Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Johannes Diebler, Anke Spannenberg and Thomas Werner[*]

Leibniz-Institut für Katalyse e. V. an der Universität Rostock,

Albert-Einstein-Strasse 29a, 18059 Rostock, Germany.

1. General

All reactions were performed in 7 cm^3 pressure tube (GL 14) with screw-cap. Thin layer chromatography was performed on *Merck* TLC-plates with fluorescence indication (silica type 60, F_{254}), spots were visualized using UV-light. Filtration was performed using silica with a grain size of 40–63 µm from *Macherey-Nagel*. Deuterated chloroform was purchased from *Deutero*. Deuterated dimethyl sulfoxide was purchased from *Sigma-Aldrich* and dried over CaH_2. NMR spectra were recorded on *Bruker 300 Fourier*, *Bruker AV 300* and *Bruker AV 400* spectrometers.

The chemical shifts (δ) for ^{1}H and ^{13}C are given in parts per million (ppm). Shifts are referenced to 7.27, 77.00 ppm in $CDCl_3$ and 2.49, 39.5 ppm in DMSO-d_6. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s= singlet, d= doublet, dd= double doublet, t= triplet, q= quadruplet, p= pentet, m= multiplet. Gas chromatography was performed on *Agilent 7890A GC System*, mass spectra were measured on downstream *5975C inert XL MSD* mass detector also from *Agilent*. The reported GC yields are based on a calibrated area of *n*-hexadecane as internal standard. Elemental analysis was performed on a *TruSpec CHNS Micro* from *Leco*. High resolution mass spectra (HRMS) were obtained from a *MAT 95 XP* from *Thermo* (EI). DSC analyses were performed with a DSC 1 STARe System (400 W) from Mettler Toledo and alumina sample pans and lid. The measurements were made in an argon atmosphere and a heating rate of 10 $K \cdot min^{-1}$ (20 $K \cdot min^{-1}$ for compound **2s**).

Solvents:

The following solvents have been used as received: *tert*-butanol (*Alfa-Aesar*), dichloromethane (*Walter*), ethanol (*Walter*), *n*-heptane (*Roth*), tetrahydrofuran (Extra Dry, *Acros*), toluene (Extra Dry, *Acros*).

Reagents:

All reagents were purchased from commercial sources and used as received without further purification. 1,2-butylene oxide (*Sigma-Aldrich*, 99%), 1,2-epoxyhex-5-ene (*Sigma-Aldrich*, 97%), 1,2-epoxyhexane (*Sigma-Aldrich*, 97%), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (*TCI*, 98%), 2-(4-chlorophenyl)oxirane (*Alfa Aesar*, 98%), 2,3-dimethyl-2,3-epoxybutane (*Sigma-Aldrich*, 99%), 2,3-epoxypropylbenzene (*Sigma-Aldrich*, 98%), allyl glycidyl ether (*Alfa Aesar*, 97%), butadiene monoxide (*Alfa Aesar*, 98%), carbon disulfide (*Sigma-Aldrich*, >99%), *cis*-2,3-epoxybutane (*Alfa Aesar*, 98%), cyclohexene sulfide (*Sigma-Aldrich*, 85%), cyclohexeneoxide (*Alfa Aesar*, 98%), cyclooctene oxide (*Sigma-Aldrich*, 99%), epichlorohydrin (*Acros*, 99%), epithiochlorohydrine (*Acros*, 97%), ethylene sulfide (*Sigma-Aldrich*, 98%), glycidyl methacrylate (*Acros*, 97%), glycidyl phenyl ether (*Alfa Aesar*, 99%), *n*-hexadecane (*Alfa Aesar*, 99%), *iso*-butylene oxide (*Alfa Aesar*, 99%),

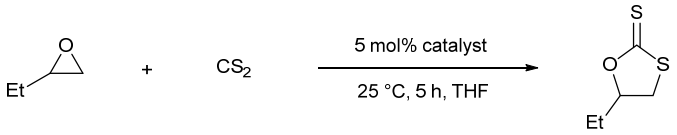
iso-butylene sulfide (*TCI*, >98%), isoprene monoxide (*Alfa Aesar*, 97%), lithium bromide (*Sigma-Aldrich*, 99%), lithium chloride (*Sigma-Aldrich*, >99%), lithium ethoxide (*Sigma-Aldrich*, 95%), lithium iodide (*Sigma-Aldrich*, 99.9%), lithium isopropoxide (*ABCR*, 94%), lithium methoxide (*Sigma-Aldrich*, 98%), lithium *tert*-butoxide (*Alfa Aesar*, 99.9%), (+)-limonene 1,2-epoxide (*Sigma-Aldrich*, >97%), (1*S*,2*S*)-(−)-1-phenylpropylene oxide (*Sigma-Aldrich*, 98%), potassium bromide (*Sigma-Aldrich*, >99%), potassium chloride (*Sigma-Aldrich*, 99%), potassium ethoxide (*Alfa Aesar*, 95%), potassium iodide (*Sigma-Aldrich*, >99%), potassium methylate (*Merck*), potassium *tert*-butoxide (*Sigma-Aldrich*, >99%), propylene oxide (*Acros*, 99%), (*R*)-propylene oxide (*TCI*, 98%), propylene sulfide (*Sigma-Aldrich*, >96%), sodium bromide (*ABCR*, 99%), sodium chloride (*Carl Roth*, >99%), sodium ethoxide (*Sigma-Aldrich*, 95%), sodium iodide (*Sigma-Aldrich*, >99%), sodium *iso*-propoxide (*ABCR*), sodium methoxide (*Acros*, 99%), sodium *tert*-butoxide (*ABCR*, 97%), sodium *tert*-pentyloxide (*Alfa Aesar*, 95%), styrene oxide (*Sigma-Aldrich*, 97%), (*R*)-styrene oxide (*TCI*, >96%), *tert*-butyl glycidyl ether (*Sigma-Aldrich*, 99%), tetra-*n*-butylammonium bromide (*Sigma-Aldrich*, 99%), *trans*-2,3-epoxybutane (*Alfa Aesar*, 97%).

2. General Procedure (GP)

In a pressure tube epoxide **1** or thiirane **3** (1.0 equiv) was added dropwise to a mixture of CS_2 (2.0 equiv) and LiO^tBu (0.05 equiv). If not otherwise stated the tube was sealed and the mixture stirred for 5 h at 25 °C. Subsequently all volatiles were removed in vaccuo. The residue was dissolved in CH_2Cl_2 and filtered over silica (SiO_2, cyclohexane:CH_2Cl_2= 2:1). After removal of all volatiles in vaccuo the thiocarbonates **2** or **4** were obtained.

3. Additional Screening Experiments

Table S1. Addition of CS_2 to **1a** in presence of different classes of catalyst.[a]

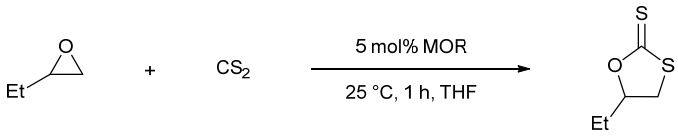


1a **2a**

Entry	Catalyst	Conversion **1a** (%)[b]	Yield **2a** (%)[b]	Selectivity **2a** (%)[b]
1	LiBr	21	16	75
2	NBu_4Br	4	0	-
3	$[HO(CH_2)_2PBu_3]I$	11	0	-
4	IPr	0	0	-
5	KO^{t}Bu	3	0	-
6	NaOMe	13	5	38
7	IPr, LiBr	3	2	66
8	KO^{t}Bu, LiBr	42	29	69
9	NaOMe, LiBr	87	76	87

[a]Reaction conditions: 2.5 mmol **1a**, 1.2 equiv CS_2, 2.5 mL THF. [b]Determined by GC with *n*-hexadecane as internal standard.

Table S2. Alkali alkoxide catalyzed addition of CS_2 to **1a** in THF.[a]

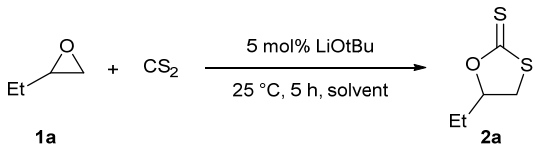


1a **2a**

Entry	MOR	Conversion **1a** (%)[b]	Yield **2a** (%)[b]	Selectivity **2a** (%)[b]
1[c]	NaOMe	13	5	38
2[c]	NaOEt	9	0	-
3	NaO^{i}Pr	7	0	-
4	NaO^{t}Bu	6	0	-
5[c]	LiOMe	2	0	-
6	LiOEt	68	59	87
7	LiO^{i}Pr	1	0	-
8	LiO^{t}Bu	90	70	78
9[c]	LiO^{t}Bu	>99	78	78

[a]Reaction conditions: 2.5 mmol **1a**, 1.2 equiv CS_2, 2.5 mL THF. [b]Determined by GC with *n*-hexadecane as internal standard. [c]*t* = 5 h.

Table S3. Influence of a solvent on the cycloaddition of **1a** and CS_2 in presence of LiO^tBu.[a]

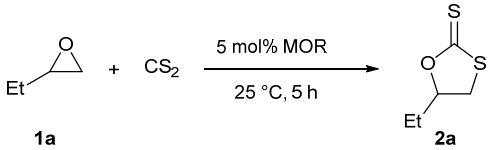


1a **2a**

entry	solvent	conversion **1a** (%)[b]	yield **2a** (%)[b]	selectivity (%)
1	THF	100	78	78
2	^{t}BuOH	12	9	75
3	EtOH	100	34	34
4	H_2O	25	12	50
5	DCM	23	10	43
6	*n*-heptane	28	13	46
7	toluene	23	14	61
8	-	>99	89	89

[a]Reaction conditions: 2.5 mmol **1a**, 2 eq. CS_2, 2.5 mL solvent. [b]Determined by GC with *n*-hexadecane as internal standard.

Table S4. Formation of **2a** in presence of alkali alkoxides.[a]

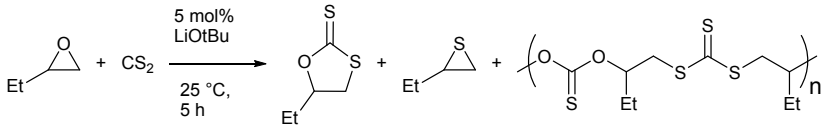


1a **2a**

entry	MOR	conversion **1a** (%)[b]	yield **2a** (%)[b]	selectivity **2a** (%)[b]
1	LiOMe	0	0	0
2	LiOEt	15	5	31
3	LiO^{i}Pr	0	0	0
4	LiO^{t}Bu	>99	89	89
5	NaOMe	42	30	71
6	NaOEt	78	62	79
7	NaO^{i}Pr	63	50	80
8	NaO^{t}Bu	72	46	64
9	NaO^{t}Pent	70	46	65
10	KOMe	0	0	0
11	KOEt	18	0	0
12	KO^{t}Bu	6	0	0

[a]Reaction conditions: 2.5 mmol **1a**, 2 equiv CS_2 [b]Determined by GC with *n*-hexadecane as internal standard.

Table S5. Influence of the catalystamount on the modelreaction.[a]



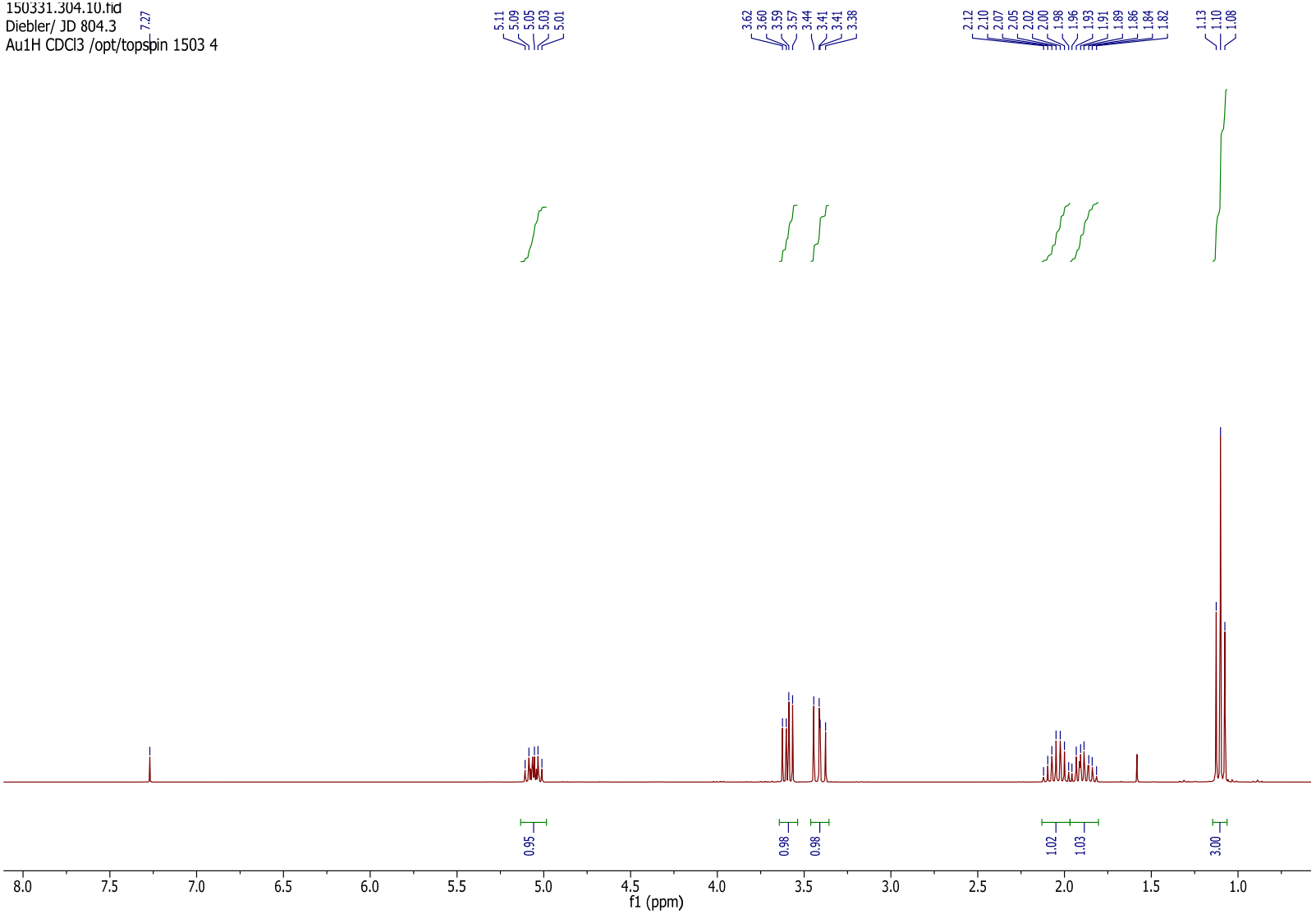
1a **2a** **3** **8**

entry	mol% LiO^tBu	conversion **1a** (%)[b]	yield **2a** (%)[c]	yield **3a** (%)[b]	yield **5a** (%)[c]
1	10	>99	85	9	1
2	5	>99	86	7	1
3	2.5	>99	82	5	10
4	2	>99	76	4	20
5	1	>99	64	3	29

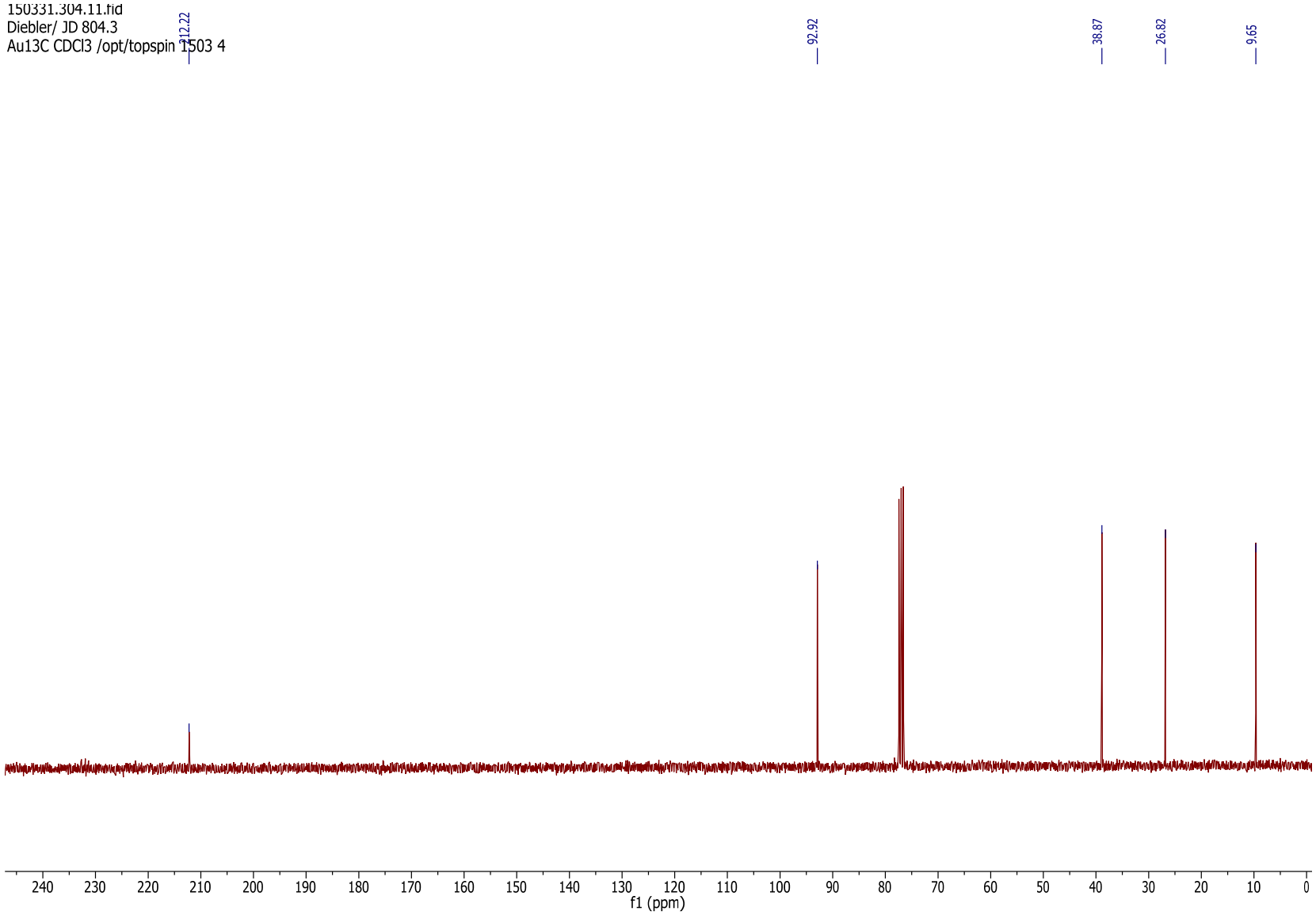
[a]Reaction conditions: 5 mmol **1a**, 2 equiv CS_2 [b]Calculated from ^{1}HNMR. [c]Isolated yield.

4. ^{1}H-NMR and ^{13}C-NMR spectra

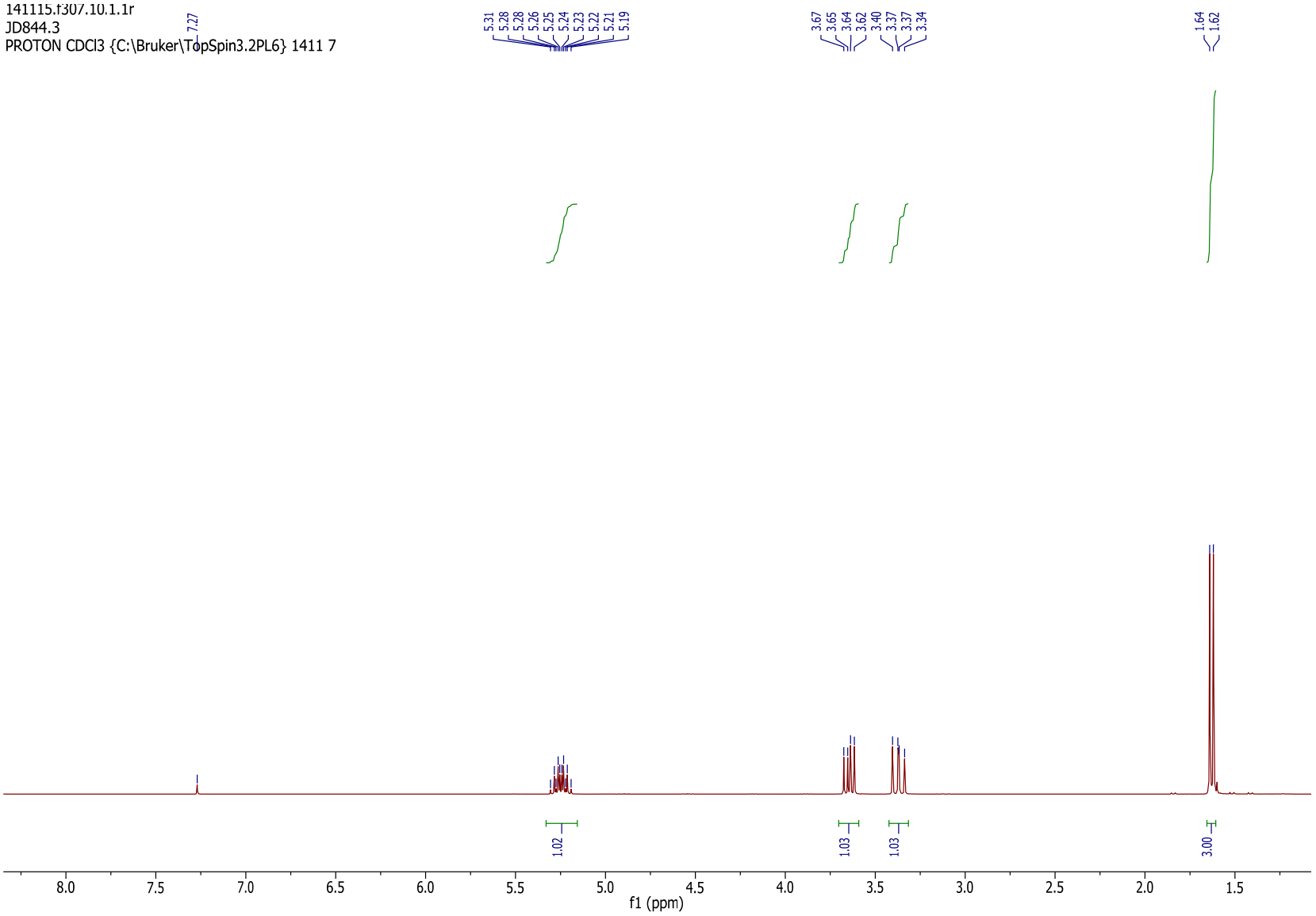
^{1}H-NMR 5-Ethyl-1,3-oxathiolane-2-thione (**2a**)



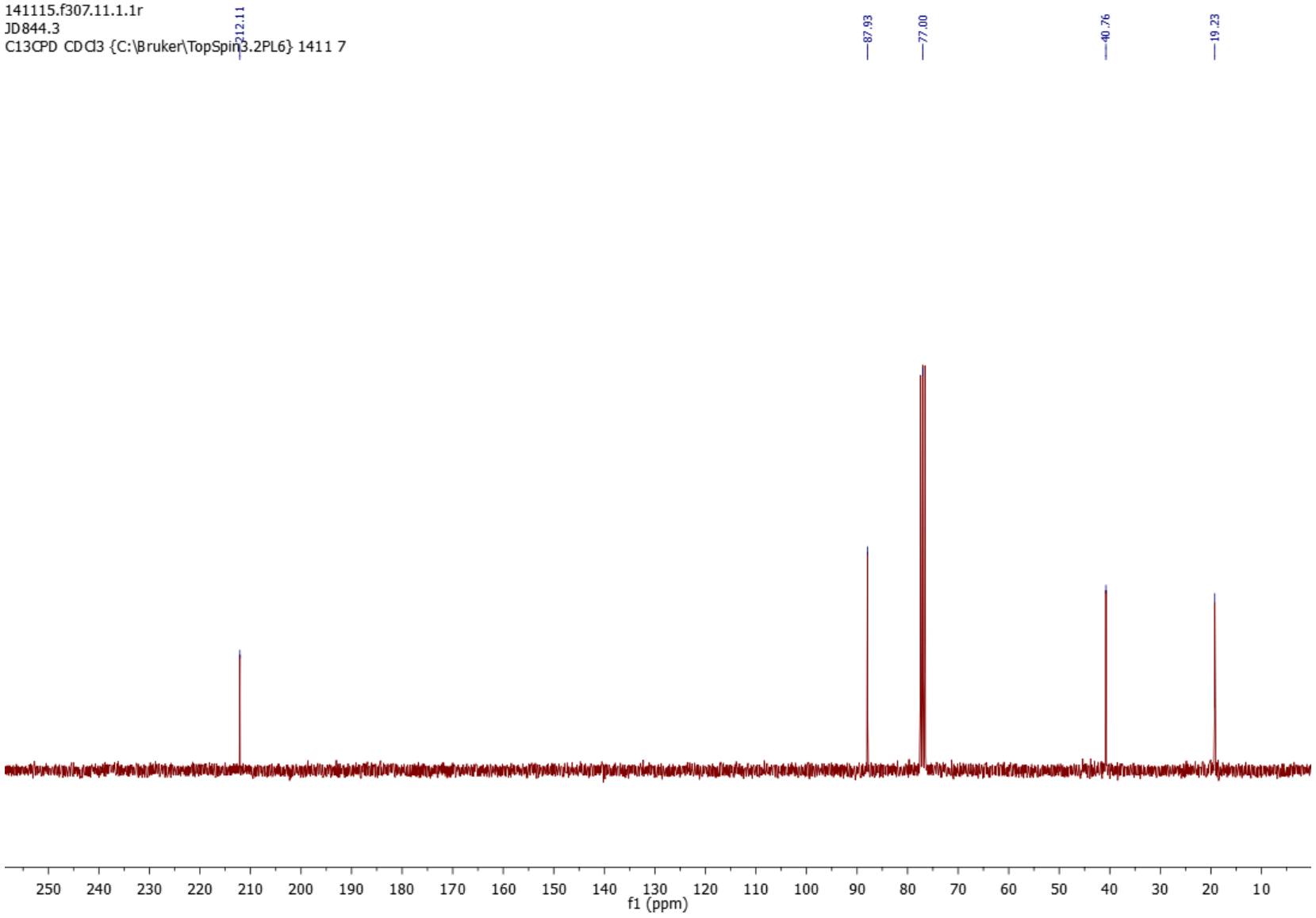
^{13}C-NMR 5-Ethyl-1,3-oxathiolane-2-thione (**2a**)



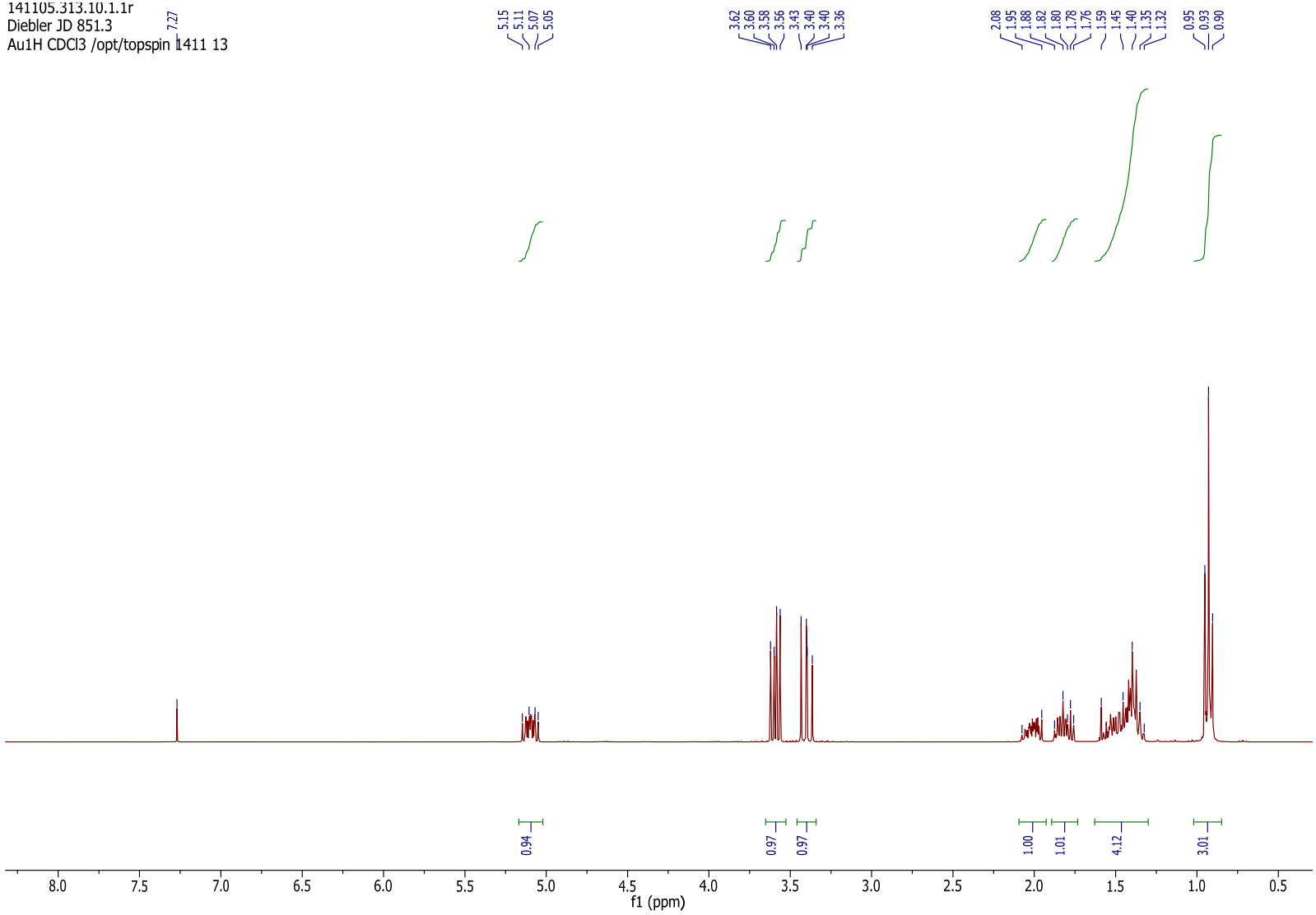
^{1}H-NMR 5-methyl-1,3-oxathiolane-2-thione (**2b**)



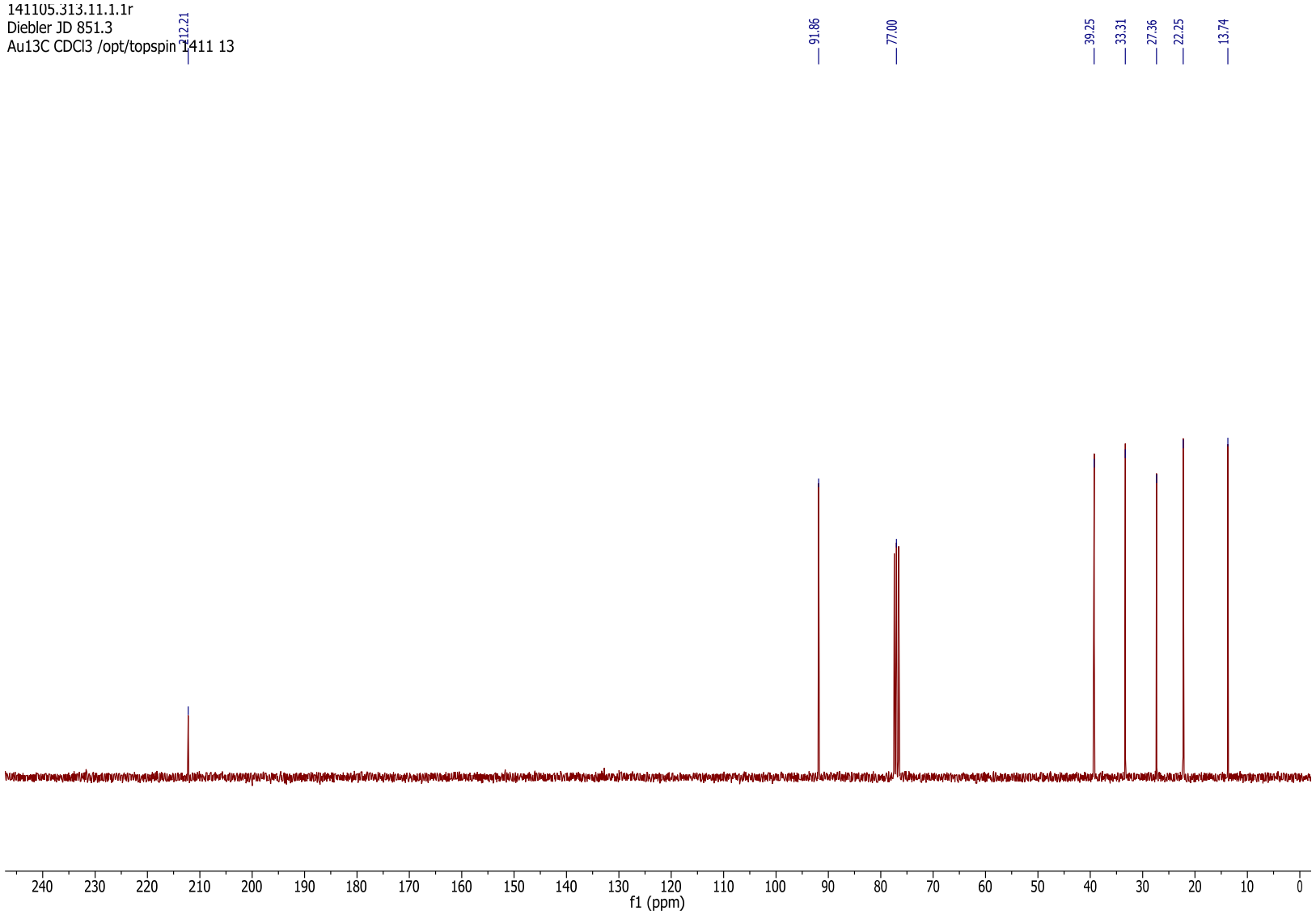
^{13}C-NMR 5-methyl-1,3-oxathiolane-2-thione (**2b**)



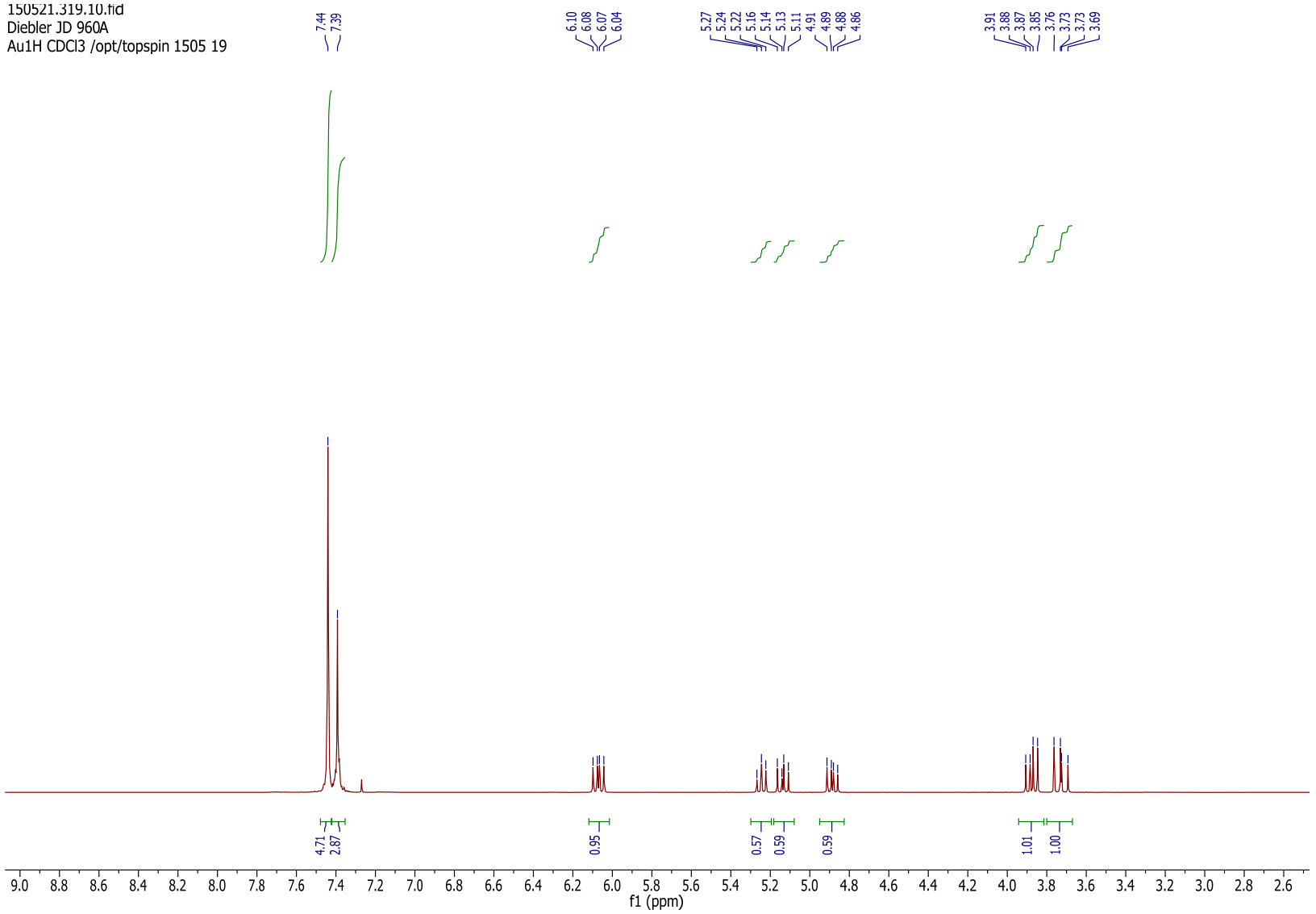
^{1}H-NMR 5-*n*-Butyl-1,3-oxathiolane-2-thione (**2c**)



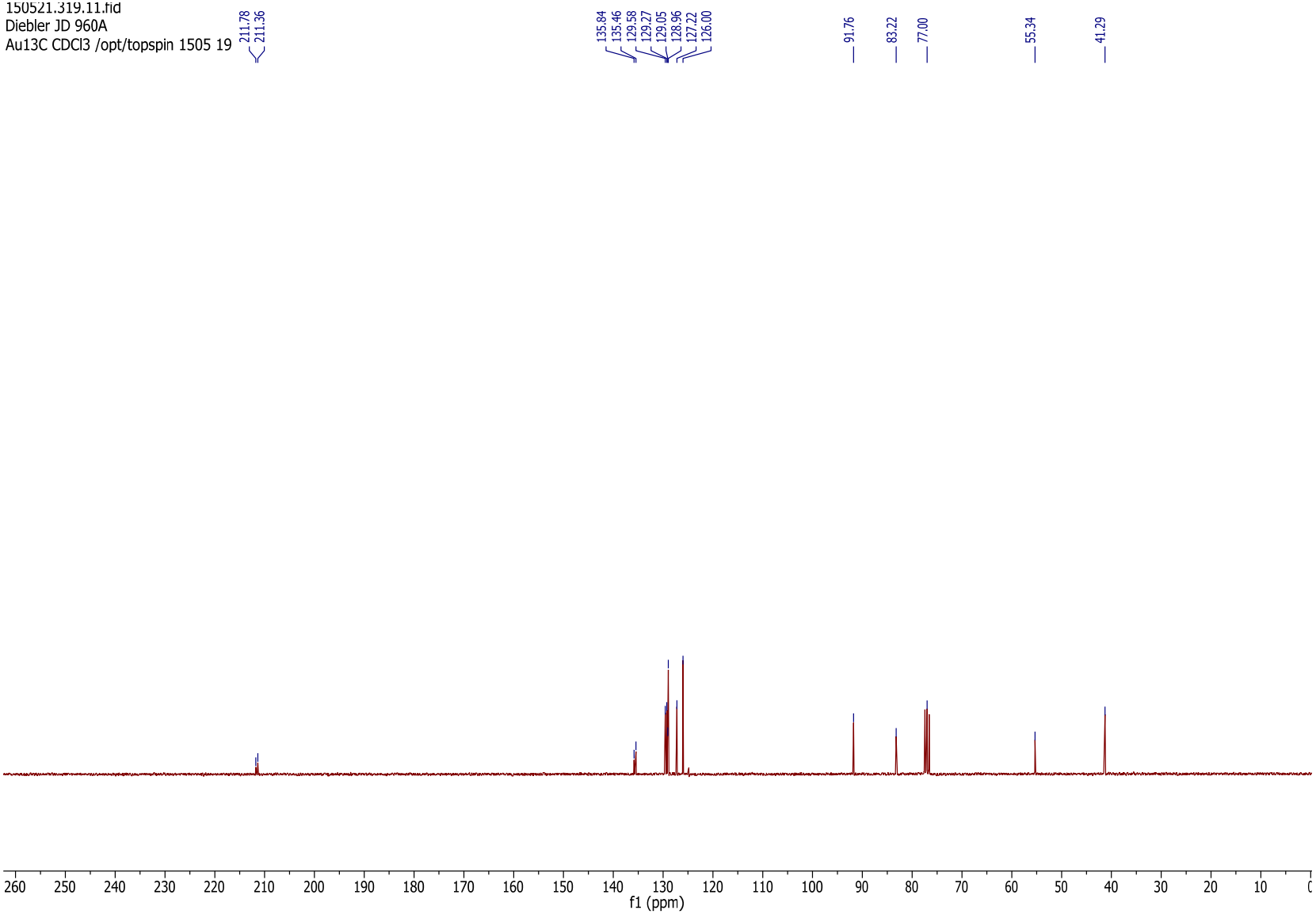
^{13}C-NMR 5-*n*-Butyl-1,3-oxathiolane-2-thione (**2c**)



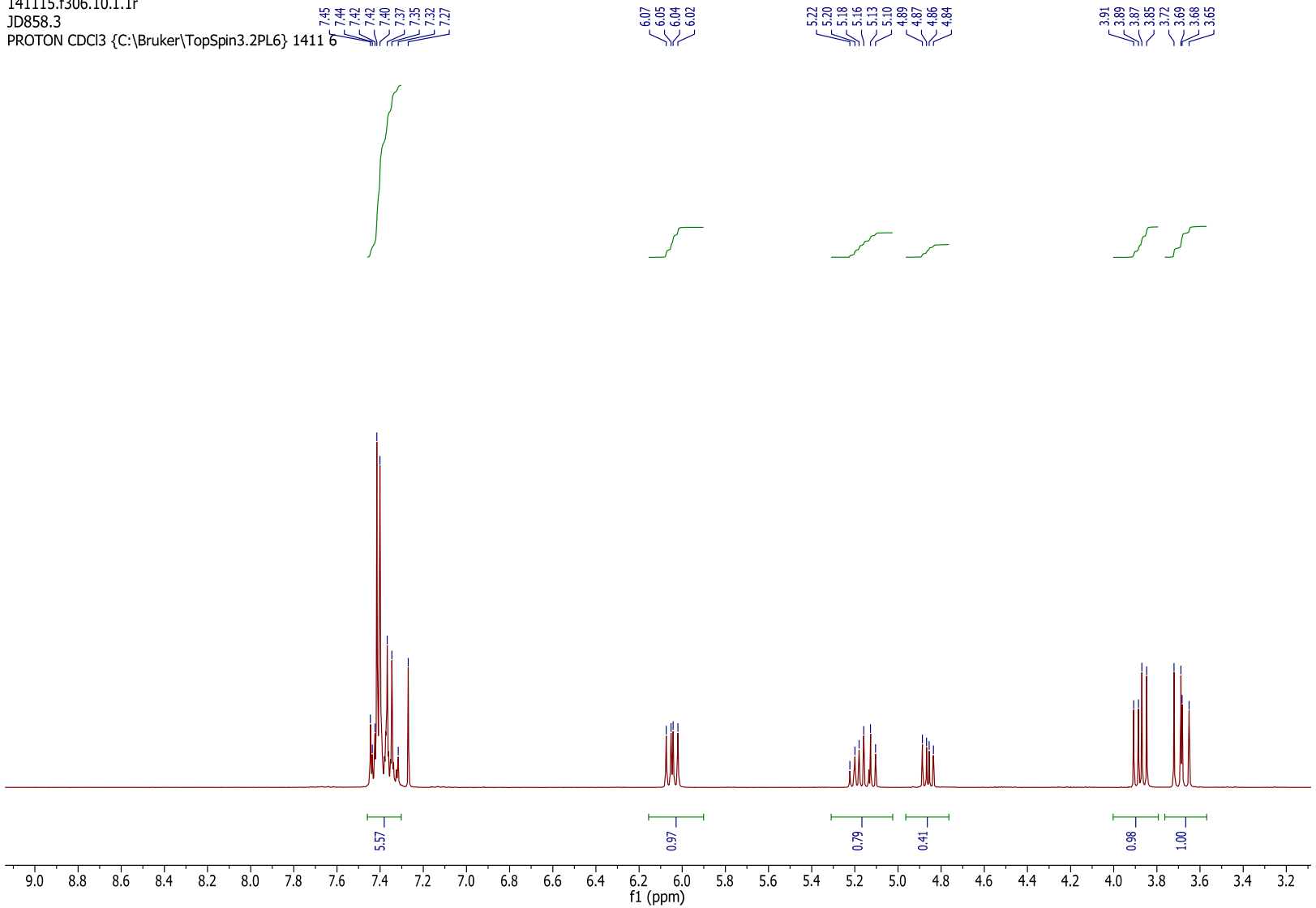
^{1}H-NMR 5-phenyl-1,3-oxathiolane-2-thione (**2d**), 4-phenyl-1,3-oxathiolane-2-thione (**2d'**)



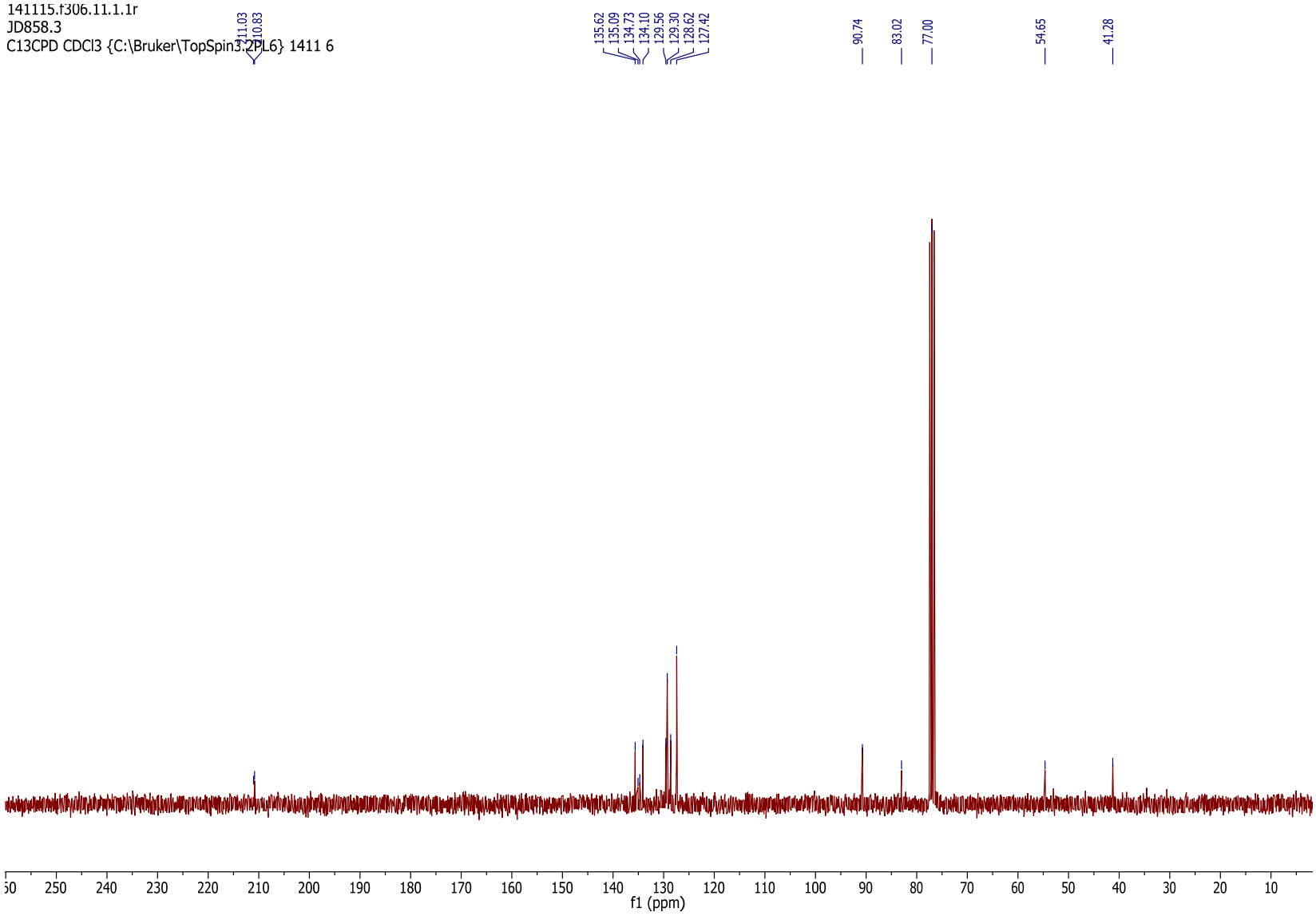
^{13}C-NMR 5-phenyl-1,3-oxathiolane-2-thione (**2d**), 4-phenyl-1,3-oxathiolane-2-thione (**2d'**)



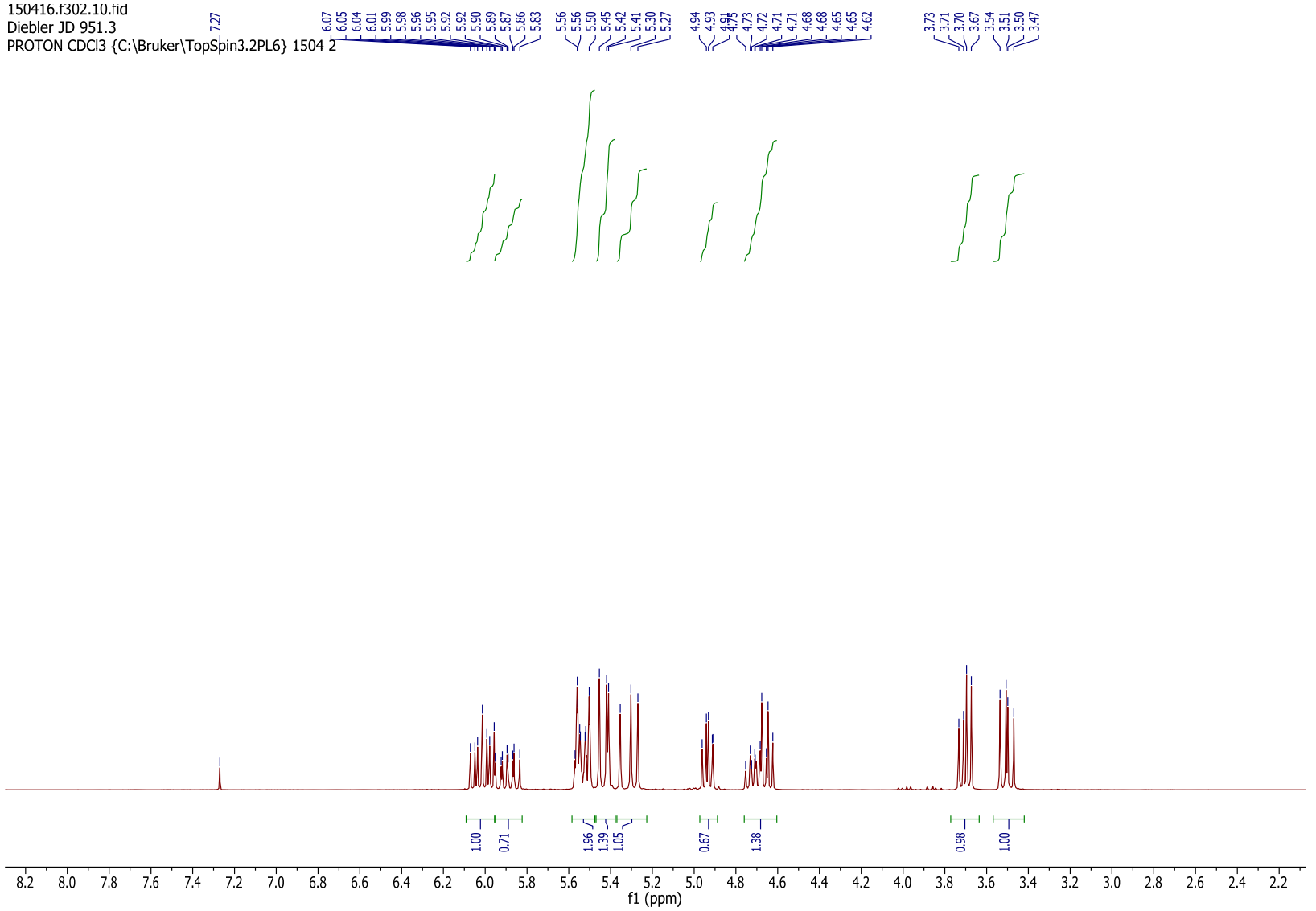
^{1}H-NMR 5-(4-chlorophenyl)-1,3-oxathiolane-2-thione (**2e**), 4-(4-chlorophenyl)-1,3-oxathiolane-2-thione (**2e'**)



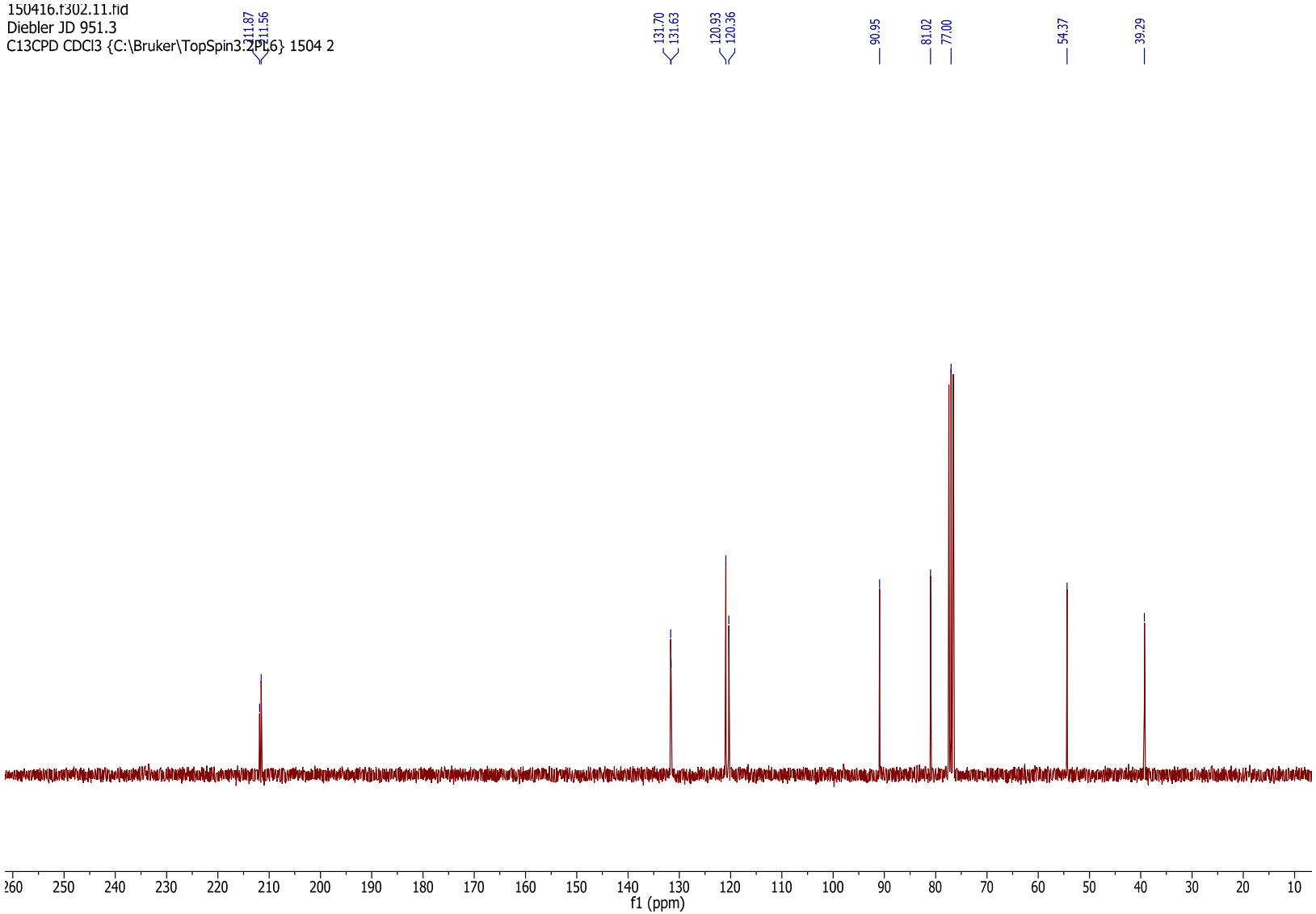
^{13}C-NMR 5-(4-chlorophenyl)-1,3-oxathiolane-2-thione (**2e**), 4-(4-chlorophenyl)-1,3-oxathiolane-2-thione (**2e'**)



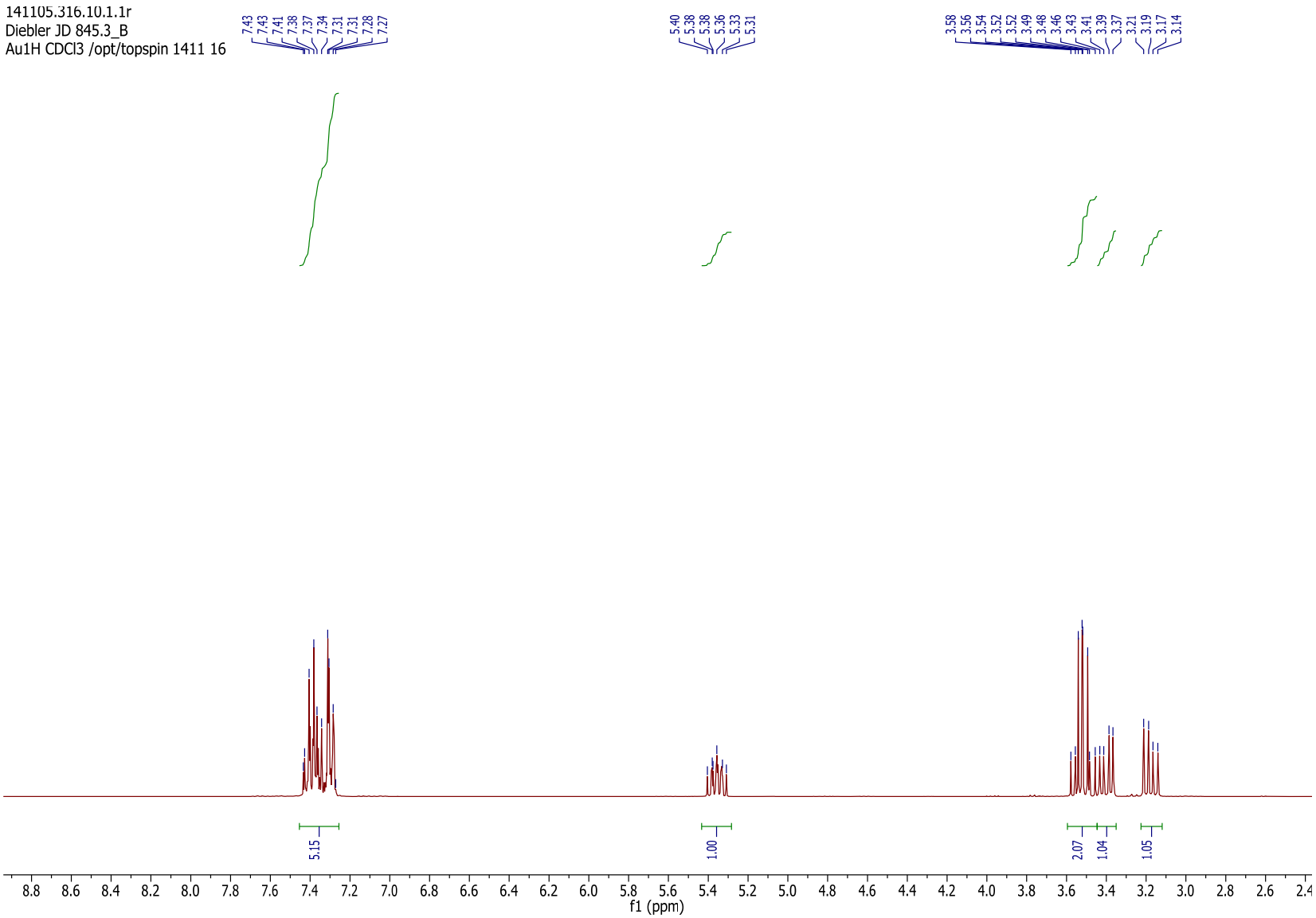
^{1}H-NMR 5-vinyl-1,3-oxathiolane-2-thione (**2f**), 4-vinyl-1,3-oxathiolane-2-thione (**2f'**)



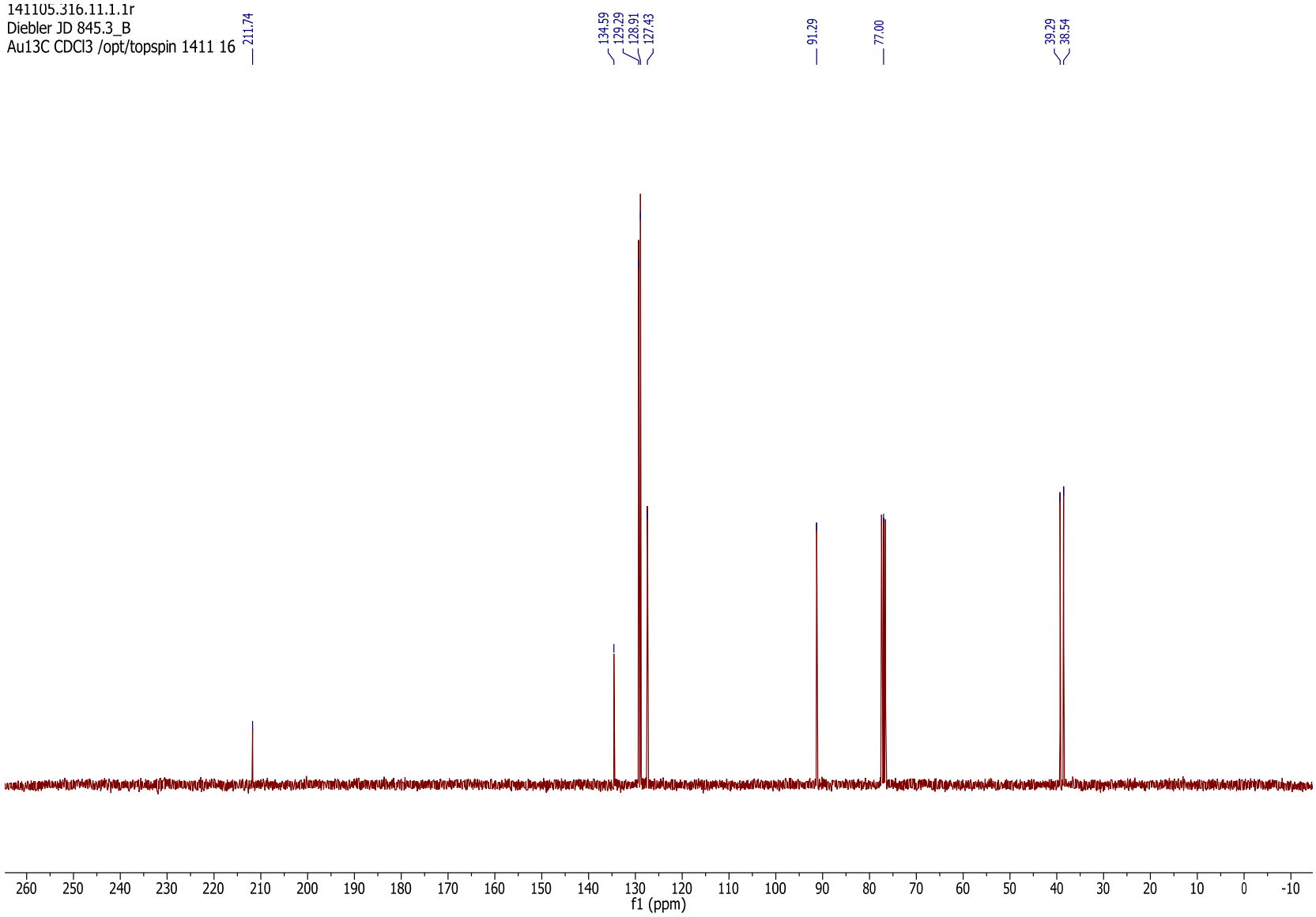
^{13}C-NMR 5-vinyl-1,3-oxathiolane-2-thione (**2f**), 4-vinyl-1,3-oxathiolane-2-thione (**2f'**)



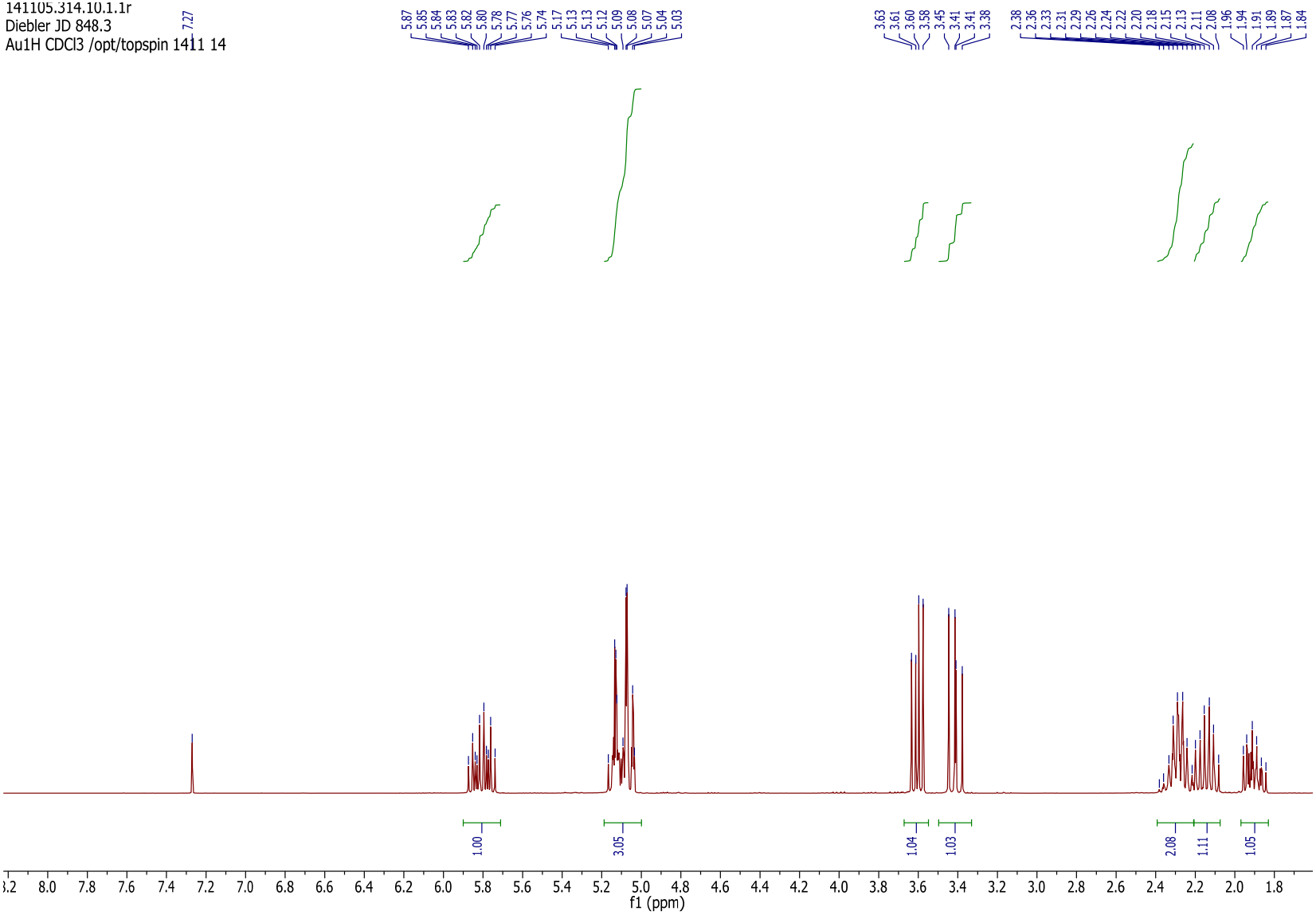
^{1}H-NMR 5-Phenylmethyl-1,3-oxathiolane-2-thione (**2g**)



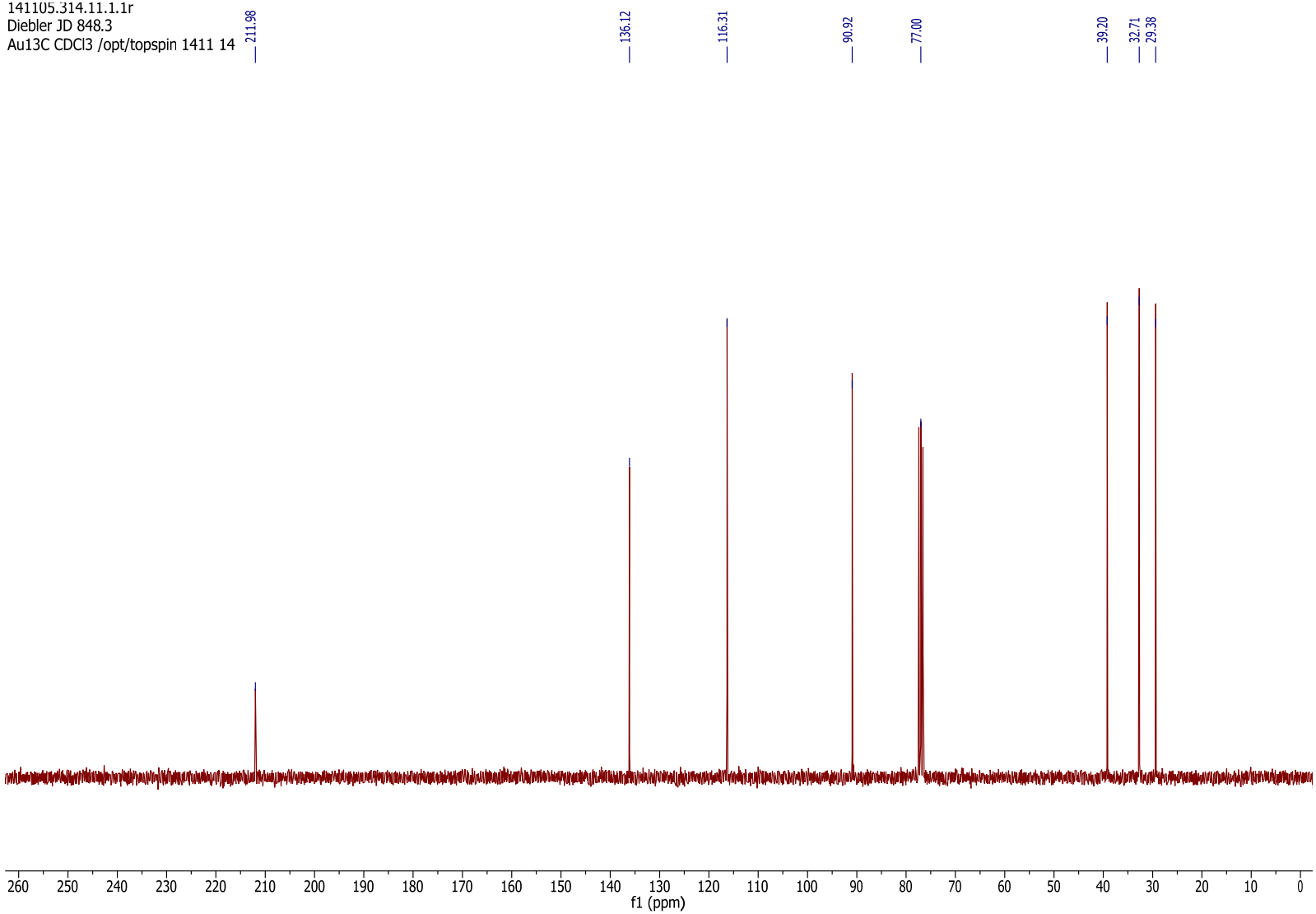
^{13}C-NMR 5-Phenylmethyl-1,3-oxathiolane-2-thione (**2g**)



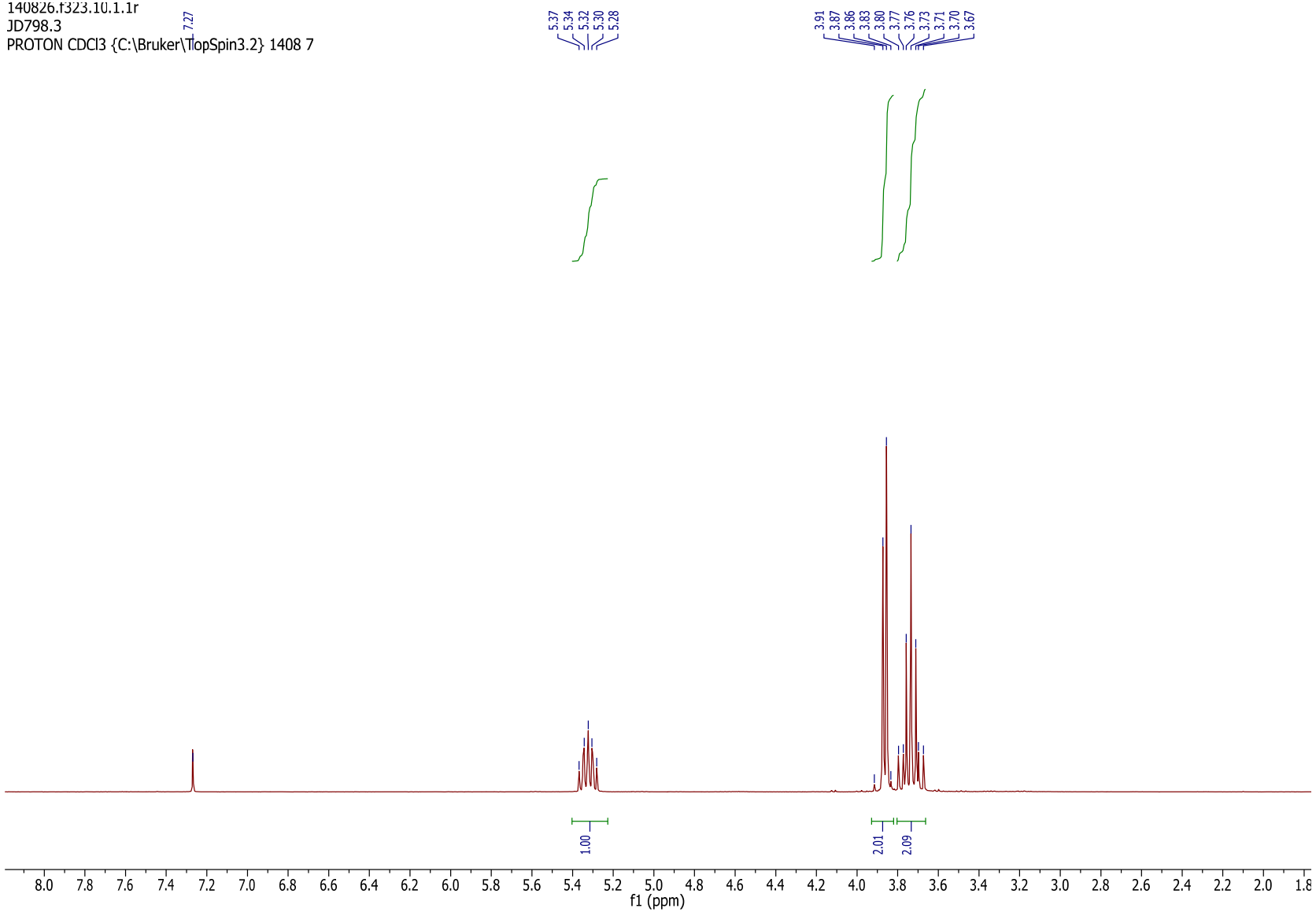
^{1}H-NMR 5-(but-3-en-1-yl)-1,3-oxathiolane-2-thione (**2h**)



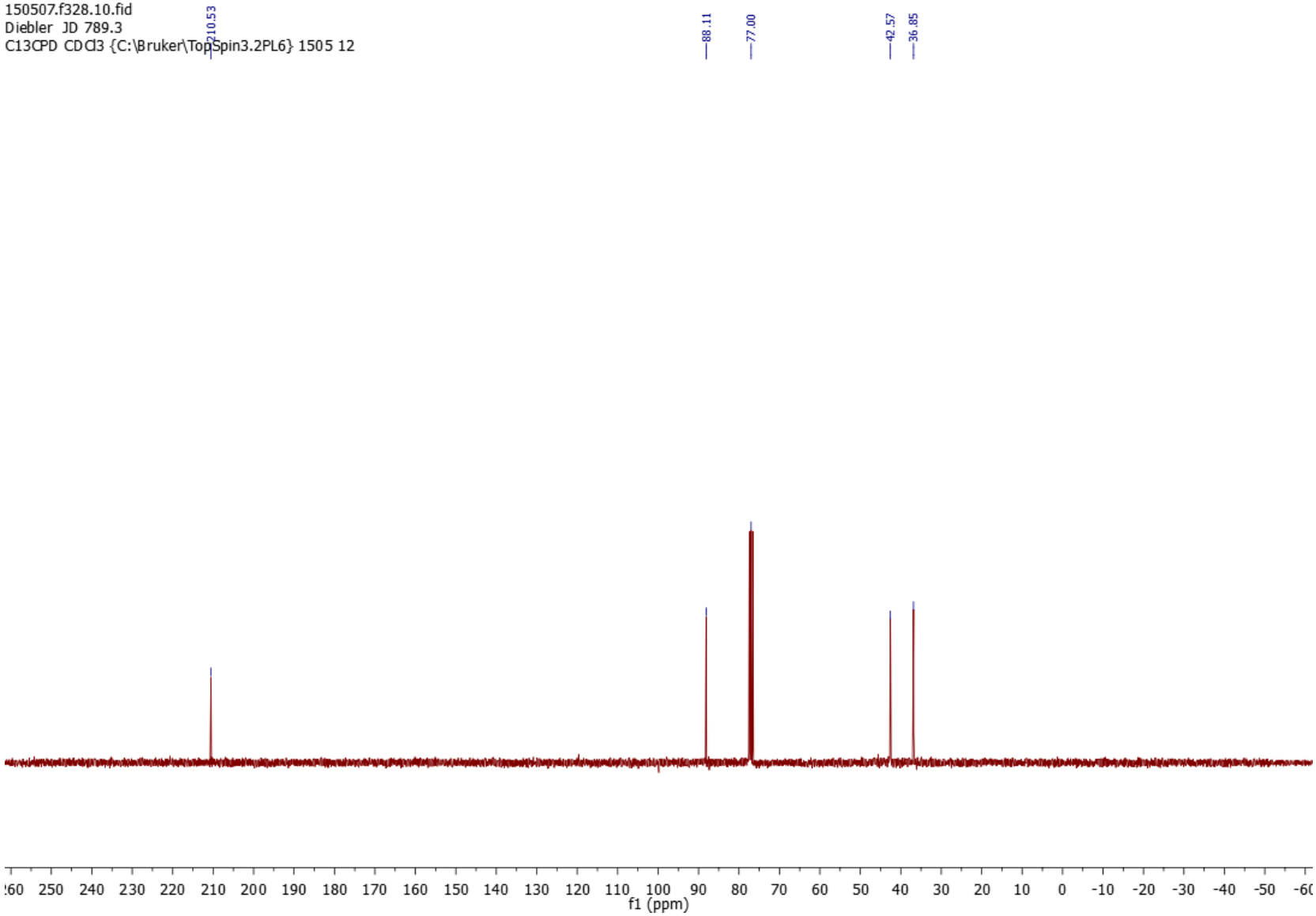
^{13}C-NMR 5-(but-3-en-1-yl)-1,3-oxathiolane-2-thione (**2h**)



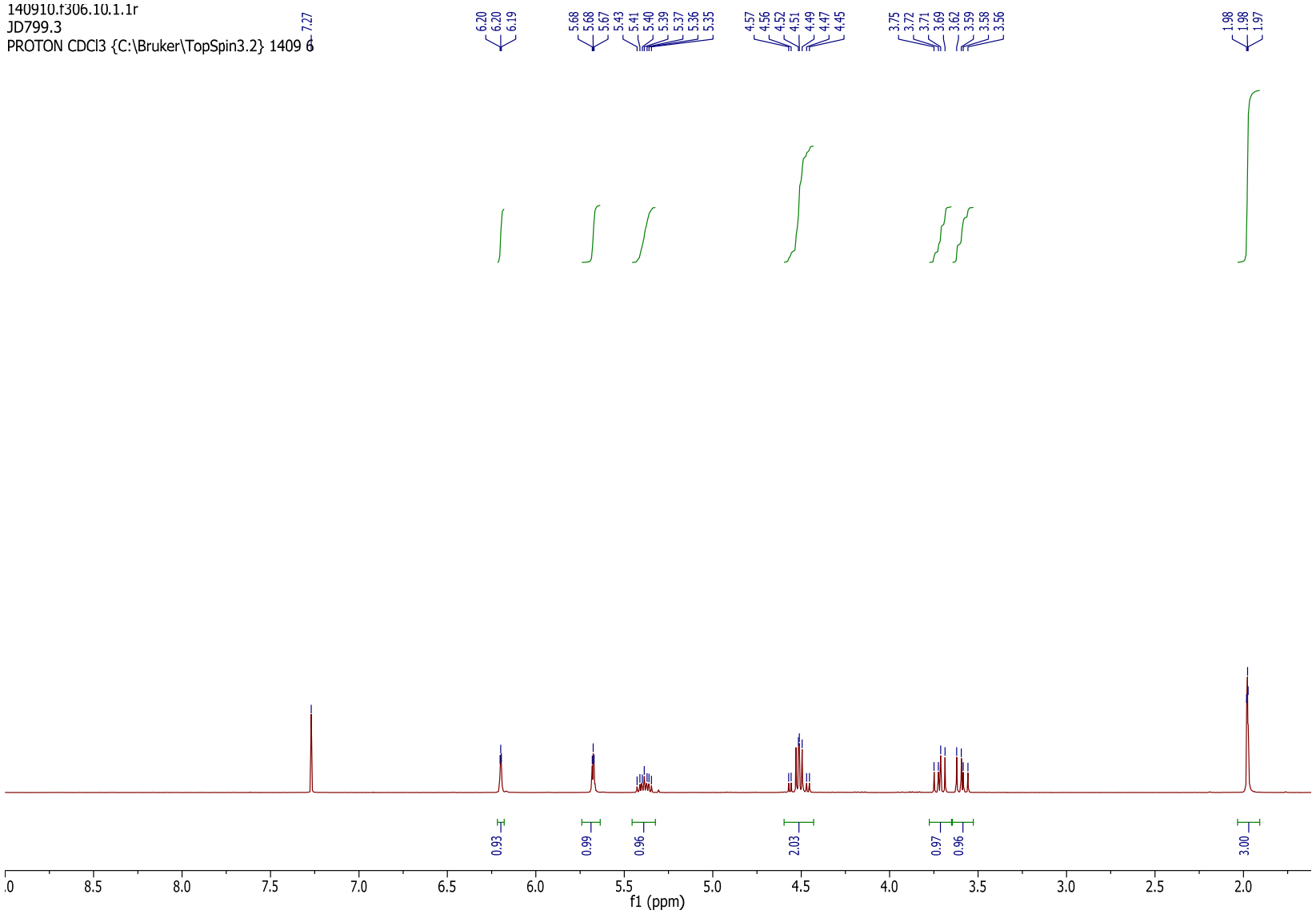
^{1}H-NMR 5-chloromethyl-1,3-oxathiolane-2-thione (**2i**)



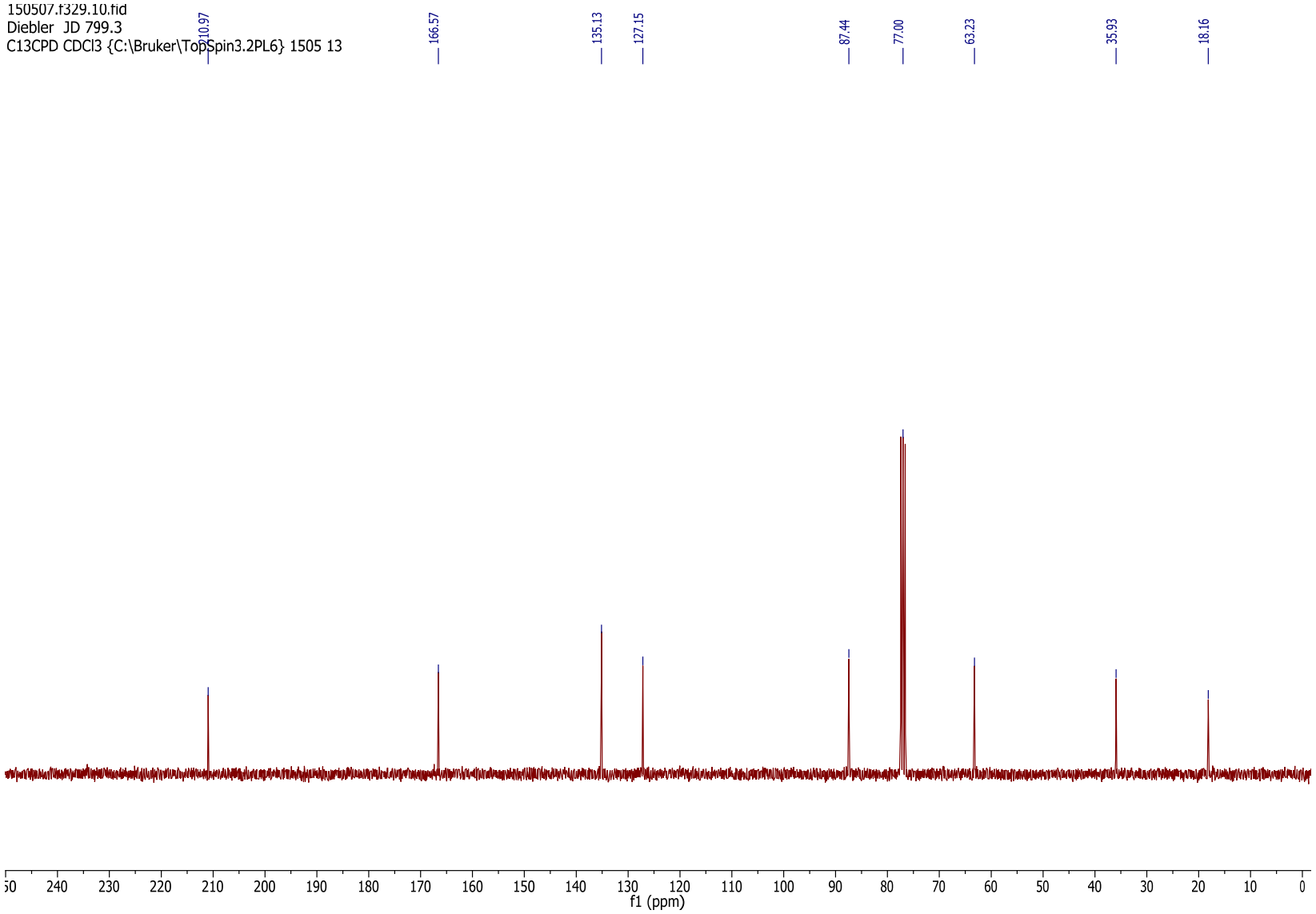
^{13}C-NMR 5-chloromethyl-1,3-oxathiolane-2-thione (**2i**)



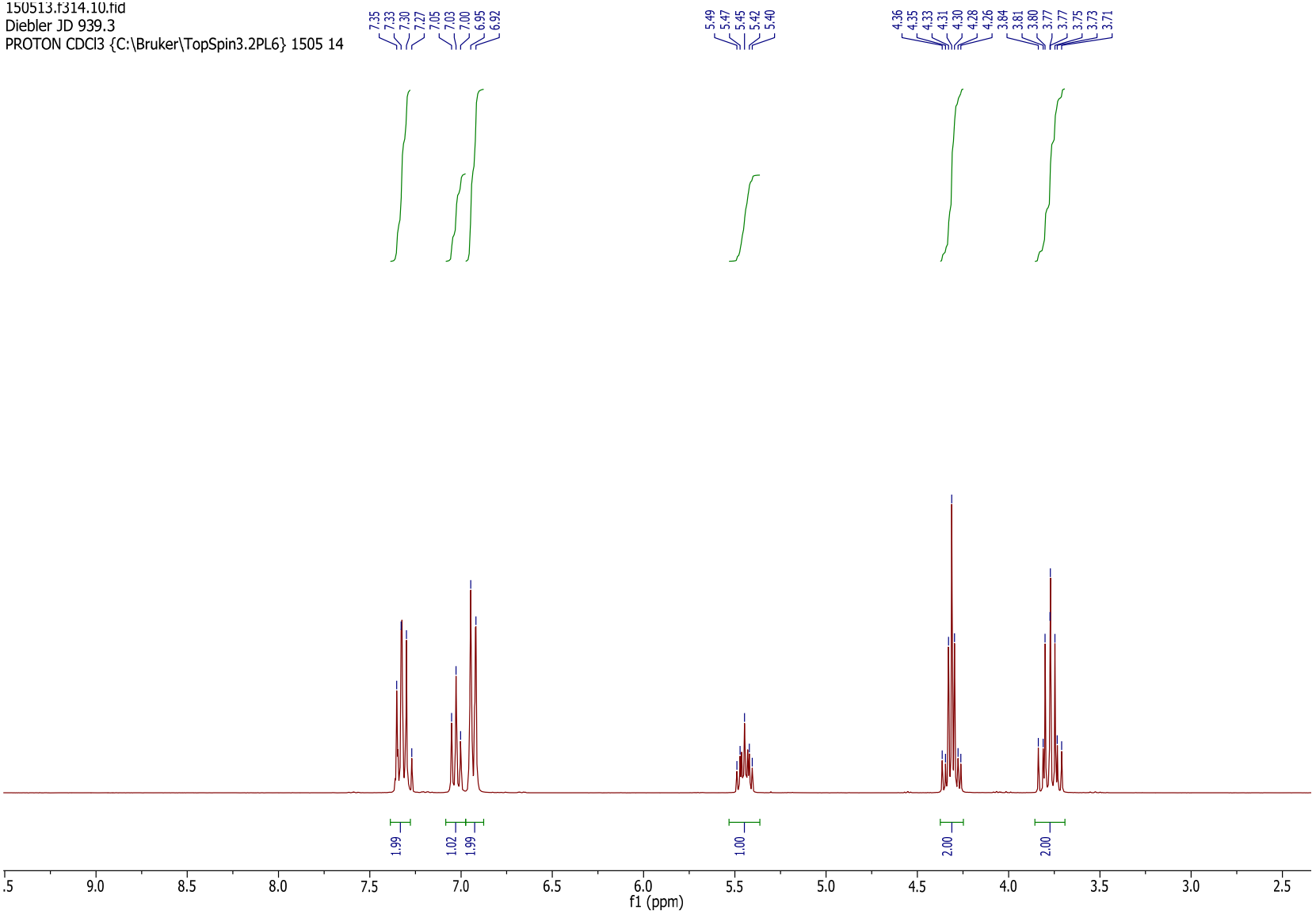
^{1}H-NMR 5-(Methacryloyloxy)methyl-1,3-oxathiolane-2-thione (**2j**)



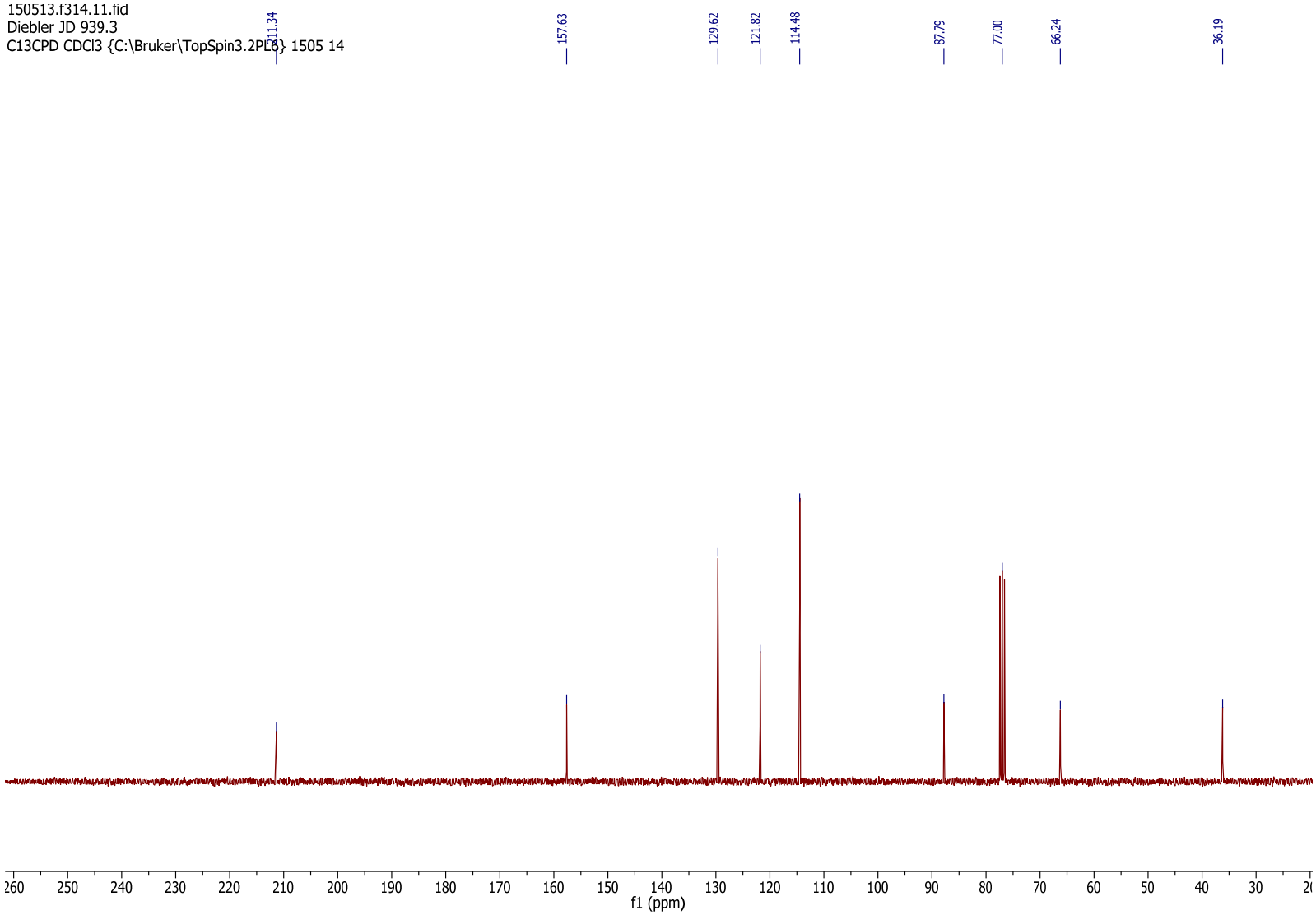
^{13}C-NMR 5-(Methacryloyloxy)methyl-1,3-oxathiolane-2-thione (**2j**)



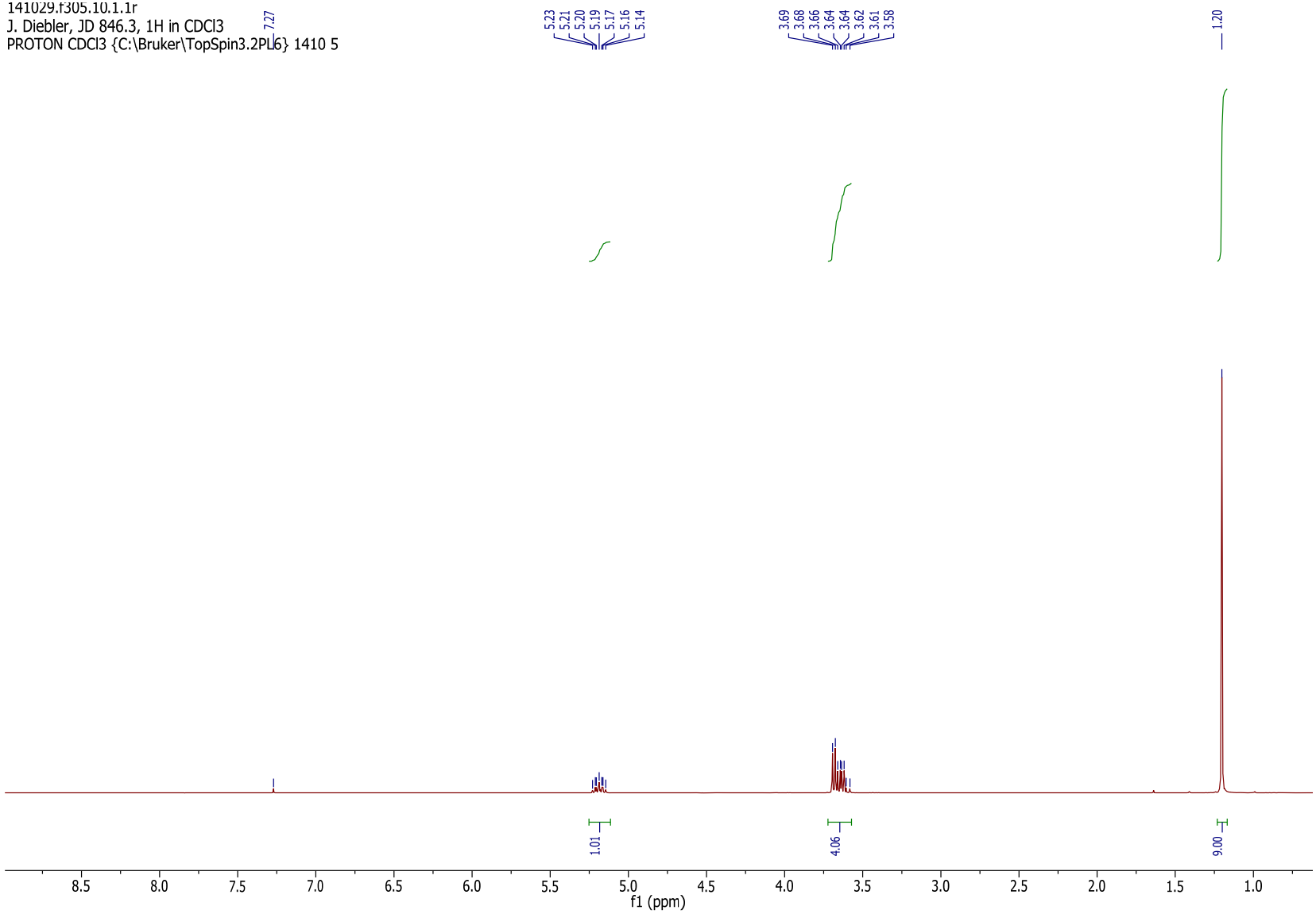
^{1}H-NMR 5-Phenoxymethyl-1,3-oxathiolane-2-thione (**2k**)



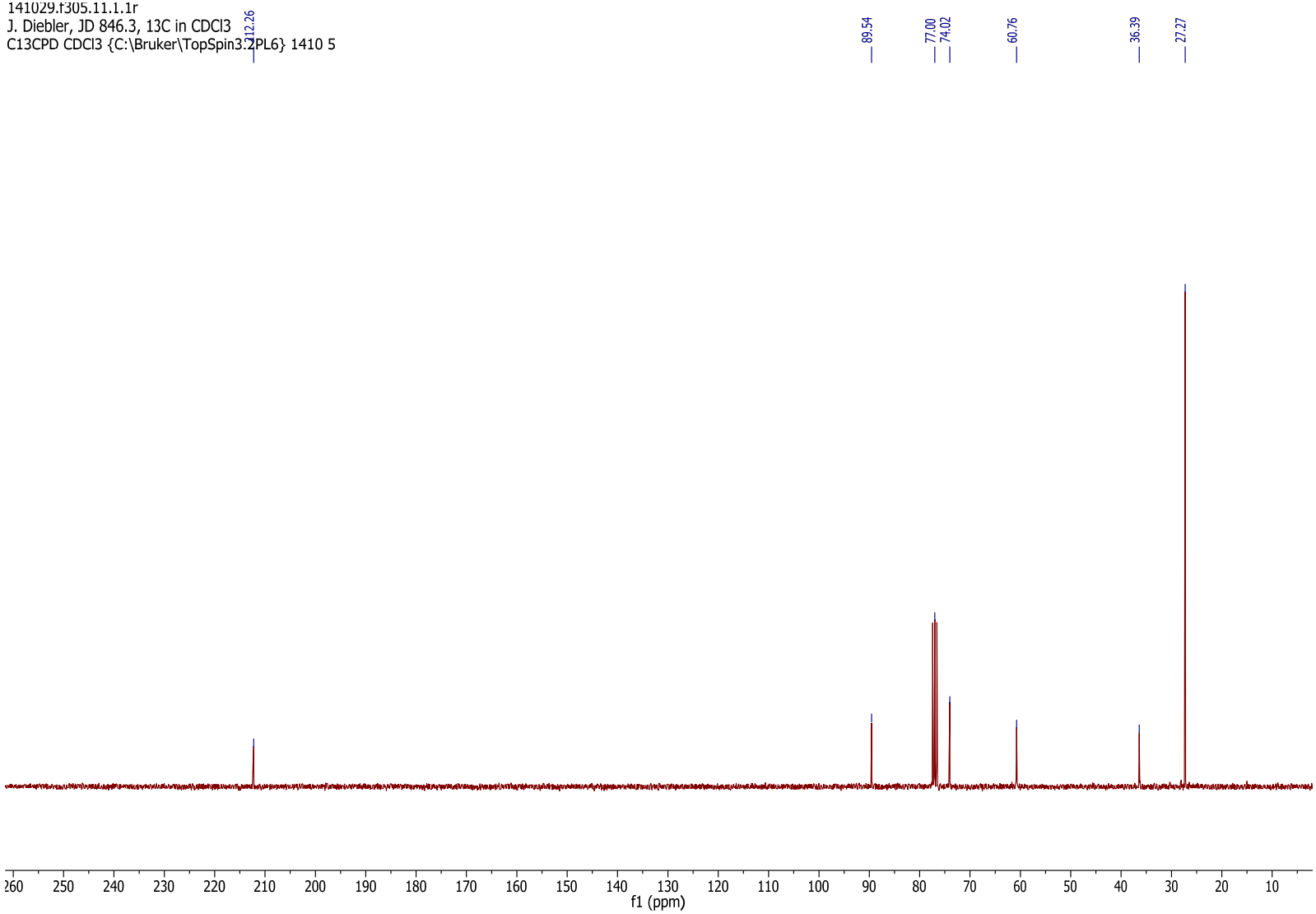
^{13}C-NMR 5-Phenoxymethyl-1,3-oxathiolane-2-thione (**2k**)



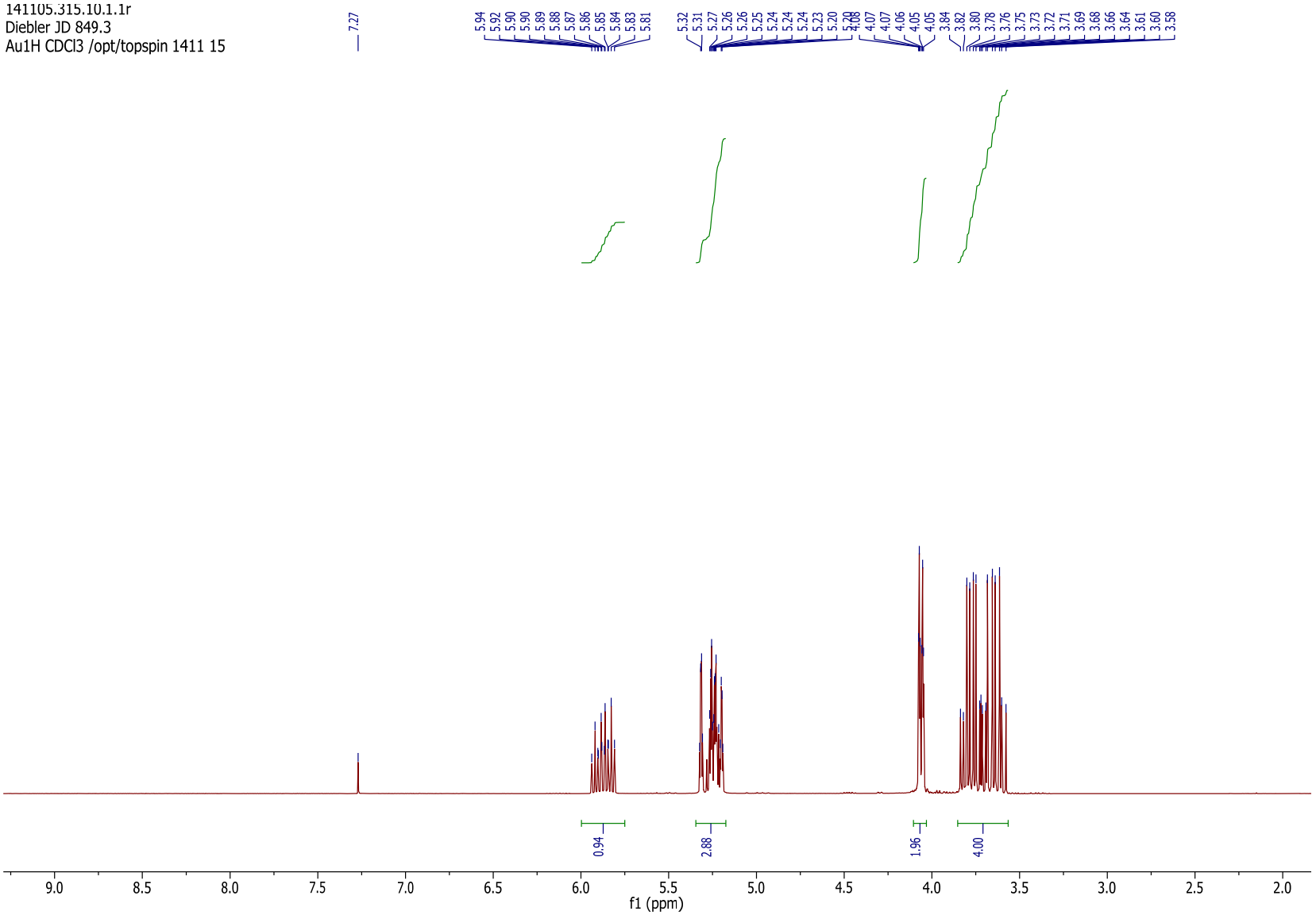
^{1}H-NMR 5-*tert*-butoxymethyl-1,3-oxathiolane-2-thione (**2l**)



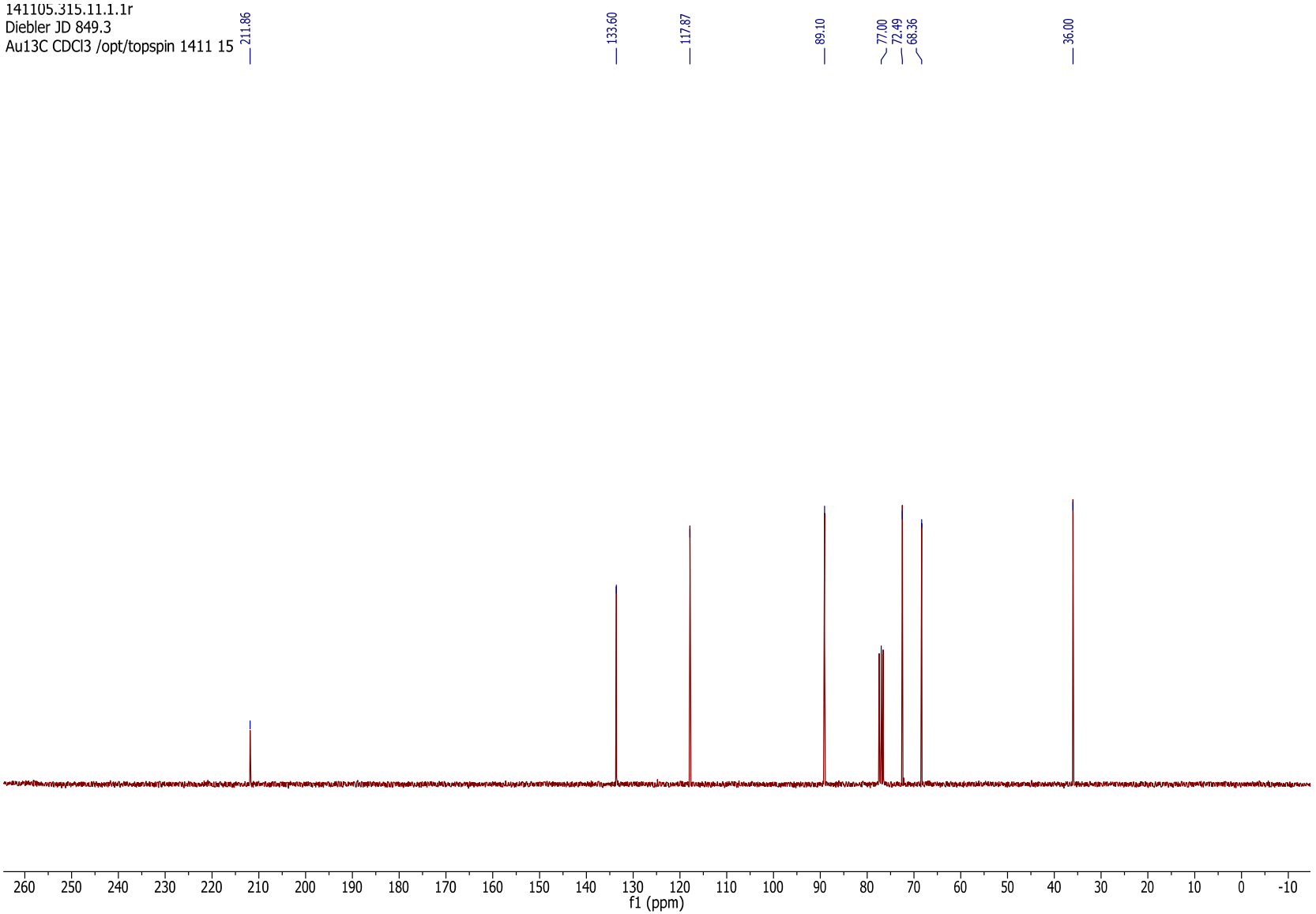
^{13}C-NMR 5-*tert*-butoxymethyl-1,3-oxathiolane-2-thione (**2l**)



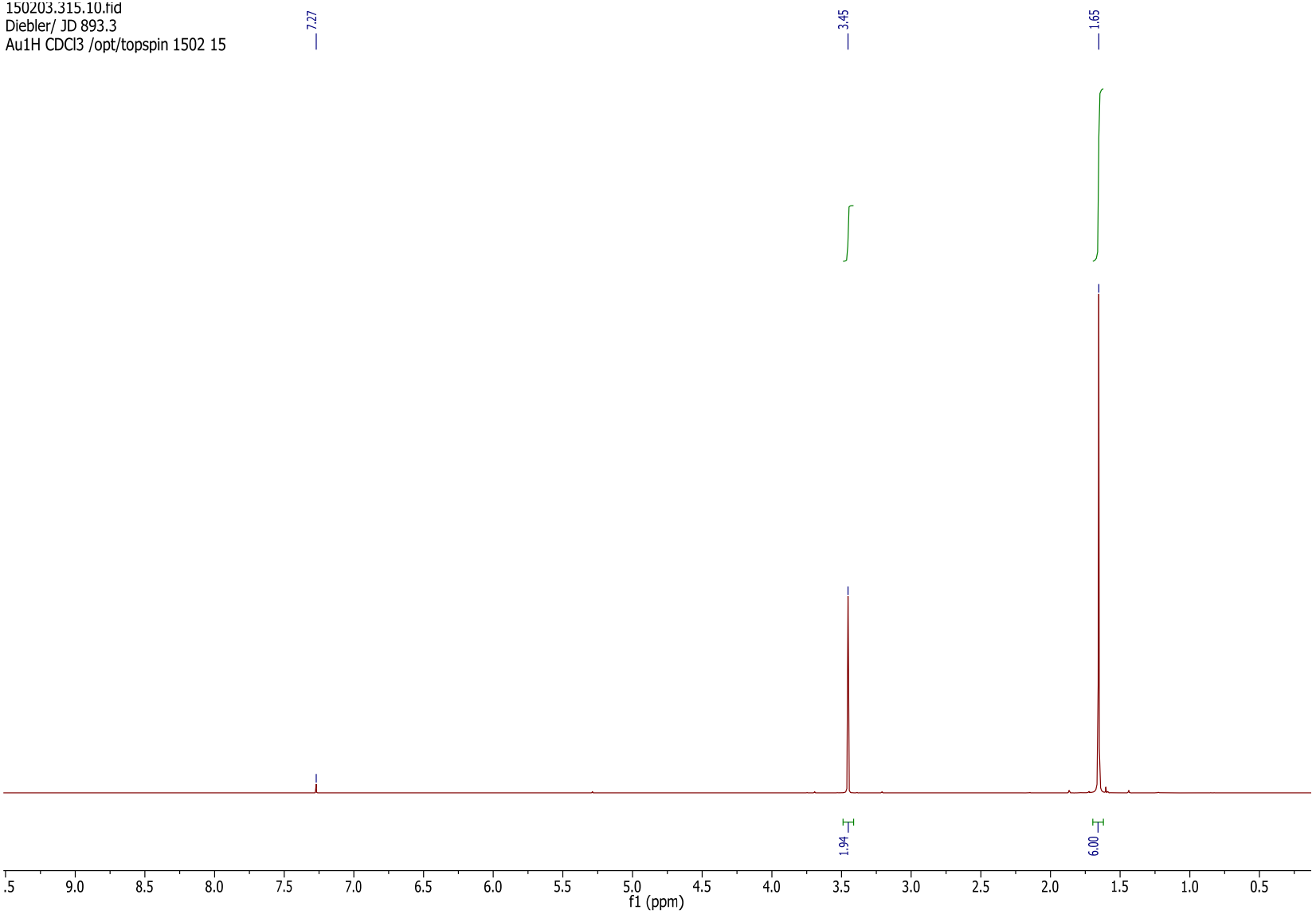
^{1}H-NMR 5-Allyloxymethyl-1,3-oxathiolane-2-thione (**2m**)



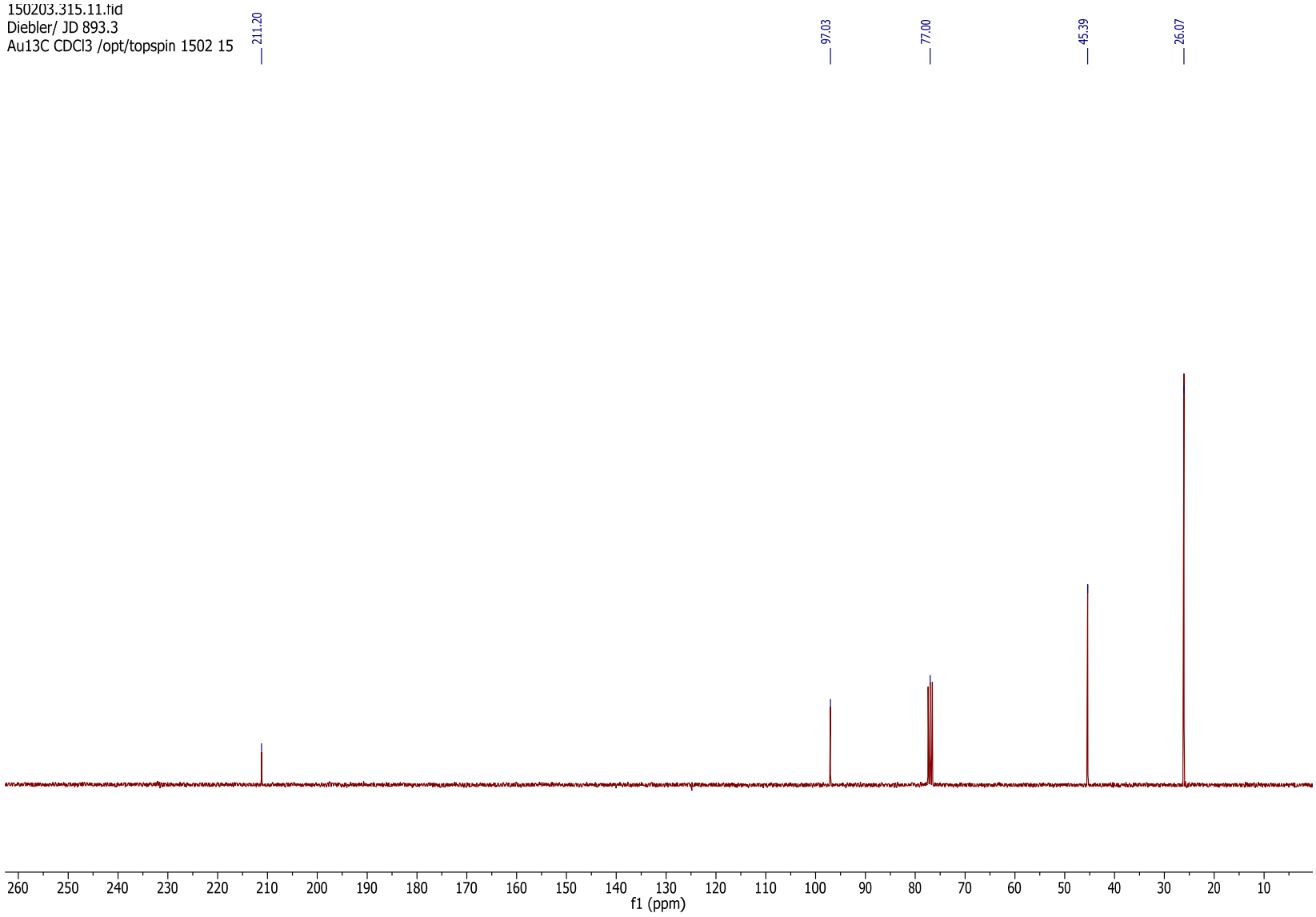
^{13}C-NMR 5-Allyloxymethyl-1,3-oxathiolane-2-thione (**2m**)



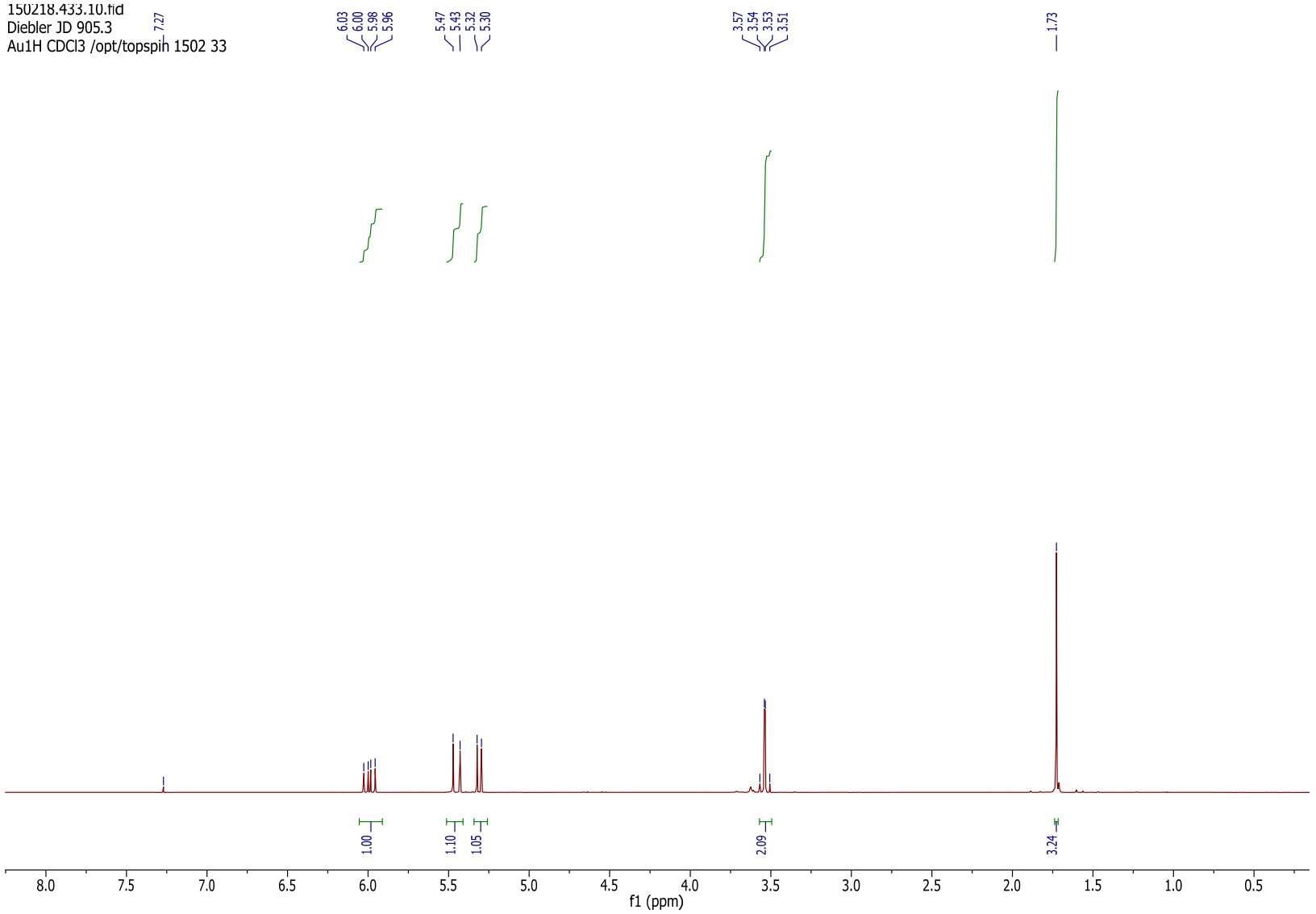
^{1}H-NMR 5,5-dimethyl-1,3-oxathiolane-2-thione (**2n**)



^{13}C-NMR 5,5-dimethyl-1,3-oxathiolane-2-thione (**2n**)

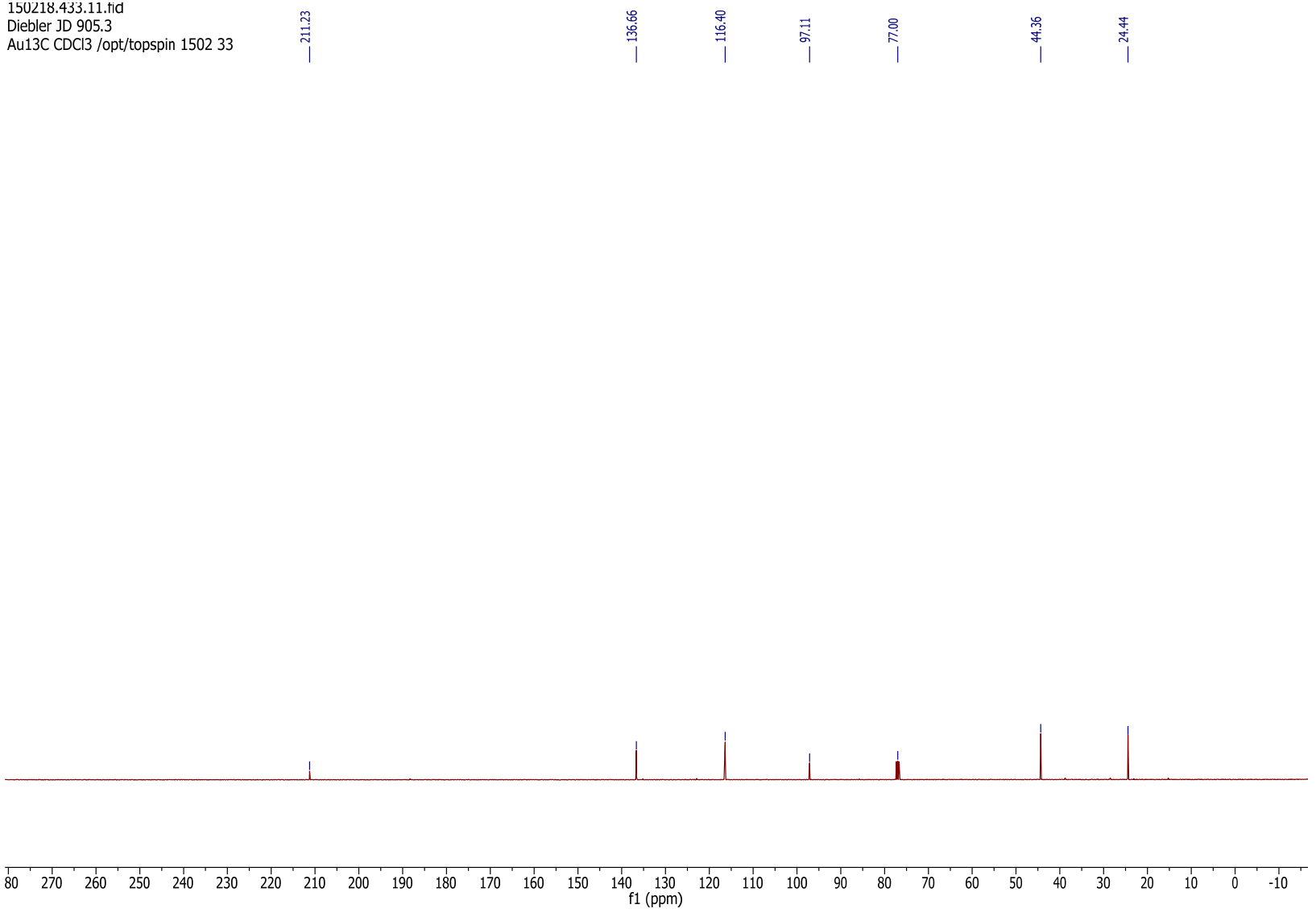


^{1}H-NMR 5-methyl-5-vinyl-1,3-oxathiolane-2-thione (**2o**)

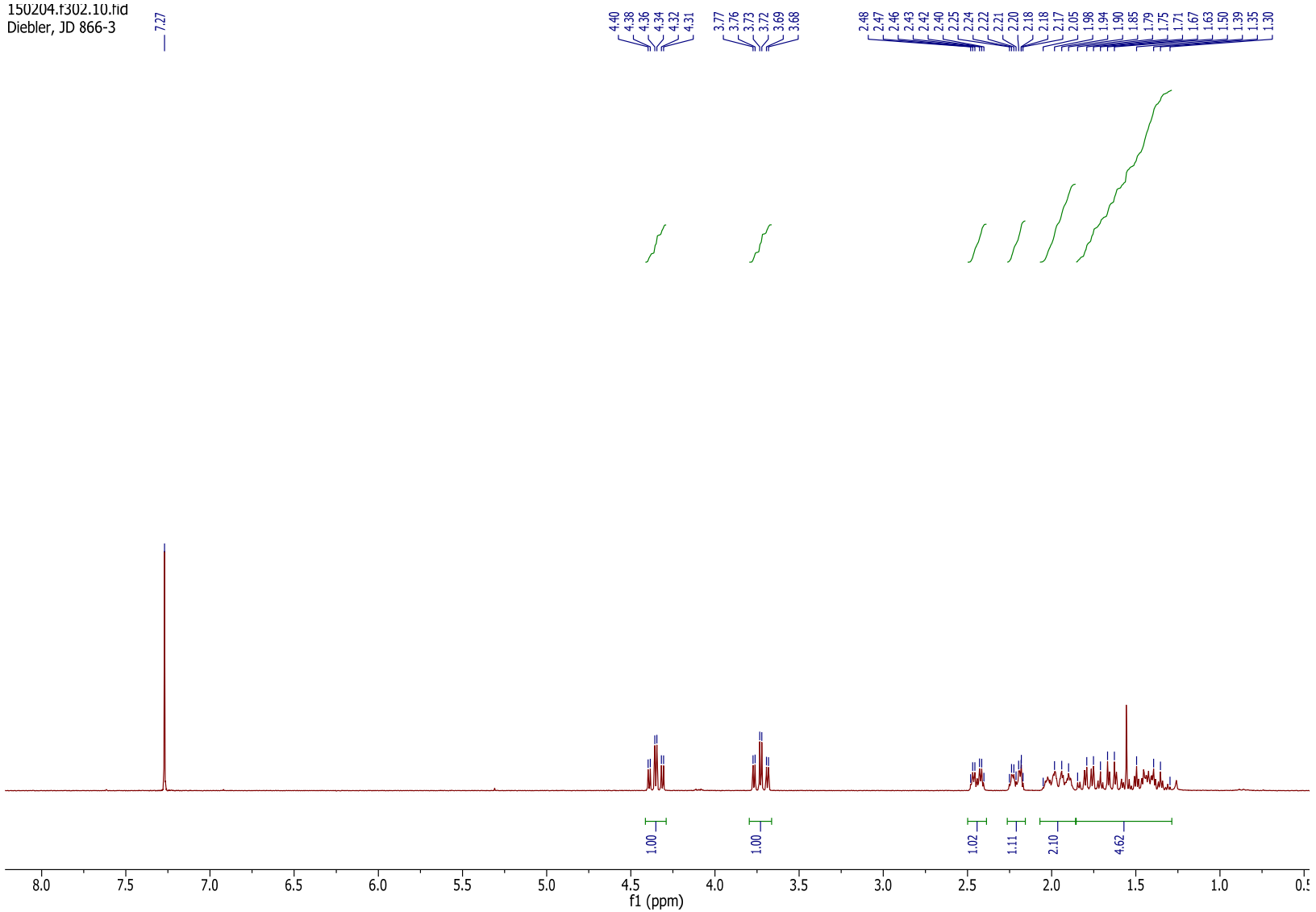


^{13}C-NMR 5-methyl-5-vinyl-1,3-oxathiolane-2-thione (**2o**)

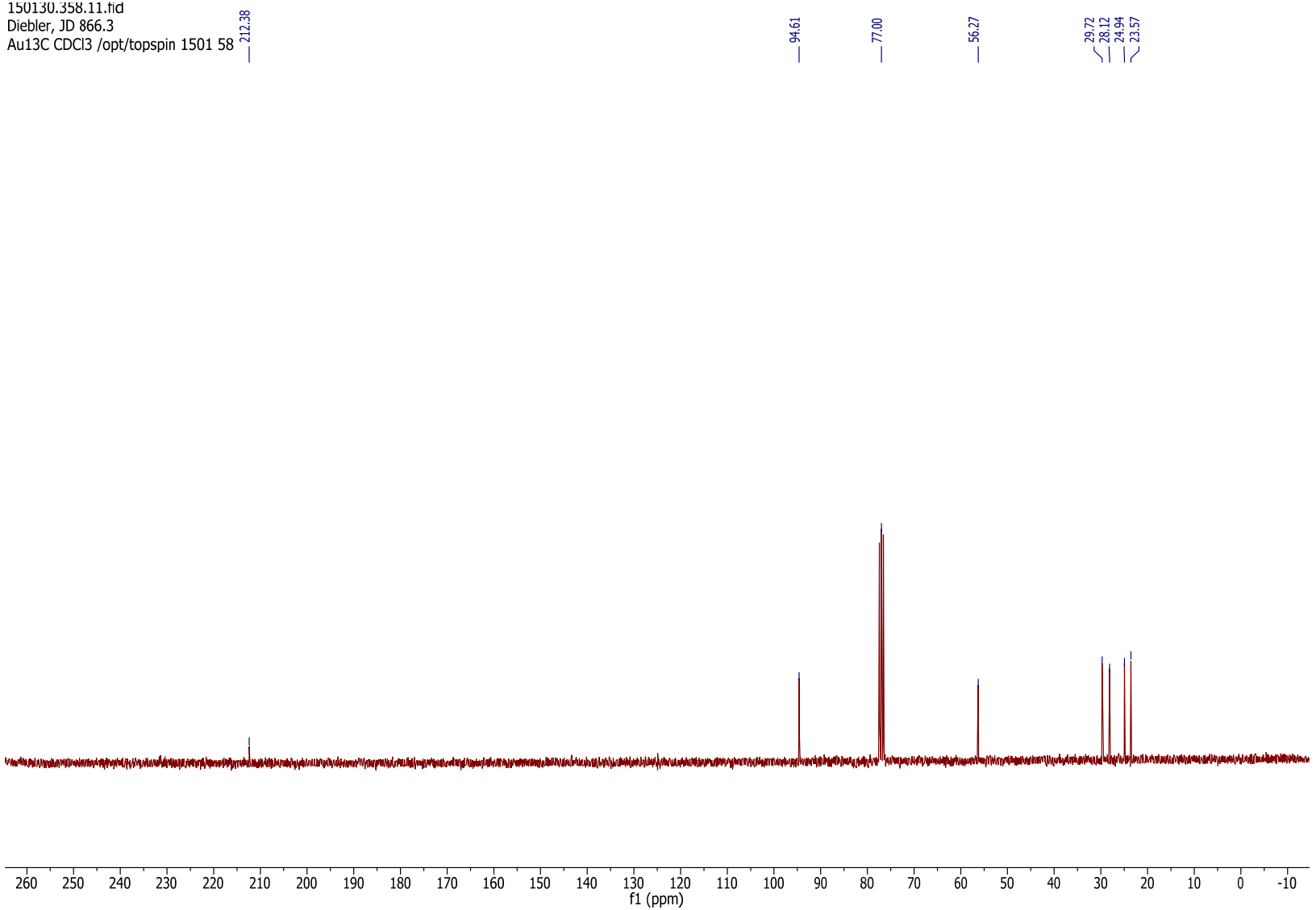
150218.433.11.fid
Diebler JD 905.3
Au13C CDCl3 /opt/topspin 1502 33



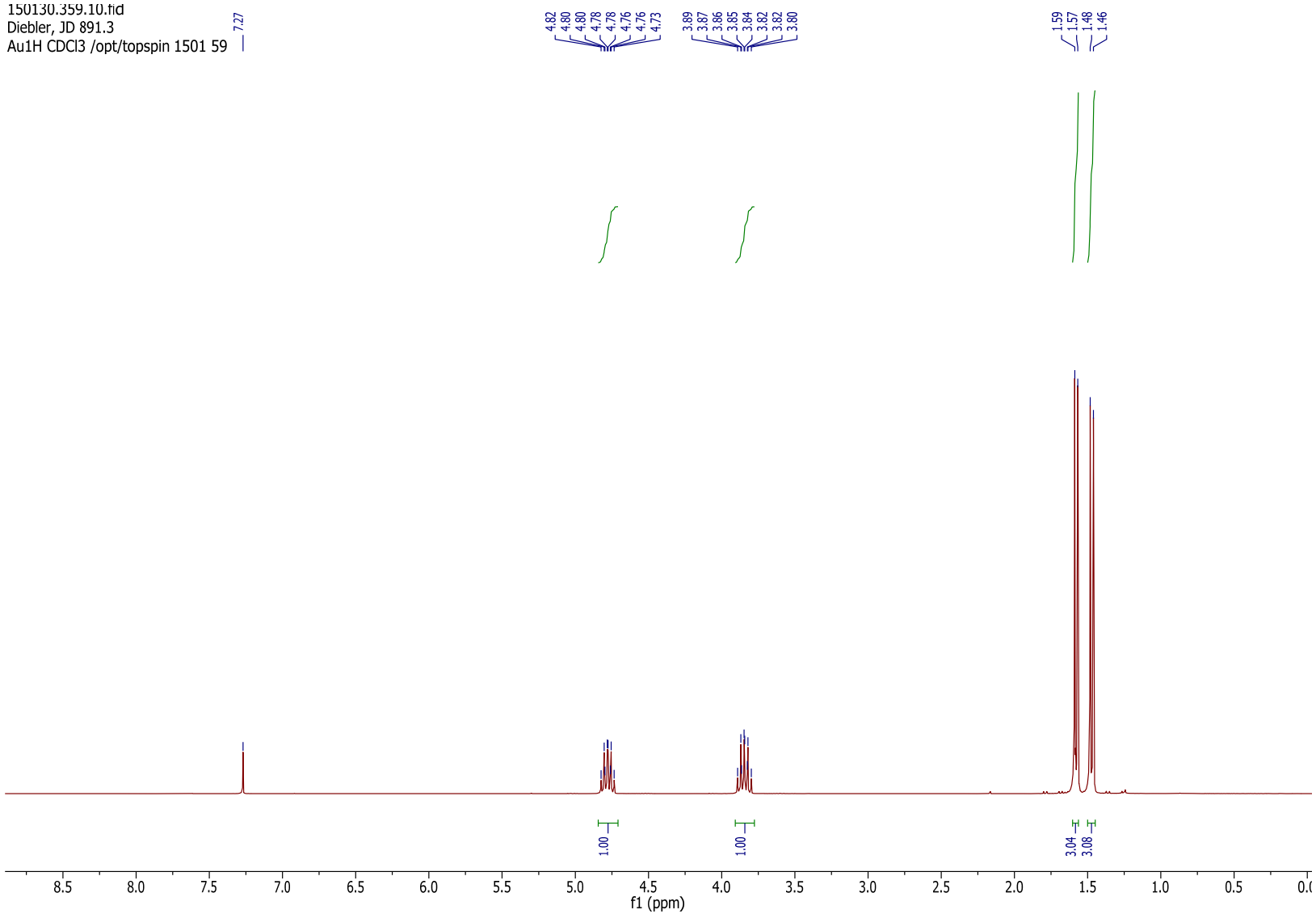
^{1}H-NMR 4,5-Tetramethylen-1,3-oxathiolane-2-thione (**2p**)



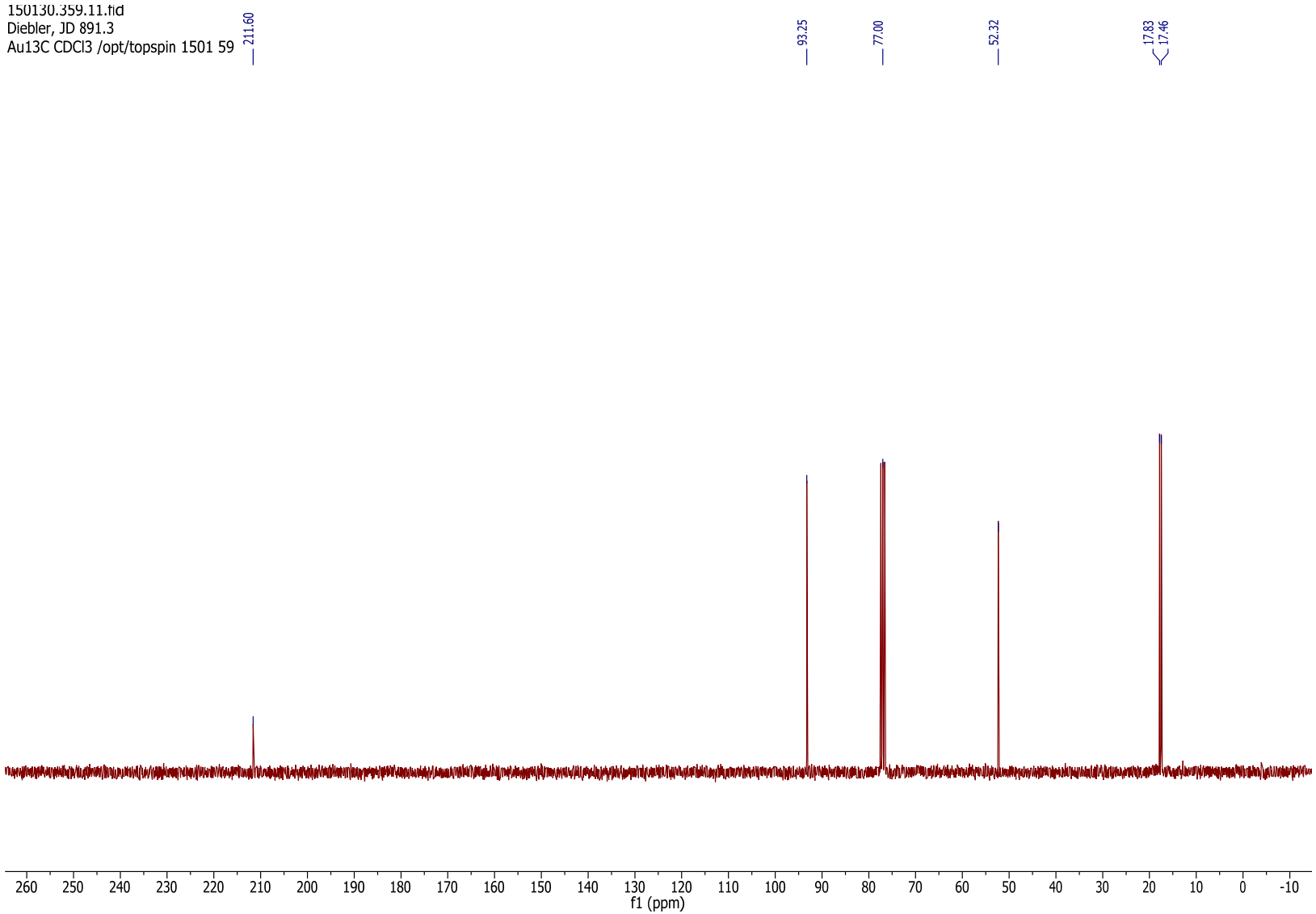
^{13}C-NMR 4,5-Tetramethylen-1,3-oxathiolane-2-thione (**2p**)



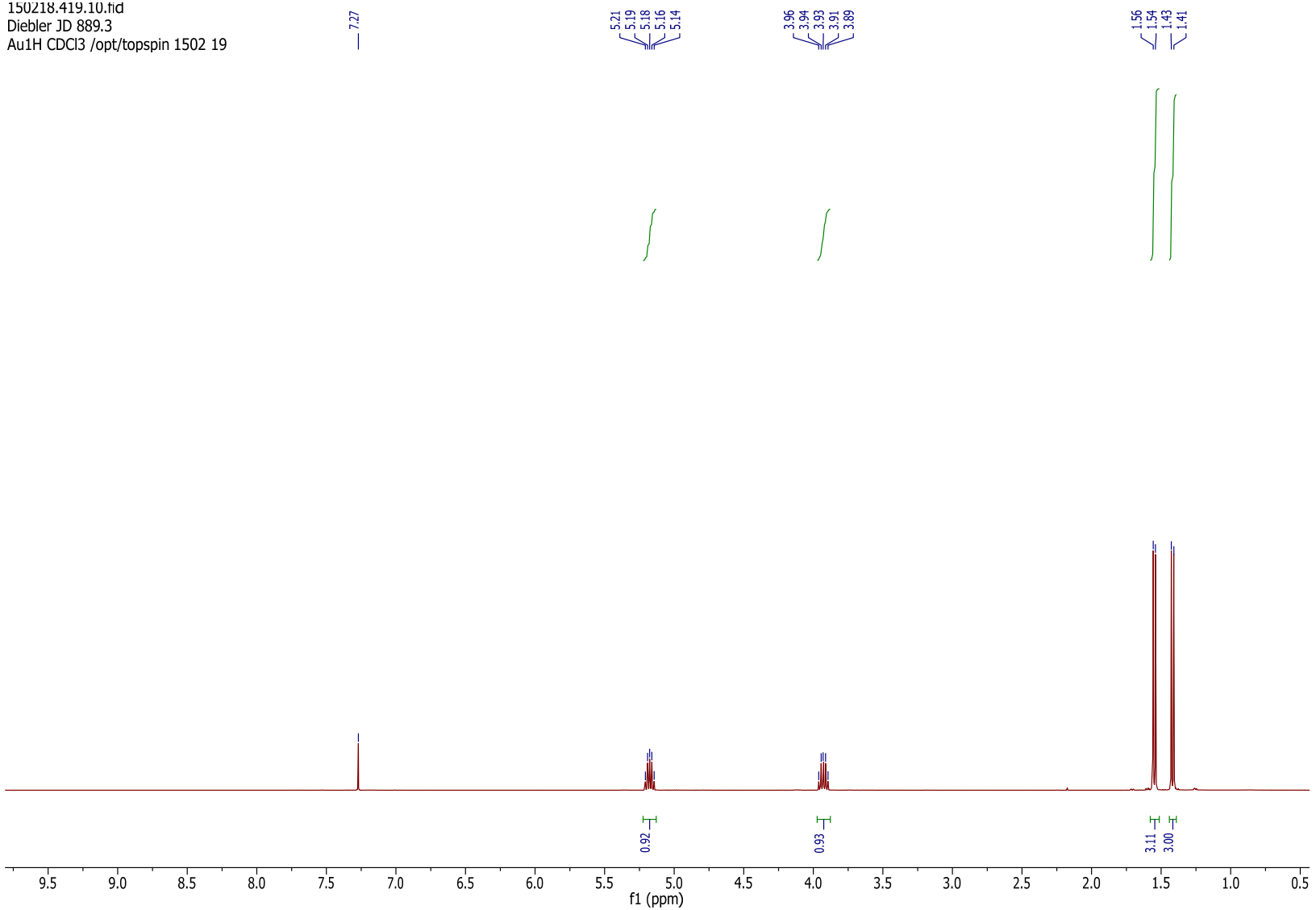
^{1}H-NMR *Trans*-4,5-dimethyl-1,3-oxathiolane-2-thione (*trans*-**2q**)



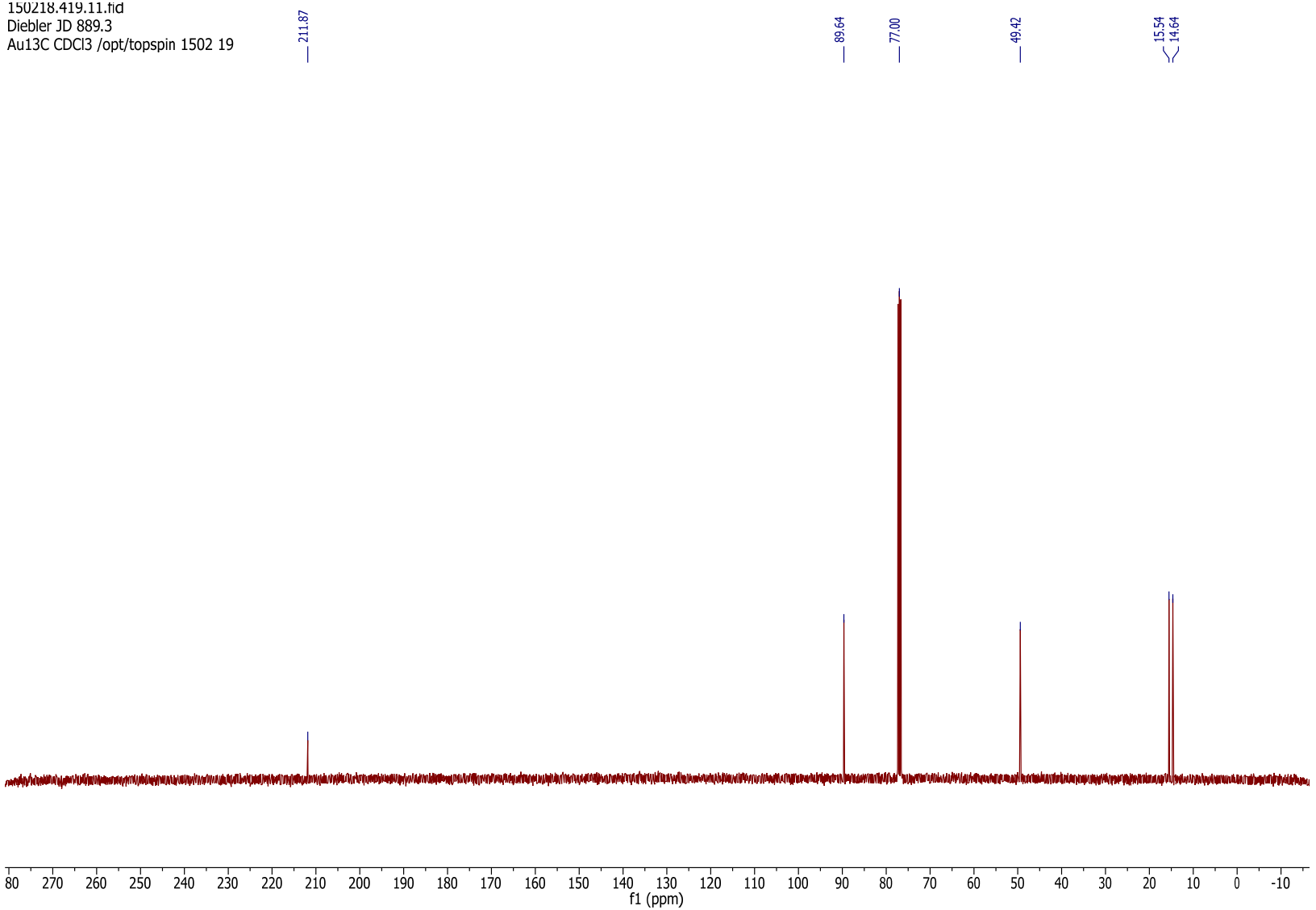
^{13}C-NMR *Trans*-4,5-dimethyl-1,3-oxathiolane-2-thione (*trans*-**2q**)



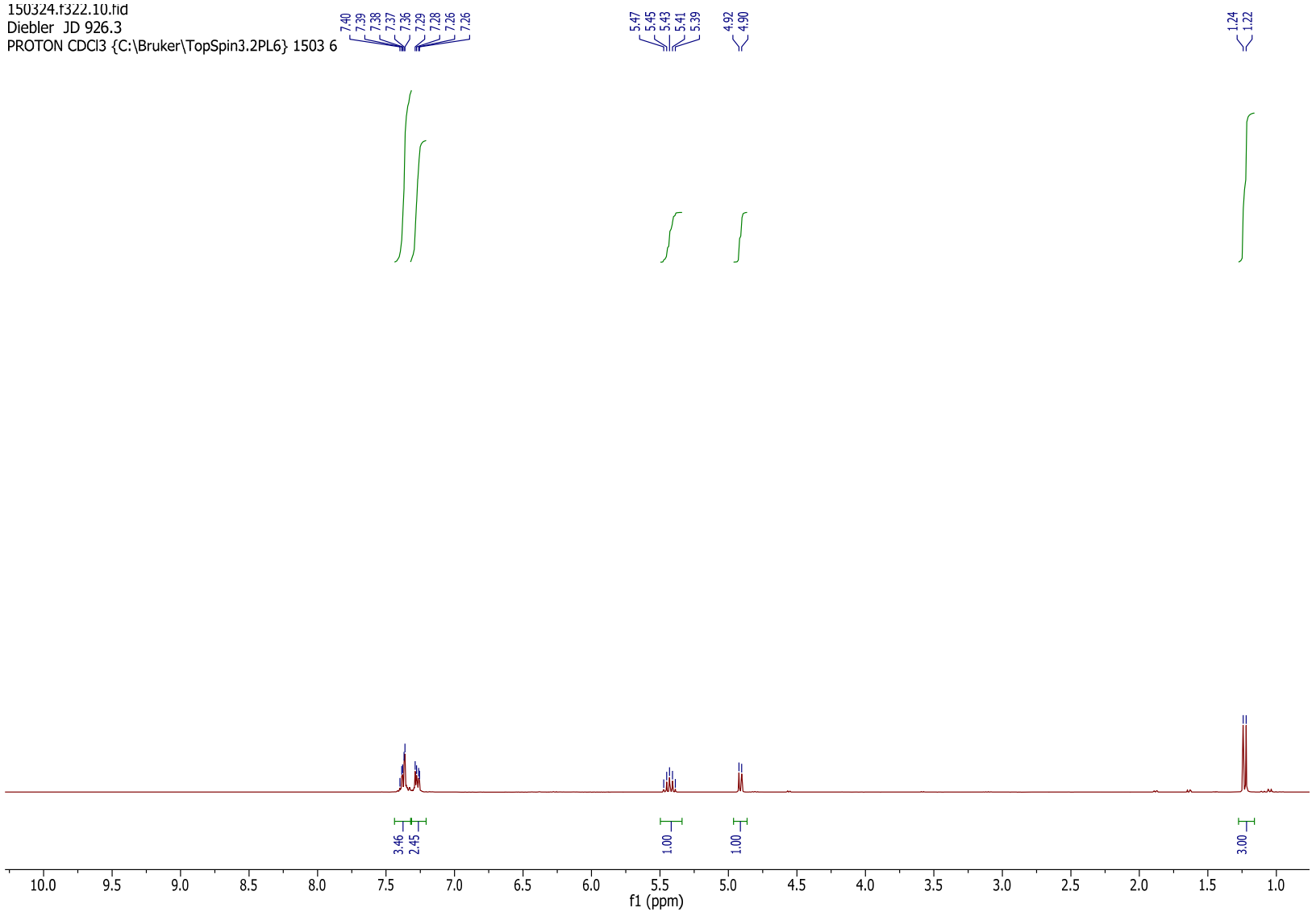
^{1}H-NMR *Cis*-4,5-dimethyl-1,3-oxathiolane-2-thione (*cis*-**2q**)



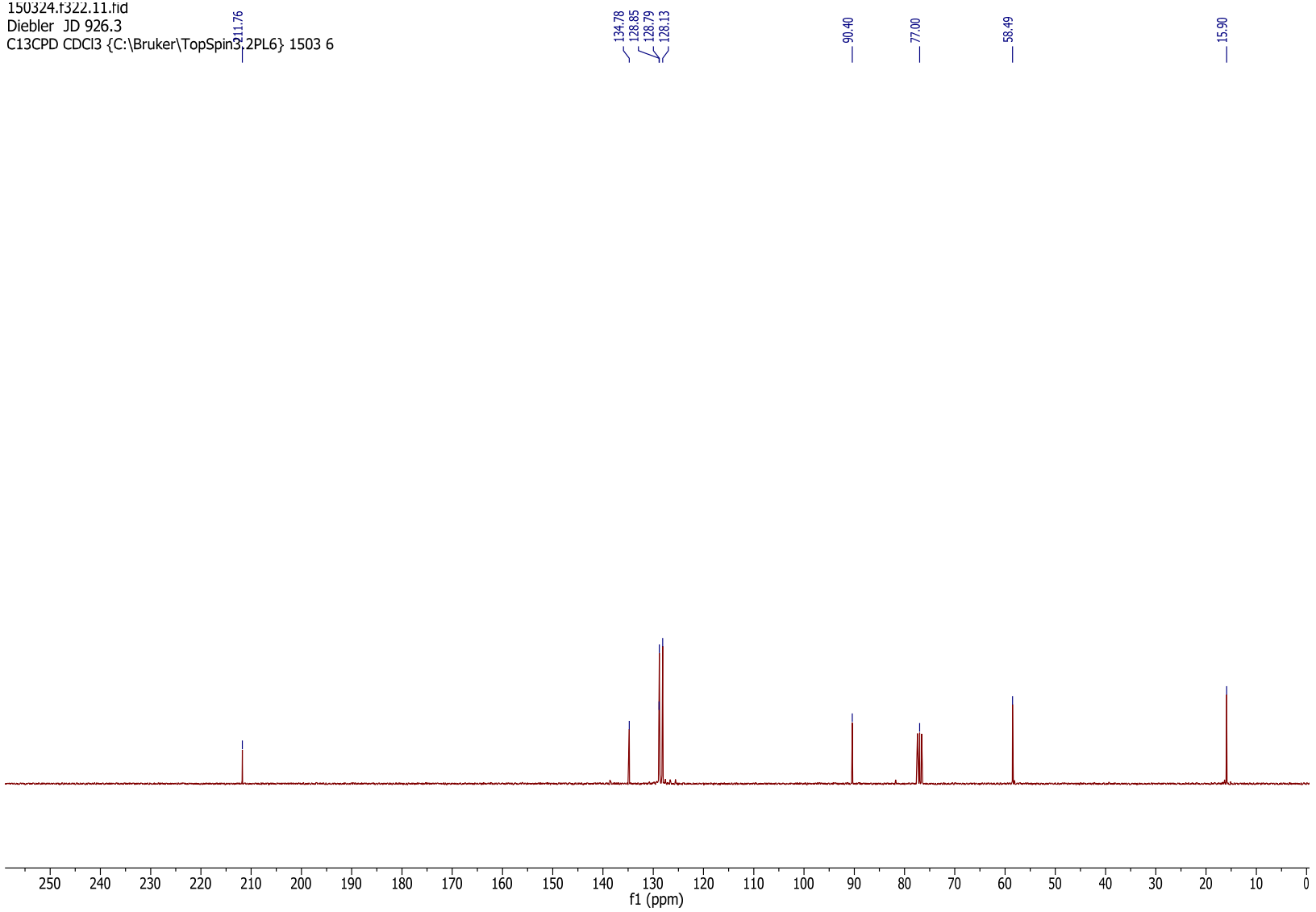
^{13}C-NMR *Cis*-4,5-dimethyl-1,3-oxathiolane-2-thione (*cis*-**2q**)



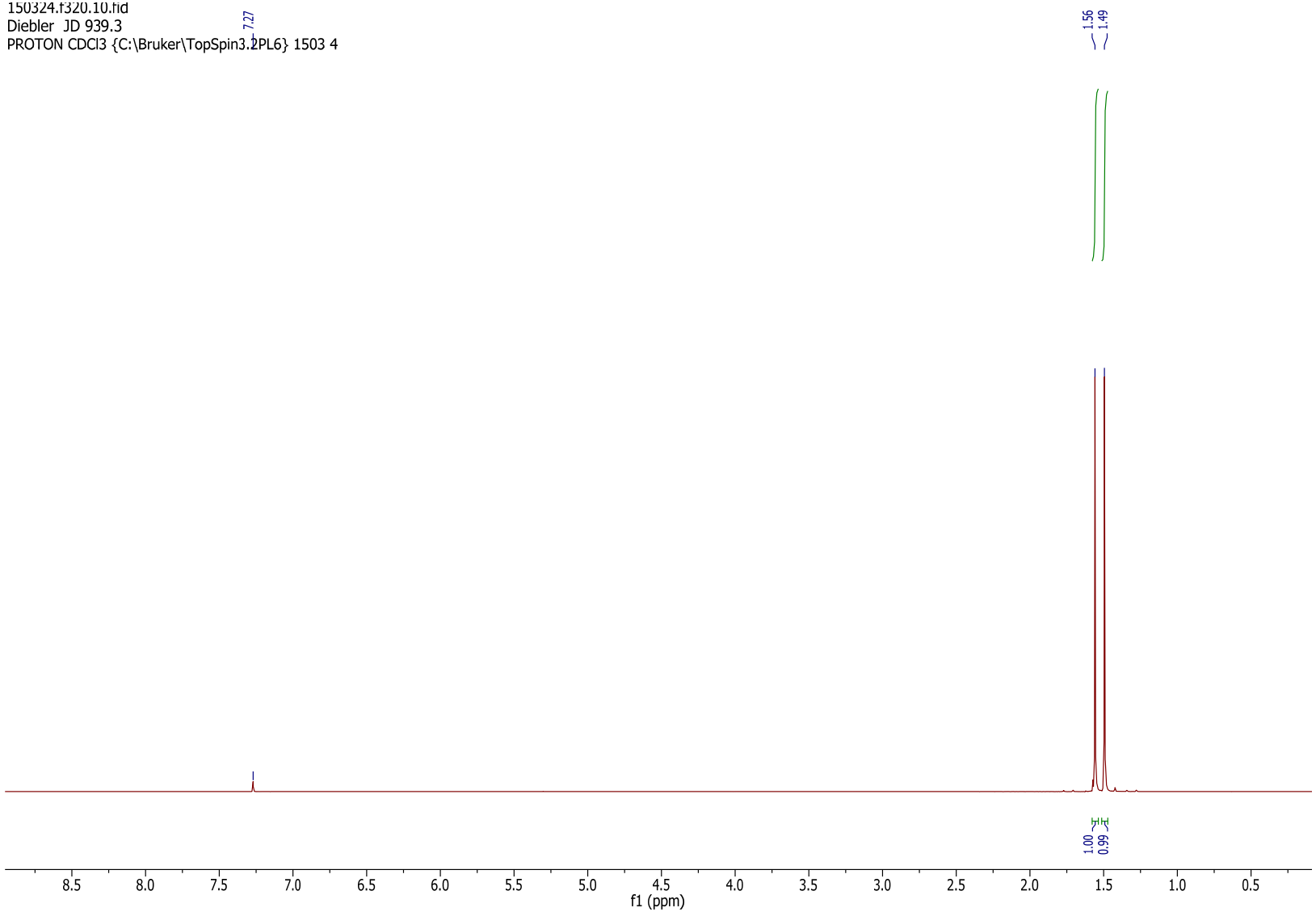
^{1}H-NMR 5-methyl-4-phenyl-1,3-oxathiolane-2-thione (**2r**)



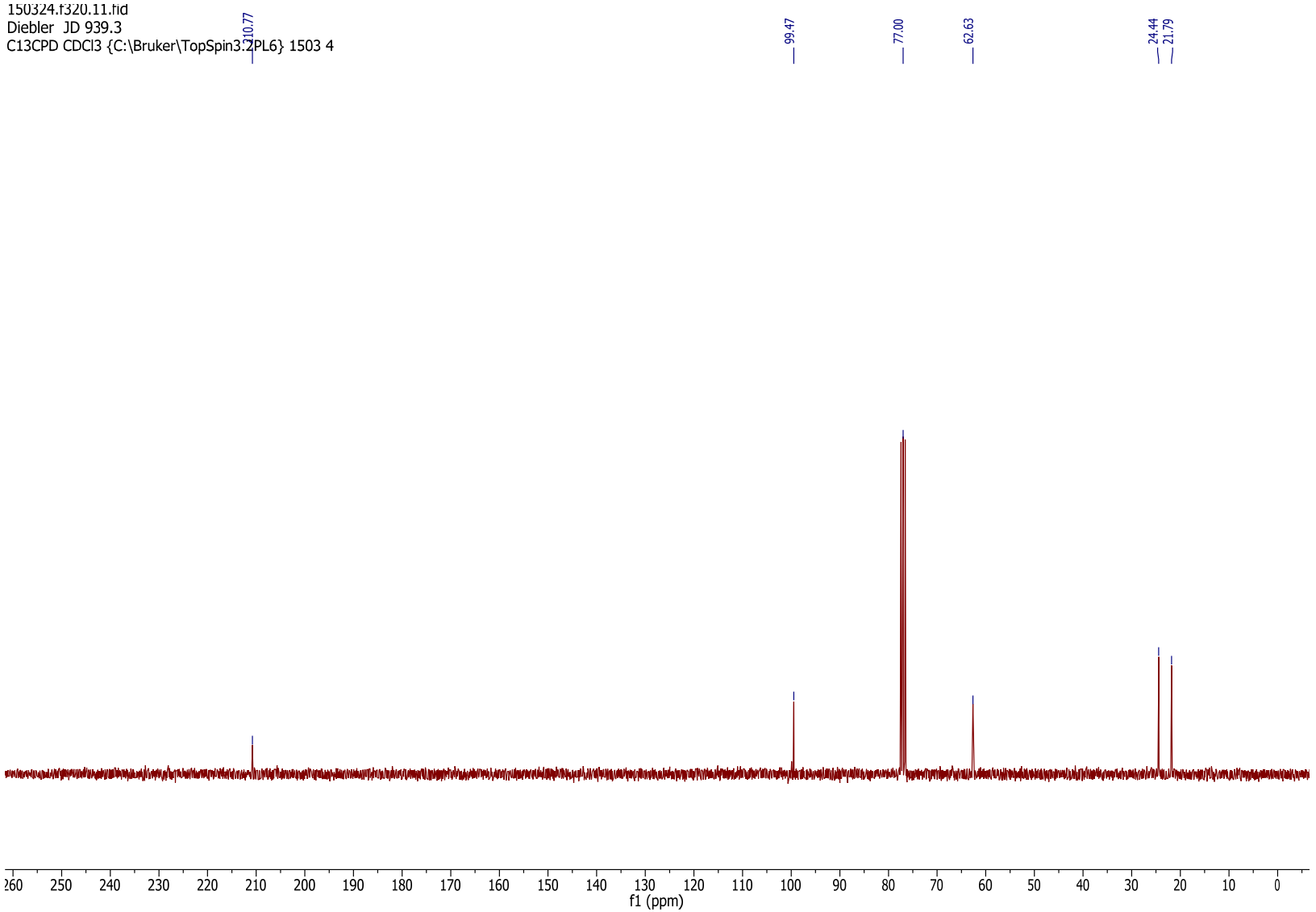
^{13}C-NMR 5-methyl-4-phenyl-1,3-oxathiolane-2-thione (**2r**)



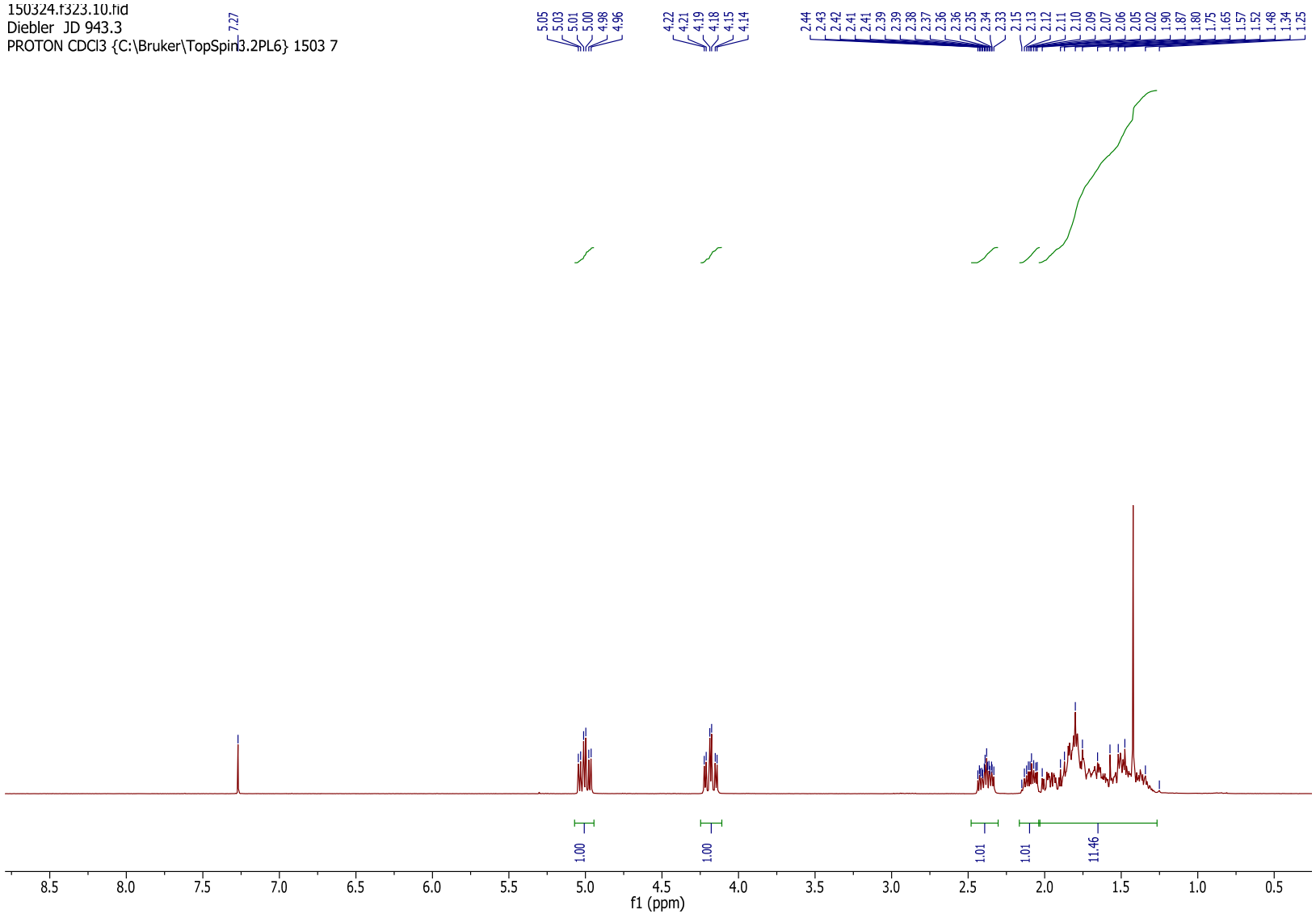
^{1}H-NMR 4,4,5,5-tetramethyl-1,3-oxathiolane-2-thione (**2s**)



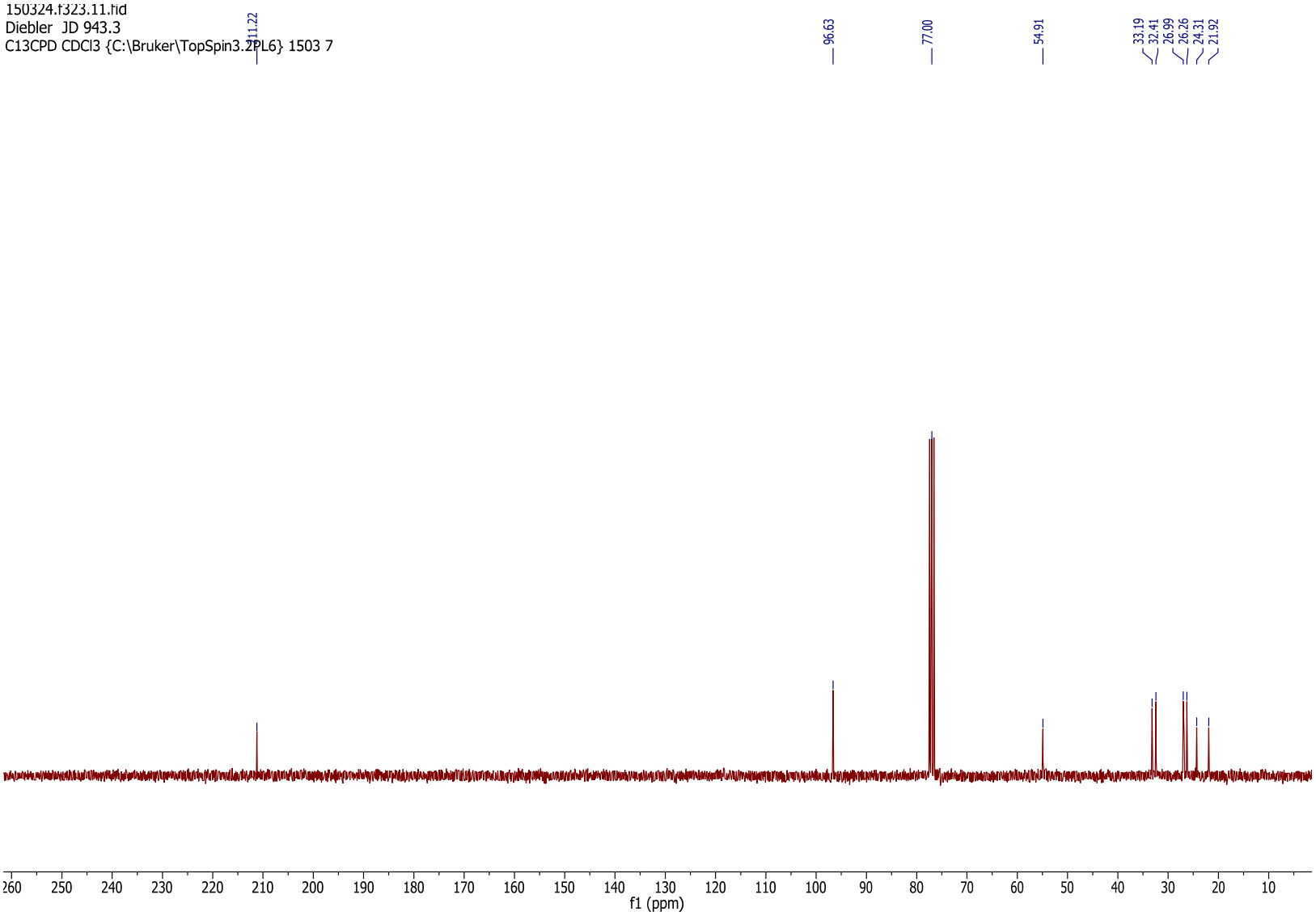
^{13}C-NMR 4,4,5,5-tetramethyl-1,3-oxathiolane-2-thione (**2s**)



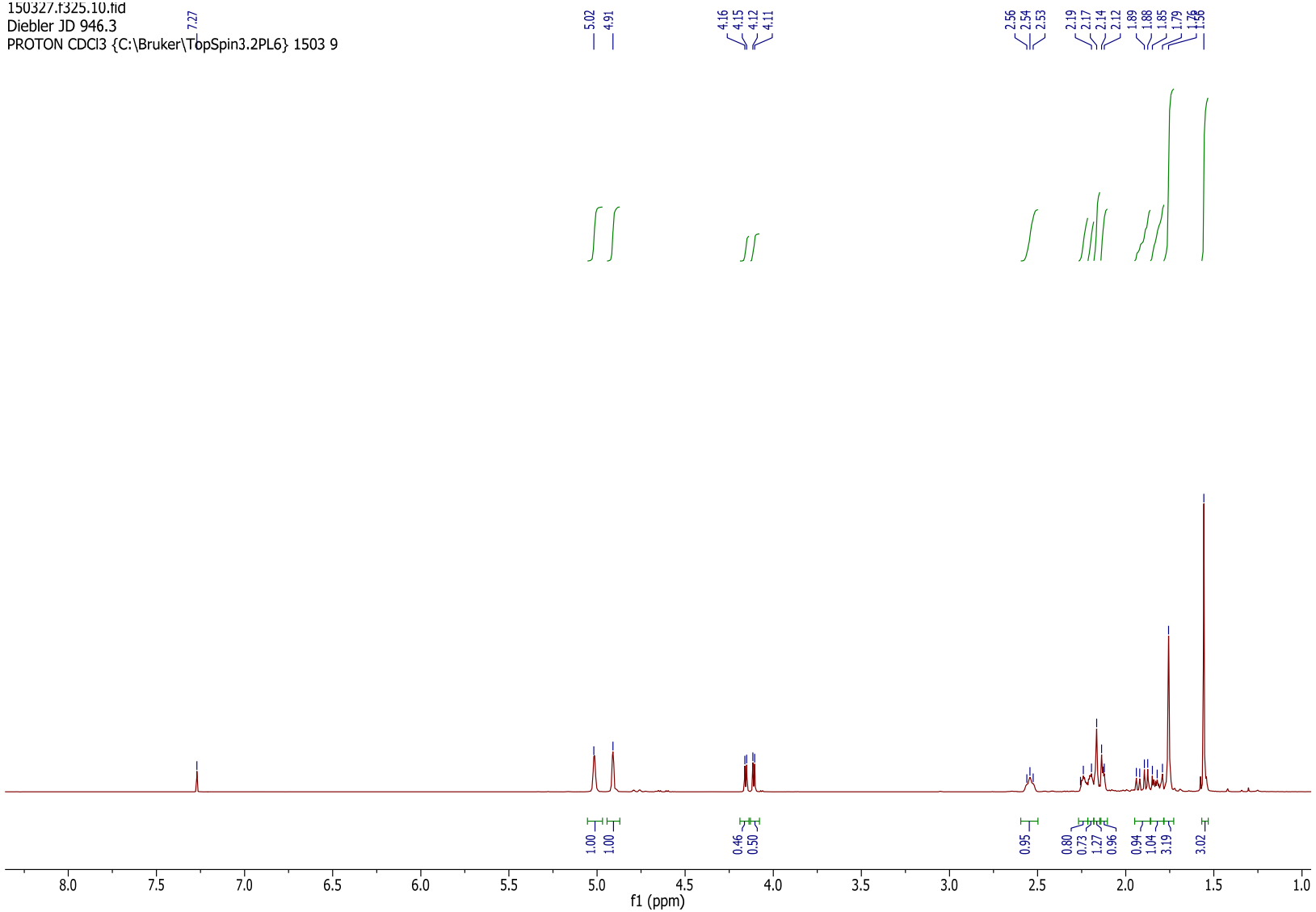
^{1}H-NMR Octahydrocycloocta[*d*][1,3]oxathiolane-2-thione (**2t**)



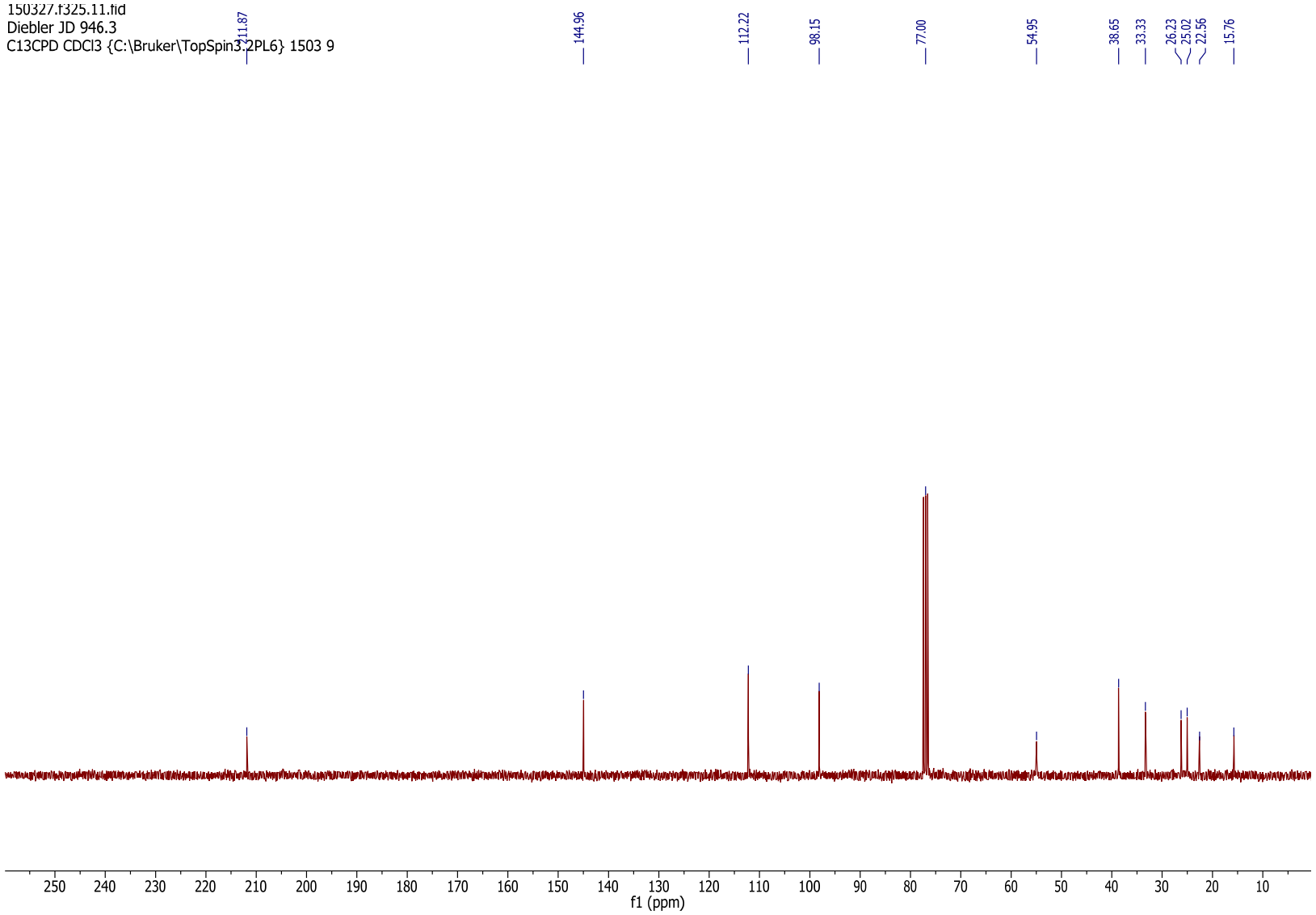
^{13}C-NMR Octahydrocycloocta[*d*][1,3]oxathiolane-2-thione (**2t**)



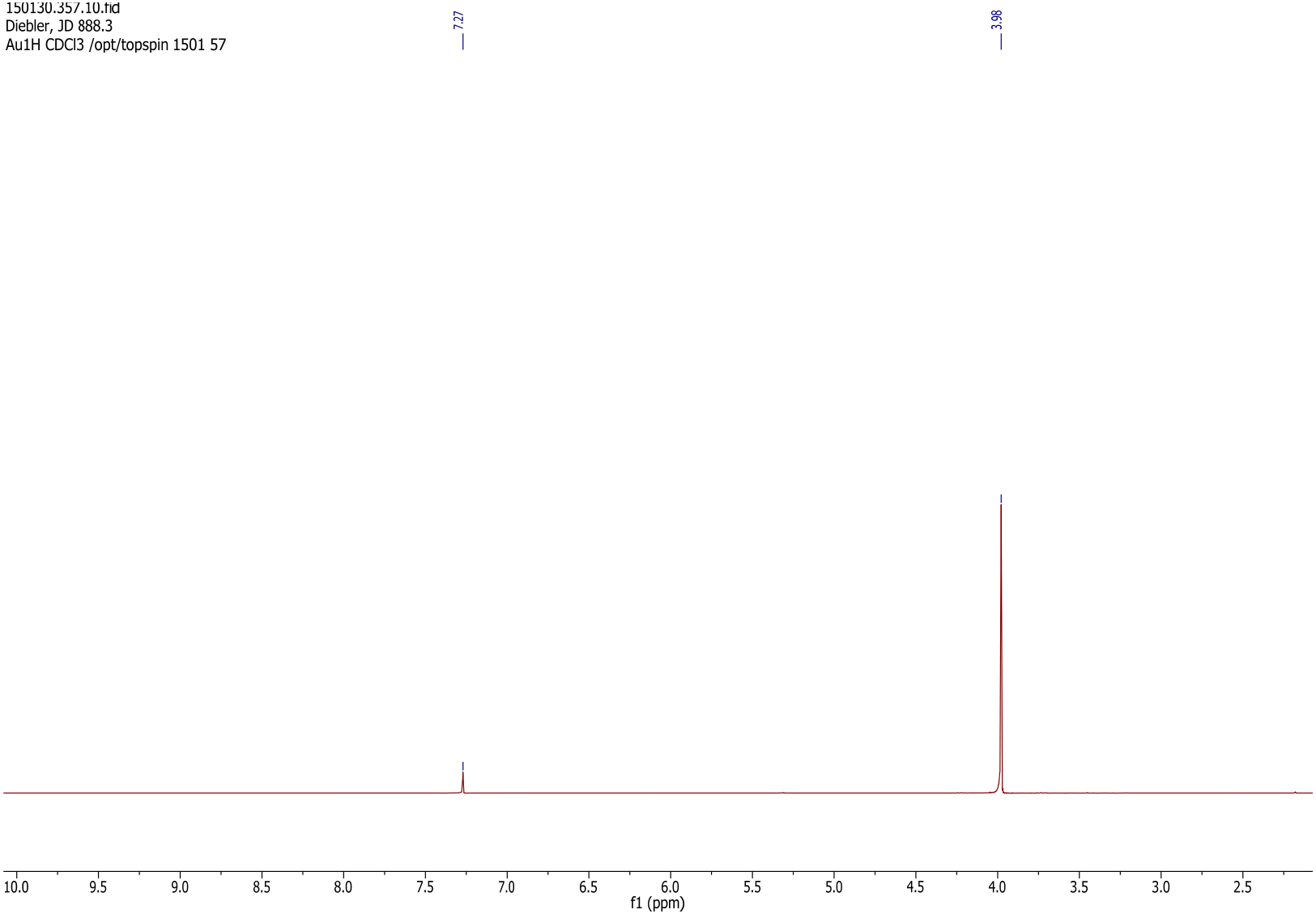
^{1}H-NMR 7a-methyl-5-(prop-1-en-2-yl) hexahydrobenzo[*d*][1,3]oxathiolane-2-thione (**2u**)



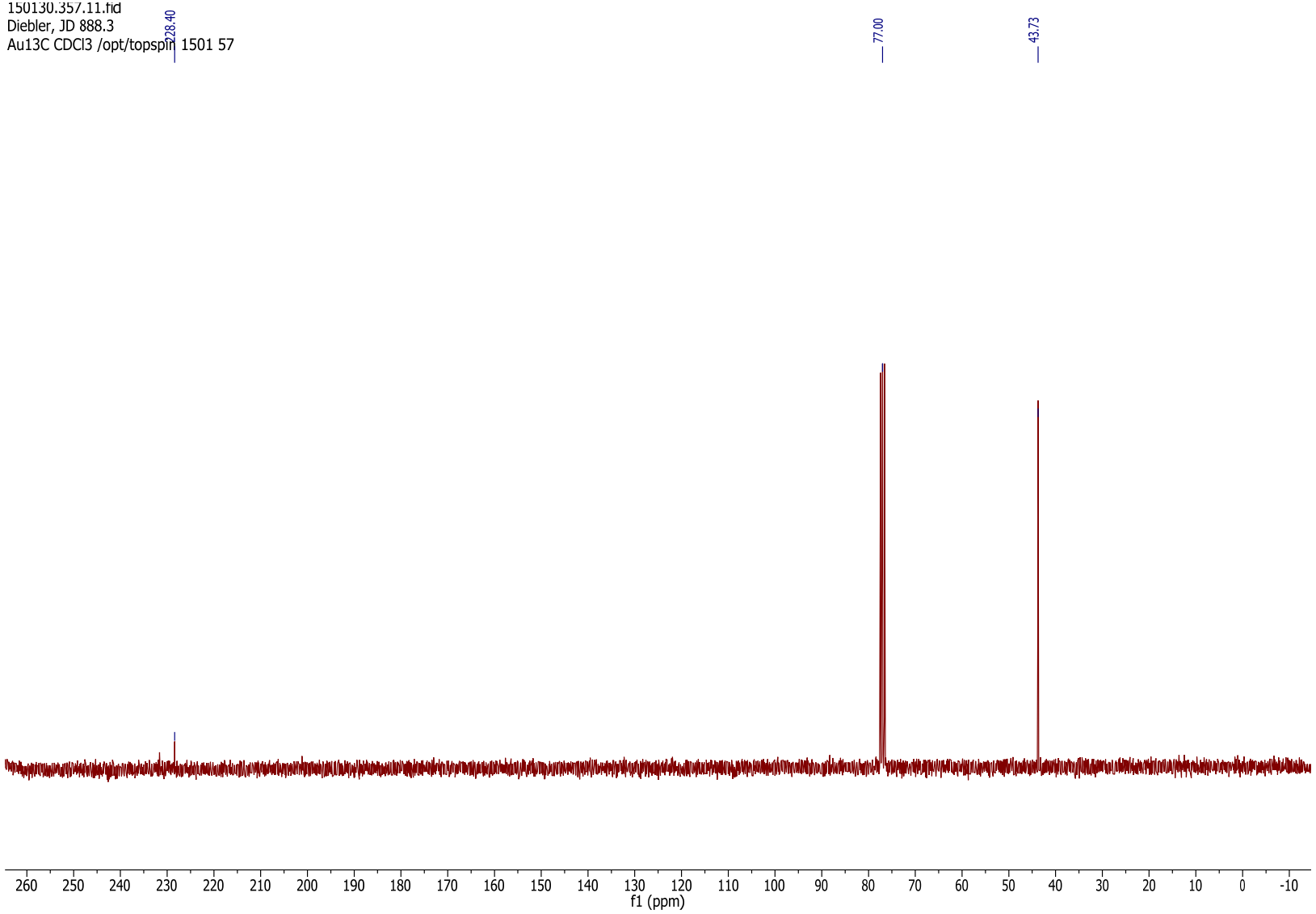
^{13}C-NMR 7a-methyl-5-(prop-1-en-2-yl) hexahydrobenzo[*d*][1,3]oxathiolane-2-thione (**2u**)



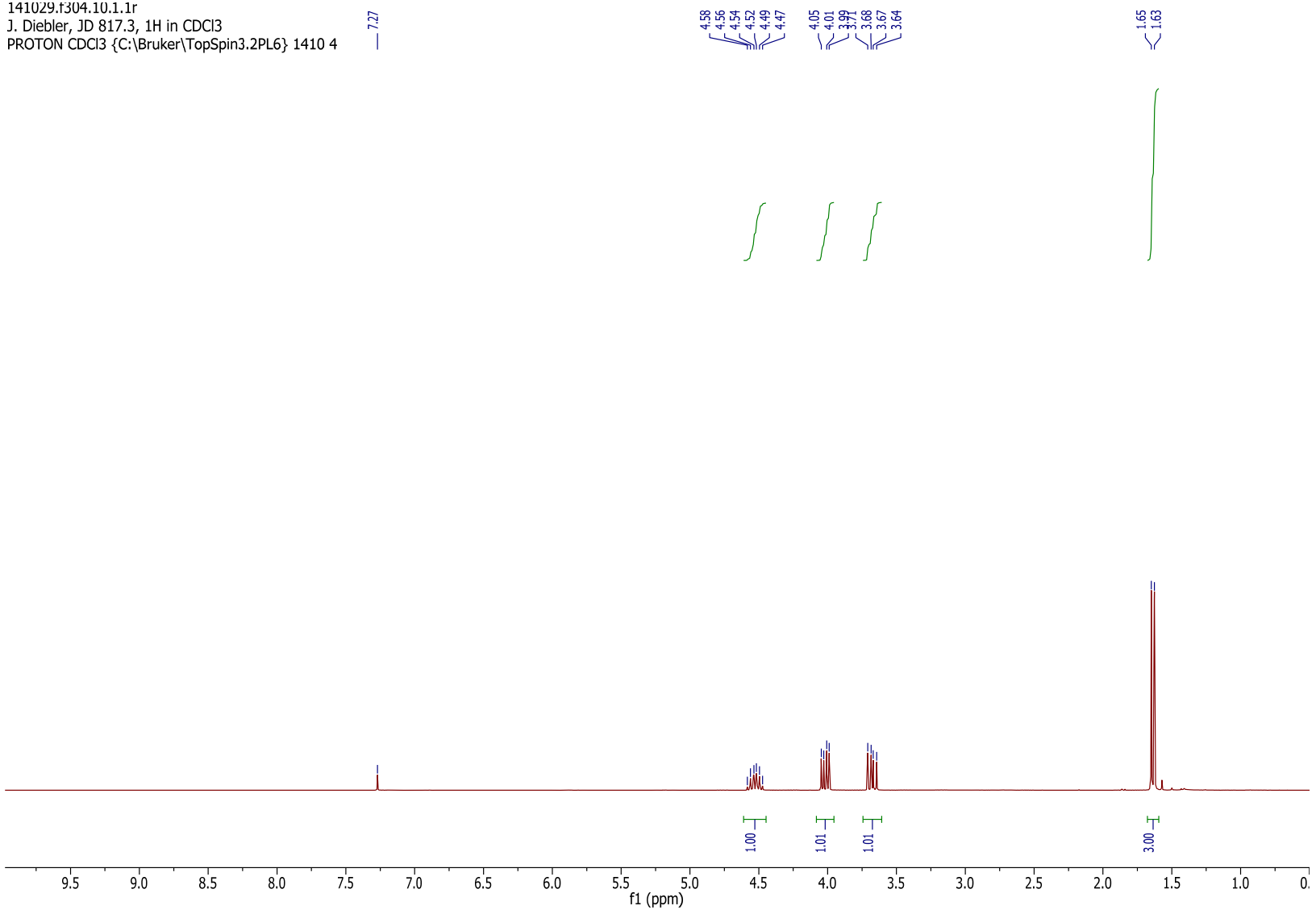
^{1}H-NMR 1,3-dithiolane-2-thione (**4a**)



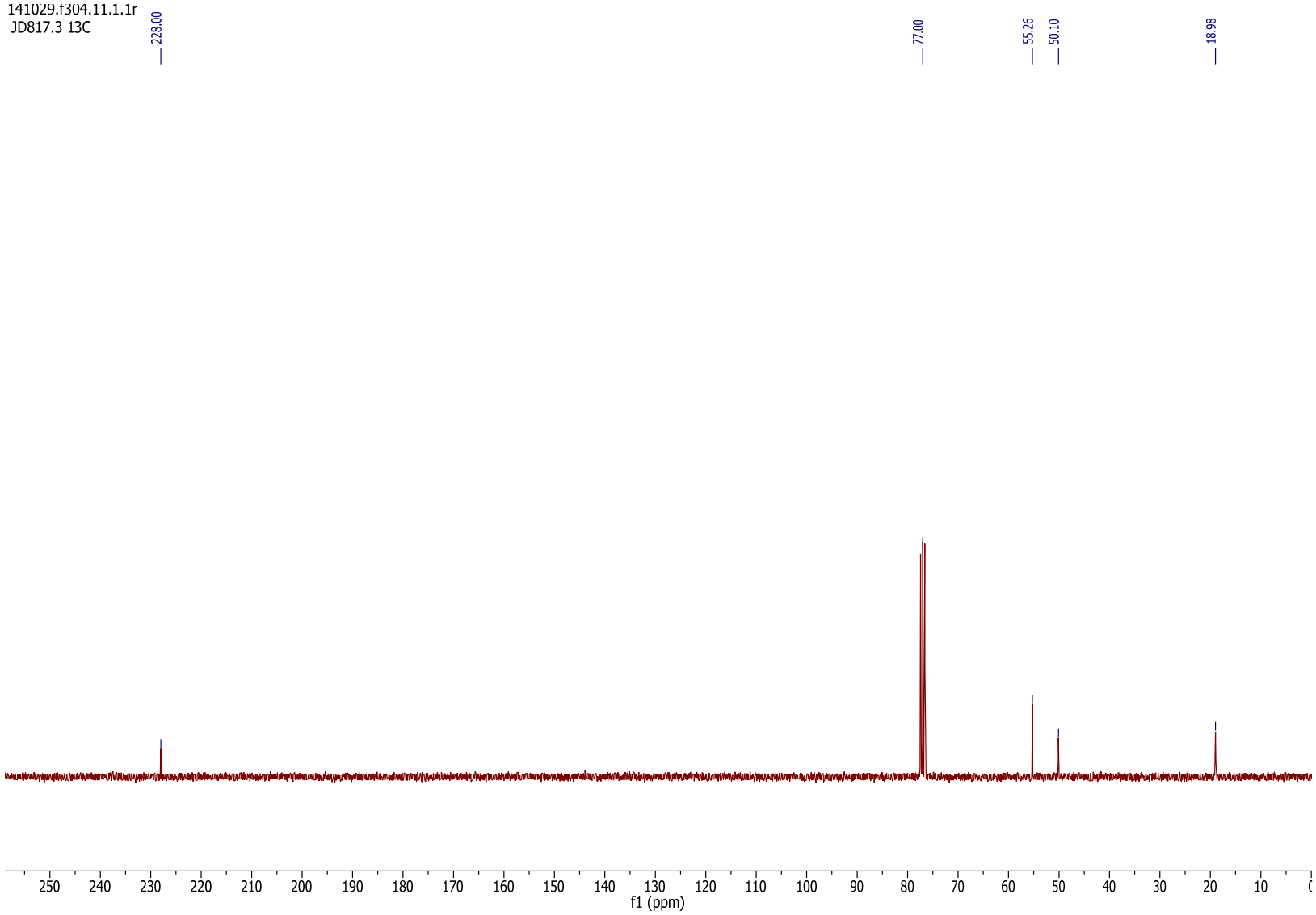
^{13}C-NMR 1,3-dithiolane-2-thione (**4a**)



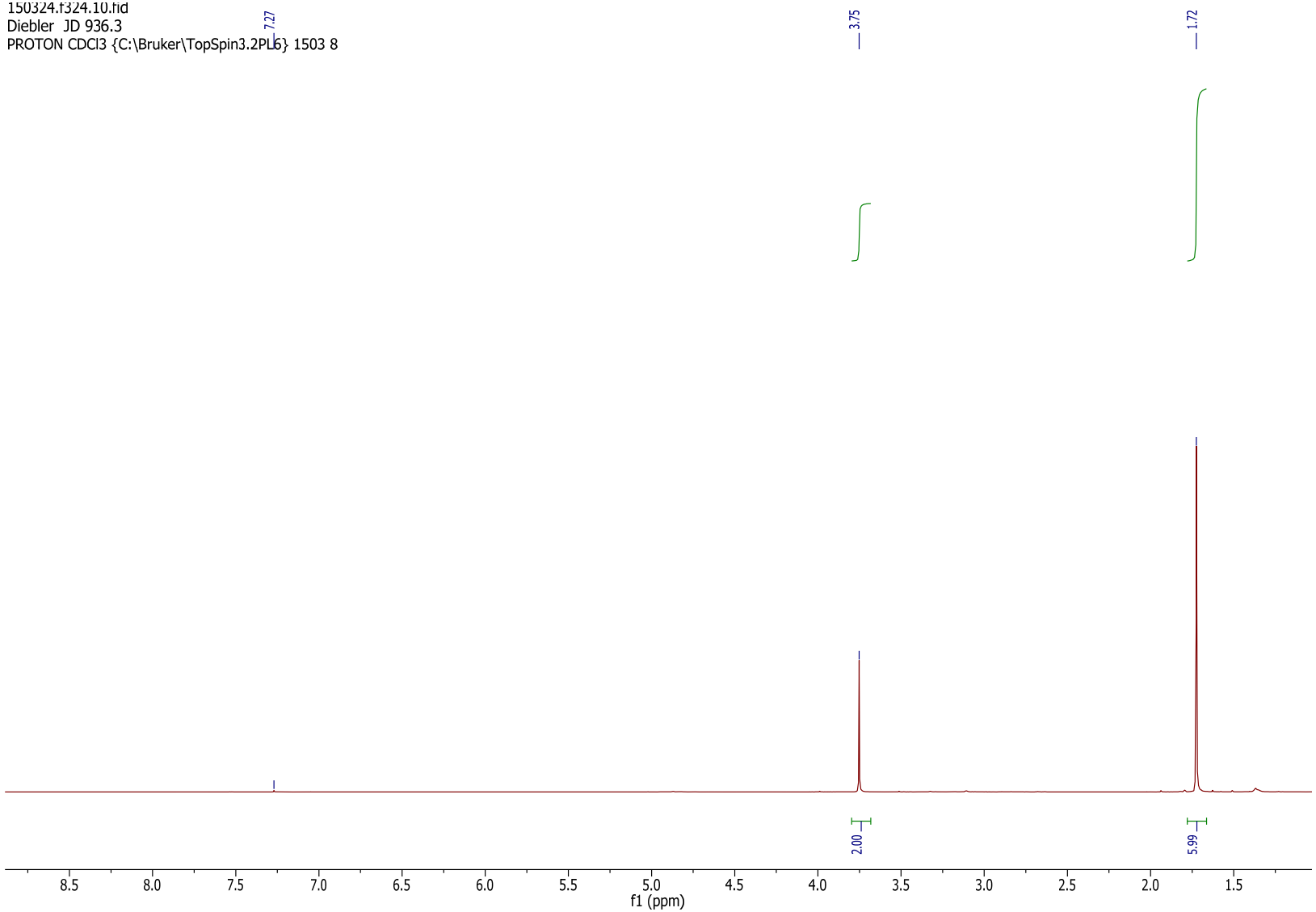
^{1}H-NMR 4-methyl-1,3-dithiolane-2-thione (**4b**)



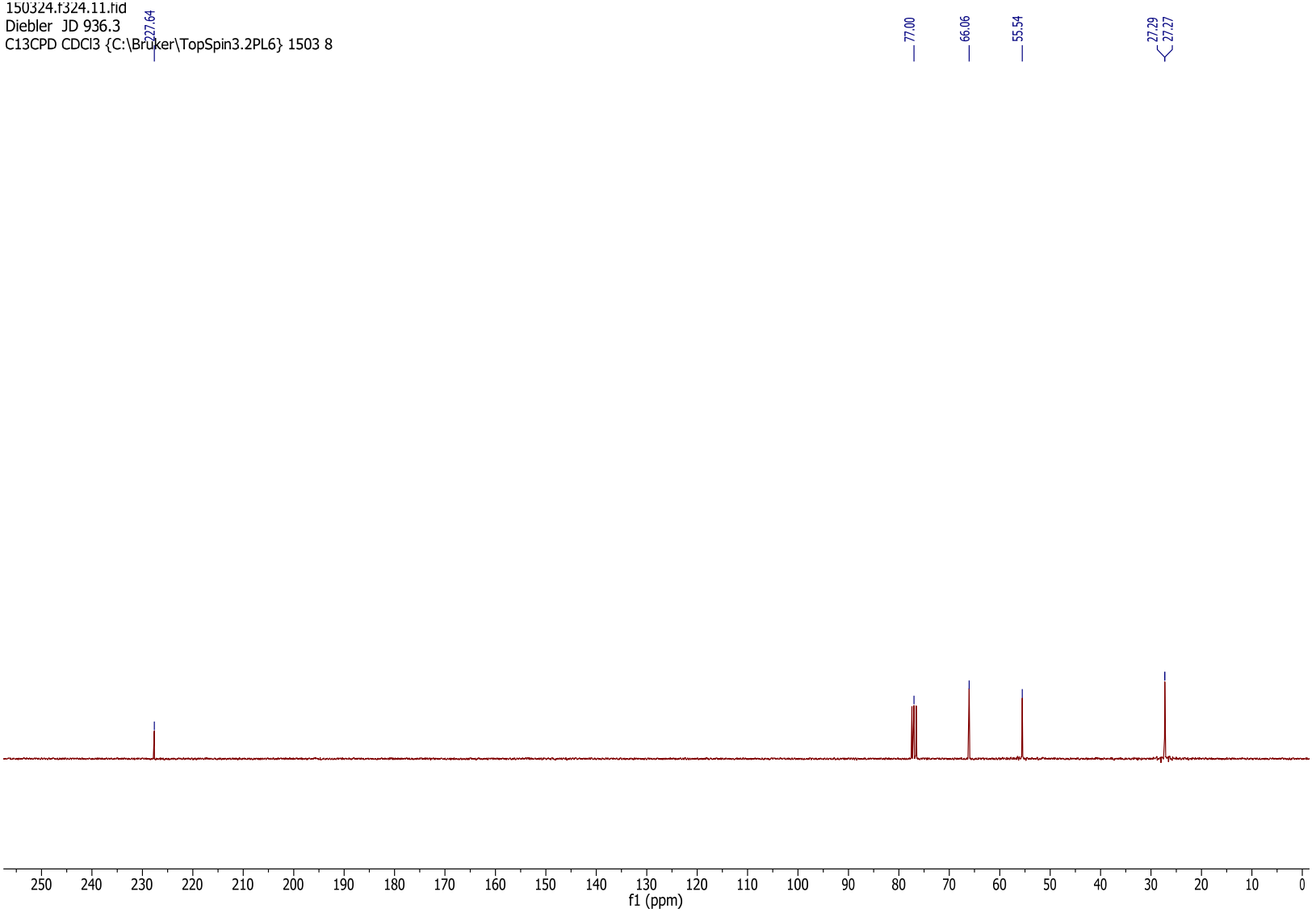
^{13}C-NMR 4-methyl-1,3-dithiolane-2-thione (**4b**)



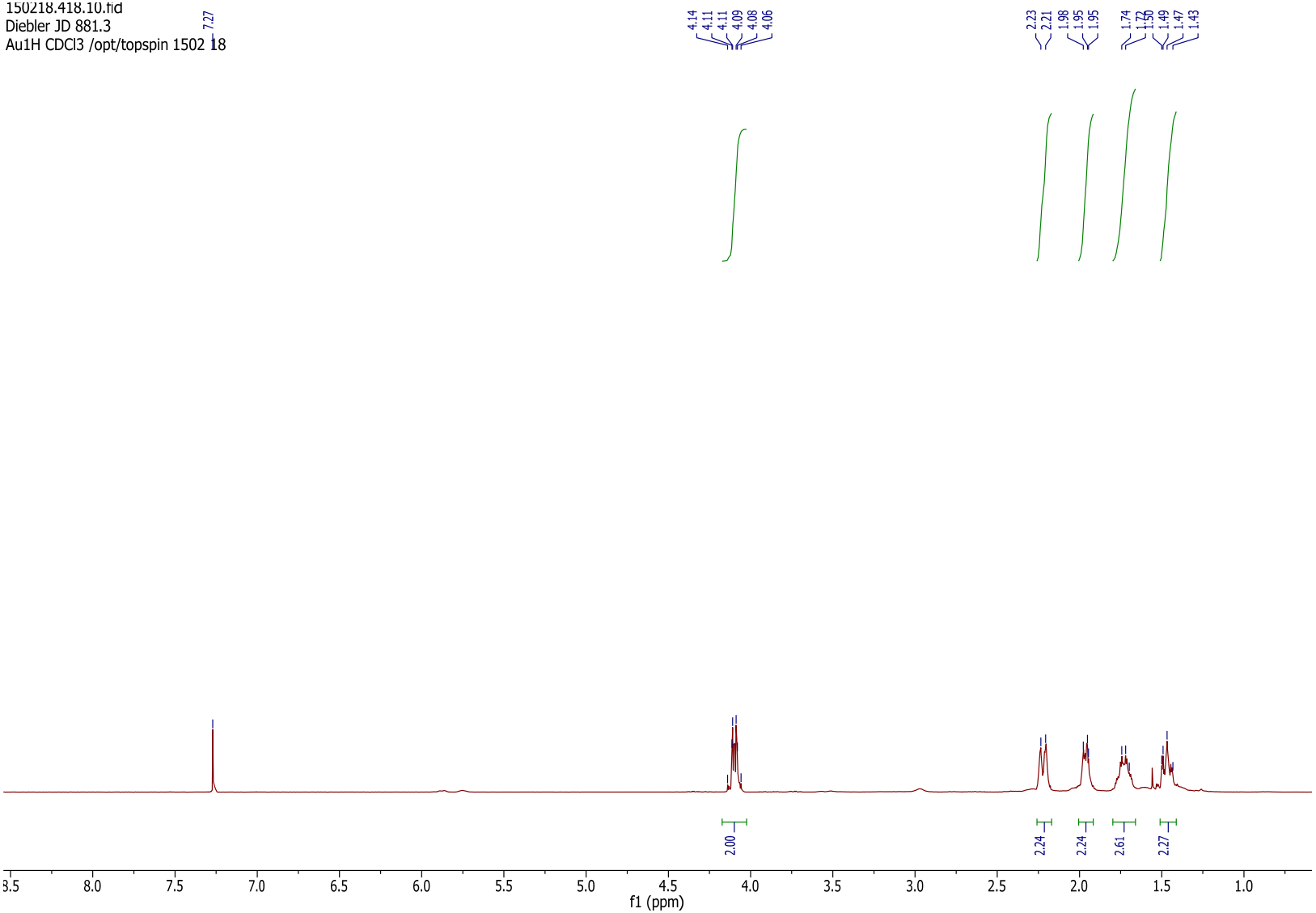
^{1}H-NMR 4,4-dimethyl-1,3-dithiolane-2-thione (**4d**)



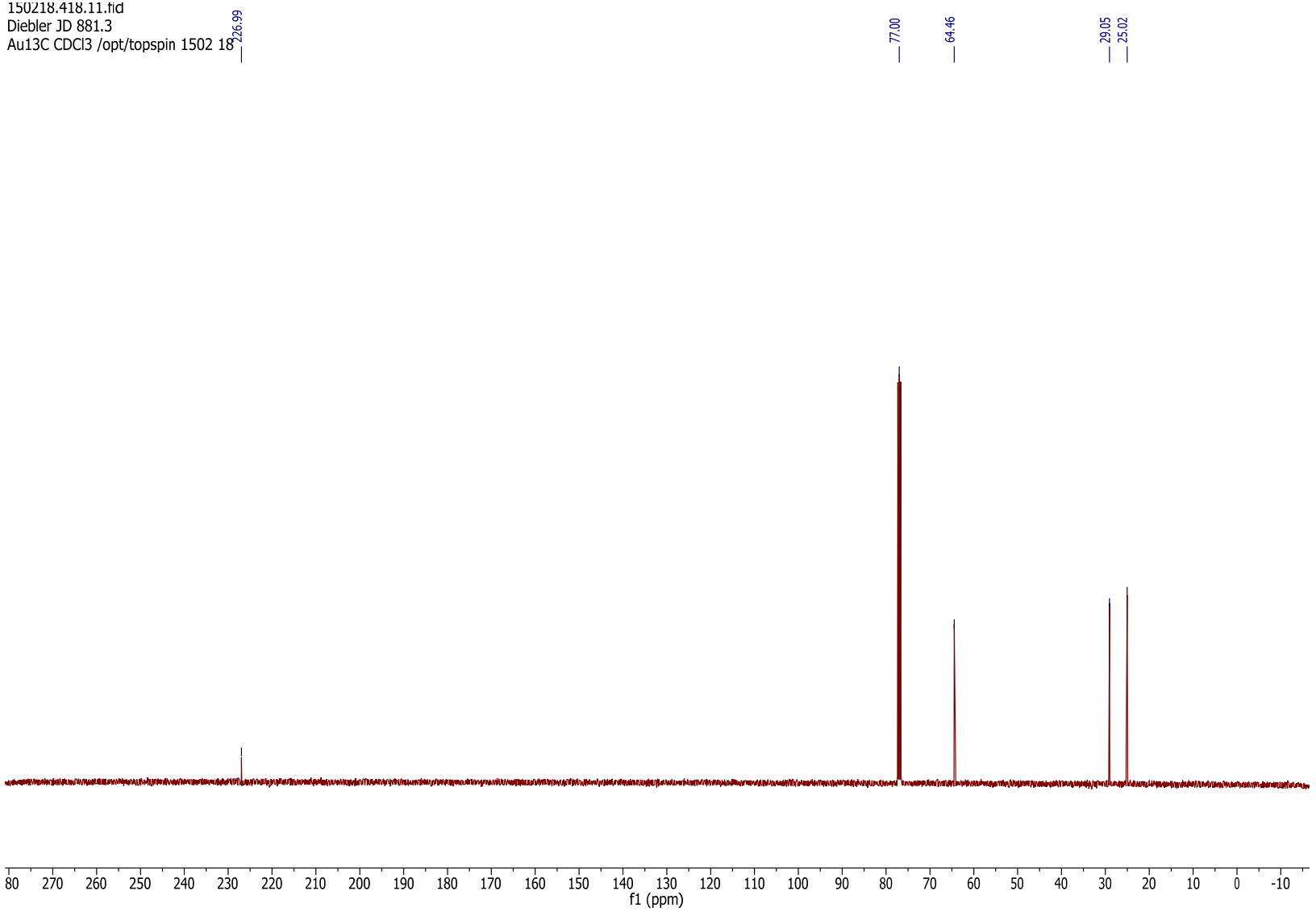
^{13}C-NMR 4,4-dimethyl-1,3-dithiolane-2-thione (**4d**)



^{1}H-NMR 4,5-tetramethylen-1,3-dithiolane-2-thione (**4e**)



^{13}C-NMR 4,5-tetramethylen-1,3-dithiolane-2-thione (**4e**)



5. X-Ray Data for 2u

X-ray crystal structure analysis of **2u**:
Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Crystallogr.* 2008, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014: G. M. Sheldrick, *Acta Crystallogr.* 2015, *C71*, 3.). XP (Bruker AXS) was used for graphical representation.
Crystal data for **2u**:
$C_{11}H_{16}OS_2$, M = 228.36, orthorhombic, space group $P2_12_12_1$, a = 8.4952(2), b = 9.1213(2), c = 14.9630(3) Å, V = 1159.44(4) Å^3, T = 150(2) K, Z = 4, 9562 reflections measured, 2938 independent reflections (R_{int} = 0.0158), final R values ($I > 2\sigma(I)$): R_1 = 0.0235, wR_2 = 0.0625, final R values (all data): R_1 = 0.0245, wR_2 = 0.0635, 129 parameters, Flack parameter x = -0.03(2).

CCDC 1478719 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6. ^{13}C NMR Spectra of the Reaction Monitoring

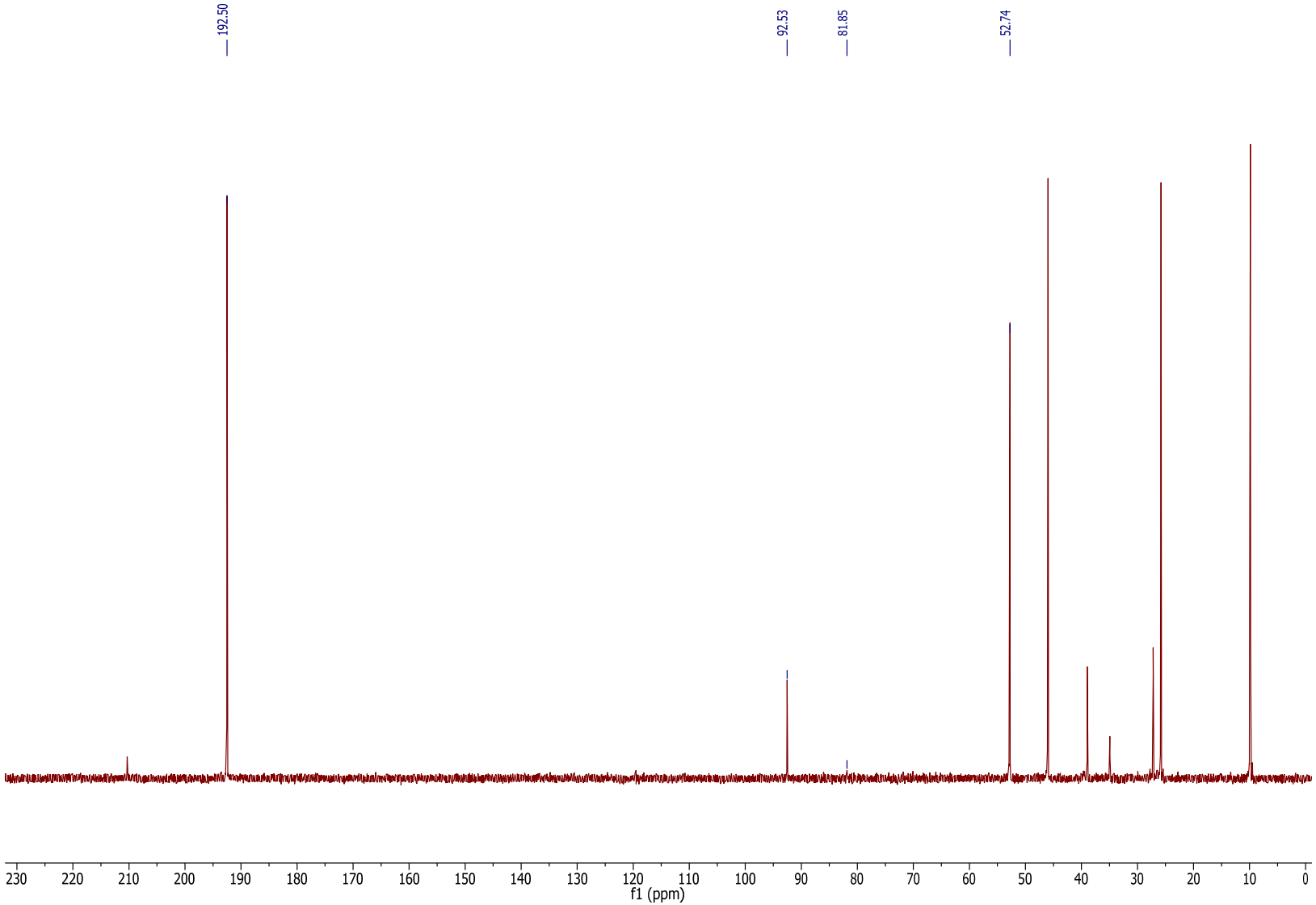


Figure S1. ^{13}C–NMR spectrum of the reaction monitoring after 0.3 h.

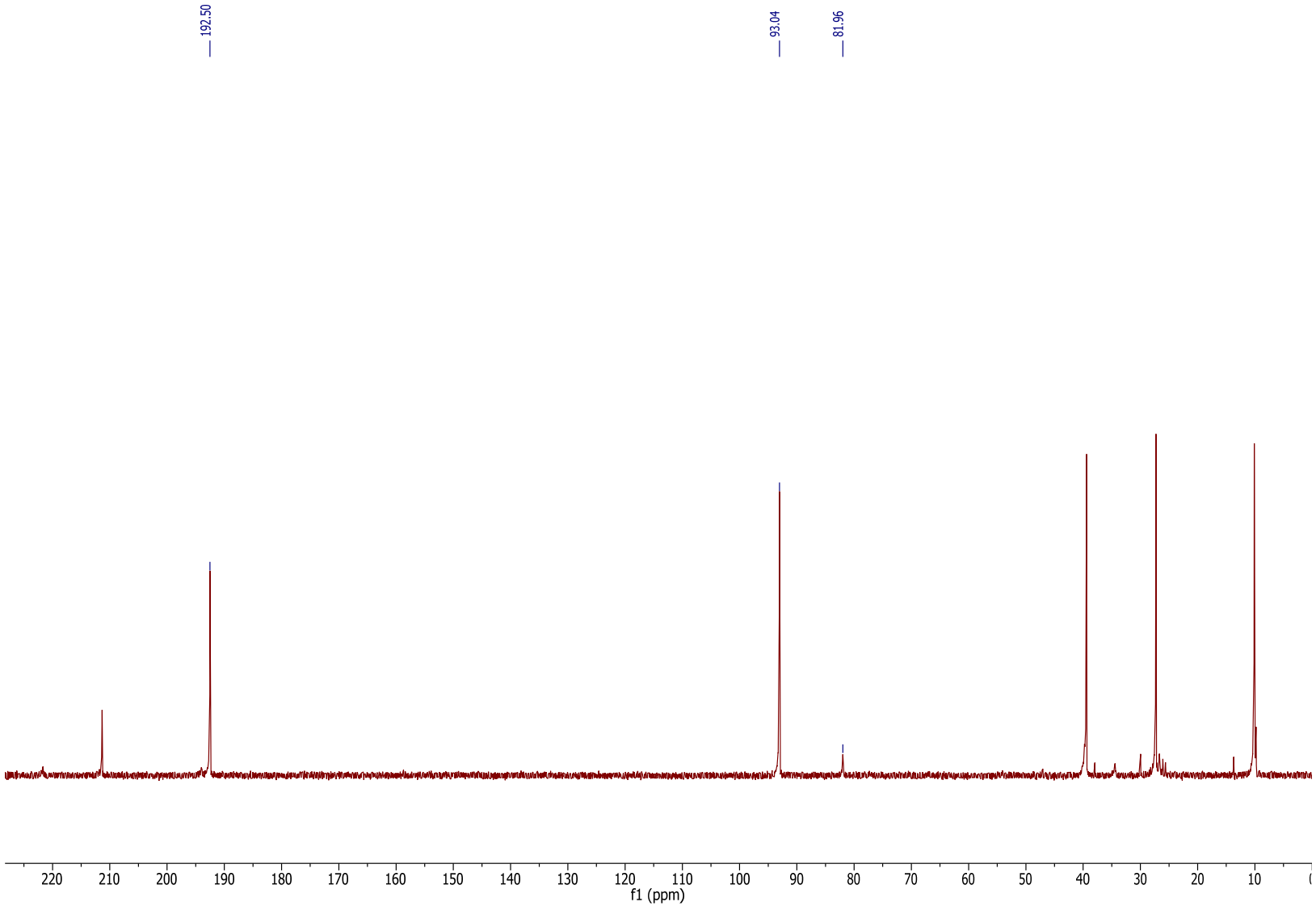


Figure S2. ^{13}C–NMR spectrum of the reaction monitoring after 1.7 h.

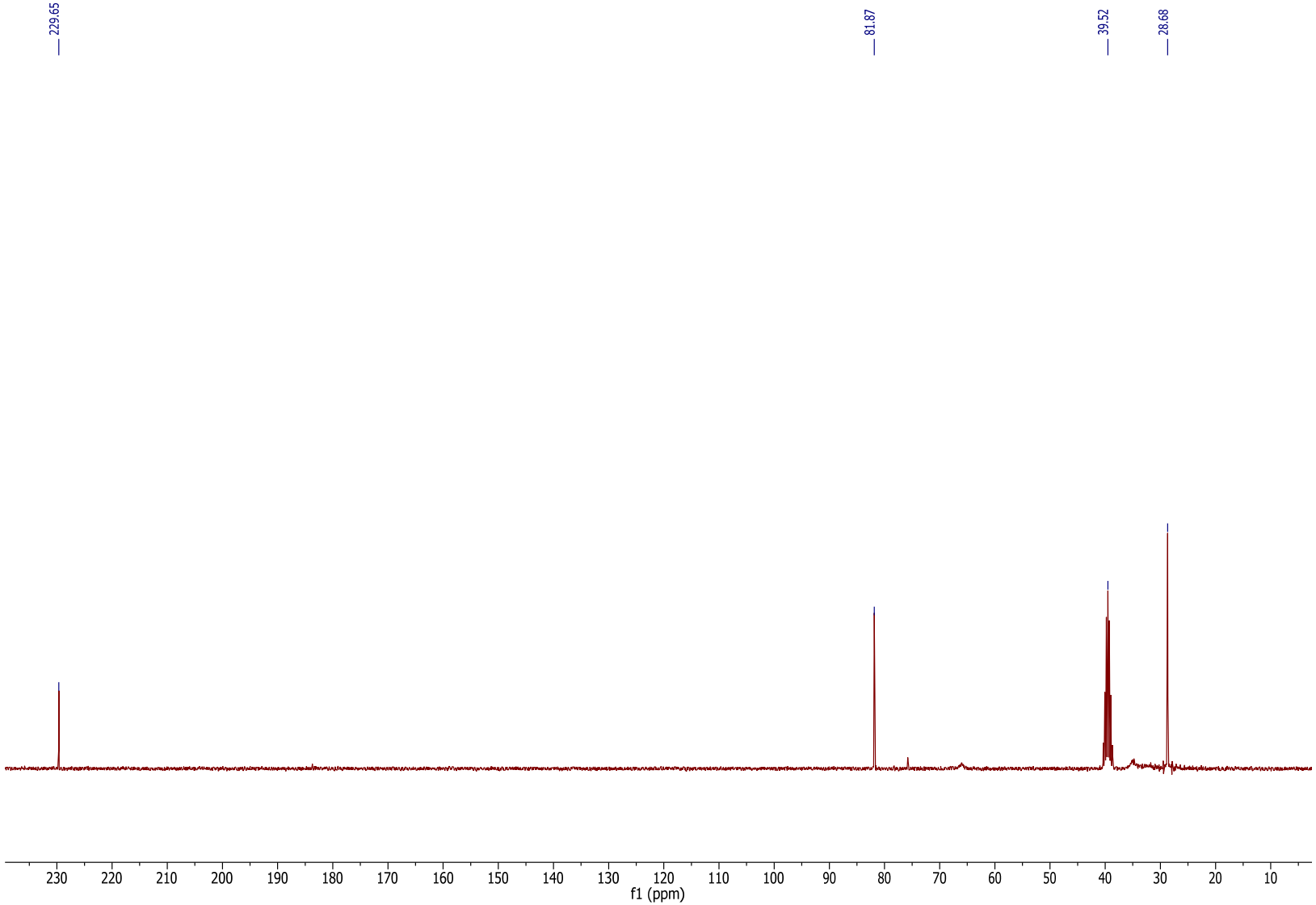


Figure S3. ^{13}C–NMR spectrum of a 1:1 mixture of LiO^{t}Bu:CS_2 in DMSO-d_6.

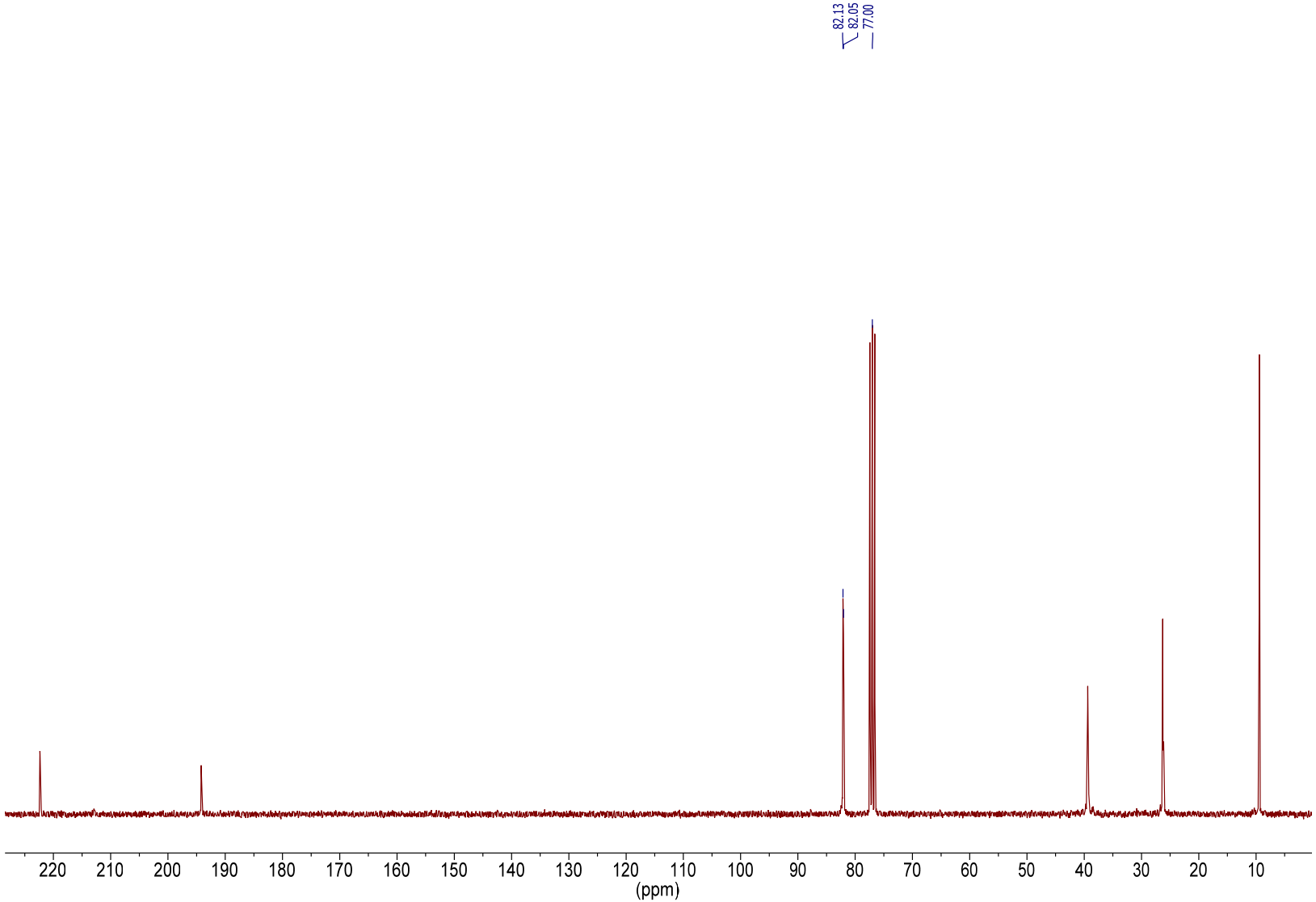
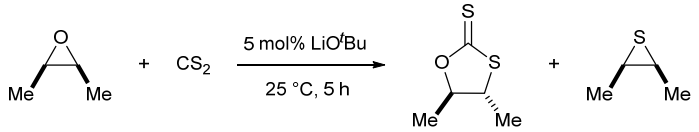


Figure S4. ^{13}C–NMR spectrum of oligomer **8** in $CDCl_3$.

7. Mechanistic Studies



cis-**1q**

trans-**2q**

cis-**3q**

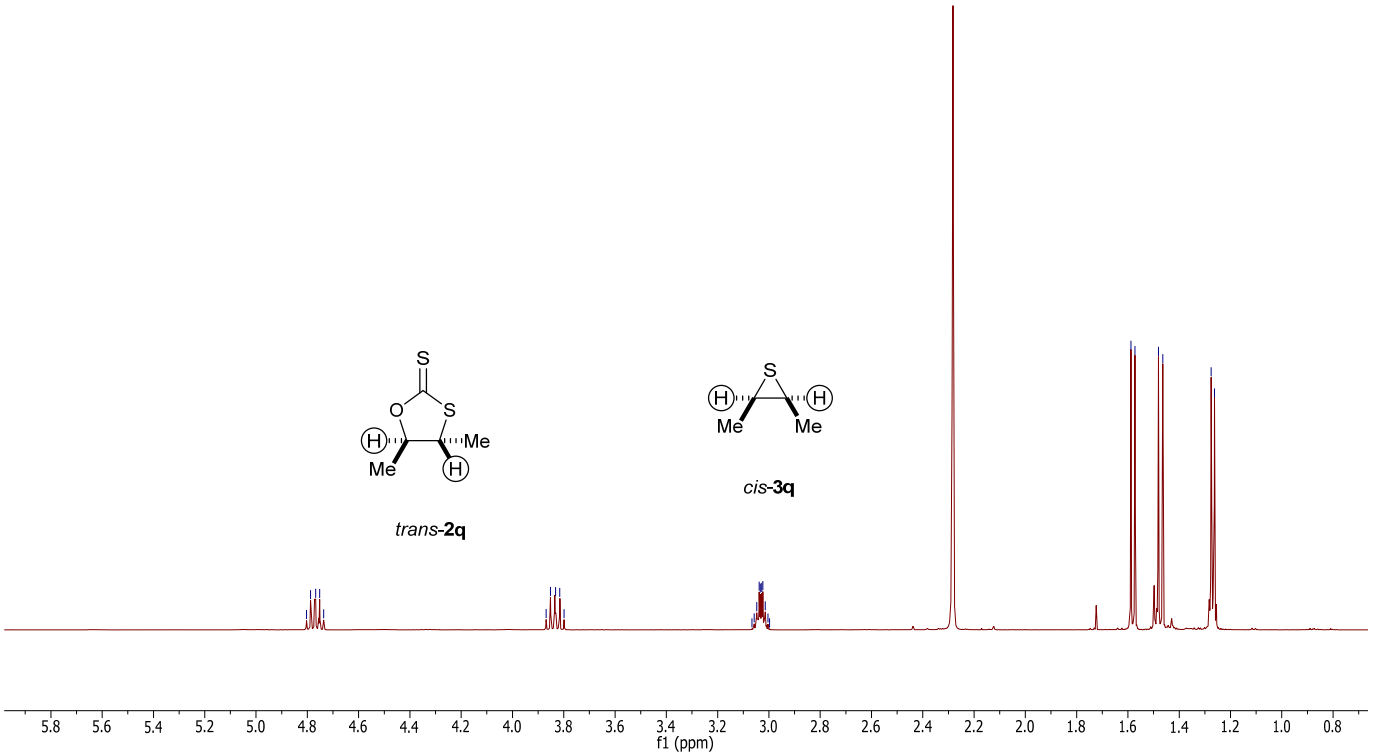


Figure S5. ^{1}H–NMR spectrum of the crude reaction mixture of the conversion of *cis*-**1q** and characteristic resonances of *trans*-**2q** and *cis*-**3q**.[1, 2]

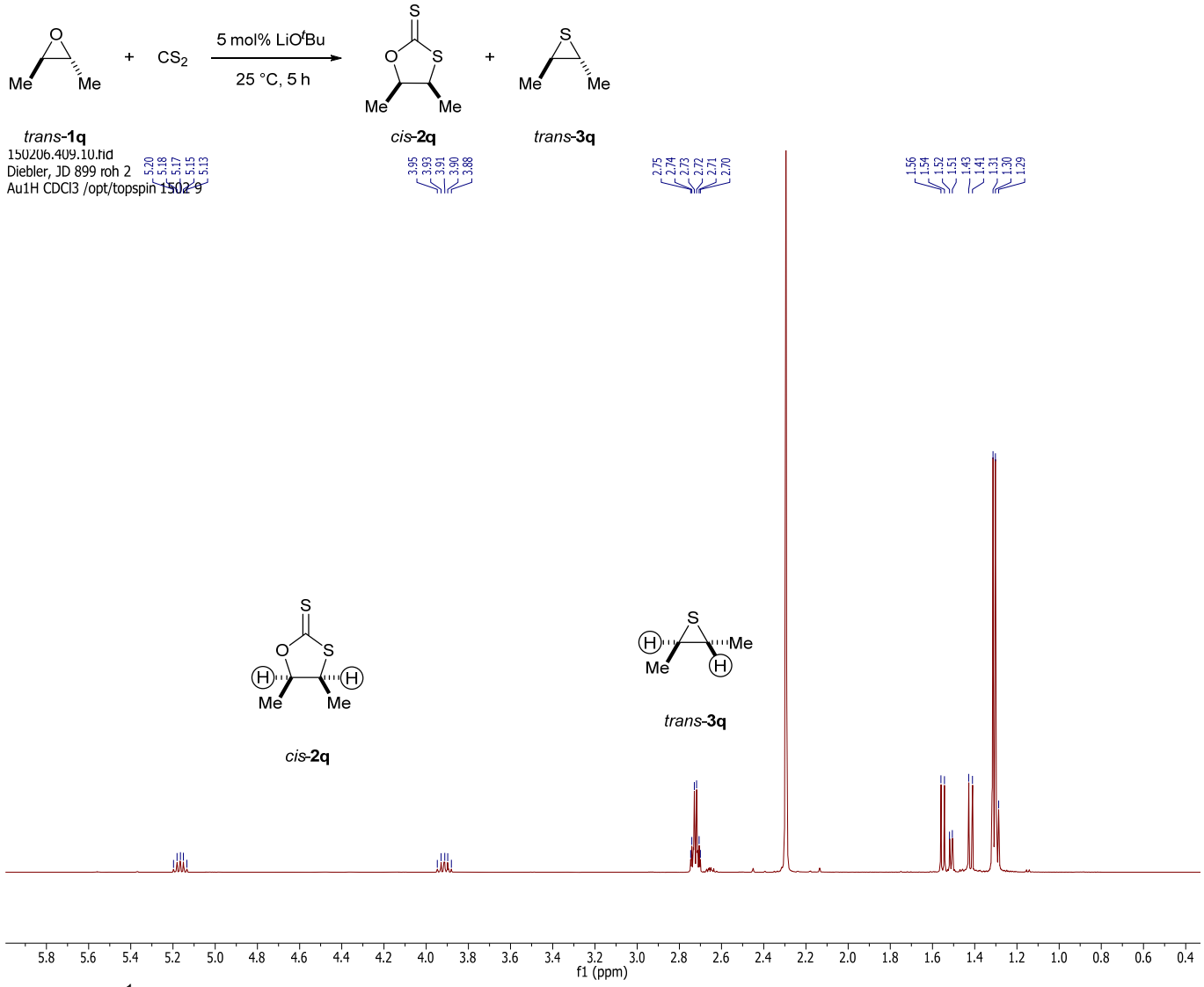


Figure S6. ^{1}H–NMR spectrum of the crude reaction mixture of the conversion of *trans*-**1q** and characteristic resonances of *cis*-**2q** and *trans*-**3q**.[1, 2]

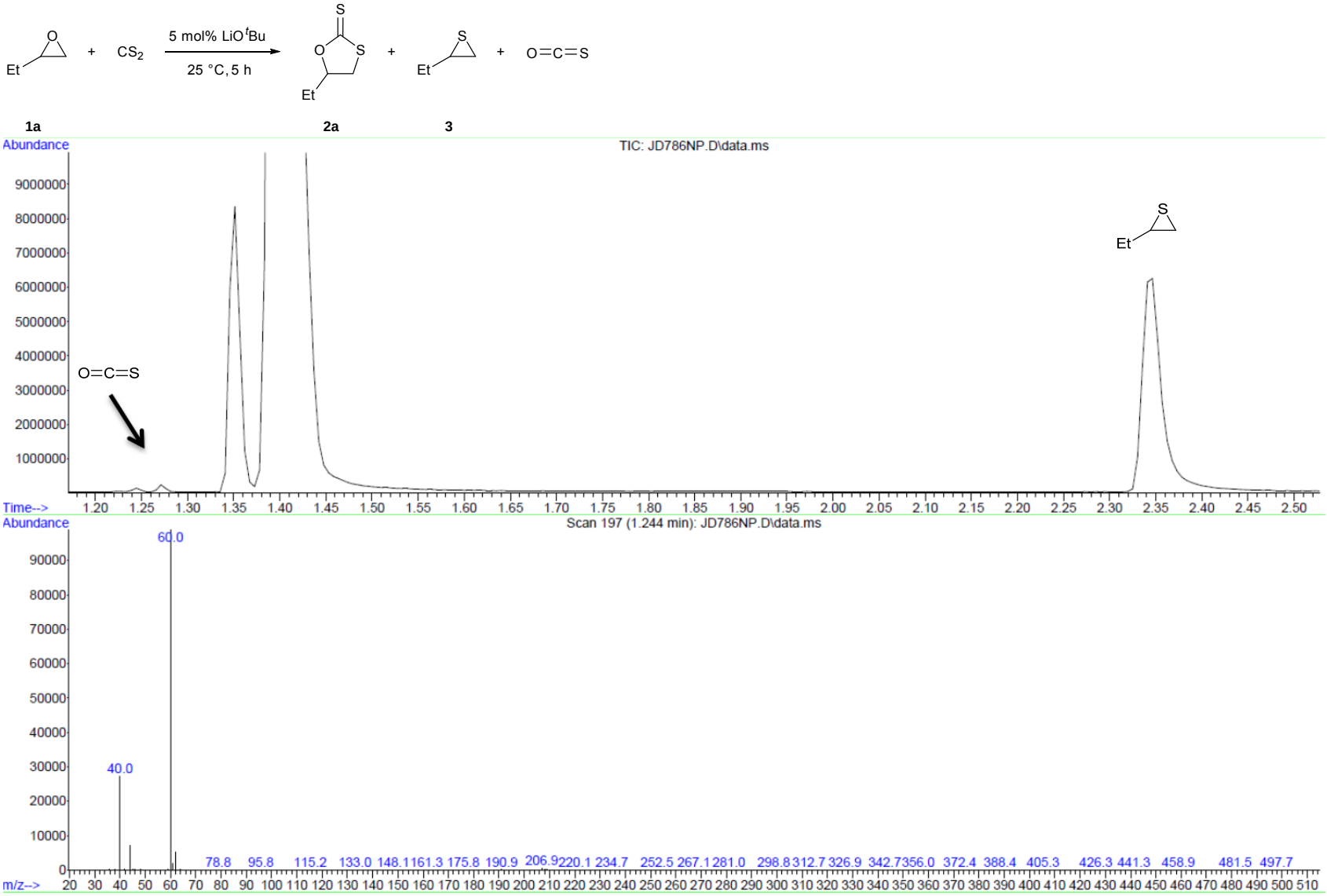


Figure S7. GC-MS of the crude reaction mixture of the conversion of **1a** under optimized reaction conditions.

8. *ee*-Determination of *ent*-2b and *ent*-2d

The enantiomeric excess (*ee*) was determined on an *Agilent* 6890 GC with a *Lipodex E* capillary GC column (25 m × 0.25 mm × 0.25 µm) from *Macherey-Nagel* as stationary phase and H_2 as carrier gas. Starting temperature was 90°C which was kept for 25 min and then raised with a rate of 6°C·min^{-1} to 180°C keeping this temperature for another 10 min. The mobile phase flow was 1 mL·min^{-1}, constantly.

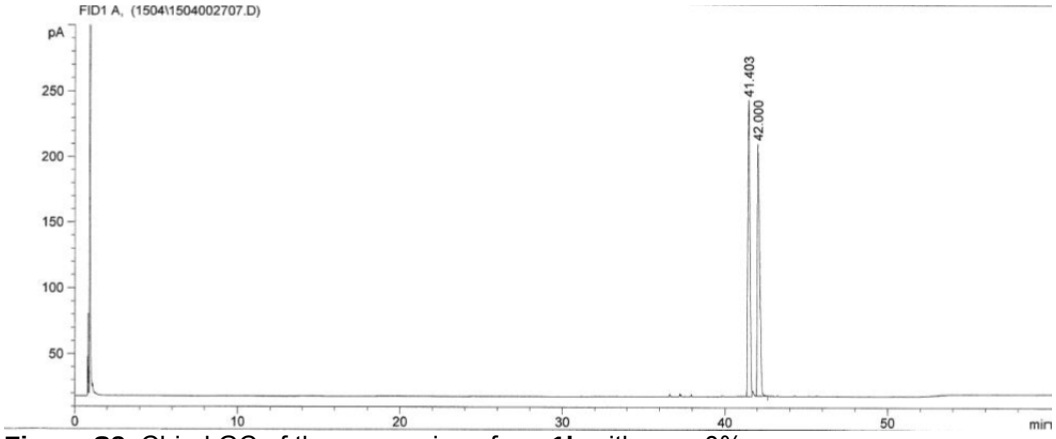


Figure S8. Chiral GC of the conversion of rac-**1b** with *ee* = 0%.

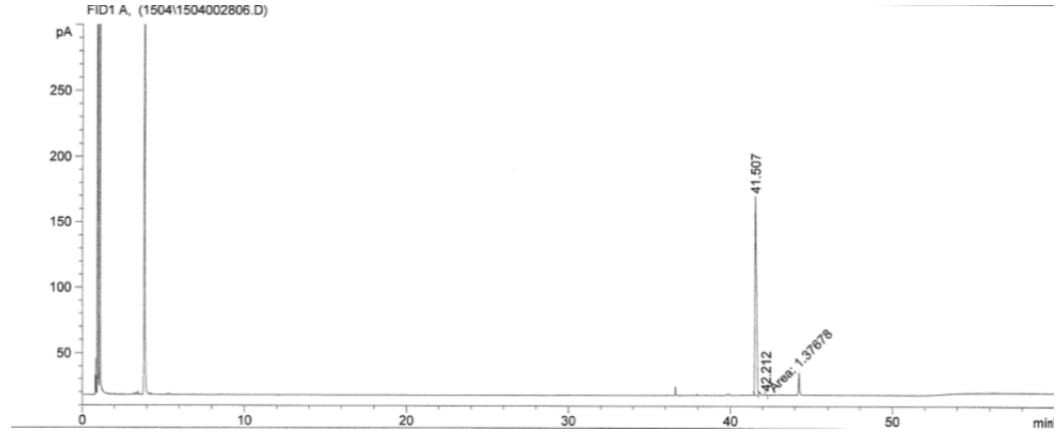
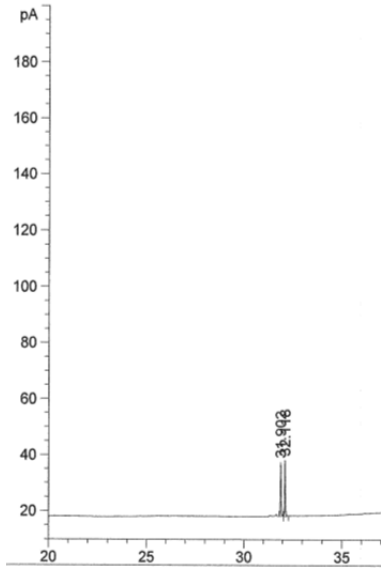


Figure S9. Chiral GC of the conversion of (*R*)-**1b** with *ee* = 99.9%.

a)



b)

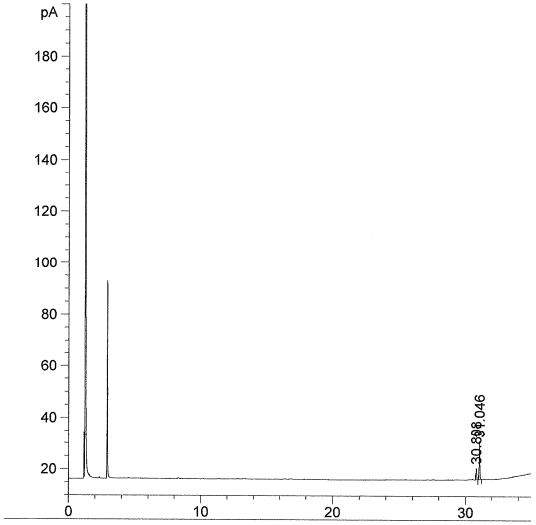


Figure S10. a) Chiral GC of the crude reaction mixture of the conversion of rac-**1d** with *ee* = 0% and τ(**2d**) = 31.9 min. b) Chiral GC of the crude reaction mixture of the conversion of (*R*)-**1d** with *ee* = 60% and τ(**2d**) = 30.8 min.

9. References

1. J. Joseph, R. K. Gosavi, A. Otter, G. Kotovych, E. M. Lown and O. P. Strausz, *J. Am. Chem. Soc.*, 1990, **112**, 8670-8678.
2. M. North and P. Villuendas, *Synlett*, 2010, 623-627.