Supporting Information

Mediation of metal chelation in cysteine-derived tetramate systems

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Table S1. Yield and H-2, H-5 chemical shifts ($CDCl_3$, 400 MHz) for thiazolidines **8-14**.

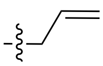
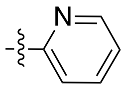
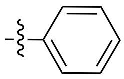
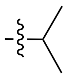
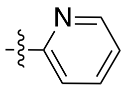
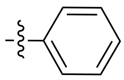
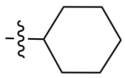
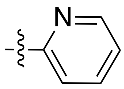
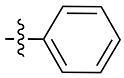
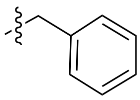
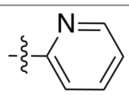
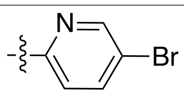
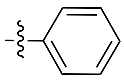
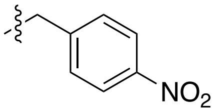
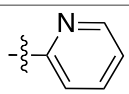
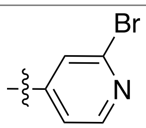
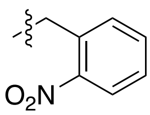
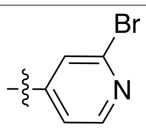
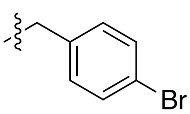
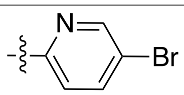
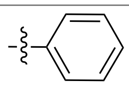
	R¹ =	**R² =**	**δ_H (ppm) for**				***cis /trans***	**Yield (%)**
			H-2		**H-5**			
			cis	***trans***	***cis***	***trans***		
8i			5.65 (d)	5.86 (d)	4.01 – 4.10 (m)	4.53 – 4.60 (m)	1 : 1	95
8iii			5.57	5.83	3.96 – 4.06 (m)	4.20 – 4.28 (m)	1.8 : 1	68
9i			5.64 (d)	5.86	3.97 (q)	4.46 (dd)	1 : 1	85
9iii			5.52	5.80	3.89 (dd)	4.05 – 4.12 (m)	1.9 : 1	83
10i			5.64	5.81	3.99	4.41 (dd)	1.1 : 1	69
10iii			5.52	5.80	3.91 (dd)	4.06 – 4.16 (m)	1.9 : 1	70
11i			5.61	5.83	4.03 (dd)	4.52 (dd)	1 : 1	45
11ii			5.61	5.82	4.06 (dd)	4.50 (dd)	1 : 1	85
11iii			5.57	5.83	3.99 – 4.08 (m)	4.22 – 4.29 (m)	1.8 : 1	50
12i			5.66	5.83	4.11 (dd)	4.66 (dd)	1 : 1	74
12iv			5.45	5.71	4.05 – 4.13 (m)		0.5 : 1	77
13iv			5.45	5.72	4.04 – 4.10 (m)		0.5 : 1	72
14ii			5.60	5.80	4.02 – 4.06 (m)	4.51 (dd)	4.5 : 1	55
14iii			5.55	5.80	3.96 – 4.05 (m)	4.25 (dd)	1.7 : 1	91

Table S2. Yield and H-2 chemical shift data ($CDCl_3$, 400 MHz) for *N*-acylthiazolidines **15-21**.

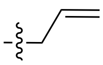
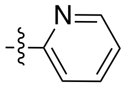
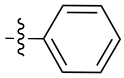
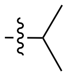
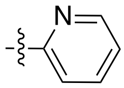
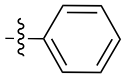
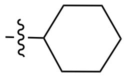
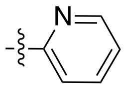
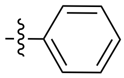
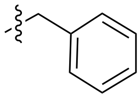
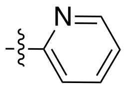
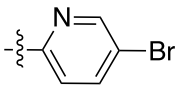
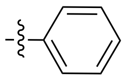
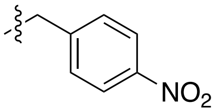
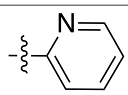
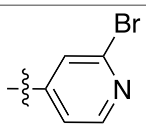
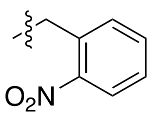
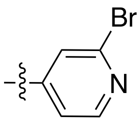
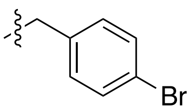
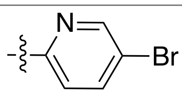
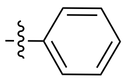
	R^1 =	R^2 =	δ_H (ppm) for H-2 (s)				*cis* /*trans*	Yield (%)
			cis		*trans*			
			Major	Minor	Major	Minor		
15i			6.16	6.43	6.13	6.20	3.1 : 1	58
15iii			6.15	6.37	6.19	6.33	1.2 : 1	74
16i			6.14	6.40	6.11	6.17	1.4 : 1	71
16iii			6.15	6.37	6.17	6.32	1 : 1	97
17i			6.14	6.39	6.10	6.17	1.2 : 1	64
17iii			6.15	6.37	6.17	6.32	1.3 : 1	99
18i			6.22	6.48	6.19	6.27	1.7 : 1	49
18ii			6.15	6.39	6.13	6.18	1 : 1	68
18iii			6.14	6.36	6.18	6.34	1.9 : 1	99
19i			6.20	6.47	6.17	6.24	8.8 : 1	99
19iv			6.14	6.20	6.13	6.15	1.5 : 1	71
20iv			6.15	6.20	6.14	-	1.1 : 1	88
21ii			6.15	6.38	6.13	-	6.5 : 1	80
21iii			6.14	6.36	6.18	6.32	2.2 : 1	61

Table S3. Yield and H-2, H-5 chemical shifts ($CDCl_3$, 400 MHz) for *C*-acylated thiazolidines **23-30**.

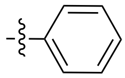
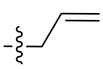
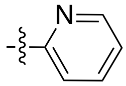
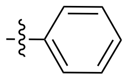
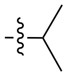
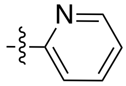
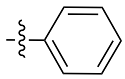
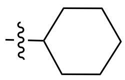
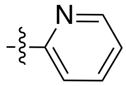
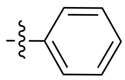
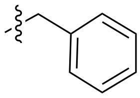
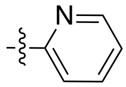
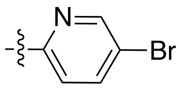
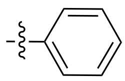
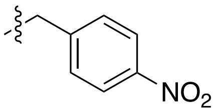
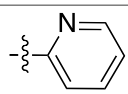
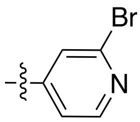
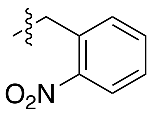
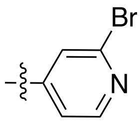
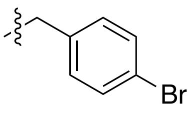
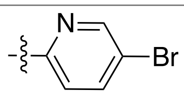
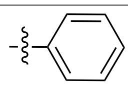
	R^1 =	R^2 =	δ_H (ppm) H2 (major) *cis*	δ_H (ppm) H2 (major) *trans*	δ_H (ppm) H2'' *C2''R*	δ_H (ppm) H2'' *C2''S*	*Cis/ trans*	*R/S*	Yield (%)
23iii	CH_3		5.77 5.95		 4.35	4.44 	*cis*	1 : 1	77
24i			5.95 6.00	-	4.62 	 4.48	*cis*	0.8 : 1	47
24iii			5.82 6.00		 4.39	4.49 	*cis*	1 : 1	54
25i			5.96 6.02	-	4.62 	 4.49	*cis*	0.7 : 1	54
25iii			5.81 6.00		 4.41	4.49 	*cis*	0.8 : 1	61
26i			5.94 6.00	(6.27 6.30)	4.60 	 4.48	(-)	0.7 : 1	68
26iii			5.82 6.01		 4.40	4.49 	*cis*	0.8 : 1	51
27i			5.98 6.02	-	4.64 	 4.51	*cis*	0.7 : 1	53
27ii			5.95 5.98	6.21 6.24	4.64 	 4.52	2.1 : 1	0.7 : 1	40
27iii			5.81 5.99		 4.38	4.46 	*cis*	0.8 : 1	70
28i			6.02 6.04	-	4.69 	 4.59	*cis*	0.7 : 1	57
28iv			5.89 6.09		4.49 	 4.48	*cis*	1 : 1	65
29iv			5.86 6.11		4.51 	 4.48	*cis*	1 : 1	40
30ii			5.95 5.97	-	4.64 	 4.53	*cis*	0.7 : 1	69
30iii			5.82 5.99		 4.37	4.46 	*cis*	1 : 1	49

Table S4. Yield, H-2, C-6, C-8, C-9 chemical shifts ($CDCl_3$) for tetramate Weinreb amides **31-39**.

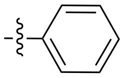
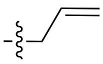
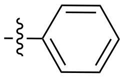
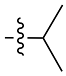
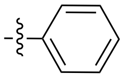
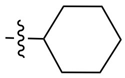
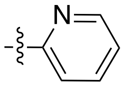
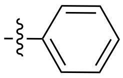
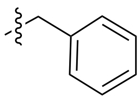
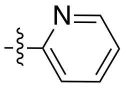
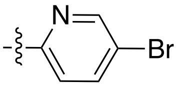
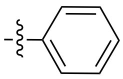
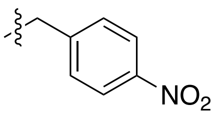
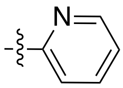
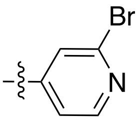
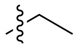
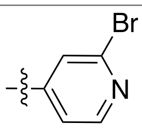
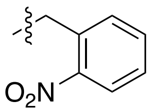
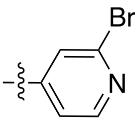
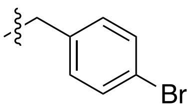
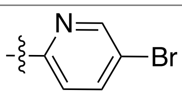
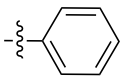
	R^1 =	R^2 =	δ (ppm) H-2	δ (ppm) C-6	δ (ppm) C-8	δ (ppm) C-9	Yield (%)
31iii	-CH_3		6.32	185.5	176.9	166.3	93
32ii			6.32	185.6	177.0	166.3	86
33iii			6.32	185.9	-	166.4	85
34i			6.38	-	-	166.5	32
34iii			6.32	185.8	176.6	166.2	63
35i			6.39	186.4	176.7	166.4	28
35ii			6.29	186.2	-	166.2	40
35iii			6.30	-	-	166.3	70
36i			6.40	186.0	177.0	166.3	20
36iv			6.18	-	-	166.1	41 (1 : 1)
37iv			6.18	-	-	166.0	
38iv			6.19	-	-	166.1	45 (1 : 1 with **37iv**)
39ii			6.31	-	177.2	166.3	35
39iii			6.31	185.3	177.2	166.3	56

Table S5. Post-column widths at half height/Hz for H-2 signals of selected tetramates.

Cpd No.	**Volume occupied by C-5 ester [a]/Å^3**	**$W_{1/2}$/Hz**	**Cpd No.**	**Volume occupied by C-5 ester [a]/Å^3**	**$W_{1/2}$/Hz**
41	73.5	15.8	**52**	73.5	19.4
42	99.9	39.6	**54**	99.9	59.8
43	107.3	34.3	**55**	107.3	27.6
44	147.1	26.4	**56**	147.1	20.6
45	144.1	38.5	**58**	144.1	2.4
46	162.3	33.3	**59**	162.3	3.3
60	73.5	22.6			
65	162.3	17.6			
76	73.5	19.3	**80**	144.1	35.3
77	99.9	6.9	**84**	90.3	42.0
78	107.3	9.5	**87**	147.1	19.6
79	147.1	6.4	**89**	144.1	30.4
81	144.1	10.9	**91**	167.1	40.5
82	162.3	8.5	**92**	167.1	27.2
83	73.5	13.4	**93**	162.3	36.7
85	99.9	42.3			
86	107.3	6.5			
88	147.1	5.1			
90	144.13	6.34			

[a] Van der Waals volume occupied by C-5 ester calculated by geometrical analysis in Marvin (20.3.0), 2020, ChemAxon.

Table S6. Physiochemical properties and activity of tetramates.[a]

Cpd No.	MW /Da	clogP	$clogD_{7.4}$	PSA /Å^2	MSA /Å^2	% PSA	HBD	HBA	MIC against *Strepto-myces*	MIC against MRSA	
									µg/ml	µg/ml	µM
41	347.39	1.74	-0.84	83.91	449.36	18.7	1	4	-	-	-
42	373.42	2.48	-0.04	83.91	482.08	17.4	1	4	-	-	-
43	375.44	2.49	0.00	83.91	510.79	16.4	1	4	-	-	-
44	415.50	3.32	0.81	83.91	572.38	14.7	1	4	31.3	62.5	150
45	423.48	3.51	0.92	83.91	557.01	15.1	1	4	62.5	-	-
46	502.38	4.31	1.66	83.91	578.02	14.5	1	4	15.6	31.3	62.2
47	395.43	2.70	1.38	83.91	493.11	17.0	1	4	n.t.	-	-
48	421.47	3.44	2.15	83.91	525.97	16.0	1	4	n.t.	-	-
49	423.48	3.46	2.18	83.91	554.49	15.1	1	4	n.t.	-	-
50	463.55	4.29	3.00	83.91	616.32	13.6	1	4	n.t.	31.3	67.4
51	471.53	4.48	3.16	83.91	601.00	14.0	1	4	n.t.	-	-
52	401.48	2.82	0.09	83.91	539.52	15.6	1	4	7.81	15.6	38.9
53	495.39	3.04	-0.10	96.80	586.45	16.5	1	5	-	-	-
54	427.52	3.56	0.88	83.91	572.86	14.6	1	4	3.91	7.81	18.3
55	429.53	3.58	0.91	83.91	602.20	13.9	1	4	7.81	7.81	18.2
56	469.50	4.41	1.72	83.91	662.98	12.7	1	4	3.91	3.91	8.33
57	557.46	4.36	1.21	96.80	660.57	14.7	1	5	15.6	15.6	28.0
58	477.58	4.60	1.84	83.91	647.55	13.0	1	4	3.91	3.91	8.19
59	556.47	5.39	2.60	83.91	668.03	12.6	1	4	0.49	1.95	3.50
60	423.48	3.35	0.76	83.91	554.67	15.1	1	4	n.t.	15.6	36.8
61	449.52	4.09	1.54	83.91	587.27	14.2	1	4	n.t.	0.98	2.18
62	451.54	4.11	1.58	83.91	616.53	13.6	1	4	n.t.	3.91	8.66
63	491.60	4.94	2.39	83.91	677.79	12.4	1	4	n.t.	0.98	1.99
64	499.59	5.13	2.51	83.91	662.21	12.7	1	4	n.t.	3.91	7.83
65	578.48	5.92	3.27	83.91	682.87	12.3	1	4	7.81	15.6	27.2
66	421.47	3.48	1.20	83.91	526.62	15.9	1	4	n.t.	15.6	37.1
67	515.38	3.70	0.96	96.80	572.87	16.9	1	5	-	-	-
68	447.51	4.22	1.98	83.91	559.30	15.0	1	4	7.81	7.81	17.5
69	449.52	4.24	2.02	83.91	588.30	14.3	1	4	7.81	1.95	4.33
70	489.59	5.07	2.83	83.91	650.24	12.9	1	4	1.95	1.95	3.98
71	577.45	5.01	2.28	96.80	647.81	14.9	1	5	15.6	15.6	27.1
72	497.57	5.26	2.95	83.91	634.90	13.2	1	4	7.81	3.91	7.86
73	576.46	6.05	3.70	83.91	655.43	12.8	1	4	n.t.	0.98	1.70
74	422.46	2.13	0.80	96.80	519.29	18.6	1	5	-	-	-
75	344.40	1.88	0.31	70.50	387.63	18.2	1	4	-	-	-
76	416.49	1.21	-2.33	95.94	560.12	17.1	2	4	62.5	62.5	150
77	442.53	1.95	-1.58	95.94	593.37	16.2	2	4	15.6	15.6	35.3
78	444.55	1.96	-1.56	95.94	621.65	15.4	2	4	15.6	15.6	35.1
79	484.61	2.79	-0.72	95.94	684.24	14.0	2	4	1.95	3.91	8.05
80	572.47	2.74	-0.88	108.83	679.81	16.0	2	5	-	-	-
81	492.59	2.99	-0.54	95.94	668.10	14.4	2	4	15.6	15.6	31.7

Table S6 Continued. Physiochemical properties and activity of tetramates.[a]

Cpd No.	MW /Da	clogP	clogD$_{7.4}$	PSA /Å^2	MSA /Å^2	% PSA	HBD	HBA	MIC against		
									Strepto-myces	MRSA	
									μg/ml	μg/ml	μM
82	571.49	3.78	0.18	95.94	687.88	13.9	2	4	125	62.5	109
83	468.57	1.34	-2.20	95.94	620.19	15.5	2	4	7.81	15.6	33.3
84	562.48	1.56	-2.06	108.83	666.16	16.3	2	5	7.81	31.3	55.6
85	494.61	2.08	-1.44	95.94	655.45	14.6	2	4	15.6	15.6	31.6
86	496.62	2.10	-1.42	95.94	680.97	14.1	2	4	1.95	7.81	15.7
87	537.68	1.89	-1.66	108.83	736.12	14.8	2	5	7.81	7.81	14.5
88	536.69	2.93	-0.59	95.94	745.30	12.9	2	4	15.6	62.5	116
89	624.55	2.87	-0.74	108.83	741.90	14.7	2	5	-	-	-
90	544.67	3.12	-0.41	95.94	731.18	13.1	2	4	31.3	62.5	115
91	590.65	2.04	-1.58	151.97	764.00	19.9	2	7	15.6	31.3	52.9
92	669.55	2.95	-0.69	151.97	781.59	19.4	2	7	31.3	62.5	93.3
93	703.45	3.67	0.03	108.83	762.27	14.3	2	5	-	-	-
94	623.56	3.91	0.32	95.94	751.84	12.8	2	4	-	-	-

[a] MW was calculated by ChemDraw 19.1.1.32; clogP, clogD$_{7.4}$, PSA, MSA, hydrogen bond donors (HBD) and acceptors (HBA) were calculated with Marvin (20.3.0), 2020, ChemAxon; % PSA was calculated by % PSA/MSA. (-) means tested but not active; n.t. means not tested. MIC values against MRSA that are < 8 μg/ml are highlighted in red.

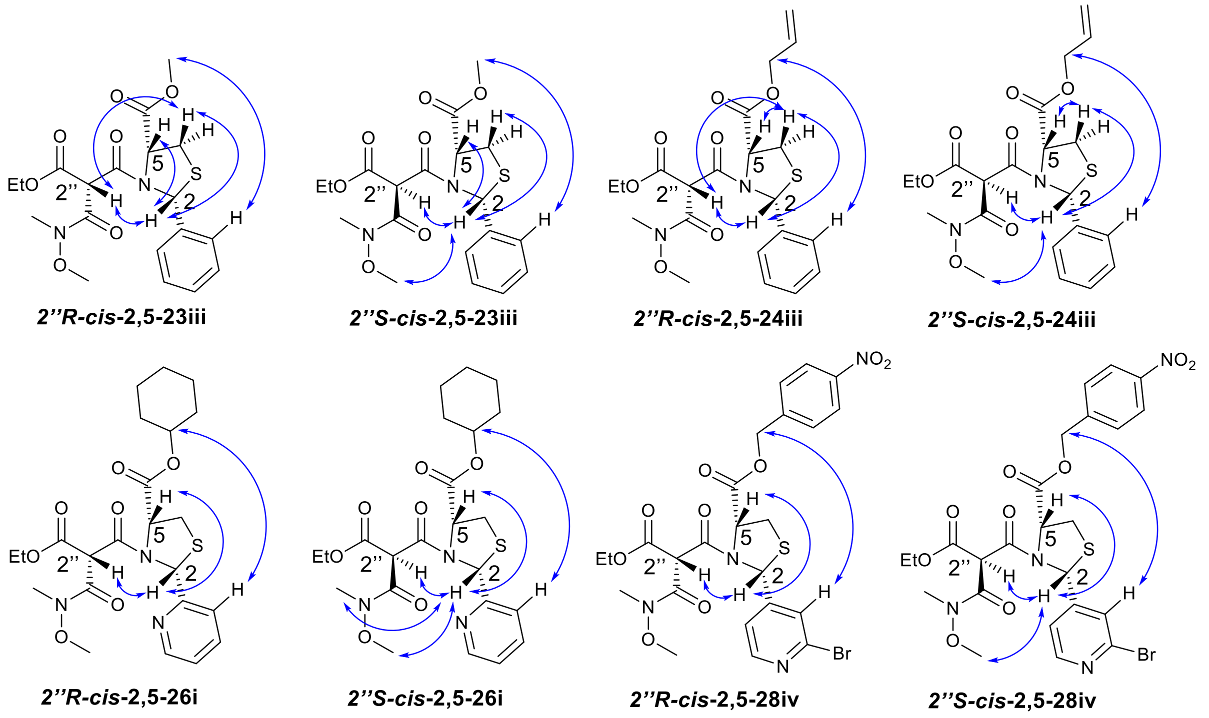


Figure S1. NOE analysis to confirm relative *cis*-2,5 stereochemistry and assign *R/S* at C2''.

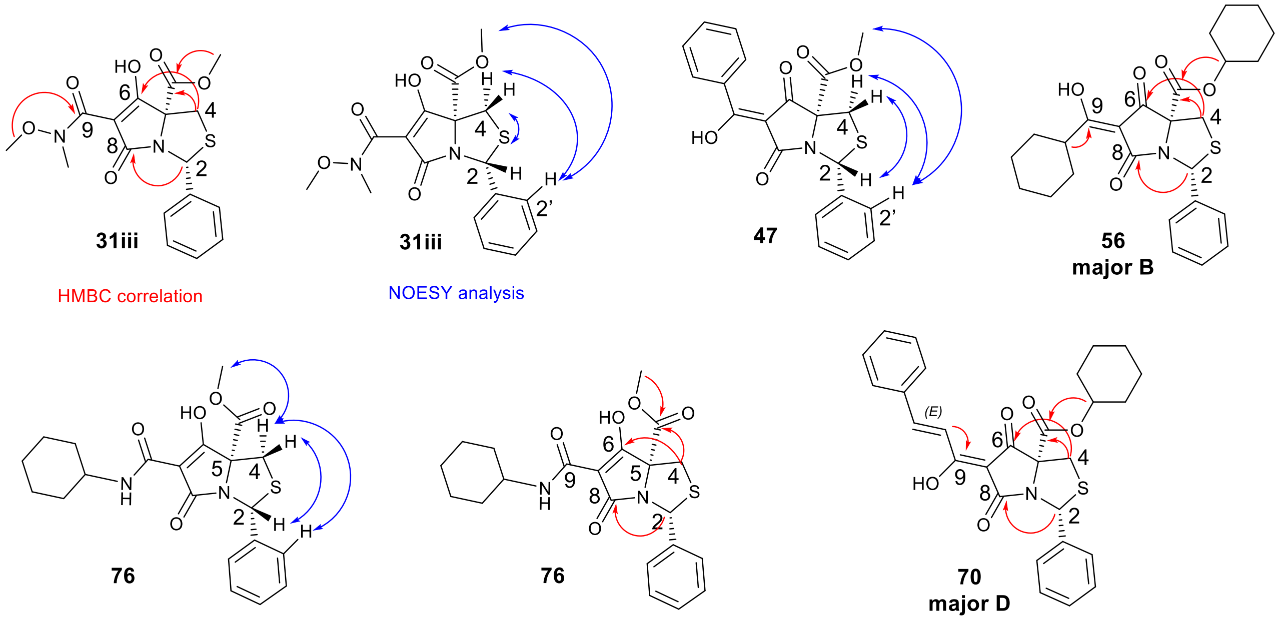
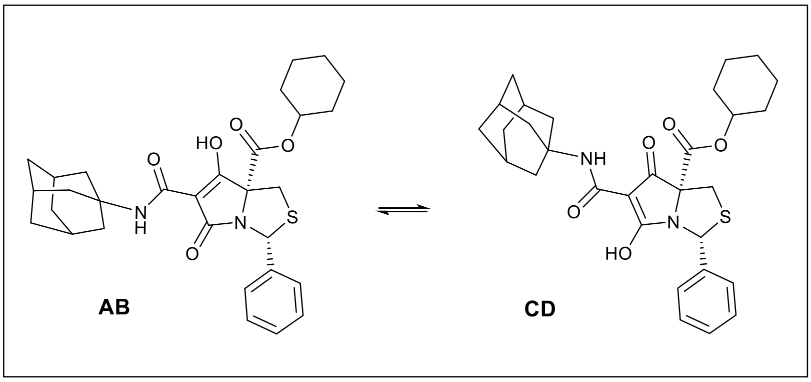


Figure S2. NOESY and HMBC correlation analysis



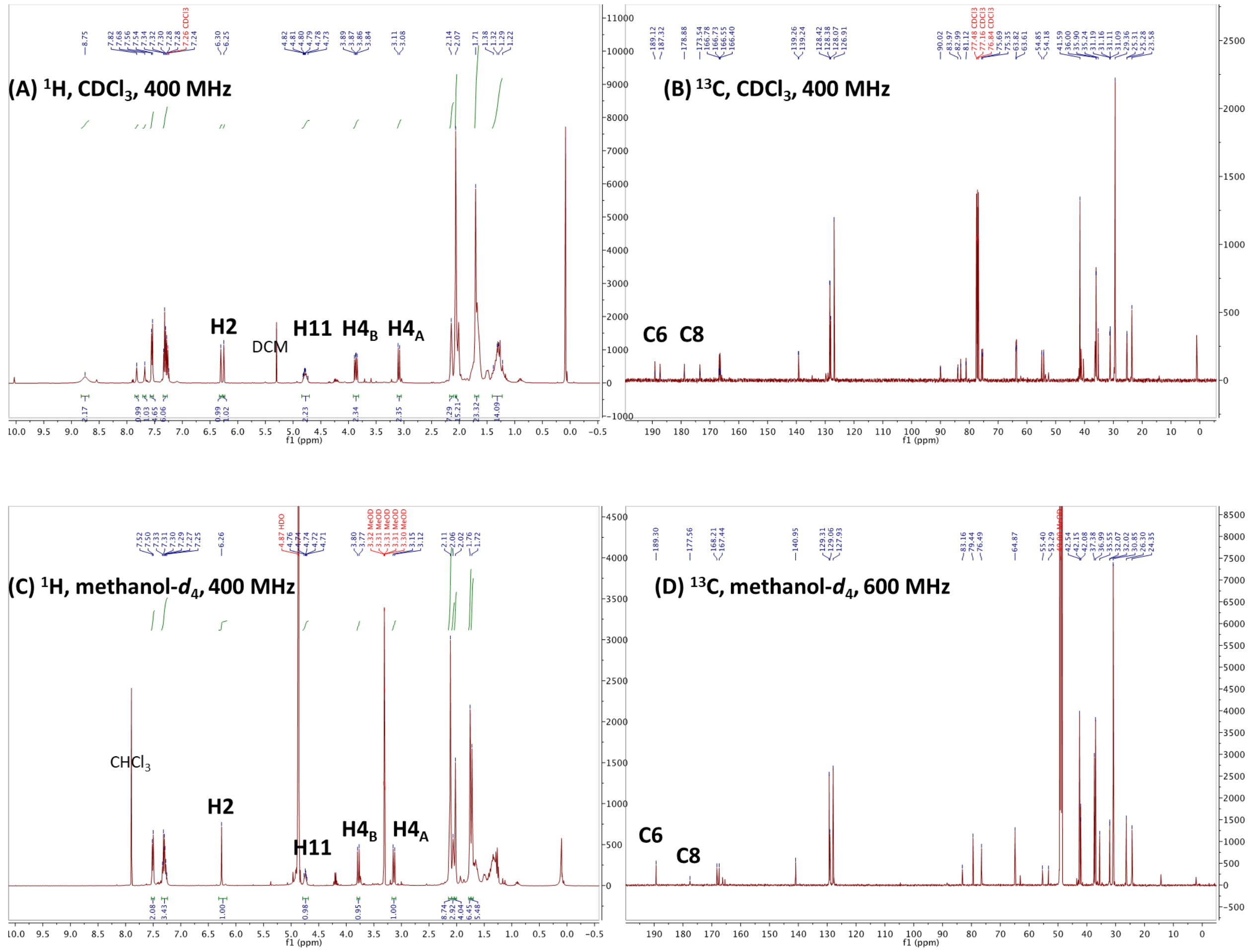


Figure S3. Comparison of NMR spectra of **88** in $CDCl_3$ and methanol-d_4 showing equilibrium between two tautomeric pairs AB and CD.

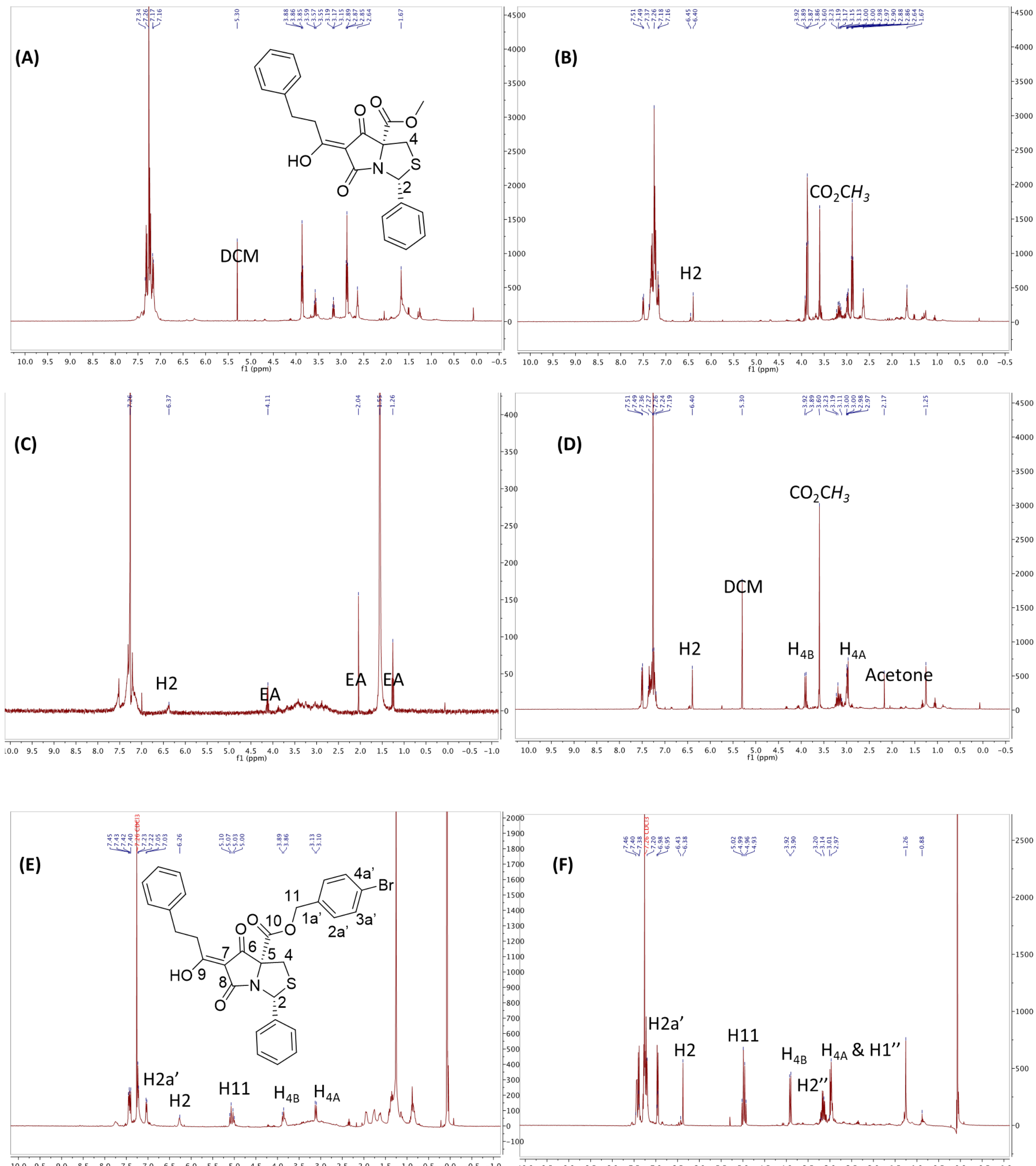


Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra indicating metal-chelation abilities of tetramate ketones **60** and **65**. (A) **60** reaction crude mixture quenched with sat. aq. NH_4Cl and extracted with EA; (B) **60** reaction crude mixture washed with 0.5 M HCl and extracted with EA; (C) **60** purified with column, before acid wash; (D) **60** purified with column, after 0.5 M HCl acid wash; (E) **65** purified with column, before acid wash; (F) **65** purified with column, after 0.5 M HCl acid wash.

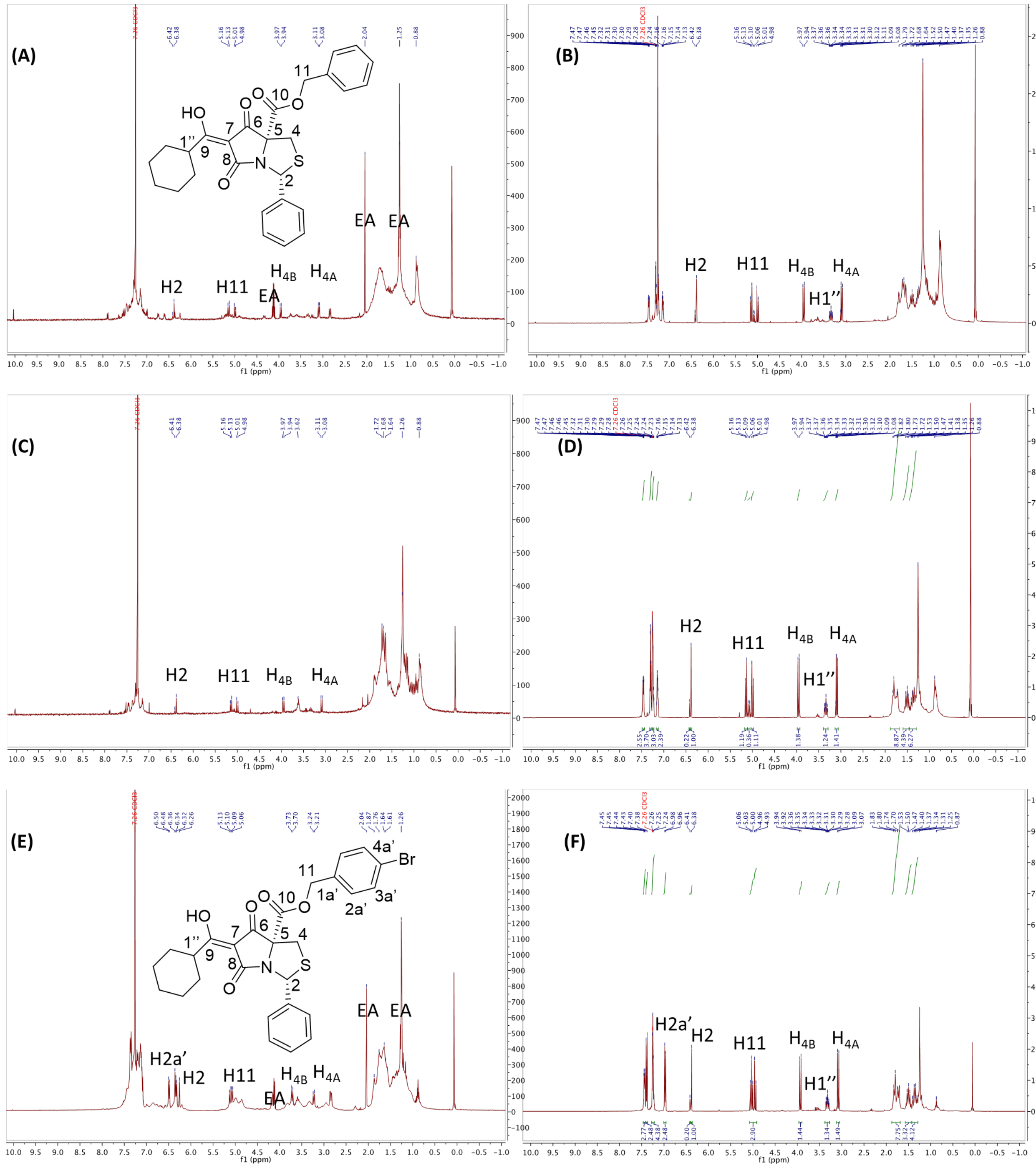


Figure S5. [1]H NMR ($CDCl_3$, 400 MHz) spectra indicating reduced metal chelating abilities of tetramate ketones **58** and **59**. (A) **58** reaction crude mixture quenched with sat. aq. NH_4Cl and extracted with EA; (B) **58** crude washed with 0.5 M HCl and extracted with EA; (C) **58** purified with column, before acid wash; (D) **58** purified with column, with 0.5 M HCl acid wash; (E) **59** purified with column, before acid wash; (F) **59** purified with column, with 0.5 M HCl acid wash.

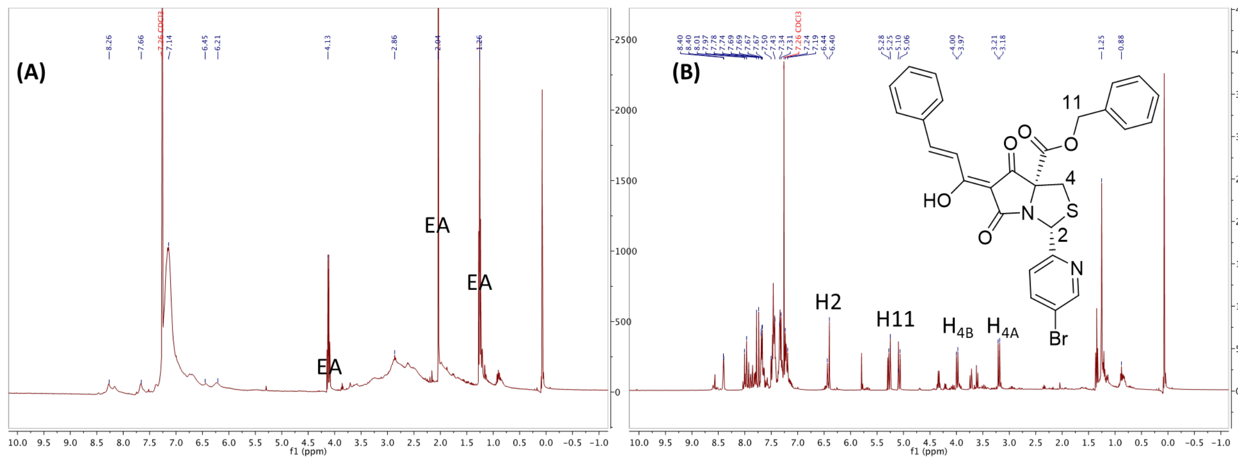


Figure S6. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for metal chelating abilities of tetramate ketone **71** with a C-2 pyridyl ring. (A) **71** purified with column, before acid wash; (B) **71** purified with column, with 5% citric acid wash.

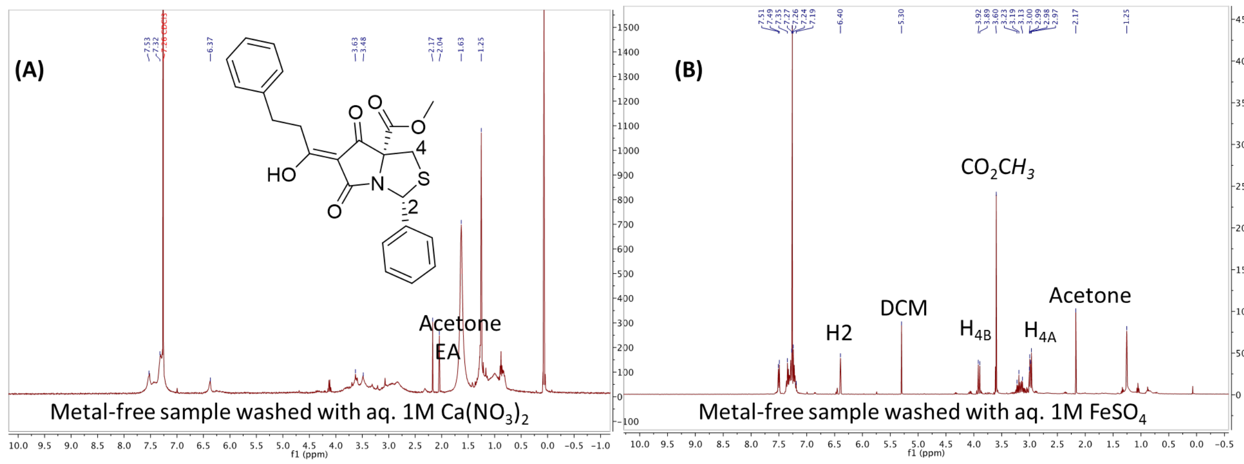


Figure S7. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra indicating a preference of **60** for binding with specific metal ions. (A) Metal-free **60** washed with aq. 1M $Ca(NO_3)_2$ solution; (B) Metal-free **60** washed with aq. 1M $FeSO_4$ solution.

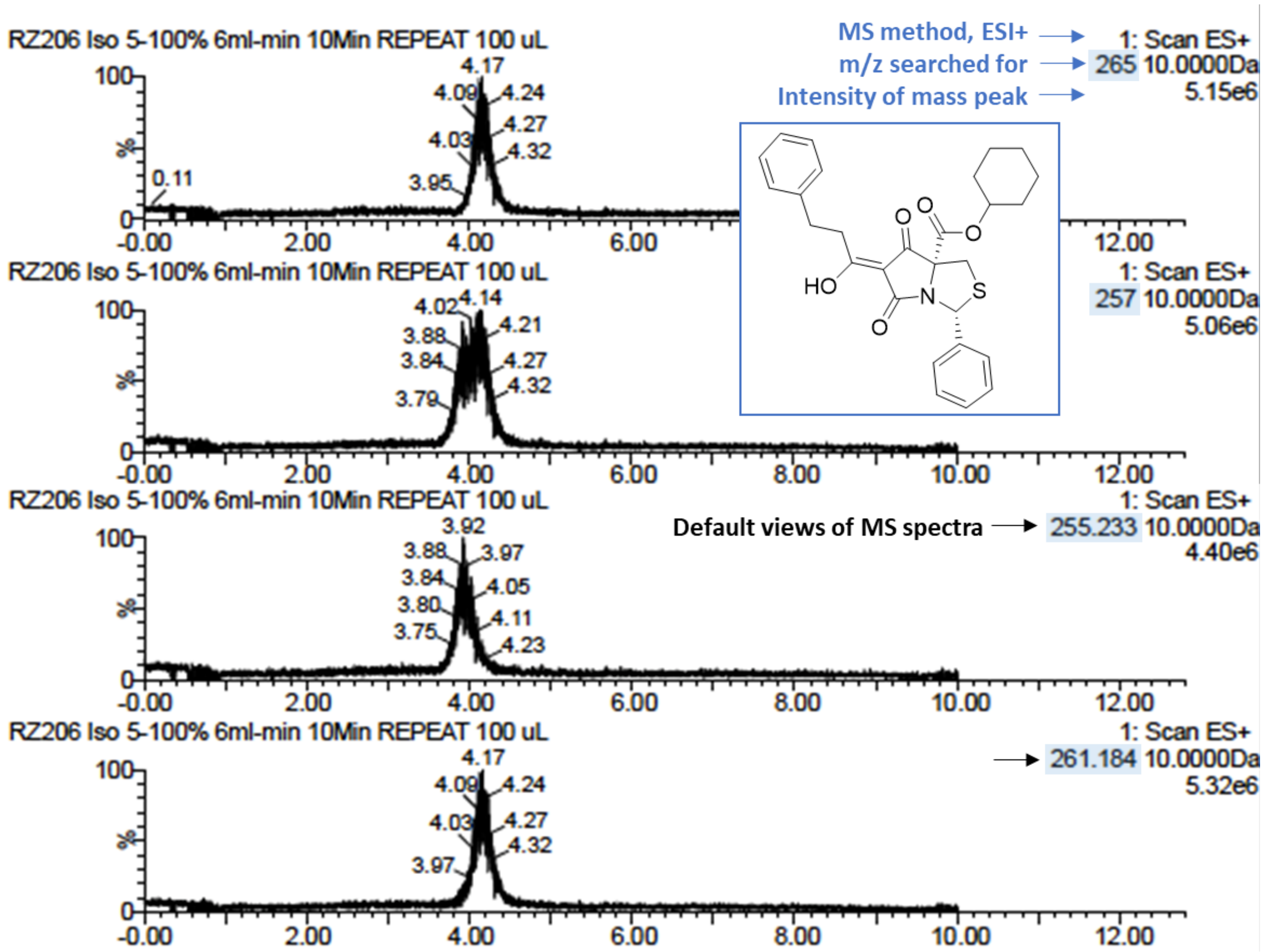


Figure S8. SFC-MS spectra for post-column metal chelated **63**. Exact mass M = 491.18; $[M+Ca]^{2+}$ m/z = 265; $[M+Mg]^{2+}$ m/z = 257. The peak intensity for searched m/z had to be comparable to those present in the default view in order to consider it as detected

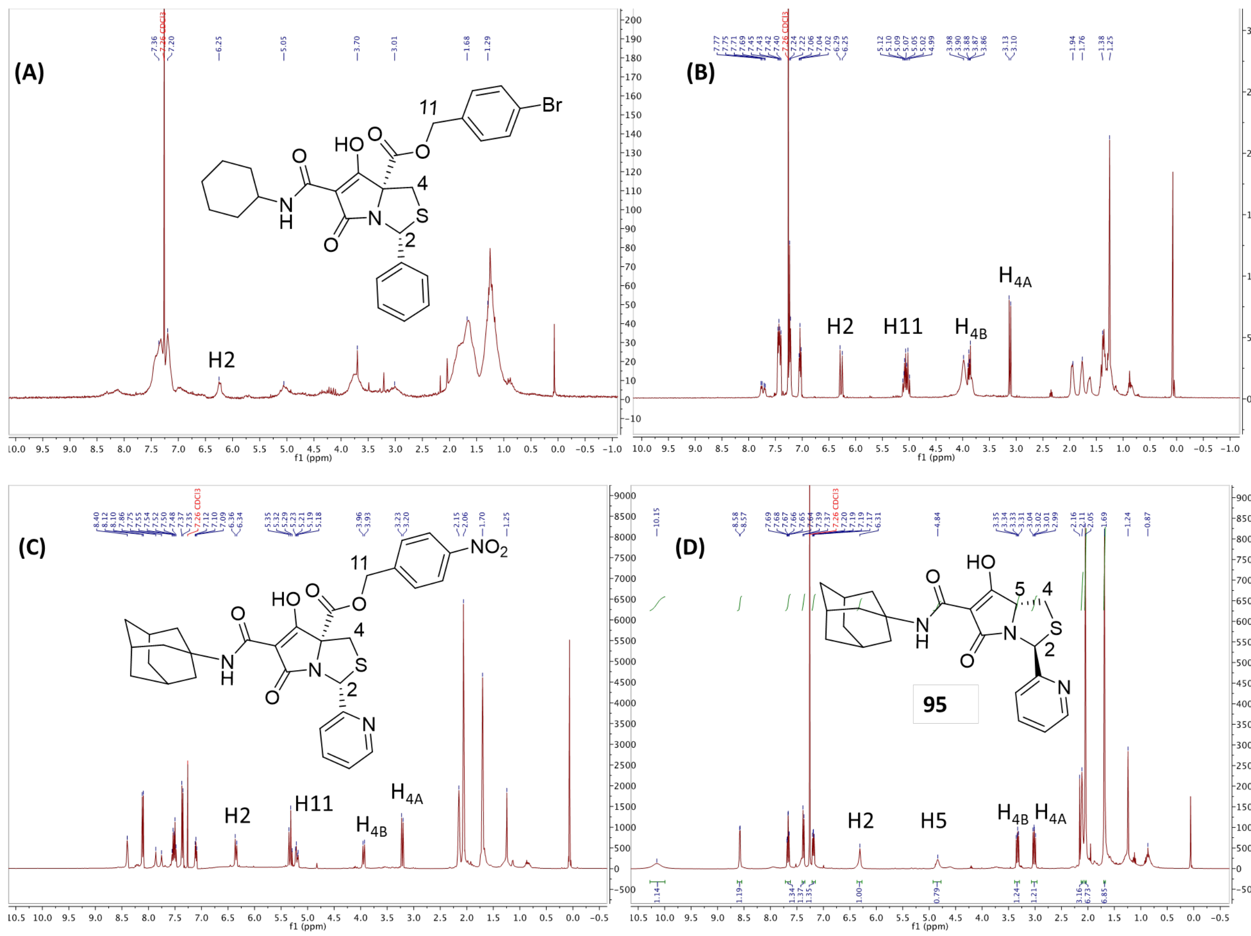


Figure S9. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra indicating metal chelating abilities of tetramate carboxamides **82** and **91**. (A) **82** purified with column, before acid wash; (B) **82** purified with column, with 0.5 M HCl acid wash; (C) **91** purified with column, with 5% citric acid wash; (D) Tetramate carboxamide **95** with no C-5 ester present, purified with column with 5% citric acid wash.

Experimental Procedures

General techniques

All reagents were obtained either from Sigma Aldrich, Alfa Aesar or Fluorochem and used without further purification. All reactions were carried out in oven-dried reaction flasks under inert (N_2) atmosphere unless not using dry solvents. Reaction times were recorded in minutes (min), hours (h) or days (d). Reactions left overnight (o.n.) lasted for 16 - 20 h. 'Petroleum ether' refers to that fraction of light petroleum ether boiling at 40-60 °C and was used as received. Temperatures below room temperature were obtained using cold baths: 0 °C (ice/water), -15 °C (ice/NaCl salt) and -78 °C (dry ice/acetone). Temperatures above room temperature were obtained with heating with oil bath. Solvents were evaporated at 40 °C unless otherwise stated under reduced pressure on a Buchi RE 111 Rotavapour attached to a Vacuubrand CVC2 pump and pressure control system. Concentrations (*c*) in the general procedures referred to the limiting reagent and were given in mmol/mL. Thin layer chromatography (TLC) was performed using Merck aluminium foil backed sheets precoated with 0.2 mm Kieselgel 60 F_{254}. Product spots were visualized by UV fluorescence (max 254 nm, for conjugated systems), staining with a $KMnO_4$ solution and heating (for unsaturated systems) or staining with ninhydrin solution and heating (for primary and secondary amines). Retention factors (R_f) were quoted to the nearest 0.01. Column chromatography was carried out using Sigma Aldrich silica gel 60, 0.040-0.063 (230-400 mesh particle size). The eluents used were determined based on the R_f values. Melting points were recorded using a Stuart Scientific SMP1 melting point instrument in open capillaries and were uncorrected. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at the stated temperature (25 °C) using the D line of sodium (wavelength at 589 nm) and a path length of 1 dm. Specific rotations $[\alpha]_D^{25}$ were calculated and reported in 10^{-1} °C cm^2 g^{-1} with concentration *c* given in g/100 ml. Infrared (IR) spectra were recorded on a Bruker Tensor 27 ATR FT-IR spectrometer with thin film (oil sample prepared in 10 mg/1ml $CHCl_3$) or powder (solid). Absorption maxima (ν_{max}) were reported in wavenumbers (cm^{-1}) and only selected peaks were reported. ^{1}H NMR spectra were recorded on AVF (400 MHz) or AVC (500 MHz) spectrometers. ^{13}C NMR spectra were recorded on Bruker AVF spectrometer at 101 MHz or on AVC spectrometer at 126 MHz with proton decoupling and cryogenic detection probe. Chemical shifts (δ) were reported in parts per million (ppm) and were referenced to the residual solvent peak in ^{1}H NMR or deuterated solvent peak in ^{13}C NMR. The abbreviations used to describe multiplicity were as follows: s (singlet), br. s (broad singlet), d (doublet), dd (double doublet), t (triplet), td (triple doublet), dt (doublet triplet), q (quartet), sept (septet), m (multiplet). Coupling constants (*J*) were given in Hertz (Hz). 2D-NOESY and 1D-NOE experiments were performed using Bruker AVB400 or AVC (500 MHz) spectrometer. HMBC experiments were recorded on Bruker AVC spectrometer. Low resolution mass spectra (*m/z*) were recorded on a Fisons Platform spectrometer using electrospray ionisation (ESI). High resolution mass spectra (HRMS) were recorded on a Bruker µTOF (ESI or APCI) spectrometer by the internal service at the Department of Chemistry, University of Oxford. The m/z values of major peaks were reported in Daltons and their intensities given as percentages of the base peaks. When halogens (X = Cl or Br) are present, MS peaks for isotopomers were included, with the relative abundance corresponded to the isotopic ratios of ^{35}Cl : ^{37}Cl = 3 : 1 and ^{79}Br : ^{81}Br = 1 : 1. Screening of compounds were performed by Oxford Antibiotic Group, Austria. For MIC determination by broth dilution assay, the samples were tested in a primary 96 well plates screening assay. The compounds were diluted in Mueller Hinton Broth (MHB) for bacterial screening to a stock solution of 1000 µg/mL, serial diluted and overlaid with a microbe solution in a concentration of 10^4 CFU/ml. The plates were incubated for 24 h at 35 °C, after which MIC values were read from the plates. For cytotoxicity testing, the synthesized compounds were tested against four different cell lines: HeLa, HEK 293, MDCK and CaCo. The cells were seeded in a 96 well plate and incubated until a confluence of 80% was achieved (under physiological conditions - 37°C, 5% CO_2 and 95% humidity). The samples were tested by serial dilution in triplicates with starting concentration of 250 µg/mL.

After 24 and 48 hours the survival of cells was evaluated by microscope and measured with Alamar Blue. IC_{50} values were obtained from the calibration curves.

General Procedure A for synthesis of L-cystine diesters 6a-g

To a stirred suspension of L-cystine (1.0 eq., 1 g, 4.2 mmol) and *p*-toluenesulphonic acid monohydrate (2.5 eq.) in cyclohexane (*c* = 0.2) was added the respective alcohol (5 eq.). The mixture was heated under reflux (80 °C) with continuous removal of water using Dean-Stark apparatus for 5 - 16 h. The reaction mixture was then cooled to room temperature and the precipitate was collected by vacuum filtration, washed with DCM and dried to give the corresponding esters of L-cystine as *p*-toluenesulphonate salts **6a-g**.

General Procedure B for synthesis of L-cysteine esters 7a-g

A round bottom flask charged with respective L-cystine diester *p*-tolunesulphonate salt (1 eq., 7.5 mmol) in DCM (*c* = 0.15) was refilled with N_2 for several times. Et_3N (2.5 eq.) was added followed by dithiothreitol (DTT, 2.5 eq.) and the mixture was stirred for 24 h. The reaction mixture was concentrated *in vacuo*; the resulting residue was dissolved in EtOAc and sat. ap. $NaHCO_3$. The combined organic layer was acidified and extracted with 0.5 M aq. HCl. The combined aqueous layer was basified with powered $NaHCO_3$ and re-extracted with EtOAc. The resulting organic layer was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The crude was further purified with flash chromatography (EtOAc/MeOH) to produce esters of L-cysteine **7a-g**.

General Procedure C for synthesis of thiazolidines 8-14

Et_3N (1.2 eq.) and the respective aldehyde (1.0 eq., 10 mmol) were added to L-cysteine methyl ester hydrochloride (1.2 eq.) in petroleum ether (*c* = 0.3). The mixture was heated under reflux at 110 °C with continuous removal of water using Dean-Stark apparatus for 18 h. The reaction mixture was then filtered and washed with diethyl ether and the combined filtrates were concentrated *in vacuo* and residue was purified by flash column chromatography to give thiazolidines.

General Procedure D for synthesis of *N*-acylthiazolidines 15-21

Mono-ethyl malonate (1.2 eq.) was added dropwise to a stirred solution of thiazolidine (1.0 eq., 9 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC, 1.2 eq.) and 4-dimethylaminopyridine (DMAP, 0.1 eq.) in DCM (c = 0.2) at 0 °C. The mixture was stirred at 0 °C for 15 min and then at room temperature for 18 h. The reaction mixture was filtered and washed with DCM and the combined filtrates were concentrated *in vacuo* and residue was purified by flash column chromatography to give *N*-acylated thiazolidines.

General Procedure E for *C*-acylation of *N*-acylthiazolidines 23-30

Dry pyridine (1.5 eq.) was added dropwise to a cooled suspension of *N*-acylthiazolidine (1.0 eq.) and magnesium bromide $MgBr_2$ (1.5 eq.) in anhydrous DCM (c = 0.15) at 0 °C. The suspension was stirred at this temperature for 30 min and a solution of methoxy(methyl)carbamic chloride **22** (1.5 eq.) in anhydrous DCM (5 ml) was added dropwise. The reaction mixture was stirred at room temperature for 24 h and then acidified with 2M aq. HCl (or 5% citric acid if pyridyl rings were present) at 0 °C. The aqueous phase extracted with EtOAc, dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography to give the tricarbonyl thiazolidines **23-30**.

General Procedure F for synthesis of tetramate esters 31-39

1,8-Diazabicycloundec-7-ene (DBU, 1.1 eq.) was added to a solution of tricarbonyl thiazolidine (1.0 eq.) in anhydrous THF and stirred at room temperature for 24 h. The reaction mixture was then cooled to 0 °C and diluted with distilled water. The mixture was partitioned between diethyl ether

(Et_2O) and water. The aqueous layer was then acidified at 0 °C with 2M aq. HCl or 5% citric acid if pyridyl rings were present, extracted with EtOAc, dried with $MgSO_4$, filtered and concentrated *in vacuo* (water bath at 25 °C) to give the Weinreb amides **31-39**. Unless otherwise stated, the crude from extraction was used for subsequent reactions without further column purification.

General procedure G for synthesis of tetramate ketone analogues 41-75

To a vigorously stirring mixture of magnesium turnings (1.1 eq.) in dry THF (*c* = 0.2), the respective bromide (1 eq.) and 2 drops of 1,2-bromoethane were added dropwise with gentle reflux. The mixture was heated at 45 °C for 1 h, until all Mg turnings were dissolved and cooled to room temperature. Pyridyl MgBr was prepared with ethyl bromide (0.2 eq.) with an excess of Mg turnings (2 eq.). *iPr*Mg-thiazole was prepared by an exchange reaction between iPr_2Mg (1.1 eq.) and 2-bromo-thiazole (1 eq.) in dry THF at room temperature for 2.5 h. The diisopropylmagnesium salt iPr_2Mg was prepared fresh according to a protocol published in literature by adding dry 1,4-dioxane (1.3 eq.) to a solution of *iPr*MgBr (1 eq.) in dry THF. The supernatant after stirring for 24 h was used directly for the exchange reaction.

The prepared Grignard reagent (2.4 eq.) was added to the Weinreb amide (1 eq.) in anhydrous THF (*c* = 0.05) dropwise at -15 °C. The reaction mixture was stirred at -15 °C for 1 h or 18 h for styrenyl MgBr and pyridyl MgBr and then quenched with sat. aq. NH_4Cl solution at -15 °C. The mixture was acidified with 2M aq. HCl or 5% citric acid if pyridyl rings were present and extracted with EtOAc. The combined organic layer was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was then purified with flash column chromatography (petroleum ether/EtOAc). The product obtained after column chromatography was dissolved in DCM and washed with 0.5 M aq. HCl or 5% citric acid if pyridyl rings were present to give tetramate ketones **41-75**.

General Procedure H for synthesis of tetramate carboxamides 76-94.

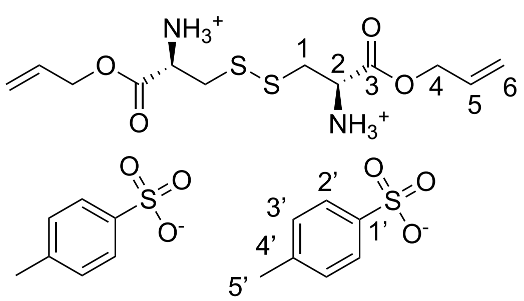
Amine (1.2 eq.) was added to a stirred solution of tetramate ester (1.0 eq., 200 mg) in THF/toluene (1 : 4, *c* = 0.05) and the mixture was heated at reflux for 18 h. It was then cooled to room temperature, concentrated *in vacuo* and residue was purified by flash column chromatography with 1% Et_3N in the eluent to give the desired product. The product was dissolved in DCM and washed with 5% citric acid. The combined organic fractions were dried with $MgSO_4$, filtered and concentrated *in vacuo* to yield the desired tetramate carboxamides.

Methoxy(methyl)carbamic chloride 22

Methoxy(methyl)carbamic chloride **22** was synthesised according to literature published procedures.[1] Dry pyridine (8.2 ml, 6 eq.) was added dropwise to a suspension of triphosgene (5 g, 1 eq.) and *N,O*-dimethylhydroxylamine hydrochloride (5 g, 3 eq.) in dry DCM (50 ml) at -78 °C. The mixture was allowed to cool to room temperature and stirred over night for 16 h. The reaction mixture was diluted with distilled water and extracted with diethyl ether. The organic layer was washed sequentially with sat. aq. $NaHCO_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo* (water bath temperature at 25 °C to avoid evaporation of the product) to give carbamic chloride **22** as a yellow oil (4.9 g, 89%). The crude oil was used directly for procedure **E** without further purifications. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.76 (s, 3H, NOCH_3), 3.32 (s, 3H, NCH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 127.2 (*C*O), 61.8 (NO*C*H_3), 36.3 (N*C*H_3).

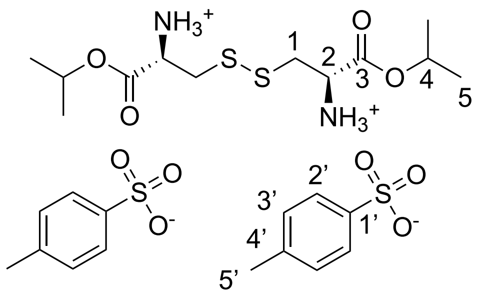
L-Cystine esters **6a-g** were synthesised from L-cystine following General Procedure **A**.

L-Cystine allyl ester *p*-toluenesulphonate, 6a



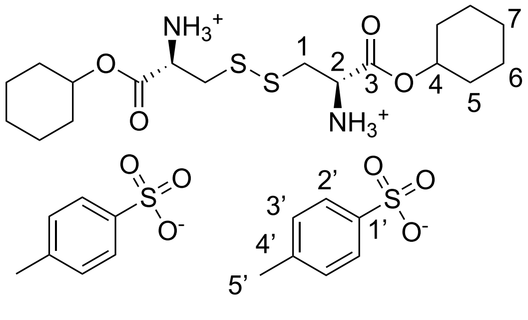
Quantitative yield (2.8 g); pale brown solid, m.p. 136 °C; $[\alpha]_D^{25}$ = -35.9 (*c* = 1.00, MeOH); ν_{max}/cm^{-1} (neat) 2981 (br. s, N-H), 1749 (s, C=O); ^{1}H NMR (methanol-d_4, 400 MHz): δ 7.71 (d, *J* = 8.2 Hz, 4H, H2'), 7.24 (d, *J* = 7.9 Hz, 4H, H3'), 5.91 – 6.06 (m, 2H, H5), 5.41 (dd, J = 17.2, 1.4 Hz, 2H, H6$_B$), 5.30 (dd, J = 10.4, 1.2 Hz, 2H, H6$_A$), 4.72 – 4.79 (m, 4H, H4), 4.45 – 4.51 (m, 2H, H2), 3.36 (dd, J = 11.8, 6.0 Hz, 2H, H1$_B$), 3.27 – 3.34 (m, 2H, H1$_A$, obscured by solvent peak), 2.37 (s, 6H, H5'); ^{13}C NMR (methanol-d_4, 101 MHz): δ 168.7 (C3), 143.4 (C1'), 141.8 (C4'), 132.4 (C5), 129.9 (C2'), 127.0 (C3'), 120.1 (C6), 68.5 (C4), 53.0 (C2), 37.9 (C1), 21.3 (C5'); *m/z* (ESI$^+$) 321 ([M+H]$^+$, 100%, M as free base); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{21}O_4N_2S_2$ [M+H]$^+$ 321.0937; found 321.0939.

L-Cystine isopropyl ester *p*-toluenesulphonate, 6b



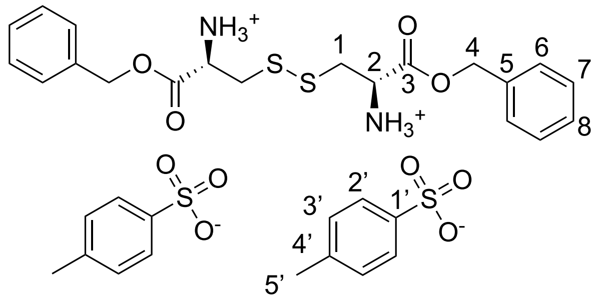
Yield (87% to quantitative, 2.5 g); white solid, m.p. 190 °C; $[\alpha]_D^{25}$ = - 47.8 (c = 0.86, MeOH); ν_{max}/cm^{-1} (neat) 2981 (br. s, N-H), 1742 (s, C=O); ^{1}H NMR (methanol-d_4, 400 MHz): δ 7.72 (d, J = 8.2 Hz, 4H, H2'), 7.25 (d, J = 7.9 Hz, 4H, H3'), 5.13 (sept, J = 6.3 Hz, 2H, H4), 4.39 (dd, J = 6.9 Hz, 2H, 5.2 Hz, H2), 3.39 (dd, J = 14.9, 5.2 Hz, 2H, H1$_B$), 3.27 – 3.34 (m, 2H, H1$_A$, obscured by solvent peak), 2.38 (s, 6H, H5'), 1.33 (s, 6H, H5$_B$), 1.32 (s, 6H, H5$_A$); ^{13}C NMR (methanol-d_4, 101 MHz): δ 168.4 (C3), 143.4 (C1'), 141.8 (C4'), 129.8 (C2'), 127.0 (C3'), 72.8 (C4), 53.2 (C2), 38.2 (C1), 21.9 (C5$_B$), 21.8 (C5$_A$), 21.3 (C5'); *m/z* (ESI$^+$) 325 ([M+H]$^+$, 100%, M as free base); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{25}O_4N_2S_2$ [M+H]$^+$ 325.1250; found 325.1249.

L-Cystine cyclohexyl ester *p*-toluenesulphonate, 6c



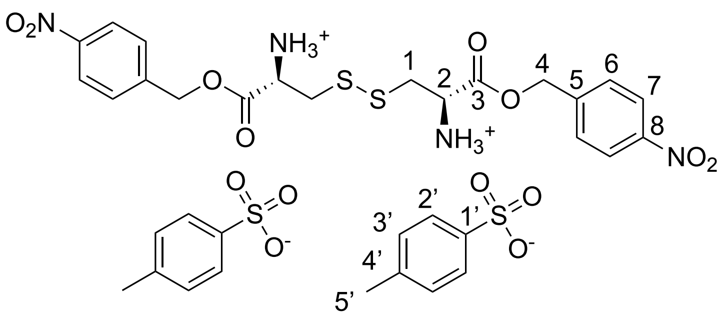
Quantitative yield (3.2 g); white solid, m.p. 196 °C; $[\alpha]_D^{25}$ = -28.9 (c = 1.1, MeOH); ν_{max}/cm^{-1} (neat) 2933 (br. s, N-H), 1745 (s, C=O); ^{1}H NMR (methanol-d_4, 400 MHz): δ 7.71 (d, J = 8.2 Hz, 4H, H2'), 7.24 (d, J = 7.9 Hz, 4H, H3'), 4.87 – 4.95 (m, 2H, H4), 4.41 (app t, J = 6.0 Hz, 2H, H2), 3.35 (dd, J = 9.6, 6.1 Hz, 2H, H1$_B$), 3.29 – 3.32 (m, 2H, H1$_A$, obscured by solvent peak), 2.37 (s, 6H, H5'), 1.90 (br. s, 4H, H5), 1.76 (br. s, 4H, H5), 1.47 – 1.63 (m, 6H, H6, H7), 1.25 – 1.48 (m, 6H, H6, H7); ^{13}C NMR (methanol-d_4, 101 MHz): δ 168.4 (C3), 143.4 (C1'), 141.8 (C4'), 129.8 (C2'), 127.0 (C3'), 77.3 (C4), 53.2 (C2), 38.3 (C1), 32.3 (C5), 32.3 (C5), 26.2 (C7), 24.6 (C6), 24.5 (C6), 21.3 (C5'); *m/z* (ESI$^+$) 405 ([M+H]$^+$, 100%, M as free base); HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{33}O_4N_2S_2$ [M+H]$^+$ 405.1876; found 405.1877.

L-Cystine benzyl ester *p*-toluenesulphonate, 6d



Quantitative yield (3.5 g); off white solid, m.p. 178 °C; $[\alpha]_D^{25}$ = -25.0 (*c* = 1.3, MeOH)(lit. -11.3 (c = 1.0 acetic acid)[2]); ν_{max}/cm^{-1} (neat) 2923 (br. s, N-H), 1748 (s, C=O); ^{1}H NMR (methanol-d_4, 400 MHz): δ 7.75 (d, *J* = 8.2 Hz, 4H, H2'), 7.40 – 7.44 (m, 4H, H6), 7.33 – 7.40 (m, 6H, H7, H8), 7.24 (d, *J* = 7.9 Hz, 4H, H3'), 5.27 (s, 4H, H4), 4.47 (app t, *J* = 5.9 Hz, 2H, H2), 3.26 – 3.33 (m, 4H, H1, obscured by solvent peak), 2.37 (s, 6H, H5'); ^{13}C NMR (methanol-d_4, 101 MHz): δ 168.8 (C3), 143.2 (C1'), 141.8 (C4'), 136.0 (C5), 129.8 (C2'), 129.8 (C7), 129.7 (C8), 129.7 (C6), 126.9 (C3'), 69.5 (C4), 53.0 (C2), 37.8 (C1), 21.3 (C5'); *m/z* (ESI$^+$) 421 ([M+H]$^+$, 100%, M as free base); HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{25}O_4N_2S_2$ [M+H]$^+$ 421.1250; found 421.1247.

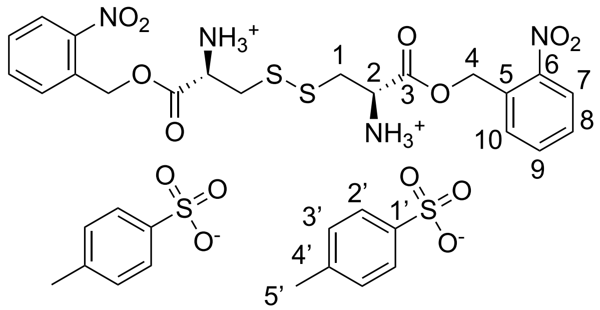
L-Cystine *p*-nitrobenzyl ester *p*-toluenesulphonate, 6e



Quantitative yield (4.3 g); yellow solid, m.p. 209 °C; $[\alpha]_D^{25}$ = -7.43 (*c* = 1.1, MeOH); ν_{max}/cm^{-1} (neat) 2981 (br. s, N-H), 1751 (s, C=O); ^{1}H NMR (methanol-d_4, 400 MHz): δ 8.17 – 8.25 (m, 4H, H7), 7.70 (d, *J* = 8.2 Hz, 4H, H2'), 7.65 (d, *J* = 8.9 Hz, 2H, H6), 7.59 (d, *J* = 8.9 Hz, 2H, H6), 7.23 (d, *J* = 7.9 Hz, 4H, H3'), 5.35 – 5.45 (m, 4H, H4), 4.57 (dd, *J* = 6.6, 5.5 Hz, 2H, H2), 3.36 – 3.42 (m, 4H, H1, obscured by solvent peak), 2.36 (s, 6H, H5'); ^{13}C NMR (methanol-d_4, 101 MHz): δ

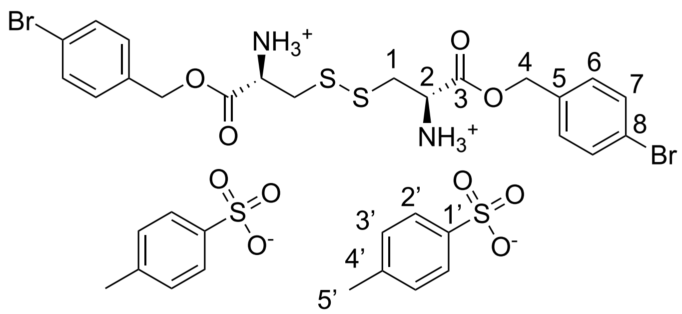
168.8 (C3), 150.9 (C8), 143.4 (C1’), 141.8 (C4’), 130.1 (C5), 129.8 (C2’), 128.2 (C7), 127.0 (C3’), 124.7 (C6), 124.4 (C6), 64.0 (C4), 53.0 (C2), 38.0 (C1), 21.3 (C5’); *m/z* (ESI$^+$) 511 ([M+H]$^+$, 100%, M as free base); HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{23}O_8N_4S_2$ [M+H]$^+$ 511.0952; found 511.0950.

L-Cystine *o*-nitrobenzyl ester *p*-toluenesulphonate, 6f



Quantitative yield (4.2 g); yellow solid, m.p. 199 °C; $[\alpha]_D^{25}$ = -14.1 (*c* = 0.95, MeOH); ν_{max}/cm^{-1} (neat) 2981 (br. s, N-H), 1753 (s, C=O); ^{1}H NMR (methanol-d_4, 400 MHz): δ 8.15 (d, *J* = 8.0 Hz, 2H, H7), 7.80 – 7.72 (m, 8H, H2’, H9 and H8), 7.68 – 7.62 (m, 2H, H10), 7.26 (d, *J* = 9.0 Hz, 4H, H3’), 5.67 (s, 4H, H4), 4.60 (dd, *J* = 6.9, 5.2 Hz, 2H, H2), 3.45 (dd, *J* = 15.0, 5.2 Hz, 2H, H1$_B$), 3.39 (m, 2H, H1$_A$, obscured by solvent peak), 2.41 (s, 6H, H5’); ^{13}C NMR (methanol-d_4, 101 MHz): δ 168.7 (C3), 149.3 (C6), 143.4 (C1’), 141.8 (C4’), 135.1 (C10), 131.5 (C5), 131.2 (C9), 130.9 (C8), 129.8 (C2’), 126.9 (C3’), 126.1 (C7), 66.3 (C4), 53.0 (C2), 38.0 (C1), 21.3 (C5’); *m/z* (ESI$^+$) 511 ([M+H]$^+$, 100%, M as free base); HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{23}O_8N_4S_2$ [M+H]$^+$ 511.0952; found 511.0951.

L-Cystine *p*-bromobenzyl ester *p*-toluenesulphonate, 6g

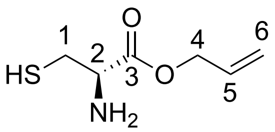


Quantitative yield (4.8 g); white solid, m.p. 194 °C; $[\alpha]_D^{25}$ = -12.9 (*c* = 0.30, MeOH); ν_{max}/cm^{-1} (neat) 2923 (br. s, N-H), 1745 (s, C=O); ^{1}H NMR (methanol-d_4, 400 MHz): δ 7.70 (d, *J* = 8.2 Hz, 4H, H2’), 7.51 (d, *J* = 8.4 Hz, 4H, H7), 7.34 (d, *J* = 8.4 Hz, 4H, H6), 7.23 (d, *J* = 7.8 Hz, 4H, H3’), 5.24 (d, *J* = 2.4 Hz, 4H, H4), 4.45 – 4.51 (m, 2H, H2), 3.27 – 3.35 (m, 4H, H1, obscured by solvent peak), 2.37 (s, 6H, H5’); ^{13}C NMR (methanol-d_4, 101 MHz): δ 168.8 (C3), (C1’ not seen), 141.8 (C4’), 135.4 (C5), 132.9 (C7), 131.7 (C6), 129.8 (C2’), 127.0 (C3’), 123.7 (C8), 68.8 (C4), 53.0

(C2), 37.9 (C1), 21.3 (C5'); *m/z* (ESI$^+$) 576 ([M+H]$^+$, 50%, M as free base), 578 ([M+H]$^+$, 100%), 580 ([M+H]$^+$, 50%); HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{23}O_4N_2Br_2S_2$ [M+H]$^+$ 576.9437, 578.9416, 580.9395; found 576.9462, 578.9439 and 580.9417.

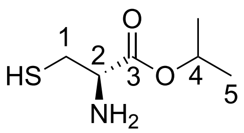
L-Cysteine esters **7a-g** were synthesised from their respective L-cystine diester *p*-toluenesulphonate salt **6a-g** (7.5 mmol) following General Procedure **B**.

L-Cysteine allyl ester, 7a



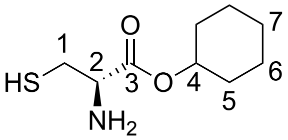
Yield (2.2 g, 82%); pale yellow oil; R_f = 0.23 (EtOAc: MeOH; 7 : 1); $[\alpha]_D^{25}$ = -76.0 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 3299 (br. s, N-H), 1734 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.85 – 5.98 (m, 1H, H5), 5.33 (d, *J* = 17.2 Hz, 1H, H6$_B$), 5.26 (d, *J* = 10.4 Hz, 1H, H6$_A$), 4.63 (d, *J* = 5.8 Hz, 2H, H4), 3.80 – 3.88 (m, 1H, H2), 3.11 – 3.18 (m, 1H, H1$_B$), 2.89 – 2.98 (m, 1H, H1$_A$), 2.17 (br. s, 3H, S*H,* N*H$_2$*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.5 (C3), 131.7 (C5), 119.1 (C6), 66.2 (C4), 53.7 (C2), 43.7 (C1); *m/z* (ESI$^+$) 162 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_6H_{12}O_2NS$ [M+H]$^+$ 162.0583; found 162.0583.

L-Cysteine isopropyl ester, 7b



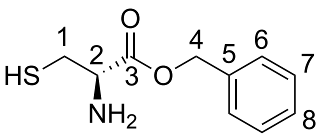
Yield (1.5 g, 65%); pale yellow oil; R_f = 0.20 (EtOAc: MeOH; 7 : 1); $[\alpha]_D^{25}$ = -6.89 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 3307 (br. s, N-H), 1733 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.04 (sept, *J* = 6.3 Hz, 1H, H4), 3.73 (dd, *J* = 7.9, 4.6 Hz, 1H, H2), 3.12 (dd, *J* = 13.5, 4.6 Hz, 1H, H1$_B$), 2.88 (dd, *J* = 13.5, 7.9 Hz, 1H, H1$_A$), 1.90 (br. s, 3H, S*H,* N*H$_2$*), 1.26 (s, 3H, H5$_B$), 1.24 (s, 3H, H5$_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.3 (C3), 69.2 (C4), 53.9 (C2), 43.9 (C1), 21.9 (C5); *m/z* (ESI$^+$) 164 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_6H_{14}O_2NS$ [M+H]$^+$ 164.0740; found 164.0740.

L-Cysteine cyclohexyl ester, 7c



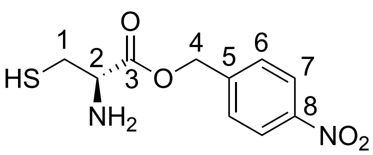
Yield (2.0 g, 71%); colourless oil; R_f = 0.20 (EtOAc: MeOH; 8 : 1); $[\alpha]_D^{25}$ = -34.5 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 3370 (br. s, N-H), 1731 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.74 – 4.88 (m, 1H, H4), 3.76 (dd, *J* = 7.8, 4.6 Hz, 1H, H2), 3.14 (dd, *J* = 13.5, 4.6 Hz, 1H, $H1_B$), 2.90 (dd, *J* = 13.5, 7.8 Hz, 1H, $H1_A$), 1.93 (br. s, 3H, S*H,* N*H₂*), 1.79 – 1.89 (m, 2H, H5), 1.64 – 1.77 (m, 2H, H5), 1.21 – 1.58 (m, 6H, H6, H7); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.3 (C3), 74.0 (C4), 54.0 (C2), 44.0 (C1), 31.6 (C5), 25.4 (C7), 23.8 (C6); *m/z* (ESI$^+$) 204 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_9H_{18}O_2NS$ [M+H]$^+$ 204.1053; found 204.1055.

L-Cysteine benzyl ester, 7d



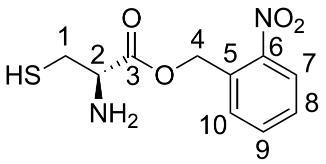
Yield (2.9 g, 83%); yellow oil; R_f = 0.40 (EtOAc: MeOH; 9 : 1); $[\alpha]_D^{25}$ = -38.0 (*c* = 0.96, $CHCl_3$)(lit. -26.6[3]-38.8[4](c = 1, 0.1 N HCl)a); ν_{max}/cm^{-1} 3304 (br. s, N-H), 1737 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (br. s, 5H, H6, H7, H8), 5.16 (s, 2H, H4), 3.82 (dd, *J* = 7.6, 4.6 Hz, 1H, H2), 3.12 (dd, *J* = 13.6, 4.6 Hz, 1H, $H1_B$), 2.90 (dd, *J* = 13.6, 7.6 Hz, 1H, $H1_A$), 1.85 (br. s, 3H, S*H,* N*H₂*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.7 (C3), 135.5 (C5), 128.8 (C7), 128.6 (C8), 128.5 (C6), 67.3 (C4), 53.8 (C2), 43.7 (C1); *m/z* (ESI$^+$) 212 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{14}O_2NS$ [M+H]$^+$ 212.0740; found 212.0745.

L-Cysteine *p*-nitrobenzyl ester, 7e



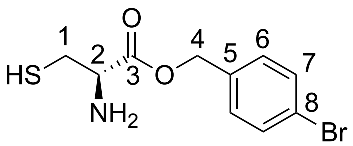
Yield (2.1 g, 50%); yellow oil; R_f = 0.15 (EtOAc: MeOH; 9 : 1); $[\alpha]_D^{25}$ = -5.13 (*c* = 0.54, $CHCl_3$); ν_{max}/cm^{-1} 3374 (br. s, N-H), 1742 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, *J* = 8.8 Hz, 2H, H7), 7.54 (d, *J* = 8.8 Hz, 2H, H6), 5.23 – 5.32 (m, 2H, H4), 3.88 (dd, *J* = 7.2, 5.0 Hz, 1H, H2), 3.13 (dd, *J* = 13.6, 5.0 Hz, 1H, $H1_B$), 2.97 (dd, *J* = 13.6, 7.2 Hz, 1H, $H1_A$), 1.72 (br. s, 3H, S*H,* N*H₂*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.4 (C3), 148.0 (C8), 142.7 (C5), 128.8 (C7), 124.1 (C6), 65.7 (C4), 56.1 (C2), 43.7 (C1); *m/z* (ESI$^+$) 257 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{13}O_4N_2S$ [M+H]$^+$ 257.0951; found 257.0952.

L-Cysteine *o*-nitrobenzyl ester, 7f



Yield (4.0 g, 94%); pale yellow oil; R_f = 0.70 (EtOAc: MeOH; 9 : 1); $[\alpha]_D^{25}$ = -15.2 (*c* = 1.37, $CHCl_3$); ν_{max}/cm^{-1} 3297 (br. s, N-H), 1742 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (dd, *J* = 8.1, 1.2 Hz, 1H, H7), 7.66 (td, *J* = 7.6, 1.3 Hz, 1H, H9), 7.63 – 7.56 (m, 1H, H8), 7.56 – 7.47 (m, 1H, H10), 5.56 (app d, *J* = 3.8 Hz, 2H, H4), 3.80 – 3.69 (m, 1H, H2), 2.89 (dd, *J* = 5.2, 3.5 Hz, 2H, H1), 1.84 (br. s, 3H, S*H,* N*H₂*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.3 (C3), 148.0 (C6), 133.9 (C10), 131.4 (C5), 129.7 (C9), 129.3 (C8), 125.3 (C7), 64.0 (C4), 56.1 (C2), 43.6 (C1); *m/z* (ESI$^+$) 257 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{13}O_4N_2S$ [M+H]$^+$ 257.0951; found 257.0952.

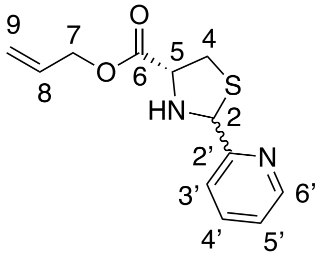
L-Cysteine *p*-bromobenzyl ester, 7g



Yield (2.5 g, 53%); white solid, m.p. 129 °C; R_f = 0.20 (100% EtOAc); $[\alpha]_D^{25}$ = -38.0 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} (neat) 1737 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 – 7.46 (m, 2H, H7), 7.27 – 7.20 (m, 2H, H6), 5.15 – 5.08 (m, 2H, H4), 3.82 (dd, *J* = 7.5, 4.7 Hz, 1H, H2), 3.10 (dd, *J* = 13.7, 4.7 Hz, 1H, $H1_B$), 2.91 (dd, *J* = 13.7, 7.5 Hz, 1H, $H1_A$), 2.09 (br. s, 3H, S*H,* N*H₂*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 173.5 (C3), 134.4 (C5), 132.0 (C7), 130.2 (C6), 122.8 (C8), 66.5 (C4), 53.8 (C2), 43.6 (C1); *m/z* (ESI$^+$) 290 and 292 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{13}O_2NBrS$ [M+H]$^+$ 289.9845 and 291.9824; found 289.9846 and 291.9826.

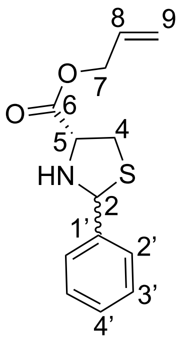
Thiazolidines **8-14** were synthesised from the respective L-cysteine esters **7a-g** with the respective aldehyde by General Procedure **C**.

(5*R*)-5-Alloxycarbonyl-2-(pyridin-2-yl)-1,3-thiazolidine, 8i



Synthesised from **7a** (1 eq. 11 mmol) with pyridine-2-carboxaldehyde; yield (2.6 g, 95%); greenish yellow oil; separable mixture of 1 : 1 *cis* and *trans* diastereomers; R_f = 0.61 (*cis*), 0.35 (*trans*) (petrol : EtOAc; 1 : 1); $[\alpha]_D^{25}$ = -47.9 (*c* = 1.04, $CHCl_3$), *cis*; $[\alpha]_D^{25}$ = -39.1 (*c* = 0.63, $CHCl_3$), *trans*; ν_{max}/cm^{-1} 3293 (br. s, N-H), 1739 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): *cis*: δ (N*H* not observed), 8.63 (d, *J* = 4.8 Hz, 1H, H6'), 7.66 (app td, *J* = 7.7, 1.8 Hz, 1H, H4'), 7.29 (d, *J* = 7.7 Hz, 1H, H3'), 7.23 (dd, *J* = 7.7, 4.8 Hz, 1H, H5'), 5.89 – 6.01 (m, 1H, H8), 5.65 (d, *J* = 8.7 Hz, 1H, H2), 5.37 (dd, *J* = 17.2, 1.5 Hz, 1H, $H9_A$), 5.28 (dd, *J* = 10.4, 1.5 Hz, 1H, $H9_A$), 4.72 (d, *J* = 5.8 Hz, 2H, H7), 4.01 – 4.10 (m, 1H, H5), 3.46 (dd, *J* = 10.0, 6.6 Hz, 1H, $H4_B$), 3.10 (app t, *J* = 9.8 Hz, 1H, $H4_A$); *trans*: δ 8.58 (d, *J* = 4.8 Hz, 1H, H6'), 7.66 (app td, *J* = 7.7, 1.8 Hz, 1H, H4'), 7.34 (d, *J* = 7.7 Hz, 1H, H3'), 7.20 (dd, *J* = 7.7, 4.8 Hz, 1H, H5'), 5.90 – 6.01 (m, 1H, H8), 5.86 (d, *J* = 6.2 Hz, 1H, H2), 5.37 (dd, *J* = 17.2, 1.4 Hz, 1H, $H9_B$), 5.29 (dd, *J* = 10.4, 1.4 Hz, 1H, $H9_A$), 4.70 (d, *J* = 5.8 Hz, 2H, H7), 4.53 – 4.60 (m, 1H, H5), 3.66 (br. s, 1H, N*H*), 3.40 (dd, *J* = 10.6, 6.8 Hz, 1H, $H4_B$), 3.35 (dd, *J* = 10.6, 4.4 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): *cis*: δ 170.5 (C6), 156.8 (C2'), 150.0 (C6'), 136.9 (C4'), 131.6 (C8), 123.5 (C3'), 122.2 (C5'), 119.3 (C9), 71.7 (C5), 66.4 (C7), 66.2 (C2), 39.5 (C4); *trans*: δ 171.5 (C6), 158.8 (C2'), 149.8 (C6'), 136.9 (C4'), 131.8 (C8), 123.1 (C3'), 121.7 (C5'), 119.1 (C9), 71.2 (C5), 66.2 (C7), 65.8 (C2), 38.9 (C4); *m/z* (ESI$^+$) 251 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{15}O_2N_2S$ [M+H]$^+$ 251.0849; found 251.0849.

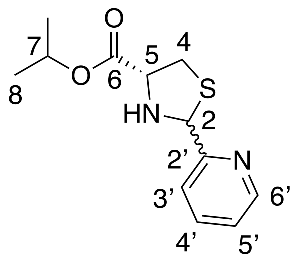
(5*R*)-5-Alloxycarbonyl-2-phenyl-1,3-thiazolidine, 8iii



Synthesised from **7a** (1 eq. 13.6 mmol) with benzaldehyde; yield (2.3 g, 68%); yellow oil; an inseparable mixture of 1.8 : 1 *cis* and *trans* diastereomers; R_f = 0.44 (petrol : EtOAc; 9 : 1); ν_{max}/cm^{-1} 3309 (br. s, N-H), 1736 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer: δ (N*H* not observed), 7.47 – 7.55 (m, 2H, H2'), 7.31 – 7.40 (m, 3H, H4' and H3'), 5.87 – 6.03 (m, 1H, H8), 5.57 (s, 1H, H2), 5.36 (dd, *J* = 17.2, 1.3 Hz, 1H, $H9_B$), 5.29 (dd, *J* = 10.4, 1.3 Hz, 1H, $H9_A$), 4.66 – 4.75 (m, 2H, H7), 3.96 – 4.06 (m, 1H, H5), 3.49 (dd, *J*

= 10.3, 7.1 Hz, 1H, $H4_B$), 3.13 (dd, *J* = 10.3, 8.9 Hz, 1H, $H4_A$); minor *trans* isomer: δ (N*H* not observed), 7.47 – 7.55 (m, 2H, H2'), 7.31 – 7.40 (m, 3H, H4' and H3'), 5.87 – 6.03 (m, 1H, H8), 5.83 (s, 1H, H2), 5.36 (dd, *J* = 17.2, 1.3 Hz, 1H, $H9_B$), 5.29 (dd, *J* = 10.4, 1.3 Hz, 1H, $H9_A$), 4.66 – 4.75 (m, 2H, H7), 4.20 – 4.28 (m, 1H, H5), 3.41 (dd, *J* = 10.6, 7.1 Hz, 1H, $H4_B$), 3.22 (dd, *J* = 10.6, 5.8 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer: δ 171.0 (C6), 138.3 (C1'), 131.5 (C8), 128.8 (C3'), 128.6 (C4'), 127.6 (C2'), 119.3 (C9), 72.8 (C5), 66.3 (C7), 65.8 (C2), 39.4 (C4); minor *trans* isomer: δ 171.6 (C6), 141.3 (C1'), 131.6 (C8), 128.8 (C3'), 128.0 (C4'), 127.0 (C2'), 119.2 (C9), 70.9 (C5), 66.2 (C7), 64.5 (C2), 38.3 (C4); *m/z* (ESI$^-$) 248 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{13}H_{14}O_2NS$ [M-H]$^-$ 248.0740; found 248.0740.

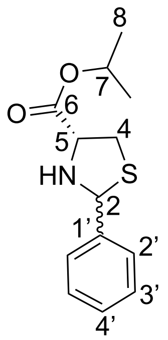
(5*R*)-5-Isopropoxycarbonyl-2-(pyridin-2-yl)-1,3-thiazolidine, 9i



Synthesised from **7b** (1 eq. 10 mmol) with pyridine-2-carboxaldehyde; yield (2.2 g, 85%); yellow oil; separable mixture of 1 : 1 *cis* and *trans* diastereomers; R_f = 0.45 (*cis*), 0.24 (*trans*) (petrol : EtOAc; 1 : 1); $[\alpha]_D^{25}$ = -67.4 (*c* = 1.18, $CHCl_3$), *cis*; $[\alpha]_D^{25}$ = -64.1 (*c* = 1.31, $CHCl_3$), *trans*; ν_{max}/cm^{-1} 3294 (br. s, N-H), 1734 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): *cis*: δ 8.62 (d, *J* = 4.8 Hz, 1H, H6'), 7.66 (app td, *J* = 7.7, 1.8 Hz, 1H, H4'), 7.28 (d, *J* = 7.7 Hz, 1H, H3'), 7.23 (dd, *J* = 7.7, 4.8 Hz, 1H, H5'), 5.64 (d, *J* = 10.7 Hz, 1H, H2), 5.14 (sept, *J* = 6.3 Hz, 1H, H7), 3.97 (dd, *J* = 10.4, 9.4 Hz, 1H, H5), 3.81 (br. s, 1H, N*H*), 3.43 (dd, *J* = 10.4, 6.6 Hz, 1H, $H4_B$), 3.06 (app t, *J* = 9.8 Hz, 1H, $H4_A$), 1.29 (app dd, *J* = 6.3, 4.0 Hz, 6H, H8); *trans*: δ (N*H* not observed), 8.57 (d, *J* = 4.8 Hz, 1H, H6'), 7.65 (app td, *J* = 7.7, 1.8 Hz, 1H, H4'), 7.34 (d, *J* = 7.7 Hz, 1H, H3'), 7.19 (dd, *J* = 7.7, 4.8 Hz, 1H, H5'), 5.86 (s, 1H, H2), 5.11 (sept, *J* = 6.3 Hz, 1H, H7), 4.46 (dd, *J* = 6.9, 4.6 Hz, 1H, H5), 3.37 (dd, *J* = 10.6, 6.9 Hz, 1H, $H4_B$), 3.27 (dd, *J* = 10.6, 4.6 Hz, 1H, $H4_A$), 1.29 (app dd, *J* = 6.3, 4.5 Hz, 6H, H8); ^{13}C NMR ($CDCl_3$, 101 MHz): *cis*: δ 170.3 (C6), 156.9 (C2'), 150.0 (C6'), 136.8 (C4'), 123.4 (C3'), 122.2 (C5'), 71.8 (C5), 69.4 (C7), 66.6 (C2), 39.6 (C4), 21.9 (C8); *trans*: δ 171.3 (C6), 159.2 (C2'), 149.7 (C6'), 136.9 (C4'), 123.0 (C3'), 121.5 (C5'), 71.3

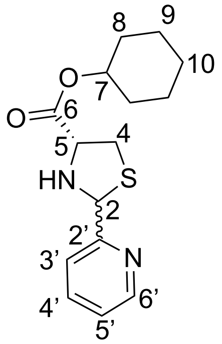
(C5), 69.3 (C7), 65.9 (C2), 39.0 (C4), 21.9 (C8); *m/z* (ESI$^+$) 253 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{17}O_2N_2S$ [M+H]$^+$ 253.1005; found 253.1007.

(5*R*)-5-Isopropoxycarbonyl-2-phenyl-1,3-thiazolidine, 9iii



Synthesised from **7b** (1 eq. 10 mmol) with benzaldehyde; yield (2.0 g, 83%); pale yellow oil; an inseparable mixture of 1.9 : 1 *cis* and *trans* diastereomers; R_f = 0.36 (petrol : EtOAc; 9 : 1); ν_{max}/cm^{-1} 3312 (br. s, N-H), 1730 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer: δ 7.49 (d, *J* = 6.6 Hz, 2H, H2'), 7.27 – 7.35 (m, 3H, H4' and H3'), 5.52 (s, 1H, H2), 5.08 (sept, *J* = 6.3 Hz, 1H, H7), 3.89 (dd, *J* = 8.9, 7.2 Hz, 1H, H5), 3.41 (dd, *J* = 10.3, 7.2 Hz, 1H, $H4_B$), 3.05 (dd, *J* = 10.2, 8.9 Hz, 1H, $H4_A$), 2.72 (br. s, 1H, N*H*), 1.24 (app dd, *J* = 6.3, 2.1 Hz, 6H, H8); minor *trans* isomer: δ 7.45 (d, *J* = 7.2 Hz, 2H, H2'), 7.27 – 7.35 (m, 3H, H4' and H3'), 5.80 (s, 1H, H2), 5.08 (sept, *J* = 6.3 Hz, 1H, H7), 4.05 – 4.12 (m, 1H, H5), 3.32 (dd, *J* = 10.5, 7.1 Hz, 1H, $H4_B$), 3.10 (dd, *J* = 10.5, 6.0 Hz, 1H, $H4_A$), 2.72 (br. s, 1H, N*H*), 1.24 (dd, *J* = 6.3, 2.1 Hz, 6H, H8); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer: δ 170.6 (C6), 138.2 (C1'), 128.6 (C3'), 127.4 (C4'), 126.9 (C2'), 72.7 (C5), 69.3 (C7), 65.8 (C2), 39.3 (C4), 21.7 (C8); minor *trans* isomer: δ 171.1 (C6), 141.5 (C1'), 128.3 (C3'), 127.7 (C4'), 126.9 (C2'), 70.9 (C5), 69.1 (C7), 64.4 (C2), 38.2 (C4), 21.7 (C8); *m/z* (ESI$^+$) 252 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{13}H_{18}O_2NS$ [M+H]$^+$ 252.1053; found 252.1053.

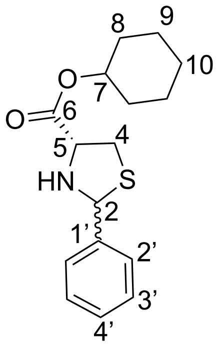
(5*R*)-5-Cyclohexyloxycarbonyl-2-(pyridin-2-yl)-1,3-thiazolidine, 10i



Synthesised from **7c** (1 eq. 4.5 mmol) with pyridine-2-carboxaldehyde; yield (0.91 g, 69%); yellow oil; separable mixture of 1.1 : 1 *cis* and *trans* diastereomers; R_f = 0.53 (*cis*), 0.31 (*trans*) (petrol : EtOAc; 3 : 2); $[\alpha]_D^{25}$ = -25.9 (*c* = 0.20, $CHCl_3$), *cis*; $[\alpha]_D^{25}$ = -35.4 (*c* = 27, $CHCl_3$), *trans*; ν_{max}/cm^{-1} 3294 (br. s, N-H), 1733 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): *cis*: δ (N*H* not observed), 8.59 (d, *J* = 4.8 Hz, 1H, H6'), 7.63

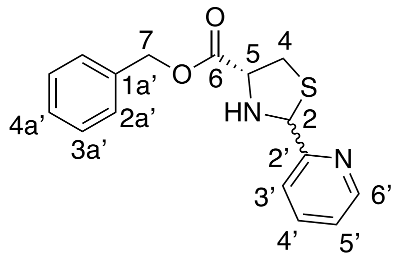
(app td, J = 7.7, 1.8 Hz, 1H, H4’), 7.27 (d, J = 7.7 Hz, 1H, H3’), 7.11 (app ddd, J = 7.7, 4.8, 1.0 Hz, 1H, H5’), 5.64 (s, 1H, H2), 4.94 – 4.82 (m, 1H, H7), 4.03 – 3.92 (m, 1H, H5), 3.42 (dd, J = 10.0, 6.6 Hz, 1H, $H4_B$), 3.05 (app t, J = 9.7 Hz, 1H, 1H, $H4_A$), 1.89 – 1.82 (m, 2H, H8), 1.75 – 1.67 (m, 2H, H8), 1.54 – 1.20 (m, 6H, H9 and H10); *trans*: δ (N*H* not observed), 8.49 (d, J = 4.8 Hz, 1H, H6’), 7.57 (app td, J = 7.7, 1.8 Hz, 1H, H4’), 7.27 (d, J = 7.7 Hz, 1H, H3’), 7.11 (app ddd, J = 7.7, 4.8, 1.1 Hz, 1H, H5’), 5.81 (s, 1H, H2), 4.88 – 4.68 (m, 1H, H7), 4.41 (dd, J = 6.9, 4.6 Hz, 1H, H5), 3.30 (dd, J = 10.5, 6.9 Hz, 1H, $H4_B$), 3.20 (dd, J = 10.5, 4.6 Hz, 1H, $H4_A$), 1.87 – 1.75 (m, 2H, H8), 1.71 – 1.62 (m, 2H, H8), 1.49 – 1.18 (m, 6H, H9 and H10); ^{13}C NMR ($CDCl_3$, 101 MHz): *cis*: δ 169.9 (C6), 159.6 (C2’), 149.6 (C6’), 136.5 (C4’), 123.1 (C3’), 121.9 (C5’), 73.7 (C7), 71.5 (C5), 66.3 (C2), 39.3 (C4), 31.2 (C8), 25.1 (C10), 23.4 (C9); *trans*: δ 171.0 (C6), 159.1 (C2’), 149.5 (C6’), 136.7 (C4’), 122.7 (C3’), 121.3 (C5’), 73.7 (C7), 71.2 (C5), 65.7 (C2), 38.8 (C4), 31.4 (C8), 25.2 (C10), 23.6 (C9); *m/z* (ESI^+) 293 ($[M+H]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{15}H_{21}O_2N_2S$ $[M+H]^+$ 293.1318; found 293.1319.

(5*R*)-5-Cyclohexyloxycarbonyl-2-phenyl-1,3-thiazolidine, 10iii



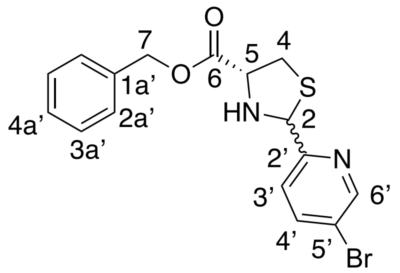
Synthesised from **7c** (1 eq. 6.9 mmol) with benzaldehyde; yield (1.4 g, 70%); pale yellow oil; an inseparable mixture of 1.9 : 1 *cis* and *trans* diastereomers; R_f = 0.22 (petrol : EtOAc; 19 : 1); ν_{max}/cm^{-1} 3312 (br. s, N-H), 1732 (s, C=O); ^1H NMR ($CDCl_3$, 400 MHz): major *cis* isomer: δ 7.48 (d, J = 7.6 Hz, 2H, H2’), 7.27 – 7.35 (m, 3H, H4’ and H3’), 5.52 (s, 1H, H2), 4.75 – 4.92 (m, 1H, H7), 3.91 (dd, J = 8.9, 7.2 Hz, 1H, H5), 3.42 (dd, J = 10.3, 7.2 Hz, 1H, $H4_B$), 3.05 (dd, J = 10.3, 8.9 Hz, 1H, $H4_A$), 2.70 (br. s, 1H, N*H*), 1.78 – 1.89 (m, 2H, H8), 1.63 – 1.74 (m, 2H, H8), 1.16 – 1.56 (m, 6H, H9 and H10); minor *trans* isomer: δ 7.44 (d, J = 7.5 Hz, 2H, H2’), 7.27 – 7.35 (m, 3H, H4’ and H3’), 5.80 (s, 1H, H2), 4.75 – 4.92 (m, 1H, H7), 4.06 – 4.16 (m, 1H, H5), 3.34 (dd, J = 10.5, 7.1 Hz, 1H, $H4_B$), 3.11 (dd, J = 10.5, 6.0 Hz, 1H, $H4_A$), 2.70 (br. s, 1H, N*H*), 1.78 – 1.89 (m, 2H, H8), 1.63 – 1.74 (m, 2H, H8), 1.16 – 1.56 (m, 6H, H9 and H10); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer: δ 170.7 (C6), 138.3 (C1’), 128.7 (C3’), 127.5 (C4’), 127.0 (C2'), 74.2 (C7), 72.8 (C5), 66.0 (C2), 39.5 (C4), 31.5 (C8), 25.3 (C10), 23.7 (C9); minor *trans* isomer: δ 171.2 (C6), 141.6 (C1'), 128.4 (C3'), 127.8 (C4'), 127.0 (C2'), 74.0 (C7), 70.9 (C5), 64.6 (C2), 38.4 (C4), 31.5 (C8), 25.3 (C10), 23.7 (C9); *m/z* (ESI$^+$) 292 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{22}O_2NS$ [M+H]$^+$ 292.1366; found 292.1365.

(5*R*)-5-Benzyloxycarbonyl-2-(pyridin-2-yl)-1,3-thiazolidine, 11i



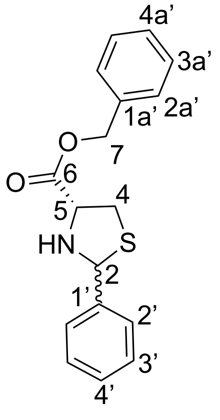
Synthesised from **7d** (1 eq. 7.4 mmol) with pyridine-2-carboxaldehyde; yield (1.0 g, 45%); pale yellow oil; an inseparable mixture of 1 : 1 *cis* and *trans* diastereomers; R_f = 0.43 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 3288 (br. s, N-H), 1736 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): *cis*: δ 8.56 (d, *J* = 5.3 Hz, 1H, H6'), 7.58 (app td, *J* = 7.8, 1.8 Hz, 1H, H4'), 7.27 – 7.31 (m, 5H, H4a', H3a', H2a'), 7.24 (d, *J* = 7.8 Hz, 1H, H3'), 7.14 – 7.19 (m, 1H, H5'), 5.61 (s, 1H, H2), 5.21 (s, 2H, H7), 4.03 (dd, *J* = 9.6, 6.7 Hz, 1H, H5), 3.81 (br. s, 1H, N*H*), 3.40 (dd, *J* = 10.1, 6.7 Hz, 1H, $H4_B$), 3.05 (app t, *J* = 9.8 Hz, 1H, $H4_A$); *trans*: δ (N*H* not observed), 8.51 (d, *J* = 4.7 Hz, 1H, H6'), 7.58 (app td, *J* = 7.7, 1.8 Hz, 1H, H4'), 7.27 – 7.34 (m, 6H, H4a', H3a', H2a' and H3'), 7.12 (dd, *J* = 7.7, 5.2 Hz, 1H, H5'), 5.83 (s, 1H, H2), 5.18 (s, 2H, H7), 4.52 (dd, *J* = 6.8, 4.4 Hz, 1H, H5), 3.32 (dd, *J* = 10.6, 6.8 Hz, 1H, $H4_B$), 3.27 (dd, *J* = 10.6, 4.4 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): *cis*: δ 170.5 (C6), 156.5 (C2'), 149.6 (C6'), 136.7 (C4'), 135.1 (C1a'), 128.4 (C4a'), 128.3 (C4a'), 128.2 (C2a'), 123.3 (C3'), 122.0 (C5'), 71.4 (C5), 67.1 (C7), 66.0 (C2), 39.2 (C4); *trans*: δ 171.4 (C6), 158.6 (C2'), 149.4 (C6'), 136.7 (C4'), 135.3 (C1a'), 128.5 (C3a'), 128.3 (C4a'), 128.1 (C2a'), 122.8 (C3'), 121.4 (C5'), 70.9 (C5), 67.0 (C7), 65.5 (C2), 38.5 (C4); *m/z* (ESI$^+$) 301 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{17}O_2N_2S$ [M+H]$^+$ 301.1005; found 301.1004.

(5*R*)-5-Benzyloxycarbonyl-2-(5-bromopyridin-2-yl)-1,3-thiazolidine, 11ii



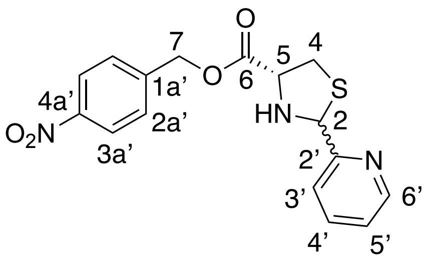
Synthesised from **7d** (1 eq. 5.6 mmol) with 5-bromopyridine-2-carbaldehyde; yield (1.8 g, 85%); yellow oil; an inseparable mixture of 1 : 1 *cis* and *trans* diastereomers; R_f = 0.25 (petrol : EtOAc; 17 : 3); ν_{max}/cm^{-1} 3292 (br. s, N-H), 1737 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, *J* = 2.3 Hz, 1H, H6' *cis*), 8.60 (d, *J* = 2.3 Hz, 1H, H6' *trans*), 7.77 (app ddd, *J* = 8.3, 6.9, 2.4 Hz, 2H, H4' *cis* and *trans*), 7.41 – 7.30 (m, 10H, H2a', H3a' and H4a', *cis* and *trans*), 7.24 (d, *J* = 8.3 Hz, 1H, H3' *trans*), 7.19 (d, *J* = 8.3 Hz, 1H, H3' *cis*), 5.82 (s, 1H, H2 *trans*), 5.61 (s, 1H, H2 *cis*), 5.26 (s, 2H, H7 *trans*), 5.23 (s, 2H, H7 *cis*), 4.50 (dd, *J* = 6.8, 4.7 Hz, 1H, H5 *trans*), 4.06 (dd, *J* = 9.5, 6.7 Hz, 1H, H5 *cis*), 3.75 (br. s, 2H, N*H*, *cis* and *trans*), 3.43 (dd, *J* = 10.1, 6.7 Hz, 1H, $H4_B$ *cis*), 3.36 (dd, *J* = 10.6, 6.8 Hz, 1H, $H4_B$ *trans*), 3.27 (dd, *J* = 10.6, 4.7 Hz, 1H, $H4_A$ *trans*), 3.07 (app t, *J* = 9.8 Hz, 1H, $H4_A$ *cis*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.4, 170.6 (C6), 158.0, 155.6 (C2'), 151.0, 150.7 (C6'), 139.4 (C4'), 135.4, 135.3 (C1a'), 128.8 (C4a'), 128.7, 128.6 (C4a'), 128.4, 128.4 (C2a'), 123.3, 122.6 (C3'), 120.2, 119.6 (C5'), 71.0, 70.5 (C5), 67.4, 67.3 (C7), 66.3, 65.6 (C2), 39.5, 38.8 (C4); *m/z* (ESI$^+$) 379 and 381 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{16}O_2N_2BrS$ [M+H]$^+$ 379.0110 and 381.0089; found 379.0112 and 381.0091.

(5*R*)-5-Benzyloxycarbonyl-2-phenyl-1,3-thiazolidine, 11iii



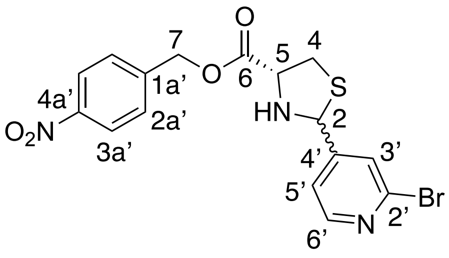
Synthesised from **7d** (1 eq. 8.7 mmol) with benzaldehyde; yield (1.3 g, 50%); pale yellow oil; an inseparable mixture of 1.8 : 1 *cis* and *trans* diastereomers; R_f = 0.72 (petrol : EtOAc; 7 : 3); ν_{max}/cm^{-1} 3031 (br. s, N-H), 1736 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer: δ 7.53 (d, *J* = 7.8 Hz, 2H, H2'), 7.32 – 7.40 (m, 8H, H4', H4a', H3', H3a', H2a'), 5.57 (s, 1H, H2), 5.25 (s, 2H, H7), 3.99 – 4.08 (m, 1H, H5), 3.48 (dd, *J* = 10.3, 7.1 Hz, 1H, $H4_B$), 3.12 (dd, *J* = 10.3, 8.9 Hz, 1H, $H4_A$), 2.72 (br. s, 1H, N*H*); minor *trans* isomer: δ 7.48 (d, *J* = 7.5 Hz, 2H, H2'), 7.32 – 7.40 (m, 8H, H4', H4a', H3', H3a', H2a'), 5.83 (s, 1H, H2), 5.23 (app d, J = 2.2 Hz, 2H, H7), 4.22 – 4.29 (m, 1H, H5), 3.41 (dd, J = 10.6, 7.1 Hz, 1H, $H4_B$), 3.22 (dd, J = 10.6, 5.8 Hz, 1H, $H4_A$), 2.72 (br. s, 1H, N*H*); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer: δ 171.2 (C6), 138.3 (C1'), 135.2 (C1a'), 128.8 (C3'), 128.7 (C3a'), 128.5 (C4a'), 128.4 (C2a'), 127.6 (C4'), 127.1 (C2'), 72.8 (C5), 67.5 (C7), 65.8 (C2), 39.4 (C4); minor *trans* isomer: δ 171.7 (C6), 141.3 (C1'), 135.4 (C1a'), 128.8 (C3'), 128.7 (C3a'), 128.6 (C4a'), 128.0 (C2a'), 127.6 (C4'), 127.1 (C2'), 70.9 (C5), 67.4 (C7), 64.5 (C2), 38.2 (C4); *m/z* (ESI$^+$) 300 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{18}O_2NS$ [M+H]$^+$ 300.1064; found 300.1055.

(5*R*)-5-(4-nitrobenzyloxycarbonyl)-2-(pyridin-2-yl)-1,3-thiazolidine, 12i



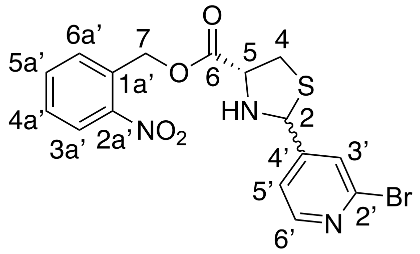
Synthesised from **7e** (1 eq. 7.8 mmol) with pyridine-2-carbaldehyde; yield (2.0 g, 74%); yellow oil; separable 1 : 1 *cis* and *trans* diastereomers; R_f = 0.38 (*cis*), 0.15 (*trans*) (petrol : EtOAc; 1 : 1); $[\alpha]_D^{25}$ = -52.5 (c = 0.97, $CHCl_3$), *cis*; $[\alpha]_D^{25}$ = -56.0 (c = 1.10, $CHCl_3$), *trans*; ν_{max}/cm^{-1} 3287 (br. s, N-H), 1743 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): *cis*: δ (N*H* not observed), 8.63 (d, J = 4.8 Hz, 1H, H6'), 8.24 (d, J = 8.8 Hz, 2H, H3a'), 7.68 (app td, J = 7.7, 1.8 Hz, 1H, H4'), 7.56 (d, J = 8.8 Hz, 2H, H2a'), 7.29 (d, J = 7.7 Hz, 1H, H3'), 7.25 (dd, J = 7.7, 4.8 Hz, 1H, H5'), 5.66 (s, 1H, H2), 5.35 (s, 2H, H7), 4.11 (dd, J = 9.3, 6.9 Hz, 1H, H5), 3.48 (dd, J = 10.1, 6.9 Hz, 1H, $H4_B$), 3.11 (app t, J = 9.8 Hz, 1H, $H4_A$); *trans*: δ (N*H* not observed), 8.57 (d, J = 4.9 Hz, 1H, H6'), 8.23 (d, J = 8.8 Hz, 2H, H3a'), 7.66 (app td, J = 7.7, 1.8 Hz, 1H, H4'), 7.55 (d, J = 8.8 Hz, 2H, H2a'), 7.31 (d, J = 7.7 Hz, 1H, H3'), 7.21 (dd, J = 7.7, 4.9 Hz, 1H, H5'), 5.83 (s, 1H, H2), 5.32 (s, 2H, H7), 4.66 (dd, J = 6.1, 4.5 Hz, 1H, H5), 3.38 – 3.43 (m, 1H, $H4_B$), 3.35 – 3.38 (m, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): *cis*: δ 170.5 (C6), 156.6 (C2'), 150.0 (C6'), 148.1 (C4a'), 142.5 (C1a'), 137.0 (C4'), 128.7 (C3a'), 124.1 (C2a'), 123.6 (C3'), 122.3 (C5'), 71.6 (C5), 66.3 (C2), 65.8 (C7), 39.5 (C4); *trans*: δ 171.5 (C6), 158.3 (C2'), 149.7 (C6'), 148.0 (C4a'), 142.7 (C1a'), 137.0 (C4'), 128.6 (C3a'), 124.0 (C2a'), 123.3 (C3'), 121.9 (C5'), 71.1 (C5), 65.8 (C2), 65.7 (C7), 38.7 (C4); *m/z* (ESI$^+$) 346 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{16}O_4N_3S$ [M+H]$^+$ 346.0856; found 346.0855.

(5*R*)-2-(2-Bromopyridin-4-yl)-5-(4-nitrobenzyloxycarbonyl)-1,3-thiazolidine, 12iv



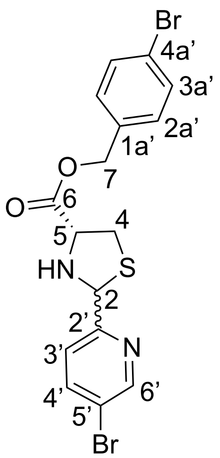
Synthesised from **7e** (1 eq. 7.4 mmol) with 2-bromopyridine-4-carbaldehyde; yield (2.4 g, 77%); yellow oil; an inseparable 0.5 : 1 *cis* and *trans* diastereomers; R_f = 0.41 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 3321 (br. s, N-H), 1739 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): minor *cis* isomer: δ (N*H* not observed), 8.23 (d, *J* = 5.1 Hz, 1H, H6’), 8.07 (d, *J* = 8.9 Hz, 2H, H3a’), 7.58 – 7.57 (m, 1H, H3’), 7.48 (d, *J* = 8.9 Hz, 2H, H2a’), 7.33 (d, *J* = 5.1 Hz, 1H, H5’), 5.45 (s, 1H, H2), 5.26 (s, 2H, H7), 4.13 – 4.05 (m, 1H, H5), 3.43 (dd, *J* = 10.4, 7.0 Hz, 1H, $H4_B$), 3.14 – 3.05 (m, 1H, $H4_A$); major *trans* isomer: δ (N*H* not observed), 8.18 (d, *J* = 5.1, 1H, H6’), 8.12 (d, *J* = 8.9 Hz, 2H, H3a’), 7.54 – 7.52 (m, 1H, H3’), 7.48 (d, *J* = 8.9 Hz, 2H, H2a’), 7.27 (d, *J* = 5.1 Hz, 1H, H5’), 5.71 (s, 1H, H2), 5.27 (s, 2H, H7), 4.13 – 4.05 (m, 1H, H5), 3.34 (dd, *J* = 10.6, 6.8 Hz, 1H, $H4_B$), 3.08 (dd, *J* = 10.6, 6.6 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): minor *cis* isomer: δ 170.3 (C6), 150.7 (C6’), 150.1 (C4’), 147.6 (C4a’), 142.2, 142.1 (C1a’ and C2’), 128.5 (C3a’), 126.8 (C3’), 123.3 (C2a’), 121.5 (C5’), 69.4 (C5), 65.2 (C7), 63.4 (C2), 38.4 (C4); major *trans* isomer: δ 170.8 (C6), 154.5 (C6’), 149.9 (C4’), 147.6 (C4a’), 142.2, 142.1 (C1a’ and C2’), 128.4 (C3a’), 125.7 (C3’), 123.7 (C2a’), 121.0 (C5’), 67.8 (C5), 65.7 (C7), 64.0 (C2), 37.8. (C4); *m/z* (ESI$^+$) 424 and 426 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{15}O_4N_3BrS$ [M+H]$^+$ 423.9961 and 425.9940; found 423.9961 and 425.9938.

(5*R*)-2-(2-Bromopyridin-4-yl)-5-(2-nitrobenzyloxycarbonyl)-1,3-thiazolidine, 13iv



Synthesised from **7f** (1 eq. 7.9 mmol) with 2-bromopyridine-4-carbaldehyde; yield (2.4 g, 72%); pale yellow oil; an inseparable 0.5 : 1 *cis* and *trans* diastereomers; R_f = 0.61 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 3291 (br. s, N-H), 1737 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (N*H* not observed), 8.29 (d, *J* = 5.1 Hz, 1H, H6' *cis*), 8.24 (d, *J* = 5.1 Hz, 1H, H6' *trans*), 8.07 (d, *J* = 8.2 Hz, 2H, H3a' *cis* and *trans*), 7.68 – 7.48 (m, 8H, H4a', H5a', H6a' and H3', *cis* and *trans*), 7.35 (d, *J* = 5.1 Hz, 1H, H5' *cis*), 7.31 – 7.28 (m, 1H, H5' *trans*), 5.72 (s, 1H, H2 *trans*), 5.65 – 5.49 (m, 4H, H7 *cis* and *trans*), 5.45 (s, 1H, H2 *cis*), 4.12 – 4.04 (m, 2H, H5 *cis* and *trans*), 3.45 (dd, *J* = 10.4, 7.0 Hz, 1H, H4$_B$ *cis*), 3.35 (dd, *J* = 10.6, 6.8 Hz, 1H, H4$_B$ *trans*), 3.17 – 3.09 (m, 2H, H4$_A$ *cis* and *trans*); ^{13}C NMR ($CDCl_3$, 101 MHz): minor *cis* isomer: δ 170.2 (C6), 150.6 (C6'), 150.4 (C4'), 147.7 (C2a'), 142.5 (C2'), 133.9 (C6a'), 130.7 (C1a'), 129.6 (C5a'), 129.5 (C4a'), 126.6 (C3'), 125.2 (C3a'), 121.5 (C5'), 69.6 (C5), 65.4 (C7), 64.2 (C2), 38.6 (C4); major *trans* isomer: δ 170.7 (C6), 154.6 (C6'), 150.1 (C4'), 147.7 (C2a'), 142.4 (C2'), 133.9 (C6a'), 130.8 (C1a'), 129.6 (C5a'), 129.4 (C4a'), 125.8 (C3'), 125.2 (C3a'), 121.2 (C5'), 67.9 (C5), 64.3 (C7), 64.2 (C2), 38.0 (C4); *m/z* (ESI$^+$) 424 and 426 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{15}O_4N_3BrS$ [M+H]$^+$ 423.9961 and 425.9940; found 423.9962 and 425.9940.

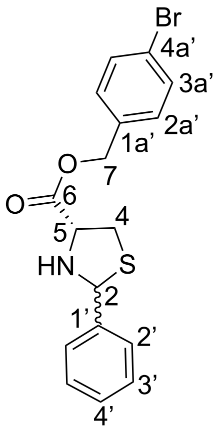
(5*R*)-5-(4-Bromobenzyloxycarbonyl)-2-(5-bromopyridin-2-yl)-1,3-thiazolidine, 14ii



Synthesised from **7g** (1 eq. 4.0 mmol) with 5-bromopyridine-2-carbaldehyde; yield (1.0 g, 55%); pale yellow solid, m.p. 125 – 130 °C; an inseparable mixture of 4.5 : 1 *cis* and *trans* diastereomers; R_f = 0.21 (petrol : EtOAc; 17 : 3); ν_{max}/cm^{-1} 3290 (br. s, N-H), 1729 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer: δ 8.66 (d, *J* = 2.1 Hz, 1H, H6'), 7.79 (dd, *J* = 8.2, 2.3 Hz, 1H, H4'), 7.50 (d, *J* = 8.4 Hz, 2H, H3a'), 7.25 (app d, *J* = 6.7 Hz, 3H, H2a' and H3'), 5.60 (s, 1H, H2), 5.20 (s, 2H, H7), 4.08 – 3.99 (m, 1H, H5), 3.75 (br. s, 1H, N*H*), 3.42 (dd, *J* = 10.1, 6.6 Hz, 1H, H4$_B$), 3.05 (app t, *J* = 9.8 Hz, 1H, H4$_A$); minor *trans* isomer: δ (N*H* not observed), 8.60 (d, *J* = 2.0 Hz, 1H, H6'), 7.77 (dd, *J* =

8.2, 2.3 Hz, 1H, H4'), 7.50 (d, *J* = 8.2 Hz, 2H, H3a'), 7.19 (d, *J* = 8.2 Hz, 3H, H2a' and H3'), 5.80 (s, 1H, H2), 5.17 (s, 2H, H7), 4.51 (dd, *J* = 6.8, 4.6 Hz, 1H, H5), 3.35 (dd, *J* = 10.7, 6.8 Hz, 1H, $H4_B$), 3.27 (dd, *J* = 10.7, 4.6 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer: δ 170.5 (C6), 155.6 (C2'), 151.1 (C6'), 139.5 (C4'), 134.3 (C1a'), 132.0 (C3a'), 130.2 (C2a'), 123.3 (C3'), 122.9 (C4a'), 120.3 (C5'), 71.0 (C5), 66.6 (C7), 66.3 (C2), 39.5 (C4); minor *trans* isomer: δ 171.4 (C6), 155.6 (C2'), 150.8 (C6'), 139.5 (C4'), 134.5 (C1a'), 132.0 (C3a'), 130.1 (C2a'), 123.3 (C3'), 122.9 (C4a'), 119.8 (C5'), 70.5 (C5), 66.6 (C7), 65.7 (C2), 38.7 (C4); *m/z* (ESI^+) 479 (50%), 480 ($[M+Na]^+$, 100%) and 483 (50%); HRMS (ESI^+) *m/z* calcd for $C_{16}H_{14}O_2N_2Br_2NaS$ $[M+Na]^+$ 478.9035, 480.9014 and 482.8993; found 478.9036, 480.9013 and 482.8991.

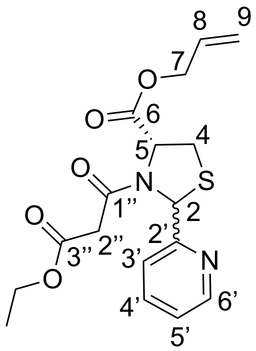
(5*R*)-5-(4-Bromobenzyloxycarbonyl)-2-phenyl-1,3-thiazolidine, 14iii



Synthesised from **7g** (1 eq. 4.4 mmol) with benzaldehyde; yield (1.5 g, 91%); pale yellow solid, m.p. 88 °C; an inseparable mixture of 1.7 : 1 *cis* and *trans* diastereomers; R_f = 0.16 (petrol : EtOAc; 9 : 1); ν_{max}/cm^{-1} 3333 (br. s, N-H), 1733 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer: δ (N*H* not observed), 7.48 – 7.53 (m, 4H, H2' and H3a'), 7.30 – 7.39 (m, 3H, H4' and H3'), 7.24 (d, *J* = 8.5 Hz, 2H, H2a'), 5.55 (s, 1H, H2), 5.17 (s, 2H, H7), 3.96 – 4.05 (m, 1H, H5), 3.46 (dd, *J* = 10.6, 7.1 Hz, 1H, $H4_B$), 3.09 (dd, *J* = 10.6, 8.9 Hz, 1H, $H4_A$); minor *trans* isomer: δ (N*H* not observed), 7.45 – 7.53 (m, 4H, H2' and H3a'), 7.30 – 7.39 (m, 3H, H4' and H3'), 7.24 (d, *J* = 8.5 Hz, 2H, H2a'), 5.80 (s, 1H, H2), 5.16 (app d, *J* = 1.5 Hz, 2H, H7), 4.25 (dd, *J* = 7.2, 5.7 Hz, 1H, H5), 3.39 (dd, *J* = 10.6, 7.2 Hz, 1H, $H4_B$), 3.19 (dd, *J* = 10.6, 5.7 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer: δ 171.1 (C6), 138.2 (C1'), 134.2 (C1a'), 132.0 (C3a'), 130.2 (C2a'), 128.8 (C3'), 128.6 (C4'), 127.5 (C2'), 122.9 (C4a'), 72.8 (C5), 66.7 (C7), 65.7 (C2), 39.3 (C4); minor *trans* isomer: δ 171.7 (C6), 141.2 (C1'), 134.4 (C1a'), 132.0 (C3a'), 130.1 (C2a'), 128.9 (C3'), 128.1 (C4'), 127.1 (C2'), 122.8 (C4a'), 71.0 (C5), 66.5 (C7), 64.5 (C2), 38.2 (C4); *m/z* (ESI$^+$) 378 and 380 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{17}O_2NBrS$ [M+H]$^+$ 378.0158 and 380.0137; found 378.0159 and 380.0137.

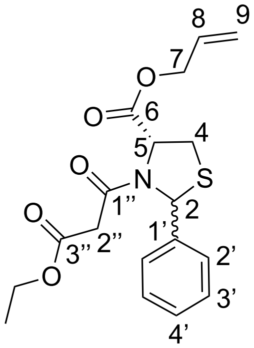
N-Acylthiazolidines **15-21** were synthesised from the respective thiazolidines **8-14** by General procedure **D**.

(5*R*)-5-Allyloxycarbonyl-1-(3-ethoxy-3-oxopropanoyl)-2-(pyridin-2-yl)-1,3-thiazolidine, 15i



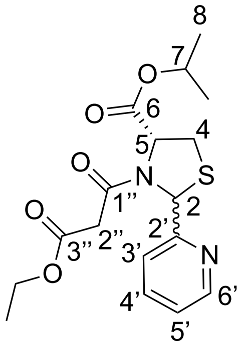
Synthesised from **8i** (1 eq. 6 mmol); yield (1.3 g, 58%); yellow oil; an inseparable mixture of 3.1 : 1 *cis* and *trans* diastereomers; R_f = 0.24 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 1735 (s, C=O), 1663 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.2 mixture of rotamers; minor *trans* isomer as a 1 : 0.7 mixture of rotamers: δ 8.54 – 8.51 (m, 1H, H6'), 8.06 (d, *J* = 7.9 Hz, 1H, H3'), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H, H4'), 7.22 – 7.18 (m, 1H, H5'), 6.43 (s, H2 *cis* minor rotamer), 6.20 (s, H2 *trans* minor rotamer), 6.16 (s, 1H, H2 *cis* major rotamer), 6.13 (s, H2 *trans* major rotamer), 5.95 – 5.84 (m, 1H, H8), 5.33 (dd, *J* = 17.2, 1.4 Hz, 2H, H9 *cis* major rotamer), 5.27 – 5.19 (m, H9 minor rotamer), 5.01 (dd, *J* = 8.2, 6.7 Hz, 1H, H5), 4.74 – 4.58 (m, 2H, H7), 4.19 – 3.98 (m, 2H, OCH_2CH_3), 3.60 – 3.00 (m, 4H, $H4_B$, $H4_A$, $H2''_A$ and $H2''_B$), 1.28 – 1.11 (m, 3H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer, major rotamer: δ 169.6 (C6), 166.4 (C3''), 165.6 (C1''), 159.4 (C2'), 149.6 (C6'), 137.6 (C4'), 131.5 (C8), 123.3 (C3'), 120.7 (C5'), 118.9 (C9), 67.7 (C7), 66.4 (C5), 64.9 (C2), 61.7 (OCH_2CH_3), 42.1 (C2''), 31.8 (C4), 14.0 (OCH_2CH_3); *m/z* (ESI$^+$) 365 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{21}O_5N_2S$ [M+H]$^+$ 365.1166; found 365.1167.

(5*R*)-5-Allyloxycarbonyl-1-(3-ethoxy-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 15iii



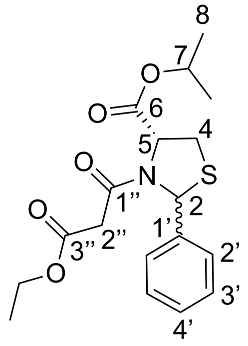
Synthesised from **8iii** (1 eq. 4.8 mmol); yield (1.3 g, 74%); yellow oil; an inseparable mixture of 1.2 : 1 *cis* and *trans* diastereomers; R_f = 0.26 (petrol : EtOAc; 4 : 1); ν_{max}/cm^{-1} 1736 (s, C=O), 1661 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.2 mixture of rotamers; minor *trans* isomer as a 1 : 0.3 mixture of rotamers: δ 7.66 (d, *J* = 7.4 Hz, 2H, H2' *cis*), 7.52 (d, *J* = 7.4 Hz, H2' minor rotamer), 7.38 (t, *J* = 7.4 Hz, 4H, H3'), 7.33 (d, *J* = 7.4 Hz, 2H, H2' *trans*), 7.22 (d, *J* = 7.4 Hz, 2H, H4'), 6.37 (s, H2 *cis* minor rotamer), 6.33 (s, H2 *trans* minor rotamer), 6.19 (s, 1H, H2 *trans* major rotamer), 6.15 (s, 1H, H2 *cis* major rotamer), 5.86 – 6.04 (m, 2H, H8 *cis* and *trans*), 5.19 – 5.44 (m, 5H, H9, H5 *trans*), 5.10 (app t, *J* = 6.8 Hz, 1H, H5, *cis* major), 4.66 – 4.80 (m, 4H, H7), 4.03 – 4.25 (m, 4H, OCH_2CH_3), 3.21 – 3.61 (m, 6H, $H4_B$, $H2''_A$, $H2''_B$), 3.11 (dd, *J* = 15.3, 8.4 Hz, 2H, $H4_A$), 1.19 – 1.35 (m, 6H, OCH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 169.5, 168.8 (C6 major and minor), 166.9, 166.4 (C3'' major and minor), 165.7, 165.5 (C1'' major, and minor), 142.2, 142.0, 139.9, 138.8 (C1' major, minor and rotamers), 131.7, 131.6, 131.1 (C8 major, minor and rotamers), 129.4, 129.2 (C3' major and minor), 128.8, 128.7, 128.4, 128.1 (C4' major, minor and rotamers), 127.2, 126.6, 125.1, 124.9 (C2' major, minor and rotamers), 120.0, 119.8, 119.1, 118.8 (C9 major, minor and rotamers), 66.5, 66.5 (C7 major and minor), 65.2, 65.0 (C5 major and minor), 64.5, 64.3, 64.1 (C2 major, minor and rotamers), 61.9, 61.9, 61.8, 61.6 (OCH_2CH_3 major, minor and rotamers), 43.6, 43.1, 42.6, 42.3 (C2'' major, minor and rotamers), 33.2, 32.6, 32.3, 31.2 (C4 major, minor and rotamers), 14.3, 14.2, 14.2, 14.1 (OCH_2CH_3 major, minor and rotamers); *m/z* (ESI$^+$) 386 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{21}O_5NNaS$ [M+Na]$^+$ 386.1033; found 386.1032.

(5*R*)-1-(3-Ethoxy-3-oxopropanoyl)-5-isopropoxycarbonyl-2-(pyridin-2-yl)-1,3-thiazolidine, 16i



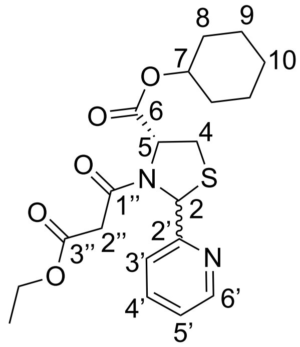
Synthesised from **9i** (1 eq. 5.4 mmol); yield (1.4 g, 71%); orange oil; an inseparable mixture of 1.4 : 1 *cis* and *trans* diastereomers; R_f = 0.32 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 1737 (s, C=O), 1665 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.2 mixture of rotamers; minor *trans* isomer as a 1 : 0.9 mixture of rotamers: δ 8.52 – 8.47 (m, 1H, H6' *cis*), 8.46 – 8.40 (m, 1H, H6' *trans*), 8.09 (d, *J* = 8.0 Hz, 1H, H3' *cis*), 7.70 (app td, *J* = 8.0, 1.8 Hz, 1H, H4' *cis*), 7.57 (app td, *J* = 6.9, 6.1, 2.3 Hz, 1H, H4' *trans*), 7.24 – 7.15 (m, 2H, H3' *trans* and H5' *cis*), 7.08 (dd, *J* = 7.0, 5.4 Hz, 1H, H5' *trans*), 6.40 (s, H2 *cis* minor rotamer), 6.17 (s, H2 *trans* minor rotamer), 6.14 (s, 1H, H2 *cis* major rotamer), 6.11 (s, 1H, H2 *trans* major rotamer), 5.24 – 4.98 (m, 3H, H7 *cis* and *trans* + H5), 4.89 (dd, *J* = 8.6, 6.6 Hz, 1H, H5), 4.17 – 3.97 (m, 4H, OCH_2CH_3 *cis* and *trans*), 3.59 – 2.95 (m, 8H, $H4_B$, $H4_A$, $H2''_A$ and $H2''_B$, *cis* and *trans*), 1.29 – 1.08 (m, 18H, OCH_2CH_3 and H8, *cis* and *trans*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 169.2, 169.0, 168.5 (C6 major, minor and rotamers), 166.9, 166.8, 166.4, 166.2 (C3'' major, minor and rotamers), 165.4, 165.2, 165.0, 164.7 (C1'' major, minor and rotamers), 160.3, 160.3, 159.5, 158.5 (C2' major, minor and rotamers), 149.9, 149.5, 149.3, 148.9 (C6' major, minor and rotamers), 137.5, 137.4, 136.8, 136.6 (C4' major, minor and rotamers), 123.2, 123.1, 122.5, 122.5 (C3' major, minor and rotamers), 120.7, 120.3, 119.6, 119.4 (C5' major, minor and rotamers), 70.5, 70.4, 69.6, 69.3 (C7 major, minor and rotamers), 67.7, 67.6, 66.4, 66.0 (C5 major, minor and rotamers), 65.2, 64.2, 64.2, 64.1 (C2 major, minor and rotamers), 61.6, 61.5, 61.3 (OCH_2CH_3 major, minor and rotamers), 43.1, 42.6, 42.3, 42.0 (C2'' major, minor and rotamers), 33.8, 33.6, 31.7, 31.3 (C4 major, minor and rotamers), 21.7, 21.6 (C8 major, minor and rotamers), 14.0, 14.0, 13.9 (OCH_2CH_3 major, minor and rotamers); *m/z* (ESI$^+$) 367 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{23}O_5N_2S$ [M+H]$^+$ 367.1322; found 367.1323.

(5*R*)-1-(3-Ethoxy-3-oxopropanoyl)-5-isopropoxycarbonyl-2-phenyl-1,3-thiazolidine, 16iii



Synthesised from **9iii** (1 eq. 4.0 mmol); yield (1.4 g, 97%); pale yellow oil; an inseparable mixture of 1 : 1 *cis* and *trans* diastereomers; R_f = 0.24 (petrol : EtOAc; 3 : 1); ν_{max}/cm^{-1} 1737 (s, C=O), 1663 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.2 mixture of rotamers; minor *trans* isomer as a 1 : 0.4 mixture of rotamers: δ 7.68 (d, *J* = 7.3 Hz, 2H, H2' *cis*), 7.53 (d, *J* = 7.4 Hz, H2' minor rotamers), 7.27 – 7.42 (m, 6H, H3' and H2' *trans*), 7.22 (d, *J* = 7.1 Hz, 2H, H4'), 6.37 (s, H2 *cis* minor rotamer), 6.32 (s, H2 *trans* minor rotamer), 6.17 (s, 1H, H2 *trans* major rotamer), 6.15 (s, 1H, H2 *cis* major rotamer), 5.26 (dd, *J* = 7.0, 1.2 Hz, 1H, H5 *trans*), 5.05 – 5.19 (m, 2H, H7), 4.99 (app t, *J* = 7.0 Hz, 1H, H5 *cis*), 4.11 – 4.16 (m, 2H, $OC\mathit{H}_2CH_3$ *trans*), 4.08 (q, *J* = 7.1 Hz, 2H, $OC\mathit{H}_2CH_3$ *cis*), 3.14 – 3.61 (m, 6H, $H4_B$, $H2''_A$, $H2''_B$), 3.10 (app dd, *J* = 15.3, 13.4 Hz, 2H, $H4_A$), 1.34 (d, *J* = 6.3 Hz, H8 *cis* and *trans* minor rotamers), 1.30 (app dd, *J* = 6.2, 2.1 Hz, 12H, H8 *cis* and *trans* major rotamers), 1.19 – 1.26 (m, 6H, $OCH_2C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 168.5 (C6 major and minor), 166.9, 166.5 (C3'' major and minor), 165.5, 165.4 (C1'' major, and minor), 140.3, 142.2, 142.2 (C1' major, minor and rotamers), 129.4, 129.1 (C3' major and minor), 128.7, 128.6, 128.3, 127.7 (C4' major, minor and rotamers), 127.2, 126.6, 125.1, 124.9 (C2' major, minor and rotamers), 70.8, 70.7, 69.7, 69.7 (C7 major, minor and rotamers), 66.5, 65.8, 65.3 (C5 major, minor and rotamers), 65.2, 64.6, 64.5, (C2 major, minor and rotamers), 62.0, 61.9, 61.7, 61.6 ($O\mathit{C}H_2CH_3$ major, minor and rotamers), 43.6, 43.0, 42.6, 42.3 (C2'' major, minor and rotamers), 34.0, 33.3, 32.2, 31.2 (C4 major, minor and rotamers), 21.9, 21.9, 21.8, 21.8 (C8 major, minor and rotamers), 14.2, 14.2, 14.1, 14.1 ($OCH_2\mathit{C}H_3$ major, minor and rotamers); *m/z* (ESI$^+$) 366 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{24}O_5NS$ [M+H]$^+$ 366.1370; found 366.1371.

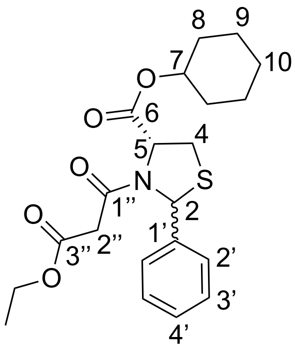
(5*R*)-5-Cyclohexyloxycarbonyl-1-(3-ethoxy-3-oxopropanoyl)-2-(pyridin-2-yl)-1,3-thiazolidine, 17i



Synthesised from **10i** (1 eq. 3.0 mmol); yield (0.8 g, 64%); orange-red oil; reaction from *cis*-**10i** produced a mixture of 4.8 : 1 *cis/trans* diastereomers, reaction from *trans*-**10i** produced a mixture of 0.2 : 1 *cis/trans* diastereomers; R_f = 0.37 (petrol : EtOAc; 1 : 1); $[\alpha]_D^{25}$ = -52.4 (c = 1.13, $CHCl_3$), *cis*; $[\alpha]_D^{25}$ = -67.1 (c = 1.65, $CHCl_3$), *trans*; ν_{max}/cm^{-1} 1737 (s, C=O), 1664 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): *cis* isomer as a 1 : 0.3 mixture of rotamers: δ 8.51 – 8.48 (m, 1H, H6'), 8.09 (d, J = 7.9 Hz, 1H, H3'), 7.69 (app td, J = 7.9, 1.7 Hz, 1H, H4'), 7.17 (dd, J = 7.9, 4.8 Hz, 1H, H5'), 6.39 (s, H2 minor rotamer), 6.14 (s, 1H, H2 major rotamer), 4.90 (dd, J = 8.6, 6.6 Hz, 1H, H5), 4.86 – 4.75 (m, 1H, H7), 4.16 – 3.96 (m, 2H, OCH_2CH$_3$), 3.31 (d, J = 15.6 Hz, 1H, H2''$_B$), 3.26 (dd, J = 12.0, 6.6 Hz, 1H, H4$_B$), 3.15 (dd, J = 12.0, 8.6 Hz, 1H, H4$_A$), 3.07 (d, J = 15.6 Hz, 1H, H2''$_A$), 1.91 – 1.75 (m, 2H, H8), 1.73 – 1.57 (m, 2H, H8), 1.54 – 1.19 (m, 6H, H9 and H10), 1.15 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); *trans* isomer as a 1 : 1 mixture of rotamers: δ 8.48 (d, J = 5.5 Hz, 1H, H6'), 8.42 (d, J = 4.3 Hz, 1H, H6'), 7.65 (app td, J = 7.8, 1.7 Hz, 1H, H4'), 7.55 (app td, J = 7.8, 1.8 Hz, 1H, H4'), 7.22 (d, J = 7.8 Hz, 1H, H3'), 7.18 (app d, J = 7.5 Hz, 2H, H3' and H5'), 7.07 (dd, J = 7.8, 4.3 Hz, 1H, H5'), 6.17 (s, 1H, H2), 6.10 (s, 1H, H2), 5.22 (app d, J = 7.0 Hz, 1H, H5), 5.06 (app d, J = 6.0 Hz, 1H, H5), 4.93 – 4.73 (m, 2H, H7), 4.15 – 4.06 (m, 2H, OCH_2CH$_3$), 3.99 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 3.73 (dd, J = 12.0, 6.1 Hz, 1H, H4$_B$), 3.52 (dd, J = 12.0, 7.1 Hz, 1H, H4$_B$), 3.38 (d, J = 12.3 Hz, 1H, H2''$_B$), 3.36 – 3.28 (m, 2H, H4$_A$), 3.25 (d, J = 15.2 Hz, 1H, H2''$_B$), 3.11 (d, J = 12.3 Hz, 1H, H2''$_A$), 2.98 (d, J = 15.2 Hz, 1H, H2''$_A$), 1.78 (br. s, 4H, H8), 1.66 (br. s, 4H, H8), 1.51 – 1.22 (m, 12H, H9 and H10), 1.18 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), 1.12 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): *cis,* major rotamer: δ 169.2 (C6), 166.3 (C3''), 165.4 (C1''), 159.5 (C2'), 149.5 (C6'), 137.4 (C4'), 123.1 (C3'), 120.6 (C5'), 74.4 (C7), 67.6 (C5), 65.2 (C2), 61.5 (OCH$_2$CH$_3$), 41.9 (C2''), 33.9 (C4), 31.7, 31.2 (C8), 25.2 (C10), 23.5 (C9), 13.9 (OCH$_2$$CH_3$); *trans,* 2 rotamers: δ 169.1, 168.5 (C6), 166.9, 166.2 (C3''), 165.0, 164.7 (C1''), 160.4, 160.3 (C2'), 149.8, 149.3 (C6'), 137.3, 136.7 (C4'), 123.1, 122.4 (C3'), 119.4, 119.4 (C5'), 75.0, 73.9 (C7), 66.5, 66.0 (C5), 64.3, 64.2 (C2), 61.5, 61.3 (OCH$_2$CH$_3$), 43.1, 42.3 (C2''), 33.6 (C4), 31.2, 31.2

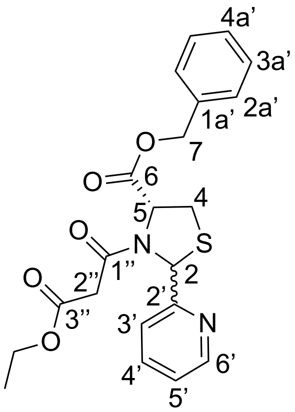
(C8), 25.2, 25.1 (C10), 23.3, 23.3 (C9), 14.0, 13.9 (OCH_2CH_3); *m/z* (ESI^+) 407 ($[M+H]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{20}H_{27}O_5N_2S$ $[M+H]^+$ 407.1635; found 407.1634.

(5*R*)-5-Cyclohexyloxycarbonyl-1-(3-ethoxy-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 17iii



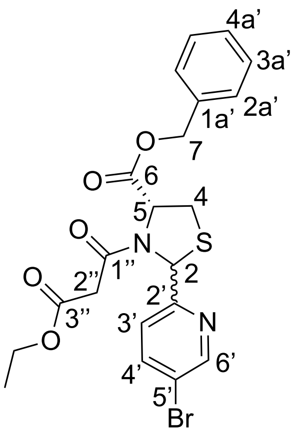
Synthesised from **10iii** (1 eq. 4 mmol); yield (1.6 g, 99%); pale yellow oil; inseparable mixture of 1.3 : 1 *cis* and *trans* diastereomers; R_f = 0.28 (petrol : EtOAc; 4 : 1); ν_{max}/cm^{-1} 1736 (s, C=O), 1663 (s, C=O); ^1H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.2 mixture of rotamers; minor *trans* isomer as a 1 : 0.4 mixture of rotamers: δ 7.68 (d, *J* = 7.3 Hz, 2H, H2' *cis*), 7.53 (d, *J* = 7.2 Hz, H2' minor rotamers), 7.26 – 7.42 (m, 6H, H3' and H2' *trans*), 7.22 (d, *J* = 7.0 Hz, 2H, H4'), 6.37 (s, H2 *trans* minor rotamer), 6.32 (s, H2 *trans* minor rotamer), 6.17 (s, 1H, H2 *trans* major rotamer), 6.15 (s, 1H, H2 *cis* major rotamer), 5.28 (dd, *J* = 6.8, 0.9 Hz, 1H, H5 *trans*), 5.14 (app d, *J* = 5.4 Hz, H5 minor rotamer), 5.01 (app t, *J* = 7.0 Hz, 1H, H5 *cis*), 4.83 – 4.95 (m, 2H, H7), 4.11 – 4.16 (m, 2H, OCH_2CH_3 *trans*), 4.08 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3 *cis*), 3.25 (s, 2H, $H2''_B$ *cis* and *trans*), 3.17 – 3.59 (m, 4H, $H2''_A$, $H4_B$), 3.10 (dd, *J* = 15.3, 13.1 Hz, 2H, $H4_A$), 1.95 (br. s, H8 minor rotamers), 1.86 (br. s, 4H, H8 *trans* major rotamer), 1.73 (br. s, 4H, H8 *cis* major rotamer), 1.34 – 1.59 (m, 12H, H9 and H10), 1.26 – 1.31 (m, OCH_2CH_3 minor rotamers), 1.22 – 1.26 (m, 3H, OCH_2CH_3 *cis* major rotamer), 1.18 – 1.22 (m, 3H, OCH_2CH_3 *trans* major rotamer); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 169.3, 169.2, 168.5 (C6 major, minor and rotamers), 167.4, 167.3, 167.0, 166.5 (C3'' major, minor and rotamers), 165.5, 165.5, 165.3, 164.7 (C1'' major, minor and rotamers), 142.3, 142.2, 140.2, 139.0 (C1' major, minor and rotamers), 129.4, 129.1 (C3' major and minor), 128.7, 128.6, 128.3, 128.1 (C4' major, minor and rotamers), 127.2, 126.6, 125.1, 124.9 (C2' major, minor and rotamers), 75.5, 75.4, 74.6, 74.4 (C7 major, minor and rotamers), 67.4, 66.5, 65.8, 65.4 (C5 major, minor and rotamers), 65.2, 64.7, 64.6, 64.3 (C2 major, minor and rotamers), 62.1, 61.9, 61.7, 61.6 (OCH_2CH_3 major, minor and rotamers), 43.6, 43.0, 42.6, 42.3 (C2'' major, minor and rotamers), 34.1, 33.4, 32.3, 31.6 (C4 major, minor and rotamers), 31.6, 31.5, 31.5, 31.3 (C8 major, minor and rotamers), 25.5, 25.5, 25.3, 25.3 (C10 major, minor and rotamers), 23.8, 23.7, 23.6 (C9 major, minor and rotamers), 14.2, 14.2, 14.2 (OCH_2CH_3 major, minor and rotamers); *m/z* (ESI$^+$) 428 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{27}O_5NNaS$ [M+Na]$^+$ 428.1502; found 428.1497.

(5*R*)-5-Benzyloxycarbonyl-1-(3-ethoxy-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 18i



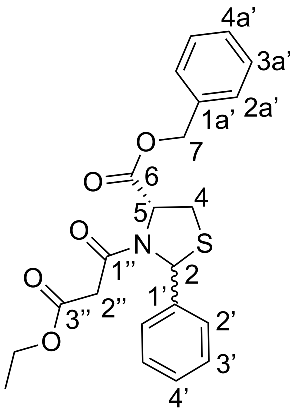
Synthesised from **11i** (1 eq. 4.2 mmol); yield (0.85 g, 49%); pale yellow oil; an inseparable 1.7 : 1 *cis* and *trans* diastereomers; R_f = 0.23 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 1740 (s, C=O), 1664 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.2 mixture of rotamers; minor *trans* isomer as a 1 : 0.7 mixture of rotamers: δ 8.58 – 8.54 (m, 2H, H6' *cis* and *trans*), 8.03 (d, *J* = 7.9 Hz, 2H, H3' *cis* and *trans*), 7.63 (app td, *J* = 7.9, 1.9 Hz, 2H, H4' *cis* and *trans*), 7.42 – 7.30 (m, 10H, H2a', H3a' and H4a', *cis* and *trans*), 7.25 – 7.20 (m, 2H, H5' *cis* and *trans*), 6.48 (s, H2 *cis* minor rotamer), 6.27 (s, H2 *trans* minor rotamer), 6.22 (s, 1H, H2 *cis* major rotamer), 6.19 (s, 1H, H2 *trans* major rotamer), 5.30 – 5.22 (m, 5H, H7 *cis* and *trans* and H5 *trans*), 5.10 (dd, *J* = 8.2, 6.7 Hz, 1H, H5 *cis*), 4.22 – 4.04 (m, 4H, OCH_2CH_3 *cis* and *trans*), 3.65 – 3.08 (m, 8H $H2''_A$, $H2''_B$, $H4_A$ and $H4_B$, *cis* and *trans*), 1.30 – 1.16 (m, 6H, OCH_2CH_3 *cis* and *trans*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.7, 169.6, 169.5, 169.0 (C6 major, minor and rotamers), 166.9, 166.9, 166.4, 166.2 (C3'' major, minor and rotamers), 165.6, 165.2, 165.0, 164.7 (C1'' major, minor and rotamers), 160.2, 160.1, 159.2, 158.4 (C2' major, minor and rotamers), 149.9, 149.5, 149.2, 148.9 (C6' major, minor and rotamers), 137.5, 137.4, 136.9, 136.7 (C4' major, minor and rotamers), 135.4, 135.1, 134.8, 134.7 (C1a' major, minor and rotamers), 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.2, 128.0 (C2a', C3a' and C4a', major, minor and rotamers), 123.2, 123.2, 122.6 (C3' major, minor and rotamers), 120.6, 120.4, 119.7, 119.5 (C5' major, minor and rotamers), 68.1, 67.6, 67.5, 67.4 (C7 major, minor and rotamers), 66.4, 66.0 (C5 *cis* and *trans*), 65.0, 64.2, 64.0 (C2 major, minor and rotamers), 61.7, 61.6, 61.5, 61.4 (O*C*H_2CH_3 major, minor and rotamers), 43.1, 42.7, 42.3, 42.0 (C2'' major, minor and rotamers), 33.9, 33.5, 31.7, 31.3 (C4 major, minor and rotamers), 14.0 (OCH_2*C*H_3 major, minor and rotamers); *m/z* (ESI^+) 415 ($[M+H]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{21}H_{23}O_5N_2S$ $[M+H]^+$ 415.1322; found 415.1321.

(5*R*)-5-(Benzyloxycarbonyl)-2-(5-bromopyridin-2-yl)-1-(3-ethoxy-3-oxopropanoyl)-1,3-thiazolidine, 18ii



Synthesised from **11ii** (1 eq. 4.8 mmol); yield (1.6 g, 68%); pale yellow oil; an inseparable mixture of 1 : 1 *cis* and *trans* diastereomers; R_f = 0.29 (petrol : EtOAc; 3 : 1); ν_{max}/cm^{-1} 1736 (s, C=O), 1663 (s, C=O); ^1H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.3 mixture of rotamers; minor *trans* isomer as a 1 : 0.9 mixture of rotamers: δ 8.60 (d, *J* = 2.2 Hz, H6' *trans* minor rotamer), 8.58 (d, *J* = 2.2 Hz, 1H, H6' *cis* rotamer), 8.53 (d, *J* = 2.2 Hz, 1H, H6' *trans* major rotamer), 7.94 (d, *J* = 8.4 Hz, 1H, H3' *cis*), 7.83 (dd, *J* = 8.3, 2.3 Hz, H4' *trans* minor rotamer), 7.73 (app td, *J* = 8.4, 2.3 Hz, 2H, H4' *cis* and trans major rotamer), 7.37 (br. s, 10H, H2a', H3a' and H4a', *cis*, *trans* and rotamers), 7.20 (d, *J* = 8.3 Hz, 1H, H3' *trans* major rotamer), 7.16 (d, *J* = 8.3 Hz, H3' *trans* minor rotamer), 6.39 (s, H2 *cis* minor rotamer), 6.18 (s, 1H, H2 *trans* major rotamer), 6.15 (s, 1H, H2 *cis* major rotamer), 6.13 (s, H2 *trans* minor rotamer), 5.38 – 5.06 (m, 6H, H7 and H5, *cis*, *trans* and rotamers), 4.25 – 4.00 (m, 4H, OCH_2CH_3, *cis*, *trans* and rotamers), 3.82 (dd, *J* = 11.9, 6.2 Hz, $H4_B$ *trans* minor rotamer), 3.56 (dd, *J* = 12.4, 7.1 Hz, 1H, $H4_B$ *trans* major rotamer), 3.44 – 3.05 (m, 7H, $H2''_B$, $H2''_A$ and $H4_A$, *cis*, *trans* and rotamers + $H4_B$ *cis*), 1.29 – 1.16 (m, 6H, OCH_2CH_3, *cis*, *trans* and rotamers); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.8, 169.7, 169.0 (C6 major, minor and rotamers), 167.0, 166.4, 166.2 (C3'' major, minor and rotamers), 165.6, 165.0, 164.8 (C1'' major, minor and rotamers), 159.2, 158.9, 158.0 (C2' major, minor and rotamers), 151.1, 150.8, 150.7, 150.2 (C6' major, minor and rotamers), 140.2, 140.1, 139.4, 139.3 (C4' major, minor and rotamers), 135.6, 135.2, 134.9 (C1a' major, minor and rotamers), 128.9, 128.8, 128.7, 128.7, 128.5, 128.2 (C2a', C3a' and C4a' major, minor and rotamers), 122.4, 121.3, 121.0 (C3' major, minor and rotamers), 120.4, 119.4 (C5' major *cis* and minor *trans*), 68.4, 67.8, 67.7, 67.3 (C7 major, minor and rotamers), 66.1, 65.6, 65.1 (C5 major, minor and rotamers), 64.3, 64.2 (C2 major *cis* and minor *trans*), 62.0, 61.9, 61.8, 61.7 (OCH_2CH_3 major, minor and rotamers), 43.2, 42.6, 42.2, 41.7 (C2'' major, minor and rotamers), 34.1, 33.8, 32.0, 31.6 (C4 major, minor and rotamers), 14.3, 14.2 (OCH_2*C*H_3 major *cis* and minor *trans*); *m/z* (ESI^+) 515 and 517 ($[M+Na]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{21}H_{21}O_5N_2BrNaS$ $[M+Na]^+$ 515.0247 and 517.0227; found 515.0249 and 517.0225.

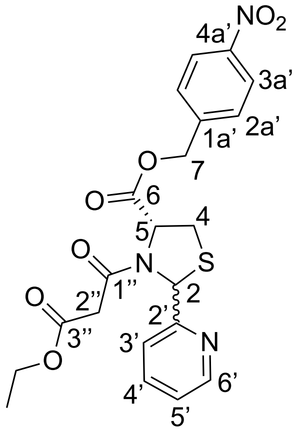
(5*R*)-5-Benzyloxycarbonyl-1-(3-ethoxy-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 18iii



Synthesised from **11iii** (1 eq. 4.4 mmol); yield (1.8 g, 99%); pale greenish yellow oil; an inseparable 1.9 : 1 *cis* and *trans* diastereomers; R_f = 0.21 (petrol : EtOAc; 4 : 1); ν_{max}/cm^{-1} 1739 (s, C=O), 1662 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.1 mixture of rotamers; minor *trans* isomer as a 1 : 0.3 mixture of rotamers: δ 8.09 – 8.12 (m, H2' minor rotamers), 7.56 – 7.65 (m, 2H, H2' *cis* major rotamer), 7.48 (d, *J* = 7.9 Hz, 2H, H2' *trans* major rotamer), 7.28 – 7.41 (m, 14H, H4a', H3', H3a', H2a'), 7.21 (d, *J* = 8.0 Hz, 2H, H4'), 6.36 (s, H2 *cis* minor rotamer), 6.34 (s, H2 *trans* minor rotamer), 6.18 (s, 1H, H2 *trans* major rotamer), 6.14 (s, 1H, H2 *cis* major rotamer), 5.37 (app d, *J* = 6.8 Hz, 1H, H5 *trans*), 5.21 – 5.32 (m, 4H, H7), 5.12 (app t, *J* = 6.8 Hz, 1H, H5 *cis*), 4.10 – 4.21 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3 *cis*), 4.04 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3 *trans*), 3.18 – 3.56 (m, 6H, H2''$_A$, H2''$_B$, H4$_B$), 3.11 (dd, *J* = 15.3, 4.7 Hz, 2H, H4$_A$), 1.24 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3 *cis*), 1.19 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3 *trans*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.6, 169.0 (C6 major and minor), 166.9, 166.4 (C3'' major and minor), 165.7, 165.6 (C1'' major and minor), 142.0, 139.8 (C1' major and minor), 135.5, 135.3 (C1a' major and minor), 130.2, 129.4, 129.1 (C3'), 128.9, 128.8, 128.7, 128.7 (C4a' and C3a'), 128.6, 128.6, 128.5, 128.2 (C4' and

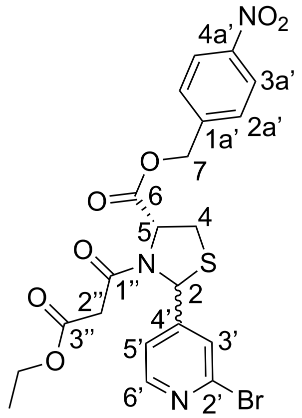
C2a’), 127.2, 126.6, 125.1, 124.9 (C2’ major, minor and rotamers), 67.7, 67.7 (C7 major and minor), 66.5 (C5 major and minor), 65.2, 65.1, 64.3 (C2 major, minor and rotamers), 61.9, 61.7, 61.6 (O*C*H_2CH_3 major, minor and rotamers), 42.6, 42.3 (C2’’ major and minor), 32.2, 31.2 (C4 major and minor), 14.2, 14.1 (OCH_2*C*H_3 major and minor); *m/z* (ESI^+) 436 ($[M+Na]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{22}H_{23}O_5NNaS$ $[M+Na]^+$ 436.1200; found 436.1191.

(5*R*)-1-(3-Ethoxy-3-oxopropanoyl)-5-(4-nitrobenzyloxycarbonyl)-2-(pyridin-2-yl)-1,3-thiazolidine, 19i



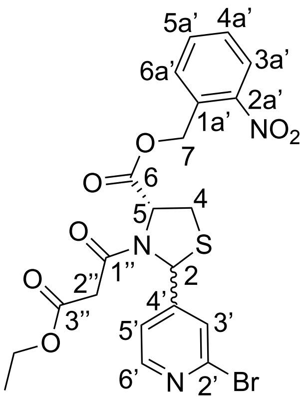
Synthesised from **12i** (1 eq. 2.4 mmol); yield (1.1 g, 99%); pale yellow oil; inseparable 8.8 : 1 *cis* and *trans* diastereomers; R_f = 0.22 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 1741 (s, C=O), 1662 (s, C=O); ^1H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.1 mixture of rotamers; minor *trans* isomer as a 1 : 0.4 mixture of rotamers: δ 8.54 (app dd, *J* = 5.2, 2.1 Hz, 1H, H6’), 8.20 (d, *J* = 8.8 Hz, 2H, H3a’), 7.98 (d, *J* = 7.9 Hz, 1H, H3’), 7.68 (app td, *J* = 7.9, 1.8 Hz, 1H, H4’), 7.54 (d, *J* = 8.8 Hz, 2H, H2a’), 7.22 (app ddd, *J* = 7.9, 5.2, 1.0 Hz, 1H, H5’), 6.47 (s, H2 *cis* minor rotamer), 6.24 (s, H2 *trans* minor rotamer), 6.20 (s, 1H, H2 *cis* major rotamer), 6.17 (s, H2 *trans* major rotamer), 5.38 (d, *J* = 13.5 Hz, 1H, $H7_B$), 5.27 (d, *J* = 13.5 Hz, 1H, $H7_A$), 5.09 (dd, *J* = 8.5, 6.6 Hz, 1H, H5), 4.15 – 4.07 (m, 2H, O$CH_2$$CH_3$), 3.40 (d, *J* = 15.7 Hz, 1H, $H2''_B$), 3.35 (dd, *J* = 12.0, 6.6 Hz, 1H, $H4_B$), 3.26 (dd, *J* = 12.0, 8.5 Hz, 1H, $H4_A$), 3.17 (d, *J* = 15.7 Hz, 1H, $H2''_A$), 1.21 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer, major rotamer: δ 169.7 (C6), 166.4 (C3’’), 165.8 (C1’’), 159.2 (C2’), 149.7 (C6’), 147.8 (C4a’), 142.5 (C1a’), 137.6 (C4’), 128.4 (C3a’), 123.9 (C2a’), 123.4 (C3’), 120.6 (C5’), 67.6 (C7), 65.9 (C5), 64.9 (C2), 61.8 (O*C*H_2CH_3), 42.1 (C2’’), 31.8 (C4), 14.1 (OCH_2*C*H_3); *m/z* (ESI^+) 460 ($[M+H]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{21}H_{22}O_7N_3S$ $[M+H]^+$ 460.1173; found 460.1173.

(5*R*)-2-(2-bromopyridin-4-yl)1-(3-ethoxy-3-oxopropanoyl)-5-(4-nitrobenzyloxycarbonyl)-1,3-thiazolidine, 19iv



Synthesised from **12iv** (1 eq. 5.5 mmol); yield (2.1 g, 71%); pale greenish yellow oil; inseparable 1.5 : 1 *cis* and *trans* diastereomers; R_f = 0.24 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 1738 (s, C=O), 1663 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.5 mixture of rotamers; minor *trans* isomer as a 1 : 0.8 mixture of rotamers: δ 8.40 – 8.27 (m, 2H, H6' *cis* and *trans*), 8.22 (d, *J* = 8.3 Hz, 4H, H3a' *cis* and *trans*), 7.83 (s, 1H, H3' *cis*), 7.62 – 7.47 (m, 4H, H2a' *cis* and *trans*), 7.39 – 7.32 (m, 2H, H5' *cis* and *trans*), 7.19 – 7.10 (m, 1H, H3' *trans*), 6.20 (s, H2 *cis* minor rotamer), 6.15 (s, H2 *trans* minor rotamer), 6.14 (s, 1H, H2 *cis* major rotamer), 6.13 (s, 1H, H2 *trans* major rotamer), 5.46 – 4.99 (m, 6H, H7 and H5), 4.28 – 4.02 (m, 4H, OCH_2CH_3), 3.56 – 3.13 (m, 8H, H2''$_B$ H2''$_A$ H4$_B$ and H4$_A$), 1.32 – 1.16 (m, 6H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 169.2 (C6 major and minor), 167.1, 166.3 (C3'' major and minor), 165.2, 165.0 (C1'' major and minor), 153.7, 153.3, 152.3 (C6' major, minor and rotamers), 151.1, 150.8, 150.4, 150.2 (C4' major, minor and rotamers), 148.0 (C4a'), 143.3, 143.1, 142.7, 142.3, 141.7, 141.5 (C1a' and C2', major, minor and rotamers), 129.0, 128.8, 128.5, 128.4 (C3a' major, minor and rotamers), 126.0, 125.4 (C3' major and minor), 124.1, 124.0 (C2a' major and minor), 121.1, 120.3, 119.4, 119.1 (C5' major, minor and rotamers), 67.0, 66.9, 66.2 (C7 major, minor and rotamers), 65.4, 65.0, 64.3, 64.3 (C5 major, minor and rotamers), 64.2, 64.0, 63.8, 63.3 (C2 major, minor and rotamers), 62.3, 62.2, 62.0, 60.5 (OCH_2CH_3 major, minor and rotamers), 43.3, 43.0, 42.5, 42.2 (C2'' major, minor and rotamers), 34.5, 33.3, 32.0, 31.3 (C4 major, minor and rotamers), 14.3, 14.2, 14.1 (OCH_2CH_3 major, minor and rotamers); *m/z* (ESI$^+$) 560 and 562 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{20}O_7N_3BrNaS$ [M+Na]$^+$ 560.0098 and 562.0078; found 560.0098 and 562.0074.

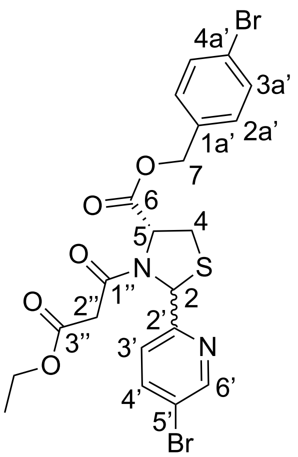
(5*R*)-2-(2-bromopyridin-4-yl)1-(3-ethoxy-3-oxopropanoyl)-5-(2-nitrobenzyloxycarbonyl)-1,3-thiazolidine, 20iv



Synthesised from **13iv** (1 eq. 5.5 mmol); Yield (2.6 g, 88%); pale greenish yellow oil; inseparable 1.1 : 1 *cis* and *trans* diastereomers; R_f = 0.26 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 1738 (s, C=O), 1663 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.6 mixture of rotamers; minor *trans* isomer as a 1 : 0.5 mixture of rotamers: δ 8.38 (d, *J* = 5.1 Hz, H6' *cis* minor rotamer), 8.35 (d, *J* = 5.1 Hz, 1H, H6' *cis* major rotamer), 8.28 (d, *J* = 5.2 Hz, 1H, H6' *trans* major rotamer), 8.19 (d, *J* = 5.1 Hz, H6' *trans* minor rotamer), 8.15 – 8.06 (m, 2H, H3a' *cis* and *trans*), 7.81 (s, 1H, H3' *cis*), 7.73 – 7.49 (m, 6H, H4a', H5a' and H6a', *cis* and *trans*), 7.39 (br. s, 1H, H5' *trans*), 7.34 (br. s, 1H, H5' *cis*), 7.18 (dd, *J* = 5.2, 1.4 Hz, 1H, H3' *trans* major rotamer), 7.13 (dd, *J* = 5.1, 1.4 Hz, H3' *trans* minor rotamer), 6.20 (s, H2 *cis* minor rotamer), 6.15 (s, 1H, H2 *cis* major rotamer), 6.14 (s, 1H, H2 *trans* major rotamer), 5.73 – 5.54 (m, 4H, H7, *cis* and *trans*), 5.36 (app d, *J* = 6.5 Hz, H5 *trans* minor rotamer), 5.28 (dd, *J* = 5.2, 1.8 Hz, 1H, H5 *trans* major rotamer), 5.18 – 5.11 (m, H5 *cis* minor rotamer), 5.03 (dd, *J* = 9.2, 6.6 Hz, 1H, H5 *cis* major rotamer), 4.31 – 3.99 (m, 4H, OCH_2CH_3 *cis* and *trans*), 3.58 – 3.11 (m, 8H, $H2''_B$ $H2''_A$ $H4_B$ and $H4_A$, *cis* and *trans*), 1.34 – 1.14 (m, 6H, OCH_2CH_3 *cis* and *trans*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.2, 169.1 (C6 major and minor), 167.3, 166.4 (C3'' major and minor), 165.2, 165.0 (C1'' major and minor), 153.8, 153.5, 152.3 (C6' major, minor and rotamers), 151.1, 150.9, 150.4, 150.2 (C4' major, minor and rotamers), 148.0 (C2a'), 143.8, 143.3, 143.1, 142.7 (C2' major, minor and rotamers), 134.2, 134.1 (C6a' major and minor), 131.3, 131.2, 130.4, 130.3 (C1a' major, minor and rotamers), 130.2, 130.0, 129.9 (C5a' major, minor and rotamers), 129.7, 129.6, 129.3, 129.2 (C4a' major, minor and rotamers), 126.1, 125.5, 125.3, 124.1 (C3' and C3a', major, minor and rotamers), 121.0, 120.3, 119.4, 119.1 (C5' major, minor and rotamers), 65.6, 65.5, 65.4, 65.1 (C7 major, minor and rotamers), 64.7, 64.6, 64.3, 64.2 (C5 major, minor and rotamers), 64.0, 63.9, 63.3 (C2 major, minor and rotamers), 62.3, 62.2, 62.0

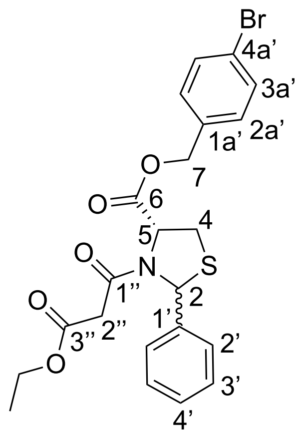
(OCH_2CH_3 major, minor and rotamers), 43.2, 42.9, 42.5, 42.2 (C2'' major, minor and rotamers), 34.5, 33.3, 32.0, 31.4 (C4), 14.3, 14.2 (OCH_2CH_3 major, minor and rotamers); *m/z* (ESI$^+$) 560 and 562 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{20}O_7N_3BrNaS$ [M+Na]$^+$ 560.0098 and 562.0078; found 560.0097 and 562.0072.

(5*R*)-5-(4-Bromobenzyloxycarbonyl)-2-(5-bromopyridin-2-yl)-1-(3-ethoxy-3-oxopropanoyl)-1,3-thiazolidine, 21ii



Synthesised from **14ii** (1 eq. 1 mmol); yield (0.5 g, 80%); yellow oil; an inseparable mixture of 6.5 : 1 *cis* and *trans* diastereomers; R_f = 0.23 (petrol : EtOAc; 3 : 1); ν_{max}/cm^{-1} 1736 (s, C=O), 1662 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.3 mixture of rotamers; minor *trans* isomer as a 1 : 1 mixture of rotamers: δ 8.58 (d, *J* = 2.1 Hz, 1H, H6'), 7.93 (d, *J* = 8.4 Hz, 1H, H3'), 7.77 (dd, *J* = 8.4, 2.2 Hz, 1H, H4'), 7.50 (d, *J* = 8.2 Hz, 2H, H3a'), 7.24 (d, *J* = 8.3 Hz, 2H, H2a'), 6.38 (s, H2 *cis* minor rotamer), 6.15 (s, obscured, H2 *trans* minor rotamer), 6.15 (s, 1H, H2 *cis* major rotamer), 6.13 (s, H2 *trans* major rotamer), 5.18 (app q, *J* = 12.3 Hz, 2H, H7), 5.10 – 5.03 (m, 1H, H5), 4.26 – 4.04 (m, 2H, OCH_2CH_3), 3.37 (d, *J* = 15.6 Hz, 1H, H2''$_B$), 3.34 – 3.29 (m, 1H, H4$_B$), 3.24 – 3.20 (m, 1H, H4$_A$), 3.17 (d, *J* = 15.6 Hz, 1H, H2''$_A$), 1.23 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): major *cis* isomer, major rotamer δ 169.8 (C6), 166.4 (C3''), 165.6 (C1''), 157.9 (C2'), 150.8 (C6'), 140.1 (C4'), 134.2 (C1a'), 132.0 (C3a'), 130.0 (C2a'), 122.8, 122.3 (C3' and C4a'), 120.5 (C5'), 67.2 (C7), 66.9 (C5), 65.0 (C2), 61.9 (OCH_2CH_3), 42.1 (C2''), 31.9 (C4), 14.1 (OCH_2CH_3); *m/z* (ESI$^+$) 571 (50%), 573 ([M+H]$^+$, 100%) and 575 (50%); HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{21}O_5N_2Br_2S$ [M+H]$^+$ 570.9532, 572.9512 and 574.9493; found 570.9532, 572.9510 and 574.9486.

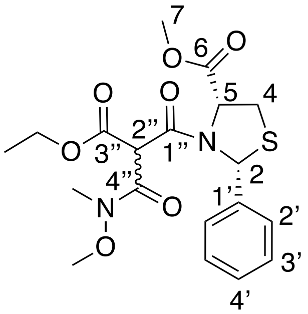
(5*R*)-5-(4-Bromobenzyloxycarbonyl)-1-(3-ethoxy-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 21iii



Synthesised from **14iii** (1 eq. 3.7 mmol); yield (1.1 g, 61%); yellow oil; an inseparable mixture of 2.2 : 1 *cis* and *trans* diastereomers; R_f = 0.21 (petrol : EtOAc; 4 : 1); ν_{max}/cm^{-1} 1735 (s, C=O), 1660 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): major *cis* isomer as a 1 : 0.1 mixture of rotamers; minor *trans* isomer as a 1 : 0.2 mixture of rotamers: δ 7.56 – 7.63 (m, 4H, H2' and H3a' *trans*), 7.44 – 7.54 (m, 4H, H2' and H3a' *cis*), 7.27 – 7.40 (m, 6H, H4' and H3'), 7.17 – 7.25 (m, 4H, H2a'), 6.36 (s, H2 *cis* minor rotamer), 6.32 (s, H2 *trans* minor rotamer), 6.18 (s, 1H, H2 *trans* major rotamer), 6.14 (s, 1H, H2 *cis* major rotamer), 5.34 (app d, *J* = 7.8 Hz, 1H, H5 *trans*), 5.15 – 5.28 (m, 4H, H7), 5.10 (app t, *J* = 6.8 Hz, 1H, H5 *cis*), 4.23 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3 *cis*), 4.05 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3 *trans*), 3.07 – 3.54 (m, 8H, $H4_A$, $H4_B$, $H2''_A$, $H2''_B$), 1.29 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3 *cis*), 1.19 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3 *trans*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.9, 169.6, 168.9 (C6 major, minor and rotamers), 166.8, 166.3 (C3'' major and minor), 165.7, 165.7 (C1'' major and minor), 141.8, 139.8 (C1' major and minor), 134.6, 134.4 (C1a' major and minor), 132.0, 131.9, 131.9, 131.7 (C3a' major, minor and rotamers), 130.2, 130.1, 129.9 (C2a' major, minor and rotamers), 129.4, 129.1 (C3' major and minor), 128.8, 128.7 (C4' major and minor), 127.2, 126.6, 125.1, 124.9 (C2' major, minor and rotamers), 122.7, 122.5 (C4a' major and minor), 67.4, 66.8, 66.5, 66.4 (C7 major and minor), 65.2, 65.0 (C5 major and minor), 64.7, 64.3 (C2 major and minor), 62.3, 61.8, 61.6 (OCH_2CH_3 major, minor and rotamers), 44.8, 42.5, 42.3, 41.6 (C2'' major and minor), 32.2, 31.4, 31.2, 29.4 (C4 major, minor and rotamers), 14.2, 14.2, 14.1 (OCH_2CH_3 major, minor and rotamers); *m/z* (ESI$^+$) 492 and 494 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{22}H_{23}O_5NBrS$ [M+H]$^+$ 492.0475 and 494.0455; found 492.0479 and 494.0457.

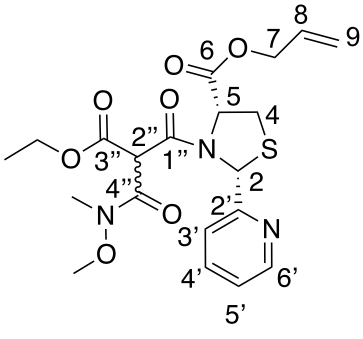
Tricarbonyl *N*-acylthiazolidines **23-30** were synthesised from the respective *N*-acylthiazolidines **15-21** by General Procedure **E**.

(2*R*,5*R*)-1-(3-Ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-5-methoxycarbonyl-2-phenyl-1,3-thiazolidine, 23iii



Synthesised from **2iii** (1 eq. 3.4 mmol); yield (1.1 g, 77%); pale yellow oil; an inseparable 1 : 1 C2'' *R/S* diastereomers; R_f = 0.20 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 1745 (s, C=O), 1669 (s, C=O); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.60 – 7.69 (m, 4H, H2'), 7.27 – 7.38 (m, 6H, H4' and H3'), 5.95 (s, 1H, H2, C2'' *R*), 5.77 (s, 1H, H2, C2'' *S*), 5.15 (app q, *J* = 6.1 Hz, 2H, H5), 4.44 (s, 1H, H2'', C2'' *S*), 4.35 (s, 1H, H2'', C2'' *R*), 4.16 – 4.30 (m, 2H, OC*H*$_2$CH$_3$), 3.97 – 4.09 (m, 2H, OC*H*$_2$CH$_3$), 3.78 (s, 6H, H7), 3.31 (s, 3H, NOC*H*$_3$), 3.27 (s, 3H, NOC*H*$_3$), 3.09 – 3.31 (m, 4H, H4), 3.07 (s, 3H, NC*H*$_3$), 3.02 (s, 3H, NC*H*$_3$), 1.26 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 1.13 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 170.1, 169.9 (C6), 165.2, 165.2 (C3''), 164.6, 164.0 (C1''), 163.9, 163.6 (C4''), 139.4, 139.2 (C1'), 129.0, 128.9 (C3'), 128.7 (C4'), 126.9, 126.5 (C2'), 66.1, 66.0 (C5), 65.1, 64.9 (C2), 62.3, 61.8 (O*C*H$_2$CH$_3$), 61.0, 60.9 (NO*C*H$_3$), 57.5, 56.8 (C2''), 52.7, 52.6 (C7), 32.6 (C4), 32.1, 32.0 (N*C*H$_3$), 14.1, 13.8 (OCH$_2$*C*H$_3$); *m/z* (ESI$^+$) 425 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{19}H_{25}O_7N_2S$ [M+H]$^+$ 425.1377; found 425.1378.

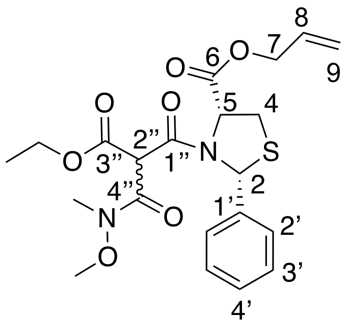
(2*R*,5*R*)-5-Allyloxycarbonyl-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-2-(pyridin-2-yl)-1,3-thiazolidine, 24i



Synthesised from **15i** (1 eq. 1.7 mmol); yield (364 mg, 47%); orange oil; an inseparable 0.8 : 1 C2'' *R/S* diastereomers; R_f = 0.22 (petrol : EtOAc; 2 : 3); ν_{max}/cm^{-1} 1745 (s, C=O), 1670 (s, C=O); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.54 – 8.51 (m, 1H, H6 minor), 8.50 – 8.47 (m, 1H, H6' major), 8.10 (app t, *J* = 8.1 Hz, 2H, H3'), 7.78 – 7.68 (m, 2H, H4'), 7.22 (dd, *J* = 8.4, 4.9 Hz, 2H, H5'), 6.00 (s, 1H, H2 major, C2'' *S*), 5.95 (s, 1H, H2 minor, C2'' *R*), 5.94 – 5.82 (m, 2H, H8), 5.36 – 5.27 (m, 2H, H9$_B$), 5.24 – 5.19 (m, 2H, H9$_A$), 5.18 – 5.08 (m, 2H, H5), 4.66 (app t,

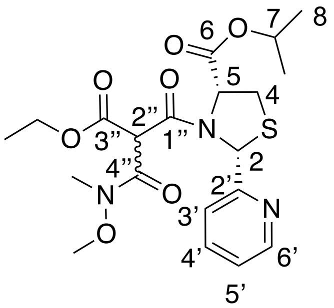
J = 5.8 Hz, 4H, H7), 4.62 (s, 1H, H2'' minor, C2'' *R*), 4.48 (s, 1H, H2'' major, C2'' *S*), 4.30 – 4.16 (m, 2H, OC*H*$_2$CH$_3$ major), 4.02 (q, J = 7.1 Hz, 2H, OC*H*$_2$CH$_3$ minor), 3.48 (s, 3H, NOC*H*$_3$ major), 3.31 (s, 3H, NOC*H*$_3$ minor), 3.30 – 3.22 (m, 4H, H4), 3.13 (s, 3H, NC*H*$_3$ major), 3.01 (s, 3H, NC*H*$_3$ minor), 1.26 (t, J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$ major), 1.11 (t, J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$ minor); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 169.5, 169.4 (C6), 164.9, 164.8 (C3''), 164.5, 164.0 (C1''), 163.8, 163.7 (C4''), 159.3, 159.0 (C2'), 149.5, 149.3 (C6'), 137.7, 137.3 (C4'), 131.4 (C8), 123.4 (C3'), 121.1 (C5'), 118.8 (C9), 67.4 (C7), 66.3 (C5), 65.1 (C2), 62.5, 61.9 (O*C*H$_2$CH$_3$), 61.2, 61.1 (NO*C*H$_3$), 57.2, 56.8 (C2''), 32.7, 32.2 (C4), 31.9, 31.8 (N*C*H$_3$), 14.0, 13.9 (OCH$_2$*C*H$_3$); *m/z* (ESI$^+$) 452 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{26}O_7N_3S$ [M+H]$^+$ 452.1486; found 452.1485.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 24iii



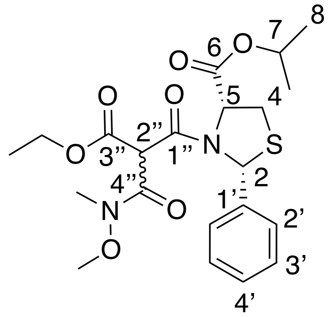
Synthesised from **15iii** (1 eq. 3.3 mmol); yield (804 mg, 54%); pale yellow oil; an inseparable 1 : 1 C2'' *R/S* diastereomers; R_f = 0.21 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 1745 (s, C=O), 1670 (s, C=O); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.62 – 7.74 (m, 4H, H2'), 7.35 – 7.42 (m, 4H, H3'), 7.29 – 7.35 (m, 2H, H4'), 6.00 (s, 1H, H2, C2'' *R*), 5.89 – 6.00 (m, 2H, H8), 5.82 (s, 1H, H2, C2'' *S*), 5.31 – 5.39 (m, 1H, H5), 5.38 (d, J = 17.2 Hz, 2H, H9$_B$), 5.28 (app dd, J = 10.5, 1.2 Hz, 2H, H9$_A$), 5.24 (dd, J = 6.1, 3.5 Hz, 1H, H5), 4.71 – 4.76 (m, 4H, H7), 4.49 (s, 1H, H2'', C2'' *S*), 4.39 (s, 1H, H2'', C2'' *R*), 4.23 – 4.37 (m, 2H, OC*H*$_2$CH$_3$), 4.09 (q, J = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.34 – 3.38 (m, 5H, NOC*H*$_3$ and H4$_B$), 3.31 (s, 3H, NOC*H*$_3$), 3.18 (dd, J = 15.2, 3.5 Hz, 2H, H4$_A$), 3.12 (s, 3H, NC*H*$_3$), 3.08 (s, 3H, NC*H*$_3$), 1.33 (t, J = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.18 (t, J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 169.5, 169.4 (C6), 165.5 (C3''), 164.3 (C1''), 164.1, 163.8 (C4''), 139.6, 139.3 (C1'), 131.7 (C8), 129.2, 129.1 (C3'), 128.9 (C4'), 127.2, 126.7 (C2'), 119.0, 119.0 (C9), 66.5, 66.5, 66.4, 66.2 (C5 and C7), 65.4, 65.2 (C2), 62.6, 62.1 (O*C*H$_2$CH$_3$), 61.2, 61.1 (NO*C*H$_3$), 57.8, 57.1 (C2''), 32.9 (C4), 32.4, 32.3 (NCH_3), 14.3, 14.1 (OCH_2CH_3); *m/z* (ESI$^+$) 473 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{26}O_7N_2NaS$ [M+Na]$^+$ 473.1353; found 473.1344.

(2*R*,5*R*)-1-(3-Ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-5-isopropoxycarbonyl-2-(pyridin-2-yl)-1,3-thiazolidine, 25i



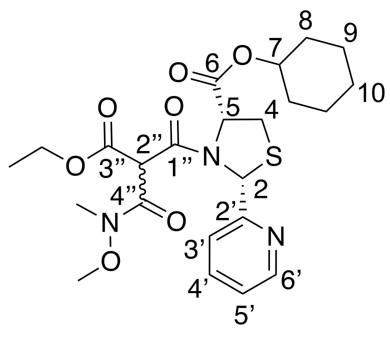
Synthesised from **16i** (1 eq. 3.0 mmol); yield (740 mg, 54%); orange oil; an inseparable 0.7 : 1 C2'' *R/S* diastereomers; R_f = 0.17 (petrol : EtOAc; 2 : 3); ν_{max}/cm^{-1} 1739 (s, C=O), 1668 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 – 8.45 (m, 2H, H6'), 8.19 (d, *J* = 7.7 Hz, 2H, H3'), 7.81 – 7.64 (m, 2H, H4'), 7.29 – 7.20 (m, 2H, H5'), 6.02 (s, 1H, H2 major, C2'' *S*), 5.96 (s, 1H, H2 minor, C2'' *R*), 5.15 – 4.97 (m, 4H, H5 and H7), 4.62 (s, 1H, H2'' minor, C2'' *R*), 4.49 (s, 1H, H2'' major, C2'' *S*), 4.33 – 4.17 (m, 2H, OCH_2CH_3 major), 4.07 – 3.98 (m, 2H, OCH_2CH_3 minor), 3.67 (s, 3H, NOCH_3 minor), 3.50 (s, 3H, NOCH_3 major), 3.36 – 3.17 (m, 4H, H4), 3.14 (s, 3H, NCH_3 major), 3.03 (s, 3H, NCH_3 minor), 1.32 – 1.11 (m, 18H, OCH_2CH_3 and H8); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.9, 168.7 (C6), 164.6, 164.6 (C3''), 163.5, 163.5 (C1''), 163.2 (C4''), 159.1, 158.9 (C2'), 149.1, 149.0 (C6'), 137.3, 137.0 (C4'), 123.1 (C3'), 120.7 (C5'), 69.2 (C7), 67.1, 67.1 (C5), 65.2, 65.2 (C2), 62.1, 61.4 (OCH_2CH_3), 60.9, 60.8 (NOCH_3), 56.8, 56.4 (C2''), 32.3, 31.8 (C4), 31.5, 31.4 (NCH_3), 21.3, 21.3 (C8), 13.7, 13.5 (OCH_2CH_3); *m/z* (ESI$^+$) 454 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{28}O_7N_3S$ [M+H]$^+$ 454.1642; found 454.1638.

(2*R*,5*R*)-1-(3-Ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-5-isopropoxycarbonyl 2-phenyl-1,3-thiazolidine, 25iii



Synthesised from **16iii** (1 eq. 4.0 mmol); yield (1.1 g, 61%); pale greenish yellow oil; an inseparable 0.8 : 1 C2'' *R/S* diastereomers; R_f = 0.30 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 1739 (s, C=O), 1668 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 – 7.74 (m, 4H, H2'), 7.35 – 7.42 (m, 4H, H3'), 7.27 – 7.35 (m, 2H, H4'), 6.00 (s, 1H, H2, C2'' *R*), 5.81 (s, 1H, H2, C2'' *S*), 5.13 (app q, *J* = 6.4 Hz, 4H, H5 and H7), 4.49 (s, 1H, H2'', C2'' *S*), 4.41 (s, 1H, H2'', C2'' *R*), 4.23 – 4.36 (m, 2H, OCH_2CH$_3$), 4.08 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 3.36 (s, 3H, NOCH_3), 3.32 (s, 3H, NOCH_3), 3.13 – 3.28 (m, 4H, H4), 3.12 (s, 3H, NCH_3), 3.08 (s, 3H, NCH_3), 1.23 – 1.37 (m, 15H, OCH$_2$CH_3 and H8), 1.17 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.3, 169.1 (C6), 165.4 (C3''), 164.2 (C1''), 163.7 (C4''), 139.9, 139.6 (C1'), 129.1, 129.1 (C3'), 128.8 (C4'), 127.2, 126.7 (C2'), 69.8, 69.7 (C7), 66.4, 66.2 (C5), 65.8, 65.6 (C2), 62.6, 62.0 (O*C*H$_2$CH$_3$), 61.2, 61.1 (NO*C*H$_3$), 57.7, 57.1 (C2''), 32.4, 32.2 (N*C*H$_3$ and C4), 21.9 (C8), 14.3, 14.1 (OCH$_2$*C*H$_3$); *m/z* (ESI$^+$) 453 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{29}O_7N_2S$ [M+H]$^+$ 453.1690; found 453.1689.

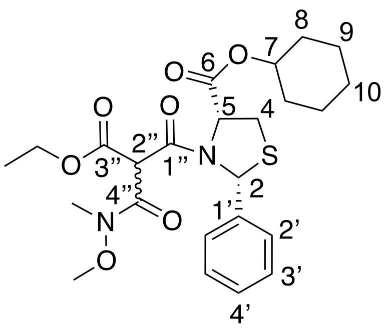
(2*R*,5*R*)-5-Cyclohexyloxycarbonyl-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 26i



Yield (345 mg, 68%), from *cis*-**17i** (1 eq. 1.0 mmol); yellow oil; an inseparable 0.7 : 1 C2'' *R/S* diastereomers; R_f = 0.28 (petrol : EtOAc; 2 : 3); ν_{max}/cm^{-1} 1740 (s, C=O), 1669 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, *J* = 5.6 Hz, 1H, H6 minor), 8.50 (d, *J* = 5.6 Hz, 1H, H6' major), 8.17 (app dd, *J* = 7.9, 3.9 Hz, 2H, H3'), 7.78 – 7.68 (m, 2H, H4'), 7.22 (dd, *J* = 7.9, 5.6 Hz, 2H, H5'), 6.00 (s, 1H, H2 major, C2'' *S*), 5.94 (s, 1H, H2 minor, C2'' *R*), 5.11 – 5.00 (m, 2H, H5), 4.88 – 4.77 (m, 2H, H7), 4.60 (s, 1H, H2'' minor, C2'' *R*), 4.48 (s, 1H, H2'' major, C2'' *S*), 4.31 – 4.17 (m, 2H, OCH_2CH$_3$ major), 4.02 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$ minor), 3.48 (s, 3H, NOCH_3 major), 3.32 (s, 3H, NOCH_3 minor), 3.30 – 3.15 (m, 4H, H4), 3.13 (s, 3H, NCH_3 major), 3.02

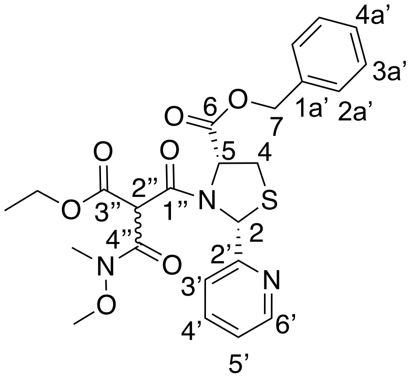
(s, 3H, 3H, NCH_3 minor), 1.92 – 1.77 (m, 4H, H8), 1.69 (br. s, 4H, H8), 1.55 – 1.30 (m, 12H, H9 and H10), 1.26 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.11 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.2, 169.0 (C6), 165.0, 164.9 (C3''), 163.8 (C1''), 163.5 (C4''), 159.5, 159.2 (C2'), 149.4, 149.3 (C6'), 137.6, 137.2 (C4'), 123.3 (C3'), 121.2, 121.1 (C5'), 74.4 (C7), 67.5, 67.5 (C5), 65.5, 65.5 (C2), 62.5, 61.8 (OCH_2CH_3), 61.2, 61.1 ($NOCH_3$), 57.2, 56.8 (C2), 32.7, 32.2 (C4), 31.9, 31.9 (NCH_3), 31.3 (C8), 25.3 (C10), 23.5 (C9), 14.0, 13.9 (OCH_2CH_3); *m/z* (ESI^+) 494 ($[M+H]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{23}H_{32}O_7N_3S$ $[M+H]^+$ 494.1955; found 494.1955.

(2*R*,5*R*)-5-Cyclohexyloxycarbonyl-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 26iii



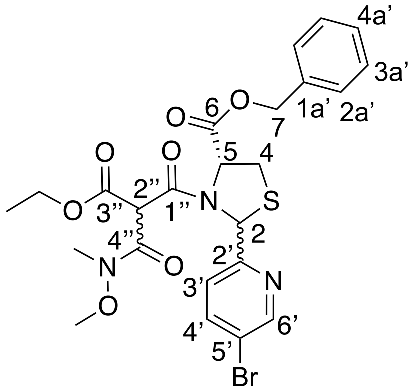
Synthesised from **17iii** (1 eq. 4.0 mmol); yield (1.0 g, 51%); pale yellow oil; an inseparable 0.8 : 1 C2'' *R/S* diastereomers, a mixture of rotamers; R_f = 0.46 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 1741 (s, C=O), 1668 (s, C=O); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64 – 7.75 (m, 4H, H2'), 7.35 – 7.43 (m, 4H, H3'), 7.29 – 7.35 (m, 2H, H4'), 6.01 (s, 1H, H2, C2'' *R*), 5.82 (s, 1H, H2, C2'' *S*), 5.22 – 5.32 (m, 1H, H5), 5.16 (app q, J = 6.1 Hz, 1H, H5), 4.80 – 4.98 (m, 2H, H7), 4.49 (s, 1H, H2'', C2'' *S*), 4.40 (s, 1H, H2'', C2'' *R*), 4.25 – 4.33 (m, 2H, OCH_2CH_3), 4.09 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 3.36 (s, 3H, $NOCH_3$), 3.32 (s, 3H, $NOCH_3$), 3.13 – 3.30 (m, 4H, H4), 3.12 (s, 3H, NCH_3), 3.08 (s, 3H, NCH_3), 1.81 – 2.00 (m, 4H, H8), 1.75 (br. s, 4H, H8), 1.43 – 1.61 (m, 6H, H9 and H10), 1.35 – 1.43 (m, 6H, H9 and H10), 1.33 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.18 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.6, 169.4, 169.2, 169.1 (C6), 165.5, 165.5, 165.0 (C3''), 164.2, 164.1 (C1''), 163.7 (C4''), 142.1, 139.9, 139.6 (C1'), 129.4, 129.4, 129.1, 129.1 (C3'), 128.8, 128.7 (C4'), 127.2, 126.7, 125.3, 125.1 (C2'), 75.6, 75.3, 74.6, 74.4 (C7), 66.4, 66.2 (C5), 65.8, 65.6 (C2), 62.6, 62.5, 62.1, 62.0 (OCH_2CH_3), 61.5, 61.2, 61.1, 60.8 ($NOCH_3$), 57.8, 57.2, 57.1 (C2''), 34.4, 33.6, 33.2, 32.9 (C4), 32.5, 32.3 (NCH_3), 31.6, 31.6, 31.5, 31.5 (C8), 25.5, 25.5, 25.4, 25.3 (C10), 23.9, 23.8, 23.7, 23.6 (C9), 14.3, 14.3, 14.1, 14.0 (OCH_2*C*H_3); *m/z* (ESI$^+$) 493 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{33}O_7N_2S$ [M+H]$^+$ 493.2003; found 493.2001.

(2*R*,5*R*)-5-Benzyloxycarbonyl-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-2-(pyridin-2-yl)-1,3-thiazolidine, 27i



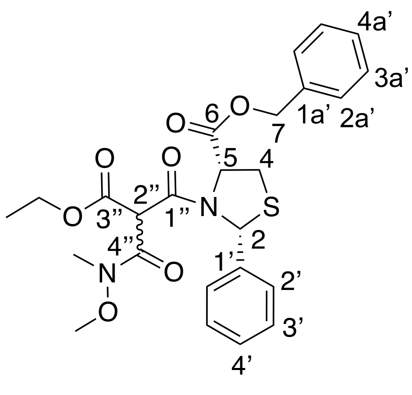
Synthesised from **18i** (1 eq. 1.4 mmol); yield (375 mg, 53%); bright yellow oil; an inseparable 0.7 : 1 C2'' *R/S* diastereomers; R_f = 0.16 (petrol : EtOAc; 2 : 3); ν_{max}/cm^{-1} 1743 (s, C=O), 1663 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, *J* = 4.6 Hz, 1H, H6' minor), 8.49 (d, *J* = 6.4 Hz, 1H, H6' major), 8.03 (d, *J* = 7.9 Hz, 2H, H3'), 7.65 – 7.52 (m, 2H, H4'), 7.35 (app t, *J* = 8.4 Hz, 10H, H2a', H3a' and H4a'), 7.24 – 7.17 (m, 2H, H5'), 6.02 (s, 1H, H2 major, C2'' *S*), 5.98 (s, 1H, H2 minor, C2'' *R*), 5.26 – 5.14 (m, 6H, H5 and H7), 4.64 (s, 1H, H2'' minor, C2'' *R*), 4.51 (s, 1H, H2'' major, C2'' *S*), 4.36 – 4.15 (m, 2H, 2H, OC*H*$_2$CH$_3$ major), 4.05 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$ minor), 3.50 (s, 3H, NOC*H*$_3$ major), 3.34 – 3.27 (m, 4H, H4), 3.26 (s, 3H, NOC*H*$_3$ minor), 3.16 (s, 3H, NC*H*$_3$ major), 3.04 (s, 3H, NC*H*$_3$ minor), 1.29 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 1.14 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.7, 169.5 (C6), 165.0, 164.9 (C3''), 164.2 (C1''), 163.9 (C4''), 159.3, 159.1 (C2'), 149.5, 149.3 (C6'), 137.7, 137.3 (C4'), 135.2, 135.2 (C1a'), 128.7, 128.6, 128.5, 128.5, 128.4, 128.4 (C2a', C3a' and C4a'), 123.4 (C3'), 121.2 (C5'), 67.7, 67.6, 67.5 (C7 and C5), 65.3 (C2), 62.6, 62.0 (O*C*H$_2$CH$_3$), 61.3, 61.1 (NO*C*H$_3$), 57.3, 56.9 (C2''), 32.8, 32.2 (C4), 32.0, 31.9 (N*C*H$_3$), 14.1, 14.0 (OCH$_2$*C*H$_3$); *m/z* (ESI$^+$) 502 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{28}O_7N_3S$ [M+H]$^+$ 502.1642; found 502.1639.

(5*R*)-5-Benzyloxycarbonyl-2-(5-bromopyridin-2-yl)-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-1,3-thiazolidine, 27ii



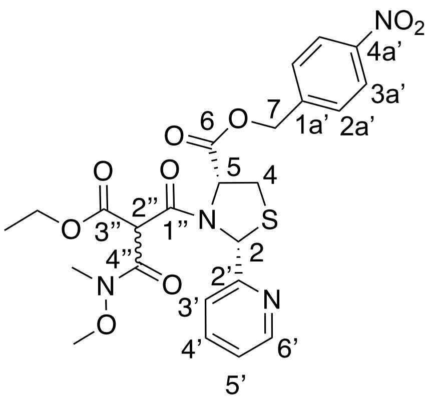
Synthesised from **18ii** (1 eq. 6.5 mmol); yield (1.5 g, 40%); yellow oil; an inseparable mixtures of diastereomers, 0.7 : 1 C2'' *R/S,* 2.1 : 1 *cis*/*trans*-2,5; R_f = 0.19 (petrol : EtOAc; 13 : 7); ν_{max}/cm^{-1} 1742 (s, C=O), 1668 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 – 8.51 (m, 2H, H6'), 7.96 (app t, *J* = 8.3 Hz, 2H, H3'), 7.79 – 7.64 (m, 2H, H4'), 7.38 – 7.33 (m, 10H, H2a', H3a' and H4a'), 5.98 (s, 1H, H2 *cis*, C2'' *S*), 5.95 (s, 1H, H2 *cis*, C2'' *R*), 5.25 – 5.15 (m, 6H, H5 and H7), 4.64 (s, 1H, H2'', C2'' *R*), 4.52 (s, 1H, H2'', C2'' *S*), 4.33 – 4.17 (m, 2H, OCH_2CH$_3$), 4.16 – 4.03 (m, 2H, OCH_2CH$_3$), 3.58 (s, 3H, NOCH_3), 3.55 (s, 3H, NOCH_3), 3.42 – 3.21 (m, 4H, H4), 3.17 (s, 3H, NCH_3), 3.06 (s, 3H, NCH_3), 1.32 – 1.22 (m, 3H, OCH$_2$CH_3), 1.18 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.8, 169.6, 169.6 (C6), 164.8, 164.4, 164.1, 163.9, 163.8, 163.7 (C3'', C1'' and C4''), 158.8, 157.9, 157.7 (C2'), 150.5, 150.5, 150.4 (C6'), 140.2, 139.8, 139.6, 139.4 (C4'), 135.2 (C1a'), 128.9, 128.8, 128.8, 128.7, 128.6, 128.5 (C2a', C3a' and C4a'), 122.8 (C3'), 120.9, 120.5 (C5'), 68.4, 67.8 (C6), 67.1, 67.0 (C5), 65.3, 63.9 (C2), 62.7, 62.2 (OCH$_2$CH$_3$), 61.4, 61.1 (NOCH$_3$), 58.3, 57.4, 57.0 (C2''), 33.5, 32.8 (C4), 32.1, 32.0 (NCH$_3$), 14.3, 14.2, 14.0 (OCH$_2$$CH_3$); *m/z* (ESI$^+$) 602 and 604 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{26}O_7N_3NaS$ [M+Na]$^+$ 602.0567 and 604.0548; found 602.0565 and 604.0542.

(2*R*,5*R*)-5-Benzyloxycarbonyl-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 27iii



Synthesised from **18iii** (1 eq. 4.6 mmol); yield (1.3 g, 57%); colourless oil; an inseparable 0.8 : 1 C2'' *R/S* diastereomers; R_f = 0.31 (petrol : EtOAc; 1 : 1); ν_{max}/cm^{-1} 1744 (s, C=O), 1671 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 – 7.65 (m, 4H, H2'), 7.34 – 7.42 (m, 12H, H3', H3a', H2a'), 7.28 – 7.33 (m, 4H, H4' and H4a'), 5.99 (s, 1H, H2, C2'' *R*), 5.81 (s, 1H, H2, C2'' *S*), 5.20 – 5.32 (m, 6H, H5 and H7), 4.46 (s, 1H, H2'', C2'' *S*), 4.38 (s, 1H, H2'', C2'' *R*), 4.26 – 4.32 (q, *J* = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 4.09 (q, *J* = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 3.25 – 3.38 (obscured, 4H, H4), 3.34 (s, 3H, NOC*H*$_3$), 3.20 (s, 3H, NOC*H*$_3$), 3.07 (s, 3H, NC*H*$_3$), 3.12 (s, 3H, NC*H*$_3$), 1.32 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.17 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 169.7, 169.5 (C6), 165.4, 165.3 (C3''), 164.9, 164.3 (C1''), 164.1, 163.8 (C4''), 139.4, 139.1 (C1'), 135.3, 135.2 (C1a'), 129.1, 129.0 (C3'), 128.8, 128.7 (C4a' and C3a'), 128.6, 128.5 (C4' and C2a'), 127.1, 126.6 (C2'), 67.8, 67.7 (C7), 66.4, 66.2 (C5), 65.5, 65.3 (C2), 62.5, 62.0 (O*C*H$_2$CH$_3$), 61.0, 61.0 (NO*C*H$_3$), 57.7, 57.0 (C2''), 32.8, 32.4 (C4), 32.2, 32.2 (N*C*H$_3$), 14.2, 14.0 (OCH$_2$*C*H$_3$); *m/z* (ESI$^+$) 523 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{25}H_{28}O_7N_2NaS$ [M+Na]$^+$ 523.1509; found 523.1508.

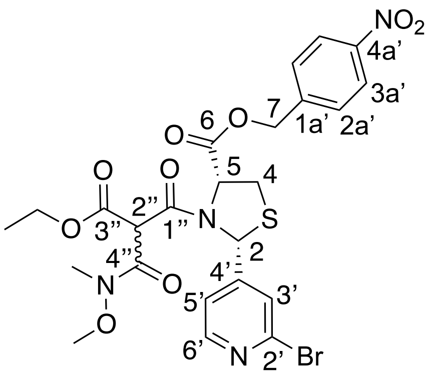
(2*R*,5*R*)-1-(3-Ethoxy-2-(methoxy(methyl)carbamoyl)-5-(4-nitrobenzyloxycarbonyl)-3-oxopropanoyl)-2-(pyridin-2-yl)-1,3-thiazolidine, 28i



Synthesised from **19i** (1 eq. 2.4 mmol); yield (745 mg, 57%); yellow oil; an inseparable 0.7 : 1 C2'' *R/S* diastereomers; *R*$_f$ = 0.23 (petrol : EtOAc; 3 : 7); ν_{max}/cm^{-1} 1747 (s, C=O), 1671 (s, C=O); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.54 (d, *J* = 4.7 Hz, 1H, H6' minor), 8.50 (d, *J* = 4.7 Hz, 1H, H6' major), 8.18 (d, *J* = 8.7 Hz, 4H, H3a'), 8.00 (d, *J* = 7.9 Hz, 2H, H3'), 7.67 (app dd, *J* = 7.9, 1.7 Hz, 2H, H4'), 7.56 (d, *J* = 8.7 Hz, 4H, H2a'), 7.23 (dd, *J* = 7.9, 4.7 Hz, 2H, H5'), 6.04 (s, 1H, H2 major, C2'' *S*), 6.02 (s, 1H, H2 minor, C2'' *R*), 5.39 – 5.25 (m, 4H, H7), 5.24 – 5.14 (m, 2H, H5), 4.69 (s, 1H, H2'' minor, C2'' *R*), 4.59 (s, 1H, H2'' major, C2'' *S*), 4.11 – 3.99 (m, 4H, OC*H*$_2$CH$_3$), 3.54 (s, 3H, NOC*H*$_3$ major), 3.43 – 3.31 (m, 4H, H4), 3.30 (s, 3H, NOC*H*$_3$ minor), 3.17 (s, 3H, NC*H*$_3$ major), 3.02 (s, 3H, NC*H*$_3$ minor), 1.28 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$ minor), 1.12 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$ major); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 169.4, 169.3 (C6), 164.8, 164.6 (C3''), 164.2, 164.1 (C1''), 163.8, 163.7 (C4''), 159.0, 158.8 (C2'), 149.4, 149.3 (C6'), 147.5 (C4a'), 142.5 (C1a'), 137.5, 137.2 (C4'), 128.3, 128.2 (C3a'), 123.6 (C2a'), 123.4, 123.3 (C3'), 120.8, 120.7 (C5'), 67.3, 67.2 (C7), 65.8 (C5), 65.0, 64.9 (C2), 62.5, 61.8, (O*C*H$_2$CH$_3$)

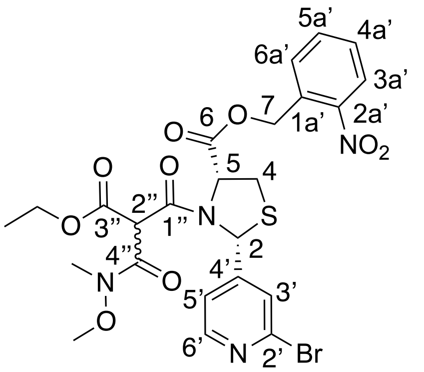
61.2, 60.9 (NOCH_3), 57.1, 56.6 (C2''), 32.6, 32.1 (C4), 31.6, 31.6 (NCH_3), 13.9, 13.8 (OCH_2CH_3); *m/z* (ESI$^+$) 547 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{27}O_9N_4S$ [M+H]$^+$ 547.1493; found 547.1487.

(2*R*,5*R*)-2-(2-Bromopyridin-4-yl)-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-5-(4-nitrobenzyloxycarbonyl)-3-oxopropanoyl)-1,3-thiazolidine, 28iv



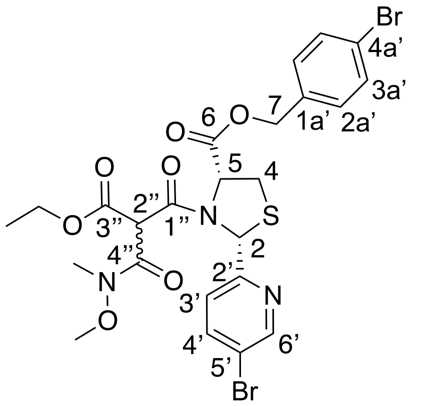
Synthesised from **19iv** (1 eq. 4.0 mmol); yield (1.6 g, 65%); pale yellow oil; an inseparable 1 : 1 C2'' *R/S* diastereomers, a mixture of rotamers; R_f = 0.26 (petrol : EtOAc; 2 : 3); ν_{max}/cm^{-1} 1747 (s, C=O), 1672 (s, C=O); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36 (d, *J* = 5.1 Hz, 1H, H6'), 8.34 (d, *J* = 5.1 Hz, 1H, H6'), 8.27 – 8.21 (m, 4H, H3a'), 7.94 (s, 1H, H3'), 7.85 (s, 1H, H3'), 7.77 (s, H3' minor rotamer), 7.74 (s, H3' minor rotamer), 7.58 (d, *J* = 8.5 Hz, 4H, H2a'), 7.55 – 7.41 (m, 2H, H5'), 6.27 (s, H2 minor rotamer), 6.26 (s, H2 minor rotamer), 6.09 (s, 1H, H2, C2'' *S*), 5.89 (s, 1H, H2, C2'' *R*), 5.45 – 5.26 (m, 6H, H5 and H7), 4.49 (s, 1H, H2'', C2'' *R*), 4.48 (s, 1H, H2'', C2'' *S*), 4.29 – 4.13 (m, 4H, OCH_2CH$_3$), 3.64 (s, NOCH_3 minor rotamer), 3.62 (s, NOCH_3 minor rotamer), 3.55 (s, 3H, NOCH_3), 3.47 (s, 3H, NOCH_3), 3.38 (dd, *J* = 12.5, 6.2 Hz, 2H, $H4_B$), 3.23 – 3.15 (m, obscured, 2H, $H4_A$), 3.20 (s, NCH_3 minor rotamer), 3.13 (s, NCH_3 minor rotamer), 3.11 (s, 3H, NCH_3), 3.01 (s, 3H, NCH_3), 1.30 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.23 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 169.4, 169.2 (C6), 165.5, 164.7, 164.2, 163.8, 163.5 (C3'', C1'' and C4''), 152.3, 151.9 (C6'), 150.7, 150.7, 150.1 (C4'), 148.1, 148.1, 148.0 (C4a'), 143.0, 142.8, 142.3, 142.3, 141.9, 141.8 (C1a' and C2'), 128.9, 128.8, 128.7, 128.6 (C3a'), 126.2, 126.0, 125.5, 125.4 (C3'), 124.0 (C2a'), 121.2, 121.2, 120.6, 120.5 (C5'), 66.7, 66.5, 66.3, 66.2, 66.1, 65.9, 65.8, 65.5 (C7 and C5), 64.2, 64.2, 64.1 (C2), 63.0, 62.8, 62.7 (OCH_2CH$_3$), 61.4, 61.3 (NOCH_3), 59.9, 59.2, 58.1, 57.3 (C2''), 35.3, 32.5, 32.4, 32.3, 32.0, 31.7 (C4 and NCH_3), 14.2, 14.2, 14.1 (OCH_2CH_3); *m/z* (ESI$^+$) 625 and 627 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{26}O_9N_4BrS$ [M+H]$^+$ 625.0598 and 627.0580; found 625.0595 and 627.0572.

(2*R*,5*R*)-2-(2-Bromopyridin-4-yl)-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-5-(2-nitrobenzyloxycarbonyl)-3-oxopropanoyl)-1,3-thiazolidine, 29iv



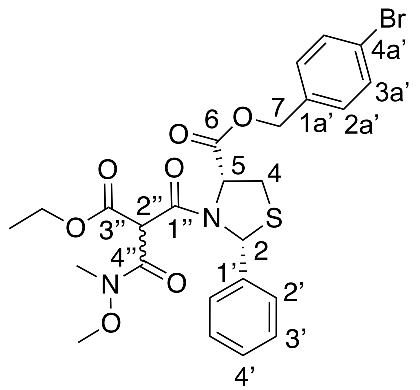
Synthesised from **20iv** (1 eq. 2.4 mmol); yield (0.6 g, 40%); yellow oil; an inseparable 1 : 1 C2'' *R/S* diastereomers, a mixture of rotamers; R_f = 0.25 (petrol : EtOAc; 2 : 3); ν_{max}/cm^{-1} 1746 (s, C=O), 16721(s, C=O); ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.38 (d, *J* = 5.2 Hz, H6' minor rotamer), 8.35 (d, *J* = 5.1 Hz, H6' minor rotamer), 8.23 (d, *J* = 5.1 Hz, 2H, H6'), 8.13 (d, *J* = 8.2 Hz, 2H, H3a'), 7.94 (s, 1H, H3'), 7.84 (s, 1H, H3'), 7.77 – 7.47 (m, 6H, H4a', H5a' and H6a'), 7.42 – 7.36 (m, 2H, H5'), 6.27 (s, H2 minor rotamer), 6.25 (s, H2 minor rotamer), 6.11 (s, 1H, H2, C2'' *S*), 5.86 (s, 1H, H2, C2'' *R*), 5.69 (br. s, 4H, H7), 5.66 – 5.55 (m, 2H, H5), 4.51 (s, 1H, H2'', C2'' *R*), 4.48 (s, 1H, H2'', C2'' *S*), 4.31 – 4.14 (m, 4H, OCH_2CH$_3$), 3.65 (s, NOCH_3 minor rotamer), 3.64 (s, NOCH_3 minor rotamer), 3.55 (s, 3H, NOCH_3), 3.47 (s, 3H, NOCH_3), 3.43 – 3.36 (m, 2H, H4$_B$), 3.26 – 3.21 (m, 2H, H4$_A$), 3.20 (s, NCH_3 minor rotamer), 3.16 (s, NCH_3 minor rotamer), 3.11 (s, 3H, NCH_3), 2.99 (s, 3H, NCH_3), 1.34 – 1.20 (m, 6H, OCH$_2$CH_3); ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz): δ 169.3, 169.2, 169.1 (C6), 165.3, 164.8, 164.6, 164.4, 164.2, 163.8, 163.5 (C3'', C1'' and C4''), 152.4, 151.9 (C6'), 150.8, 150.7, 150.0 (C4'), 147.5 (C2a'), 143.0, 142.8, 142.3 (C2'), 134.2, 134.2, 134.1, 134.0 (C6a'), 131.4, 131.4, 130.7, 130.6 (C1a'), 129.9, 129.7, 129.7, 129.6 (C5a'), 129.5, 129.5, 129.2, 129.2 (C4a'), 126.3, 125.6, 125.5, 125.2 (C3' and C3a'), 121.2, 121.2, 120.6, 120.5 (C5'), 66.0, 65.9, 65.8, 65.5, 65.2, 65.1, 64.7, 64.6, 64.2, 64.0 (C7, C5 and C2), 63.0, 63.0, 62.7, 62.7 (O*C*H$_2$CH$_3$), 61.6, 61.5, 61.4, 61.3 (NO*C*H$_3$), 59.6, 58.8, 58.2, 57.4 (C2''), 35.1, 33.5, 32.6, 32.4, 32.3, 32.0, 31.8 (C4 and N*C*H$_3$), 14.3, 14.2, 14.1 (OCH$_2$*C*H$_3$); *m/z* (ESI$^+$) 625 and 627 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{26}O_9N_4BrS$ [M+H]$^+$ 625.0598 and 627.0580; found 625.0594 and 627.0572.

(2*R*,5*R*)-5-(4-Bromobenzyloxycarbonyl)-2-(5-bromopyridin-2-yl)-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-1,3-thiazolidine, 30ii



Synthesised from **21ii** (1 eq. 0.5 mmol); yield (200 mg, 69%); pale yellow oil; an inseparable 0.7 : 1 C2'' *R/S* diastereomers; R_f = 0.17 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 1746 (s, C=O), 1672 (s, C=O); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (d, *J* = 2.1 Hz, 1H, H6'), 8.54 (d, *J* = 2.1 Hz, 1H, H6'), 7.95 (app dd, *J* = 12.1, 8.4 Hz, 2H, H3'), 7.76 (dd, *J* = 8.4, 2.3 Hz, 1H, H4'), 7.73 (dd, *J* = 8.4, 2.3 Hz, 1H, H4'), 7.49 (dd, *J* = 8.5, 2.1 Hz, 4H, H3a'), 7.24 (d, *J* = 8.5 Hz, 4H, H2a'), 5.97 (s, 1H, H2, C2'' *S*), 5.95 (s, 1H, H2, C2'' *R*), 5.23 – 5.08 (m, 6H, H7 and H5), 4.64 (s, 1H, H2'', C2'' *R*), 4.53 (s, 1H, H2'', C2'' *S*), 4.31 – 4.18 (m, 2H, OCH_2CH_3), 4.08 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 3.60 (s, 3H, $NOCH_3$), 3.56 (s, 3H, $NOCH_3$), 3.37 – 3.19 (m, 4H, H4), 3.17 (s, 3H, NCH_3), 3.05 (s, 3H, NCH_3), 1.29 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.17 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.7, 169.6 (C6), 164.9, 164.8 (C3''), 164.1, 163.9 (C1''), 163.8 (C4''), 157.9, 157.6 (C2'), 150.6, 150.4 (C6'), 140.2, 139.8 (C4'), 134.2 (C1a'), 131.9 (C3a'), 130.1 (C2a'), 122.7, 122.7 (C3' and C4a'), 120.6, 120.5 (C5'), 67.2, 67.0, 67.0, 66.9 (C7 and C5), 65.3, 65.2 (C2), 62.7, 62.2 (OCH_2CH_3), 61.4, 61.1 ($NOCH_3$), 57.4, 56.9 (C2''), 34.0 (C4), 32.0 (NCH_3), 14.2, 14.0 (OCH_2CH_3); *m/z* (ESI$^+$) 658, 660 ([M+H]$^+$, 100%) and 662; HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{26}O_7N_3Br_2S$ [M+H]$^+$ 657.9853, 659.9833 and 661.9815; found 657.9847, 659.9826 and 661.9804.

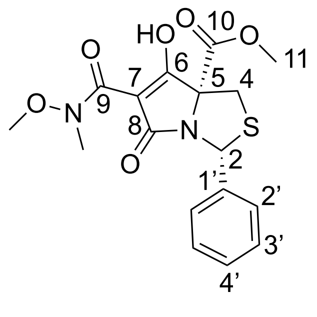
(2*R*,5*R*)-5-(4-Bromobenzyloxycarbonyl)-1-(3-ethoxy-2-(methoxy(methyl)carbamoyl)-3-oxopropanoyl)-2-phenyl-1,3-thiazolidine, 30iii



Synthesised from **21iii** (1 eq. 3.5 mmol); yield (1.0 g, 49%); yellow oil; an inseparable 1 : 1 C2'' *R/S* diastereomers; R_f = 0.17 (petrol : EtOAc; 3 : 2); ν_{max}/cm^{-1} 1742 (s, C=O), 1668 (s, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (app dd, *J* = 6.6, 2.9 Hz, 2H, H2'), 7.59 (app dd, *J* = 6.4, 3.0 Hz, 2H, H2'), 7.50 (dd, *J* = 8.4, 1.7 Hz, 4H, H3a'), 7.31 – 7.35 (m, 4H, H3'), 7.28 (app dd, *J* = 8.4, 3.1 Hz, 6H, H2a' and H4'), 5.99 (s, 1H, H2, C2'' *R*), 5.82 (s, 1H, H2, C2'' *S*), 5.14 – 5.27 (m, 6H, H5 and H7), 4.46 (s, 1H, H2'', C2'' *S*), 4.37 (s, 1H, H2'', C2'' *R*), 4.24 – 4.33 (m, 2H, OC*H*$_2$CH$_3$), 4.09 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.24 – 3.30 (m, 4H, H4), 3.34 (s, 3H, NOC*H*$_3$), 3.21 (s, 3H, NOC*H*$_3$), 3.14 (s, 3H, NC*H*$_3$), 3.08 (s, 3H, NC*H*$_3$), 1.32 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.17 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.7, 169.5 (C6), 165.5, 165.3 (C1''), 164.4, 164.1 (C3''), 163.9 (C4''), 139.4, 139.2 (C1'), 134.4, 134.3 (C1a'), 131.9 (C3a'), 130.2, 130.1 (C2a'), 129.2, 129.1 (C3'), 128.9 (C4'), 127.1, 126.6 (C2'), 122.7, 122.6 (C4a'), 66.9, 66.9 (C7), 66.4, 66.2 (C5), 65.5, 65.3 (C2), 62.6, 62.1 (O*C*H$_2$CH$_3$), 61.1, 61.1 (NO*C*H$_3$), 57.7, 57.0 (C2''), 32.9, 32.4 (C4), 32.2, 32.3 (N*C*H$_3$), 14.3, 14.1 (OCH$_2$*C*H$_3$); *m/z* (ESI$^+$) 601 and 603 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{25}H_{27}O_7N_2BrNaS$ [M+Na]$^+$ 601.0615, 603.0596; found 601.0611 and 603.0591.

Tetramate Weinreb amides **31-39** were synthesised from the respective tricarbonyl *N*-acylthiazolidines **23-30** by General Procedure **F**.

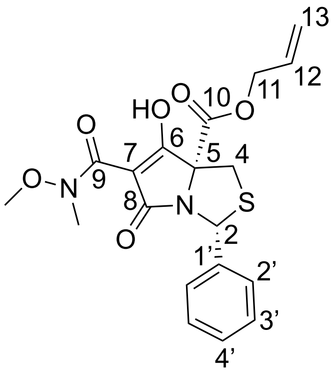
(2*R*,5*R*)-1-Aza-6-hydroxy-5-methoxycarbonyl-7-(methoxy(methyl)carbamoyl)-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]-oct-6-ene, 31iii



Synthesised from **23iii** (1 eq. 2.6 mmol); yield (912 mg, 93%); pale yellow foamy oil; R_f = 0.31 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 7.51 (d, *J* = 6.8 Hz, 2H, H2'), 7.28 – 7.36 (m, 3H, H3' and H4'), 6.32 (s, 1H, H2), 3.90 (d, *J* = 11.5 Hz, 1H, H4$_B$), 3.80 (s, 3H, NOC*H*$_3$), 3.69 (s, 3H, H11), 3.51 (br. s, 3H, NC*H*$_3$), 3.12 (d, *J* = 11.5 Hz, 1H, H4$_A$); ^{13}C NMR ($CDCl_3$, 101

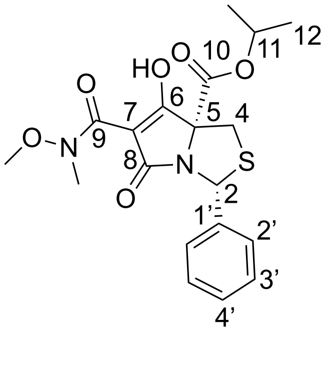
MHz): δ 185.5 (C6), 176.9 (C8), 167.9 (C10), 166.3 (C9), 138.9 (C1'), 128.5 (C3'), 128.3 (C4'), 126.9 (C2'), 80.4 (C7), 64.7 (C5), 62.3 (C2), 61.2 (NO*C*H_3), 53.5 (C11), 35.7 (C4), 35.3 (N*C*H_3); *m/z* (ESI$^+$) 379 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{19}O_6N_2S$ [M+H]$^+$ 379.0958; found 379.0959.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]-oct-6-ene, 32iii



Synthesised from **24iii** (1 eq. 1.7 mmol); yield (590 mg, 86%); yellow oil; R_f = 0.21 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 7.51 (d, *J* = 7.0 Hz, 2H, H2'), 7.25 – 7.36 (m, 3H, H3' and H4'), 6.32 (s, 1H, H2), 5.67 – 5.83 (m, 1H, H12), 5.24 (dd, *J* = 17.2, 1.4 Hz, 1H, $H13_B$), 5.19 (dd, *J* = 10.4, 1.4 Hz, 1H, $H13_A$), 4.58 (d, *J* = 5.8 Hz, 2H, H11), 3.91 (d, *J* = 11.5 Hz, 1H, $H4_B$), 3.80 (s, 3H, NOC*H*$_3$), 3.51 (br. s, 3H, NC*H*$_3$), 3.12 (d, *J* = 11.5 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 185.6 (C6), 177.0 (C8), 167.2 (C10), 166.3 (C9), 139.0 (C1'), 131.2 (C12), 128.5 (C3'), 128.2 (C4'), 127.0 (C2'), 119.2 (C13), 80.5 (C7), 67.2 (C11), 64.8 (C5), 62.3 (C2), 61.2 (NO*C*H_3), 35.7 (C4), 35.2 (N*C*H_3); *m/z* (ESI$^+$) 405 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{19}H_{21}O_6N_2S$ [M+H]$^+$ 405.1115; found 405.1115.

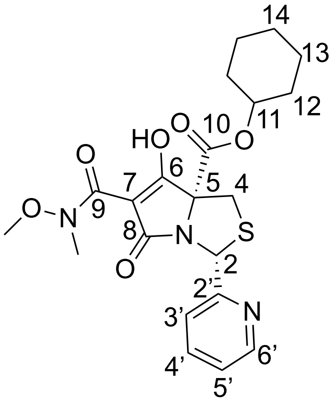
(2*R*,5*R*)-1-Aza-6-hydroxy-5-isopropoxycarbonyl-7-(methoxy(methyl)carbamoyl)-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]-oct-6-ene, 33iii



Synthesised from **25iii** (1 eq. 2.2 mmol); yield (760 mg, 85%); yellow oil; R_f = 0.23 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 7.53 (d, *J* = 6.4 Hz, 2H, H2'), 7.25 – 7.35 (m, 3H, H3' and H4'), 6.32 (s, 1H, H2), 5.00 (sept, *J* = 6.3 Hz, 1H, H11), 3.90 (d, *J* = 11.5 Hz, 1H, $H4_B$), 3.80 (s, 3H, NOC*H*$_3$), 3.52 (br. s, 3H, NC*H*$_3$), 3.10 (d, *J* = 11.5 Hz, 1H, $H4_A$), 1.16 (d, *J* = 6.3 Hz, 3H, $H12_B$), 1.10 (d, *J* = 6.3 Hz, 3H, $H12_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 185.9

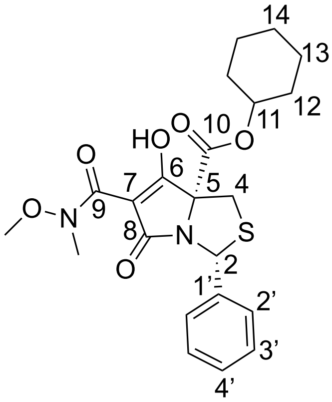
(C6), (C8 not shown), 166.5 (C10), 166.4 (C9), 139.0 (C1'), 128.5 (C3'), 128.2 (C4'), 127.0 (C2'), 80.4 (C7), 70.9 (C11), 64.6 (C5), 62.4 (NO*C*H_3 and C2), 35.6 (N*C*H_3 and C4), 21.5 ($C12_B$), 21.4 ($C12_A$); *m/z* (ESI^-) 405 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{19}H_{21}O_6N_2S$ $[M-H]^-$ 405.1126; found 405.1123.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-2-(pyridin-2-yl)-3-thiabicyclo[3.3.0]-oct-6-ene, 34i



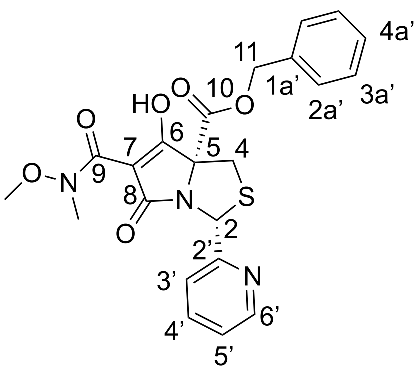
Synthesised from **26i** (1 eq. 0.7 mmol); yield (100 mg, 32%); yellow foamy oil; R_f = 0.12 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.52 (d, *J* = 4.0 Hz, 1H, H6'), 7.74 – 7.58 (m, 2H, H3' and H4'), 7.18 (app t, *J* = 5.3 Hz, 1H, H5'), 6.38 (s, 1H, H2), 4.86 – 4.74 (m, 1H, H11), 3.93 (d, *J* = 11.5 Hz, 1H, $H4_B$), 3.82 (s, 3H, NOC*H_3*), 3.53 (br. s, 3H, NC*H_3*), 3.15 (d, *J* = 11.5 Hz, 1H, $H4_A$), 1.80 – 1.69 (m, 2H, H12), 1.69 – 1.59 (m, 2H, H12), 1.52 – 1.43 (m, 2H, H13), 1.41 – 1.29 (m, 4H, H13 and H14); ^{13}C NMR ($CDCl_3$, 101 MHz): δ (C6, C8 not shown), 166.5 (C10 and C9), 158.8 (C2'), 149.2 (C6'), 137.0 (C4'), 122.9 (C3'), 120.3 (C5'), 81.1 (C7), 75.5 (C11), 65.2 (C5), 62.5 (NO*C*H_3 and C2), 35.7 (C4 and N*C*H_3), 31.2 (C12), 25.3 (C14), 23.6 (C13); *m/z* (ESI^-) 446 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{21}H_{24}N_3O_6S$ $[M-H]^-$ 446.1391; found 446.1400.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]-oct-6-ene, 34iii



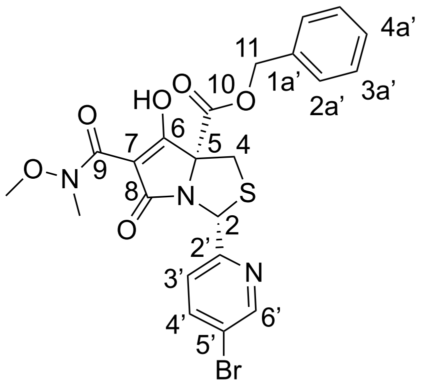
Synthesised from **26iii** (1 eq. 2.0 mmol); yield (570 mg, 63%); yellow foamy oil; R_f = 0.26 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 7.53 (d, *J* = 6.9 Hz, 2H, H2’), 7.27 – 7.34 (m, 3H, H3’ and H4’), 6.32 (s, 1H, H2), 4.70 – 4.85 (m, 1H, H11), 3.91 (d, *J* = 11.5 Hz, 1H, $H4_B$), 3.81 (s, 3H, NOCH_3), 3.53 (br. s, 3H, NCH_3), 3.11 (d, *J* = 11.5 Hz, 1H, $H4_A$), 1.59 – 1.78 (m, 4H, H12), 1.20 – 1.39 (m, 6H, H13 and H14); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 185.8 (C6), 176.6 (C8), 166.4 (C10), 166.2 (C9), 138.9 (C1’), 128.3 (C3’), 128.1 (C4’), 126.9 (C2’), 80.4 (C7), 75.3 (C11), 64.5 (C5), 62.2 (NO*C*H_3 and C2), 35.4 (C4 and N*C*H_3), 31.0 (C12), 31.0 (C12), 25.2 (C14), 23.4 (C13); *m/z* (ESI$^+$) 447 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{22}H_{27}O_6N_2S$ [M+H]$^+$ 447.1584; found 447.1583.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-2-(pyridin-2-yl)-3-thiabicyclo[3.3.0]-oct-6-ene, 35i



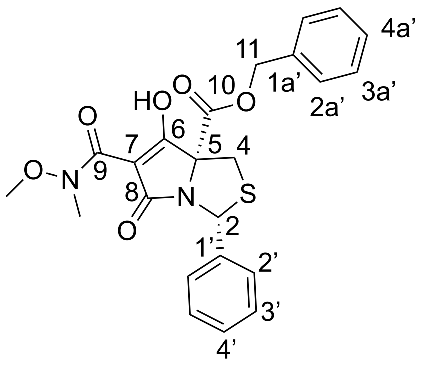
Synthesised from **27i** (1 eq. 0.8 mmol); yield (95 mg, 28%); brown oil; R_f = 0.17 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.40 (d, *J* = 4.7 Hz, 1H, H6’), 7.49 – 7.43 (m, 2H, H3’ and H4’), 7.32 – 7.27 (m, 3H, H3a’ and H4a’), 7.27 – 7.20 (m, 2H, H2a’), 7.14 – 7.08 (m, 1H, H5’), 6.39 (s, 1H, H2), 5.24 – 5.13 (m, 2H, H11), 3.99 (d, *J* = 11.6 Hz, 1H, $H4_B$), 3.80 (s, 3H, NOCH_3), 3.52 (br. s, 3H, NCH_3), 3.22 (d, *J* = 11.6 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 186.4 (C6), 176.7 (C8), 167.1 (C10), 166.4 (C9), 158.6 (C2’), 149.1 (C6’), 137.1 (C4’), 135.2 (C1a’), 128.7 (C3a’), 128.5 (C4a’), 128.4 (C2a’), 122.9 (C3’), 120.2 (C5’), 81.3 (C7), 68.3 (C11), 65.4 (C5), 62.4 (NO*C*H_3 and C2), 35.8 (C4), 35.5 (N*C*H_3); *m/z* (ESI$^-$) 454 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{22}H_{20}O_6N_3S$ [M-H]$^-$ 454.1078; found 454.1066.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-2-(5-bromopyridin-2-yl)-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-3-thiabicyclo[3.3.0]-oct-6-ene, 35ii



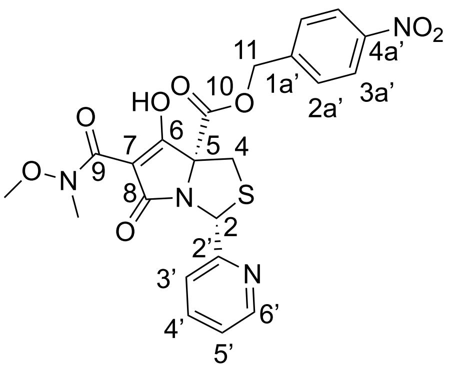
Synthesised from **27ii** (1 eq. 2.6 mmol); yield (550 mg, 40%); yellow oil; R_f = 0.23 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.33 (d, *J* = 2.1 Hz, 1H, H6'), 7.48 (dd, *J* = 8.4, 2.3 Hz, 1H, H4'), 7.36 – 7.25 (m, 4H, H3', H3a' and H4a'), 7.22 (d, *J* = 6.6 Hz, 2H, H2a'), 6.29 (s, 1H, H2), 5.24 (d, *J* = 12.2 Hz, 1H, $H11_B$), 5.11 (d, *J* = 12.2 Hz, 1H, $H11_A$), 3.95 (d, *J* = 11.6 Hz, 1H, $H4_B$), 3.79 (s, 3H, NOCH_3), 3.50 (br. s, 3H, NCH_3), 3.18 (d, *J* = 11.6 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 186.2 (C6), (C8 not shown), 167.0 (C10), 166.2 (C9), 157.0 (C2'), 150.1 (C6'), 139.3 (C4'), 134.9 (C1a'), 128.6 (C2a', C4a' and C3a'), 122.5 (C3'), 119.7 (C5'), 81.0 (C7), 68.4 (C11), 64.7 (C5), 63.5 (C2), 62.5 (NO*C*H_3), 35.8 (C4), 33.7 (N*C*H_3); *m/z* (ESI$^-$) 532 and 534 ([M-H]$^-$, 100%); $C_{22}H_{19}O_6N_3SBr$ ([M-H]$^-$).

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]-oct-6-ene, 35iii



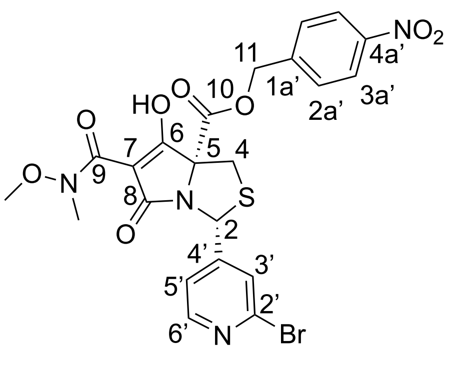
Synthesised from **27iii** (1 eq. 2.4 mmol); yield (764 mg, 70%); yellow oil; R_f = 0.31 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 7.41 – 7.56 (m, 2H, H2'), 7.29 – 7.43 (m, 7H, H4a', H3', H3a', H2a'), 7.19 – 7.34 (m, 1H, H4', obscured by solvent peak), 6.33 (s, 1H, H2), 5.17 (s, 2H, H11), 3.96 (d, *J* = 11.6 Hz, 1H, $H4_B$), 3.81 (s, 3H, NOCH_3), 3.54 (br. s, 3H, NCH_3), 3.16 (d, *J* = 11.6 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ (C6, C8 not shown), 167.2 (C10), 166.3 (C9), 138.7 (C1'), 134.9 (C1a'), 128.6 (C3'), 128.6 (C3a'), 128.5 (C4'), 128.5 (C4a'), 128.3 (C2a'), 127.0 (C2'), 80.6 (C7), 68.4 (C11), 64.9 (C5), 62.4 (NO*C*H_3 and C2), 35.7 (C4), 34.4 (N*C*H_3); *m/z* (ESI$^+$) 455 ([M+H]$^+$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{23}H_{21}O_6N_2S$ [M-H]$^-$ 453.1126; found 453.1130.

(2*R*,5*R*)-1-Aza-6-hydroxy-7-(methoxy(methyl)carbamoyl)-5-(4-nitrobenzyloxycarbonyl)-8-oxo-2-(pyridin-2-yl)-3-thiabicyclo[3.3.0]-oct-6-ene, 36i



Synthesised from **28i** (1 eq. 1.4 mmol); yield (135 mg, 20%); brown oil; R_f = 0.25 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.35 (d, *J* = 4.3 Hz, 1H, H6'), 8.03 (d, *J* = 8.7 Hz, 2H, H3a'), 7.51 (app t, *J* = 7.6 Hz, 1H, H4'), 7.43 (d, *J* = 7.8 Hz, 1H, H3'), 7.31 (d, *J* = 8.7 Hz, 2H, H2a'), 7.12 – 7.02 (m, 1H, H5'), 6.36 (s, 1H, H2), 5.25 (d, *J* = 13.4 Hz, 1H, $H11_A$), 5.19 (d, *J* = 13.4 Hz, 1H, $H11_B$), 3.93 (d, *J* = 11.6 Hz, 1H, $H4_B$), 3.76 (s, 3H, NOCH_3), 3.45 (br. s, 3H, NCH_3), 3.19 (d, *J* = 11.6 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 186.0 (C6), 177.0 (C8), 167.2 (C10), 166.3 (C9), 158.3 (C2'), 148.8 (C6'), 147.8 (C4a'), 142.4 (C1a'), 137.3 (C4'), 128.3 (C2a'), 123.8 (C3a'), 123.0 (C3'), 120.4 (C5'), 81.2 (C7), 66.5 (C11), 65.2 (C5), 62.6 (C2 and NOCH_3), 35.8 (NCH_3 and C4); *m/z* (ESI$^-$) 499 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{22}H_{19}O_8N_4S$ [M-H]$^-$ 499.0929; found 499.0938.

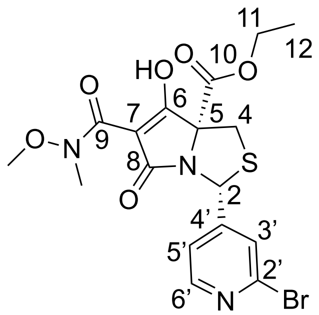
(2*R*,5*R*)-1-Aza-2-(2-bromopyridin-4-yl)-6-hydroxy-7-(methoxy(methyl)carbamoyl)-5-(4-nitrobenzyloxycarbonyl)-8-oxo-3-thiabicyclo[3.3.0]-oct-6-ene, 36iv



Synthesised from **28iv** (1 eq. 2.3 mmol); yield (550 mg, 41% as inseparable mixture with **37iv**, 1 : 1 molar ratio); yellow oil; R_f = 0.31 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.28 (d, *J* = 5.1 Hz, 1H, H6'), 8.13 (d, *J* = 8.8 Hz, 2H, H3a'), 7.63 (s, 1H, H3'), 7.49 (d, *J* = 5.1 Hz, 1H, H5'), 7.36 (d, *J* = 8.8 Hz, 2H, H2a'), 6.18 (s, 1H, H2), 5.29 – 5.18 (m, 2H, H11), 3.87 (dd, *J* = 11.7, 1H, $H4_B$), 3.80 (s, 3H, NOCH_3), 3.49 (br. s, 3H, NCH_3), 3.16 (d, *J* = 11.7 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ (C6 and C8 not shown), 166.6 (C10), 166.1 (C9), 151.4 (C6'), 150.2 (C4'), 147.9 (C4a'), 142.5 (C2'), 141.7

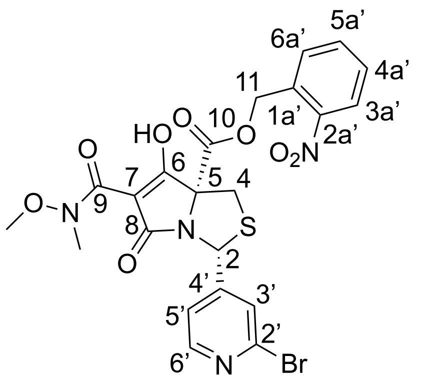
(C1a'), 128.4 (C2a'), 125.8 (C3'), 123.9 (C3a'), 120.9 (C5'), 80.3 (C7), 66.8 (C11), 63.7 (C5), 62.5 (C2 and NO*C*H_3), 36.2 (N*C*H_3 and C4); *m/z* (ESI$^-$) 577 and 579 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{22}H_{18}O_8N_4BrS$ [M-H]$^-$ 577.0022 and 579.0000; found 577.0034 and 579.0015.

(2*R*,5*R*)-1-Aza-2-(2-bromopyridin-4-yl)-5-ethoxycarbonyl-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-3-thiabicyclo[3.3.0]-oct-6-ene, 37iv



By-product from an inseparable mixture with **36iv** or **38iv**, 1 : 1 molar ratio; yellow oil; R_f = 0.31 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.21 (d, *J* = 5.1 Hz, 1H, H6'), 7.59 (s, 1H, H3'), 7.32 – 7.29 (m, 1H, H5'), 6.18 (s, 1H, H2'), 4.22 – 4.14 (m, 2H, H11), 3.85 (dd, *J* = 11.5, 1H, $H4_B$), 3.79 (s, 3H, NOC*H_3*), 3.49 (br. s, 3H, NC*H_3*), 3.11 (d, *J* = 11.5 Hz, 1H, $H4_A$), 1.19 (t, *J* = 7.1 Hz, 3H, H12); ^{13}C NMR ($CDCl_3$, 101 MHz): δ (C6 and C8 not shown), 166.6 (C10), 166.0 (C9), 151.1 (C6'), 150.2 (C4'), 142.4 (C2'), 127.0 (C3'), 120.8 (C5'), 80.1 (C7), 63.3 (C5), 62.4 (C2 and NO*C*H_3), 61.2 (C11), 36.0 (N*C*H_3 and C4), 14.0 (C12); *m/z* (ESI$^-$) 470 and 472 ([M-H]$^-$, 100%); $C_{17}H_{17}O_6N_3BrS$ ([M-H]$^-$).

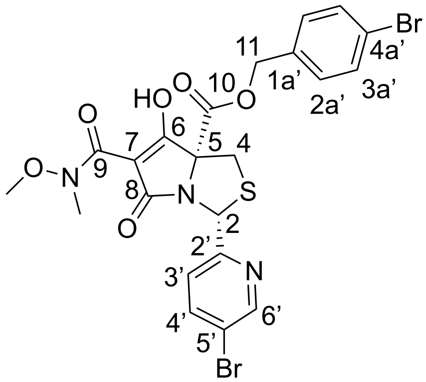
(2*R*,5*R*)-1-Aza-2-(2-bromopyridin-4-yl)-6-hydroxy-7-(methoxy(methyl)carbamoyl)-5-(2-nitrobenzyloxycarbonyl)-8-oxo-3-thiabicyclo[3.3.0]-oct-6-ene, 38iv



Synthesised from **29iv** (1 eq. 0.9 mmol); yield (233 mg, 45% as inseparable mixture with **37iv**, 1 : 1 molar ratio); yellow oil; R_f = 0.31 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.31 (d, *J* = 5.1 Hz, 1H, H6'), 8.06 (d, *J* = 8.1 Hz, 1H, H3a'), 7.66 (s, 1H, H3'), 7.59 – 7.51 (m, 1H, H5a'), 7.51 – 7.44 (m, 1H, H5'), 7.44 – 7.38 (m, 1H, H4a'), 7.40 – 7.34 (m, 1H, H6a'), 6.19 (s, 1H, H2), 5.61 (d, *J* = 14.4 Hz, 1H, $H11_B$), 5.52 (d, *J* = 14.4 Hz, 1H, $H11_A$), 3.90 (d, *J* = 11.7 Hz, 1H, $H4_B$), 3.83 (s, 3H, NOC*H_3*), 3.52 (br.

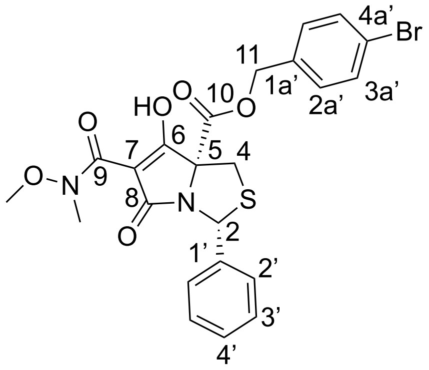
s, 3H, NCH_3), 3.18 (d, J = 11.7 Hz, 1H, H4_A); ^{13}C NMR ($CDCl_3$, 101 MHz): δ (C6 and C8 not shown), 166.4 (C10), 166.1 (C9), 151.4 (C6'), 150.2 (C4'), 147.5 (C2a'), 142.5 (C2'), 134.1 (C6a'), 133.8 (C1a'), 130.5 (C5a'), 129.4 (C4a'), 125.8 (C3'), 125.2 (C3a'), 120.9 (C5'), 80.3 (C7), 65.3 (C11), 63.3 (C5), 62.6 (C2 and NOCH_3), 36.0 (NCH$_3$ and C4); *m/z* (ESI^-) 577 and 579 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{22}H_{18}O_8N_4BrS$ $[M-H]^-$ 577.0022 and 579.0000; found 577.0034 and 579.0015.

(2*R*,5*R*)-1-Aza-5-(4-bromobenzyloxycarbonyl)-2-(5-bromopyridin-2-yl)-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-3-thiabicyclo[3.3.0]-oct-6-ene, 39ii



Synthesised from **30ii** (1 eq. 0.3 mmol); yield (65 mg, 35%); pale yellow oil; R_f = 0.29 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.36 (s, 1H, H6'), 7.59 (dd, J = 8.3, 2.0 Hz, 1H, H4'), 7.43 (d, J = 8.3 Hz, 2H, H3a'), 7.33 (d, J = 8.3 Hz, 1H, H3'), 7.12 (d, J = 8.3 Hz, 2H, H2a'), 6.31 (s, 1H, H2), 5.19 (d, J = 12.4 Hz, 1H, H11_B), 5.08 (d, J = 12.4 Hz, 1H, H11_A), 3.94 (d, J = 11.6 Hz, 1H, H4_B), 3.81 (s, 3H, NOCH_3), 3.52 (br. s, 3H, NCH_3), 3.20 (d, J = 11.6 Hz, 1H, H4_A); ^{13}C NMR ($CDCl_3$, 101 MHz): δ (C6 not shown), 177.2 (C8), 167.1 (C10), 166.3 (C9), 157.1 (C2'), 150.2 (C6'), 139.4 (C4'), 134.0 (C1a'), 131.8 (C3a'), 130.2 (C2a'), 122.8 (C4a'), 121.6 (C3'), 119.9 (C5'), 81.0 (C7), 67.5 (C11), 64.8 (C5), 63.5 (C2), 63.1 (NOCH$_3$), 35.9 (C4), 33.8 (NCH$_3$); *m/z* (ESI^-) 610 (50%), 612 ($[M-H]^-$, 100%) and 614 (50%); HRMS (ESI^-) *m/z* calcd for $C_{22}H_{18}O_6N_3Br_2S$ $[M-H]^-$ 609.9289, 611.9269 and 613.6250; found 609.9273, 611.9252 and 613.9229.

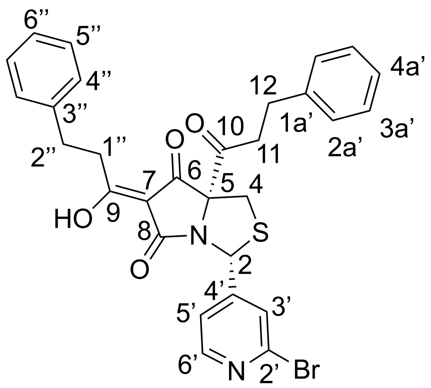
(2*R*,5*R*)-1-Aza-5-(4-bromobenzyloxycarbonyl)-6-hydroxy-7-(methoxy(methyl)carbamoyl)-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]-oct-6-ene, 39iii



Synthesised from **30iii** (1 eq. 1.7 mmol); yield (496 mg, 56%); purified with column chromatography and wash with 0.5 M HCl solution after column; yellow oil; R_f = 0.34 (EtOAc : MeOH; 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 7.42 – 7.45 (m, 2H, H2'), 7.40 (d, *J* = 8.4 Hz, 2H, H3a'), 7.21 – 7.25 (m, 3H, H4' and H3'), 7.05 (d, *J* = 8.5 Hz, 2H, H2a'), 6.30 (s, 1H, H2), 5.06 (s, 2H, H11), 3.91 (d, *J* = 11.6 Hz, 1H, $H4_B$), 3.78 (s, 3H, NOCH_3), 3.50 (br. s, 3H, NCH_3), 3.13 (d, *J* = 11.6 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 185.3 (C6), 177.2 (C8), 167.1 (C10), 166.3 (C9), 138.6 (C1'), 133.9 (C1a'), 131.8 (C3a'), 130.1 (C2a'), 128.5 (C3'), 128.3 (C4'), 126.9 (C2'), 122.6 (C4a'), 80.6 (C7), 67.5 (C11), 64.8 (C5), 62.4 (C2), 61.5 (NO*C*H_3), 35.7 (C4), 34.4 (N*C*H_3); *m/z* (ESI$^-$) 531 and 533 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{23}H_{20}O_6N_2BrS$ [M-H]$^-$ 531.0220 and 533.0200; found 531.0233 and 533.0213.

Tetramate ketones **40-75** were synthesised from the respective tetramate Weinreb amides **31-39** by General Procedure **G** with the corresponding Grignard reagent (R^{3}MgBr for the synthesis of **41-74**, R^{3}Mg*i*Pr for the synthesis of **75**).

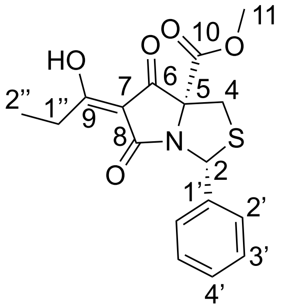
(2*R*,5*R*)-1-Aza-2-(2-bromopyridin-4-yl)-7-[(*Z*)-1-hydroxy-3-phenylpropylidene]-6,8-dioxo-5-(3-phenylpropanoyl)dihydro-3-thiabicyclo[3.3.0]-octane, 40



Synthesised from **38iv** (1 eq. 50 mg, 0.1 mmol) with $PhCH_2CH_2MgBr$; yield (23 mg, 44%); brown oil; R_f = 0.39 (100% EtOAc); $[\alpha]_D^{25}$ = -23.0 (*c* = 1.13, $CHCl_3$); ν_{max}/cm^{-1} 1711 (s, C=O), 1654 (s, C=O), 1585 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.34 (d, *J* = 5.1 Hz, 1H, H6'), 7.66 (s, 1H, H3'), 7.31 – 7.12 (m, 10H, H2a', H3a', H4a', H4'', H5'' and H6''), 6.98 (d, *J* = 5.1 Hz, 1H, H5'), 6.27 (s, 1H, H2), 3.91 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.26 – 2.55 (m, 9H, H1'', H2'', H11, H12 and $H4_A$); ^{13}C NMR ($CDCl_3$, 101

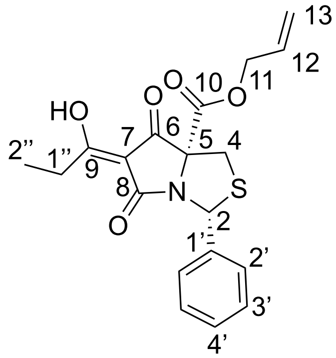
MHz): δ 199.6 (C10), 190.8 (C6), 186.9 (C9), 176.1 (C8), 150.7 (C6'), 149.9 (C4'), 143.0 (C2'), 140.1 (C1a'), 139.0 (C3''), 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1 (C2a', C3a', C4a', C4'', C5''), 126.8 (C6''), 126.5 (C3'), 121.5 (C5'), 100.6 (C7), 87.7 (C5), 61.8 (C2), 38.8 (C11), 34.6 (C4), 34.1 (C1''), 32.0 (C2''), 29.4 (C12); *m/z* (ESI$^-$) 575 and 577 ([M+H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{29}H_{24}O_2N_2BrS$ [M-H]$^-$ 575.0635 and 577.0616; found 575.0634 and 575.0614.

(2*R*,5*R*)-1-Aza-7-[(*E*)-1-hydroxypropylidene]-5-methoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, **41**



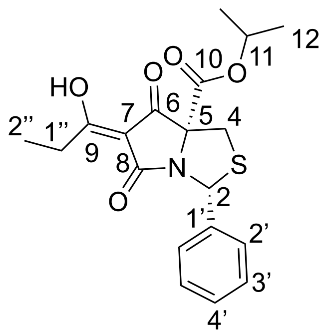
Synthesised from **31iii** (1 eq. 20 mg, 0.05 mmol) with ethylmagnesium bromide; yield (13 mg, 71%); yellow oil; R_f = 0.31 (100% EtOAc); $[\alpha]_D^{25}$ = +272 (*c* = 1.3, $CHCl_3$); ν_{max}/cm^{-1} 1751 (s, C=O), 1713 (s, C=O), 1655 (s, C=O), 1598 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 4.1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.51 (d, *J* = 7.3 Hz, 2H, H2'), 7.38 – 7.29 (m, 3H, H3' and H4'), 6.47 (s, H2 minor), 6.42 (s, 1H, H2 major), 3.94 (d, *J* = 11.3 Hz, 1H, $H4_B$), 3.61 (s, 3H, H11), 3.09 (d, *J* = 11.3 Hz, 1H, $H4_A$), 2.88 (q, *J* = 7.5 Hz, 2H, H1''), 1.22 (d, *J* = 7.5 Hz, 3H, H2''); ^{13}C NMR ($CDCl_3$, 101 MHz): AB tautomer shown only: δ 192.3 (C6), 187.3 (C9), 175.6 (C8), 167.1 (C10), 138.2 (C1'), 128.6 (C3'), 127.2 (C2' and C4'), 100.0 (C7), 82.1 (C5), 63.7 (C2), 53.5 (C11), 35.4 (C4), 26.7 (C1''), 9.7 (C2''); *m/z* (ESI$^-$) 346 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{17}H_{16}O_5NS$ [M-H]$^-$ 346.0755; found 346.0758.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-7-[(*E*)-1-hydroxypropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 42



Synthesised from **32iii** (1 eq. 23 mg, 0.06 mmol) with ethylmagnesium bromide; yield (10 mg, 45%); yellow oil; R_f = 0.37 (100% EtOAc); $[\alpha]_D^{25}$ = +229 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1714 (s, C=O), 1656 (s, C=O), 1604 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 3.7 : 1 AB/CD tautomers: δ (O*H* not observed), 7.52 (d, *J* = 6.9 Hz, 2H, H2’), 7.36 – 7.28 (m, 3H, H3’ and H4’), 6.46 (s, H2 minor), 6.42 (s, 1H, H2 major), 5.74 – 5.61 (m, 1H, H12), 5.24 – 5.14 (m, 2H, H13), 4.59 – 4.43 (m, 2H, H11), 3.95 (d, *J* = 11.3 Hz, 1H, $H4_B$), 3.09 (d, *J* = 11.3 Hz, 1H, $H4_A$), 2.89 (q, *J* = 7.5 Hz, 2H, H1’’), 1.22 (t, *J* = 7.5 Hz, 3H, H2’’); ^{13}C NMR ($CDCl_3$, 101 MHz): AB tautomer shown only: δ 192.3 (C6), 187.3 (C9), 175.8 (C8), 166.3 (C10), 138.2 (C1’), 131.0 (C12), 128.6, 128.6 (C3’ and C4’), 127.2 (C2’), 119.5 (C13), 100.0 (C7), 82.3 (C5), 67.4 (C11), 63.8 (C2), 35.4 (C4), 26.7 (C1’’), 9.7 (C2’’); *m/z* (ESI$^-$) 372 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{19}H_{18}O_5NS$ [M-H]$^-$ 372.0900; found 372.0915.

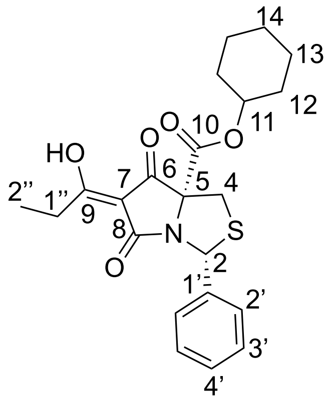
(2*R*,5*R*)-1-Aza-7-[(*E*)-1-hydroxypropylidene]-5-isopropoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 43



Synthesised from **33iii** (1 eq. 22 mg, 0.05 mmol) with ethylmagnesium bromide; yield (8 mg, 40%); yellow oil; R_f = 0.29 (100% EtOAc); $[\alpha]_D^{25}$ = +124 (*c* = 0.78, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1715 (s, C=O), 1656 (s, C=O), 1608 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 4.2 : 1 AB/CD tautomers: δ (O*H* not observed), 7.53 (d, *J* = 7.3 Hz, 2H, H2’), 7.36 – 7.28 (m, 3H, H3’ and H4’), 6.46 (s, H2 minor), 6.41 (s, 1H, H2), 4.93 (sept, *J* = 6.3 Hz, 1H, H11), 3.94 (d, *J* = 11.3 Hz, 1H, $H4_B$), 3.06 (d, *J* = 11.3 Hz, 1H, $H4_A$), 2.93 – 2.83 (m, 2H, H1’’), 1.23 (t, *J* = 7.6 Hz, 3H, H2’’), 1.13 (d, *J* = 6.3 Hz, 3H, $H12_B$), 1.00 (d, *J* = 6.3 Hz, 3H, $H12_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): AB tautomer shown only: δ 192.0 (C6), 187.6 (C9), 175.9 (C8), 166.0 (C10), 138.4 (C1’), 128.6 (C3’), 128.5 (C4’), 127.2 (C2’), 100.1 (C7), 82.4 (C5), 71.1 (C11), 63.7 (C2), 35.3 (C4), 26.7 (C1’’), 21.5 (C12), 21.3 (C12),

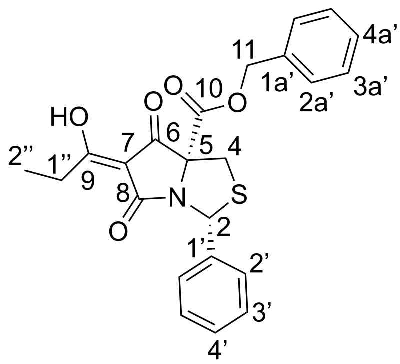
9.8 (C2''); m/z (ESI$^-$) 374 ([M-H]$^-$, 100%); HRMS (ESI$^-$) m/z calcd for $C_{19}H_{20}O_5NS$ [M-H]$^-$ 374.1068; found 374.1071.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-7-[(*E*)-1-hydroxypropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 44



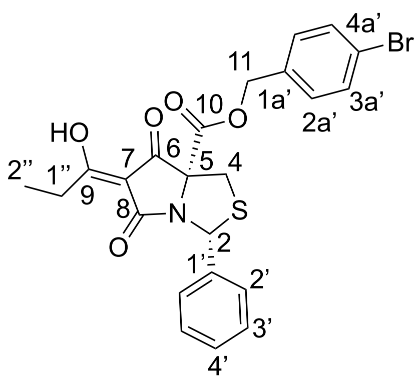
Synthesised from **34iii** (1 eq. 43 mg, 0.1 mmol) with ethylmagnesium bromide; yield (32 mg, 80%); yellow oil; R_f = 0.33 (100% EtOAc); $[\alpha]_D^{25}$ = +208 (c = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1713 (s, C=O), 1654 (s, C=O), 1601 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 4.5 : 1 AB/CD tautomers: δ (O*H* not observed), 7.53 (d, J = 7.1 Hz, 2H, H2'), 7.36 – 7.26 (m, 3H, H3' and H4'), 6.44 (s, H2 minor), 6.40 (s, 1H, H2 major), 4.79 – 4.68 (m, 1H, H11), 3.93 (d, J = 11.3 Hz, 1H, $H4_B$), 3.07 (d, J = 11.3 Hz, 1H, $H4_A$), 2.95 – 2.81 (m, 2H, H1''), 1.74 – 1.67 (m, 2H, H12), 1.62 – 1.54 (m, 4H, H12, H13), 1.49 – 1.41 (m, 2H, H13), 1.37 – 1.27 (m, 2H, H14), 1.22 (t, J = 7.5 Hz, 3H, H2''); ^{13}C NMR ($CDCl_3$, 101 MHz): AB tautomer shown only: δ 191.9 (C6), 187.7 (C9), 175.8 (C8), 165.8 (C10), 138.4 (C1'), 128.6 (C3'), 128.5 (C4'), 127.2 (C2'), 100.1 (C7), 82.5 (C5), 75.6 (C11), 63.7 (C2), 35.1 (C4), 31.0, 30.9 (C12), 26.6 (C1''), 25.3 (C14), 23.4, 23.4 (C13), 9.8 (C2''); m/z (ESI$^-$) 414 ([M-H]$^-$, 100%); HRMS (ESI$^-$) m/z calcd for $C_{22}H_{24}O_5NS$ [M-H]$^-$ 414.1381; found 414.1389.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-7-[(*E*)-1-hydroxypropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 45



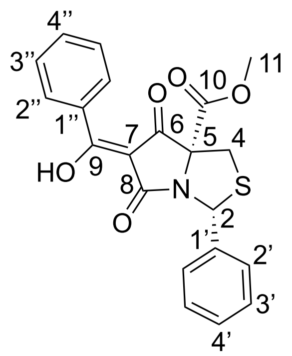
Synthesised from **35iii** (1 eq. 35 mg, 0.08 mmol) with ethylmagnesium bromide; yield (14 mg, 43%); yellow oil; R_f = 0.41 (100% EtOAc); $[\alpha]_D^{25}$ = +75.6 (c = 0.40, $CHCl_3$); ν_{max}/cm^{-1} 1746 (s, C=O), 1714 (s, C=O), 1657 (s, C=O), 1602 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 4.2 : 1 AB/CD tautomers: δ (O*H* not observed), 7.47 (m, 2H, H2'), 7.30 – 7.25 (m, 6H, obscured by solvent, H3', H3a', H4' and H4a'), 7.14 (dd, J = 6.4, 2.8 Hz, 2H, H2a'), 6.44 (s, H2 minor) 6.40 (s, 1H, H2 major), 5.12 (d, J = 12.3 Hz, 1H, $H11_A$), 5.00 (d, J = 12.3 Hz, 1H, $H11_B$), 3.96 (d, J = 11.4 Hz, 1H, $H4_B$), 3.10 (d, J = 11.4 Hz, 1H, $H4_A$), 2.87 (q, J = 7.6 Hz, 2H, H1''), 1.21 (t, J = 7.6 Hz, 3H, H2''); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): AB tautomer shown only: δ 192.3 (C6), 187.3 (C9), 175.9 (C8), 166.6 (C10), 138.2 (C1'), 134.7 (C1a'), 128.7, 128.7 (C3' and C3a'), 128.6, 128.6, 128.4 (C2a', C4', C4a'), 127.2 (C2'), 100.1 (C7), 82.4 (C5), 68.6 (C11), 64.0 (C2), 35.4 (C5), 26.7 (C1''), 9.7 (C2''); *m/z* (ESI$^-$) 422 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{23}H_{20}O_5NS$ [M-H]$^-$ 422.1068; found 422.1075.

(2*R*,5*R*)-1-Aza-5-(4-bromobenzyloxycarbonyl)-7-[(*E*)-1-hydroxypropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 46



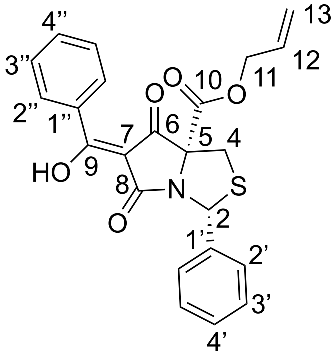
Synthesised from **39iii** (1 eq. 46 mg, 0.09 mmol) with ethylmagnesium bromide; yield (18 mg, 42%); yellow oil; R_f = 0.40 (100% EtOAc); $[\alpha]_D^{25}$ = +169 (c = 0.80, $CHCl_3$); ν_{max}/cm^{-1} 1749 (s, C=O), 1713 (s, C=O), 1655 (s, C=O), 1600 (s, C=C); ^{1}H NMR ($CDCl_3$, 600 MHz): a mixture of 3.3 : 1 AB/CD tautomers: δ (O*H* not observed), 7.49 – 7.42 (m, 2H, H2'), 7.40 (d, J = 8.4 Hz, 2H, H3a'), 7.29 – 7.21 (m, obscured by solvent, 3H, H3' and H4'), 6.97 (d, J = 8.4 Hz, 2H, H2a'), 6.42 (s, H2 minor), 6.40 (s, 1H, H2 major), 5.02 (d, J = 12.4 Hz, 1H, $H11_B$), 4.96 (d, J = 12.4 Hz, 1H, $H11_A$), 3.95 (d, J = 11.4 Hz, 1H, $H4_B$), 3.10 (d, J = 11.4 Hz, 1H, $H4_A$), 2.87 (q, J = 7.6 Hz, 2H, H1''), 1.22 (t, J = 7.6 Hz, 3H, H2''); ^{13}C NMR ($CDCl_3$, 101 MHz): AB tautomer shown only: δ 192.5 (C6), 187.3 (C9), 175.9 (C8), 166.6 (C10), 138.1 (C1'), 133.8 (C1a'), 131.9 (C3a'), 130.1 (C2a'), 128.7 (C3'), 128.6 (C4'), 127.2 (C2'), 122.8 (C4a'), 98.5 (C7), 82.3 (C5), 67.7 (C11), 63.9 (C2), 35.4 (C4), 26.7 (C1''), 9.7 (C2''); *m/z* (ESI$^-$) 500 and 502 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{23}H_{19}O_5NBrS$ [M-H]$^-$ 500.0173 and 502.0153; found 500.0180 and 502.0159.

(2*R*,5*R*)-1-Aza-7-[(*Z*)-hydroxyl(phenyl)methylene]-5-methoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 47



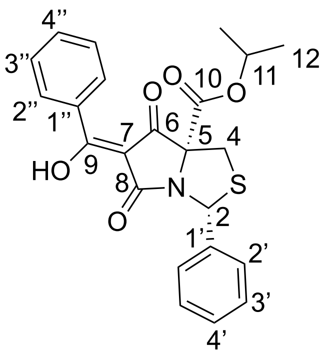
Synthesised from **31iii** (1 eq. 30 mg, 0.08 mmol) with phenylmagnesium bromide; yield (10 mg, 33%); pale yellow oil; R_f = 0.43 (100% EtOAc); $[\alpha]_D^{25}$ = +186 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1750 (s, C=O), 1709 (s, C=O), 1652 (s, C=O), 1591 (s, C=C), 1560 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.18 (d, *J* = 7.5 Hz, 2H, H2''), 7.64 (t, *J* = 7.5 Hz, 1H, H4''), 7.53 (app dt, *J* = 15.6, 7.5 Hz, 4H, H2' and H3''), 7.35 (app dt, *J* = 15.4, 7.1 Hz, 3H, H4' and H3'), 6.49 (s, 1H, H2), 3.98 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.65 (s, 3H, H11), 3.14 (d, *J* = 11.4 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 185.9 (C6), 182.9 (C9), 177.7 (C8), 167.1 (C10), 138.1 (C1'), 134.8 (C1''), 130.1 (C3''), 128.7 (C3'), 128.4 (C4' and C4''), 127.2 (C2' and C2''), 96.8 (C7), 81.5 (C5), 64.2 (C2), 53.6 (C11), 35.7 (C4); *m/z* (ESI$^+$) 418 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{17}O_5NNaS$ [M+Na]$^+$ 418.0720; found 418.0720.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-7-[(*Z*)-hydroxyl(phenyl)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 48



Synthesised from **32iii** (1 eq. 21 mg, 0.05 mmol) with phenylmagnesium bromide; yield (10 mg, 46%); yellow oil; R_f = 0.50 (100% EtOAc); $[\alpha]_D^{25}$ = +2.04 (c = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1750 (s, C=O), 1708 (s, C=O), 1650 (s, C=O), 1591 (s, C=C), 1559 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.2 : 1 AB/CD tautomers: δ (O*H* not observed), 8.17 (d, *J* = 7.9 Hz, 2H, H2''), 7.64 (t, *J* = 7.5 Hz, 1H, H4''), 7.53 (app dt, *J* = 15.6, 7.4 Hz, 4H, H2' and H3''), 7.34 (app dt, *J* = 10.9, 6.8 Hz, 3H, H4' and H3'), 6.49 (s, 1H, H2 major), 6.40 (s, H2 minor), 5.62 – 5.79 (m, 1H, H12), 5.14 – 5.32 (m, 2H, H13), 4.47 – 4.64 (m, 2H, H11), 3.99 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.14 (d, *J* = 11.4 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): a mixture of AB/CD tautomers: δ 189.9 (C6 AB), 185.9 (C6 CD), 182.9 (C9 CD), 181.5 (C6 AB), 177.9 (C8 CD), 177.1 (C8 AB), 166.6, 166.4 (C10), 139.7, 138.1 (C1'), 134.8, 134.4 (C1''), 131.0 (C12), 130.2, 130.0 (C3''), 129.0 (C3'), 128.7 (C4''), 128.4 (C4'), 127.2 (C2'), 126.6 (C2''), 118.4 (C13), 100.5 (C7 AB), 99.0 (C7 CD), 81.6 (C5), 70.0, 67.5 (C11), 64.4, 62.9 (C2), 35.7, 33.8 (C4); *m/z* (ESI$^+$) 444 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{23}H_{19}O_5NNaS$ [M+Na]$^+$ 444.0876; found 444.0876.

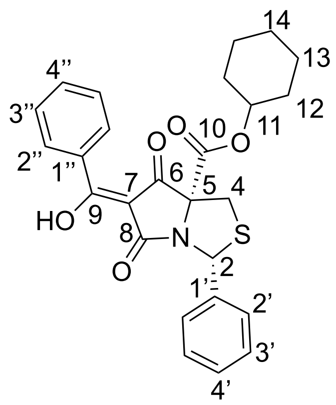
(2*R*,5*R*)-1-Aza-7-[(*Z*)-hydroxyl(phenyl)methylene]-5-isopropoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 49



Synthesised from **33iii** (1 eq. 50 mg, 0.1 mmol) with phenylmagnesium bromide; yield (32 mg, 62%); pale yellow oil; R_f = 0.56 (100% EtOAc); $[\alpha]_D^{25}$ = +235 (c = 0.93, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1709 (s, C=O), 1652 (s, C=O), 1592 (s, C=C), 1560 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.17 (d, *J* = 7.4 Hz, 2H, H2''), 7.64 (t, *J* = 7.4 Hz, 1H, H4''), 7.58 (d, *J* = 7.2 Hz, 2H, H2'), 7.51 (t, *J* = 7.4 Hz, 2H, H3''), 7.34 (app dt, *J* = 13.4, 7.2 Hz, 3H, H4' and H3'), 6.49 (s, 1H, H2), 4.98 (sept, *J* = 6.3 Hz, 1H, H11), 3.98 (d, *J* = 11.3 Hz, 1H, $H4_B$), 3.11 (d, *J* = 11.3 Hz, 1H, $H4_A$), 1.17 (d, *J* = 6.3 Hz, 3H, $H12_B$), 1.03 (d, *J* = 6.3 Hz, 3H, $H12_A$); ^{13}C NMR ($CDCl_3$, 101

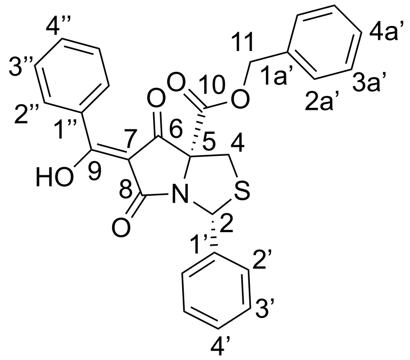
MHz): δ 186.2 (C6), 182.6 (C9), 177.9 (C8), 166.0 (C10), 138.3 (C1'), 134.7 (C1''), 130.1 (C3''), 128.6 (C3'), 128.4 (C4' and C4''), 127.2 (C2' and C2''), 99.0 (C7), 81.7 (C5), 71.2 (C11), 64.2 (C2), 35.5 (C4), 21.6 ($C12_B$), 21.3 ($C12_A$); *m/z* (ESI^+) 424 ($[M+H]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{23}H_{22}O_5NS$ $[M+H]^+$ 424.1213; found 424.1213.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-7-[(*Z*)-hydroxyl(phenyl)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 50



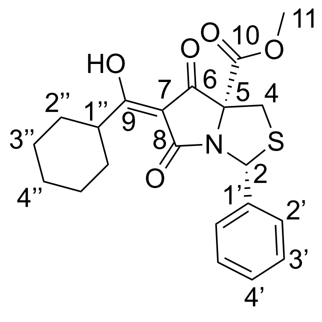
Synthesised from **34iii** (1 eq. 55 mg, 0.1 mmol) with phenylmagnesium bromide; yield (30 mg, 53%); yellow oil; R_f = 0.54 (100% EtOAc); $[\alpha]_D^{25}$ = +180 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1746 (s, C=O), 1709 (s, C=O), 1653 (s, C=O), 1593 (s, C=C), 1560 (s, C=C); ^1H NMR ($CDCl_3$, 400 MHz): a 0.1 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 8.16 (d, *J* = 7.4 Hz, 2H, H2''), 7.64 (t, *J* = 7.4 Hz, 1H, H4''), 7.57 (d, *J* = 7.2 Hz, 2H, H2'), 7.51 (t, *J* = 7.4 Hz, 2H, H3''), 7.34 (app dt, *J* = 12.6, 6.9 Hz, 3H, H3' and H4'), 6.50 (s, H2 minor tautomer), 6.48 (s, 1H, H2 major tautomer), 4.72 – 4.83 (m, 1H, H11), 3.98 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.12 (d, *J* = 11.4 Hz, 1H, $H4_A$), 1.55 – 1.68 (m, 4H, H12), 1.16 – 1.43 (m, 6H, H13 and H14); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 186.4 (C6), 182.5 (C9), 177.9 (C8), 166.0 (C10), 138.3 (C1'), 134.7 (C1''), 131.0, 130.1 (C3''), 128.6 (C3'), 128.6 (C4''), 128.4 (C4'), 127.2 (C2' and C2''), 99.1 (C7), 81.9 (C5), 75.8 (C11), 64.3 (C2), 35.4 (C4), 31.1 (C12), 31.0 (C12), 25.3 (C14), 23.5 (C13), 23.5 (C13); *m/z* (ESI^-) 462 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{26}H_{24}O_5NS$ $[M-H]^-$ 462.1381; found 462.1383.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-7-[(*Z*)-hydroxyl(phenyl)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 51



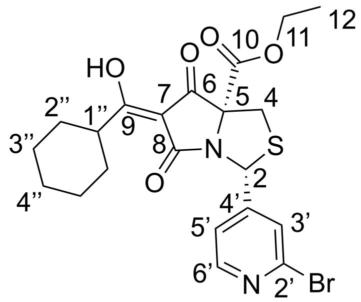
Synthesised from **35iii** (1 eq. 42 mg, 0.09 mmol) with phenylmagnesium bromide; yield (13 mg, 30%); orange oil; R_f = 0.50 (100% EtOAc); $[\alpha]_D^{25}$ = +1.69 (c = 1.3, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1708 (s, C=O), 1651 (s, C=O), 1591 (s, C=C), 1557 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.13 (d, J = 7.5 Hz, 2H, H2’’), 7.64 (t, J = 7.5 Hz, 1H, H4’’), 7.47 – 7.52 (m, 4H, H2’ and H3’’), 7.27 – 7.32 (m, 6H, H3’, H3a’, H4’ and H4a’), 7.18 (dd, J = 6.6, 2.9 Hz, 2H, H2a’), 6.47 (s, 1H, H2), 5.17 (d, J = 12.2 Hz, 1H, $H11_B$), 5.05 (d, J = 12.2 Hz, 1H, $H11_A$), 4.00 (d, J = 11.5 Hz, 1H, $H4_B$), 3.15 (d, J = 11.5 Hz, 1H, $H4_A$); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 185.9 (C6), 182.9 (C9), 178.0 (C8), 166.7 (C10), 138.0 (C1’), 134.8 (C1a’), 134.7 (C1’’), 130.2 (C3’’), 128.7 (C3’ and C3a’), 128.6, 128.5, 128.4 (C2'', C2a’, C4’, C4a’, C4’’), 127.2 (C2’), 99.0 (C7), 81.8 (C5), 68.7 (C11), 64.6 (C2), 35.7 (C4); *m/z* (ESI$^+$) 472 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{27}H_{22}O_5NS$ [M+H]$^+$ 472.1213; found 472.1214.

(2*R*,5*R*)-1-Aza-7-[(*E*)-cyclohexyl(hydroxy)methylene]-5-methoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 52



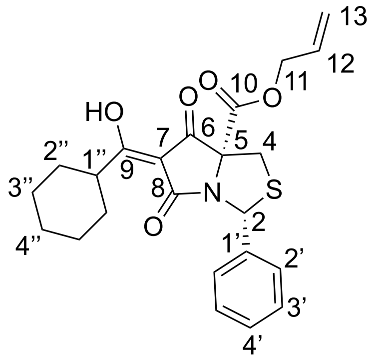
Synthesised from **31iii** (1 eq. 35 mg, 0.09 mmol) with cyclohexylmagnesium bromide; yield (13 mg, 35%); yellow oil; R_f = 0.29 (petrol: EtOAc; 7 : 3); $[\alpha]_D^{25}$ = +155 (c = 1.1, $CHCl_3$); ν_{max}/cm^{-1} 1751 (s, C=O), 1713 (s, C=O), 1653 (s, C=O), 1598 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a 3.8 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 7.51 (d, J = 7.5 Hz, 2H, H2’), 7.33 (app dt, J = 14.4, 7.0 Hz, 3H, H4’ and H3’), 6.44 (s, H2 minor tautomer), 6.41 (s, 1H, H2 major tautomer), 3.94 (d, J = 11.3 Hz, 1H, $H4_B$), 3.64 (s, H11 minor tautomer), 3.62 (s, 3H, H11 major tautomer), 3.30 – 3.39 (m, 1H, H1’’), 3.08 (d, J = 11.3 Hz, 1H, $H4_A$), 1.69 – 1.86 (m, 6H, H3’’ and H2’’), 1.45 – 1.59 (m, 2H, H3’’), 1.30 – 1.44 (m, 2H, H4’’); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 195.3 (C6), 187.1 (C9), 182.4 (C9 minor tautomer), 176.1 (C8), 167.1 (C10), 138.3 (C1’), 128.6 (C3’ and C4’), 127.2 (C2’), 99.0 (C7), 82.1 (C5), 63.7 (C2), 53.5 (C11), 41.5 (C1''), 35.5 (C4), 28.9 (C2''), 28.8 (C2''), 25.6 (C3''), 25.6 (C3''), 25.5 (C4''); *m/z* (ESI$^-$) 400 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{21}H_{22}O_5NS$ [M-H]$^-$ 400.1224; found 400.1227.

(2*R*,5*R*)-1-Aza-2-(2-bromopyridin-4-yl)-7-[(*E*)-cyclohexyl(hydroxy)methylene]-5-ethoxycarbonyl-6,8-dioxo-3-thiabicyclo[3.3.0]-octane, 53



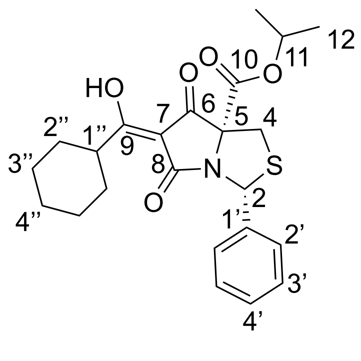
Synthesised from **37iv** (1 eq. 32 mg, 0.07 mmol) with cyclohexylmagnesium bromide; yield (11 mg, 33%); brown oil; R_f = 0.26 (petrol ether : EtOAc; 1 : 4); $[\alpha]_D^{25}$ = +149 (*c* = 1.06, $CHCl_3$); ν_{max}/cm^{-1} 1748 (s, C=O), 1715 (s, C=O), 1656 (s, C=O), 1586 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 3.3 : 1 AB/CD tautomers: δ (O*H* not observed), 8.34 (d, *J* = 5.1 Hz, 1H, H6'), 7.66 (s, 1H, H3'), 7.38 (d, J = 5.1 Hz, 1H, H5'), 6.30 (s, H2 minor), 6.28 (s, 1H, H2 major), 4.16 (q, *J* = 7.1 Hz, 2H, H11), 3.93 (d, *J* = 11.4 Hz, 1H, H4$_B$), 3.40 – 3.32 (m, 1H, H1''), 3.09 (d, *J* = 11.4 Hz, 1H, H4$_A$), 1.88 – 1.72 (m, 6H, H3'' and H2''), 1.59 – 1.46 (m, 2H, H3''), 1.43 – 1.31 (m, 2H, H4''), 1.17 (t, *J* = 7.1 Hz, 3H, H12); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 195.9 (C6), 186.3 (C9), 176.4 (C8), 166.1 (C10), 150.7 (C6'), 150.4 (C4'), 142.7 (C2'), 125.9 (C3'), 121.1 (C5'), 98.6 (C7), 82.3 (C5), 63.7 (C2 minor), 63.5 (C2 major), 62.2 (C11 minor), 61.7 (C11 major), 41.5 (C1''), 35.9 (C4), 28.9 (C2''), 28.8 (C2''), 25.6 (C3''), 25.5 (C3''), 25.5 (C4''), 14.0 (C12); *m/z* (ESI$^-$) 493 and 495 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{21}H_{22}O_5N_2BrS$ [M-H]$^-$ 493.0438 and 495.0418; found 493.0430 and 493.0407.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-7-[(*E*)-cyclohexyl(hydroxy)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 54



Synthesised from **32iii** (1 eq. 24 mg, 0.06 mmol) with cyclohexylmagnesium bromide; yield (10 mg, 39%); pale yellow oil; R_f = 0.42 (100% EtOAc); $[\alpha]_D^{25}$ = +11.0 (c = 0.70, $CHCl_3$); ν_{max}/cm^{-1} 1751 (s, C=O), 1715 (s, C=O), 1654 (s, C=O), 1599 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 4.0 : 1 AB/CD tautomers: δ (O*H* not observed), 7.52 (d, J = 6.4 Hz, 2H, H2'), 7.28 – 7.35 (m, 3H, H3' and H4'), 6.44 (s, H2 minor tautomer), 6.41 (s, 1H, H2 major tautomer), 5.61 – 5.74 (m, 1H, H12), 5.14 – 5.25 (m, 2H, H13), 4.45 – 4.59 (m, 2H, H11), 3.95 (d, J = 11.3 Hz, 1H, H4$_B$), 3.29 – 3.42 (m, 1H, H1''), 3.08 (d, J = 11.3 Hz, 1H, H4$_A$), 1.70 – 1.86 (m, 6H, H3'' and H2''), 1.45 – 1.59 (m, 2H, H3''), 1.32 – 1.44 (m, 2H, H4''); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 195.3 (C6), 187.1 (C9), 176.3 (C8), 166.4 (C10), 138.3 (C1'), 131.0 (C12), 128.6 (C3'), 128.6 (C4'), 127.2 (C2'), 119.5 (C13), 99.0 (C7), 82.3 (C5), 67.4 (C11), 63.8 (C2), 41.4 (C1''), 35.5 (C4), 28.9 (C2''), 28.8 (C2''), 25.6 (C3''), 25.6 (C3''), 25.5 (C4''); m/z (ESI$^-$) 426 ([M-H]$^-$, 100%); HRMS (ESI$^-$) m/z calcd for $C_{23}H_{24}O_5NS$ [M-H]$^-$ 426.1381; found 426.1385.

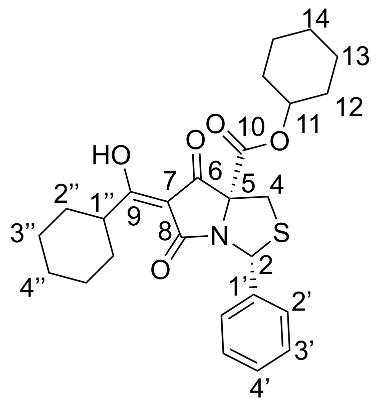
(2*R*,5*R*)-1-Aza-7-[(*E*)-cyclohexyl(hydroxy)methylene]-5-isopropoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 55



Synthesised from **33iii** (1 eq. 32 mg, 0.08 mmol) with cyclohexylmagnesium bromide; yield (10 mg, 30%); yellow oil; R_f = 0.26 (petrol ether : EtOAc; 3 : 7); $[\alpha]_D^{25}$ = +163 (c = 0.60, $CHCl_3$); ν_{max}/cm^{-1} 1748 (s, C=O), 1714 (s, C=O), 1655 (s, C=O), 1601 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 4.0 : 1 AB/CD tautomers: δ (O*H* not observed), 7.53 (d, J = 7.3 Hz, 2H, H2'), 7.28 – 7.36 (m, 3H, H3' and H4'), 6.43 (s, H2 minor tautomer), 6.40 (s, 1H, H2 major tautomer), 4.94 (sept, J = 6.3 Hz, 1H, H11), 3.93 (d, J = 11.3 Hz, 1H, H4$_B$), 3.36 (tt, J = 11.6, 3.2 Hz, 1H, H1''), 3.06 (d, J = 11.3 Hz, 1H, H4$_A$), 1.68 – 1.88 (m, 6H, H3'' and H2''), 1.45 – 1.60 (m, 2H, H3''), 1.31 – 1.45 (m, 2H, H4''), 1.14 (d, J = 6.3 Hz, 3H, H12$_B$), 1.01 (d, J =

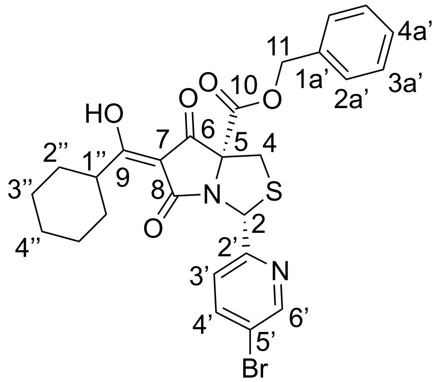
6.3 Hz, 3H, H12$_A$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 195.1 (C6), 187.4 (C9), 176.4 (C8), 166.0 (C10), 138.5 (C1'), 128.6 (C3'), 128.5 (C4'), 127.2 (C2'), 99.0 (C7), 82.4 (C5), 71.1 (C11), 63.7 (C2), 41.4 (C1''), 35.4 (C4), 28.9 (C2''), 28.7 (C2''), 25.6 (C3''), 25.6 (C3''), 25.5 (C4''), 21.5 (C12$_B$), 21.3 (C12$_A$); *m/z* (ESI$^-$) 428 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{23}H_{26}O_5NS$ [M-H]$^-$ 428.1537; found 428.1539.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-7-[(*E*)-cyclohexyl(hydroxy)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 56



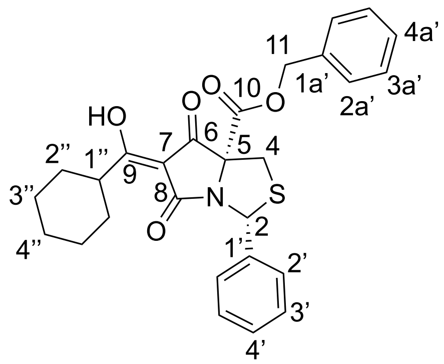
Synthesised from **34iii** (1 eq. 30 mg, 0.07 mmol) with cyclohexylmagnesium bromide; yield (18 mg, 57%); pale yellow oil; R_f = 0.47 (petrol ether : EtOAc; 7 : 3); $[\alpha]_D^{25}$ = +3.12 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1713 (s, C=O), 1655 (s, C=O), 1600 (s, C=C); ^1H NMR ($CDCl_3$, 400 MHz): a mixture of 4.3 : 1 AB/CD tautomers: δ (O*H* not observed), 7.53 (d, *J* = 6.3 Hz, 2H, H2'), 7.28 – 7.35 (m, 3H, H3' and H4'), 6.42 (s, H2 minor tautomer), 6.39 (s, 1H, H2 major tautomer), 4.68 – 4.80 (m, 1H, H11), 3.93 (d, *J* = 11.3 Hz, 1H, H4$_B$), 3.36 (tt, *J* = 11.5, 3.1 Hz, 1H, H1''), 3.06 (d, *J* = 11.3 Hz, 1H, H4$_A$), 1.65 – 1.89 (m, 8H, H12 and H2''), 1.40 – 1.65 (m, 8H, H3'' and H13), 1.32 – 1.39 (m, 4H, H4'' and H14); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 195.0 (C6), 187.6 (C9), 176.4 (C8), 165.9 (C10 major tautomer), 164.7 (C10 minor tautomer), 138.5 (C1'), 128.6 (C3'), 128.5 (C4'), 127.2 (C2'), 99.1 (C7), 82.5 (C5), 75.6 (C11), 63.8 (C2 major tautomer), 62.3 (C2 minor tautomer), 41.3 (C1''), 35.2 (C4), 31.1 (C12), 31.0 (C12), 28.9 (C2''), 28.7 (C2''), 25.6 (C3''), 25.6 (C3''), 25.5 (C4''), 25.3 (C14), 23.5 (C13), 23.5 (C13); *m/z* (ESI$^+$) 492 ([M+Na]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{26}H_{31}O_5NNaS$ [M+Na]$^+$ 492.1815; found 492.1816.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-2-(5-bromopyridin-2-yl)-7-[(*E*)-cyclohexyl(hydroxy)methylene]-6,8-dioxo-3-thiabicyclo[3.3.0]-octane, 57



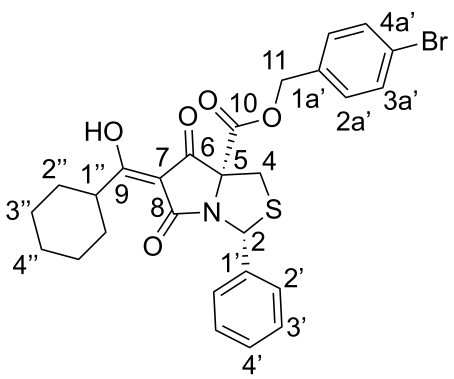
Synthesised from **35ii** (1 eq. 50 mg, 0.09 mmol) with cyclohexylmagnesium bromide; yield (15 mg, 29%); orange oil; R_f = 0.32 (100% EtOAc); $[\alpha]_D^{25}$ = +41.0 (c = 0.99, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1712 (s, C=O), 1655 (s, C=O), 1598 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 3.7 : 1 AB/CD tautomers: δ (O*H* not observed), 8.56 (d, *J* = 2.0 Hz, 1H, H6'), 7.84 – 7.76 (m, 1H, H4'), 7.37 – 7.28 (m, 3H, H3a' and H4a'), 7.24 – 7.15 (m, 3H, H2a' and H3'), 6.38 (s, H2 minor tautomer), 6.35 (s, 1H, H2 major tautomer), 5.21 (d, *J* = 12.3 Hz, 1H, $H11_B$), 5.11 (d, *J* = 12.3 Hz, 1H, $H11_A$), 3.94 (d, *J* = 11.5 Hz, 1H, $H4_B$), 3.39 – 3.34 (m, 1H, H1''), 3.14 (d, *J* = 11.5 Hz, 1H, $H4_A$), 1.86 – 1.70 (m, 6H, H3'' and H2''), 1.55 – 1.46 (m, 2H, H3''), 1.42 – 1.35 (m, 2H, H4''); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 195.7 (C6 AB), 194.3 (C6 CD), 187.0 (C9 AB), 186.0 (C9 CD), 176.8 (C8 AB), 172.9 (C8 CD), 166.8 (C10 CD), 166.5 (C10 AB), 156.5, 156.4 (C2'), 151.3, 150.4 (C6'), 139.5, 139.4 (C4'), 134.7 (C1a'), 128.7 (C3a'), 128.6 (C4a'), 127.1 (C2a'), 122.9, 121.6 (C3'), 120.2, 120.0 (C5'), 102.0 (C7 CD), 98.9 (C7 AB), 85.1, 83.3 (C5), 68.6 (C11), 64.3 (C2), 41.5, 41.3 (C1''), 35.8 (C4), 28.9, 28.9, 28.8, 28.7 (C2''), 25.7, 25.6, 25.6, 25.5, 25.5, 25.5 (C3'' and C4''); *m/z* (ESI$^-$) 555 and 557 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{26}H_{24}O_5N_2BrS$ [M-H]$^-$ 555.0595 and 557.0574; found 555.0590 And 557.0578.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-7-[(*E*)-cyclohexyl(hydroxy)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 58



Synthesised from **35iii** (1 eq. 72 mg, 0.2 mmol) with cyclohexylmagnesium bromide; yield (28 mg, 37%); yellow oil; R_f = 0.67 (100% EtOAc); $[\alpha]_D^{25}$ = +45.1 (c = 0.60, $CHCl_3$); ν_{max}/cm^{-1} 1749 (s, C=O), 1712 (s, C=O), 1656 (s, C=O), 1597 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 4.6 : 1 AB/CD tautomers: δ (O*H* not observed), 7.49 – 7.44 (m, 2H, H2'), 7.32 – 7.27 (m, 3H, H3' and H4'), 7.26 – 7.23 (m, 3H, H3a' and H4a'), 7.17 – 7.12 (m, 2H, H2a'), 6.42 (s, H2 minor tautomer), 6.38 (s, 1H, H2 major tautomer), 5.14 (d, *J* = 12.3 Hz, 1H, $H11_B$), 5.00 (d, *J* = 12.3 Hz, 1H, $H11_A$), 3.96 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.34 (tt, *J* = 11.6, 3.2 Hz, 1H, H1''), 3.10 (d, *J* = 11.4 Hz, 1H, $H4_A$), 1.88 – 1.68 (m, 6H, H3'' and H2''), 1.60 – 1.46 (m, 2H, H3''), 1.45 – 1.30 (m, 2H, H4''); ^{13}C NMR ($CDCl_3$, 101 MHz): AB major: δ 195.3 (C6), 187.1 (C9), 176.4 (C8), 166.6 (C10), 138.2 (C1'), 134.7 (C1a'), 128.7, 128.6, 128.6, 128.5 (C3' and C3a'), 128.4, 128.3 (C4' and C4a'), 127.2, 127.1 (C2' and C2a'), 99.0 (C7), 82.4 (C5), 68.5 (C11), 64.0 (C2), 41.4 (C1''), 35.4 (C4), 28.9 (C2''), 28.7 (C2''), 25.6 (C3''), 25.6 (C3''), 25.5 (C4''); *m/z* (ESI$^+$) 478 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{27}H_{28}O_5NS$ [M+H]$^+$ 478.1683; found 478.1682.

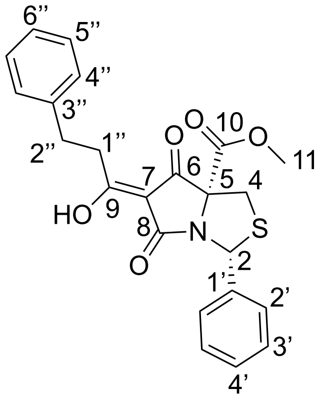
(2*R*,5*R*)-1-Aza-5-(4-bromobenzyloxycarbonyl)-7-[(*E*)-cyclohexyl(hydroxy)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 59



Synthesised from **39iii** (1 eq. 37 mg, 0.07 mmol) with cyclohexylmagnesium bromide; yield (14 mg, 36%); yellow oil; R_f = 0.68 (100% EtOAc); $[\alpha]_D^{25}$ = +66.0 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1750 (s, C=O), 1712 (s, C=O), 1655 (s, C=O), 1595 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 5.1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.48 – 7.41 (m, 3H, H2' and H4'), 7.39 (d, *J* = 8.4 Hz, 2H, H3a'), 7.28 – 7.22 (m, 2H, obscured by solvent peak, H3'), 6.97 (d, *J* = 8.4 Hz, 2H, H2a'), 6.41 (s, H2 minor tautomer), 6.38 (s, 1H, H2 major tautomer), 5.08 – 4.91 (m, 2H, H11) 3.93 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.32 (tt, *J* = 11.6, 3.3 Hz, 1H, H1''), 3.08 (d, *J* = 11.4 Hz, 1H, $H4_A$), 1.87 – 1.69 (m, 6H, H3'' and H2''), 1.57 – 1.44 (m, 2H, H3'), 1.43 – 1.29 (m, 2H, H4''); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 195.5 (C6 AB), 186.9 (C9 AB), 176.4 (C8 AB), 166.6 (C10), 138.2 (C1'), 133.7 (C1a'), 131.9 (C3a' minor), 131.8 (C3a' major), 130.1 (C2a' major), 130.0 (C2a' minor), 128.6 (C3'), 128.6 (C4'), 127.2 (C2' minor), 127.1 (C2' major), 122.7 (C4a'), 98.9 (C7), 82.3 (C5), 67.8 (C11 minor), 67.6 (C11 major), 63.9 (C2), 41.5 (C1''), 35.4 (C4), 28.9

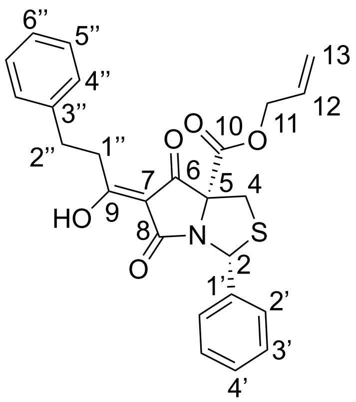
(C2''), 28.7 (C2''), 25.6 (C3''), 25.5 (C4''); *m/z* (ESI$^-$) 554 and 556 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{27}H_{25}O_5NBrS$ [M-H]$^-$ 554.0642 and 556.0623; found 554.0265 and 556.0628.

(2*R*,5*R*)-1-Aza-7-[(*Z*)-1-hydroxy-3-phenylpropylidene]-5-methoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 60



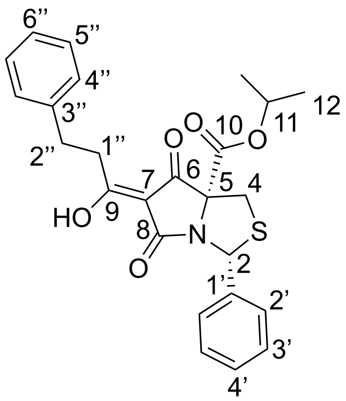
Synthesised from **31iii** (1 eq. 40 mg, 0.1 mmol) with phenethylmagnesium bromide; yield (18 mg, 40%); pale yellow oil; R_f = 0.37 (100% EtOAc); $[\alpha]_D^{25}$ = +148 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1752 (s, C=O), 1715 (s, C=O), 1655 (s, C=O), 1601 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 7.50 (d, *J* = 7.7 Hz, 2H, H2'), 7.19 – 7.38 (m, 8H, H4', H3', H4'', H5'' and H6''), 6.40 (s, 1H, H2), 3.91 (d, *J* = 11.3 Hz, 1H, H4$_B$), 3.60 (s, 3H, H11), 3.10 – 3.24 (m, 2H, H2''), 2.99 (d, *J* = 8.1 Hz, 2H, H1''), 2.98 (d, *J* = 11.3 Hz, 1H, H4$_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.8 (C6), 187.1 (C9), 175.3 (C8), 167.0 (C10), 139.4 (C3''), 138.2 (C1'), 128.7 (C3' and C5''), 128.6, 128.6 (C4' and C4''), 127.2 (C2'), 126.7 (C6''), 100.8 (C7), 82.1 (C5), 63.7 (C2), 53.5 (C11), 35.3 (C4), 34.7 (C1''), 32.0 (C2''); *m/z* (ESI$^+$) 424 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{23}H_{22}O_5NS$ [M+H]$^+$ 424.1213; found 424.1215.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-7-[(*Z*)-1-hydroxy-3-phenylpropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 61



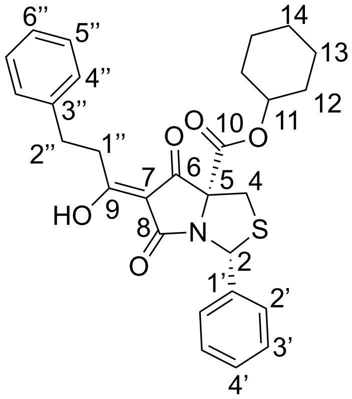
Synthesised from **32iii** (1 eq. 27 mg, 0.07 mmol) with phenethylmagnesium bromide; yield (10 mg, 33%); yellow oil; R_f = 0.54 (100% EtOAc); $[\alpha]_D^{25}$ = +2.91 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1711 (s, C=O), 1652 (s, C=O), 1600 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.8 : 1 AB/CD tautomers: δ (O*H* not observed), 7.55 (d, *J* = 7.2 Hz, 2H, H2' minor tautomer), 7.51 (d, *J* = 6.9 Hz, 2H, H2' major tautomer), 7.17 – 7.40 (m, 16H, H4', H3', H4'', H5'' and H6''), 6.41 (s, 1H, H2 minor, AB), 6.40 (s, 1H, H2 major, CD), 5.58 – 5.73 (m, 2H, H12), 5.10 – 5.26 (m, 4H, H13), 4.41 – 4.58 (m, 4H, H11), 4.08 (d, *J* = 11.4 Hz, 1H, $H4_B$ minor tautomer), 3.92 (d, *J* = 11.4 Hz, 1H, $H4_B$ major tautomer), 3.08 – 3.34 (m, 4H, H2''), 2.85 – 3.04 (m, 6H, H1'' and $H4_A$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 191.5 (C6 AB), 189.8 (C6 CD), 188.1 (C9 AB), 187.2 (C9 CD), 175.5 (C8 CD), 174.7 (C8 AB), 166.2 (C10), 140.4, 139.4 (C3''), 138.1, 137.8 (C1'), 130.9 (C12), 129.0, 128.7 (C3'), 128.6, 128.6 (C5''), 128.6, 128.5 (C4''), 128.3, 128.1 (C4'), 127.2, 126.7 (C2'), 126.5, 126.3 (C6''), 119.5 (C13), 102.3 (C7 AB), 100.8 (C7 CD), 87.3, 82.2 (C5), 70.1, 67.4 (C11), 64.2, 63.3 (C2), 35.3 (C4), 34.7, 34.5 (C1''), 32.1, 32.0 (C2''); *m/z* (ESI^+) 472 ($[M+Na]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{25}H_{23}O_5NNaS$ $[M+Na]^+$ 472.1189; found 472.1193.

(2*R*,5*R*)-1-Aza-7-[(*Z*)-1-hydroxy-3-phenylpropylidene]-5-isopropoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 62



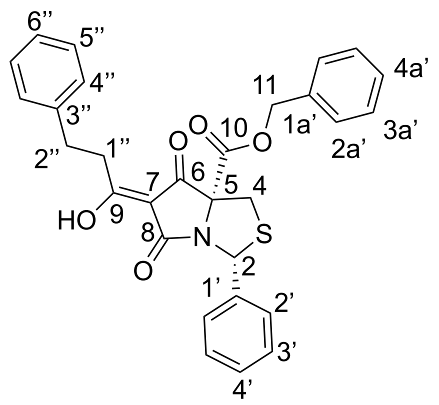
Synthesised from **33iii** (1 eq. 74 mg, 0.2 mmol) with phenethylmagnesium bromide; yield (37 mg, 45%); pale yellow oil; R_f = 0.44 (100% EtOAc); $[\alpha]_D^{25}$ = +153 (*c* = 1.1, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1713 (s, C=O), 1653 (s, C=O), 1600 (s, C=C); ^1H NMR ($CDCl_3$, 400 MHz): a mixture of 0.1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.53 (d, *J* = 7.0 Hz, 2H, H2'), 7.17 – 7.38 (m, 8H, H4', H3', H4'', H5'' and H6''), 6.41 (s, H2 minor tautomer), 6.40 (s, 1H, H2 major tautomer), 4.87 – 4.98 (m, 1H, H11), 4.08 (d, *J* = 11.3 Hz, $H4_B$ minor tautomer), 3.91 (d, *J* = 11.3 Hz, 1H, $H4_B$, major tautomer), 3.08 – 3.28 (m, 2H, H2''), 2.97 – 3.09 (m, 2H, H1''), 2.96 (d, *J* = 11.3 Hz, 1H, $H4_A$), 1.12 (d, *J* = 6.3 Hz, 3H, $H12_B$), 0.99 (d, *J* = 6.3 Hz, 3H, $H12_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): CD major only: δ 189.5 (C6), 187.5 (C9), 175.6 (C8), 165.9 (C10), 139.4 (C3''), 138.3 (C1'), 128.7 (C3' and C5''), 128.6, 128.5 (C4' and C4''), 127.2 (C2'), 126.7 (C6''), 100.8 (C7), 82.4 (C5), 71.1 (C11), 63.6 (C2), 35.2 (C4), 34.7 (C1''), 32.0 (C2''), 21.5 ($C12_B$), 21.2 ($C12_A$); *m/z* (ESI$^+$) 452 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{25}H_{26}O_5NS$ [M+H]$^+$ 452.1526; found 452.1527.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-7-[(*Z*)-1-hydroxy-3-phenylpropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 63



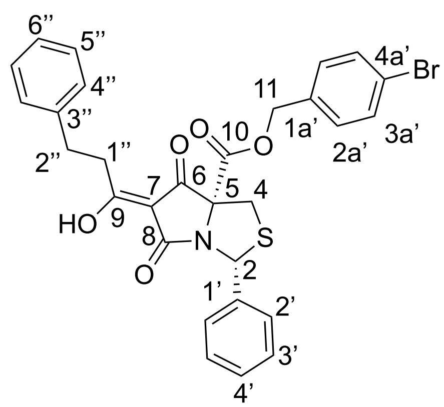
Synthesised from **34iii** (1 eq. 55 mg, 0.1 mmol) with phenethylmagnesium bromide; yield (44 mg, 73%); yellow oil; R_f = 0.47 (100% EtOAc); $[\alpha]_D^{25}$ = +114 (*c* = 0.98, $CHCl_3$); ν_{max}/cm^{-1} 1746 (s, C=O), 1714 (s, C=O), 1654 (s, C=O), 1602 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.2 : 1 AB/CD tautomers: δ (O*H* not observed), 7.54 (d, *J* = 7.0 Hz, 2H, H2'), 7.19 – 7.38 (m, 8H, H4', H3', H4'', H5'' and H6''), 6.42 (s, H2 minor tautomer), 6.40 (s, 1H, H2 major tautomer), 4.68 – 4.78 (m, 1H, H11), 4.09 (d, *J* = 11.1 Hz, $H4_B$ minor tautomer), 3.92 (d, *J* = 11.3 Hz, 1H, $H4_B$ major tautomer), 3.13 – 3.24 (m, 2H, H2''), 2.95 – 3.05 (m, 2H, H1''), 2.99 (d, *J* = 11.3 Hz, 1H, $H4_A$), 1.54 – 1.65 (m, 4H, H12), 1.16 – 1.38 (m, 6H, H14 and H13); ^{13}C NMR ($CDCl_3$, 101 MHz): CD major only: δ 189.4 (C6), 187.6 (C9), 175.6 (C8), 165.8 (C10), 139.5 (C3''), 138.3 (C1'), 128.7 (C3' and C5''), 128.6, 128.5 (C4' and C4''), 127.2 (C2'), 126.7 (C6''), 100.9 (C7), 82.5 (C5), 75.7 (C11), 63.7 (C2), 35.1 (C4), 34.7 (C1''), 32.0 (C2''), 31.1 (C12), 30.9 (C12), 25.3 (C14), 23.5 (C13); *m/z* (ESI$^-$) 490 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{28}H_{28}O_5NS$ [M-H]$^-$ 490.1694; found 490.1697.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-7-[(*Z*)-1-hydroxy-3-phenylpropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 64



Synthesised from **35iii** (1 eq. 27 mg, 0.06 mmol) with phenethylmagnesium bromide; yield (12 mg, 40%); pale yellow oil; R_f = 0.51 (100% EtOAc); $[\alpha]_D^{25}$ = +1.46 (c = 1.2, CHCl$_3$); ν_{max}/cm^{-1} 1749 (s, C=O), 1713 (s, C=O), 1654 (s, C=O), 1599 (s, C=C); ^{1}H NMR (CDCl$_3$, 400 MHz): δ (O*H* not observed), 7.46 (dd, J = 6.4, 2.9 Hz, 2H, H2'), 7.21 – 7.31 (m, 11H, H4', H4a', H3', H3a', H4'', H5'' and H6''), 7.13 (dd, J = 6.4, 2.9 Hz, 2H, H2a'), 6.38 (s, 1H, H2), 5.11 (d, J = 12.2 Hz, 1H, H11$_B$), 4.99 (d, J = 12.2 Hz, 1H, H11$_A$), 3.93 (d, J = 11.4 Hz, 1H, H4$_B$), 3.11 – 3.19 (m, 2H, H2''), 3.00 (d, J = 11.4 Hz, 1H, H4$_A$), 2.93 – 2.98 (m, 2H, H1''); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 189.8 (C6), 187.1 (C9), 175.6 (C8), 166.5 (C10), 139.4 (C3''), 138.1 (C1'), 134.6 (C1a'), 128.7, 128.5, 128.4 (C2a', C3', C3a', C4', C4a', C4'', C5''), 127.2 (C2'), 126.7 (C6''), 100.8 (C7), 82.4 (C5), 68.6 (C11), 63.9 (C2), 35.3 (C4), 34.8 (C1''), 32.0 (C2''); *m/z* (ESI$^+$) 500 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{29}H_{26}O_5NS$ [M+H]$^+$ 500.1526; found 500.1525.

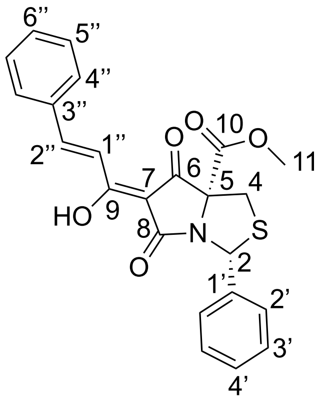
(2*R*,5*R*)-1-Aza-5-(4-bromobenzyloxycarbonyl)-7-[(*Z*)-1-hydroxy-3-phenylpropylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 65



Synthesised from **39iii** (1 eq. 30 mg, 0.06 mmol) with phenethylmagnesium bromide; yield (10 mg, 31%); pale yellow oil; R_f = 0.50 (100% EtOAc); $[\alpha]_D^{25}$ = +54.0 (c = 0.50, CHCl$_3$); ν_{max}/cm^{-1} 1749 (s, C=O), 1713 (s, C=O), 1627 (s, C=O), 1599 (s, C=C); ^{1}H NMR (CDCl$_3$, 400 MHz): a mixture of 0.1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.47 – 7.41 (m, 2H, H2'), 7.39 (d, J = 8.4 Hz, 2H, H3a'), 7.30 – 7.19 (m, 8H, H4', H3', H4'', H5'' and H6''), 6.96 (d, J = 8.4 Hz, 2H, H2a'), 6.43 (s, H2 minor, AB), 6.38 (s, 1H, H2 major, CD), 5.00 (d, J = 12.4 Hz, 1H, H11$_B$), 4.94 (d, J = 12.4 Hz, 1H, H11$_A$), 3.91 (d, J = 11.4 Hz, 1H, H4$_B$), 3.22 – 3.11 (m, 2H, H2''), 3.00 – 2.94 (m, 3H, H4$_A$

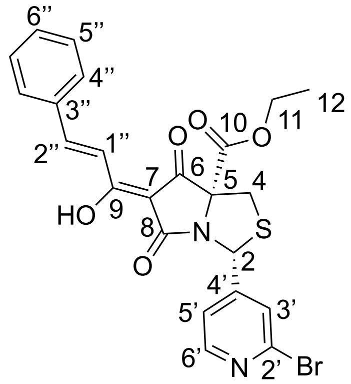
and H1''); ^{13}C NMR ($CDCl_3$, 101 MHz): CD major only: δ 190.1 (C6), 187.1 (C9), 175.6 (C8), 166.5 (C10), 139.5 (C3''), 138.1 (C1'), 133.4 (C1a'), 132.0 (C3a'), 130.2 (C2a'), 128.8, 128.8, 128.6 (C3', C4', C4'', C5''), 127.3 (C2'), 126.8 (C6''), 122.9 (C4a'), 100.8 (C7), 82.4 (C5), 67.8 (C11), 63.9 (C2), 35.4 (C4), 34.9 (C1''), 32.1 (C2''); *m/z* (ESI$^-$) 576 and 578 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{29}H_{23}O_5NBrS$ [M-H]$^-$ 576.0475 and 578.0456; found 576.0492 and 578.0474.

(2*R*,5*R*)-1-Aza-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-5-methoxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 66



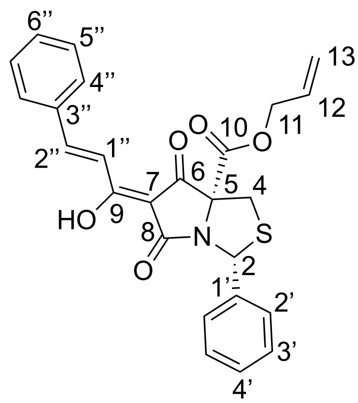
Synthesised from **31iii** (1 eq. 40 mg, 0.1 mmol) with β-styrylmagnesium bromide; yield (26 mg, 58%); yellow oil; R_f = 0.51 (100% EtOAc); $[\alpha]_D^{25}$ = +214 (*c* = 0.95, $CHCl_3$); ν_{max}/cm^{-1} 1750 (s, C=O), 1706 (s, C=O), 1652 (s, C=O), 1625 (s, C=C), 1581 (s, C=C), 1563 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a 0.26 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 7.96 (d, *J* = 16.0 Hz, 1H, H1''), 7.73 (d, *J* = 16.0 Hz, 1H, H2''), 7.66 (dd, *J* = 7.6, 1.9 Hz, 2H, H4''), 7.54 (d, *J* = 7.5 Hz, 2H, H2'), 7.28 – 7.47 (m, 6H, H3', H4', H5'' and H6''), 6.51 (s, H2 minor tautomer), 6.46 (s, 1H, H2 major tautomer), 3.98 (d, *J* = 11.3 Hz, 1H, H4_B), 3.64 (s, 3H, H11), 3.14 (d, *J* = 11.3 Hz, 1H, H4_A); ^{13}C NMR ($CDCl_3$, 101 MHz): CD major only: δ 187.5 (C6), 176.2 (C9), 176.0 (C8), 167.2 (C10), 146.9 (C2''), 138.4 (C1'), 134.3 (C3''), 131.9 (C4''), 129.4, 129.3 (C3' and C5''), 128.6, 128.6 (C4' and C6''), 127.2 (C2'), 117.4 (C1''), 99.5 (C7), 82.2 (C5), 63.9 (C2), 53.5 (C11), 35.5 (C4); *m/z* (ESI$^-$) 420 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{23}H_{18}O_5NS$ [M-H]$^-$ 420.0911; found 420.0914.

(2*R*,5*R*)-1-Aza-2-(2-bromopyridin-4-yl)-5-ethoxycarbonyl-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-6,8-dioxo-thiabicyclo[3.3.0]-octane, 67



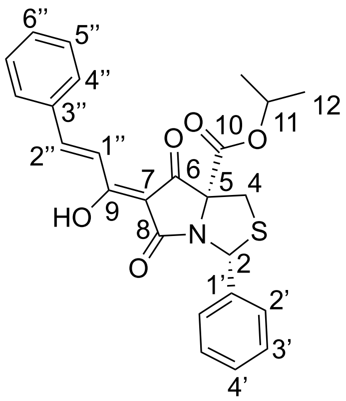
Synthesised from **37iv** (1 eq. 98 mg, 0.2 mmol) with β-styrylmagnesium bromide; yield (33 mg, 31%); orange oil; R_f = 0.16 (petrol ether : EtOAc; 3 : 7); $[\alpha]_D^{25}$ = +89.6 (*c* = 1.11, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1708 (s, C=O), 1653 (s, C=O), 1622 (s, C=C), 1580 (s, C=C), 1561 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a 0.34 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 8.35 (d, *J* = 5.0 Hz, 1H, H6'), 7.99 (d, *J* = 16.0 Hz, 1H, H1''), 7.73 (d, *J* = 16.0 Hz, 1H, H2''), 7.70 – 7.61 (m, 3H, H3' and H4''), 7.50 – 7.35 (m, 4H, H5', H5'' and H6''), 6.36 (s, H2 minor tautomer), 6.32 (s, 1H, H2 major tautomer), 4.17 (q, *J* = 7.1 Hz, 2H, H11), 3.96 (d, *J* = 11.4 Hz, 1H, H4$_B$), 3.19 (d, *J* = 11.5 Hz, H4$_A$ minor), 3.15 (d, *J* = 11.4 Hz, 1H, H4$_A$ major), 1.18 (t, *J* = 7.1 Hz, 3H, H12); ^{13}C NMR ($CDCl_3$, 101 MHz): major CD tautomer only: δ 186.7 (C6), 176.6 (C9), 176.3 (C8), 166.2 (C10), 150.7 (C6'), 150.4 (C4'), 147.7 (C2''), 142.7 (C2'), 134.1 (C3''), 132.2 (C4''), 129.6, 129.3 (C5''), 128.5 (C6''), 125.9 (C3'), 121.1 (C5'), 117.1 (C1''), 99.0 (C7), 82.4 (C5), 63.5 (C2), 61.8 (C11), 35.9 (C4), 14.0 (C12); *m/z* (ESI$^-$) 513 and 515 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{23}H_{18}O_5N_2BrS$ [M-H]$^-$ 513.0125 and 515.0105; found 513.0116 and 515.0093.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 68



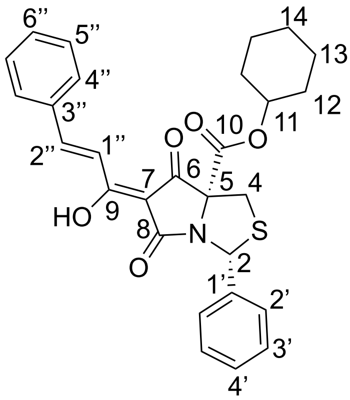
Synthesised from **32iii** (1 eq. 22 mg, 0.05 mmol) with β-styrylmagnesium bromide; yield (14 mg, 58%); yellow oil; R_f = 0.32 (petrol ether : EtOAc; 3 : 7); $[\alpha]_D^{25}$ = +6.83 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1749 (s, C=O), 1706 (s, C=O), 1652 (s, C=O), 1625 (s, C=C), 1581 (s, C=C), 1564 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a 0.17 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 7.96 (d, *J* = 15.9 Hz, 1H, H1''), 7.73 (d, *J* = 15.9 Hz, 1H, H2''), 7.67 (dd, *J* = 7.5, 1.9 Hz, 2H, H4''), 7.55 (d, *J* = 7.0 Hz, 2H, H2'), 7.31 – 7.47 (m, 6H, H3', H4', H5'' and H6''), 6.51 (s, H2 minor tautomer), 6.46 (s, 1H, H2 major tautomer), 5.63 – 5.75 (m, 1H, H12), 5.15 – 5.26 (m, 2H, H13), 4.49 – 4.56 (m, 2H, H11), 3.99 (d, *J* = 11.4 Hz, 1H, H4$_B$), 3.14 (d, *J* = 11.4 Hz, 1H, H4$_A$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): major CD tautomer: δ 187.5 (C6), 176.2 (C9), 176.1 (C8), 166.5 (C10), 146.9 (C2''), 138.3 (C1'), 134.2 (C3''), 131.9 (C4''), 131.0 (C12), 129.5, 129.3 (C3' and C5''), 128.6, 128.6 (C4' and C6''), 127.2 (C2'), 119.6 (C13), 117.4 (C1''), 99.5 (C7), 82.3 (C5), 67.5 (C11), 64.0 (C2), 35.5 (C4); minor AB tautomer: δ 196.3 (C6), 176.7 (C9), 175.0 (C8), 169.0 (C10), 146.0 (C2''), 139.9 (C1'), 134.4 (C3''), 131.6 (C4''), 130.9 (C12), 129.6, 129.2 (C3' and C5''), 128.6, 128.5 (C4' and C6''), 126.6 (C2'), 119.6 (C13), 117.6 (C1''), 101.1 (C7), 80.6 (C5), 70.5 (C11), 62.5 (C2), 35.7 (C4); *m/z* (ESI$^-$) 446 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{25}H_{20}O_5NS$ [M-H]$^-$ 446.1068; found 446.1070.

(2*R*,5*R*)-1-Aza-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-5-isopropyloxycarbonyl-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 69



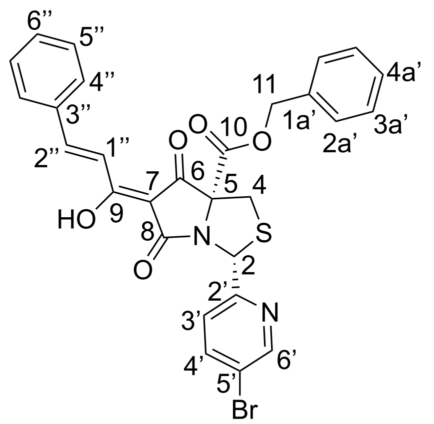
Synthesised from **33iii** (1 eq. 40 mg, 0.1 mmol) with β-styrylmagnesium bromide; yield (34 mg, 77%); yellow oil; R_f = 0.34 (petrol ether : EtOAc; 3 : 7); $[\alpha]_D^{25}$ = +287 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1744 (s, C=O), 1707 (s, C=O), 1652 (s, C=O), 1625 (s, C=C), 1581 (s, C=C), 1565 (s, C=C); ^1H NMR ($CDCl_3$, 400 MHz): a 0.28 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 7.96 (d, *J* = 16.0 Hz, 1H, H1''), 7.74 (d, *J* = 16.0 Hz, 1H, H2''), 7.67 (dd, *J* = 7.4, 1.9 Hz, 2H, H4''), 7.57 (d, *J* = 7.2 Hz, 2H, H2'), 7.29 – 7.47 (m, 6H, H3', H4', H5'' and H6''), 6.50 (s, H2 minor tautomer), 6.46 (s, 1H, H2 major tautomer), 4.95 (sept, *J* = 6.2 Hz, 1H, H11), 3.97 (d, *J* = 11.3 Hz, 1H, H4$_B$), 3.11 (d, *J* = 11.3 Hz, 1H, H4$_A$), 1.16 (d, *J* = 6.2 Hz, 3H, H12$_B$), 1.02 (d, *J* = 6.2 Hz, 3H, H12$_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): major CD tautomer: δ 187.7 (C6), 176.3 (C9), 176.0 (C8), 166.1 (C10), 146.7 (C2''), 138.5 (C1'), 134.3 (C3''), 131.9 (C4''), 129.4, 129.2 (C3' and C5''), 128.6, 128.5 (C4' and C6''), 127.3 (C2'), 117.5 (C1''), 99.6 (C7), 82.5 (C5), 71.2 (C11), 63.8 (C2), 35.5 (C4), 21.5 (C12$_B$), 21.3 (C12$_A$); minor AB tautomer: δ 196.7 (C6), 176.5 (C9), (C8 not shown), 169.1 (C10), 147.3 (C2''), 139.1 (C1'), 134.3 (C3''), 132.0 (C4''), 129.5, 129.3 (C3' and C5''), 128.6, 128.3 (C4' and C6''), 127.3 (C2'), 116.7 (C1''), 101.8 (C7), 80.8 (C5), 71.3 (C11), 64.1 (C2), 35.6 (C4), 21.5 ($C12_B$), 21.3 ($C12_A$); *m/z* (ESI^+) 472 ($[M+Na]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{25}H_{23}O_5NNaS$ $[M+Na]^+$ 472.1189; found 472.1190.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 70



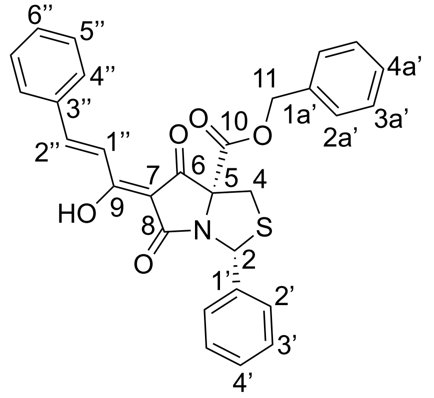
Synthesised from **34iii** (1 eq. 57 mg, 0.1 mmol) with β-styrylmagnesium bromide; yield (33 mg, 53%); yellow oil; R_f = 0.32 (petrol ether : EtOAc; 1 : 4); $[\alpha]_D^{25}$ = +7.30 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1743 (s, C=O), 1706 (s, C=O), 1651 (s, C=O), 1625 (s, C=C), 1581 (s, C=C), 1564 (s, C=C); ^1H NMR ($CDCl_3$, 400 MHz): a 0.28 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 7.95 (d, *J* = 16.0 Hz, 1H, H1''), 7.74 (d, *J* = 16.0 Hz, 1H, H2''), 7.67 (dd, *J* = 7.5, 1.9 Hz, 2H, H4''), 7.56 (d, *J* = 7.0 Hz, 2H, H2'), 7.29 – 7.45 (m, 6H, H3', H4', H5'' and H6''), 6.49 (s, H2 minor tautomer), 6.45 (s, 1H, H2 major tautomer), 4.69 – 4.79 (m, 1H, H11), 3.97 (d, *J* = 11.3 Hz, 1H, $H4_B$), 3.12 (d, *J* = 11.3 Hz, 1H, $H4_A$), 1.55 – 1.65 (m, 4H, H12), 1.16 – 1.39 (m, 6H, H14 and H13); ^{13}C NMR ($CDCl_3$, 101 MHz): major CD tautomer: δ 187.9 (C6), 176.3 (C9), 175.9 (C8), 166.0 (C10), 146.7 (C2''), 138.5 (C1'), 134.3 (C3''), 131.8 (C4''), 129.4, 129.2 (C3' and C5''), 128.6, 128.5 (C4' and C6''), 127.2 (C2'), 117.4 (C1''), 99.6 (C7), 82.6 (C5), 75.8 (C11), 63.9 (C2), 35.4 (C4), 31.1 (C12), 31.0 (C12), 25.3 (C14), 23.6 (C13), 23.5 (C13); minor AB tautomer: δ 196.8 (C6), 176.5 (C9), (C8 not shown), 169.1 (C10), 147.3 (C2''), 139.1 (C1'), 134.3 (C3''), 132.0 (C4''), 129.5, 129.3 (C3' and C5''), 128.5, 128.3 (C4' and C6''), 127.2 (C2'), 116.7 (C1''), 101.9 (C7), 80.9 (C5), 75.9 (C11), 64.3 (C2), 35.5 (C4), 31.1 (C12), 31.0 (C12), 25.3 (C14), 23.6 (C13), 23.5 (C13); *m/z* (ESI^-) 488 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{28}H_{26}O_5NS$ $[M-H]^-$ 488.1537; found 488.1542.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-2-(5-bromopyridin-2-yl)-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-6,8-dioxo-3-thiabicyclo[3.3.0]-octane, 71



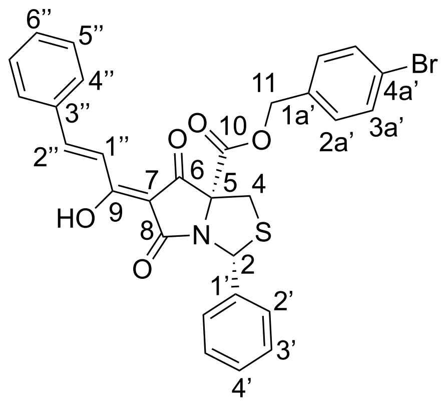
Synthesised from **35ii** (1 eq. 38 mg, 0.07 mmol) with β-styrylmagnesium bromide; yield (12 mg, 29%); bright yellow oil; R_f = 0.16 (petrol: EtOAc; 2 : 3); $[\alpha]_D^{25}$ = +125.7 (*c* = 1.20, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1706 (s, C=O), 1651 (s, C=O), 1625 (s, C=C), 1581 (s, C=C), 1563 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a 0.43 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 8.40 (d, *J* = 2.1 Hz, 1H, H6'), 7.99 (d, *J* = 16.0 Hz, 1H, H1''), 7.76 (d, *J* = 16.0 Hz, 1H, H2''), 7.72 – 7.65 (m, 3H, H4' and H4''), 7.53 – 7.29 (m, 5H, H3a', H5'' and H6''), 7.26 – 7.16 (m, 4H, H2a', H3' and H4a'), 6.44 (s, H2 minor), 6.40 (s, 1H, H2 major tautomer), 5.26 (d, *J* = 12.2 Hz, 1H, $H11_B$), 5.08 (d, *J* = 12.2 Hz, 1H, $H11_A$), 3.99 (d, *J* = 11.5 Hz, 1H, $H4_B$), 3.20 (d, *J* = 11.5 Hz, 1H, $H4_A$); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): major CD tautomer: δ 187.4 (C6), 176.7 (C9), 176.5 (C8), 166.6 (C10), 156.5 (C2'), 150.4 (C6'), 147.4 (C2''), 139.4 (C4'), 134.7 (C1a'), 134.2 (C3''), 132.1 (C4''), 129.5, 129.3 (C5''), 128.8, 128.7, 128.7 (C2a', C3a', C4a' and C6''), 121.6 (C3'), 120.0 (C5'), 117.2 (C1''), 102.8 (C7), 83.3 (C5), 68.7 (C11), 64.5 (C2), 35.9 (C4); minor AB tautomer: δ 196.1 (C6), 177.0 (C9), 175.5 (C8), 166.9 (C10), 156.7 (C2'), 151.4 (C6'), 148.0 (C2''), 139.5 (C4'), 134.6 (C1a'), 134.4 (C3''), 131.7 (C4''), 129.6, 129.2 (C5''), 128.8, 128.7, 128.6 (C2a', C3a', C4a' and C6''), 122.8 (C3'), 120.2 (C5'), 117.7 (C1''), 99.3 (C7), 85.3 (C5), 68.8 (C11), 63.2 (C2), 33.7 (C4); *m/z* (ESI$^-$) 575 and 577 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{28}H_{20}O_5N_2BrS$ [M-H]$^-$ 575.0282 and 577.0261; found 575.0275 and 577.0258.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 72



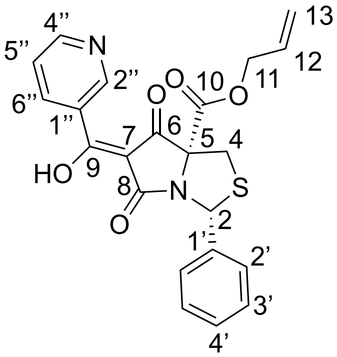
Synthesised from **35iii** (1 eq. 25 mg, 0.05 mmol) with β-styrylmagnesium bromide; yield (15 mg, 55%); bright yellow oil; R_f = 0.27 (petrol: EtOAc; 3 : 7); $[\alpha]_D^{25}$ = +56.3 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1705 (s, C=O), 1652 (s, C=O), 1624 (s, C=C), 1580 (s, C=C), 1562 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a 0.26 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 7.96 (d, *J* = 15.9 Hz, 1H, H1''), 7.73 (d, *J* = 15.9 Hz, 1H, H2''), 7.64 – 7.69 (m, 2H, H4''), 7.47 – 7.51 (m, 2H, H2'), 7.29 – 7.47 (m, 8H, H3', H3a', H4', H5'' and H6''), 7.12 – 7.20 (m, 3H, H2a' and H4a'), 6.49 (s, H2 minor tautomer), 6.44 (s, 1H, H2 major tautomer), 5.11 (d, *J* = 12.3 Hz, 1H, $H11_B$), 5.05 (d, *J* = 12.3 Hz, 1H, $H11_A$), 4.00 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.15 (d, *J* = 11.4 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): major CD tautomer only: δ 187.4 (C6), 176.3 (C9), 176.2 (C8), 166.8 (C10), 146.9 (C2''), 138.3 (C1'), 134.7 (C1a'), 134.3 (C3''), 131.9 (C4''), 129.5, 129.3 (C3' and C5''), 128.7, 128.7, 128.6, 128.6, 128.5 (C2a', C3a', C4', C4a' and C6''), 127.2 (C2'), 117.4 (C1''), 99.6 (C7), 82.5 (C5), 68.7 (C11), 64.2 (C2), 35.6 (C4); *m/z* (ESI$^-$) 496 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{29}H_{22}O_5NS$ [M-H]$^-$ 496.1224; found 496.1216.

(2*R*,5*R*)-1-Aza-5-(4-bromobenzyloxycarbonyl)-7-[(*Z*,2*E*)-1-hydroxy-3-phenylallylidene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 73



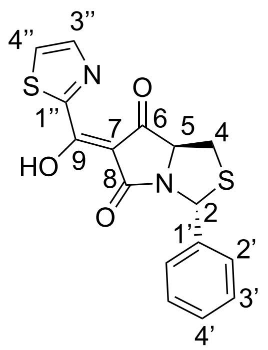
Synthesised from **39iii** (1 eq. 40 mg, 0.07 mmol) with β-styrylmagnesium bromide; yield (25 mg, 59%); bright yellow oil; R_f = 0.38 (petrol: EtOAc; 3 : 7); $[\alpha]_D^{25}$ = +67.0 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1747 (s, C=O), 1706 (s, C=O), 1651 (s, C=O), 1625 (s, C=C), 1581 (s, C=C), 1563 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a 0.23 : 1 mixture of AB/CD tautomers: δ (O*H* not observed), 7.96 (d, *J* = 16.0 Hz, 1H, H1''), 7.71 (d, *J* = 16.0 Hz, 1H, H2''), 7.63 – 7.70 (m, 2H, H4''), 7.41 – 7.51 (m, 6H, H2', H3' and H5''), 7.40 (d, *J* = 8.4 Hz, 2H, H3a'), 7.25 – 7.30 (m, 2H, H4' and H6''), 6.99 (d, *J* = 8.4 Hz, 2H, H2a'), 6.49 (s, H2 minor tautomer), 6.44 (s, 1H, H2 major tautomer), 5.01 (s, 2H, H11), 3.98 (d, *J* = 11.4 Hz, 1H, $H4_B$), 3.14 (d, *J* = 11.4 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): major CD tautomer only: δ 187.3 (C6), 176.3 (C9), 176.2 (C8), 166.7 (C10), 147.1 (C2''), 138.2 (C1'), 134.2 (C3''), 133.7 (C1a'), 132.0 (C3a'), 131.8 (C4''), 130.1 (C2a'), 129.5, 129.3 (C3' and C5''), 128.6, 128.6 (C4' and C6''), 127.2 (C2'), 122.7 (C4a'), 117.3 (C1''), 99.4 (C7), 82.3 (C5), 67.7 (C11), 64.0 (C2), 35.6 (C4); *m/z* (ESI^-) 574 and 576 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{29}H_{21}O_5NBrS$ $[M-H]^-$ 574.0329 and 576.0311; found 574.0319 and 576.0295.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-7-[(*Z*)-hydroxy(pyridin-3-yl)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 74



Synthesised from **32iii** (1 eq. 170 mg, 0.4 mmol) with pyridin-3-ylmagnesium bromide; yield (21 mg, 12%); organe-red oil; R_f = 0.38 (100% EtOAc); $[\alpha]_D^{25}$ = +73.1 (*c* = 1.04, $CHCl_3$); ν_{max}/cm^{-1} 1741 (s, C=O), 1687 (s, C=O), 1631 (s, C=C); ^1H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 9.38 (s, 1H, H2''), 8.83 (s, 2H, H4'' and H6''), 7.80 – 7.73 (m, 1H, H5''), 7.56 (d, *J* = 7.2 Hz, 2H, H2'), 7.35 – 7.27 (m, 3H, H3' and H4'), 6.47 (s, 1H, H2), 5.83 – 5.69 (m, 1H, H12), 5.24 (dd, *J* = 17.2, 1.5 Hz, 1H, $H13_B$), 5.15 (dd, *J* = 10.4, 1.5 Hz, 1H, $H13_A$), 4.56 (d, *J* = 5.9 Hz, 2H, H11), 3.95 (d, *J* = 11.3 Hz, 1H, $H4_B$), 3.15 (d, *J* = 11.3 Hz, 1H, $H4_A$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): CD tautomer: δ 189.6 (C6), 181.6 (C9), 176.2 (C8), 168.4 (C10), 151.5 (C2''), 148.5 (C4''), 144.0 (C1''), 140.2 (C1'), 138.5 (C6''), 131.6 (C12), 128.4 (C3' and C4'), 127.0 (C2'), 124.5 (C5''), 118.9 (C13), 99.4 (C7), 81.3 (C5), 66.9 (C11), 64.8 (C2), 36.3 (C4); *m/z* (ESI^+) 423 ($[M+H]^+$, 100%); HRMS (ESI^+) *m/z* calcd for $C_{22}H_{19}O_5NS$ $[M+H]^+$ 423.1009; found 423.1007.

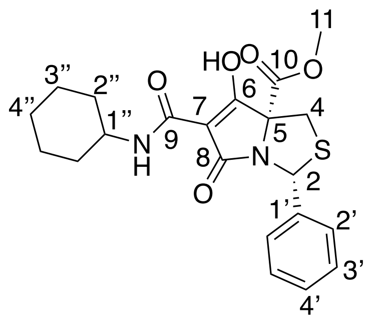
(2*R*,5*S*)-1-aza-7-[(*Z*)-hydroxy(thiazol-2-yl)methylene]-6,8-dioxo-2-phenyl-3-thiabicyclo[3.3.0]-octane, 75



Synthesised from **32iii** (1 eq. 82 mg, 0.2 mmol) with isopropyl(thiazol-2-yl)magnesium; yield (16 mg, 23%); yellow oil; R_f = 0.23 (EtOAc : MeOH; 7 : 1); $[\alpha]_D^{25}$ = +5.63 (c = 0.84, $CHCl_3$); ν_{max}/cm^{-1} 1703 (s, C=O), 1613 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (O*H* not observed), 8.02 (d, *J* = 3.3 Hz, 1H, H3''), 7.85 (d, *J* = 3.3 Hz, 1H, H4''), 7.49 (d, *J* = 7.4 Hz, 2H, H2'), 7.34 (t, *J* = 7.4 Hz, 2H, H3'), 7.28 (d, *J* = 7.4 Hz, 1H, H4'), 6.47 (s, 1H, H2), 4.72 (app t, *J* = 7.5 Hz, 1H, H5), 3.36 (dd, *J* = 11.1, 7.2 Hz, 1H, $H4_B$), 3.08 (dd, *J* = 11.1, 8.1 Hz, 1H, $H4_A$); ^{13}C NMR ($CDCl_3$, 101 MHz): CD tautomer: δ 189.2 (C6), 177.9 (C9), 173.0 (C8), 156.9 (C1''), 151.5 (C4''), 138.6 (C1'), 131.0 (C3''), 128.7 (C3'), 127.1 (C4'), 126.6 (C2'), 91.0 (C7), 67.6 (C5), 63.2 (C2), 33.9 (C4); *m/z* (ESI$^-$) 343 ([M-H]$^-$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{12}O_3N_2NaS_2$ [M+Na]$^+$ 367.0182; found 367.0187.

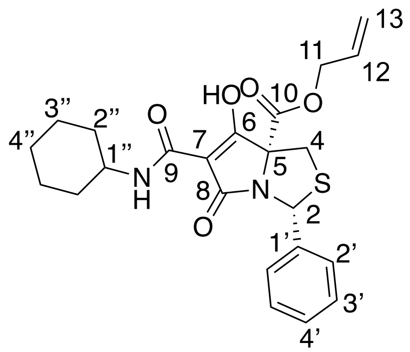
Tetramate carboxamides **76-94** were synthesised from the respective tetramate Weinreb amides **31-39** by General Procedure **H** with the corresponding amine (R^3NH_2).

(2*R*,5*R*)-1-Aza-7-(cyclohexylaminocarbonyl)-6-hydroxy-5-methoxycarbonyl-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 76



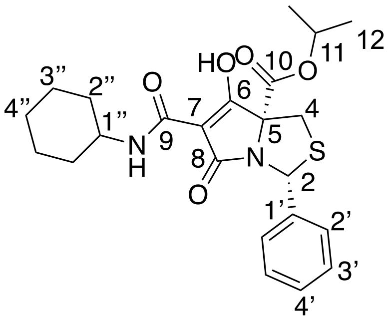
Synthesised from **31iii** (1 eq. 60 mg, 0.2 mmol) with cyclohexylamine; yield (20 mg, 30%); yellow oil; R_f = 0.72 (100% EtOAc); $[\alpha]_D^{25}$ = +147 (c = 1.00, $CHCl_3$); ν_{max}/cm^{-1} 1746 (s, C=O), 1691 (s, C=O), 1624 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.79 (br. s, 1H, N*H*), 7.72 (br. s, 1H, N*H*), 7.51 (d, *J* = 7.3 Hz, 4H, H2' AB and CD), 7.33 (t, *J* = 7.3 Hz, 4H, H3' AB and CD), 7.27 (d, *J* = 7.3 Hz, 2H, H4' AB and CD), 6.31 (s, 1H, H2 CD), 6.27 (s, 1H, H2 AB), 3.89 – 3.80 (m, 4H, H1'' and $H4_B$, AB and CD), 3.70 (s, 3H, H11 AB), 3.67 (s, 3H, H11 CD), 3.11 (d, *J* = 11.5 Hz, 2H, $H4_A$, AB and CD), 2.00 – 1.87 (m, 4H, H3''), 1.82 – 1.71 (m, 4H, H3''), 1.68 – 1.55 (m, 4H, H2''), 1.44 – 1.28 (m, 8H, H2'' and H4''); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 189.0 (C6 CD), 187.1 (C6 AB), 178.4 (C8 CD), 173.2 (C8 AB), 168.0 (C10 CD), 167.7 (C10 AB), 165.9 (C9 CD), 165.8 (C9 AB), 139.2, 139.1 (C1'), 128.6, 128.6 (C3'), 128.3 (C4'), 127.0 (C2'), 89.4, 83.7 (C7), 82.6, 80.9 (C5), 63.9, 63.7 (C2), 53.6, 53.4 (C11), 50.0, 49.3 (C1''), 35.3, 35.2 (C4), 32.6, 32.6 (C2''), 25.2, 25.2 (C3''), 24.4 (C4''); *m/z* (ESI^-) 415 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{21}H_{23}O_5N_2S$ $[M-H]^-$ 415.1333; found 415.1340.

(2*R*,5*R*)-5-Allyloxycarbonyl-1-aza-7-(cyclohexylaminocarbonyl)-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 77



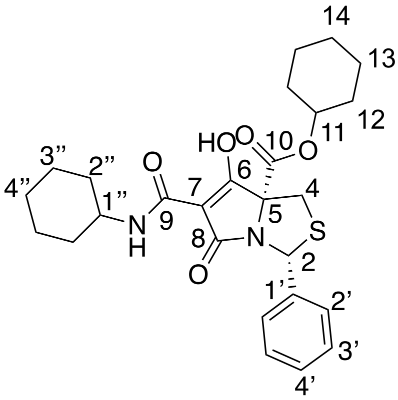
Synthesised from **32iii** (1 eq. 80 mg, 0.2 mmol) with cyclohexylamine; yield (42 mg, 48%); yellow oil; R_f = 0.69 (100% EtOAc); $[\alpha]_D^{25}$ = +92.6 (*c* = 1.05, $CHCl_3$); ν_{max}/cm^{-1} 1746 (s, C=O), 1691 (s, C=O), 1625 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ (O*H* not observed), 7.78 (br. s, 1H, N*H*), 7.71 (br. s, 1H, N*H*), 7.52 (d, *J* = 7.4 Hz, 4H, H2' AB and CD), 7.34 – 7.23 (m, 6H, H3' and H4' AB and CD), 6.31 (s, 1H, H2 CD), 6.26 (s, 1H, H2 AB), 5.82 – 5.68 (m, 2H, H12 AB and CD), 5.30 – 5.15 (m, 4H, H13 AB and CD), 4.64 – 4.49 (m, 4H, H11 AB and CD), 3.92 – 3.78 (m, 4H, H1'' and $H4_B$, AB and CD), 3.11 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 1.98 – 1.90 (m, 4H, H3''), 1.80 – 1.72 (m, 4H, H3''), 1.65 – 1.57 (m, 4H, H2''), 1.41 – 1.28 (m, 8H, H2'' and H4''); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 188.8 (C6 CD), 187.0 (C6 AB), 178.5 (C8 CD), 173.3 (C8 AB), 167.1 (C10 CD), 166.8 (C10 AB), 165.9 (C9 CD), 165.7 (C9 AB), 139.1, 139.1 (C1'), 131.2, 131.1 (C12), 128.5 (C3'), 128.2 (C4'), 127.0 (C2'), 119.4, 119.2 (C13), 89.5, 83.7 (C7), 82.7, 81.0 (C5), 67.3, 67.1 (C11), 63.9, 63.7 (C2), 49.9, 49.2 (C1''), 35.3, 35.2 (C4), 32.6 (C2''), 25.2, 25.1 (C3''), 24.4 (C4''); *m/z* (ESI^-) 441 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{23}H_{25}O_5N_2S$ $[M-H]^-$ 441.1490; found 441.1494.

(2*R*,5*R*)-1-Aza-7-(cyclohexylaminocarbonyl)-6-hydroxy-5-isopropyloxycarbonyl-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 78



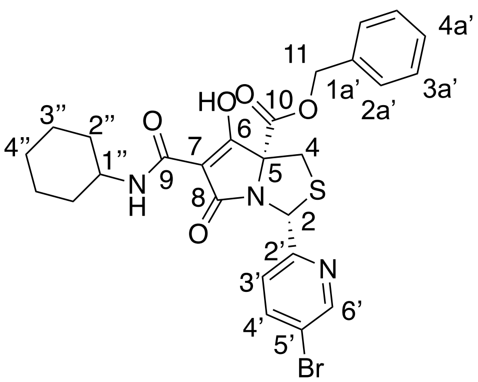
Synthesised from **33iii** (1 eq. 34 mg, 0.08 mmol) with cyclohexylamine; yield (18 mg, 49%); yellow oil; R_f = 0.47 (100% EtOAc); $[\alpha]_D^{25}$ = +141 (*c* = 0.90, $CHCl_3$); ν_{max}/cm^{-1} 1739 (s, C=O), 1693 (s, C=O), 1627 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1.1 : 1 AB/CD tautomers: δ 7.78 (br. s, 1H, N*H*), 7.68 (br. s, 1H, N*H*), 7.54 (d, *J* = 7.2 Hz, 4H, H2' AB and CD), 7.35 – 7.27 (m, 6H, H3' and H4' AB and CD), 6.31 (s, 1H, H2 CD), 6.26 (s, 1H, H2 AB), 5.68 (br. s, 2H, O*H* AB and CD), 5.05 – 4.93 (m, 2H, H11 AB and CD), 3.92 – 3.80 (m, 4H, H1'' and $H4_B$, AB and CD), 3.09 (app dd, *J* = 11.5, 1.3 Hz, 2H, $H4_A$ AB and CD), 1.99 – 1.93 (m, 4H, H3''), 1.81 – 1.74 (m, 4H, H3''), 1.69 – 1.58 (m, 4H, H2''), 1.42 – 1.31 (m, 8H, H2'' and H4''), 1.17 (app t, *J* = 6.2 Hz, 6H, $H12_B$ AB and CD), 1.11 (d, *J* = 6.2 Hz, 3H, $H12_A$), 1.08 (d, *J* = 6.2 Hz, 3H, $H12_A$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 188.6 (C6 CD), 187.4 (C6 AB), 178.7 (C8 CD), 173.4 (C8 AB), 166.9 (C10 CD), 166.5 (C10 AB), 165.9 (C9 CD), 165.7 (C9 AB), 139.3, 139.3 (C1'), 128.5, 128.5 (C3'), 128.2, 128.2 (C4'), 127.1, 127.0 (C2'), 90.2, 83.7 (C7), 82.9, 81.0 (C5), 71.1, 70.7 (C11), 63.8, 63.6 (C2), 50.0, 49.1 (C1''), 35.3 (C4), 32.7, 32.6 (C2''), 25.3, 25.2 (C3''), 24.5 (C4''), 21.6, 21.6 ($C12_B$), 21.5, 21.4 ($C12_A$); *m/z* (ESI$^+$) 445 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{23}H_{29}O_5N_2S$ [M+H]$^+$ 445.1792; found 445.1791.

(2*R*,5*R*)-1-Aza-5-cyclohexyloxycarbonyl-7-(cyclohexylaminocarbonyl)-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 79



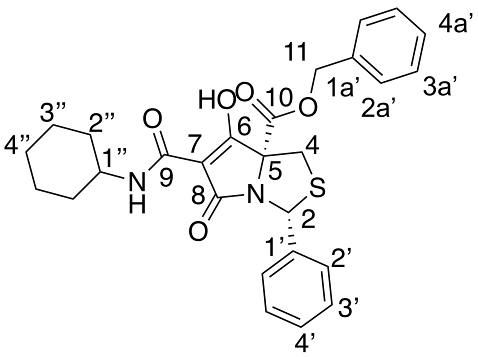
Synthesised from **34iii** (1 eq. 48 mg, 0.1 mmol) with cyclohexylamine; yield (32 mg, 61%); yellow oil; R_f = 0.70 (100% EtOAc); $[\alpha]_D^{25}$ = +185 (c = 1.20, $CHCl_3$); ν_{max}/cm^{-1} 1739 (s, C=O), 1692 (s, C=O), 1626 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1.1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.78 (br. s, 1H, N*H*), 7.67 (br. s, 1H, N*H*), 7.54 (d, *J* = 8.0 Hz, 4H, H2' AB and CD), 7.35 – 7.25 (m, 6H, H3' and H4' AB and CD), 6.30 (s, 1H, H2 CD), 6.25 (s, 1H, H2 AB), 4.85 – 4.71 (m, 2H, H11 AB and CD), 3.91 – 3.79 (m, 4H, H1'' and $H4_B$, AB and CD), 3.09 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.00 – 1.89 (m, 4H), 1.83 – 1.71 (m, 8H), 1.71 – 1.54 (m, 8H), 1.54 – 1.27 (m, 20H) (H2'', 3'', 4'', H12, 13, 14, AB and CD, a total of 40 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 188.6 (C6 CD), 187.5 (C6 AB), 178.7 (C8 CD), 173.4 (C8 AB), 166.8 (C10 CD), 166.4 (C10 AB), 165.9 (C9 CD), 165.7 (C9 AB), 139.3 (C1'), 128.5, 128.5 (C3'), 128.2, 128.2 (C4'), 127.0 (C2'), 90.4, 83.8 (C7), 83.1, 81.1 (C5), 75.8, 75.4 (C11), 63.9, 63.7 (C2), 50.0, 49.1 (C1''), 35.3, 35.2 (C4), 32.7, 32.6 (C2''), 31.2, 31.2, 31.2, 31.2 (C12), 25.4, 25.3, 25.3, 25.2 (C3'', C14), 24.5 (C4''), 23.6, 23.6 (C13); *m/z* (ESI$^-$) 483 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{26}H_{31}O_5N_2S$ [M-H]$^-$ 483.1948; found 483.1969.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-2-(5-bromopyridin-2-yl)-7-(cyclohexylaminocarbonyl)-6-hydroxy-8-oxo-3-thiabicyclo[3.3.0]oct-6-ene, 80



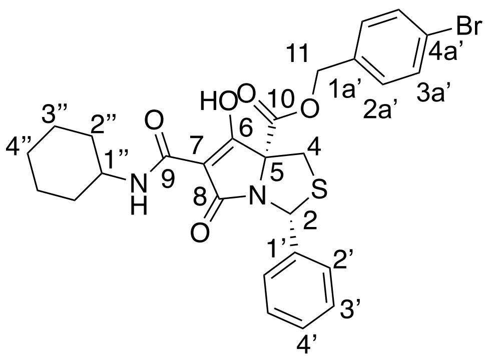
Synthesised from **35ii** (1 eq. 83 mg, 0.2 mmol) with cyclohexylamine; yield (31 mg, 35%); yellow oil; R_f = 0.71 (100% EtOAc); $[\alpha]_D^{25}$ = +96.8 (c = 1.02, $CHCl_3$); ν_{max}/cm^{-1} 1743 (s, C=O), 1692 (s, C=O), 1625 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ (O*H* not observed), 8.59 – 8.53 (m, 1H, H6'), 8.35 (d, *J* = 2.0 Hz, 1H, H6'), 7.87 (br. s, 1H, N*H*), 7.78 (dd, *J* = 8.2, 2.4 Hz, 2H, H4' AB and CD), 7.69 (br. s, 1H, N*H*), 7.49 – 7.44 (m, 2H, H3' AB and CD), 7.38 – 7.29 (m, 8H, H2a' and H3a', AB and CD), 7.25 – 7.22 (m, 2H, H4a' AB and CD), 6.27 (s, 1H, H2 CD), 6.24 (s, 1H, H2 AB), 5.27 (d, J = 12.3 Hz, 2H, $H11_B$ AB and CD), 5.08 (app dd, J = 12.3, 6.6 Hz, 2H, $H11_A$ AB and CD), 3.91 (app dd, J = 11.6, 4.0 Hz, 2H, $H4_B$ AB and CD), 3.88 – 3.79 (m, 2H, H1'' AB and CD), 3.17 (d, J = 11.6 Hz, 2H, $H4_A$ AB and CD), 1.99 – 1.93 (m, 4H, H3''), 1.81 – 1.72 (m, 4H, H3''), 1.67 – 1.59 (m, 4H, H2''), 1.44 – 1.35 (m, 8H, H2'' and H4''); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 189.4 (C6 CD), 187.1 (C6 AB), 178.6 (C8 CD), 173.5 (C8 AB), 167.5 (C10 CD), 167.3 (C10 AB), 165.8 (C9 CD), 165.8 (C9 AB), 157.4, 157.3 (C2'), 151.2, 150.1 (C6'), 139.3 (C4'), 135.0, 134.8 (C1a'), 128.7, 128.7 (C3a', C4a' and C2a'), 122.8, 121.5 (C3'), 120.0, 119.7 (C5'), 88.8, 85.2 (C7), 83.6, 81.9 (C5), 68.5, 68.3 (C11), 64.1, 63.0 (C2), 50.0, 49.4 (C1''), 35.6, 35.5 (C4), 32.6, 32.6 (C2''), 25.2, 25.1 (C3''), 24.4 (C4''); *m/z* (ESI^-) 570 and 572 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{26}H_{25}O_5N_3BrS$ $[M-H]^-$ 570.0704 and 572.0685; found 570.0700 and 572. 0678.

(2*R*,5*R*)-1-Aza-5-benzyloxycarbonyl-7-(cyclohexylaminocarbonyl)-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 81



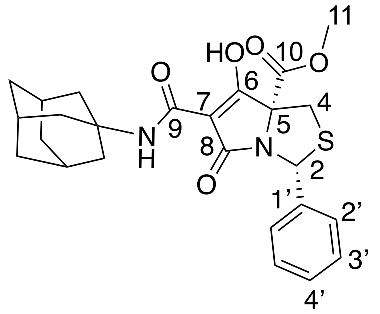
Synthesised from **35iii** (1 eq. 37 mg, 0.08 mmol) with cyclohexylamine; yield (14 mg, 35%); pale yellow oil; R_f = 0.68 (100% EtOAc); $[\alpha]_D^{25}$ = +62.9 (c = 0.70, $CHCl_3$); ν_{max}/cm^{-1} 1744 (s, C=O), 1693 (s, C=O), 1625 (s, C=C); ^1H NMR ($CDCl_3$, 500 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ 7.78 (br. s, 1H, N*H*), 7.69 (br. s, 1H, N*H*), 7.51 – 7.41 (m, 4H, H2' AB and CD), 7.36 – 7.29 (m, 6H, H3' and H4' AB and CD), 7.25 – 7.16 (m, 10H, H2a', H3a' and H4a', AB and CD), 6.49 (br. s, 2H, O*H* AB and CD), 6.29 (s, 1H, H2 CD), 6.25 (s, 1H, H2 AB), 5.18 – 5.06 (m, 4H, H11 AB and CD), 3.90 (app dd, J = 11.5, 8.5 Hz, 2H, $H4_B$ AB and CD), 3.78 – 3.71 (m, 2H, H1''AB and CD), 3.12 (d, J = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.01 – 1.88 (m, 4H), 1.88 – 1.81 (m, 2H), 1.81 – 1.72 (m, 4H), 1.67 – 1.59 (m, 2H), 1.41 – 1.33 (m, 8H), (H2'', 3'', 4'', AB and CD, a total of 20 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 188.9 (C6 CD), 187.1 (C6 AB), 178.7 (C8 CD), 173.5 (C8 AB), 167.5 (C10 CD), 167.2 (C10 AB), 165.9 (C9 CD), 165.8 (C9 AB), 139.1, 139.0 (C1'), 135.0, 134.8 (C1a'), 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.2 (C3', C4', C3a', C4a' and C2a'), 127.0 (C2'), 89.6, 83.8 (C7), 82.9, 81.2 (C5), 68.6, 68.3 (C11), 64.2, 63.9 (C2), 50.0, 49.3 (C1''), 35.4, 35.3 (C4), 32.7, 32.6 (C2''), 25.2, 25.2 (C3''), 24.4 (C4''); *m/z* (ESI$^+$) 493 ([M+H]$^+$, 100%); HRMS (ESI$^+$) *m/z* calcd for $C_{27}H_{29}O_5N_2S$ [M+H]$^+$ 493.1792; found 493.1791.

(2*R*,5*R*)-1-Aza-5-(4-bromobenzyloxycarbonyl)-7-(cyclohexylaminocarbonyl)-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 82



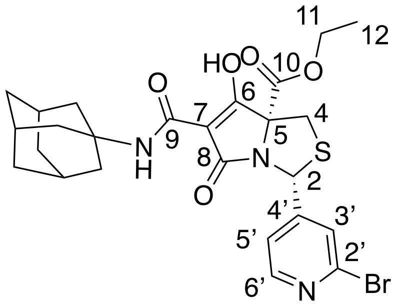
Synthesised from **39iii** (1 eq. 24 mg, 0.04 mmol) with cyclohexylamine; yield (12 mg, 47%); pale yellow oil; R_f = 0.60 (100% EtOAc); $[\alpha]_D^{25}$ = +148 (*c* = 0.60, $CHCl_3$); ν_{max}/cm^{-1} 1744 (s, C=O), 1692 (s, C=O), 1625 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ 7.77 (br. s, 1H, N*H*), 7.71 (br. s, 1H, N*H*), 7.49 – 7.37 (m, 8H, H2' and H3a', AB and CD), 7.26 – 7.19 (m, 6H, H3' and H4', AB and CD), 7.09 – 6.98 (m, 4H, H2a' AB and CD), 6.29 (s, 1H, H2 CD), 6.25 (s, 1H, H2 AB), 5.13 – 4.97 (m, 4H, H11 AB and CD), 3.98 (br. s, 2H, O*H* AB and CD), 3.90 – 3.82 (m, 4H, H1'' and $H4_B$, AB and CD), 3.12 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.00 – 1.89 (m, 4H, H3''), 1.83 – 1.70 (m, 4H, H3''), 1.70 – 1.54 (m, 4H, H2''), 1.43 – 1.31 (m, 8H, H2'' and H4''); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 189.0 (C6 CD), 186.9 (C6 AB), 178.6 (C8 CD), 173.4 (C8 AB), 167.4 (C10 CD), 167.1 (C10 AB), 165.9 (C9 CD), 165.8 (C9 AB), 139.1, 139.0 (C1'), 134.0, 133.8 (C1a'), 131.8, 131.8 (C3a'), 130.1, 130.1 (C2a'), 128.5, 128.5 (C3'), 128.3, 128.3 (C4'), 127.0, 127.0 (C2'), 122.7, 122.6 (C4a'), 89.2, 83.7 (C7), 82.8, 81.1 (C5), 67.7, 67.4 (C11), 64.0, 63.8 (C2), 50.0, 49.3 (C1''), 35.4, 35.3 (C4), 32.6, 32.6 (C2''), 25.2, 25.2 (C3''), 24.4 (C4''); *m/z* (ESI$^-$) 569 and 571 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{27}H_{26}O_5N_2BrS$ [M-H]$^-$ 569.0751 and 571.0732; found 569.0757 and 571.0732.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-1-aza-6-hydroxy-5-methoxycarbonyl-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 83



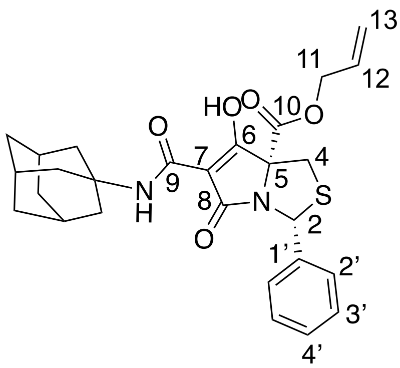
Synthesised from **31iii** (1 eq. 55 mg, 0.1 mmol) with 1-adamantylamine; yield (38 mg, 56%); greenish yellow oil; R_f = 0.65 (EtOAc : petrol; 4 : 1); $[\alpha]_D^{25}$ = +162 (*c* = 1.00, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1688 (s, C=O), 1626 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ (O*H* not observed), 7.82 (br. s, 1H, N*H*), 7.72 (br. s, 1H, N*H*), 7.51 (d, *J* = 7.7 Hz, 4H, H2' AB and CD), 7.37 – 7.27 (m, 6H, H3' and H4', AB and CD), 6.31 (s, 1H, H2 CD), 6.26 (s, 1H, H2 AB), 3.86 (d, *J* = 11.5 Hz, 2H, $H4_B$ AB and CD), 3.70 (s, 3H, H11 AB), 3.67 (s, 3H, H11 CD), 3.10 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.14 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.05 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.69 (br. s, 12H, Adamantyl-CH_2 AB and CD); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 189.4 (C6 CD), 187.0 (C6 AB), 178.6 (C8 CD), 173.4 (C8 AB), 168.0 (C10 CD), 167.7 (C10 AB), 166.8 (C9 CD), 166.7 (C9 AB), 139.2, 139.1 (C1'), 128.6, 128.5 (C3'), 128.3 (C4'), 126.9 (C2'), 89.2, 84.0 (C7), 82.6, 81.0 (C5), 63.9, 63.8 (C2), 55.0, 54.5 (C11), 53.6, 53.4 (Adamantyl-*C*), 41.6 (Adamantyl-*C*H$_2$), 36.0, 36.0 (Adamantyl-*C*H$_2$), 35.3, 35.2 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI$^-$) 467 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{25}H_{27}O_5N_2S$ [M-H]$^-$ 467.1646; found 467.1653.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-1-aza-2-(2-bromopyridin-4-yl)-5-ethoxycarbonyl-6-hydroxy-8-oxo-3-thiabicyclo[3.3.0]oct-6-ene, 84



Synthesised from **37iv** (1 eq. 63 mg, 0.1 mmol) with 1-adamantylamine; yield (39 mg, 52%); yellow oil; R_f = 0.30 (100% EtOAc); $[\alpha]_D^{25}$ = +58.8 (c = 0.95, $CHCl_3$); ν_{max}/cm^{-1} 1743 (s, C=O), 1689 (s, C=O), 1626 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1 : 1 AB/CD tautomers: δ 8.31 (d, J = 5.1 Hz, 2H, H6' AB and CD), 7.88 (br. s, 1H, NH), 7.68 (s, 2H, H3' AB and CD), 7.63 (br. s, 1H, NH), 7.38 (d, J = 5.1 Hz, 2H, H5' AB and CD), 6.18 (s, 1H, H2 CD), 6.14 (s, 1H, H2 AB), 5.61 (br. s, 2H, OH AB and CD), 4.37 – 4.10 (m, 4H, H11 AB and CD), 3.92 – 3.83 (m, 2H, $H4_B$ AB and CD), 3.11 (app dd, J = 11.5, 3.3 Hz, 2H, $H4_A$ AB and CD), 2.15 (br. s, 6H, Adamantyl-CH AB and CD), 2.06 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.71 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.24 – 1.18 (m, 6H, H12 AB and CD); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.7 (C6 CD), 186.6 (C6 AB), 178.5 (C8 CD), 173.5 (C8 AB), 167.0 (C10), 166.8 (C9 CD), 166.7 (C9 AB), 151.5 (C6'), 150.3 (C4'), 142.7 (C2'), 127.1, 125.9 (C3'), 121.0, 120.9 (C5'), 87.1, 83.8 (C7), 82.7, 81.3 (C5), 63.4, 63.2 (C2), 61.7, 61.6 (C11), 55.3, 54.8 (Adamantyl-C), 41.7 (Adamantyl-CH$_2$), 36.0, 35.9 (Adamantyl-CH$_2$), 35.8, 35.7 (C4), 29.4 (Adamantyl-CH), 14.1 (C12); m/z (ESI$^-$) 560 and 562 ([M-H]$^-$, 100%); HRMS (ESI$^-$) m/z calcd for $C_{25}H_{27}O_5N_3BrS$ [M-H]$^-$ 560.0849 and 562.0830; found 560.0852 and 562.0828.

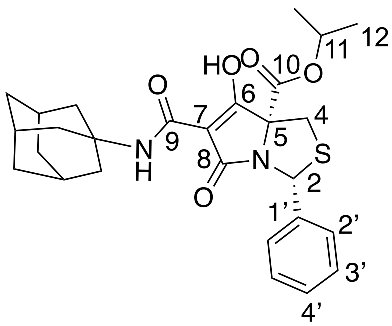
(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-5-allyloxycarbonyl-1-aza-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 85



Synthesised from **32iii** (1 eq. 76 mg, 0.2 mmol) with 1-adamantylamine; yield (43 mg, 46%); pale yellow oil; R_f = 0.76 (EtOAc : petrol; 7 : 3); $[\alpha]_D^{25}$ = +53.9 (c = 1.08, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1689 (s, C=O), 1626 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1 : 1 AB/CD tautomers: δ (OH not observed), 7.81 (br. s, 1H, NH), 7.71 (br. s, 1H, NH), 7.52 (d, J = 7.4 Hz, 4H, H2' AB and CD), 7.33 – 7.26 (m, 6H, H3' and H4', AB and CD), 6.31 (s, 1H, H2 CD), 6.26 (s, 1H, H2 AB), 5.83 – 5.68 (m, 2H, H12 AB and CD), 5.30 –

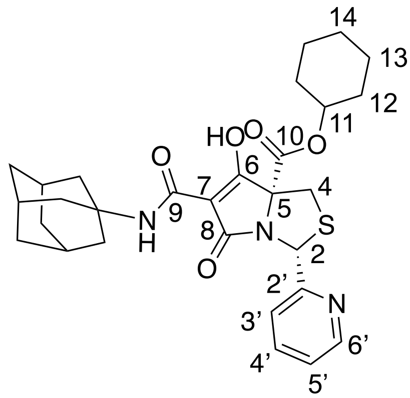
5.16 (m, 4H, H13 AB and CD), 4.64 – 4.49 (m, 4H, H11 AB and CD), 3.87 (app dd, *J* = 11.5, 6.5 Hz, 2H, $H4_B$ AB and CD), 3.10 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.14 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.05 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.70 (br. s, 12H, Adamantyl-CH_2 AB and CD); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.3 (C6 CD), 187.0 (C6 AB), 178.8 (C8 CD), 173.5 (C8 AB), 167.2 (C10 CD), 166.9 (C10 AB), 166.8 (C9 CD), 166.7 (C9 AB), 139.2, 139.1 (C1'), 131.3, 131.1 (C12), 128.5, 128.5 (C3'), 128.2 (C4'), 127.0 (C2'), 119.4, 119.3 (C13), 89.4, 84.0 (C7), 82.7, 81.1 (C5), 67.4, 67.2 (C11), 63.9, 63.8 (C2), 55.0, 54.4 (Adamantyl-*C*), 41.7 (Adamantyl-*C*H_2), 36.0, 36.0 (Adamantyl-*C*H_2), 35.3, 35.3 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI^-) 493 ($[M-H]^-$, 100%); HRMS (ESI^-) *m/z* calcd for $C_{27}H_{29}O_5N_2S$ $[M-H]^-$ 493.1803; found 493.1808.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-1-aza-6-hydroxy-5-isopropyloxycarbonyl-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 86



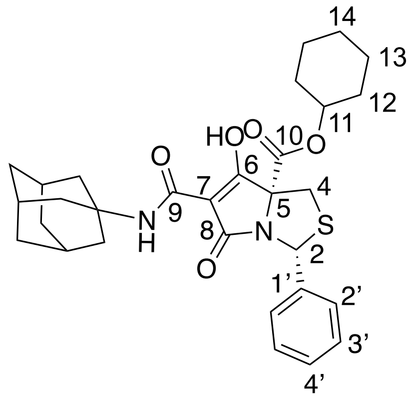
Synthesised from **33iii** (1 eq. 125 mg, 0.3 mmol) with 1-adamantylamine; yield (67 mg, 44%); pale yellow oil; R_f = 0.76 (EtOAc : petrol; 7 : 3); $[\alpha]_D^{25}$ = +133 (*c* = 0.96, $CHCl_3$); ν_{max}/cm^{-1} 1739 (s, C=O), 1692 (s, C=O), 1629 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.80 (br. s, 1H, N*H*), 7.67 (br. s, 1H, N*H*), 7.53 (d, *J* = 7.4 Hz, 4H, H2' AB and CD), 7.34 – 7.23 (m, 6H, H3' and H4', AB and CD), 6.30 (s, 1H, H2 CD), 6.24 (s, 1H, H2 AB), 5.05 – 4.90 (m, 2H, H11 AB and CD), 3.85 (app dd, *J* = 11.5, 8.3 Hz, 2H, $H4_B$ AB and CD), 3.07 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.13 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.05 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.69 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.16 (app t, *J* = 6.3 Hz, 6H, $H12_B$ AB and CD), 1.08 (app dd, *J* = 10.3, 6.3 Hz, 6H, $H12_A$ AB and CD); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.0 (C6 CD), 187.2 (C6 AB), 178.9 (C8 CD), 173.5 (C8 AB), 166.8 (C10 CD), 166.8 (C10 AB), 166.6 (C9 CD), 166.5 (C9 AB), 139.3, 139.3 (C1'), 128.4, 128.4 (C3'), 128.1 (C4'), 127.0, 127.0 (C2'), 89.9, 83.9 (C7), 82.9, 81.0 (C5), 71.0, 70.7 (C11), 63.7, 63.5 (C2), 54.9, 54.2 (Adamantyl-*C*), 41.6 (Adamantyl-*C*H$_2$), 36.0, 35.9 (Adamantyl-*C*H$_2$), 35.3 (C4), 29.4 (Adamantyl-*C*H), 21.6, 21.4 (C12); *m/z* (ESI$^-$) 495 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{27}H_{31}O_5N_2S$ [M-H]$^-$ 495.1948; found 495.1964.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-5-cyclohexyloxycarbonyl-1-aza-6-hydroxy-8-oxo-2-(pyridin-2-yl)-3-thiabicyclo[3.3.0]oct-6-ene, 87



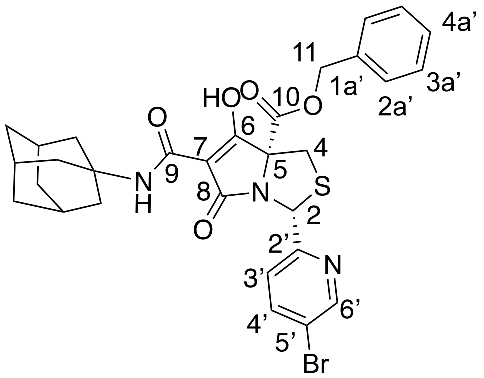
Synthesised from **34i** (1 eq. 45 mg, 0.1 mmol) with 1-adamantylamine; yield (18 mg, 33%); yellow oil; R_f = 0.65 (EtOAc : petrol; 9 : 1); $[\alpha]_D^{25}$ = +64.3 (*c* = 0.40, $CHCl_3$); ν_{max}/cm^{-1} 1730 (s, C=O), 1690 (s, C=O), 1631 (s, C=C); ^{1}H NMR ($CDCl_3$, 600 MHz): a mixture of 1 : 1 AB/CD tautomers: δ (O*H* not observed), 8.56 – 8.49 (m, 2H, H6' AB and CD), 7.86 (s br. s, 1H, N*H*), 7.69 (br. s, 1H, N*H*), 7.67 (app d, *J* = 5.8 Hz, 4H, H4' and H3', AB and CD), 7.18 (t, *J* = 5.8 Hz, 2H, H5' AB and CD), 6.35 (s, 1H, H2 CD), 6.31 (s, 1H, H2 AB), 4.85 – 4.73 (m, 2H, H11 AB and CD), 3.87 (app dd, *J* = 11.4, 7.5 Hz, 2H, H4$_B$ AB and CD), 3.12 (app dd, *J* = 11.4, 2.8 Hz, 2H, H4$_A$ AB and CD), 2.15 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.07 (br. s, 12H, Adamantyl-C*H*$_2$ AB and CD), 1.71 (br. s, 20H, Adamantyl-C*H*$_2$ and H12, AB and CD), 1.36 – 1.27 (m, 12H, H14 and H13, AB and CD); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 189.5 (C6 CD), 187.4 (C6 AB), 179.0 (C8 CD), 173.6 (C8 AB), 166.9 (C10 CD), 166.7 (C10 AB), 166.7 (C9 CD), 166.4 (C9 AB), 159.1 (C2'), 149.2 (C6'), 136.9 (C4'), 122.8 (C3'), 120.2 (C5'), 89.7, 84.0 (C7), 83.8, 81.9, (C5), 75.7, 75.4 (C11), 64.6, 64.3 (C2), 55.0, 54.4 (Adamantyl-*C*), 41.7, 41.7 (Adamantyl-*C*H$_2$), 36.1, 36.0 (Adamantyl-*C*H$_2$), 35.5, 35.5 (C4), 31.3, 31.3 (C12), 29.5 (Adamantyl-*C*H), 25.4, 25.4 (C14), 23.6 (C13); *m/z* (ESI$^-$) 536 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{29}H_{34}O_5N_3S$ [M-H]$^-$ 536.2225; found 536.2220.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-5-cyclohexyloxycarbonyl-1-aza-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 88



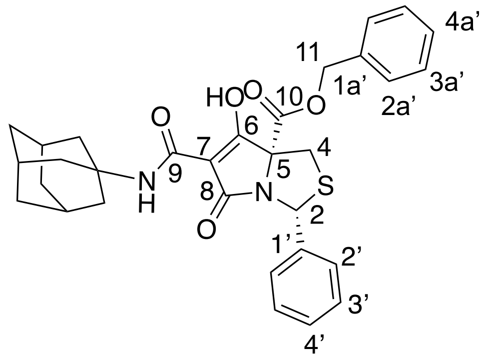
Synthesised from **34iii** (1 eq. 115 mg, 0.3 mmol) with 1-adamantylamine; yield (78 mg, 57%); yellow oil; R_f = 0.89 (EtOAc : petrol; 7 : 3); $[\alpha]_D^{25}$ = +99.4 (*c* = 0.98, $CHCl_3$); ν_{max}/cm^{-1} 1739 (s, C=O), 1690 (s, C=O), 1628 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1 : 1 AB/CD tautomers: δ 8.75 (br. s, 2H, O*H* AB and CD), 7.82 (br. s, 1H, N*H*), 7.68 (br. s, 1H, N*H*), 7.55 (d, *J* = 7.6 Hz, 4H, H2’ AB and CD), 7.34 – 7.27 (m, 6H, H3’ and H4’, AB and CD), 6.30 (s, 1H, H2 CD), 6.25 (s, 1H, H2 AB), 4.84 – 4.71 (m, 2H, H11 AB and CD), 3.87 (app dd, *J* = 11.4, 8.0 Hz, 2H, $H4_B$ AB and CD), 3.09 (d, *J* = 11.4 Hz, 2H, $H4_A$ AB and CD), 2.14 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.07 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.71 (br. s, 20H, Adamantyl-CH_2 and H12, AB and CD), 1.54 – 1.23 (m, 12H, H14 and H13, AB and CD); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.1 (C6 CD), 187.3 (C6 AB), 178.9 (C8 CD), 173.5 (C8 AB), 166.8 (C10 CD), 166.7 (C10 AB), 166.5 (C9 CD), 166.4 (C9 AB), 139.3, 139.2 (C1’), 128.4, 128.4 (C3’), 128.1 (C4’), 126.9 (C2’), 90.0, 84.0 (C7), 83.0, 81.1 (C5), 75.7, 75.4 (C11), 63.8, 63.6 (C2), 54.8, 54.2 (Adamantyl-*C*), 41.6 (Adamantyl-*C*H_2), 36.0, 35.9 (Adamantyl-*C*H_2), 35.2 (C4), 31.2, 31.2, 31.1, 31.1 (C12), 29.4 (Adamantyl-*C*H), 25.3, 25.3 (C14), 23.6 (C13); *m/z* (ESI$^-$) 535 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{30}H_{35}O_5N_2S$ [M-H]$^-$ 535.2272; found 535.2277.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-5-benzyloxycarbonyl-2-(5-bromopyridin-2-yl)-1-aza-6-hydroxy-8-oxo-3-thiabicyclo[3.3.0]oct-6-ene, 89



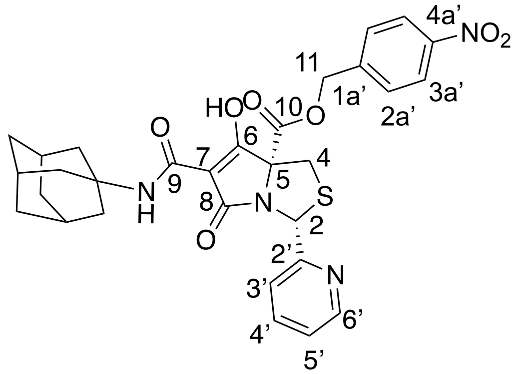
Synthesised from **35ii** (1 eq. 73 mg, 0.1 mmol) with 1-adamantylamine; yield (29 mg, 34%); pale yellow oil; R_f = 0.78 (EtOAc : petrol; 3 : 2); $[\alpha]_D^{25}$ = +86.1 (*c* = 0.97, $CHCl_3$); ν_{max}/cm^{-1} 1743 (s, C=O), 1688 (s, C=O), 1626 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ (O*H* not observed), 8.35 (app dd, *J* = 8.9, 1.9 Hz, 2H, H6' AB and CD), 7.89 (br. s, 1H, N*H*), 7.69 (br. s, 1H, N*H*), 7.48 – 7.42 (m, 2H, H4' AB and CD), 7.39 – 7.29 (m, 10H, H2a', H3a' and H4a', AB and CD), 7.23 (d, *J* = 7.1 Hz, 2H, H3' AB and CD), 6.26 (s, 1H, H2 CD), 6.23 (s, 1H, H2 AB), 5.28 (app dd, *J* = 12.2, 1.6 Hz, 2H, $H11_B$ AB and CD), 5.07 (app dd, *J* = 12.2, 7.6 Hz, 2H, $H11_A$ AB and CD), 3.90 (app dd, *J* = 11.5, 4.0 Hz, 2H, $H4_B$ AB and CD), 3.16 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.14 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.06 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.70 (br. s, 12H, Adamantyl-CH_2); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.8 (C6 CD), 187.0 (C6 AB), 178.9 (C8 CD), 173.6 (C8 AB), 167.3 (C10 CD), 167.1 (C10 AB), 166.7 (C9), 157.4, 157.3 (C2'), 150.1 (C6'), 139.3 (C4'), 135.0, 134.9 (C1a'), 128.7, 128.7, 128.7 (C3a', C4a', C2a'), 121.6 (C3'), 120.0, 119.6 (C5'), 88.8, 84.0 (C7), 83.6, 82.0 (C5), 68.5, 68.3 (C11), 64.1, 64.0 (C2), 55.1, 54.6 (Adamantyl-*C*), 41.7, 41.6 (Adamantyl-*C*H_2), 36.0, 35.9 (Adamantyl-*C*H_2), 35.7, 35.6 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI$^+$) 624 and 626 ([M+H]$^+$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{30}H_{31}O_5N_3BrS$ [M+H]$^+$ 624.1162 and 626.1144; found 624.0368 and 626.1137.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-5-benzyloxycarbonyl-1-aza-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 90



Synthesised from **35iii** (1 eq. 71 mg, 0.2 mmol) with 1-adamantylamine; yield (57 mg, 67%); yellow oil; R_f = 0.78 (EtOAc : petrol; 7 : 3); $[\alpha]_D^{25}$ = +65.7 (c = 0.95, $CHCl_3$); ν_{max}/cm^{-1} 1742 (s, C=O), 1688 (s, C=O), 1627 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1 : 1 AB/CD tautomers: δ (O*H* not observed), 7.82 (br. s, 1H, N*H*), 7.69 (br. s, 1H, N*H*), 7.48 – 7.44 (m, 4H, H2' AB and CD), 7.33 – 7.28 (m, 6H, H3' and H4', AB and CD), 7.24 – 7.17 (m, 10H, H2a', H3a' and H4a', AB and CD), 6.28 (s, 1H, H2 CD), 6.23 (s, 1H, H2 AB), 5.20 – 5.04 (m, 4H, H11 AB and CD), 3.89 (app dd, J = 11.5, 6.4 Hz, 2H, H4$_B$ AB and CD), 3.11 (d, J = 11.5 Hz, 2H, H4$_A$ AB and CD), 2.13 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.05 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.69 (br. s, 12H, Adamantyl-CH_2); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.3 (C6 CD), 187.0 (C6 AB), 178.9 (C8 CD), 173.6 (C8 AB), 167.5 (C10 CD), 167.2 (C10 AB), 166.7 (C9 CD), 166.6 (C9 AB), 139.1, 139.0 (C1'), 134.9, 134.8 (C1a'), 128.6, 128.6, 128.5, 128.5, 128.4, 128.4 (C3', C3a', C2a'), 128.1 (C4' and C4a'), 126.9 (C2'), 89.4, 84.1 (C7), 82.8, 81.2 (C5), 68.5, 68.3 (C11), 64.1, 63.9 (C2), 54.9, 54.4 (Adamantyl-*C*), 41.6, 41.6 (Adamantyl-*C*H_2), 36.0, 35.9 (Adamantyl-*C*H_2), 35.4, 35.3 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI$^-$) 543 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{31}H_{31}O_5N_2S$ [M-H]$^-$ 543.1959; found 543.1968.

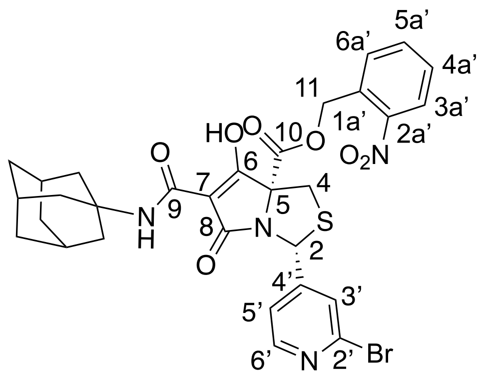
(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-5-(4-nitrobenzyloxycarbonyl)-1-aza-6-hydroxy-8-oxo-2-(pyridin-2-yl)-3-thiabicyclo[3.3.0]oct-6-ene, 91



Synthesised from **36i** (1 eq. 42 mg, 0.08 mmol) with 1-adamantylamine; yield (26 mg, 52%); pale yellow oil; R_f = 0.41 (100% EtOAc); $[\alpha]_D^{25}$ = +142.8 (c = 0.87, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1689 (s, C=O), 1627 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.8 : 1 AB/CD tautomers: δ (O*H* not observed), 8.40 (br. s, 2H, H6' AB and CD), 8.11 (d, J = 8.3 Hz, 4H, H3a' AB and

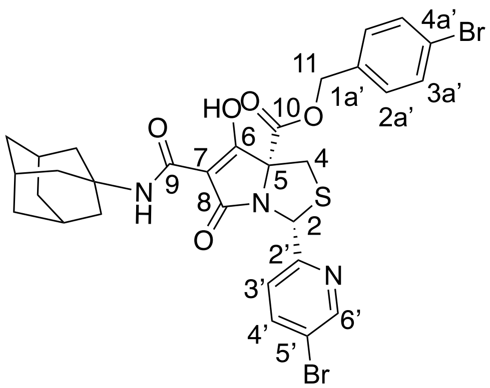
CD), 7.86 (br. s, 1H, N*H* CD), 7.75 (br. s, 1H, N*H* AB), 7.58 – 7.45 (m, 4H, H4' and H3', AB and CD), 7.36 (d, *J* = 8.5 Hz, 4H, H2a' AB and CD), 7.15 – 7.05 (m, 2H, H5' AB and CD), 6.36 (s, 1H, H2 CD), 6.34 (s, 1H, H2 AB), 5.39 – 5.17 (m, 4H, H11 AB and CD), 3.94 (d, *J* = 11.6 Hz, 2H, $H4_B$ AB and CD), 3.21 (d, *J* = 11.6 Hz, 2H, $H4_A$ AB and CD), 2.15 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.06 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.70 (br. s, 12H, Adamantyl-CH_2 AB and CD); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.1 (C6 CD), 187.1 (C6 AB), 179.0 (C8 CD), 173.8 (C8 AB), 167.4 (C10 CD), 167.2 (C10 AB), 166.7 (C9), 158.7 (C2'), 149.1 (C6'), 147.8 (C4a'), 142.5 (C1a'), 136.9 (C4'), 128.3 (C2a'), 123.8 (C3a'), 122.8 (C3'), 120.2 (C5'), 88.4, 84.0 (C7), 83.5, 82.0 (C5), 66.5, 66.3 (C11), 64.6, 64.5 (C2), 55.2, 54.7 (Adamantyl-*C*), 41.7, 41.6 (Adamantyl-*C*H_2), 35.9 (Adamantyl-*C*H_2), 35.5, 35.4 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI$^-$) 589 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{30}H_{29}O_7N_4S$ [M-H]$^-$ 589.1762; found 589.1757.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-1-aza-2-(2-bromopyridin-4-yl)-6-hydroxy-5-(2-nitrobenzyloxycarbonyl)-8-oxo-3-thiabicyclo[3.3.0]-oct-6-ene, 92



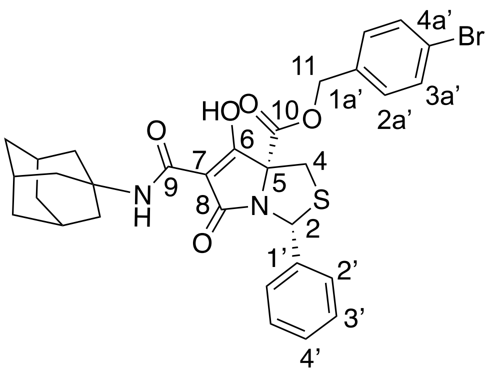
Synthesised from **38iv** (1 eq. 42 mg, 0.07 mmol) with 1-adamantylamine; yield (21 mg, 43%); yellow oil; R_f = 0.20 (100% EtOAc); $[\alpha]_D^{25}$ = +1.84 (*c* = 1.05, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1689 (s, C=O), 1629 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 1 : 1 AB/CD tautomers: δ (N*H* and O*H* not observed), 8.32 (d, *J* = 5.1 Hz, 1H, H6'), 8.22 (d, *J* = 5.1 Hz, 1H, H6'), 8.09 (d, *J* = 8.1 Hz, 1H, H3a'), 7.89 (d, *J* = 8.1 Hz, 1H, H3a'), 7.68 (s, 1H, H3'), 7.61 (s, 1H, H3'), 7.55 (d, *J* = 7.7 Hz, 2H, H5a' AB and CD), 7.48 (t, *J* = 7.7 Hz, 2H, H4a' AB and CD), 7.41 (d, *J* = 7.7 Hz, 2H, H6a' AB and CD), 7.38 (d, *J* = 5.1 Hz, 1H, H5'), 7.34 (d, *J* = 5.1 Hz, 1H, H5'), 6.18 (s, 1H, H2 CD), 6.14 (s, 1H, H2 AB), 5.63 – 5.56 (m, 4H, H11 AB and CD), 3.89 – 3.84 (m, 2H, $H4_B$ AB and CD), 3.14 (d, *J* = 11.6 Hz, 2H, $H4_A$ AB and CD), 2.15 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.06 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.71 (br. s, 12H, Adamantyl-CH_2 AB and CD); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.7 (C6 CD), 186.5 (C6 AB), 178.5 (C8 CD), 173.5 (C8 AB), 167.0 (C10 CD), 166.8 (C10 AB), 166.7 (C9 CD), 166.7 (C9 AB), 151.5 (C6'), 150.3, 150.3 (C4'), 147.5 (C2a'), 142.6 (C2'), 134.0 (C6a'), 132.6 (C1a'), 129.3, 129.3 (C5a'), 129.1, 129.0 (C4a'), 125.9, 125.9 (C3'), 125.3, 125.3 (C3a'), 121.0, 120.9 (C5'), 87.6, 82.7 (C7), 81.5, 81.1 (C5), 65.4, 65.2 (C11), 63.4, 63.2 (C2), 55.4, 55.1 (Adamantyl-*C*), 41.6 (Adamantyl-*C*H_2), 36.0, 35.9 (Adamantyl-*C*H_2), 35.7, 35.7 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI$^-$) 667 and 669 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{30}H_{28}O_7N_4BrS$ [M-H]$^-$ 667.0868 and 669.0847; found 667.0860 and 669.0840.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-1-aza-5-(4-bromobenzyloxycarbonyl)-2-(5-bromopyridin-2-yl)-6-hydroxy-8-oxo-3-thiabicyclo[3.3.0]oct-6-ene, 93



Synthesised from **39ii** (1 eq. 40 mg, 0.06 mmol) with 1-adamantylamine; yield (20 mg, 44%); pale yellow oil; R_f = 0.54 (100% EtOAc); $[\alpha]_D^{25}$ = +144 (*c* = 1.0, $CHCl_3$); ν_{max}/cm^{-1} 1743 (s, C=O), 1689 (s, C=O), 1627 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ 8.36 (app dd, *J* = 8.0, 2.0 Hz, 2H, H6' AB and CD), 7.87 (br. s, 1H, N*H*), 7.70 (br. s, 1H, N*H*), 7.56 (app dt, *J* = 8.4, 2.4 Hz, 2H, H4' AB and CD), 7.44 (d, *J* = 8.3 Hz, 4H, H3a' AB and CD), 7.35 (d, *J* = 8.4 Hz, 2H, H3' AB and CD), 7.11 (d, *J* = 8.3 Hz, 4H, H2a' AB and CD), 6.27 (s, 1H, H2 CD), 6.23 (s, 1H, H2 AB), 5.63 (br. s, 2H, O*H* AB and CD), 5.21 (app dd, *J* = 12.4, 2.6 Hz, 2H, $H11_B$ AB and CD), 5.03 (app dd, *J* = 12.4, 6.2 Hz, 2H, $H11_A$ AB and CD), 3.89 (app dd, *J* = 11.6, 4.1 Hz, 2H, $H4_B$ AB and CD), 3.17 (app dd, *J* = 11.6, 1.1 Hz, 2H, $H4_A$ AB and CD), 2.15 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.06 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.70 (br. s, 12H, Adamantyl-CH_2); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.9 (C6 CD), 187.0 (C6 AB), 178.9 (C8 CD), 173.6 (C8 AB), 167.3 (C10 CD), 167.1 (C10 AB), 166.7 (C9 CD), 166.7 (C9 AB), 157.5, 157.3 (C2'), 150.2 (C6'), 139.3 (C4'), 134.1, 133.9 (C1a'), 131.9 131.8 (C3a'), 130.2 (C2a'), 122.8, 122.7 (C4a'), 121.6 (C3'), 119.8, 119.8 (C5'), 88.5, 83.9 (C7), 83.5, 82.0 (C5), 67.6, 67.4 (C11), 64.1, 64.0 (C2), 55.2, 54.7 (Adamantyl-*C*), 41.7, 41.6 (Adamantyl-*C*H_2), 36.0, 35.9 (Adamantyl-*C*H_2), 35.6, 35.5 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI$^+$) 702 (50%), 704 ([M+H]$^+$, 100%) and 706 (50%); HRMS (ESI$^+$) *m/z* calcd for $C_{30}H_{30}O_5N_3Br_2S$ [M+H]$^+$ 702.0267, 704.0249 and 706.0232; found 702.0265, 704.0243 and 706.0220.

(2*R*,5*R*)-7-(Adamantylaminocarbonyl)-1-aza-5-(4-bromobenzyloxycarbonyl)-6-hydroxy-8-oxo-2-phenyl-3-thiabicyclo[3.3.0]oct-6-ene, 94



Synthesised from **39iii** (1 eq. 29 mg, 0.05 mmol) with 1-adamantylamine; yield (16 mg, 47%); pale yellow oil; R_f = 0.29 (EtOAc : petrol; 2 : 3); $[\alpha]_D^{25}$ = +152 (*c* = 0.80, $CHCl_3$); ν_{max}/cm^{-1} 1745 (s, C=O), 1689 (s, C=O), 1626 (s, C=C); ^{1}H NMR ($CDCl_3$, 400 MHz): a mixture of 0.9 : 1 AB/CD tautomers: δ 7.80 (br. s, 1H, N*H*), 7.71 (br. s, 1H, N*H*), 7.46 – 7.39 (m, 8H, H2' and H3a', AB and CD), 7.25 – 7.20 (m, 6H, H3' and H4', AB and CD), 7.04 (app t, *J* = 7.8 Hz, 4H, H2a' AB and CD), 6.29 (s, 1H, H2 CD), 6.24 (s, 1H, H2 AB), 5.79 (br. s, 2H, O*H* AB and CD), 5.11 – 5.01 (m, 4H, H11 AB and CD), 3.87 (app dd, *J* = 11.5, 6.7 Hz, 2H, $H4_B$ AB and CD), 3.11 (d, *J* = 11.5 Hz, 2H, $H4_A$ AB and CD), 2.14 (br. s, 6H, Adamantyl-C*H* AB and CD), 2.05 (br. s, 12H, Adamantyl-CH_2 AB and CD), 1.70 (br. s, 12H, Adamantyl-CH_2); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 189.4 (C6 CD), 186.9 (C6 AB), 178.8 (C8 CD), 173.6 (C8 AB), 167.4 (C10 CD), 167.2 (C10 AB), 166.8 (C9 CD), 166.7 (C9 AB), 139.1, 139.0 (C1'), 134.0, 133.9 (C1a'), 131.8, 131.8 (C3a'), 130.1, 130.1 (C2a'), 128.5, 128.5 (C3'), 128.2 (C4'), 127.0, 127.0 (C2'), 122.7, 122.6 (C4a'), 88.8, 84.0 (C7), 82.8, 81.2 (C5), 67.6, 67.4 (C11), 64.0, 63.9 (C2), 55.1, 54.6 (Adamantyl-*C*), 41.7, 41.7 (Adamantyl-*C*H_2), 36.0, 36.0 (Adamantyl-*C*H_2), 35.4, 35.3 (C4), 29.4 (Adamantyl-*C*H); *m/z* (ESI$^-$) 621 and 623 ([M-H]$^-$, 100%); HRMS (ESI$^-$) *m/z* calcd for $C_{31}H_{30}O_5N_2BrS$ [M-H]$^-$ 621.1064 and 623.1046; found 621.1073 and 623.1052.

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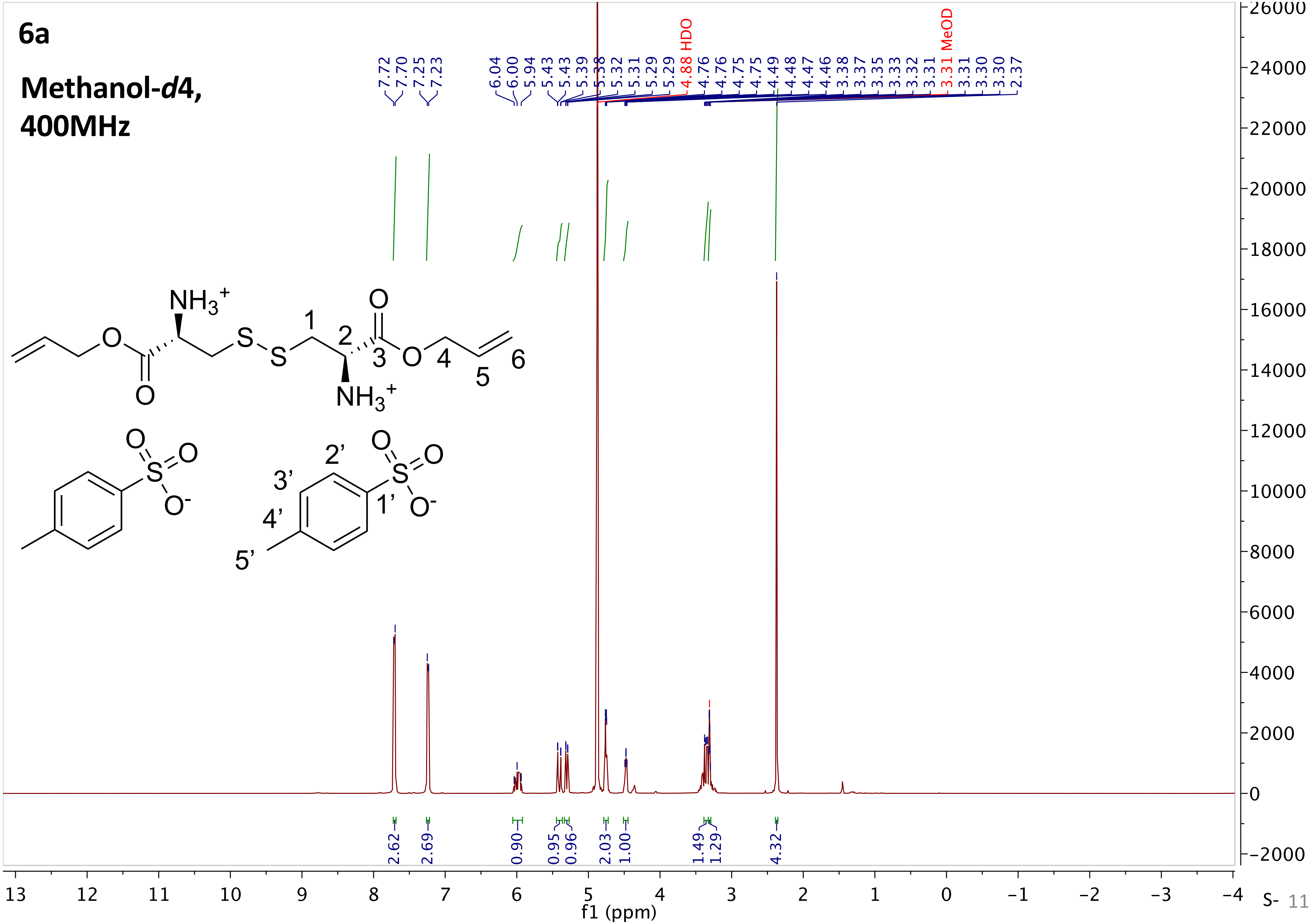
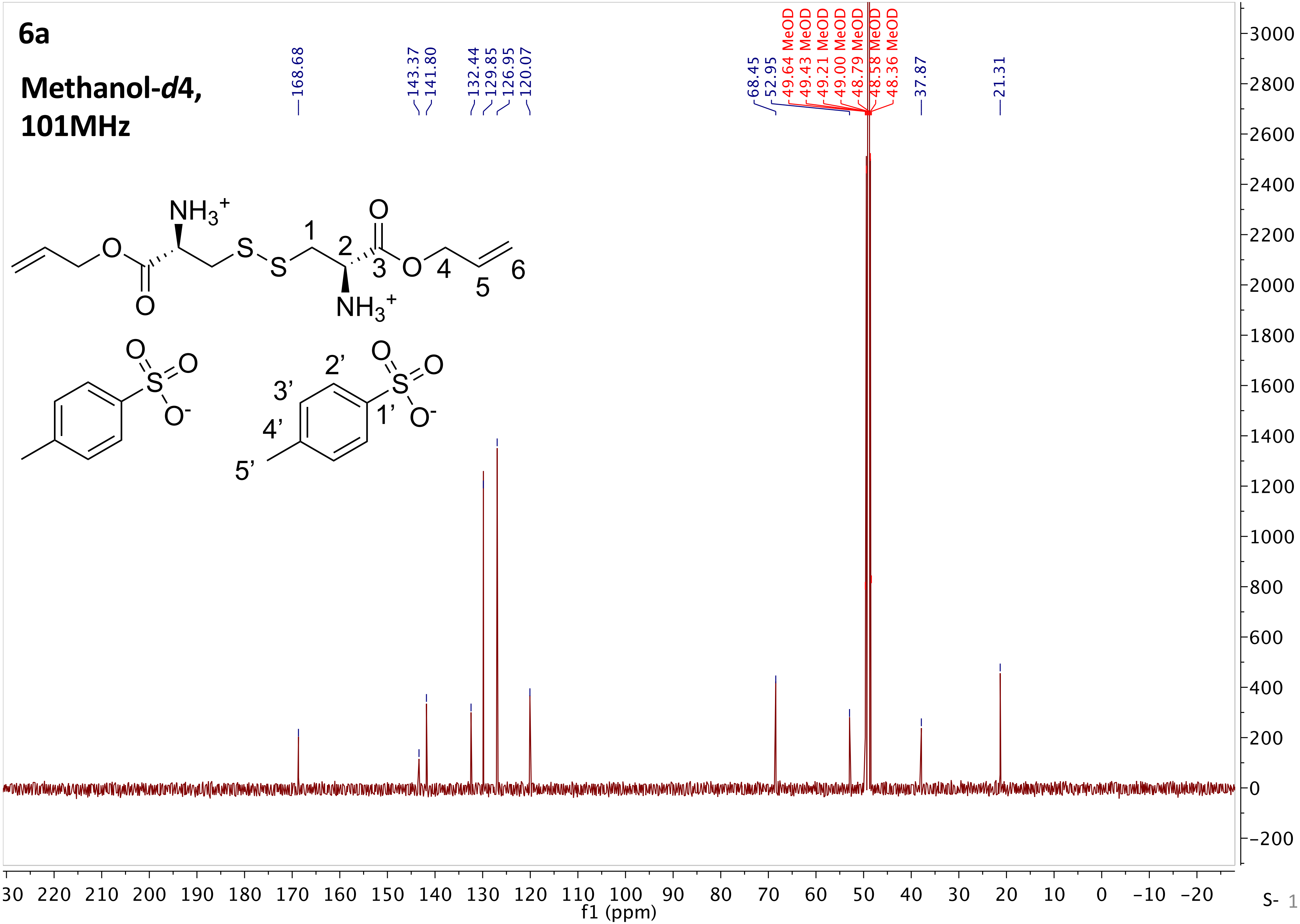
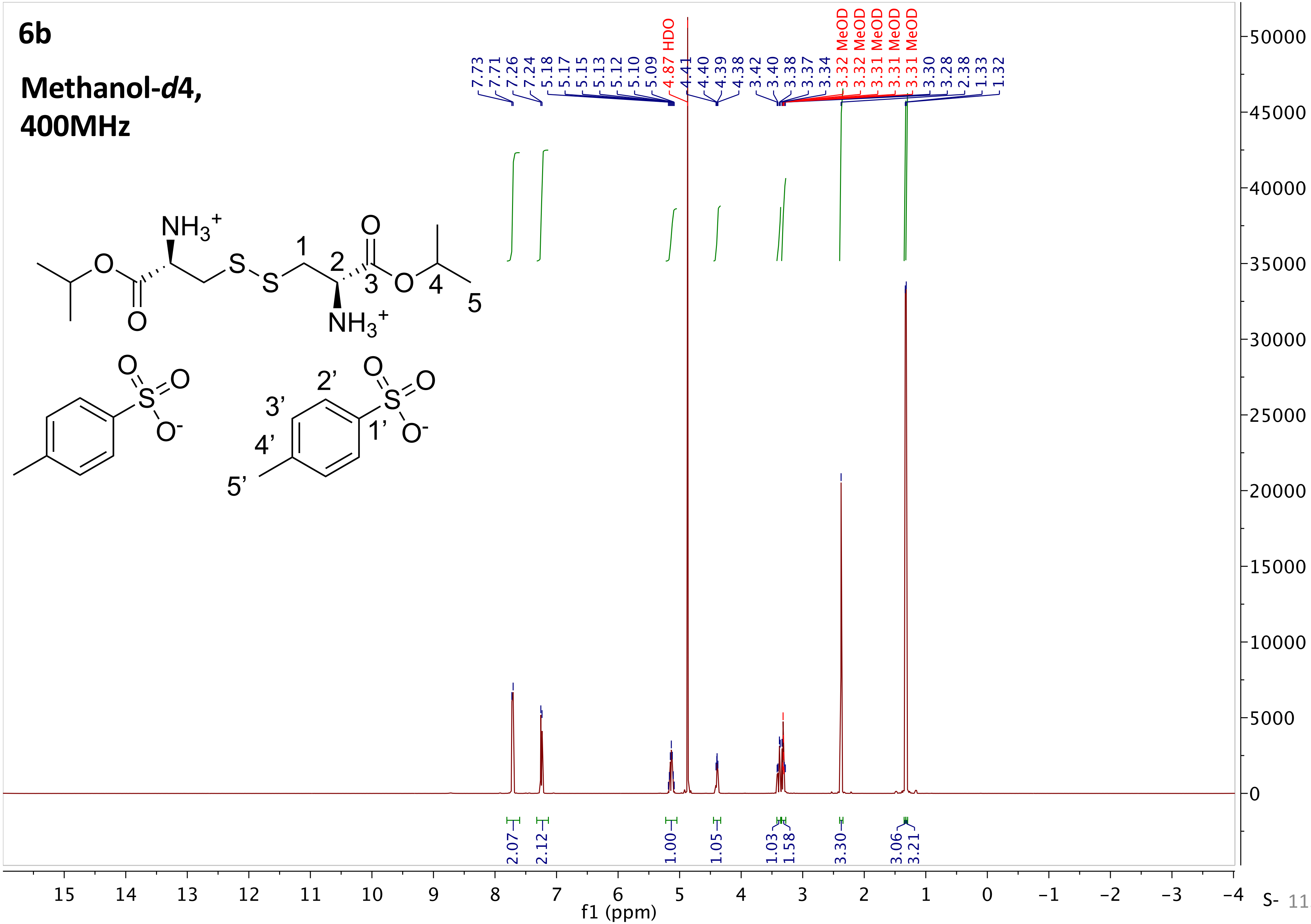
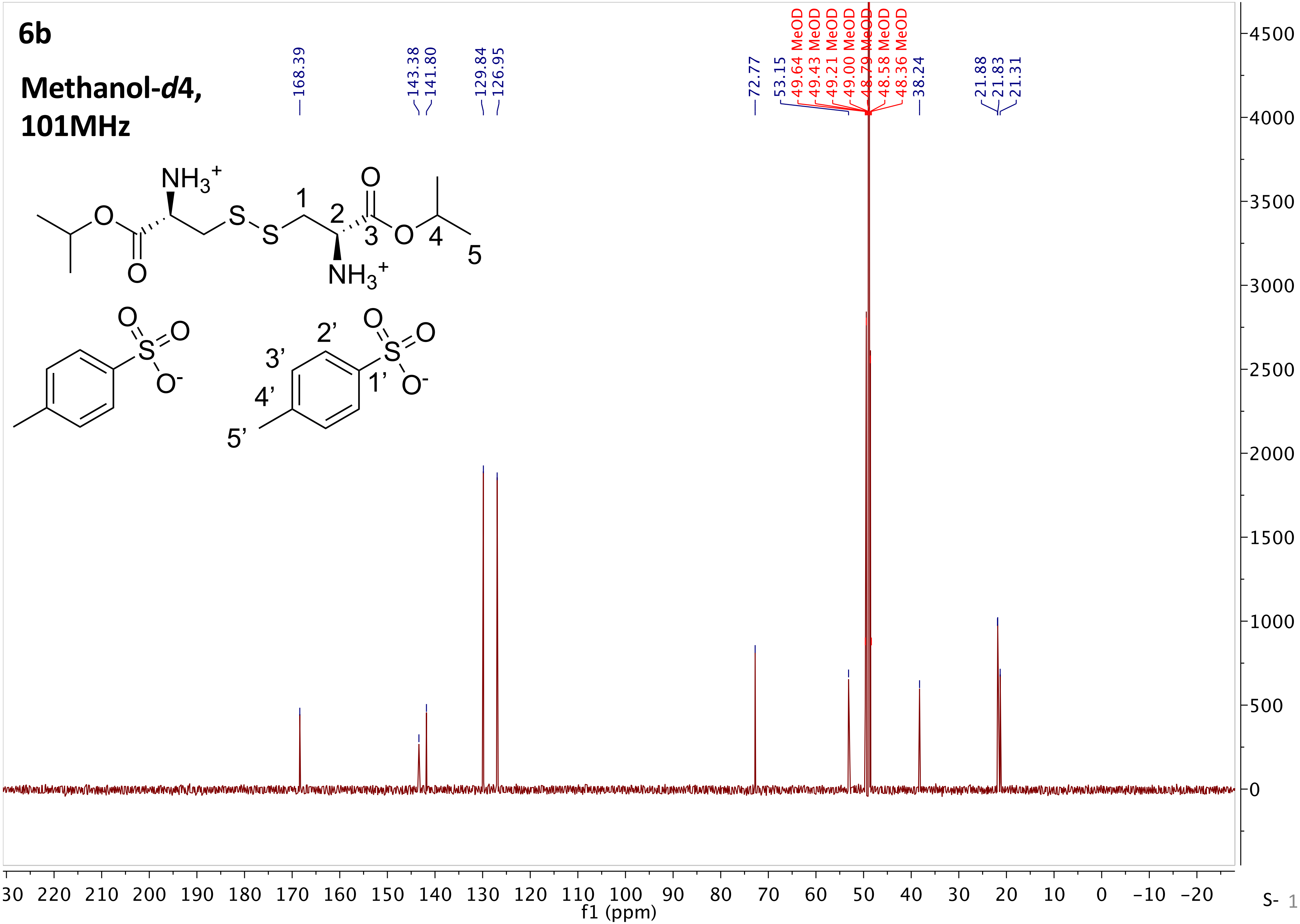
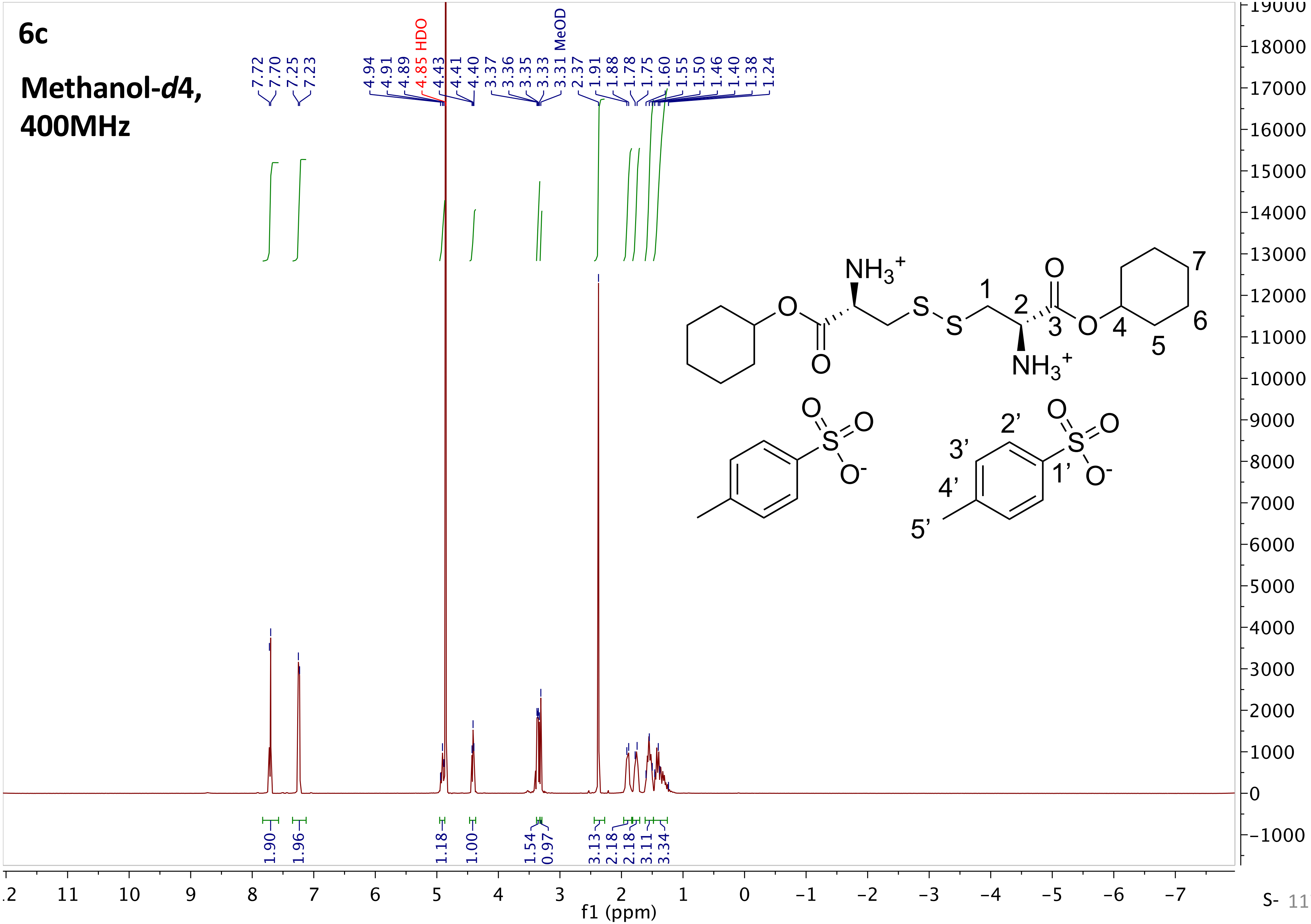

6a
Methanol-d4,
400MHz
7.72
7.70
7.25
7.23
6.04
6.00
5.94
5.43
5.43
5.39
5.38
5.32
5.31
5.29
5.29
4.88 HDO
4.76
4.76
4.75
4.75
4.49
4.48
4.47
4.46
3.38
3.37
3.35
3.33
3.32
3.31
3.31 MeOD
3.31
3.30
3.30
2.37
2.62
2.69
0.90
0.95
0.96
2.03
1.00
1.49
1.29
4.32
f1 (ppm)

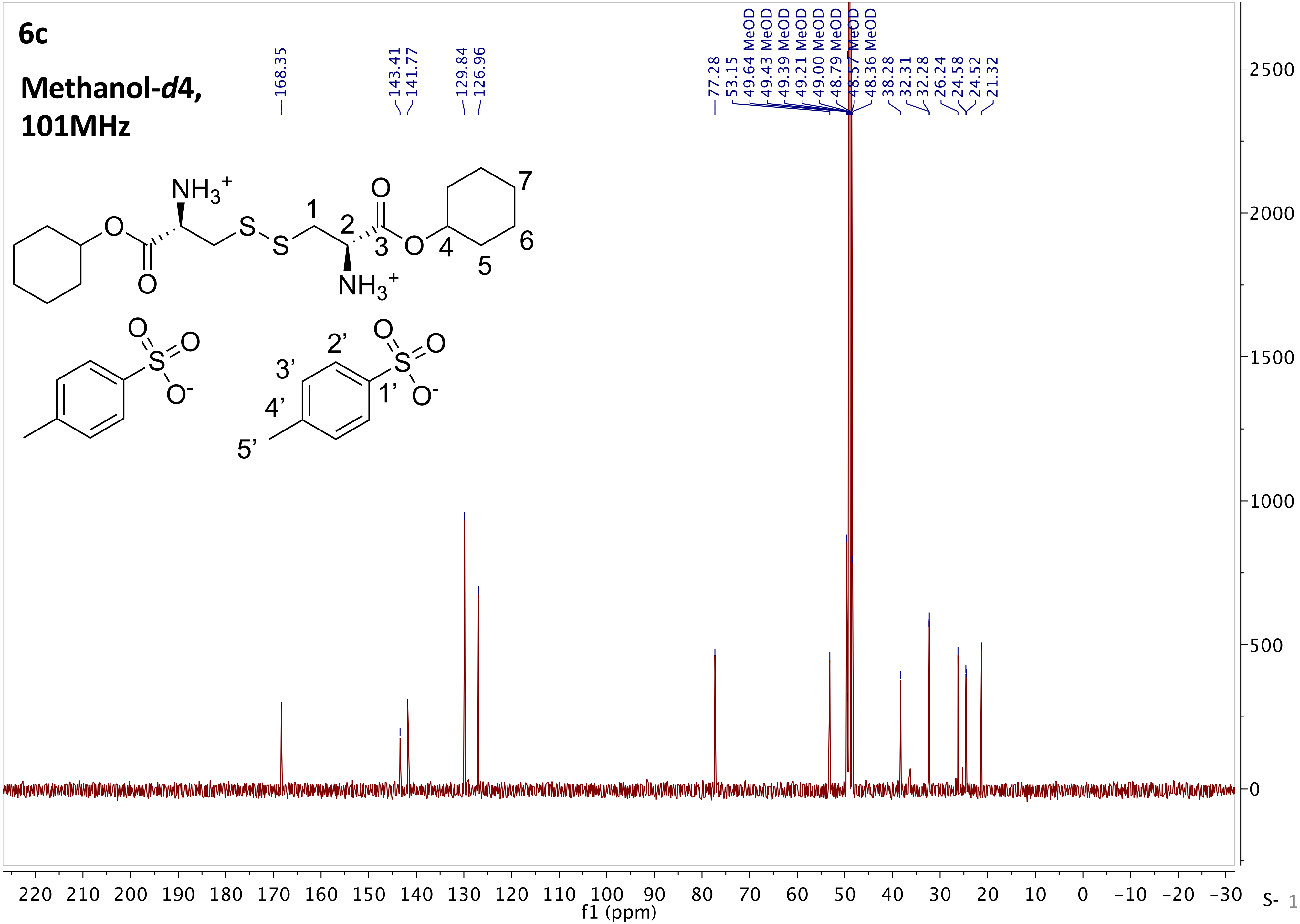


6a
Methanol-d4,
101MHz
168.68
143.37
141.80
132.44
129.85
126.95
120.07
68.45
52.95
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.58 MeOD
48.36 MeOD
37.87
21.31
f1 (ppm)


6b
Methanol-d4,
400MHz
NH3+
O
O
S
S
1
2
3
4
5
NH3+
O
O
O
O
S
O-
2'
3'
4'
5'
1'
O
O
S
O-
7.73
7.71
7.26
7.24
5.18
5.17
5.15
5.13
5.12
5.10
5.09
4.87 HDO
4.41
4.40
4.39
4.38
3.42
3.40
3.38
3.37
3.34
3.32 MeOD
3.32 MeOD
3.31 MeOD
3.31 MeOD
3.31 MeOD
3.30
3.28
2.38
1.33
1.32
2.07
2.12
1.00
1.05
1.03
1.58
3.30
3.06
3.21
f1 (ppm)


6b
Methanol-d4,
101MHz
168.39
143.38
141.80
129.84
126.95
72.77
53.15
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.58 MeOD
48.36 MeOD
38.24
21.88
21.83
21.31
f1 (ppm)


6c
Methanol-d4,
400MHz
7.72
7.70
7.25
7.23
4.94
4.91
4.89
4.85 HDO
4.43
4.41
4.40
3.37
3.36
3.35
3.33
3.31 MeOD
2.37
1.91
1.88
1.78
1.75
1.60
1.55
1.50
1.46
1.40
1.38
1.24
1.90
1.96
1.18
1.00
1.54
0.97
3.13
2.18
2.18
3.11
3.34
f1 (ppm)
NH3+
O
S
S
1
2
3
4
5
6
7
2'
3'
4'
5'
1'
O-


6c
Methanol-d4,
101MHz
168.35
143.41
141.77
129.84
126.96
77.28
53.15
49.64 MeOD
49.43 MeOD
49.39 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
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32.28
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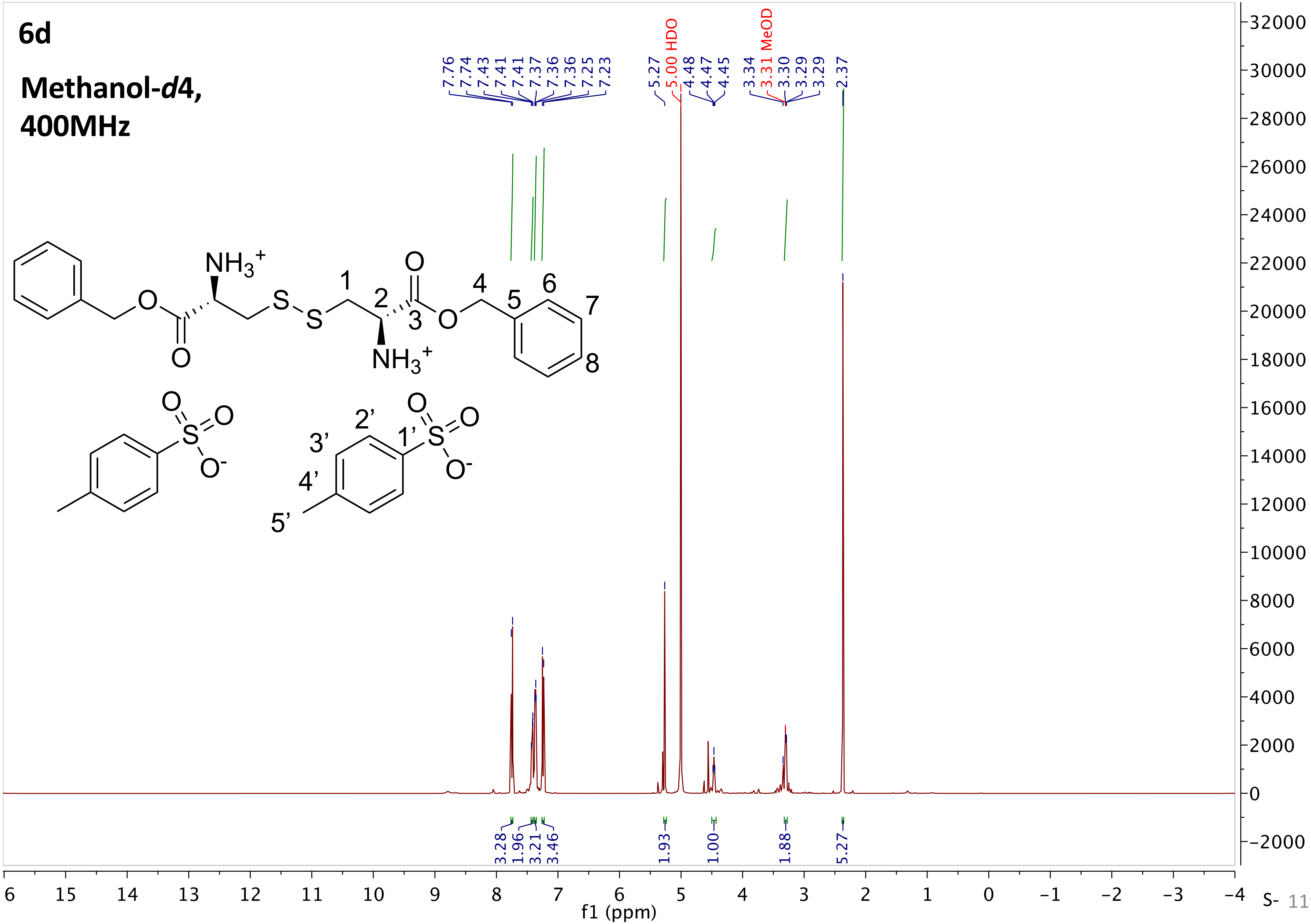
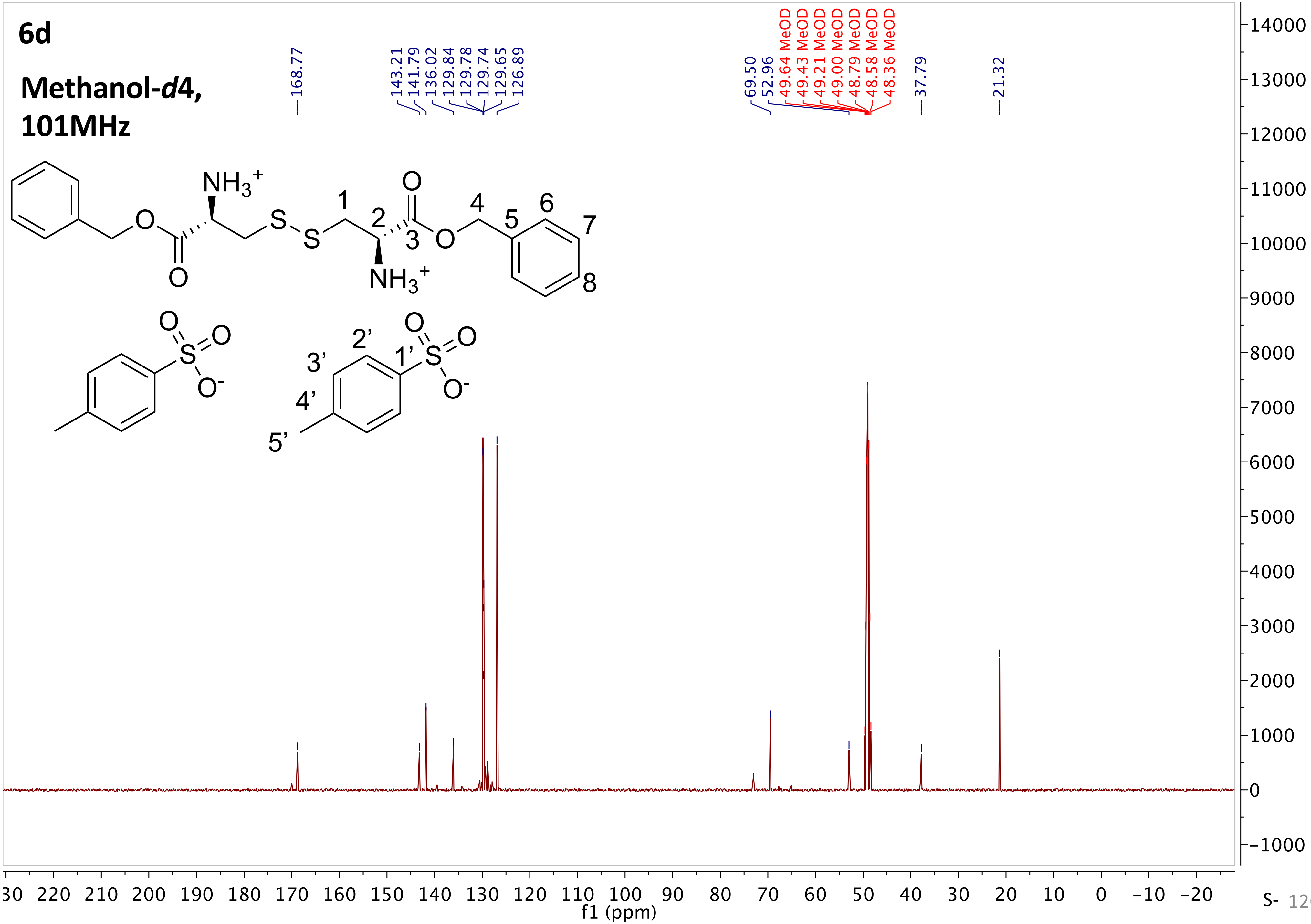
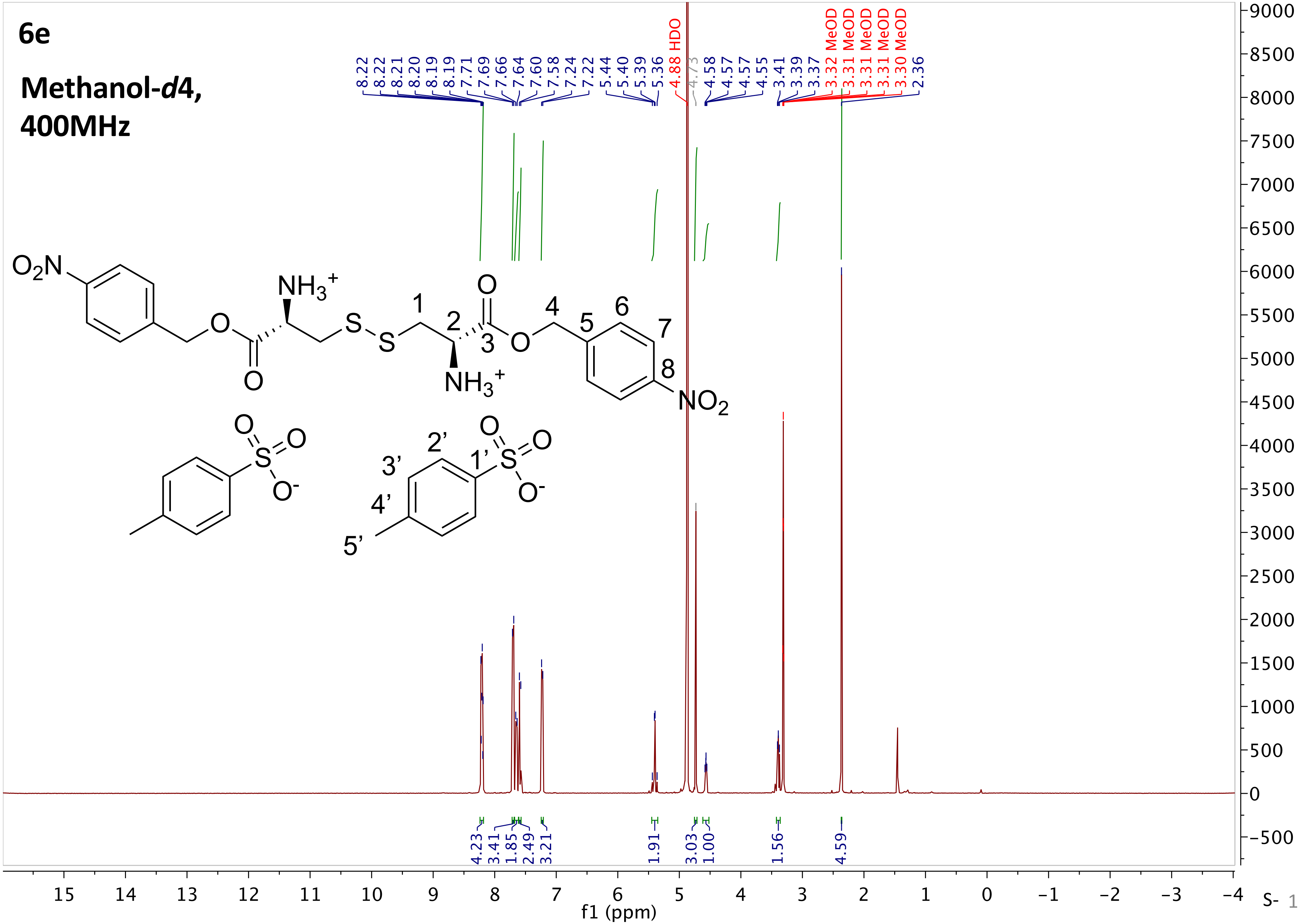
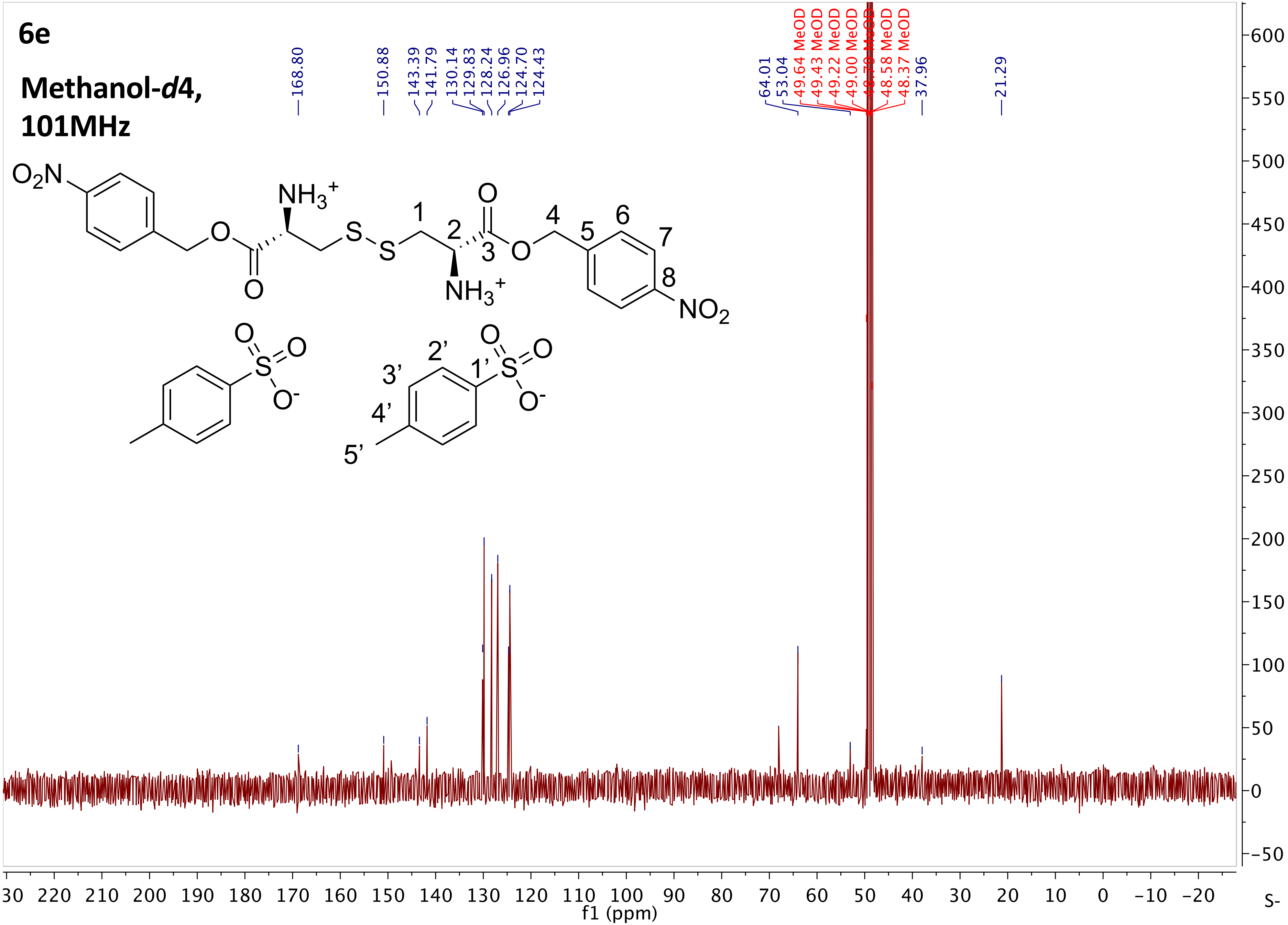
24.58
24.52
21.32
f1 (ppm)


6d
Methanol-d4,
400MHz
7.76 7.74 7.43 7.41 7.41 7.37 7.36 7.36 7.25 7.23
5.27 5.00 HDO 4.48 4.47 4.45
3.34 3.31 MeOD 3.30 3.29 3.29 2.37
3.28 1.96 3.21 3.46 1.93 1.00 1.88 5.27
f1 (ppm)


6d
Methanol-d4,
101MHz
168.77
143.21
141.79
136.02
129.84
129.78
129.74
129.65
126.89
69.50
52.96
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.58 MeOD
48.36 MeOD
37.79
21.32
f1 (ppm)

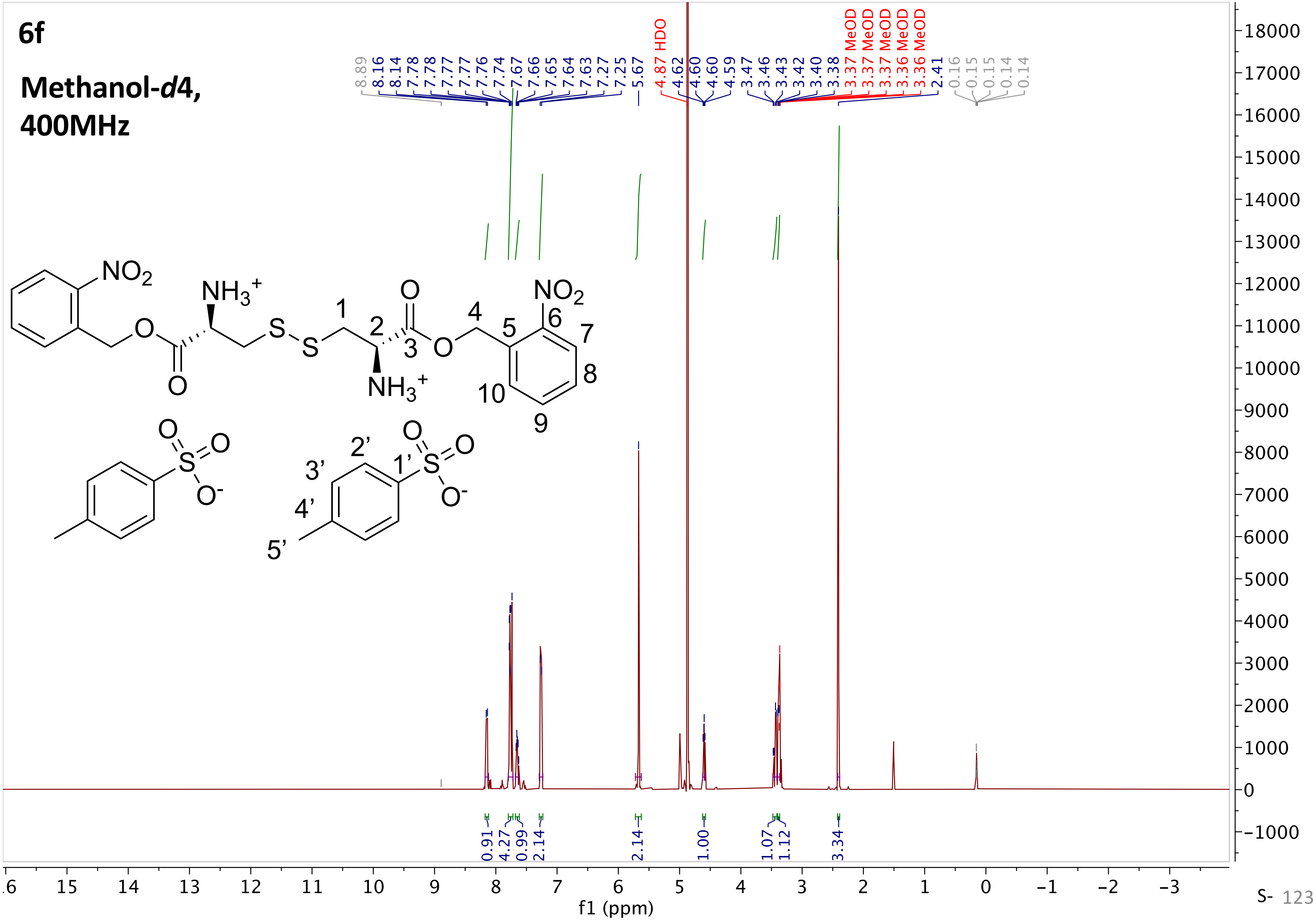

6e
Methanol-d4, 400MHz
8.22 8.22 8.21 8.20 8.19 8.19 7.71 7.69 7.66 7.64 7.60 7.58 7.24 7.22 5.44 5.40 5.39 5.36 4.88 HDO 4.73 4.58 4.57 4.57 4.55 3.41 3.39 3.37 3.32 MeOD 3.31 MeOD 3.31 MeOD 3.31 MeOD 3.30 MeOD 2.36
4.23 3.41 1.85 2.49 3.21 1.91 3.03 1.00 1.56 4.59
f1 (ppm)

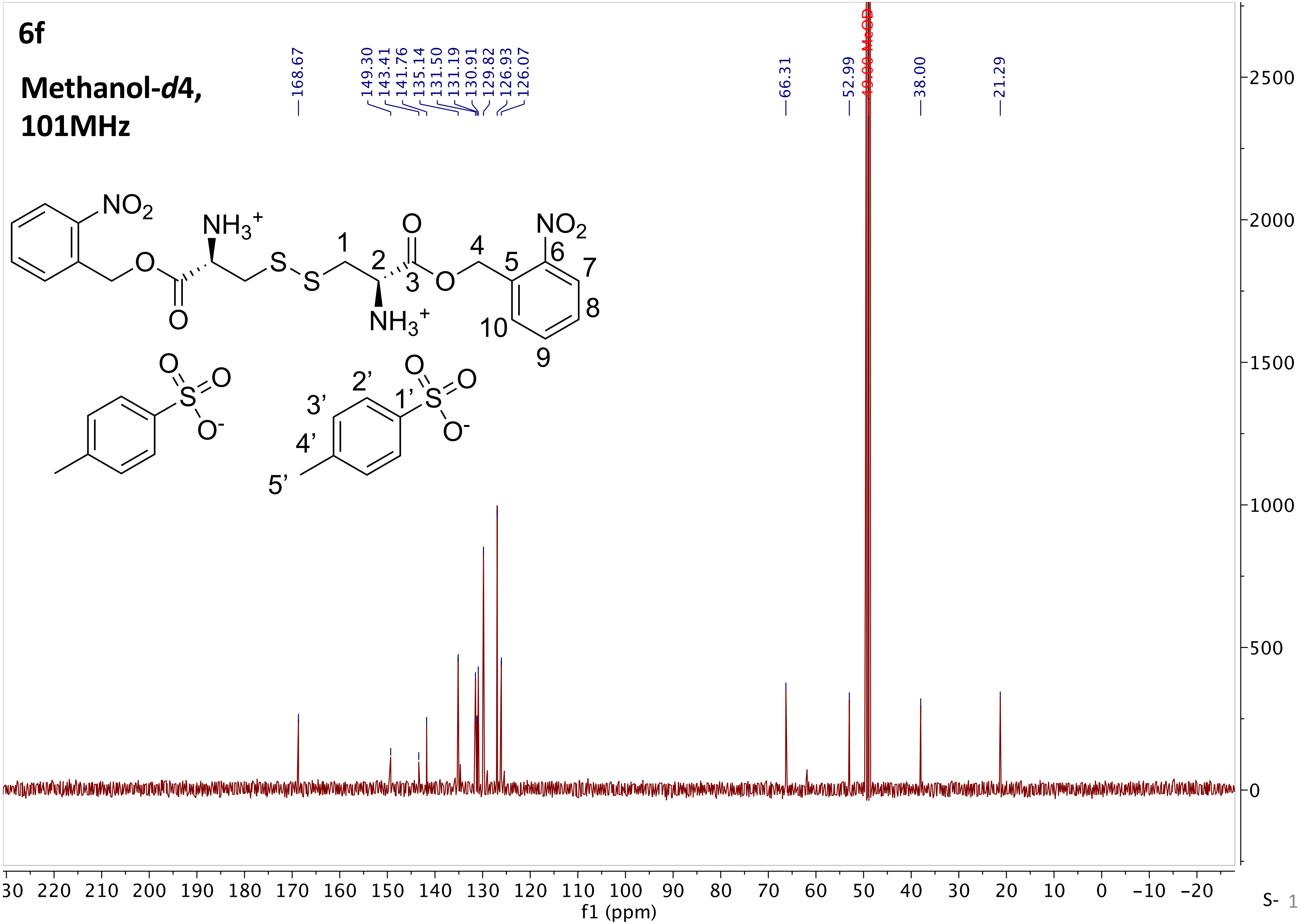


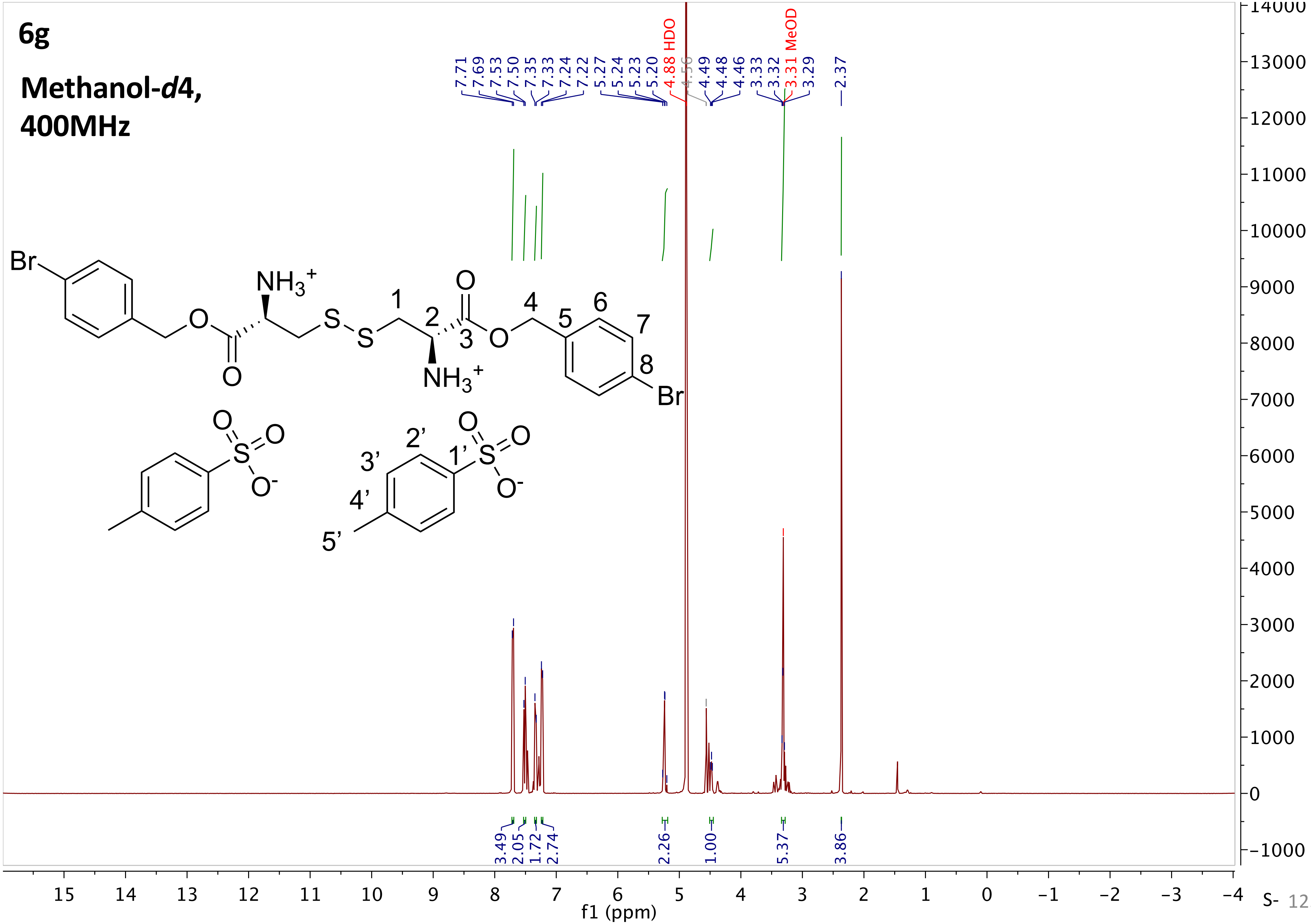
6e
Methanol-d4, 101MHz
168.80
150.88
143.39
141.79
130.14
129.83
128.24
126.96
124.70
124.43
64.01
53.04
49.64 MeOD
49.43 MeOD
49.22 MeOD
49.00 MeOD
48.79 MeOD
48.58 MeOD
48.37 MeOD
37.96
21.29
f1 (ppm)

6f

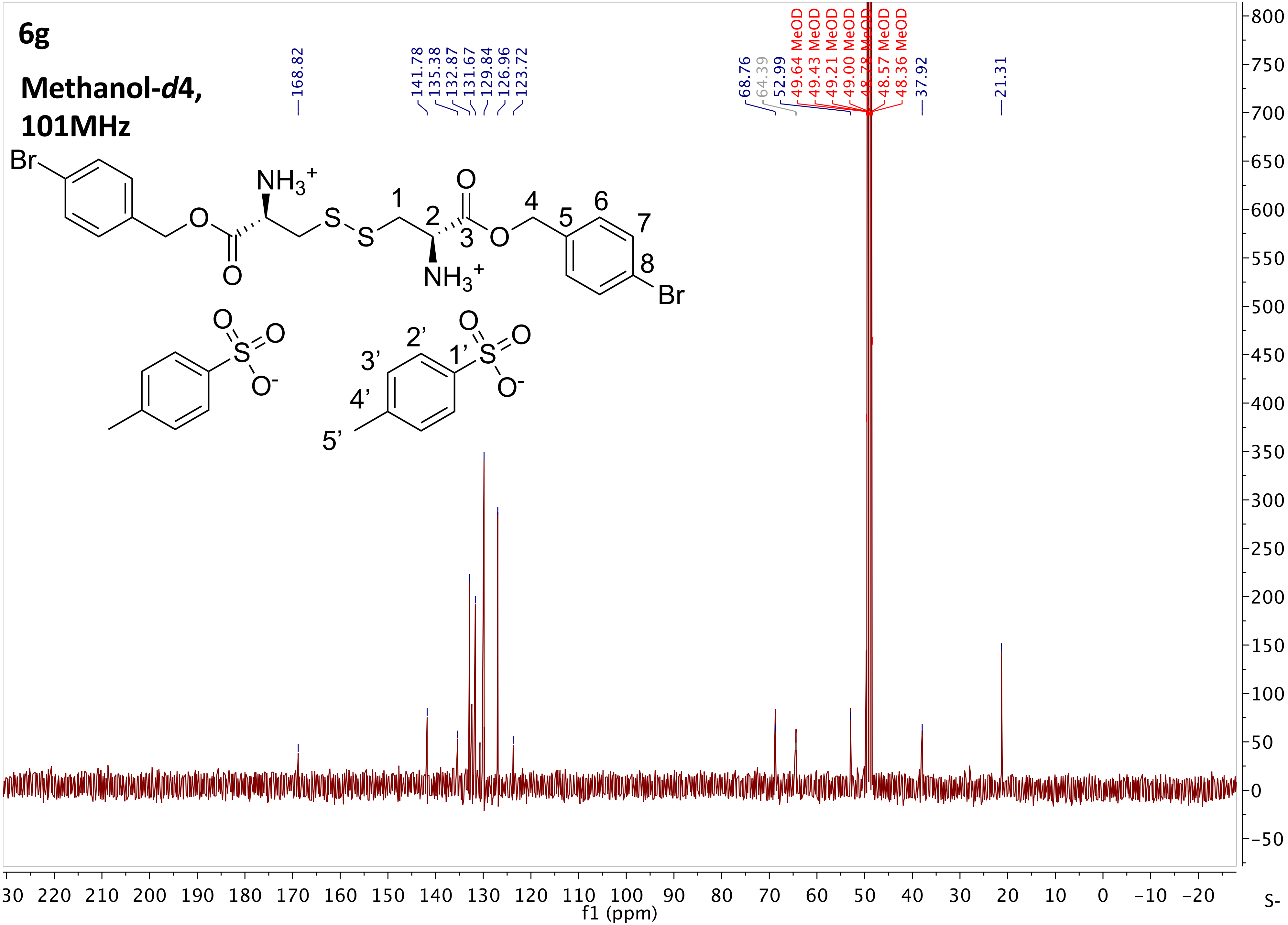
Methanol-*d*4, 400MHz



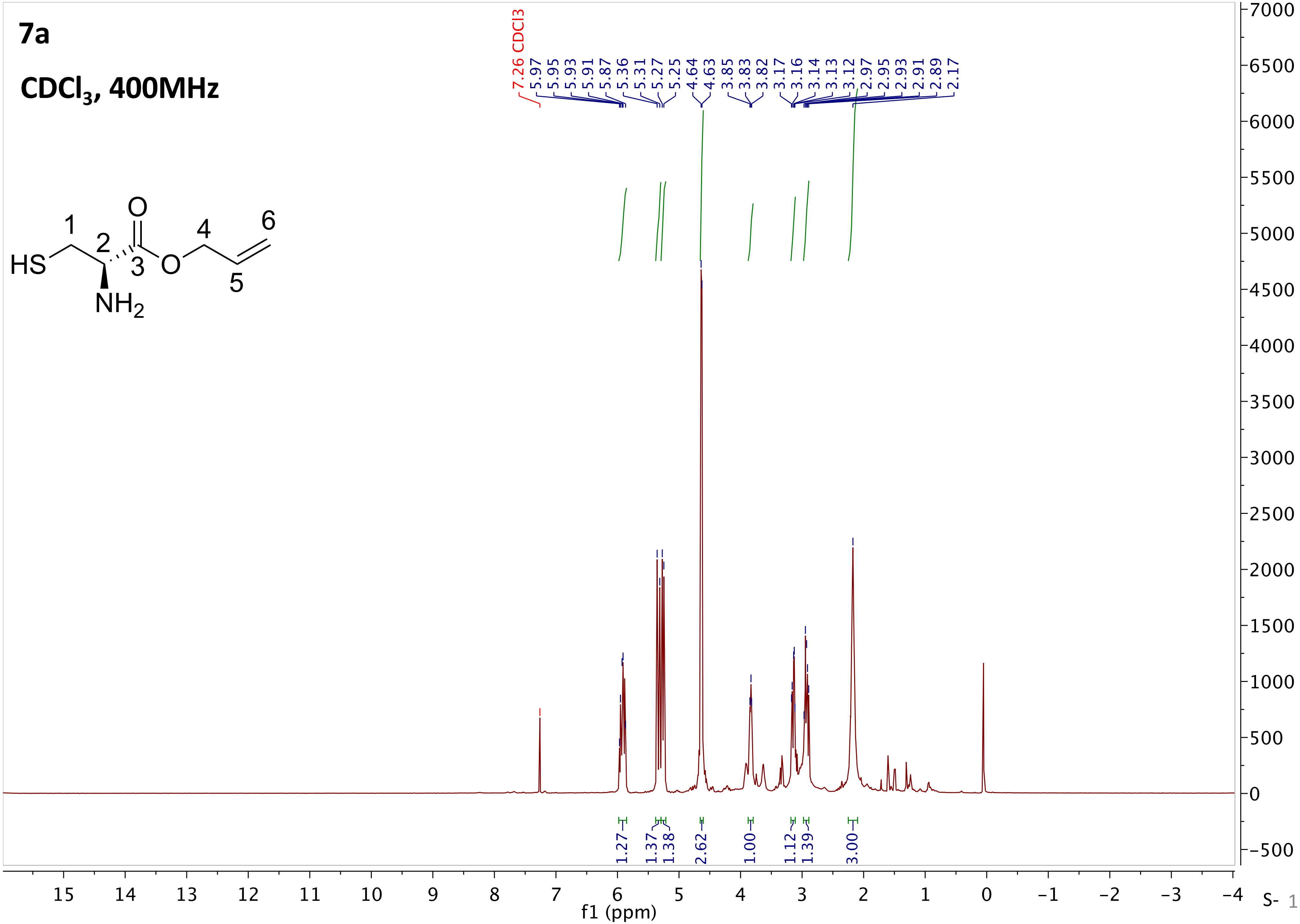

6f
Methanol-d4,
101MHz
168.67
149.30
143.41
141.76
135.14
131.50
131.19
130.91
129.82
126.93
126.07
66.31
52.99
49.00 MeOD
38.00
21.29
f1 (ppm)

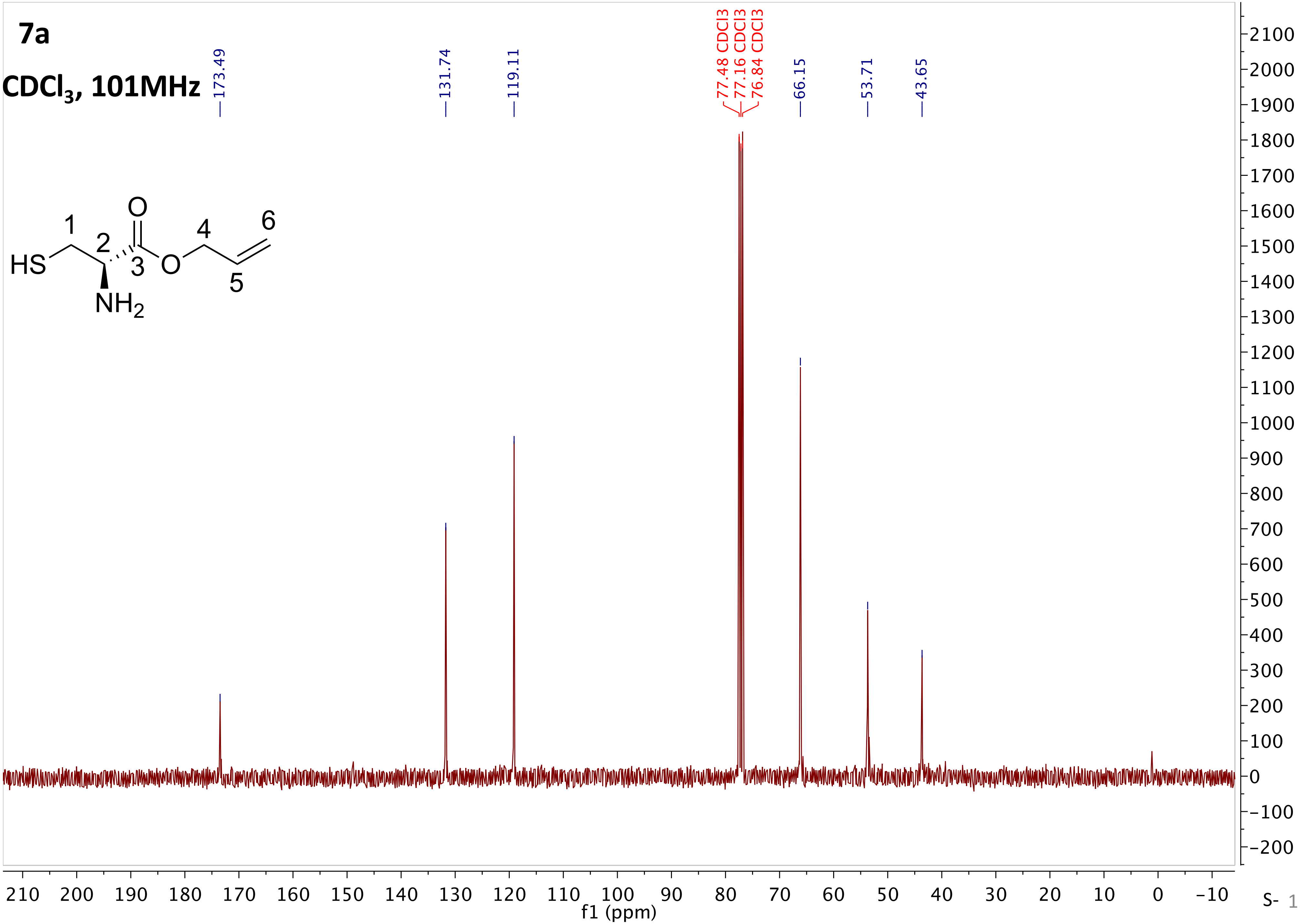


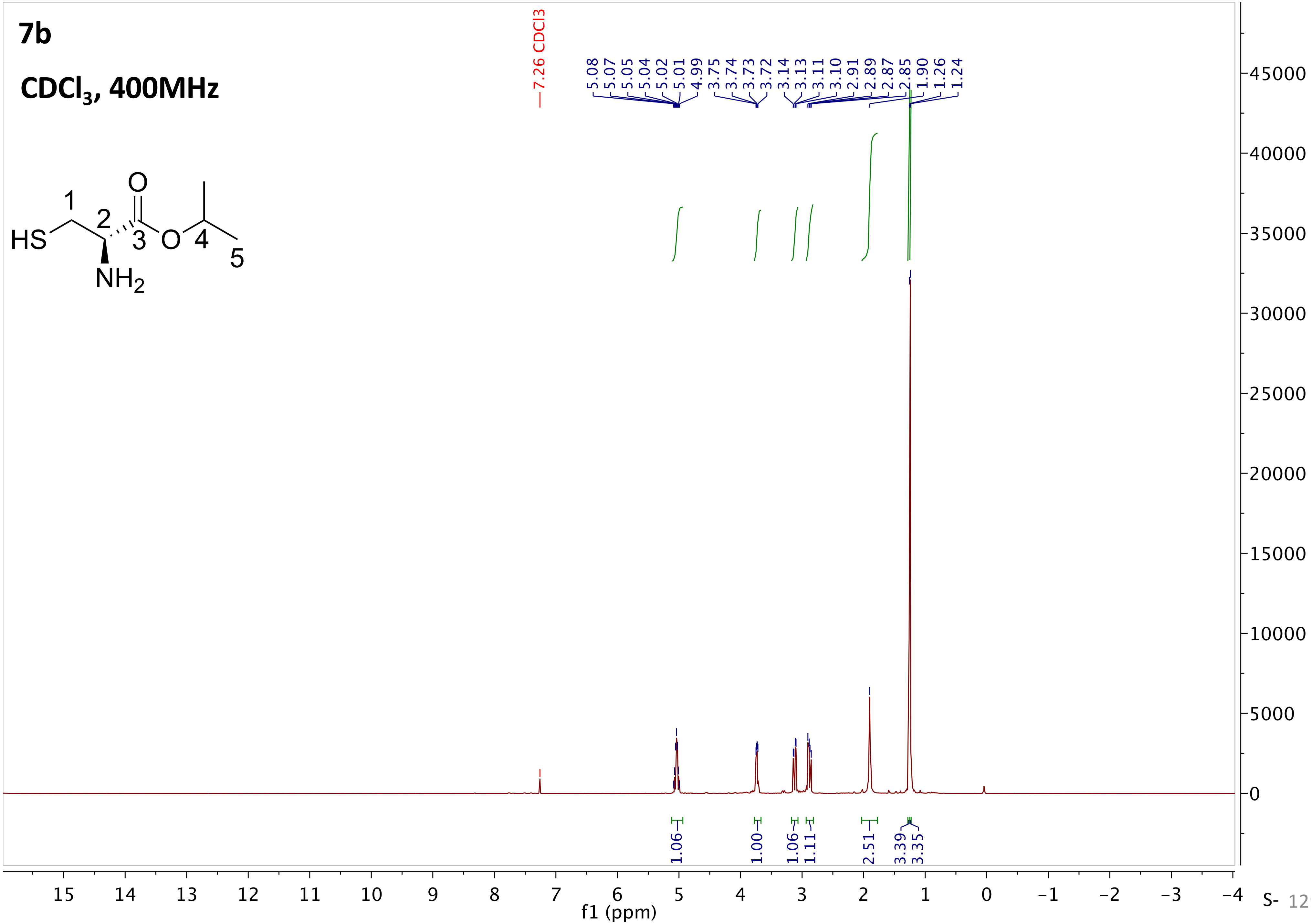
6g
Methanol-*d*4,
400MHz
7.71
7.69
7.53
7.50
7.35
7.33
7.24
7.22
5.27
5.24
5.23
5.20
4.88 HDO
4.56
4.49
4.48
4.46
3.33
3.32
3.31 MeOD
3.29
2.37
3.49
2.05
1.72
2.74
2.26
1.00
5.37
3.86
f1 (ppm)

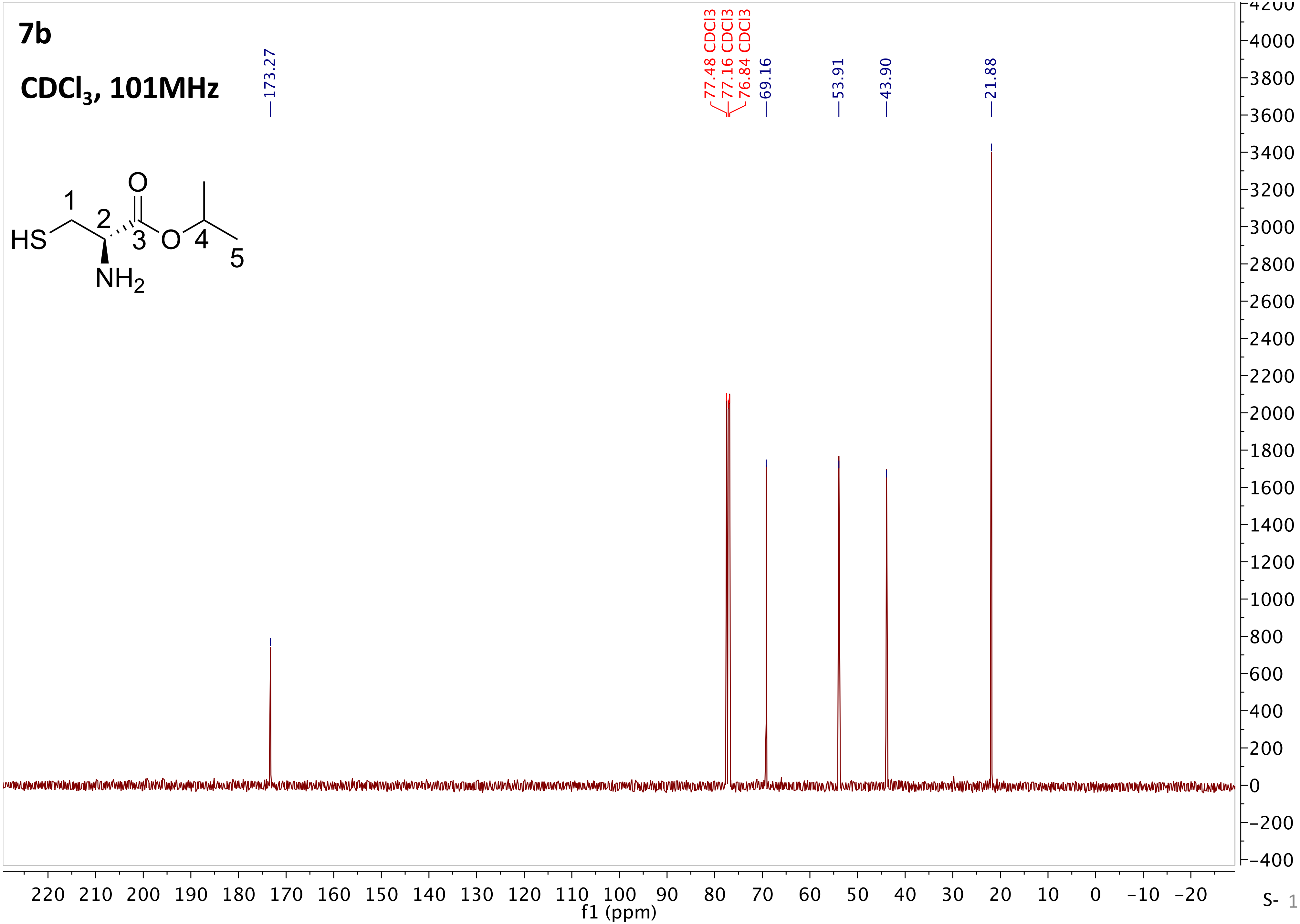


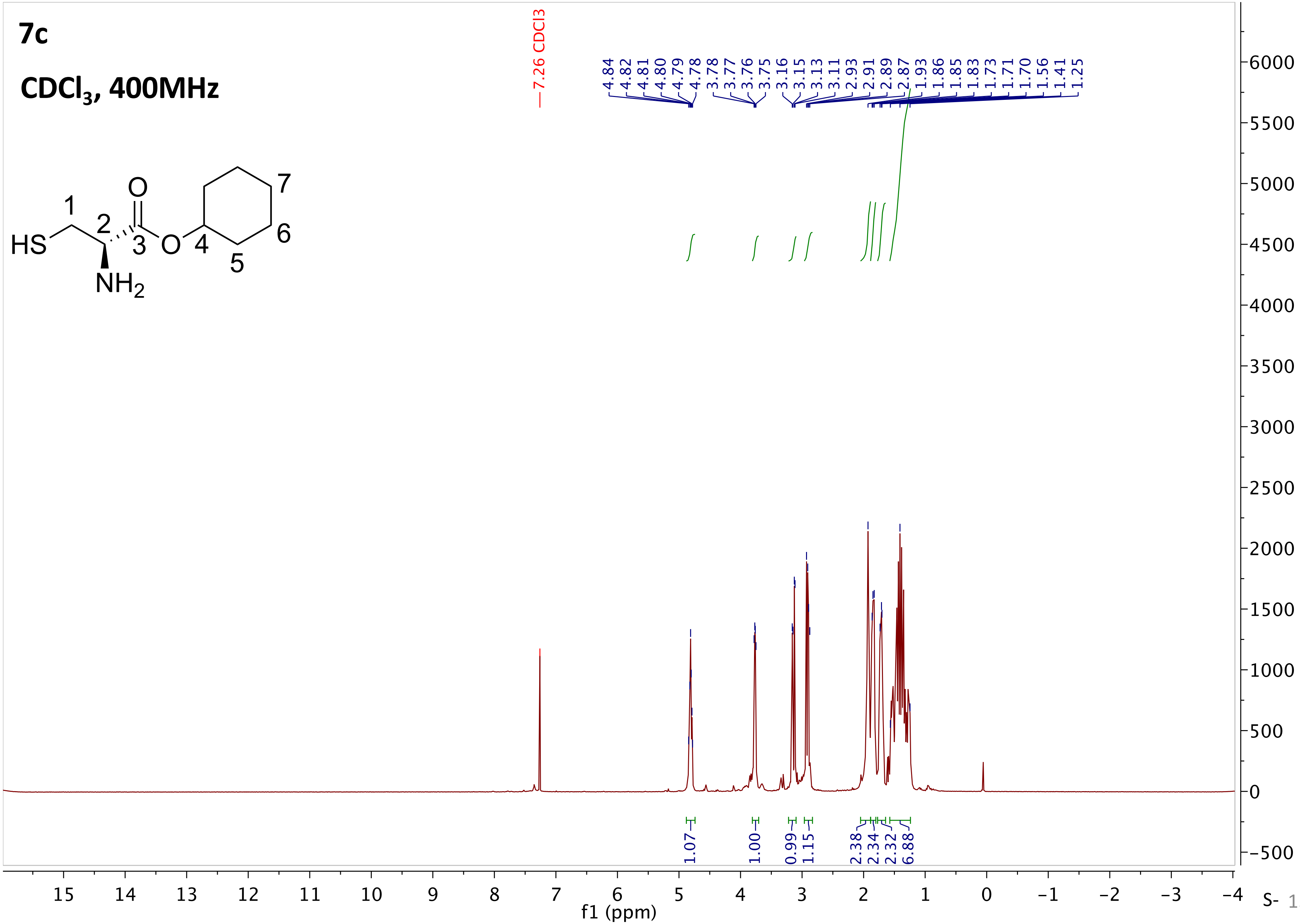
6g
Methanol-d4,
101MHz
168.82
141.78
135.38
132.87
131.67
129.84
126.96
123.72
68.76
64.39
52.99
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.78 MeOD
48.57 MeOD
48.36 MeOD
37.92
21.31
f1 (ppm)


7a
CDCl3, 400MHz
7.26 CDCl3
5.97
5.95
5.93
5.91
5.87
5.36
5.31
5.27
5.25
4.64
4.63
3.85
3.83
3.82
3.17
3.16
3.14
3.13
3.12
2.97
2.95
2.93
2.91
2.89
2.17
1.27
1.37
1.38
2.62
1.00
1.12
1.39
3.00
f1 (ppm)

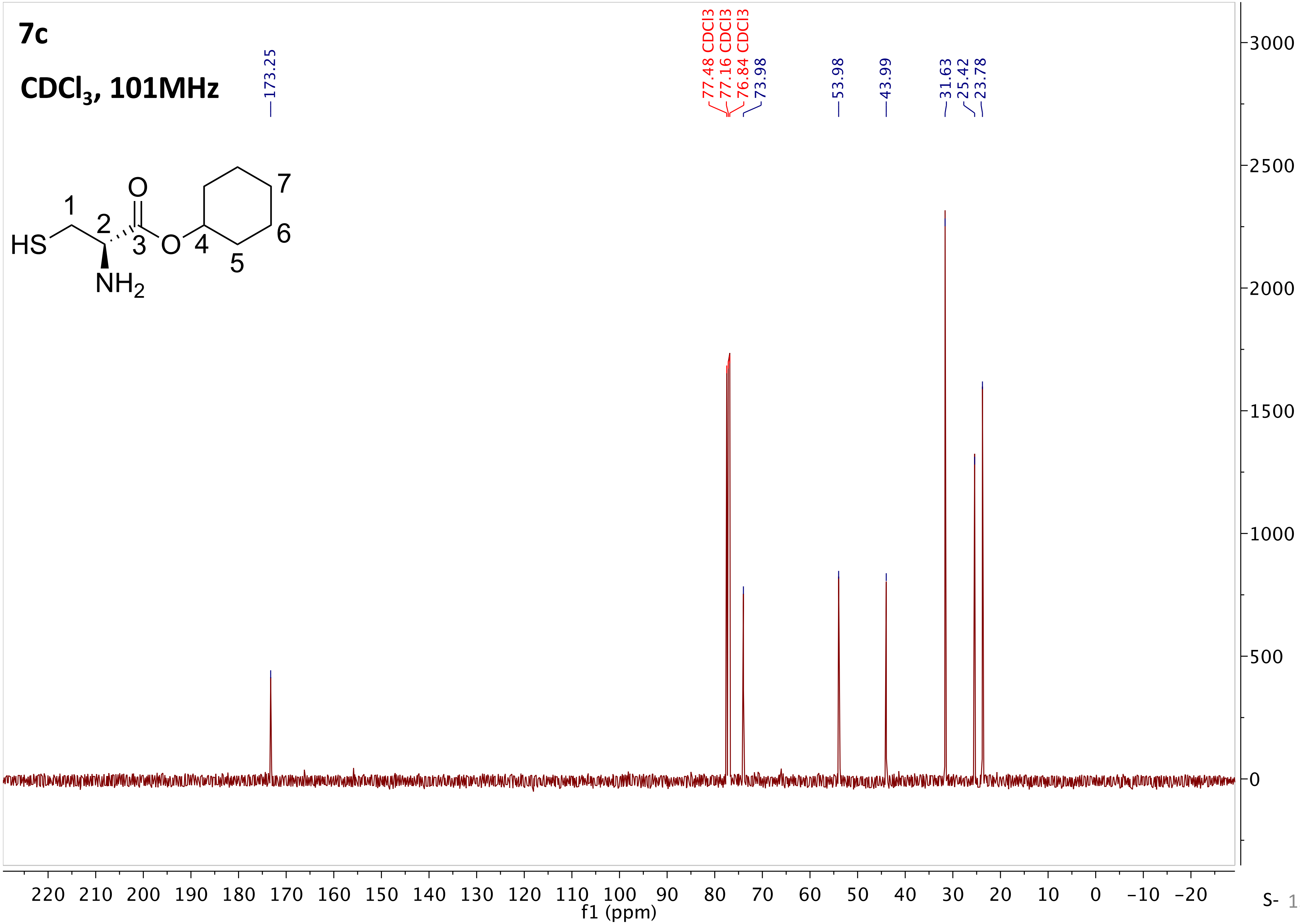

7a
CDCl3, 101MHz
173.49
131.74
119.11
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.15
53.71
43.65
HS
NH2
O
1
2
3
4
5
6
f1 (ppm)


7b
CDCl3, 400MHz
HS
1
2
3
4
5
O
O
NH2
7.26 CDCl3
5.08
5.07
5.05
5.04
5.02
5.01
4.99
3.75
3.74
3.73
3.72
3.14
3.13
3.11
3.10
2.91
2.89
2.87
2.85
1.90
1.26
1.24
1.06
1.00
1.06
1.11
2.51
3.39
3.35
f1 (ppm)


7b
CDCl3, 101MHz
HS
NH2
O
O
1
2
3
4
5
173.27
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.16
53.91
43.90
21.88
f1 (ppm)



7c
CDCl3, 400MHz
HS
NH2
O
1
2
3
4
5
6
7
7.26 CDCl3
4.84
4.82
4.81
4.80
4.79
4.78
3.78
3.77
3.76
3.75
3.16
3.15
3.13
3.11
2.93
2.91
2.89
2.87
1.93
1.86
1.85
1.83
1.73
1.71
1.70
1.56
1.41
1.25
1.07
1.00
0.99
1.15
2.38
2.34
2.32
6.88
f1 (ppm)



7c
CDCl3, 101MHz
173.25
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.98
53.98
43.99
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25.42
23.78
HS
NH2
O
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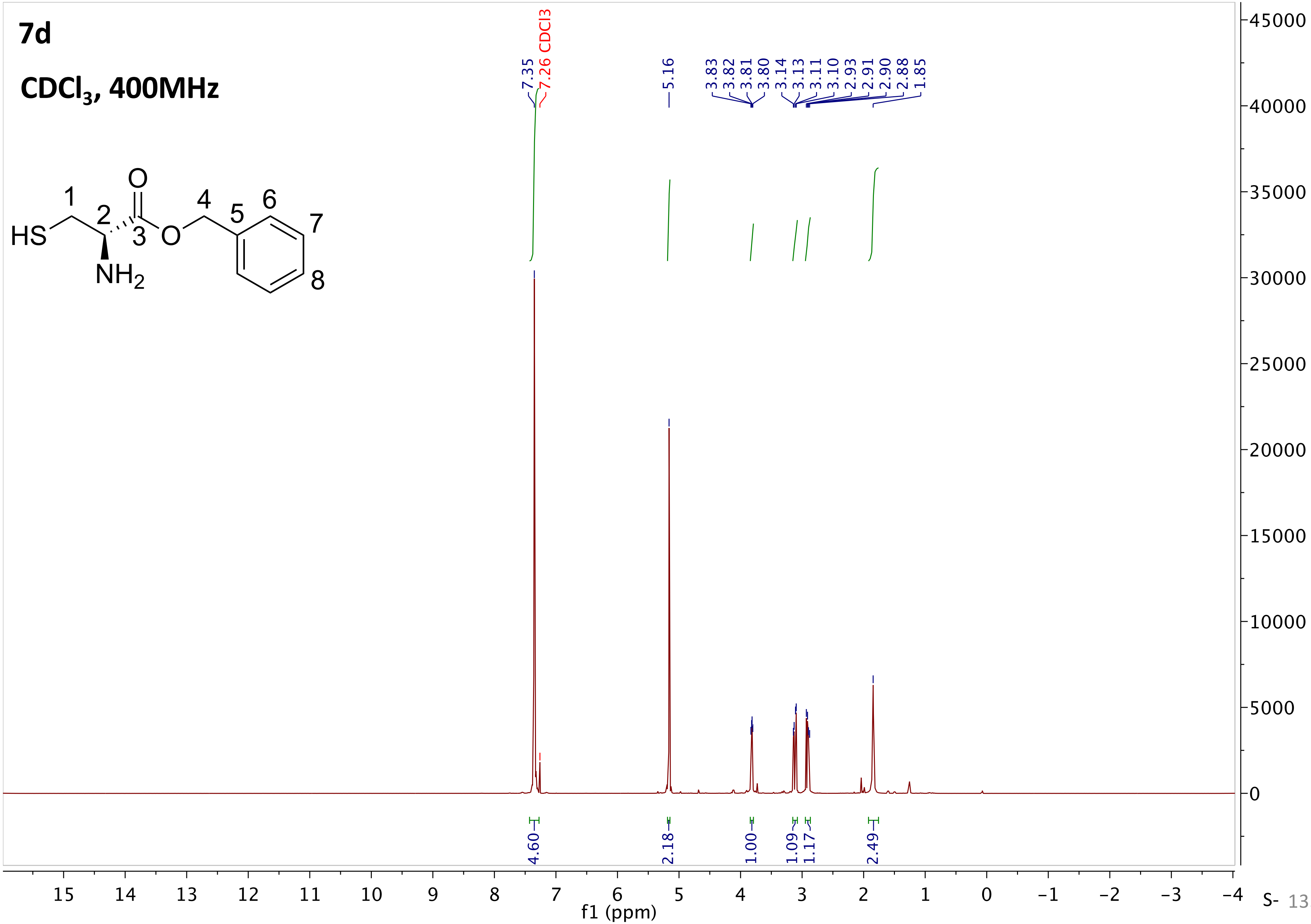
2
3
4
5
6
7
f1 (ppm)


7d
CDCl3, 400MHz
HS
NH2
O
O
1
2
3
4
5
6
7
8
7.35
7.26 CDCl3
5.16
3.83
3.82
3.81
3.80
3.14
3.13
3.11
3.10
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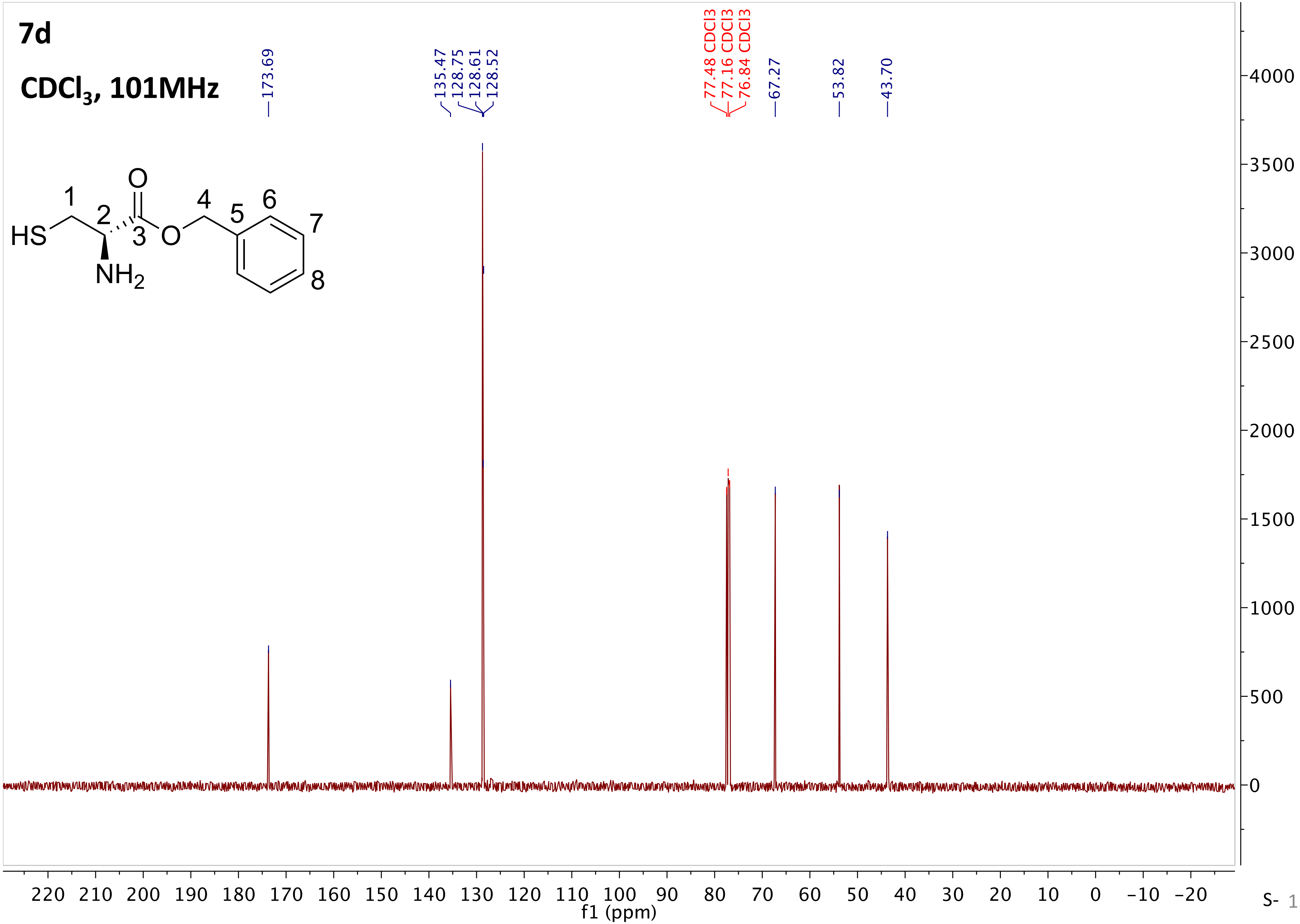
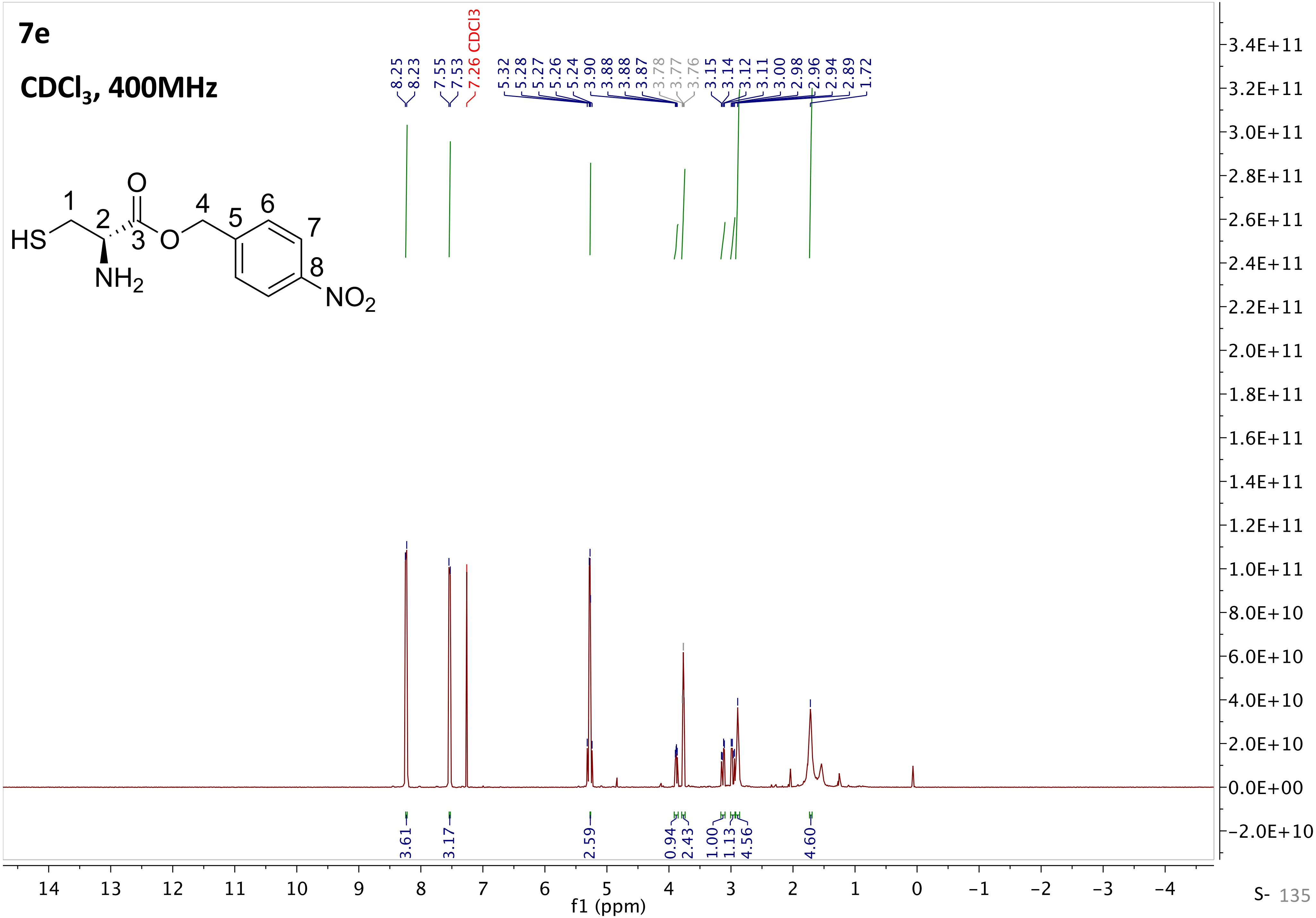
1.17
2.49
f1 (ppm)

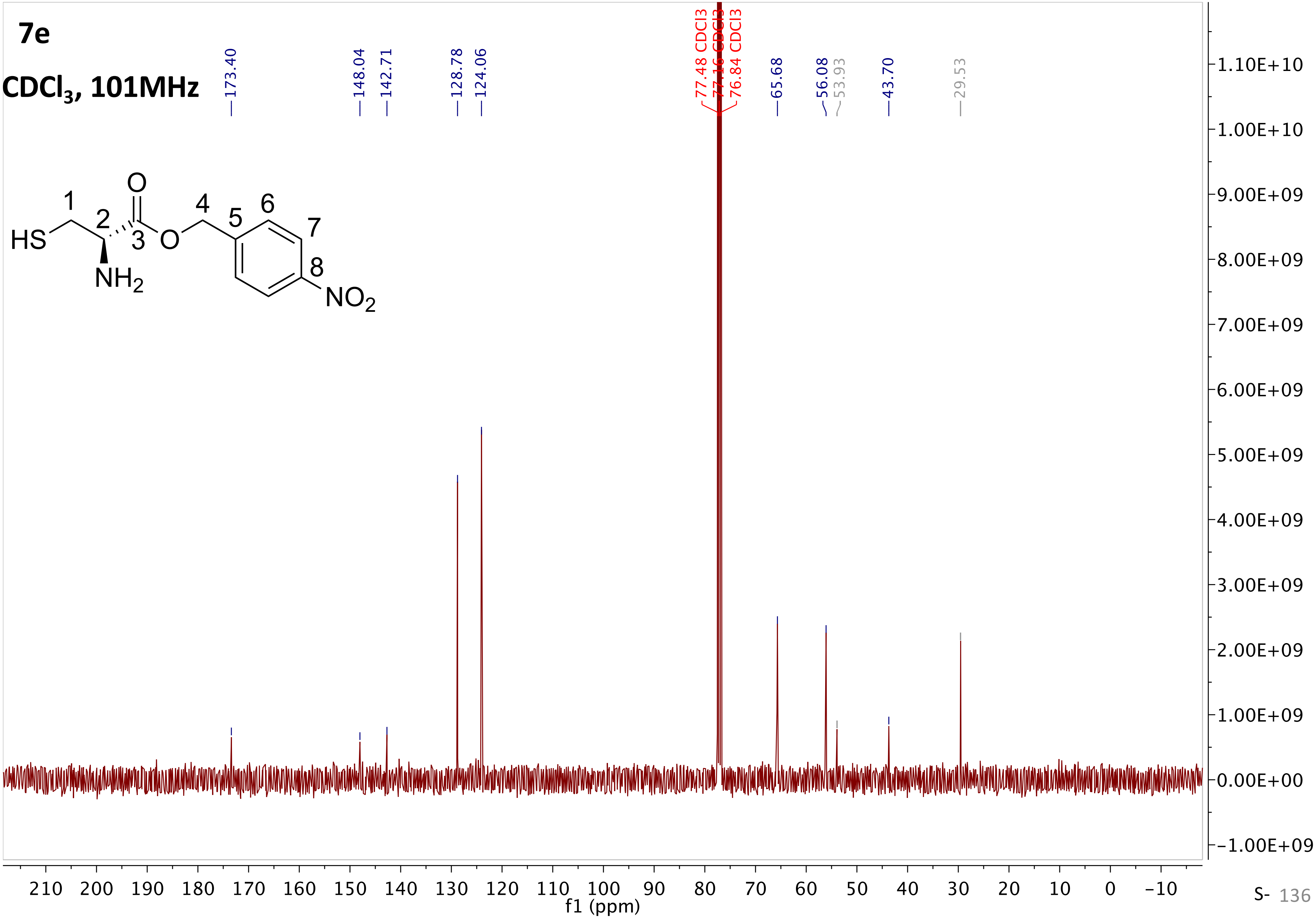


7d
CDCl3, 101MHz
173.69
135.47
128.75
128.61
128.52
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.27
53.82
43.70
HS
NH2
O
1
2
3
4
5
6
7
8
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

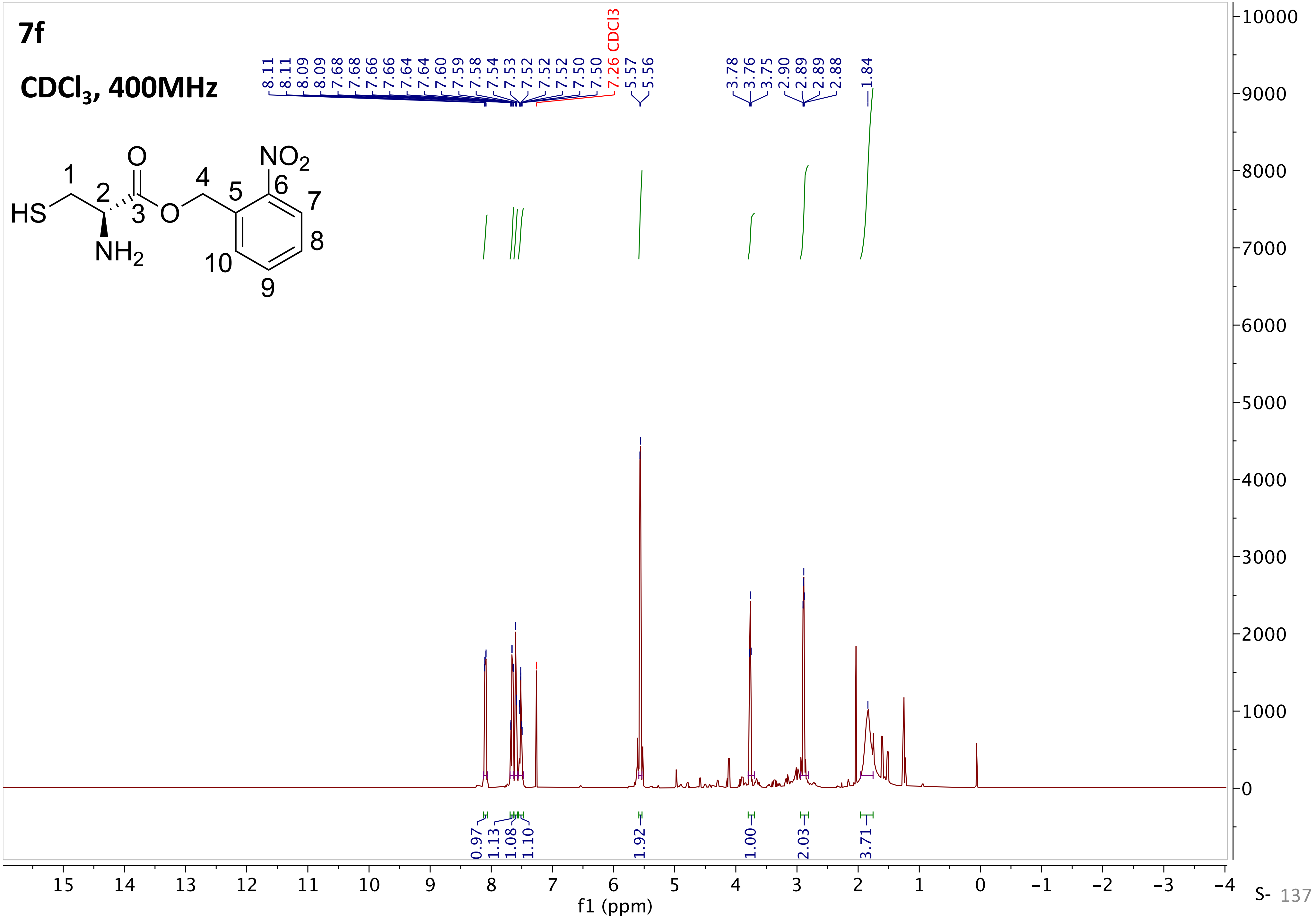
7e

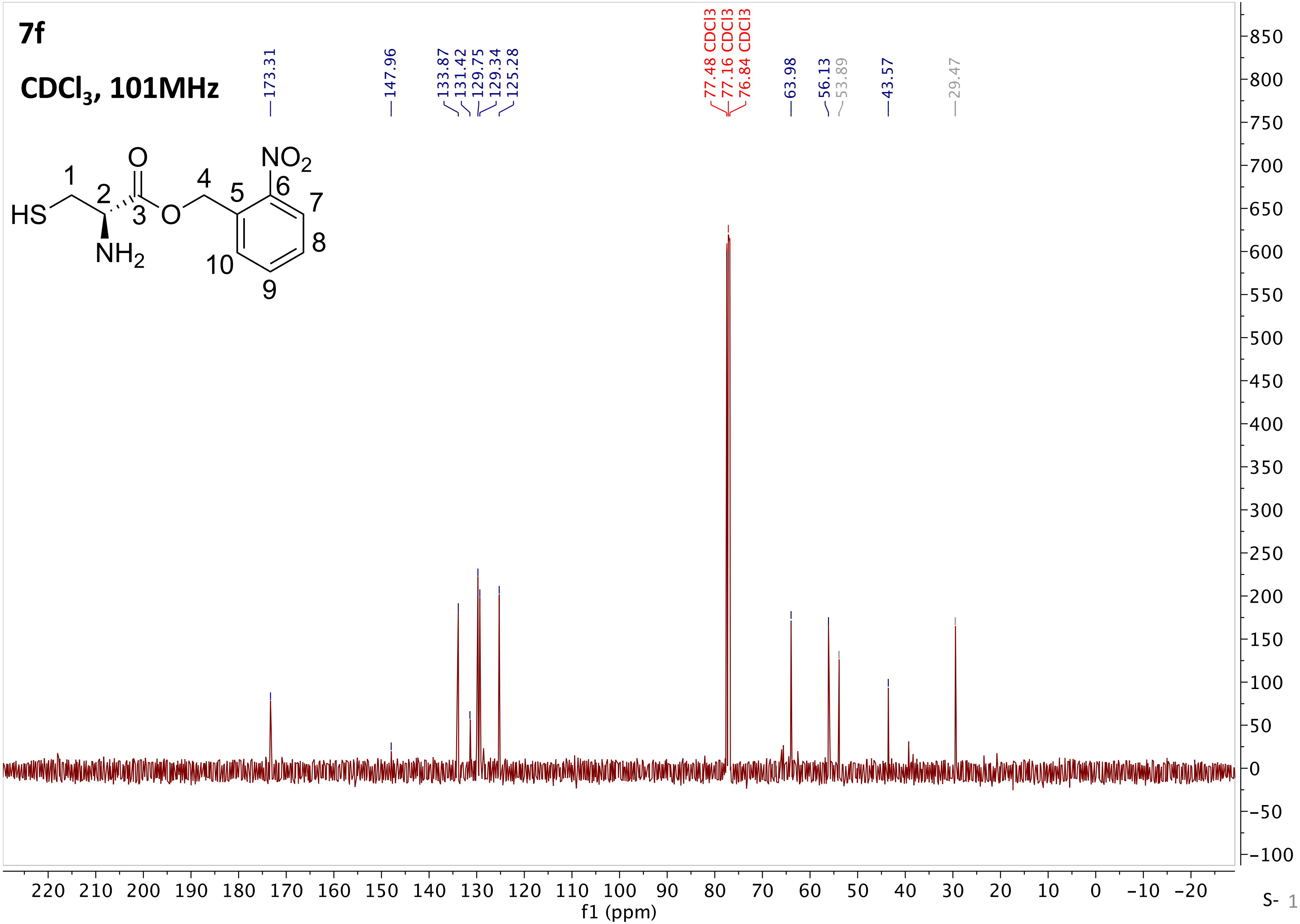
$CDCl_3$, 400MHz

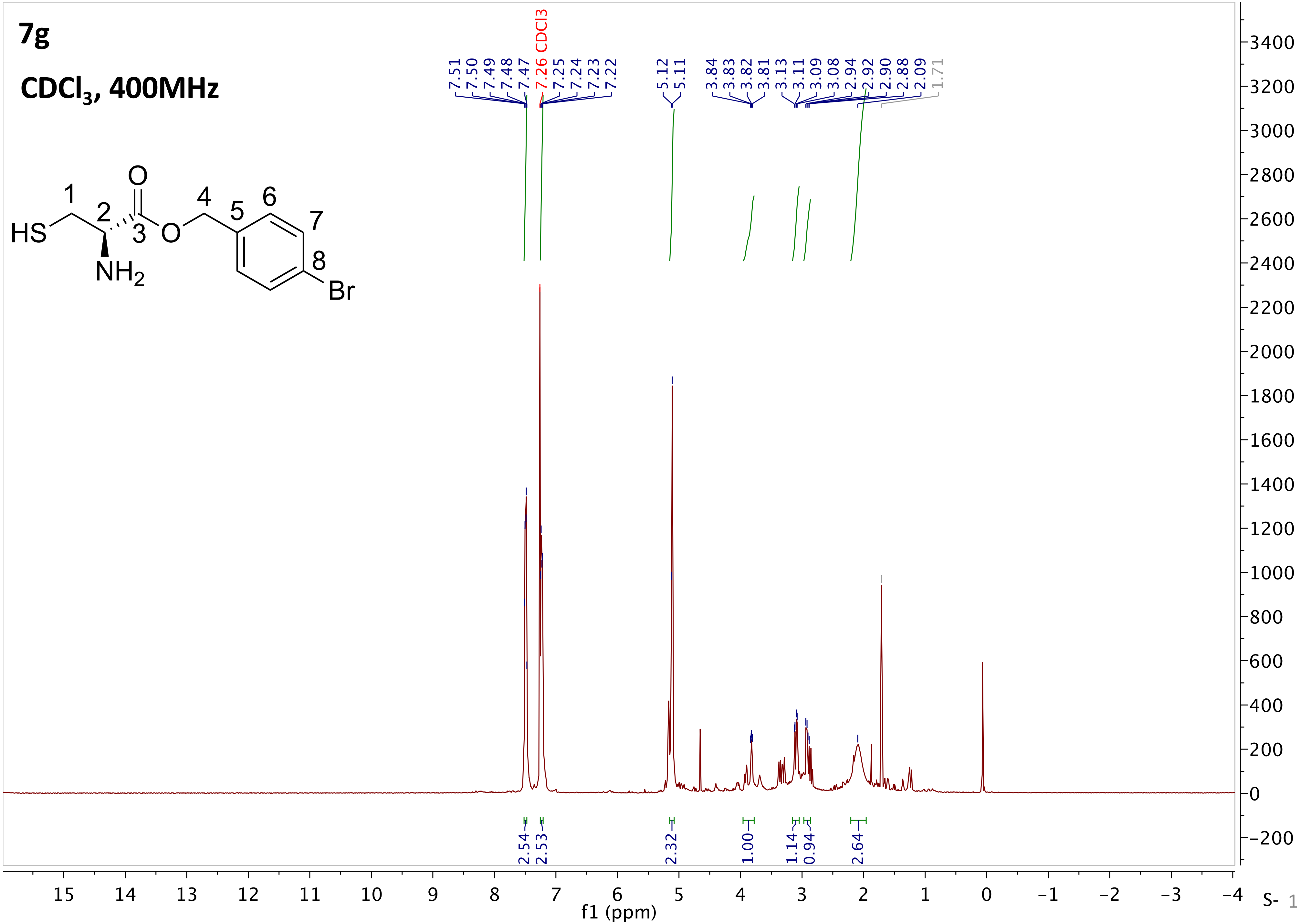


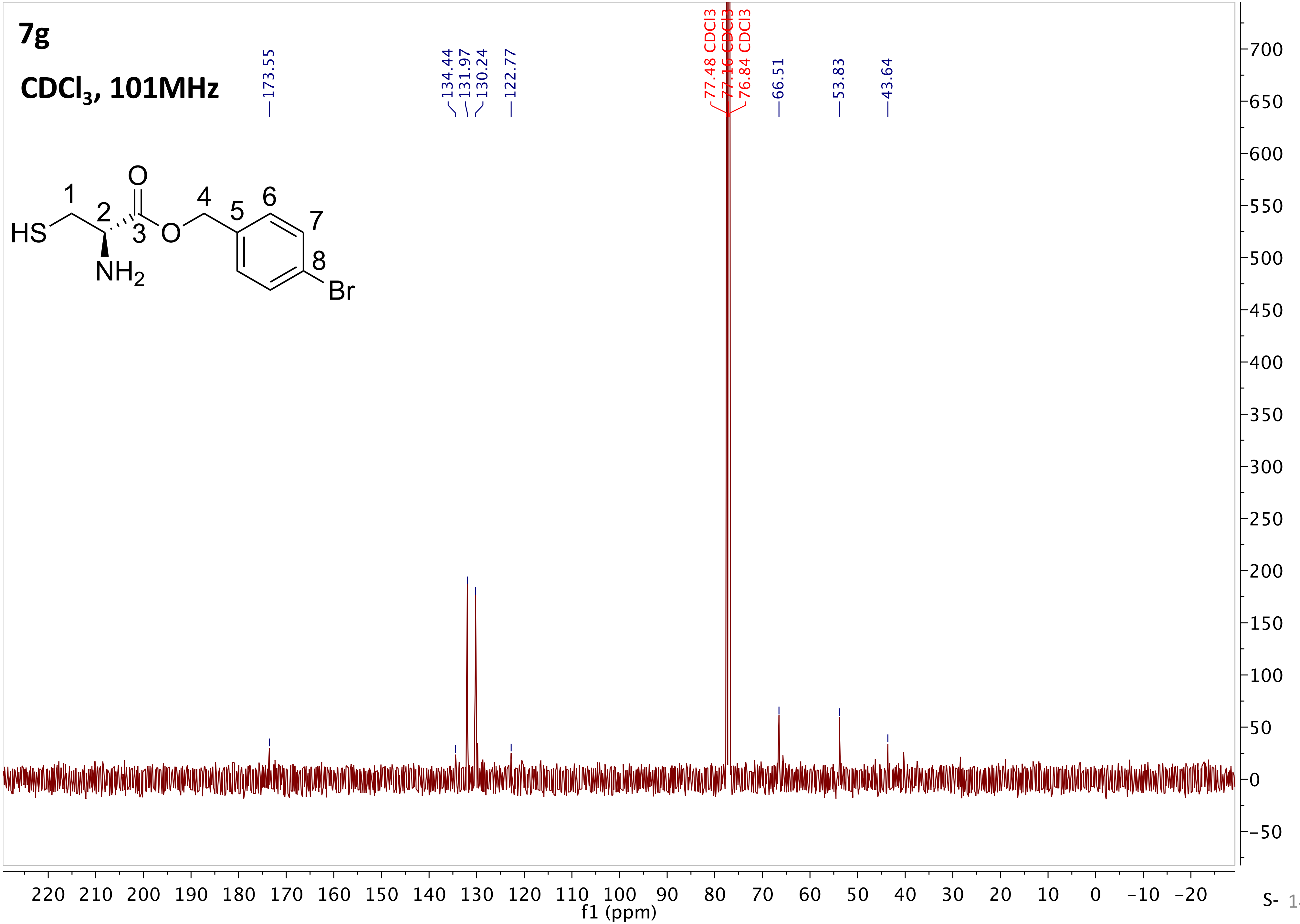


7e
CDCl3, 101MHz
173.40
148.04
142.71
128.78
124.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.68
56.08
53.93
43.70
29.53
HS
NH2
O
NO2
1
2
3
4
5
6
7
8
f1 (ppm)

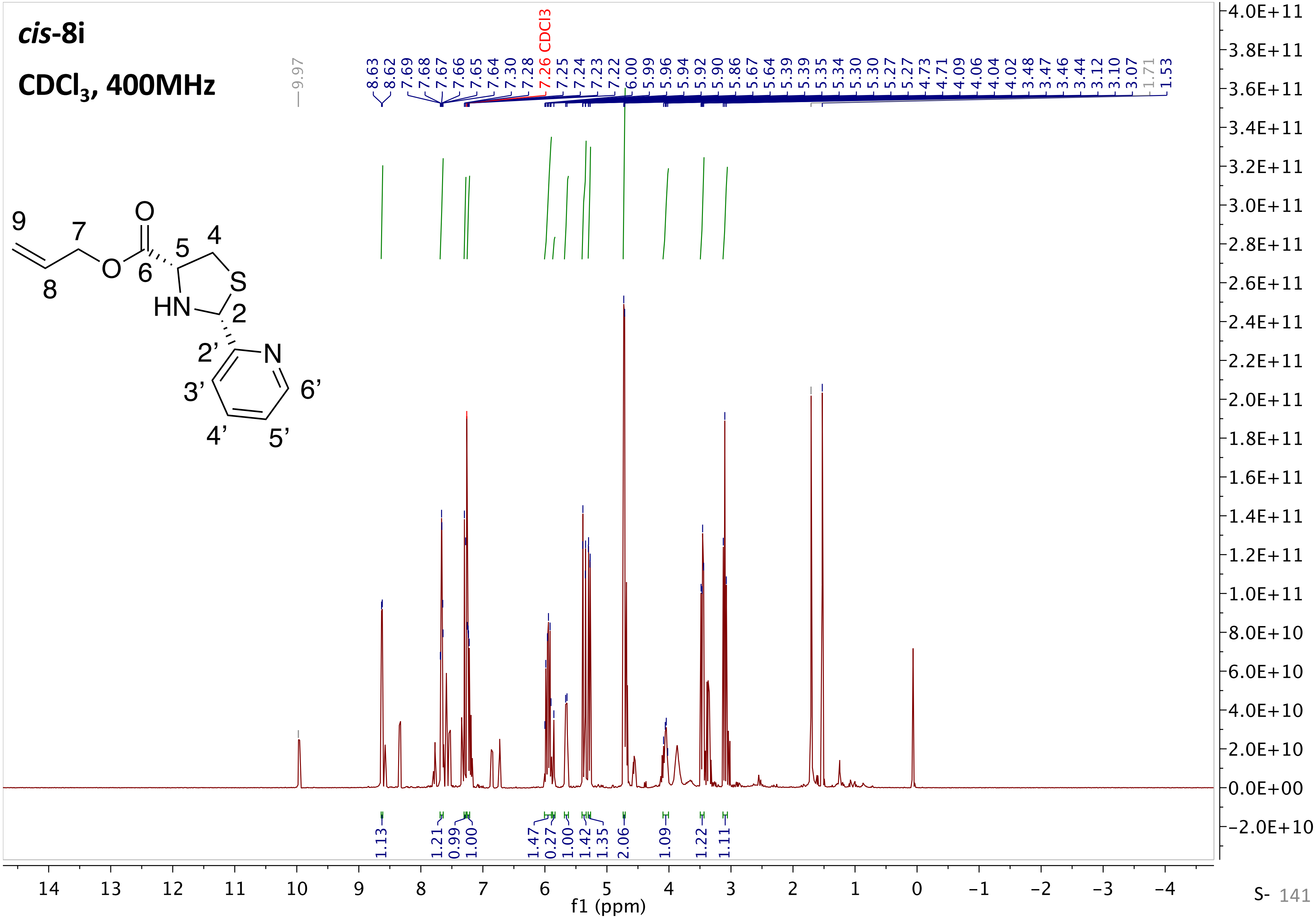

7f
CDCl3, 400MHz
8.11
8.11
8.09
8.09
7.68
7.68
7.66
7.66
7.64
7.64
7.60
7.59
7.58
7.54
7.53
7.52
7.52
7.52
7.50
7.50
7.26 CDCl3
5.57
5.56
3.78
3.76
3.75
2.90
2.89
2.89
2.88
1.84
0.97
1.13
1.08
1.10
1.92
1.00
2.03
3.71
f1 (ppm)


7f
CDCl3, 101MHz
173.31
147.96
133.87
131.42
129.75
129.34
125.28
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.98
56.13
53.89
43.57
29.47
HS
NH2
O
O
NO2
1
2
3
4
5
6
7
8
9
10
f1 (ppm)

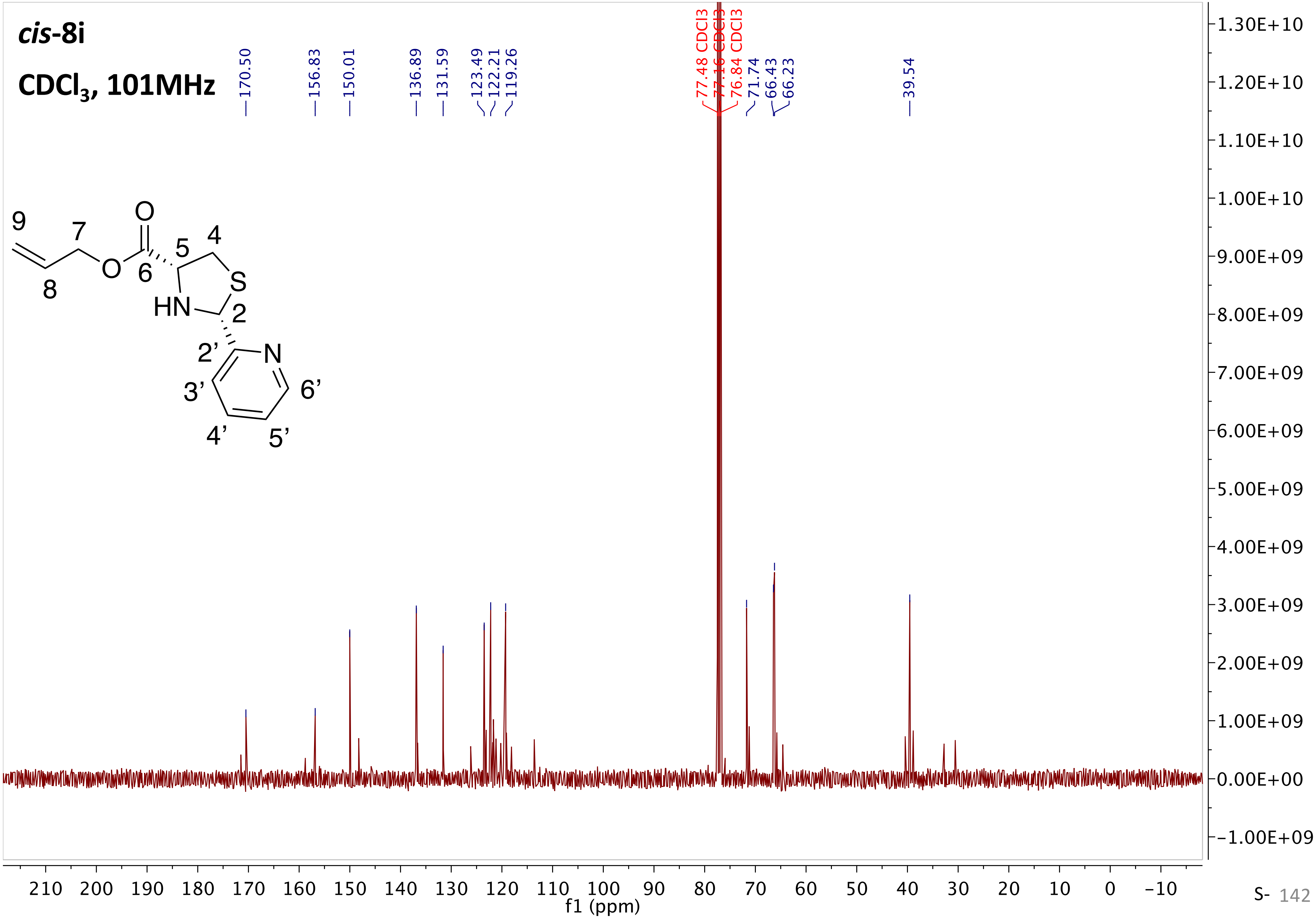

7g
CDCl3, 400MHz
HS
NH2
O
O
Br
1
2
3
4
5
6
7
8
7.51 7.50 7.49 7.48 7.47 7.26 CDCl3 7.25 7.24 7.23 7.22
5.12 5.11
3.84 3.83 3.82 3.81 3.13 3.11 3.09 3.08 2.94 2.92 2.90 2.88 2.09 1.71
2.54 2.53 2.32 1.00 1.14 0.94 2.64
f1 (ppm)



7g
CDCl3, 101MHz
173.55
134.44
131.97
130.24
122.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.51
53.83
43.64
HS
NH2
O
O
Br
1
2
3
4
5
6
7
8
f1 (ppm)

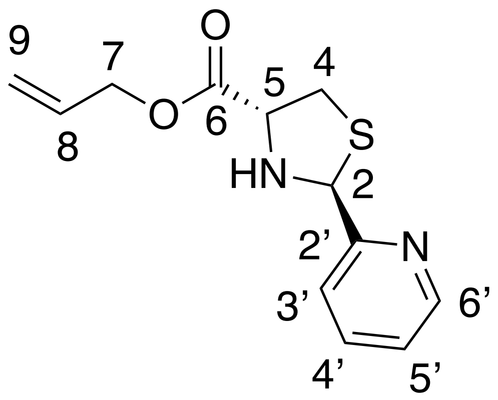


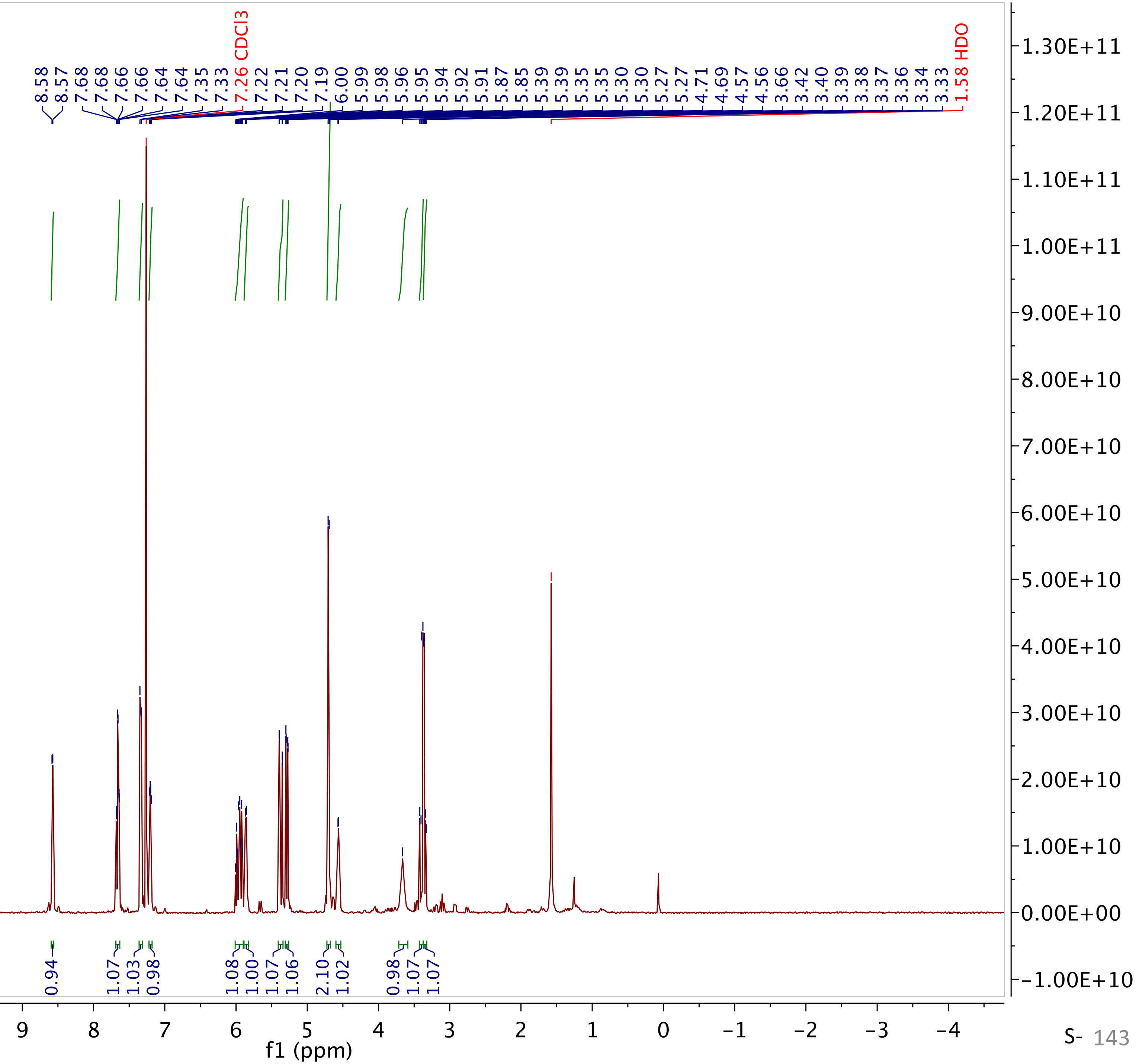
cis-8i
CDCl3, 400MHz
9.97
8.63 8.62 7.69 7.68 7.67 7.66 7.65 7.64 7.30 7.28 7.26 CDCl3 7.25 7.24 7.23 7.22 6.00 5.99 5.96 5.94 5.92 5.90 5.86 5.67 5.64 5.39 5.39 5.35 5.34 5.30 5.30 5.27 5.27 4.73 4.71 4.09 4.06 4.04 4.02 3.48 3.47 3.46 3.44 3.12 3.10 3.07 1.71 1.53
9
7
O
5
4
O
6
S
8
HN
2
2’
N
3’
6’
4’
5’
1.13
1.21
0.99
1.00
1.47
0.27
1.00
1.42
1.35
2.06
1.09
1.22
1.11
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)
4.0E+11 3.8E+11 3.6E+11 3.4E+11 3.2E+11 3.0E+11 2.8E+11 2.6E+11 2.4E+11 2.2E+11 2.0E+11 1.8E+11 1.6E+11 1.4E+11 1.2E+11 1.0E+11 8.0E+10 6.0E+10 4.0E+10 2.0E+10 0.0E+00 −2.0E+10

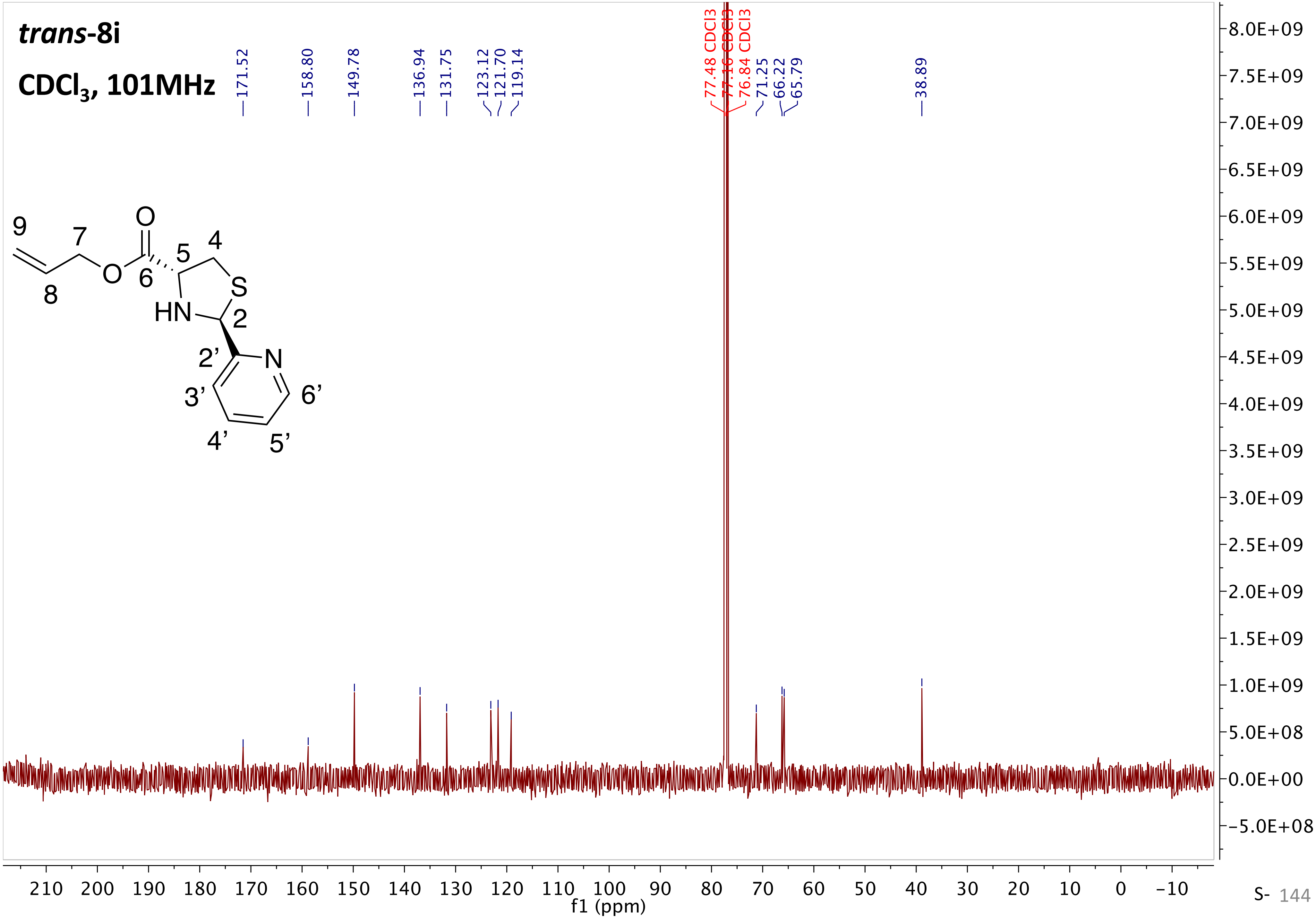

cis-8i
CDCl3, 101MHz
170.50
156.83
150.01
136.89
131.59
123.49
122.21
119.26
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.74
66.43
66.23
39.54
9
7
O
5
4
6
S
8
HN
2
2'
N
3'
6'
4'
5'
f1 (ppm)

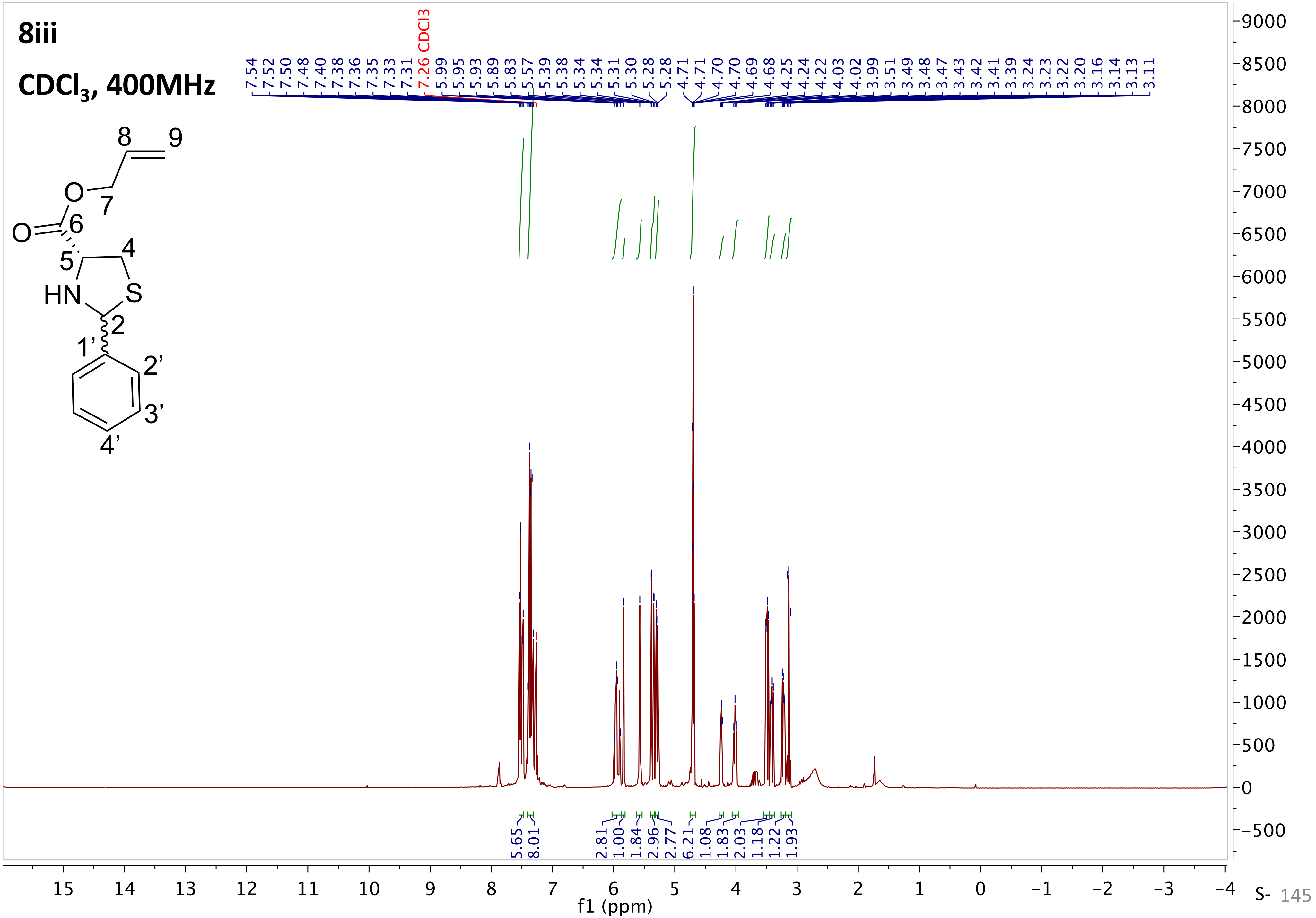
trans-8i

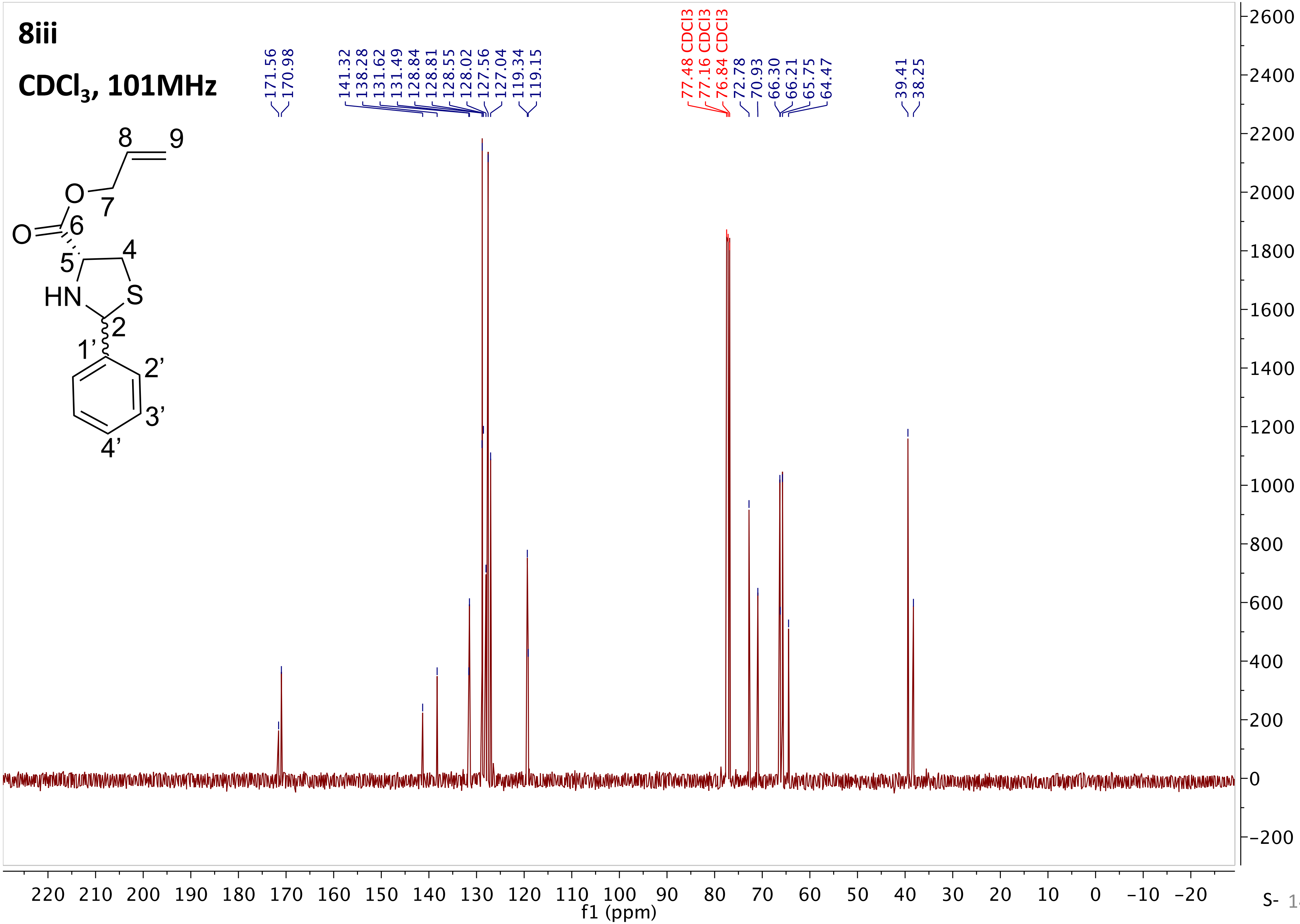
$CDCl_3$, 400MHz

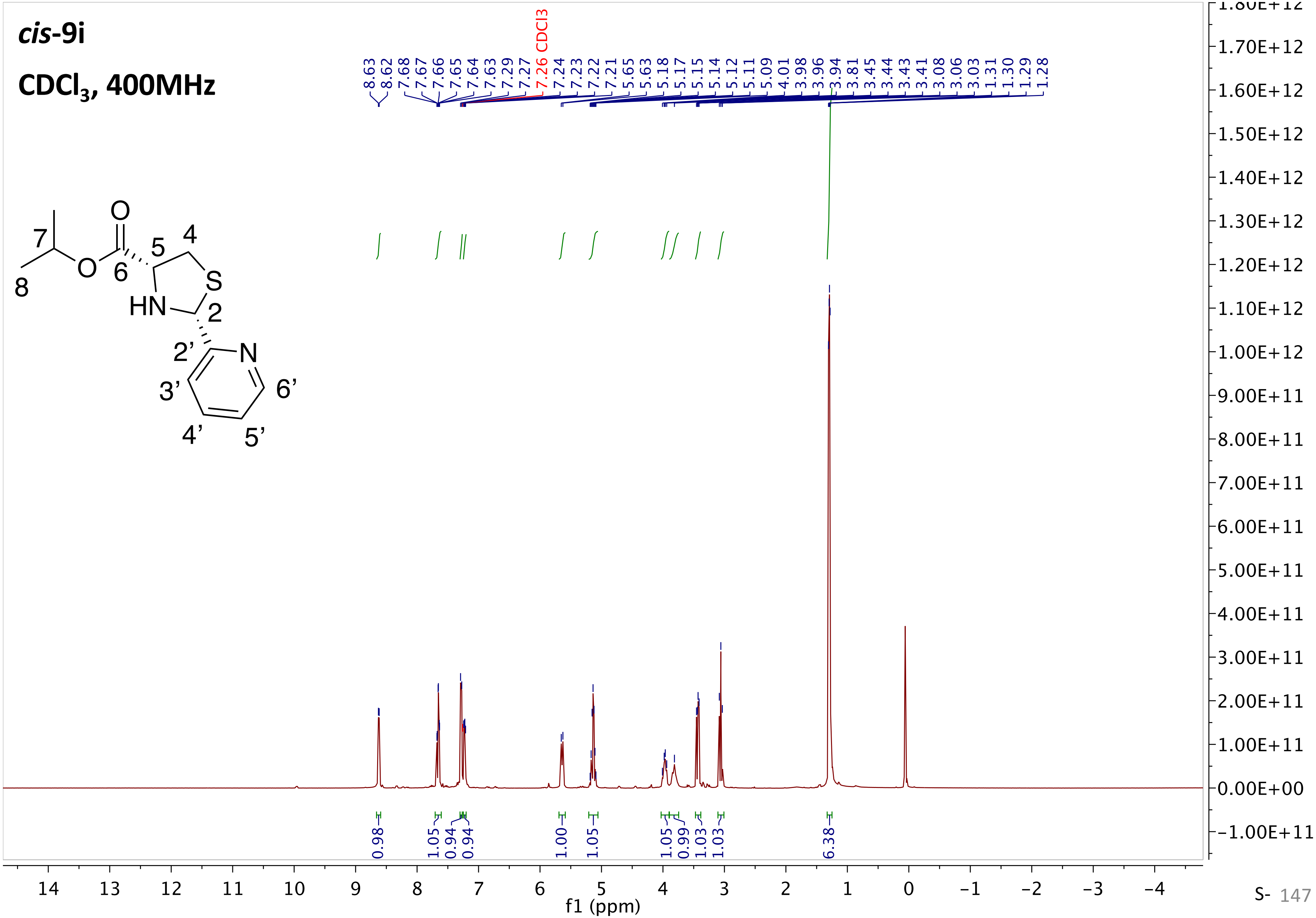




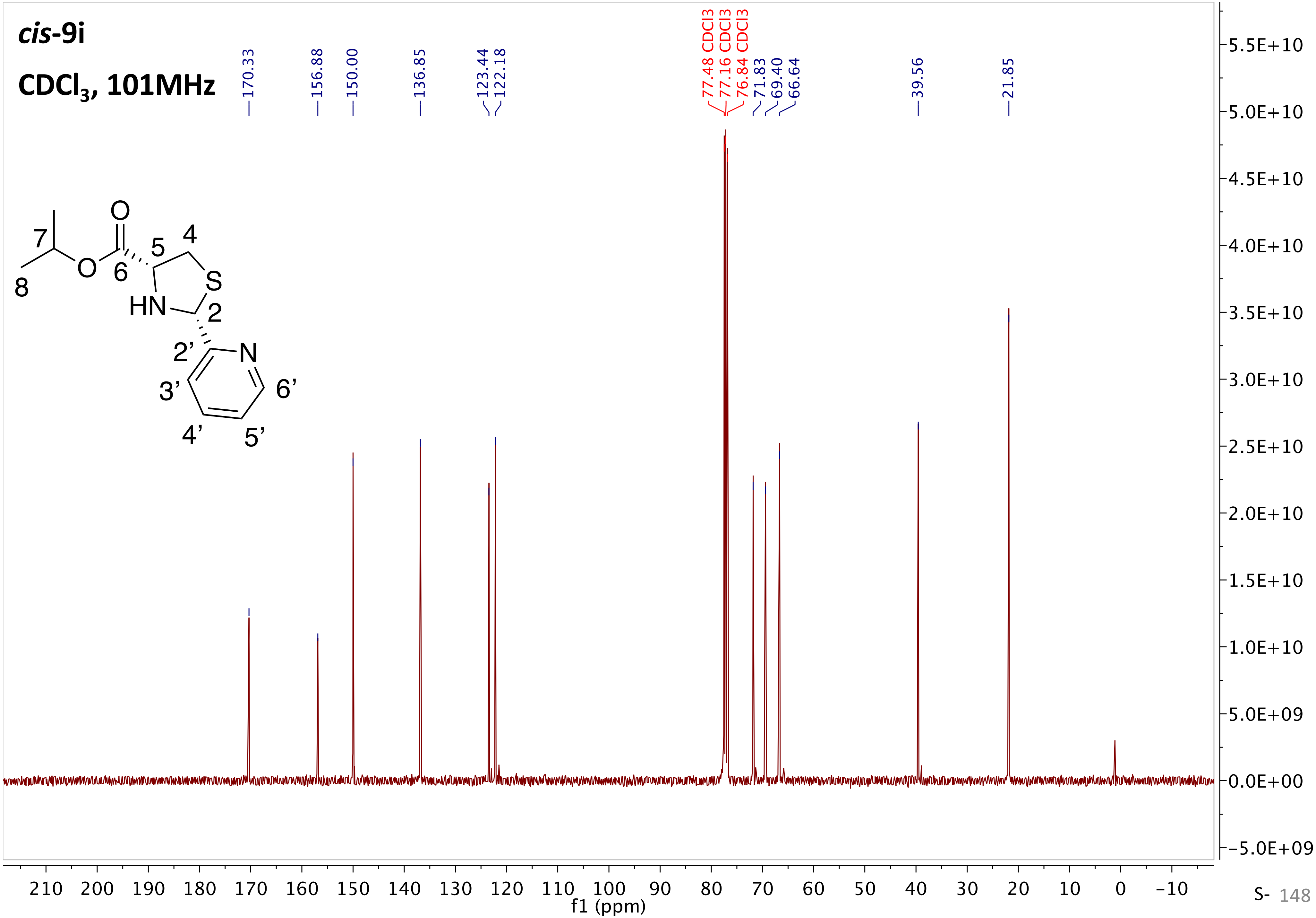

trans-8i
CDCl3, 101MHz
171.52
158.80
149.78
136.94
131.75
123.12
121.70
119.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.25
66.22
65.79
38.89
9
7
O
4
5
O
6
S
8
HN
2
2'
N
3'
6'
4'
5'
f1 (ppm)


8iii
$CDCl_3$, 400MHz
f1 (ppm)

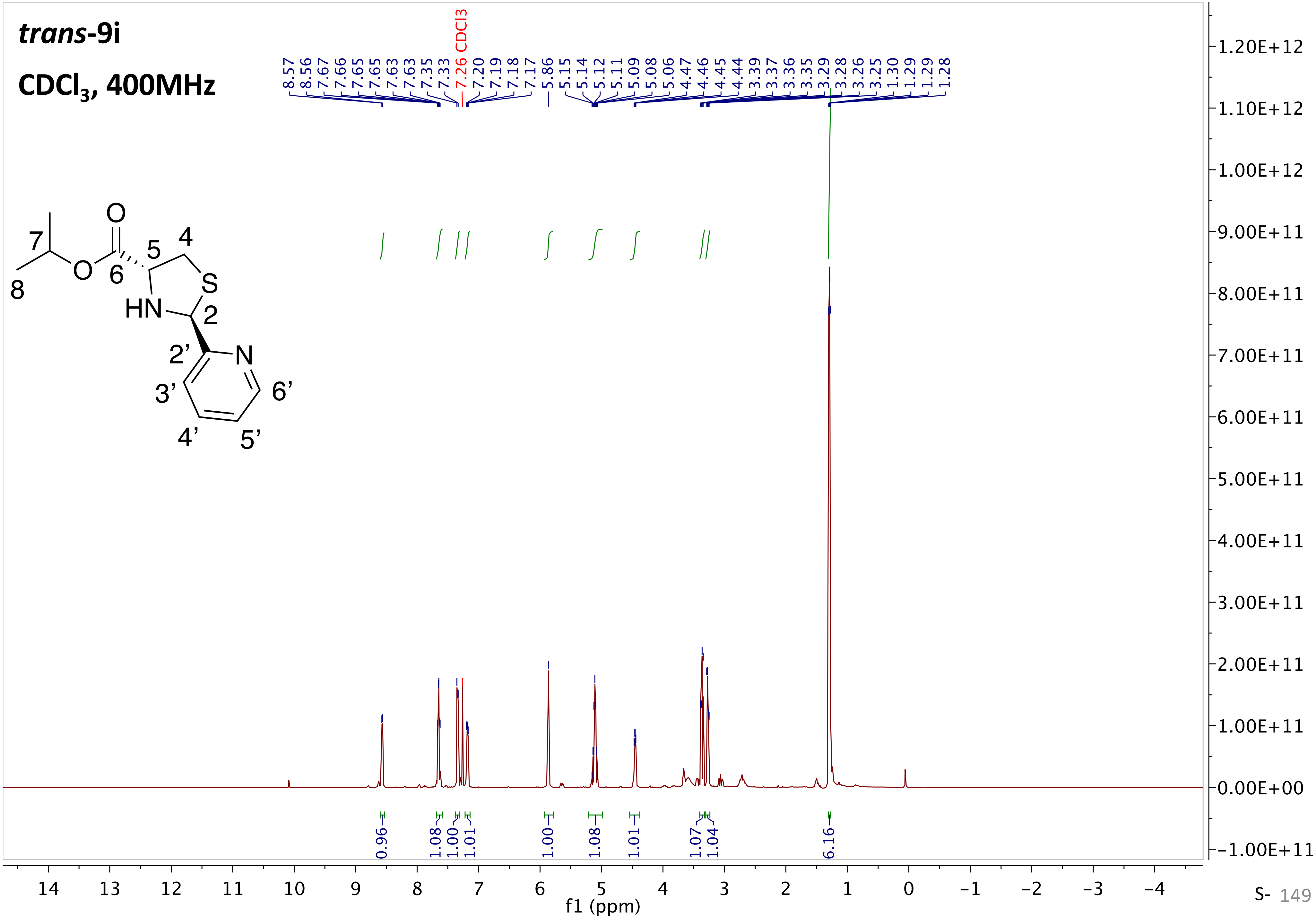

8iii
CDCl3, 101MHz
171.56
170.98
141.32
138.28
131.62
131.49
128.84
128.81
128.55
128.02
127.56
127.04
119.34
119.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.78
70.93
66.30
66.21
65.75
64.47
39.41
38.25
f1 (ppm)

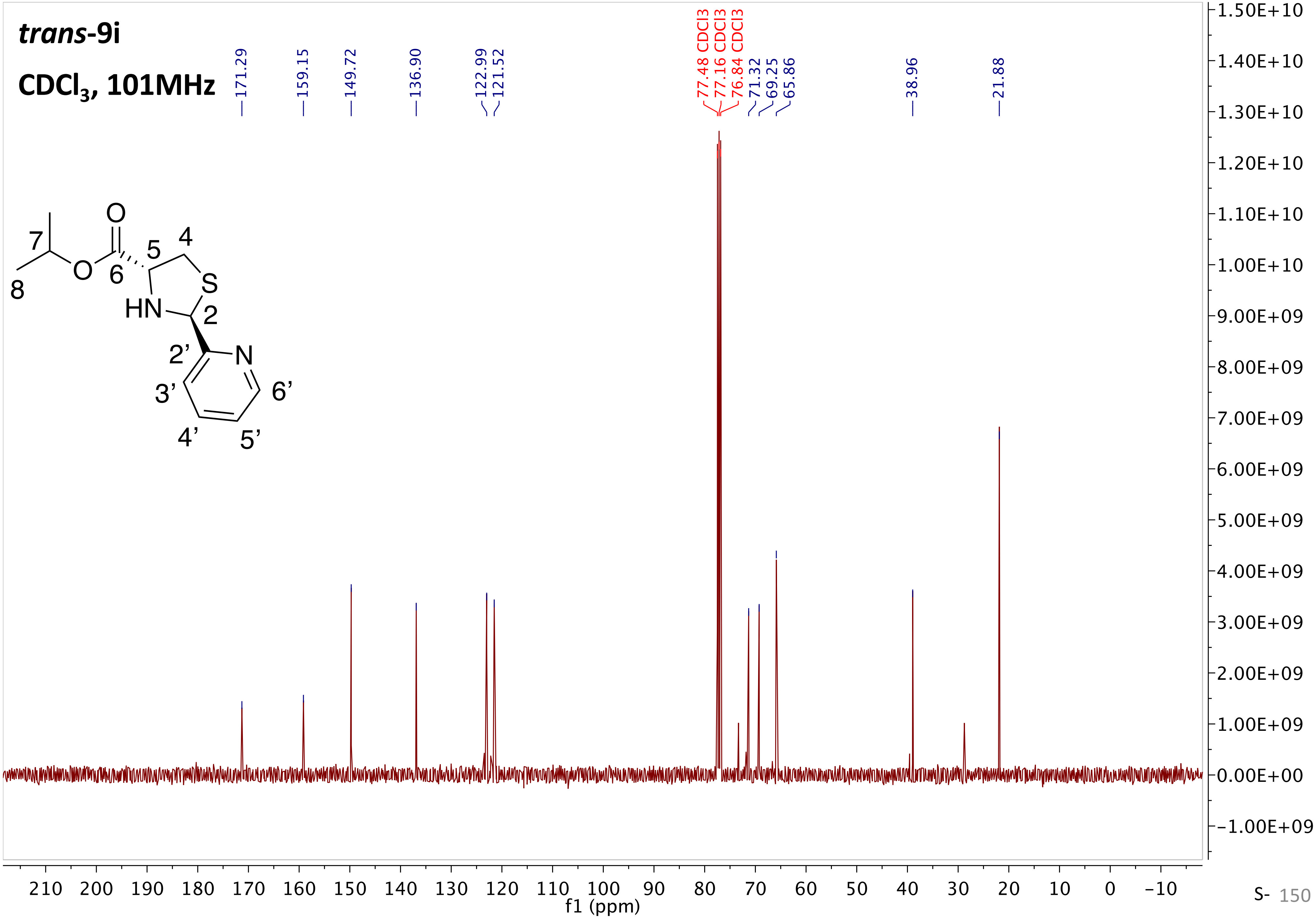


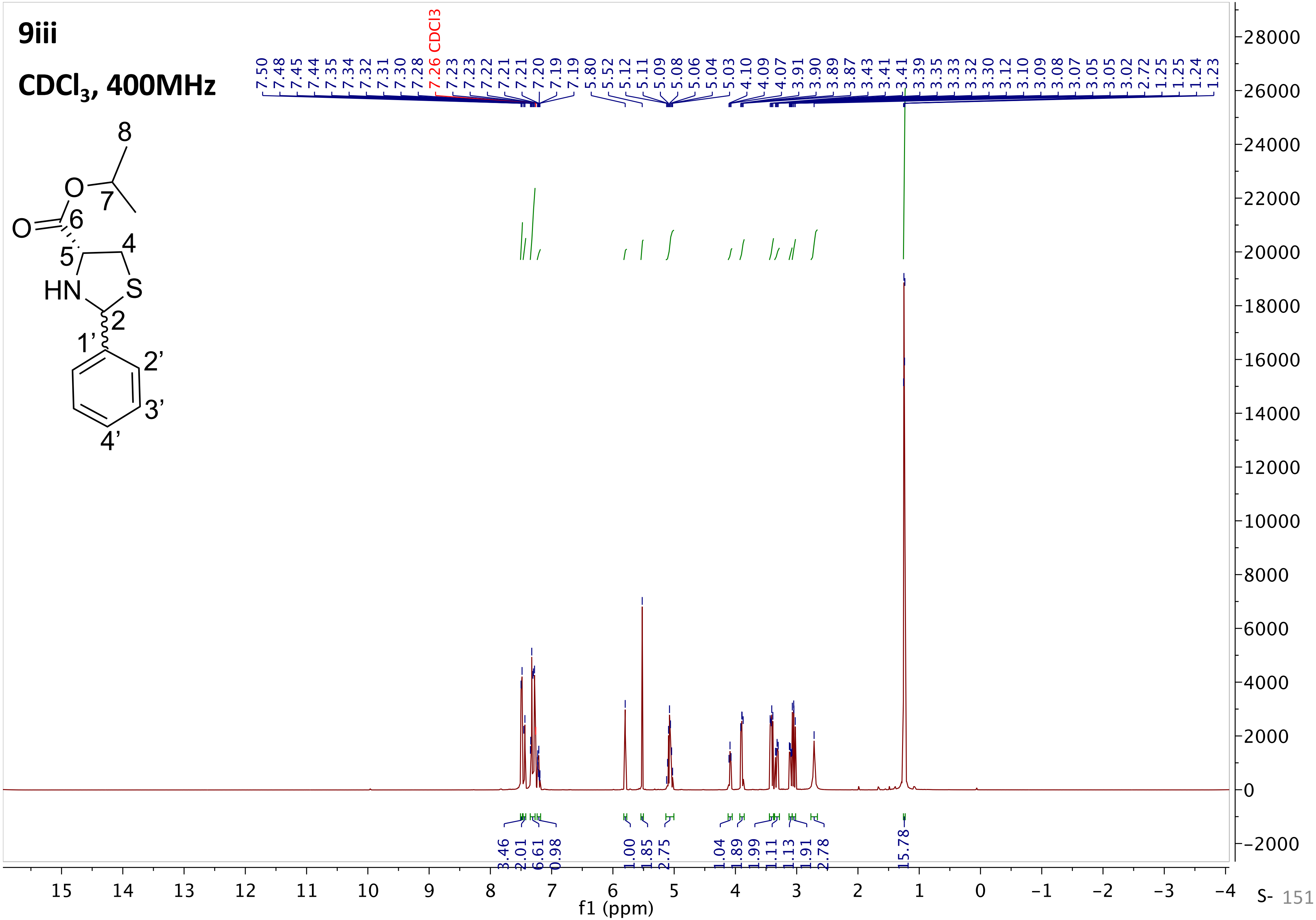
cis-9i
CDCl3, 400MHz
8.63 8.62 7.68 7.67 7.66 7.65 7.64 7.63 7.29 7.27 7.26 CDCl3 7.24 7.23 7.22 7.21 5.65 5.63 5.18 5.17 5.15 5.14 5.12 5.11 5.09 4.01 3.98 3.96 3.94 3.81 3.45 3.44 3.43 3.41 3.08 3.06 3.03 1.31 1.30 1.29 1.28
0.98 1.05 0.94 0.94 1.00 1.05 1.05 0.99 1.03 1.03 6.38
f1 (ppm)

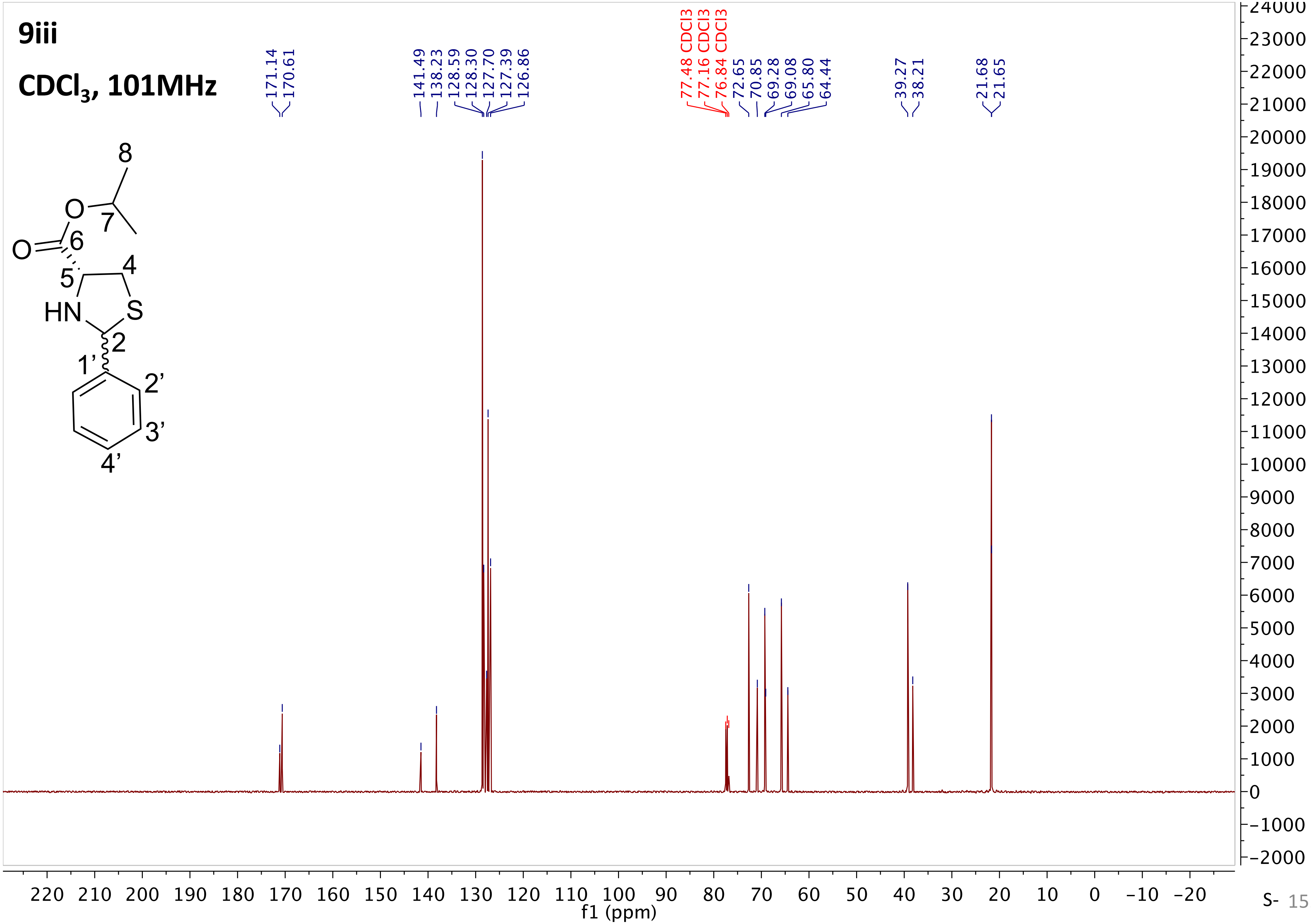


cis-9i
CDCl3, 101MHz
170.33
156.88
150.00
136.85
123.44
122.18
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.83
69.40
66.64
39.56
21.85
f1 (ppm)


trans-9i
CDCl3, 400MHz
8.57 8.56 7.67 7.66 7.65 7.65 7.63 7.63 7.35 7.33 7.26 CDCl3 7.20 7.19 7.18 7.17 5.86 5.15 5.14 5.12 5.11 5.09 5.08 5.06 4.47 4.46 4.45 4.44 3.39 3.37 3.36 3.35 3.29 3.28 3.26 3.25 1.30 1.29 1.29 1.28
0.96 1.08 1.00 1.01 1.00 1.08 1.01 1.07 1.04 6.16
f1 (ppm)

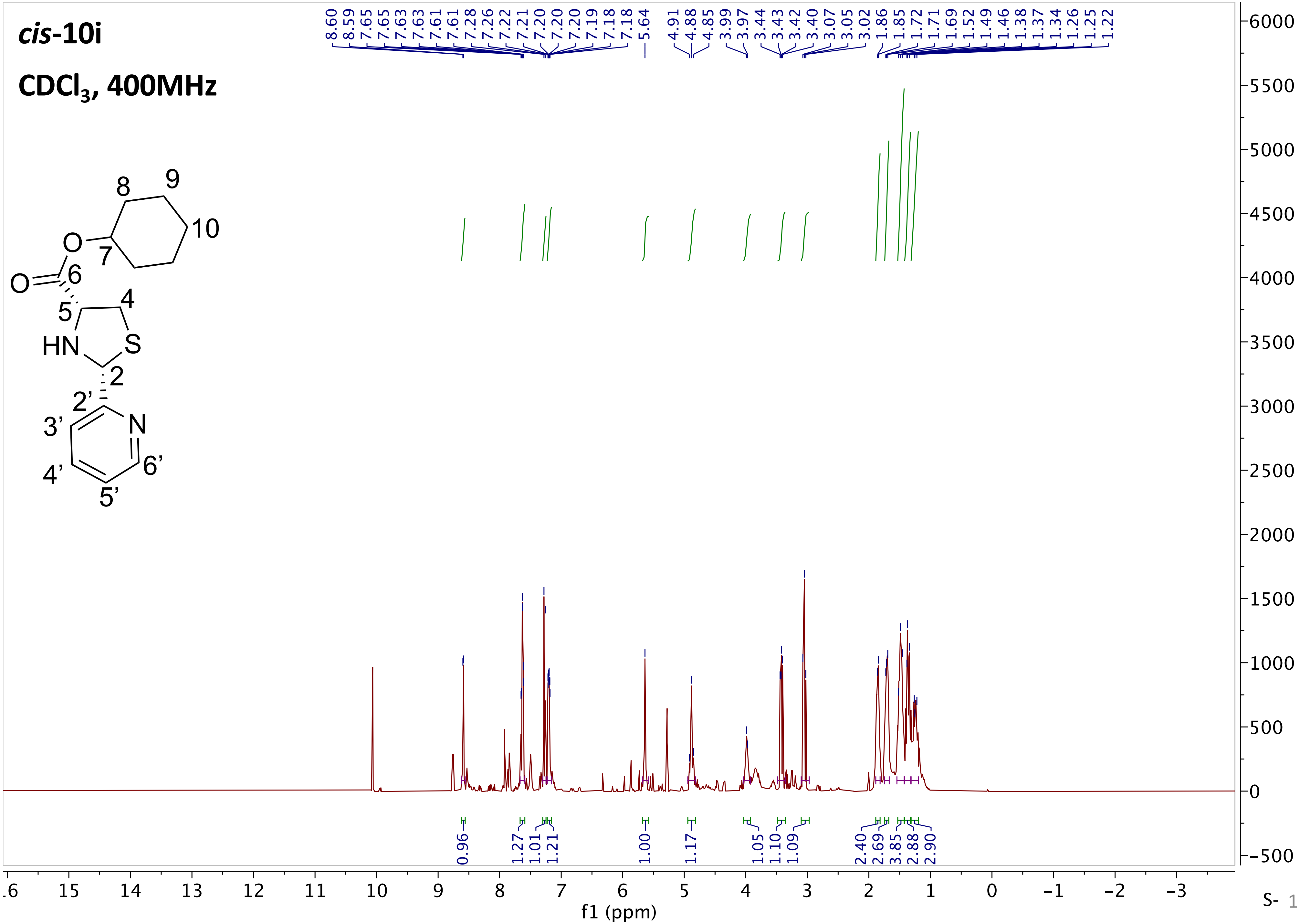

trans-9i
CDCl3, 101MHz
171.29
159.15
149.72
136.90
122.99
121.52
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.32
69.25
65.86
38.96
21.88
O
7
5
4
O
6
S
8
HN
2
2’
N
3’
6’
4’
5’
1.50E+10
1.40E+10
1.30E+10
1.20E+10
1.10E+10
1.00E+10
9.00E+09
8.00E+09
7.00E+09
6.00E+09
5.00E+09
4.00E+09
3.00E+09
2.00E+09
1.00E+09
0.00E+00
−1.00E+09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

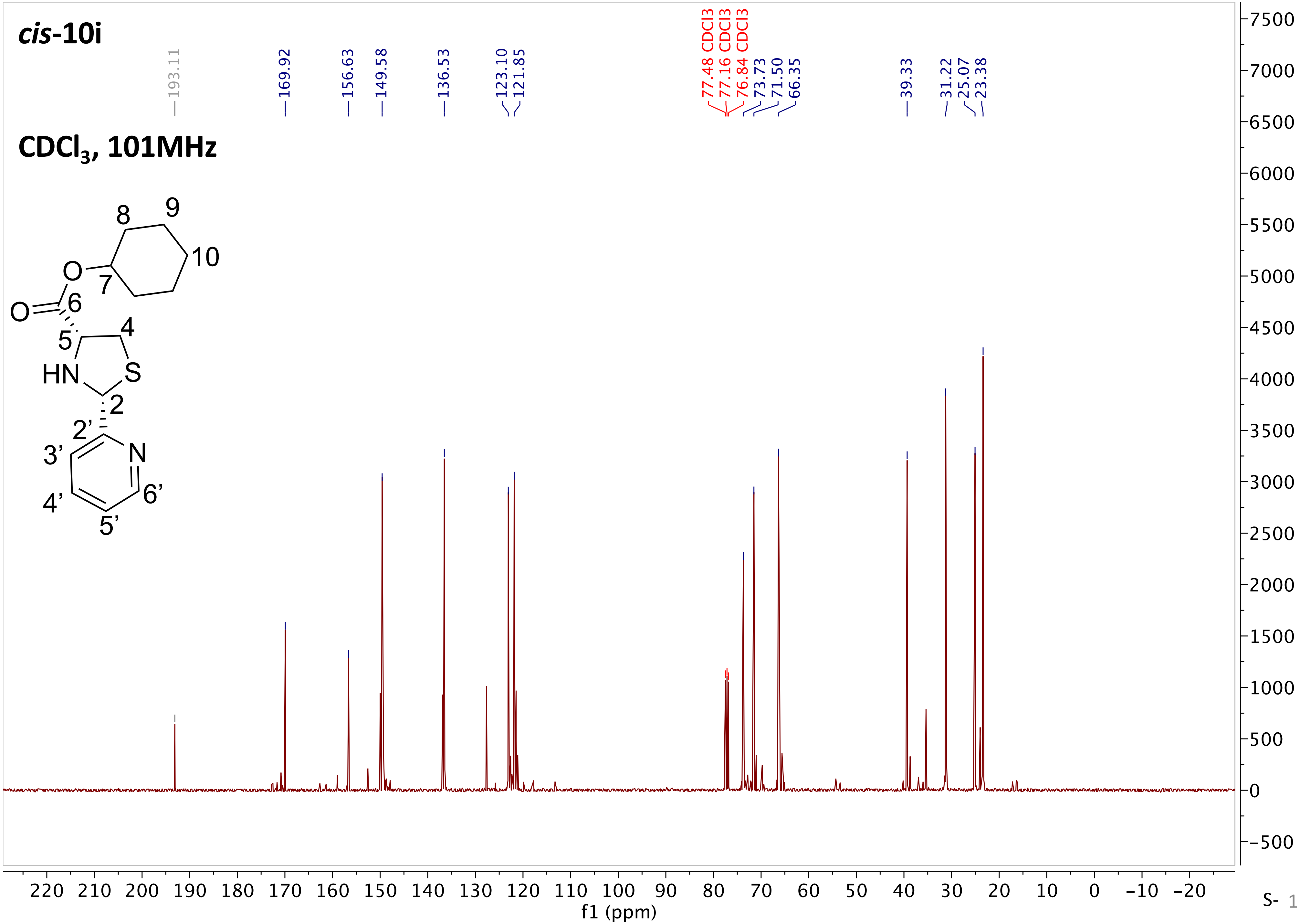

9iii
CDCl3, 400MHz
7.50 7.48 7.45 7.44 7.35 7.34 7.32 7.31 7.30 7.28 7.26 CDCl3 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.19 5.80 5.52 5.12 5.11 5.09 5.08 5.06 5.04 5.03 4.10 4.09 4.07 3.91 3.90 3.89 3.87 3.43 3.41 3.41 3.39 3.35 3.33 3.32 3.30 3.12 3.10 3.09 3.08 3.07 3.05 3.05 3.02 2.72 1.25 1.25 1.24 1.23
3.46 2.01 6.61 0.98 1.00 1.85 2.75 1.04 1.89 1.99 1.11 1.13 1.91 2.78 15.78
8
7
6
5
4
O
O
HN
S
2
1’
2’
3’
4’
f1 (ppm)


9iii
CDCl3, 101MHz
171.14
170.61
141.49
138.23
128.59
128.30
127.70
127.39
126.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.65
70.85
69.28
69.08
65.80
64.44
39.27
38.21
21.68
21.65
f1 (ppm)

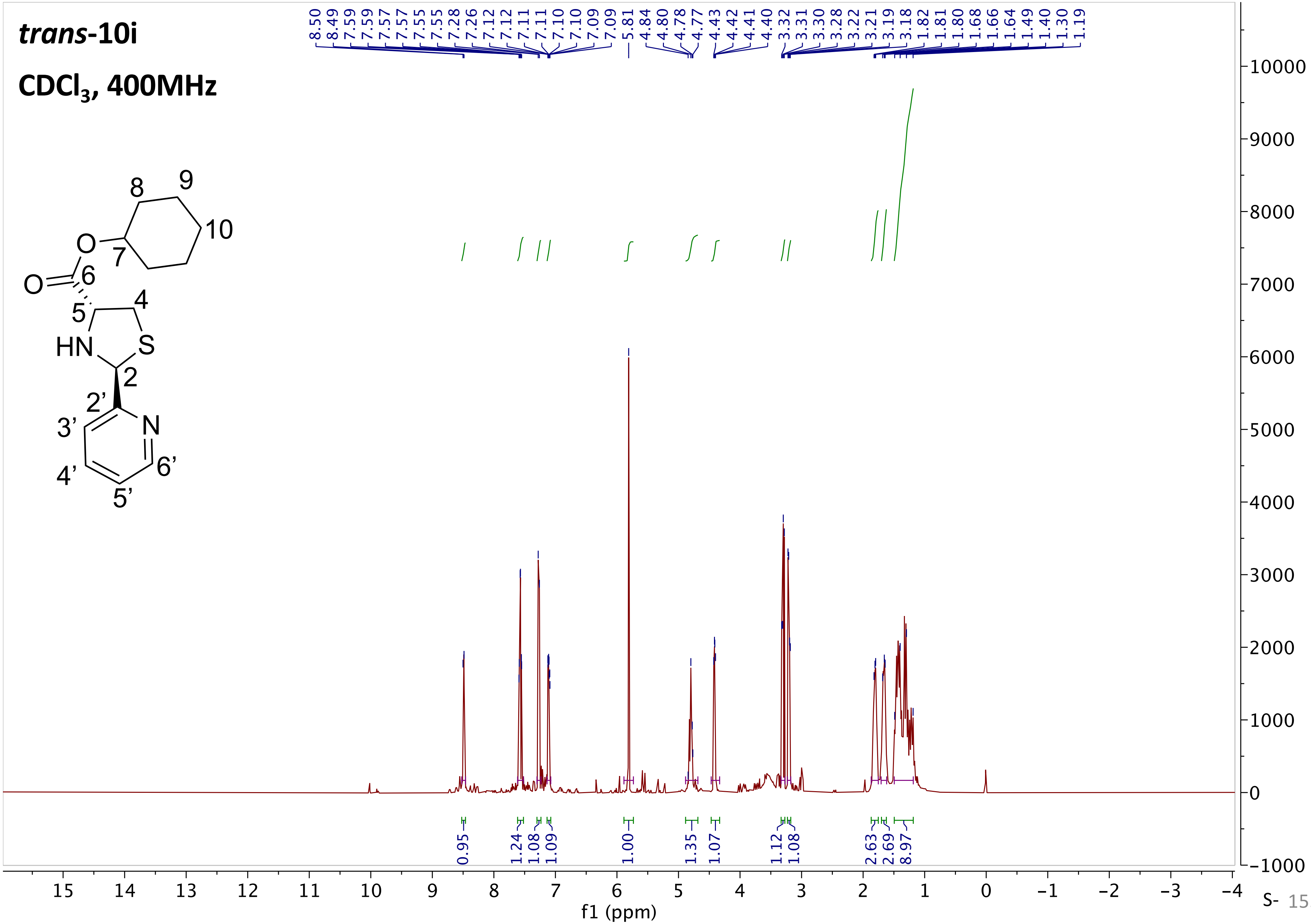
***cis*-10i**

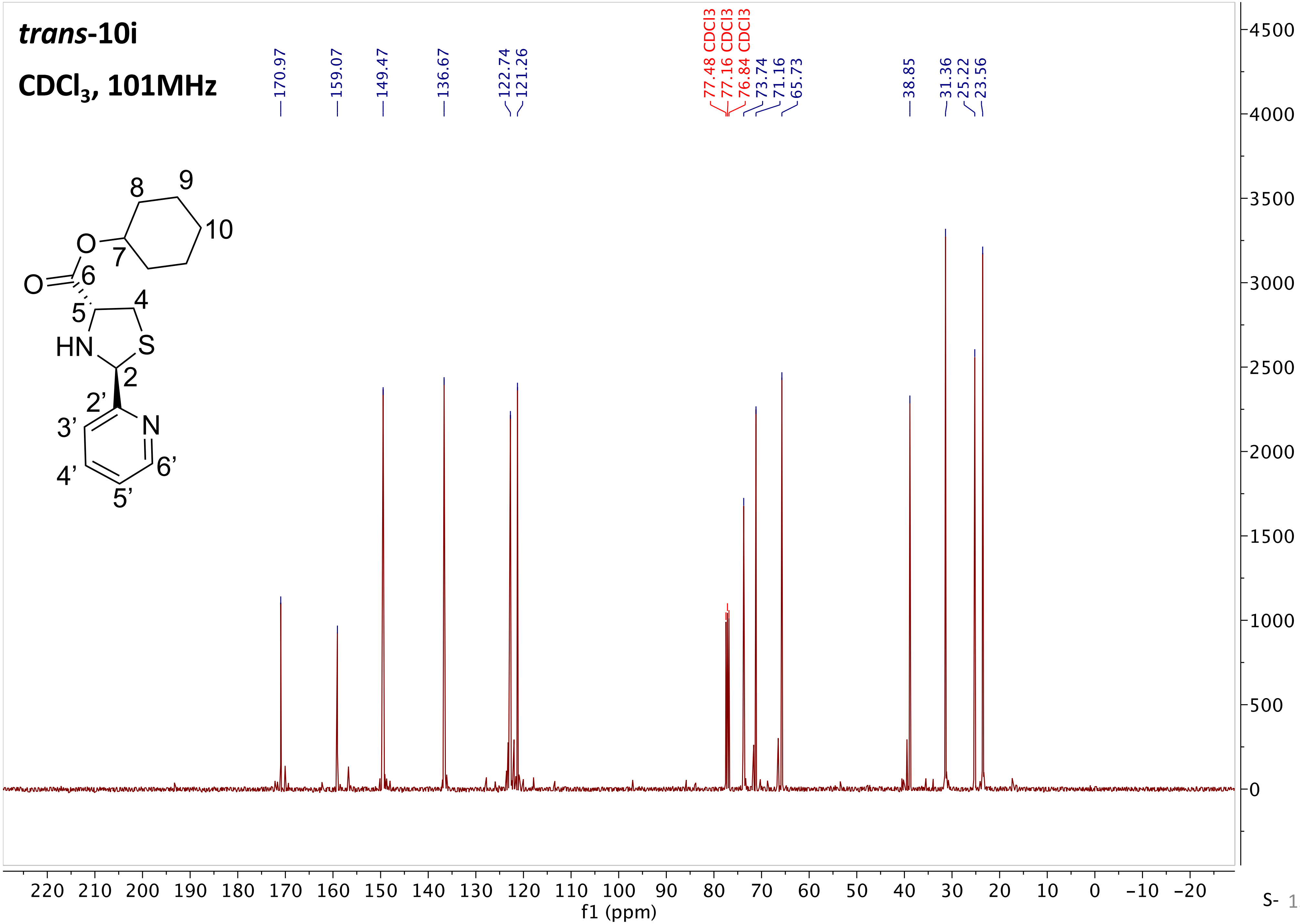
$CDCl_3$, 400MHz





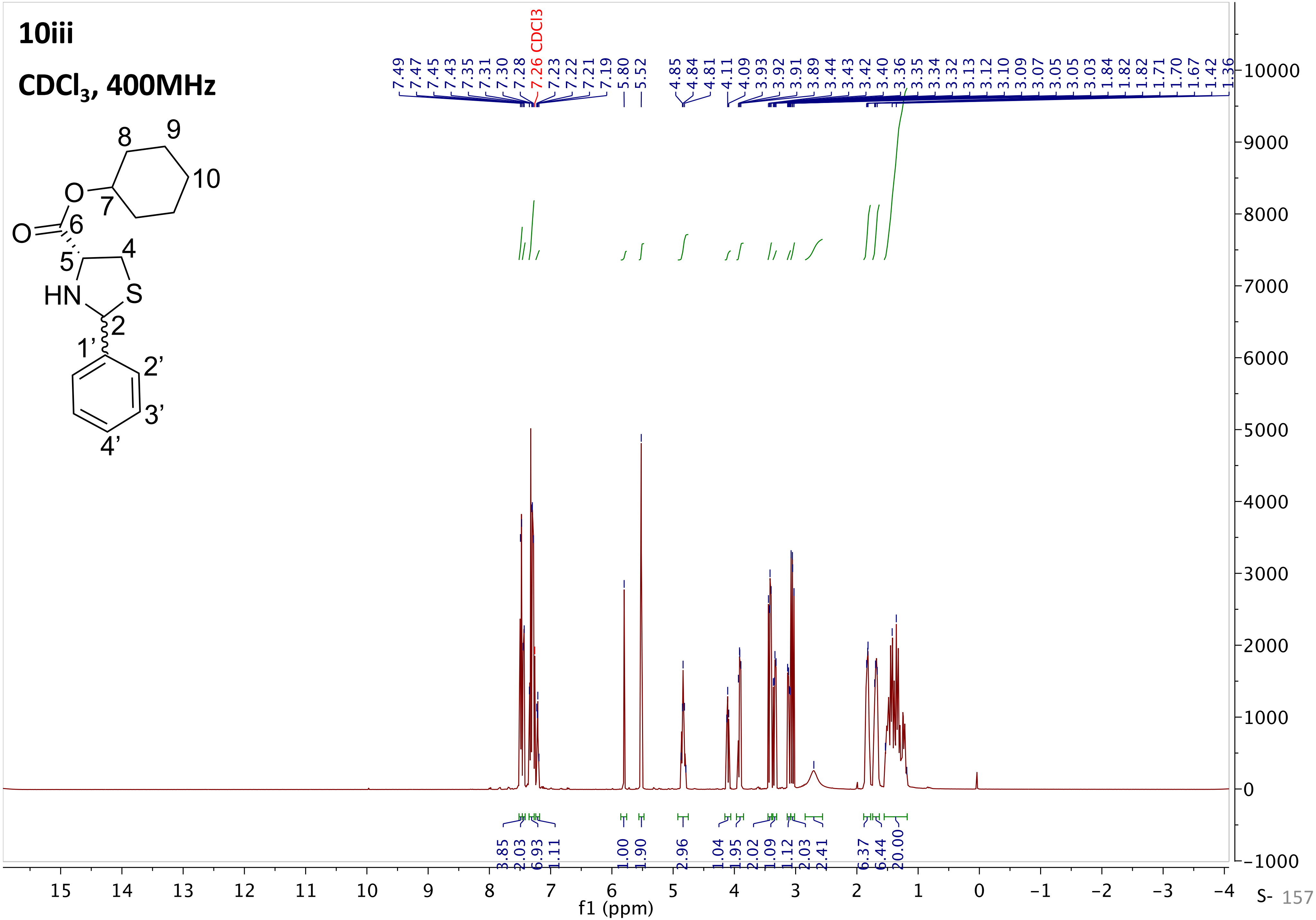
cis-10i
CDCl3, 101MHz
193.11
169.92
156.63
149.58
136.53
123.10
121.85
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.73
71.50
66.35
39.33
31.22
25.07
23.38
8
9
10
O
7
O
6
5
4
HN
S
2
2'
3'
N
4'
6'
5'
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


trans-10i
CDCl3, 400MHz
8.50 8.49 7.59 7.59 7.57 7.57 7.55 7.55 7.28 7.26 7.12 7.12 7.11 7.11 7.10 7.10 7.09 7.09 5.81 4.84 4.80 4.78 4.77 4.43 4.42 4.41 4.40 3.32 3.31 3.30 3.28 3.22 3.21 3.19 3.18 1.82 1.81 1.80 1.68 1.66 1.64 1.49 1.40 1.30 1.19
0.95 1.24 1.08 1.09 1.00 1.35 1.07 1.12 1.08 2.63 2.69 8.97
f1 (ppm)


trans-10i
$CDCl_3$, 101MHz
170.97
159.07
149.47
136.67
122.74
121.26
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.74
71.16
65.73
38.85
31.36
25.22
23.56
8
9
10
O
7
O
6
5
4
HN
S
2
2'
3'
N
4'
5'
6'
f1 (ppm)

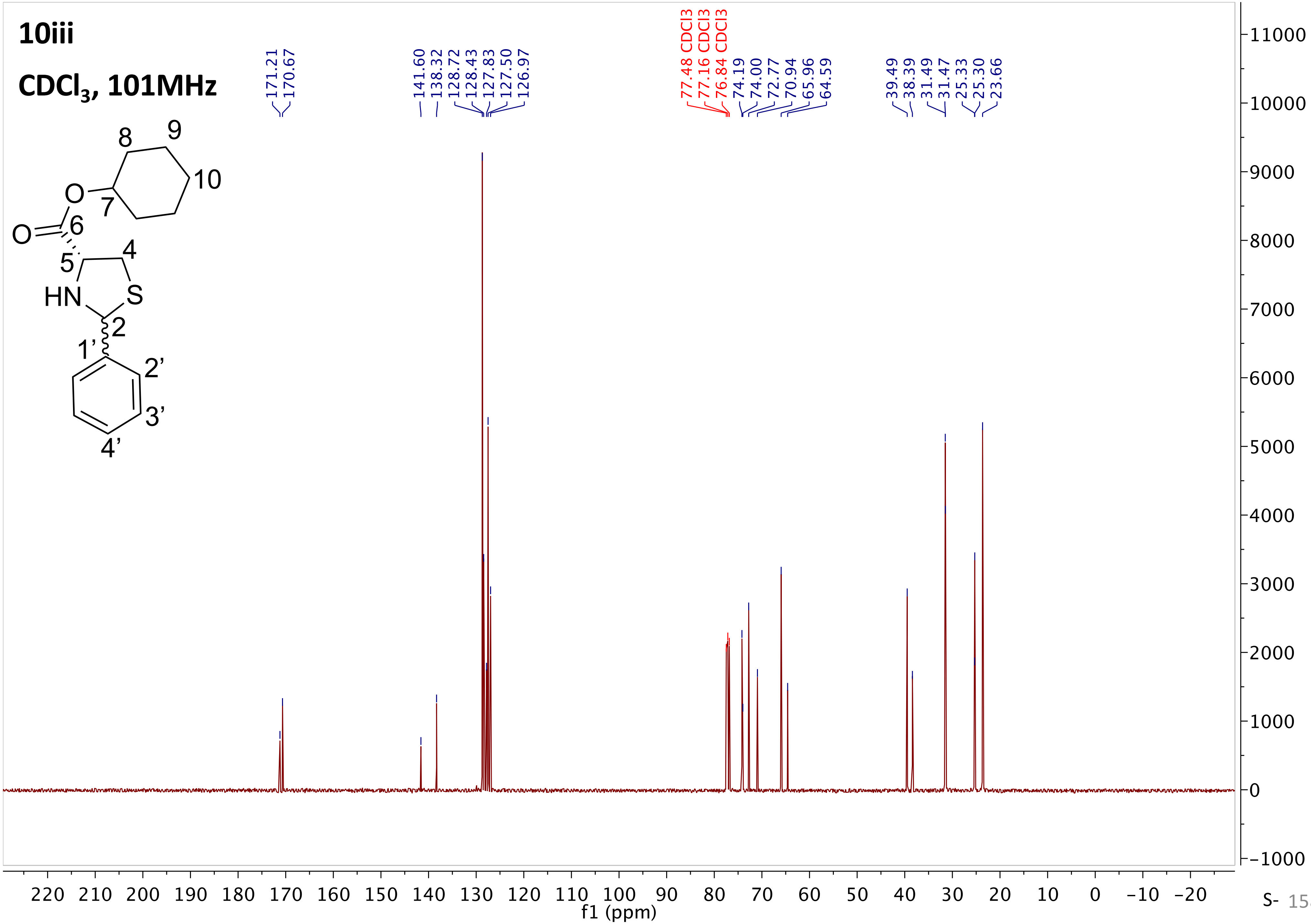
10iii

$CDCl_3$, 400MHz



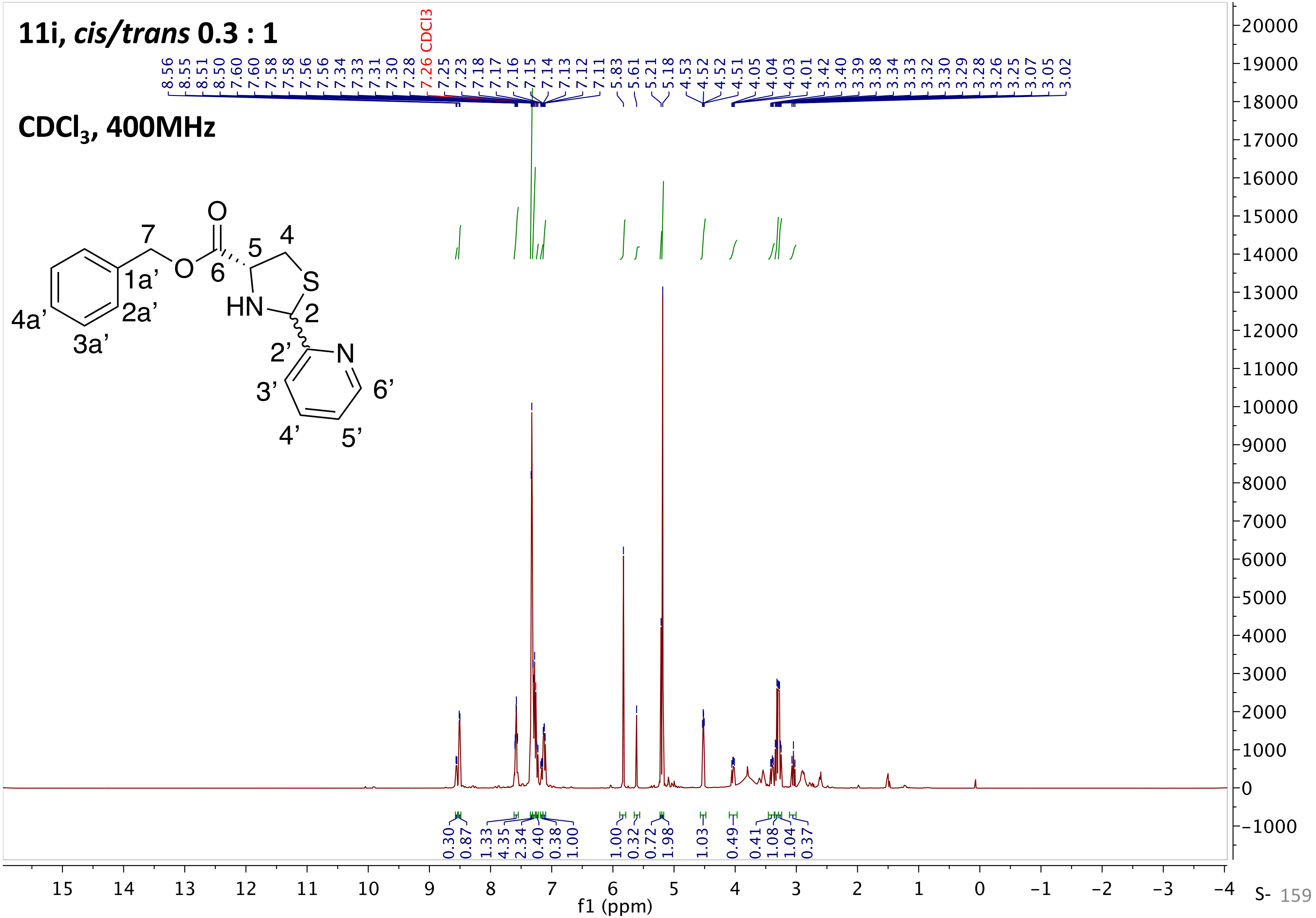
10iii

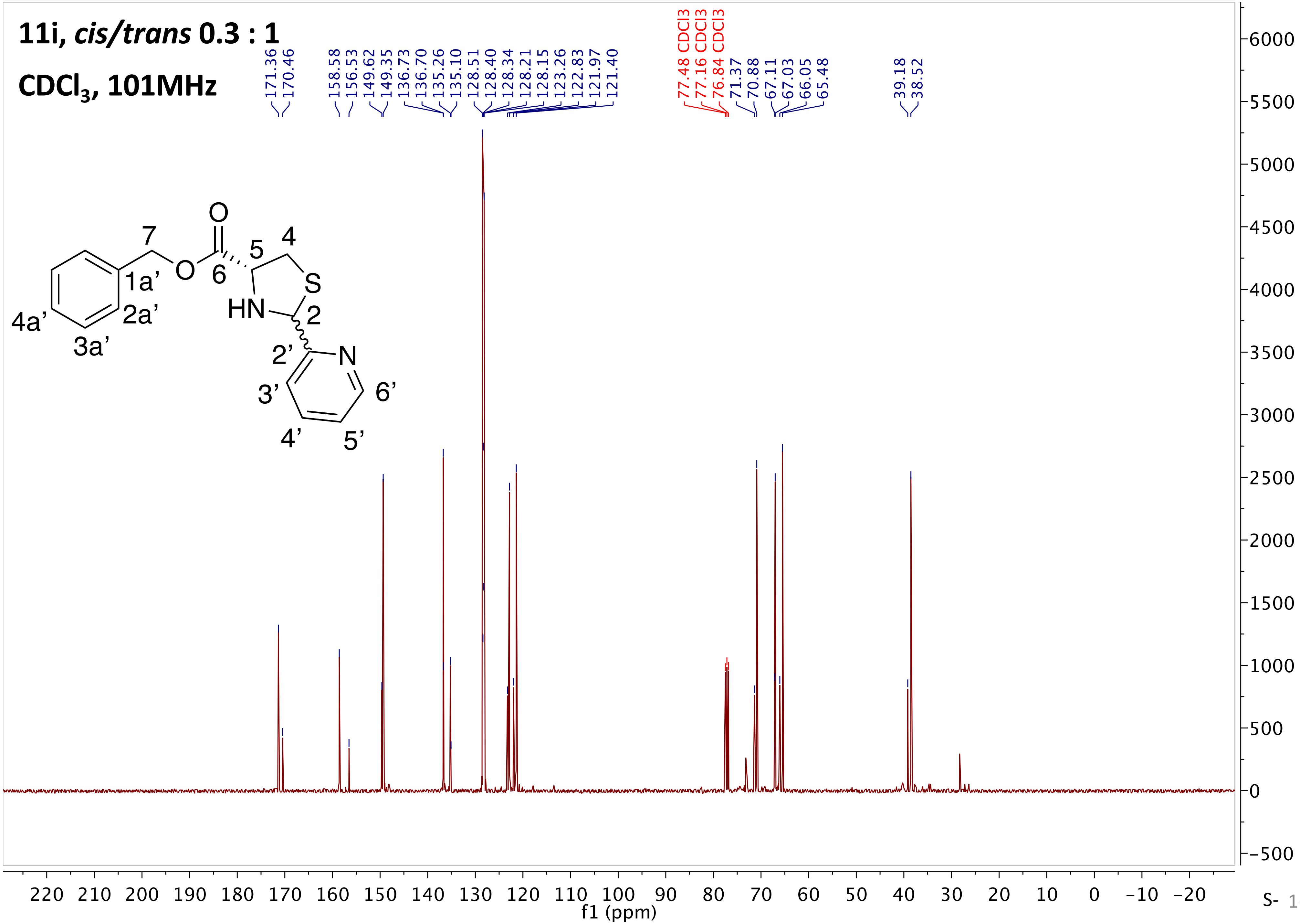
$CDCl_3$, 101MHz



11i, *cis/trans* 0.3 : 1

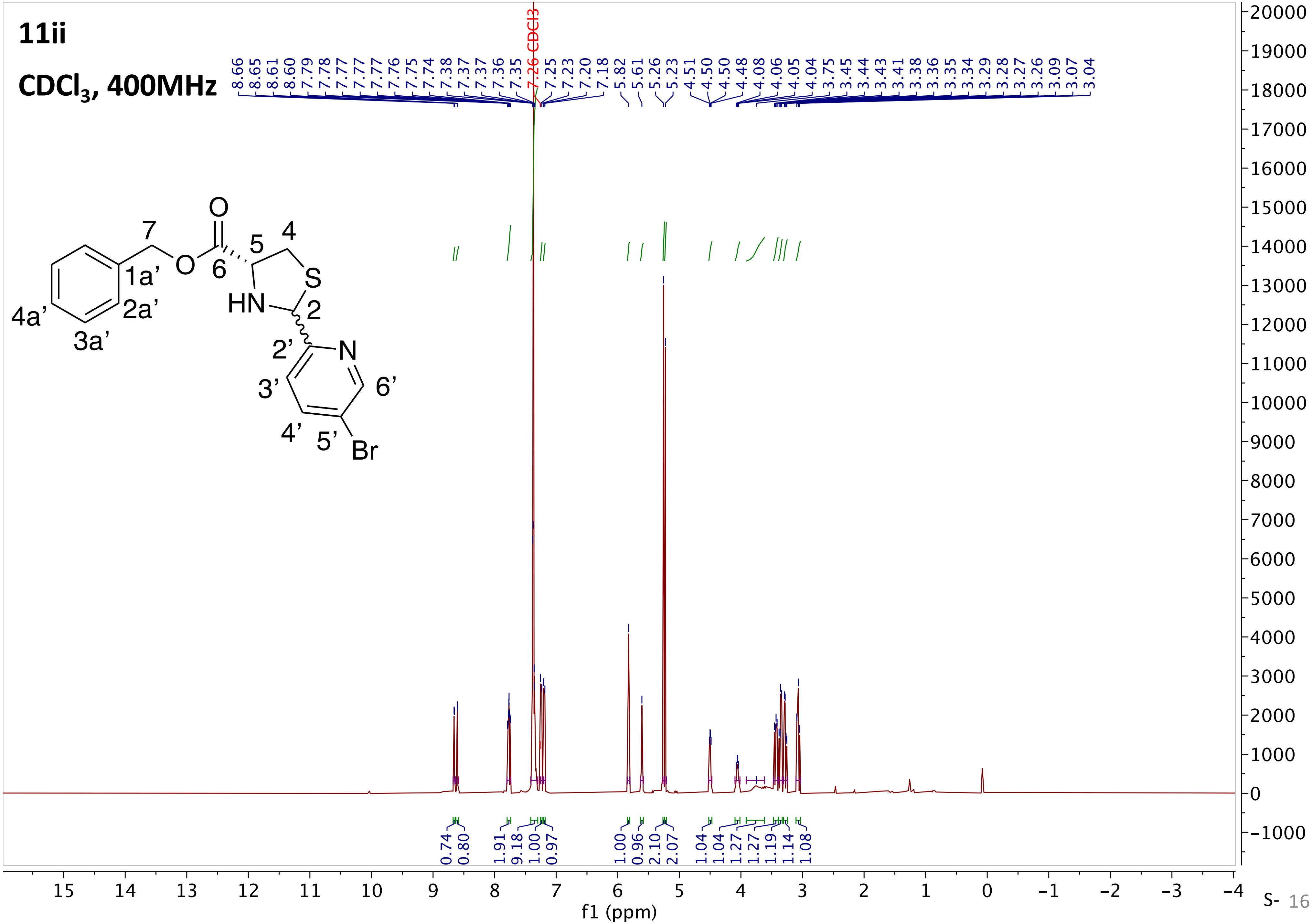
CDCl$_3$, 400MHz

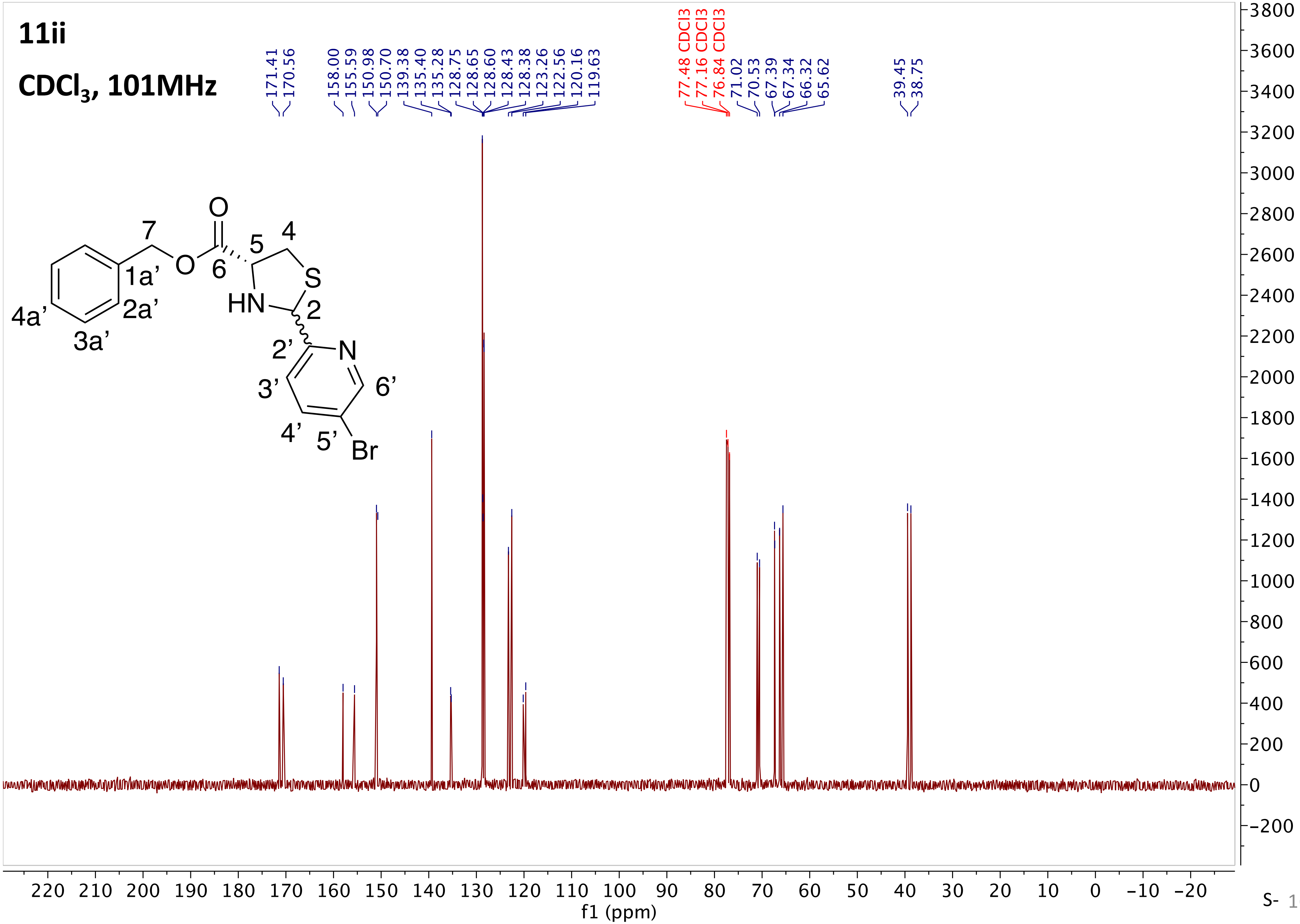


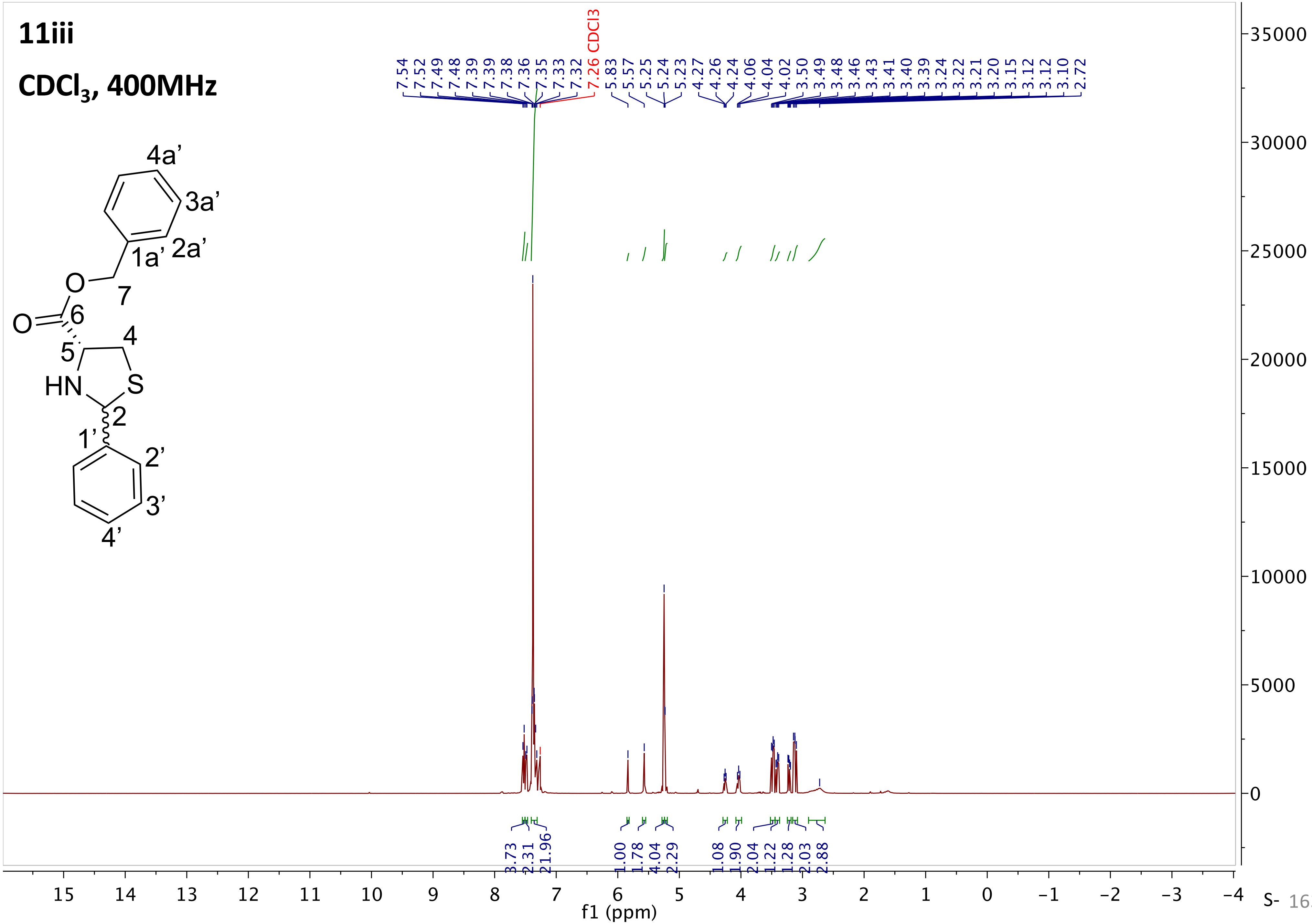

11i, cis/trans 0.3 : 1
CDCl3, 101MHz
171.36
170.46
158.58
156.53
149.62
149.35
136.73
136.70
135.26
135.10
128.51
128.40
128.34
128.21
128.15
123.26
122.83
121.97
121.40
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.37
70.88
67.11
67.03
66.05
65.48
39.18
38.52
f1 (ppm)

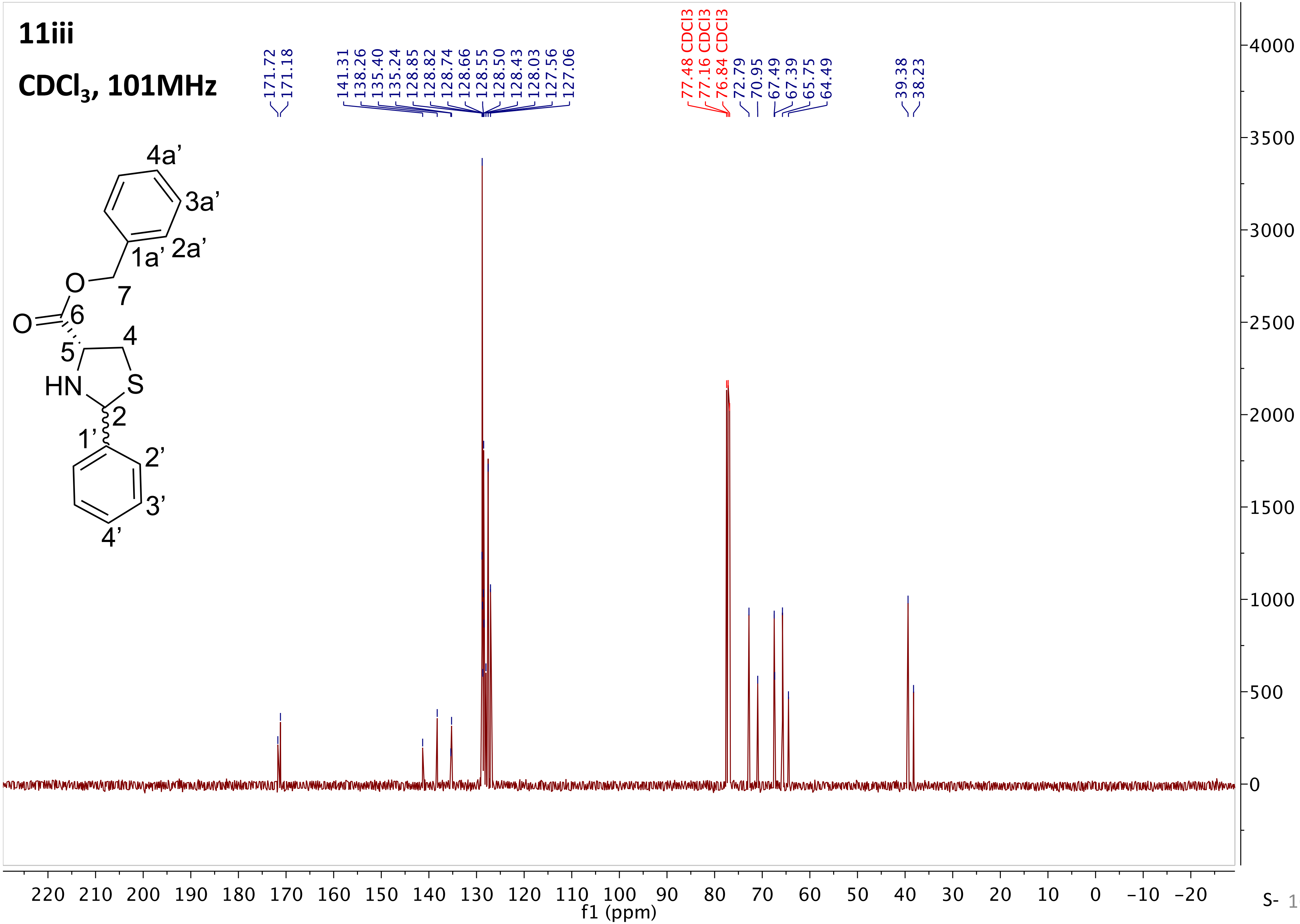
11ii

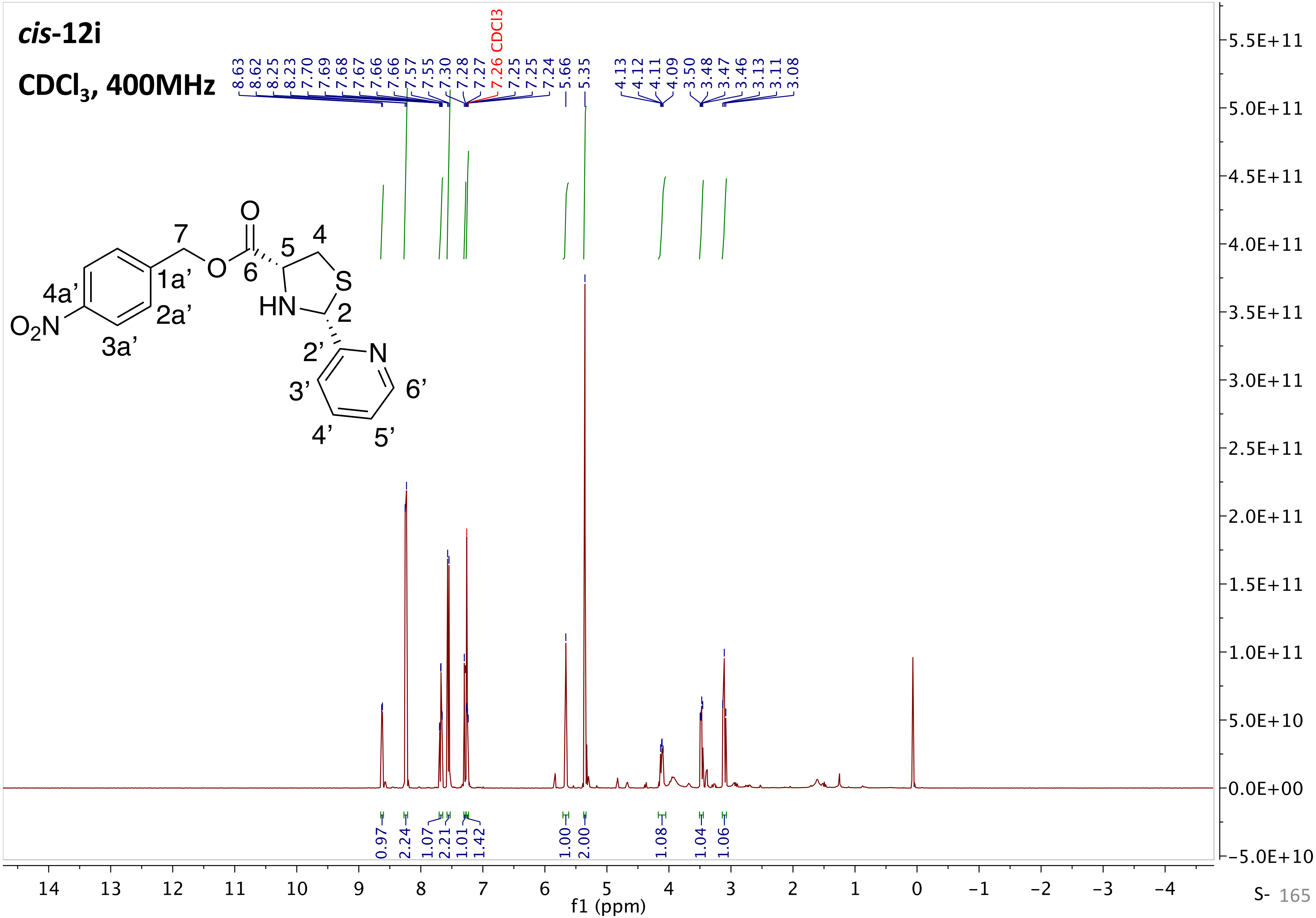
$CDCl_3$, 400MHz



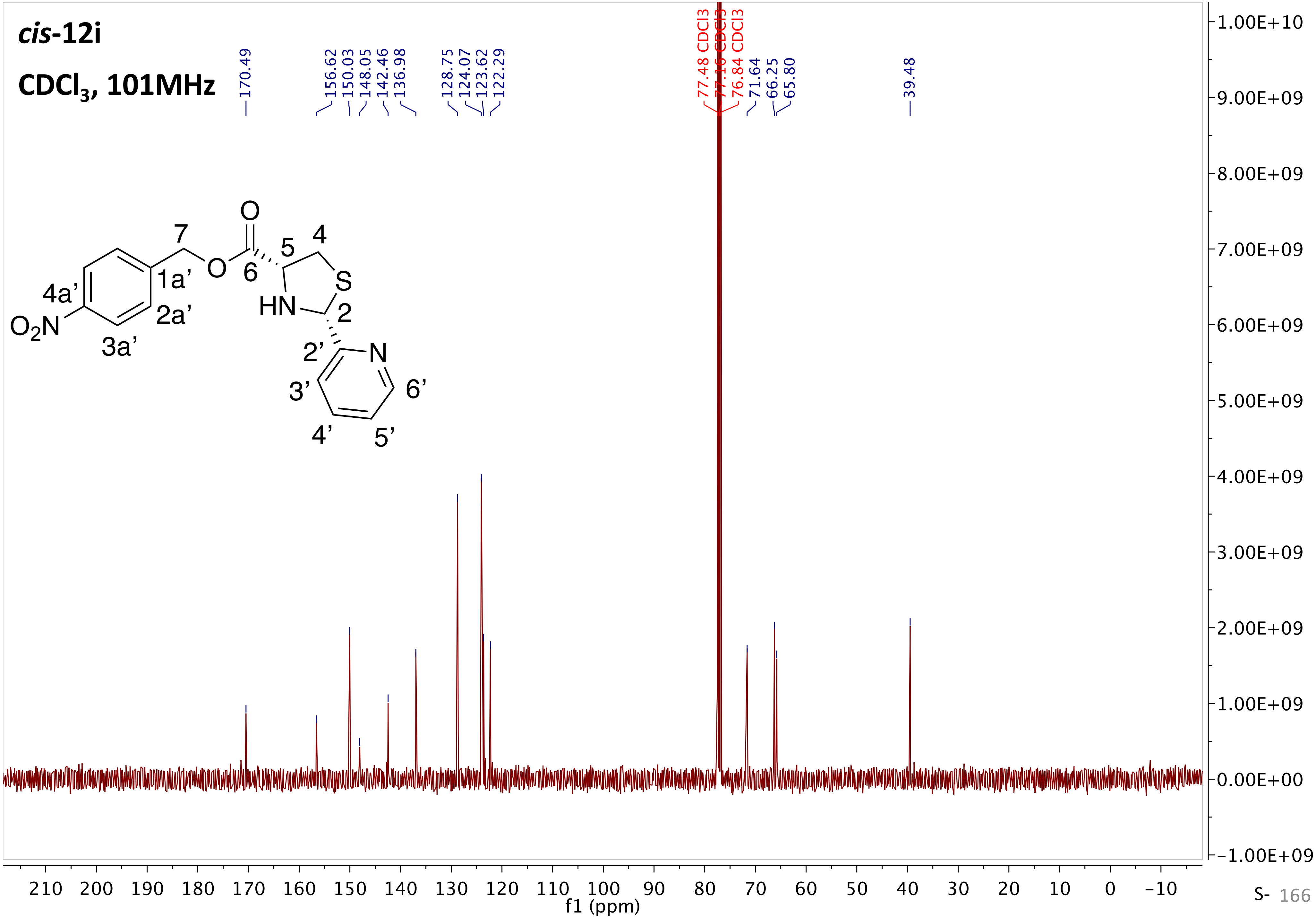

11ii
CDCl3, 101MHz
171.41
170.56
158.00
155.59
150.98
150.70
139.38
135.40
135.28
128.75
128.65
128.60
128.43
128.38
123.26
122.56
120.16
119.63
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.02
70.53
67.39
67.34
66.32
65.62
39.45
38.75
f1 (ppm)

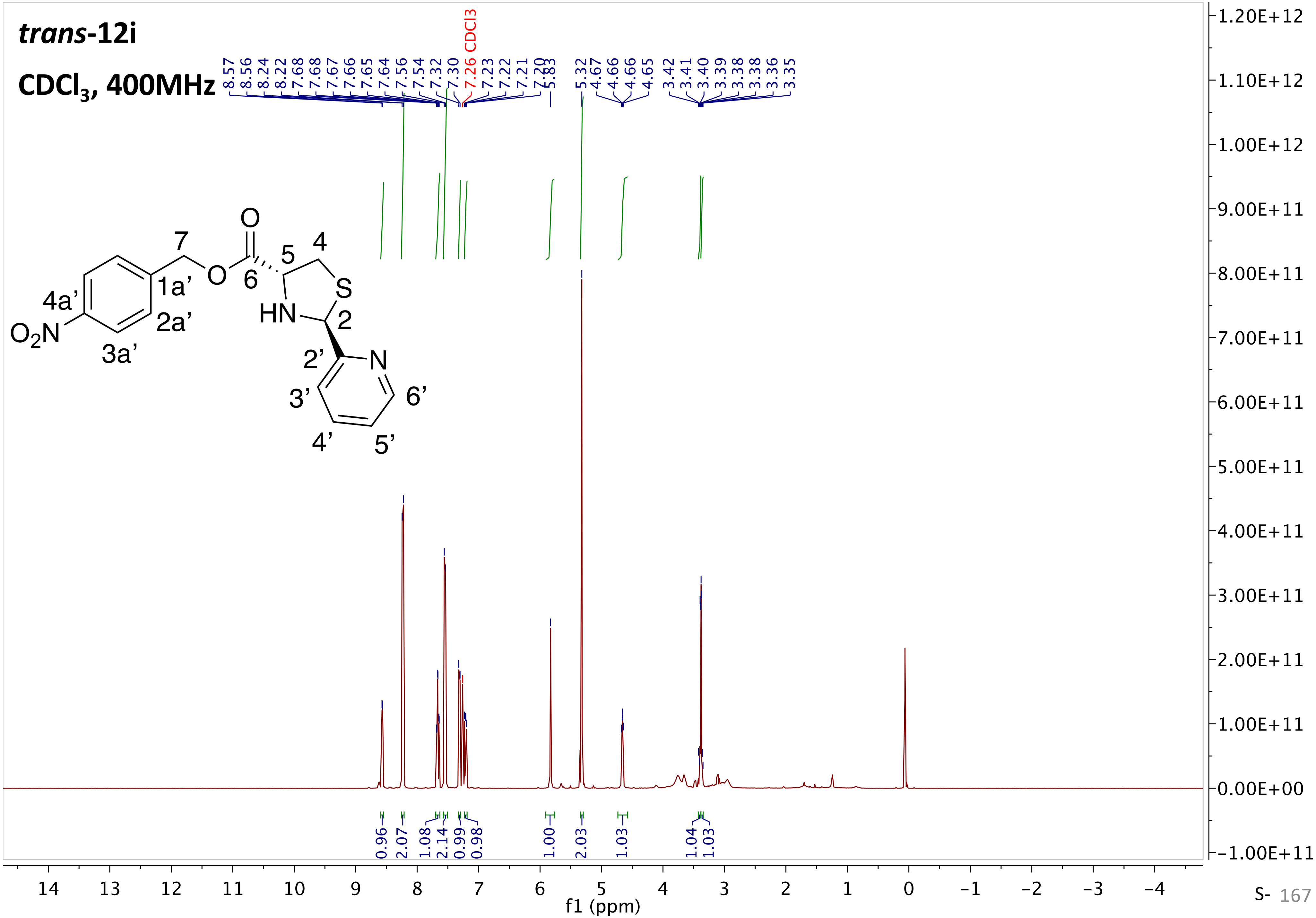

11iii
CDCl3, 400MHz
7.54 7.52 7.49 7.48 7.39 7.39 7.38 7.36 7.35 7.33 7.32 7.26 CDCl3 5.83 5.57 5.25 5.24 5.23 4.27 4.26 4.24 4.06 4.04 4.02 3.50 3.49 3.48 3.46 3.43 3.41 3.40 3.39 3.24 3.22 3.21 3.20 3.15 3.12 3.12 3.10 2.72
3.73 2.31 21.96 1.00 1.78 4.04 2.29 1.08 1.90 2.04 1.22 1.28 2.03 2.88
4a'
3a'
2a'
1a'
O
7
O
6
5
4
HN
S
2
1'
2'
3'
4'
35000
30000
25000
20000
15000
10000
5000
0
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)

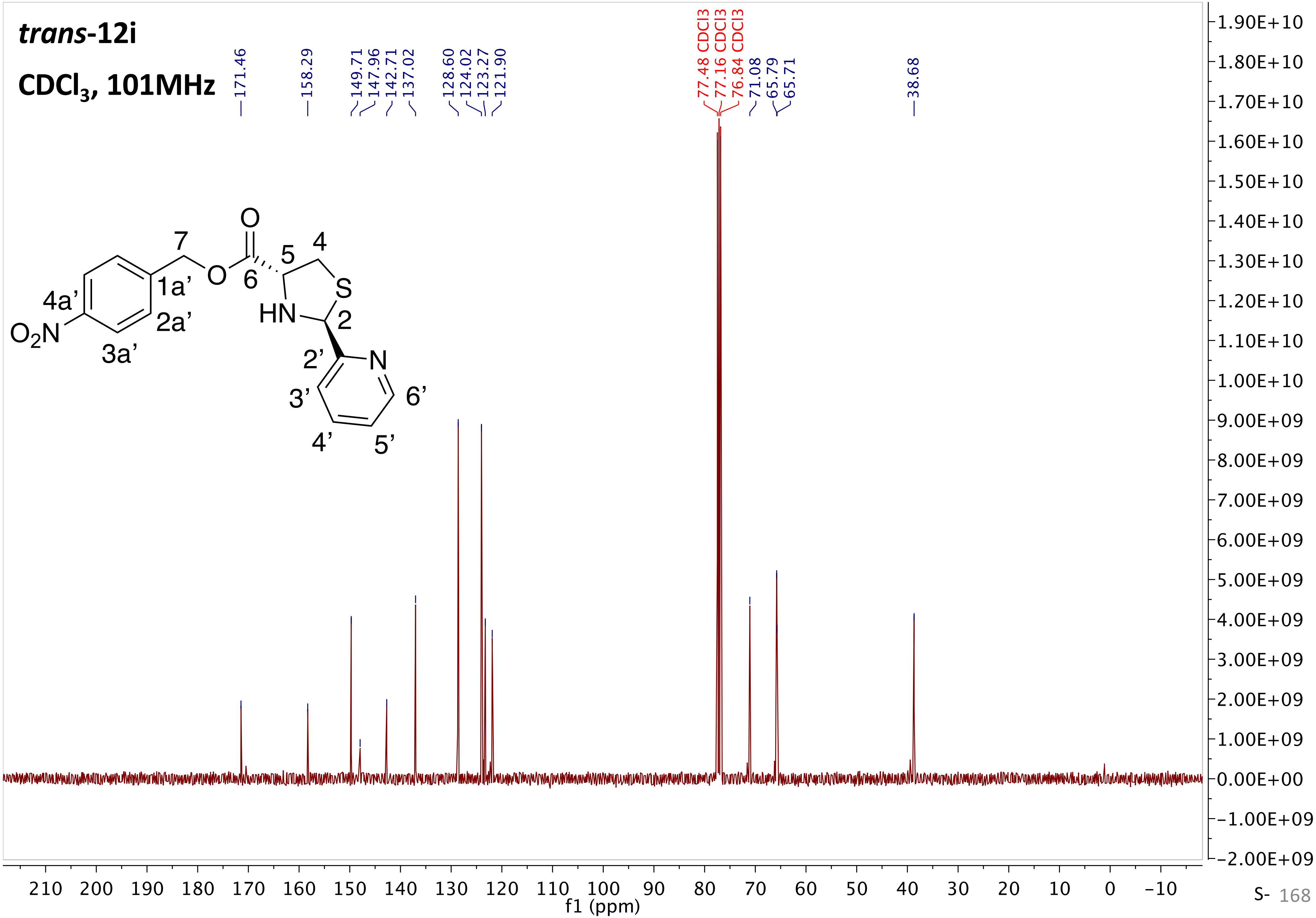

11iii
CDCl3, 101MHz
171.72
171.18
141.31
138.26
135.40
135.24
128.85
128.82
128.74
128.66
128.55
128.50
128.43
128.03
127.56
127.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.79
70.95
67.49
67.39
65.75
64.49
39.38
38.23
4a'
3a'
2a'
1a'
O
7
O
6
5
4
HN
S
2
1'
2'
3'
4'
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



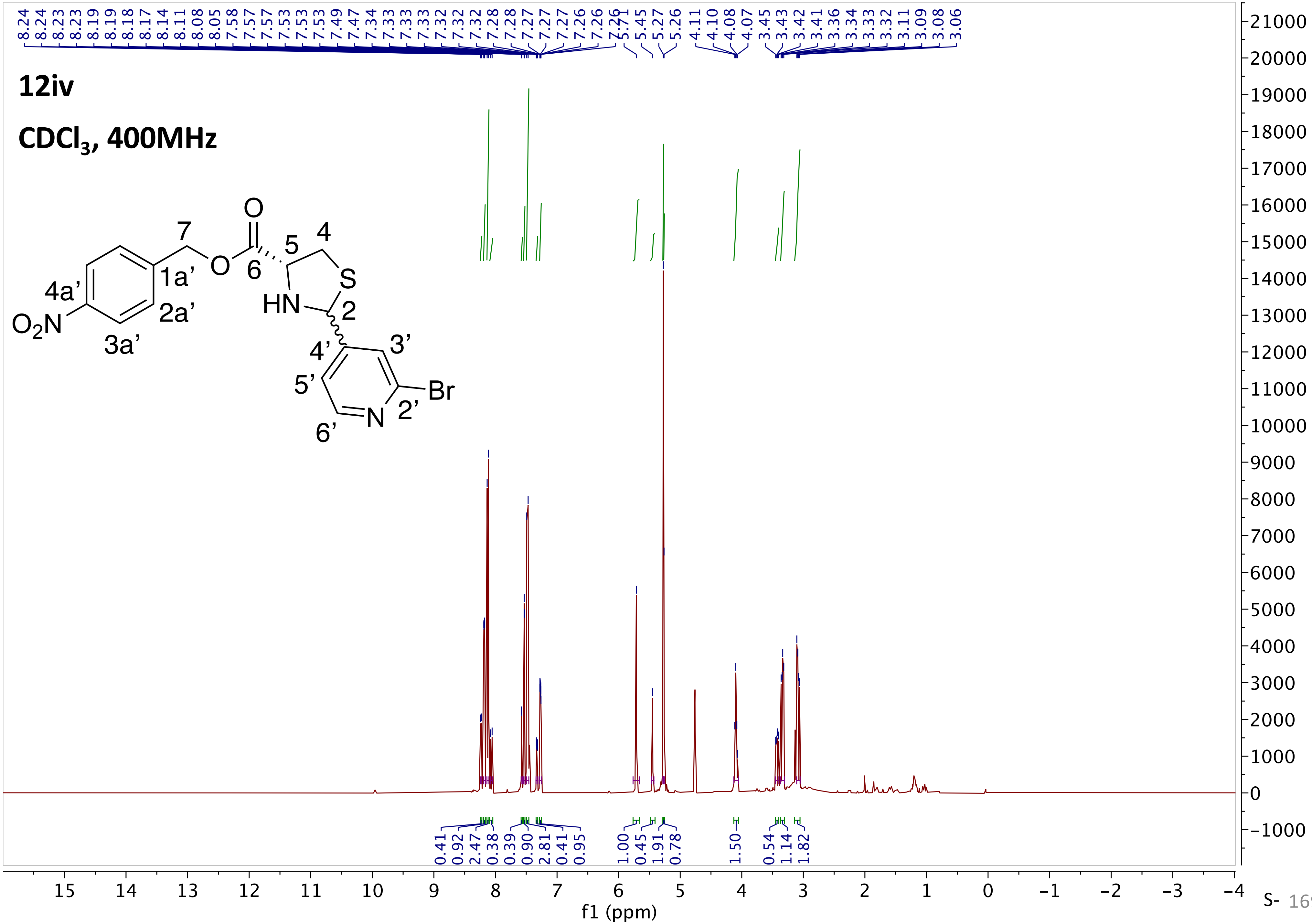
cis-12i
$CDCl_3$, 400MHz
8.63
8.62
8.25
8.23
7.70
7.69
7.68
7.67
7.66
7.66
7.57
7.55
7.30
7.28
7.27
7.26 CDCl3
7.25
7.25
7.24
5.66
5.35
4.13
4.12
4.11
4.09
3.50
3.48
3.47
3.46
3.13
3.11
3.08
0.97
2.24
1.07
2.21
1.01
1.42
1.00
2.00
1.08
1.04
1.06
f1 (ppm)

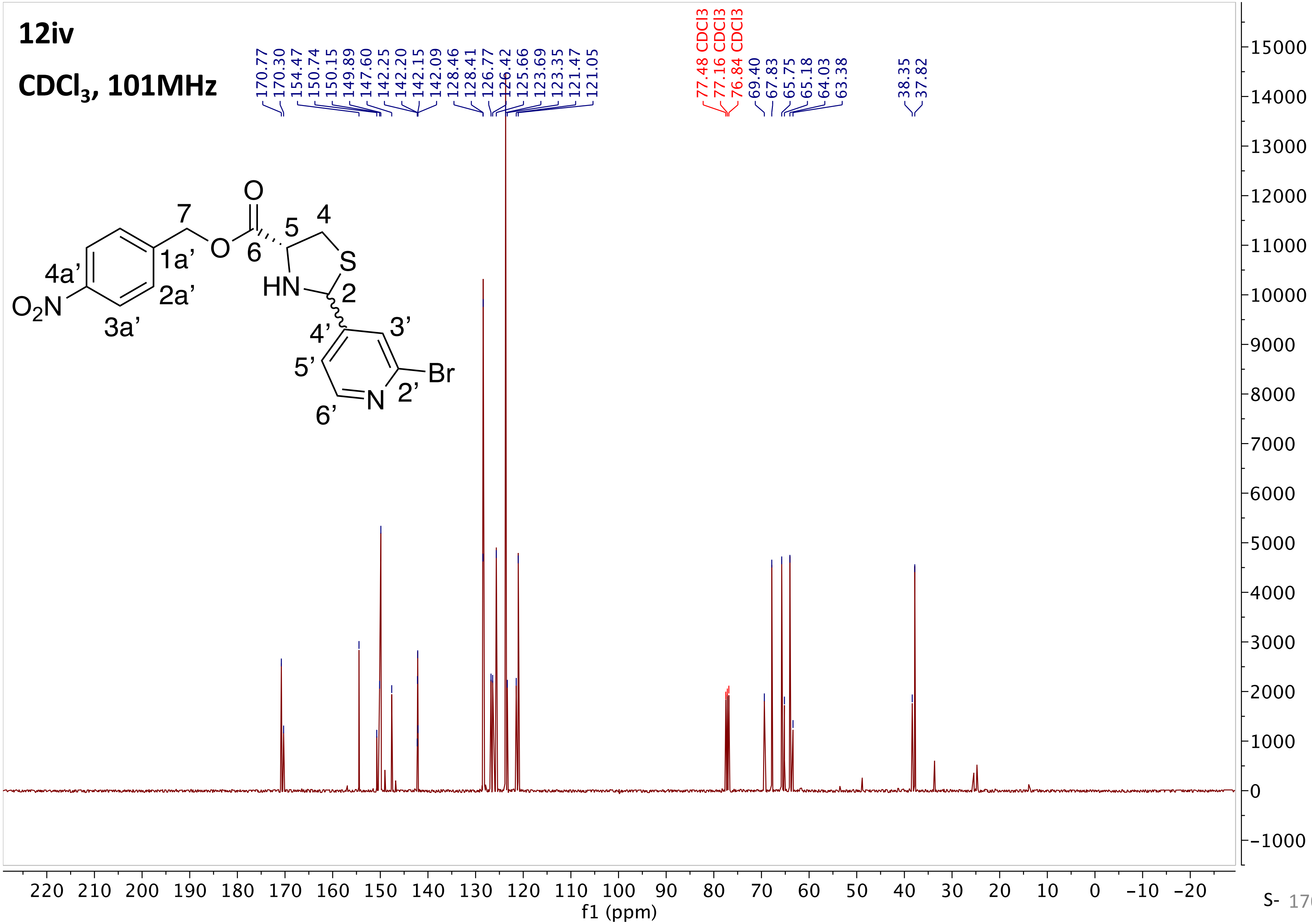

cis-12i
CDCl3, 101MHz
170.49
156.62
150.03
148.05
142.46
136.98
128.75
124.07
123.62
122.29
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.64
66.25
65.80
39.48
f1 (ppm)


trans-12i
CDCl3, 400MHz
8.57 8.56 8.24 8.22 7.68 7.68 7.67 7.66 7.65 7.64 7.56 7.54 7.32 7.30 7.26 CDCl3 7.23 7.22 7.21 7.20 5.83 5.32 4.67 4.66 4.66 4.65 3.42 3.41 3.40 3.39 3.38 3.38 3.36 3.35
0.96 2.07 1.08 2.14 0.99 0.98 1.00 2.03 1.03 1.04 1.03
f1 (ppm)



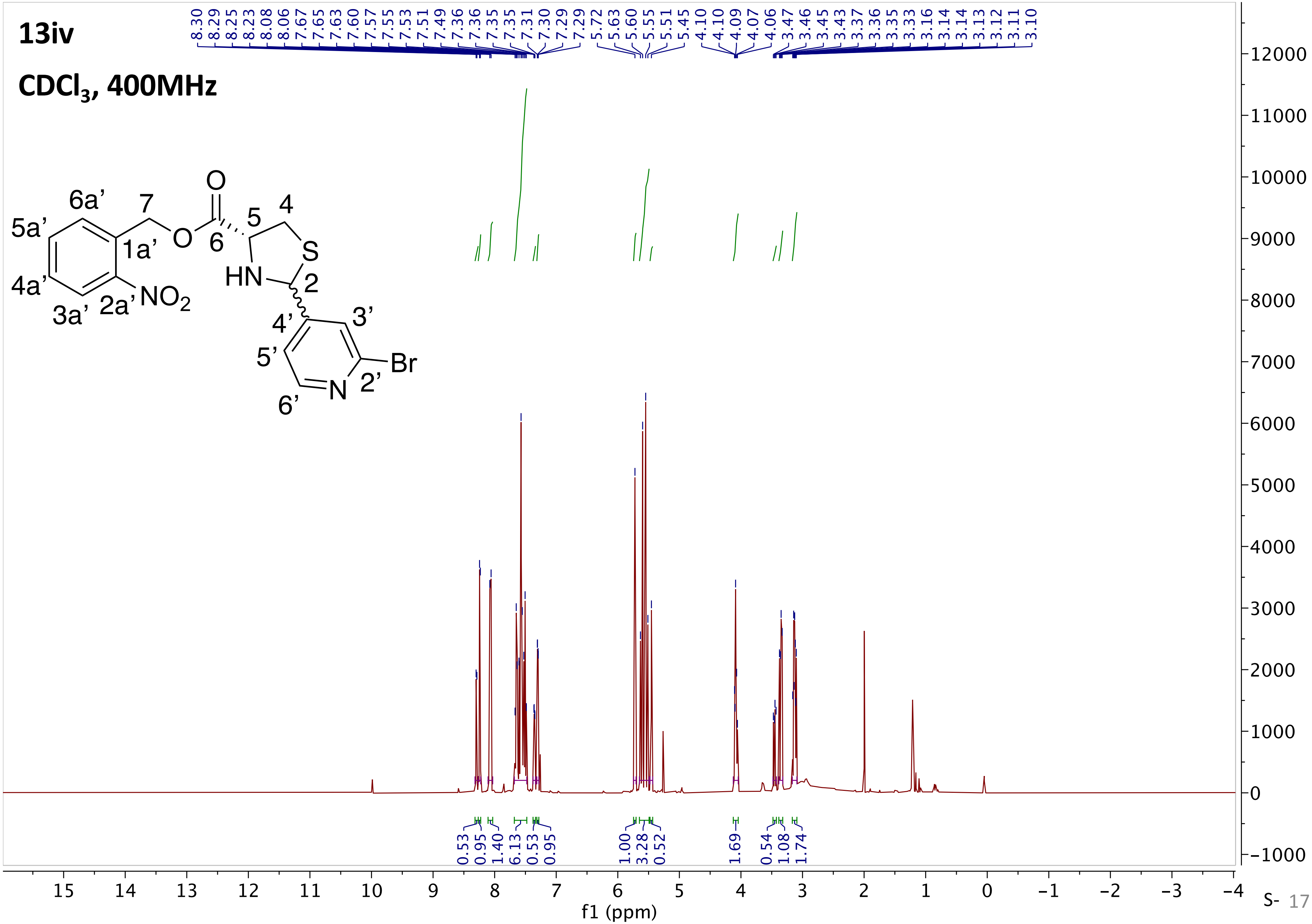
trans-12i
CDCl3, 101MHz
171.46
158.29
149.71
147.96
142.71
137.02
128.60
124.02
123.27
121.90
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.08
65.79
65.71
38.68
f1 (ppm)

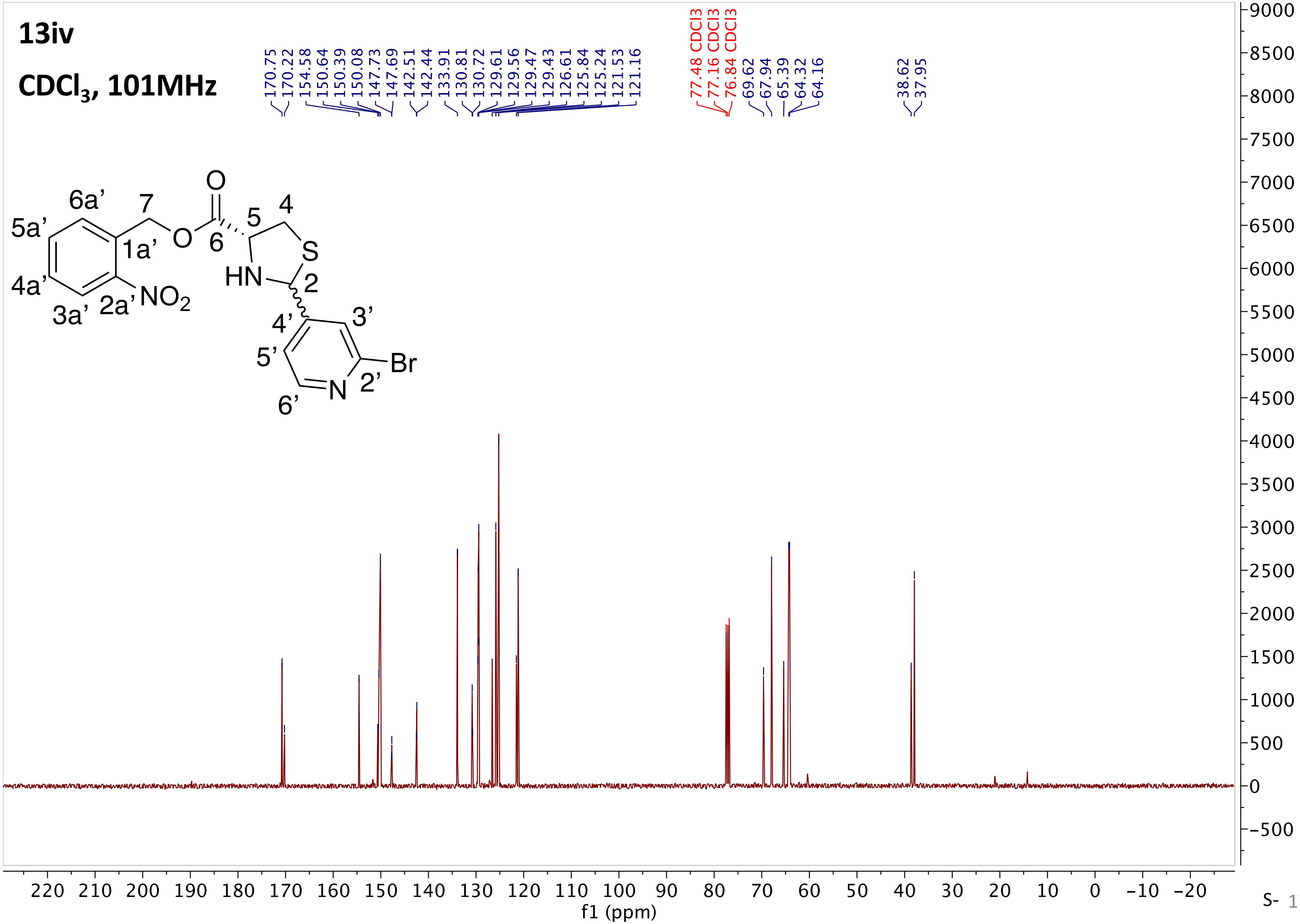

12iv
CDCl3, 400MHz
O
7
5
4
1a'
O
6
S
4a'
HN
2
2a'
O2N
3a'
4'
3'
5'
Br
2'
N
6'
f1 (ppm)


12iv
$CDCl_3$, 101MHz
170.77
170.30
154.47
150.74
150.15
149.89
147.60
142.25
142.20
142.15
142.09
128.46
128.41
126.77
126.42
125.66
123.69
123.35
121.47
121.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.40
67.83
65.75
65.18
64.03
63.38
38.35
37.82
O
7
5
4
6
S
1a'
4a'
HN
2
2a'
O_2N
3a'
4'
3'
5'
Br
2'
N
6'
f1 (ppm)

13iv

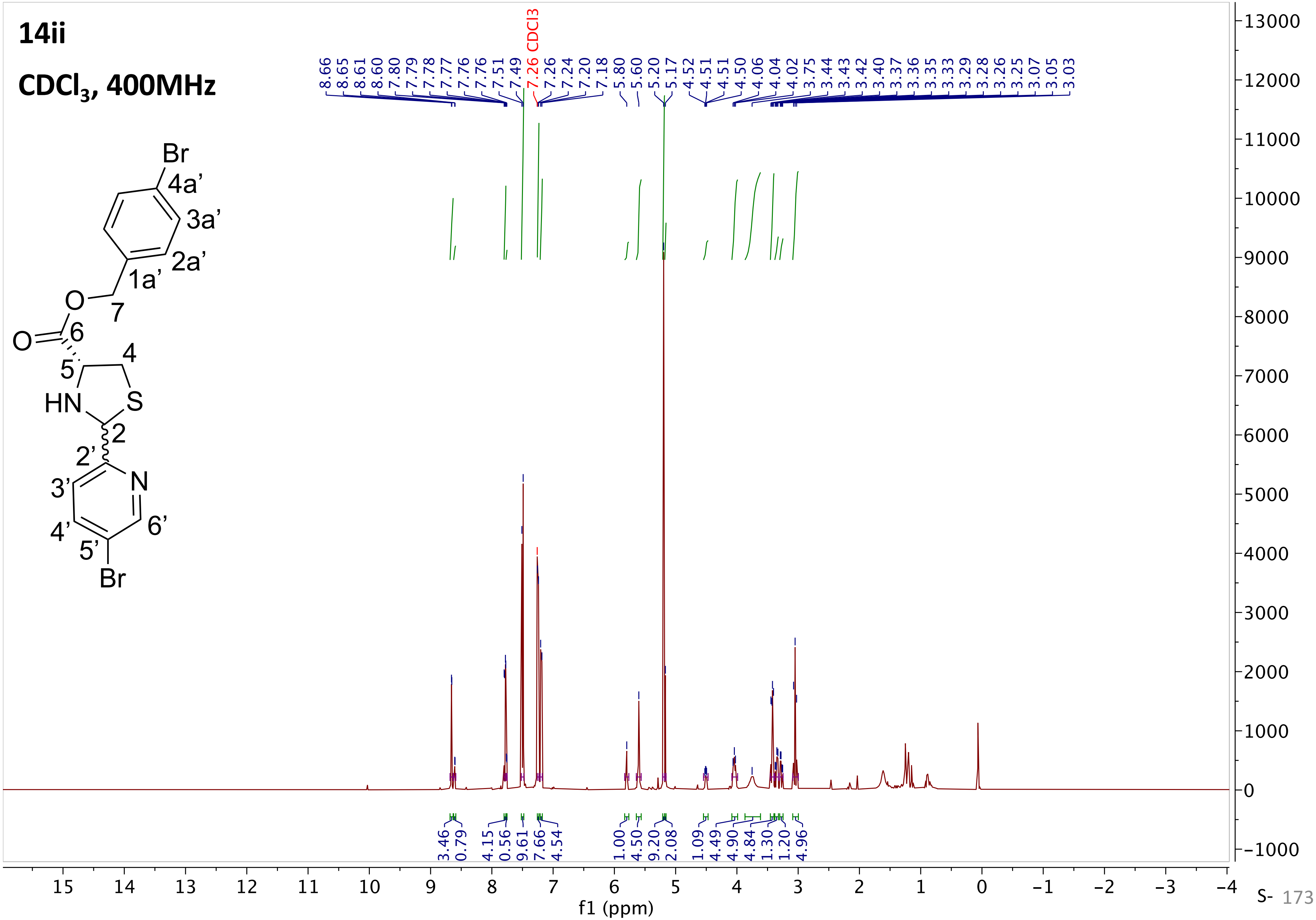
$CDCl_3$, 400MHz




13iv
CDCl3, 101MHz
170.75
170.22
154.58
150.64
150.39
150.08
147.73
147.69
142.51
142.44
133.91
130.81
130.72
129.61
129.56
129.47
129.43
126.61
125.84
125.24
121.53
121.16
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.62
67.94
65.39
64.32
64.16
38.62
37.95
f1 (ppm)

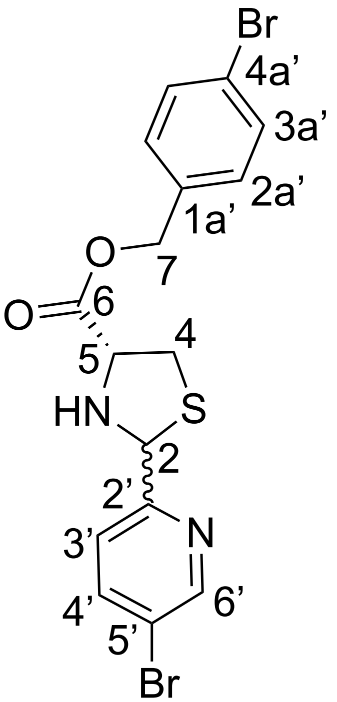
14ii

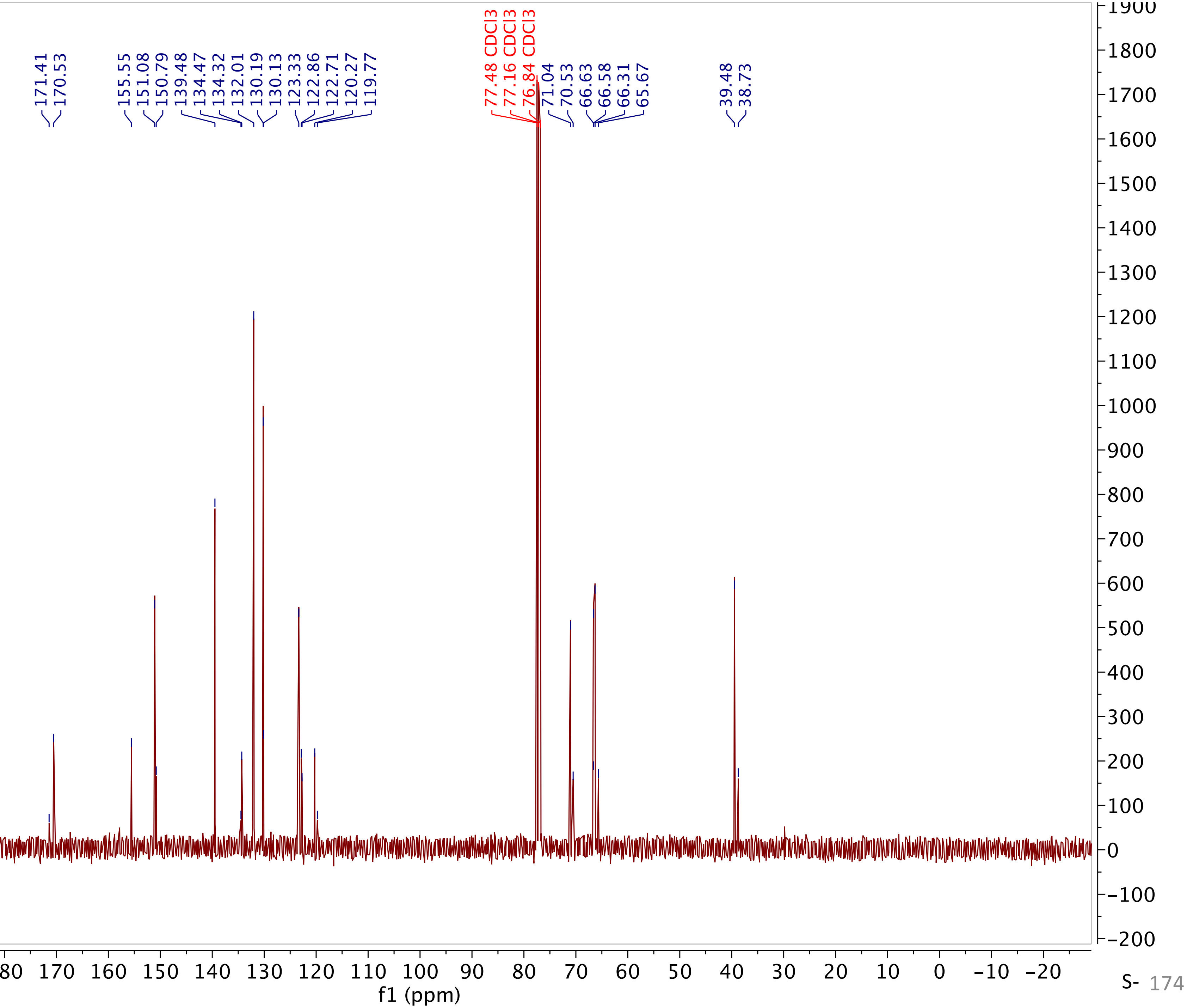
$CDCl_3$, 400MHz



14ii

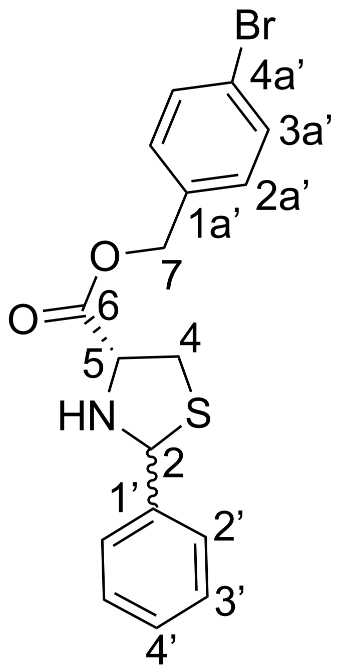
$CDCl_3$, 101MHz

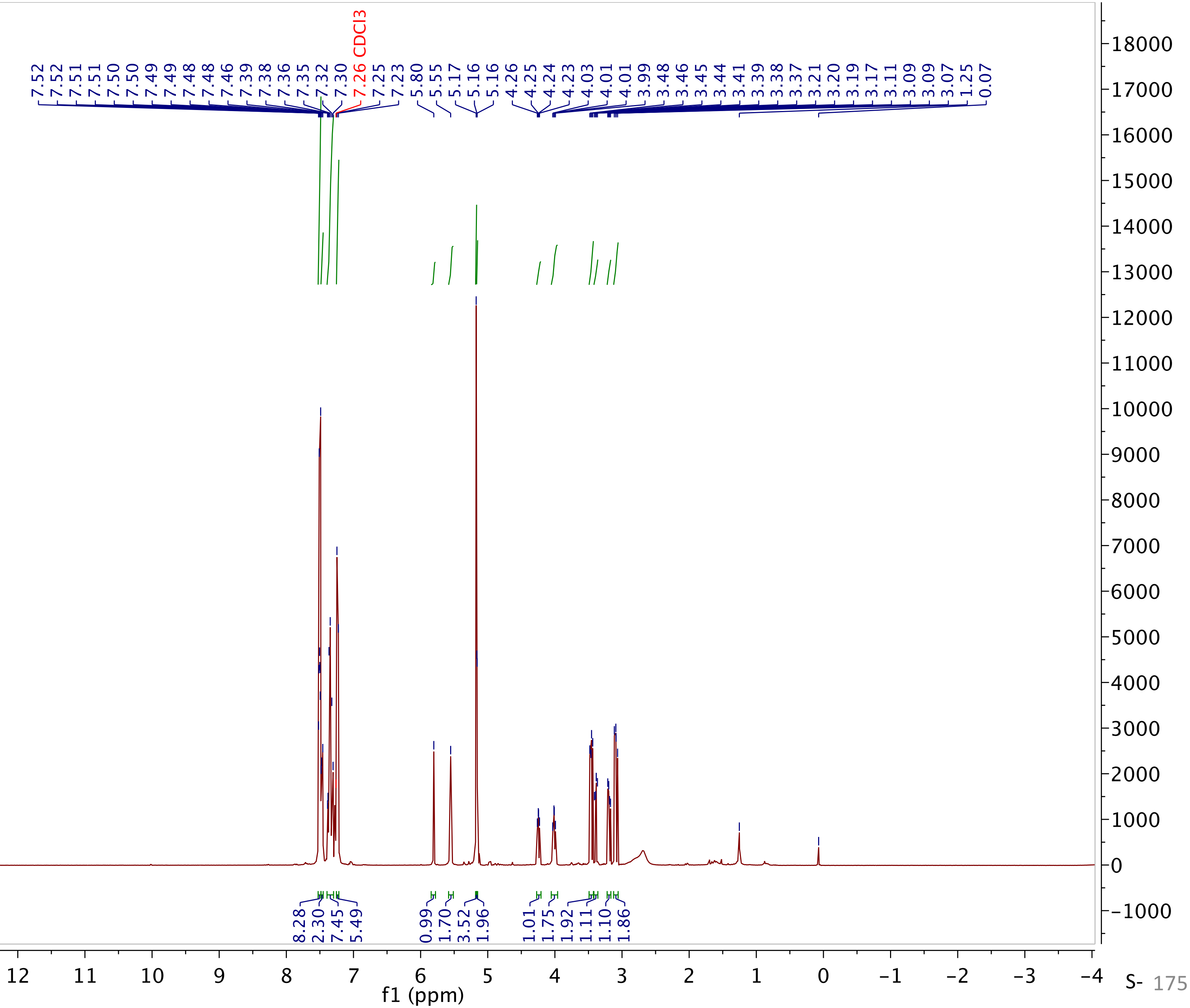


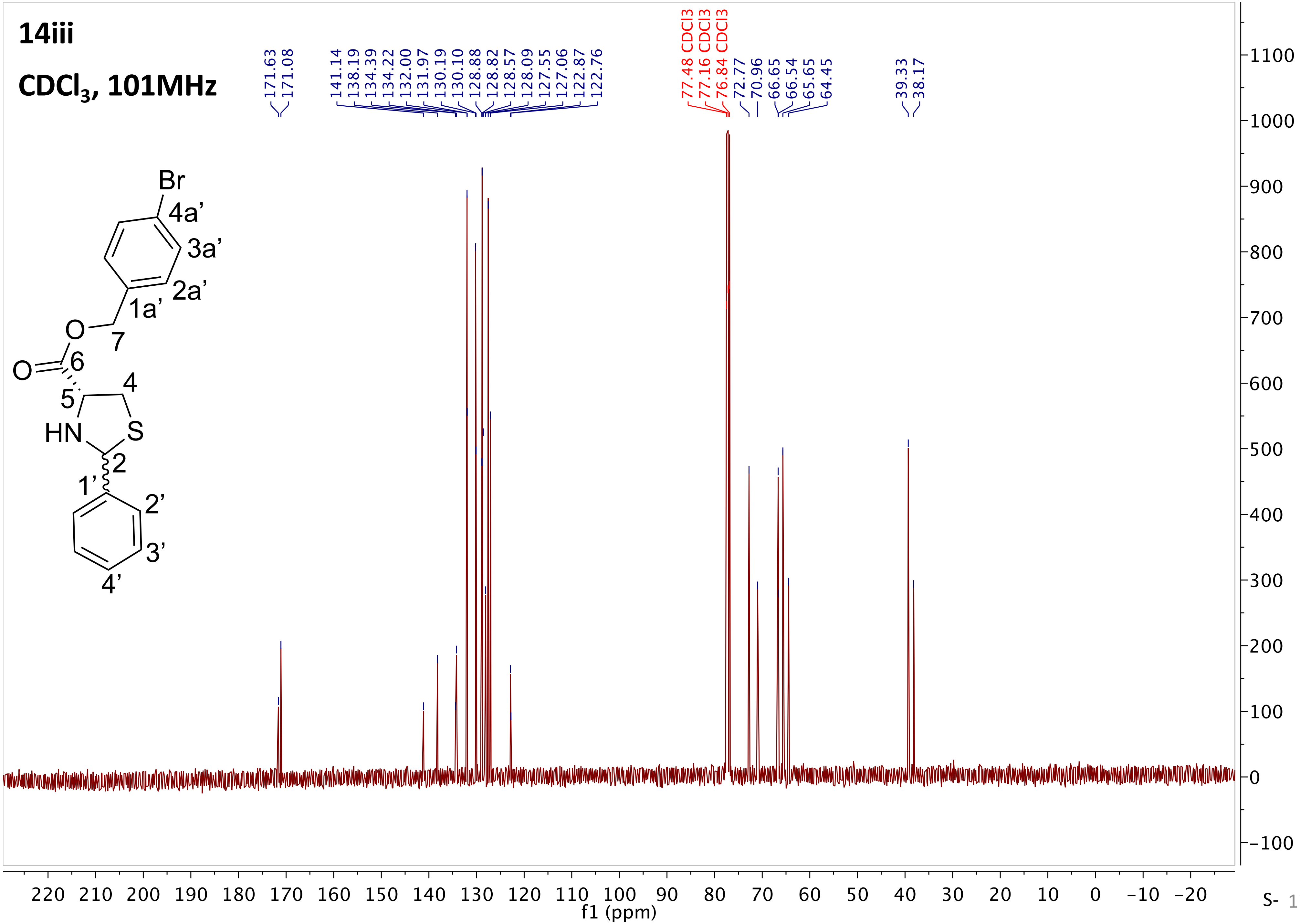


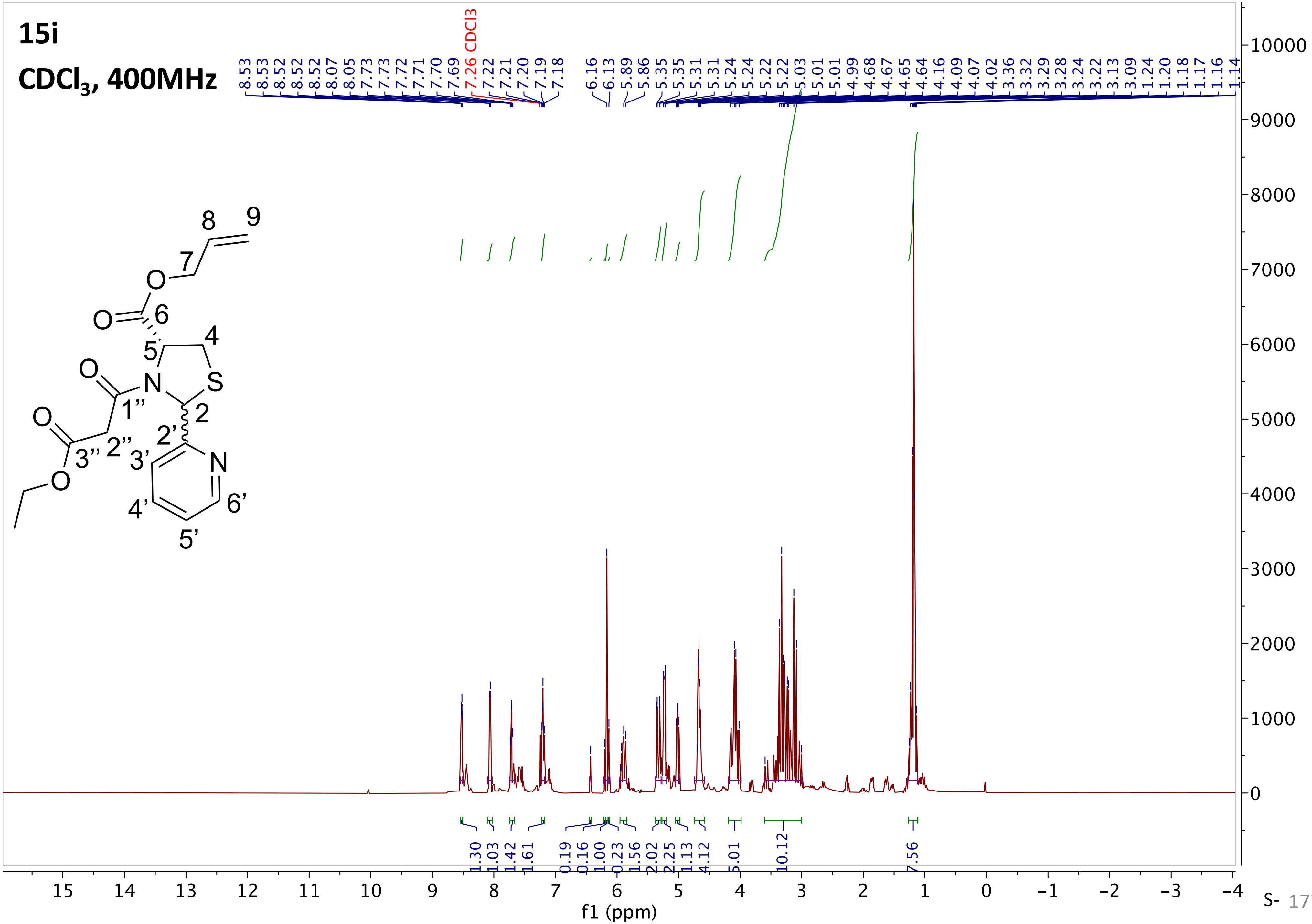
14iii

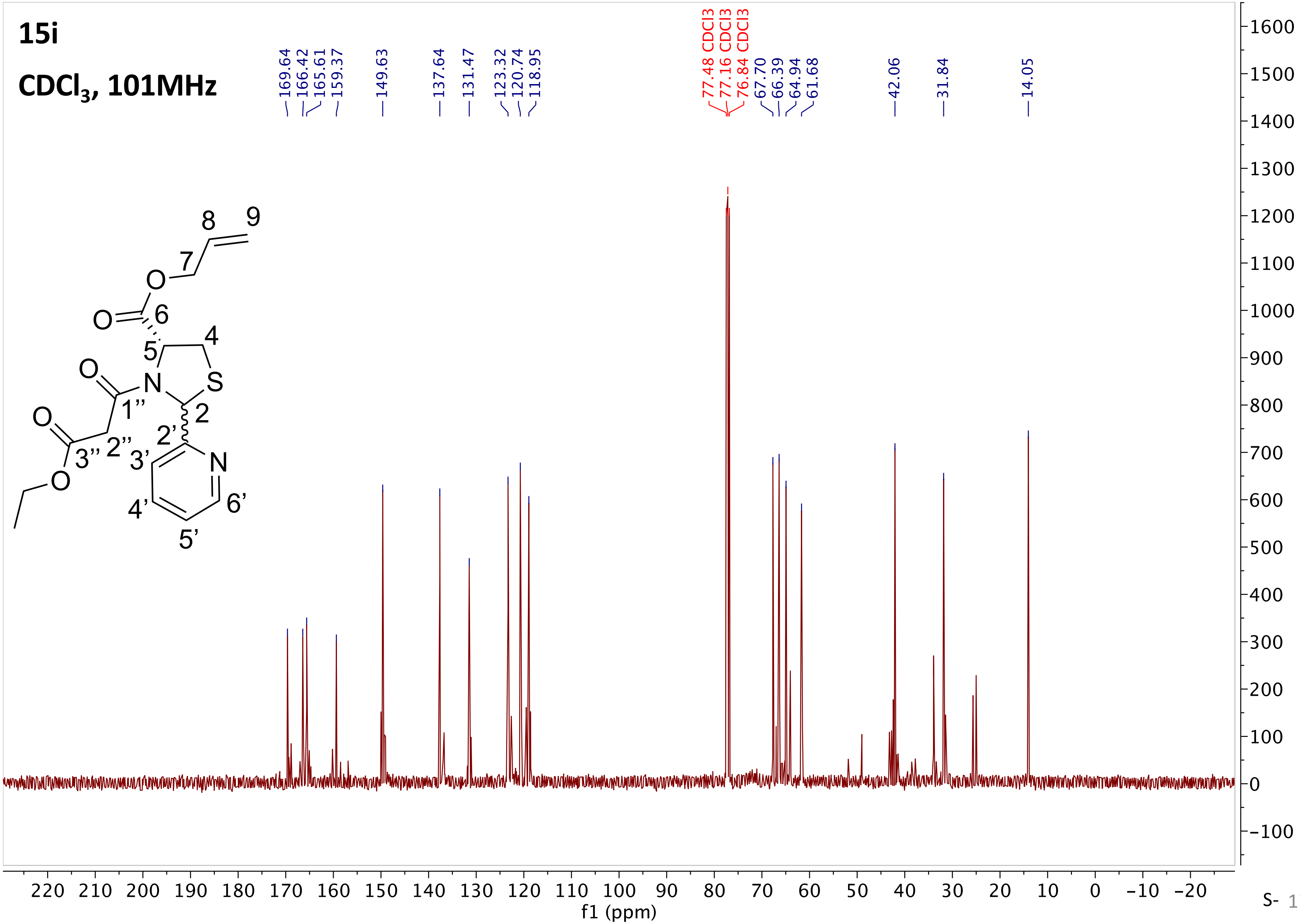
$CDCl_3$, 400MHz

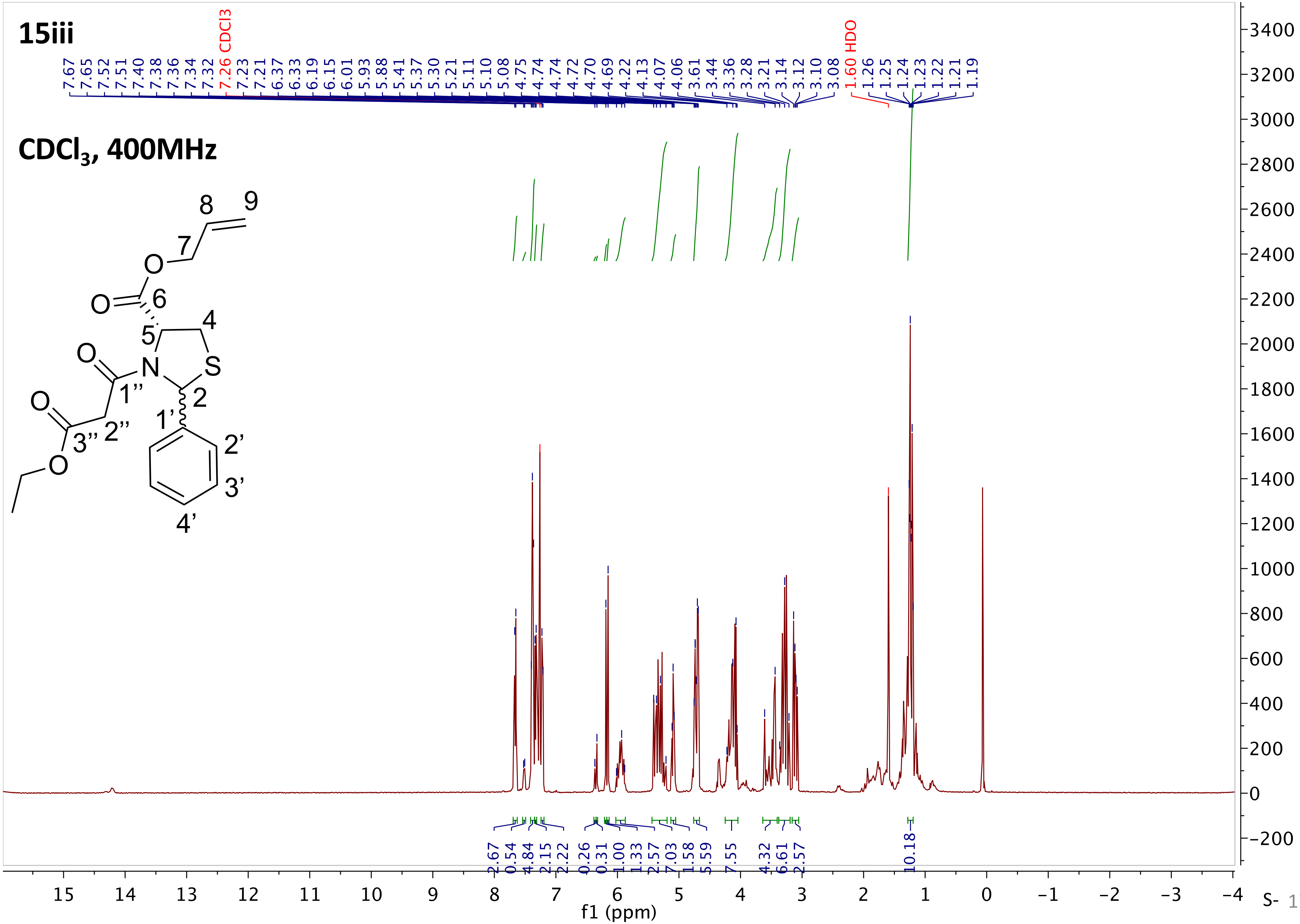




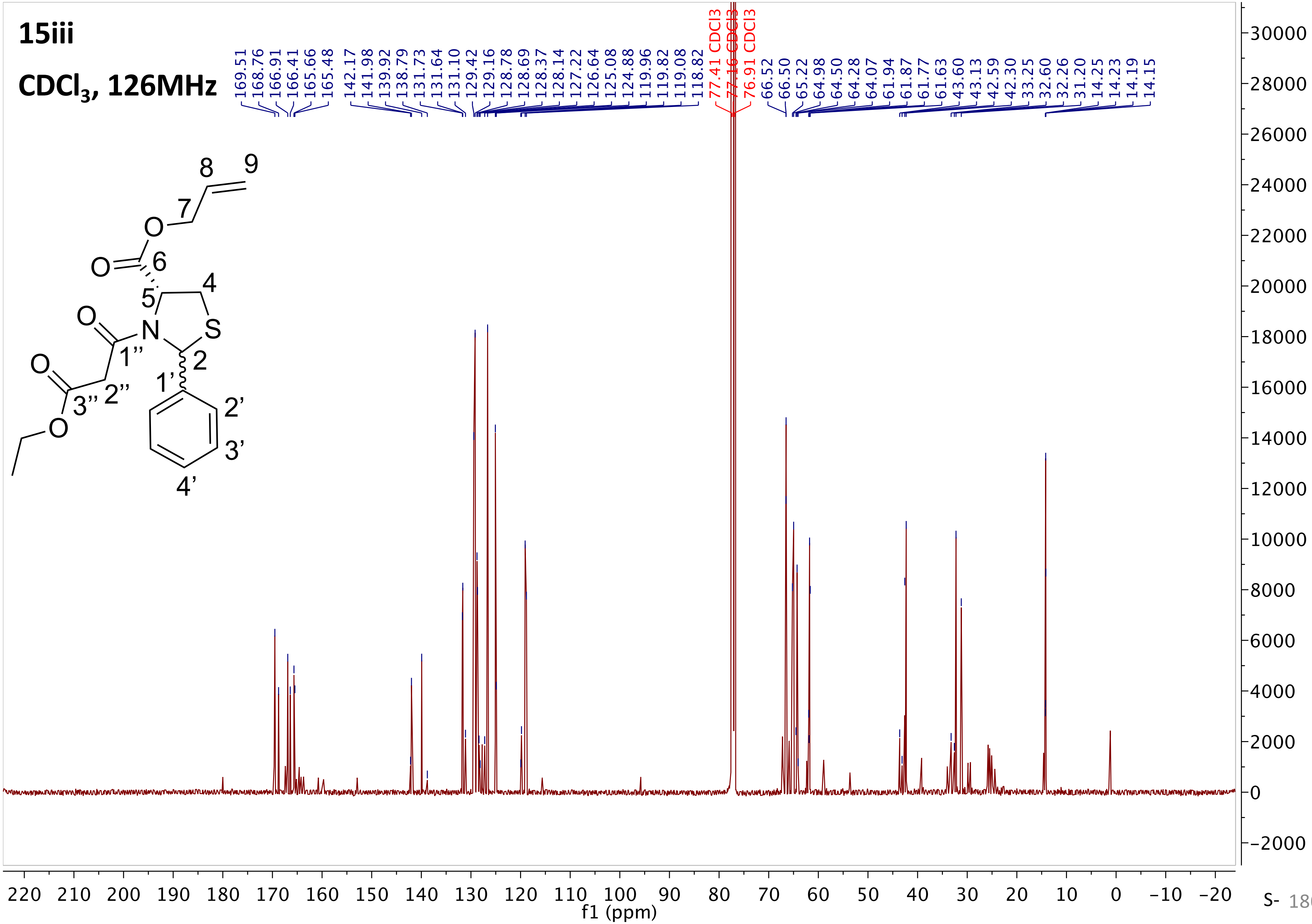

14iii
CDCl3, 101MHz
171.63
171.08
141.14
138.19
134.39
134.22
132.00
131.97
130.19
130.10
128.88
128.82
128.57
128.09
127.55
127.06
122.87
122.76
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.77
70.96
66.65
66.54
65.65
64.45
39.33
38.17
Br
4a'
3a'
2a'
1a'
O
7
6
O
5
4
HN
S
2
1'
2'
3'
4'
f1 (ppm)

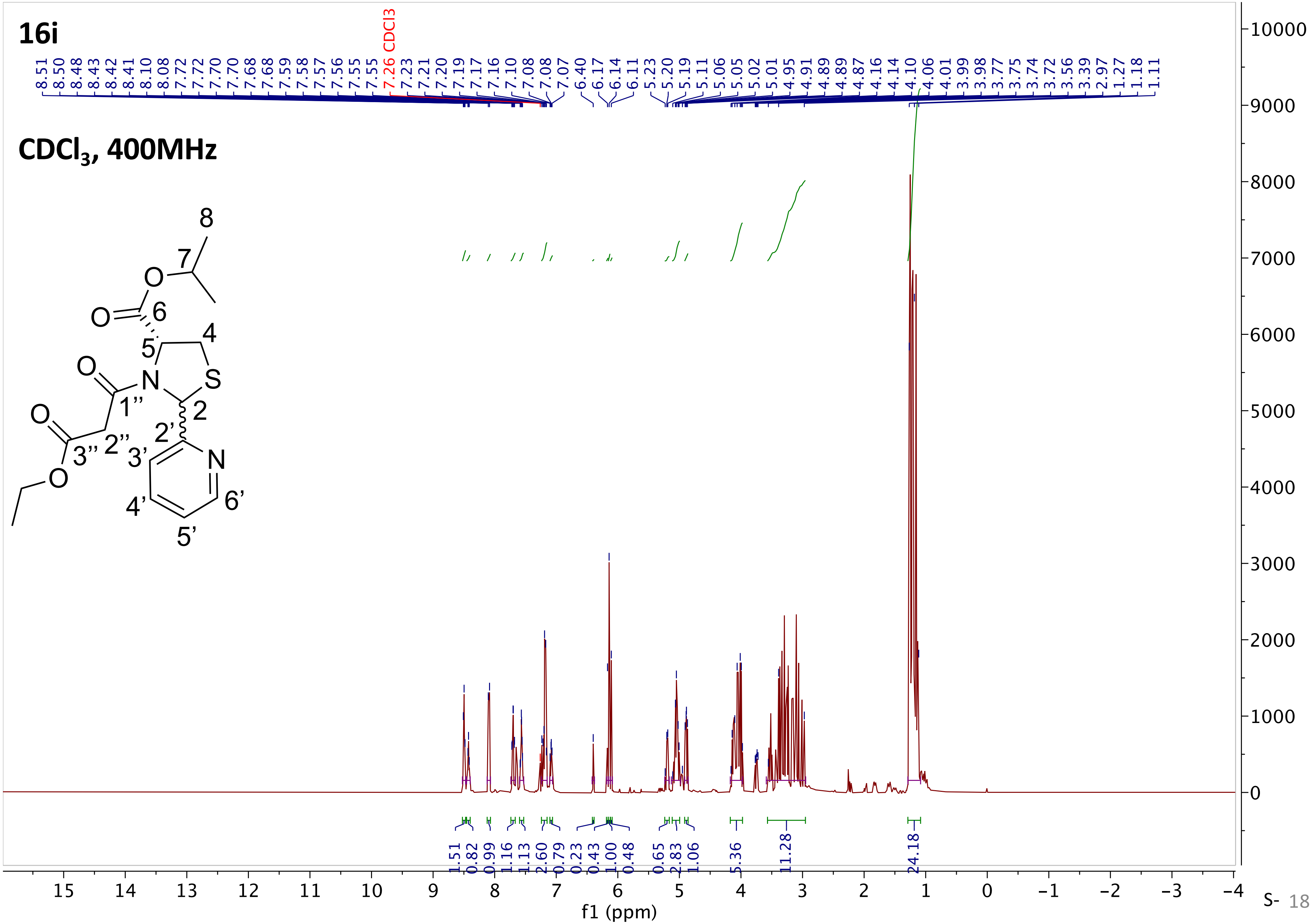

15i
CDCl$_3$, 400MHz
f1 (ppm)

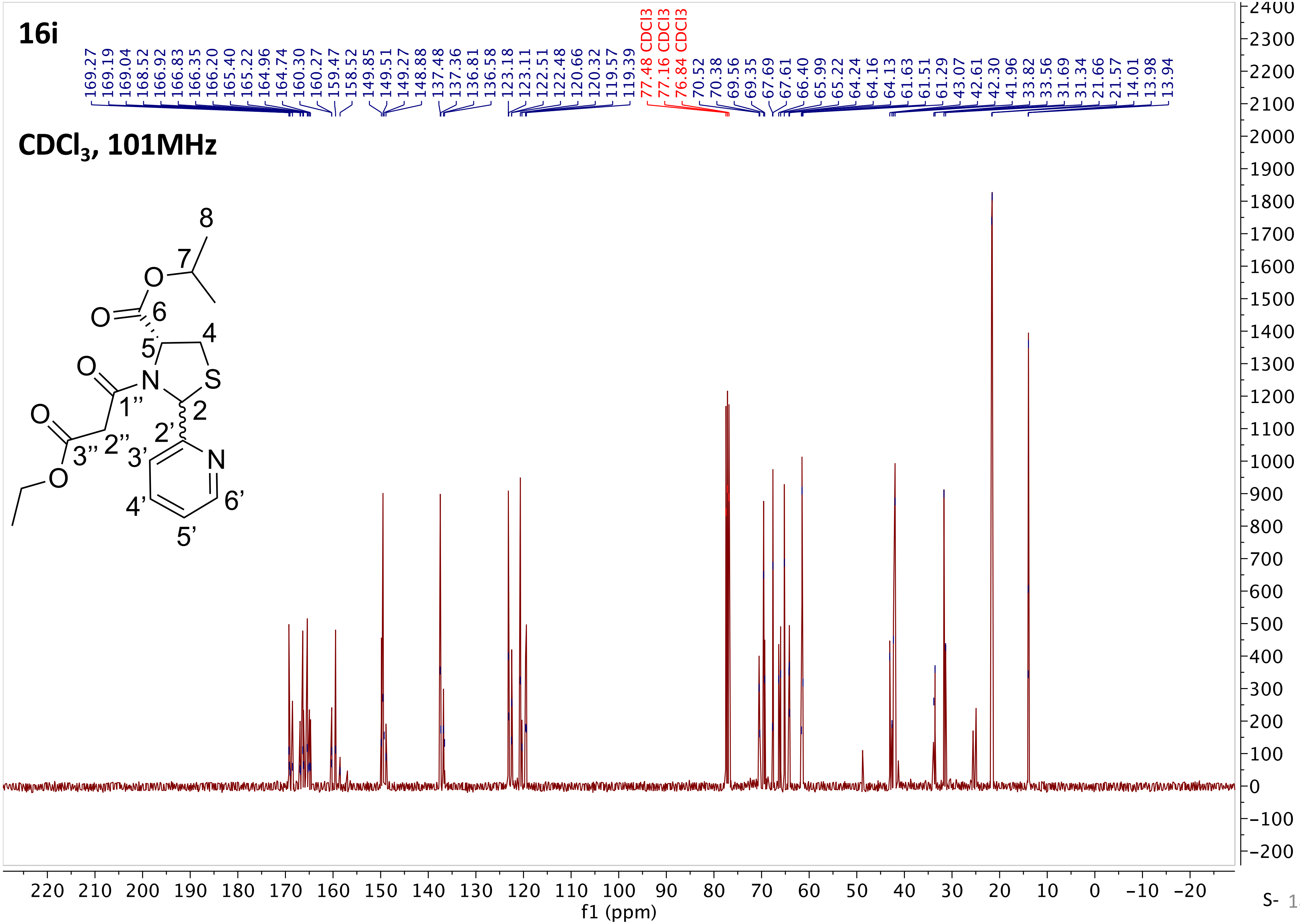

15i
CDCl3, 101MHz
169.64
166.42
165.61
159.37
149.63
137.64
131.47
123.32
120.74
118.95
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.70
66.39
64.94
61.68
42.06
31.84
14.05
f1 (ppm)



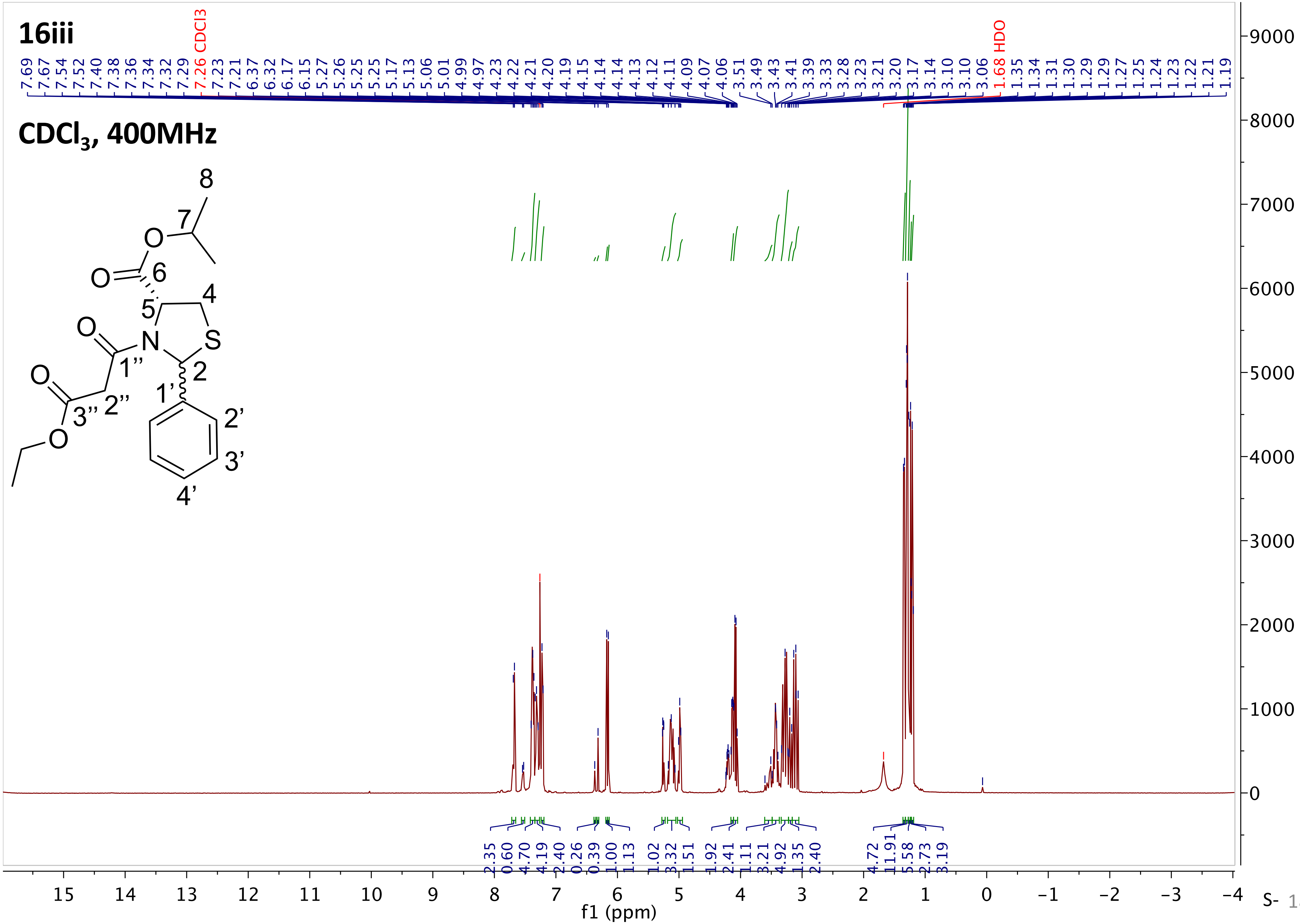
15iii
CDCl3, 400MHz
7.67 7.65 7.52 7.51 7.40 7.38 7.36 7.34 7.32 7.26 CDCl3 7.23 7.21 6.37 6.33 6.19 6.15 6.01 5.93 5.88 5.41 5.37 5.30 5.21 5.11 5.10 5.08 4.75 4.74 4.74 4.72 4.70 4.69 4.22 4.13 4.07 4.06 3.61 3.44 3.36 3.28 3.21 3.14 3.12 3.10 3.08 1.60 HDO 1.26 1.25 1.24 1.23 1.22 1.21 1.19
2.67 0.54 4.84 2.15 2.22 0.26 0.31 1.00 1.33 2.57 7.03 1.58 5.59 7.55 4.32 6.61 2.57 10.18
f1 (ppm)


15iii
CDCl3, 126MHz
169.51
168.76
166.91
166.41
165.66
165.48
142.17
141.98
139.92
138.79
131.73
131.64
131.10
129.42
129.16
128.78
128.69
128.37
128.14
127.22
126.64
125.08
124.88
119.96
119.82
119.08
118.82
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.52
66.50
65.22
64.98
64.50
64.28
64.07
61.94
61.87
61.77
61.63
43.60
43.13
42.59
42.30
33.25
32.60
32.26
31.20
14.25
14.23
14.19
14.15
f1 (ppm)

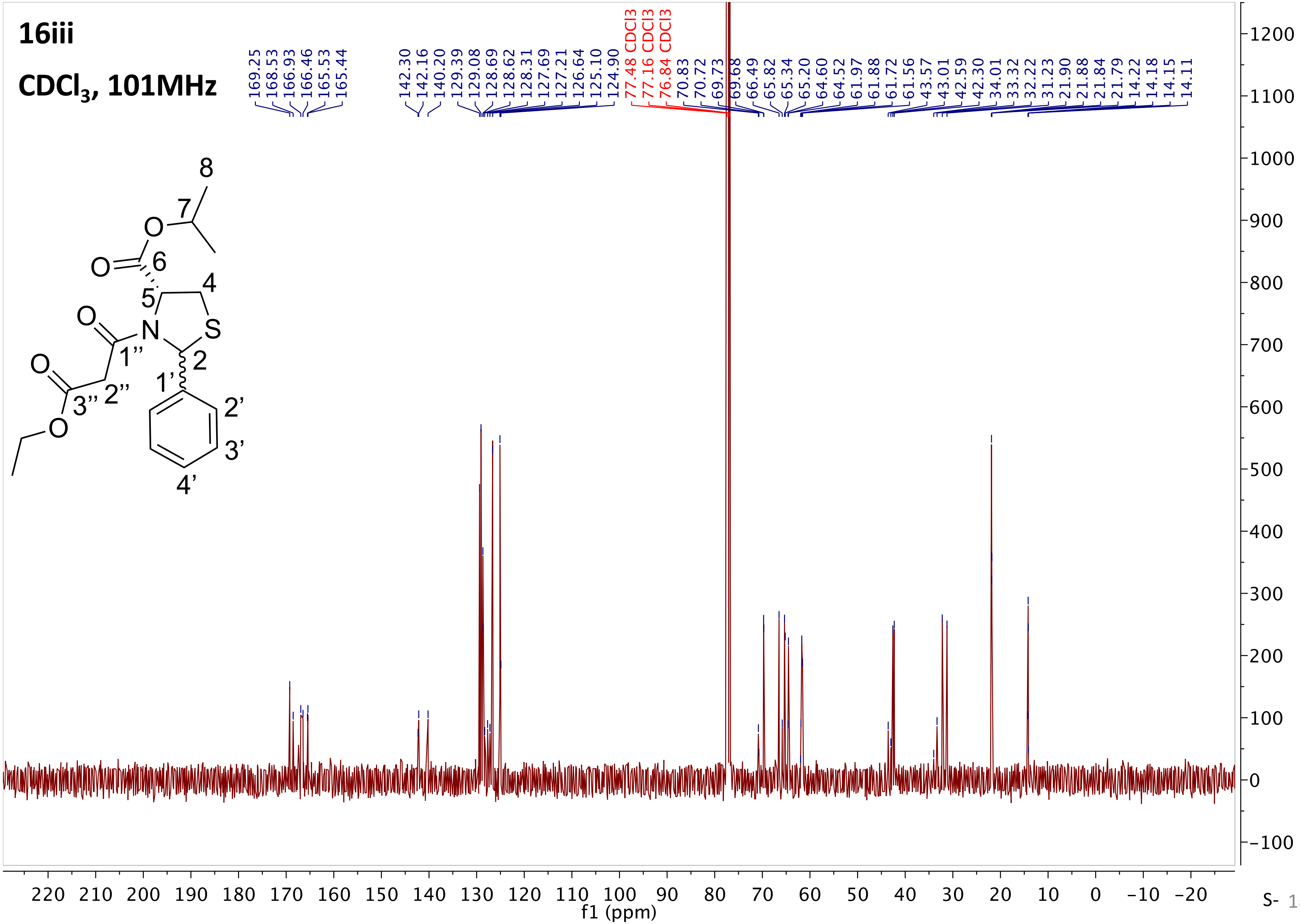

16i
CDCl$_3$, 400MHz
8.51 8.50 8.48 8.43 8.42 8.41 8.10 8.08 7.72 7.72 7.70 7.70 7.68 7.68 7.59 7.58 7.57 7.56 7.55 7.55 7.26 CDCl3 7.23 7.21 7.20 7.19 7.17 7.16 7.10 7.08 7.08 7.07 6.40 6.17 6.14 6.11 5.23 5.20 5.19 5.11 5.06 5.05 5.02 5.01 4.95 4.91 4.89 4.89 4.87 4.16 4.14 4.10 4.06 4.01 3.99 3.98 3.77 3.75 3.74 3.72 3.56 3.39 2.97 1.27 1.18 1.11
1.51 0.82 0.99 1.16 1.13 2.60 0.79 0.23 0.43 1.00 0.48 0.65 2.83 1.06 5.36 11.28 24.18
f1 (ppm)

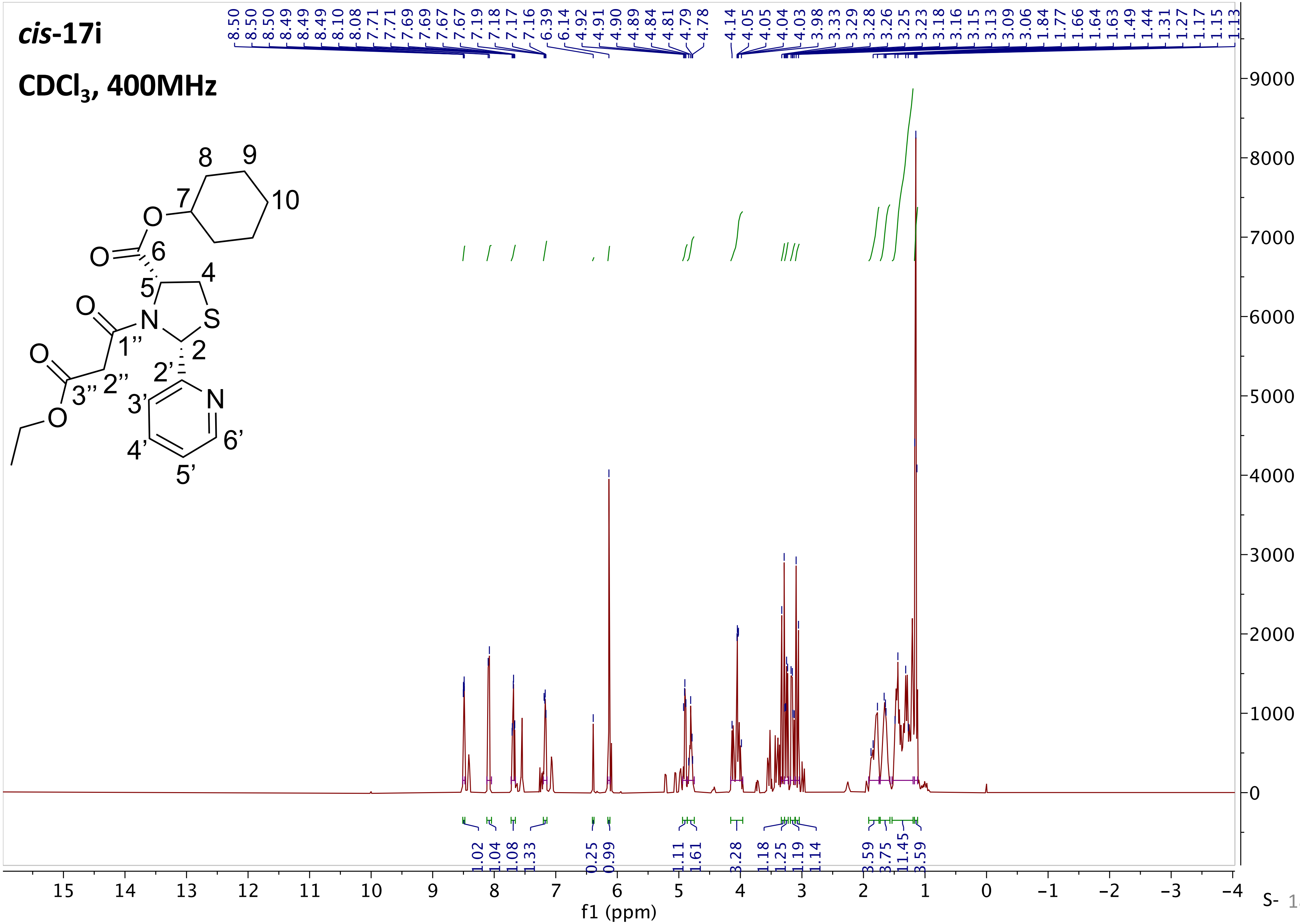


16i
CDCl3, 101MHz
169.27 169.19 169.04 168.52 166.92 166.83 166.35 166.20 165.40 165.22 164.96 164.74 160.30 160.27 159.47 158.52 149.85 149.51 149.27 148.88 137.48 137.36 136.81 136.58 123.18 123.11 122.51 122.48 120.66 120.32 119.57 119.39
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
70.52 70.38 69.56 69.35 67.69 67.61 66.40 65.99 65.22 64.24 64.16 64.13 61.63 61.51 61.29 43.07 42.61 42.30 41.96 33.82 33.56 31.69 31.34 21.66 21.57 14.01 13.98 13.94
f1 (ppm)



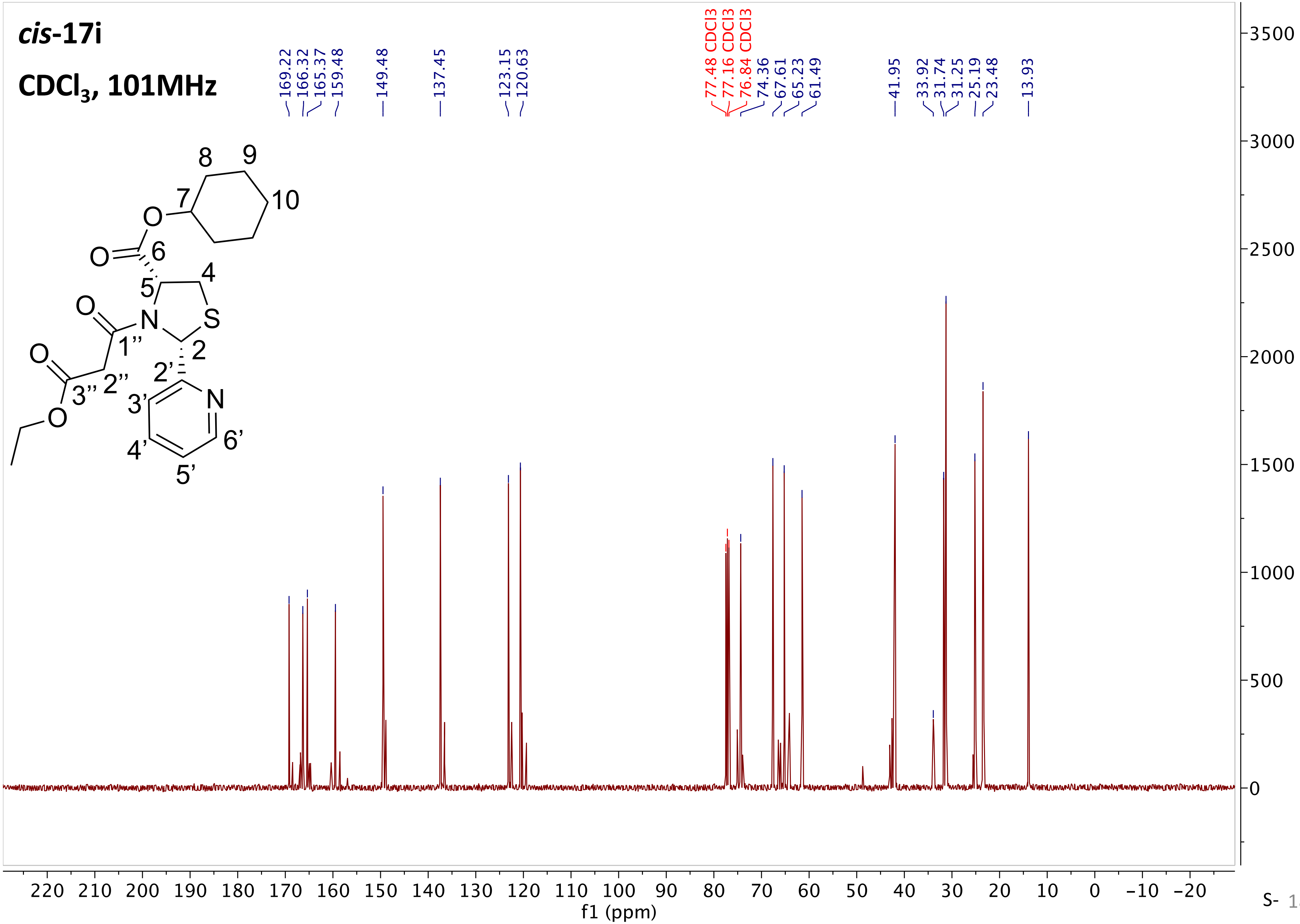
16iii
CDCl$_3$, 400MHz
7.69 7.67 7.54 7.52 7.40 7.38 7.36 7.34 7.32 7.29 7.26 CDCl3 7.23 7.21 6.37 6.32 6.17 6.15 5.27 5.26 5.25 5.25 5.17 5.13 5.06 5.01 4.99 4.97 4.23 4.22 4.21 4.20 4.19 4.15 4.14 4.14 4.13 4.12 4.11 4.09 4.07 4.06 3.51 3.49 3.43 3.41 3.39 3.33 3.28 3.23 3.21 3.20 3.17 3.14 3.10 3.10 3.06 1.68 HDO 1.35 1.34 1.31 1.30 1.29 1.29 1.27 1.25 1.24 1.23 1.22 1.21 1.19
2.35 0.60 4.70 4.19 2.40 0.26 0.39 1.00 1.13 1.02 3.32 1.51 1.92 2.41 1.11 3.21 4.92 1.35 2.40 4.72 11.91 5.58 2.73 3.19
f1 (ppm)

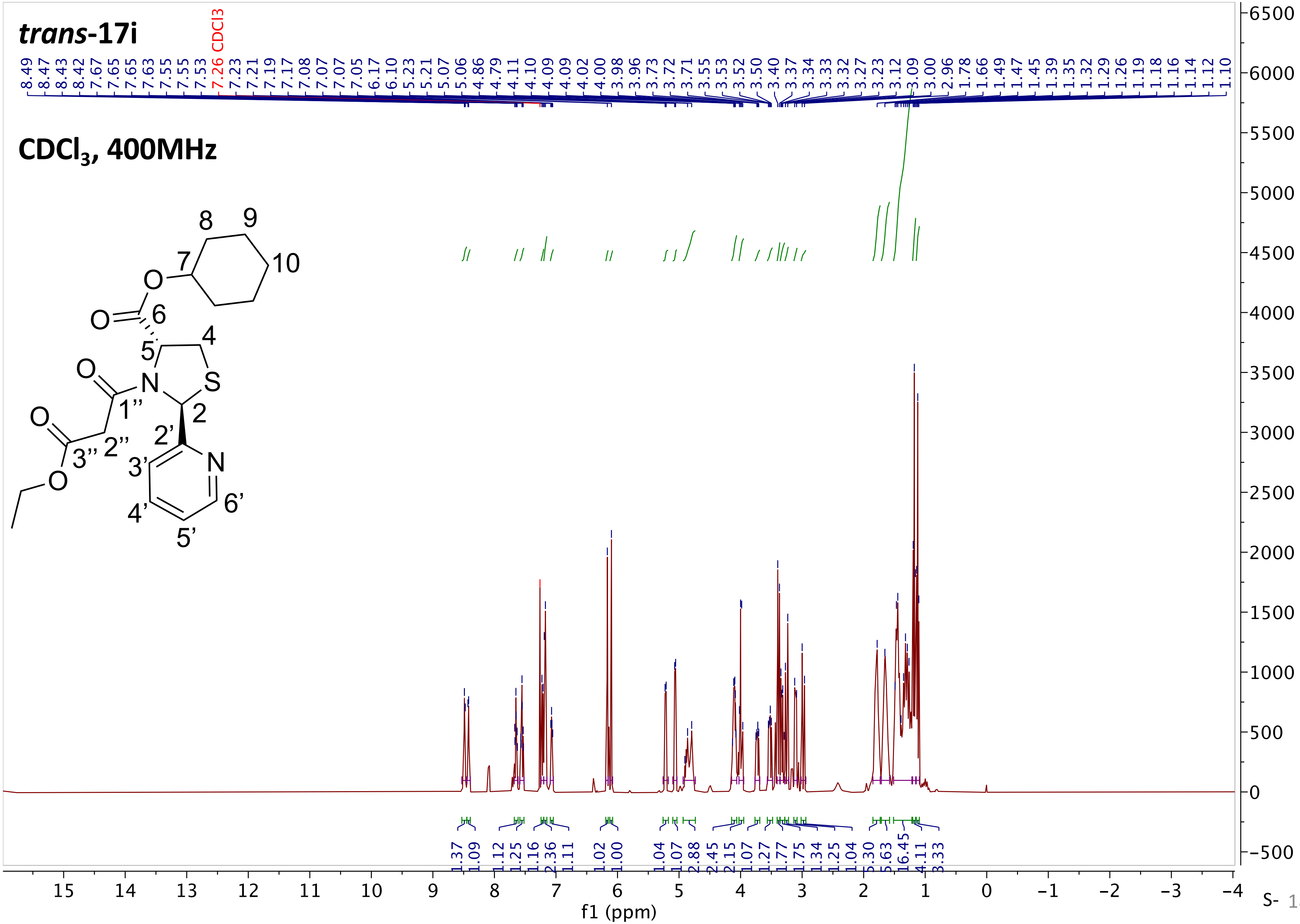

16iii
CDCl3, 101MHz
169.25
168.53
166.93
166.46
165.53
165.44
142.30
142.16
140.20
129.39
129.08
128.69
128.62
128.31
127.69
127.21
126.64
125.10
124.90
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.83
70.72
69.73
69.68
66.49
65.82
65.34
65.20
64.60
64.52
61.97
61.88
61.72
61.56
43.57
43.01
42.59
42.30
34.01
33.32
32.22
31.23
21.90
21.88
21.84
21.79
14.22
14.18
14.15
14.11
f1 (ppm)


cis-17i
CDCl3, 400MHz
8.50 8.50 8.50 8.49 8.49 8.49 8.10 8.08 7.71 7.71 7.69 7.69 7.67 7.67 7.19 7.18 7.17 7.16 6.39 6.14 4.92 4.91 4.90 4.89 4.84 4.81 4.79 4.78
4.14 4.05 4.05 4.04 4.03 3.98 3.33 3.29 3.28 3.26 3.25 3.23 3.18 3.16 3.15 3.13 3.09 3.06 1.84 1.77 1.66 1.64 1.63 1.49 1.44 1.31 1.27 1.17 1.15 1.13
1.02 1.04 1.08 1.33 0.25 0.99 1.11 1.61 3.28 1.18 1.25 1.19 1.14 3.59 3.75 11.45 3.59
f1 (ppm)

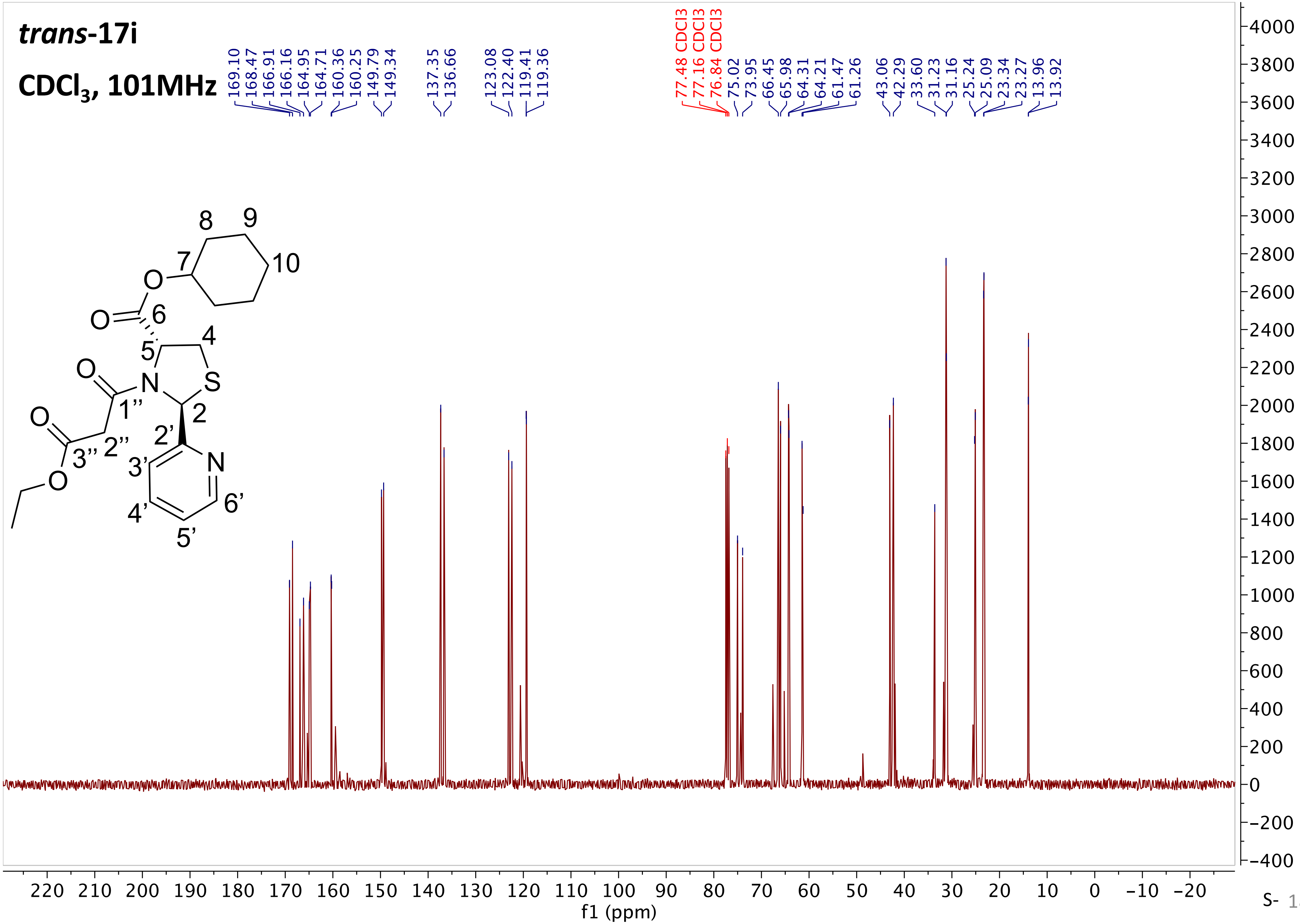
***cis*-17i**

$CDCl_3$, 101MHz

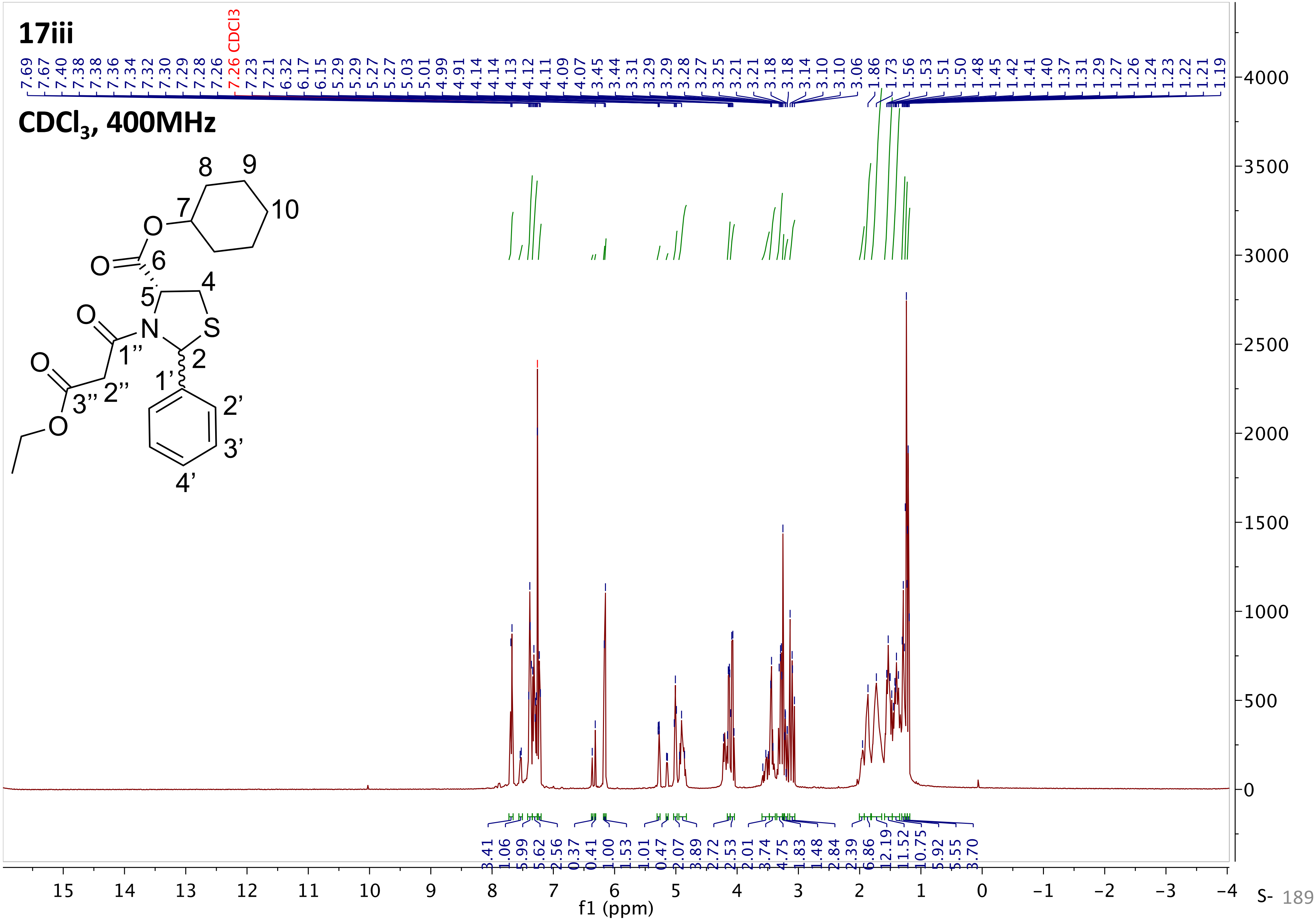




trans-17i
CDCl$_3$, 400MHz
8.49 8.47 8.43 8.42 7.67 7.65 7.65 7.63 7.55 7.55 7.53 7.26 CDCl3 7.23 7.21 7.19 7.17 7.08 7.07 7.07 7.05 6.17 6.10 5.23 5.21 5.07 5.06 4.86 4.79 4.11 4.10 4.09 4.09 4.02 4.00 3.98 3.96 3.73 3.72 3.71 3.55 3.53 3.52 3.50 3.40 3.37 3.34 3.33 3.32 3.27 3.23 3.12 3.09 3.00 2.96 1.78 1.66 1.49 1.47 1.45 1.39 1.35 1.32 1.29 1.26 1.19 1.18 1.16 1.14 1.12 1.10
1.37 1.09 1.12 1.25 1.16 2.36 1.11 1.02 1.00 1.04 1.07 2.88 2.45 2.15 1.07 1.27 1.77 1.75 1.34 1.25 1.04 5.30 5.63 16.45 4.11 3.33
f1 (ppm)



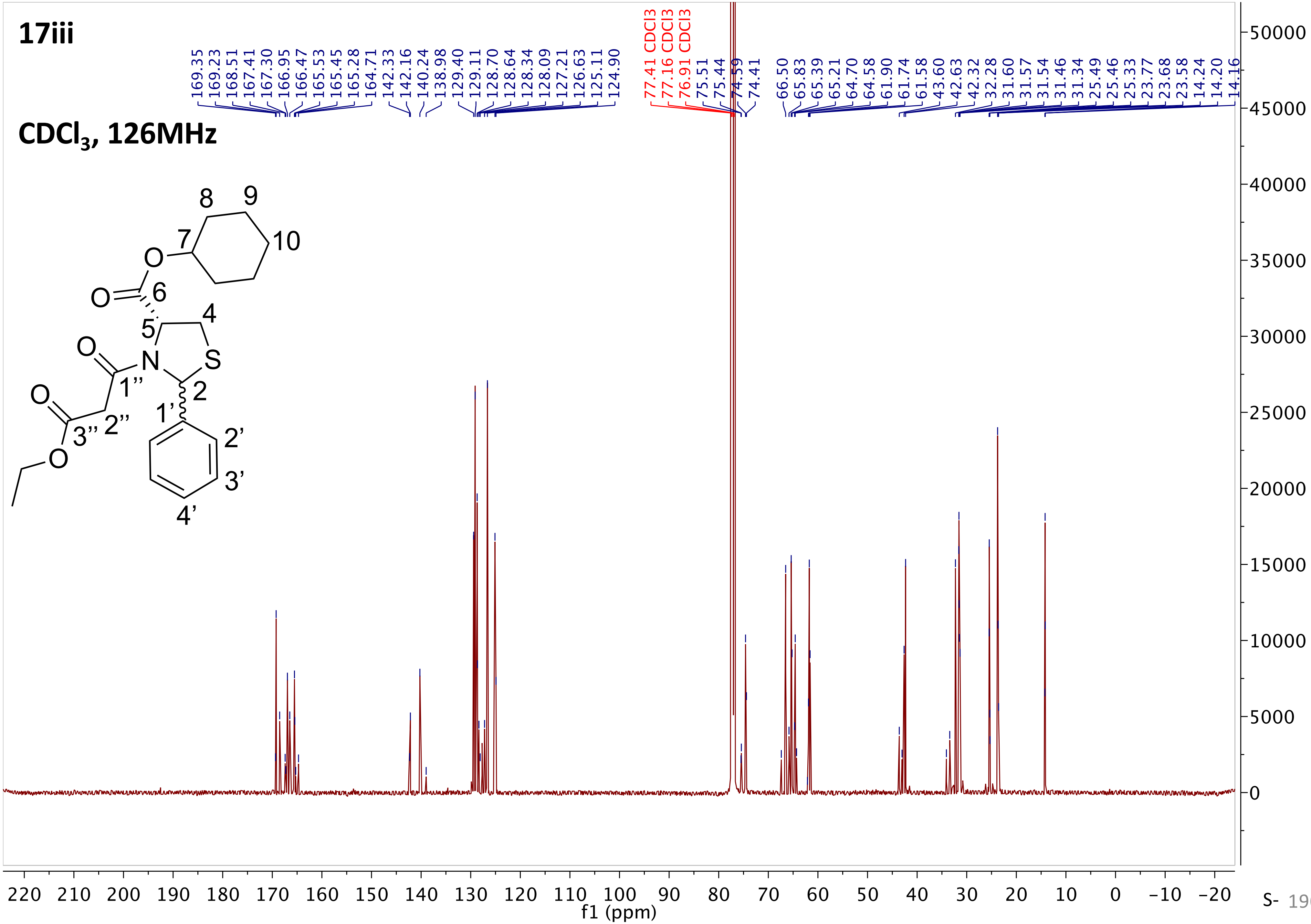
trans-17i
CDCl3, 101MHz
169.10
168.47
166.91
166.16
164.95
164.71
160.36
160.25
149.79
149.34
137.35
136.66
123.08
122.40
119.41
119.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.02
73.95
66.45
65.98
64.31
64.21
61.47
61.26
43.06
42.29
33.60
31.23
31.16
25.24
25.09
23.34
23.27
13.96
13.92
f1 (ppm)

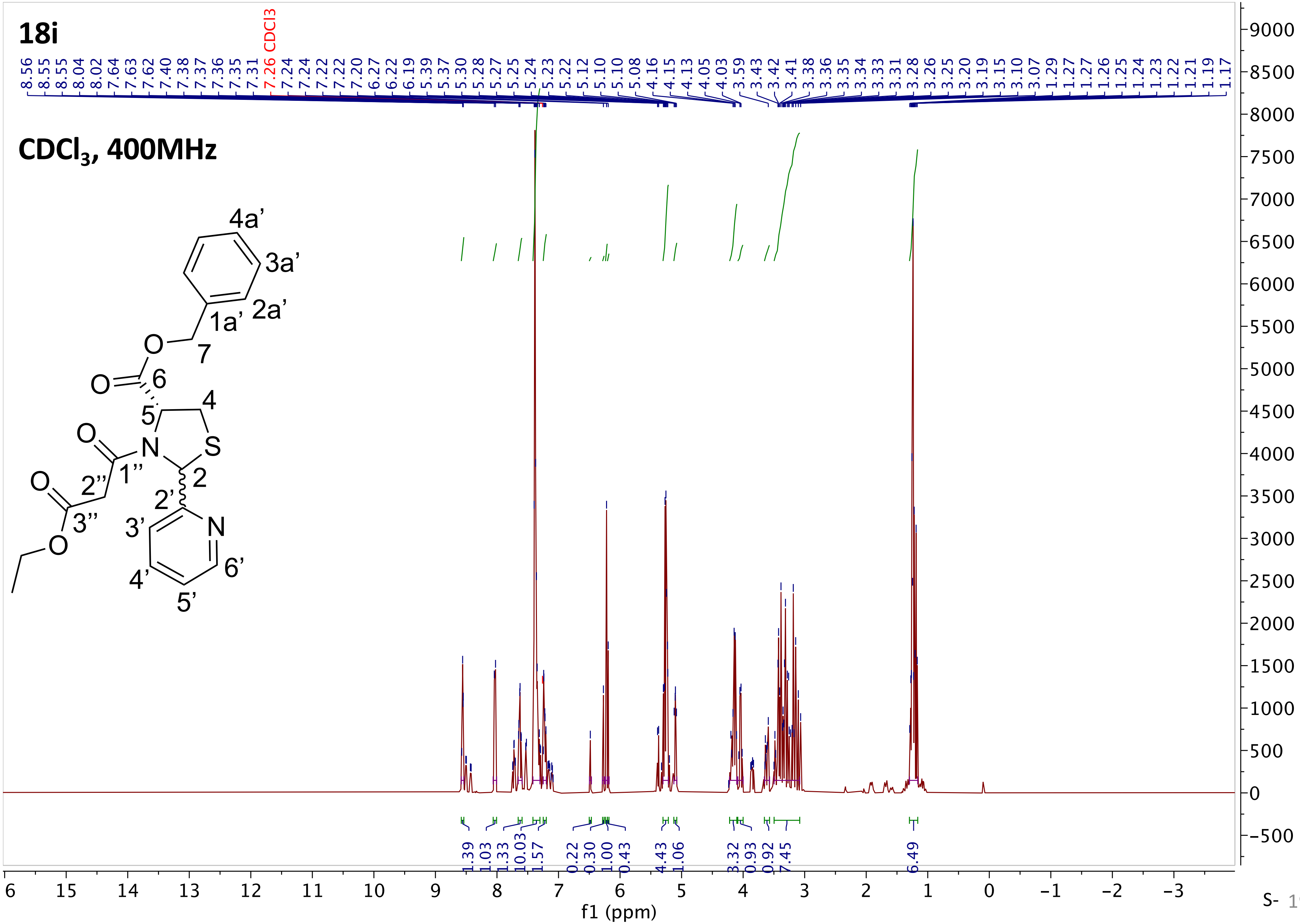


17iii
CDCl3, 400MHz
f1 (ppm)

17iii

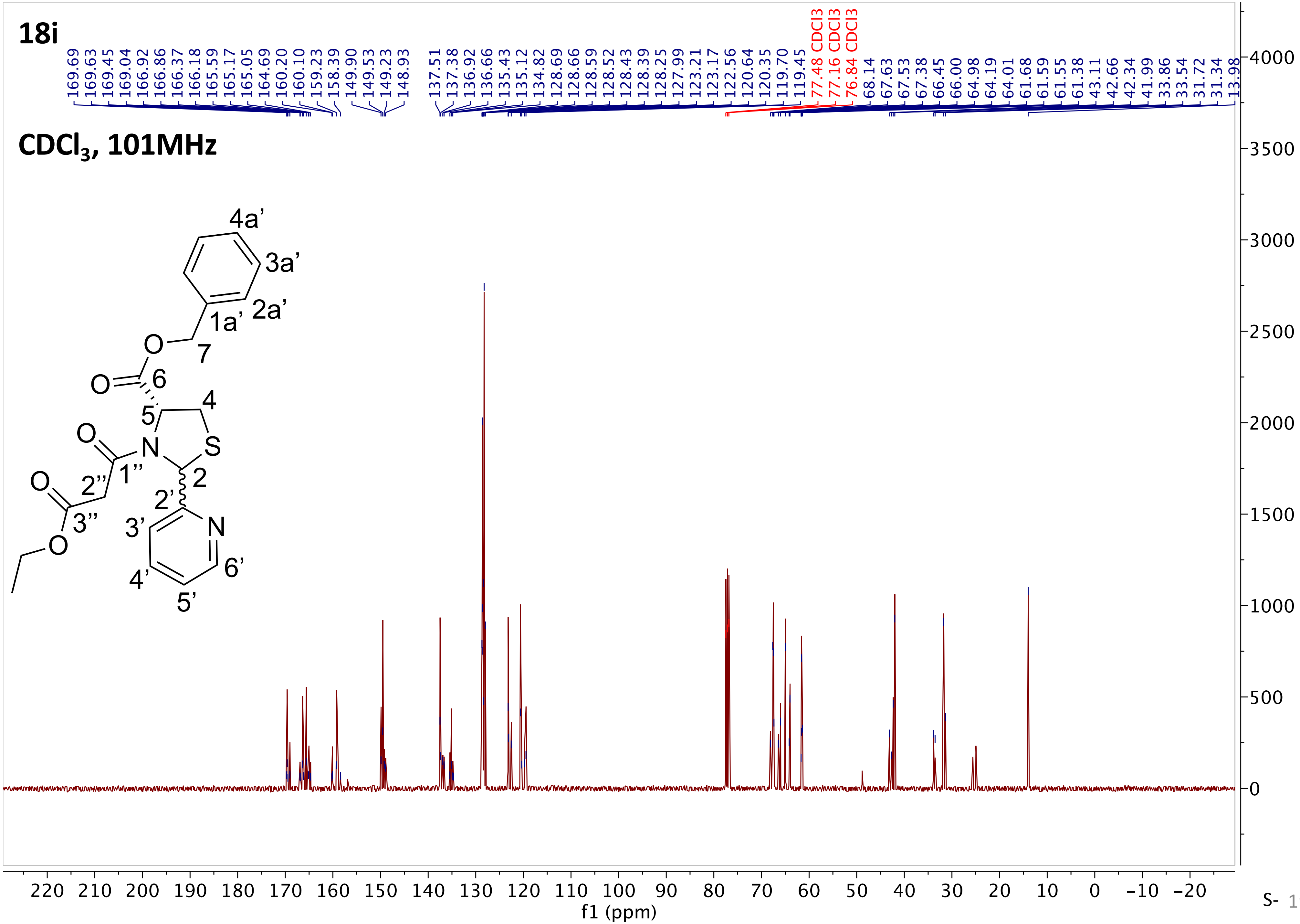
$CDCl_3$, 126MHz




18i
CDCl$_3$, 400MHz
f1 (ppm)

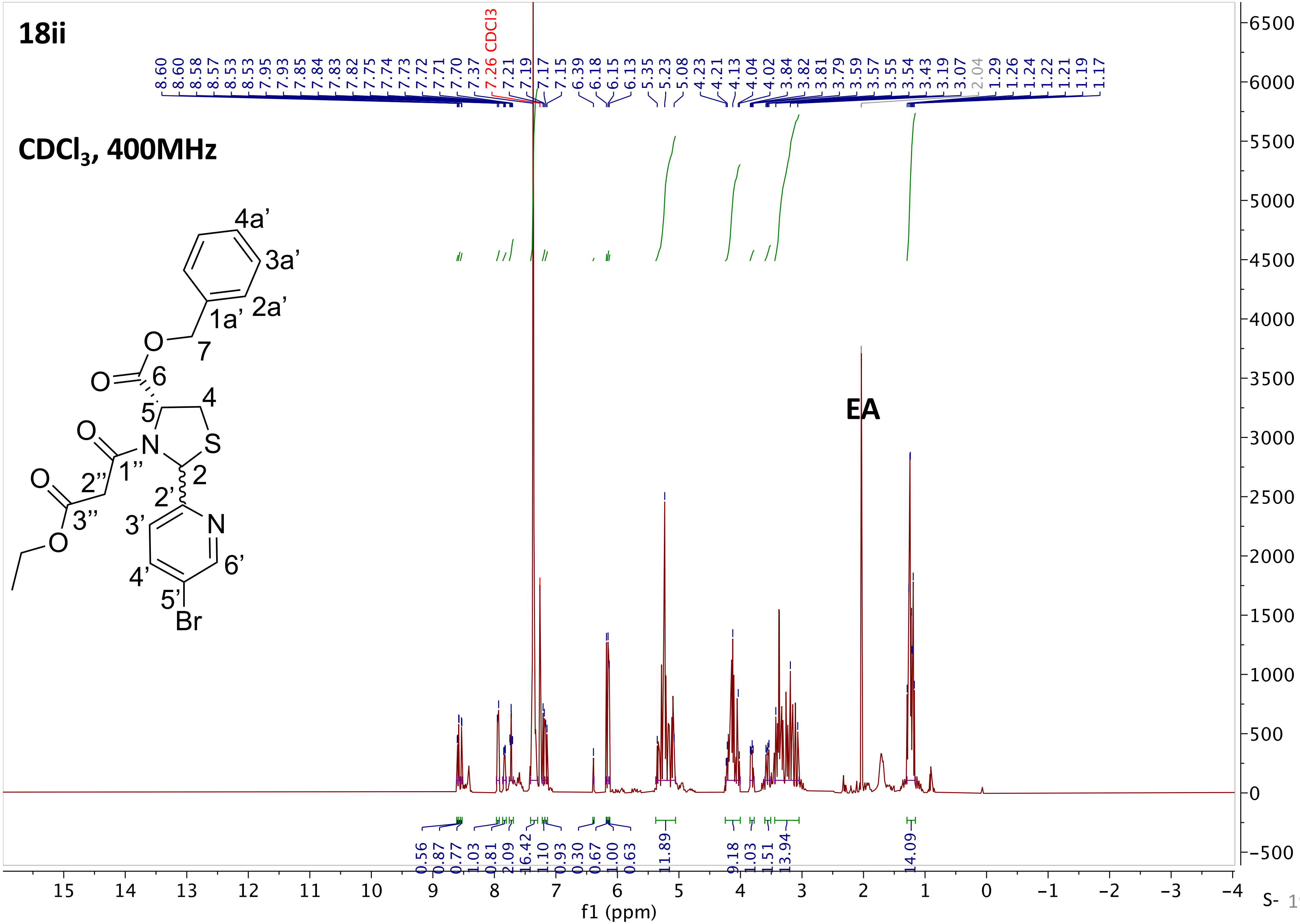
18i

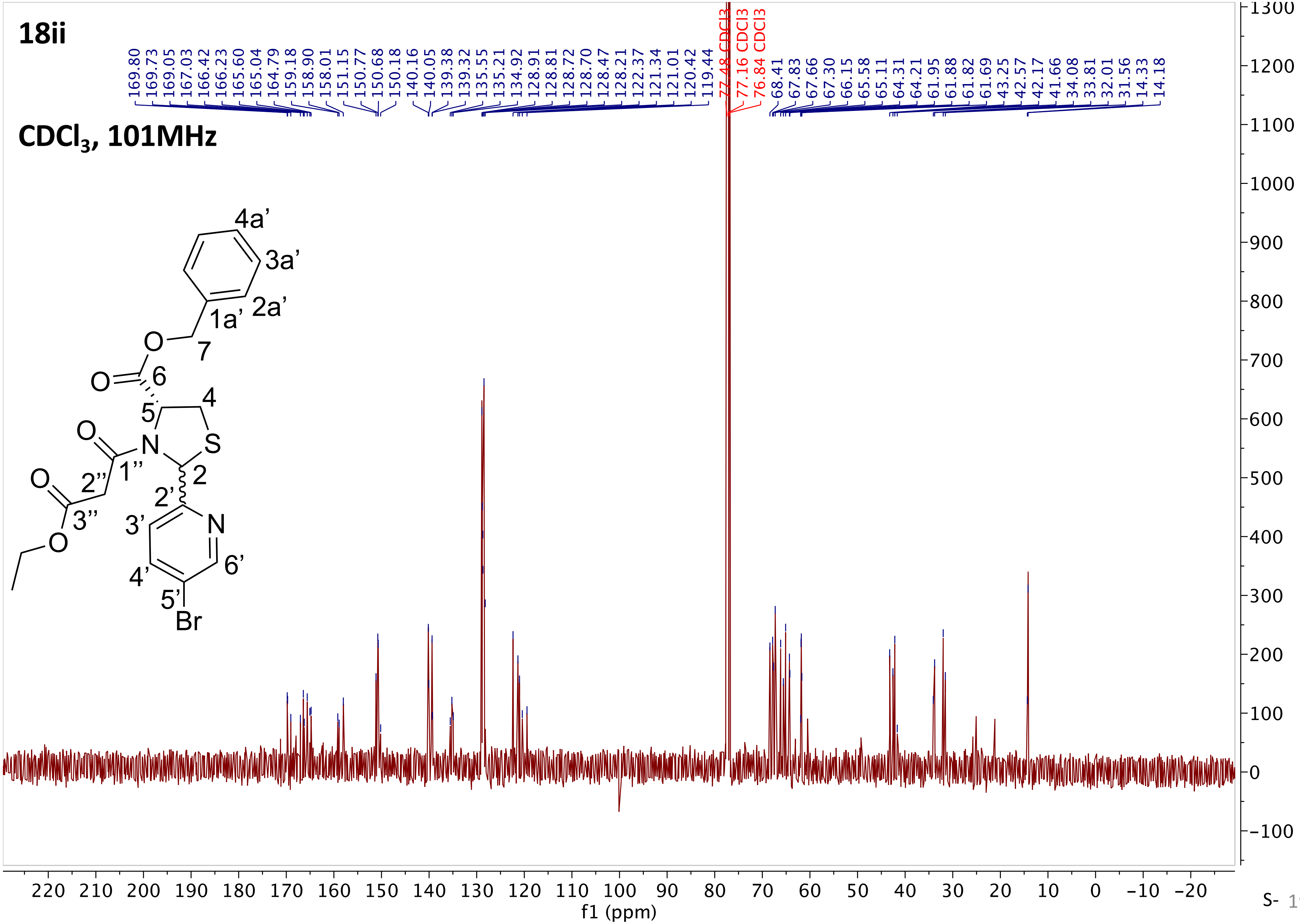
$CDCl_3$, 101MHz

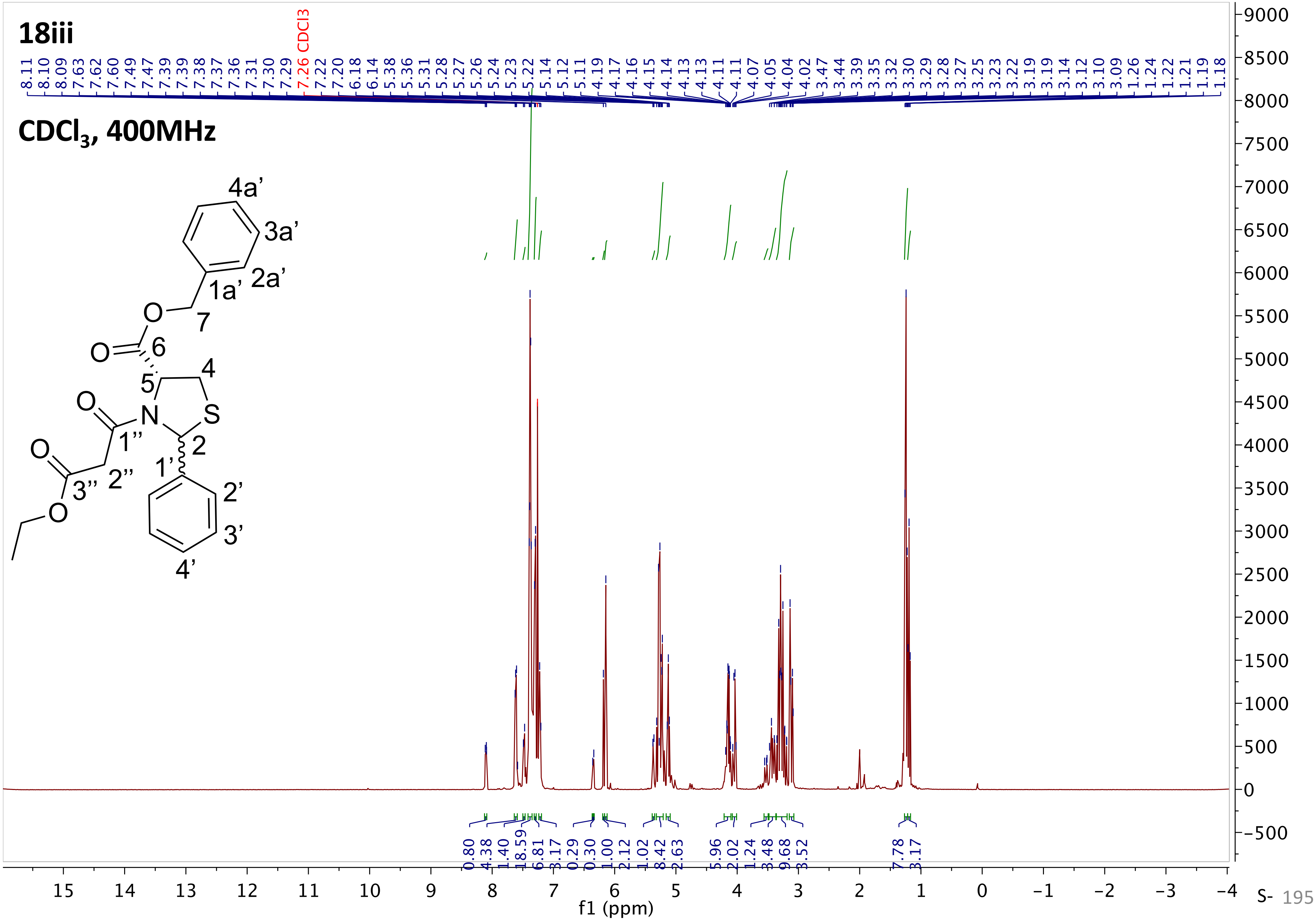


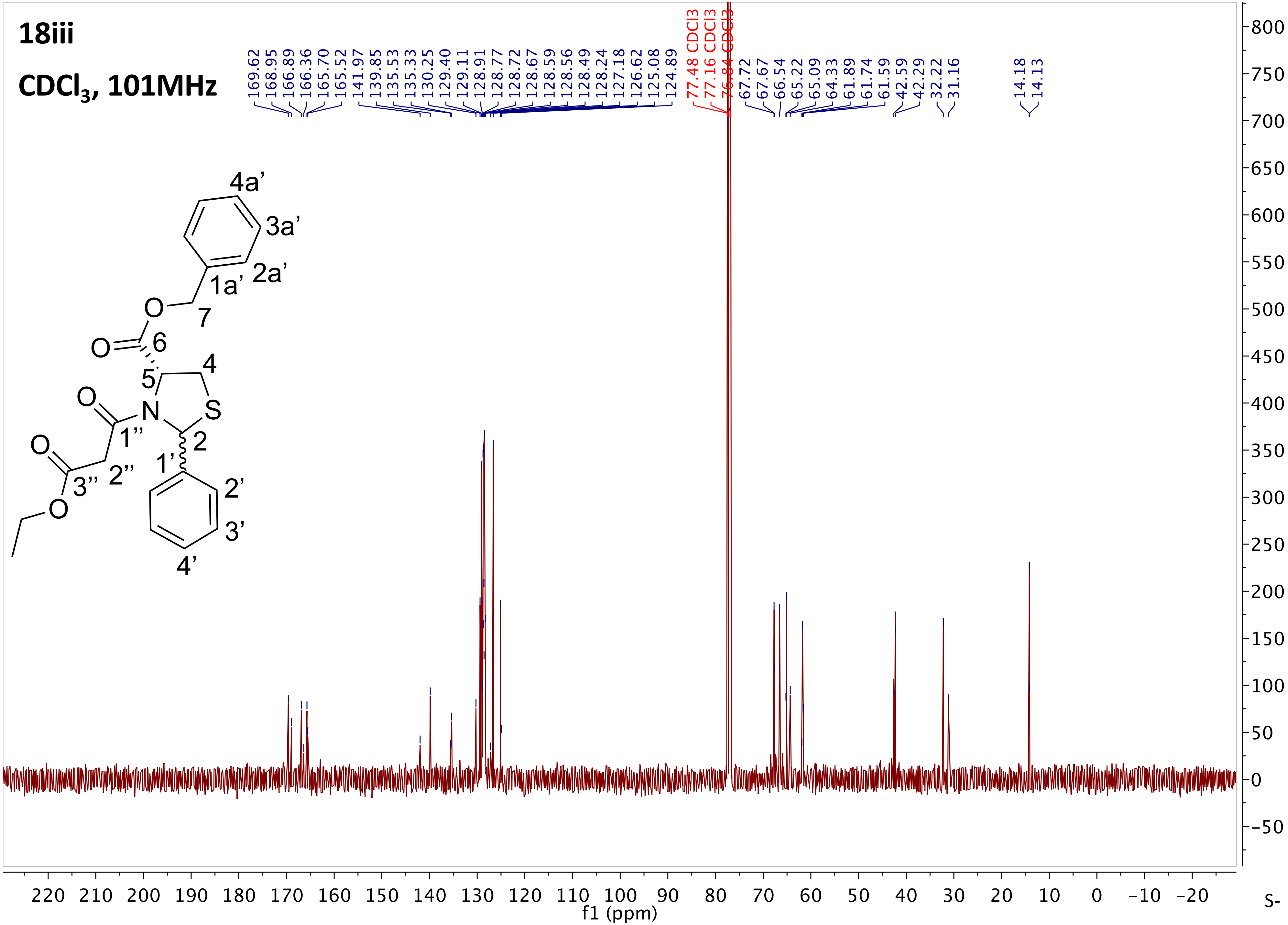
18ii

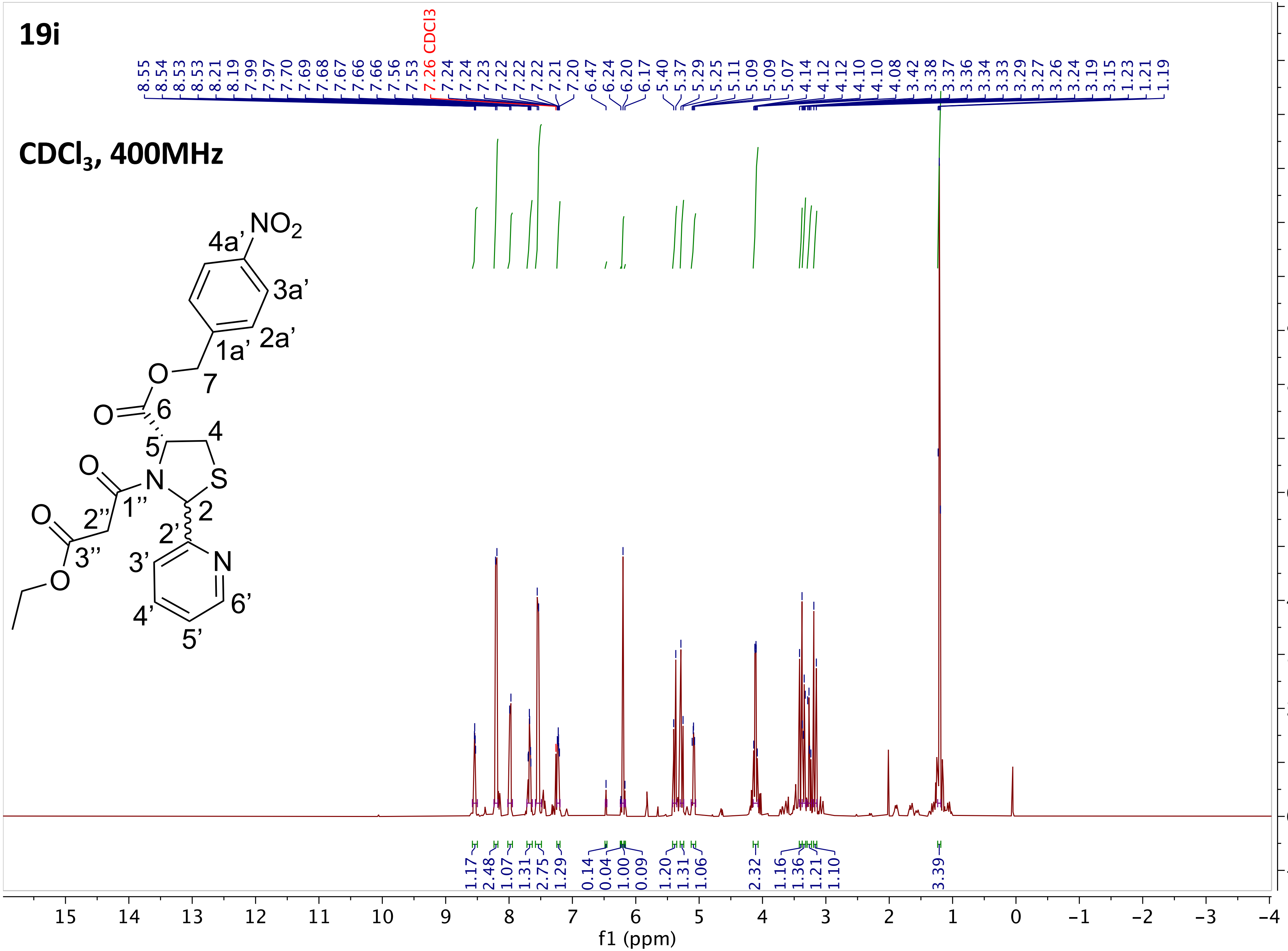
CDCl$_3$, 400MHz

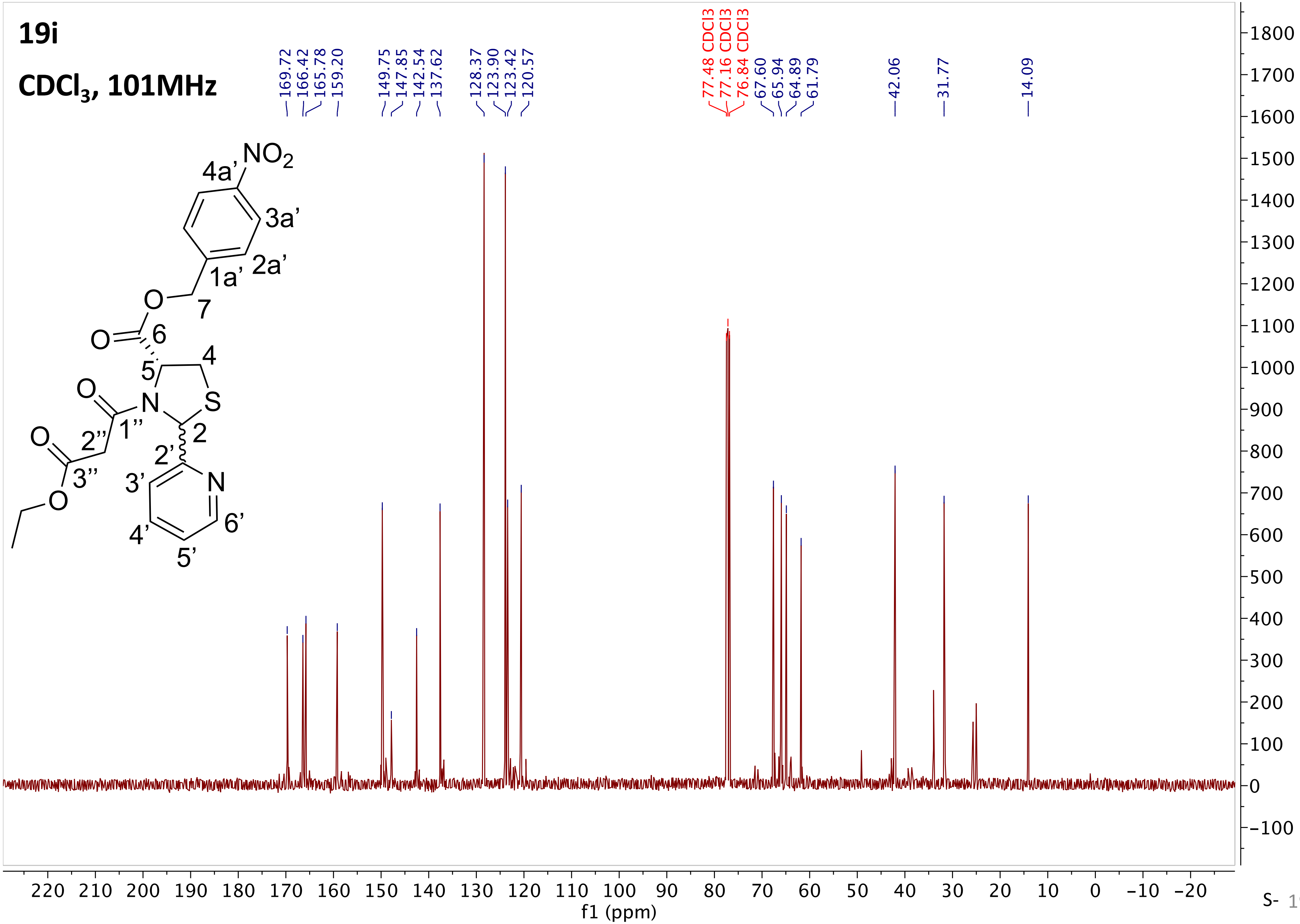



18ii
CDCl$_3$, 101MHz
169.80
169.73
169.05
167.03
166.42
166.23
165.60
165.04
164.79
159.18
158.90
158.01
151.15
150.77
150.68
150.18
140.16
140.05
139.38
139.32
135.55
135.21
134.92
128.91
128.81
128.72
128.70
128.47
128.21
122.37
121.34
121.01
120.42
119.44
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.41
67.83
67.66
67.30
66.15
65.58
65.11
64.31
64.21
61.95
61.88
61.82
61.69
43.25
42.57
42.17
41.66
34.08
33.81
32.01
31.56
14.33
14.18
f1 (ppm)


18iii
CDCl3, 400MHz
7.26 CDCl3
f1 (ppm)

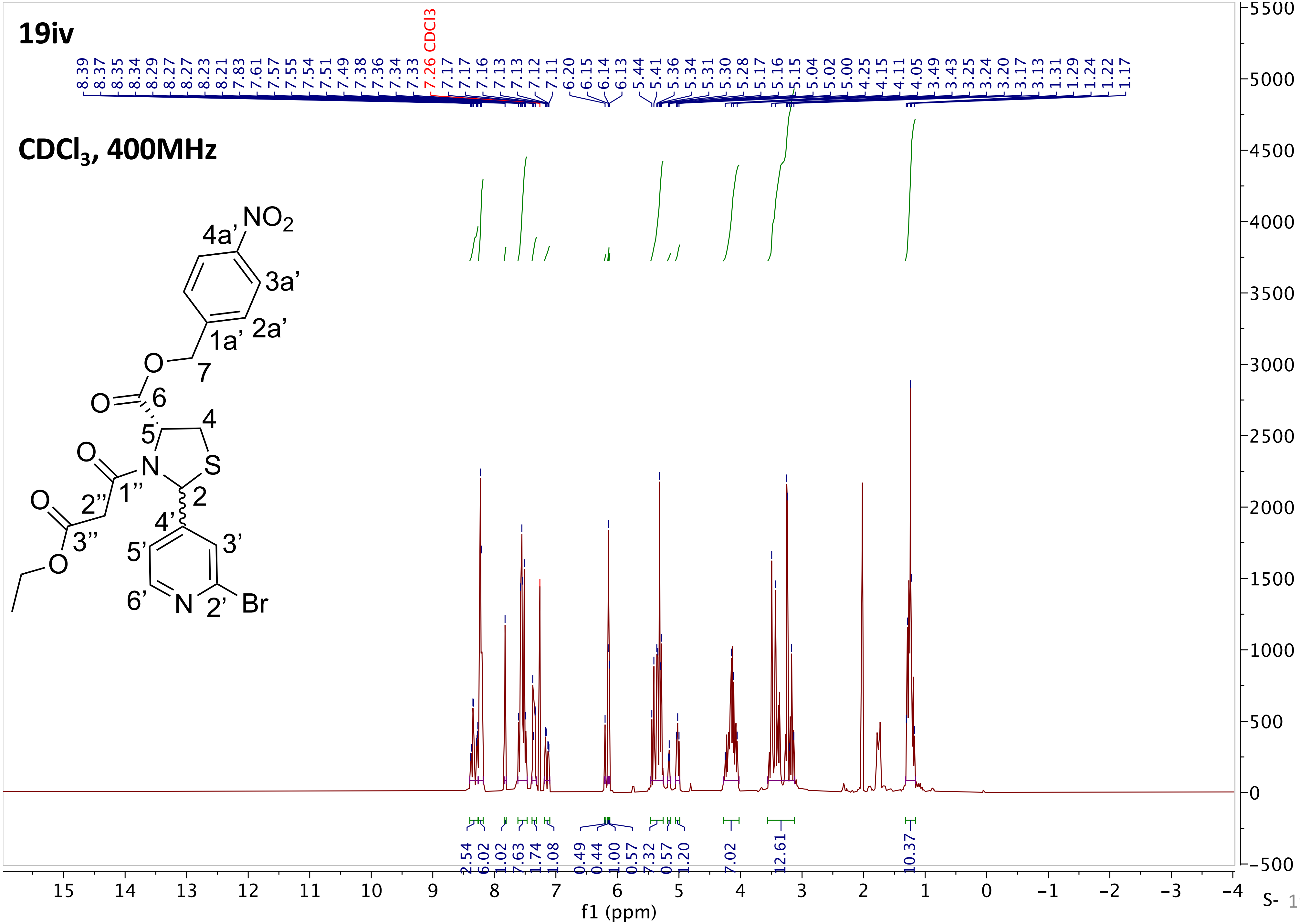

18iii
CDCl3, 101MHz
169.62
168.95
166.89
166.36
165.70
165.52
141.97
139.85
135.53
135.33
130.25
129.40
129.11
128.91
128.77
128.72
128.67
128.59
128.56
128.49
128.24
127.18
126.62
125.08
124.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.72
67.67
66.54
65.22
65.09
64.33
61.89
61.74
61.59
42.59
42.29
32.22
31.16
14.18
14.13
f1 (ppm)

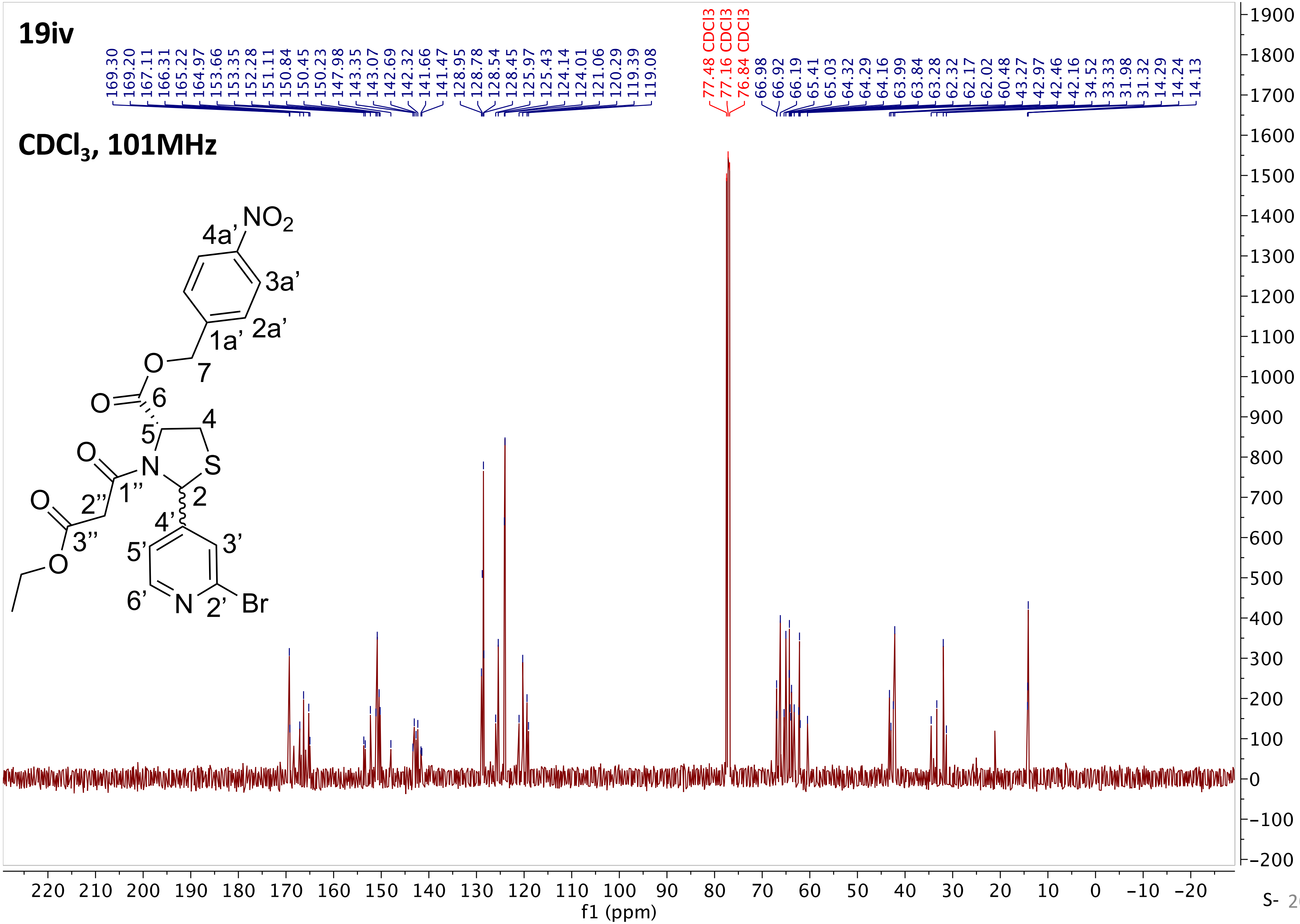

19i
CDCl3, 400MHz
8.55 8.54 8.53 8.53 8.21 8.19 7.99 7.97 7.70 7.69 7.68 7.67 7.66 7.66 7.56 7.53 7.26 CDCl3 7.24 7.24 7.23 7.22 7.22 7.22 7.21 7.20 6.47 6.24 6.20 6.17 5.40 5.37 5.29 5.25 5.11 5.09 5.09 5.07 4.14 4.12 4.12 4.10 4.10 4.08 3.42 3.38 3.37 3.36 3.34 3.33 3.29 3.27 3.26 3.24 3.19 3.15 1.23 1.21 1.19
1.17 2.48 1.07 1.31 2.75 1.29 0.14 0.04 1.00 0.09 1.20 1.31 1.06 2.32 1.16 1.36 1.21 1.10 3.39
NO2
4a'
3a'
2a'
1a'
O
7
O
6
5
4
O
N
S
1''
2''
O
2
2'
3''
3'
N
O
4'
6'
5'
f1 (ppm)

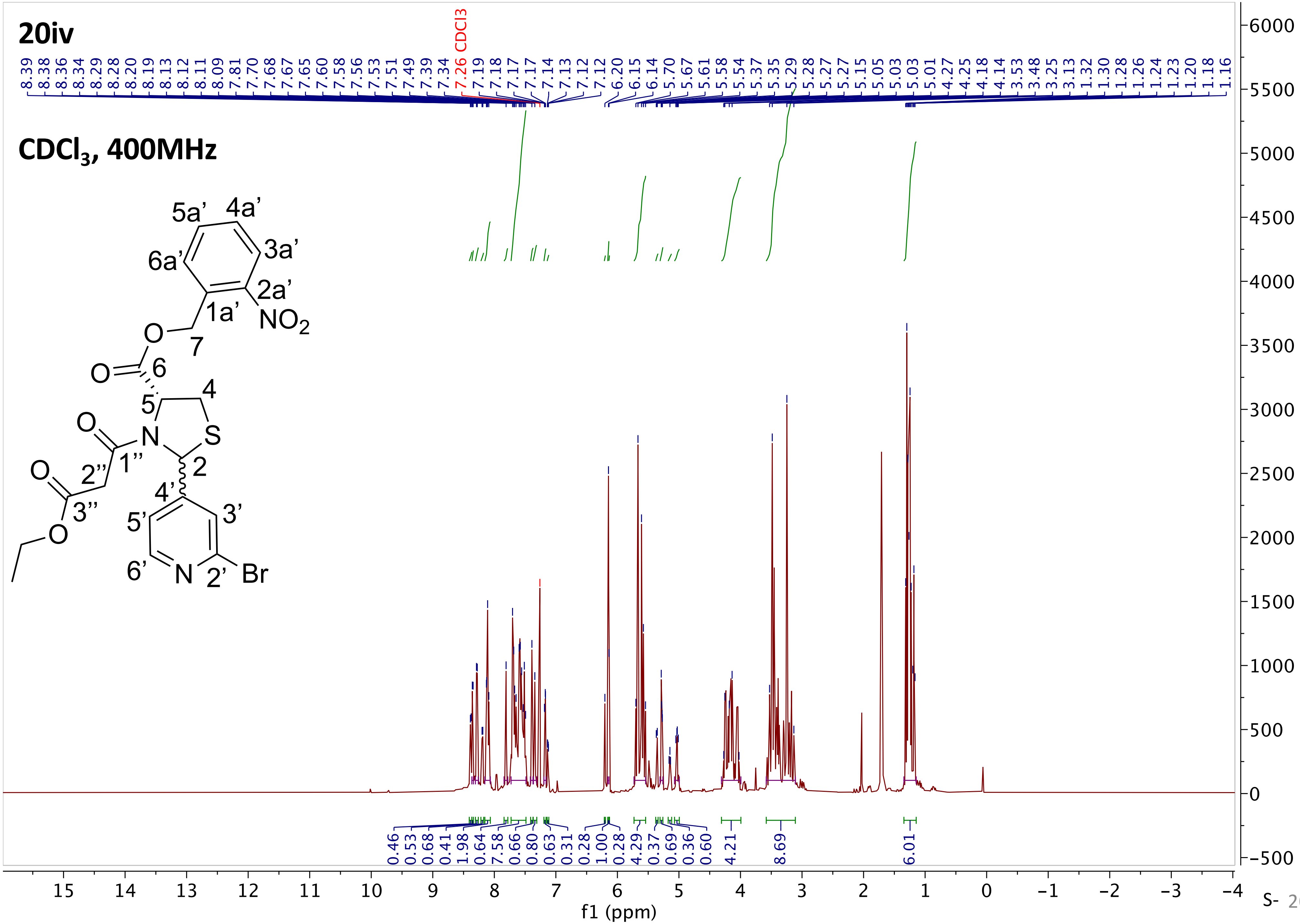

19i
CDCl3, 101MHz
169.72
166.42
165.78
159.20
149.75
147.85
142.54
137.62
128.37
123.90
123.42
120.57
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.60
65.94
64.89
61.79
42.06
31.77
14.09
f1 (ppm)

19iv

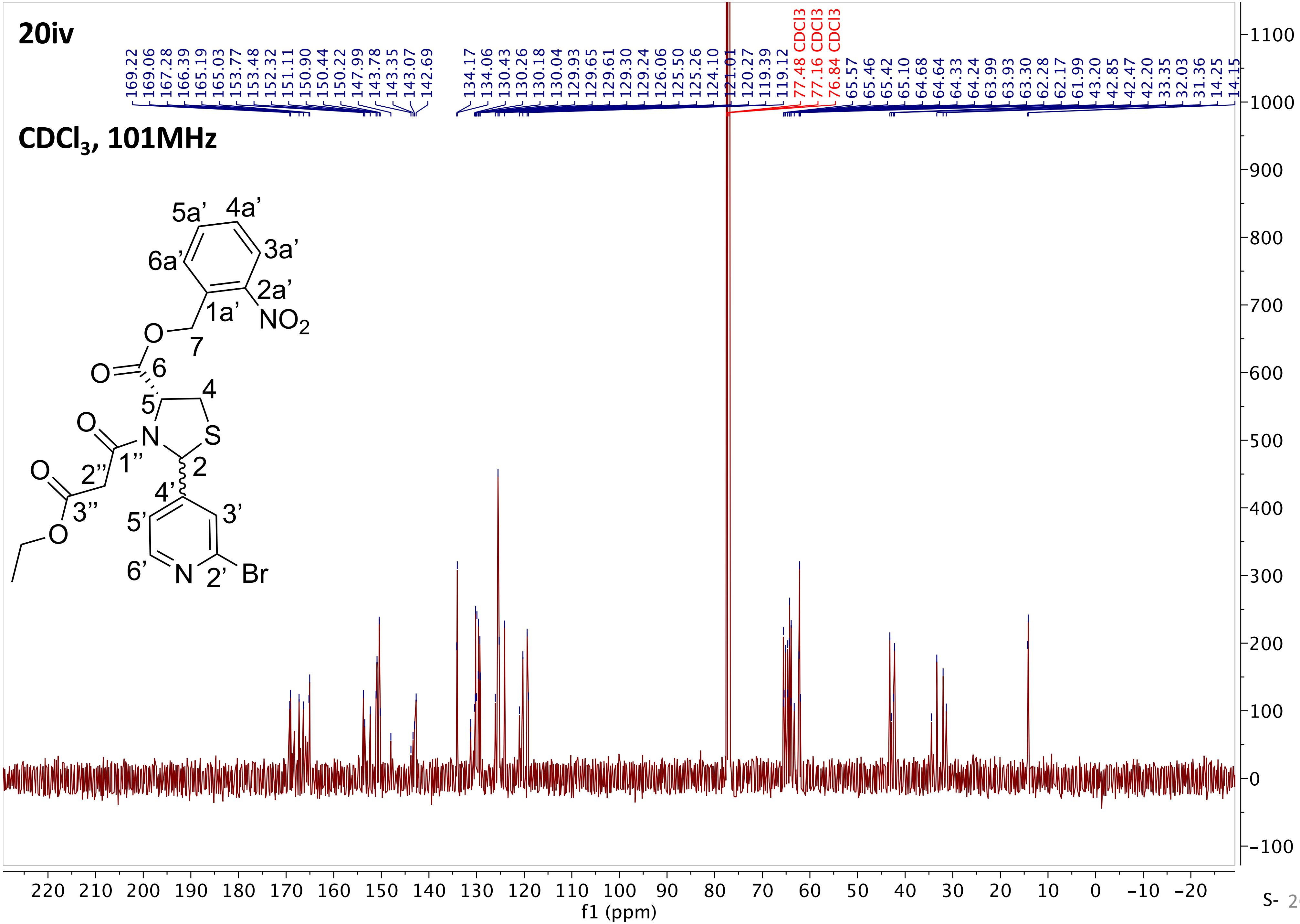
$CDCl_3$, 400MHz




19iv
CDCl3, 101MHz
169.30 169.20 167.11 166.31 165.22 164.97 153.66 153.35 152.28 151.11 150.84 150.45 150.23 147.98 143.35 143.07 142.69 142.32 141.66 141.47 128.95 128.78 128.54 128.45 125.97 125.43 124.14 124.01 121.06 120.29 119.39 119.08
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
66.98 66.92 66.19 65.41 65.03 64.32 64.29 64.16 63.99 63.84 63.28 62.32 62.17 62.02 60.48 43.27 42.97 42.46 42.16 34.52 33.33 31.98 31.32 14.29 14.24 14.13
NO2
4a'
3a'
2a'
1a'
O
7
O
6
4
5
O
N
S
2''
1''
2
O
4'
3'
5'
3''
O
6'
N
2'
Br
f1 (ppm)

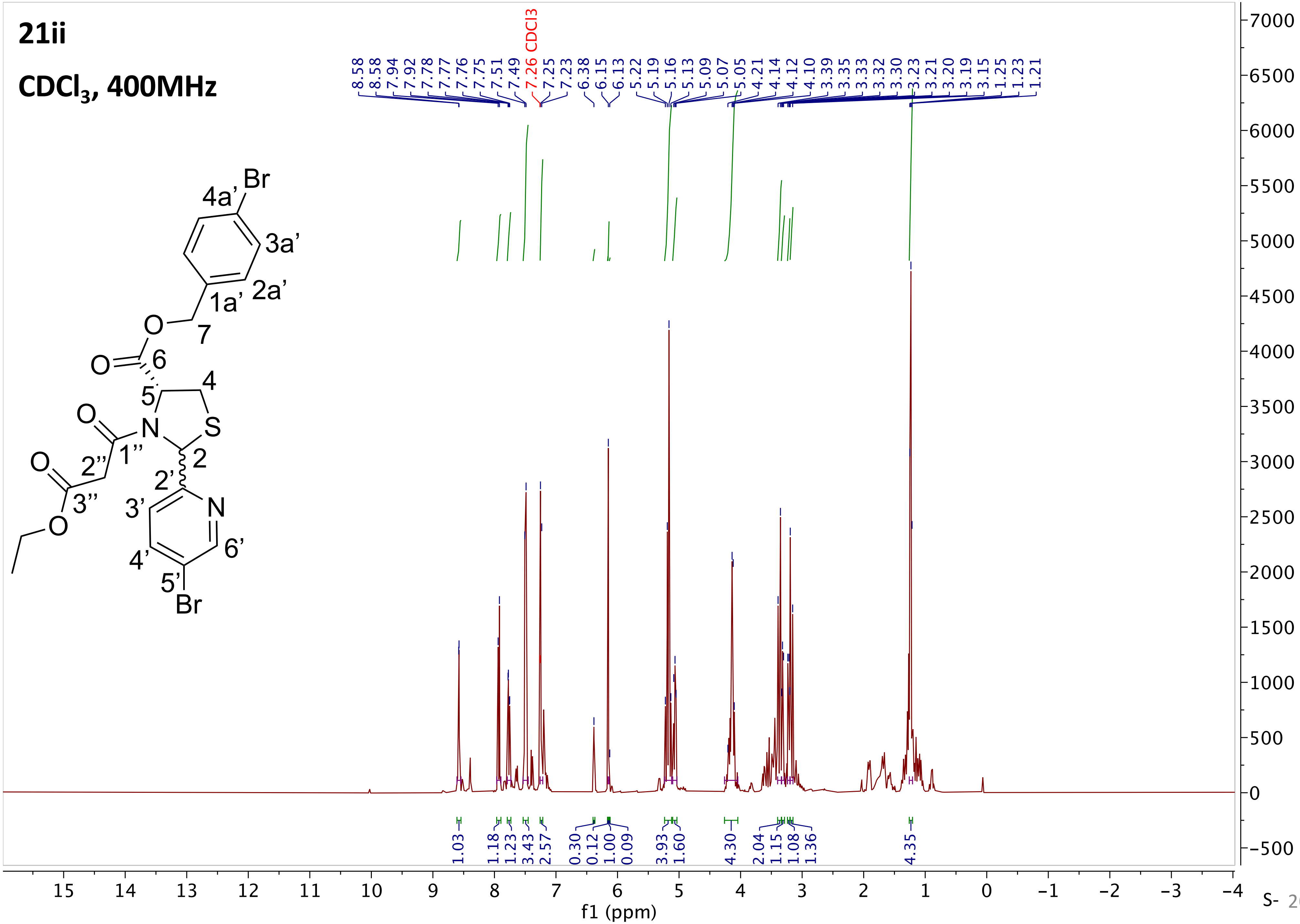


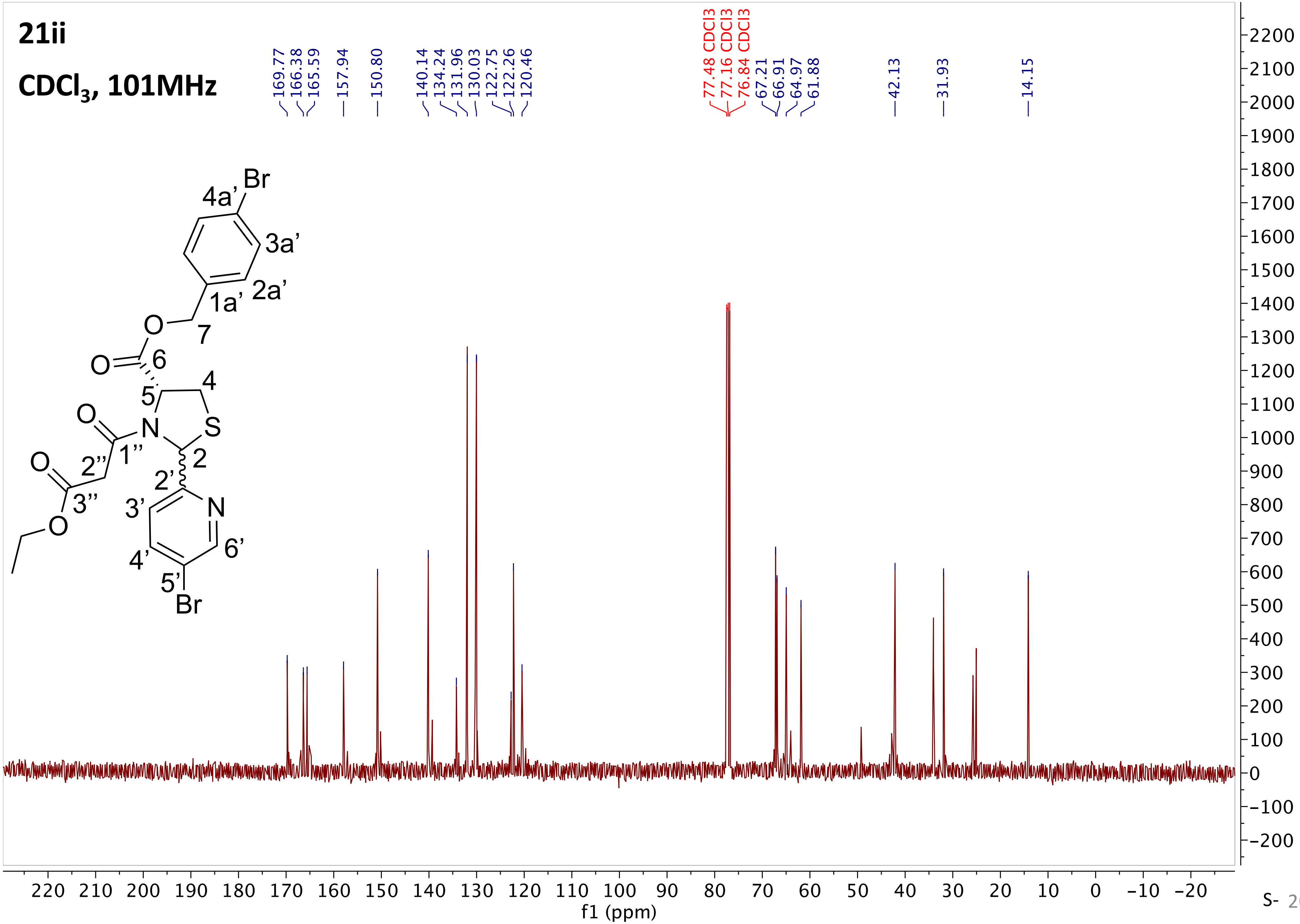
20iv
CDCl3, 400MHz
7.26 CDCl3
f1 (ppm)


20iv
CDCl3, 101MHz
169.22
169.06
167.28
166.39
165.19
165.03
153.77
153.48
152.32
151.11
150.90
150.44
150.22
147.99
143.78
143.35
143.07
142.69
134.17
134.06
130.43
130.26
130.18
130.04
129.93
129.65
129.61
129.30
129.24
126.06
125.50
125.26
124.10
121.01
120.27
119.39
119.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.57
65.46
65.42
65.10
64.68
64.64
64.33
64.24
63.99
63.93
63.30
62.28
62.17
61.99
43.20
42.85
42.47
42.20
33.35
32.03
31.36
14.25
14.15
f1 (ppm)

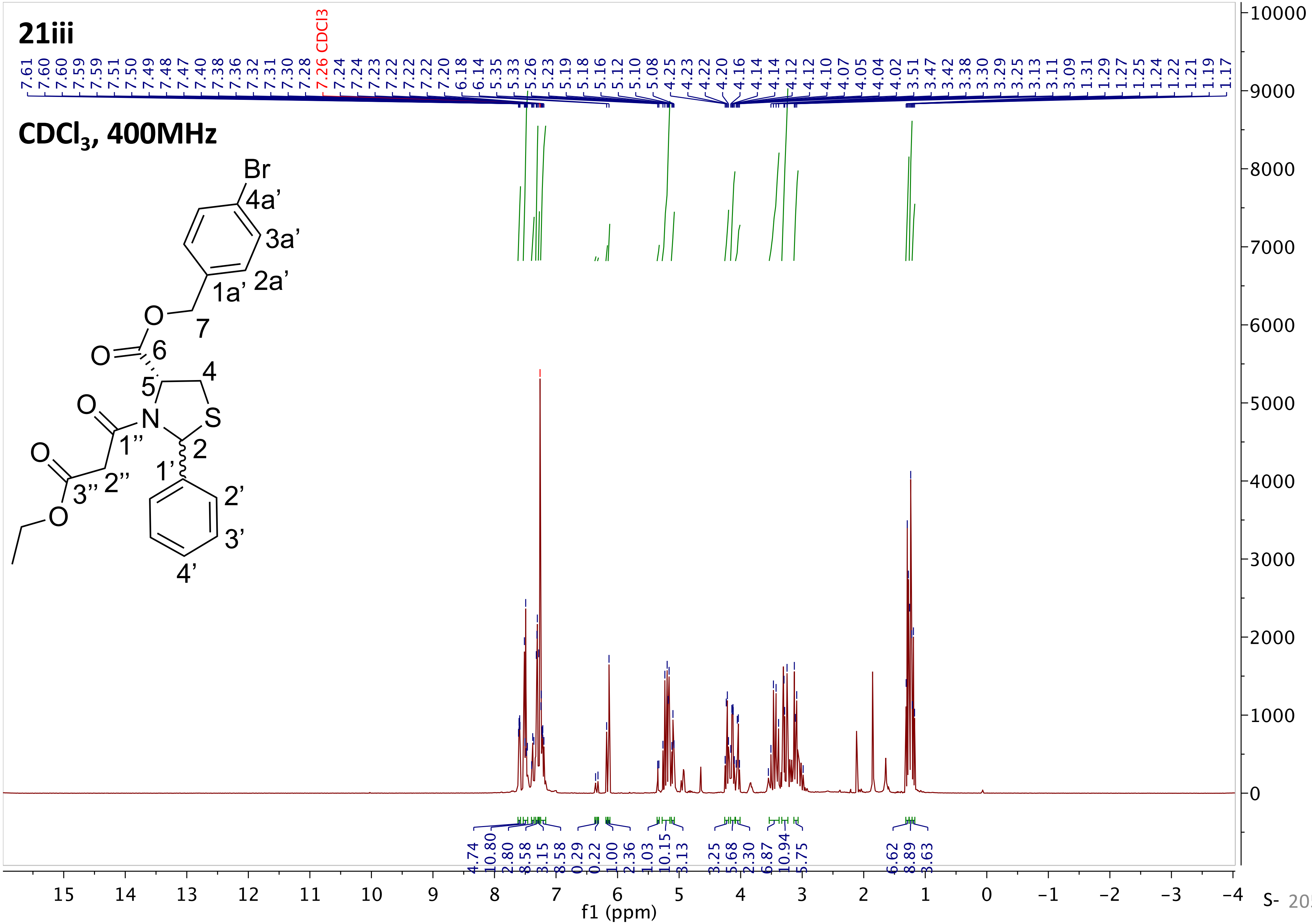
21ii

$CDCl_3$, 400MHz





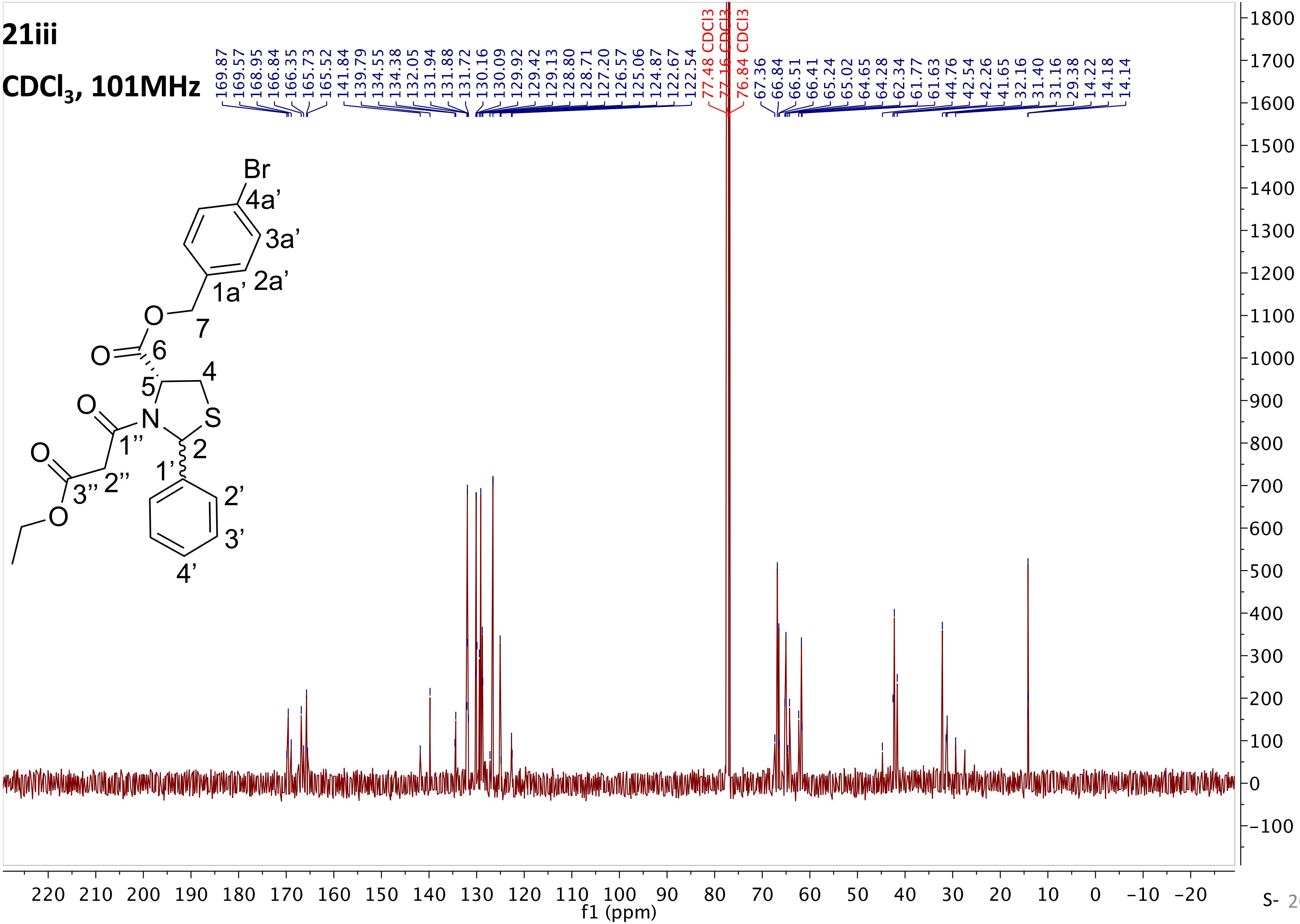
21ii
$CDCl_3$, 101MHz
169.77
166.38
165.59
157.94
150.80
140.14
134.24
131.96
130.03
122.75
122.26
120.46
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.21
66.91
64.97
61.88
42.13
31.93
14.15
f1 (ppm)



21iii
CDCl3, 400MHz
7.26 CDCl3
f1 (ppm)

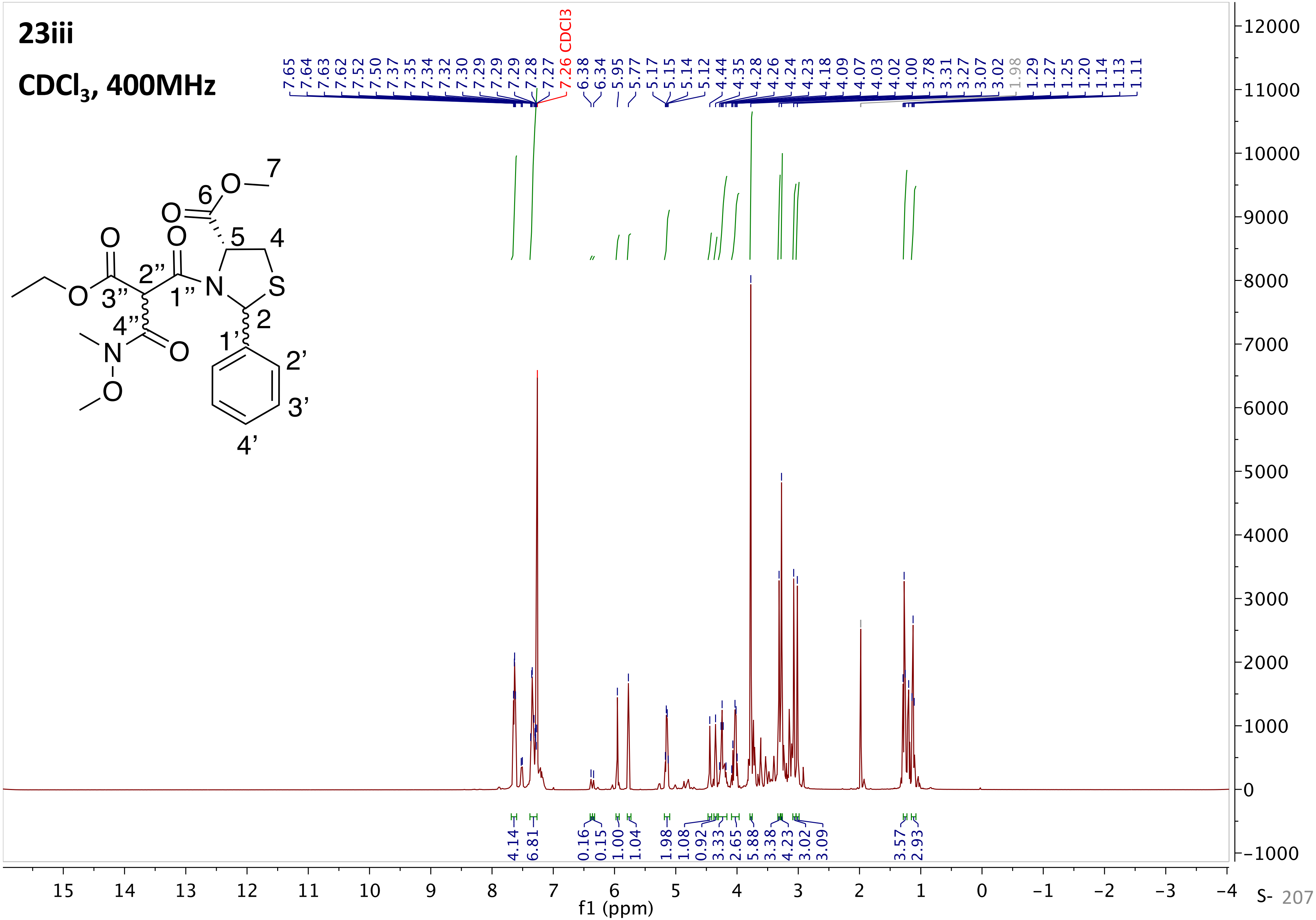
21iii

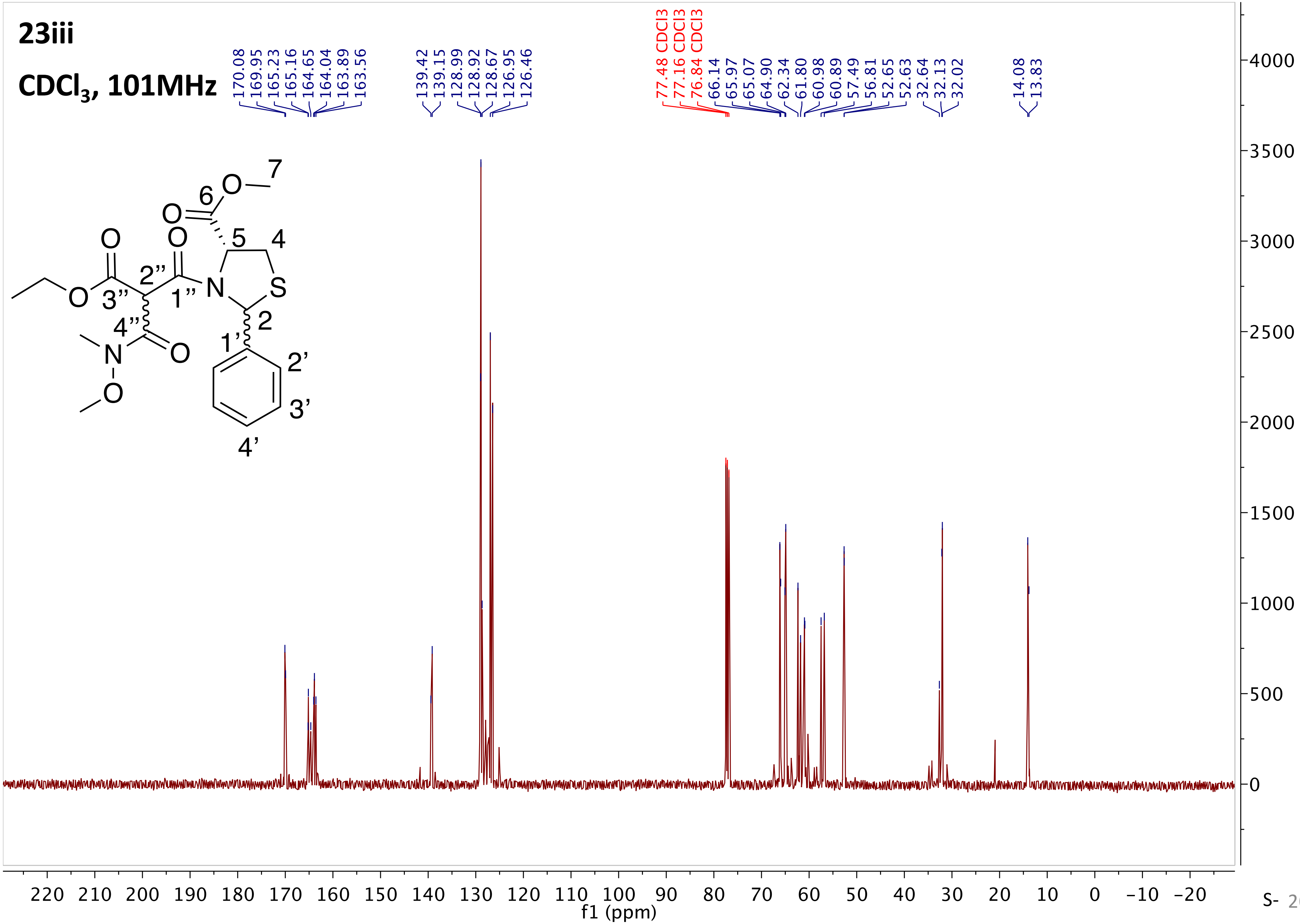
$CDCl_3$, 101MHz

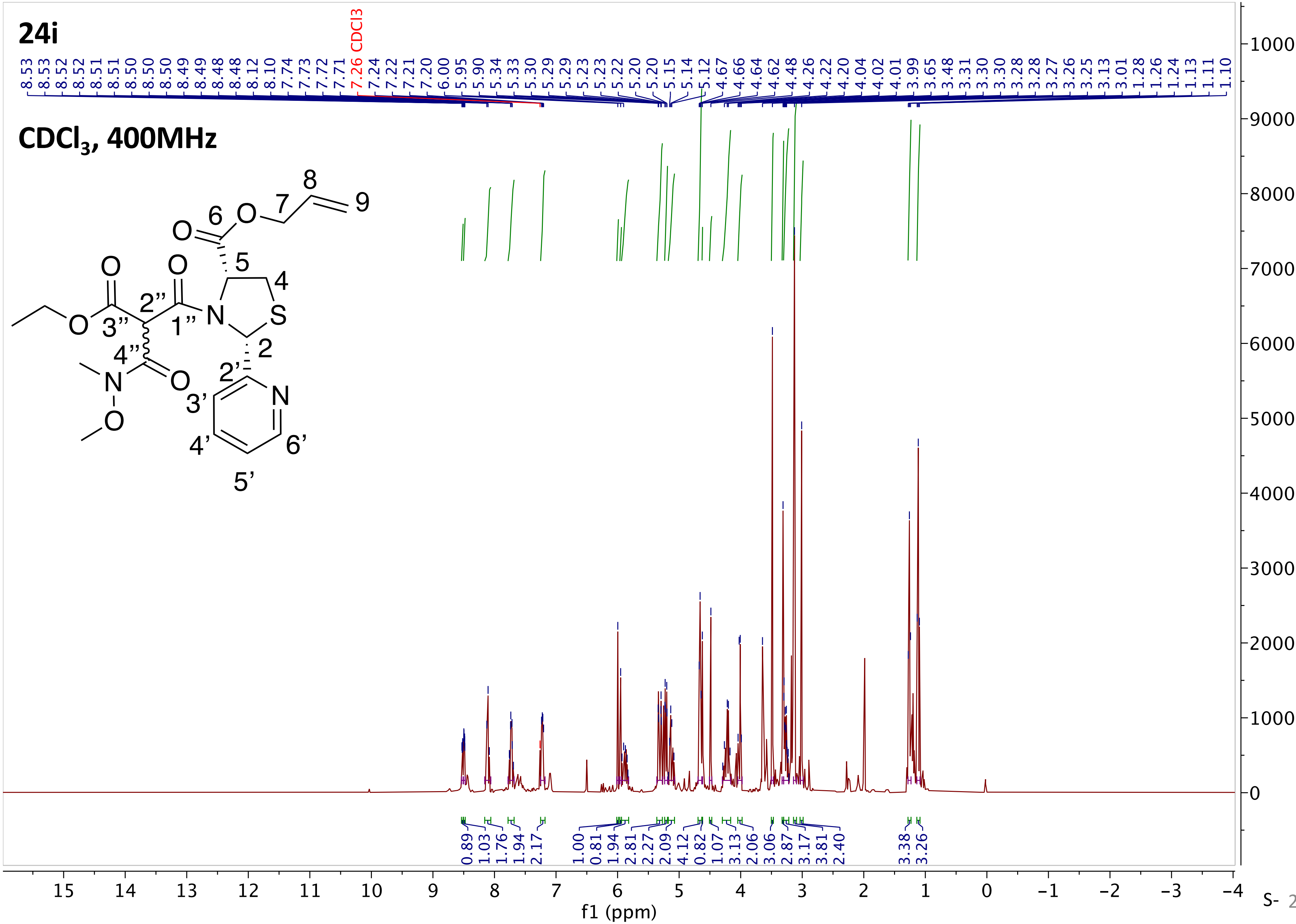


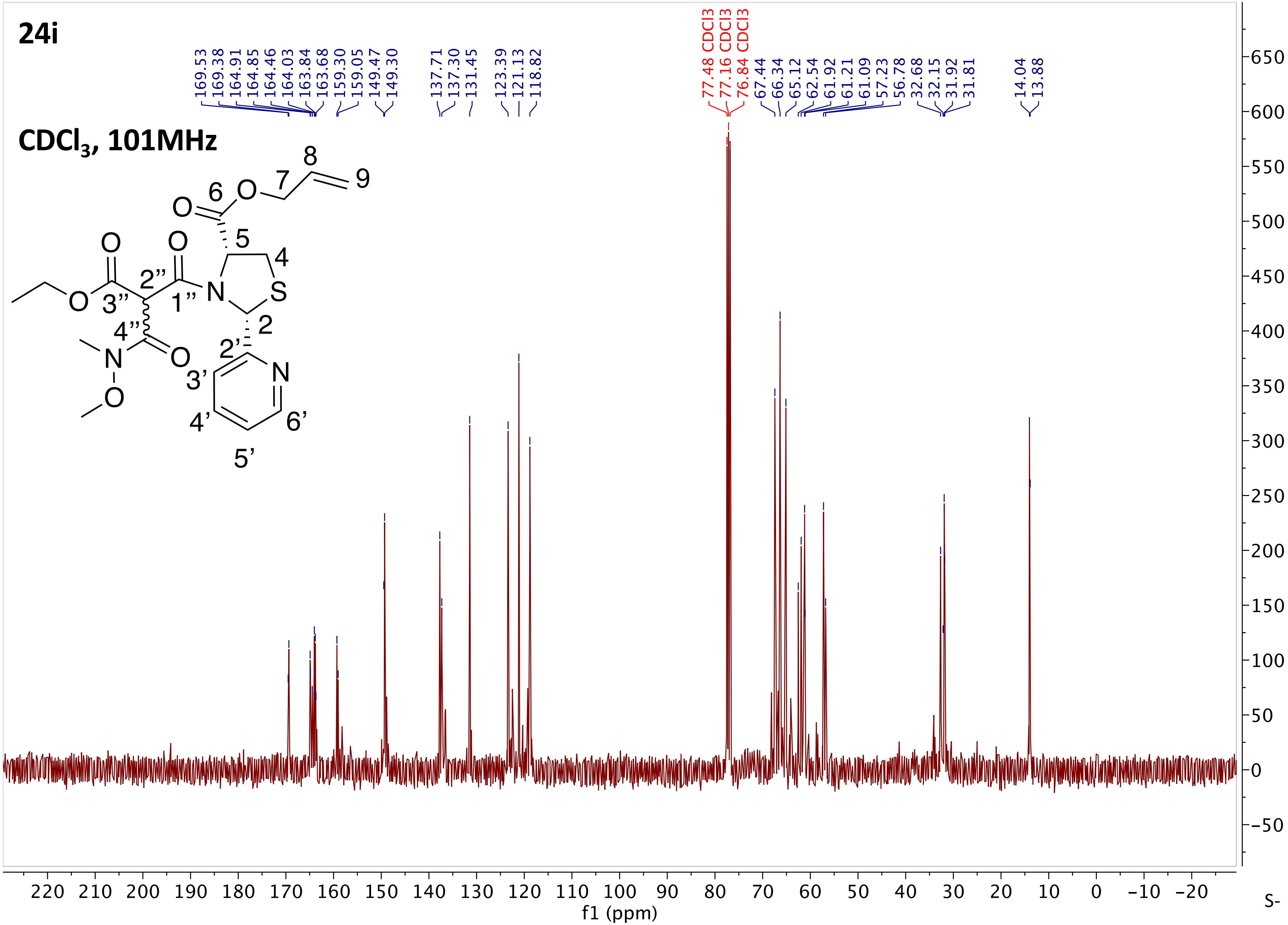
23iii

$CDCl_3$, 400MHz

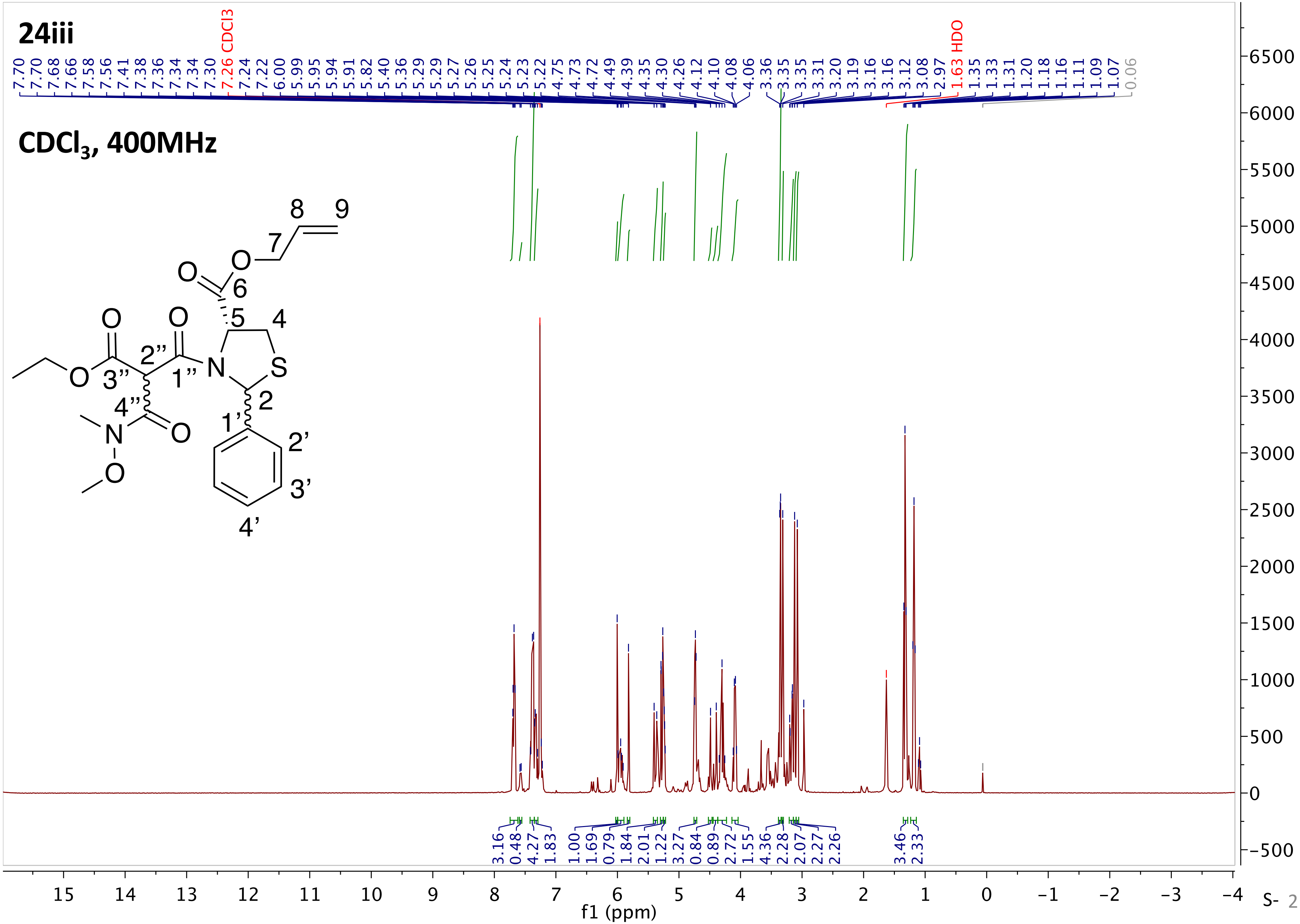



23iii
CDCl3, 101MHz
170.08
169.95
165.23
165.16
164.65
164.04
163.89
163.56
139.42
139.15
128.99
128.92
128.67
126.95
126.46
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.14
65.97
65.07
64.90
62.34
61.80
60.98
60.89
57.49
56.81
52.65
52.63
32.64
32.13
32.02
14.08
13.83
f1 (ppm)


24i
CDCl3, 400MHz
8.53 8.53 8.52 8.52 8.51 8.51 8.50 8.50 8.50 8.49 8.48 8.48 8.12 8.10 7.74 7.73 7.72 7.71 7.26 CDCl3 7.24 7.22 7.21 7.20 6.00 5.95 5.90 5.34 5.33 5.30 5.29 5.29 5.23 5.23 5.22 5.20 5.20 5.15 5.14 5.12 4.67 4.66 4.64 4.62 4.48 4.26 4.22 4.20 4.04 4.02 4.01 3.99 3.65 3.48 3.31 3.30 3.30 3.28 3.28 3.27 3.26 3.25 3.13 3.01 1.28 1.26 1.24 1.13 1.11 1.10
0.89 1.03 1.76 1.94 2.17 1.00 0.81 1.94 2.81 2.27 2.09 4.12 0.82 1.07 3.13 2.06 3.06 2.87 3.17 3.81 2.40 3.38 3.26
f1 (ppm)

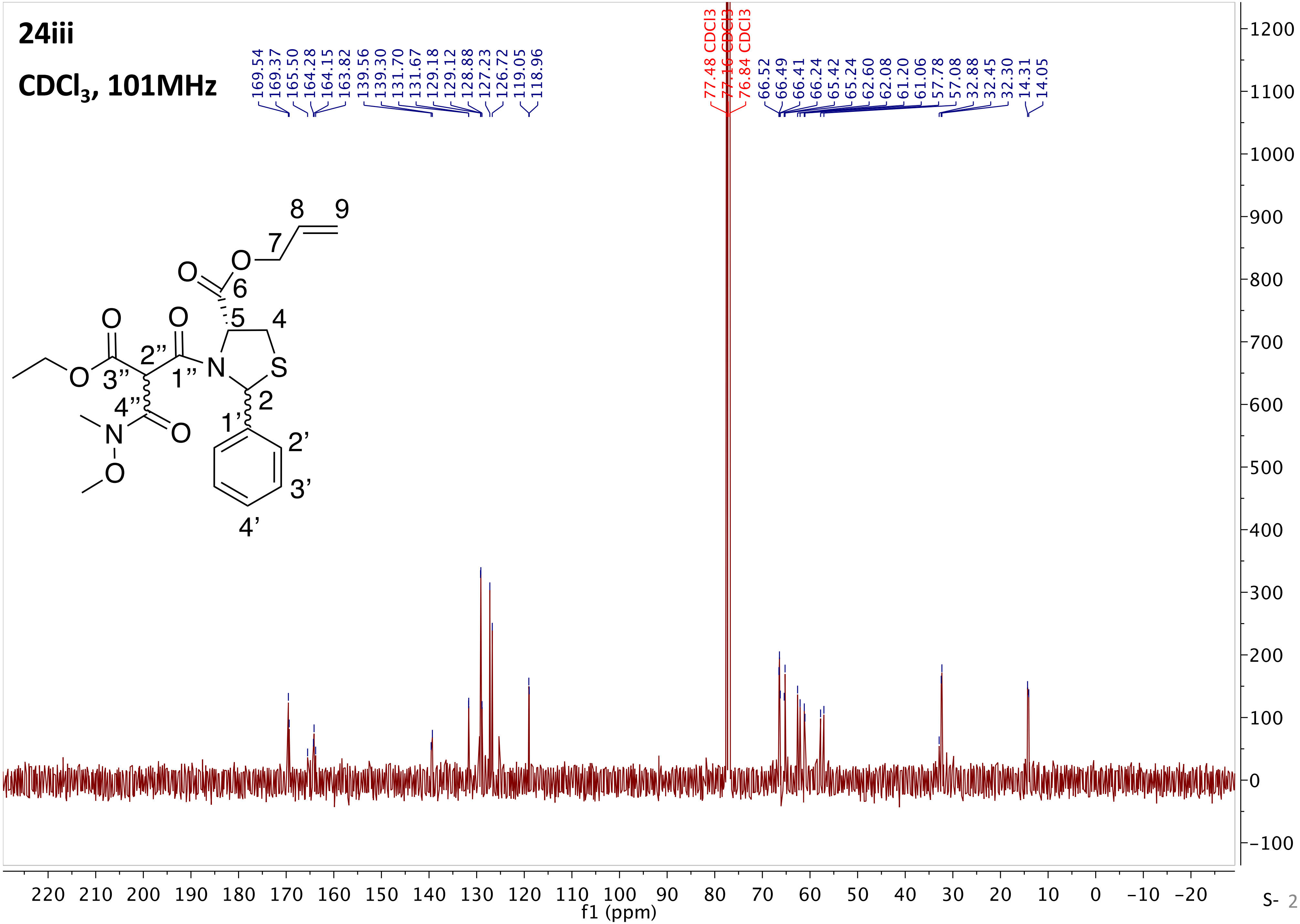


24i
CDCl3, 101MHz
169.53 169.38 164.91 164.85 164.46 164.03 163.84 163.68 159.30 159.05 149.47 149.30 137.71 137.30 131.45 123.39 121.13 118.82
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
67.44 66.34 65.12 62.54 61.92 61.21 61.09 57.23 56.78 32.68 32.15 31.92 31.81 14.04 13.88
f1 (ppm)


24iii
CDCl3, 400MHz
f1 (ppm)

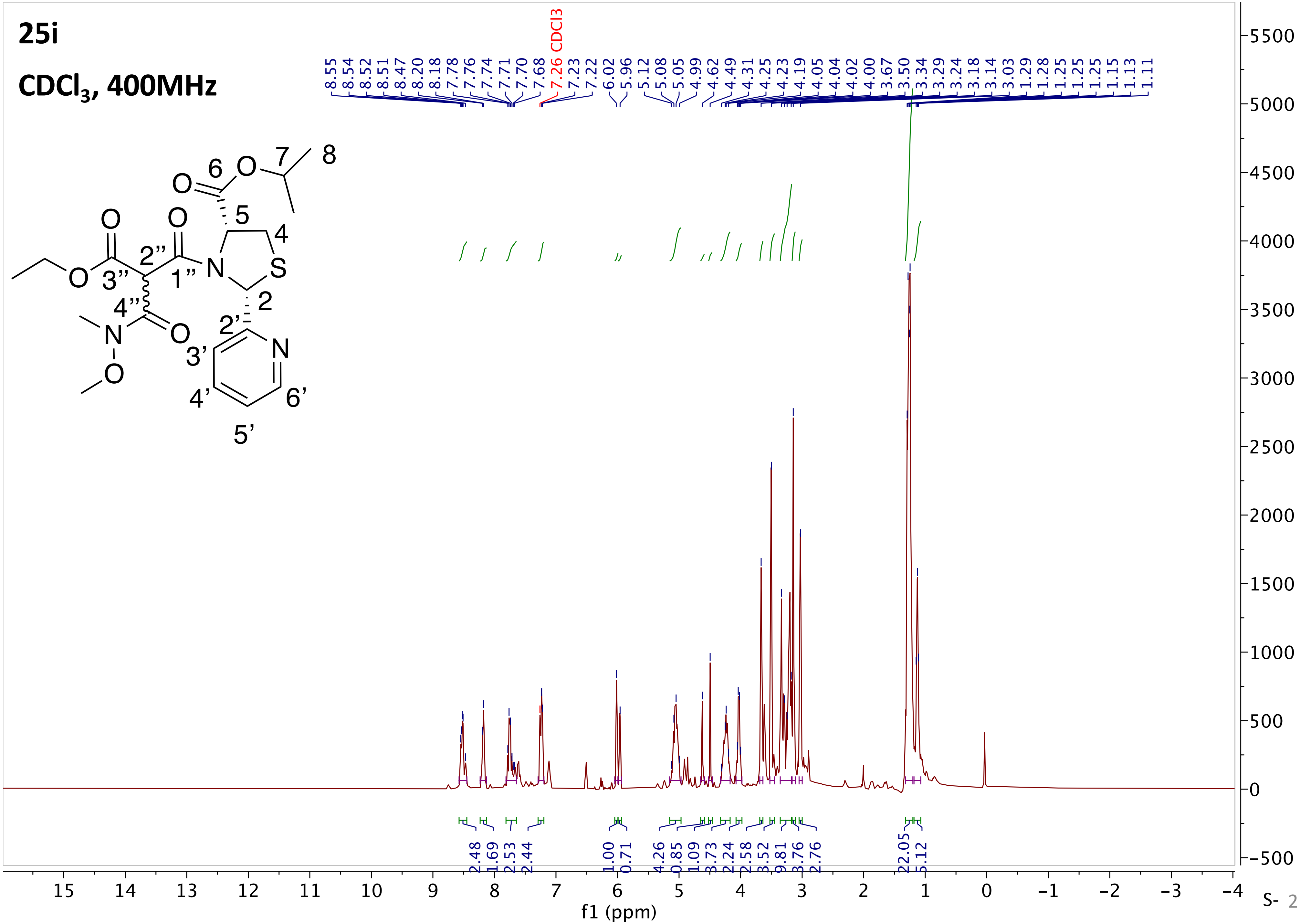
24iii

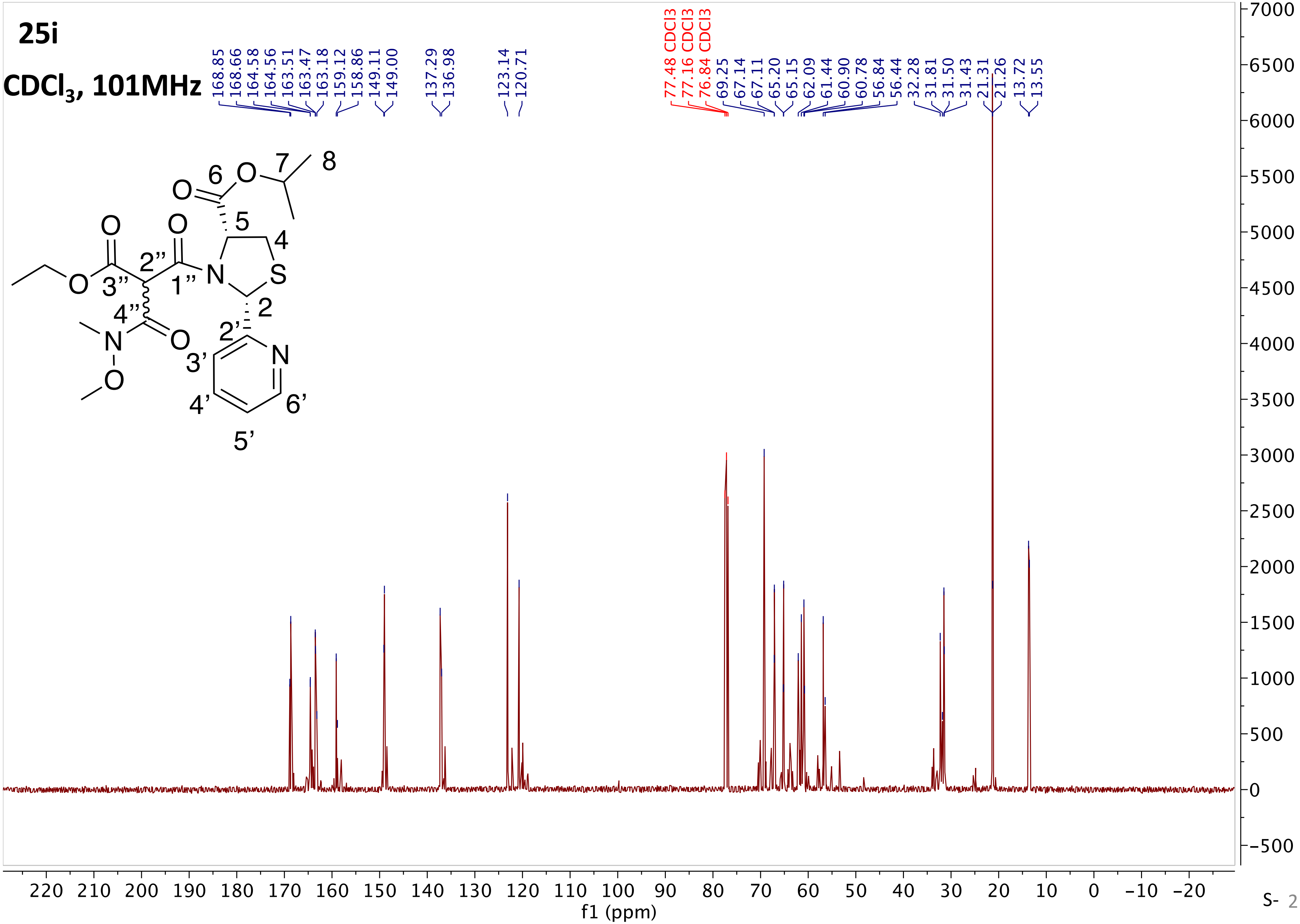
$CDCl_3$, 101MHz



25i

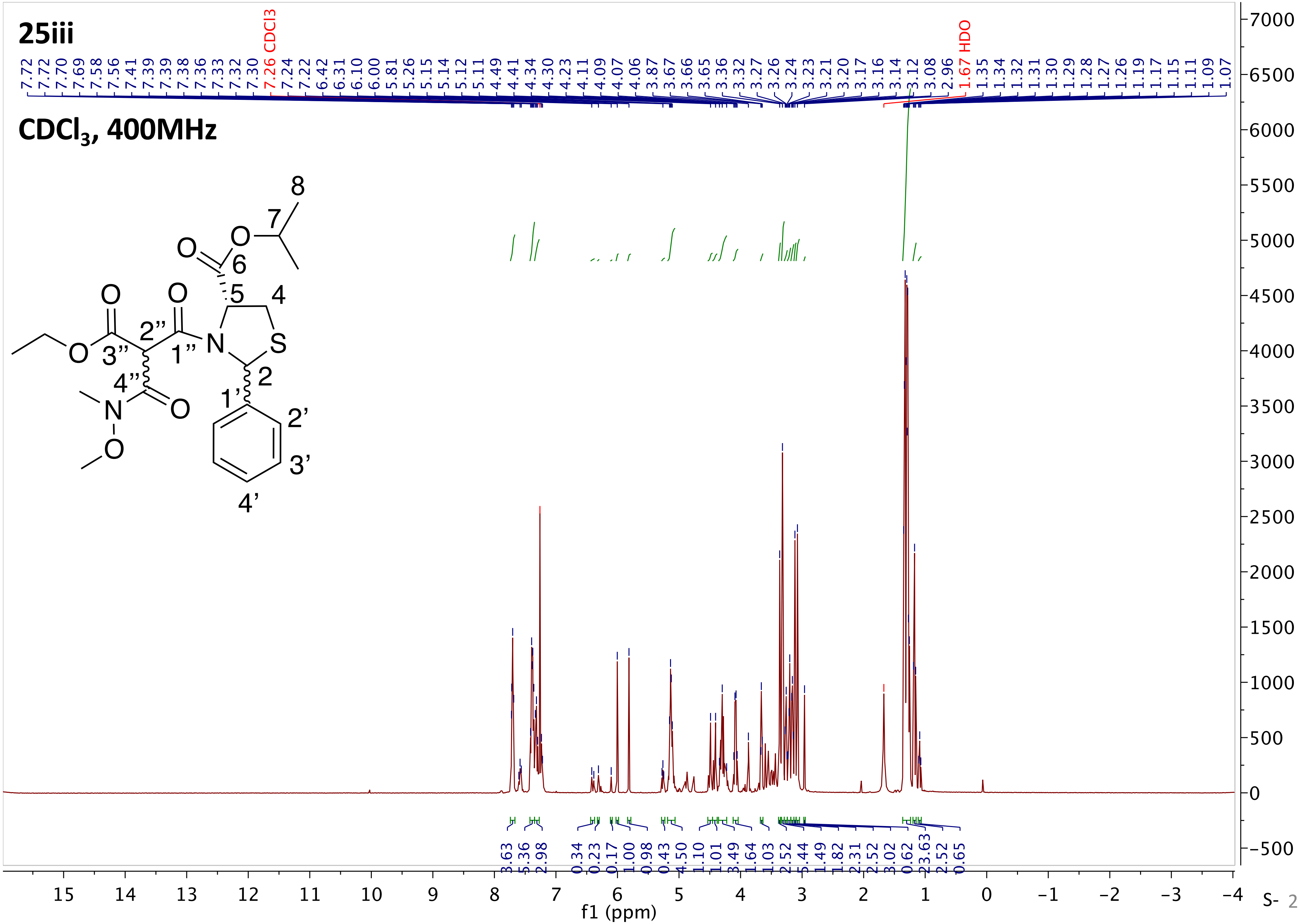
CDCl$_3$, 400MHz

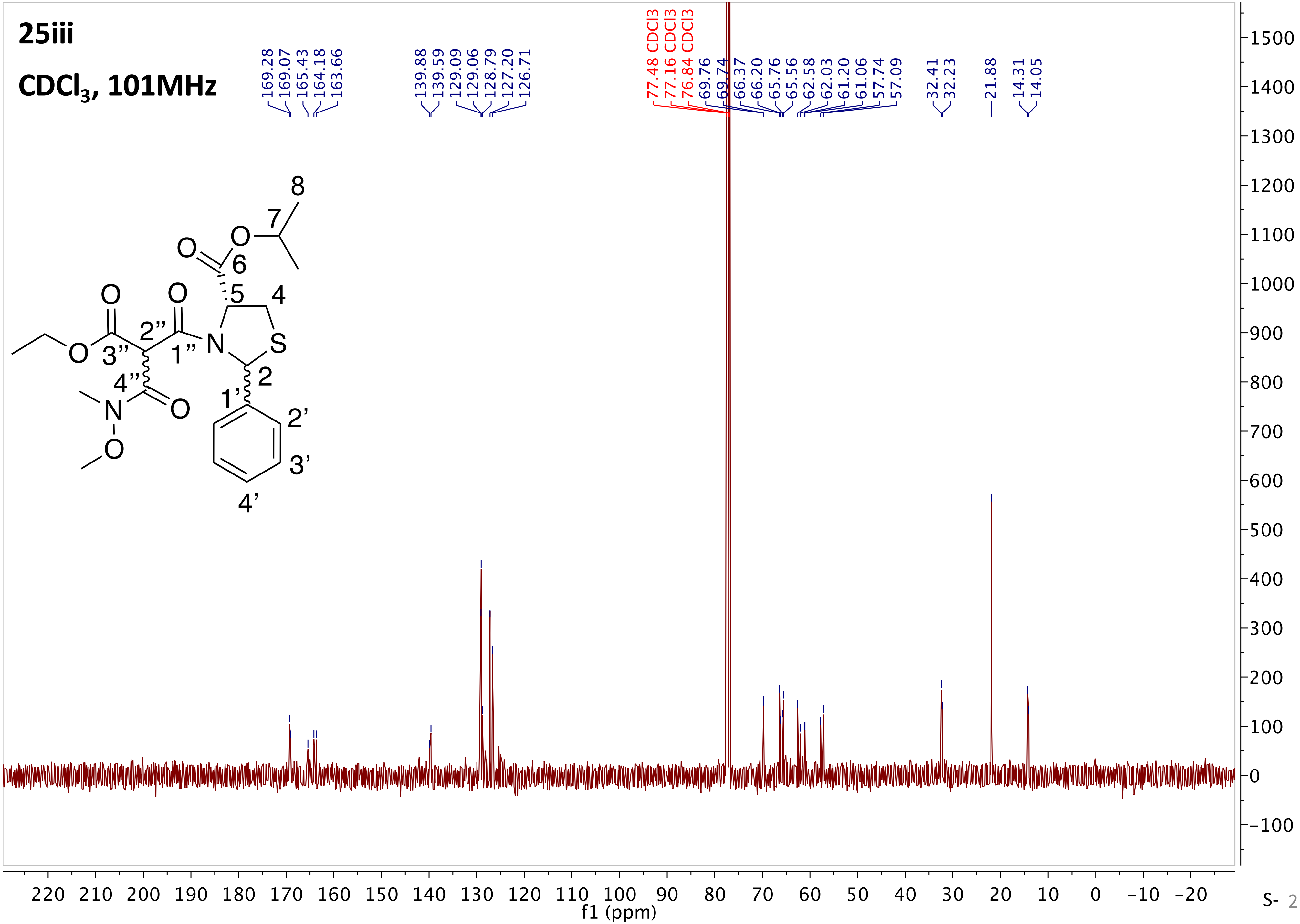



25i
CDCl3, 101MHz
168.85
168.66
164.58
164.56
163.51
163.47
163.18
159.12
158.86
149.11
149.00
137.29
136.98
123.14
120.71
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.25
67.14
67.11
65.20
65.15
62.09
61.44
60.90
60.78
56.84
56.44
32.28
31.81
31.50
31.43
21.31
21.26
13.72
13.55
f1 (ppm)

25iii

$CDCl_3$, 400MHz

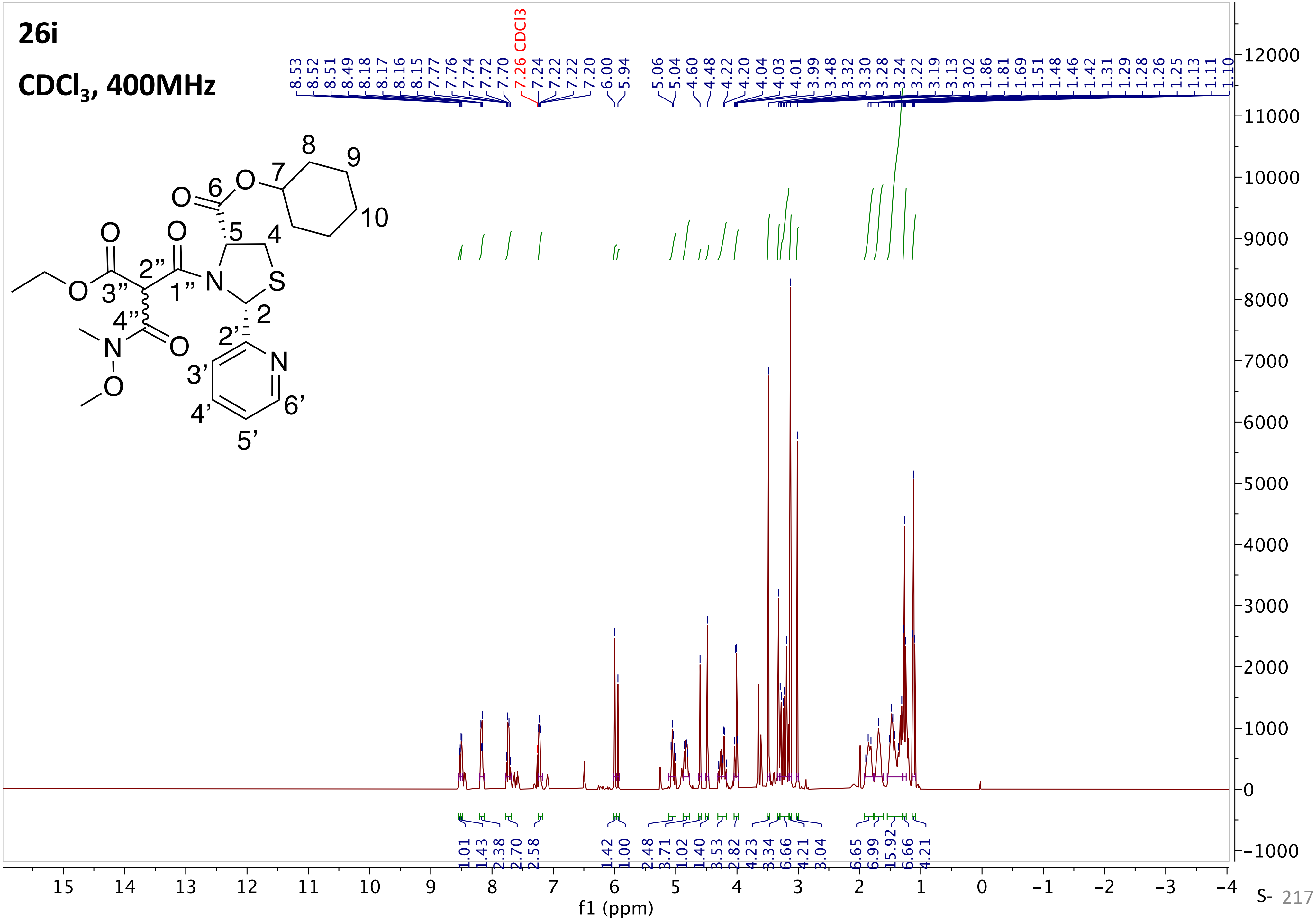


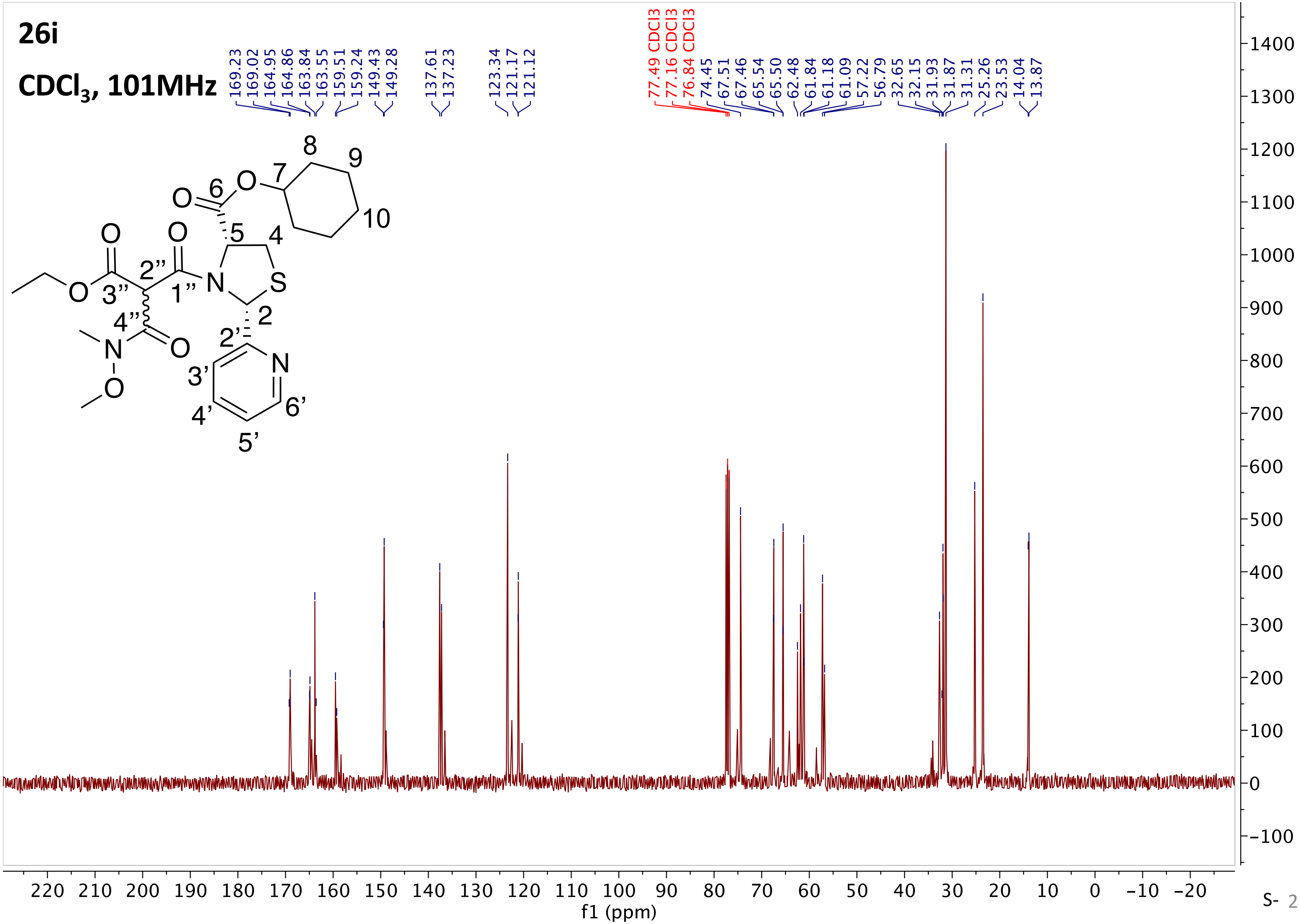


25iii
CDCl3, 101MHz
169.28
169.07
165.43
164.18
163.66
139.88
139.59
129.09
129.06
128.79
127.20
126.71
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.76
69.74
66.37
66.20
65.76
65.56
62.58
62.03
61.20
61.06
57.74
57.09
32.41
32.23
21.88
14.31
14.05
f1 (ppm)

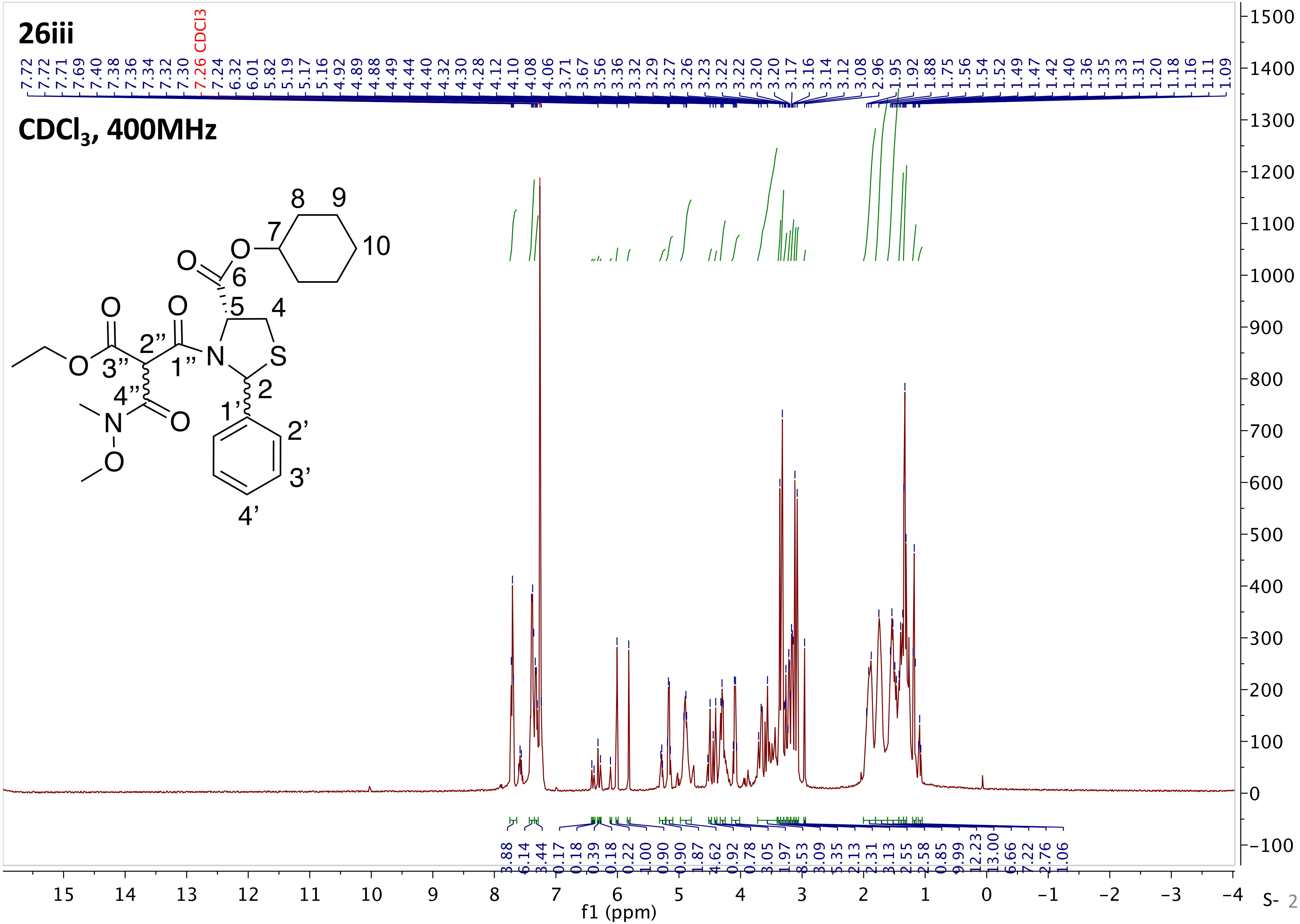
26i

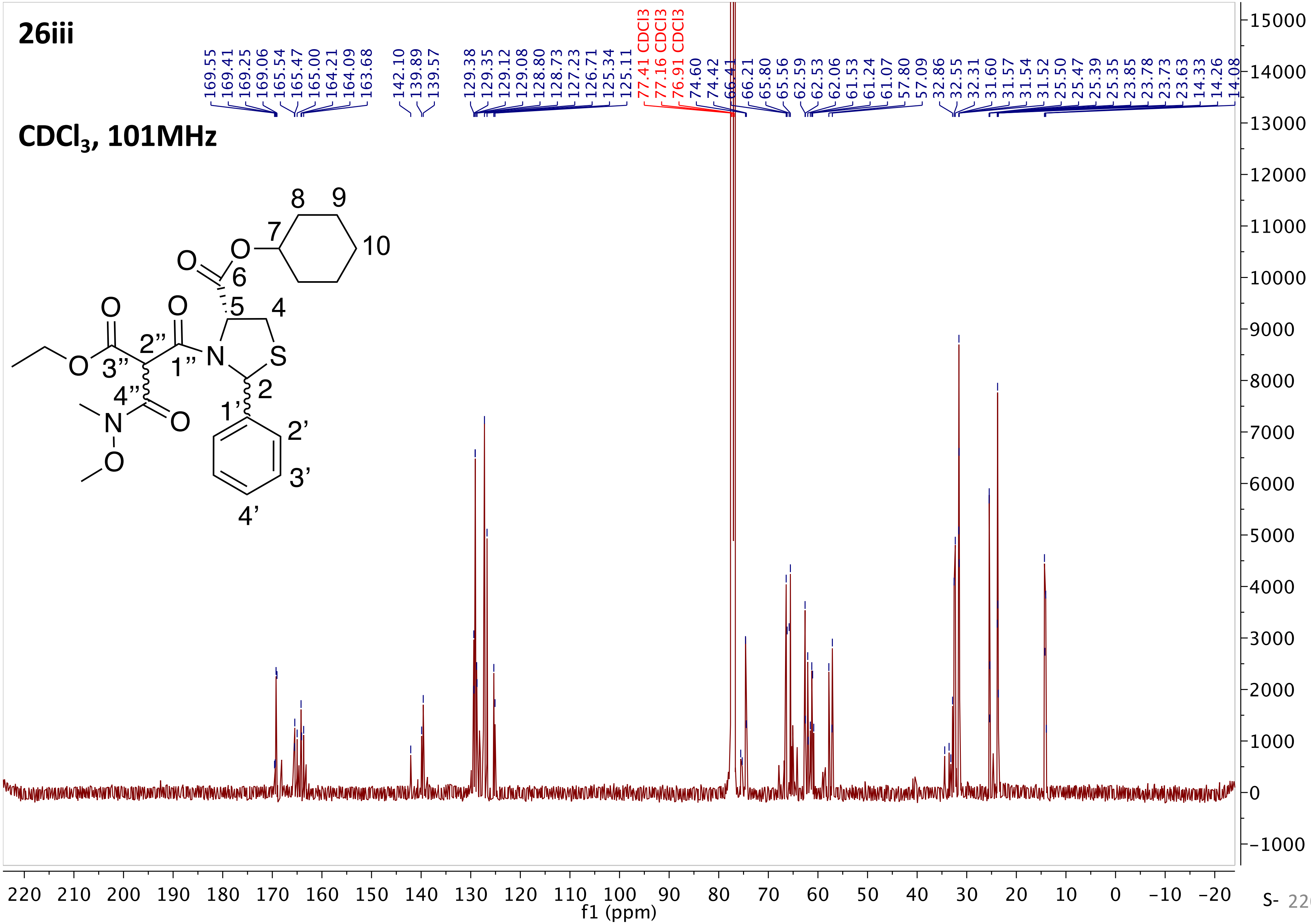
$CDCl_3$, 400MHz

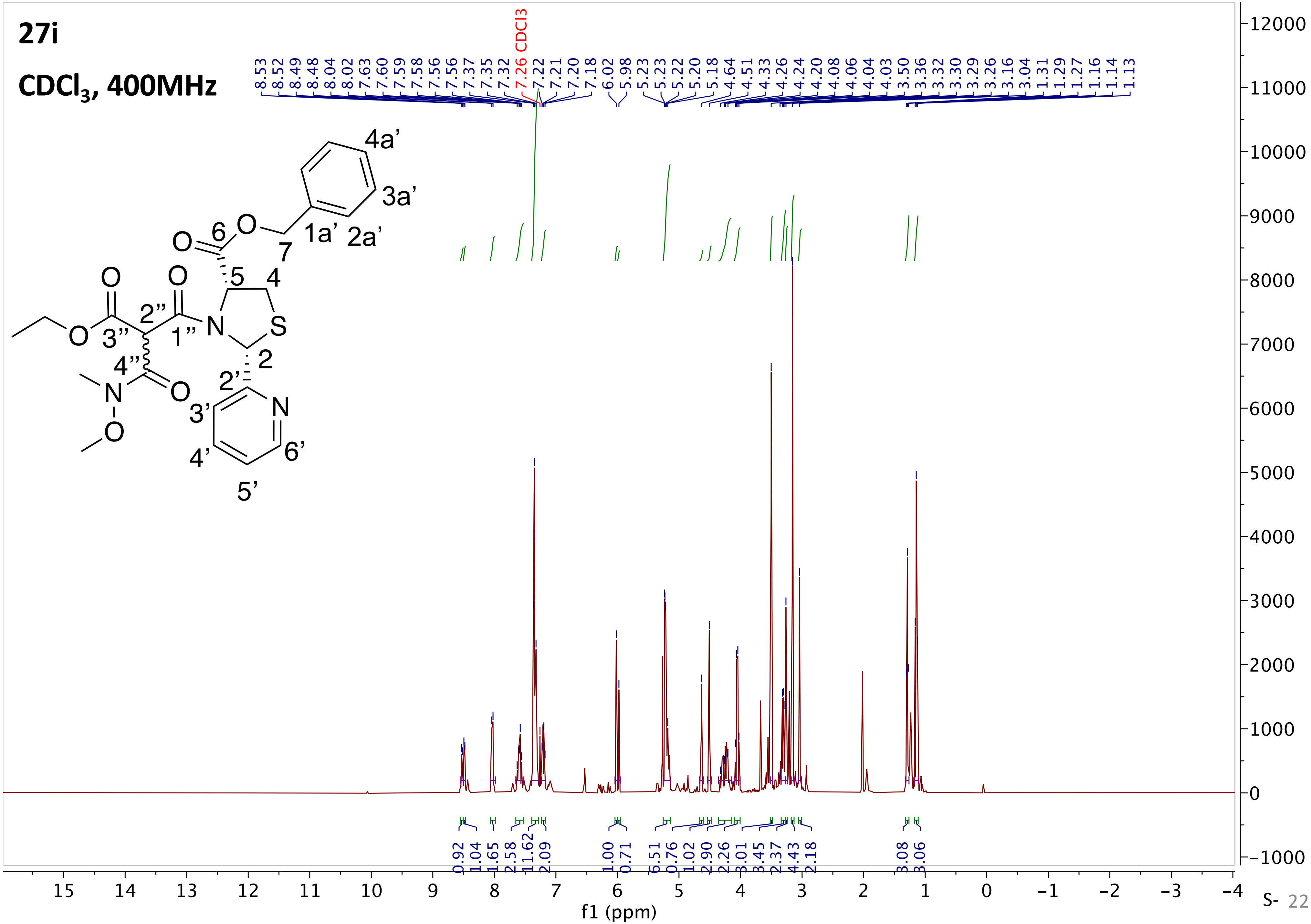


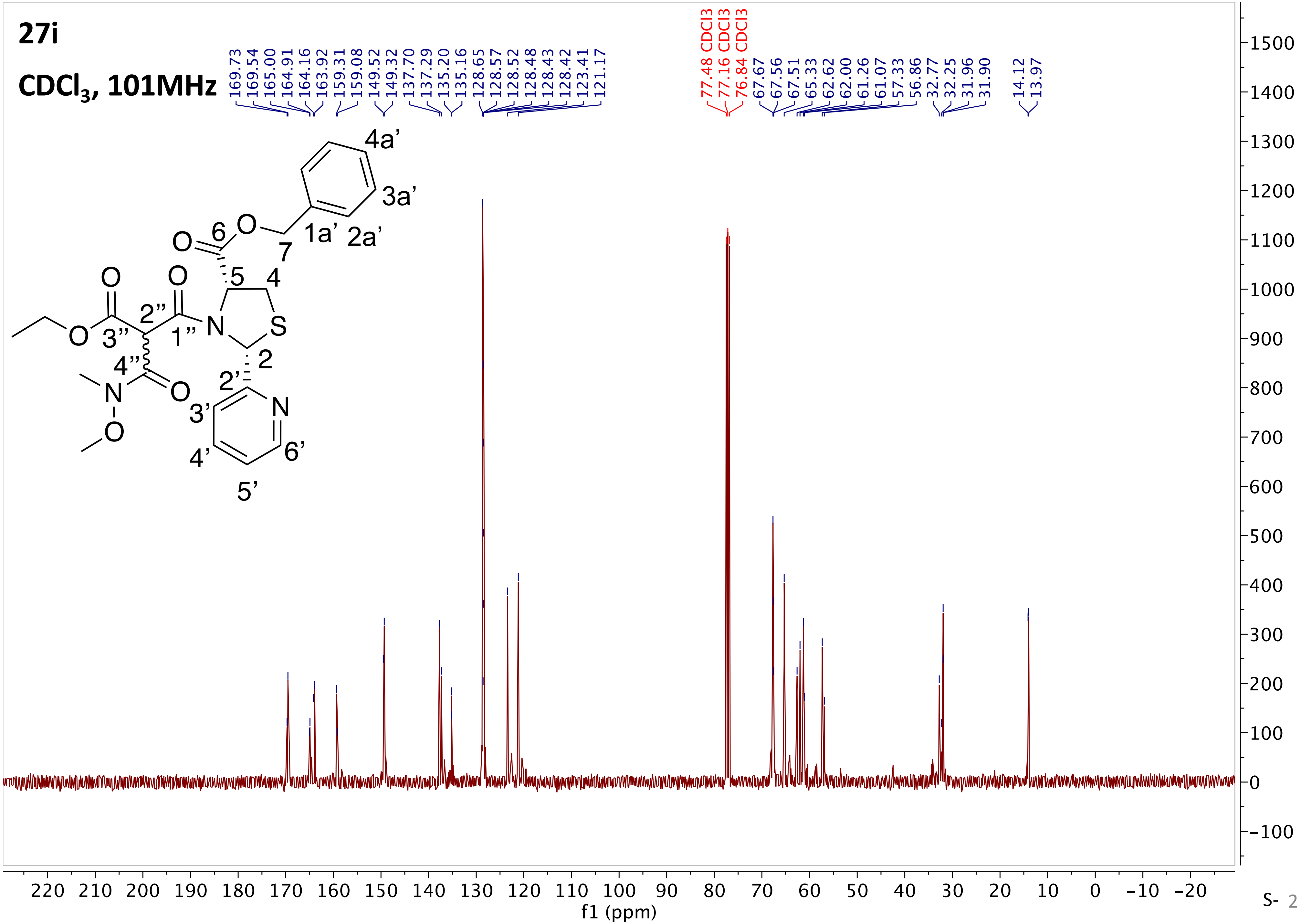


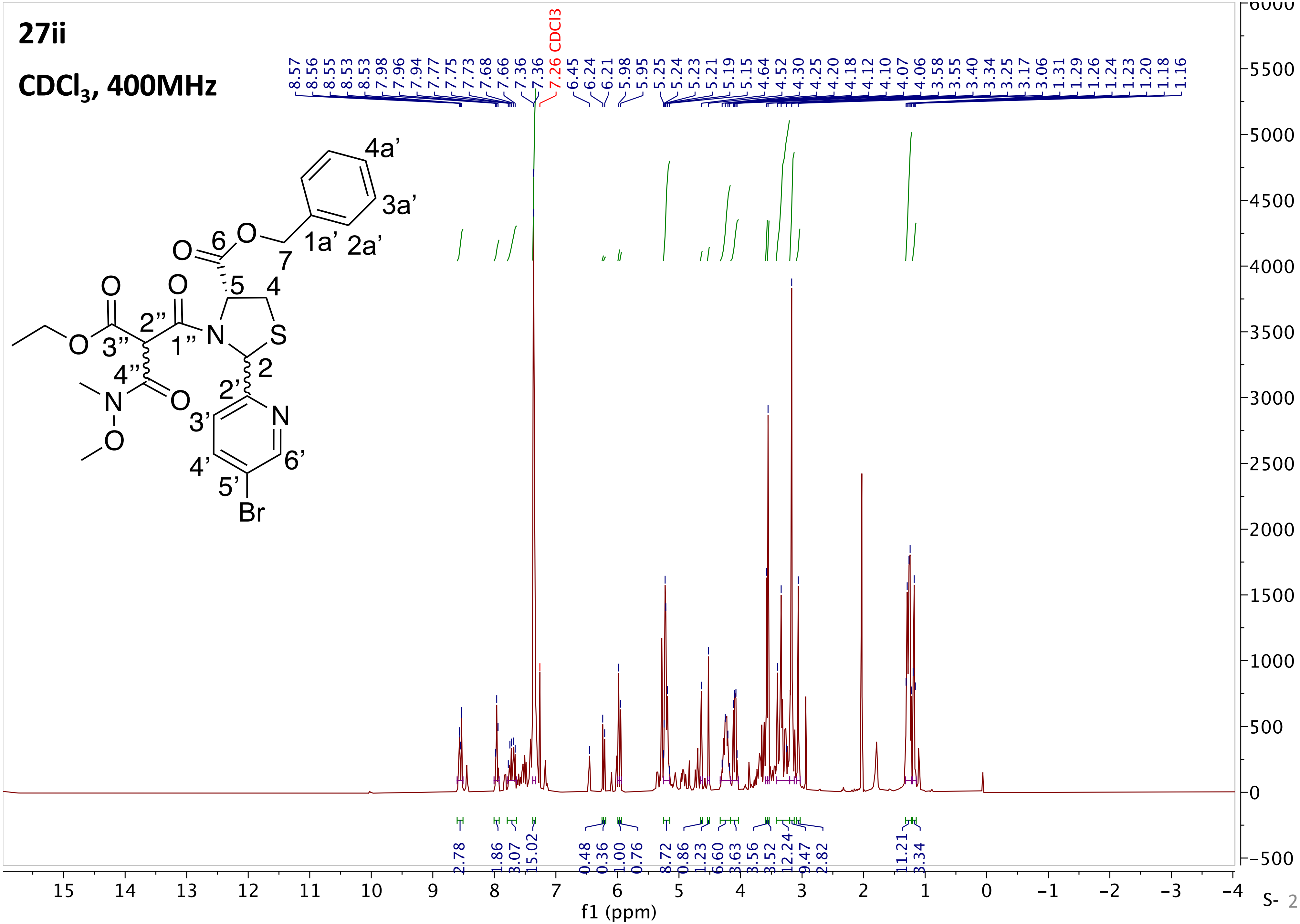
26i
CDCl3, 101MHz
169.23
169.02
164.95
164.86
163.84
163.55
159.51
159.24
149.43
149.28
137.61
137.23
123.34
121.17
121.12
77.49 CDCl3
77.16 CDCl3
76.84 CDCl3
74.45
67.51
67.46
65.54
65.50
62.48
61.84
61.18
61.09
57.22
56.79
32.65
32.15
31.93
31.87
31.31
25.26
23.53
14.04
13.87
f1 (ppm)

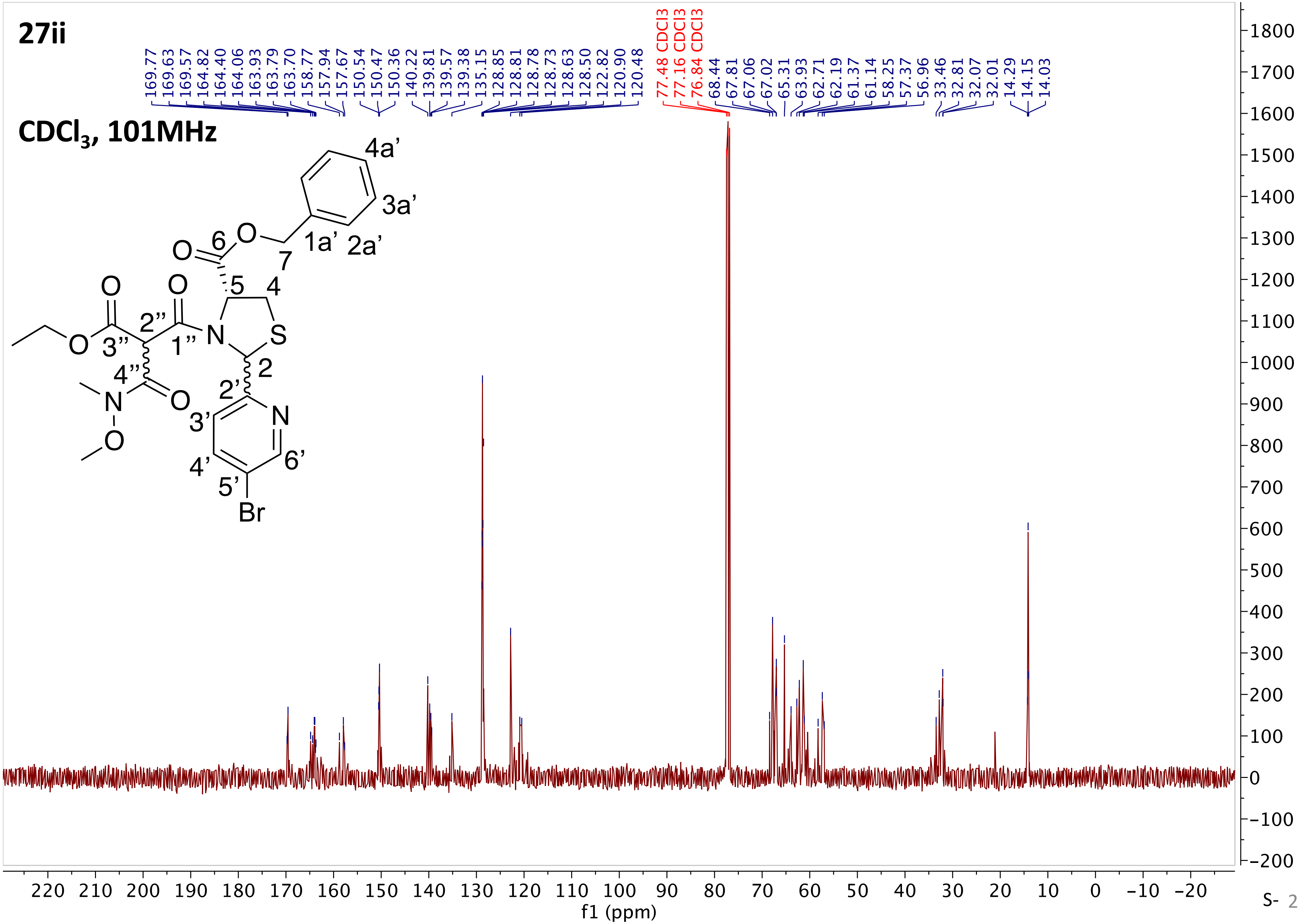

26iii
$CDCl_3$, 400MHz
f1 (ppm)

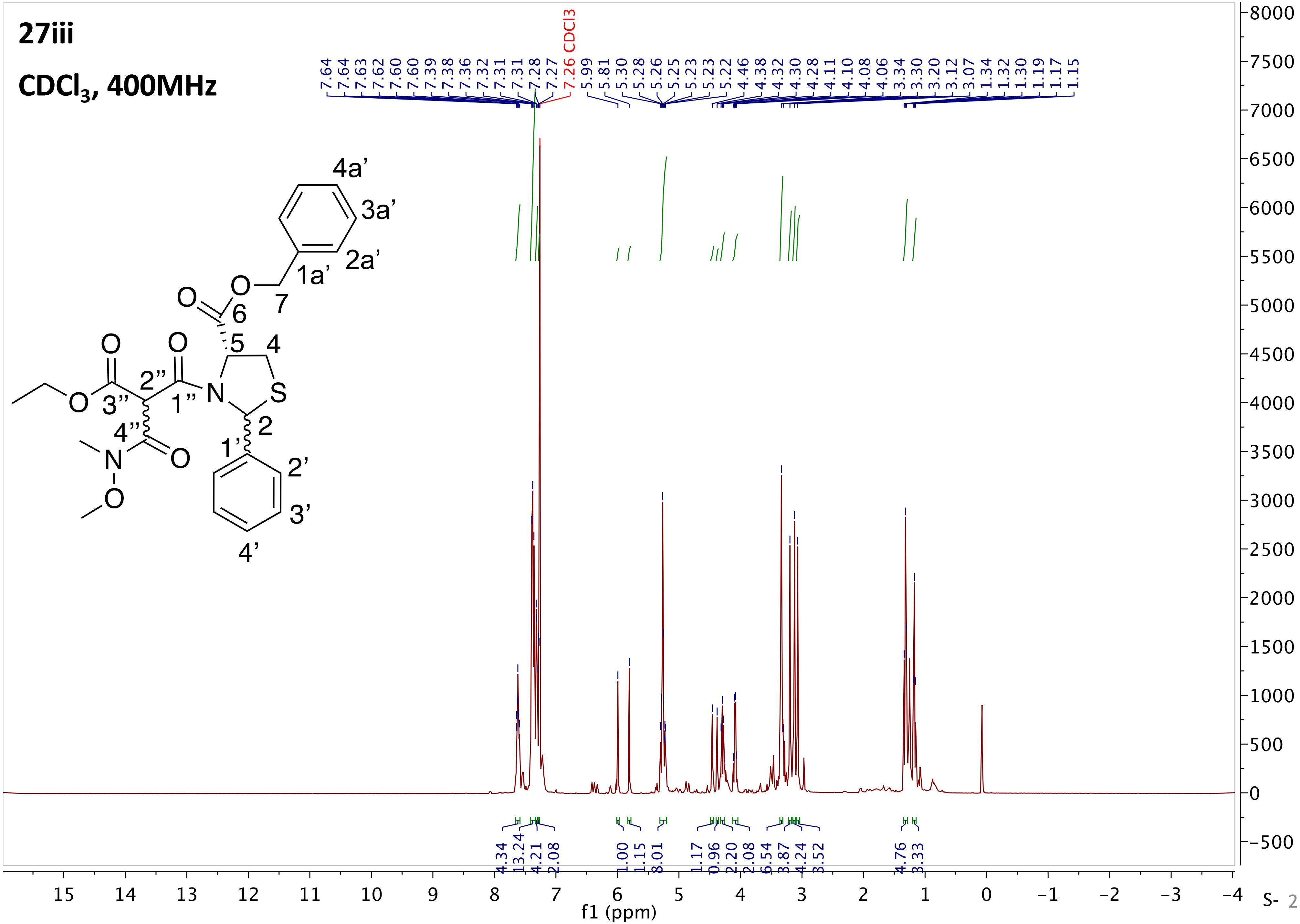

26iii
CDCl3, 101MHz
169.55
169.41
169.25
169.06
165.54
165.47
165.00
164.21
164.09
163.68
142.10
139.89
139.57
129.38
129.35
129.12
129.08
128.80
128.73
127.23
126.71
125.34
125.11
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
74.60
74.42
66.41
66.21
65.80
65.56
62.59
62.53
62.06
61.53
61.24
61.07
57.80
57.09
32.86
32.55
32.31
31.60
31.57
31.54
31.52
25.50
25.47
25.39
25.35
23.85
23.78
23.73
23.63
14.33
14.26
14.08
f1 (ppm)

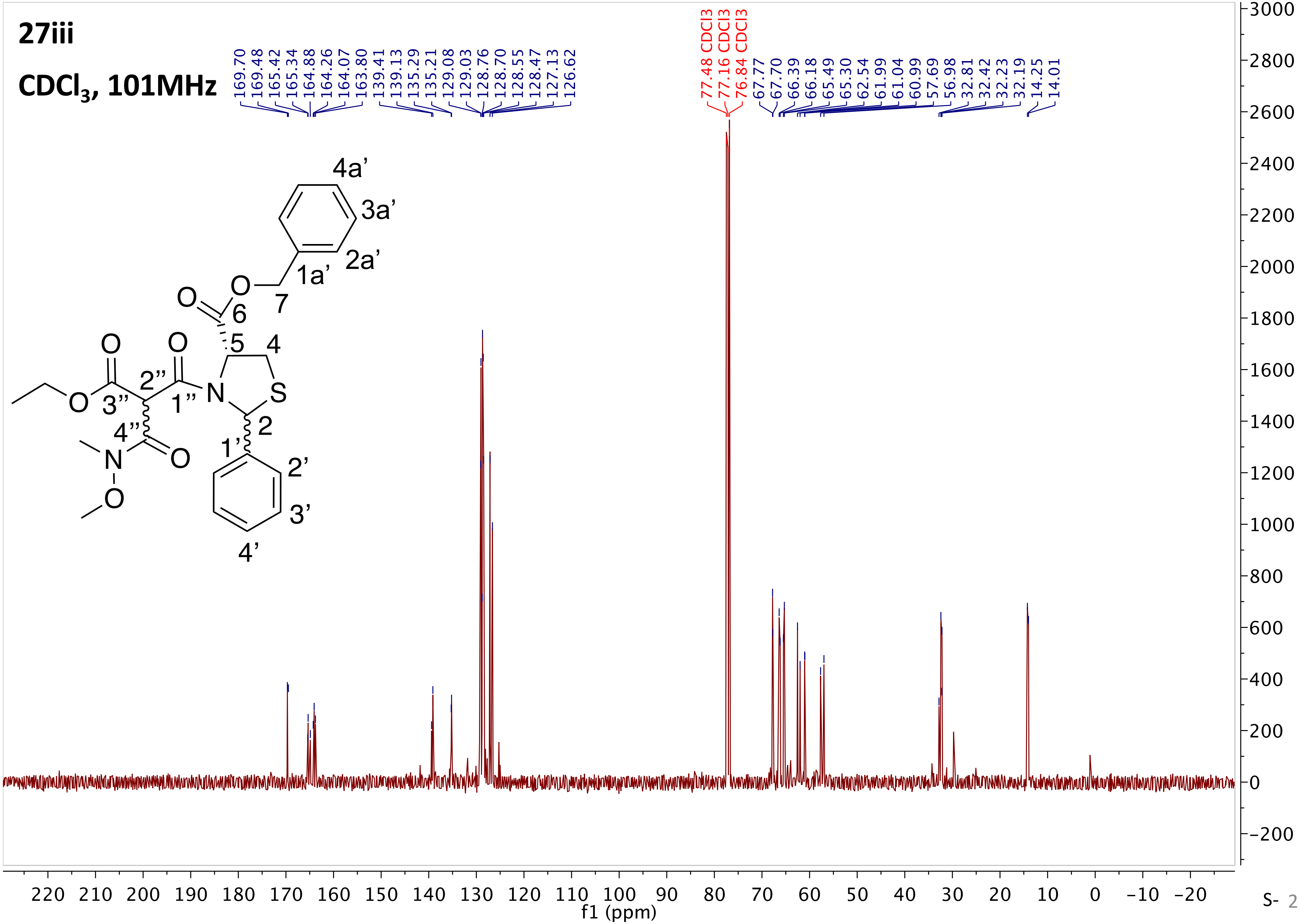

27i
CDCl3, 400MHz
8.53 8.52 8.49 8.48 8.04 8.02 7.63 7.60 7.59 7.58 7.56 7.56 7.37 7.35 7.32 7.26 CDCl3 7.22 7.21 7.20 7.18 6.02 5.98 5.23 5.23 5.22 5.20 5.18 4.64 4.51 4.33 4.26 4.24 4.20 4.08 4.06 4.04 4.03 3.50 3.36 3.32 3.30 3.29 3.26 3.16 3.04 1.31 1.29 1.27 1.16 1.14 1.13
0.92 1.04 1.65 2.58 11.62 2.09 1.00 0.71 6.51 0.76 1.02 2.90 2.26 3.01 3.45 2.37 4.43 2.18 3.08 3.06
f1 (ppm)

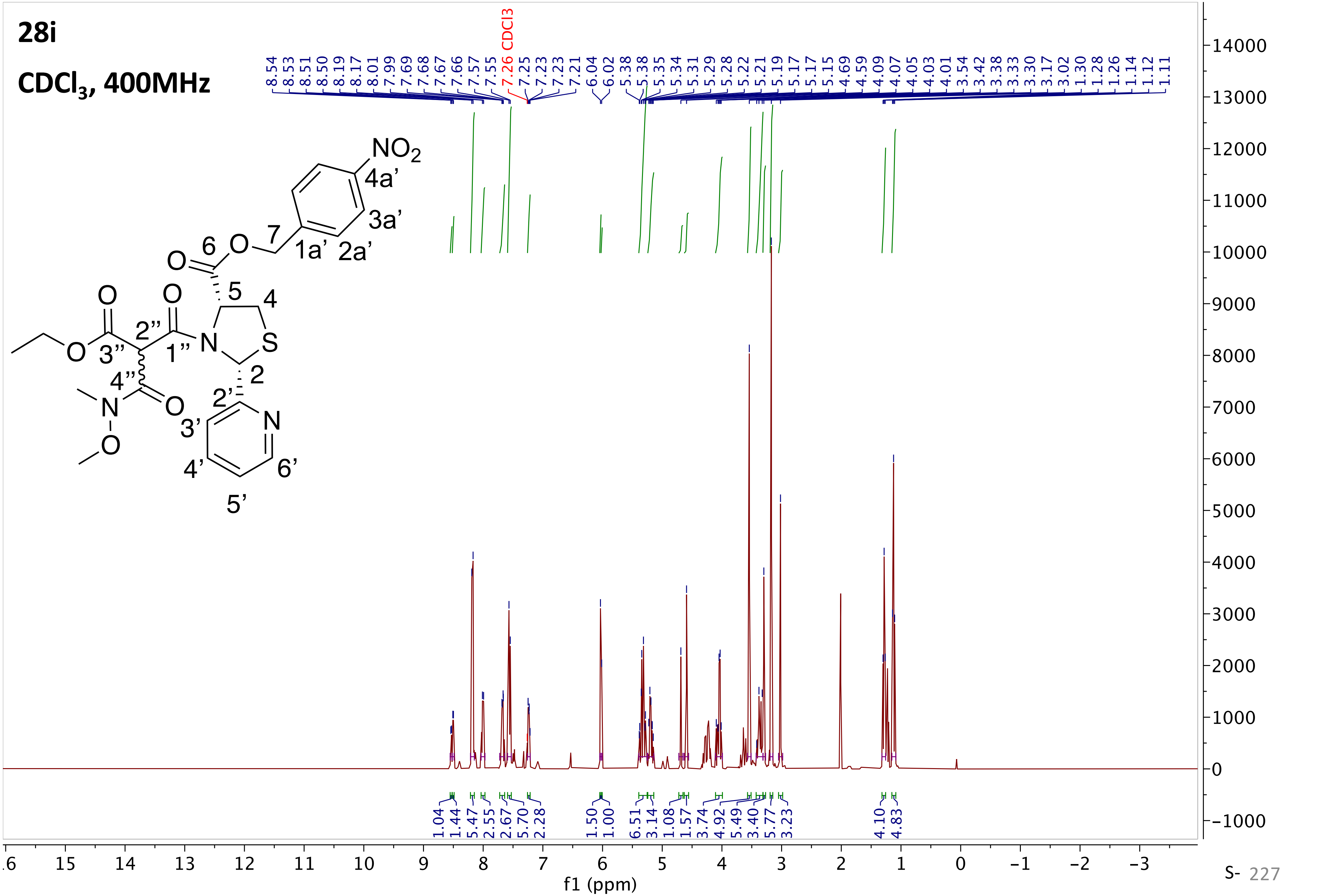

27i
CDCl$_3$, 101MHz
169.73
169.54
165.00
164.91
164.16
163.92
159.31
159.08
149.52
149.32
137.70
137.29
135.20
135.16
128.65
128.57
128.52
128.48
128.43
128.42
123.41
121.17
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.67
67.56
67.51
65.33
62.62
62.00
61.26
61.07
57.33
56.86
32.77
32.25
31.96
31.90
14.12
13.97
f1 (ppm)


27ii
$CDCl_3$, 400MHz
8.57 8.56 8.55 8.53 8.53 7.98 7.96 7.94 7.77 7.75 7.73 7.68 7.66 7.36 7.36 7.26 CDCl3 6.45 6.24 6.21 5.98 5.95 5.25 5.24 5.23 5.21 5.19 5.15 4.64 4.52 4.30 4.25 4.20 4.18 4.12 4.10 4.07 4.06 3.58 3.55 3.40 3.34 3.25 3.17 3.06 1.31 1.29 1.26 1.24 1.23 1.20 1.18 1.16
2.78 1.86 3.07 15.02 0.48 0.36 1.00 0.76 8.72 0.86 1.23 6.60 3.63 3.56 3.52 12.24 9.47 2.82 11.21 3.34
f1 (ppm)


27ii
CDCl3, 101MHz
169.77 169.63 169.57 164.82 164.40 164.06 163.93 163.79 163.70 158.77 157.94 157.67 150.54 150.47 150.36 140.22 139.81 139.57 139.38 135.15 128.85 128.81 128.78 128.73 128.63 128.50 122.82 120.90 120.48
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
68.44 67.81 67.06 67.02 65.31 63.93 62.71 62.19 61.37 61.14 58.25 57.37 56.96 33.46 32.81 32.07 32.01 14.29 14.15 14.03
4a'
3a'
2a'
1a'
7
O
6
O
5
4
S
N
2
1''
2''
3''
4''
O
O
O
N
O
2'
3'
4'
5'
6'
N
Br
f1 (ppm)

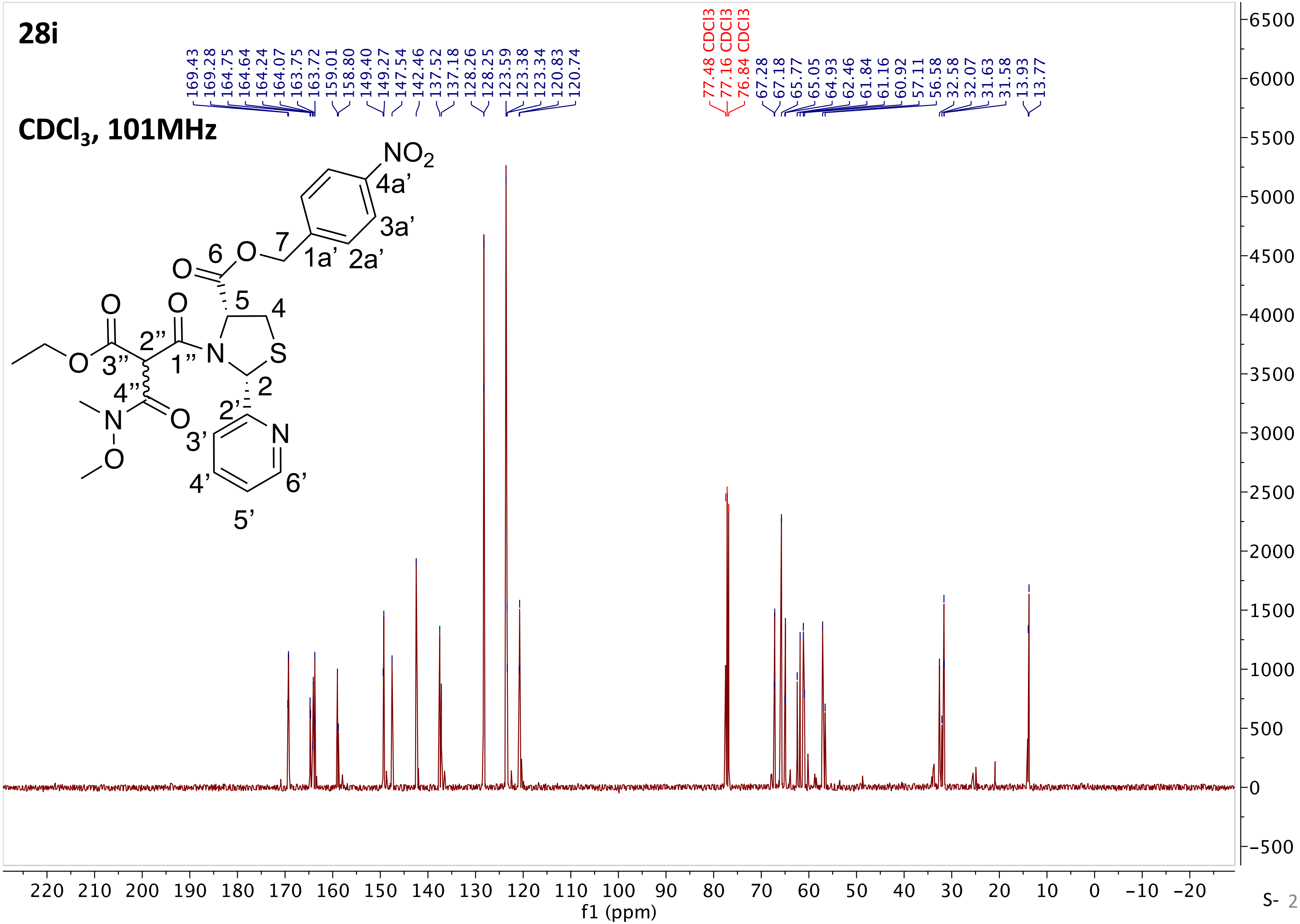

27iii
CDCl3, 400MHz
CDCl3
f1 (ppm)

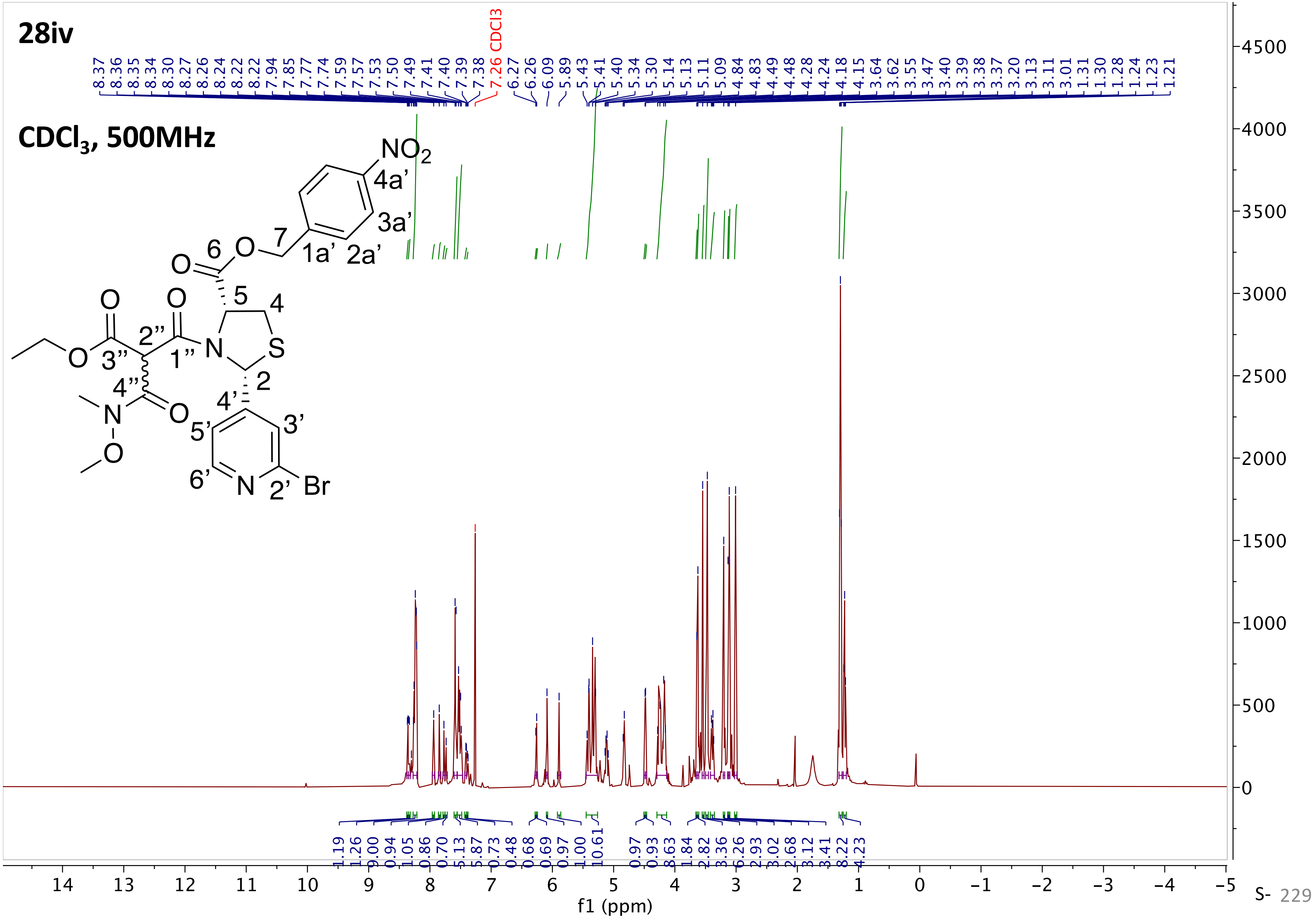

27iii
CDCl3, 101MHz
169.70
169.48
165.42
165.34
164.88
164.26
164.07
163.80
139.41
139.13
135.29
135.21
129.08
129.03
128.76
128.70
128.55
128.47
127.13
126.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.77
67.70
66.39
66.18
65.49
65.30
62.54
61.99
61.04
60.99
57.69
56.98
32.81
32.42
32.23
32.19
14.25
14.01
4a'
3a'
2a'
1a'
7
6
5
4
O
S
N
2
2''
1''
3''
4''
1'
2'
3'
4'
f1 (ppm)

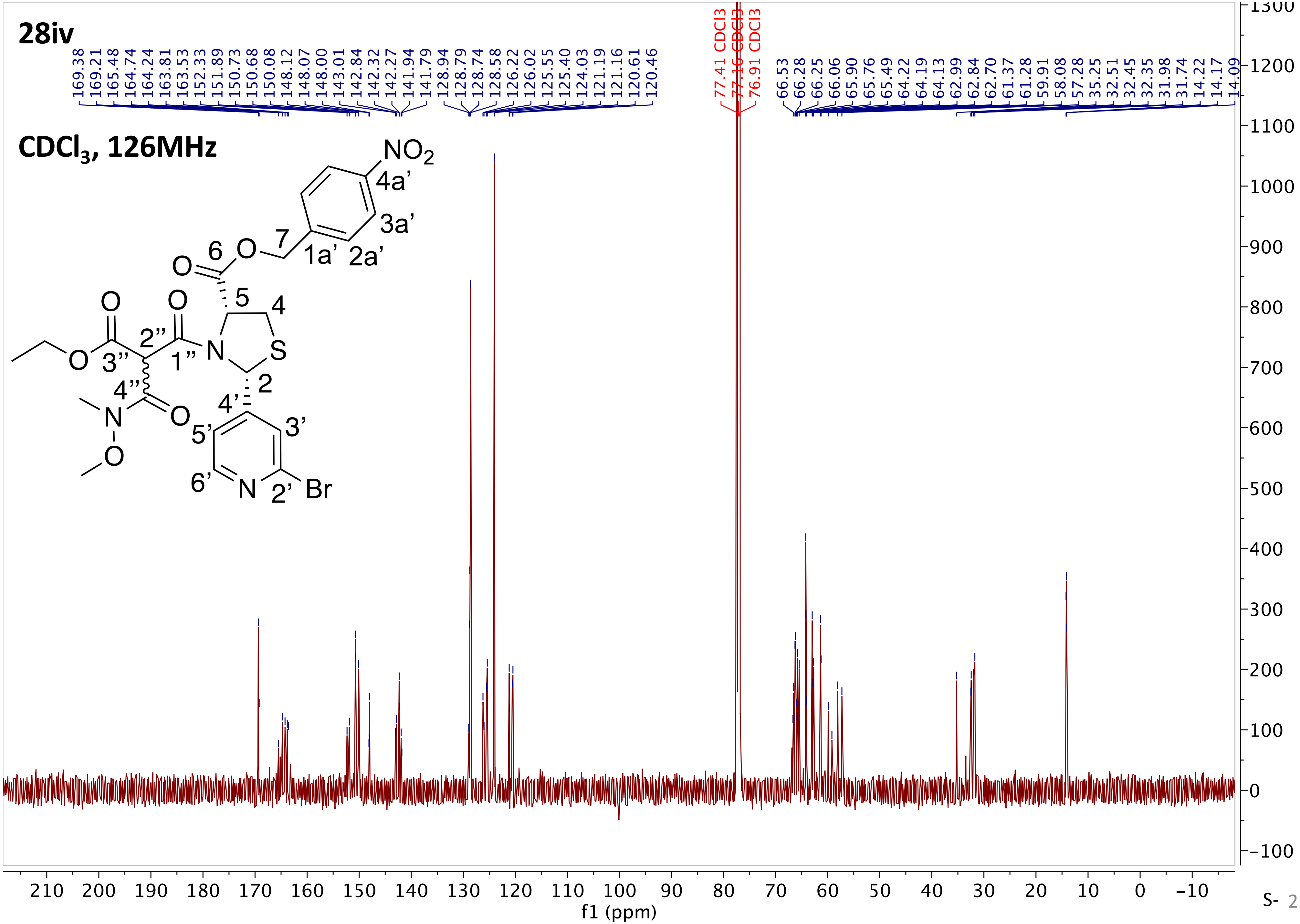

28i
CDCl3, 400MHz
7.26 CDCl3
f1 (ppm)

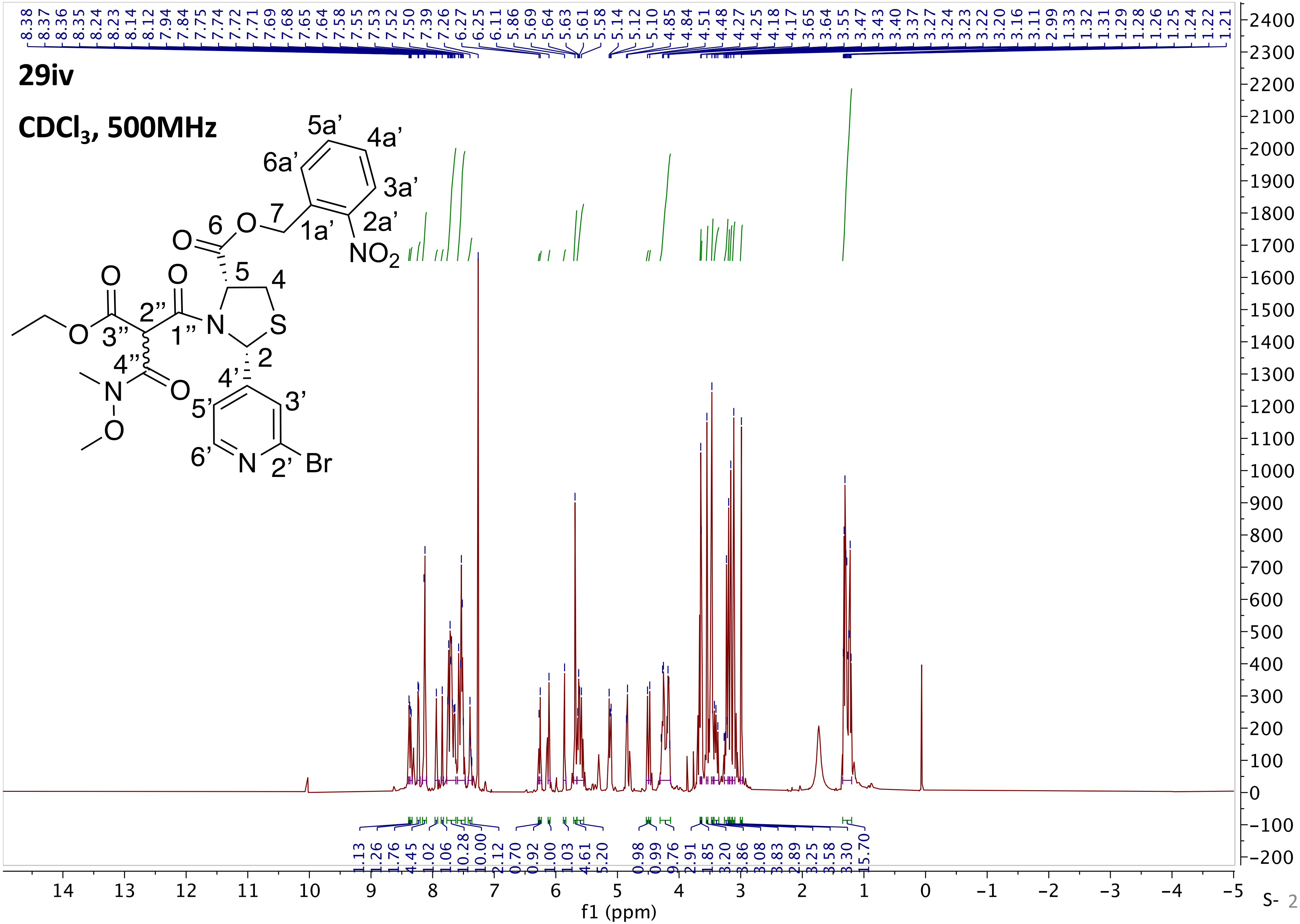
28i

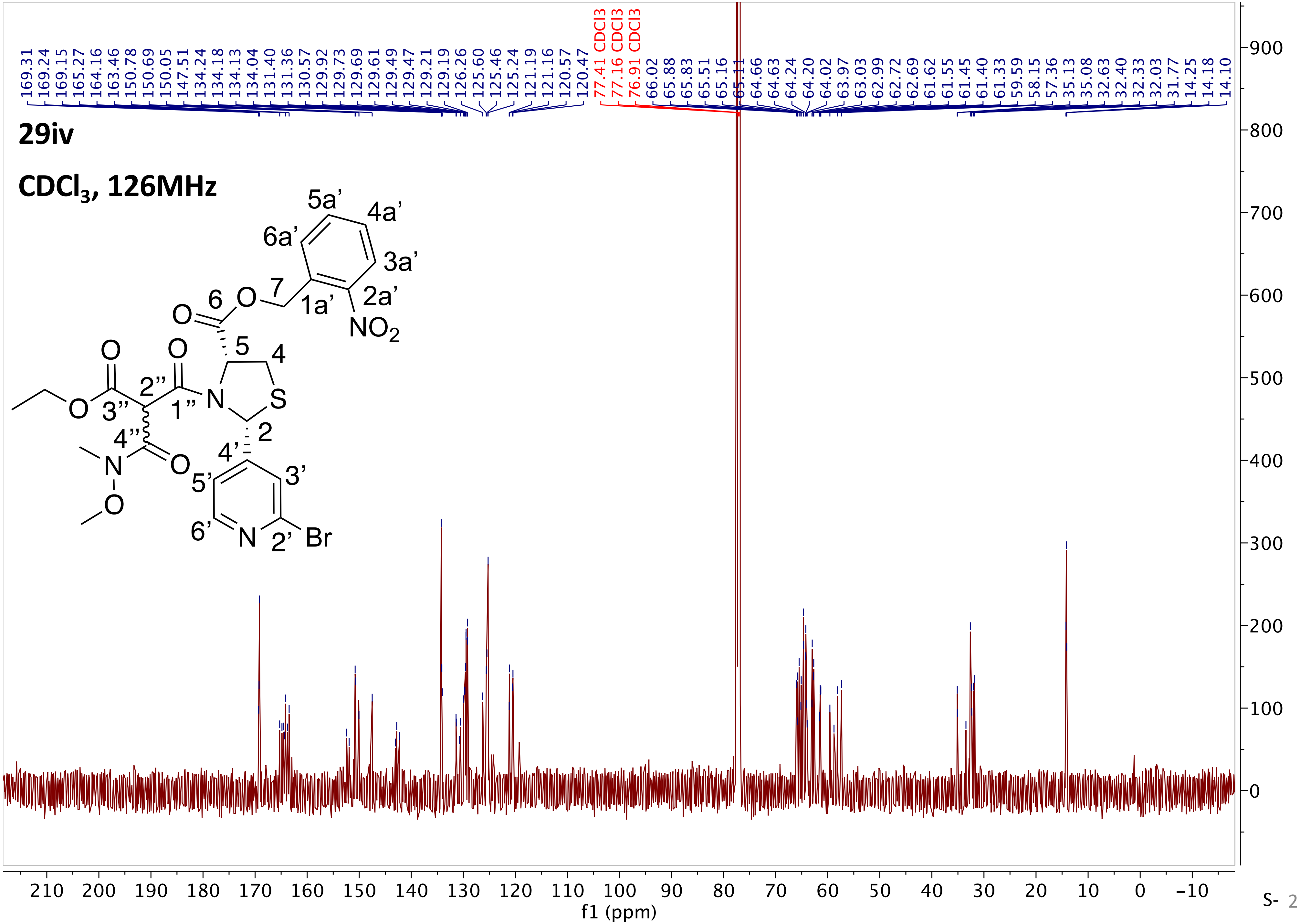
$CDCl_3$, 101MHz




28iv
CDCl3, 500MHz
f1 (ppm)
7.26 CDCl3

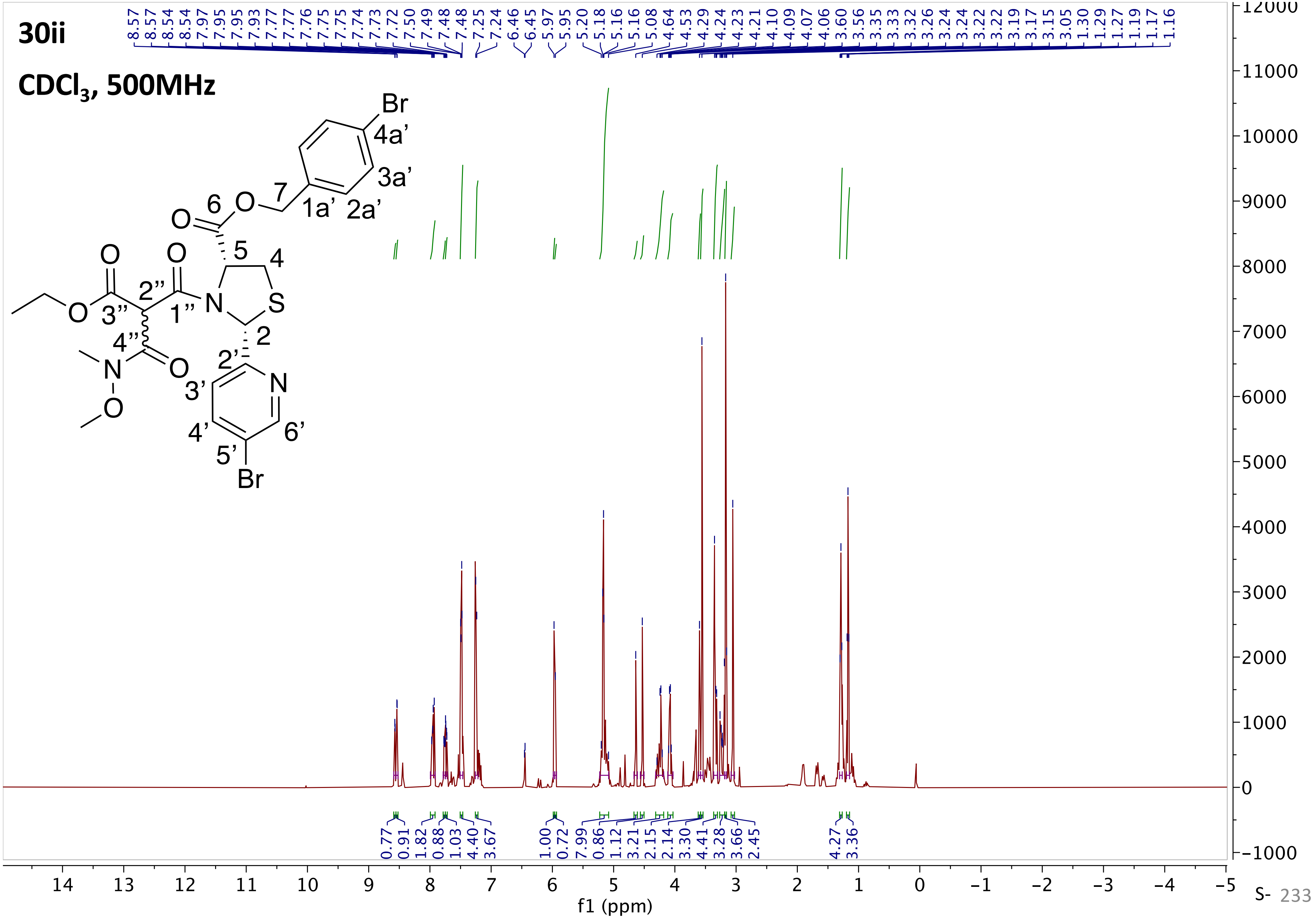

28iv
CDCl3, 126MHz
169.38
169.21
165.48
164.74
164.24
163.81
163.53
152.33
151.89
150.73
150.68
150.08
148.12
148.07
148.00
143.01
142.84
142.32
142.27
141.94
141.79
128.94
128.79
128.74
128.58
126.22
126.02
125.55
125.40
124.03
121.19
121.16
120.61
120.46
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.53
66.28
66.25
66.06
65.90
65.76
65.49
64.22
64.19
64.13
62.99
62.84
62.70
61.37
61.28
59.91
58.08
57.28
35.25
32.51
32.45
32.35
31.98
31.74
14.22
14.17
14.09
f1 (ppm)


29iv
CDCl3, 500MHz
f1 (ppm)


29iv
CDCl3, 126MHz
169.31
169.24
169.15
165.27
164.16
163.46
150.78
150.69
150.05
147.51
134.24
134.18
134.13
134.04
131.40
131.36
130.57
129.92
129.73
129.69
129.61
129.49
129.47
129.21
129.19
126.26
125.60
125.46
125.24
121.19
121.16
120.57
120.47
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.02
65.88
65.83
65.51
65.16
65.11
64.66
64.63
64.24
64.20
64.02
63.97
63.03
62.99
62.72
62.69
61.62
61.55
61.45
61.40
61.33
59.59
58.15
57.36
35.13
35.08
32.63
32.40
32.33
32.03
31.77
14.25
14.18
14.10
f1 (ppm)

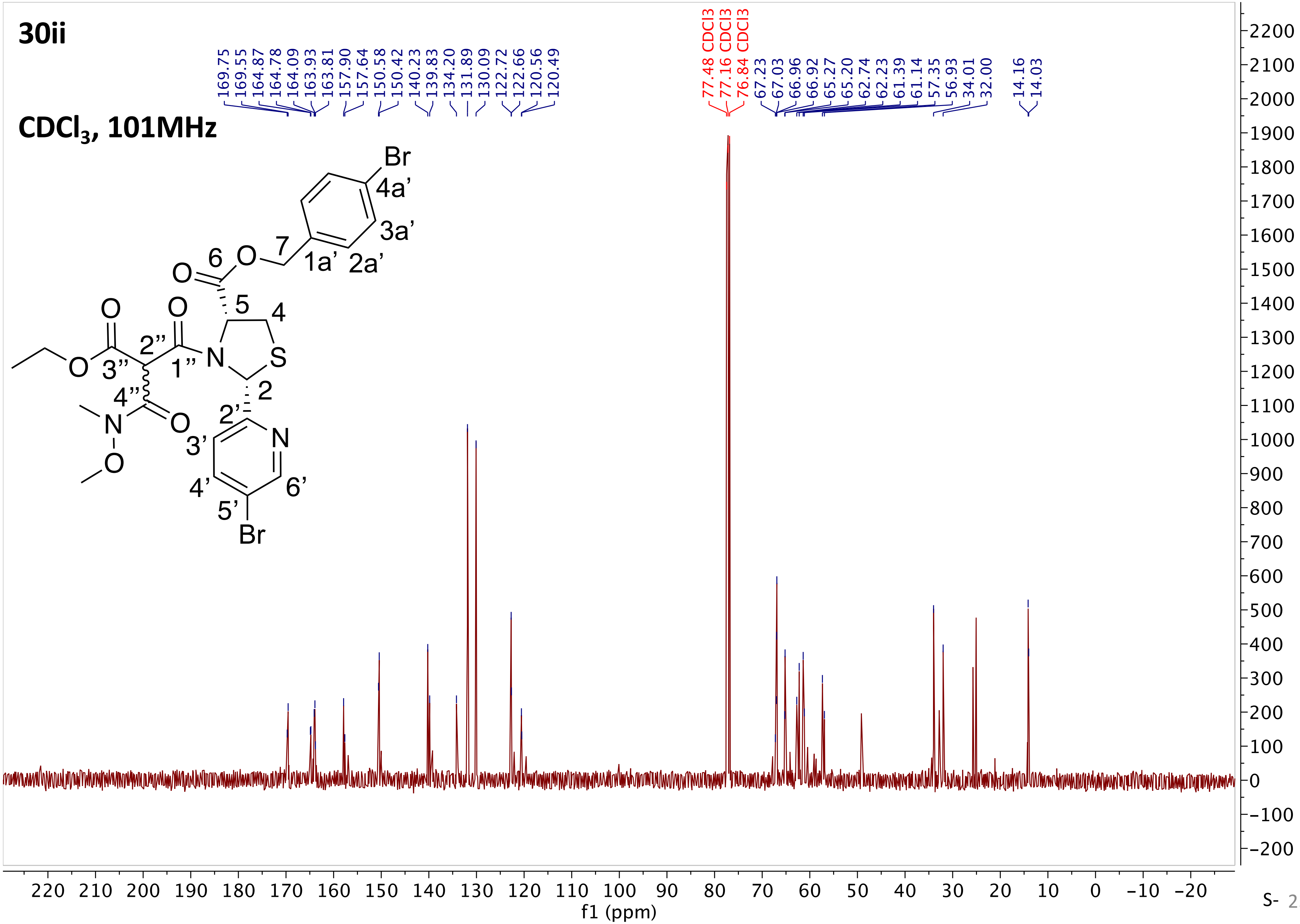
30ii

$CDCl_3$, 500MHz



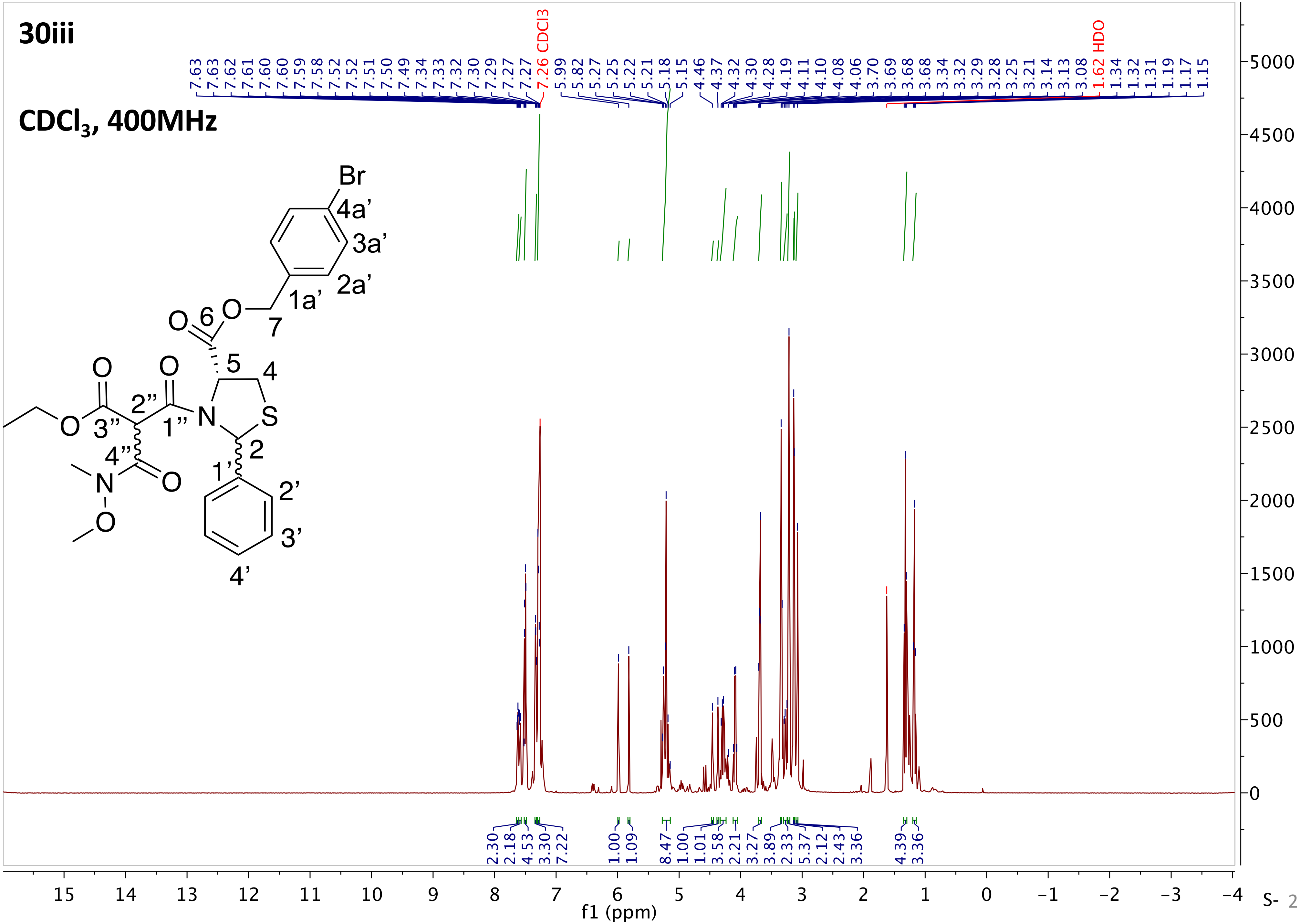
30ii

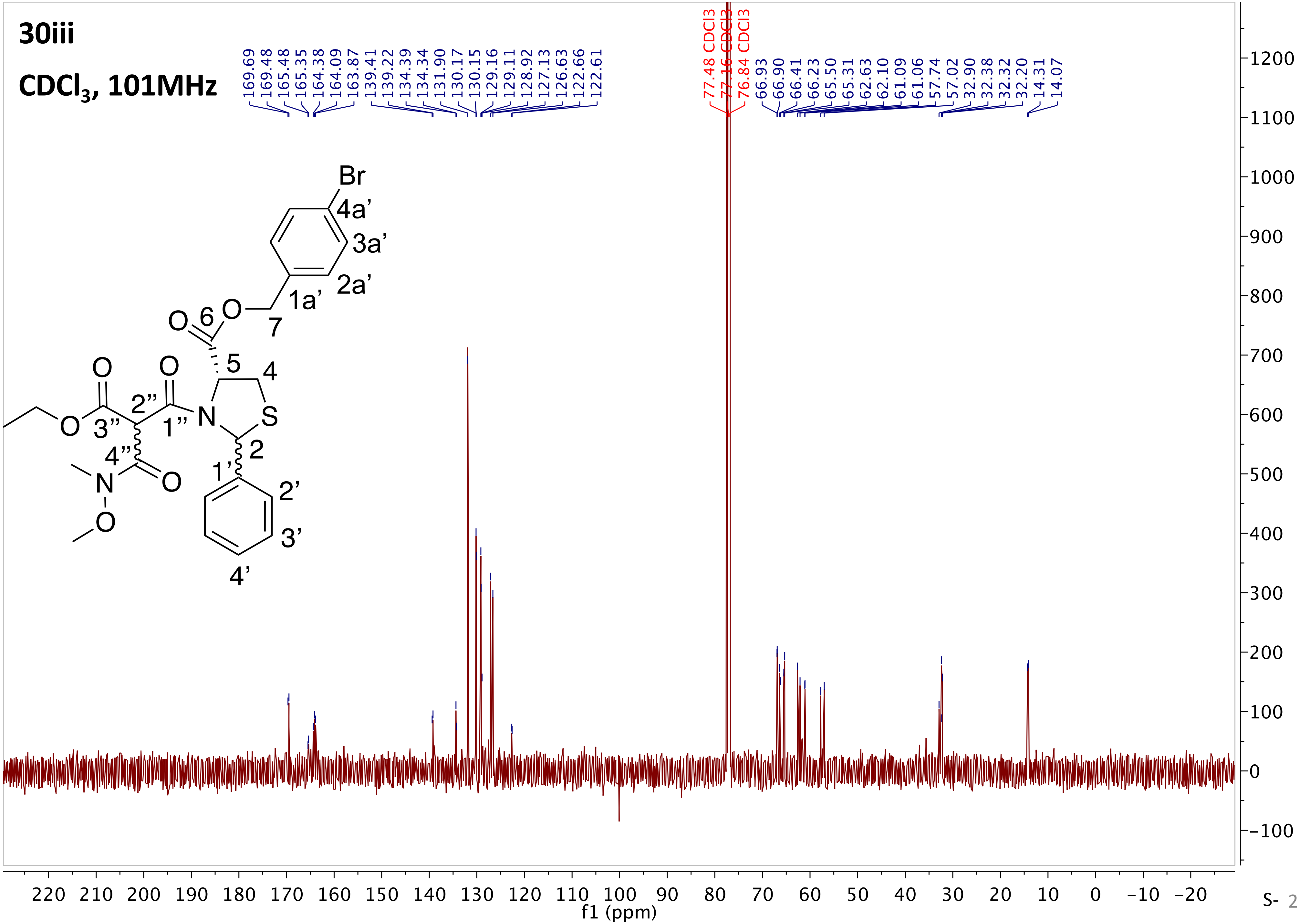
$CDCl_3$, 101MHz

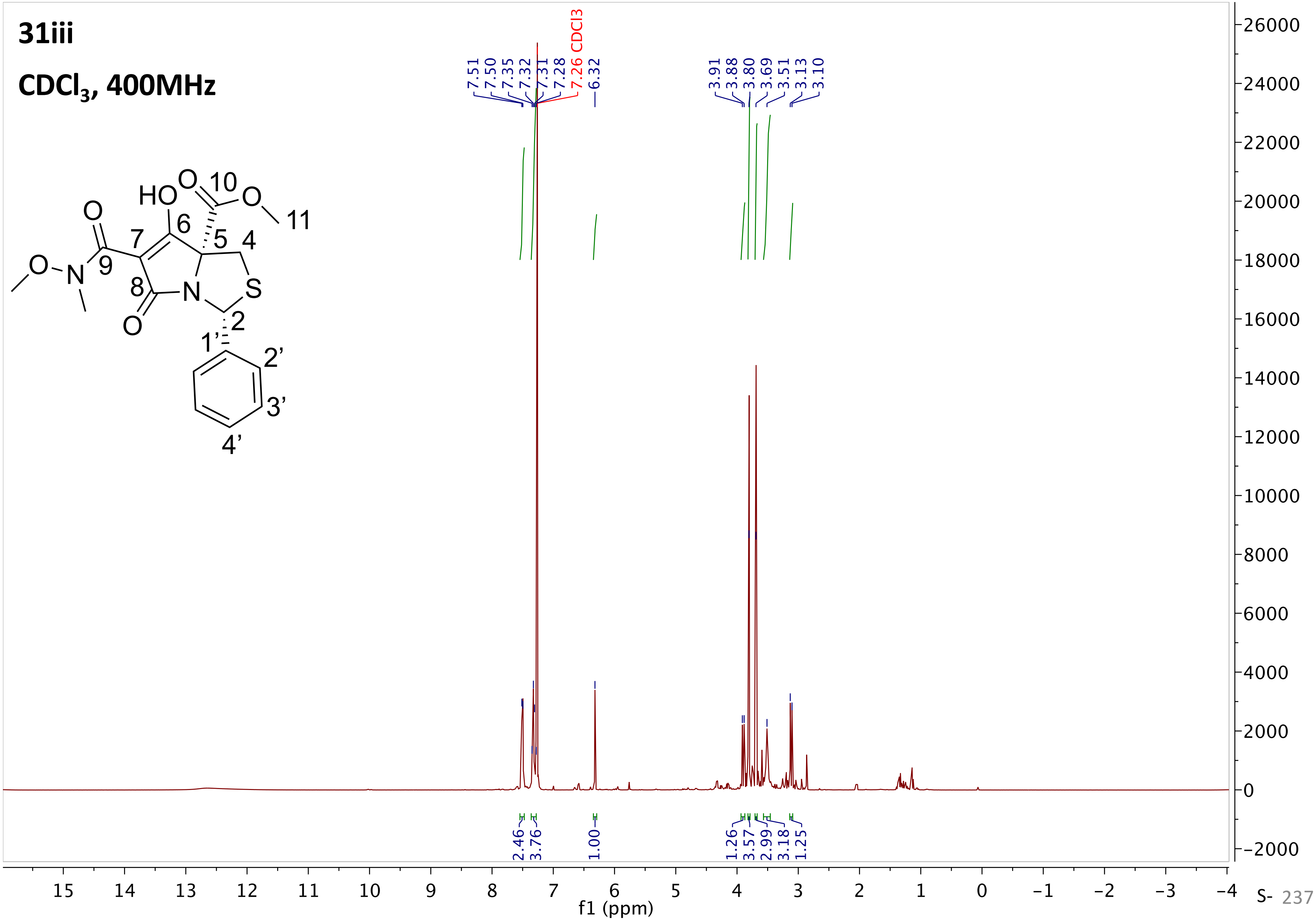


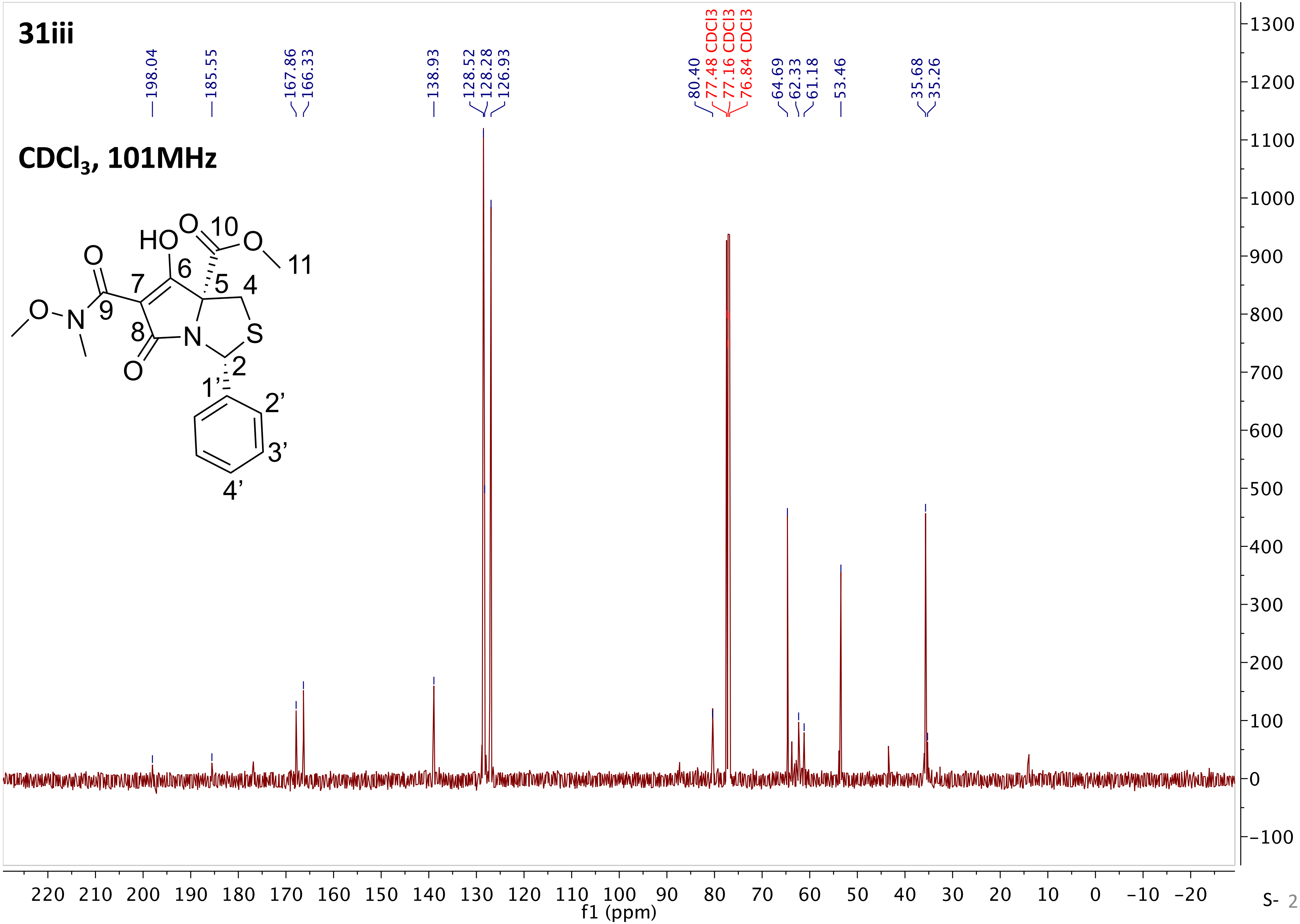
30iii

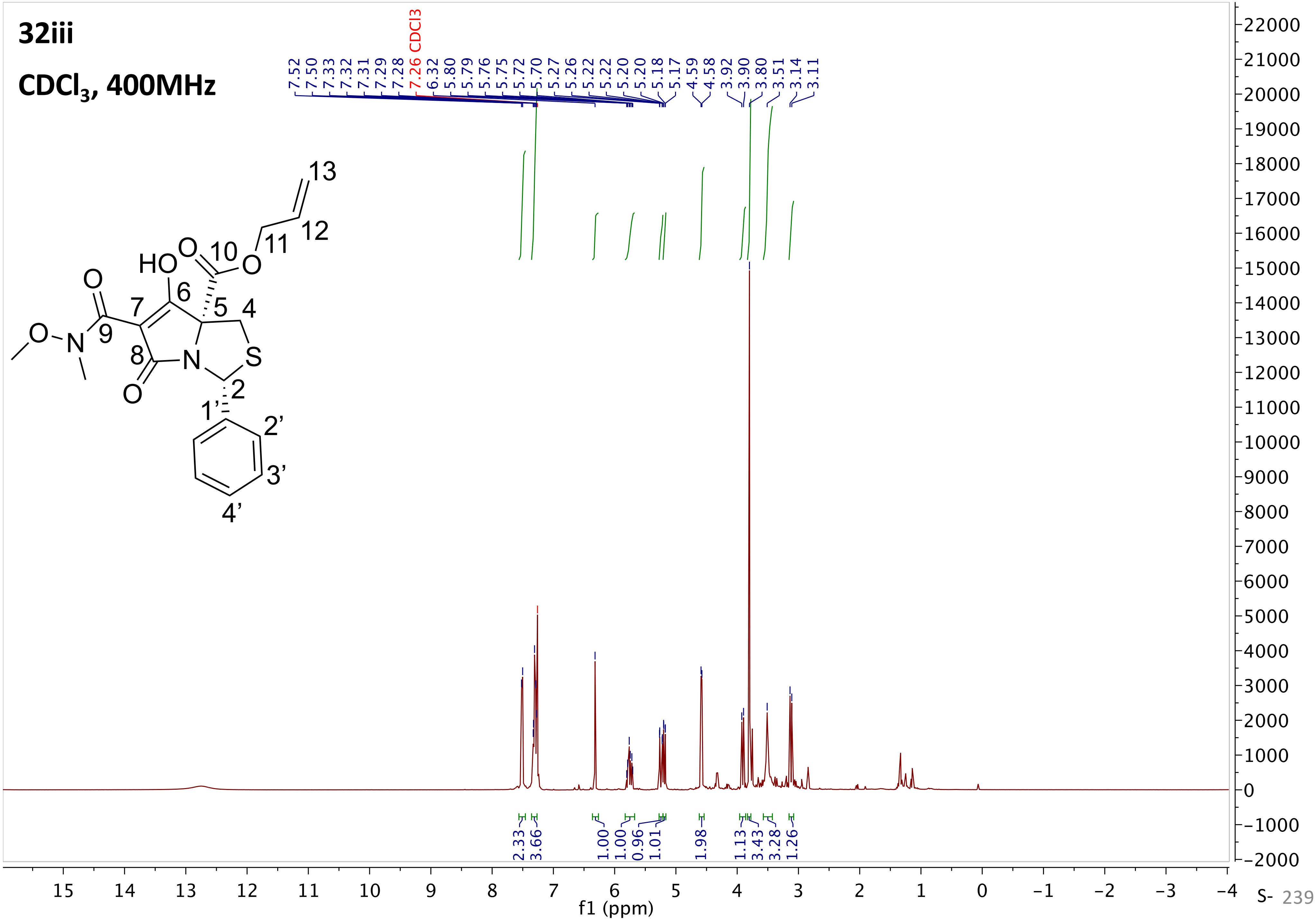
$CDCl_3$, 400MHz



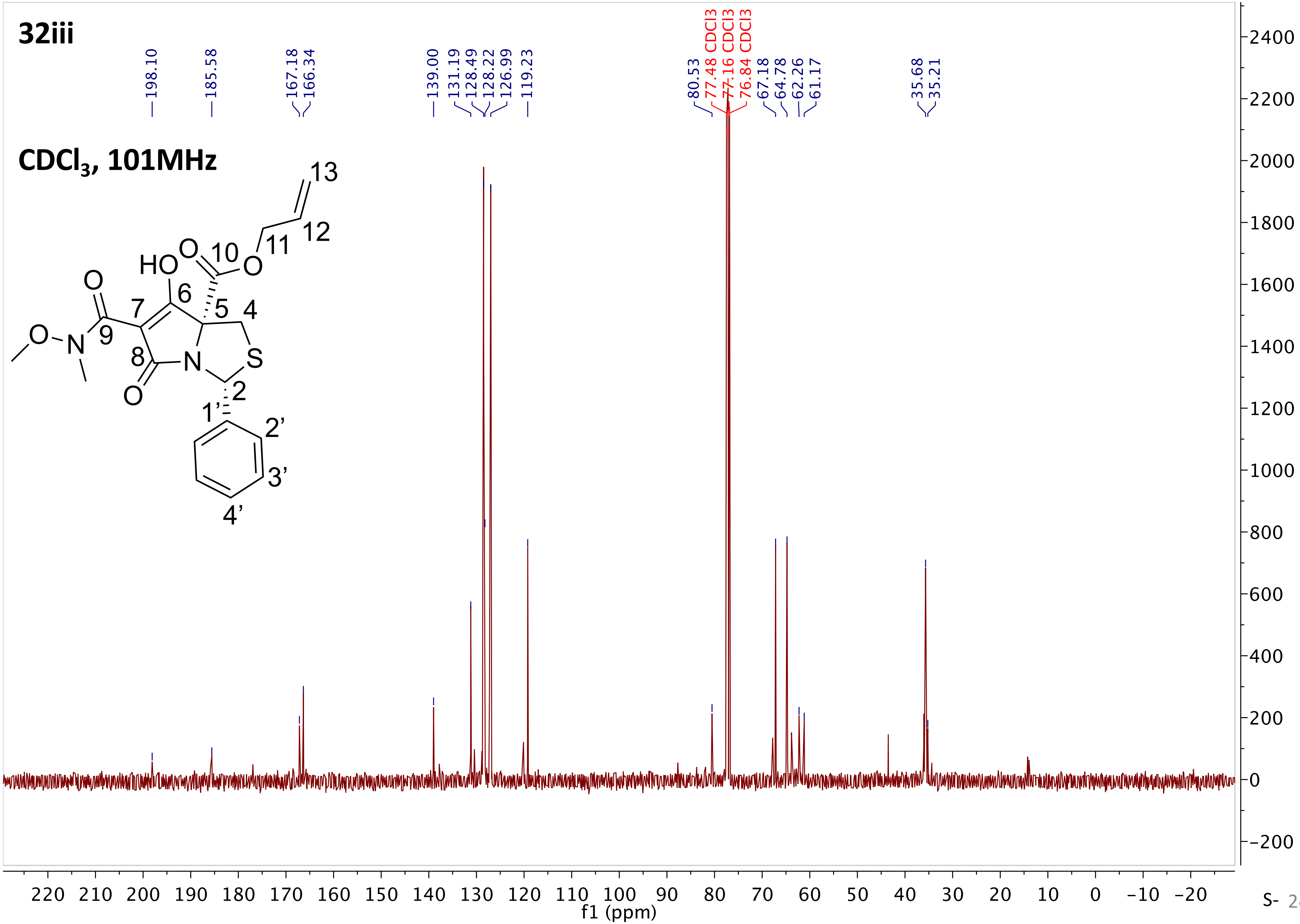

30iii
CDCl3, 101MHz
169.69
169.48
165.48
165.35
164.38
164.09
163.87
139.41
139.22
134.39
134.34
131.90
130.17
130.15
129.16
129.11
128.92
127.13
126.63
122.66
122.61
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.93
66.90
66.41
66.23
65.50
65.31
62.63
62.10
61.09
61.06
57.74
57.02
32.90
32.38
32.32
32.20
14.31
14.07
Br
4a'
3a'
2a'
1a'
O
6
O
7
5
4
O
O
2''
N
S
O
3''
1''
2
4''
1'
2'
N
O
O
3'
4'
f1 (ppm)


31iii
CDCl3, 400MHz
7.51
7.50
7.35
7.32
7.31
7.28
7.26 CDCl3
6.32
3.91
3.88
3.80
3.69
3.51
3.13
3.10
2.46
3.76
1.00
1.26
3.57
2.99
3.18
1.25
f1 (ppm)


31iii
CDCl3, 101MHz
198.04
185.55
167.86
166.33
138.93
128.52
128.28
126.93
80.40
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
64.69
62.33
61.18
53.46
35.68
35.26
f1 (ppm)



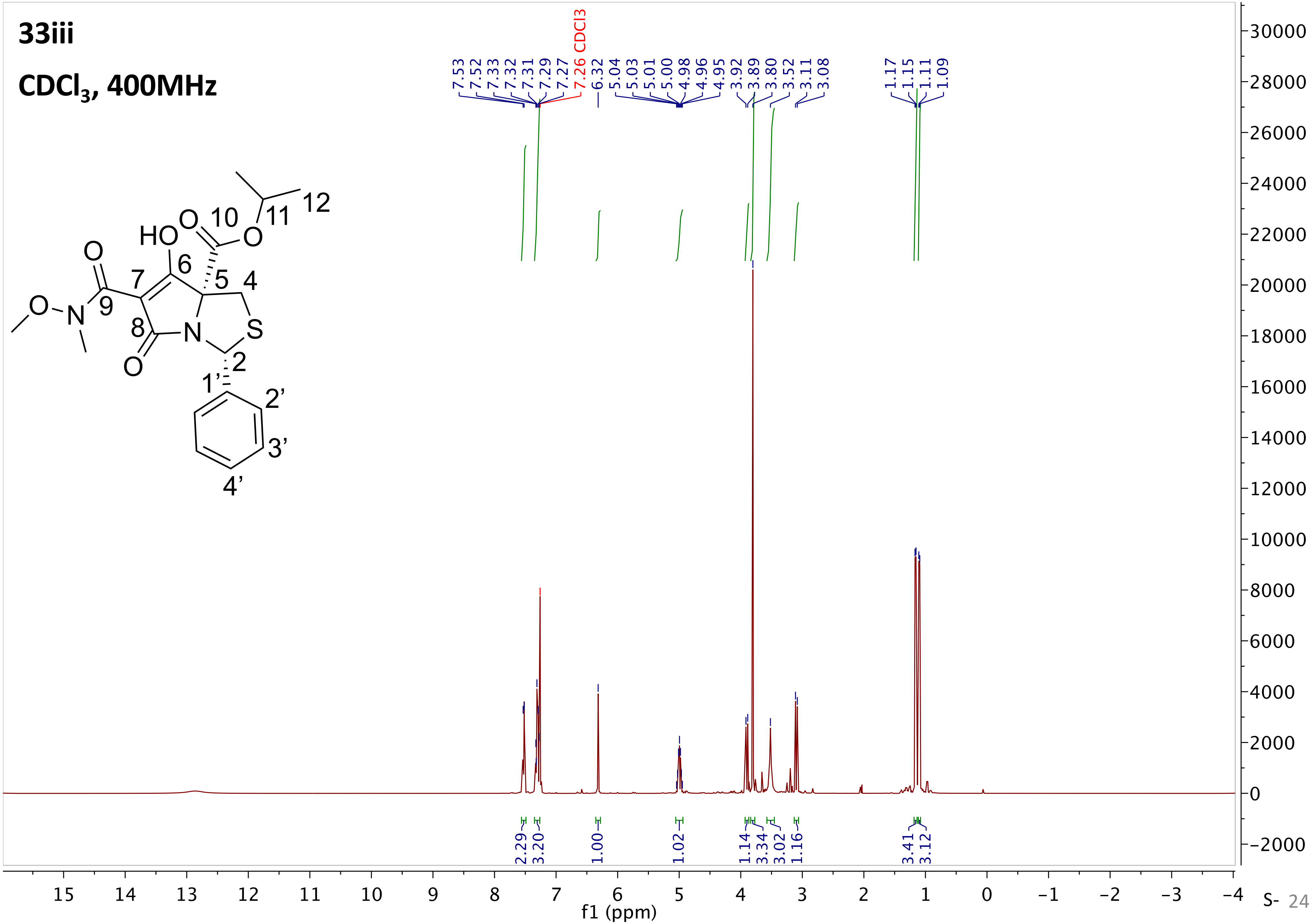
32iii
CDCl3, 400MHz
7.52 7.50 7.33 7.32 7.31 7.29 7.28 7.26 CDCl3 6.32 5.80 5.79 5.76 5.75 5.72 5.70 5.27 5.26 5.22 5.22 5.20 5.20 5.18 5.17 4.59 4.58 3.92 3.90 3.80 3.51 3.14 3.11
2.33 3.66 1.00 1.00 0.96 1.01 1.98 1.13 3.43 3.28 1.26
f1 (ppm)

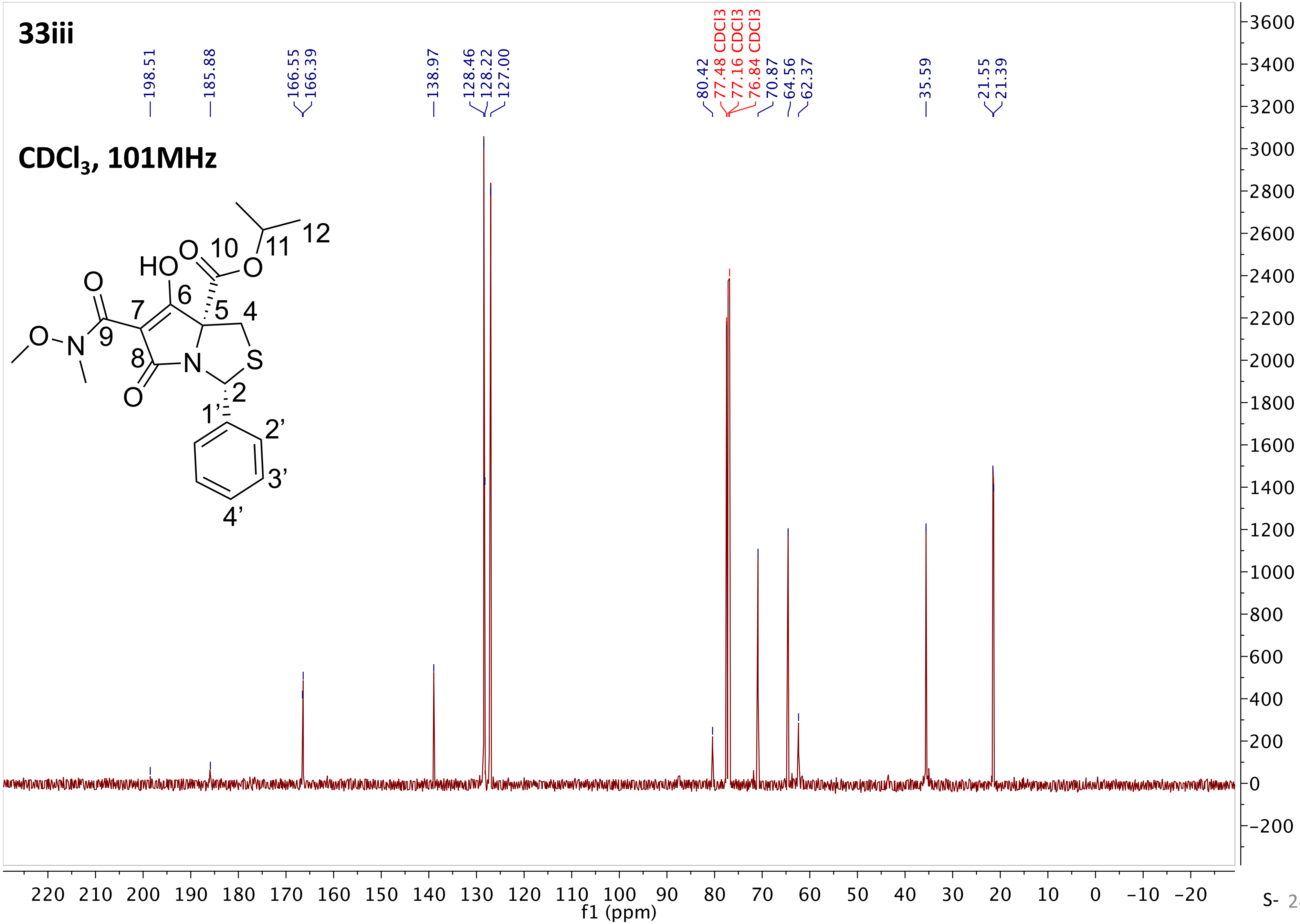


32iii
CDCl3, 101MHz
198.10
185.58
167.18
166.34
139.00
131.19
128.49
128.22
126.99
119.23
80.53
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.18
64.78
62.26
61.17
35.68
35.21
f1 (ppm)

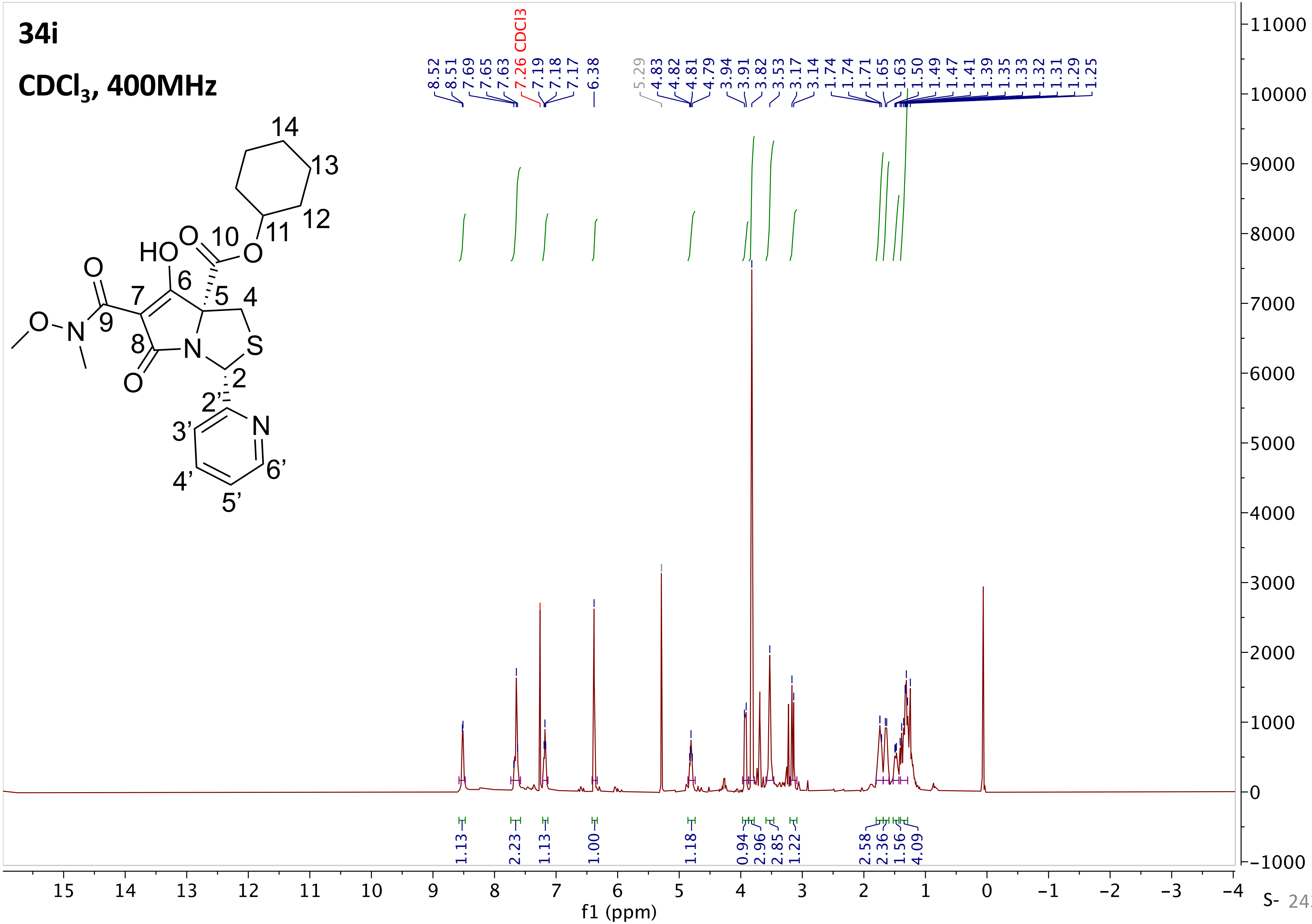
33iii

CDCl$_3$, 400MHz



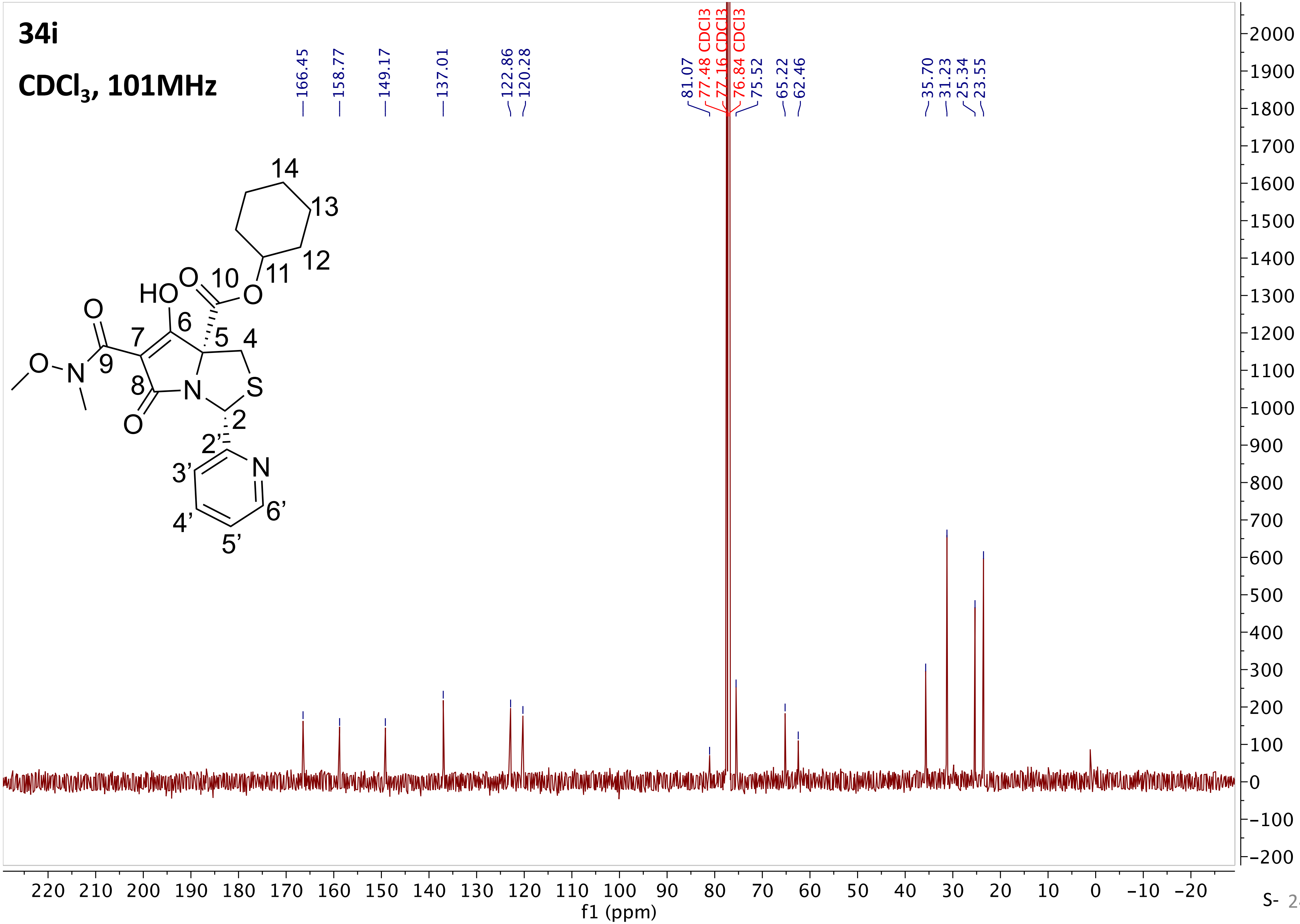


33iii
CDCl3, 101MHz
198.51
185.88
166.55
166.39
138.97
128.46
128.22
127.00
80.42
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.87
64.56
62.37
35.59
21.55
21.39
f1 (ppm)


34i
CDCl3, 400MHz
8.52 8.51 7.69 7.65 7.63 7.26 CDCl3 7.19 7.18 7.17 6.38 5.29 4.83 4.82 4.81 4.79 3.94 3.91 3.82 3.53 3.17 3.14 1.74 1.74 1.71 1.65 1.63 1.50 1.49 1.47 1.41 1.39 1.35 1.33 1.32 1.31 1.29 1.25
1.13 2.23 1.13 1.00 1.18 0.94 2.96 2.85 1.22 2.58 2.36 1.56 4.09
f1 (ppm)

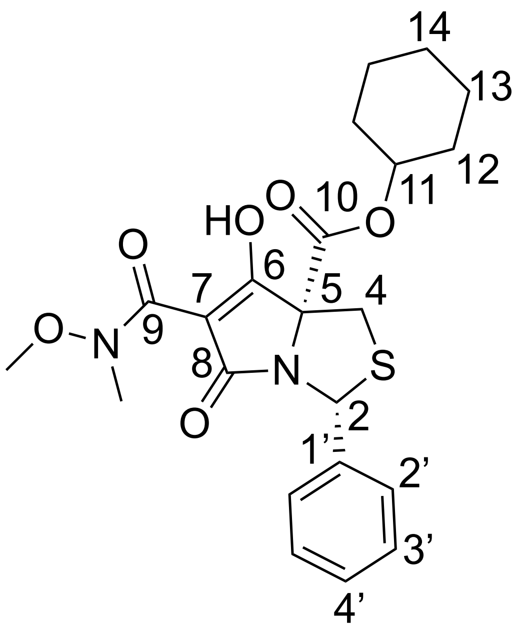
34i

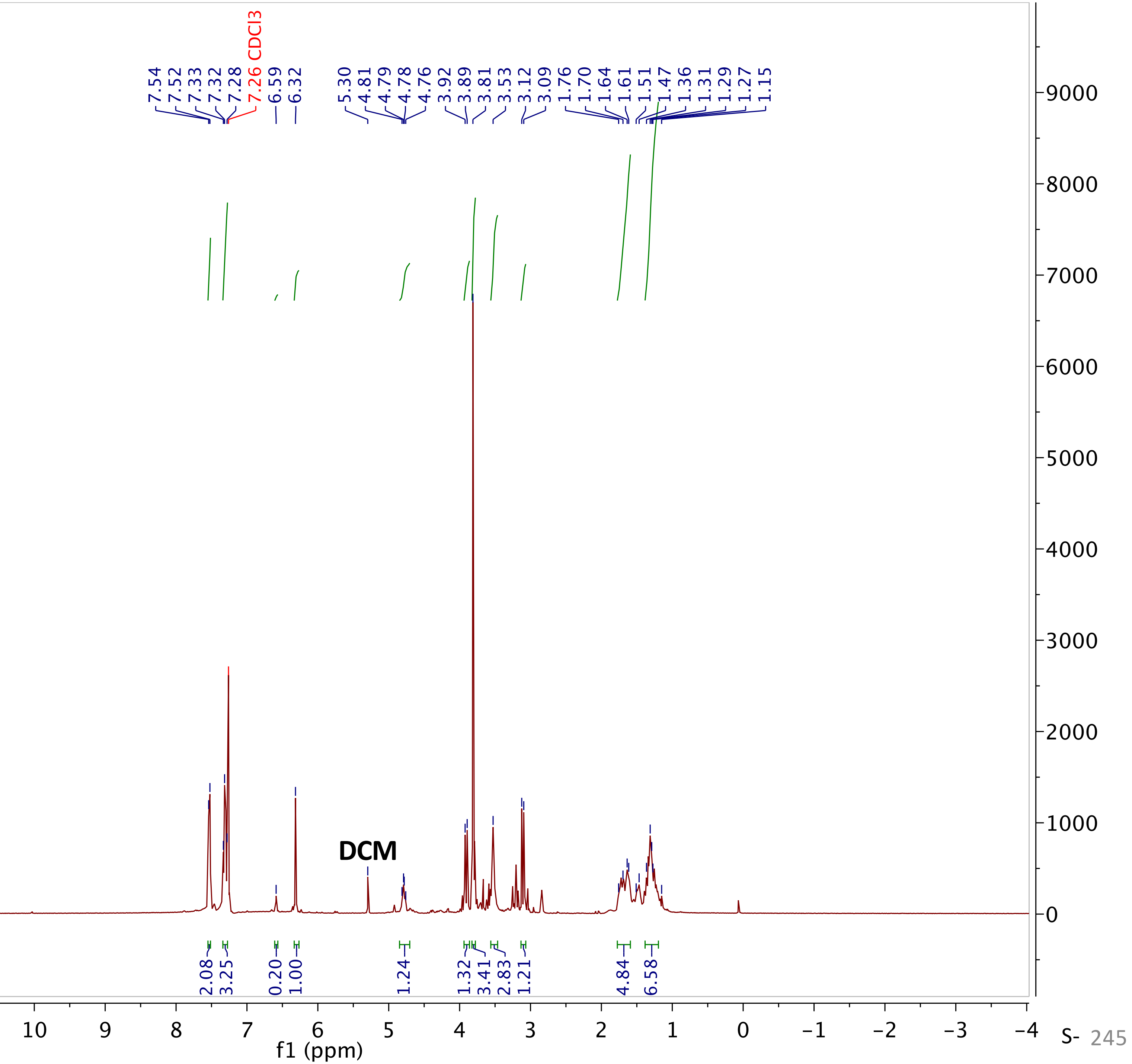
$CDCl_3$, 101MHz

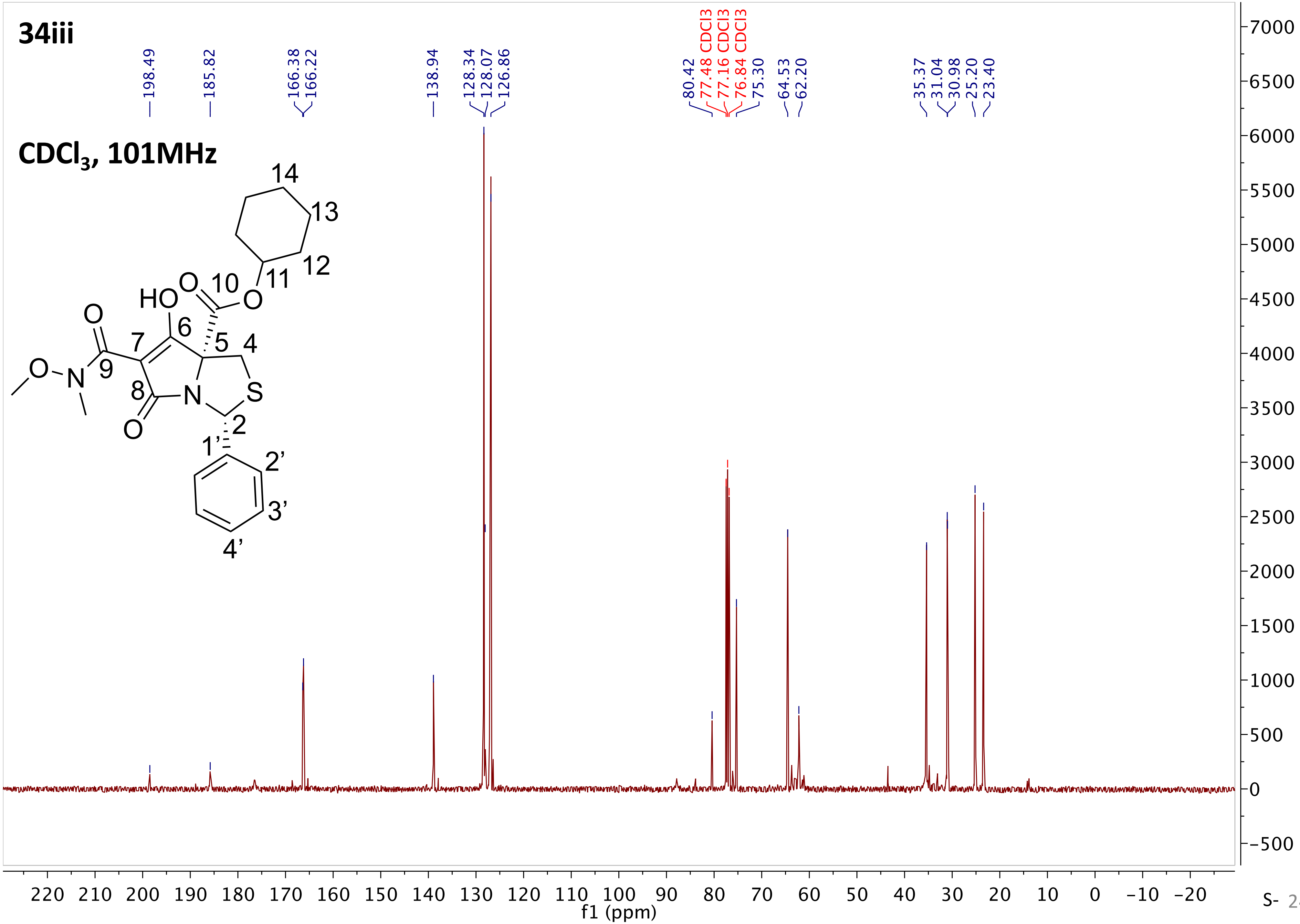


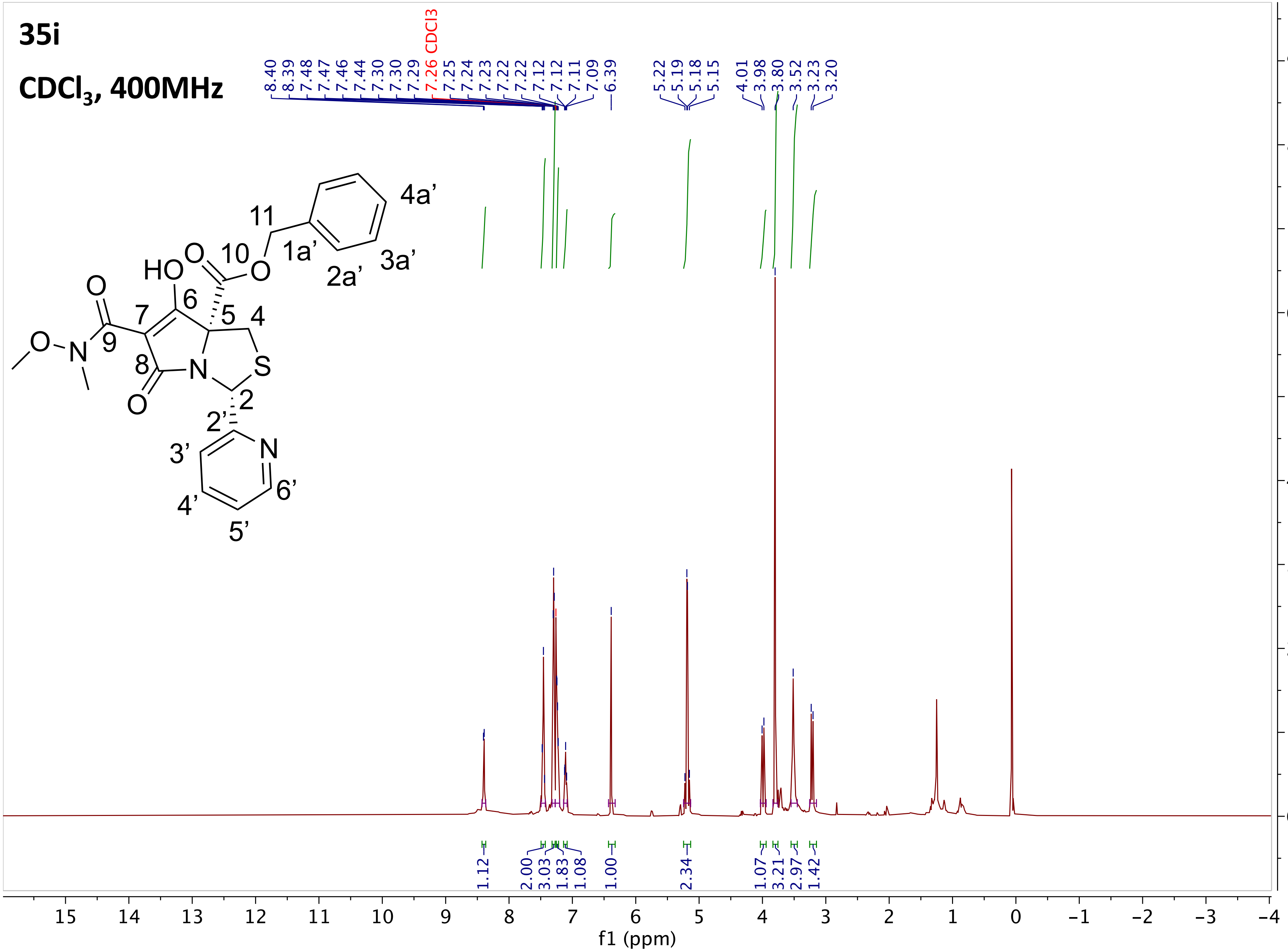
34iii

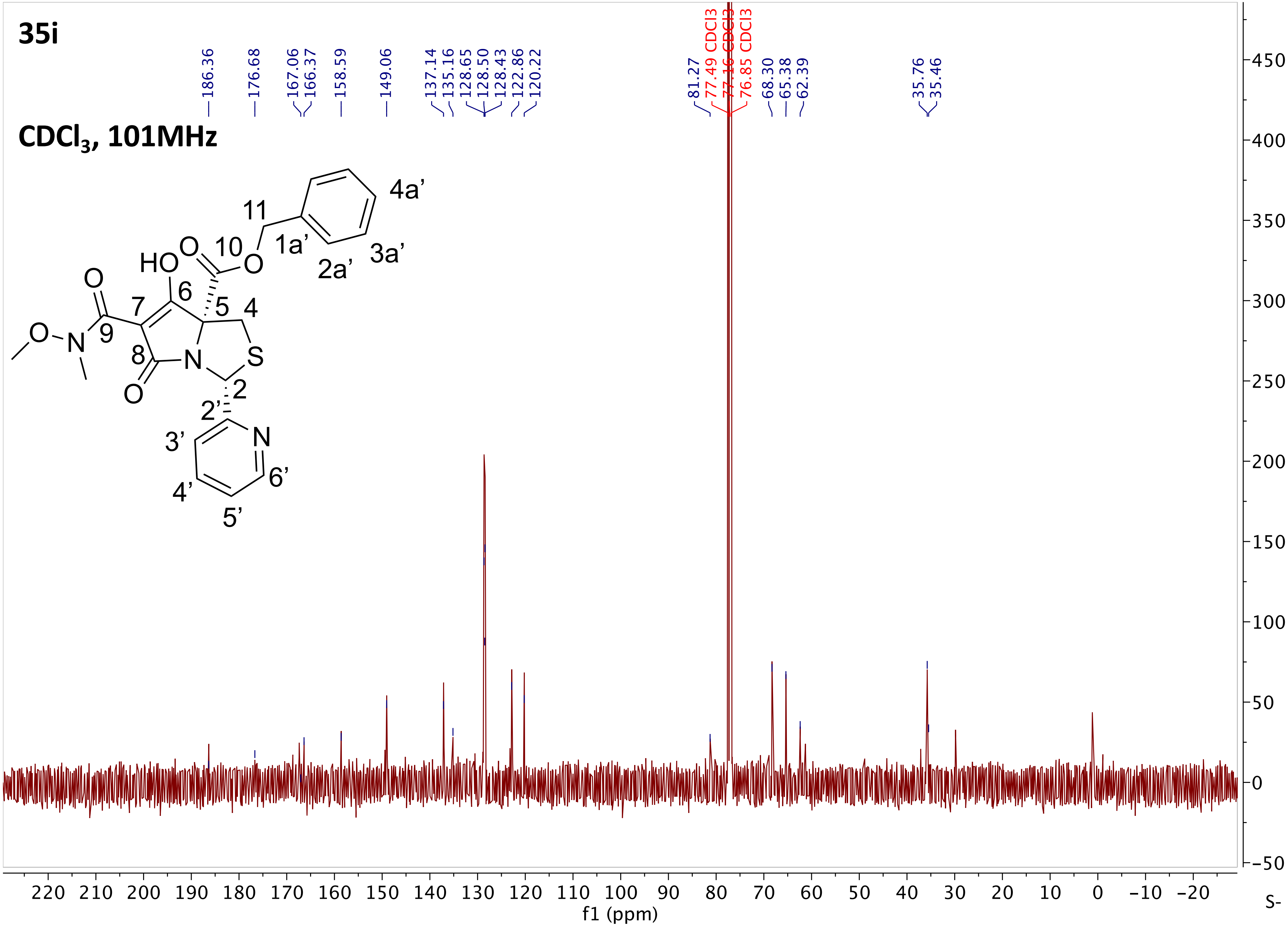
$CDCl_3$, 400MHz

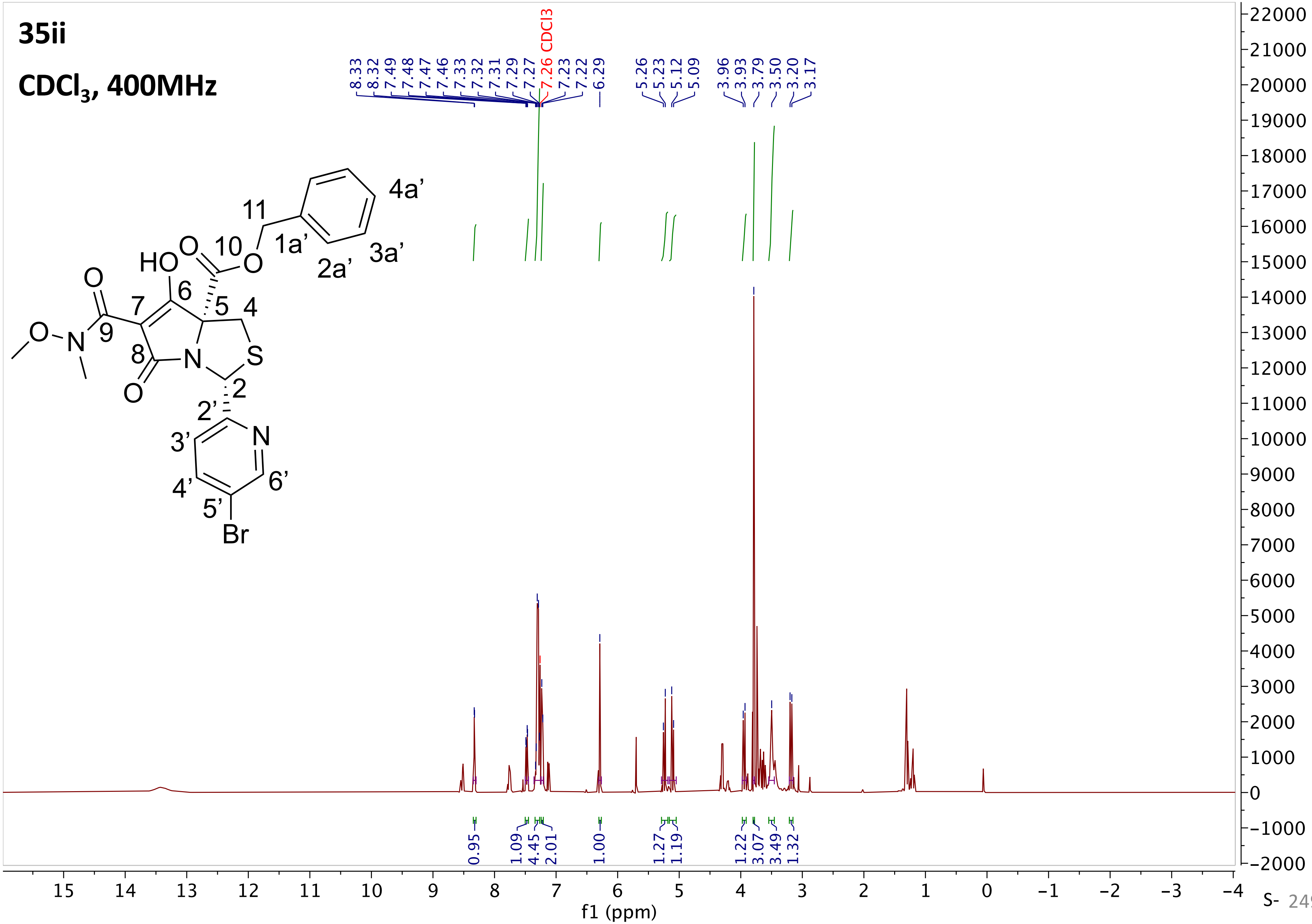




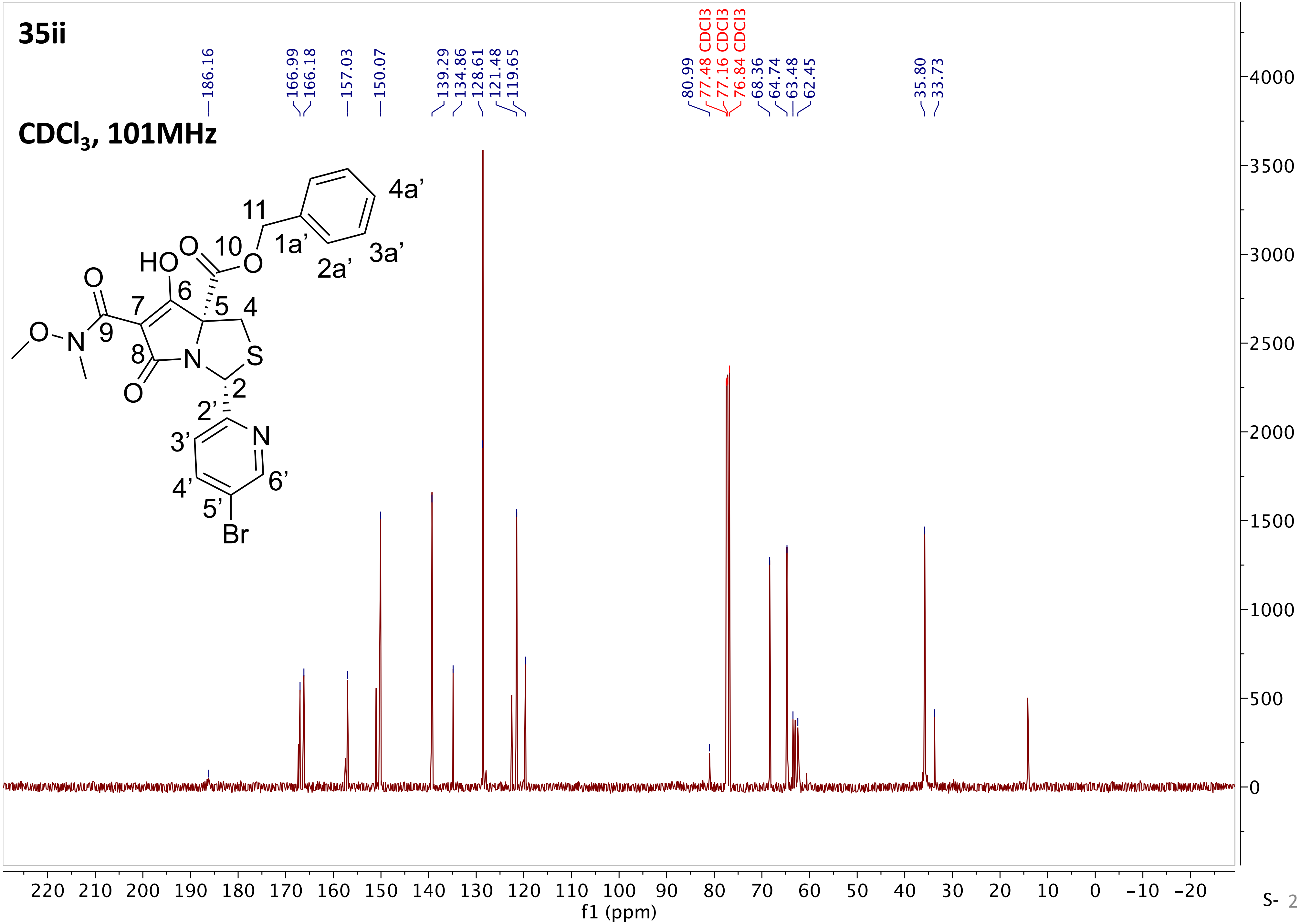

34iii
CDCl3, 101MHz
198.49
185.82
166.38
166.22
138.94
128.34
128.07
126.86
80.42
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.30
64.53
62.20
35.37
31.04
30.98
25.20
23.40
f1 (ppm)

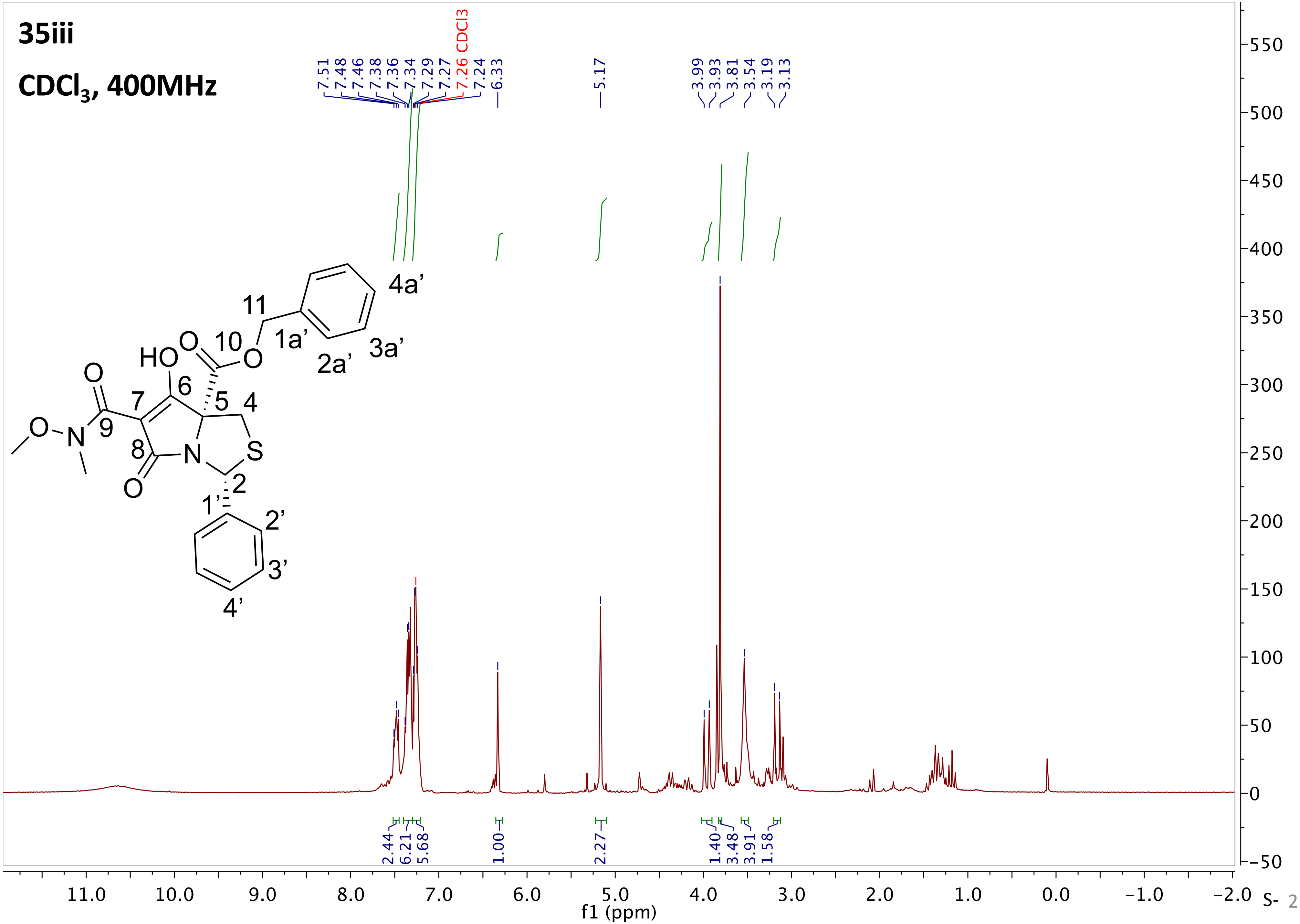

35i
CDCl3, 400MHz
8.40 8.39 7.48 7.47 7.46 7.44 7.30 7.30 7.29 7.26 CDCl3 7.25 7.24 7.23 7.22 7.22 7.12 7.12 7.11 7.09 6.39
5.22 5.19 5.18 5.15
4.01 3.98 3.80 3.52 3.23 3.20
1.12 2.00 3.03 1.83 1.08 1.00 2.34 1.07 3.21 2.97 1.42
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)
9000 8000 7000 6000 5000 4000 3000 2000 1000 0
HO O O 10 11 1a' 2a' 3a' 4a' 6 5 4 7 9 8 N S 2 2' 3' 4' 5' 6' N O N O


35i
CDCl3, 101MHz
186.36
176.68
167.06
166.37
158.59
149.06
137.14
135.16
128.65
128.50
128.43
122.86
120.22
81.27
77.49 CDCl3
77.16 CDCl3
76.85 CDCl3
68.30
65.38
62.39
35.76
35.46
f1 (ppm)

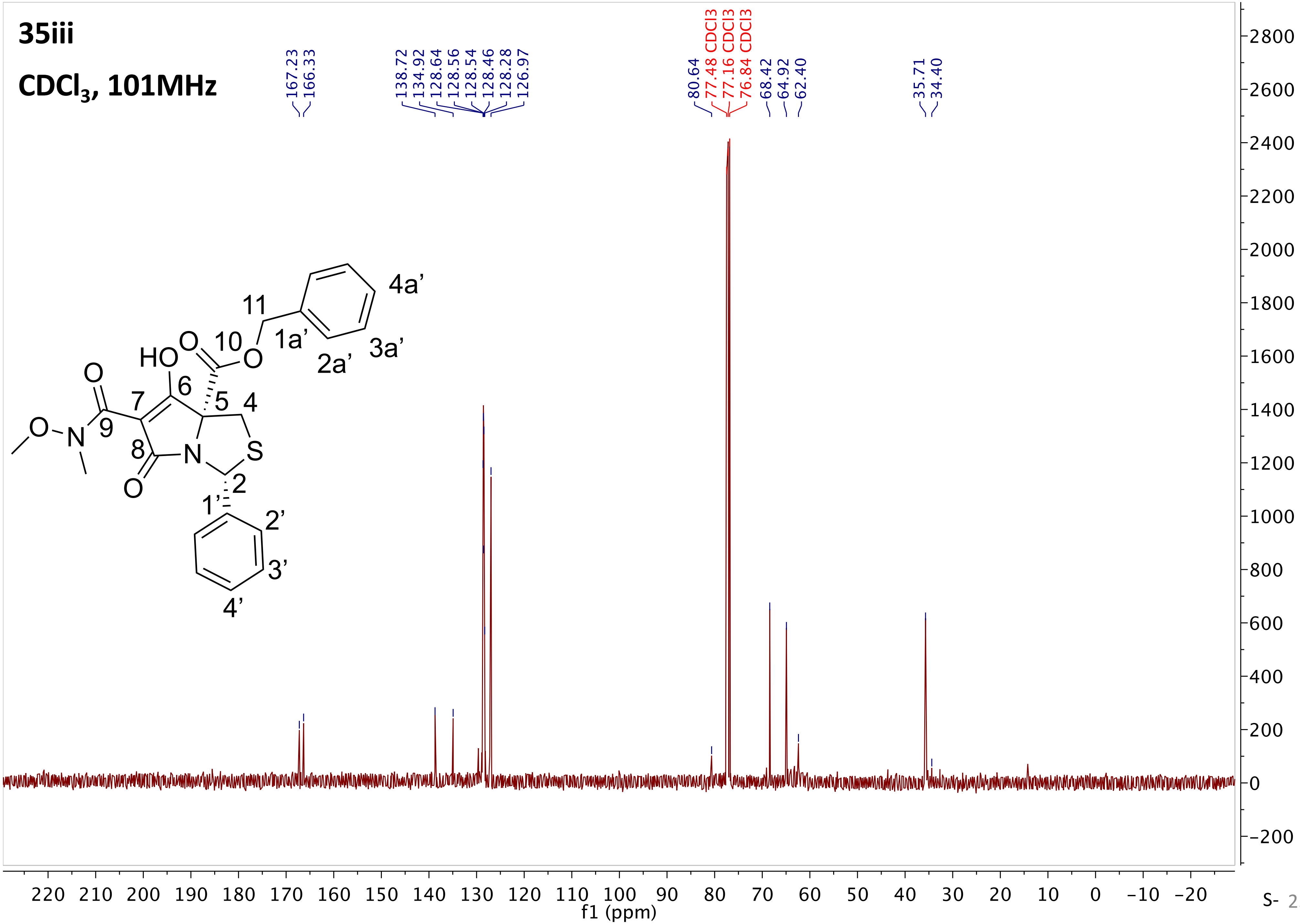


35ii
CDCl3, 400MHz
8.33 8.32 7.49 7.48 7.47 7.46 7.33 7.32 7.31 7.29 7.27 7.26 CDCl3 7.23 7.22 6.29
5.26 5.23 5.12 5.09 3.96 3.93 3.79 3.50 3.20 3.17
0.95 1.09 4.45 2.01 1.00 1.27 1.19 1.22 3.07 3.49 1.32
f1 (ppm)

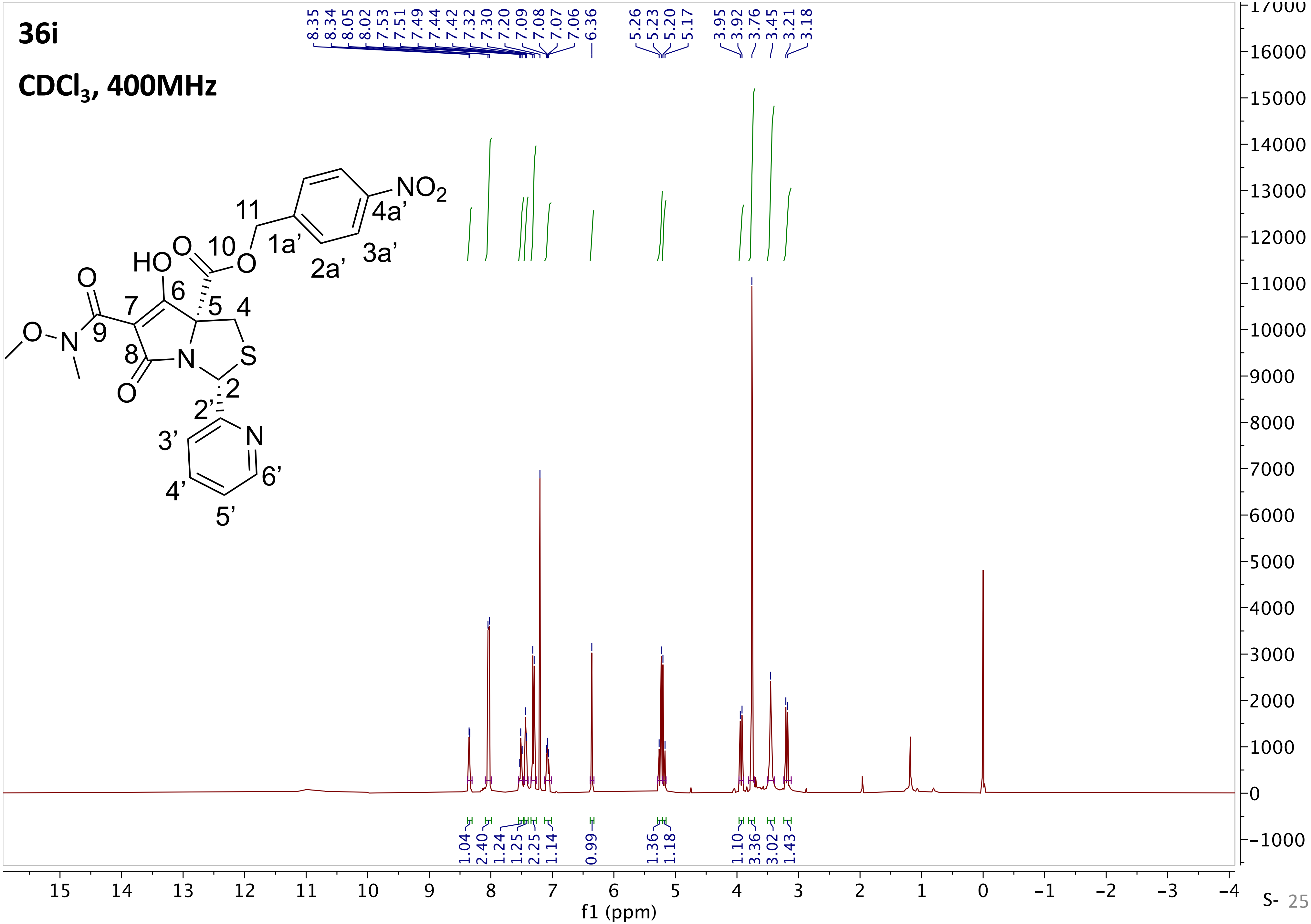

35ii
CDCl3, 101MHz
186.16
166.99
166.18
157.03
150.07
139.29
134.86
128.61
121.48
119.65
80.99
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.36
64.74
63.48
62.45
35.80
33.73
f1 (ppm)

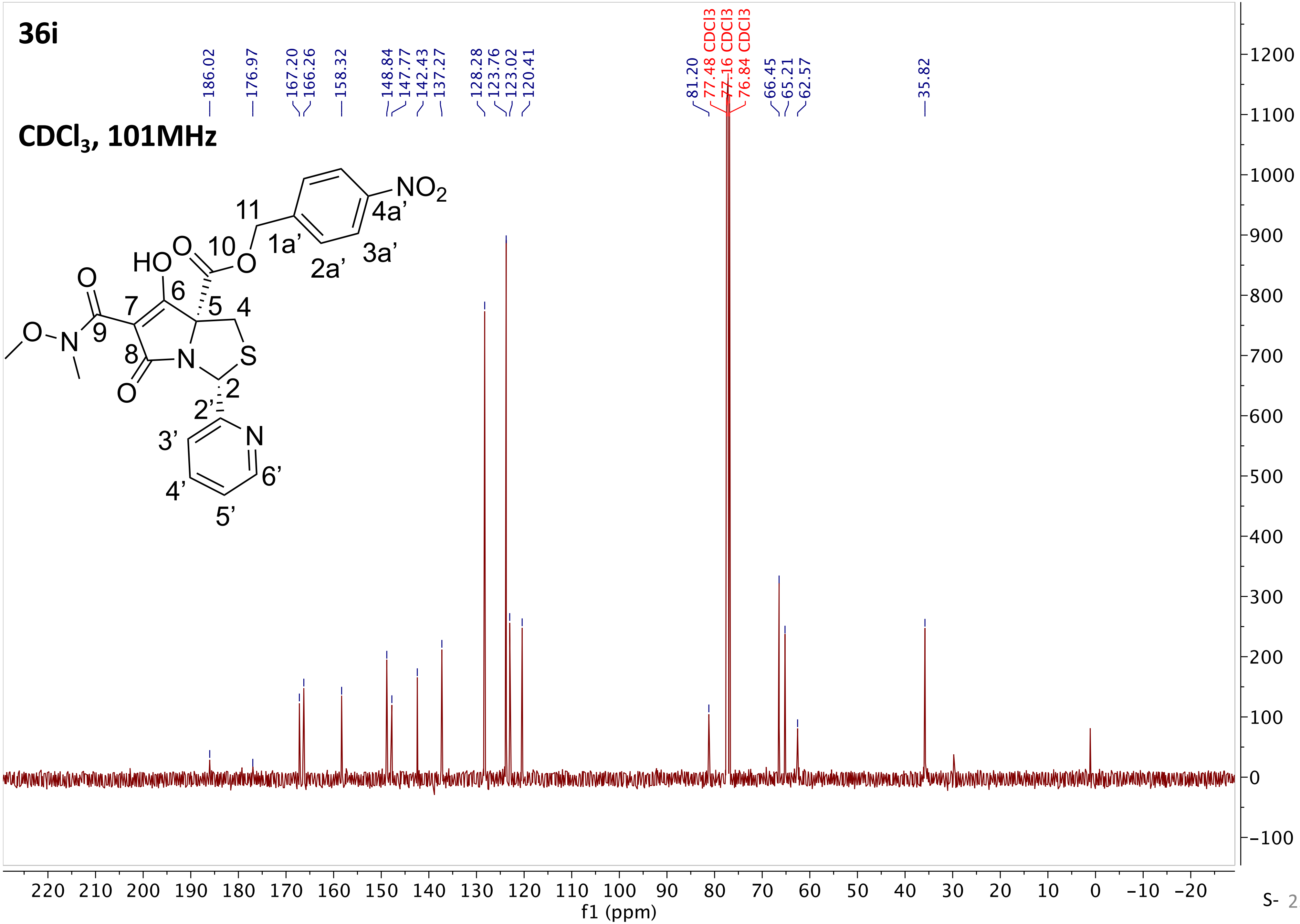


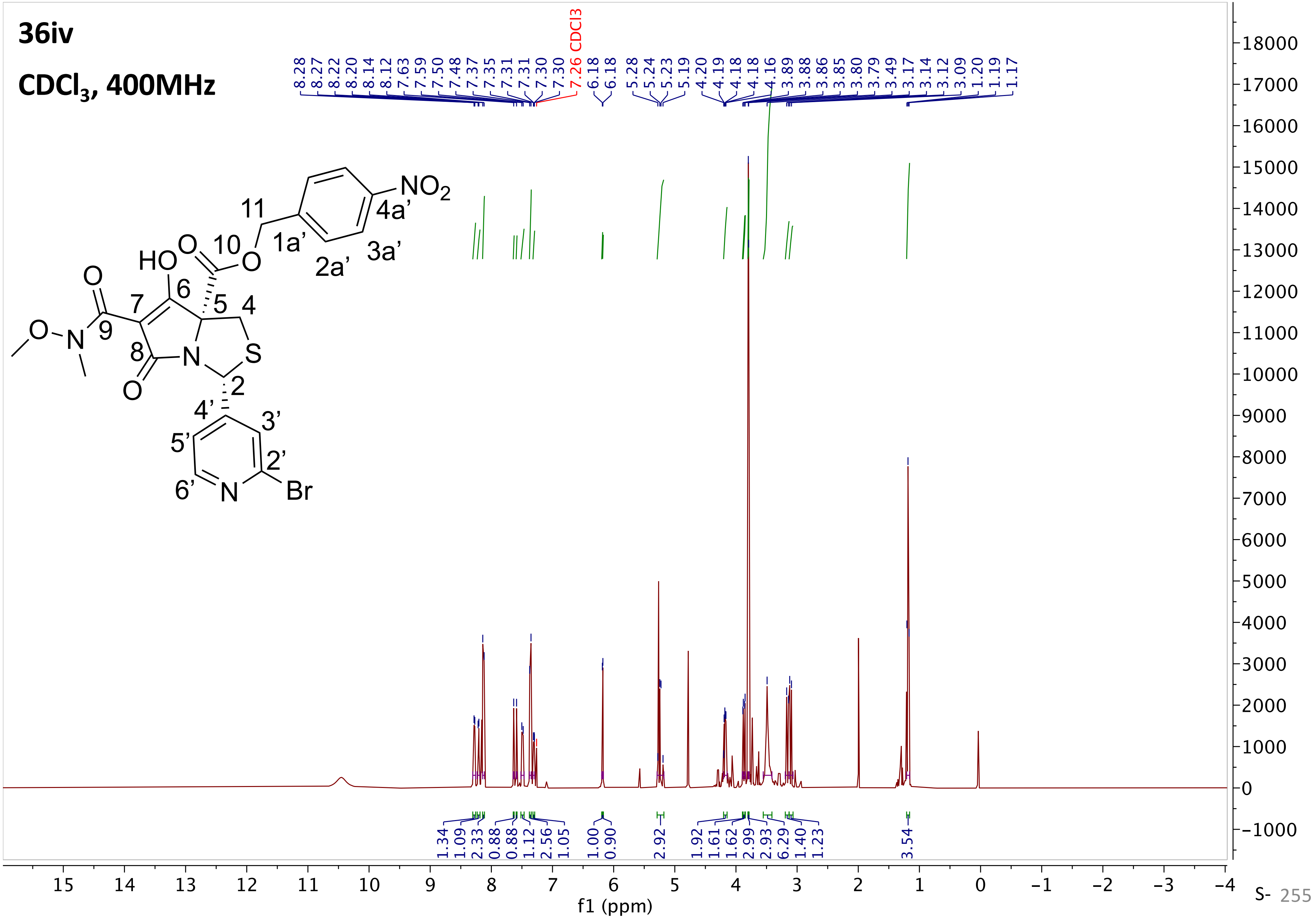
35iii
CDCl3, 400MHz
7.51
7.48
7.46
7.38
7.36
7.34
7.29
7.27
7.26 CDCl3
7.24
6.33
5.17
3.99
3.93
3.81
3.54
3.19
3.13
2.44
6.21
5.68
1.00
2.27
1.40
3.48
3.91
1.58
f1 (ppm)

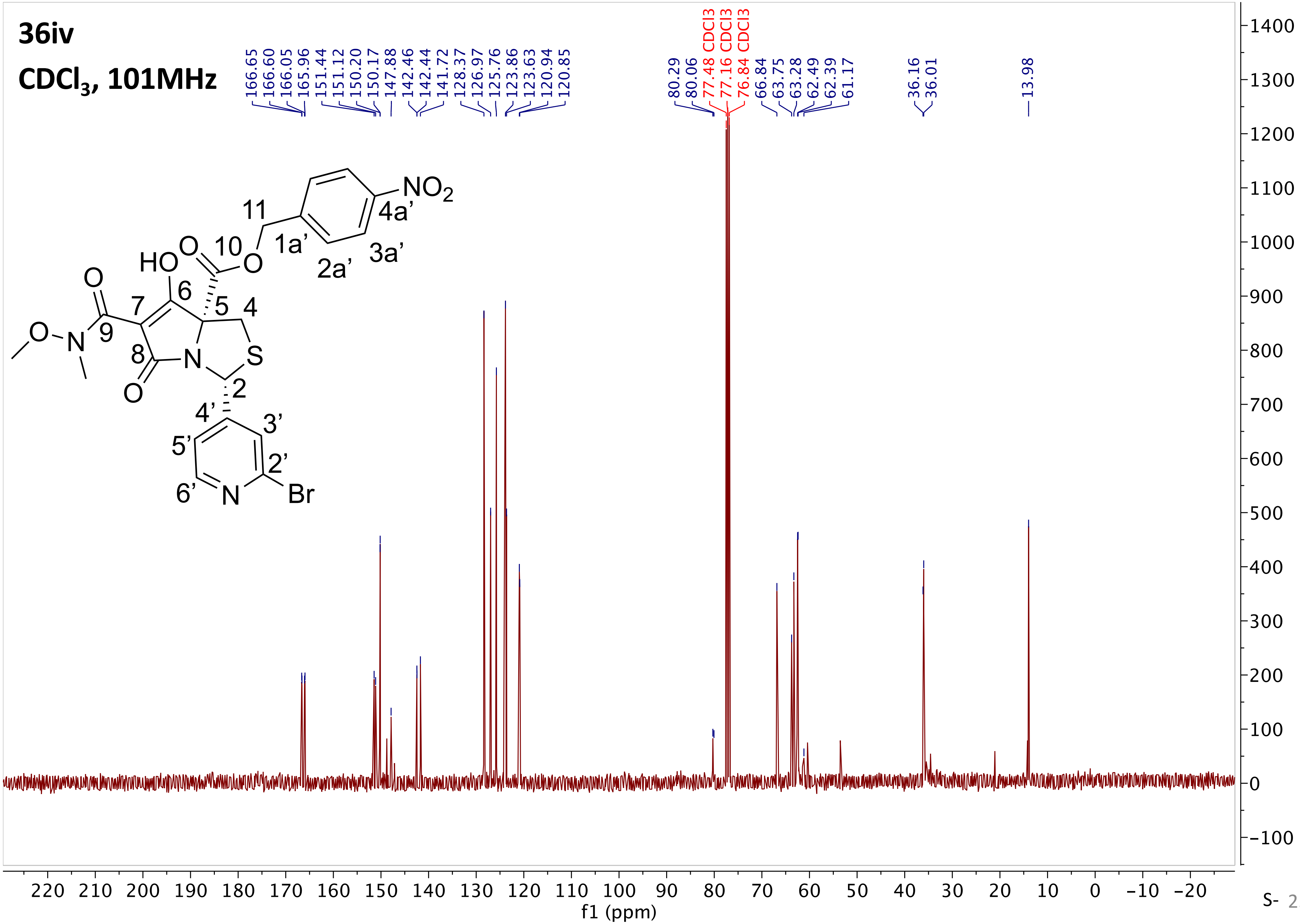


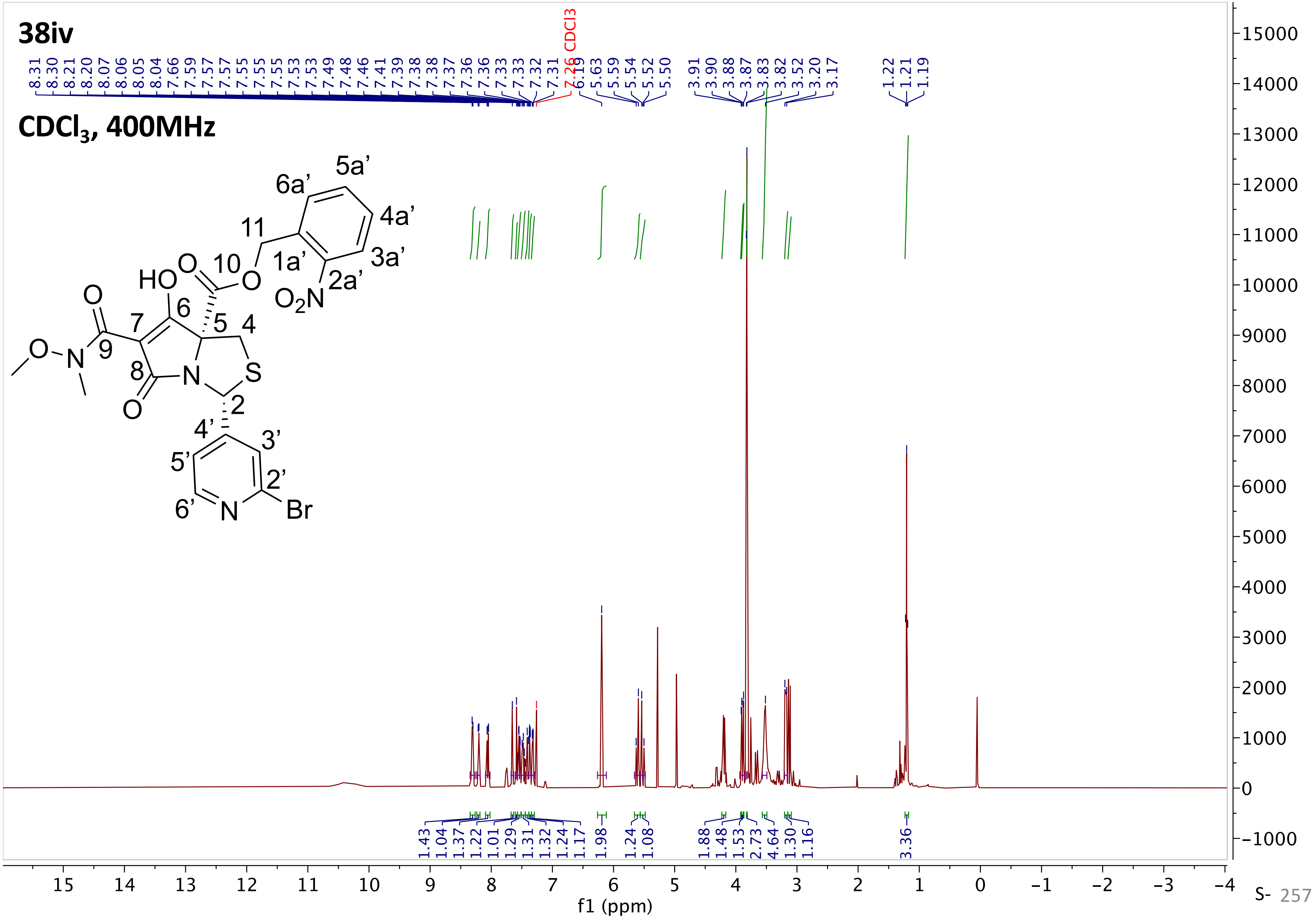
35iii
CDCl3, 101MHz
167.23
166.33
138.72
134.92
128.64
128.56
128.54
128.46
128.28
126.97
80.64
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.42
64.92
62.40
35.71
34.40
f1 (ppm)

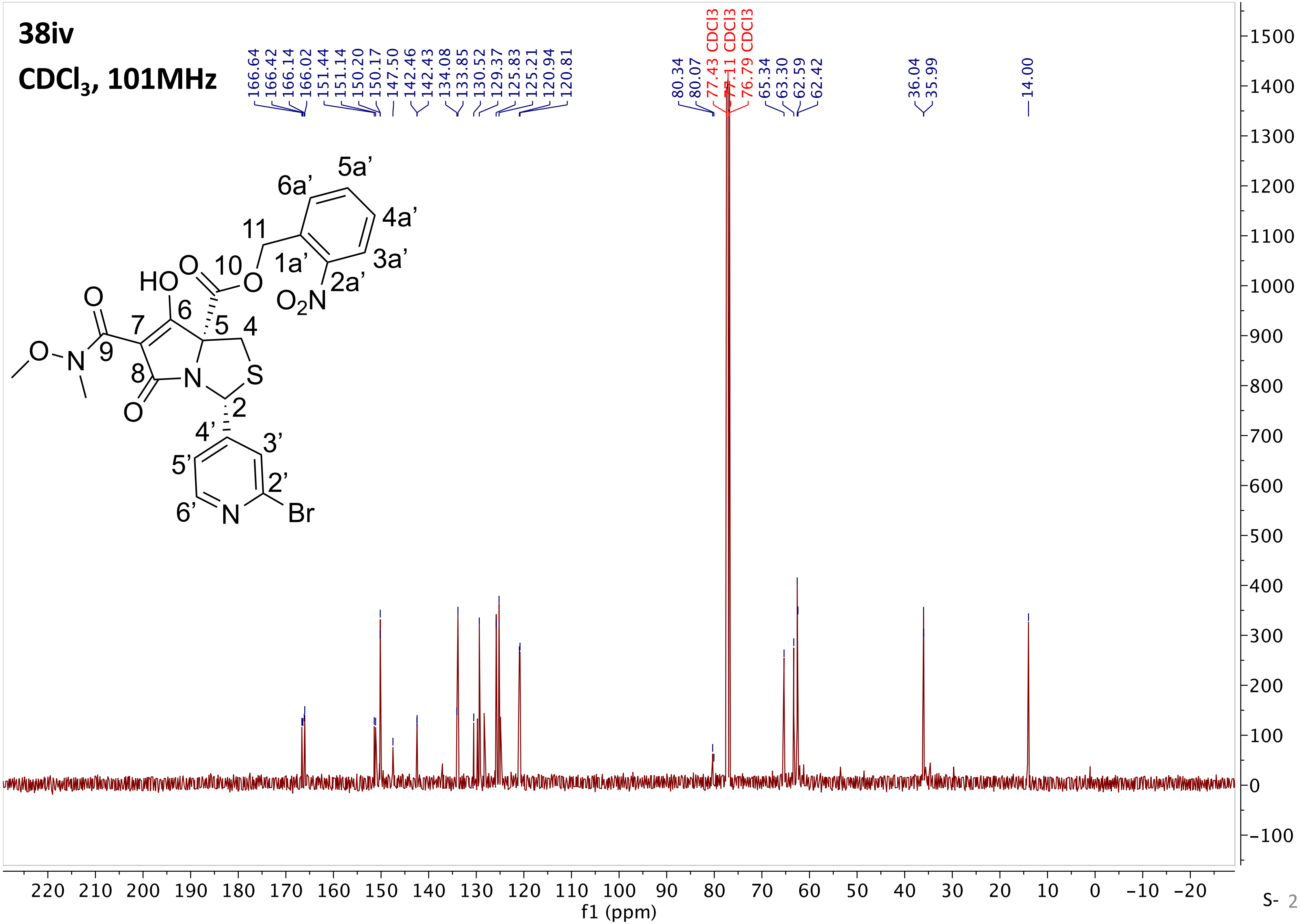

36i
CDCl3, 400MHz
8.35 8.34 8.05 8.02 7.53 7.51 7.49 7.44 7.42 7.32 7.30 7.20 7.09 7.08 7.07 7.06 6.36 5.26 5.23 5.20 5.17 3.95 3.92 3.76 3.45 3.21 3.18
1.04 2.40 1.24 1.25 2.25 1.14 0.99 1.36 1.18 1.10 3.36 3.02 1.43
f1 (ppm)

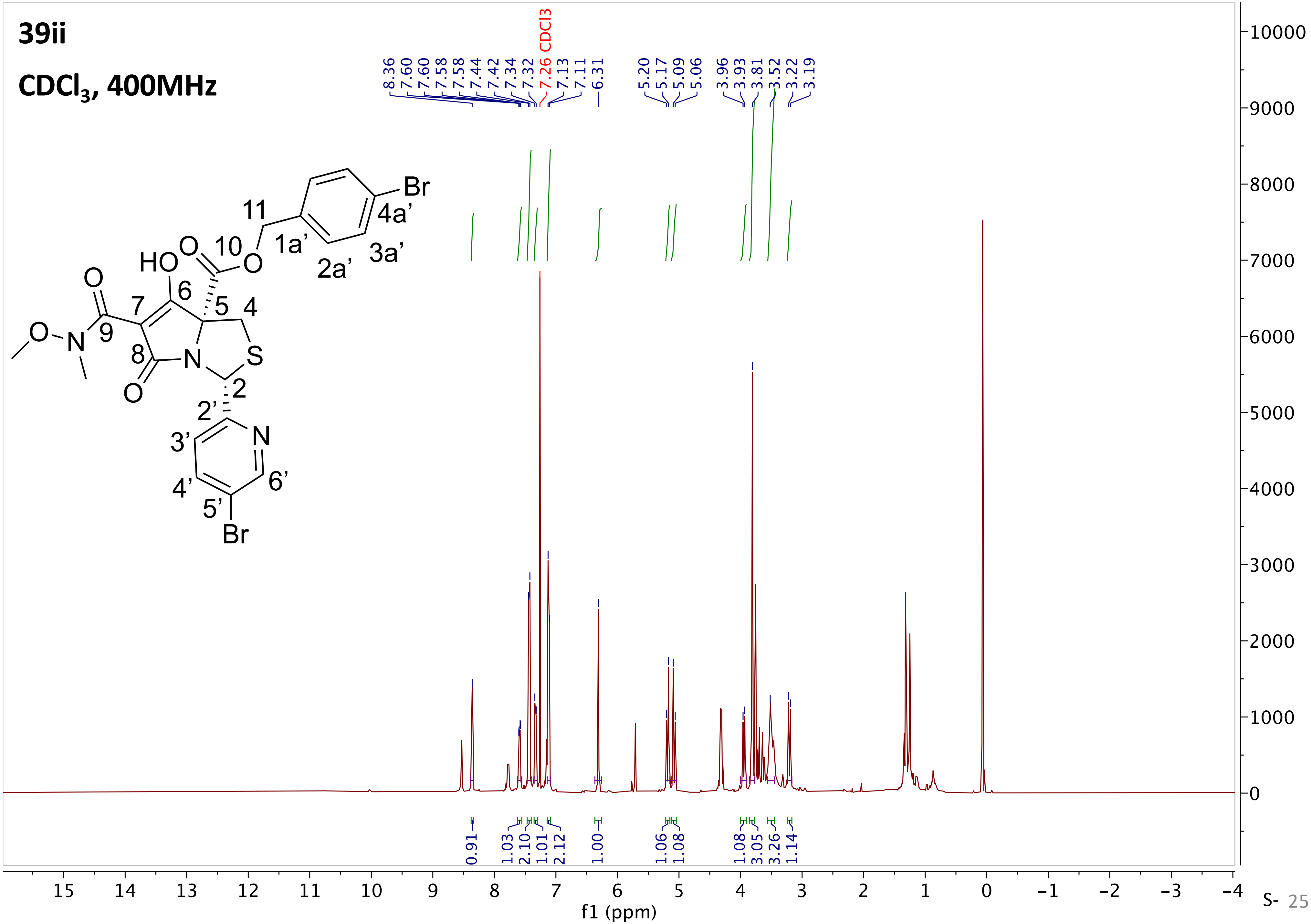

36i
CDCl3, 101MHz
186.02
176.97
167.20
166.26
158.32
148.84
147.77
142.43
137.27
128.28
123.76
123.02
120.41
81.20
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.45
65.21
62.57
35.82
NO2
11
4a'
10
1a'
3a'
2a'
HO
O
6
5
4
7
9
8
N
S
2
2'
3'
4'
5'
6'
f1 (ppm)


36iv
CDCl3, 400MHz
f1 (ppm)


36iv
CDCl3, 101MHz
166.65
166.60
166.05
165.96
151.44
151.12
150.20
150.17
147.88
142.46
142.44
141.72
128.37
126.97
125.76
123.86
123.63
120.94
120.85
80.29
80.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.84
63.75
63.28
62.49
62.39
61.17
36.16
36.01
13.98
f1 (ppm)

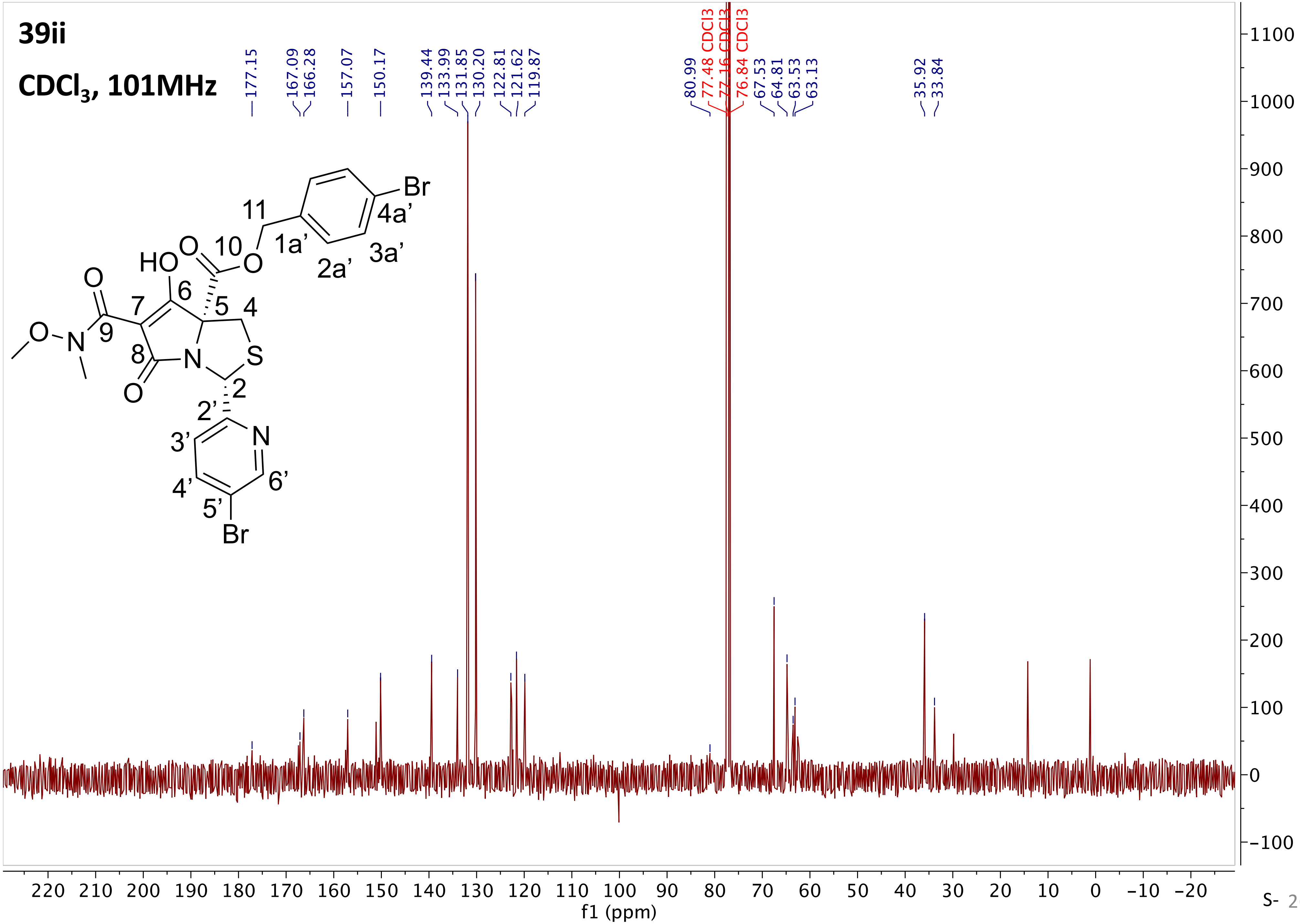

38iv
CDCl3, 400MHz
7.26 CDCl3
f1 (ppm)


38iv
CDCl3, 101MHz
166.64
166.42
166.14
166.02
151.44
151.14
150.20
150.17
147.50
142.46
142.43
134.08
133.85
130.52
129.37
125.83
125.21
120.94
120.81
80.34
80.07
77.43 CDCl3
77.11 CDCl3
76.79 CDCl3
65.34
63.30
62.59
62.42
36.04
35.99
14.00
f1 (ppm)


39ii
CDCl3, 400MHz
8.36
7.60
7.60
7.58
7.58
7.44
7.42
7.34
7.32
7.26 CDCl3
7.13
7.11
6.31
5.20
5.17
5.09
5.06
3.96
3.93
3.81
3.52
3.22
3.19
0.91
1.03
2.10
1.01
2.12
1.00
1.06
1.08
1.08
3.05
3.26
1.14
f1 (ppm)

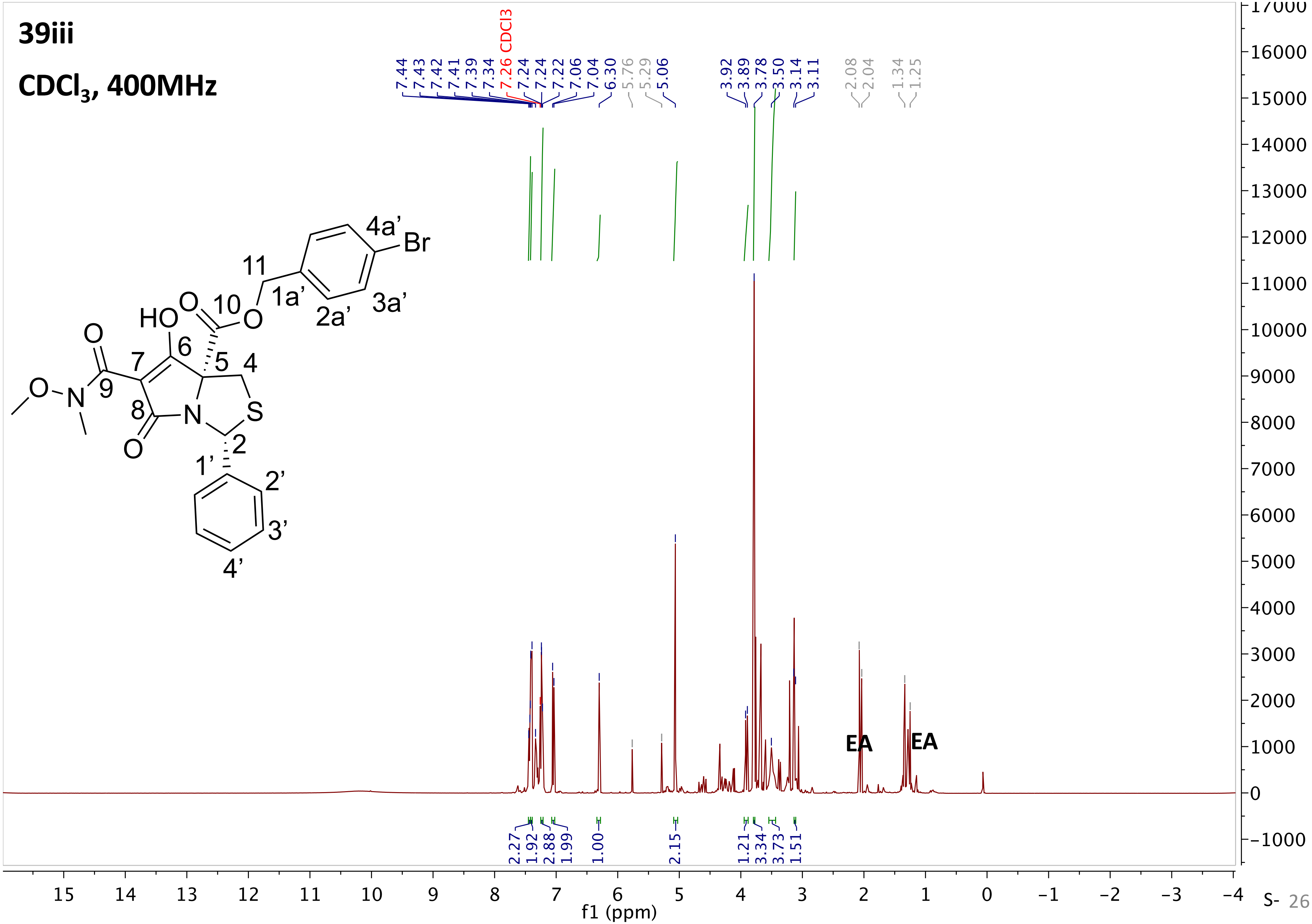
39ii

$CDCl_3$, 101MHz



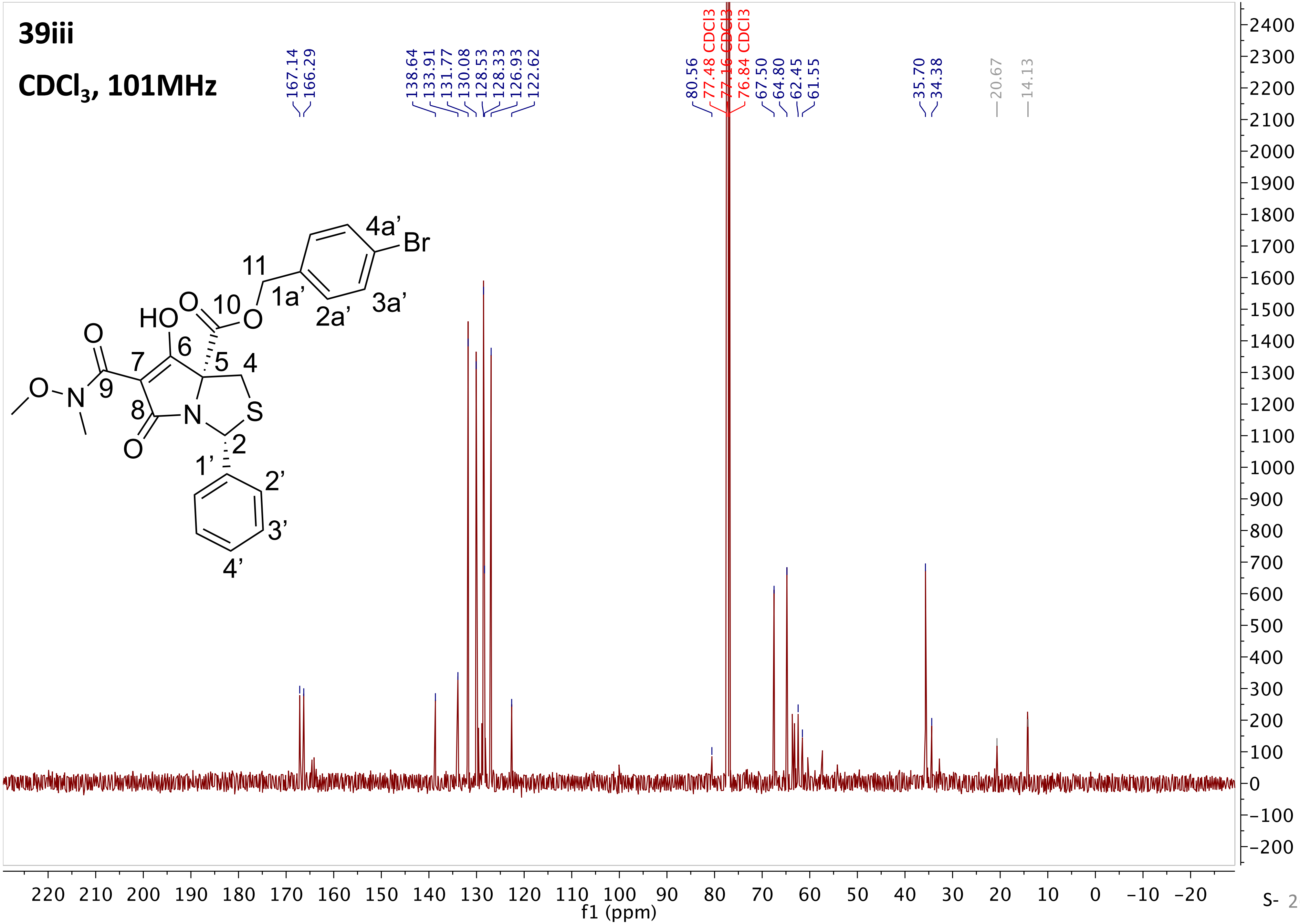
39iii

$CDCl_3$, 400MHz



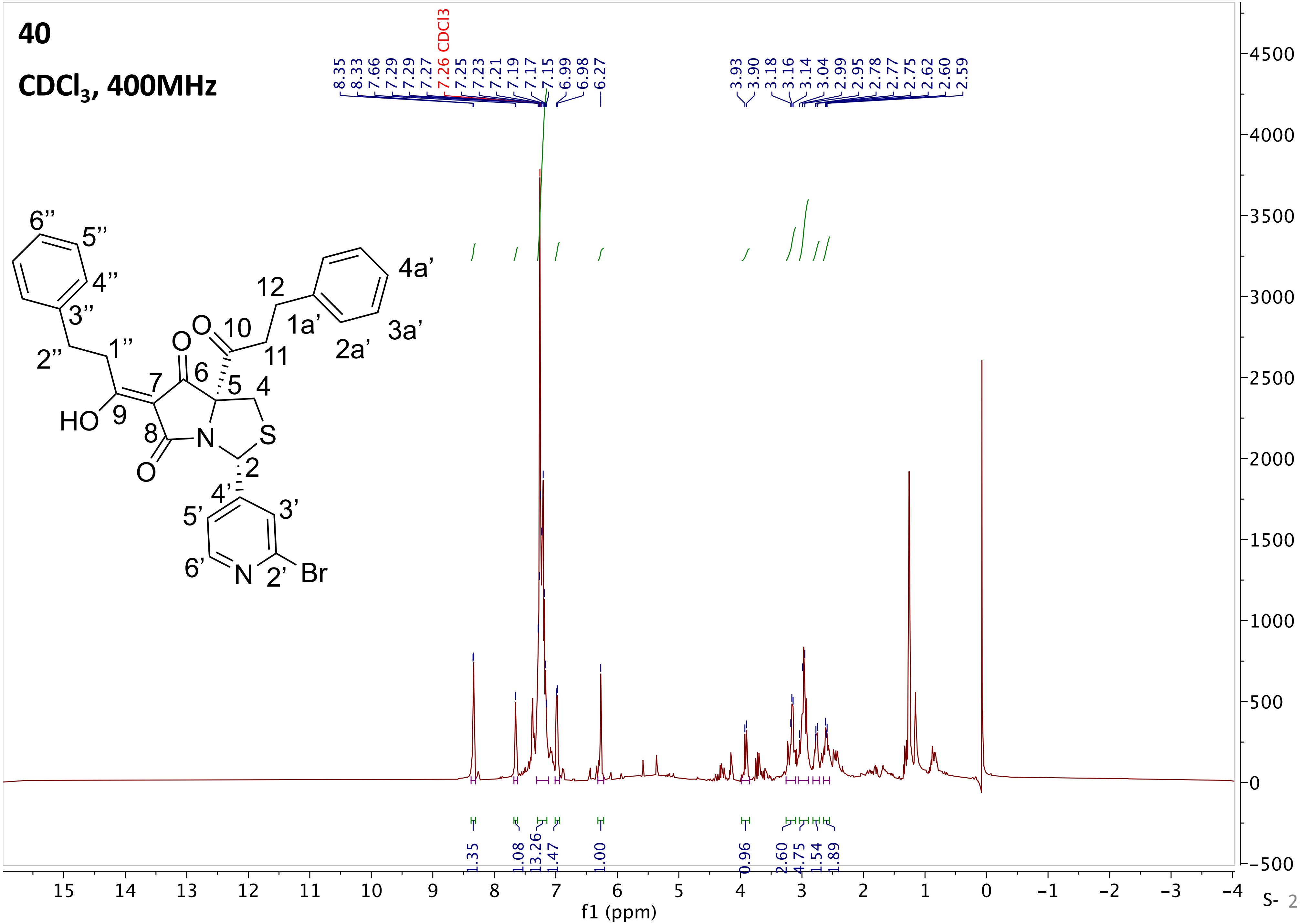
39iii

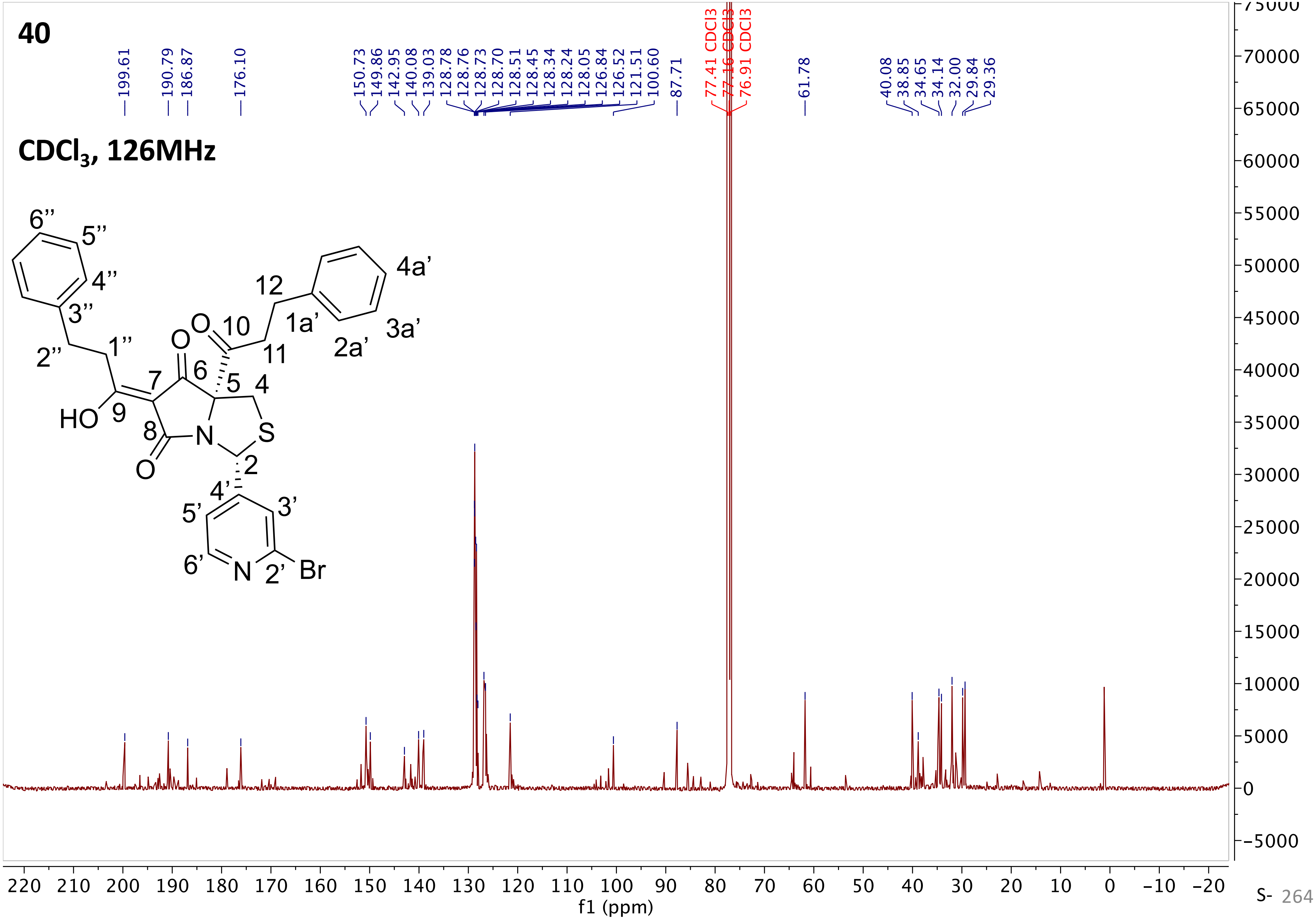
$CDCl_3$, 101MHz



40

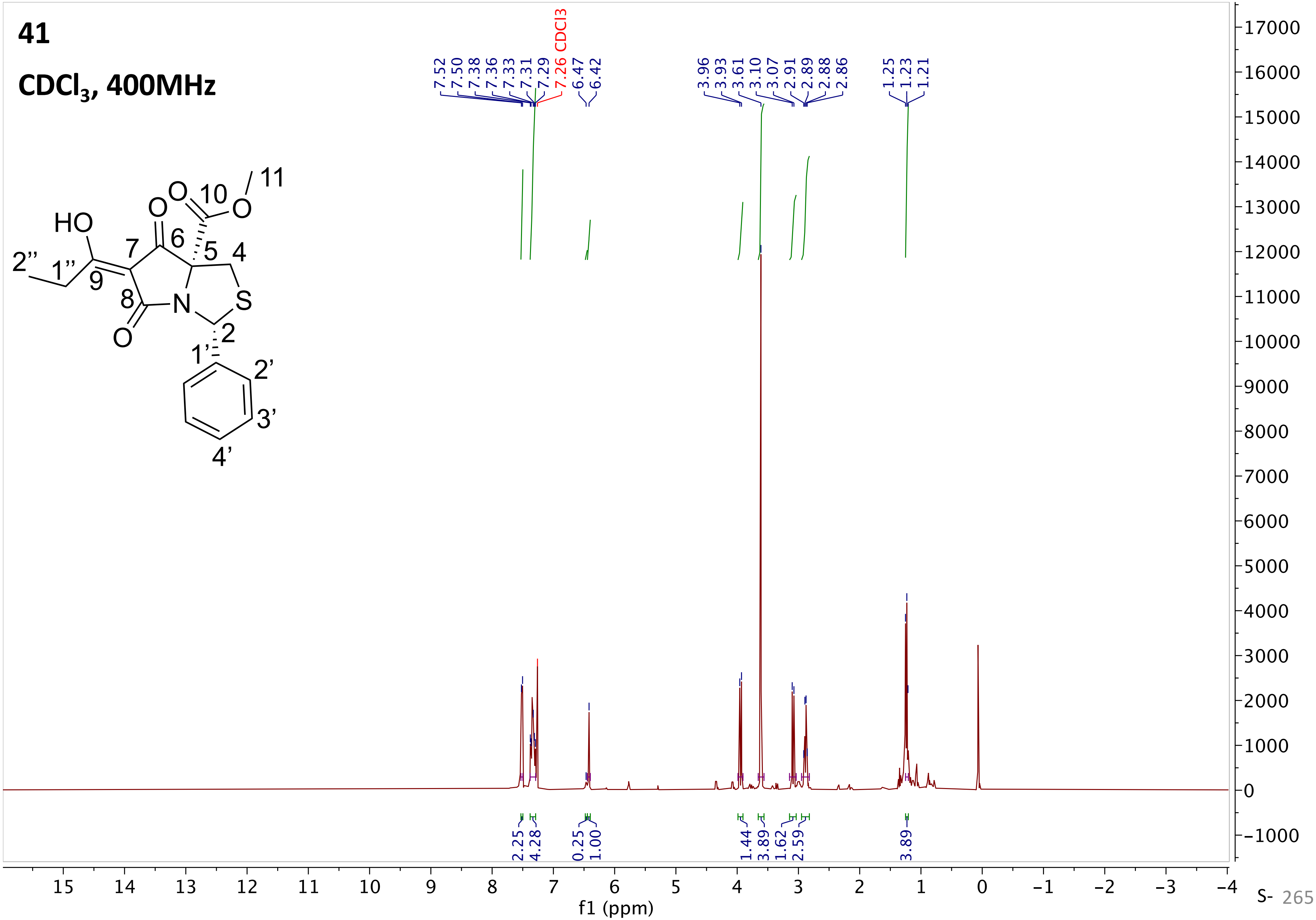
$CDCl_3$, 400MHz




40
CDCl3, 126MHz
199.61
190.79
186.87
176.10
150.73
149.86
142.95
140.08
139.03
128.78
128.76
128.73
128.70
128.51
128.45
128.34
128.24
128.05
126.84
126.52
121.51
100.60
87.71
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
61.78
40.08
38.85
34.65
34.14
32.00
29.84
29.36
f1 (ppm)
HO
Br

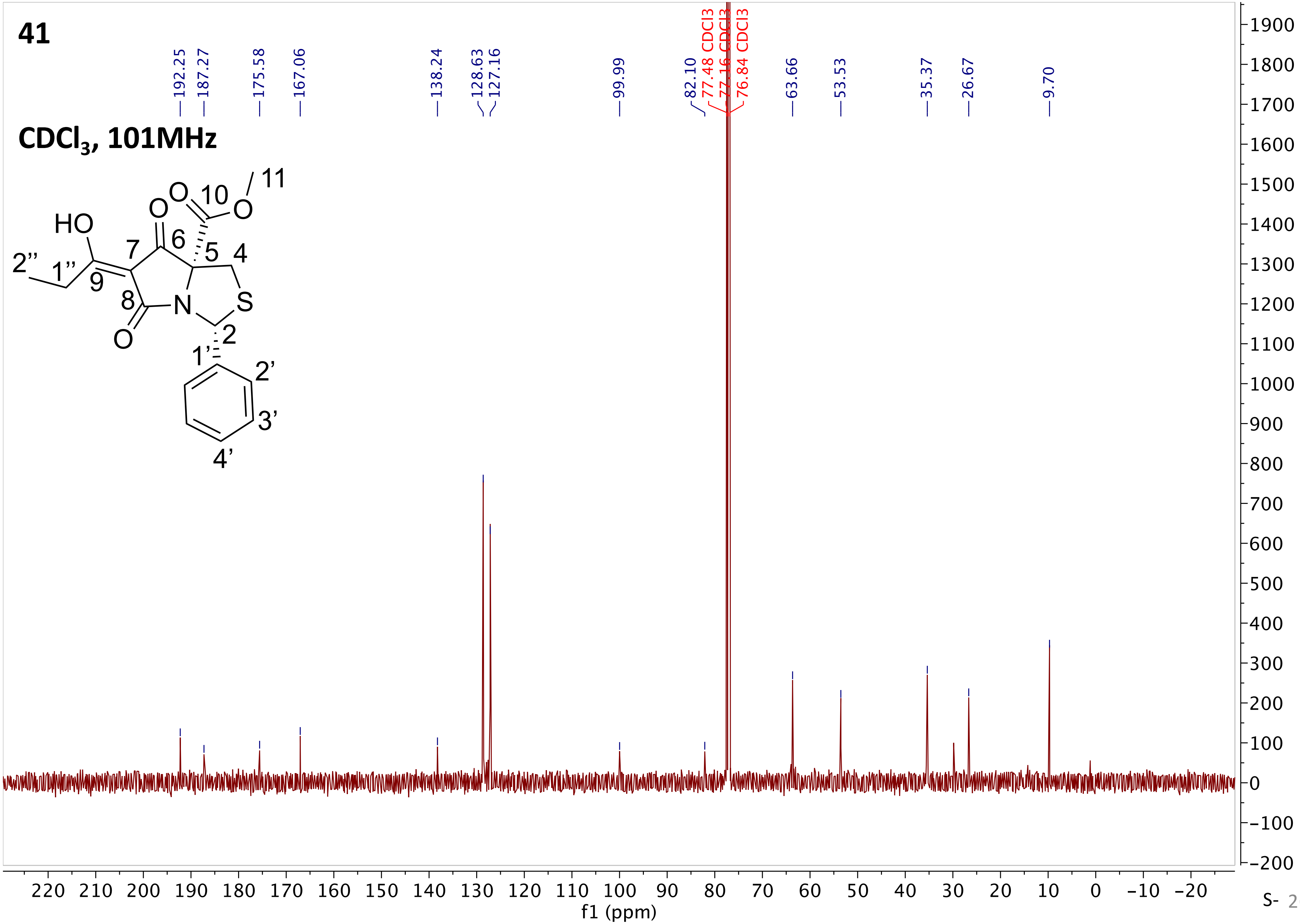
41

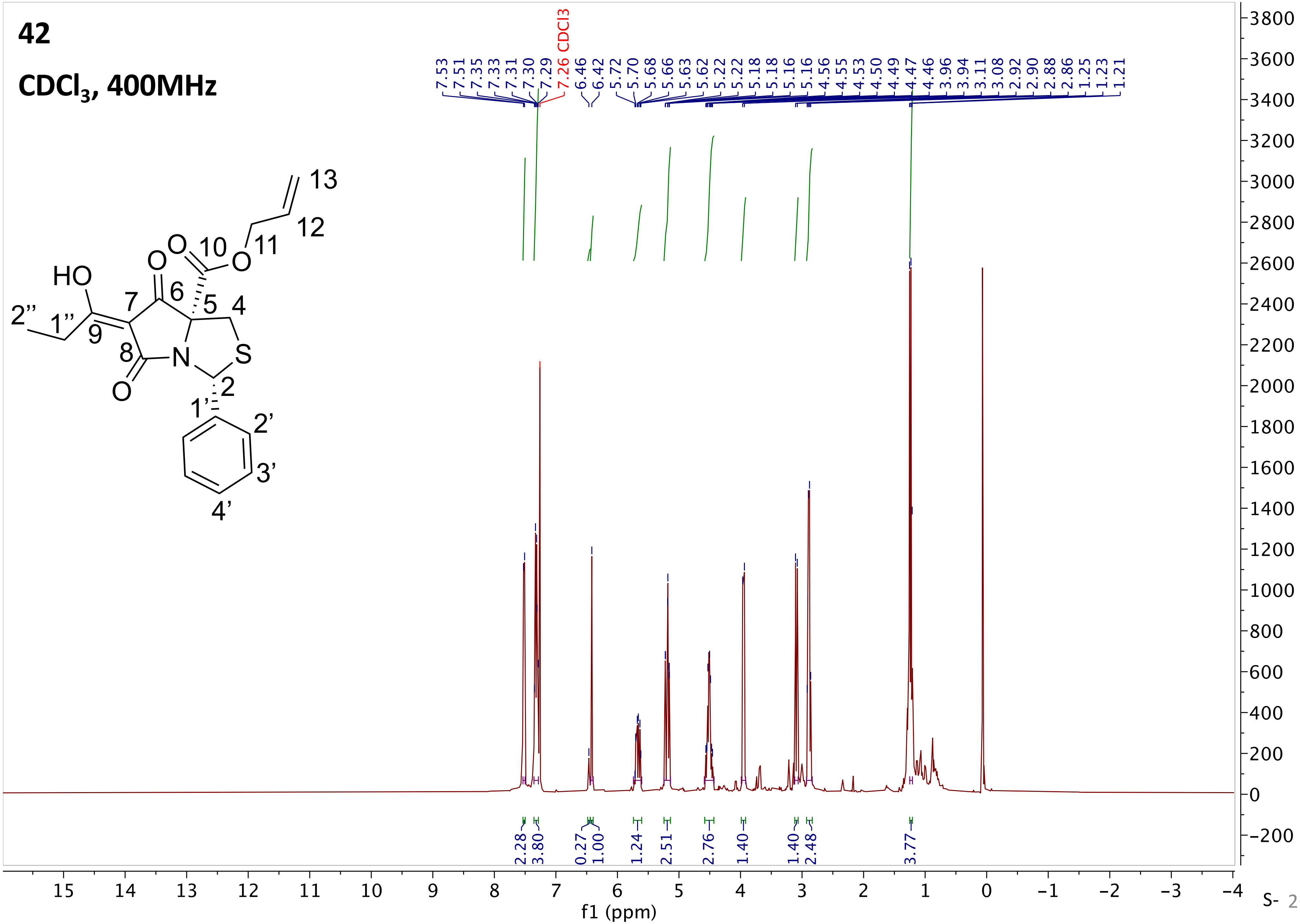
$CDCl_3$, 400MHz

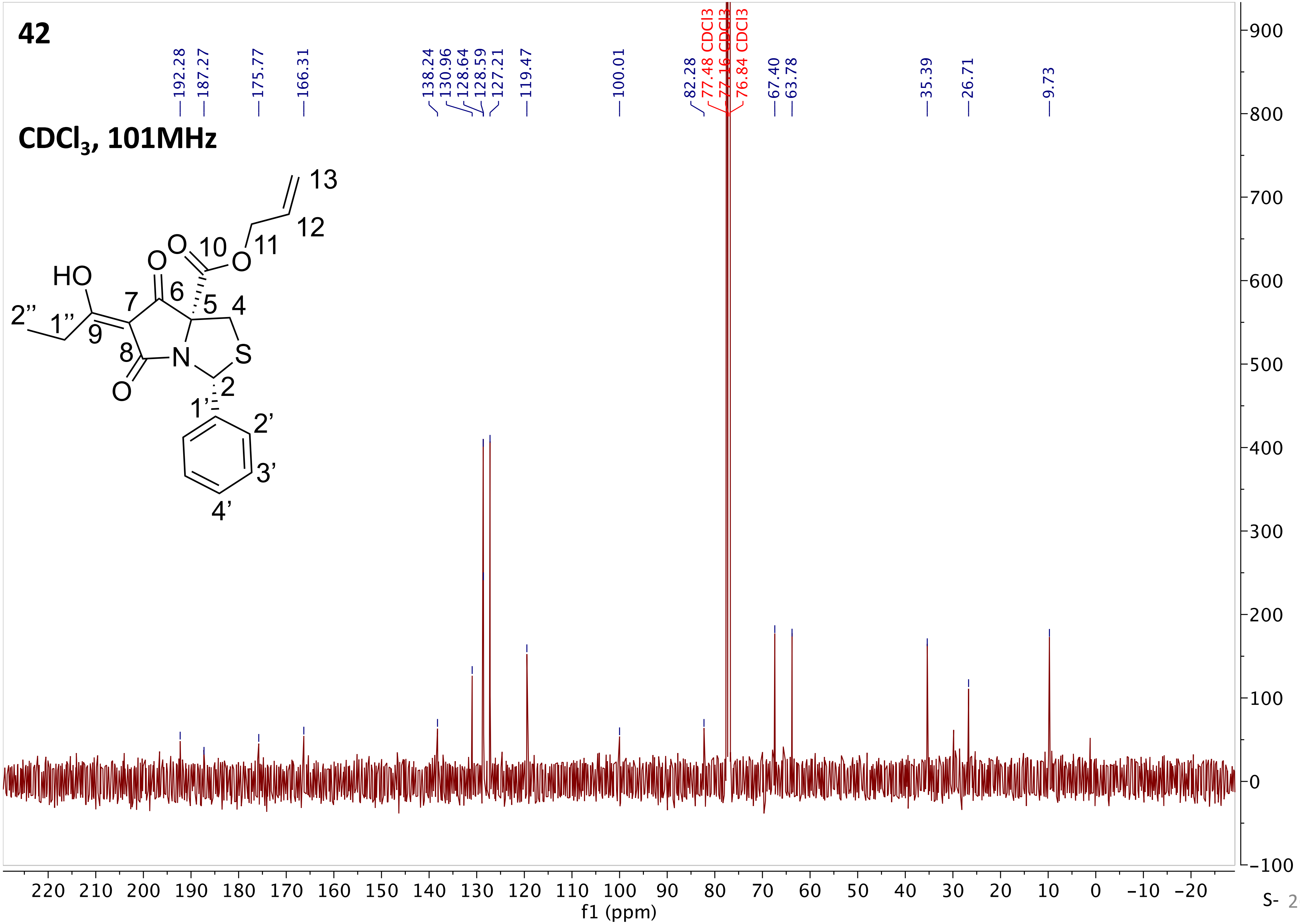


41

$CDCl_3$, 101MHz



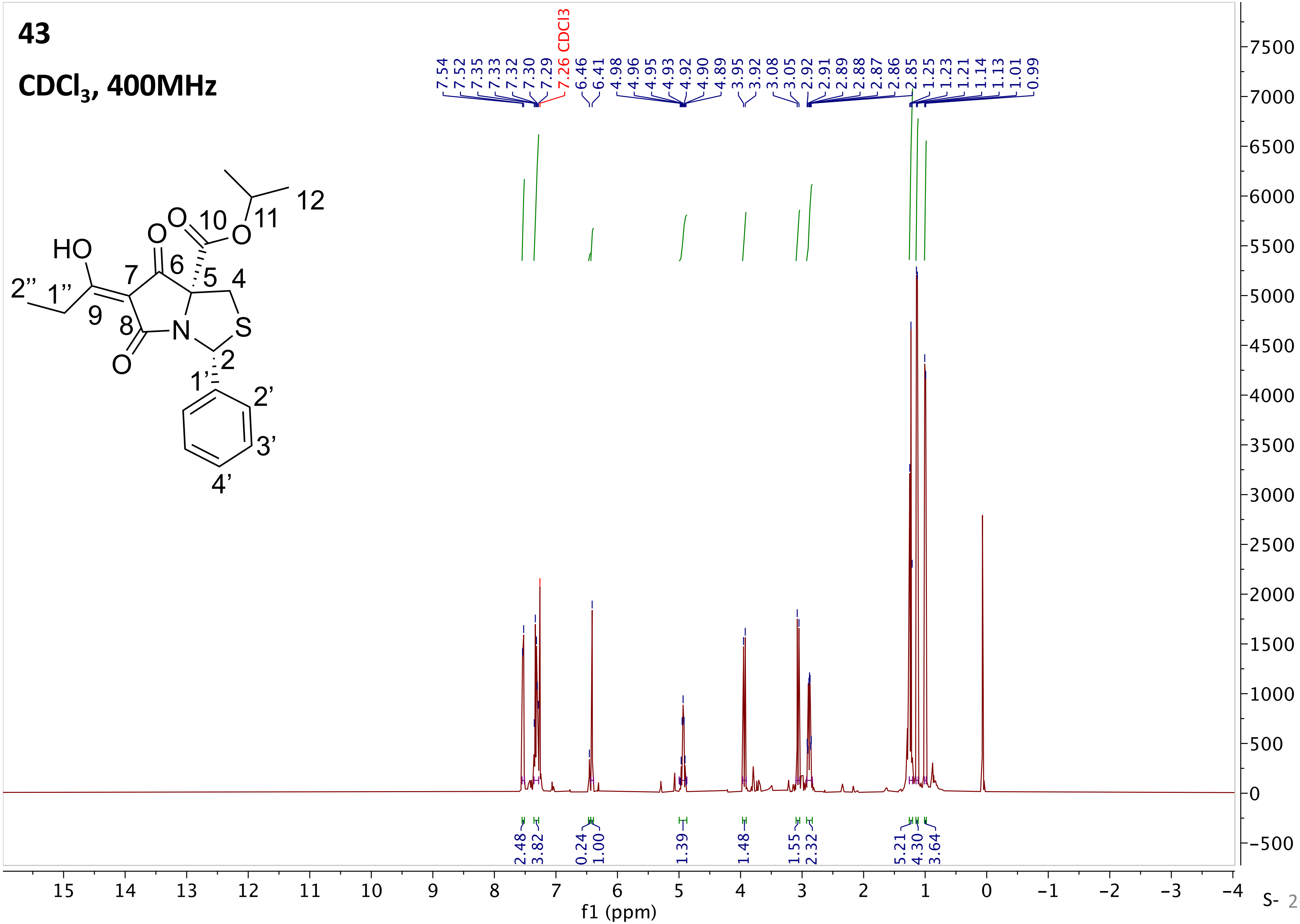

42
CDCl3, 400MHz
7.53 7.51 7.35 7.33 7.31 7.30 7.29 7.26 CDCl3 6.46 6.42 5.72 5.70 5.68 5.66 5.63 5.62 5.22 5.22 5.18 5.18 5.16 5.16 4.56 4.55 4.53 4.50 4.49 4.47 4.46 3.96 3.94 3.11 3.08 2.92 2.90 2.88 2.86 1.25 1.23 1.21
2.28 3.80 0.27 1.00 1.24 2.51 2.76 1.40 1.40 2.48 3.77
HO
O
O
O
O
O
N
S
2''
1''
2
1'
2'
3'
4'
4
5
6
7
8
9
10
11
12
13
f1 (ppm)

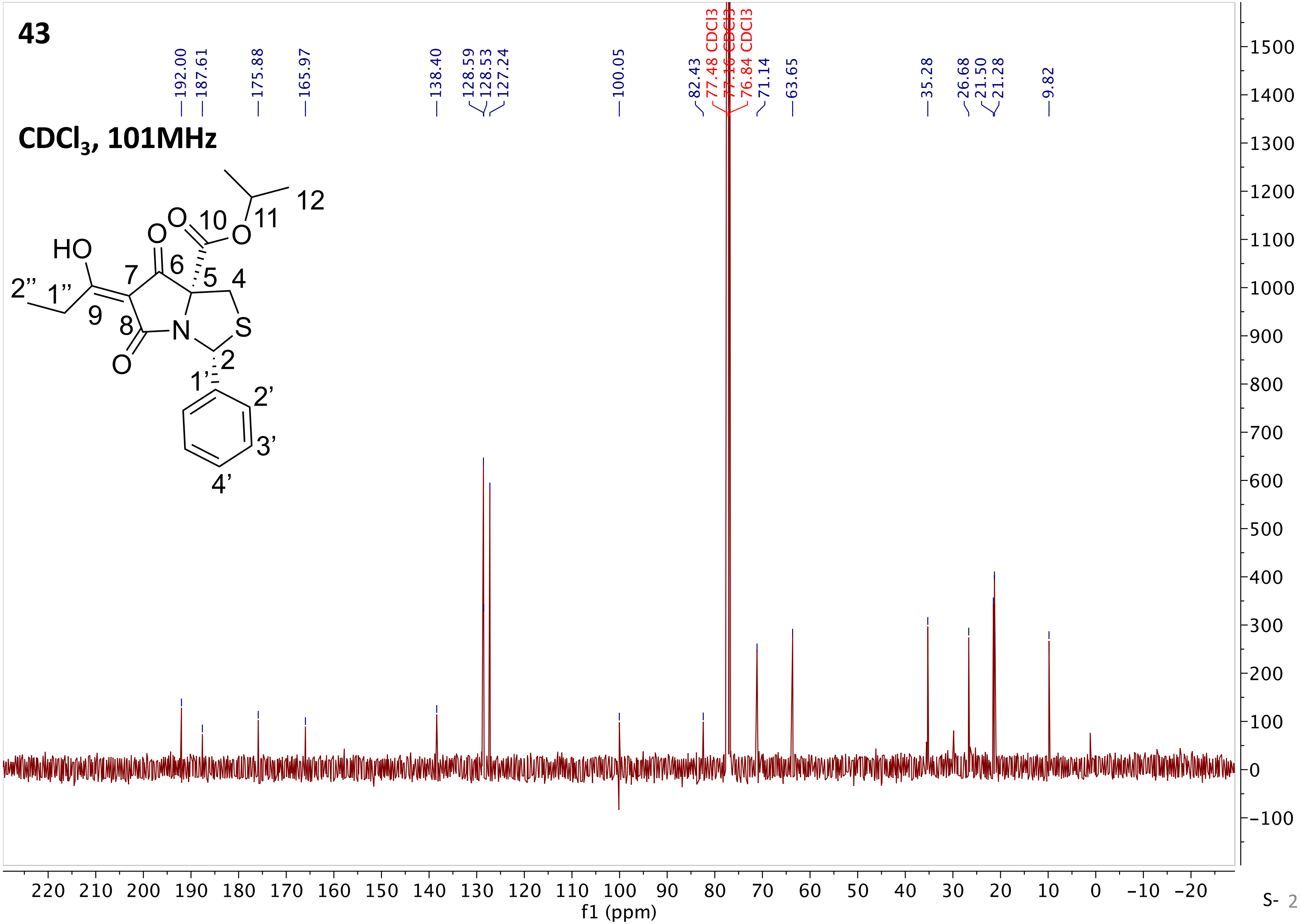


42
CDCl3, 101MHz
192.28
187.27
175.77
166.31
138.24
130.96
128.64
128.59
127.21
119.47
100.01
82.28
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.40
63.78
35.39
26.71
9.73
f1 (ppm)

43

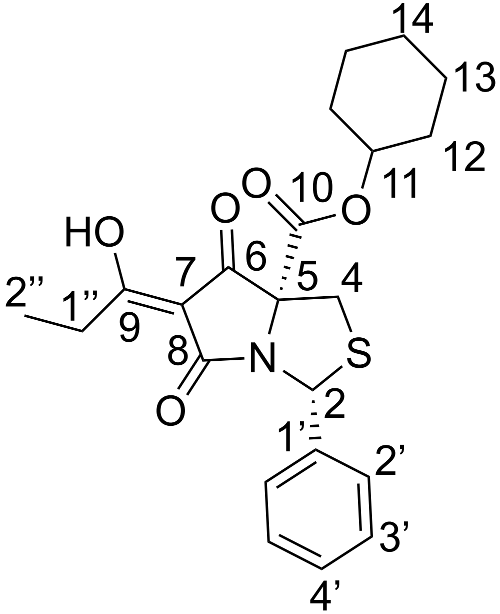
$CDCl_3$, 400MHz

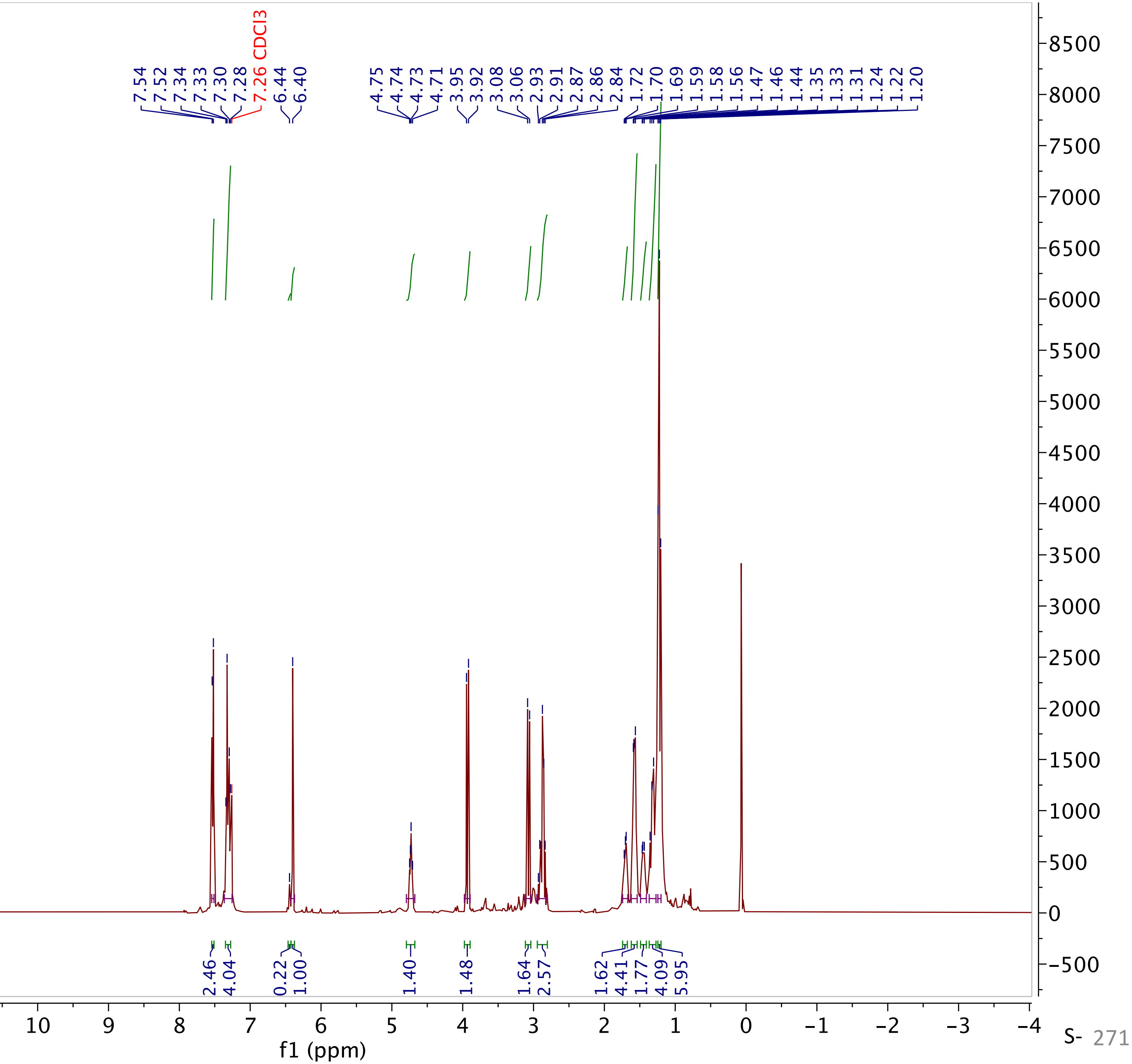


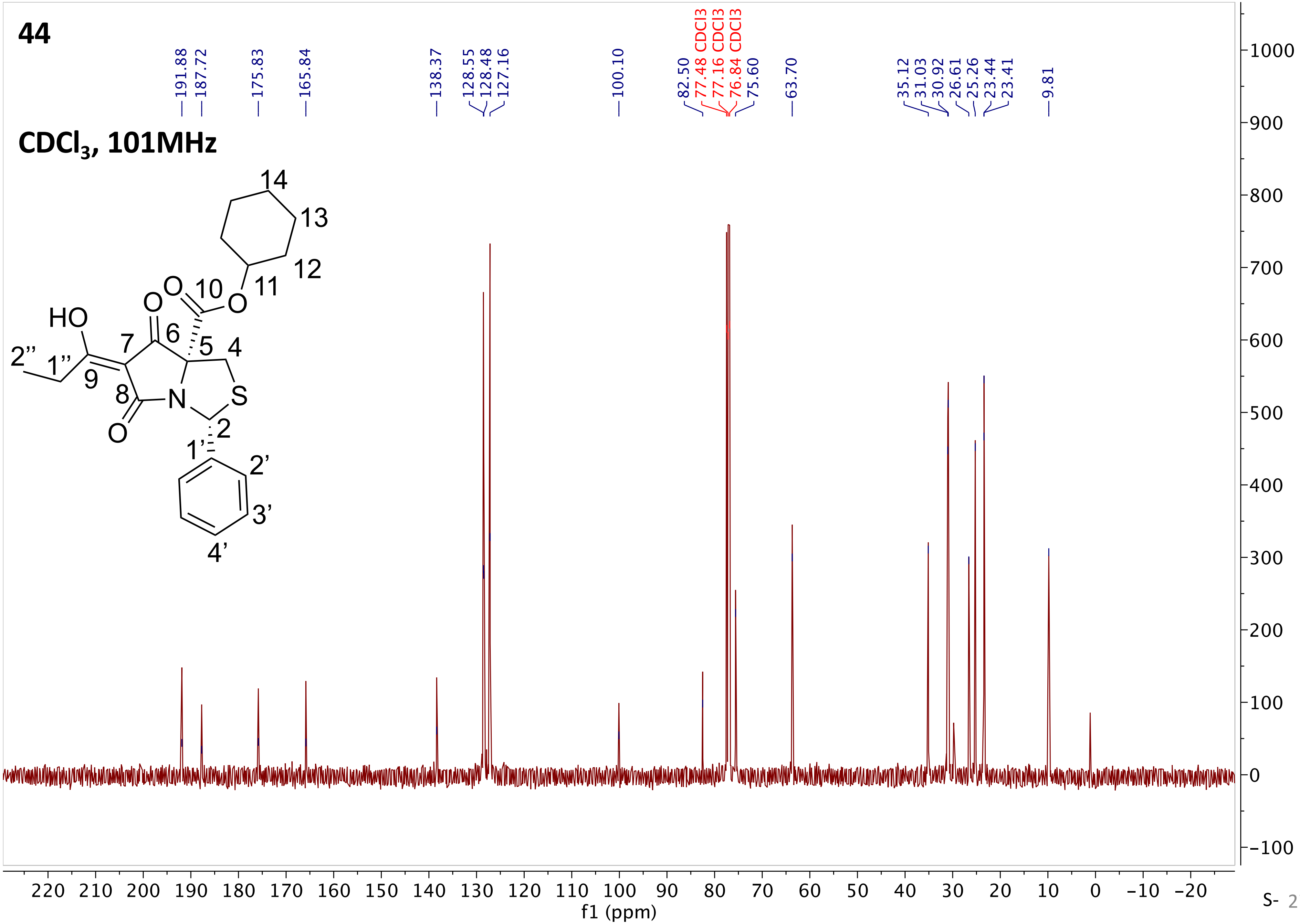

43
CDCl3, 101MHz
192.00
187.61
175.88
165.97
138.40
128.59
128.53
127.24
100.05
82.43
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.14
63.65
35.28
26.68
21.50
21.28
9.82
f1 (ppm)

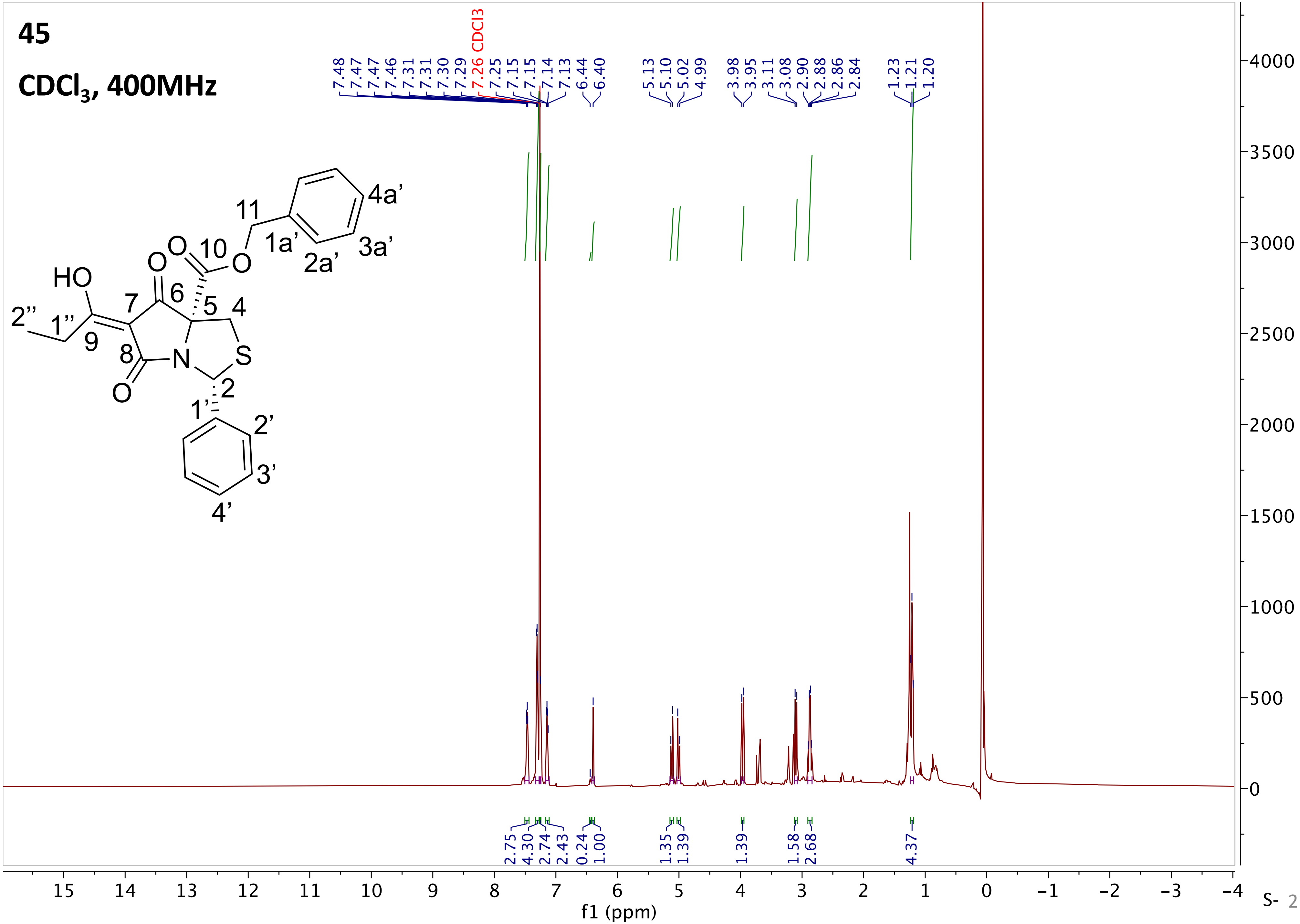
44

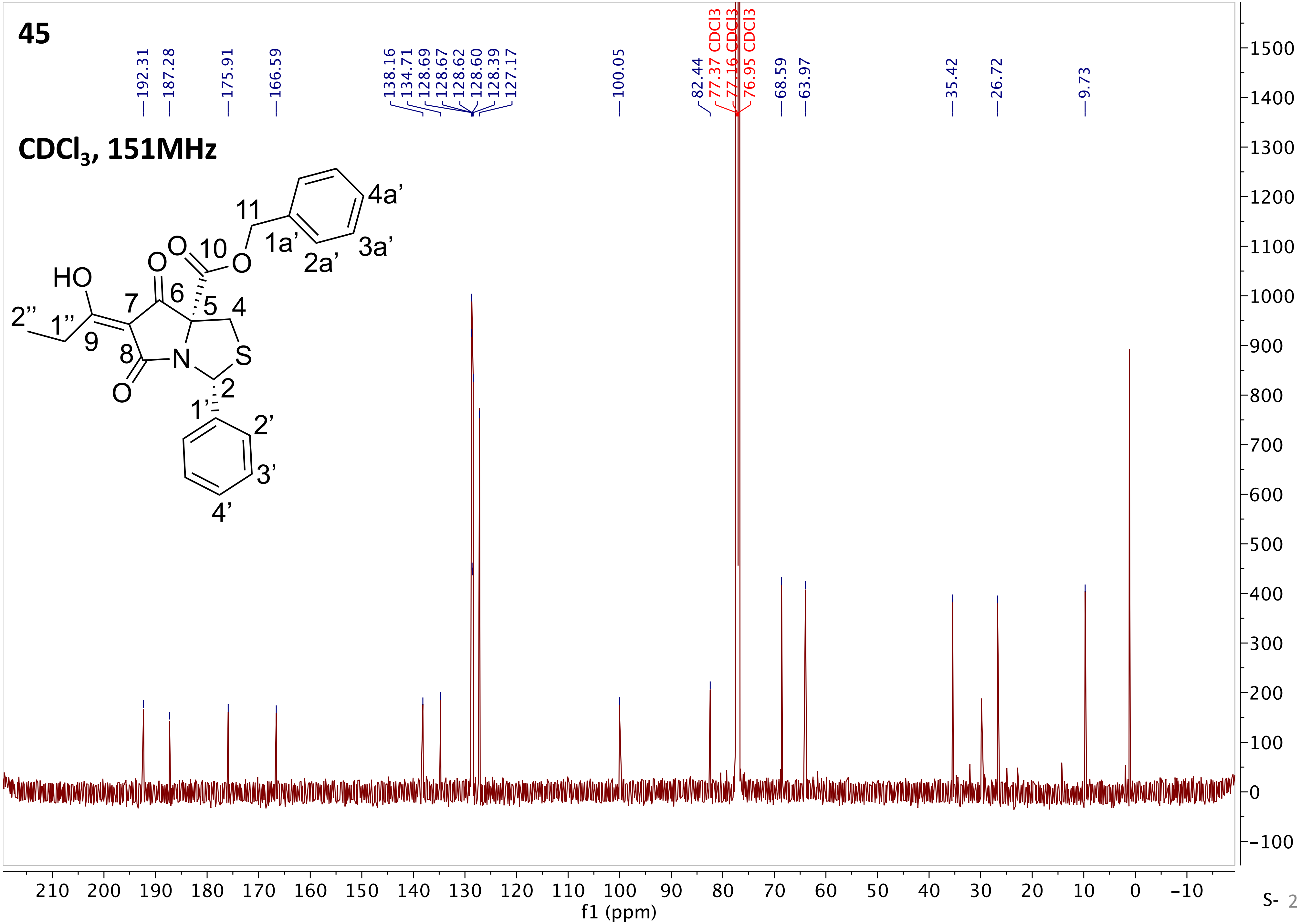
$CDCl_3$, 400MHz





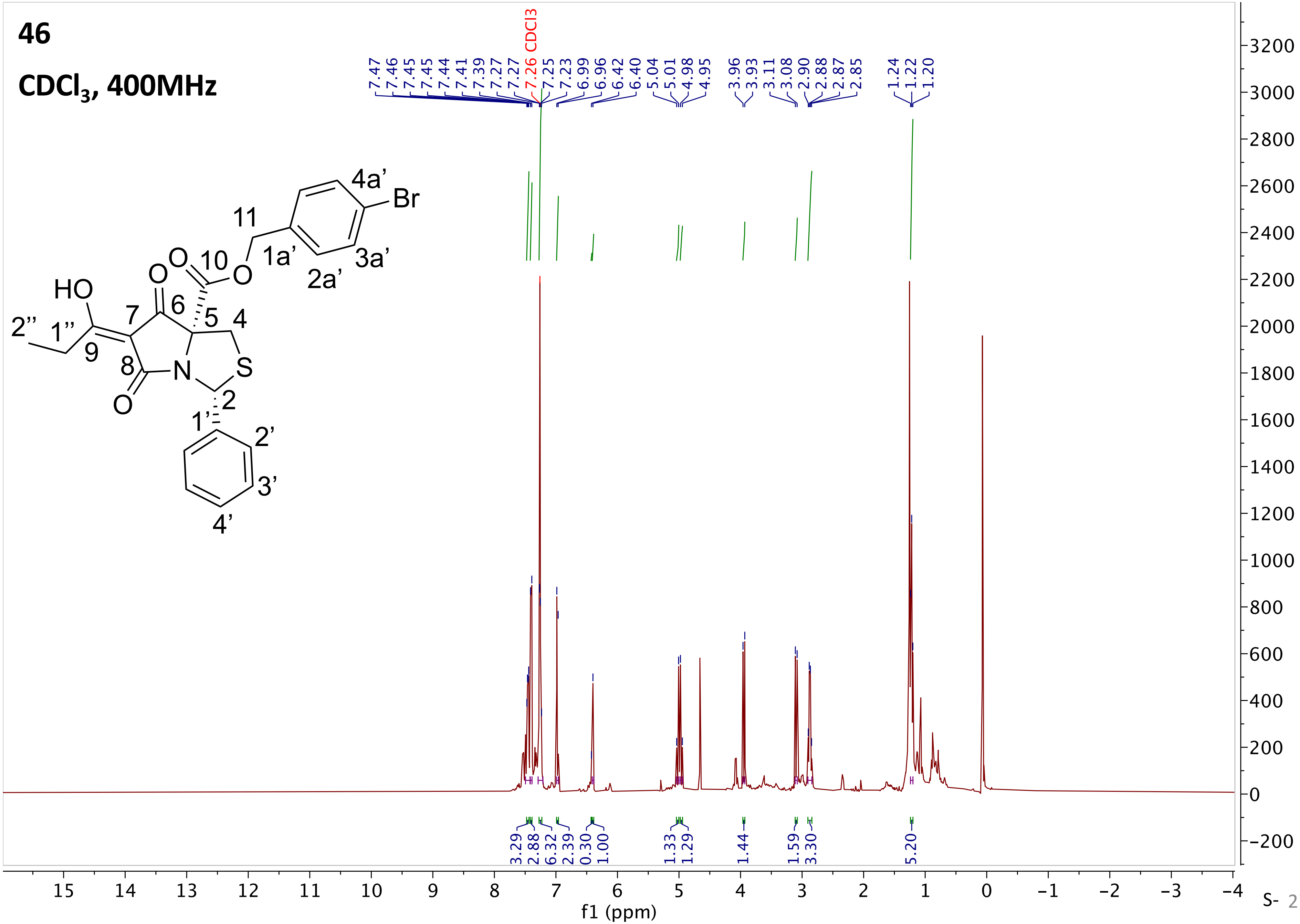

44
$CDCl_3$, 101MHz
191.88
187.72
175.83
165.84
138.37
128.55
128.48
127.16
100.10
82.50
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.60
63.70
35.12
31.03
30.92
26.61
25.26
23.44
23.41
9.81
f1 (ppm)


45
CDCl3, 400MHz
7.48 7.47 7.47 7.46 7.31 7.31 7.30 7.29 7.26 CDCl3 7.25 7.15 7.15 7.14 7.13 6.44 6.40 5.13 5.10 5.02 4.99 3.98 3.95 3.11 3.08 2.90 2.88 2.86 2.84 1.23 1.21 1.20
2.75 4.30 2.74 2.43 0.24 1.00 1.35 1.39 1.39 1.58 2.68 4.37
f1 (ppm)
HO
O
N
S
11
10
1a'
2a'
3a'
4a'
1'
2'
3'
4'
1''
2''


45
CDCl3, 151MHz
192.31
187.28
175.91
166.59
138.16
134.71
128.69
128.67
128.62
128.60
128.39
127.17
100.05
82.44
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
68.59
63.97
35.42
26.72
9.73
f1 (ppm)

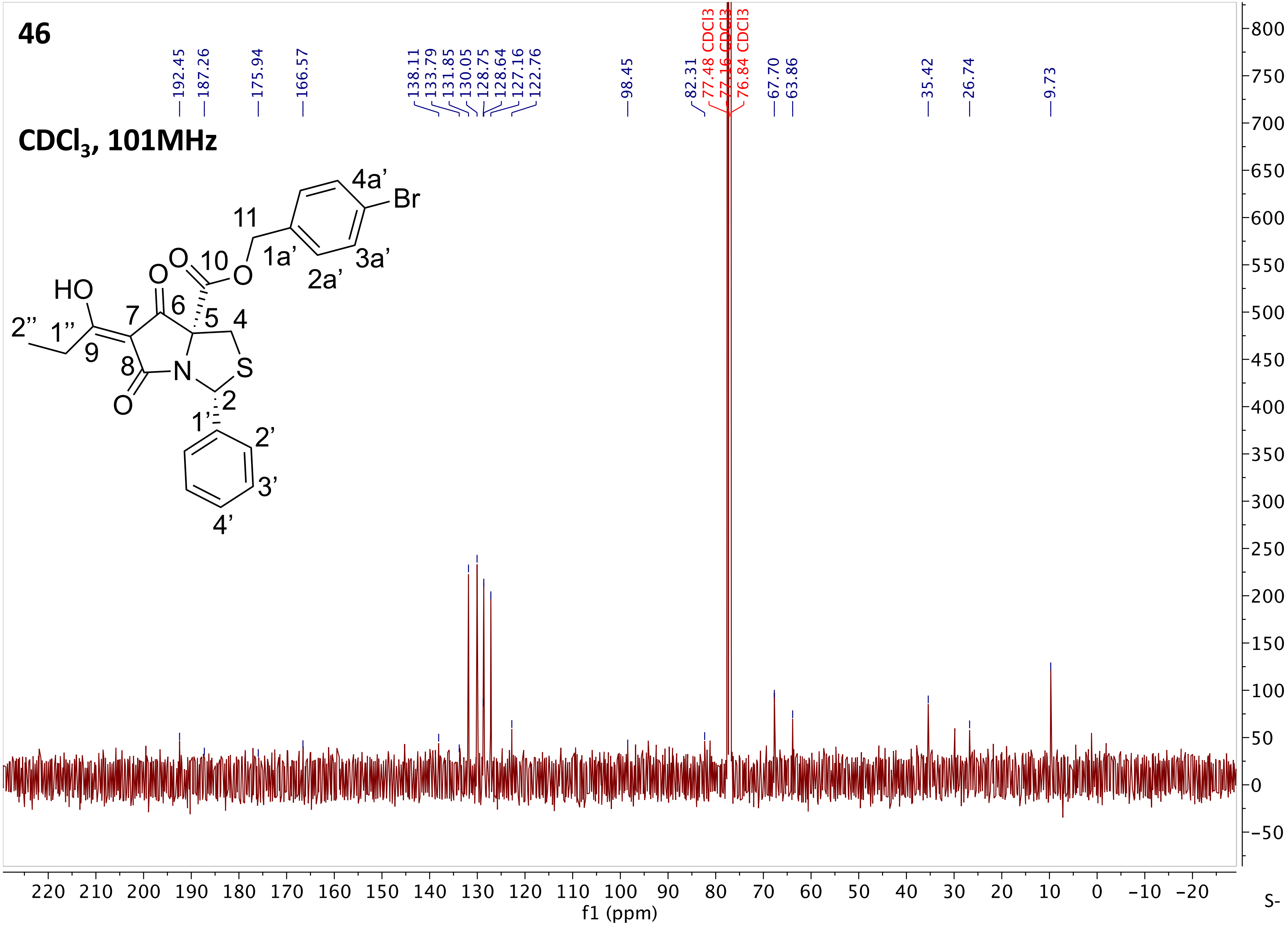
46

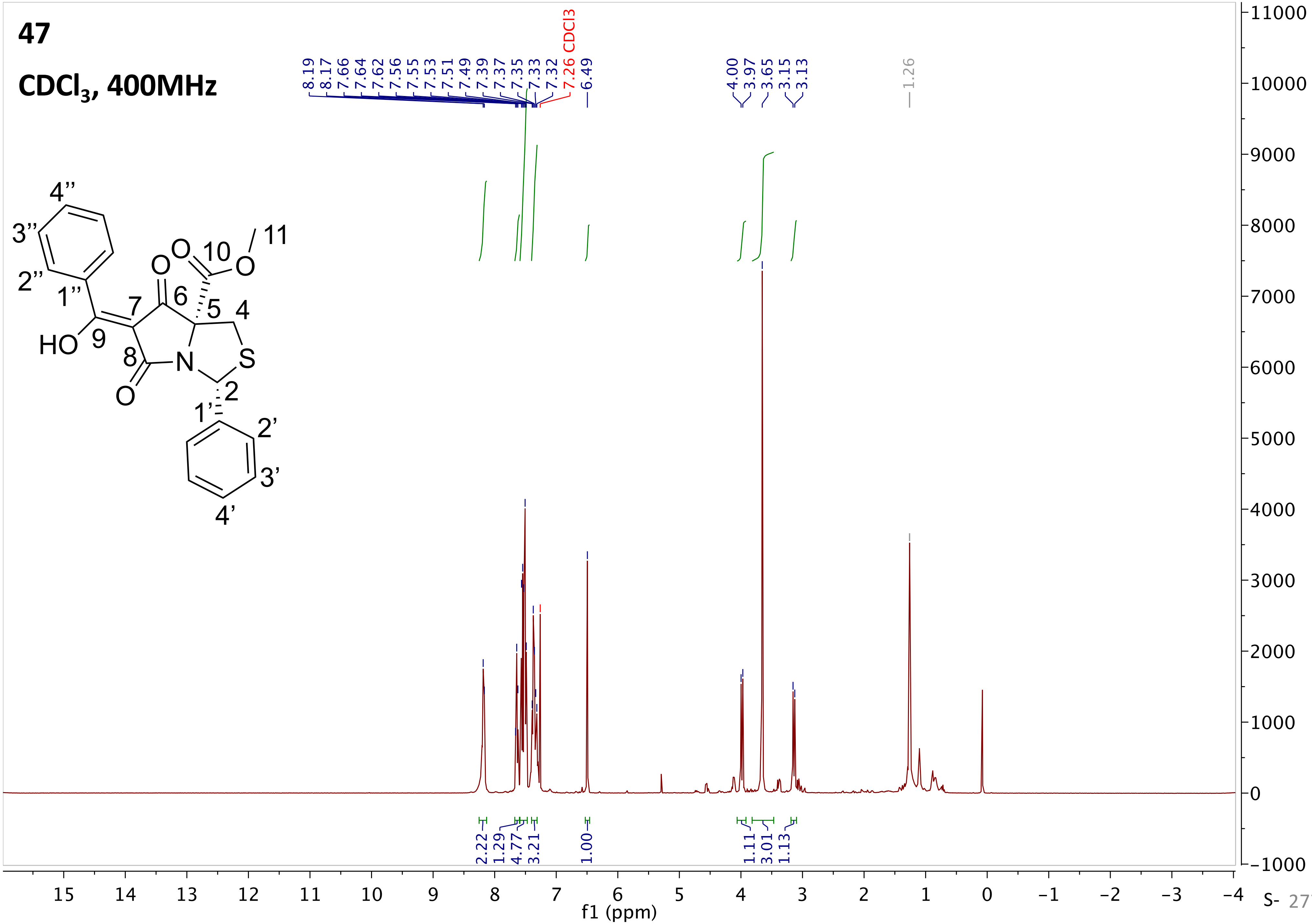
$CDCl_3$, 400MHz

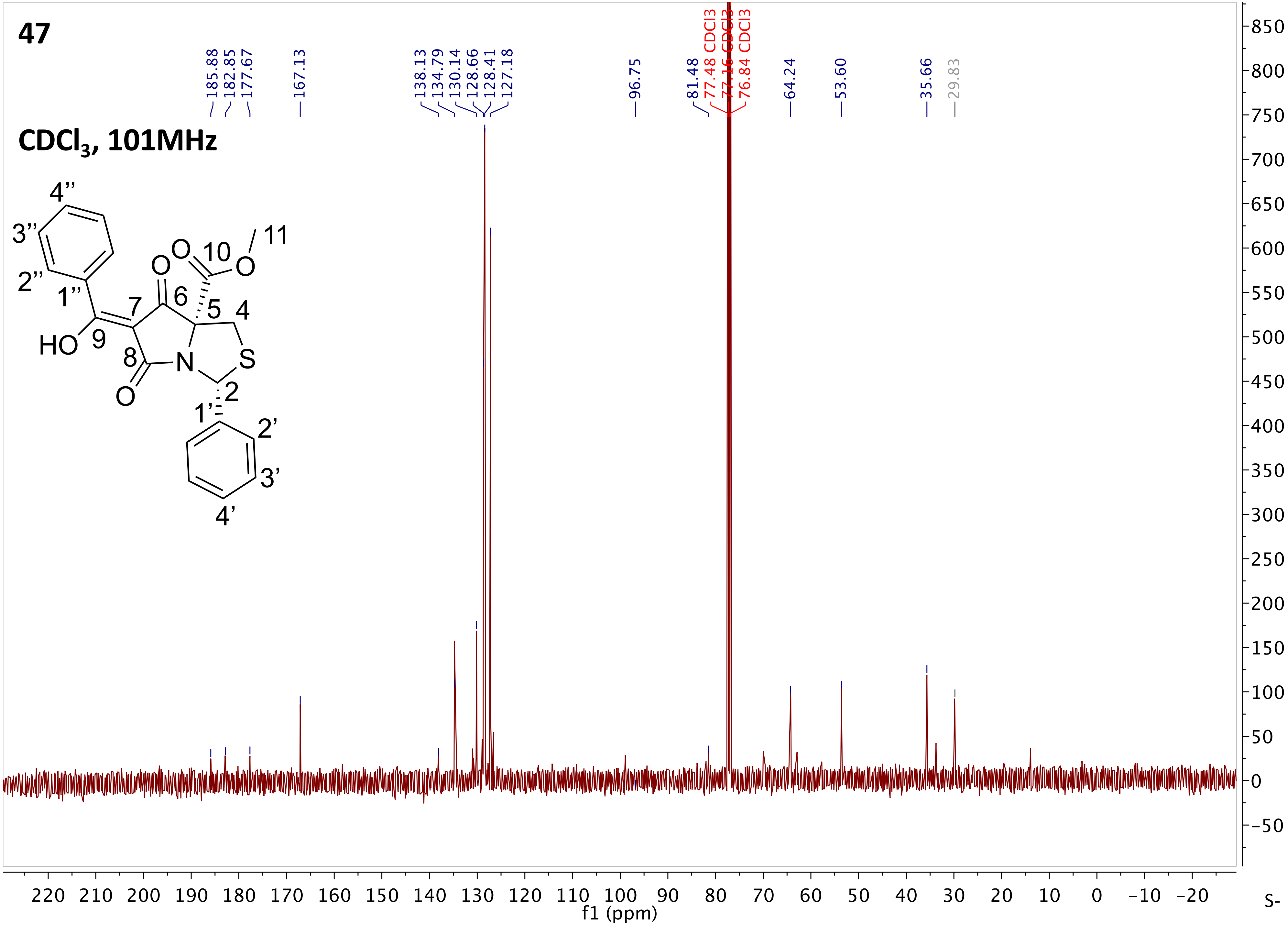


46

$CDCl_3$, 101MHz



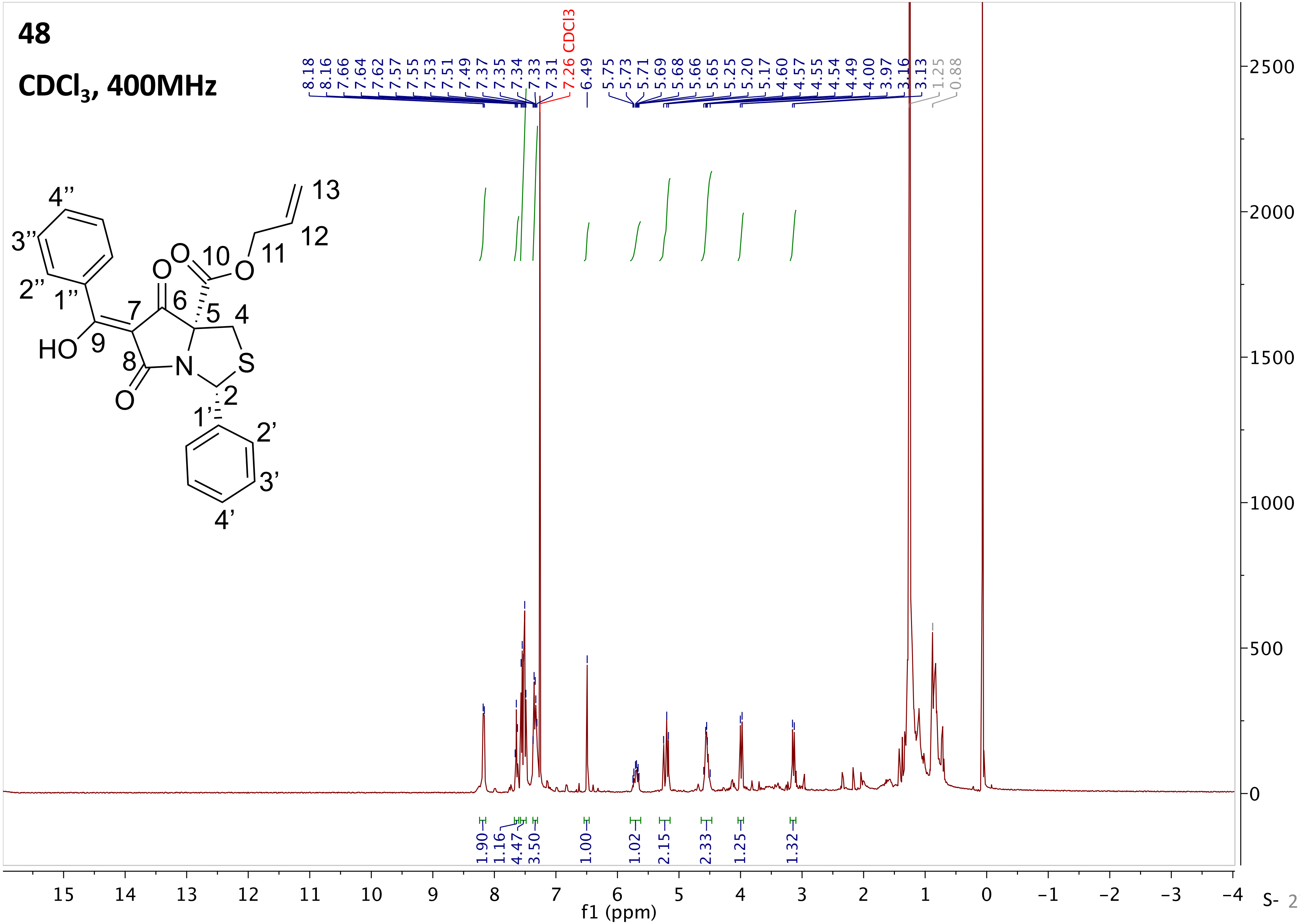

47
CDCl3, 400MHz
f1 (ppm)

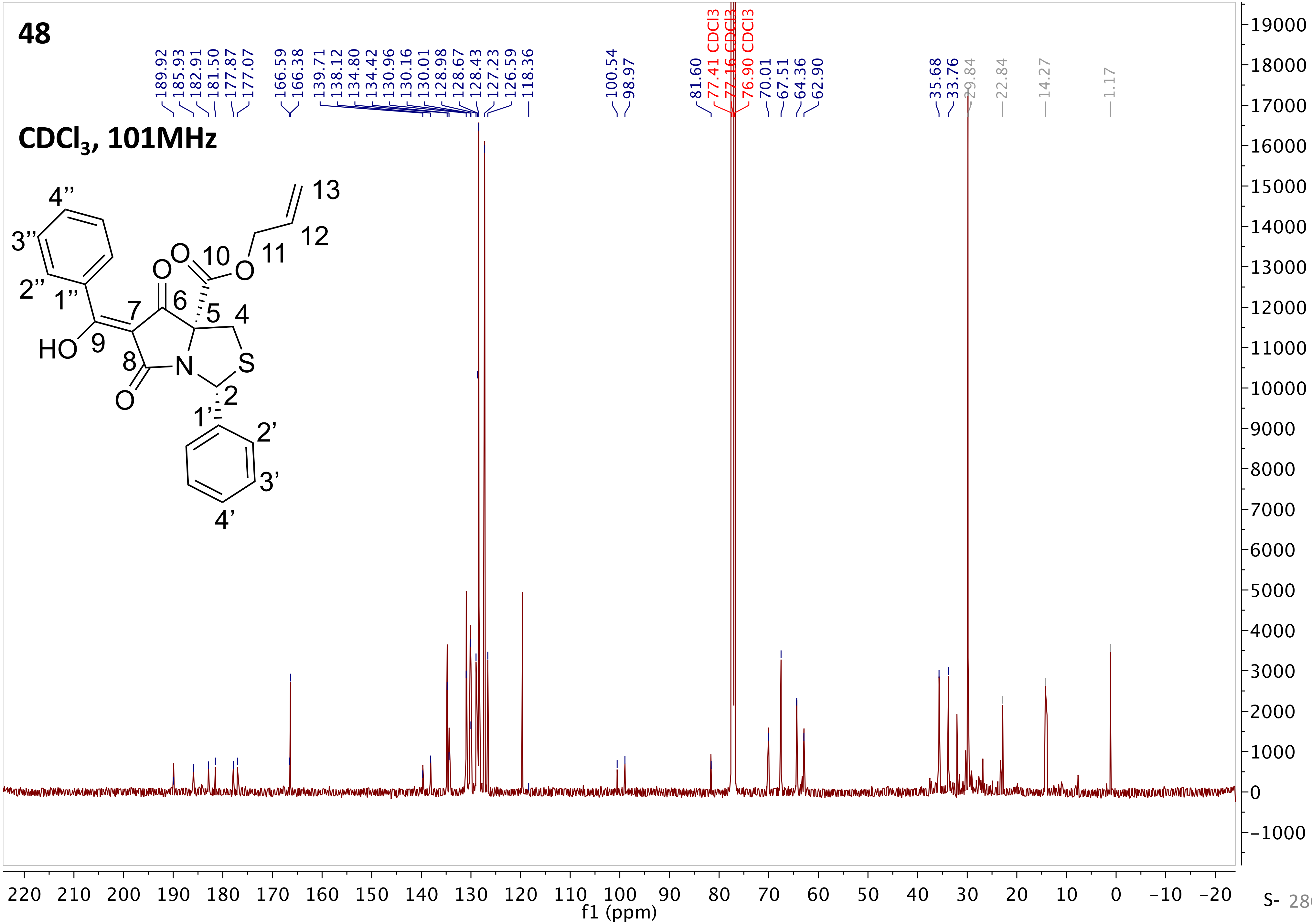


47
CDCl3, 101MHz
185.88
182.85
177.67
167.13
138.13
134.79
130.14
128.66
128.41
127.18
96.75
81.48
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
64.24
53.60
35.66
29.83
f1 (ppm)

48

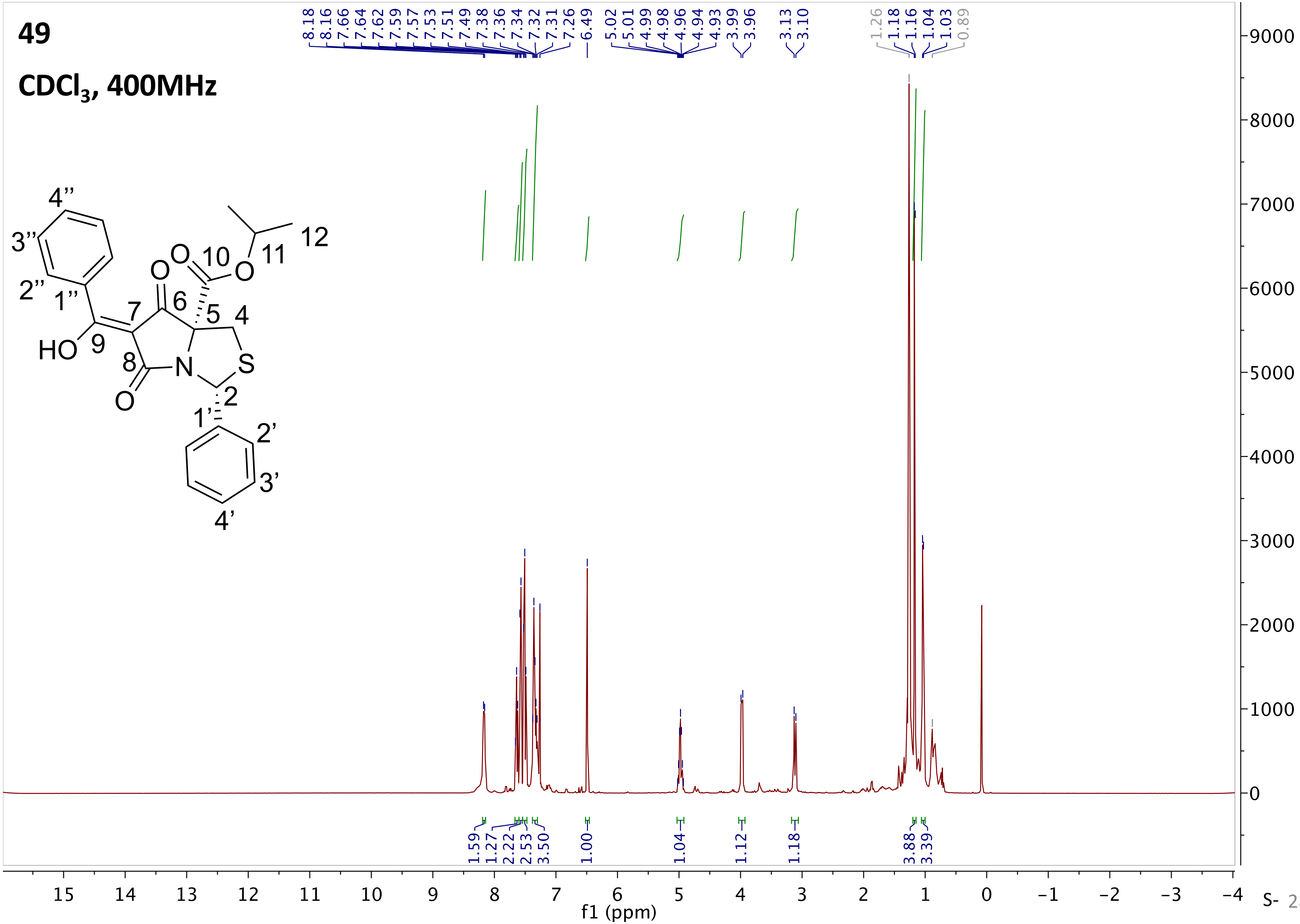
CDCl$_3$, 400MHz




48
CDCl3, 101MHz
189.92
185.93
182.91
181.50
177.87
177.07
166.59
166.38
139.71
138.12
134.80
134.42
130.96
130.16
130.01
128.98
128.67
128.43
127.23
126.59
118.36
100.54
98.97
81.60
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
70.01
67.51
64.36
62.90
35.68
33.76
29.84
22.84
14.27
1.17
f1 (ppm)

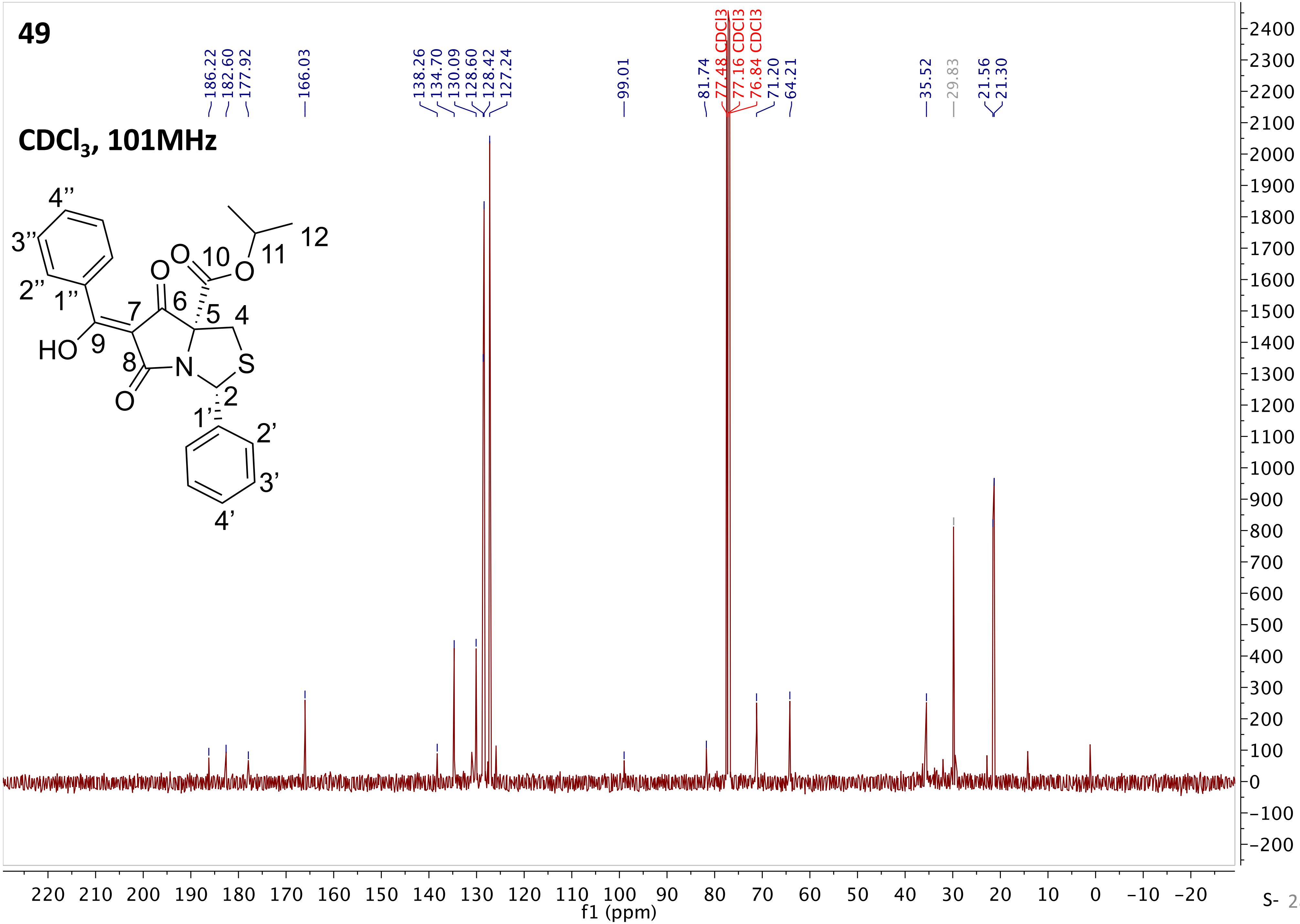
49

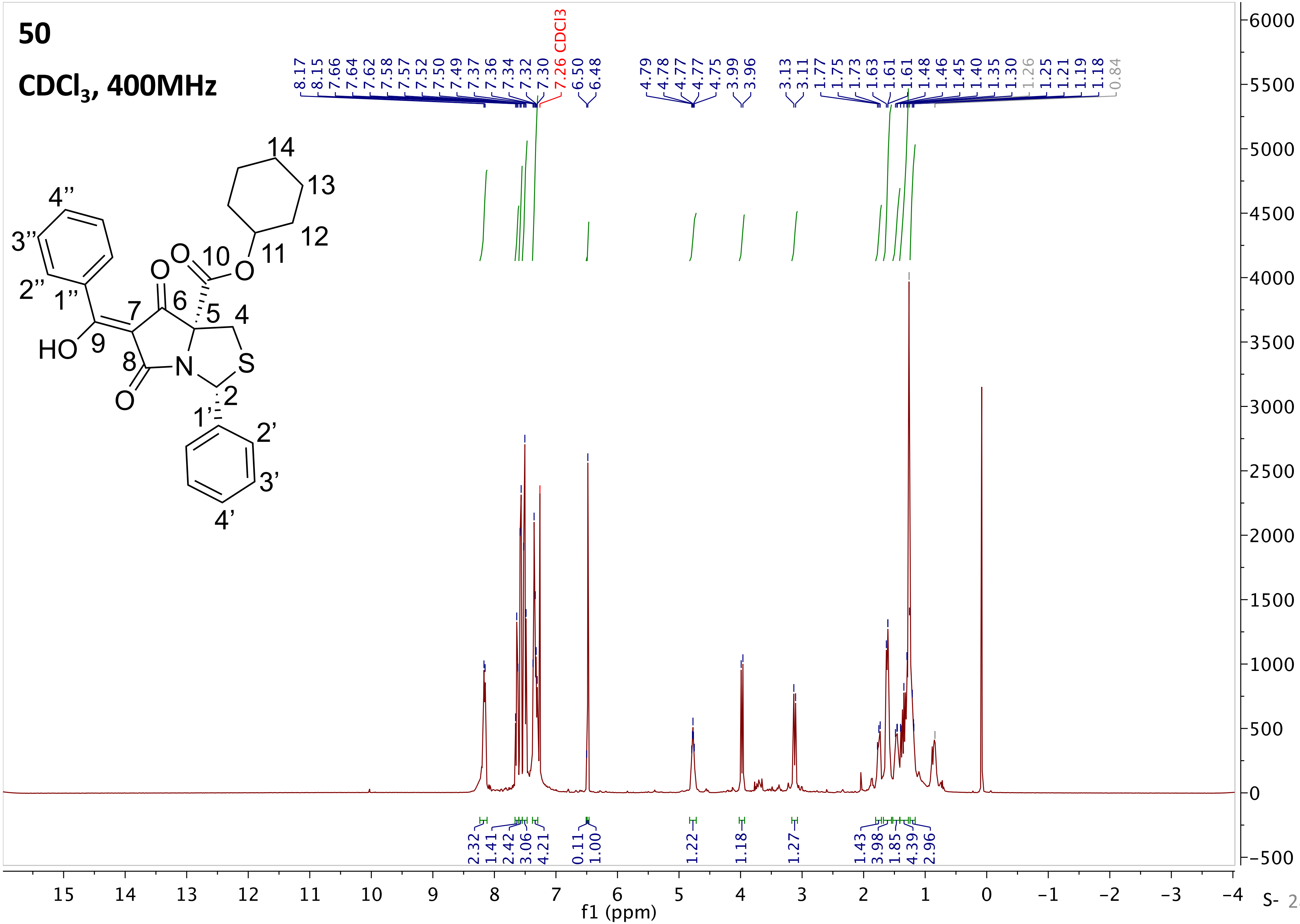
$CDCl_3$, 400MHz



49

CDCl$_3$, 101MHz

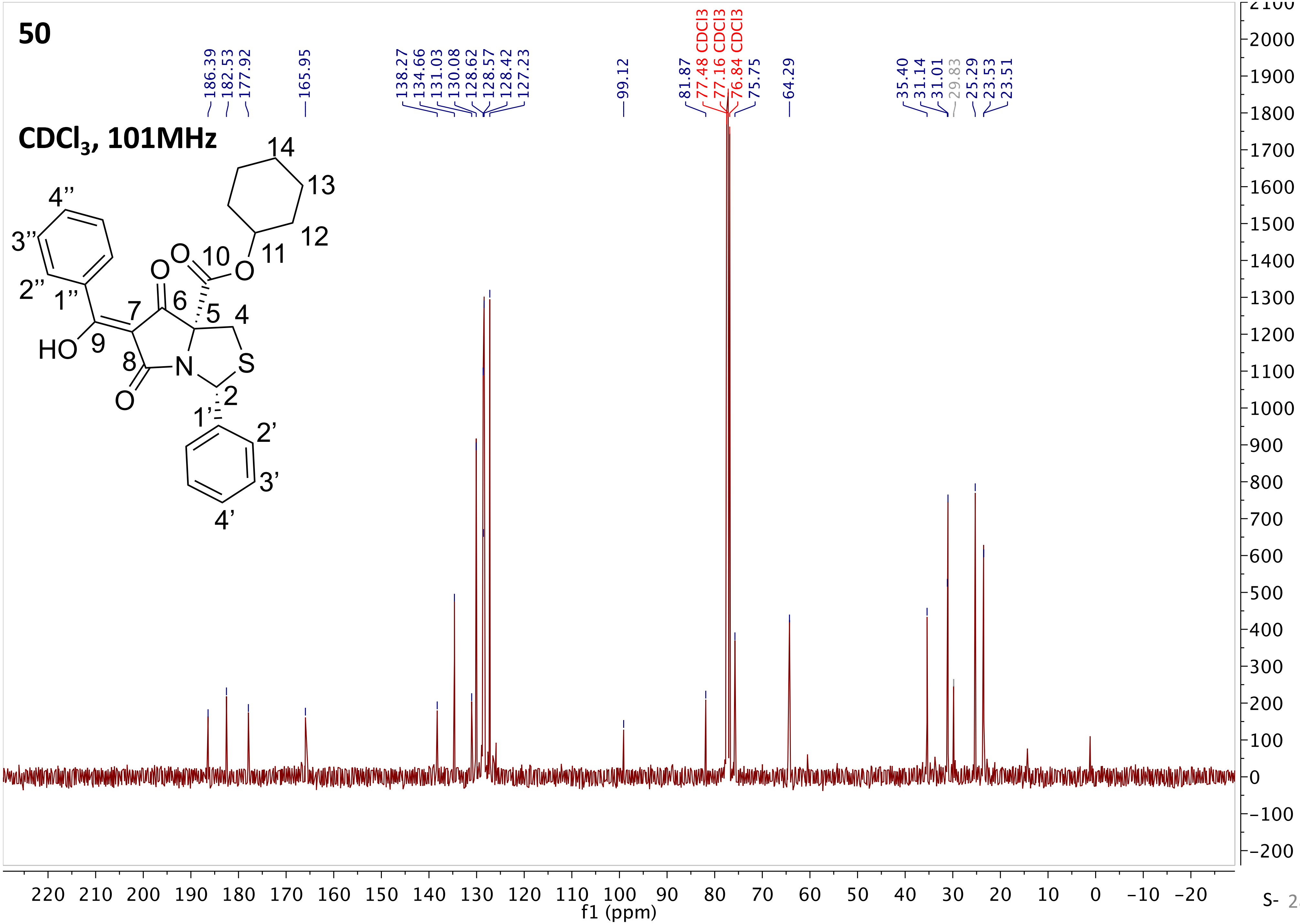


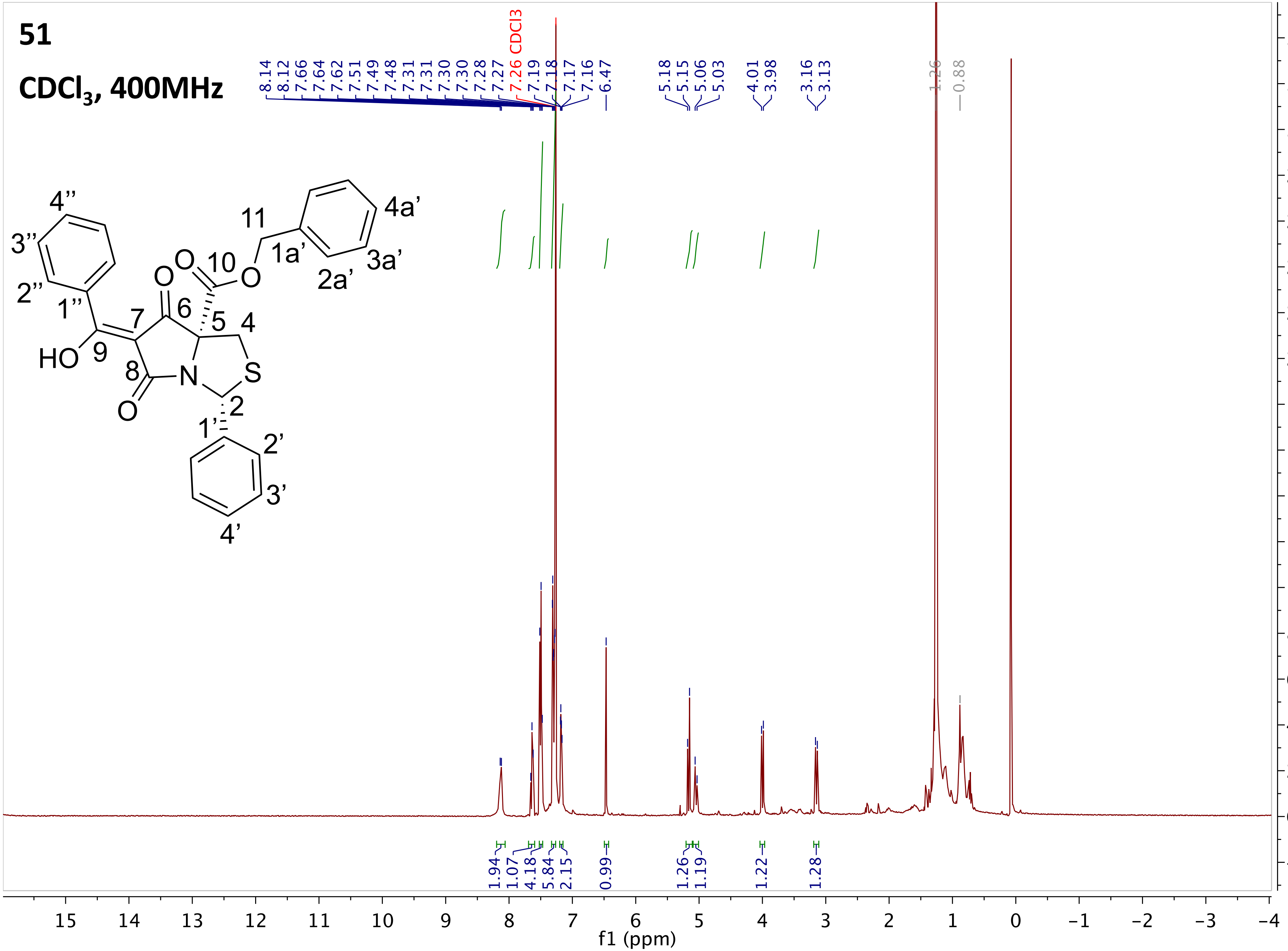


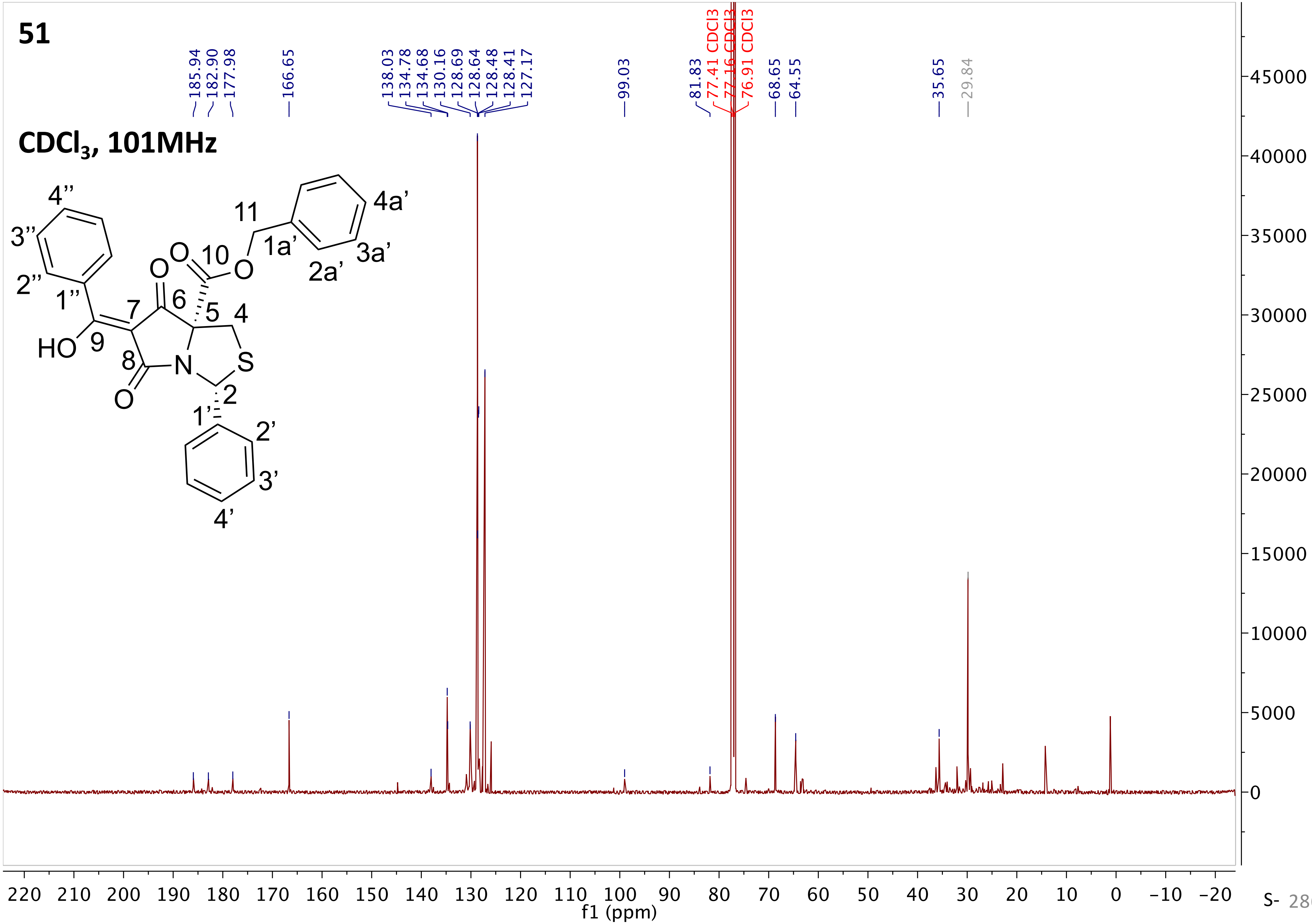
50
CDCl3, 400MHz
8.17 8.15 7.66 7.64 7.62 7.58 7.57 7.52 7.50 7.49 7.37 7.36 7.34 7.32 7.30 7.26 CDCl3 6.50 6.48 4.79 4.78 4.77 4.77 4.75 3.99 3.96 3.13 3.11 1.77 1.75 1.73 1.63 1.61 1.61 1.48 1.46 1.45 1.40 1.35 1.30 1.26 1.25 1.21 1.19 1.18 0.84
2.32 1.41 2.42 3.06 4.21 0.11 1.00 1.22 1.18 1.27 1.43 3.98 1.85 4.39 2.96
f1 (ppm)

50

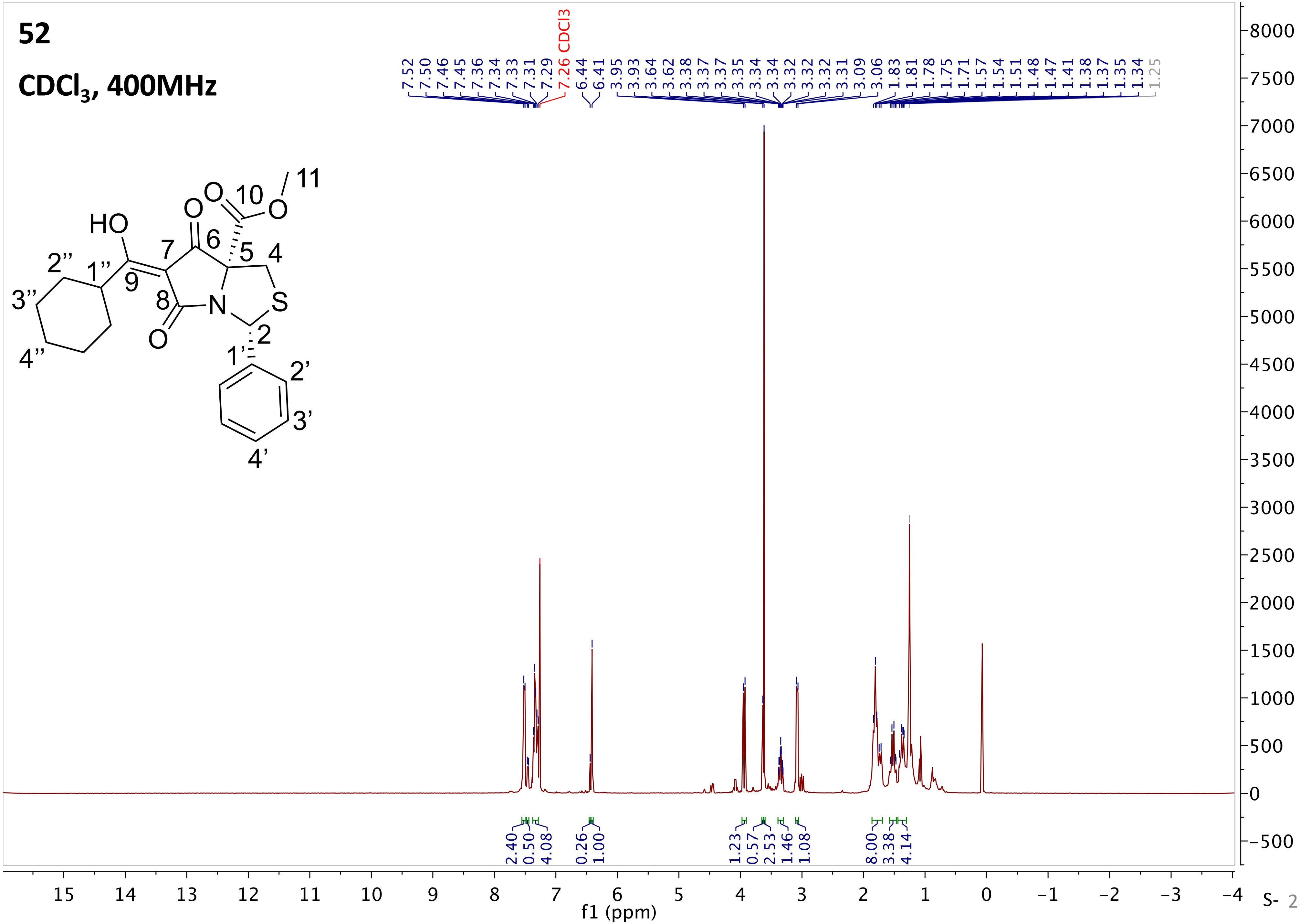
CDCl$_3$, 101MHz

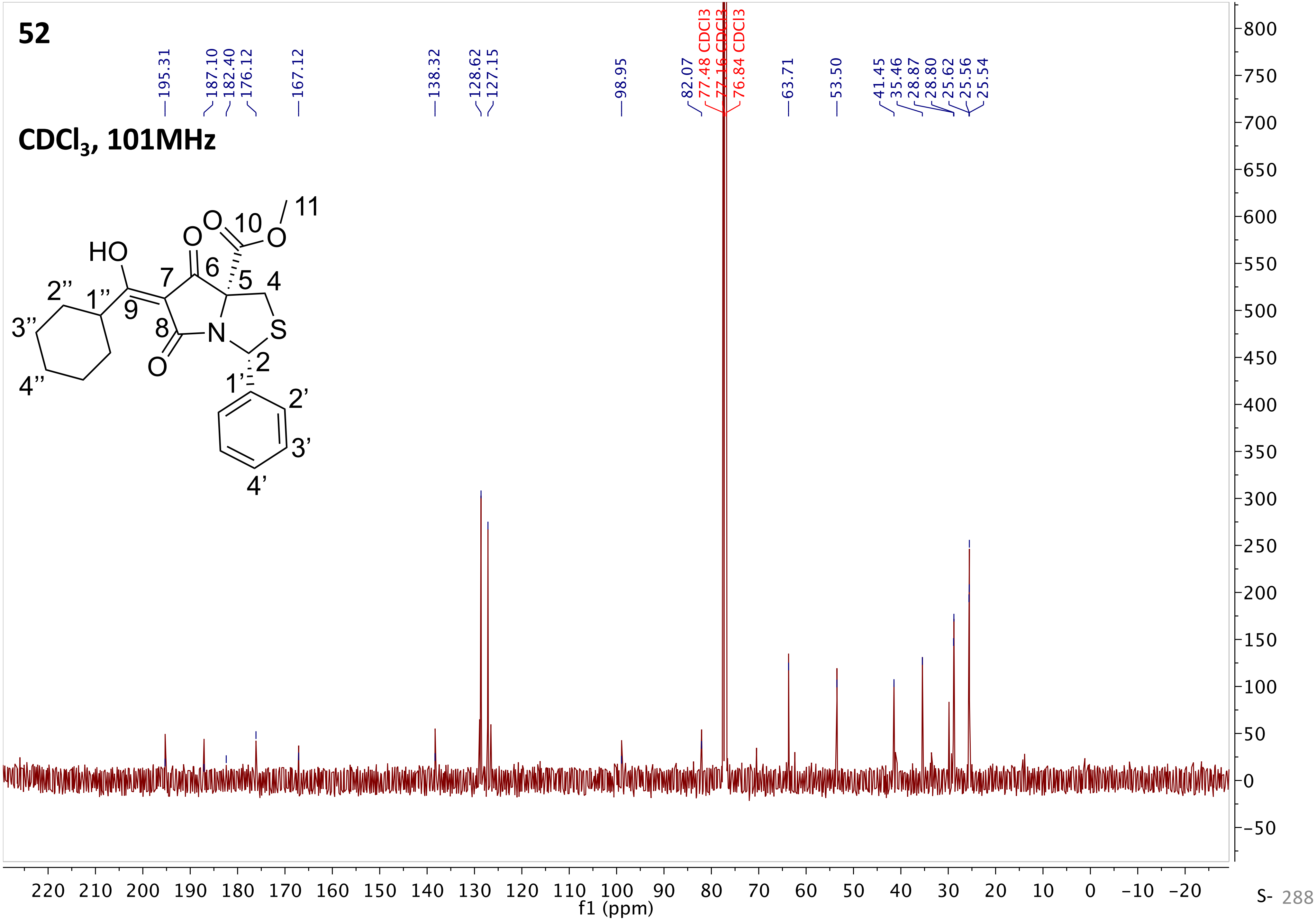


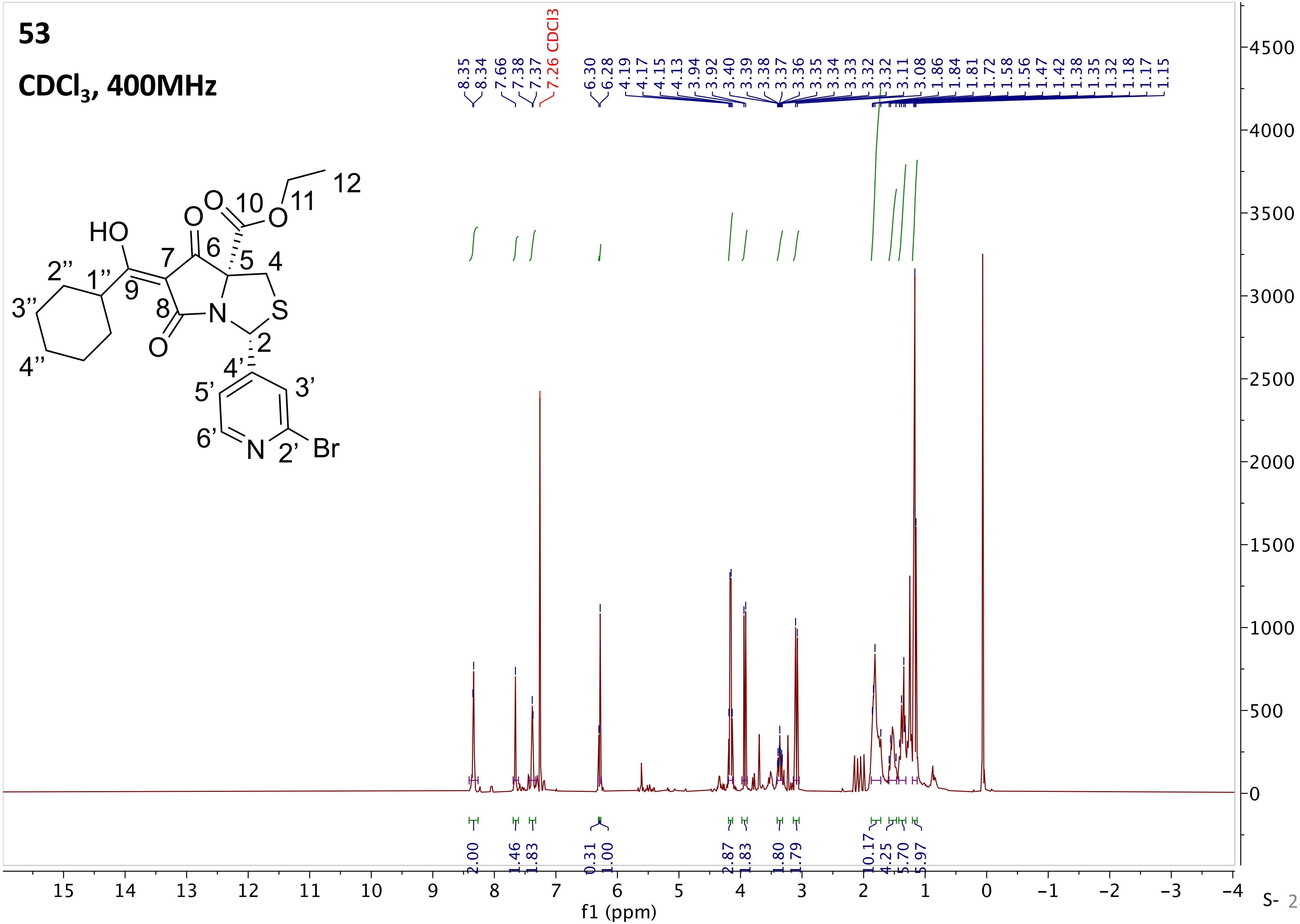

51
$CDCl_3$, 400MHz
8.14 8.12 7.66 7.64 7.62 7.51 7.49 7.48 7.31 7.31 7.30 7.30 7.28 7.27 7.26 CDCl3 7.19 7.18 7.17 7.16 6.47
5.18 5.15 5.06 5.03 4.01 3.98 3.16 3.13 1.26 0.88
1.94 1.07 4.18 5.84 2.15 0.99 1.26 1.19 1.22 1.28
4'' 3'' 2'' 1'' 7 HO 9 8 O N 2 S 4 5 6 O 10 O 11 1a' 2a' 3a' 4a' 1' 2' 3' 4'
f1 (ppm)



51
CDCl3, 101MHz
185.94
182.90
177.98
166.65
138.03
134.78
134.68
130.16
128.69
128.64
128.48
128.41
127.17
99.03
81.83
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.65
64.55
35.65
29.84
f1 (ppm)

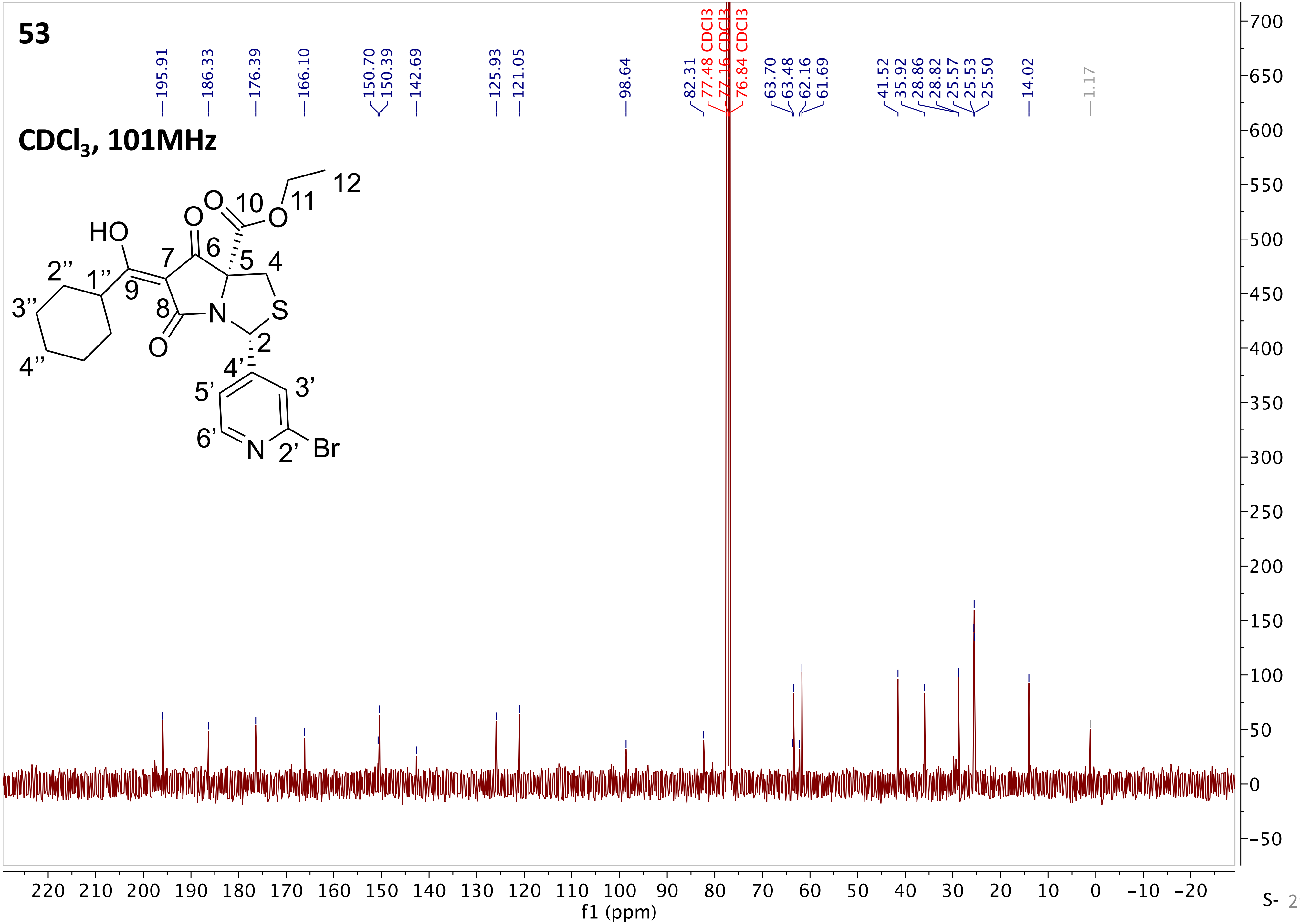

52
CDCl3, 400MHz
f1 (ppm)


52
CDCl3, 101MHz
195.31
187.10
182.40
176.12
167.12
138.32
128.62
127.15
98.95
82.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.71
53.50
41.45
35.46
28.87
28.80
25.62
25.56
25.54
f1 (ppm)


53
CDCl3, 400MHz
8.35 8.34 7.66 7.38 7.37 7.26 CDCl3 6.30 6.28 4.19 4.17 4.15 4.13 3.94 3.92 3.40 3.39 3.38 3.37 3.36 3.35 3.34 3.33 3.32 3.32 3.11 3.08 1.86 1.84 1.81 1.72 1.58 1.56 1.47 1.42 1.38 1.35 1.32 1.18 1.17 1.15
HO
O
O
O
O
N
S
N
Br
1'' 2'' 3'' 4'' 2 4 5 6 7 8 9 10 11 12 2' 3' 4' 5' 6'
2.00 1.46 1.83 0.31 1.00 2.87 1.83 1.80 1.79 10.17 4.25 5.70 5.97
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)
4500 4000 3500 3000 2500 2000 1500 1000 500 0

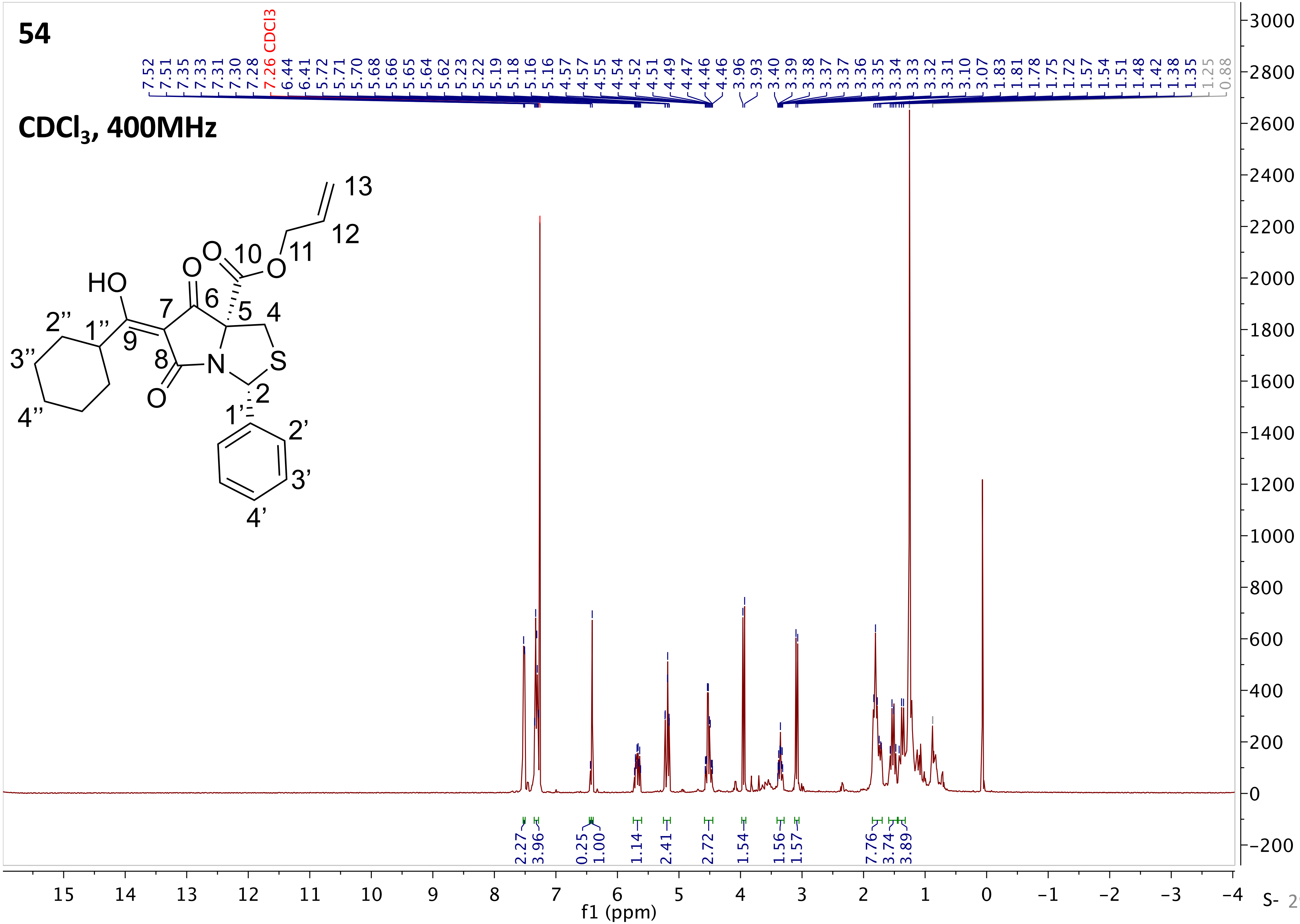
53

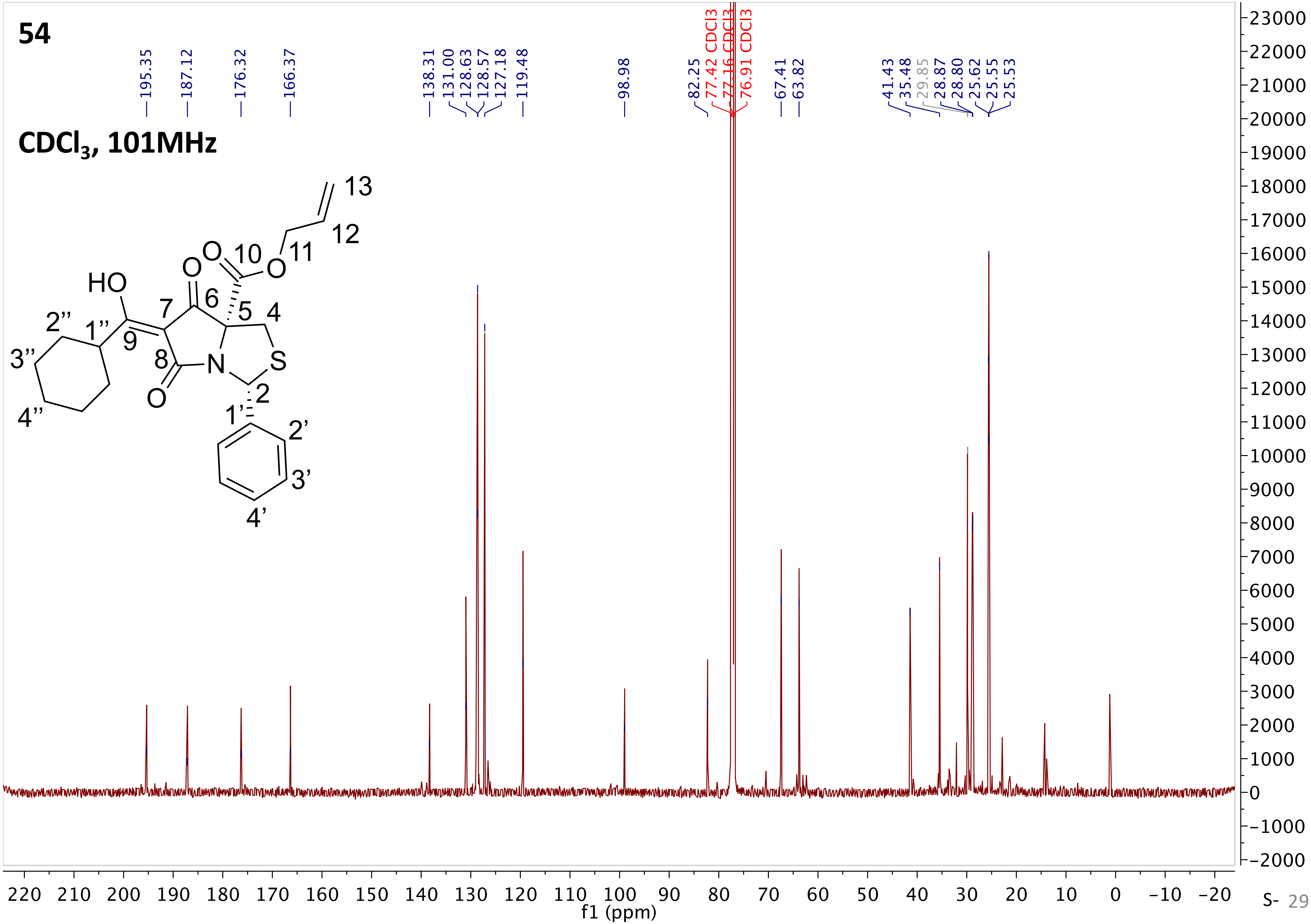
$CDCl_3$, 101MHz



54

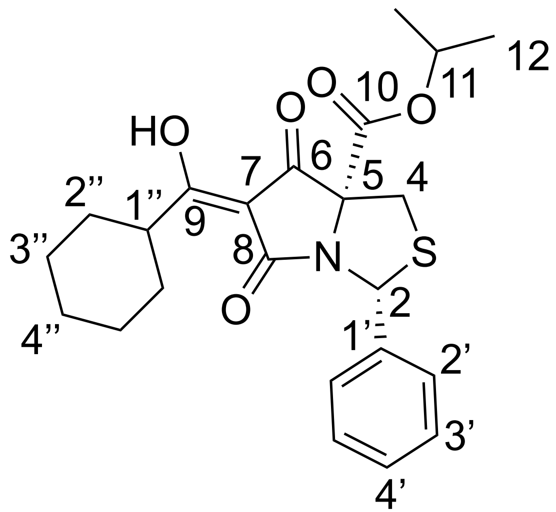
$CDCl_3$, 400MHz

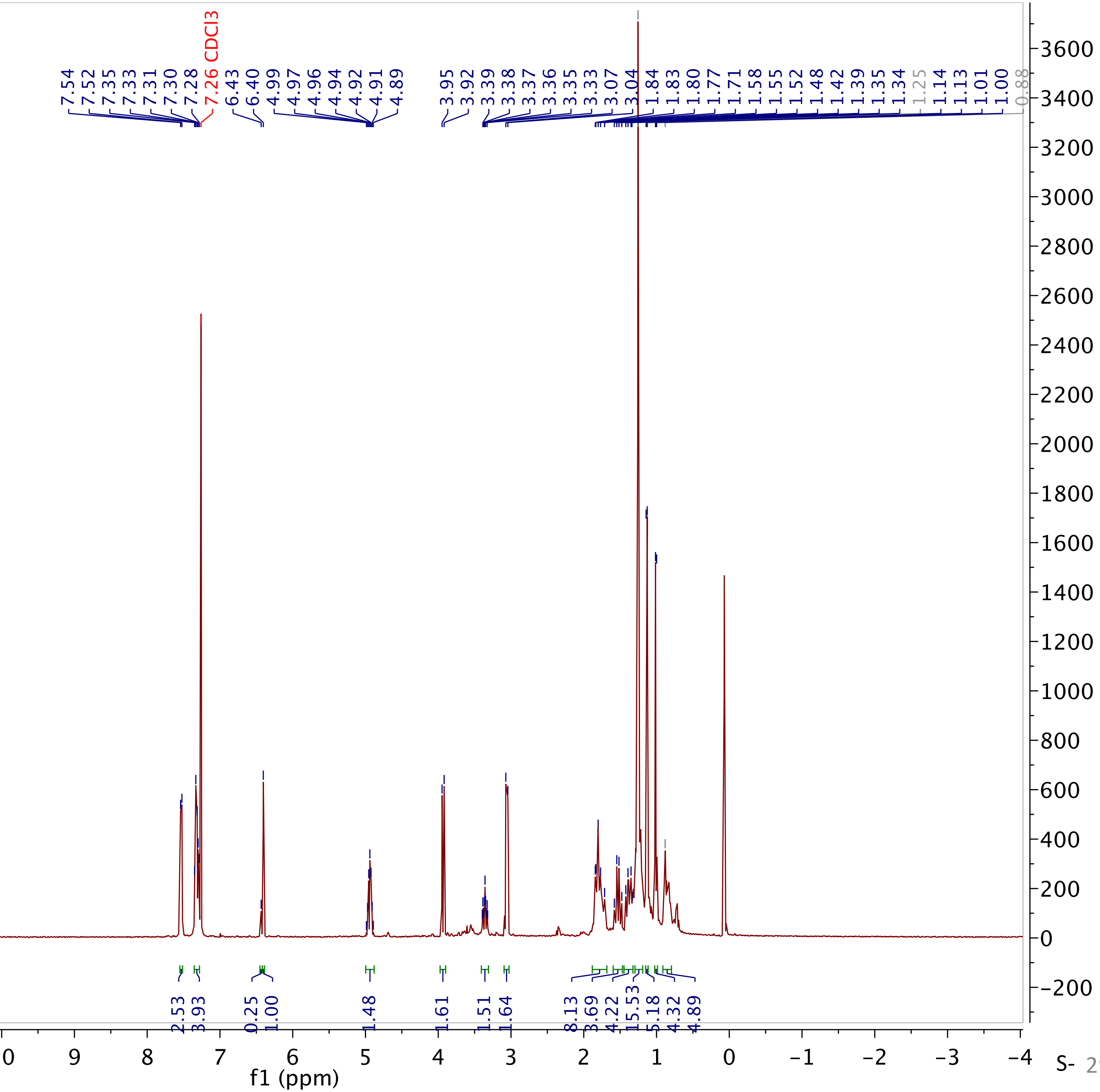



54
CDCl3, 101MHz
195.35
187.12
176.32
166.37
138.31
131.00
128.63
128.57
127.18
119.48
98.98
82.25
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
67.41
63.82
41.43
35.48
29.85
28.87
28.80
25.62
25.55
25.53
HO
O
O
O
O
N
S
f1 (ppm)

55

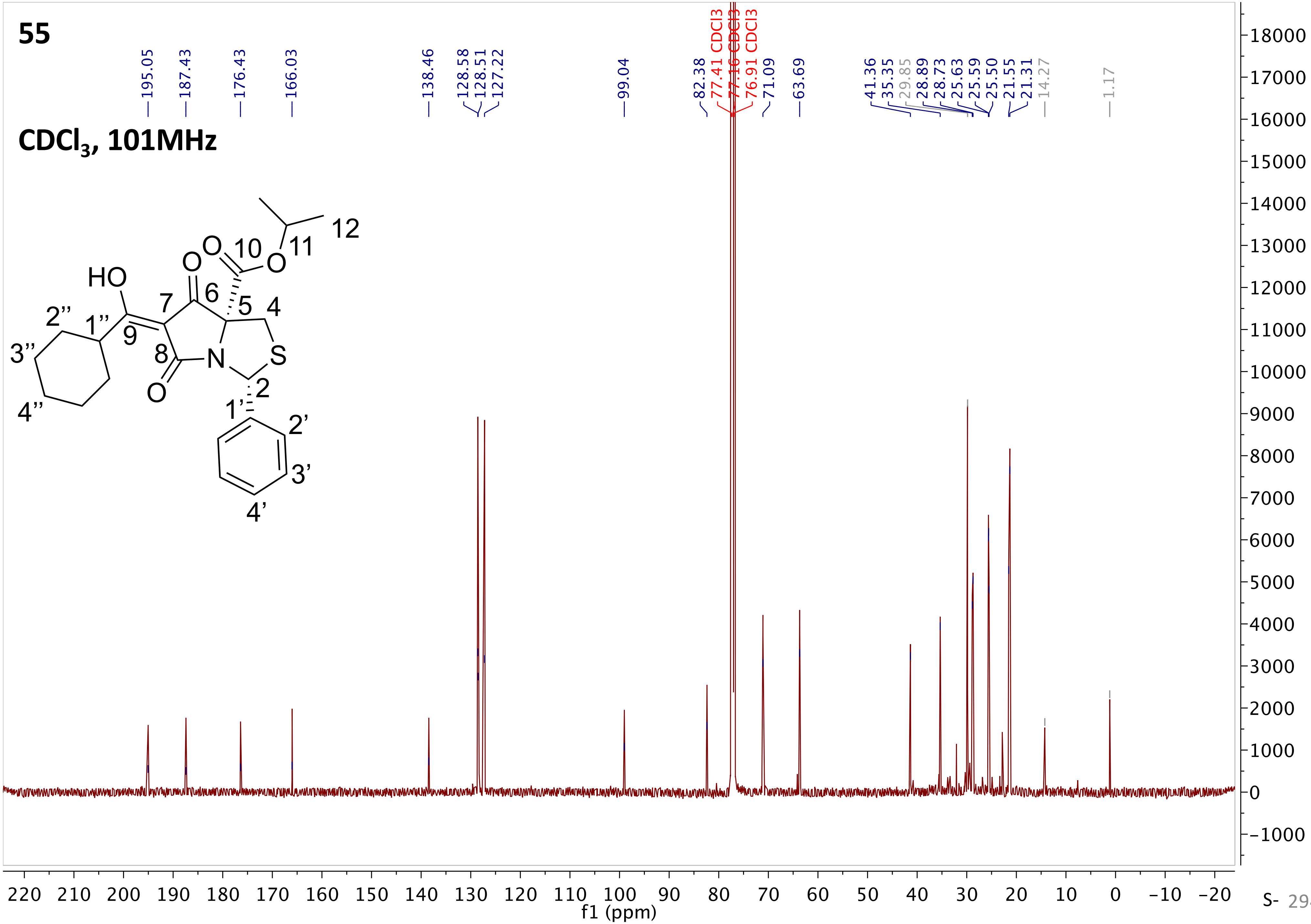
$CDCl_3$, 400MHz

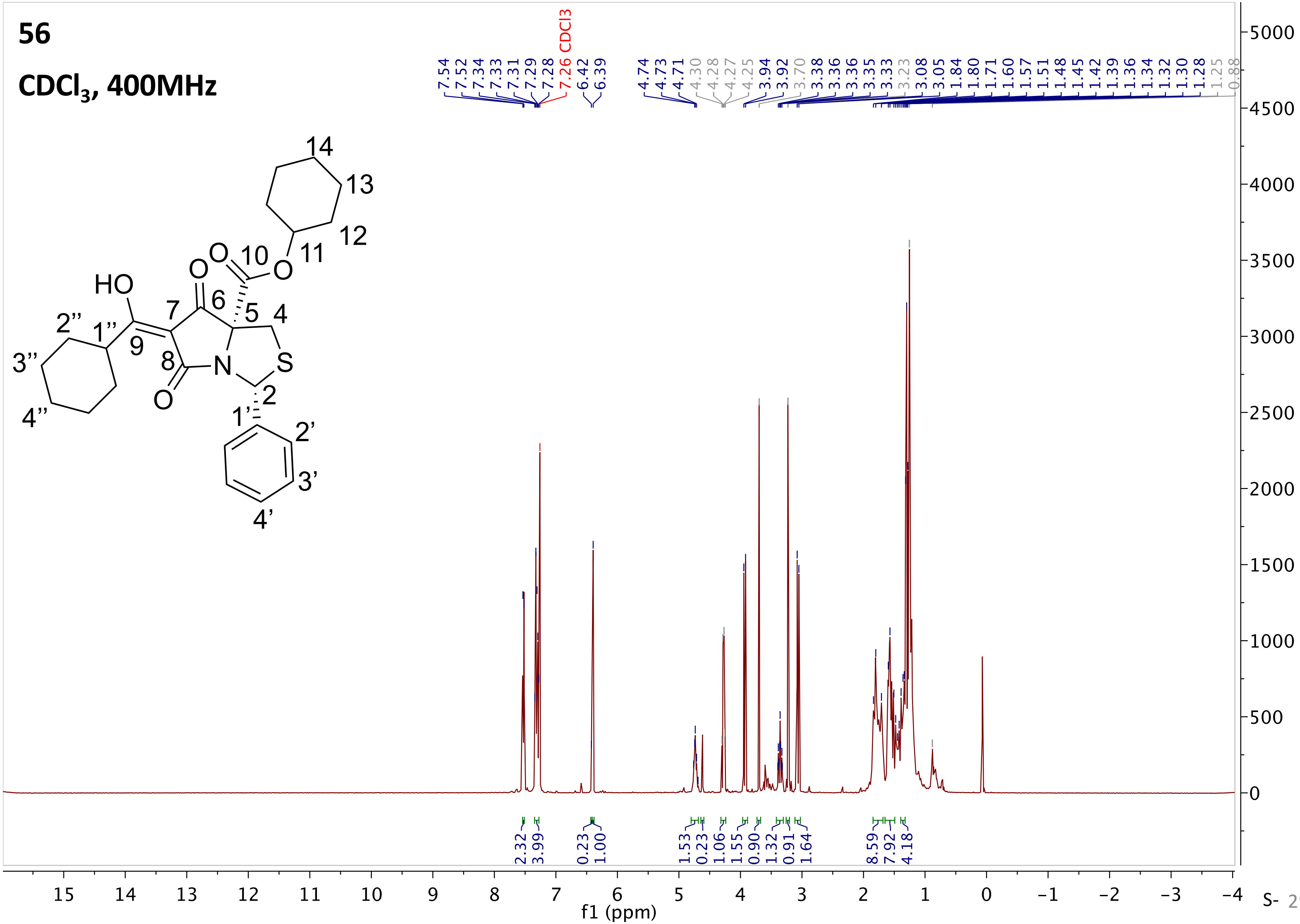


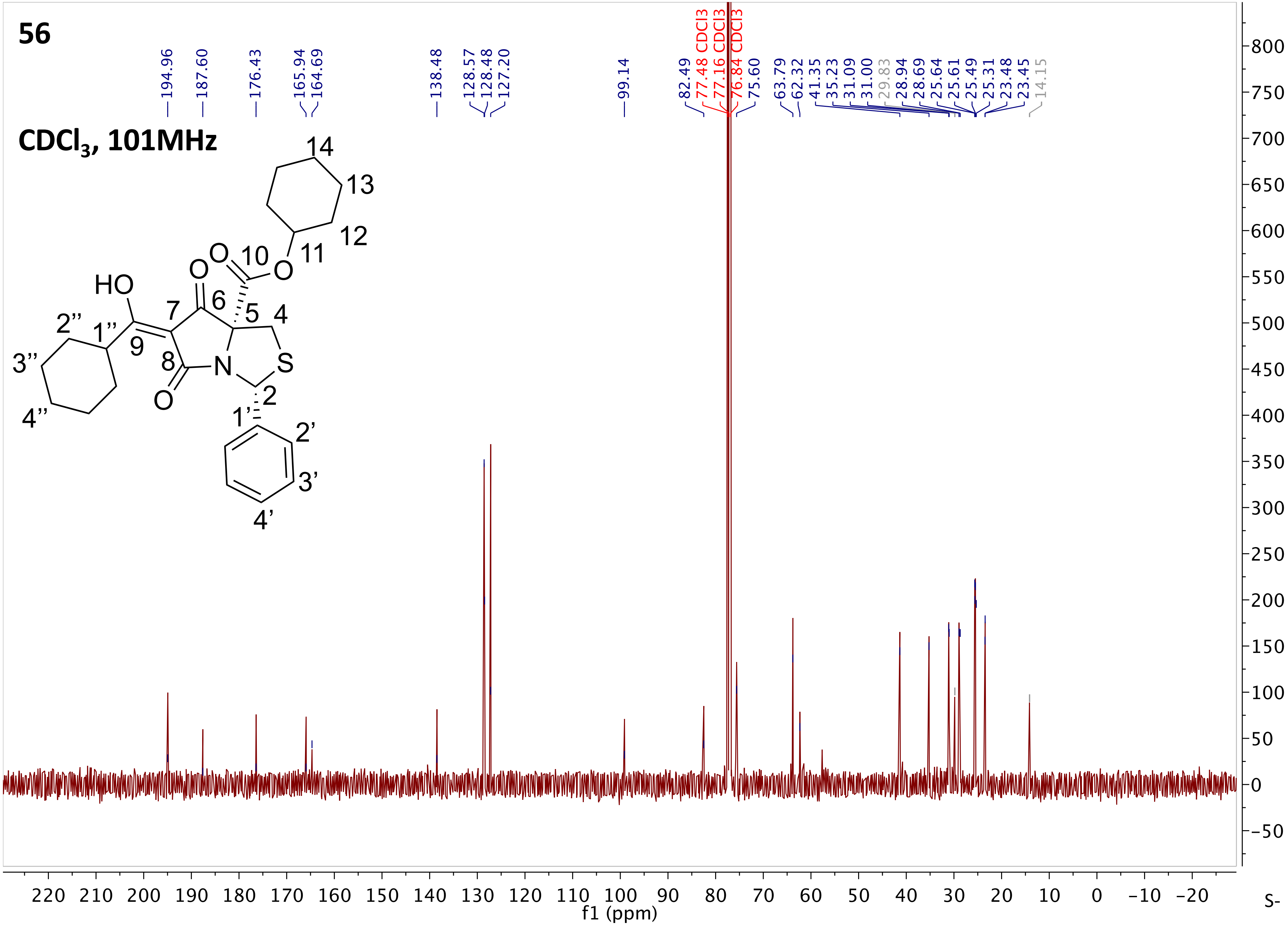


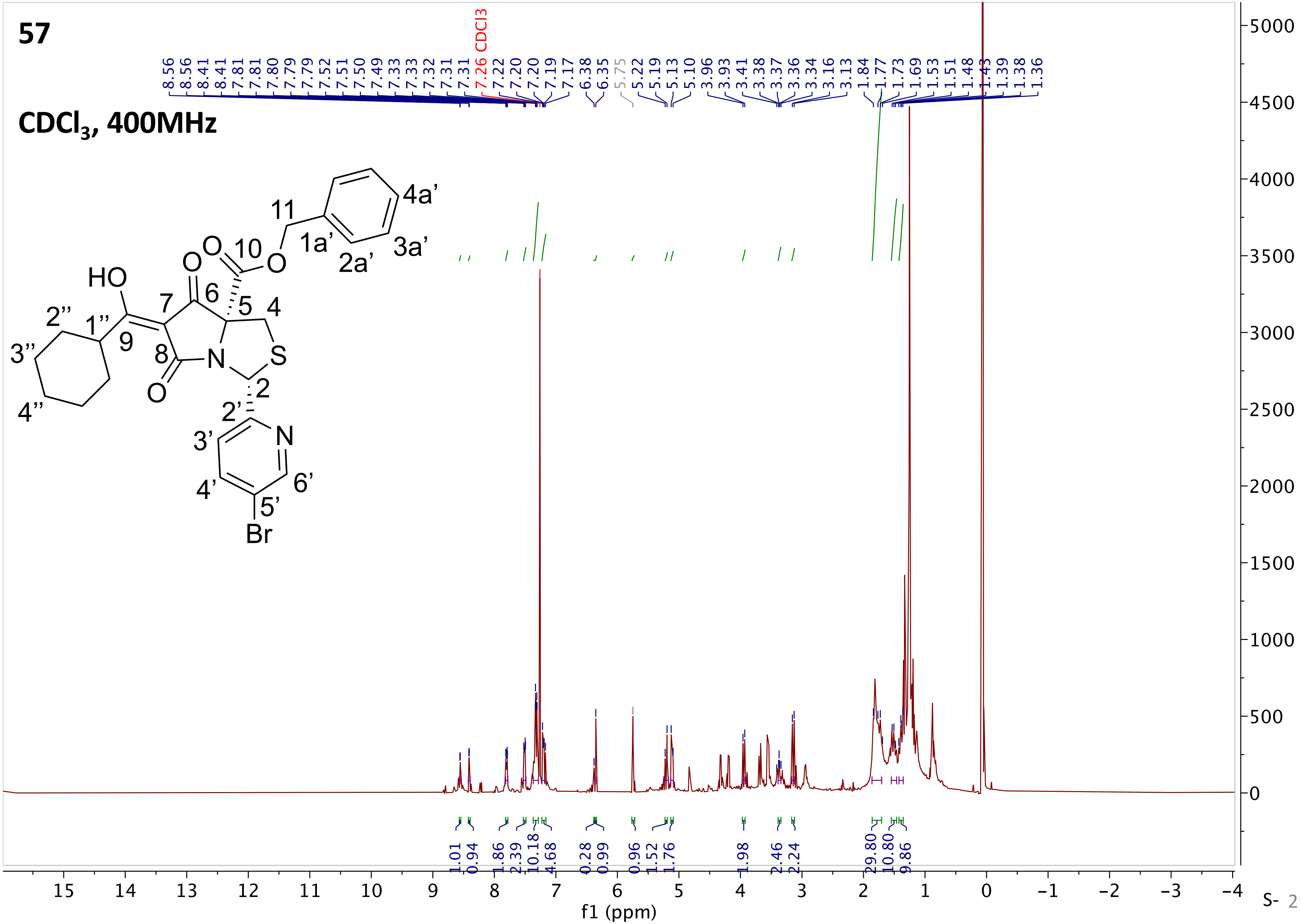
55

CDCl$_3$, 101MHz

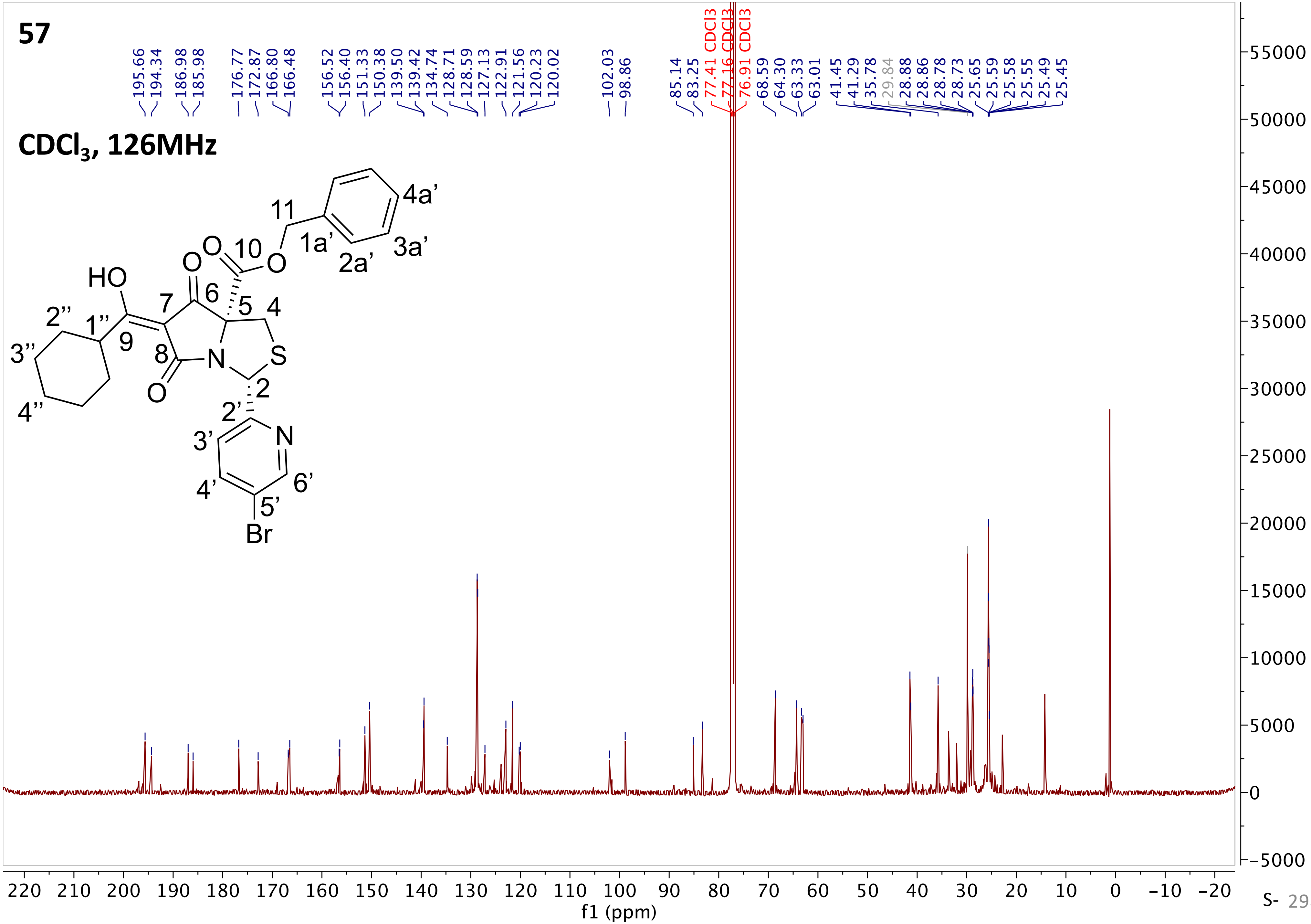


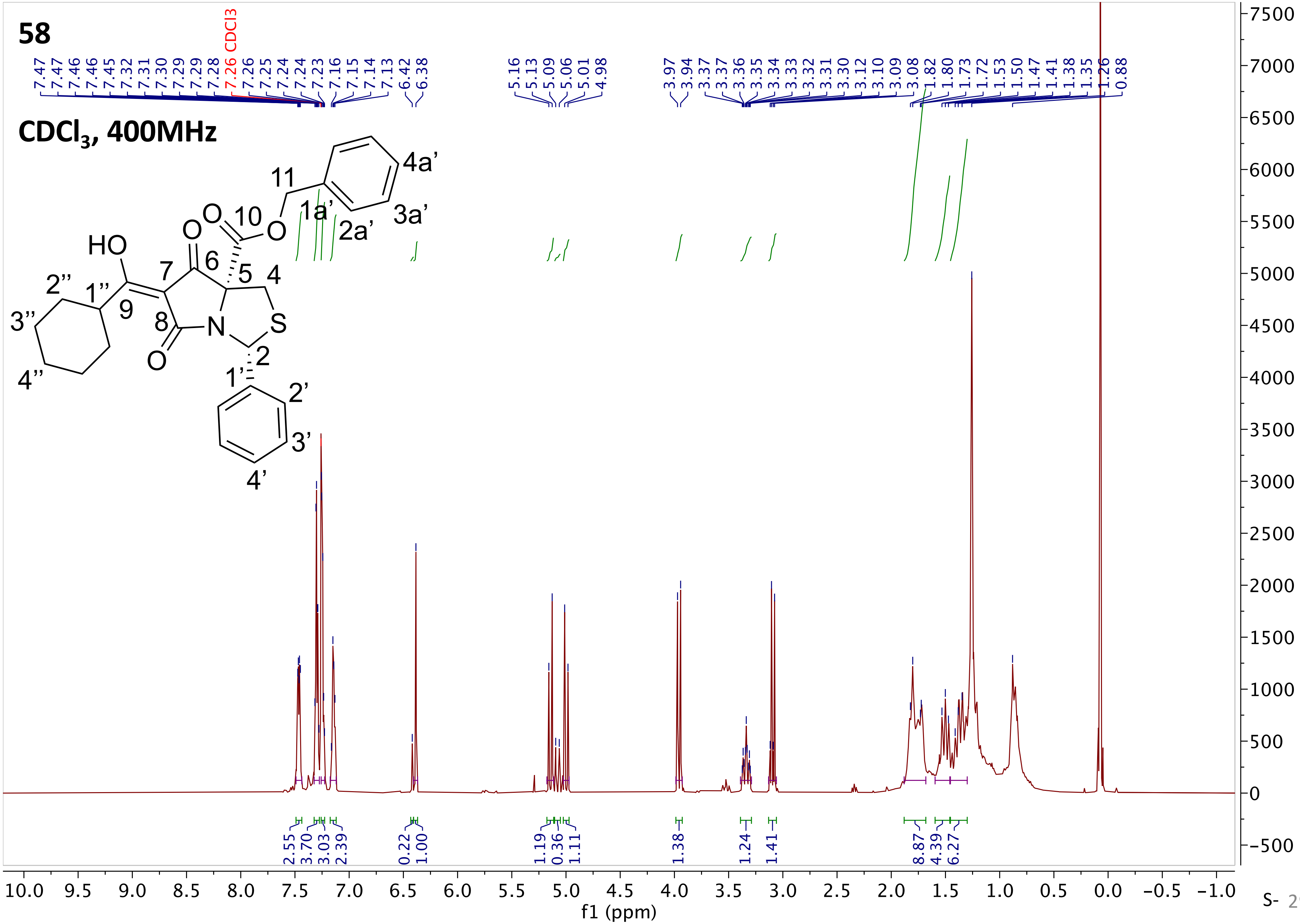

56
CDCl3, 400MHz
7.54 7.52 7.34 7.33 7.31 7.29 7.28 7.26 CDCl3 6.42 6.39 4.74 4.73 4.71 4.30 4.28 4.27 4.25 3.94 3.92 3.70 3.38 3.36 3.36 3.35 3.33 3.23 3.08 3.05 1.84 1.80 1.71 1.60 1.57 1.51 1.48 1.45 1.42 1.39 1.36 1.34 1.32 1.30 1.28 1.25 0.88
2.32 3.99 0.23 1.00 1.53 0.23 1.06 1.55 0.90 1.32 0.91 1.64 8.59 7.92 4.18
f1 (ppm)
HO
O
O
O
O
N
S
2
4
5
6
7
8
9
10
11
12
13
14
1'
2'
3'
4'
1''
2''
3''
4''


56
CDCl3, 101MHz
194.96
187.60
176.43
165.94
164.69
138.48
128.57
128.48
127.20
99.14
82.49
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.60
63.79
62.32
41.35
35.23
31.09
31.00
29.83
28.94
28.69
25.64
25.61
25.49
25.31
23.48
23.45
14.15
HO
O
O
O
O
N
S
f1 (ppm)



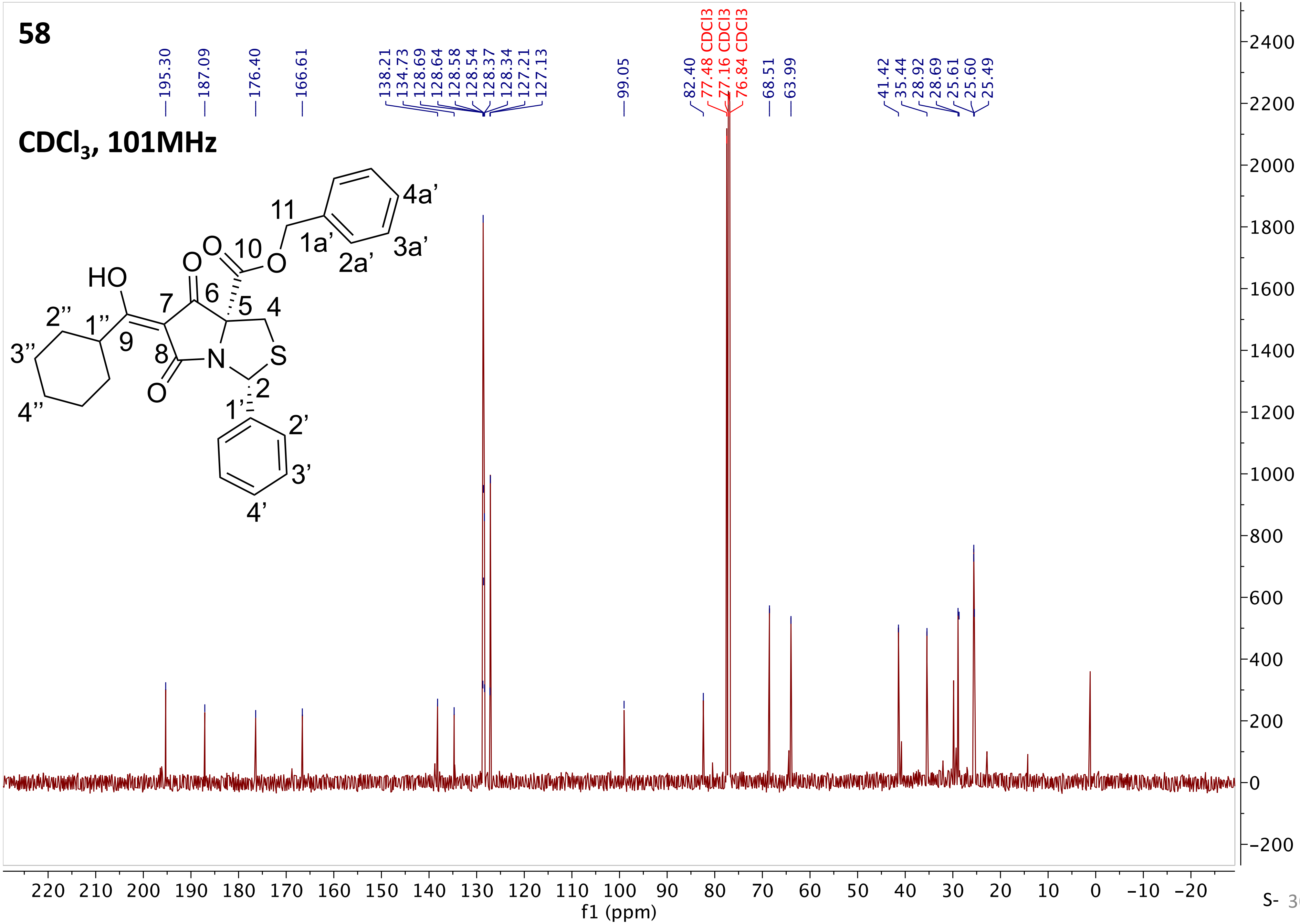
57
$CDCl_3$, 400MHz
8.56 8.56 8.41 8.41 7.81 7.81 7.80 7.79 7.79 7.52 7.51 7.50 7.49 7.33 7.33 7.32 7.31 7.31 7.26 CDCl3 7.22 7.20 7.20 7.19 7.17 6.38 6.35 5.75 5.22 5.19 5.13 5.10 3.96 3.93 3.41 3.38 3.37 3.36 3.34 3.16 3.13 1.84 1.77 1.73 1.69 1.53 1.51 1.48 1.43 1.39 1.38 1.36
1.01 0.94 1.86 2.39 10.18 4.68 0.28 0.99 0.96 1.52 1.76 1.98 2.46 2.24 29.80 10.80 9.86
HO
O
O
O
O
N
S
N
Br
1''
2''
3''
4''
1a'
2a'
3a'
4a'
2'
3'
4'
5'
6'
2
4
5
6
7
8
9
10
11
f1 (ppm)

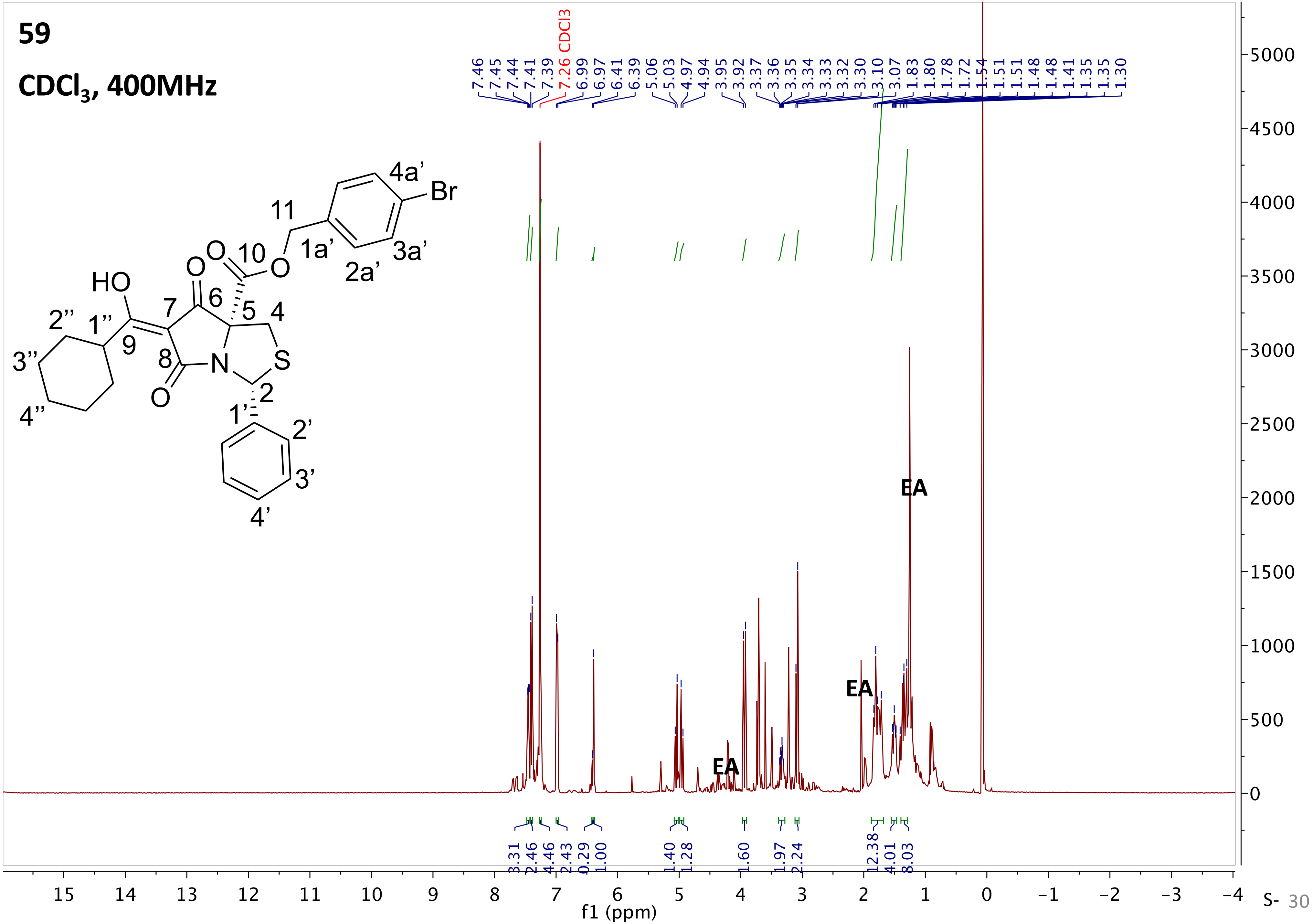

57
CDCl3, 126MHz
195.66
194.34
186.98
185.98
176.77
172.87
166.80
166.48
156.52
156.40
151.33
150.38
139.50
139.42
134.74
128.71
128.59
127.13
122.91
121.56
120.23
120.02
102.03
98.86
85.14
83.25
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.59
64.30
63.33
63.01
41.45
41.29
35.78
29.84
28.88
28.86
28.78
28.73
25.65
25.59
25.58
25.55
25.49
25.45
f1 (ppm)


58
CDCl3, 400MHz
7.47 7.47 7.46 7.46 7.45 7.32 7.31 7.30 7.29 7.29 7.28 7.26 CDCl3 7.26 7.25 7.24 7.24 7.23 7.16 7.15 7.14 7.13 6.42 6.38
5.16 5.13 5.09 5.06 5.01 4.98
3.97 3.94 3.37 3.37 3.36 3.35 3.34 3.33 3.32 3.31 3.30 3.12 3.10 3.09 3.08 1.82 1.80 1.73 1.72 1.53 1.50 1.47 1.41 1.38 1.35 1.26 0.88
2.55 3.70 3.03 2.39 0.22 1.00 1.19 0.36 1.11 1.38 1.24 1.41 8.87 4.39 6.27
f1 (ppm)

58

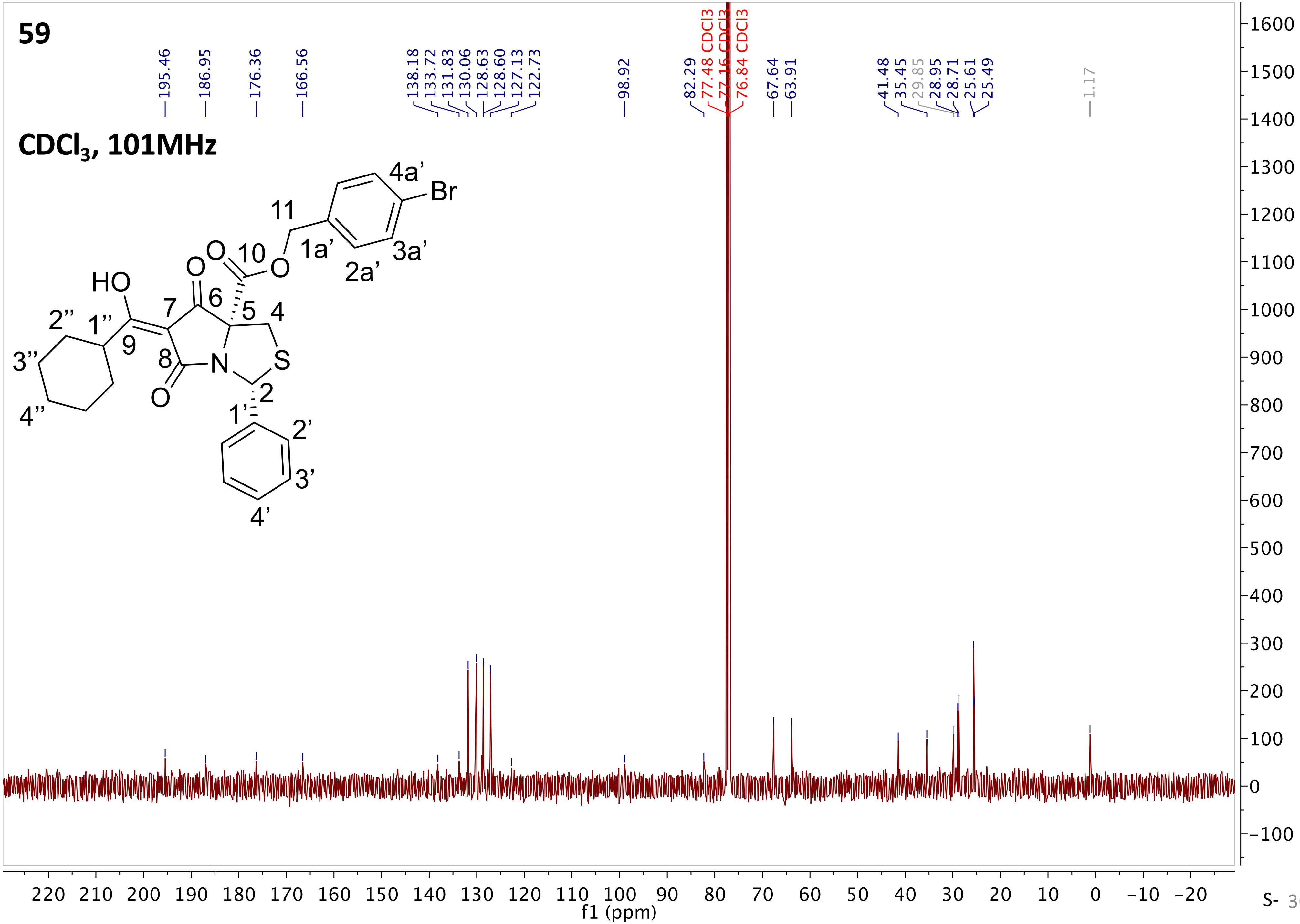
$CDCl_3$, 101MHz

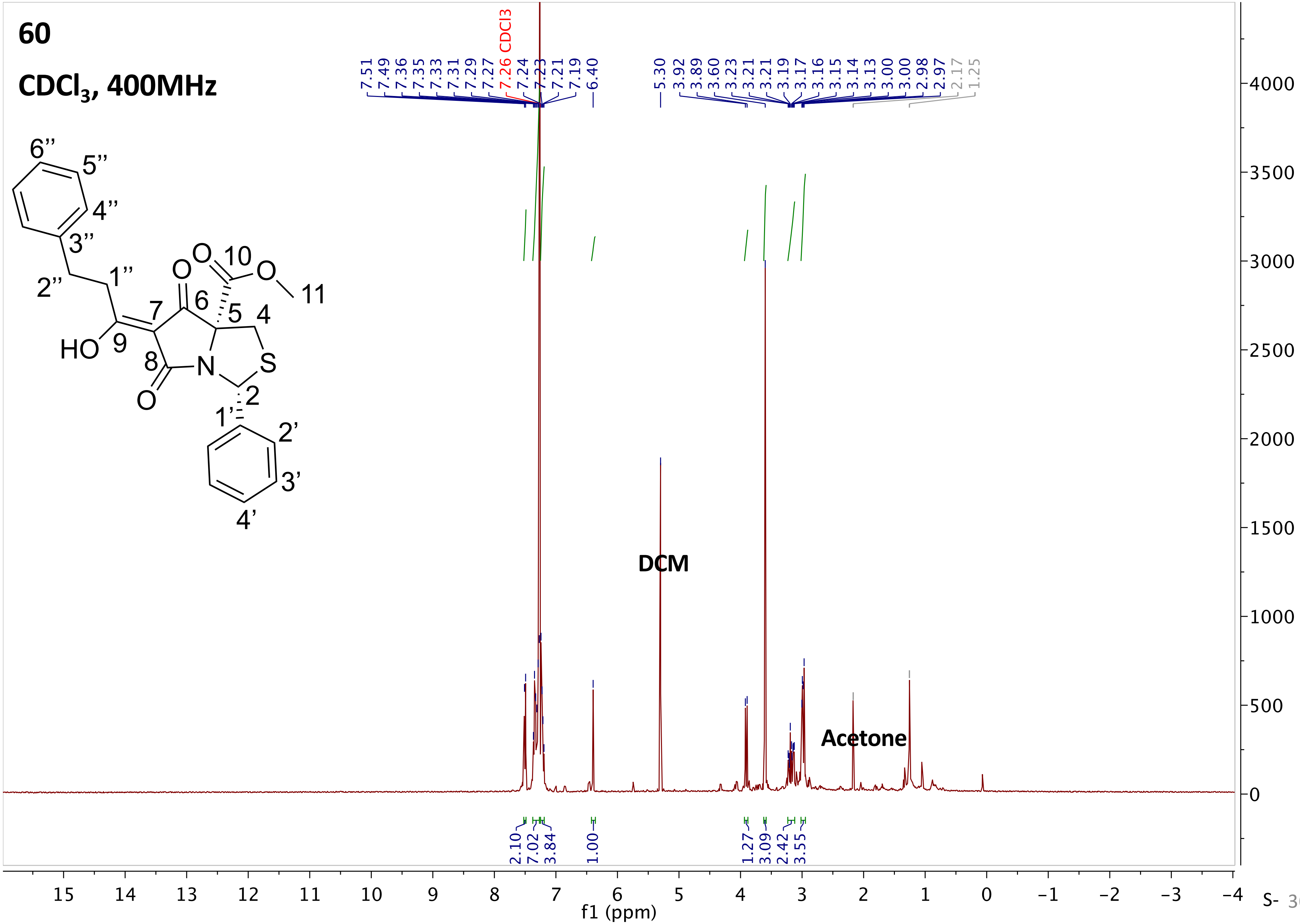


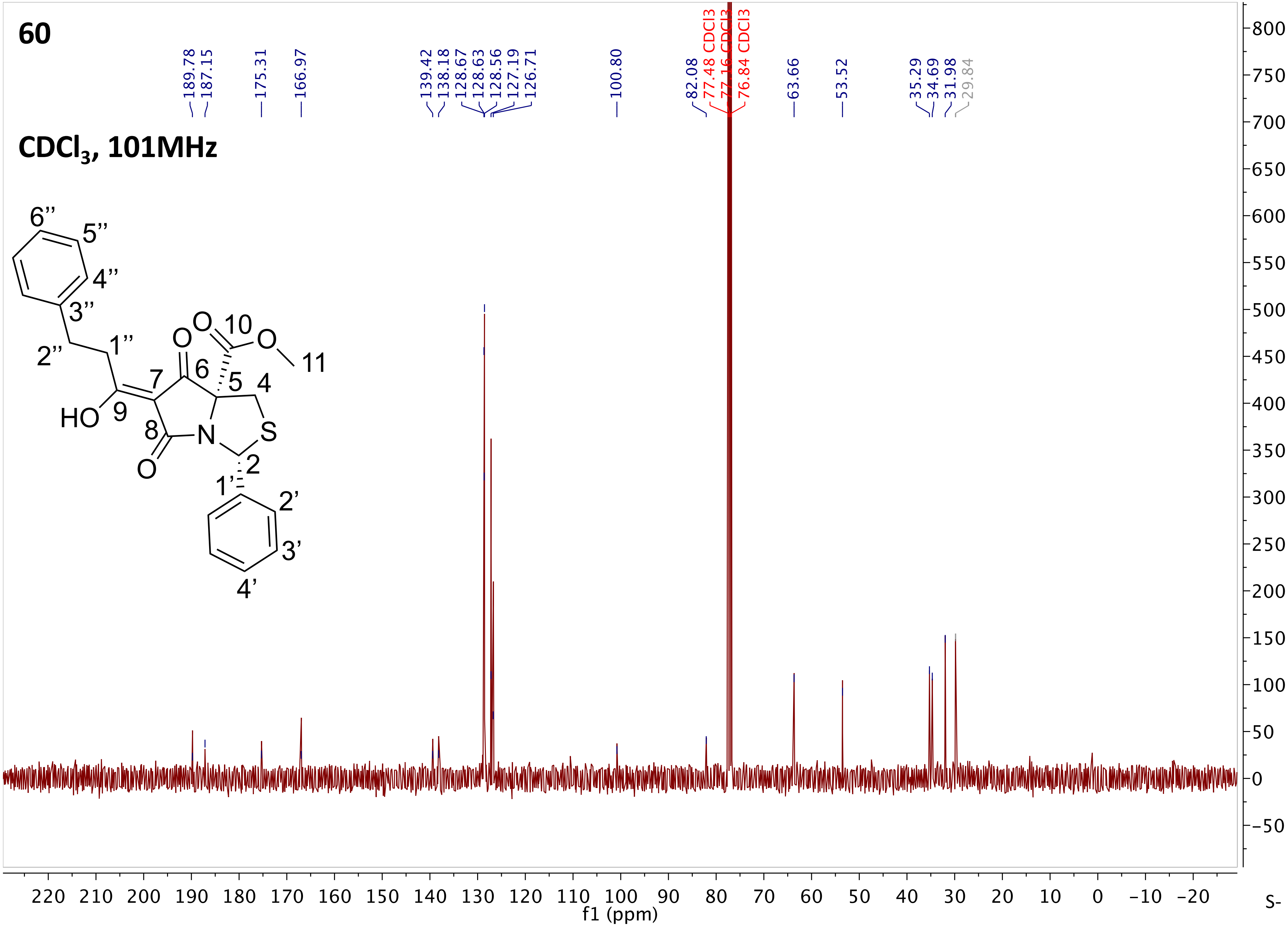

59
CDCl$_3$, 400MHz
7.46 7.45 7.44 7.41 7.39 7.26 CDCl3 6.99 6.97 6.41 6.39 5.06 5.03 4.97 4.94 3.95 3.92 3.37 3.36 3.35 3.34 3.33 3.32 3.30 3.10 3.07 1.83 1.80 1.78 1.72 1.54 1.51 1.51 1.48 1.48 1.41 1.35 1.35 1.30
HO
O
O
O
O
Br
N
S
EA
EA
EA
3.31 2.46 4.46 2.43 0.29 1.00 1.40 1.28 1.60 1.97 2.24 12.38 4.01 8.03
f1 (ppm)

59

$CDCl_3$, 101MHz



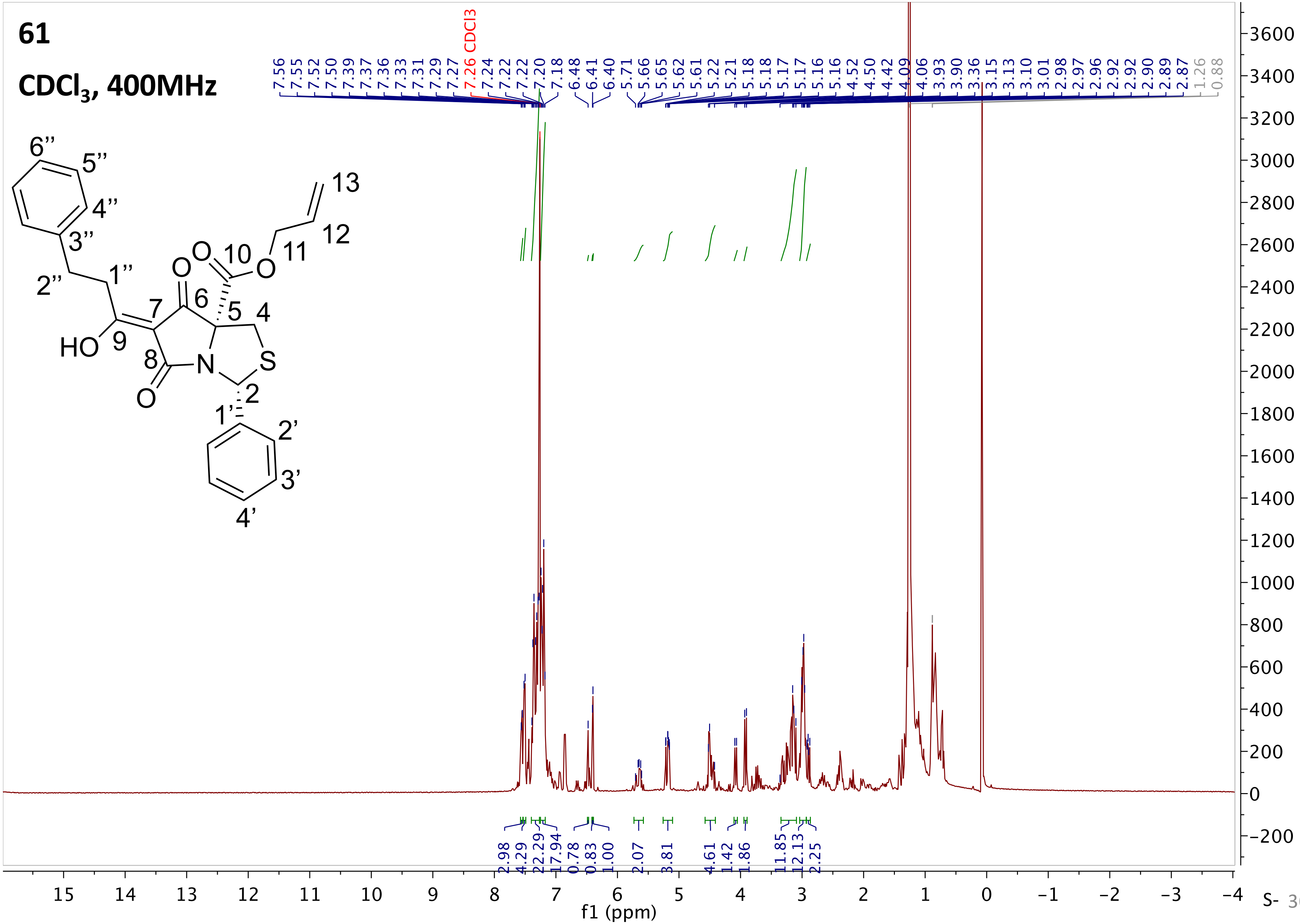

60
CDCl$_3$, 400MHz
7.51 7.49 7.36 7.35 7.33 7.31 7.29 7.27 7.26 CDCl3 7.24 7.23 7.21 7.19 6.40
5.30 3.92 3.89 3.60 3.23 3.21 3.21 3.19 3.17 3.16 3.15 3.14 3.13 3.00 3.00 2.98 2.97 2.17 1.25
DCM
Acetone
2.10 7.02 3.84 1.00 1.27 3.09 2.42 3.55
f1 (ppm)

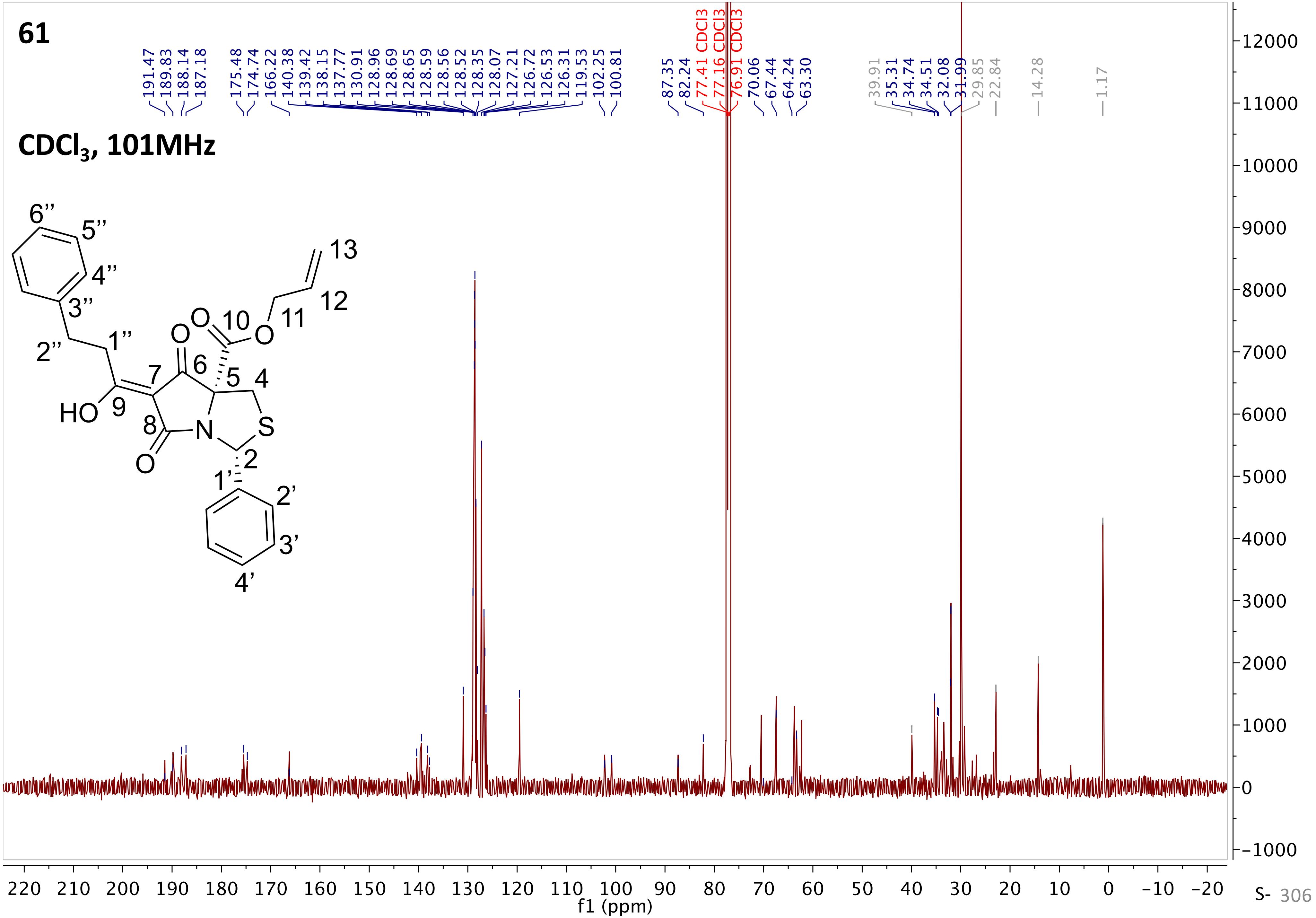


60
CDCl3, 101MHz
189.78
187.15
175.31
166.97
139.42
138.18
128.67
128.63
128.56
127.19
126.71
100.80
82.08
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.66
53.52
35.29
34.69
31.98
29.84
f1 (ppm)

61

$CDCl_3$, 400MHz

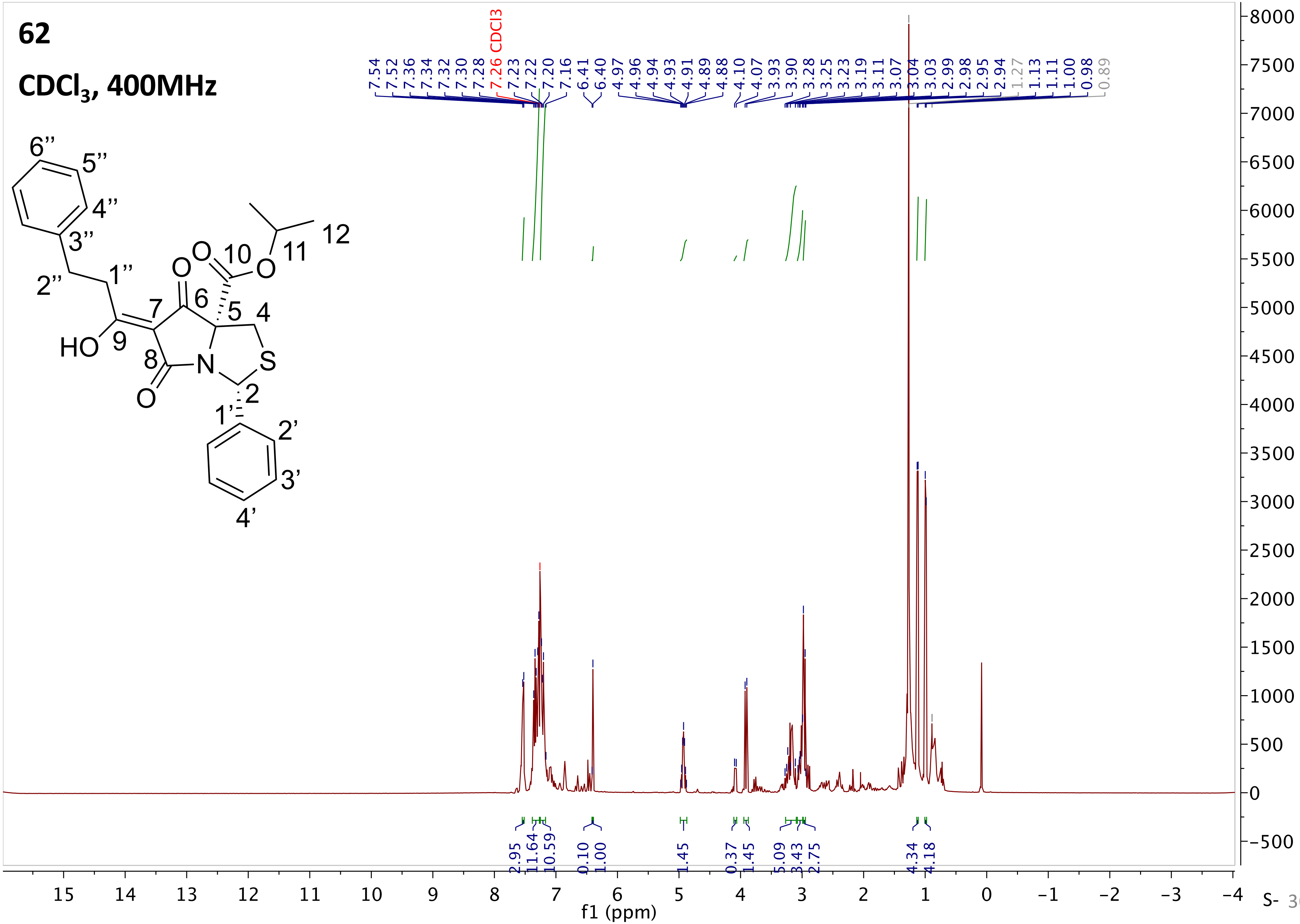




61
CDCl3, 101MHz
191.47
189.83
188.14
187.18
175.48
174.74
166.22
140.38
139.42
138.15
137.77
130.91
128.96
128.69
128.65
128.59
128.56
128.52
128.35
128.07
127.21
126.72
126.53
126.31
119.53
102.25
100.81
87.35
82.24
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
70.06
67.44
64.24
63.30
39.91
35.31
34.74
34.51
32.08
31.99
29.85
22.84
14.28
1.17
f1 (ppm)

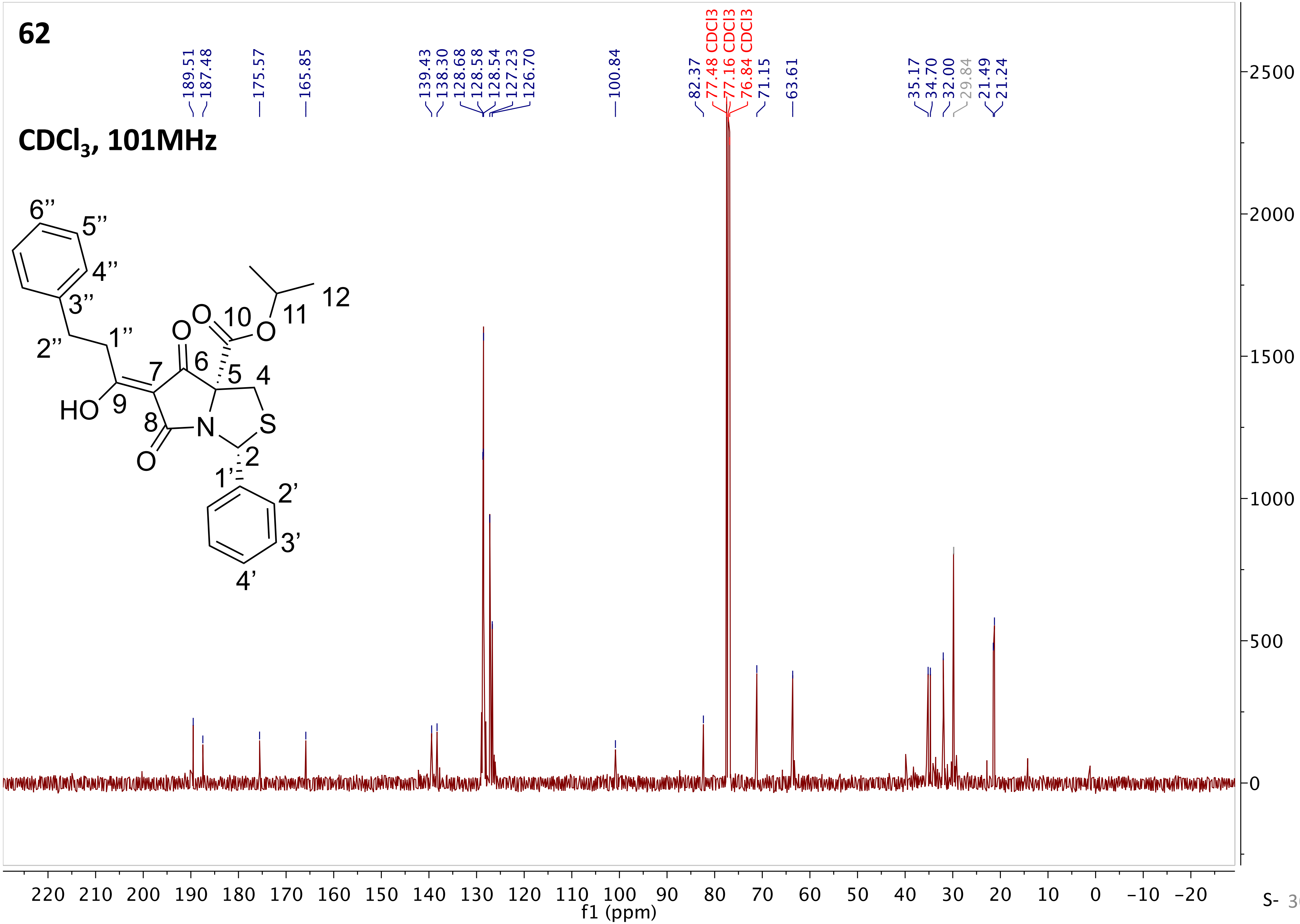
62

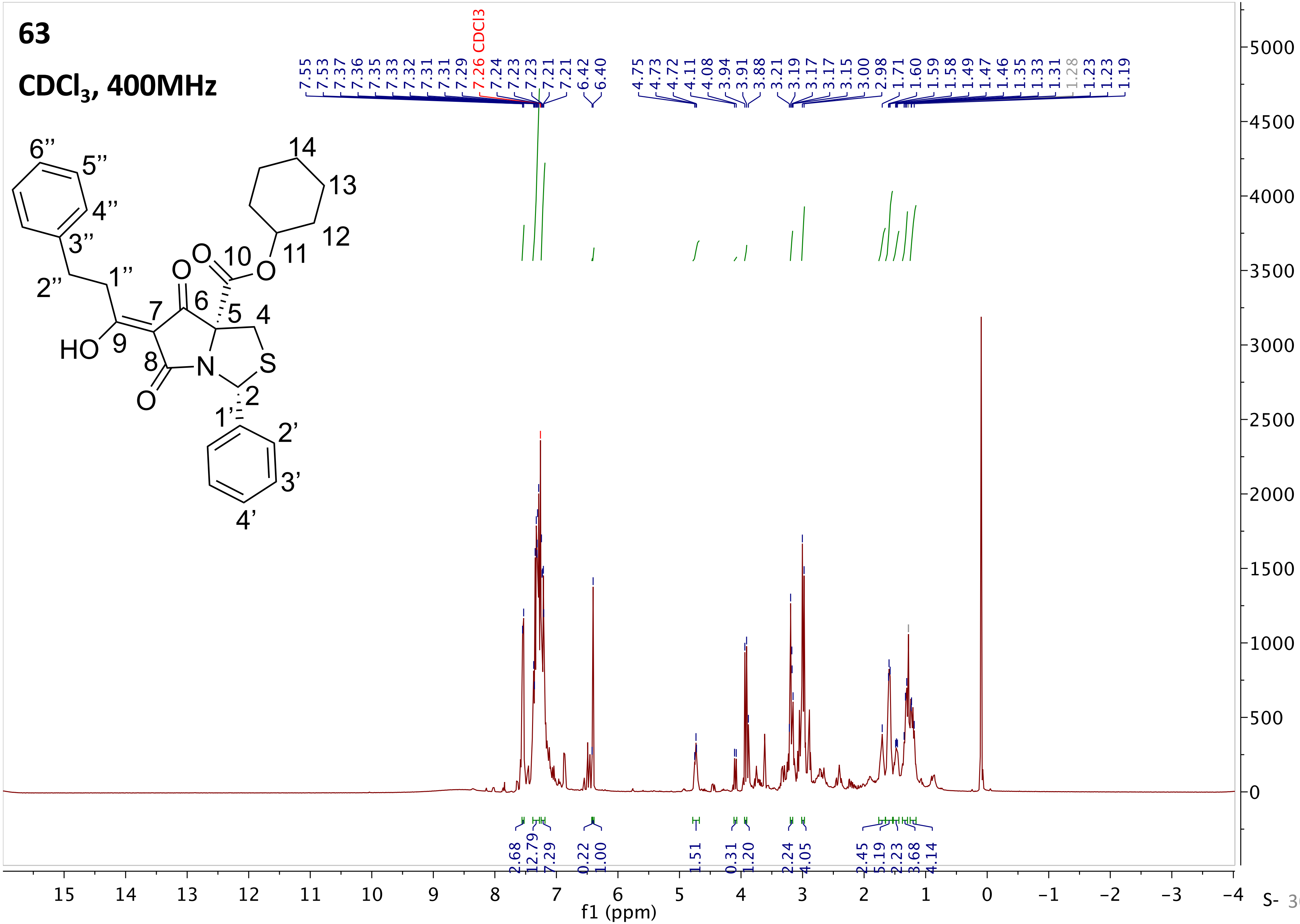
$CDCl_3$, 400MHz

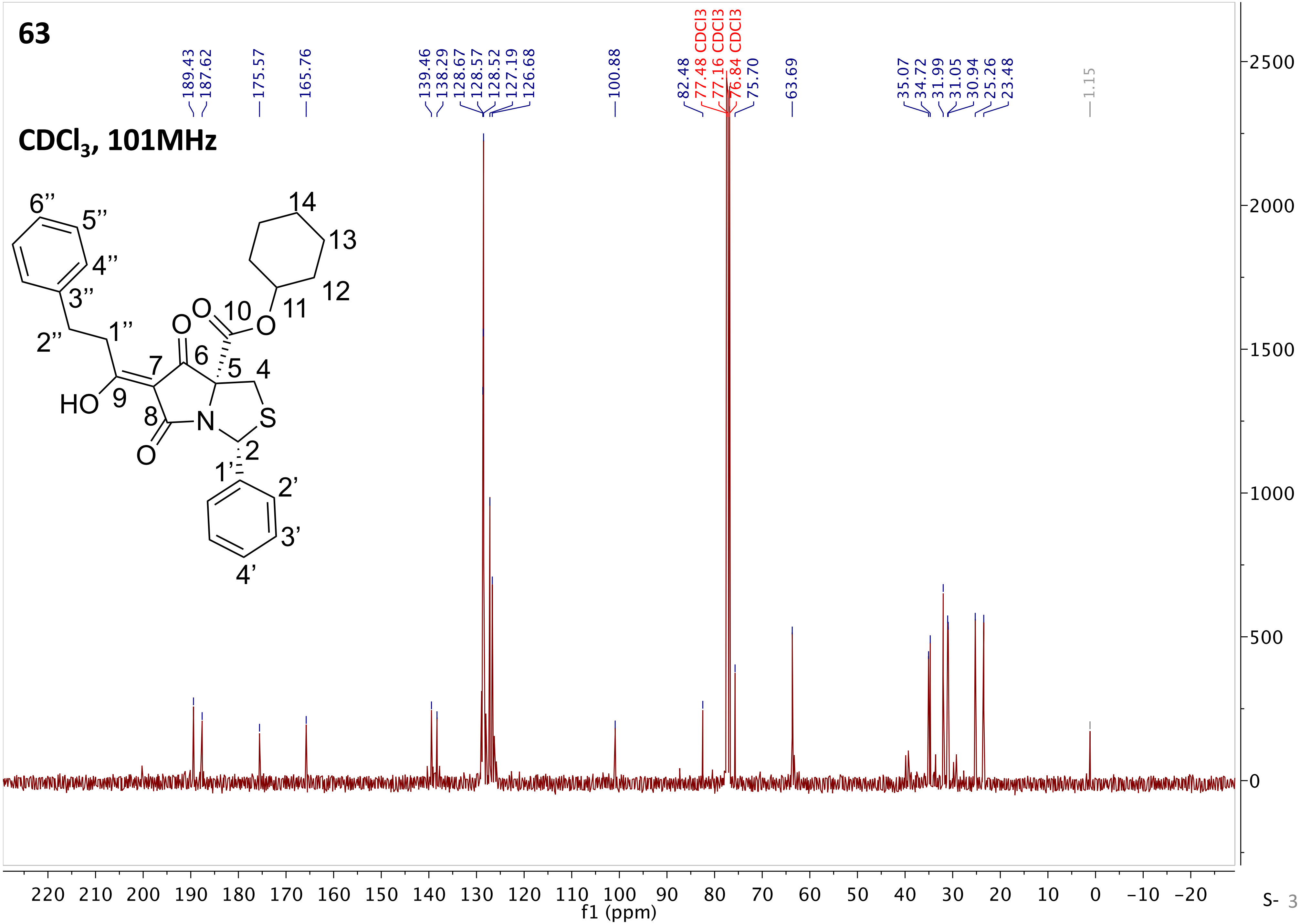


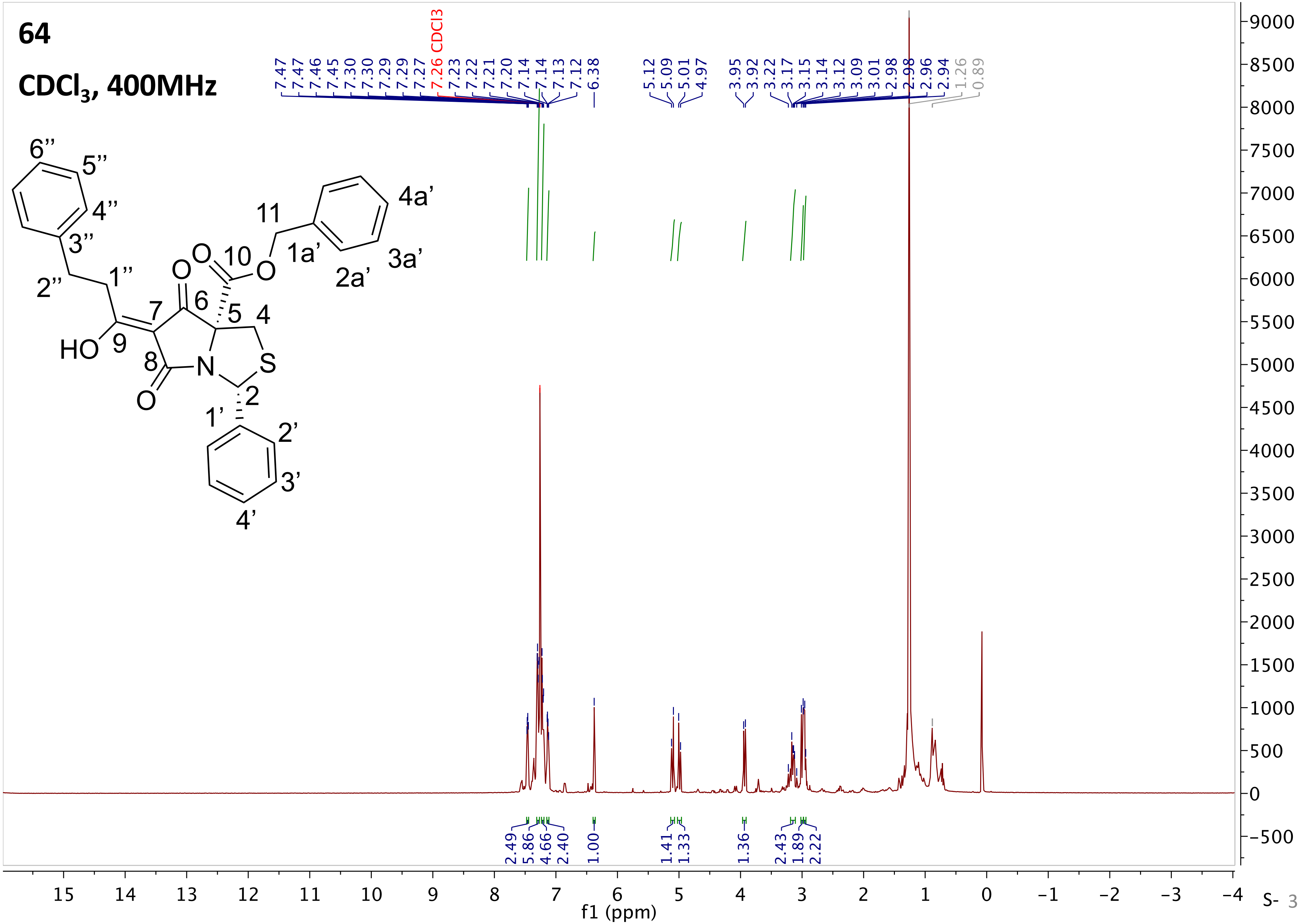
62

CDCl$_3$, 101MHz




63
CDCl3, 400MHz
f1 (ppm)

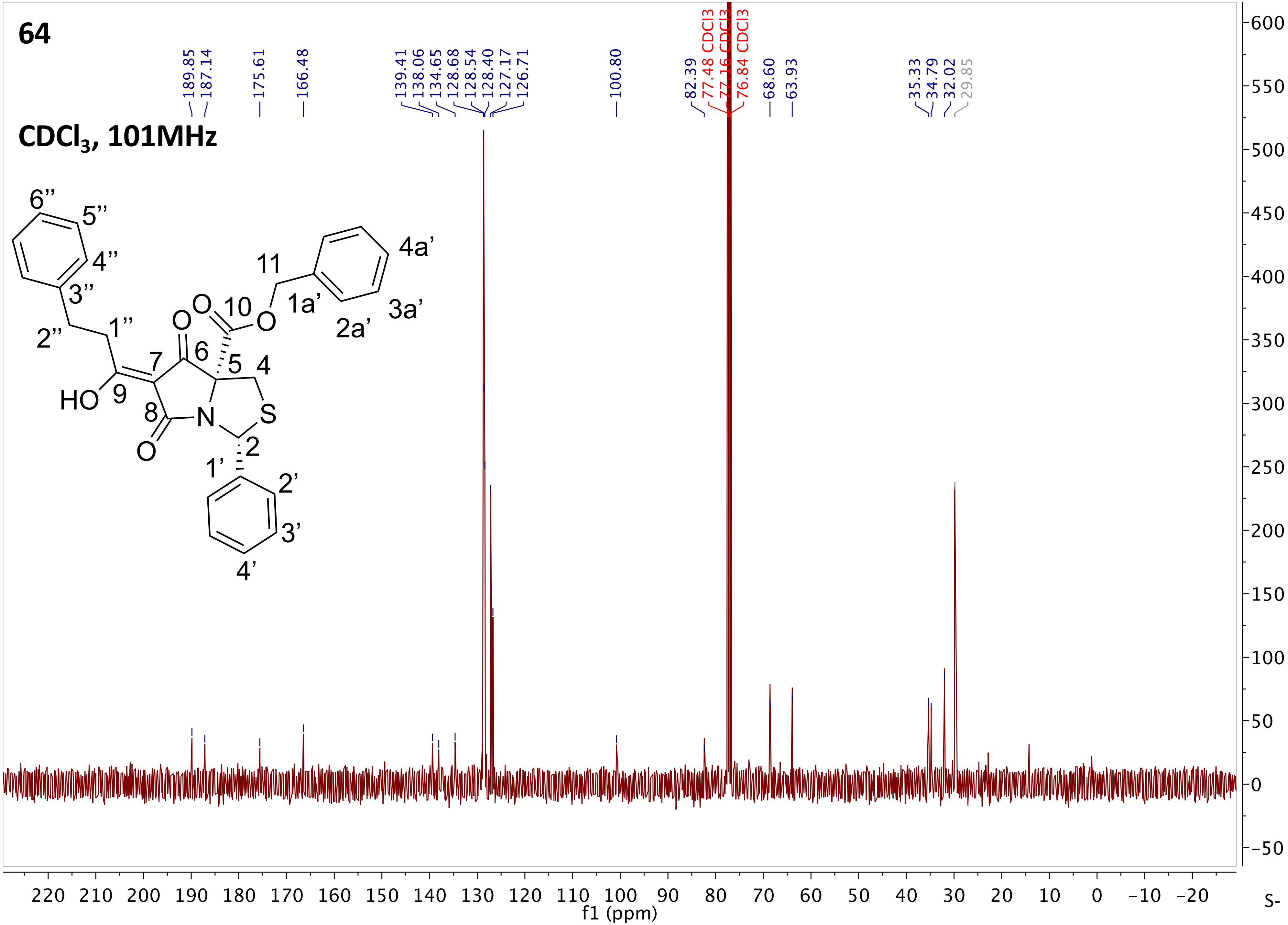

63
CDCl3, 101MHz
189.43
187.62
175.57
165.76
139.46
138.29
128.67
128.57
128.52
127.19
126.68
100.88
82.48
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.70
63.69
35.07
34.72
31.99
31.05
30.94
25.26
23.48
1.15
f1 (ppm)



64
CDCl3, 400MHz
7.47 7.47 7.46 7.45 7.30 7.30 7.29 7.29 7.27 7.26 CDCl3 7.23 7.22 7.21 7.20 7.14 7.14 7.13 7.12 6.38 5.12 5.09 5.01 4.97 3.95 3.92 3.22 3.17 3.15 3.14 3.12 3.09 3.01 2.98 2.98 2.96 2.94 1.26 0.89
2.49 5.86 4.66 2.40 1.00 1.41 1.33 1.36 2.43 1.89 2.22
f1 (ppm)

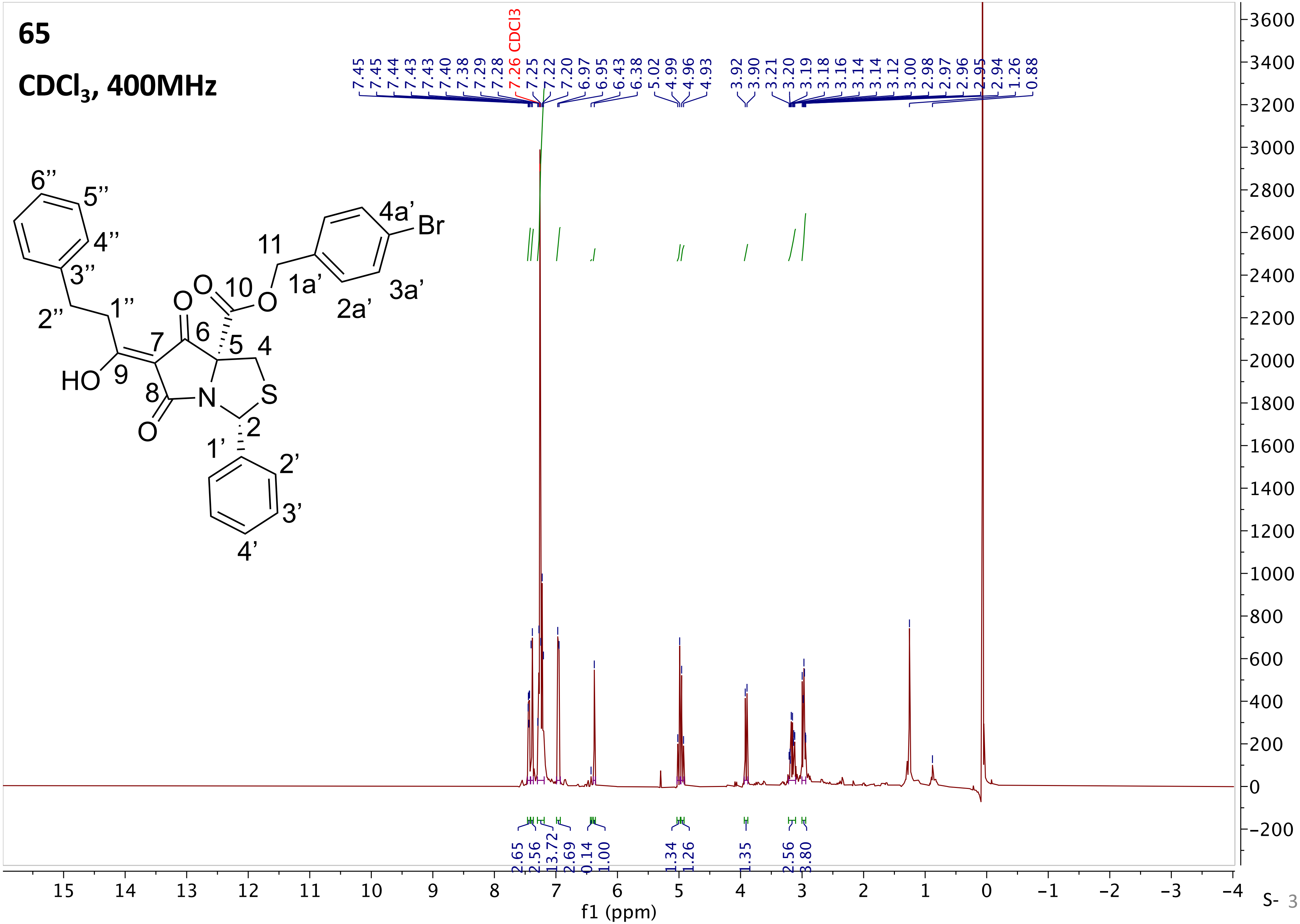
64

$CDCl_3$, 101MHz



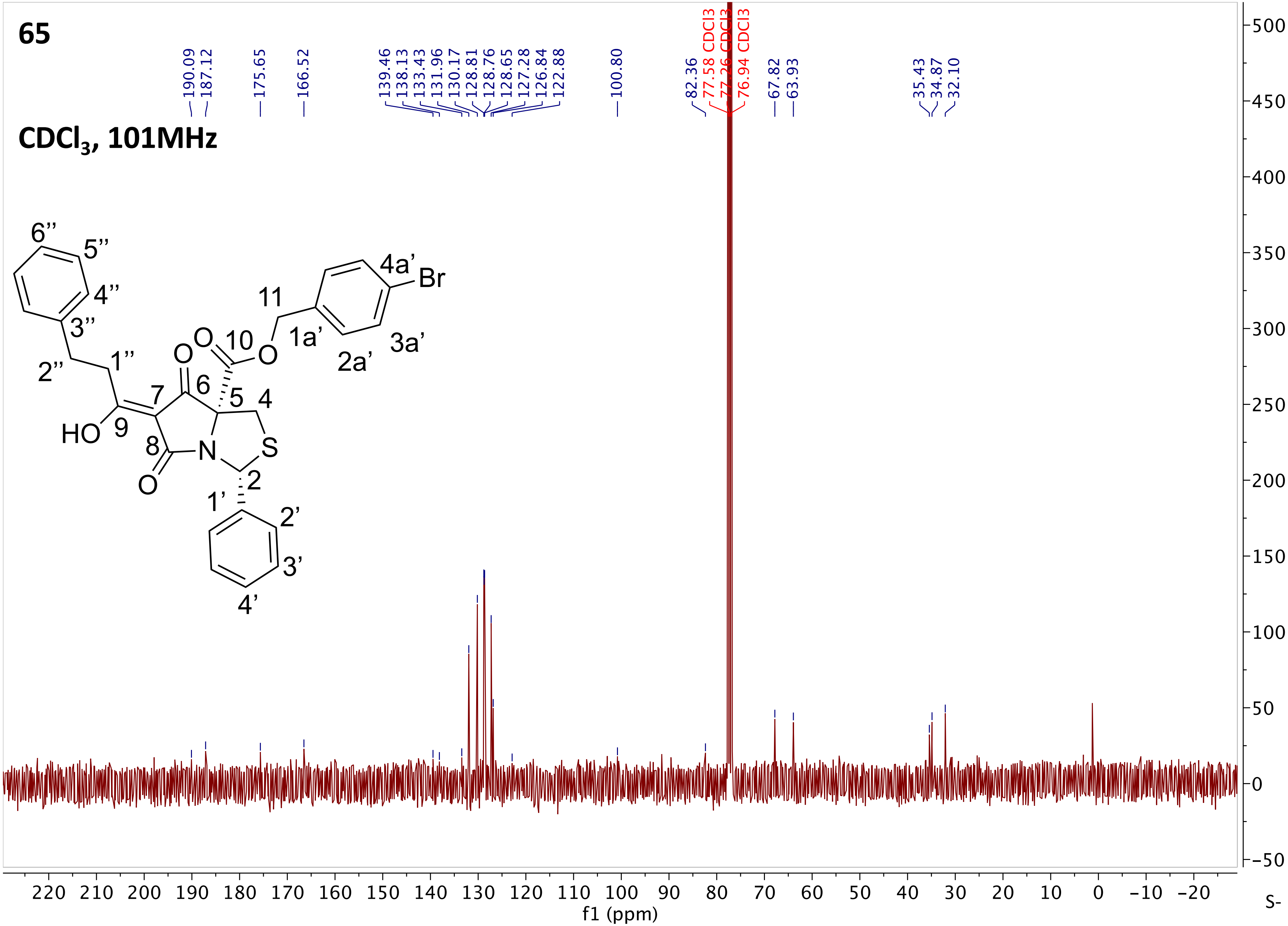
65

CDCl$_3$, 400MHz



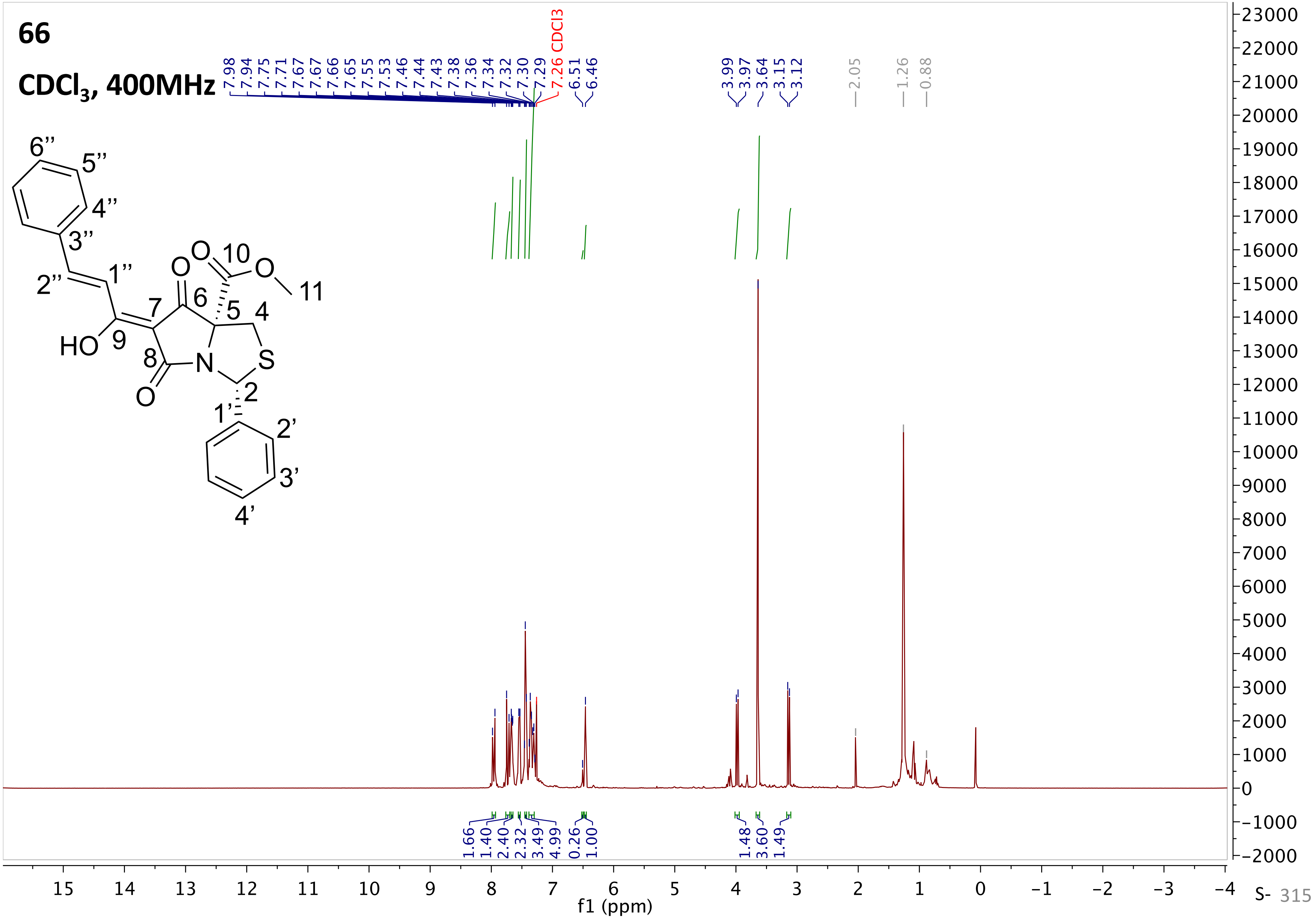
65

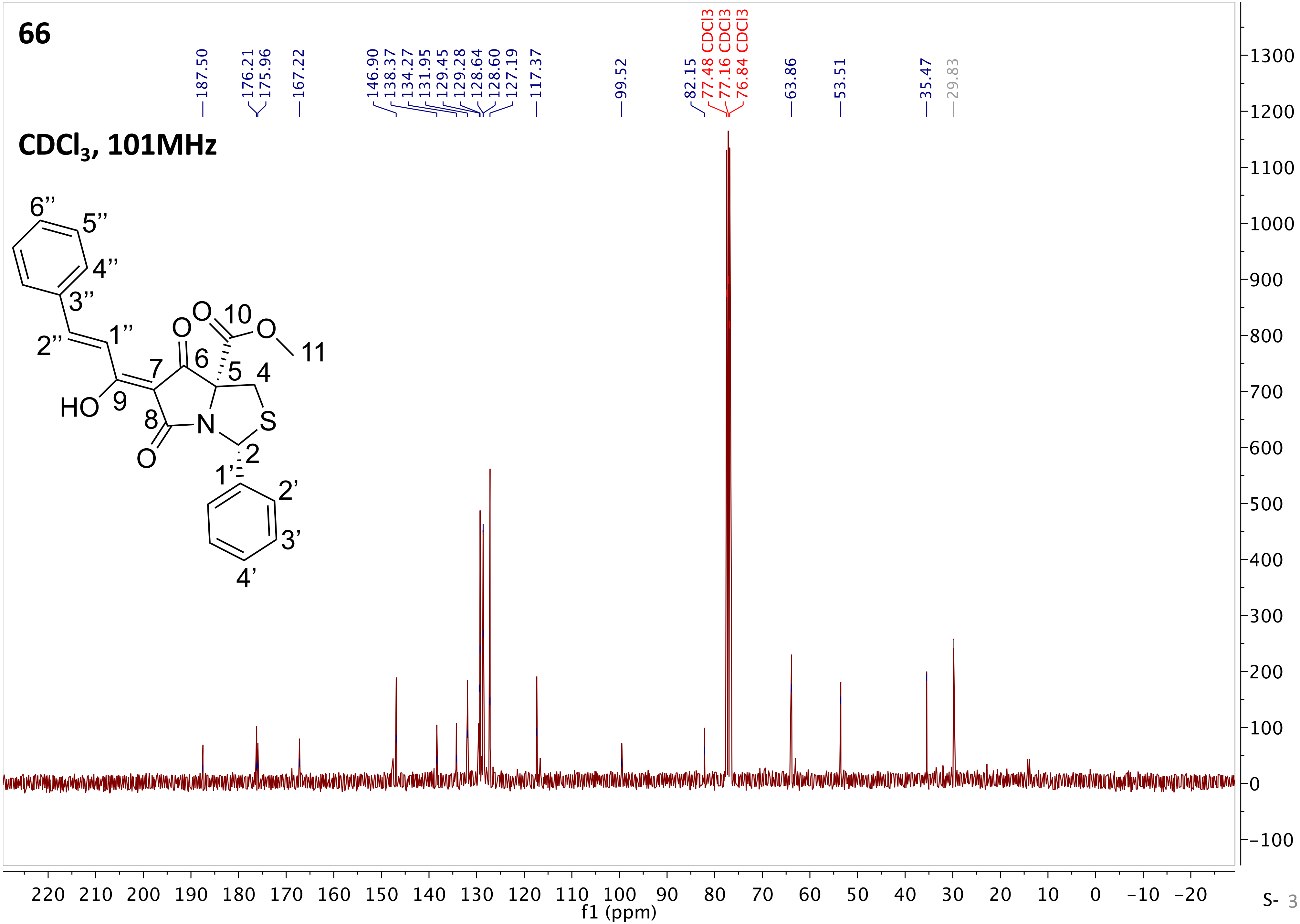
$CDCl_3$, 101MHz



66

$CDCl_3$, 400MHz

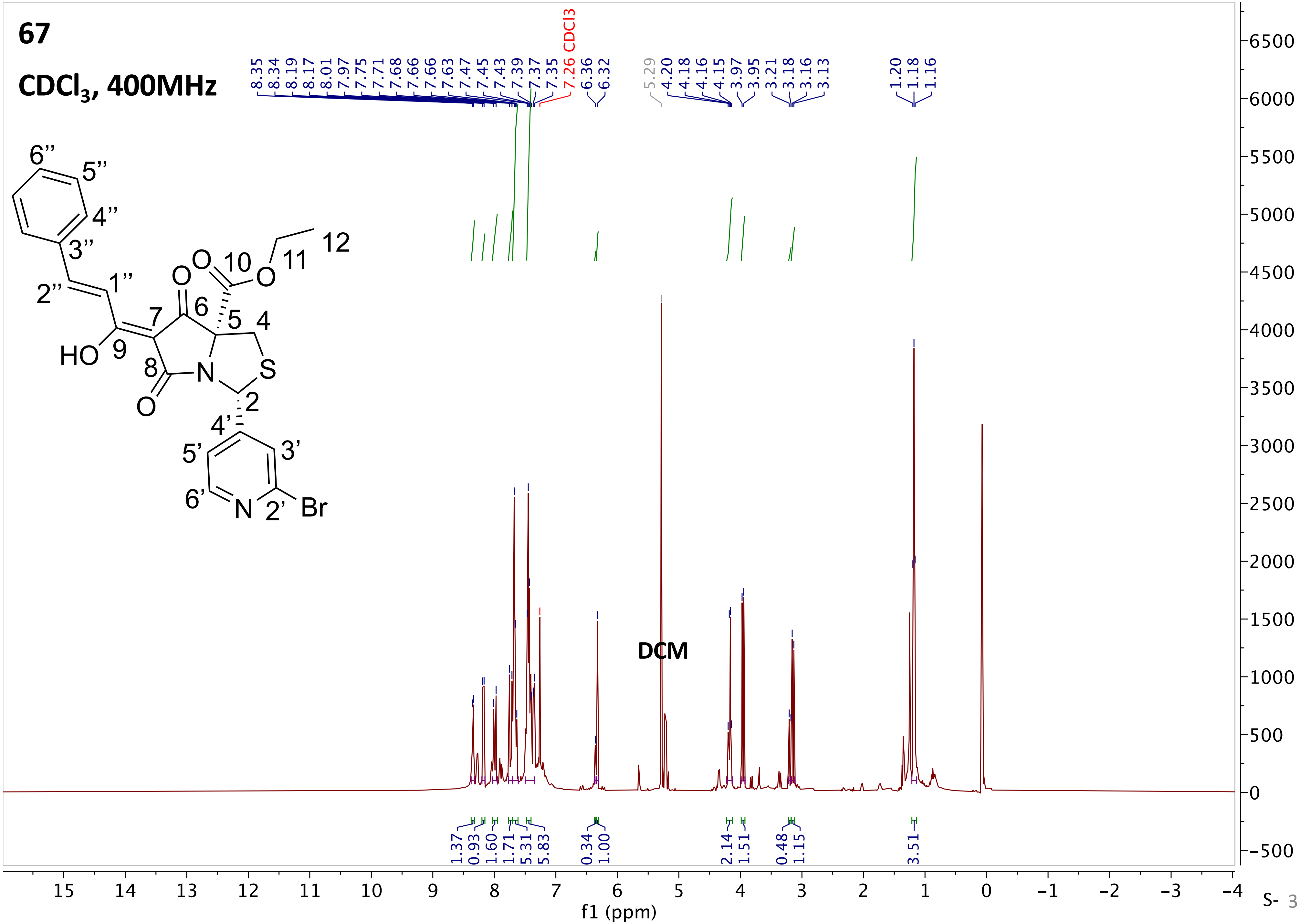


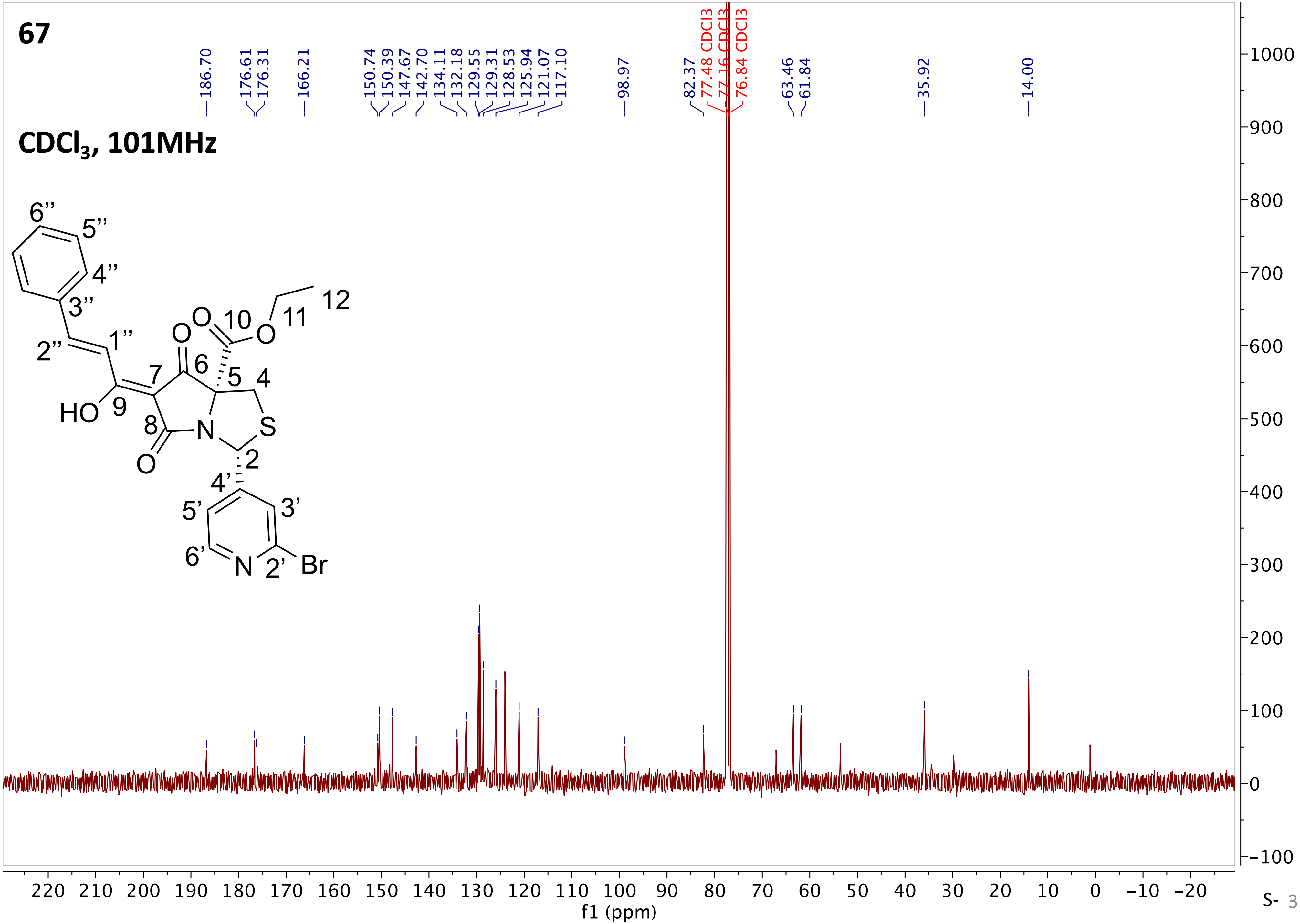


66
CDCl3, 101MHz
187.50
176.21
175.96
167.22
146.90
138.37
134.27
131.95
129.45
129.28
128.64
128.60
127.19
117.37
99.52
82.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.86
53.51
35.47
29.83
f1 (ppm)

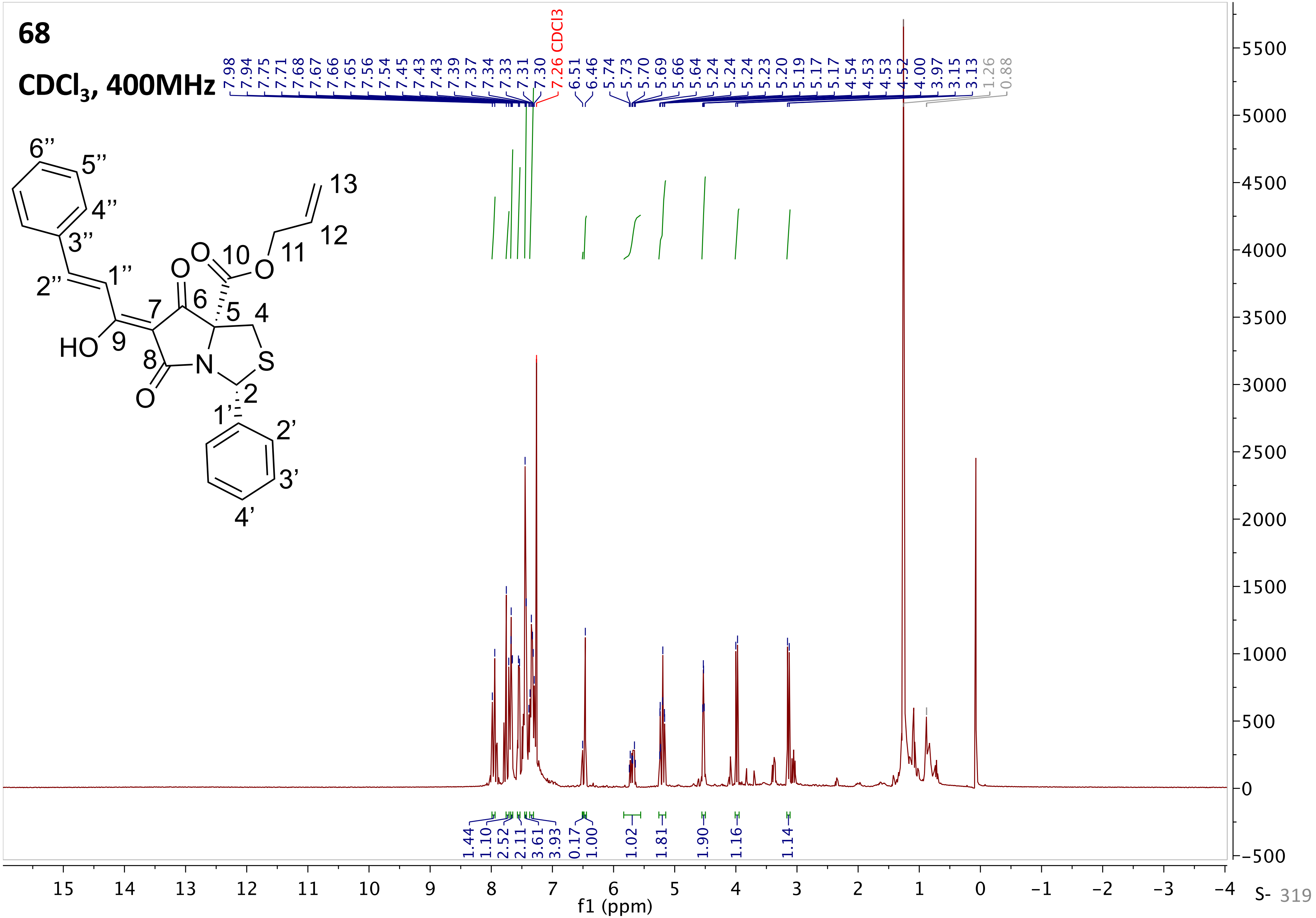
67

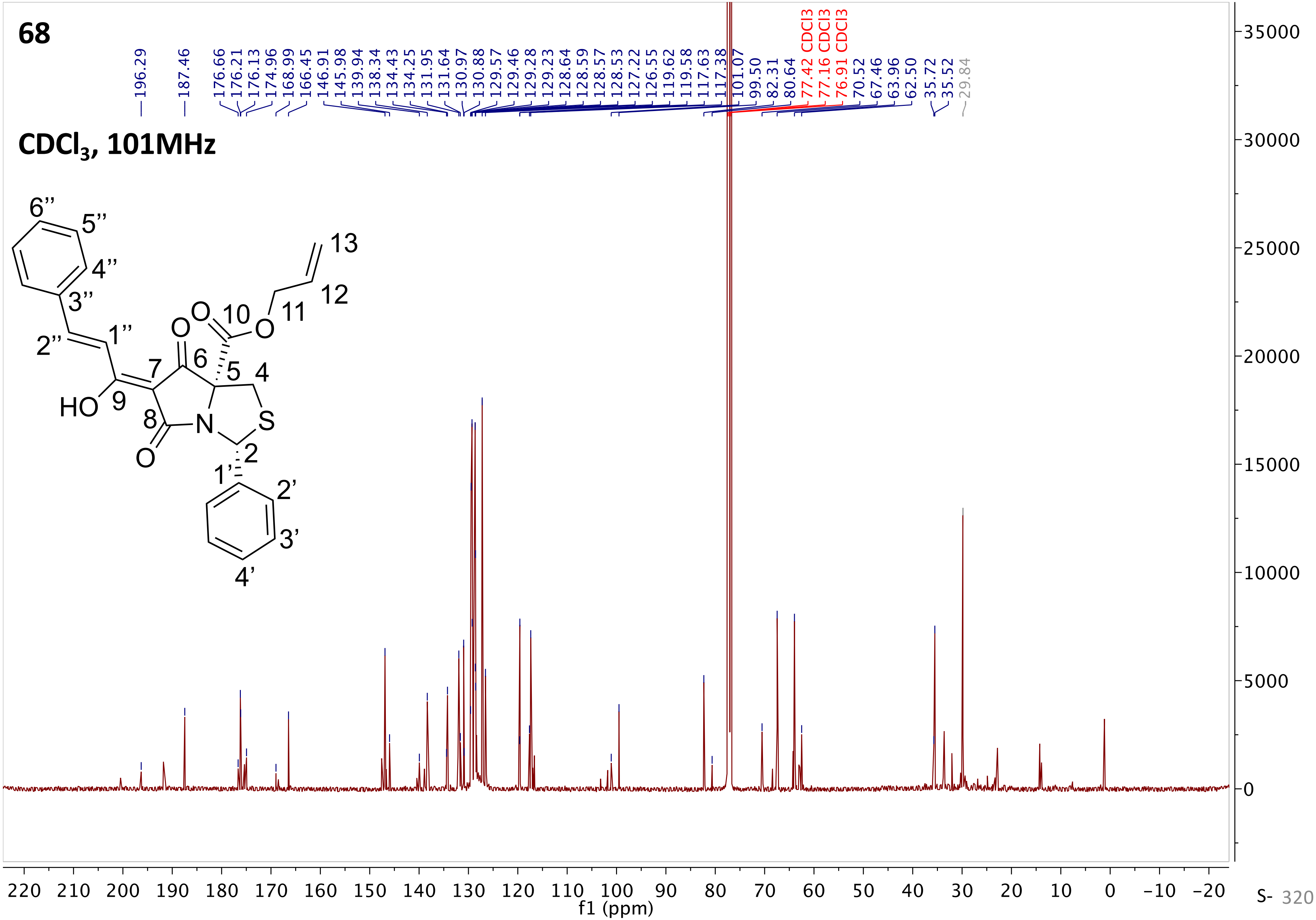
$CDCl_3$, 400MHz

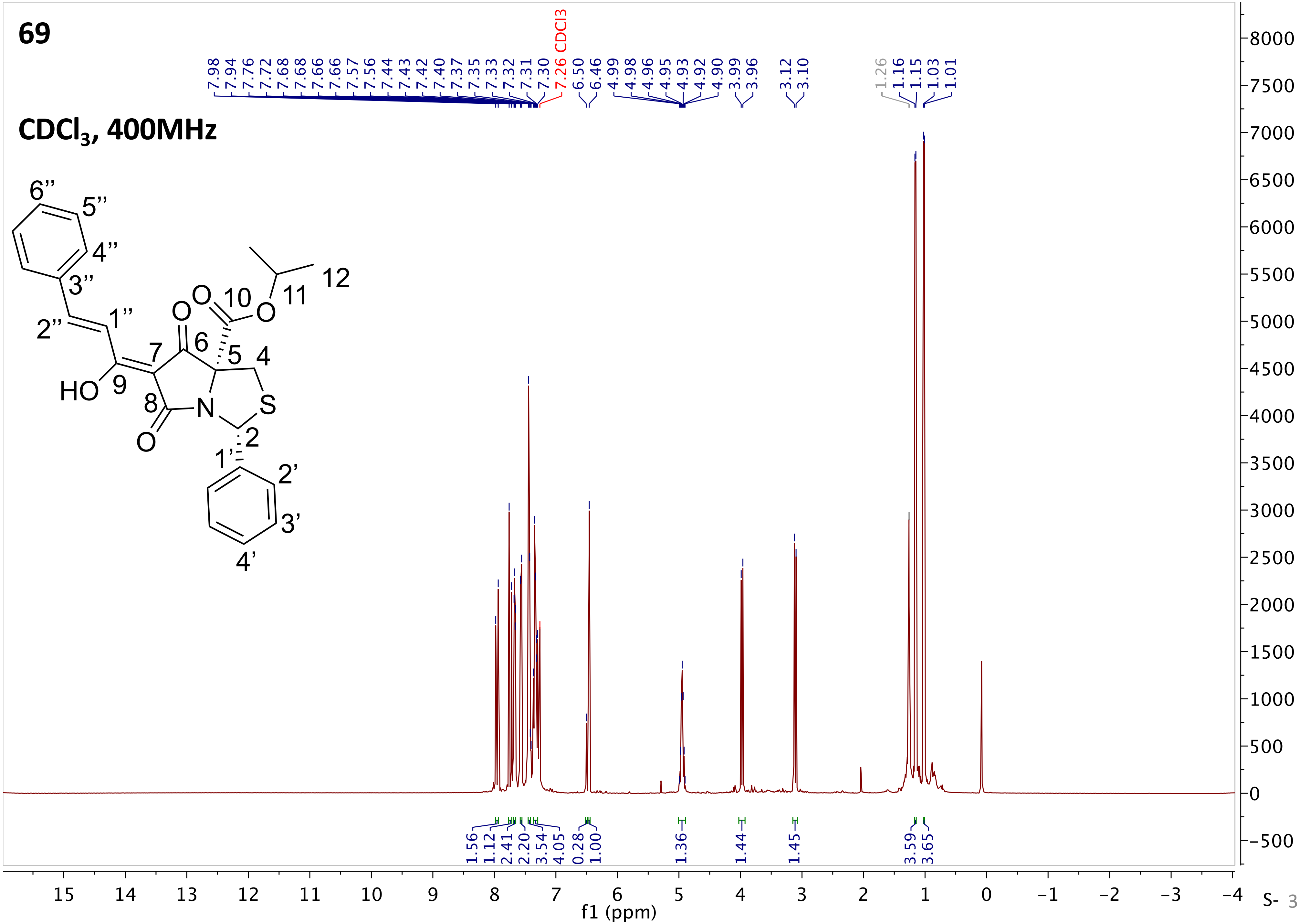




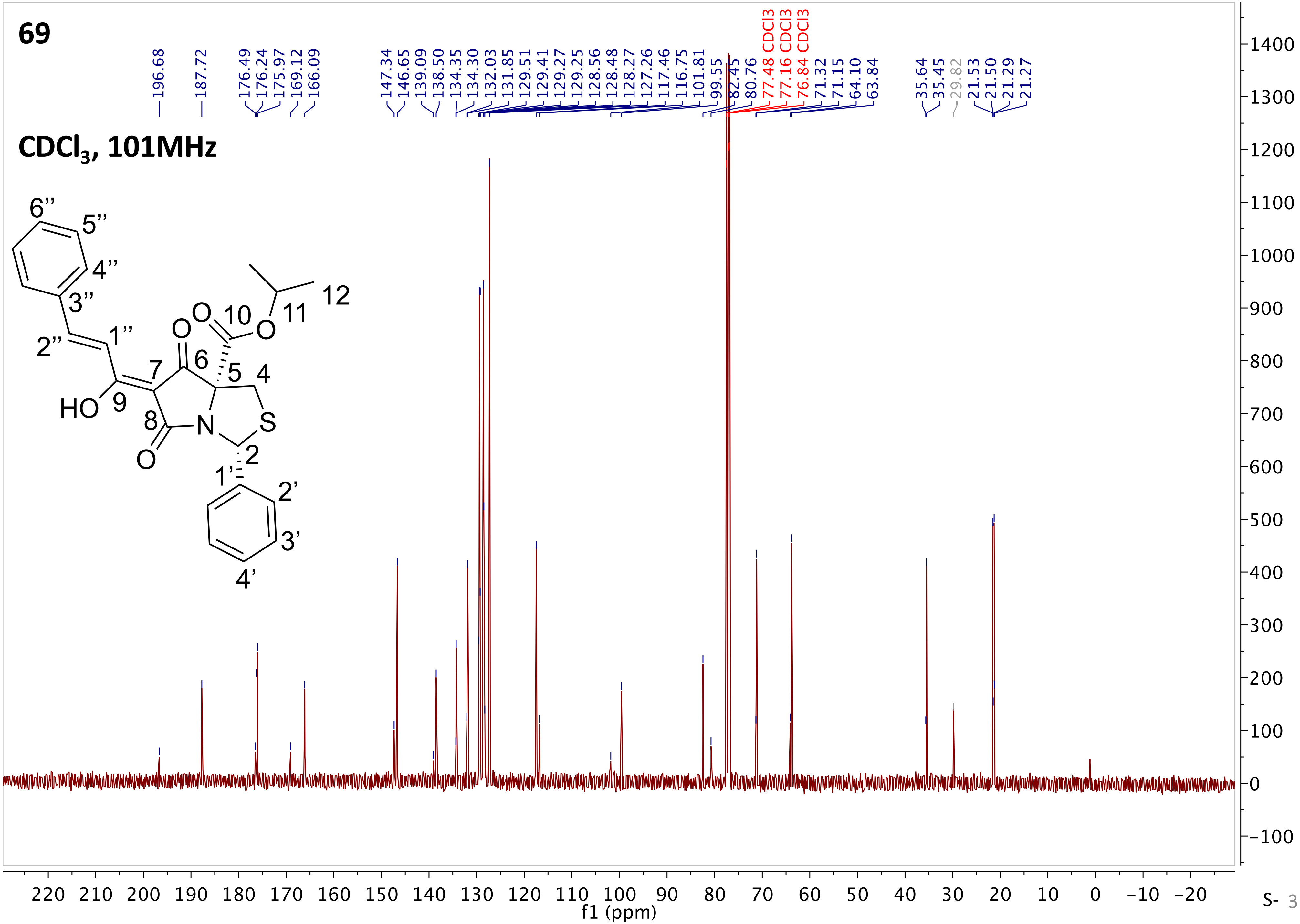
67
CDCl$_3$, 101MHz
186.70
176.61
176.31
166.21
150.74
150.39
147.67
142.70
134.11
132.18
129.55
129.31
128.53
125.94
121.07
117.10
98.97
82.37
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.46
61.84
35.92
14.00
f1 (ppm)


68
CDCl3, 400MHz
7.98 7.94 7.75 7.71 7.68 7.67 7.66 7.65 7.56 7.54 7.45 7.43 7.43 7.39 7.37 7.34 7.33 7.31 7.30 7.26 CDCl3 6.51 6.46 5.74 5.73 5.70 5.69 5.66 5.64 5.24 5.24 5.24 5.23 5.20 5.19 5.17 5.17 4.54 4.53 4.53 4.52 4.00 3.97 3.15 3.13 1.26 0.88
1.44 1.10 2.52 2.11 3.61 3.93 0.17 1.00 1.02 1.81 1.90 1.16 1.14
f1 (ppm)


68
CDCl3, 101MHz
196.29
187.46
176.66
176.21
176.13
174.96
168.99
166.45
146.91
145.98
139.94
138.34
134.43
134.25
131.95
131.64
130.97
130.88
129.57
129.46
129.28
129.23
128.64
128.59
128.57
128.53
127.22
126.55
119.62
119.58
117.63
117.38
101.07
99.50
82.31
80.64
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
70.52
67.46
63.96
62.50
35.72
35.52
29.84
f1 (ppm)

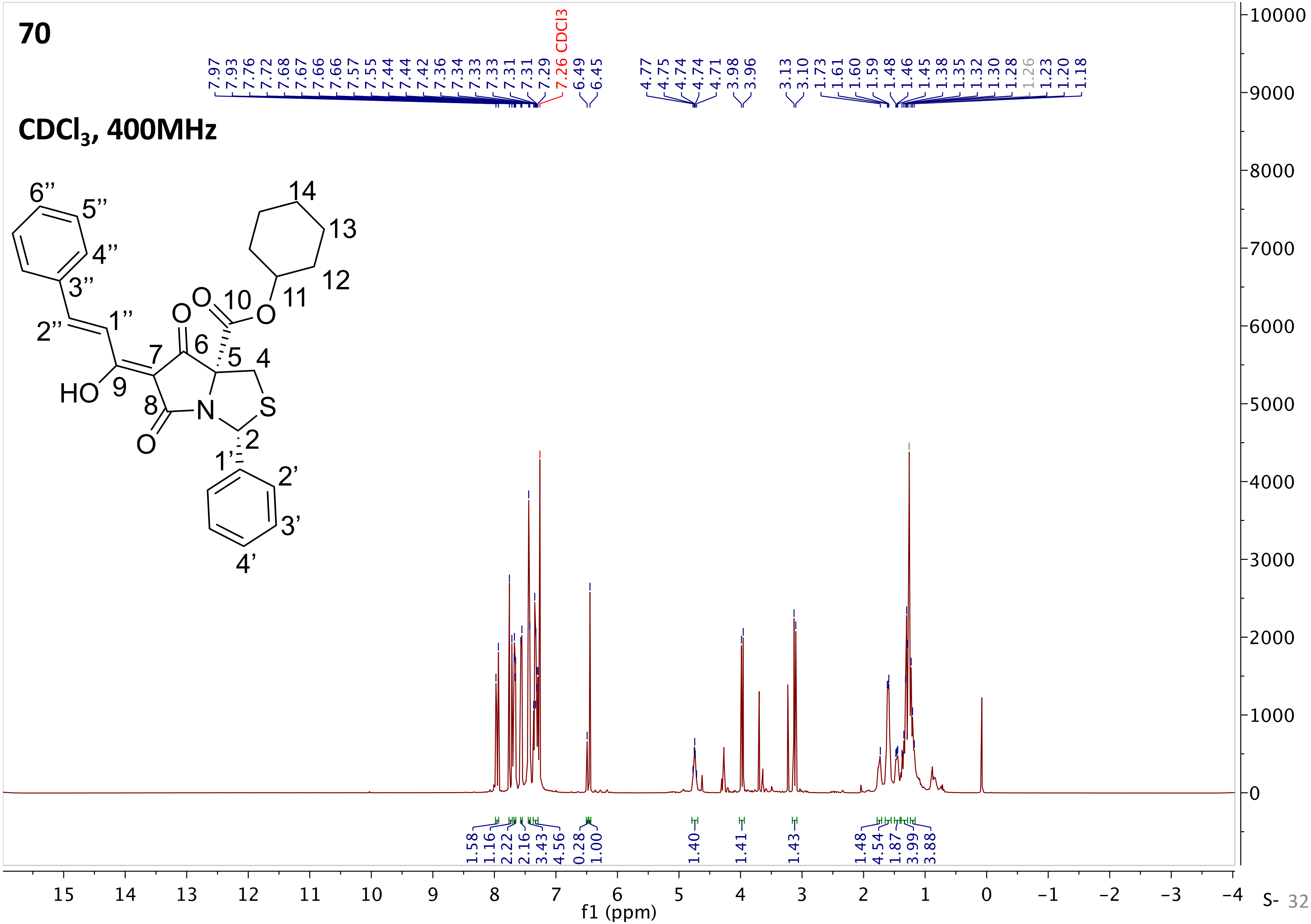


69
CDCl3, 400MHz
7.98 7.94 7.76 7.72 7.68 7.68 7.66 7.66 7.57 7.56 7.44 7.43 7.42 7.40 7.37 7.35 7.33 7.32 7.31 7.30 7.26 CDCl3 6.50 6.46 4.99 4.98 4.96 4.95 4.93 4.92 4.90 3.99 3.96 3.12 3.10 1.26 1.16 1.15 1.03 1.01
1.56 1.12 2.41 2.20 3.54 4.05 0.28 1.00 1.36 1.44 1.45 3.59 3.65
f1 (ppm)


69
CDCl$_3$, 101MHz
196.68
187.72
176.49
176.24
175.97
169.12
166.09
147.34
146.65
139.09
138.50
134.35
134.30
132.03
131.85
129.51
129.41
129.27
129.25
128.56
128.48
128.27
127.26
117.46
116.75
101.81
99.55
82.45
80.76
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.32
71.15
64.10
63.84
35.64
35.45
29.82
21.53
21.50
21.29
21.27
f1 (ppm)

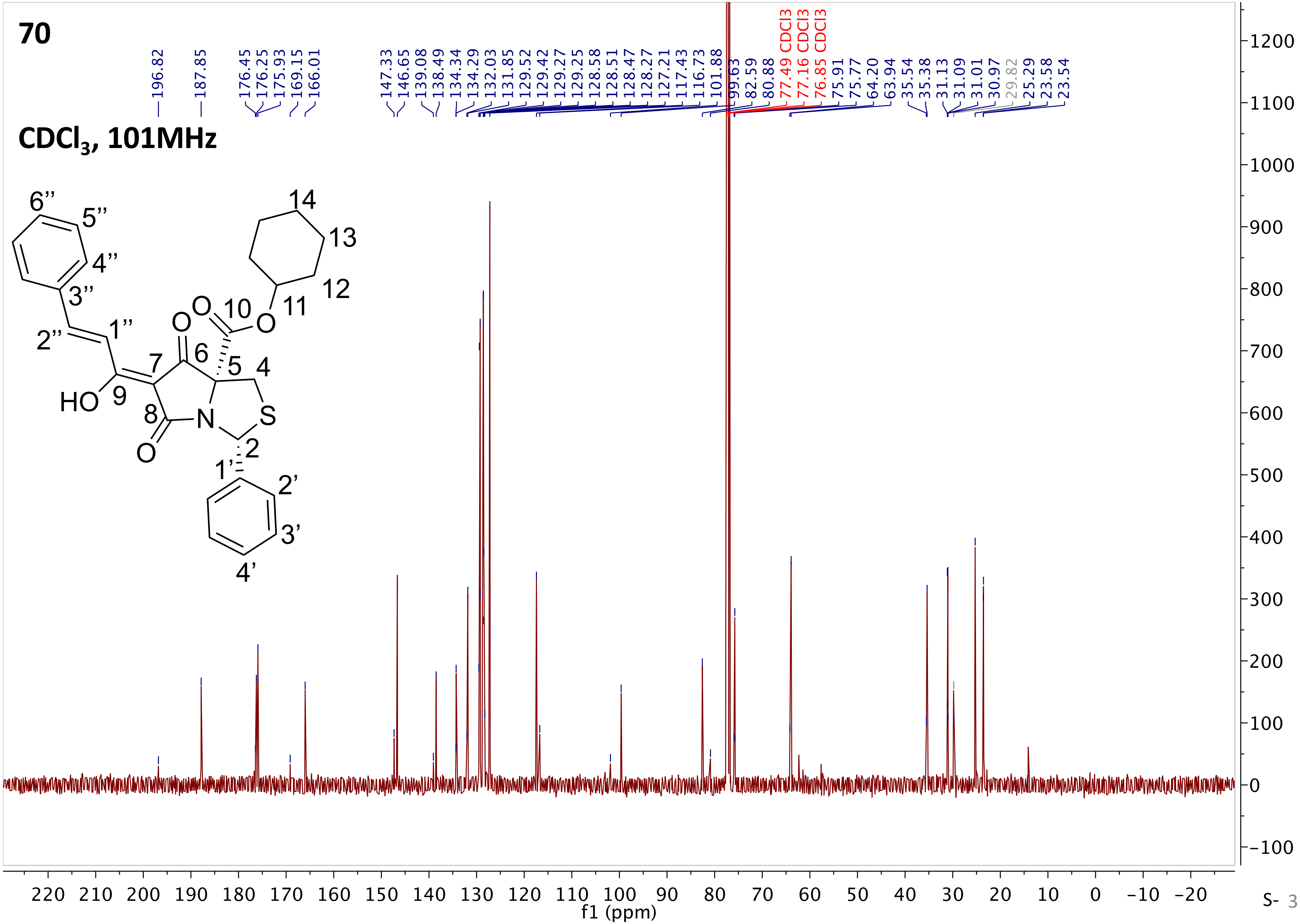
70

CDCl$_3$, 400MHz



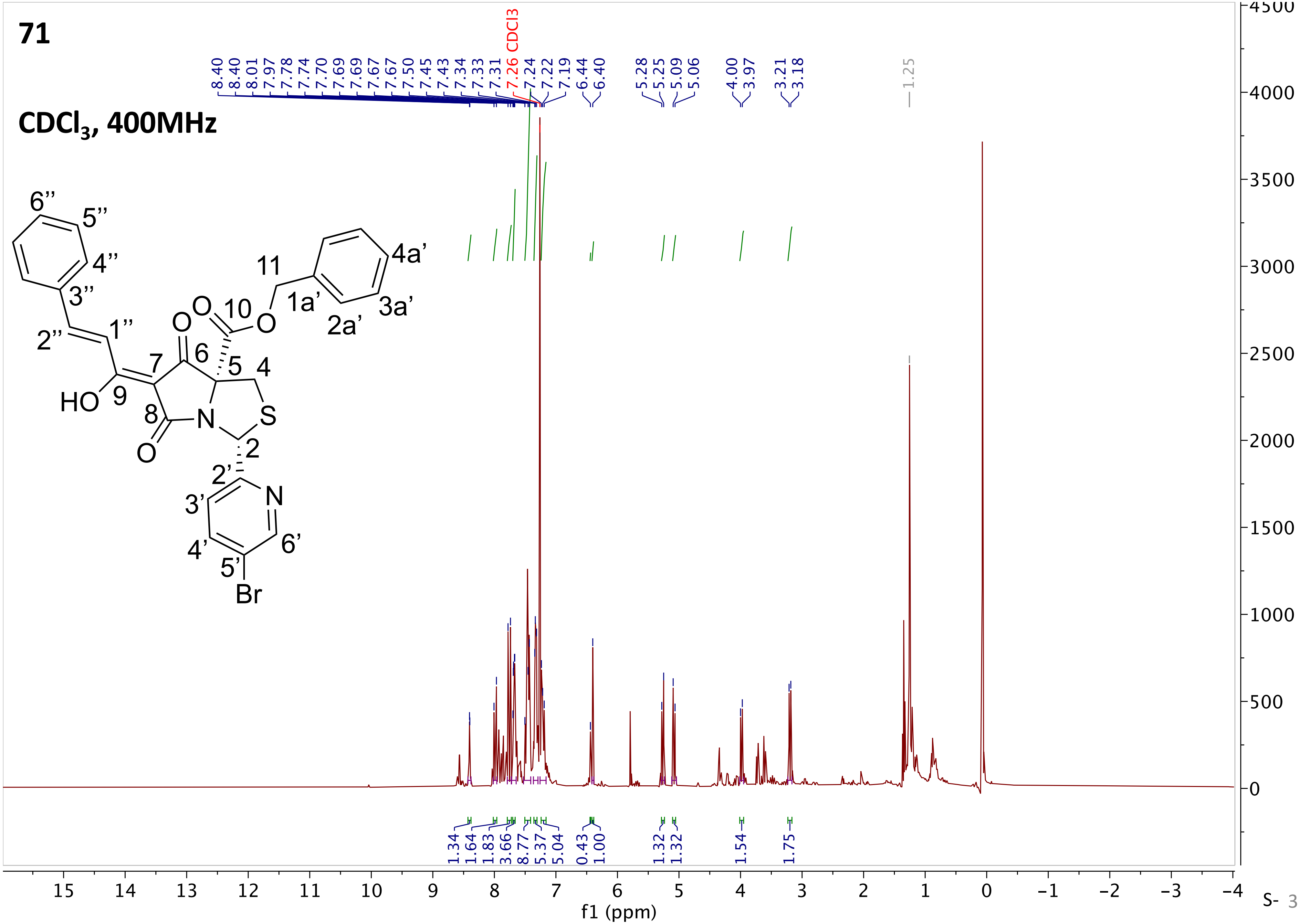
70

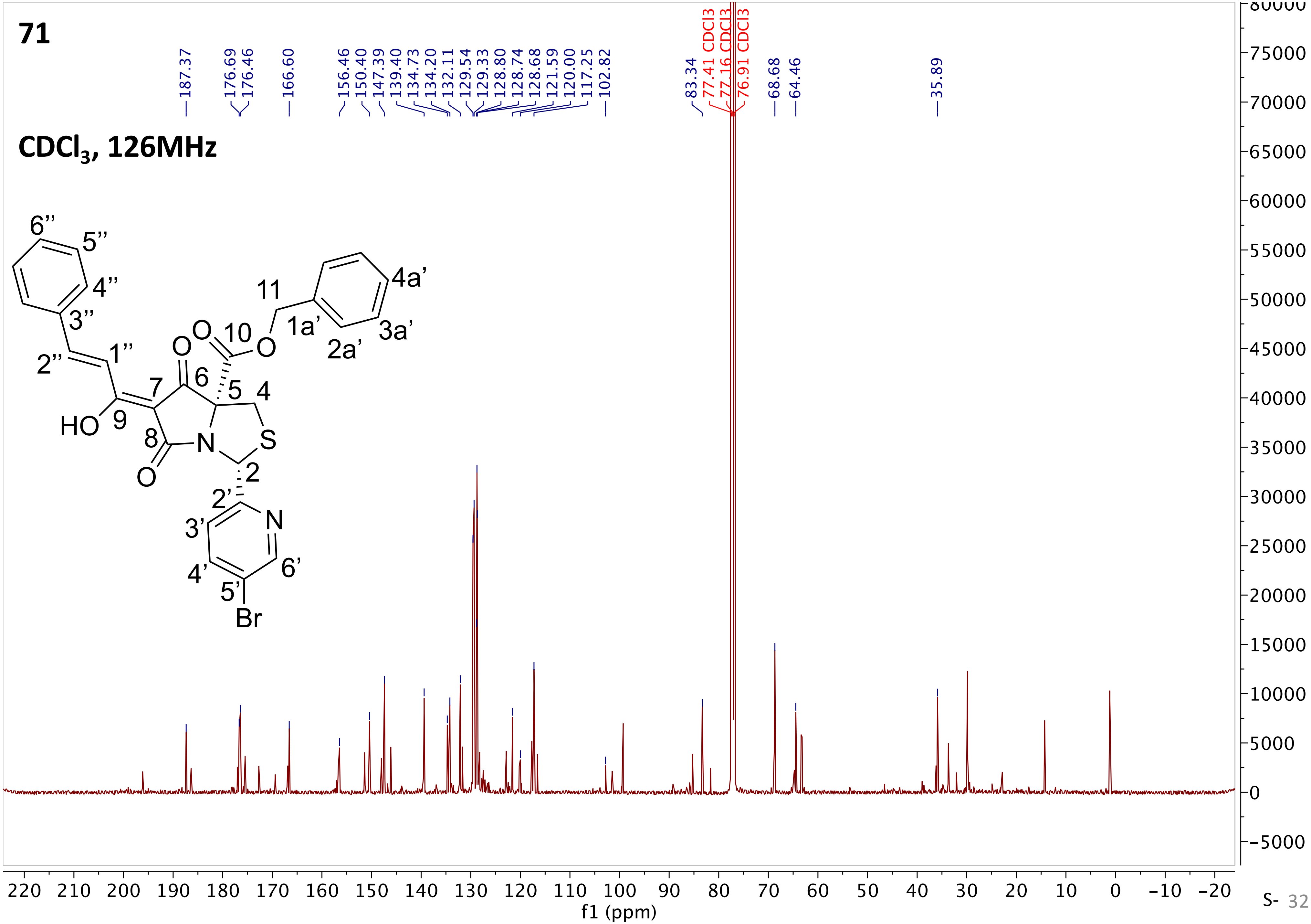
$CDCl_3$, 101MHz

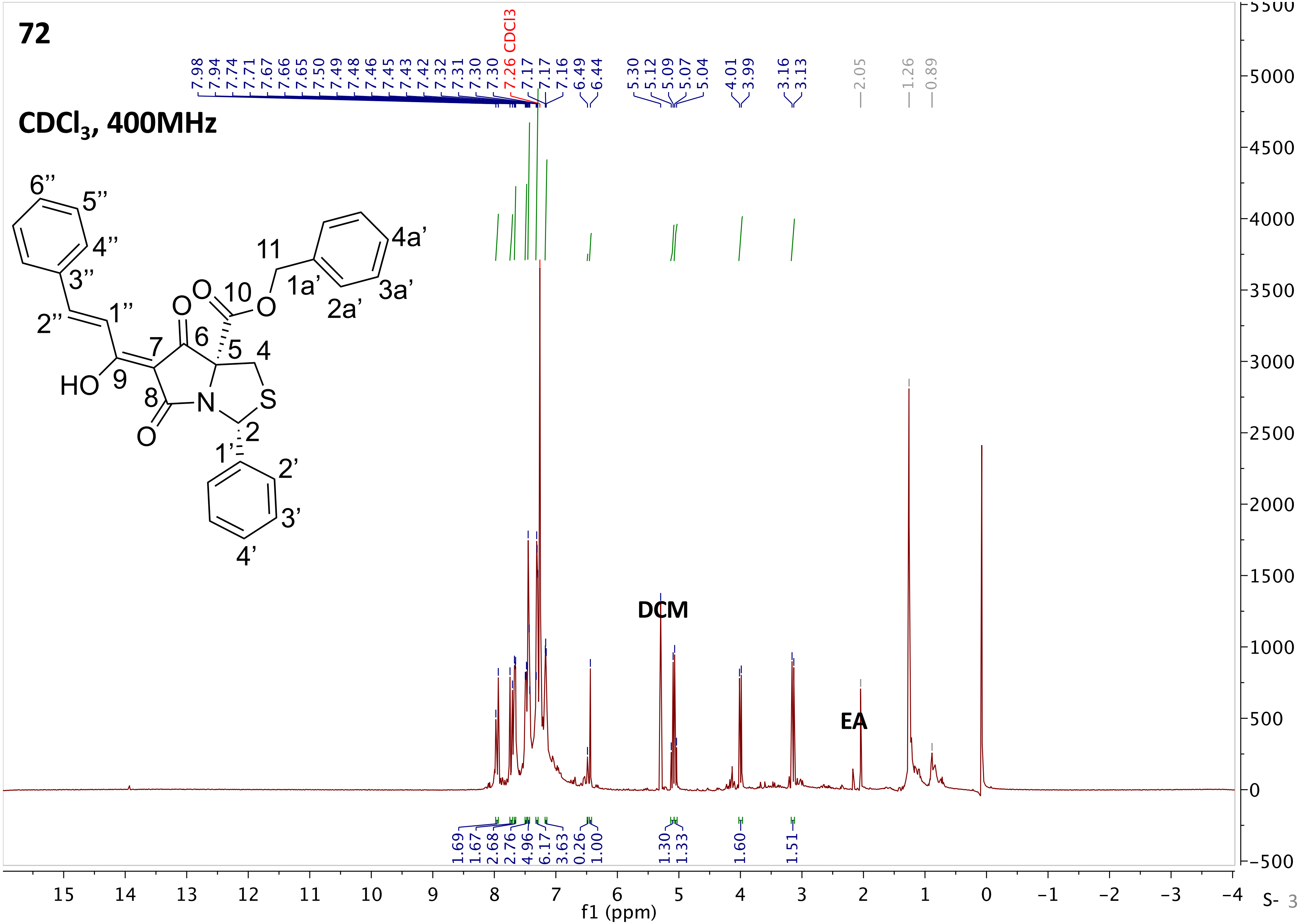


71

$CDCl_3$, 400MHz

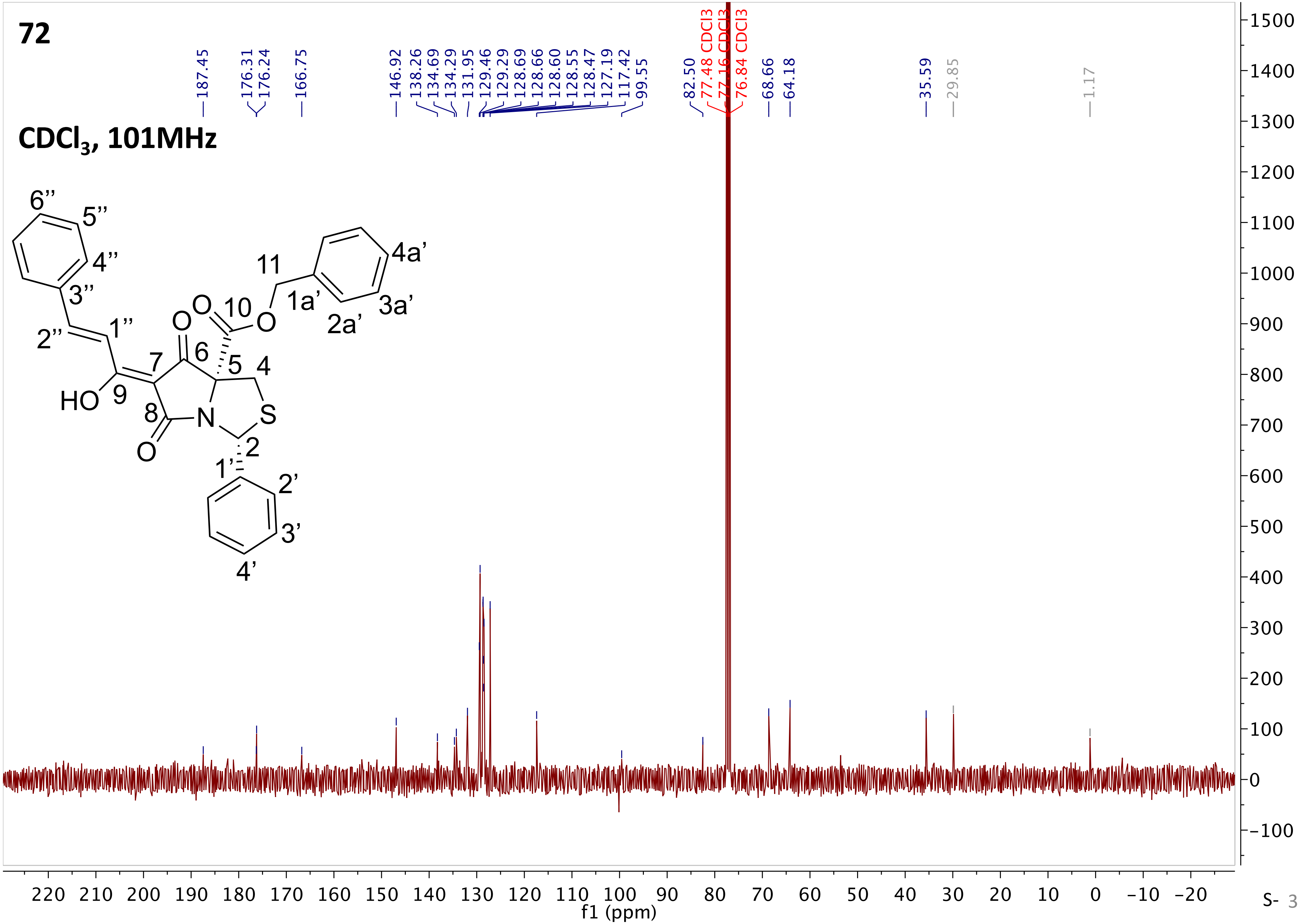



71
CDCl3, 126MHz
187.37
176.69
176.46
166.60
156.46
150.40
147.39
139.40
134.73
134.20
132.11
129.54
129.33
128.80
128.74
128.68
121.59
120.00
117.25
102.82
83.34
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.68
64.46
35.89
6''
5''
4''
3''
2''
1''
11
10
4a'
1a'
3a'
2a'
O
O
O
6
7
5
4
HO
9
8
N
S
O
2
2'
N
3'
6'
4'
5'
Br
f1 (ppm)


72
CDCl$_3$, 400MHz
7.98 7.94 7.74 7.71 7.67 7.66 7.65 7.50 7.49 7.48 7.46 7.45 7.43 7.42 7.32 7.31 7.30 7.30 7.26 CDCl3 7.17 7.17 7.16 6.49 6.44 5.30 5.12 5.09 5.07 5.04 4.01 3.99 3.16 3.13 2.05 1.26 0.89
DCM
EA
1.69 1.67 2.68 2.76 4.96 6.17 3.63 0.26 1.00 1.30 1.33 1.60 1.51
f1 (ppm)

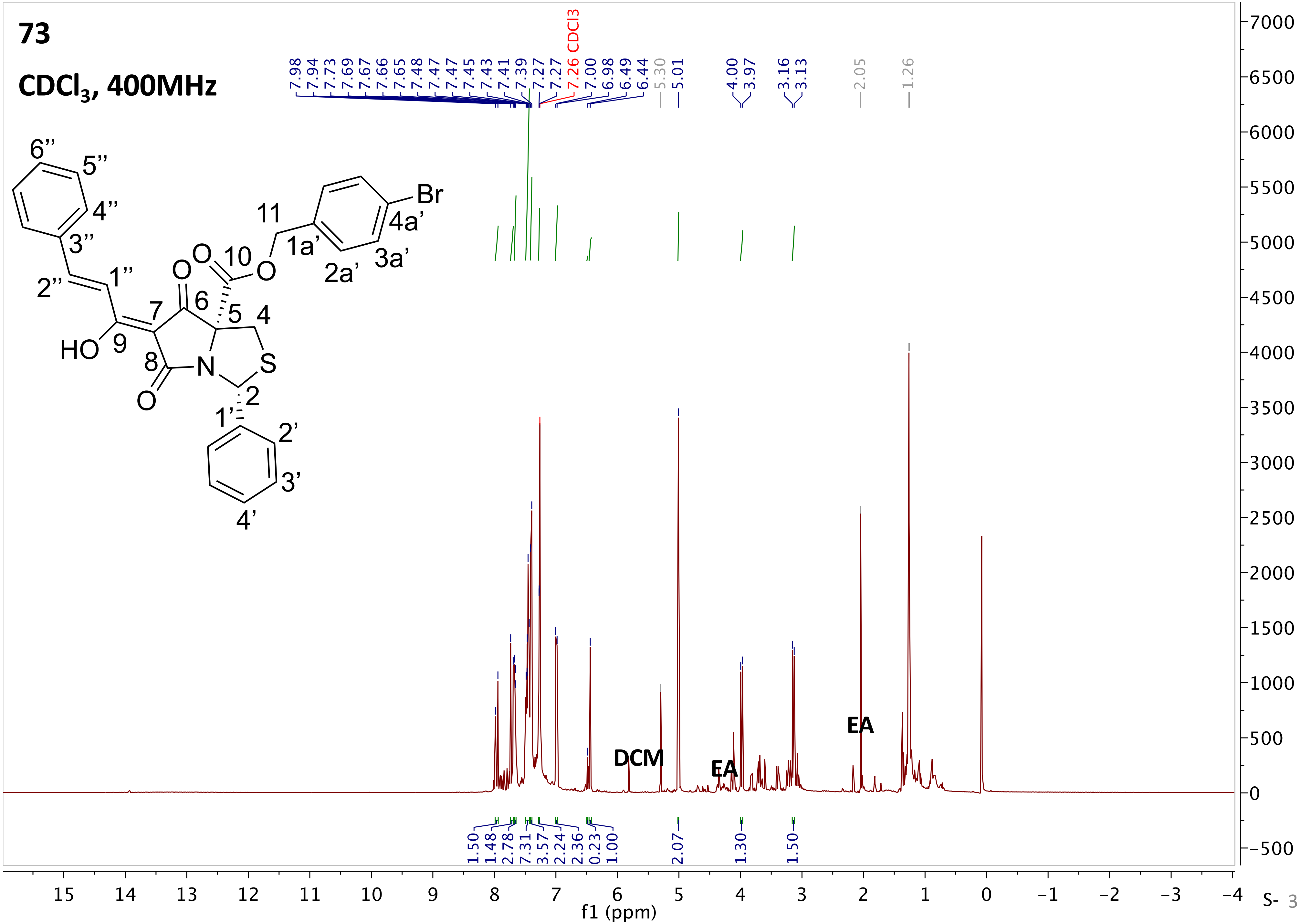
72

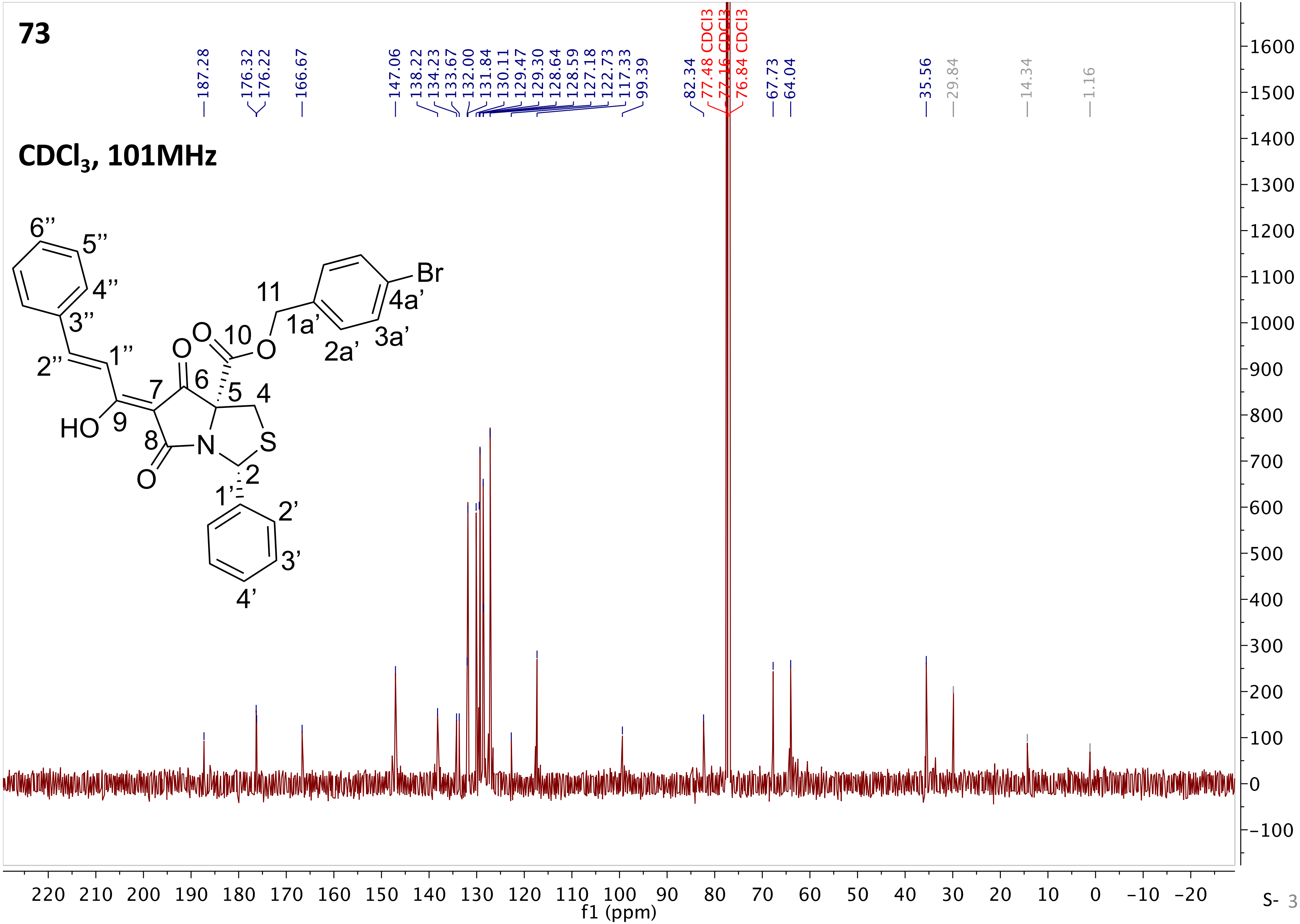
$CDCl_3$, 101MHz

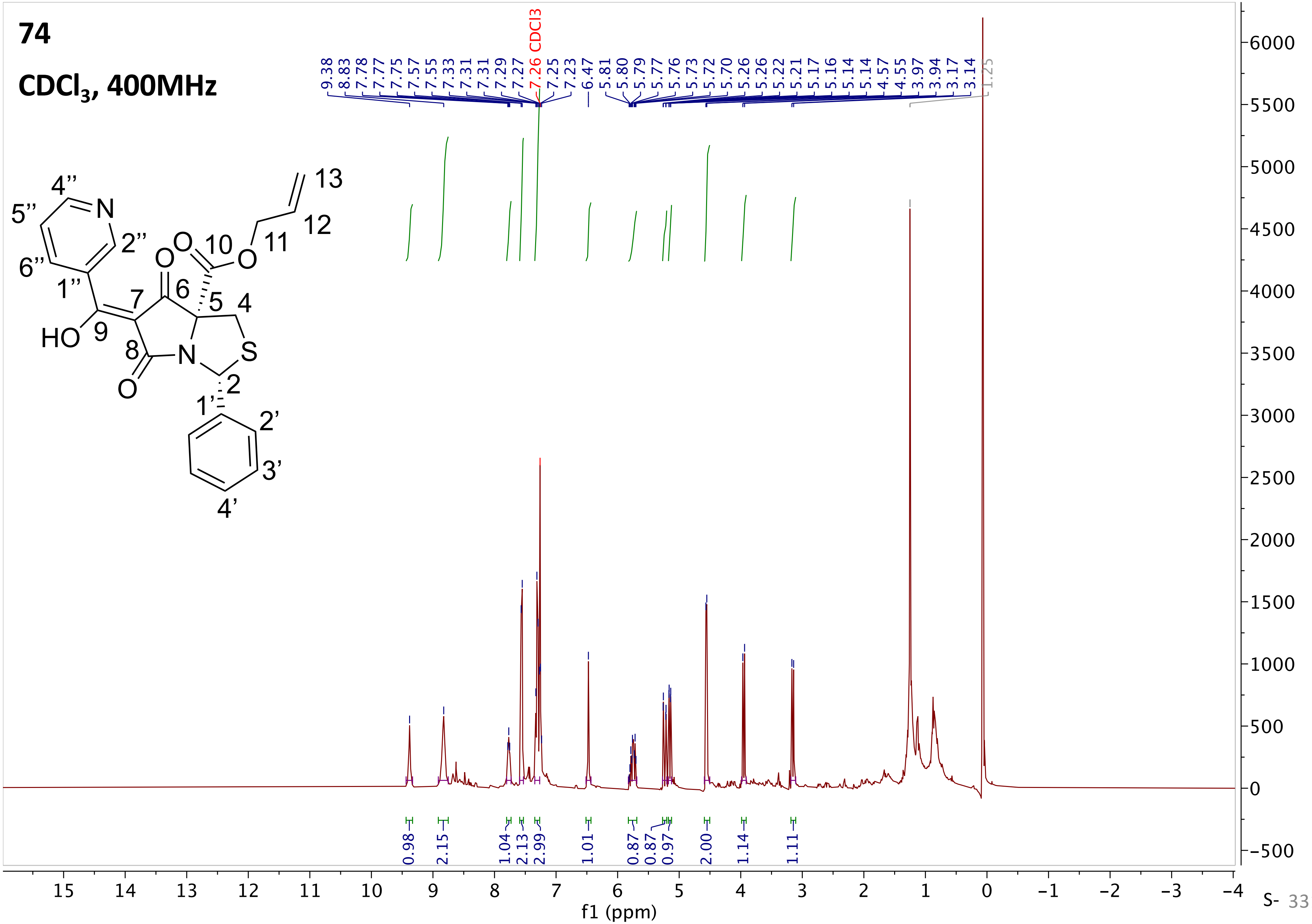


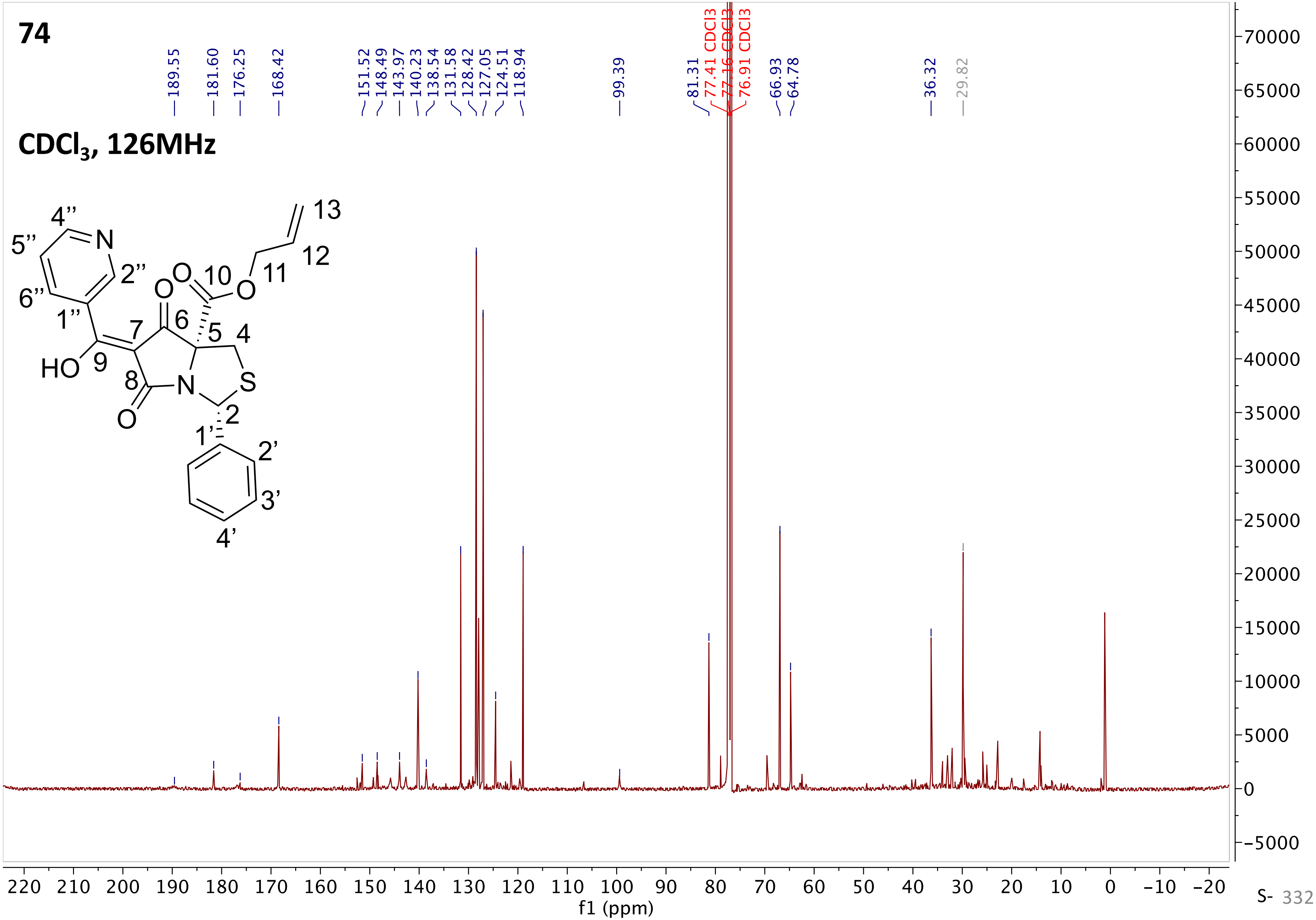
73

CDCl$_3$, 400MHz




73
CDCl3, 101MHz
187.28
176.32
176.22
166.67
147.06
138.22
134.23
133.67
132.00
131.84
130.11
129.47
129.30
128.64
128.59
127.18
122.73
117.33
99.39
82.34
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.73
64.04
35.56
29.84
14.34
1.16
f1 (ppm)

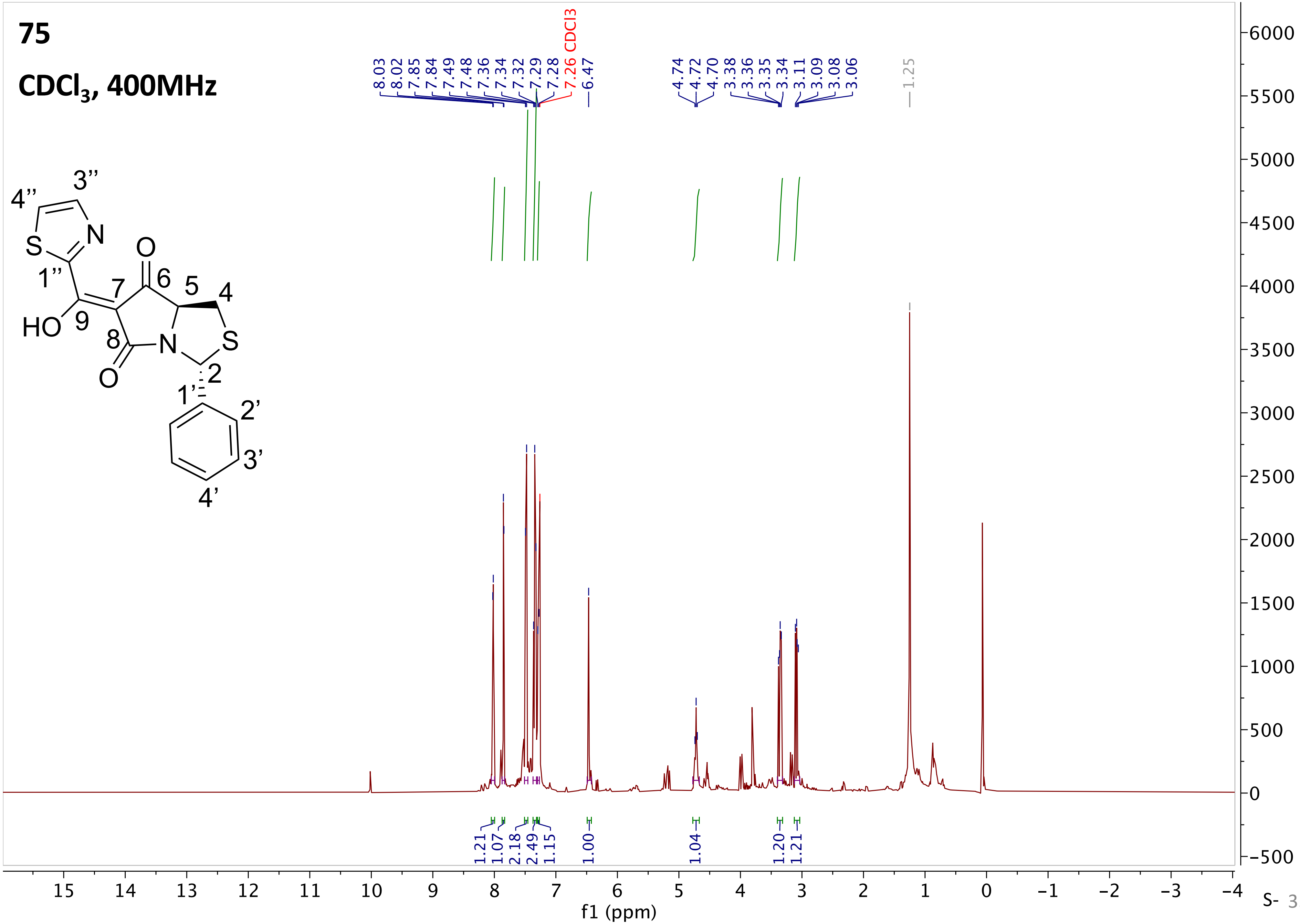

74
CDCl3, 400MHz
9.38 8.83 7.78 7.77 7.75 7.57 7.55 7.33 7.31 7.31 7.29 7.27 7.26 CDCl3 7.25 7.23 6.47 5.81 5.80 5.79 5.77 5.76 5.73 5.72 5.70 5.26 5.26 5.22 5.21 5.17 5.16 5.14 5.14 4.57 4.55 3.97 3.94 3.17 3.14 1.25
0.98 2.15 1.04 2.13 2.99 1.01 0.87 0.87 0.97 2.00 1.14 1.11
f1 (ppm)

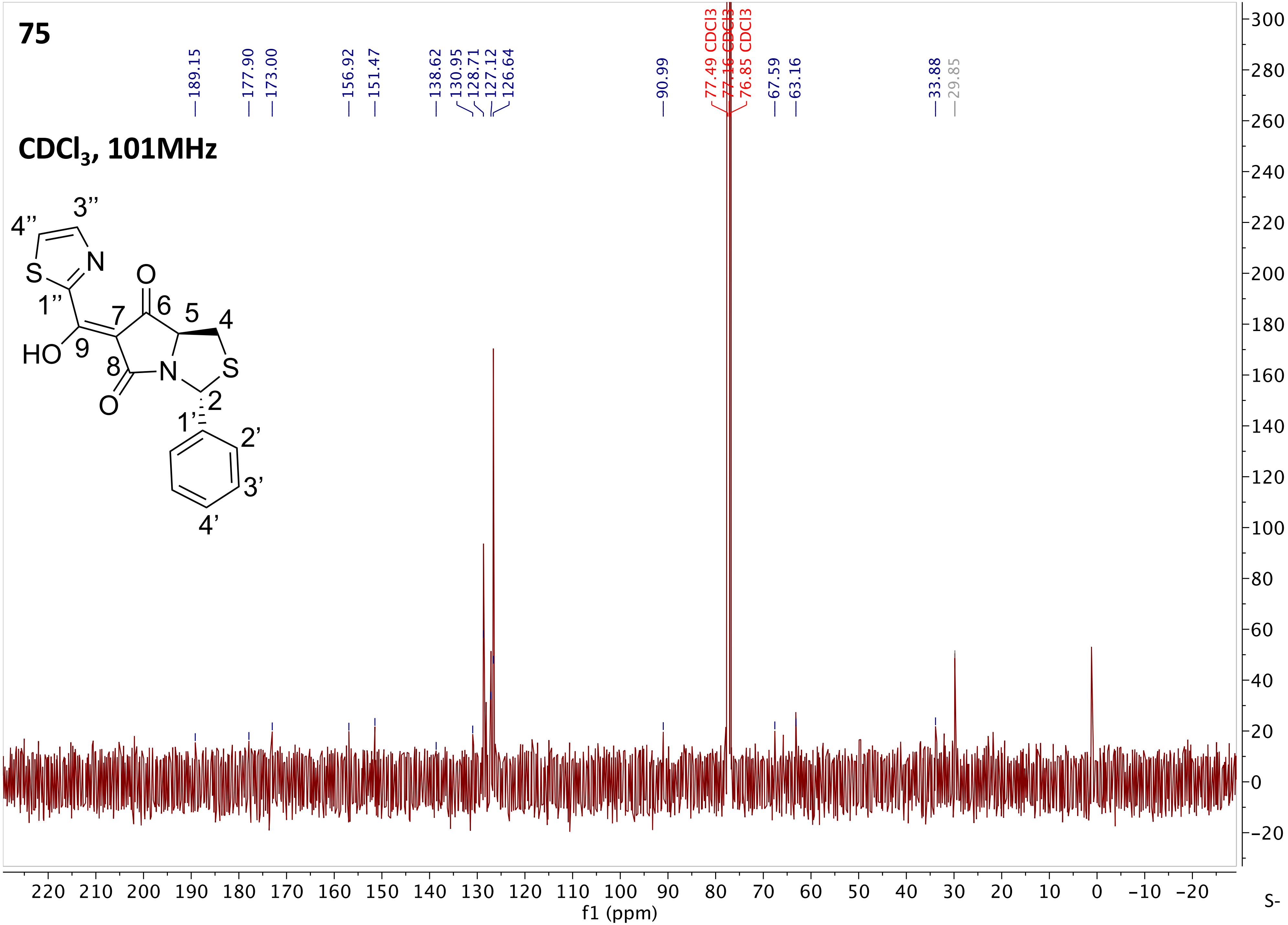


74
CDCl3, 126MHz
189.55
181.60
176.25
168.42
151.52
148.49
143.97
140.23
138.54
131.58
128.42
127.05
124.51
118.94
99.39
81.31
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.93
64.78
36.32
29.82
f1 (ppm)

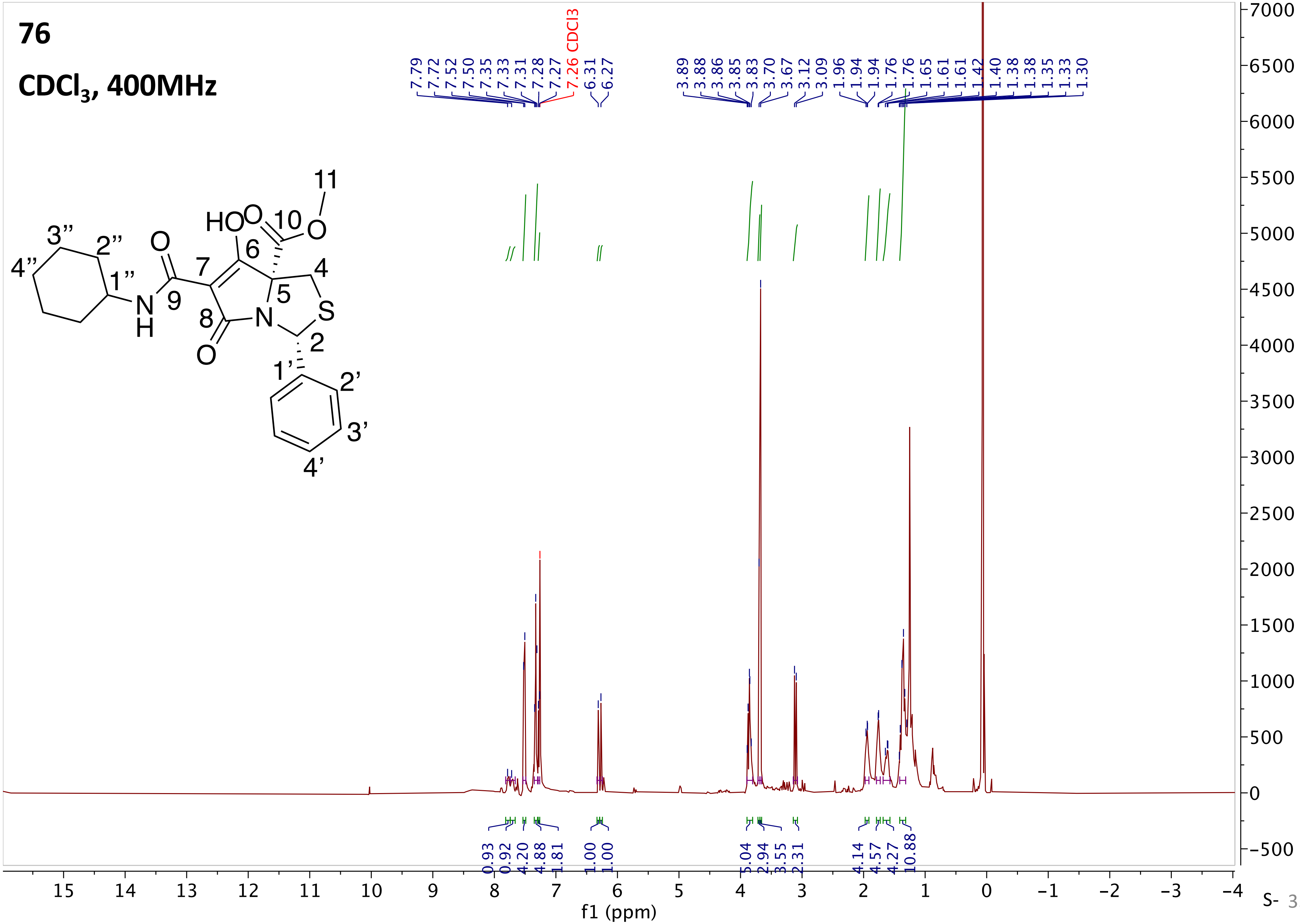
75

$CDCl_3$, 400MHz

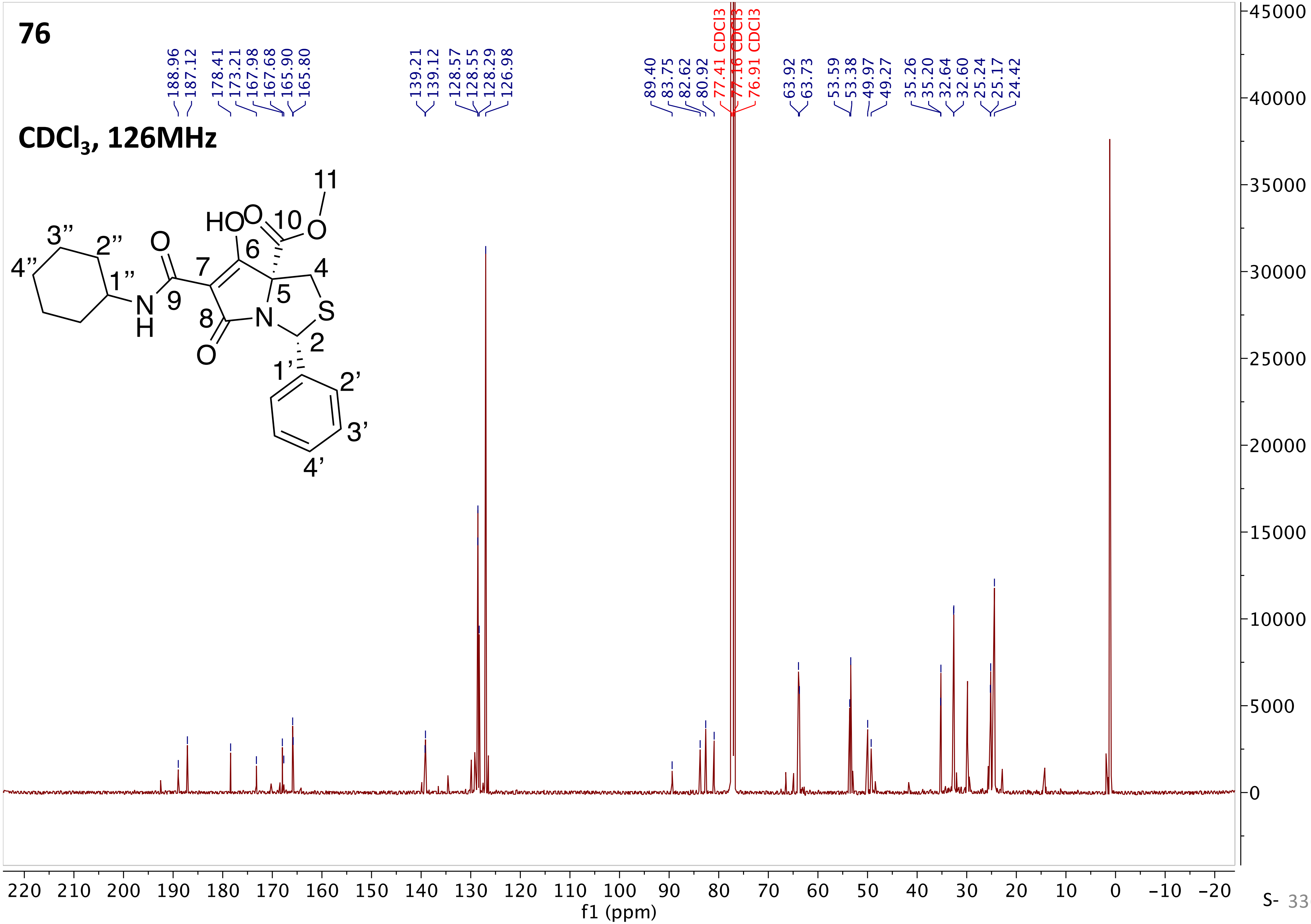


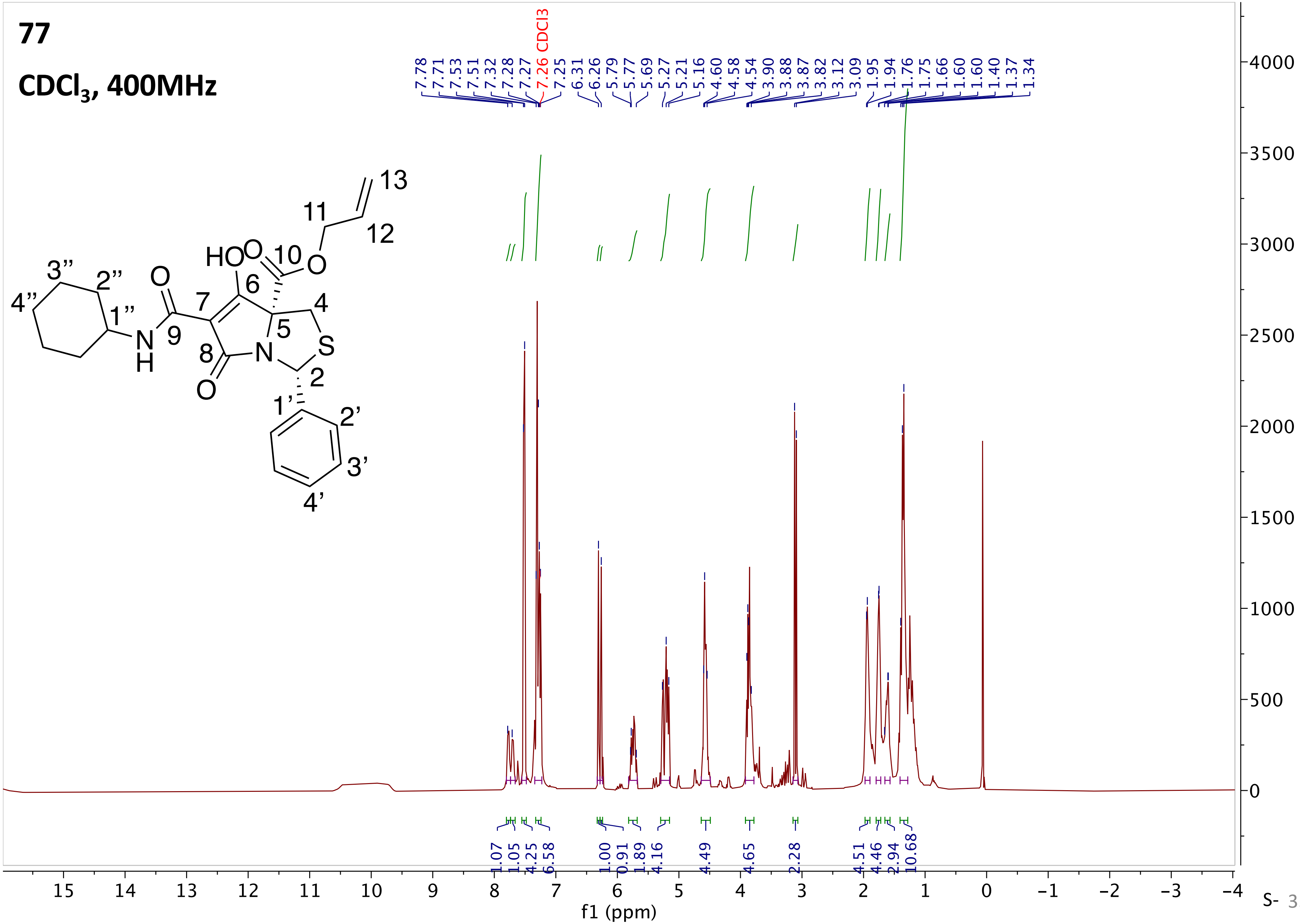


75
CDCl3, 101MHz
189.15
177.90
173.00
156.92
151.47
138.62
130.95
128.71
127.12
126.64
90.99
77.49 CDCl3
77.16 CDCl3
76.85 CDCl3
67.59
63.16
33.88
29.85
f1 (ppm)



76
CDCl3, 400MHz
7.79 7.72 7.52 7.50 7.35 7.33 7.31 7.28 7.27 7.26 CDCl3 6.31 6.27
3.89 3.88 3.86 3.85 3.83 3.70 3.67 3.12 3.09 1.96 1.94 1.94 1.76 1.76 1.65 1.61 1.61 1.42 1.40 1.38 1.38 1.35 1.33 1.30
0.93 0.92 4.20 4.88 1.81 1.00 1.00 5.04 2.94 3.55 2.31 4.14 4.57 4.27 10.88
f1 (ppm)

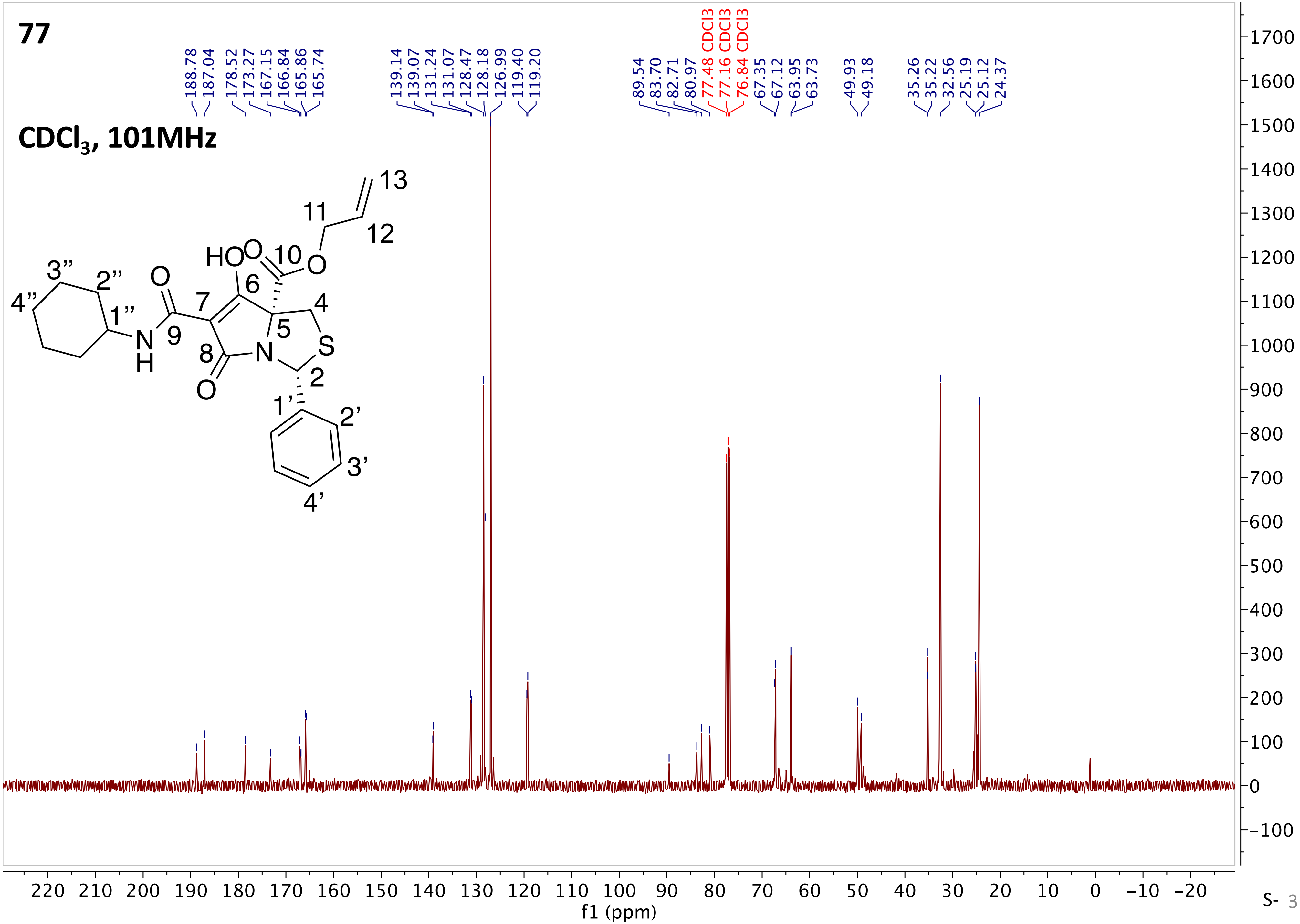

76
CDCl3, 126MHz
188.96
187.12
178.41
173.21
167.98
167.68
165.90
165.80
139.21
139.12
128.57
128.55
128.29
126.98
89.40
83.75
82.62
80.92
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
63.92
63.73
53.59
53.38
49.97
49.27
35.26
35.20
32.64
32.60
25.24
25.17
24.42
f1 (ppm)



77
CDCl3, 400MHz
7.78 7.71 7.53 7.51 7.32 7.28 7.27 7.26 CDCl3 7.25 6.31 6.26 5.79 5.77 5.69 5.27 5.21 5.16 4.60 4.58 4.54 3.90 3.88 3.87 3.82 3.12 3.09 1.95 1.94 1.76 1.75 1.66 1.60 1.60 1.40 1.37 1.34
1.07 1.05 4.25 6.58 1.00 0.91 1.89 4.16 4.49 4.65 2.28 4.51 4.46 2.94 10.68
f1 (ppm)

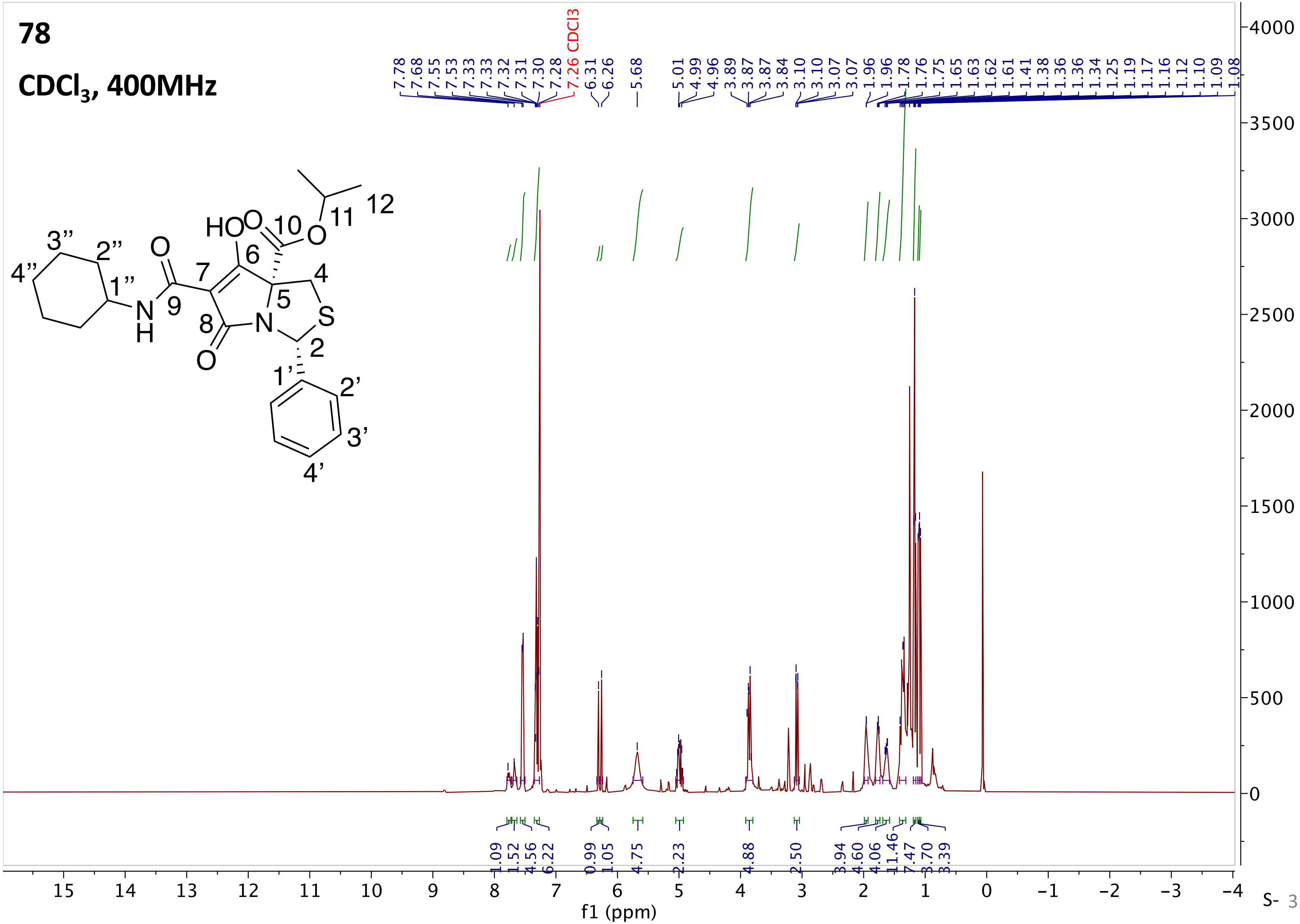
77

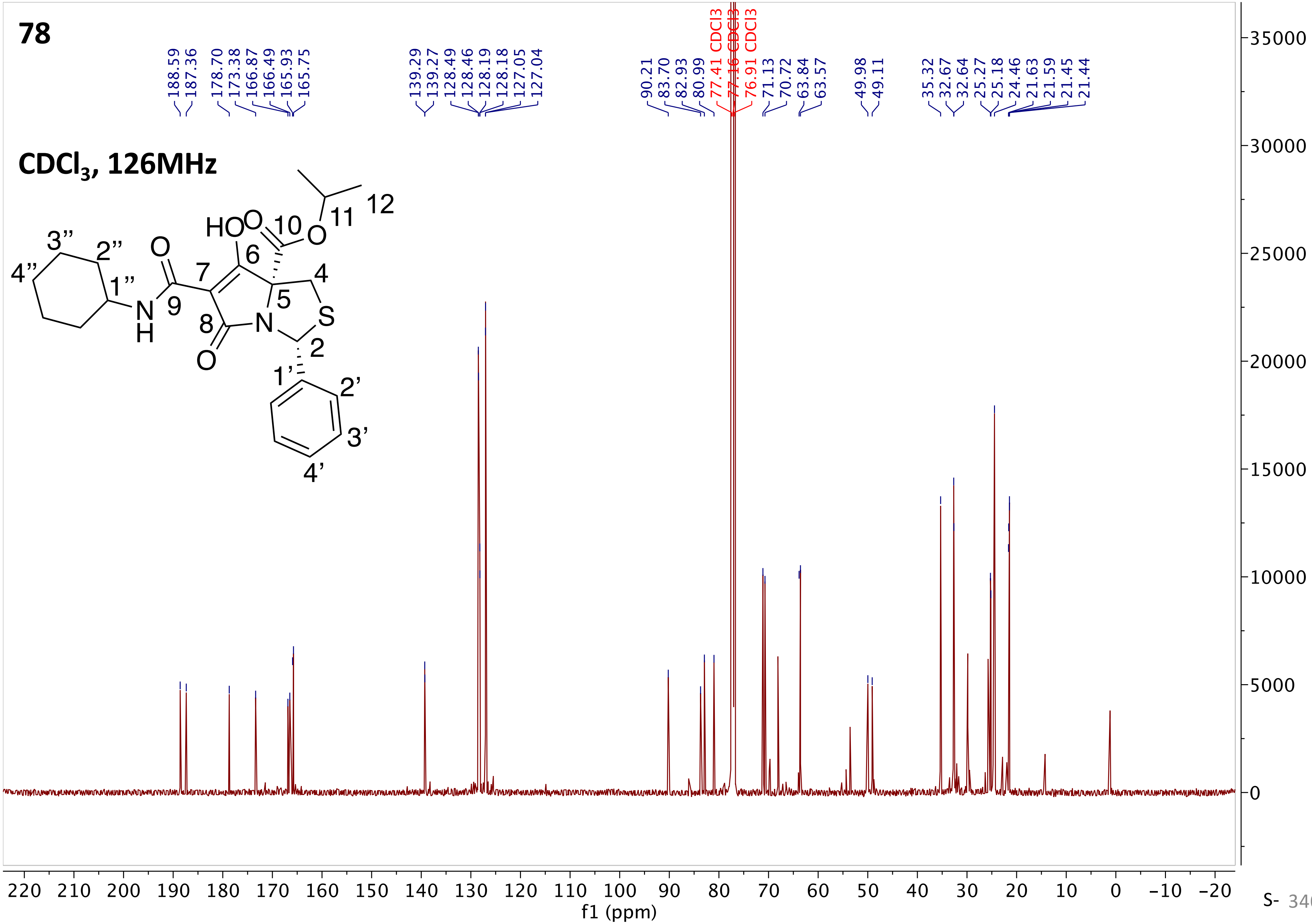
CDCl$_3$, 101MHz

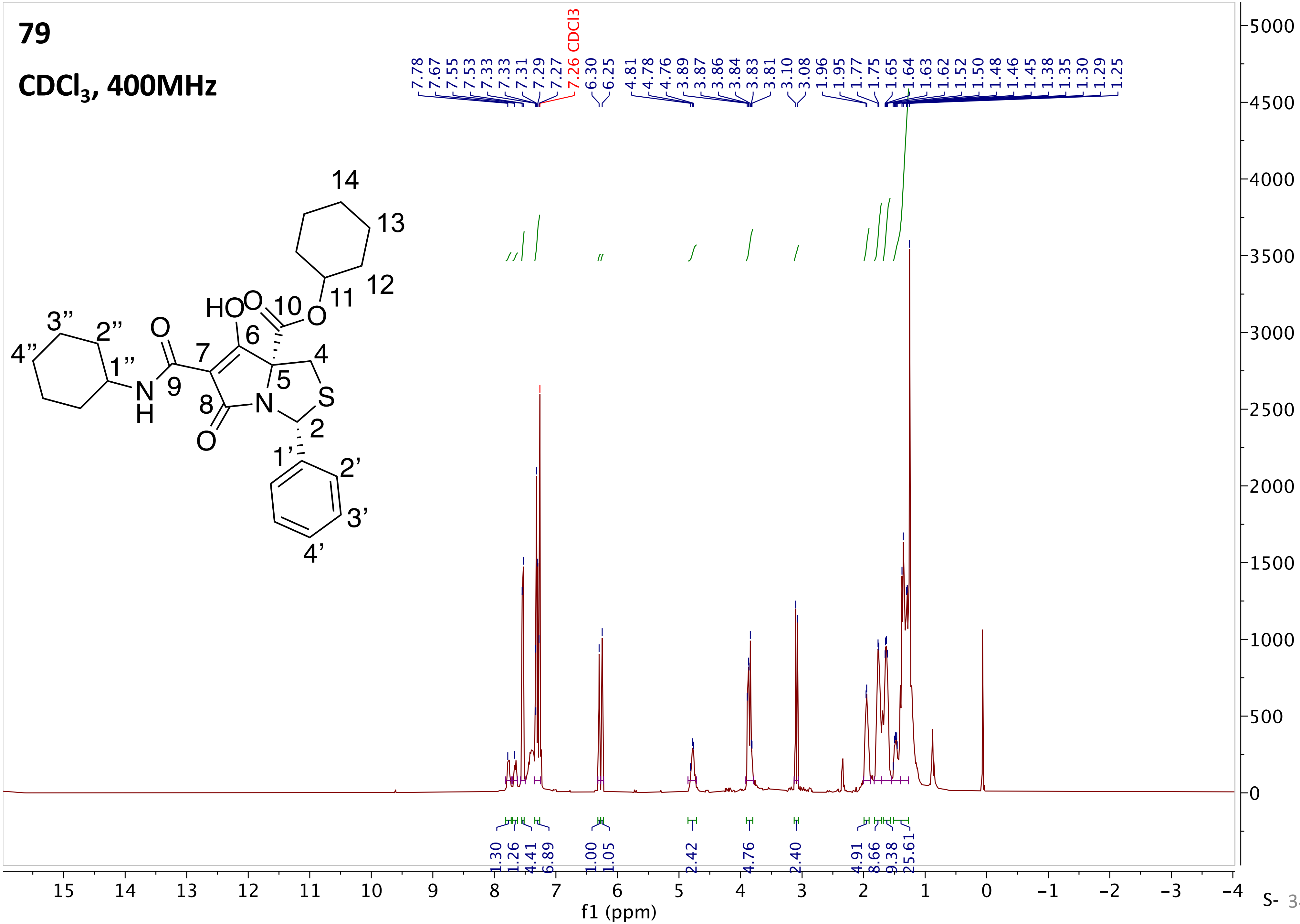


78

$CDCl_3$, 400MHz

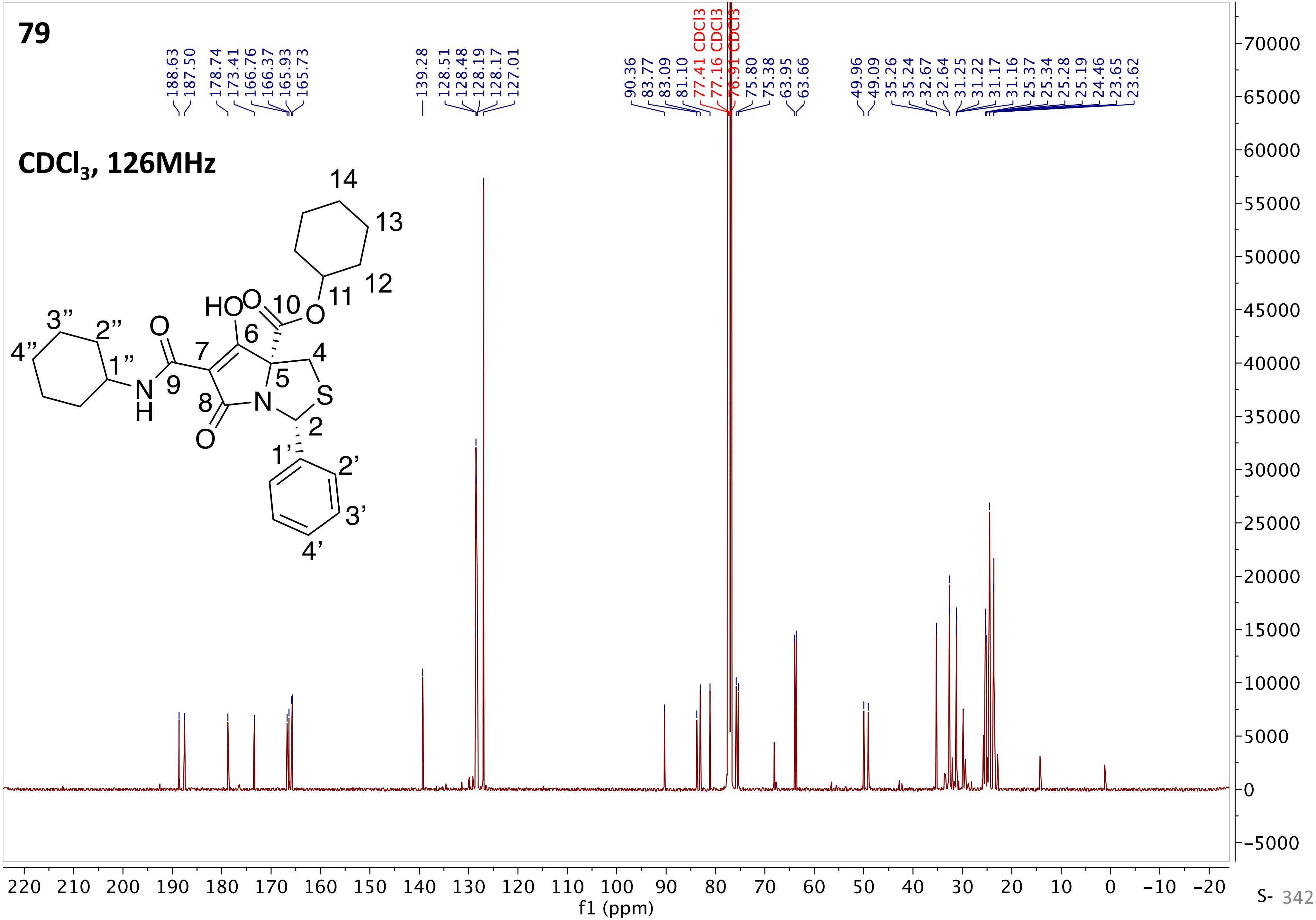


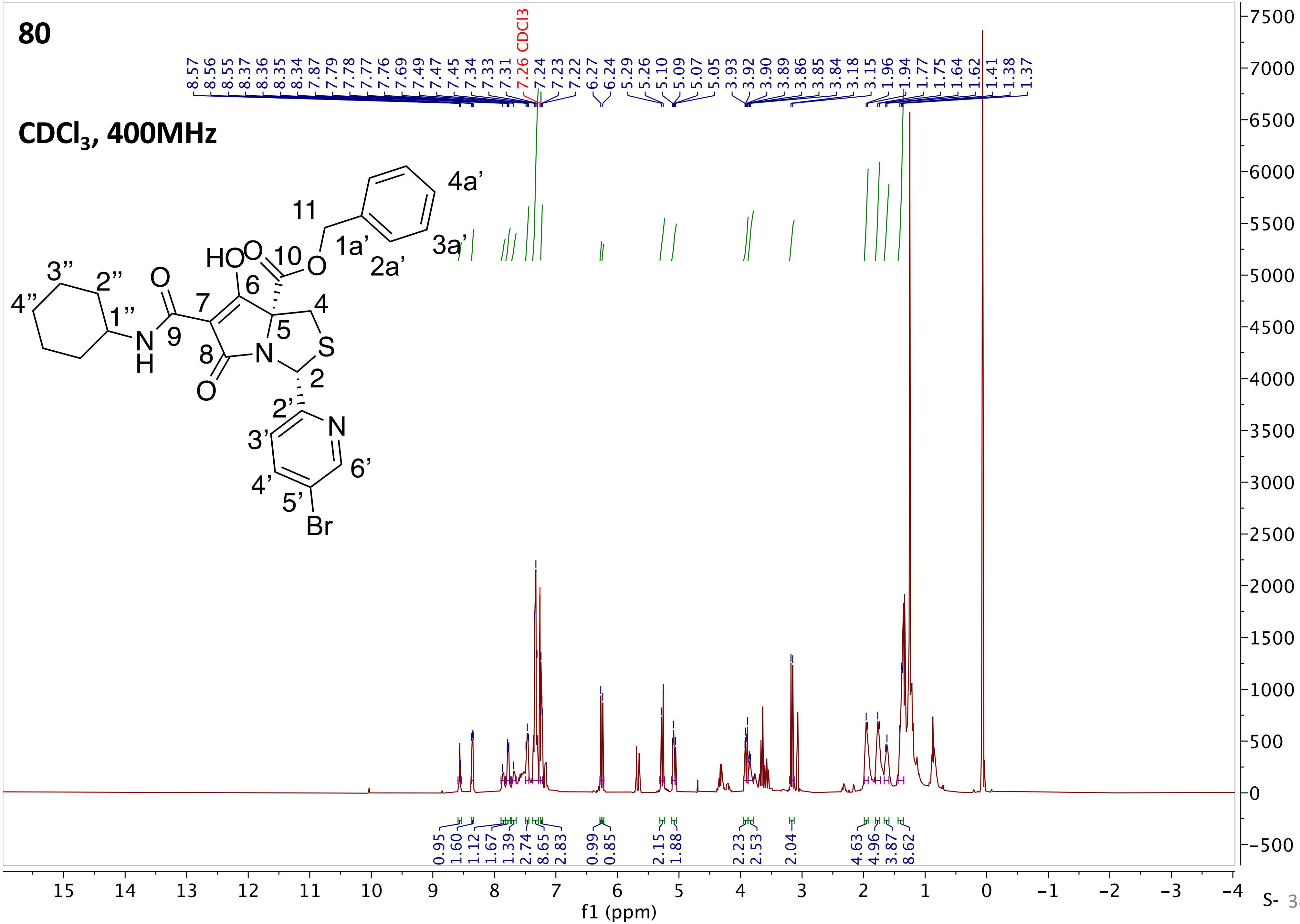

78
CDCl3, 126MHz
188.59
187.36
178.70
173.38
166.87
166.49
165.93
165.75
139.29
139.27
128.49
128.46
128.19
128.18
127.05
127.04
90.21
83.70
82.93
80.99
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
71.13
70.72
63.84
63.57
49.98
49.11
35.32
32.67
32.64
25.27
25.18
24.46
21.63
21.59
21.45
21.44
HO
O
10
O
11
12
6
7
O
9
N
H
8
O
N
5
4
S
2
1'
2'
3'
4'
1''
2''
3''
4''
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
35000 30000 25000 20000 15000 10000 5000 0

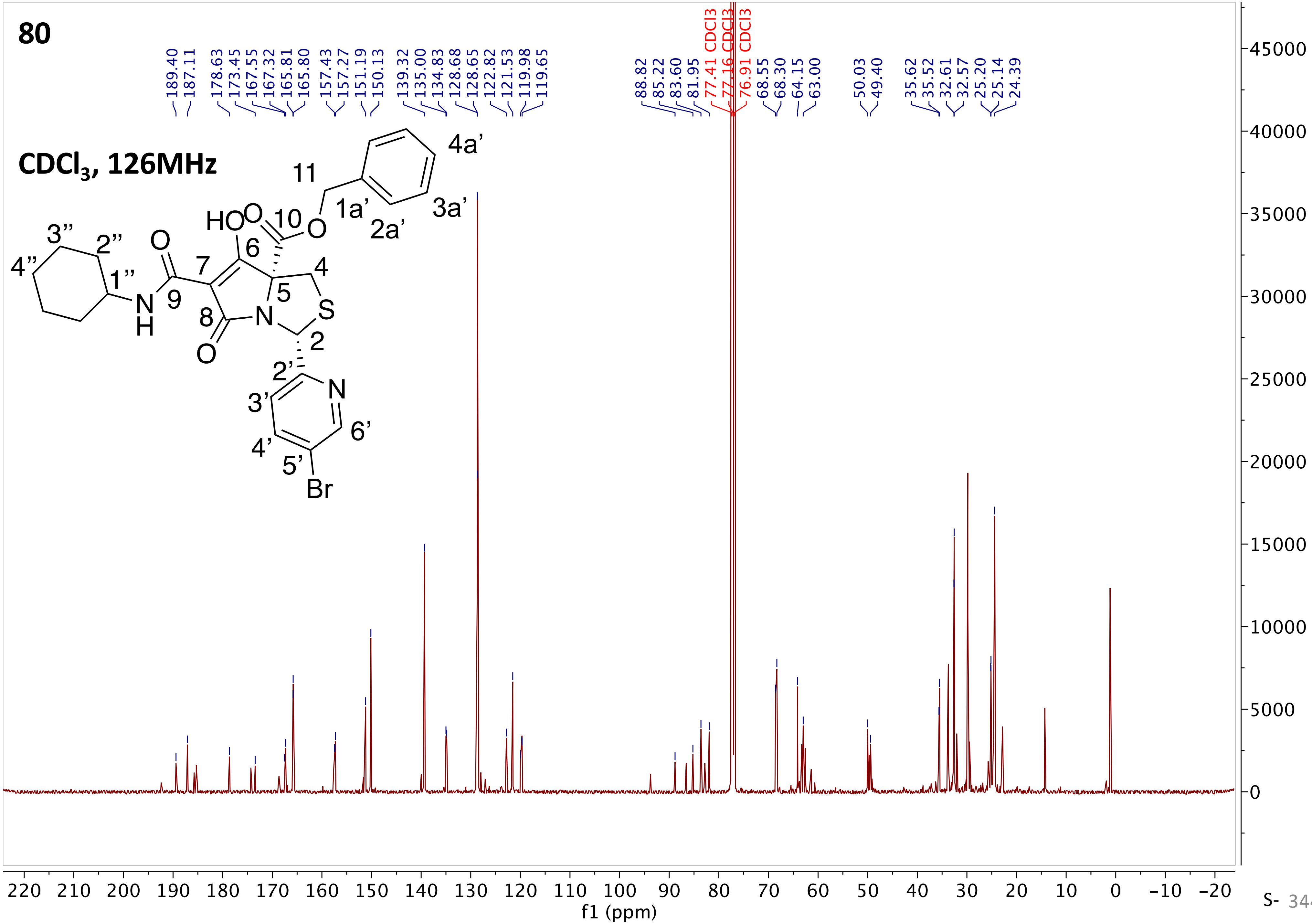

79
CDCl3, 400MHz
7.78
7.67
7.55
7.53
7.33
7.33
7.31
7.29
7.27
7.26 CDCl3
6.30
6.25
4.81
4.78
4.76
3.89
3.87
3.86
3.84
3.83
3.81
3.10
3.08
1.96
1.95
1.77
1.75
1.65
1.64
1.63
1.62
1.52
1.50
1.48
1.46
1.45
1.38
1.35
1.30
1.29
1.25
1.30
1.26
4.41
6.89
1.00
1.05
2.42
4.76
2.40
4.91
8.66
9.38
25.61
f1 (ppm)

79

CDCl$_3$, 126MHz

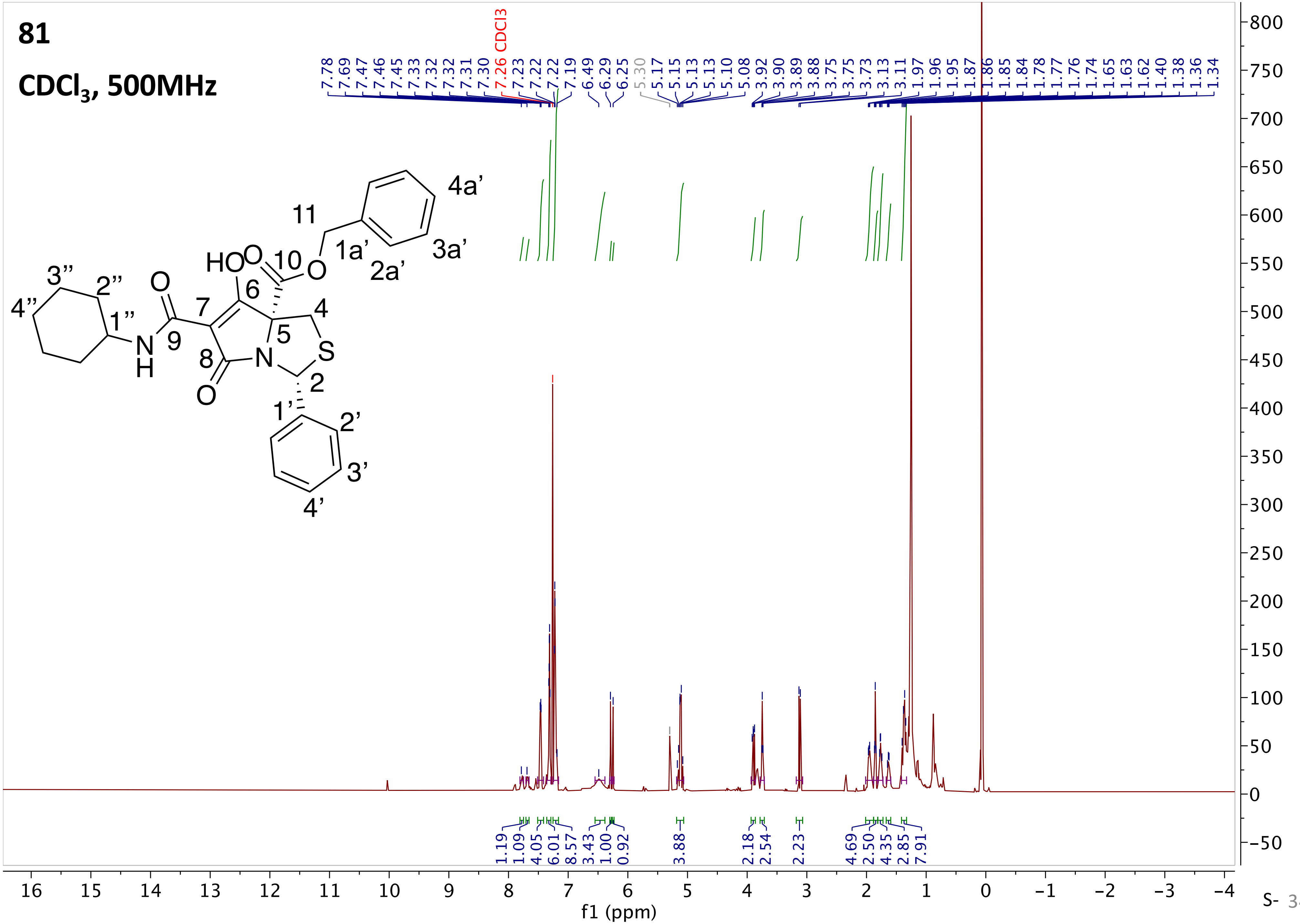


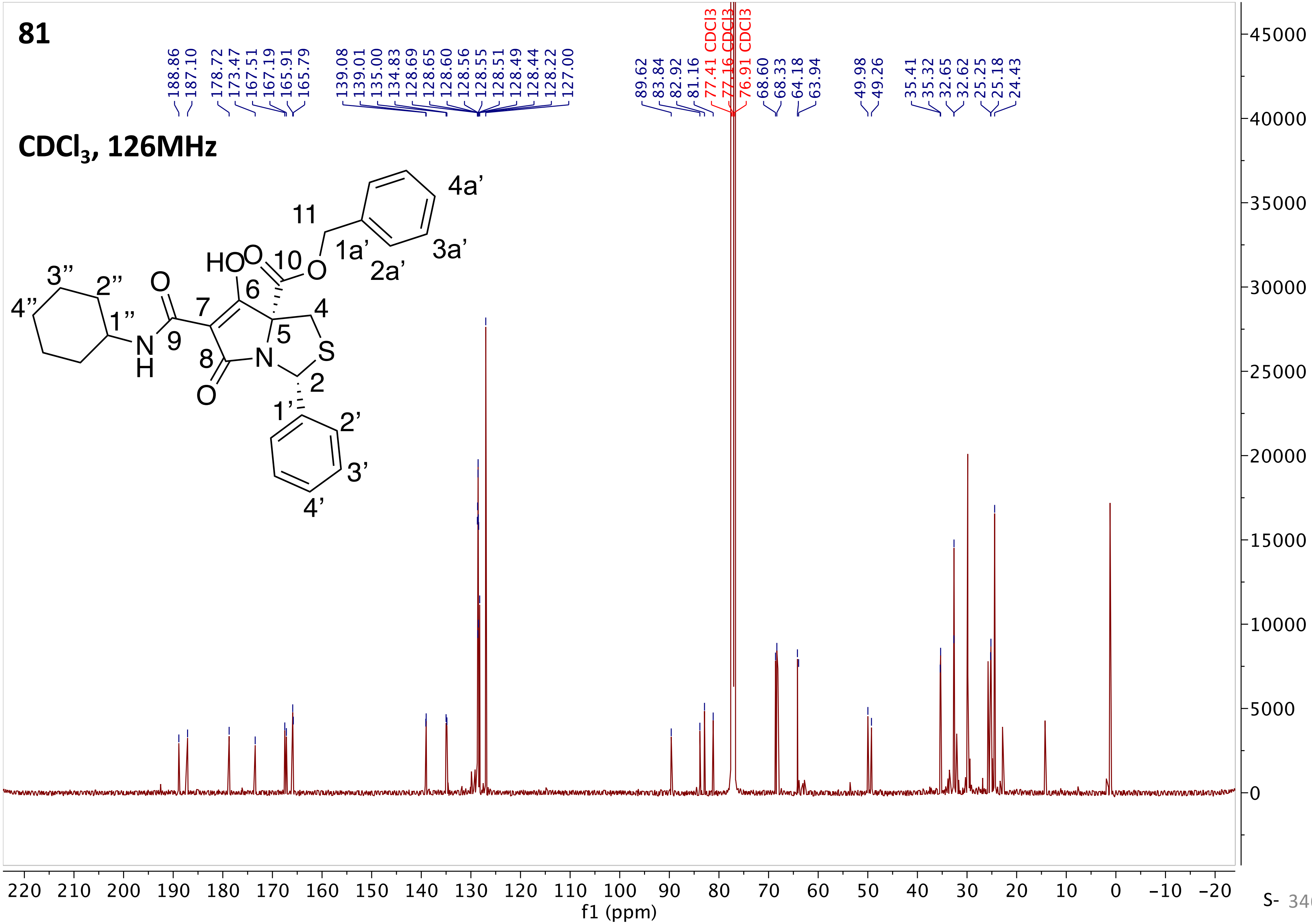

80
CDCl$_3$, 400MHz
7.26 CDCl3
8.57 8.56 8.55 8.37 8.36 8.35 8.34 7.87 7.79 7.78 7.77 7.76 7.69 7.49 7.47 7.45 7.34 7.33 7.31 7.24 7.23 7.22 6.27 6.24 5.29 5.26 5.10 5.09 5.07 5.05 3.93 3.92 3.90 3.89 3.86 3.85 3.84 3.18 3.15 1.96 1.94 1.77 1.75 1.64 1.62 1.41 1.38 1.37
0.95 1.60 1.12 1.67 1.39 2.74 8.65 2.83 0.99 0.85 2.15 1.88 2.23 2.53 2.04 4.63 4.96 3.87 8.62
f1 (ppm)

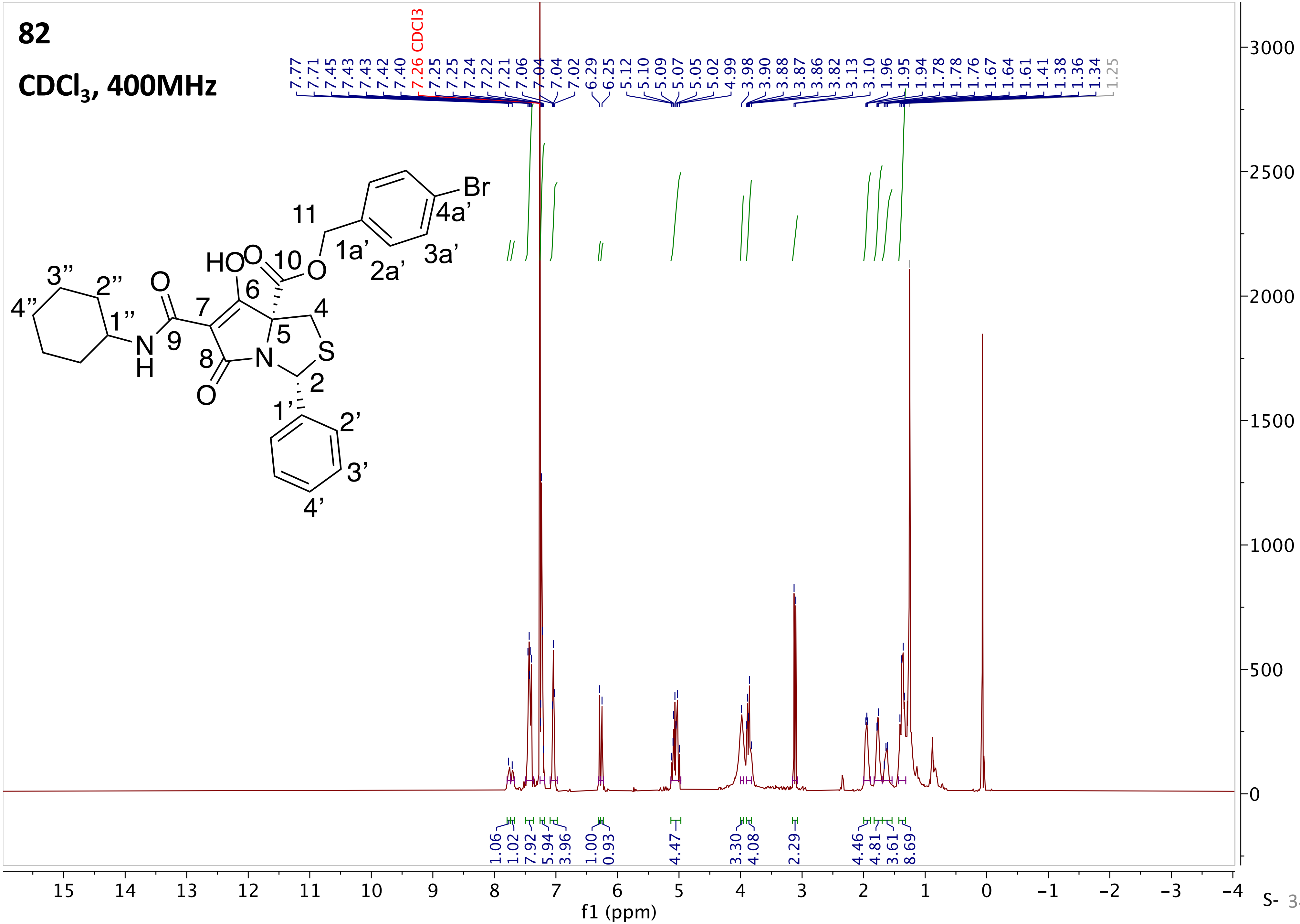

80
CDCl3, 126MHz
189.40
187.11
178.63
173.45
167.55
167.32
165.81
165.80
157.43
157.27
151.19
150.13
139.32
135.00
134.83
128.68
128.65
122.82
121.53
119.98
119.65
88.82
85.22
83.60
81.95
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.55
68.30
64.15
63.00
50.03
49.40
35.62
35.52
32.61
32.57
25.20
25.14
24.39
f1 (ppm)

81

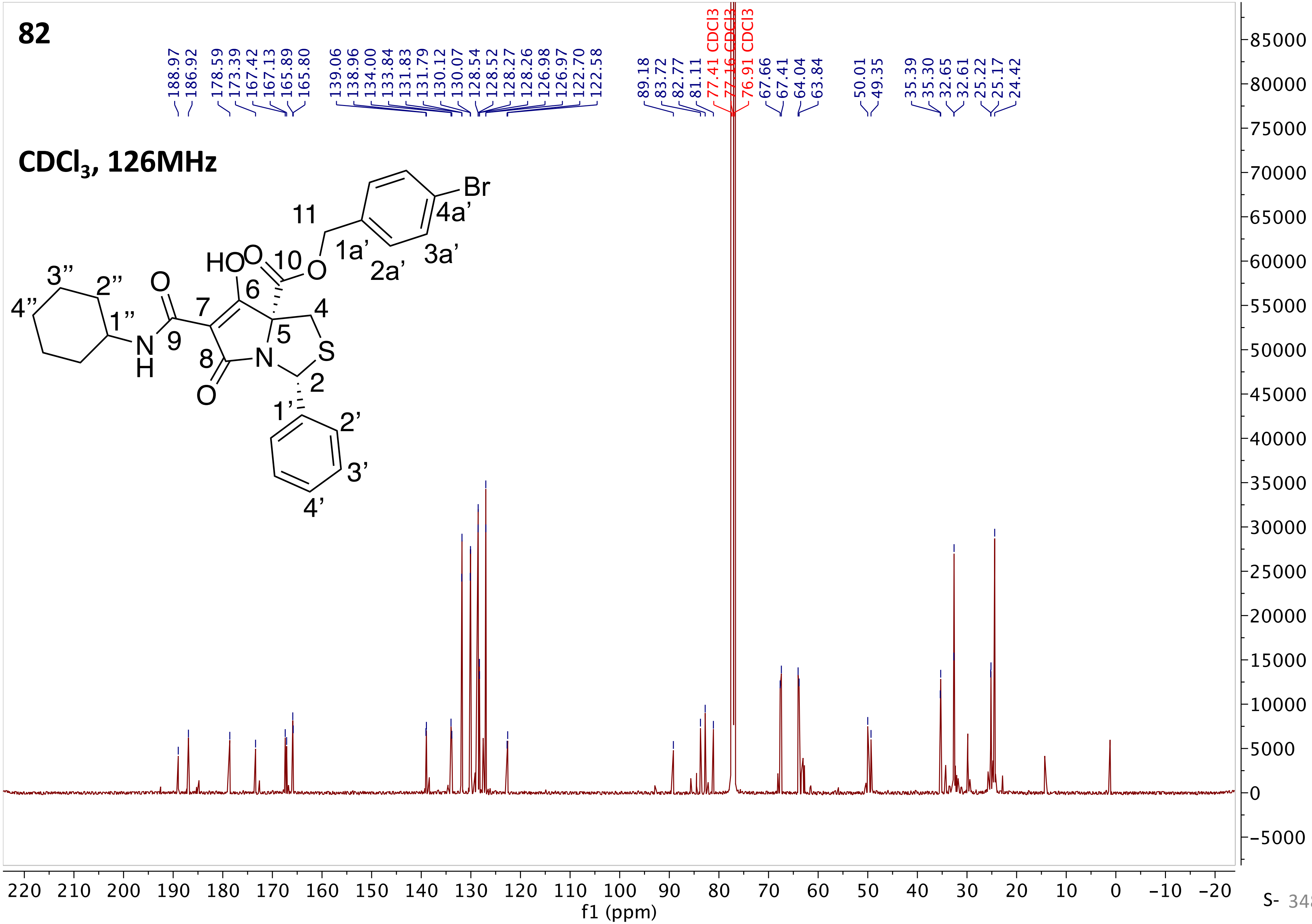
$CDCl_3$, 500MHz




81
CDCl3, 126MHz
188.86
187.10
178.72
173.47
167.51
167.19
165.91
165.79
139.08
139.01
135.00
134.83
128.69
128.65
128.60
128.56
128.55
128.51
128.49
128.44
128.22
127.00
89.62
83.84
82.92
81.16
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.60
68.33
64.18
63.94
49.98
49.26
35.41
35.32
32.65
32.62
25.25
25.18
24.43
f1 (ppm)

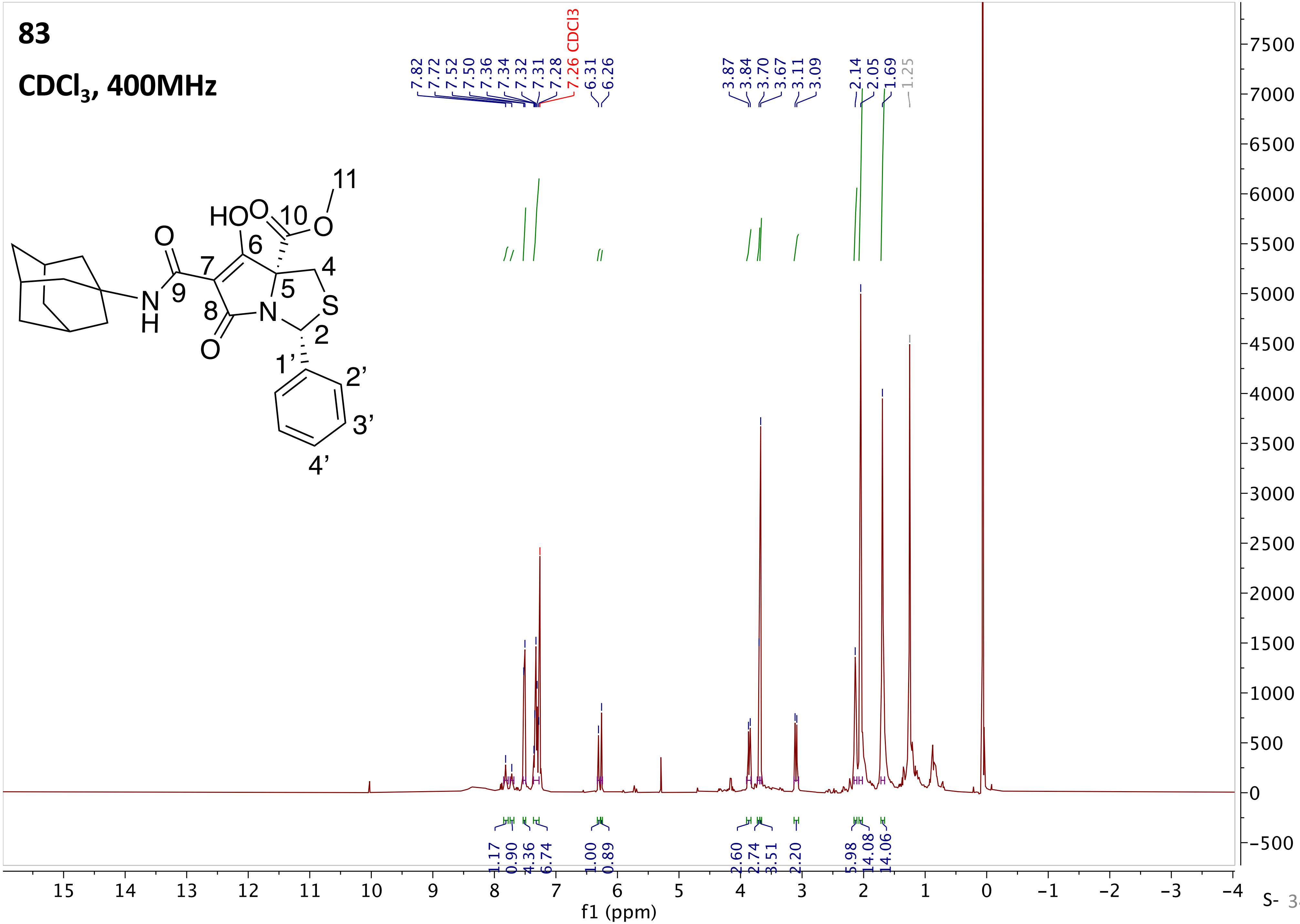


82
CDCl3, 400MHz
7.77 7.71 7.45 7.43 7.43 7.42 7.40 7.26 CDCl3 7.25 7.25 7.24 7.22 7.21 7.06 7.04 7.04 7.02 6.29 6.25 5.12 5.10 5.09 5.07 5.05 5.02 4.99 3.98 3.90 3.88 3.87 3.86 3.82 3.13 3.10 1.96 1.95 1.94 1.78 1.78 1.76 1.67 1.64 1.61 1.41 1.38 1.36 1.34 1.25
1.06 1.02 7.92 5.94 3.96 1.00 0.93 4.47 3.30 4.08 2.29 4.46 4.81 3.61 8.69
f1 (ppm)


82
CDCl3, 126MHz
188.97
186.92
178.59
173.39
167.42
167.13
165.89
165.80
139.06
138.96
134.00
133.84
131.83
131.79
130.12
130.07
128.54
128.52
128.27
128.26
126.98
126.97
122.70
122.58
89.18
83.72
82.77
81.11
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.66
67.41
64.04
63.84
50.01
49.35
35.39
35.30
32.65
32.61
25.22
25.17
24.42
f1 (ppm)

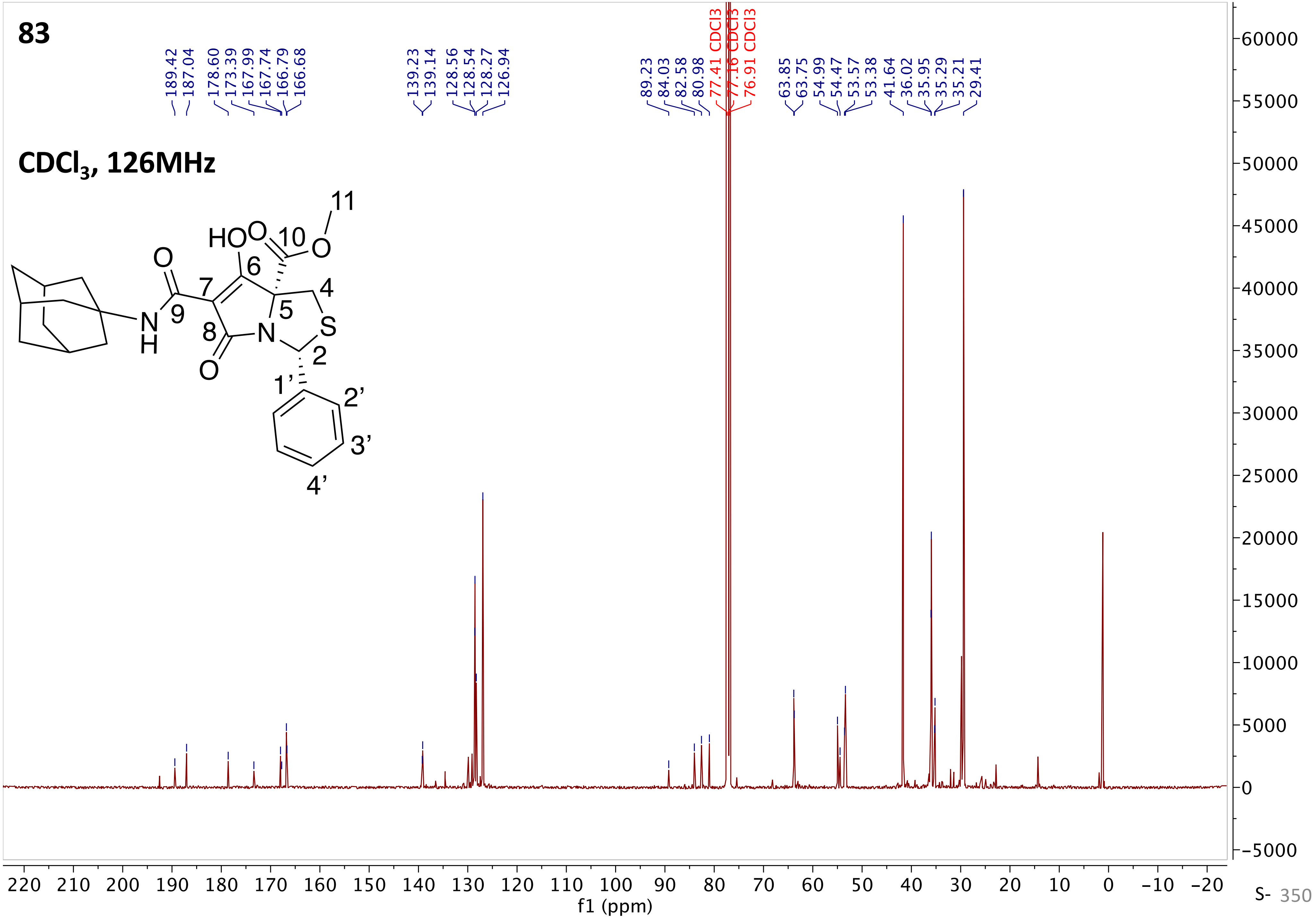
83

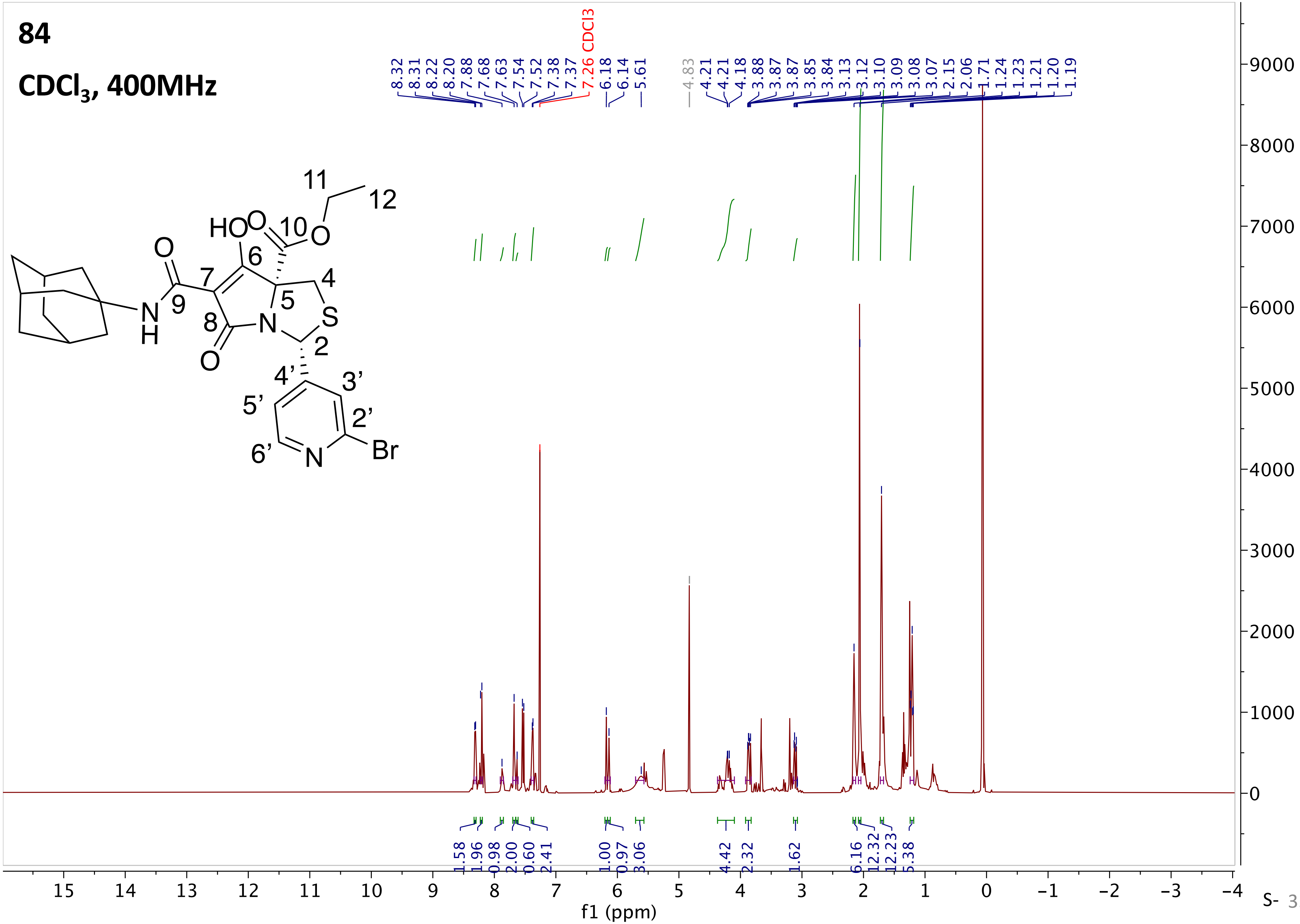
$CDCl_3$, 400MHz

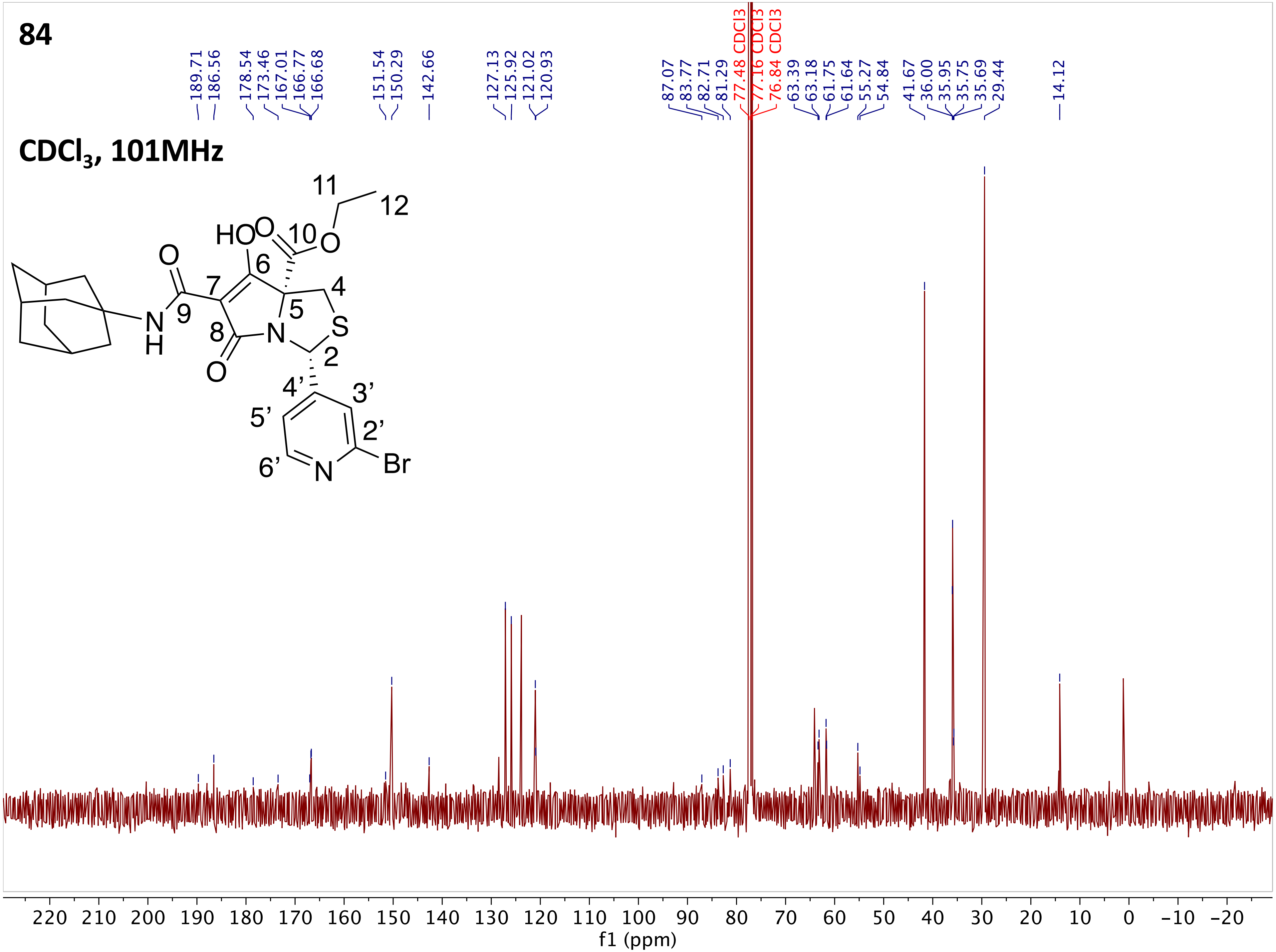


83

$CDCl_3$, 126MHz



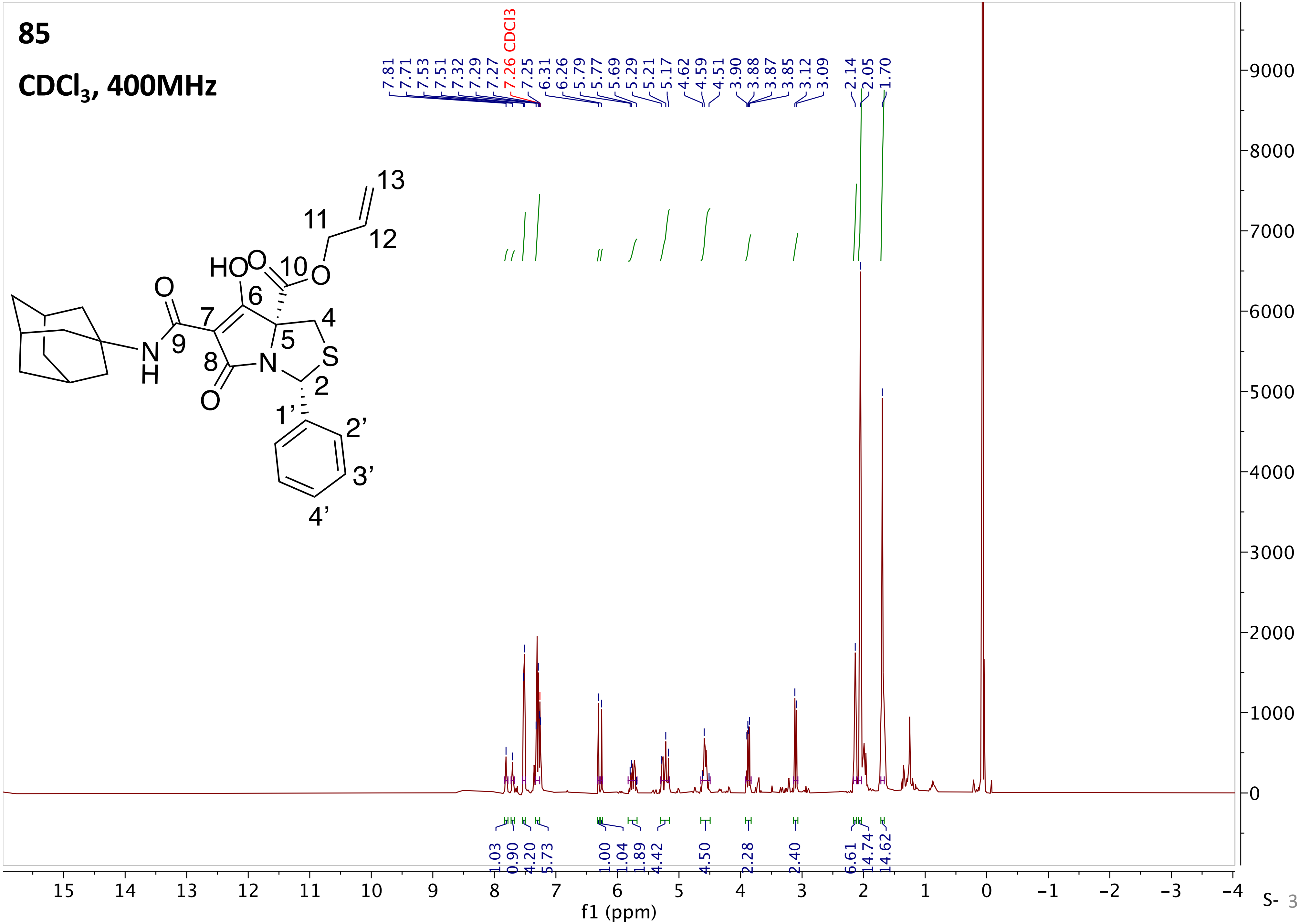

84
$CDCl_3$, 400MHz
11
12
HO
O
10
O
O
6
7
4
N
H
9
5
S
8
N
2
O
4'
3'
5'
2'
6'
N
Br
8.32
8.31
8.22
8.20
7.88
7.68
7.63
7.54
7.52
7.38
7.37
7.26 CDCl3
6.18
6.14
5.61
4.83
4.21
4.21
4.18
3.88
3.87
3.87
3.85
3.84
3.13
3.12
3.10
3.09
3.08
3.07
2.15
2.06
1.71
1.24
1.23
1.21
1.20
1.19
1.58
1.96
0.98
2.00
0.60
2.41
1.00
0.97
3.06
4.42
2.32
1.62
6.16
12.32
12.23
5.38
f1 (ppm)



84
CDCl3, 101MHz
189.71
186.56
178.54
173.46
167.01
166.77
166.68
151.54
150.29
142.66
127.13
125.92
121.02
120.93
87.07
83.77
82.71
81.29
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.39
63.18
61.75
61.64
55.27
54.84
41.67
36.00
35.95
35.75
35.69
29.44
14.12
f1 (ppm)

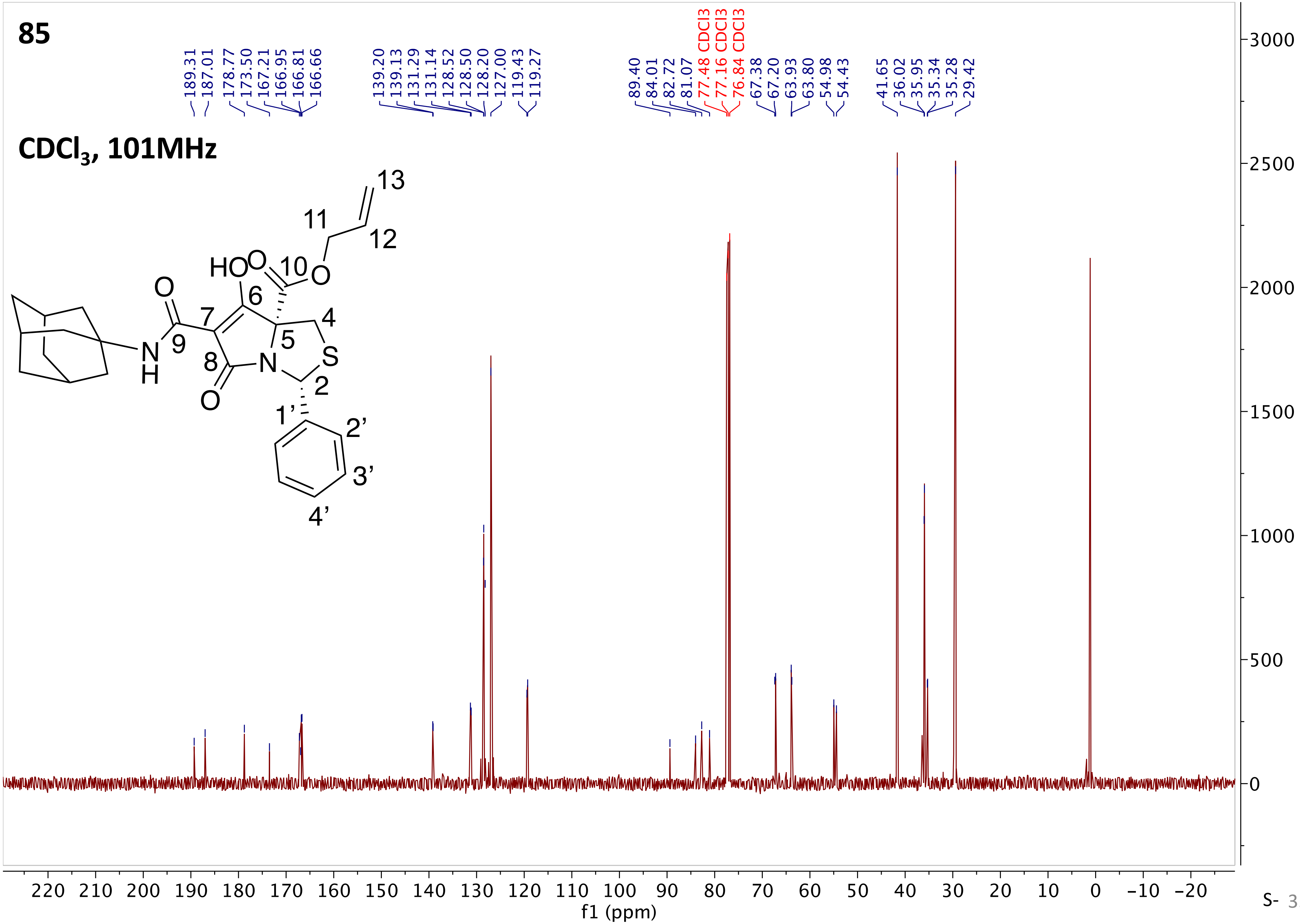
85

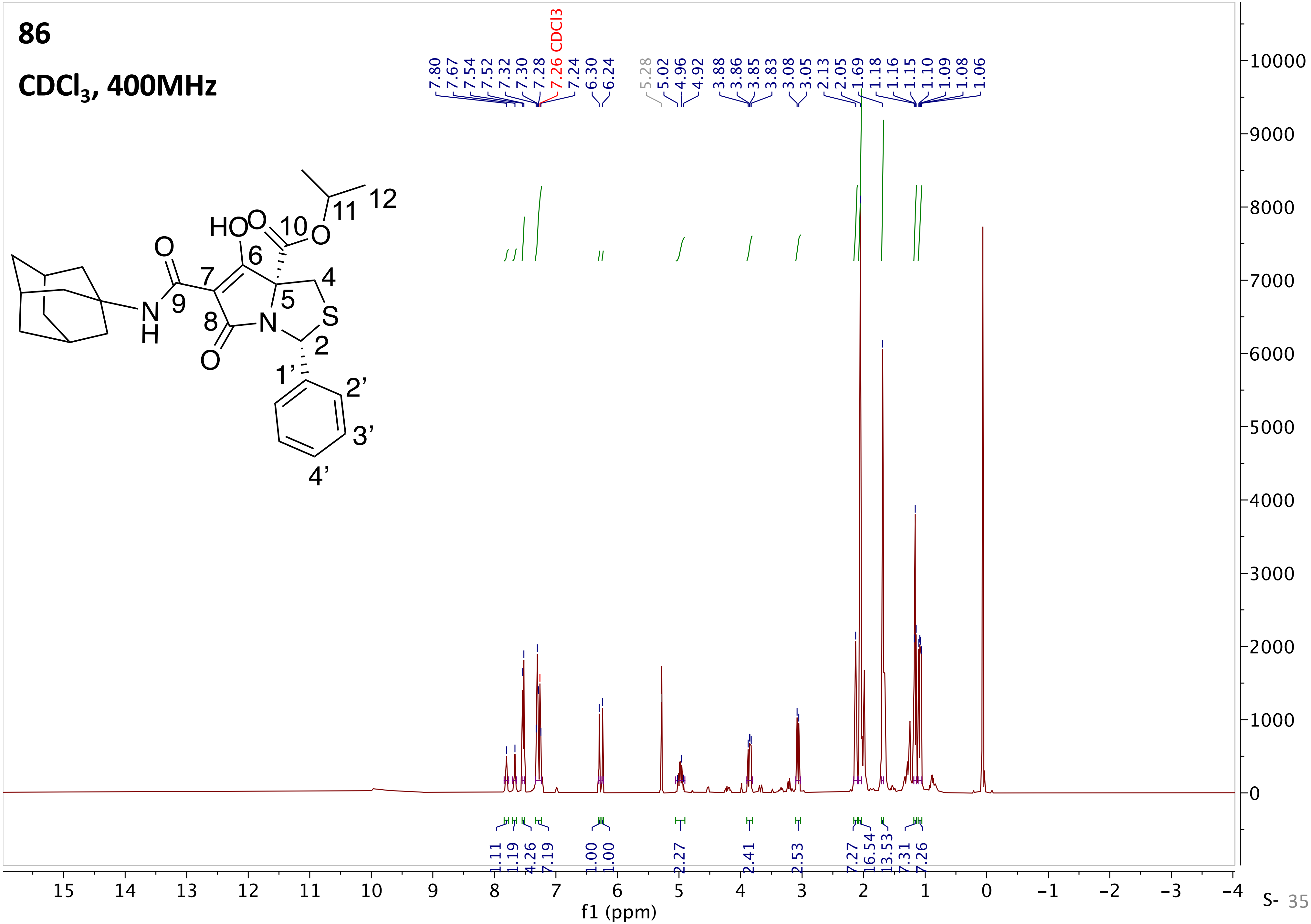
$CDCl_3$, 400MHz

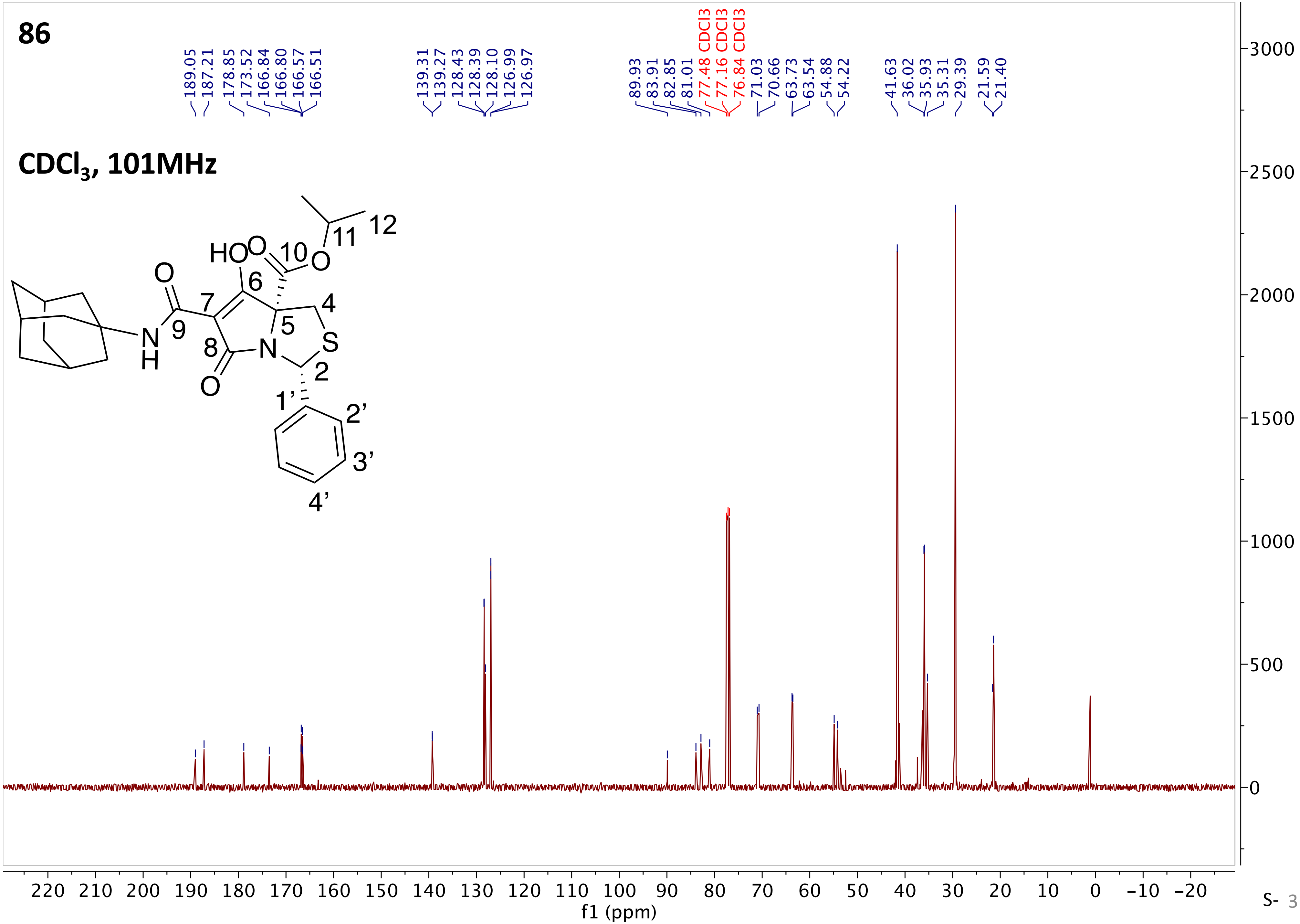


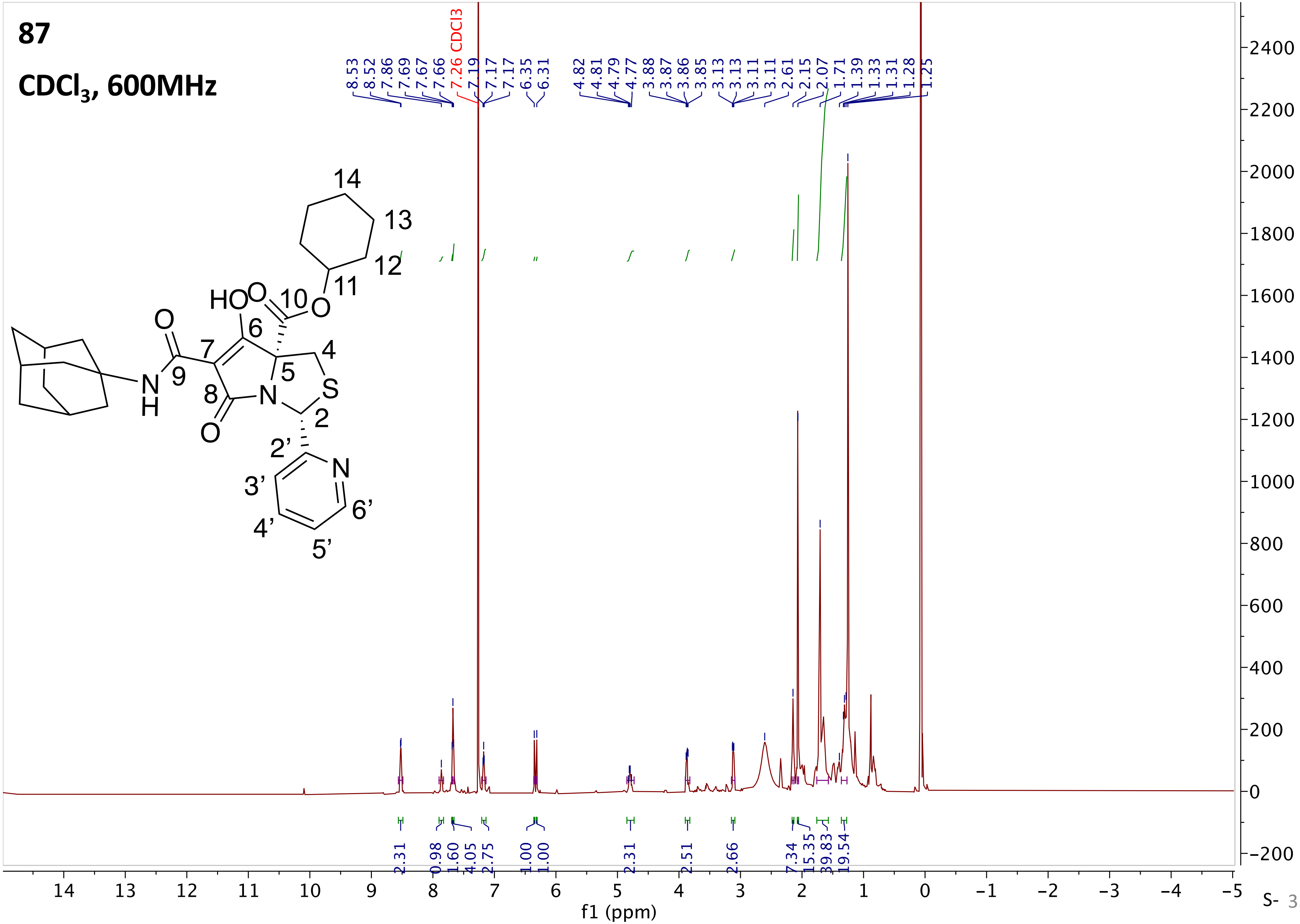
85

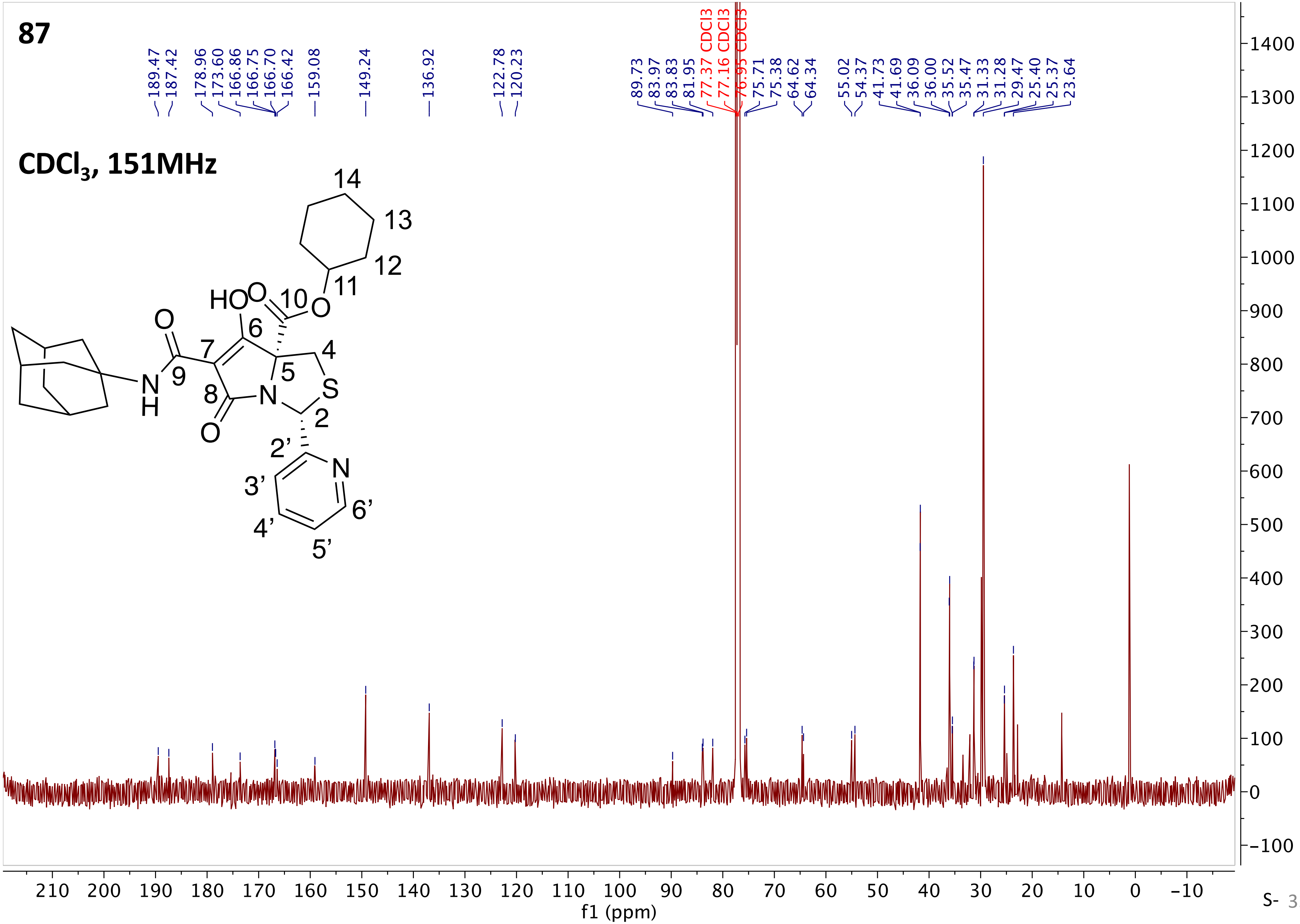
$CDCl_3$, 101MHz




86
CDCl3, 400MHz
7.80 7.67 7.54 7.52 7.32 7.30 7.28 7.26 CDCl3 7.24 6.30 6.24 5.28 5.02 4.96 4.92 3.88 3.86 3.85 3.83 3.08 3.05 2.13 2.05 1.69 1.18 1.16 1.15 1.10 1.09 1.08 1.06
1.11 1.19 4.26 7.19 1.00 1.00 2.27 2.41 2.53 7.27 16.54 13.53 7.31 7.26
HO O 10 O 11 12 O 7 6 4 9 N H 5 S 8 N 2 O 1' 2' 3' 4'
f1 (ppm)

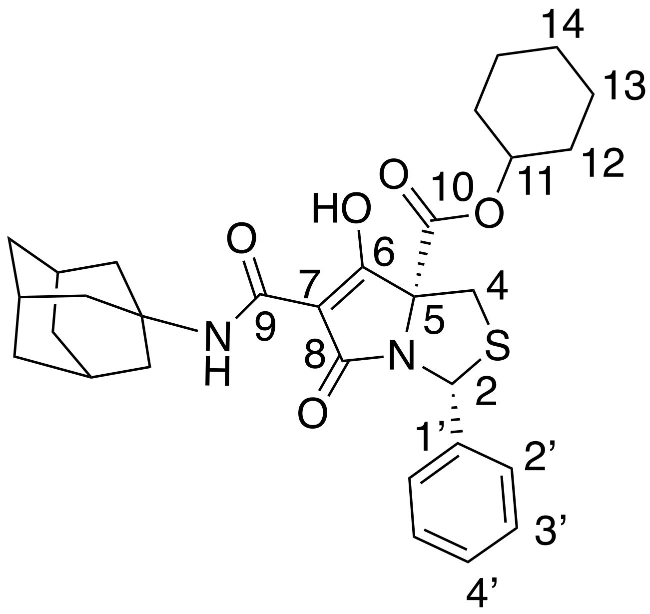

86
CDCl3, 101MHz
189.05
187.21
178.85
173.52
166.84
166.80
166.57
166.51
139.31
139.27
128.43
128.39
128.10
126.99
126.97
89.93
83.91
82.85
81.01
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.03
70.66
63.73
63.54
54.88
54.22
41.63
36.02
35.93
35.31
29.39
21.59
21.40
HO
O
10
O
11
12
6
4
O
7
5
S
N
9
8
N
H
2
O
1'
2'
3'
4'
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

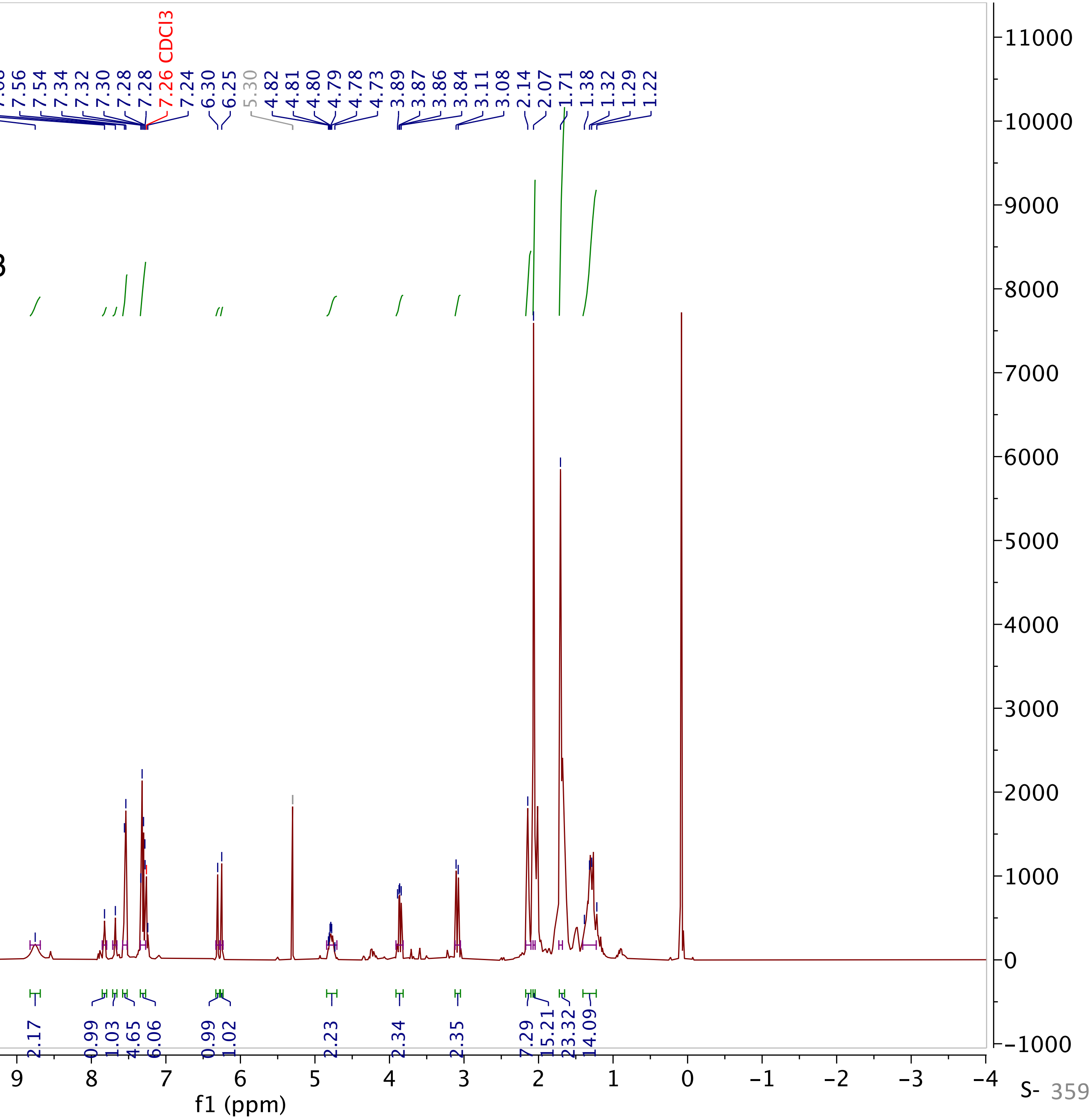

87
CDCl3, 600MHz
CDCl3
8.53
8.52
7.86
7.69
7.67
7.66
7.26
7.19
7.17
7.17
6.35
6.31
4.82
4.81
4.79
4.77
3.88
3.87
3.86
3.85
3.13
3.13
3.11
3.11
2.61
2.15
2.07
1.71
1.39
1.33
1.31
1.28
1.25
2.31
0.98
1.60
4.05
2.75
1.00
1.00
2.31
2.51
2.66
7.34
15.35
39.83
19.54
f1 (ppm)

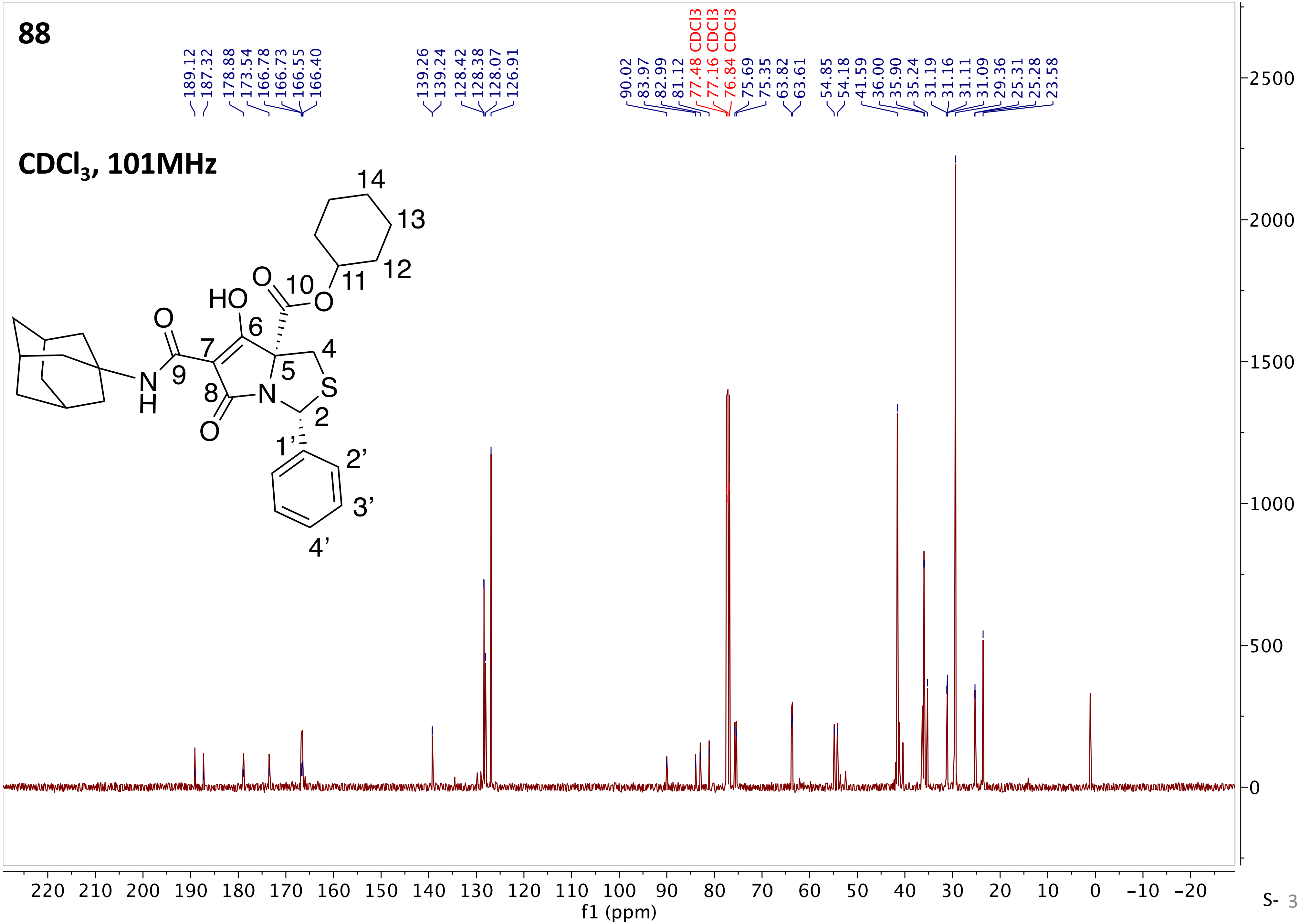

87
CDCl3, 151MHz
189.47
187.42
178.96
173.60
166.86
166.75
166.70
166.42
159.08
149.24
136.92
122.78
120.23
89.73
83.97
83.83
81.95
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
75.71
75.38
64.62
64.34
55.02
54.37
41.73
41.69
36.09
36.00
35.52
35.47
31.33
31.28
29.47
25.40
25.37
23.64
f1 (ppm)

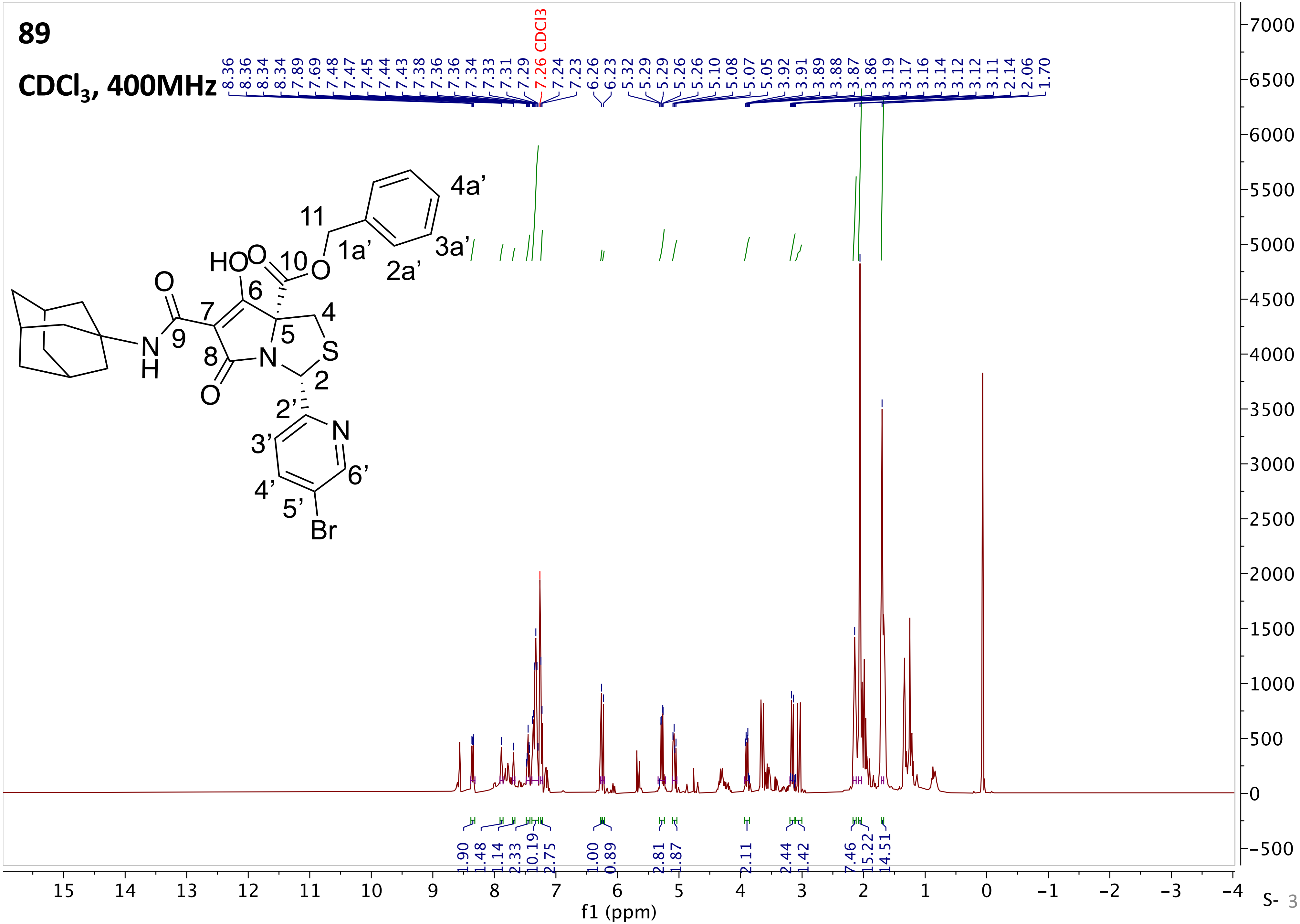
88

$CDCl_3$, 400MHz

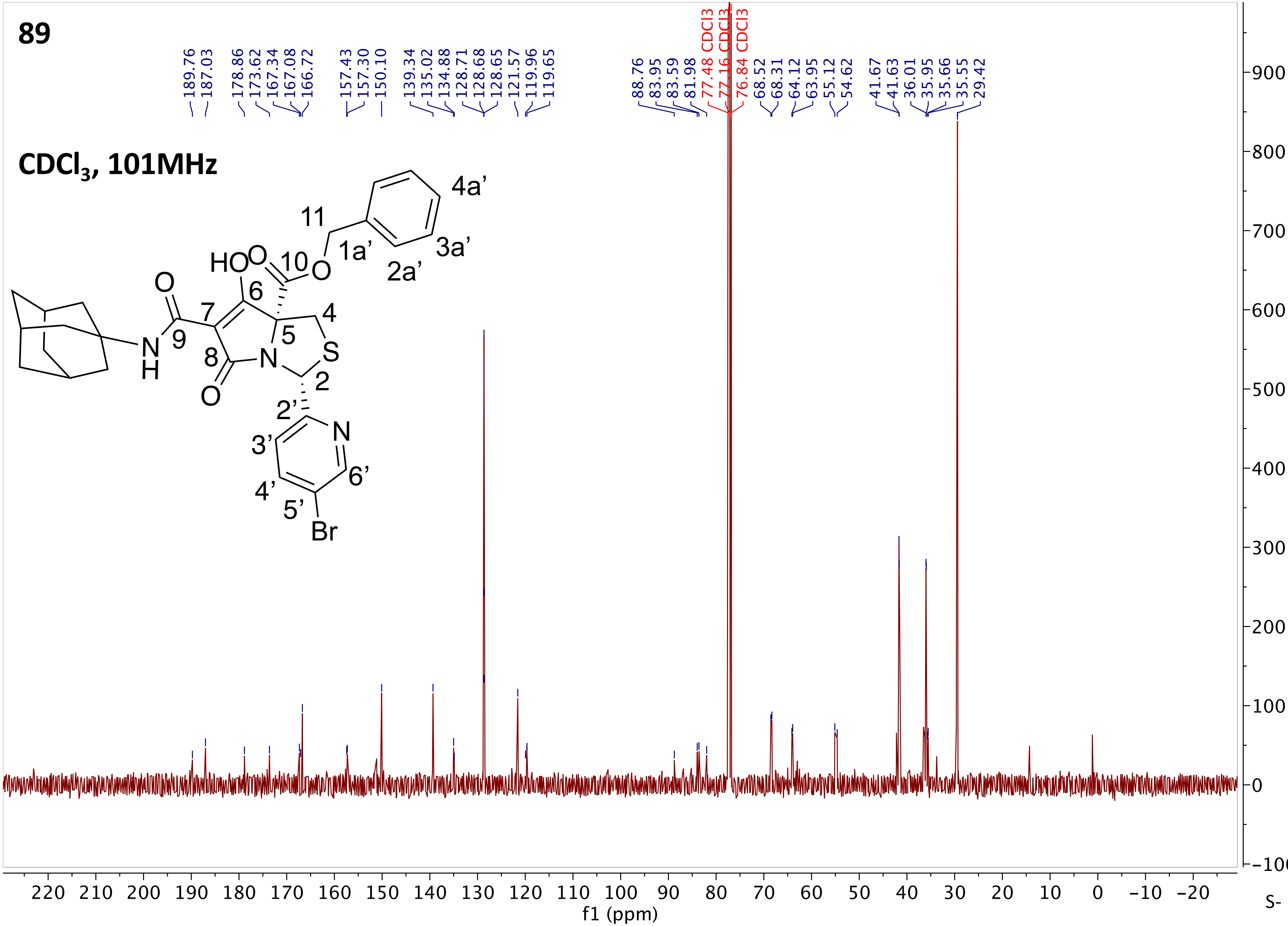




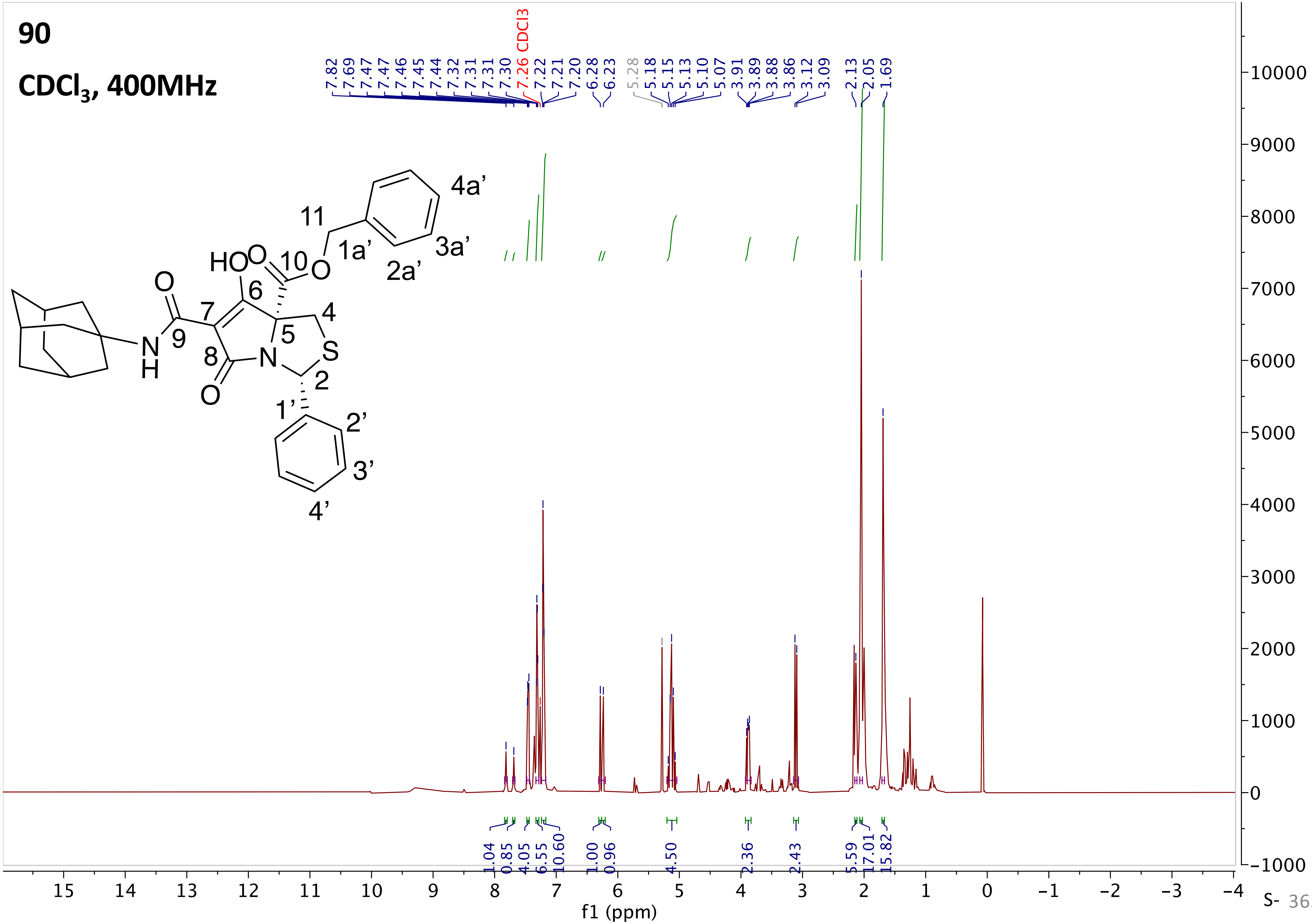

88
CDCl3, 101MHz
189.12
187.32
178.88
173.54
166.78
166.73
166.55
166.40
139.26
139.24
128.42
128.38
128.07
126.91
90.02
83.97
82.99
81.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.69
75.35
63.82
63.61
54.85
54.18
41.59
36.00
35.90
35.24
31.19
31.16
31.11
31.09
29.36
25.31
25.28
23.58
f1 (ppm)

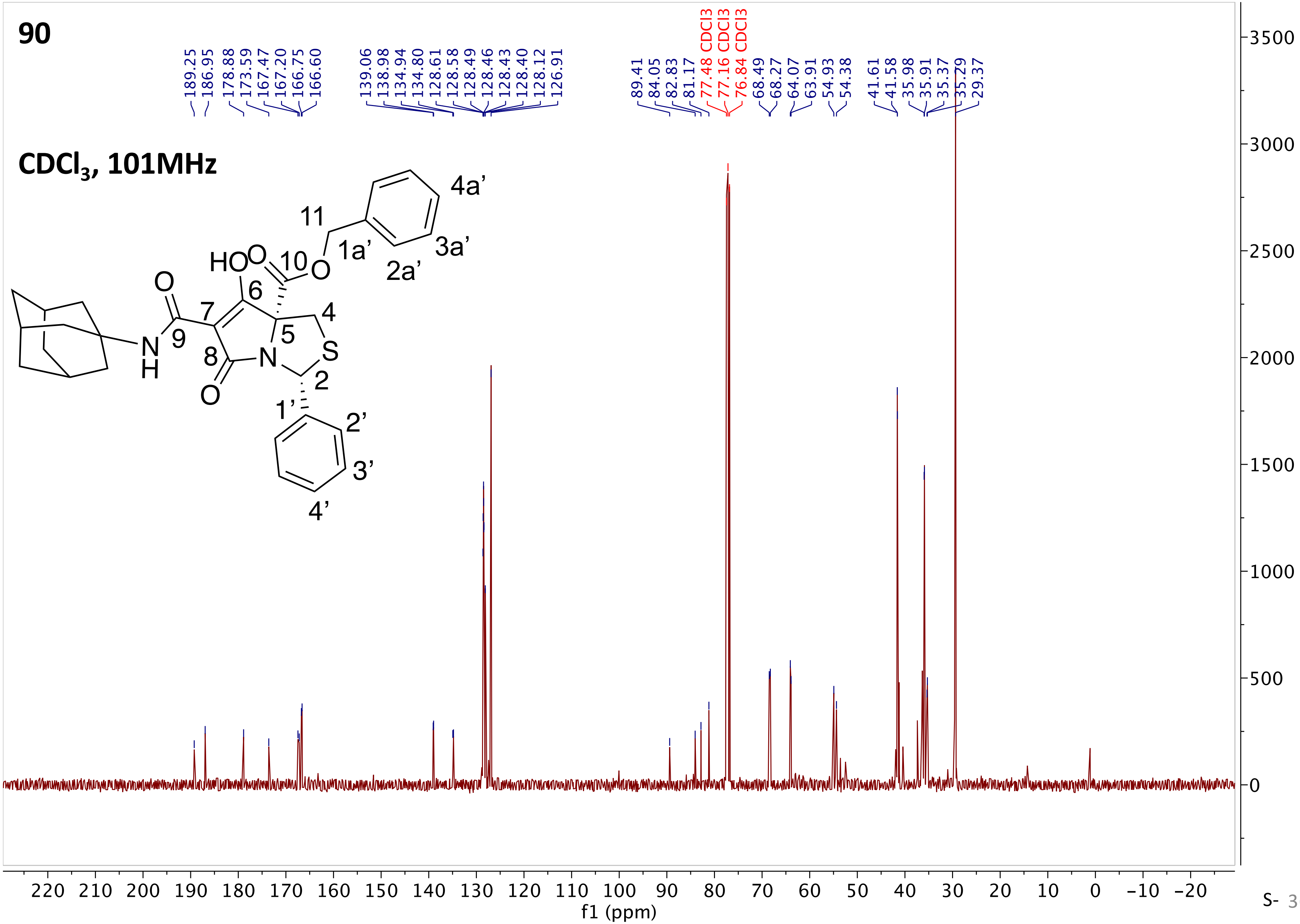


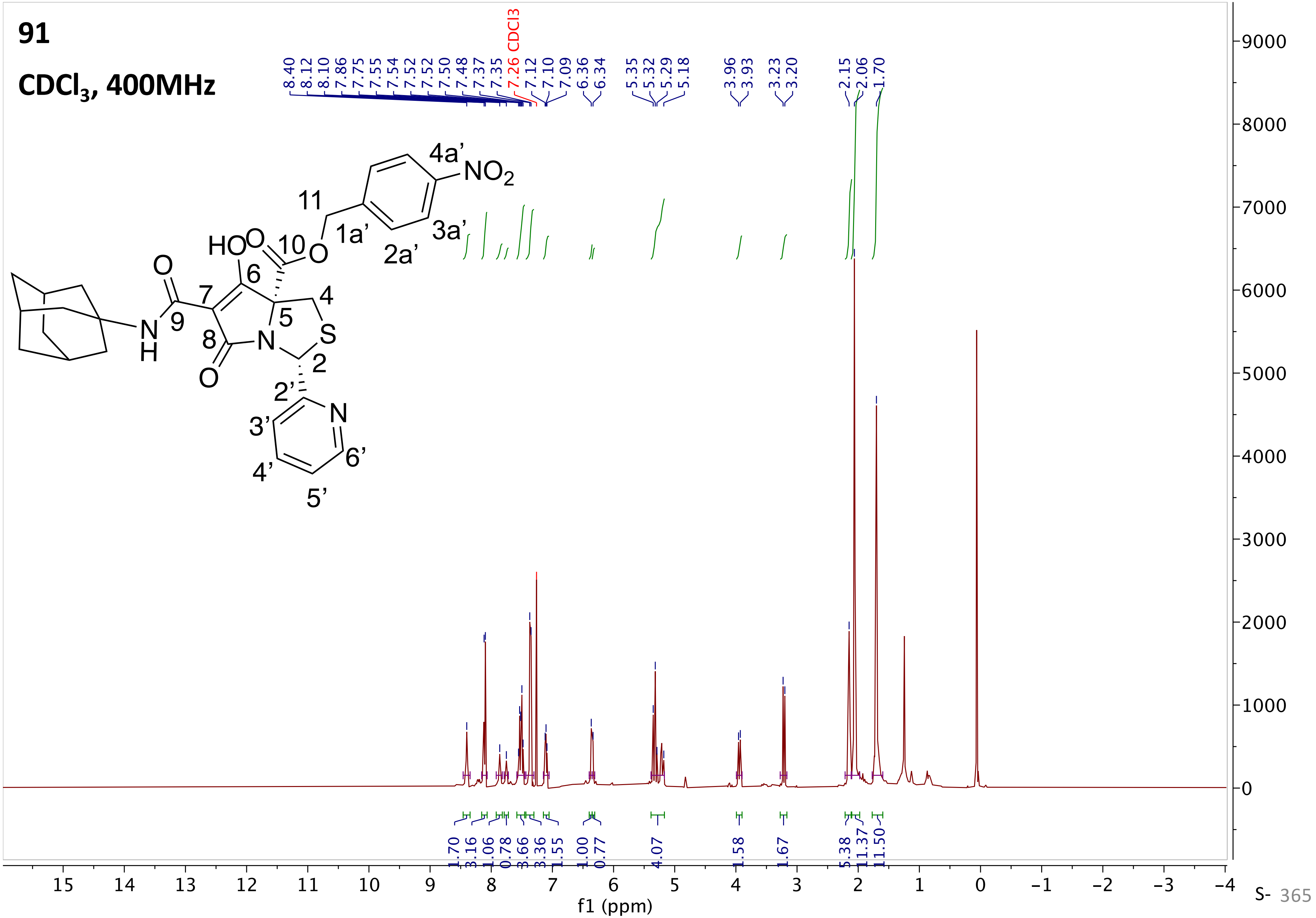
89
CDCl3, 400MHz
8.36 8.36 8.34 8.34 7.89 7.69 7.48 7.47 7.45 7.44 7.43 7.38 7.36 7.36 7.34 7.33 7.31 7.29 7.26 CDCl3 7.24 7.23 6.26 6.23 5.32 5.29 5.29 5.26 5.26 5.10 5.08 5.07 5.05 3.92 3.91 3.89 3.88 3.87 3.86 3.19 3.17 3.16 3.14 3.12 3.12 3.11 2.14 2.06 1.70
1.90 1.48 1.14 2.33 10.19 2.75 1.00 0.89 2.81 1.87 2.11 2.44 1.42 7.46 15.22 14.51
f1 (ppm)



89
CDCl3, 101MHz
189.76
187.03
178.86
173.62
167.34
167.08
166.72
157.43
157.30
150.10
139.34
135.02
134.88
128.71
128.68
128.65
121.57
119.96
119.65
88.76
83.95
83.59
81.98
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.52
68.31
64.12
63.95
55.12
54.62
41.67
41.63
36.01
35.95
35.66
35.55
29.42
f1 (ppm)

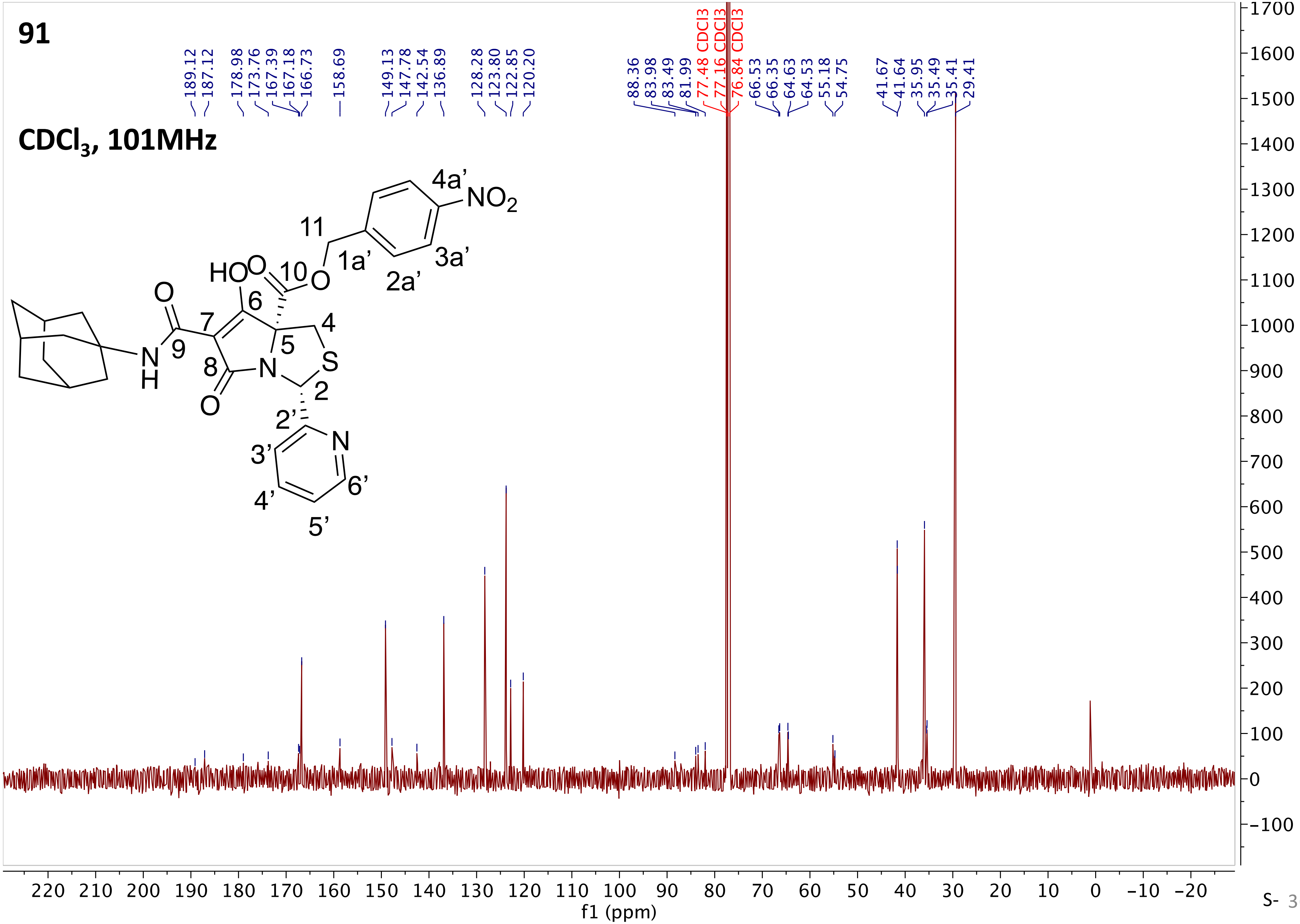

90
CDCl3, 400MHz
7.82 7.69 7.47 7.47 7.46 7.45 7.44 7.32 7.31 7.31 7.30 7.26 CDCl3 7.22 7.21 7.20 6.28 6.23 5.28 5.18 5.15 5.13 5.10 5.07 3.91 3.89 3.88 3.86 3.12 3.09 2.13 2.05 1.69
1.04 0.85 4.05 6.55 10.60 1.00 0.96 4.50 2.36 2.43 5.59 17.01 15.82
f1 (ppm)

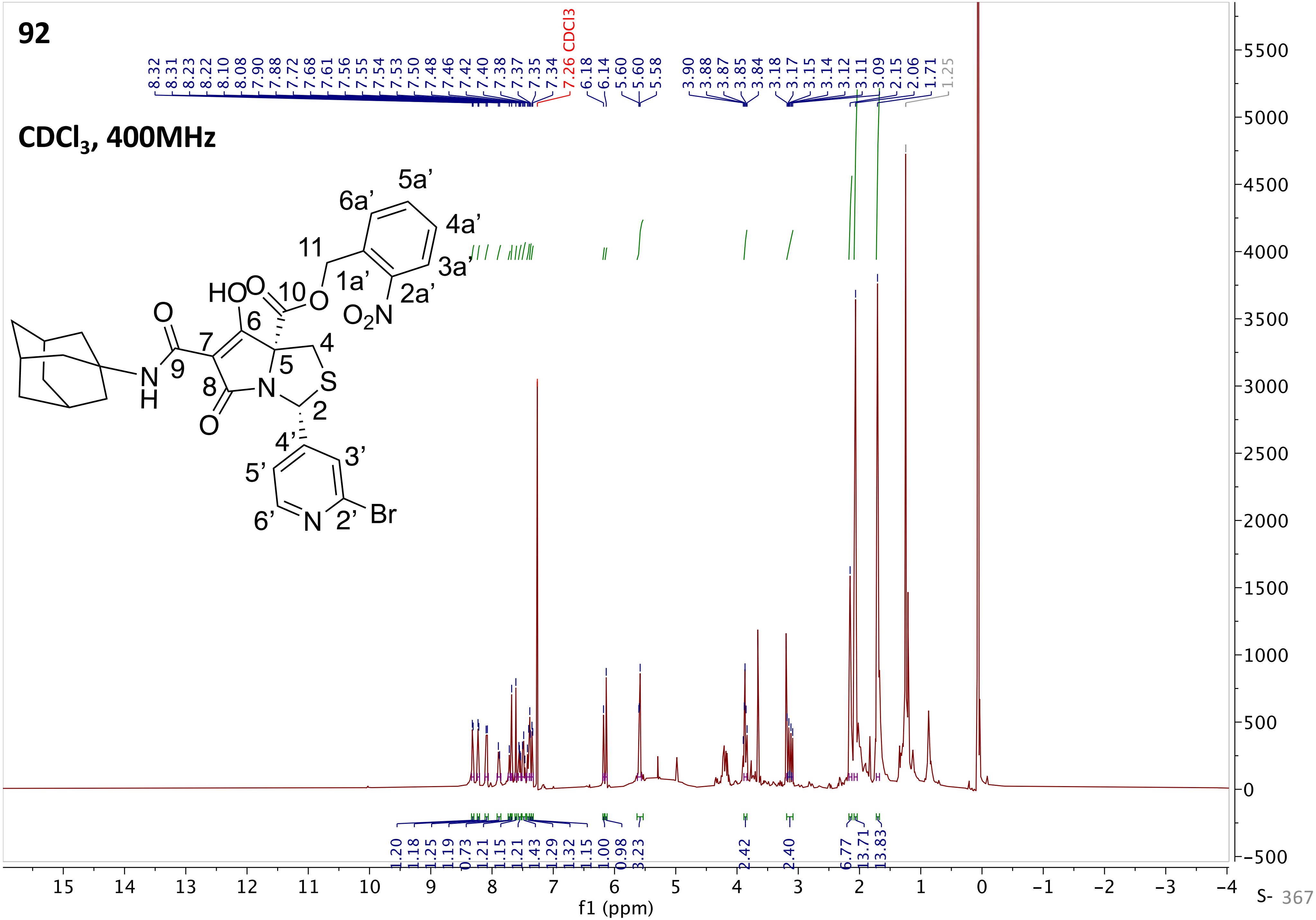

90
CDCl3, 101MHz
189.25
186.95
178.88
173.59
167.47
167.20
166.75
166.60
139.06
138.98
134.94
134.80
128.61
128.58
128.49
128.46
128.43
128.40
128.12
126.91
89.41
84.05
82.83
81.17
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.49
68.27
64.07
63.91
54.93
54.38
41.61
41.58
35.98
35.91
35.37
35.29
29.37
f1 (ppm)


91
CDCl3, 400MHz
8.40 8.12 8.10 7.86 7.75 7.55 7.54 7.52 7.52 7.50 7.48 7.37 7.35 7.26 CDCl3 7.12 7.10 7.09 6.36 6.34 5.35 5.32 5.29 5.18 3.96 3.93 3.23 3.20 2.15 2.06 1.70
1.70 3.16 1.06 0.78 3.66 3.36 1.55 1.00 0.77 4.07 1.58 1.67 5.38 11.37 11.50
f1 (ppm)

91

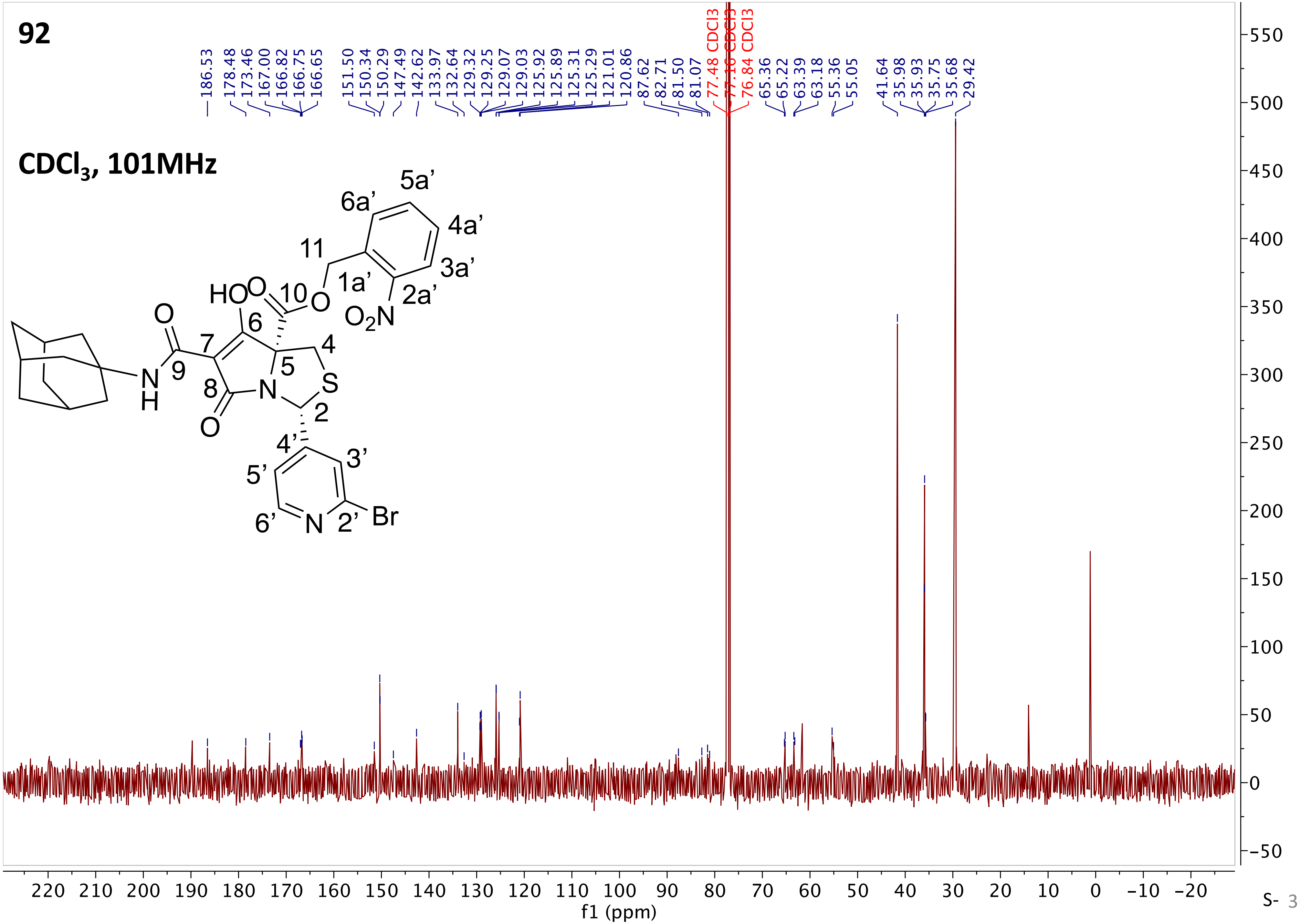
$CDCl_3$, 101MHz




92
CDCl3, 400MHz
8.32 8.31 8.23 8.22 8.10 8.08 7.90 7.88 7.72 7.68 7.61 7.56 7.55 7.54 7.53 7.50 7.48 7.46 7.42 7.40 7.38 7.37 7.35 7.34 7.26 CDCl3 6.18 6.14 5.60 5.60 5.58 3.90 3.88 3.87 3.85 3.84 3.18 3.17 3.15 3.14 3.12 3.11 3.09 2.15 2.06 1.71 1.25
1.20 1.18 1.25 1.19 0.73 1.21 1.15 1.21 1.43 1.29 1.32 1.15 1.00 0.98 3.23 2.42 2.40 6.77 13.71 13.83
f1 (ppm)

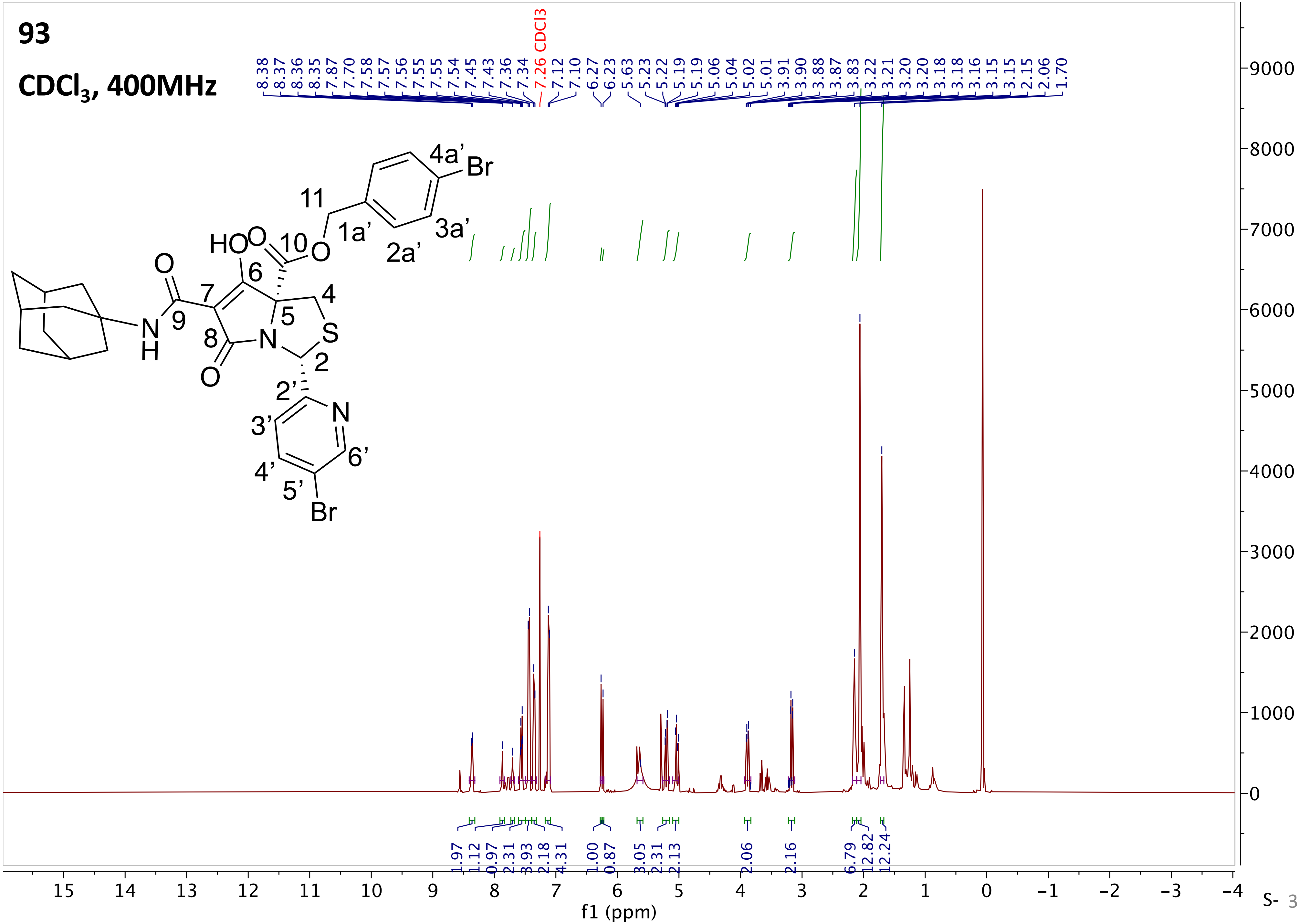
92

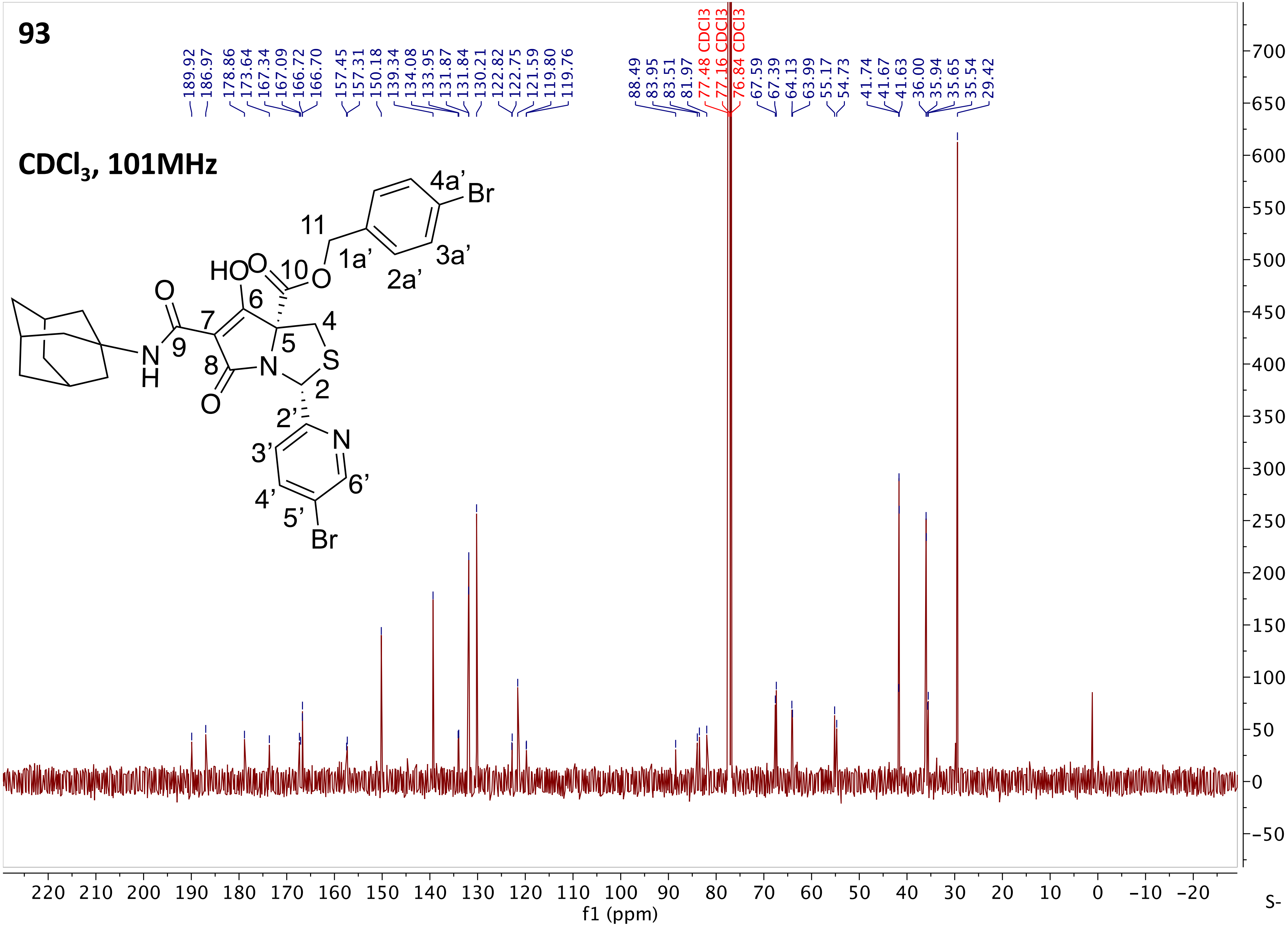
CDCl$_3$, 101MHz



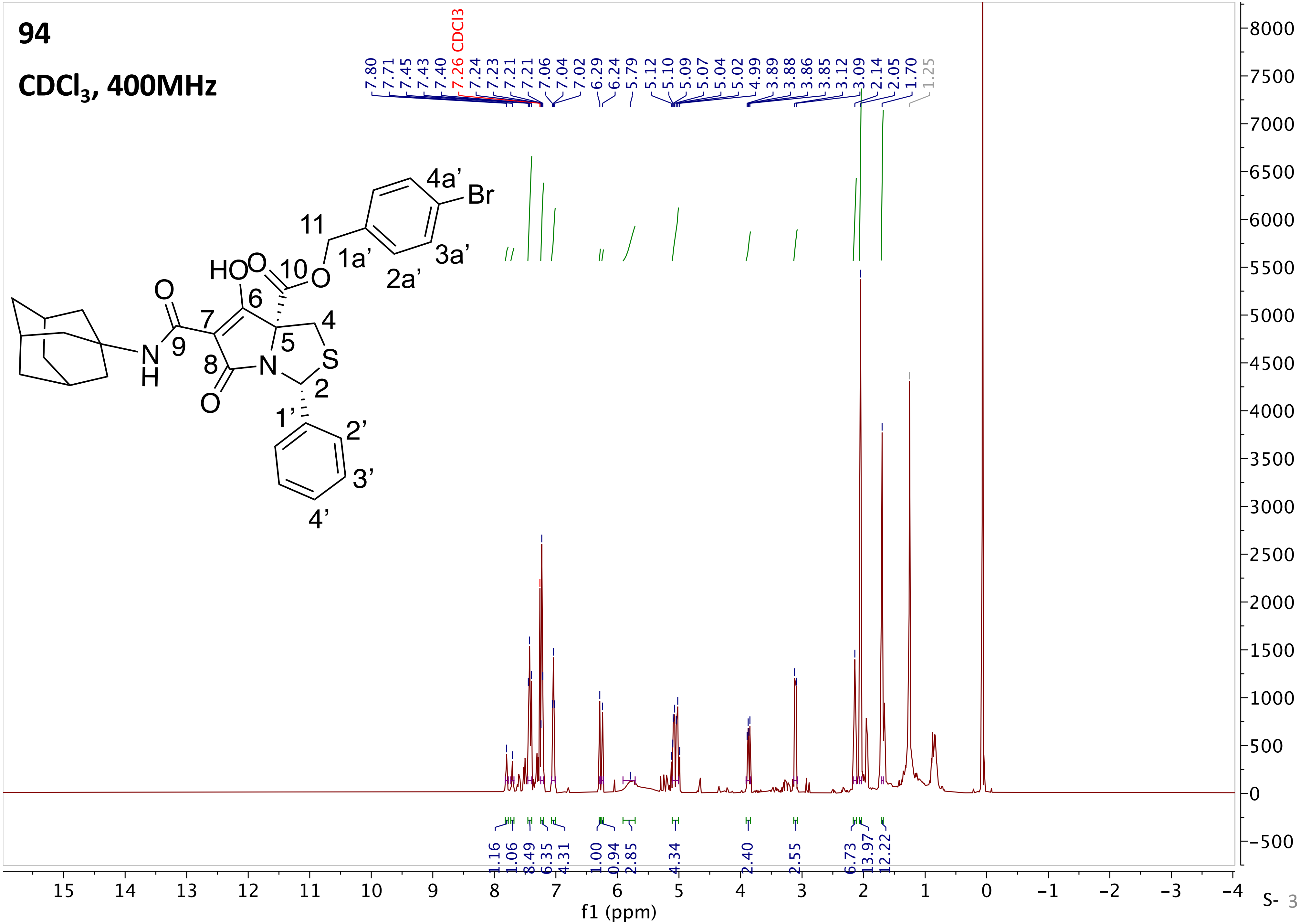
93

$CDCl_3$, 400MHz





93
CDCl3, 101MHz
189.92
186.97
178.86
173.64
167.34
167.09
166.72
166.70
157.45
157.31
150.18
139.34
134.08
133.95
131.87
131.84
130.21
122.82
122.75
121.59
119.80
119.76
88.49
83.95
83.51
81.97
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.59
67.39
64.13
63.99
55.17
54.73
41.74
41.67
41.63
36.00
35.94
35.65
35.54
29.42
f1 (ppm)


94
CDCl3, 400MHz
7.80 7.71 7.45 7.43 7.40 7.26 CDCl3 7.24 7.23 7.21 7.21 7.06 7.04 7.02 6.29 6.24 5.79 5.12 5.10 5.09 5.07 5.04 5.02 4.99 3.89 3.88 3.86 3.85 3.12 3.09 2.14 2.05 1.70 1.25
1.16 1.06 8.49 6.35 4.31 1.00 0.94 2.85 4.34 2.40 2.55 6.73 13.97 12.22
HO O 10 O 11 1a' 2a' 3a' 4a' Br
O 9 N H 7 6 5 4 S 2 N 8 O 1' 2' 3' 4'
f1 (ppm)

94

$CDCl_3$, 101MHz