

Synthesis of Functionalized Spirocyclic Oxetanes through Paternò-Büchi Reactions of Cyclic Ketones and Maleic Acid Derivatives

Supporting Information

Double-Anonymous Submission

1. Synthetic Procedures and Analytical Data of New Compounds	- 2 -
1.1 General Information	- 2 -
1.2. Optimization reactions	- 3 -
1.3. General Procedure	- 12 -
1.4. Synthetic procedures	- 13 -
2. Crystal structures	- 34 -
3. References	- 35 -
4. ^1H / ^{13}C NMR Spectra of New Compounds	- 36 -

1. Synthetic Procedures and Analytical Data of New Compounds

1.1 General Information

Reagents were purchased in the highest purity available from Acros Organics, Alfa Aesar or Sigma Aldrich. Anhydrous solvents used in reactions were purchased from Acros Organics equipped with AcroSeal™ and all other solvents used were of reagent grade. Reaction vessels were oven dried and cooled under an argon atmosphere prior to use and experiments were performed under argon gas. Reactions were monitored by thin-layer chromatography (TLC) and/or ¹H NMR spectroscopic analysis.

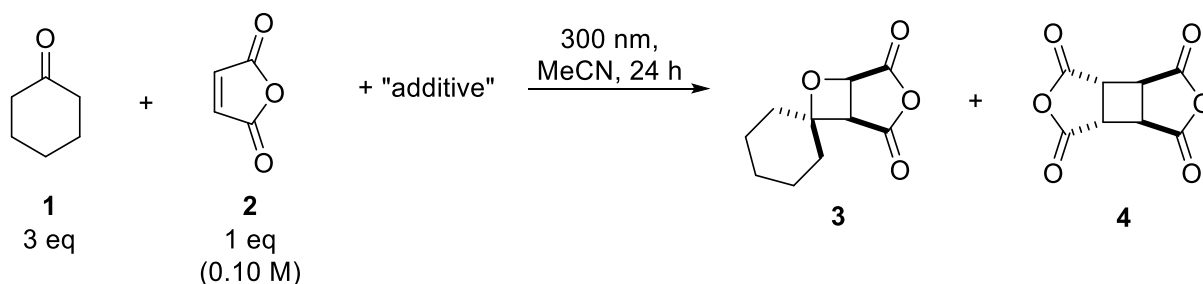
Photochemical reactions were performed in Duran phototubes (20-mL or 50-mL volume) using a Rayonet RPR-100 photochemical batch reactor equipped with 16 lamps (300 nm). When operating, the approximate temperature inside the reactor chamber is 40 °C. Flow reactions were performed using Vapourtec UV-150 photochemical reactor. Steady state emission and excitation spectra were recorded on an Agilent Technologies Cary Eclipse spectrophotometer.

Analytical TLC was carried out using Merck pre-coated aluminium-backed TLC silica gel plates (silica gel 60 F₂₅₄) and the plates were visualised by UV light (254 nm) and by staining with either potassium permanganate or *p*-anisaldehyde stain (a solution of concentrated H₂SO₄ (5 mL), glacial acetic acid (1.5 mL) and *p*-anisaldehyde (3.7 mL) in absolute ethanol (135 mL); prepared with vigorous stirring). Most oxetanes were visualized using the *p*-anisaldehyde stain, showing as a dark blue spot. Normal phase flash column chromatography on silica gel was carried out using silica gel from VWR (40-63 microns).

¹H NMR spectroscopic data were obtained on either 300 or 400 MHz instruments and ¹³C{¹H} NMR data were obtained at 101 MHz (Bruker Ultrashield 400 Plus) at 298 K unless otherwise specified. The chemical shifts are reported in parts per million (δ) relative to residual CHCl₃ (δ_H = 7.26 ppm) and CDCl₃ (δ_C = 77.2 ppm, central line), residual d₅-DMSO (δ_H = 2.50 ppm) and d₆-DMSO (δ_C = 39.5 ppm, central line), residual C₆D₆ (δ_H = 7.16 ppm) and (δ_C = 128.1 ppm), residual CHD₂CN (δ_H = 1.93 ppm) and CD₃CN (δ_C = 1.3 ppm). The assignment of the signals in the ¹H and ¹³C NMR spectra was achieved through 2D-NMR techniques: COSY, HSQC and HMBC. Coupling constants (*J*) are quoted in Hertz. Infrared spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrometer. Melting points were performed on a Sanyo Gallenkamp capillary melting point apparatus and are uncorrected. High resolution mass spectrometry data were recorded using electron spray ionization (ESI) or atmospheric pressure chemical ionization (APCI) on a Shimadzu LCMS-IT-TOF mass spectrometer. UV/Vis spectra were recorded using an Agilent Cary 60 UV-Vis spec spectrophotometer. For X-ray crystallography, a suitable crystal was selected and mounted on a Mitegen loop using Paratone-N oil on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.2(5) K during data collection. Using Olex2,¹ the structure was solved with the ShelXT structure solution program using direct methods and refined with the ShelXL refinement package using least squares minimisation.^{2,3} Figures and tables were prepared using Olex2 software.¹

1.2. Optimization reactions

1.2.1. Table S1: Effect of additives and wavelengths on the Paternò-Büchi reaction of cyclohexanone and maleic anhydride



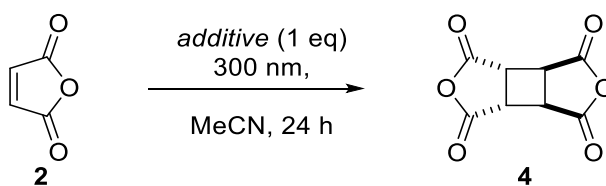
A solution of maleic anhydride (98 mg, 1.00 mmol), cyclohexanone (0.32 mL, 3.00 mmol) and additive in anhydrous MeCN (10 mL) was purged with argon for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300\ nm$). The reaction was stopped after 24 h and the consumption of maleic anhydride was calculated by 1H NMR spectroscopy (solvent suppression).

Additive	Eq.	Wavelength (nm)	2 (%)	3 (%)	4 (%)	E(S) and E(T) of additive (nm)	Conversion of 2 into	
							3 (%)	4 (%)
-	-	250	96	3	1	-	3	1
-	-	300	0	75	25	-	60	40
-	-	350	99	0	1	-	0	1
-	-	365	100	0	0	-	0	0
-	-	385	100	0	0	-	0	0
no cyclohexanone	-	300	79	-	21	-	0	42
<i>p</i> -methoxybenzophenone	1	300	24	0	61	E(S) = 285 ⁴ ; E(T) = 414	0	76
<i>p</i> -dicyanobenzene	1	300	60	31	9	E(S) = 290; E(T) = 406	29	11
benzophenone	1	300	94	6	0	E(S) = 384; E(T) = 413	6	0
	0.1	300	66	26	4		25	8
	1	365	100	0	0		0	0
	0.5	365	100	0	0		0	0
	1	385	100	0	0		0	0
	0.5	385	100	0	0		0	0
<i>p</i> -tolunitrile	1	300	59	40	1	E(S) = 278; E(T) = 378	39	2
5-phenyl-1H-tetrazole	1	300	61	36	1	E(S) = 270 ⁵ ; E(T) = 360	35	2
	1	350	100	0	0		0	0
	1	365	100	0	0		0	0

	1	385	100	0	0		0	0
xanthone	1	350	100	0	0	E(S) = 368; E(T) = 386	0	0
Anisole	1	300	31	12	43	E(S) = 278; E(T) = 354	9	60
<i>p</i> -Xylene	1	254	95	5	0	E(S) = 274; E(T) = 355	5	0
	1	300	65	34	1		34	1
	1	365	100	0	0		0	0
	1	385	100	0	0		0	0
Toluene	1	300	66	33	1	E(S) = 269; E(T) = 345	33	1
	1	254	96	3	1		3	1
Fluorobenzene	1	300	64	35	1	E(S) = 266; E(T) = 341	35	1
	1	254	96	4	0		4	0
<i>p</i> -Xylene ^a	1	300	0	97	3	E(S) = 274; E(T) = 355	95	5

Table S1^a = 72 h irradiation.

1.2.2. Table S2: Effect of additives on reagents

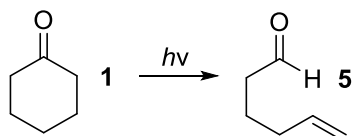


A solution of maleic anhydride (98 mg, 1.00 mmol) and additive (1.00-3.00 mmol) in anhydrous MeCN (10 mL) was purged with argon for 15 minutes, then irradiated at room temperature ($\lambda = 300$ nm). The reaction was stopped at 24 h and the consumption of maleic anhydride was judged by ¹H NMR spectroscopy (solvent suppression).

Additive	Eq. of additive	2 (%)	4 (%)
4,4-dichlorobenzophenone	1	93	7
4-fluorobenzophenone	1	98	2
Benzophenone	1	100	0
4-methoxybenzophenone	1	23	77
<i>p</i> -dicyanobenzene	1	79	21
<i>m</i> -tolunitrile	1	96	4
<i>p</i> -tolunitrile	1	98	2
<i>o</i> -tolunitrile	1	96	4
anisole	1	24	76
4-acetylpyridine	1	94	6
phenyl-tetrazole	1	97	3
1,4-dichlorobenzene	1	97	3
<i>p</i> -xylene	1	99	1
<i>p</i> -xylene	3	99	1
toluene	1	98	2

-	0	79	21
---	---	----	----

Table S2A: Amount of polymer product was not determined (an internal standard may interfere with the reaction)..

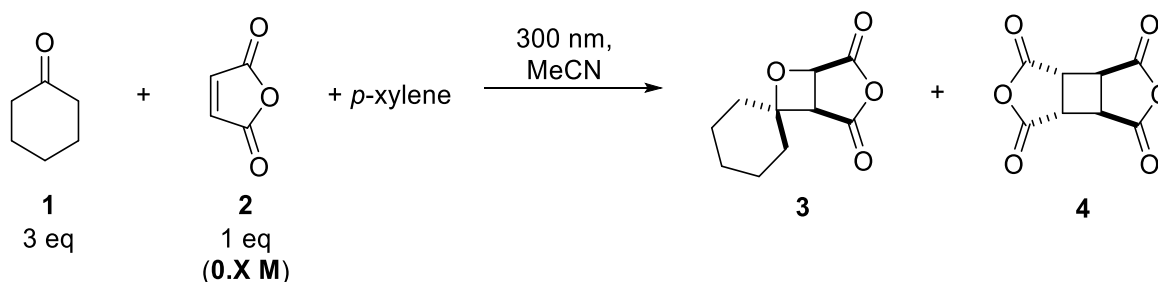


A solution of cyclohexanone (0.32 mL, 3.00 mmol) and additive (0.33 - 1 mmol) in anhydrous MeCN (10 mL) was purged with argon for 15 minutes, then irradiated at room temperature ($\lambda = 300$ nm). The reaction was stopped at 24 h and the consumption of maleic anhydride was judged by ^1H NMR spectroscopy (solvent suppression).

Additive	Eq. of additive	5 (%)	1 (%)
<i>m</i> -tolunitrile	1	1%	99
<i>p</i> -tolunitrile	1	6%	94
<i>p</i> -xylene	0.33	6%	94
<i>p</i> -xylene	1	3%	97
<i>p</i> -xylene	2	1%	99
-	0	9%	91

Table S2B

1.2.3. Table S3 – Effect of concentration on the Paternò-Büchi reaction with 1 eq. of *p*-xylene

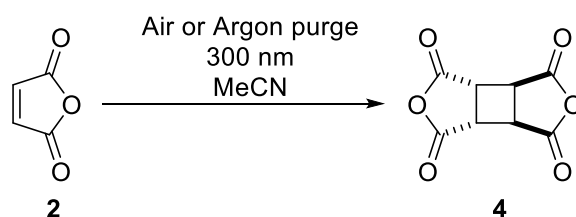


A solution of maleic anhydride (98 mg, 1.00 mmol), cyclohexanone (0.32 mL, 3.00 mmol) and *p*-xylene (0.12 mL, 1.00 mmol) in anhydrous MeCN was purged with argon for 15 minutes, then irradiated at room temperature ($\lambda = 300$ nm) until complete consumption of the maleic anhydride as judged by ^1H NMR spectroscopy (solvent suppression).

2 [M]	Reaction time (h)	3 (%)	4 (%)
0.16	86	98	2
0.14	120	98	2
0.12	86	98	2
0.1	86	97	3
0.08	72	98	2
0.06	72	98	3
0.04	60	96	4
0.02	48	93	7

Table S 3 Amount of polymer product was not determined (an internal standard may interfere with the reaction).

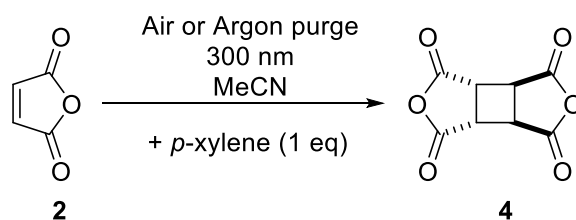
1.2.4. Table S4 - Testing reaction under oxygen atmosphere



A solution of maleic anhydride (98 mg, 1.00 mmol) in anhydrous MeCN (0.10 M, 10 mL) was prepared in a Duran phototube and purged with argon or air for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm), the reactions were tracked by ^1H NMR spectroscopy (solvent suppression).

Time (h)	Argon purge		Air purge	
	% MA	% dimer	% MA	% dimer
2	97	3	98	2
4	94	6	97	3
6	93	7	95	5
8	91	9	93	7
10	90	10	92	8
12	88	12	90	10
24	81	19	82	18

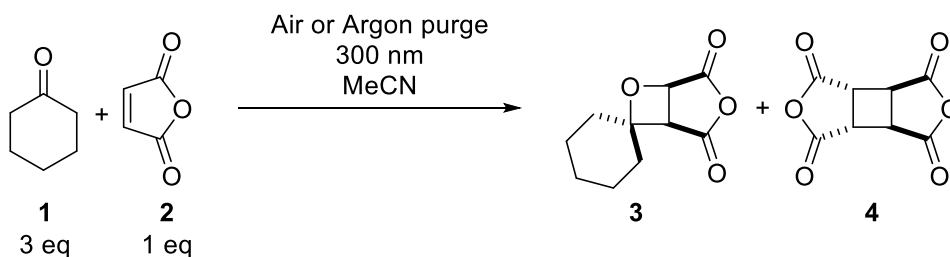
Table S4A



A solution of maleic anhydride (98 mg, 1.00 mmol) and *p*-xylene (0.12 mL, 1.00 mmol) in anhydrous MeCN (0.10 M, 10 mL) was prepared in a Duran phototube and purged with argon or air for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm), the reactions were tracked by ^1H NMR spectroscopy (solvent suppression).

Time (h)	Argon purge		Air purge	
	% MA	% dimer	% MA	% dimer
2	100	0	100	0
4	100	0	100	0
6	100	0	100	0
8	100	0	100	0
10	100	0	100	0
12	100	0	100	0
24	100	0	100	0

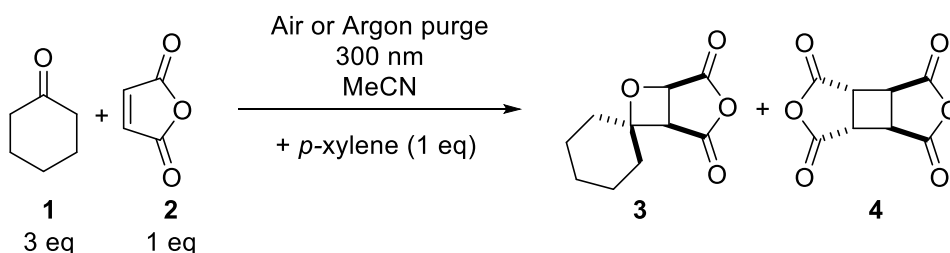
Table S4B



A solution of maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3 mmol) in anhydrous MeCN (0.10 M, 10 mL) was prepared in a Duran phototube and purged with argon or air for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm), the reactions were tracked by ^1H NMR spectroscopy (solvent suppression).

Time (h)	Argon purge			Air purge		
	% MA	% dimer	% oxetane	% MA	% dimer	% oxetane
2	94	2	4	96	2	2
4	90	4	5	91	4	5
6	87	6	7	88	5	7
8	83	7	10	86	6	9
10	81	8	11	83	7	10
12	78	9	13	79	8	13
24	63	15	22	67	13	20

Table S4C

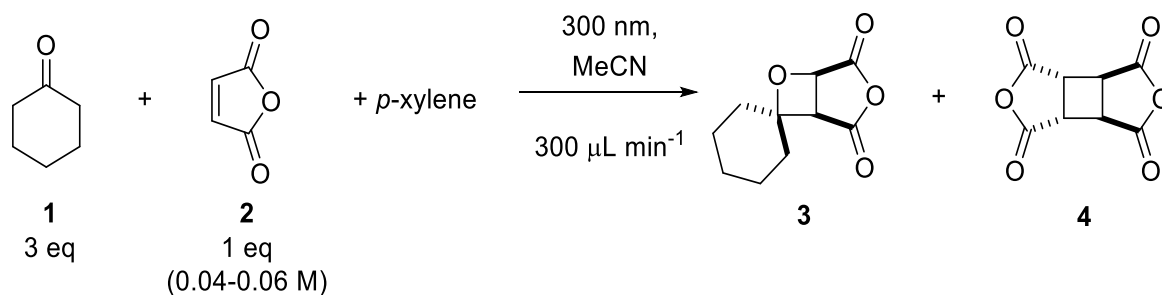


A solution of maleic anhydride (98 mg, 1.00 mmol), cyclohexanone (0.32 mL, 3 mmol) and *p*-xylene (0.12 mL, 1.00 mmol) in anhydrous MeCN (0.10 M, 10 mL) was prepared in a Duran phototube and purged with argon or air for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm), the reactions were tracked by ^1H NMR spectroscopy (solvent suppression).

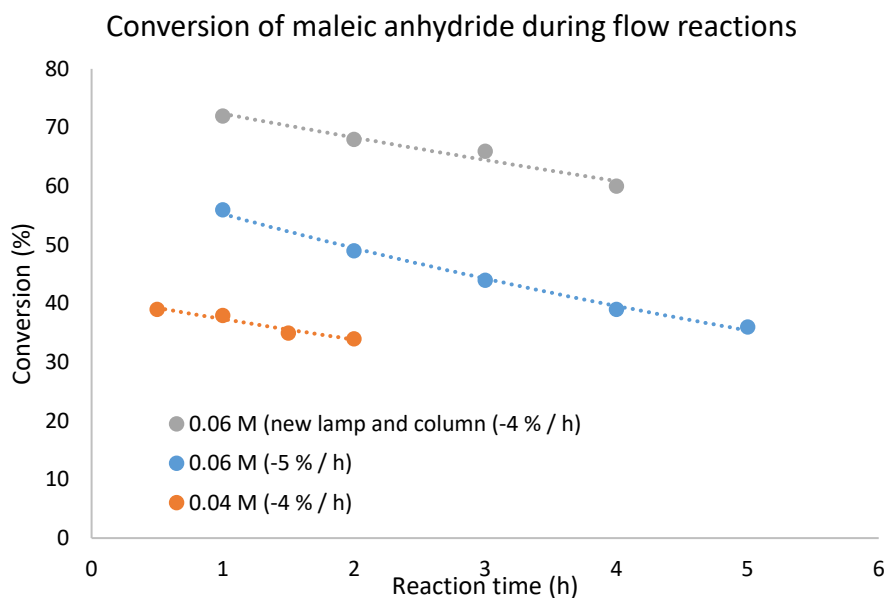
Time (h)	Argon purge			Air purge		
	% MA	% dimer	% oxetane	% MA	% dimer	% oxetane
2	96	0	4	98	0	2
4	94	0	6	94	0	6
6	90	0	9	92	0	7
8	87	0	12	90	0	9
10	84	0	15	89	0	11
12	83	0	17	87	0	12
24	70	1	29	78	0	22

Table S4D

1.2.5. Testing of the Paternò-Büchi reaction under flow conditions

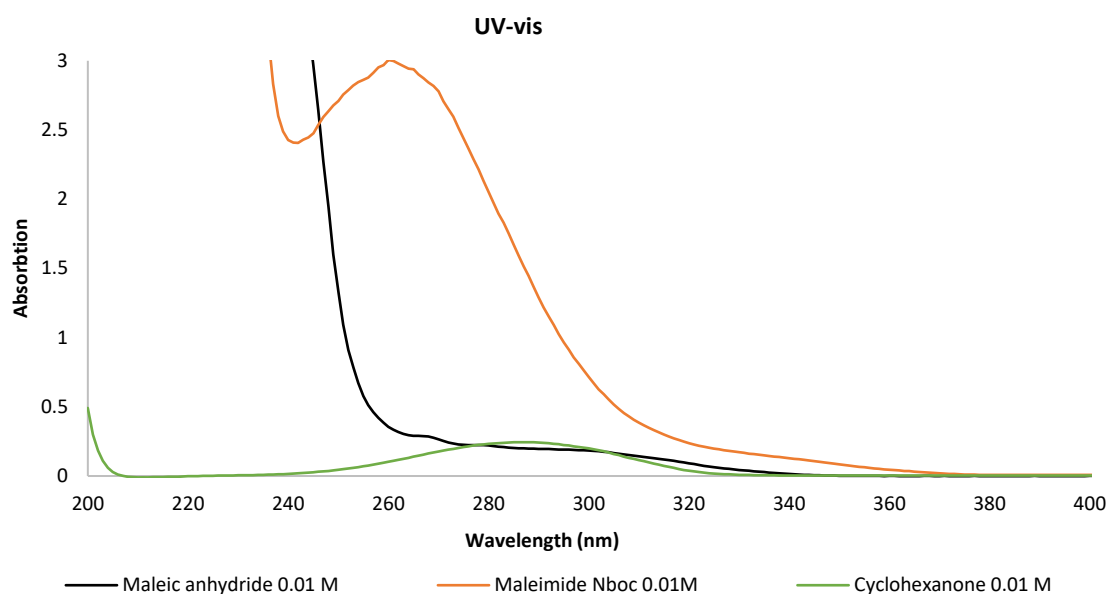


A solution of maleic anhydride (1.0 eq), cyclohexanone (3.0 eq) and p-xylene (1.0 eq) in anhydrous MeCN was purged with argon for 15 minutes, then irradiated at room temperature ($\lambda = 300 \text{ nm}$, $300 \mu\text{Lmin}^{-1}$) in a Vapourtec UV-150 photochemical reactor. Reaction mixtures were collected ever 30-60 minutes and the consumption of the maleic anhydride as judged by ^1H NMR spectroscopy (solvent suppression). The maleic anhydride was not fully consumed, and the consumption decreased over time, suggesting reactor fouling. Therefore, flow conditions were not further investigated.



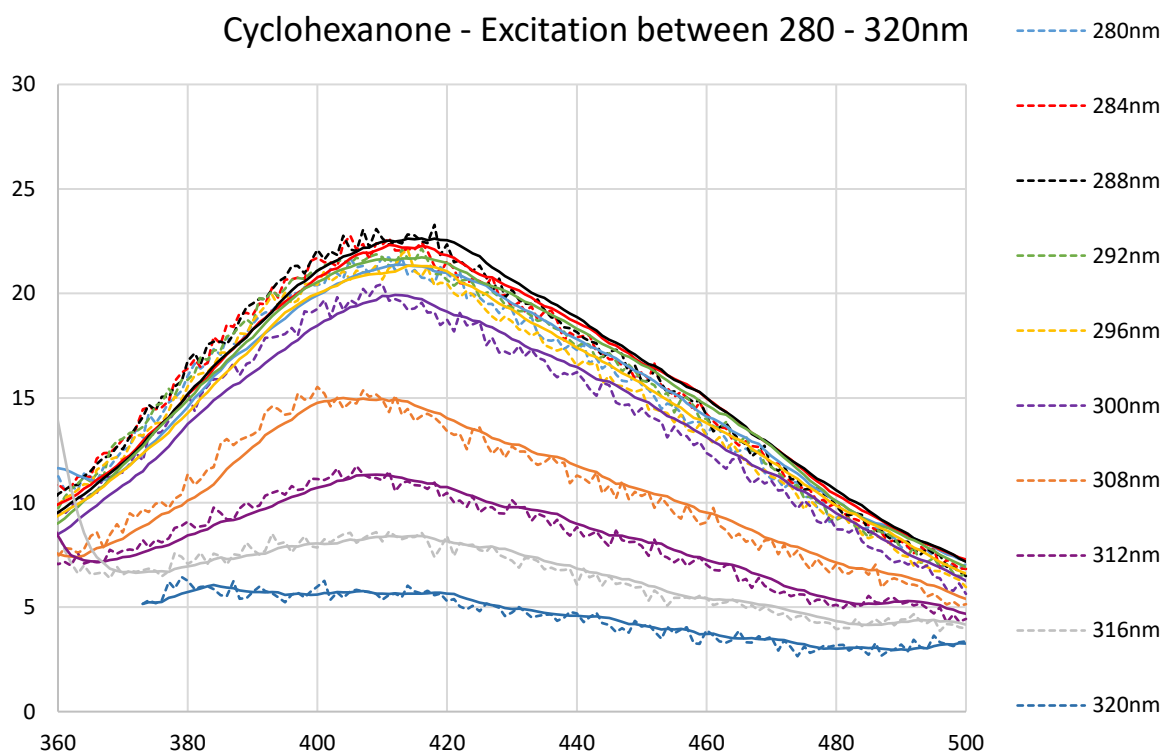
Graph 1 Conversion of maleic anhydride in the Paternò-Büchi reaction under flow conditions.

1.2.6. UV-Vis Data

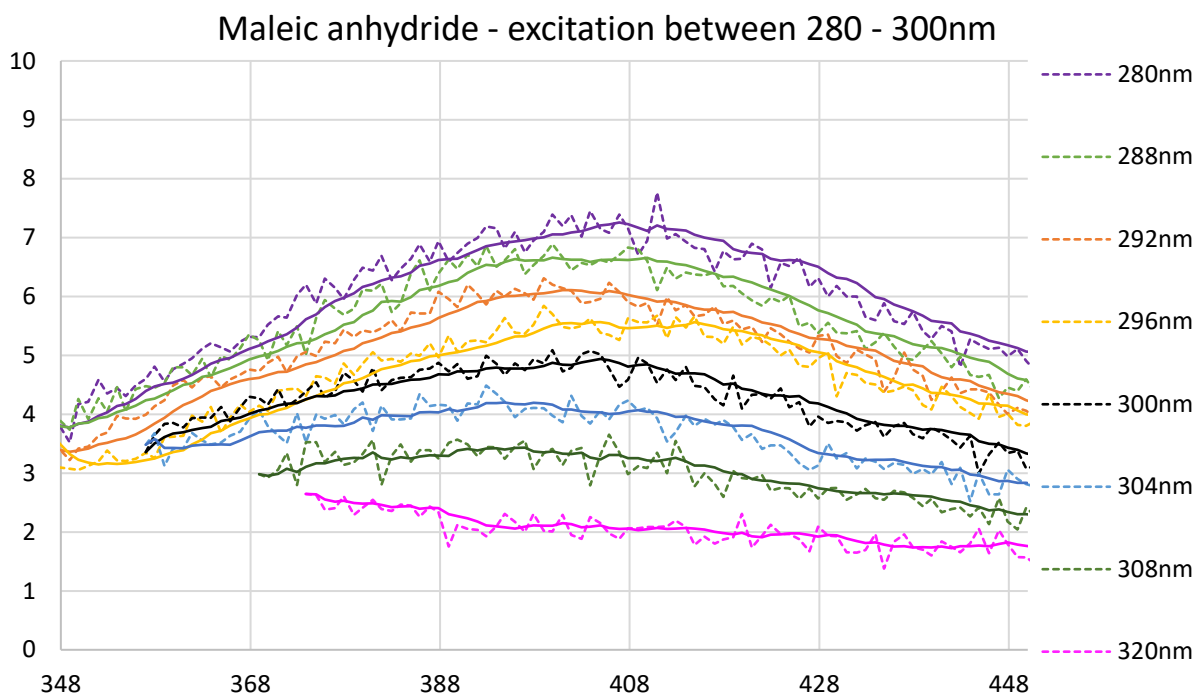


Graph 2 UV-vis spectra of in MeCN ($M = 0.01M$).

1.2.7. Phosphorescence Data



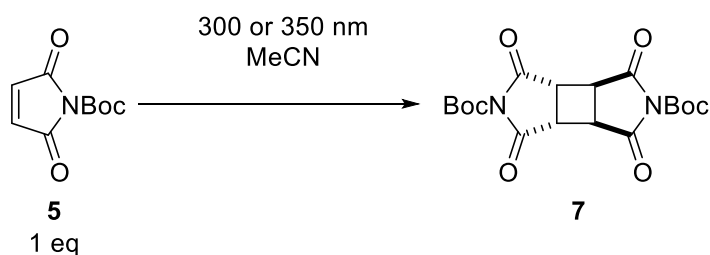
Graph 3 Excitations between 280 nm and 320 nm show a clear phosphorescence signal, with $\lambda_{(max)} = 418 \text{ nm}$ (69 kcal mol^{-1}). Solvent: MeCN.



Graph 4 Excitations between 280 nm and 320 nm show a very weak phosphorescence signal which was not very reproducible with $\lambda_{(max)} = 408 \text{ nm}$ (70 kcal mol^{-1}). Solvent: MeCN.

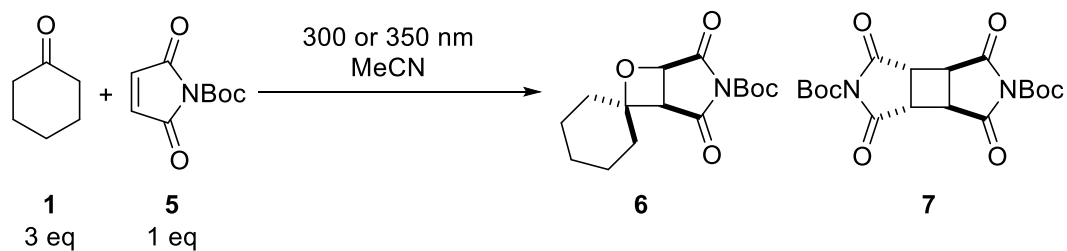
1.2.1. Table S5: Effect of additives and wavelengths on the Paternò-Büchi reaction of cyclohexanone and N-Boc-maleimide

A solution of N-Boc-maleimide (1 eq) in anhydrous MeCN (0.10 M) was prepared and purged with argon for 15 minutes, the solution was placed in a Duran phototube (NMR tube). Next, cyclohexanone (3 eq) and/or additives were added followed by irradiation at approximately 40 °C ($\lambda = 300 \text{ nm}$ or 350 nm), the reactions were tracked by ^1H NMR spectroscopy (solvent suppression).



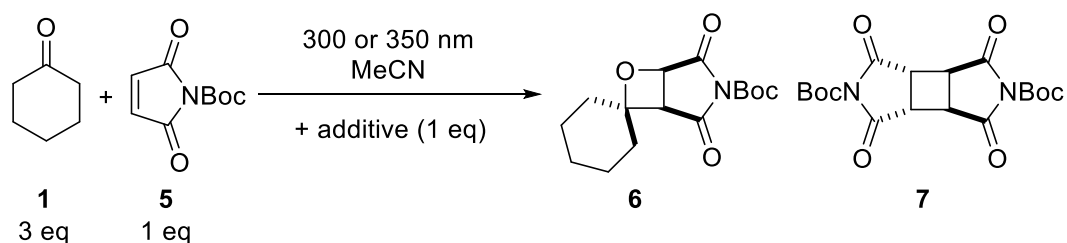
Time (h)	300 nm		350 nm	
	% alkene	% dimer	% alkene	% dimer
1	92	8	91	9
3	78	22	71	29
6	60	40	60	40
10	32	68	31	69

Table S5A



Time (h)	300 nm			350 nm		
	% alkene	% dimer	% oxetane	% alkene	% dimer	% oxetane
1	89	9	2	92	8	0
3	66	26	8	70	30	0
6	31	54	14	46	54	0
10	0	78	22	17	83	0

Table S5B

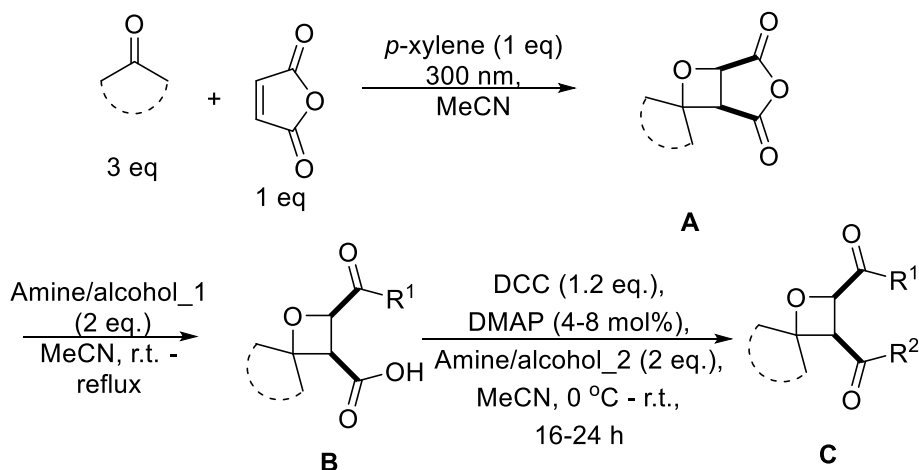


Additive	Time (h)	300 nm		
		% alkene	% dimer	% oxetane
<i>p</i> -xylene	1	97	1	2
	3	87	4	9
	6	80	6	14
	10	54	15	30
<i>m</i> -tolunitrile	1	93	4	4
	3	81	9	10
	6	62	19	19
	10	34	34	31
anisole	1	51	49	0
	3	45	54	1
	6	34	57	10
	10	23	61	16
toluene	1	95	1	4
	3	88	3	9
	6	74	6	19
	10	41	17	43
Additive	Time (h)	350 nm		
xanthone	1	94	6	0
	3	84	16	0
	6	62	38	0
	10	32	68	0
benzophenone	1	88	12	0
	3	64	36	0

	6	30	70	0
	10	0	100	0
<i>m</i> -tolunitrile	1	97	3	0
	3	91	9	0
	6	81	19	0
	10	66	34	0

Table S5C

1.3. General Procedure

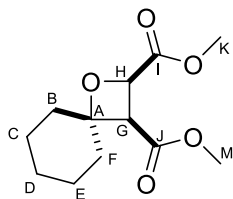


A solution of maleic anhydride (1.0 eq, scale specified for each procedure), ketone (3.0 eq) and *p*-xylene (1.0 eq) in anhydrous MeCN (0.1 M, with respect to maleic anhydride) was prepared in a Duran phototube and purged with argon for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm) until complete consumption of the maleic anhydride, as judged by ^1H NMR spectroscopy (solvent suppression). Next, the solution was decanted into a round-bottomed flask, and amine/alcohol_1 (1-2.0 eq) was added. The reaction mixture was stirred at room temperature or reflux for 24-72 h (specified for each procedure) until full consumption of oxetane **A**, as judged by ^1H NMR spectroscopy (solvent suppression). The solvent was evaporated under reduced pressure to give the crude product **B**. Crude product **B** was dried under high vacuum overnight to fully remove unreacted alcohol/amine_1, then dissolved in anhydrous MeCN (0.3-0.5 M) under nitrogen. Next, DMAP (5 mol%) was added, followed by amine/alcohol_2 (2.0 eq). The reaction mixture was cooled to 0 °C and DCC (1.2 eq) was added portion-wise. The reaction was slowly warmed to room temperature and stirred overnight. The precipitated urea was filtered off and the filtrate was concentrated under reduced pressure to give crude product **C**. Purification by flash column chromatography on silica gel gave the purified oxetane product (column details specified for each procedure).

1.4. Synthetic procedures

rac-(2*R*,3*R*)-Dimethyl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate **10**

(WM-05-29)



Chemical Formula: C₁₂H₁₈O₅

Molecular Weight: 242.27

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using methanol (0.10 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 19:1-9:1 hexane-EtOAc) gave **10** (98 mg, 0.33 mmol, 42%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.05 (d, *J* = 8.8 Hz, 1H, H^H), 3.80 (s, 3H, H^K), 3.69 (d, *J* = 8.8 Hz, 1H, H^G), 3.68 (s, 3H, H^M), 1.87-1.29 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 171.3 (C^I), 168.8 (C^J), 85.6 (C^A), 71.6 (C^H), 52.1 (C^{K/M}), 51.9 (C^{K/M}), 51.0 (C^G), 39.4 (C^{B/F}), 33.6 (C^{B/F}), 24.8 (C^{C/D/E}), 22.2 (C^{C/D/E}), 21.6 (C^{C/D/E}).

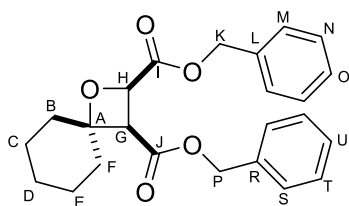
FTIR (ATR) ν (cm⁻¹): 2931 (C-H), 1761 (C=O), 1735 (C=O).

HRMS: ESI C₁₂H₁₈O₅ [M + Na]⁺ predicted: 265.1046, found at 265.1039.

R_f: (acetone-hexane, 1:4) = 0.41.

rac-(2*R*,3*R*)-Dibenzyl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate **11**

(WM-04-71,80)



Chemical Formula: C₂₄H₂₆O₅

Molecular Weight: 394.47

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzyl alcohol (0.20 mL, 2.00 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using benzyl alcohol (0.20 mL, 2.00 mmol). Purification by flash chromatography (eluent 7:3 hexane-EtOAc) gave **11** (100 mg, 0.29 mmol, 29%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.30 (m, 10H, H^{M, N, O, S, T, U}), 5.21 (d, *J* = 12.2 Hz, 1H, H^{K/P}), 5.08-5.05 (m, 3H, H^{K, P}), 5.07 (d, *J* = 8.9 Hz, 1H, H^H), 3.73 (d, *J* = 8.9 Hz, 1H, H^G), 1.80-1.26 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 170.6 (C^I), 168.1 (C^J), 135.5 (C^{L/R}), 135.2 (C^{L/R}), 128.7 (C^{N/T}), 128.6 (2

peaks, ($C^{N/T}$ and $C^{M/S}$), 128.5 ($C^{M/S}$), 128.5 ($C^{O/U}$), 127.7 ($C^{O/U}$), 85.9 (C^A), 71.6 (C^H), 66.9 ($C^{K/P}$), 66.8 ($C^{K/P}$), 51.0 (C^G), 39.6 ($C^{B/F}$), 33.5 ($C^{B/F}$), 24.8 ($C^{C/D/E}$), 22.3 ($C^{C/D/E}$), 21.6 ($C^{C/D/E}$).

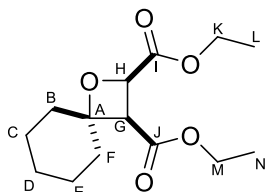
FTIR (ATR) ν (cm^{-1}): 2933 (C-H), 1735 (C=O).

HRMS: ESI $C_{24}H_{26}O_5$ $[M + Na]^+$ predicted: 417.1672, found at 417.1663.

R_f = (EtOAc-hexane, 2:3) = 0.47

rac*-(2*R*,3*R*)-Diethyl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate **12*

(WM-04-74,87)



Chemical Formula: $C_{14}H_{22}O_5$

Molecular Weight: 270.33

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using ethanol (0.12 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step (using ethanol (0.12 mL, 2.00 mmol)). Purification by flash chromatography (eluent 19:1-9:1 hexane-acetone) gave **12** (92 mg, 0.34 mmol, 34%) as a colourless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.02 (d, $J = 8.8$ Hz, 1H, H^H), 4.26-4.22 (m, 2H, $H^{K/M}$), 4.22-4.10 (m, 2H, $H^{K/M}$), 3.67 (d, $J = 8.8$ Hz, 1H, H^G), 1.93-1.61 (m, 10H, $H^{B, C, D, E, F}$), 1.32-1.22 (m, 6H, $H^{L, N}$).

^{13}C NMR (101 MHz, CDCl_3) δ 170.9 (C^I), 168.3 (C^I), 85.5 (C^A), 71.7 (C^H), 61.3 ($C^{K/M}$), 61.0 ($C^{K/M}$), 51.1 (C^G), 40.9 ($C^{B/F}$), 39.5 ($C^{B/F}$), 33.5 ($C^{C/D/E}$), 24.9 ($C^{C/D/E}$), 22.3 ($C^{C/D/E}$), 14.2 ($C^{L/M}$), 14.1 ($C^{L/M}$).

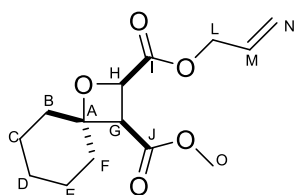
FTIR (ATR) ν (cm^{-1}): 2933 (C-H), 1731 (C=O).

HRMS: ESI $C_{14}H_{22}O_5$ $[M + Na]^+$ predicted: 293.1359, found at 293.1346.

R_f (acetone-hexane, 1:9) = 0.32.

rac*-(2*R*,3*R*)-2-Allyl 3-methyl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate **13*

(WM-05-46)



Chemical Formula: $C_{14}H_{20}O_5$

Molecular Weight: 268.3090

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using allyl alcohol (0.14 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 1:4 EtOAc-hexane) gave **13** (81 mg, 0.31 mmol, 31%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 5.95 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H, H^M), 5.34 (dq, *J* = 17.2, 1.5 Hz, 1H, H^N), 5.24 (ddd, *J* = 10.4, 2.5, 1.2 Hz, 1H, H^N), 5.05 (d, *J* = 8.8 Hz, 1H, H^H), 4.74 (ddt, *J* = 13.0, 5.9, 1.3 Hz, 1H, H^L), 4.67 (ddt, *J* = 13.0, 5.9, 1.3 Hz, 1H, H^L), 3.70 (d, *J* = 8.8 Hz, 1H, H^G), 3.68 (s, 3H, H^O), 1.87-1.31 (m, 10H, H^{B/C/D/E/F}).

¹³C NMR (101 MHz, CDCl₃) δ 170.5 (C^I), 168.7 (C^I), 132.0 (C^M), 118.7 (C^N), 85.7 (C^A), 71.6 (C^H), 65.8 (C^L), 51.9 (C^O), 51.0 (C^G), 39.5 (C^{B/F}), 33.5 (C^{B/F}), 24.8 (C^{C/D/E}), 22.2 (C^{C/D/E}), 21.6 (C^{C/D/E}).

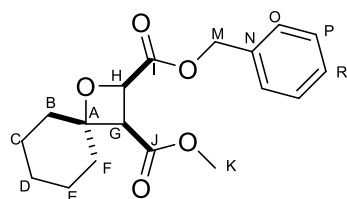
FTIR (ATR) ν (cm⁻¹): 2933 (C-H), 1735 (C=O).

HRMS: ESI C₁₄H₂₀NO₅ [M + Na]⁺ predicted: 291.1203, found: 219.1202.

R_f: (EtOAc-hexane, 1:4) = 0.31.

rac*-(2*R*,3*R*)-2-Benzyl 3-methyl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate **14*

(WM-06-90)



Chemical Formula: C₁₈H₂₂O₅

Molecular Weight: 318.37

1 mmol scale - Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzyl alcohol (0.10 mL, 1 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step methanol (0.10 mL, 2 mmol). Purification by flash chromatography (eluent 9:1-3:2 hexane-EtOAc) gave **14** (70 mg, 0.22 mmol, 22%) as a colourless oil.

30 mmol scale Using the general procedure, maleic anhydride (2.94 g, 30 mmol) and cyclohexanone (9.60 mL, 90.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzyl alcohol (3.12 mL, 30 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (60 mL) and used in the final step methanol (2.42 mL, 60 mmol). Purification by flash chromatography (eluent 9:1-3:2 hexane-EtOAc) gave **14** (2.26 mg, 6.1 mmol, 20%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.31 (m, 5H, H^{O,P,R}), 5.27 (d, *J* = 12.2 Hz, 1H, H^M), 5.21 (d, *J* = 12.2 Hz, 1H, H^M), 5.07 (d, *J* = 8.9 Hz, 1H, H^H), 3.70 (d, *J* = 8.9 Hz, 1H, H^G), 3.59 (s, 3H, H^K), 1.92-1.30 (m, 10H, H^{B,C,D,E,F}).

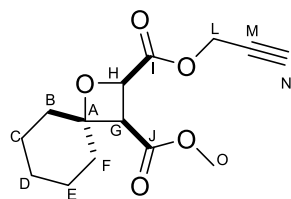
¹³C NMR (101 MHz, CDCl₃) δ 170.6 (C^I), 168.7 (C^I), 135.5 (C^N), 128.7 (C^P), 128.5 (C^O), 128.3 (C^R), 85.7 (C^A), 71.6 (C^H), 66.9 (C^M), 51.8 (C^K), 50.9 (C^G), 39.5 (C^{B/F}), 33.5 (C^{B/F}), 24.8 (C^{C/D/E}), 22.2 (C^{C/D/E}), 21.6 (C^{C/D/E}).

FTIR (ATR) ν (cm⁻¹): 2931 (C-H), 1735 (C=O).

HRMS: APCI C₁₈H₂₂O₅ [M + H]⁺ predicted: 319.1540, found at 319.1531.

rac-(2R,3R)-3-Methyl 2-prop-2-yn-1-yl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate 15

(WM-05-67)



Chemical Formula: C₁₄H₁₈O₅

Molecular Weight: 266.29

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using propargyl alcohol (0.12 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (4 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 9:1-4:1 hexane-EtOAc) gave **15** (40 mg, 0.17 mmol, 17%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.07 (d, *J* = 8.8 Hz, 1H, H^H), 4.86 (dd, *J* = 15.6, 2.5 Hz, 1H, H^I), 4.82 (dd, *J* = 15.6, 2.5 Hz, 1H, H^L), 3.71 (d, *J* = 8.8 Hz, 1H, H^G), 3.68 (s, 3H, H^O), 2.48 (t, *J* = 2.5 Hz, 1H, H^N), 1.90-1.29 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 170.1 (C^I), 168.6 (C^L), 86.0 (C^A), 77.3 (C^N), 75.2 (C^H), 71.4 (C^M), 52.5 (C^L), 52.0 (C^O), 51.0 (C^G), 39.5 (C^{B/F}), 33.5 (C^{B/F}), 24.8 (C^{C/D/E}), 22.2 (C^{C/D/E}), 21.5 (C^{C/D/E}).

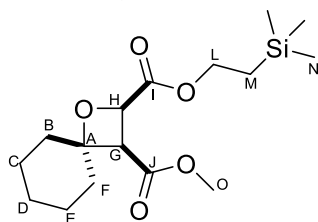
FTIR (ATR) ν (cm⁻¹): 2933 (C-H), 2120 (weak, C≡C), 1764 (C=O), 1735 (C=O).

HRMS: ESI C₁₄H₁₈O₅ [M + H]⁺ predicted: 267.1227, found: 267.1240.

R_f: (EtOAc-hexane, 1:4) = 0.16.

(2R,3R)-3-Methyl 2-(2-(trimethylsilyl)ethyl) 1-oxaspiro[3.5]nonane-2,3-dicarboxylate 16

(WM-05-69)



Chemical Formula: C₁₆H₂₈O₅Si

Molecular Weight: 328.48

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using 2-(trimethylsilyl)ethanol (0.29 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step, using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 19:1-9:1 hexane-EtOAc) gave **16** (60 mg, 0.19 mmol, 19%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.01 (d, *J* = 8.8 Hz, 1H, H^H), 4.45 – 4.21 (m, 4H, H^{L, M}), 3.69 (d, *J* = 8.8 Hz, 1H, H^G), 3.69 (s, 3H, H^O), 1.92-1.62 (m, 10H, H^{B, C, D, E, F}), 0.04 (s, 9H, H^N).

¹³C NMR (101 MHz, CDCl₃) δ 170.9 (C^I), 168.8 (C^L), 85.5 (C^A), 71.6 (C^H), 63.5 (C^L), 51.8 (C^G), 50.9 (C^O),

39.5 (C^{B/F}), 33.6 (C^{B/F}), 24.8 (C^{C/D/E}), 22.3 (C^{C/D/E}), 21.6 (C^{C/D/E}), 17.3 (C^M), -1.5 (C^N).

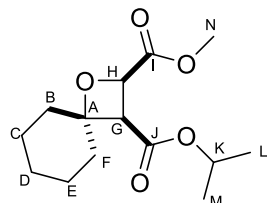
FTIR (ATR) ν (cm⁻¹): 2935 (C-H), 1740 (C=O).

HRMS: ESI C₁₆H₂₈O₅Si [M + Na]⁺ predicted: 351.1603, found at 351.1603.

R_f: (EtOAc-hexane, 2:3) = 0.52

rac*-(2*R*,3*R*)-3-Isopropyl 2-methyl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate **17*

(WM-06-04)



Chemical Formula: C₁₄H₂₂O₅

Molecular Weight: 270.33

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using methanol (0.10 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product B was obtained, then dissolved in MeCN (3 mL) and used in the final step using isopropanol (0.15 mL, 2.00 mmol). Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **17** (61 mg, 0.23 mmol, 23%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 5.06 (d, *J* = 8.8 Hz, 1H, H^H), 5.02 (sept, *J* = 6.2 Hz, 1H, H^K), 3.80 (s, 1H, H^M), 3.62 (d, *J* = 8.8 Hz, 1H, H^G), 1.91-1.63 (m, 10H, H^{B, C, D, E, F}), 1.24 (d, *J* = 6.3 Hz, 3H, H^{L/M}), 1.23 (d, *J* = 6.3 Hz, 3H, H^{L/M}).

¹³C NMR (101 MHz, CDCl₃) δ 171.4 (C^I), 167.9 (C^J), 85.6 (C^A), 71.8 (C^H), 68.8 (C^K), 52.0 (C^N), 51.4 (C^G), 39.4 (C^{B/F}), 33.5 (C^{B/F}), 24.9 (C^{C/D/E}), 22.3 (C^{C/D/E}), 21.8 (C^{C/D/E}), 21.8 (C^{M/L}), 21.6 (C^{M/L}).

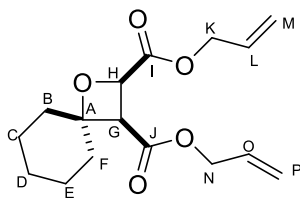
FTIR (ATR) ν (cm⁻¹): 2933 (C-H), 1763 (C=O), 1729 (C=O).

HRMS: ESI C₁₄H₂₂O₅ [M + Na]⁺, predicted: 293.1359, found: 293.1351.

R_f (EtOAc – hexane, 2:3) = 0.20

rac*-(2*R*,3*R*)-Diallyl 1-oxaspiro[3.5]nonane-2,3-dicarboxylate **18*

(WM-06-28)



Chemical Formula: C₁₆H₂₂O₅

Molecular Weight: 294.35

Using the general procedure, maleic anhydride (490 mg, 5.00 mmol) and cyclohexanone (1.60 mL, 15.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using allyl alcohol (0.70 mL, 7.50 mmol) and stirring at reflux for 48 h in the second step, the crude product B was obtained, then dissolved in MeCN (25 mL) and used in the final step using allyl alcohol (0.70 mL, 7.50 mmol).

Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **18** (361 mg, 1.23 mmol, 26%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.00 – 5.83 (m, 2H, H^{L/O}), 5.37 – 5.28 (m, 2H, H^{P/M}), 5.28-5.21 (m, 2H, H^{P/M}), 5.06 (d, *J* = 8.8 Hz, 1H, H^H), 4.76-4.62 (m, 2H, H^{N/K}), 4.62-4.52 (m, 2H, H^{N/K}), 3.72 (d, *J* = 8.8 Hz, 1H, H^G), 1.99-1.31 (m, 10H, H^{B, C, D, E, F}).

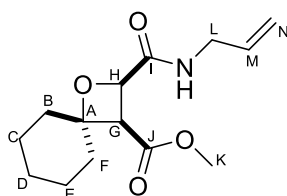
¹³C NMR (101 MHz, CDCl₃) δ 170.5 (C^I), 168.0 (C^J), 132.0 (C^{L/O}), 131.6 (C^{L/O}), 119.1 (C^{M/P}), 118.6 (C^{M/P}), 85.7 (C^A), 71.6 (C^H), 65.8 (C^{K/N}), 65.7 (C^{K/N}), 51.1 (C^G), 39.6 (C^{B/F}), 33.5 (C^{B/F}), 24.8 (C^{C/D/E}), 22.3 (C^{C/D/E}), 21.6 (C^{C/D/E}).

FTIR (ATR) ν (cm⁻¹): 2933 (C-H), 1735 (C=O).

HRMS: ESI C₁₆H₂₂O₅ [M + Na]⁺ predicted: 317.1353, found at 317.1353

rac-(2*R*,3*R*)-Methyl 2-(allylcarbamoyl)-1-oxaspiro[3.5]nonane-3-carboxylate **19**

(WM-05-50)



Chemical Formula: C₁₄H₂₁NO₄

Molecular Weight: 267.3250

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using allyl amine (0.22 mL, 2.00 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 3:2 hexane-EtOAc) gave **19** (68 mg, 0.25 mmol, 25%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 6.86 (s, 1H, N-H), 5.90 (ddt, *J* = 15.9, 10.3, 5.6 Hz, 1H, H^M), 5.33-5.24 (m, 1H, H^N), 5.16 (ddd, *J* = 10.3, 1.7, 1.1 Hz, 1H, H^N), 4.94 (d, *J* = 8.8 Hz, 1H, H^H), 4.07-3.89 (m, 2H, H^L), 3.66 (s, 3H, H^K), 3.62 (d, *J* = 8.8 Hz, 1H, H^G), 1.96-1.15 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 170.3 (C^I), 168.8 (C^J), 134.1 (C^M), 116.5 (C^N), 85.1 (C^A), 72.6 (C^H), 51.8 (C^K), 50.2 (C^G), 41.3 (C^L), 39.5 (C^{B/F}), 33.8 (C^{B/F}), 24.7 (C^{C/D/E}), 22.4 (C^{C/D/E}), 21.8 (C^{C/D/E}).

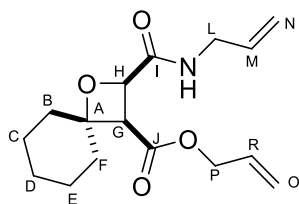
FTIR (ATR) ν (cm⁻¹): 3298 (N-H), 2931 (C-H), 1748 (C=O, ester), 1654 (C=O, amide).

HRMS: ESI C₁₄H₂₁NO₄ [M + H]⁺ predicted: 268.1543, found: 268.1554.

R_f: (EtOAc-hexane, 2:3) = 0.16.

rac-(2R,3R)-Allyl 2-(allylcarbamoyl)-1-oxaspiro[3.5]nonane-3-carboxylate 20

(WM-06-09)



Chemical Formula: C₁₆H₂₃NO₄

Molecular Weight: 293.36

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using allyl amine (0.14 mL, 2.00 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and directly used in the final step using allyl alcohol (0.14 mL, 2.00 mmol). Purification by flash chromatography (eluent 9:1-4:1 hexane-EtOAc) gave **20** (45 mg, 0.15 mmol, 15%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.86 (s, 1H, N-H), 5.96-5.83 (m, 2H, H^{M, R}), 5.36-5.13 (m, 4H, H^{N, O}), 4.96 (d, *J* = 8.8 Hz, 1H, H^H), 4.58 (s - broad, 1H, H^P), 4.57 (s - broad, 1H, H^P), 4.01-3.95 (m, 2H, H^L), 3.65 (d, *J* = 8.8 Hz, 1H, H^G), 1.96-1.20 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 170.2 (C^I), 168.0 (C^I), 134.1 (C^R), 131.8 (C^M), 118.9 (C^O), 116.5 (C^N), 85.1 (C^A), 72.7 (C^H), 65.6 (C^P), 50.3 (C^G), 41.3 (C^L), 39.6 (C^{B/F}), 33.8 (C^{B/F}), 24.8 (C^{C/D/E}), 22.4 (C^{C/D/E}), 21.8 (C^{C/D/E}).

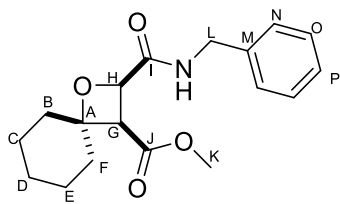
FTIR (ATR) ν (cm⁻¹): 3324 (broad, N-H), 2931 (C-H), 1738 (C=O, ester), 1671 (C=O, amide).

HRMS: APCI C₁₆H₂₃O₅ [M + Na]⁺ predicted: 316.1519, found at 316.1515.

R_f: (EtOAc-hexane, 2:3) = 0.16.

rac-(2R,3R)-Methyl 2-(benzylcarbamoyl)-1-oxaspiro[3.5]nonane-3-carboxylate 21

(WM-05-48)



Chemical Formula: C₁₈H₂₃NO₄

Molecular Weight: 317.3850

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzylamine (0.22 mL, 2.00 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (4 mL) and directly used in the final step, using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 7:3 to 1:4 hexane-EtOAc) gave **21** (60 mg, 0.19 mmol, 19%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.39-7.28 (m, 5H, H^{N, O, P}), 7.07 (s, 1H, N-H), 5.00 (d, *J* = 8.8 Hz, 1H, H^H), 4.57 (s - broad, 1H, H^L), 4.55 (br s, 1H, H^L), 3.68 (s, 3H, H^K), 3.66 (d, *J* = 8.8 Hz, 1H, H^G), 1.93-1.21 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 170.4 (C^I), 168.8 (C^J), 138.0 (C^M), 128.7 (C^O), 127.9 (C^N), 127.5 (C^P), 85.1 (C^A), 72.7 (C^H), 51.9 (C^K), 50.2 (C^G), 43.1 (C^L), 39.6 (C^{B/F}), 33.8 (C^{B/F}), 24.7 (C^{C/D/E}), 22.4 (C^{C/D/E}), 21.8 (C^{C/D/E}).

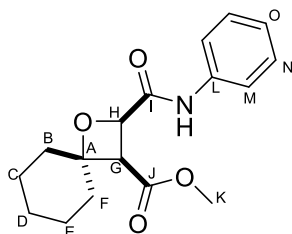
FTIR (ATR) ν (cm⁻¹): 3412 (broad, N-H), 2931 (C-H), 1735 (C=O, ester), 1669 (C=O, amide).

HRMS: ESI C₃₆H₄₆N₂O₈ [M + Na]⁺ predicted: 657.3164, found at 657.3160.

R_f: (EtOAc-hexane, 2:3) = 0.13.

rac-(2*R*,3*R*)-Methyl 2-(phenylcarbamoyl)-1-oxaspiro[3.5]nonane-3-carboxylate **22**

(WM-05-56)



Chemical Formula: C₁₇H₂₁NO₄

Molecular Weight: 303.3580

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using aniline (0.10 mL, 1.10 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step, using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 3:2 hexane-EtOAc) gave **22** (63 mg, 0.22 mmol, 23%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1H, N-H) 7.61-7.57 (m, 2H, H^N), 7.38-7.31 (m, 2H, H^M), 7.20-7.16 (m, 1H, H^O), 5.04 (d, *J* = 8.7 Hz, 1H, H^H), 3.71 (d, *J* = 8.7 Hz, 1H, H^G), 3.67 (s, 3H, H^K), 1.91-1.23 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 168.7 (C^J), 168.6 (C^I), 137.0 (C^L), 129.1 (C^N), 124.6 (C^O), 120.1 (C^M), 85.5 (C^A), 72.7 (C^H), 52.0 (C^K), 50.6 (C^G), 39.6 (C^{B/F}), 33.8 (C^{B/F}), 24.7 (C^{C/D/E}), 22.4 (C^{C/D/E}), 21.8 (C^{C/D/E}).

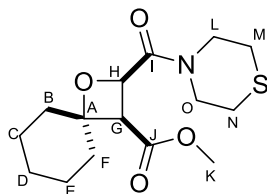
FTIR (ATR) ν (cm⁻¹): 3375 (broad, N-H), 2931 (C-H), 1735 (C=O, ester), 1686 (C=O, amide).

HRMS: ESI C₂₄H₂₆O₅ [M + Na]⁺ predicted: 304.1543, found at 304.1543.

R_f: (EtOAc-hexane, 2:3) = 0.21.

rac-(2*R*,3*R*)-Methyl 2-(thiomorpholine-4-carbonyl)-1-oxaspiro[3.5]nonane-3-carboxylate **23**

(WM-05-52)



Chemical Formula: C₁₅H₂₃NO₄S

Molecular Weight: 313.4120

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using thiomorpholine (0.11 mL, 1.10 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was

obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 3:2 hexane-EtOAc) gave **23** (99 mg, 0.32 mmol, 32%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 5.23 (d, *J* = 8.3 Hz, 1H, H^H), 4.20 (ddd, *J* = 13.5, 6.1, 2.8 Hz, 1H, H^{L/O}), 4.07 (ddd, *J* = 13.5, 6.1, 2.8 Hz, 1H, H^{L/O}), 3.71 (s, 3H, H^K), 3.63 (d, *J* = 8.3 Hz, 1H, H^G), 3.62 – 3.51 (m, 2H, H^{L/O}), 2.89-2.74 (m, 2H, H^{M/N}), 2.61-2.53 (m, 1H, H^{M/N}), 2.48 (dd, *J* = 12.8, 5.5 Hz, 1H, H^{M/N}), 1.90-1.60 (m, 5H, H^{B, C, D, E, F}), 1.56-1.26 (m, 5H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 169.5 (C^I), 168.5 (C^J), 84.0 (C^A), 73.4 (C^H), 52.0 (C^K), 51.8 (C^{L/O}), 47.4 (C^{L/O}), 45.1 (C^G), 38.7 (C^{B/F}), 33.6 (C^{B/F}), 27.6 (C^{M/N}), 27.3 (C^{M/N}), 24.9 (C^{C/D/E}), 22.5 (C^{C/D/E}), 21.8 (C^{C/D/E}).

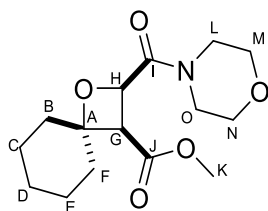
FTIR (ATR) ν (cm⁻¹): 2927 (C-H), 1735 (C=O, ester), 1656 (C=O, amide).

HRMS: ESI C₁₅H₂₃NO₄S [M + H]⁺ predicted: 314.1421, found: 314.1408.

R_f: (EtOAc-hexane, 2:3) = 0.10.

rac*-(2*R*,3*R*)-Methyl 2-(morpholine-4-carbonyl)-1-oxaspiro[3.5]nonane-3-carboxylate **24*

(WM-05-58)



Chemical Formula: C₁₅H₂₃NO₅

Molecular Weight: 297.35

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using morpholine (0.10 mL, 1.10 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 4:1 hexane-EtOAc) gave **24** (92 mg, 0.31 mmol, 31%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.26 (d, *J* = 8.4 Hz, 1H, H^H), 3.71 (s, 3H, H^K), 3.64 (d, *J* = 8.4 Hz, 1H, H^G), 3.76-3.48 (m, 8H, H^{L, M, N, O}), 1.91-1.28 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 169.4 (C^I), 168.4 (C^J), 84.4 (C^A), 73.3 (C^H), 66.9 (C^{M/N}), 66.5 (C^{M/N}), 51.8 (C^K and C^G), 45.1 (C^{L/O}), 42.6 (C^{L/O}), 38.9 (C^{B/F}), 33.6 (C^{B/F}), 24.9 (C^{C/D/E}), 22.5 (C^{C/D/E}), 21.7 (C^{C/D/E}).

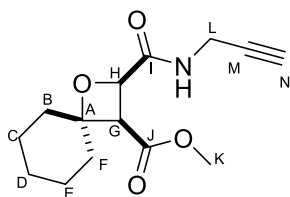
FTIR (ATR) ν (cm⁻¹): 2926 (C-H), 1735 (C=O, ester), 1653 (C=O, amide).

HRMS: ESI C₁₅H₂₃ONO₅ [M + H]⁺ predicted: 298.1639, found: 298.1649.

R_f: (EtOAc-hexane, 1:4) = 0.19.

rac-(2R,3R)-Methyl 2-(prop-2-yn-1-ylcarbamoyl)-1-oxaspiro[3.5]nonane-3-carboxylate 25

(WM-05-54)



Chemical Formula: C₁₄H₁₉NO₄

Molecular Weight: 265.3090

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using propargylamine (0.13 mL, 2.00 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 3:2 hexane-EtOAc) gave **25** (78 mg, 0.33 mmol, 33%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.95 (s, 1H, N-H), 4.95 (d, *J* = 8.7 Hz, 1H, H^H), 4.22 (ddd, *J* = 17.6, 6.1, 2.6 Hz, 1H, H^L), 4.10 (ddd, *J* = 17.6, 4.9, 2.6 Hz, 1H, H^L), 3.68 (s, 3H, H^K), 3.63 (d, *J* = 8.7 Hz, 1H, H^G), 2.26 (t, *J* = 2.6 Hz, 1H, H^N), 1.93-1.20 (m, 10H, H^{B, C, D, E, F}).

¹³C NMR (101 MHz, CDCl₃) δ 170.2 (C^I), 168.7 (C^J), 85.3 (C^A), 79.2 (C^M), 72.6 (C^H), 71.7 (C^N), 51.9 (C^K), 50.4 (C^G), 39.5 (C^{B/F}), 33.8 (C^{B/F}), 28.7 (C^L), 24.7 (C^{C/D/E}), 22.4 (C^{C/D/E}), 21.8 (C^{C/D/E}).

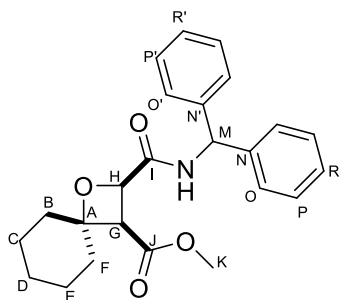
FTIR (ATR) ν (cm⁻¹): 3280 (broad, N-H), 2931 (C-H), 1735 (C=O, ester), 1671 (C=O, amide).

HRMS: ESI C₁₄H₁₉NO₄ [M + H]⁺ predicted: 266.1387, found: 366.1374.

R_f: (EtOAc-hexane, 2:3) = 0.27.

rac-(2R,3R)-Methyl 2-(benzhydrylcarbamoyl)-1-oxaspiro[3.5]nonane-3-carboxylate 26

(WM-05-51)



Chemical Formula: C₂₄H₂₇NO₄

Molecular Weight: 393.4830

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzhydrylamine (0.19 mL, 1.10 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 3:2 hexane-EtOAc) gave **26** (80 mg, 0.20 mmol, 20%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.24 (m, 10H, H^{N, O, P, R, N', O', P', R'}), 6.33 (d, *J* = 8.4 Hz, 1H, H^M), 5.00 (d, *J* = 8.9 Hz, 1H, H^H), 3.66 (d, *J* = 8.9 Hz, 1H, H^G), 3.59 (s, 3H, H^K), 1.98-1.14 (m, 10H, H^{B/C/D/E/F}).

¹³C NMR (101 MHz, CDCl₃) δ 169.5 (C^I), 168.6 (C^J), 141.5 (C^{N/N'}), 141.4 (C^{N/N'}), 128.6 (C^{O/O'}), 128.5 (C^{O/O'}), 127.8 (C^{P/P'}), 127.6 (C^{P/P'}), 127.4 (C^{R/R'}), 127.4 (C^{R/R'}), 85.3 (C^A), 72.7 (C^H), 56.3 (C^K), 51.8 (C^G), 50.3 (C^M), 39.7 (C^{B/F}), 33.8 (C^{B/F}), 24.7 (C^{C/D/E}), 22.4 (C^{C/D/E}), 21.9 (C^{C/D/E}).

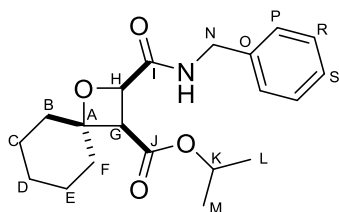
FTIR (ATR) ν (cm⁻¹): 3315 (broad, N-H), 2931 (C-H), 1735 (C=O, ester), 1675 (C=O, amide).

HRMS: ESI: C₂₄H₂₇NO₄ [M + H]⁺ predicted: 394.2013, found: 394.1997.

R_f: (EtOAc-hexane, 2:3) = 0.20.

rac*-(2*R*,3*R*)-Isopropyl 2-(benzylcarbamoyl)-1-oxaspiro[3.5]nonane-3-carboxylate **27*

(WM-05-91)



Chemical Formula: C₂₀H₂₇NO₄

Molecular Weight: 345.44

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclohexanone (0.32 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzylamine (0.11 mL, 2.00 mmol) and stirring at room temperature for 16 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in final step using isopropanol (0.15 mL, 2.00 mmol). Purification by flash chromatography (eluent 19:1-9:1 hexane-EtOAc) gave **27** (114 mg, 0.33 mmol, 35%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.39-7.27 (m, 5H, H^{P,R,S}), 7.05 (s, 1H, N-H), 5.10-5.03 (m, 1H, H^K), 5.00 (d, *J* = 8.7 Hz, 1H, H^H), 4.65 (dd, *J* = 14.9, 6.5 Hz, 1H, H^N), 4.47 (dd, *J* = 14.9, 5.2 Hz, 1H, H^N), 3.59 (d, *J* = 8.7 Hz, 1H, H^G), 1.96-1.27 (m, 10H, H^{B, C, D, E, F}), 1.25 (d, *J* = 4.6 Hz, 3H, H^{L/M}), 1.23 (d, *J* = 4.5 Hz, 3H, H^{L/M}).

¹³C NMR (101 MHz, CDCl₃) δ 170.4 (C^I), 167.8 (C^J), 138.0 (C^O), 128.7 (C^R), 127.9 (C^P), 127.4 (C^S), 85.1 (C^A), 72.9 (C^H), 68.6 (C^K), 50.7 (C^G), 43.0 (C^N), 39.5 (C^{B/F}), 33.7 (C^{B/F}), 24.8 (C^{C/D/E}), 22.4 (C^{C/D/E}), 21.9 (C^{C/D/E}), 21.9 (C^{L/M}), 21.8 (C^{L/M}).

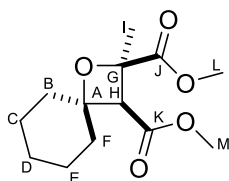
FTIR (ATR) ν (cm⁻¹): 3461 (broad, N-H), 2931 (C-H), 1731 (C=O, ester), 1765 (C=O, amide).

HRMS ESI C₂₀H₂₇NO₄ [M + Na]⁺ predicted: 368.1829, found: 368.1832.

R_f: (EtOAc-hexane, 2:3) = 0.26.

rac*-(2*R*,3*R*)-2,3-Dimethyl 2-methyl-1-oxaspiro[3.5]nonane-2,3-dicarboxylate **28*

(WM-07-62)



Chemical Formula: C₁₃H₂₀O₅

Molecular Weight: 256.2980

A solution of 2-methylmaleic anhydride (112 mg, 1.00 mmol), cyclohexanone (0.32 mL, 3.00 mmol) and *p*-xylene (0.12 mL, 1.00 mmol) in anhydrous MeCN (0.1 M, 10 mL) was prepared in a Duran phototube and purged with argon for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm) until complete consumption of the 2-methylmaleic anhydride (168 h), as judged by ¹H NMR spectroscopy (solvent suppression). Next, the solution was decanted into a round-bottomed flask, and methanol (0.10 mL, 2 mmol) was added. The reaction mixture was stirred at reflux for 48 h until full consumption of oxetane **A**, as judged by ¹H NMR spectroscopy (solvent suppression). The solvent was evaporated under reduced pressure to give the crude product **B**. Crude **B** was then dissolved in anhydrous MeCN (3 mL) under nitrogen. Next, DMAP (10 mg, 5 mol%) was added, followed by methanol (0.10 mL, 2.0 mmol). The reaction mixture was cooled to 0 °C and DCC (226 mg, 1.2 mmol) was added portion-wise. The reaction was slowly warmed to room temperature and stirred overnight. The precipitated urea was filtered off and the filtrate was concentrated under reduced pressure to give crude product **C**. Purification by flash chromatography (eluent: 9:1 hexane-EtOAc) gave **28** (82 mg, 0.32 mmol, 32 %) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 3.81 (s, 3H, H^I), 3.69 (s, 3H, H^M), 3.37 (s, 1H, H^H), 1.92 – 1.77 (m, 4H, H^{B, C, D, E, F}), 1.73 – 1.68 (m, 3H, H^I), 1.54 – 1.27 (m, 4H, H^{B, C, D, E}).

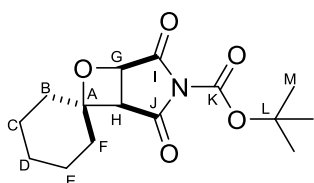
¹³C NMR (101 MHz, CDCl₃) δ 173.2 (C^J), 168.9 (C^K), 81.5 (C^A), 78.3 (C^G), 57.1 (C^H), 52.4 (C^L), 51.8 (C^M), 41.2 (C^I), 33.1 (C^{B/C/D/E/F}), 27.7 (C^{B/C/D/E/F}), 24.8 (C^{B/C/D/E/F}), 22.1 (C^{B/C/D/E/F}), 21.9 (C^{B/C/D/E/F}).

FTIR (ATR) ν (cm⁻¹): 2931 (C-H), 1736 (C=O).

MS: APCI C₁₃H₂₀O₅ [M+H]⁺ predicted: 257.1384, found: 257.1378.

rac*-(2*R*,3*R*)-Tert-butyl 2,4-dioxo-7-oxa-3-azaspiro[bicyclo[3.2.0]heptane-6,1'-cyclohexane]-3-carboxylate **29*

(WM-09-24)



Chemical Formula: C₁₅H₂₁NO₅

Molecular Weight: 295.3350

A solution of N-Boc-maleimide (200 mg, 1.00 mmol), cyclohexanone (0.30 mL, 3.00 mmol) and *p*-xylene (0.60 mL, 6.00 mmol) in anhydrous MeCN (0.05 M, 20 mL) was prepared in a Duran phototube

and purged with argon for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm) until complete consumption of the N-Boc-maleimide (20 h), as judged by ^1H NMR spectroscopy (solvent suppression). The solvent was removed under reduced pressure to give crude product **29**. Purification by flash chromatography (eluent: 1:9 acetone-heptane) gave **29** (90 mg, 0.31 mmol, 31 %) as a colourless oil.

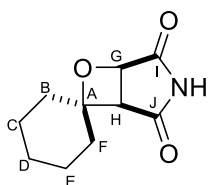
^1H NMR (400 MHz, CDCl_3) δ 4.95 (d, $J = 5.7$ Hz, 1H, H^{G}), 3.40 (d, $J = 5.7$ Hz, 1H, H^{H}), 1.62 (s, 9H, H^{M}), 1.98 – 1.27 (m, 10H, $\text{H}^{\text{B, C, D, E, F}}$).

^{13}C NMR (101 MHz, CDCl_3) δ 170.4 (C^{I}), 170.4 (C^{J}), 146.4 (C^{K}), 88.3 (C^{A}), 86.8 (C^{L}), 72.1 (C^{G}), 48.1 (C^{H}), 39.1 ($\text{C}^{\text{B/C/D/E/F}}$), 35.3 ($\text{C}^{\text{B/C/D/E/F}}$), 27.7 (C^{M}), 24.5 ($\text{C}^{\text{B/C/D/E/F}}$), 22.0 ($\text{C}^{\text{B/C/D/E/F}}$), 21.7 ($\text{C}^{\text{B/C/D/E/F}}$).

FTIR (ATR) ν (cm^{-1}): 2935 (C-H), 1763 (C=O), 1725 (C=O).

rac-(2*R*,3*R*)-7-Oxa-3-azaspiro[bicyclo[3.2.0]heptane-6,1'-cyclohexane]-2,4-dione **30**

(WM-09-09)



Chemical Formula: $\text{C}_{10}\text{H}_{13}\text{NO}_3$

Molecular Weight: 195.2180

A solution of malaimide (50 mg, 0.50 mmol), cyclohexanone (0.15 mL, 1.50 mmol) and *p*-xylene (0.30 mL, 3.00 mmol) in anhydrous MeCN (0.05 M, 10 mL) was prepared in a Duran phototube and purged with argon for 15 minutes, then irradiated at approximately 40 °C ($\lambda = 300$ nm) until complete consumption of the malaimide (23 h), as judged by ^1H NMR spectroscopy (solvent suppression). The solvent was removed under reduced pressure to give crude product **30**. Purification by flash chromatography (eluent: 1:4 to 2:3 EtOAc-heptane) gave **30** (20 mg, 0.10 mmol, 20 %) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1H, N-H), 4.95 (d, $J = 5.6$ Hz, 1H, H^{G}), 3.41 (d, $J = 5.6$ Hz, 1H, H^{H}), 2.01 – 1.35 (m, 10H, $\text{H}^{\text{B, C, D, E, F}}$).

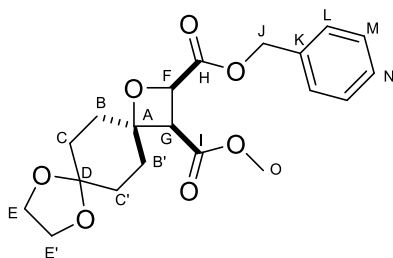
^{13}C NMR (101 MHz, CDCl_3) δ 174.6 (C^{I}), 174.0 (C^{J}), 87.9 (C^{G}), 73.4 (C^{A}), 49.3 (C^{H}), 39.0 ($\text{C}^{\text{B/C/D/E/F}}$), 35.2 ($\text{C}^{\text{B/C/D/E/F}}$), 24.5 ($\text{C}^{\text{B/C/D/E/F}}$), 22.0 ($\text{C}^{\text{B/C/D/E/F}}$), 21.8 ($\text{C}^{\text{B/C/D/E/F}}$).

FTIR (ATR) ν (cm^{-1}): 3218 (broad, N-H), 2935 (C-H), 1718 (C=O).

Melting point: 160-164 °C

2-Benzyl 3-methyl *rac*-(2*R*,3*R*)-1,8,11-trioxadispiro[3.2.47.24]tridecane-2,3-dicarboxylate **31**

(WM-06-34)



Chemical Formula: C₂₀H₂₄O₇

Molecular Weight: 376.41

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and 1,4-cyclohexanedione monoethylene acetal (460 mg, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzyl alcohol (0.21 mL, 2.00 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **31** (80 mg, 0.21 mmol, 21%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.42-7.31 (m, 5H, H^{L, M, N}), 5.29 (d, *J* = 12.2 Hz, 1H, H^I), 5.22 (d, *J* = 12.2 Hz, 1H, H^J), 5.10 (d, *J* = 8.9 Hz, 1H, H^F), 4.00-3.91 (m, 4H, H^{E, E'}), 3.78 (d, *J* = 8.9 Hz, 1H, H^G), 3.63 (s, *J* = 2.7 Hz, 3H, H^O), 2.25-1.53 (m, 8H, H^{B, B', C, C'}).

¹³C NMR (101 MHz, CDCl₃) δ 170.5 (C^I), 168.5 (C^J), 135.5 (C^K), 128.6 (C^M), 128.5 (C^L), 128.4 (C^N), 107.6 (C^D), 84.4 (C^A), 71.8 (C^F), 67.0 (C^J), 64.4 (C^{E/E'}), 64.3 (C^{E/E'}), 51.9 (C^O), 50.1 (C^G), 36.6 (C^{B, B', C, C'}), 30.7 (C^{B, B', C, C'}), 29.7 (C^{B, B', C, C'}).

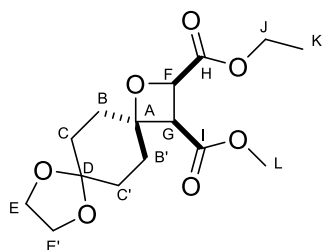
FTIR (ATR) ν (cm⁻¹): 2952 (C-H), 1735 (C=O).

HRMS: ESI C₂₀H₂₄O₇ [M + Na]⁺ predicted: 399.1397, found at 399.1397.

R_f: (EtOAc-hexane, 1:1) = 0.30.

2-Ethyl 3-methyl *rac*-(2*R*,3*R*)-1,8,11-trioxadispiro[3.2.47.24]tridecane-2,3-dicarboxylate **32**

(WM-06-33)



Chemical Formula: C₁₅H₂₂O₇

Molecular Weight: 314.33

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and 1,4-cyclohexanedione monoethylene acetal (460 mg, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using ethanol (0.11 mL, 2.00 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **32** (77 mg, 0.26 mmol, 26%) as colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.04 (d, *J* = 8.9 Hz, 1H, H^F), 4.33-4.23 (m, 2H, H^J), 3.98-3.89 (m, 4H, H^E), 3.75 (d, *J* = 8.9 Hz, 1H, H^G), 3.68 (s, *J* = 2.0 Hz, 3H, H^L), 2.20-1.50 (m, 8H, H^{B, B', C, C'}), 1.30 (t, *J* = 7.2 Hz, 3H, H^K).

¹³C NMR (101 MHz, CDCl₃) δ 170.6 (C^H), 168.6 (C^I), 107.6 (C^D), 84.2 (C^A), 71.8 (C^F), 64.4 (C^{E/E'}), 64.3 (C^{E/E'}), 61.3 (C^J), 51.9 (C^L), 50.1 (C^G), 36.5 (C^{B, B', C, C'}), 30.7 (C^{B, B', C, C'}), 30.5 (C^{B, B', C, C'}), 29.7 (C^{B, B', C, C'}), 14.1 (C^K).

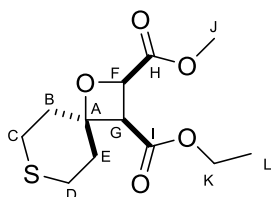
FTIR (ATR) ν (cm⁻¹): 2952 (C-H), 1735 (C=O).

HRMS: ESI C₁₅H₂₂O₄ [M + Na]⁺ predicted: 337.1258, found at 337.1245.

R_f: (EtOAc-hexane, 1:1) = 0.20.

rac*-(2*R*,3*R*)-3-Ethyl 2-methyl 1-oxa-7-thiaspiro[3.5]nonane-2,3-dicarboxylate **33*

(WM-07-03)



Chemical Formula: C₁₂H₁₈O₅S

Molecular Weight: 274.33

Using the general procedure, maleic anhydride (490 mg, 5.00 mmol) and tetrahydro-4H-thiopyran-4-one (1.75 mg, 15.00 mmol) used in the Paternò-Büchi reaction. The reaction was irradiated for 2 weeks. Using methanol (0.50 mL, 10.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (25 mL) and used in the final step using ethanol (0.60 mL, 10.00 mmol). Purification by flash chromatography (eluent: 9:1 to 3:1 hexane-EtOAc) gave **33** (275 mg, 1.00 mmol, 20%) as yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 5.05 (d, *J* = 8.9 Hz, 1H, H^F), 4.16 (q, *J* = 7.1 Hz, 2H, H^K), 3.81 (s, *J* = 1.8 Hz, 3H, H^J), 3.66 (d, *J* = 8.9 Hz, 1H, H^G), 2.98-2.89 (m, 2H, H^{C/D}), 2.55-2.29 (m, 4H, H^{B/C/D/E}), 2.17-2.08 (m, 1H, H^{B/E}), 1.97-1.87 (m, 1H, H^{B/E}), 1.27 (t, *J* = 7.1 Hz, 3H, H^L).

¹³C NMR (101 MHz, CDCl₃) δ 171.0 (C^H), 167.6 (C^I), 83.9 (C^A), 72.0 (C^F), 61.3 (C^K), 52.2 (C^J), 51.3 (C^G), 40.3 (C^{B/E}), 34.7 (C^{B/E}), 24.5 (C^{C/D}), 23.8 (C^{C/D}), 14.2 (C^L).

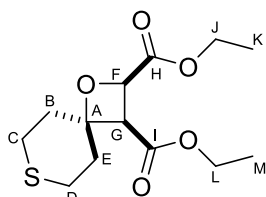
FTIR (ATR) ν (cm⁻¹): 2931 (C-H), 1731 (C=O).

HRMS: APCI C₁₂H₁₈O₅S [M + H]⁺, predicted at 275.0948, found at 275.0948.

R_f: (EtOAc-hexane, 3:7) = 0.29.

rac*-(2*R*,3*R*)-Diethyl 1-oxa-7-thiaspiro[3.5]nonane-2,3-dicarboxylate **34*

(WM-06-59)



Chemical Formula: C₁₃H₂₀O₅S

Molecular Weight: 288.36

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and tetrahydro-4H-thiopyran-4-one (350 mg, 3.00 mmol) used in the Paternò-Büchi reaction. The reaction was irradiated for 2 weeks. Using ethanol (0.12 mL, 2.00 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using ethanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent: 9:1 to 3:1 hexane-EtOAc) gave **34** (62 mg, 0.22 mmol, 22%).

¹H NMR (400 MHz, CDCl₃) δ 5.02 (d, *J* = 9.0 Hz, 1H, H^F), 4.28 (dt, *J* = 14.4, 7.2 Hz, 1H, H^I), 4.27 (dt, *J* = 14.3, 7.2 Hz, 1H, H^J), 4.16 (q, *J* = 7.2 Hz, 2H, H^L), 3.65 (d, *J* = 9.0 Hz, 1H, H^G), 2.98-2.90 (m, 2H, H^{C/D}), 2.55-2.43 (m, 2H, H^{C/D}), 2.39-2.29 (m, 2H, H^{B/E}), 2.17-2.09 (m, 1H, H^{B/E}), 1.97-1.89 (m, 1H, H^{B/E}), 1.30 (t, *J* = 7.1 Hz, 4H), 1.26 (t, *J* = 6.8 Hz, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 170.5 (C^H), 167.6 (C^I), 83.8 (C^A), 72.0 (C^F), 61.3 (C^{J/L}), 61.2 (C^{J/L}), 51.2 (C^G), 40.3 (C^{B/E}), 34.7 (C^{B/E}), 24.5 (C^{C/D}), 23.9 (C^{C/D}), 14.2 (C^{K/M}), 14.1 (C^{K/M}).

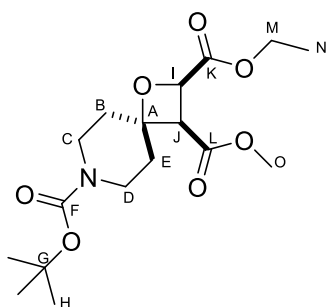
FTIR (ATR) ν (cm⁻¹): 2980 (C-H), 1731 (C=O).

HRMS: APCI C₁₃H₂₀O₅S [M + Na]⁺, predicted: 311.0924, found at 311.0931.

R_f: (EtOAc-hexane, 1:4) = 0.41.

rac-(2*R*,3*R*)-7-*tert*-Butyl 2-ethyl 3-methyl 1-oxa-7-azaspiro[3.5]nonane-2,3,7-tricarboxylate **35**

(WM-06-77/WM-06-92)



Chemical Formula: C₁₇H₂₇NO₇

Molecular Weight: 357.40

1 mmol scale - Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and 1-Boc-4-piperidone (597 mg, 3.00 mmol) used in the Paternò-Büchi reaction (86 h irradiation). Using ethanol (0.12 mL, 2.00 mmol) and stirring at reflux for 86 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 7:3 hexane-EtOAc) gave **35** (49 mg, 0.14 mmol, 14%) as yellow oil.

5 mmol scale - Using the general procedure, maleic anhydride (490 mg, 5.00 mmol) and 1-Boc-4-piperidone (2.98 g, 15.00 mmol) used in the Paternò-Büchi reaction (86 h irradiation). Using ethanol (0.60 mL, 10.00 mmol) and stirring at reflux for 86 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (25 mL) and used in the final step using methanol (0.50 mL, 10.00 mmol). Purification by flash chromatography (eluent 7:3 hexane-EtOAc) gave **35** (246mg, 0.69 mmol, 14%) as yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 5.05 (d, *J* = 8.9 Hz, 1H, H^I), 4.34-4.21 (m, 2H, H^M), 3.74 (d, *J* = 8.9 Hz, 1H, H^J), 3.69 (s, 3H, H^O), 3.31-3.22 (m, 2H, H^{B/C/D/E}), 2.13-1.97 (m, 2H, H^{B/C/D/E}), 1.93-1.82 (m, 1H, H^{B/C/D/E}), 1.71-1.63 (m, 1H, H^{B/C/D/E}), 1.44 (s, 9H, H^H), 1.30 (t, *J* = 7.2 Hz, 3H, H^N).

¹³C NMR (101 MHz, CDCl₃) δ 170.3 (C^K), 168.1 (C^L), 154.6 (C^F), 83.4 (C^A), 79.8 (C^G), 72.0 (C^I), 61.4 (C^M),

52.0 (C^O), 50.4 (C^J), 38.4 (C^{C+D}), 33.1 (C^{B+E}), 28.3 (C^N), 14.1 (C^H).

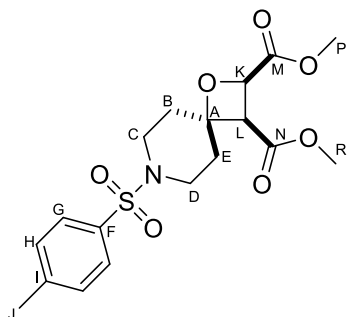
FTIR (ATR) ν (cm⁻¹): 2976 (C-H), 1735 (C=O, ester), 1686 (C=O, next to N).

HRMS: APCI C₁₇H₂₇NO₇ [M + Na]⁺ predicted: 380.1680, found at 380.1667.

R_f: (EtOAc-hexane, 2:3) = 0.23.

rac*-(2*R*,3*R*)-Dimethyl 7-tosyl-1-oxa-7-azaspiro[3.5]nonane-2,3-dicarboxylate **36*

(WM-06-55)



Chemical Formula: C₁₈H₂₃NO₇S

Molecular Weight: 397.44

Using the general procedure, maleic anhydride (147 mg, 1.50 mmol) and 1-tosyl-4-piperidinone (570 mg, 4.50 mmol) used in the Paternò-Büchi reaction (168 h irradiation; 80 % conversion). Using methanol (0.15 mL, 3.00 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (7 mL) and used in the final step using methanol (0.15 mL, 3.00 mmol). Purification by flash chromatography (eluent: 7:3 hexane-EtOAc) gave **36** (91 mg, 0.22 mmol, 21%) as a colourless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.63-7.59 (m, 2H, H^G), 7.30 (dd, J = 8.5, 0.6 Hz, 2H, H^H), 4.99 (d, J = 8.9 Hz, 1H, H^K), 3.78 (s, 3H, H^{P/R}), 3.73 (d, J = 8.9 Hz, 1H, H^L), 3.67 (s, 3H, H^{P/R}), 3.63-3.52 (m, 2H, H^{C/D}), 2.67-2.59 (m, 2H, H^{C/D}), 2.42 (s, 3H, H^I), 2.24 (ddd, J = 13.4, 5.5, 2.9 Hz, 1H, H^{B/E}), 2.08 (ddd, J = 13.0, 5.8, 2.2 Hz, 2H, H^{B/E}), 1.79-1.71 (m, 1H, H^{B/E}).

¹³C NMR (101 MHz, CDCl₃) δ 170.6 (C^M), 167.9 (C^N), 143.8 (C^I), 132.7 (C^G), 129.8 (C^H), 127.7 (C^F), 82.2 (C^A), 72.0 (C^K), 52.3 (C^{P/R}), 52.2 (C^{P/R}), 49.9 (C^L), 42.0 (C^{C/D}), 41.5 (C^{C/D}), 37.7 (C^{B/F}), 32.6 (C^{B/F}), 21.5 (C^J).

FTIR (ATR) ν (cm⁻¹): 2926 (C-H), 1742 (C=O).

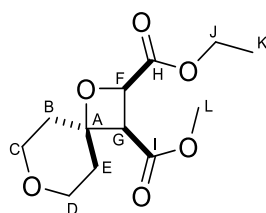
HRMS: APCI C₁₈H₂₃NO₇S [M + H]⁺ predicted: 398.1268, found at: 398.1269.

R_f: (EtOAc-hexane, 2:3) = 0.11

Melting point: 130 - 136 °C.

rac*-(2*R*,3*R*)-2-Ethyl 3-methyl 1,7-dioxaspiro[3.5]nonane-2,3-dicarboxylate **37*

(WM-06-49)



Chemical Formula: C₁₂H₁₈O₆

Molecular Weight: 258.27

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and tetrahydro-4H-pyran-4-one (0.30 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (96 h irradiation). Using ethanol (0.12 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step (using methanol 0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **37** (79 mg, 0.31 mmol, 31%) as colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.06 (d, *J* = 8.9 Hz, 1H, H^F), 4.33-4.23 (m, 2H, H^I), 3.81-3.73 (m, 3H, H^{C, D}), 3.75 (d, *J* = 8.9 Hz, 1H, H^G), 3.70 (s, 3H, H^L), 3.68-3.62 (m, 1H, H^{C/D}), 2.09 (dt, *J* = 13.5, 3.7 Hz, 1H, H^{B/E}), 2.01 (m, 2H, H^{B/E}), 1.87-1.77 (m, 1H, H^{B/E}), 1.30 (t, *J* = 7.2 Hz, 3H, H^K).

¹³C NMR (101 MHz, CDCl₃) δ 170.4 (C^H), 168.1 (C^I), 82.5 (C^A), 71.9 (C^F), 63.6 (C^{C/D}), 63.3 (C^{C/D}), 61.4 (C^J), 52.0 (C^L), 50.7 (C^G), 39.3 (C^{B/E}), 34.1 (C^{B/E}), 14.1 (C^K).

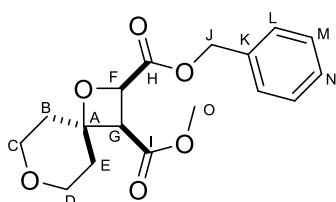
FTIR (ATR) ν (cm⁻¹): 2957 (C-H), 1735 (C=O).

HRMS: APCI C₁₂H₁₈O₆ [M + H]⁺ predicted: 259.1176, found at 259.1168.

R_f: (EtOAc-hexane, 2:3) = 0.14.

rac*-(2*R*,3*R*)-2-Benzyl 3-methyl 1,7-dioxaspiro[3.5]nonane-2,3-dicarboxylate **38*

(WM-06-50)



Chemical Formula: C₁₇H₂₀O₆

Molecular Weight: 320.34

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and tetrahydro-4H-pyran-4-one (0.30 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (96 h irradiation). Using benzyl alcohol (0.21 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **38** (86 mg, 0.27 mmol, 27%) as colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.32 (m, 5H, H^{L, M, N}), 5.27 (d, *J* = 12.1 Hz, 1H, H^I), 5.20 (d, *J* = 12.1 Hz, 1H, H^J), 5.10 (d, *J* = 8.9 Hz, 1H, H^F), 3.76 (d, *J* = 8.9 Hz, 1H, H^G), 3.80-3.63 (m, 4H, H^{C, D}), 3.61 (s, 1H, H^O), 2.10 (dt, *J* = 13.5, 3.7 Hz, 1H, H^{B/E}), 2.03-1.98 (m, 2H, H^{B/E}), 1.87-1.78 (m, 1H, H^{B/E}).

¹³C NMR (101 MHz, CDCl₃) δ 170.3 (C^H), 168.1 (C^I), 135.3 (C^K), 128.7 (C^M), 128.6 (C^L), 128.4 (C^N), 82.7 (C^A), 71.9 (C^F), 67.1 (C^J), 63.5 (C^{C/D}), 63.3 (C^{C/D}), 52.0 (C^O), 50.7 (C^G), 39.4 (C^{B/E}), 34.1 (C^{B/E}).

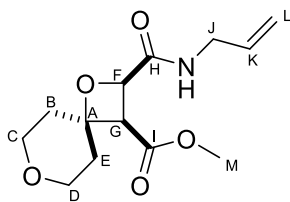
FTIR (ATR) ν (cm⁻¹): 2953 (C-H), 1735 (C=O)

HRMS: APCI C₁₇H₂₀O₆ [M + Na]⁺ predicted: 343.1152, found at 343.1142.

R_f: (EtOAc-hexane, 3:7) = 0.13.

rac*-(2*R*,3*R*)-Methyl 2-(allylcarbamoyl)-1,7-dioxaspiro[3.5]nonane-3-carboxylate **39*

(WM-06-46)



Chemical Formula: C₁₃H₁₉NO₅

Molecular Weight: 269.30

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and tetrahydro-4H-pyran-4-one (0.30 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (96 h irradiation). Using allyl amine (0.14 mL, 2.00 mmol) and stirring at room temperature for 24 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (3 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **39** (42 mg, 0.16 mmol, 16%) as colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.81 (s, 1H, N-H), 5.91 (ddd, *J* = 16.0, 10.8, 5.6 Hz, 1H, H^K), 5.32-5.26 (m, 1H, H^L), 5.21-5.15 (m, 1H, H^I), 5.01 (d, *J* = 8.8 Hz, 1H, H^F), 4.01 (m, 2H, H^J), 3.82-3.74 (m, 2H, H^{C/D}), 3.70 (d, *J* = 8.8 Hz, 1H, H^G), 3.69 (s, 1H, H^M), 3.54 (dt, *J* = 16.9, 5.1 Hz, 1H, H^{C/D}), 2.05-1.84 (m, 5H, H^{B, E, C/D}).

¹³C NMR (101 MHz, CDCl₃) δ 169.7 (C^H), 168.3 (C^I), 133.9 (C^K), 116.7 (C^L), 81.8 (C^A), 72.8 (C^F), 63.8 (C^{C/D}), 63.3 (C^{C/D}), 52.1 (C^M), 50.2 (C^G), 41.3 (C^J), 39.4 (C^{B/E}), 34.5 (C^{B/E}).

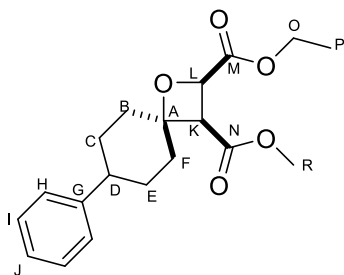
FTIR (ATR) ν (cm⁻¹): 3404 (N-H), 2857 (C-H), 1736 (C=O, ester), 1664 (C=O, amide).

HRMS: APCI C₁₃H₁₉NO₅ [M + H]⁺ predicted: 270.1336, found at: 270.1325.

R_f: (EtOAc-hexane, 1:4) = 0.10.

rac*-(2*R*,3*R*)-2-Ethyl 3-methyl 7-phenyl-1-oxaspiro[3.5]nonane-2,3-dicarboxylate **40*

(WM-06-71)



Chemical Formula: C₁₉H₂₄O₅

Molecular Weight: 332.40

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and 4-phenylcyclohexanone (520 mg, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using ethanol (0.12 mL, 2.00 mmol) and stirring at reflux for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol).

Purification by flash chromatography (eluent 9:1 hexane-EtOAc) gave **40** (101 mg, 0.30 mmol, 30%) as yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, *J* = 10.5, 4.3 Hz, 2H, H^I), 7.23-7.13 (m, 3H, H^{H,J}), 5.08 (d, *J* = 8.8 Hz, 1H, H^L), 4.30 (m, 2H, H^O), 3.85 (d, *J* = 8.8 Hz, 1H, H^K), 3.74 (s, 3H, H^R), 2.55-2.49 (m, 2H, H^{D,B/C/F/E}), 2.34-2.27 (m, 1H, H^{B/C/F/E}), 1.89 (m, 4H, H^{B/C/F/E}), 1.72-1.63 (m, 2H, H^{B/C/F/E}), 1.32 (t, *J* = 7.1 Hz, 3H, H^P), 1.25-1.20 (m, 1H, H^{B/C/D/E}).

¹³C NMR (101 MHz, CDCl₃) δ 170.6 (C^M), 169.0 (C^N), 145.8 (C^G), 128.5 (C^I), 126.6 (C^H), 126.3 (C^J), 85.5 (C^A), 71.3 (C^L), 61.3 (C^O), 52.0 (C^R), 50.4 (C^K), 42.6 (C^D), 40.0 (C^{B/C/E/F}), 33.9 (C^{B/C/E/F}), 30.4 (C^{B/C/E/F}), 29.9 (C^{B/C/E/F}), 14.2 (C^P).

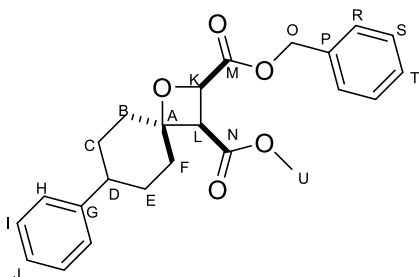
FTIR (ATR) ν (cm⁻¹): 2931 (C-H), 1757 and 1731 (C=O).

HRMS: APCI C₁₉H₂₄O₅ [M + H]⁺ predicted: 333.1697, found at 333.1695.

R_f: (EtOAc-hexane, 1:4) = 0.09.

rac*-(2*R*,3*R*)-2-Benzyl 3-methyl 7-phenyl-1-oxaspiro[3.5]nonane-2,3-dicarboxylate **41*

(WM-06-72)



Chemical Formula: C₂₄H₂₆O₅

Molecular Weight: 394.47

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and 4-phenylcyclohexanone (520 mg, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzyl alcohol (0.20 mL, 2.00 mmol) and stirring at reflux for 72 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 9:1 hexane-EtOAc) gave **41** (65 mg, 0.16 mmol, 16%) as yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.39-7.12 (m, 10H, H^{H,I,J,R,S,T}), 5.25 (s, 2H, H^O), 5.11 (d, *J* = 8.9 Hz, 1H, H^K), 3.85 (d, *J* = 8.9 Hz, 1H, H^L), 3.65 (s, 3H, H^U), 2.59-2.49 (m, 2H, H^{D,B/C/F/E}), 2.33-2.25 (m, 1H, H^{B/C/F/E}), 2.00-1.78 (m, 3H, H^{B/C/F/E}), 1.72-1.60 (m, 2H, H^{B/C/F/E}), 1.28-1.18 (m, 1H, H^{B/C/F/E}).

¹³C NMR (101 MHz, CDCl₃) δ 170.5 (C^M), 168.9 (C^N), 145.7 (C^G), 135.4 (C^P), 128.7 (C^{I/S/R}), 128.5 (C^{I/S/R}), 128.5 (C^{I/S/R}), 128.4 (C^{T/J}), 126.6 (C^H), 126.3 (C^{T/J}), 85.7 (C^A), 71.3 (C^K), 67.0 (C^O), 51.9 (C^U), 50.4 (C^L), 42.6 (C^D), 40.0 (C^{B/C/E/F}), 33.9 (C^{B/C/E/F}), 30.4 (C^{B/C/E/F}), 29.9 (C^{B/C/E/F}).

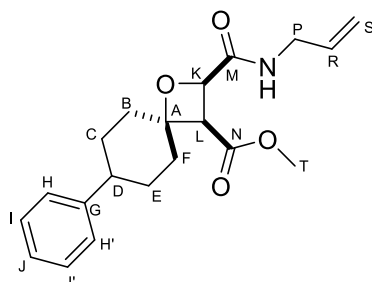
FTIR (ATR) ν (cm⁻¹): 2929 (C-H), 1759 and 1733 (C=O).

HRMS: APCI C₂₄H₂₆O₅ [M + H]⁺, predicted: 395.1853, found at 395.1853.

R_f: (EtOAc-hexane, 1:4) = 0.12.

rac-(2R,3R)-Methyl 2-(allylcarbamoyl)-7-phenyl-1-oxaspiro[3.5]nonane-3-carboxylate 42

(WM-06-73)

Chemical Formula: C₂₀H₂₅NO₄

Molecular Weight: 343.42

Using the general procedure, maleic anhydride (98 mg, 1.00 mmol) and 4-phenylcyclohexanone (520 mg, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using allyl amine (0.14 mL, 2.00 mmol) and stirring at room temperature for 24 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (4 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol). Purification by flash chromatography (eluent 1:1 hexane-EtOAc) gave **42** (81 mg, 0.24 mmol, 24%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.34-7.27 (m, 2H, H^I), 7.24-7.17 (m, 1H, H^I), 7.14 (dd, *J* = 5.2, 3.3 Hz, 2H, H^H), 6.90 (s, 1H, N-H), 5.93 (ddt, *J* = 17.2, 10.3, 5.6 Hz, 1H, H^R), 5.31 (ddd, *J* = 17.2, 3.1, 1.7 Hz, 1H, H^S), 5.19 (dq, *J* = 10.3, 1.4 Hz, 1H, H^S), 5.01 (d, *J* = 8.8 Hz, 1H, H^K), 4.09-3.91 (m, 2H, H^P), 3.79 (d, *J* = 8.8 Hz, 1H, H^L), 3.73 (s, 3H, H^T), 2.58-2.47 (m, 2H, H^{B/C/F/E}), 2.36-2.29 (m, 1H, H^{B/C/F/E}), 1.97 (dd, *J* = 9.8, 6.8 Hz, 1H, H^{B/C/F/E}), 1.92-1.78 (m, 2H, H^{B/C/F/E}), 1.69-1.54 (m, 2H, H^{B/C/F/E}), 1.18 (dd, *J* = 12.2, 3.5 Hz, 1H, H^{B/C/F/E}).

¹³C NMR (101 MHz, CDCl₃) δ 170.1 (C^M), 169.0 (C^N), 145.5 (C^G), 134.0 (C^R), 128.5 (C^{I/H}), 126.6 (C^{I/H}), 126.4 (C^S), 116.6 (C^J), 85.1 (C^A), 72.5 (C^K), 52.0 (C^T), 49.5 (C^P), 42.6 (C^P), 41.3 (C^S), 40.0 (C^{B/C/E/F}), 34.0 (C^{B/C/E/F}), 30.4 (C^{B/C/E/F}), 30.0 (C^{B/C/E/F}).

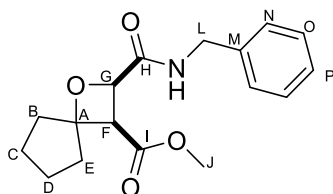
FTIR (ATR) ν (cm⁻¹): 3412 (broad, N-H), 2931 (C-H), 1735 (C=O, ester), 1671 (C=O, amide)

HRMS: APCI C₂₀H₂₅NO₄ [M + H]⁺, predicted at 344.1856, found at 344.1839.

R_f: (EtOAc-hexane, 4:1) = 0.26.

rac-(2R,3R)-Methyl 2-(benzylcarbamoyl)-1-oxaspiro[3.4]octane-3-carboxylate 43

(WM-05-72)

Chemical Formula: C₁₇H₂₁NO₄

Exact Mass: 303.15

Using the general procedure, maleic anhydride (98 mg, 1 mmol) and cyclopentanone (0.26 mL, 3.00 mmol) were used in the Paternò-Büchi reaction (86 h irradiation). Using benzyl amine (0.11 mL, 2.00 mmol) and stirring at room temperature for 48 h in the second step, the crude product **B** was obtained, then dissolved in MeCN (5 mL) and used in the final step using methanol (0.10 mL, 2.00 mmol).

Purification by flash chromatography (eluent 4:1-3:2 hexane-EtOAc) gave **43** (30 mg, 0.10 mmol, 10%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.40-7.27 (m, 5H, H^{N, O, P}), 7.01 (br s, 1H, N-H), 5.02 (d, *J* = 8.6 Hz, 1H, H^G), 4.55 (d, *J* = 5.9 Hz, 2H, H^I), 3.91 (d, *J* = 8.6 Hz, 1H, H^F), 3.68 (s, 3H, H^J), 2.26-1.02 (m, 10H, H^{B, C, D, E}).

¹³C NMR (101 MHz, CDCl₃) δ 170.1 (C^H), 169.4 (C^I), 138.0 (C^M), 128.7 (C^O), 127.9 (C^P), 127.5 (C^N), 92.9 (C^A), 72.8 (C^G), 51.9 (C^J), 49.5 (C^F), 43.0 (C^L), 40.5 (C^{B, E}), 36.1 (C^{B, E}), 22.7 (C^{C, D}), 22.5 (C^{C, D}).

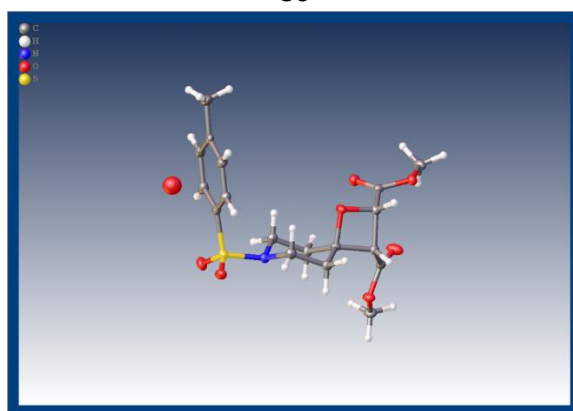
FTIR (ATR) ν (cm⁻¹): 3404 (broad, N-H), 2950 (C-H), 1735 (C=O, ester), 1669 (C=O, amide).

HRMS: ESI C₁₇H₂₁NO₄ [M + H]⁺ predicted: 304.1543, found at 304.1537.

R_f: (EtOAc-hexane, 1:1) = 0.20.

2. Crystal structures

36



Identification code	SC139_autored
Empirical formula	C ₁₈ H ₂₃ NO _{7.06} S
Formula weight	398.43
Temperature/K	100.00(16)
Crystal system	monoclinic
Space group	I2/a
a/Å	19.2318(2)
b/Å	8.22860(10)
c/Å	24.0575(2)
α /°	90
β /°	94.6890(10)
γ /°	90
Volume/Å ³	3794.38(7)
Z	8
ρ_{calc} /cm ³	1.395
μ /mm ⁻¹	1.881
F(000)	1684.0
Crystal size/mm ³	0.17 × 0.14 × 0.12
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	7.374 to 152.528

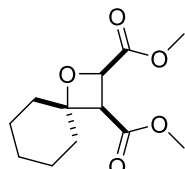
Index ranges	-19 ≤ h ≤ 24, -10 ≤ k ≤ 7, -30 ≤ l ≤ 27
Reflections collected	15168
Independent reflections	3947 [R _{int} = 0.0185, R _{sigma} = 0.0127]
Data/restraints/parameters	3947/0/252
Goodness-of-fit on F ²	1.066
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0332, wR ₂ = 0.0890
Final R indexes [all data]	R ₁ = 0.0338, wR ₂ = 0.0895
Largest diff. peak/hole / e Å ⁻³	0.31/-0.49
Largest diff. peak/hole / e Å ⁻³	0.32/-0.20

3. References

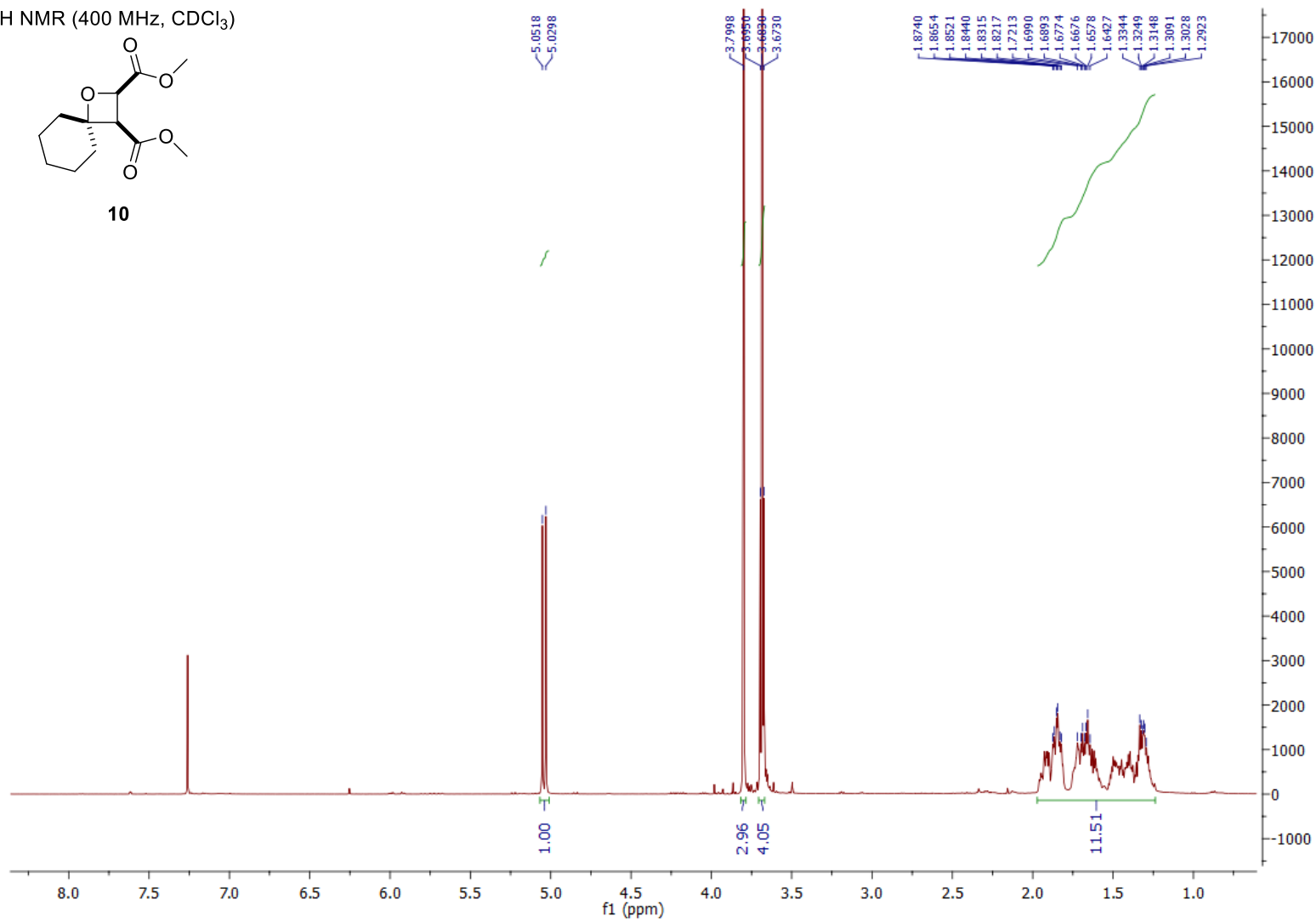
1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
2. Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122.
3. Sheldrick, G. M. SHELXT - Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8
4. Boscá F., Cosa G., Miranda M. A., Scaiano J. C., *Photochem. Photobiol. Sci.*, **2002**, *1*, 704-708
5. Gryczyński I, Kowski A. *Zeitschrift für Naturforschung A.*, **1982**, *37* (11), 1259-1261

4. ^1H / ^{13}C NMR Spectra of New Compounds

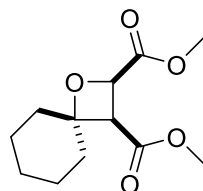
^1H NMR (400 MHz, CDCl_3)



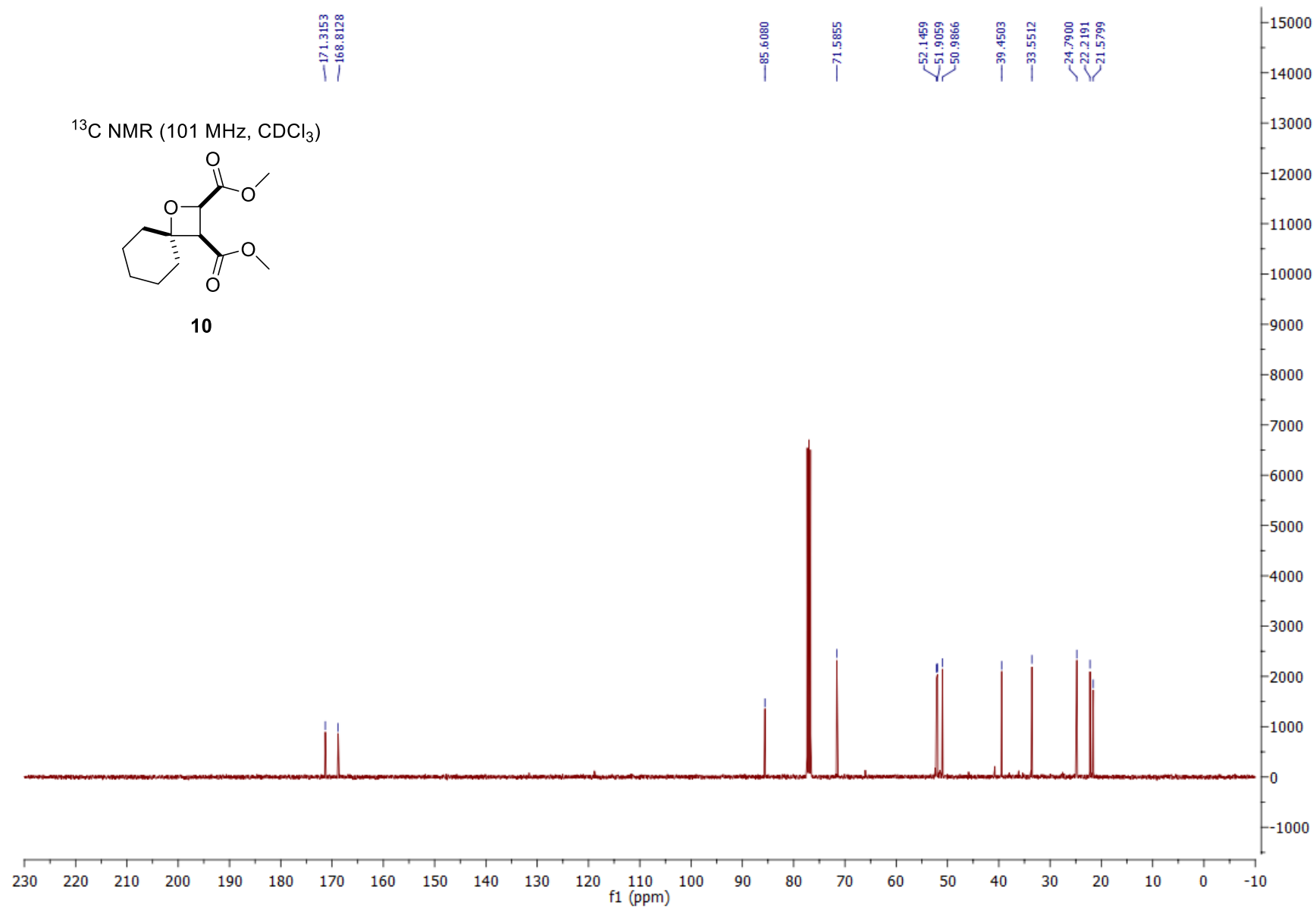
10

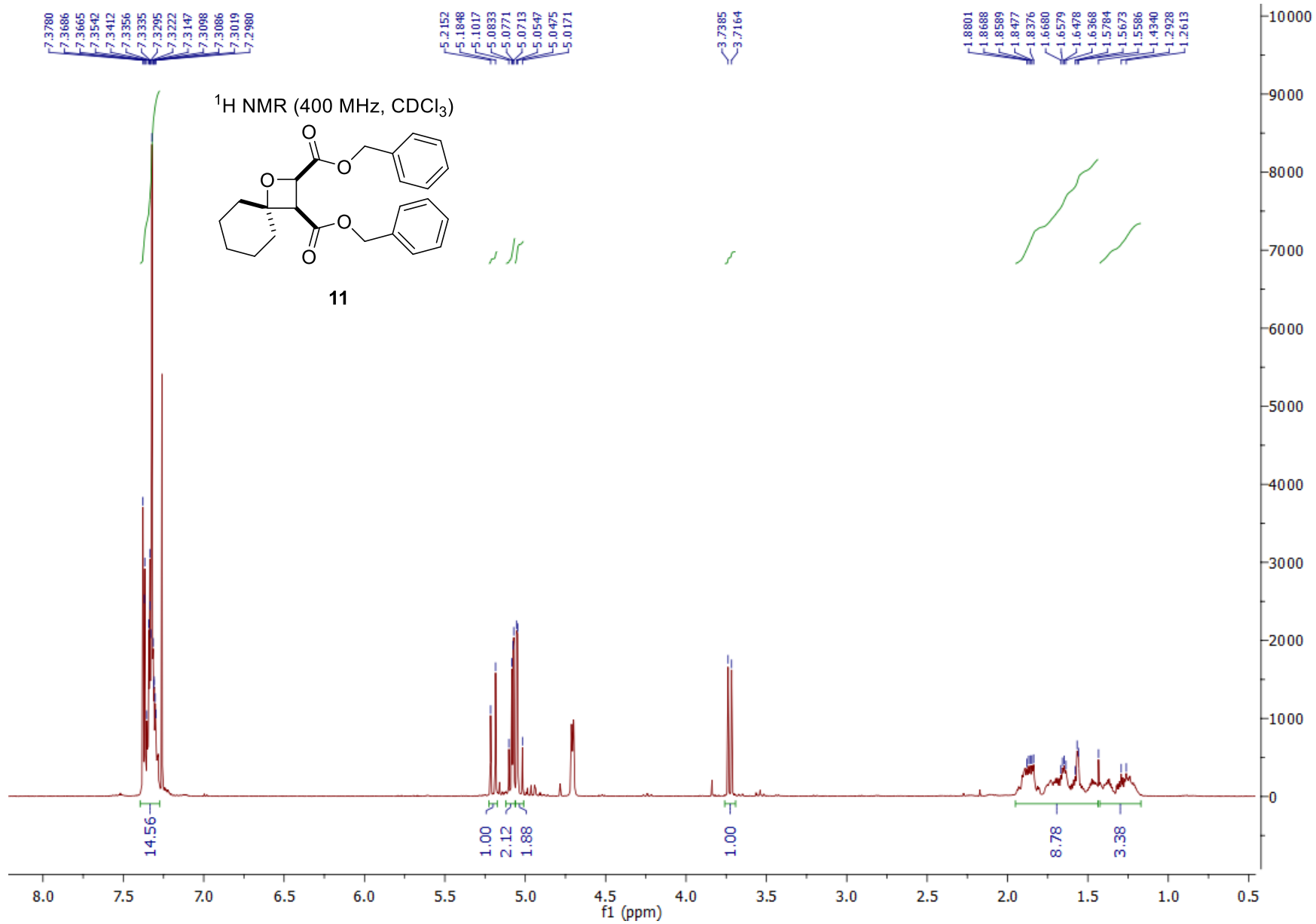


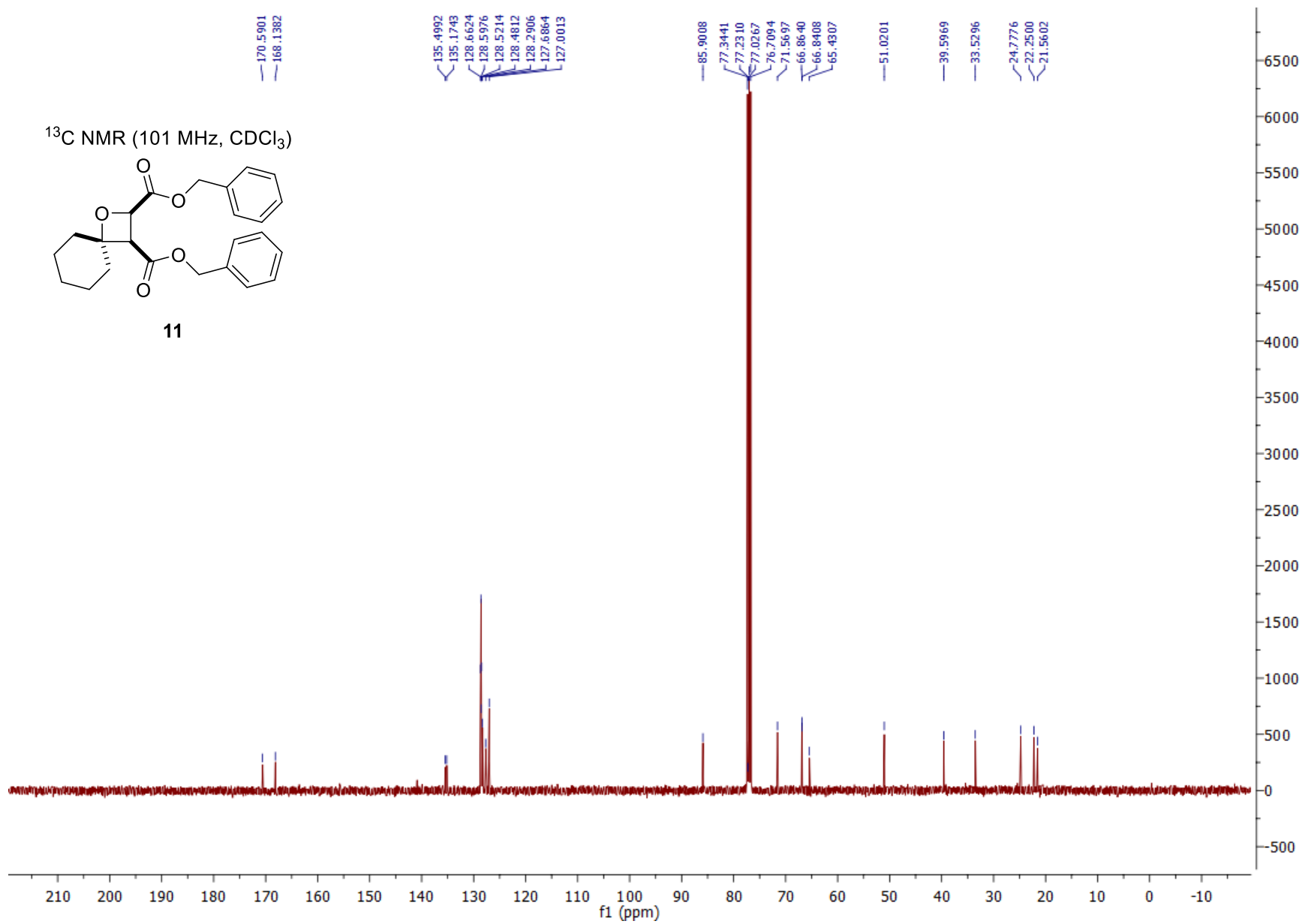
¹³C NMR (101 MHz, CDCl₃)



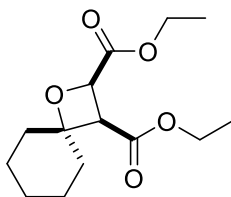
10



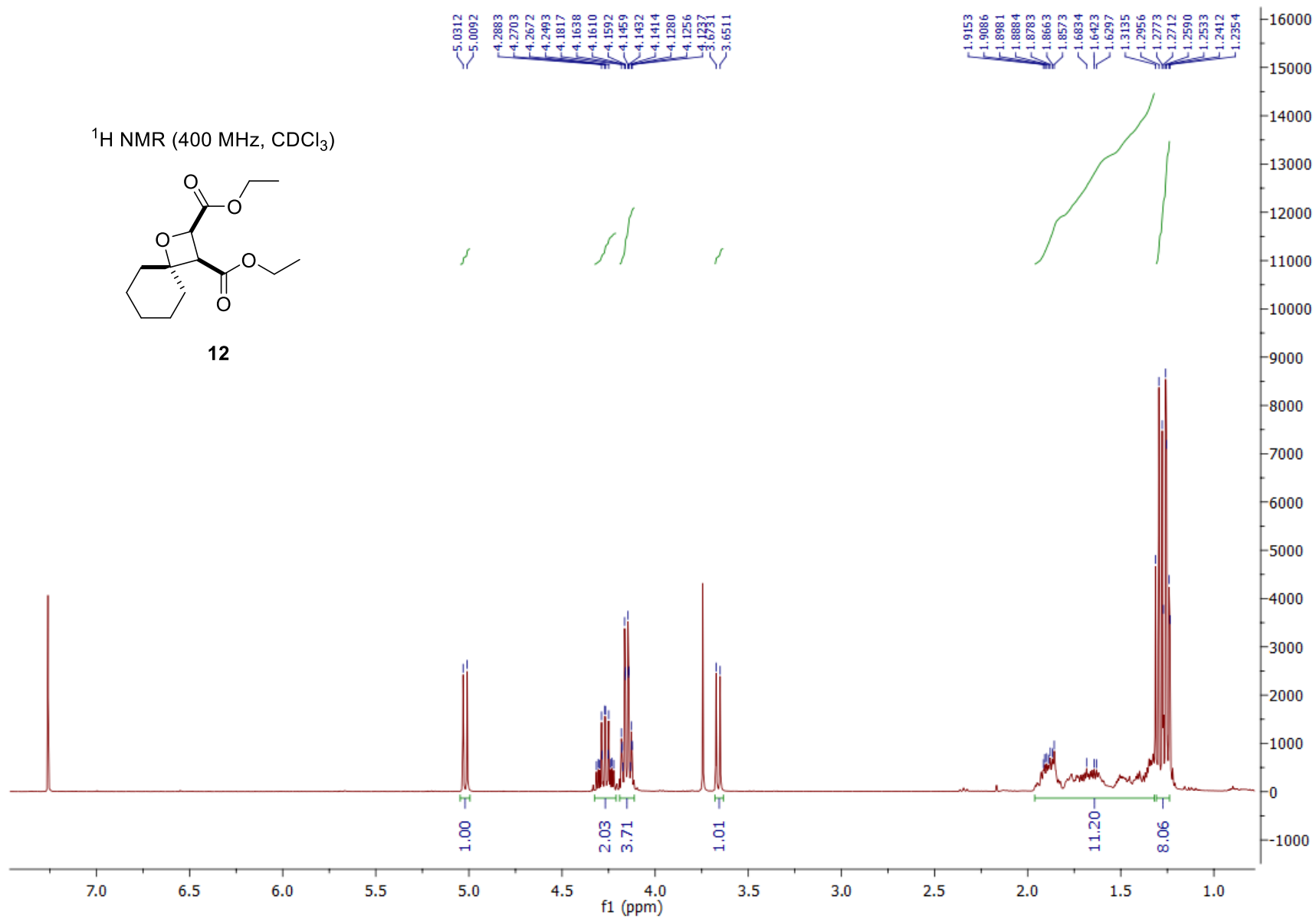




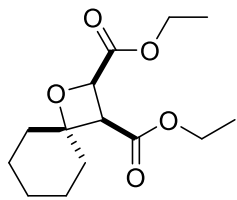
^1H NMR (400 MHz, CDCl_3)



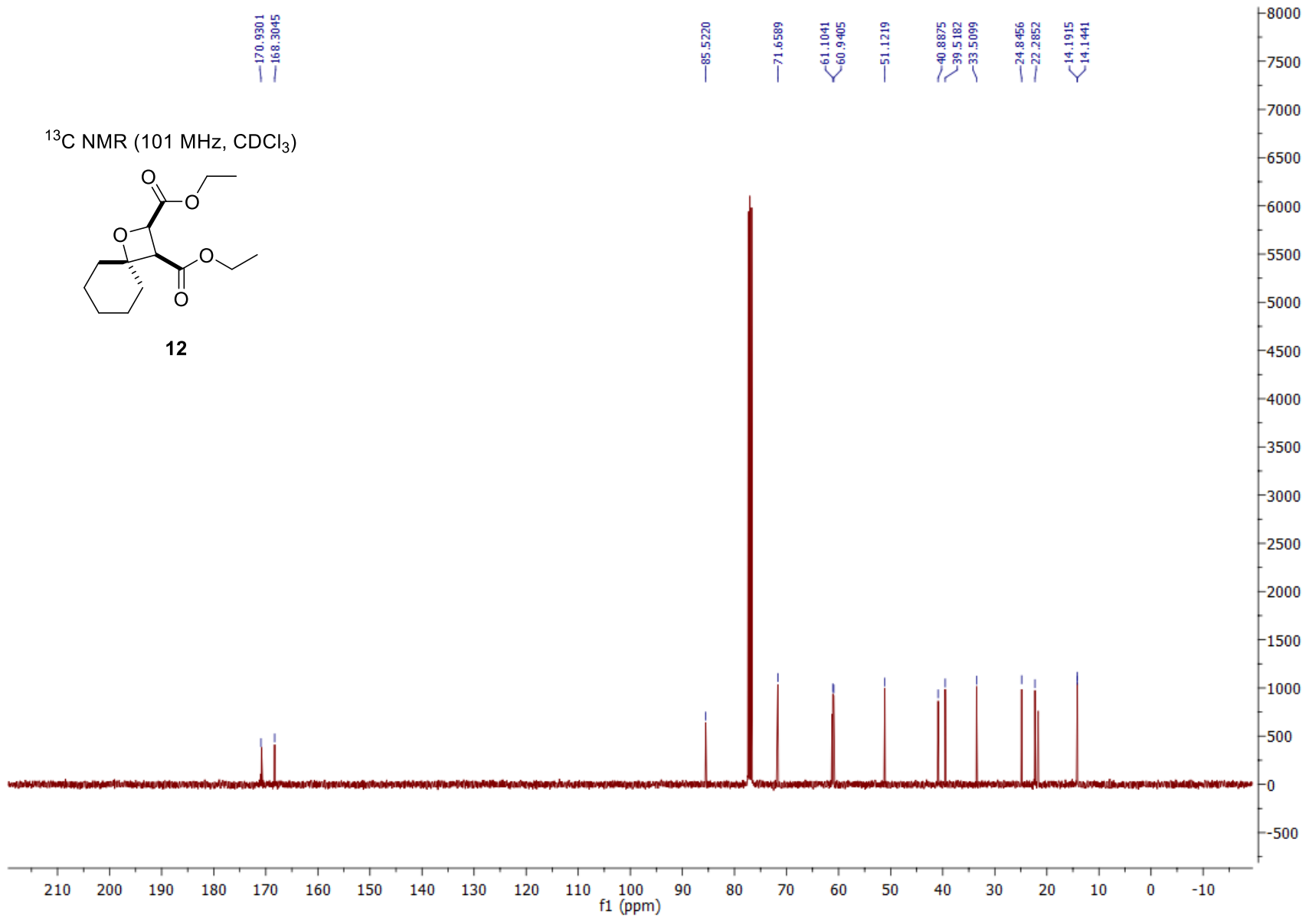
12

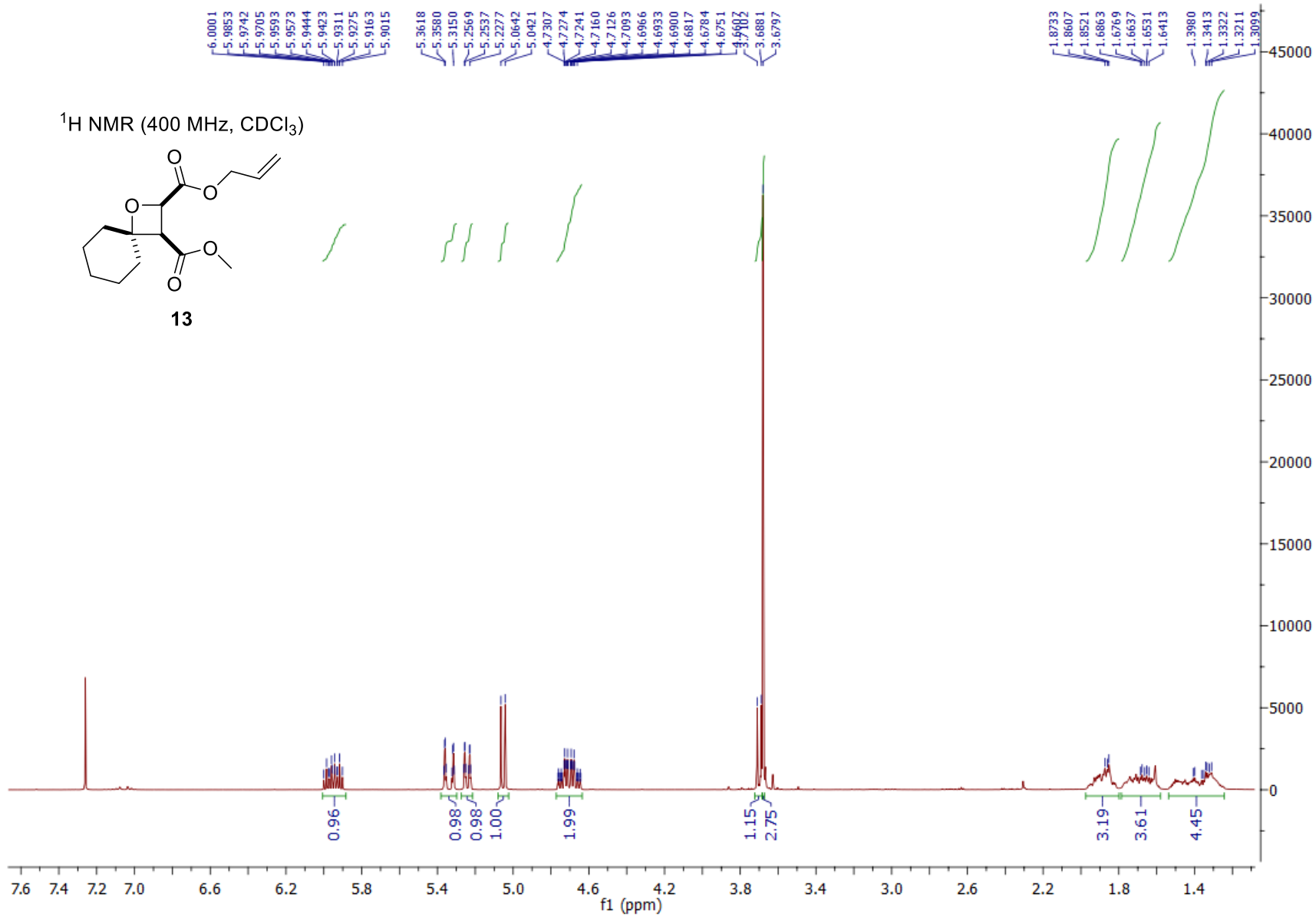


¹³C NMR (101 MHz, CDCl₃)

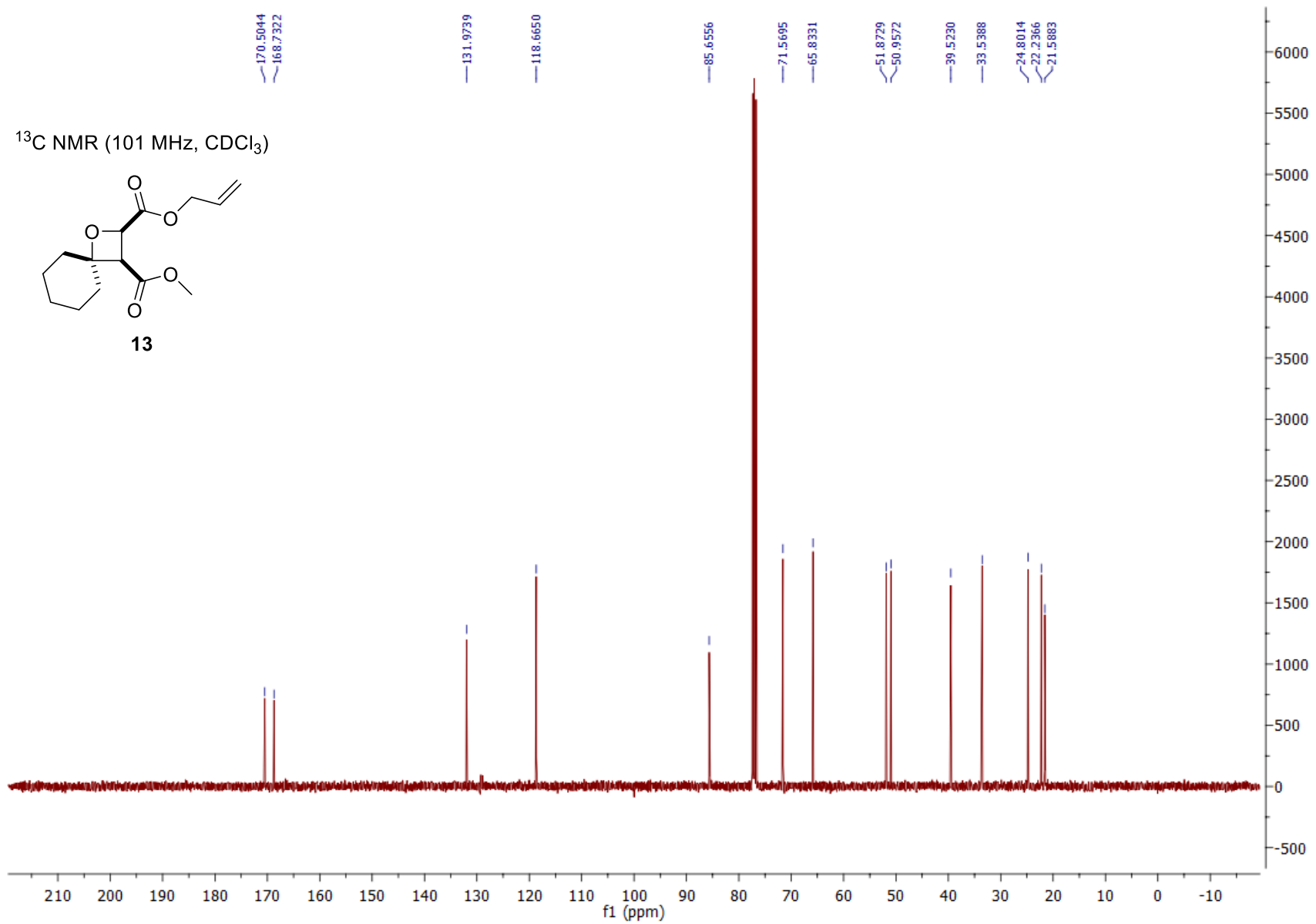
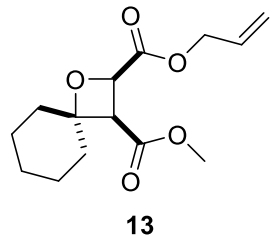


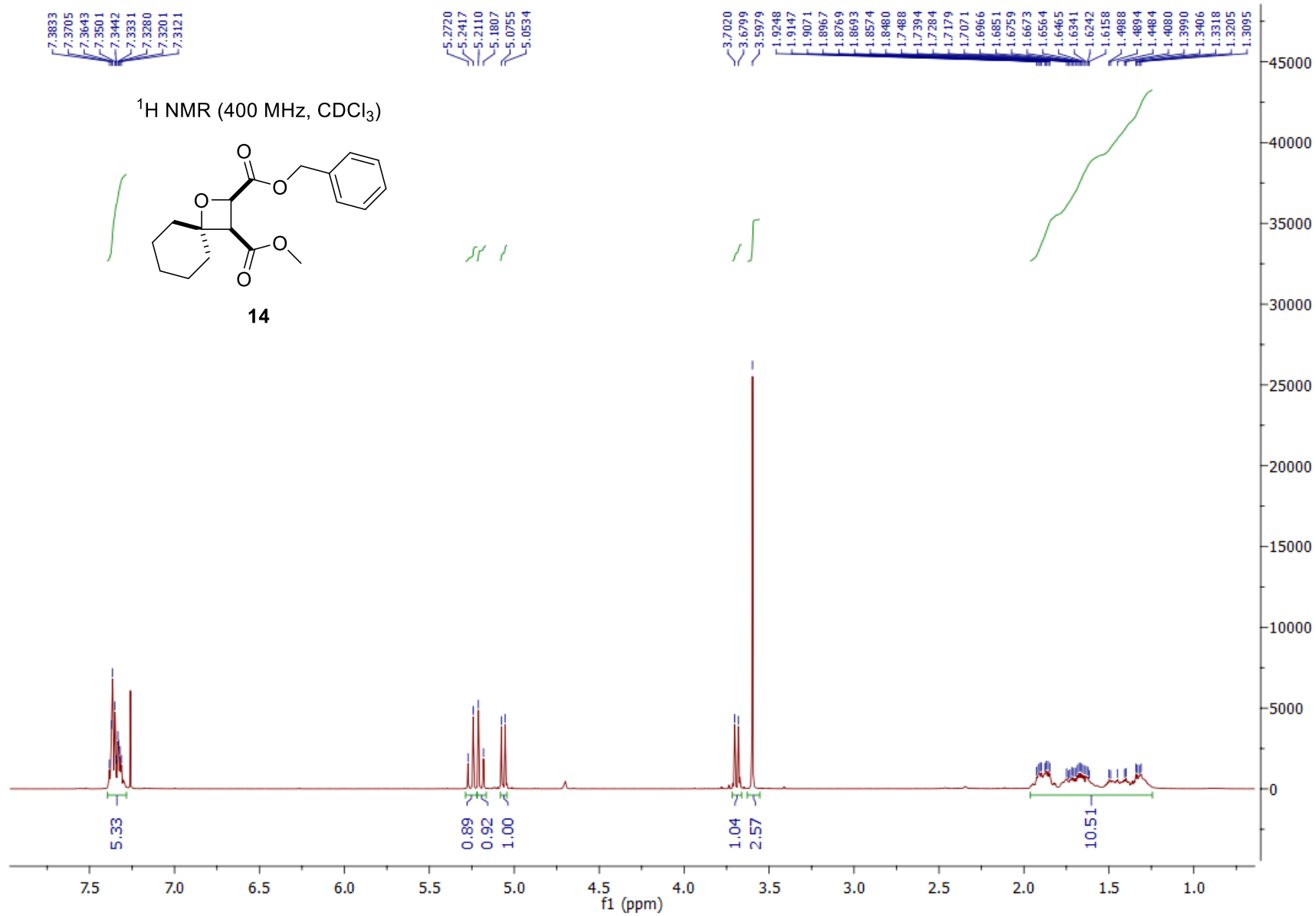
12



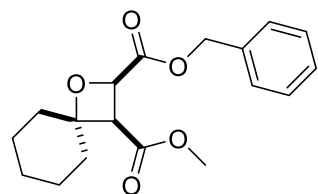


¹³C NMR (101 MHz, CDCl₃)

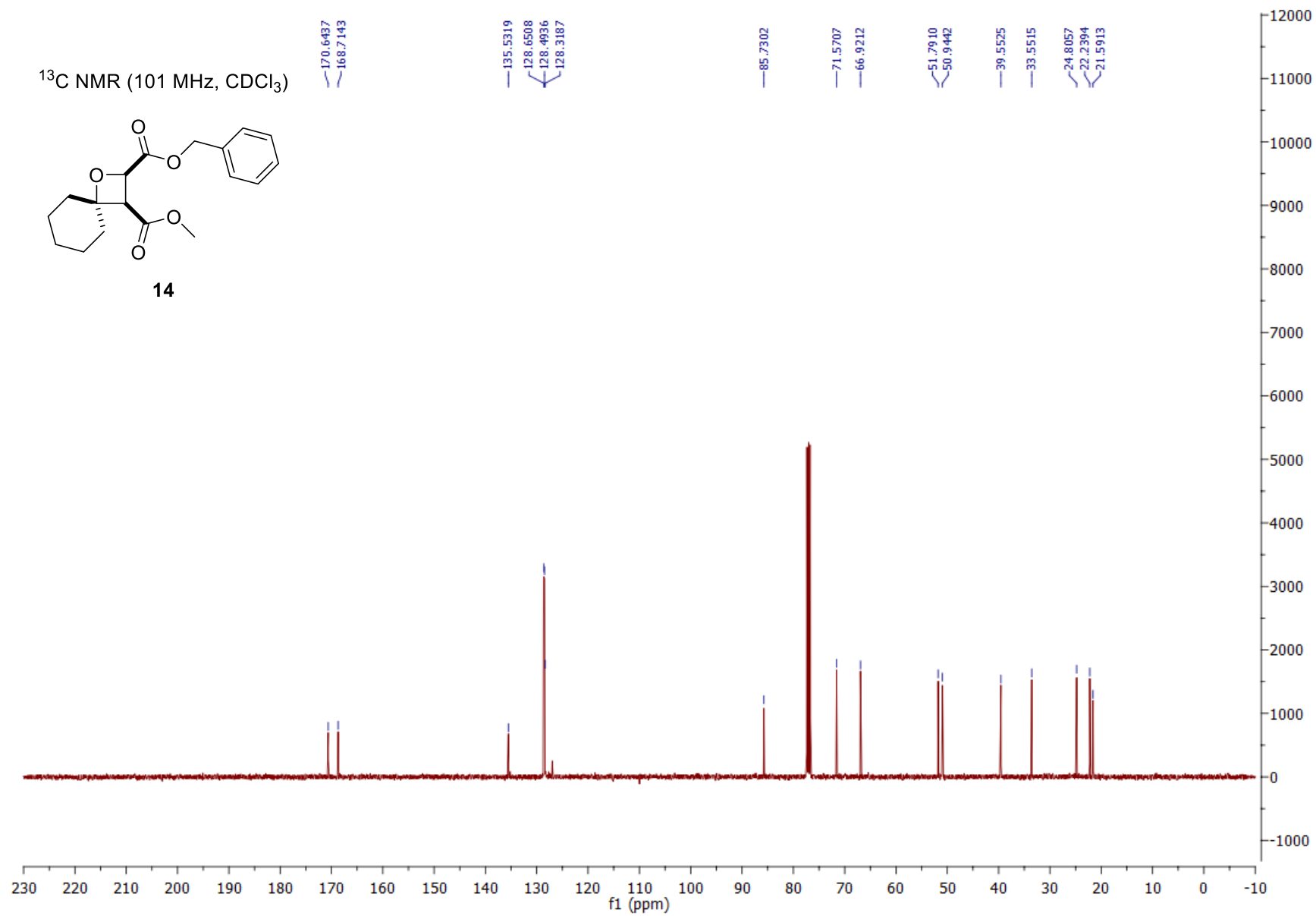


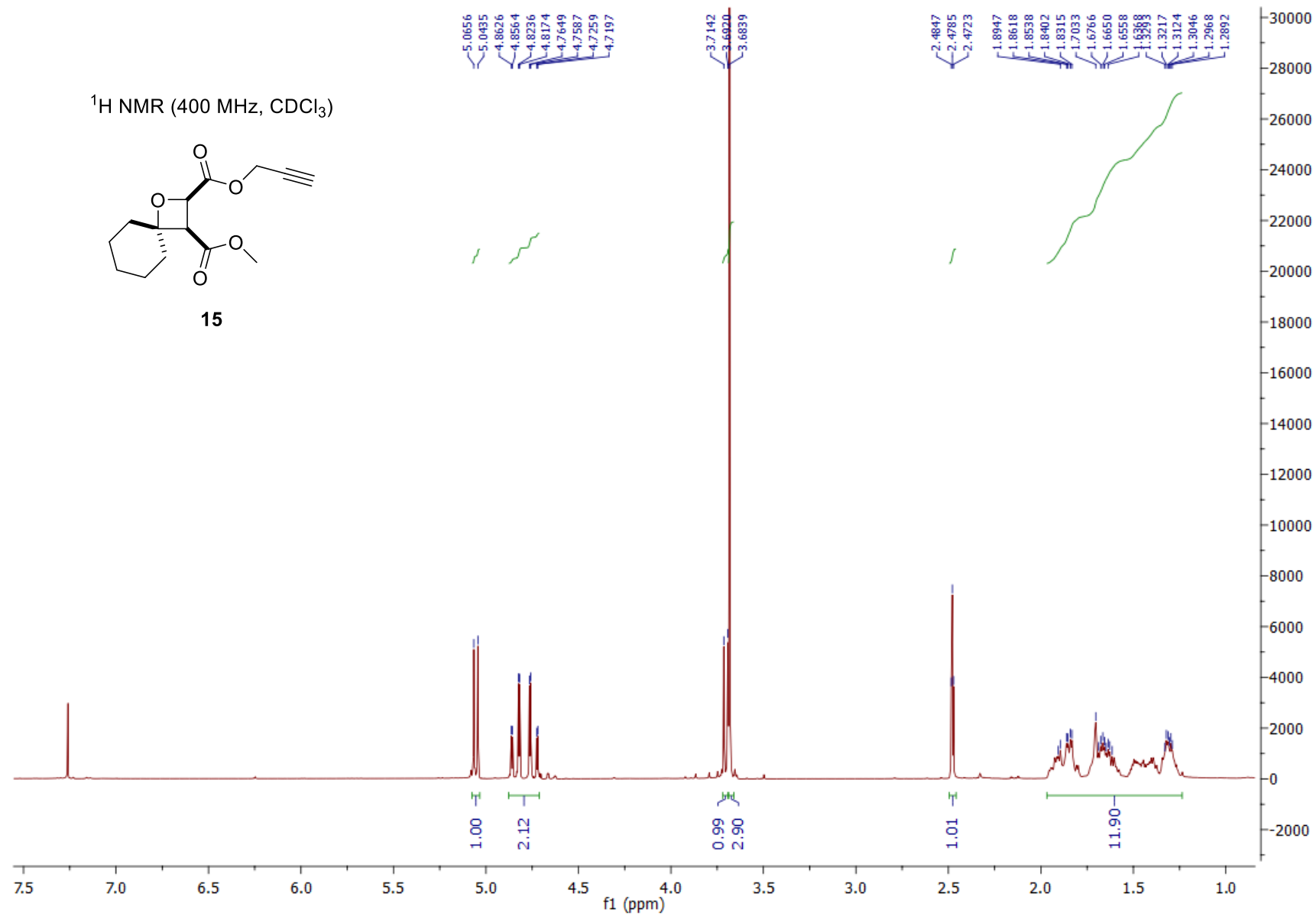


^{13}C NMR (101 MHz, CDCl_3)

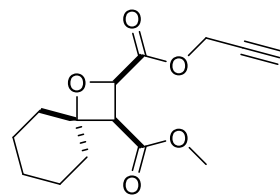


14

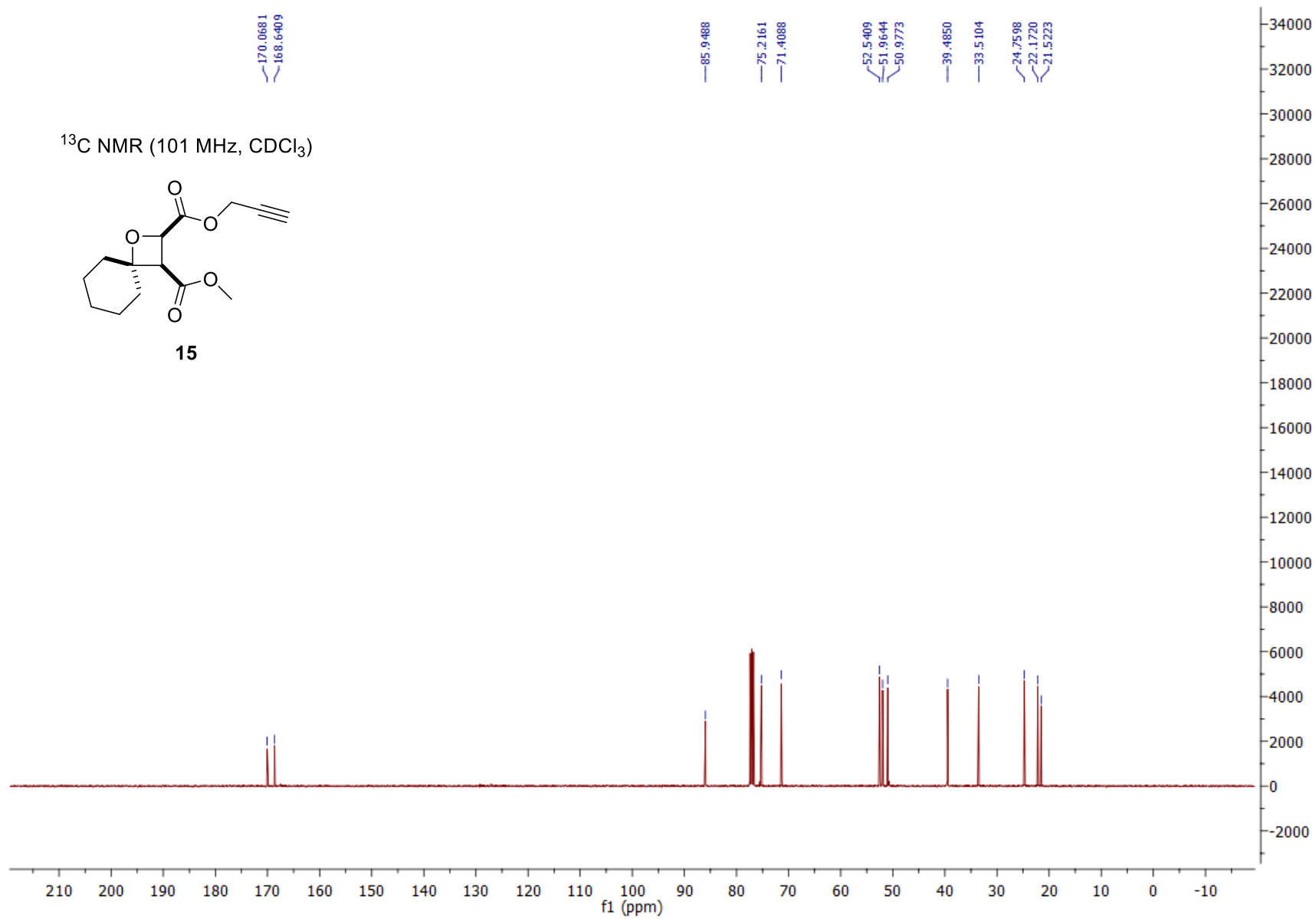


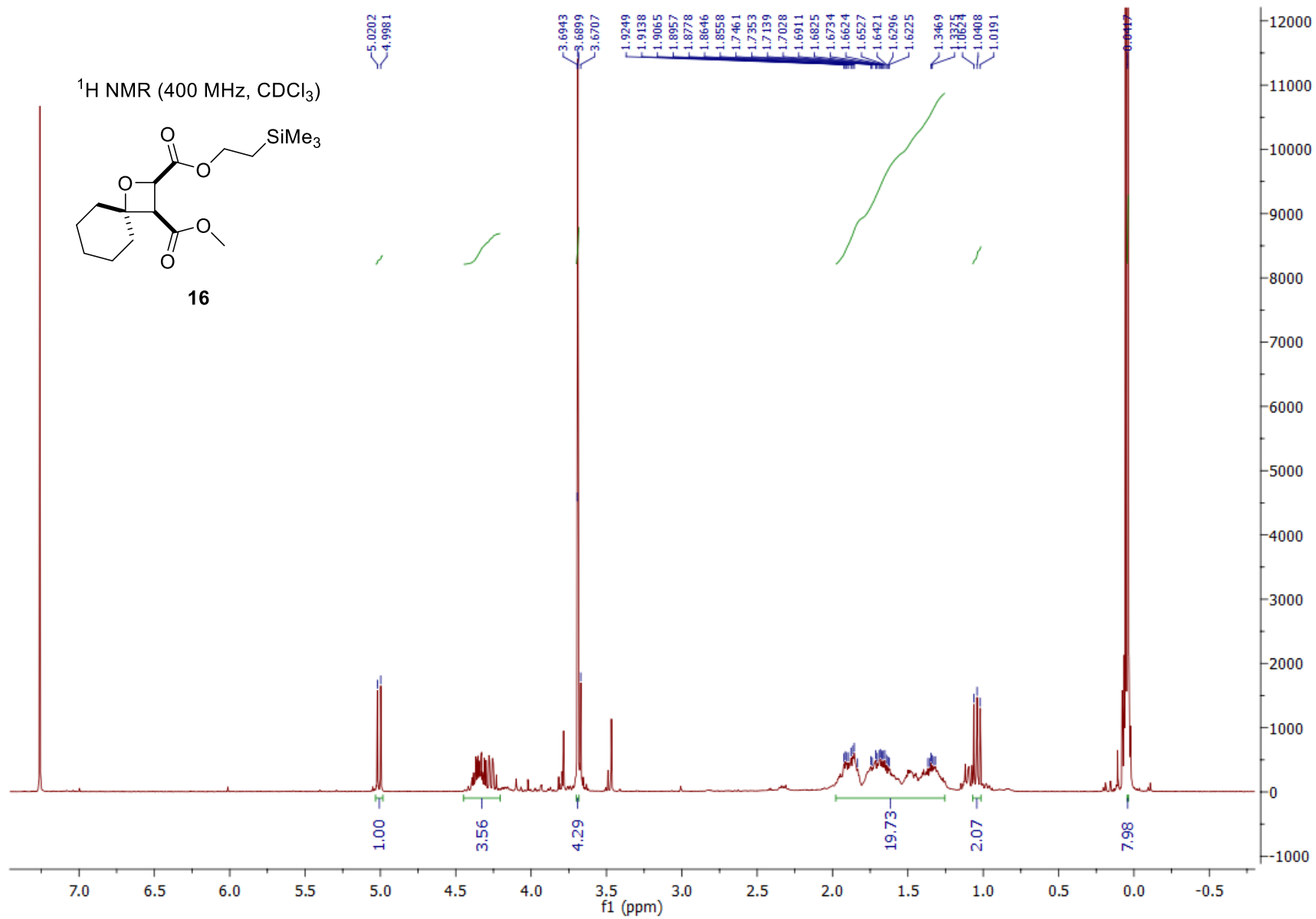


^{13}C NMR (101 MHz, CDCl_3)

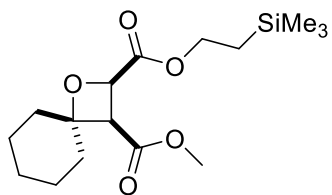


15

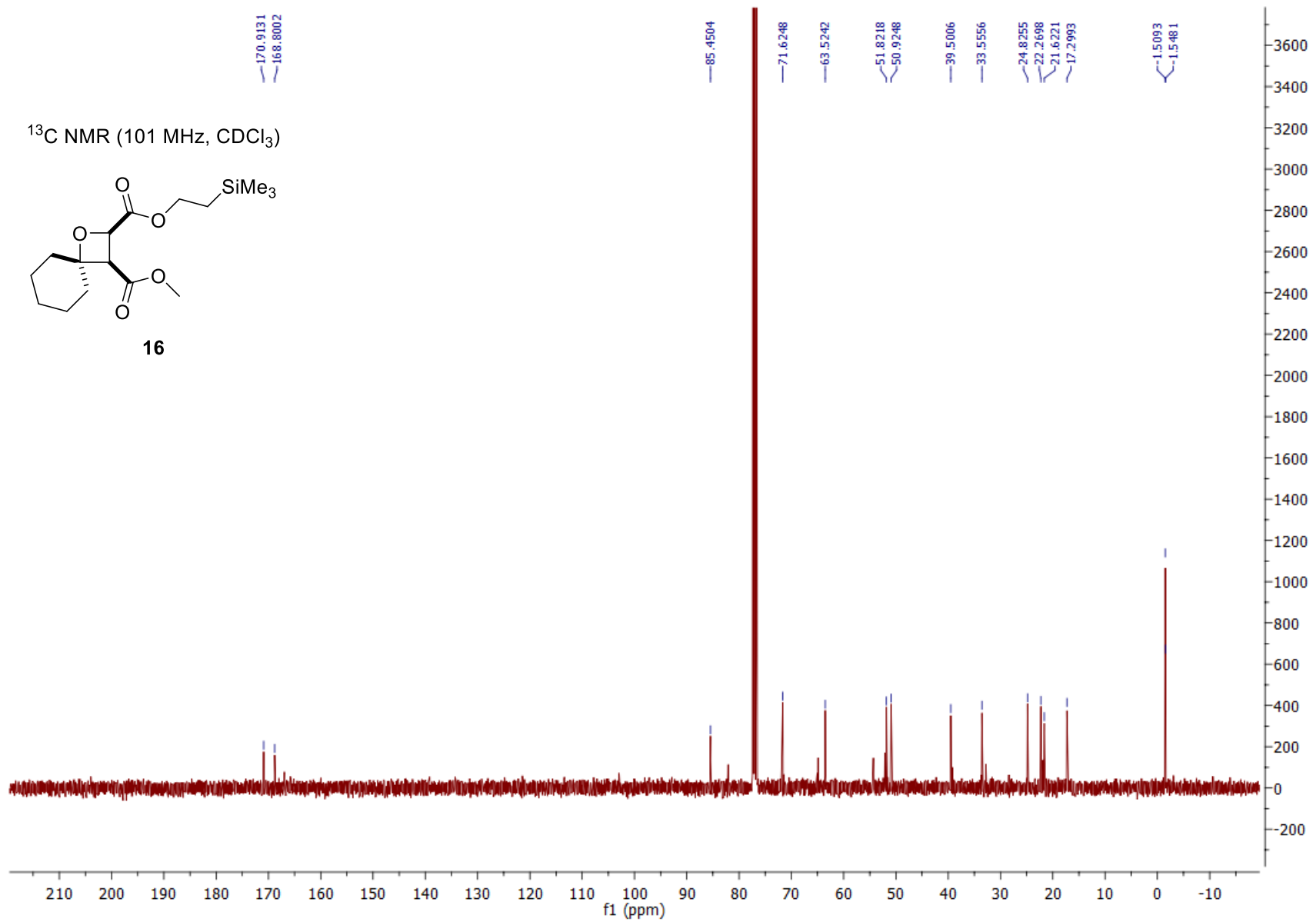




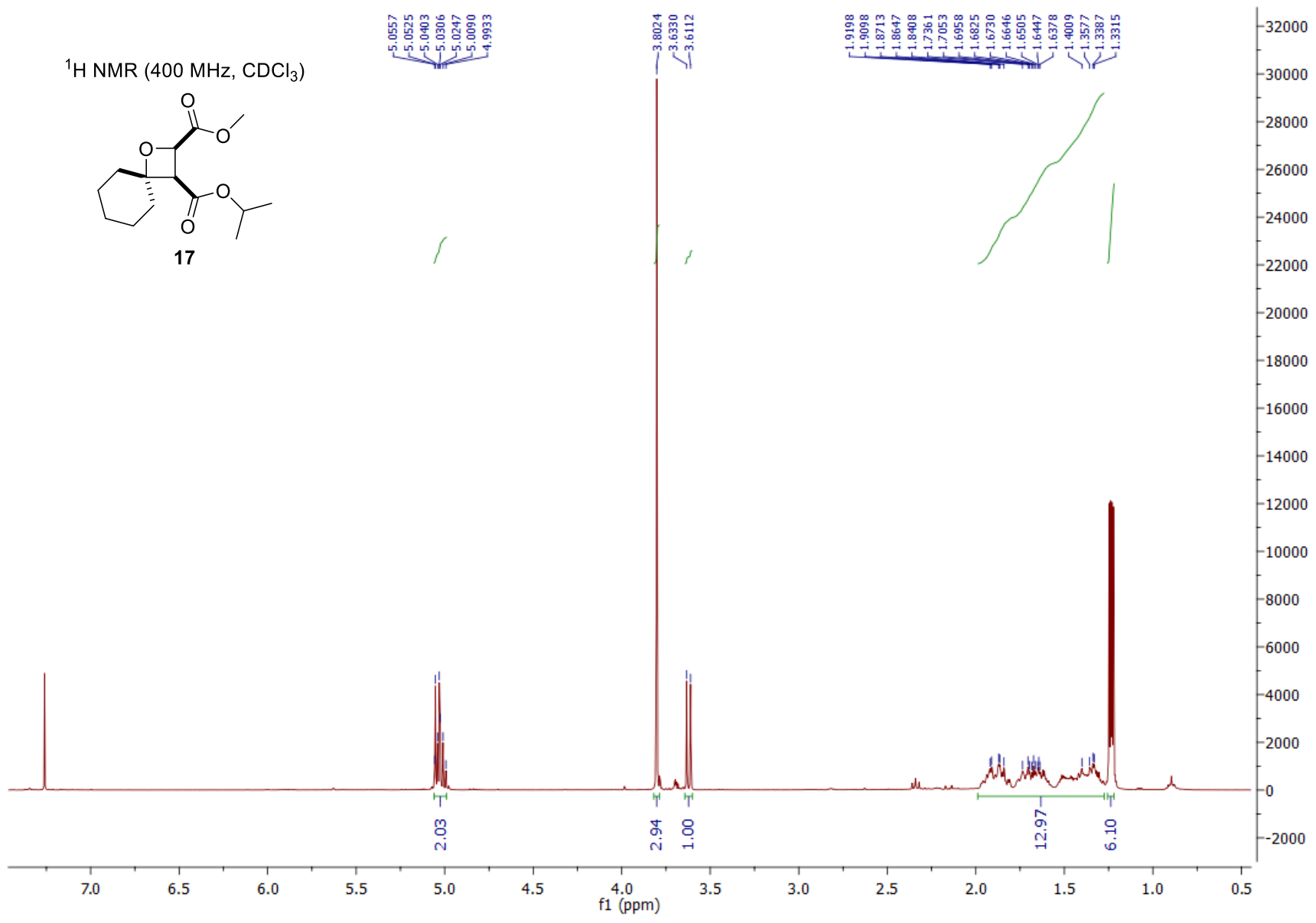
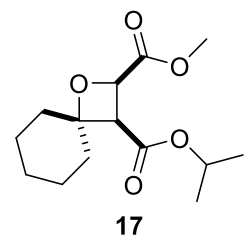
^{13}C NMR (101 MHz, CDCl_3)



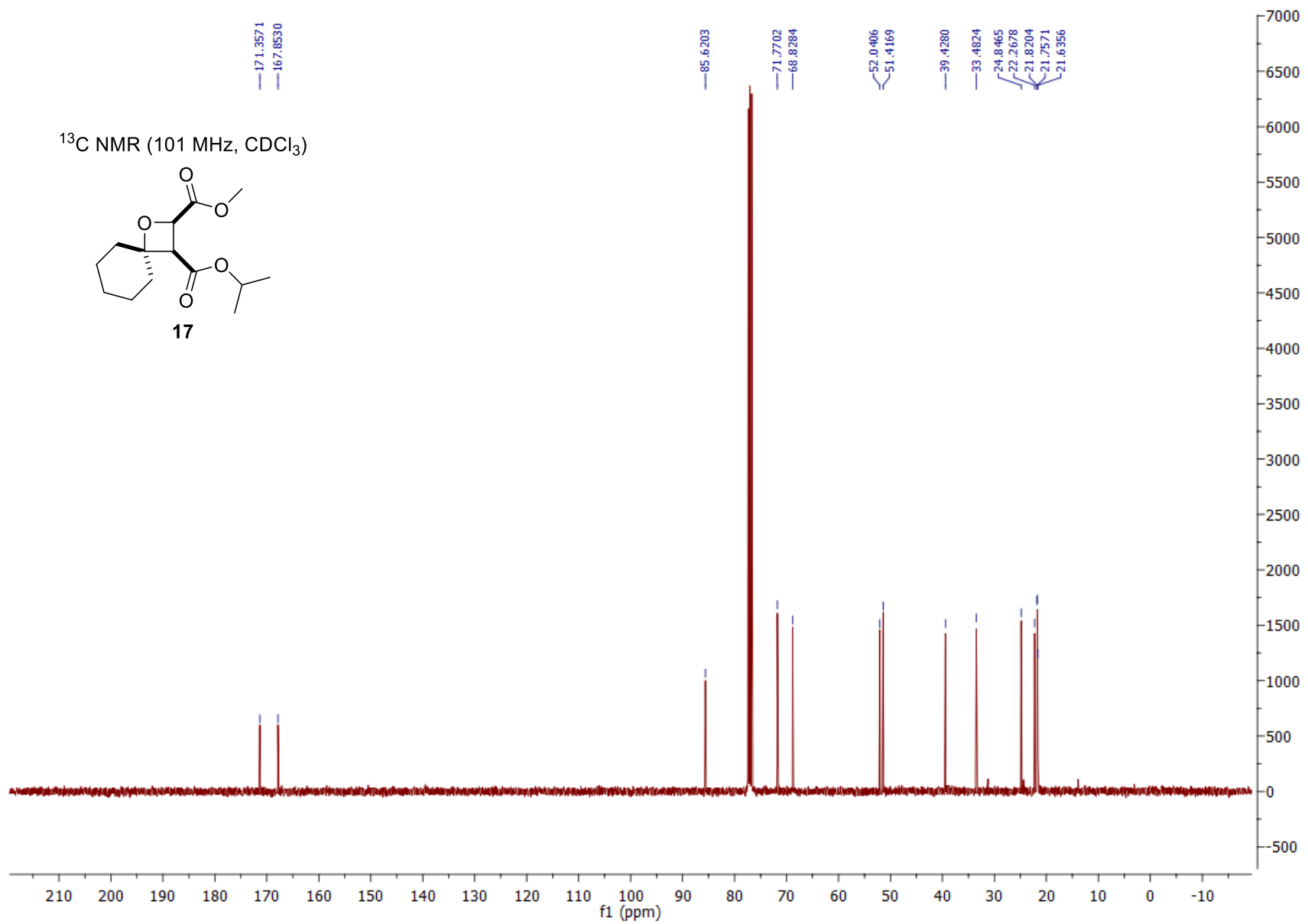
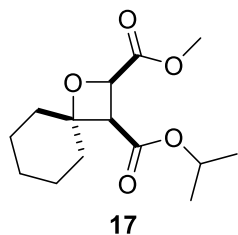
16



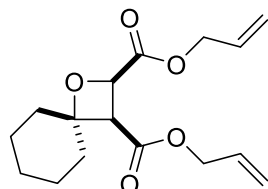
¹H NMR (400 MHz, CDCl₃)



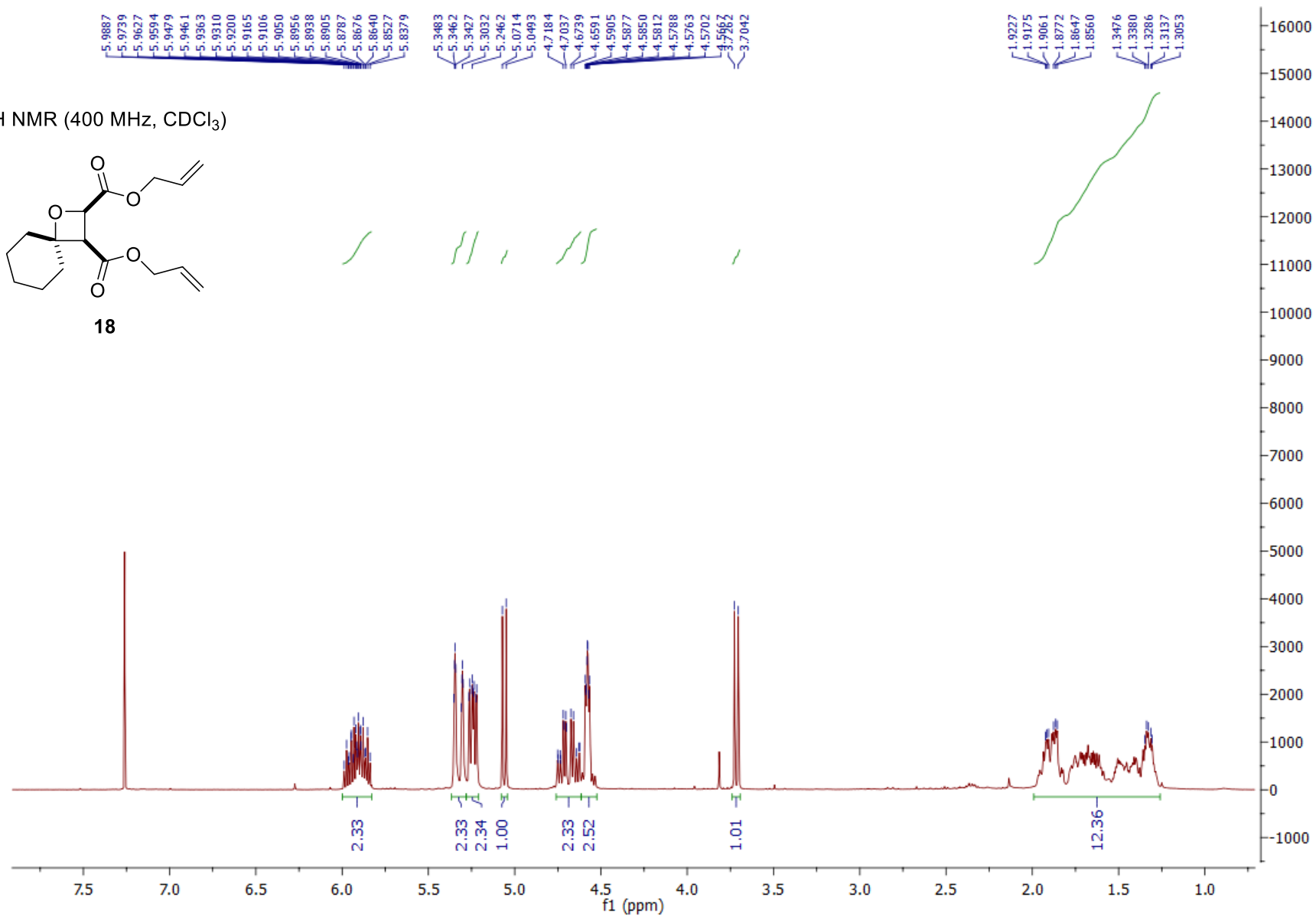
^{13}C NMR (101 MHz, CDCl_3)



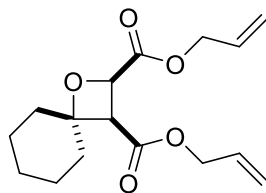
¹H NMR (400 MHz, CDCl₃)



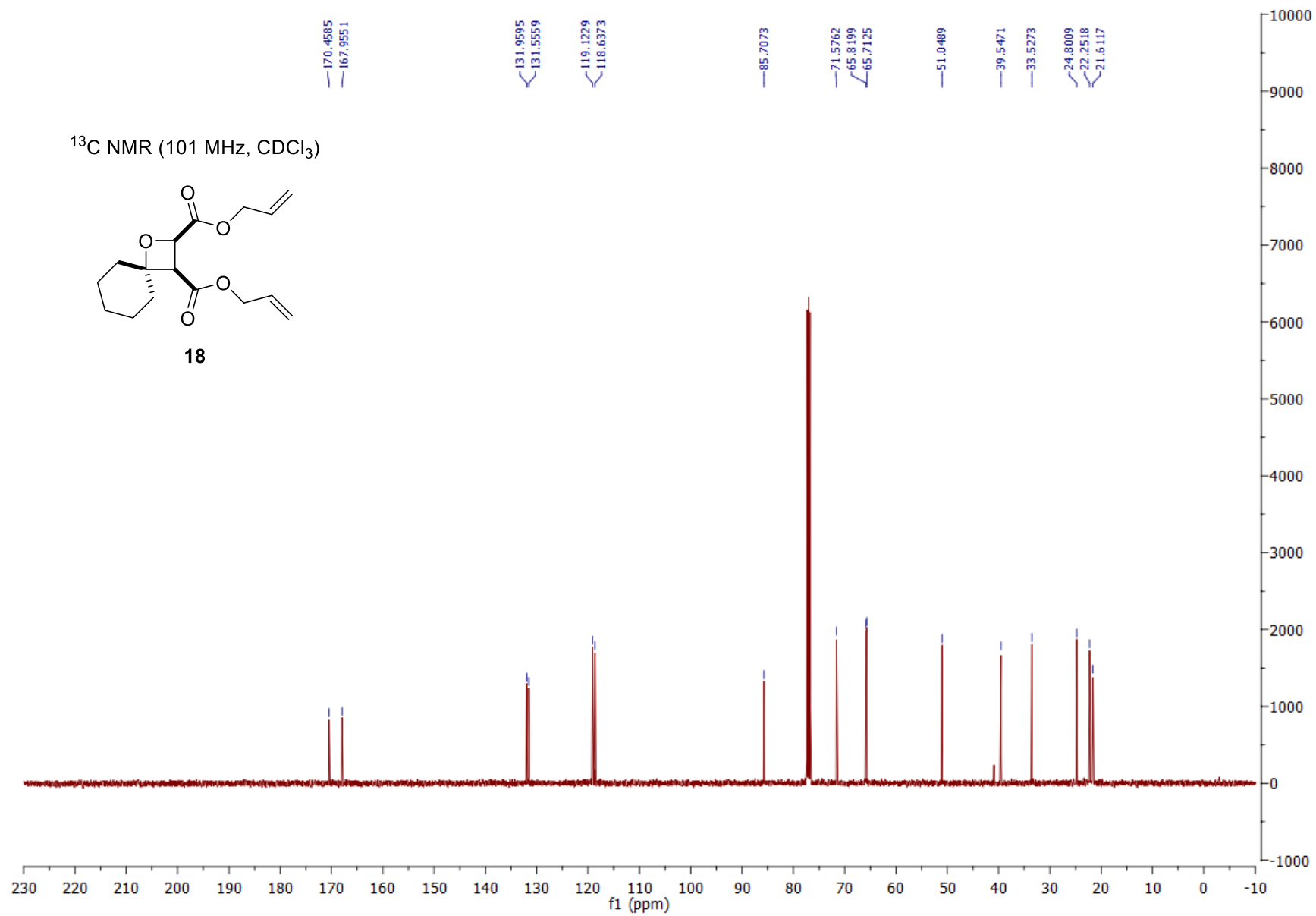
18



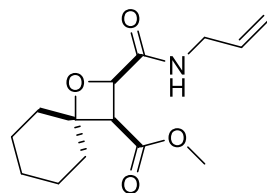
^{13}C NMR (101 MHz, CDCl_3)



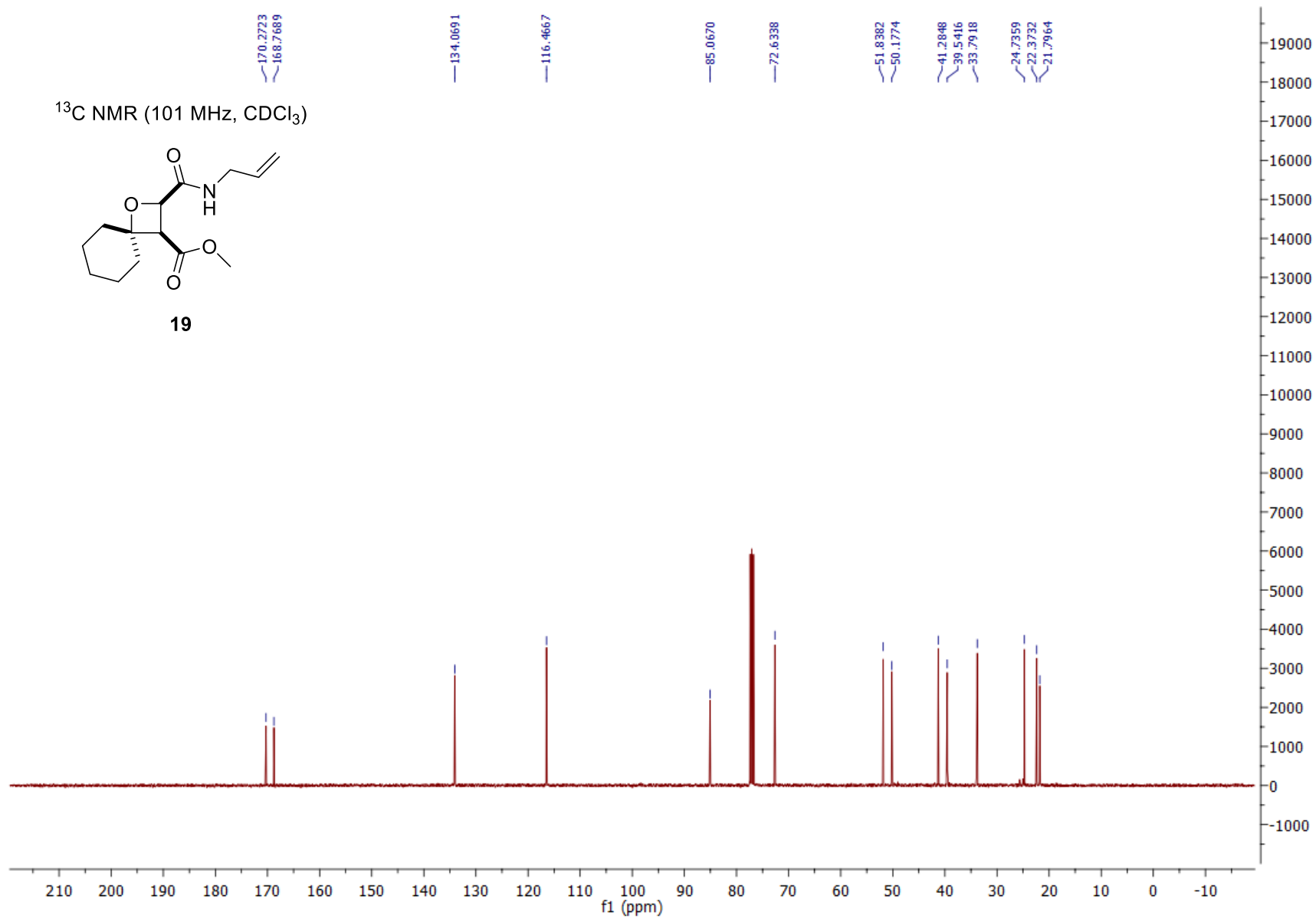
18

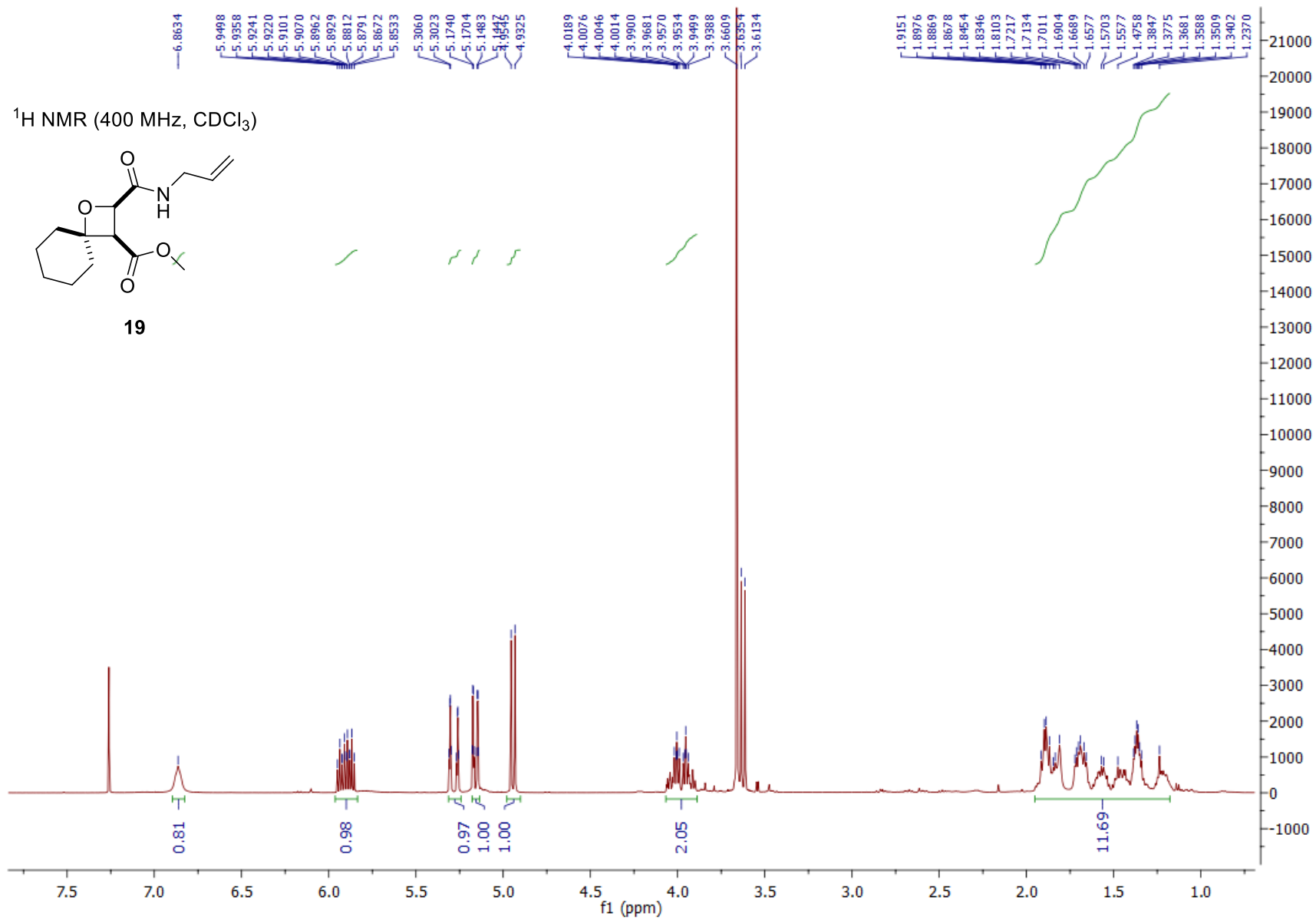


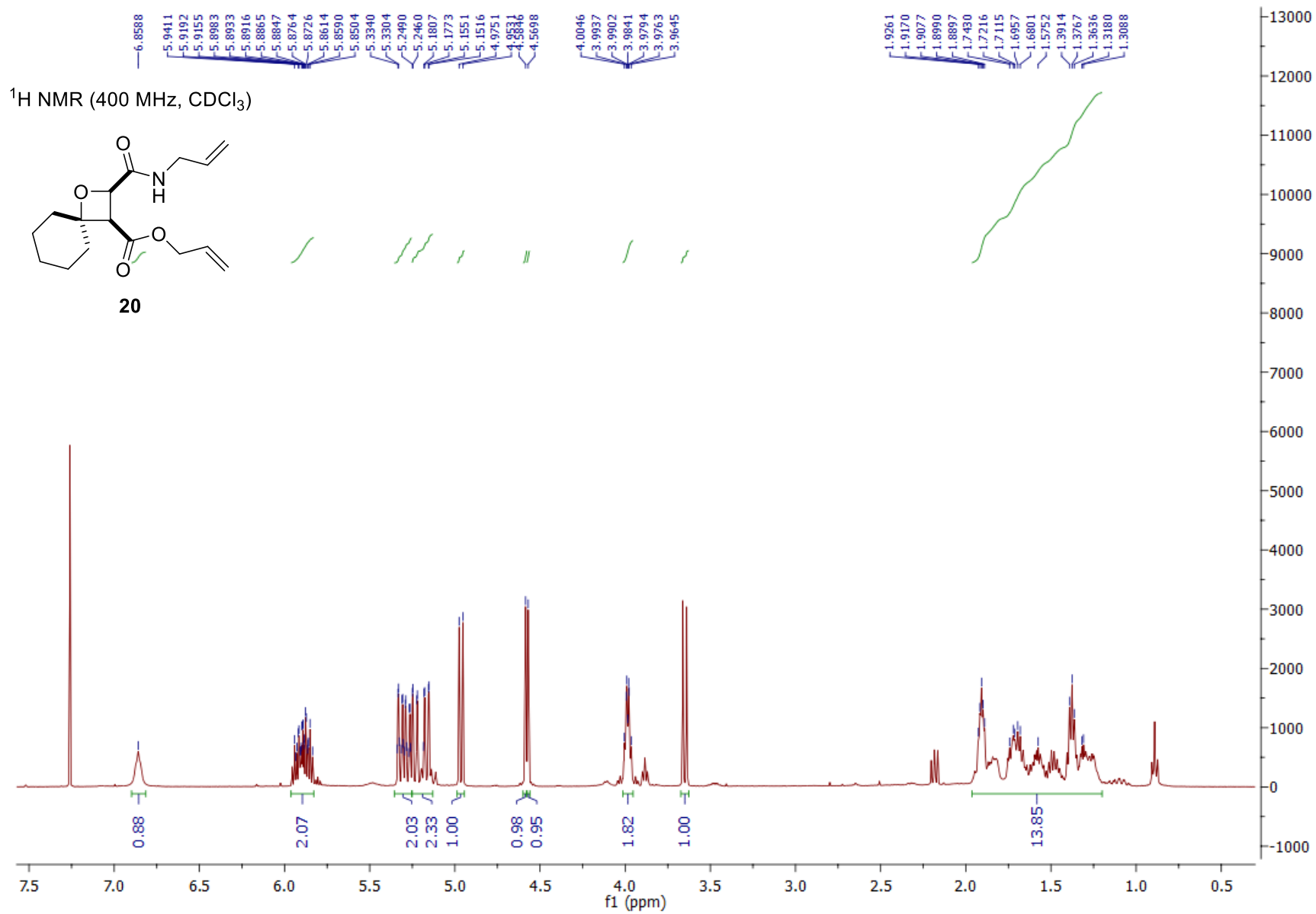
¹³C NMR (101 MHz, CDCl₃)



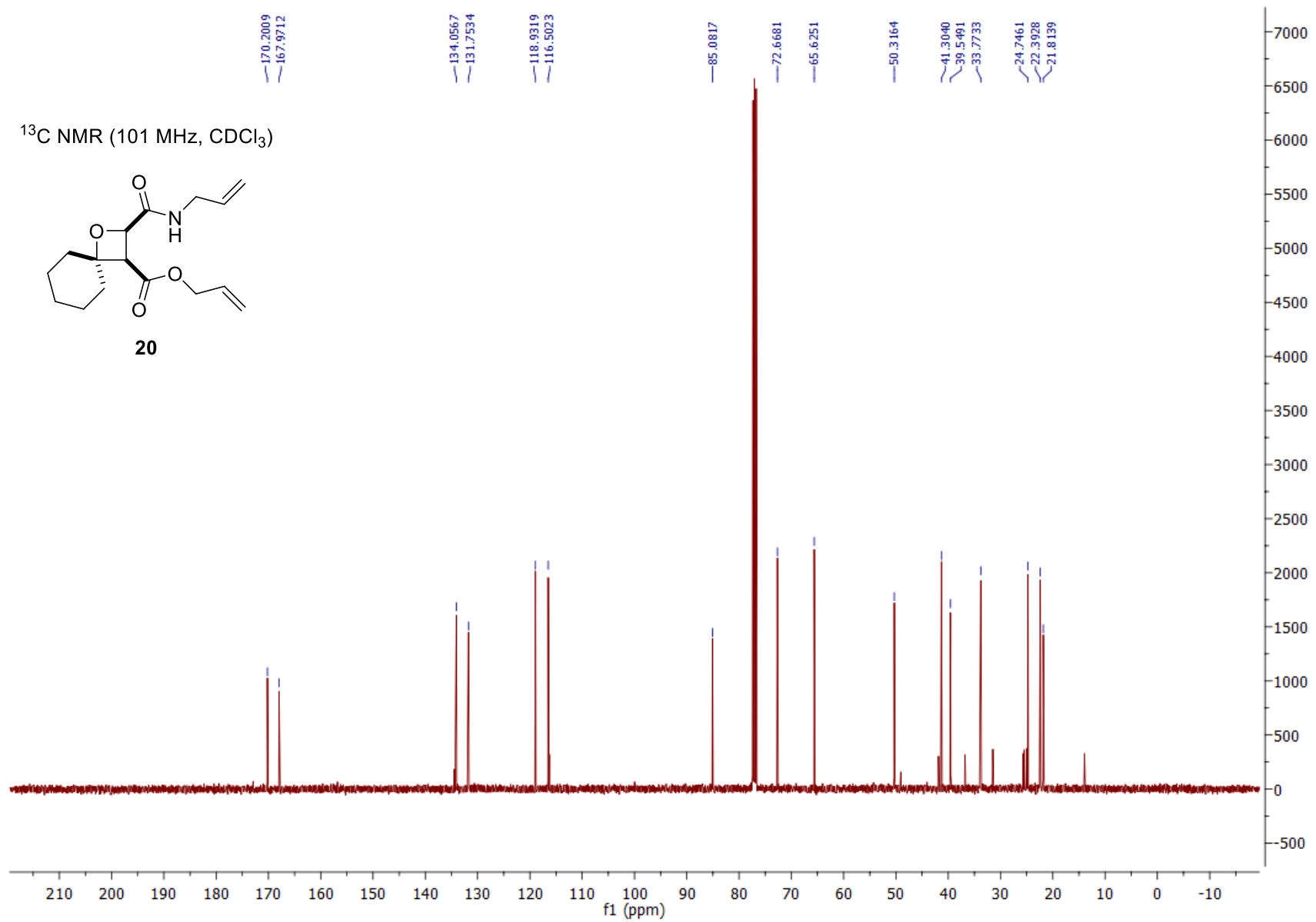
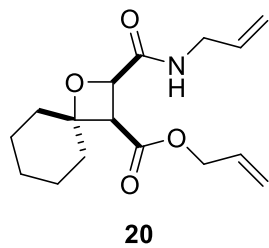
19

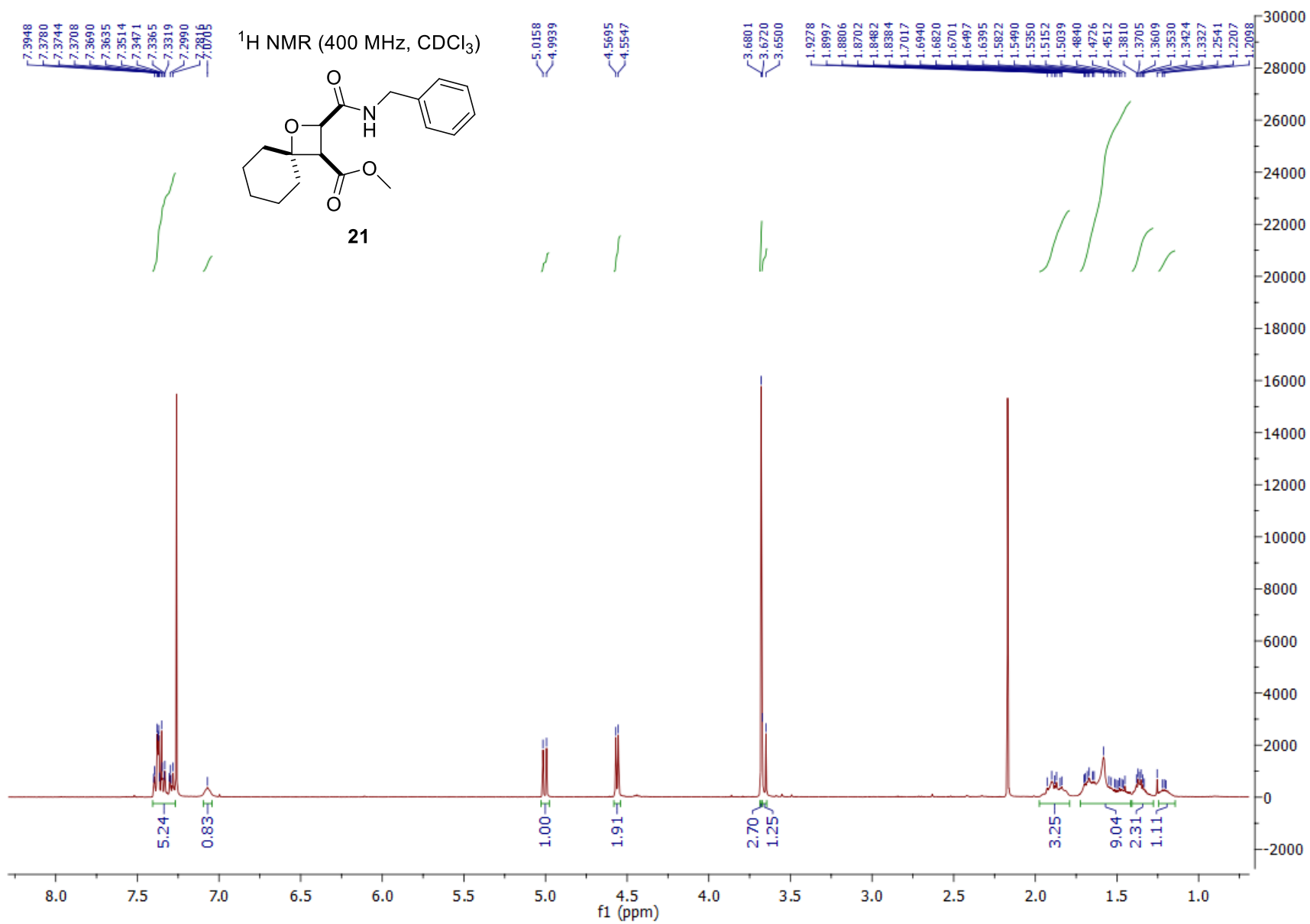


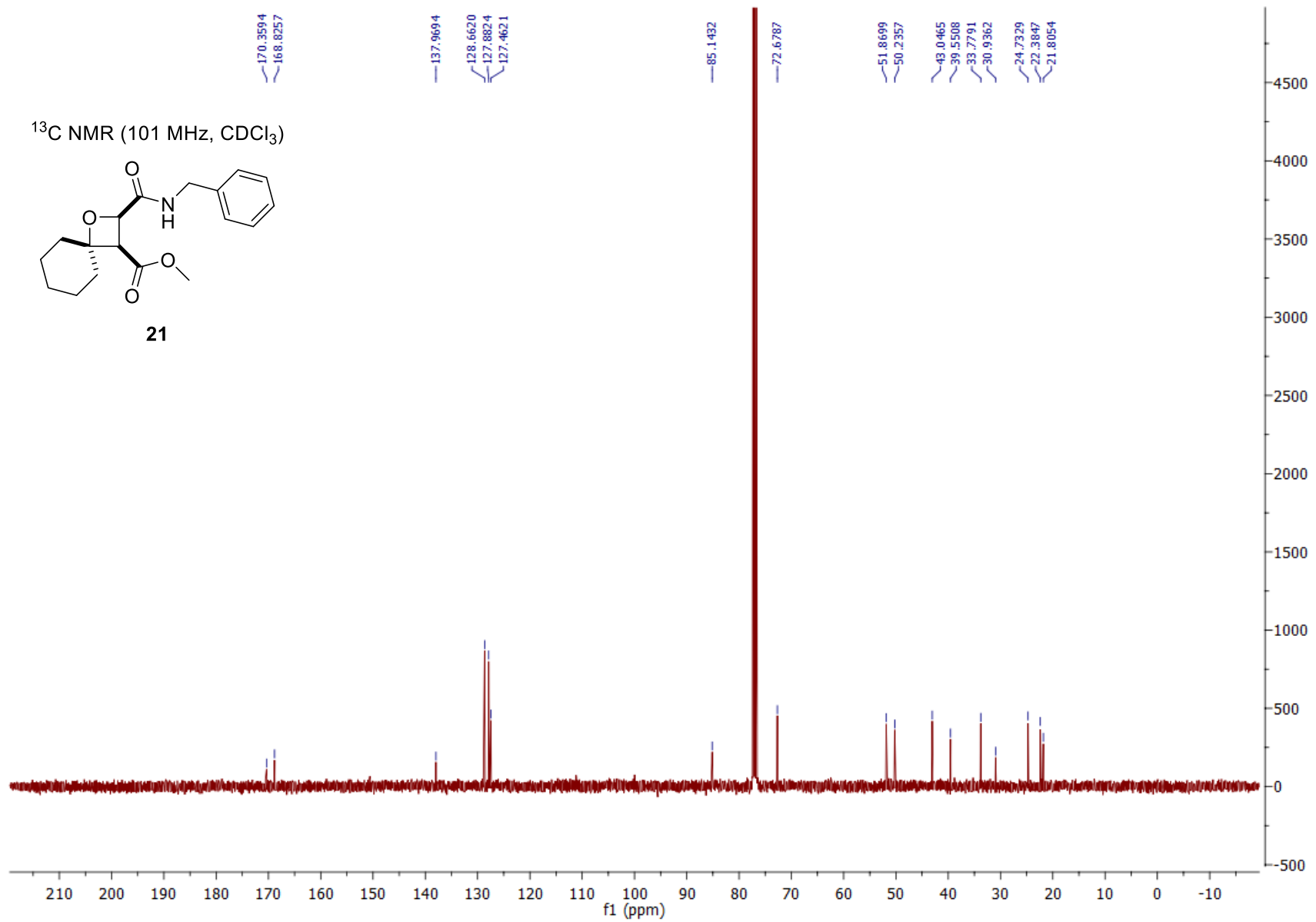




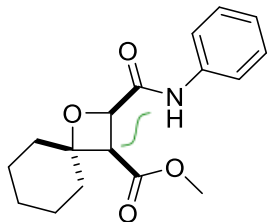
^{13}C NMR (101 MHz, CDCl_3)



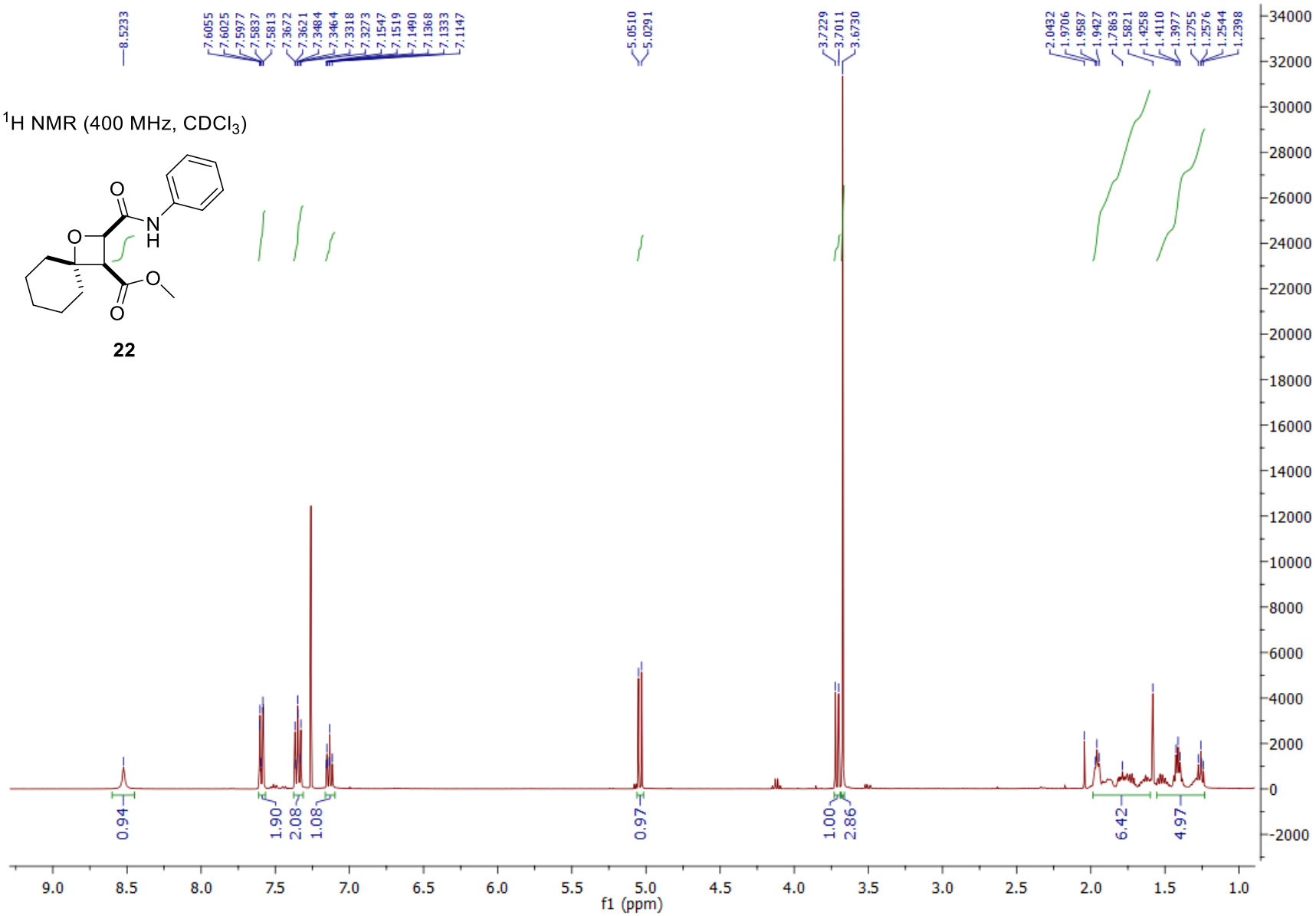




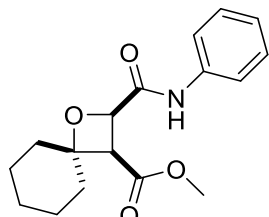
^1H NMR (400 MHz, CDCl_3)



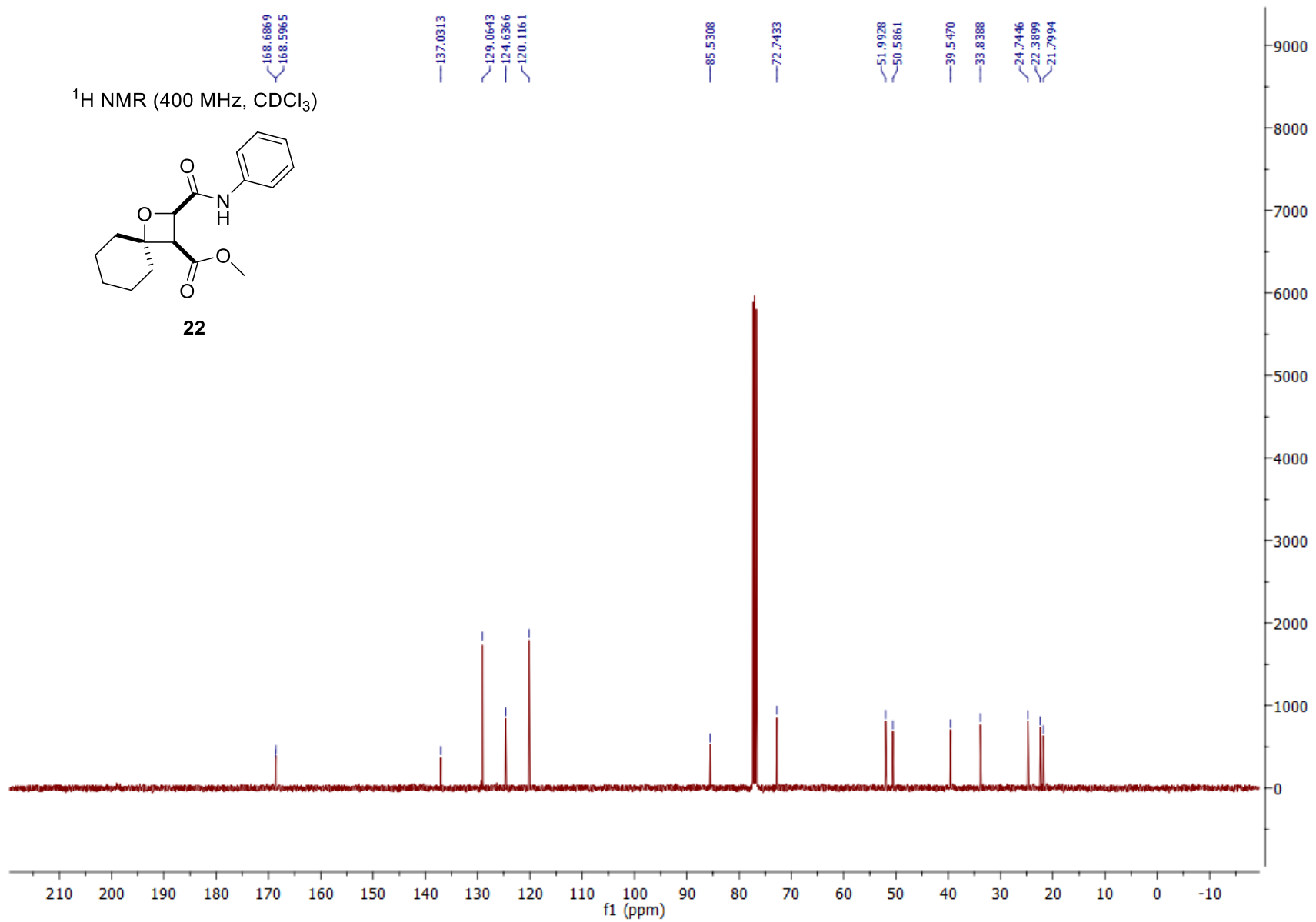
22

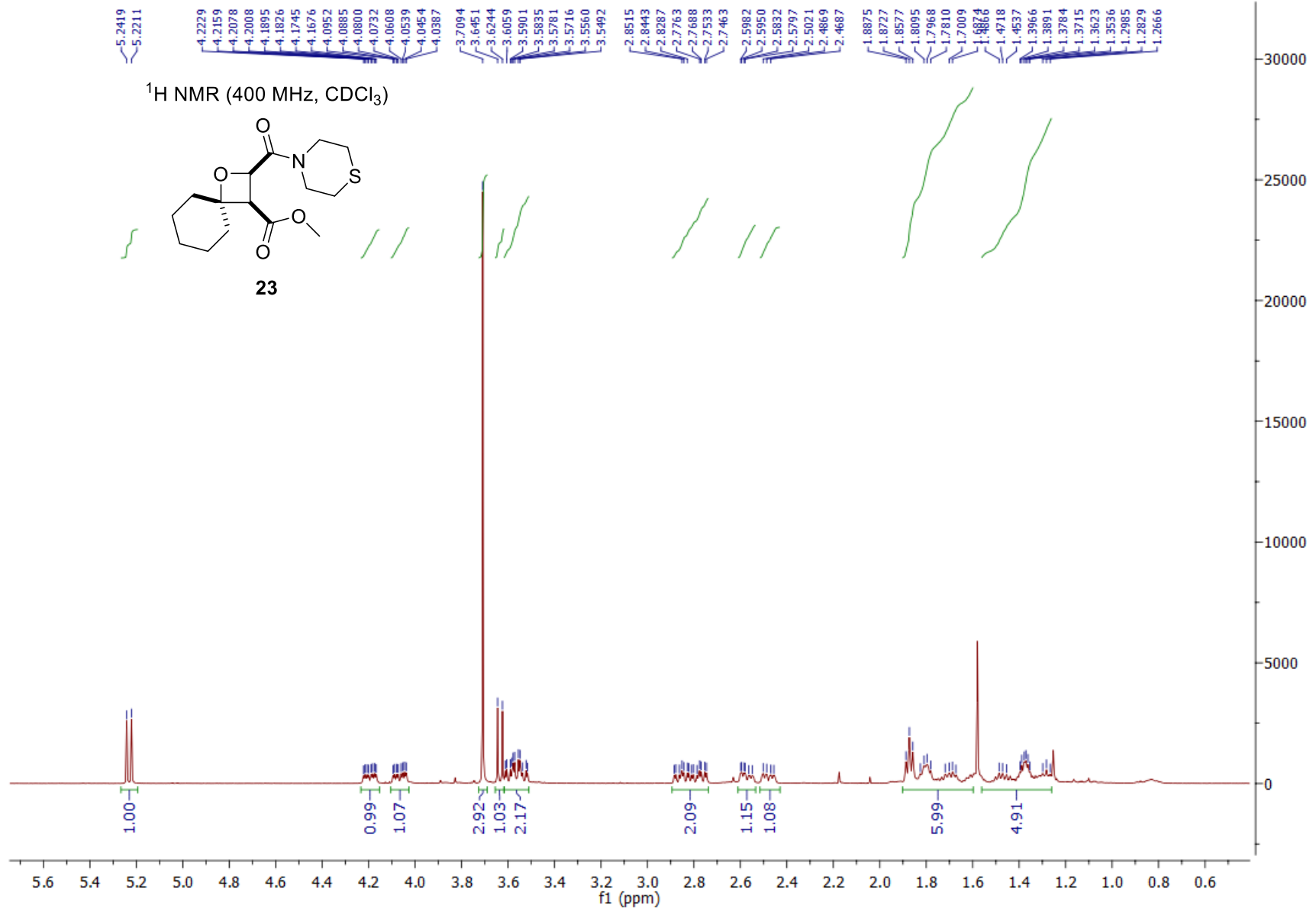


¹H NMR (400 MHz, CDCl₃)

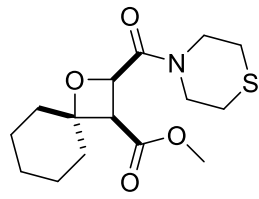


22

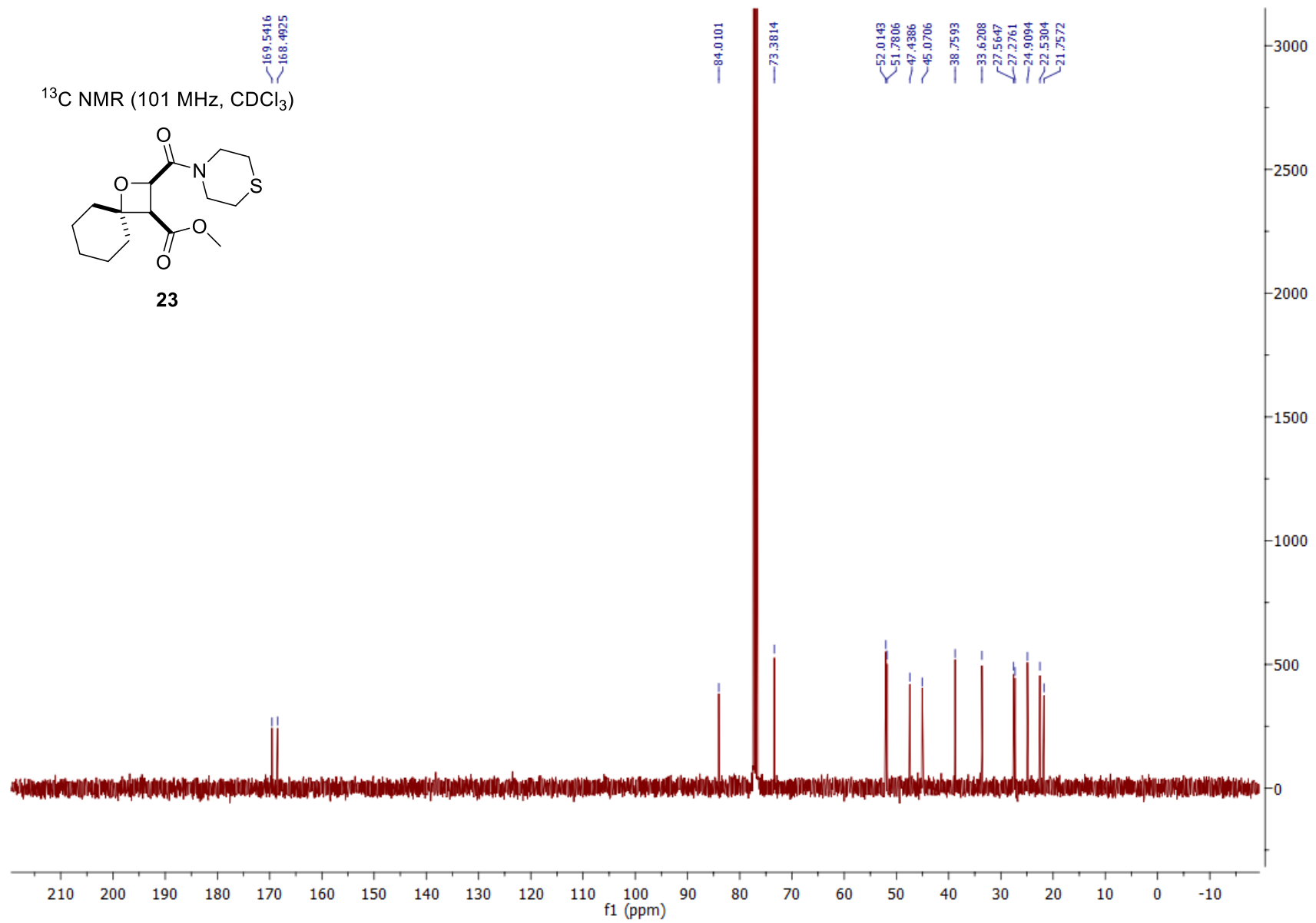




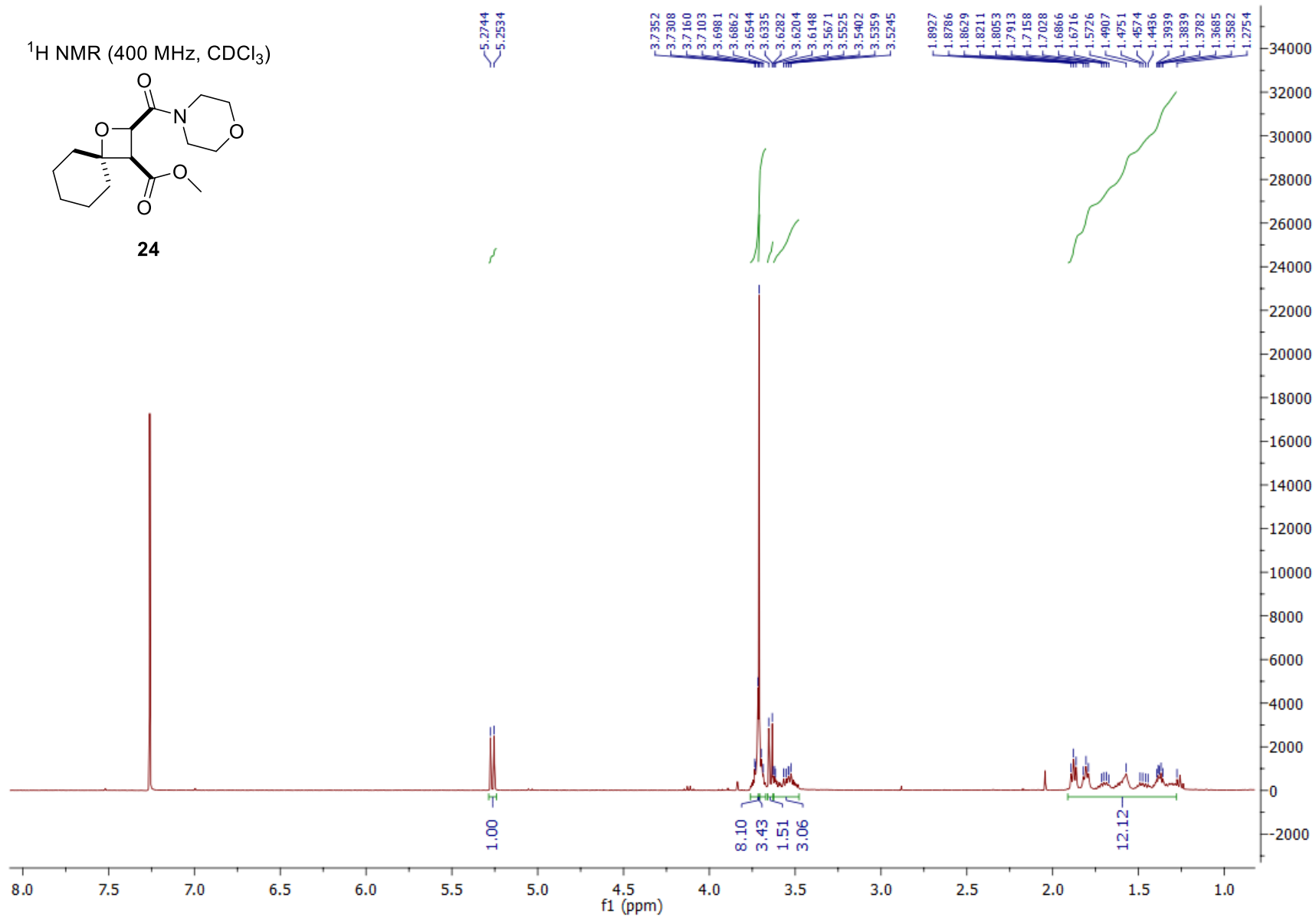
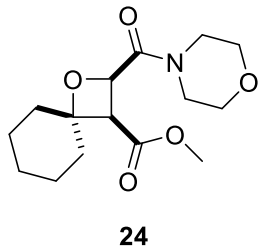
¹³C NMR (101 MHz, CDCl₃)



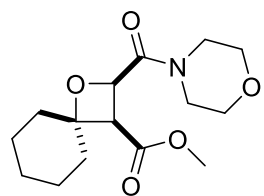
23



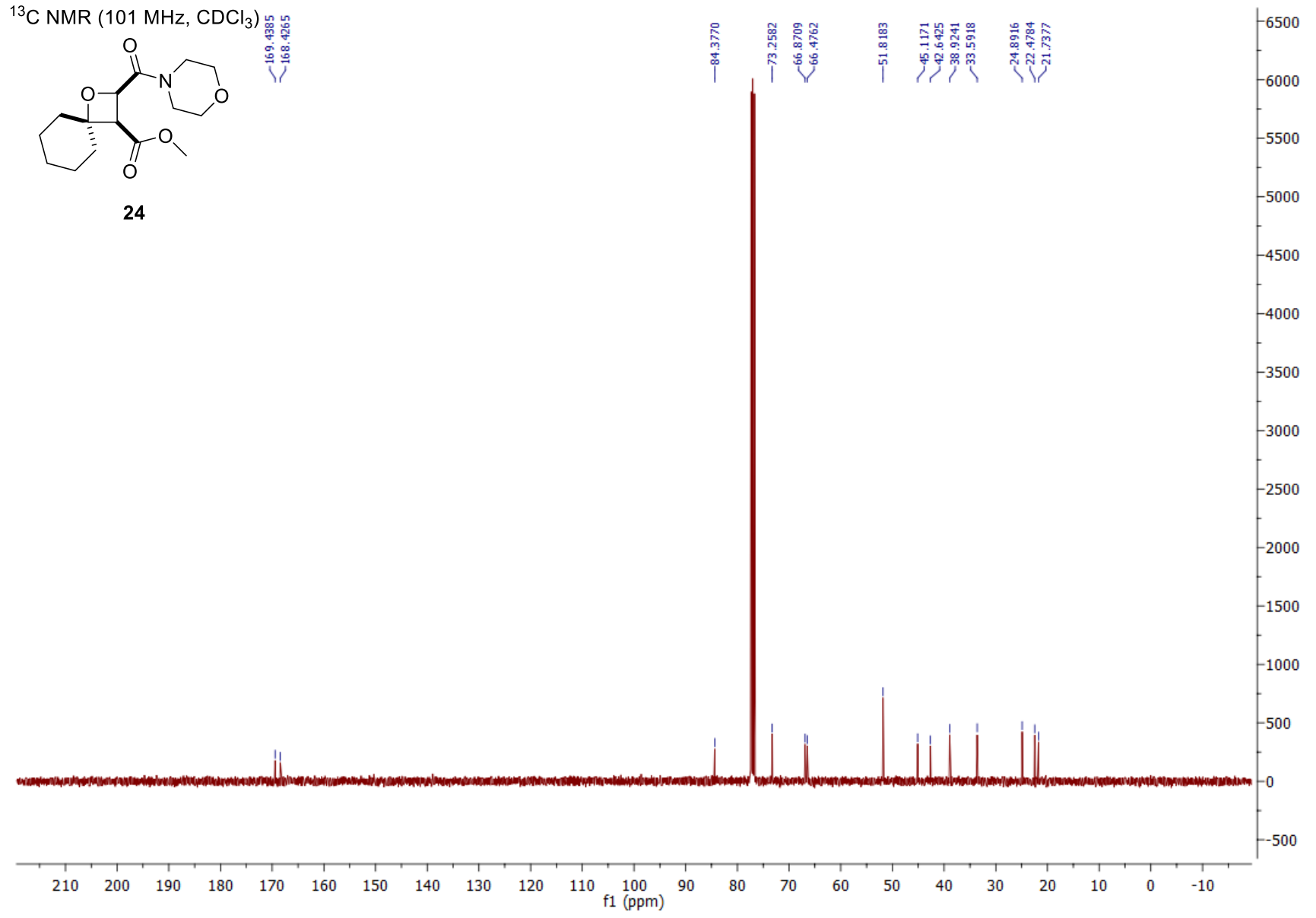
^1H NMR (400 MHz, CDCl_3)

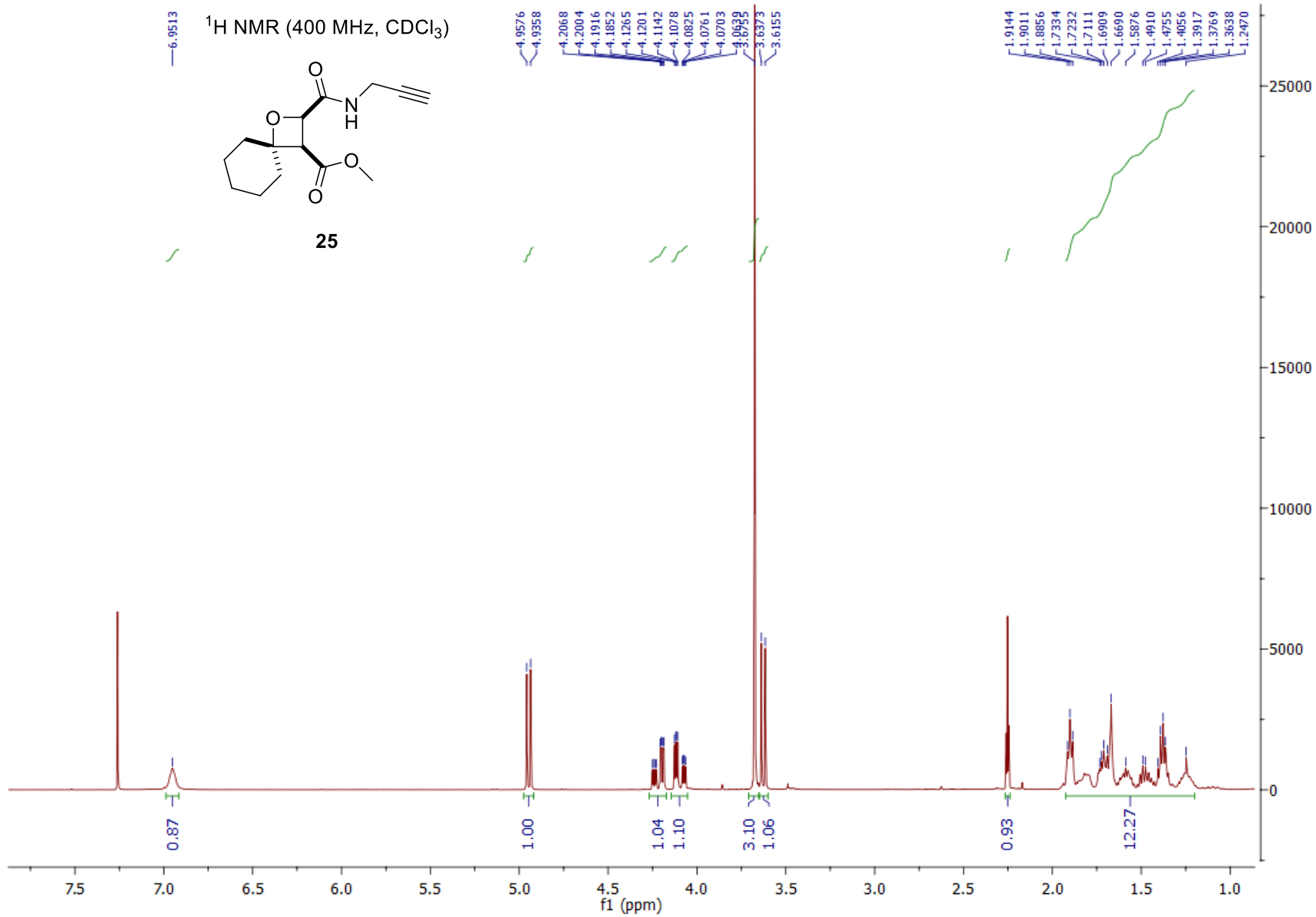


¹³C NMR (101 MHz, CDCl₃)

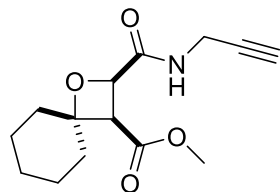


24

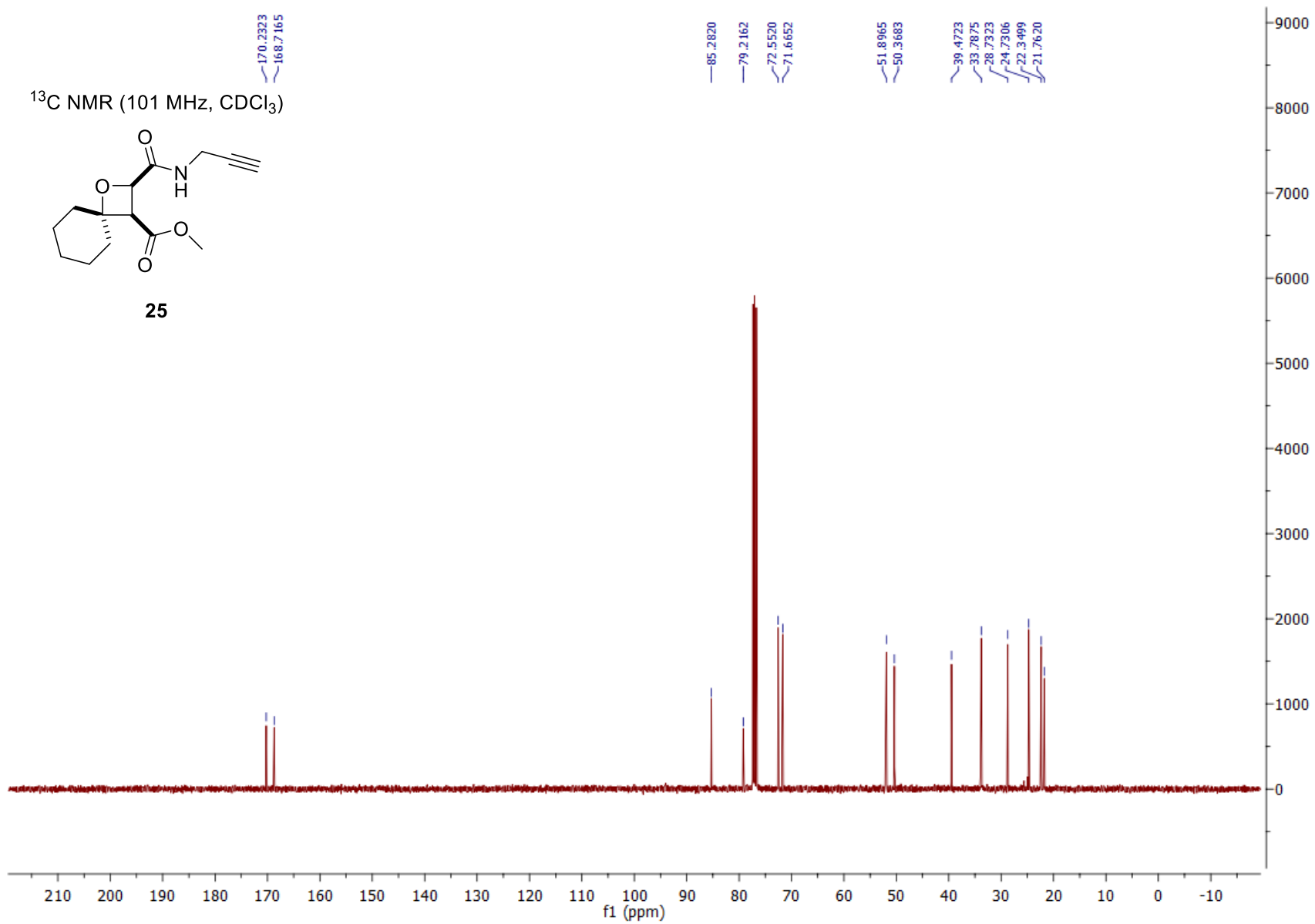


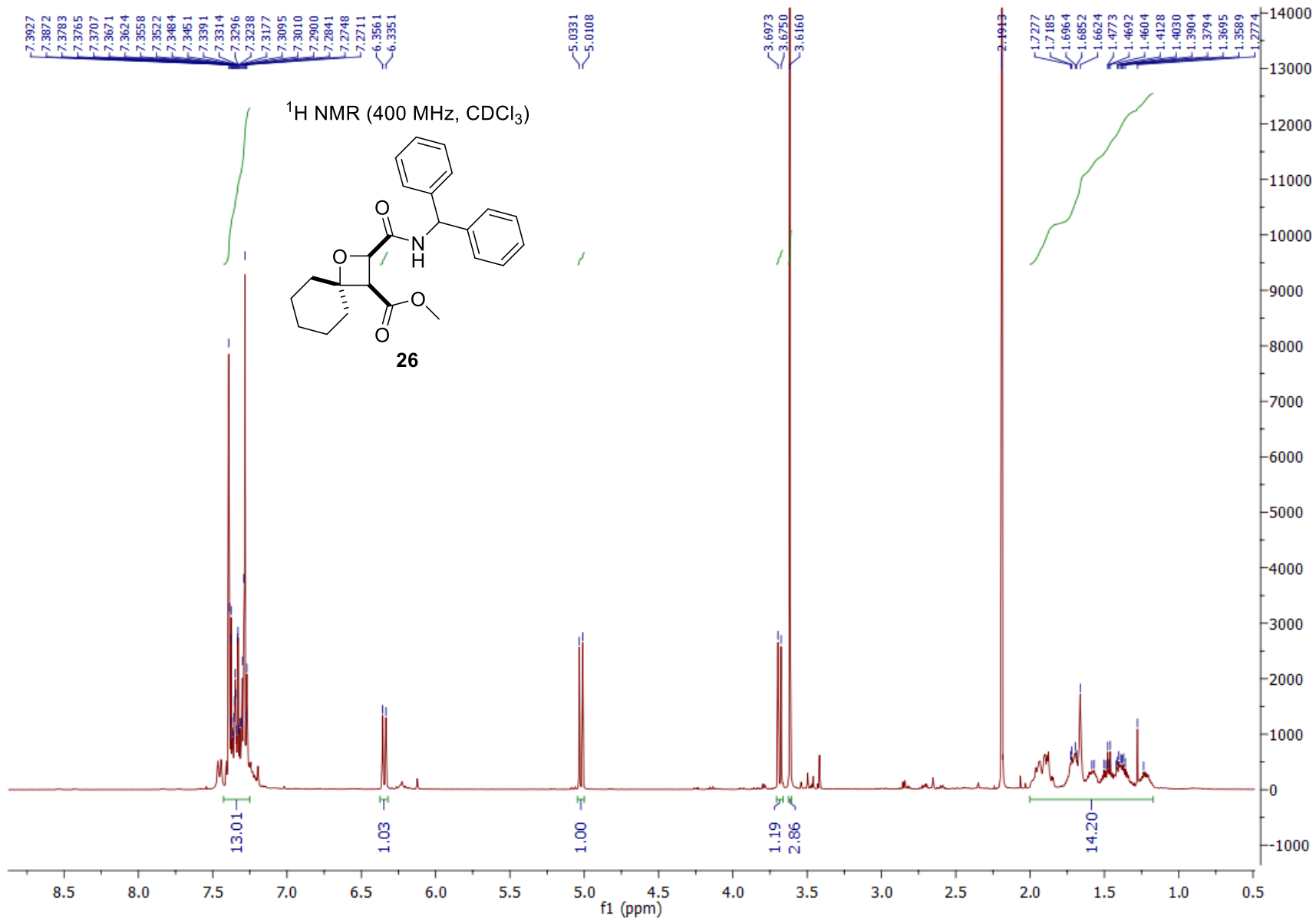


¹³C NMR (101 MHz, CDCl₃)

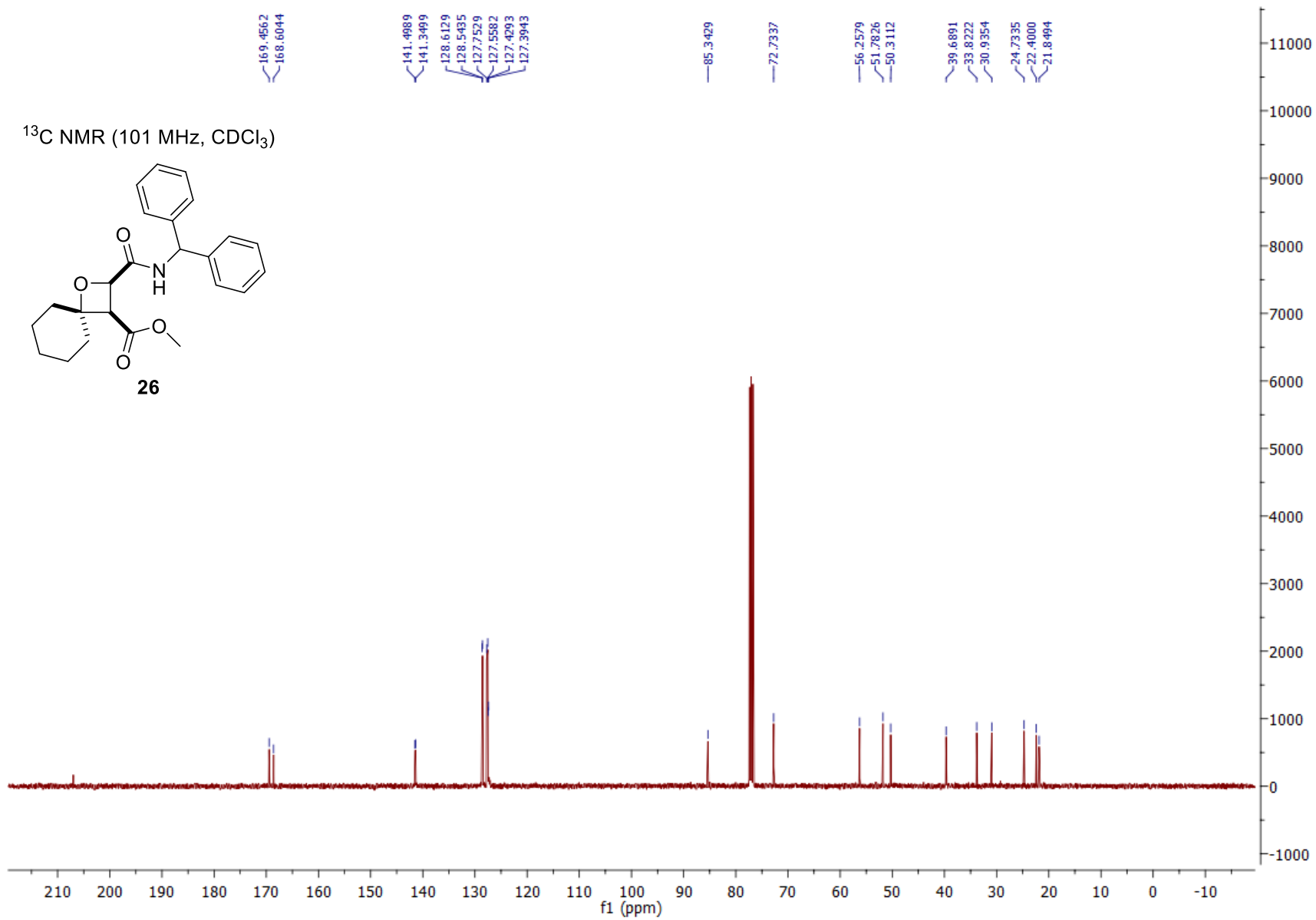
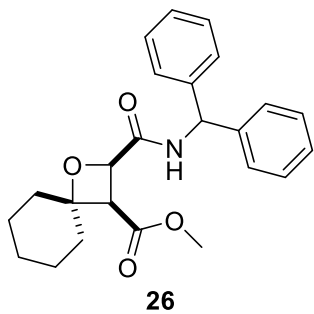


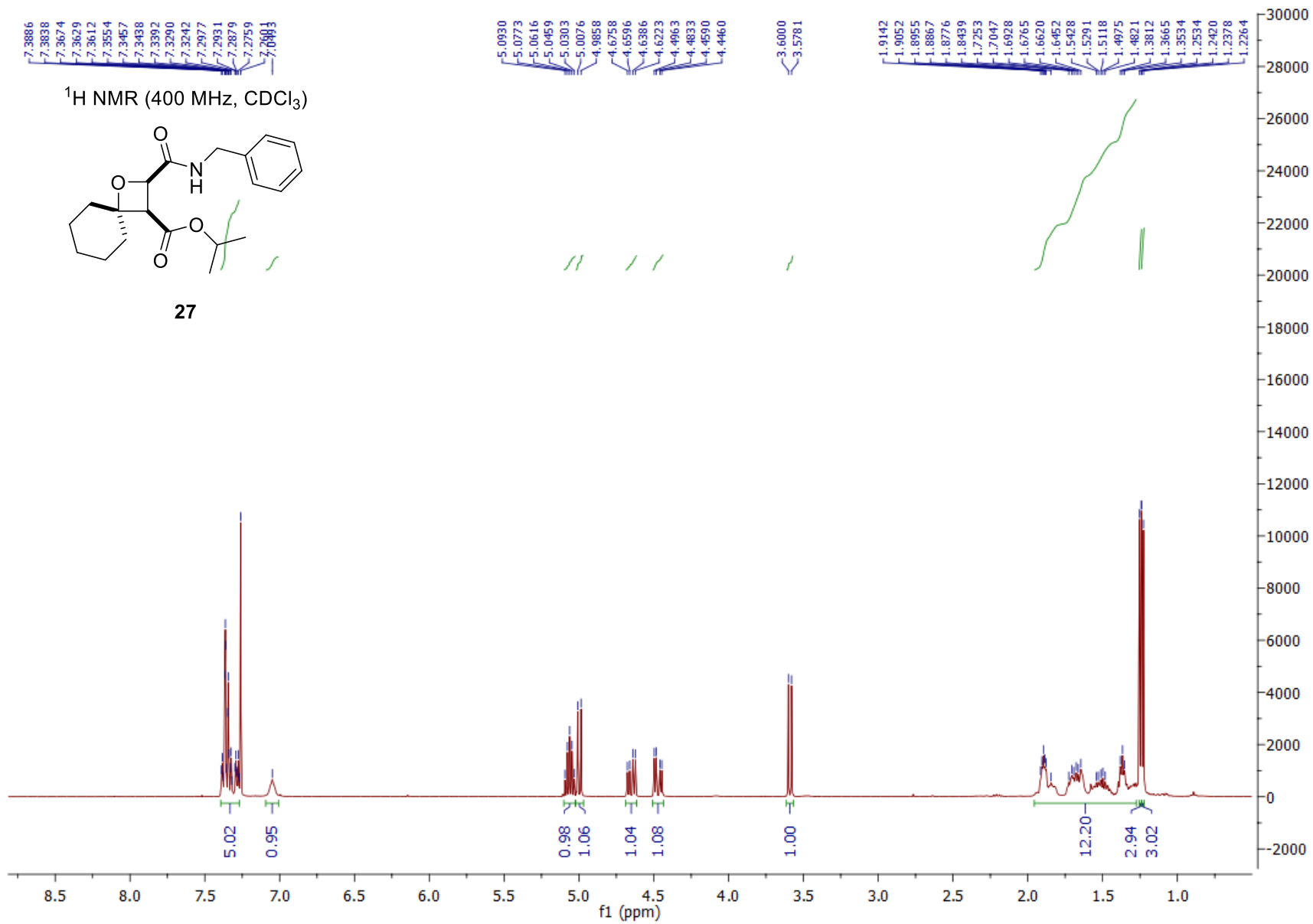
25



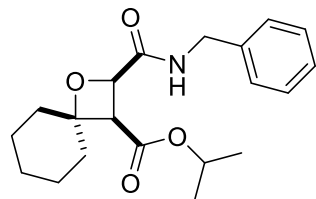


¹³C NMR (101 MHz, CDCl₃)

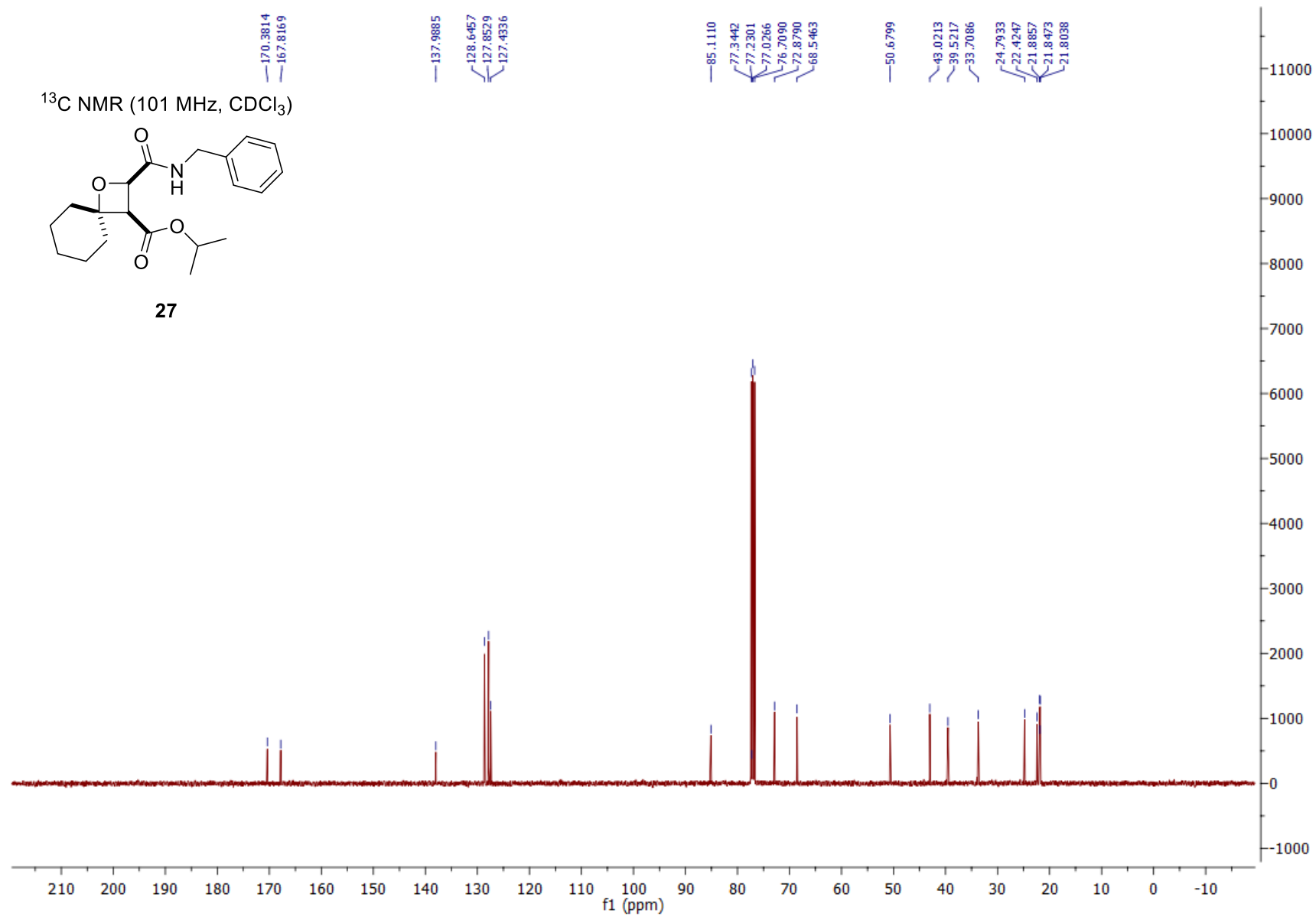




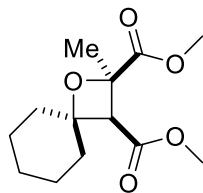
¹³C NMR (101 MHz, CDCl₃)



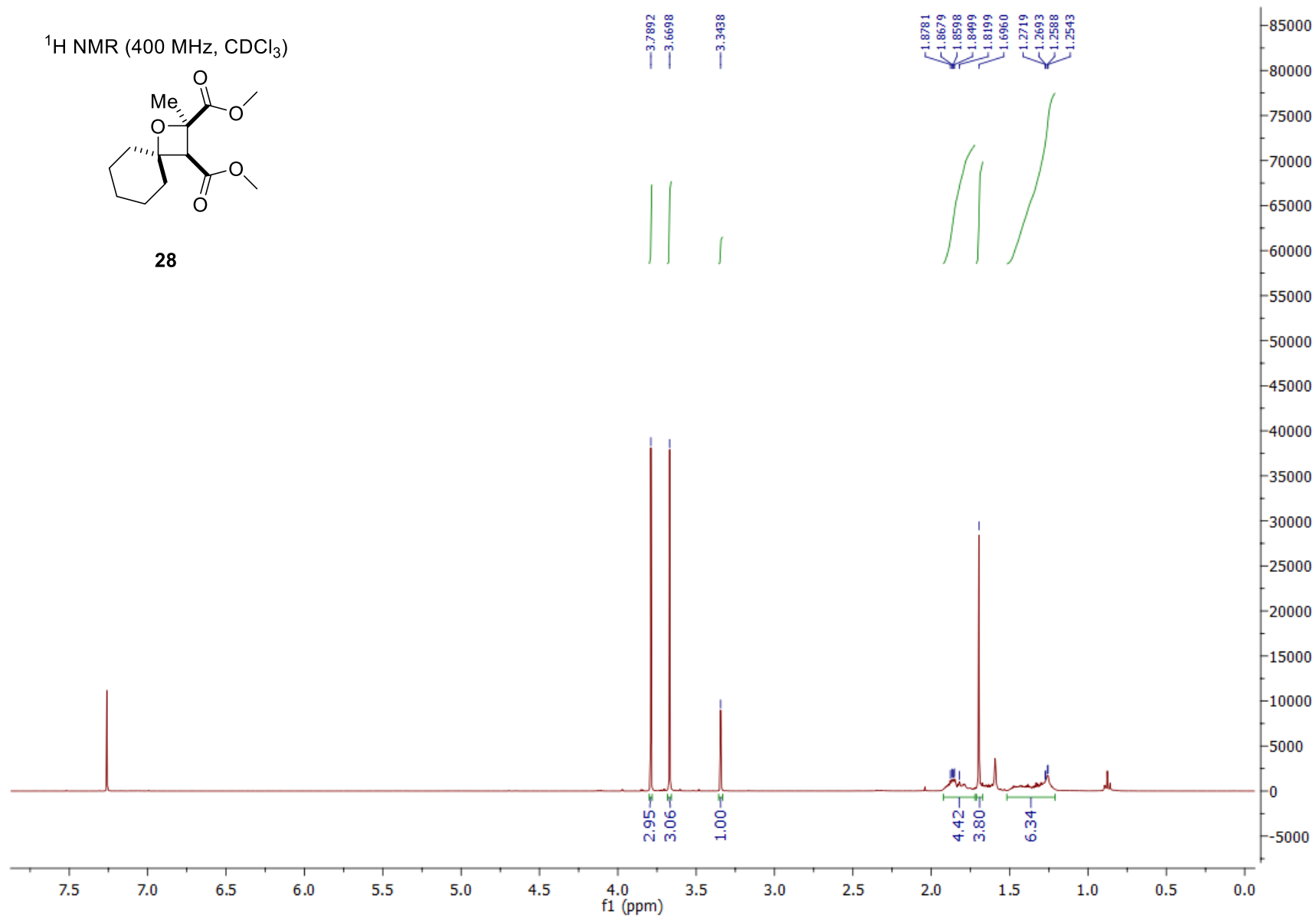
27

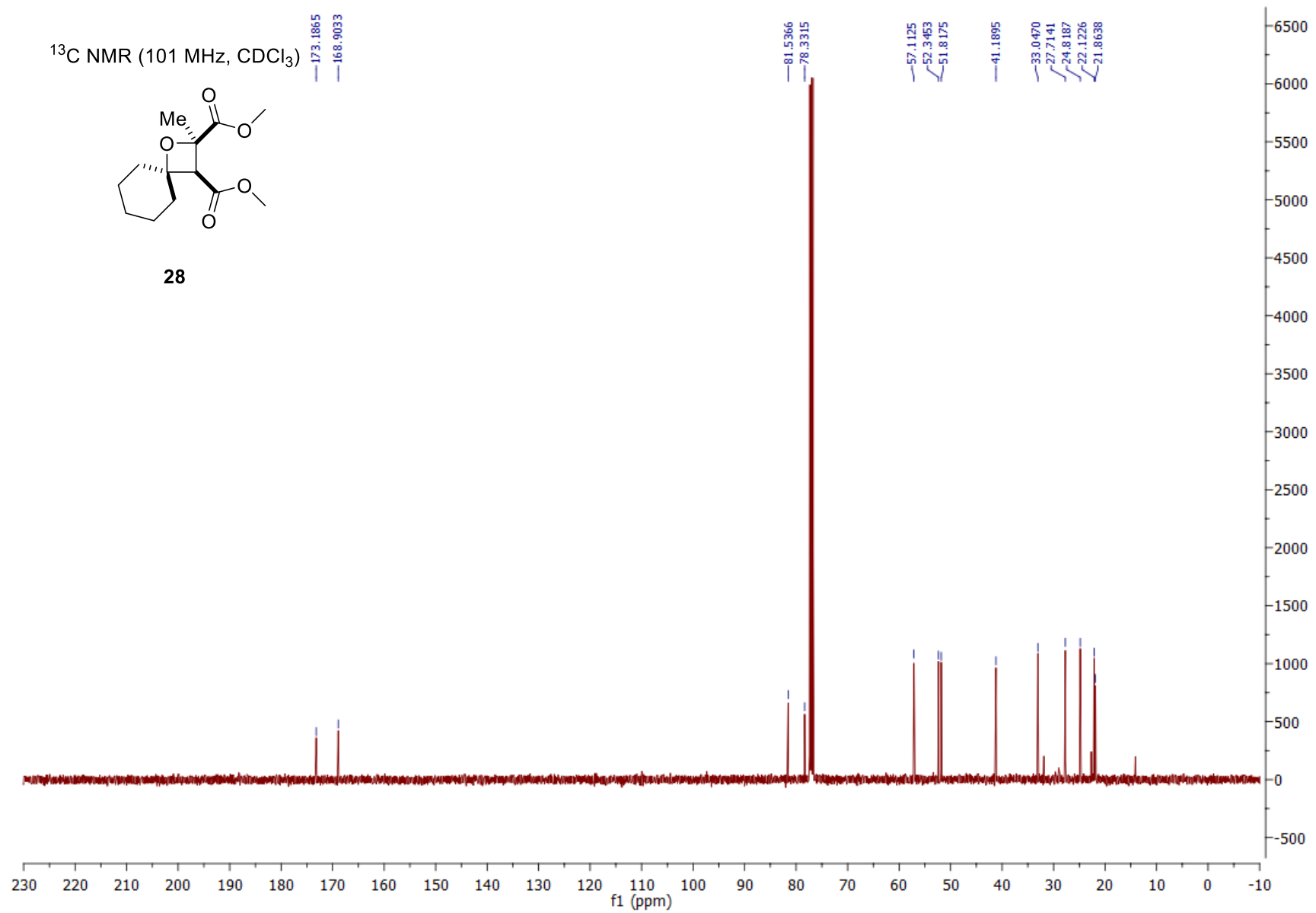


¹H NMR (400 MHz, CDCl₃)

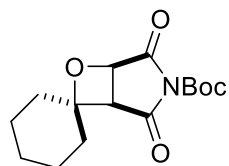


28

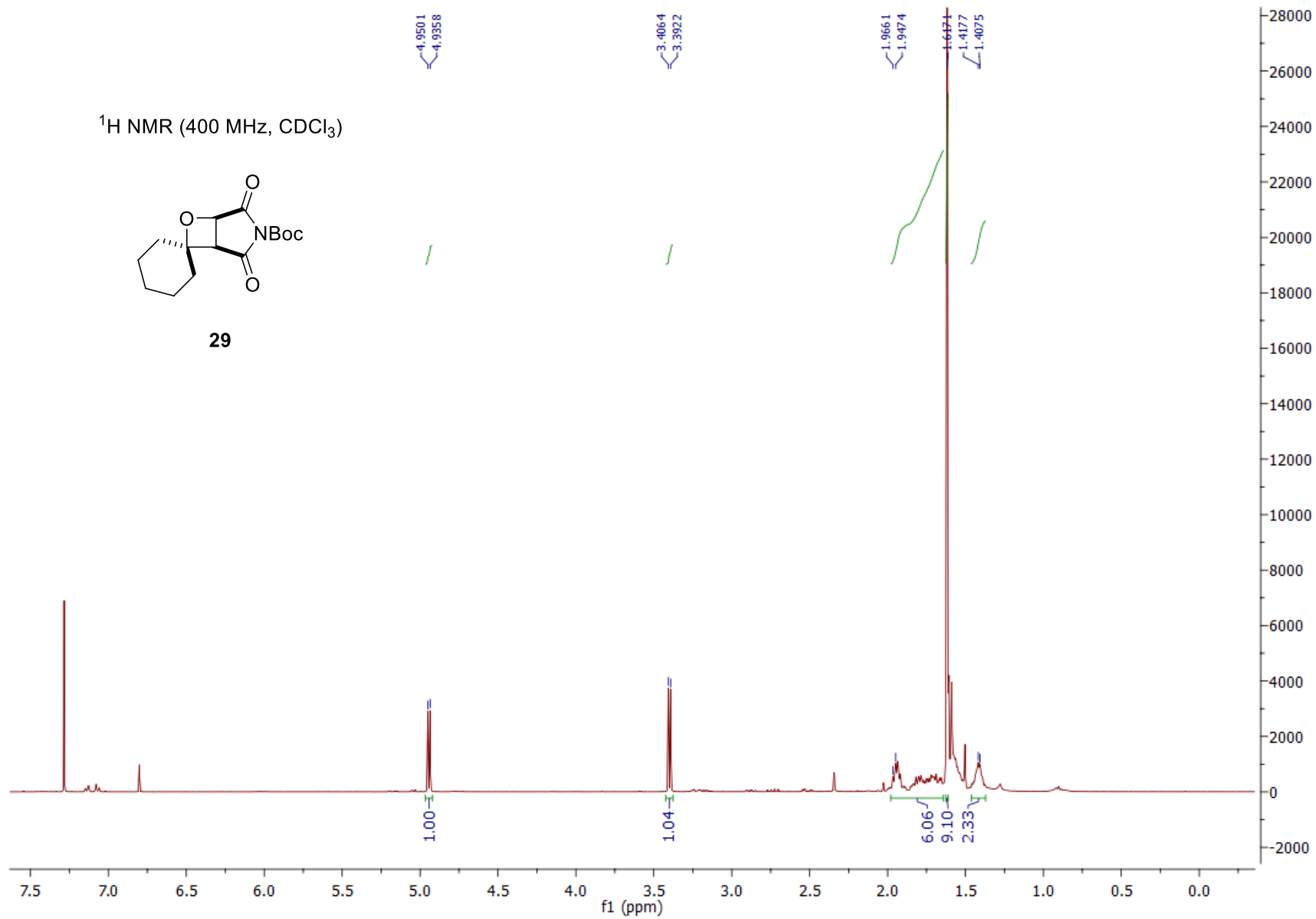




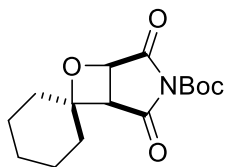
¹H NMR (400 MHz, CDCl₃)



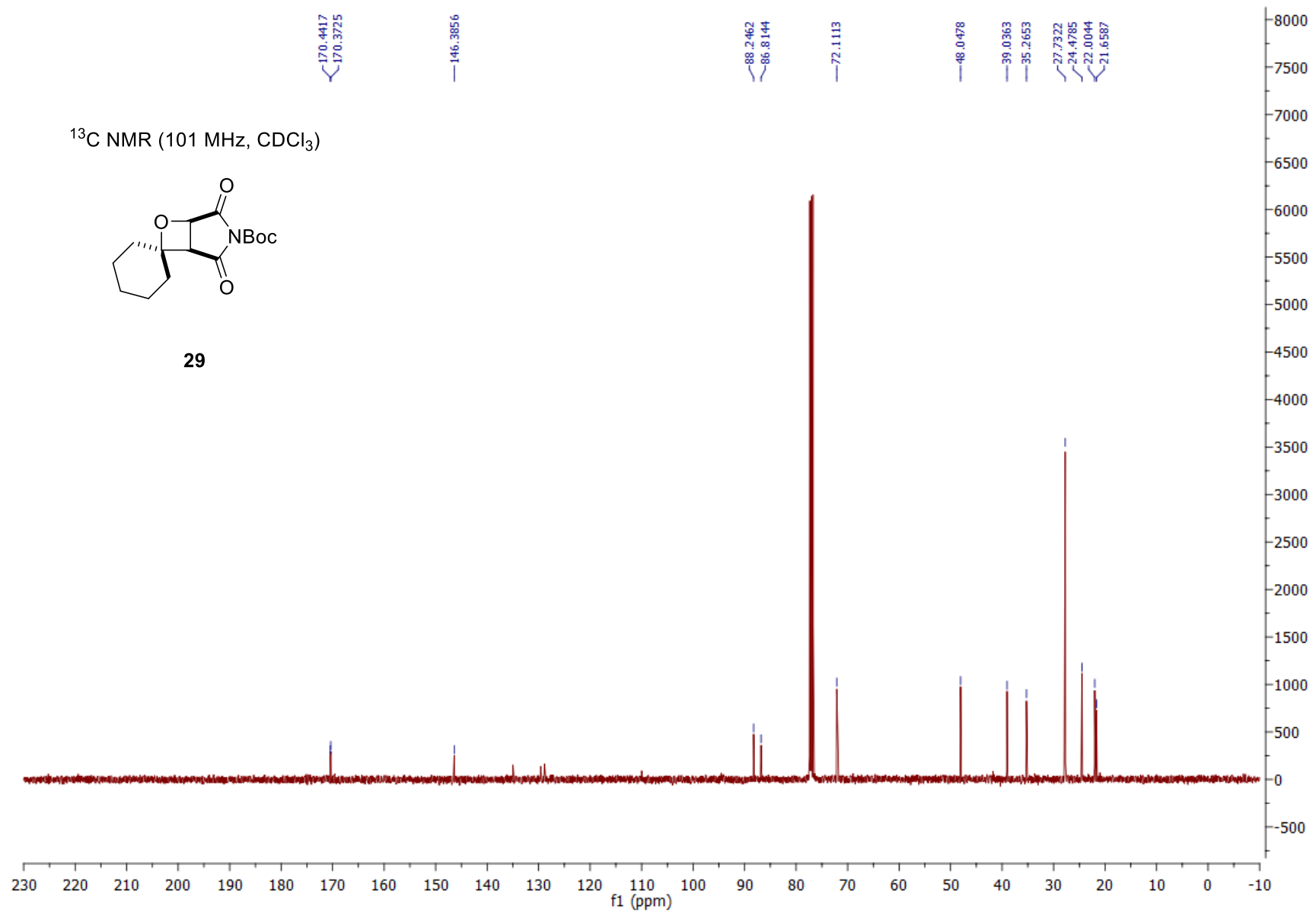
29

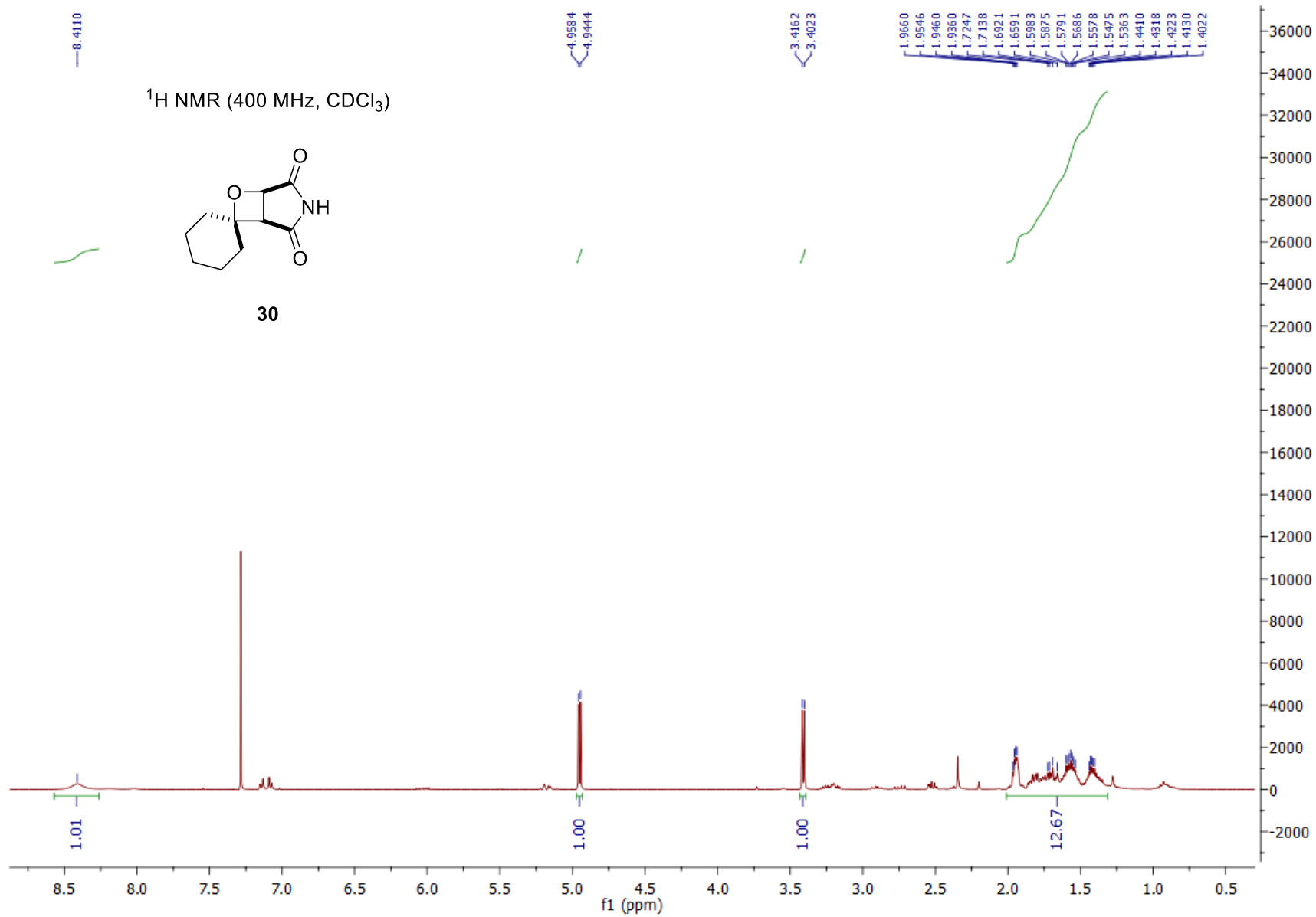


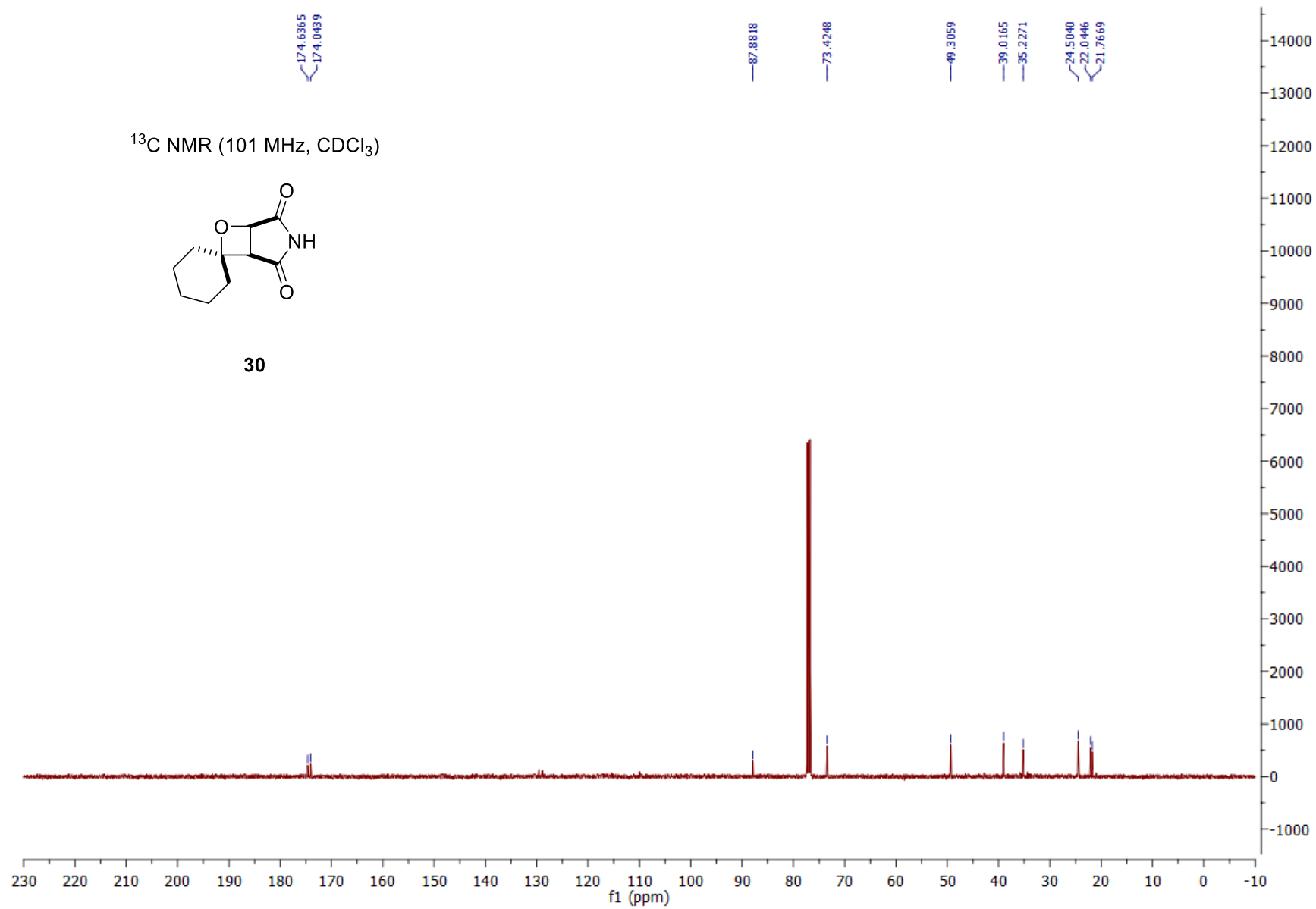
^{13}C NMR (101 MHz, CDCl_3)

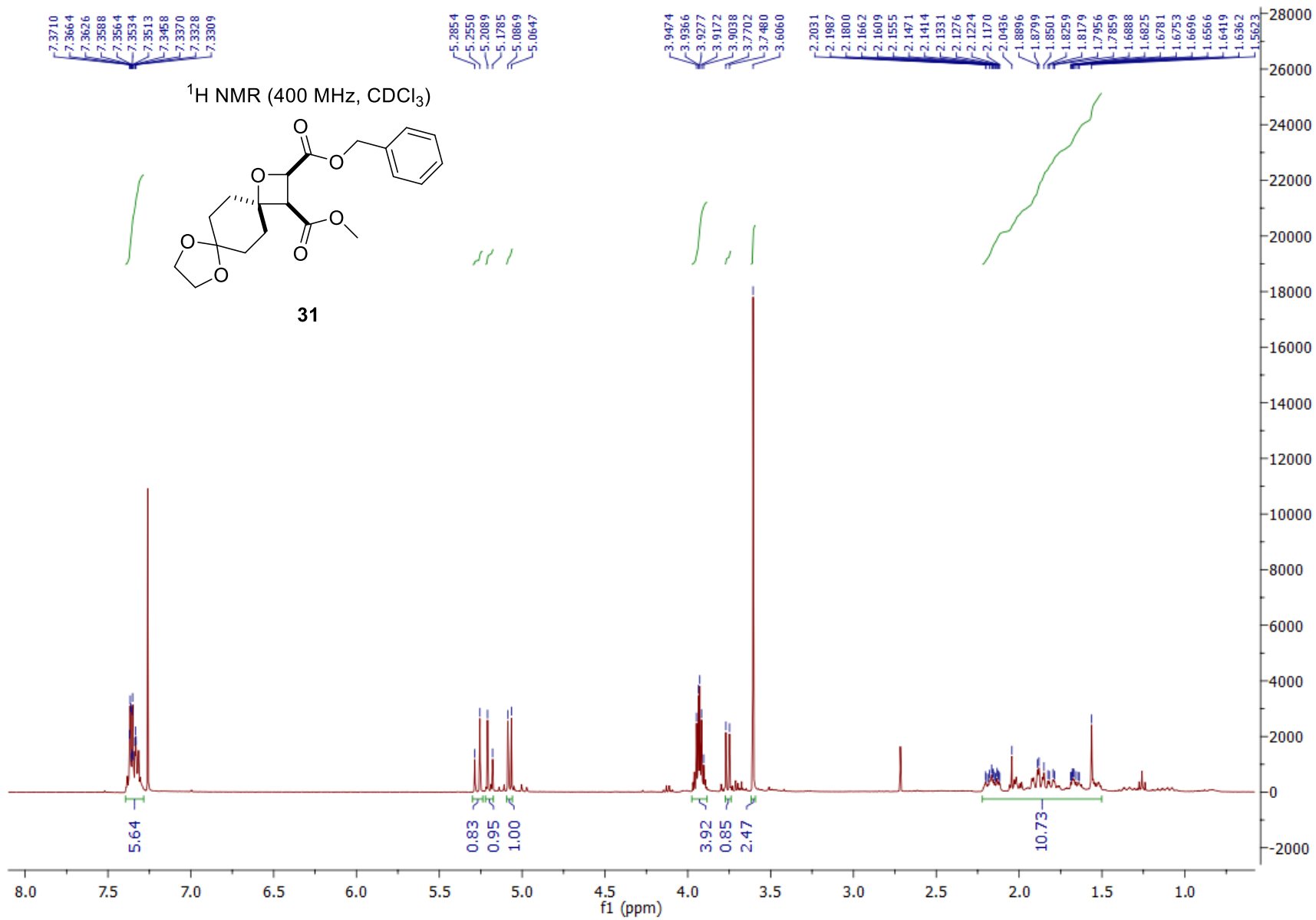


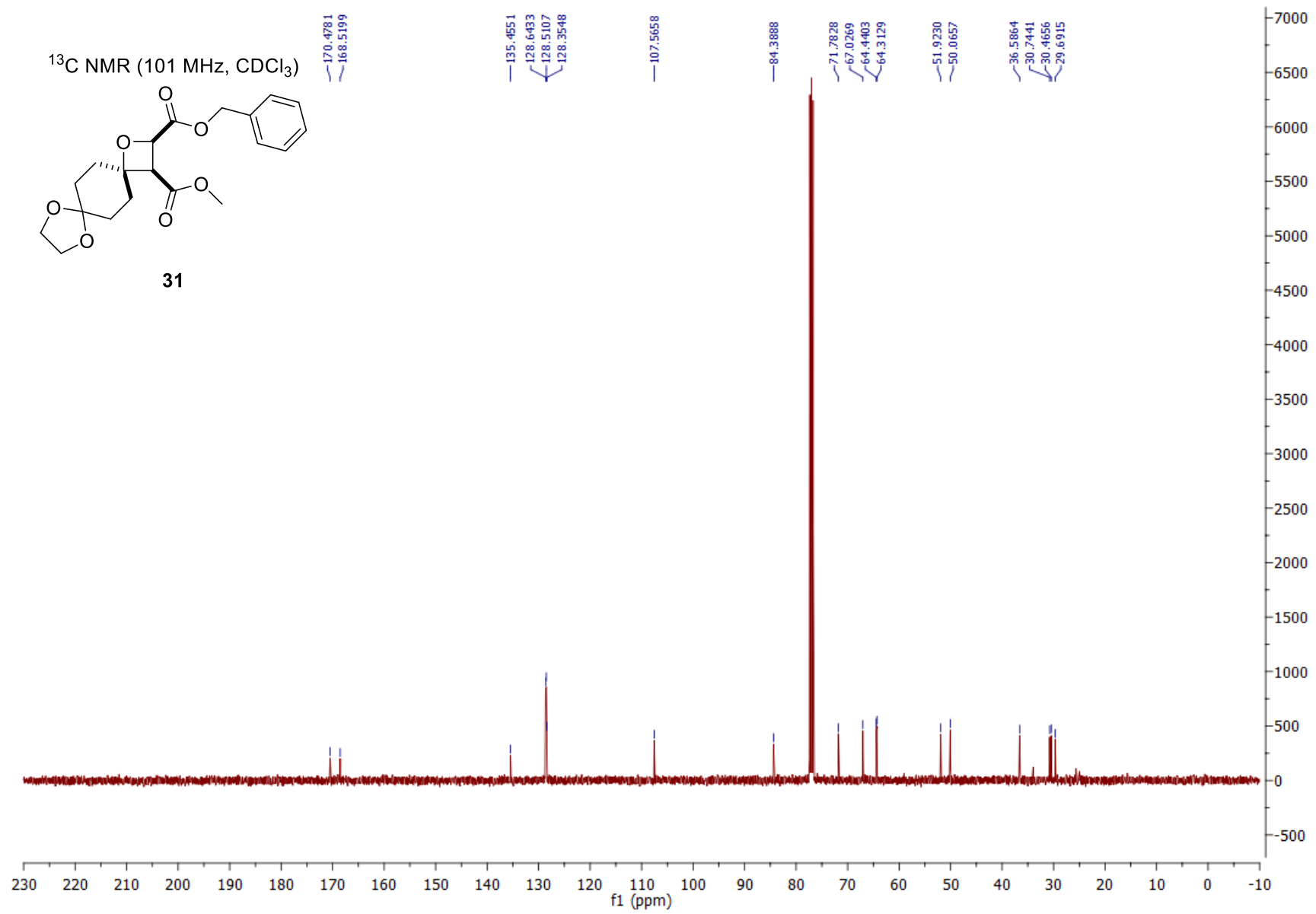
29



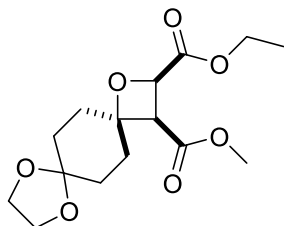




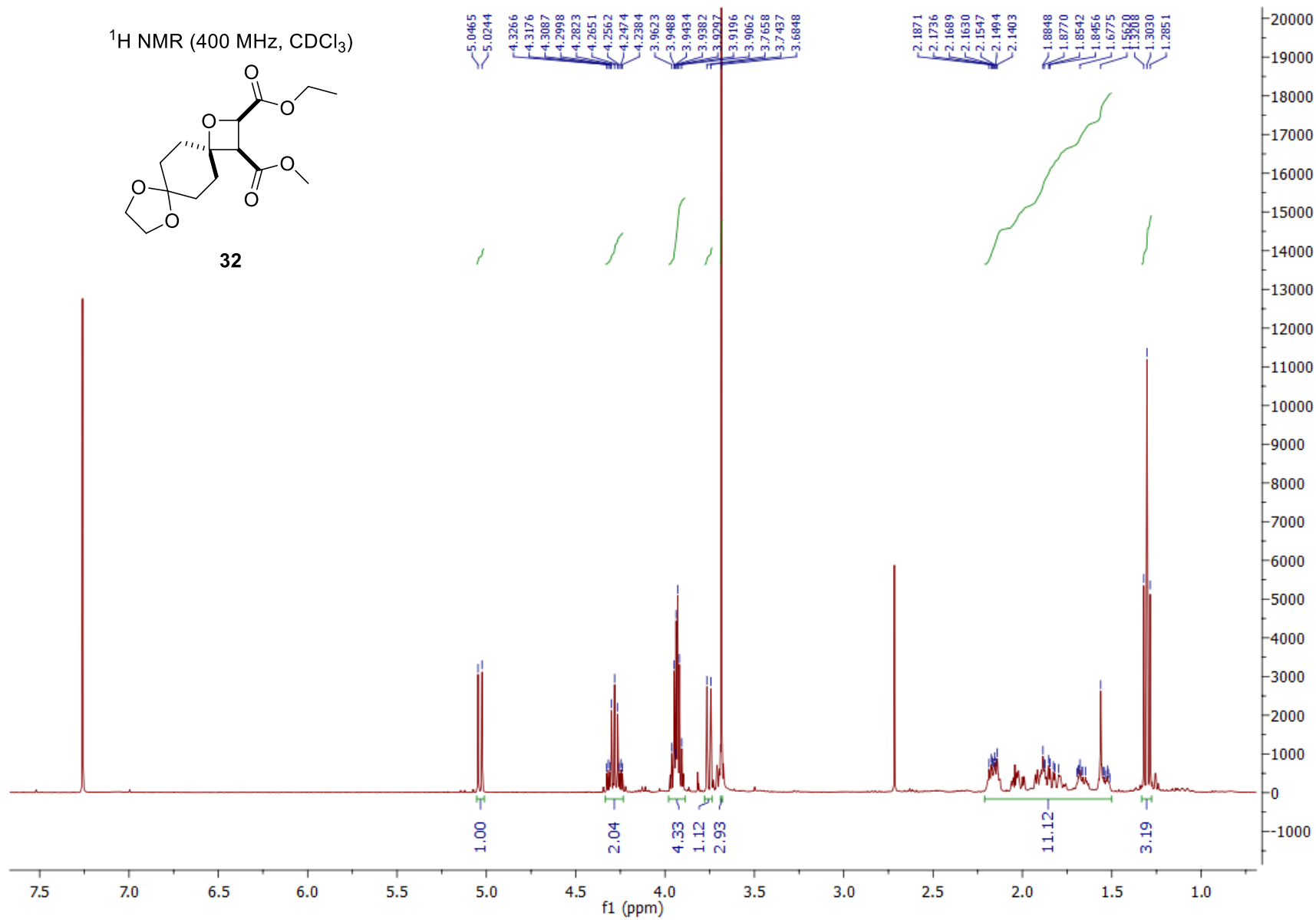


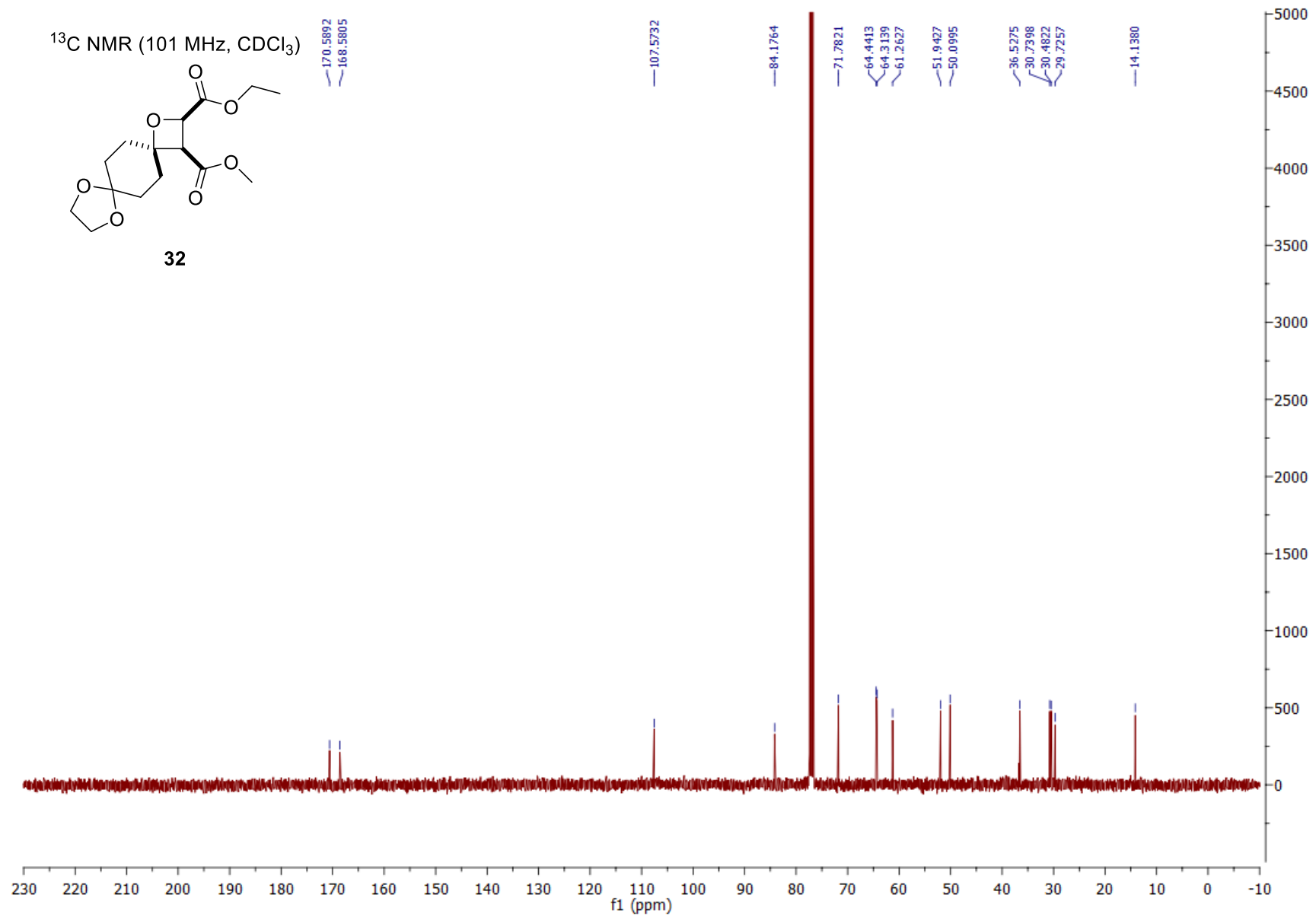


¹H NMR (400 MHz, CDCl₃)

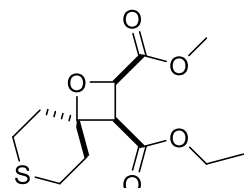


32

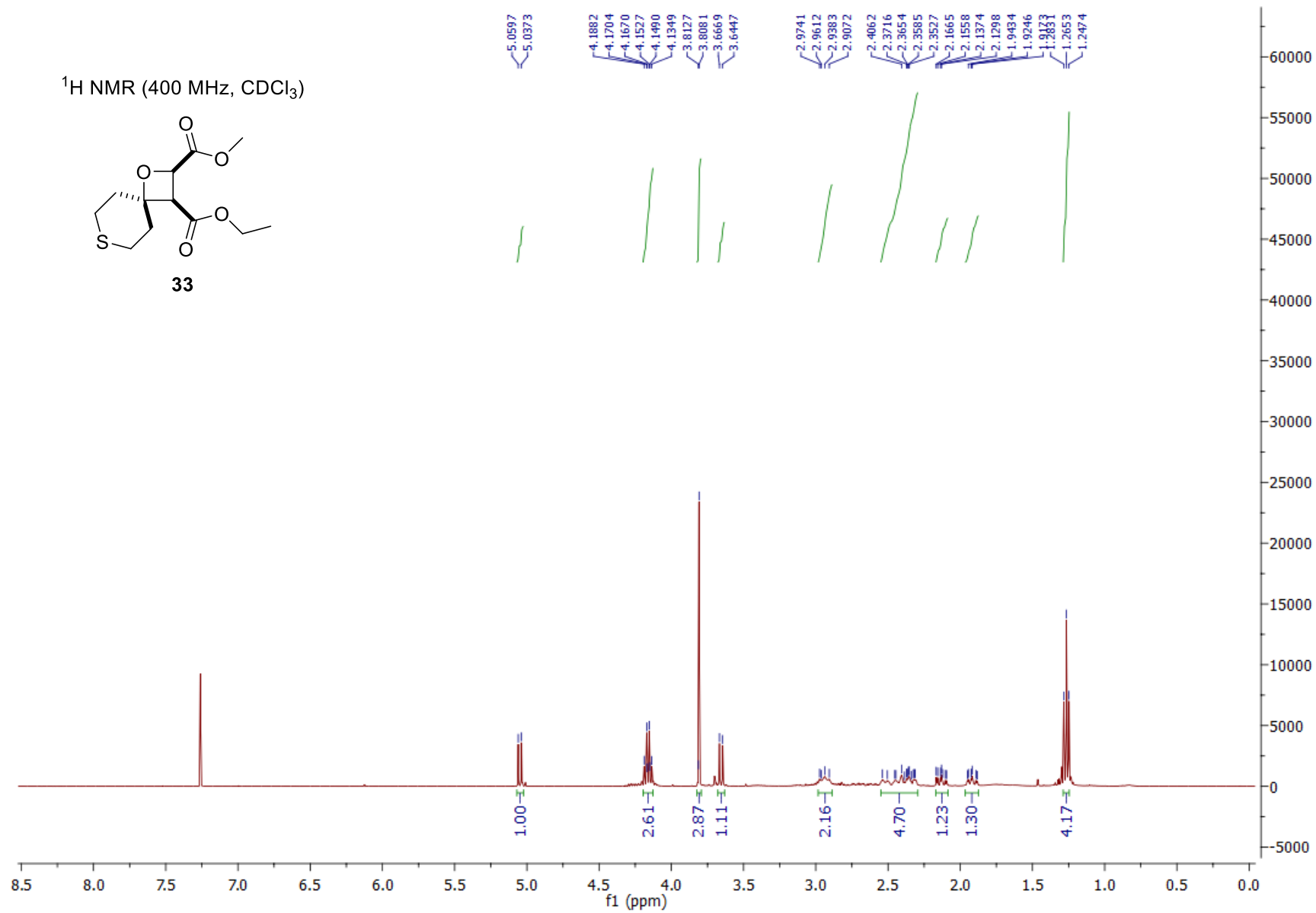




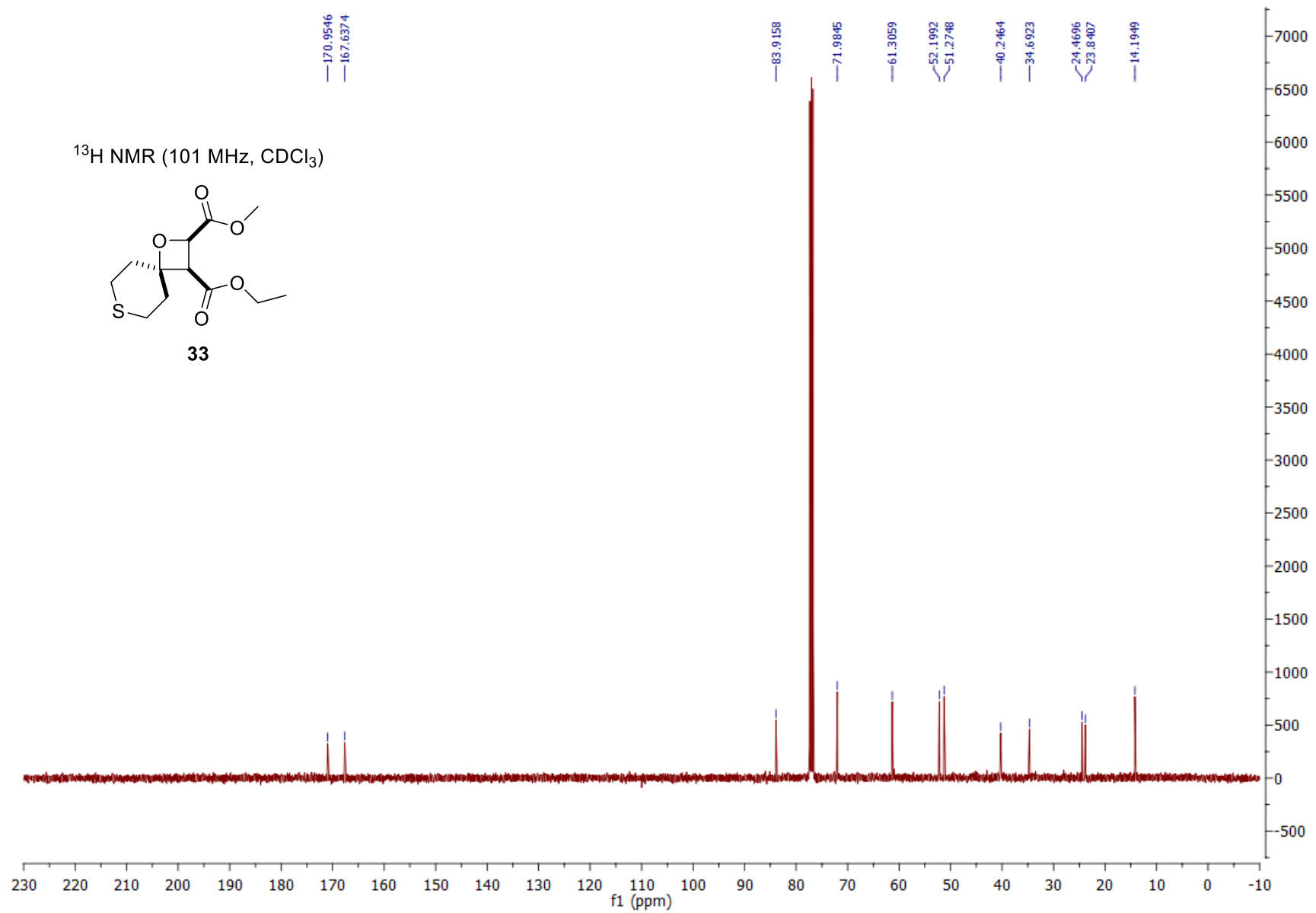
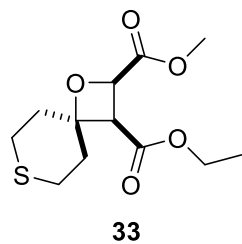
¹H NMR (400 MHz, CDCl₃)



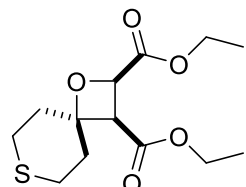
33



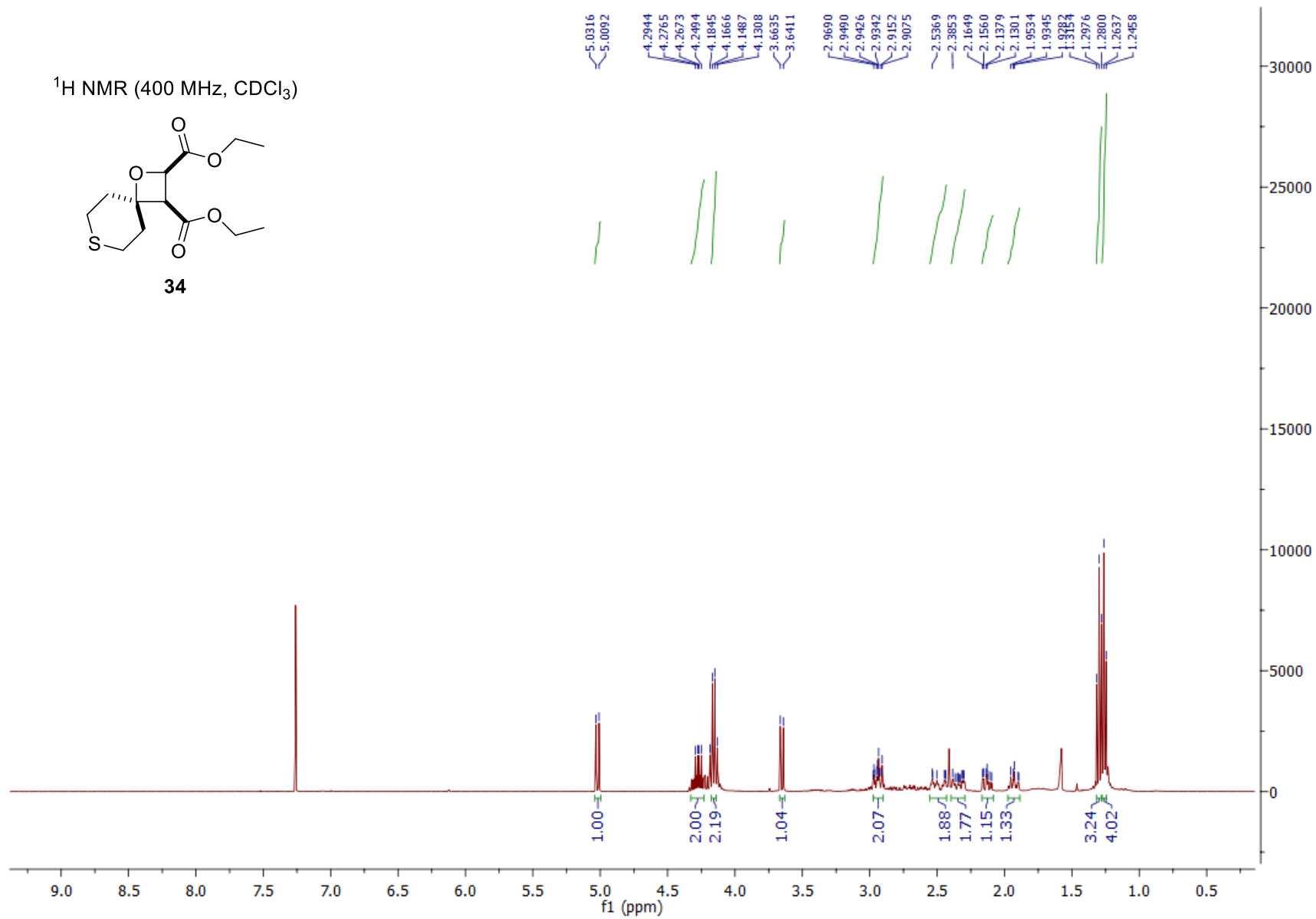
^{13}H NMR (101 MHz, CDCl_3)



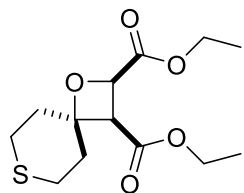
¹H NMR (400 MHz, CDCl₃)



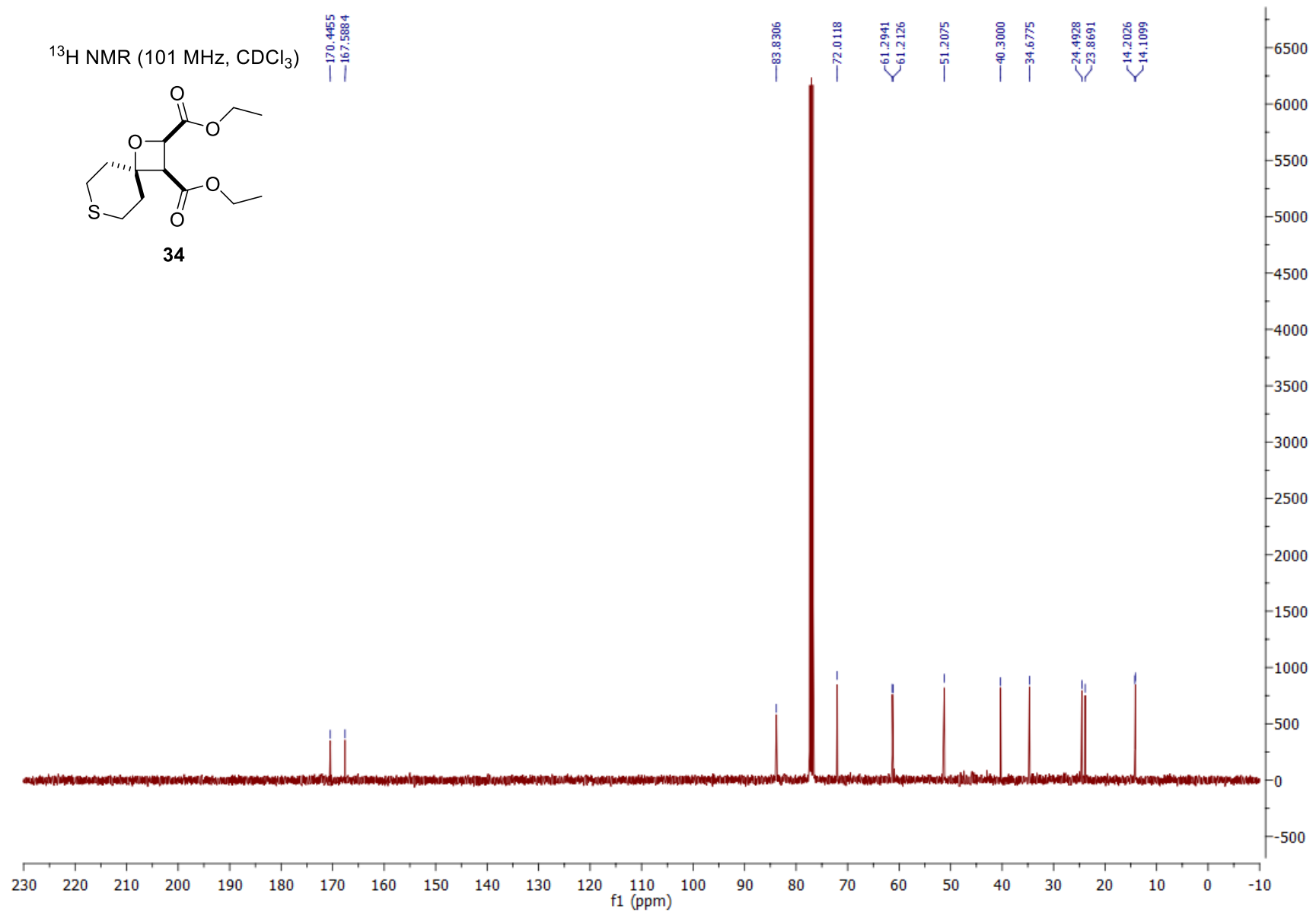
34



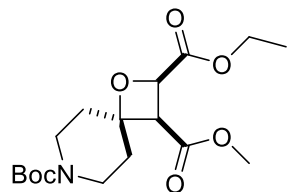
^{13}H NMR (101 MHz, CDCl_3)



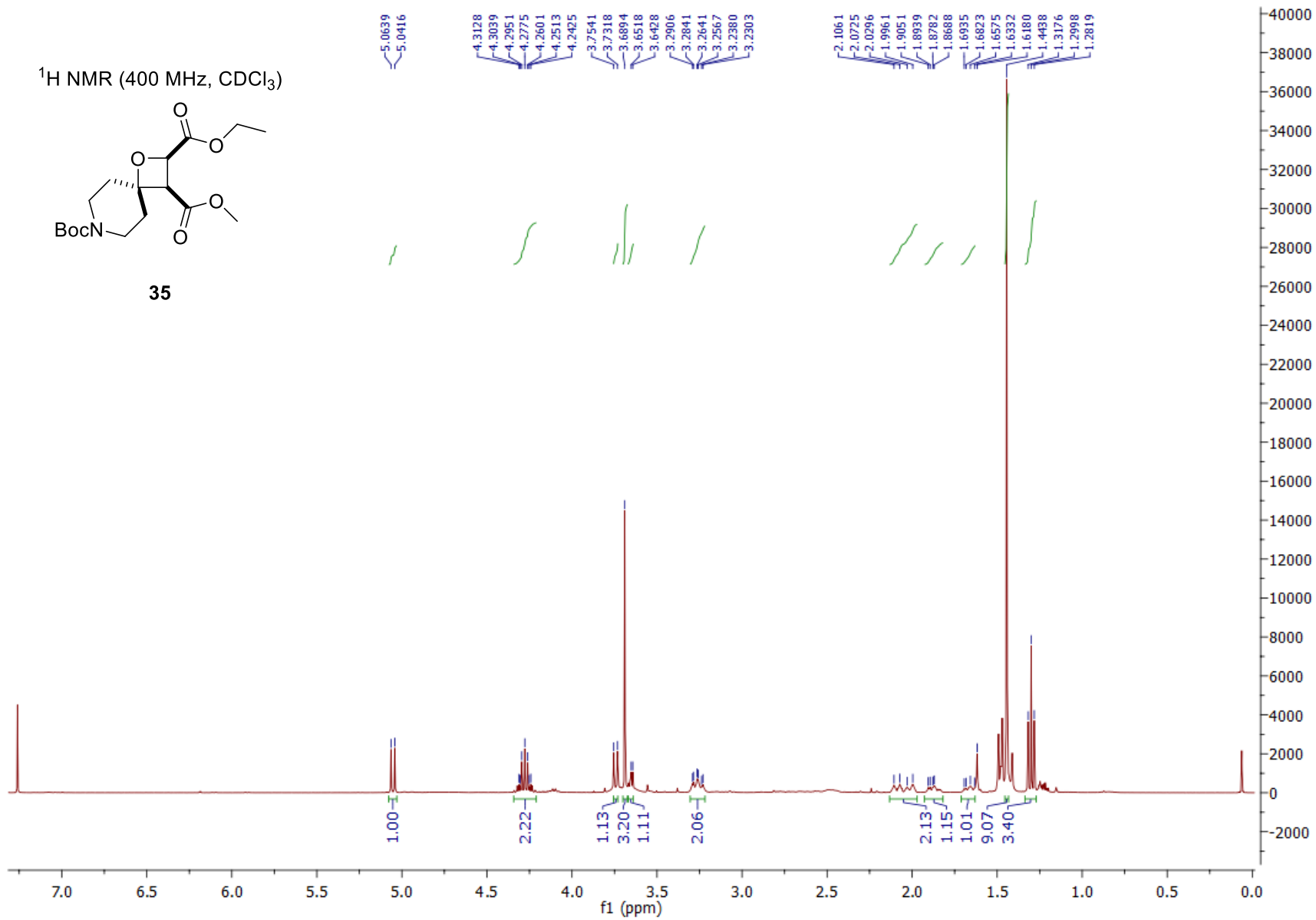
34



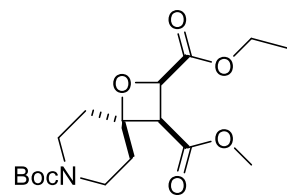
¹H NMR (400 MHz, CDCl₃)



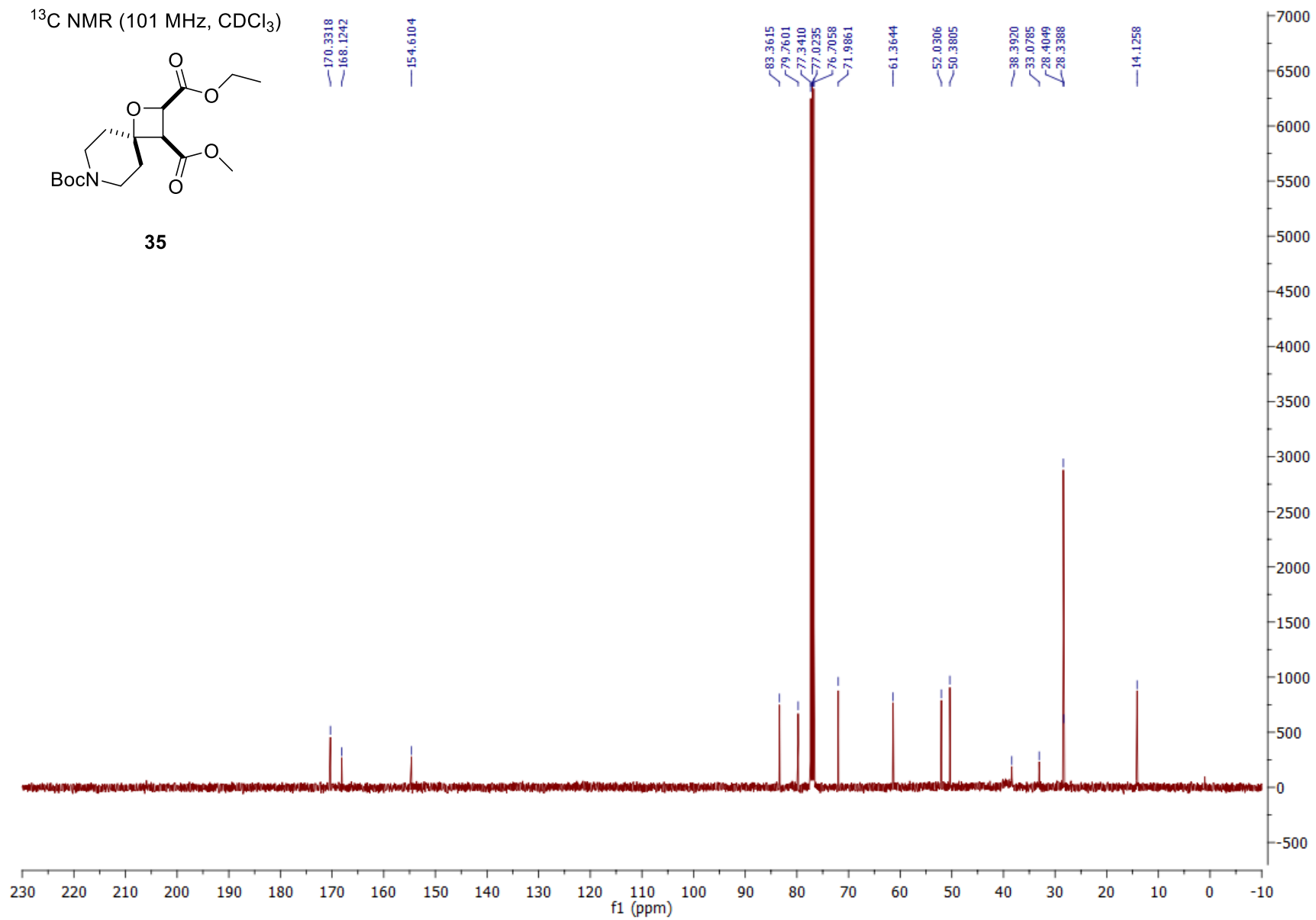
35

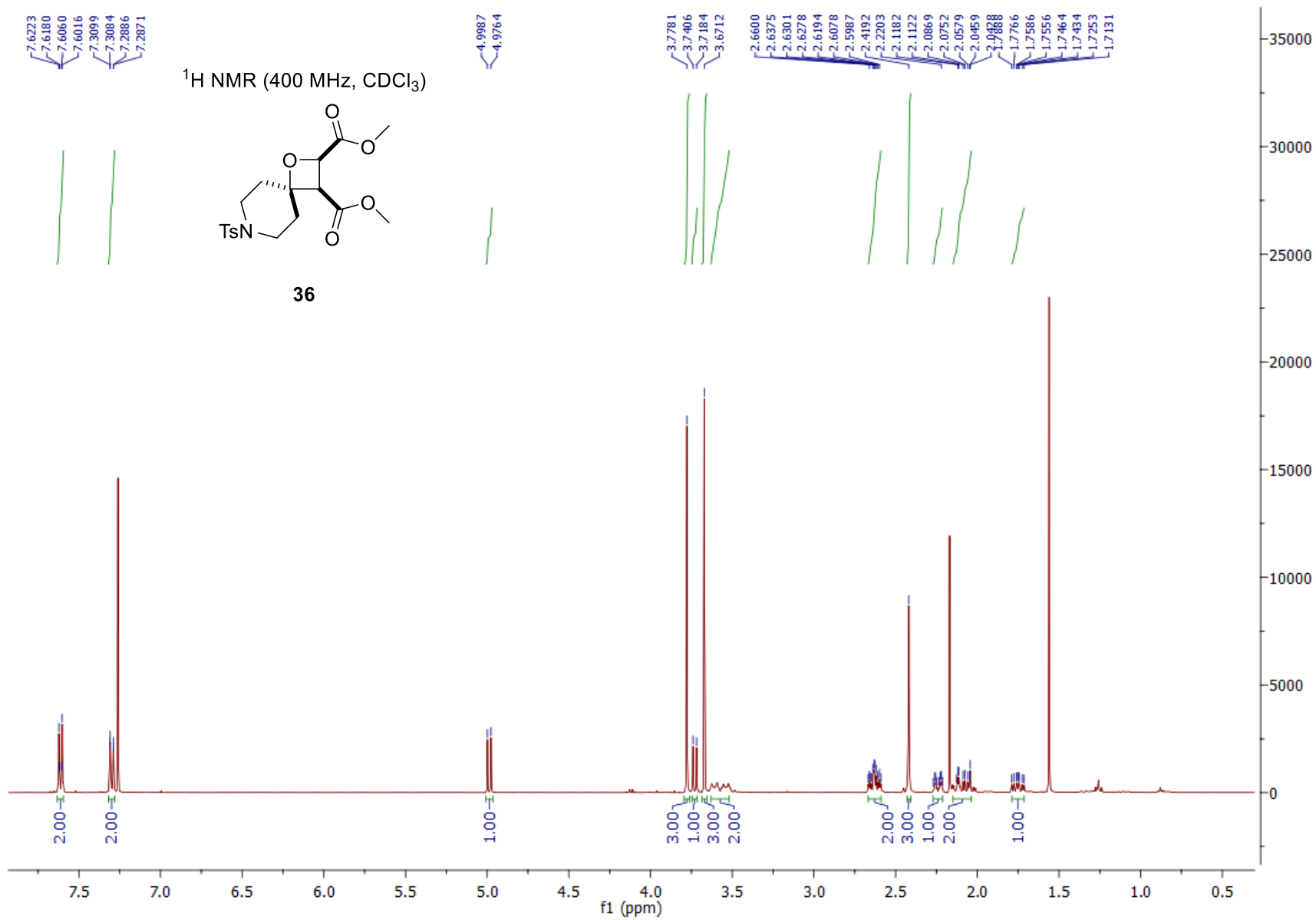


¹³C NMR (101 MHz, CDCl₃)

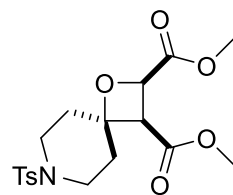


35

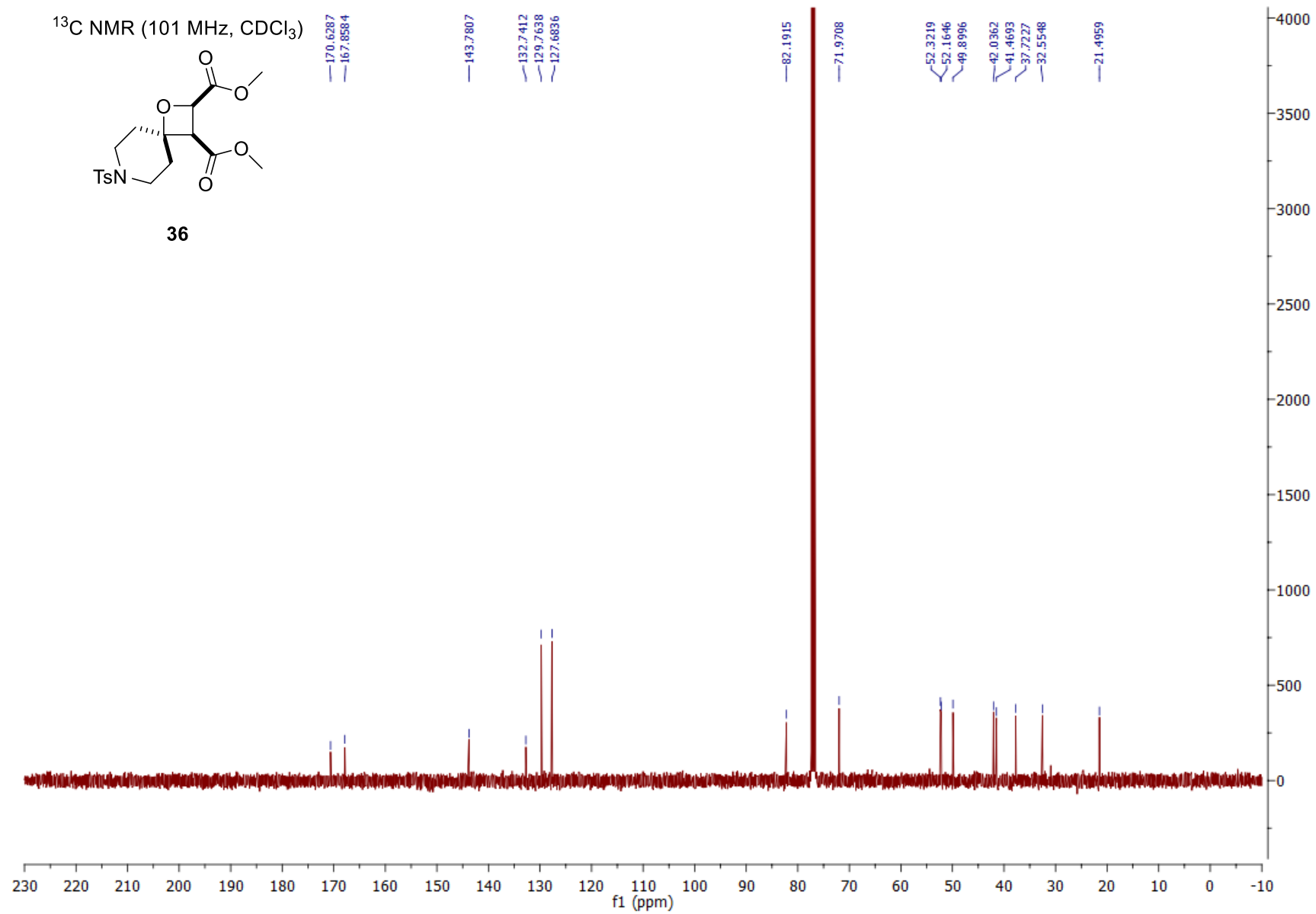




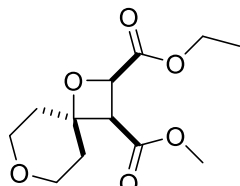
^{13}C NMR (101 MHz, CDCl_3)



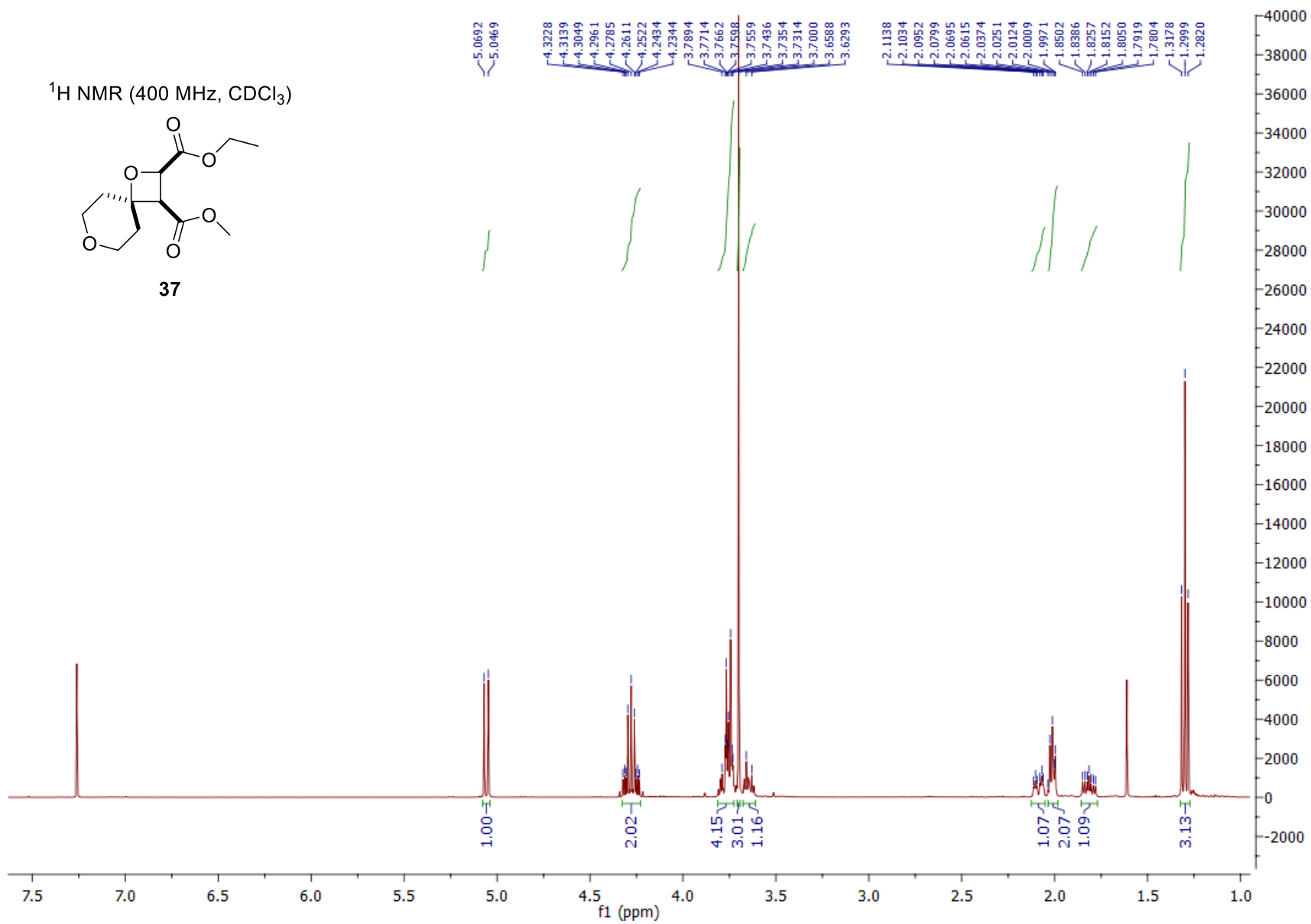
36



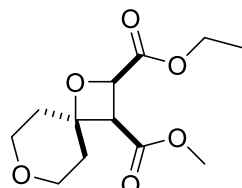
¹H NMR (400 MHz, CDCl₃)



37



¹³C NMR (101 MHz, CDCl₃)



37

170.3586
168.1296

82.4978

71.9346

63.5549

63.2789

61.3539

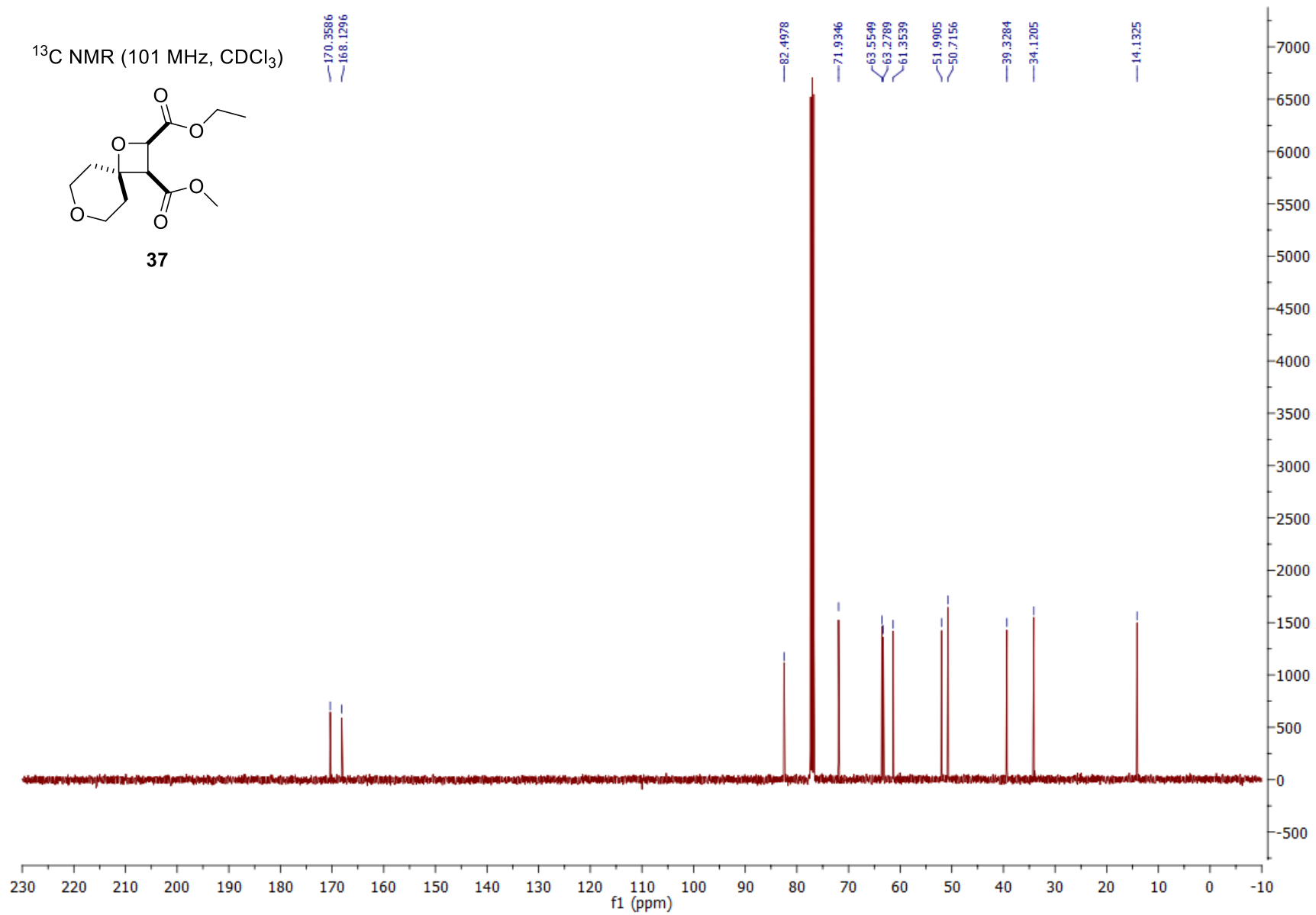
51.9905

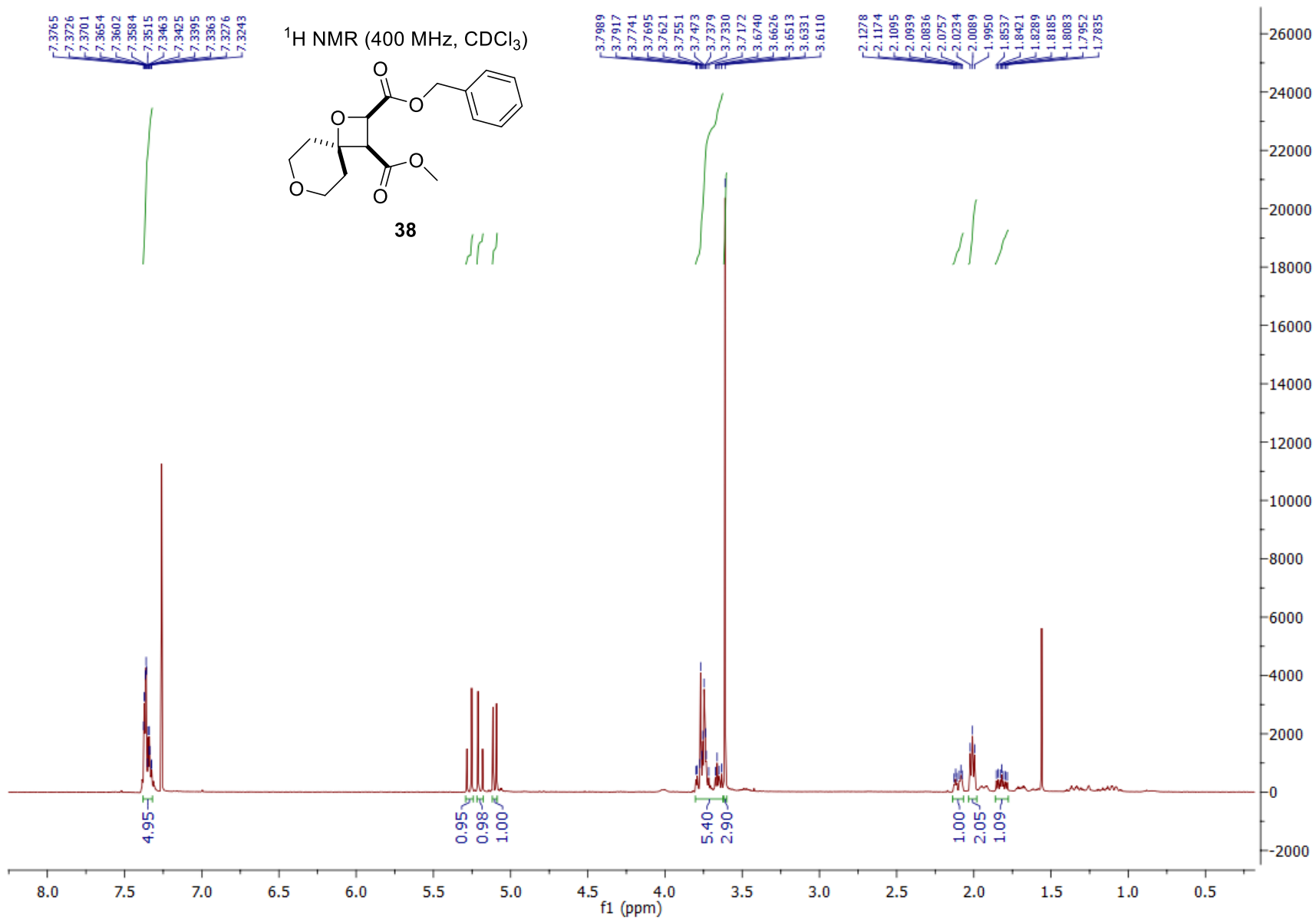
50.7156

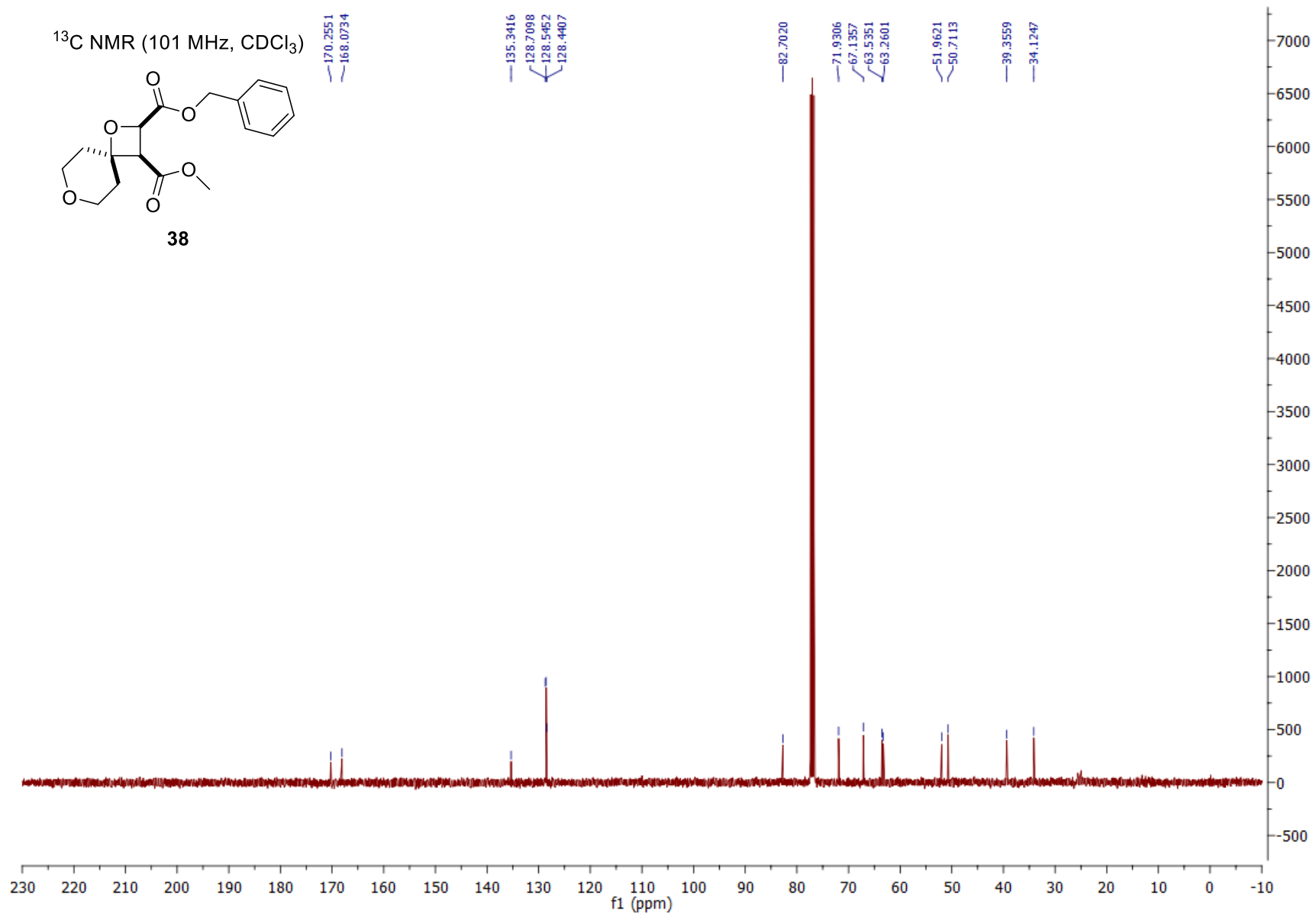
39.3284

34.1205

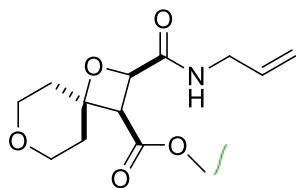
14.1325



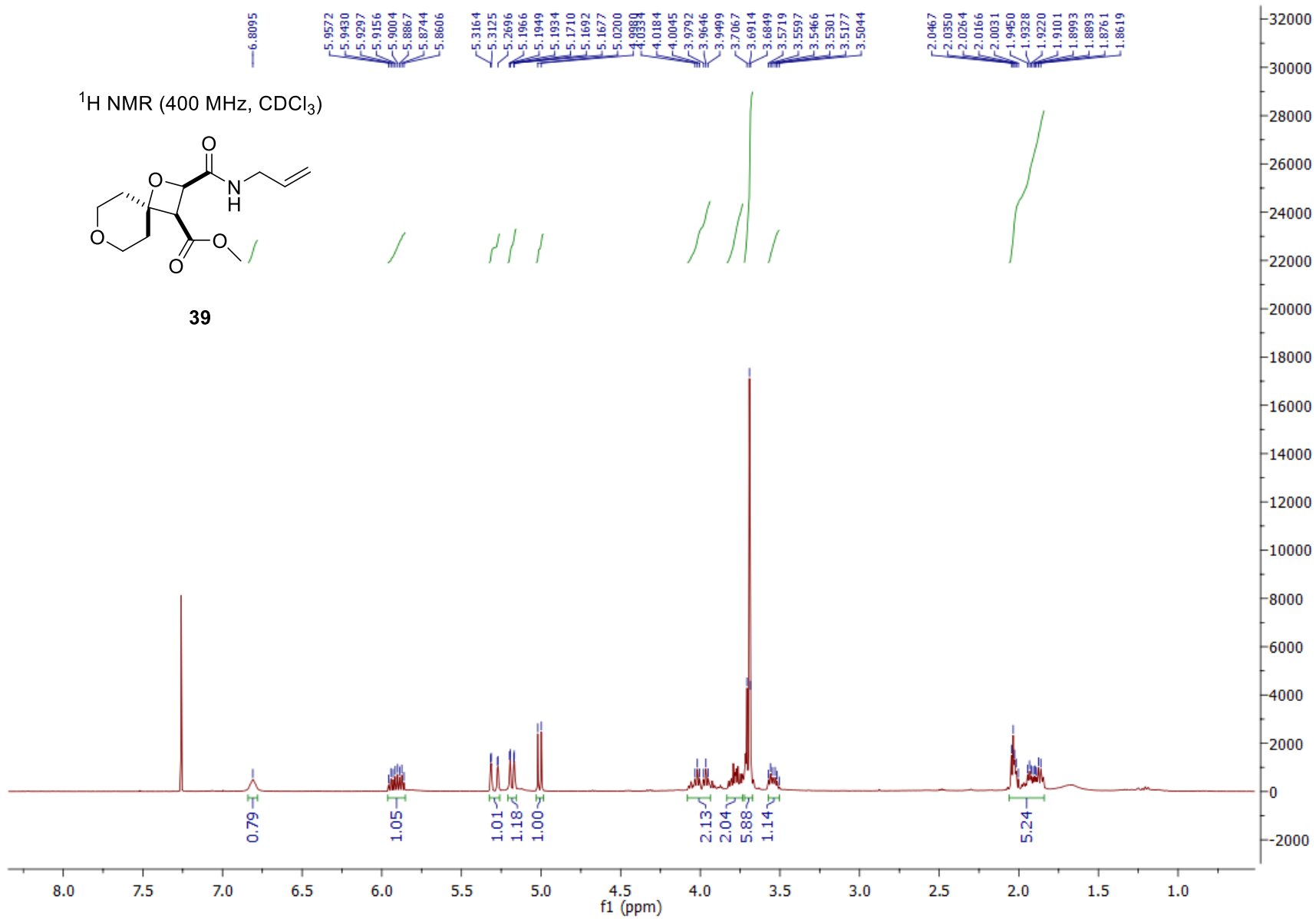




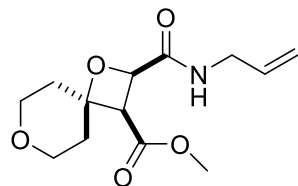
¹H NMR (400 MHz, CDCl₃)



39



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



39

169.7319
168.3026

133.9398

116.6536

81.8189

72.8296

63.7682

63.3306

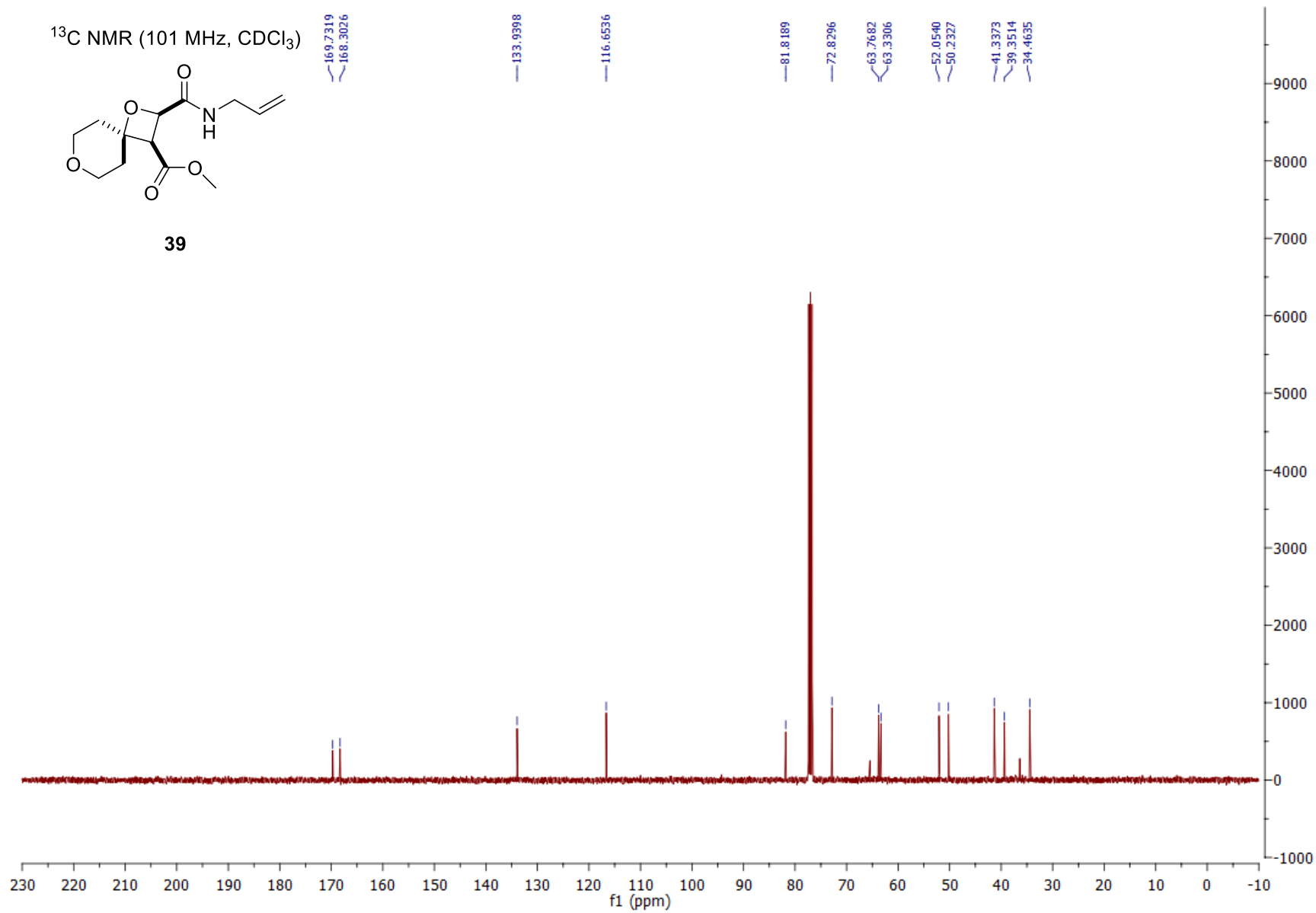
52.0540

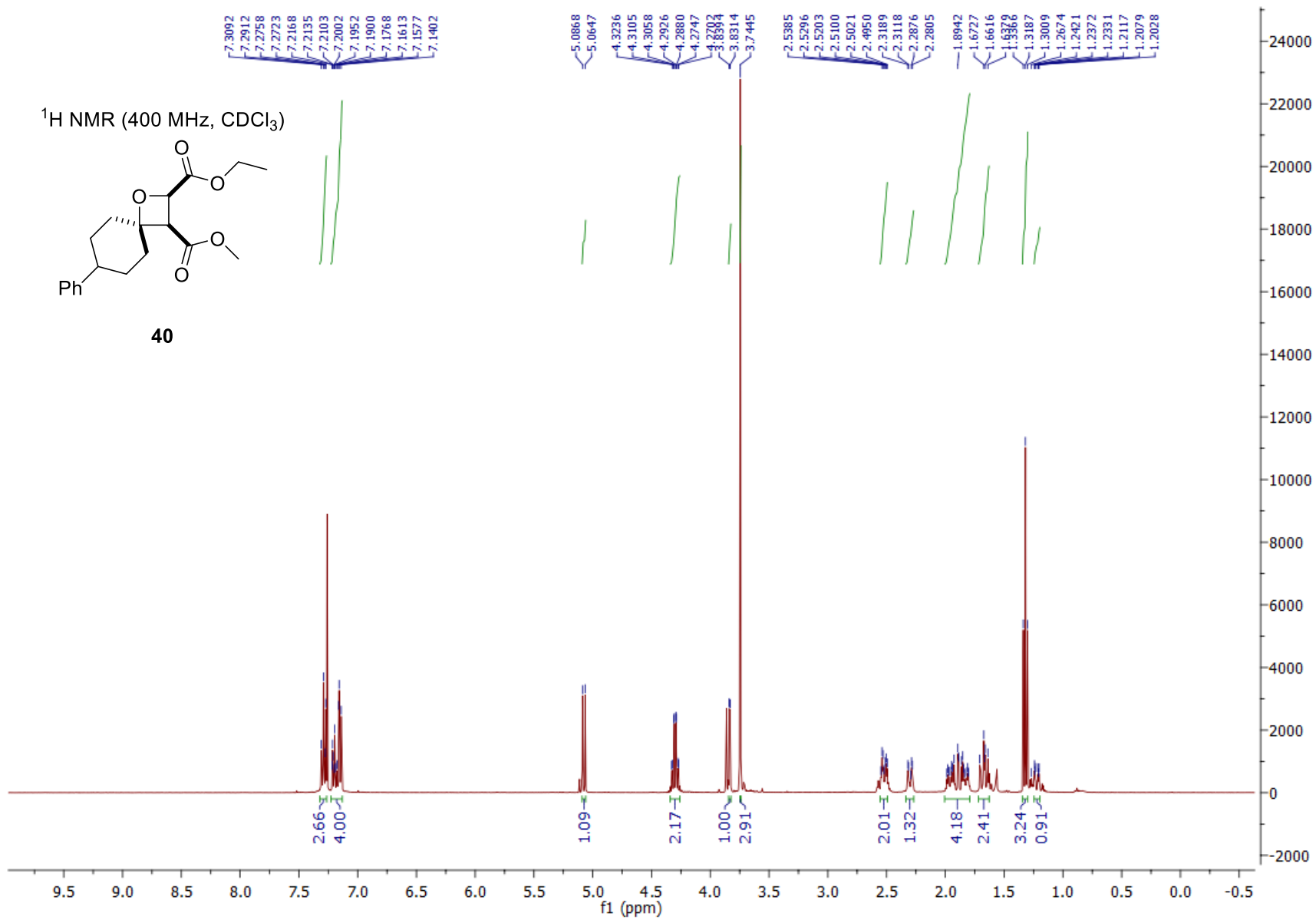
50.2327

41.3373

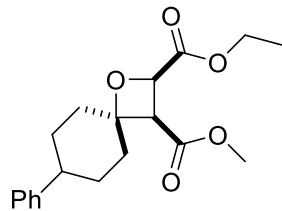
39.3514

34.4635

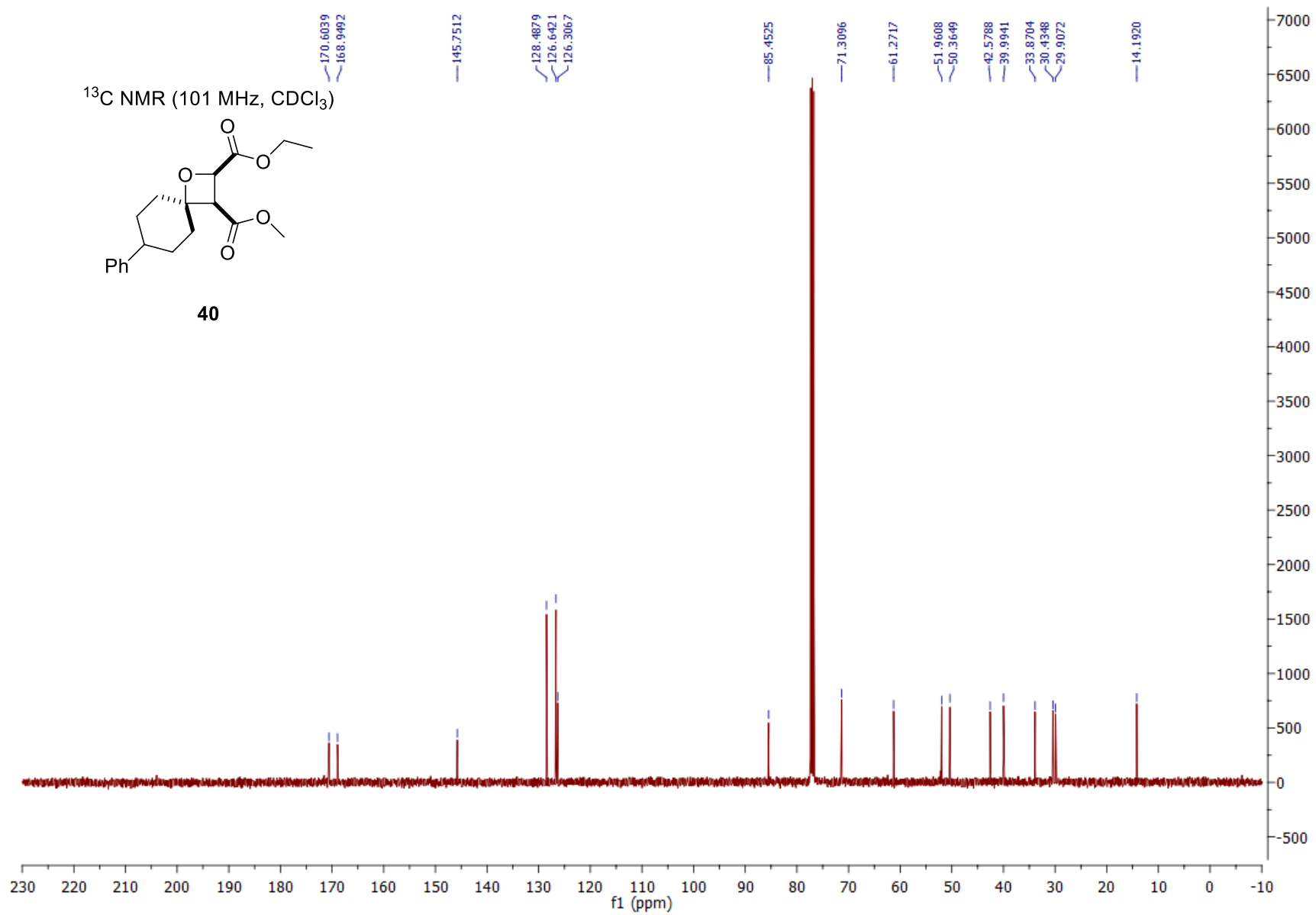


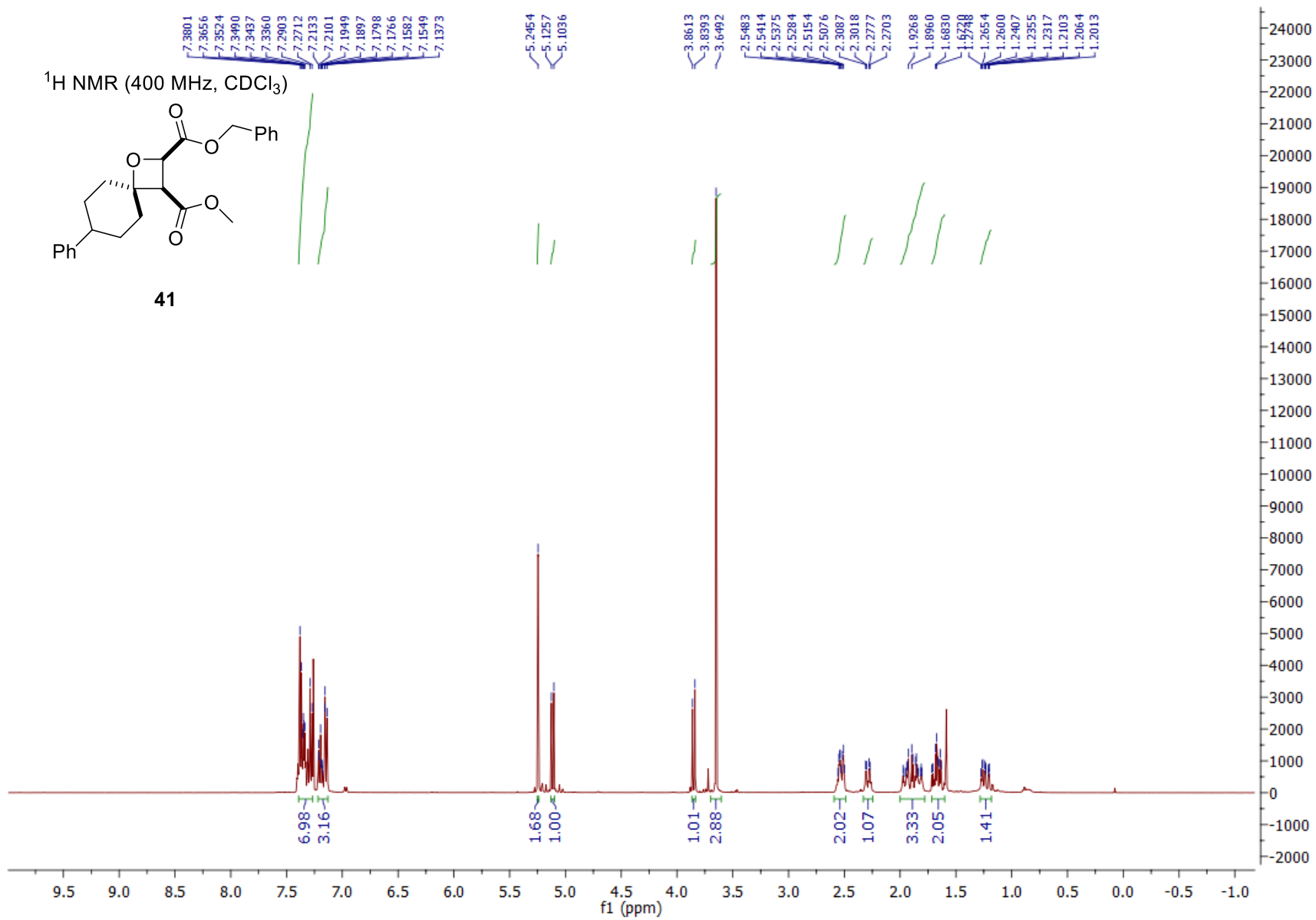


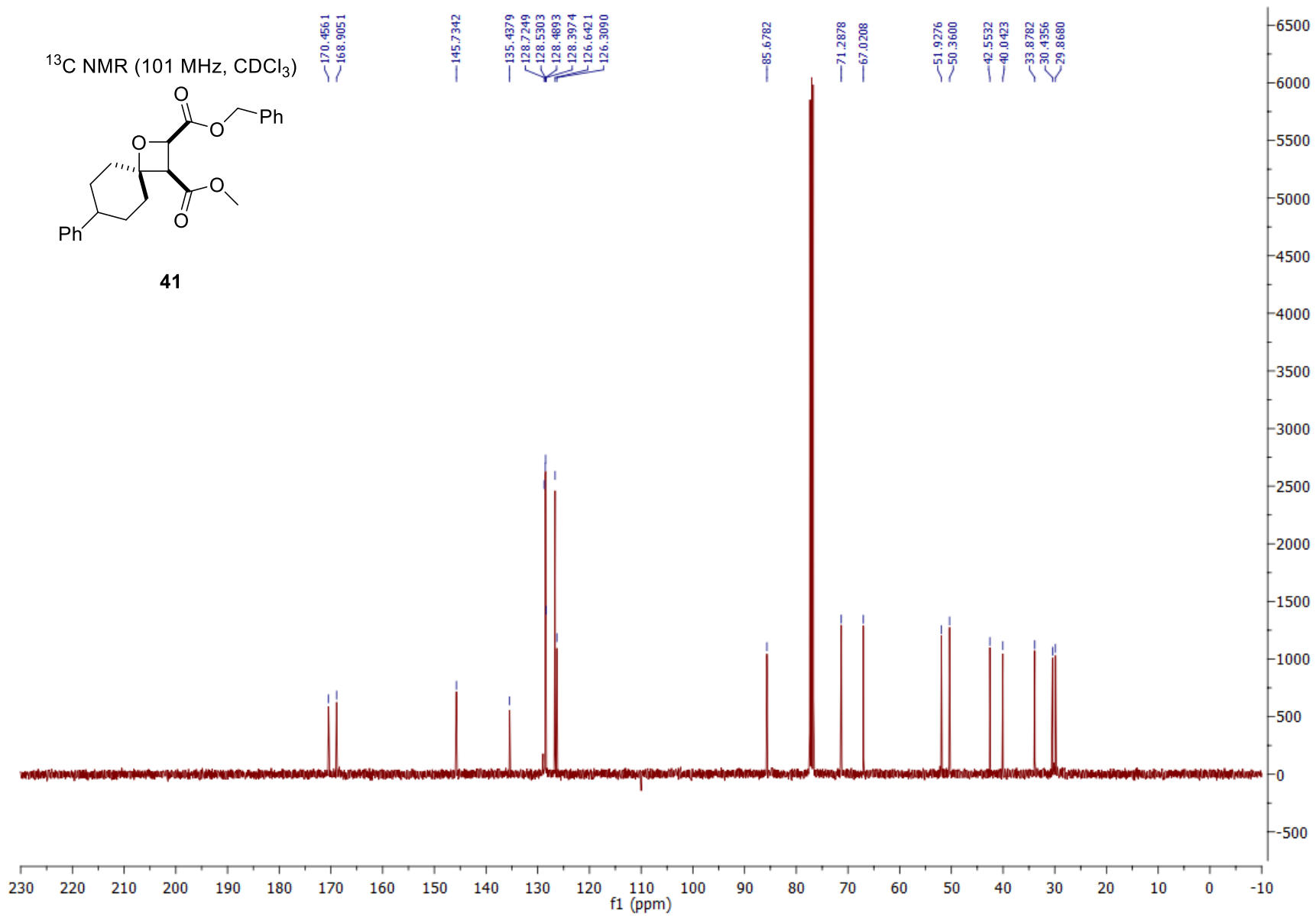
¹³C NMR (101 MHz, CDCl₃)

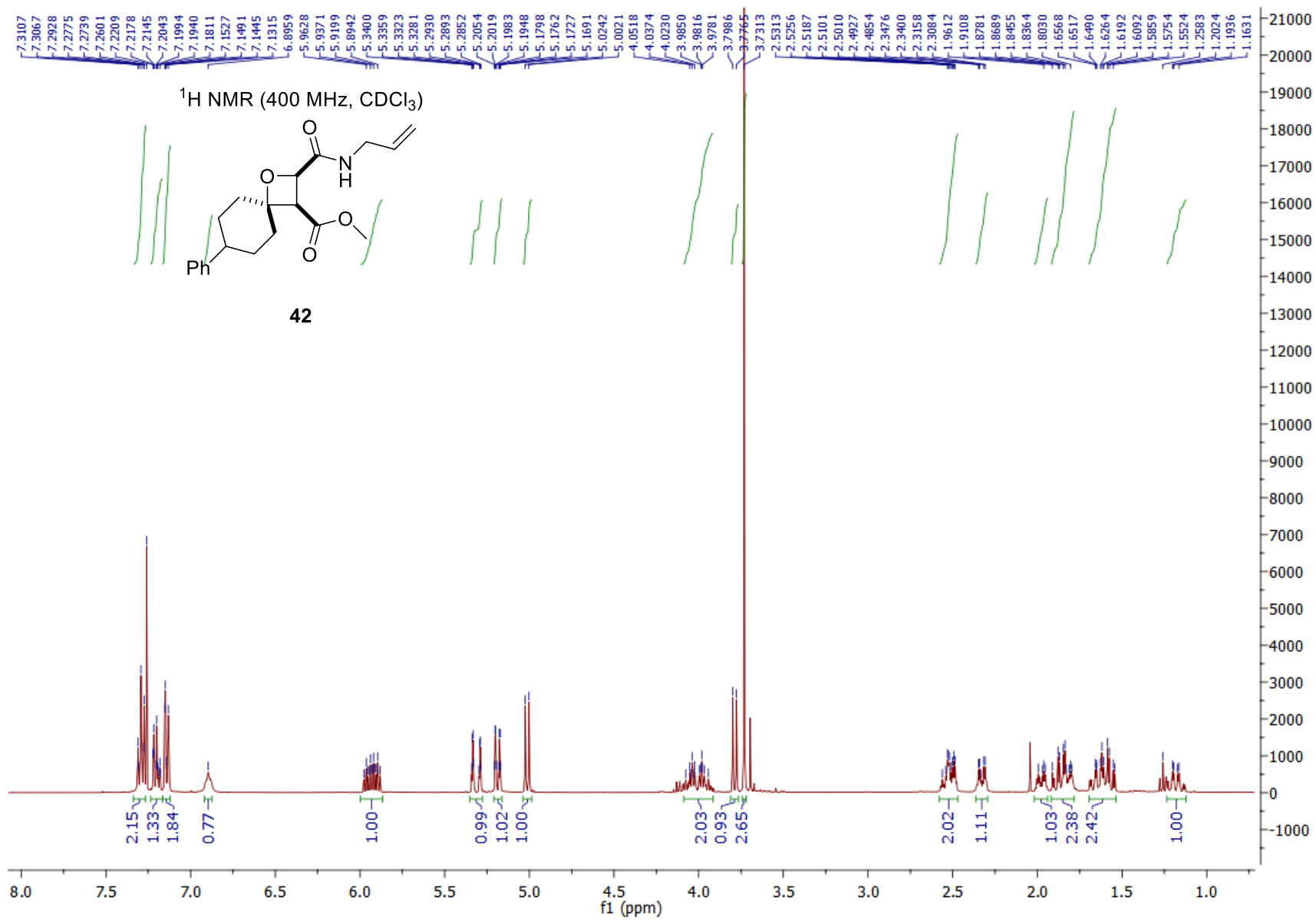


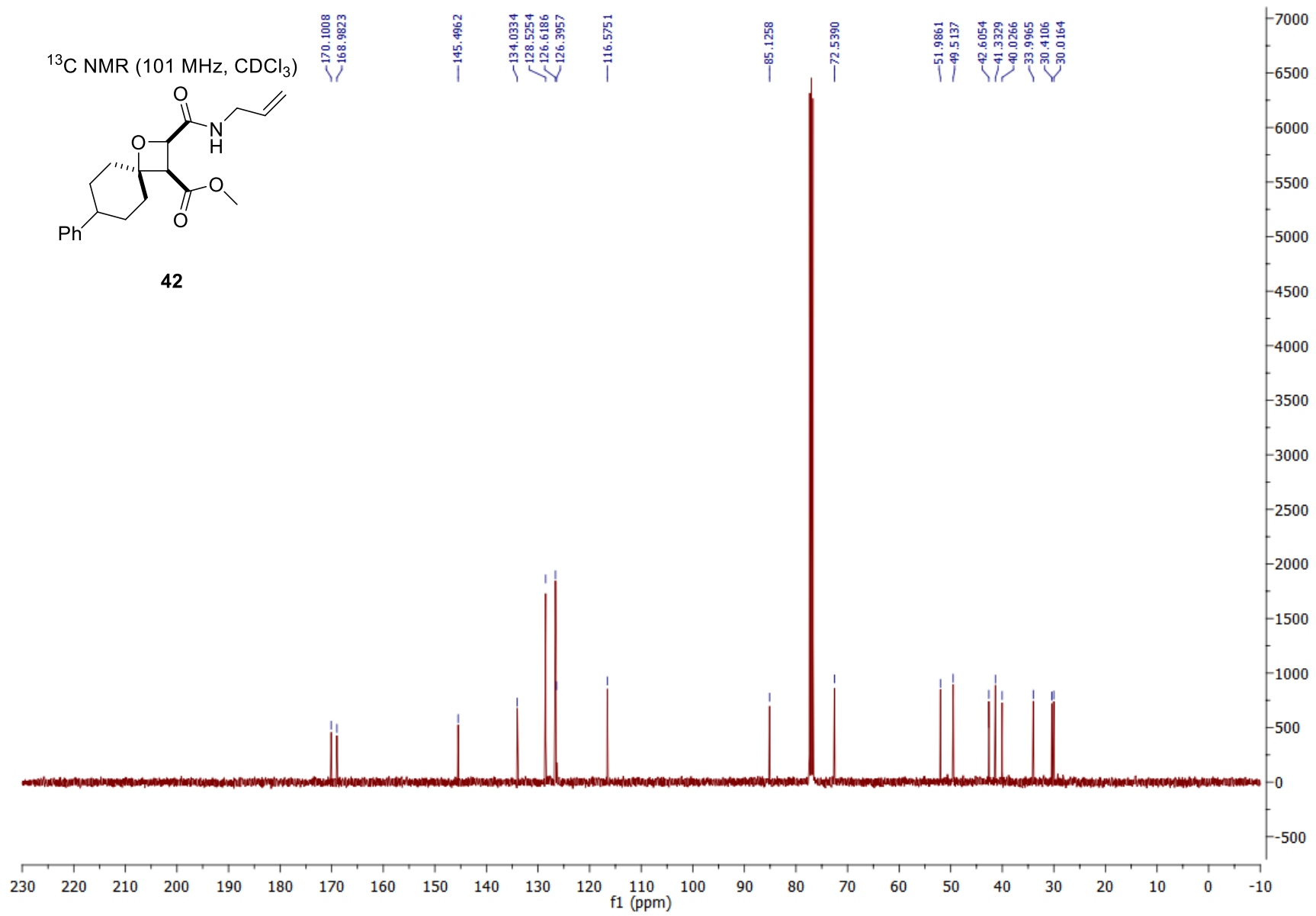
40

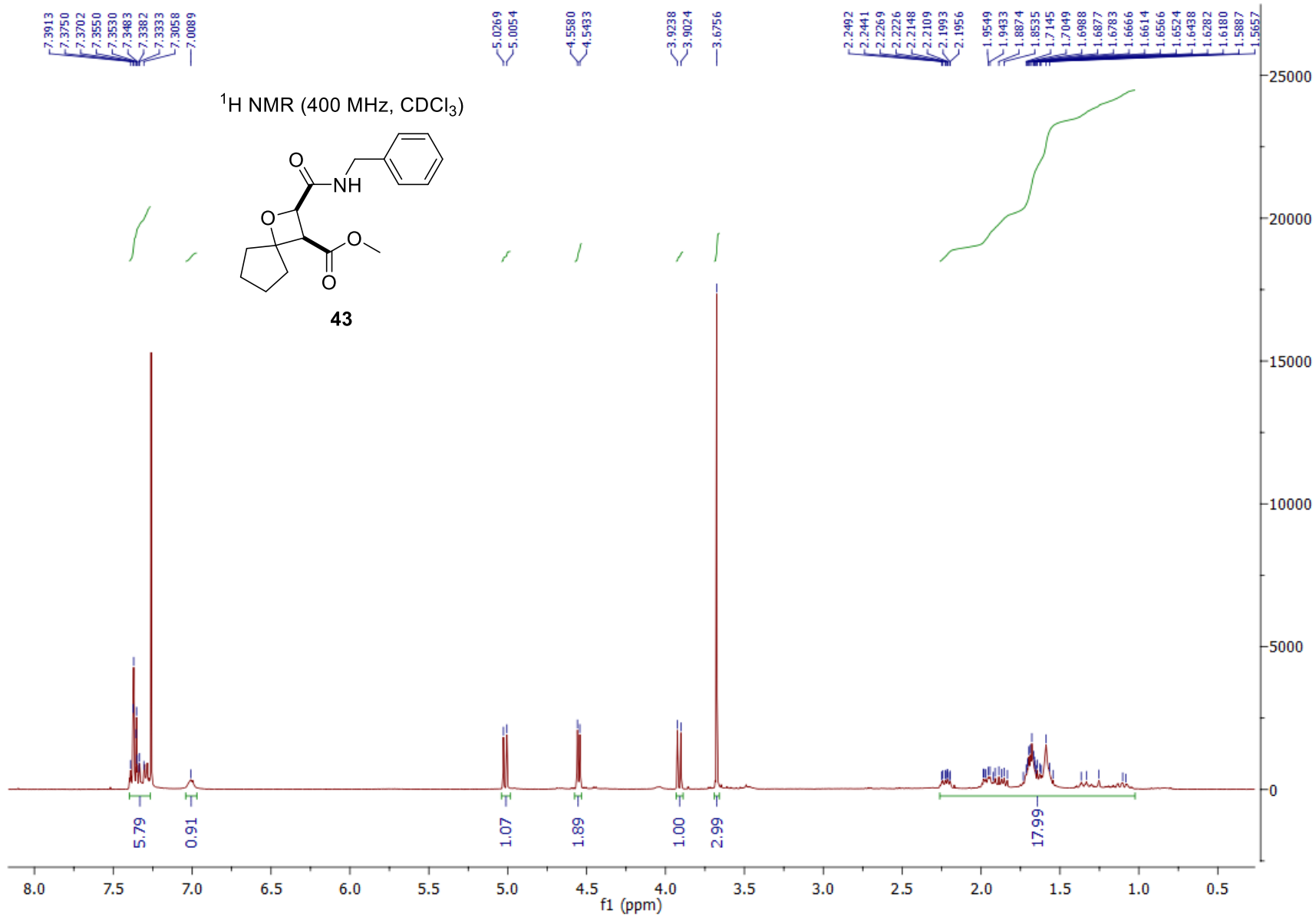












¹³C NMR (101 MHz, CDCl₃)

