Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information:

Iron-catalysed Alkene and Heteroarene H/D Exchange by Reversible Protonation of Iron-hydride Intermediates

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1. General Experimental

***Reaction Setup*:** All reactions were performed in oven (185 °C) and/or flamed-dried glassware under an atmosphere of anhydrous nitrogen or argon, unless otherwise indicated. All air- and moisture sensitive reactions were carried out using standard vacuum line and Schlenk techniques, or in a glovebox with a purified argon atmosphere. All glassware was cleaned using base (KOH, ^{i}PrOH) and acid (HCl_{aq}) baths. All reported reaction temperatures correspond to external bath temperatures. Room temperature (r.t) was approximately 16-19 °C. "Brine" refers to a saturated solution of sodium chloride in H_2O.

***NMR Spectroscopy*:** ^{1}H, ^{2}H, ^{11}B, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on Bruker Avance III 400 and 500 MHz; Bruker AVI 400 MHz; Bruker Avance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent peak ($CHCl_3$: 7.27 ppm, 77.00 ppm; CH_2Cl_2: 5.32 ppm, 54.00 ppm; d_8-THF: 1.73 ppm, 25.37; CD_3CN: 1.94 ppm, 1.39 ppm). Multiplicities are indicated by app. (apparent), br. (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet). Coupling constants, *J*, are reported in Hertz and rounded to the nearest 0.1 Hz. Integration is provided and assignments are indicated. ^{1}H and ^{13}C assignments are corroborated through 2-D NMR experiments (COSY, HSQC, HMBC).

***Infrared Spectroscopy*:** Infra-red (IR) spectra were recorded on a Shimadzu IRAffinity-1 spectrometer (model no. A213749) spectrometer. Relevant peaks are reported in cm^{-1}.

***Mass Spectrometry*:** Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry, Mass Spectrometry Laboratory. High-resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Electron Impact (EI^+) spectra were performed at 70 eV using methane as the carrier gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Chemical Ionization (CI^+) spectra were performed with methane reagent gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Electrospray Ionization (ESI^+) spectra were performed using a time-of-flight (TOF) mass analyzer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

***Melting Points*:** Melting points (mp) were determined on a Stuart Scientific SMP10 melting point apparatus in capillary tubes and are uncorrected.

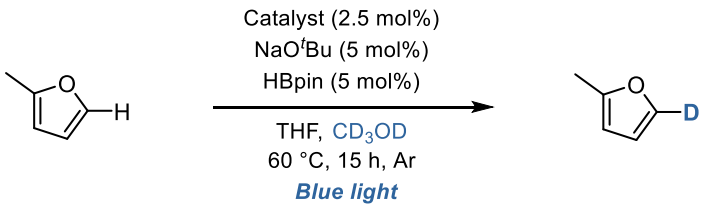
***Chromatography*:** Analytical thin-layer chromatography was performed on aluminium-backed silica plates (Merck 60 F_{254}). Pet. ether refers to petroleum ether 40-60. Product spots were visualised by UV light at 254 nm, and subsequently developed using potassium permanganate solution if appropriate. Flash column chromatography was performed on silica gel (Merck Kielselgel 60, 40-63 μm) unless otherwise stated.

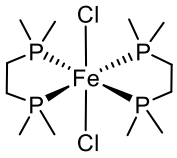
***Solvents*:** All solvents for air- and moisture sensitive techniques were obtained from an anhydrous solvent system (Innovative Technology). Anhydrous d_8-tetrahydrofuran was distilled from sodium/benzophenone. d_4-Methanol was purchased from Cambridge Isotope Laboratories and used as received. d_3-Methanol (CD_3OH) and d_1-methanol (CH_3OD) were purchased from Euriso-top and used as received. Reaction solvents tetrahydrofuran (THF) (Fisher, HPLC grade), ether (Et_2O) (Fisher, BHT stabilized ACS grade), and dichloromethane (CH_2Cl_2) (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvent toluene (ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Reaction solvent ethanol (absolute, VWR) was used as received. Solvents for filtration, transfers, chromatography, and recrystallization were dichloromethane (CH_2Cl_2) (ACS grade, amylene stabilized), ether (Et_2O) (Fisher, BHT stabilized ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), hexane (Optima), methanol (MeOH) (ACS grade), pentane (ACS grade), and petroleum ether (40–60°C, ACS grade).

***Chemicals*:** All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros organics, Tokyo Chemical Industries UK, Fluorochem and Apollo Scientific or synthesised within the laboratory. Iron(II) chloride was purchased from Strem Chemicals Inc. (UK); anhydrous iron(II) chloride, 98% (product number 93-2631. Lot 19226800, 44.00000% Fe, expect 44.059%). 1,2-Bis(dimethylphosphino)ethane (dmpe) was purchased from Sigma-Aldrich, Inc. (261939).

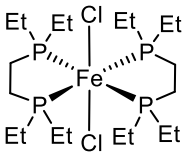
***Lamp*:** Kessil A160WE LED Aquarium Light - Tuna Blue

2. Table S1 - Choice of Pre-catalyst

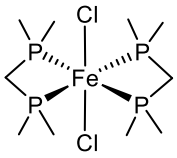




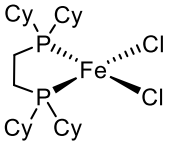
$dmpe_2FeCl_2$



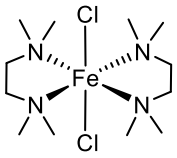
$depe_2FeCl_2$



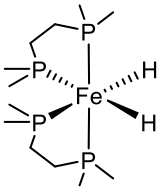
$dmpm_2FeCl_2$



$dcypeFeCl_2$



$tmeda_2FeCl_2$



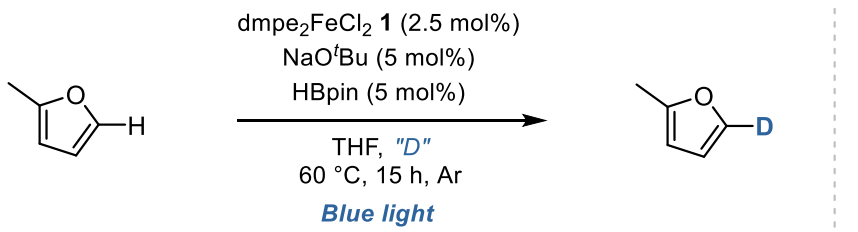
$dmpe_2FeH_2$

Entry	Catalyst	Deuterium incorporation (%)[a]
1	-	0
2	$dmpe_2FeCl_2$	97
3	$dmpe_2FeCl_2$ (2.0 mol%)	92
4	$dmpe_2FeCl_2$ (1.0 mol%)	92
5	$dmpe_2FeH_2$	88
6	dmpe (no Fe)	0
7	$FeCl_2$ (no dmpe)	0
8	$depe_2FeCl_2$	0
9	$dmpm_2FeCl_2$	0
10	$dcypeFeCl_2$	0
11	$tmeda_2FeCl_2$	0

[a]Reaction conditions: 2-methylfuran **3a** (0.33 mmol), [Fe] **1** (2.5 mol%), NaO^{t}Bu (5 mol%), HBpin (5 mol%), THF (0.2 mL), d_4-CD_3OD (0.2 mL), blue-light irradiation, 15 h.

Procedure: A 1.75 mL sample vial with screw-cap lid was loaded with [*Catalyst*] (8.2 µmol, 2.5 mol%) and NaO^{t}Bu (1.6 mg, 16.4 µmol, 5 mol%) before the addition of HBpin (1 drop, *ca.* 5 µL, 5 mol%), THF (0.2 mL) and CD_3OD (0.2 mL). Any remaining HBpin at this stage was destroyed by reaction with CD_3OD, releasing HD. 2-Methylfuran (30 µL, 0.33 mmol) was added and the vial sealed and irradiated. On completion, the vial was opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. Deuterium incorportation was determined by integration of residual proton 'H' resonances in the ^1H NMR spectra.

3. Table S2 - Choice of “D” Source



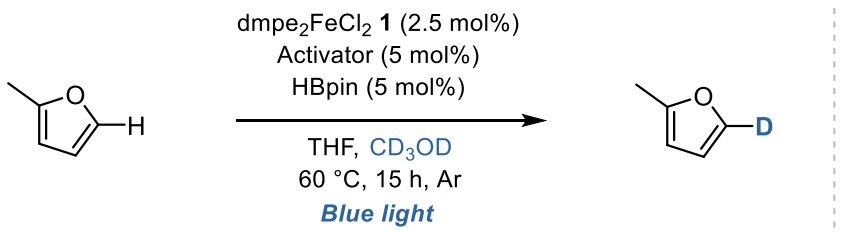
dmpe$_2$FeCl$_2$ **1**

Entry	“D” source	Deuterium incorporation (%)[a]
1	-	0
2	CD_3OD	97
3	CD_3OH	0
4	CH_3OD	90
5	d_1-EtOD	75
6	d_1-EtOD: CD_3OD 95:5	80
7	d_8-^{i}PrOD	38
8	d_1-^{t}BuOD	0
9	d_2-D_2O	18
10	d_6-acetone	0
11	d_6-benzene	0
12	d_3-acetonitrile	0
13	d_8-THF	5
14	d_6-DMSO	0

[a]Reaction conditions: 2-methylfuran **3a** (0.33 mmol), [Fe] **1** (2.5 mol%), NaO^{t}Bu (5 mol%), HBpin (5 mol%), THF (0.2 mL), *deuterium source* (0.2 mL), blue-light irradiation, 15 h.

Procedure: A 1.75 mL sample vial with screw-cap lid was loaded with [dmpe$_2$FeCl$_2$] **1** (3.5 mg, 8.2 µmol, 2.5 mol%) and NaO^{t}Bu (1.6 mg, 16.4 µmol, 5 mol%) before the addition of HBpin (1 drop, *ca.* 5 µL, 5 mol%), THF (0.2 mL) and *deuterium source* (0.2 mL). 2-Methylfuran **3a** (30 µL, 0.33 mmol) was added and the vial sealed and irradiated. On completion, the vial was opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. Deuterium incorportation was determined by integration of residual C-H resonances in the ^{1}H NMR spectra.

4. Table S3 - Choice of Activator



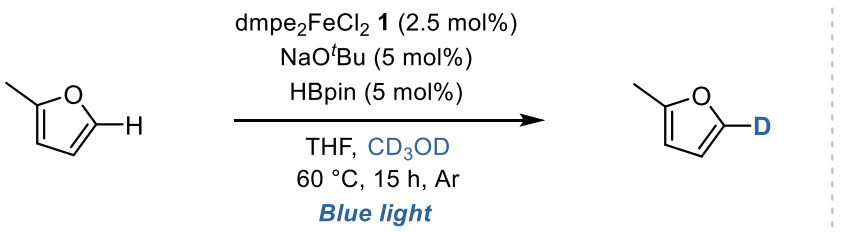
$dmpe_2FeCl_2$ **1**

Entry	Activator	Deuterium incorporation (%)[a]
1	*none*	11
2	NaO^tBu	97
3	NaHMDS	30
4	KF	74
5	TMPLi	45
6	Na(2-ethylhexanoate)	0
7	KO^tBu	90
8	LiOMe	95
9	$NaBHEt_3$ (no HBpin)	45
10	LiH (no HBpin)	79
11	$LiAlH_4$ (no HBpin)	50

[a]Reaction conditions: 2-methylfuran **3a** (0.33 mmol), [Fe] **1** (2.5 mol%), activator (5 mol%), HBpin (5 mol%), THF (0.2 mL), d_4-CD_3OD (0.2 mL), blue-light irradiation, 15 h.

Procedure: A 1.75 mL sample vial with screw-cap lid was loaded with [$dmpe_2FeCl_2$] **1** (3.5 mg, 8.2 µmol, 2.5 mol%) and '*Activator*' (16.4 µmol, 5 mol%) before the addition of HBpin (1 drop, *ca.* 5 µL, 5 mol%), THF (0.2 mL) and CD_3OD (0.2 mL). 2-Methylfuran **3a** (30 µL, 0.33 mmol) was added and the vial sealed and irradiated. On completion, the vial was opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. Deuterium incorportation was determined by integration of residual proton 'H' resonances in the ^1H NMR spectra.

5. Table S4 - Overview of Control Reactions for Arene Deuteration

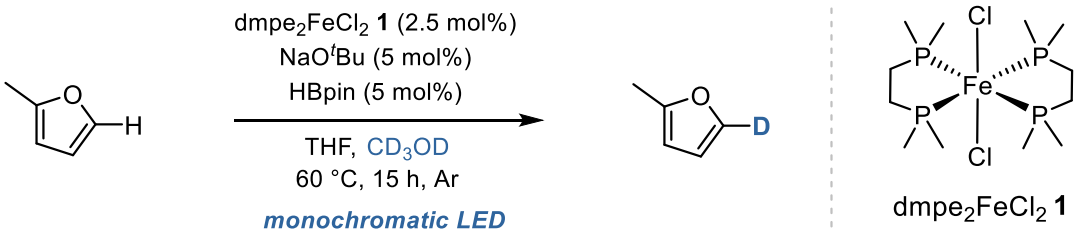


dmpe$_2$FeCl$_2$ **1**

Entry	Variation from standard conditions	Deuterium incorporation (%)[a]
1	*none*	97
2	No [dmpe$_2$FeCl$_2$] **1**	0
3	No CD_3OD	0
4	dmpe (no $FeCl_2$)	0
5	$FeCl_2$ (no dmpe)	0
6	No light (60 ºC)	0
7	No THF	94
8	No HBpin	80
9	No HBpin and no THF	82
10	No NaO^{t}Bu	11
11	[dmpe$_2$FeCl$_2$] **1** (2 mol%)	92
12	[dmpe$_2$FeCl$_2$] **1** (1 mol%)	94
13	[dmpe$_2$FeH$_2$] **2**	88

[a]Reaction conditions: 2-methylfuran (0.33 mmol), [Fe] (2.5 mol%), activator (5 mol%), HBpin (5 mol%), THF (0.2 mL), d_4-CD_3OD (0.2 mL), blue-light irradiation, 15 h.

6. Table S5 - Choice of Irradiation Wavelength

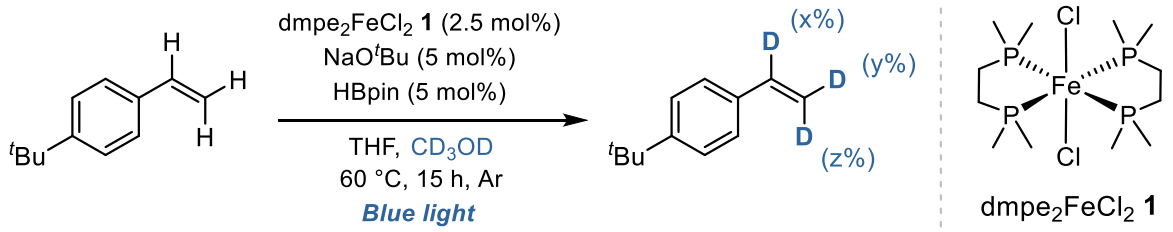


Entry	Wavelength (nm)	Current (mA)	Deuterium incorporation (%)[a]
1	365	100	46
2	365	200	58
3	365	350	66
4	420	100	69
5	420	200	75
6	420	350	95
7	450	100	50
8	450	200	72
9	450	350	>99
10	525	100	58
11	525	200	72
12	525	350	94

[a]Reaction conditions: 2-methylfuran **3a** (0.33 mmol), [Fe] **1** (2.5 mol%), activator (5 mol%), HBpin (5 mol%), THF (0.2 mL), d_4-CD_3OD (0.2 mL), LED-light irradiation, 20 h.

Procedure: A 1.75 mL sample vial with screw-cap lid was loaded with [$dmpe_2FeCl_2$] **1** (3.5 mg, 8.2 µmol, 2.5 mol%) and NaO^{t}Bu (1.6 mg, 16.4 µmol, 5 mol%) before the addition of HBpin (1 drop, *ca.* 5 µL, 5 mol%), THF (0.2 mL) and CD_3OD (0.2 mL). *n.b* Any remaining HBpin at this stage is destroyed by reaction with CD_3OD, releasing HD. 2-Methylfuran **3a** (30 µL, 0.33 mmol) was added and the vial sealed and irradiated. Irradiation was conducted using a Pacer Photochemistry LED illuminator (Pacer International). On completion, the vial is opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. On completion, the vial was opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. Deuterium incorportation was determined by integration of residual C-H resonances in the ^{1}H NMR spectra.

7. Table S6 - Overview of Control Reactions for Alkene Deuteration

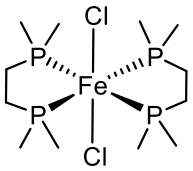


Entry	Variation from standard conditions	Deuterium incorporation (%)[a]		
		(x)	(y)	(z)
1	*none*	82	84	84
2	No [$dmpe_2FeCl_2$] **1**	0	0	0
3	No CD_3OD	0	0	0
4	dmpe (no $FeCl_2$)	0	0	0
5	$FeCl_2$ (no dmpe)	0	0	0
6	No light (60 ºC)	30	3	5
7	No light (80 ºC)	21	5	5
8	No HBpin	28	21	21
9	No NaO^{t}Bu	0	0	0
10	BnONa act. (no HBpin)	0	0	0
11	LiOMe act. (no HBpin)	14	9	9

[a]Reaction conditions: 2-methylfuran (0.33 mmol), [Fe] (2.5 mol%), activator (5 mol%), HBpin (5 mol%), THF (0.2 mL), d_4-CD_3OD (0.2 mL), blue light irradiation, 15 h.

8. Preparation of Pre-catalysts

dmpe$_2$FeCl$_2$ **1**



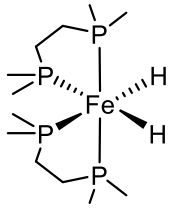
Following the reported procedure,[1] 1,2-bis(dimethylphosphino)ethane (dmpe, 800 mg, 5.3 mmol, 2 equiv.) was added dropwise (over *ca.* 30 seconds) to a stirred solution of iron(II) dichloride (340 mg, 2.7 mmol) in anhydrous tetrahydrofuran (30 mL). The mixture was stirred for 18 hours, the solvent was removed *in vacuo* (30 ºC, 400 to 20 mbar) and the solid dissolved in anhydrous dichloromethane (8 mL), filtered and the solvent removed *in vacuo* to give [dmpe$_2$FeCl$_2$] **1** (1.08 g, 2.5 mmol, 93%) as a light green amorphous solid.

^{31}P NMR: (162 MHz, d_8-THF)

59.5.

Data were in accordance with those previously reported.[1-2]

$dmpe_2FeH_2$ **2**



According to a modification of the procedure reported by Darcel,[3] a lithium triethylborohydride solution (1.7 M in THF, 0.91 mL, 1.54 mmol, 2.2 equiv.) was added dropwise to a stirred solution of $dmpe_2FeCl_2$ **1** (300 mg, 0.70 mmol) in anhydrous diethyl ether (15 mL). The mixed was stirred for 2 hours with an observed colour change to yellow/orange. Conversion was monitored by ^1H and ^{31}P NMR spectroscopy to ensure full conversion of $dmpe_2FeHCl$ intermediate. The solvent was removed *in vacuo* and the resultant solid extracted with pentane (3 x 10 mL). The solution was evaporated to dryness *in vacuo*. The crude product was sublimated (40 – 80 °C, 1 x 10^{-2} mbar for several hours) to yield [$dmpe_2FeH_2$] **2** as a pale yellow precipitate in high purity (186 mg, 0.52 mmol, 74%).

^1H NMR: (500 MHz, THF)

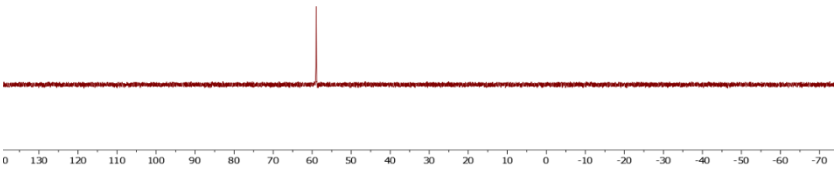
−14.06 (ddq, J = 57.7, 37.9, 18.9 Hz, 1H). *Hydride region only.*

^{31}P NMR: (202 MHz, THF)

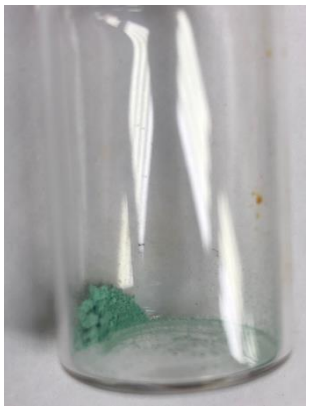
77.18 (t, J = 26.6 Hz), 67.51 (t, J = 26.6 Hz).

Data were in accordance with those previously reported.[4]

9. Air- and Moisture-Stability of [$dmpe_2FeCl_2$] **1**



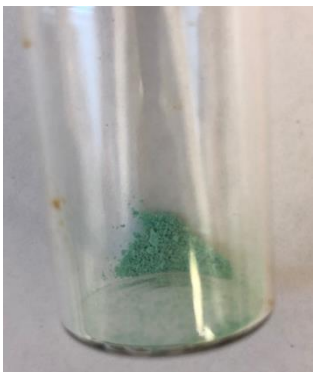
a) Freshly prepared [$dmpe_2FeCl_2$] 1 and corresponding ^{31}P NMR spectra (162 MHz, THF).



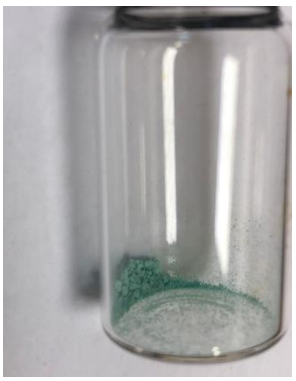
b) after 1 day in air

c) after 2 days in air

d) after 3 days in air

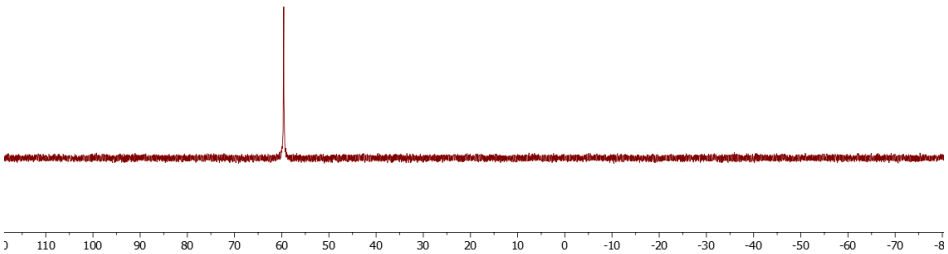


e) after 5 days in air



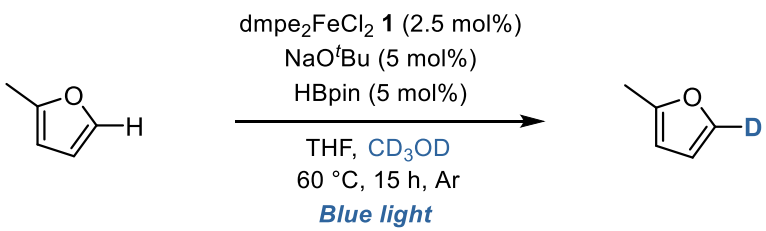
f) after 6 days in air

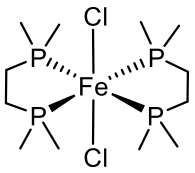
g) after 10 days in air



h) after 14 days in air and corresponding ^{31}P NMR spectra (162 MHz, THF).

10. Table S7 - Use of [$dmpe_2FeCl_2$] **1** Stored in Air



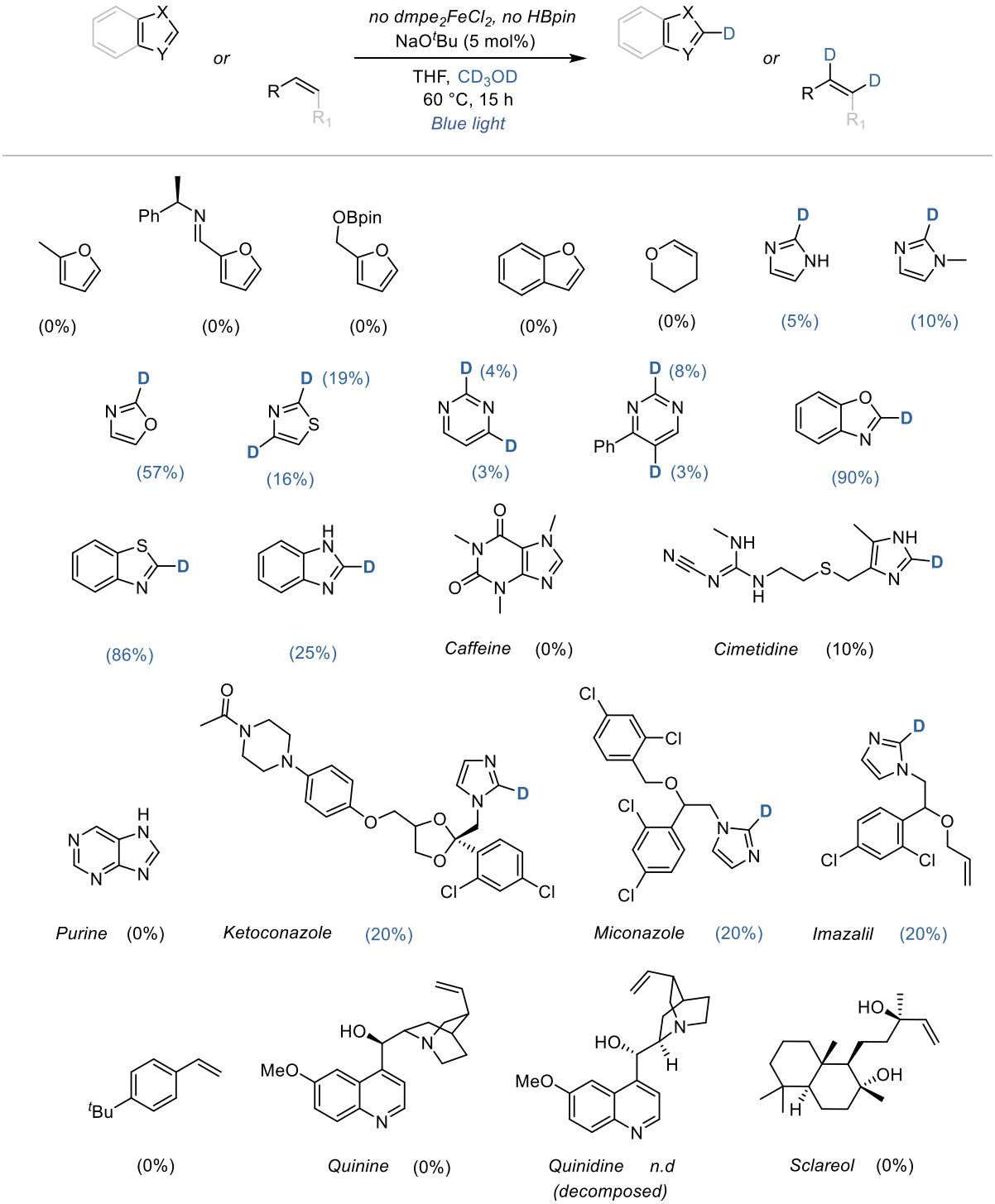


$dmpe_2FeCl_2$ **1**

Entry	Variation from standard conditions	Deuterium incorporation (%)[a]
1	*none*	97
2	[$dmpe_2FeCl_2$] **1** Stored in air for 14 days	92
3	[$dmpe_2FeCl_2$] **1** Stored in air for 31 days	91

Procedure: A 1.75 mL sample vial with screw-cap lid was loaded with [$dmpe_2FeCl_2$] **1** (3.5 mg, 8.2 µmol, 2.5 mol%) and NaO^{t}Bu (1.6 mg, 16.4 µmol, 5 mol%) before the addition of HBpin (1 drop, *ca.* 5 µL, 10 mol%), THF (0.2 mL) and CD_3OD (0.2 mL). *n.b* Any remaining HBpin at this stage is destroyed by reaction with CD_3OD, releasing HD. 2-Methylfuran **3a** (30 µL, 0.33 mmol) is added and the vial sealed and irradiated. On completion, the vial is opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. On completion, the vial was opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. Deuterium incorportation was determined by integration of residual C-H resonances in the ^{1}H NMR spectra.

11. Table S8 - Base-mediated (Background) H/D Exchange

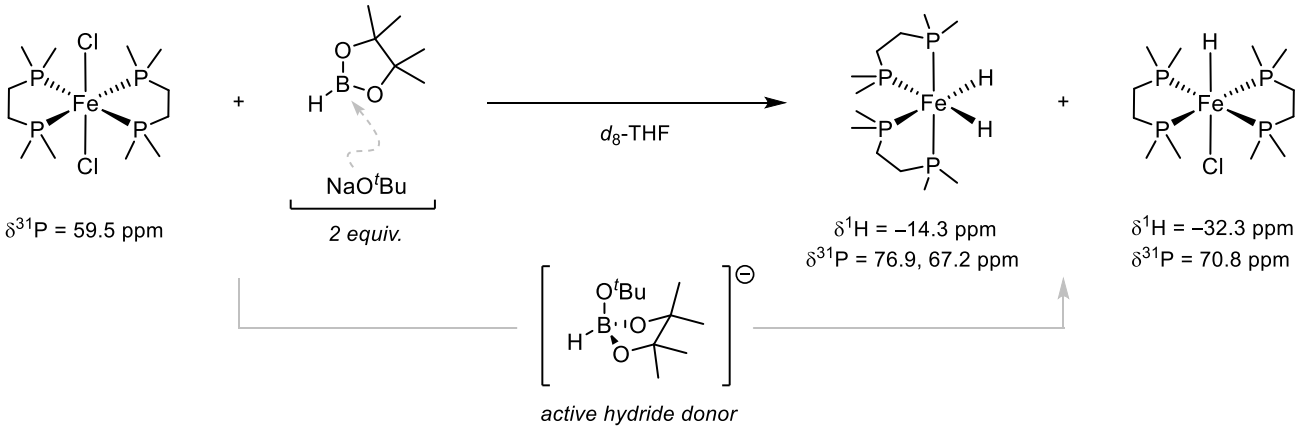


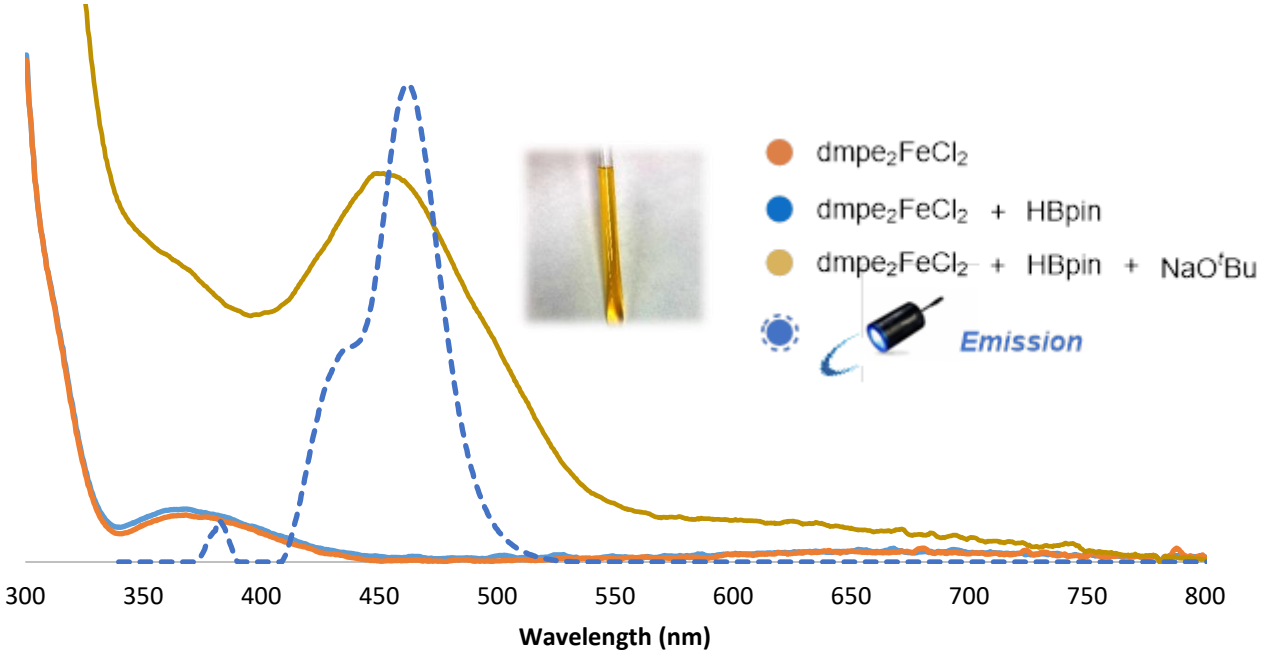
A 1.75 mL sample vial with screw-cap lid was loaded with NaO^{t}Bu (1.6 mg, 16.4 µmol, 5 mol%) before the addition of CD_3OD (0.2 mL). Substrate (arene/alkene, 0.33 mmol) was added and the vial sealed and irradiated under the same reaction conditions that were used with iron-catalyst present. Background base-mediated H/D exchange was observed for some *N*-heterocyclic arenes, values presented are %D incorporation. Deuterium incorportation was determined by integration of residual proton 'H' resonances in the ^{1}H NMR spectra. *n.b. When dmpe$_2$FeCl$_2$ is used in combination with NaO^{t}Bu and HBpin, the NaO^{t}Bu is consumed and converted into ^{t}BuOBpin and NaCl.*[5]

12. Mechanistic investigations

I) Activation studies

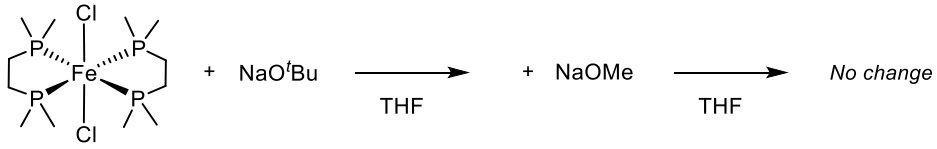
a) Reaction of [dmpe$_2$FeCl$_2$] **1** with pinacolborane (HBpin) and NaO^{t}Bu in d_8-THF:





In a J-Young's NMR tube, pinacolborane (10 µL, 70 µmol) was added to a mixture of [dmpe$_2$FeCl$_2$] **1** (10 mg, 24 µmol) and sodium *tert*-butoxide (5 mg, 50 µmol) in anhydrous d_8-THF. The tube was shaken and the mixture immediately turned yellow.

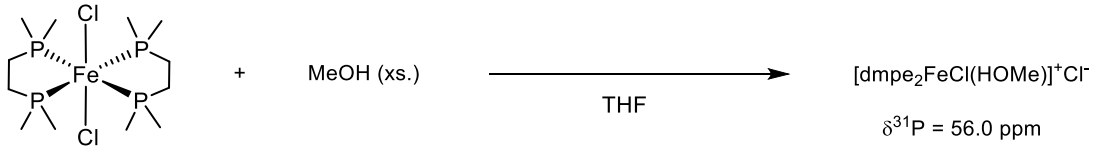
b) Reaction of [dmpe$_2$FeCl$_2$] 1 with NaO^{t}Bu and NaOMe in THF.



δ^{31}P = 59.5 ppm

In a J-Young's NMR tube, sodium *tert*-butoxide (1.4 mg, 14 µmol) was added to a mixture of [dmpe$_2$FeCl$_2$] **1** (3 mg, 8 µmol) in anhydrous THF (0.4 mL). The tube was shaken and the mixture remained green. Sodium methoxide (0.6 mg, 14 µmol) was subsequently added to the tube and shaken, no change was observed.

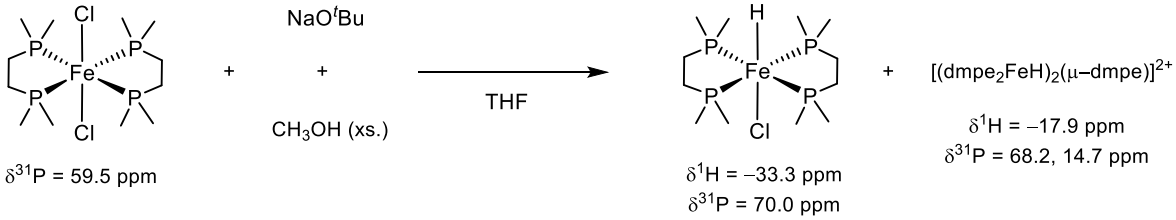
c) Reaction of [dmpe$_2$FeCl$_2$] 1 with CH_3OH in THF.



δ^{31}P = 59.5 ppm

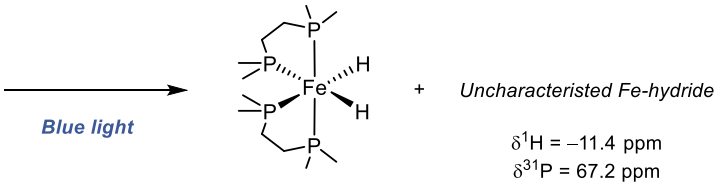
In a J-Young's NMR tube, anhydrous CH_3OH (0.2 mL) was added to a mixture of [dmpe$_2$FeCl$_2$] **1** (3 mg, 8 µmol) in anhydrous THF (0.2 mL). The tube was shaken and the mixture turned pale yellow.[6]

c) Reaction of [dmpe$_2$FeCl$_2$] **1** with NaO^{t}Bu and CH_3OH in THF.



δ^{31}P = 59.5 ppm

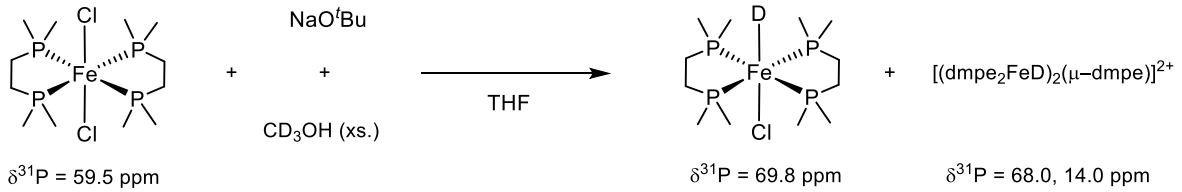
δ^1H = –33.3 ppm
δ^{31}P = 70.0 ppm



δ^1H = –13.4 ppm
δ^{31}P = 73.8, 64.9 ppm

In a J-Young's NMR tube, anhydrous CH_3OH (0.2 mL) was added to a mixture of [dmpe$_2$FeCl$_2$] **1** (3 mg, 8 µmol) and sodium *tert*-butoxide (1.4 mg, 14 µmol) in anhydrous THF (0.2 mL). The tube was shaken and the mixture immediately turned yellow/orange with the formation of [dmpe$_2$FeHCl] observed by ^{1}H and ^{31}P NMR spectroscopy. Upon blue light irradiation the formation of [dmpe$_2$FeH$_2$] 2 and an uncharacterised iron-hydride species was observed by ^{1}H and ^{31}P NMR spectroscopy.

d) Reaction of [dmpe$_2$FeCl$_2$] **1** with NaO^{t}Bu and CD_3OH in THF.



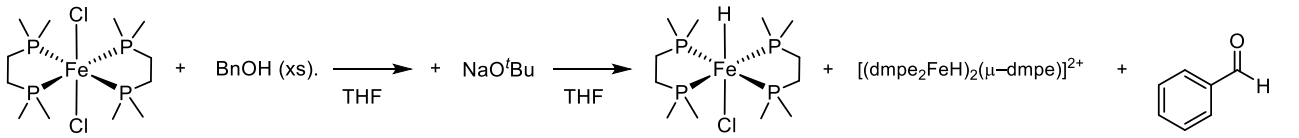
δ^{31}P = 59.5 ppm

δ^{31}P = 69.8 ppm

δ^{31}P = 68.0, 14.0 ppm

In a J-Young's NMR tube, anhydrous CD_3OH (0.2 mL) was added to a solution of [dmpe$_2$FeCl$_2$] **1** (3 mg, 8 μmol) and sodium *tert*-butoxide (1.4 mg, 14 μmol) in anhydrous THF (0.2 mL). The tube was shaken and the mixture immediately turned yellow/orange with the formation of [dmpe$_2$FeDCl] observed by ^{31}P NMR spectroscopy. Upon standing the iron deuterides exchanged with d_3-methanol to give iron hydrides and d_4-MeOD.

e) Reaction of [dmpe$_2$FeCl$_2$] **1** with BnOH and NaO^{t}Bu in THF.



δ^{31}P = 59.5 ppm

δ^{1}H = –33.3 ppm
δ^{31}P = 70.0 ppm

δ^{1}H = –17.9 ppm
δ^{31}P = 68.2, 14.7 ppm

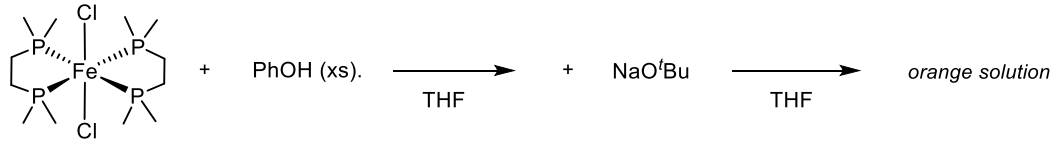
δ^{13}C = 192.1 ppm

In a J-Young's NMR tube, benzyl alcohol (0.2 mL, 1.90 mmol) was added to a solution of [dmpe$_2$FeCl$_2$] **1** (3 mg, 8 μmol) in anhydrous THF (0.2 mL). The tube was shaken and the solution remained pale green. Upon addition of sodium *tert*-butoxide (1.4 mg, 14 μmol) the solution became orange and an insoluble precipitate was formed. The formation of [dmpe$_2$FeHCl] was observed by ^{1}H and ^{31}P NMR spectroscopy. The formation of benzaldehyde was observed by ^{13}C NMR spectroscopy and mass spectrometry.

MS: (HRMS – EI$^+$)

Found 106.041029 ($C_7H_6O_1$), requires 106.04132.

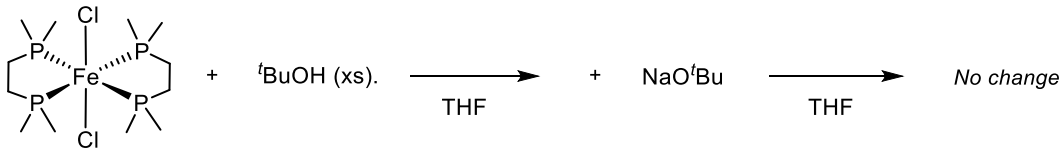
f) Reaction of [dmpe$_2$FeCl$_2$] **1** with PhOH and NaO^{t}Bu in THF.



δ^{31}P = 59.5 ppm

In a J-Young's NMR tube, phenol (0.56 g, 6.00 mmol) was added to a solution of [dmpe$_2$FeCl$_2$] **1** (3 mg, 8 µmol) in anhydrous THF. The tube was shaken and the solution remained pale green. Upon addition of sodium *tert*-butoxide (1.4 mg, 14 µmol) the solution became orange and an insoluble beige precipitate was formed. No difference could be observed in the solution by ^{1}H and ^{31}P NMR spectroscopy.

g) Reaction of [dmpe$_2$FeCl$_2$] **1** with ^{t}BuOH and NaO^{t}Bu in THF.

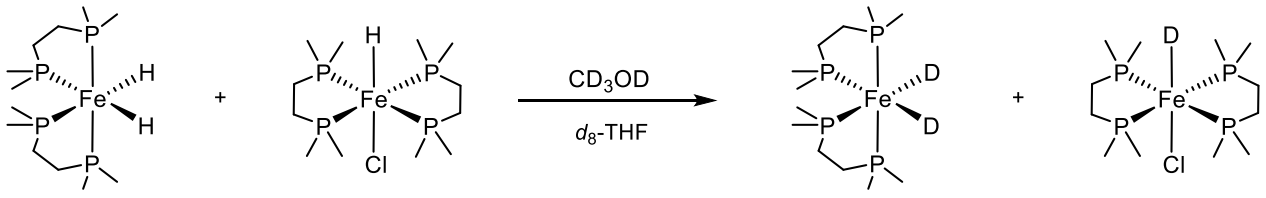


δ^{31}P = 59.5 ppm

In a J-Young's NMR tube, *tert*-butanol (0.44 g, 6.00 mmol) was added to a mixture of [dmpe$_2$FeCl$_2$] **1** (3 mg, 8 µmol) in anhydrous THF (0.2 mL). The tube was shaken and the mixture remained green. No difference could be observed in the solution by ^{1}H and ^{31}P NMR spectroscopy.

II) Iron-hydride exchange studies, C-H metallation, and catalyst turnover.

a) Reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with CD_3OD:



δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

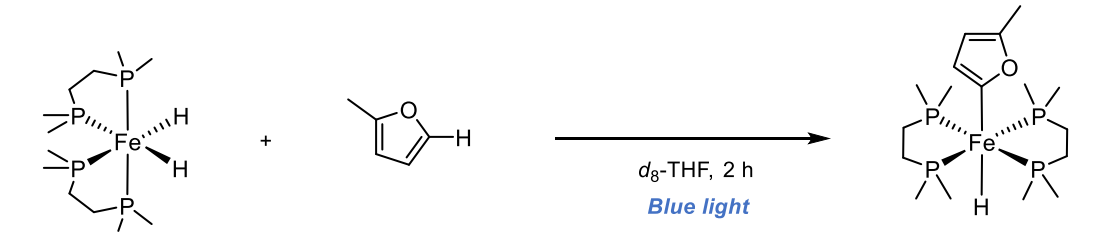
δ^1H = –32.3 ppm
δ^{31}P = 70.8 ppm

δ^2H = –14.6 ppm
δ^{31}P = 77.7, 66.6 ppm

δ^2H = –32.6 ppm
δ^{31}P = 70.7 ppm

CD_3OD (50 µL, 1.25 mmol) was added to a reaction mixture containing [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] in d_8-THF (*ca.* 25 µmol [Fe]). The mixture was shaken and left to react for 1 hour at room temperature before removing the solvent *in vacuo* (20 ºC, 0.1 mbar). Anhydrous tetrahydrofuran (0.5 mL) was added before the acquisition of NMR spectra.

b) Reaction of [dmpe$_2$FeH$_2$] **2** with 2-methylfuran **3a**:



δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

δ^1H = –18.9 ppm
δ^{31}P = 77.9-75.9 ppm

2-Methylfuran **3a** (15 µL, 160 µmol) was added to a reaction mixture containing [dmpe$_2$FeH$_2$] **2** in d_8-THF (*ca.* 25 µmol [Fe]). The mixture was shaken and irradiated with blue light (Kessil Tuna Blue A160WE) for 2 hours. Yellow like crystals were produced from slow cooling a saturated pentane solution at −30 °C.

[trans-dmpe$_2$Fe(H)(2-methylfuryl)] trans-**5**

MS: (HRMS – EI$^+$)

Found 438.12041 ($C_{17}H_{38}O_1{}^{56}Fe_1P_4$), requires 438.12171.

^{1}H NMR: (500 MHz, d_8-THF)

5.44 (s, 1H), 5.22 (s, 1H), 2.16 (s, 3H), −18.9 (quin. J = 45 Hz, 1H).

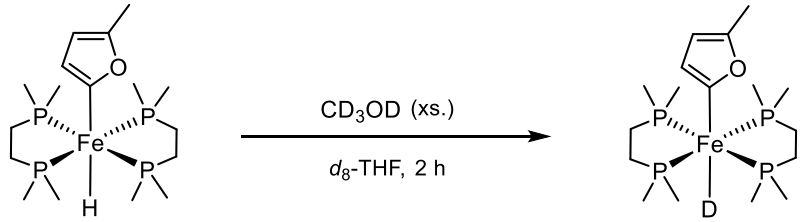
^{13}C NMR: (151 MHz, d_8-THF) *furyl ligand only*

150.0, 120.5, 104.5, 13.4. (*resonance for C-Fe not observed)*

^{31}P NMR: (202 MHz, d_8-THF)

77.9-75.9 (m).

c) Reaction of [*trans*-dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** with CD_3OD:



δ^1H = –18.9 ppm
δ^{31}P = 77.9-75.9 ppm

δ^2H = –18.5 ppm
δ^{31}P = 77.3 ppm

Anhydrous CD_3OD (50 µL, 1.25 mmol) was added to [dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** (30 µmol) in d_8-THF (0.5 mL).

*[trans-dmpe$_2$Fe(D)(2-methylfuryl] **[D]**-trans-**5***

MS: (HRMS – EI$^+$)

Found 439.12855 ($C_{17}H_{37}D_1O_1{}^{56}Fe_1P_4$), requires 439.12799.

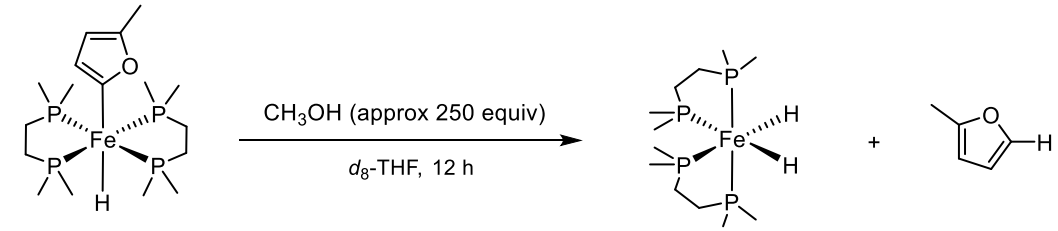
^{2}H NMR: (77 MHz, THF)

−18.5 (q, *J* = 6.9 Hz, 1D).

^{31}P NMR: (202 MHz, d_8-THF)

77.3 (t, *J* = 6.4 Hz).

d) Reaction of [*trans*-dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** with CH_3OH to produce **3a**:



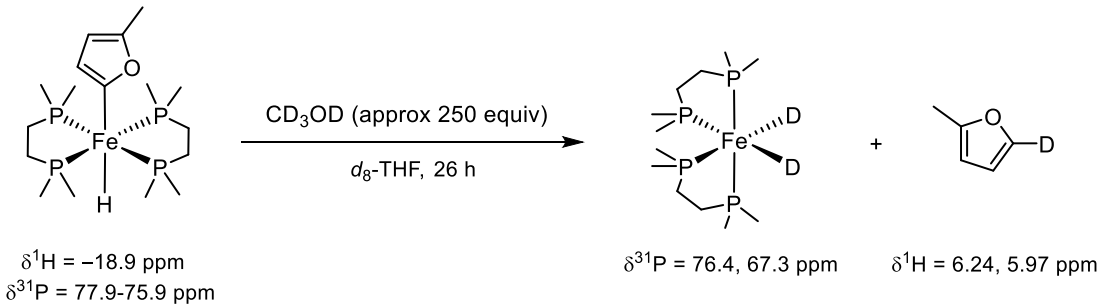
δ^1H = –18.9 ppm
δ^{31}P = 77.9-75.9 ppm

δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

δ^1H = 7.31, 6.24, 5.97 ppm

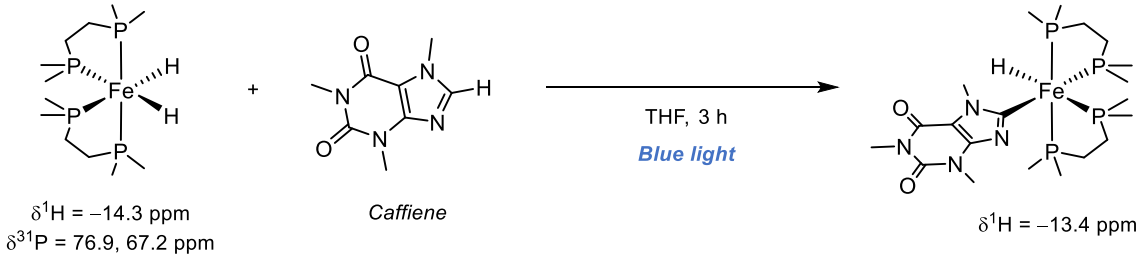
A solution of [*trans*-dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** (30 µmol) and CH_3OH (approx. 100 equiv) in d_8-THF (0.5 mL) was left at room temperature and monitored for 12 h.

e) Reaction of [*trans*-dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** with CD_3OD to produce **[D]-3a**:



A solution of [*trans*-dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** (30 µmol) and CD_3OD (approx. 250 equiv) in d_8-THF (0.5 mL) was left at room temperature and monitored for 26 h.

f) Reaction of [dmpe$_2$FeH$_2$] **2** with Caffiene **3s**:



Caffiene **3s** (31 mg, 160 µmol) was added to a reaction mixture containing [dmpe$_2$FeH$_2$] **2** in d_8-THF (*ca.* 25 µmol [Fe]). The mixture was shaken and irradiated with blue light (Kessil Tuna Blue A160WE) for 3 hours. Yellow block crystals were produced from slow cooling a saturated pentane solution at −30 °C.

*[cis-dmpe$_2$Fe(H)(caffeine)] cis-**6***

MS: (HRMS – EI$^+$)

Found 550.16387 ($C_{20}H_{42}N_4O_2{}^{56}Fe_1P_4$), requires 550.16022.

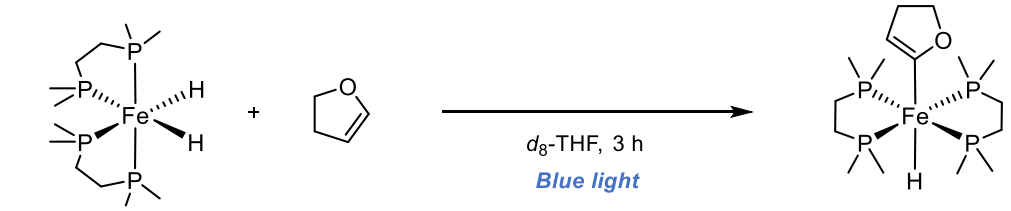
^{1}H NMR: (500 MHz, THF) *hydride region only*

−13.14−13.60 (m, 1H).

^{31}P NMR: (202 MHz, THF)

78.1-77.1 (m), 71.1-70.1 (m), 62.4-61.5 (m), 58.4-57.6 (m).

g) Reaction of [dmpe$_2$FeH$_2$] **2** with 2,3-dihydrofuran **4g**:



δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

δ^1H = –18.3 ppm
δ^{31}P = 76.6 ppm

2,3-Dihydrofuran 4**g** (8 µL, 105 µmol) was added to a reaction mixture containing [dmpe$_2$FeH$_2$] **2** (20 mg, 76 µmol) in d_8-THF. The mixture was shaken and irradiated with blue light (Kessil Tuna Blue A160WE) for 3 hours. Yellow block-like crystals were produced from slow cooling a saturated pentane solution at −30 °C.

*[trans-dmpe$_2$Fe(H)(2,3-dihydrofuryl)] trans-***7**

MS: (HRMS – EI$^+$)

Found 426.12171 ($C_{16}H_{38}O_1{}^{56}Fe_1P_4$), requires 426.12171.

^{1}H NMR: (500 MHz, C_6D_6)

4.02 (t, J = 8.8 Hz, 2H, furyl-C*H*$_2$), 3.99 (t, J = 1.8 Hz ,1H, furyl-C*H*), 2.62 (td, J = 8.8, 1.7 Hz, 2H, furyl-C*H*$_2$), 1.89 (m, 4H, PC*H*$_2$), 1.46 – 1.43 (m, 4H, PC*H*$_2$), 1.41 (s, 12H, PC*H*$_3$), 1.20 (s, 12H, PC*H*$_3$), -18.30 (p, J = 45.6 Hz, 1H, Fe-*H*).

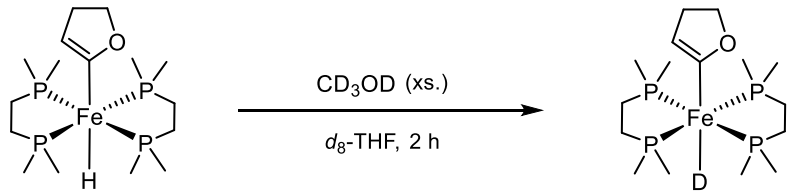
^{13}C NMR: (151 MHz, C_6D_6)

105.9 (furyl-*C*H), 67.5 (furyl-*C*H$_2$), 32.3-32.8 (P*C*H$_2$, furyl-*C*H$_2$), 26.2 (P*C*H$_3$), 17.8 (P*C*H$_3$). (*resonance for C-Fe not observed)*

^{31}P NMR: (202 MHz, C_6D_6)

76.6 (d, J = 38.8 Hz).

h) Reaction of [*trans*-dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7** with CD_3OD:



δ^1H = –18.9 ppm
δ^{31}P = 77.9-75.9 ppm

δ^2H = –18.3 ppm
δ^{31}P = 76.8 ppm

Anhydrous CD_3OD (0.25 mL) was added to [*trans*-dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7** (30 µmol) in d_8-THF (0.25 mL).

[trans-dmpe$_2$Fe(D)(2,3-dihydrofuryl] ***[D]****-trans-****7***

MS: (HRMS – EI$^+$)

Found 427.120297 ($C_{16}H_{37}D_1O_1{}^{56}Fe_1P_4$), requires 427.12798.

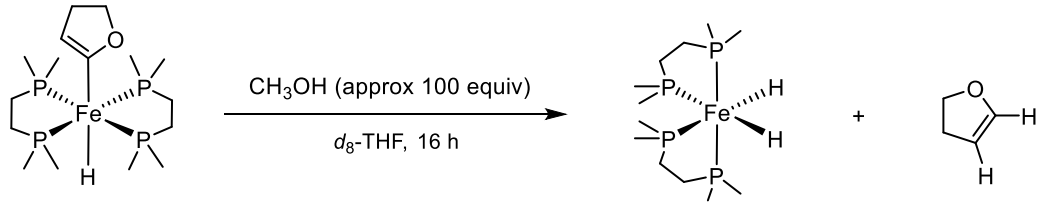
^{2}H NMR: (77 MHz, THF)

−18.3 (q, *J* = 6.9 Hz, 1D).

^{31}P NMR: (202 MHz, d_8-THF)

76.8 (t, *J* = 7.5 Hz).

i) Reaction of [*trans*-dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7** with CH_3OH to produce **4g**:



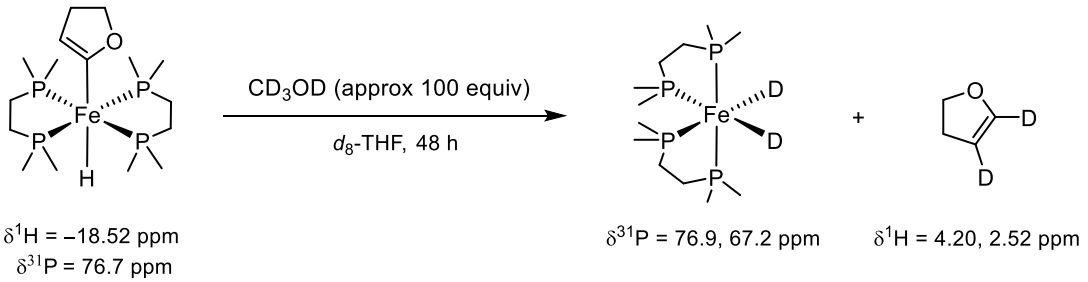
δ^1H = –18.52 ppm
δ^{31}P = 76.7 ppm

δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

δ^1H = 6.32, 4.92, 4.23, 2.57 ppm

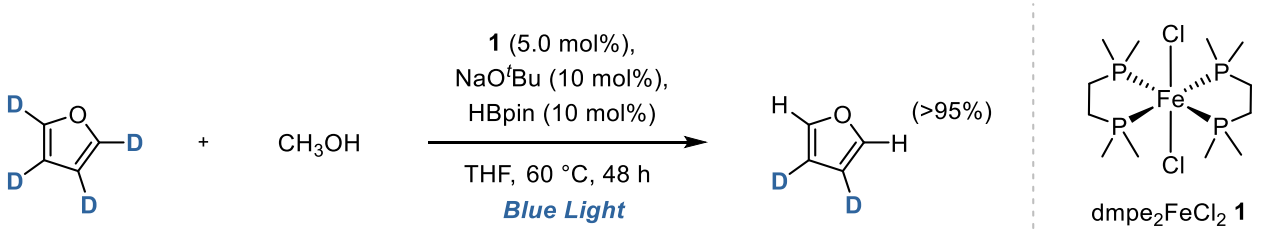
A solution of [*trans*-dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7** (30 µmol) and CH_3OH (approx. 100 equiv) in d_8-THF (0.5 mL) was left at room temperature and monitored for 18 h.

j) Reaction of [*trans*-dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7** with CD_3OD to produce **[D]-4g**:



A solution of [*trans*-dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7** (30 µmol) and CD_3OD (approx. 250 equiv) in d_8-THF (0.5 mL) was left at room temperature and monitored for 48 h.

III) Protodedeuteration of d_4-furan



Following an altered version of the general deuteration procedure, d_4-furan (24µL, 0.33 mmol) was reacted with CH_3OH to give *d*$_2$*3D,4D*-furan. Deuterium incorporation was determined by ^{1}H NMR spectroscopy.

d$_2$-[*3D*,*4D*]-furan

MS: (HRMS [M+H]+ – CI+)

Found 70.038421 ($C_4H_2D_2O_1$), requires 70.03822

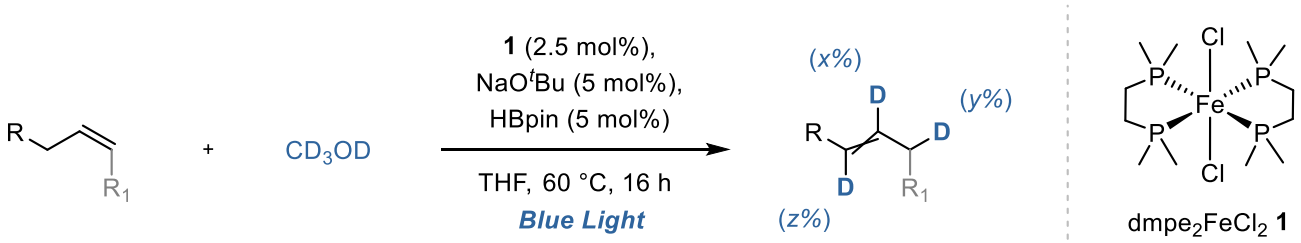
^{1}H NMR: (500 MHz, $CDCl_3$)

(s, 0.89H), 6.39 (s, 0.01H).

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

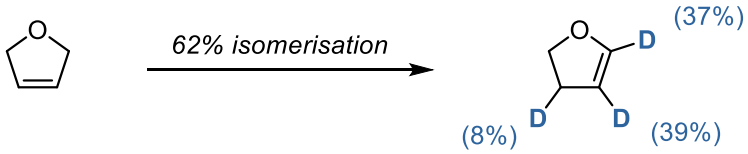
13C NMR (126 MHz, CDCl3) δ 142.47, 109.18 (t, *J* = 27.2 Hz).

IIII) Alkene isomerisation studies



Following the general deuteration procedure, 'alkene' (0.33 mmol) was reacted to give the isomerised alkene. Extent of isomerisation and deuterium incorporation were determined by ^{1}H and ^{2}H NMR spectroscopy.

a) 2,5-Dihydrofuran



2,3-Dihydrofuran-d_3

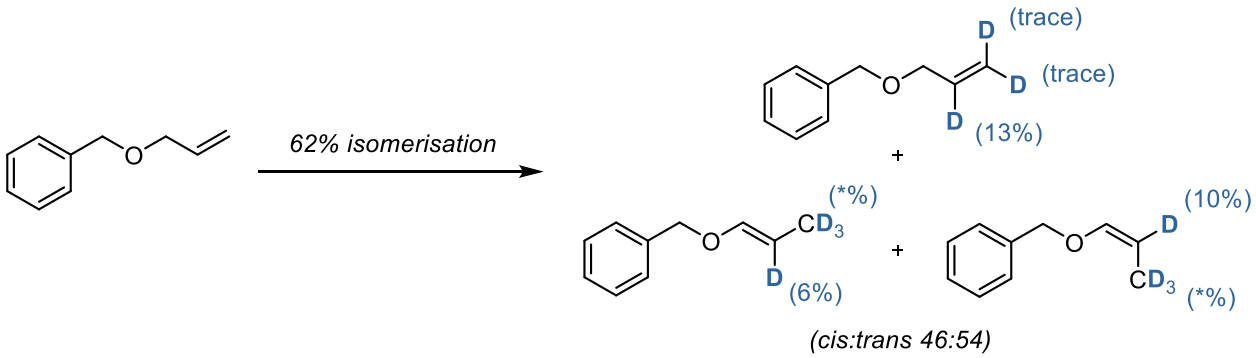
^{1}H NMR: (500 MHz, $CDCl_3$)

6.33 (d, J = 2.3 Hz, 0.63H), 4.90 (dd, J = 4.3, 2.5 Hz, 0.61H), 4.31 (t, J = 9.4 Hz, 2H), 2.65 – 2.58 (m, 1.85H).

^{2}H NMR: (77 MHz, $CDCl_3$)

6.37 (s), 5.01 (s), 2.62 (m).

b) Allyl benzyl ether



*Deuterium incoporation could not be quantified due to overlapping signals with 'hydrogenated' product, propylbenzylether (9%).

Allyl benzyl ether-*α,β,β-d*$_3$

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

7.40 – 7.27 (m, 5H), 5.97 (ddt, J = 17.2, 10.4, 5.6 Hz, 0.87H), 5.32 (dq, J = 17.2, 1.7 Hz, 1H), 5.21 (dq, J = 10.4, 1.3 Hz, 1H), 4.54 (s, 2H), 4.04 (dt, J = 5.6, 1.4 Hz, 2H).

^{2}H NMR: (77 MHz, $CDCl_3$)

6.00 (m).

(*E*)-((Prop-1-en-1-yloxy)methyl)benzene-*d*

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

7.41 – 7.27 (m, 5H), 6.04 (dq, J = 6.2, 1.7 Hz, 1H), 4.80 (s, 2H), 4.48 – 4.42 (m, 0.94H), 1.63 (dd, J = 6.9, 1.7 Hz, *H).

^{2}H NMR: (77 MHz, $CDCl_3$)

4.50 (m), 1.65 (m).

(*Z*)-((Prop-1-en-1-yloxy)methyl)benzene-*d*

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

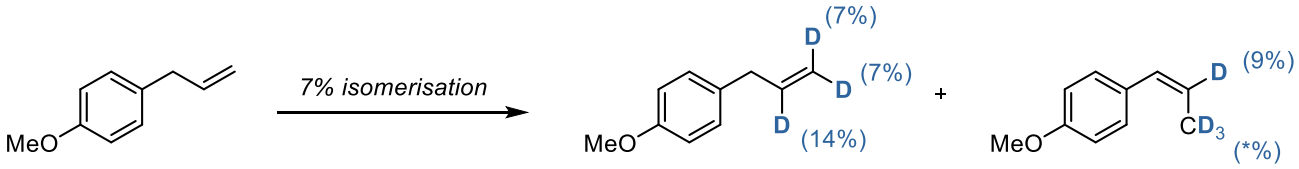
7.48 – 7.27 (m, 5H), 6.32 (dq, J = 12.5, 1.6 Hz, 1H), 4.90 (dq, J = 12.4, 6.7 Hz, 0.9H), 4.80 (s, 2H), 1.57 (dd, J = 6.7, 1.6 Hz, *H).

^{2}H NMR: (77 MHz, $CDCl_3$)

4.94 (m), 1.58 (m).

Data were in accordance with those previously reported.[7]

c) 4-Allylanisole



*Deuterium incoporation could not be quantified due to overlapping signals with 'hydrogenated' product, 4-*n*-propylanisole (5%). Deterium peaks for the *(Z)*-anethole product couldn't not be observed due to the low level of isomerisation. No (*E*)-anethole product was observed.

Allylanisole-*d*[3]

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

7.12 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.97 (ddt, J = 16.8, 10.1, 6.7 Hz, 0.86H), 5.15 – 5.01 (m, 1.86H), 3.80 (s, 3H), 3.39 – 3.31 (m, 2H).

^{2}H NMR: (77 MHz, $CHCl_3$)

6.00 (m), 5.09 (m), 0.95.

(*Z*)-Anethole-*d*

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

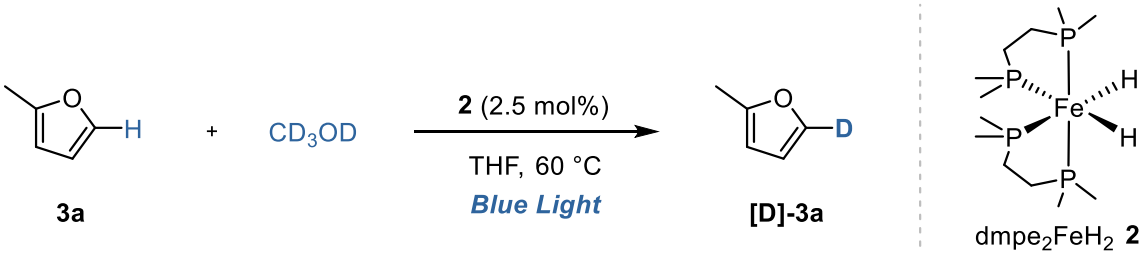
7.26 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.39 (dd, J = 11.4, 2.1 Hz, 1H), 5.71 (dq, J = 11.5, 7.1 Hz, 0.91H), 3.83 (s, 3H) 1.89 (d, *H).

Data were in accordance with those previously reported.[8]

IV) On/Off experiments

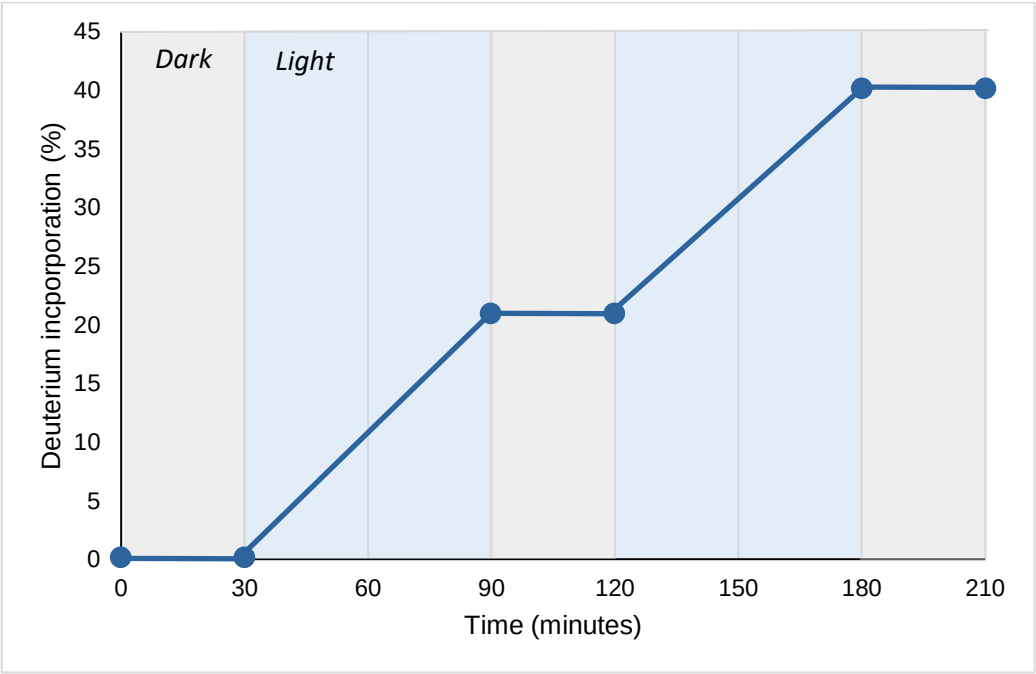
In a glove box with a purified argon atmosphere, [$dmpe_2FeH_2$] **2** (2.0 mg, 0.008 mmol, 2.5 mol%) and anhydrous THF (0.2 mL) were added to a Young's tap NMR tube. After addition of 2-methylfuran **2a** (30 µL, 0.33 mmol) *or* 4-*tert*-butylstyrene **4a** (60 µL, 0.33 mmol) and CD_3OD (0.2 mL), the tube was sealed, removed from the glove box and irradiated with blue light on and off. Deuterium incorporation was determined by reference to non-exchangable hydrogen atoms within the substrates using ^1H NMR spectroscopy.

a) 2-Methyl furan **3a**

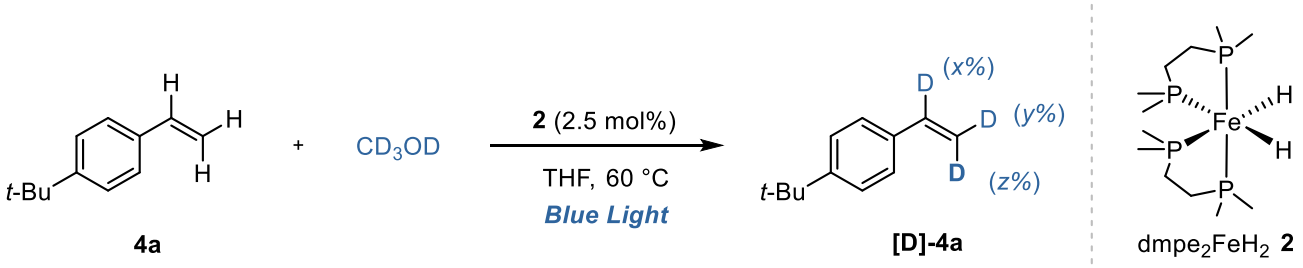


3a **[D]-3a** $dmpe_2FeH_2$ **2**

Entry	Total time (minutes)	Increment	Deuterium incorporation (%)
1	0	N/A	0
2	30	+ 30 minutes dark	0
3	60	+ 30 minutes light	21
4	90	+ 30 minutes dark	21
5	120	+ 30 minutes light	40
6	150	+ 30 minutes dark	40



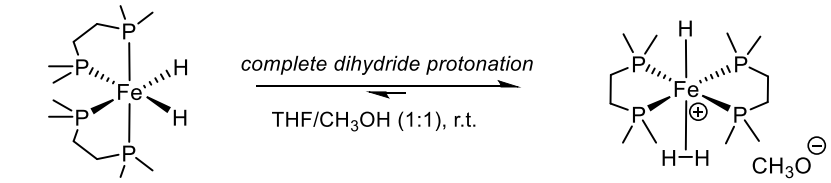
b) 4-*tert*-Butylstyrene **4a**



Entry	Total time (minutes)	Increment	Deuterium incorporation (%)		
			x	y	z
1	0	N/A	0	0	0
2	30	+ 30 minutes dark	0	0	0
3	60	+ 30 minutes light	15	7	7
4	90	+ 30 minutes dark	15	7	7
5	120	+ 30 minutes light	24	12	14
6	150	+ 30 minutes dark	24	12	14

V) Iron-hydride protonation studies

a) Reaction of [dmpe$_2$FeH$_2$] **2** with CD_3OH:

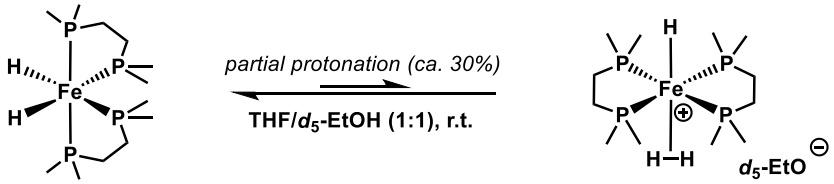


δ^1H = -14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

δ^1H = *n.d* (broad resonance)
δ^{31}P = 68.5 ppm

Anhydrous CD_3OH (200 µL) was added to [dmpe$_2$FeH$_2$] **2** (5.0 mg, 14 µmol) in THF (0.2 mL).

b) Reaction of [dmpe$_2$FeH$_2$] **2** with d_5-EtOH:



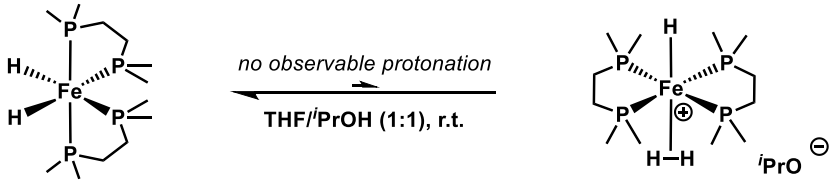
δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

FeH_2 : FeH_3 = 70:30

δ^1H = *n.d* (broad resonance)
δ^{31}P = 68.3 ppm

Anhydrous d_5-ethanol (200 µL) was added to [dmpe$_2$FeH$_2$] **2** (5.0 mg, 14 µmol) in THF (0.2 mL).

c) Reaction of [dmpe$_2$FeH$_2$] **2** with ^{i}PrOH:

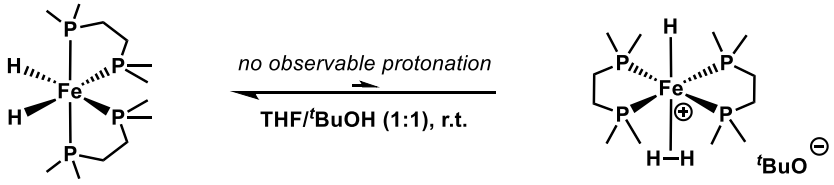


δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

not observed

Anhydrous isopropanol (200 µL) was added to [dmpe$_2$FeH$_2$] **2** (4.5 mg, 14 µmol) in THF (0.2 mL).

d) Reaction of [dmpe$_2$FeH$_2$] **2** with ^{t}BuOH:



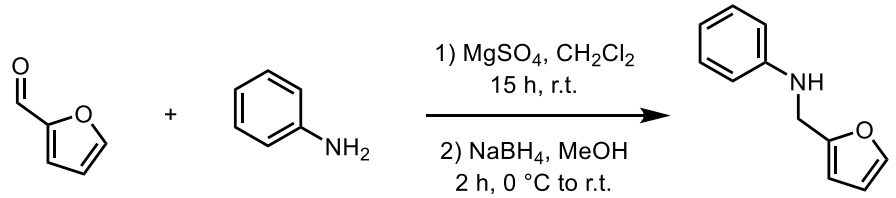
δ^1H = –14.3 ppm
δ^{31}P = 76.9, 67.2 ppm

not observed

Anhydrous *tert*-butanol (200 µL) was added to [dmpe$_2$FeH$_2$] **2** (4.5 mg, 14 µmol) in THF (0.2 mL).

13. Substrate synthesis and characterisation

N-(Furan-2-ylmethyl)aniline **3c**



Aniline (5.40 mL, 60 mmol) was added dropwise (over *ca*. 1 minute) to a stirred solution of furfural (5.0 mL, 60 mmol) and magnesium sulfate (17.40 g, 144 mmol) in anhydrous dichloromethane (50 mL). The reaction was stirred for 15 hours at room temperature, filtered (to remove magnesium sulfate) and the solvent removed *in vacuo* (30 ºC, 500 to 100 mbar) before the addition of methanol (80 mL) and sodium borohydride (4.50 g, 118 mmol, 3 x portions at 0 ºC). *n.b Caution addition of sodium borohydride is exothermic.* The reaction was warmed to room temperature, stirred for 2 hours and the solvent removed *in vacuo* (30 ºC, 500 to 20 mbar). The product was purified by Kugelrohr distillation (170 ºC, 2.0 mbar) to give *N*-(furan-2-ylmethyl)aniline **3c** (6.75 g, 39 mmol, 65%) as a colourless oil.

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

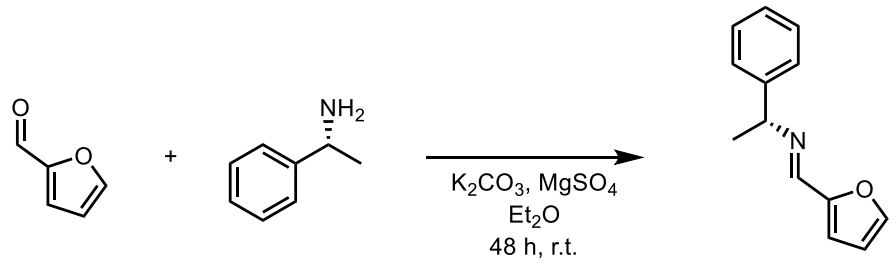
7.40-7.38 (m, 1H), 7.24-7.19 (m, 2H), 6.79-6.75 (m, 1H), 6.71 (app. d, J = 7.5 Hz, 2 H), 6.35 (dd, J = 3.3, 1.8 Hz, 1H), 6.27-6.25 (m, 1H), 4.35 (d, J = 5.0 Hz, 2H), 4.03 (br. s, $\Delta\nu_{1/2}$ = 22.1 Hz, 1H).

^{13}C NMR: (150 MHz, $CDCl_3$)

152.8, 147.7, 142.0, 129.3, 118.1, 113.2, 110.4, 107.0, 41.5.

Data were in accordance with those previously reported.[9]

(1*R*)-*N*-(Furan-2-ylmethylidene)-1-phenylethanamine **3d**



(*R*)-α-Methylbenzylamine (7.63 mL, 60 mmol) was added to a stirred mixture of furfural (5.0 mL, 60 mmol), potassium carbonate (15.13 g, 109 mmol) and magnesium sulfate (20.0 g, 167 mmol) in anhydrous diethylether (180 mL). The reaction mixture was stirred at room temperature for 48 hours, filtered and the solvent removed *in vacuo* (30 ºC, 500 to 200 mbar). The product was purified by Kugelrohr distillation (170 ºC, 1.0 mbar) to give (1*R*)-*N*-(furan-2-ylmethylidene)-1-phenylethanamine **3d** (3.55 g, 17.8 mmol, 30%) as a yellow oil.

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

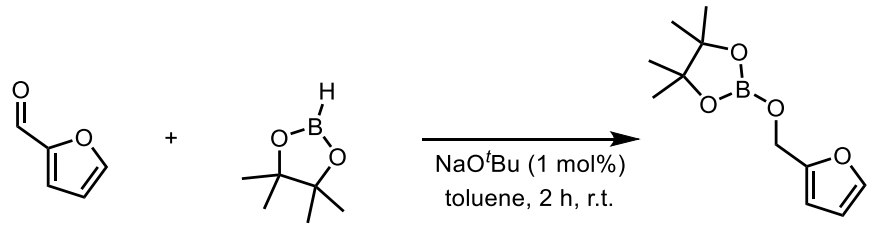
8.17 (s, 1H), 7.54 (d, *J* = 1.4 Hz, 1H), 7.44-7.41 (m, 2H), 7.38-7.34 (m, 2H), 7.28-7.24 (m, 1H), 6.76 (d, *J* = 3.4 Hz, 1H), 6.49 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.53 (q, *J* = 6.5 Hz, 1H), 1.65 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

151.6, 148.4, 144.8, 144.6, 128.5, 127.0, 126.8, 114.3, 111.6, 69.9, 24.5.

Data were in accordance with those previously reported.[10]

4,4,5,5-Tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane **3e**



Furfural (4.31 mL, 52.0 mmol) was added to a stirred mixture of sodium *tert*-butoxide (50 mg, 0.52 mmol) in anhydrous toluene (100 mL). Pinacolborane (8.7 mL, 60 mmol) was added portionwise (4 at 20 minute intervals) – *n.b* caution, addition of pinacolborane is exothermic. The reaction mixture was stirred at room temperature for 2 hours, the solvent removed *in vacuo* (40 °C, 400 to 30 mbar) and the product purified by Kugelrohr distillation (60 °C, 0.3 mbar) to give 4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane 3e (10.6 g, 47.3 mmol, 91%) as a yellow oil.

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

7.40 (dd, J = 1.8, 0.7 Hz, 1H), 6.35-6.30 (m, 2H), 4.85 (s, 2H), 1.29 (s, 12H).

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

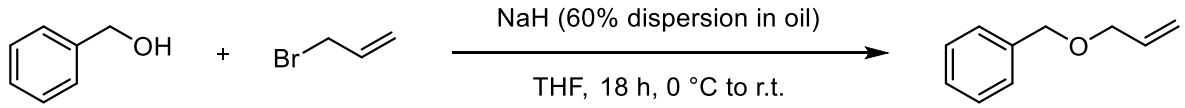
152.5, 142.5, 110.3, 108.3, 83.1, 59.2, 24.6.

^{11}B NMR: (101 MHz, $CDCl_3$)

22.0 (br. s, $\Delta\nu_{1/2}$ = 93.5 Hz)

Data were in accordance with those previously reported.[11]

Allylbenzyl ether



According to a modification of the procedure reported by Williams,[12] a solution of benzyl alcohol (3.1 mL, 30 mmol) in anhydrous THF (10 mL) was added slowly to a stirring solution of sodium hydride (1.30 g, 33 mmol, 60% dispersion in oil) in anhydrous THF (30 mL) at 0 °C under an N_2 atmosphere. The solution was stirred at 0 °C for 1 hour. Allyl bromide (2.85 mL, 33 mmol) was then added to the solution dropwise. After stirred at 0 °C for 1 hour, the reaction mixture was allowed to reach room temperature and subsequently stirred for 16 hours. The reaction mixture was poured into a saturated ammonium chloride solution (100 mL) and the product extracted with ethyl acetate (3 x 50 mL). The organic layers were washed with saturate sodium bicarbonate (50 mL) and brine (100 mL), then dried ($MgSO_4$) and concentrated *in vacuo* to give allylbenzyl ether as a colourless oil (2.67 g, 18 mmol, 60%).

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

7.38 – 7.28 (m, 5H), 5.96 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.32 (dq, J = 17.2, 1.7 Hz, f1H), 5.21 (dq, J = 10.4, 1.4 Hz, 1H), 4.53 (s, 2H), 4.04 (dt, J = 5.6, 1.4 Hz, 2H).

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

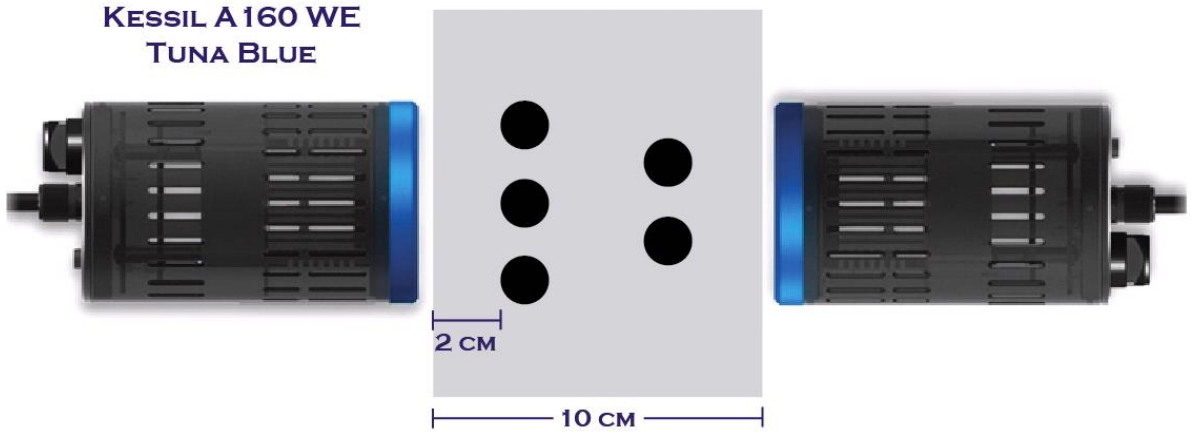
138.5, 134.9, 128.5, 127.9, 127.7, 117.3, 72.3, 71.3.

Data were in accordance with those previously reported.[12]

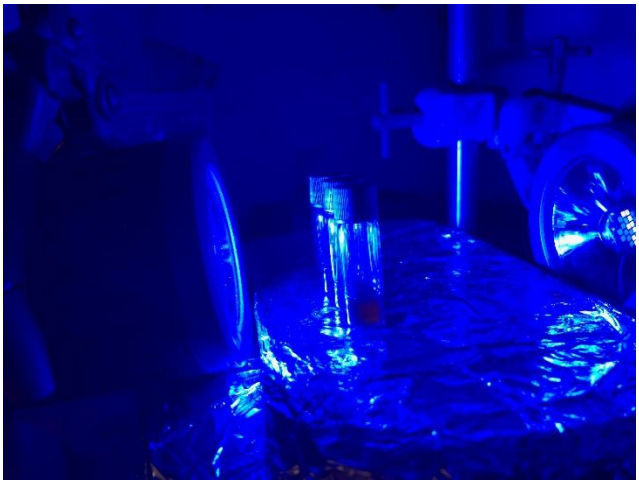
14. General reaction Procedure: Iron-catalysed Deuteration

A 1.75 mL sample vial with screw-cap lid is loaded with [$dmpe_2FeCl_2$] **1** (3.5 mg, 8.2 μmol, 2.5 mol%) and NaO^tBu (1.6 mg, 16.4 μmol, 5 mol%) before the addition of HBpin (1 drop, *ca.* 5 μL, 5 mol%), THF (0.2 mL) and CD_3OD (0.2 mL). *n.b* Any remaining HBpin at this stage is destroyed by reaction with CD_3OD, releasing HD. Substrate (arene/alkene, 0.33 mmol) is added and the vial sealed and irradiated. On completion, the vial is opened, diluted with Et_2O (0.5 mL), the mixture filtered (SiO_2 plug) and the solvent removed *in vacuo* (30 °C, 300 to 10 mbar) to give the deuterated product. Deuterium incorporation was determined by integration of residual C-H resonances in the ^1H NMR spectra.

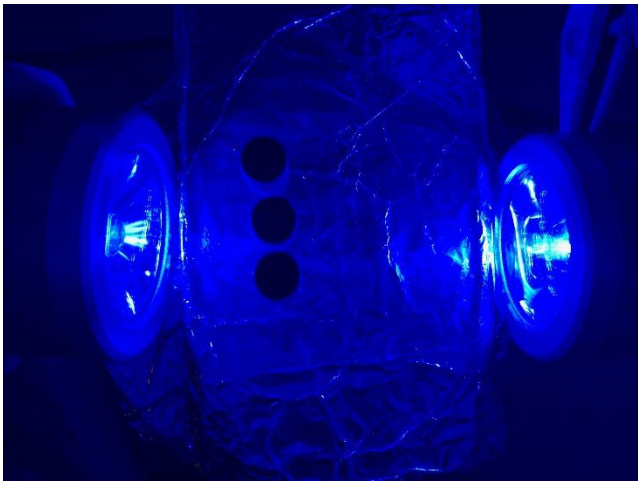
Volatile substrates/products: The general procedure was altered to avoid loss of material. Product recovery/yield was determined by the addition of an internal standard (1,3,5-trimethoxybenzene).



a) Schematic overview of reaction setup



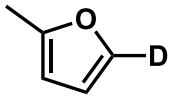
b) Side-on view



c) Aerial view

15. Product data

2-Methyl-5D-furan **[D]-3a**



Following the general deuteration procedure, 2-methylfuran **3a** (27 mg, 0.33 mmol) was reacted to give 2-methyl-5D-furan **[D]-3a**. Trimethoxybenzene was added as an internal standard to quantify recovery (87%, *5D*-97% incorporation).

MS: (HRMS – EI^+)

Found 83.04674 ($C_5H_5D_1O_1$), requires 83.04759.

^{1}H NMR: (500 MHz, CD_3OD)

7.32-7.30 (m, 0.03 H), 6.26 (d, *J* = 2.9 Hz, 1H), 5.99-5.97 (m, 1H), 2.27 (s, 3H).

^{2}H NMR: (77 MHz, CH_3OH)

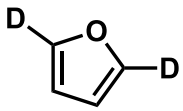
7.34 (s).

^{13}C NMR: (125 MHz, $CD_3OD/CDCl_3$)

155.9, <u>144.4 (t, *J* = 31 Hz)</u>, 113.9, 109.2, 17.1.

n.b underlined ^{13}C resonances denote labelled position(s)

2,5D-furan **[D]-3b**



Following the general deuteration procedure, furan **3b** (23 mg, 0.33 mmol) was reacted to give 2,5-D-furan **[D]-3b***.* Trimethoxybenzene was added as an internal standard to quantify recovery (54%, *2,5D*-91% incorporation).

MS: (HRMS $[M+H]^+ – Cl^+$)

Found 71.04532 ($C_4H_3D_2O_1$), requires 71.04605.

^{1}H NMR: (500 MHz, CD_3OD)

7.51 (s, 0.09H), 6.42 (s, 2H).

^{2}H NMR: (77 MHz, $CH_{3p}OH$)

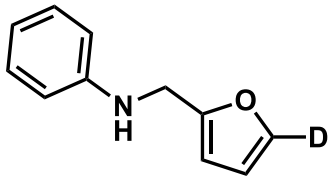
7.50 (s).

^{13}C NMR: (125 MHz, CD_3OD)

142.4, <u>142.3, 142.1 (t, *J* = 31 Hz), 142.0 (t, *J* = 31 Hz)</u>.

n.b underlined ^{13}C resonances denote labelled position(s)

N-(5D-Furan-2-ylmethyl)aniline **[D]-3c**



Following the general deuteration procedure, *N*-(furan-2-ylmethyl)aniline **3c** (57 mg, 0.33 mmol) was reacted to give *N-(5D-furan-2-ylmethyl)aniline* **[D]-3c** (50 mg, 87%, D-incorporation: 87%) as a yellow oil.

MS: (HRMS – EI^+)

Found 174.08804 ($C_{11}H_{10}D_1O_1N_1$), requires 174.08979.

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

7.39 (dd, *J* = 1.7, 0.9 Hz, 0.13H), 7.24-7.18 (m, 2H), 6.79-6.75 (m, 1H), 6.73-6.68 (m, 2H), 6.34 (d, *J* = 3.4 Hz, 1H), 6.27-6.25 (m, 1H), 4.35 (d, *J* = 5.2 Hz, 2H), 4.03 (br. s, 1H).

^{2}H NMR: (77 MHz, $CDCl_3$)

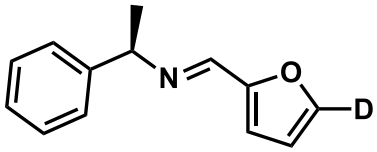
7.33 (s).

^{13}C NMR: (125 MHz, $CDCl_3$)

152.7, 147.7, <u>141.9, 141.7 (t, *J* = 31.6 Hz)</u>, 129.2, 118.0, 113.2, 110.3, 110.1, 107.1, 41.5.

n.b underlined ^{13}C resonances denote labelled position(s)

(1*R*)-*N*-(5D-Furan-2ylmethylidene)-1-phenylethanamine **[D]-3d**



Following the general deuteration procedure, (1*R*)-*N*-(furan-2ylmethylidene)-1-phenylethanamine **3d** was reacted to give *(1R)-N-(5D-furan-2ylmethylidene)-1-phenylethanamine* **[D]-3d** (66 mg, >95%, D-incorporation: 44%) as a yellow oil.

MS: (HRMS – EI^+)

Found 200.10498 ($C_{13}H_{12}D_1O_1N_1$), requires 200.10544.

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

8.17 (s, 1H), 7.55-7.53 (m, 0.56H), 7.45-7.40 (m, 2H), 7.38-7.34 (m, 2H), 7.26 (tt, *J* = 7.4, 2.0 Hz, 1H), 6.76 (d, J = 3.4 Hz, 1H), 6.49 (dd, J = 3.4, 1.7 Hz, 1H), 4.53 (q, *J* = 6.7 Hz, 1H), 1.65 (d, *J* = 6.7 Hz, 3H).

^{2}H NMR: (77 MHz, $CHCl_3$)

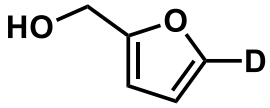
7.59 (s).

^{13}C NMR: (125 MHz, $CDCl_3$)

151.6, 148.4, 144.8, <u>144.6, 144.5 (t, *J* = 31.3 Hz)</u>, 128.5, 127.0, 126.8, 114.3, 111.6, 69.9, 24.5.

n.b underlined ^{13}C resonances denote labelled position(s)

2-(Hydroxymethyl)-5D-furan **[D]-3e**



Following the general deuteration procedure, 4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane **3e** (74 mg, 0.33 mmol) was reacted to give *2-(hydroxymethyl)-5D-furan* **[D]-3e** (29 mg, 91%, *5D*-80% incorporation) as a colourless oil.

MS: (HRMS – EI^+)

Found 99.04247 ($C_5H_5D_1O_2$), requires 99.04251.

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

7.43 (dd, *J* = 1.8, 0.9 Hz, 0.2H), 6.36 (d, *J* = 3.3 Hz, 1H), 6.32 (app. d, *J* = 3.2 Hz, 1H), 4.64 (s, 2H), 1.74 (br. s, 1H).

^{2}H NMR: (77 MHz, $CHCl_3$)

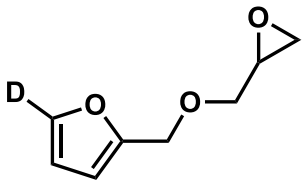
7.48 (s).

^{13}C NMR: (125 MHz, $CDCl_3$)

154.0, 153.9, <u>142.6, 142.4 (t, *J* = 31 Hz)</u>, 110.4, 110.2, 107.8, 57.6.

n.b underlined ^{13}C resonances denote labelled position(s)

2-[(2,3-Epoxypropoxy)methyl]-*5D*-furan **[D]-3f**



Following the general deuteration procedure, 2-[(2,3-epoxypropoxy)methyl]furan **3f** (51 mg, 0.33 mmol) was reacted to give *2-[(2,3-epoxypropoxy)methyl]-5D-furan* **[D]-3f** (31.0 mg, 0.20 mmol, 61%, 58% D-incorporation) as a colourless oil.

MS: (HRMS – EI^+)

Found 155.06842 ($C_8H_9D_1O_3$), requires 155.06872.

^{1}H NMR: (500 MHz, CD_3OD)

7.50 (s, 0.42H), 6.41-6.37 (m, 2H), 4.57-4.47 (m, 2H), 3.78 (dd, *J* = 11.7, 2.6 Hz, 1H), 3.37 (dd, *J* = 11.4, 6.1 Hz, 1H), 3.16-3.10 (m, 1H), 2.78 (t, *J* = 4.8 Hz, 1H), 2.59 (dd, *J* = 5.0, 2.6 Hz, 1H).

^{2}H NMR: (77 MHz, CD_3OD)

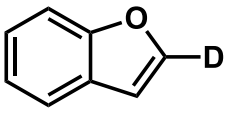
7.52 (s).

^{13}C NMR: (125 MHz, CD_3OD)

151.6, 151.5, <u>142.8, 142.6 (t, *J* = 31.1 Hz)</u>, 109.9, 109.7 (t, *J* = 2.0 Hz), 109.2, 70.4, 64.4, 50.3, 43.3.

n.b underlined ^{13}C resonances denote labelled position(s)

1D-Benzofuran **[D]-3g**



Following the general deuteration procedure, benzofuran **3g** (39 mg, 0.33 mmol) was reacted to give *1D*-benzofuran **[D]-3g** (38.0 mg, 0.32 mmol, 97%, 92% D-incorporation) as a yellow oil.

By a modification of the general deuteration procedure, the reaction was conducted using benzofuran **g** (1.10 g, 9.3 mmol), [$dmpe_2FeCl_2$] **1** (98.0 mg, 230 µmol, 2.5 mol%), NaO^tBu (44.0 mg, 460 µmol, 5 mol%), pinacolborane (66 µL, 460 µmol, 5 mol%), tetrahydrofuran (5 mL) and CD_3OD (5 mL). The reaction mixture was irradiated for 48 h, filtered (10 g SiO_2 plug, EtOAc) and the solvent removed *in vacuo* (30 °C, 400 to 20 mbar) to give *1D*-benzofuran **[D]-**3g as a yellow oil. Trimethoxybenzene was added as an internal standard to quantify recovery (84%, 85% incorporation).

MS: (HRMS – EI^+)

Found 119.04599 ($C_8H_5D_1O_1$), requires 119.04759.

^{1}H NMR: (500 MHz, CD_3OD)

7.74 (d, *J* = 2.2 Hz, 0.08 H), 7.63-7.60 (m, 1H), 7.49 (dq, *J* = 8.3, 0.6 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.23 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.84-6.82 (m, 1H).

^{2}H NMR: (77 MHz, CH_3OH)

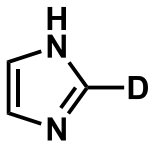
7.74 (s).

^{13}C NMR: (125 MHz, CD_3OD)

155.0, <u>144.9, 144.7 (t, *J* = 31.1 Hz)</u>, 127.5, 123.8, 122.4, 120.8, 110.7, 106.1, 105.9 (t, *J* = 2.0 Hz).

n.b underlined ^{13}C resonances denote labelled position(s)

2D-Imidazole **[D]-3h**



Following the general deuteration procedure, imidazole **3h** (22 mg, 0.33 mmol) was reacted to give *2D-imidazole* **[D]-3h** (22 mg, 0.33 mmol). Trimethoxybenzene was added as an internal standard to quantify recovery (>95%, *2D*-84% incorporation).

MS: (HRMS – EI^+)

Found 69.04310 ($C_3H_3D_1N_2$), requires 69.04318.

^{1}H NMR: (500 MHz, CD_3OD)

7.69 (s, 0.16H), 7.07 (s, 2H).

^{2}H NMR: (77 MHz, CD_3OD)

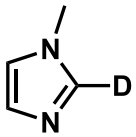
7.87 (br. s).

^{13}C NMR: (125 MHz, CD_3OD)

<u>134.9, 134.7 (t, J = 32 Hz)</u>, 121.2 (br. s, $\Delta\nu_{1/2}$ = 36 Hz).

n.b underlined ^{13}C resonances denote labelled position(s)

2D-N-Methylimidazole **[D]-3i**



Following the general deuteration procedure, *N*-methylimidazole **3i** (27 mg, 0.33 mmol) was reacted to give *2D-N-methylimidazole* **[D]-3i**. Trimethoxybenzene was added as an internal standard to quantify recovery (>95%, *2D*-92% incorporation).

MS: (HRMS – EI^+)

Found 84.06789 ($C_4H_6D_1N_2$), requires 84.06665.

^{1}H NMR: (500 MHz, CD_3OD)

7.59 (s, 0.08H), 7.07 (s, 1H), 6.96 (s, 1H), 3.74 (s, 3H).

^{2}H NMR: (77 MHz, CH_3OH)

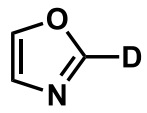
7.60 (s).

^{13}C NMR: (125 MHz, CD_3OD)

<u>137.7, 137.5 (t, *J* = 33.0 Hz)</u>, 127.6, 120.4, 32.1.

n.b underlined ^{13}C resonances denote labelled position(s)

2D-Oxazole **[D]-3j**



Following the general deuteration procedure, oxazole **3j** (23 mg, 0.33 mmol) was reacted to give *2D-oxazole* **[D]-3j**. Trimethoxybenzene was added as an internal standard to quantify recovery (79%, *2D*-70% incorporation).

MS: (HRMS – EI^+)

Found 71.03537 ($C_3H_3D_1O_1N_1$), requires 71.03502.

^{1}H NMR: (500 MHz, CD_3OD)

8.25 (s, 0.3), 8.00-7.93 (m, 1H), 7.27-7.18 (m, 1H).

^{2}H NMR: (77 MHz, CD_3OD)

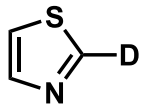
8.24 (s).

^{13}C NMR: (125 MHz, CD_3OD)

<u>152.2, 152.0 (t, *J* = 35.2 Hz)</u>, 139.6, 139.5, 125.6.

n.b underlined ^{13}C resonances denote labelled position(s)

2D-Thiazole **[D]-3k**



Following the general deuteration procedure, thiazole **3k** (28 mg, 0.33 mmol) was reacted to give *2D-thiazole* **[D]-3k**. Trimethoxybenzene was added as an internal standard to quantify recovery (90%, *2D*-76% incorporation).

MS: (HRMS – EI^+)

Found 87.01212 ($C_3H_3D_1N_1{}^{32}S_z$), requires 87.01217.

^{1}H NMR: (500 MHz, CD_3OD)

9.06 (s, 0.24H), 8.00-7.93 (m, 1H), 7.71-7.64 (m, 1H).

^{2}H NMR: (77 MHz, CD_3OD)

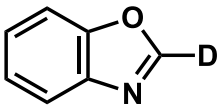
9.08 (s).

^{13}C NMR: (125 MHz, CD_3OD)

<u>153.9, 153.6 (t, *J* = 32.3 Hz)</u>, 142.5, 142.4 (t, *J* = 2.1 Hz), 119.2.

n.b underlined ^{13}C resonances denote labelled position(s)

2D-Benzoxazole **[D]-3l**



Following the general deuteration procedure, benzoxazole **3l** (27 mg, 0.33 mmol) was reacted to give *2D-benzoxazole* **[D]-3l** (25 mg, 96%, 40% D-incorporation) as a yellow oil.

^{1}H NMR: (500 MHz, CD_3OD)

8.48 (s, 0.6H), 7.78-7.75 (m, 1H), 7.70-7.66 (m, 1H), 7.49-7.41 (m, 2H).

^{2}H NMR: (77 MHz, CH_3OH)

8.43 (s).

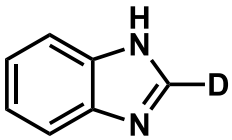
^{13}C NMR: (125 MHz, CD_3OD)

<u>153.7, 153.5 (t, *J* = 34.9 Hz)</u>, 149.9, 139.4, 125.6, 124.6, 119.6.

n.b underlined ^{13}C resonances denote labelled position(s)

Data were in accordance with those previously reported[7].

1D-Benzimidazole **[D]-3m**



Following the general deuteration procedure, benzimidazole **3m** (39 mg, 0.33 mmol) was reacted to give *1D*-benzimidazole **[D]-3m** (33.5 mg, 0.28 mmol, 85%, 86% D-incorporation) as a colourless amorphous solid.

MS: (HRMS – EI^+)

Found 119.05805 ($C_7H_5D_1N_2$), requires 119.05883.

MPt: 173-176 °C (CD_3OD)

^{1}H NMR: (500 MHz, CD_3OD)

8.16 (s, 0.07 H), 7.65-7.60 (m, 2H), 7.27 (dt, *J* = 9.4, 3.1 Hz, 2H).

^{2}H NMR: (77 MHz, CD_3OD)

8.15 (br. s), 7.84 (s, N*D*).

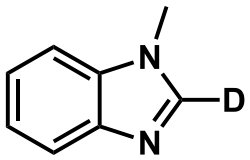
^{13}C NMR: (125 MHz, CD_3OD)

<u>141.1, 140.9 (t, *J* = 32.6 Hz)</u>, 122.4, 114.8 (br. s, $\Delta\nu_{1/2}$ = 226.5 Hz).

1 x ^{13}C resonance not observed

n.b underlined ^{13}C resonances denote labelled position(s)

1-Methyl-2-d_1-benzimidazole **[D]-3n**



Following the general deuteration procedure, 1-methylbenzimidazole **3n** (44 mg, 0.33 mmol) was reacted to give *1-methyl-2-d_1-benzimidazole* **[D]-3n** (32 mg, 82%, D-incorporation: 2-D = 92%) as a yellow oil.

MS: (HRMS – EI^+)

Found 133.07605 ($C_8H_7D_1N_2$), requires 133.07448.

^{1}H NMR: (500 MHz, CD_3OD)

8.11-8.08 (m, 0.08H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.56-7.51 (m, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 3.90 (s, 3H).

^{2}H NMR: (77 MHz, CH_3OH)

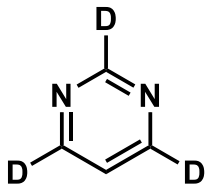
8.12 (s).

^{13}C NMR: (125 MHz, CD_3OD)

<u>143.8, 143.6 (t, *J* = 32 Hz)</u>, 142.5, 134.4, 122.8, 122.0, 118.6, 109.7, 29.9.

n.b underlined ^{13}C resonances denote labelled position(s)

2,4,6-d_3-Pyrimidine **[D]-3o**



Following the general deuteration procedure, pyrimidine **3o** (26 mg, 0.33 mmol) was reacted to give *2,4,6-d_3-pyrimidine* **[D]-3o**. Trimethoxybenzene was added as an internal standard to quantify recovery (90%, D-incorporation: 2-D = 36%, 4,6-D = 18%).

MS: (HRMS – EI^+)

Found 81.04116 ($C_4H_3D_1N_2$), requires 81.04318. (*mono-deutero*)

^{1}H NMR: (500 MHz, CD_3OD)

9.18 (s, 0.69H), 8.81 (d, *J* = 4.8 Hz, 1.64H), 7.57-7.52 (m, 1H).

^{2}H NMR: (77 MHz, CH_3OH)

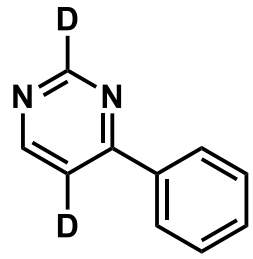
9.20 (s), 8.85 (s).

^{13}C NMR: (125 MHz, $CDCl_3$)

<u>158.0, 157.7 (t, *J* = 32.0 Hz)</u>, <u>157.0, 156.7 (t, *J* = 27 Hz)</u>, 122.0-121.9.

n.b underlined ^{13}C resonances denote labelled position(s)

4-Phenyl-2,5-d_2-pyrimidine **[D]-3p**



Following the general deuteration procedure, 4-phenylpyrimidine **3p** (51 mg, 0.33 mmol) was reacted to give *4-phenyl-2,5-d_2-pyrimidine* **[D]-3p** (49 mg, 95%, D-incorporation: 2-D = 77%, 5-D = 31%) as a yellow amorphous solid.

MS: (HRMS – EI^+)

Found 159.08591 ($C_{10}H_5D_3N_2$), requires 159.08758.

MPt: 65-66 °C (CD_3OD)

^{1}H NMR: (500 MHz, CD_3OD)

9.19 (s, 0.23H), 8.79 (d, *J* = 5.5 Hz, 0.69H), 8.20-8.14 (m, 2H), 8.00-7.97 (m, 1H), 7.58-7.52 (m, 3H).

^{2}H NMR: (77 MHz, CH_3OH)

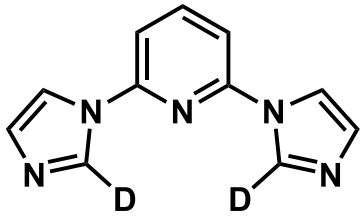
9.20 (s), 8.81 (s).

^{13}C NMR: (125 MHz, CD_3OD)

164.3, <u>158.2, 157.9 (t, *J* = 31.3 Hz)</u>, <u>157.2, 156.9 (t, *J* = 26.5 Hz)</u>, 136.1, 131.0, 128.8, 127.0, 117.3-117.1.

n.b underlined ^{13}C resonances denote labelled position(s)

2,6-Bis(1-imidazolyl)pyridine-d_2 **[D]-3q**



Following the general deuteration procedure, 2,6-bis(1-imidazolyl)pyridine **3q** (69 mg, 0.33 mmol) was reacted to give *2,6-bis(1-imidazolyl)pyridine-d_2* **[D]-3q** (51 mg, 72%, D-incorporation: 80%) as a yellow amorphous solid.

MS: (HRMS – EI^+)

Found 213.09757 ($C_{11}H_7D_2N_5$), requires 213.09780.

MPt: 98-100 °C (CD_3OD)

^{1}H NMR: (500 MHz, CD_3OD)

8.66 (s, 0.41H), 8.13 (t, *J* = 8.1 Hz, 1H), 7.99 (s, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.19 (s, 2H).

^{2}H NMR: (77 MHz, CH_3OH)

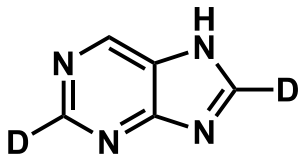
8.70 (br. s, $\Delta\nu_{1/2}$ = 4.7 Hz).

^{13}C NMR: (125 MHz, CD_3OD)

148.1, 142.8, <u>135.3, 135.1 (t, *J* = 31.0 Hz)</u>, 129.4, 116.6, 110.3.

n.b underlined ^{13}C resonances denote labelled position(s)

7H-Purine-2,8-d_2 **[D]-3r**



Following the general deuteration procedure, purine **3r** (40 mg, 0.33 mmol) was reacted to give 7H-*purine-2,8-d_2* **[D]-3r** (34 mg, 84%, D-incorporation: 2-position 80%, 8-position 22%) as an off-white amorphous solid.

MS: (HRMS – EI^+)

Found 121.05016 ($C_5H_3D_1N_4$), requires 121.04932.

MPt: 208-210 °C (CD_3OD)

^{1}H NMR: (500 MHz, CD_3OD)

9.11 (br. s, 0.78H), 8.95 (s, 1H), 8.57 (br. s, 0.2H).

^{2}H NMR: (77 MHz, CH_3OH)

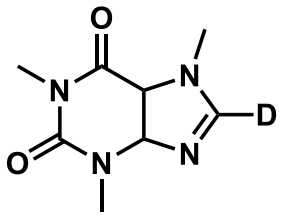
9.08 (br. s), 8.53 (br. s)

^{13}C NMR: (150 MHz, CD_3OD)

<u>156.2 (br. s), 153.4</u>, <u>147.6 (br. s), 146.3 (br. s)</u>, 131.3 (br. s).

n.b underlined ^{13}C resonances denote labelled position(s)

Caffeine-d_1 **[D]-3s**



Following the general deuteration procedure, caffeine **3s** (65 mg, 0.33 mmol) was reacted to give *caffeine-d_1* **[D]-3s** (58.8 mg, 90%, 68% D-incorporation) as an off-white amorphous solid.

MS: (HRMS – EI^+)

Found 197.09973 ($C_8H_{11}D_1O_2N_4$), requires 197.10175.

MPt: 236-238 °C ($CDCl_3$)

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

7.51 (s, 0.32H), 3.99 (s, 3H), 3.59 (s, 3H), 3.40 (s, 3H).

^{2}H NMR: (77 MHz, CH_3OH)

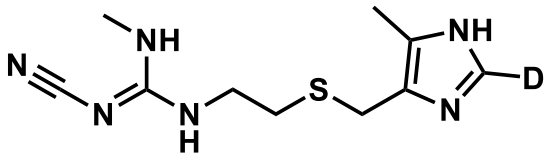
7.86 (s).

^{13}C NMR: (125 MHz, $CDCl_3$)

155.5, 151.8, 148.7, <u>141.4, 141.2 (t, *J* = 32 Hz)</u>, 107.6, 33.6, 29.7, 27.9.

n.b underlined ^{13}C resonances denote labelled position(s)

Cimetidine-d_1 **[D]-3t**



Following the general deuteration procedure, cimetidine **3t** (83 mg, 0.33 mmol) was reacted to give *cimetidine-d_1* **[D]-3t** (49.7 mg, 82%, D-incorporation: 76%) as a colourless microcrystalline solid.

MS: (HRMS – EI^+)

Found 253.12360 ($C_{10}H_{15}D_1N_6{}^{32}S_1$), requires 253.12145.

MPt: 159-161 °C (CD_3OD)

^{1}H NMR: (500 MHz, CD_3OD)

7.50 (s, 0.24H), 3.73 (s, 3H), 3.37 (t, *J* = 6.7 Hz, 2H), 2.81 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 3H).

^{2}H NMR: (77 MHz, CH_3OH)

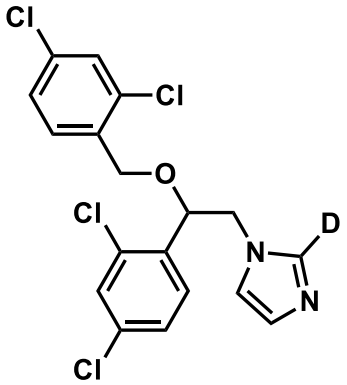
7.50 (br. s)

^{13}C NMR: (125 MHz, CD_3OD)

160.6, <u>133.3, 133.1 (t, *J* = 33 Hz)</u>, 118.6, 40.7, 30.2, 27.3, 25.9, 8.7. *(2 x resonances not observed)*

n.b underlined ^{13}C resonances denote labelled position(s)

Miconazole-d_1 **[D]-3u**



Following the general deuteration procedure, miconazole **3u** (136 mg, 0.33 mmol) was reacted to give *miconazole-d_1* **[D]-3u** (121 mg, 88%, D-incorporation: 99%) as a colourless amorphous solid.

MS: (HRMS – EI^+)

Found 414.99083 ($C_{18}H_{13}D_1O_1N_2{}^{35}Cl_4$), requires 414.99175.

MPt: 59-62 °C ($CDCl_3$)

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

7.54 (s, 1H), 7.48-7.34 (m, 3H), 7.30 (s, 2H), 7.09 (br. s, $\Delta\nu_{1/2}$ = 64 Hz, 1H), 6.98 (br. s, $\Delta\nu_{1/2}$ = 66 Hz, 1H), 5.15 (d, J = 4.7 Hz, 1H), 4.48 (ABq, $\Delta\nu_{AB}$ = 50.0 Hz, J_{AB} = 12.5 Hz, 2H), 4.37 (br. s, 1H), 4.32 (br. s, $\Delta\nu_{1/2}$ = 36 Hz, 1H).

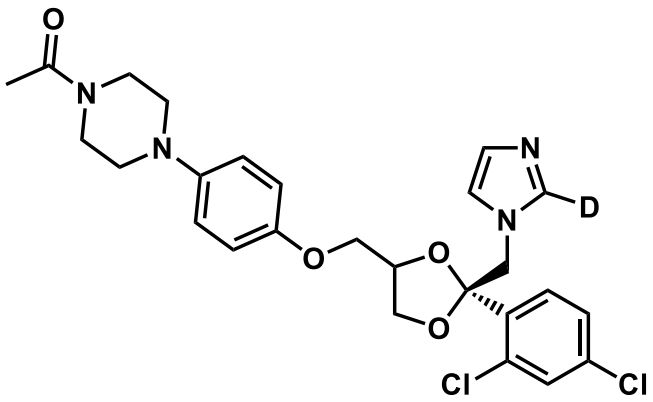
^{2}H NMR: (77 MHz, CH_3OH)

7.60 (br. s, $\Delta\nu_{1/2}$ = 8.5 Hz).

^{13}C NMR: (125 MHz, $CDCl_3$)

134.7, 134.2, 134.1, 133.9, 133.8, 133.5, 130.6, 129.1, 128.9, 128.7, 127.6, 127.0, 120.0 (br. $\Delta\nu_{1/2}$ = 100 Hz), 77.2, 67.7, 50.8 (br. $\Delta\nu_{1/2}$ = 60 Hz). *(deuterated carbon not observed)*

Ketoconazole-d_1 **[D]-3b**



Following the general deuteration procedure, ketoconazole **3v** (175 mg, 0.33 mmol) was reacted to give *ketoconazole-d_1* **[D]-3v** (166 mg, 94%, D-incorporation: 99%) as a colourless amorphous solid.

MS: (HRMS – EI^+)

Found 531.15535 ($C_{26}H_{27}D_1O_4N_4{}^{35}Cl_2$), requires 531.15449.

MPt: 135-138 °C (CD_3OD)

^{1}H NMR: (500 MHz, CD_3OD)

7.67 (d, *J* = 9.8 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.37 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 4.77-4.50 (m, 2H), 4.42-4.32 (m, 1H), 3.91 (dd, *J* = 8.3, 7.0 Hz, 1H), 3.81-3.64 (m, 6H), 3.52 (dd, *J* = 9.8, 5.5 Hz, 1H), 3.09 (t, *J* = 4.6 Hz, 2H), 3.03 (t, *J* = 5.0 Hz, 2H), 2.15 (s, 3H).

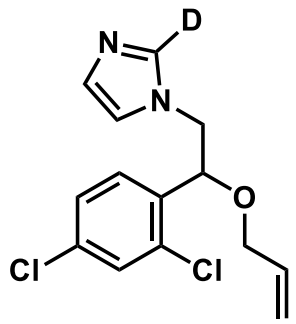
^{2}H NMR: (77 MHz, CH_3OH)

7.74 (br. s, $\Delta\nu_{1/2}$ = 10 Hz).

^{13}C NMR: (125 MHz, CD_3OD)

170.3, 153.3, 145.8, 135.5, 134.9, 133.0, 130.8, 129.9, 127.0, 118.7, 115.0, 108.0, 75.0, 67.8, 66.8, 50.9, 50.5, 46.2, 41.4, 19.8.

Imazalil-d_1 **[D]-3w**



Following the general deuteration procedure, imazalil **3w** (98 mg, 0.33 mmol) was reacted to give *imazalil-d_1* **[D]-3w** (121 mg, 88%, D-incorporation: 90%) as a viscous yellow oil.

^{1}H NMR: (500 MHz, CD_3OD)

7.58-7.50 (m, 1H), 7.49-7.41 (m, 0.5H), 7.39 (dd, *J* = 8.5, 2.1, 0.3H), 7.36 (d, *J* = 1.2 Hz, 1.5H), 7.31 (d, *J* = 1.3 Hz, 0.4H), 7.10-7.04 (m, 1H), 6.97-6.92 (m, 1H), 5.90-5.75 (m, 1H), 5.17 (qq, *J* = 17.2, 1.8 Hz, 2H), 5.06 (dd, *J* = 7.1, 3.3 Hz, 1H), 4.49 (ABq, $\Delta\nu_{AB}$ = 50.0 Hz, J_{AB} = 12.3 Hz, 0.4H), 4.38-4.20 (m, 2H), 3.89 (ABqddt, $\Delta\nu_{AB}$ = 76.0 Hz, J_{AB} = 13.0, 4.9, 1.7 Hz, 1.6H). *(mixture of rotamers)*

^{2}H NMR: (77 MHz, CH_3OH)

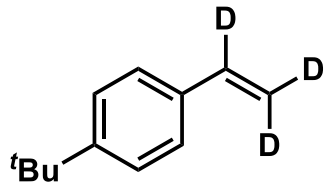
7.57 (br. s, $\Delta\nu_{1/2}$ = 4.6 Hz).

^{13}C NMR: (125 MHz, CD_3OD)

<u>137.6 (t, *J* = 32Hz)</u>, 134.7, 134.4, 134.2, 134.1, 133.8, 133.5, 133.3, 130.6, 129.1, 129.0, 128.9, 128.7, 127.6, 127.5, 127.4, 127.3, 127.0, 120.2, 120.0, 116.3, 77.1, 76.3, 70.0, 67.7, 50.7. *(mixture of rotamers)*

n.b underlined ^{13}C resonances denote labelled position(s)

4-*tert*-Butylstyrene-*α,β,β-d*$_3$ **[D]-4a**



Following the general deuteration procedure, 4-*tert*-butylstyrene **4a** (53 mg, 0.33 mmol) was reacted to give *4-tert-butylstyrene-α,β,β-d*$_3$ **[D]-4a** (34 mg, 85%, D-incorporation: *α*-82%, *ca. β*-84%) as a yellow oil.

MS: (HRMS – EI$^+$)

Found 163.14391 ($C_{12}H_{13}D_3$), requires 163.14348.

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

7.37 (s, 4H), 6.76-6.69 (m, 0.18H), 5.76-5.68 (m, 0.16H), 5.23-5.18 (m, 0.16H), 1.35 (s, 9H).

^{2}H NMR: (77 MHz, $CHCl_3$)

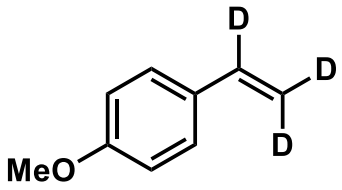
6.76 (br. s), 5.76 (br. s), 5.25 (br. s).

^{13}C NMR: (125 MHz, $CDCl_3$)

150.9, <u>136.6, 136.5, 136.4</u>, 134.9, 134.8, 127.5, 126.0, 125.9, 125.5, 125.2, <u>113.0, 112.9, 112.8, 112.6, 112.4</u>, 31.3.

n.b underlined ^{13}C resonances denote labelled position(s)

4-Methoxystyrene-*α,β,β-d*$_3$ **[D]-4b**



Following the general deuteration procedure, 4-methoxystyrene **4b** (44 mg, 0.33 mmol) was reacted to give 4-methoxystyrene-*α,β,β-d*$_3$ **[D]-4b** (27 mg, 62%, D-incorporation: *α*-71%, *β*-71%) as a yellow oil.

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

7.40-7.32 (m, 2H), 6.90-6.82 (m, 2H), 6.68-6.60 (m, 0.28H), 5.61-5.56 (m, 0.29H), 5.14-5.09 (m, 0.29H), 3.81 (s, 3H).

^{2}H NMR: (77 MHz, THF/CD_3OD)

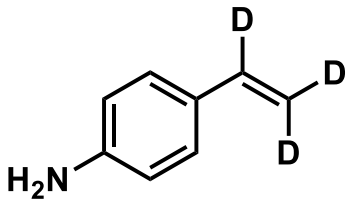
6.74 (br. s), 5.68 (br. s), 5.14 (br. s).

^{13}C NMR: (125 MHz, $CDCl_3$)

159.8, 136.4, 136.3, 136.1, 135.9, 130.8, 127.8, 114.3, 111.8, 111.7, 111.6, 111.4, 55.7.

n.b underlined ^{13}C resonances denote labelled position(s)

4-Aminostyrene-*α,β,β-d*$_3$ **[D]-4c**



Following the general deuteration procedure, 4-aminostyrene **4c** (39 mg, 0.33 mmol) was reacted to give *4-aminostyrene-α,β,β-d*$_3$ **[D]-4c** (36 mg, 89%, D-incorporation: *α*-69%, *β*-61%) as a yellow oil.

MS: (HRMS – EI$^+$)

Found 122.09106 ($C_8H_6D_3N_1$), requires 122.09178.

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

7.28-7.23 (m, 2H), 6.70-6.64 (m, 2H), 6.65-6.60 (m, 0.31H), 5.60-5.53 (m, 0.39H), 5.09-5.03 (m, 0.39H), 3.72 (br. s, 2H).

^{2}H NMR: (77 MHz, $CHCl_3$)

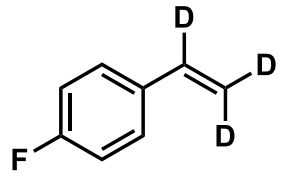
6.76-6.63 (m), 5.67-5.57 (m), 5.18-5.01 (m).

^{13}C NMR: (125 MHz, $CDCl_3$)

146.2, 136.6, 136.5, 136.4, 128.6, 128.4, 127.3, 115.0, 110.0, 109.9, 109.8, 109.6, 109.4.

n.b underlined ^{13}C resonances denote labelled position(s)

4-Fluorostyrene-*α,β,β-d*$_3$ **[D]-4d**



Following the general deuteration procedure, 4-fluorostyrene **4d** (40 mg, 0.33 mmol) was reacted to give *4-fluorostyrene-α,β,β-d*$_3$ **[D]-4d** (24 mg, 58%, D-incorporation: *α*-63%, *ca. β*-53%) as a volatile colourless liquid.

MS: (HRMS – EI^+)

Found 125.07070 ($C_8H_4D_3F_1$), requires 125.07146.

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

7.43-7.37 (m, 2H), 7.07-7.01 (m, 2H), 6.75-6.67 (m, 0.37H), 5.72-5.65 (m, 0.47H), 5.27-5.20 (m, 0.47H).

^{2}H NMR: (77 MHz, $CHCl_3$)

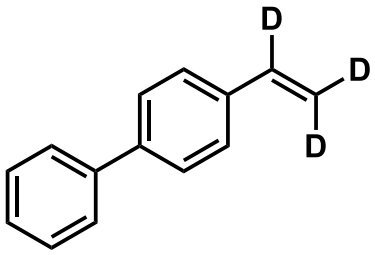
6.75 (br. s), 5.73 (br. s), 5.29 (br. s).

^{13}C NMR: (125 MHz, $CDCl_3$)

162.5 (d, *J* = 246.3 Hz), 135.7, 135.6, 135.5, 135.4, 135.2, 135.0, 133.8, 133.7, 127.8 (d, *J* = 7.9 Hz), 127.7 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.7 Hz), 113.5, 113.4, 113.3, 113.0, 112.9.

n.b underlined ^{13}C resonances denote labelled position(s)

4-Vinylbiphenyl-*α,β,β-d*$_3$ **[D]-4e**



Following the general deuteration procedure, 4-vinylbiphenyl **4e** (59 mg, 0.33 mmol) was reacted to give 4-*vinylbiphenyl-α,β,β-d*$_3$ **[D]-4e** (59 mg, 97%, D-incorporation: *α*-78%, *ca. β*-75%) as an off-white amorphous solid.

MS: (HRMS – EI^+)

Found 183.11204 ($C_{14}H_9D_3$), requires 183.11218.

MPt: 102-105 °C ($CDCl_3$)

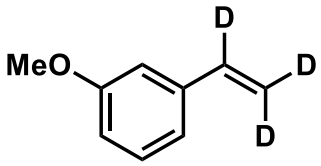
^{1}H NMR: (500 MHz, $CDCl_3$)

7.66-7.57 (m, 4H), 7.54-7.44 (m, 4H), 7.37 (tt, *J* = 6.9, 1.3 Hz, 1H), 6.82-6.75 (m, 0.22H), 5.85-5.77 (0.25H), 5.33-5.27 (m, 0.25H).

^{2}H NMR: (77 MHz, $CHCl_3$)

6.83 (s), 5.86 (s), 5.34 (s).

3-Methoxystyrene-*α,β,β-d*$_3$ **[D]-4f**



Following the general deuteration procedure, 4-methoxystyrene **4f** (46 µL, 0.33 mmol) was reacted to give *3-methoxystyrene-α,β,β-d*$_3$ **[D]-4f** (38 mg, 86%, D-incorporation: *α*-45%, *ca. β*-45%) as a colourless liquid.

MS: (HRMS – EI$^+$)

Found 137.09168 ($C_8H_7D_3O_1$), requires 125.137.09145.

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

7.24 (t, J = 7.9 Hz, 1H), 7.02 (ddq, J = 7.6, 1.5, 0.8 Hz, 1H), 6.96 zp(p, J = 1.1 Hz, 1H), 6.82 (ddd, J = 8.1, 2.6, 0.9 Hz, 1H), 6.77 – 6.67 (m, 0.55 H), 5.79 – 5.70 (m, 0.55 H), 5.29 – 5.22 (m, 0.55 H), 3.83 (s, 3H).

^{2}H NMR: (77 MHz, $CDCl_3$)

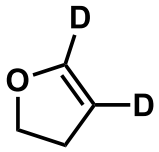
6.74 (m), 5.80-5.78 (m), 5.30 (m).

^{13}C NMR: (125 MHz, $CDCl_3$)

159.96, 139.19, 139.17, 139.12, 136.93, 136.85, 136.83, 136.80, 136.74, 136.69, 136.61, 136.52, 136.42, 136.34, 129.64, 119.06, 119.04, 114.26, 114.11, 114.04, 113.85, 113.82, 113.66, 113.63, 113.58, 113.57, 111.68, 111.65, 55.35.

n.b underlined ^{13}C resonances denote labelled position(s)

2,3-Dihydro-*4D,5D*-furan **[D]-4g**



Following the general deuteration procedure, 2,3-dihydrofuran **4g** (23 mg, 0.33 mmol) was reacted to give *2,3-dihydro-4D,5D-furan* **[D]-4g**. Trimethoxybenzene was added as an internal standard to quantify recovery (77%, *3D*-62%, *4D*-62% incorporation).

MS: (HRMS – EI^+)

Found 72.05629 ($C_4H_4D_2O_1$), requires 72.05542.

^{1}H NMR: (500 MHz, CD_3OD)

6.34 (s, 0.37 H), 4.97 (s, 0.37 H), 4.26 (t, *J* = 9.0 Hz, 2H), 2.59 (t, *J* = 9.7 Hz, 2H).

^{2}H NMR: (77 MHz, CD_3OD)

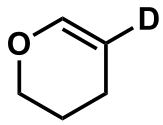
6.38 (s), 5.03 (s).

^{13}C NMR: (125 MHz, CD_3OD)

<u>145.3, 145.2, 145.1, 145.0, 144.9, 144.8</u>, <u>99.1, 98.9, 98.7, 98.5</u>, 97.4, 29.7.

n.b underlined ^{13}C resonances denote labelled position(s)

2,3-Dihydro-*5D*-pyran **[D]-4h**



Following the general deuteration procedure, 2,3-dihydropyran **4h** (28 mg, 0.33 mmol) was reacted to give *2,3-dihydro-5D-pyran* **[D]-4h**. Trimethoxybenzene was added as an internal standard to quantify recovery (84%, *5D*-40% incorporation).

MS: (HRMS – EI^+)

Found 86.07169 ($C_5H_8D_1O_1$), requires 86.07107.

^{1}H NMR: (500 MHz, CD_3OD)

6.35-6.29 (m, 1H), 4.66 (dt, *J* = 6.7, 3.5 Hz, 0.59H), 3.95 (t, *J* = 5.0 Hz, 2H), 2.04-1.95 (m, 2H), 1.89-1.82 (m, 2H).

^{2}H NMR: (77 MHz, CD_3OD)

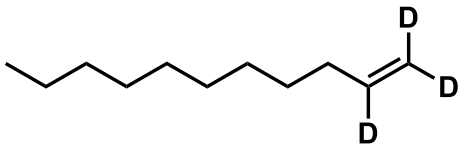
4.73-4.68 (m).

^{13}C NMR: (125 MHz, CD_3OD)

143.7, <u>100.3, 100.0 (t, *J* = 24.8)</u>, 65.3, 22.5, 19.1.

n.b underlined ^{13}C resonances denote labelled position(s)

Undecene-*α,β,β-d*$_3$ **[D]-4i**



Following the general deuteration procedure, undecene **4i** (68 µL, 0.33 mmol) was reacted to give undecene-*α,β,β-d*$_3$ **[D]-4i** (30.0 mg, 61%, D-incorporation: *α*-50%, *ca. β*-37%) as a pale yellow oil. Traces of (*E*)-undec-2-ene and undecane were observed by ^{1}H, ^{2}H, and ^{13}C NMR spectroscopy.

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

5.82 (ddt, J = 17.0, 10.3, 6.7 Hz, 0.5H), 5.04 – 4.85 (m, 1.2H), 2.08 – 1.99 (m, 2H), 1.45 – 1.20 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H).

^{2}H NMR: (77 MHz, $CDCl_3$)

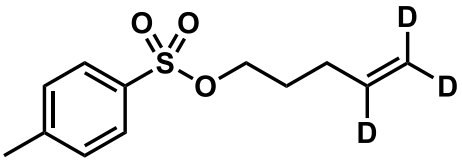
5.86 (m), 5.03 (m), 4.97 (m).

^{13}C NMR: (125 MHz, $CDCl_3$)

<u>139.43, 139.34, 139.31, 139.28, 139.22, 139.10, 138.91, 114.22, 114.13, 114.08, 113.95, 113.81, 113.76, 113.62,</u> 33.98, 32.05, 29.63, 29.45, 29.33, 29.12, 22.83, 14.25.

n.b underlined ^{13}C resonances denote labelled position(s)

Toluene-4-sulfonic acid pent-4-enyl ester-*α,β,β-d*$_3$ **[D]-4j**



Following the general deuteration procedure, toluene-4-sulfonic acid pent-4-enyl ester **4j** (79 mg, 0.33 mmol) was reacted to give *toluene-4-sulfonic acid pent-4-enyl ester-α,β,β-d*$_3$ **[D]-4j** (75.0 mg, 95%, D-incorporation: *α*-48%, *β*-20%) as a colourless oil.

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

7.84-7.78 (m, 2H), 7.40-7.33 (m, 2H), 5.77-5.67 (m, 0.52), 5.01-4.93 (m, 1.59H), 4.06 (t, *J* = 6.5 Hz, 2H), 2.48 (s, 3H), 2.14-2.08 (m, 2H), 1.80-1.73 (m, 2H).

^{2}H NMR: (77 MHz, $CHCl_3$)

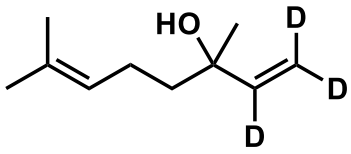
5.83-5.52 (m), 5.05-4.92 (m).

^{13}C NMR: (125 MHz, $CDCl_3$)

144.7, <u>136.6</u>, 133.3, 129.8, 127.9, <u>115.9, 115.7</u>, 66.8, 29.4, 28.0, 21.6.

n.b underlined ^{13}C resonances denote labelled position(s)

Linalool-*α,β,β-d*$_3$ **[D]-4k**



Following the general deuteration procedure, linalool **4k** (51 mg, 0.33 mmol) was reacted to give *linalool-α,β,β-d*$_3$ **[D]-4k** (49.7 mg, 96%, D-incorporation: *α*-36%, *ca. β*-10%) as a yellow oil.

MS: (HRMS – EI$^+$)

Found 155.14185 ($C_{10}H_{17}D_1O_1$), requires 155.14149. (*mono-deutero*)

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

5.94 (dd, *J* = 17.6, 11.3 Hz, 0.64H), 5.26-5.21 (m, 0.91H), 5.18-5.12 (m, 1H), 5.10-5.06 (m, 0.89H), 2.12-1.97 (m, 2H), 1.70 (s, 3H), 1.63 (s, 3H), 1.61-1.56 (m, 2H), 1.30 (s, 3H).

^{2}H NMR: (77 MHz, CH_3OH)

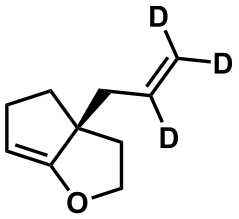
5.92 (app. t, *J* = 2.2 Hz). (*β-D's not observed)*

^{13}C NMR: (125 MHz, $CDCl_3$)

<u>145.1-144.5</u>, 132.0, 131.7, 124.6, 124.3, <u>111.7, 111.6</u>, 73.5-73.3, 42.1, 42.0, 27.9, 27.8, 25.7, 22.8, 22.6, 17.7,17.6.

n.b underlined ^{13}C resonances denote labelled position(s)

(*S*)-5-Allyl-2-oxabicyclo[3.3.0]oct-8-ene-*α,β,β-d*$_3$ **[D]-4l**



Following the general deuteration procedure, (*S*)-5-allyl-2-oxabicyclo[3.3.0]oct-8-ene **4l** (50 mg, 0.33 mmol) was reacted to give *(S)-5-allyl-2-oxabicyclo[3.3.0]oct-8-ene-α,β,β-d*$_3$ **[D]-4l** (47.7 mg, 94%, D-incorporation: *α*-62%, *β*-48%) as a colourless oil.

MS: (HRMS – EI^+)

Found 151.11020 ($C_{10}H_{13}D_1O_1$), requires 151.11019. (*mono-deutero*)

^{1}H NMR: (500 MHz, CD_3OD)

5.96-5.86 (m, 0.38H), 5.16-5.05 (m, 1.05H), 4.52-4.45 (m, 2H), 4.31 (d, *J* = 3.3 Hz, 1H), 2.73-2.65 (m, 1H), 2.37 (ddd, *J* = 14.5, 8.5, 3.7, 1H), 2.30-2.19 (m, 2H), 2.03-1.97 (m, 2H), 1.74-1.63 (m, 2H).

^{2}H NMR: (77 MHz, CH_3OH)

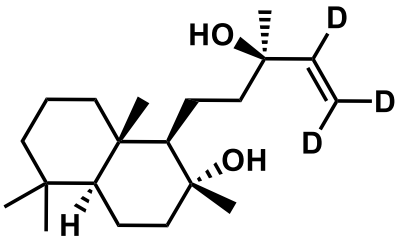
5.98-5.83 (m), 5.16-5.03 (m).

^{13}C NMR: (125 MHz, $CDCl_3$)

168.4, <u>135.5-134.8 (m)</u>, <u>116.5-115.8 (m)</u>, 87.9, 75.8, 54.0, 38.2-37.8 (m), 35.1, 34.4, 32.3.

n.b underlined ^{13}C resonances denote labelled position(s)

Sclareol-*α,β,β-d*$_3$ **[D]-4m**



Following the general deuteration procedure, sclareol **4m** (101 mg, 0.33 mmol) was reacted to give sclareol-*α,β,β-d*$_3$ **[D]-4m** (70 mg, 98%, D-incorporation: *α*-47%, *ca. β*-12%) as a colourless amorphous solid.

MS: (HRMS – EI$^+$)

Found 309.27643 ($C_{20}H_{35}D_1O_2$), requires 309.27726. (*mono-deutero*)

MPt: 78-81 °C ($CDCl_3$)

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

5.95 (dd, *J* = 17.0, 10 Hz, 0.53H), 5.27-5.20 (m, 0.89H), 5.10-5.00 (m, 0.86H), 1.86 (dt, *J* = 12.8, 3.3 Hz, 1H), 1.71-1.48 (m, 7H), 1.48-1.32 (m, 4H), 1.28-1.24 (m, 3H), 1.21-1.11 (m, 5H), 1.02-0.91 (m, 2H), 0.88 (s, 3H), 0.83-0.78 (m, 6H).

^{2}H NMR: (77 MHz, CH_3OH)

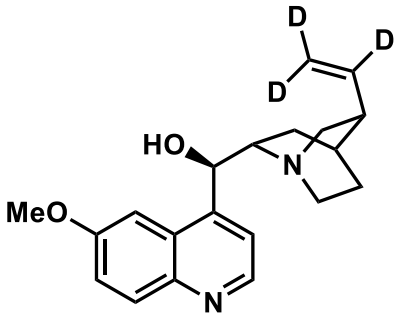
5.95 (m). *(β-D's not observed)*

^{13}C NMR: (125 MHz, CD_3OD)

<u>145.2, 145.1, 144.9 (t, *J* = 24.4 Hz), 144.5</u>, <u>111.0, 110.9, 110.4, 110.3</u>, 73.9, 72.8, 72.7, 61.2, 61.0, 60.8, 55.3, 55.2, 44.2, 43.9, 43.6, 43.3, 41.2, 38.9, 38.5, 32.6, 32.4, 31.1, 30.8, 28.9, 28.6, 28.2, 26.4, 24.0, 23.7, 23.4, 20.7, 19.7, 18.3, 17.6, 14.6, 14.5.

n.b underlined ^{13}C resonances denote labelled position(s)

Quinine-*α,β,β-d*$_3$ **[D]-4n**



By a modification of the general deuteration procedure, the reaction was conducted using quinine **4n** (1.10 g, 3.4 mmol), [dmpe$_2$FeCl$_2$] **1** (36.0 mg, 85 µmol, 2.5 mol%), NaO^{t}Bu (16.0 mg, 170 µmol, 5 mol%), pinacolborane (24 µL, 170 µmol, 5 mol%), tetrahydrofuran (2 mL) and CD_3OD (2 mL). The reaction mixture was irradiated for 48 h, filtered (5 g SiO_2 plug, CH_2Cl_2) and the solvent removed *in vacuo* (30 °C, 400 to 20 mbar). The product was recrystallized from petroleum ether/MeOH (*ca.* 20:1) to give *quinine-α,β,β-d*$_3$ **[D]-4n** (1.0 g, 91%, D-incorporation: *α*-79%, *β*-29%) as an off-white amorphous solid.

MS: (HRMS – EI$^+$)

Found 325.19124 ($C_{20}H_{23}D_1O_2N_2$), requires 325.18951. (*mono-deutero*)

MPt: 180-184 °C (petroleum ether/MeOH)

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

8.76 (d, *J* = 4.4 Hz, 1H), 8.05 (d, *J* = 9.2 Hz, 1H), 7.54 (d, *J* = 4.3 Hz, 1H), 7.39 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.30 (d, *J* = 2.8 Hz, 1H), 5.85-5.75 (m, 0.21H), 5.56 (d, *J* = 4.5 Hz, 1H), 5.03-4.94 (m, 1.43H), 3.95 (s, 3H), 3.45-3.35 (m, 1H), 3.25-3.18 (m, 1H), 3.13 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.75-2.65 (m, 2H), 2.34-2.26 (m, 1H), 1.88-1.83 (m, 1H), 1.77-1.62 (m, 4H).

^{2}H NMR: (77 MHz, $CHCl_3$)

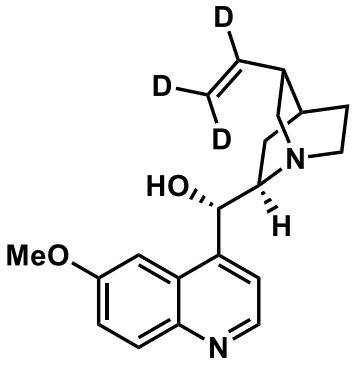
5.87-5.70 (m), 5.03-4.90 (m).

^{13}C NMR: (125 MHz, $CDCl_3$)

157.8, 147.8, 147.2, 144.5, <u>142.0, 141.7 (t, *J* = 24 Hz)</u>, 131.9, 126.8, 121.6, 118.4, <u>114.2</u>, 101.3, 72.5, 60.0, 57.1, 55.7, 43.2, 40.0, 27.9, 27.8, 22.3.

n.b underlined ^{13}C resonances denote labelled position(s)

Quinidine-*α,β,β-d*$_3$ **[D]-4o**



Following the general deuteration procedure, quinidine **4o** (107 mg, 0.33 mmol) was reacted to give *quinidine-α,β,β-d*$_3$ [**D]-4o** (104 mg, 96%, D-incorporation: *α*-67%, *β*-23%) as a colourless amorphous solid.

MS: (HRMS – EI$^+$)

Found 325.18926 ($C_{20}H_{23}D_1O_2N_2$), requires 325.18951. (*mono-deutero*)

MPt: 175-180 °C (CH_3OH)

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

8.65 (d, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.54 (d, *J* = 4.5 Hz, 1H), 7.32 (dd, *J* = 9.7, 2.7 Hz, 1H), 7.18 (d, *J* = 3.0 Hz, 1H), 6.09-5.99 (m, 0.33H), 5.59 (d, *J* = 4.1 Hz, 1H), 5.07-5.02 (m, 1.55H), 3.86 (s, 3H), 3.33 (ddd, *J* = 13.6, 9.2, 2.0 Hz, 1H), 3.07 (td, *J* = 9.7, 3.6 Hz, 1H), 2.95-2.86 (m, 2H), 2.78 (dt, *J* = 12.3, 8.8 Hz, 1H), 2.27-2.21 (m, 1H), 2.08-2.01 (m, 1H), 1.79-1.75 (m, 1H), 1.61-1.45 (m, 2H), 1.2-1.13 (m, 1H).

^{2}H NMR: (77 MHz, CH_3OH)

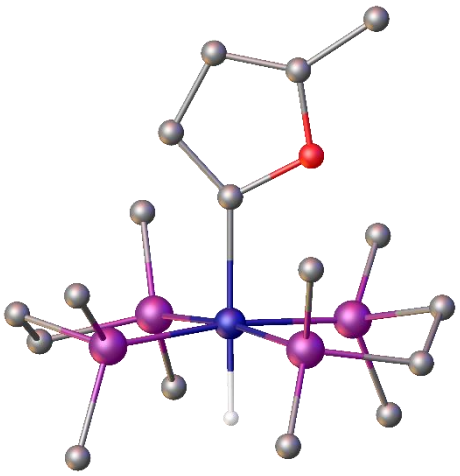
6.15-6.00 (m), 5.12-4.97 (m).

^{13}C NMR: (125 MHz, $CDCl_3$)

157.7, 147.6, 144.2, <u>140.6, 140.3 (t, *J* = 27 Hz)</u>, 131.5, 126.6, 121.5, 118.4, <u>114.4</u>, 101.2, 72.0, 59.7, 55.6, 50.2, 49.6, 40.0, 28.2, 26.4, 21.1.

n.b underlined ^{13}C resonances denote labelled position(s)

16. Crystal Data and Experimental – *trans*-**5**



Experimental. Single pale yellow plate crystals of *trans*-**5** recrystallised from pentane by slow cooling. A suitable crystal with dimensions 0.62 × 0.20 × 0.07 mm^3 was selected and mounted on a MITIGEN holder in Paratone oil. on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady T = 119.99(10) K during data collection. The structure was solved with the olex2.solve 1.3-beta solution program using iterative methods and by using Olex2 as the graphical interface. The model was refined with ShelXL 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{17}H_{38}FeOP_4$, M_r = 438.20, triclinic, P-1 (No. 2), a = 8.9533(2) Å, b = 10.1488(3) Å, c = 13.3681(4) Å, α = 90.181(2)°, β = 106.444(3)°, γ = 106.680(2)°, V = 1111.27(6) Å^3, T = 119.99(10) K, Z = 2, Z' = 1, μ(Mo K$_\alpha$) = 0.969, 28848 reflections measured, 7639 unique (R_{int} = 0.0347) which were used in all calculations. The final wR_2 was 0.0743 (all data) and R_1 was 0.0390 (I≥2 σ(I)).

Compound	*trans*-5
Formula	$C_{17}H_{38}FeOP_4$
$D_{calc.}$/ g cm^{-3}	1.310
μ/mm^{-1}	0.969
Formula Weight	438.20
Colour	pale yellow
Shape	plate
Size/mm^3	0.62×0.20×0.07
T/K	119.99(10)
Crystal System	triclinic
Space Group	P-1
a/Å	8.9533(2)
b/Å	10.1488(3)
c/Å	13.3681(4)
α/°	90.181(2)
β/°	106.444(3)
γ/°	106.680(2)
V/Å^3	1111.27(6)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_\alpha$
Θ_{min}/°	3.329
Θ_{max}/°	32.850
Measured Refl's.	28848
Indep't Refl's	7639
Refl's I≥2 σ(I)	6581
R_{int}	0.0347
Parameters	360
Restraints	0
Largest Peak	0.517
Deepest Hole	-0.325
GooF	1.094
wR_2 (all data)	0.0743
wR_2	0.0707
R_1 (all data)	0.0503
R_1	0.0390

Structure Quality Indicators

Reflections:	d min (Mo) 0.66	I/σ(I) 24.7	Rint 3.47%	complete 100% (IUCr) 100%
Refinement:	Shift -0.001	Max Peak 0.5	Min Peak -0.3	GooF 1.094

A pale yellow plate-shaped crystal with dimensions 0.62 × 0.20 × 0.07 mm^3 was mounted on a MITIGEN holder in Paratone oil.. Data were collected using a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 119.99(10) K.

Data were measured using ω scans using Mo K$_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro. The maximum resolution that was achieved was Θ = 32.850° (0.66 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro. The unit cell was refined using CrysAlisPro on 11006 reflections, 38% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro. The final completeness is 99.80 % out to 32.850° in Θ. A gaussian absorption correction was performed using CrysAlisPro 1.171.40.61a. Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient μ of this material is 0.969 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.546 and 1.000.

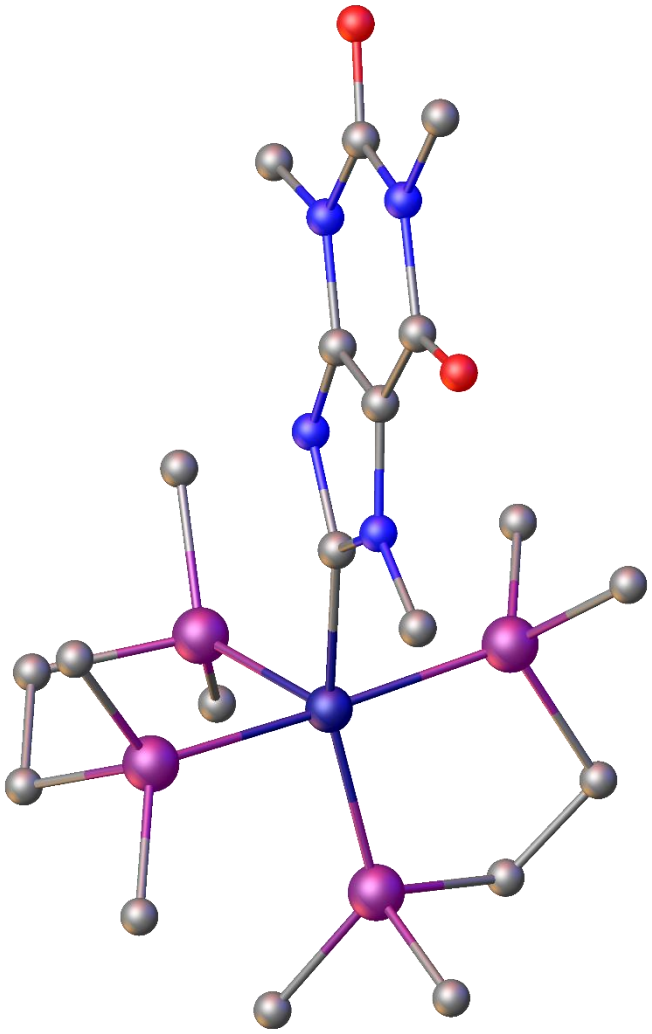
The structure was solved and the space group *P*-1 (# 2) determined by the olex2.solve 1.3-beta structure solution program using using iterative methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: H atoms were identified from a difference Fourier map and freely refined.

_exptl_absorpt_process_details: CrysAlisPro 1.171.40.61a. Numerical absorption correction based on gaussian integration over a multifaceted crystal modelEmpirical absorption correction using spherical harmonicsas implemented in SCALE3 ABSPACK.

CCDC Deposition Number 2073340

cis-**6**



Experimental. Single yellow block crystals of *cis*-**6** recrystallised from pentane by slow cooling. A suitable crystal with dimensions 0.50 × 0.37 × 0.23 mm^3 was selected and mounted on a MITIGEN holder in Paratone oil. on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady T = 100.0 K during data collection. The structure was solved with the ShelXT solution program using dual methods and by using Olex2 as the graphical interface. The model was refined with ShelXL 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{20}H_{42}FeN_4O_2P_4$, M_r = 550.30, monoclinic, $P2_1/n$ (No. 14), a = 10.4604(6) Å, b = 17.5579(11) Å, c = 14.6107(9) Å, β = 91.861(2)°, α = γ = 90°, V = 2682.0(3) Å^3, T = 100.0 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.825, 241200 reflections measured, 11736 unique (R_{int} = 0.0279) which were used in all calculations. The final wR_2 was 0.0932 (all data) and R_1 was 0.0403 (I≥2 σ(I)).

Compound	*cis*-6
Formula	$C_{20}H_{42}FeN_4O_2P_4$
$D_{calc.}$/ g cm^{-3}	1.363
μ/mm^{-1}	0.825
Formula Weight	550.30
Colour	yellow
Shape	block
Size/mm^3	0.50×0.37×0.23
T/K	100.0
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	10.4604(6)
b/Å	17.5579(11)
c/Å	14.6107(9)
α/°	90
β/°	91.861(2)
γ/°	90
V/Å^3	2682.0(3)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.267
Θ_{max}/°	35.598
Measured Refl's.	241200
Indep't Refl's	11736
Refl's I≥2 σ(I)	10664
R_{int}	0.0279
Parameters	429
Restraints	262
Largest Peak	0.558
Deepest Hole	-0.558
GooF	1.196
wR_2 (all data)	0.0932
wR_2	0.0911
R_1 (all data)	0.0453
R_1	0.0403

Structure Quality Indicators

Reflections:	d min (Mo) 0.61	I/σ(I) 73.6	Rint 2.79%	complete 100%
Refinement:	Shift 0.001	Max Peak 0.6	Min Peak -0.6	GooF 1.196

A yellow block-shaped crystal with dimensions 0.50 × 0.37 × 0.23 mm^3 was mounted on a MITIGEN

holder in Paratone oil. Data were collected using a Bruker D8 VENTURE diffractometer equipped with an Oxford Cryosystems Cryostream 800 low-temperature device operating at T = 100.0 K.

Data were measured using ϕ and ω scans using MoK$_\alpha$ radiation. . The maximum resolution that was achieved was Θ = 35.598° (0.61 Å).

The unit cell was refined using SAINT (Bruker, V8.40A, after 2013) on 9509 reflections, 4% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.40A, after 2013). The final completeness is 100.00 % out to 35.598° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR_2(int) was 0.1129 before and 0.0479 after correction. The Ratio of minimum to maximum transmission is 0.8873. The $\lambda/2$ correction factor is Not present. . The absorption coefficient μ of this material is 0.825 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.663 and 0.747.

The structure was solved and the space group $P2_1/n$ (# 14) determined by the ShelXT structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

_*refine_special_details*: The dmpe ligands were modelled as disodered (approx 2:1 ratio) consistent with peaks in a difference map. Displacement ellipsoid and geometric restraints were used. Despite this , some of the minor component ellipsoids remain rather elongated.#==========
========#>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<#==========
=== Format: alert-number_ALERT_alert-type_alert-level text213_ALERT_2_B Atom C1A has ADP max/min Ratio ..... 4.2 prolat220_ALERT_2_B NonSolvent Resd 1 C U_{eq}(max)/U_{eq}(min) Range 6.6 RatioSee above for a comment on disorder and ellipsoids#==========
========213_ALERT_2_C Atom C3 has ADP max/min Ratio ..... 3.1 prolat213_ALERT_2_C Atom C2A has ADP max/min Ratio ..... 3.5 prolat213_ALERT_2_C Atom C3A has ADP max/min Ratio ..... 3.8 prolat213_ALERT_2_C Atom C4A has ADP max/min Ratio ..... 3.1 prolat213_ALERT_2_C Atom C6A has ADP max/min Ratio ..... 3.2 prolat222_ALERT_3_C NonSolvent Resd 1 H U_{iso}(max)/U_{iso}(min) Range 6.7 Ratio906_ALERT_3_C Large K Value in the Analysis of Variance ..... 3.123 CheckSee above for a comment on disorder and ellipsoids918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) . 1 Check977_ALERT_2_C Check Negative Difference Density on H19C -0.31 eA-3#==========
=

_*exptl_absorpt_process_details*: SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction.wR_2(int) was 0.1129 before and 0.0479 after correction.The Ratio of minimum to maximum transmission is 0.8873.The $\lambda/2$ correction factor is Not present.

CCDC Deposition Number 2073339.

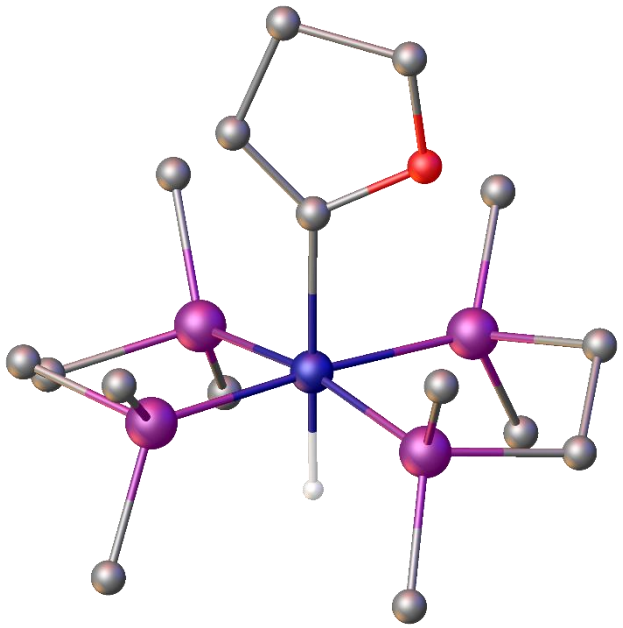
THE UNIVERSITY of EDINBURGH
Crystal Structure Service

Dr Gary S. Nichol
Crystallography Service Manager
Phone: +44 (0)131 650 4806
E–mail: g.s.nichol@ed.ac.uk

Submitted by: Luke Britton
Solved by: Gary S Nichol

R_1=3.36

Crystal Data and Experimental



Experimental. Single translucent dark yellow block-shaped crystals of *trans*-**7** recrystallised from a mixture of pentane and THF by slow cooling. A suitable crystal with dimensions 0.33 × 0.19 × 0.19 mm^3 was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady T = 120.01(10) K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 1.5-beta (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{16}H_{38}FeOP_4$, M_r = 426.19, monoclinic, $P2_1/n$ (No. 14), a = 14.6983(3) Å, b = 17.3967(3) Å, c = 17.9529(4) Å, β = 108.957(2)°, α = γ = 90°, V = 4341.61(16) Å^3, T = 120.01(10) K, Z = 8, Z' = 2, μ(Mo K$_\alpha$) = 0.990, 114056 reflections measured, 13141 unique (R_{int} = 0.0487) which were used in all calculations. The final wR_2 was 0.0754 (all data) and R_1 was 0.0336 (I≥2 σ(I)).

Compound	*trans*-**7**
Formula	$C_{16}H_{38}FeOP_4$
$D_{calc.}$/ g cm^{-3}	1.304
μ/mm^{-1}	0.990
Formula Weight	426.19
Colour	translucent dark yellow
Shape	block-shaped
Size/mm^3	0.33×0.19×0.19
T/K	120.01(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	14.6983(3)
b/Å	17.3967(3)
c/Å	17.9529(4)
α/°	90
β/°	108.957(2)
γ/°	90
V/Å^3	4341.61(16)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	Mo K$_\alpha$
Θ_{min}/°	3.156
Θ_{max}/°	31.324
Measured Refl's.	114056
Indep't Refl's	13141
Refl's I≥2 σ(I)	10498
R_{int}	0.0487
Parameters	727
Restraints	153
Largest Peak	0.671
Deepest Hole	-0.487
GooF	1.043
wR_2 (all data)	0.0754
wR_2	0.0689
R_1 (all data)	0.0494
R_1	0.0336

Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=62.6° 0.68	I/σ(I) 30.8	Rint 4.87%	Full 50.5° 92% to 62.6° 99.8
Refinement:	Shift 0.001	Max Peak 0.7	Min Peak -0.5	GooF 1.043

A translucent dark yellow block-shaped-shaped crystal with dimensions 0.33 × 0.19 × 0.19 mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 120.01(10) K.

Data were measured using ω scans with Mo K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.41.99a (Rigaku OD, 2021). The maximum resolution that was achieved was Θ = 31.324° (0.68 Å).

The unit cell was refined using CrysAlisPro 1.171.41.99a (Rigaku OD, 2021) on 34876 reflections, 31% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.41.99a (Rigaku OD, 2021). The final completeness is 99.80 % out to 31.324° in Θ. A multi-scan absorption correction was performed using CrysAlisPro 1.171.41.99a (Rigaku Oxford Diffraction, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient μ of this material is 0.990 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.864 and 1.000.

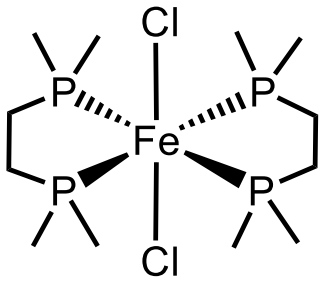
The structure was solved and the space group $P2_1/n$ (# 14) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

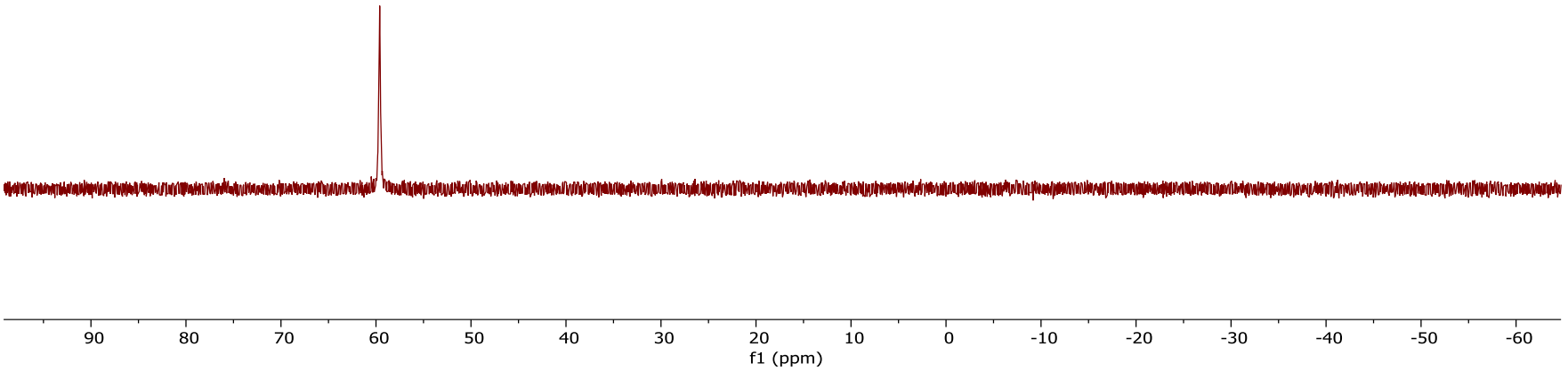
_refine_special_details: Atoms O51 to C54 were modelled as disordered, corresponding with a 180 degree rotation about the Fe51-C51 bond. Displacement ellipsoid and geometric restraints were used on the disorder components (roughly 2:1 disorder ratio). Disordered H atoms were placed using HADD in Olex2. All other H atoms were identified from a difference map and freely refined.

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

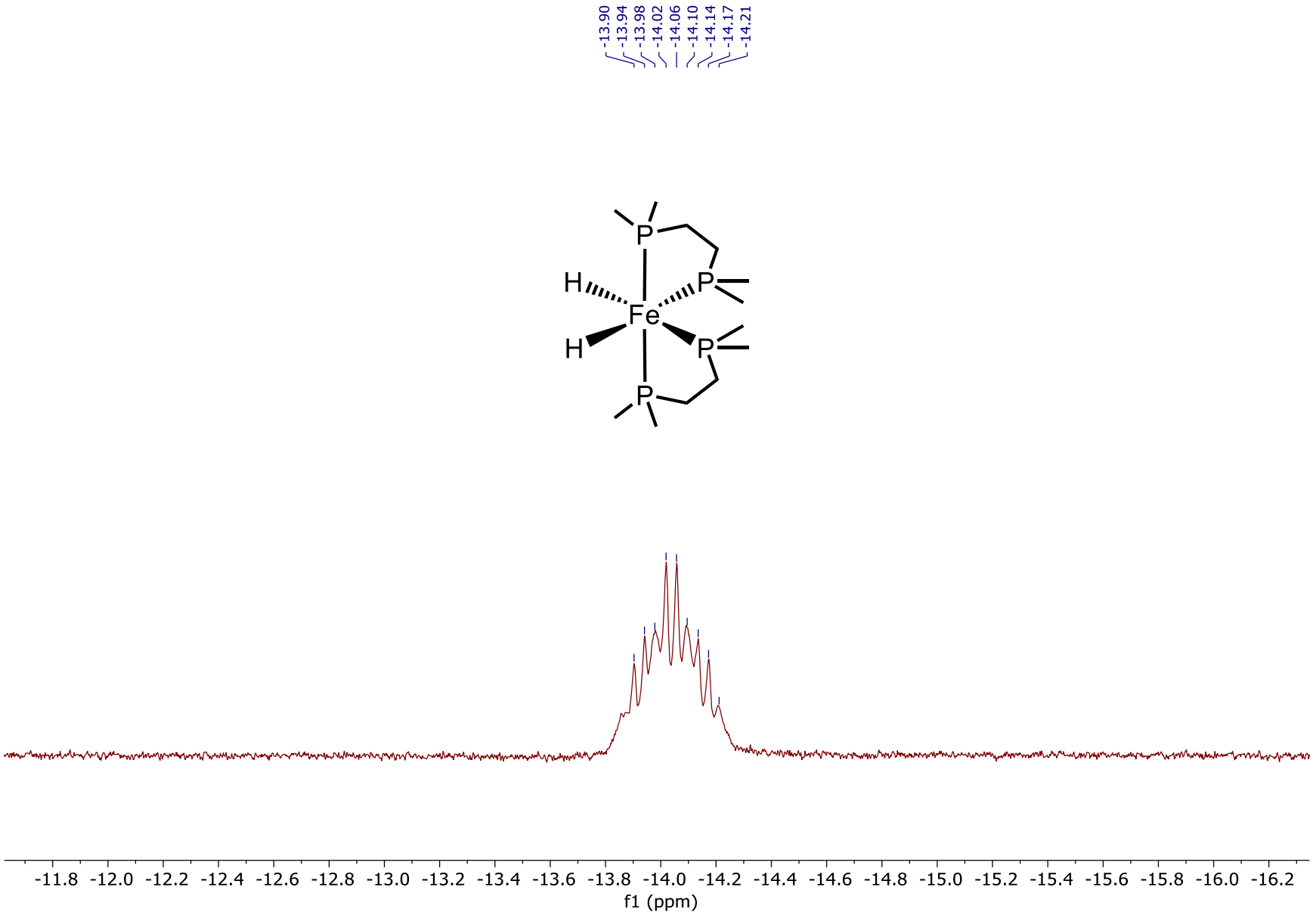
CCDC Deposition Number 2159501

17. NMR spectra – Pre-catalysts

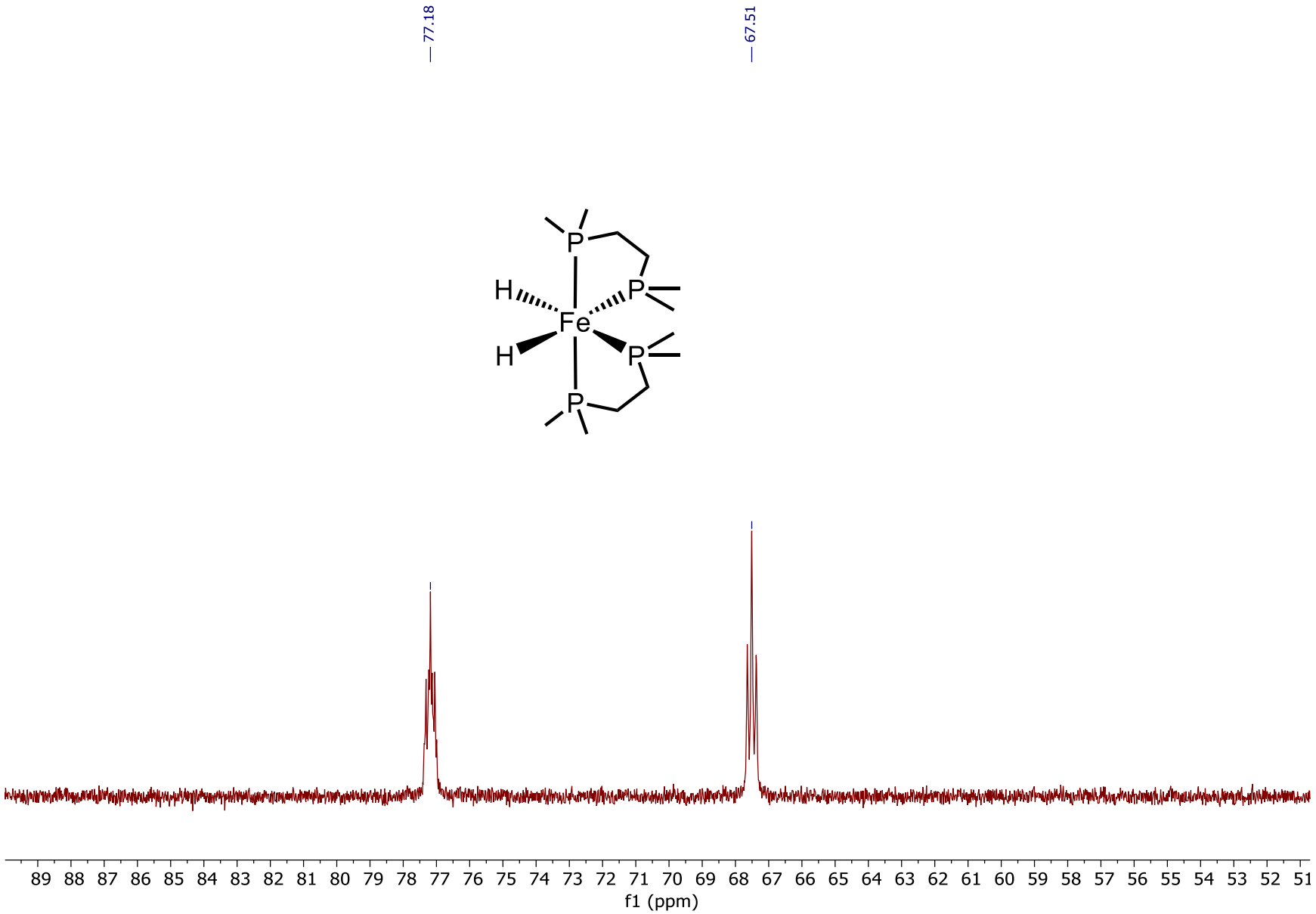




^{31}P NMR (162 MHz, d_8-THF) of [dmpe$_2$FeCl$_2$] **1**.

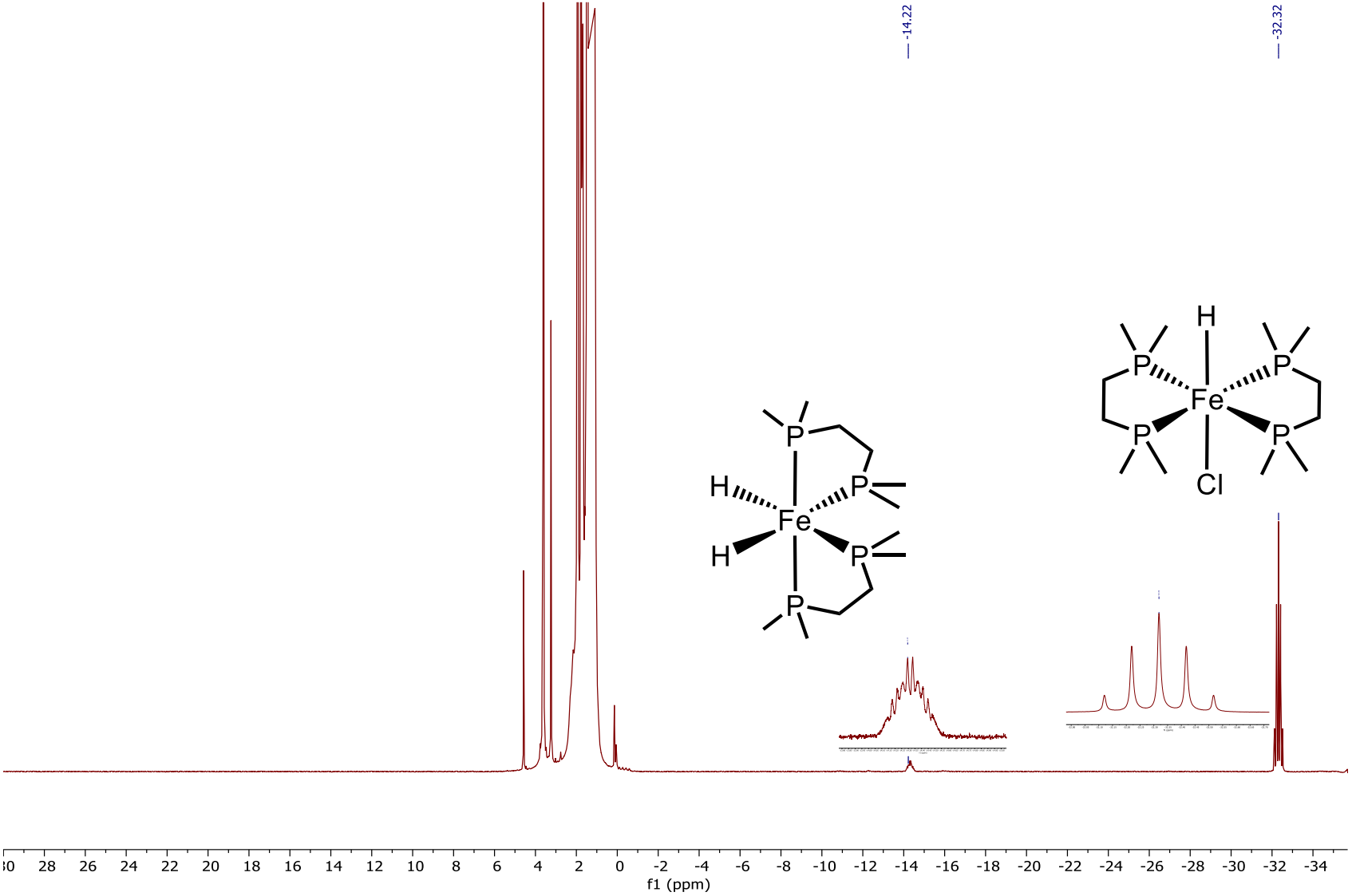


^{1}H NMR (500 MHz, THF) of [dmpe$_2$FeH$_2$] **2**.

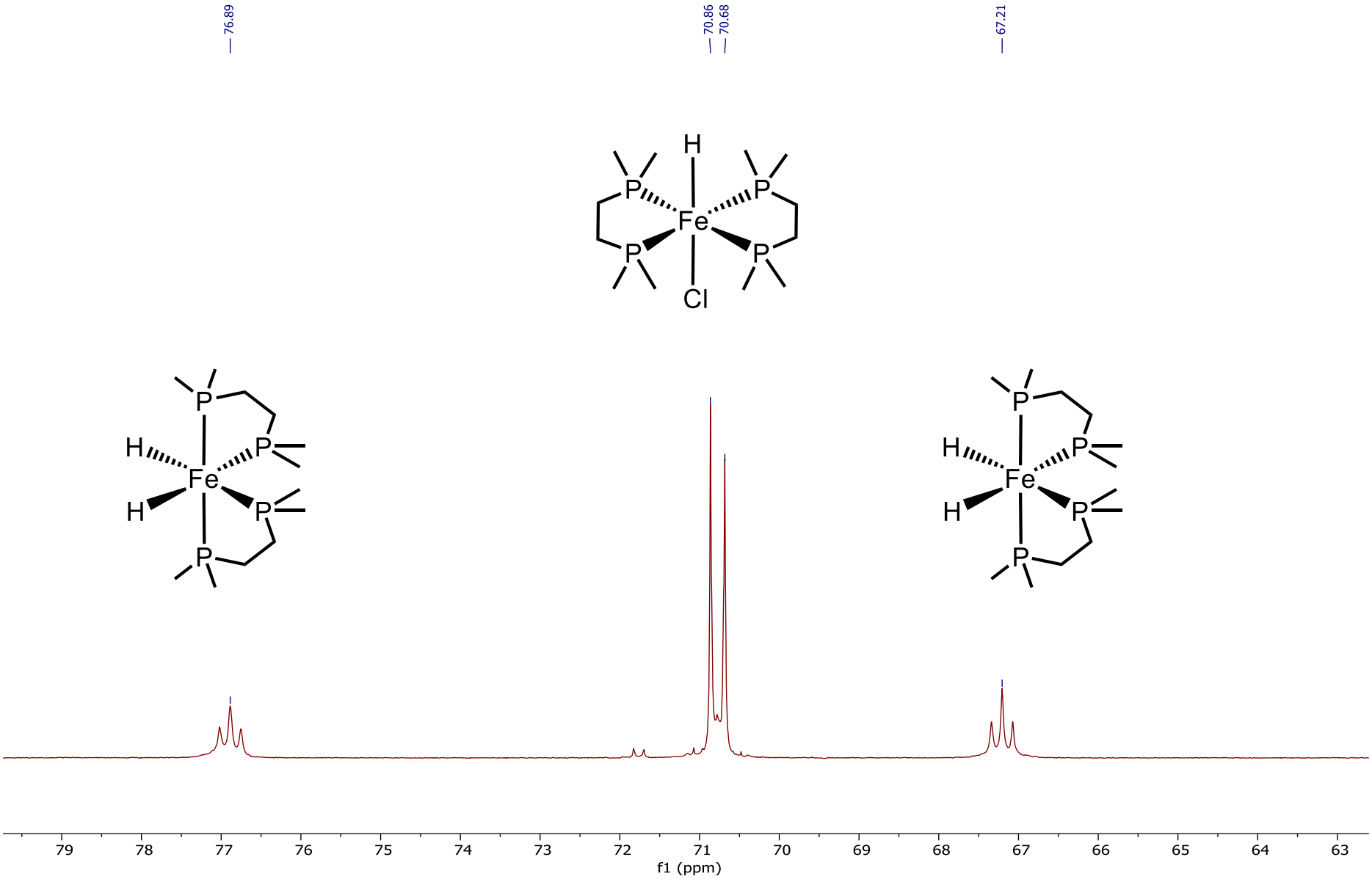


^{31}P NMR (202 MHz, THF) of [dmpe$_2$FeH$_2$] **2**.

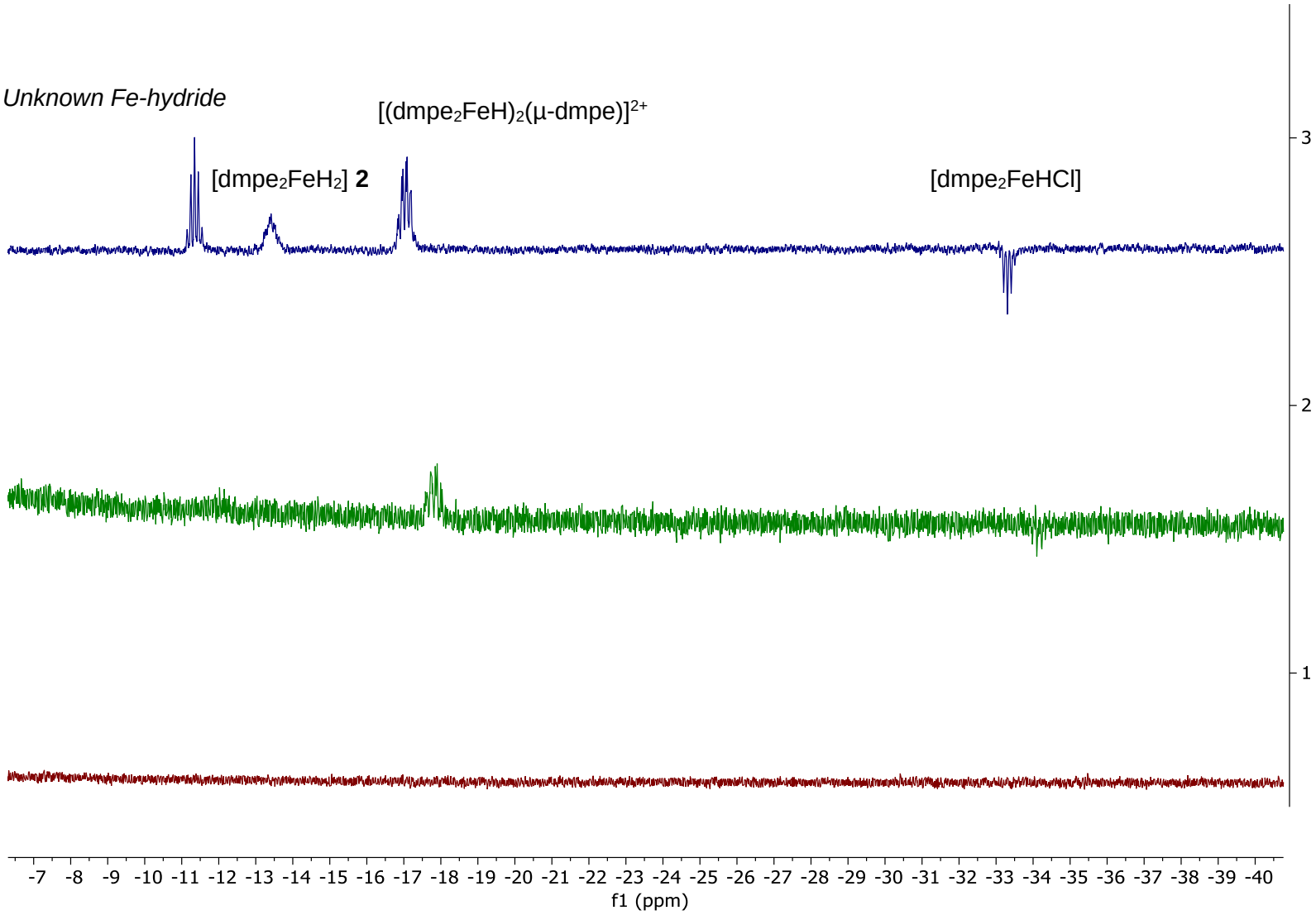
NMR spectra - Activation studies



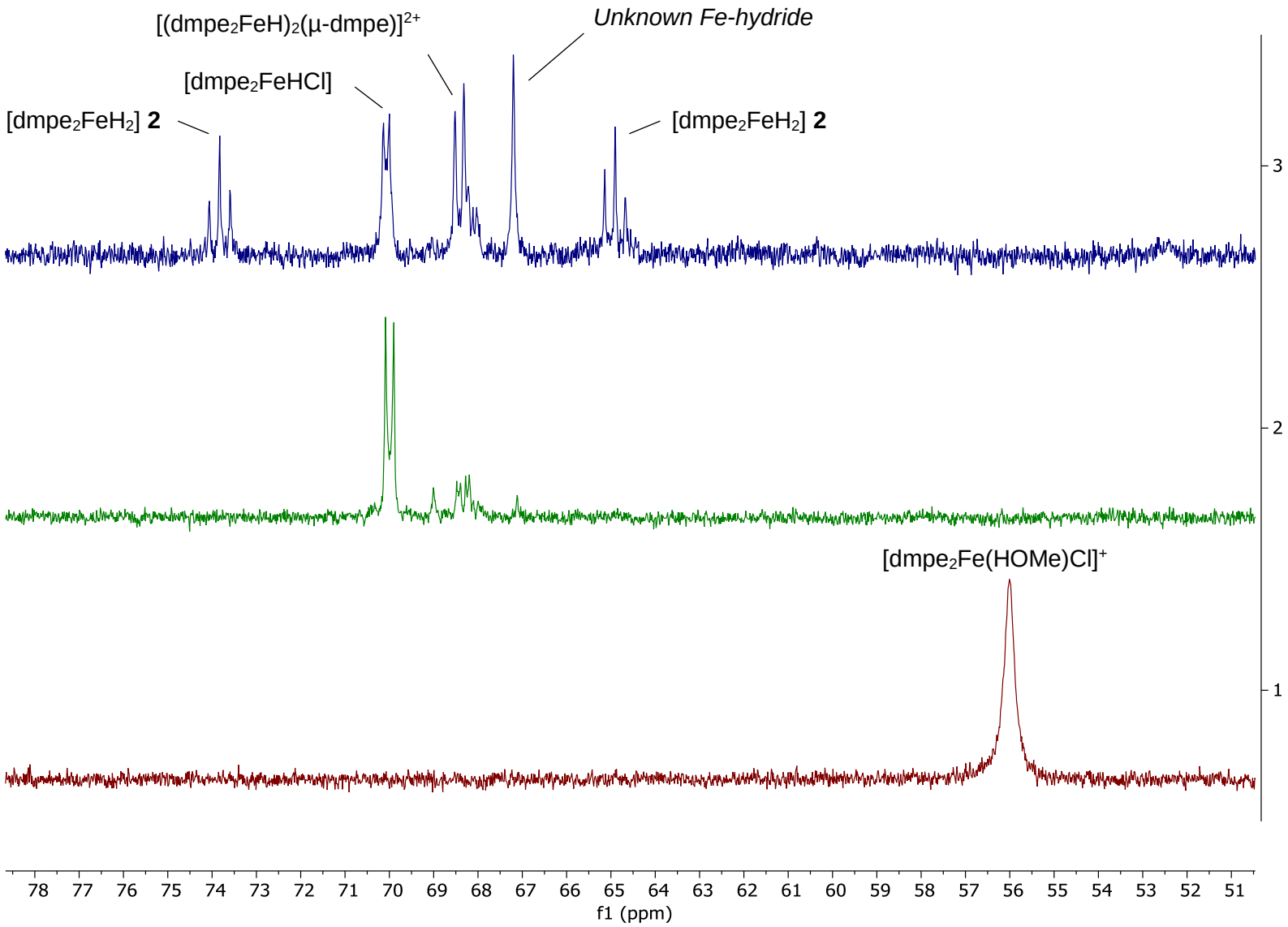
^{1}H NMR (500 MHz, d^{8}-THF) for the reaction of [dmpe$_2$FeCl$_2$] **1** + HBpin + NaO^{t}Bu.



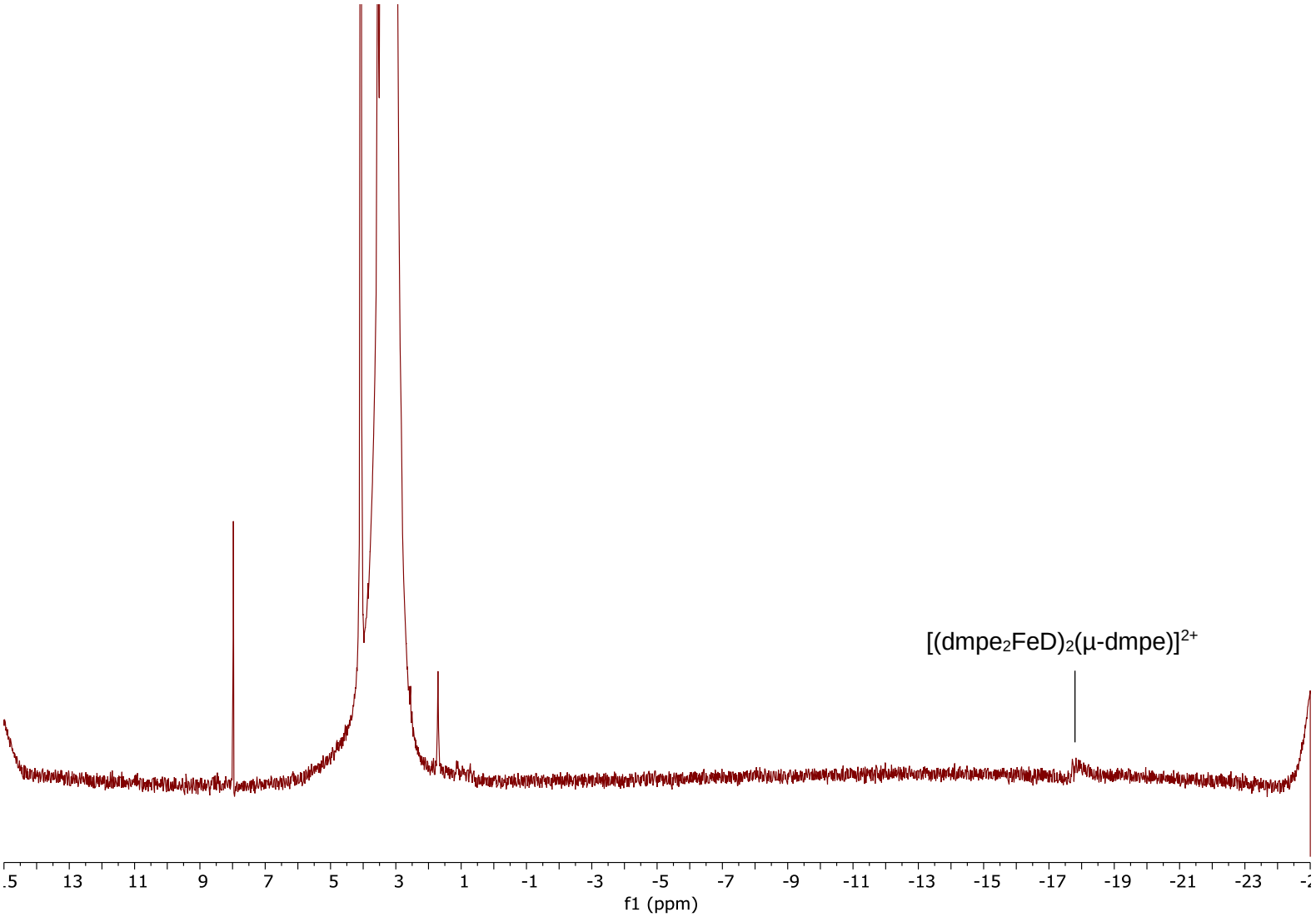
^{31}P NMR (202 MHz, d^8-THF) of the reaction of [dmpe$_2$FeCl$_2$] **1** + HBpin + NaO^{t}Bu.



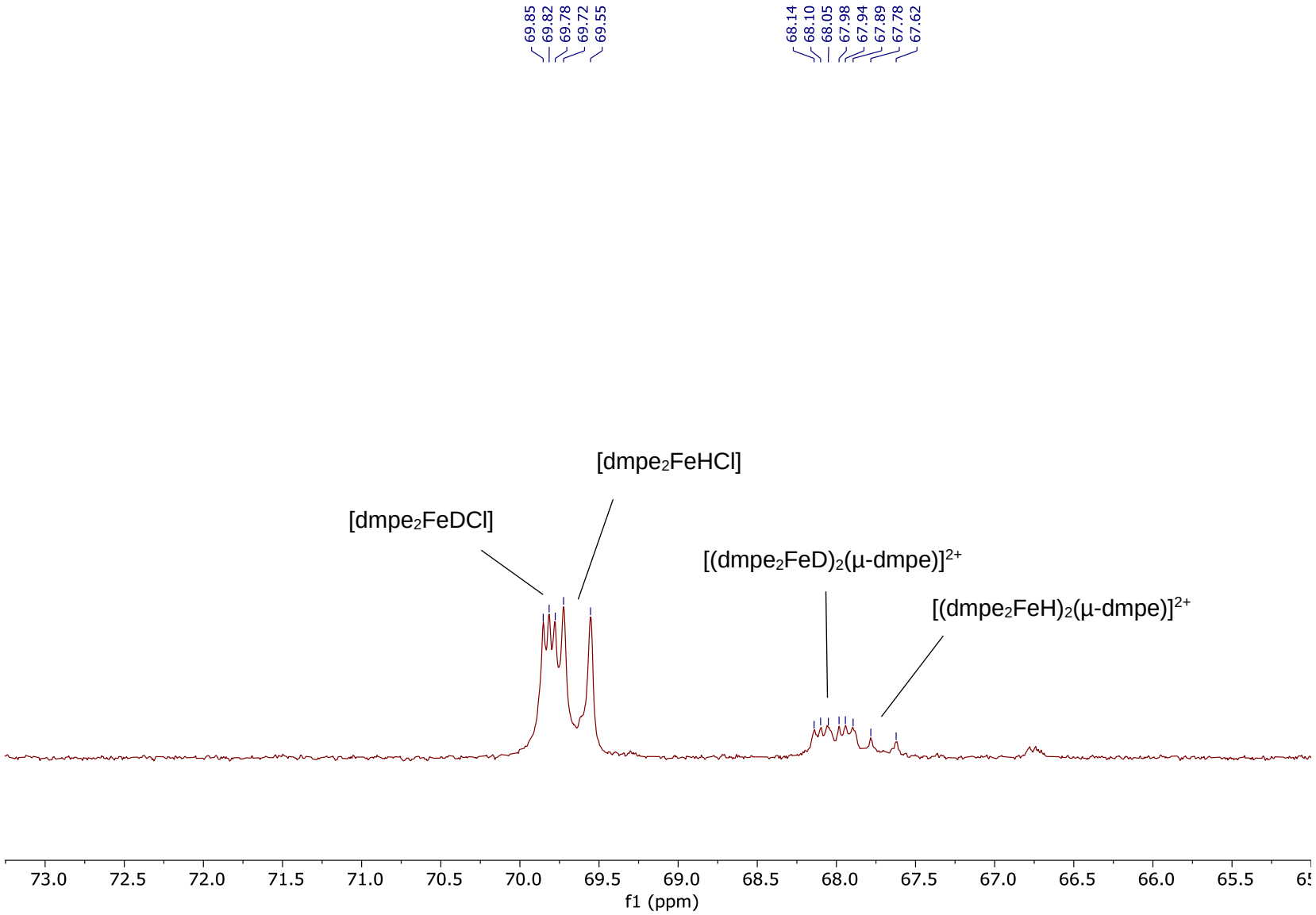
^{1}H NMR (500 MHz, THF) for the reaction of [dmpe$_2$FeCl$_2$] **1** + CH_3OH in THF. (1) Before the addition of NaO^{t}Bu. (2) After the addition of NaO^{t}Bu. (3) after 30 minutes of blue light irradiation – hydride region only.



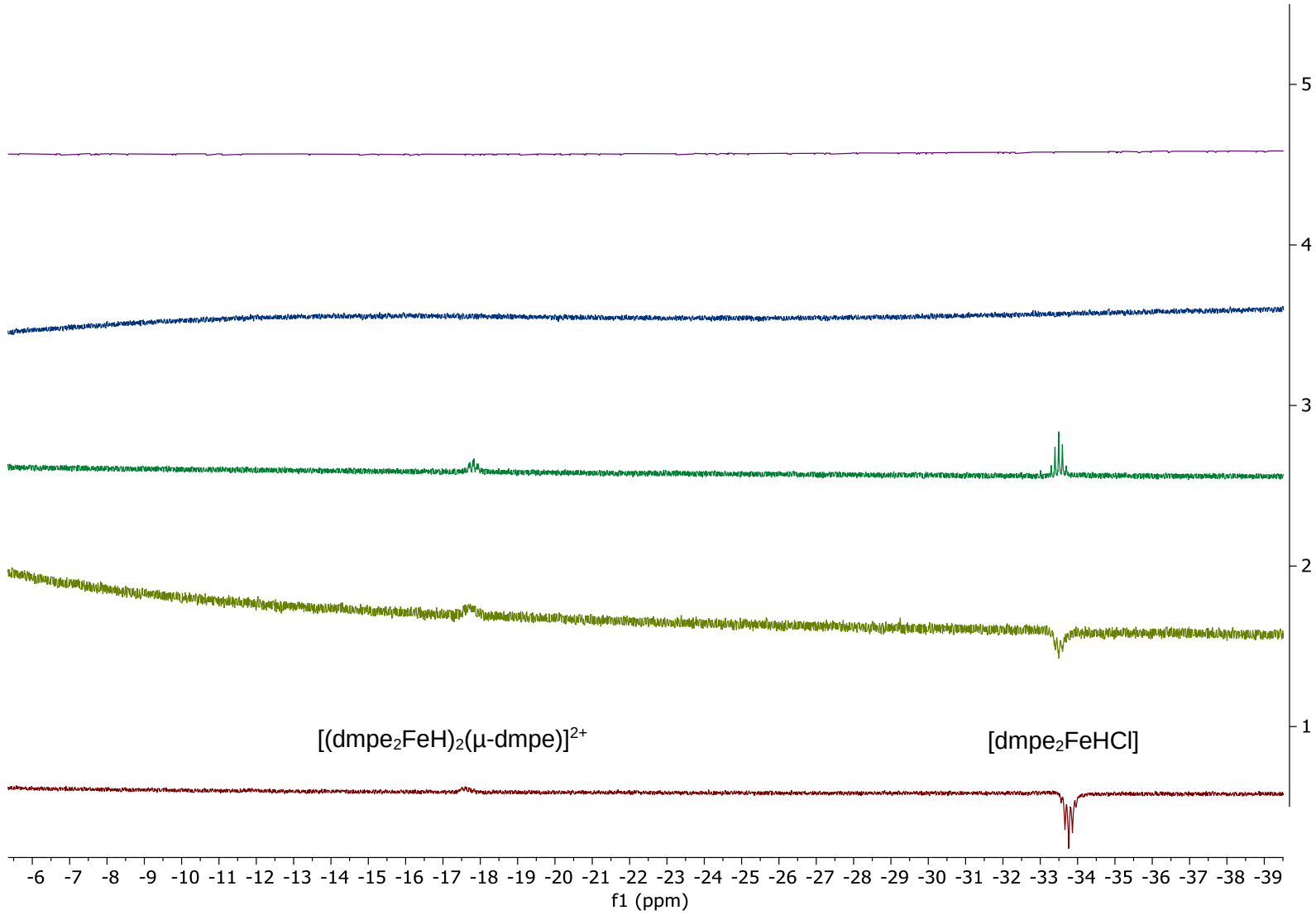
^{31}P NMR (126 MHz, THF) for the reaction of [dmpe$_2$FeCl$_2$] **1** + CH_3OH in THF. (1) Before the addition of NaO^{t}Bu. (2) After the addition of NaO^{t}Bu. (3) After 30 minutes of blue light irradiation.



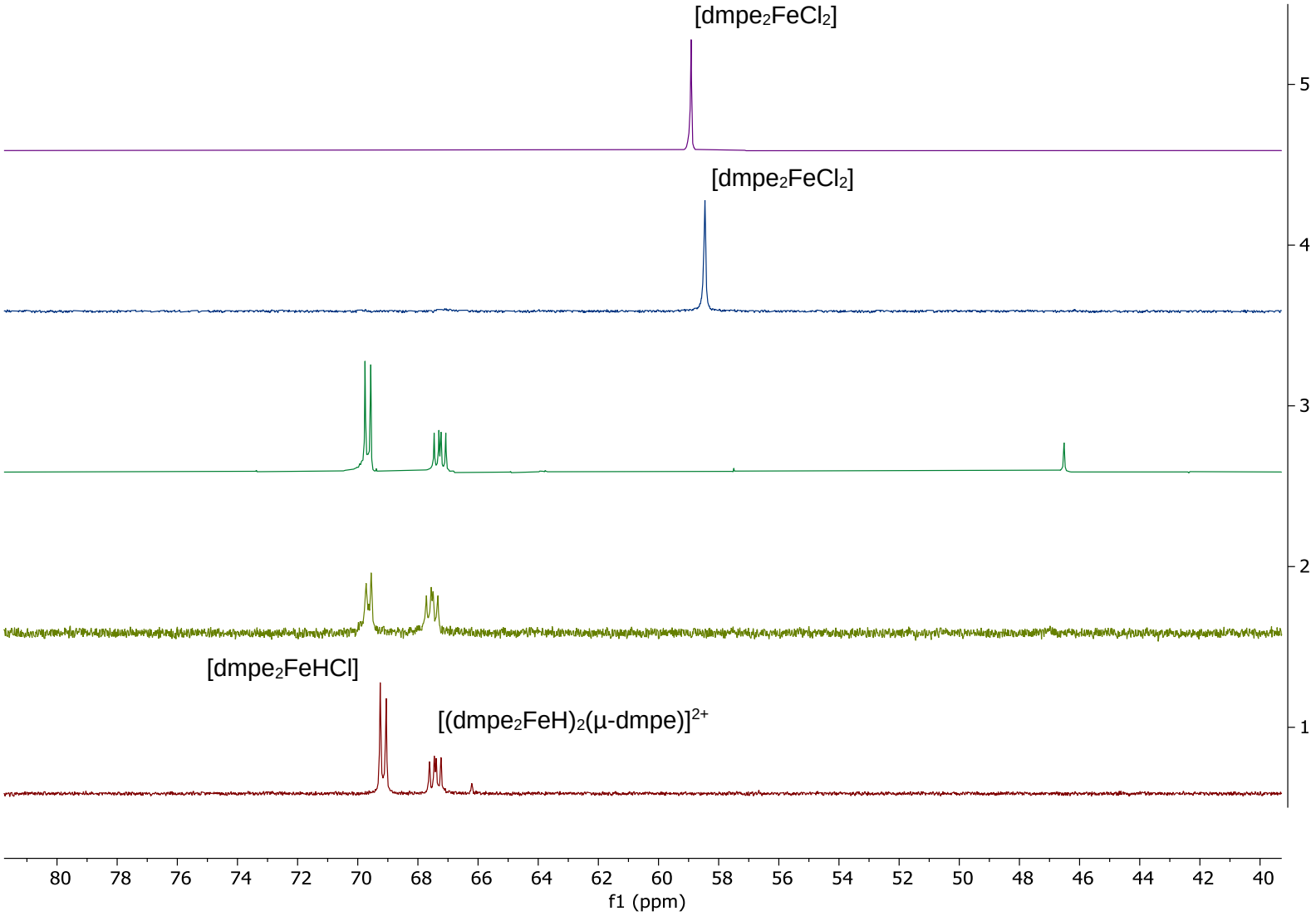
^{2}H NMR (77 MHz, THF) for the reaction of (1) [dmpe$_2$FeCl$_2$] **1** + CD$_3$OH + NaO^{t}Bu in THF.



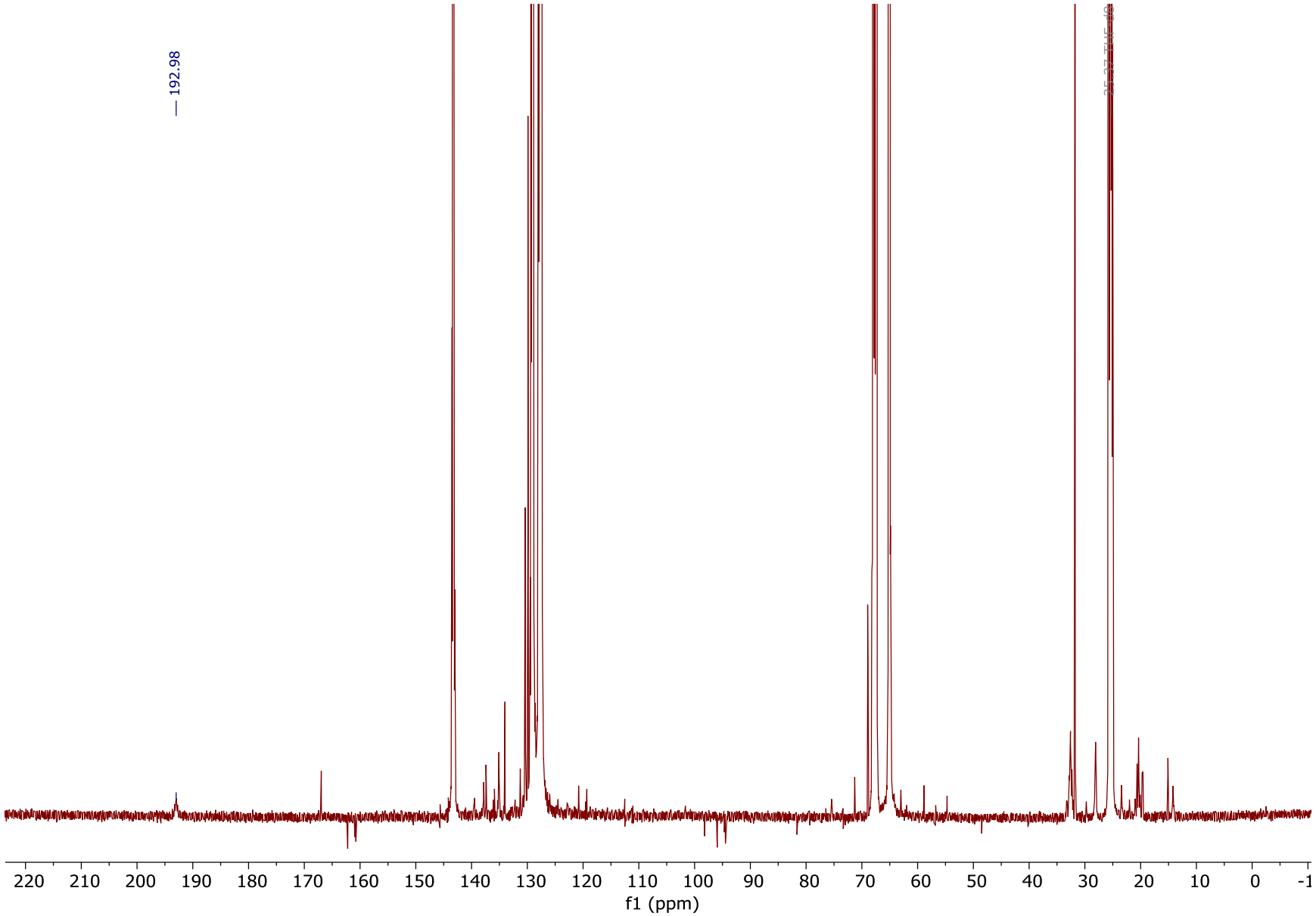
^{31}P NMR (126 MHz, THF) for the reaction of (1) [dmpe$_2$FeCl$_2$] **1** + CD_3OH + NaO^{t}Bu in THF.



^{1}H NMR (500 MHz, THF) for the reaction of [dmpe$_2$FeCl$_2$] **1** + 'alcohol' + NaO^{t}Bu in THF. (1) Methanol. (2) Ethanol. (3) Benzyl alcohol (4) Phenol. (5) *tert*-Butanol – hydride region only.

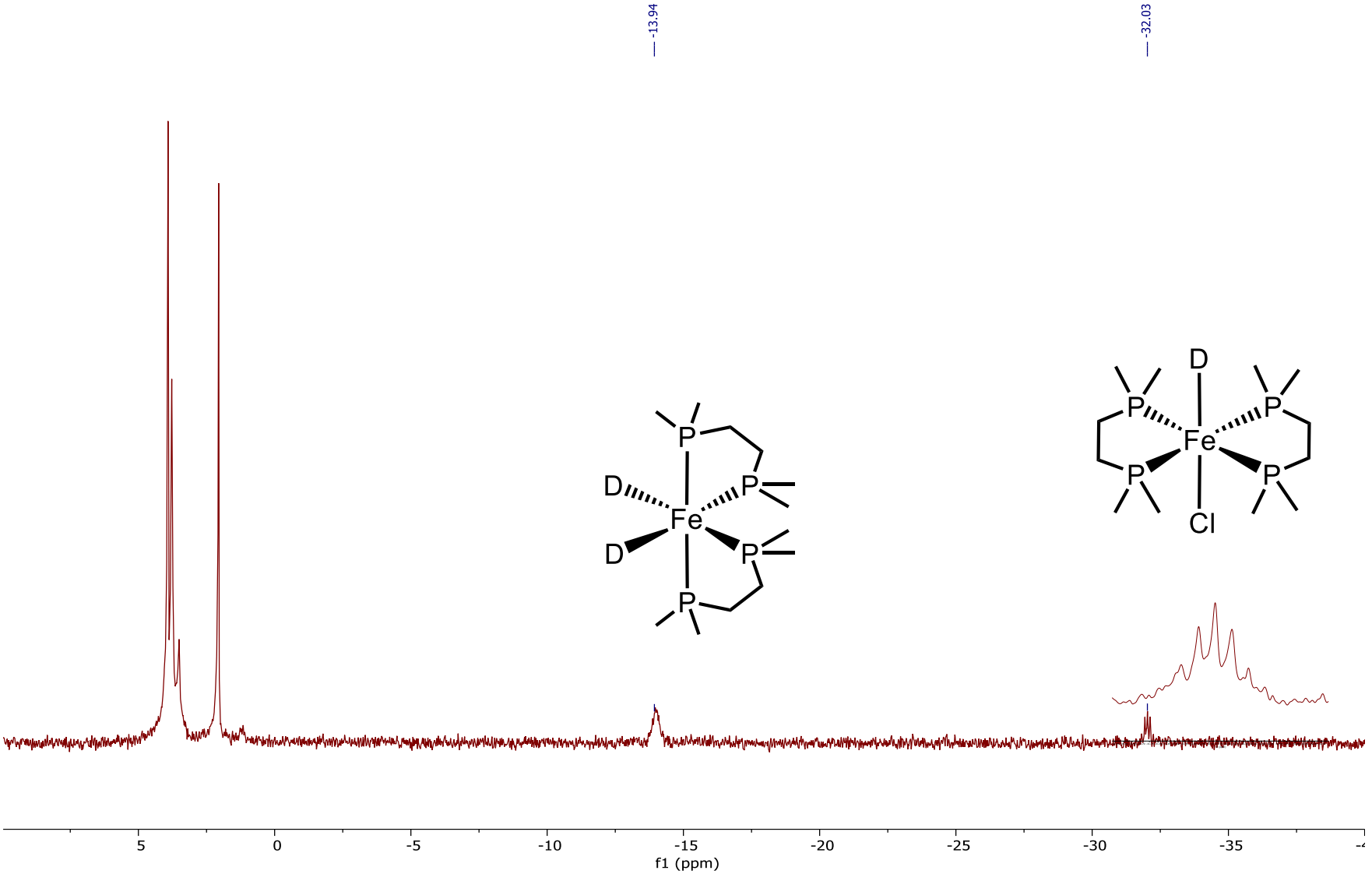


^{31}P NMR (126 MHz, THF) for the reaction of [dmpe$_2$FeCl$_2$] **1** + 'alcohol' + NaO^{t}Bu in THF. (1) Methanol. (2) Ethanol. (3) Benzyl alcohol (4) Phenol. (5) *tert*-Butanol.

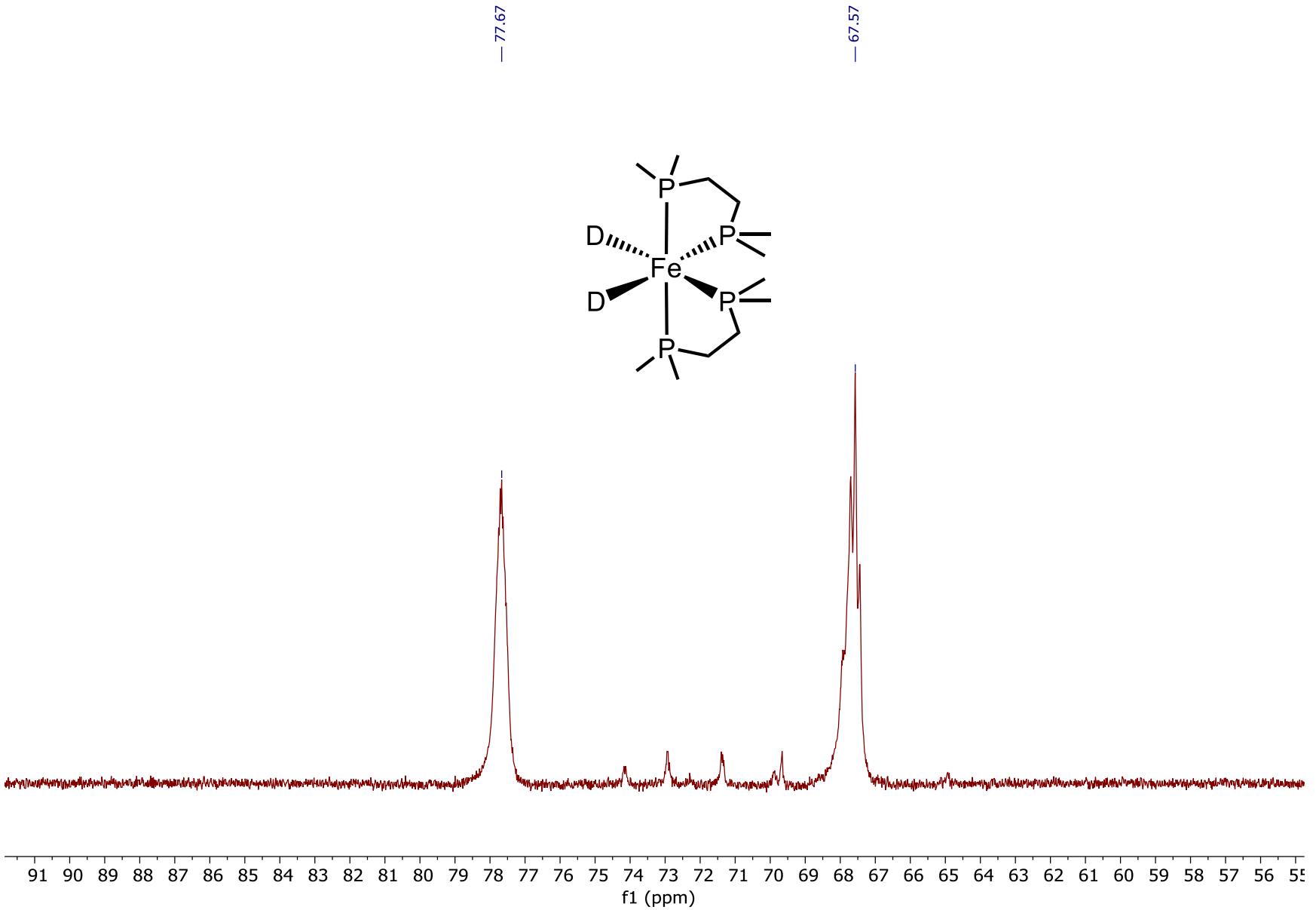


^{13}C NMR (126 MHz, THF) for the reaction of [dmpe$_2$FeCl$_2$] **1** + benzyl alcohol + NaO^{t}Bu in THF, generation of benzldehyde.

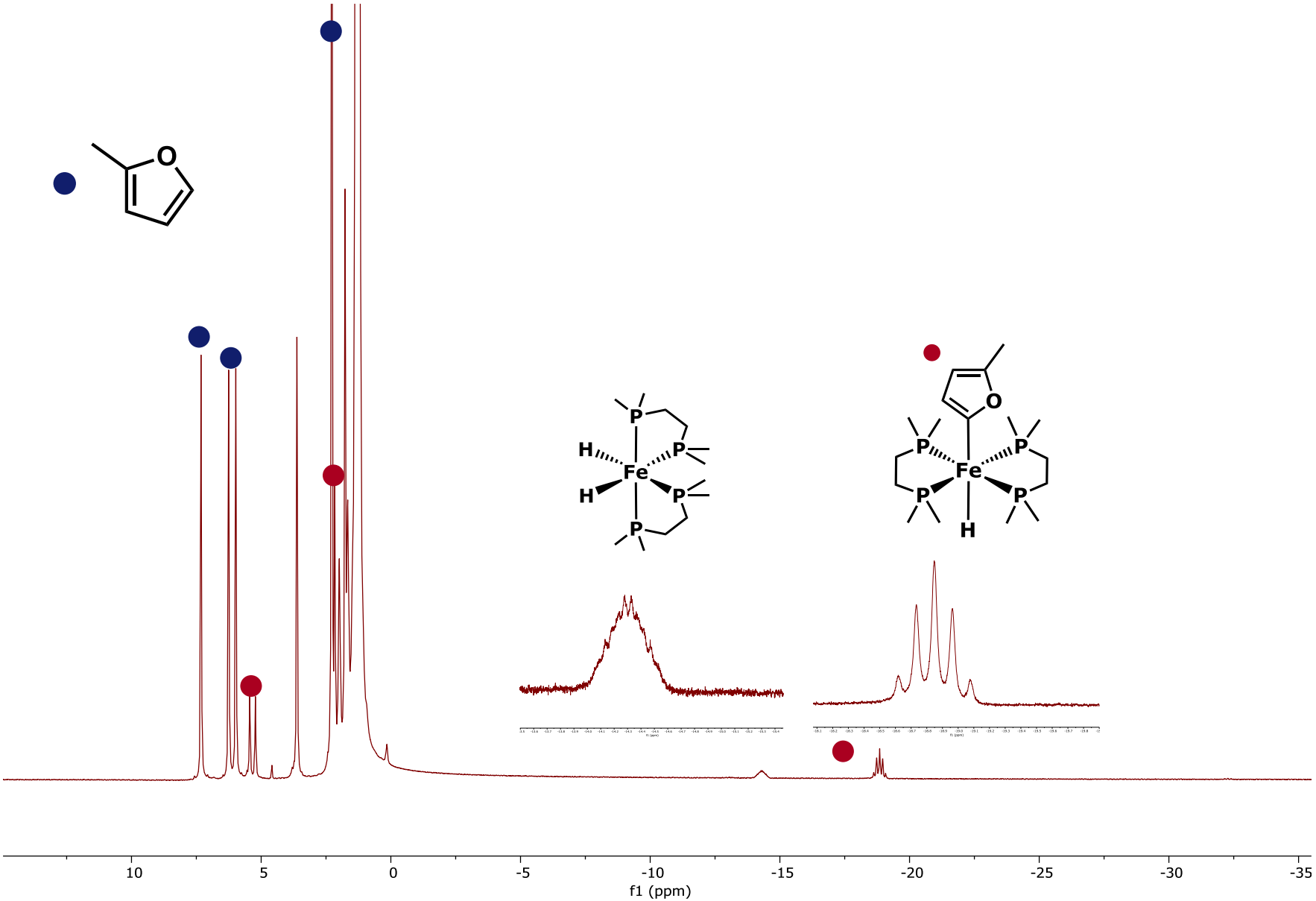
NMR spectra - H/D exchange



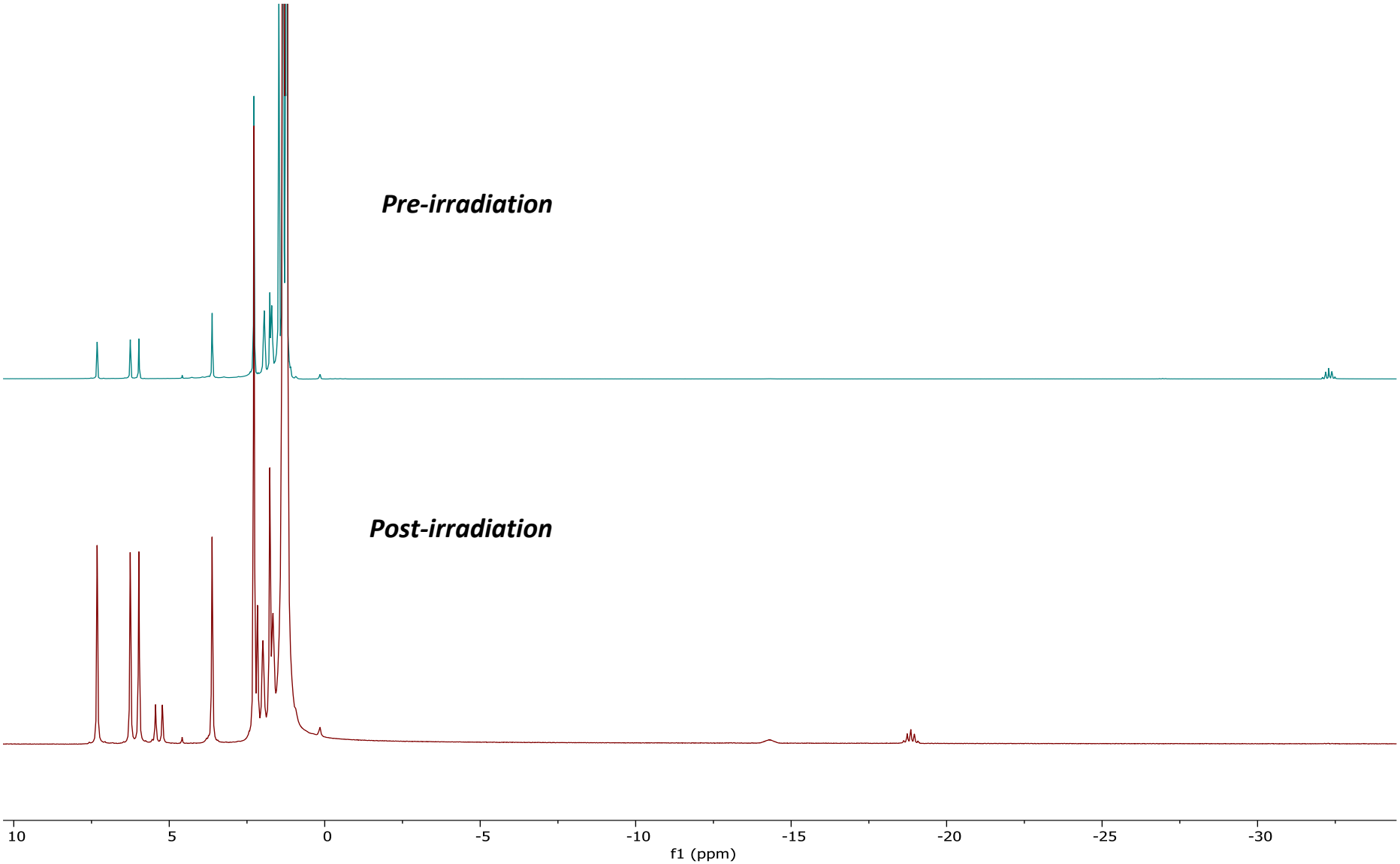
^{2}H NMR (77 MHz, THF) of the reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with CD$_3$OD.



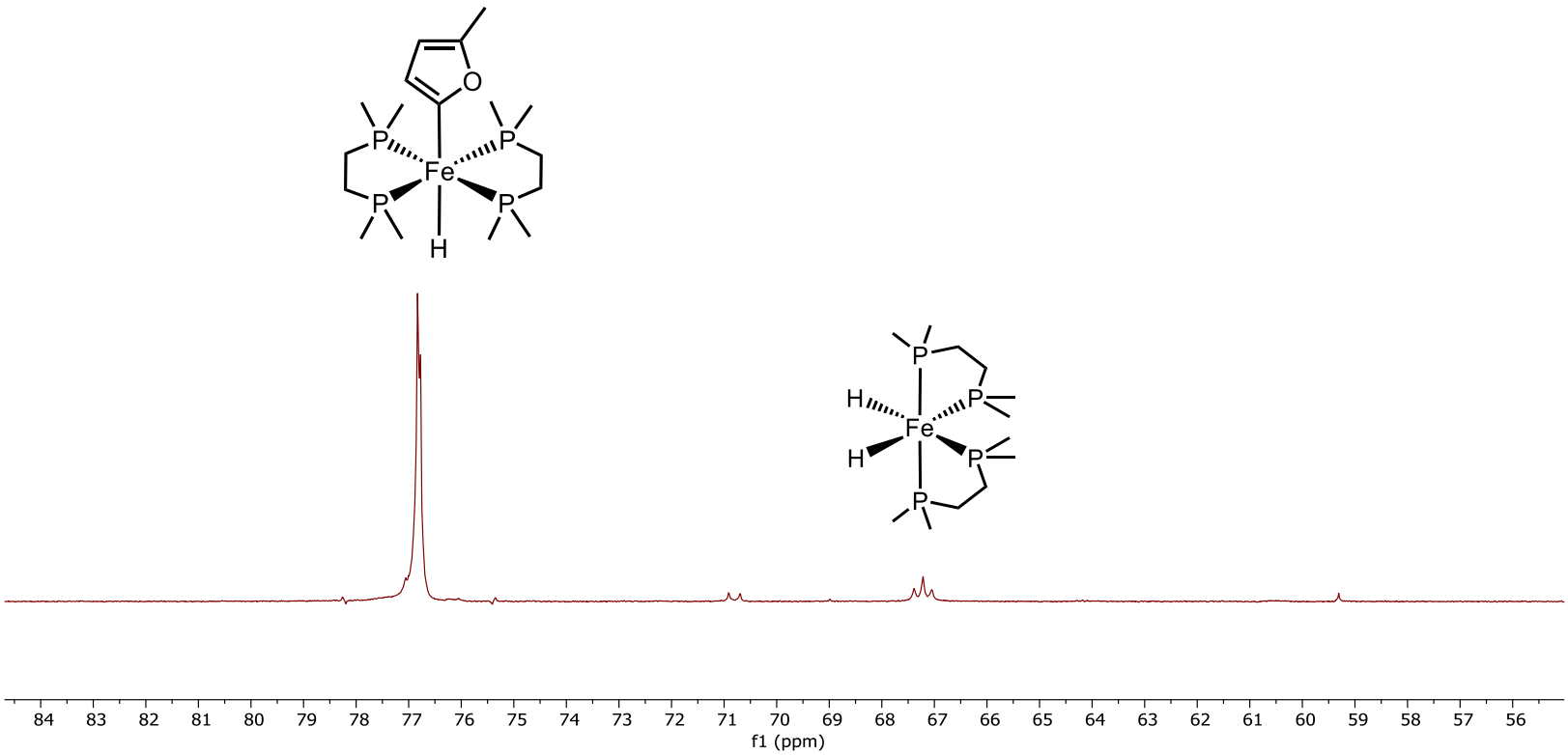
^{31}P NMR (126 MHz, THF) of the reaction of [dmpe$_2$FeH$_2$] **2** with CD_3OD.



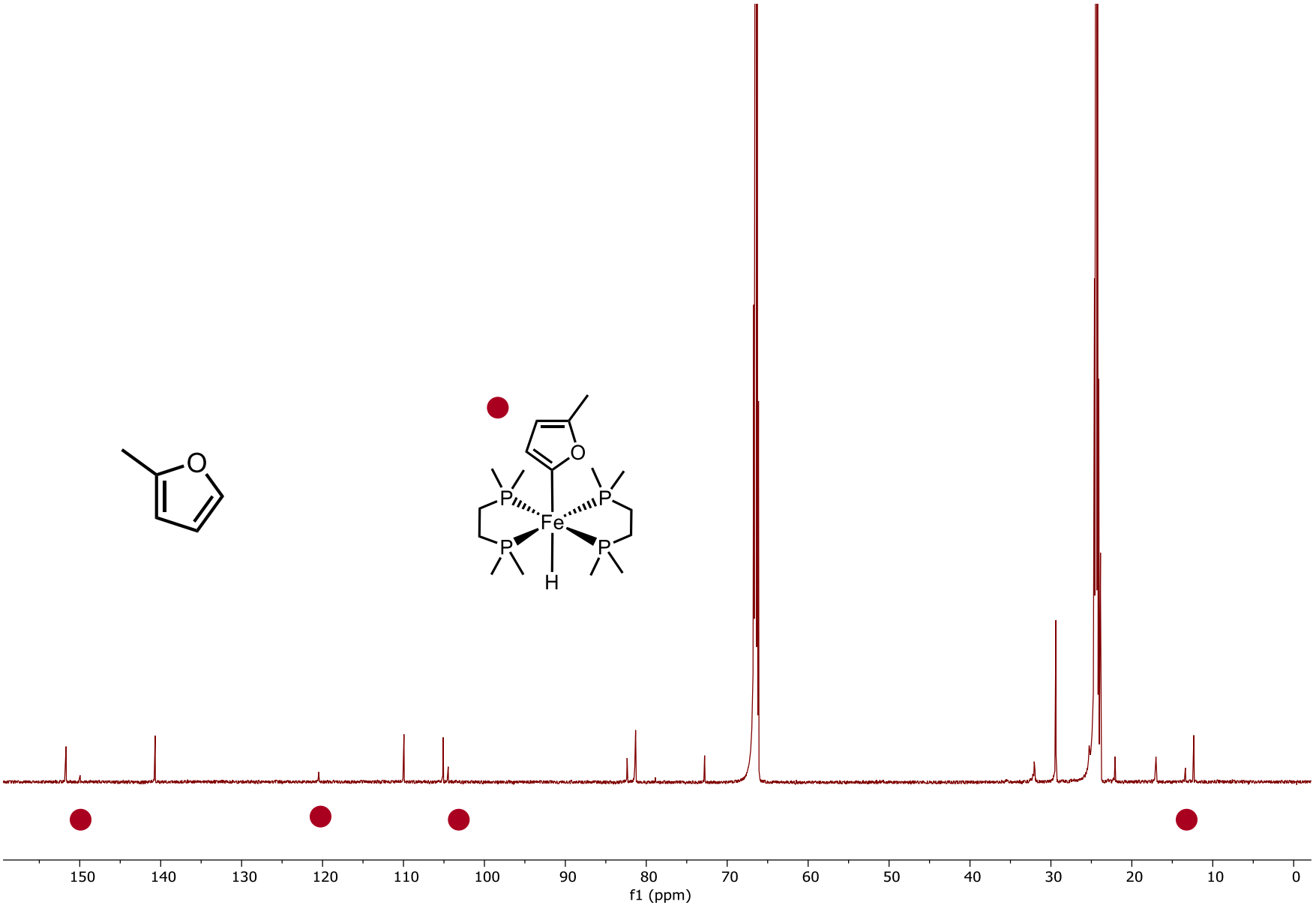
^{1}H NMR (400 MHz, d^{8}-THF) for the reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with 2-methylfuran **3a**.



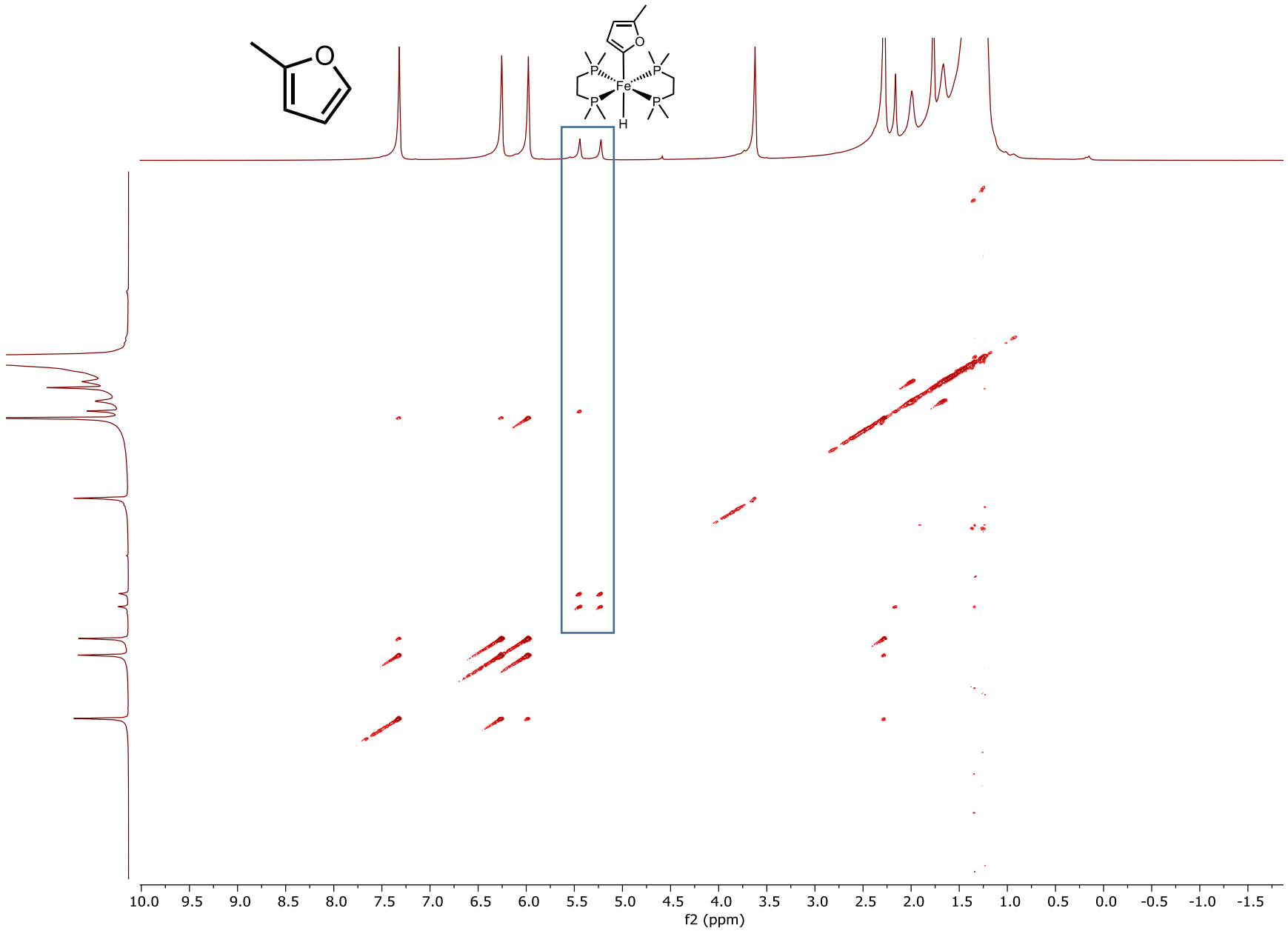
^{1}H NMR (400 MHz, d^{8}-THF) stacked comparison for the reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with 2-methylfuran **3a**. Top = before irradiation, bottom = post-irradiation.



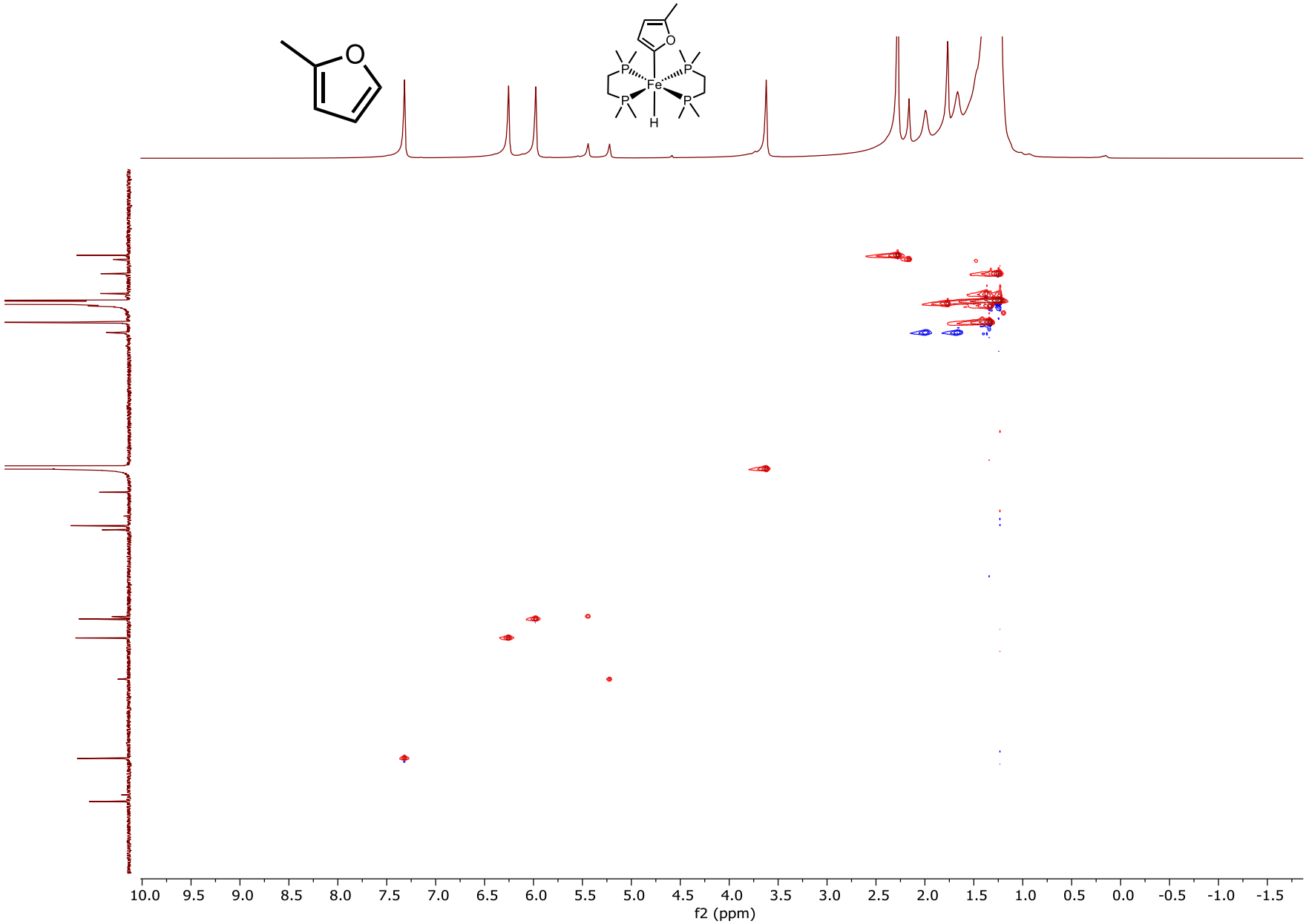
^{31}P NMR (162 MHz, d^8-THF) of the reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with 2-methylfuran **3a**.



^{13}C NMR (151 MHz, d^8-THF) for the reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with 2-methylfuran **3a**.

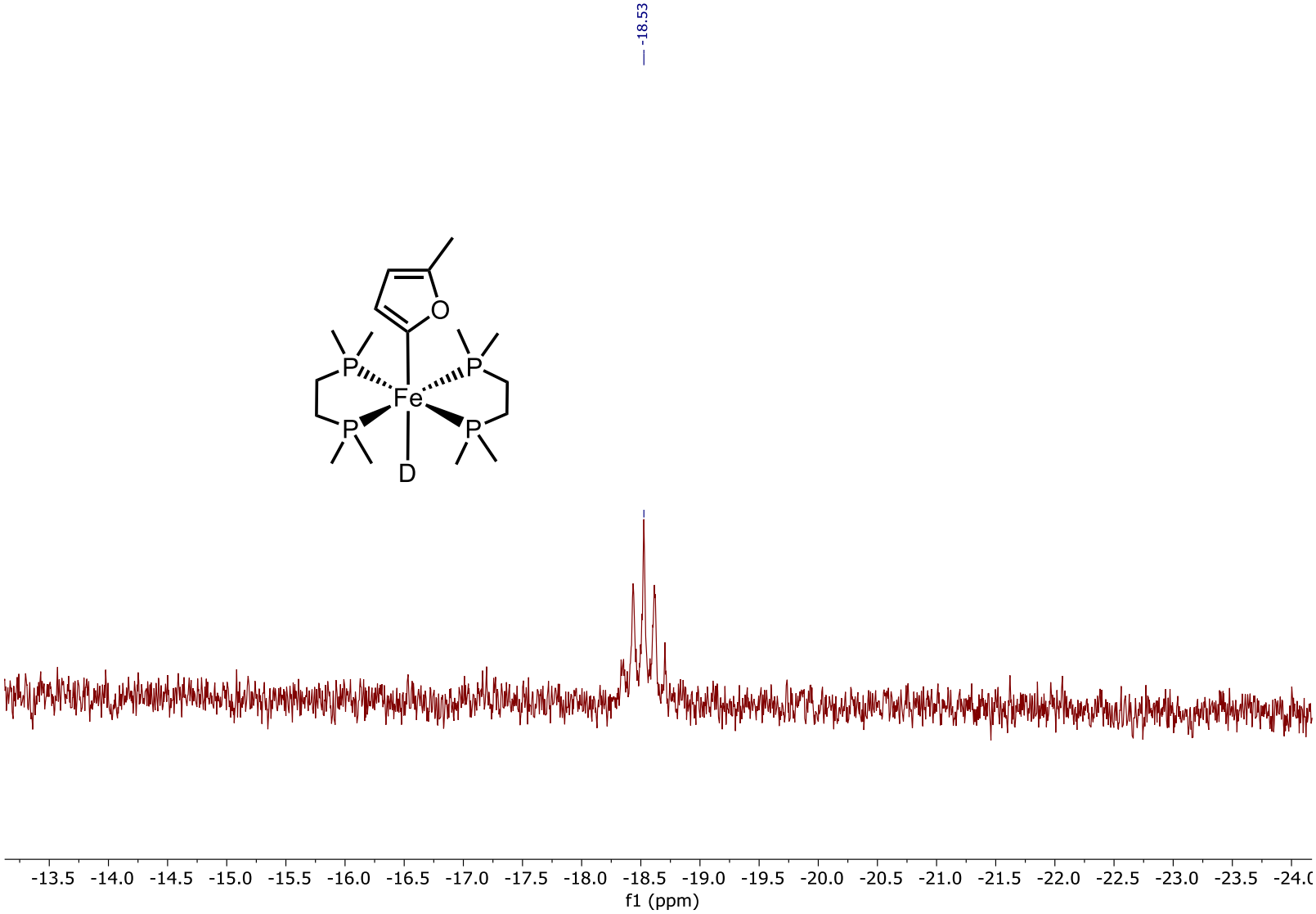


^{1}H-^{1}H COSY NMR (600 MHz, d^{8}-THF) for the reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with 2-methylfuran **3a**.

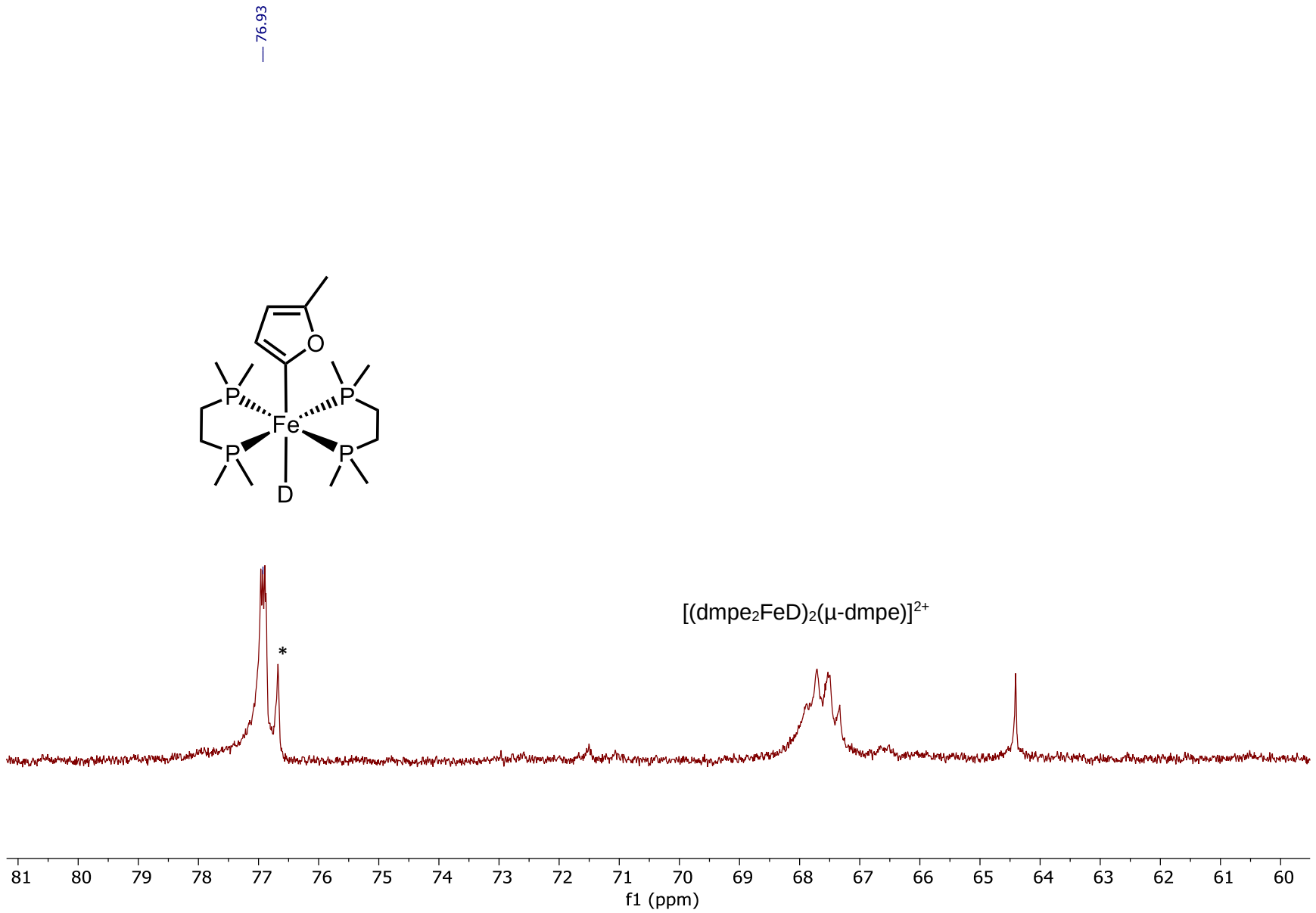


^{1}H-^{13}C HSQC NMR (600, 151 MHz, *d*^{8}-THF) for the reaction of [dmpe$_2$FeH$_2$] **2** and [dmpe$_2$FeHCl] with 2-methylfuran **3a**.

NMR spectra – Fe-aryl H/D exchange

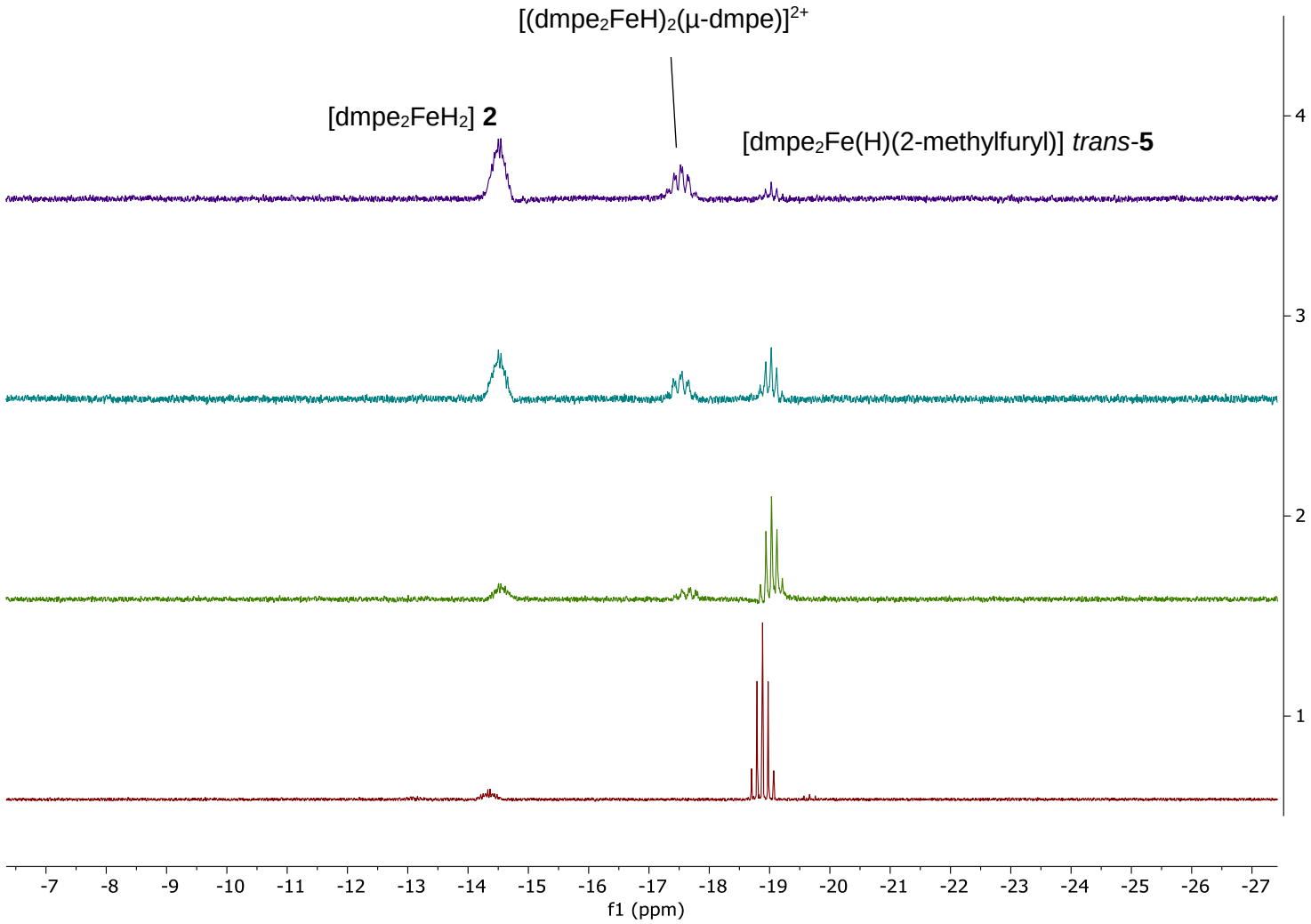


^{2}H NMR (77 MHz, THF) of [dmpe$_2$Fe(D)(2-methylfuryl)] **[D]**-*trans*-**5**. *Deuteride region only*

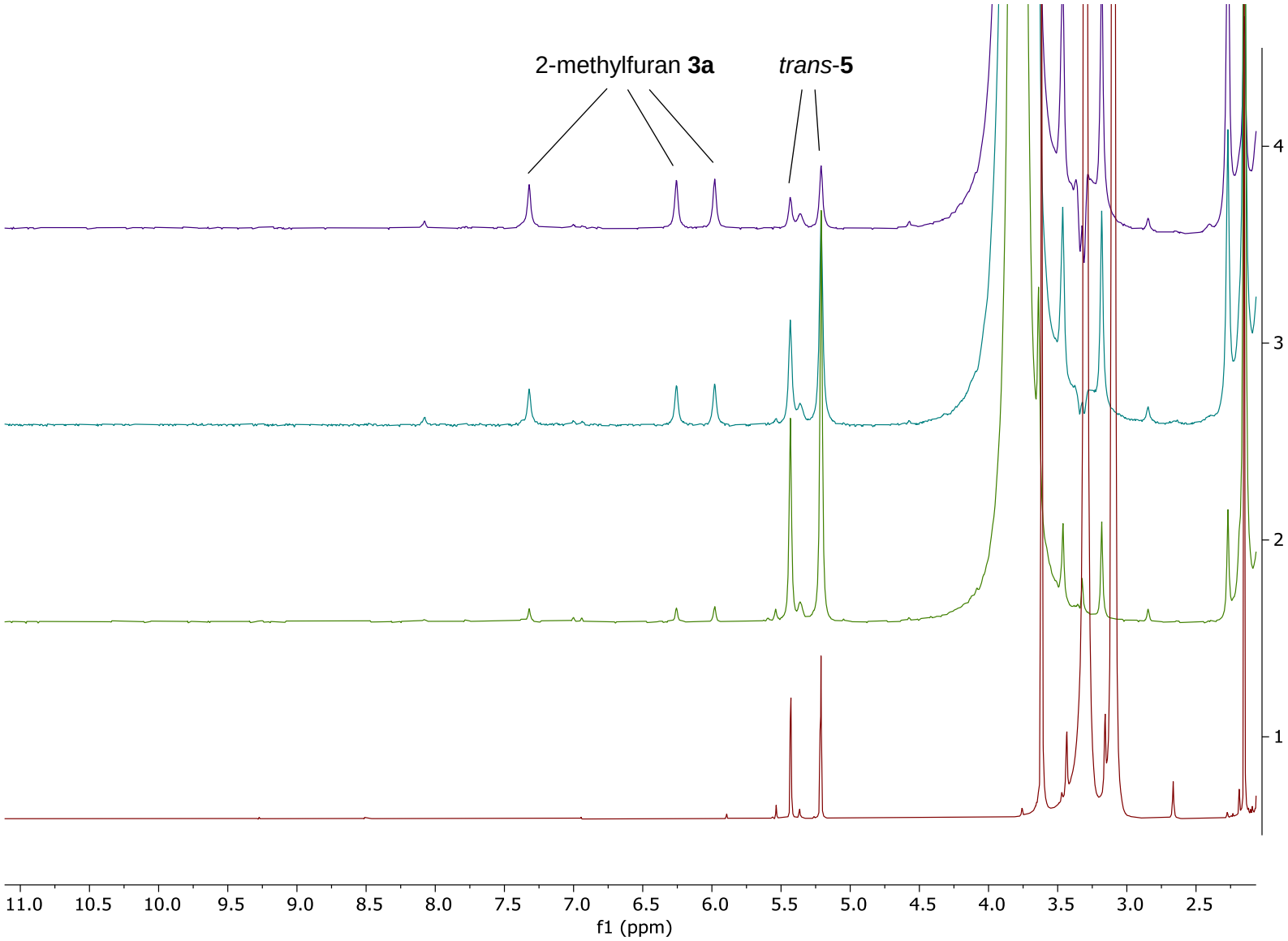


^{31}P NMR (202 MHz, d^8-THF) of [dmpe$_2$Fe(D)(2-methylfuryl)] **[D]**-*trans*-**5**. (*) denotes residual ^{1}H isotopologue - dmpe$_2$FeH(2-methylfuryl)

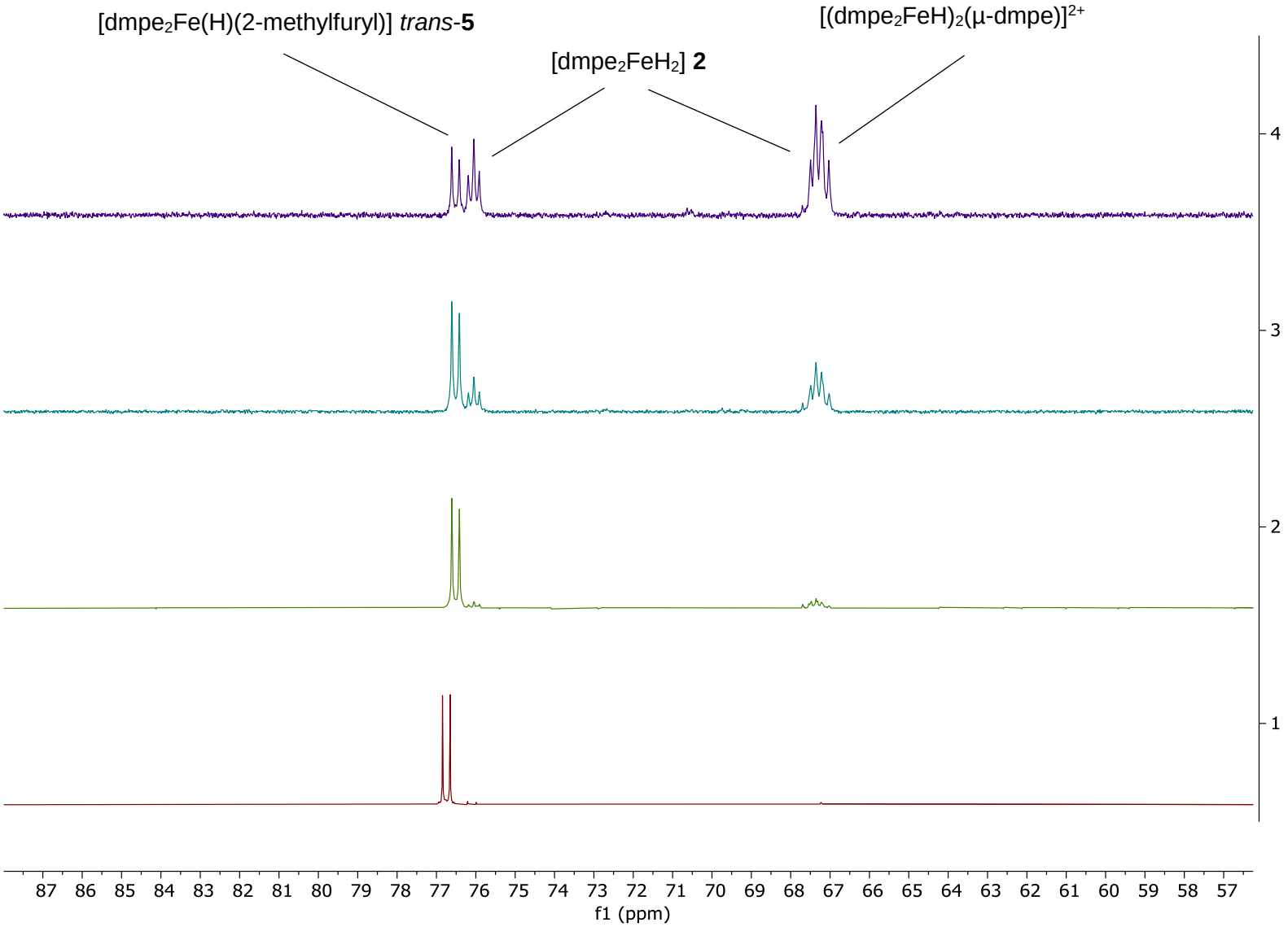
NMR spectra – Fe-aryl turnover



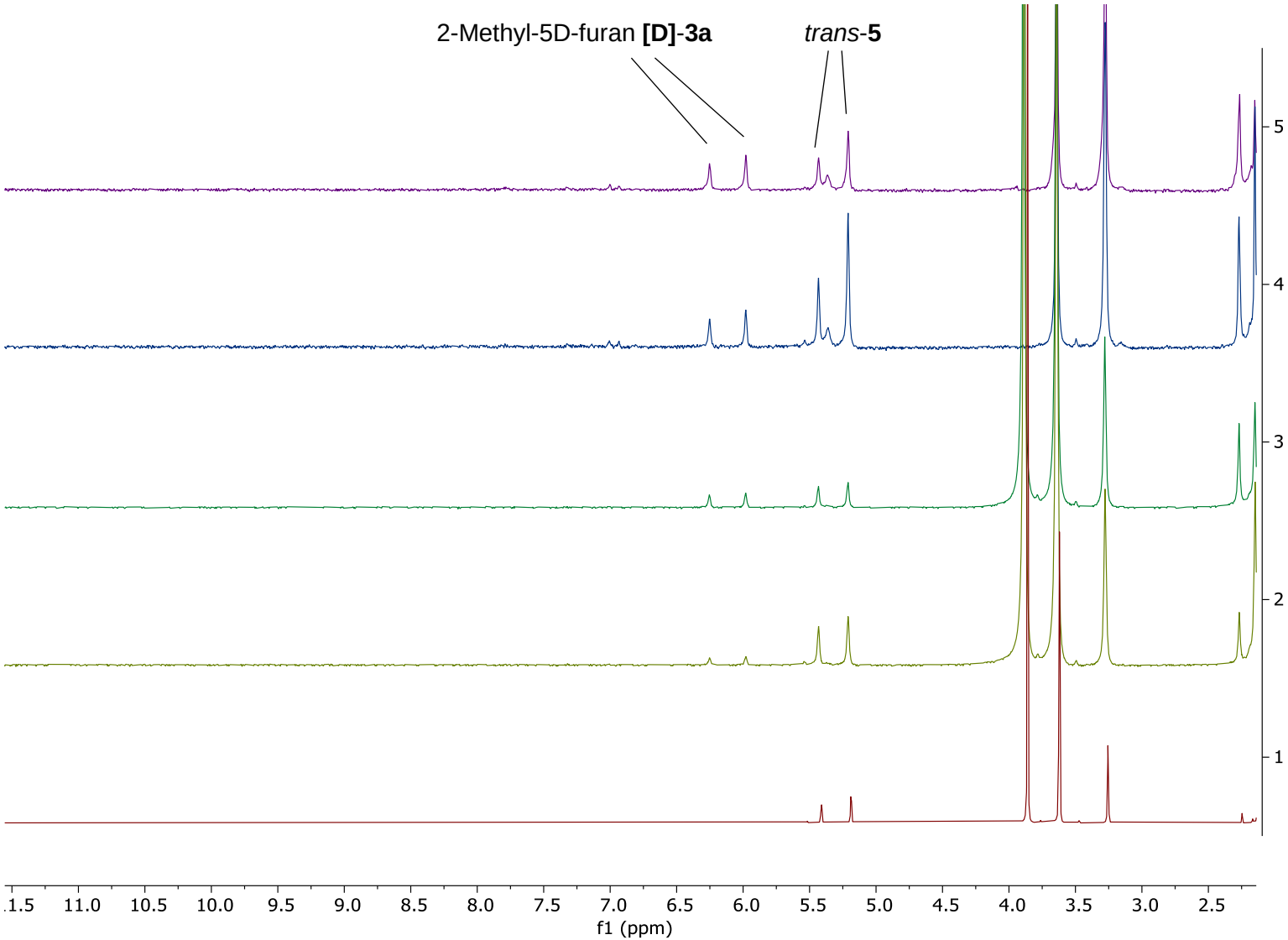
^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** + CH_3OH in d_8-THF (1) Before addition of CH_3OH. (2) After the addition of CH_3OH (approx. 250 equiv.). (3) after 4 h at rt. (4) after 12 h at rt. – hydride region only.



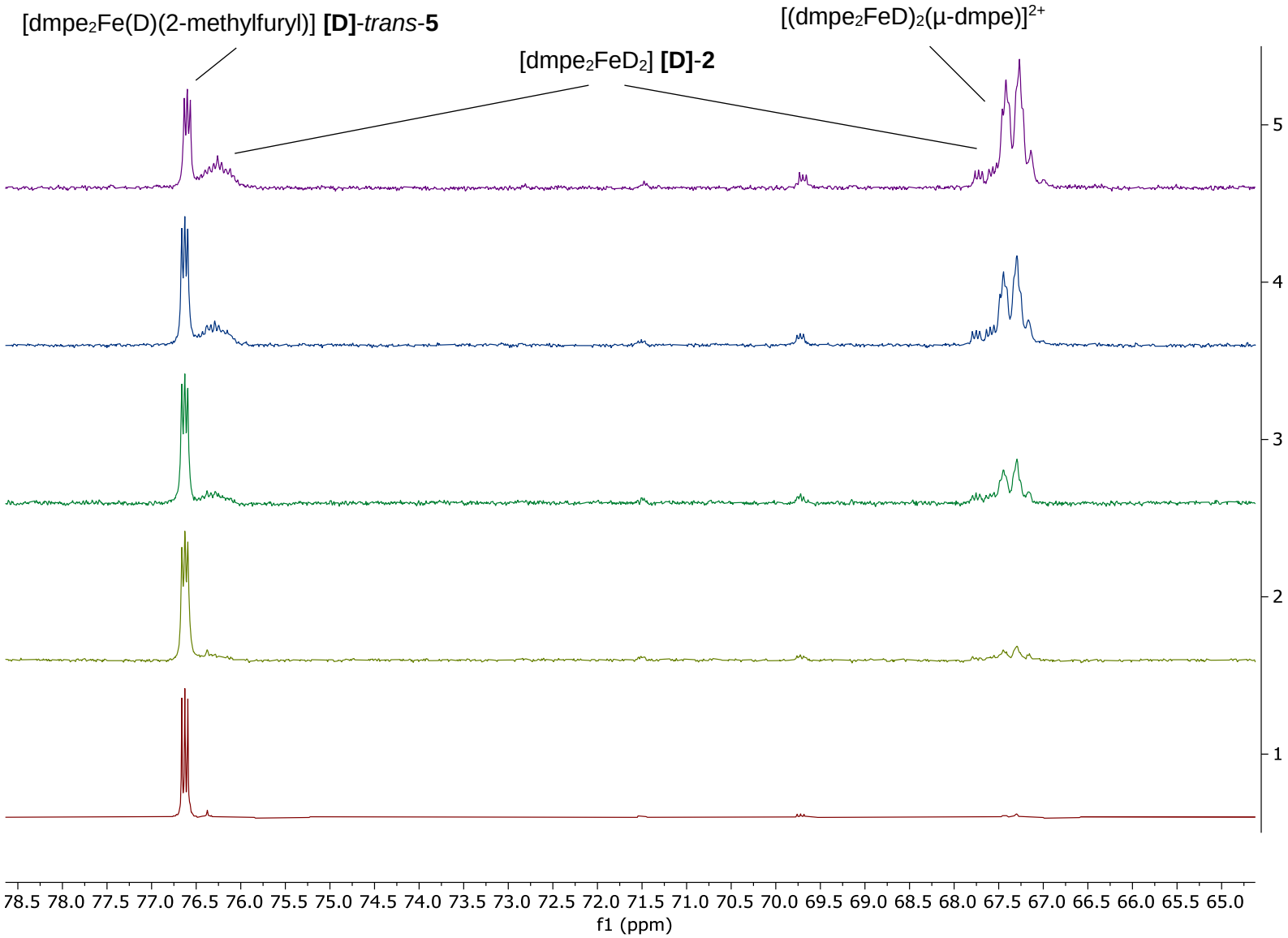
^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** + CH_3OH in d_8-THF (1) Before addition of CH_3OH. (2) After the addition of CH_3OH (approx. 250 equiv.). (3) after 4 h at rt. (4) after 12 h at rt.



^{31}P NMR (202 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** + CH_3OH in d_8-THF (1) Before addition of CH_3OH. (2) After the addition of CH_3OH (approx. 250 equiv.). (3) after 4 h at rt. (4) after 12 h at rt.

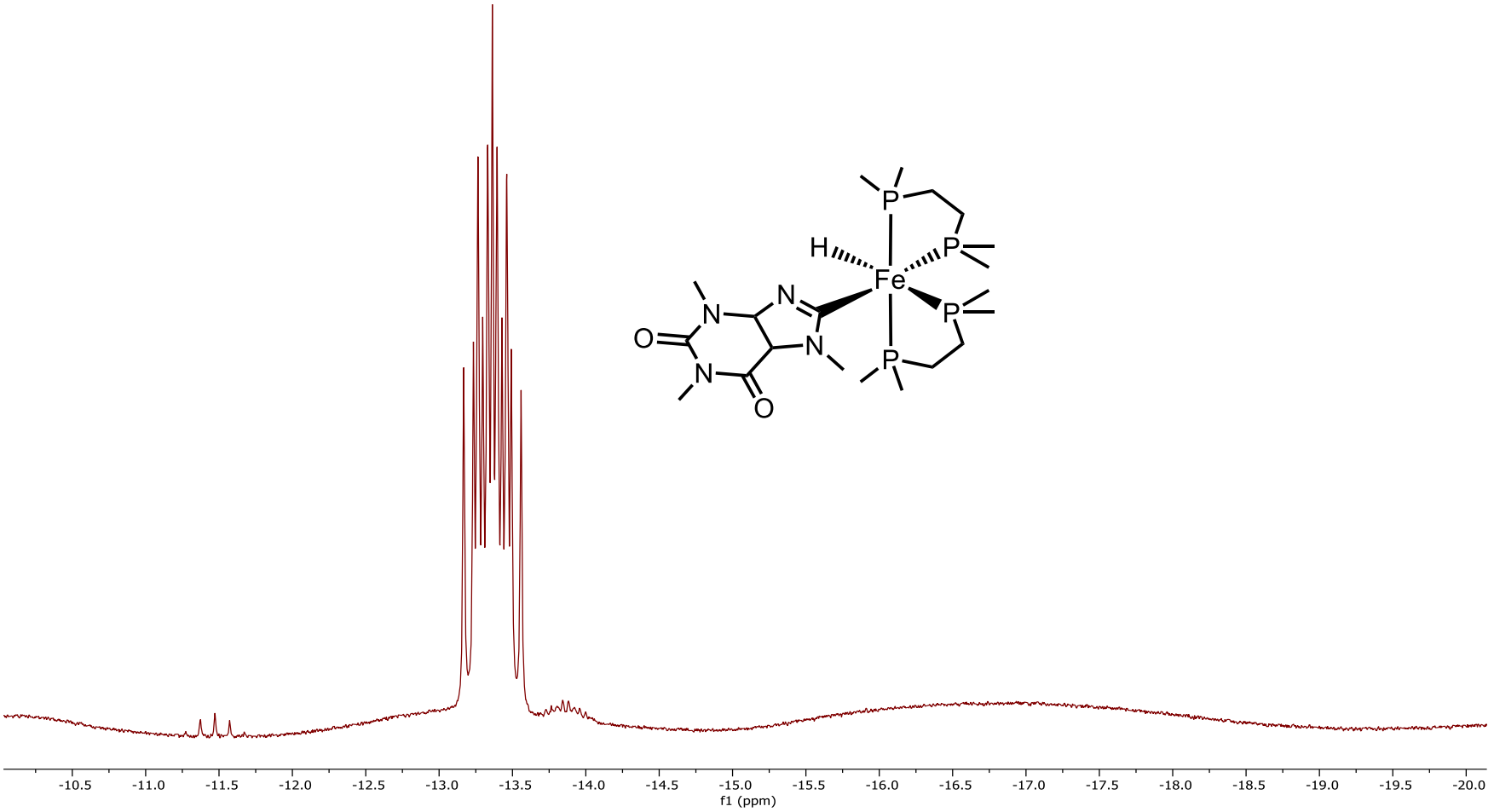


^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** + CD_3OD in d_8-THF (1) After the addition of CH_3OH (approx. 250 equiv.). (2) after 4 h at rt. (3) after 12 h at rt. (4) after 18 h at rt. (5) after 26 h at rt.

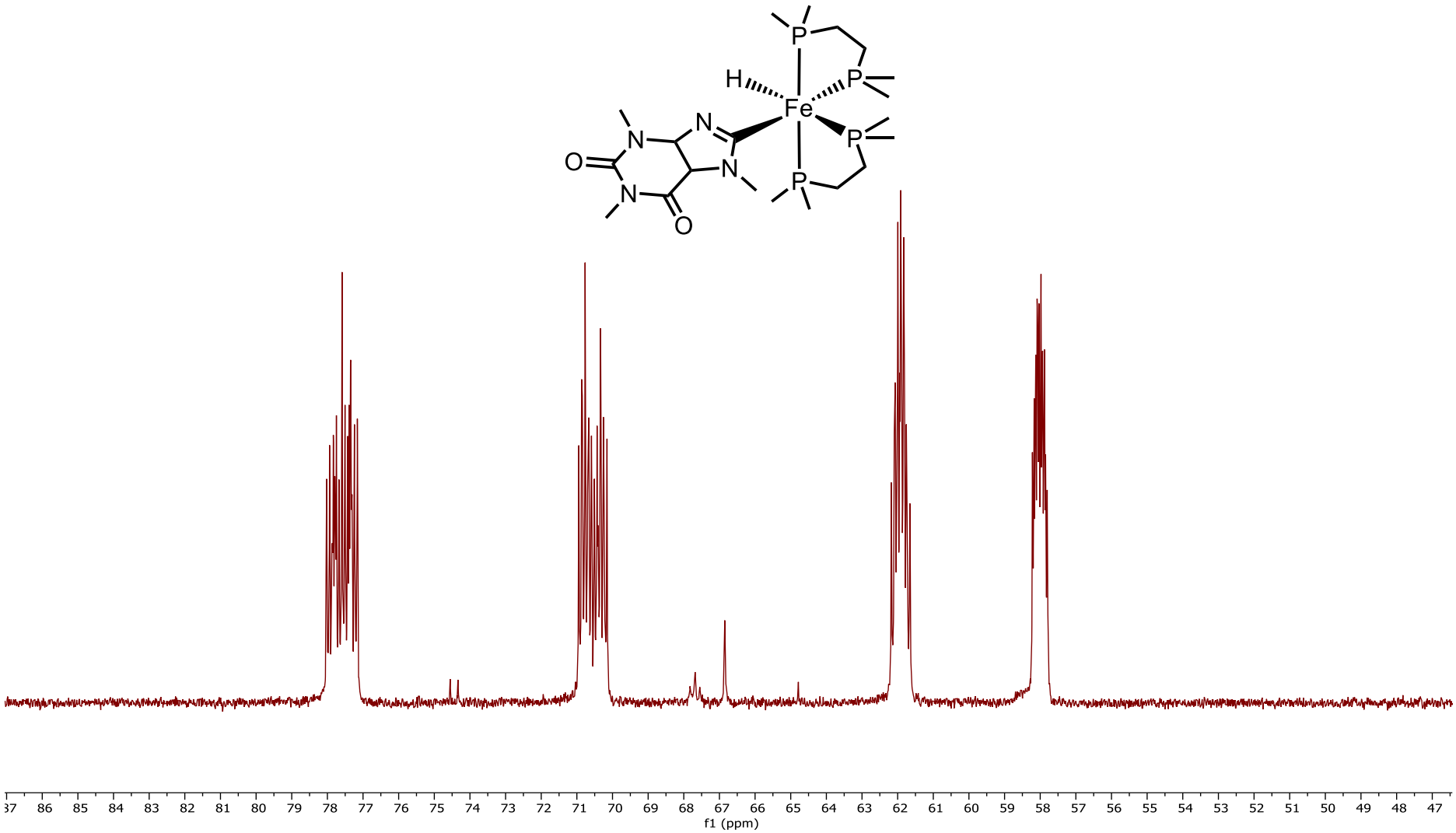


^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2-methylfuryl)] *trans*-**5** + CD_3OD in d_8-THF (1) After the addition of CH_3OH (approx. 250 equiv.). (2) after 4 h at rt. (3) after 12 h at rt. (4) after 18 h at rt. (5) after 26 h at rt.

NMR spectra – Additional Fe arene C-H metallation

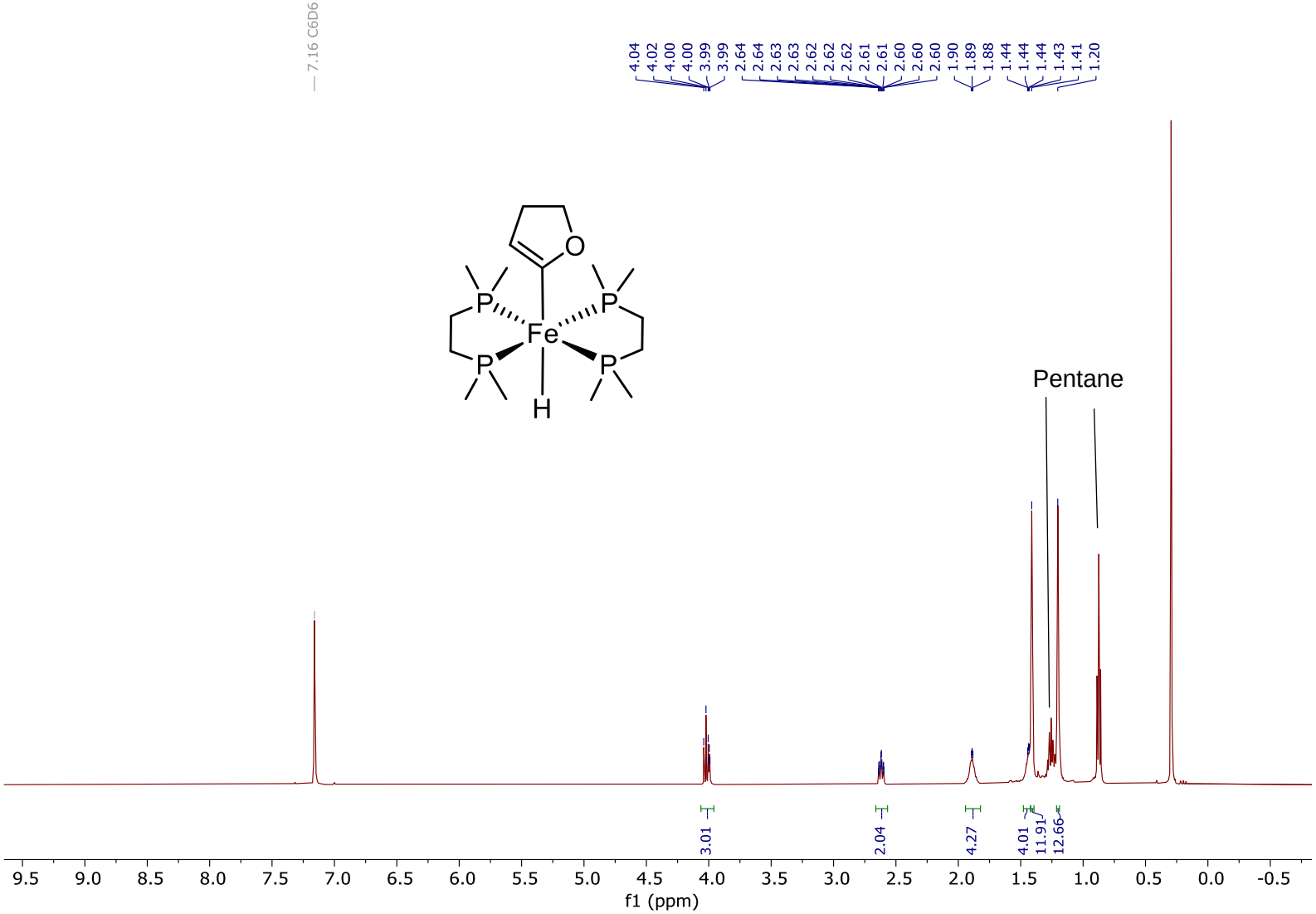


^{1}H NMR (500 MHz, THF) of [dmpe$_2$Fe(H)caffeine] *cis*-**6**.

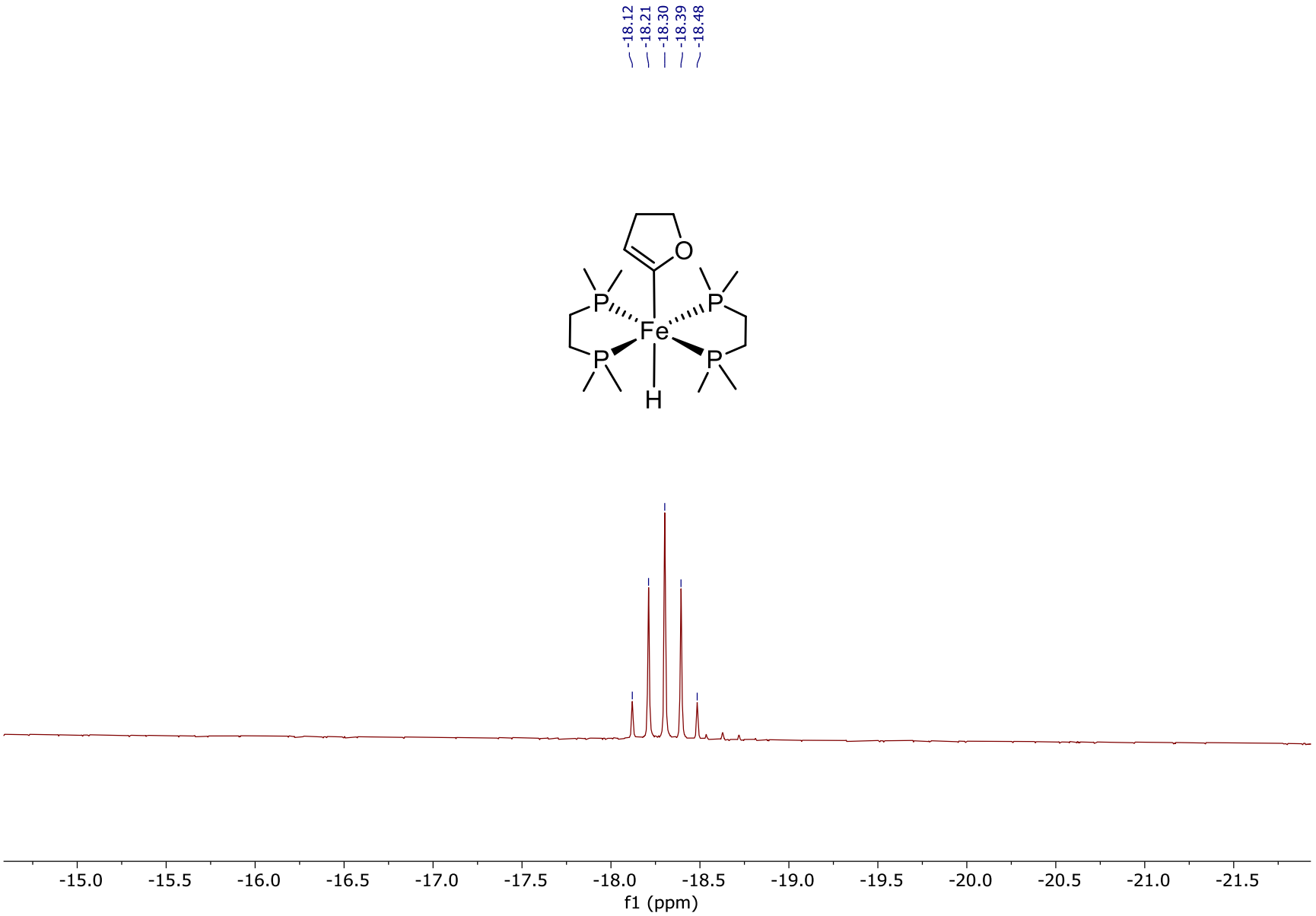


^{31}P NMR (202 MHz, THF) of [dmpe$_2$Fe(H)caffeine] *cis*-**6**.

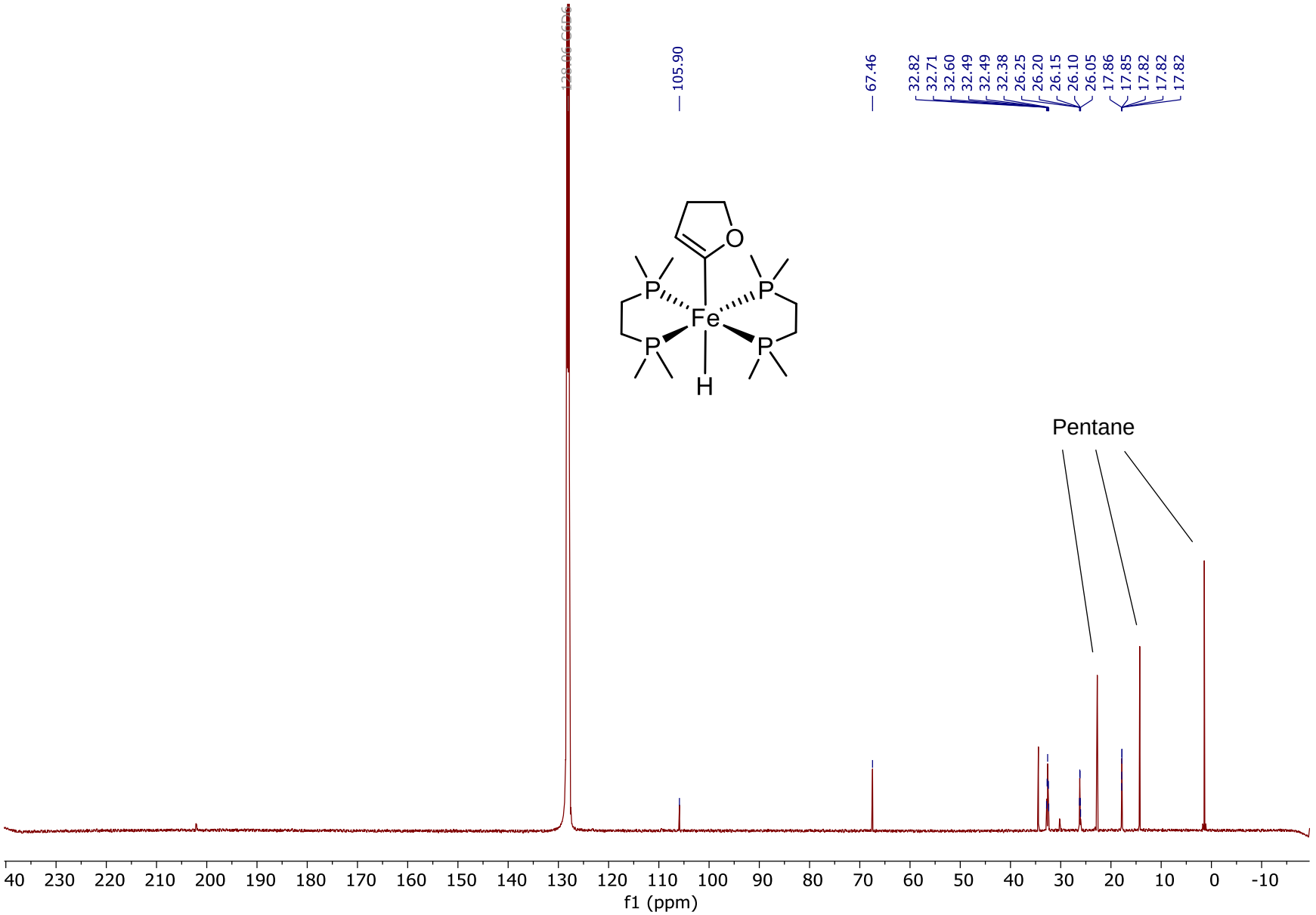
NMR spectra – Fe alkene C-H metallation



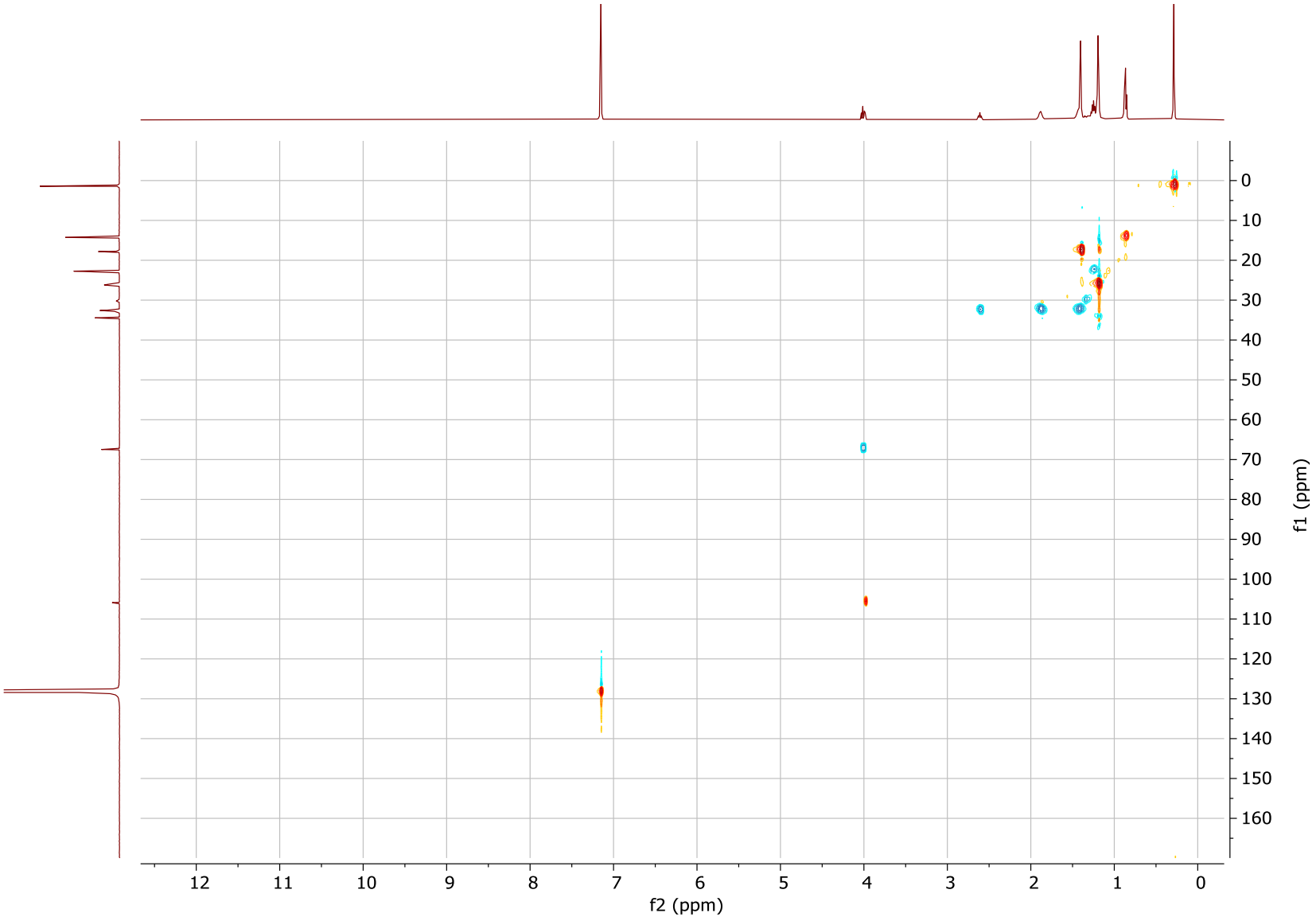
^{1}H NMR (500 MHz, C_6D_6) of [dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7**.



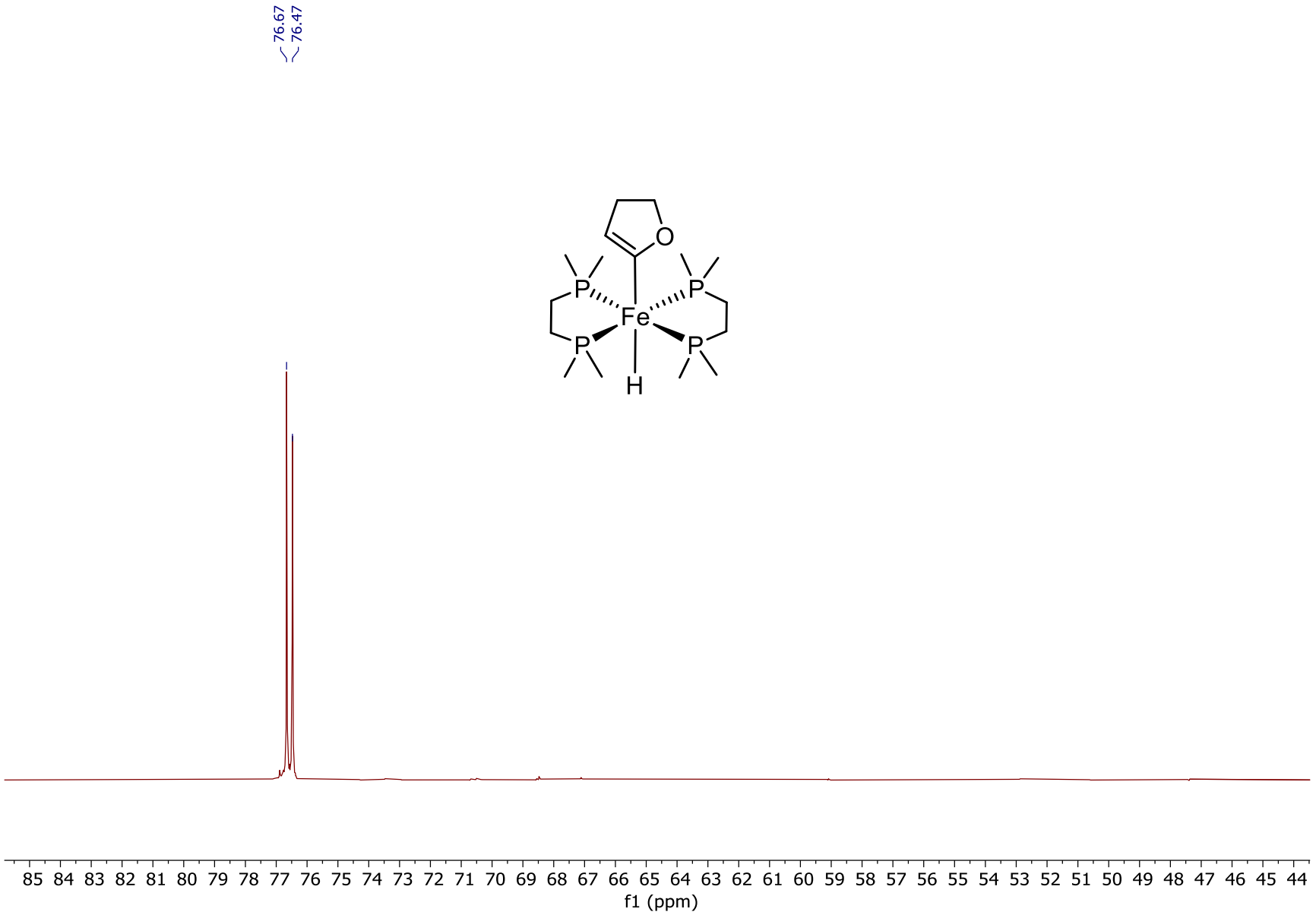
^{1}H NMR (500 MHz, C_6D_6) of [dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7** – *Hydride region only*.



^{13}C NMR (126 MHz, C_6D_6) of [dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7**.

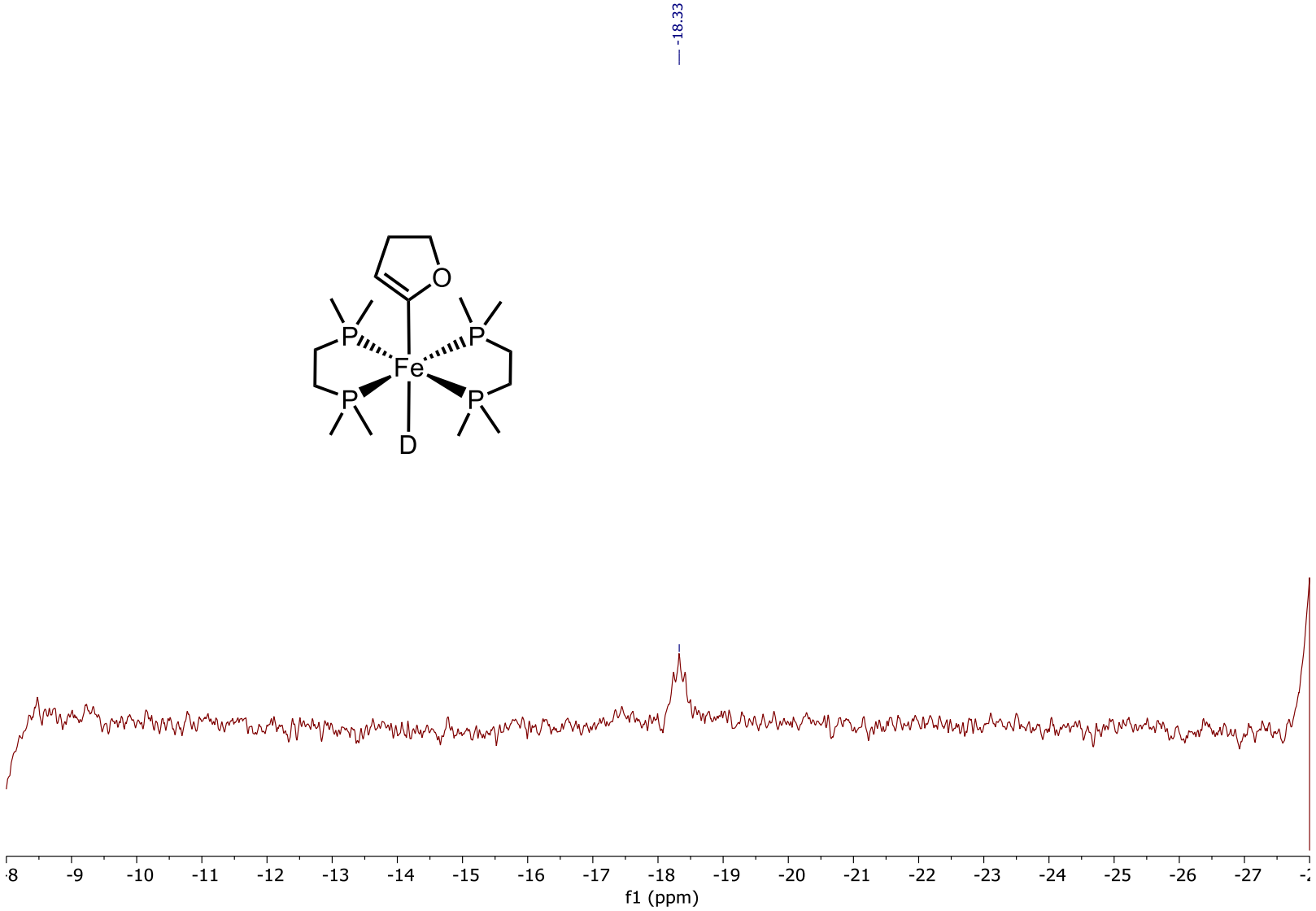


^{1}H-^{13}C HSQC NMR (500, 126 MHz, C_6D_6) with DEPT editing of [dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7**.

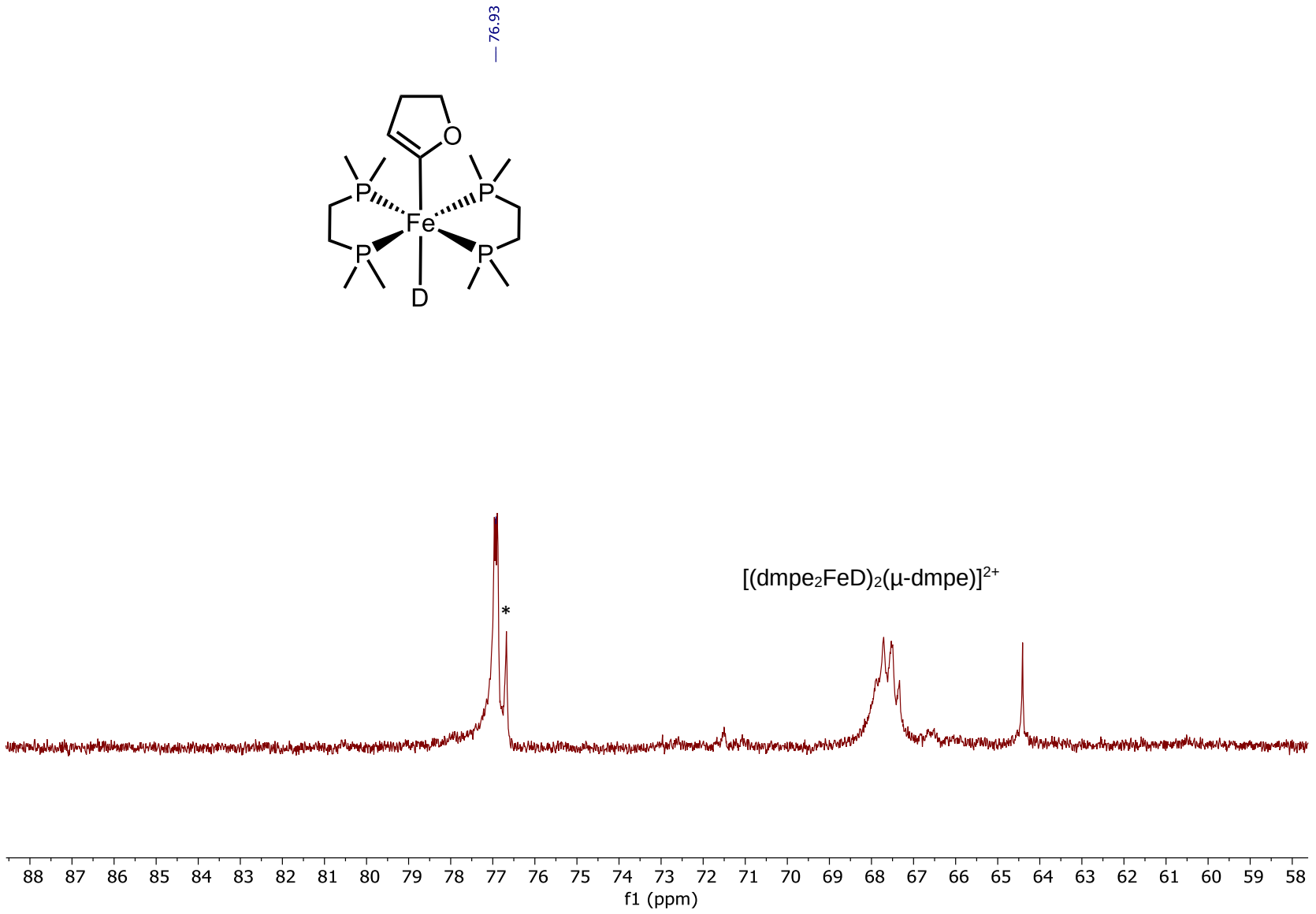


^{31}P NMR (202 MHz, C_6D_6) of [dmpe$_2$Fe(H)(2,3-dihydrofuryl)] *trans*-**7**.

NMR spectra – Fe-alkenyl H/D exchange

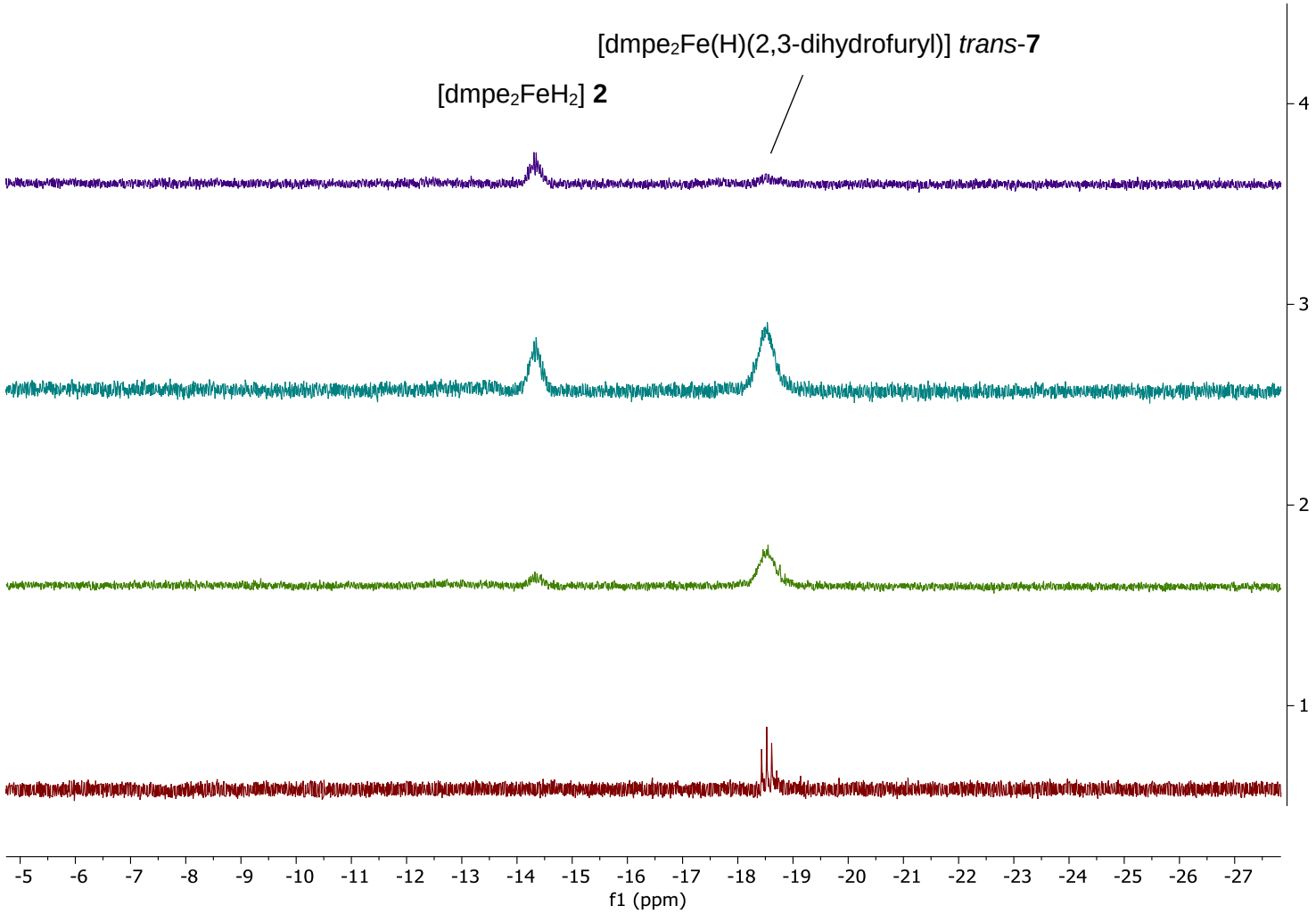


^{2}H NMR (77 MHz, THF) of [dmpe$_2$Fe(D)(2,3-dihydrofuryl)] **[D]**-*trans*-**7** – *Deuteride region only*.

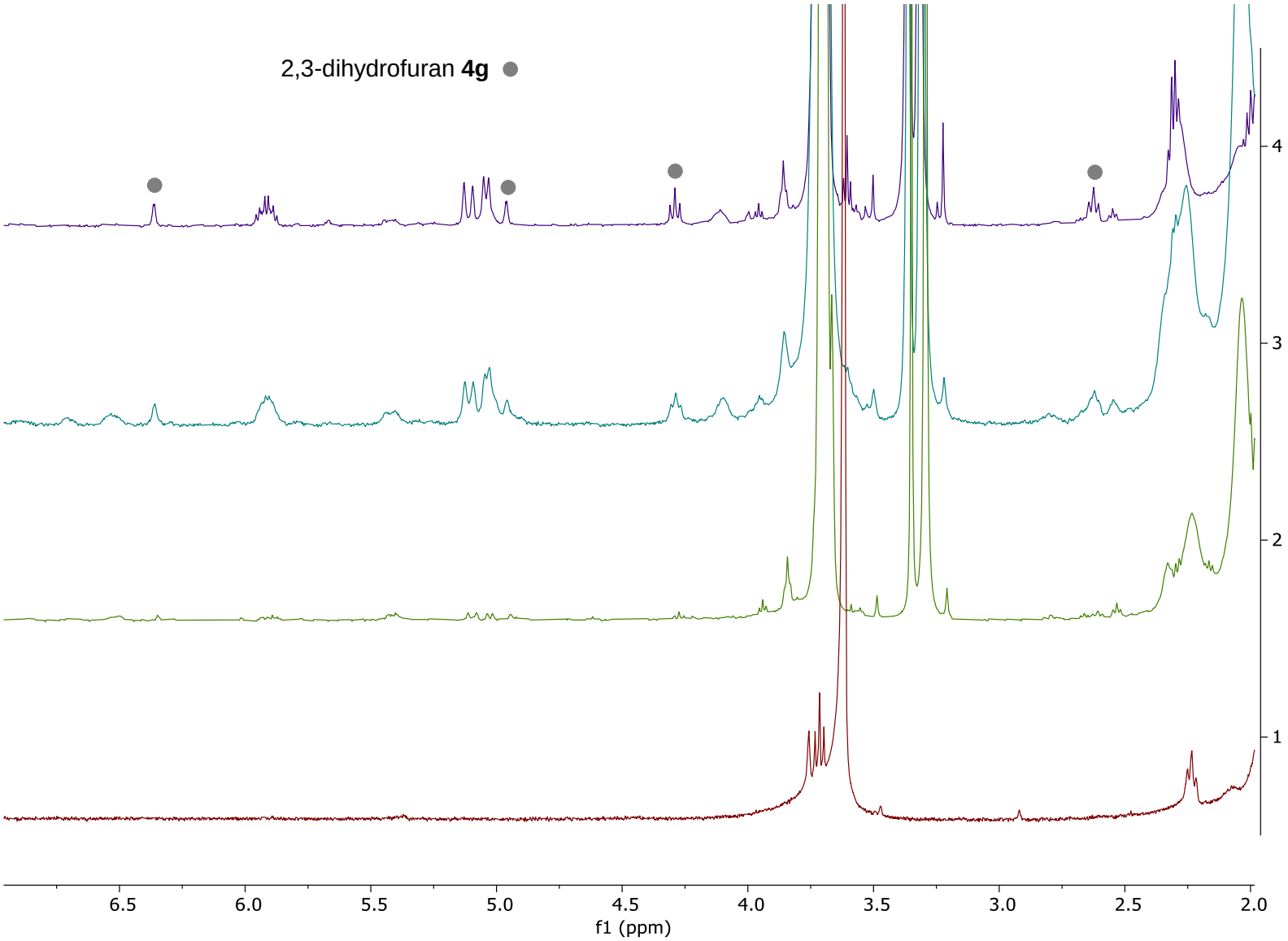


^{31}P NMR (202 MHz, d^8-THF) of [dmpe$_2$Fe(D)(2,3-dihydrofuryl)] **[D]**-*trans*-**7**. (*) denotes residual ^{1}H isotopologue - [dmpe$_2$Fe(H)(2,3-dihydrofuryl)].

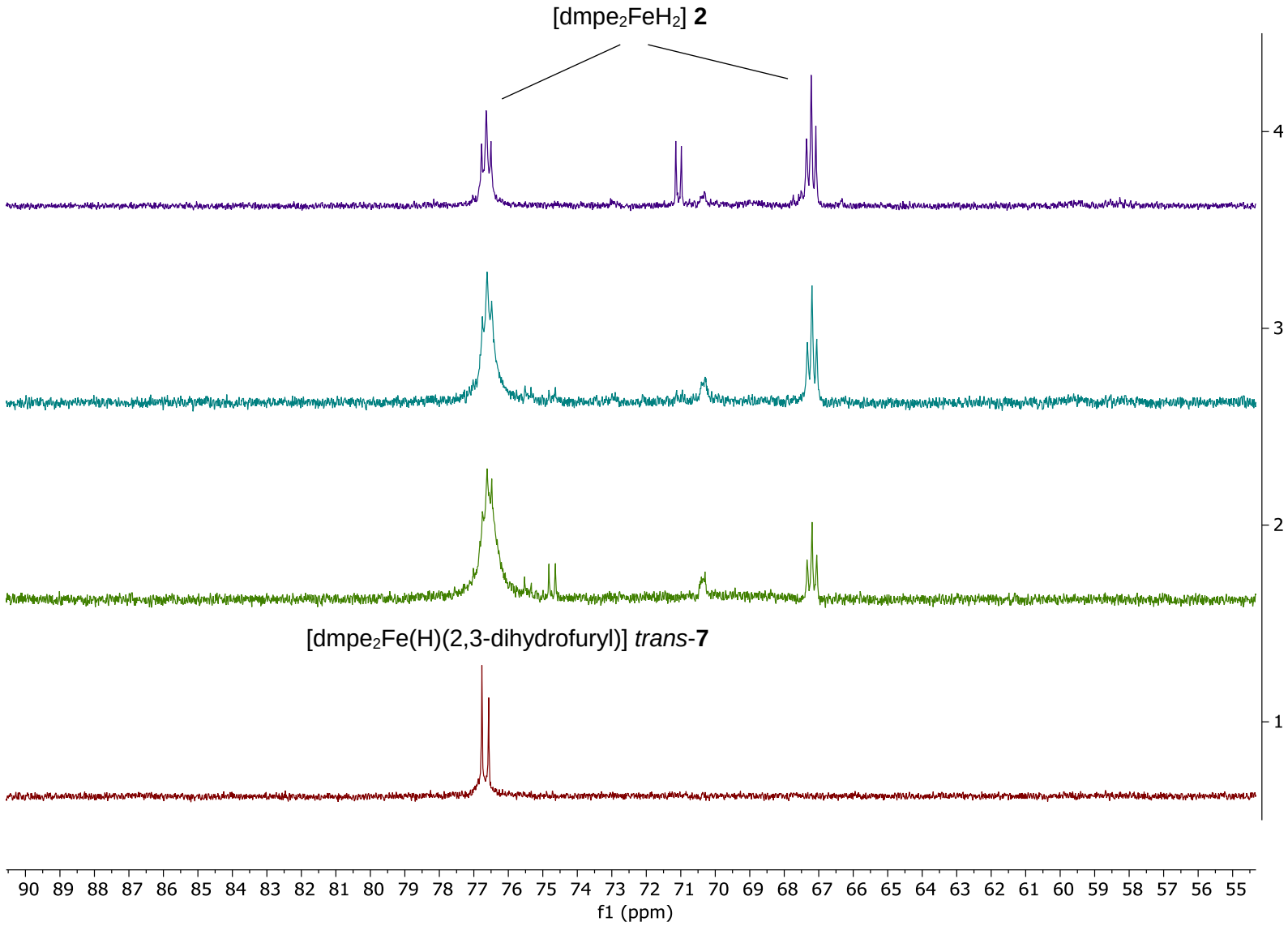
NMR spectra – Fe-alkenyl turnover



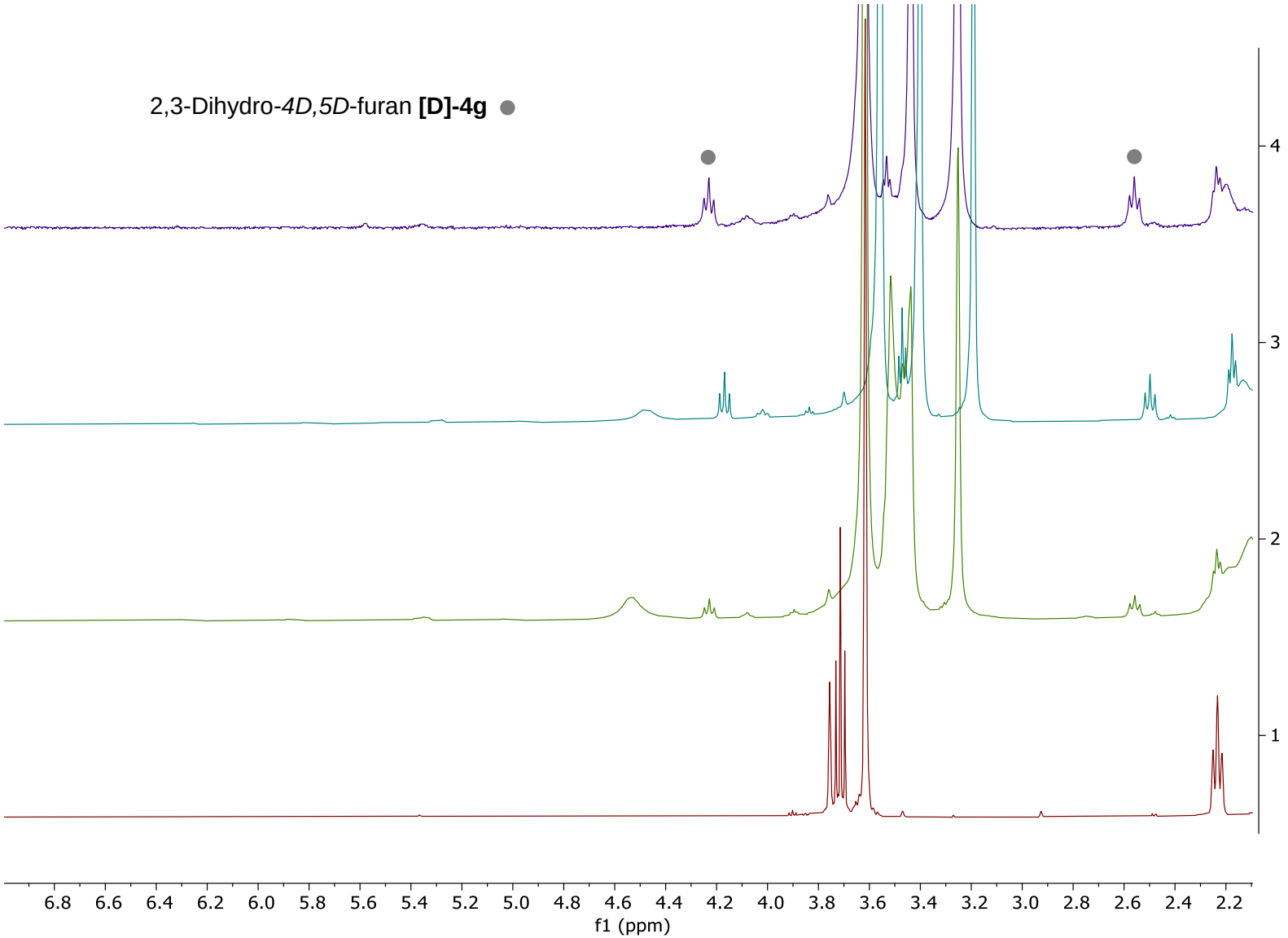
^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2,3-dihydrolfuryl)] *trans*-**7** + CH_3OH in d_8-THF (1) Before addition of CH_3OH. (2) After the addition of CH_3OH (approx. 100 equiv.). (3) after 4 h at rt. (4) after 18 h at rt. – hydride region only.



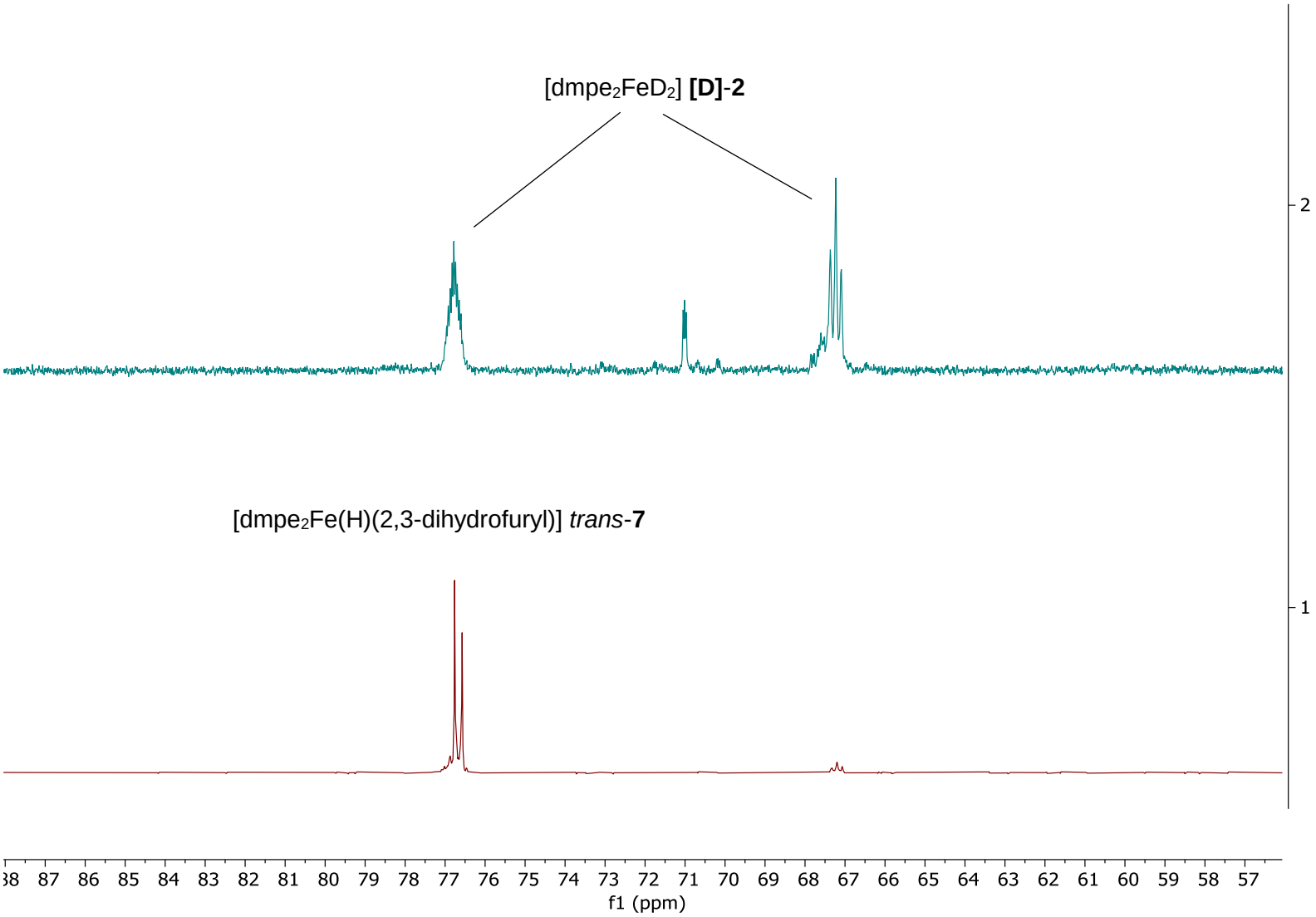
^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2,3-dihydrolfuryl)] *trans*-**7** + CH_3OH in d_8-THF (1) Before addition of CH_3OH. (2) After the addition of CH_3OH (approx. 100 equiv.). (3) after 4 h at rt. (4) after 18 h at rt.



^{31}P NMR (202 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2,3-dihydrolfuryl)] *trans*-**7** + CH_3OH in d_8-THF (1) Before addition of CH_3OH. (2) After the addition of CH_3OH (approx. 100 equiv.). (3) after 4 h at rt. (4) after 18 h at rt.

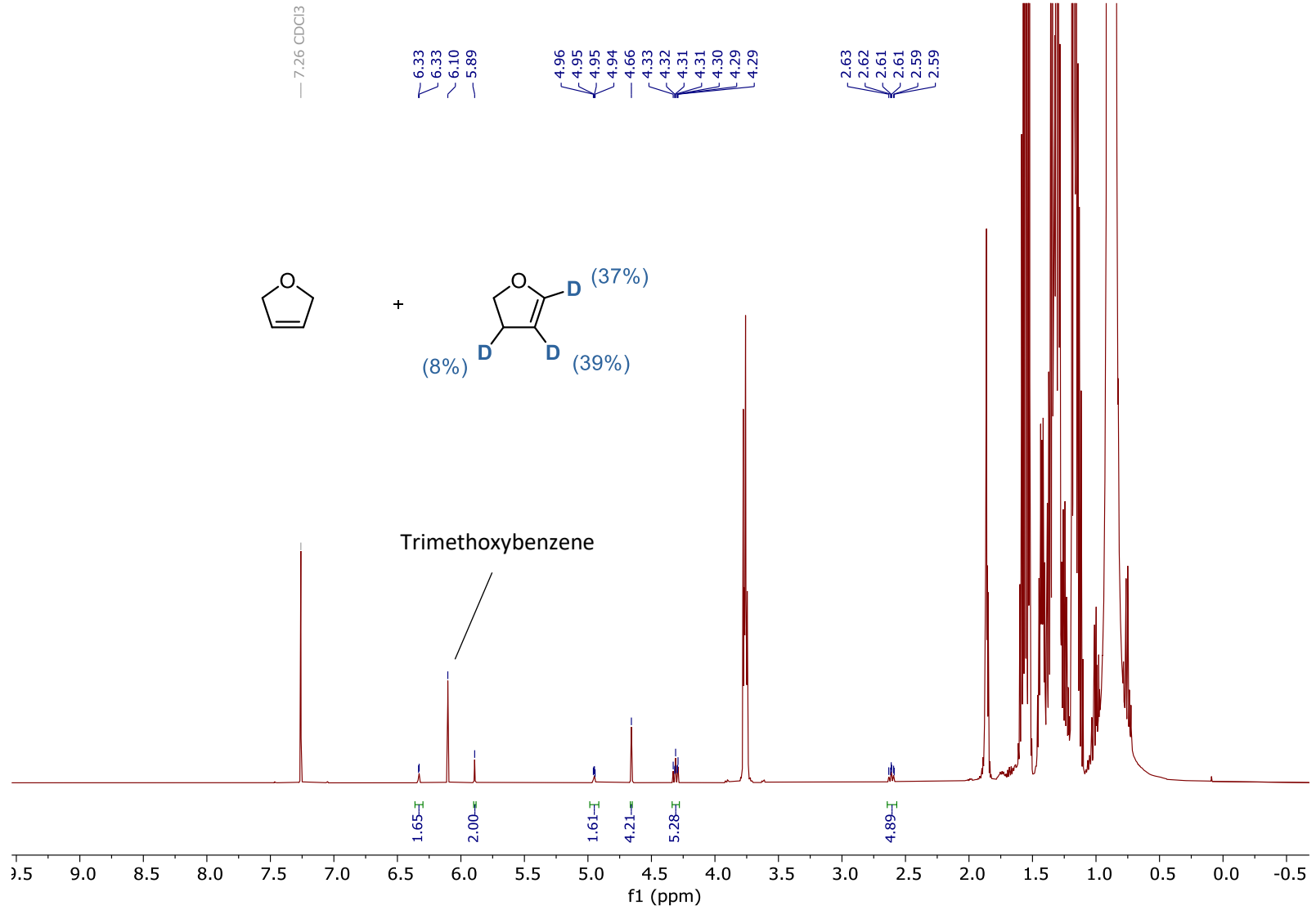


^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2,3-dihydrolfuryl)] *trans*-**7** + CD_3OD in d_8-THF (1) Before addition of CD_3OD. (2) After the addition of CD_3OD (approx. 100 equiv.). (3) After 4 h at rt. (4) After 18 h at rt.

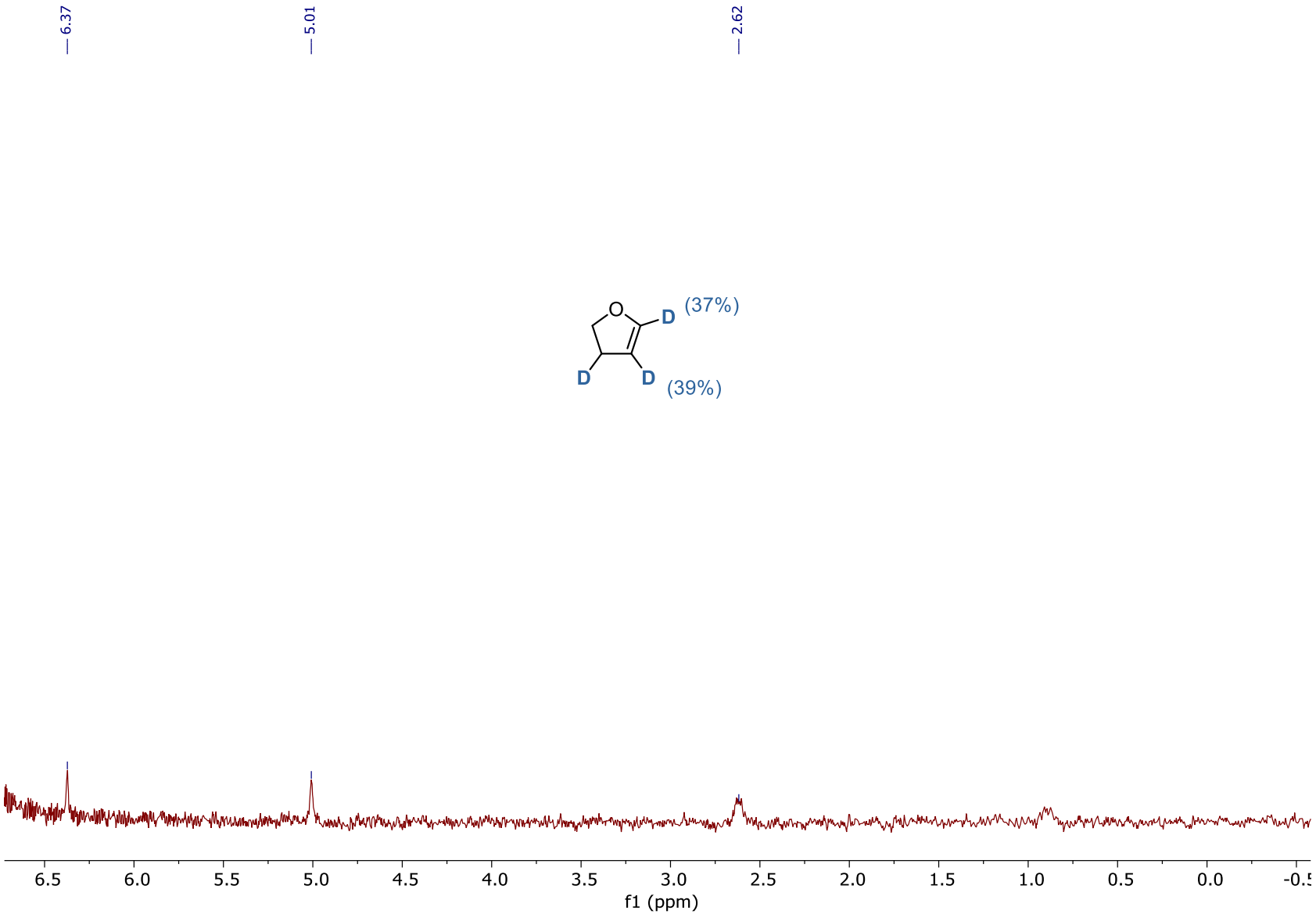


^{1}H NMR (500 MHz, d_8-THF) for the reaction of [dmpe$_2$Fe(H)(2,3-dihydrolfuryl)] *trans*-**7** + CD_3OD in d_8-THF (1) Before addition of CD_3OD. (2) After 18 h at rt.

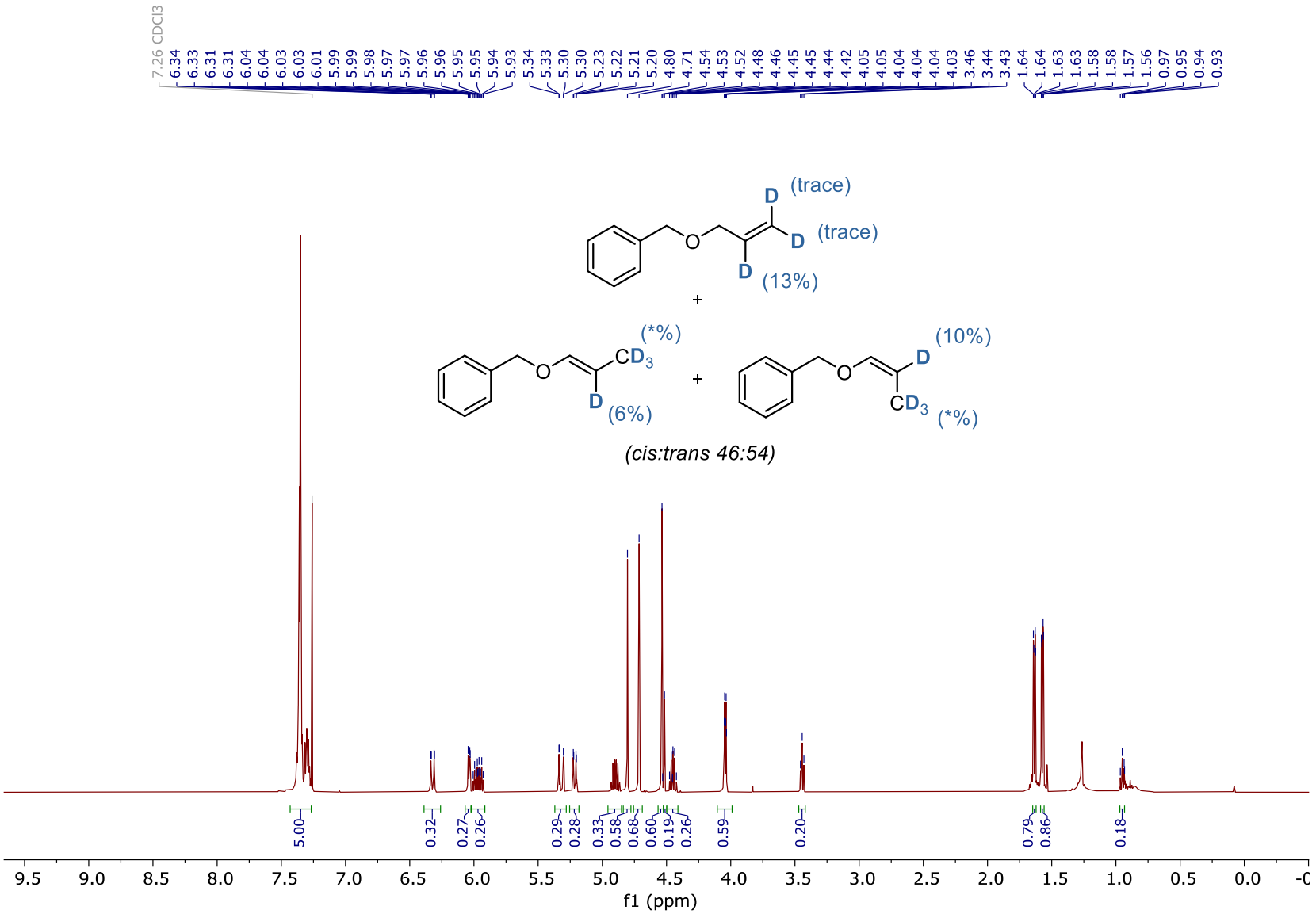
NMR spectra – Fe-catalysed alkene isomerisation



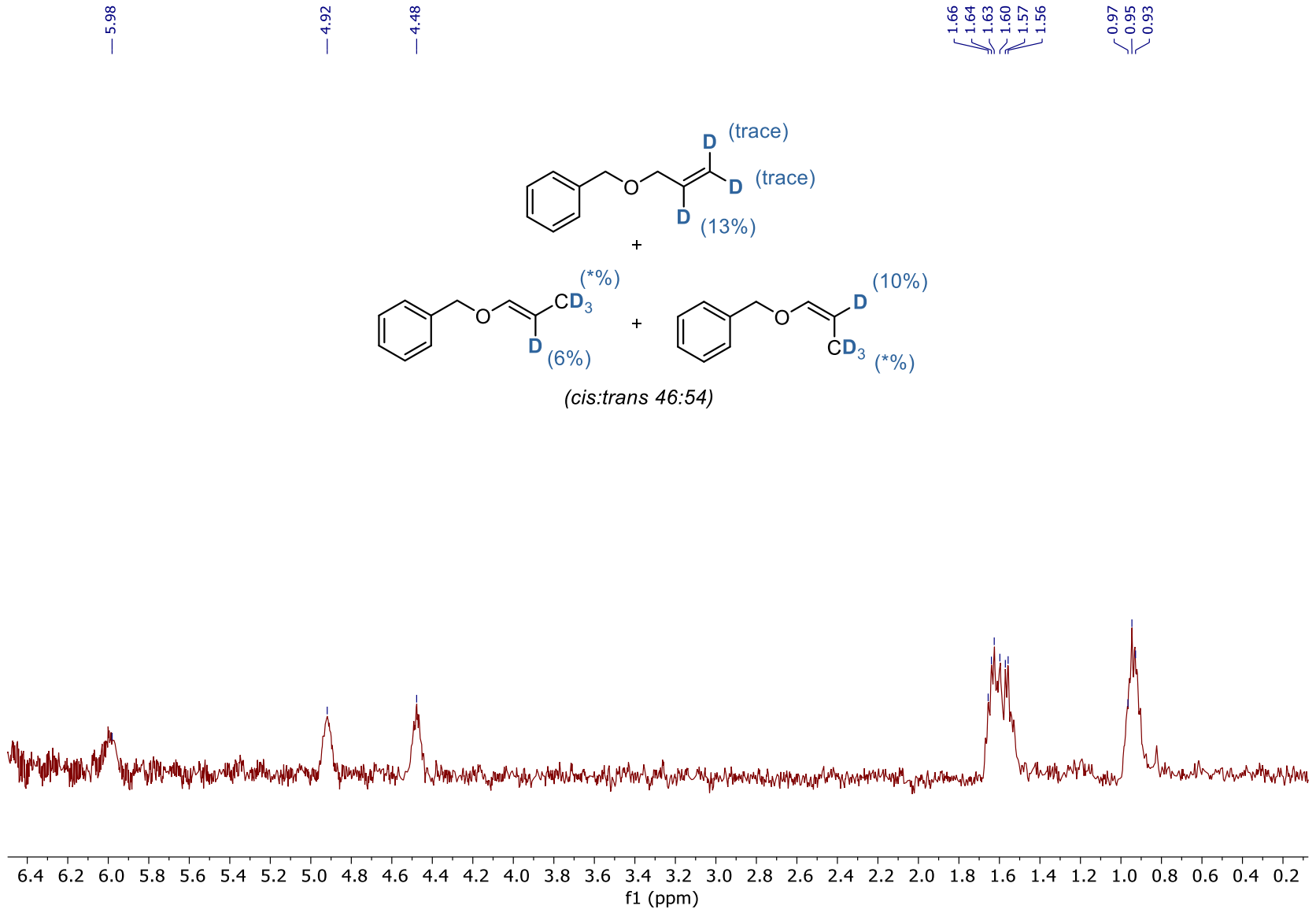
^{1}H NMR (500 MHz, $CDCl_3$) of 2,5-dihydrofuran and 2,3-dihydrofuran-d_3.



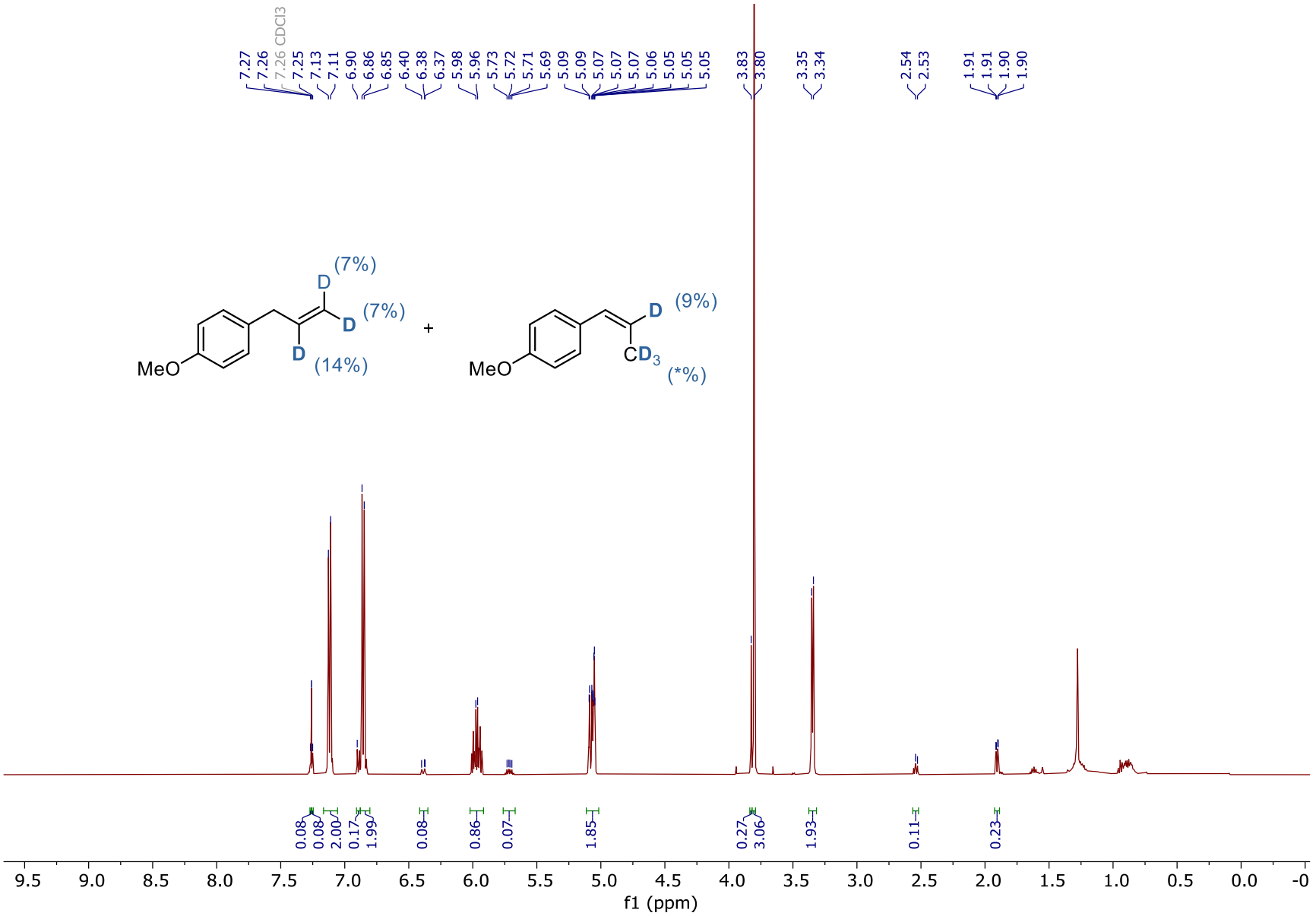
^{2}H NMR (77 MHz, $CDCl_3$) of 2,3-dihydrofuran-d_3.



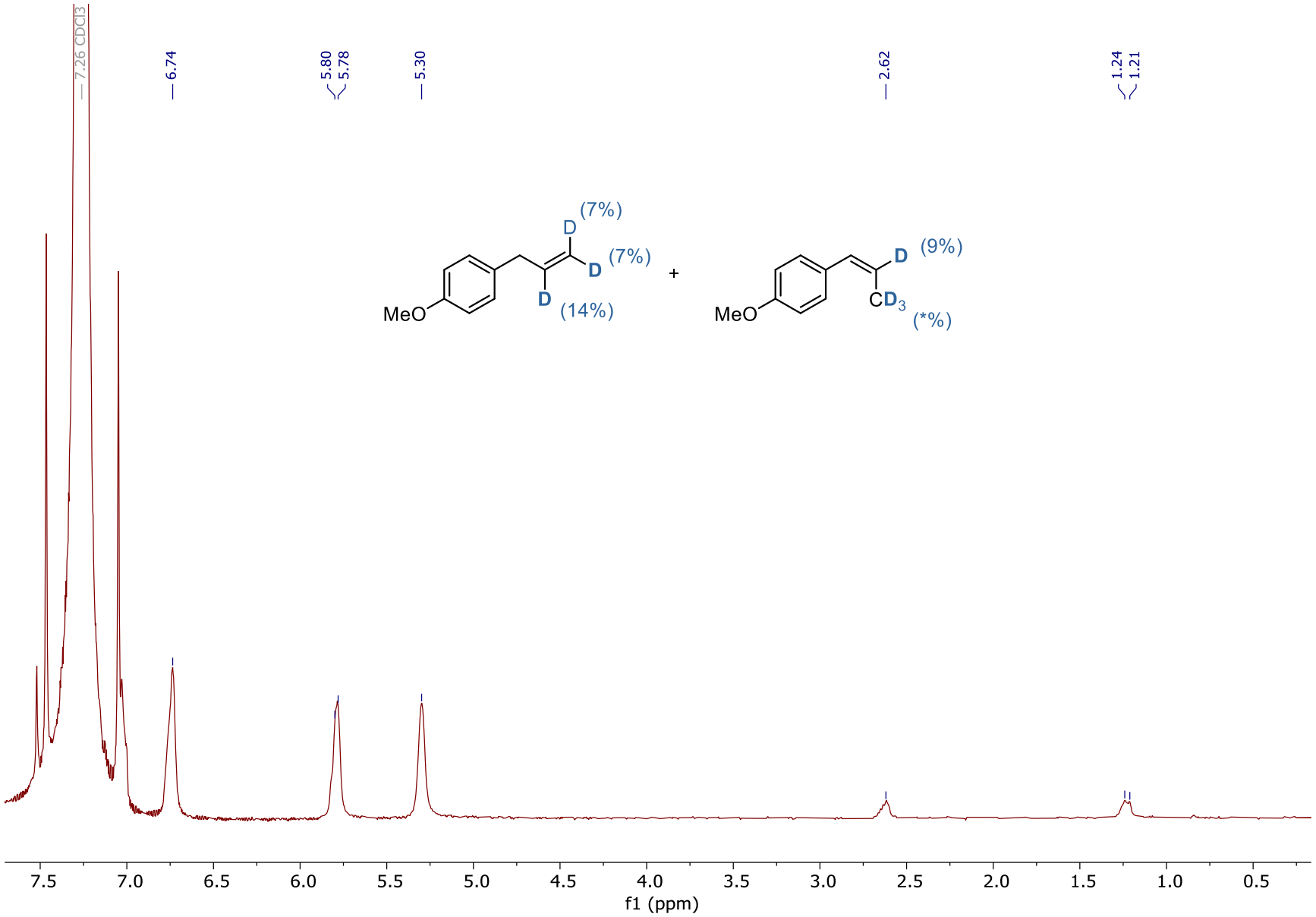
^{1}H NMR (500 MHz, $CDCl_3$) of allyl benzyl ether-*α,β,β-d*$_3$ and (*E*)-((prop-1-en-1-yloxy)methyl)benzene-*d* and (*Z*)-((prop-1-en-1-yloxy)methyl)benzene-*d.*



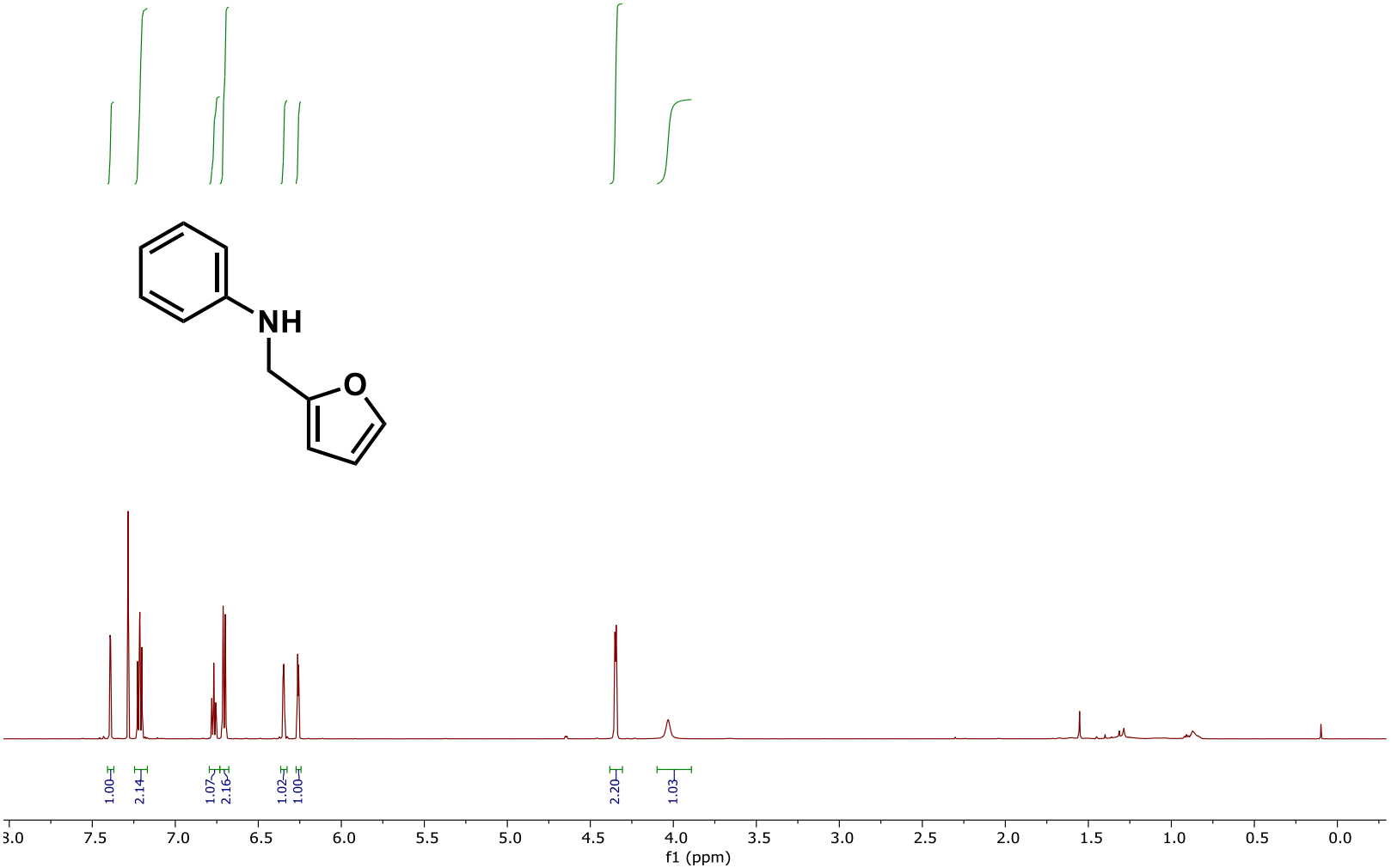
^{2}H NMR (77 MHz, $CDCl_3$) of allyl benzyl ether-*α,β,β-d*$_3$ and (*E*)-((prop-1-en-1-yloxy)methyl)benzene-*d* and (*Z*)-((prop-1-en-1-yloxy)methyl)benzene-*d.*



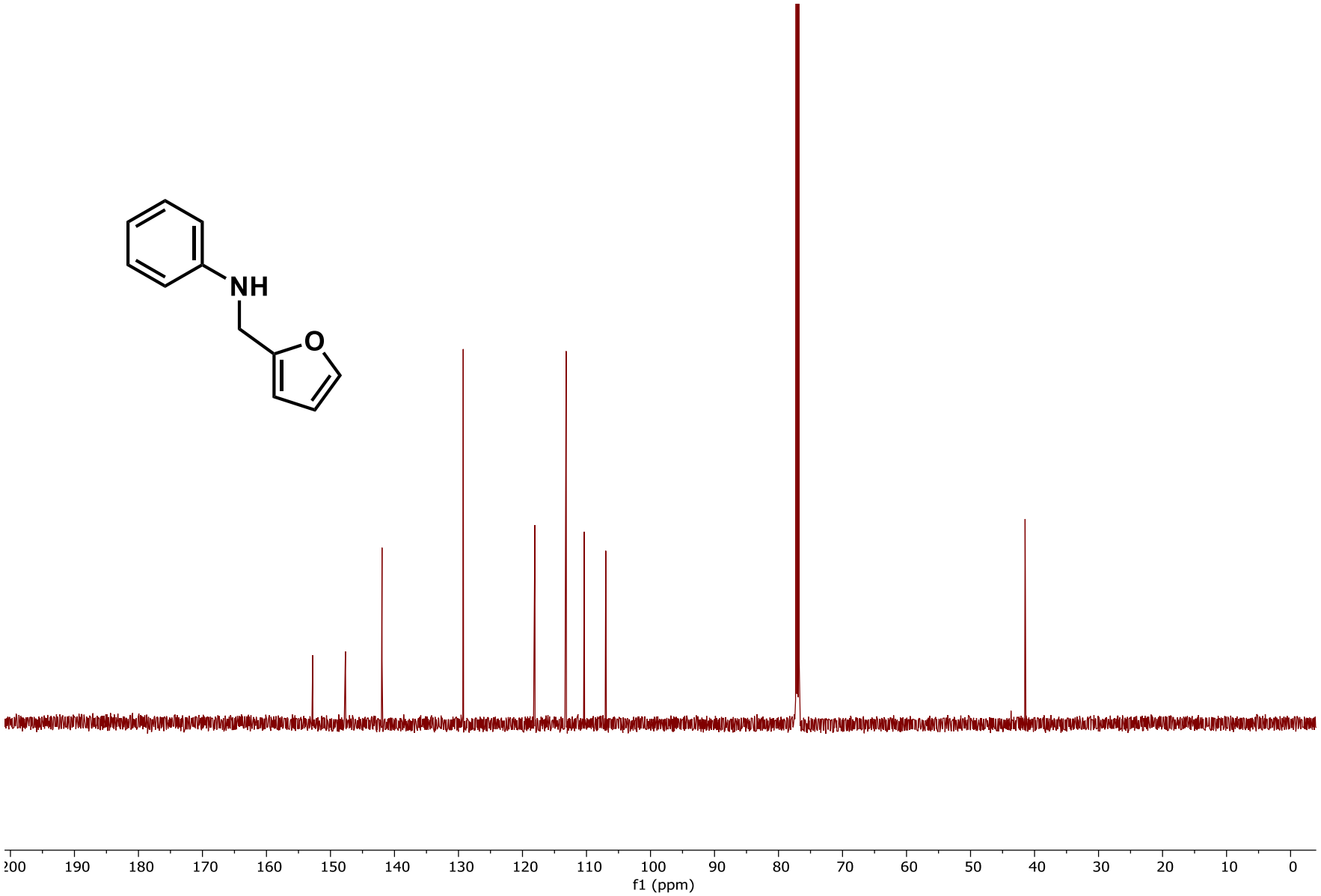
^{1}H NMR (500 MHz, $CDCl_3$) of allylanisole-d_3 and (*Z*)-anethole-*d.*



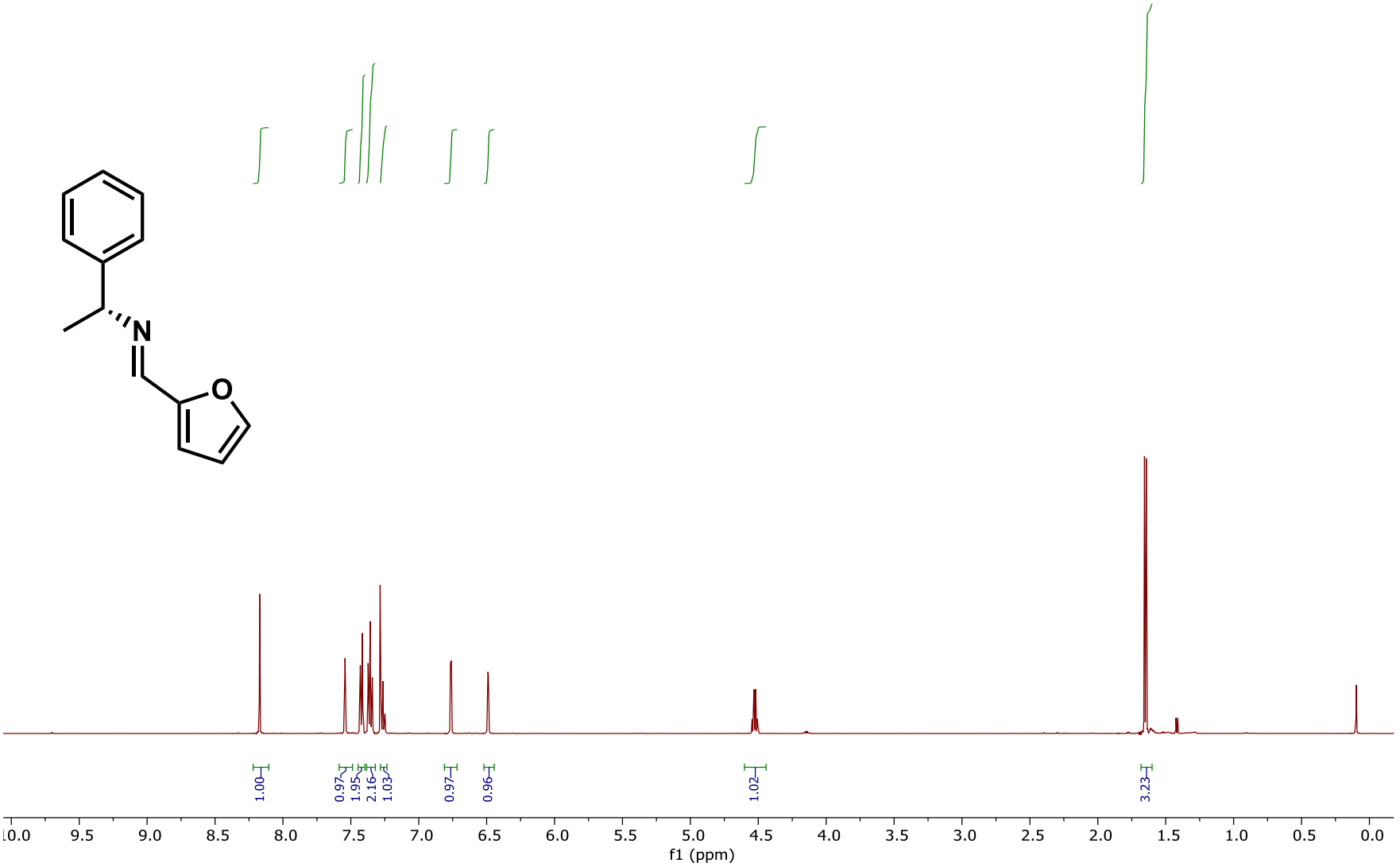
^{2}H NMR (77 MHz, $CDCl_3$) of allylanisole-d_3 and (*Z*)-anethole-*d.*



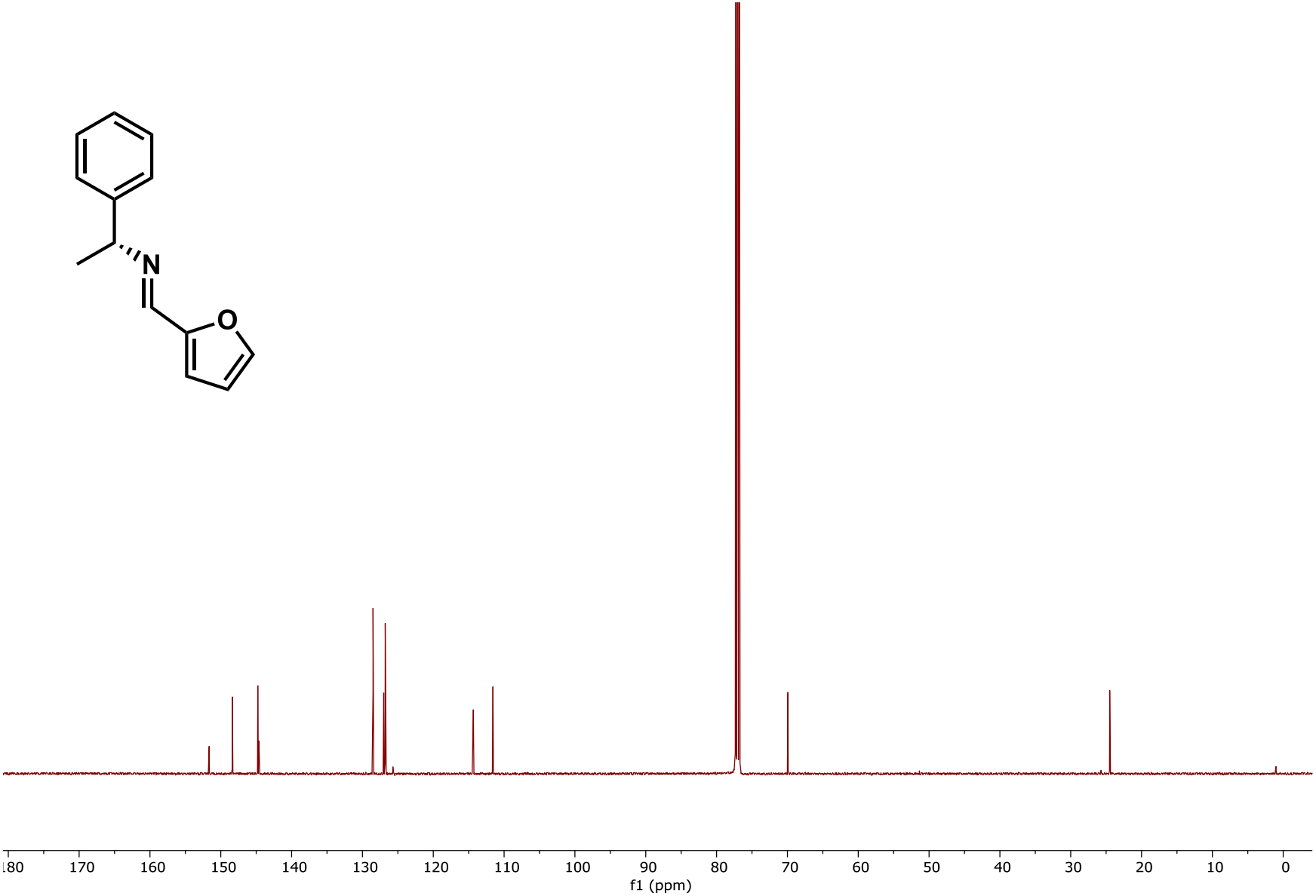
^{1}H NMR (600 MHz, $CDCl_3$) of *N*-(furan-2-ylmethyl)aniline **3c**.



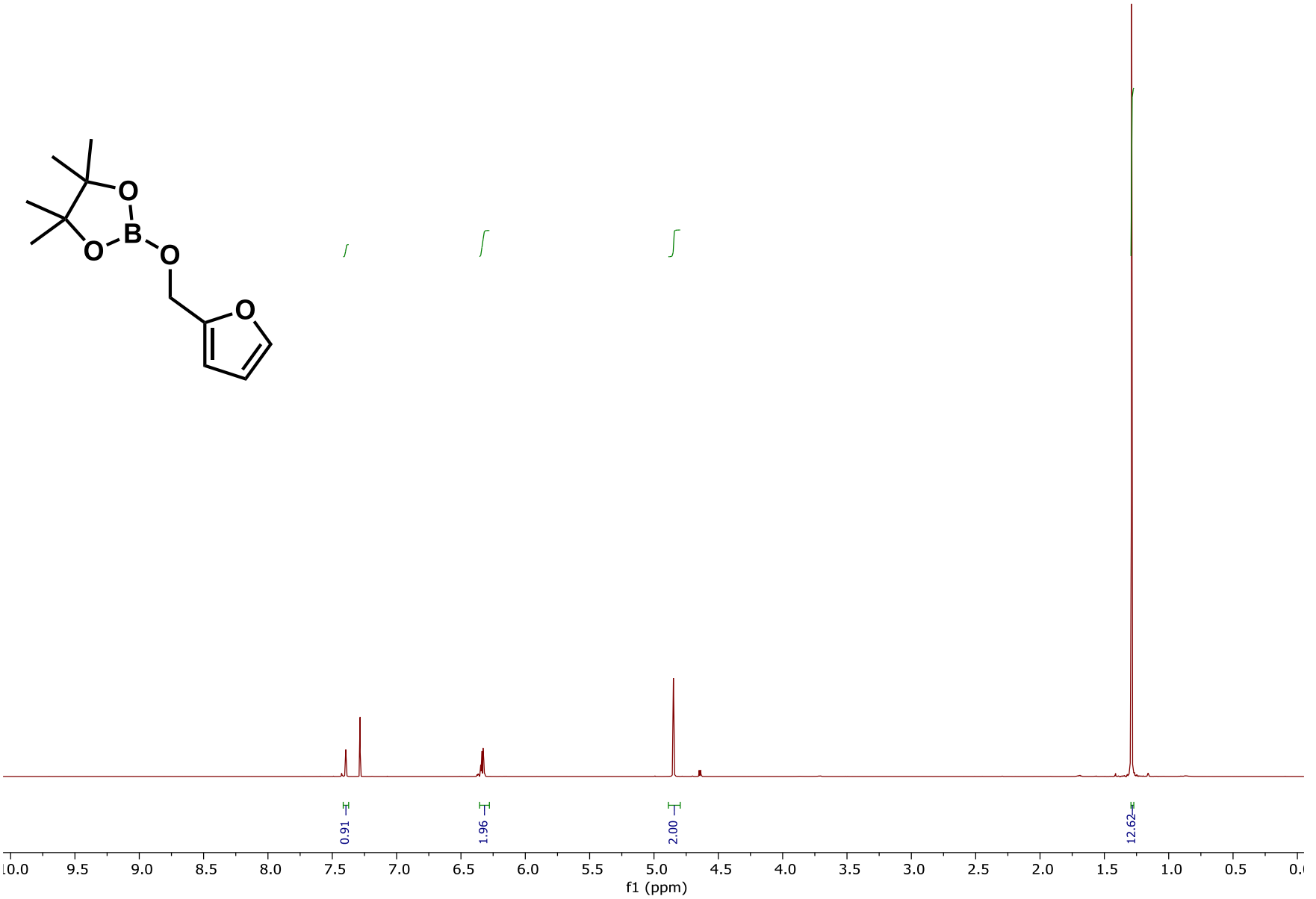
^{1}H NMR (150 MHz, $CDCl_3$) of *N*-(furan-2-ylmethyl)aniline **3c**.



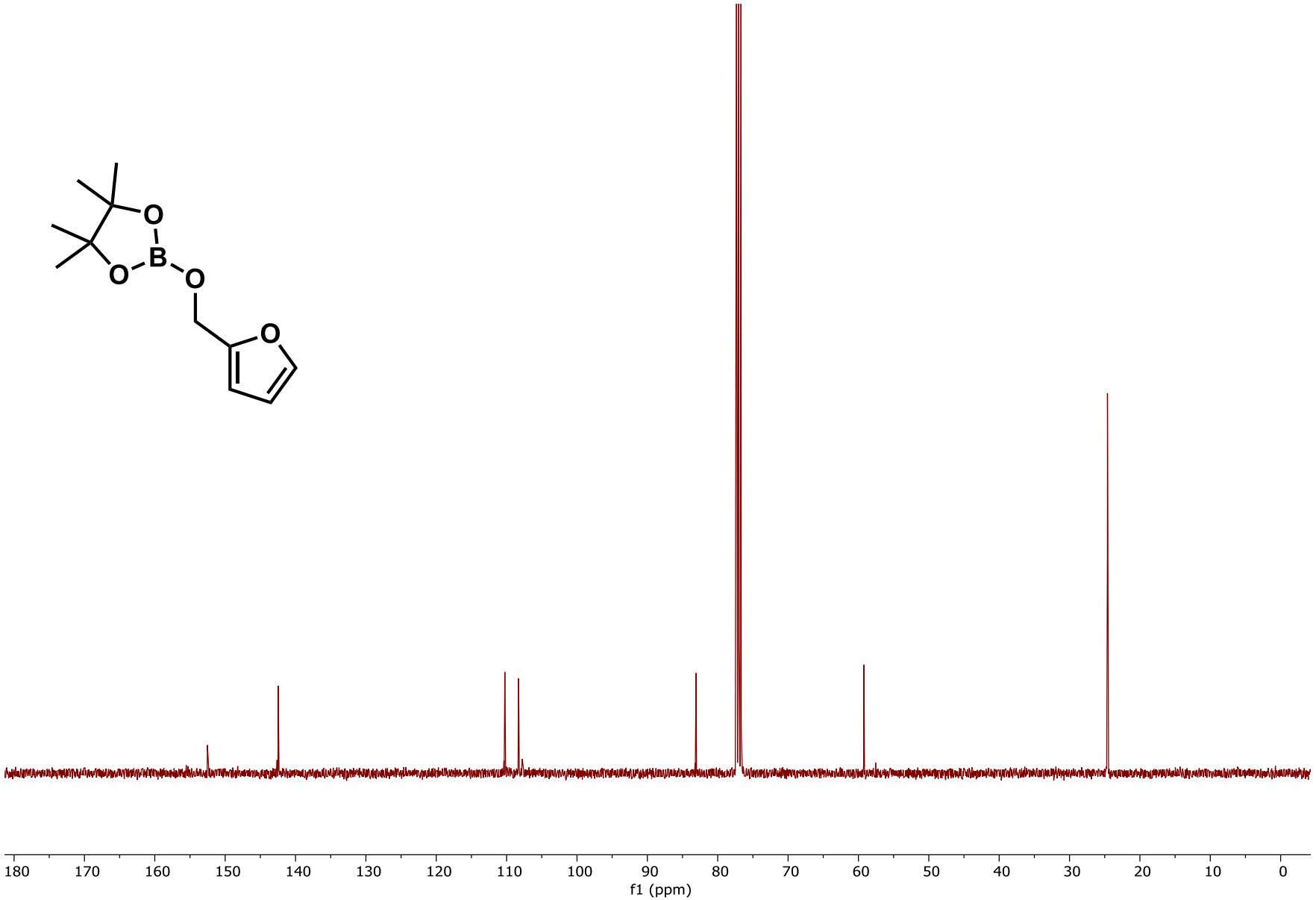
^{1}H NMR (500 MHz, $CDCl_3$) of (1*R*)-*N*-(furan-2ylmethylidene)-1-phenylethanamine **3d**.



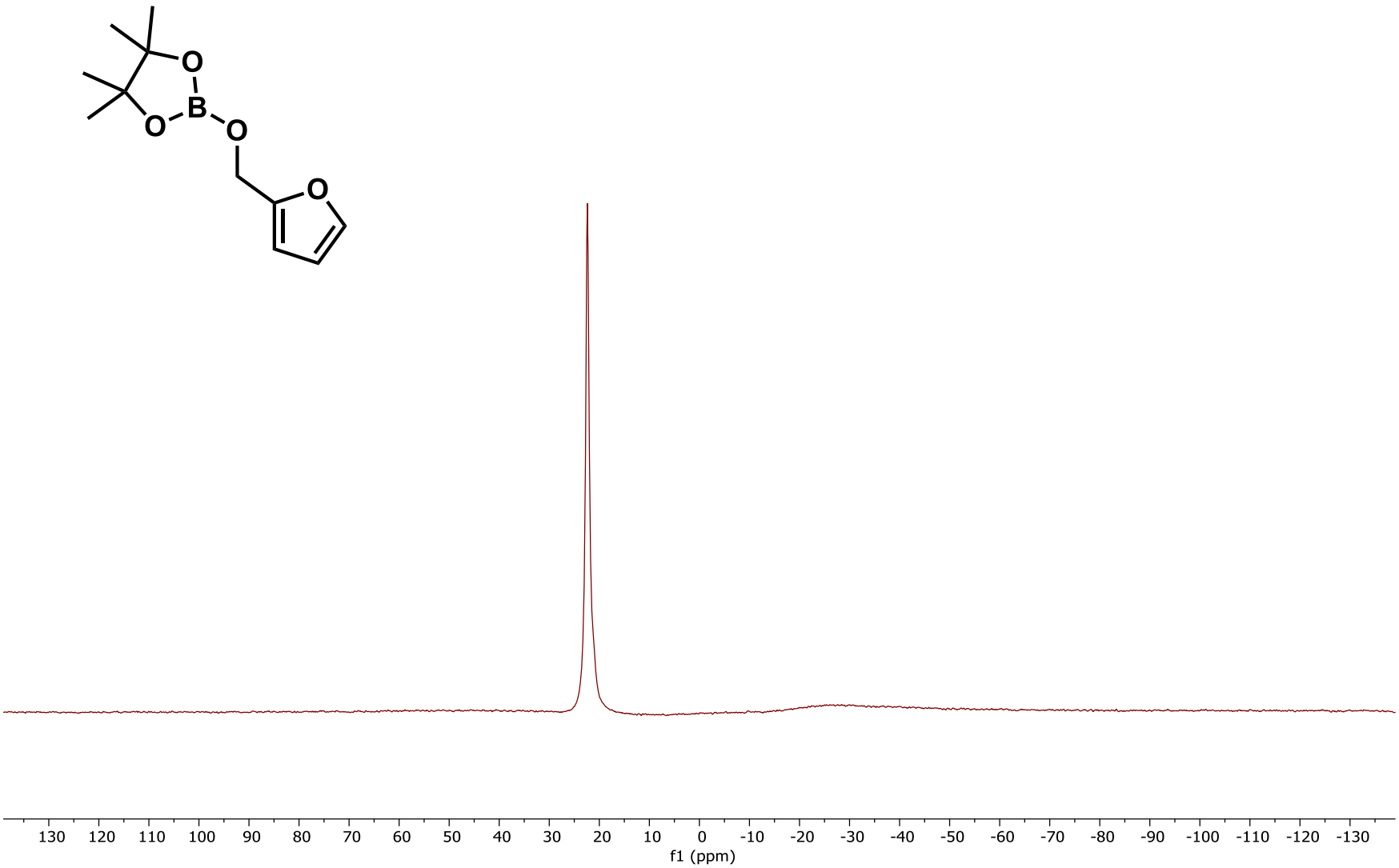
^{13}C NMR (125 MHz, $CDCl_3$) of (1*R*)-*N*-(furan-2ylmethylidene)-1-phenylethanamine **3d**.



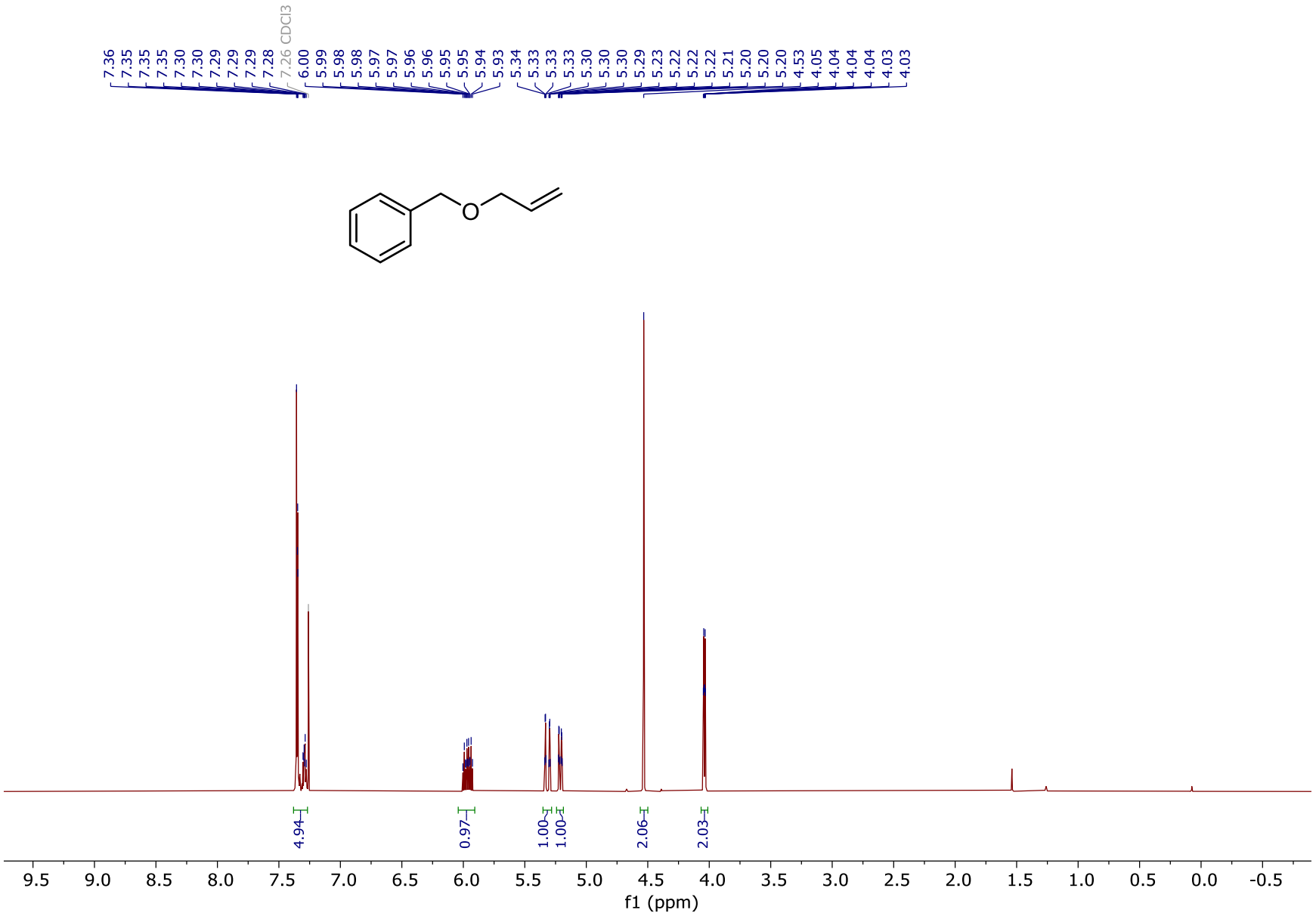
^{1}H NMR (500 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane **3e**.



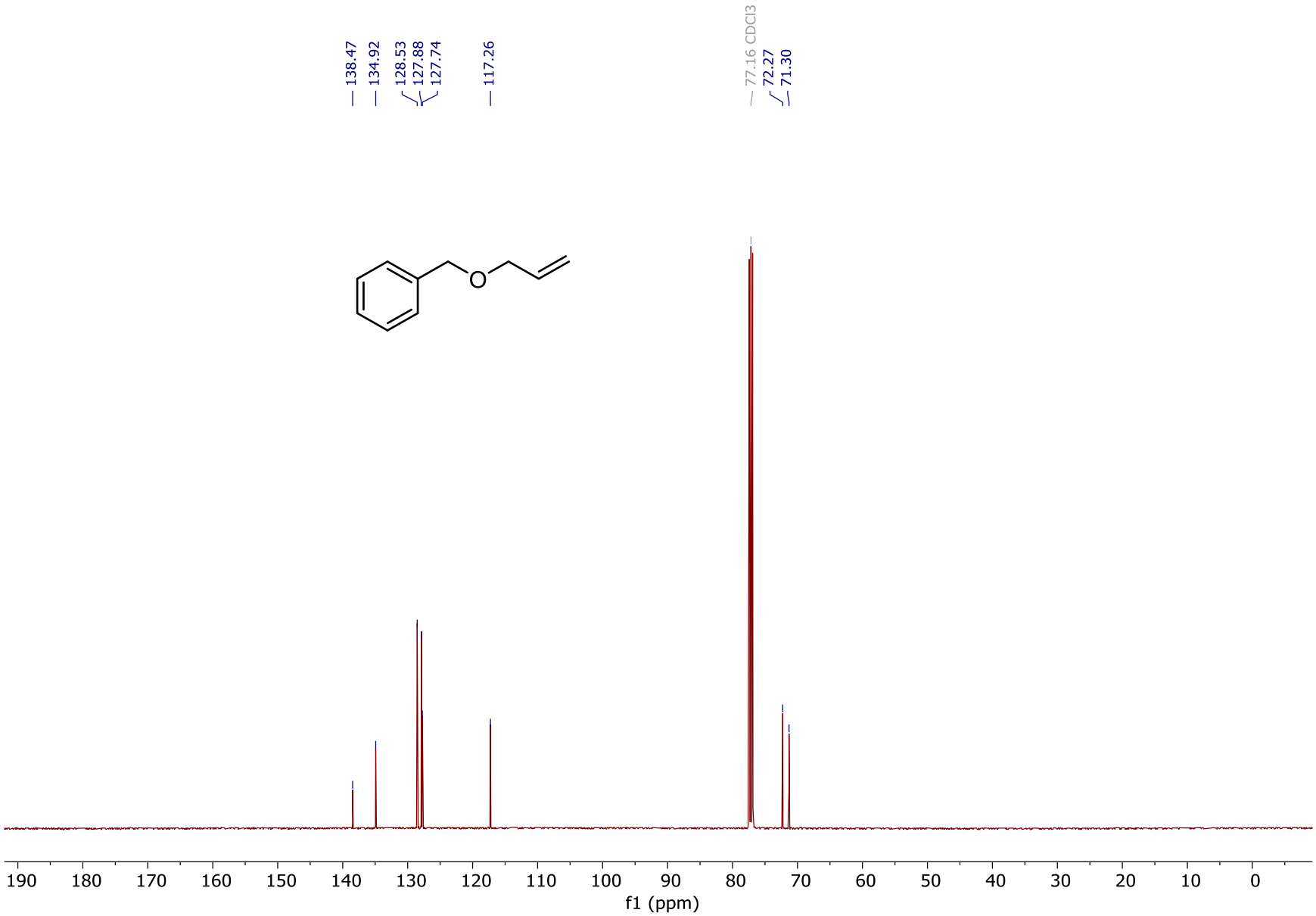
^{13}C NMR (101 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane **3e**.



^{11}B NMR (128 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane **3e**.

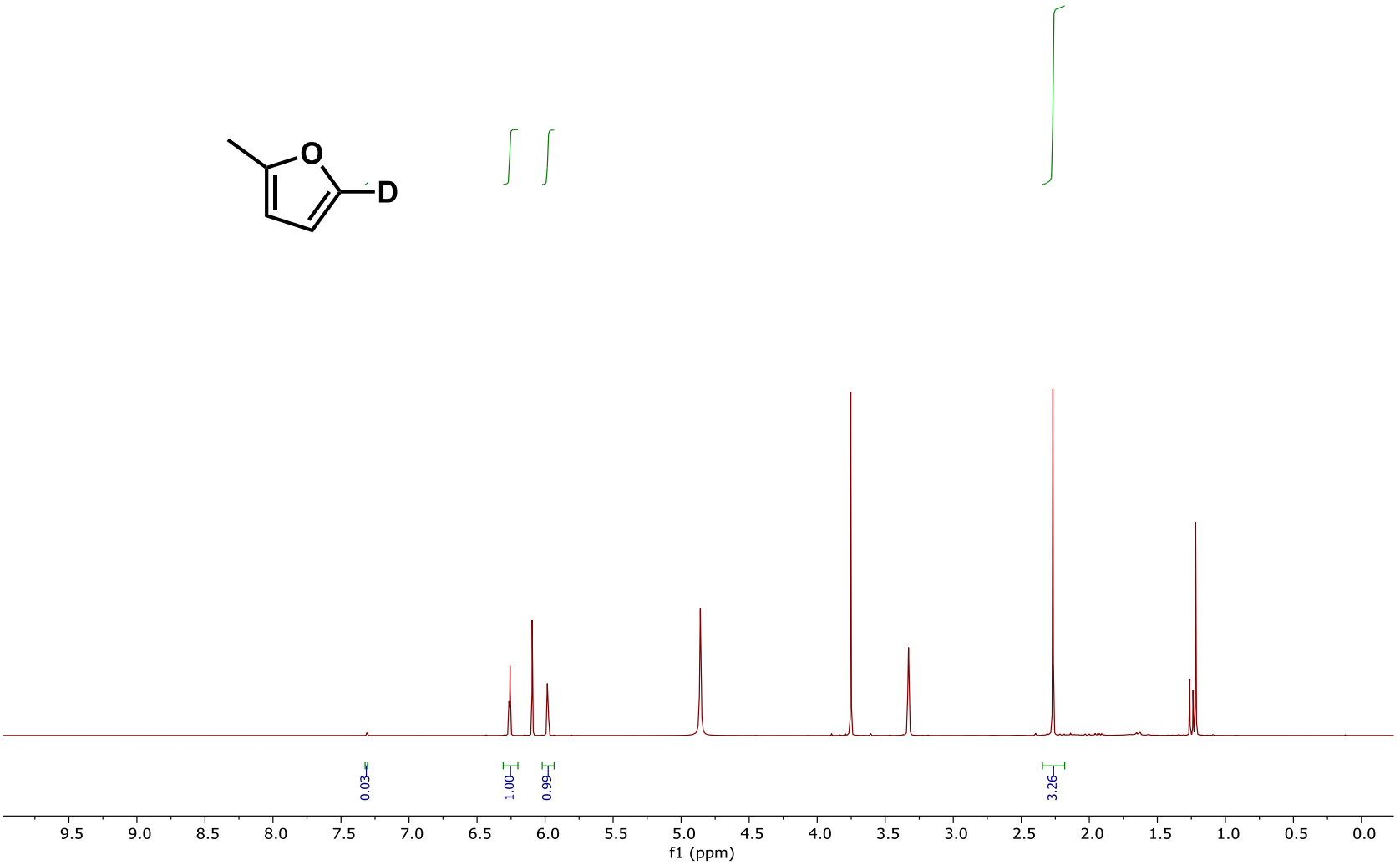


^{1}H NMR (500 MHz, $CDCl_3$) of allybenzyl ether.

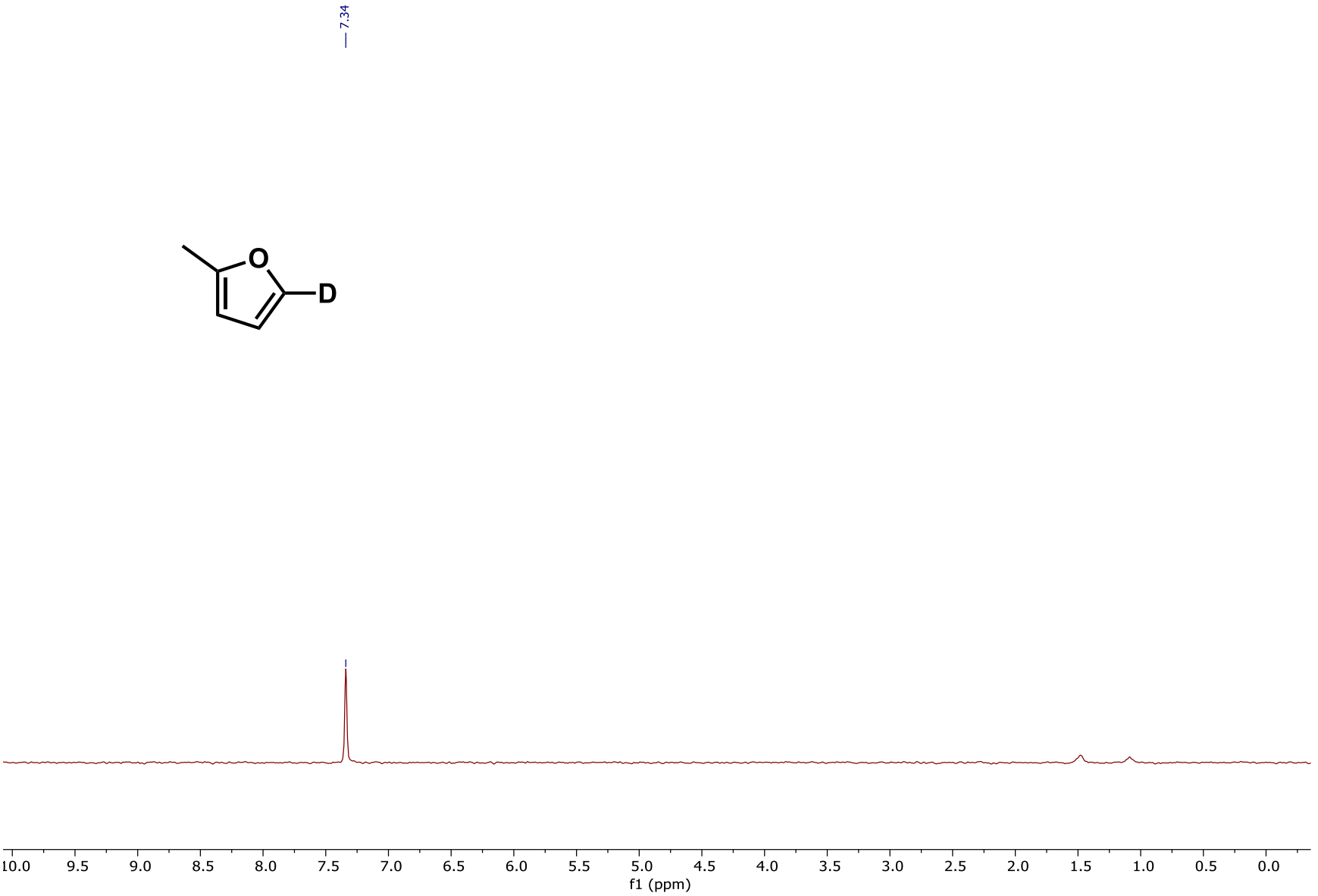


^{13}C NMR (126 MHz, $CDCl_3$) of allybenzyl ether.

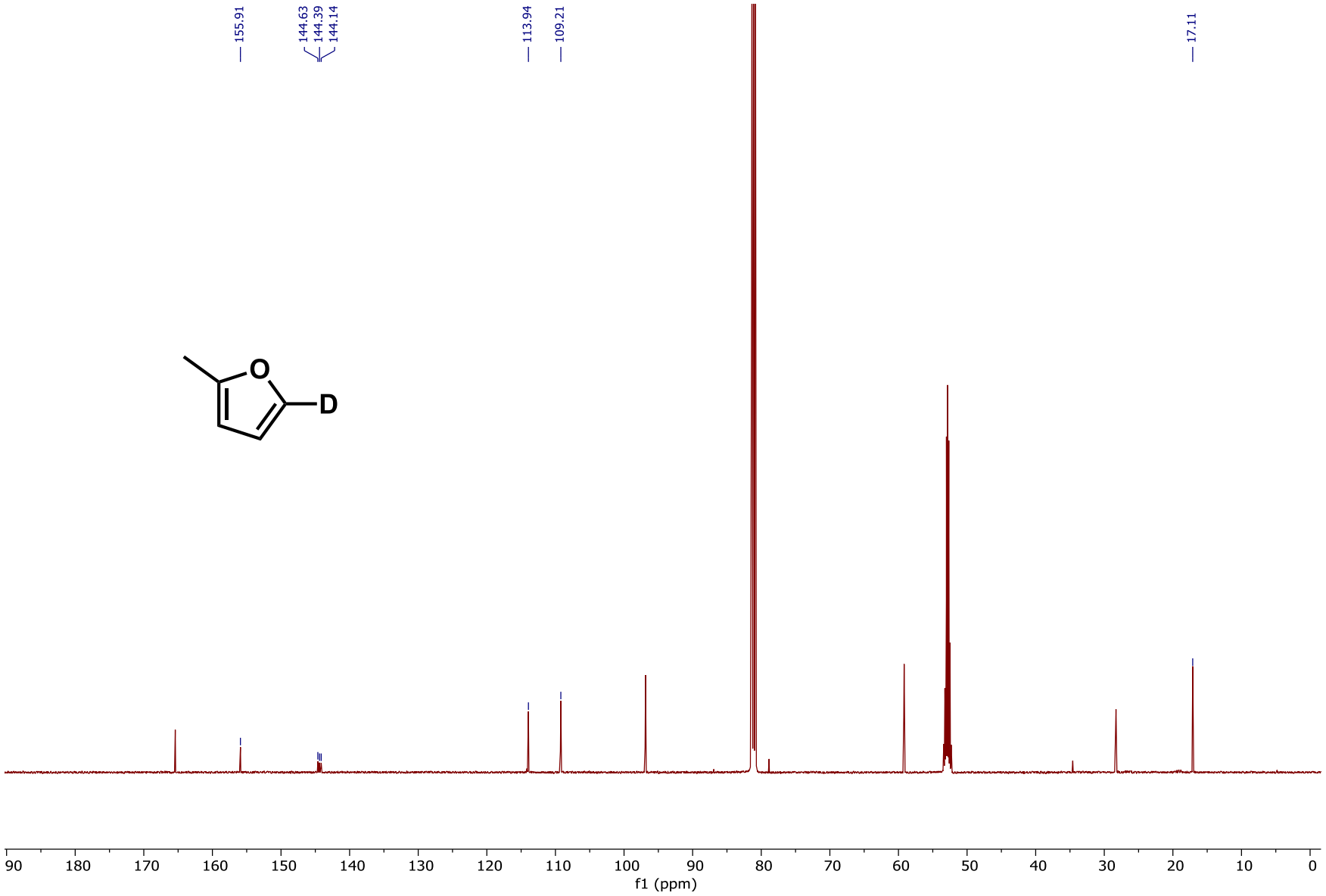
NMR spectra – product characterisation



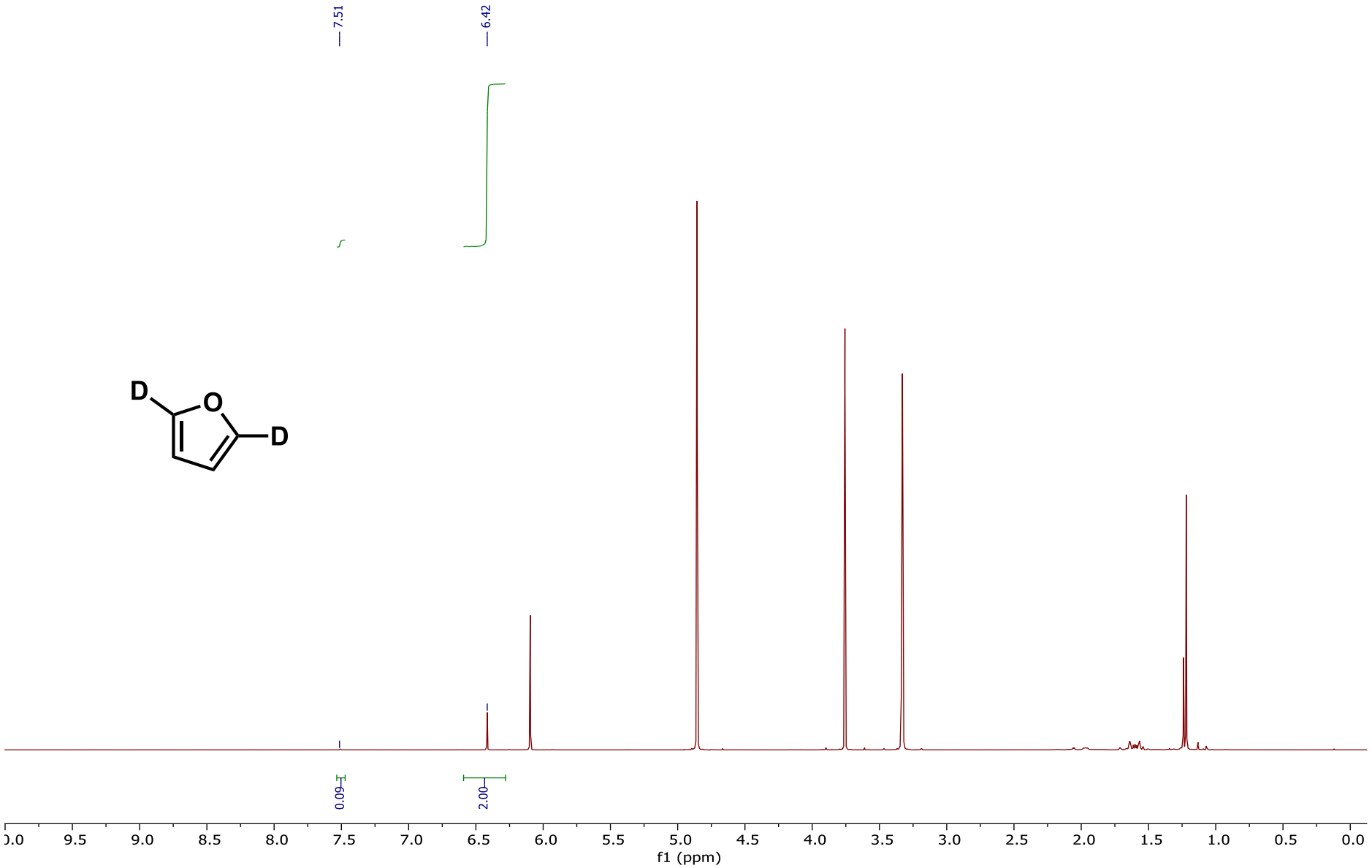
^{1}H NMR (500 MHz, CD_3OD) of 2-methyl-5D-furan **[D]-3a**.



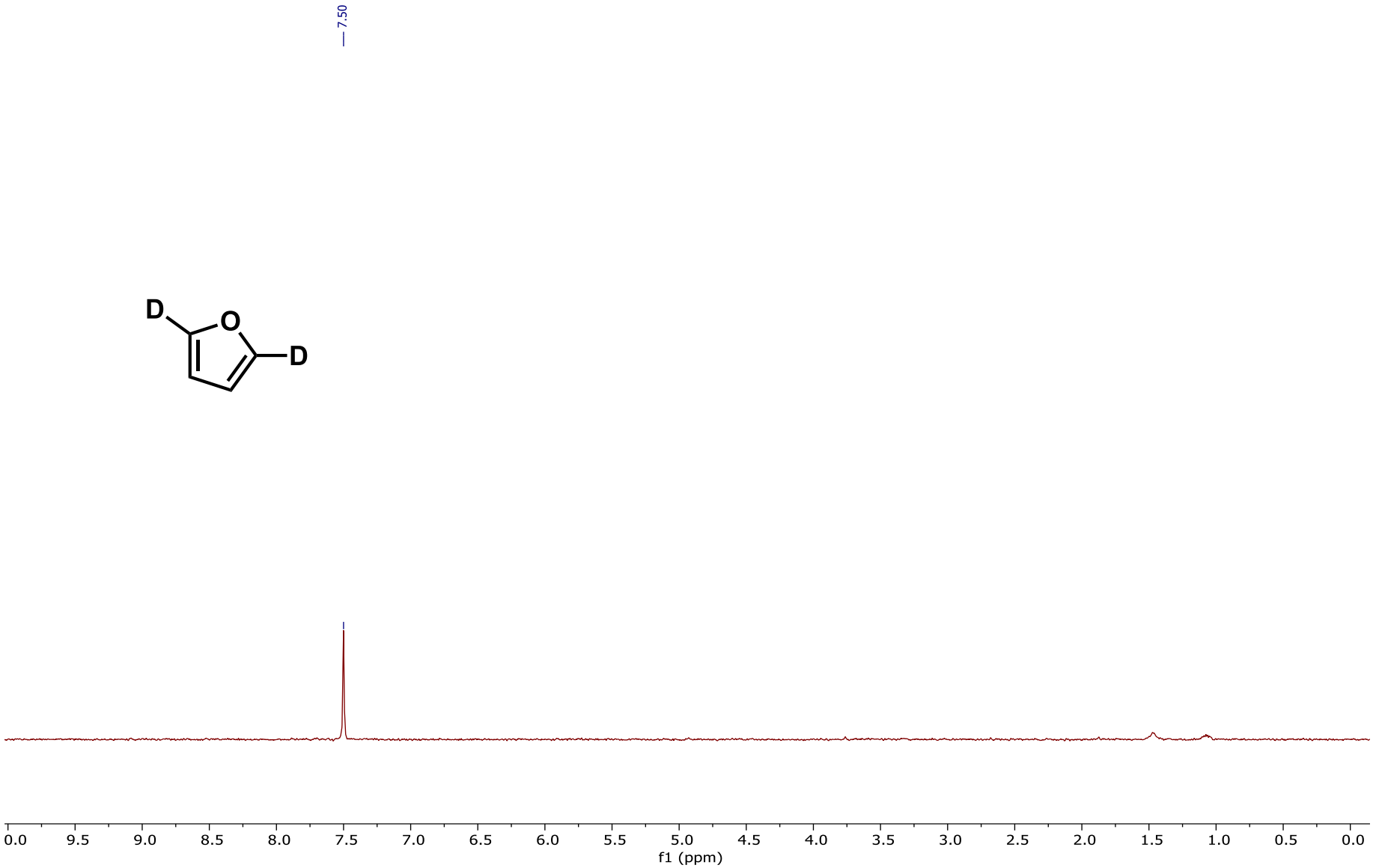
^{2}H NMR (77 MHz, CH_3OH) of 2-methyl-5D-furan **[D]-3a**.



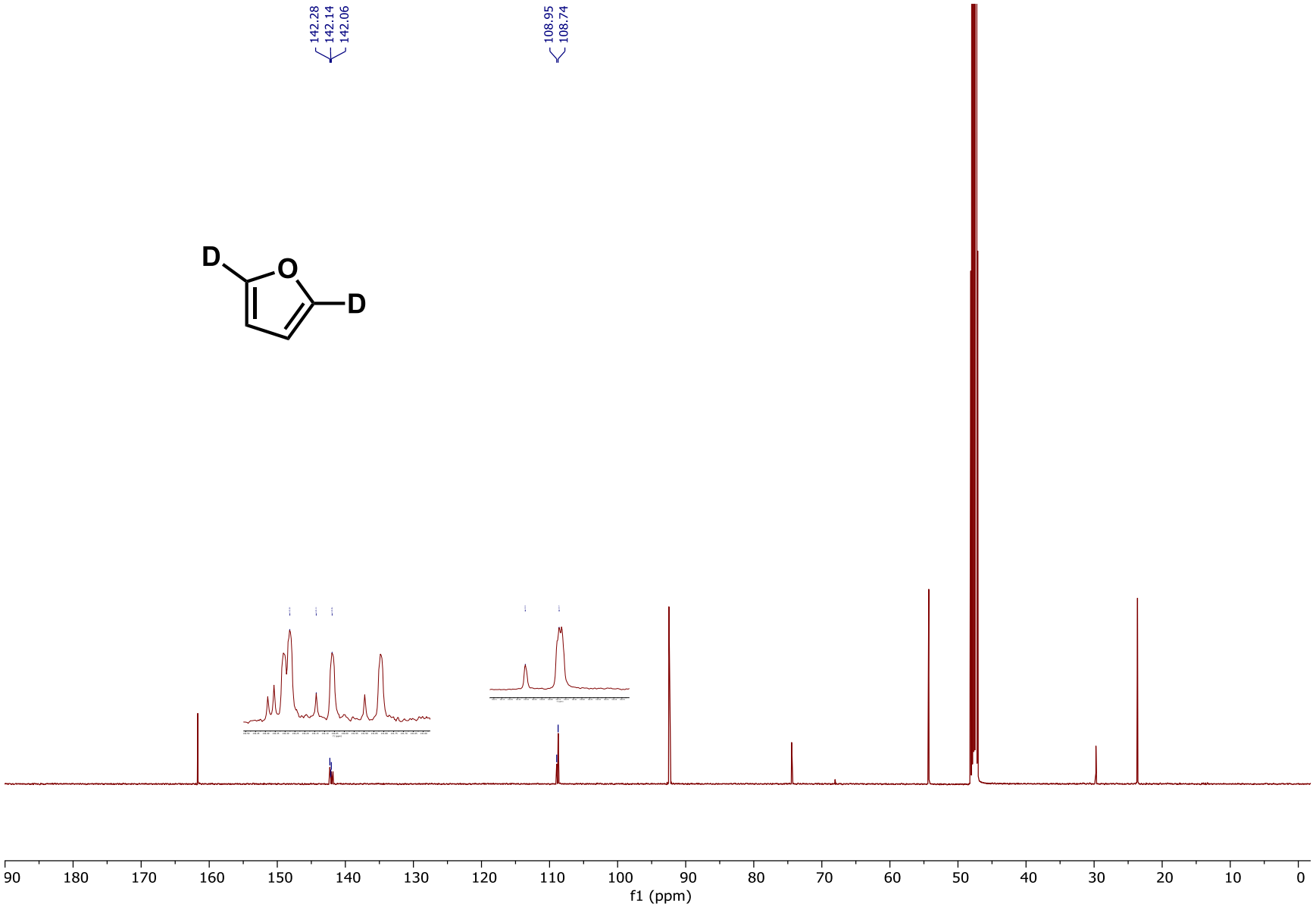
^{13}C NMR (125 MHz, $CD_3OD/CDCl_3$) of 2-methyl-5D-furan **[D]-3a**.



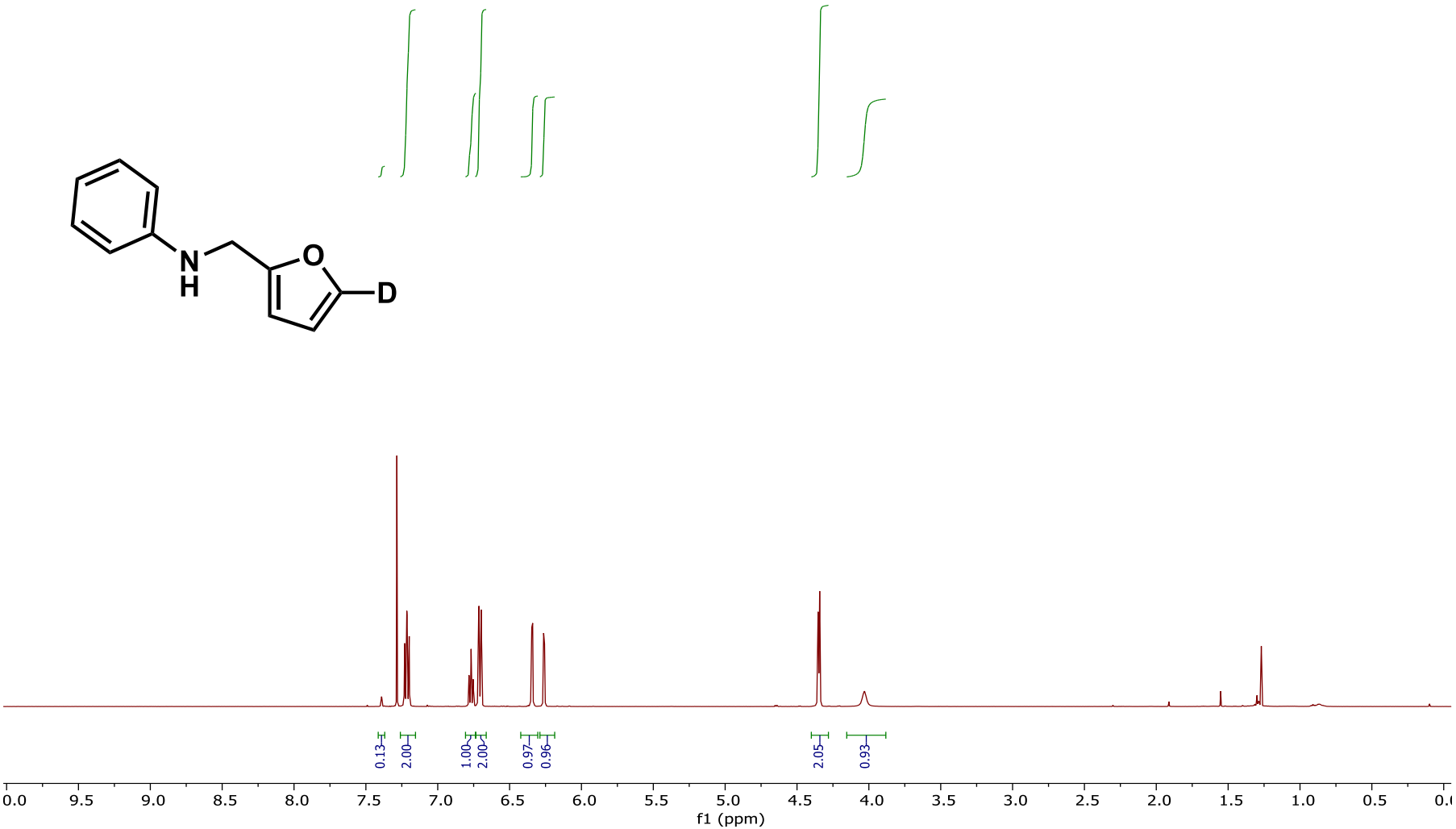
^{1}H NMR (500 MHz, CD_3OD) of 2,5-D-furan **[D]-3b**.



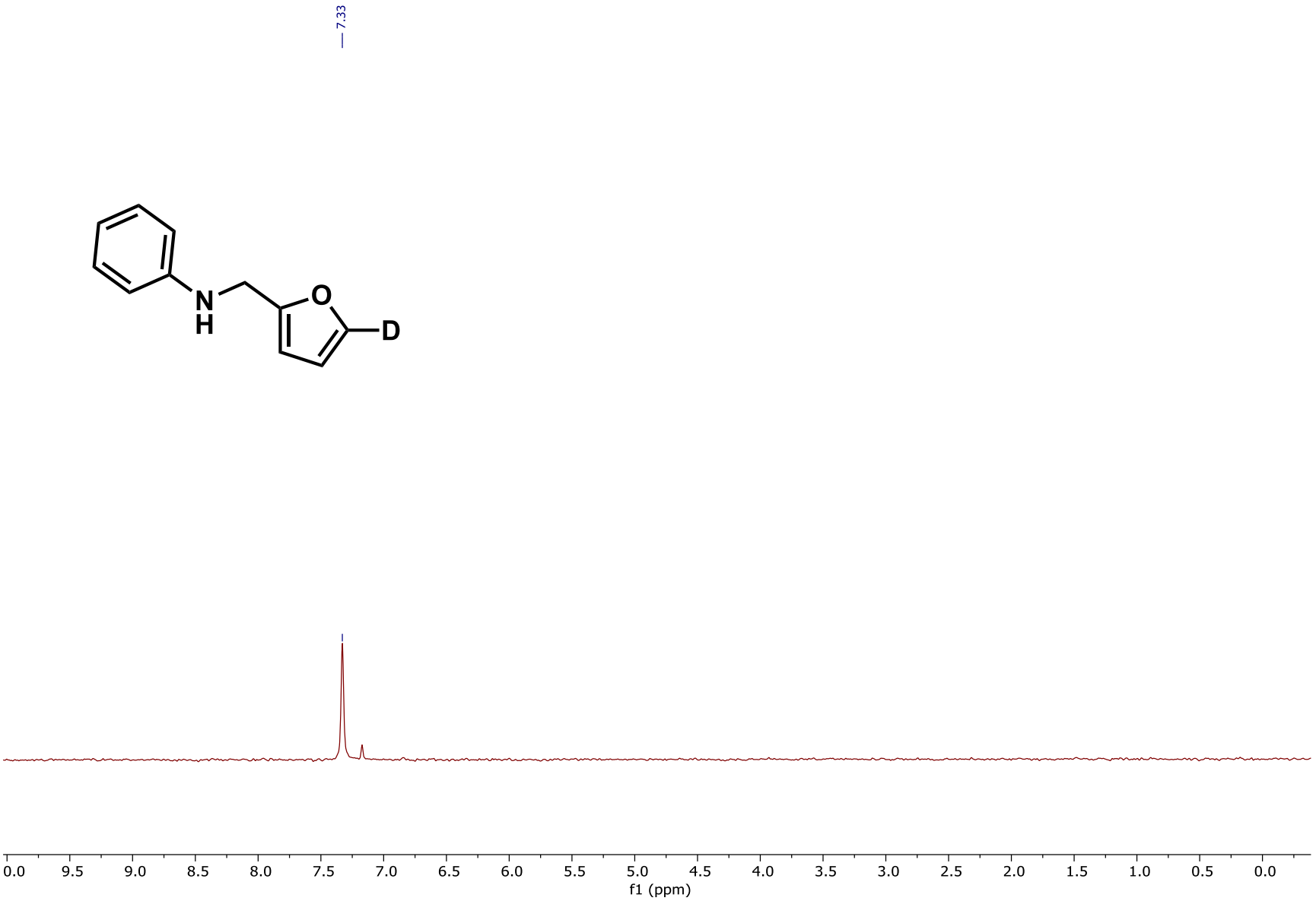
^{2}H NMR (77 MHz, CH_3OH) of 2,5-D-furan **[D]-3b**.



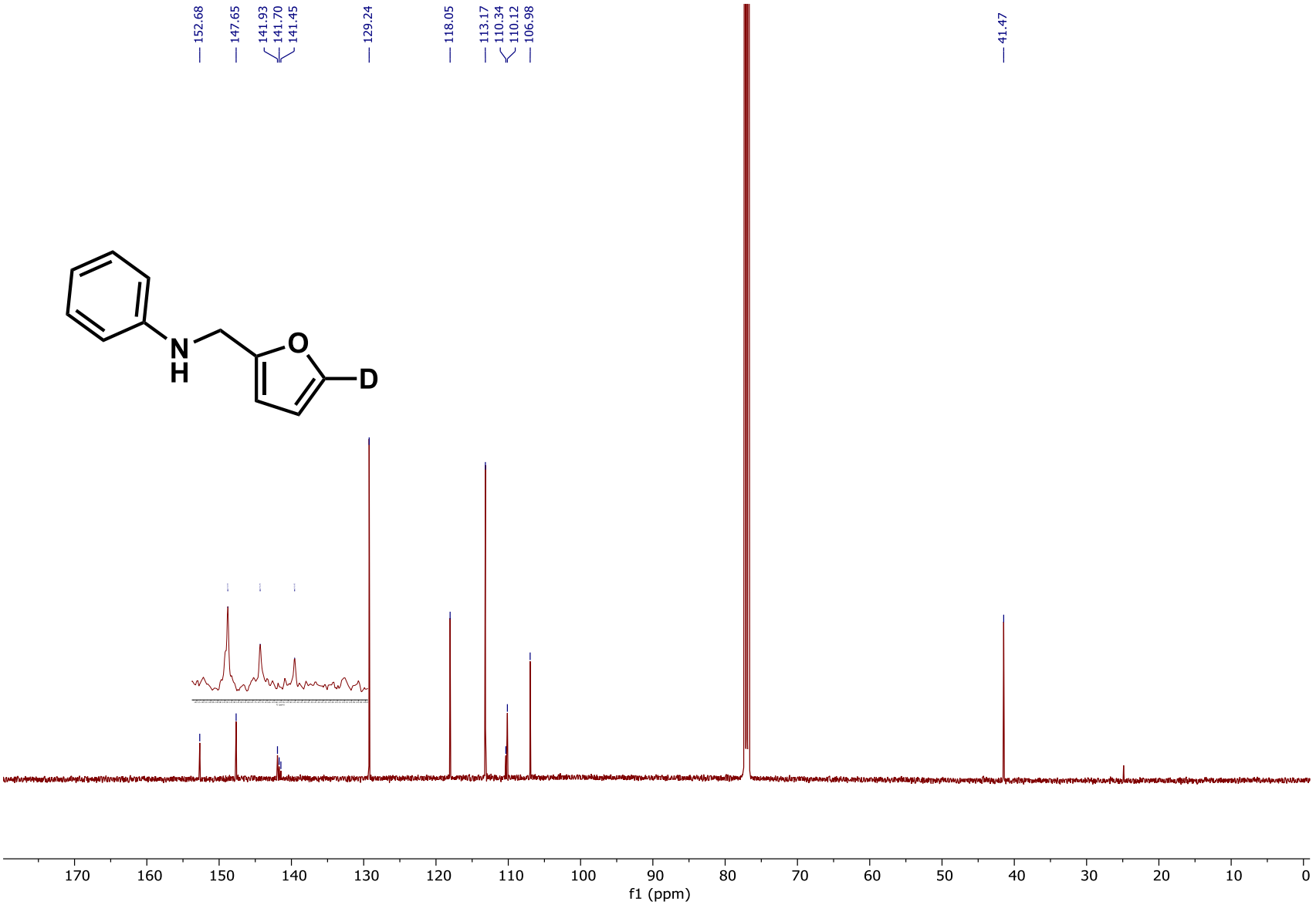
^{13}C NMR (125 MHz, CD_3OD) of 2,5-D-furan **[D]-3b**.



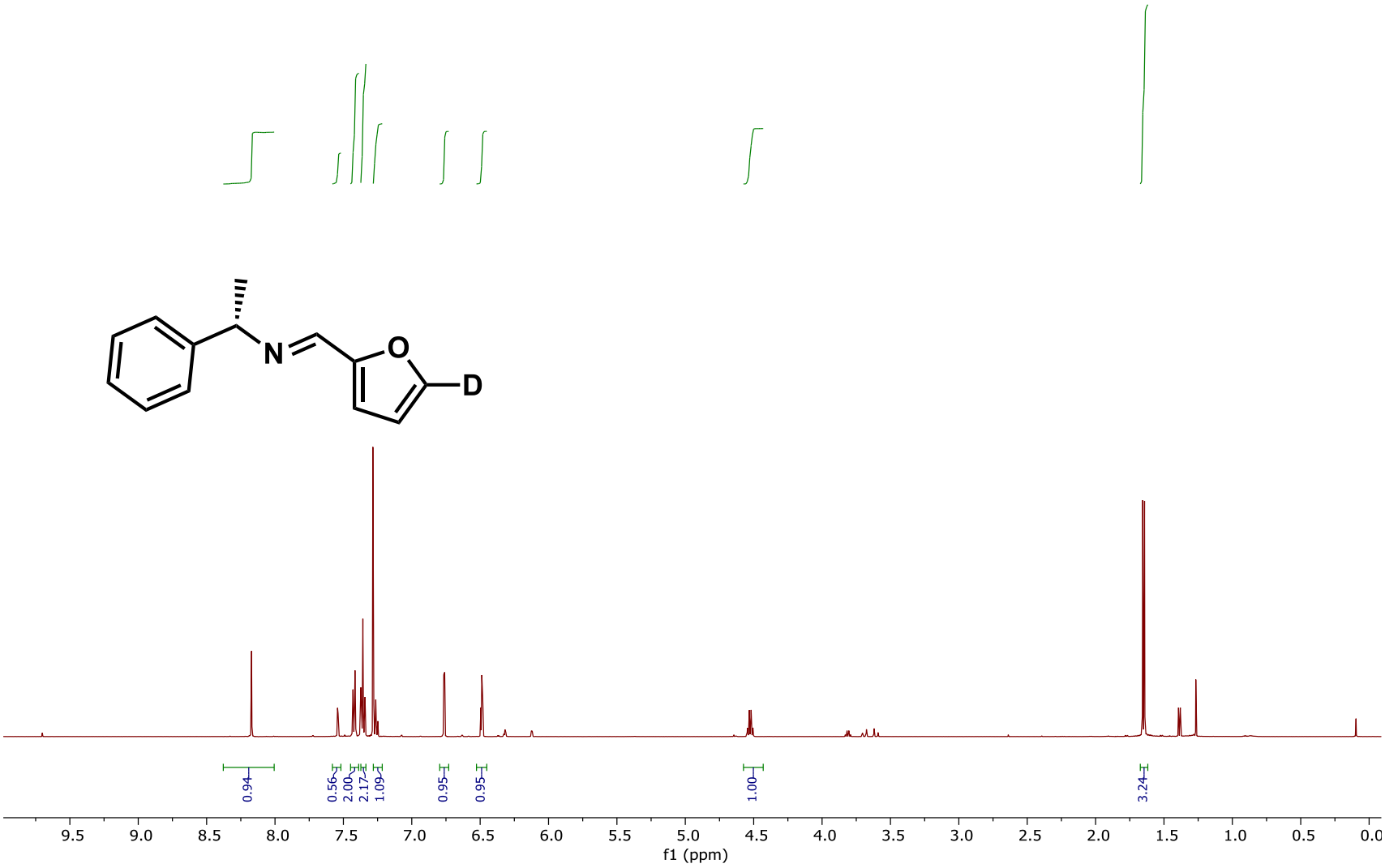
^{1}H NMR (500 MHz, $CDCl_3$) of *N*-(5D-furan-2-ylmethyl)aniline **[D]-3c**.



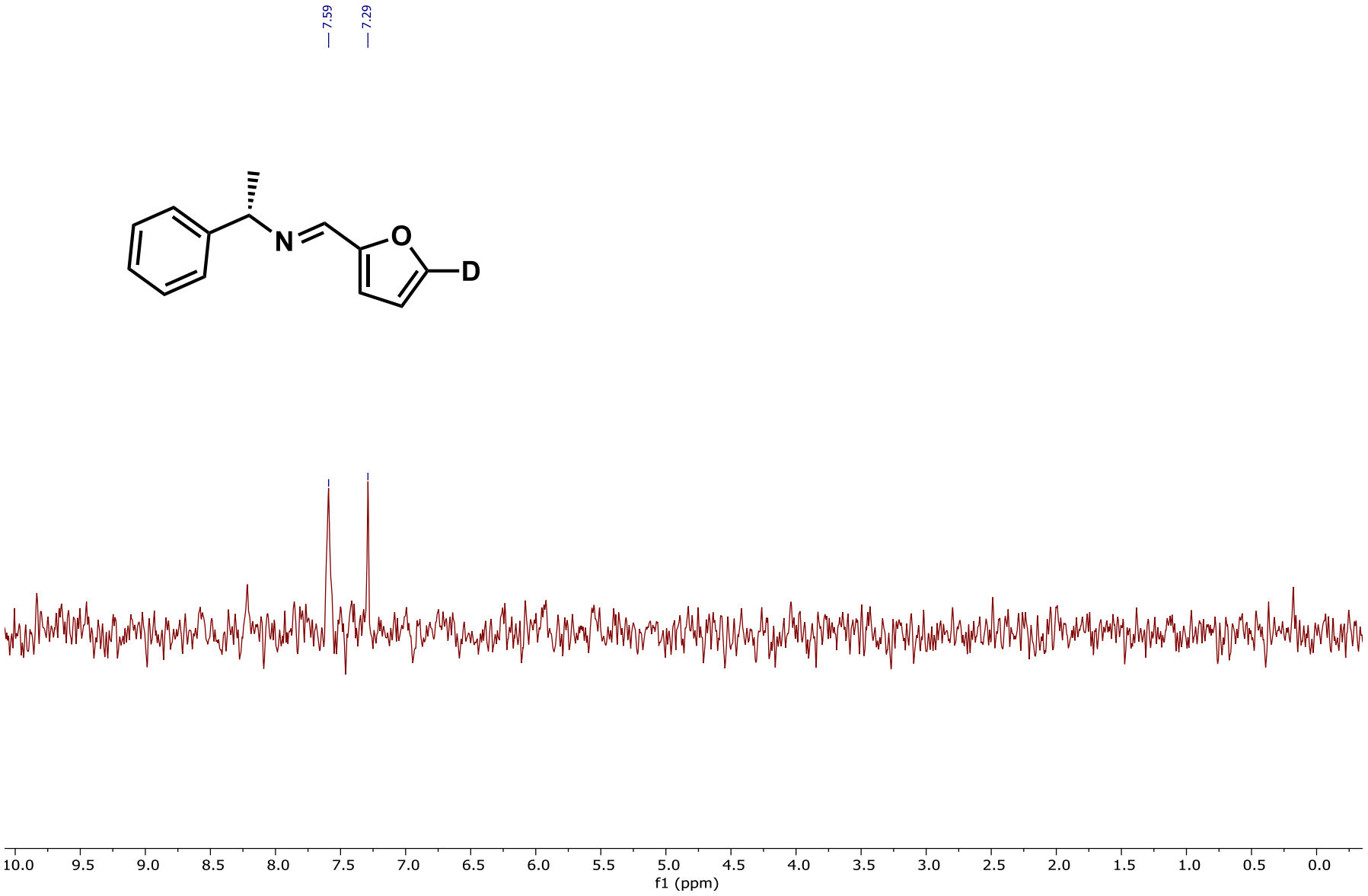
^{2}H NMR (77 MHz, $CHCl_3$) of *N*-(5D-furan-2-ylmethyl)aniline **[D]-3c**.



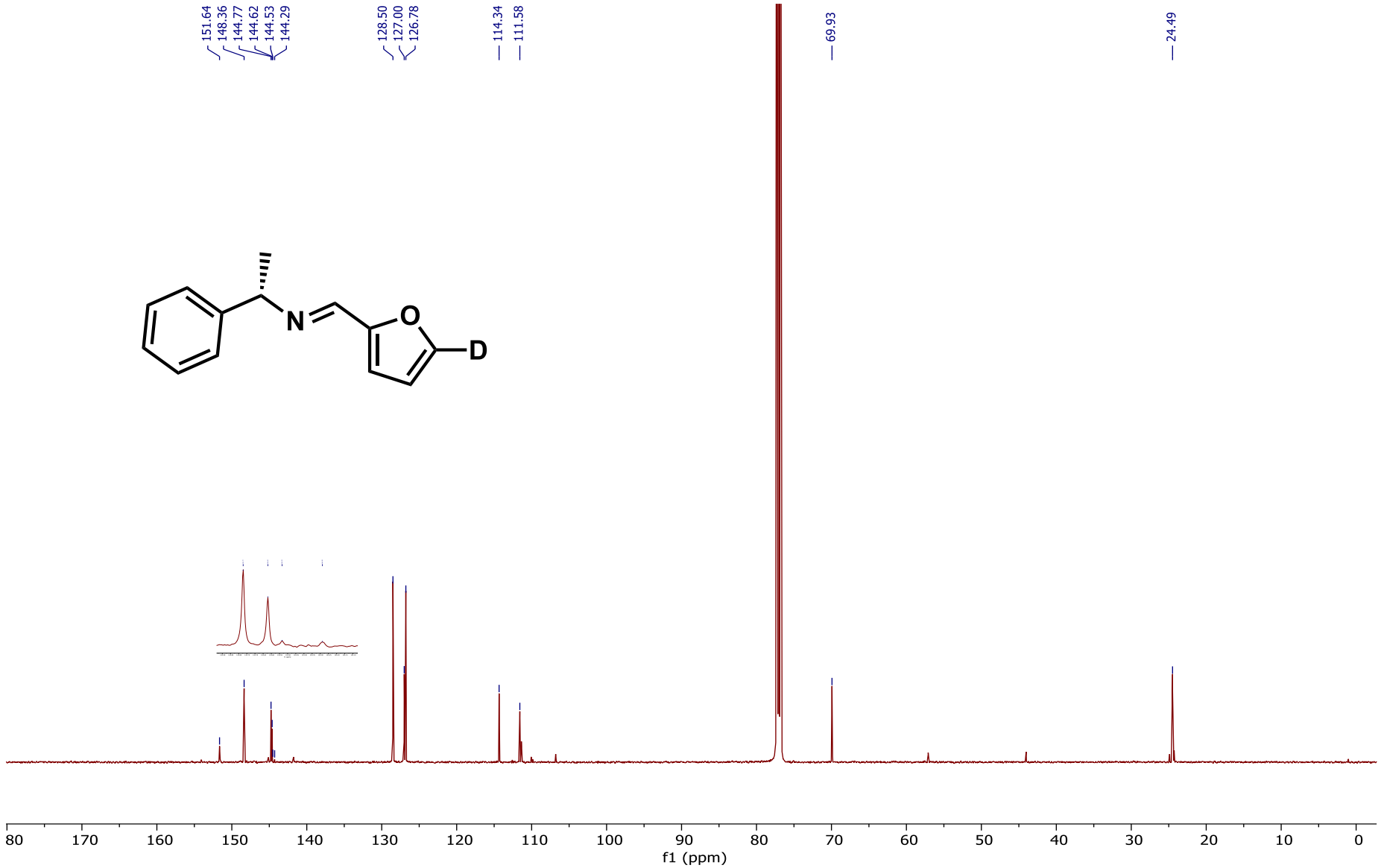
^{13}C NMR (125 MHz, $CDCl_3$) of *N*-(5D-furan-2-ylmethyl)aniline **[D]-3c**.



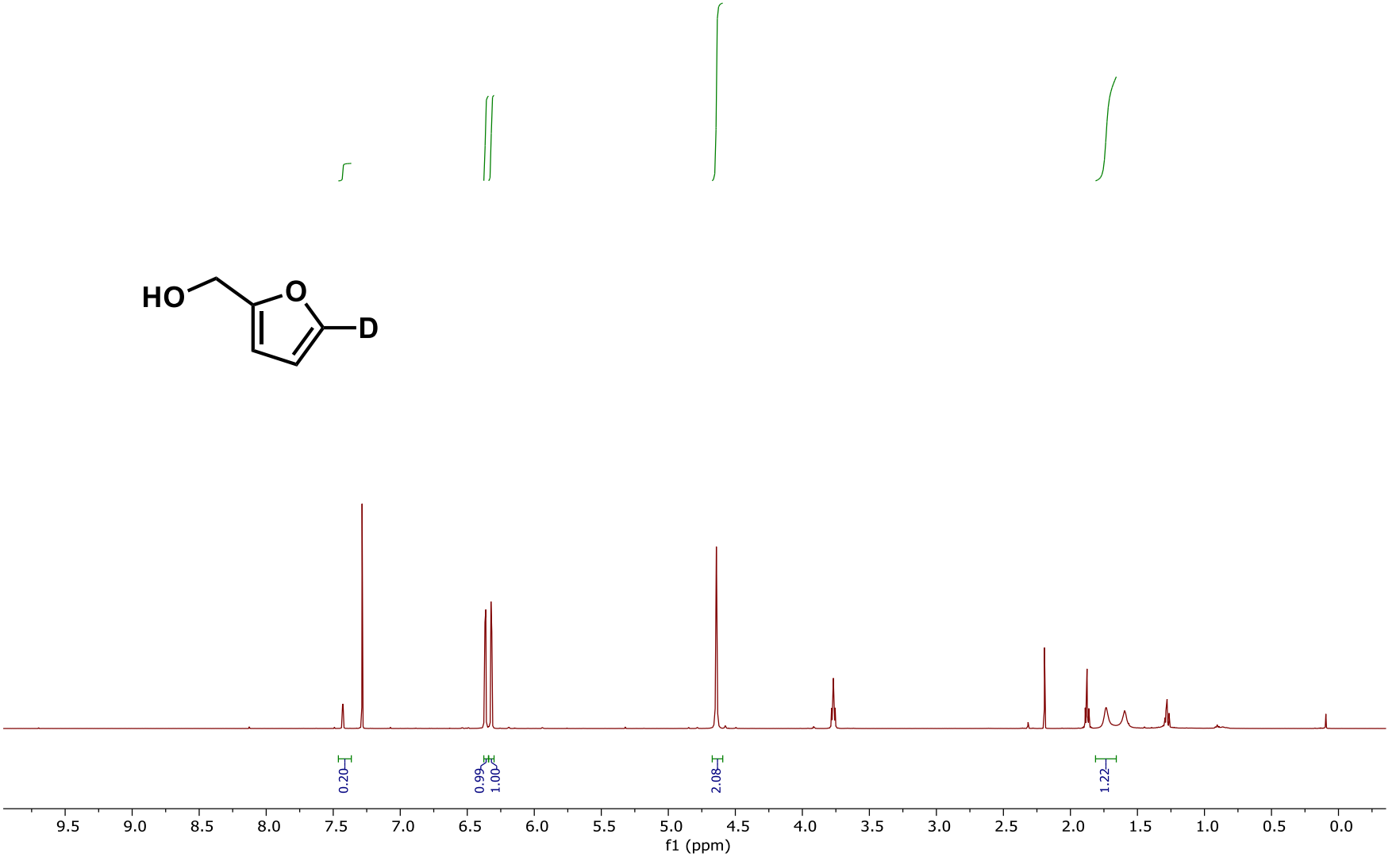
^{1}H NMR (500 MHz, $CDCl_3$) of (1*R*)-*N*-(5D-furan-2ylmethylidene)-1-phenylethanamine **[D]-3d**.



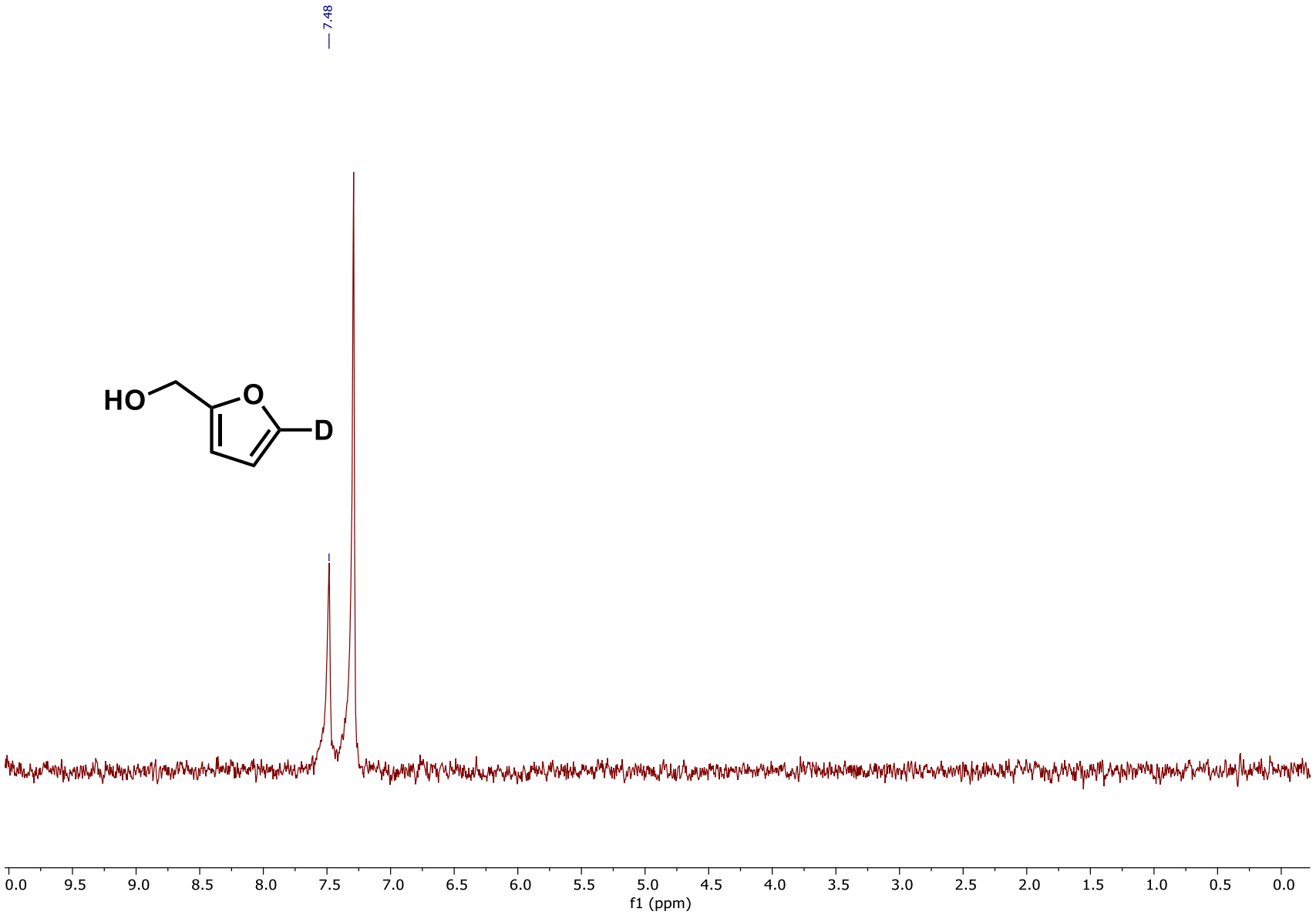
^{2}H NMR (77 MHz, $CHCl_3$) of (1*R*)-*N*-(5D-furan-2ylmethylidene)-1-phenylethanamine **[D]-3d**.



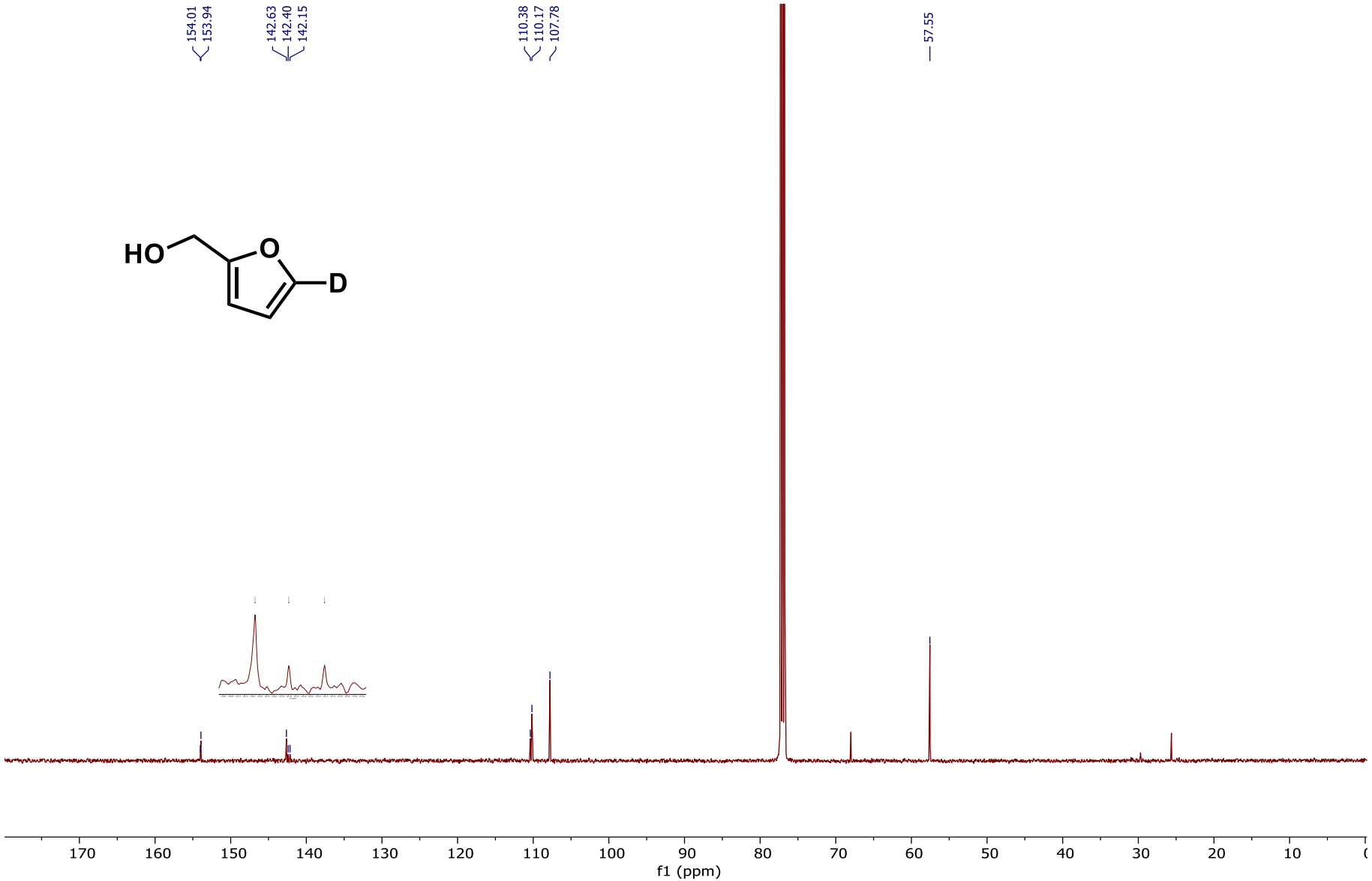
^{13}C NMR (125 MHz, $CDCl_3$) of (1*R*)-*N*-(5D-furan-2ylmethylidene)-1-phenylethanamine **[D]-3d**.



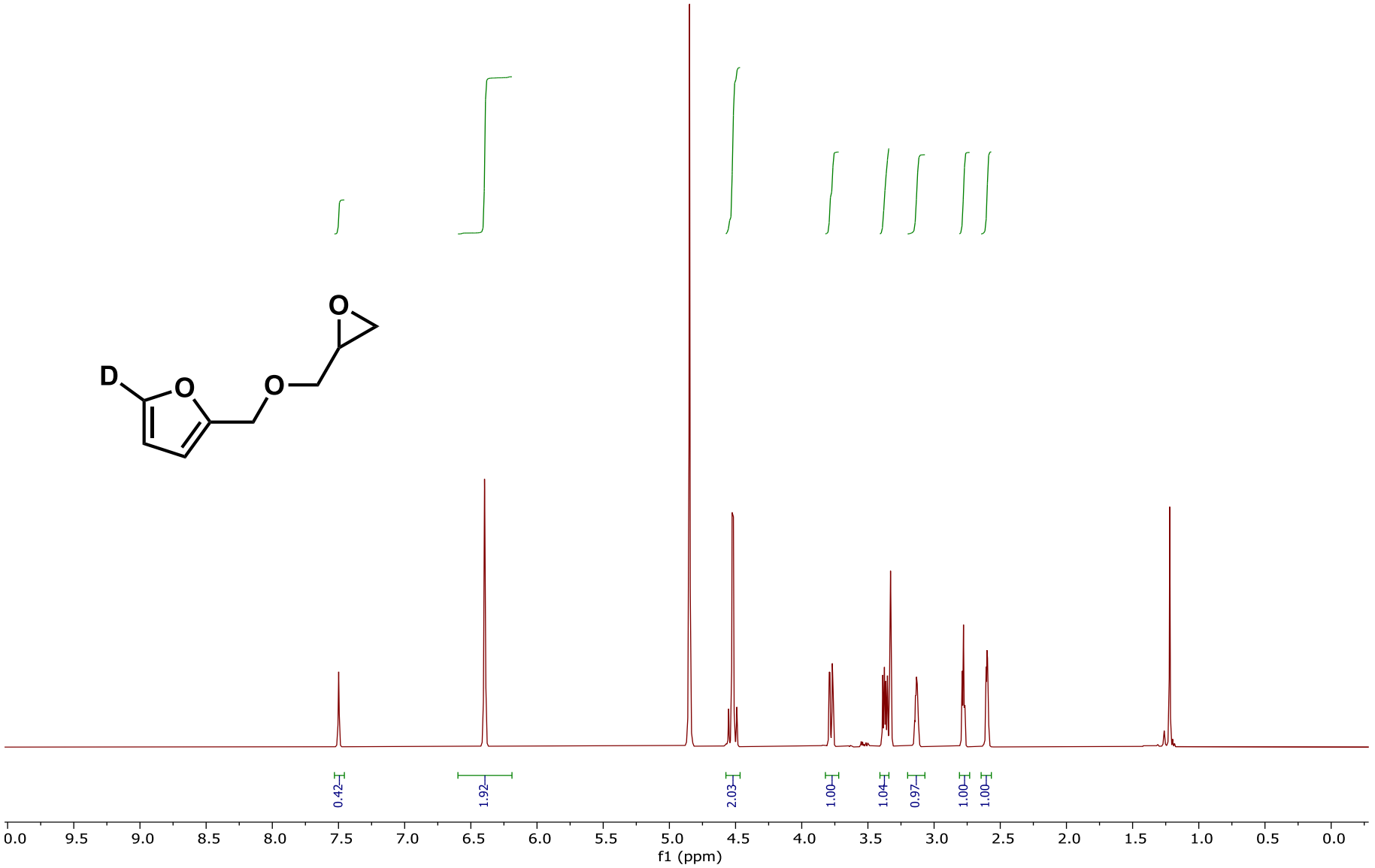
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(hydroxymethyl)-5D-furan **[D]-3e**.



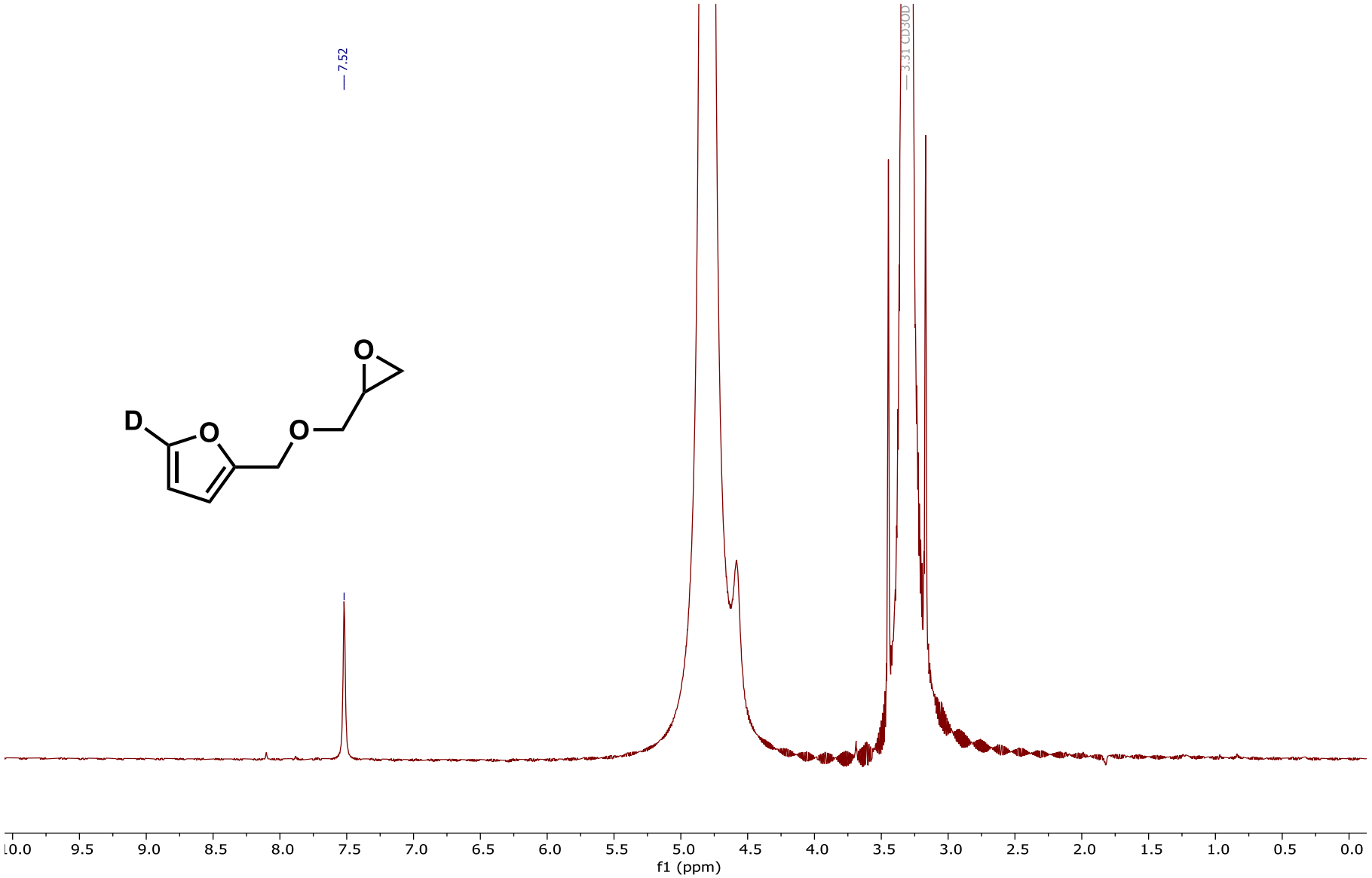
^{2}H NMR (500 MHz, $CHCl_3$) of 2-(hydroxymethyl)-5D-furan **[D]-3e**.



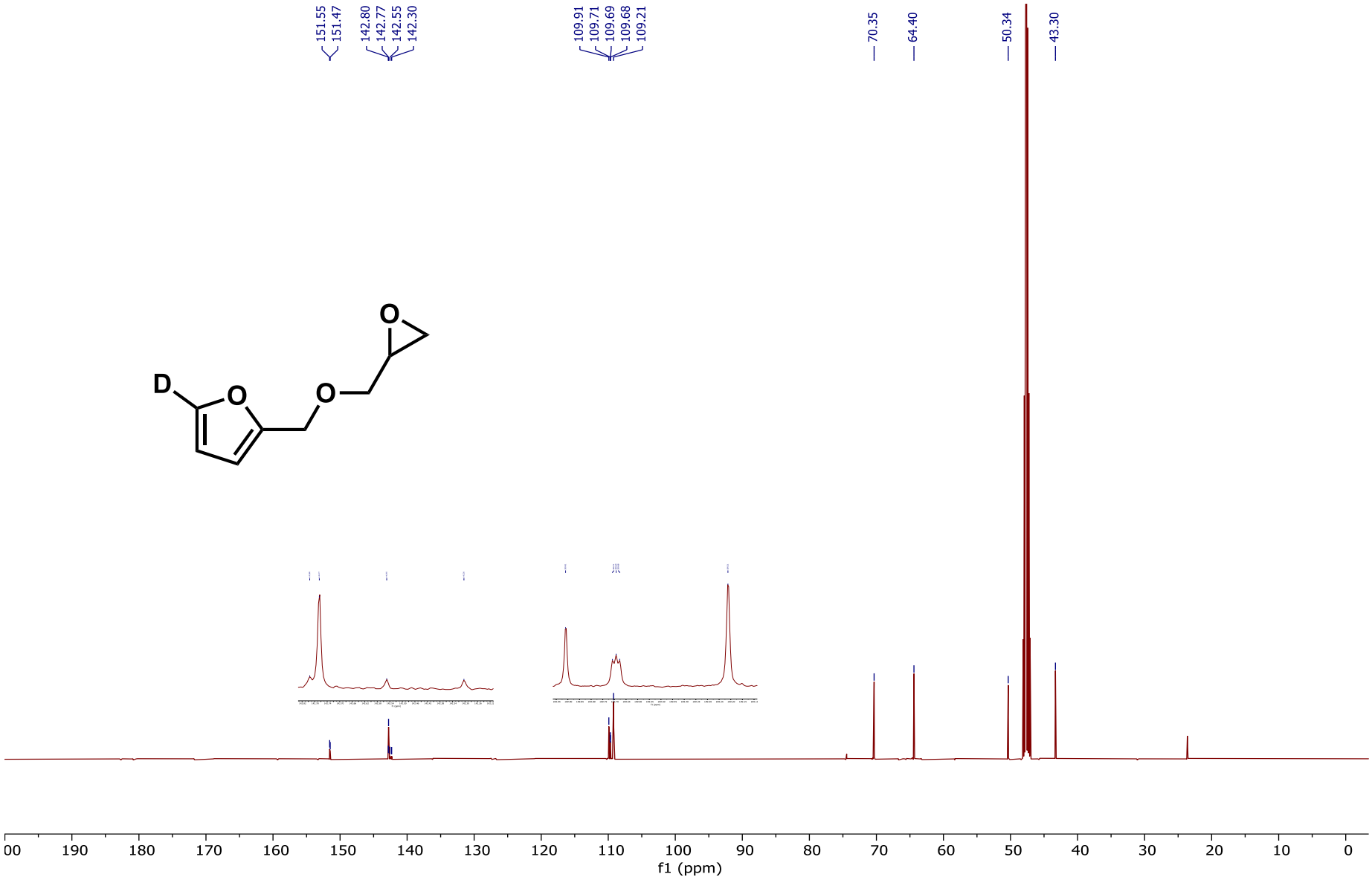
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(hydroxymethyl)-5D-furan **[D]-3e**.



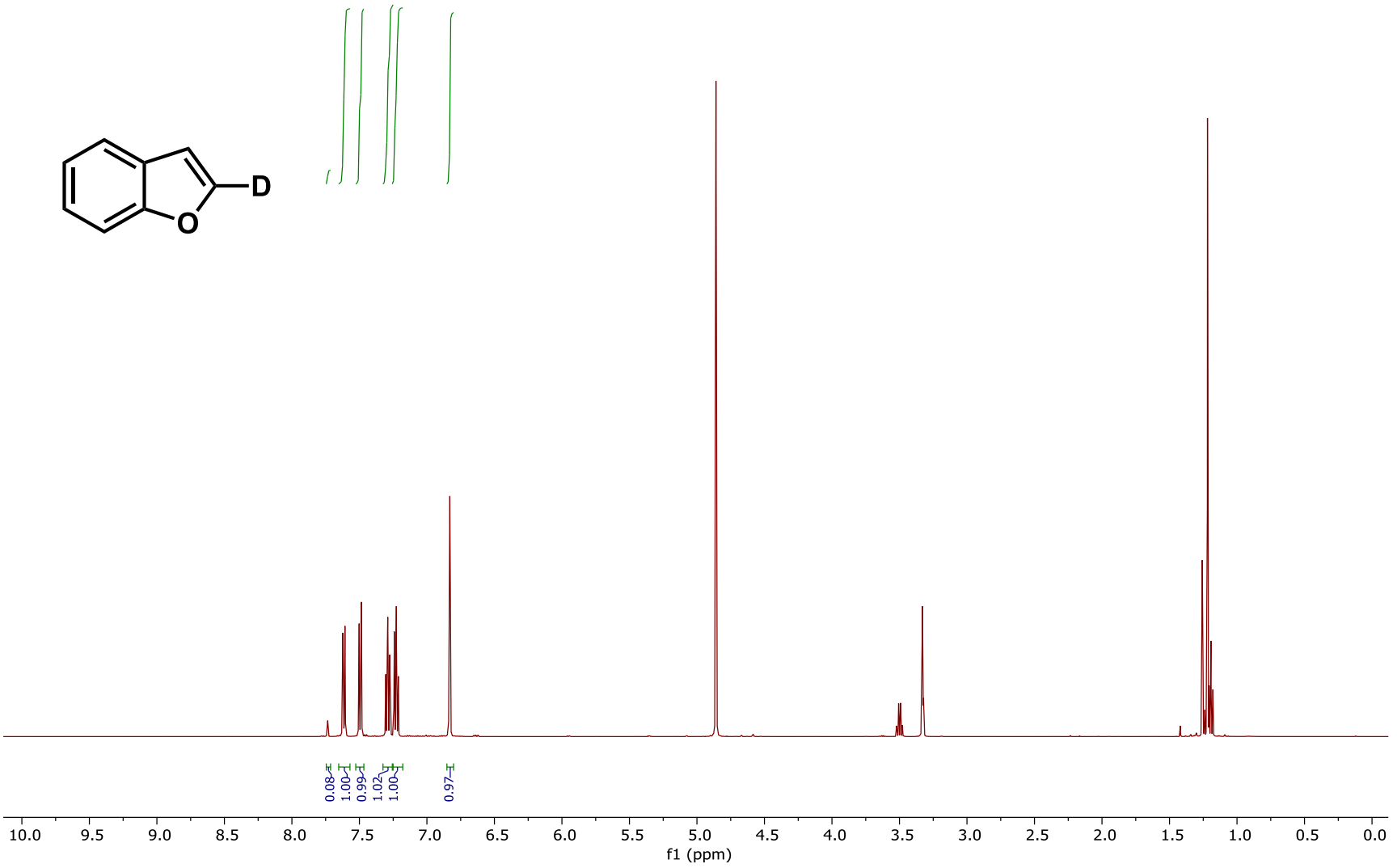
^{1}H NMR (500 MHz, CD_3OD) of 2-[(2,3-epoxypropoxy)methyl]-*5D*-furan **[D]-3f**.



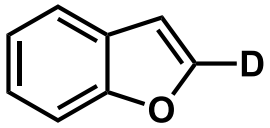
^{2}H NMR (77 MHz, CD_3OD) of 2-[(2,3-epoxypropoxy)methyl]-*5D*-furan **[D]-3f**.

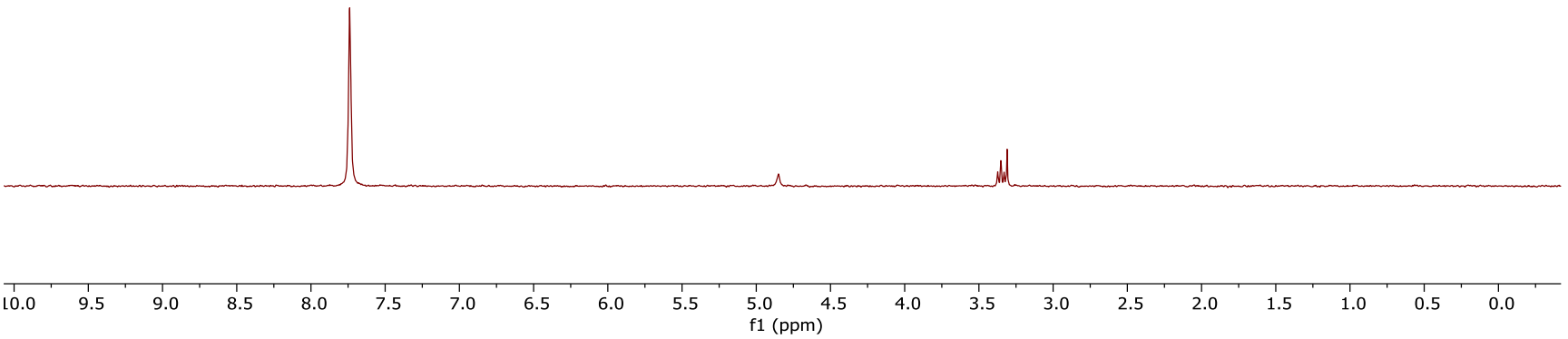


^{13}C NMR (125 MHz, CD_3OD) of 2-[(2,3-epoxypropoxy)methyl]-*5D*-furan **[D]-3f**.

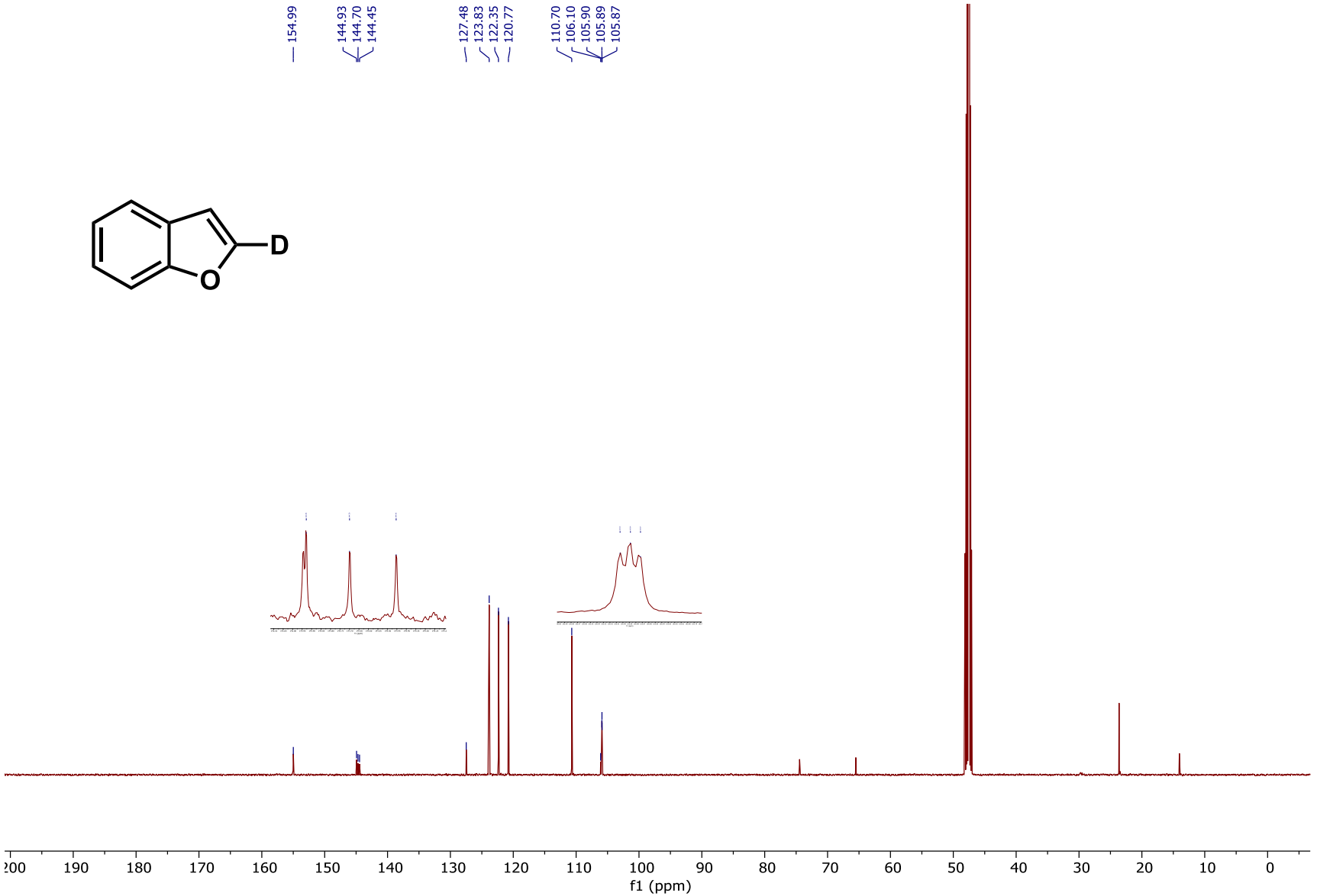


^{1}H NMR (500 MHz, CD_3OD) of *1D*-benzofuran **[D]-3g**.

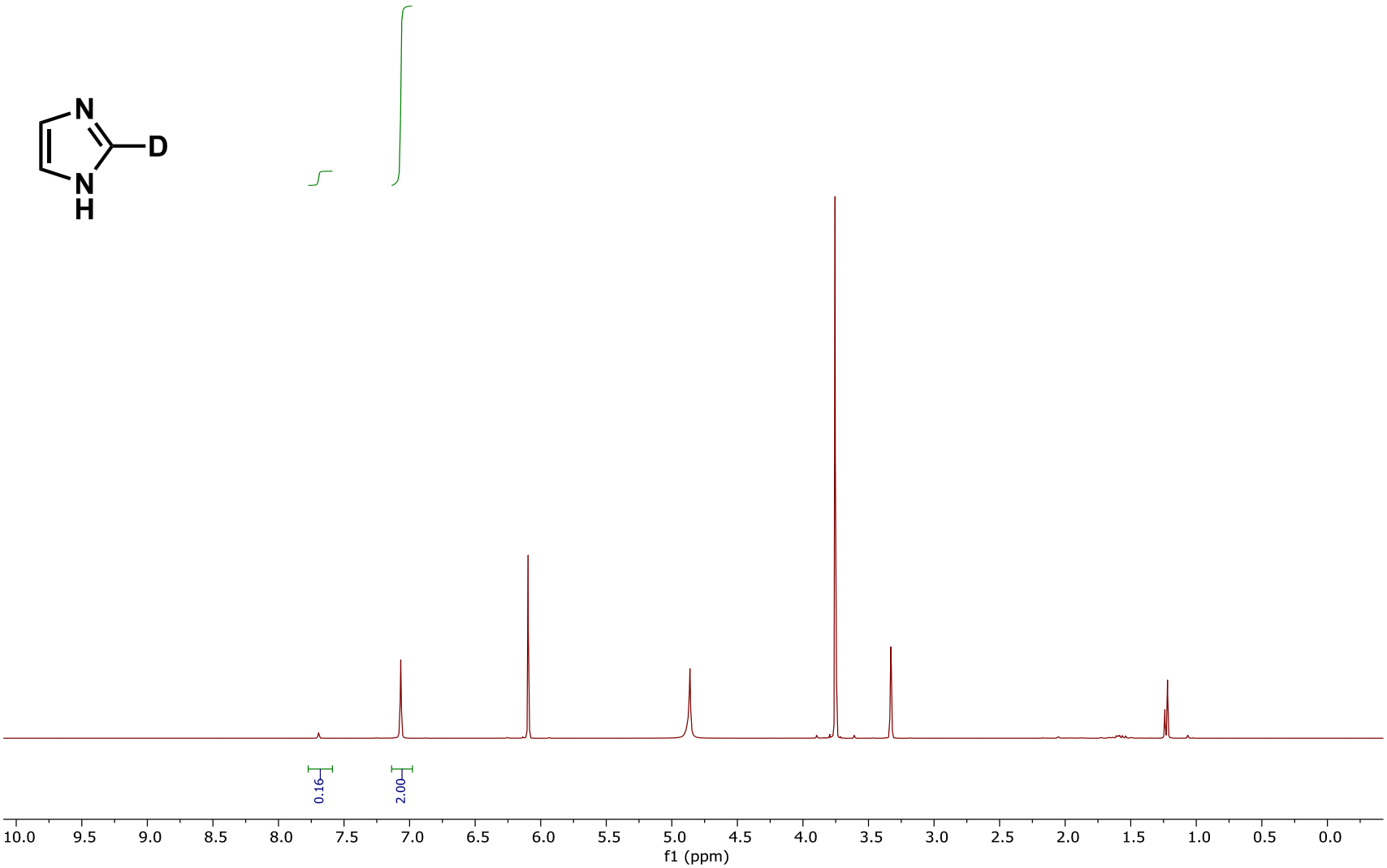




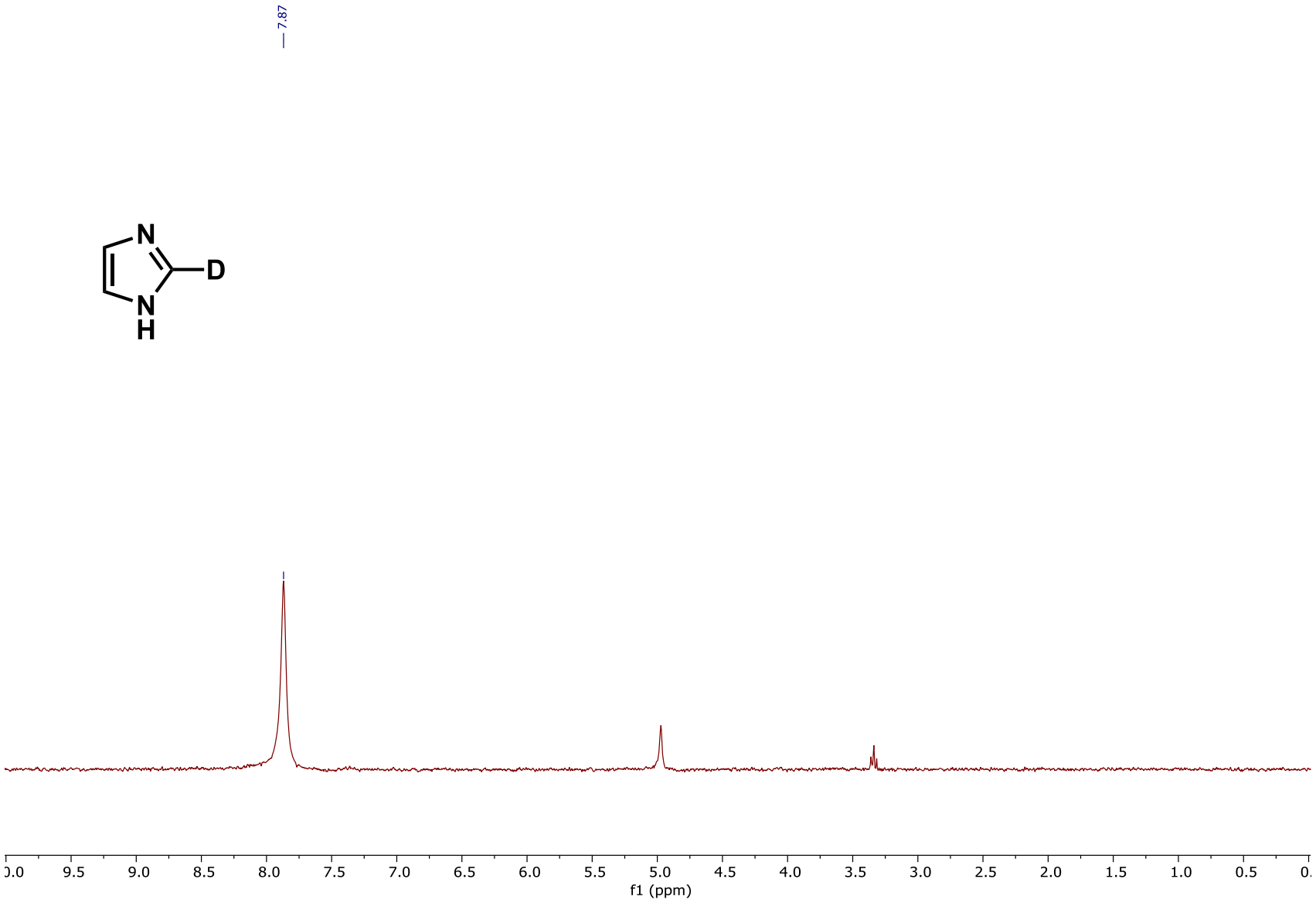
^{2}H NMR (77 MHz, CH_3OH) of *1D*-benzofuran **[D]-3g**.



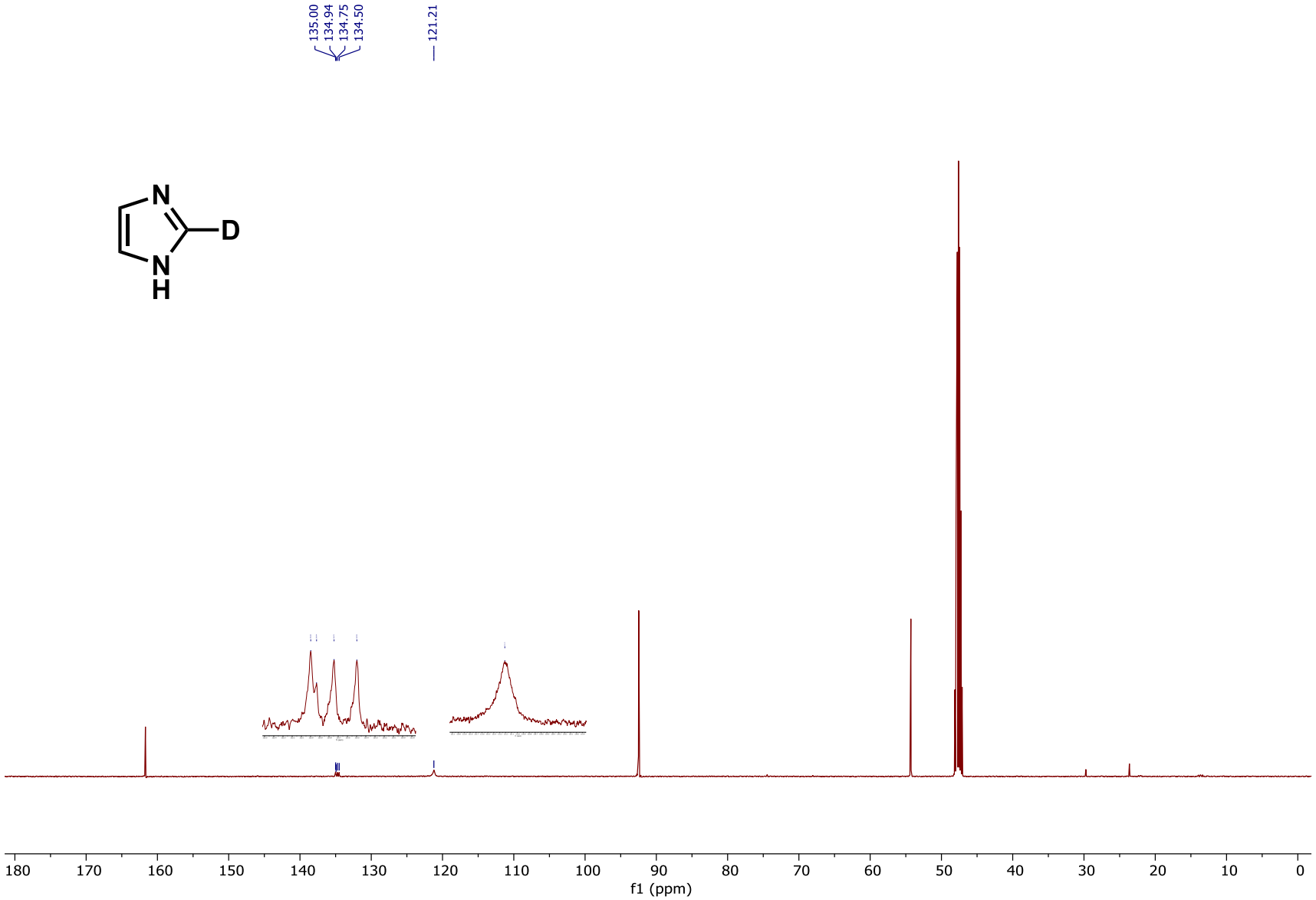
^{13}C NMR (125 MHz, CD_3OD) of *1D*-benzofuran**[D]-3g**.



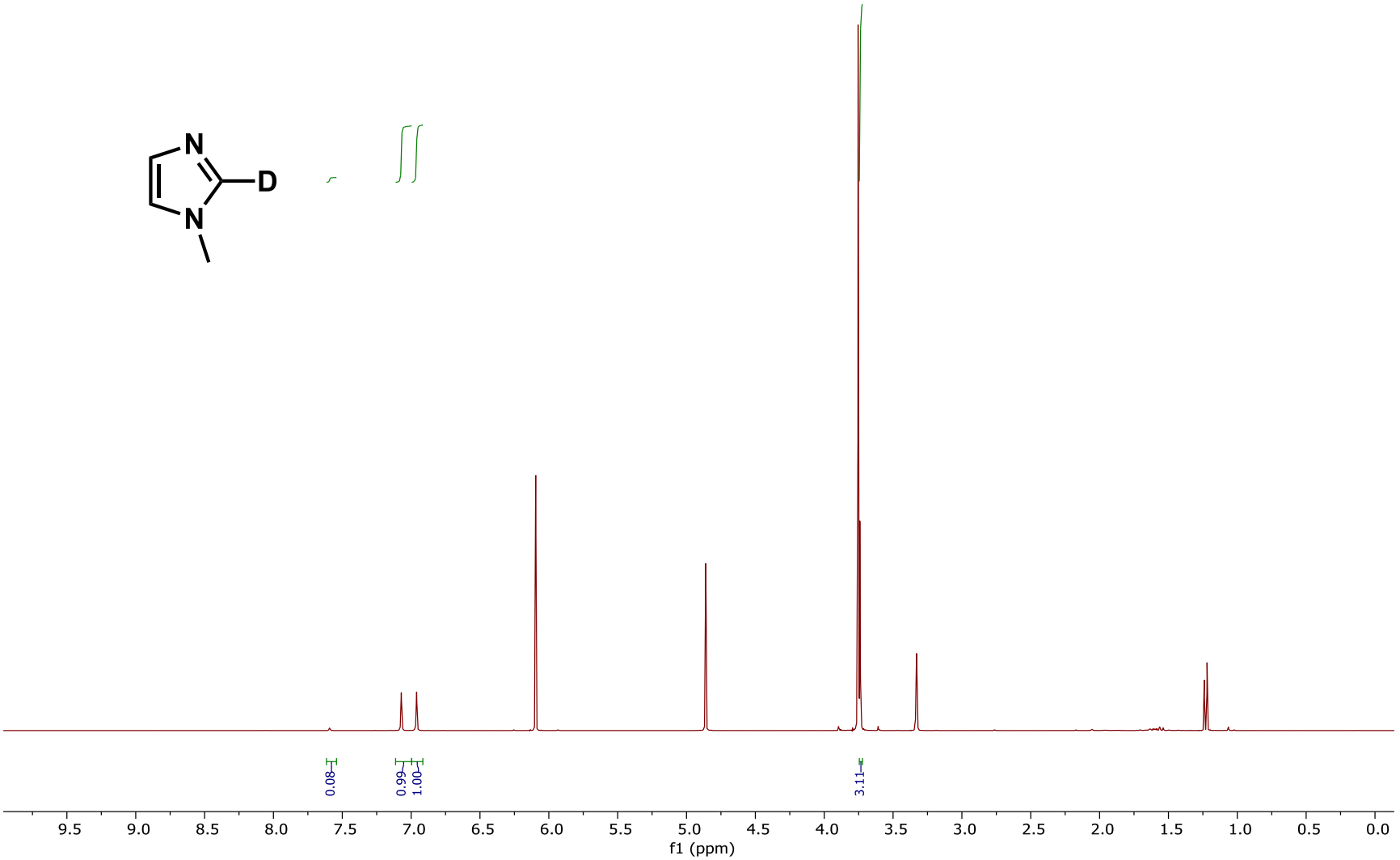
^{1}H NMR (500 MHz, CD_3OD) of 2*D*-imidazole **[D]-3h**.



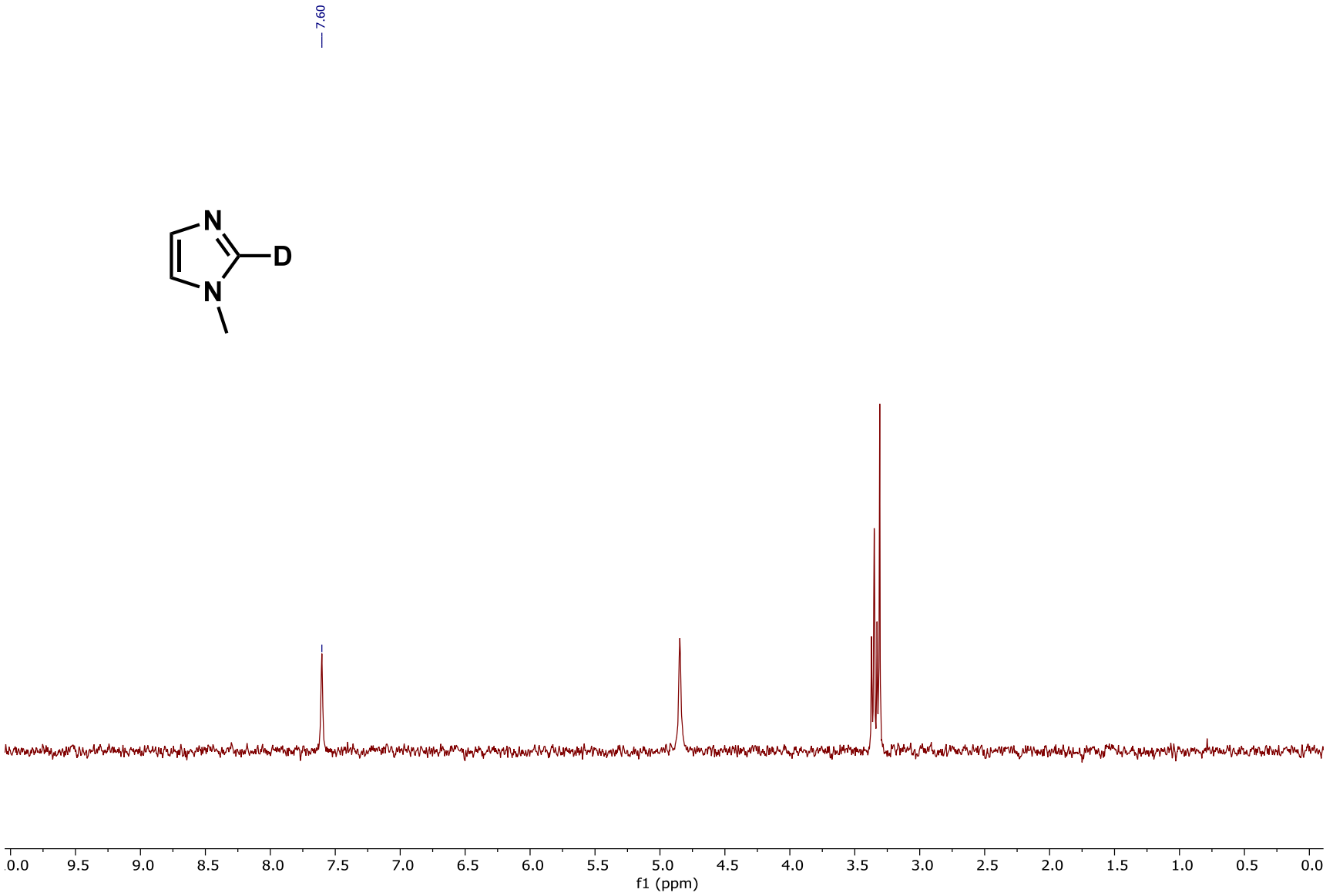
^{2}H NMR (77 MHz, CH_3OH) of 2*D*-imidazole **[D]-3h**.



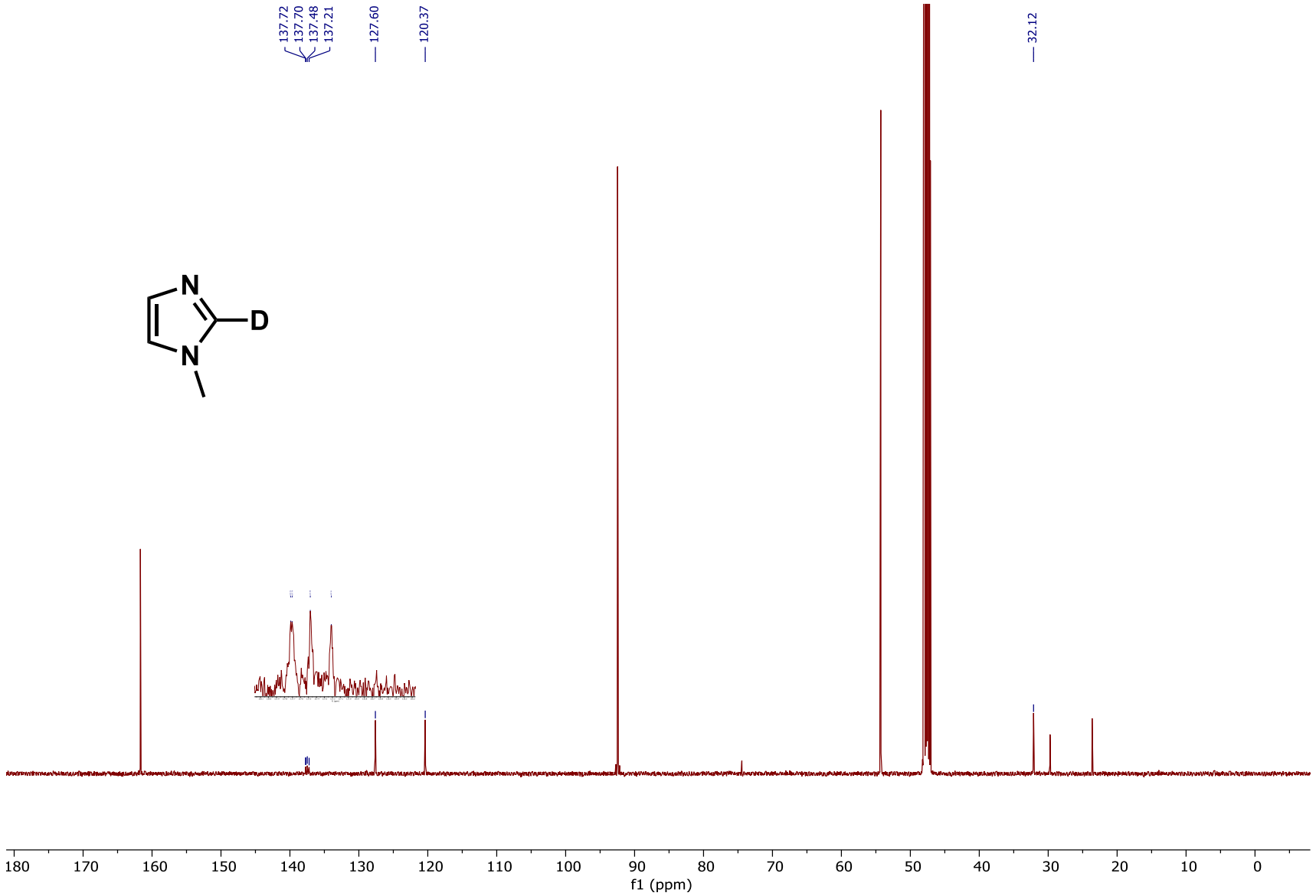
^{13}C NMR (125 MHz, CD_3OD) of *2D*-imidazole **[D]-3h**.



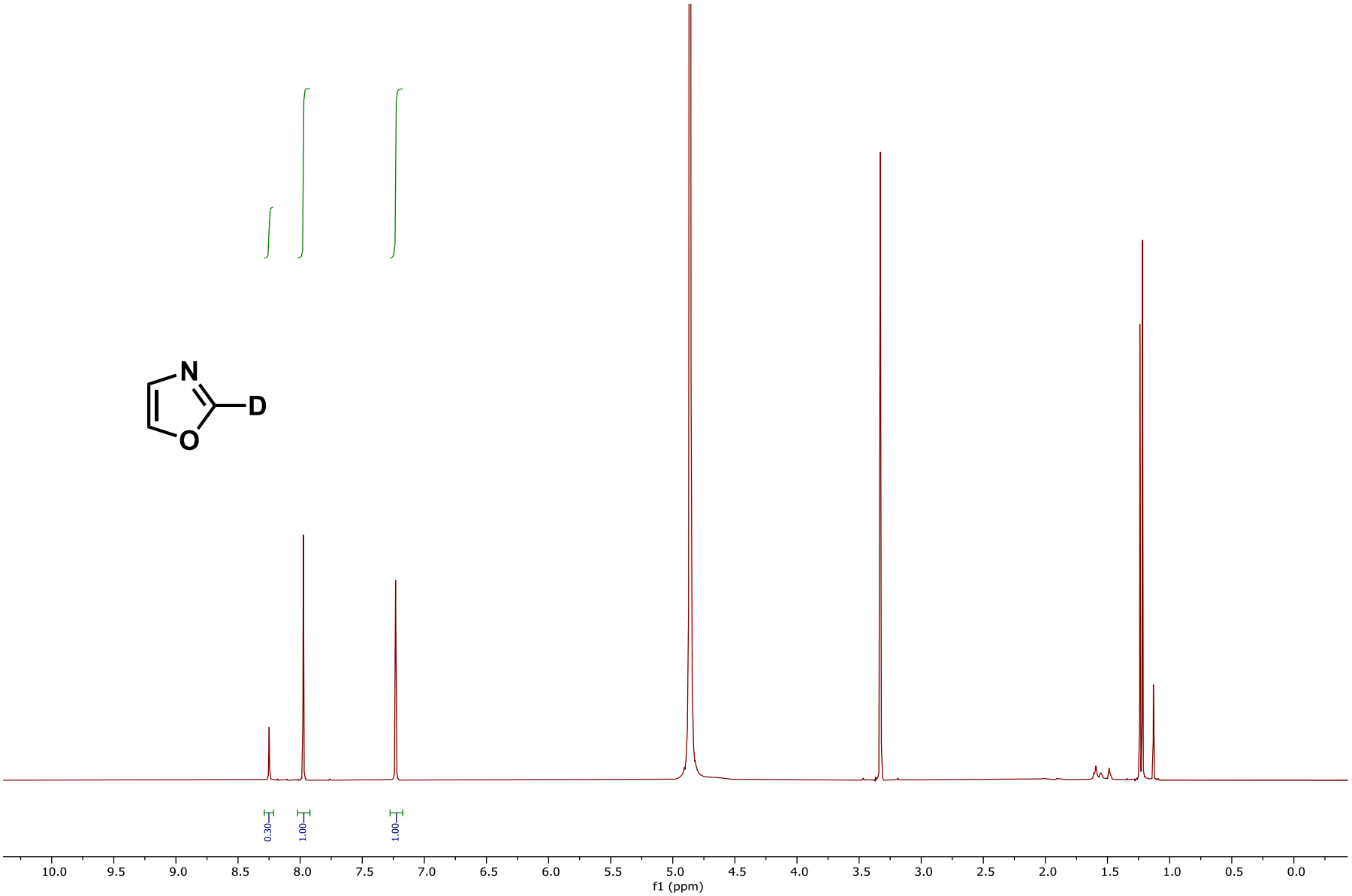
^{1}H NMR (500 MHz, CD_3OD) of 2*D*-*N*-methylimidazole **[D]-3i**.



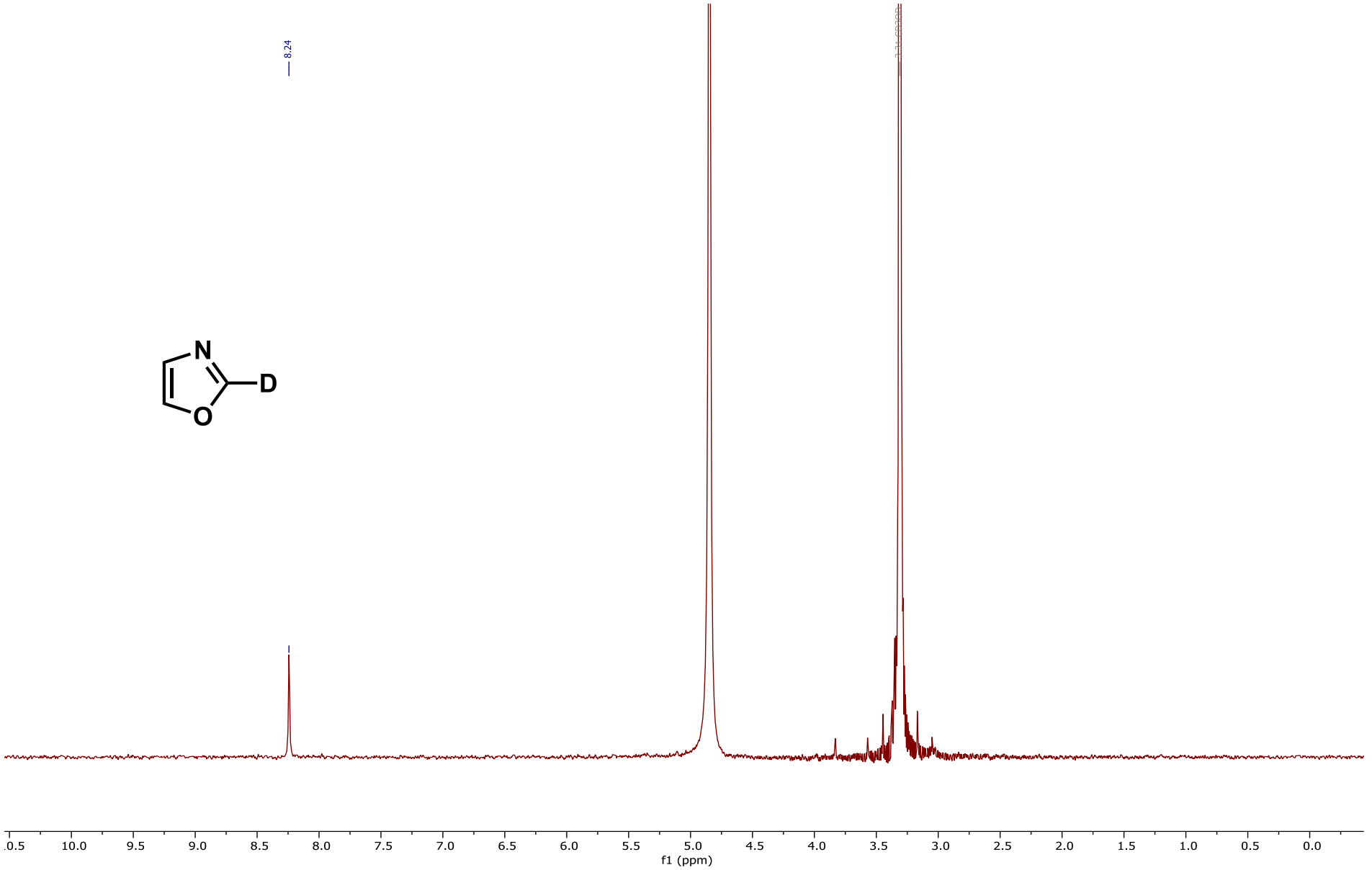
^{2}H NMR (500 MHz, CH_3OH) of 2*D*-*N*-methylimidazole **[D]-3i**.



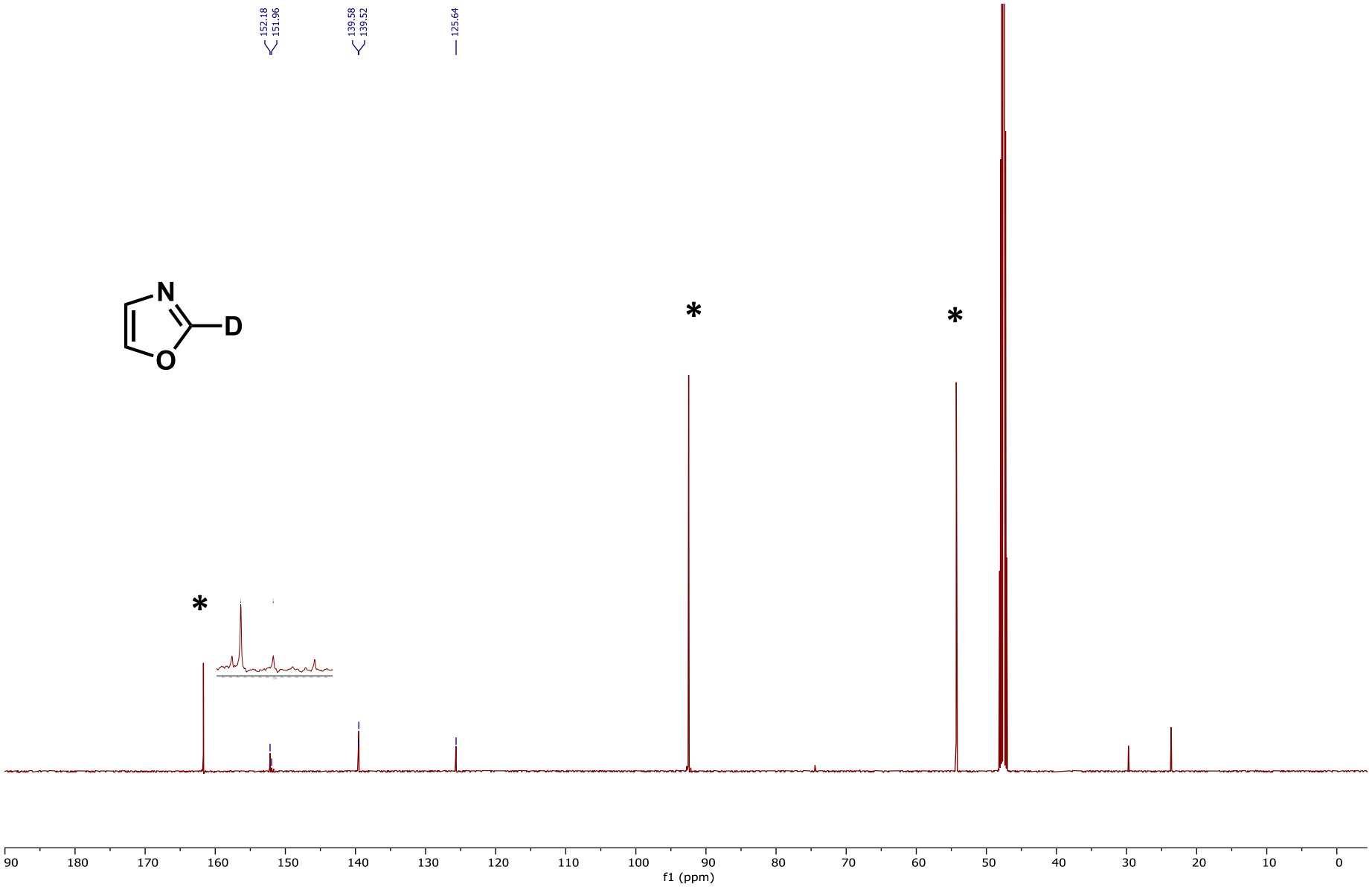
^{13}C NMR (125 MHz, CD_3OD) of 2*D*-*N*-methylimidazole **[D]-3i**.



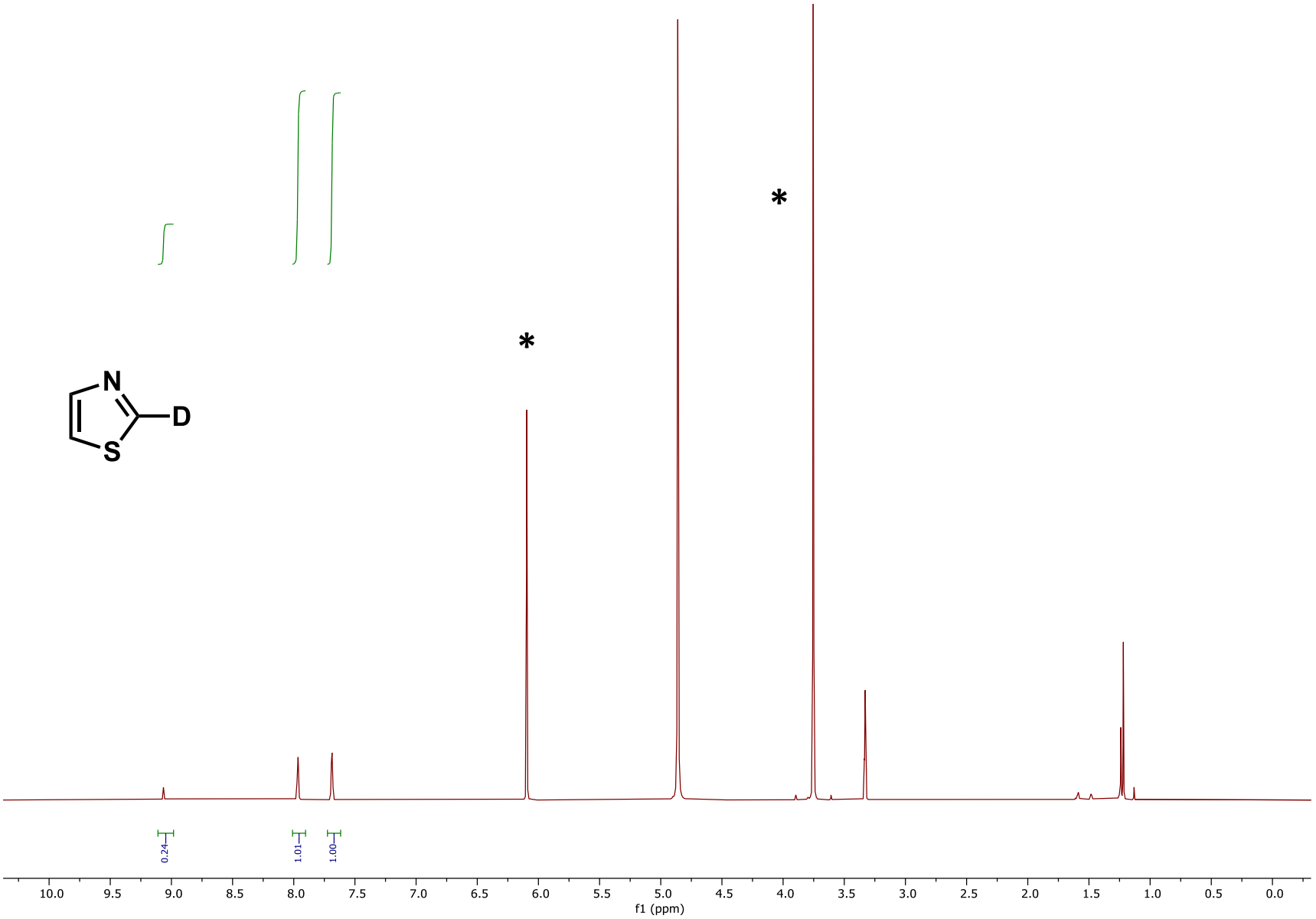
^{1}H NMR (500 MHz, CD_3OD) of 2D-thiazole **[D]-3j**.



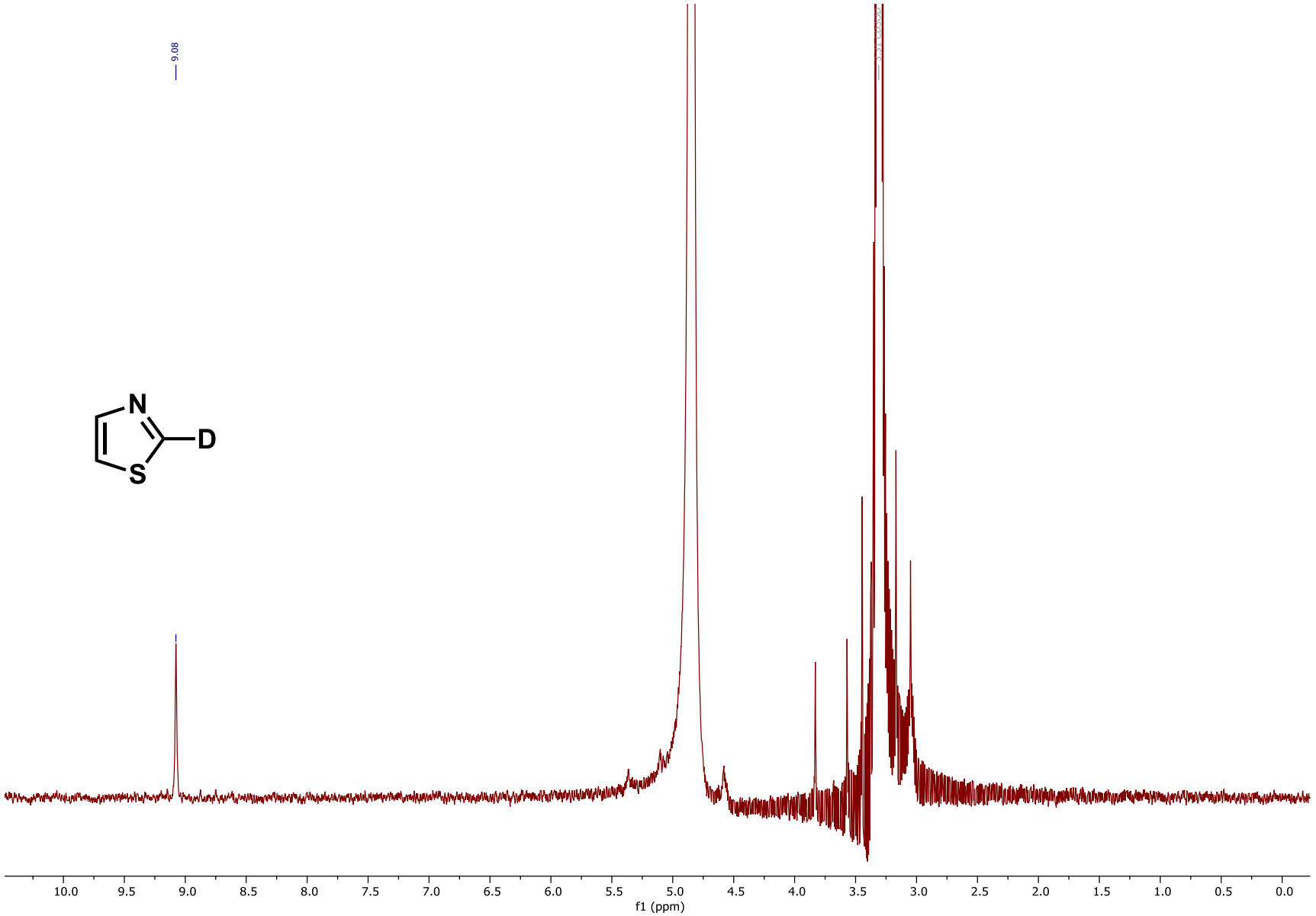
^{2}H NMR (77 MHz, CD_3OD) of 2D-oxazole **[D]-3j**.



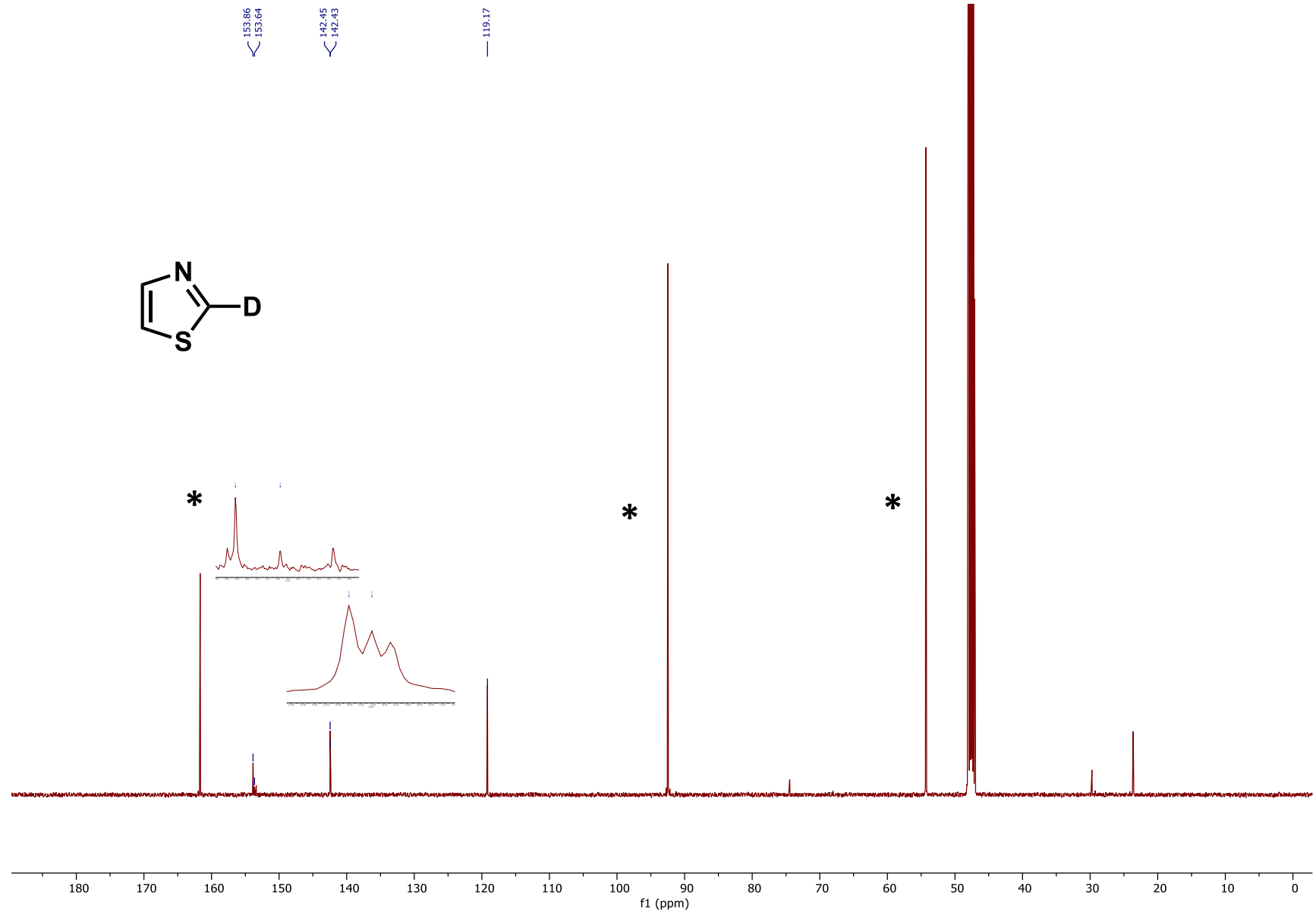
^{13}C NMR (125 MHz, CD_3OD) of 2D-oxazole **[D]-3j**. (*) Denotes resonances from 1,3,5-trimethoxybenzene.



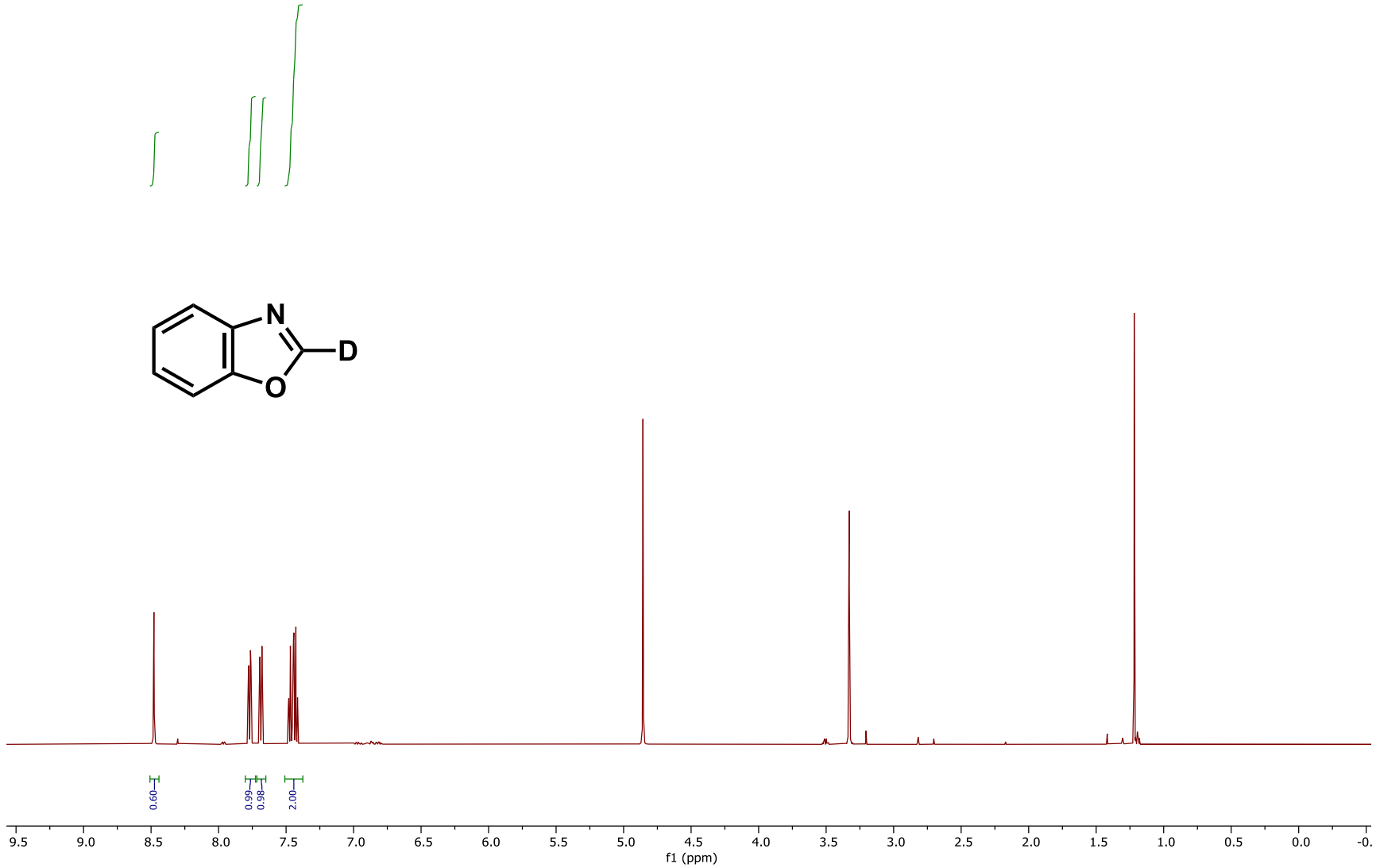
^{1}H NMR (500 MHz, CD_3OD) of 2D-thiazole **[D]-3k**. (*) Denotes resonances from 1,3,5-trimethoxybenzene.



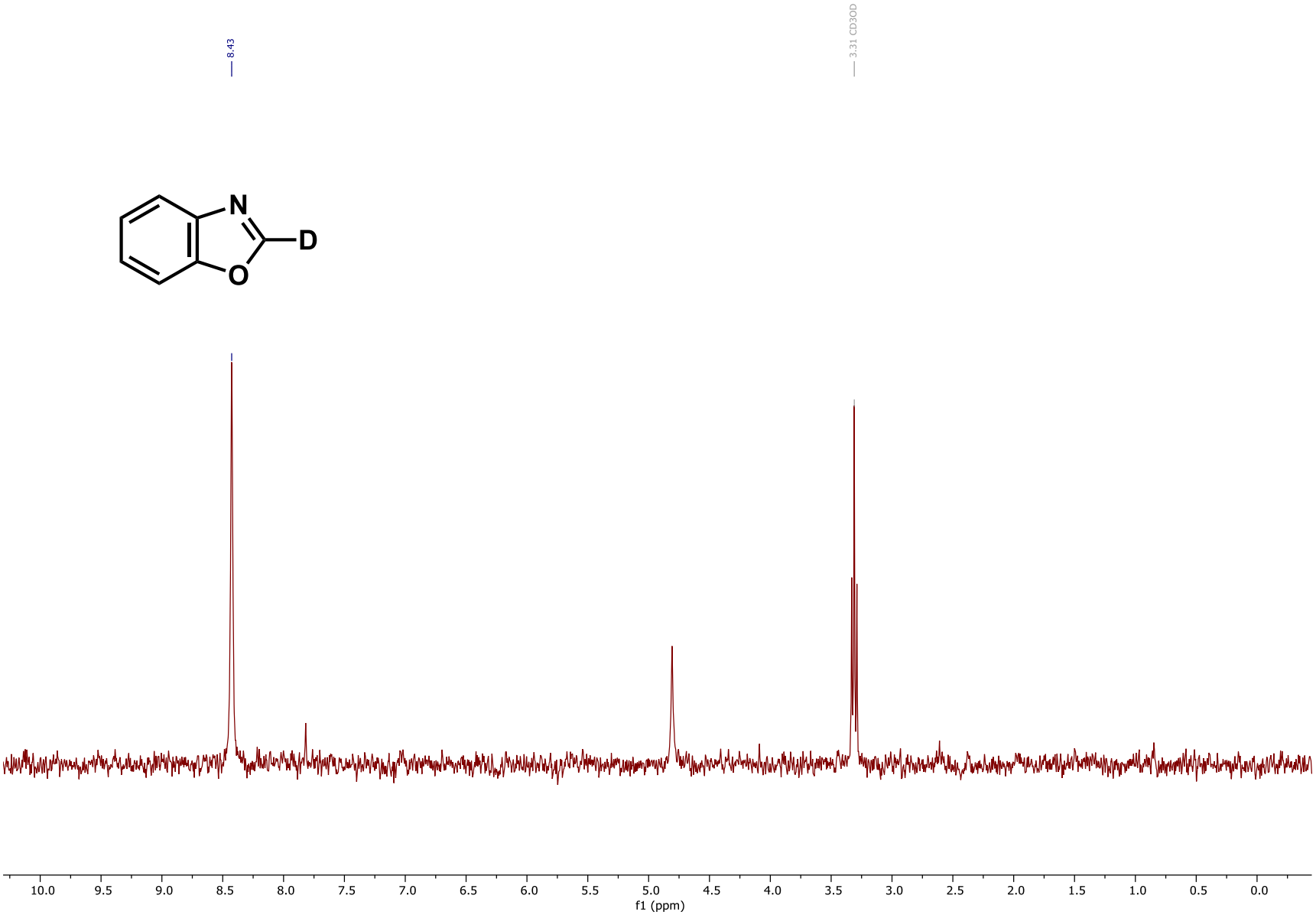
^{2}H NMR (77 MHz, CD_3OD) of 2D-thiazole**[D]-3k**.



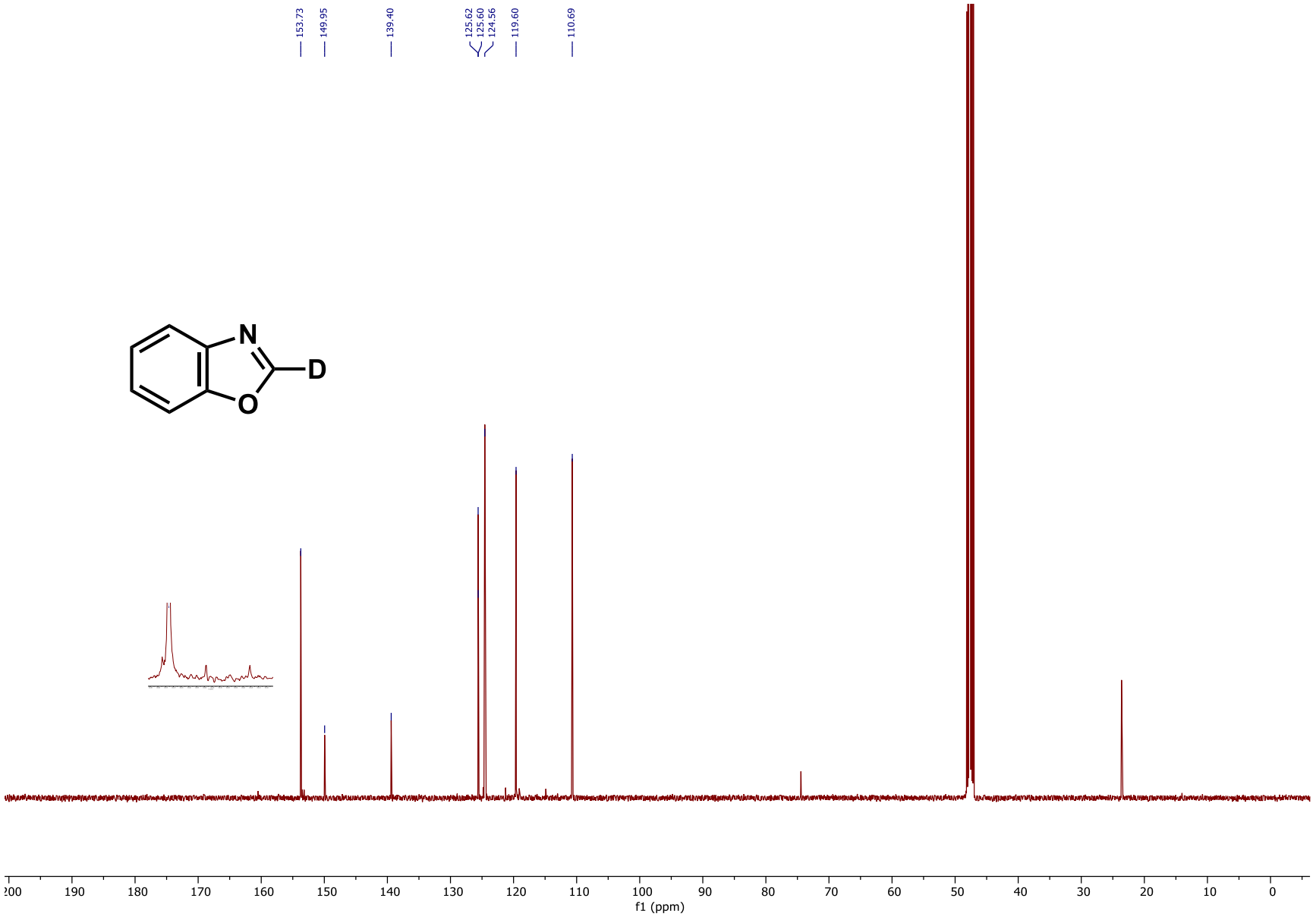
^{13}C NMR (125 MHz, CD_3OD) of 2D-thiazole **[D]-3k**. (*) Denotes resonances from 1,3,5-trimethoxybenzene.



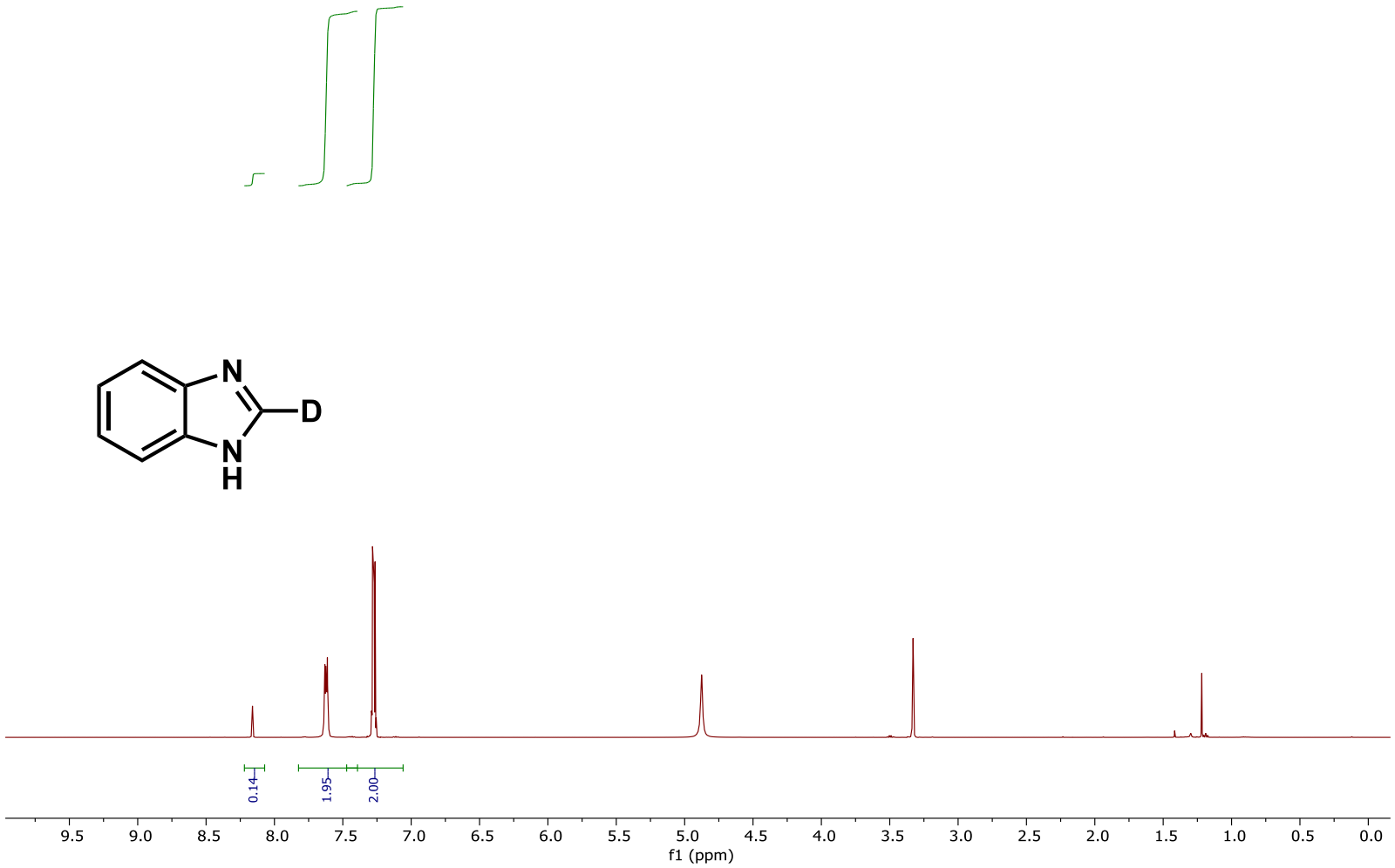
^{1}H NMR (500 MHz, CD_3OD) of 2D-benzoxazole **[D]-3l**.



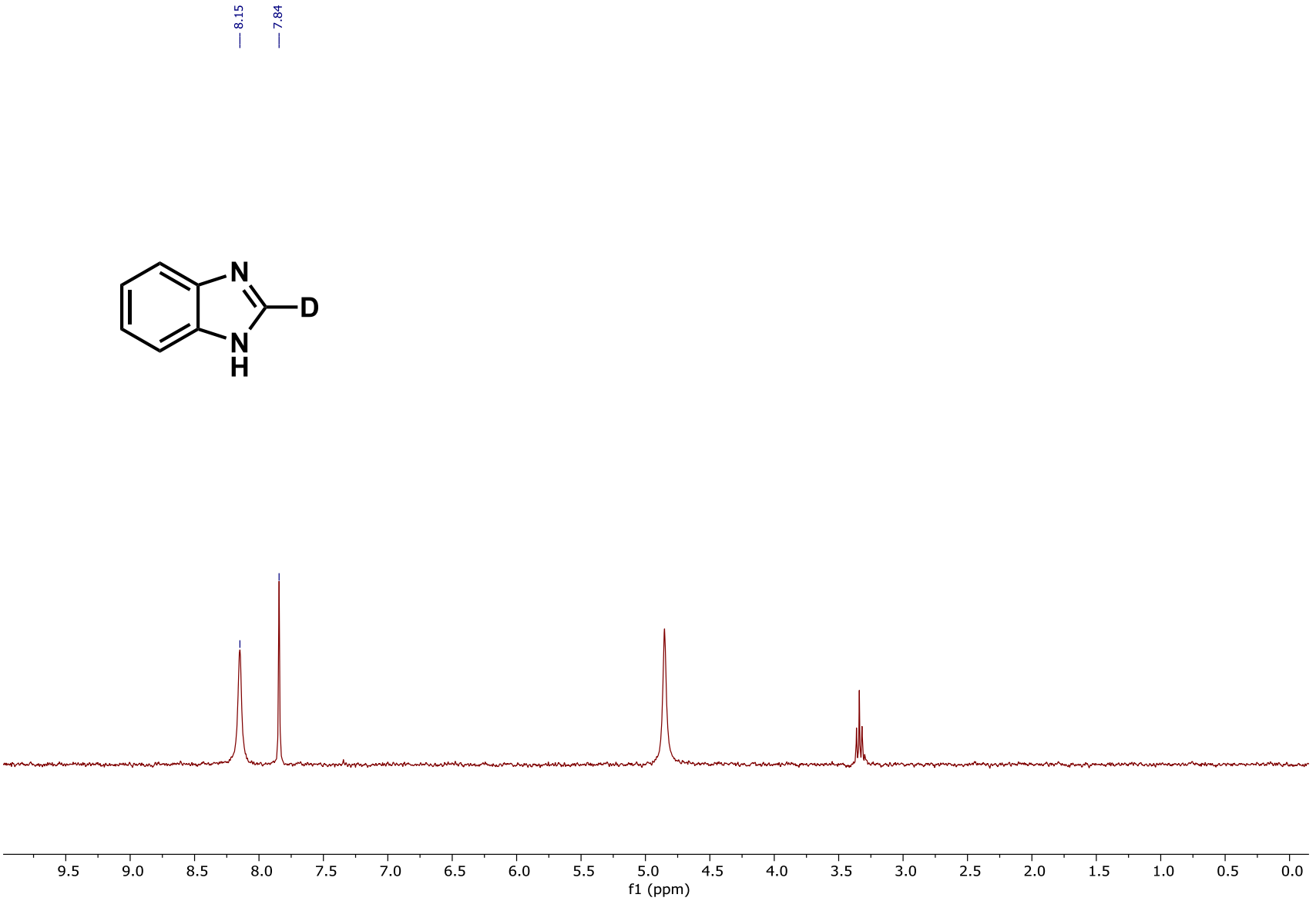
^{2}H NMR (77 MHz, CH_3OH) of 2D-benzoxazole **[D]-3l** – containing residual d_4-MeOD.



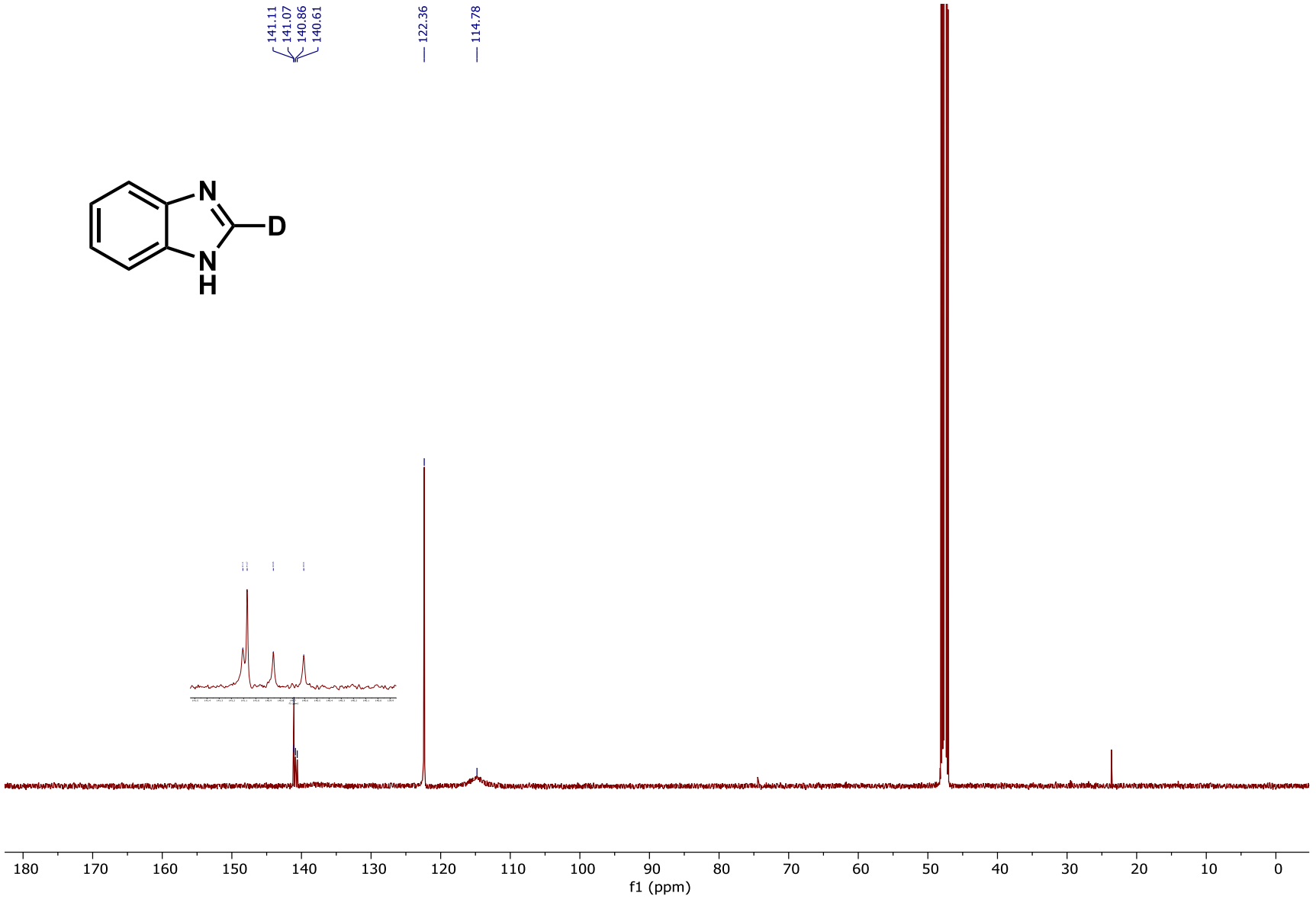
^{13}C NMR (125 MHz, CD_3OD) of 2D-benzoxazole **[D]-3l**.



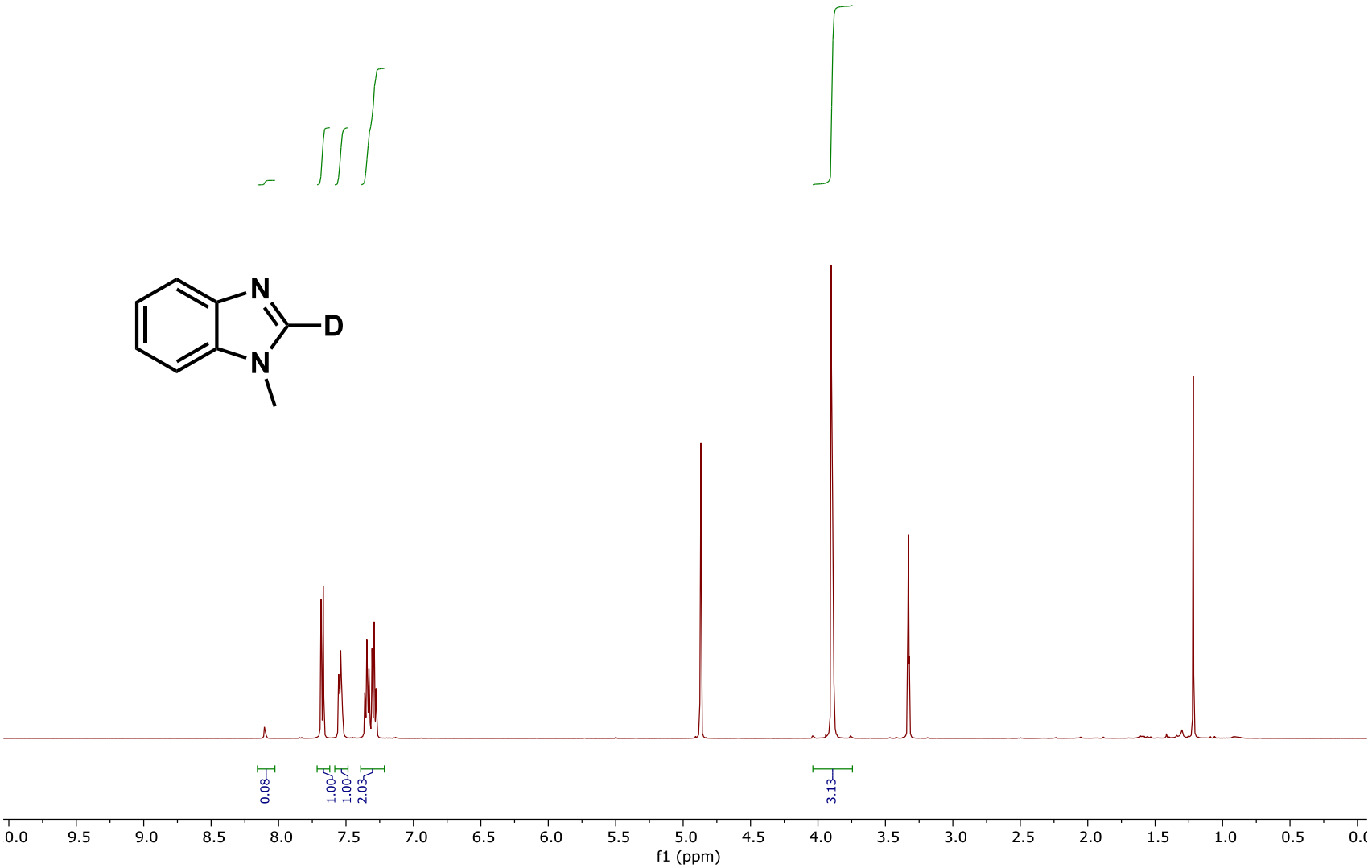
^{1}H NMR (500 MHz, CD_3OD) of *1D*-benzimidazole **[D]-3m**.



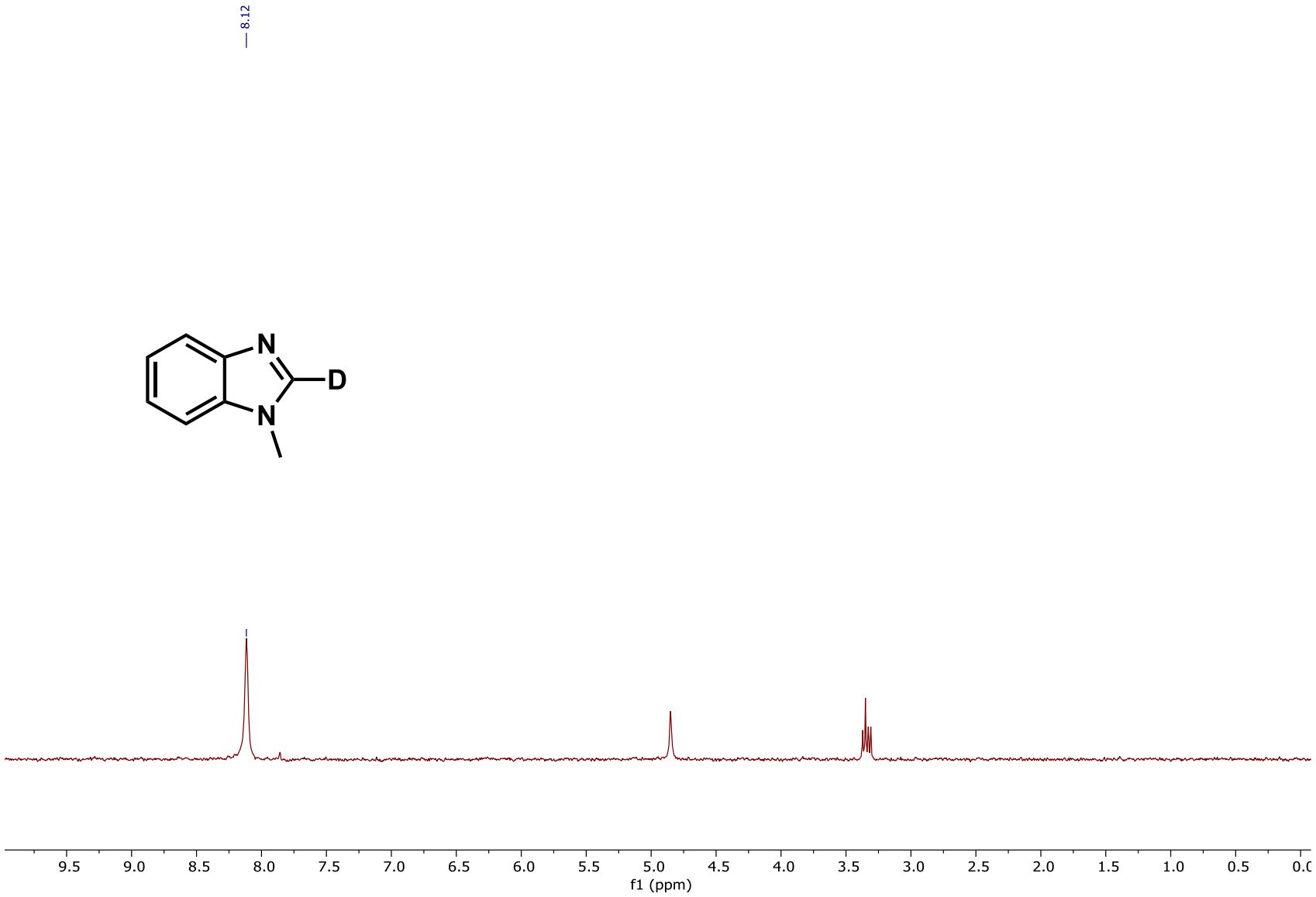
^{2}H NMR (77 MHz, CH_3OH) of *1D*-benzimidazole **[D]-3m** – containing residual d_4-MeOD.



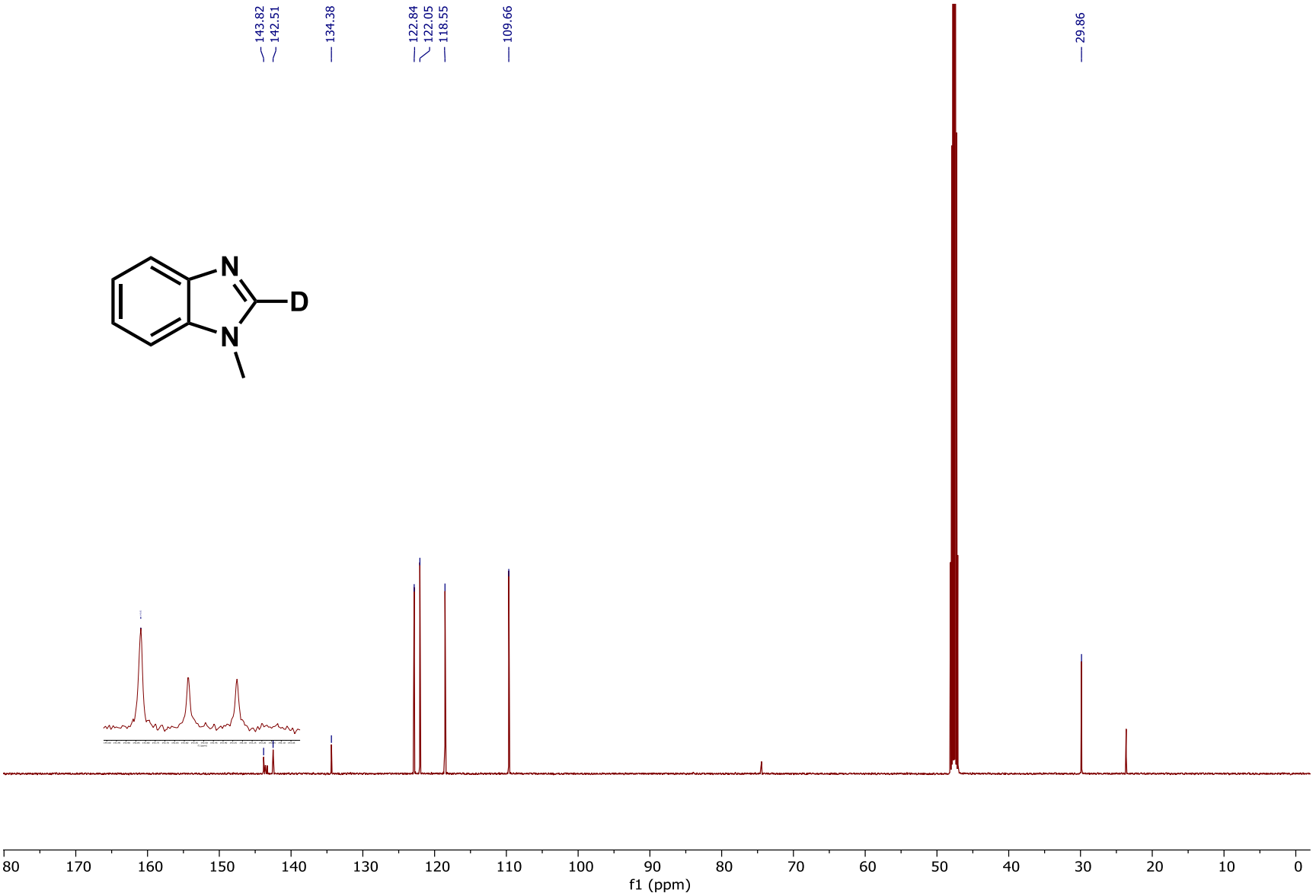
^{13}C NMR (125 MHz, CD_3OD) of *1D*-benzimidazole **[D]-3m**.



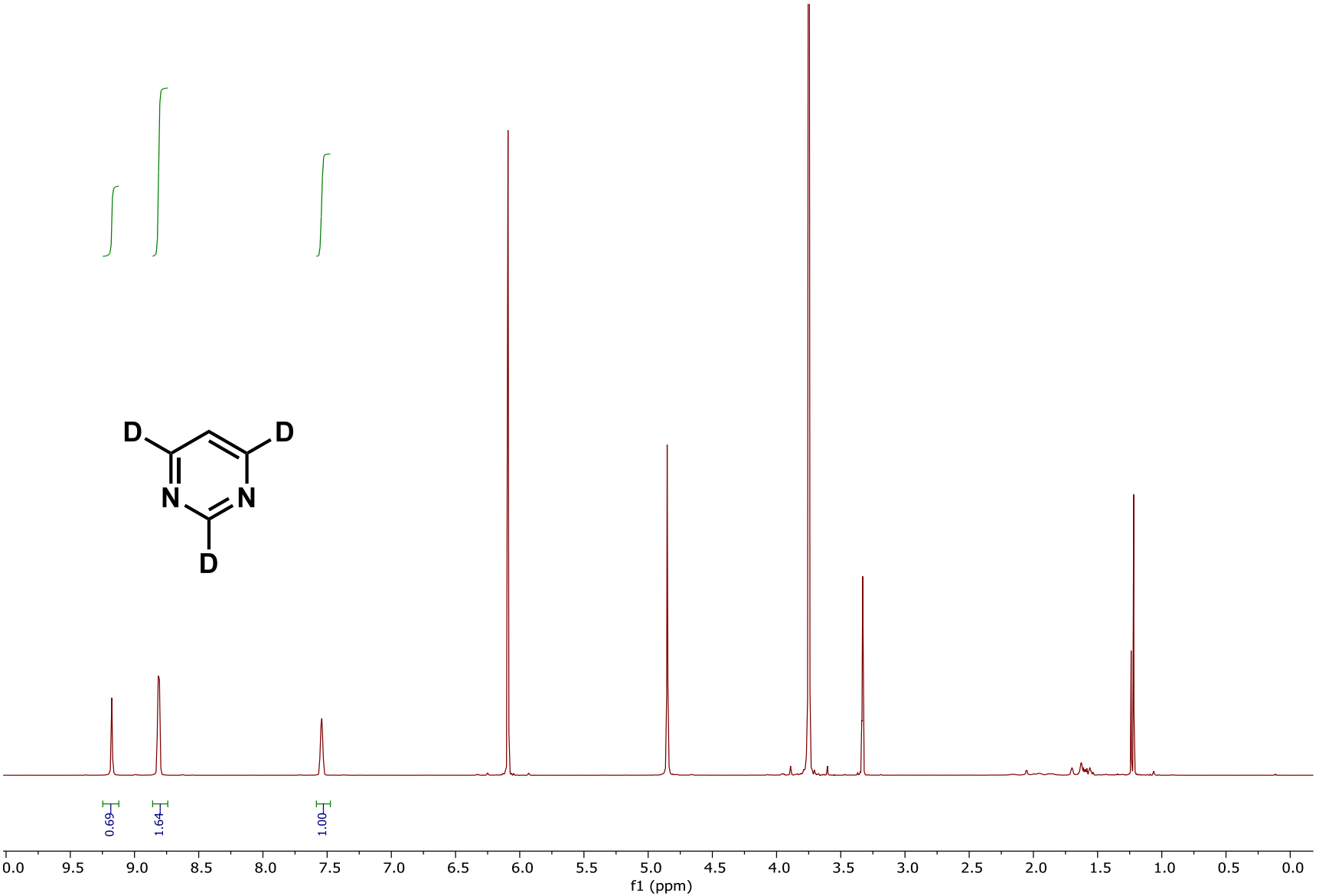
^{1}H NMR (500 MHz, CD_3OD) of 1-methyl-2-d_1-benzimidazole **[D]-3n**.



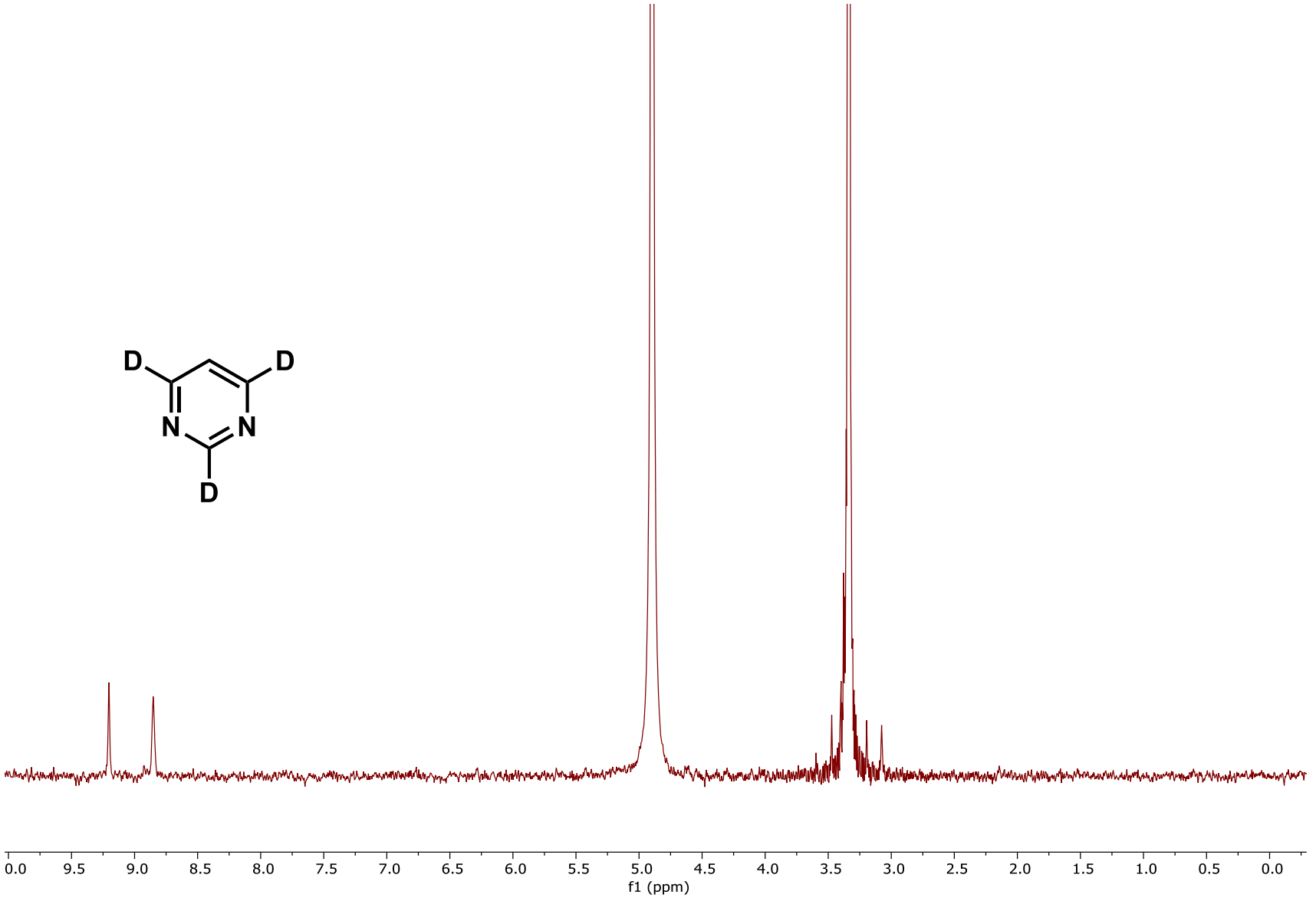
^{2}H NMR (77 MHz, CH_3OH) of 1-methyl-2-d_1-benzimidazole **[D]-3n**.



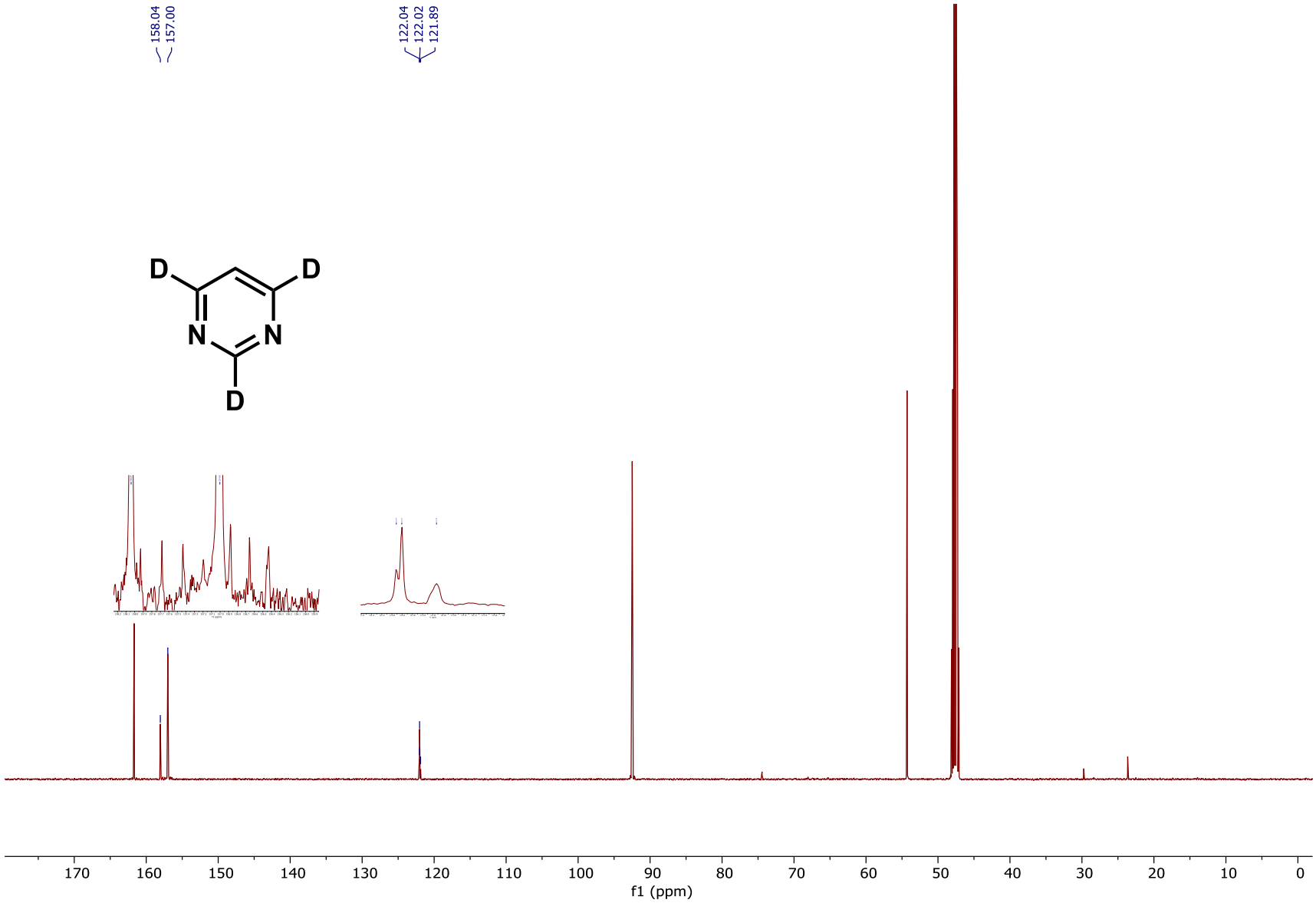
^{13}C NMR (125 MHz, CD_3OD) of 1-methyl-2-d_1-benzimidazole **[D]-3n**.



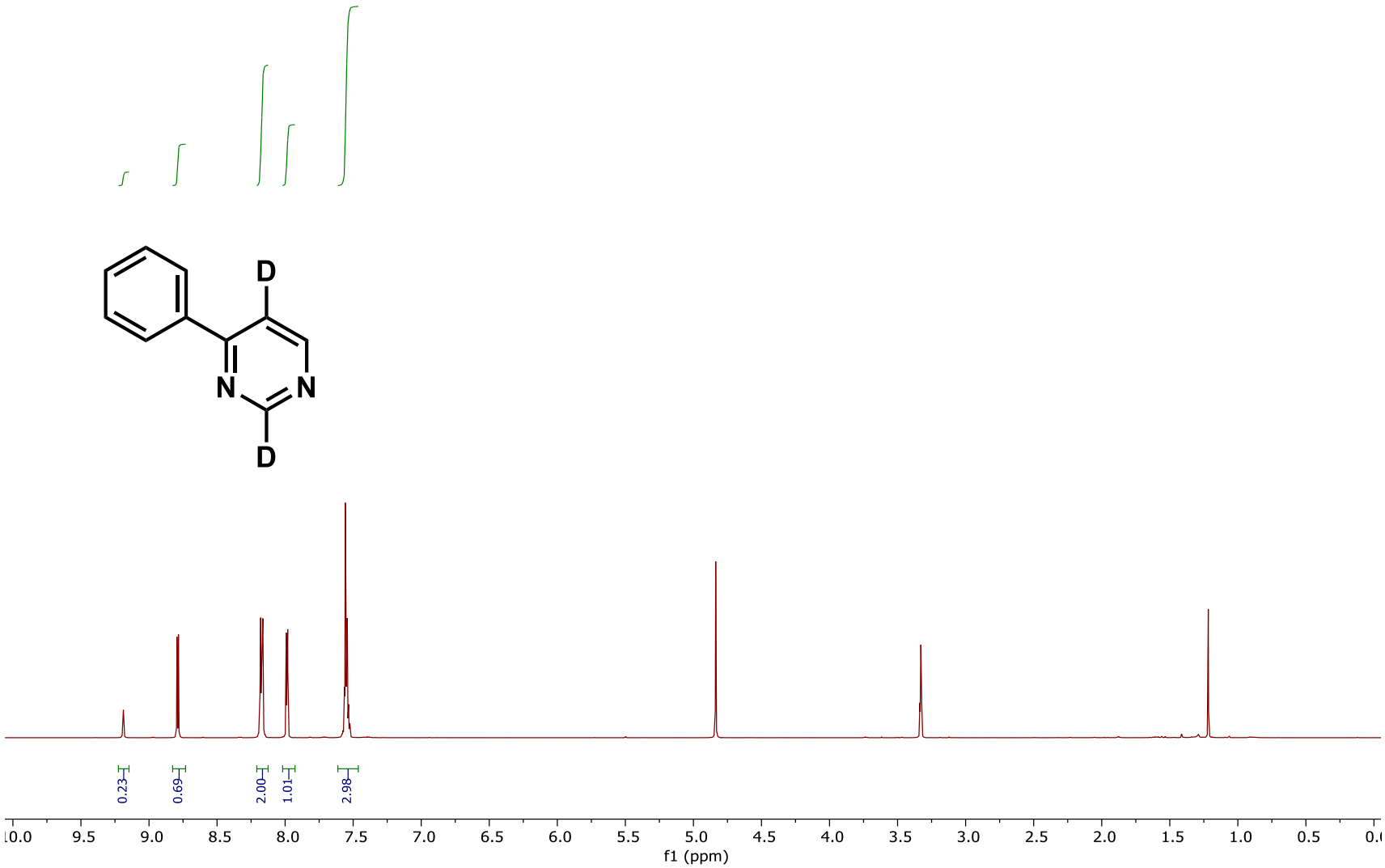
^{1}H NMR (500 MHz, CD_3OD) of 2,4,6-d_3-pyrimidine **[D]-3o**.



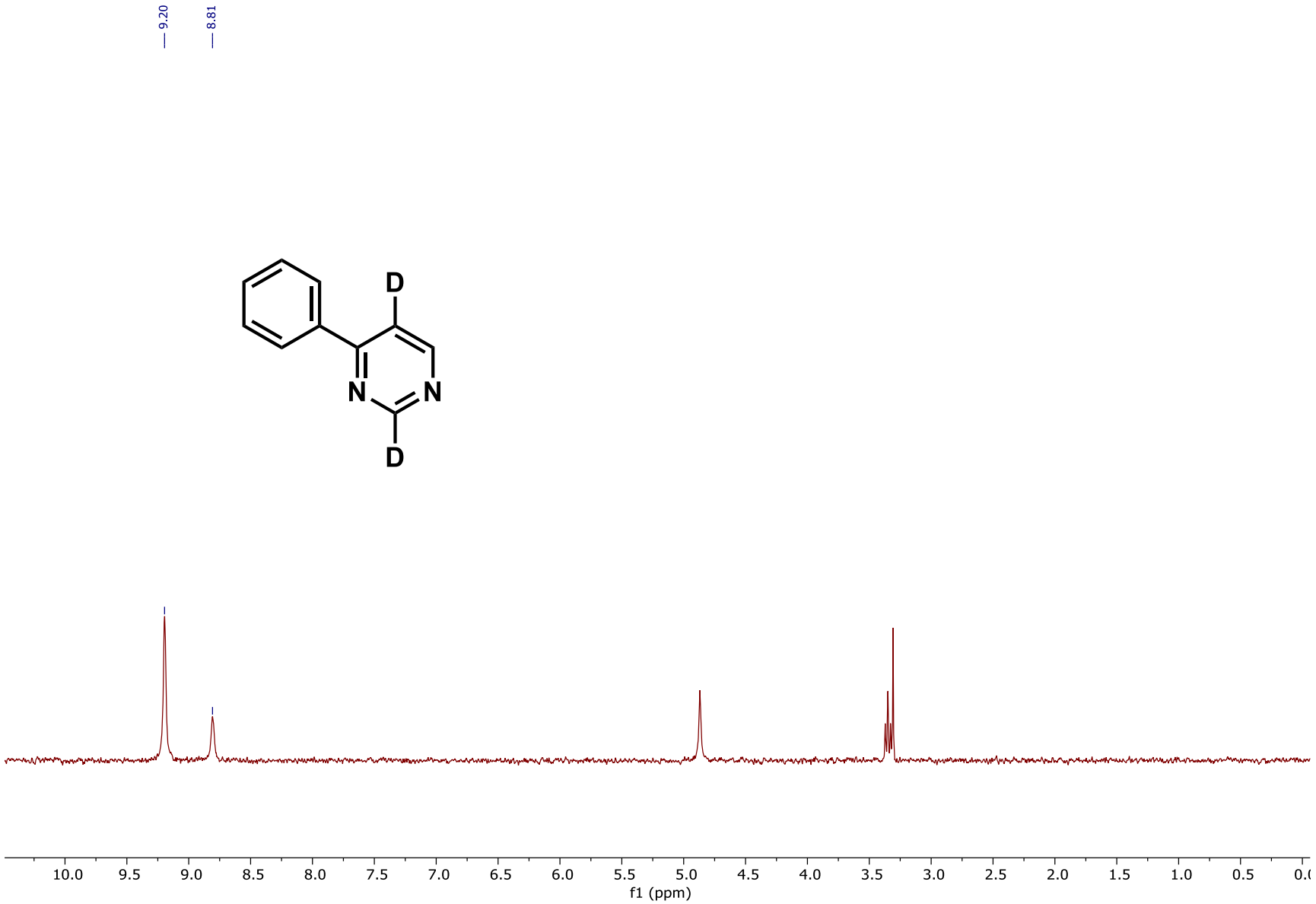
^{2}H NMR (77 MHz, CD_3OD) of 2,4,6-d_3-pyrimidine **[D]-3o**.



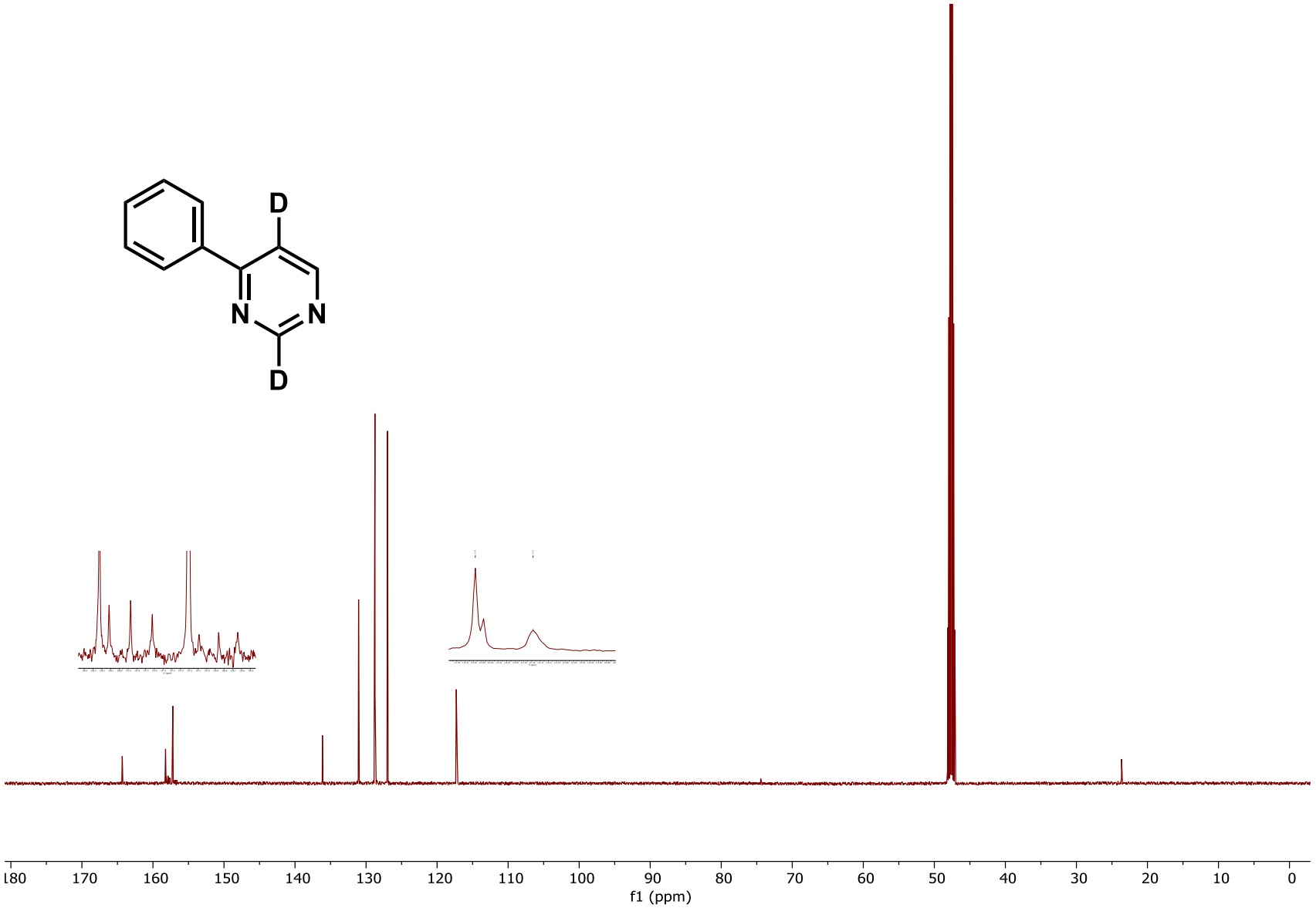
^{13}C NMR (125 MHz, CD_3OD) of 2,4,6-d_3-pyrimidine **[D]-3o**.



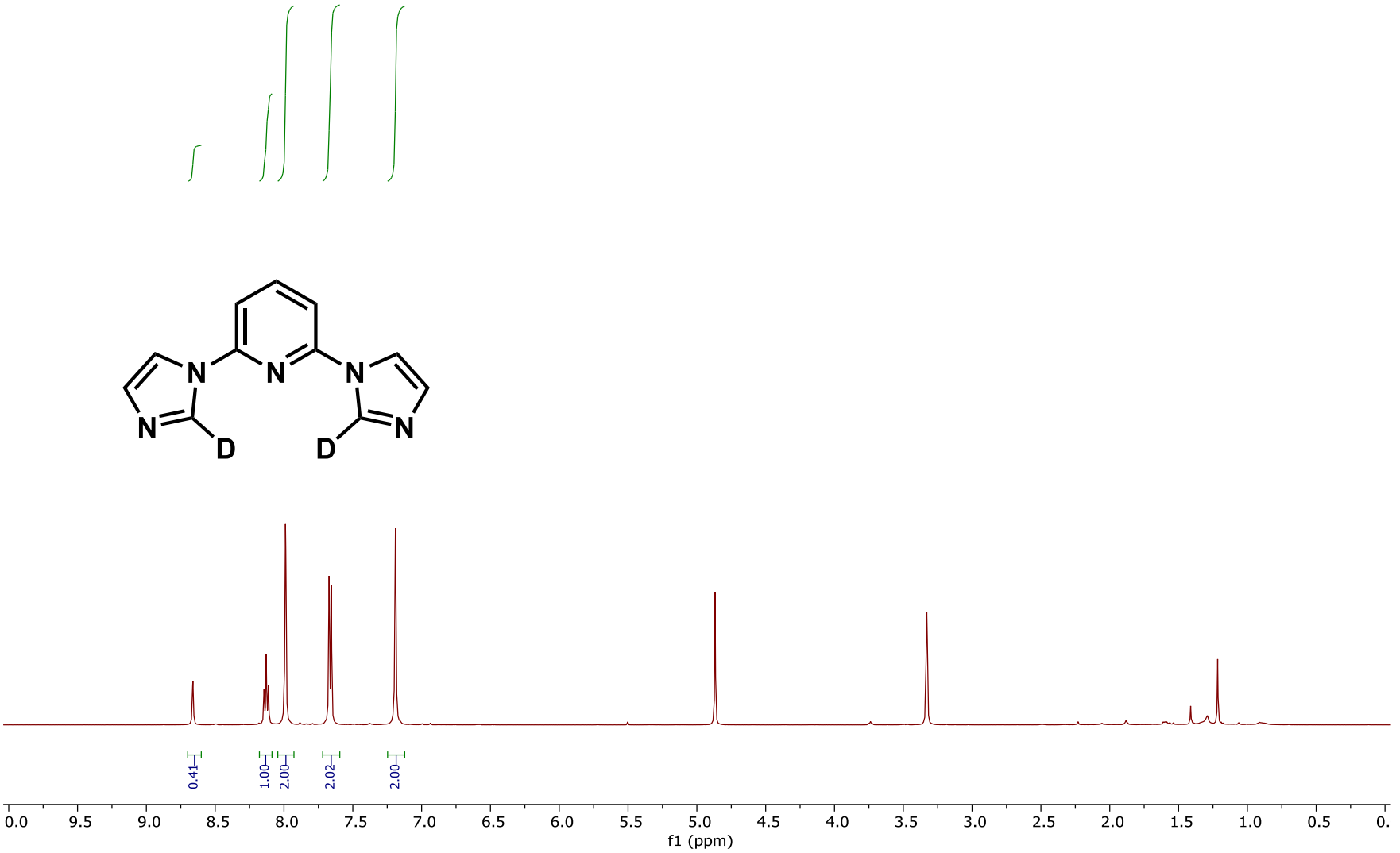
^{1}H NMR (500 MHz, CD_3OD) of 4-phenyl-2,5-d_2-pyrimidine **[D]-3p**.



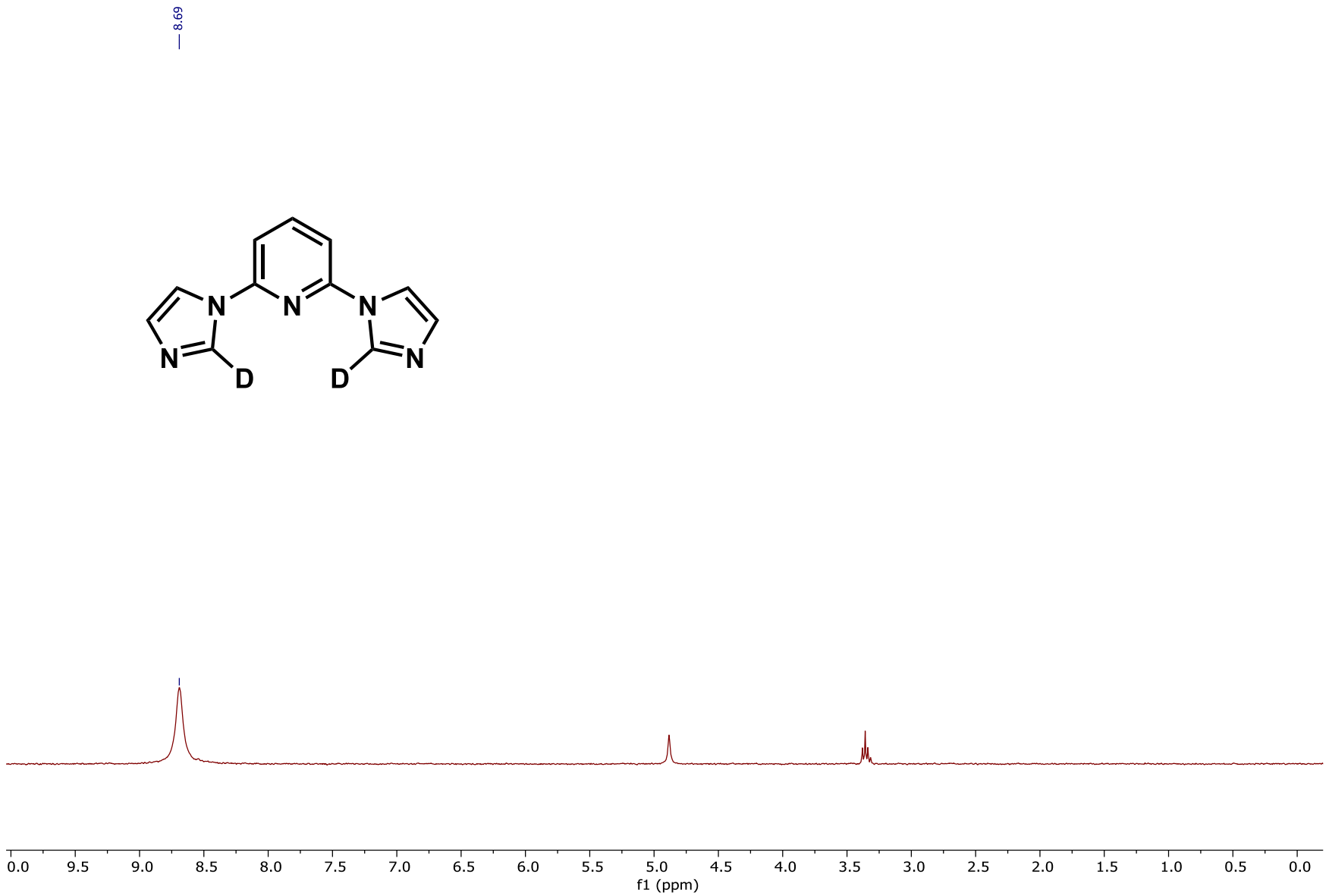
^{2}H NMR (77 MHz, CH_3OH) of 4-phenyl-2,5-d_2-pyrimidine **[D]-3p** – containing residual d_4-MeOD.



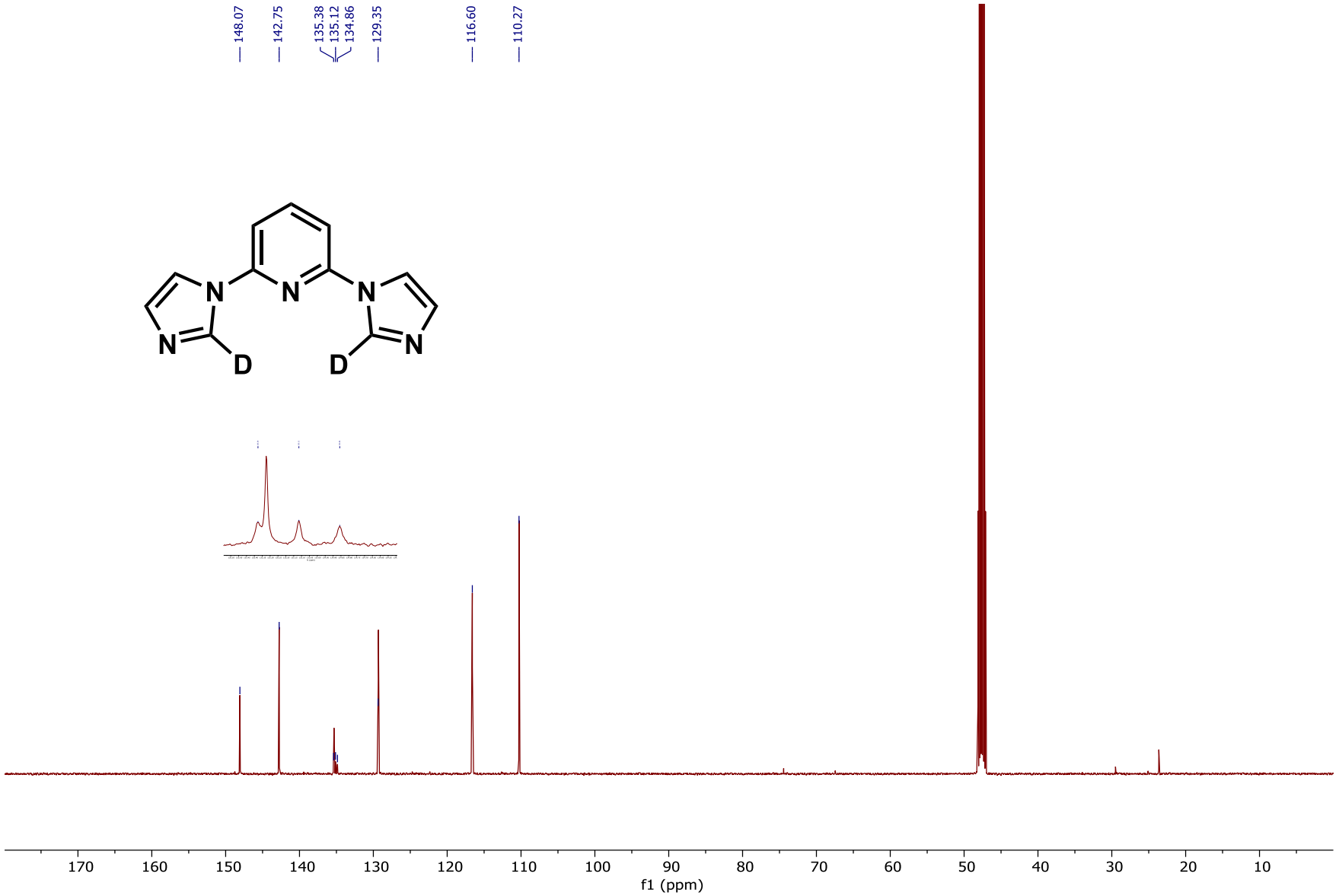
^{13}C NMR (125 MHz, CD_3OD) of 4-phenyl-2,5-d_2-pyrimidine **[D]-3p**.



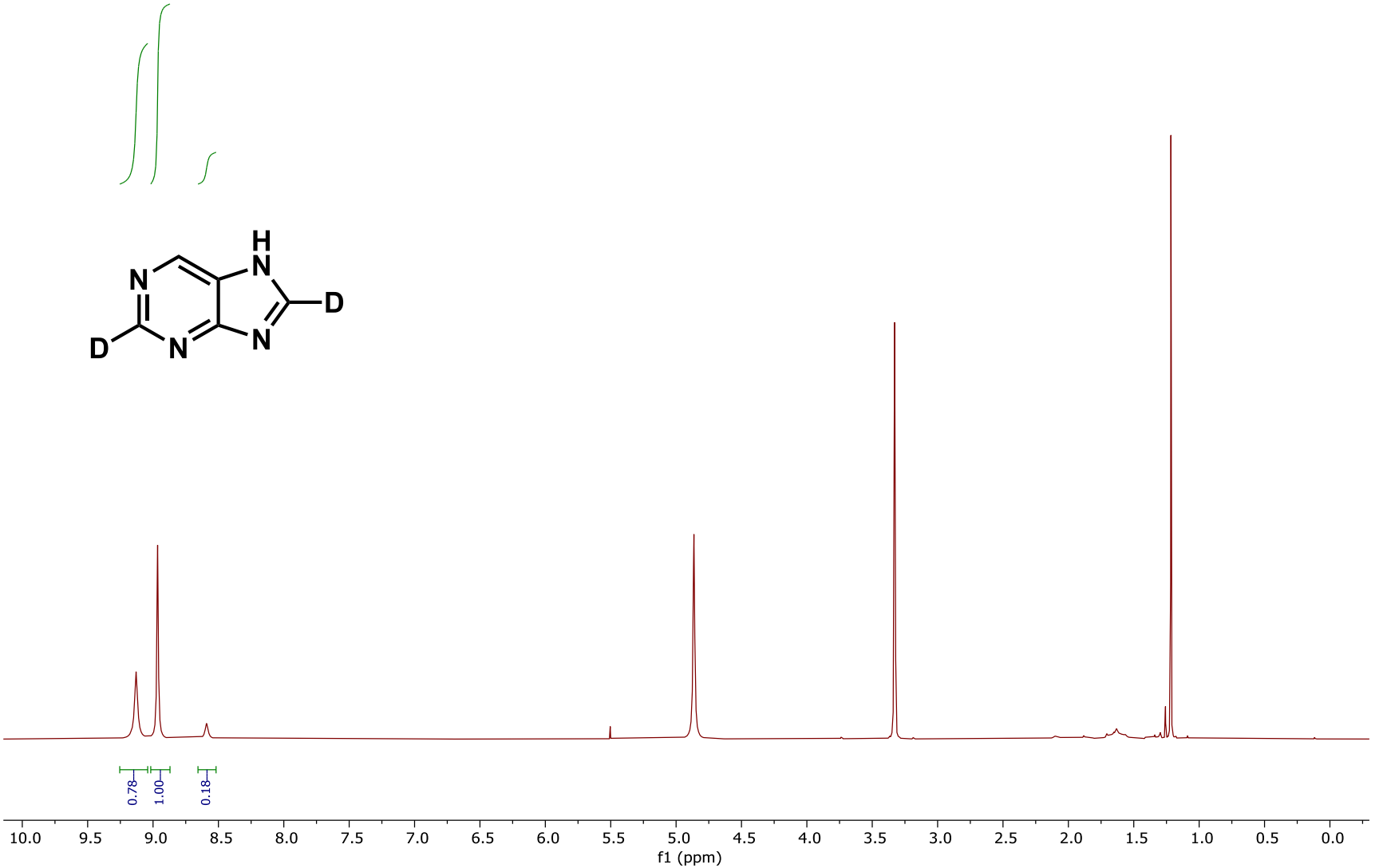
^{1}H NMR (500 MHz, CD_3OD) of 2,6-bis(1-imidazolyl)pyridine-*d*$_1$ **[D]-3q**.



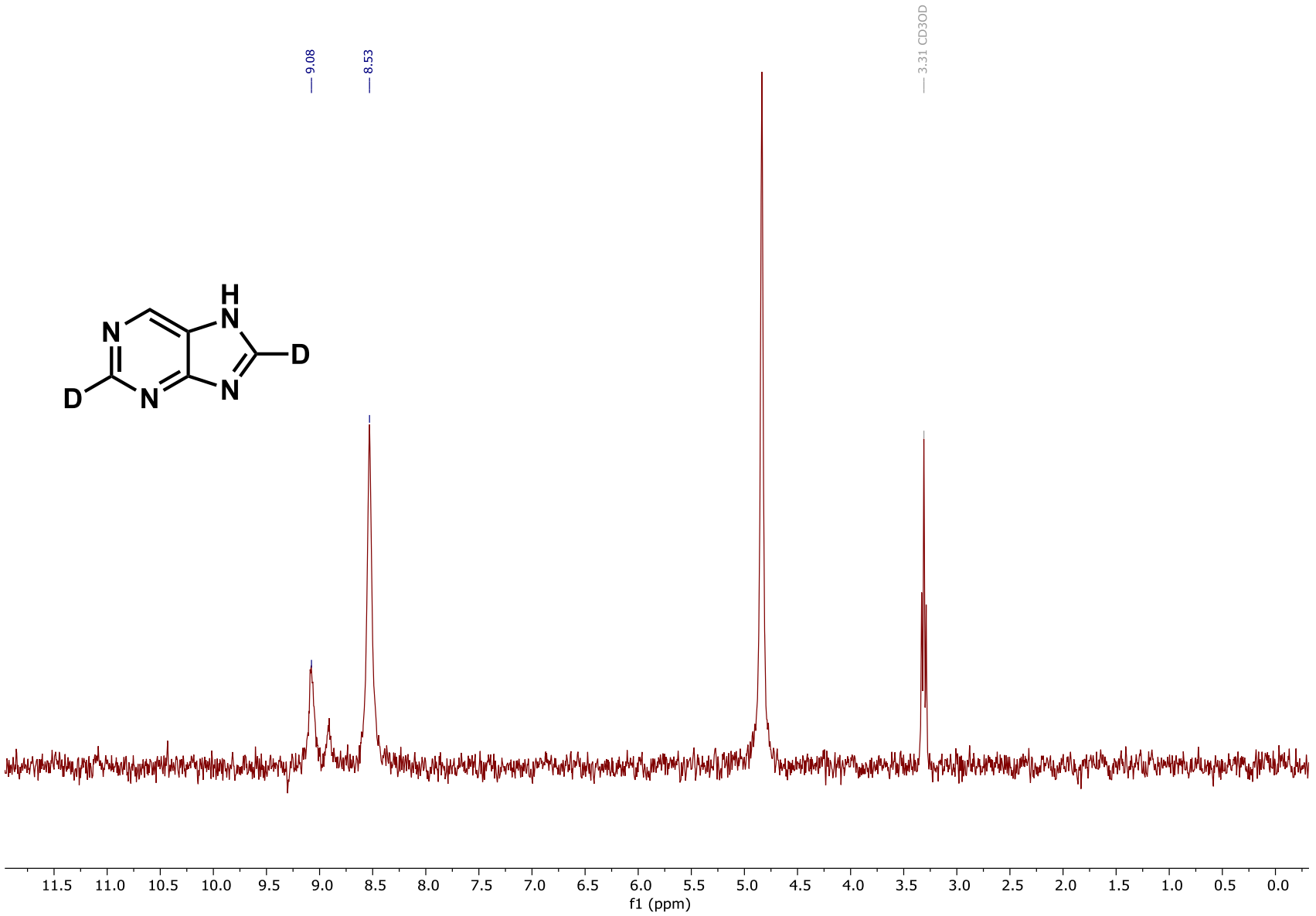
^{2}H NMR (77 MHz, CH_3OH) of 2,6-bis(1-imidazolyl)pyridine-d_1 **[D]-3q** – containing residual d_4-MeOD.



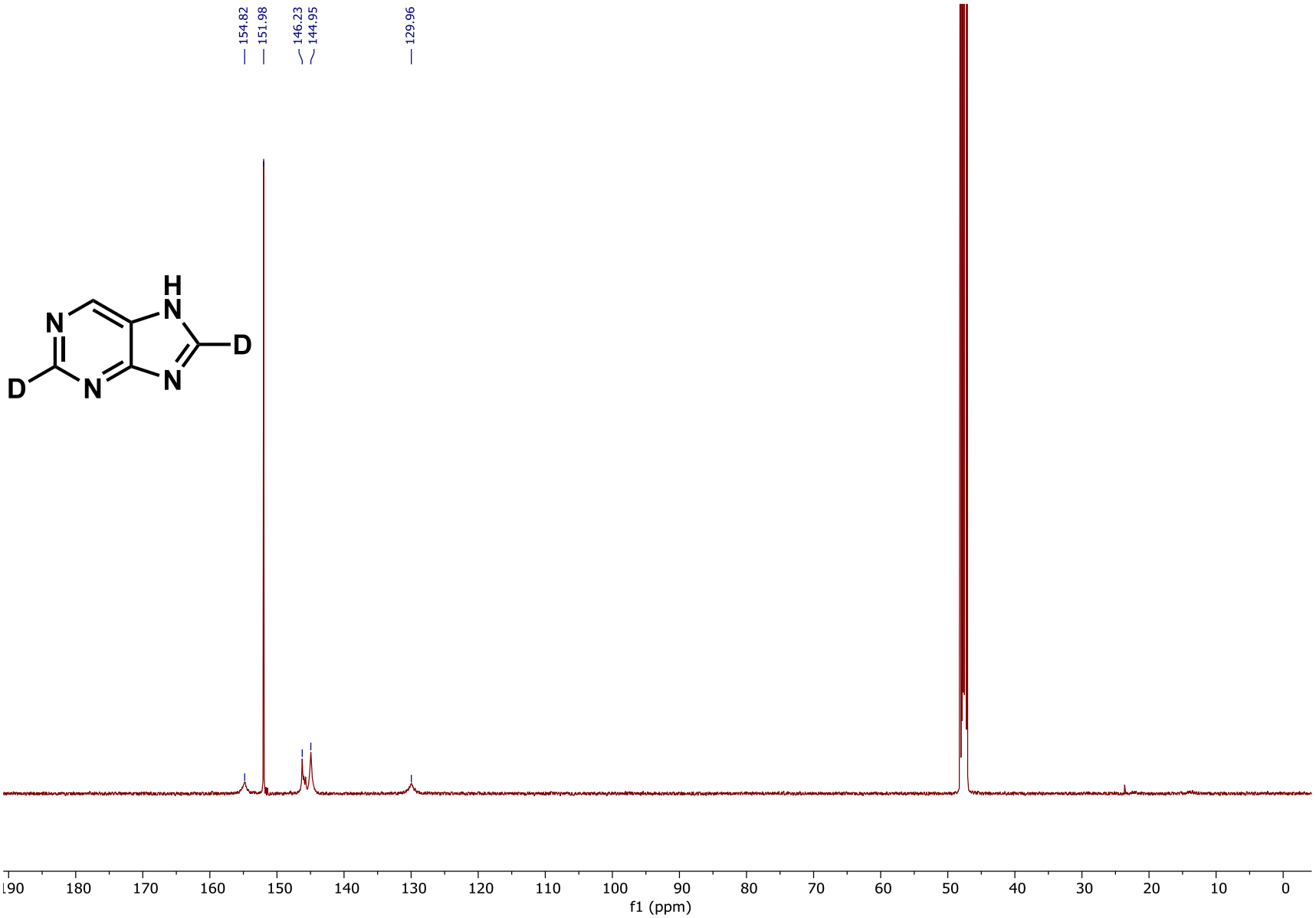
^{13}C NMR (125 MHz, CD_3OD) of 2,6-bis(1-imidazolyl)pyridine-d_1 **[D]-3q**.



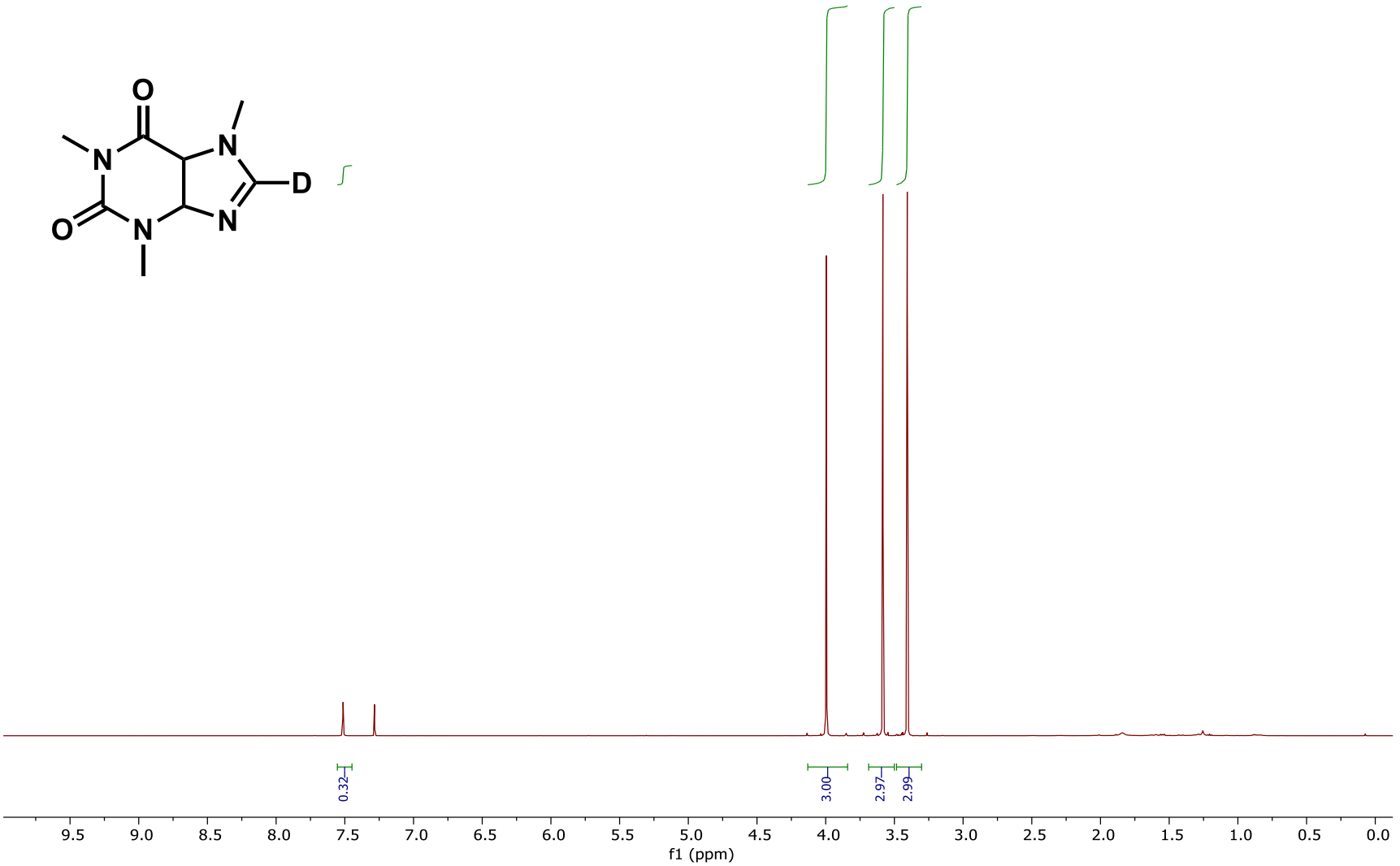
^{1}H NMR (500 MHz, CD_3OD) of of 7H-purine-2,8-d_2 **[D]-3r**.



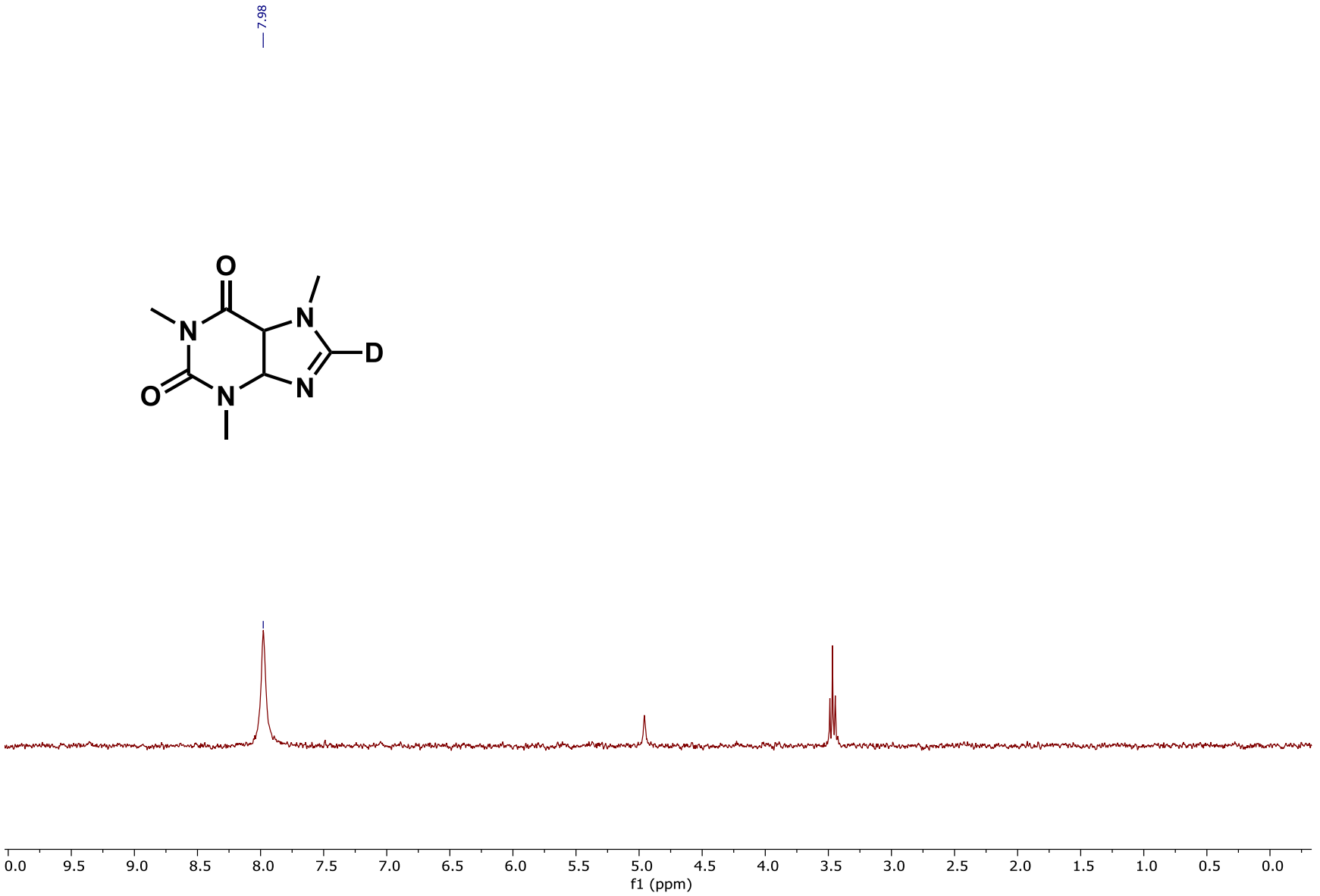
^{2}H NMR (77 MHz, CH_3OH) of of 7H-purine-2,8-d_2 **[D]-3r** – containing residual d_4-MeOD.



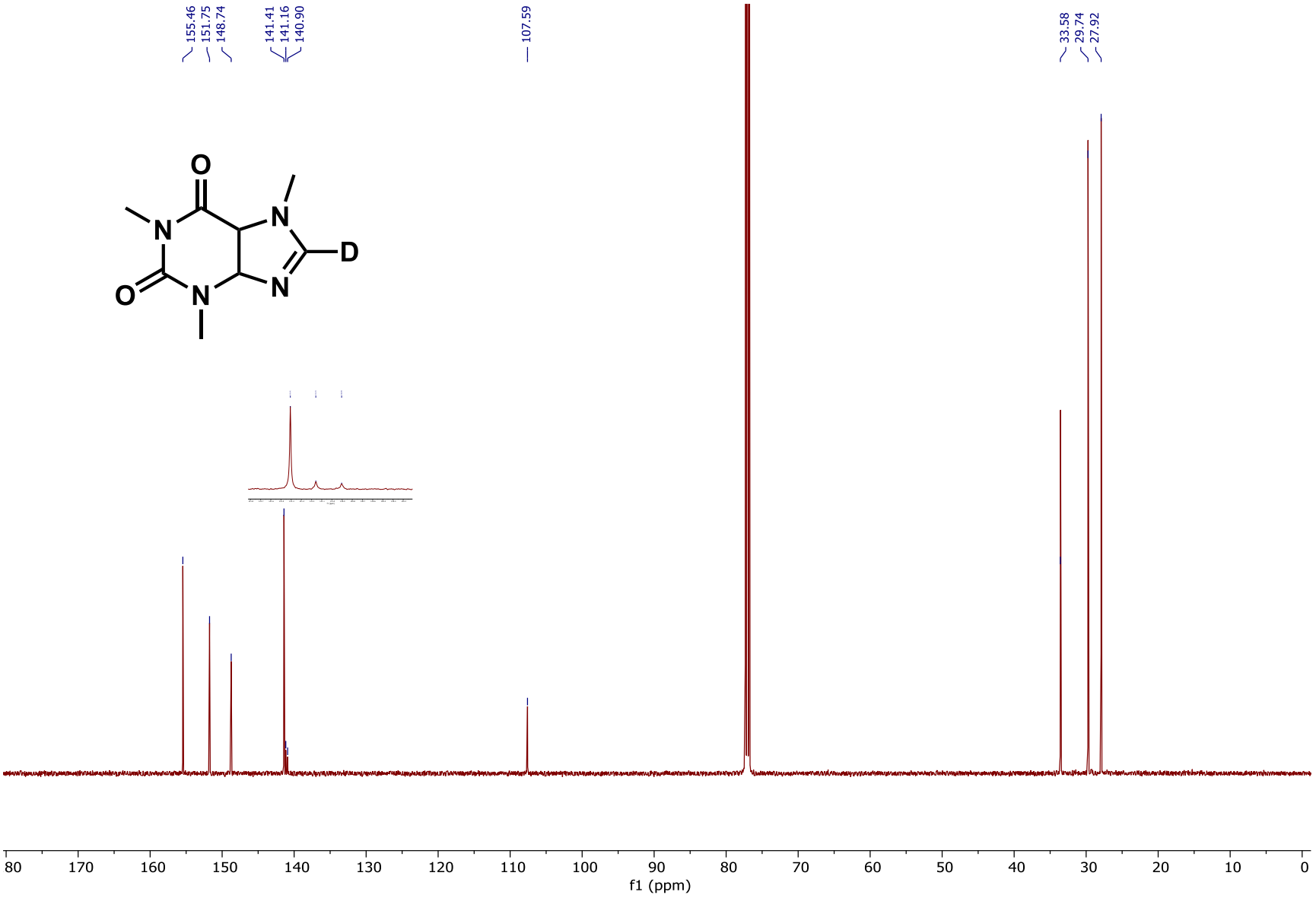
^{13}C NMR (150 MHz, CD_3OD) of 7H-purine-2,8-d_2 **[D]-3r**.



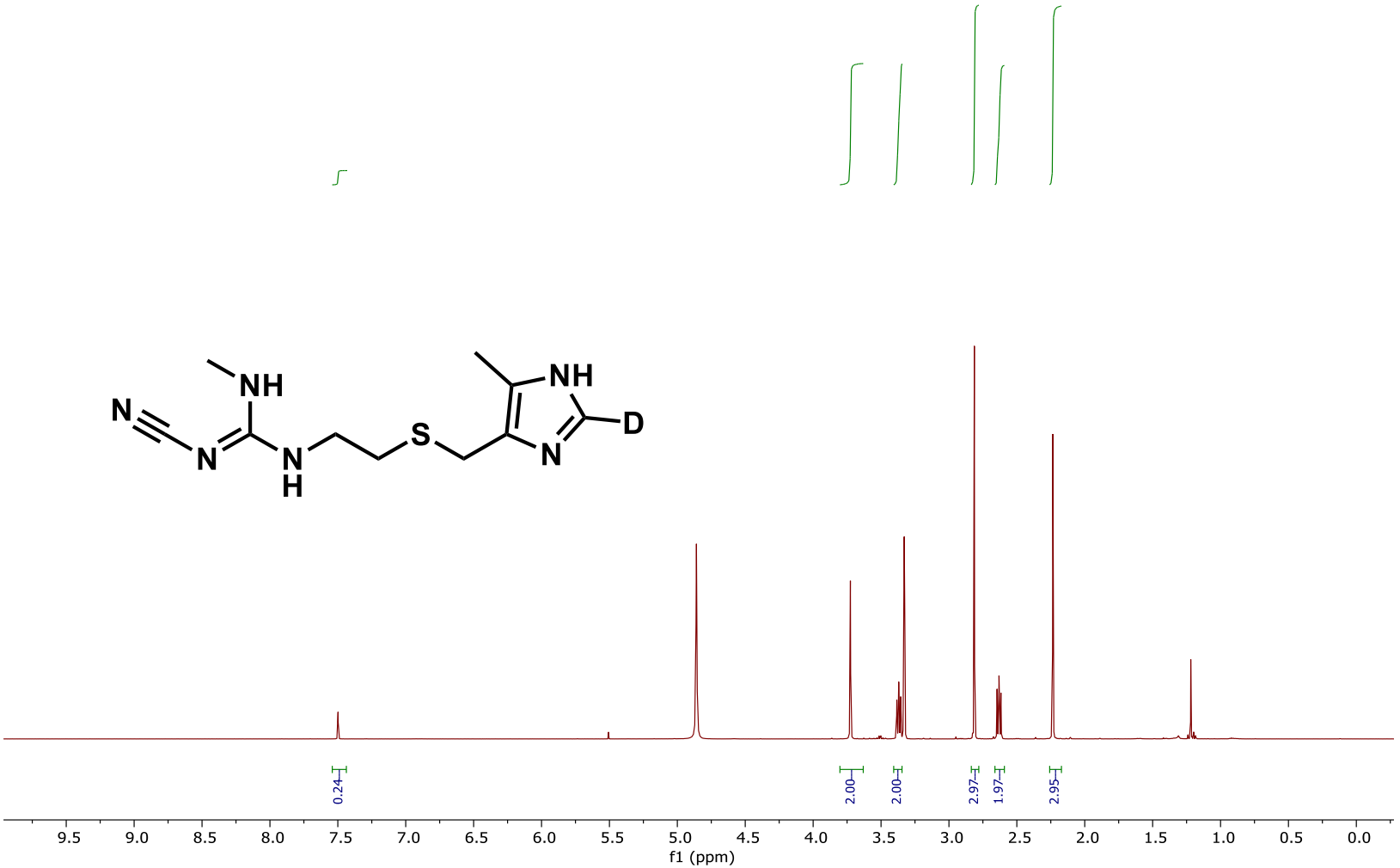
^{1}H NMR (500 MHz, $CDCl_3$) of Caffeine-d_1 **[D]-3s**.



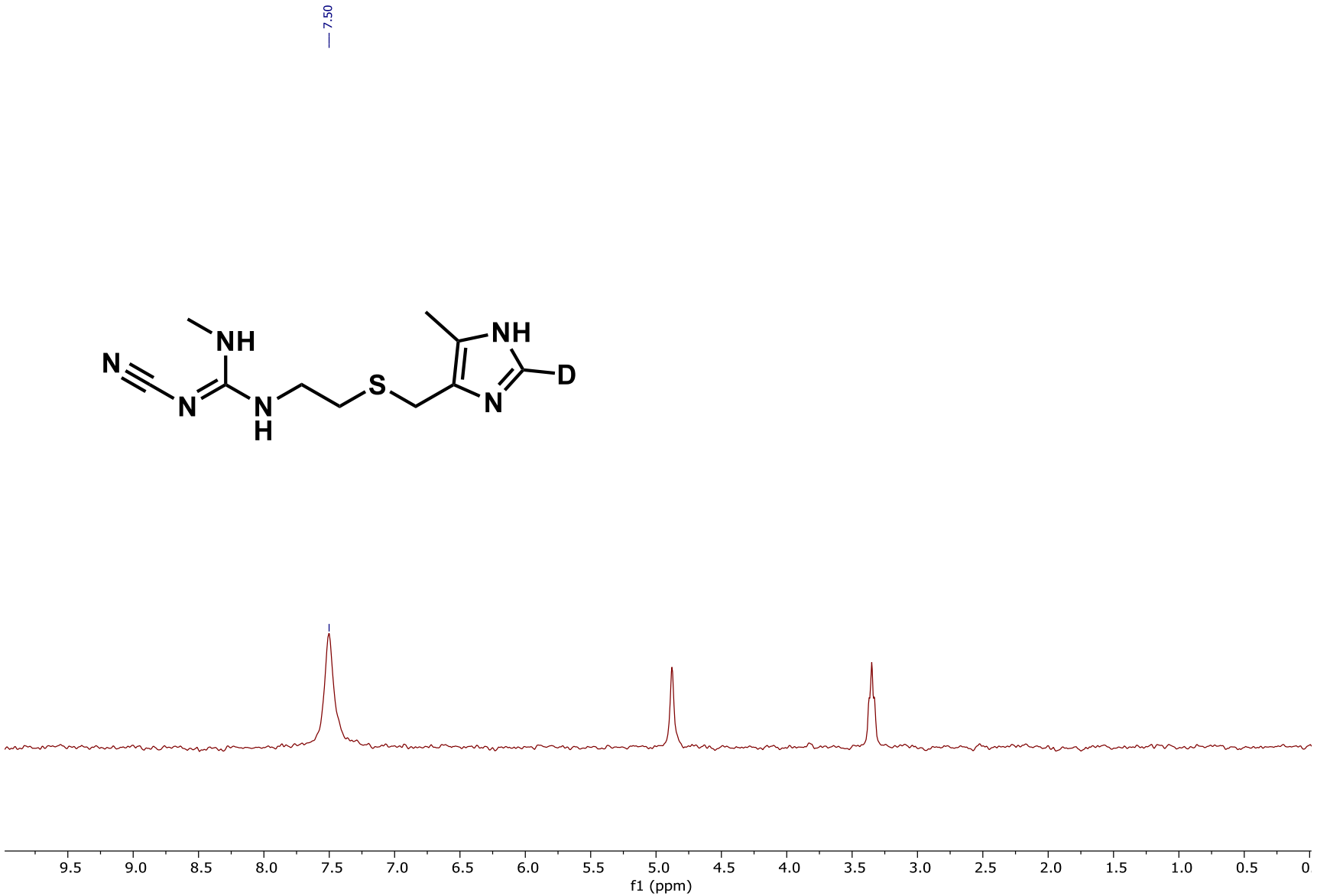
^{2}H NMR (77 MHz, $CHCl_3$) of Caffeine-*d*$_1$ **[D]-3s** – containing residual *d*$_4$-MeOD.



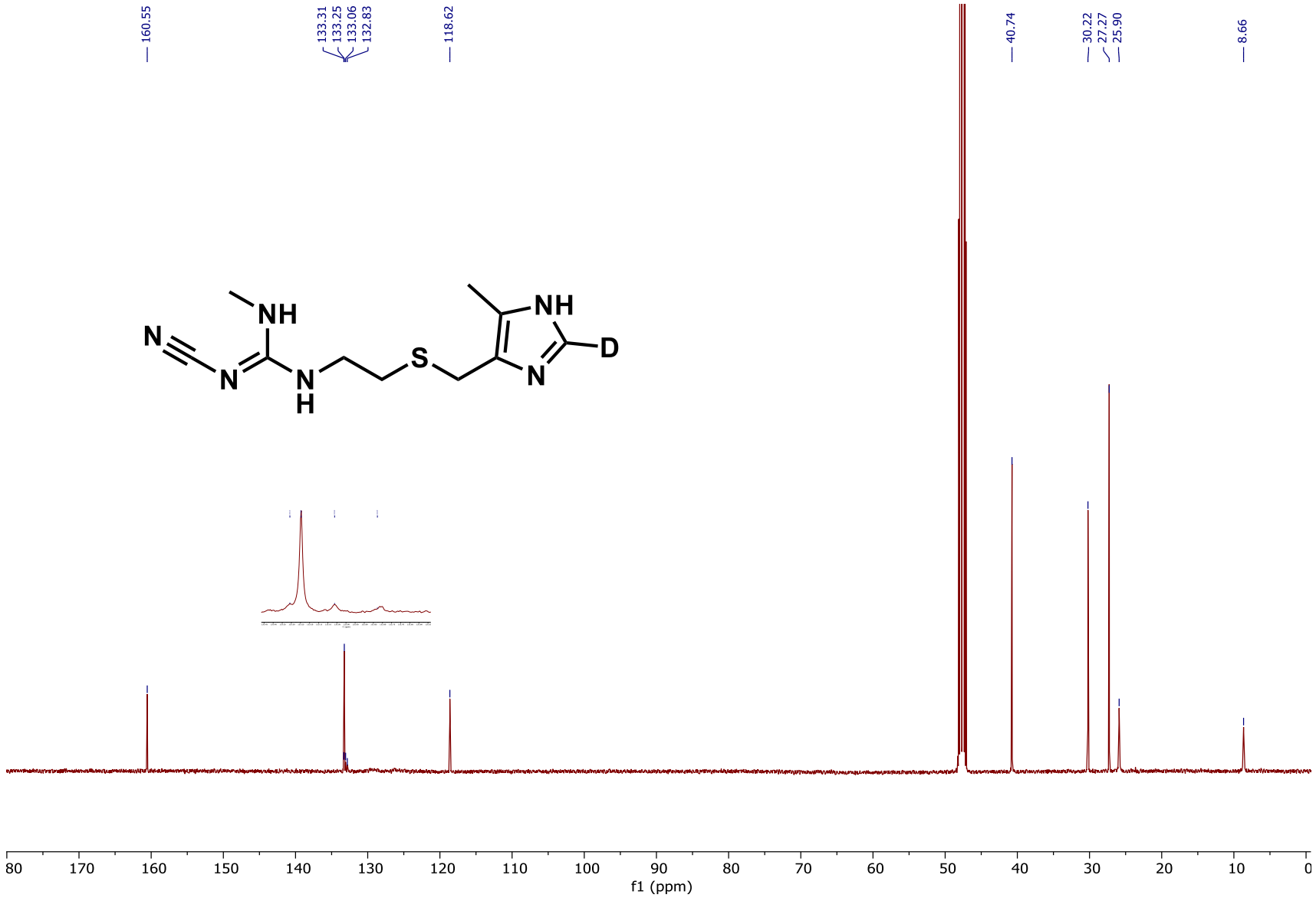
^{13}C NMR (125 MHz, $CDCl_3$) of Caffeine-*d*$_1$ **[D]-3s**.



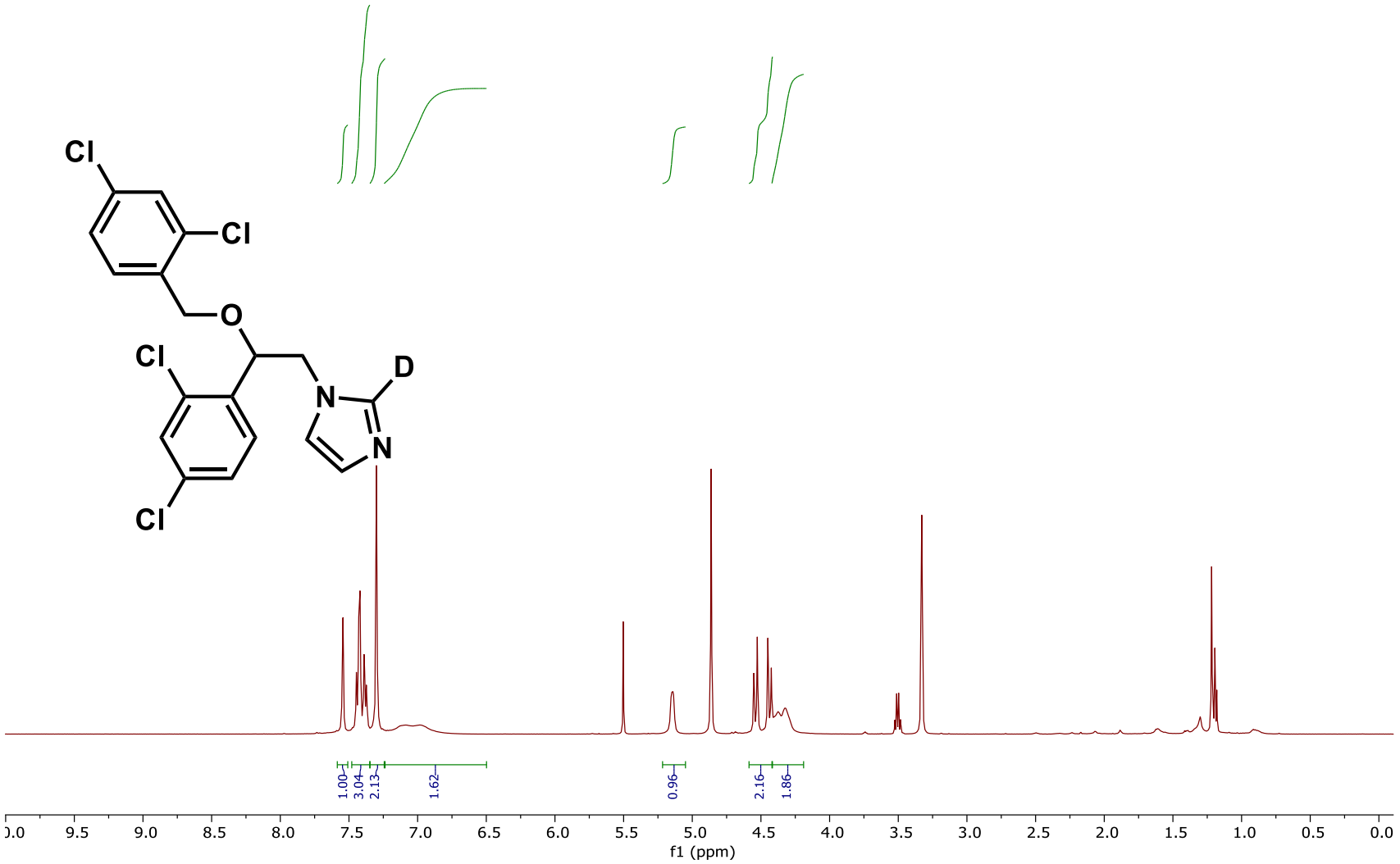
^{1}H NMR (500 MHz, CD_3OD) of Cimetidine-d_1 **[D]-3t**.



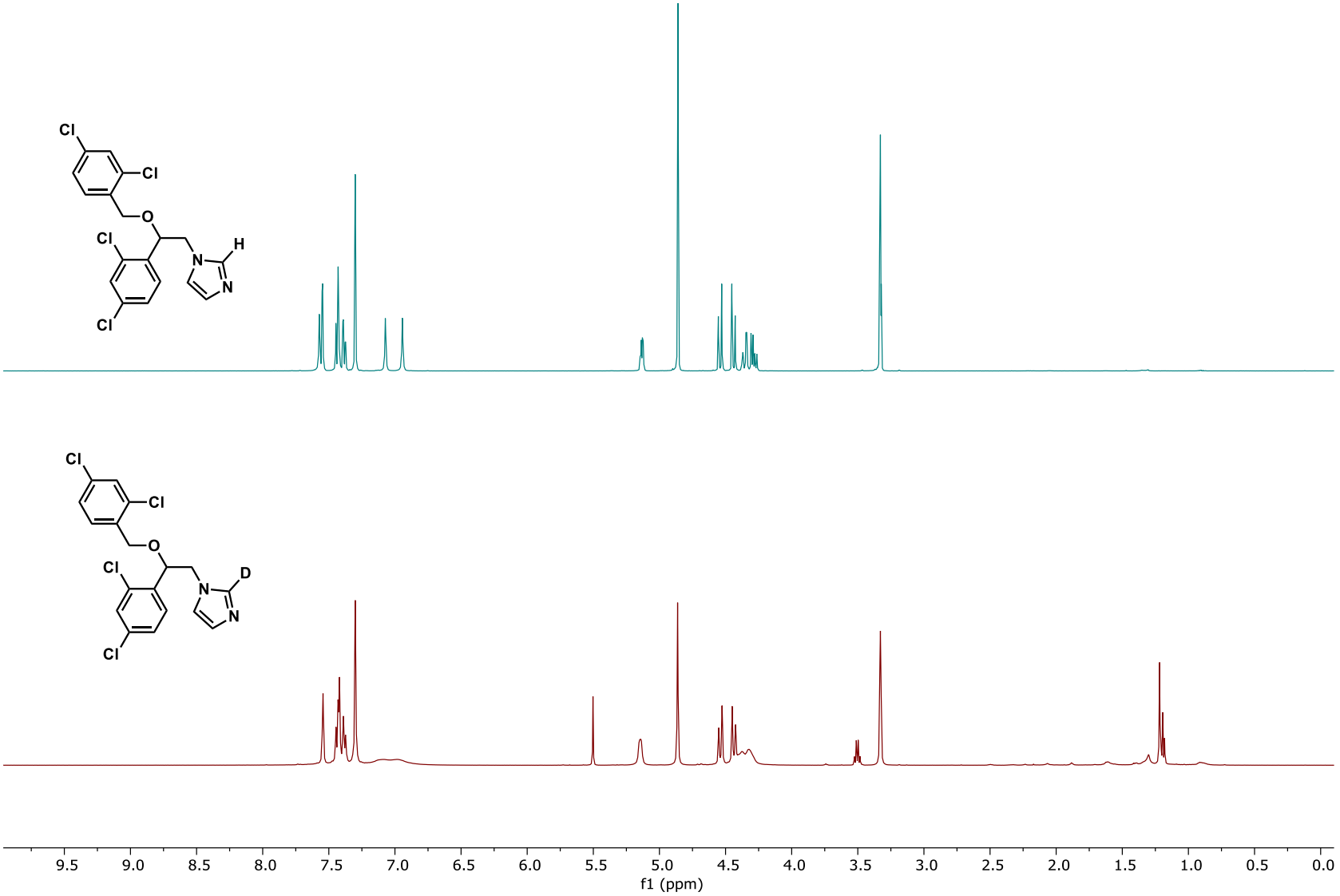
^{2}H NMR (77 MHz, CH_3OH) of Cimetidine-d_1 **[D]-3t** – containing residual d_4-MeOD.



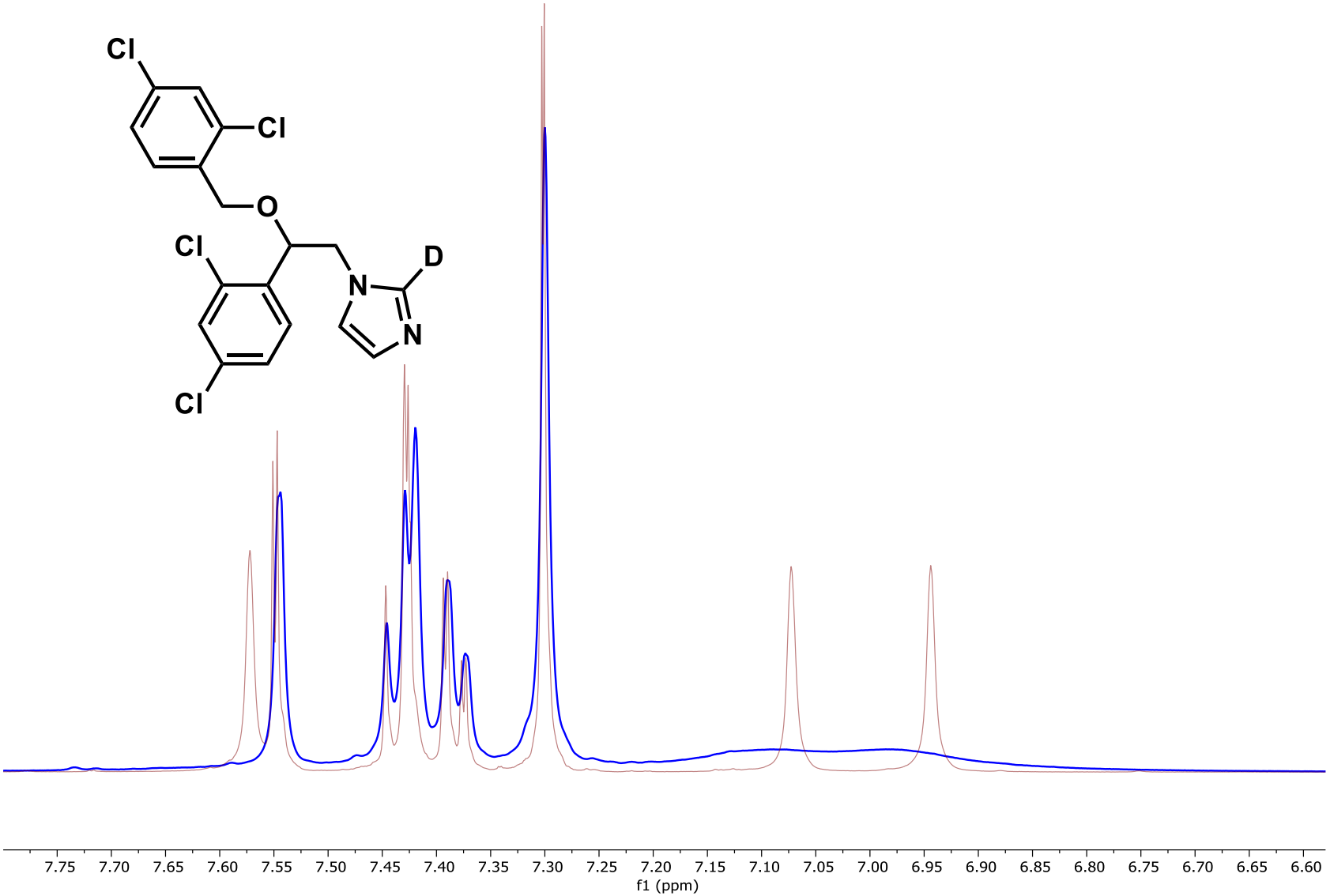
^{13}C NMR (125 MHz, CD_3OD) of Cimetidine-d_1 **[D]-3t**.



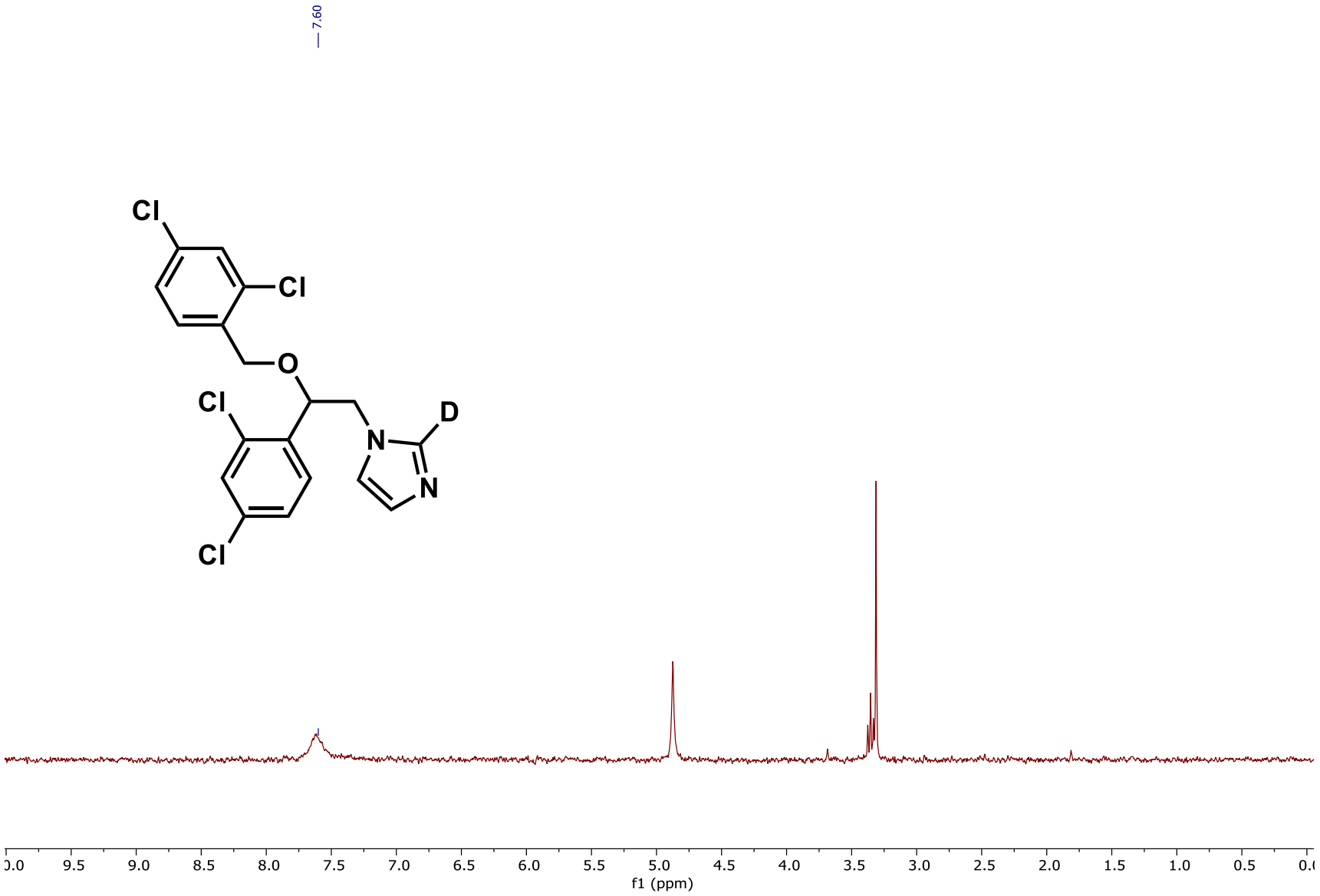
^{1}H NMR (500 MHz, CD_3OD) of Miconazole-*d*$_1$ **[D]-3u**.



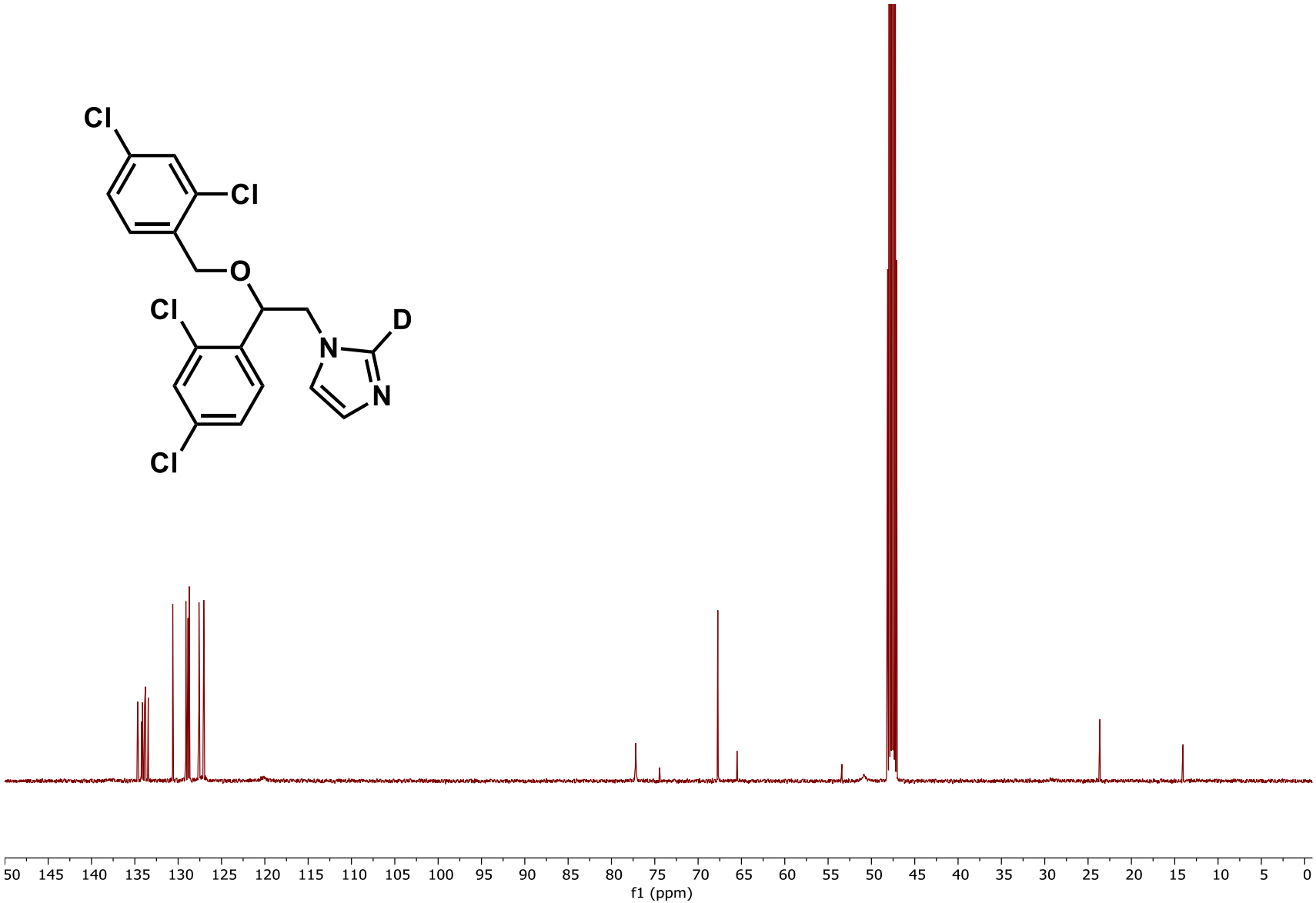
^{1}H NMR (500 MHz, CD_3OD) stacked comparison of Miconazole **3u** (top) and Miconazole-d_1 **[D]-3u** (bottom).



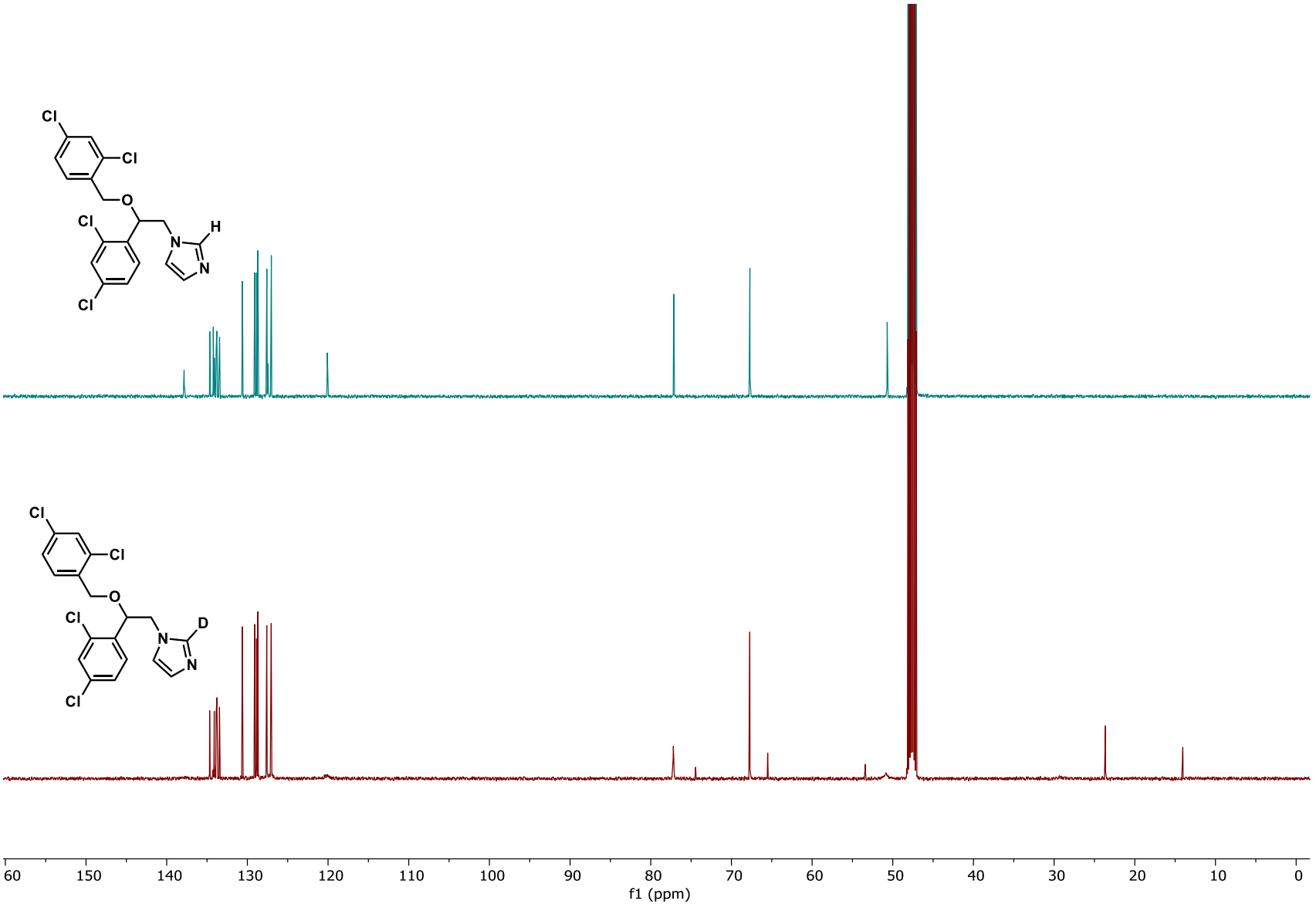
^{1}H NMR (500 MHz, CD_3OD) downfield region, superimposed comparison of Miconazole **3u** (maroon) and Miconazole-d_1 **[D]-3u** (blue).



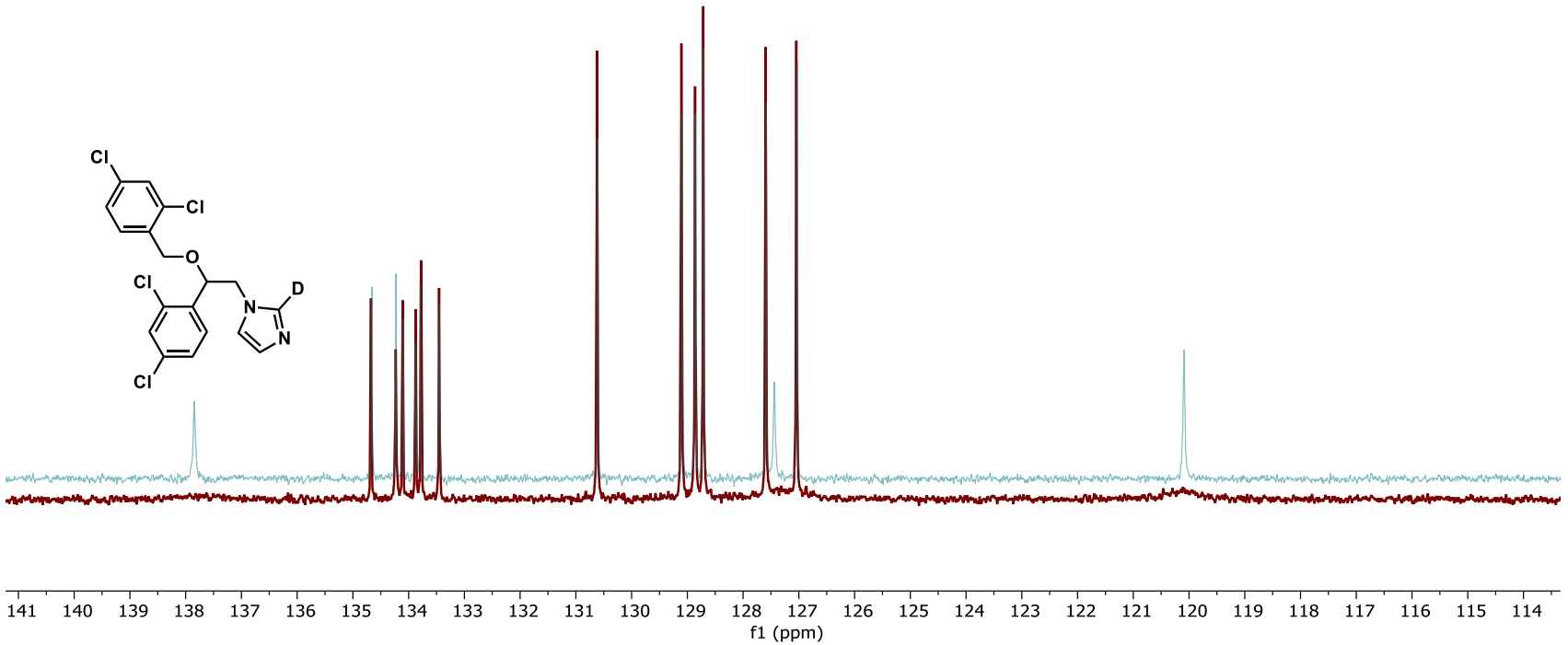
^{2}H NMR (77 MHz, CH_3OH) of Miconazole-d_1 **[D]-3u** – containing residual d_4-MeOD.



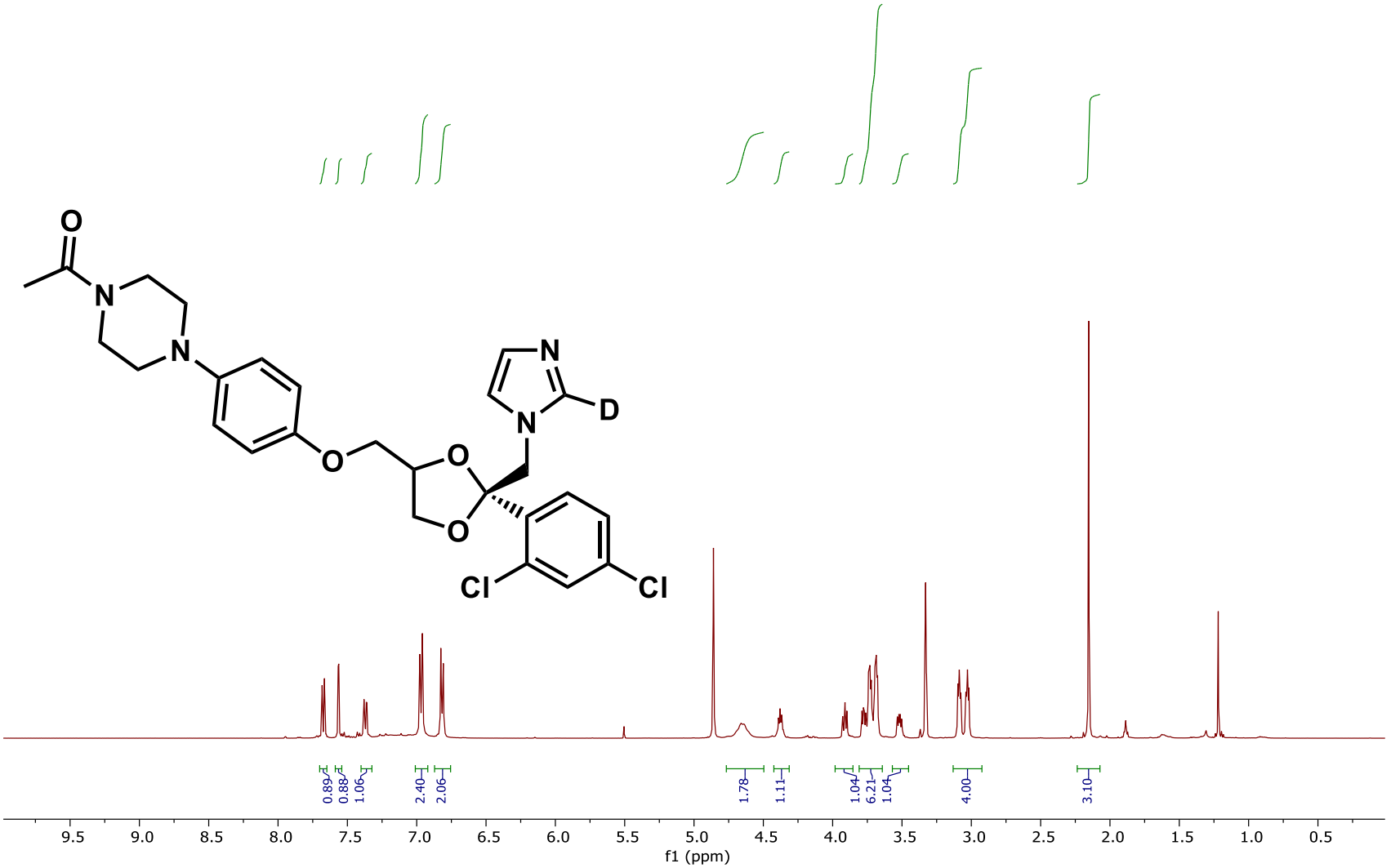
^{13}C NMR (125 MHz, CD_3OD) of Miconazole-*d*$_1$ **[D]-3u**.



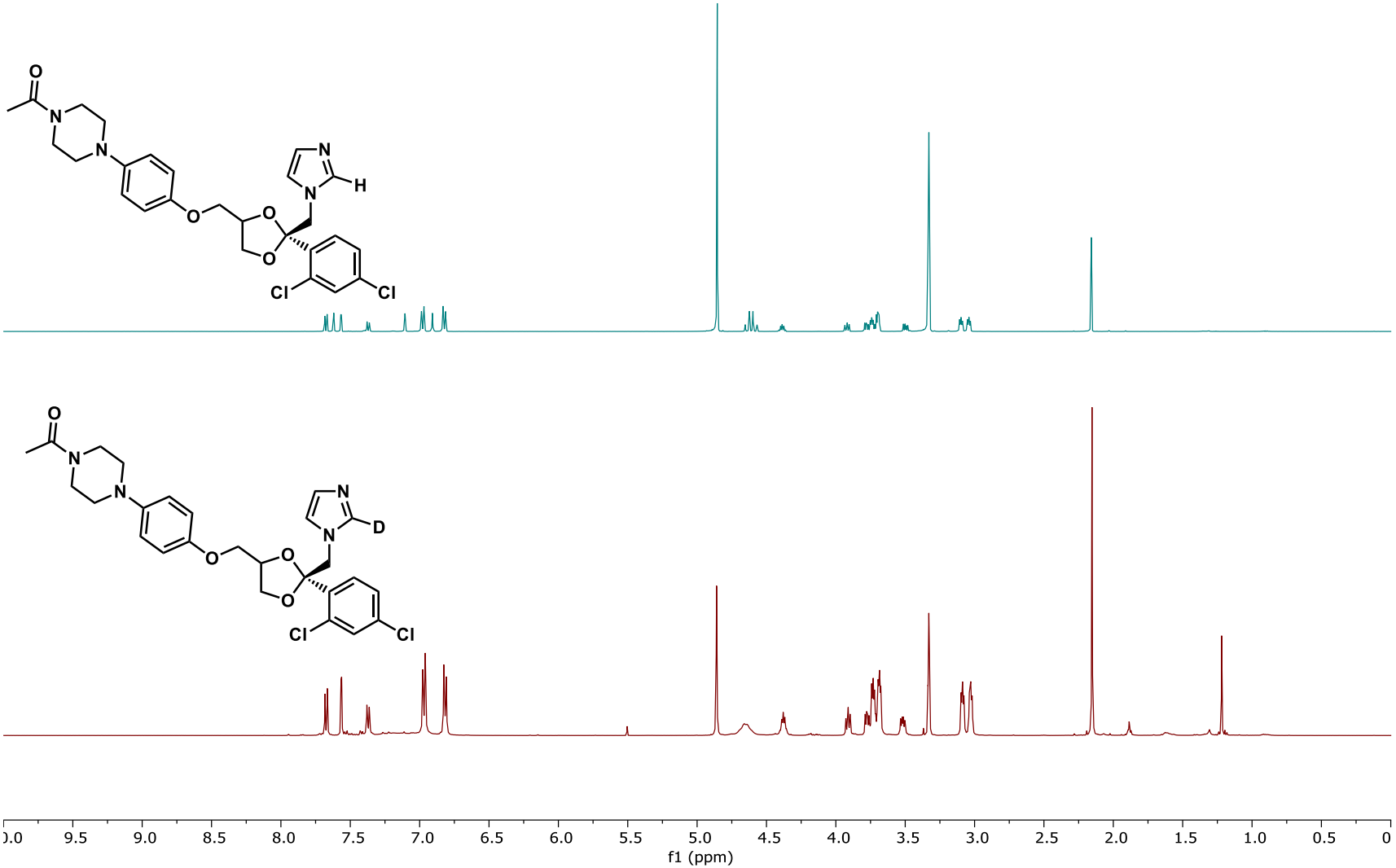
^{13}C NMR (125 MHz, CD_3OD) stacked comparison of Miconazole **3u** (top) and Miconazole-*d*$_1$ **[D]-3u** (bottom).



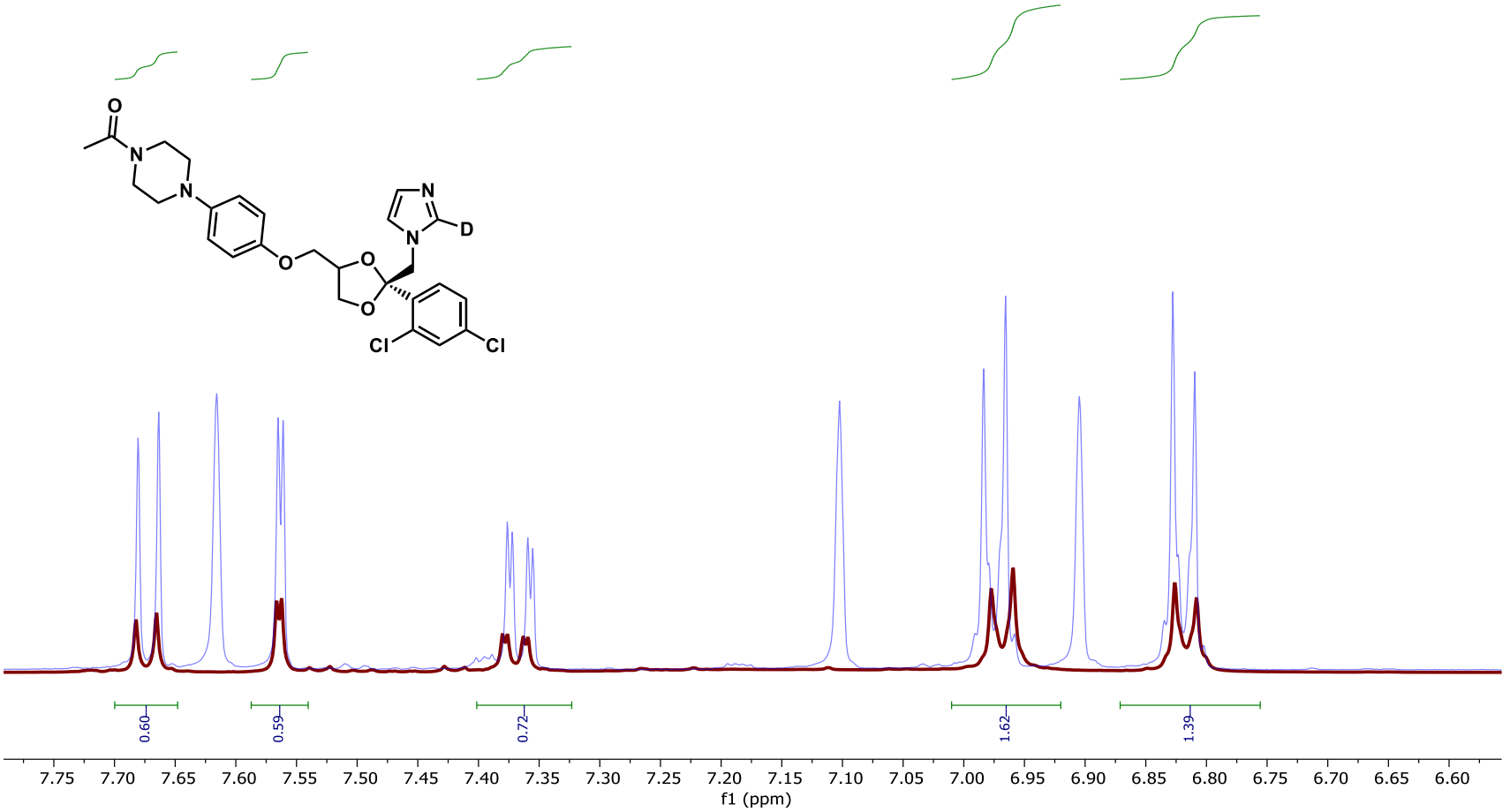
^{13}C NMR (125 MHz, CD_3OD) downfield region, superimposed comparison of Miconazole **3u** (cyan) and Miconazole-*d*$_1$ **[D]-3u** (maroon).



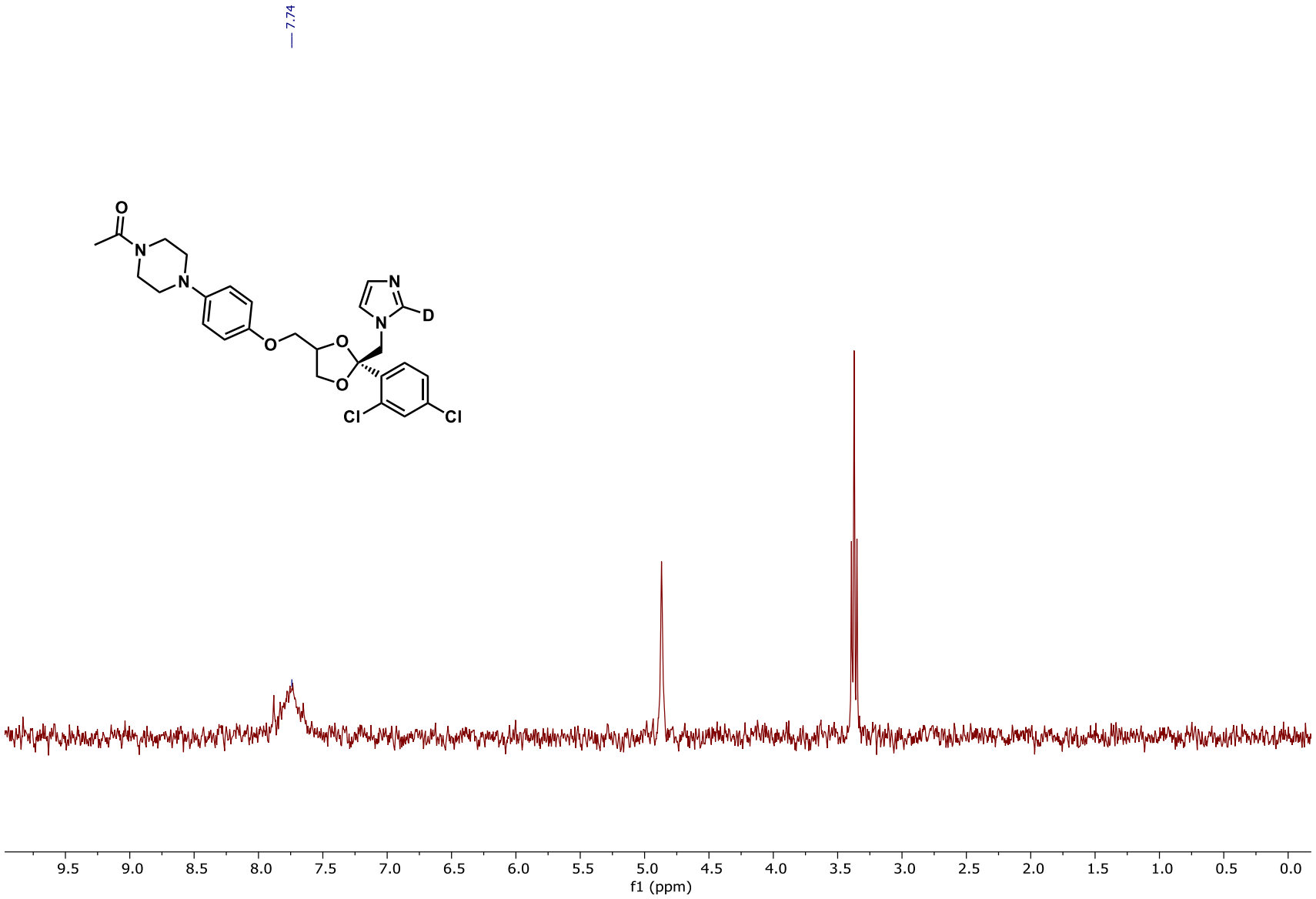
^{1}H NMR (500 MHz, CD_3OD) of Ketoconazole-d_1 **[D]-3v**.



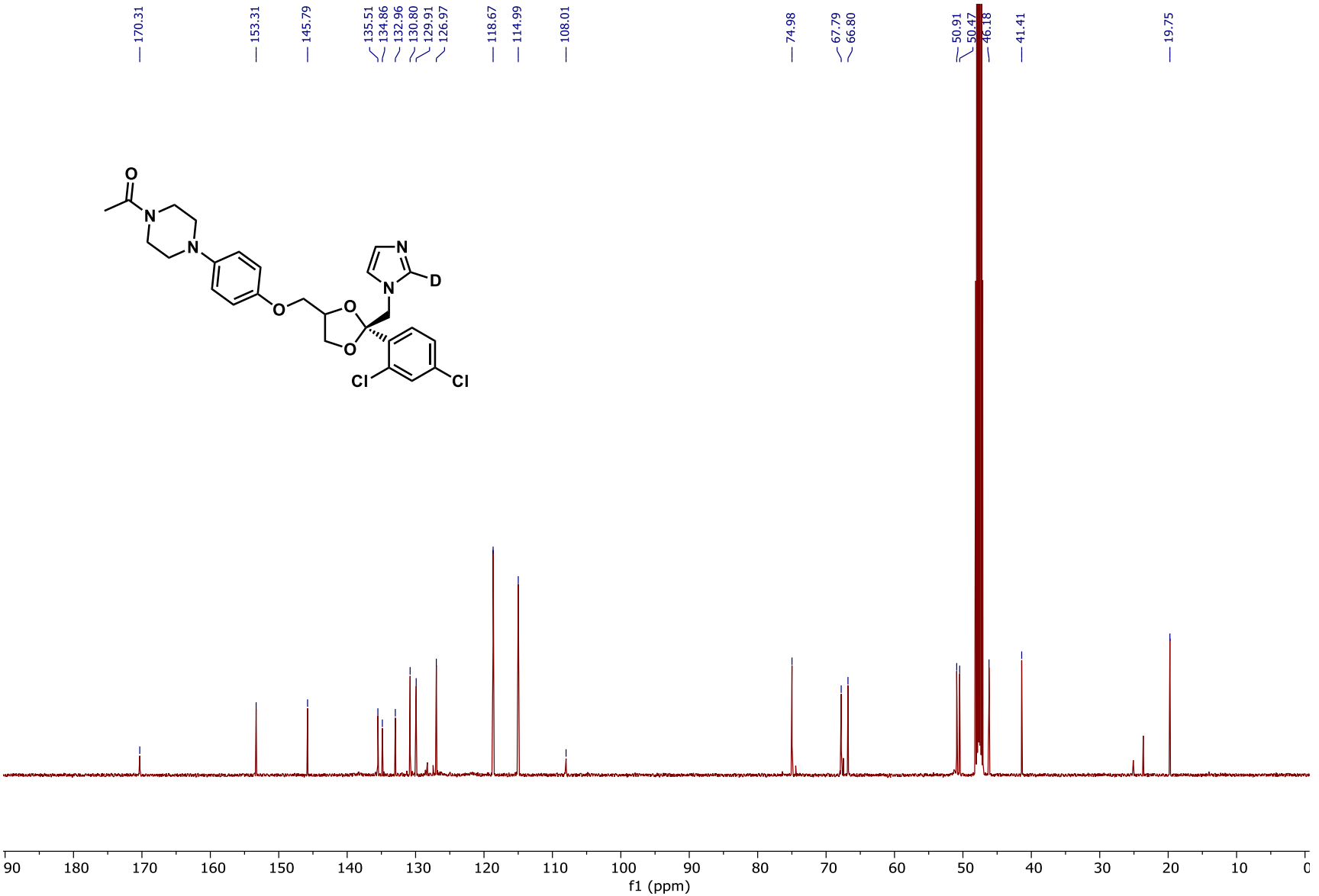
^{1}H NMR (500 MHz, CD_3OD) stacked comparison of Ketoconazole **3v** (top) and Ketoconazole-*d*$_1$ **[D]-3v** (bottom).



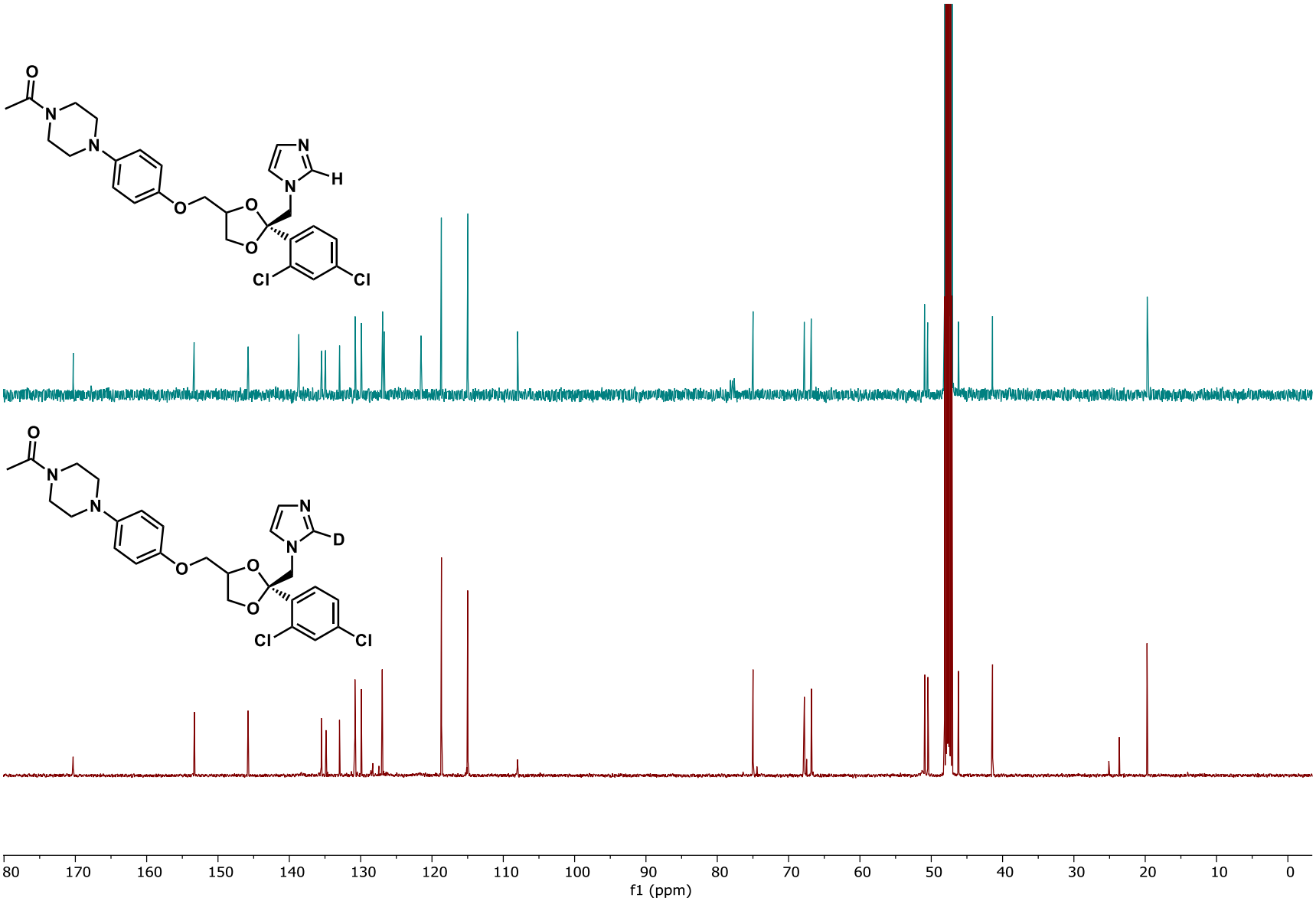
^{1}H NMR (500 MHz, CD_3OD) downfield region, superimposed comparison of Ketoconazole **3v** (blue) and Ketoconazole-*d*$_1$ **[D]-3v** (maroon).



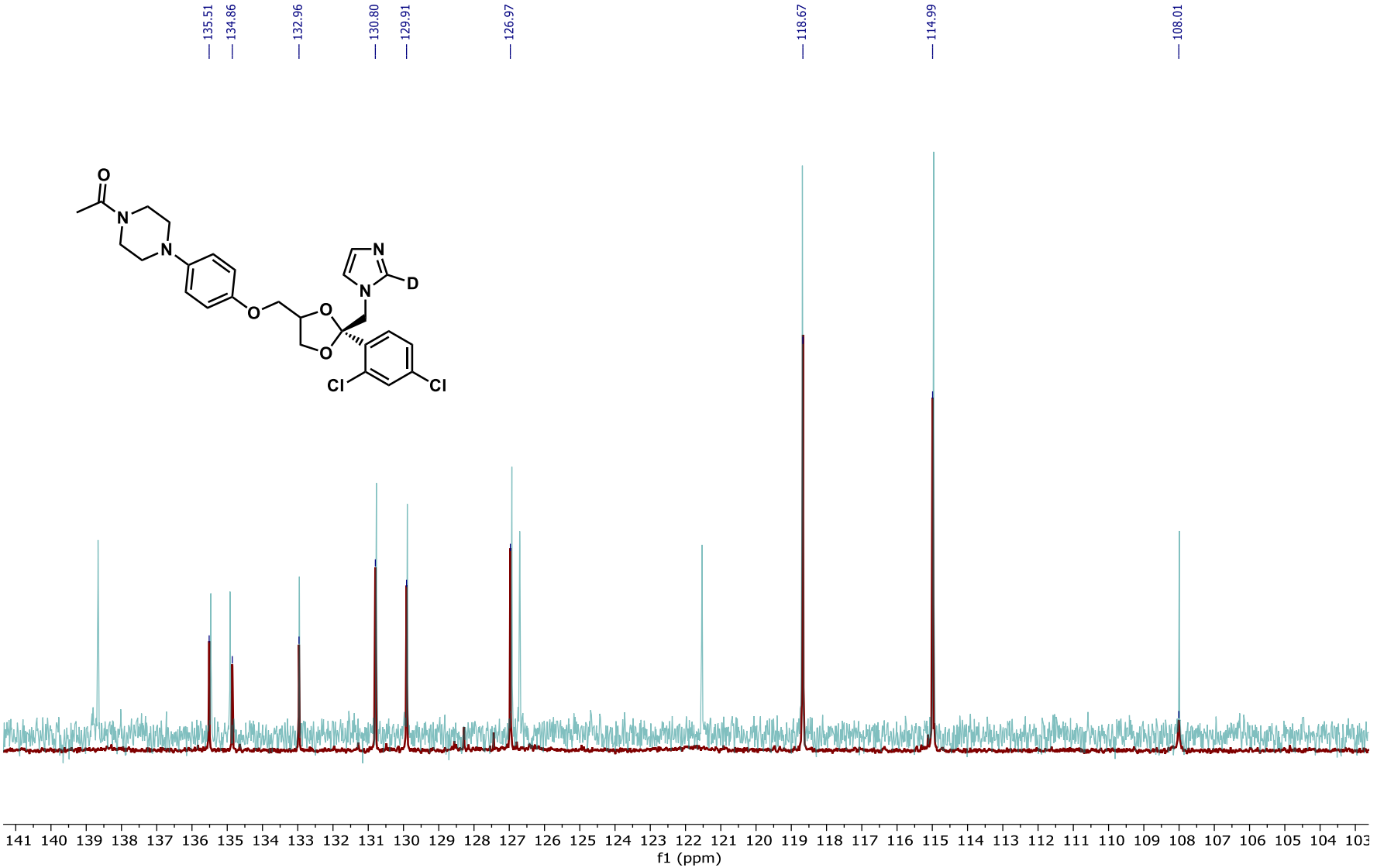
^{2}H NMR (77 MHz, CH_3OH) of Ketoconazole-*d*$_1$ **[D]-3v** – containing residual *d*$_4$-MeOD.



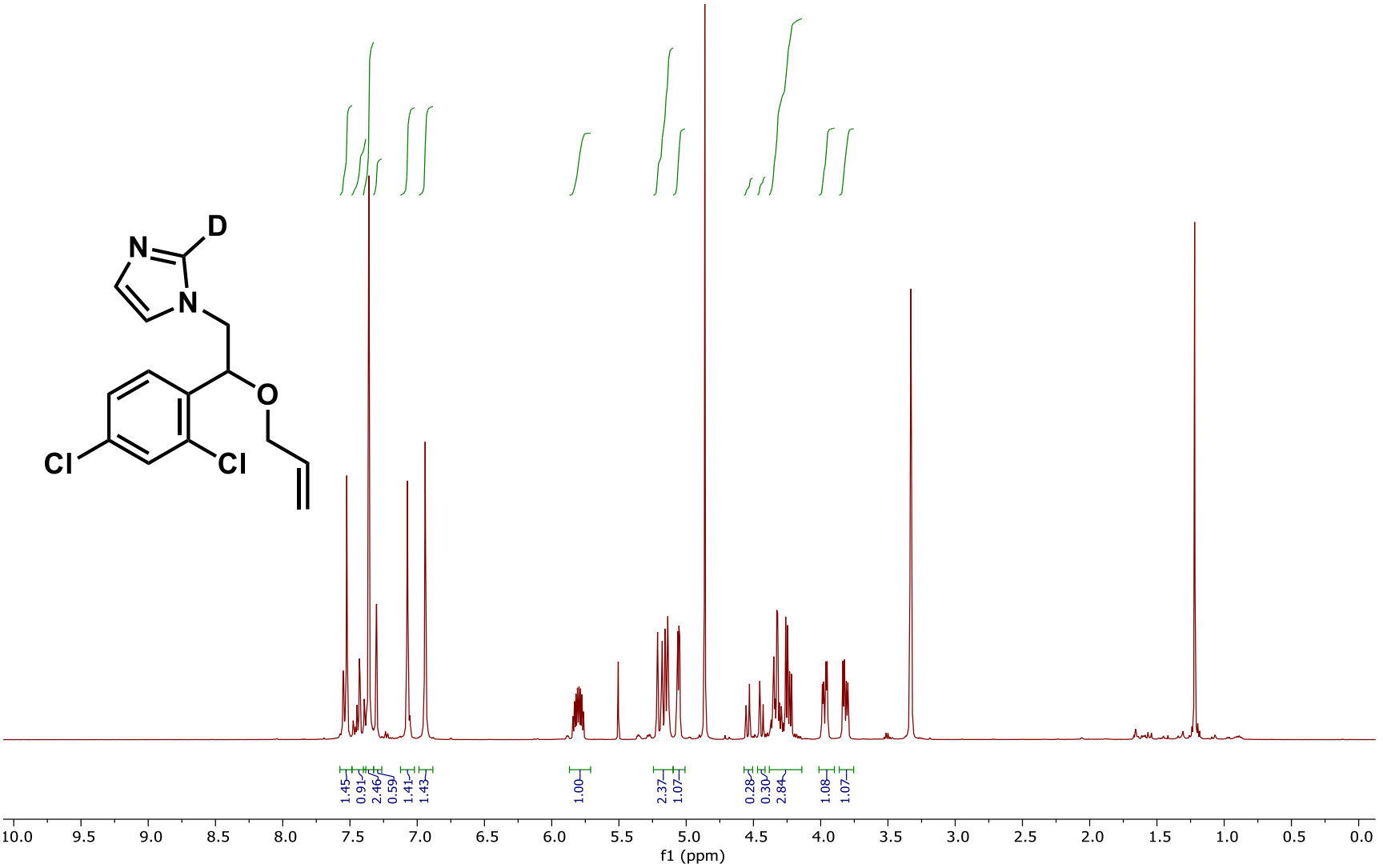
^{13}C NMR (125 MHz, CD_3OD) of Ketoconazole-*d*$_1$ **[D]-3v**.



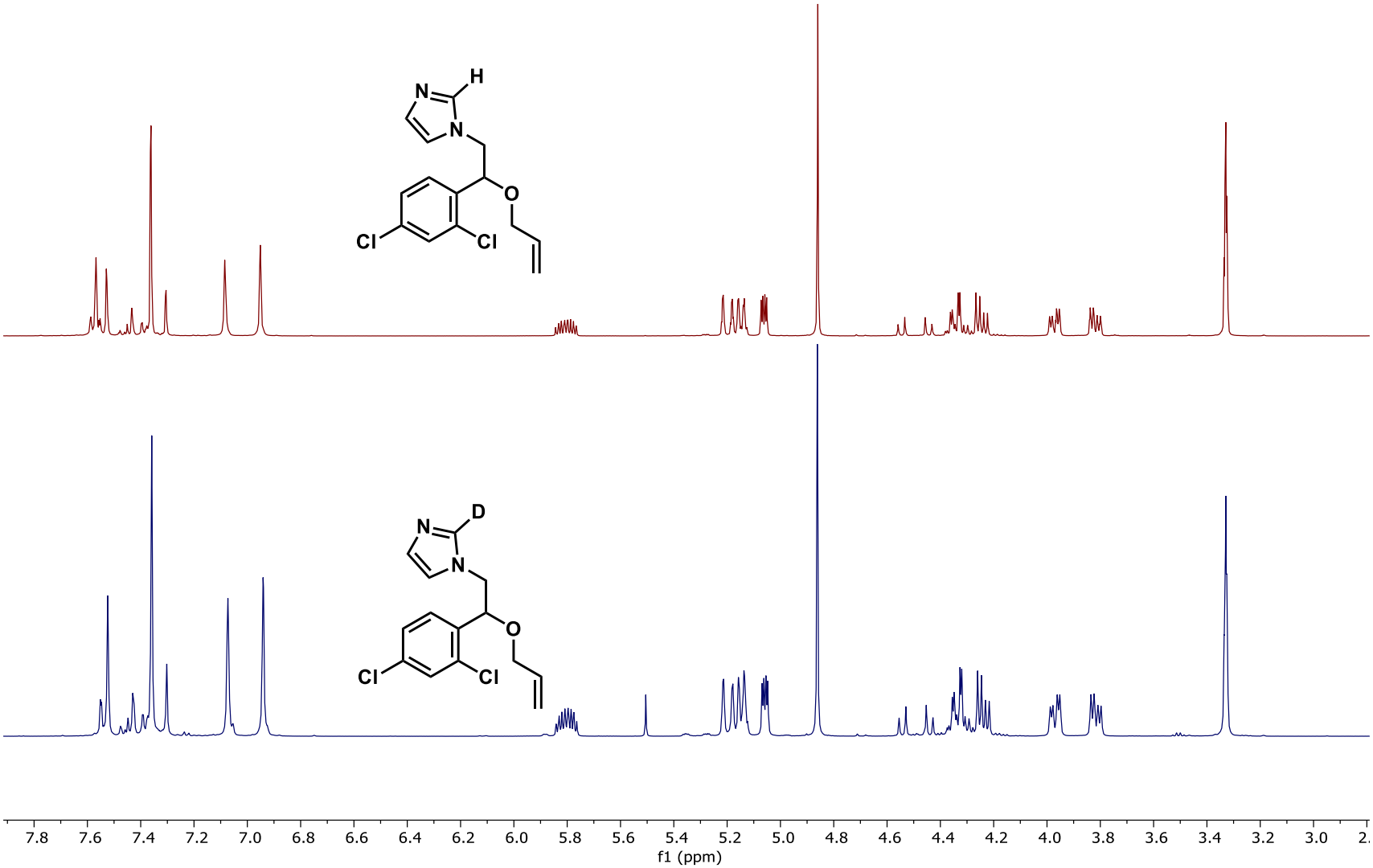
^{13}C NMR (125 MHz, CD_3OD) stacked comparison of Ketoconazole **3v** (top) and Ketoconazole-*d*$_1$ **[D]-3v** (bottom).



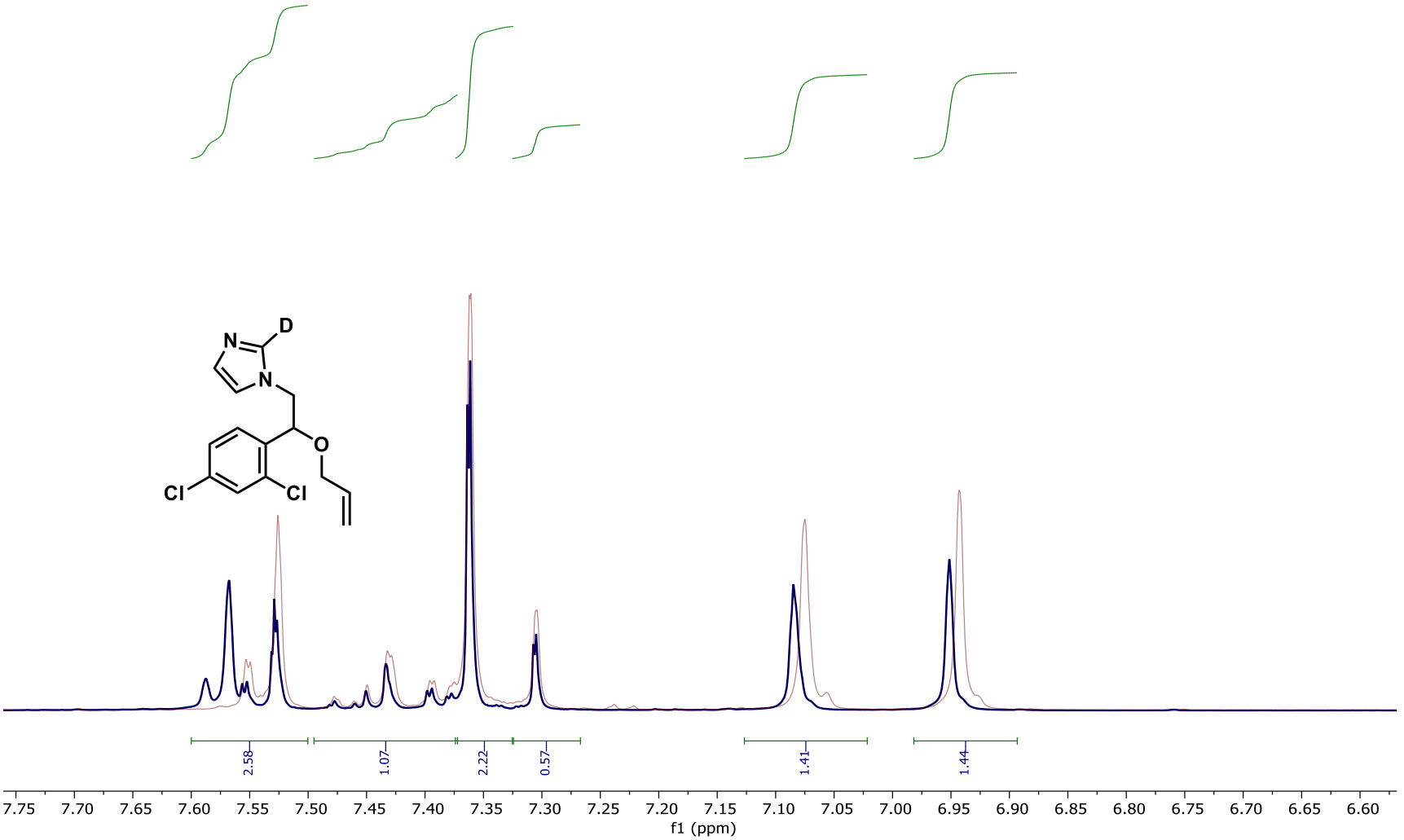
^{13}C NMR (141 to 103 ppm, 125 MHz, CD_3OD) superimposed comparison of Ketoconazole **3v** (cyan) and Ketoconazole-*d*$_1$ **[D]-3v** (maroon) – *showing 3 unobserved imidazole ^{13}C resonances.*



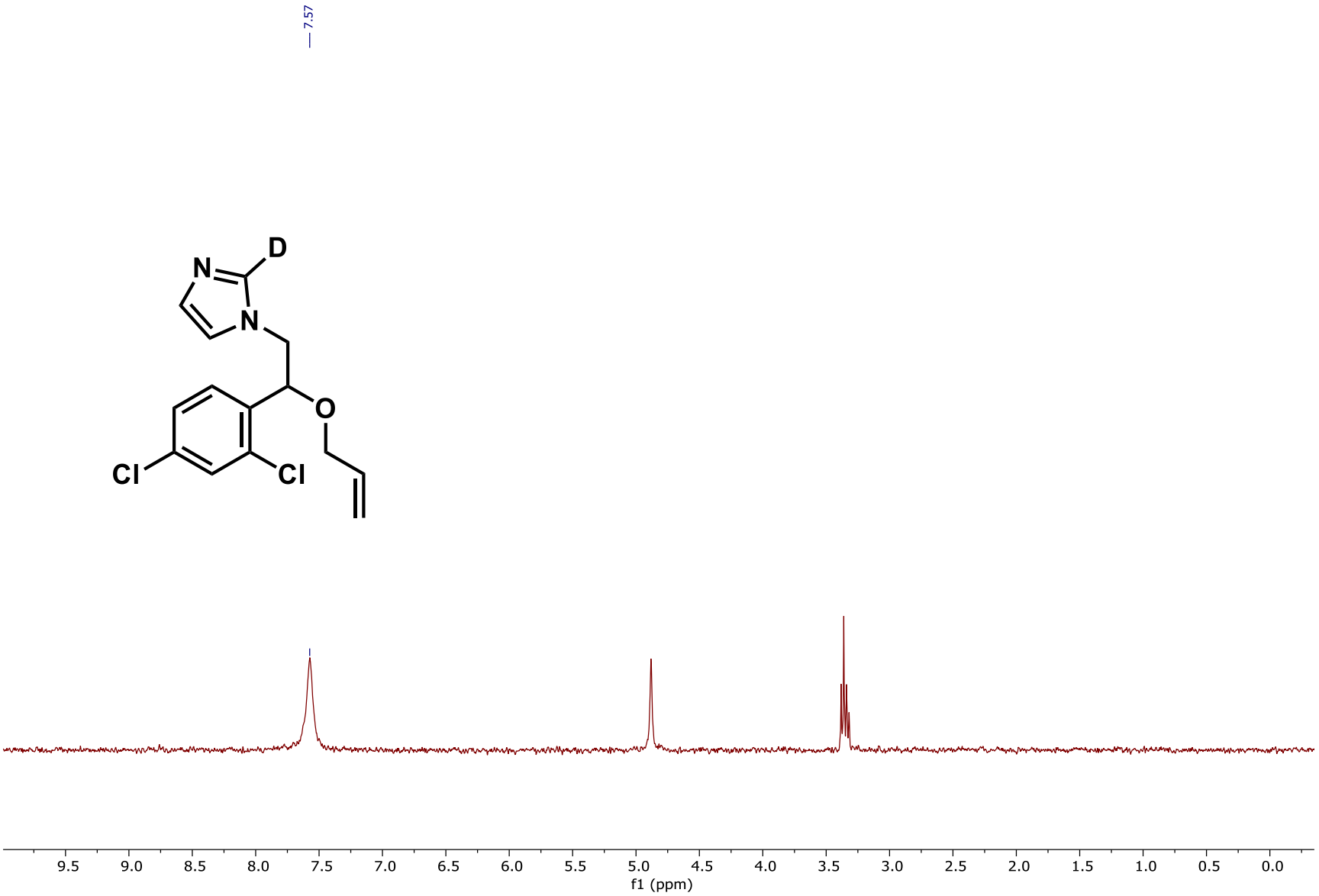
^{1}H NMR (500 MHz, CD_3OD) of Imazalil-*d*$_1$ **[D]-3w**.



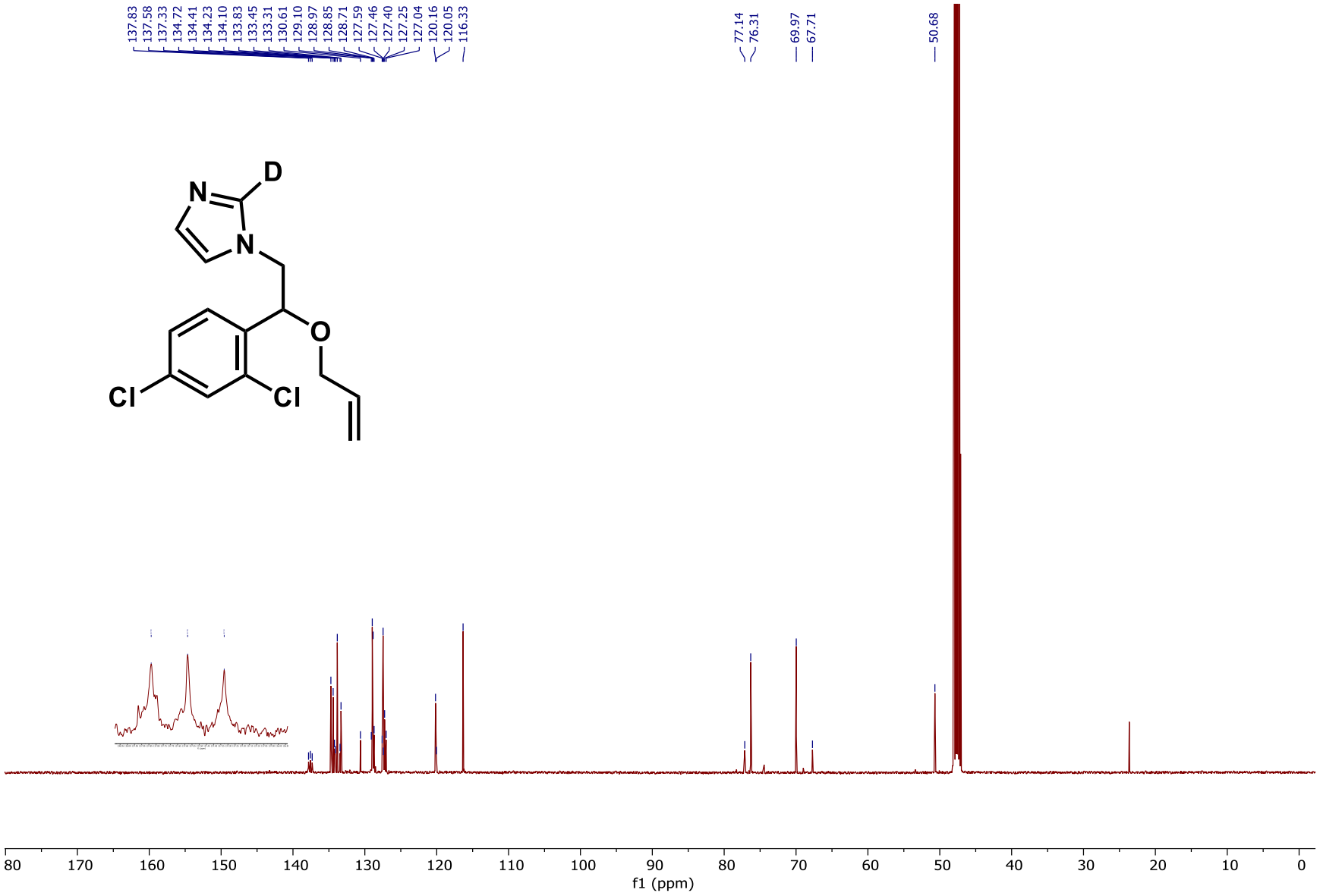
^{1}H NMR (500 MHz, CD_3OD) stacked comparison of Imazalil **3w** (top) and Imazalil-*d*$_1$ **[D]-3w** (bottom).



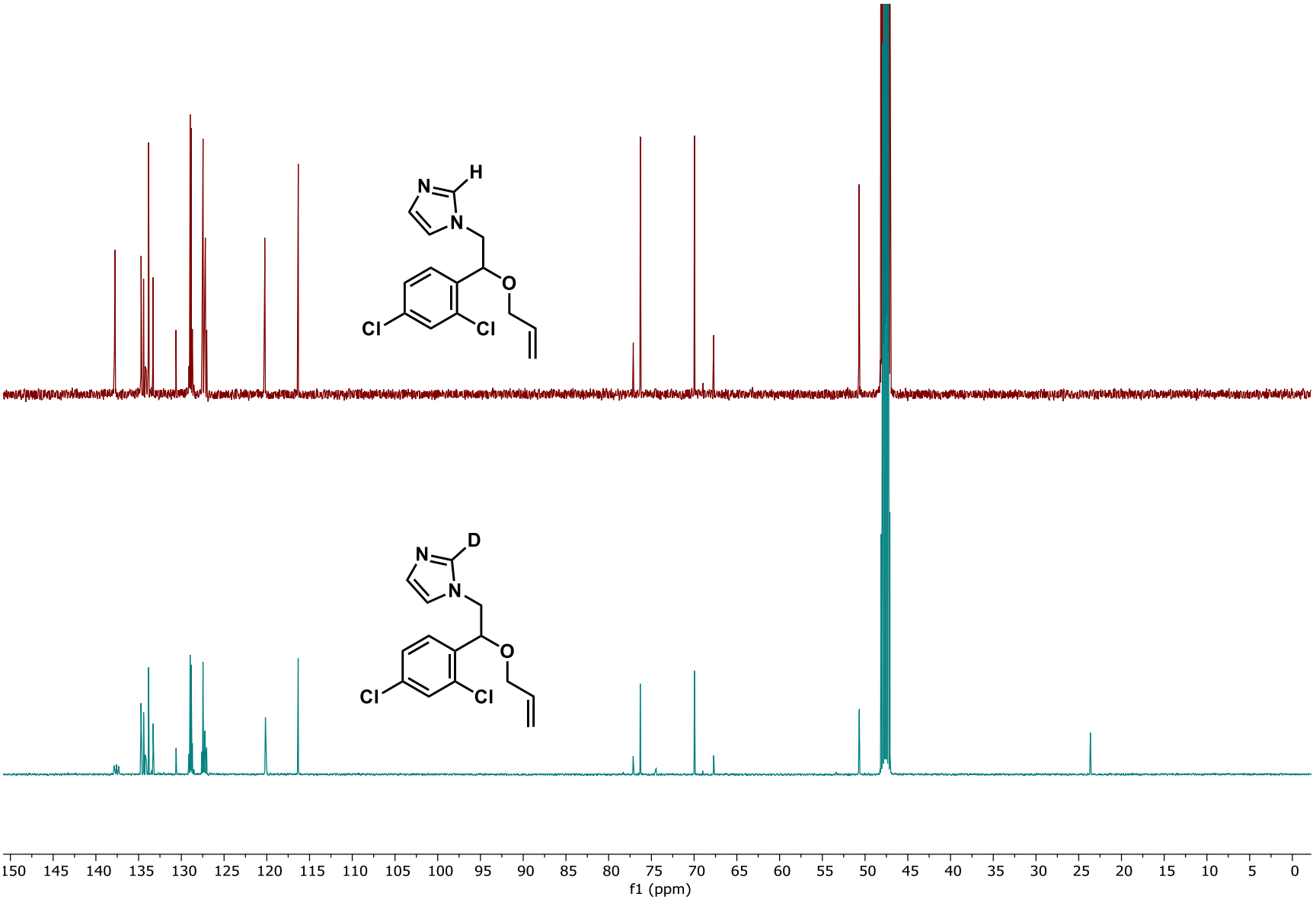
^{1}H NMR (500 MHz, CD_3OD) superimposed comparison of Imazalil **3w** (blue) and Imazalil-*d*$_1$ **[D]-3w** (maroon).



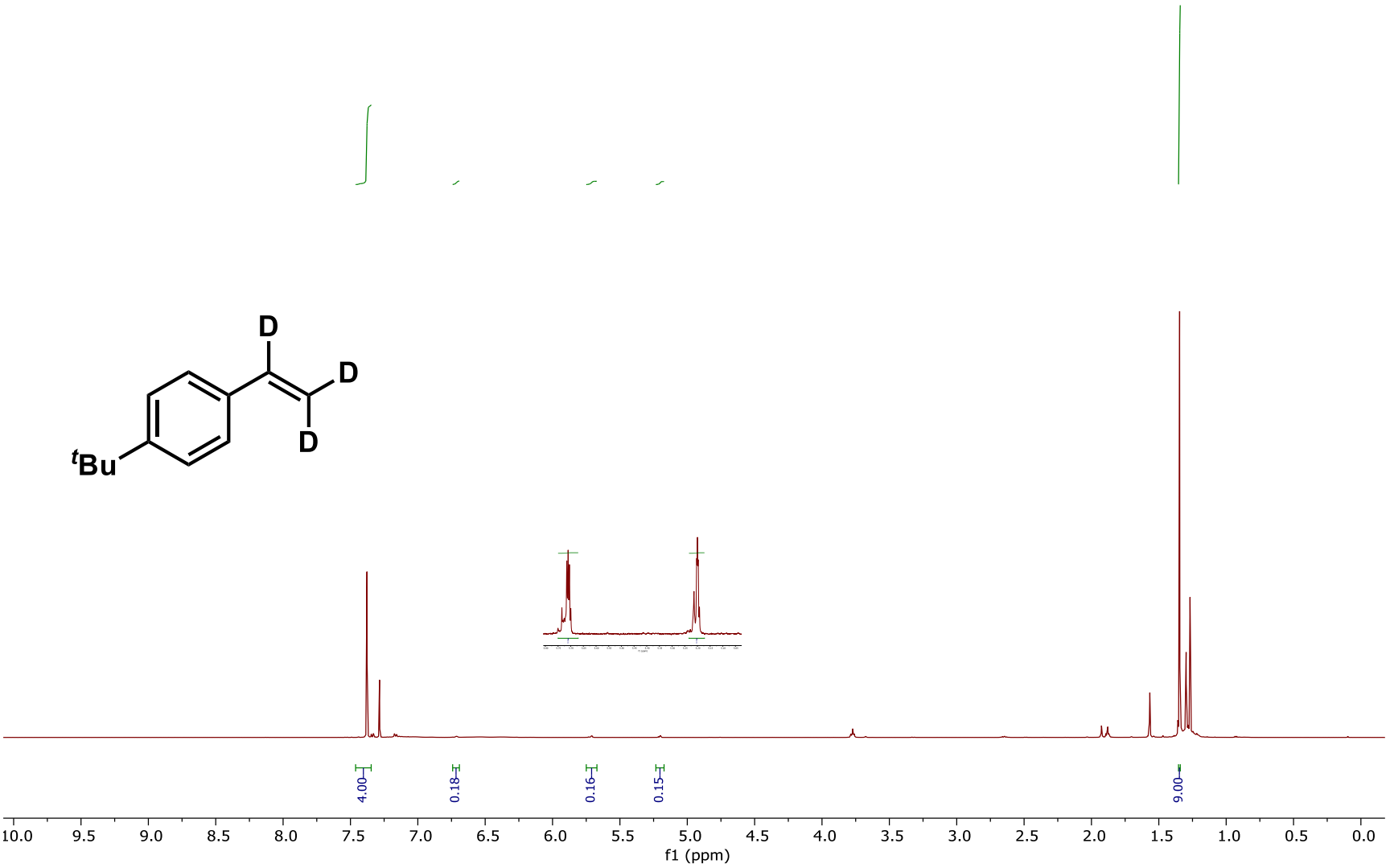
^{2}H NMR (500 MHz, CH_3OH) of Imazalil-*d*$_1$ **[D]-3w** – containing residual *d*$_4$-MeOD.



^{13}C NMR (125 MHz, CD_3OD) of Imazalil-*d*$_1$ **[D]-3w**.

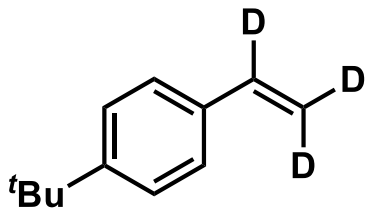


^{13}C NMR (125 MHz, CD_3OD) of stacked comparison of Imazalil **3w** (top) and Imazalil-*d*$_1$ **[D]-3w** (bottom).

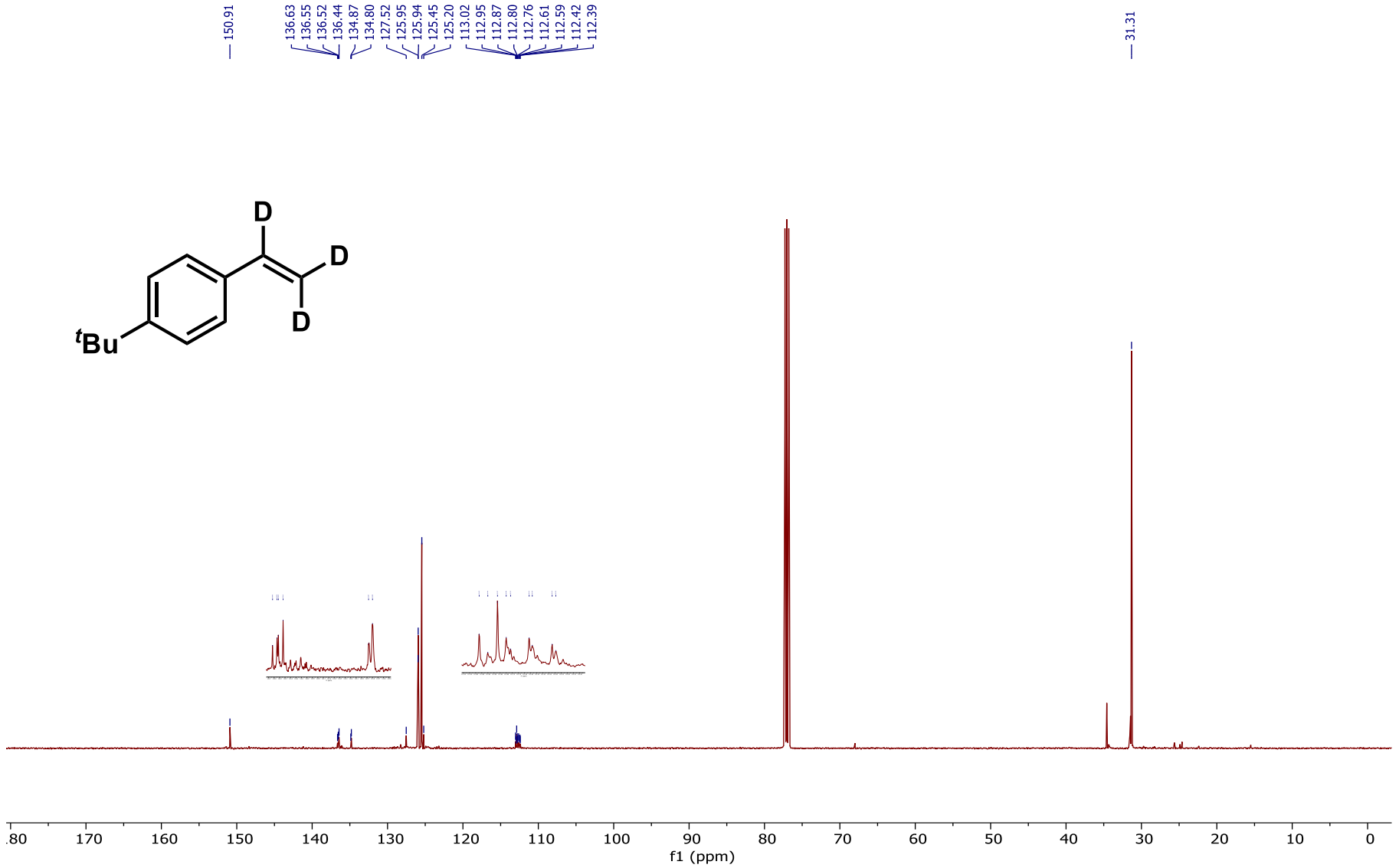


^{1}H NMR (500 MHz, $CDCl_3$) of 4-*tert*-butylstyrene-*α,β,β-d*$_3$ **[D]-4a.**

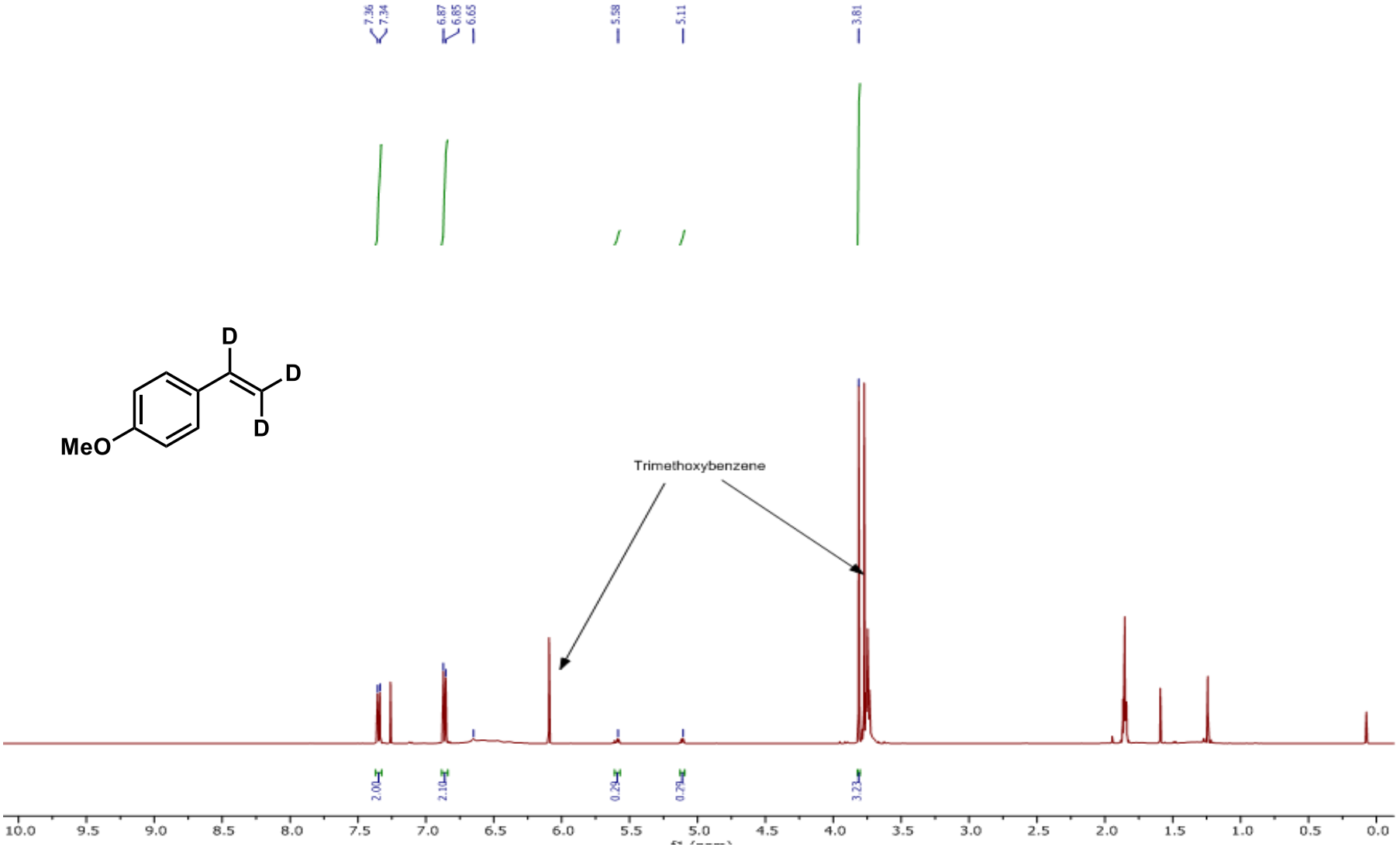
.



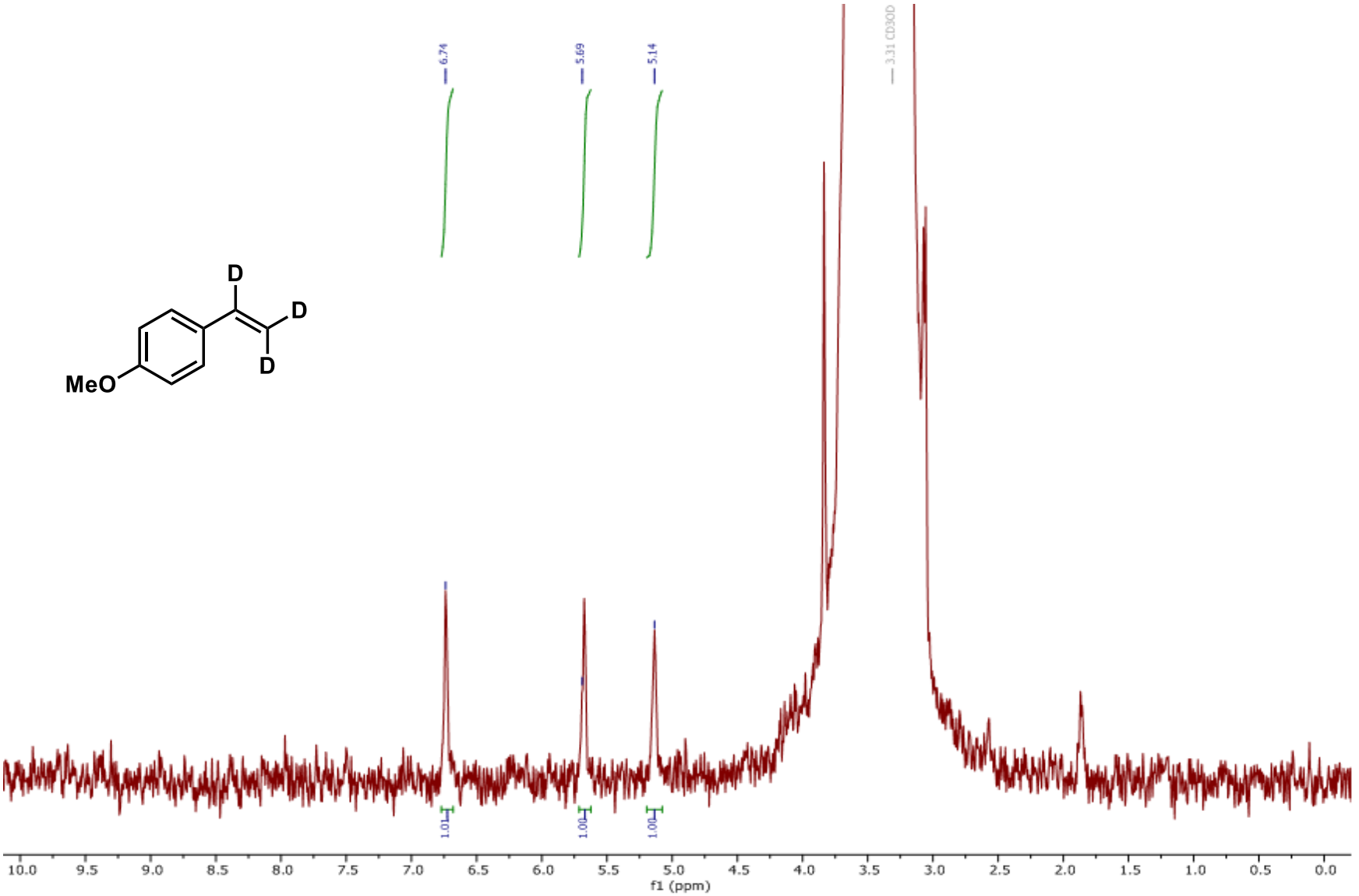
^{2}H NMR (77 MHz, $CHCl_3$) of 4-*tert*-butylstyrene-*α,β,β-d*$_3$ **[D]-4a.**



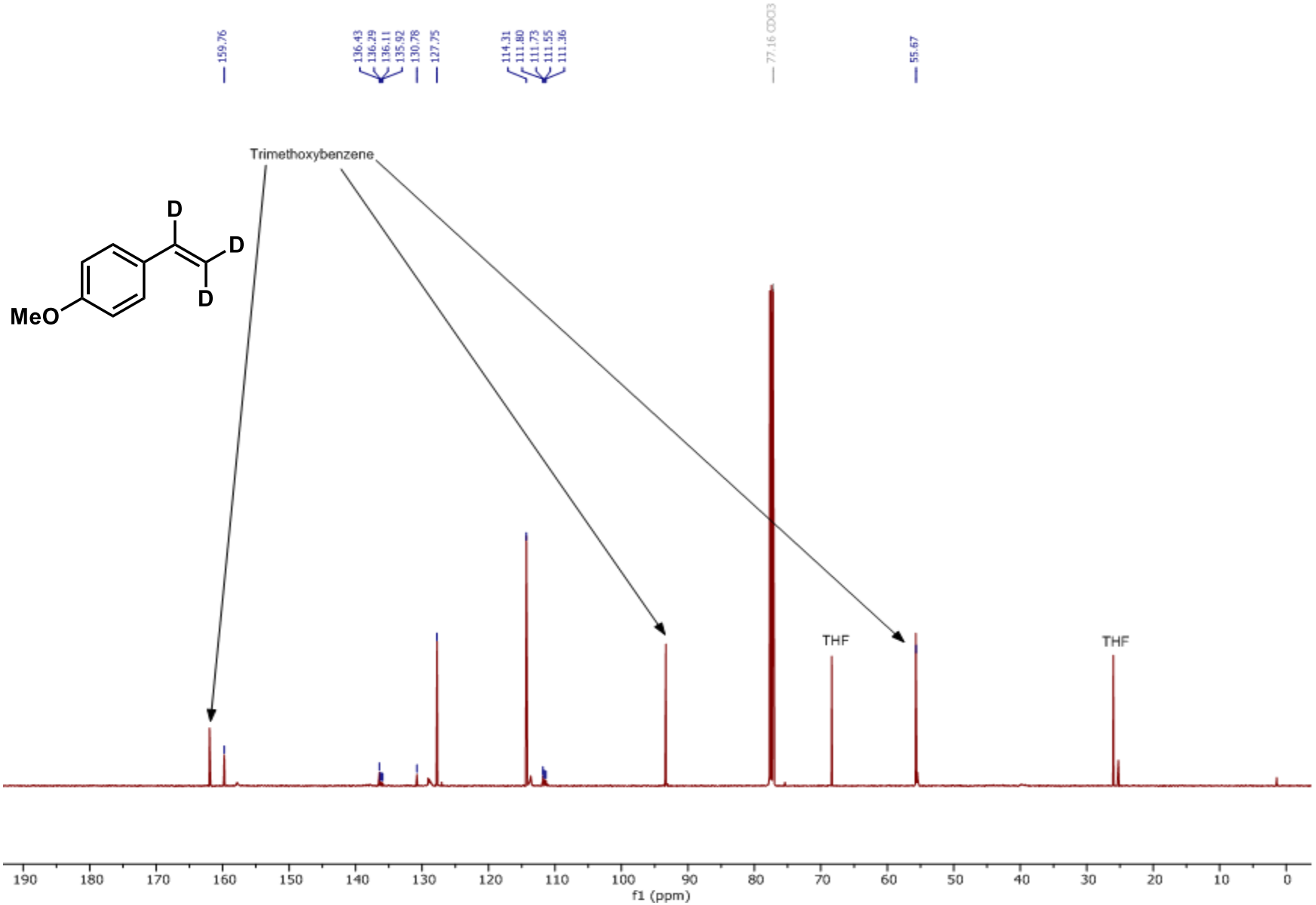
^{13}C NMR (125 MHz, $CHCl_3$) of 4-*tert*-butylstyrene-*α,β,β-d*$_3$ **[D]-4a.**



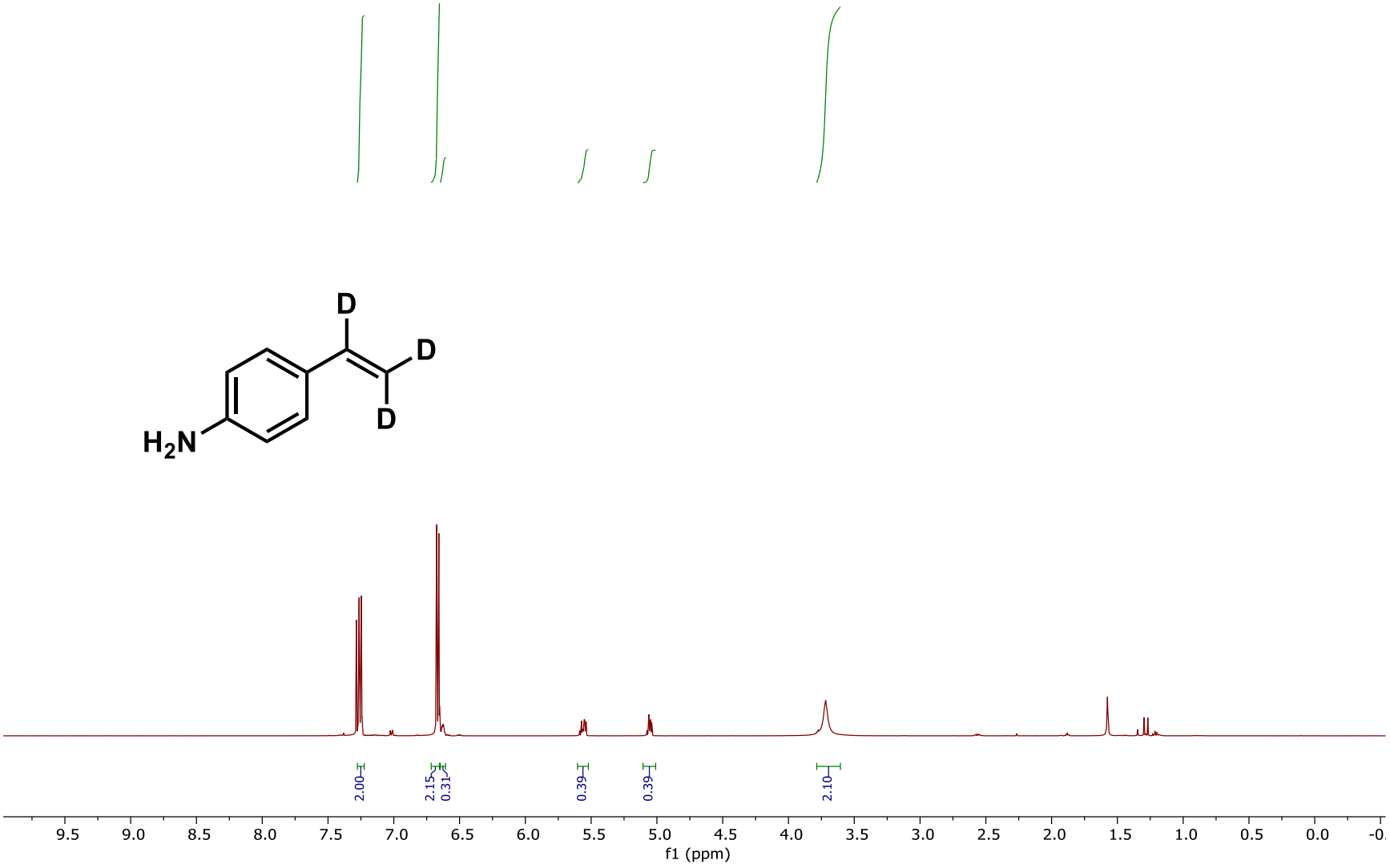
^{1}H NMR (500 MHz, $CDCl_3$/THF/CD_3OD) of 4-methoxystyrene-*α,β,β-d*$_3$ **[D]-4b.**



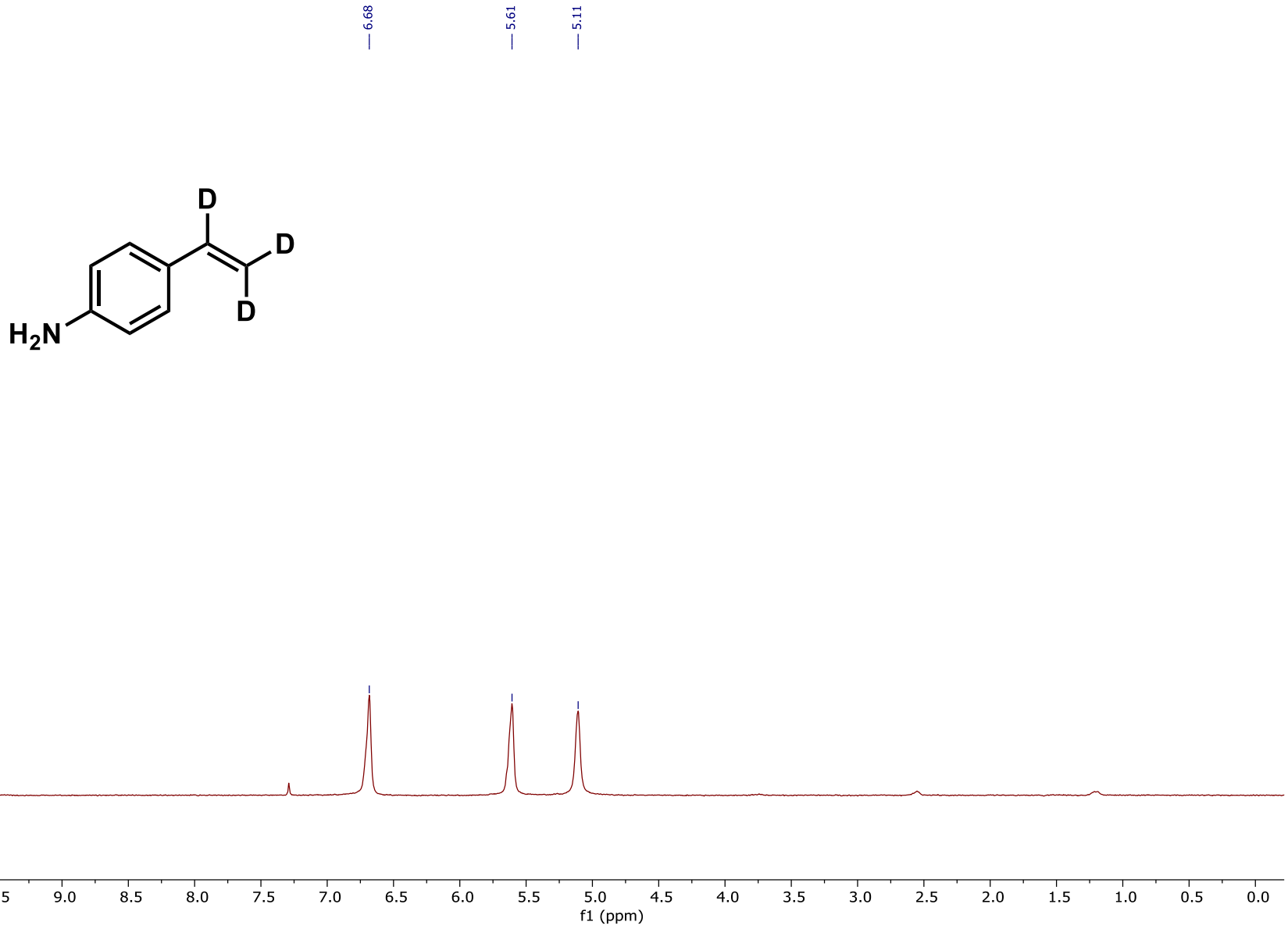
^{2}H NMR (77 MHz, THF/CD_3OD) of 4-methoxystyrene-*α,β,β-d*$_3$ **[D]-4b.**



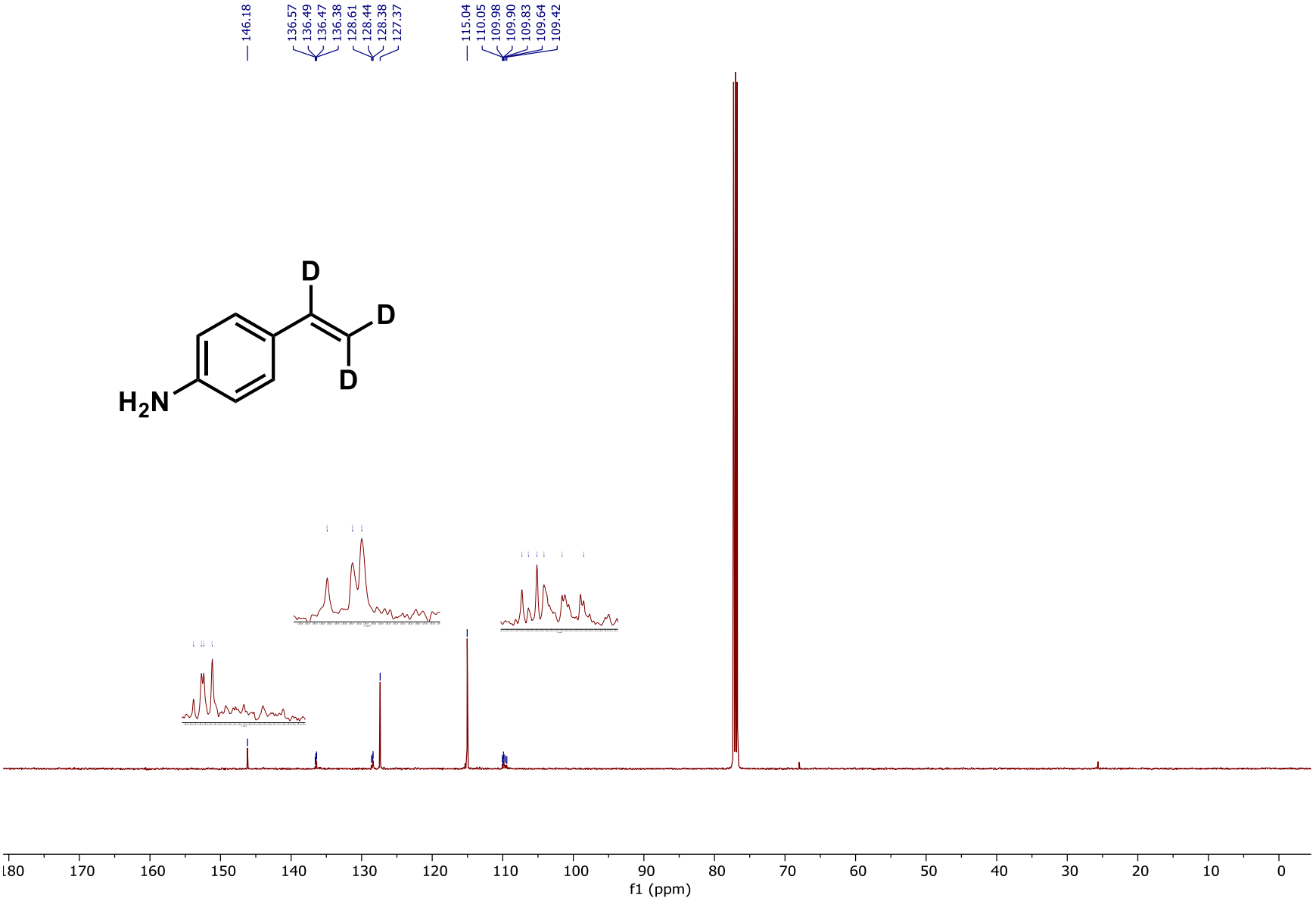
^{13}C NMR (125 MHz, $CDCl_3$/THF/CD_3OD) of 4-methoxystyrene-*α,β,β-d*$_3$ **[D]-4b**.



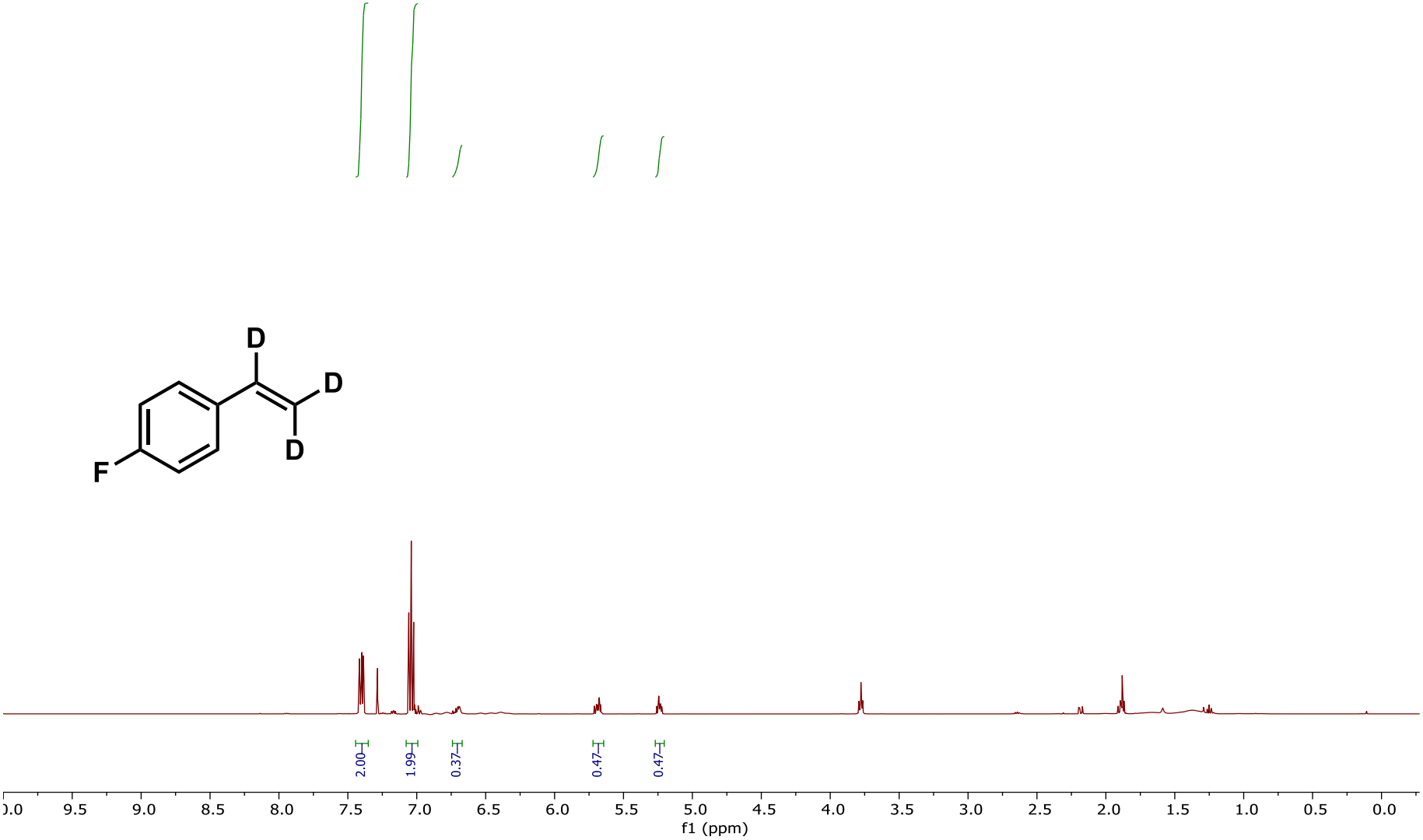
^{1}H NMR (500 MHz, $CDCl_3$) of 4-aminostyrene-*α,β,β-d*$_3$ **[D]-4c.**



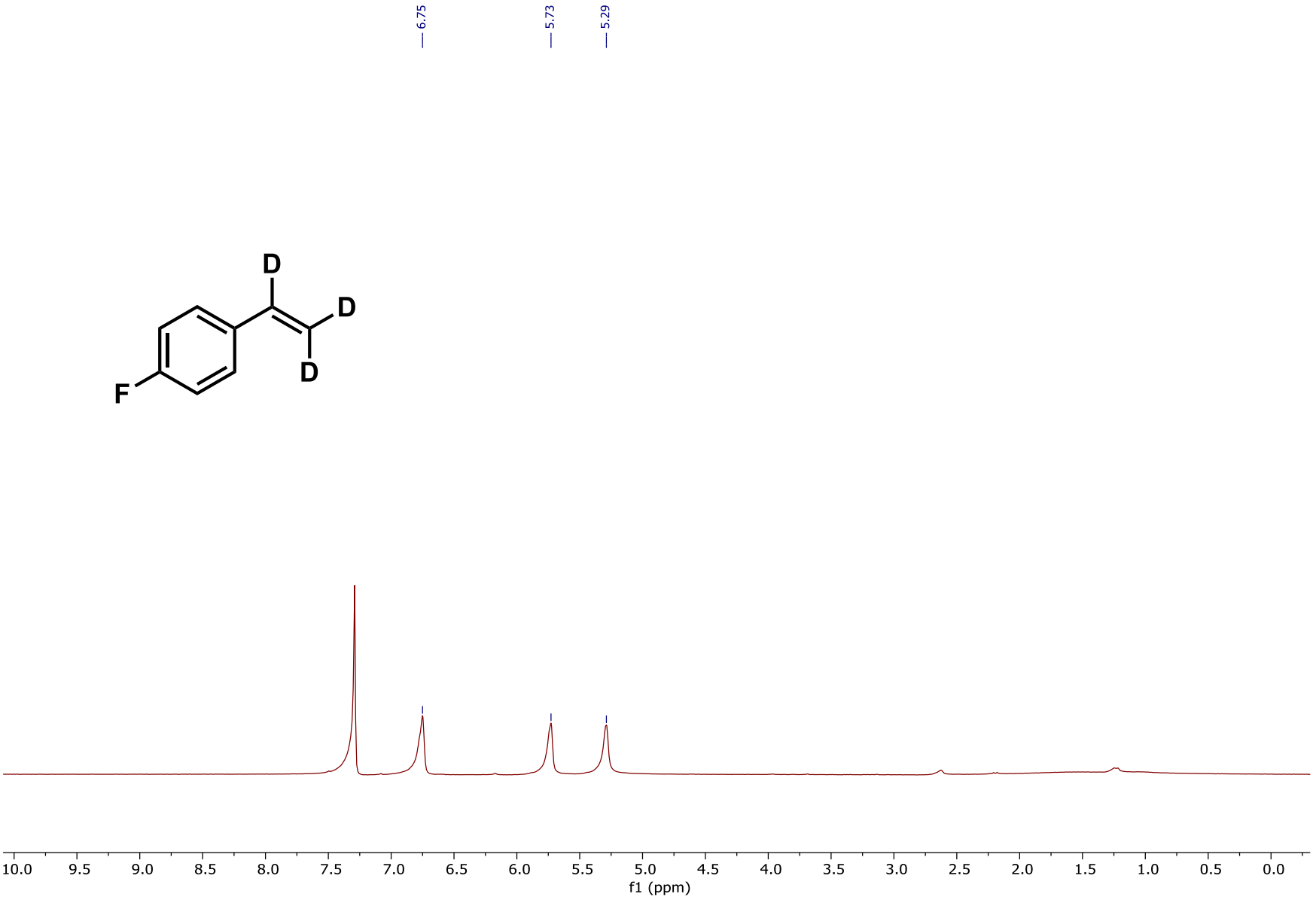
^{2}H NMR (77 MHz, $CHCl_3$) of 4-aminostyrene-*α,β,β-d*$_3$ **[D]-4c.**



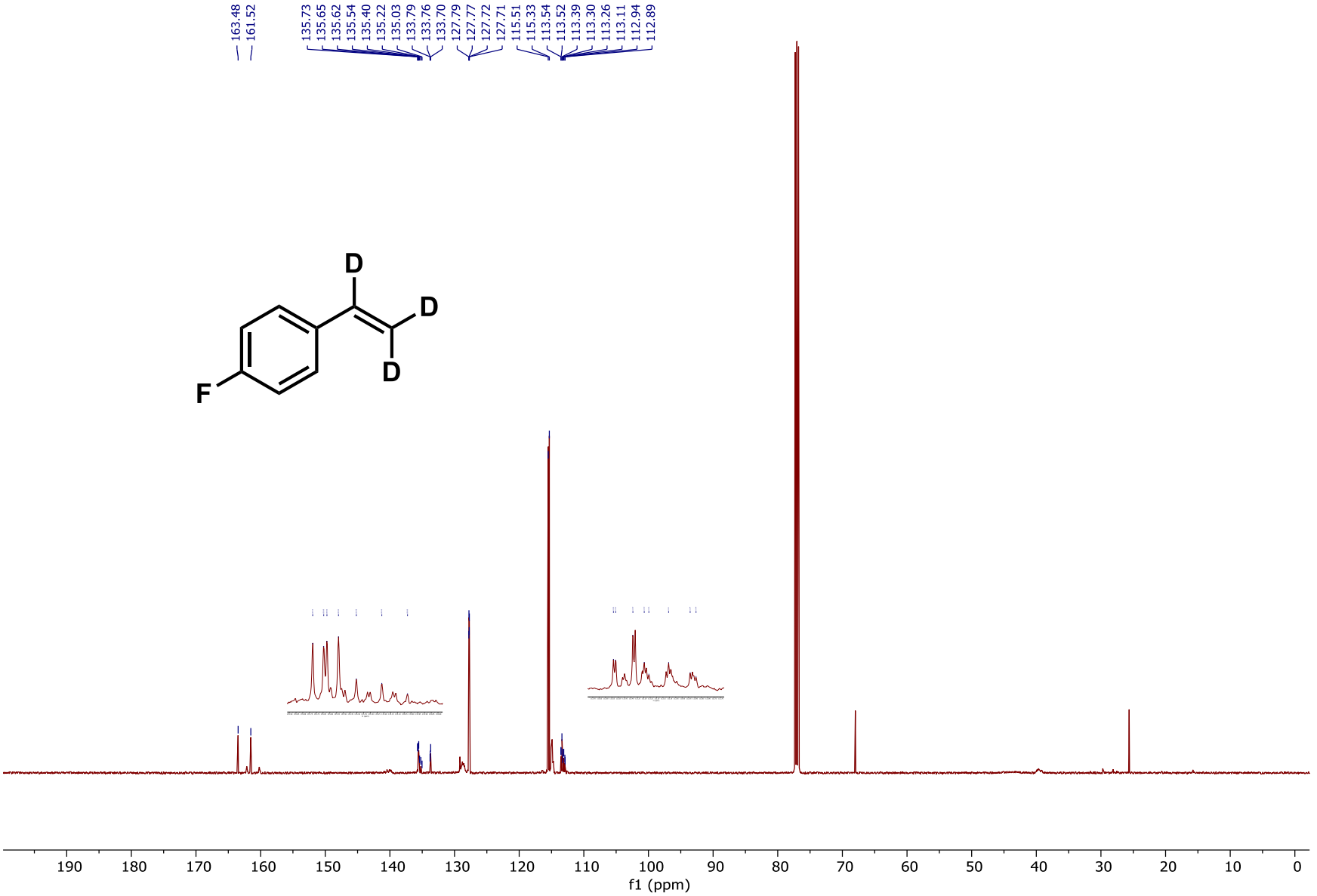
^{13}C NMR (125 MHz, $CDCl_3$) of 4-aminostyrene-*α,β,β-d*$_3$ **[D]-4c.**



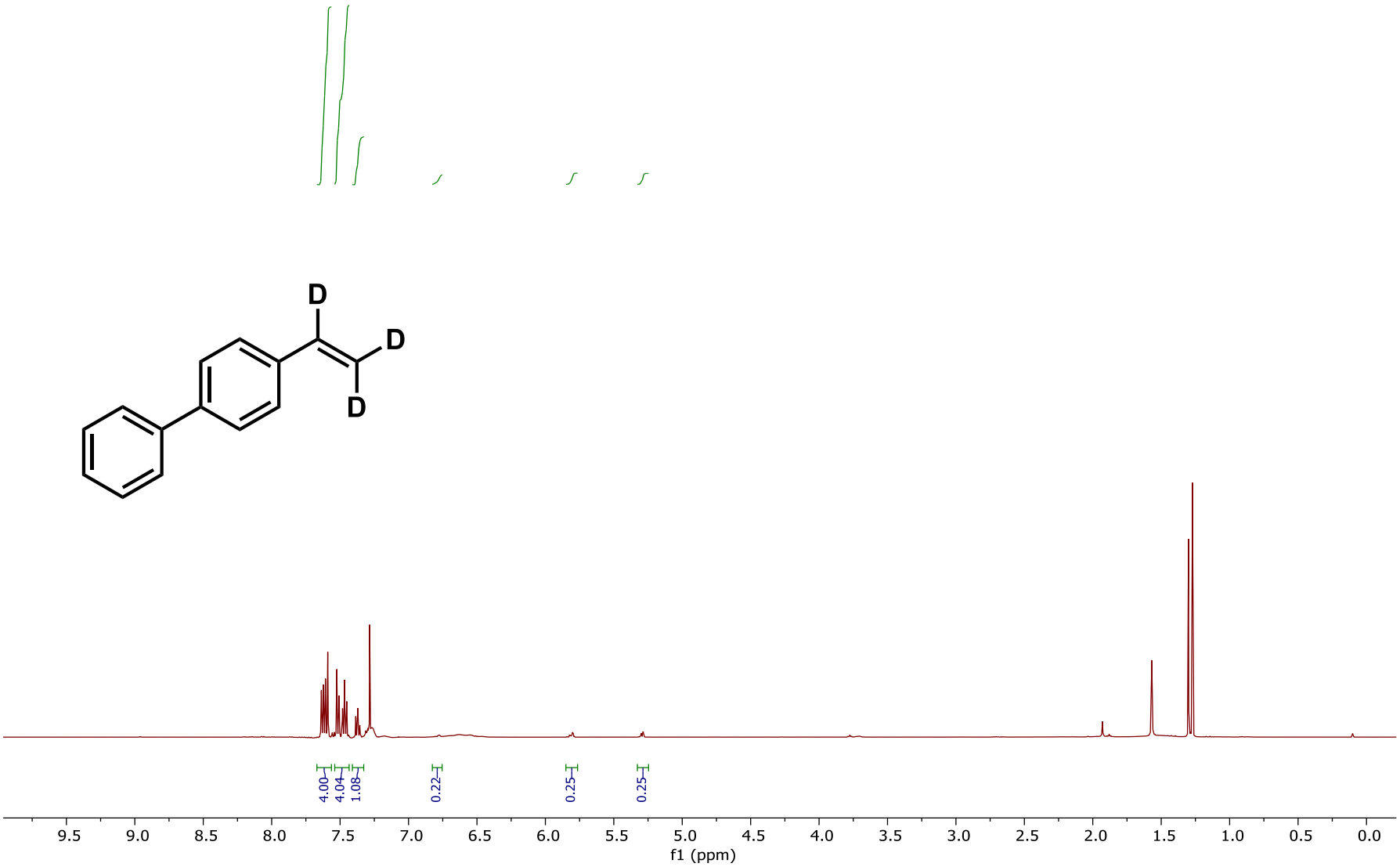
^{1}H NMR (500 MHz, $CDCl_3$) of 4-fluorostyrene-*α,β,β-d*$_3$ **[D]-4d.**



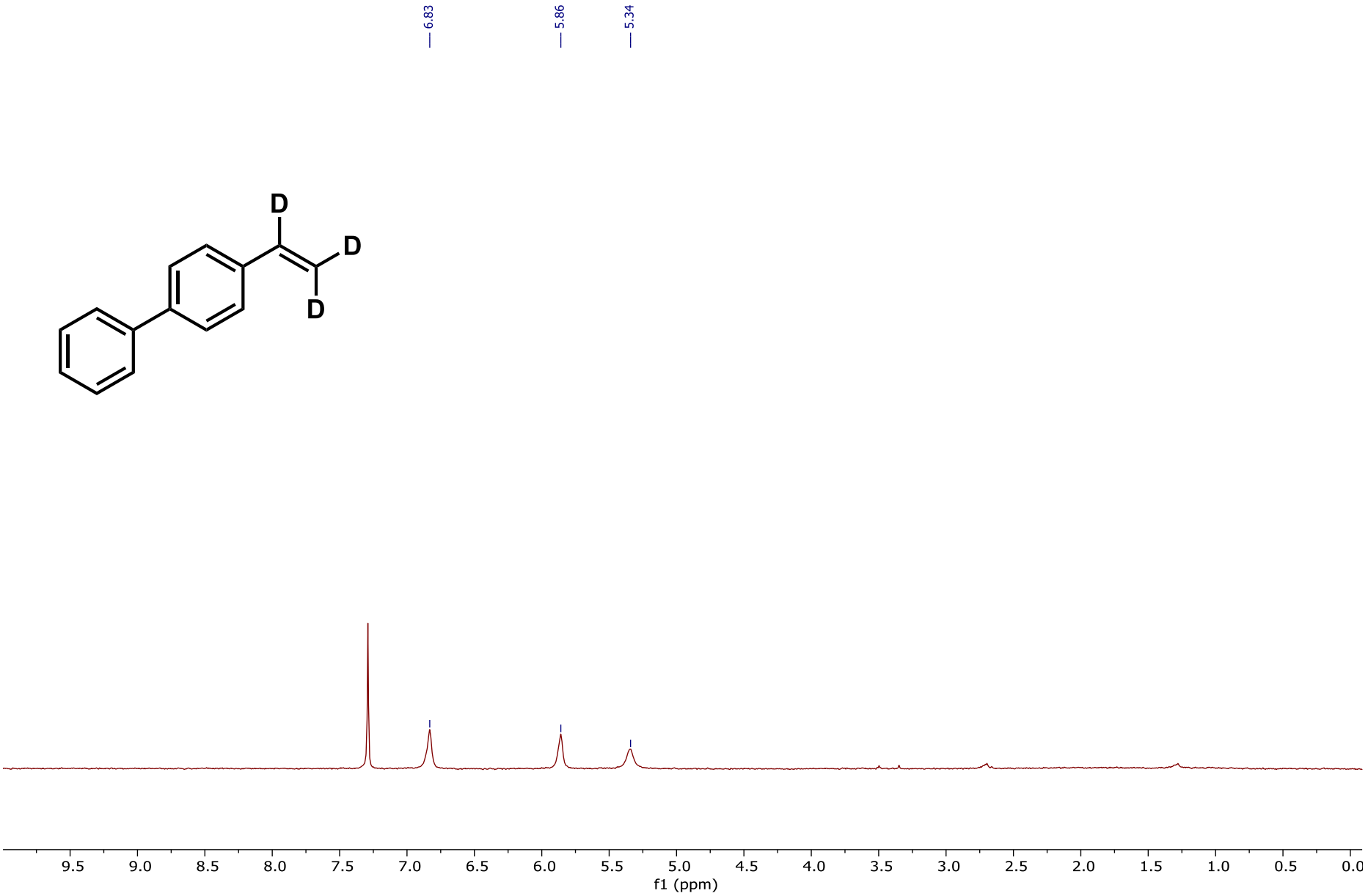
^{2}H NMR (77 MHz, $CHCl_3$) of 4-fluorostyrene-*α,β,β-d*$_3$ **[D]-4d.**



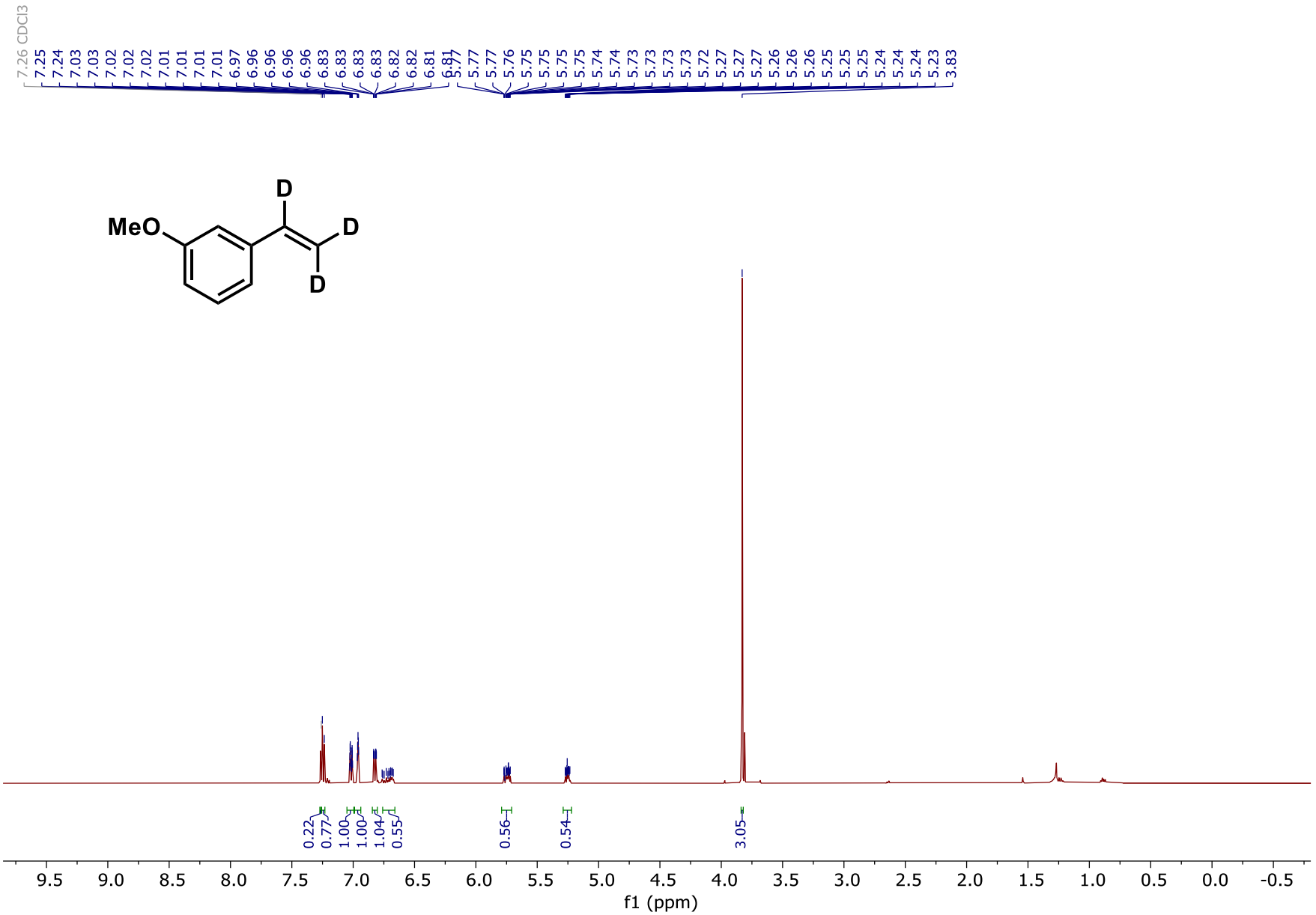
^{13}C NMR (125 MHz, $CDCl_3$) of 4-fluorostyrene-*α,β,β-d*$_3$ **[D]-4d.**



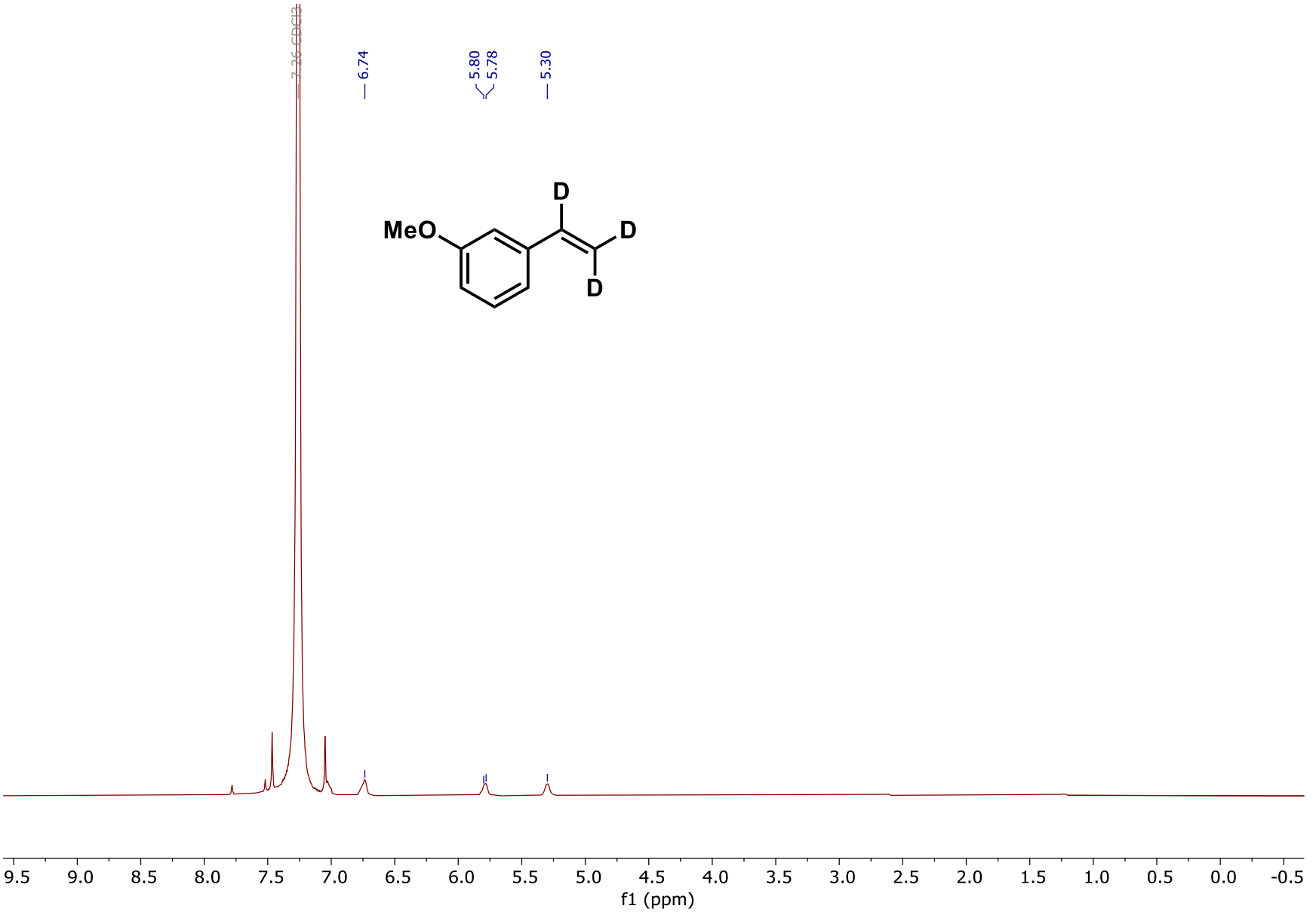
^{1}H NMR (500 MHz, $CDCl_3$) of 4-vinylbiphenyl-*α,β,β-d*$_3$ **[D]-4e.**



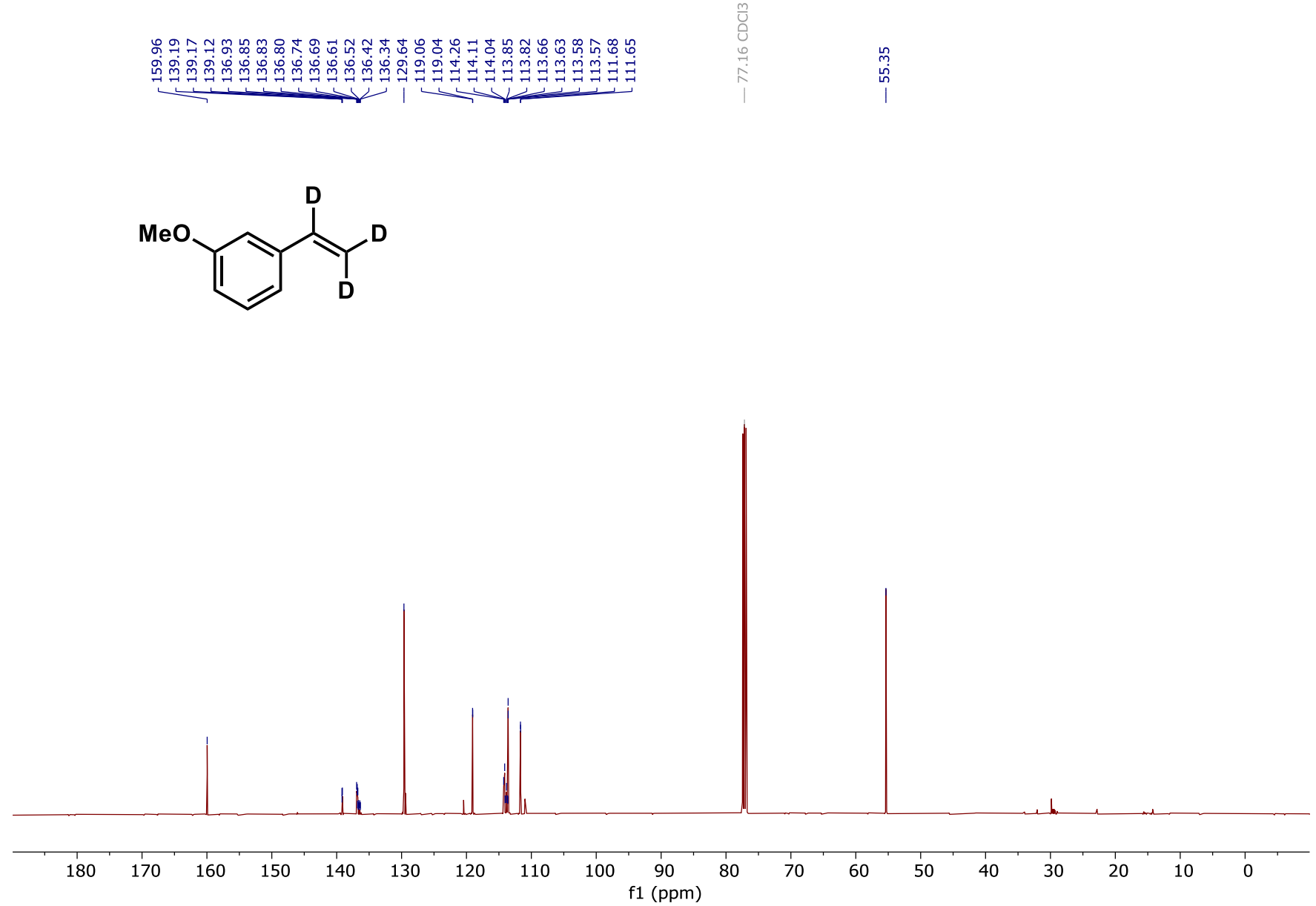
^{2}H NMR (77 MHz, $CHCl_3$) of 4-vinylbiphenyl-*α,β,β-d*$_3$ **[D]-4e.**



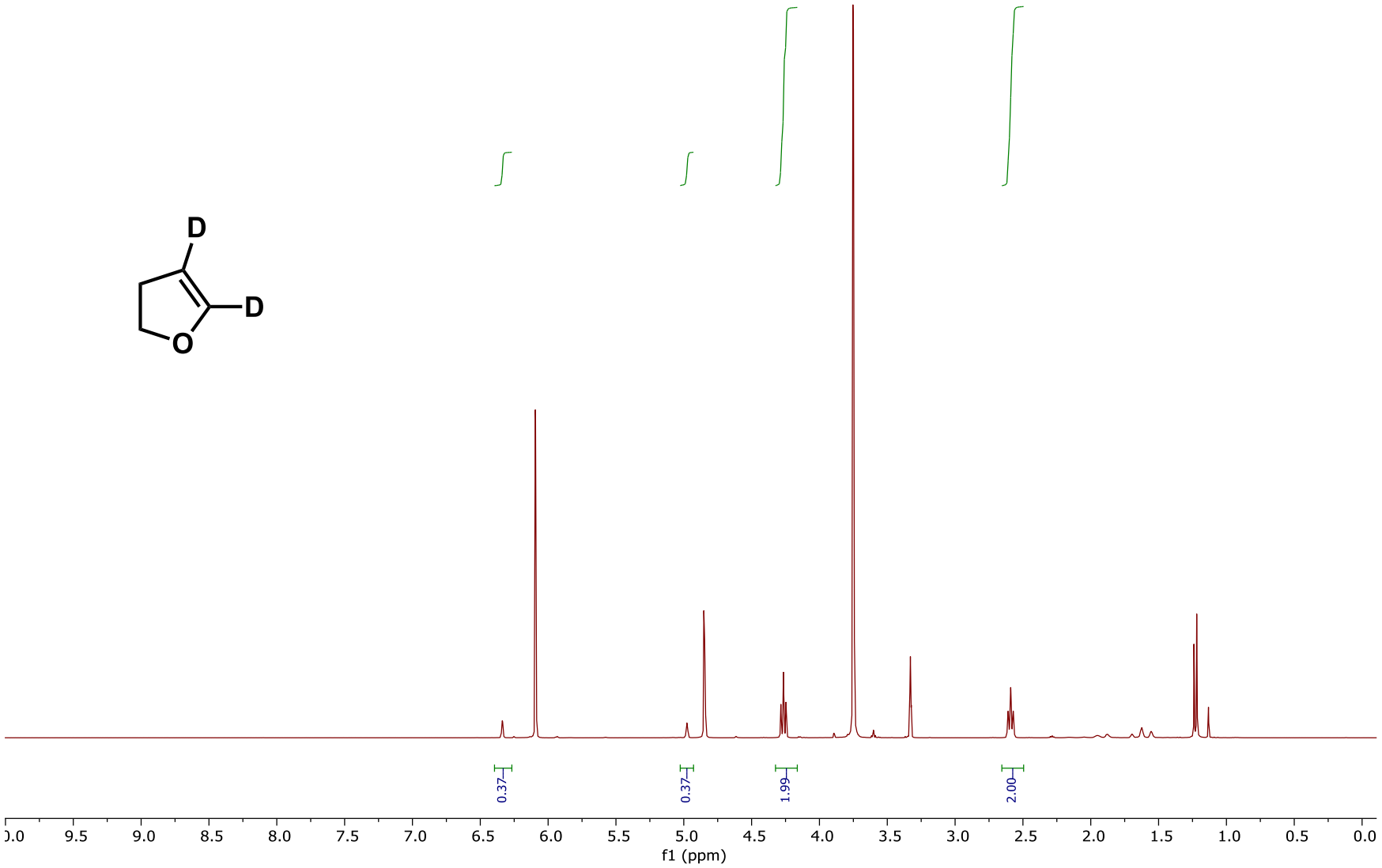
^{1}H NMR (500 MHz, $CDCl_3$) of 3-methoxystyrene-*α,β,β-d*$_3$ **[D]-4f.**



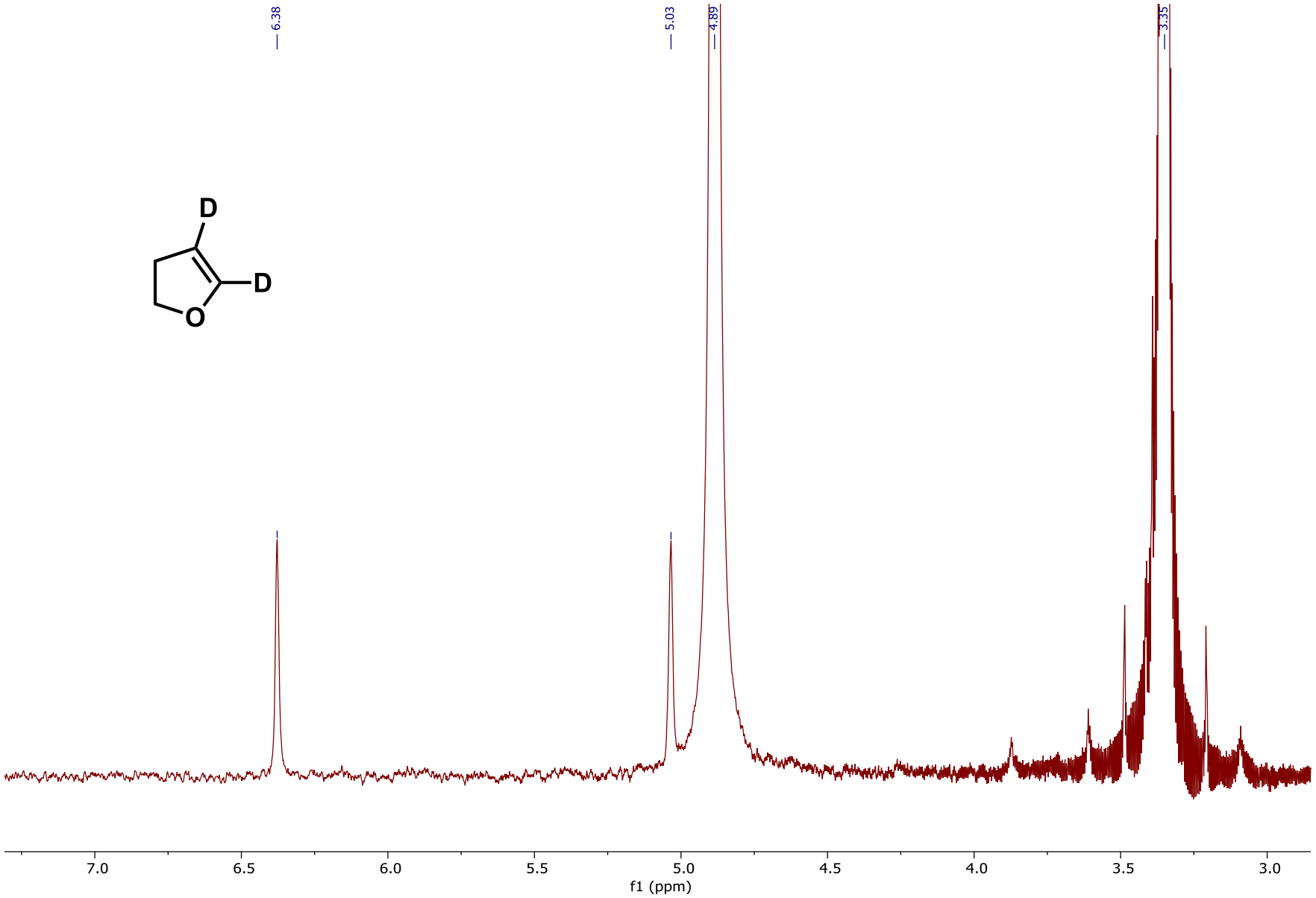
^{2}H NMR (77 MHz, $CDCl_3$) of 3-methoxystyrene-*α,β,β-d*$_3$ **[D]-4f**.



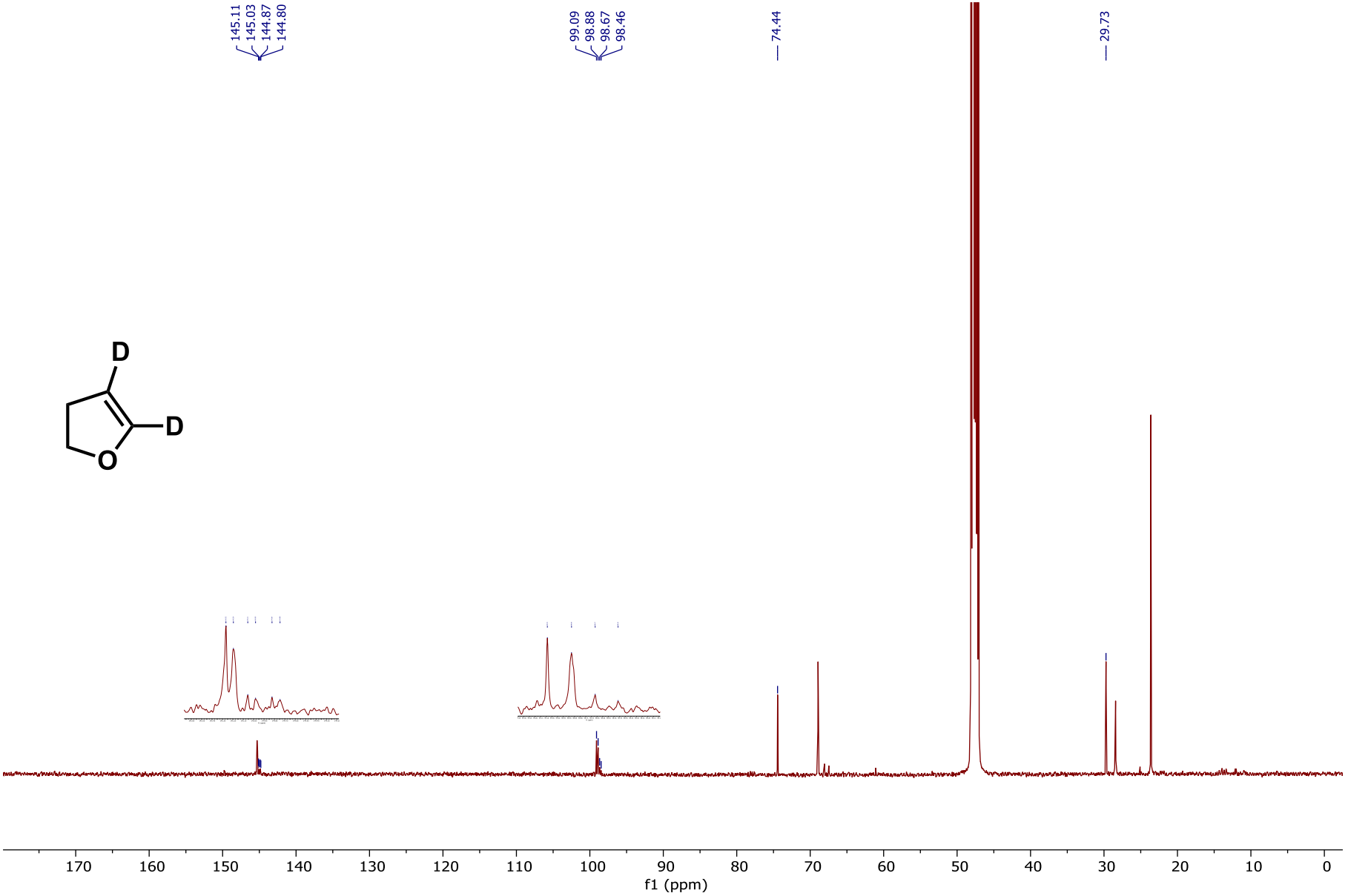
^{13}C NMR (126 MHz, $CDCl_3$) of 3-methoxystyrene-*α,β,β-d*$_3$ **[D]-4f.**



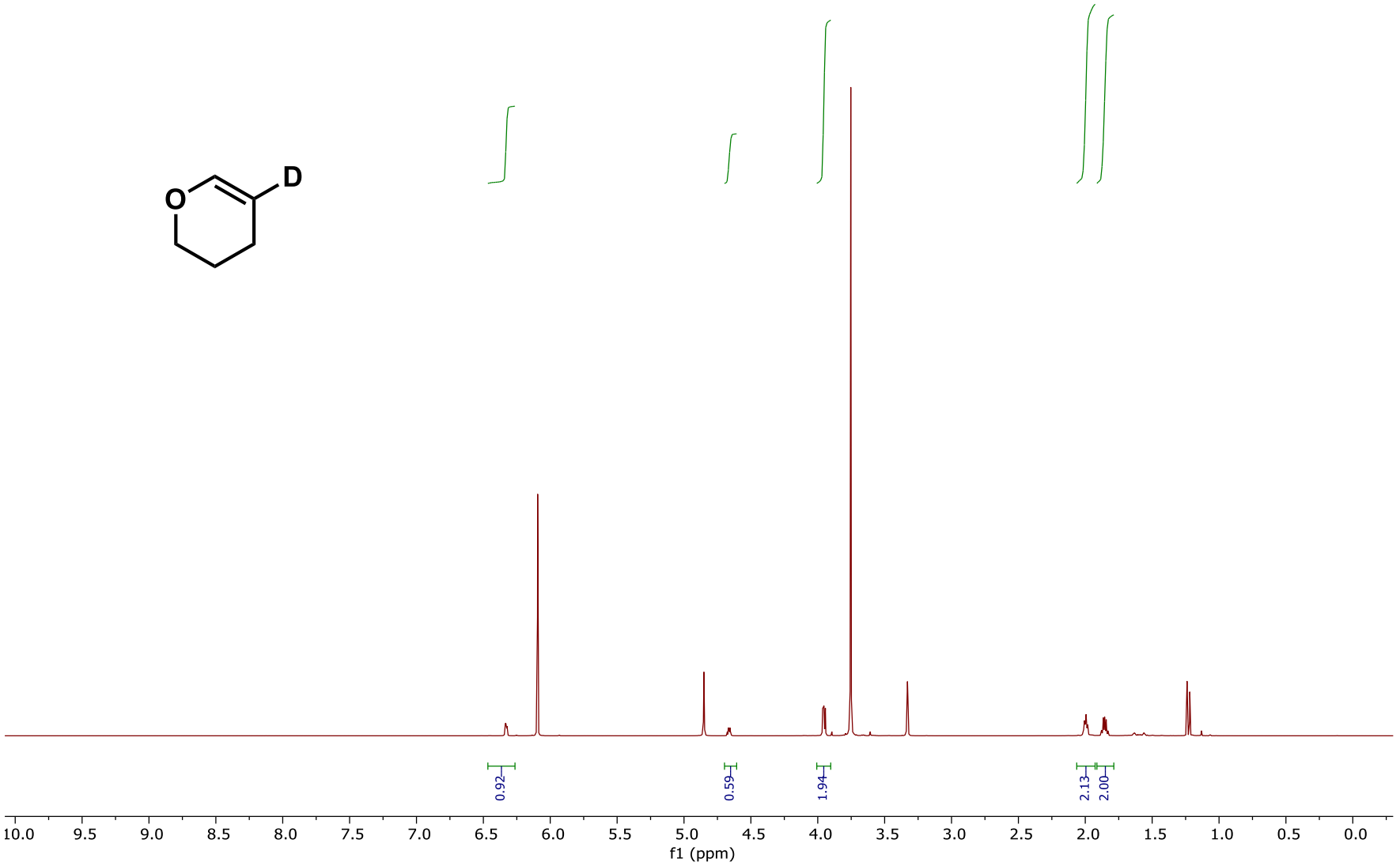
^{1}H NMR (500 MHz, CD_3OD) of 2,3-dihydro-*3D,4D*-furan **[D]-4g.**



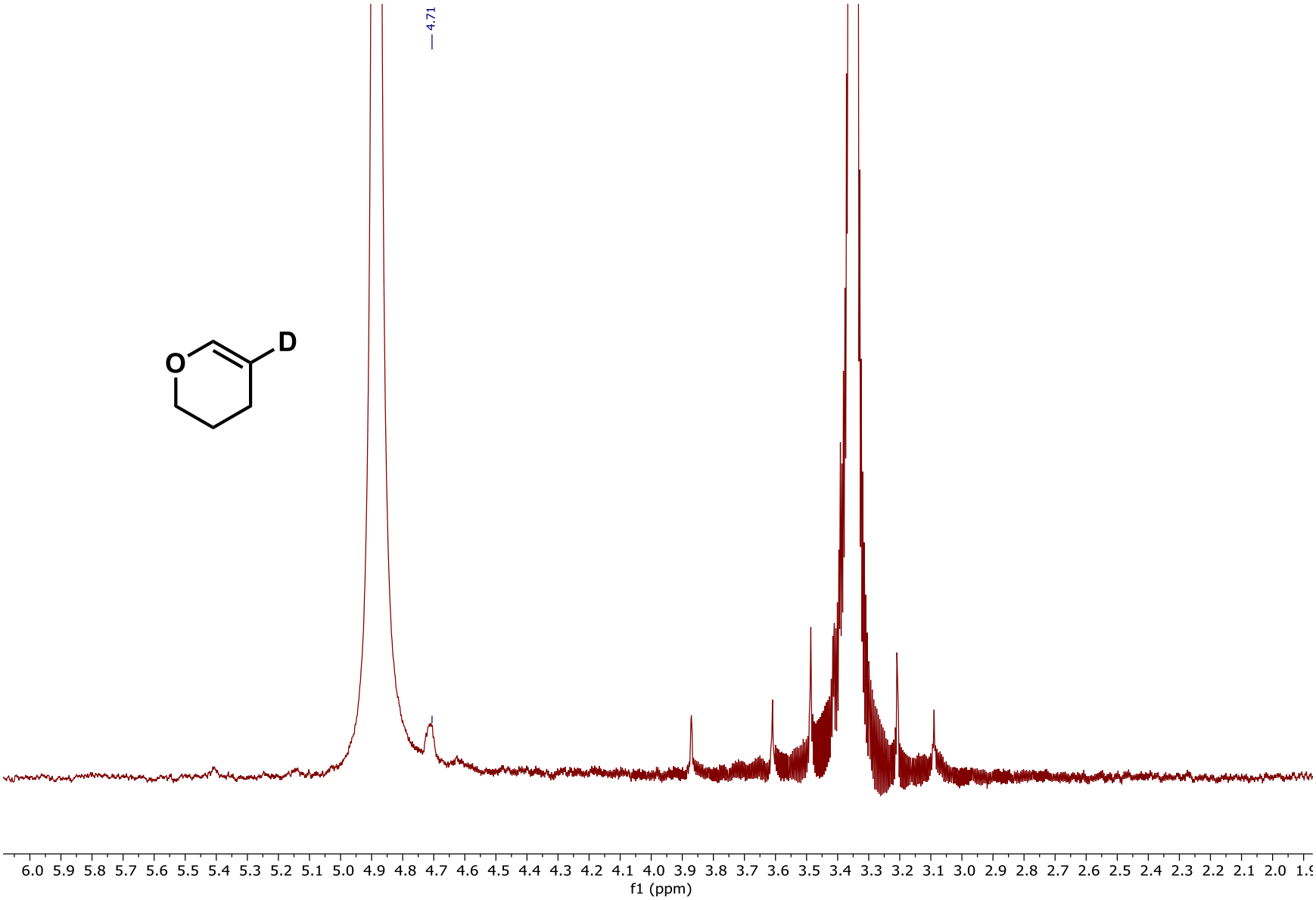
^{2}H NMR (77 MHz, CD_3OD) of 2,3-dihydro-*3D,4D*-furan **[D]-4g.**



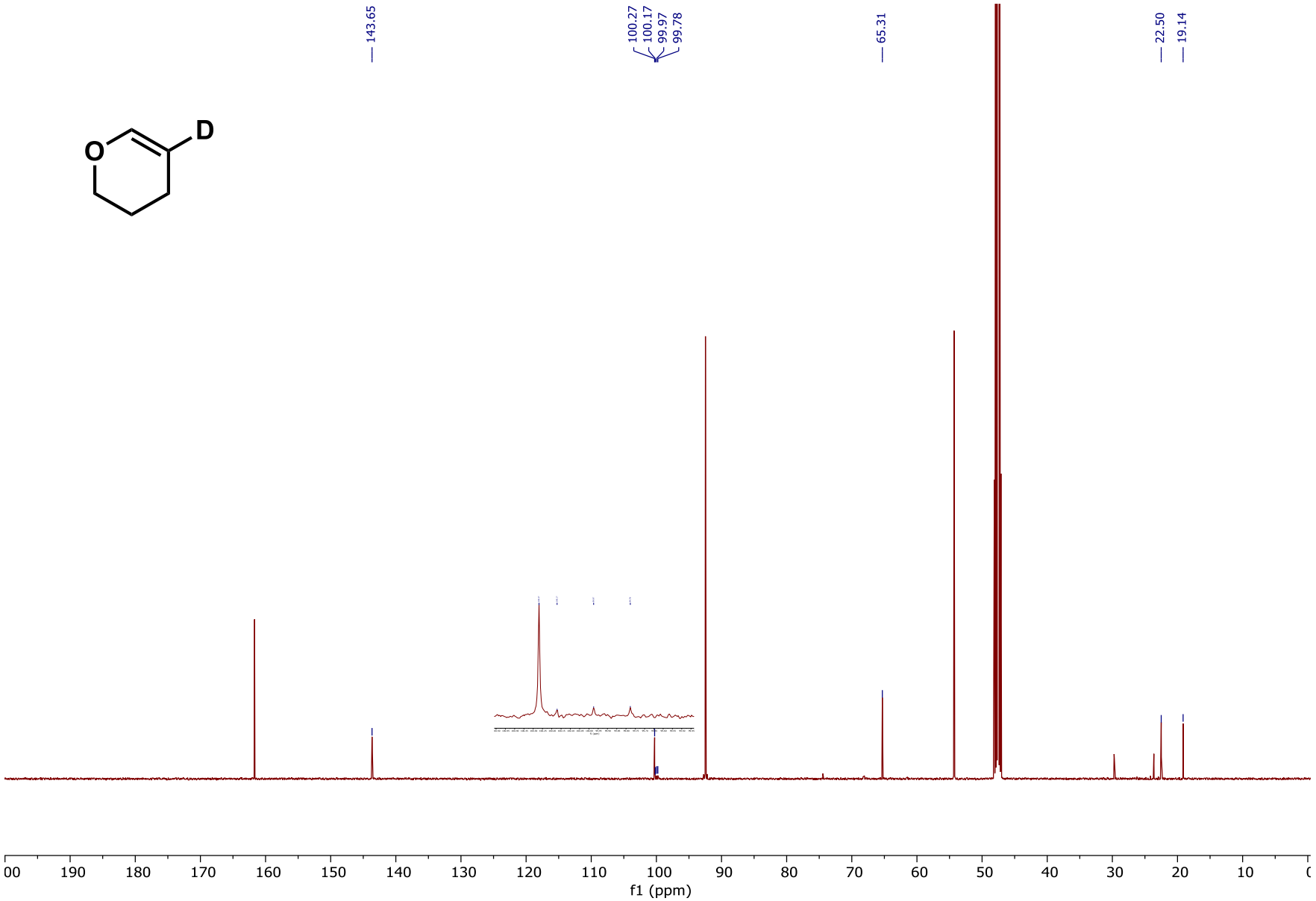
^{13}C NMR (125 MHz, CD_3OD) of 2,3-dihydro-*3D,4D*-furan **[D]-4g**.



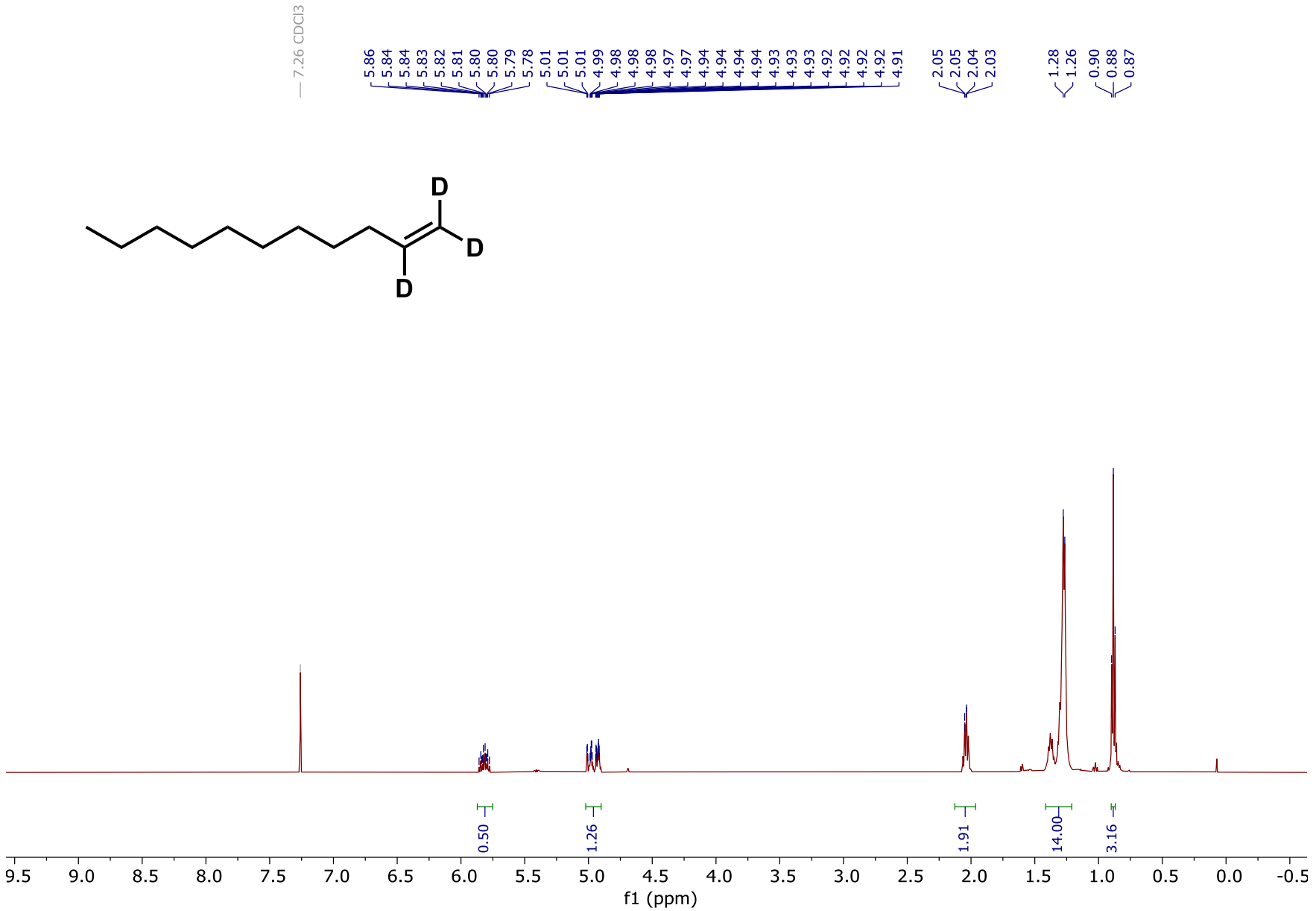
^{1}H NMR (500 MHz, CD_3OD) of *5D*-3,4-dihydropyran **[D]-4h.**



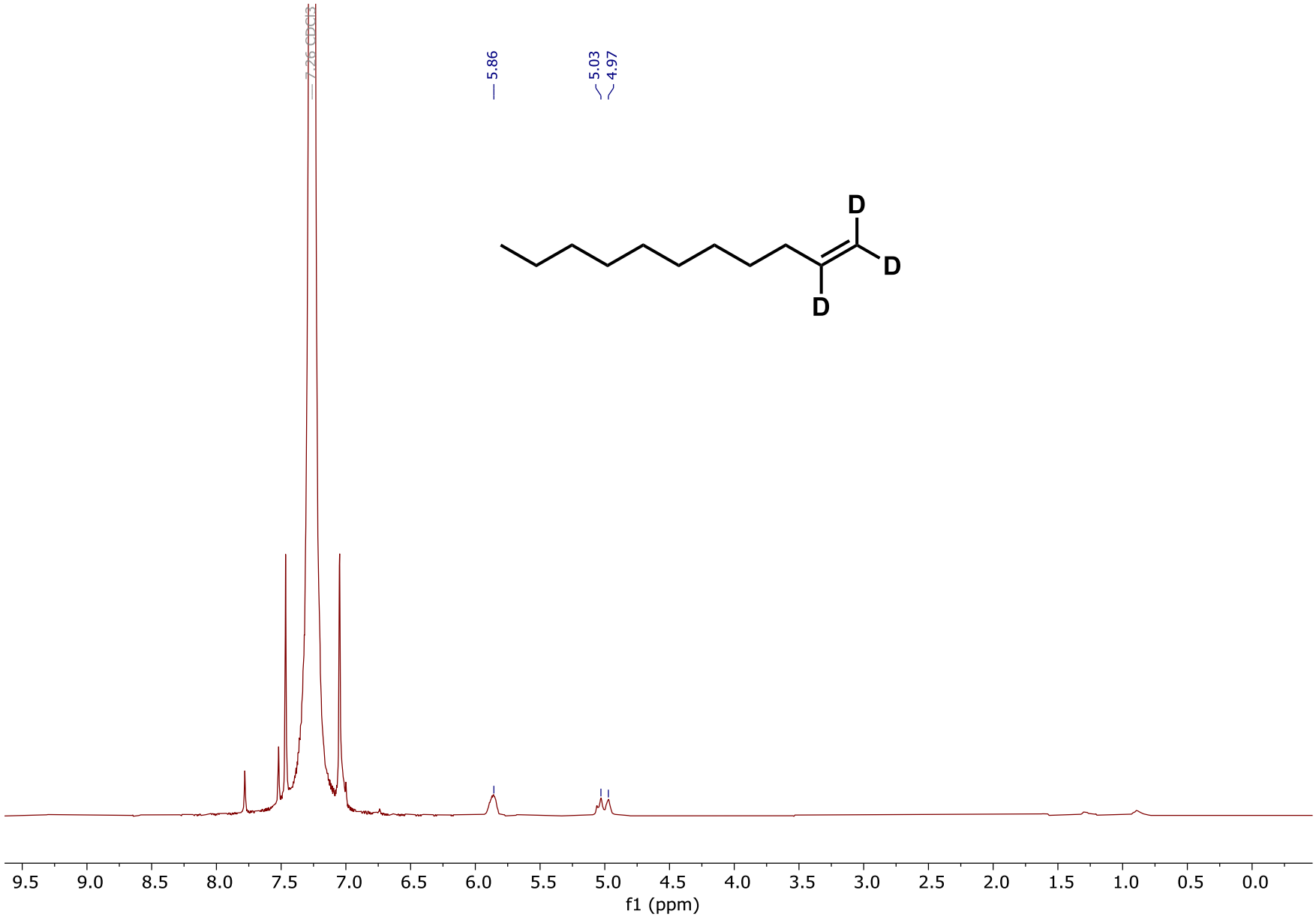
^{2}H NMR (500 MHz, CD_3OD) of *5D*-3,4-dihydropyran **[D]-4h.**



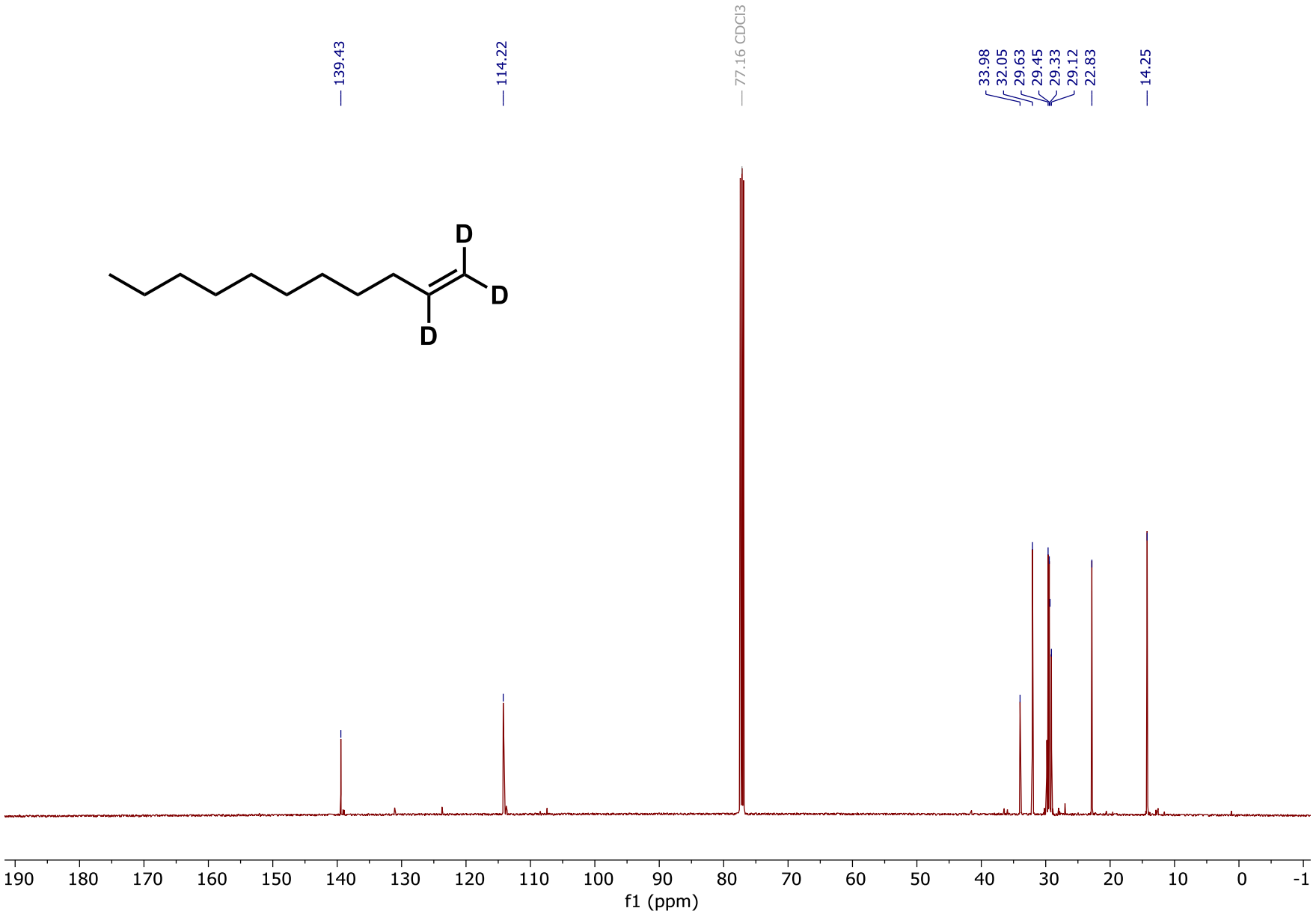
^{13}C NMR (125 MHz, CD_3OD) of *5D*-3,4-dihydropyran **[D]-4h.**



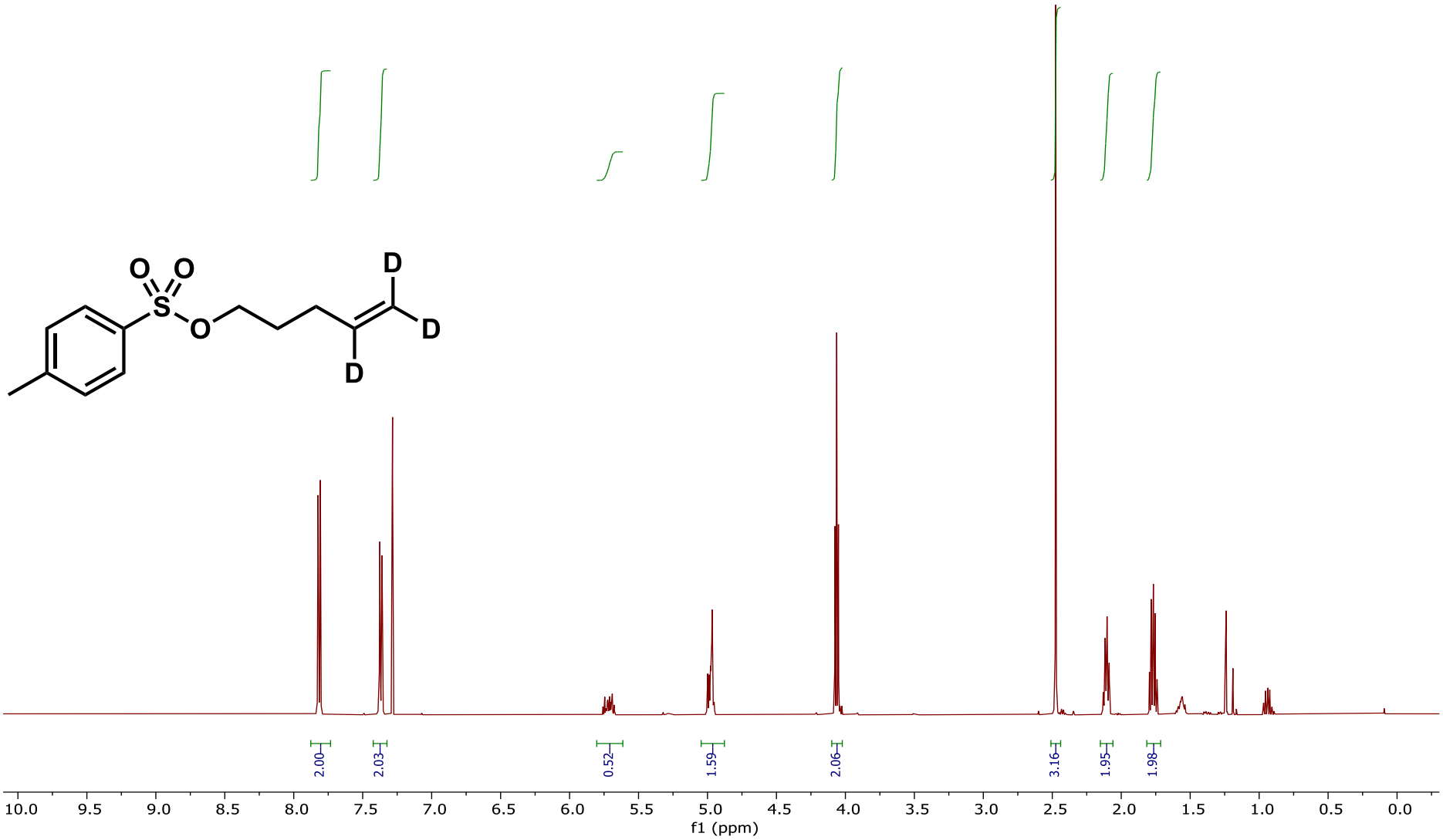
^{1}H NMR (500 MHz, $CDCl_3$) of undecene-*α,β,β-d*$_3$ **[D]-4i.**



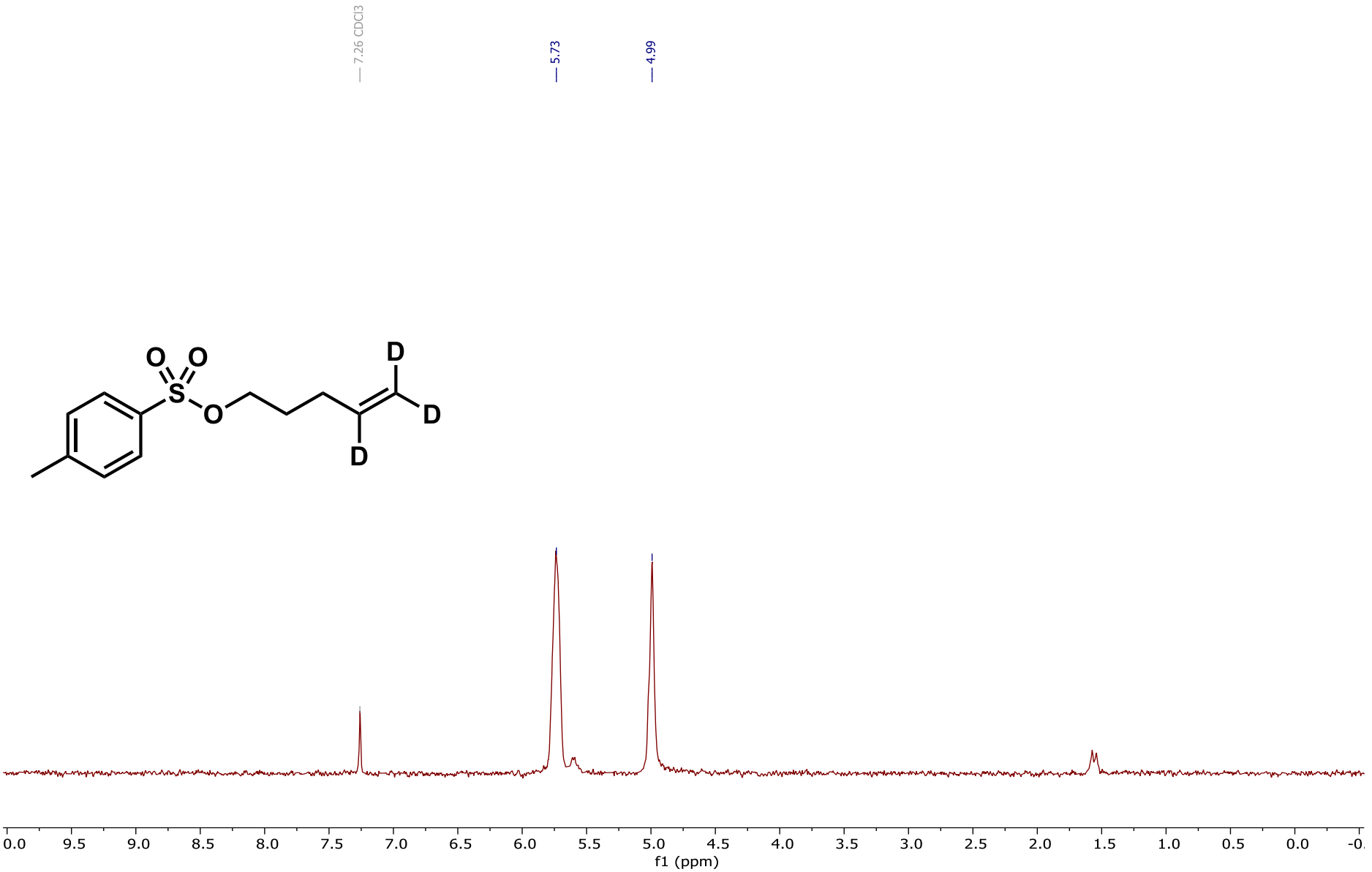
^{2}H NMR (77 MHz, $CDCl_3$) of undecene-*α,β,β-d*$_3$ **[D]-4i.**



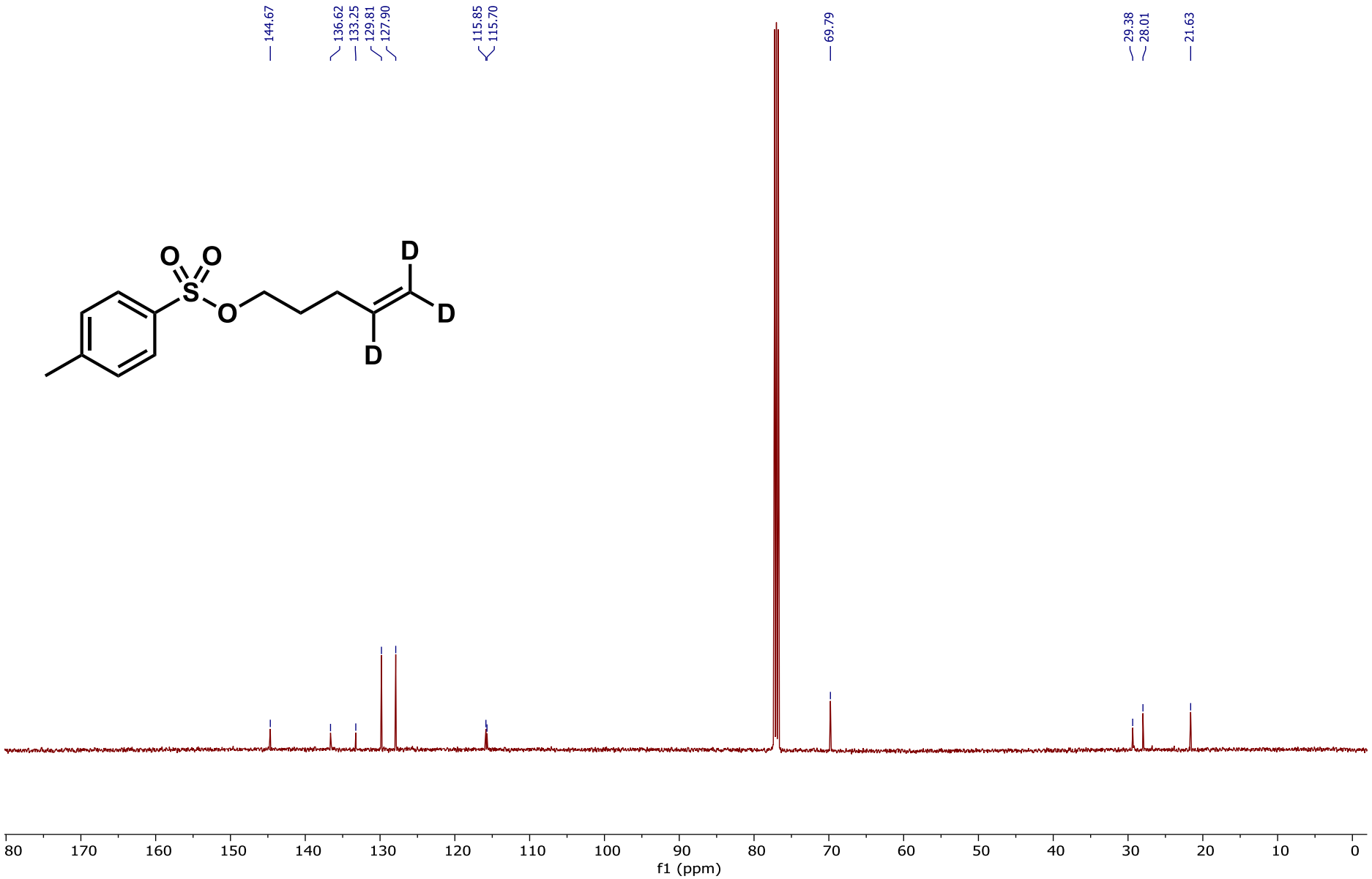
^{13}C NMR (126 MHz, $CDCl_3$) of undecene-*α,β,β-d*$_3$ **[D]-4i.**



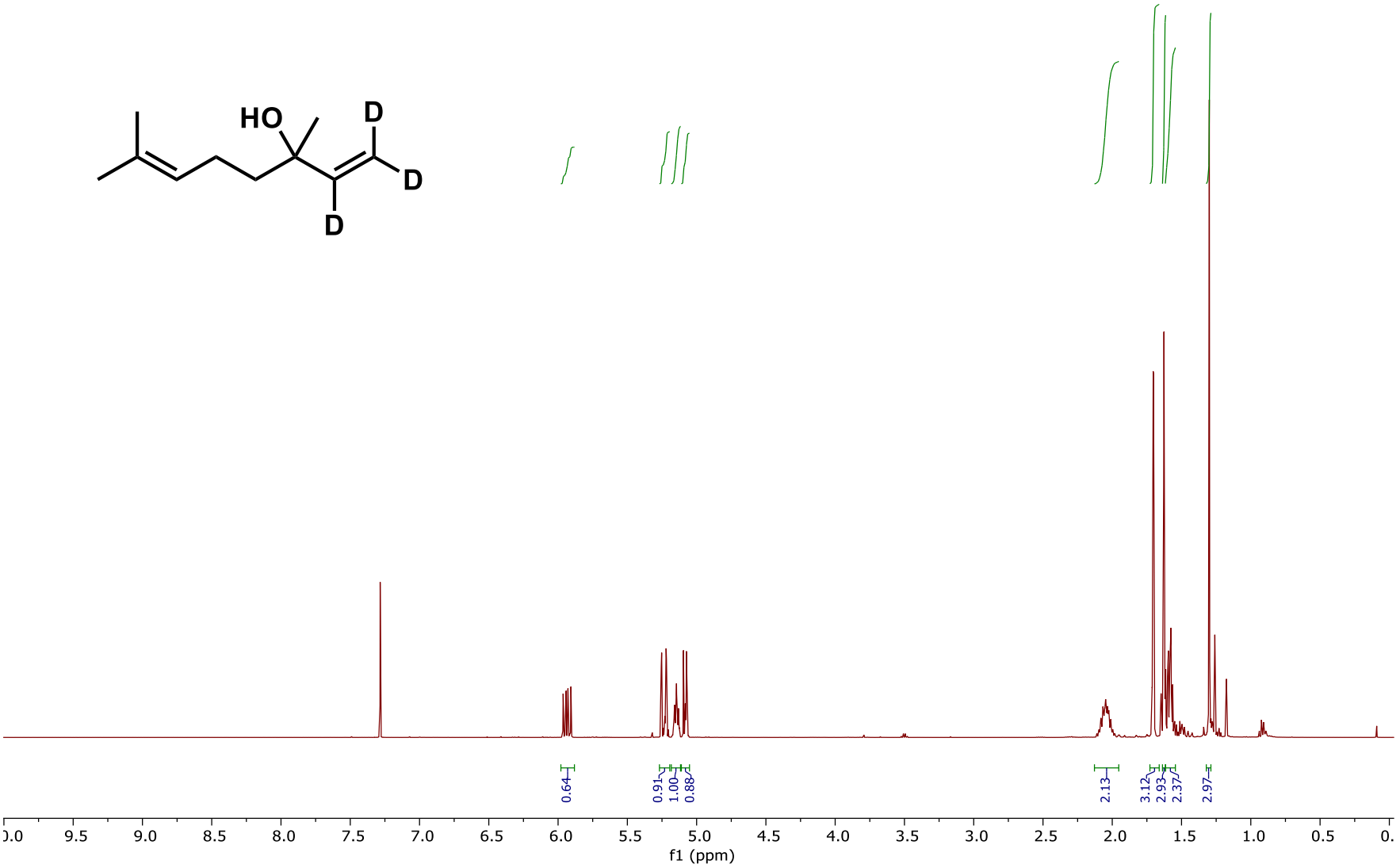
^{1}H NMR (500 MHz, $CDCl_3$) of toluene-4-sulfonic acid pent-4-enyl ester-d_3 **[D]-4j.**



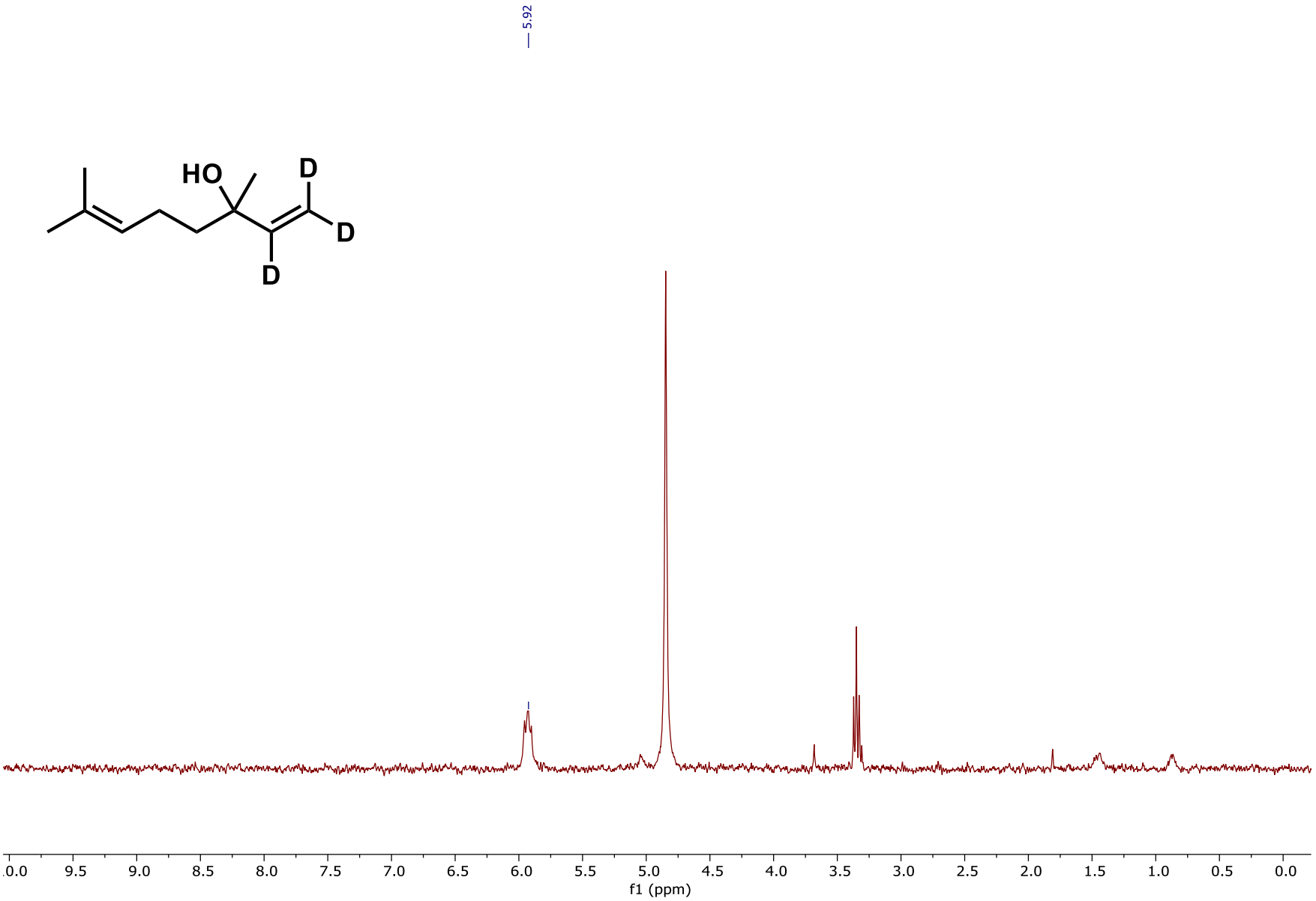
^{2}H NMR (77 MHz, $CHCl_3$) of toluene-4-sulfonic acid pent-4-enyl ester-d_3 **[D]-4j.**



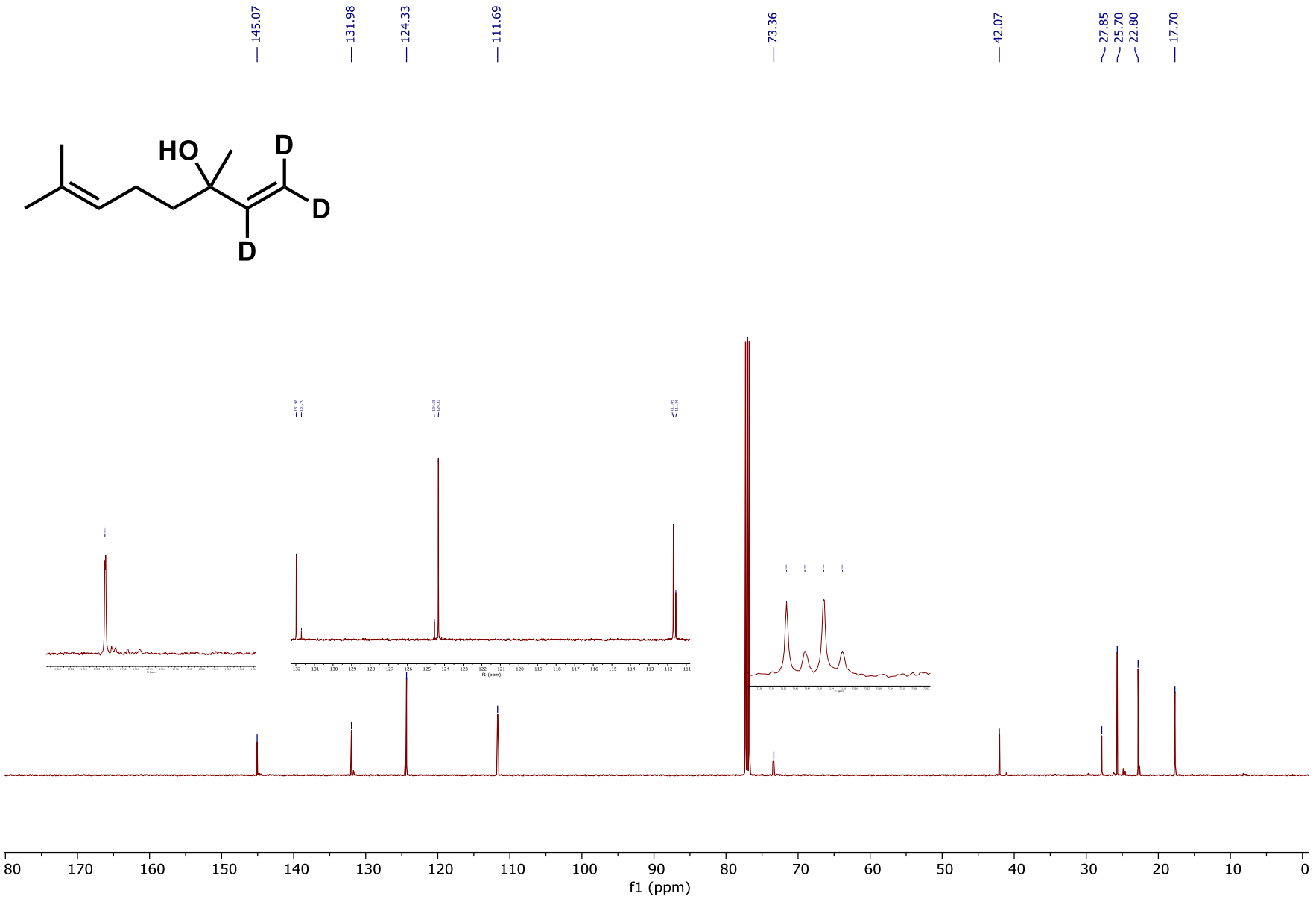
^{13}C NMR (125 MHz, $CDCl_3$) of toluene-4-sulfonic acid pent-4-enyl ester-d_3 **[D]-4j.**



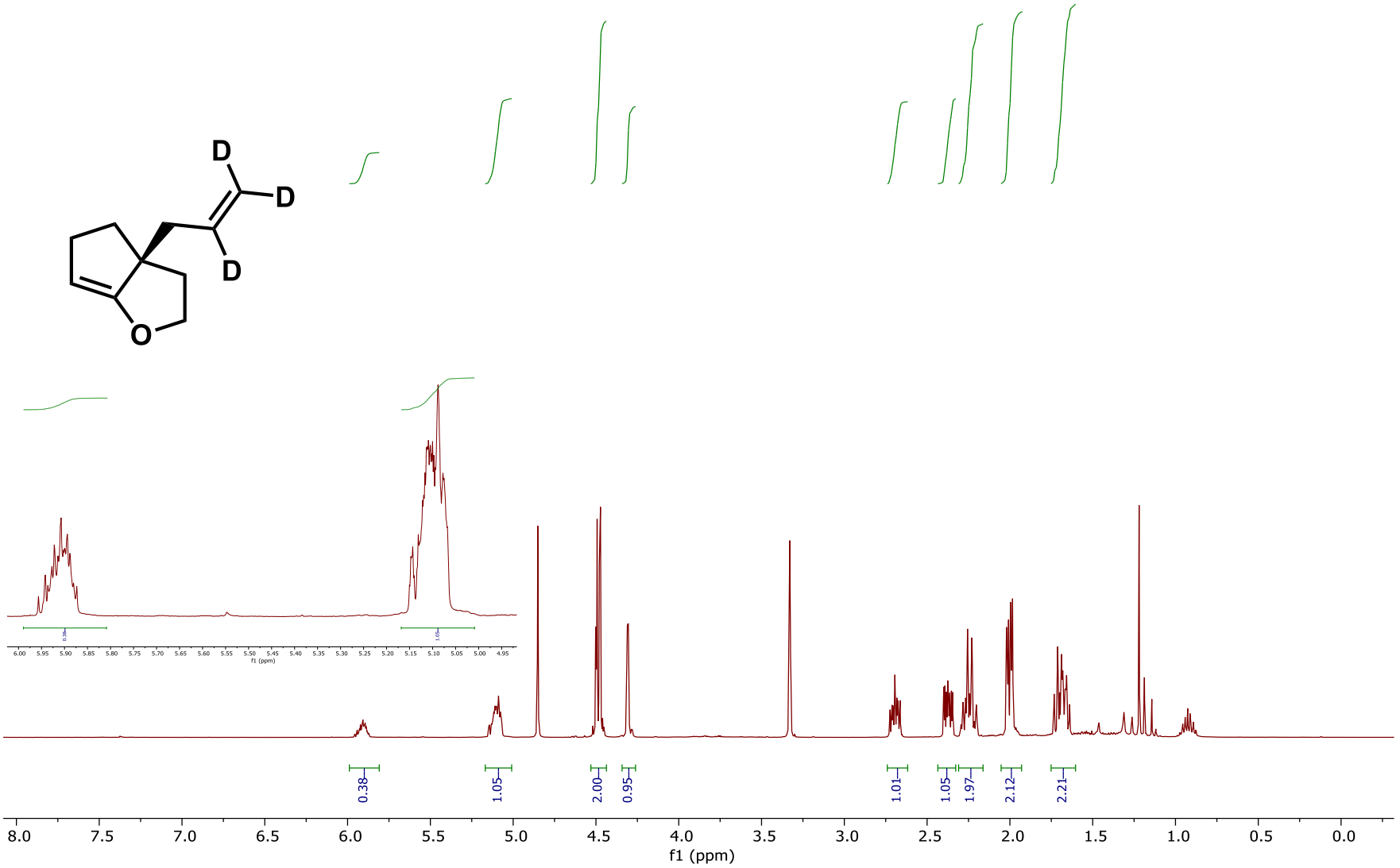
^{1}H NMR (500 MHz, $CDCl_3$) of Linalool-*α,β,β-d*$_3$ **[D]-4k.**



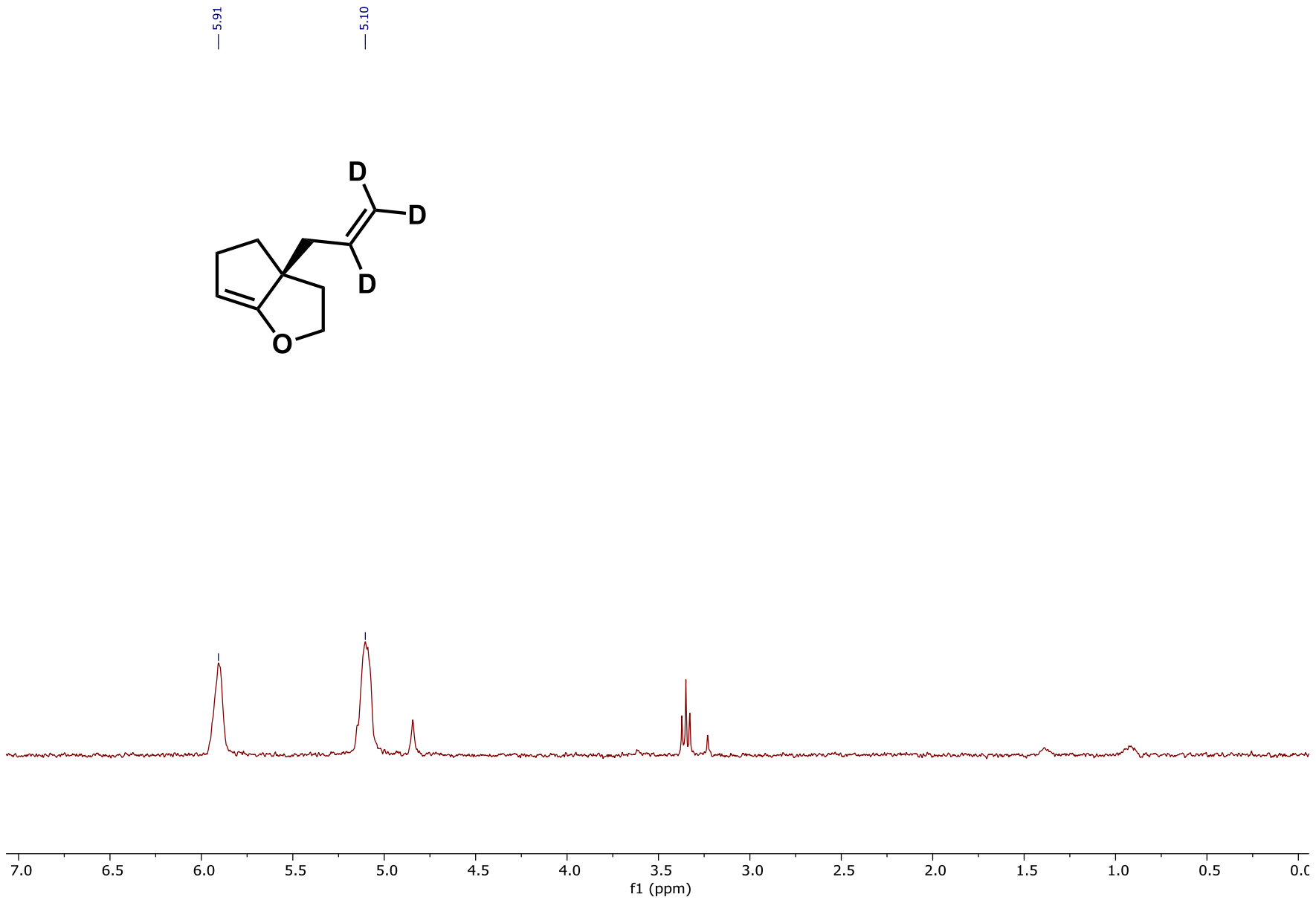
^{2}H NMR (77 MHz, $CDCl_3$) of Linalool-*α,β,β-d*$^{=}$ **[D]-4k.**



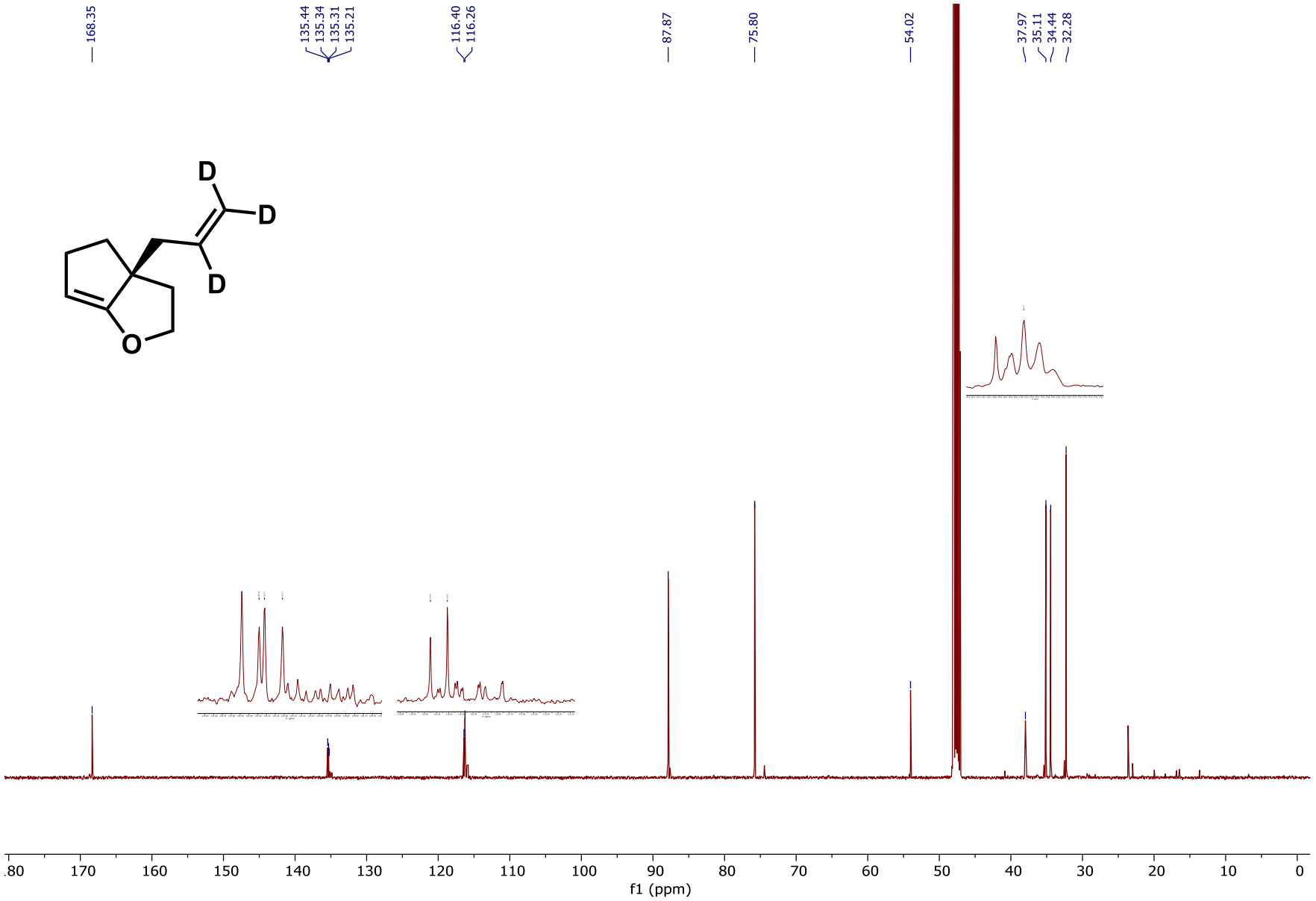
^{13}C NMR (125 MHz, $CDCl_3$) of Linalool-*α,β,β-d*$^{=}$ **[D]-4k.**



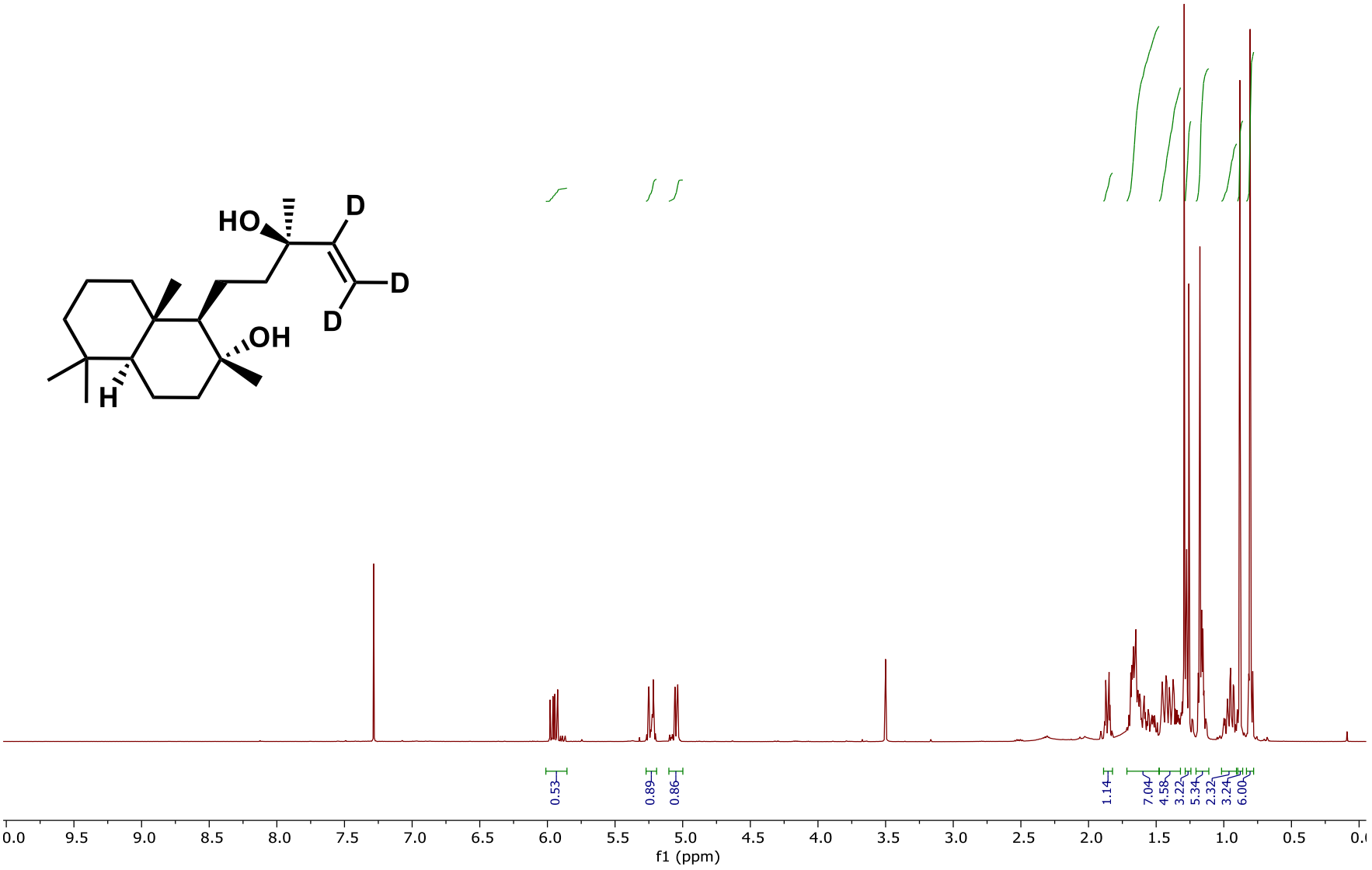
^{1}H NMR (500 MHz, CD_3OD) of (*S*)-5-Allyl-2-oxabicyclo[3.3.0]oct-8-ene-*α,β,β-d*$_{=}$ **[D]-4l.**



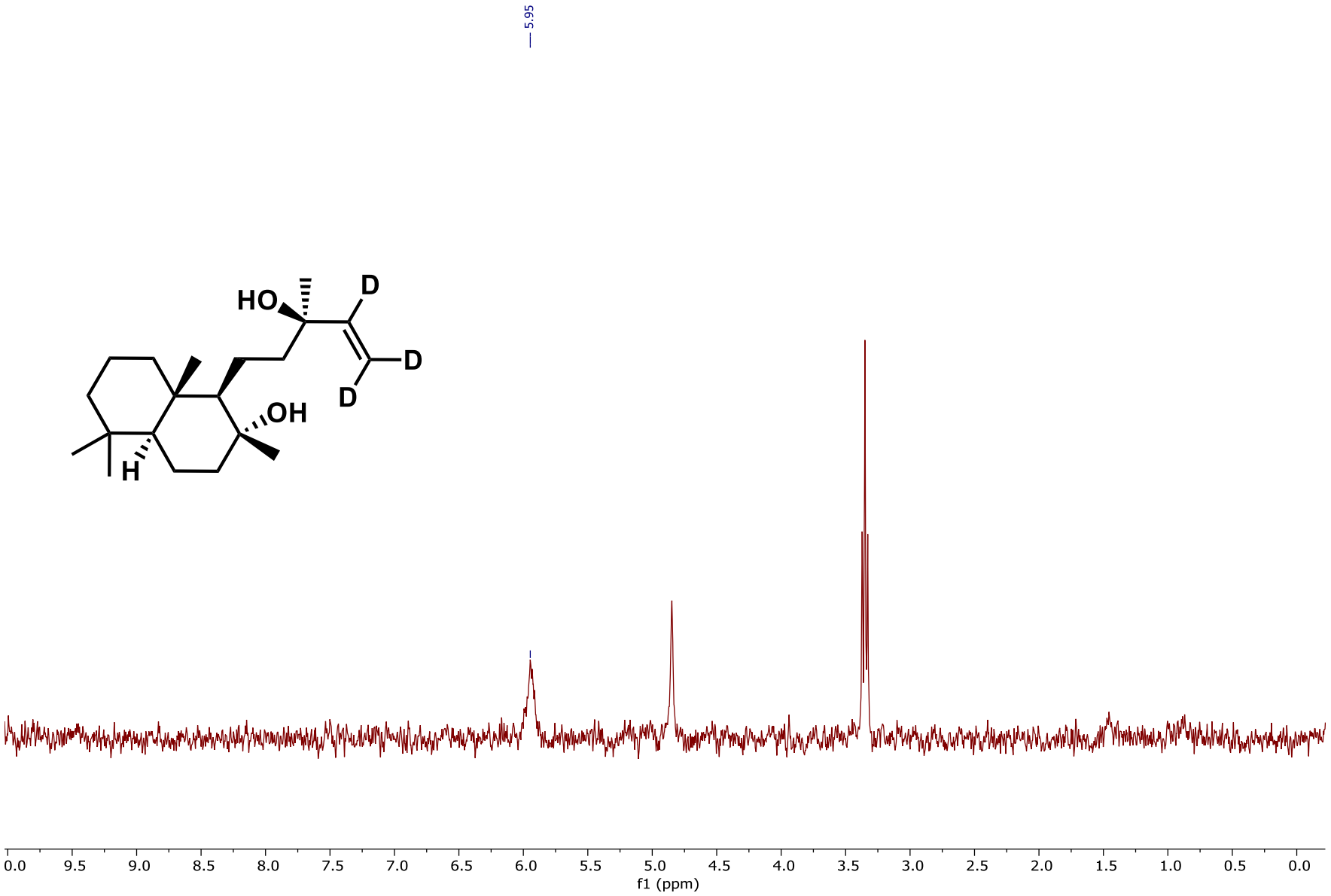
^{2}H NMR (77 MHz, CH_3OH) of (*S*)-5-Allyl-2-oxabicyclo[3.3.0]oct-8-ene-*α,β,β-d*$_3$ **[D]-4l.**



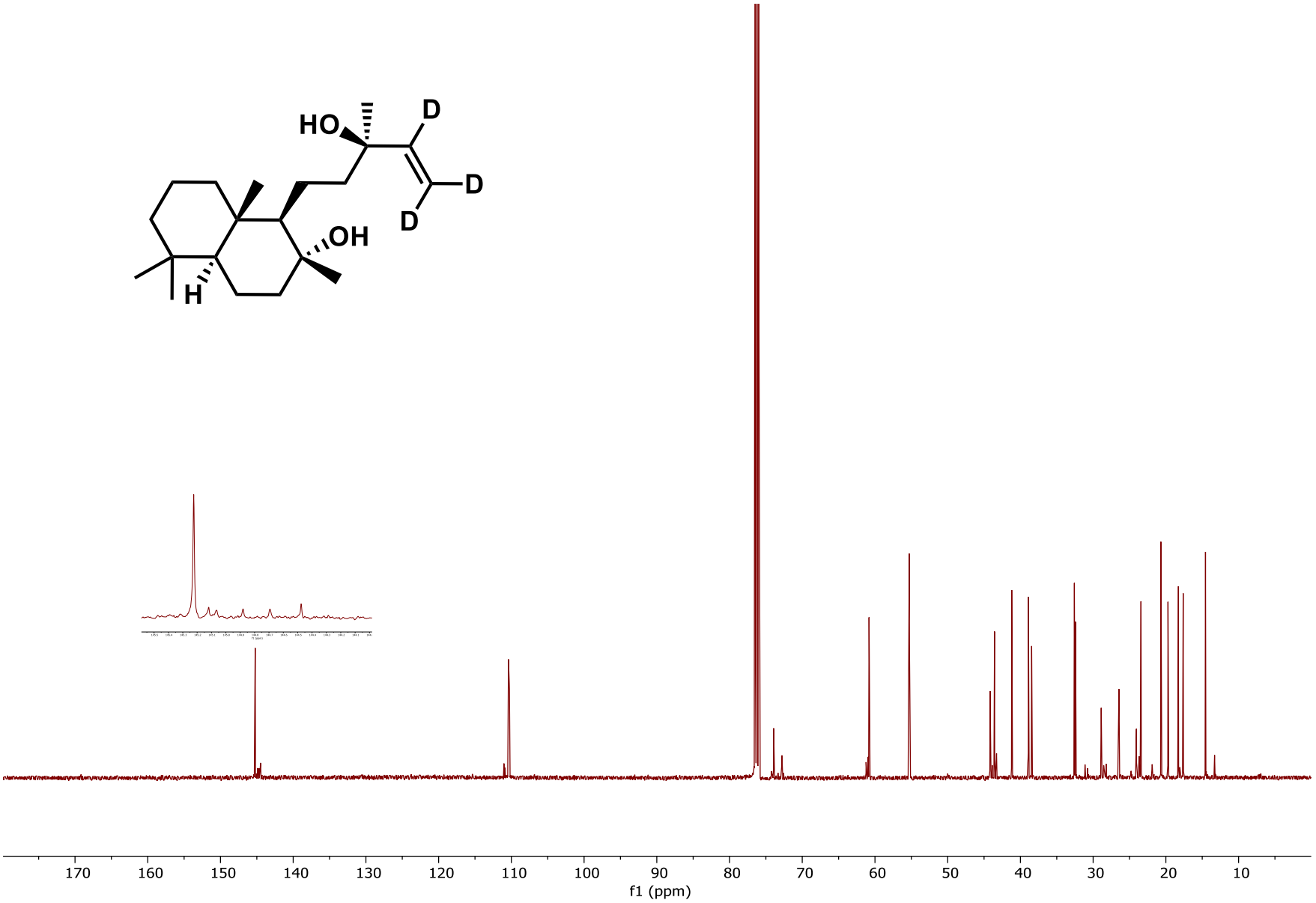
^{13}C NMR (125 MHz, CD_3OD) of (*S*)-5-Allyl-2-oxabicyclo[3.3.0]oct-8-ene-*α,β,β-d*$_3$ **[D]-4l.**



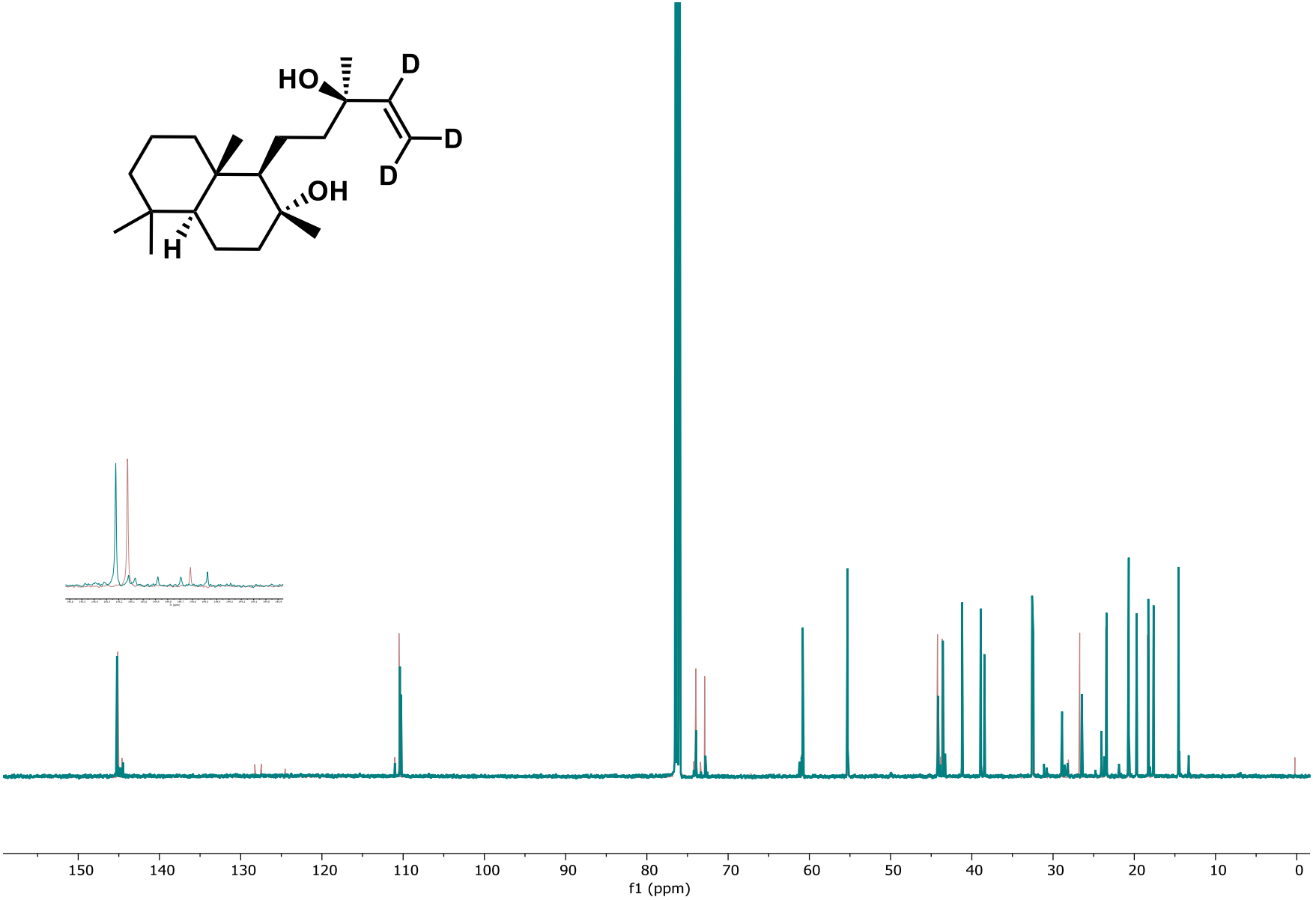
^{1}H NMR (500 MHz, $CDCl_3$) of Sclareol-*α,β,β-d*$_3$ **[D]-4m.**



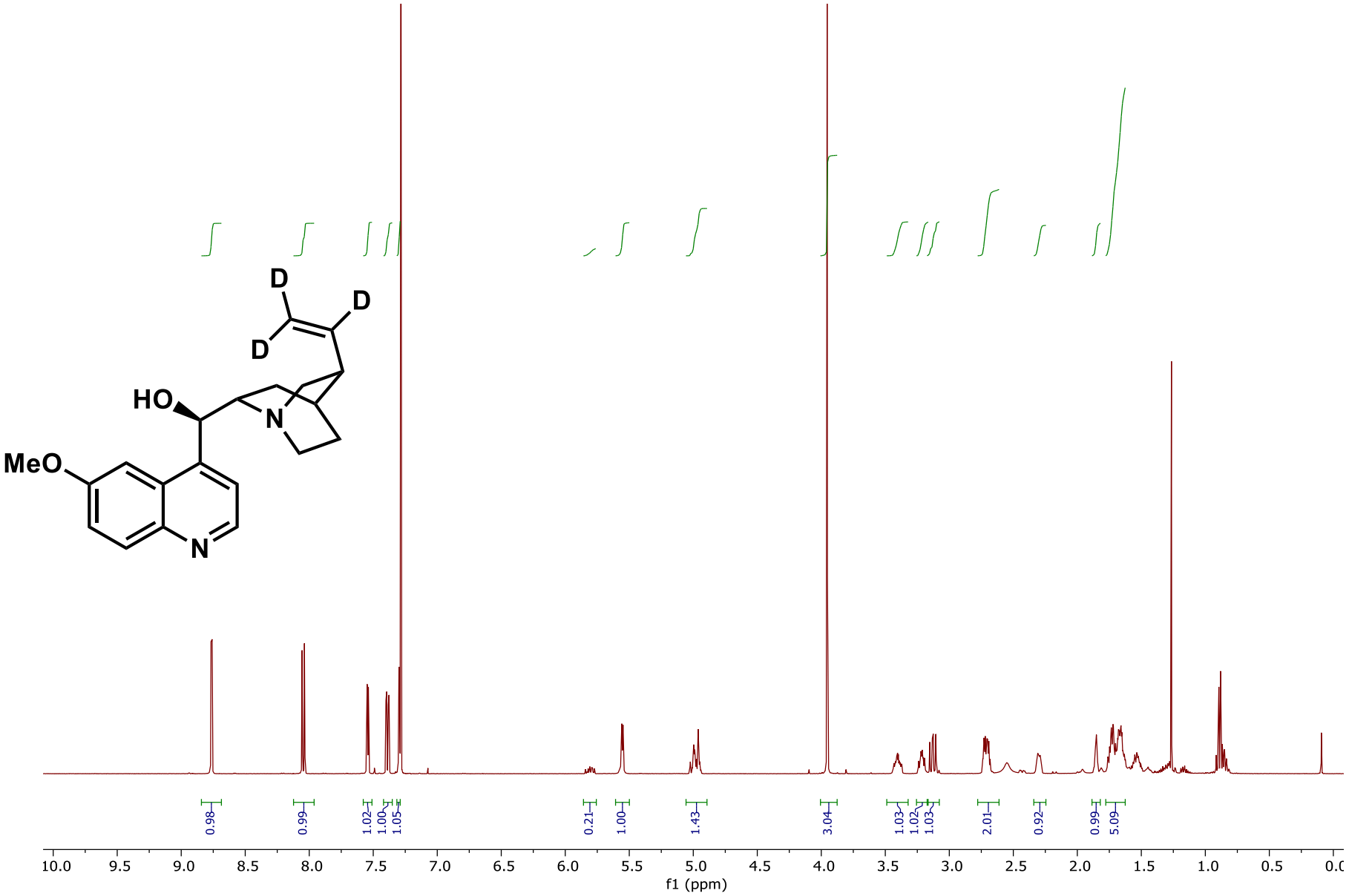
^{2}H NMR (77 MHz, $CDCl_3$) of Sclareol-*α,β,β-d*$_3$ **[D]-4m.**



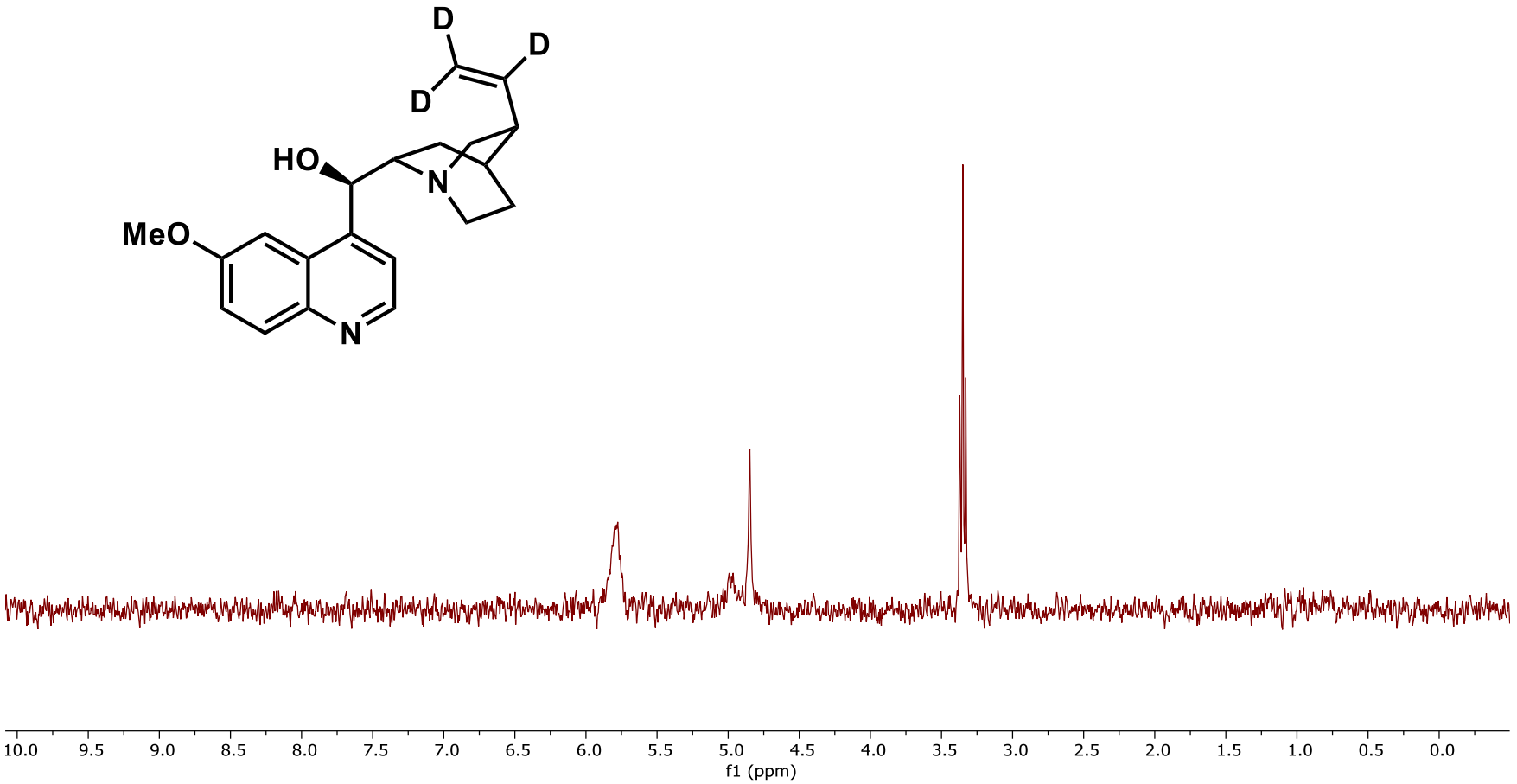
^{13}C NMR (125 MHz, $CDCl_3$) of Sclareol-*α,β,β-d*$_3$ **[D]-4m.**



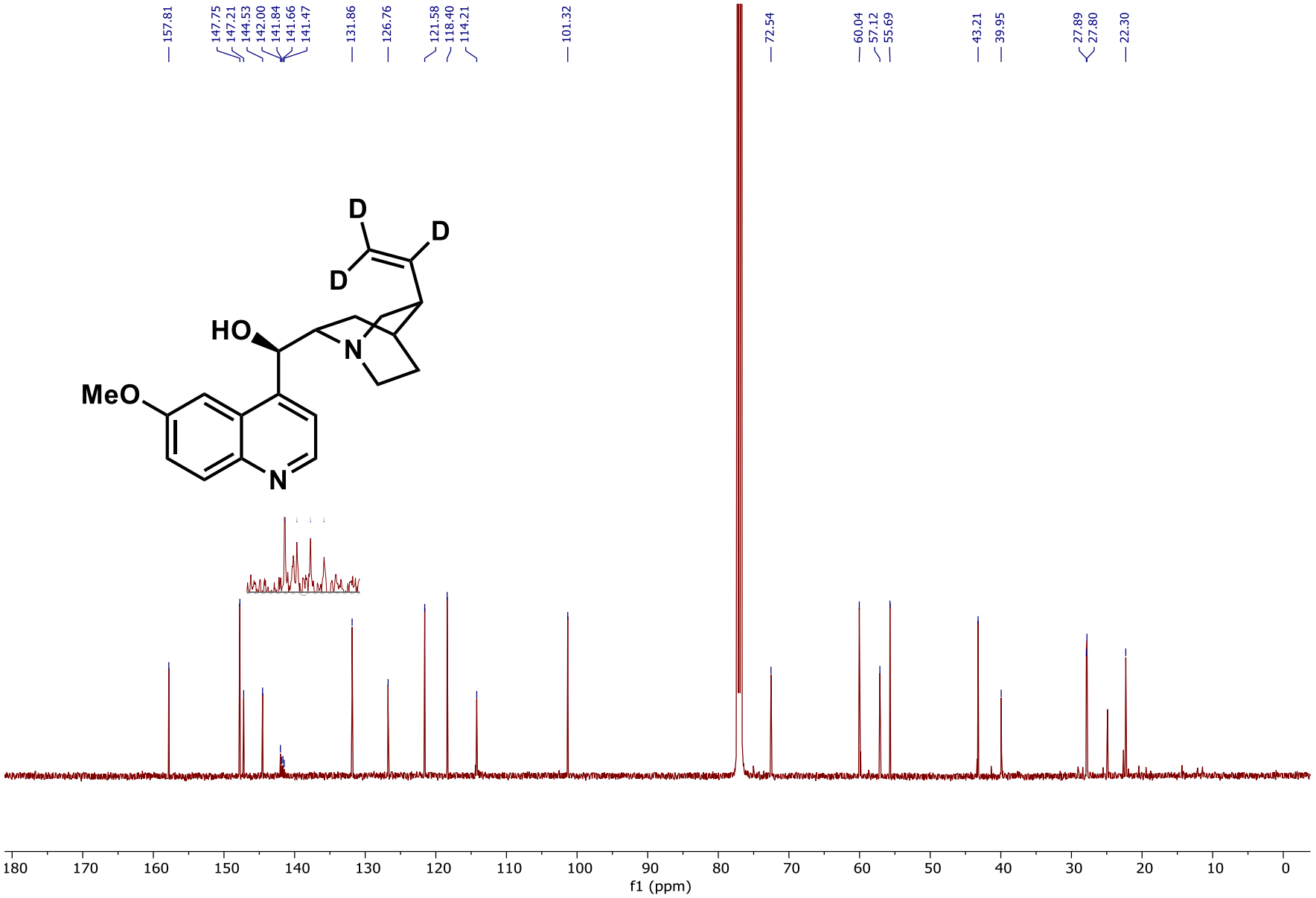
^{13}C NMR (125 MHz, $CDCl_3$) superimposed comparison of Sclareol **4m** (maroon) and Sclareol-*α,β,β-d*$_3$ **[D]-4m** *(green/cyan).*



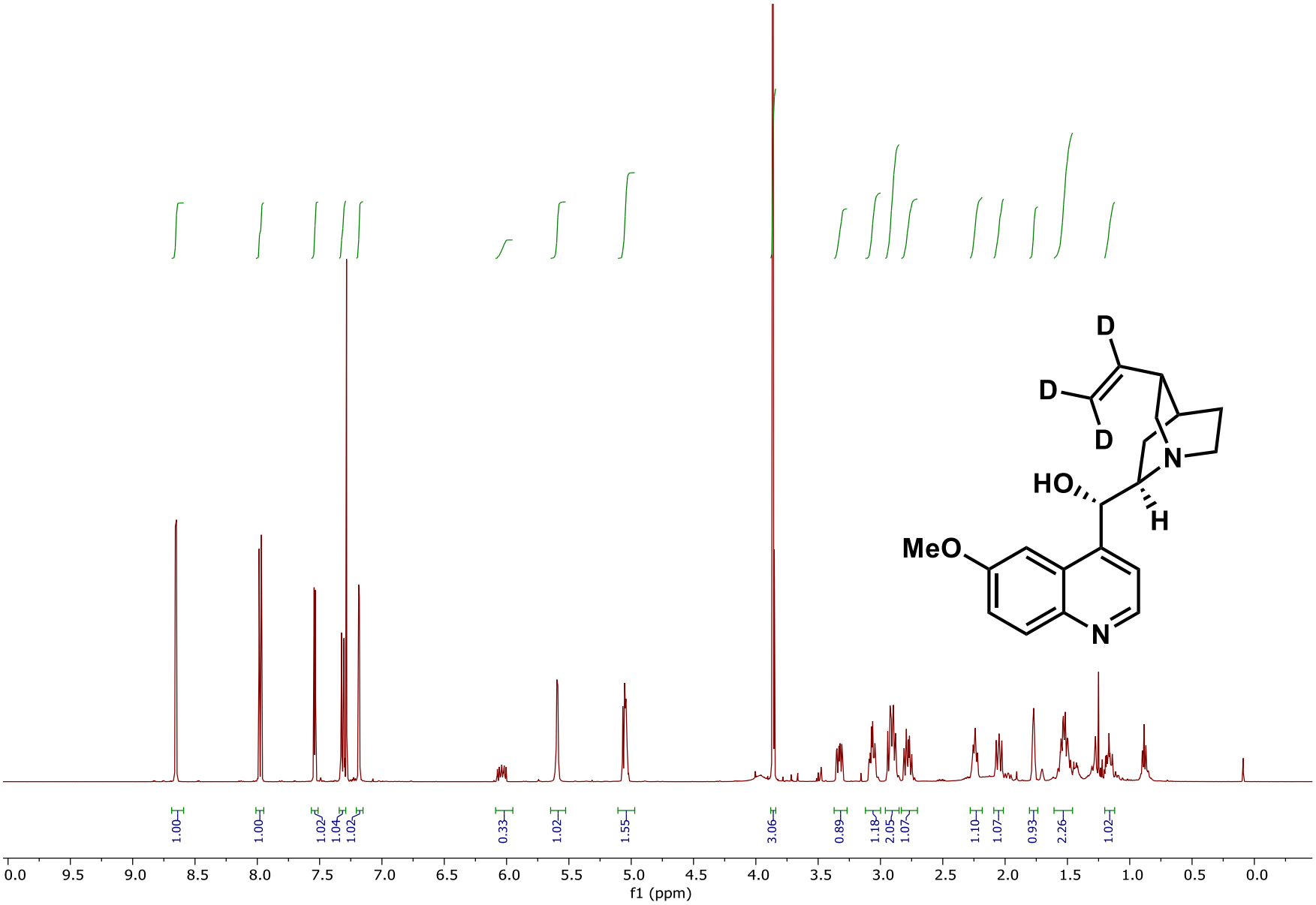
^{1}H NMR (500 MHz, $CDCl_3$) of Quinine-*α,β,β-d*$_3$ **[D]-4n.**



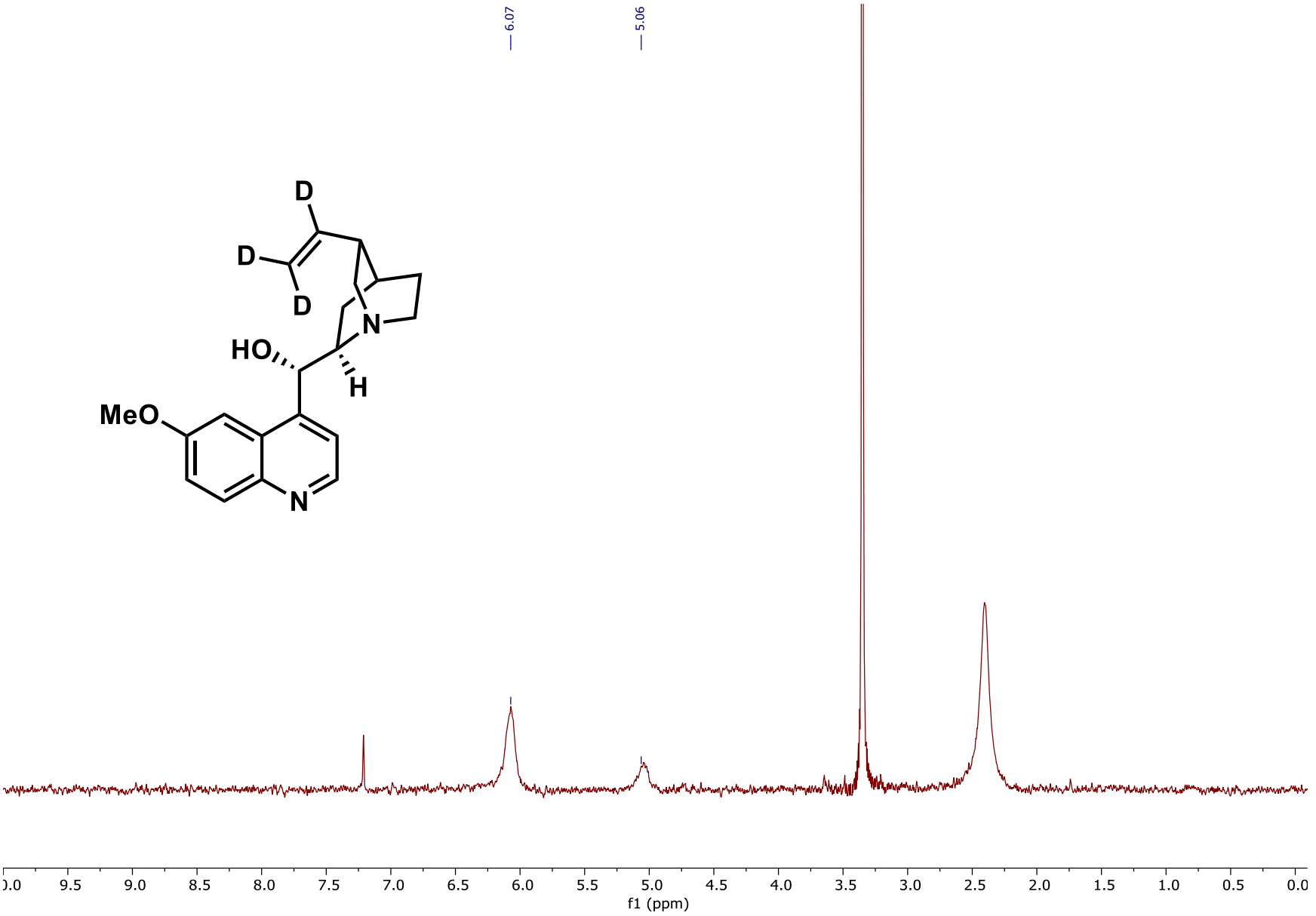
^{2}H NMR (77 MHz, $CDCl_3$) of Quinine-*α,β,β-d*$_3$ **[D]-4n** – containing residual d_4-MeOD.



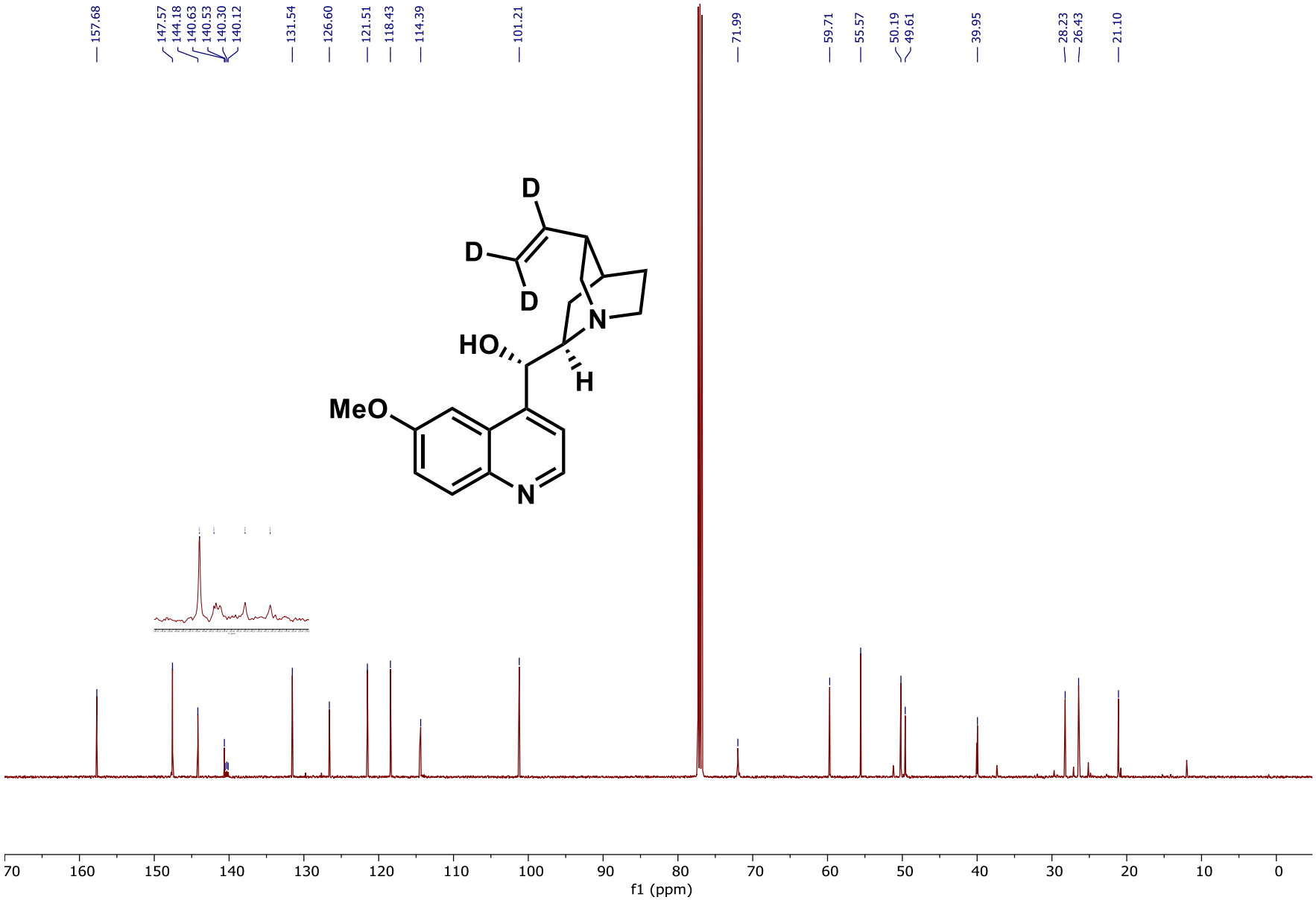
^{13}C NMR (125 MHz, $CDCl_3$) of Quinine-*α,β,β-d*$_3$ **[D]-4n.**



^{1}H NMR (500 MHz, $CDCl_3$) of Quinidine-*α,β,β-d*$_3$ **[D]-4o.**



^{2}H NMR (500 MHz, CH_3OH) of Quinidine-*α,β,β-d*$_3$ **[D]-4o** – containing residual d_4-MeOD.



^{13}C NMR (125 MHz, $CDCl_3$) of Quinidine-*α,β,β-d*$_3$ **[D]-4o.**

18. References

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