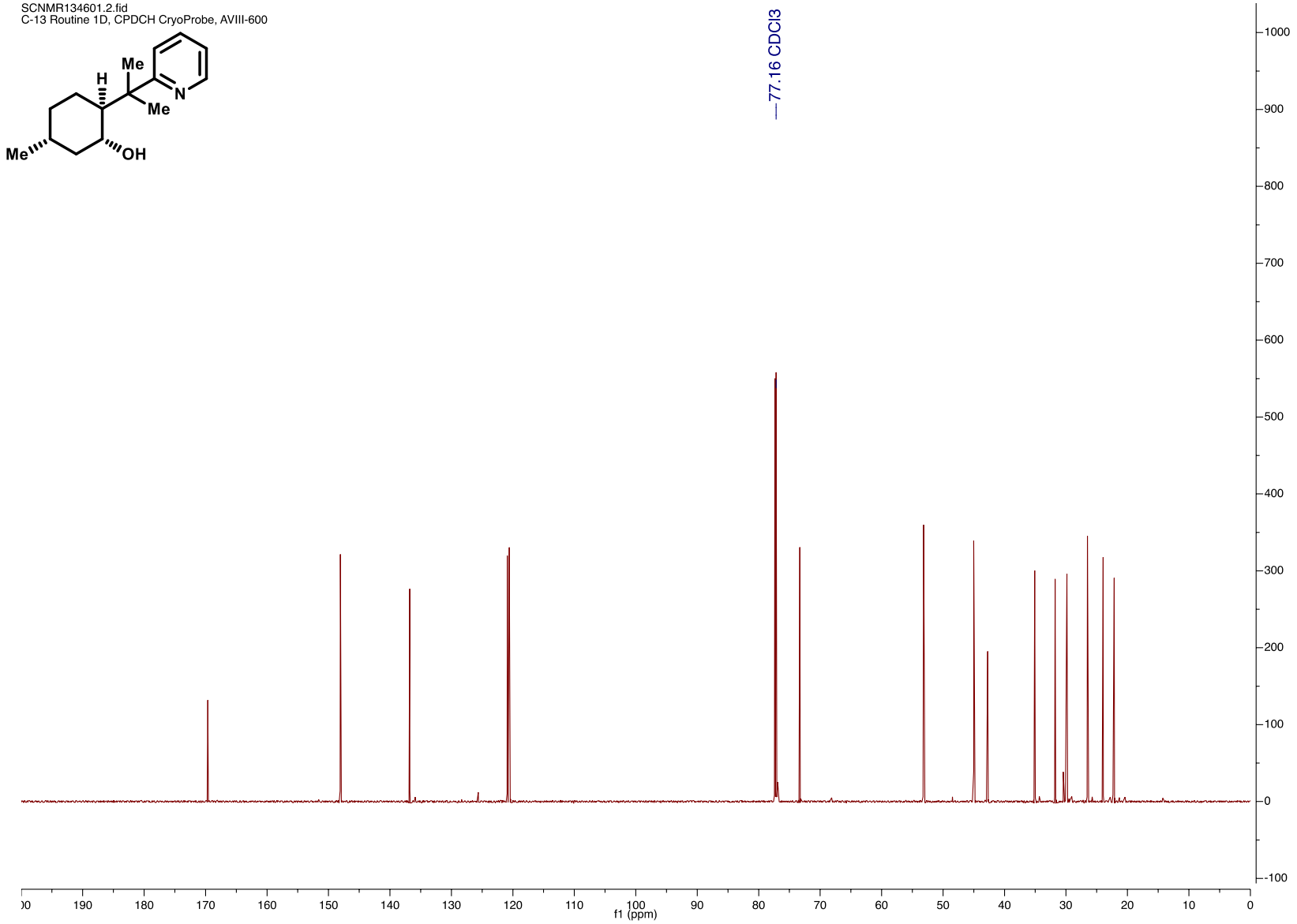

SCNMR120102 2-pyridyl sm.2.fid
C-13 DEPTQ (APT) 1D, CPDCH CryoProbe, AVIII-600
155.68
150.06
144.99
138.02
127.35
123.17
112.90
85.64
77.37
77.16 CDCl3
76.95
50.86
41.94
33.76
31.74
30.53
21.98
19.89
H
Me
Me
O
S
O
O
N
f1 (ppm)

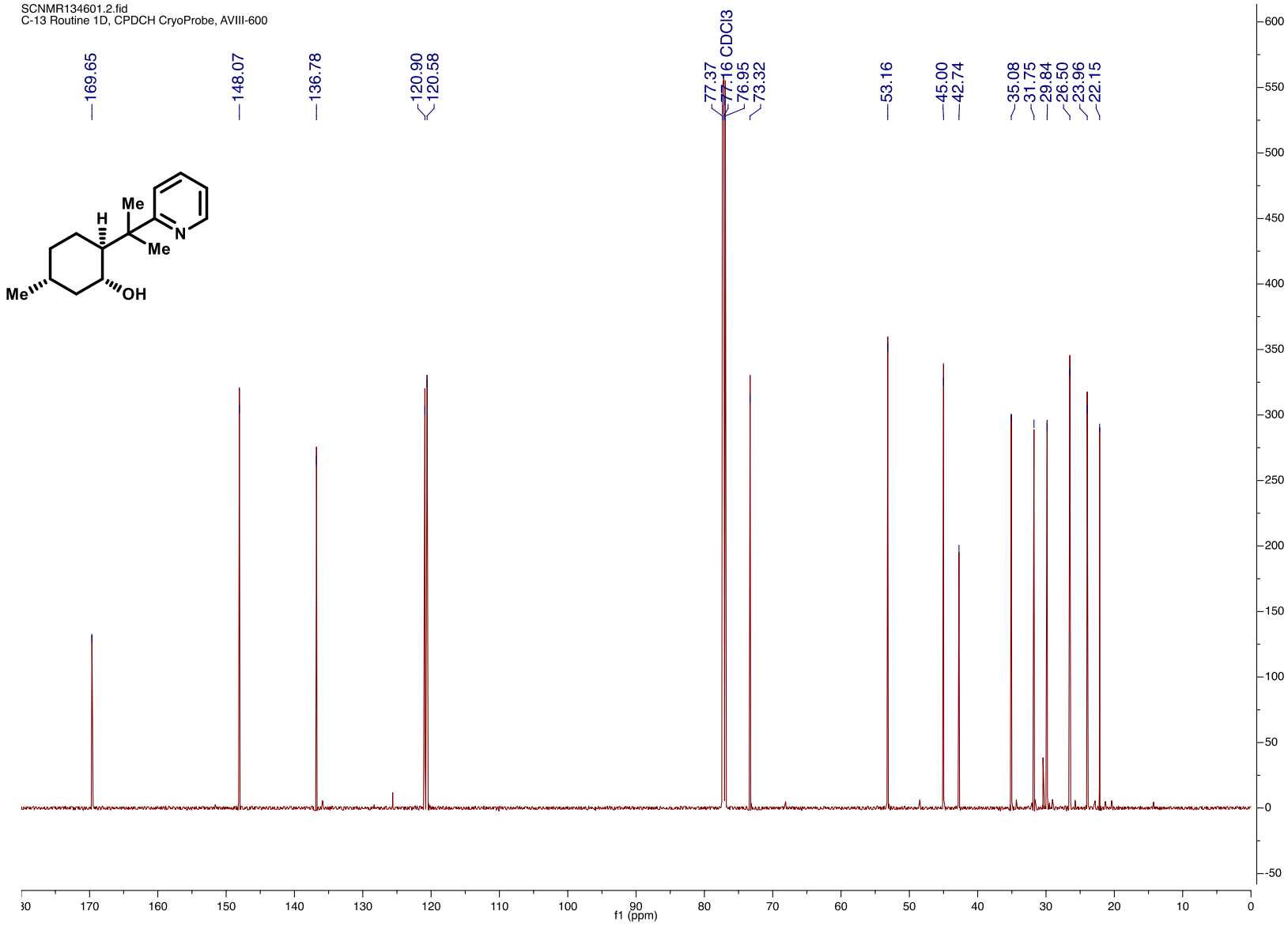
10: ^{1}H-NMR


SCNMR134601.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
H
N
Me
Me
OH
f1 (ppm)

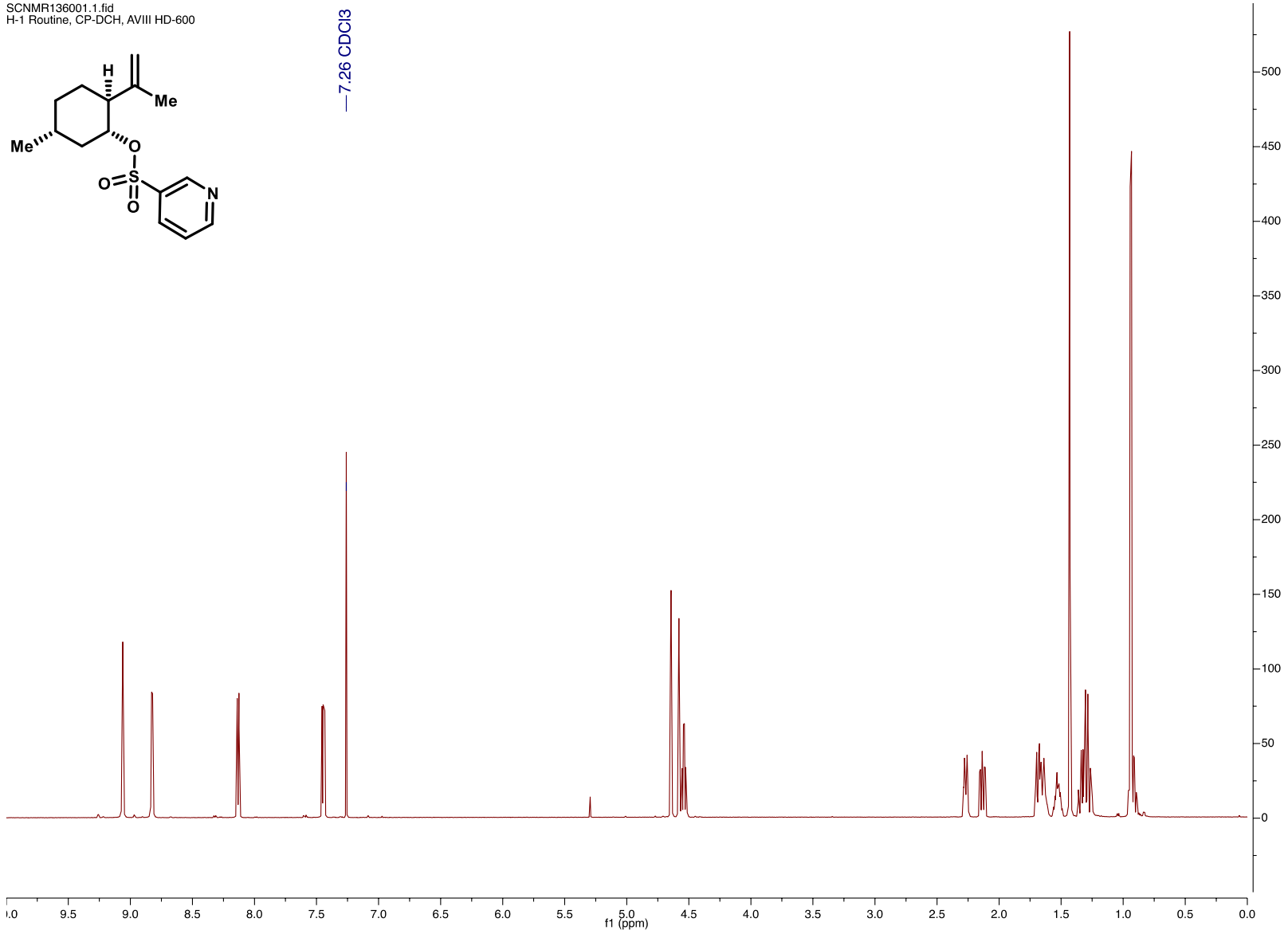

SCNMR134601-1.fid
H-1 Routine 1D PROTON /AV III HD 500
Me
H
N
Me
Me
OH
f1 (ppm)

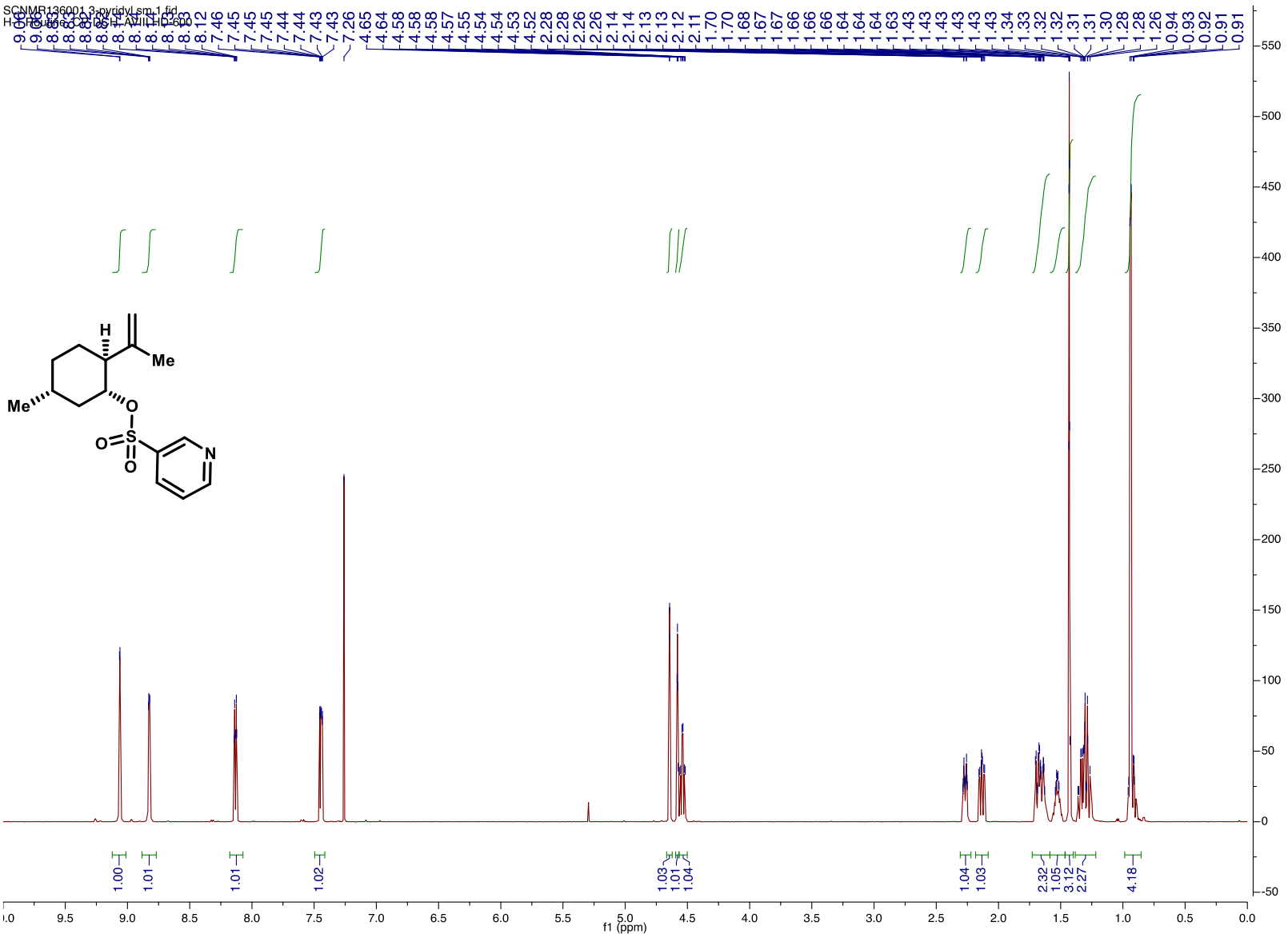
10: ^{13}C-NMR


SCNMR134601.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
H
N
Me
Me
OH
77.16 CDCl3
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

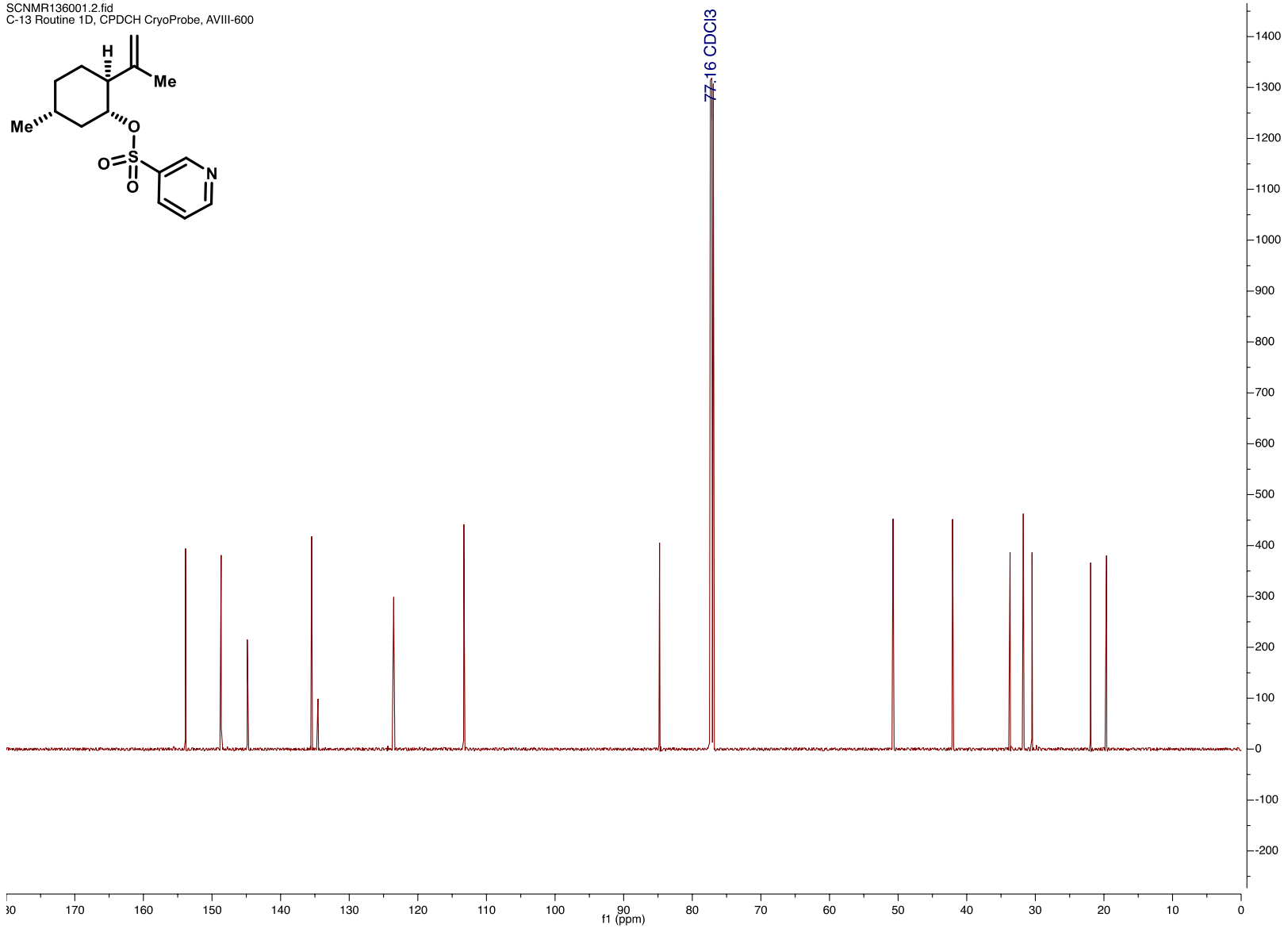

SCNMR134601.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
169.65
148.07
136.78
120.90
120.58
77.37
77.16 CDCl3
76.95
73.32
53.16
45.00
42.74
35.08
31.75
29.84
26.50
23.96
22.15
Me
H
N
Me
Me
OH
f1 (ppm)

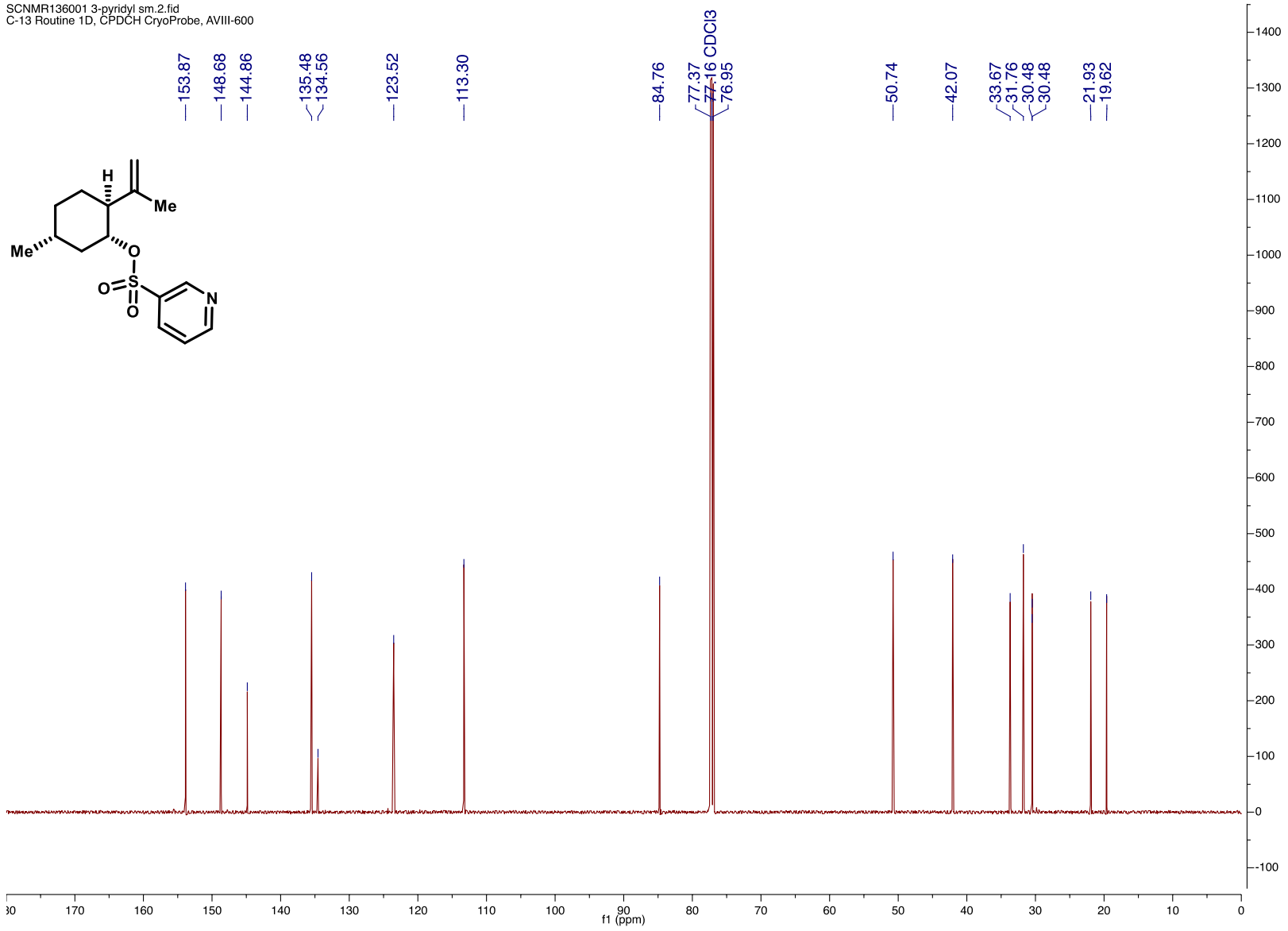
SI-13: ^{1}H-NMR


SCNMR136001.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
H
Me
Me
O
S
O
O
N
500
450
400
350
300
250
200
150
100
50
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
f1 (ppm)

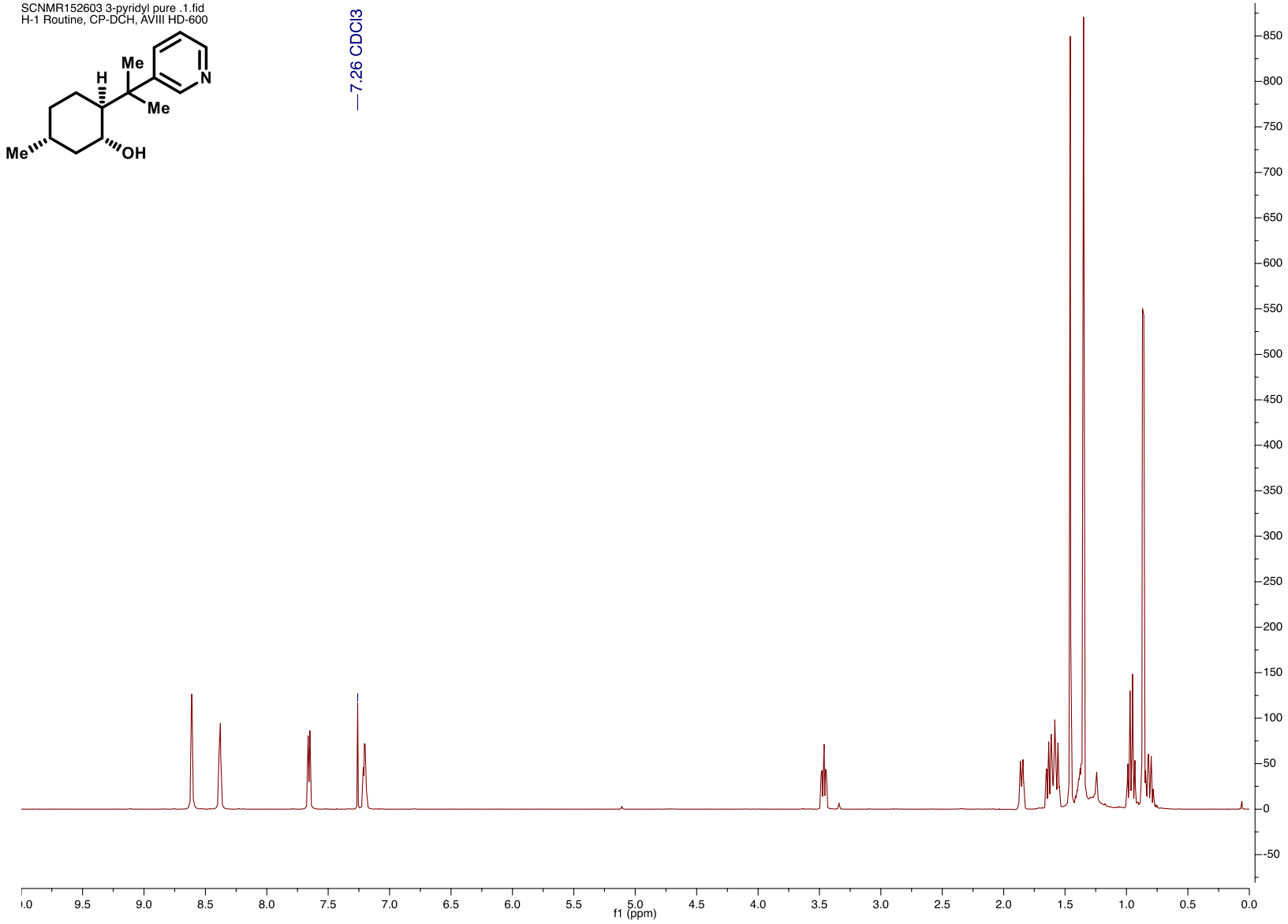

SCNMR136001-3-pyridyl-sm-1.fid
H-CRUDE-27SEP2021-AVIII-HD-600
H
Me
Me
O
O
S
O
O
N
f1 (ppm)

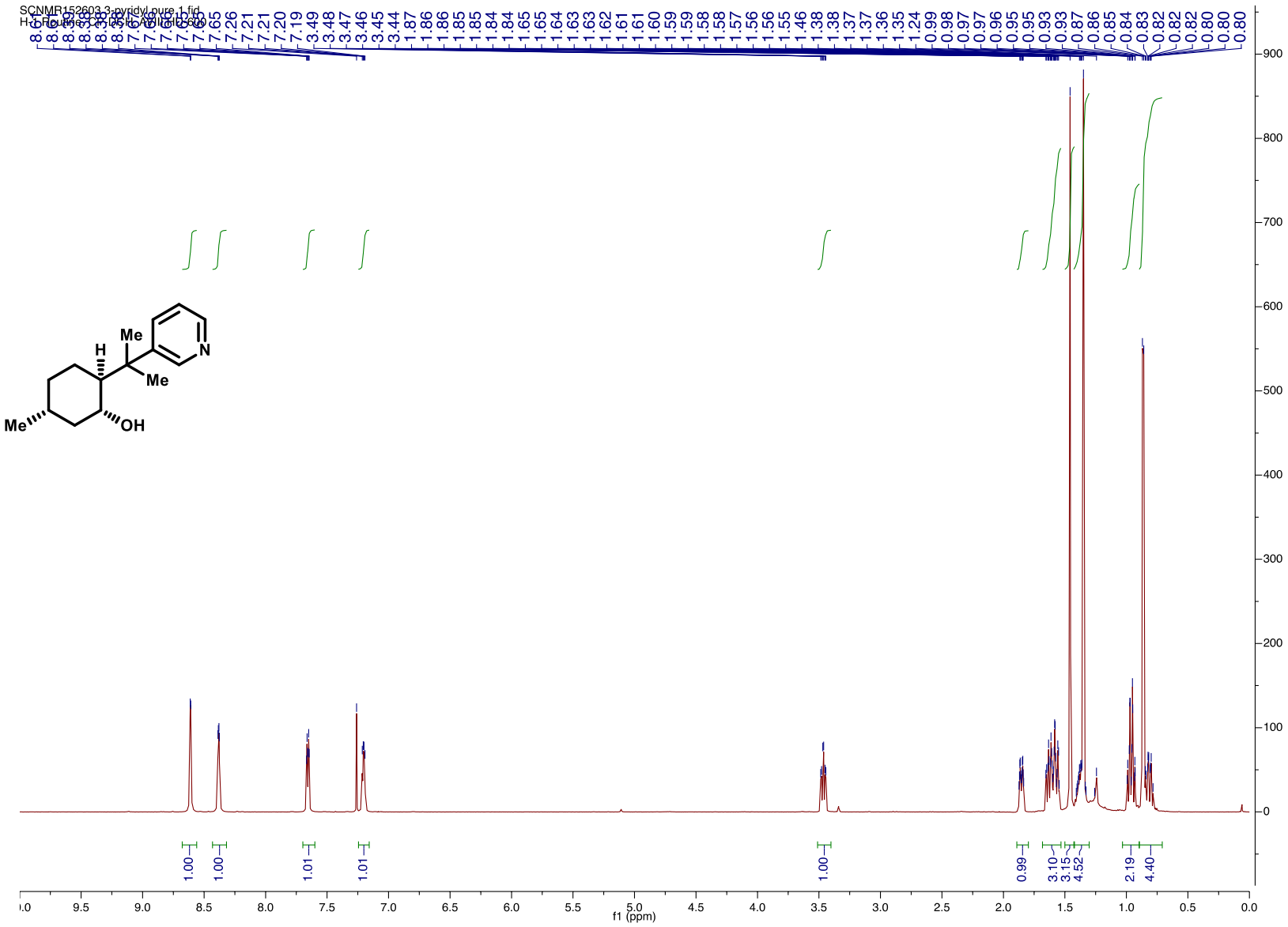
SI-13: ^{13}C-NMR


SCNMR136001.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
77.16 CDCl3
H
Me
Me
O
S
O
O
N
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

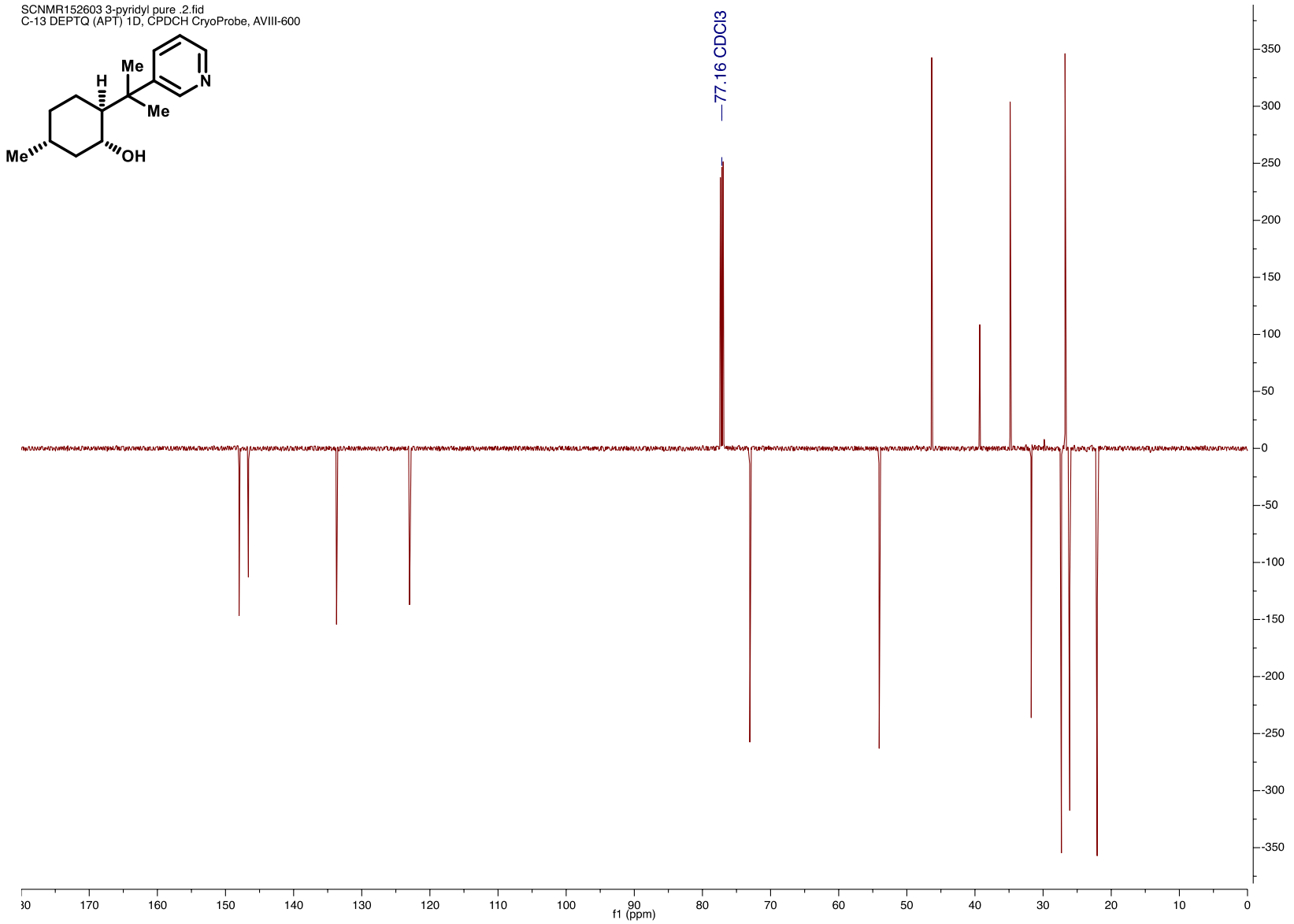

SCNMR136001 3-pyridyl sm.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
153.87
148.68
144.86
135.48
134.56
123.52
113.30
84.76
77.37
77.16 CDCl3
76.95
50.74
42.07
33.67
31.76
30.48
30.48
21.93
19.62
H
Me
Me
O
O
S
O
N
f1 (ppm)

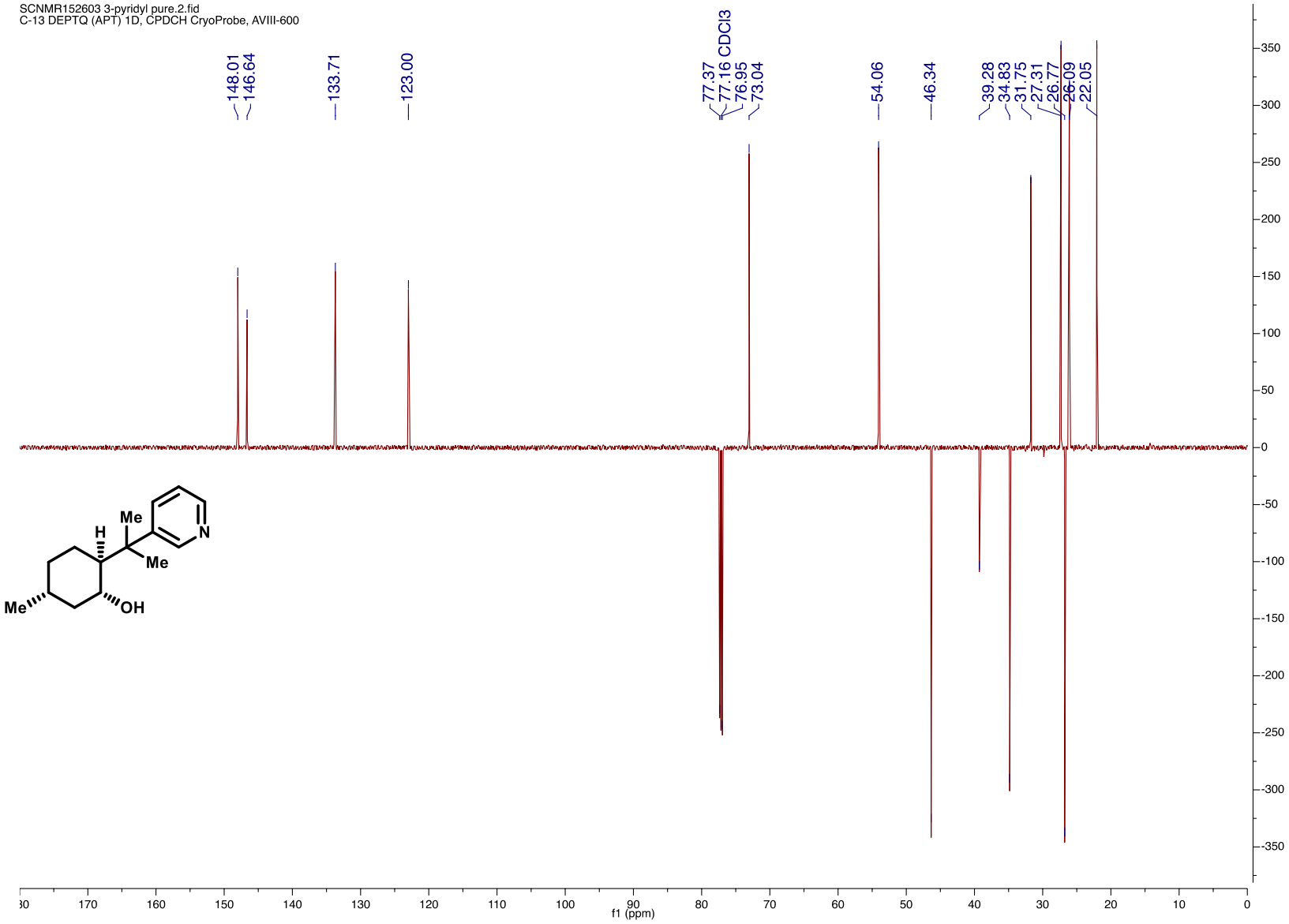
11: ^{1}H-NMR, $CDCl_3$



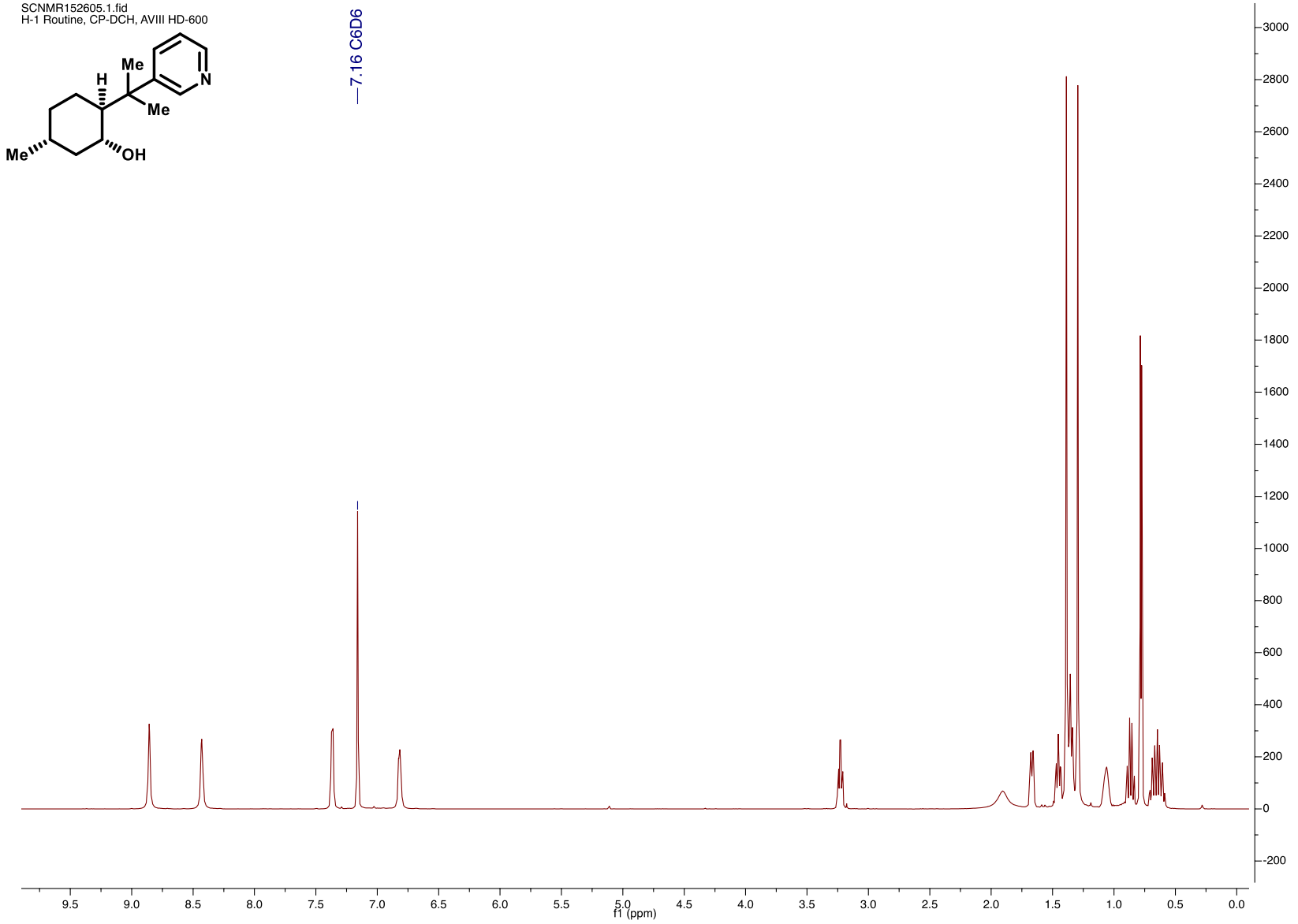

SCNMR152603-3-pyridyl-pure-1.fid
H-1 Routine 1 d 25 °C Alina 500
8.58 8.58 8.57 8.57 8.56 8.56 7.66 7.65 7.65 7.65 7.26 7.21 7.21 7.20 7.19 3.49 3.48 3.47 3.46 3.45 3.44 1.87 1.86 1.86 1.85 1.85 1.84 1.84 1.65 1.65 1.64 1.63 1.63 1.62 1.61 1.61 1.60 1.59 1.59 1.58 1.58 1.57 1.56 1.56 1.55 1.46 1.38 1.38 1.37 1.37 1.36 1.35 1.24 0.99 0.98 0.97 0.97 0.96 0.95 0.95 0.93 0.93 0.87 0.86 0.85 0.84 0.83 0.82 0.82 0.82 0.80 0.80 0.80
Me
H
N
Me
Me
Me
OH
1.00
1.00
1.01
1.01
1.00
0.99
3.10
3.15
4.52
2.19
4.40
f1 (ppm)

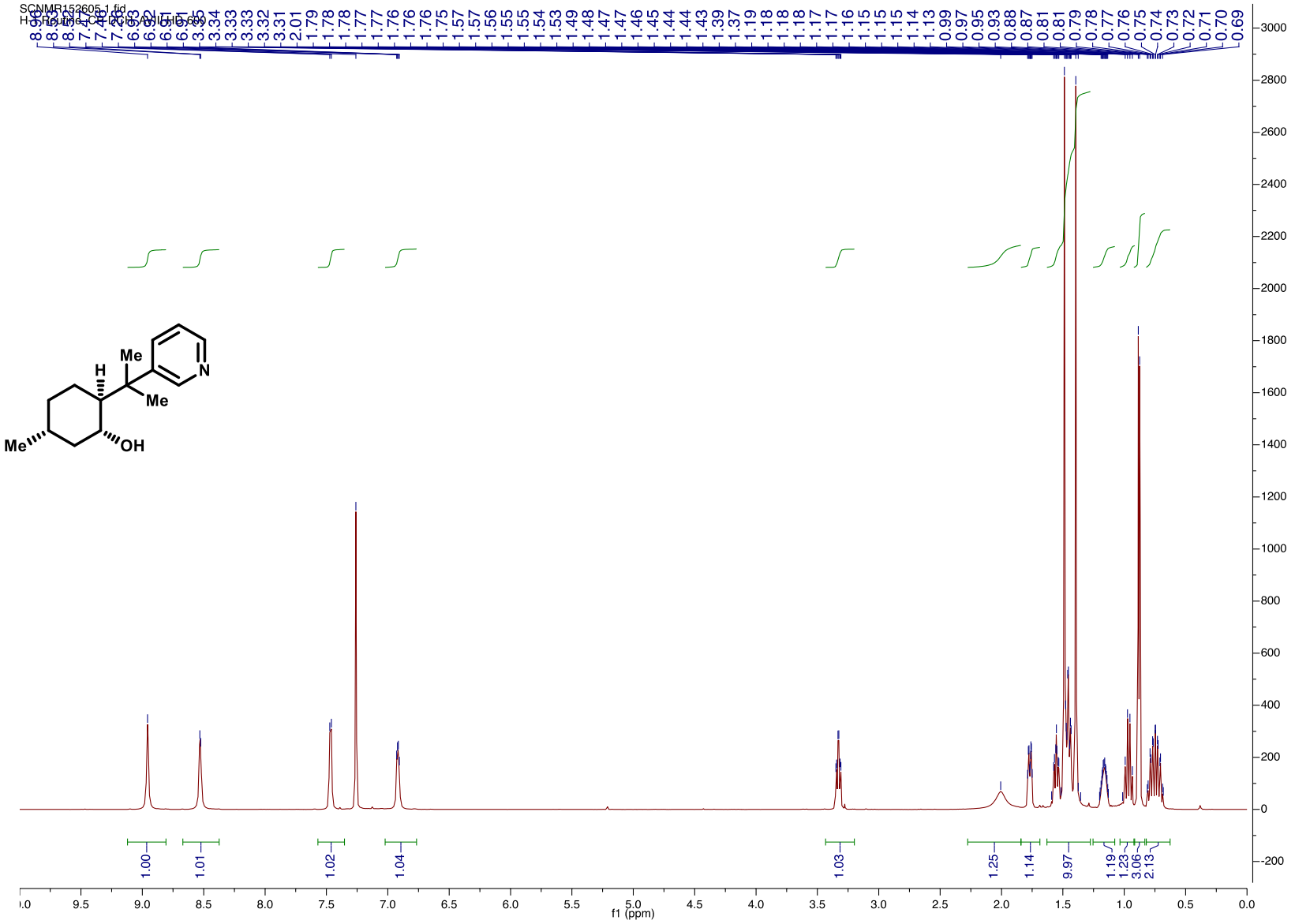
11: ^{13}C-NMR, DEPT-Q, $CDCl_3$



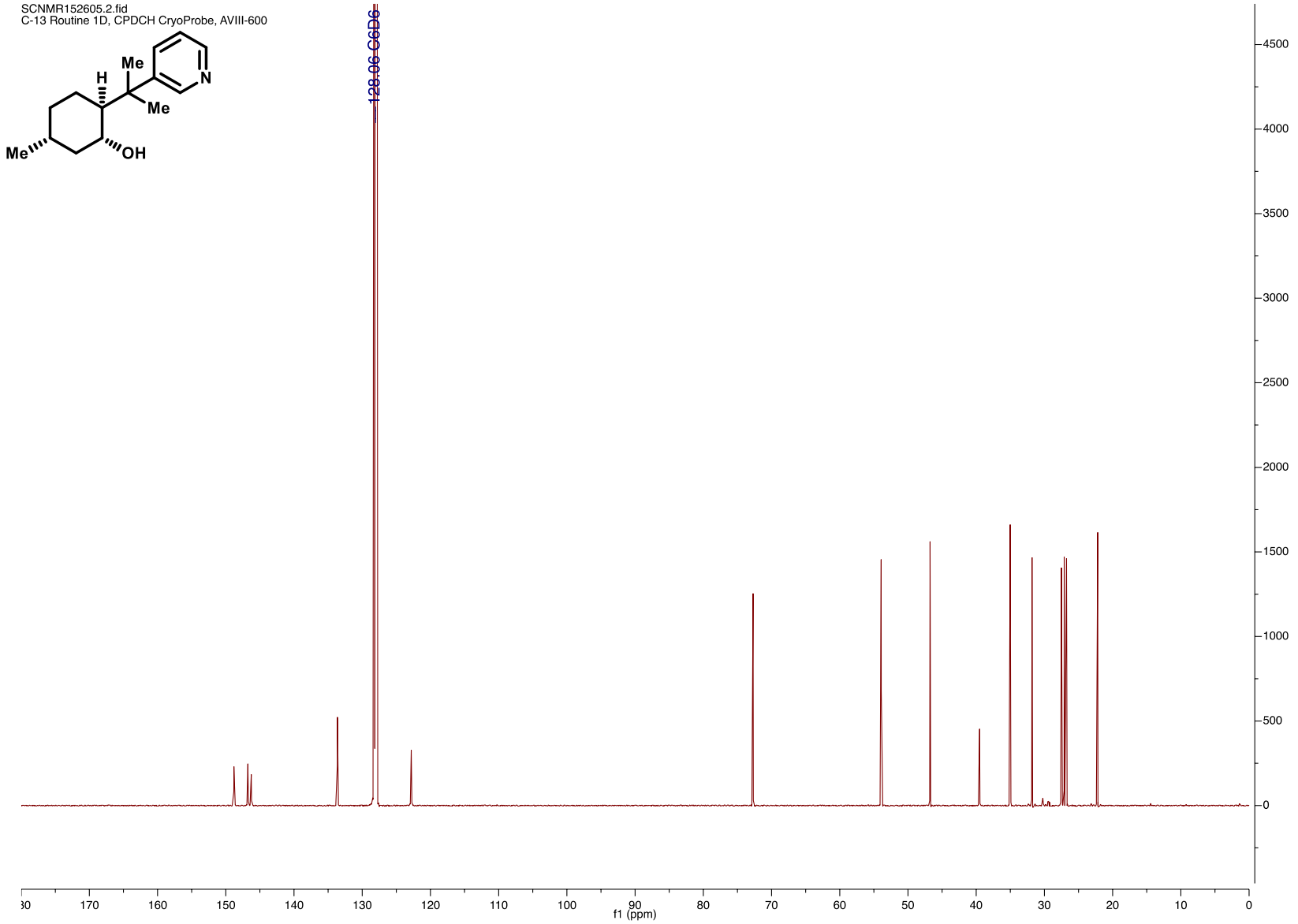

SCNMR152603 3-pyridyl pure.2.fid
C-13 DEPTQ (APT) 1D, CPDCH CryoProbe, AVIII-600
148.01
146.64
133.71
123.00
77.37
77.16 CDCl3
76.95
73.04
54.06
46.34
39.28
34.83
31.75
27.31
26.77
26.09
22.05
Me
H
Me
N
Me
OH
f1 (ppm)

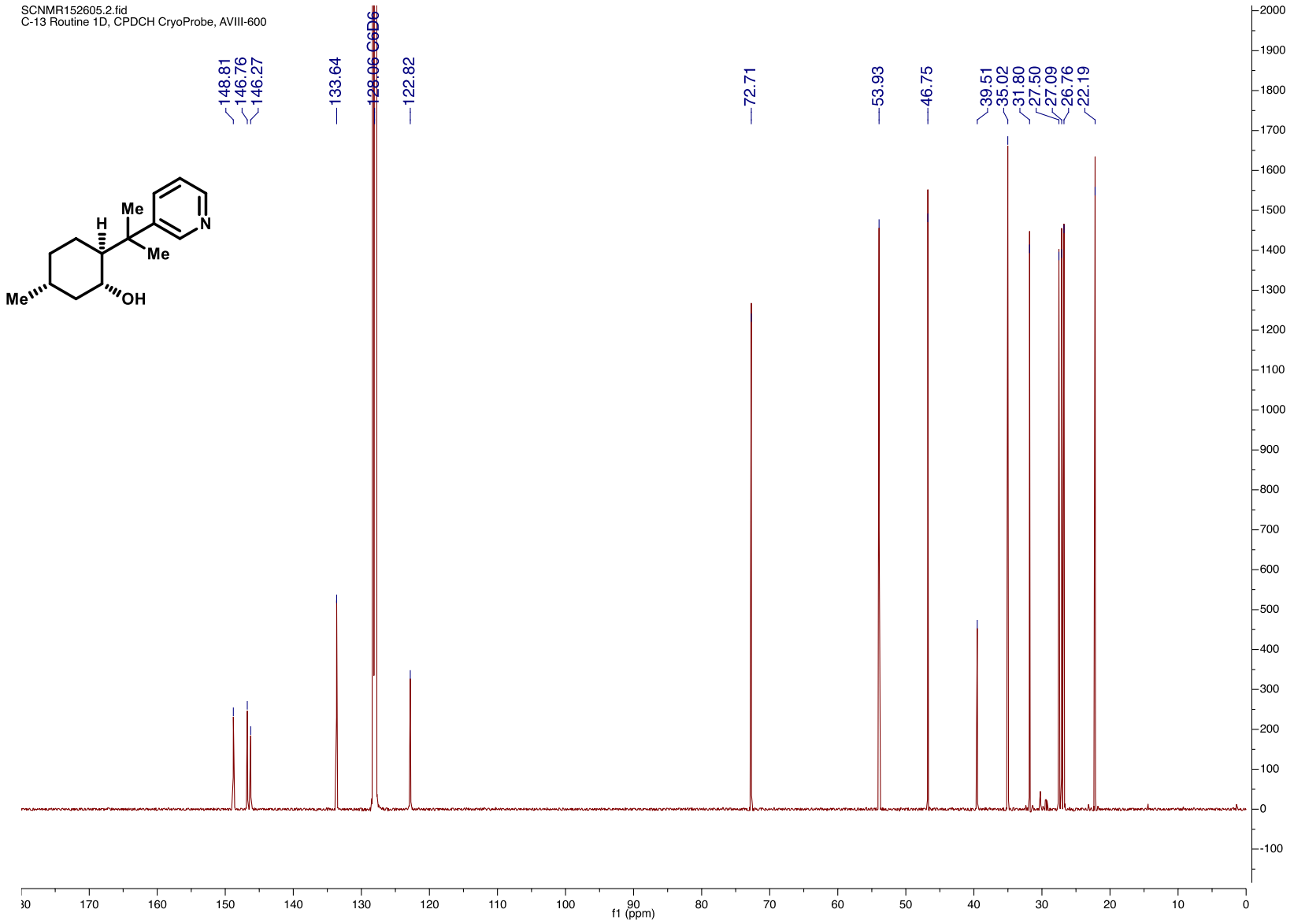
11: ^{1}H-NMR, C_6D_6



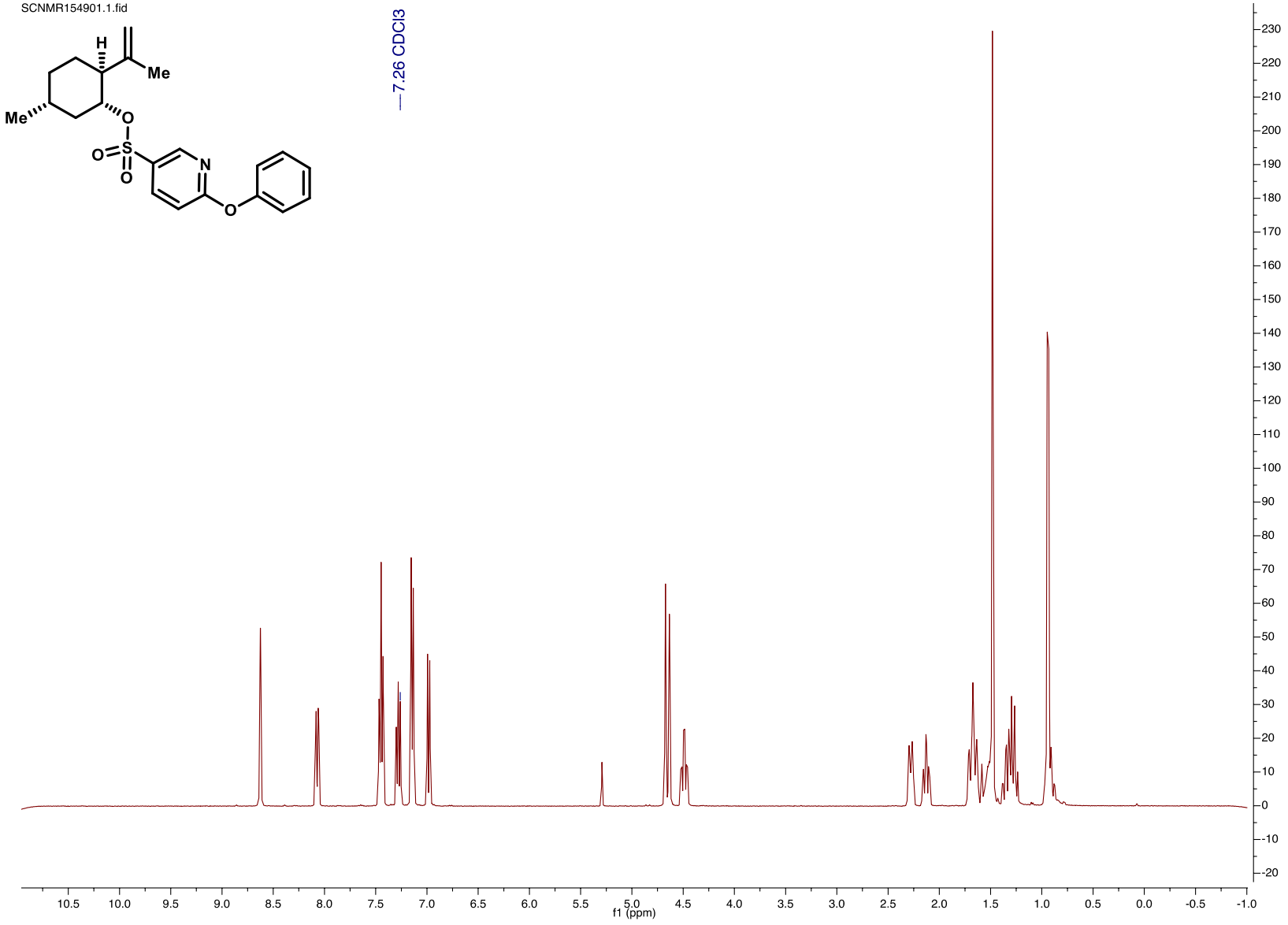

SCNMR152605-1.fid
Me
H
Me
N
Me
OH
1.00
1.01
1.02
1.04
1.03
1.25
1.14
9.97
1.19
1.23
3.06
2.13
f1 (ppm)

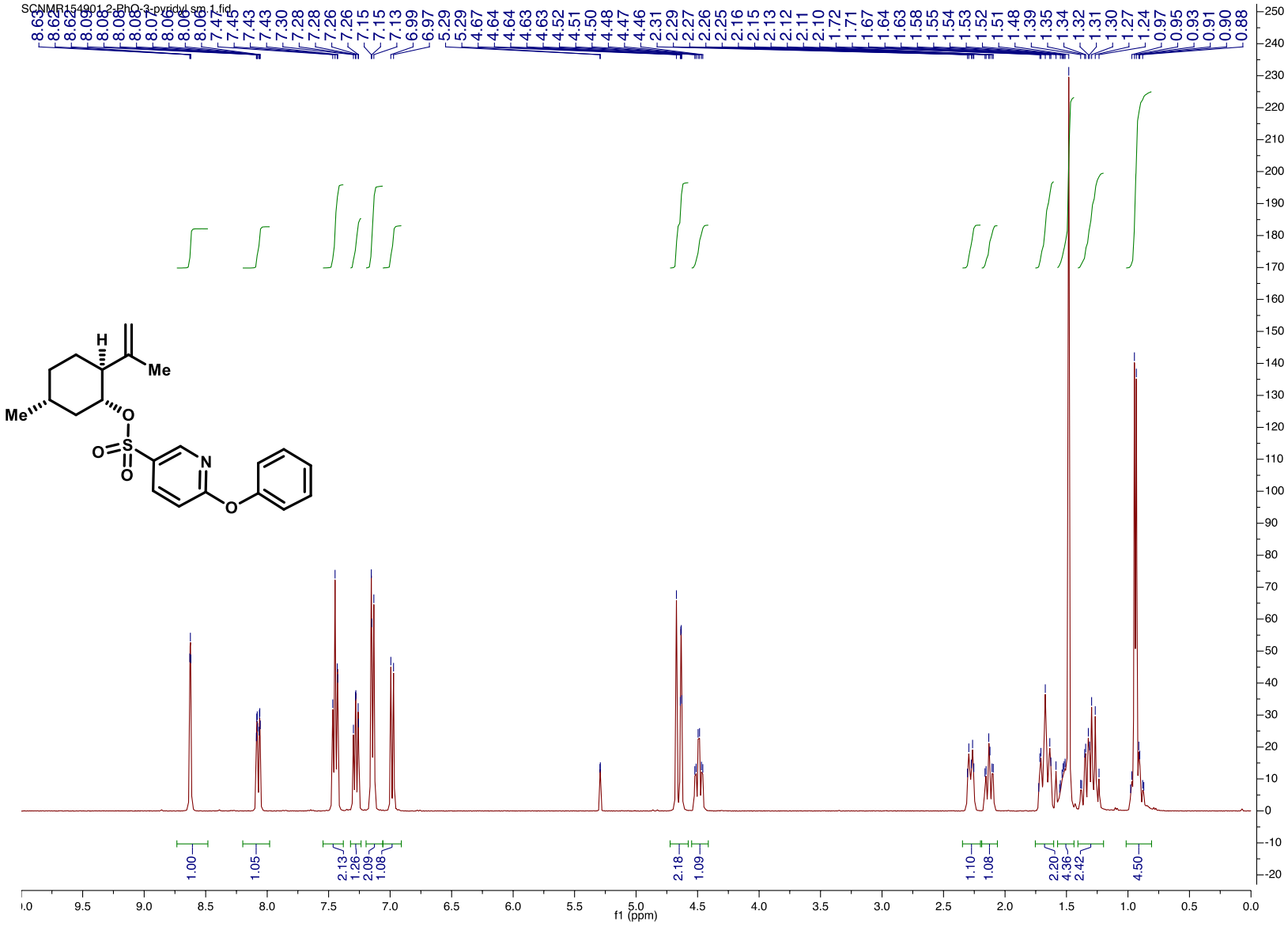
11: ^{13}C-NMR, C_6D_6



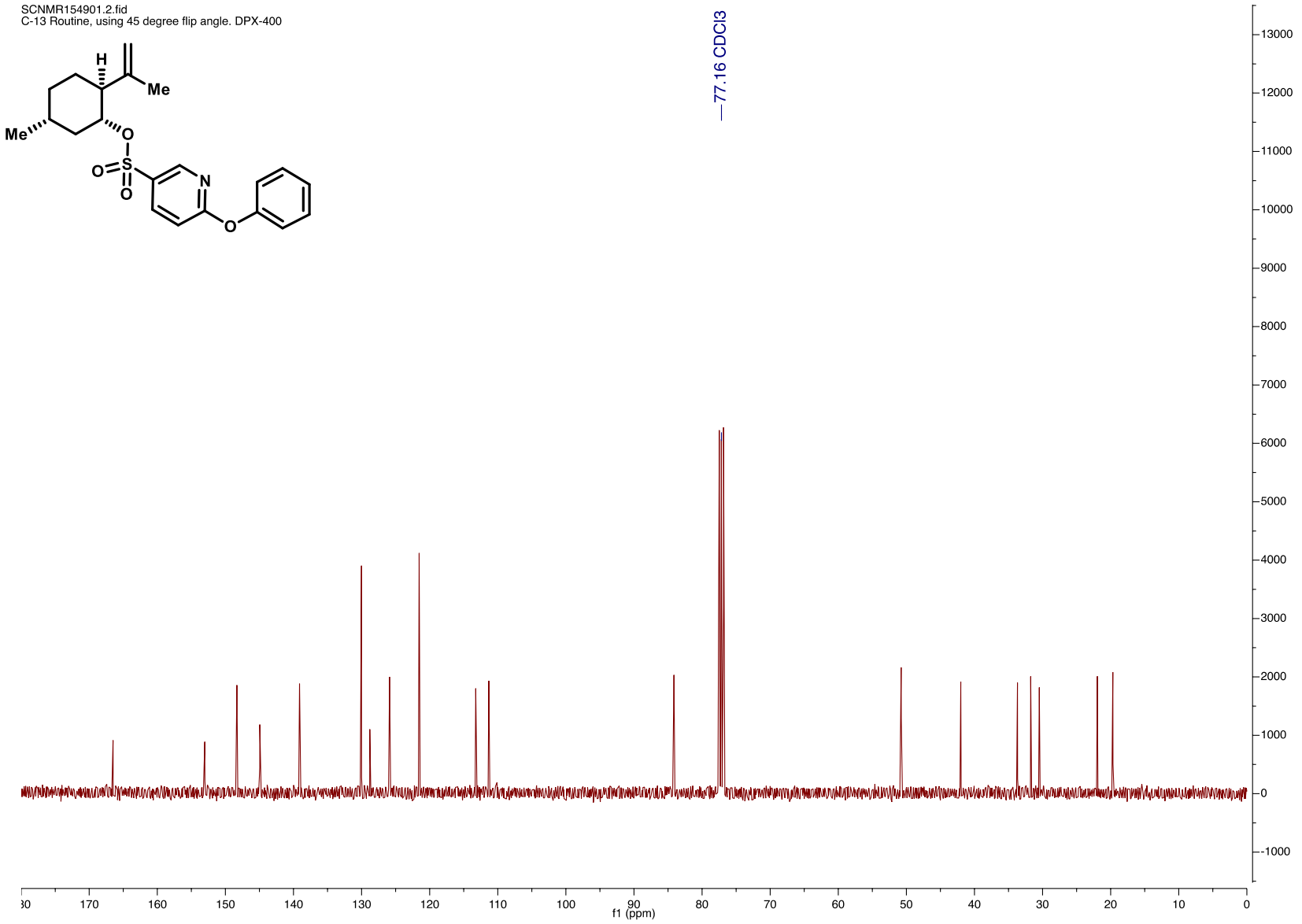

SCNMR152605.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
148.81
146.76
146.27
133.64
129.06 C6D6
122.82
72.71
53.93
46.75
39.51
35.02
31.80
27.50
27.09
26.76
22.19
Me
H
Me
N
Me
Me
OH
f1 (ppm)

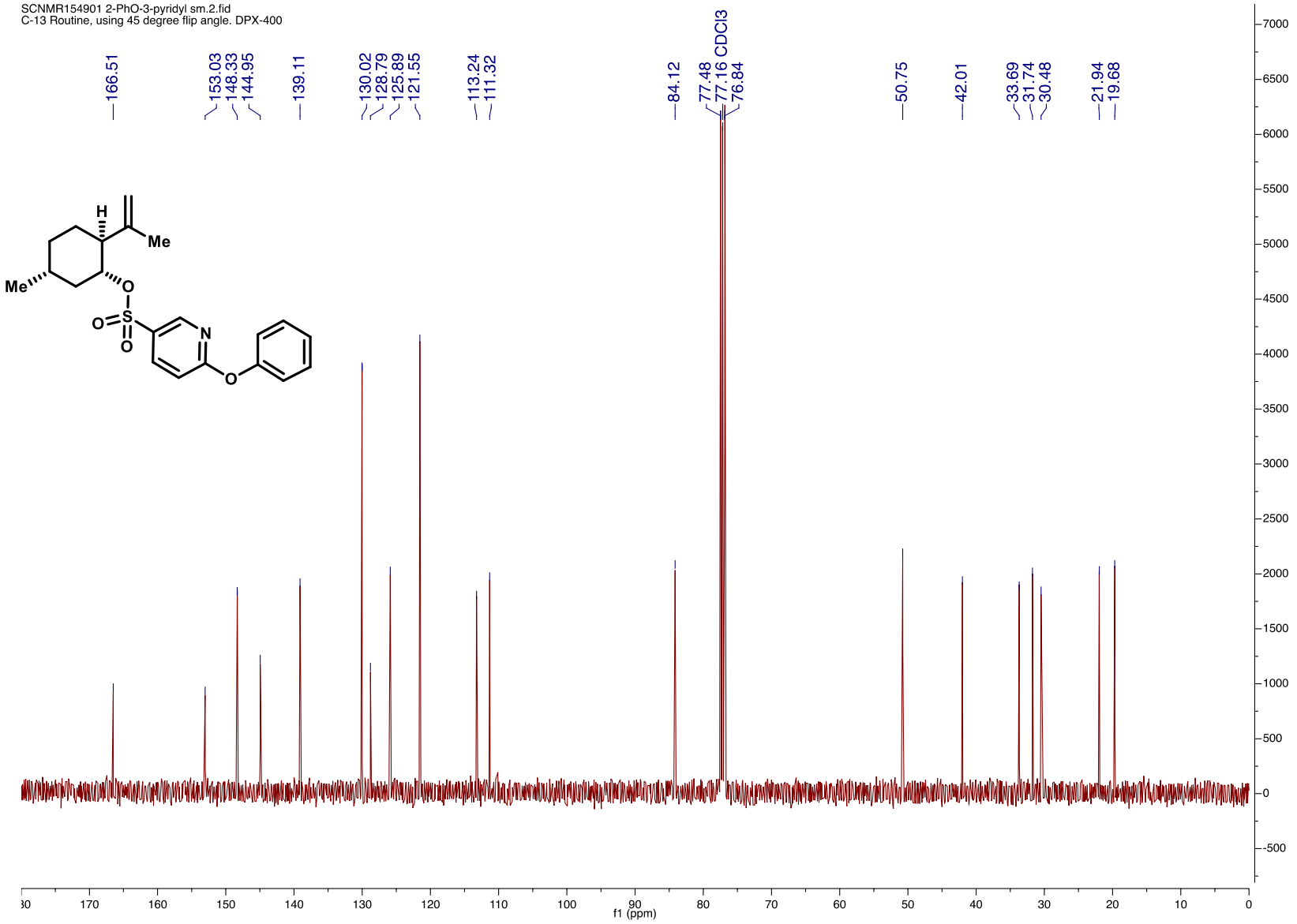
SI-14: ^{1}H-NMR


SCNMR154901.1.fid
7.26 CDCl3
H
Me
Me
O
O
S
O
O
N
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
10.5
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)

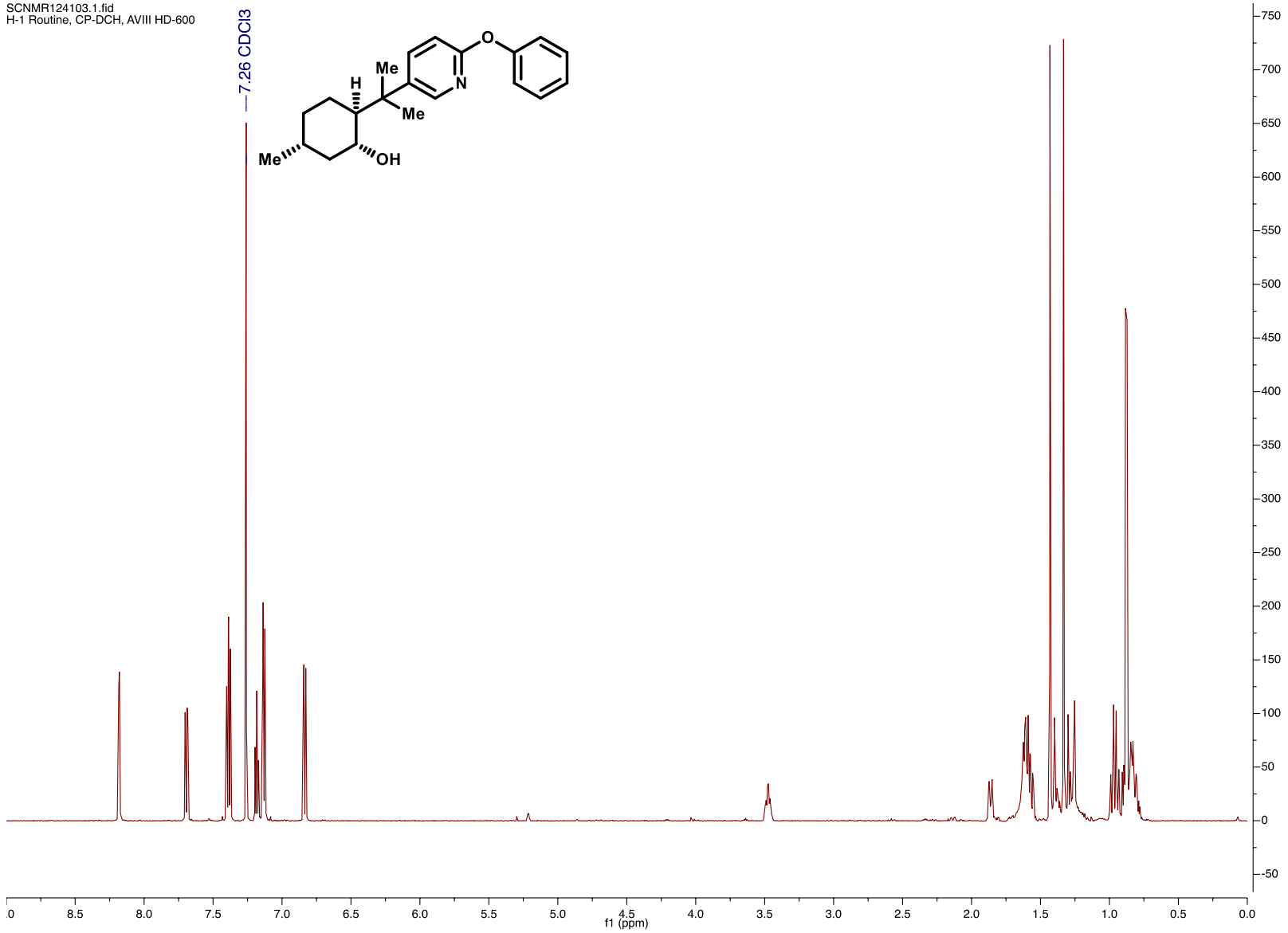

SCNMR154901-2-PhO-3-pyridyl-sm-1.fid
8.63 8.63 8.62 8.62 8.09 8.08 8.08 8.08 8.08 8.07 8.07 8.06 8.06 8.06 8.06 8.06 7.47 7.45 7.43 7.43 7.30 7.28 7.28 7.26 7.26 7.15 7.15 7.13 6.99 6.97
5.29 5.29 4.67 4.64 4.64 4.63 4.63 4.52 4.51 4.50 4.48 4.47 4.46 2.31 2.29 2.27 2.26 2.25 2.16 2.15 2.13 2.12 2.11 2.10 1.72 1.71 1.67 1.64 1.63 1.58 1.55 1.54 1.53 1.52 1.51 1.48 1.39 1.35 1.34 1.32 1.31 1.30 1.27 1.24 0.97 0.95 0.93 0.91 0.90 0.88
H
Me
Me
O
O
S
O
O
N
O
1.00
1.05
2.13
1.26
2.09
1.08
2.18
1.09
1.10
1.08
2.20
4.36
2.42
4.50
f1 (ppm)

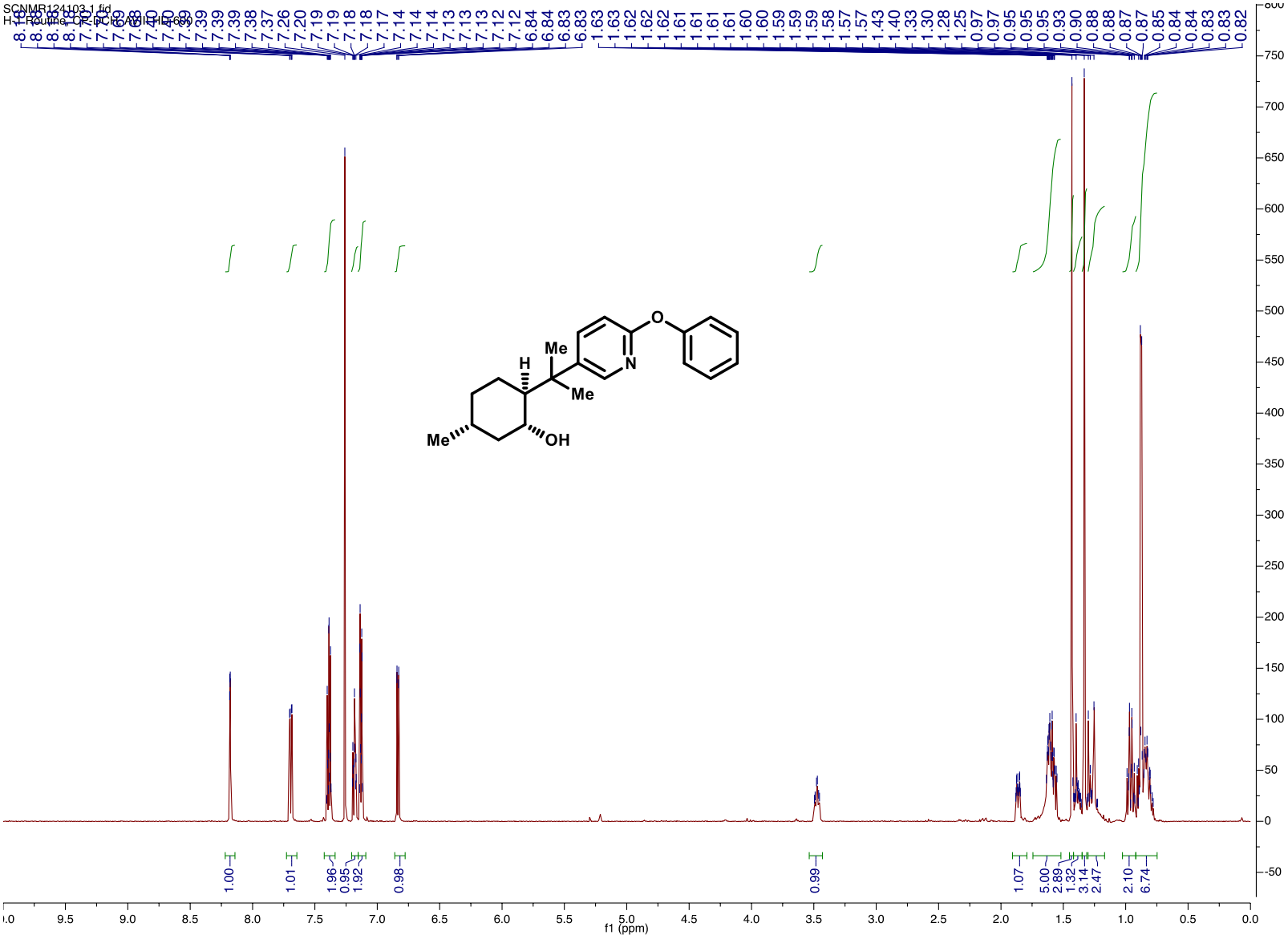
SI-14: ^{13}C-NMR


SCNMR154901.2.fid
C-13 Routine, using 45 degree flip angle. DPX-400
—77.16 CDCl3
f1 (ppm)

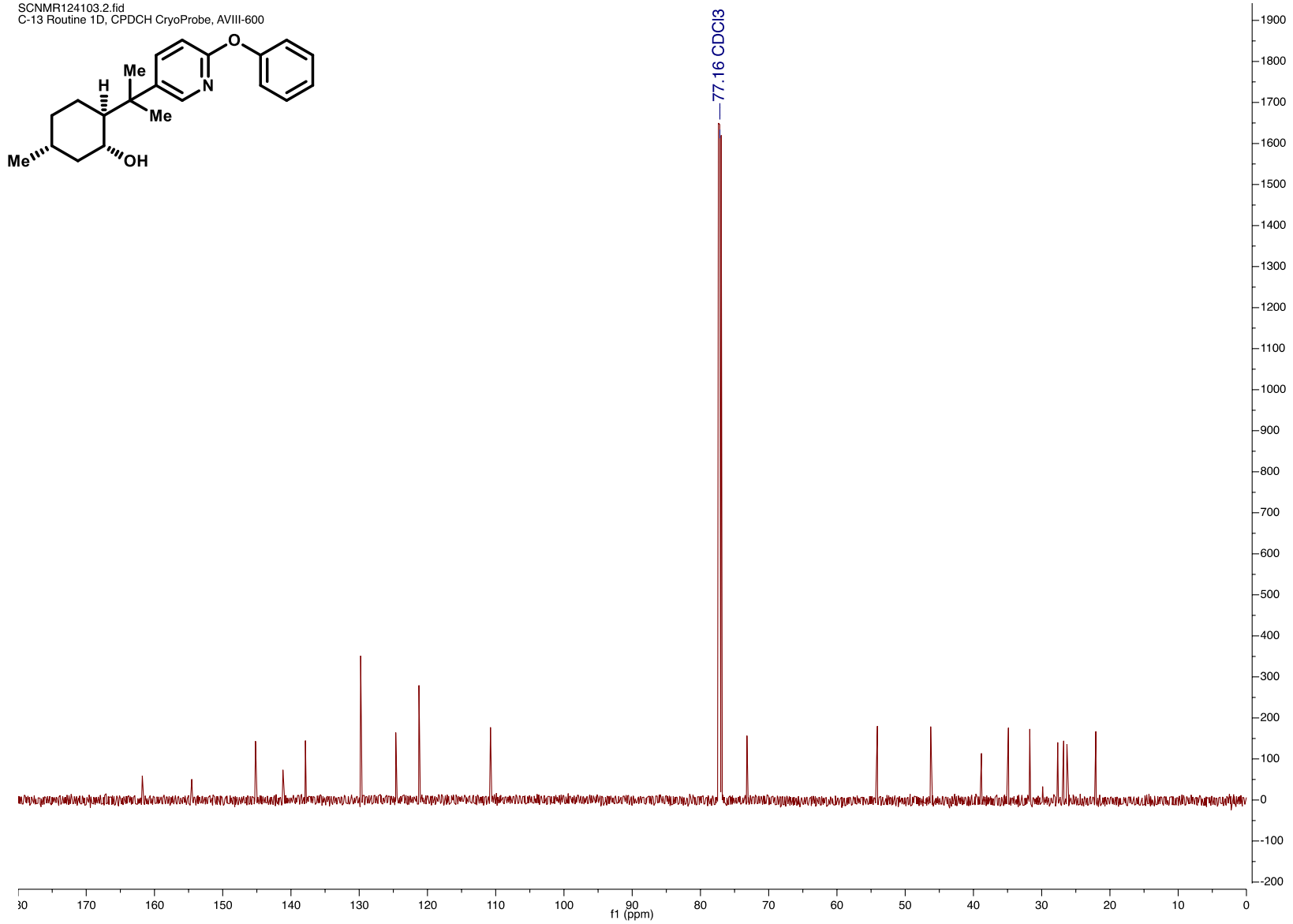

SCNMR154901 2-PhO-3-pyridyl sm.2.fid
C-13 Routine, using 45 degree flip angle. DPX-400
166.51
153.03
148.33
144.95
139.11
130.02
128.79
125.89
121.55
113.24
111.32
84.12
77.48
77.16 CDCl3
76.84
50.75
42.01
33.69
31.74
30.48
21.94
19.68
H
Me
Me
O
S
O
O
N
O
f1 (ppm)

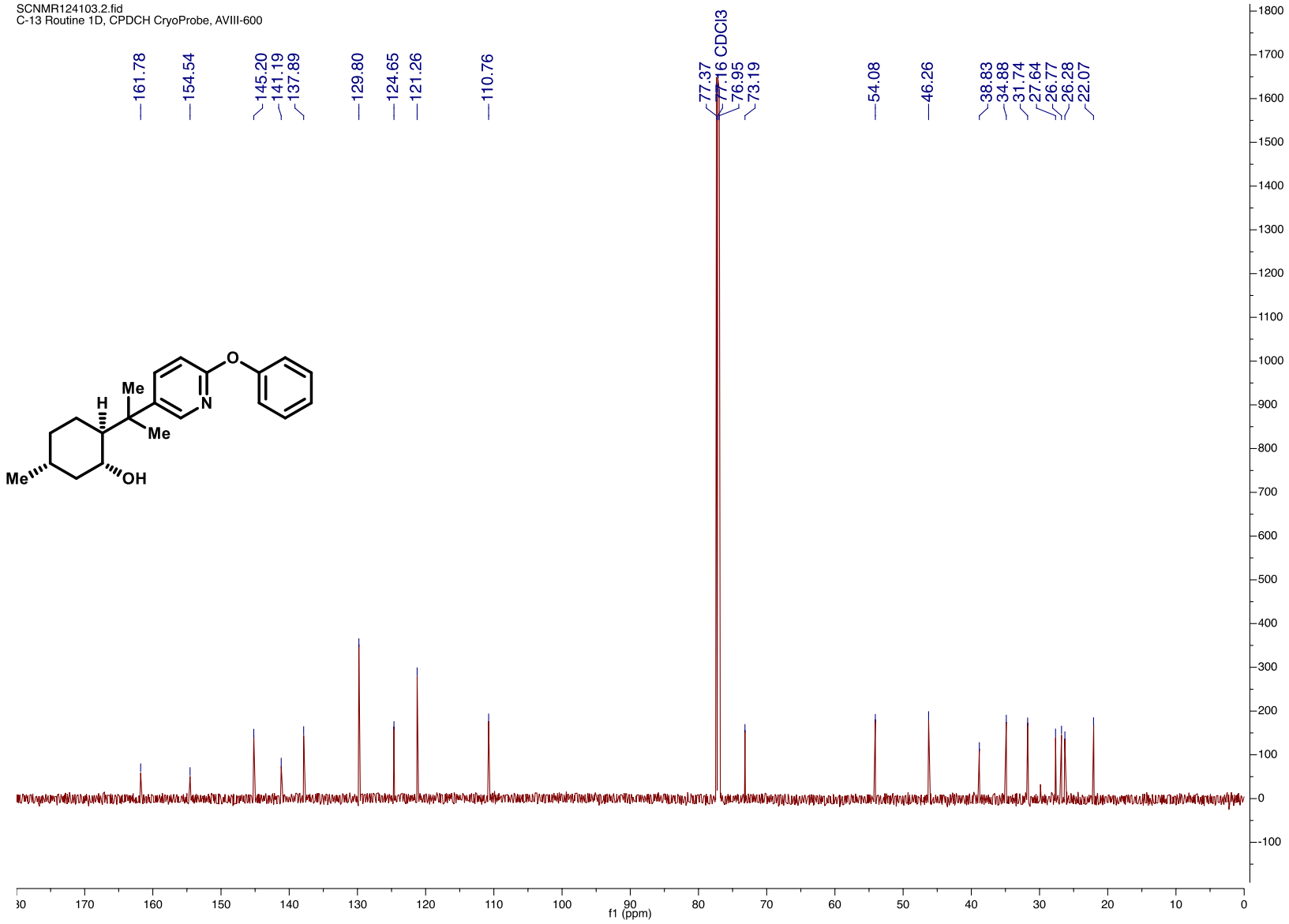
12: ^{1}H-NMR


SCNMR124103.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
H
Me
N
O
Me
OH
f1 (ppm)

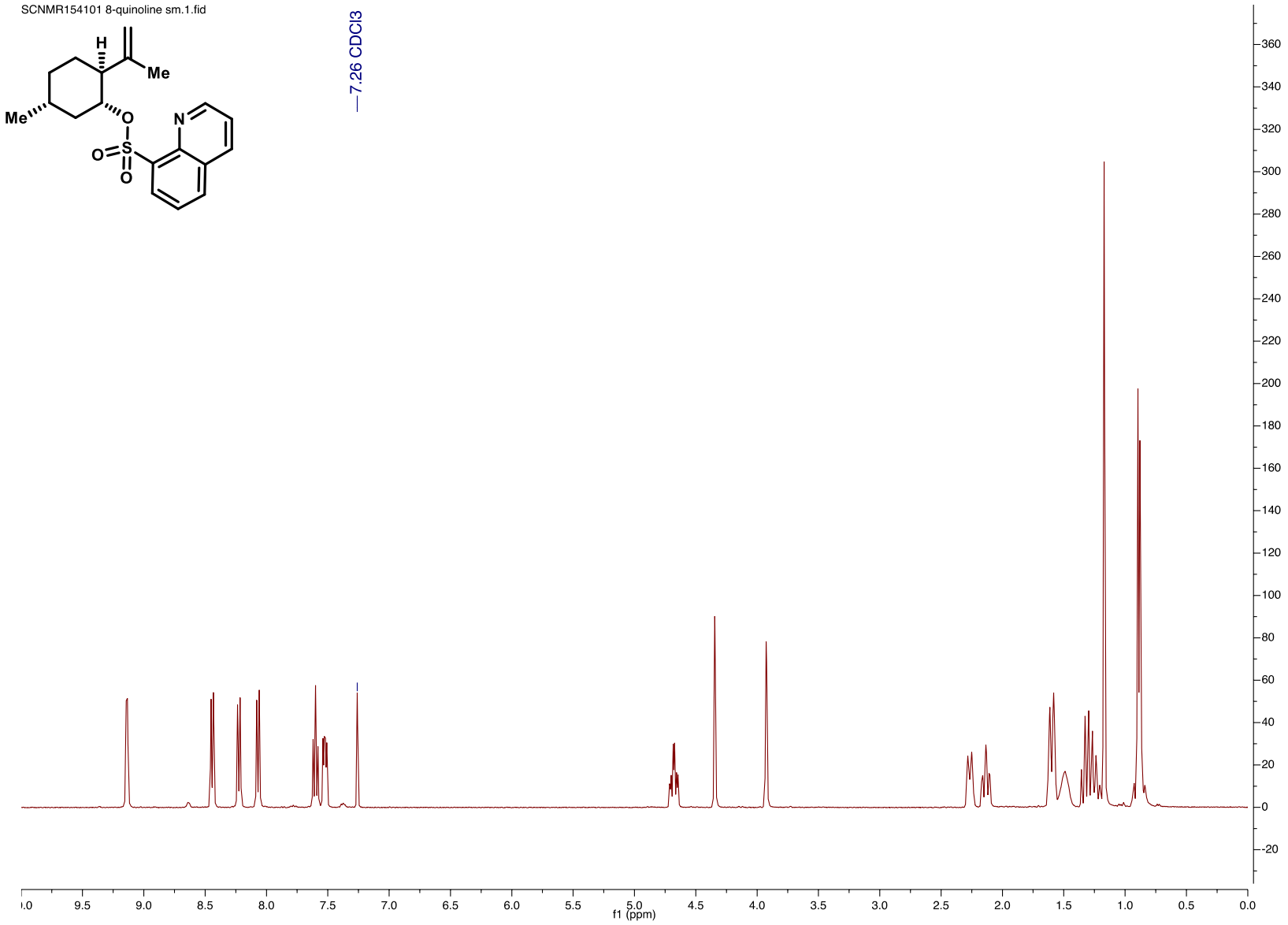

SCNMR124103-1.fid
H-1 Routine, QF-PCH-AV-HD-469
8.18 8.18 8.17 8.17 7.39 7.38 7.37 7.26 7.20 7.19 7.19 7.18 7.18 7.17 7.14 7.14 7.14 7.13 7.13 7.12 7.12 6.84 6.84 6.83 6.83 1.63 1.63 1.62 1.62 1.62 1.61 1.61 1.61 1.61 1.60 1.60 1.59 1.59 1.59 1.58 1.57 1.57 1.43 1.40 1.33 1.30 1.28 1.25 0.97 0.97 0.95 0.95 0.95 0.93 0.90 0.88 0.88 0.87 0.87 0.85 0.84 0.84 0.83 0.83 0.82
O
N
H
Me
Me
Me
OH
1.00
1.01
1.96
0.95
1.92
0.98
0.99
1.07
5.00
2.89
1.32
3.14
2.47
2.10
6.74
f1 (ppm)

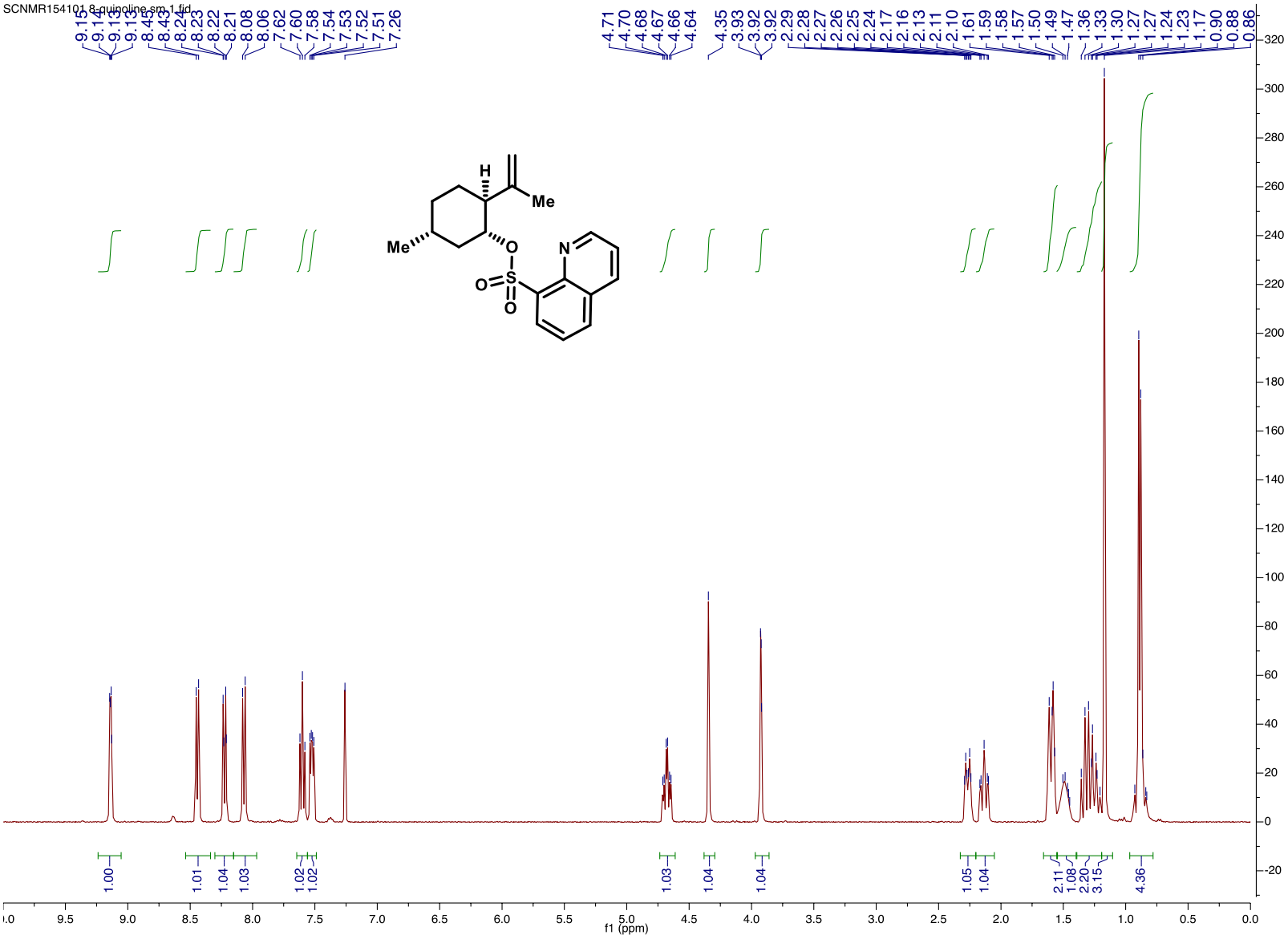
12: ^{13}C-NMR


SCNMR124103.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
77.16 CDCl3
f1 (ppm)

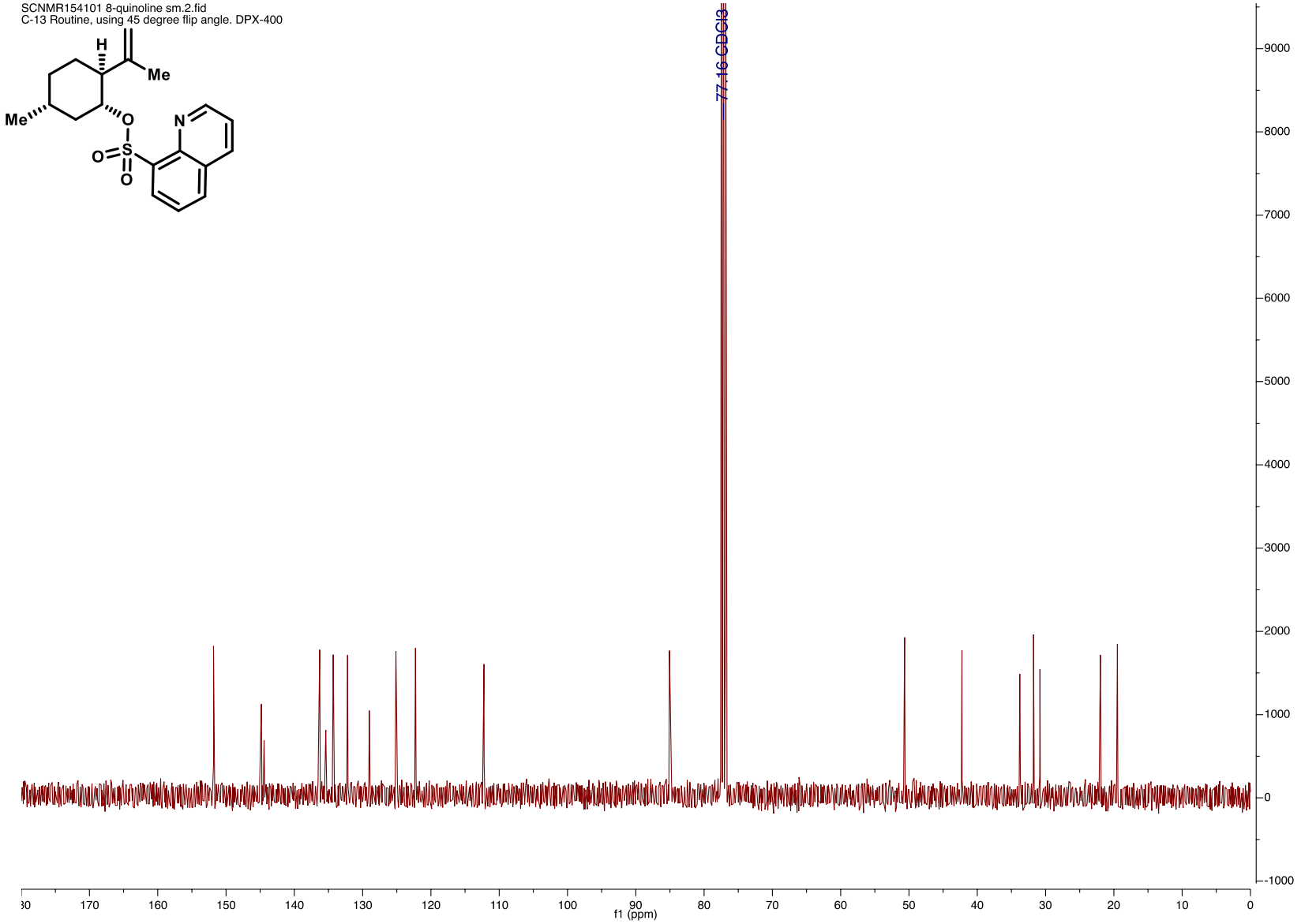

SCNMR124103.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
161.78
154.54
145.20
141.19
137.89
129.80
124.65
121.26
110.76
77.37
77.16 CDCl3
76.95
73.19
54.08
46.26
38.83
34.88
31.74
27.64
26.77
26.28
22.07
Me
H
Me
Me
OH
O
N
f1 (ppm)

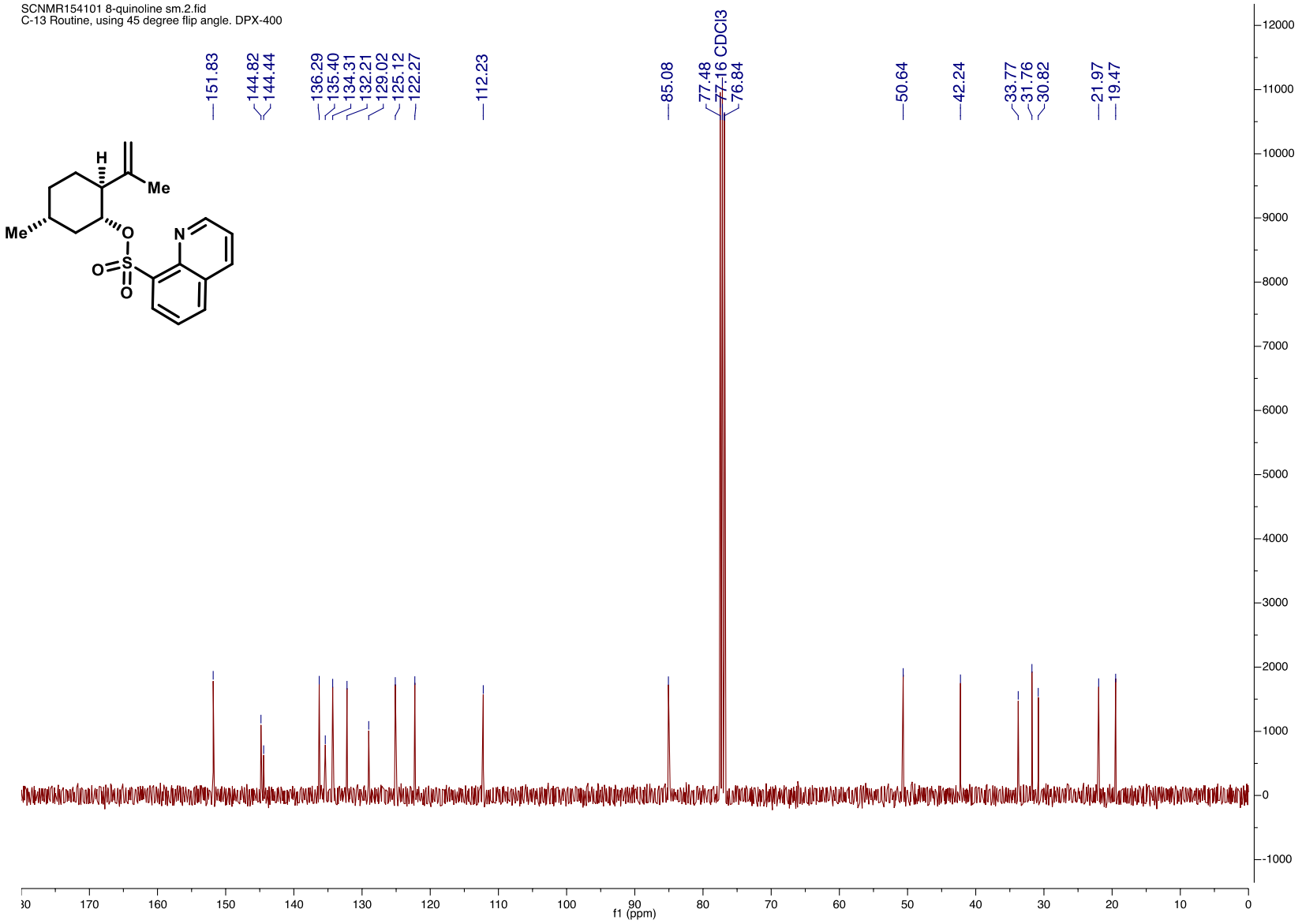
SI-15: ^{1}H-NMR


SCNMR154101 8-quinoline sm.1.fid
7.26 CDCl3
H
Me
Me
O
N
O
S
O
O
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
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
f1 (ppm)

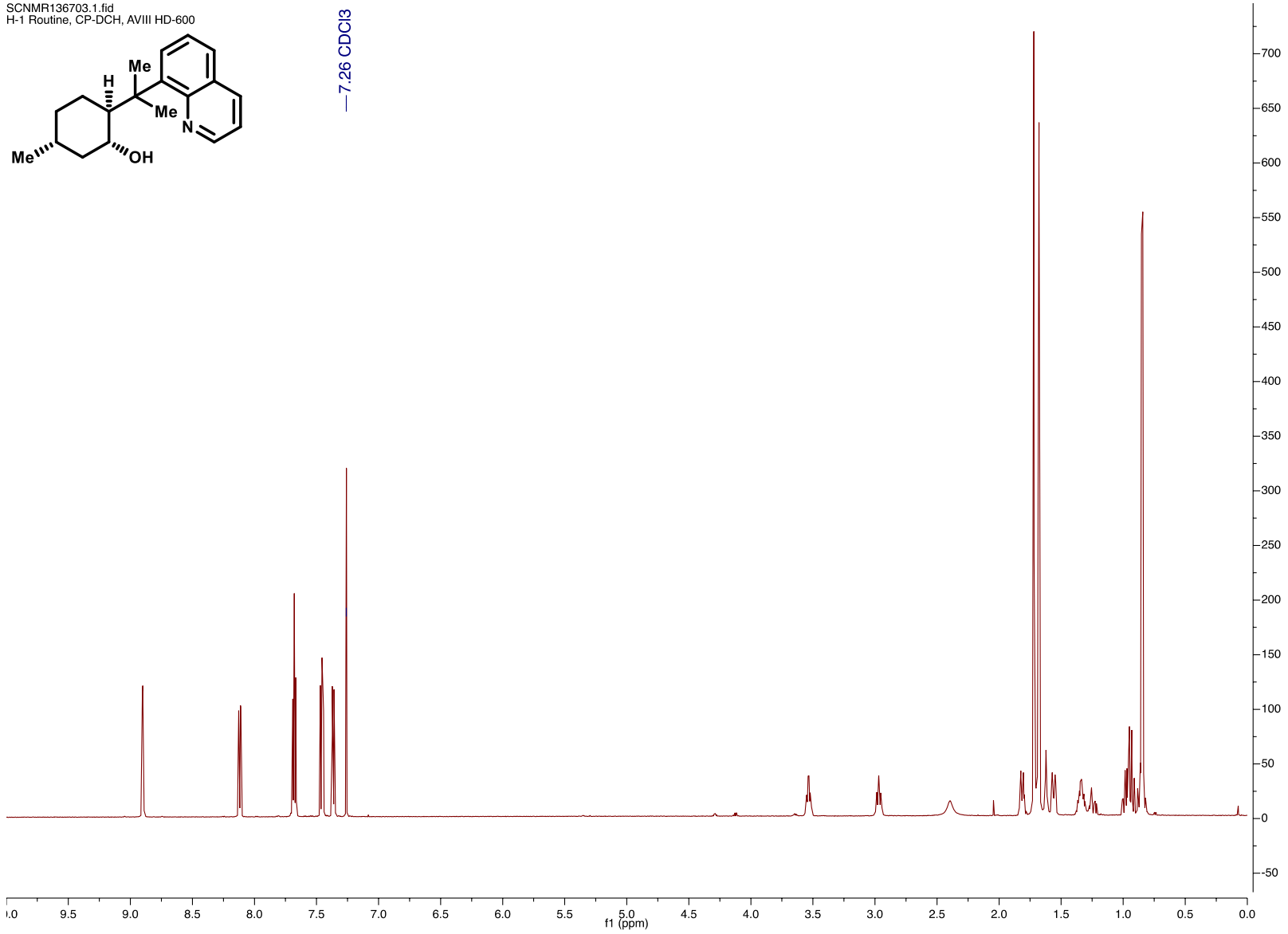

SCNMR154101 8-quinoline.sm.1.fid
9.15
9.14
9.13
8.45
8.44
8.24
8.23
8.22
8.21
8.08
8.06
7.62
7.60
7.58
7.54
7.53
7.52
7.51
7.26
4.71
4.70
4.68
4.67
4.66
4.64
4.35
3.93
3.92
3.92
2.29
2.28
2.27
2.26
2.25
2.24
2.17
2.16
2.13
2.11
2.10
1.61
1.59
1.58
1.57
1.50
1.49
1.47
1.36
1.33
1.30
1.27
1.27
1.24
1.23
1.17
0.90
0.88
0.86
H
Me
Me
O
N
O
S
O
O
1.00
1.01
1.04
1.03
1.02
1.02
1.03
1.04
1.04
1.05
1.04
2.11
1.08
2.20
3.15
4.36
f1 (ppm)

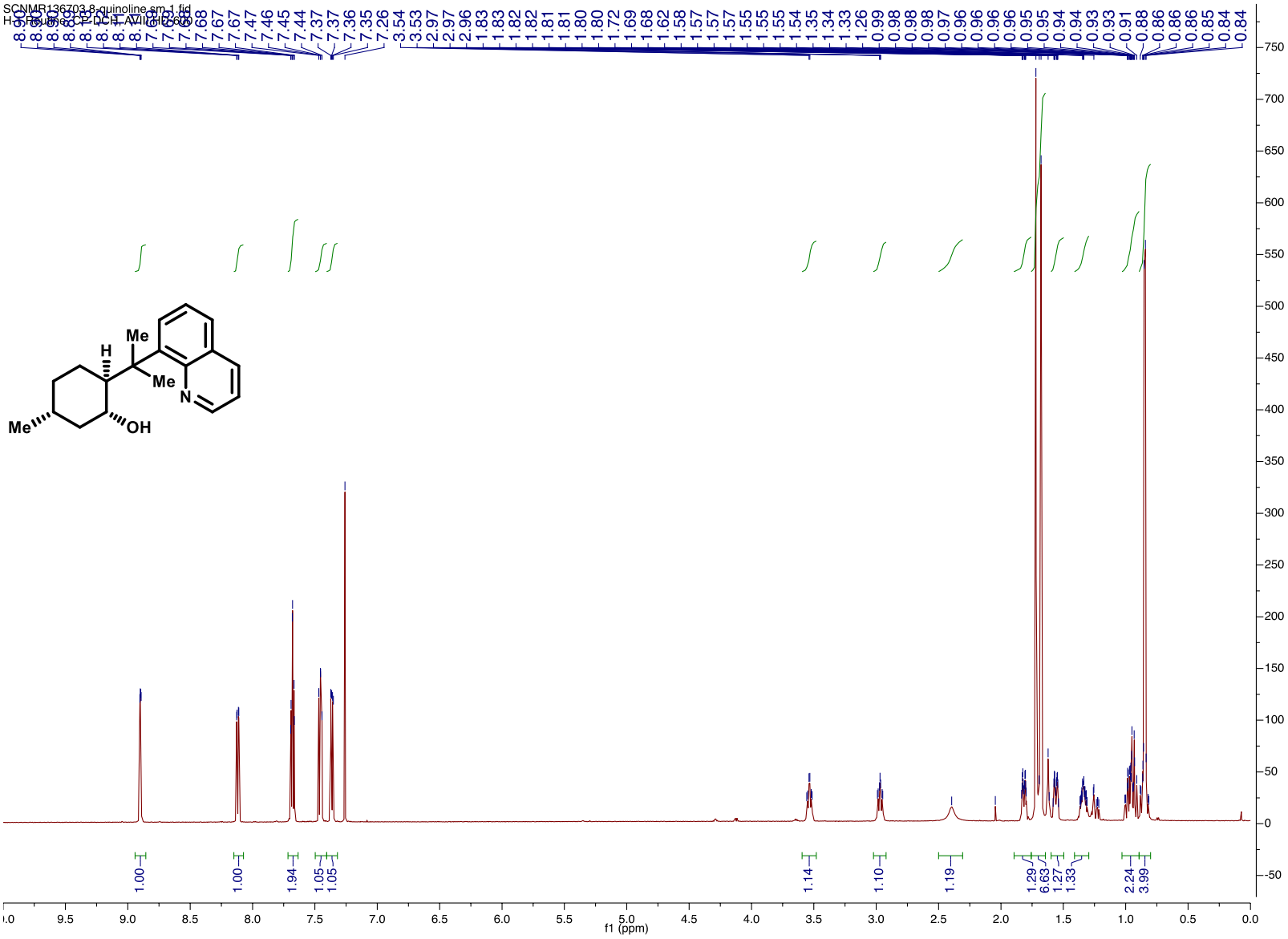
SI-15: ^{13}C-NMR


SCNMR154101 8-quinoline sm.2.fid
C-13 Routine, using 45 degree flip angle. DPX-400
H
Me
Me
O
N
O
S
O
O
77.16 CDCl3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

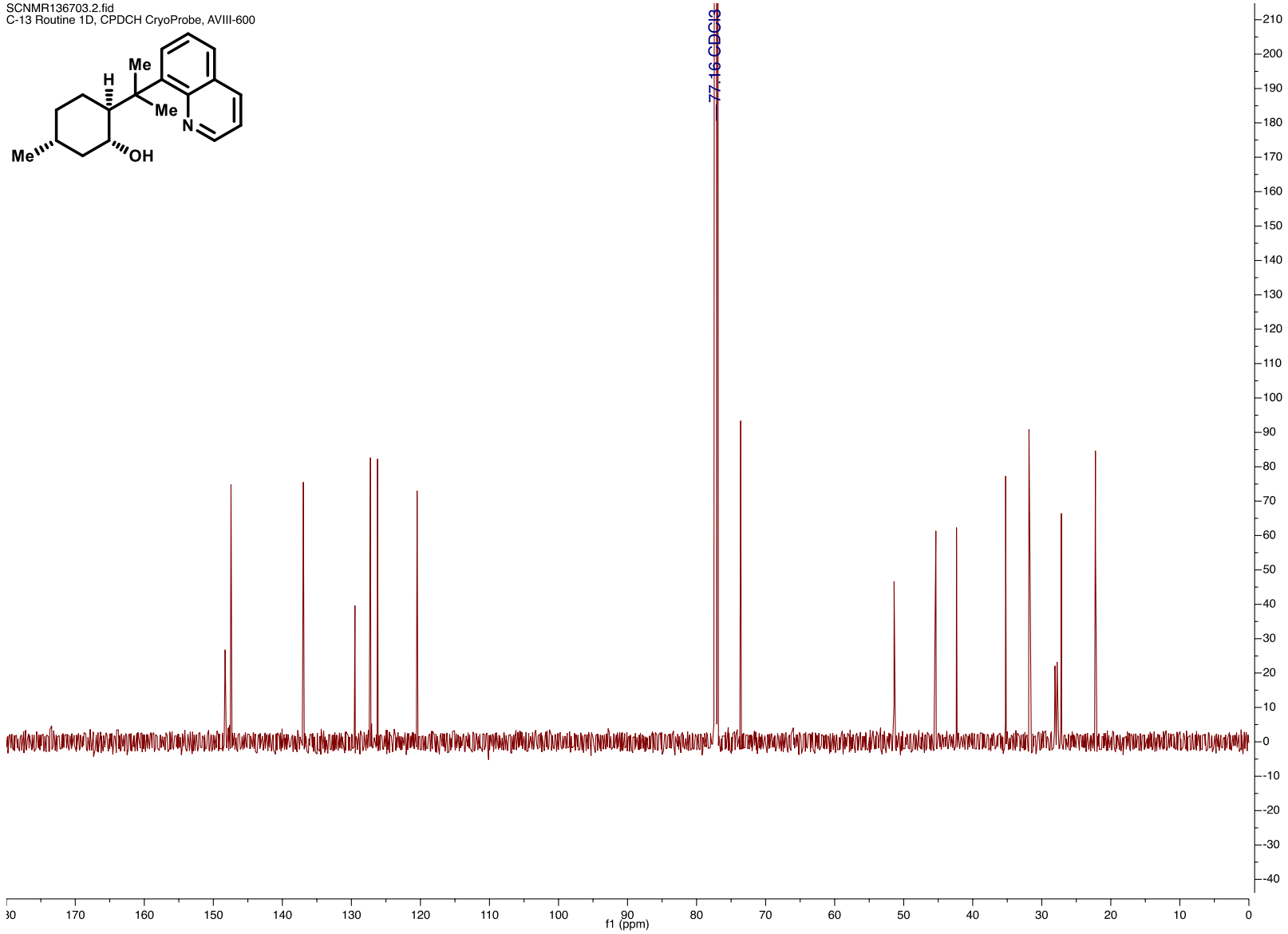

SCNMR154101 8-quinoline sm.2.fid
C-13 Routine, using 45 degree flip angle. DPX-400
151.83
144.82
144.44
136.29
135.40
134.31
132.21
129.02
125.12
122.27
112.23
85.08
77.48
77.16 CDCl3
76.84
50.64
42.24
33.77
31.76
30.82
21.97
19.47
H
Me
Me
O
N
O
S
O
O
f1 (ppm)

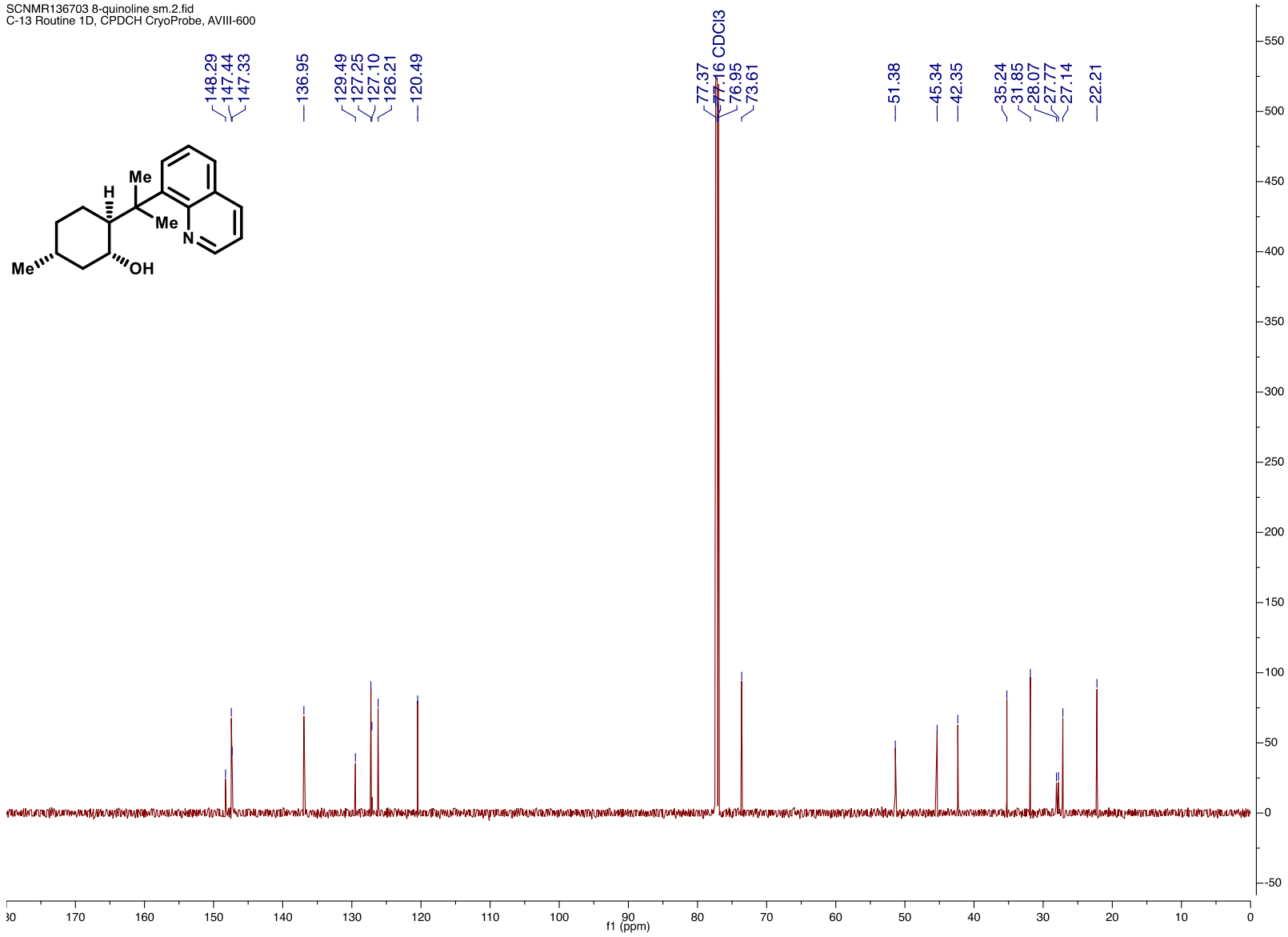
13: ^{1}H-NMR


SCNMR136703.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
Me
H
Me
Me
N
Me
OH
f1 (ppm)

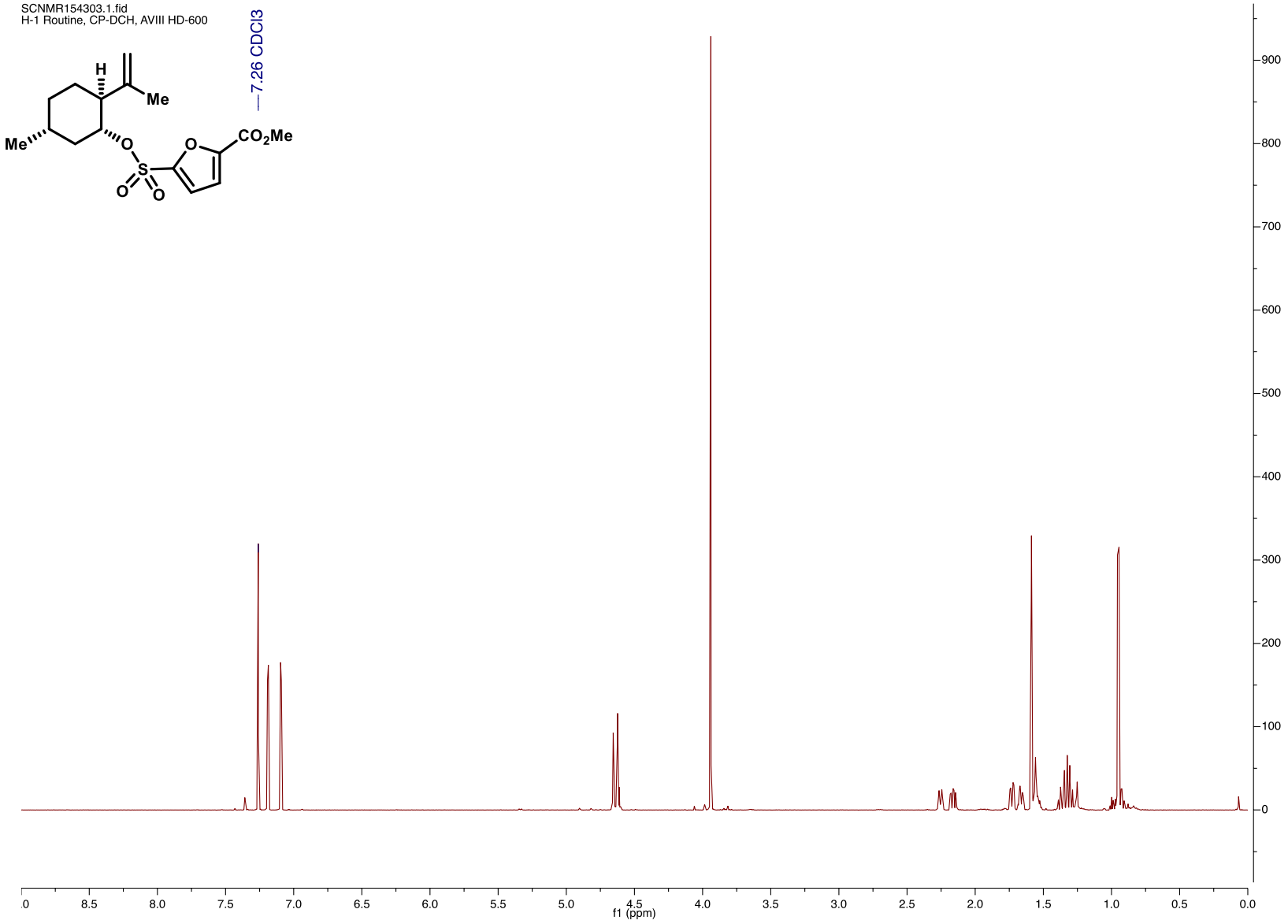

SCNMR136703.8-quinoline sm 1.fid
H_CHLOROFORM-D1_AV III HD 600
Me
H
Me
Me
N
Me
OH
f1 (ppm)

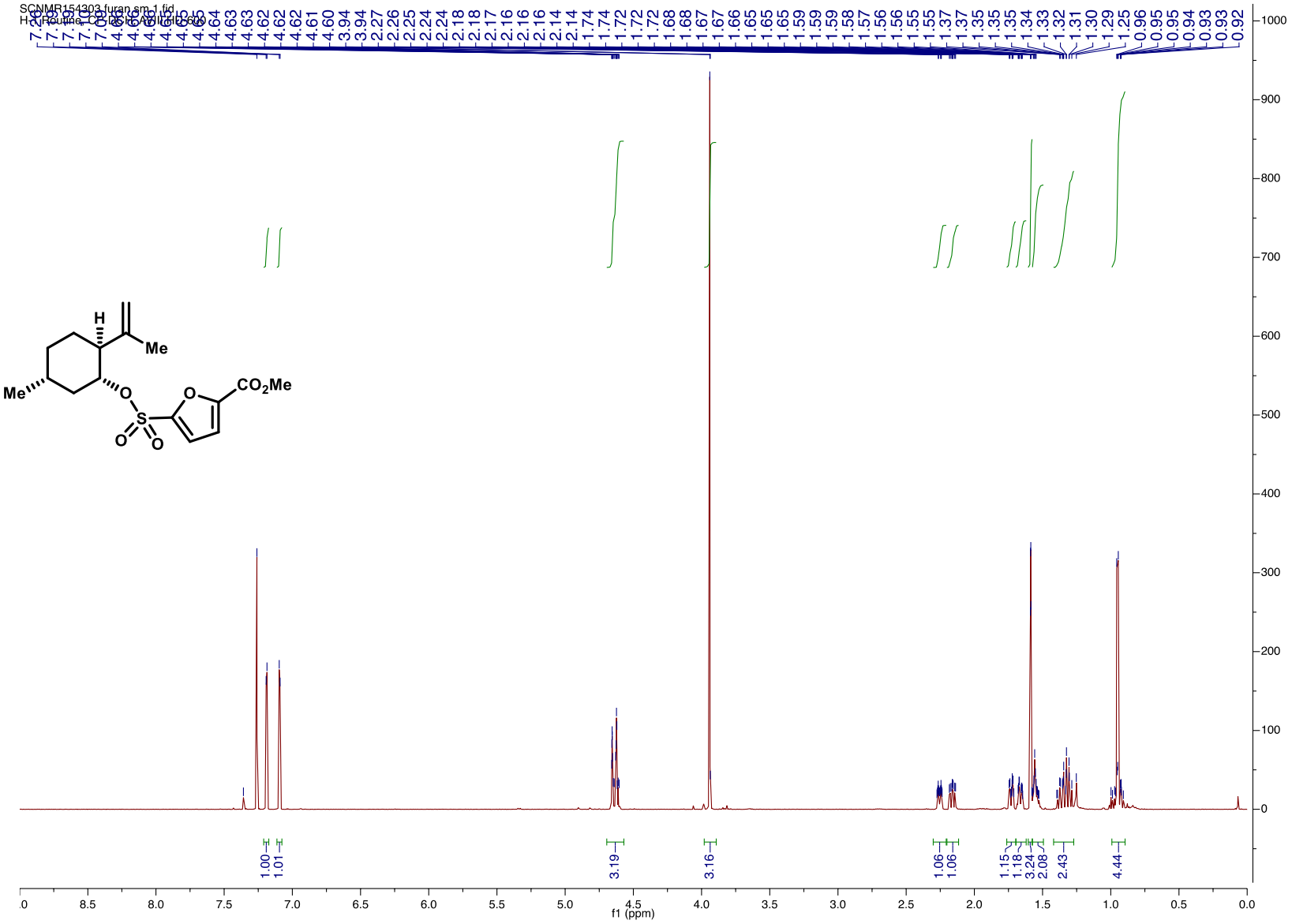
13: ^{13}C-NMR


SCNMR136703.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
H
Me
Me
N
OH
77.16 CDCl3
f1 (ppm)

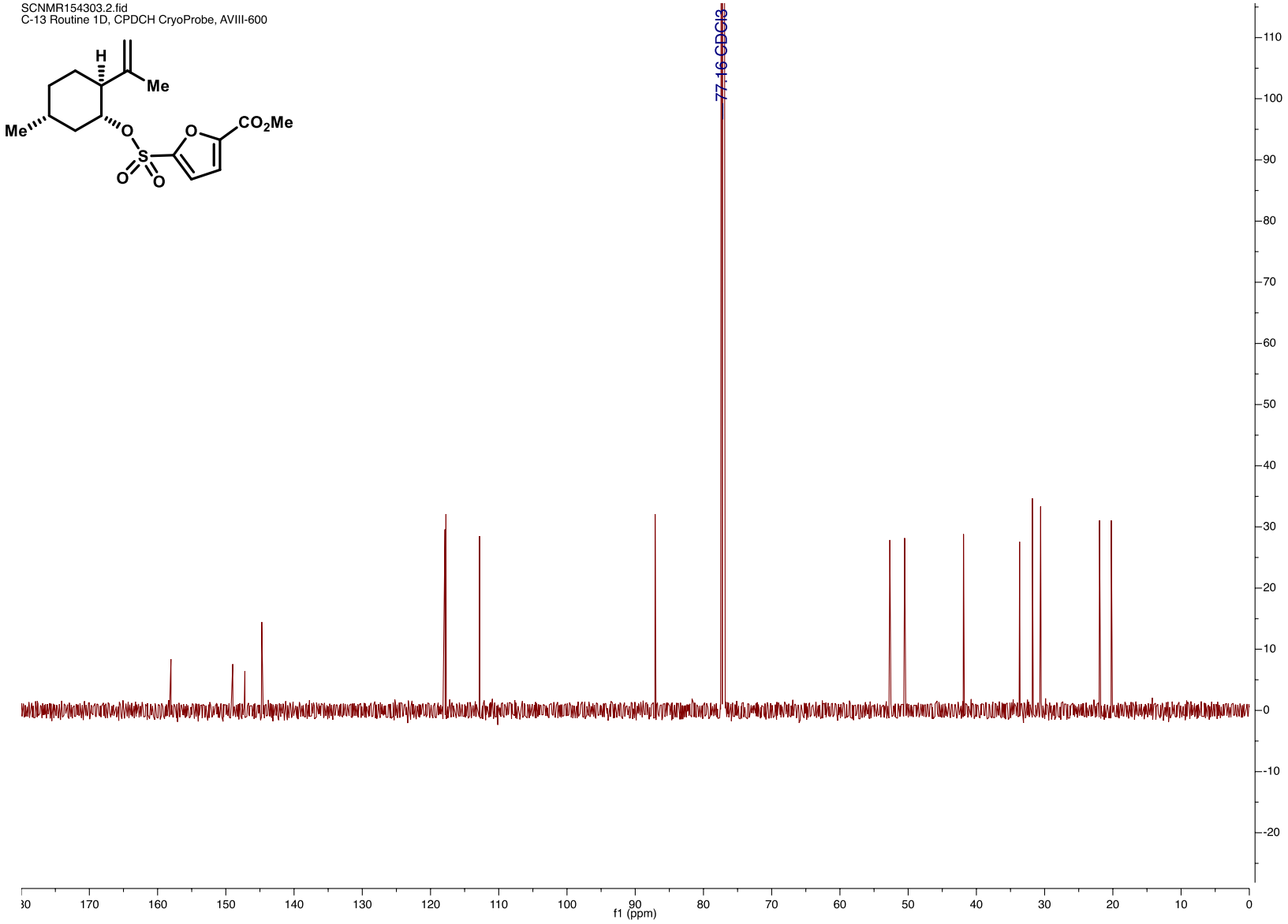

SCNMR136703 8-quinoline sm.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
148.29
147.44
147.33
136.95
129.49
127.25
127.10
126.21
120.49
77.37
77.16 CDCl3
76.95
73.61
51.38
45.34
42.35
35.24
31.85
28.07
27.77
27.14
22.21
Me
H
Me
Me
N
Me
OH
f1 (ppm)

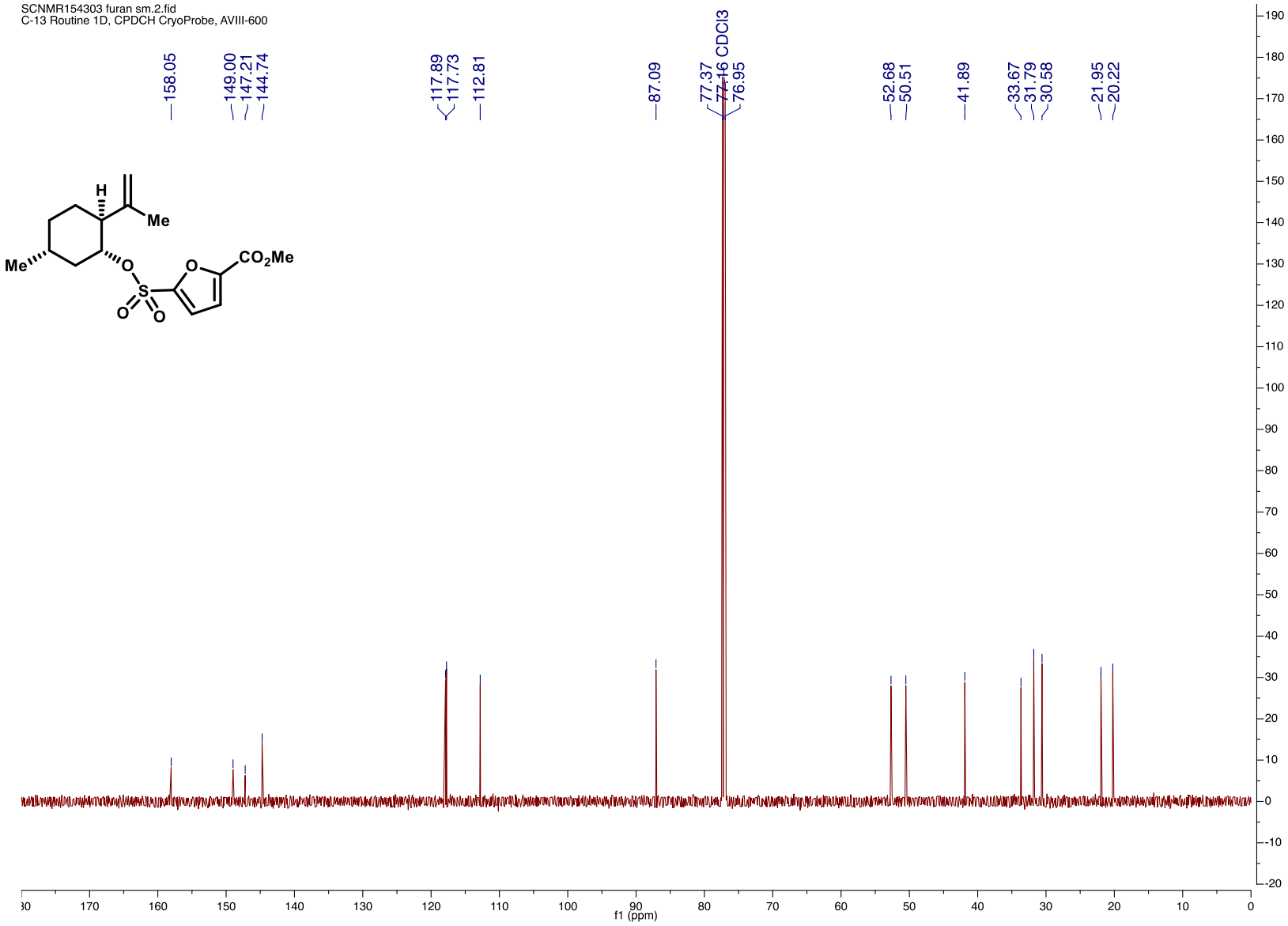
SI-16: ^{1}H-NMR


SCNMR154303.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
H
Me
Me
O
S
O
O
O
CO2Me
900
800
700
600
500
400
300
200
100
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
f1 (ppm)

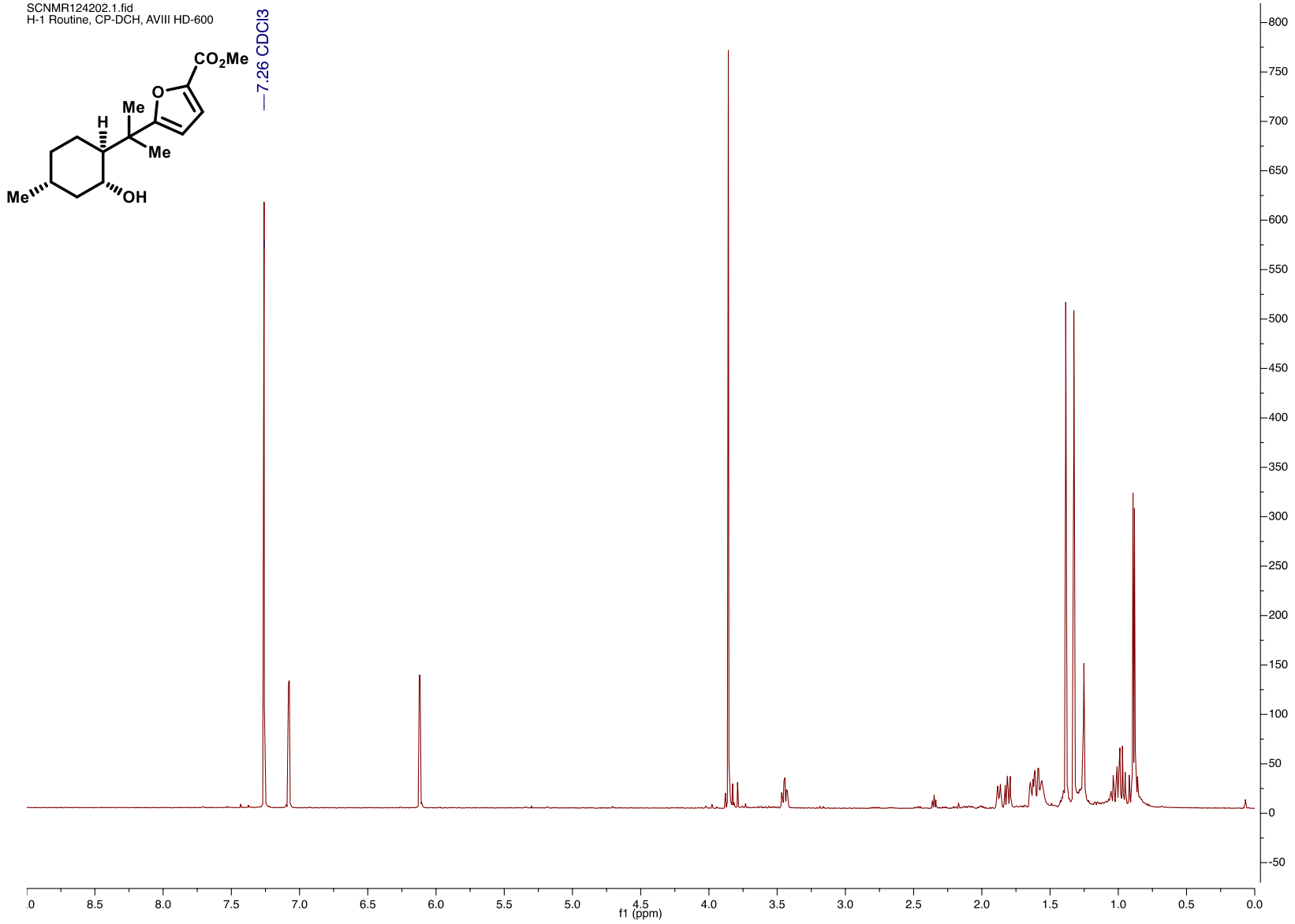

SCNMR154303-furan-sm-1.fid
H-1 Routine, CDCl3 (Acquisition Time 2.60
H
Me
Me
O
S
O
O
O
O
CO2Me
1.00
1.01
3.19
3.16
1.06
1.06
1.15
1.18
3.24
2.08
2.43
4.44
f1 (ppm)

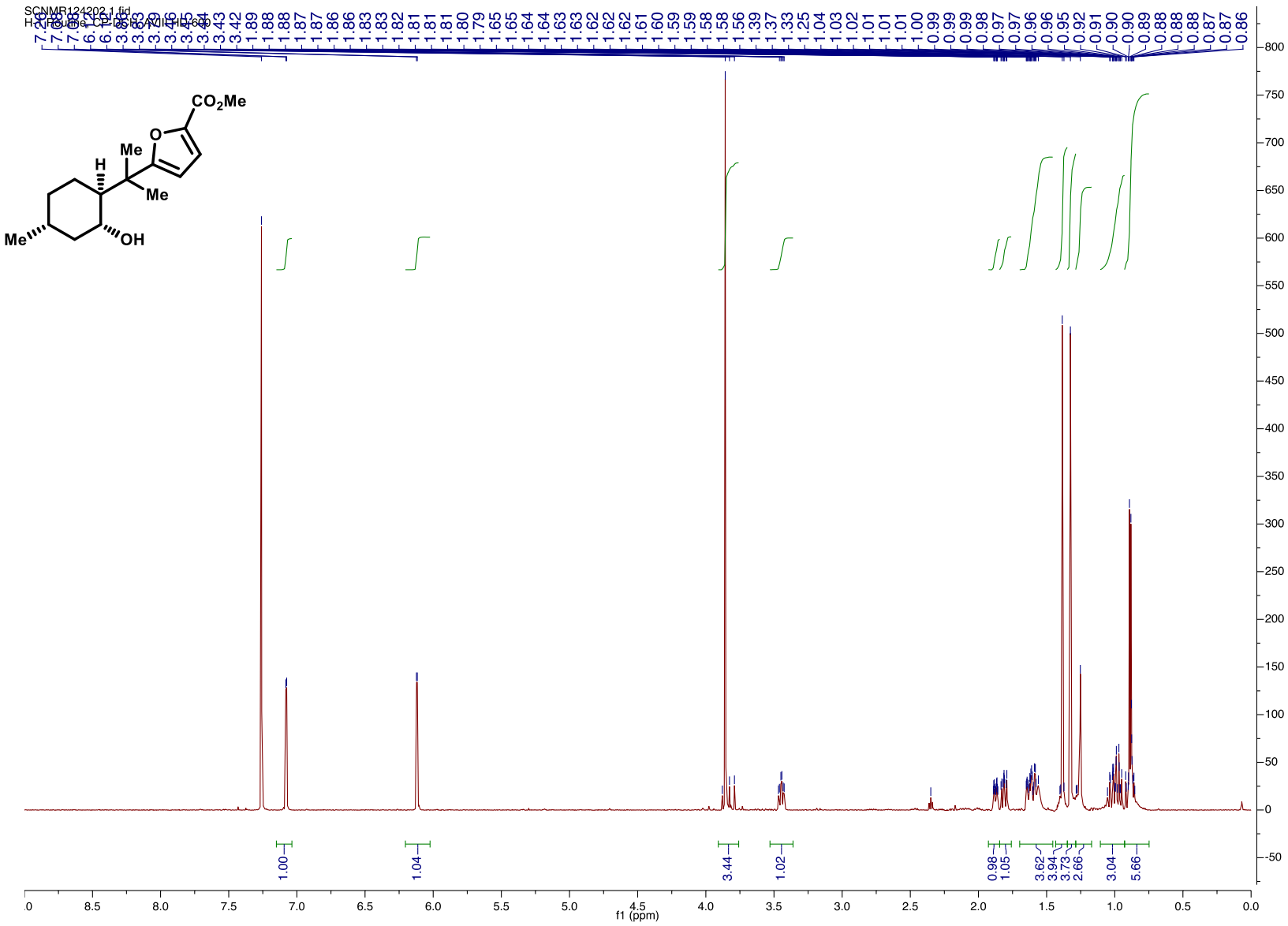
SI-16: ^{13}C-NMR


SCNMR154303.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
77.16 CDCl3
f1 (ppm)

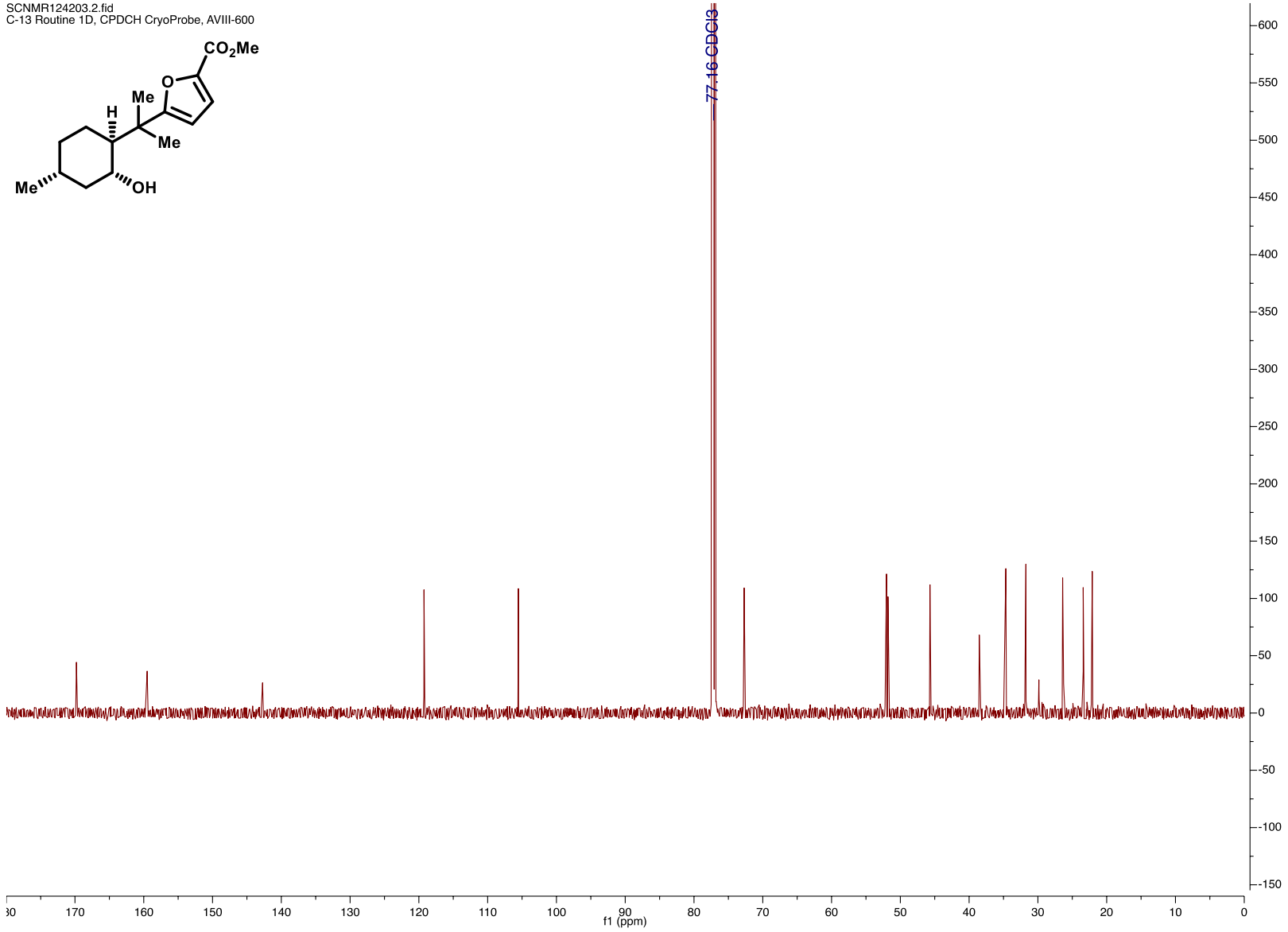

SCNMR154303 furan sm.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
158.05
149.00
147.21
144.74
117.89
117.73
112.81
87.09
77.37
77.16 CDCl3
76.95
52.68
50.51
41.89
33.67
31.79
30.58
21.95
20.22
H
Me
Me
O
S
O
O
O
CO2Me
f1 (ppm)

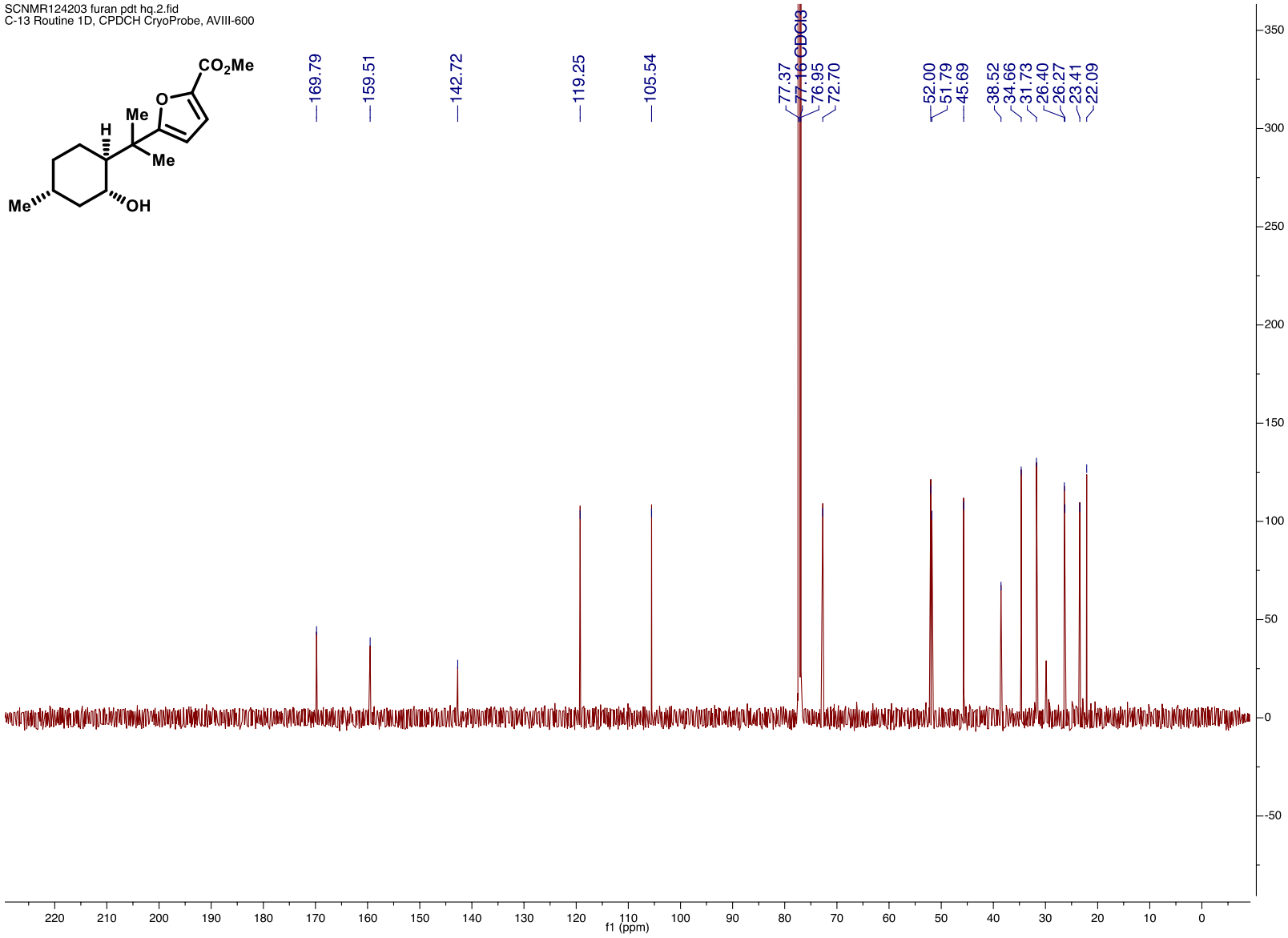
14: ^{1}H-NMR


SCNMR124202.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
CO2Me
O
Me
H
Me
Me
OH
f1 (ppm)

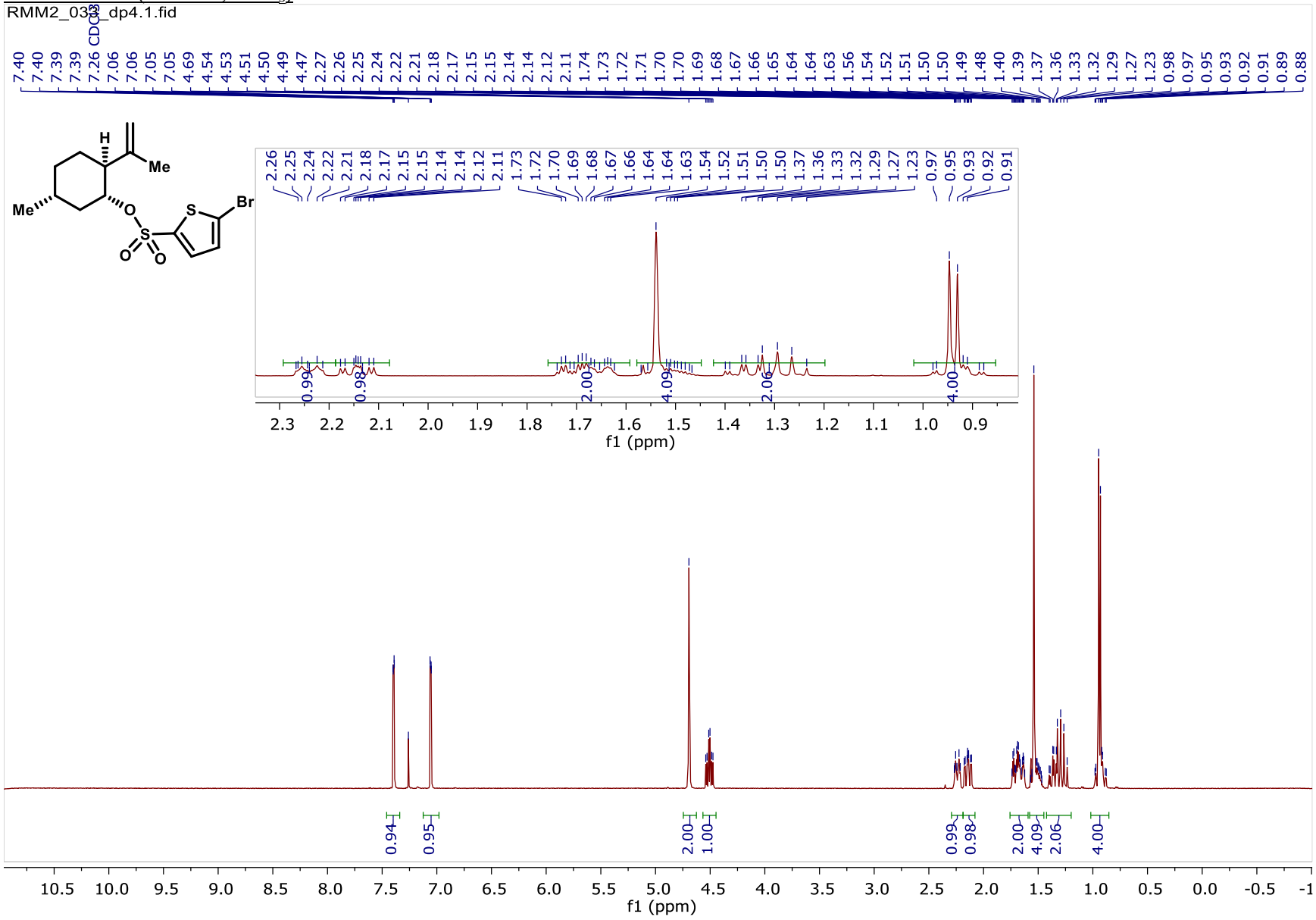

SCNMR124202.1.fid
H-Proton_CP-DUL.ex3
CO2Me
O
Me
H
Me
Me
OH
f1 (ppm)

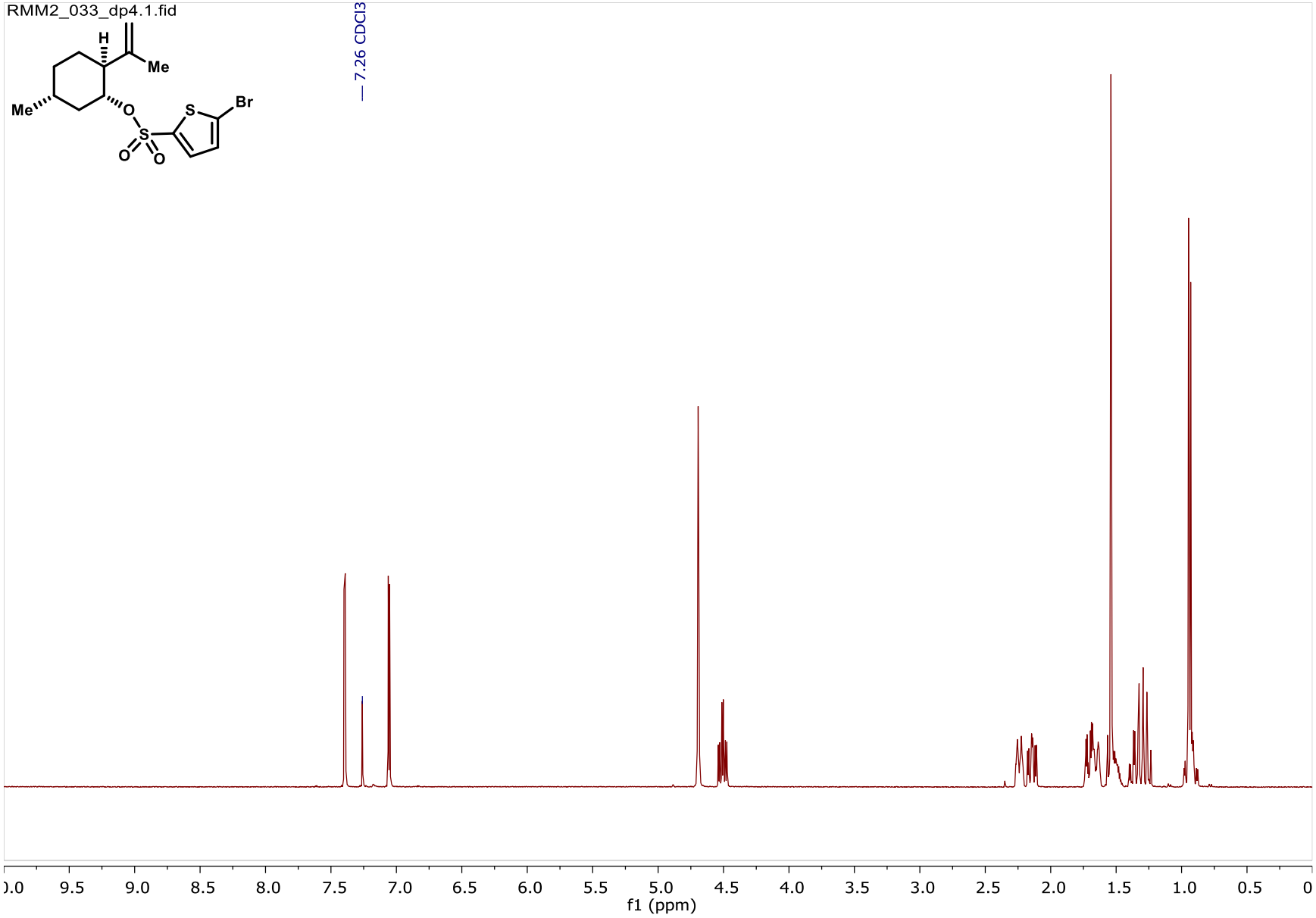
14: ^{13}C-NMR


SCNMR124203.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
CO2Me
O
Me
H
Me
Me
OH
77.16 CDCl3
f1 (ppm)

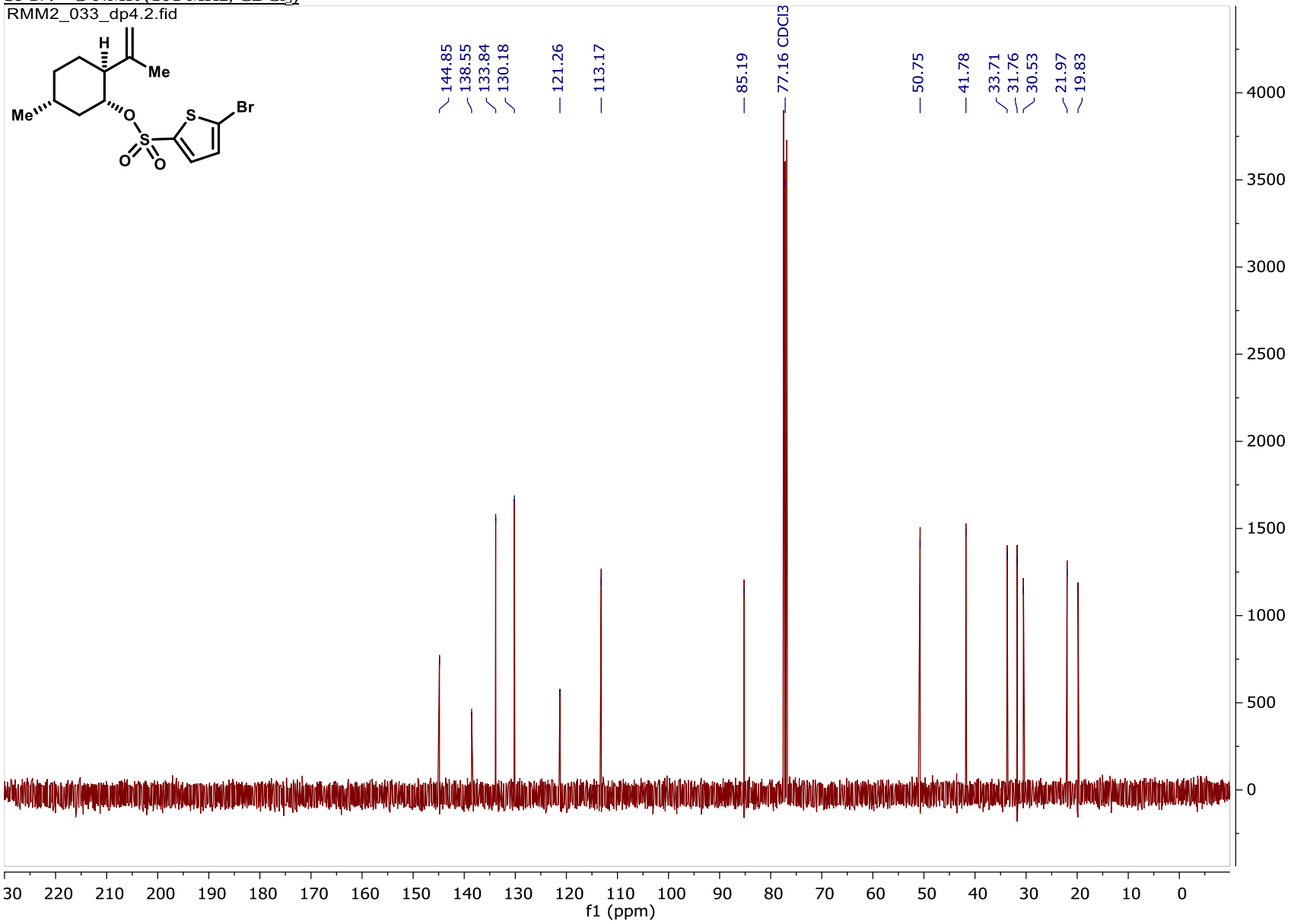

SCNMR124203 furan pdt hq.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
CO2Me
O
Me
H
Me
Me
OH
169.79
159.51
142.72
119.25
105.54
77.37
77.16 CDCl3
76.95
72.70
52.00
51.79
45.69
38.52
34.66
31.73
26.40
26.27
23.41
22.09
f1 (ppm)

SI-17: ^{1}H-NMR (400 MHz, $CDCl_3$)

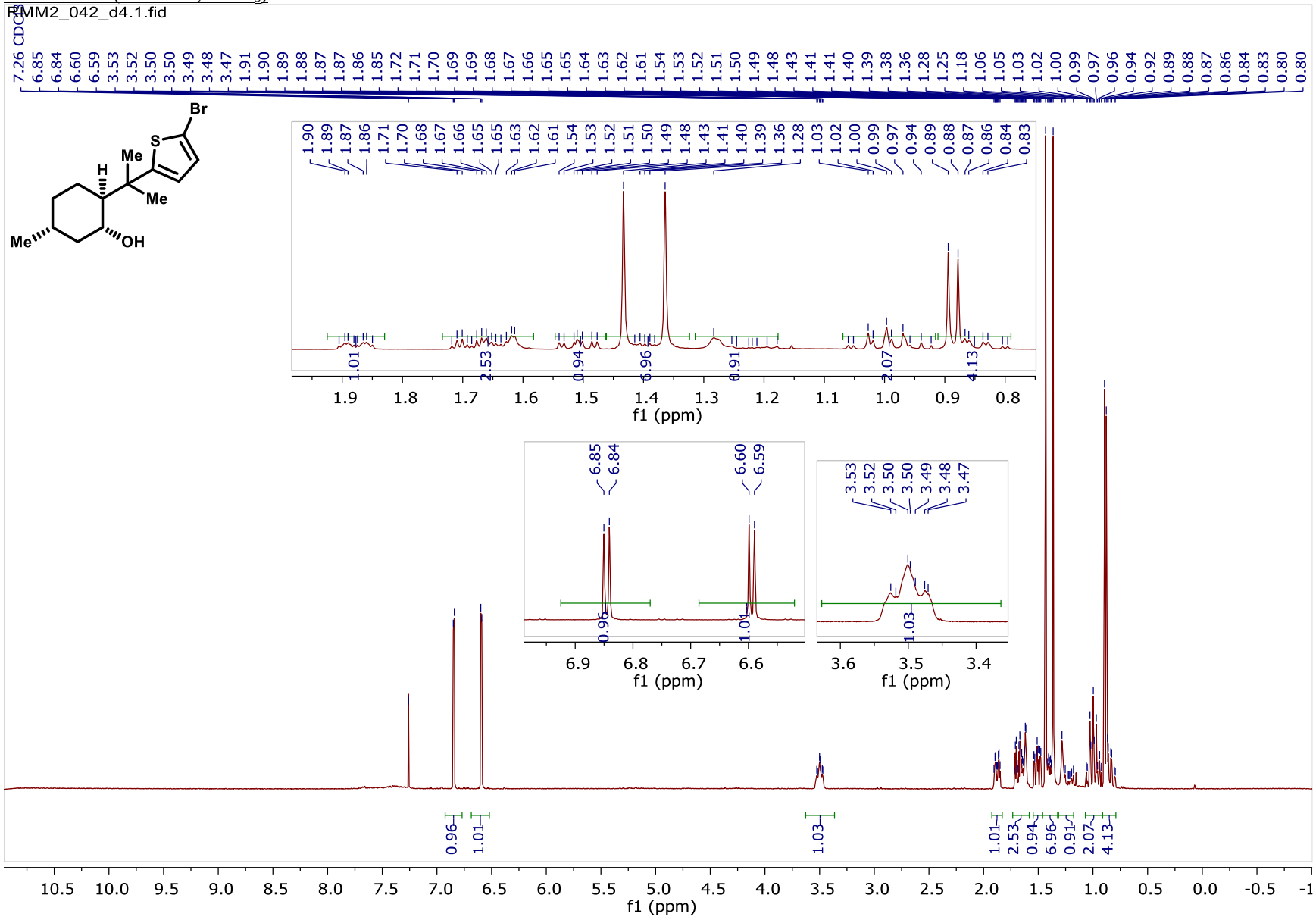


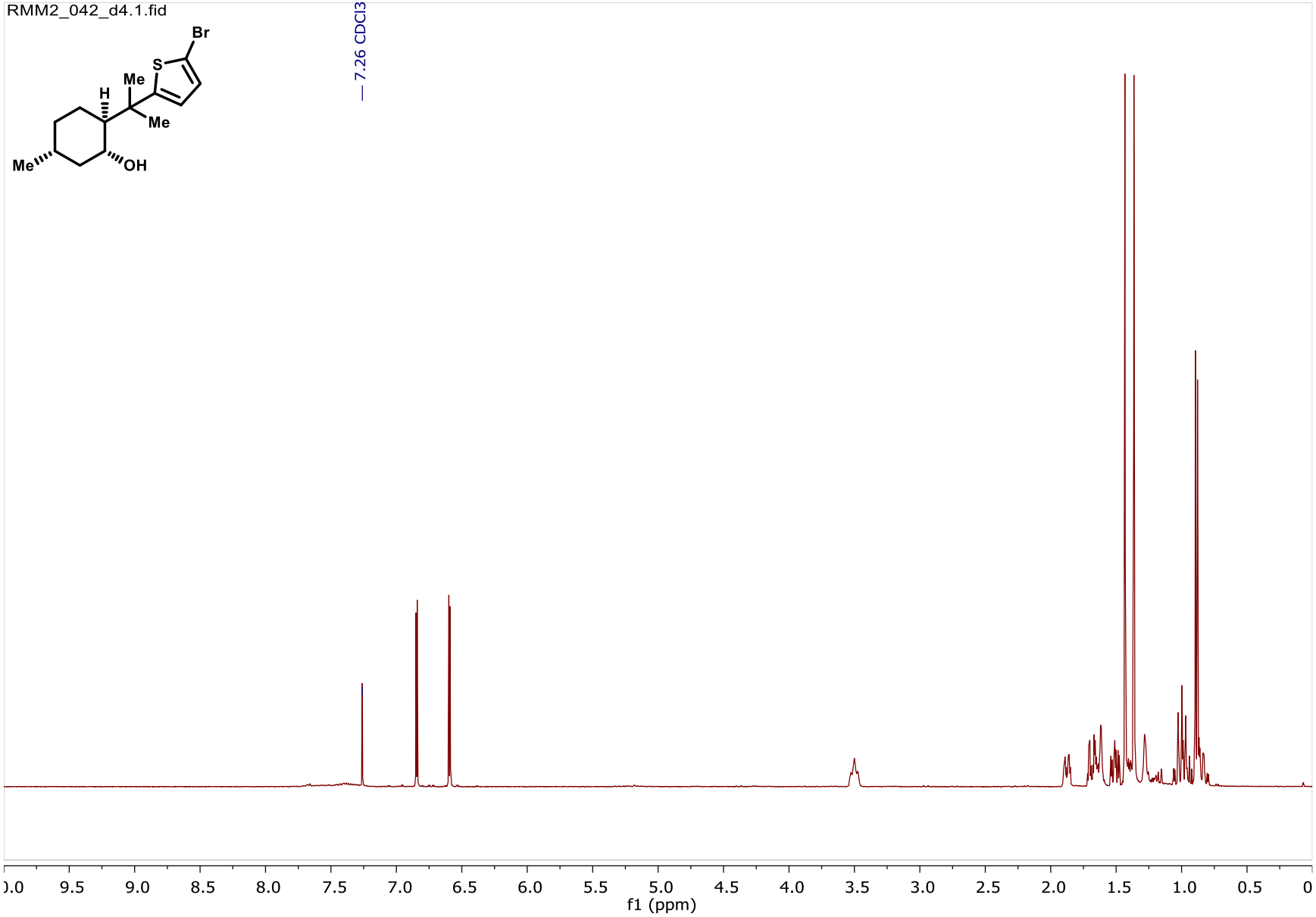

RMM2_033_dp4.1.fid
— 7.26 CDCl3
H
Me
Me
O
S
Br
S
O
O
f1 (ppm)

SI-17: ^{13}C-NMR (101 MHz, $CDCl_3$)

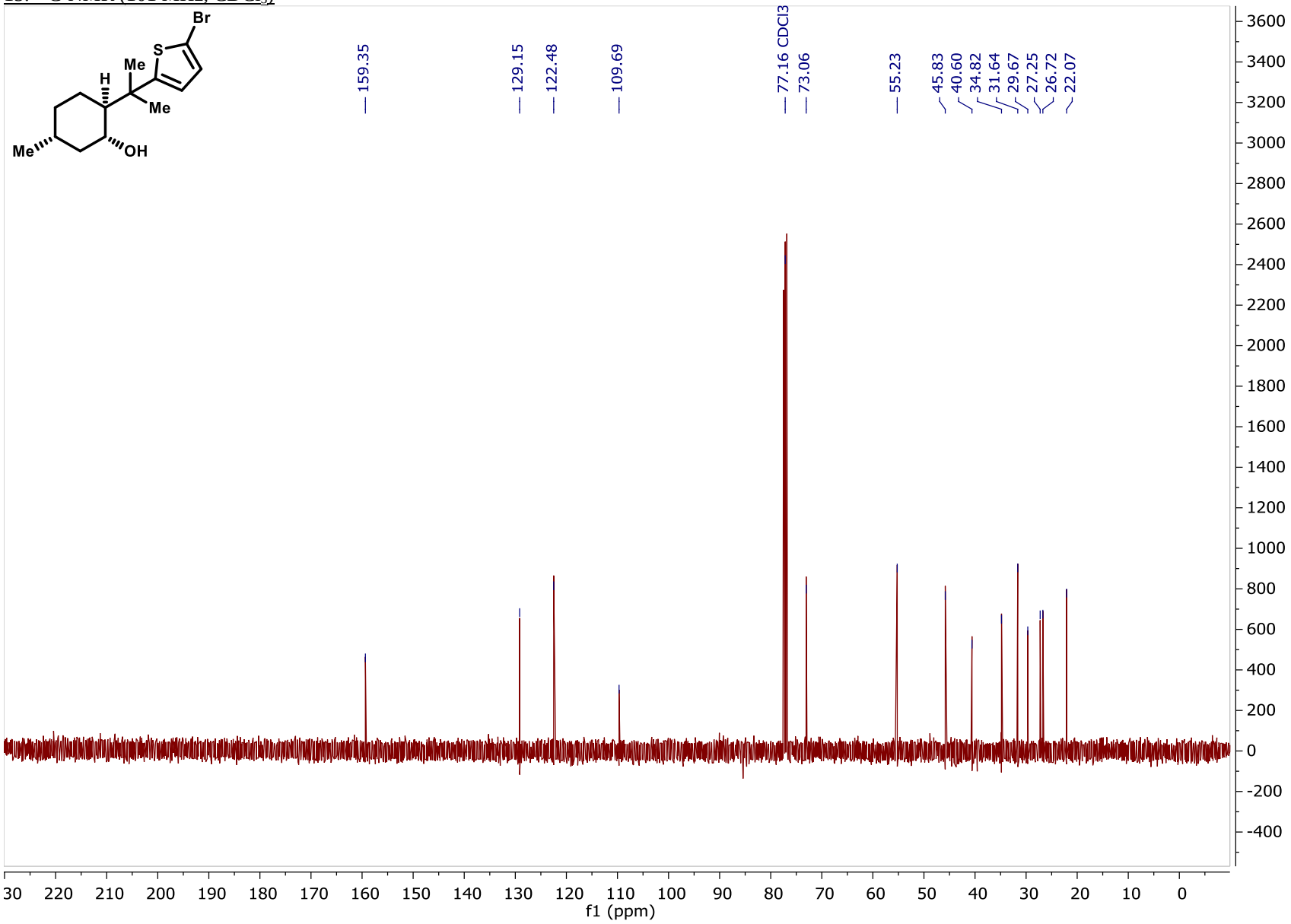


15: ^{1}H-NMR (400 MHz, $CDCl_3$)

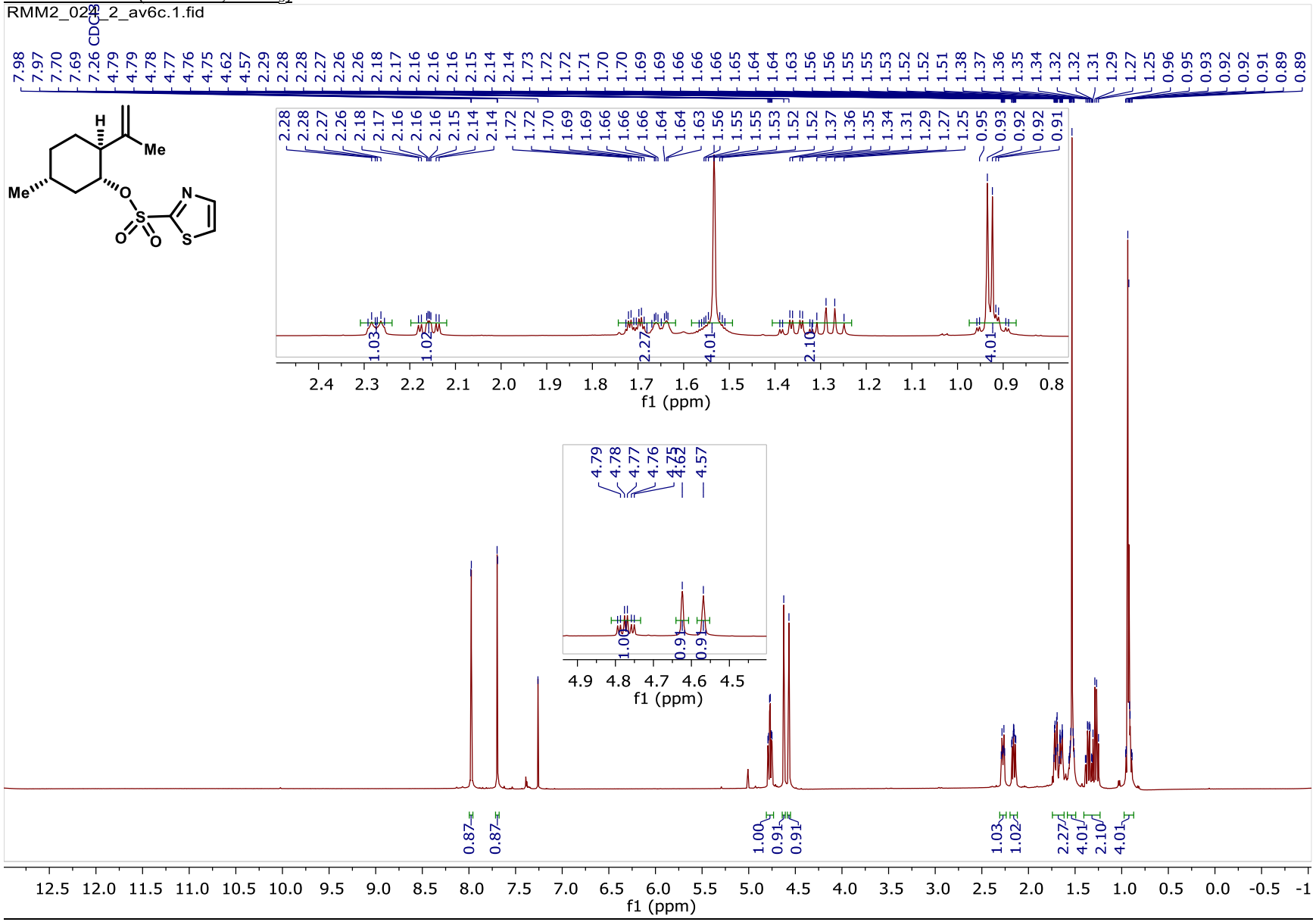


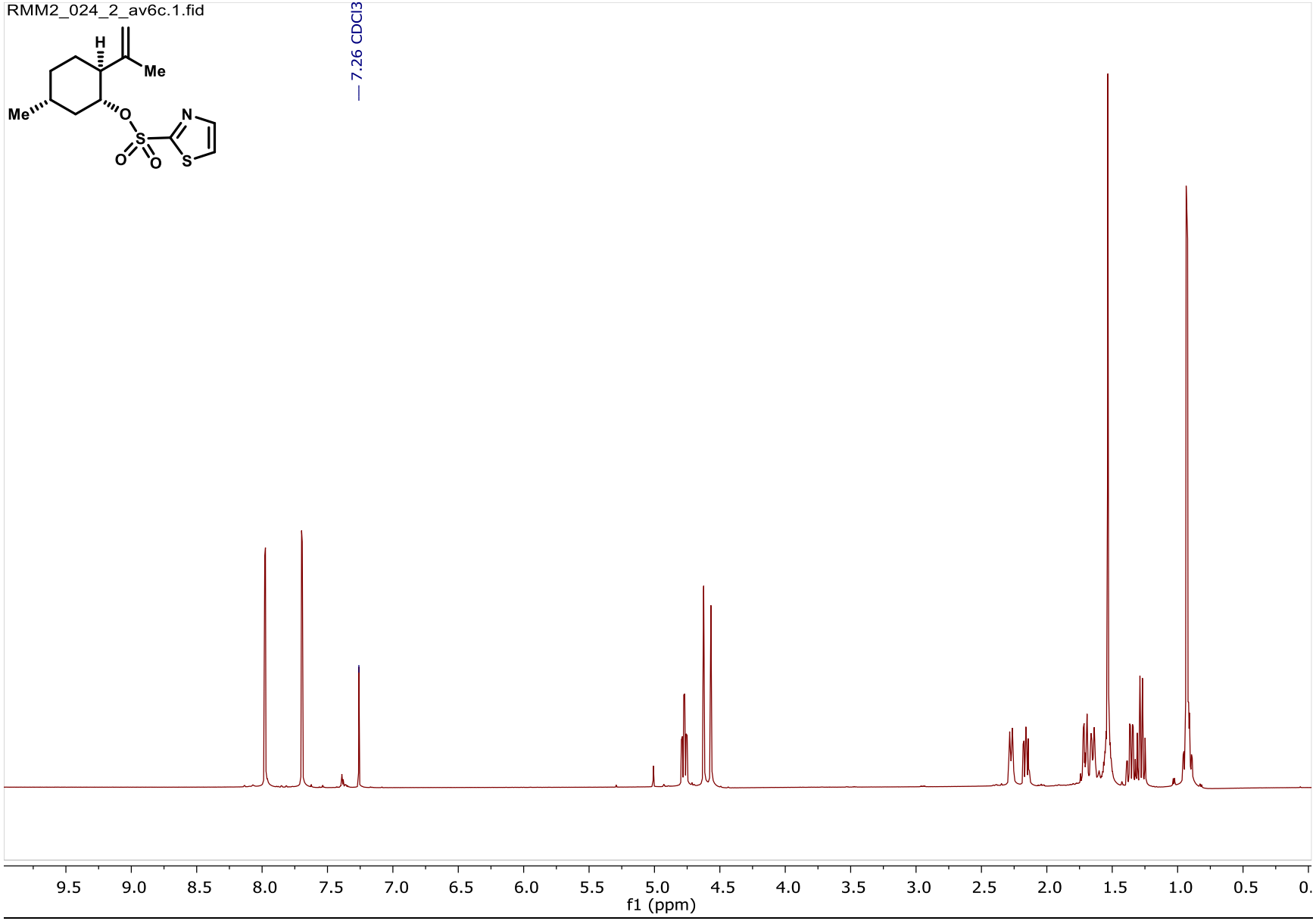

RMM2_042_d4.1.fid
Br
S
Me
H
Me
Me
OH
7.26 CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

15: ^{13}C-NMR (101 MHz, $CDCl_3$)

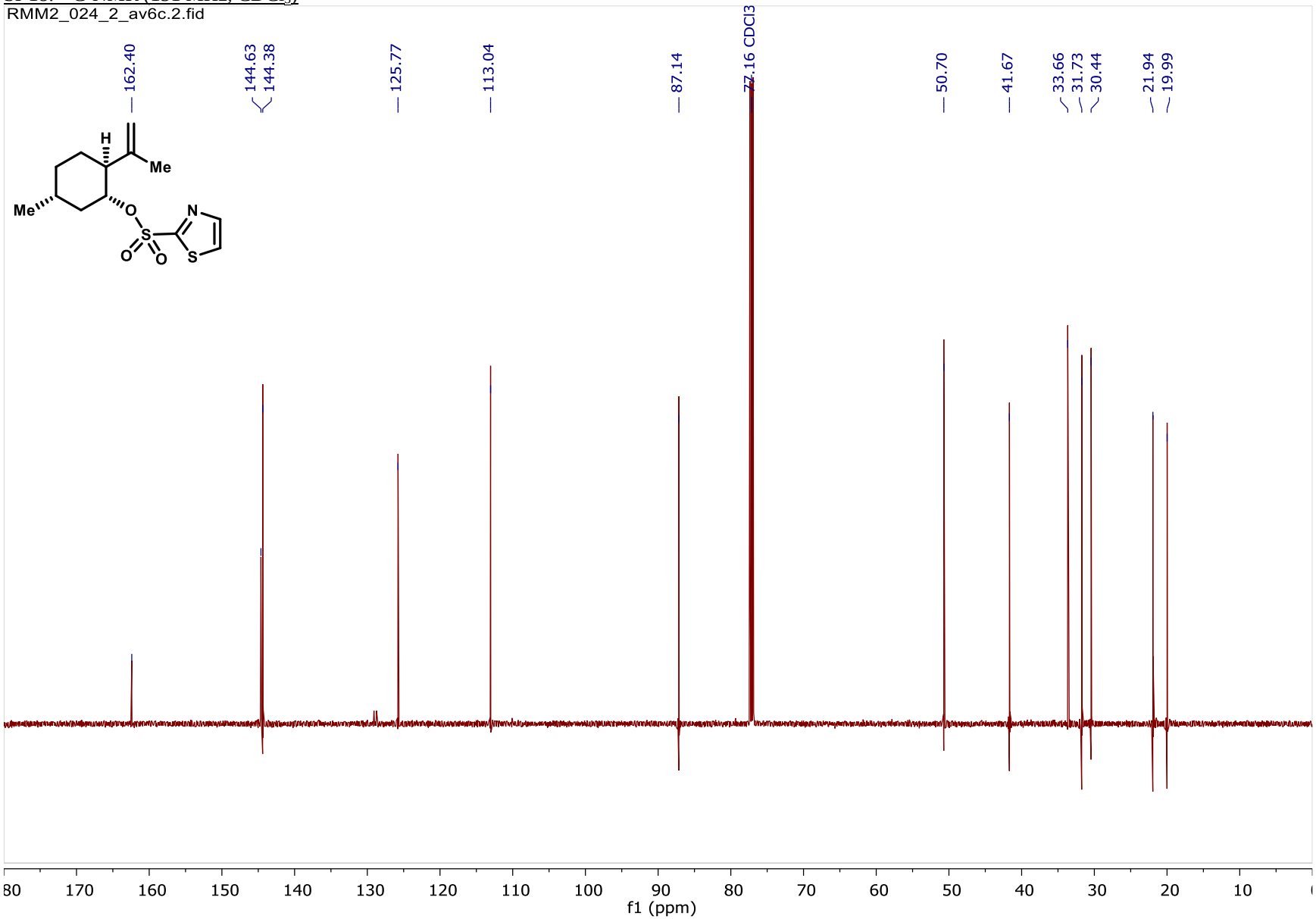


SI-18: ^{1}H-NMR (600 MHz, $CDCl_3$)

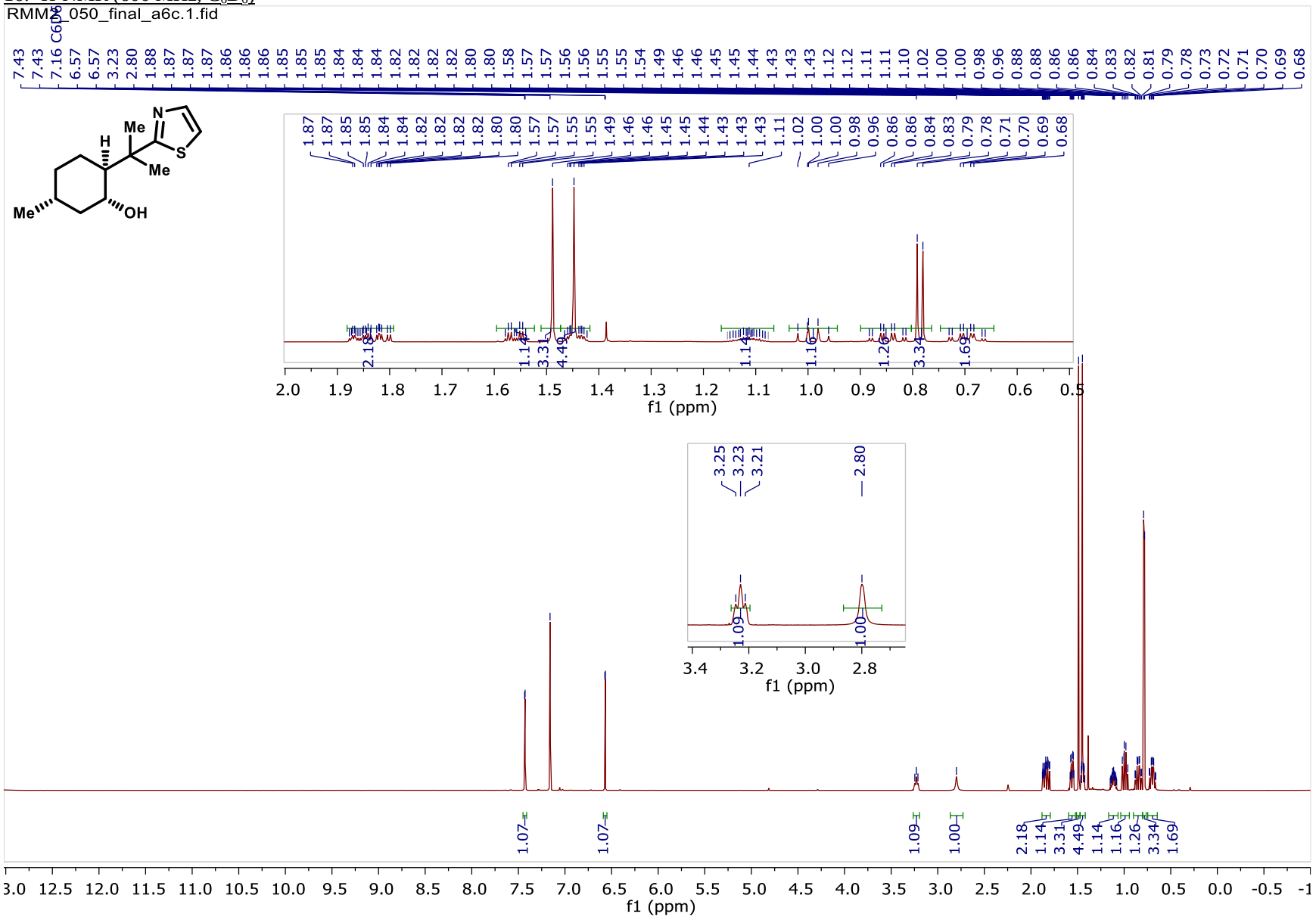


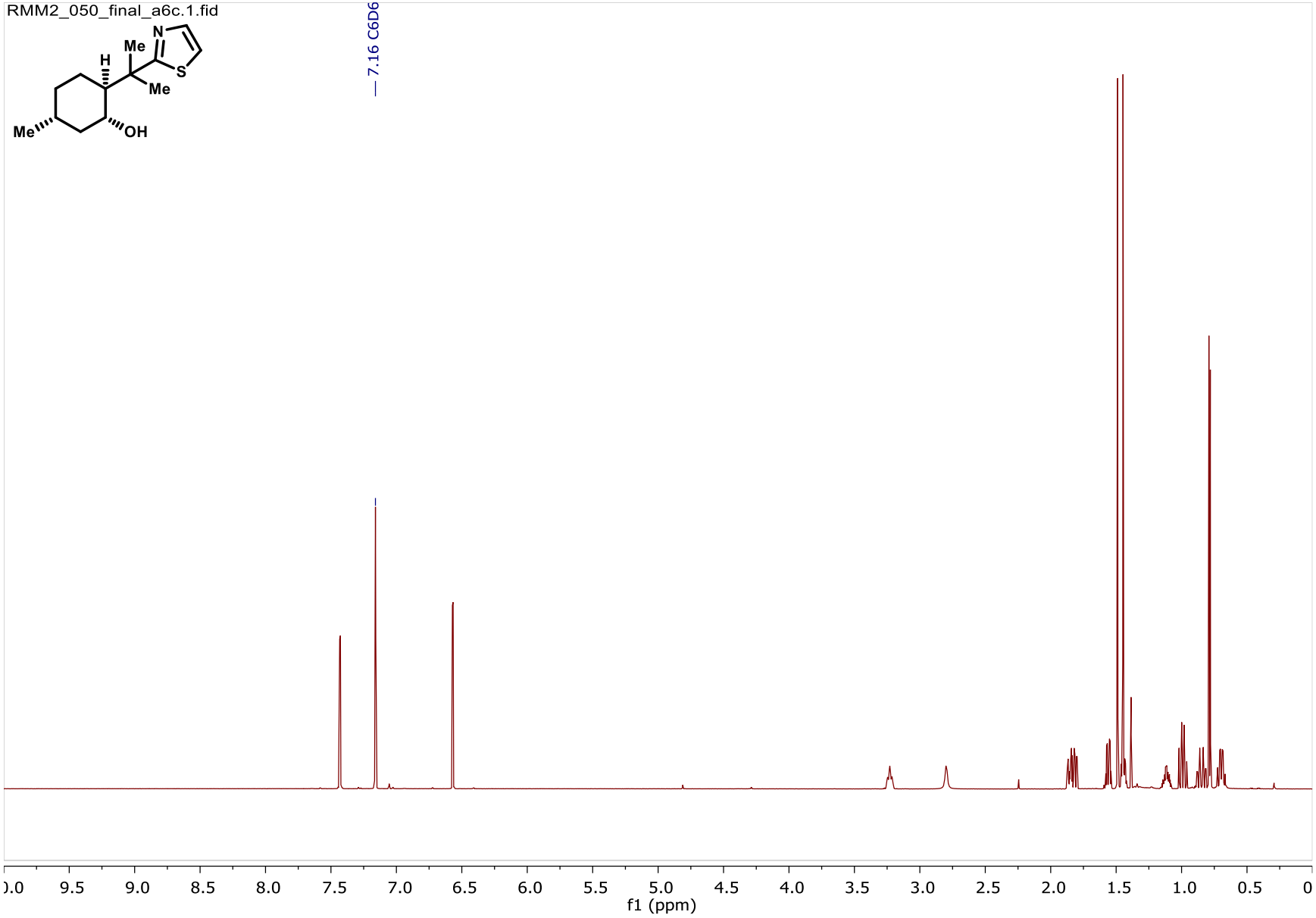

RMM2_024_2_av6c.1.fid
7.26 CDCl3
H
Me
Me
O
S
O
O
N
S
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

SI-18: ^{13}C-NMR (151 MHz, $CDCl_3$)

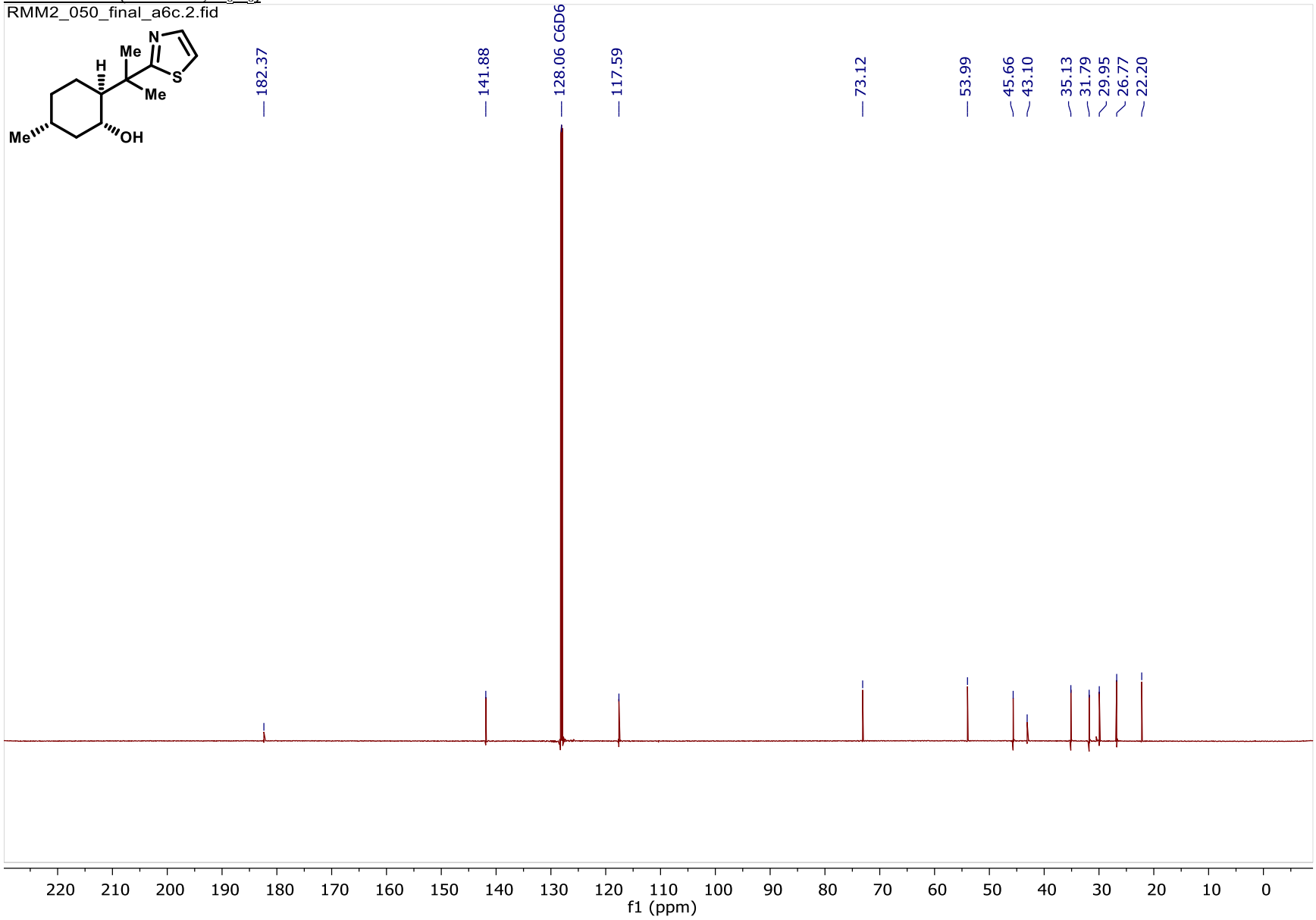


16: ^{1}H-NMR (600 MHz, C_6D_6)

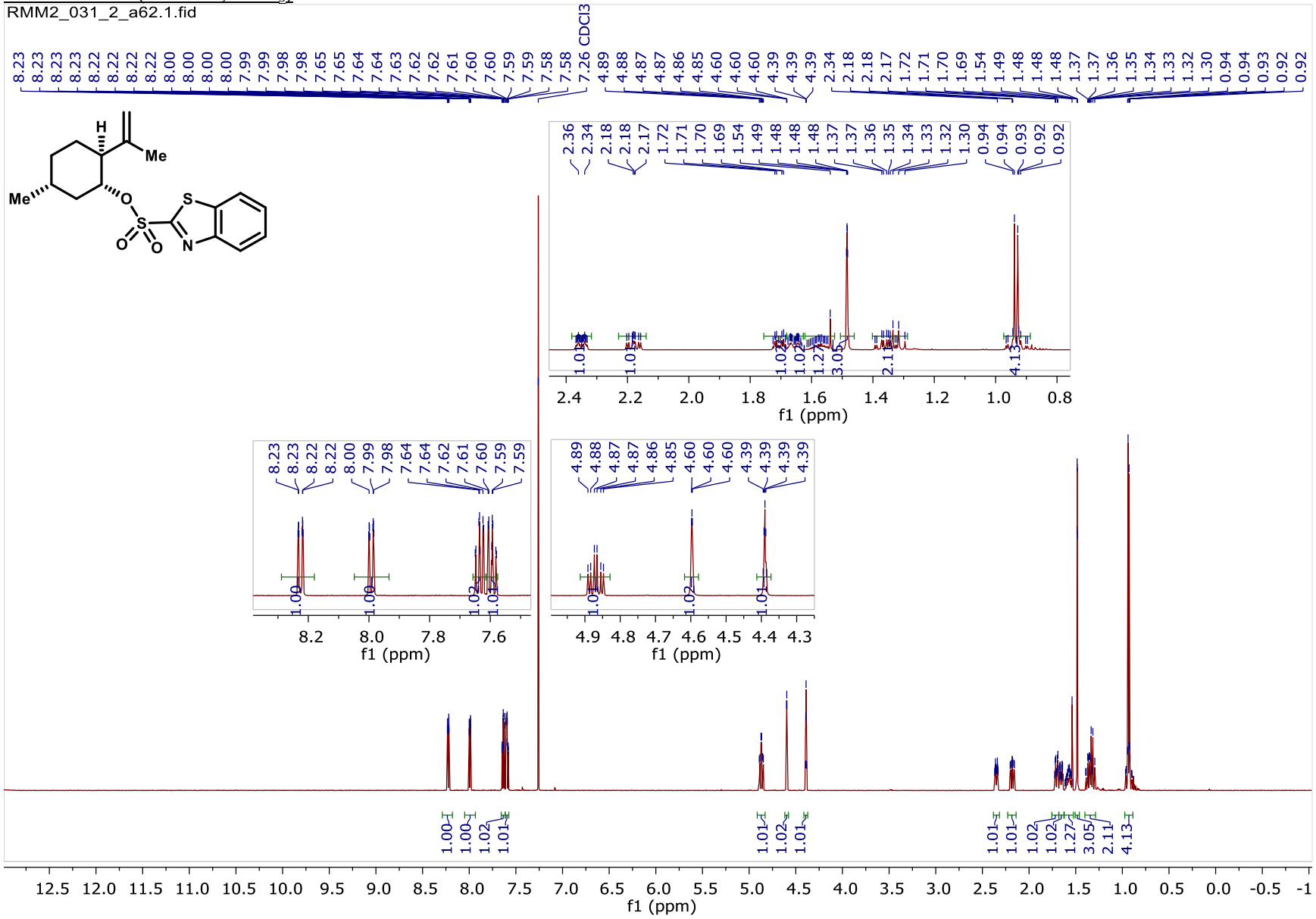


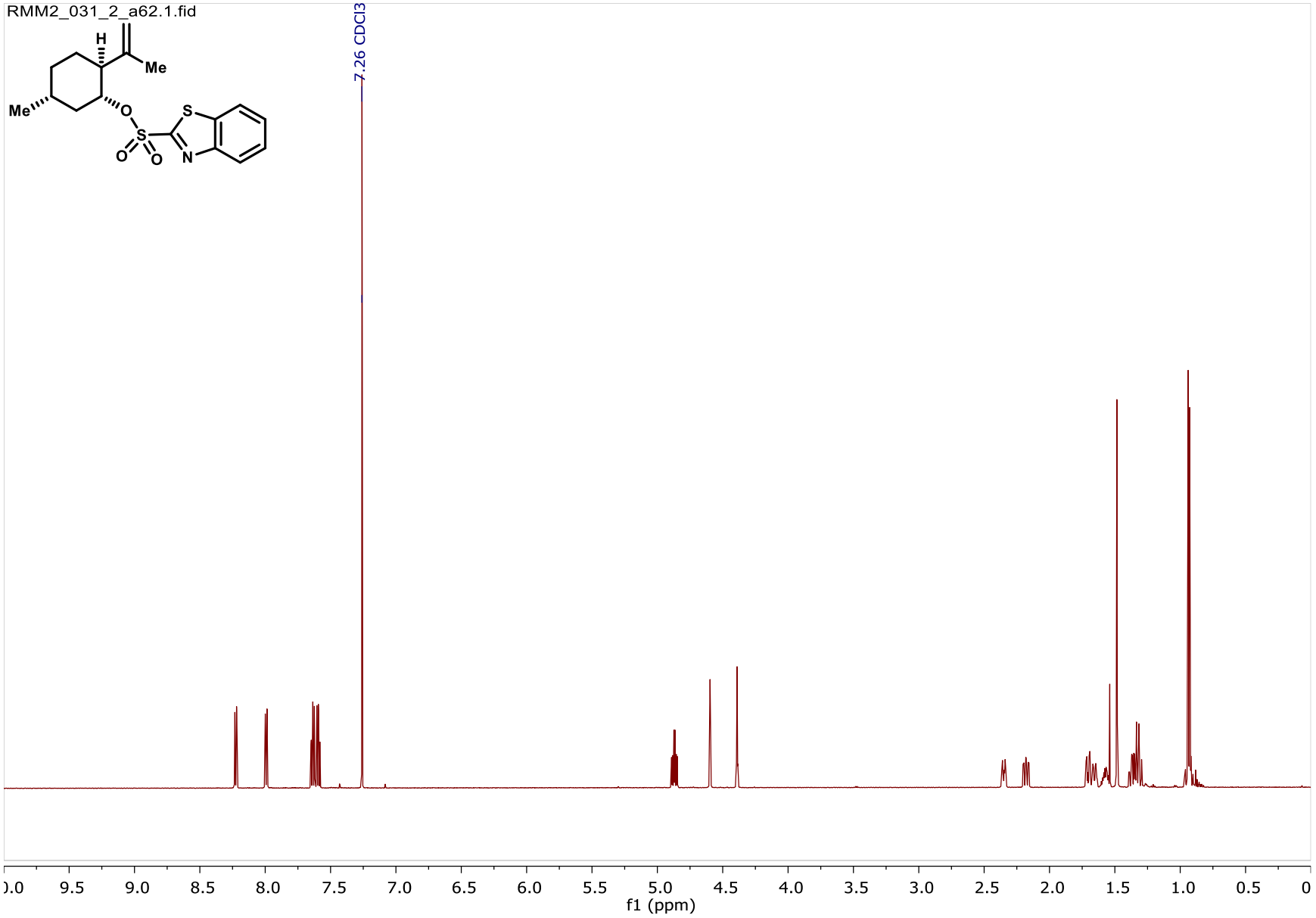

RMM2_050_final_a6c.1.fid
7.16 C6D6
N
Me
H
S
Me
Me
OH
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

16: ^{13}C-NMR (151 MHz, C_6D_6)

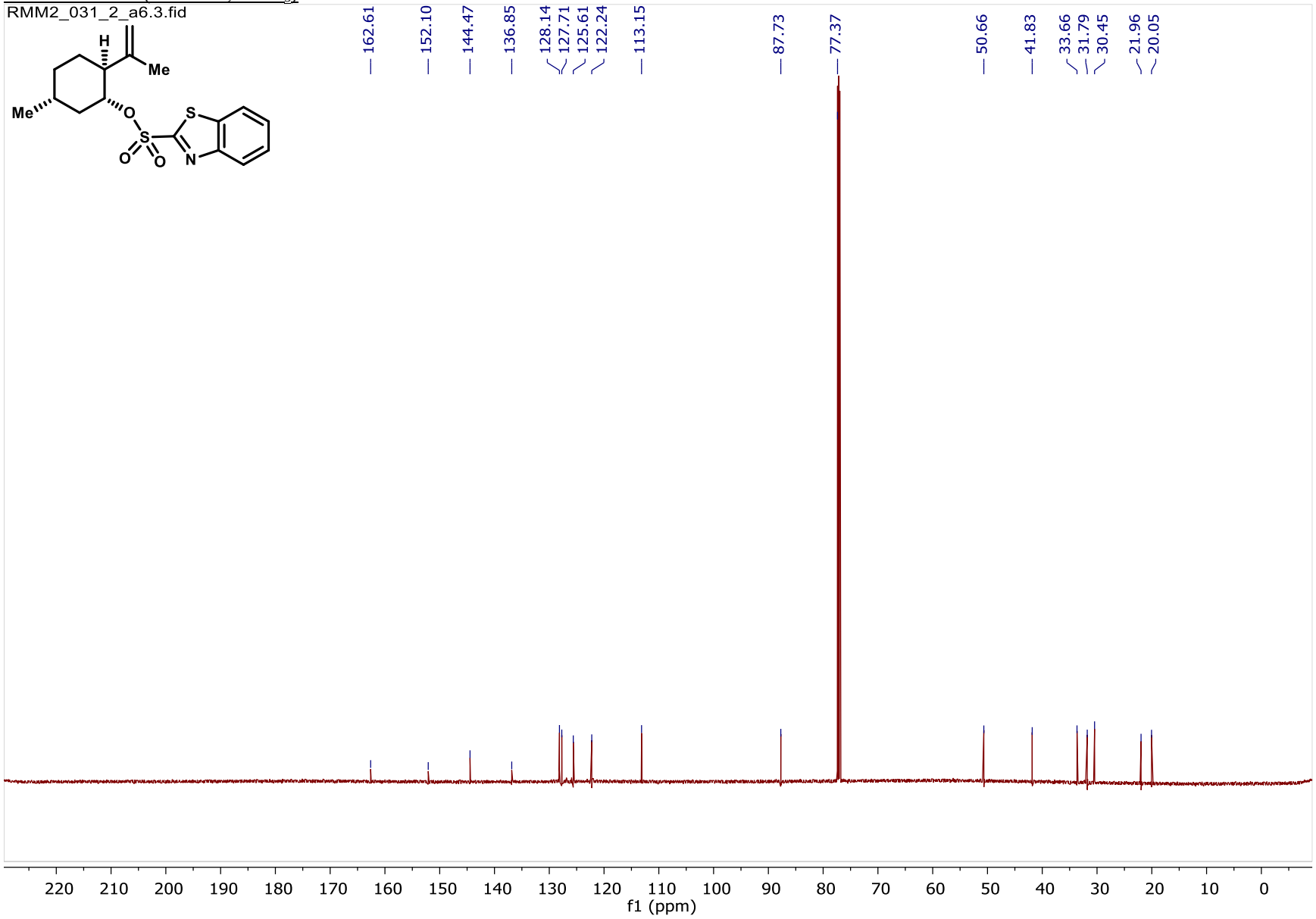


SI-19: ^{1}H-NMR (600 MHz, $CDCl_3$)

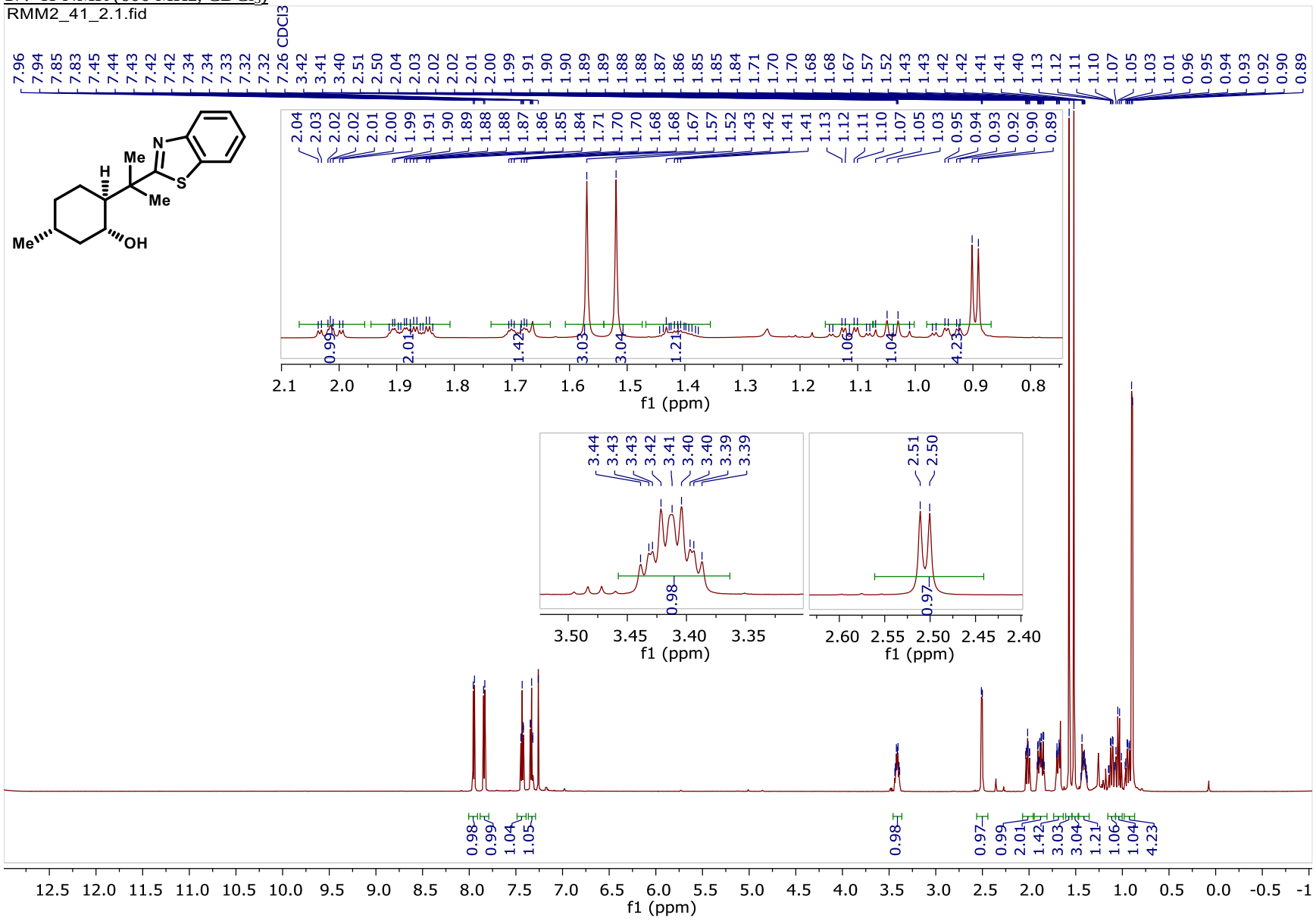


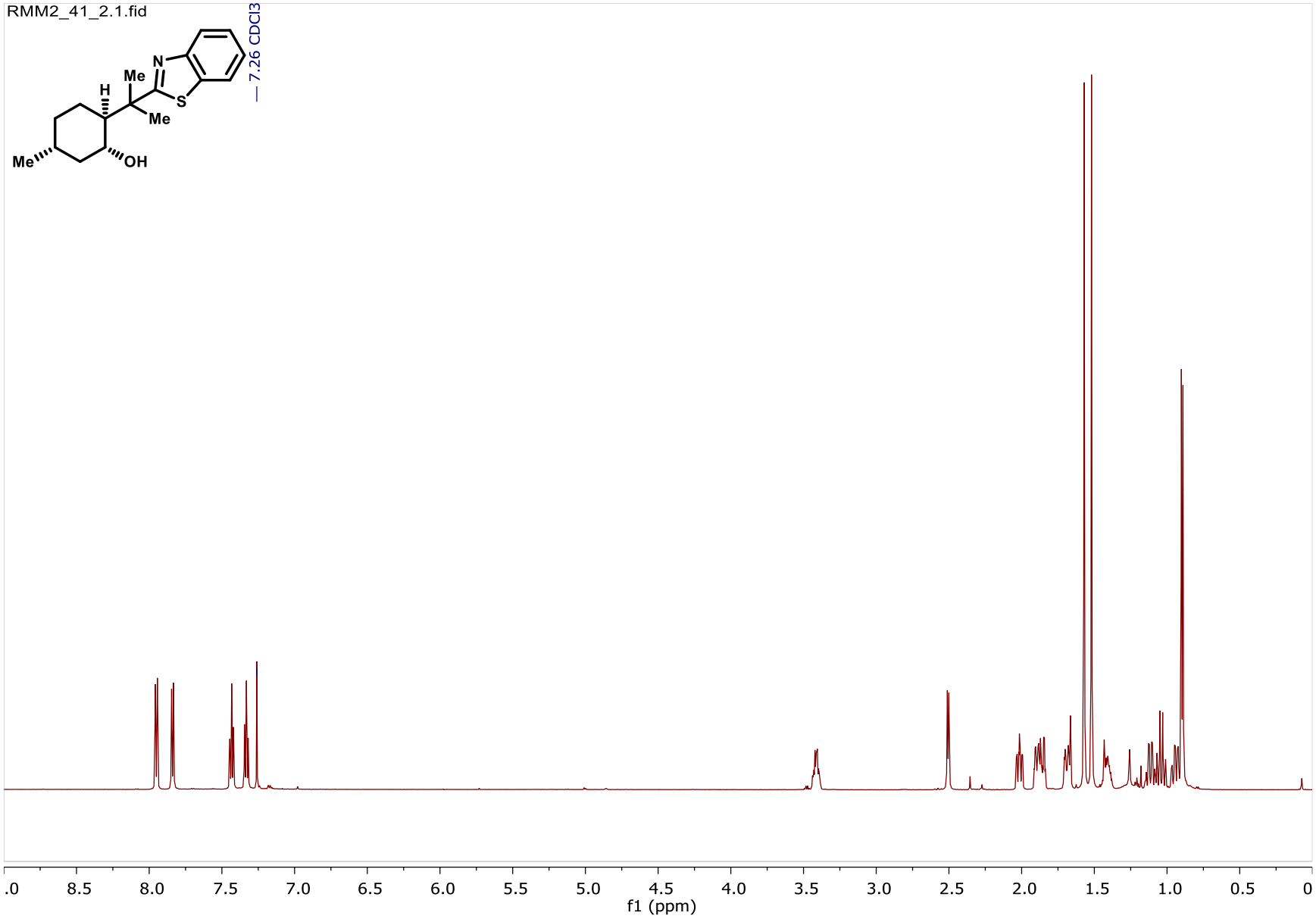

RMM2_031_2_a62.1.fid
7.26 CDCl3
H
Me
Me
O
S
O
O
S
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

SI-19: ^{13}C-NMR (151 MHz, $CDCl_3$)

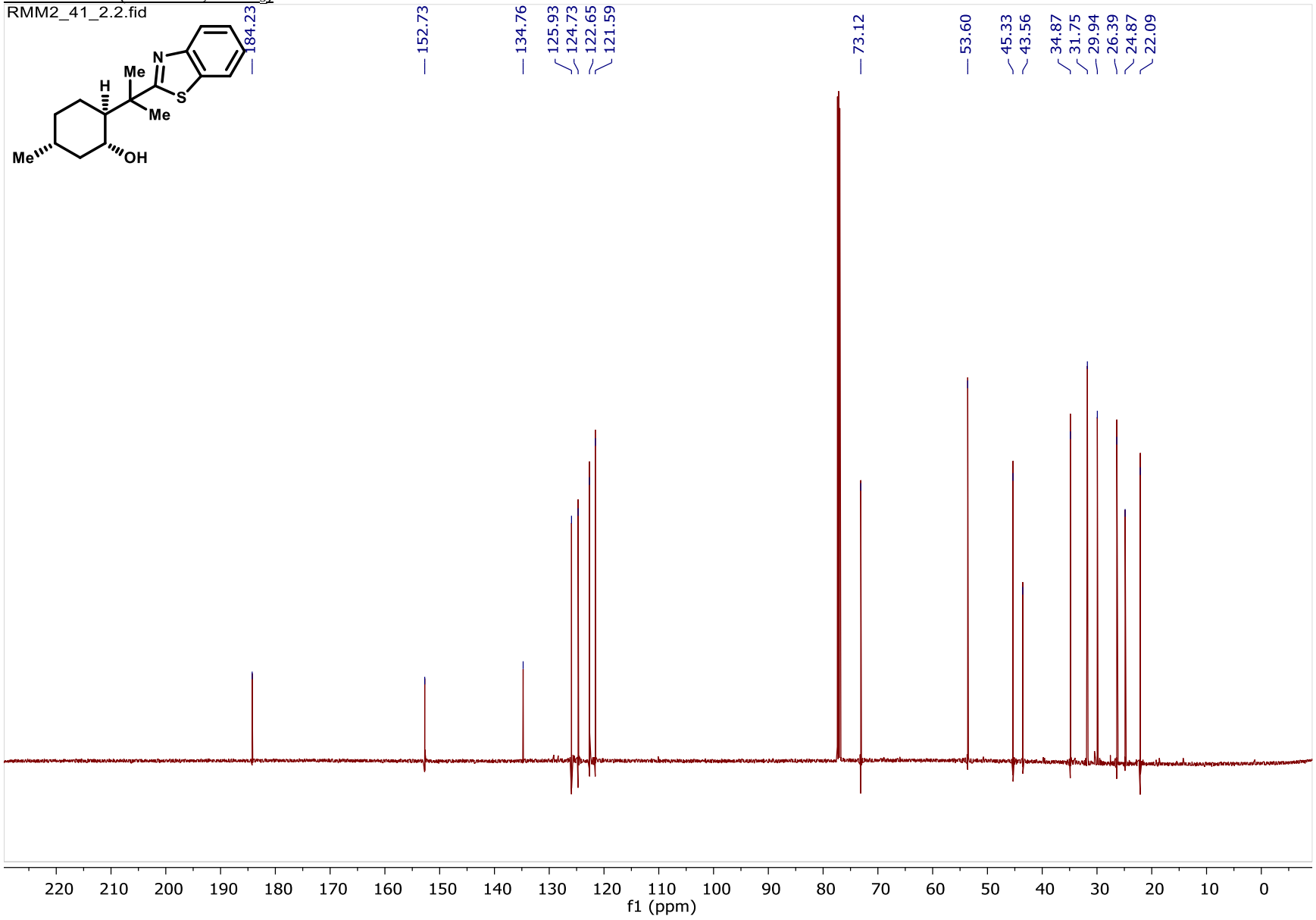


17: ^{1}H-NMR (600 MHz, $CDCl_3$)

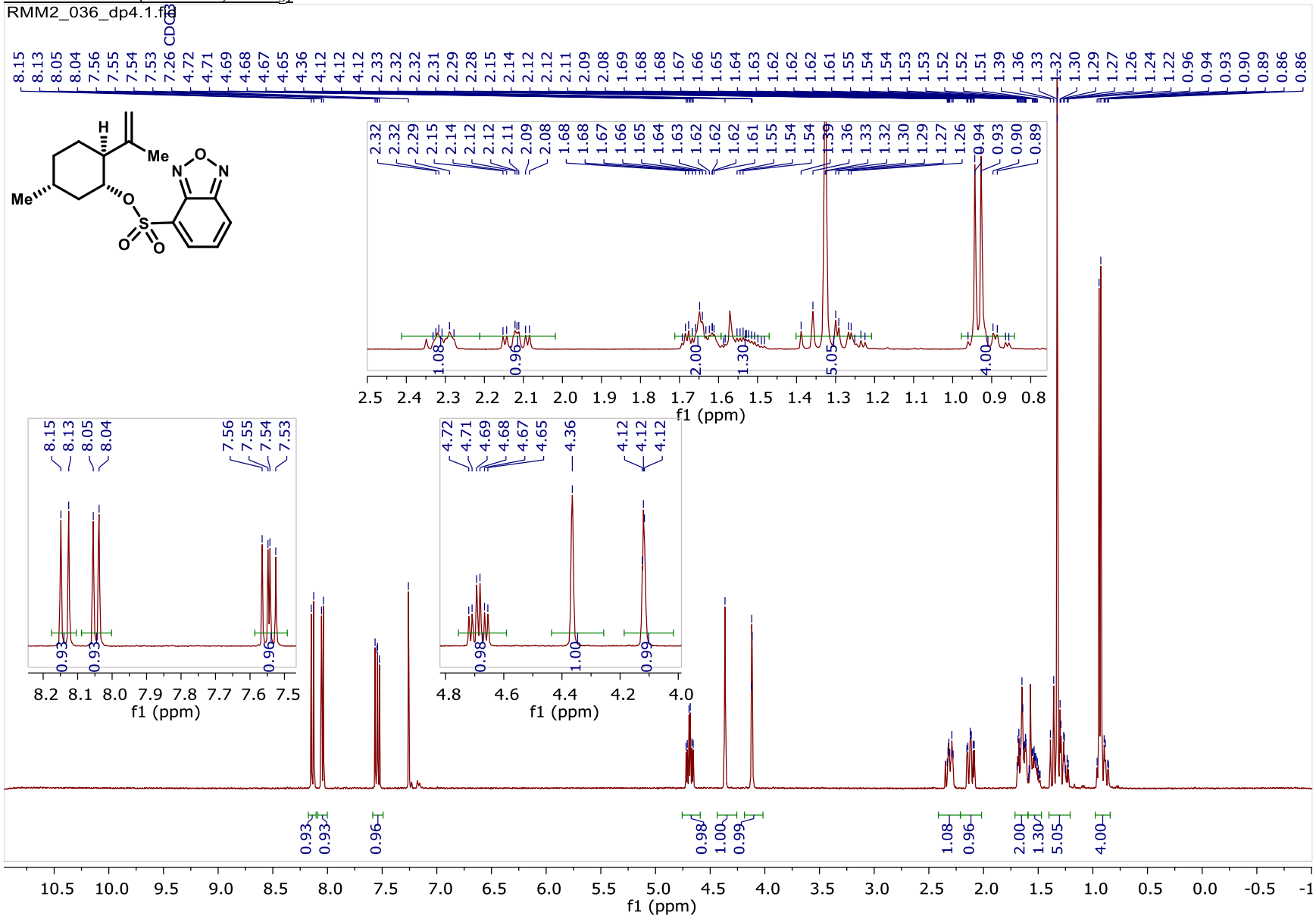


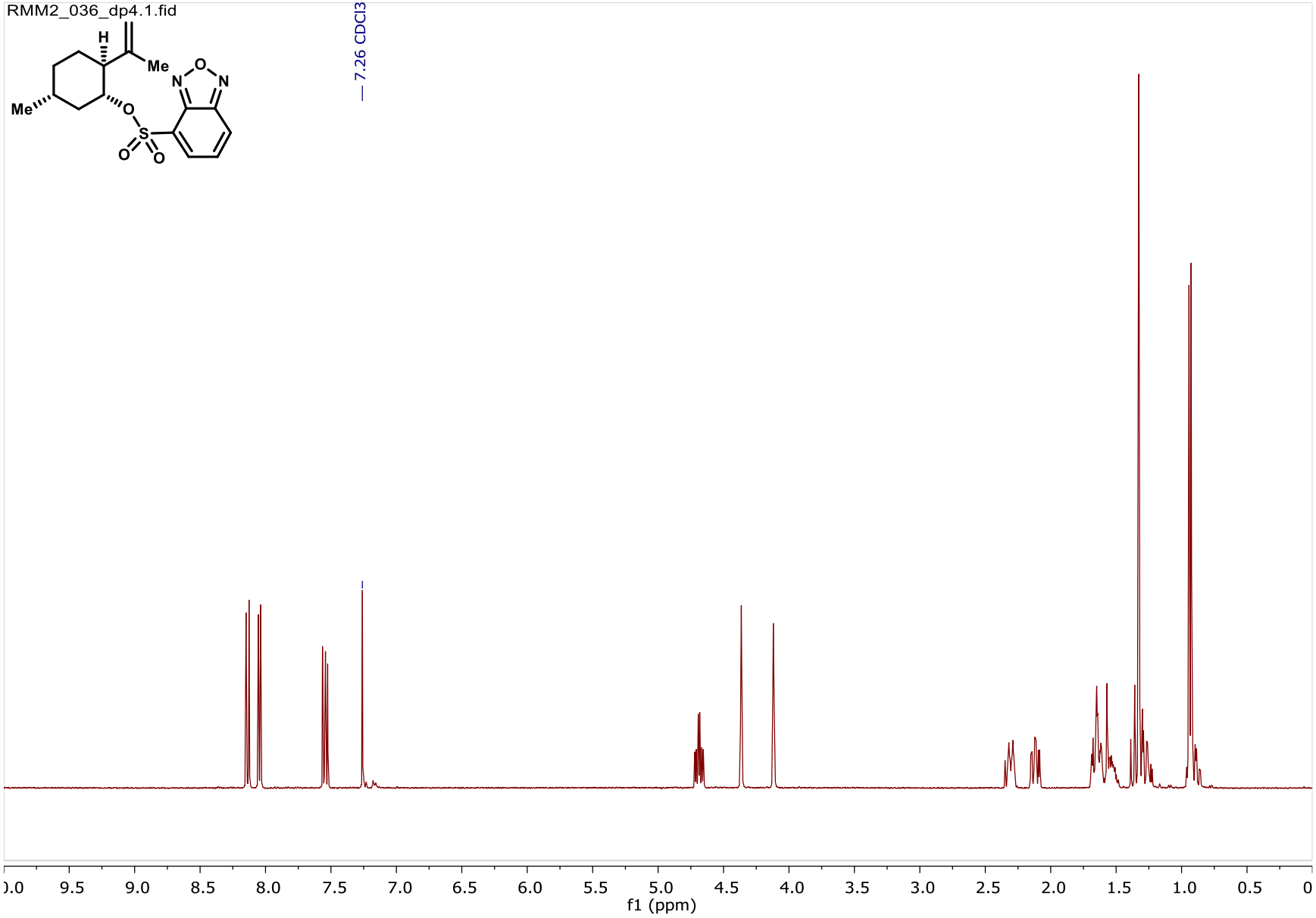

RMM2_41_2.1.fid
— 7.26 CDCl3
N
Me
H
S
Me
Me
OH
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

17: ^{13}C-NMR (151 MHz, $CDCl_3$)

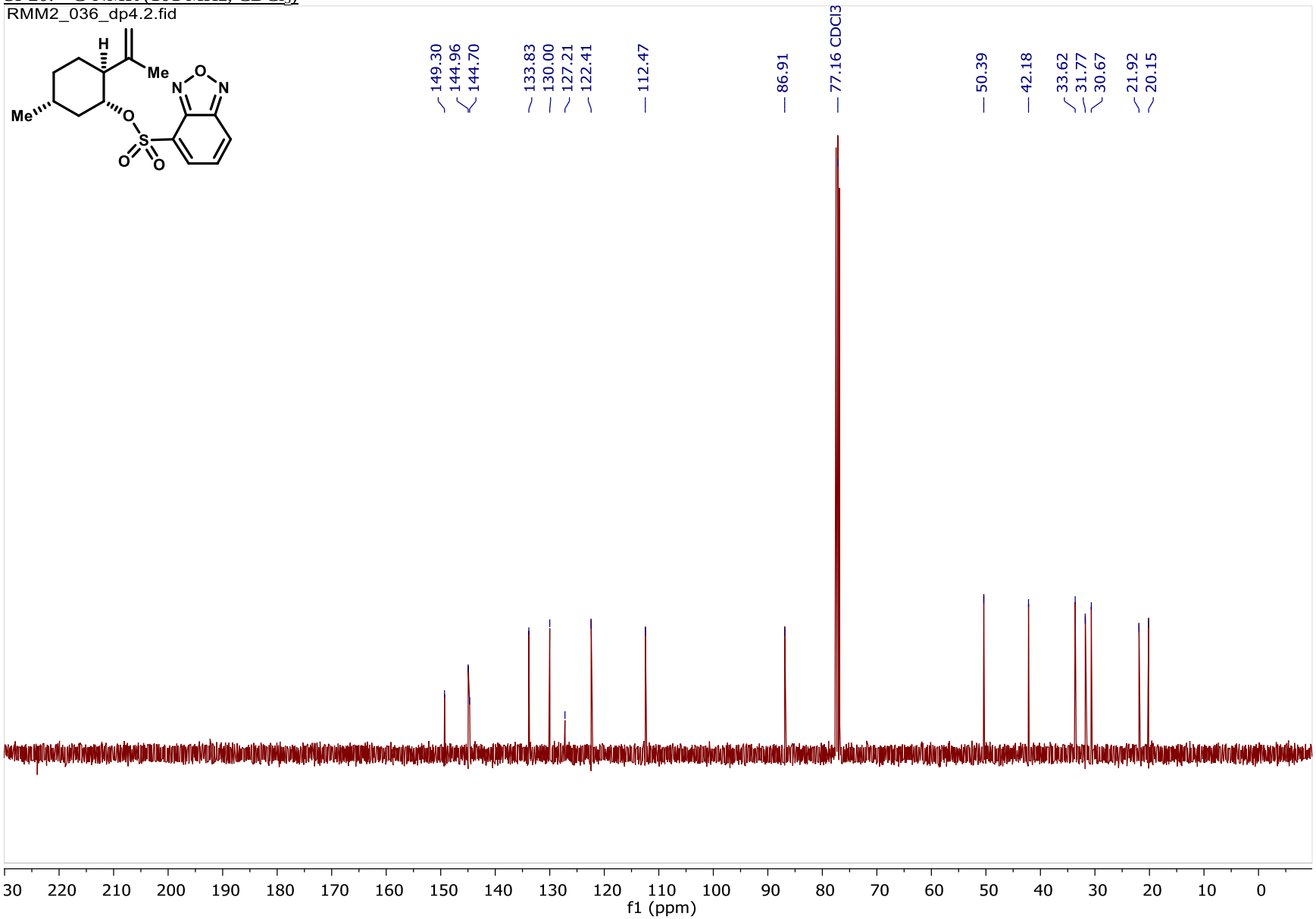


SI-20: ^{1}H-NMR (400 MHz, $CDCl_3$)

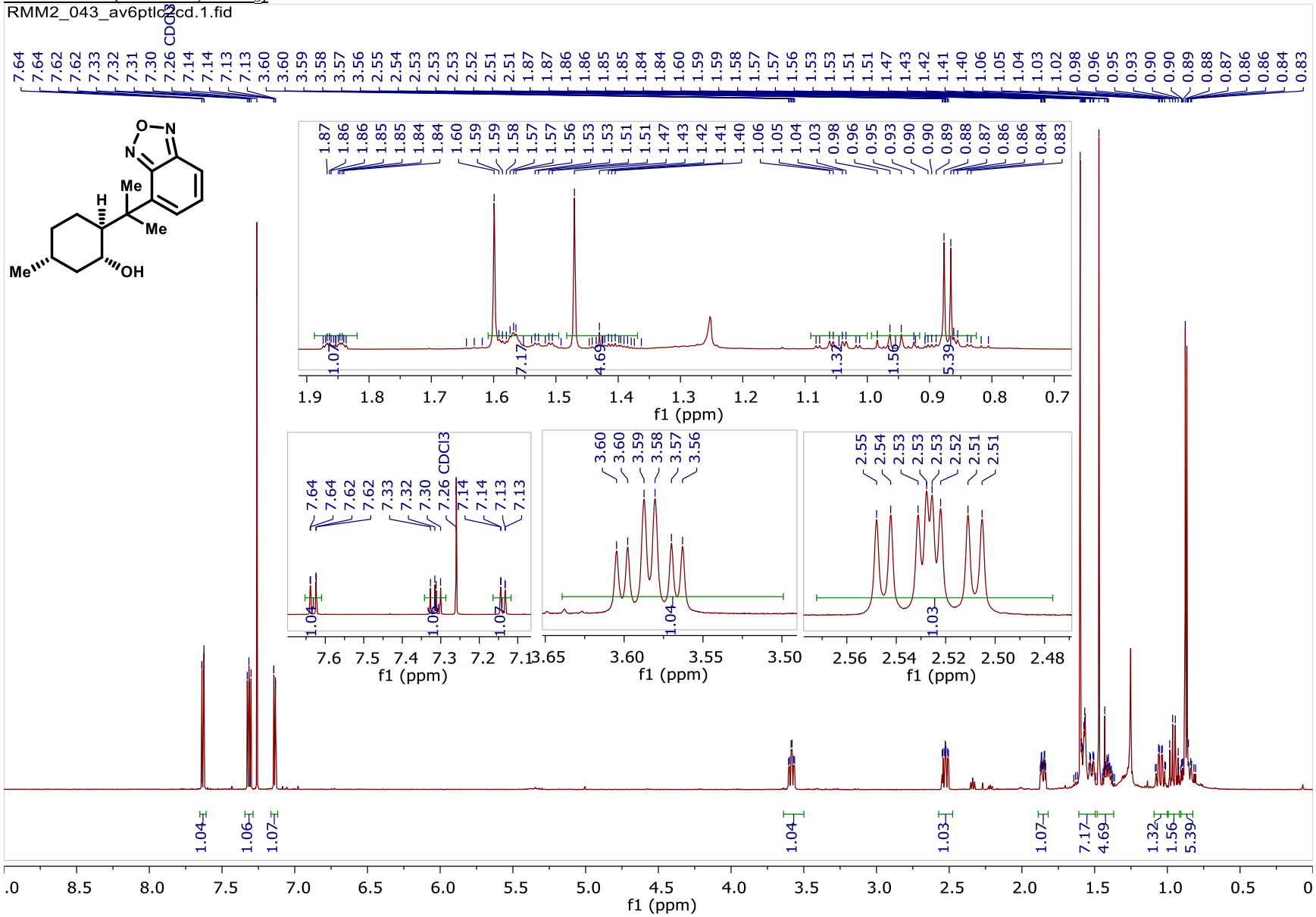


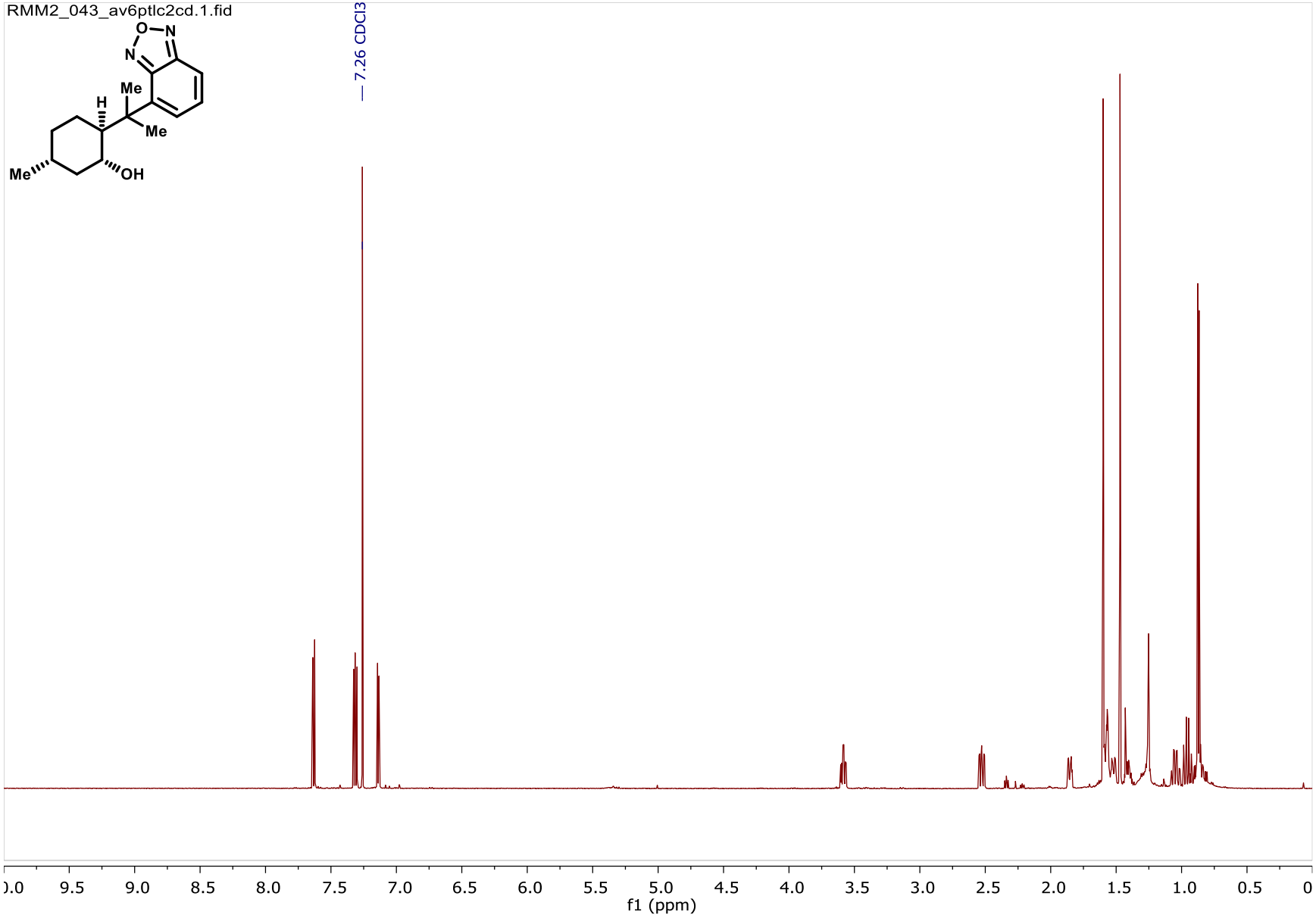

RMM2_036_dp4.1.fid
— 7.26 CDCl3
H
Me
Me
O
N
O
N
S
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

SI-20: ^{13}C-NMR (101 MHz, $CDCl_3$)

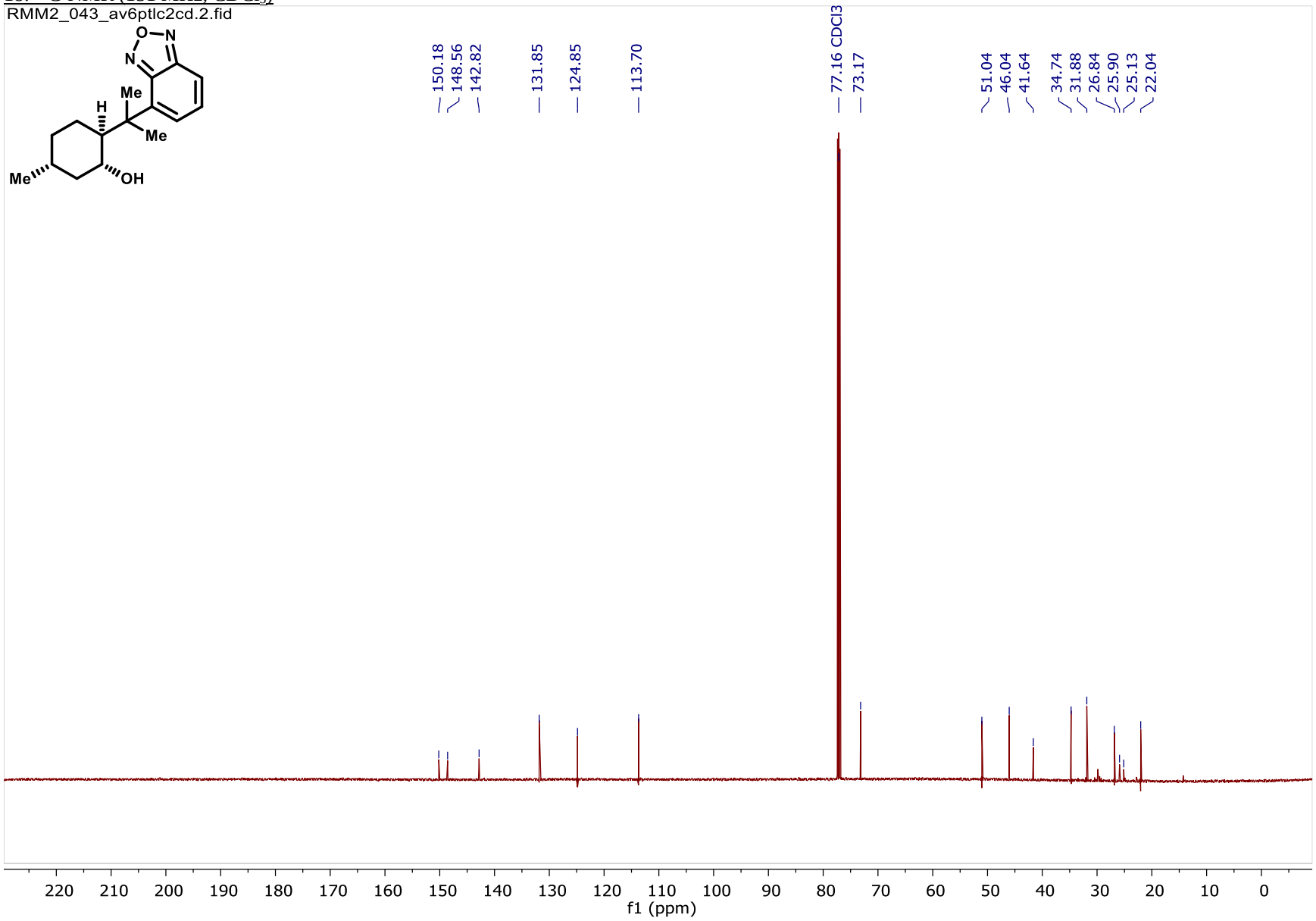


18: ^{1}H-NMR (600 MHz, $CDCl_3$)

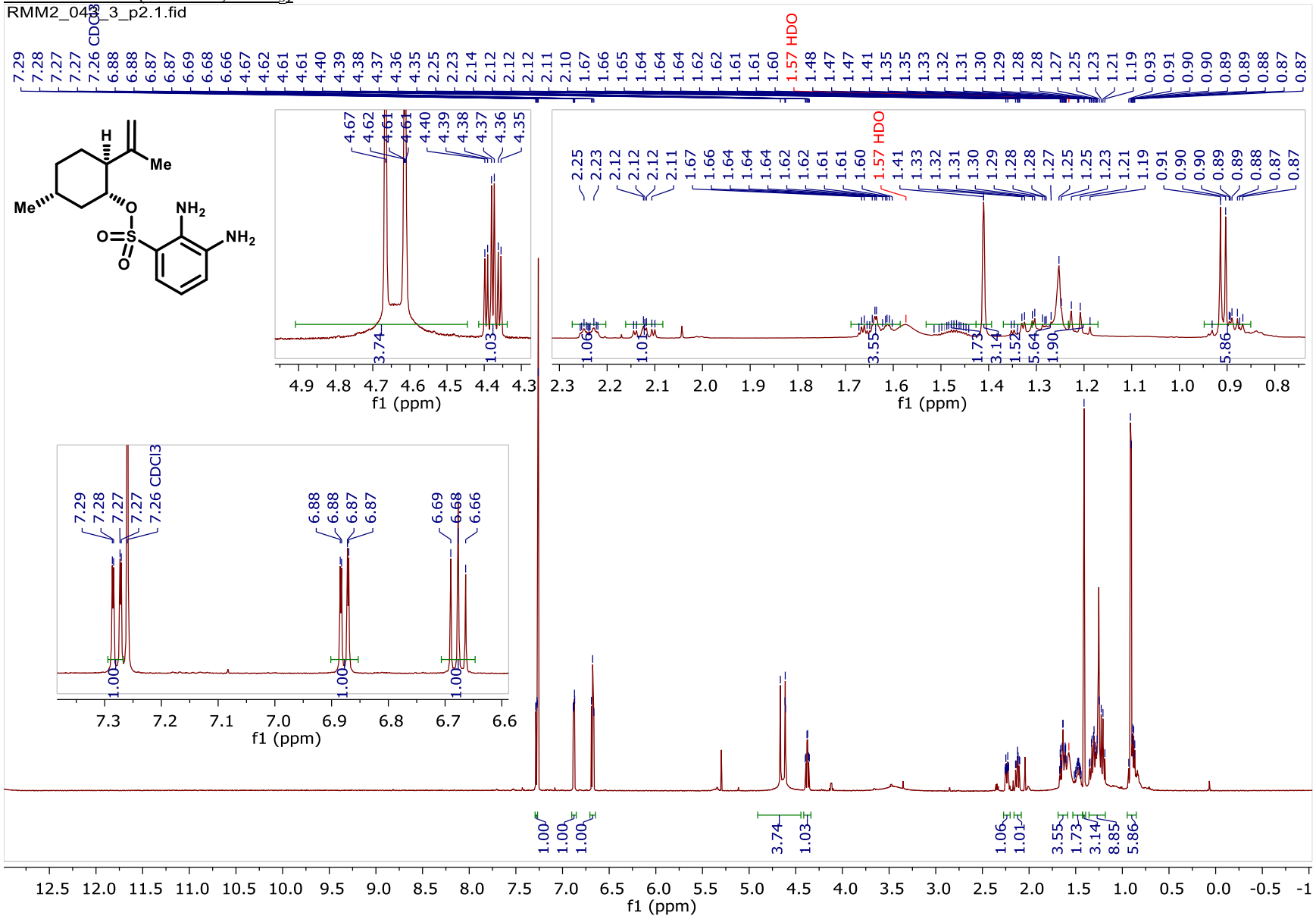


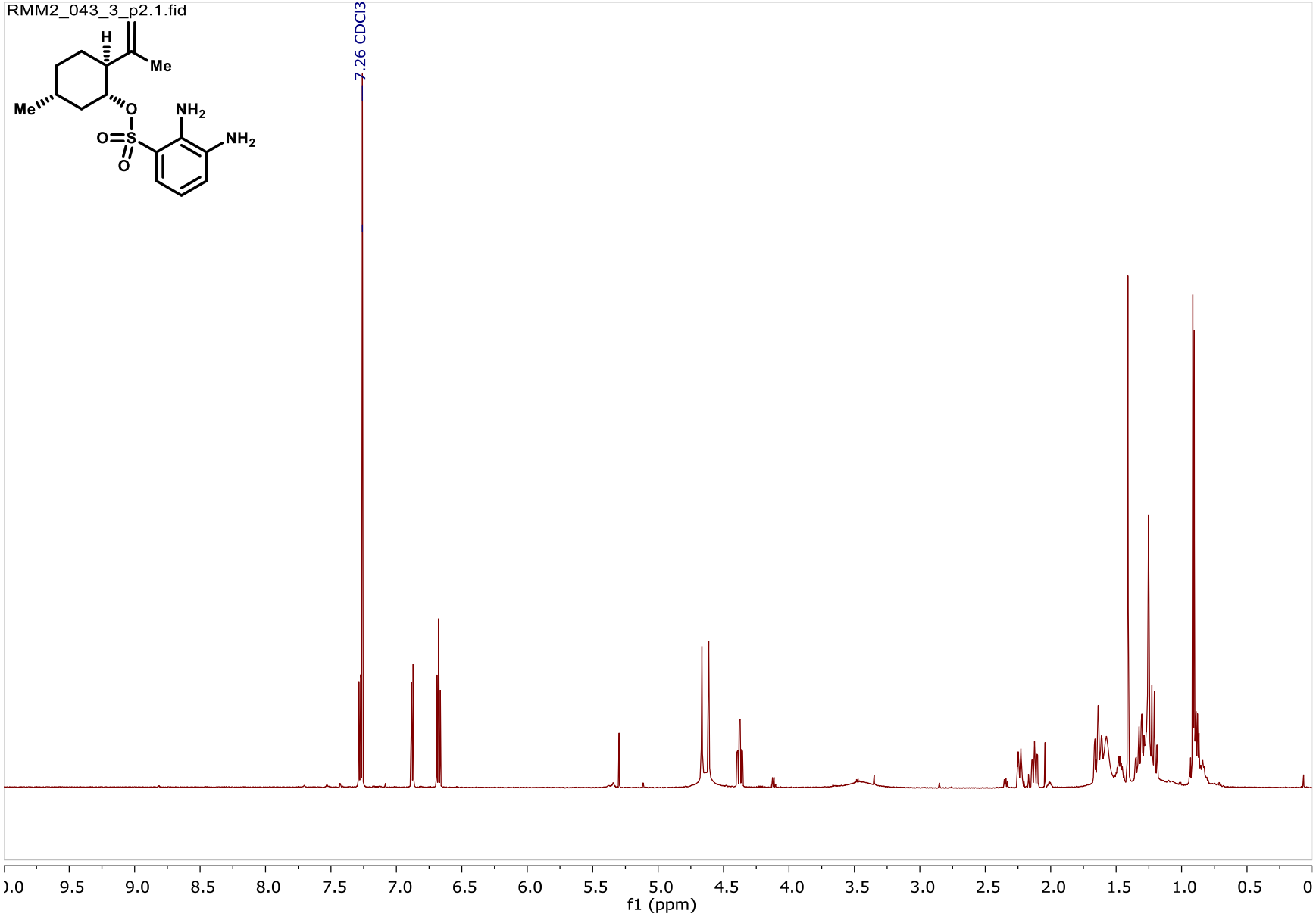

RMM2_043_av6ptlc2cd.1.fid
7.26 CDCl3
O
N
N
Me
H
Me
Me
OH
f1 (ppm)

18: ^{13}C-NMR (151 MHz, $CDCl_3$)

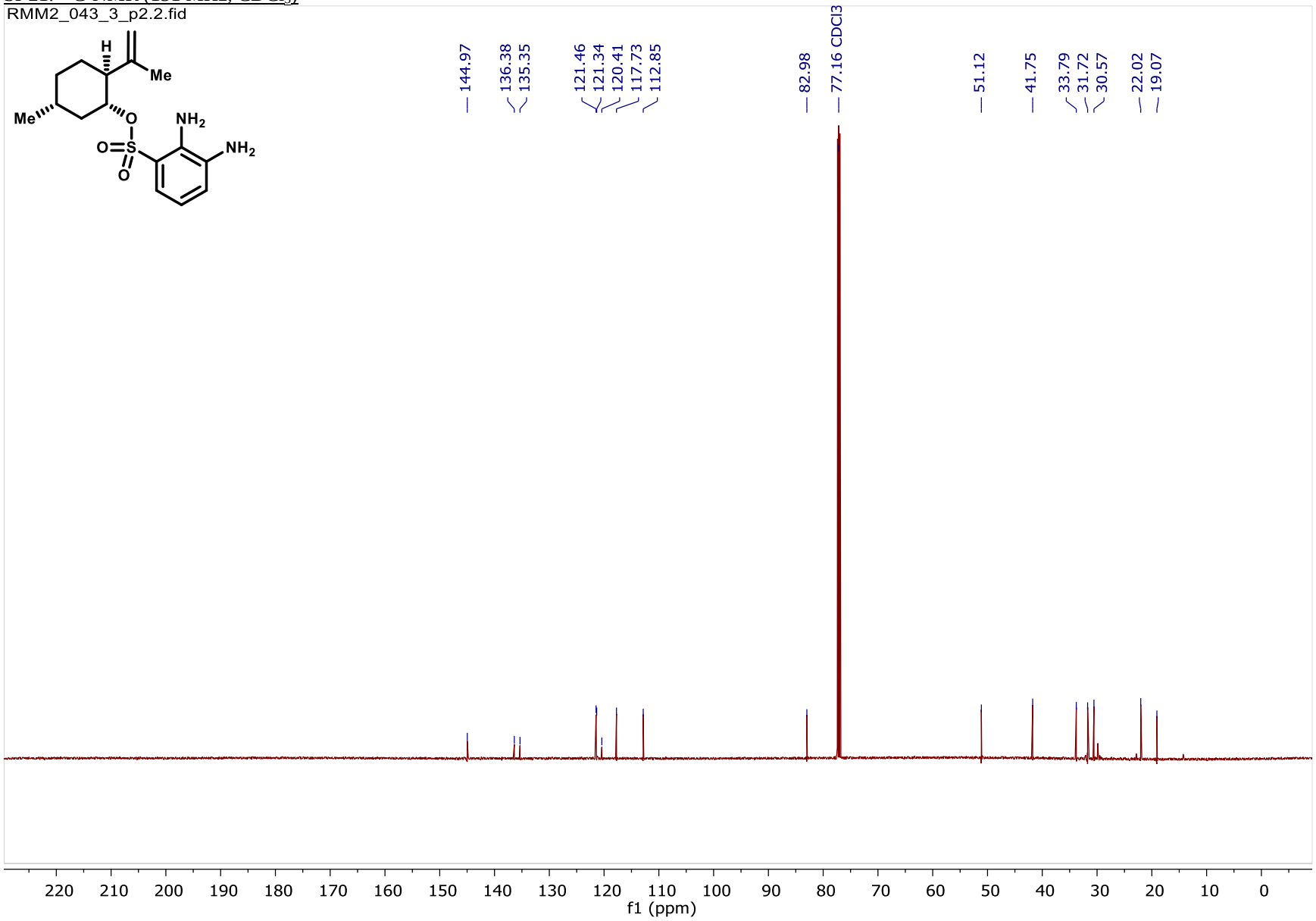


SI-21: ^{1}H-NMR (600 MHz, $CDCl_3$)

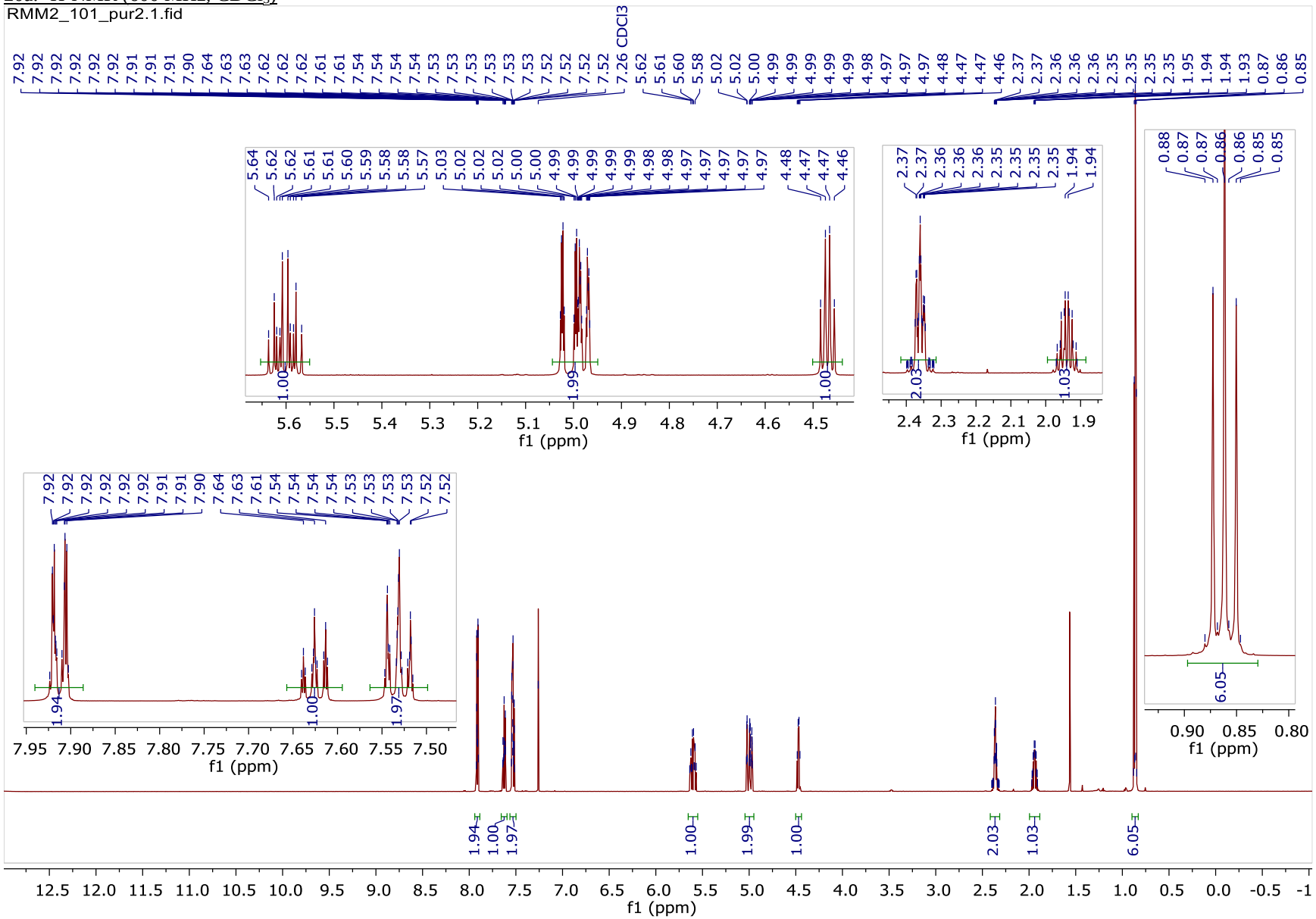


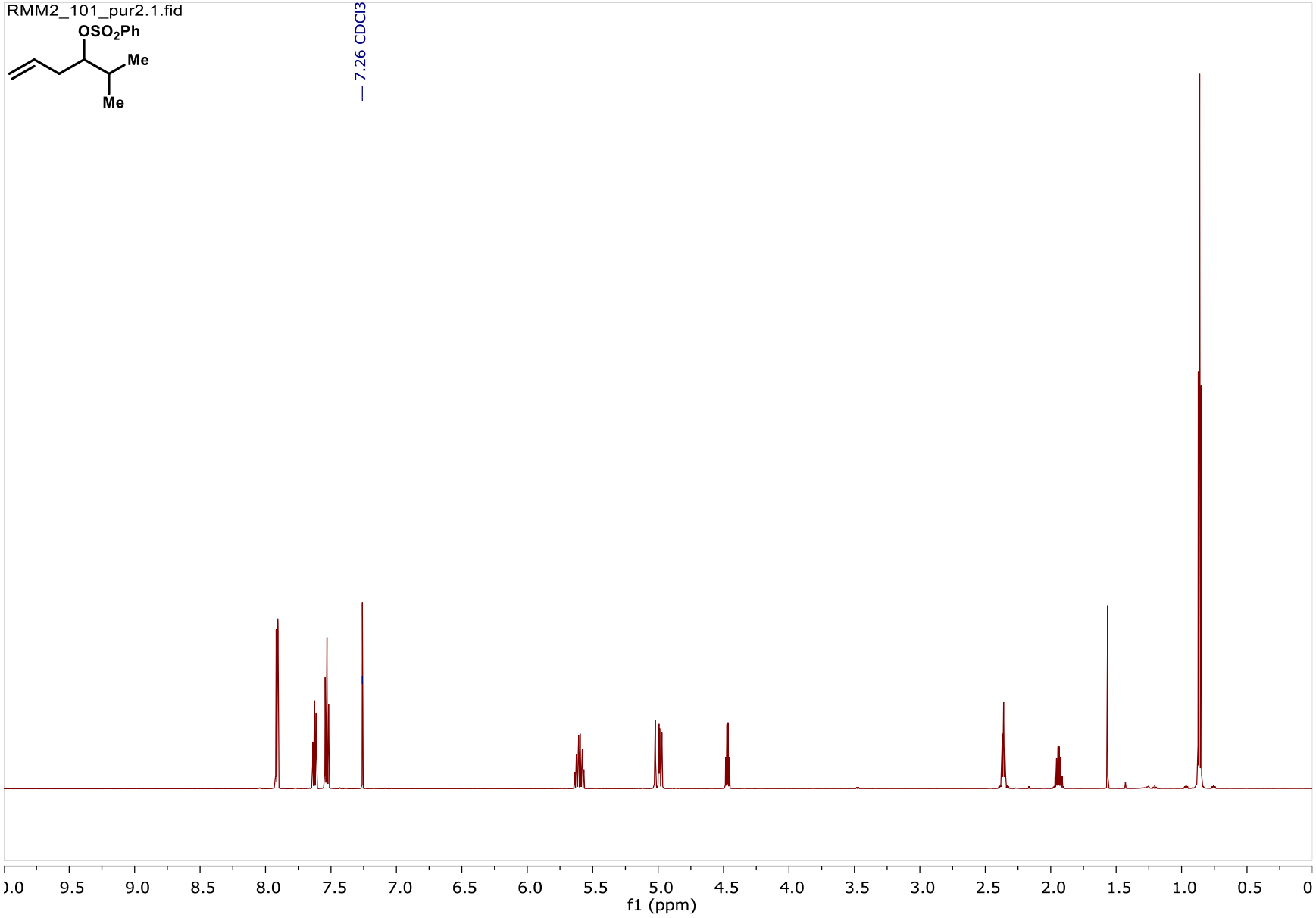

RMM2_043_3_p2.1.fid
7.26 CDCl3
H
Me
Me
O
NH2
O=S
NH2
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

SI-21: ^{13}C-NMR (151 MHz, $CDCl_3$)

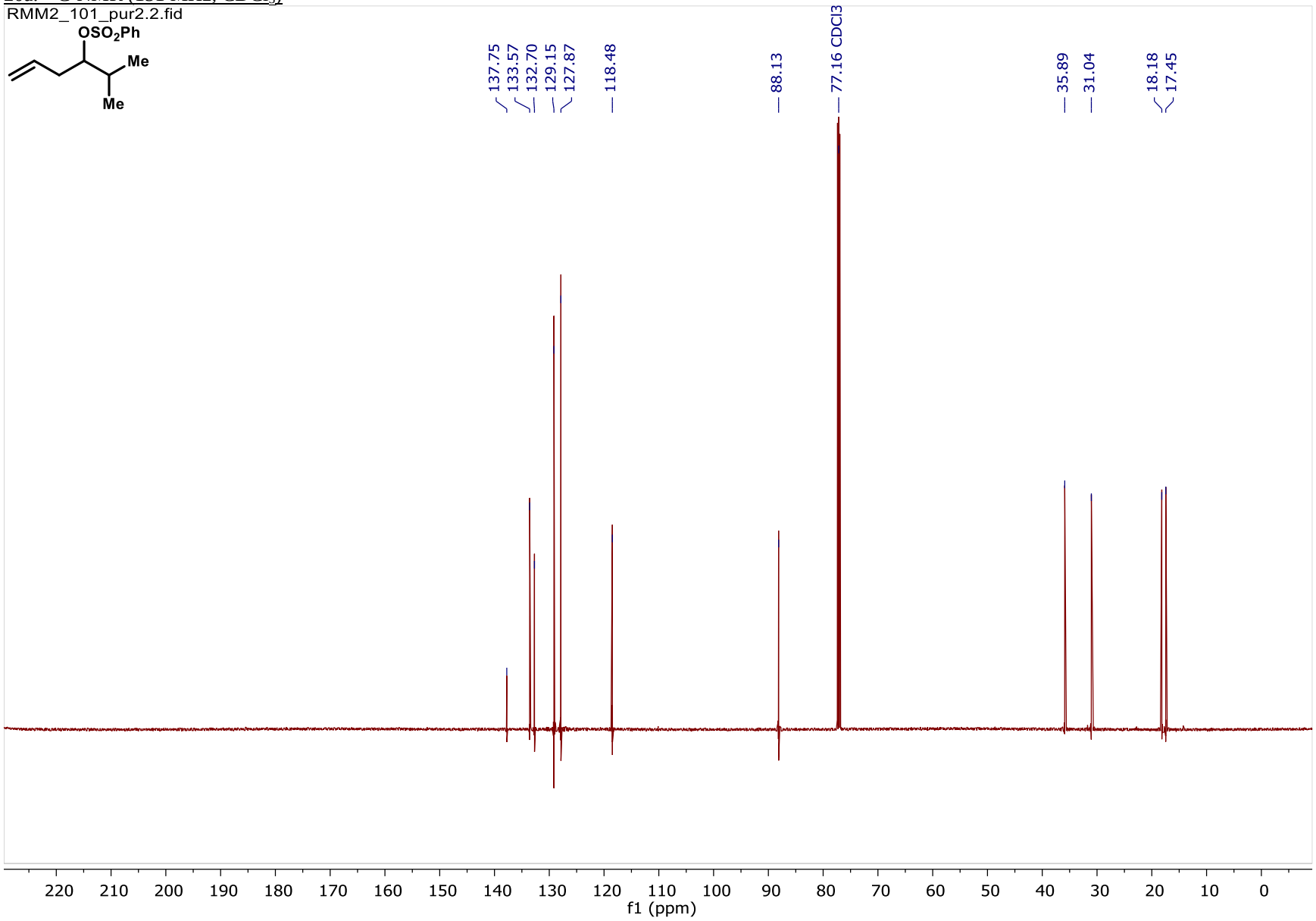


20a: ^{1}H-NMR (600 MHz, $CDCl_3$)

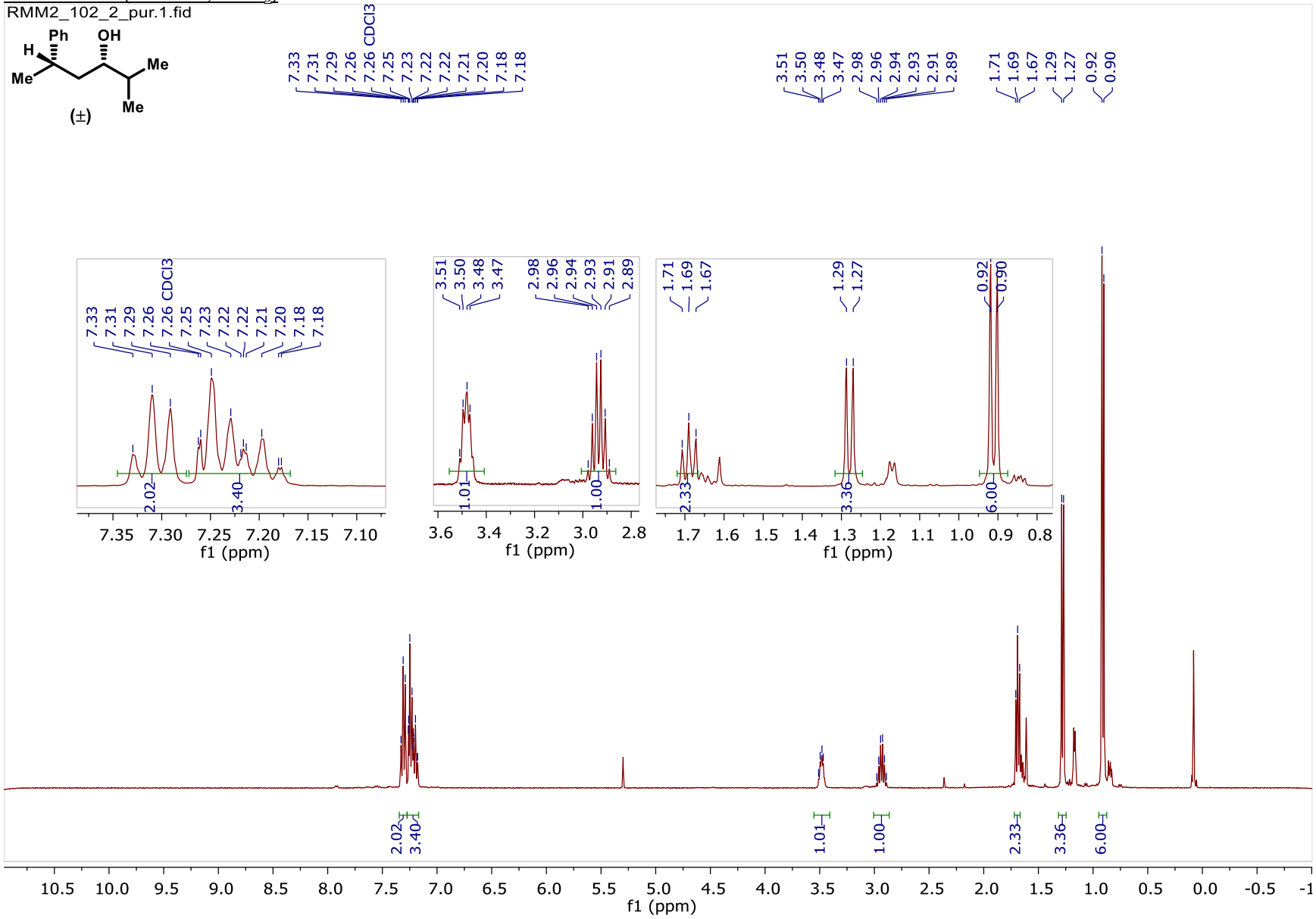


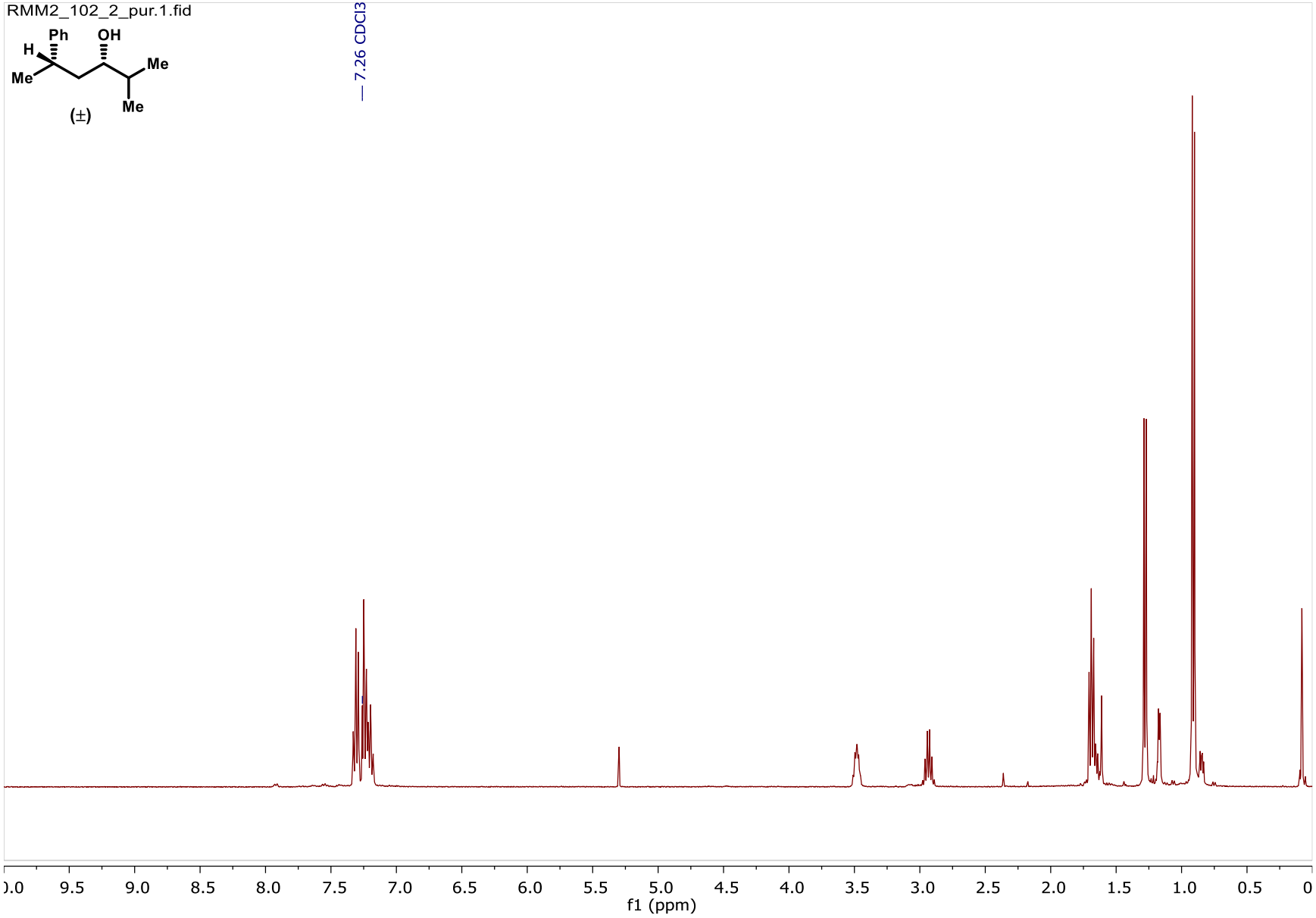

RMM2_101_pur2.1.fid
OSO2Ph
Me
Me
7.26 CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

20a: ^{13}C-NMR (151 MHz, $CDCl_3$)

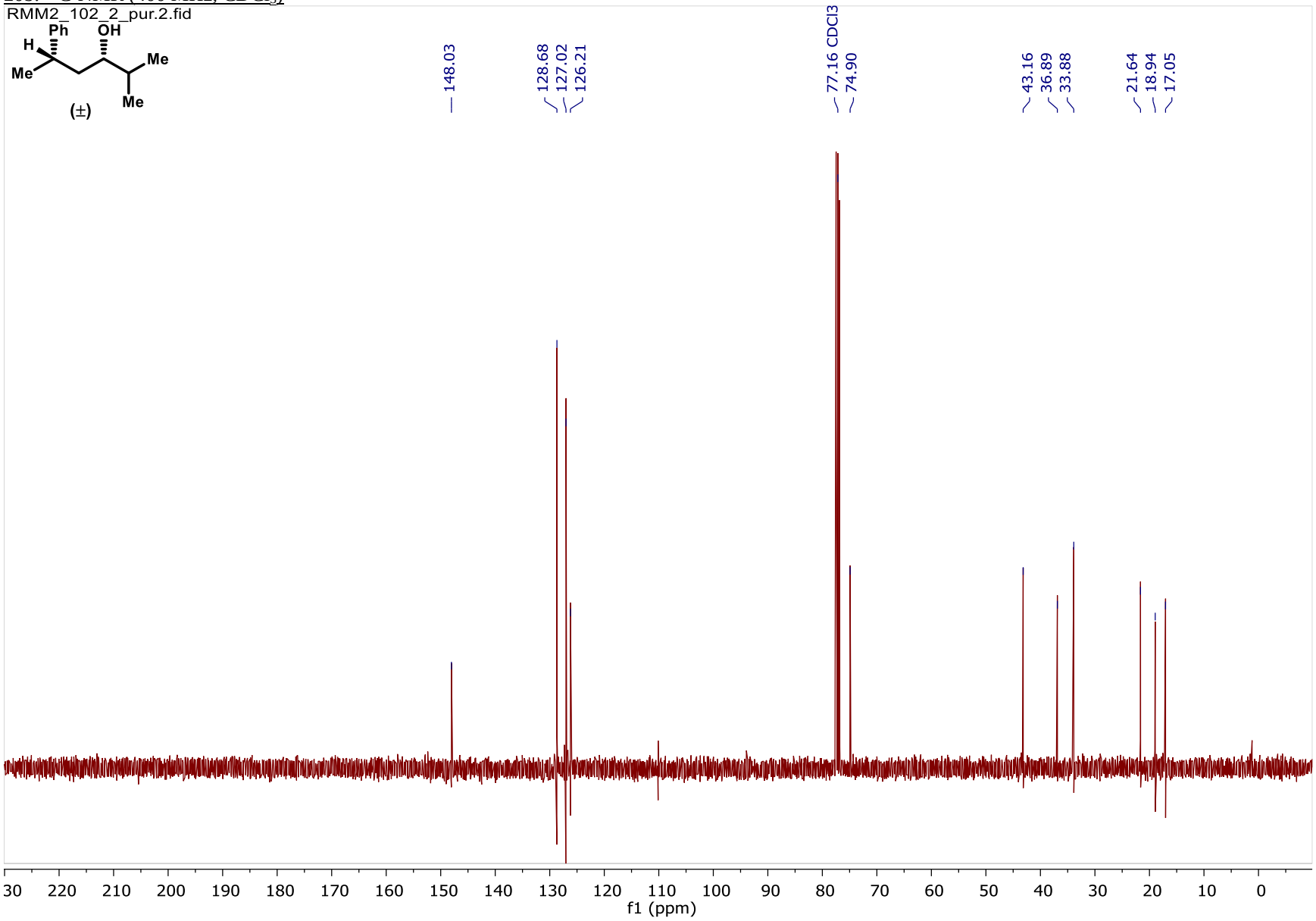


20b: ^{1}H-NMR (400 MHz, $CDCl_3$)

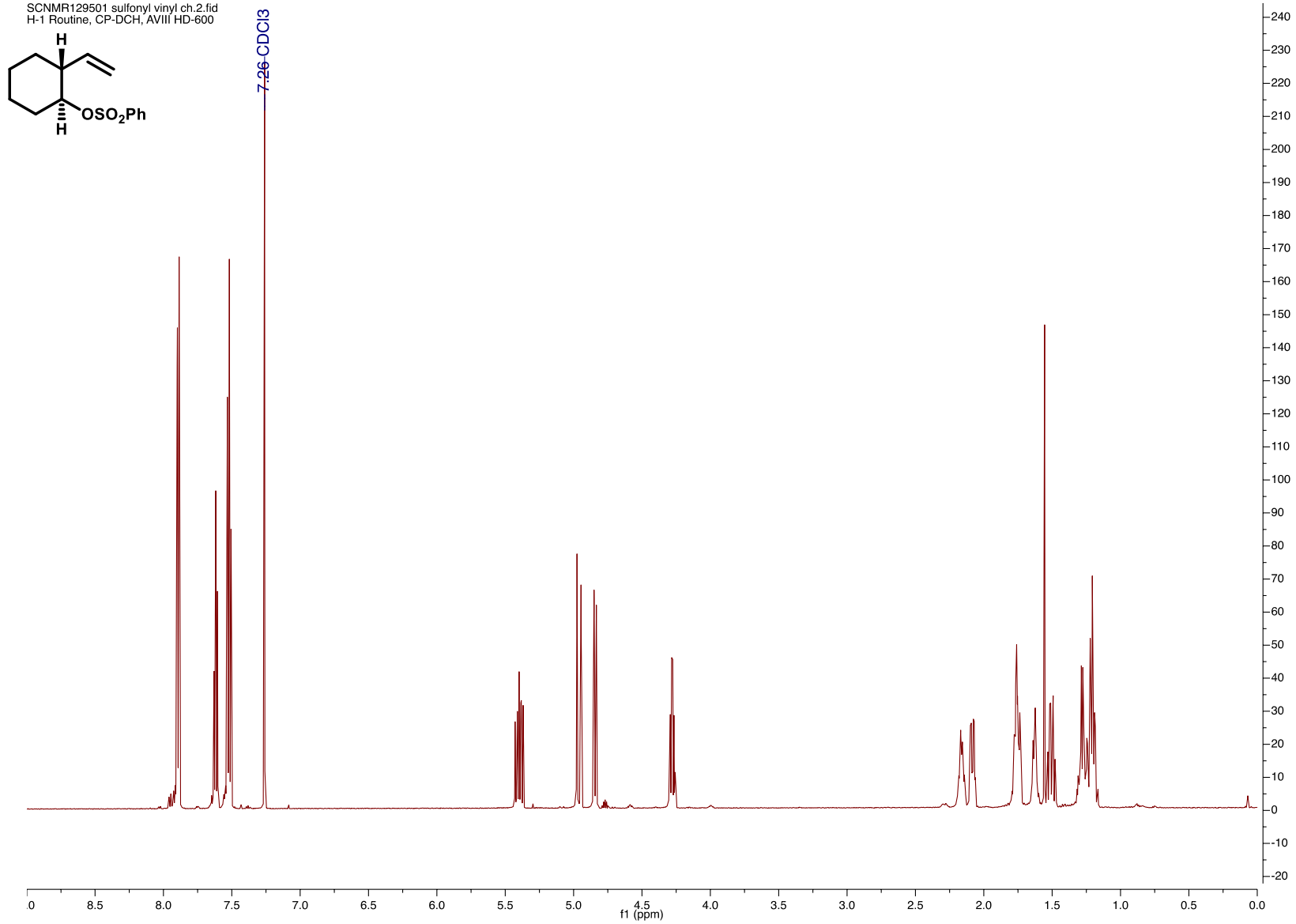


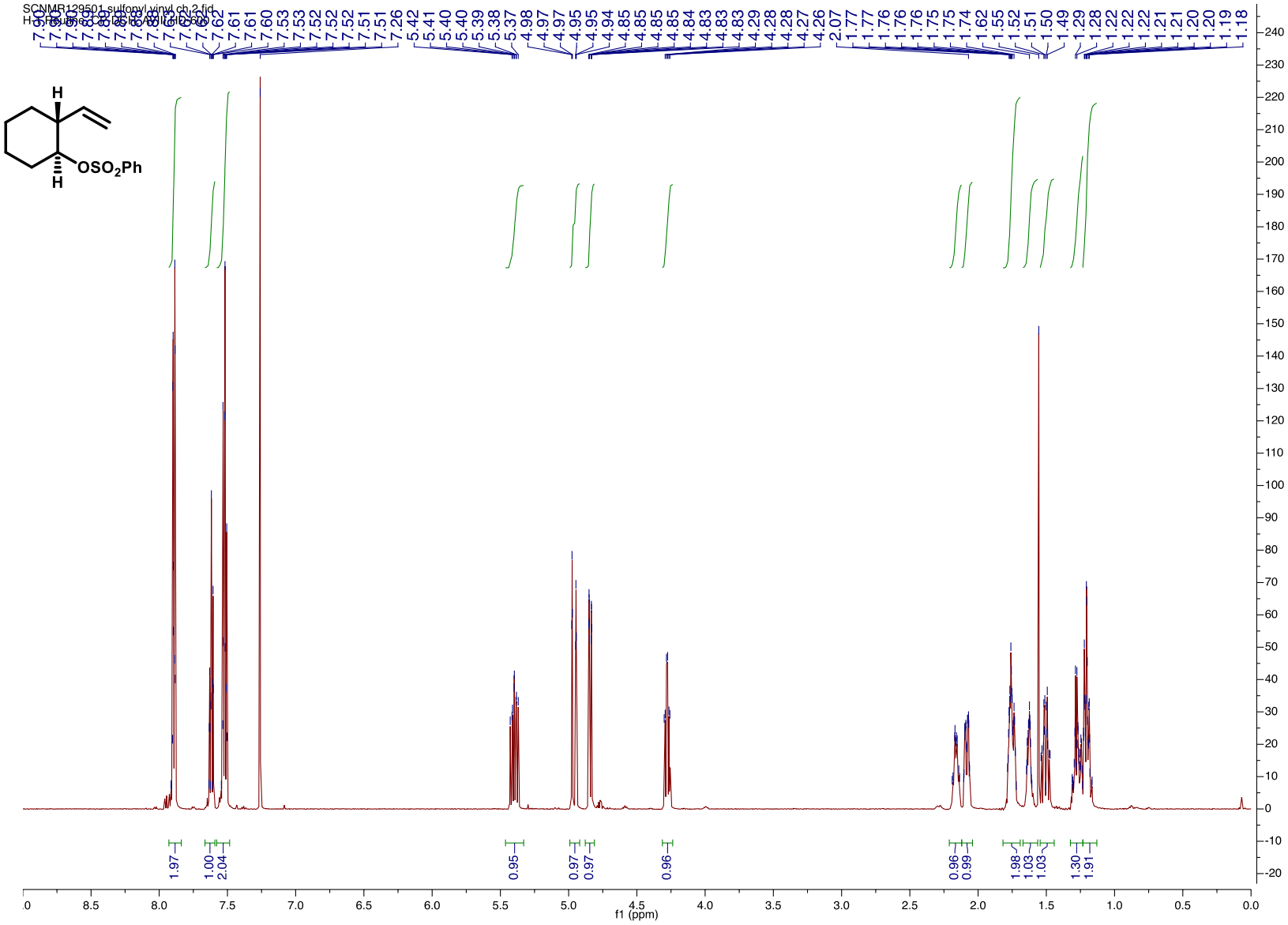

RMM2_102_2_pur.1.fid
Ph
OH
H
Me
Me
Me
(±)
7.26 CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

20b: ^{13}C-NMR (400 MHz, $CDCl_3$)

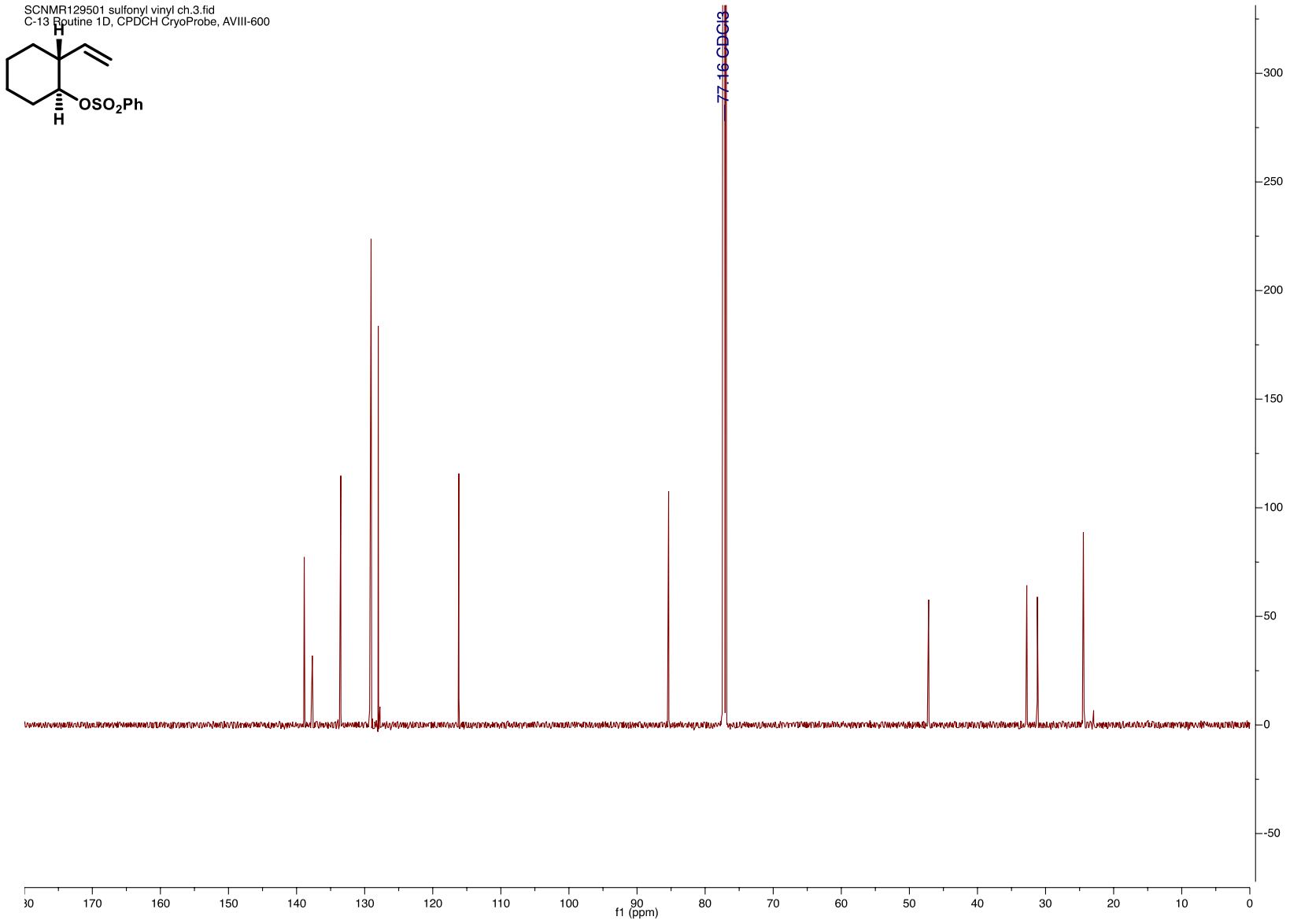


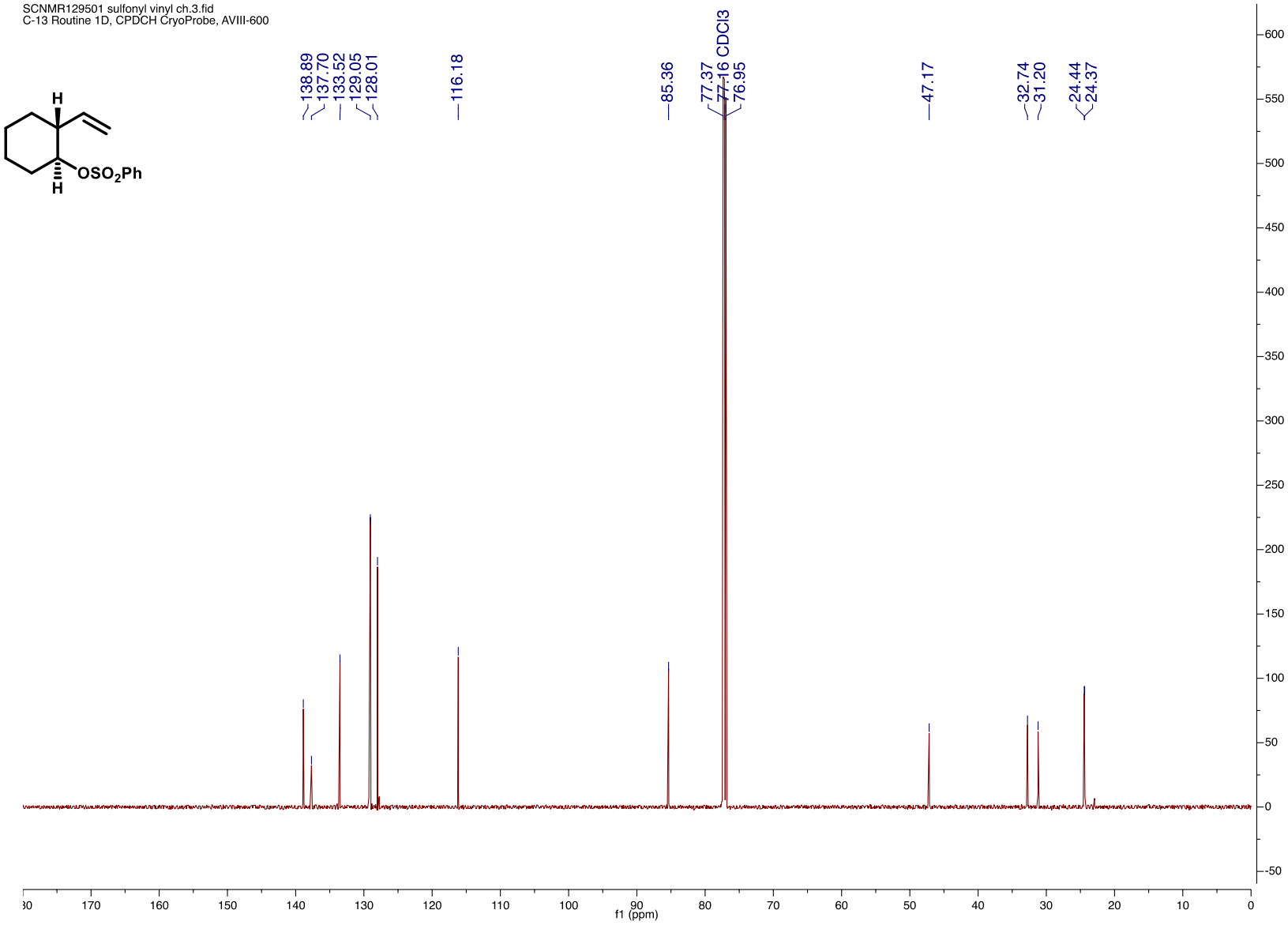
21a: ^{1}H-NMR


SCNMR129501 sulfonyl vinyl ch.2.fid
H-1 Routine, CP-DCH, AVIII HD-600
H
OSO2Ph
H
7.26-CDCl3
f1 (ppm)

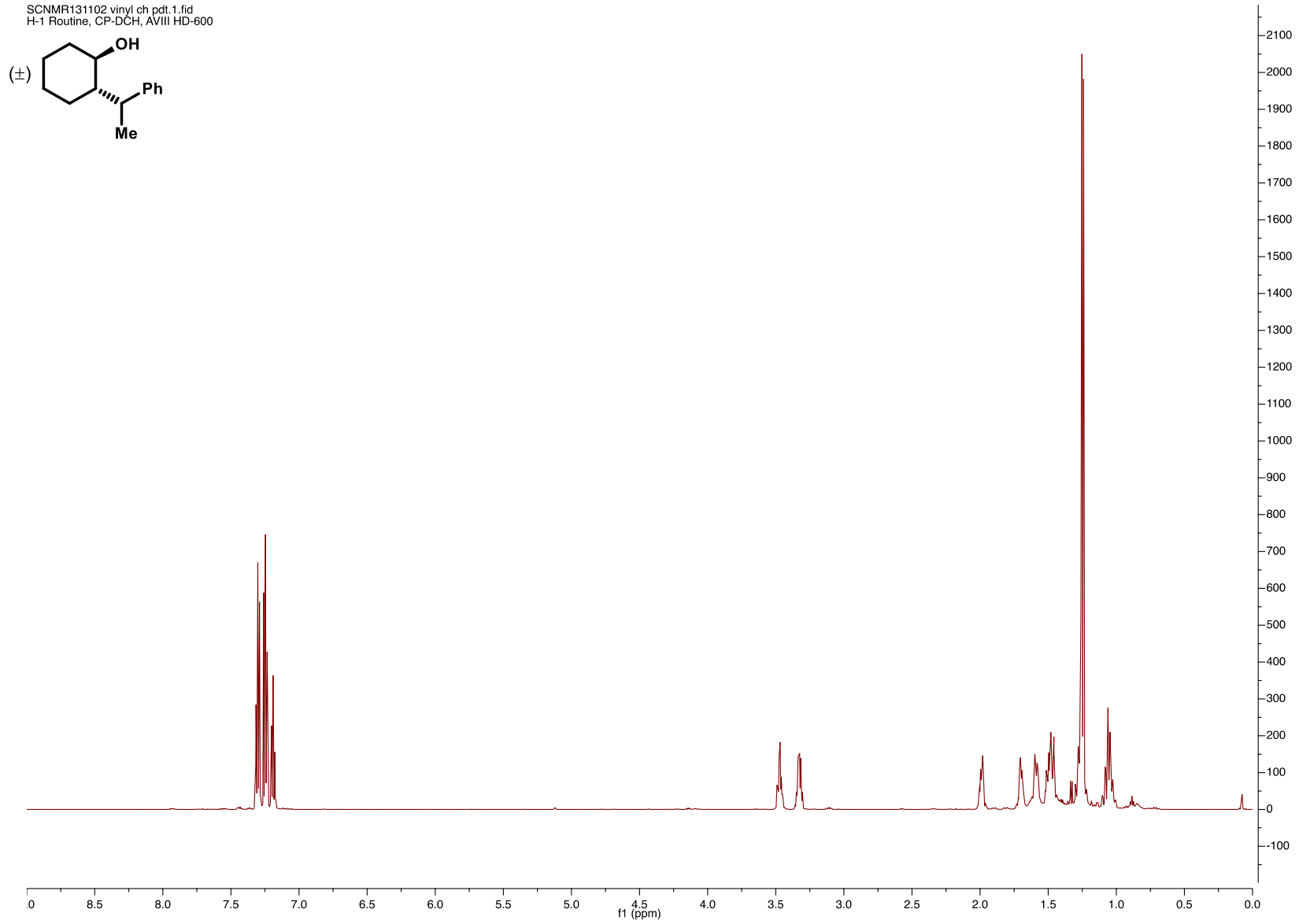

SCNMR129501 sulfonyl vinyl ch 2.fid
H-Routine 5 mm BBO 400S1 H-BB-D-05 Z SP
H
OSO2Ph
H
f1 (ppm)

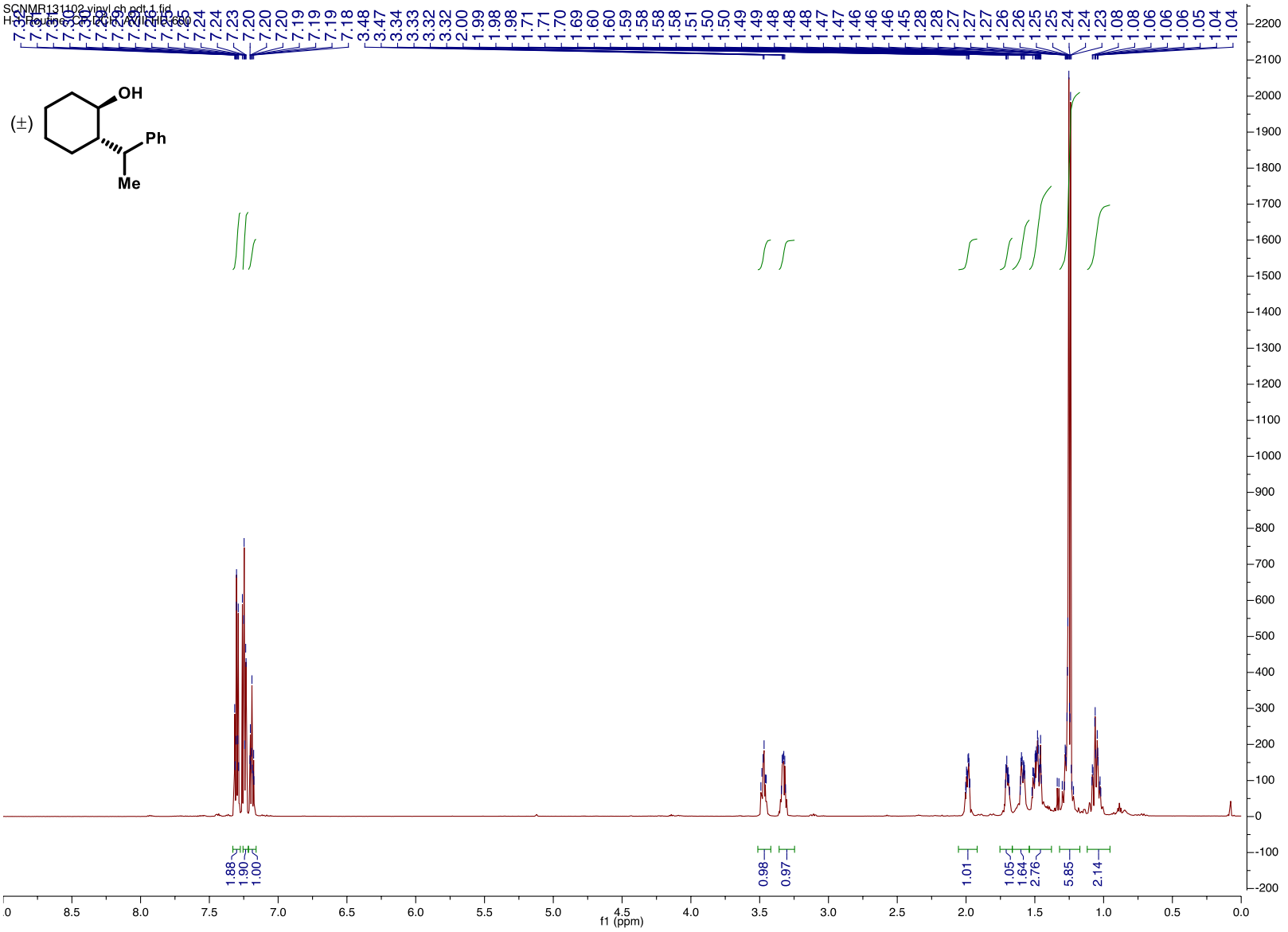
21a: ^{13}C-NMR


SCNMR129501 sulfonyl vinyl ch.3.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
H
OSO2Ph
H
77.16 CDCl3
300
250
200
150
100
50
0
-50
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

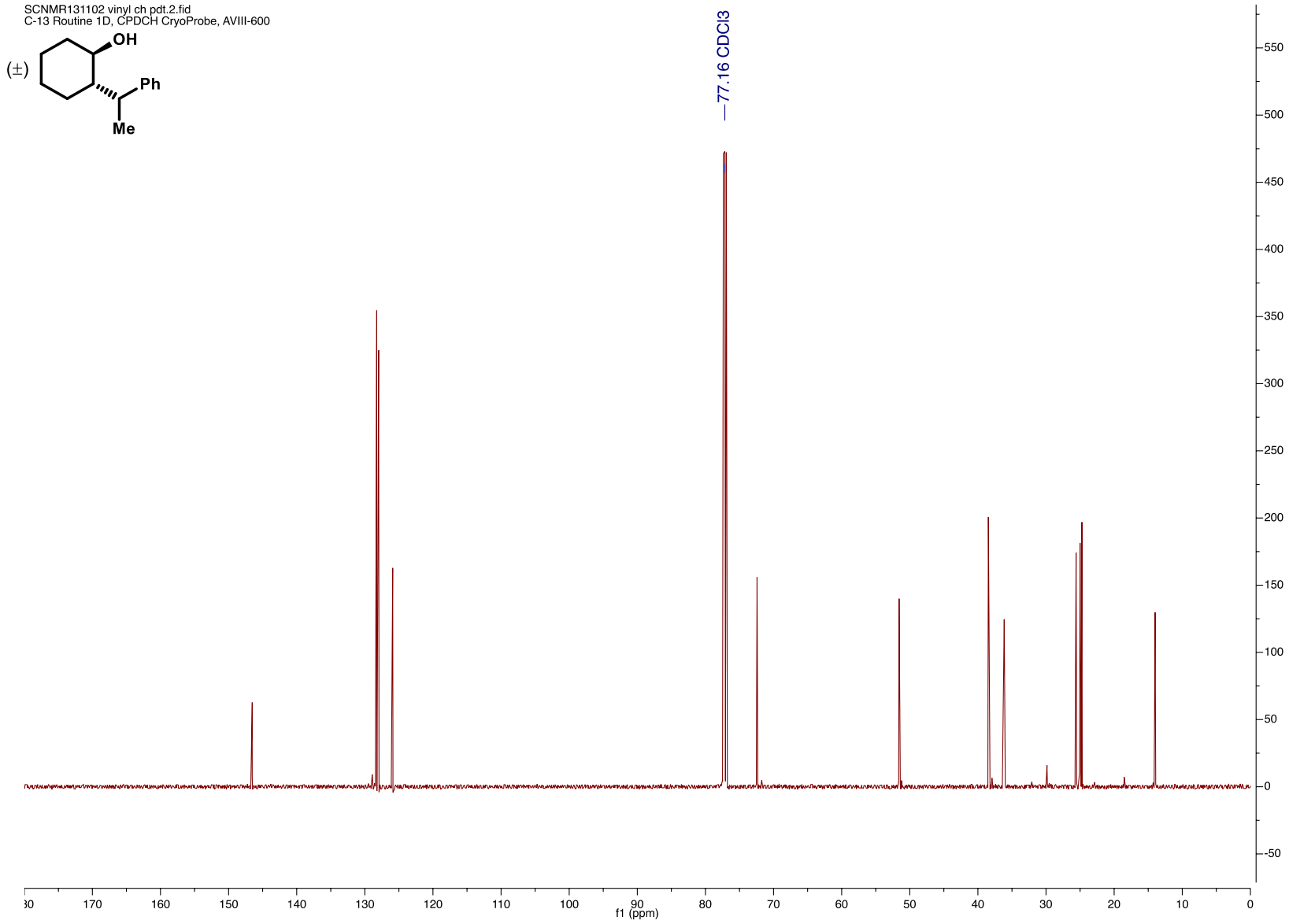

SCNMR129501 sulfonyl vinyl ch.3.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
H
OSO2Ph
H
138.89
137.70
133.52
129.05
128.01
116.18
85.36
77.37
77.16 CDCl3
76.95
47.17
32.74
31.20
24.44
24.37
f1 (ppm)

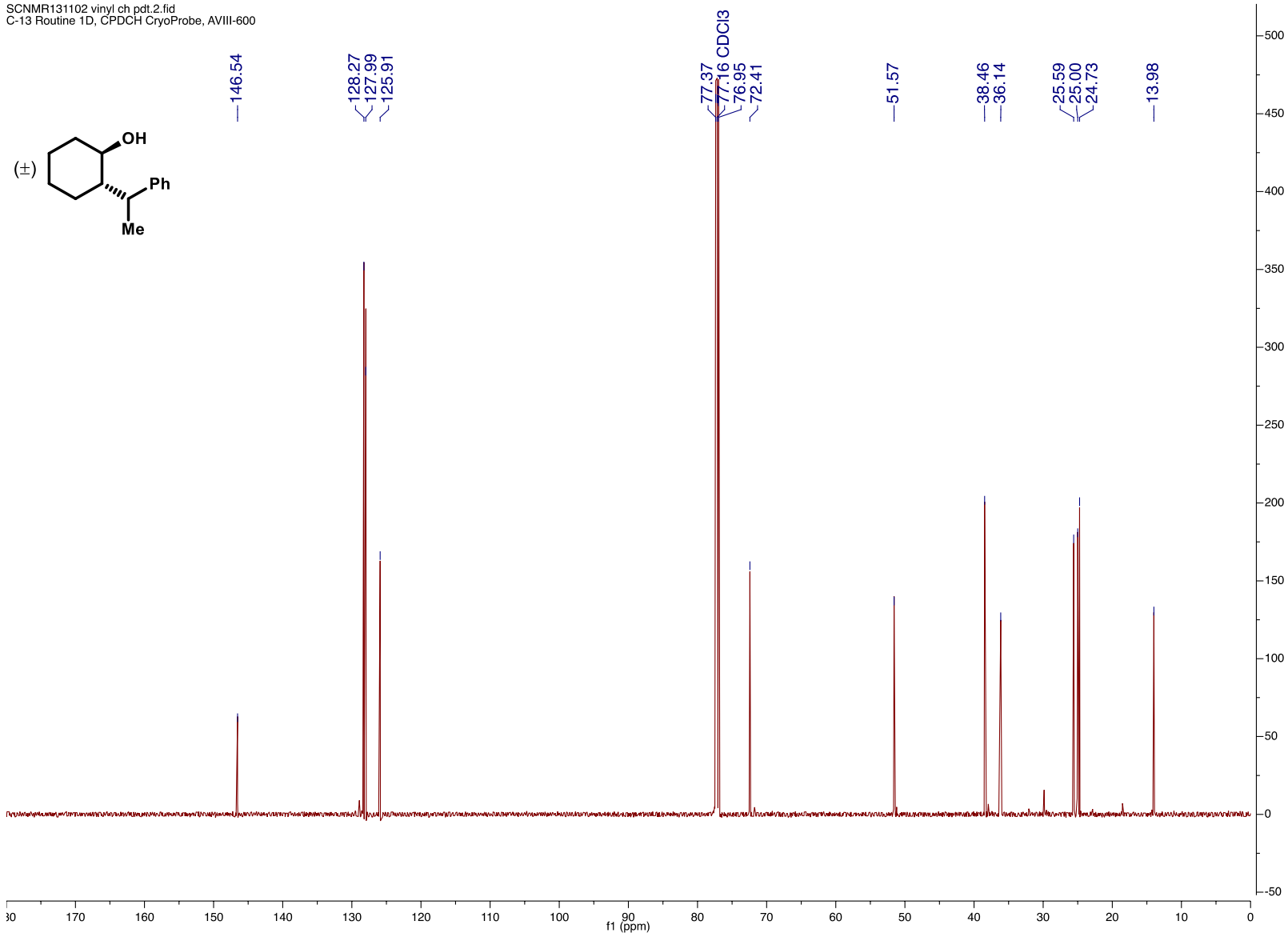
21b: ^{1}H-NMR


SCNMR131102 vinyl ch pdt.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
(±)
OH
Ph
Me
f1 (ppm)

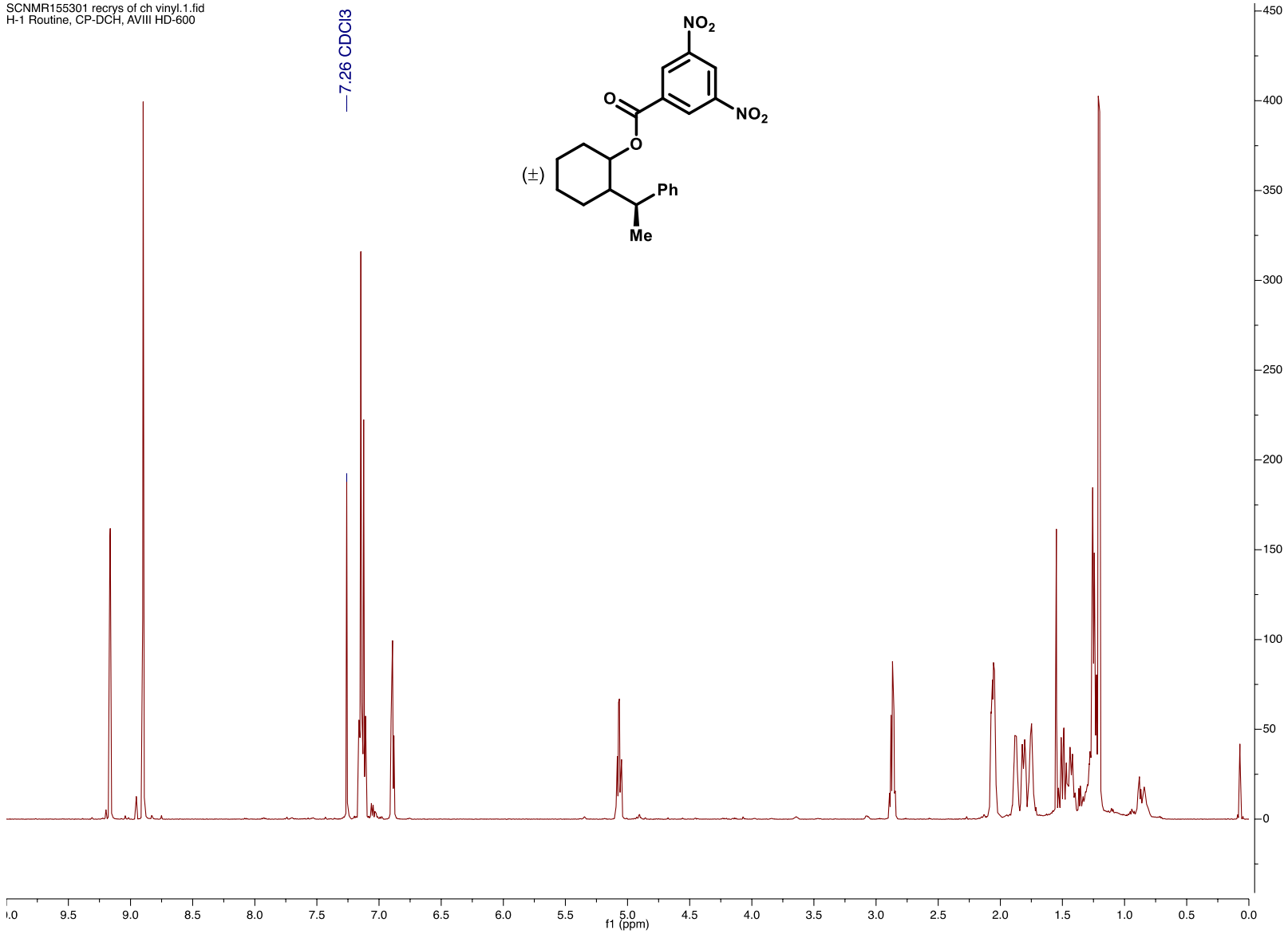

SCNMR131102 vinyl ch pdt 1 fid
(±)
OH
Ph
Me
1.88
1.90
1.00
0.98
0.97
1.01
1.05
1.64
2.76
5.85
2.14
f1 (ppm)

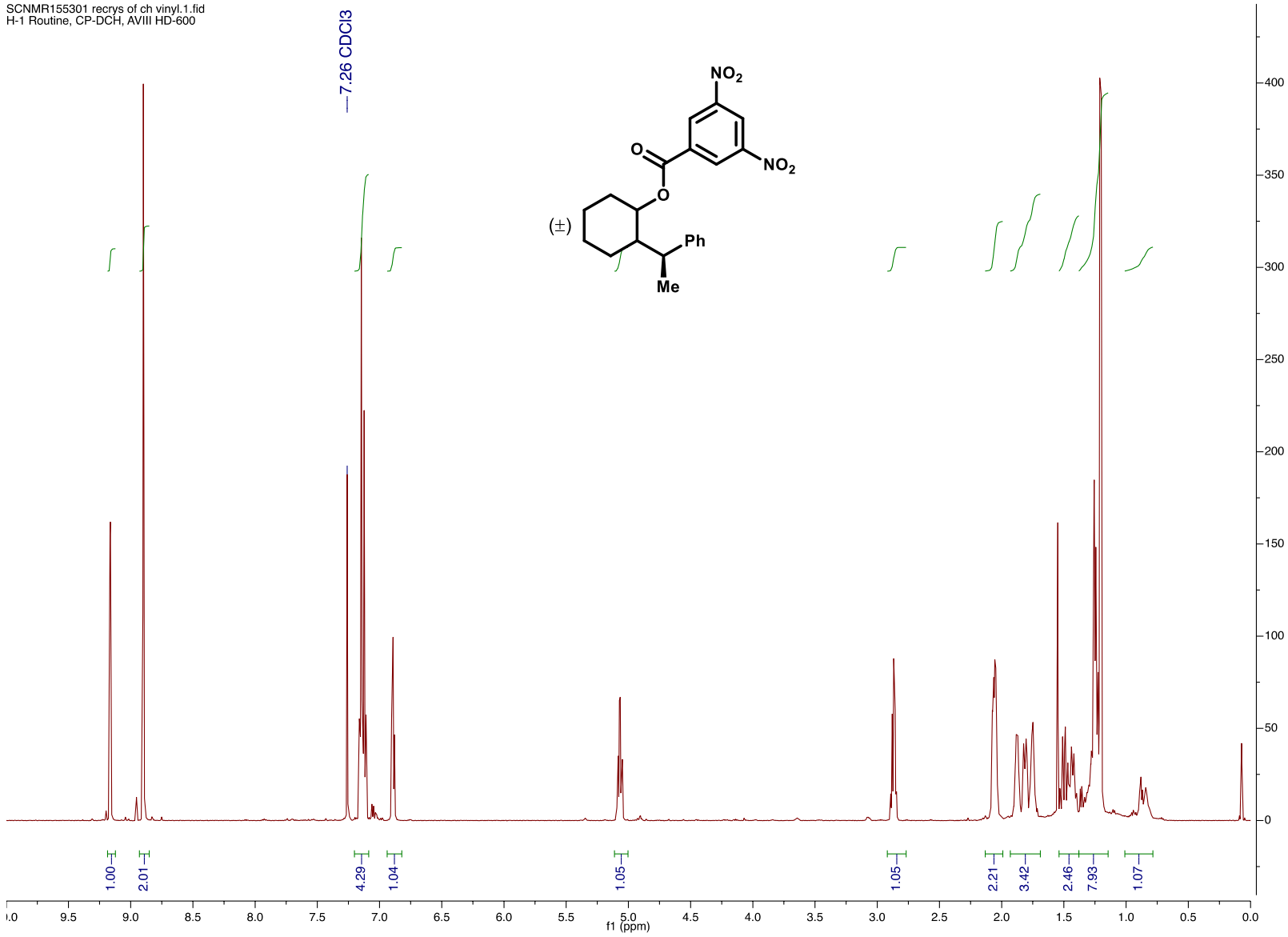
21b: ^{13}C-NMR


SCNMR131102 vinyl ch pdt.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
(±)
OH
Ph
Me
77.16 CDCl3
f1 (ppm)

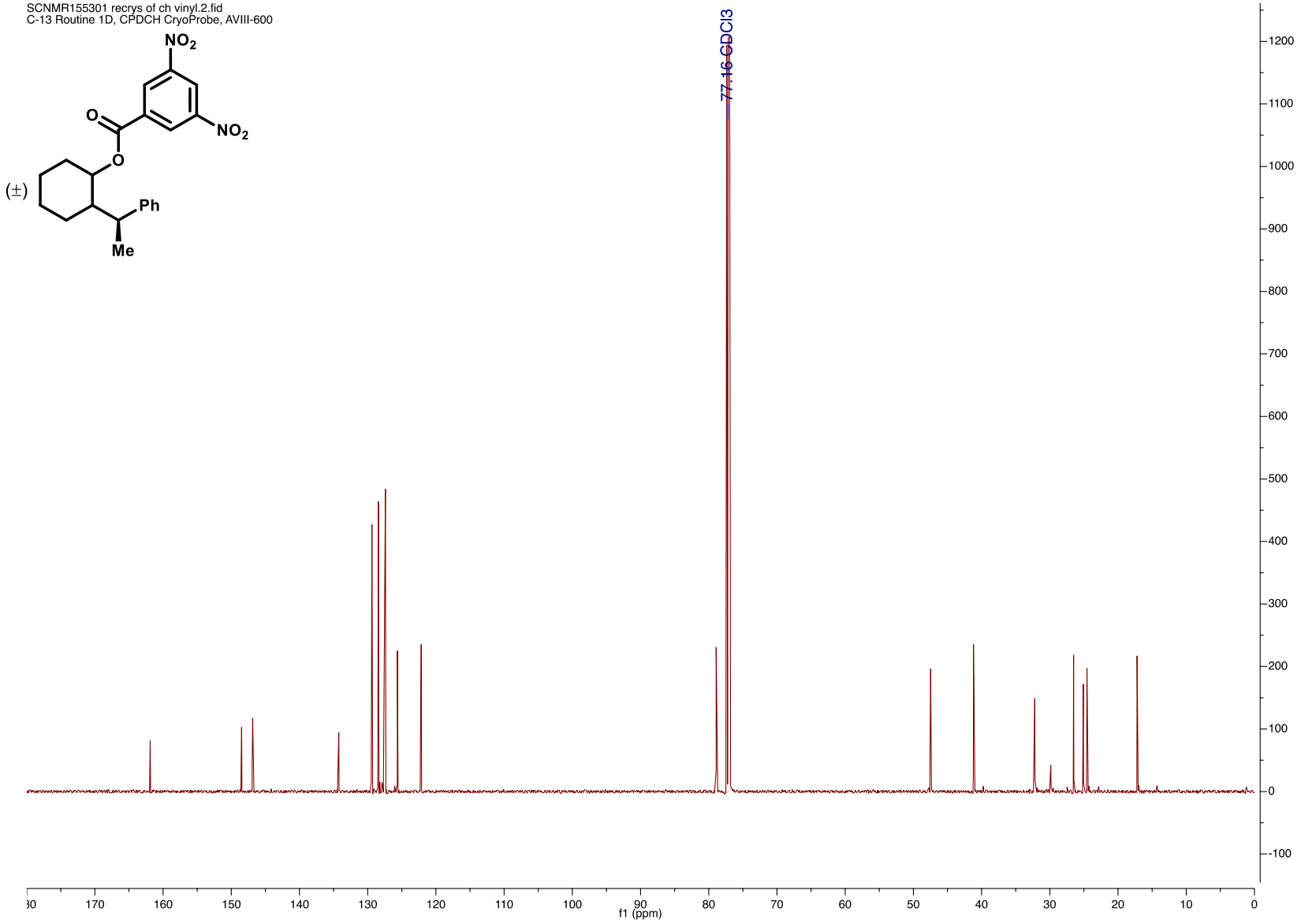

SCNMR131102 vinyl ch pdt.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
146.54
128.27
127.99
125.91
77.37
77.16 CDCl3
76.95
72.41
51.57
38.46
36.14
25.59
25.00
24.73
13.98
(±)
OH
Ph
Me
f1 (ppm)

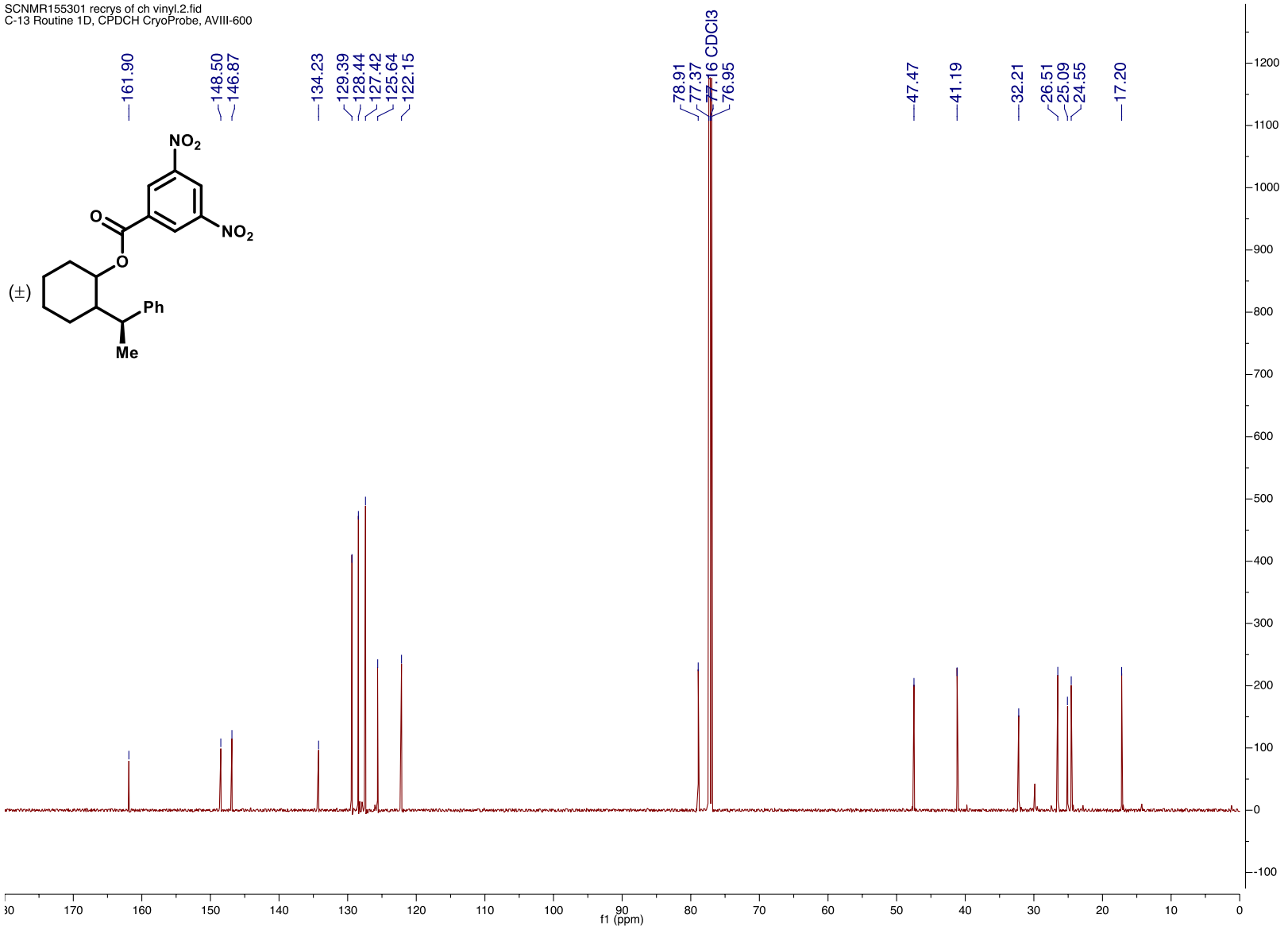
SI-23: ^{1}H-NMR


SCNMR155301 recrys of ch vinyl.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
NO2
NO2
O
O
(±)
Ph
Me
f1 (ppm)


SCNMR155301 recrys of ch vinyl.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.26 CDCl3
NO2
NO2
O
O
(±)
Ph
Me
1.00
2.01
4.29
1.04
1.05
1.05
2.21
3.42
2.46
7.93
1.07
f1 (ppm)

SI-23: ^{13}C-NMR


SCNMR155301 recrys of ch vinyl.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
NO2
NO2
O
O
(±)
Ph
Me
77.16 CDCl3
f1 (ppm)


SCNMR155301 recrys of ch vinyl.2.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
161.90
148.50
146.87
134.23
129.39
128.44
127.42
125.64
122.15
78.91
77.37
77.16 CDCl3
76.95
47.47
41.19
32.21
26.51
25.09
24.55
17.20
NO2
NO2
O
O
(±)
Ph
Me
f1 (ppm)