Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Synthesis of 2,4-bifunctionalised cyclopentenones from 2-furaldehyde

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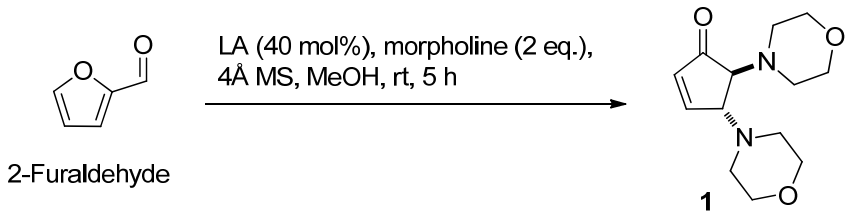
Sections Included:

General Remarks

All reactions were carried out at atmospheric pressure with stirring at room temperature unless otherwise stated. Reagents and solvents were purchased from commercial sources and used as supplied or purified by conventional methods. Methanol and acetonitrile were dried with activated 4Å molecular sieves overnight, then decanted onto CaH_2, refluxed under argon for 3 h and distilled onto freshly activated 4Å molecular sieves. 2-furaldehyde was purified by distilling under vacuum. Reactions were monitored by TLC analysis carried out on silica gel SIL G/UV254 coated onto aluminium plates purchased from VWR. Visualization was carried out under a UV lamp operating at 254 nm wavelength and by staining with a solution of phosphomolybdic acid in ethanol (12 g/250 mL) followed by heating. Flash column chromatography was carried out with silica gel 60 (0.04-0.063 mm, 230-400 mesh) purchased from Merck. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ (unless another solvent is stated) on Brucker NMR spectrometers operating at ambient room temperature probe. ^1H spectra were recorded at 400, 500 or 600 MHz and ^{13}C spectra were recorded at 125 or 150 MHz, using residual solvents as internal reference. Were necessary, DEPT135, COSY, HMQC, HMBC and NOESY spectra have been used to ascertain structure. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer operating in ATR mode. Melting points were measured on a Gallenkamp apparatus and are uncorrected. Experimental procedures for all isolated compounds are presented. All yields quoted are isolated yields, unless otherwise stated, and when multiple products are obtained, data are presented in terms of order isolated. General methods for reactions followed by HPLC analysis are reported.

General method for diamine 1 synthesis from 2-furaldehyde studies by HPLC analysis



To a solution of 2-furaldehyde in dry MeCN (0.083 M) was added morpholine (2 eq.), 4Å molecular sieves (0.2 g/mmol of 2-furaldehyde) and the selected Lewis acid (0.4 eq.). The mixture was stirred for 5 hours at room temperature after which reaction samples of 0.100 mL were taken, diluted in H_2O (5 mL) and filtered through a syringe filter (13 mm with 0.2 μm PTFE membrane). Samples were analysed with the method described below (page S11).

Table S1 – Results for Lewis acid screening for samples after 5 hours reaction time.

Entry	Lewis acid (0.4 equiv.)	Furaldehyde (%)	**1** (%)
1	n.u.	84	2
2	$Dy(OTf)_3$	26	67
3	$TiCl_4$	37	52
4	$AlCl_3$	22	68
5	$BF_3•Et_2O$	17	72
6	$SnCl_2$	17	83
7	$SnCl_4$	33	68
8	$Sn(Bu)_3Cl$	51	48
9	BCl_3	35	64
10	$Al(Me)_2Cl$	15	82
11	BBr_3	28	64
12	$Al(Et)_2Cl$	20	74
13	$Al(O^tBu)_3$	91	0
14	$NiCl_2$	34	66

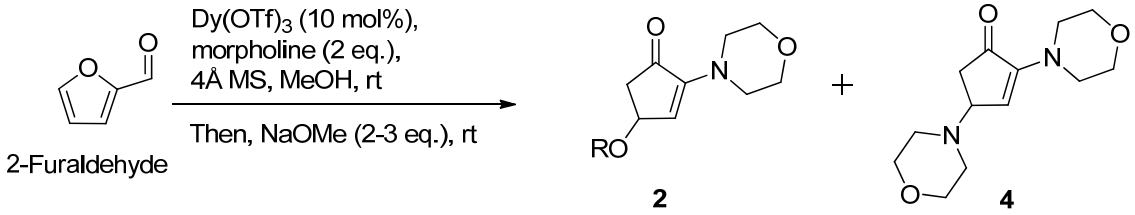
Reaction conditions: 2-furaldehyde in MeCN (0.083 M), morpholine (2 eq.), 4Å molecular sieves, rt; yields determined by HPLC; n.u. – none utilised.

Table S2 – Results for Lewis acid screening for samples after 5 hours reaction time.

Entry	Lewis acid (0.4 equiv.)	Furaldehyde (%)	**1** (%)
1	$CoCl_2$	18	81
2	$PdCl_2$	89	0
3	$RuCl_3$	39	55

Reaction conditions: 2-furaldehyde in MeCN (0.083 M), morpholine (2 eq.), 4Å molecular sieves, rt; yields determined by HPLC.

General method for synthesis of enone 2 studies by ^{1}H NMR analysis



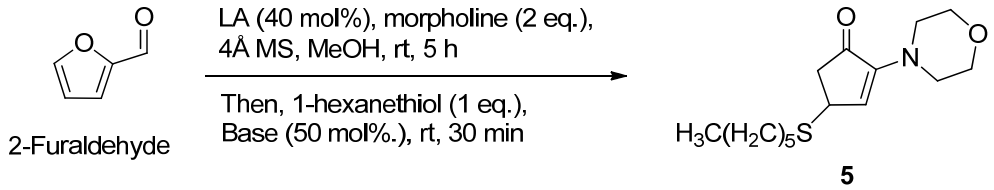
To a solution of 2-furaldehyde in dry MeCN (0.125 M) was added morpholine (2 eq.), $Dy(OTf)_3$ (0.1 eq.) and 4Å molecular sieves (0.2 g/mmol of 2-furaldehyde). The mixture was stirred at room temperature for 5 hours. Then, NaOMe (0.5-8 eq.) was added and the mixture was stirred at room temperature for 30 minutes. Afterwards, the reaction mixture was quenched with water, filtered through a short plug of celite and the filter cake was washed twice with DCM. Added brine to the filtrate and separated layers. The aqueous layer was extracted one more time with DCM. The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was dissolved in deuterated chloroform being analysed by ^{1}H NMR.

Table S3 – Effect of NaOMe equivalents on the ration of products **2** and **4** by ^{1}H NMR.

Entry	Time (min)	NaOMe (equiv.)	**2**:**4** ratio by ^{1}H NMR
1	30	0.5	No conversion from **1**
2	30	1.0	**2**:**1** ratio of 40:60
3	30	1.5	73:27
4	30	2.0	74:26
5	30	4.0	71:29
6	30	6.0	70:30
7	30	8.0	67:33

Reaction conditions: 2-furaldehyde in MeOH (0.125 M), morpholine (2 eq.), $Dy(OTf)_3$ (0.1 eq.), 4Å molecular sieves, rt, 5h. Then, NaOMe was added, rt, 30 min.

General method for enone 5 synthesis from 2-furaldehyde studies by HPLC analysis

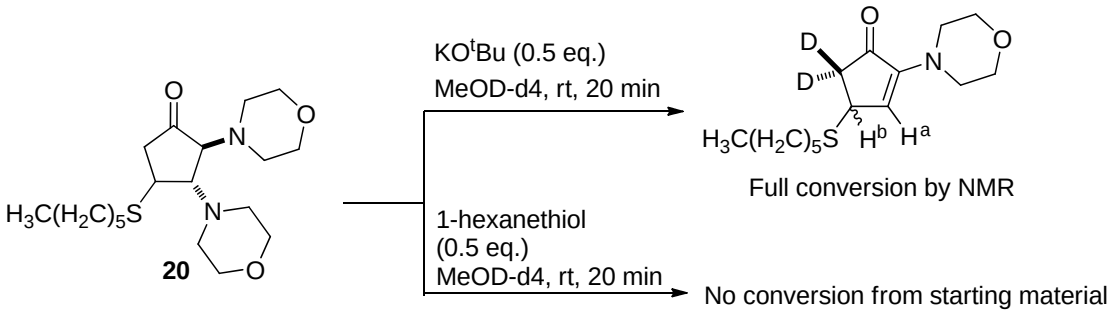


To a solution of 2-furaldehyde in dry MeCN (0.083 M) was added morpholine (2 eq.), 4Å molecular sieves (0.2 g/mmol of 2-furaldehyde) and the selected Lewis acid (0.4 eq.) The mixture was stirred for 5 hours at room temperature. Then, 1-hexanethiol (1 eq.) and the selected base (0.5 eq.) were added and the mixture was stirred for 30 minutes at room temperature at which time reaction samples of 0.100 mL were taken, diluted in 2:3 H_2O/MeCN (5 mL) and filtered through a syringe filter (13 mm with 0.2 μm PTFE membrane). Samples were analysed with the method described below (page S11).

HPLC method for enone 5 synthesis from 2-furaldehyde studies

The resulting samples for **1** synthesis from 2-furaldehyde studies were analysed on a Varian Pro Star Model 500 HPLC system equipped with a Phenomenex Jupiter reverse phase 10μm C18 250×4 mm column. Samples were injected (10 μL) and eluted at a flow rate of 1.0 mL/min through a reverse phase column with the following solvent system program: 0-1 minutes 95:5 (H_2O/MeCN), 1-14 minutes 90:10 (H_2O/MeCN), 14-16 minutes 95:5 (H_2O/MeCN). Acquisition time was 16 minutes. 2-furaldehyde (retention time 8.00 min) absorbance was measured at 254 nm and diamine **1** (retention time 7.03 min) absorbance was measured at 214 nm. Samples for synthesis of enone **5** from 2-furaldehyde were diluted in 2:3 H_2O/MeCN (5 mL) and filtered through a syringe filter (13 mm with 0.2 μm PTFE membrane). Samples for quantification of 2-furaldehyde and diamine **1** were analysed according with method described for diamine **1** synthesis from 2-furaldehyde studies (above). Samples for quantification of enone **5** were injected (10 μL) and eluted at a flow rate of 1.0 mL/min through a reverse phase column with the following solvent system program: 0-20 minutes 20:80 (H_2O/MeCN). Acquisition time was 16 minutes. Enone **5** (retention time 5.04 min) absorbance was measured at 214 nm. Chromatogram peak area (mAU/min) was converted into molar amounts using calibration plots of pure compound standard solutions of 2-furaldehyde, **1** and **5**.

Deuteration studies of the synthesis of enone 5 from diamine 20 by ^{1}H NMR



A solution of diamine **20** (19 mg, 0.05 mmol) in MeOD-d4 (0.5 mL) was analysed by ^{1}H NMR. Then, a solution of KO^{t}Bu (3 mg, 0.025 mmol) in MeOD-d4 (0.5 mL) was added. The mixture was analysed by ^{1}H NMR 20 minutes later. Another solution of diamine **20** (11 mg, 0.03 mmol) in MeOD-d4 (0.5 mL) was analysed by ^{1}H NMR. Then, 1-hexanethiol (0.0042 mL 0.03 mmol) was added. The mixture was analysed by ^{1}H NMR 20 minutes later.

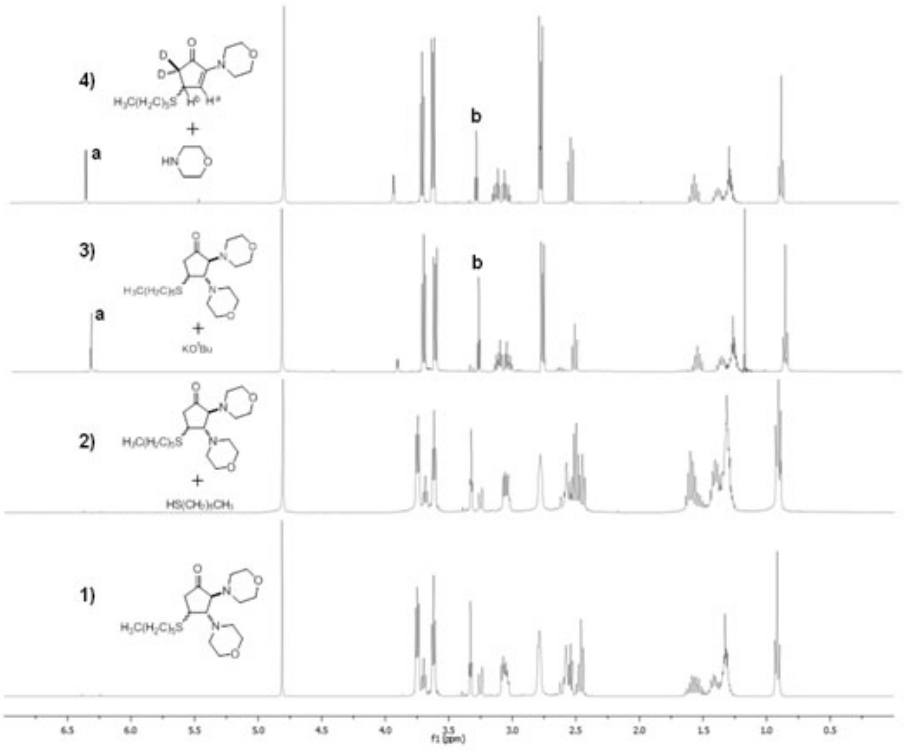
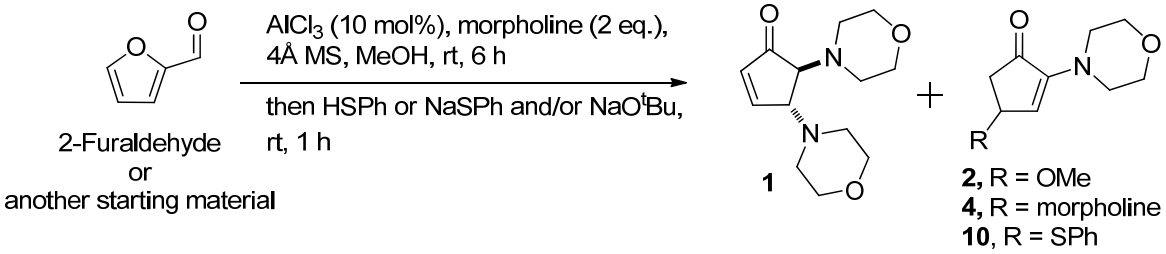


Figure S1 – Studies by ^{1}H NMR at 400 MHz in MeOD-d4: diamine **20** (0.06-0.1 M). 1) Diamine **20** before adding reagents. 2) 20 minutes after adding 1-hexanethiol (1 eq.). 3) 20 minutes after adding KO^{t}Bu (0.5 eq.). 4) Control sample of enone **5** with morpholine (1:1 ratio). Note: several protons for diamine **20** overlap with each other.

Reaction studies of 2-furaldehyde with thiophenol specie under different conditions



To a solution of 2-furaldehyde (0.041 mL, 0.5 mmol) in MeOH (2 mL) was added morpholine (0.086 mL, 1 mmol) and $AlCl_3$ (6.7 mg, 0.05 mmol). The mixture was stirred at room temperature for 5 hours. Then, thiophenol or sodium thiophenolate was added with or without base (NaO^tBu) and the mixture was stirred at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM. The mixture was washed with AcOH/NaOAc buffer solution at pH 5 and brine. The aqueous layer was further extracted with DCM. The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v). A similar procedure in terms of concentrations, time events and work up was followed for control experiments with other starting materials.

Table S4 – Results for experiments varying thiophenol, sodium thiophenolate and NaO^{t}Bu.

Entry[a]	Starting Material	HSPh (eq.)	NaSPh (eq.)	NaO^{t}Bu (eq.)	**10** (%)	**2** (%)	**1** (%)	**4** (%)
1	Furaldehyde	1	n.u.	n.u.	42	n.o.	19	n.o.
2	Furaldehyde	n.u.	1	n.u.	4	3	80	n.o.
3	Furaldehyde	1	n.u.	0.25	68	n.o.	29	n.o.
4	Furaldehyde	n.u.	1	0.25	n.o.	67	0.4	21
5	Furaldehyde	0.75	0.25	n.u.	42	n.o.	27	n.o.
6	Furaldehyde	1	n.u.	1	8	69	n.o.	13
7	Furaldehyde	1	n.u.	0.9	17	60	n.o.	18
8	Furaldehyde	1	n.u.	0.6	26	47	n.o.	10
9	Furaldehyde	n.u.	n.u.	0.25	n.o.	46	n.o.	26
10[b]	**1**	1	n.u.	1	2	66	n.o.	7
11[c]	**10**	n.u.	n.u.	0.25	81	6	n.o.	n.o.
12[d]	**10**	n.u.	n.u.	0.25	93	6	n.o.	n.o.
13[c]	**10**	n.u.	n.u.	1	9	29	n.o.	n.o.

[a] – Conditions: 2-furaldehyde in MeOH (0.25 M), morpholine (2 eq.), $AlCl_3$ (10 mol%), 4Å MS (0.1 g/mmol of 2-furaldehyde), rt, 5 h. Afterwards added thiophenol or sodium thiolate and base if indicated, rt, 1 h. [b] – Conditions: **1** in MeOH (0.25 M) with thiophenol and base, rt, 1 h. [c] – Conditions: **10** in MeOH (0.25 M) with base, rt, 7 h. [d] – Conditions: **10** in MeOH (0.25 M) with $AlCl_3$ (10 mol%), morpholine (1 eq.), 4Å MS and base, rt, 7 h. Yields for isolated products by flash chromatography on silica gel. n.u. – none utilised; n.o. – none observed.

Deuteration studies of enone 23 with neutral or basic conditions by ^{1}H NMR

A solution of enone **23** (16 mg, 0.1 mmol) in D_2O (0.4 mL) and MeOD-d4 (0.2 mL) was analysed by ^{1}H NMR 1 day, 2 days and 9 days later. Another solution of enone **23** (16 mg, 0.1 mmol) in D_2O (0.4 mL) and MeOD-d4 (0.2 mL) was analysed by ^{1}H NMR 20 minutes later. Then, K_2CO_3 (4 mg, 0.03 mmol) was added. The mixture was analysed by ^{1}H NMR 4 hours later.

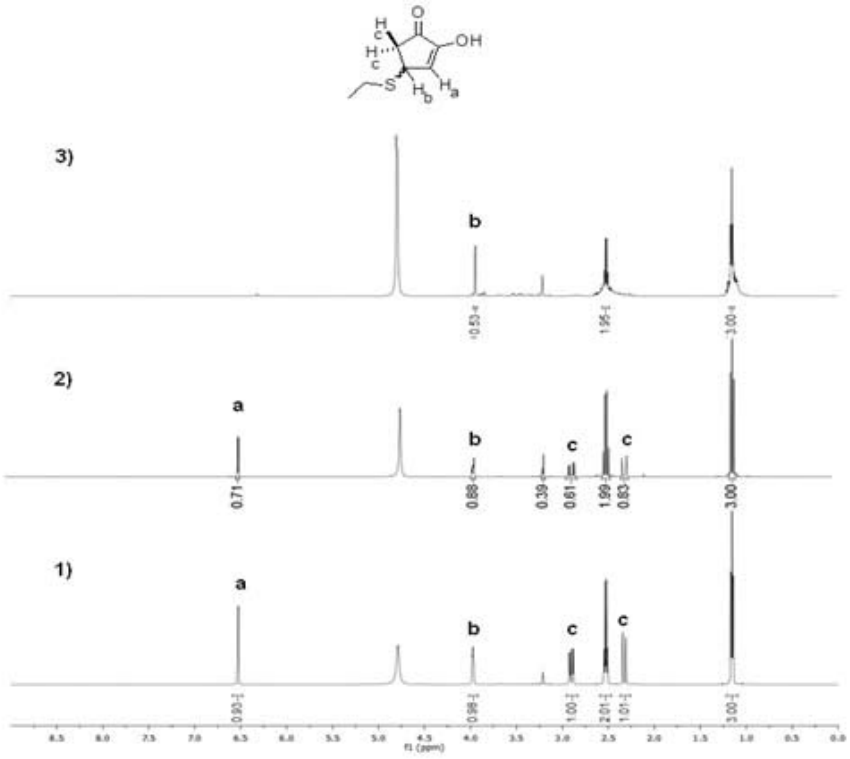
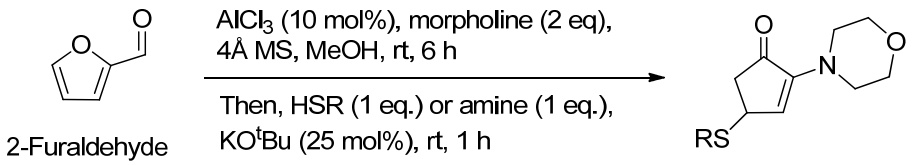


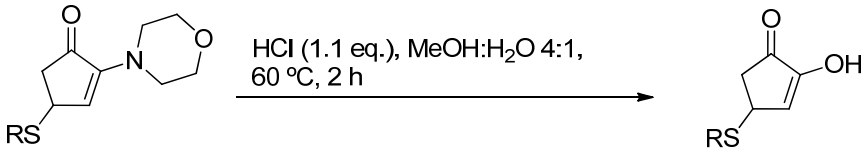
Figure S2 – Deuteration studies by ^{1}H NMR at 400 MHz in D_2O:MeOD-d4 2:1 ratio: enone **23** (0.25 M). 1) Enone **23** in neutral pH at the start of experiment. 2) Enone **23** in neutral pH after 9 days. 3) Enone **23** 1 hour after adding K_2CO_3 (0.3 eq.).

General method for 2-morpholino-4-thio cyclopentenone syntheses from 2-furaldehyde



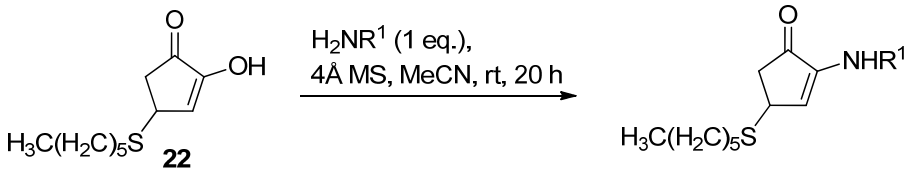
To a solution of 2-furaldehyde in dry MeOH (0.25 M) was added morpholine (2 eq.), 4Å molecular sieves (0.2 g/mmol of 2-furaldehyde) and $AlCl_3$ (0.1 eq.). The mixture was stirred at room temperature for 6 hours. Then, thiol (1 eq.) was added, followed by addition of KO^tBu (0.25 eq.) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM. To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (0.68 M in total acetates) and brine. The organic layer was separated and the aqueous layer was further extracted with DCM (twice). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica.

General method for syntheses of 2-hydroxyl cyclopentenones



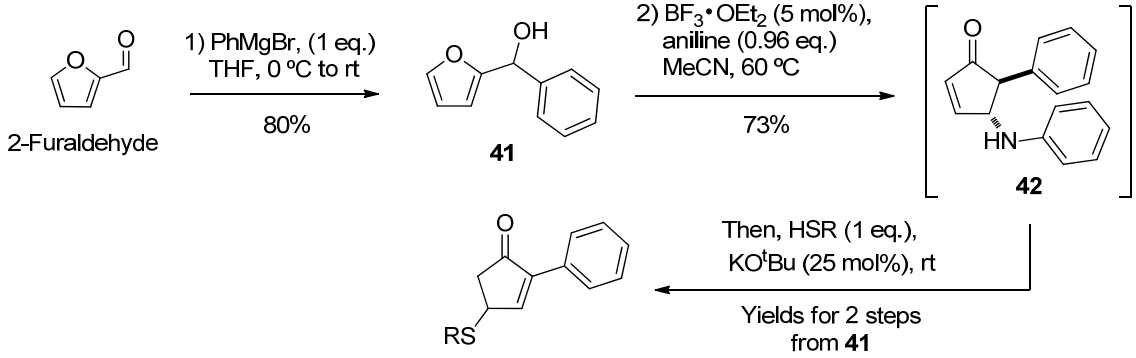
To a solution of the selected 2-morpholino-4-thio cyclopentenone (0.2 M) in a mixture of MeOH/water (4:1 v/v) was added HCl 37% (1.1 eq.). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water and DCM were added and layers were separated. Aqueous layer was further extracted with DCM. Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid or an orange oil which was purified by flash chromatography on silica.

General method for 2-amino-4-thio cyclopentenones syntheses



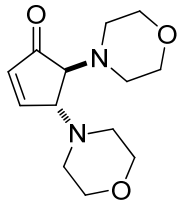
To a solution of diketone **22** in dry MeCN (0.25 M) was added the selected amine (1 eq.) and 4Å molecular sieves (0.2 g/mmol of diketone **22**). The mixture was stirred at room temperature for 20 hours. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM. The filtrate was concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica.

General method for 2-amino-4-thio cyclopentenones syntheses



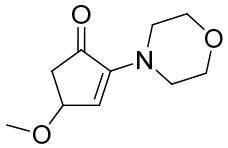
To a solution of compound **41** in MeCN (0.25 M) was added aniline (0.96 eq.) and BF_3•OEt_2 (5 mol%). The mixture was stirred at 80 ºC for 2 hours. Then, thiol (1 eq.) was added, followed by addition of KO^tBu (0.25 eq.) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was quenched with brine, extracted with EtOAc, dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica.

***trans*-4,5-dimorpholinocyclopent-2-enone 1**



To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), $AlCl_3$ (67 mg, 0.5 mmol) and 4Å molecular sieves (1 g). The mixture was stirred at room temperature for 6 hours. Afterwards, the reaction was quenched with AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and filtered through a short plug of celite. To the mixture was added DCM (60 mL) and layers were separated. The aqueous layer was further extracted with DCM (2×20 mL). Combined organic layers were washed with water (10 mL), then dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **1** as a yellow oil that crystallizes upon standing (0.94 g, 3.7 mmol, 74%). Data for **1** in accordance with reference:[1] ^{1}H NMR (500 MHz, $CDCl_3$) 2.53-2.62 (m, 6H, morpholine), 2.78 (overlapped t, J = 5.0 Hz, 2H, morpholine), 3.24 (d, J = 3.0 Hz, 1H, COC*H*), 3.67 (t, J = 5.0 Hz, 4H, morpholine), 3.68 (t, J = 5.0 Hz, 4H, morpholine), 3.75 (q, J = 2.5 Hz, 1H, COCH=CHC*H*N), 6.19 (dd, J = 6.5, 2.5 Hz, 1H, COC*H*=CH), 7.56 (dd, J = 6.5, 2.5 Hz, 1H, COCH=C*H*); ^{13}C NMR (125 MHz, $CDCl_3$) 49.9 (morpholine), 50.2 (morpholine), 66.6 (COC*H*), 67.2 (morpholine), 67.3 (morpholine), 68.2 (COCH=CHC*H*N), 135.5 (COC*H*=CH), 160.7 (COCH=C*H*), 206.2 (*C*=O).

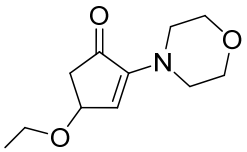
4-methoxy-2-morpholinocyclopent-2-enone 2



To a solution of 2-furaldehyde (0.041 mL, 0.5 mmol) in dry MeOH (4 mL) was added morpholine (0.086 mL, 1 mmol), $Dy(OTf)_3$ (30 mg, 0.05 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 5 hours. Then, sodium methoxide (81 mg, 1.5 mmol) was added and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction was quenched with water (6 mL), filtered through a short plug of celite and the filter cake was washed with DCM (2×6 mL). Filtrate layers were separated and the aqueous layer was extracted one more time with DCM (6 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **2** as a low melting point yellow solid (68 mg, 0.34 mmol, 67%) and **4** as a yellow oil (22 mg, 0.04 mmol, 18%). Note: compound **2** is not stable as an isolated solid and will progressively turn into a dark oil over time. Data for **2**: IR (film) ν_{max} 2960, 2857, 1703, 1607, 1262, 1113, 890, 725. ^{1}H NMR (500 MHz, $CDCl_3$) 2.34-2.30 (dd, J = 18.4, 1.8 Hz, 1H, COCH_2), 2.71-2.66 (dd, J = 18.4, 5.9 Hz, 1H, COCH_2), 3.18-3.10 (overlapped t, J = 4.8 Hz, 4H, morpholine), 3.35 (s, 3H, OCH_3), 3.72 (t, overlapped peaks, J = 4.8 Hz, 4H, morpholine), 4.39 (m, J = 3.1, 1.85 Hz, 1H, C*H*OMe), 6.17 (d, J = 3.0 Hz, 1H, COC=C*H*); ^{13}C NMR (125 MHz, $CDCl_3$) 42.5 (CO*C*H_2), 47.8 (morpholine), 56.5 (O*C*H_3), 66.5 (morpholine), 74.4 (*C*HOMe), 128.0 (COC=*C*H), 151.4 (CO*C*=CH), 201.2 (*C*=O). HRMS (EI) $[M]^+$ found 197.10483, $C_{10}H_{15}O_3N$ requires 197.10464. Data for **4**: IR (film) ν_{max} 2959, 2855, 1702, 1610, 1451, 1260, 1112, 1008, 889, 726. ^{1}H NMR (500 MHz, $CDCl_3$) 2.43-2.39 (dd, overlapped peaks, J = 18.5, 2.6 Hz, 1H, COCH_2), 2.49-2.46 (dd, overlapped peaks, J = 18.5, 6.0 Hz, 1H, COCH_2), 2.54-2.49 (m, overlapped peaks, 4H, morpholine), 3.16-3.09 (m, 4H, morpholine), 3.69-3.68 (m, overlapped peaks, 1H, $COCH_2CH$N), 3.72-3.70 (t, overlapped peaks, J = 4.6 Hz, 4H, morpholine), 3.75 (t, J = 4.6 Hz, 4H,

morpholine), 6.22 (d, *J* = 2.9 Hz, 1H, COC=C*H*); ^{13}C NMR (125 MHz, $CDCl_3$) 38.0 (CO*C*H_2), 48.0 (morpholine), 49.9 (morpholine), 60.2 (COCH_2*C*HN), 66.5 (morpholine), 67.0 (morpholine), 129.5 (COC=*C*H), 151.6 (CO*C*=CH), 201.9 (*C*=O). HRMS (EI) $[M]^+$ found 252.14731, $C_{13}H_{20}O_3N_2$ requires 252.14684.

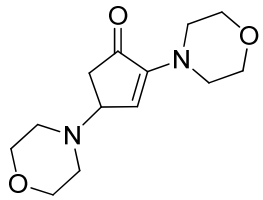
4-ethoxy-2-morpholinocyclopent-2-enone 3



To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry ethanol (20 mL) was added morpholine (0.86 mL, 10 mmol), $AlCl_3$ (67 mg, 0.5 mmol) and 4Å molecular sieves (1 g). The mixture was stirred at room temperature for 6 hours. Then, sodium ethoxide (0.68 g, 10 mmol) was added and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **3** as a low melting point yellow solid (0.38 g, 1.8 mmol, 36%) and **4** as a yellow oil (0.66 g, 2.6 mmol, 52%). Note: compound **3** is not stable as an isolated solid and will progressively turn into a dark oil over time. Data for **3**: IR (film) ν_{max} 2970, 2855, 1706, 1607, 1262, 1115, 1018, 888. ^{1}H NMR (600 MHz, $CDCl_3$) 1.15 (t, *J* = 7.0 Hz, 3H, C*H*$_3$), 2.28 (dd, *J* = 18.4, 1.7 Hz, 1H, COC*H*$_2$), 2.66 (dd, *J* = 18.4, 5.8 Hz, 1H, COC*H*$_2$), 3.15-3.04 (t, overlapped peaks, *J* = 4.8 Hz, 4H, morpholine), 3.48 (t, *J* = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 3.67 (t, overlapped peaks, *J* = 4.2 Hz, 4H, morpholine), 4.43 (m, *J* = 3.0 Hz, 1H, C*H*OEt), 6.14 (d, *J* = 2.9 Hz, 1H COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 15.6 (*C*H$_3$), 43.1 (CO*C*H$_2$), 47.8

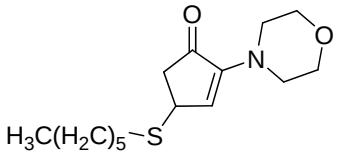
(morpholine), 64.6 (O*C*H$_2$CH$_3$), 66.5 (morpholine), 72.9 (*C*HOEt), 128.7 (COC=*C*H), 151.3 (CO*C*=CH), 201.4 (*C*=O). HRMS (EI) [M]$^+$ found 211.12065, $C_{11}H_{17}NO_3$ requires 211.12029. Data for **4**: ^{1}H NMR (600 MHz, $CDCl_3$) 2.41-2.38 (dd, *J* = 18.6, 2.5 Hz, 1H, COC*H*$_2$), 2.48-2.44 (dd, overlapped peaks, *J* = 18.6, 5.9 Hz, 1H, COC*H*$_2$), 2.53-2.48 (m, overlapped peaks, 4H, morpholine), 3.09 (m, 4H, morpholine), 3.70-3.68 (m, overlapped peaks, 5H, morpholine and COH$_2$C*H*N), 3.71 (t, overlapped peaks, *J* = 4.9 Hz, 4H, morpholine), 6.19 (d, *J* = 2.9 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 37.8 (CO*C*H$_2$), 48.0 (morpholine), 49.7 (morpholine), 60.2 (COCH$_2$*C*HN), 66.5 (morpholine), 66.8 (morpholine), 129.2 (COC=*C*H), 151.7 (CO*C*=CH), 201.9 (*C*=O).

2,4-dimorpholinocyclopent-2-enone 4



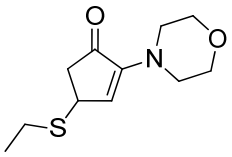
See experimental method for 4-methoxy-2-morpholinocyclopent-2-enone **2** (pages S19-S20). Data for **4**: IR (film) ν_{max} 2959, 2855, 1702, 1610, 1451, 1260, 1112, 1008, 889, 726. ^{1}H NMR (500 MHz, $CDCl_3$) 2.43-2.39 (dd, overlapped peaks, *J* = 18.5, 2.6 Hz, 1H, COC*H*$_2$), 2.49-2.46 (dd, overlapped peaks, *J* = 18.5, 6.0 Hz, 1H, COC*H*$_2$), 2.54-2.49 (m, overlapped peaks, 4H, morpholine), 3.16-3.09 (m, 4H, morpholine), 3.69-3.68 (m, overlapped peaks, 1H, COCH$_2$C*H*N), 3.72-3.70 (t, overlapped peaks, *J* = 4.6 Hz, 4H, morpholine), 3.75 (t, *J* = 4.6 Hz, 4H, morpholine), 6.22 (d, *J* = 2.9 Hz, 1H, COC=C*H*); ^{13}C NMR (125 MHz, $CDCl_3$) 38.0 (CO*C*H$_2$), 48.0 (morpholine), 49.9 (morpholine), 60.2 (COCH$_2$C*H*N), 66.5 (morpholine), 67.0 (morpholine), 129.5 (COC=*C*H), 151.6 (CO*C*=CH), 201.9 (*C*=O). HRMS (EI) [M]$^+$ found 252.14731, $C_{13}H_{20}O_3N_2$ requires 252.14684.

4-(hexylthio)-2-morpholinocyclopent-2-enone 5



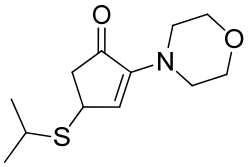
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, 1-hexanethiol (0.7 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **5** as an orange oil (1.112 g, 3.9 mmol, 79%). Data for **5**: IR (film) ν_{max} 2924, 2854, 1703, 1601, 1260, 1118, 1026, 889. ^{1}H NMR (600 MHz, $CDCl_3$) 0.87 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 1.31-1.24 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.38 (quintet, J = 7.3 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.58 (quintet, J = 7.5, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.46-2.43 (dd, J = 19.1, 1.7 Hz, 1H, $COCH_2$), 2.52 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.92-2.88 (dd, J = 19.1, 6.3 Hz, 1H, $COCH_2$), 3.17-3.09 (t, overlapped peaks, J = 4.8 Hz, 4H, morpholine), 3.76 (t, J = 4.8, 4H, morpholine), 3.90 (m, J = 3.0, 1.8 Hz, 1H, $COCH_2CHS$), 6.19 (d, J = 3.0 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 22.6 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 29.9 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.8 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 39.5 ($COCH_2CH$), 44.5 ($COCH_2$), 48.1 (morpholine), 66.6 (morpholine), 132.0 (COC=CH), 150.6 (COC=CH), 202.7 (C=O). HRMS (EI) $[M]^+$ found 283.16062, $C_{15}H_{25}NO_2S$ requires 283.16005.

4-(ethylthio)-2-morpholinocyclopent-2-enone 6



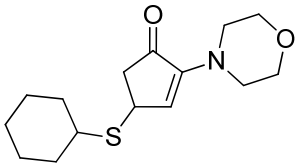
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, ethanethiol (0.37 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **6** as an orange oil (0.829 g, 3.6 mmol, 73%). Data for **6**: IR (film) ν_{max} 2962, 2854, 1700, 1600, 1260, 1114, 1025, 889. ^{1}H NMR (600 MHz, $CDCl_3$) 1.27 (t, J = 7.4, 3H, CH_3), 2.46 (dd, J = 19.1, 1.7 Hz, 1H, COCH_2), 2.56 (q, J = 7.4 Hz, 2H, SCH_2CH$_3$), 2.90 (dd, J = 19.1, 6.3 Hz, 1H, COCH_2), 3.17-3.08 (t, overlapped peaks, J = 4.7 Hz, 4H, morpholine), 3.76 (t, J = 4.8, 4H, morpholine), 3.92 (m, J = 3.1, 1.2 Hz, 1H, COCH$_2$CHSEt), 6.19 (d, J = 3.1 Hz, 1H, COC=CH); ^{13}C NMR (150 MHz, $CDCl_3$) 15.1 (CH$_3$), 24.8 (SCH$_2$CH$_3$), 39.3 (CHSEt), 44.5 (COCH$_2$), 48.1 (morpholine), 66.6 (morpholine), 131.9 (COC=CH), 150.6 (COC=CH), 202.6 (C=O). HRMS (EI) $[M]^+$ found 227.09694, $C_{11}H_{17}NO_2S$ requires 227.09745.

4-(isopropylthio)-2-morpholinocyclopent-2-enone 7



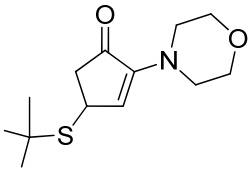
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, 2-propanethiol (0.464 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **7** as an orange oil (0.924 g, 3.8 mmol, 77%). Data for **7**: IR (film) ν_{max} 2958, 2857, 1702, 1601, 1381, 1261, 1114, 1025, 889. ^{1}H NMR (600 MHz, $CDCl_3$) 1.29 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 2.47 (dd, J = 19.1, 1.7 Hz, 1H, $COCH_2$), 2.92 (dd, J = 19.1, 6.2 Hz, 1H, $COCH_2$), 3.02 (septet, J = 6.7 Hz, 1H, $CH(CH_3)_2$), 3.15-3.09 (t, overlapped peaks, J = 4.2 Hz, 4H, morpholine), 3.76 (t, J = 4.8, 4H, morpholine), 3.94 (m, J = 3.1, 1.3 Hz, 1H, $COCH_2CHS$), 6.19 (d, J = 3.2 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 24.0 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 35.6 ($CH(CH_3)_2$), 38.6 ($COCH_2CH$), 45.3 ($COCH_2$), 48.0 (morpholine), 66.6 (morpholine), 132.0 (COC=*C*H), 150.4 (CO*C*=CH), 202.7 (*C*=O). HRMS (EI) $[M]^+$ found 241.11286, $C_{12}H_{19}NO_2S$ requires 241.11310.

4-(cyclohexylthio)-2-morpholinocyclopent-2-enone 8



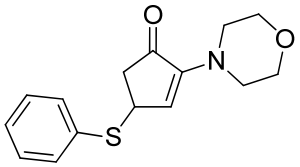
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, cyclohexanethiol (0.625 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **8** as an orange oil (1.005 g, 3.6 mmol, 72%). Data for **8**: IR (film) ν_{max} 2922, 2852, 1700, 1602, 1448, 1261, 1112, 1027, 889, 733. ^{1}H NMR (600 MHz, $CDCl_3$) 1.39-1.22 (m, overlapped peaks, 5H, cyclohexane), 1.60 (m, J = 12.4, 4.1 Hz, 1H, cyclohexane), 1.75 (m, J = 12.5, 3.7 Hz, 2H, cyclohexane), 1.95 (m, J = 3.6 Hz, 2H, cyclohexane), 2.46 (dd, J = 19.1, 1.7 Hz, 1H, COC*H*$_2$), 2.75-2.71 (m, J = 10.4, 3.6 Hz, 1H, cyclohexane), 2.91 (dd, J = 19.1, 6.2 Hz, 1H, COC*H*$_2$), 3.12 (t, J = 4.8 Hz, 4H, morpholine), 3.75 (t, J = 4.8, 4H, morpholine), 3.96 (m, J = 3.1, 1.1 Hz, 1H, COCH$_2$C*H*S), 6.18 (d, J = 3.1 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 25.8 (cyclohexane), 26.1 (cyclohexane), 26.2 (cyclohexane), 34.2 (cyclohexane), 34.4 (cyclohexane), 38.3 (COCH$_2$*C*H), 44.0 (cyclohexane), 45.4 (CO*C*H$_2$), 48.1 (morpholine), 66.6 (morpholine), 132.3 (COC=*C*H), 150.4 (CO*C*=CH), 202.7 (*C*=O). HRMS (EI) $[M]^+$ found 281.14355, $C_{15}H_{23}NO_2S$ requires 281.14440.

4-(*tert*-butylthio)-2-morpholinocyclopent-2-enone 9



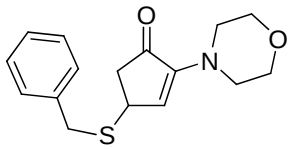
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, 2-methyl-2-propanethiol (0.56 mL, 5 mmol) was added, followed by addition of KO^{t}Bu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **9** as a yellow-white solid (0.975 g, 3.8 mmol, 76%). Data for **9**: mp 67-69 ºC. IR (pellet) ν_{max} 3071, 2955, 2860, 1701, 1602, 1454, 1268, 1113, 1025, 887, 741. ^{1}H NMR (600 MHz, $CDCl_3$) 1.37 (s, 9H, CC*H*$_3$), 2.54 (dd, *J* = 19.2, 1.7 Hz, 1H, COC*H*$_2$), 2.98 (dd, *J* = 19.1, 6.2 Hz, 1H, COC*H*$_2$), 3.15-3.09 (overlapped t, *J* = 4.9 Hz, 4H, morpholine), 3.76 (t, *J* = 4.9 Hz, 4H, morpholine), 3.93 (m, *J* = 3.2 Hz, 1H, COCH$_2$C*H*S), 6.15 (d, *J* = 3.2 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 31.6 (C*C*H$_3$), 37.3 (COCH$_2$*C*HS), 44.2 (*C*CH$_3$), 47.1 (CO*C*H$_2$), 48.1 (morpholine), 66.6 (morpholine), 132.7 (COC=*C*H), 150.2 (CO*C*=CH), 203.0 (*C*=O). HRMS (EI) $[M]^+$ found 255.12922, $C_{13}H_{21}NO_2S$ requires 255.12875.

2-morpholino-4-(phenylthio)-cyclopent-2-enone 10



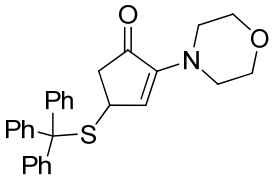
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, thiophenol (0.513 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **10** as a white-yellow low melting point solid (0.973 g, 3.5 mmol, 71%). Data for **10**: mp 80-82 ºC. IR (film) ν_{max} 3058, 2978, 2842, 1696, 1609, 1479, 1375, 1257, 1110, 1029, 889, 724, 685. ^{1}H NMR (600 MHz, $CDCl_3$) 2.50 (dd, J = 19.2, 1.7 Hz, 1H, COCH_2), 2.90 (dd, J = 19.2, 6.2 Hz, 1H, COCH_2), 3.13-3.08 (overlapped t, J = 4.4 Hz, 4H, morpholine), 3.75 (t, J = 4.8, 4H, morpholine), 4.30 (m, J = 3.1, 1.3 Hz, 1H, $COCH_2CHS$), 6.19 (d, J = 3.2 Hz, 1H, COC=C*H*), 7.33-7.29 (m, 3H, Ph), 7.41-7.39 (m, 2H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 42.8 ($COCH_2CHS$), 43.7 ($COCH_2$), 47.9 (morpholine), 66.5 (morpholine), 127.9 (Ph), 129.2 (overlapped, Ph), 130.7 (Ph), 132.8 (overlapped, COC=*C*H and Ph), 133.6 (Ph), 150.8 (CO*C*=CH), 202.1 (*C*=O). HRMS (EI) $[M]^+$ found 275.09643, $C_{15}H_{17}NO_2S$ requires 275.09745.

4-(benzylthio)-2-morpholinocyclopent-2-enone 11



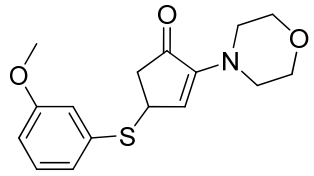
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, α-toluenethiol (0.587 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **11** as a white-yellow low melting point solid (1.154 g, 4.0 mmol, 80%). Data for **11**: mp 64-66 ºC. IR (film) ν_{max} 2961, 2850, 1701, 1591, 1384, 1254, 1116, 1026, 888, 831, 712. ^{1}H NMR (600 MHz, $CDCl_3$) 2.33 (dd, J = 19.2, 1.8 Hz, 1H, COCH_2), 2.72 (dd, J = 19.2, 6.3 Hz, 1H, COCH_2), 2.98-2.93 (overlapped t, J = 4.8 Hz, 2H, morpholine), 3.07-3.03 (overlapped t, J = 4.8 Hz, 2H, morpholine), 3.66 (t, J = 4.8, 4H, morpholine), 3.70 (s, 2H, CH_2Ph), 3.74 (m, J = 3.1, 1.2 Hz, 1H, $COCH_2CHS$), 5.99 (d, J = 3.2 Hz, 1H, COC=CH), 7.18 (m, J = 4.2 Hz, 1H, Ph), 7.25 (d, J = 4.4 Hz, 4H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 35.6 (CH_2Ph), 39.3 ($COCH_2CHS$), 44.1 (COCH_2), 47.9 (morpholine), 66.4 (morpholine), 127.2 (Ph), 128.7 (Ph), 128.9 (overlapped, Ph), 131.3 (overlapped, COC=CH and Ph), 138.4 (Ph), 150.4 (COC=CH), 202.2 (C=O). HRMS (EI) $[M]^+$ found 289.11351, $C_{16}H_{19}NO_2S$ requires 289.11310.

2-morpholino-4-(tritylthio)-cyclopent-2-enone 12



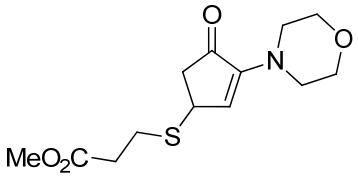
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, trityl thiol (1.38 g, 5 mmol) was added, followed by addition of KO^{t}Bu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **12** as a yellow-white solid (1.40 g, 3.2 mmol, 63%). Data for **12**: mp 160-162 ºC. IR (pellet) ν_{max} 2954, 2828, 1706, 1550, 1262, 1116, 1026, 889, 746, 697. ^{1}H NMR (600 MHz, $CDCl_3$) 2.07 (dd, J = 19.5, 1.7 Hz, 1H, COCH_2), 2.19 (dd, J = 19.5, 6.2 Hz, 1H, COCH_2), 3.06 (t, J = 4.7 Hz, 4H, morpholine), 3.55 (m, J = 3.1 Hz, 1H, $COCH_2CHS$), 3.73 (t, J = 4.7 Hz, 4H, morpholine), 5.89 (d, J = 3.1 Hz, 1H, COC=CH), 7.24 (overlapped t, J = 7.3 Hz, 3H, Ph), 7.31 (overlapped t, J = 7.4 Hz, 6H, Ph), 7.49 (overlapped d, J = 7.6 Hz, 6H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 40.8 ($COCH_2CHS$), 44.4 (COCH_2), 48.0 (morpholine), 66.6 (morpholine), 67.9 (CPh_3), 127.1 (Ph), 128.3 (Ph, overlapped), 129.7 (Ph, overlapped), 131.8 (COC=CH), 144.6 (Ph), 150.0 (COC=CH), 202.7 (C=O). HRMS (EI) $[M+H]^+$ found 442.1847, $C_{28}H_{28}NO_2S$ requires 442.1841.

4-(3-methoxyphenylthio)-2-morpholinocyclopent-2-enone 13



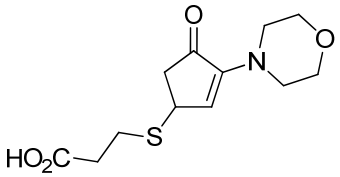
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, 3-methoxybenzylmercaptan (0.62 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/EtOAc (10:1 v/v) to afford **13** as an orange solid (1.07 g, 3.5 mmol, 70%). Data for **13**: mp 58-61 ºC. IR (film) ν_{max} 2966, 2865, 1693, 1577, 1476, 1245, 1116, 1024, 886, 775. ^{1}H NMR (500 MHz, $CDCl_3$) 2.52-2.49 (dd, J = 19.2, 1.7 Hz, 1H, COCH_2), 2.93-2.88 (dd, J = 19.2, 6.2 Hz, 1H, COCH_2), 3.15 (overlapped t, J = 4.8 Hz, 4H, morpholine), 3.74 (t, J = 4.8 Hz, 4H, morpholine), 3.79 (s, 3H, OCH_3), 4.32 (m, J = 3.0 Hz, 1H, COCH$_2$CHS), 6.18 (d, J = 3.1 Hz, 1H, COC=CH), 6.81 (dd, J = 8.3, 0.7 Hz, 1H, Ph), 6.92 (q, J = 2.4 Hz, 1H, Ph), 6.97 (dq, J = 7.6, 0.8 Hz, 1H, Ph), 7.22 (t, J = 7.9 Hz, 1H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) 42.6 (COCH$_2$*C*HS), 43.7 (CO*C*H$_2$), 47.9 (morpholine), 55.4 (O*C*H$_3$), 66.5 (morpholine), 113.3 (Ph), 117.6 (Ph), 124.3 (Ph), 130.0 (Ph), 130.4 (COC=*C*H), 135.1 (Ph), 150.8 (CO*C*=CH), 159.9 (Ph), 201.9 (*C*=O). HRMS (EI) $[M+H]^+$ found 306.1158, $C_{16}H_{20}NO_3S$ requires 306.1164.

Methyl 3-(3-morpholino-4-oxocyclopent-2-enylthio)-propanoate 14



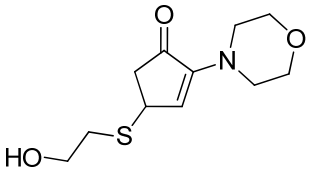
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, methyl-3-mercaptopropionate (0.542 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/EtOAc (10:1 v/v) to afford **14** as an orange oil (0.973 g, 3.5 mmol, 71%). Data for **14**: IR (film) ν_{max} 2954, 2867, 1706, 1600, 1357, 1254, 1196, 1115, 1024, 889, 735. ^{1}H NMR (600 MHz, $CDCl_3$) 2.45 (d, J = 19.2 Hz, 1H, COC*H*$_2$), 2.62 (t, J = 7.2 Hz, 2H, C*H*$_2$CH$_2$COOMe), 2.81 (t, J = 7.2 Hz, 2H, CH$_2$C*H*$_2$COOMe), 2.91 (dd, J = 19.2, 6.3 Hz, 1H, COC*H*$_2$), 3.18-3.09 (overlapped t, J = 4.9 Hz, 4H, morpholine), 3.70 (s, 3H, COOC*H*$_3$), 3.76 (t, J = 4.8, 4H, morpholine), 3.94 (m, J = 3.1 Hz, 1H, COCH$_2$C*H*S), 6.17 (d, J = 2.8 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 25.7 (*C*H$_2$CH$_2$COOMe), 34.8 (CH$_2$*C*H$_2$COOMe), 39.8 (COCH$_2$*C*HS), 44.4 (CO*C*H$_2$), 48.0 (morpholine), 52.1 (COO*C*H$_3$), 66.6 (morpholine), 131.1 (COC=*C*H), 150.1 (CO*C*=CH), 172.2 (*C*OOMe), 202.3 (*C*=O). HRMS (EI) $[M]^+$ found 285.10215, $C_{13}H_{19}NO_4S$ requires 285.10293.

3-(3-morpholino-4-oxocyclopent-2-enylthio)-propanoic acid 15



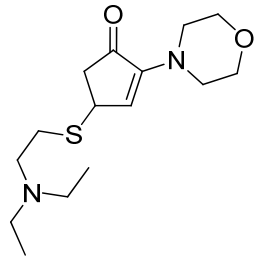
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (10 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, a solution of 3-mercaptopropionic acid (0.436 mL, 5 mmol) with KO^{t}Bu (0.56 g, 5 mmol) in dry MeOH (10 mL) was added, followed by further addition of KO^{t}Bu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was quenched with HCl 2M (5 mL), followed by addition of AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (5 mL). The mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **15** as an orange oil that crystallizes into an orange-brown solid upon standing (0.743 g, 2.7 mmol, 55%). Data for **15**: mp 109-112 ºC. IR (film) ν_{max} 2987, 2872, 2651, 2575, 1707, 1601, 1247, 1174, 1104, 1023, 885, 836, 731. ^{1}H NMR (600 MHz, $CDCl_3$) 2.47 (dd, J = 19.2, 1.7 Hz, 1H, COC*H*$_2$), 2.66 (t, J = 7.1 Hz, 2H, C*H*$_2$CH$_2$COOH), 2.81 (t, J = 7.2 Hz, 2H, CH$_2$C*H*$_2$COOH), 2.93 (dd, J = 19.2, 6.3 Hz, 1H, COC*H*$_2$), 3.19-3.10 (overlapped t, J = 4.8 Hz, 4H, morpholine), 3.77 (t, J = 4.8, 4H, morpholine), 3.96 (m, J = 3.1 Hz, 1H, COCH$_2$C*H*S), 6.18 (d, J = 3.1 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 25.3 (*C*H$_2$CH$_2$COOH), 34.8 (CH$_2$*C*H$_2$COOH), 39.9 (COCH$_2$*C*HS), 44.3 (CO*C*H$_2$), 48.0 (morpholine), 66.5 (morpholine), 131.1 (COC=*C*H), 150.8 (CO*C*=CH), 177.1 (*C*OOH), 202.4 (*C*=O). HRMS (EI) $[M-H]^+$ found 270.0810, $C_{12}H_{16}NO_4S$ requires 270.0800.

4-(2-hydroxyethylthio)-2-morpholinocyclopent-2-enone 16



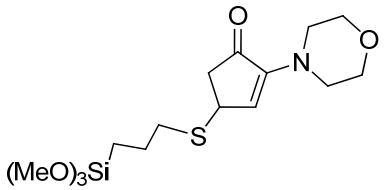
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, 2-mercaptoethanol (0.35 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **16** as an orange oil (0.940 g, 3.9 mmol, 77%). Data for **16**: IR (film) ν_{max} 3402, 2956, 2856, 1698, 1599, 1380, 1260, 1112, 1024, 888. ^{1}H NMR (600 MHz, $CDCl_3$) 2.45 (dd, J = 19.2, 1.7 Hz, 1H, COCH_2), 2.74 (dt, J = 6.2, 2.4 Hz, 2H, CH_2CH$_2$OH), 2.92 (dd, J = 19.2, 6.4 Hz, 1H, COCH_2), 3.11-3.08 (overlapped t, J = 4.8 Hz, 2H, CH$_2$CH_2OH), 3.18-3.15 (overlapped t, J = 4.8 Hz, 2H, morpholine), 3.76-3.74 (overlapped peaks, t, J = 4.9 Hz, 6H, morpholine), 3.97 (m, J = 3.1 Hz, 1H, COCH$_2$CHS), 6.17 (d, J = 3.1 Hz, 1H, COC=CH); ^{13}C NMR (150 MHz, $CDCl_3$) 33.8 (CH$_2$CH_2OH), 39.5 (COCH$_2$*C*HS), 44.5 (CO*C*H$_2$), 48.0 (morpholine), 61.3 (CH_2CH$_2$OH), 66.5 (morpholine), 131.2 (COC=*C*H), 150.8 (CO*C*=CH), 202.4 (*C*=O). HRMS (EI) $[M]^+$ found 243.09161, $C_{11}H_{17}NO_3S$ requires 243.09236.

4-(2-(diethylamino)ethylthio)-2-morpholinocyclopent-2-enone 17



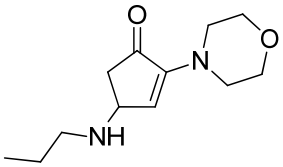
To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, 2-(diethylamino)-ethanethiol (0.75 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (20 mL, 0.68 M in total acetates) and brine (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **17** as an orange oil (1.127 g, 3.8 mmol, 76%). Data for **17**: IR (film) ν_{max} 2965, 2821, 1702, 1600, 1381, 1261, 1116, 1026, 889. ^{1}H NMR (600 MHz, $CDCl_3$) 1.00 (t, J = 7.1 Hz, 6H, NCH_2CH_3), 2.45 (dd, J = 19.2, 1.7 Hz, 1H, $COCH_2$), 2.54-2.50 (q, J = 7.1 Hz, 4H, NCH_2CH_3), 2.65-2.58 (m, overlapped peaks, 4H, $CH_2CH_2NEt_2$), 2.92 (dd, J = 19.2, 6.4 Hz, 1H, $COCH_2$), 3.16-3.09 (overlapped t, J = 4.8 Hz, 4H, morpholine), 3.76-3.74 (overlapped peaks, t, J = 4.9 Hz, 4H, morpholine), 3.97 (m, J = 3.1 Hz, 1H, $COCH_2CHS$), 6.17 (d, J = 3.1 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 11.9 (NCH_2CH_3), 28.4 (SCH_2CH_2N), 39.6 ($COCH_2CHS$), 44.6 ($COCH_2$), 47.1 (NCH_2CH_3), 48.0 (morpholine), 53.2 (SCH_2CH_2N), 66.6 (morpholine), 131.7 (COC=*C*H), 150.7 (CO*C*=CH), 202.5 (*C*=O). HRMS (EI) $[M]^+$ found 298.17123, $C_{15}H_{26}N_2O_2S$ requires 298.17094.

4-(3-(trimethoxysilyl)-propylthio)-2-morpholinocyclopent-2-enone 18



To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry MeOH (20 mL) was added morpholine (0.86 mL, 10 mmol), 4Å molecular sieves (1 g) and $AlCl_3$ (67 mg, 0.5 mmol). The mixture was stirred at room temperature for 6 hours. Then, (3-mercaptopropyl)-trimethoxysilane (0.93 mL, 5 mmol) was added, followed by addition of KO^tBu (140 mg, 1.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (60 mL). DCM (140 mL) was added to the filtrate mixture, which was concentrated under reduced pressure to a volume of 20 mL. More DCM (100 mL) was added and the mixture was again concentrated under reduced pressure to 20 mL. The mixture was filtered off and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **18** as an orange oil (0.94 g, 2.6 mmol, 52%). Data for **18**: IR (film) ν_{max}.2942, 2839, 1703, 1601, 1450, 1262, 1069, 889, 810. ^{1}H NMR (600 MHz, $CDCl_3$) 0.76-73 (overlapped t, J = 6.1 Hz, 2H, $(OMe)_3SiCH_2CH_2CH_2$), 1.73-1.69 (m, 2H, $(OMe)_3SiCH_2CH_2CH_2$), 2.46-2.43 (dd, J = 19.1, 1.6 Hz, 1H, $COCH_2$), 2.57-2.54 (overlapped t, J = 7.4 Hz, 2H, $(OMe)_3SiCH_2CH_2CH_2$), 2.92-2.88 (dd, J = 19.2, 6.3 Hz, 1H, $COCH_2$), 3.17-3.09 (overlapped t, J = 4.8 Hz, 4H, morpholine), 3.55 (s, 7H, $Si(OCH_3)_3$), 3.76 (t, J = 4.8 Hz, 4H, morpholine), 3.90 (m, J = 3.0 Hz, 1H, $COCH_2CHS$), 6.19 (d, J = 3.1 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 8.8 ($(OMe)_3SiCH_2CH_2CH_2$), 23.5 ($(OMe)_3SiCH_2CH_2CH_2$), 33.7 ($(OMe)_3SiCH_2CH_2CH_2$), 39.4 ($COCH_2CHS$), 44.5 ($COCH_2$), 48.1 (morpholine), 50.7 ($Si(OCH_3)_3$), 66.6 (morpholine), 132.0 (COC=*C*H), 150.6 (CO*C*=CH), 202.6 (*C*=O). HRMS (EI) $[M+H]^+$ found 362.14552, $C_{15}H_{28}NO_5SSi$ requires 362.14575.

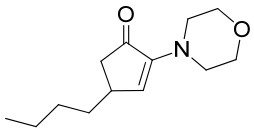
2-morpholino-4-(propylamino)-cyclopent-2-enone 19



To a solution of 2-furaldehyde (0.041 mL, 0.5 mmol) in dry MeOH (2 mL) was added morpholine (0.086 mL, 1 mmol), $AlCl_3$ (6.7 mg, 0.05 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 6 hours. Then, *n*-propylamine (0.041 mL, 0.5 mmol) was added, followed by addition of KO^tBu (14 mg, 0.125 mmol) and the mixture was stirred at room temperature for 2 days. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (20 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (6 mL, 0.68 M in total acetates). The organic layer was separated and the aqueous layer was further extracted with DCM (10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a dark oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **3** as an orange oil (21 mg, 0.11 mmol, 21%), compound **19** as an orange oil (33 mg, 0.14 mmol, 29%), and compound **2** as a yellow oil (26 mg, 0.1 mmol, 20%). Data for **3**: (600 MHz, $CDCl_3$) 2.37-2.33 (dd, J = 18.4, 1.8 Hz, 1H, COCH_2), 2.74-2.70 (dd, J = 18.4, 5.8 Hz, 1H, COCH_2), 3.21-3.12 (overlapped t, J = 4.8 Hz, 4H, morpholine), 3.38 (s, 3H, OCH_3), 3.76 (t, overlapped peaks, J = 4.8 Hz, 4H, morpholine), 4.42 (m, J = 3.0, 1.8 Hz, 1H, C*H*OMe), 6.21 (d, J = 3.0 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 42.5 (CO*C*H_2), 47.8 (morpholine), 56.5 (O*C*H_3), 66.5 (morpholine), 74.4 (*C*HOMe), 128.0 (COC=*C*H), 151.4 (CO*C*=CH), 201.2 (*C*=O). Data for **19**: IR (film) ν_{max} 3368, 2959, 2856, 1702, 1634, 1452, 1276, 1113, 1006, 853, 730. ^{1}H NMR (600 MHz, $CDCl_3$) 0.94 (t, J = 7.4 Hz, 3H, $NCH_2CH_2CH_3$), 1.57 (sextet, J = 7.1 Hz, 2H, $NCH_2CH_2CH_3$), 2.40-2.36 (dd, J = 18.9, 2.0 Hz, 1H, COCH_2), 2.50-2.46 (dd, J = 18.9, 5.8 Hz, 1H, COCH_2), 2.53 (t, overlapped peaks, J = 4.4 Hz, 4H, morpholine), 2.95 (quartet, J = 6.0 Hz, 2H, $NCH_2CH_2CH_3$), 3.73 (t, overlapped peaks, J = 4.6 Hz, 4H, morpholine), 3.78 (m, J = 2.9 Hz, 1H, $COCH_2CHN$), 3.98 (t, J = 5.0 Hz, 1H, N*H*), 5.79 (d, J = 3.0 Hz, 1H, COC=C*H*);

^{13}C NMR (150 MHz, $CDCl_3$) 11.7 ($NCH_2CH_2\mathit{C}H_3$), 22.2 ($NCH_2\mathit{C}H_2CH_3$), 36.3 ($N\mathit{C}H_2CH_2CH_3$), 46.1 ($CO\mathit{C}H_2$), 49.9 (morpholine), 61.4 ($COCH_2C\mathit{H}N$), 67.1 (morpholine), 117.2 (COC=*C*H), 147.4 (CO*C*=CH), 201.9 (*C*=O). HRMS (EI) $[M+H]^+$ found 225.16030, $C_{12}H_{21}N_2O_2$ requires 225.15999. Data for **2**: ^{1}H NMR (600 MHz, $CDCl_3$) 2.43-2.39 (dd, overlapped peaks, J = 18.5, 2.3 Hz, 1H, $COC\mathit{H}_2$), 2.50-2.47 (dd, overlapped peaks, J = 18.5, 6.0 Hz, 1H, $COC\mathit{H}_2$), 2.53-2.49 (m, overlapped peaks, 4H, morpholine), 3.13 (m, J = 5.0 Hz, 4H, morpholine), 3.70-3.67 (m, overlapped peaks, 1H, $COH_2C\mathit{H}N$), 3.71 (t, overlapped peaks, J = 4.6 Hz, 4H, morpholine), 3.75 (t, J = 4.6 Hz, 4H, morpholine), 6.22 (d, J = 2.9 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 38.0 ($CO\mathit{C}H_2$), 48.0 (morpholine), 50.0 (morpholine), 60.2 ($COCH_2C\mathit{H}N$), 66.6 (morpholine), 67.0 (morpholine), 129.6 (COC=*C*H), 151.7 (CO*C*=CH), 202.0 (*C*=O).

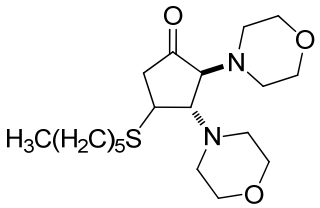
4-butyl-2-morpholinocyclopent-2-enone 20



CuI (0.925 g, 5 mmol) was suspended in dry Et_2O (20 mL) under argon. The mixture was cooled down to 0 ºC. Next, a 2.5 M solution of *n*-butyllithium in hexanes (4 mL, 10 mmol) was added dropwise over 15 minutes. Then, the mixture was cooled down to –78 ºC and added dropwise a solution of **1** (1.26 g, 5 mmol) in 1:1 Et_2O:THF (20 mL) over 30 minutes. The mixture was stirred at –78 ºC for 10 minutes and then was allowed to rise to room temperature and stir for an additional 60 minutes. Then, the reaction was quenched with ice (20 g). The mixture was extracted with Et_2O (2×40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (4:1 v/v) to afford **20** as a yellow oil (0.882 g, 3.9 mmol, 79%). Data for **20**: IR (film) ν_{max} 2956, 2920, 2854, 1699, 1606, 1451, 1380, 1261, 1117, 1024, 891. ^{1}H NMR (500 MHz, $CDCl_3$) 0.90 (t, J = 7.0 Hz, 3H, $CH_2CH_2CH_2C\mathit{H}_3$), 1.38-1.31 (m, overlapped peaks, 5H, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 1.50-1.46 (m, overlapped peaks, 1H,

$CH_2CH_2CH_2CH_3$), 2.05-2.01 (dd, J = 19.0, 2.0 Hz, 1H, $COCH_2$), 2.61-2.56 (dd, J = 19.0, 6.5 Hz, 1H, $COCH_2$), 2.70 (m, 1H, $COCH_2CH$), 3.07 (overlapped t, J = 4.5 Hz, 4H, morpholine), 3.78 (overlapped t, J = 4.5 Hz, 4H, morpholine), 6.31 (d, J = 3.0 Hz, 1H, COC=C*H*); ^{13}C NMR (125 MHz, $CDCl_3$) 14.1 ($CH_2CH_2CH_2CH_3$), 22.8 ($CH_2CH_2CH_2CH_3$), 29.8 ($CH_2CH_2CH_2CH_3$), 35.7 ($CH_2CH_2CH_2CH_3$), 36.0 ($COCH_2CH$), 42.4 ($COCH_2$), 48.5 (morpholine), 66.7 (morpholine), 138.0 (COC=*C*H), 150.1 (CO*C*=CH), 204.8 (*C*=O). HRMS (EI) $[M]^+$ found 223.15701, $C_{13}H_{21}NO_2$ requires 223.15663.

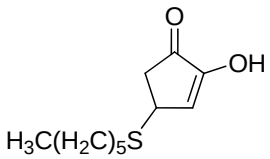
trans-4-(hexylthio)-2,3-dimorpholinocyclopentanone 21



To a solution of 2-furaldehyde (82 µL, 1 mmol) in dry MeOH (4 mL) was added morpholine (172 µL, 2 mmol), $AlCl_3$ (13.4 mg, 0.1 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 5 hours. Then, 1-hexanethiol (140 µL, 1 mmol), was added and the mixture was stirred for 24 hours. Afterwards, the reaction was filtered through a short plug of celite and the filter cake was washed with DCM (30 mL). To the filtrate was added water (10 mL). The organic layer was separated and the aqueous layer was further extracted with DCM (10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/EtOAc/ethanol (30:1:1 v/v) to afford **5** as a yellow oil (76 mg, 0.27 mmol, 27%), compound **21** as a yellow oil that crystallizes into a yellow solid upon standing (87 mg, 0.23 mmol, 23%), and compound **1** as a yellow oil (19.5 mg, 0.077 mmol, 8%). Data for **5**: ^{1}H NMR (600 MHz, $CDCl_3$) 0.85 (t, J = 7.0 Hz, 3H, $S(CH_2)_5CH_3$), 1.29-1.22 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.35 (quintet, J = 7.3 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.56 (quintet, J = 7.4, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.44-2.40 (dd, J = 19.1, 1.8 Hz, 1H, $COCH_2$), 2.50

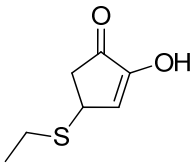
(t, J = 7.4 Hz, 2H, SCH_2CH$_2$(CH$_2$)$_3$CH$_3$), 2.90-2.86 (dd, J = 19.1, 6.2 Hz, 1H, COCH_2), 3.15-3.07 (t, overlapped peaks, J = 4.8 Hz, 4H, morpholine), 3.74 (t, J = 4.8, 4H, morpholine), 3.88 (m, J = 3.0, 1.8 Hz, 1H, COCH$_2$CHS), 6.18 (d, J = 3.0 Hz, 1H, COC=CH); ^{13}C NMR (150 MHz, CDCl$_3$) 14.1 (S(CH$_2$)$_5$$CH_3$), 22.6 (S(CH$_2$)$_4$$CH_2CH_3$), 28.7 (S(CH$_2$)$_3$$CH_2CH_2CH_3$), 29.9 (S(CH$_2$)$_2CH_2$(CH$_2$)$_2CH_3$), 30.7 (SCH$_2$$CH_2$(CH$_2$)$_3CH_3$), 31.5 (S$CH_2CH_2$(CH$_2$)$_3CH_3$), 39.5 (COCH$_2$$C$H), 44.5 (CO$CH_2$), 48.0 (morpholine), 66.6 (morpholine), 132.0 (COC=CH), 150.6 (COC=CH), 202.6 (C=O). Data for **21**: mp 87-92 ºC. IR (film) ν_{max} 2954, 2848, 1739, 1455, 1252, 1112, 1007, 865, 730. ^{1}H NMR (500 MHz, CDCl$_3$) 0.86 (t, J = 6.0 Hz, 3H, S(CH$_2$)$_5$CH_3), 1.30-1.23 (m, overlapped peaks, 4H, S(CH$_2$)$_3$CH_2CH_2CH$_3$), 1.37-1.31 (m, overlapped peaks, 2H, S(CH$_2$)$_2$CH_2(CH$_2$)$_2$CH$_3$), 1.55-1.47 (m, overlapped peaks, 2H, SCH$_2$CH_2(CH$_2$)$_3$CH$_3$), 2.40-2.32 (m, overlapped peaks, 2H, SCH_2CH$_2$(CH$_2$)$_3$CH$_3$), 2.57-2.53 (q, overlapped peaks, J = 8.0, 4.0 Hz, 2H, COCH_2CHS), 2.61-2.57 (dd, overlapped peaks, J = 15.0, 1.3 Hz, 1H, COCH_2CHS), 2.91 (dd, J = 8.0, 4.5 Hz, 1H, COCHNCHN), 2.71 (m, 4H, morpholine), 3.13 (m, 4H, morpholine), 3.00 (m, overlapped peaks, 2H,), 3.26 (d, J = 8.0 Hz, 1H, COCHN), 3.61-3.59 (t, overlapped peaks, J = 3.0 Hz, 4H, morpholine), 3.74 (t, J = 4.0 Hz, 4H, morpholine); ^{13}C NMR (125 MHz, CDCl$_3$) 14.1 (S(CH$_2$)$_5$$CH_3$), 22.6 S(CH$_2$)$_4$$CH_2CH_3$), 28.8 (S(CH$_2$)$_3$$CH_2CH_2CH_3$), 29.2 (S(CH$_2$)$_2CH_2$(CH$_2$)$_2CH_3$), 30.3 (SCH$_2$$CH_2$(CH$_2$)$_3CH_3$), 31.5 (S$CH_2CH_2$(CH$_2$)$_3CH_3$), 40.8 (COCH$_2$$C$HS), 44.8 (morpholine), 52.5 (COCH$_2$), 65.3 (COCHNCHN), 67.0 (morpholine, overlapped), 67.5 (morpholine), 72.1 (COCHN), 214.5 (C=O). HRMS (EI) [M]$^+$ found 370.22742, C$_{19}$H$_{34}$N$_2$O$_3$S requires 370.2284. Data for **1**: ^{1}H NMR (600 MHz, CDCl$_3$) 2.67-2.57 (m, 6H, morpholine), 2.80 (overlapped t, J = 4.5 Hz, 2H, morpholine), 3.29 (d, J = 3.0 Hz, 1H COCH), 3.68 (t, J = 4.6 Hz, 4H, morpholine), 3.73 (t, J = 4.6 Hz, 4H, morpholine), 3.80 (q, J = 2.1 Hz, 1H, COCH=CHCHN), 6.21 (dd, J = 6.5, 1.9 Hz, 1H, COCH=CH), 7.59 (dd, J = 6.5, 2.2 Hz, 1H, COCH=CH); ^{13}C NMR (150 MHz, CDCl$_3$) 50.0 (morpholine), 50.2 (morpholine), 66.7 (COCH), 67.2 (morpholine), 67.4 (morpholine), 68.2 (COCH=CHCHN), 135.6 (COCH=CH), 160.8 (COCH=CH), 206.2 (C=O).

4-(hexylthio)-2-hydroxycyclopent-2-enone 22



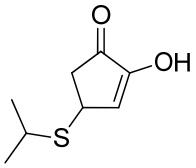
To a solution of enone **5** (0.142 g, 0.5 mmol) in MeOH (2 mL) and water (0.5 mL) was added HCl 37% (0.047 mL, 0.55 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (2 mL) and DCM (6 ml) were added and layers were separated. Aqueous layer was further extracted with DCM (6 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **22** as a pale yellow low melting point solid (89 mg, 0.4 mmol, 83%). Data for **22**: mp 64-66 ºC. IR (film) ν_{max} 3269, 2923, 2856, 1698, 1648, 1383, 1183, 1105, 926, 871. ^{1}H NMR (600 MHz, $CDCl_3$) 0.86 (t, J = 7.0 Hz, 3H, $S(CH_2)_5CH_3$), 1.30-1.23 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.35 (quintet, J = 7.7 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.56 (quintet, J = 7.4, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.46-2.43 (dd, J = 19.6, 1.4 Hz, 1H, $COCH_2$), 2.51 (dt, J = 7.7, 2.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.95-2.90 (dd, J = 19.6, 5.9 Hz, 1H, $COCH_2$), 3.92 (m, J = 3.1, 1.4 Hz, 1H, $COCH_2CHS$), 6.50 (d, J = 3.1 Hz, 1H, COC=CH), 6.57 (br, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$) 14.1 ($S(CH_2)_5CH_3$), 22.6 $S(CH_2)_4CH_2CH_3$), 28.7 ($S(CH_2)_3CH_2CH_2CH_3$), 29.8 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.6 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 38.5 ($COCH_2CH$), 41.7 ($COCH_2$), 130.7 (COC=CH), 153.4 (COC=CH), 202.3 (C=O). HRMS (EI) $[M+H]^+$ found 215.11002, $C_{11}H_{19}O_2S$ requires 215.11058.

4-(ethylthio)-2-hydroxycyclopent-2-enone 23



To a solution of enone **6** (0.227 g, 1 mmol) in MeOH (4 mL) and water (1 mL) was added HCl 37% (0.094 mL, 1.1 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (4 mL) and DCM (12 ml) were added and layers were separated. Aqueous layer was further extracted with DCM (12 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **23** as a pale yellow low melting point solid (0.125 g, 0.79 mmol, 79%). Data for **23**: mp 46-48 ºC. IR (film) ν_{max} 3257, 2971, 2927, 2866, 1698, 1647, 1386, 1183, 1102, 925, 869. ^{1}H NMR (600 MHz, $CDCl_3$) 1.24 (t, J = 7.4 Hz, 3H, CH_3), 2.46-2.42 (dd, J = 19.6, 1.4 Hz, 1H, COCH_2), 2.56-2.52 (dq, J = 7.4, 2.9 Hz, 2H, SCH_2CH$_3$), 2.94-2.90 (dd, J = 19.6, 5.9 Hz, 1H, COCH_2), 3.92 (m, J = 3.1, 1.4 Hz, 1H, COCH$_2$CHSEt), 6.49 (d, J = 3.1 Hz, 1H, COC=CH), 6.76 (br, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$) 15.0 (*C*H$_3$), 24.6 (S*C*H$_2$CH$_3$), 38.3 (*C*HSEt), 41.8 (CO*C*H$_2$), 130.9 (COC=*C*H), 153.5 (CO*C*=CH), 202.4 (*C*=O). HRMS (EI) $[M]^+$ found 158.03950, $C_7H_{10}O_2S$ requires 158.03960.

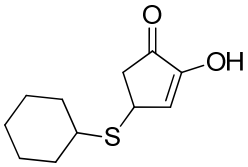
2-hydroxy-4-(isopropylthio)-cyclopent-2-enone 24



To a solution of enone **7** (0.241 g, 1 mmol) in MeOH (4 mL) and water (1 mL) was added HCl 37% (0.094 mL, 1.1 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (4 mL) and DCM (12 ml) were added and layers were separated. Aqueous layer was further extracted with DCM (12 mL). Combined organic layers were dried ($MgSO_4$), filtered and

concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **24** as a pale yellow low melting point solid (0.141 g, 0.82 mmol, 82%). Data for **24**: mp 60-62 ºC. IR (film) ν_{max} 3144, 2958, 2928, 2865, 1682, 1612, 1396, 1258, 1091, 926, 858. ^{1}H NMR (600 MHz, $CDCl_3$) 1.27-1.25 (overlapped d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 2.45-2.42 (dd, J = 19.5, 1.3 Hz, 1H, COCH_2), 2.94-2.90 (dd, J = 19.5, 5.9 Hz, 1H, COCH_2), 3.00 (septet, J = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 3.95 (m, J = 3.1, 1.4 Hz, 1H, COCH$_2$CHS), 6.49 (d, J = 3.1 Hz, 1H COC=CH), 6.84 (br, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$) 23.9 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 35.6 (*C*H(CH$_3$)$_2$), 37.5 (COCH$_2$*C*H), 42.6 (CO*C*H$_2$), 131.0 (COC=*C*H), 153.3 (CO*C*=CH), 202.5 (*C*=O). HRMS (EI) $[M]^+$ found 172.05541, $C_8H_{12}O_2S$ requires 172.05525.

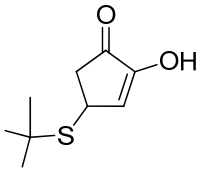
4-(cyclohexylthio)-2-hydroxycyclopent-2-enone 25



To a solution of enone **8** (0.281 g, 1 mmol) in MeOH (4 mL) and water (1 mL) was added HCl 37% (0.094 mL, 1.1 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (4 mL) and DCM (12 ml) were added and layers were separated. Aqueous layer was further extracted with DCM (12 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **25** as a pale yellow low melting point solid (0.195 g, 0.92 mmol, 92%). Data for **25**: mp 80-83 ºC (decomposes). IR (film) ν_{max} 3124, 2923, 2848, 1682, 1610, 1397, 1270, 1096, 999, 928, 853. ^{1}H NMR (600 MHz, $CDCl_3$) 1.37-1.17 (m, overlapped peaks, 5H, cyclohexane), 1.58-1.56 (dt, J = 12.5, 4.0 Hz, 1H, cyclohexane), 1.73-1.71 (dt, J = 12.5, 3.8 Hz, 2H, cyclohexane), 1.91 (d, J = 12.7 Hz, 2H, cyclohexane), 2.45-2.41 (dd, J = 19.6, 1.3 Hz, 1H, COCH_2), 2.73-2.69 (tt,

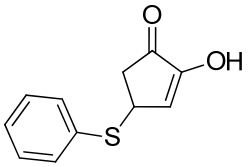
J = 10.4, 3.7 Hz, 1H, cyclohexane), 2.94-2.90 (dd, *J* = 19.6, 5.9 Hz, 1H, COC*H*$_2$), 3.97 (m, *J* = 3.0, 1.2 Hz, 1H, COCH$_2$C*H*S), 6.48 (d, *J* = 3.0 Hz, 1H, COC=C*H*), 6.77 (br, 1H, O*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 25.7, 26.1 (two overlapped peaks), 34.1 (cyclohexane), 34.4 (cyclohexane), 37.3 (COCH$_2$*C*H), 42.7 (CO*C*H$_2$), 43.9 (cyclohexane), 131.1 (COC=*C*H), 153.3 (CO*C*=CH), 202.5 (*C*=O). HRMS (EI) $[M]^+$ found 212.08682, $C_{11}H_{16}O_2S$ requires 212.08655.

4-(*tert*-butylthio)-2-hydroxycyclopent-2-enone 26



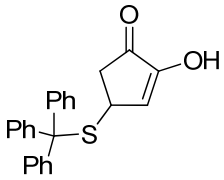
To a solution of enone **9** (0.255 g, 1 mmol) in MeOH (4 mL) and water (1 mL) was added HCl 37% (0.094 mL, 1.1 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (4 mL) and DCM (12 ml) were added and layers were separated. Aqueous layer was further extracted with DCM (12 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **26** as a pale yellow low melting point solid (0.176 g, 0.94 mmol, 94%). Data for **26**: mp 112-115 ºC (decomposes). IR (film) ν_{max} 3327, 2963, 2864, 1689, 1646, 1387, 1160, 1109, 928, 868. ^{1}H NMR (600 MHz, $CDCl_3$) 1.36 (s, 9H, CC*H*$_3$), 2.53-2.50 (dd, *J* = 19.5, 1.3 Hz, 1H, COC*H*$_2$), 3.00-2.97 (dd, *J* = 19.5, 5.8 Hz, 1H, COC*H*$_2$), 3.95 (m, *J* = 3.1, 1.2 Hz, 1H, COCH$_2$C*H*S), 6.45 (d, *J* = 3.1 Hz, 1H, COC=C*H*), 6.55 (br, 1H, O*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 31.5 (C*C*H$_3$), 36.2 (COCH$_2$*C*HS), 44.2 (*C*CH$_3$), 44.3 (CO*C*H$_2$), 131.3 (COC=*C*H), 152.9 (CO*C*=CH), 202.6 (*C*=O). HRMS (EI) $[M]^+$ found 186.07011, $C_9H_{14}O_2S$ requires 186.07090.

2-hydroxy-4-(phenylthio)-cyclopent-2-enone 27



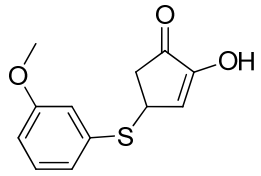
To a solution of enone **10** (0.138 g, 0.5 mmol) in a mixture of EtOAc (4mL), MeOH (1 mL) and water (0.5 mL) was added HCl 37% (0.047 mL, 0.55 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (2 mL) and EtOAc (6 ml) were added and layers were separated. Aqueous layer was further extracted with EtOAc (6 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **27** as a pale yellow low melting point solid (0.067 g, 0.24 mmol, 49%). Data for **27**: mp 95-98 ºC. IR (film) ν_{max} 3242, 3058, 1715, 1688, 1647, 1377, 1186, 1105, 930, 869. ^{1}H NMR (600 MHz, $CDCl_3$) 2.50-2.47 (dd, *J* = 19.6, 1.4 Hz, 1H, COC*H*$_2$), 2.93-2.89 (dd, *J* = 19.6, 5.9 Hz, 1H, COC*H*$_2$), 4.30 (m, *J* = 3.1, 1.4 Hz, 1H, COCH$_2$C*H*S), 6.25 (br, 1H, O*H*), 6.52 (d, *J* = 3.0 Hz, 1H, COC=C*H*), 7.34-7.30 (m, overlapped peaks, 3H, Ph), 7.43-7.41 (m, overlapped peaks, 2H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 40.8 (CO*C*H$_2$), 41.8 (COCH$_2$*C*HS), 128.2 (Ph), 129.3 (overlapped, Ph), 129.6 (Ph), 132.8 (overlapped, COC=*C*H and Ph), 133.2 (Ph), 153.6 (CO*C*=CH), 201.6 (*C*=O). HRMS (EI) $[M+H]^+$ found 207.04813, $C_{11}H_{11}O_2S$ requires 207.04798.

2-hydroxy-4-(tritylthio)-cyclopent-2-enone 28



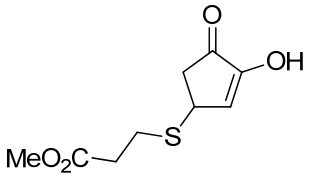
To a solution of enone **12** (0.442 g, 1 mmol) in a mixture of EtOAc (4mL), MeOH (1 mL) and water (0.5 mL) was added HCl 37% (0.094 mL, 1.1 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (2 mL) and EtOAc (12 ml) were added and layers were separated. Aqueous layer was further extracted with EtOAc (12 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **28** as a pale yellow low melting point solid (0.304 g, 0.82 mmol, 82%). Data for **28**: mp 88-92 ºC. IR (film) ν_{max} 3312, 3032, 1698, 1652, 1388, 1192, 1107, 906, 854. ^{1}H NMR (600 MHz, $CDCl_3$) 2.09-2.06 (dd, J = 19.9, 1.3 Hz, 1H, COCH_2), 2.22-2.18 (dd, J = 19.9, 5.9 Hz, 1H, COCH_2), 3.58 (m, J = 3.0, 1.4 Hz, 1H, $COCH_2CHS$), 6.25 (d, J = 3.0 Hz, 1H, COC=CH), 6.45 (br, 1H, OH), 7.26 (t, overlapped peaks, J = 7.3 Hz, 3H, Ph), 7.33 (t, overlapped peaks, J = 7.5 Hz, 6H, Ph), 7.33 (d, overlapped peaks, J = 8.6 Hz, 6H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 39.8 ($COCH_2CHS$), 41.8 ($COCH_2$), 68.1 (CPh_3), 127.2 (Ph), 128.4 (Ph, overlapped), 129.7 (Ph, overlapped), 130.3 (COC=CH), 144.5 (Ph), 152.8 (COC=CH), 202.4 (C=O). HRMS (EI, CI, FAB) could only see peak for (CPh_3) which masks everything.

4-(3-methoxyphenylthio)-2-hydroxycyclopent-2-enone 29



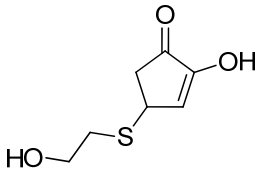
To a solution of enone **13** (0.305 g, 1 mmol) in a mixture of EtOAc (4mL), MeOH (1 mL) and water (0.5 mL) was added HCl 37% (0.094 mL, 1.1 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (4 mL) and EtOAc (12 ml) were added and layers were separated. Aqueous layer was further extracted with EtOAc (12 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **29** as a pale yellow low melting point solid (0.164 g, 0.69 mmol, 69%). Data for **29**: mp 81-84 ºC. IR (film) ν_{max} 3251, 3014, 1709, 1689, 1646, 1575, 1375, 1244, 1186, 1030, 840. ^{1}H NMR (600 MHz, $CDCl_3$) 2.50-2.47 (dd, J = 19.6, 1.4 Hz, 1H, COCH_2), 2.94-2.89 (dd, J = 19.6, 5.9 Hz, 1H, COCH_2), 3.79 (s, 3H, OCH_3), 4.32. (m, J = 3.0, 1.4 Hz, 1H, COCH$_2$CHS), 6.52 (d, J = 3.0 Hz, 1H, COC=CH), 6.60 (br, 1H, OH), 6.83-6.81 (ddd, J = 8.3, 2.6, 0.8 Hz, 1H, Ph), 6.94 (t, J = 2.1 Hz, 1H, Ph), 6.99-6.97 (dq, J = 7.6, 0.8 Hz, 1H, Ph), 7.22 (t, J = 8.0 Hz, 1H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 40.9 (COCH$_2$), 41.7 (COCH$_2$$C$HS), 55.5 (O$CH_3$), 113.8 (Ph), 117.9 (Ph), 124.8 (Ph), 129.8 (Ph), 130.1 (COC=CH), 134.4 (Ph), 153.8 (COC=CH), 159.9 (Ph), 201.8 (C=O). HRMS (EI) $[M]^+$ found 236.05024, $C_{12}H_{12}O_3S$ requires 236.05017.

Methyl-3-(3-hydroxy-4-oxocyclopent-2-enylthio)-propanoate 30



To a solution of enone **14** (0.285 g, 1 mmol) in a mixture of MeOH (4 mL) and water (1 mL) was added HCl 37% (0.094 mL, 1.1 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (4 mL) and DCM (12 ml) were added and layers were separated. Aqueous layer was further extracted with DCM (12 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **30** as an orange oil (0.170 g, 0.78 mmol, 78%). Data for **30**: IR (film) ν_{max} 3336, 2954, 2930, 2850, 1700, 1652, 1387, 1193, 1100, 910, 727. ^{1}H NMR (600 MHz, $CDCl_3$) 2.41-2.38 (dd, J = 19.6, 1.1 Hz, 1H, COCH_2), 2.58 (t, J = 7.2 Hz, 2H, CH_2CH$_2$COOMe), 2.76 (t, J = 7.0 Hz, 2H, CH$_2$CH_2COOMe), 2.91-2.87 (dd, J = 19.6, 5.9 Hz, 1H, COCH_2), 3.64 (s, 3H, COOCH_3), 3.93 (m, J = 3.1, 1.6 Hz, 1H, COCH$_2$CHS), 6.44 (d, J = 3.1 Hz, 1H, COC=CH), 7.03 (br, 1H, OH); ^{13}C NMR (150 MHz, $CDCl_3$) 25.4 (*C*H$_2$CH$_2$COOMe), 34.7 (CH$_2$*C*H$_2$COOMe), 38.7 (COCH$_2$*C*HS), 41.7 (CO*C*H$_2$), 52.1 (COO*C*H$_3$), 130.3 (COC=*C*H), 153.9 (CO*C*=CH), 172.5 (*C*OOMe), 202.0 (*C*=O). HRMS (EI) $[M]^+$ found 216.04489 $C_9H_{12}O_4S$ requires 216.04508.

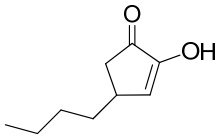
4-(2-hydroxyethylthio)-2-hydroxycyclopent-2-enone 31



To a solution of enone **16** (0.060 g, 0.25 mmol) in a mixture of EtOAc (1mL), MeOH (0.25 mL) and water (0.125 mL) was added HCl 37% (0.024 mL, 0.28 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, added EtOAc (100 ml) and concentrated under reduced pressure to a volume of 10 mL. Then, more EtOAc was added (100 mL) and the mixture was

concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with DCM/MeOH (20:1 v/v) to afford **31** as an orange oil (0.035 g, 0.20 mmol, 80%). Data for **31**: IR (film) ν_{max} 3376, 2954, 2885, 2512, 2242, 1695, 1634, 1365, 1107, 1032, 871. ^{1}H NMR (600 MHz, MeOD-d4) 2.35-2.31 (dd, *J* = 19.4, 1.4 Hz, 1H, COC*H*$_2$), 2.68 (t, *J* = 6.7 Hz, 2H, C*H*$_2$CH$_2$OH), 2.92-2.88 (dd, *J* = 19.4, 6.0 Hz, 1H, COC*H*$_2$), 3.70-3.65 (t, overlapped peaks, *J* = 6.6 Hz, 2H, CH$_2$C*H*$_2$OH), 4.01 (m, *J* = 3.1, 1.4 Hz, 1H, COCH$_2$C*H*S), 6.39 (d, *J* = 3.1 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, CDCl$_3$) 36.5 (CH$_2$C*H*$_2$OH), 42.3 (COCH$_2$*C*HS), 46.1 (CO*C*H$_2$), 65.4 (C*H*$_2$CH$_2$OH), 134.1 (COC=*C*H), 158.6 (CO*C*=CH), 206.4 (*C*=O). HRMS (EI) [M]$^+$ found 174.03542, $C_7H_{10}O_3S$ requires 174.03506.

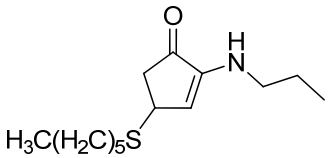
4-butyl-2-hydroxycyclopent-2-enone 32



To a solution of compound **21** (0.224 g, 1 mmol) in THF (4 mL) and water (1 mL) was added HCl 37% (0.170 mL, 2 mmol). The mixture was stirred at 60 ºC for 2 hours. Afterwards, water (10 mL) was added and the mixture was extracted with EtOAc (2×20 mL). Combined organic layers were dried (MgSO$_4$), filtered and concentrated under reduced pressure to yield a yellow low melting point solid which was purified by flash chromatography on silica with toluene/EtOH (10:1 v/v) to afford **32** as a pale yellow low melting point solid (0.125 g, 0.81 mmol, 81%). Data for **32**: IR (film) ν_{max} 3343, 2956, 2924, 2857, 1691, 1392, 1193, 1102, 847, 785, 690. mp: 101-102 ºC. ^{1}H NMR (500 MHz, CDCl$_3$) 0.88 (t, *J* = 7.0 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.39-1.31 (m, overlapped peaks, 5H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.50-1.46 (m, overlapped peaks, 1H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.05-2.01 (dd, *J* = 19.0, 2.0 Hz, 1H, COC*H*$_2$), 2.61-2.57 (dd, *J* = 19.0, 6.5 Hz, 1H, COC*H*$_2$), 2.72 (m, 1H, COCH$_2$C*H*), 6.4 (br, 1H, O*H*), 6.52 (d, *J* = 3.0 Hz, 1H, COC=C*H*); ^{13}C NMR (125 MHz, CDCl$_3$) 14.0 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 22.7 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 29.7 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 34.6 (COCH$_2$C*H*), 35.5 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 39.5 (CO*C*H$_2$), 134.7

(COC=*C*H), 152.6 (CO*C*=CH), 204.2 (*C*=O). HRMS (EI) $[M]^+$ found 154.09864, $C_9H_{14}O_2$ requires 154.09883.

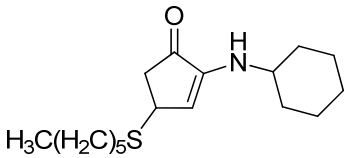
4-(hexylthio)-2-(propylamino)-cyclopent-2-enone 33



To a solution of enone **22** (0.054 g, 0.25 mmol) in dry MeCN (2 mL) was added *n*-propylamine (0.021 mL, 0.25 mmol) and 4Å molecular sieves (0.05 g). The mixture was stirred at room temperature for 20 hours. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with EtOAc (6 mL). To the filtrate was added AcOH/NaOAc buffer solution at pH 5 (2 mL, 0.68 M in total acetates). The organic layer was separated and the aqueous layer was further extracted with EtOAc (6 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with petroleum ether/DCM/EtOAc (10:10:1 v/v) to afford **33** as a clear oil with a slight brown hue (0.033 g, 0.13 mmol, 51%) that gets progressively darker over time. Data for **33**: IR (film) ν_{max} 3375, 2957, 2926, 2856, 1703, 1633, 1497, 1158, 928, 807, 732. ^{1}H NMR (600 MHz, $CDCl_3$) 0.87 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 0.93 (t, J = 7.4 Hz, 3H, $NCH_2CH_2CH_3$), 1.29-1.23 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.36 (quintet, J = 7.3 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.60-1.53 (m, overlapped peaks, 4H, $SCH_2CH_2(CH_2)_3CH_3$ and $NCH_2CH_2CH_3$), 2.45-2.41 (dd, J = 19.4, 1.6 Hz, 1H, $COCH_2$), 2.51 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.91-2.87 (dd, J = 19.4, 6.1 Hz, 1H, $COCH_2$), 2.95-2.93 (q, J = 5.5 Hz, 2H, $NCH_2CH_2CH_3$), 3.98-3.91 (br, overlapped peaks, 1H, N*H*), 3.96 (m, J = 3.1, 1.5 Hz, 1H, $COCH_2CHS$), 5.75 (d, J = 3.1 Hz, 1H, COC=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 11.6 ($NCH_2CH_2CH_3$), 14.2 ($S(CH_2)_5CH_3$), 22.3 ($NCH_2CH_2CH_3$), 22.6 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 30.0

($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.7 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 40.8 ($COCH_2CH$), 43.3 ($COCH_2$), 46.1 ($NCH_2CH_2CH_3$), 119.6 (COC=CH), 146.6 (COC=CH), 202.4 (C=O). HRMS (EI) $[M+H]^+$ found 256.17327, $C_{14}H_{26}NOS$ requires 256.17354.

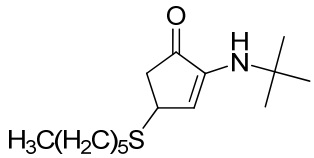
2-(cyclohexylamino)-4-(hexylthio)-cyclopent-2-enone 34



To a solution of enone **22** (0.108 g, 0.5 mmol) in dry MeCN (2 mL) was added cyclohexylamine (0.057 mL, 0.5 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 20 hours. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (15 mL). The filtrate was concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (20:1 v/v) to afford **34** as a clear oil with a slight brown hue (0.094 g, 0.32 mmol, 64%) that gets progressively darker over time. Data for **34**: IR (film) ν_{max} 3363, 2926, 2853, 1704, 1629, 1493, 1450, 1153, 1137, 929, 806, 732. ^{1}H NMR (600 MHz, $CDCl_3$) 0.84 (t, J = 7.1 Hz, 3H, $S(CH_2)_5CH_3$), 1.11 (m, J = 7.3 Hz, 2H, cyclohexane), 1.31-1.16 (m, overlapped peaks, 7H, $S(CH_2)_3CH_2CH_2CH_3$ and cyclohexane), 1.35 (quintet, J = 7.3 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.60-1.53 (quintet, overlapped peaks, J = 7.2 Hz, 3H, $SCH_2CH_2(CH_2)_3CH_3$ and cyclohexane), 1.71-1.68 (m, overlapped peaks, 2H, cyclohexane), 1.92 (dq, J = 12.4, 2.7 Hz, 2H, cyclohexane), 2.42-2.38 (dd, J = 19.4, 1.5 Hz, 1H, $COCH_2$), 2.42 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.88-2.84 (dd, J = 19.4, 6.1 Hz, 1H, $COCH_2$), 2.99-2.94 (m, 1H, cyclohexane), 3.89 (d, J = 7.3 Hz, 1H, NH), 3.95 (m, J = 3.1, 1.5 Hz, 1H, $COCH_2CHS$), 5.72 (d, J = 3.1 Hz, 1H, COC=CH); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 22.6 $S(CH_2)_4CH_2CH_3$), 24.8 (cyclohexane), 25.9 (cyclohexane), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 30.0 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.6 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 32.6

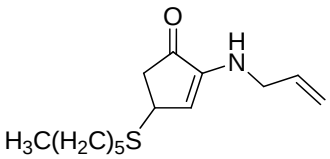
(cyclohexane), 40.9 ($COCH_2CH$), 43.1 ($COCH_2$), 52.5 (cyclohexane), 119.2 (COC=CH), 145.1 (COC=CH), 202.8 (C=O). HRMS (EI) $[M-H]^+$ found 294.18930, $C_{17}H_{28}NOS$ requires 294.18916.

2-(*tert*-butylamino)-4-(hexylthio)-cyclopent-2-enone 35



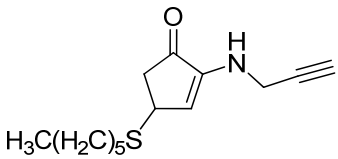
To a solution of enone **22** (0.108 g, 0.5 mmol) in dry MeCN (2 mL) was added *tert*-butylamine (0.053 mL, 0.5 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 20 hours. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (15 mL). The filtrate was concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (20:1 v/v) to afford **35** as a clear oil with a slight brown hue (0.032 g, 0.12 mmol, 24%) that gets progressively darker over time. Data for **35**: IR (film) ν_{max} 3386, 2958, 2926, 2856, 1707, 1628, 1502, 1458, 1365, 1232, 1120, 930, 809. ^{1}H NMR (600 MHz, $CDCl_3$) 0.88 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 1.31-1.25 (m and s, overlapped peaks, 13H, $S(CH_2)_3CH_2CH_2CH_3$ and CCH_3), 1.37 (quintet, J = 7.4 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.58 (quintet, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.42-2.38 (dd, J = 19.5, 1.6 Hz, 1H, $COCH_2$), 2.50 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.87-2.83 (dd, J = 19.5, 6.1 Hz, 1H, $COCH_2$), 3.99 (m, J = 3.1, 1.6 Hz, 1H, $COCH_2CHS$), 4.06 (br, 1H, NH), 5.87 (d, J = 3.1 Hz, 1H, COC=CH); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 22.7 $S(CH_2)_4CH_2CH_3$), 28.5 (CCH_3), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 30.1 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.4 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 41.2 ($COCH_2CH$), 42.2 ($COCH_2$), 50.3 ($CCH_3$), 120.0 (COC=CH), 142.9 (COC=CH), 203.9 (C=O). HRMS (EI) $[M+H]^+$ found 270.18899, $C_{15}H_{28}NOS$ requires 270.18916.

2-(allylamino)-4-(hexylthio)-cyclopent-2-enone 36



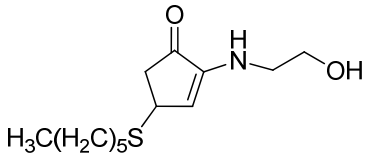
To a solution of enone **22** (0.108 g, 0.5 mmol) in dry MeCN (2 mL) was added allylamine (0.038 mL, 0.5 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 20 hours. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (8 mL). The filtrate was concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with DCM to afford **36** as a clear oil with a slight brown hue (0.084 g, 0.33 mmol, 66%) that gets progressively darker over time. Data for **36**: IR (film) ν_{max} 3375, 2954, 2924, 2855, 1703, 1632, 1494, 1147, 924, 812. ^{1}H NMR (600 MHz, $CDCl_3$) 0.86 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 1.30-1.23 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.35 (quintet, J = 7.3 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.56 (quintet, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.44-2.41 (dd, J = 19.4, 1.5 Hz, 1H, $COCH_2$), 2.50 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.91-2.87 (dd, J = 19.4, 6.0 Hz, 1H, $COCH_2$), 3.63 (br, 2H, NCH_2), 3.96 (m, J = 3.1, 1.4 Hz, 1H, $COCH_2CHS$), 4.12 (br, 1H, NH), 5.15-5.13 (dd, J = 10.3, 1.4 Hz, 1H, $NCH_2CH=CH_2$), 5.21-5.18 (dd, J = 17.2, 1.5 Hz, 1H $NCH_2CH=CH_2$), 5.79 (d, overlapped peaks, J = 3.1 Hz, 1H, $COC=CH$), 5.84-5.77 (m overlapped peaks, 1H, $NCH_2CH=CH_2$); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 22.6 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 30.0 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.6 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 40.7 ($COCH_2CH$), 43.1 ($COCH_2$), 46.7 ($NCH_2CH=CH_2$), 116.6 ($NCH_2CH=CH_2$), 120.8 ($NCH_2CH=CH_2$), 134.0 ($COC=CH$), 146.2 ($COC=CH$), 202.3 ($C=O$). HRMS (EI) $[M+H]^+$ found 254.15732, $C_{14}H_{24}NOS$ requires 254.15786.

4-(hexylthio)-2-(prop-2-ynylamino)-cyclopent-2-enone 37



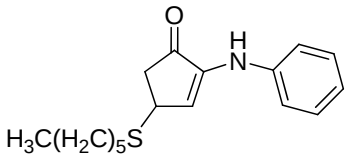
To a solution of enone **22** (0.108 g, 0.5 mmol) in dry MeCN (2 mL) was added propargylamine (0.034 mL, 0.5 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 20 hours. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (8 mL). The filtrate was concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with DCM to afford **37** as a brown oil (0.038 g, 0.15 mmol, 31%) that gets progressively darker over time. Data for **37**: IR (film) ν_{max} 3369, 3292, 2954, 2924, 2855, 1702, 1634, 1490, 1143, 928, 821. ^{1}H NMR (600 MHz, $CDCl_3$) 0.87 (t, J = 6.8 Hz, 3H, $S(CH_2)_5CH_3$), 1.30-1.23 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.37 (quintet, J = 7.3 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.58 (quintet, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.22 (t, J = 2.5 Hz, 1H, NCH_2CCH), 2.46-2.43 (dd, J = 19.4, 1.5 Hz, 1H, $COCH_2$), 2.50 (dt, J = 7.6, 2.8 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.93-2.89 (dd, J = 19.4, 6.1 Hz, 1H, $COCH_2$), 3.82 (d, J = 2.3 Hz, 2H, NCH_2CCH), 4.00 (m, J = 3.0, 1.5 Hz, 1H, $COCH_2CHS$), 4.20 (br, 1H, NH), 5.98 (d, J = 3.1 Hz, 1H, COC=CH); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 22.7 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 29.9 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.6 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 33.7 ($NCH_2CCH$), 40.6 ($COCH_2CH$), 43.1 ($COCH_2$), 72.0 ($NCH_2CCH$), 79.4 ($NCH_2CCH$), 122.7 (COC=CH), 145.4 (COC=CH), 201.9 (C=O). HRMS (EI) $[M]^+$ found 251.13462, $C_{14}H_{21}NOS$ requires 251.13438.

2-(2-hydroxyethylamino)-4-(hexylthio)-cyclopent-2-enone 38



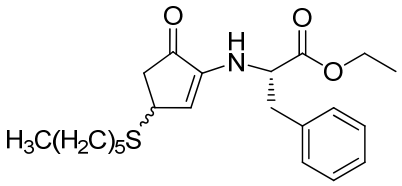
To a solution of enone **22** (0.108 g, 0.5 mmol) in dry MeCN (2 mL) was added ethanolamine (0.030 mL, 0.5 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 20 hours. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (8 mL). The filtrate was concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with DCM/ethanol (20:1 v/v) to afford **38** as a brown oil (0.066 g, 0.25 mmol, 51%) that gets progressively darker over time. Data for **38**: IR (film) ν_{max} 3379, 2954, 2925, 2856, 1698, 1631, 1498, 1458, 1152, 1061, 908, 728. ^{1}H NMR (600 MHz, $CDCl_3$) 0.85 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 1.29-1.23 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.35 (quintet, J = 7.3 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.56 (quintet, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.44-2.40 (dd, J = 19.5, 1.4 Hz, 1H, $COCH_2$), 2.51 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.91-2.86 (dd, J = 19.5, 6.0 Hz, 1H, $COCH_2$), 3.14 (m, J = 5.2, 2.5 Hz, 2H, $NHCH_2CH_2OH$), 3.73 (t, J = 5.2 Hz, 2H, $NHCH_2CH_2OH$), 3.95 (m, J = 3.3, 1.6 Hz, 1H, $COCH_2CHS$), 4.38 (t, J = 5.2 Hz, 1H, $NHCH_2CH_2OH$), 5.84 (d, J = 3.1 Hz, 1H, COC=CH); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 22.6 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 29.9 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.9 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 40.6 ($COCH_2CH$), 43.3 ($COCH_2$), 46.5 ($NHCH_2CH_2OH$), 60.8 ($NHCH_2CH_2OH$), 120.9 (COC=CH), 146.6 (COC=CH), 202.8 (C=O). HRMS (EI) $[M+H]^+$ found 258.15262, $C_{13}H_{24}NO_2S$ requires 258.15277.

4-(hexylthio)-2-(phenylamino)-cyclopent-2-enone 39



To a solution of enone **22** (0.108 g, 0.5 mmol) in dry MeCN (2 mL) was added aniline (0.046 mL, 0.5 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 20 hours (incomplete conversion). Then, the mixture was stirred at 70 ºC for 20 hours (incomplete conversion) after which $AlCl_3$ (6.7 mg, 0.05 mmol) was added and the mixture was stirred at 70 ºC for another 20 hours (complete conversion). Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (15 mL). To the filtrate was added water (5 mL) and layers were separated. The aqueous layer was further extracted with DCM (15 mL). Combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with DCM to afford **39** as a brown oil (0.038 g, 0.15 mmol, 31%) that gets progressively darker over time. Data for **39**: IR (film) ν_{max} 3337, 2954, 2924, 2855, 1706, 1631, 1598, 1529, 1498, 1444, 1295, 1095, 929, 747, 689. ^{1}H NMR (600 MHz, $CDCl_3$) 0.88 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 1.32-1.26 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.39 (quintet, J = 7.4 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.61 (quintet, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.54-2.50 (dd, J = 19.5, 1.6 Hz, 1H, $COCH_2$), 2.57 (t, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.99-2.95 (dd, J = 19.5, 6.2 Hz, 1H, $COCH_2$), 4.09 (m, J = 3.1, 1.6 Hz, 1H, $COCH_2CHS$), 6.31 (br, 1H, NH), 6.60 (d, J = 3.1 Hz, 1H, COC=CH), 6.97 (t, J = 7.4 Hz, 1H, Ph), 7.05 (d, overlapped peaks, J = 7.6 Hz, 2H, Ph), 7.31 (t, overlapped peaks, J = 7.6 Hz, 2H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 22.7 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 29.9 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.8 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 41.0 ($COCH_2CH$), 42.0 ($COCH_2$), 117.2 (overlapped, Ph), 121.7 (COC=CH), 123.7 (Ph), 129.6 (overlapped, Ph), 140.3 (Ph), 141.1 (COC=CH), 202.5 (C=O). HRMS (EI) $[M]^+$ found 289.14987, $C_{17}H_{23}NOS$ requires 289.15003.

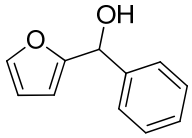
(*S*)-ethyl 2-(3-(hexylthio)-5-oxocyclopent-1-enylamino)-3-phenylpropanoate 40



To a solution of enone **22** (0.108 g, 0.5 mmol) in dry MeOH (2 mL) was added L-phenylalanine ethyl ester hydrochloride (0.115 g, 0.5 mmol) and 4Å molecular sieves (0.1 g). The mixture was stirred at room temperature for 2 days. Afterwards, the reaction mixture was filtered through a short plug of celite and the filter cake was washed with DCM (8 mL). The filtrate was concentrated under reduced pressure to yield a dark brown oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (10:1 v/v) to afford a separable diastereomeric mixture of diastereomer **40a** as a brown oil (0.034 g, 0.087 mmol, 17%) and diastereomer **40b** as a brown oil (0.040 g, 0.10 mmol, 20%). Both isolated diastereomers get progressively darker over time. Data for **40a**: IR (film) ν_{max} 3363, 2954, 2926, 2856, 1736, 1708, 1632, 1495, 1455, 1190, 1146, 1029, 929, 813, 742, 699. ^{1}H NMR (600 MHz, $CDCl_3$) 0.88 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 1.20 (t, J = 7.1 Hz, 3H, $COOCH_2CH_3$), 1.31-1.25 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.36 (quintet, J = 7.6 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.55 (quintet, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.43-2.40 (dd, J = 19.4, 1.5 Hz, 1H, $COCH_2$), 2.47 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.89-2.85 (dd, J = 19.4, 6.1 Hz, 1H, $COCH_2$), 3.03-3.00 (dd, J = 13.7, 7.1 Hz, 1H, $PhCH_2$), 3.12-3.09 (dd, J = 13.7, 5.9 Hz, 1H, $PhCH_2$), 3.90 (m, J = 2.9, 1.5 Hz, 1H, $COCH_2CHS$), 4.05 (dt, J = 6.8 Hz, 1H, $NHCHCOOEt$), 4.16-4.10 (m, overlapped peaks, J = 7.4 Hz, 2H, $COOCH_2CH_3$), 4.51 (d, J = 8.4 Hz, 1H, NH), 5.72 (d, J = 3.1 Hz, 1H, COC=CH), 7.14 (d, J = 7.0 Hz, 2H, Ph), 7.24-7.21 (m, overlapped peaks, J = 7.3 Hz, 1H, Ph), 7.29-7.25 (m, overlapped peaks, J = 7.5, 7.0 Hz, 2H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 14.3 ($COOCH_2CH_3$), 22.7 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 29.9 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.4 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5

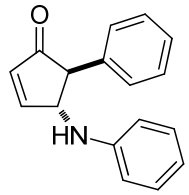
($SCH_2CH_2(CH_2)_3CH_3$), 38.3 (CH_2Ph), 40.5 ($COCH_2CH$), 43.0 ($COCH_2$), 58.5 ($NHCHCOOEt$), 61.4 ($COOCH_2CH_3$), 121.7 (Ph), 127.2 (COC=CH), 128.7 (overlapped, Ph), 129.3 (overlapped, Ph), 136.3 (Ph), 144.9 (COC=CH), 171.8 (COOEt), 201.6 (C=O). HRMS (EI) $[M-H]^+$ found 388.19428, $C_{22}H_{30}NO_3S$ requires 388.19464. Data for **40b**: IR (film) ν_{max} 3377, 2956, 2925, 2856, 1737, 1708, 1632, 1495, 1455, 1190, 1147, 1029, 929, 816, 742, 699. ^1H NMR (600 MHz, $CDCl_3$) 0.88 (t, J = 6.9 Hz, 3H, $S(CH_2)_5CH_3$), 1.18 (t, J = 7.1 Hz, 3H, $COOCH_2CH_3$), 1.31-1.25 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.36 (quintet, J = 7.6 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.57 (quintet, J = 7.6 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.44-2.401 (dd, J = 19.4, 1.5 Hz, 1H, $COCH_2$), 2.49 (t, J = 7.4 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.90-2.86 (dd, J = 19.4, 6.1 Hz, 1H, $COCH_2$), 3.06-3.02 (dd, J = 13.7, 6.8 Hz, 1H, $PhCH_2$), 3.12-3.09 (dd, J = 13.7, 6.3 Hz, 1H, $PhCH_2$), 3.93 (m, J = 3.0, 1.4 Hz, 1H, $COCH_2CHS$), 4.05 (q, J = 6.6 Hz, 1H, $NHCHCOOEt$), 4.15-4.10 (m, overlapped peaks, J = 7.1 Hz, 2H, $COOCH_2CH_3$), 4.50 (d, J = 8.4 Hz, 1H, NH), 5.75 (d, J = 3.1 Hz, 1H, COC=CH), 7.15 (d, J = 7.0 Hz, 2H, Ph), 7.25-7.22 (m, overlapped peaks, J = 7.0 Hz, 1H, Ph), 7.30-7.27 (m, overlapped peaks, J = 7.5, 7.0 Hz, 2H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 14.2 ($S(CH_2)_5CH_3$), 14.3 ($COOCH_2CH_3$), 22.7 $S(CH_2)_4CH_2CH_3$), 28.8 ($S(CH_2)_3CH_2CH_2CH_3$), 29.9 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.8 ($SCH_2CH_2(CH_2)_3CH_3$), 31.5 ($SCH_2CH_2(CH_2)_3CH_3$), 38.3 ($CH_2Ph$), 40.6 ($COCH_2CH$), 43.0 ($COCH_2$), 58.3 ($NHCHCOOEt$), 61.4 ($COOCH_2CH_3$), 121.4 (Ph), 127.2 (COC=CH), 128.7 (overlapped, Ph), 129.3 (overlapped, Ph), 136.1 (Ph), 150.0 (COC=CH), 171.9 (COOEt), 201.6 (C=O). HRMS (EI) $[M-H]^+$ found 388.19413, $C_{22}H_{30}NO_3S$ requires 388.19464.

(furan-2-yl)-(phenyl)-methanol 41



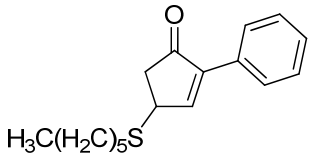
This compound was synthesised through an adaptation of the reported procedure.[2] To a solution of 2-furaldehyde (0.41 mL, 5 mmol) in dry tetrahydrofuran (5 mL) cooled to 0 ºC was added dropwise a 3 M solution of phenylmagnesium bromide in diethyl ether (1.8 mL, 5.4 mmol). A slow rate of addition is crucial for a high yield and should be equal or lower than 0.125 mL/min. The mixture was stirred while allowing it to rise to room temperature and then stirred for an additional 60 minutes. Then, the mixture was quenched with 5M ammonium chloride solution (30 mL). Next, the mixture was extracted with diethyl ether (3×60 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield **41** as a colourless oil (0.842 g, 4.8 mmol, 97%) which was deemed pure enough for the next synthetic step. Data for **41** in accordance with reference:[2] IR (film) ν_{max} 3358, 3062, 3030, 1493, 1452, 1141, 1008, 927, 813, 728, 697. ^{1}H NMR (600 MHz, $CDCl_3$) 2.49 (br, 1H, O*H*), 5.83 (s, 1H, C*H*OH), 6.12 (d, *J* = 3.3 Hz, 1H, COC=C*H*), 6.32 (dd, *J* = 3.2, 1.8 Hz, 1H, COC=CHC*H*), 7.35-7.32 (m, overlapped peaks, *J* = 7.3, 1.3 Hz, 2H, Ph and COC*H*=CH), 7.40-7.37 (m, overlapped peaks, *J* = 8.6, 7.7 Hz, 2H, Ph), 7.47-7.44 (m, overlapped peaks, *J* = 8.9, 7.0 Hz, 2H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) 70.2 (*C*HOH), 107.6 (COC=*C*H), 110.3 (COC=CH*C*H), 126.7 (Ph), 128.2 (Ph), 128.6 (Ph), 140.9 (Ph), 148.3 (CO*C*H=CH), 156.0 (CO*C*=CH). HRMS (EI) $[M]^+$ found 174.06839, $C_{11}H_{10}O_2$ requires 174.06808.

***trans*-5-phenyl-4-(phenylamino)-cyclopent-2-enone 42**



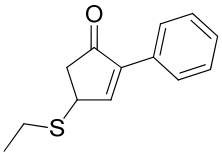
To a solution of compound **41** (0.174 g, 1 mmol) in dry MeCN (6 mL) was added aniline (0.092 mL, 1 mmol) and $Dy(OTf)_3$ (30 mg, 0.05 mmol). The mixture was stirred at 80 ºC for 4 hours. Then, the mixture was quenched with water (10 mL). The mixture was extracted with DCM (3×20 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil that was purified by flash chromatography on silica with petroleum ether/EtOAc (4:1 v/v) to afford **42** as a pale yellow solid (0.182 g, 0.73 mmol, 73%). Data for **42** in accordance with reference:[3] mp 83-86 ºC. IR (film) ν_{max} 3369, 1708, 1694, 1600, 1515, 1496, 1313, 1254, 1131, 918, 881, 746, 691. ^{1}H NMR (600 MHz, $CDCl_3$) 3.41 (d, *J* = 2.6 Hz, 1H, COC*H*Ph), 4.14 (br, 1H, N*H*), 4.76 (q, *J* = 1.5 Hz, 1H, COCHPhC*H*N), 6.41 (dd, *J* = 5.7, 1.6 Hz, 1H, COC*H*=CH), 6.54 (d, *J* = 7.8 Hz, 2H, Ph), 6.78 (t, *J* = 7.3 Hz, 1H, Ph), 7.17-7.14 (m, overlapped peaks, *J* = 8.5 Hz, 4H, Ph), 7.34-7.31 (m, overlapped peaks, *J* = 7.4 Hz, 1H, Ph), 7.39-7.36 (m, overlapped peaks, *J* = 7.6 Hz, 2H, Ph), 7.75 (dd, *J* = 5.7, 2.3 Hz, 1H, COCH=C*H*); ^{13}C NMR (150 MHz, $CDCl_3$) 60.2 (CO*C*HPh), 63.4 (COCHPh*C*HN), 114.0 (Ph), 118.7 (Ph), 127.6 (Ph), 128.2 (Ph), 129.2 (Ph), 129.6 (Ph), 134.7 (CO*C*H=CH), 138.2 (Ph), 146.4 (Ph), 162.2 (COCH=*C*H), 206.9 (*C*=O). HRMS (EI) $[M]^+$ found 249.11474, $C_{17}H_{15}NO$ requires 249.11536.

4-(hexylthio)-2-phenylcyclopent-2-enone 43



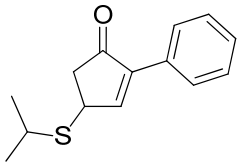
To a solution of compound **41** (0.087 g, 0.5 mmol) in dry MeCN (2 mL) was added aniline (0.044 mL, 0.48 mmol) and BF_3•OEt_2 (0.003 mL, 0.025 mmol). The mixture was stirred at 80 ºC for 2 hours. Then, added 1-hexanethiol (0.068 mL, 0.48 mmol), followed by addition of MeOH (1 mL) and KO^{t}Bu (0.014 g, 0.125 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was quenched with brine (10 mL) and the mixture was extracted with EtOAc (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (15:1 v/v) to afford **43** as a yellow oil (0.053 g, 0.19 mmol, 39%). Data for **43**: IR (film) ν_{max} 3058, 2954, 2925, 2855, 1705, 1494, 1447, 1303, 1128, 935, 762, 692. ^{1}H NMR (500 MHz, $CDCl_3$) 0.88 (t, J = 7.0 Hz, 3H, $S(CH_2)_5CH_3$), 1.32-1.26 (m, overlapped peaks, 4H, $S(CH_2)_3CH_2CH_2CH_3$), 1.39 (quintet, J = 7.0 Hz, 2H, $S(CH_2)_2CH_2(CH_2)_2CH_3$), 1.61 (quintet, J = 7.5, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.57 (t, J = 7.5 Hz, 2H, $SCH_2CH_2(CH_2)_3CH_3$), 2.63-2.59 (dd, J = 19.0, 2.0 Hz, 1H, $COCH_2$), 3.09-3.04 (dd, J = 19.0, 6.5 Hz, 1H, $COCH_2$), 4.03 (dt, J = 6.5, 3.0 Hz, 1H, $COCH_2CHS$), 7.40-7.34 (m, overlapped peaks, J = 7.1 Hz, 3H, Ph), 7.66 (d, J = 3.0 Hz, 1H, COC=CH), 7.72-7.70 (m, overlapped peaks, J = 7.0 Hz, 2H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) 14.1 ($S(CH_2)_5CH_3$), 22.6 $S(CH_2)_4CH_2CH_3$), 28.7 ($S(CH_2)_3CH_2CH_2CH_3$), 29.9 ($S(CH_2)_2CH_2(CH_2)_2CH_3$), 30.5 ($SCH_2CH_2(CH_2)_3CH_3$), 31.4 ($SCH_2CH_2(CH_2)_3CH_3$), 41.2 ($COCH_2CHS$), 44.6 ($COCH_2$), 127.3 (overlapped, Ph), 128.6 (overlapped, Ph), 129.0 (Ph), 130.8 (Ph), 143.2 (COC=CH), 157.5 (COC=CH), 205.1 (C=O). HRMS (EI) $[M]^+$ found 274.13840, $C_{17}H_{22}OS$ requires 274.13859.

4-(ethylthio)-2-phenylcyclopent-2-enone 44



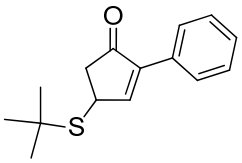
To a solution of compound **41** (0.174 g, 1 mmol) in dry MeCN (4 mL) was added aniline (0.088 mL, 0.96 mmol) and BF_3•OEt_2 (0.006 mL, 0.05 mmol). The mixture was stirred at 80 ºC for 2 hours. Then, added ethanethiol (0.074 mL, 1 mmol), followed by addition of MeOH (2 mL) and KO^{t}Bu (0.028 g, 0.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was quenched with brine (10 mL) and the mixture was extracted with EtOAc (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (10:1 v/v) to afford **44** as an orange oil (0.045 g, 0.21 mmol, 21%). Data for **44**: IR (film) ν_{max} 3057, 2968, 2925, 2870, 1702, 1494, 1447, 1304, 1267, 1128, 935, 762, 692. ^{1}H NMR (500 MHz, $CDCl_3$) 1.31 (t, J = 7.0 Hz, 3H, SCH_2CH_3), 2.64-2.59 (q, overlapped peaks, 2H, SCH_2CH_3), 2.63-2.59 (dd, J = 19.0, 2.5 Hz, 1H, $COCH_2$), 3.10-3.05 (dd, J = 19.0, 6.5 Hz, 1H, $COCH_2$), 4.05 (dt, J = 6.5, 2.5 Hz, 1H, $COCH_2CHS$), 7.41-7.33 (m, overlapped peaks, 3H, Ph), 7.67 (d, J = 3.0 Hz, 1H, COC=C*H*), 7.72-7.70 (m, overlapped peaks, 2H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) 15.1 (SCH_2CH_3), 24.6 (SCH_2CH_3), 41.0 ($COCH_2CHS$), 44.6 ($COCH_2$), 127.3 (overlapped, Ph), 128.6 (overlapped, Ph), 129.0 (Ph), 130.8 (Ph), 143.3 (COC=CH), 157.4 (COC=CH), 205.0 (C=O). HRMS (EI) $[M]^+$ found 218.07621, $C_{13}H_{14}OS$ requires 218.07599.

4-(isopropylthio)-2-phenylcyclopent-2-enone 45



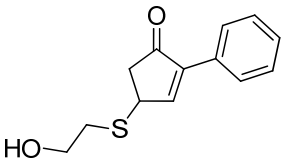
To a solution of compound **41** (0.174 g, 1 mmol) in dry MeCN (4 mL) was added aniline (0.088 mL, 0.96 mmol) and BF_3•OEt_2 (0.006 mL, 0.05 mmol). The mixture was stirred at 80 ºC for 2 hours. Then, added 2-propanethiol (0.093 mL, 1 mmol), followed by addition of MeOH (2 mL) and KO^{t}Bu (0.028 g, 0.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was quenched with brine (10 mL) and the mixture was extracted with EtOAc (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (10:1 v/v) to afford **45** as an orange oil (0.089 g, 0.38 mmol, 39%). Data for **45**: IR (film) ν_{max} 3056, 2960, 2924, 2865, 1703, 1494, 1447, 1304, 1129, 935, 762, 693. ^{1}H NMR (500 MHz, $CDCl_3$) 1.34 (2 overlapped d's, J = 6.5 Hz, 6H, SCH(CH_3)$_2$), 2.64-2.59 (dd, J = 19.0, 2.0 Hz, 1H, COCH_2), 3.06 (dd, J = 19.0, 6.5 Hz, 1H, COCH_2), 3.09 (m, J = 6.5 Hz, 1H, SCH(CH$_3$)$_2$), 4.07 (dt, J = 6.5, 2.0 Hz, 1H, COCH$_2$CHS), 7.40-7.34 (m, overlapped peaks, 3H, Ph), 7.67 (d, J = 3.0 Hz, 1H, COC=CH), 7.71-7.69 (m, overlapped peaks, 2H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) 23.9 (SCH(CH$_3$)$_2$), 24.2 (SCH(CH$_3$)$_2$), 35.7 (SCH(CH$_3$)$_2$) 40.4 (COCH$_2$$C$HS), 45.5 (CO$CH_2$), 127.4 (overlapped, Ph), 128.6 (overlapped, Ph), 128.9 (Ph), 130.9 (Ph), 143.0 (COC=CH), 157.5 (COC=CH), 205.1 (C=O). HRMS (EI) [M]$^+$ found 232.09188, $C_{14}H_{16}OS$ requires 232.09164.

4-(*tert*-butylthio)-2-phenylcyclopent-2-enone 46



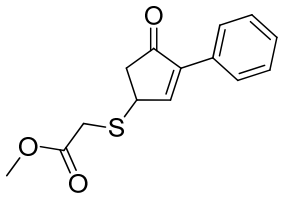
To a solution of compound **41** (0.174 g, 1 mmol) in dry MeCN (4 mL) was added aniline (0.088 mL, 0.96 mmol) and BF_3•OEt_2 (0.006 mL, 0.05 mmol). The mixture was stirred at 80 ºC for 2 hours. Then, added 2-methyl-2-propanethiol (0.113 mL, 1 mmol), followed by addition of MeOH (2 mL) and KO^tBu (0.028 g, 0.25 mmol) and the mixture was stirred for 2 hours at room temperature. Afterwards, the reaction mixture was quenched with brine (10 mL) and the mixture was extracted with EtOAc (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (10:1 v/v) to afford **46** as a yellow-brown solid (0.149 g, 0.61 mmol, 61%). Data for **46**: mp: 101-102 ºC. IR (solid) ν_{max} 3064, 2964, 2926, 2862, 1701, 1497, 1364, 1135, 933, 769, 695. ^{1}H NMR (500 MHz, $CDCl_3$) 1.42 (s, 9H, $SC(CH_3)_3$), 2.68-2.64 (dd, J = 19.0, 2.0 Hz, 1H, $COCH_2$), 3.14-3.09 (dd, J = 19.0, 6.5 Hz, 1H, $COCH_2$), 4.04 (dt, J = 6.5, 2.0 Hz, 1H, $COCH_2CHS$), 7.39-7.31 (m, overlapped peaks, 3H, Ph), 7.62 (d, J = 3.0 Hz, 1H, COC=CH), 7.71-7.69 (m, overlapped peaks, 2H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) 31.5 ($SC(CH_3)_3$), 39.1 ($COCH_2CHS$), 44.4 ($SC(CH_3)_3$), 47.2 ($COCH_2$), 127.3 (overlapped, Ph), 128.5 (overlapped, Ph), 128.9 (Ph), 130.9 (Ph), 142.7 (COC=CH), 158.1 (COC=CH), 205.3 (C=O). HRMS (EI) $[M]^+$ found 246.10706 $C_{15}H_{18}OS$ requires 246.10729.

4-((2-hydroxyethyl)thio)-2-phenylcyclopent-2-enone 47



To a solution of compound **41** (0.174 g, 1 mmol) in dry MeCN (4 mL) was added aniline (0.088 mL, 0.96 mmol) and BF_3•OEt_2 (0.006 mL, 0.05 mmol). The mixture was stirred at 80 ºC for 2 hours. Then, added 2-mercaptoethanol (0.07 mL, 1 mmol), followed by addition of MeOH (2 mL) and KO^{t}Bu (0.028 g, 0.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was quenched with brine (10 mL) and the mixture was extracted with EtOAc (2×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield an orange oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (10:1 v/v) to afford **47** as an orange oil (0.099 g, 0.42 mmol, 42%). Data for **47**: IR (film) ν_{max} 3399, 3057, 2921, 2874, 1698, 1494, 1304, 1130, 1044, 929, 763, 728, 693. ^{1}H NMR (500 MHz, $CDCl_3$) 2.50 (br, 1H, O*H*), 2.61-2.57 (dd, *J* = 19.0, 2.0 Hz, 1H, COC*H*$_2$), 2.77 (dt, *J* = 6.0, 2.5 Hz, 2H, HOCH$_2$C*H*$_2$S), 3.08-3.03 (dd, *J* = 19.0, 6.5 Hz, 1H, COC*H*$_2$), 3.77 (dt, *J* = 6.0, 2.5 Hz, 2H, HOC*H*$_2$CH$_2$S), 4.08 (dt, *J* = 6.5, 2.0 Hz, 1H, COCH$_2$C*H*S), 7.39-7.32 (m, overlapped peaks, 3H, Ph), 7.65 (d, *J* = 3.0 Hz, 1H, COC=C*H*), 7.70-7.68 (m, overlapped peaks, 2H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) 33.6 (HOCH$_2$*C*H$_2$S), 41.1 (COCH$_2$*C*HS), 44.6 (CO*C*H$_2$), 61.6 (HO*C*H$_2$CH$_2$S), 127.3 (overlapped, Ph), 128.6 (overlapped, Ph), 129.1 (Ph), 130.6 (Ph), 143.5 (CO*C*=CH), 157.1 (COC=*C*H), 205.0 (*C*=O). HRMS (EI) $[M]^+$ found 234.07121, $C_{13}H_{14}O_2S$ requires 234.07090.

methyl 2-((4-oxo-3-phenylcyclopent-2-en-1-yl)thio)acetate 48



To a solution of compound **41** (0.174 g, 1 mmol) in dry MeCN (4 mL) was added aniline (0.088 mL, 0.96 mmol) and BF_3•OEt_2 (0.006 mL, 0.05 mmol). The mixture was stirred at 80 ºC for 2 hours. Then, added methylthioglycolate (0.089 mL, 1 mmol), followed by addition of MeOH (2 mL) and KO^{t}Bu (0.028 g, 0.25 mmol) and the mixture was stirred for 60 minutes at room temperature. Afterwards, the reaction mixture was quenched with brine (10 mL) and the mixture was extracted with EtOAc (3×20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a dark orange oil which was purified by flash chromatography on silica with petroleum ether/EtOAc (4:1 v/v) to afford **48** as an orange oil (0.127 g, 0.49 mmol, 49%). Data for **48**: IR (film) ν_{max} 3356, 2954, 2926, 2857, 1702, 1397, 1280, 1128, 764, 694. ^{1}H NMR (500 MHz, $CDCl_3$) 2.59-2.55 (dd, J = 19.0, 2.0 Hz, 1H, COCH_2), 3.07-3.02 (dd, J = 19.0, 6.5 Hz, 1H, COCH_2), 3.28 (s, 1H, SCH_2CO$_2$CH$_3$), 3.30 (s, 1H, SCH_2CO$_2$CH$_3$), 3.68 (s, 3H, SCH$_2$CO$_2$CH_3), 4.18 (dt, J = 6.5, 2.0 Hz, 1H, COCH$_2$CHS), 7.38-7.32 (m, overlapped peaks, 3H, Ph), 7.66 (d, J = 3.0 Hz, 1H, COC=CH), 7.70-7.68 (m, overlapped peaks, 2H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) 32.3 (SCH$_2$CO$_2$CH$_3$), 41.7 (COCH$_2$$C$HS), 44.0 (CO$CH_2$), 52.7 (SCH$_2CO_2$$CH_3$), 127.4 (overlapped, Ph), 128.6 (overlapped, Ph), 129.1 (Ph), 130.6 (Ph), 143.9 (COC=CH), 156.1 (COC=CH), 170.7 (SCH$_2$$CO_2CH_3$), 204.4 ($C$=O). HRMS (EI) $[M]^+$ found 262.06576, $C_{14}H_{14}O_3S$ requires 262.06582.

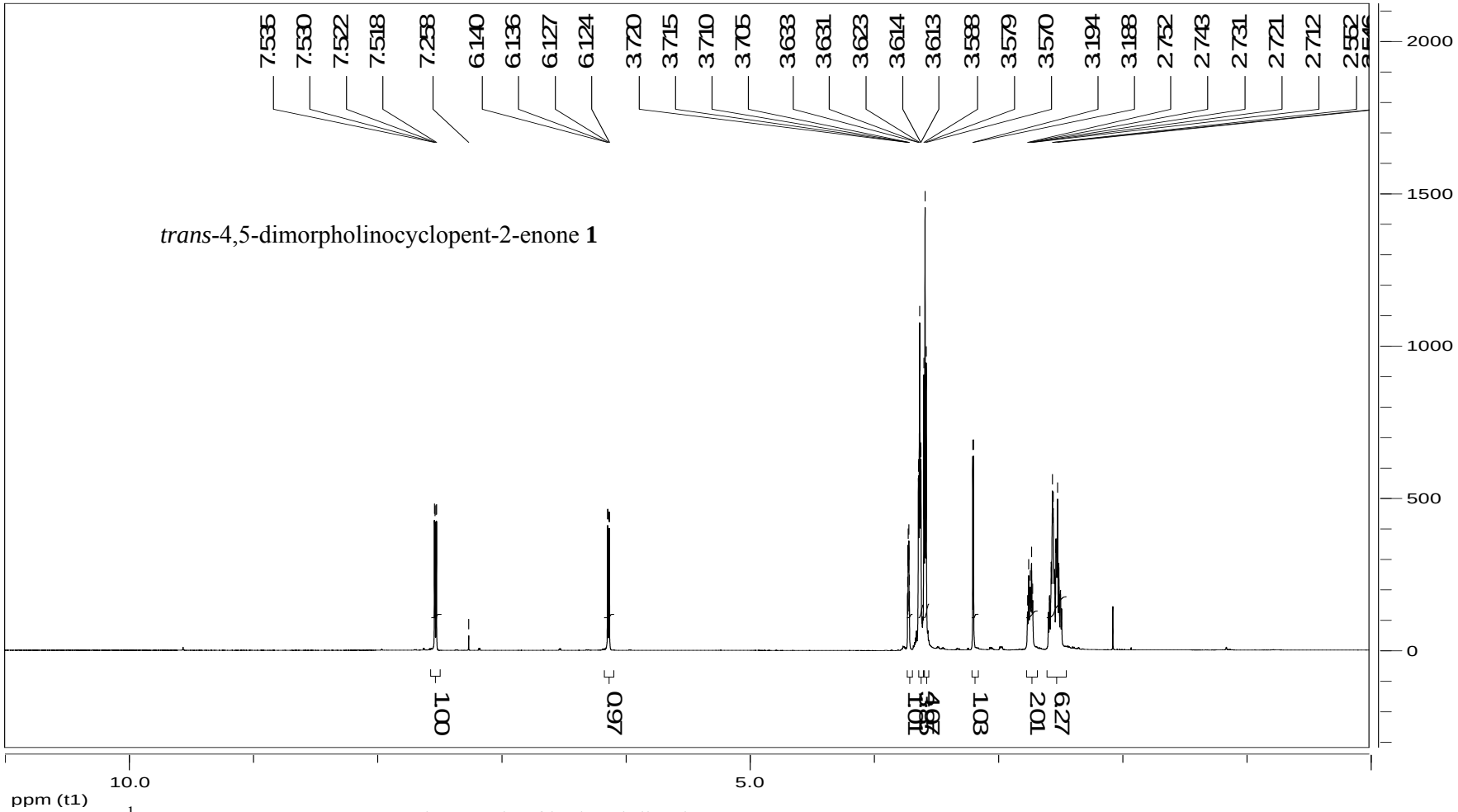


Figure S3 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated diamine **1**.

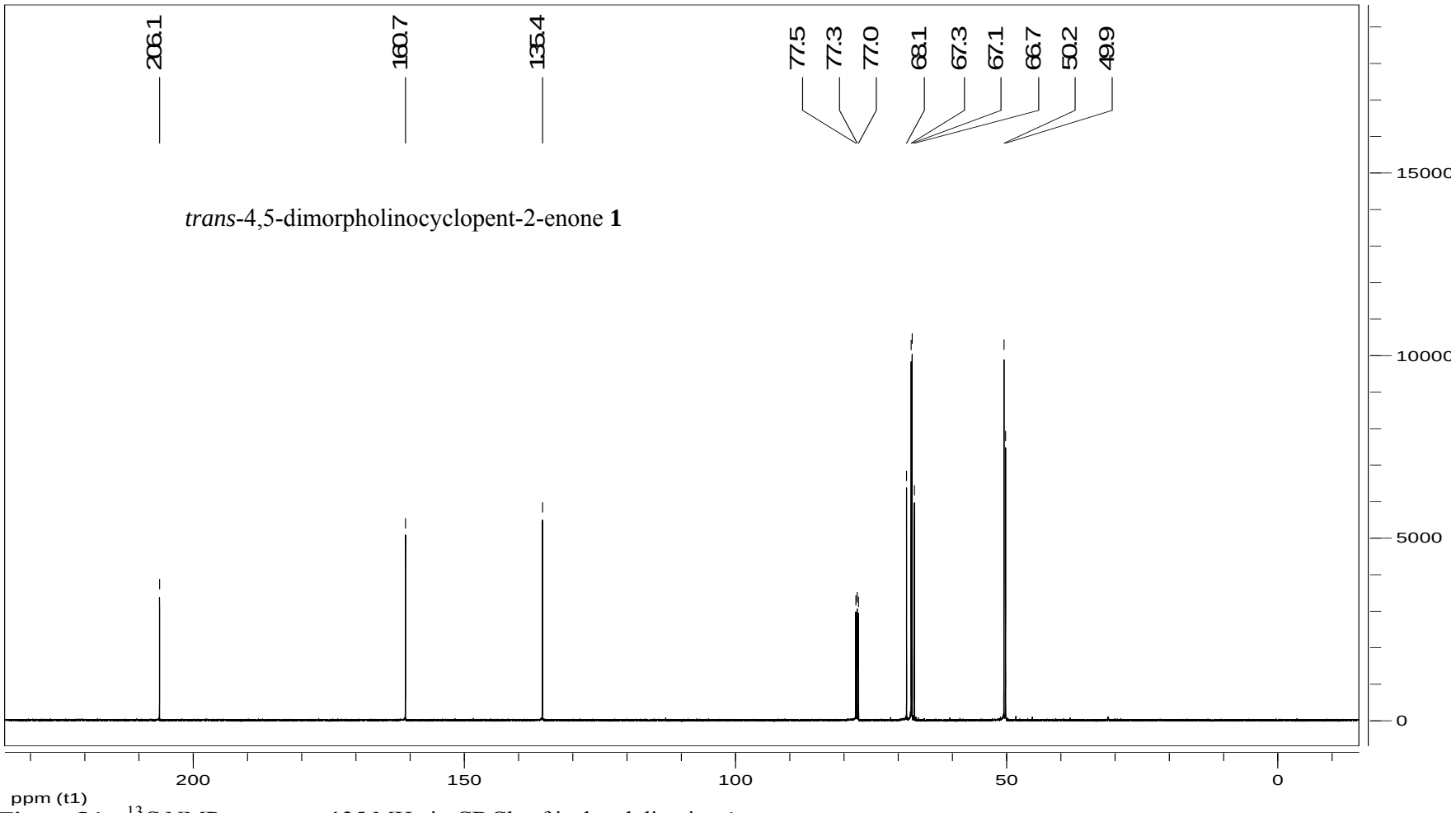


Figure S4 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated diamine **1**.

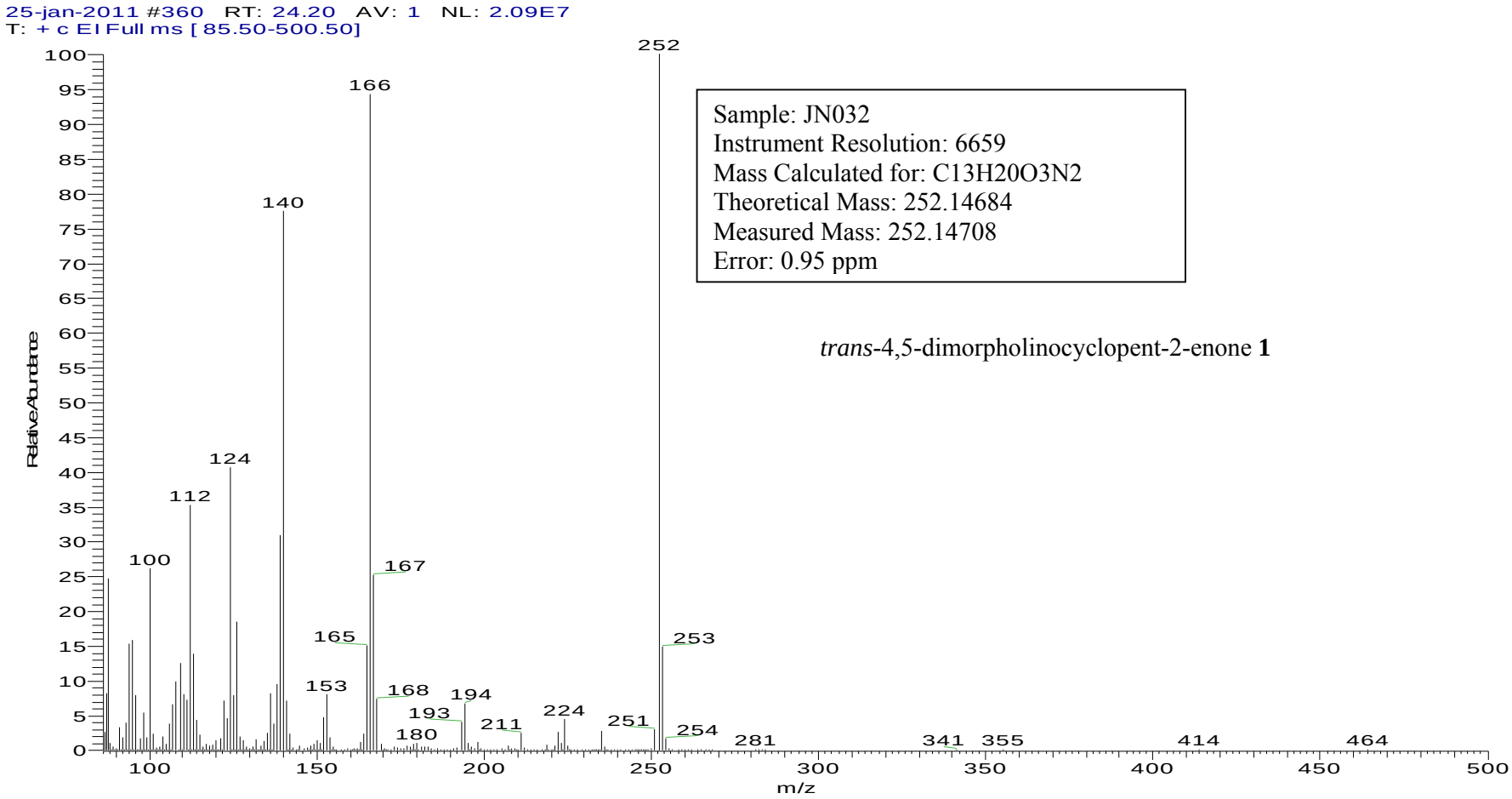


Figure S5 – EI mass spectra for exact mass measurement of isolated diamine **1**.

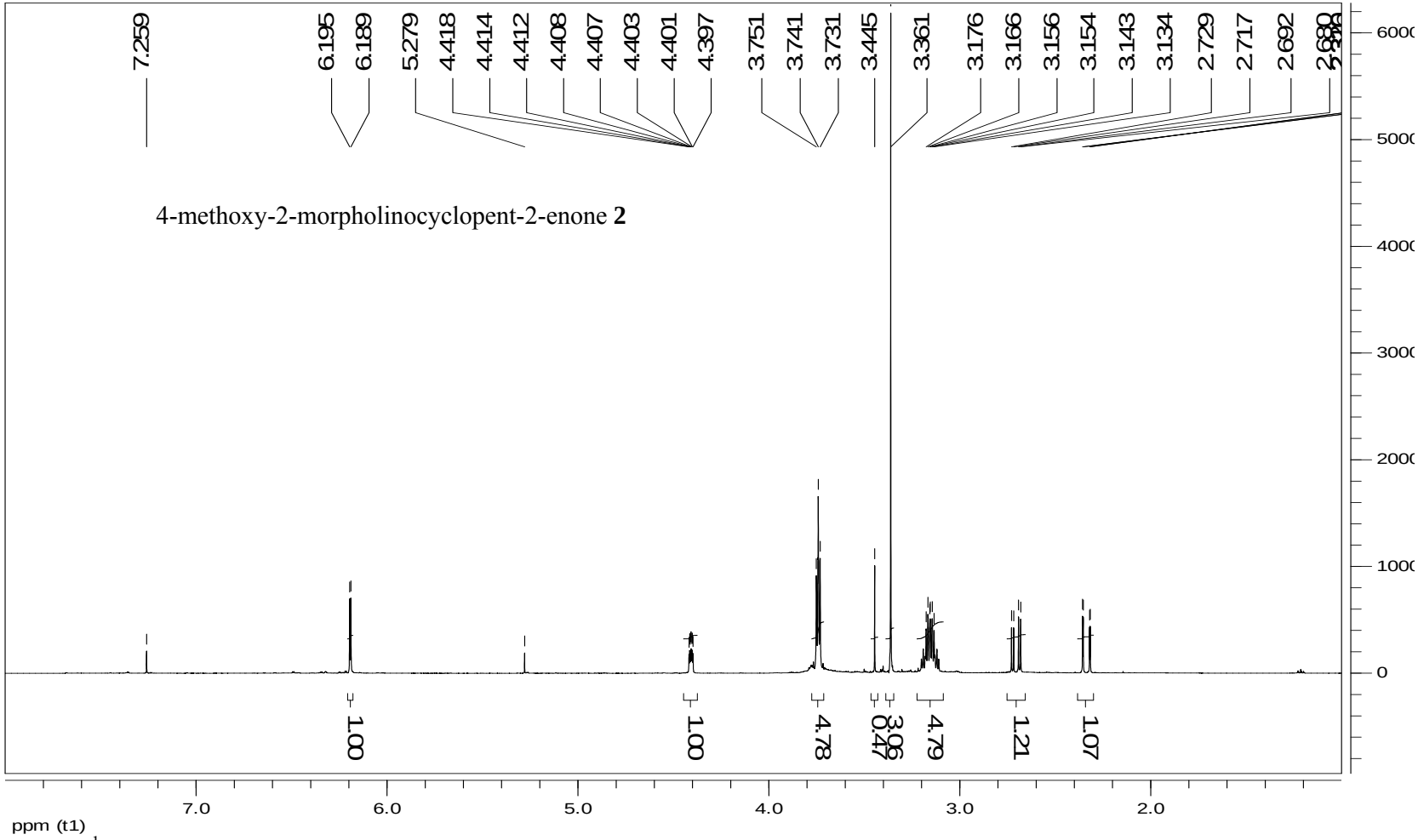


Figure S6 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated enone **2**.

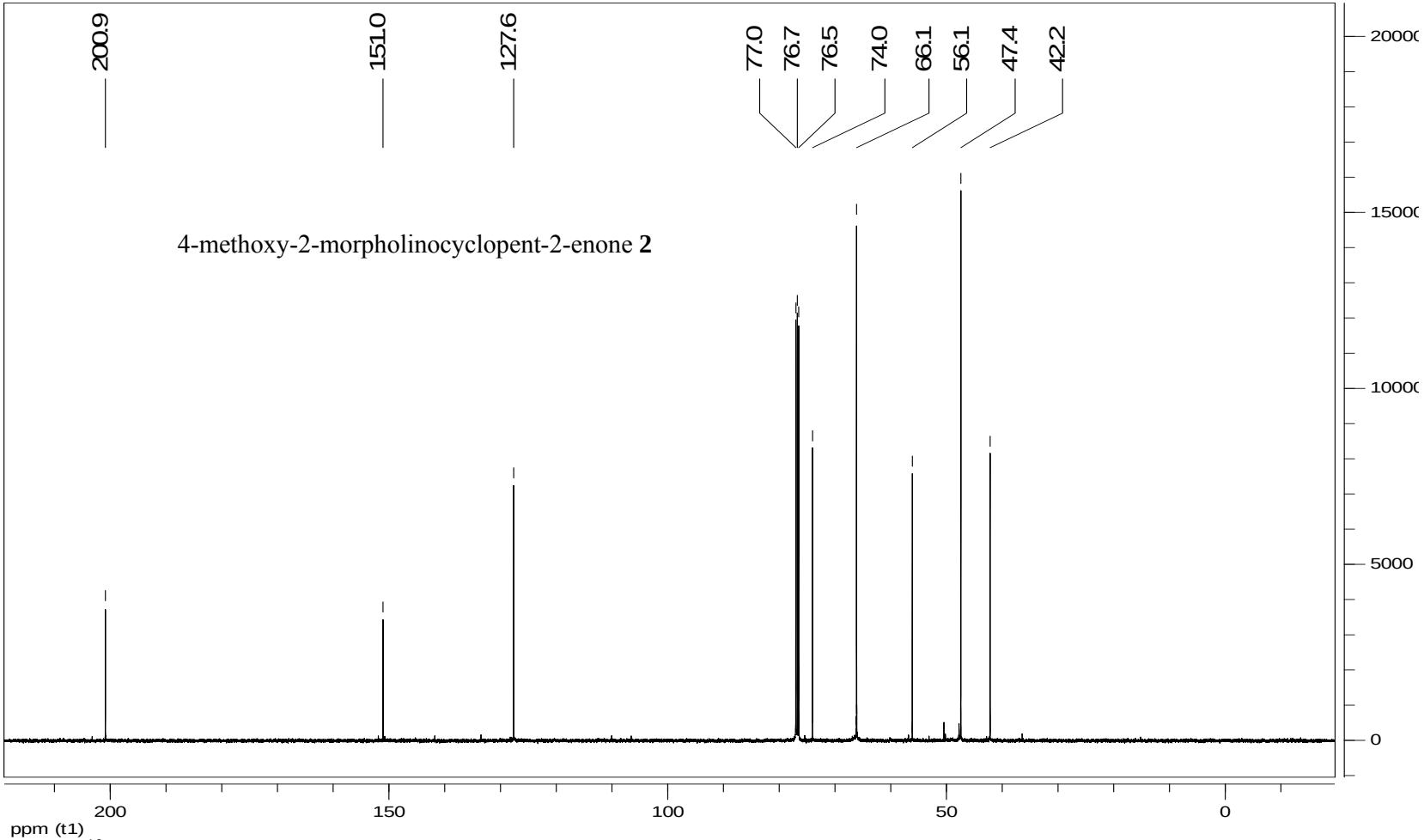
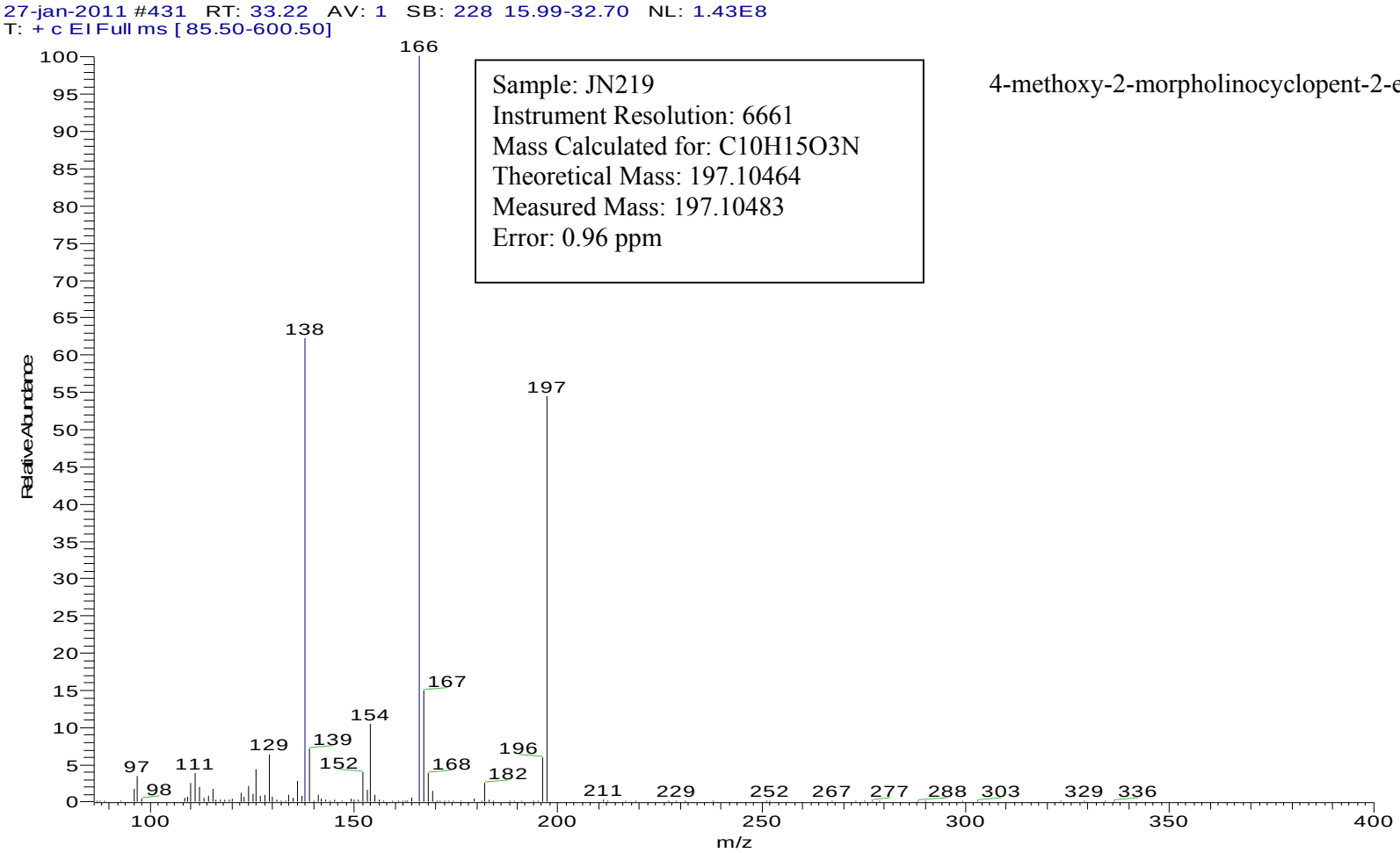


Figure S7 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated enone **2**.



4-methoxy-2-morpholinocyclopent-2-enone **2**

Figure S8 – EI mass spectra for exact mass measurement of isolated enone **2**.

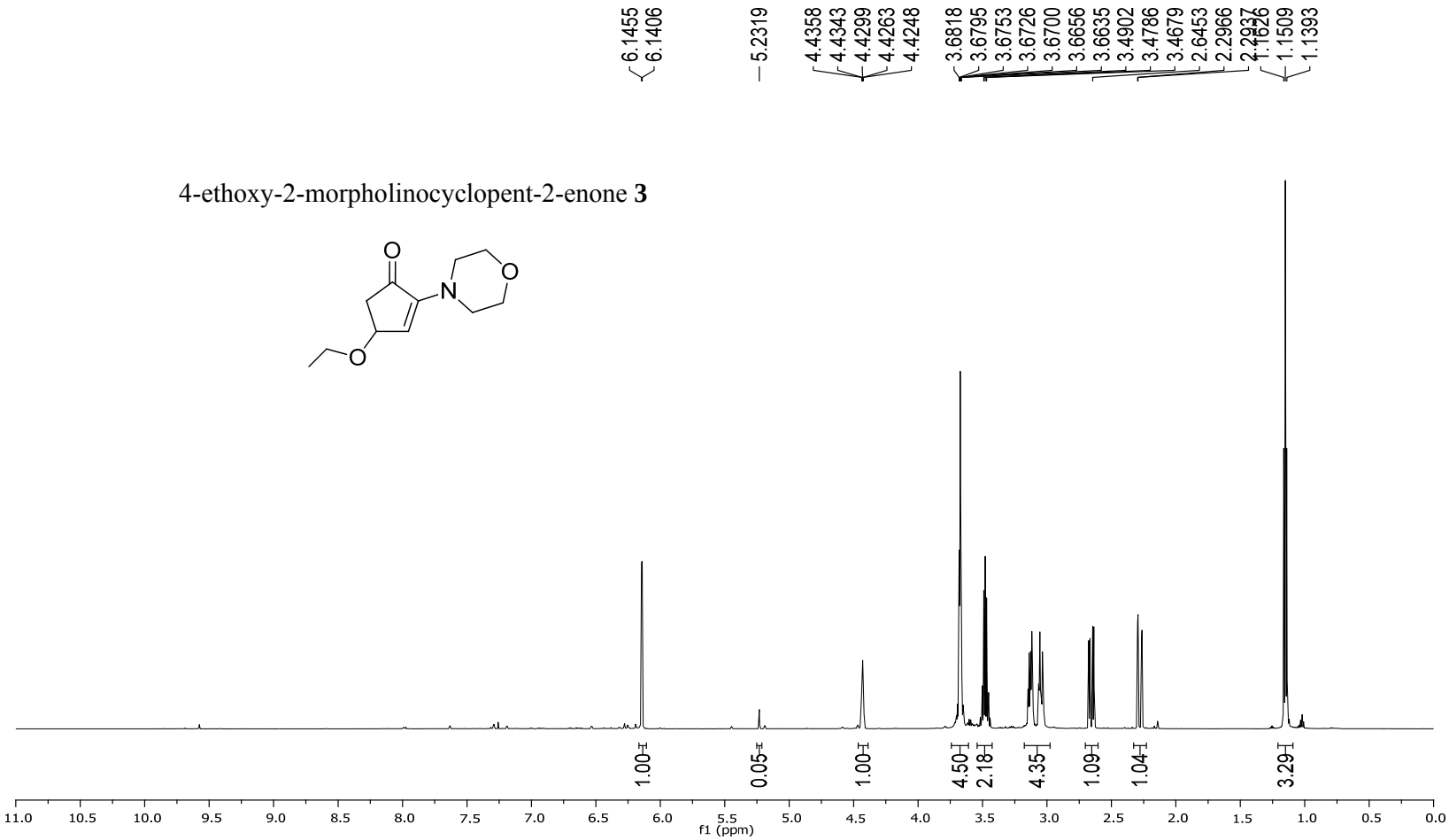


Figure S9 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **3**.

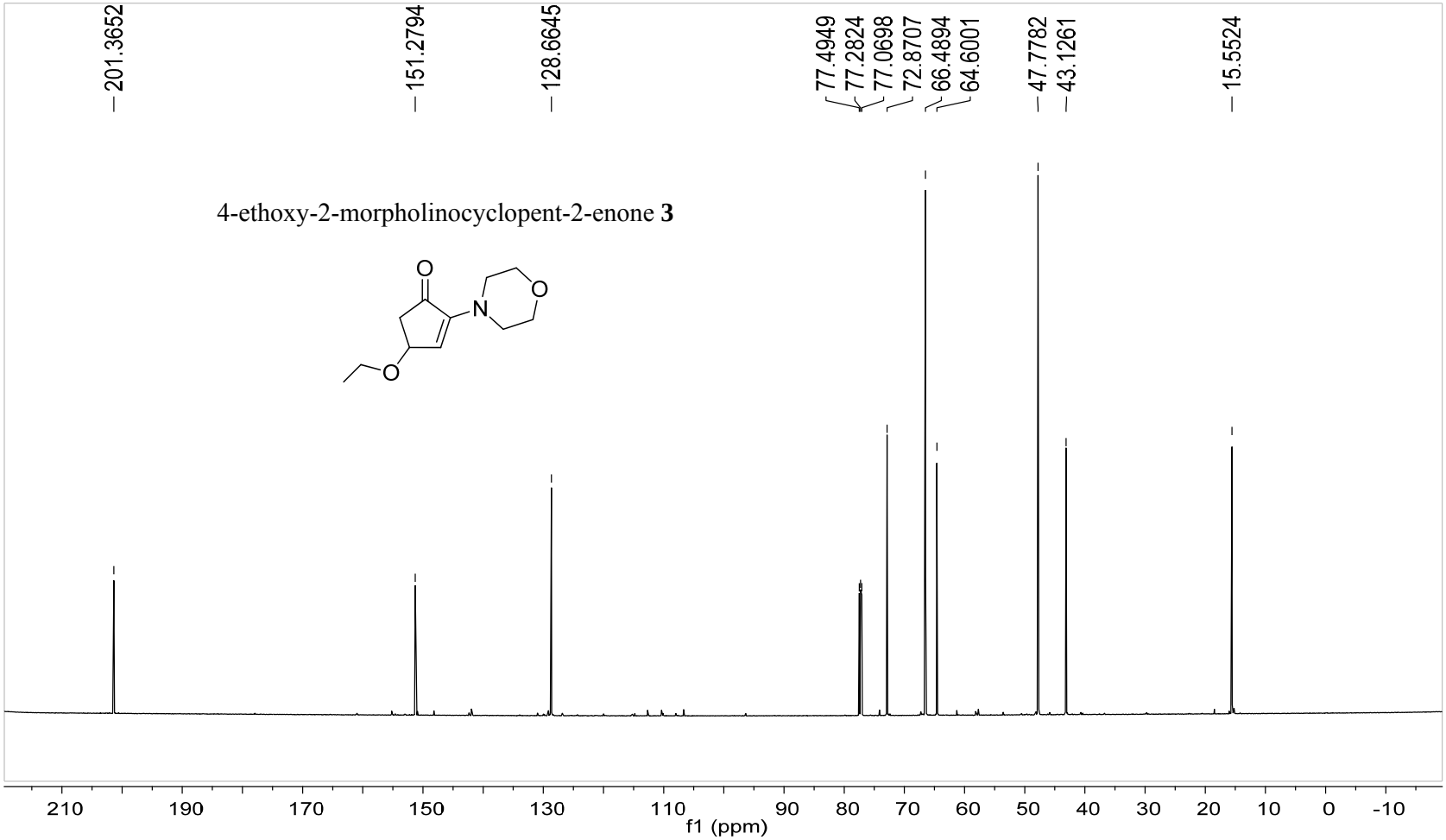


Figure S10 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **3**.

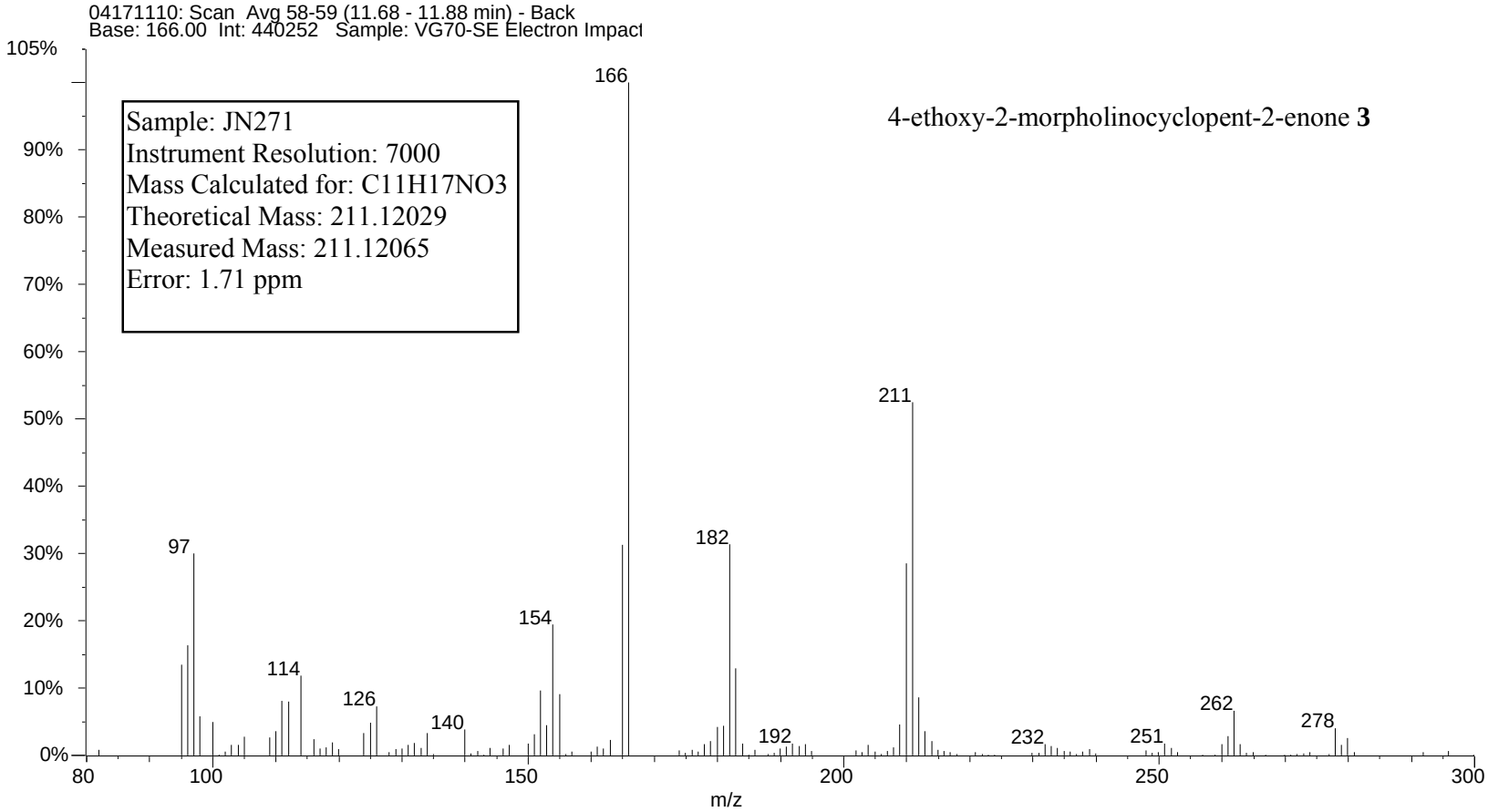


Figure S11 – EI mass spectra for exact mass measurement of isolated enone **3**.

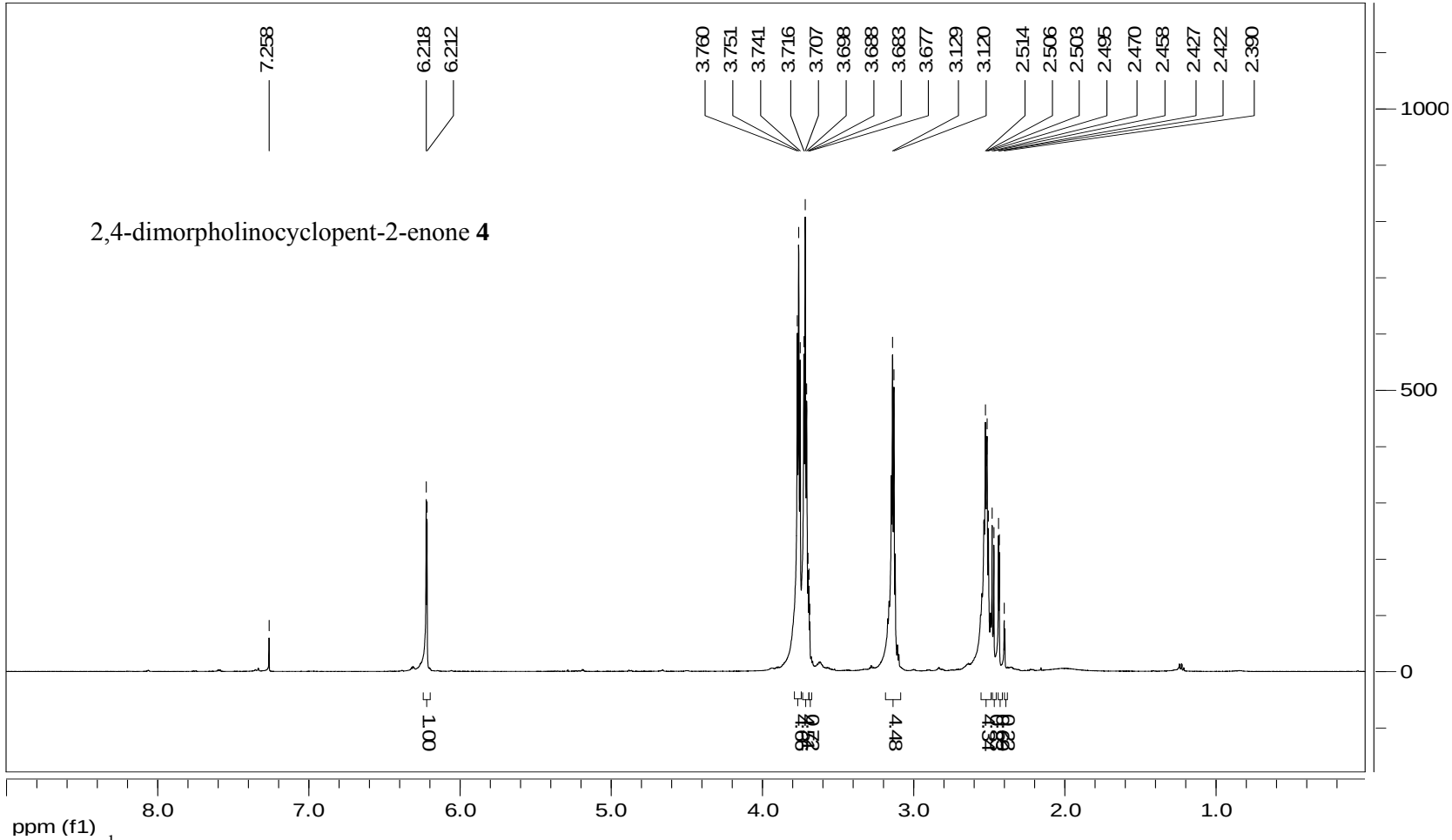


Figure S12 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated diamine **4**.

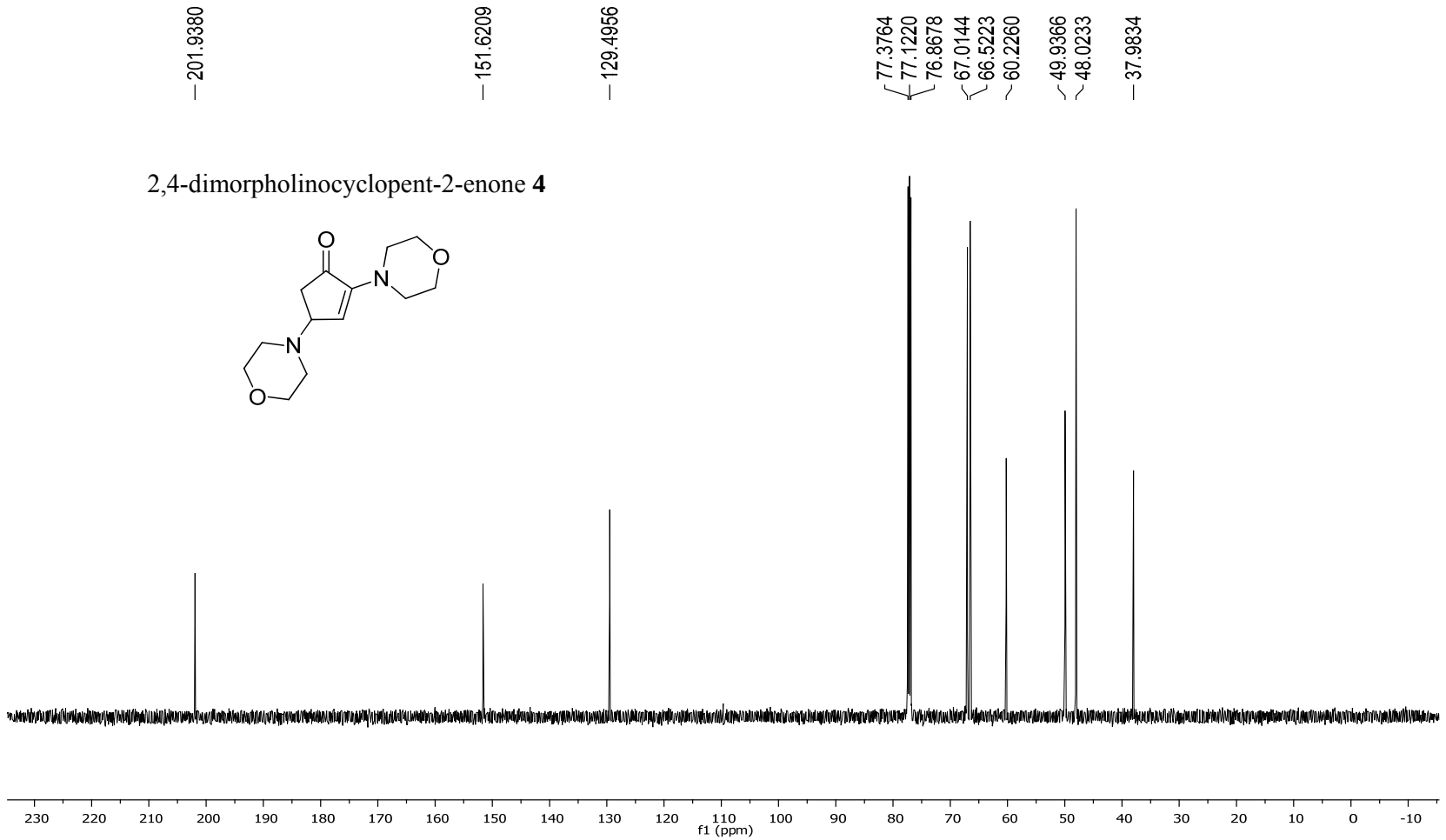


Figure S13 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated diamine **4**.

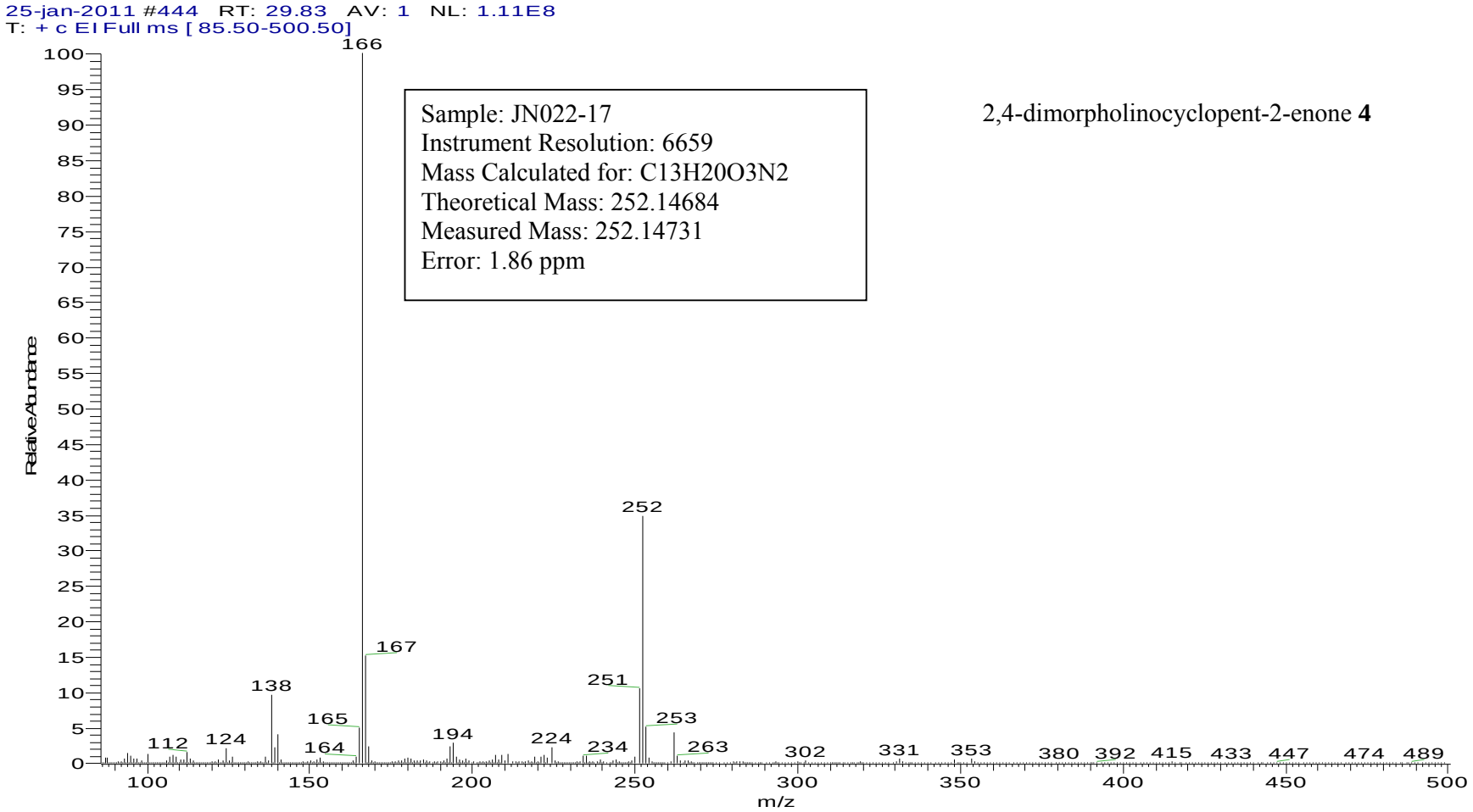


Figure S14 – EI mass spectra for exact mass measurement of isolated diamine **4**.

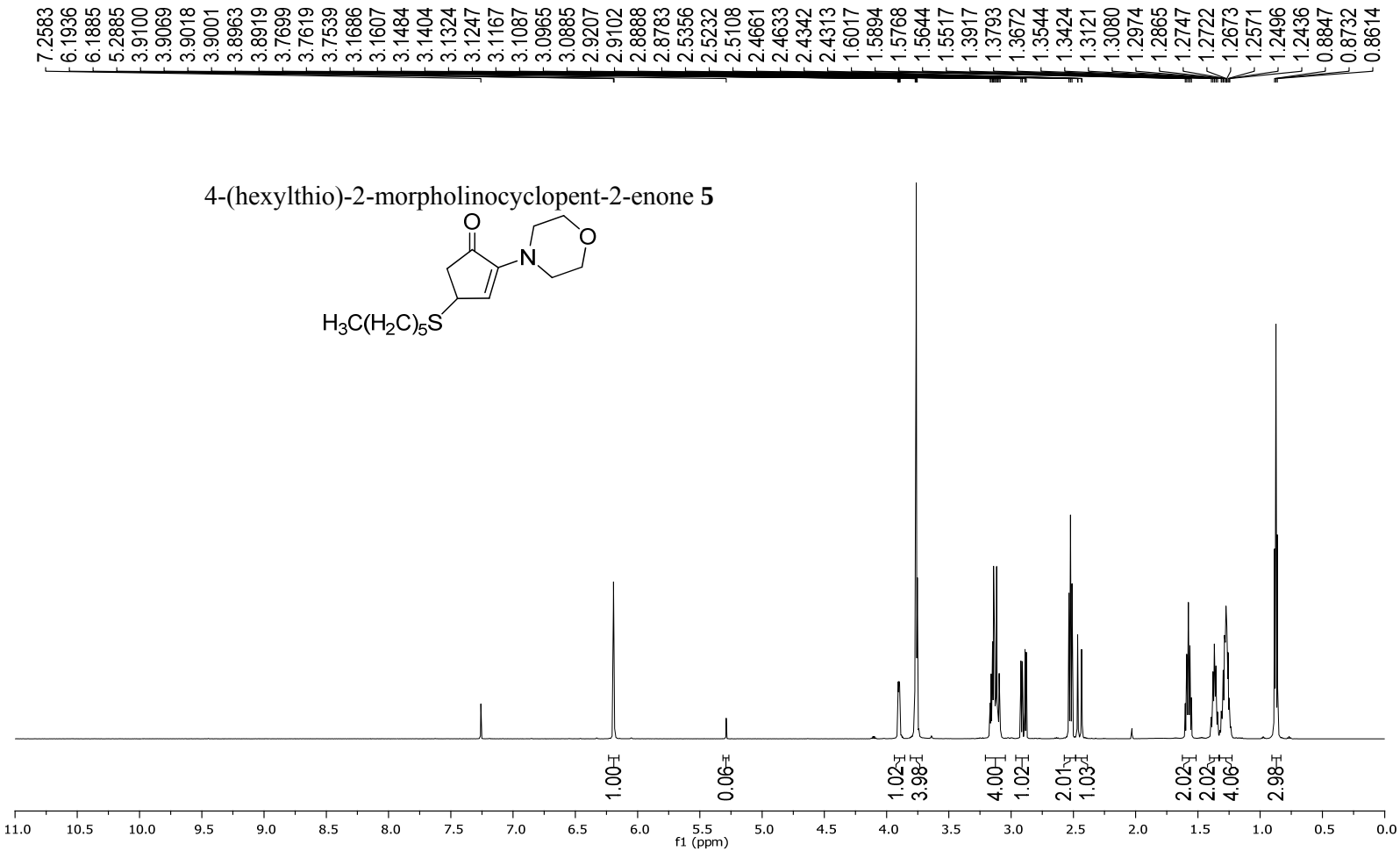


Figure S15 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **5**.

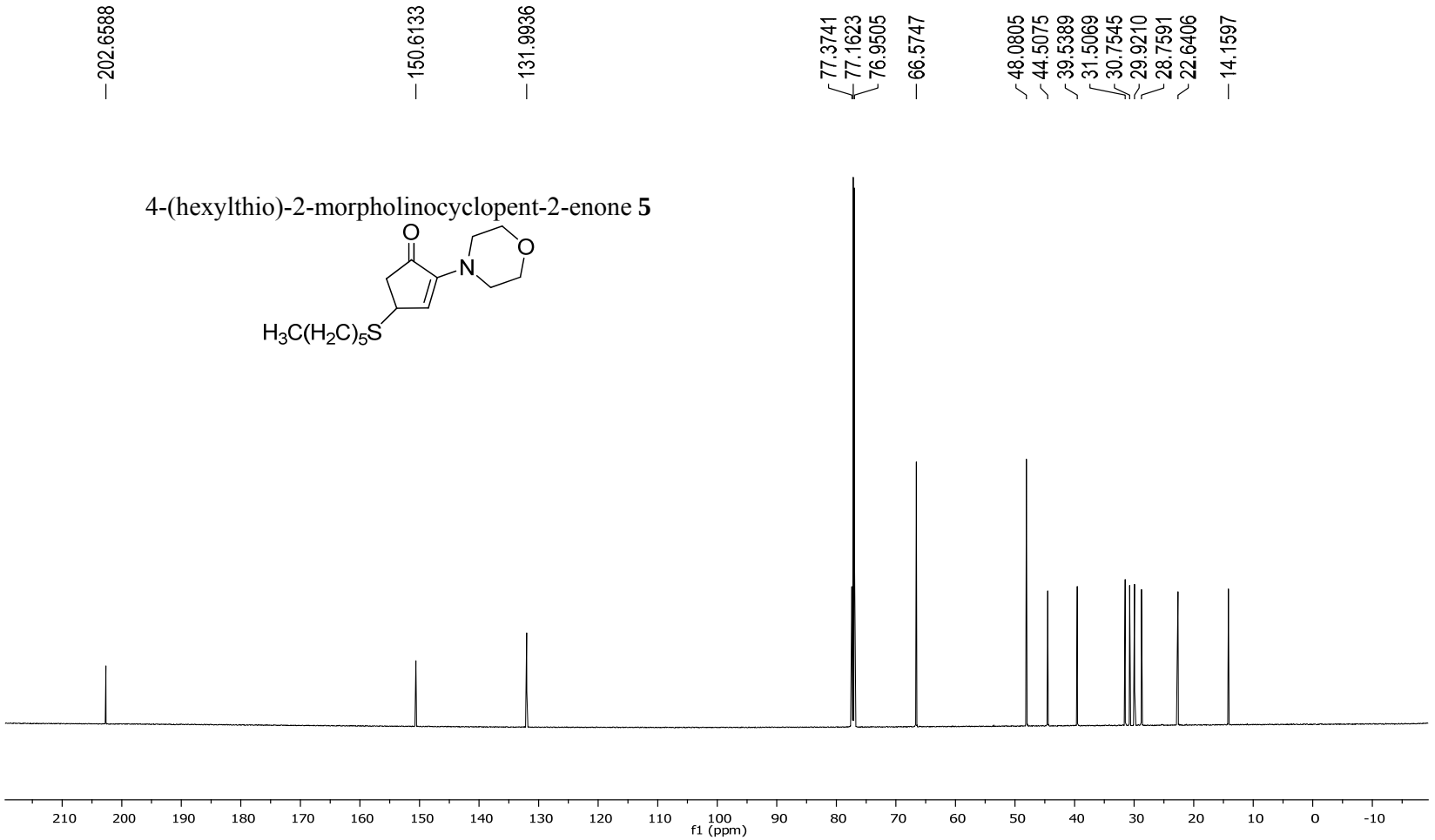


Figure S16 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **5**.

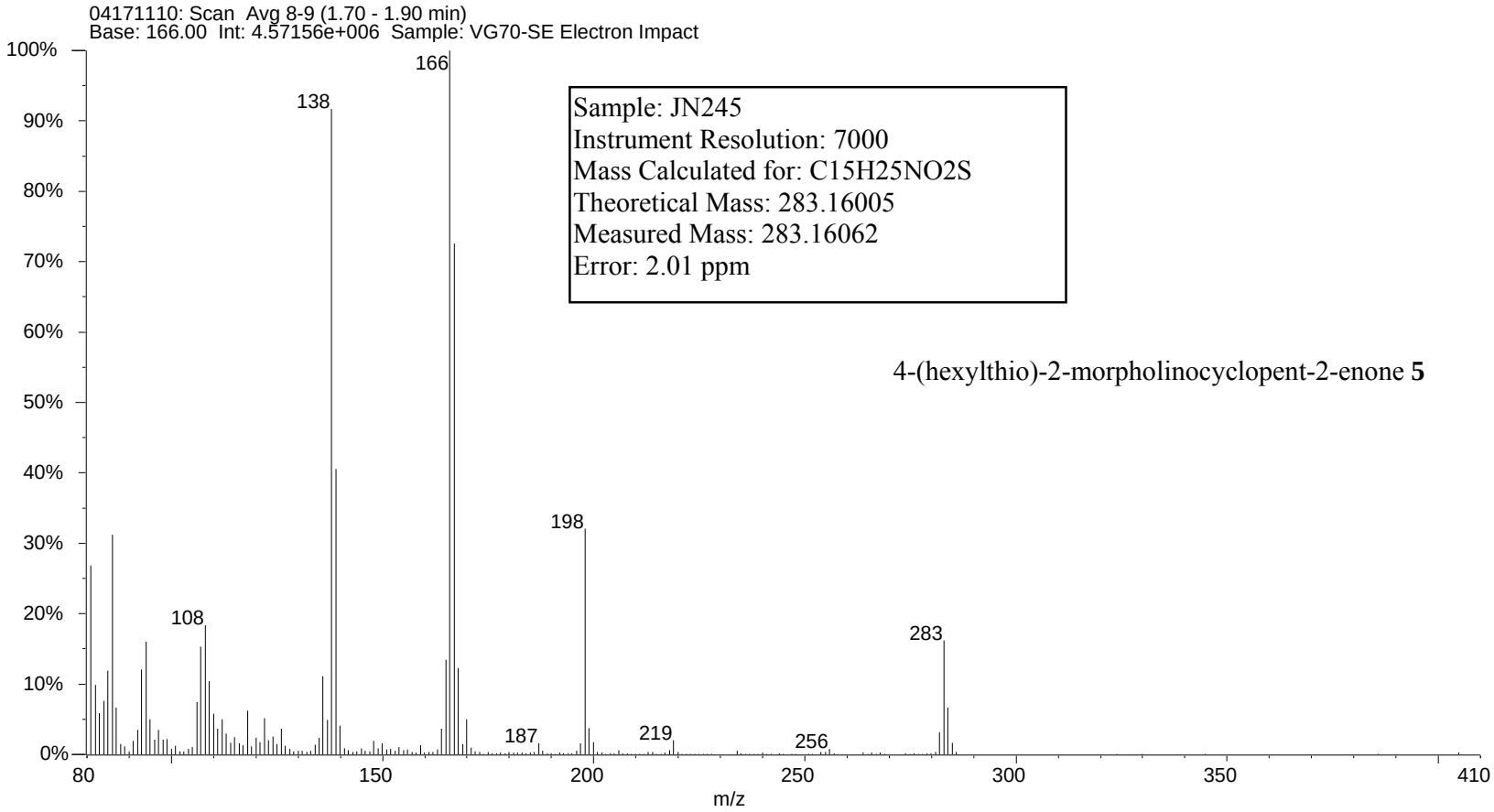


Figure S17 – EI mass spectra for exact mass measurement of isolated enone **5**.

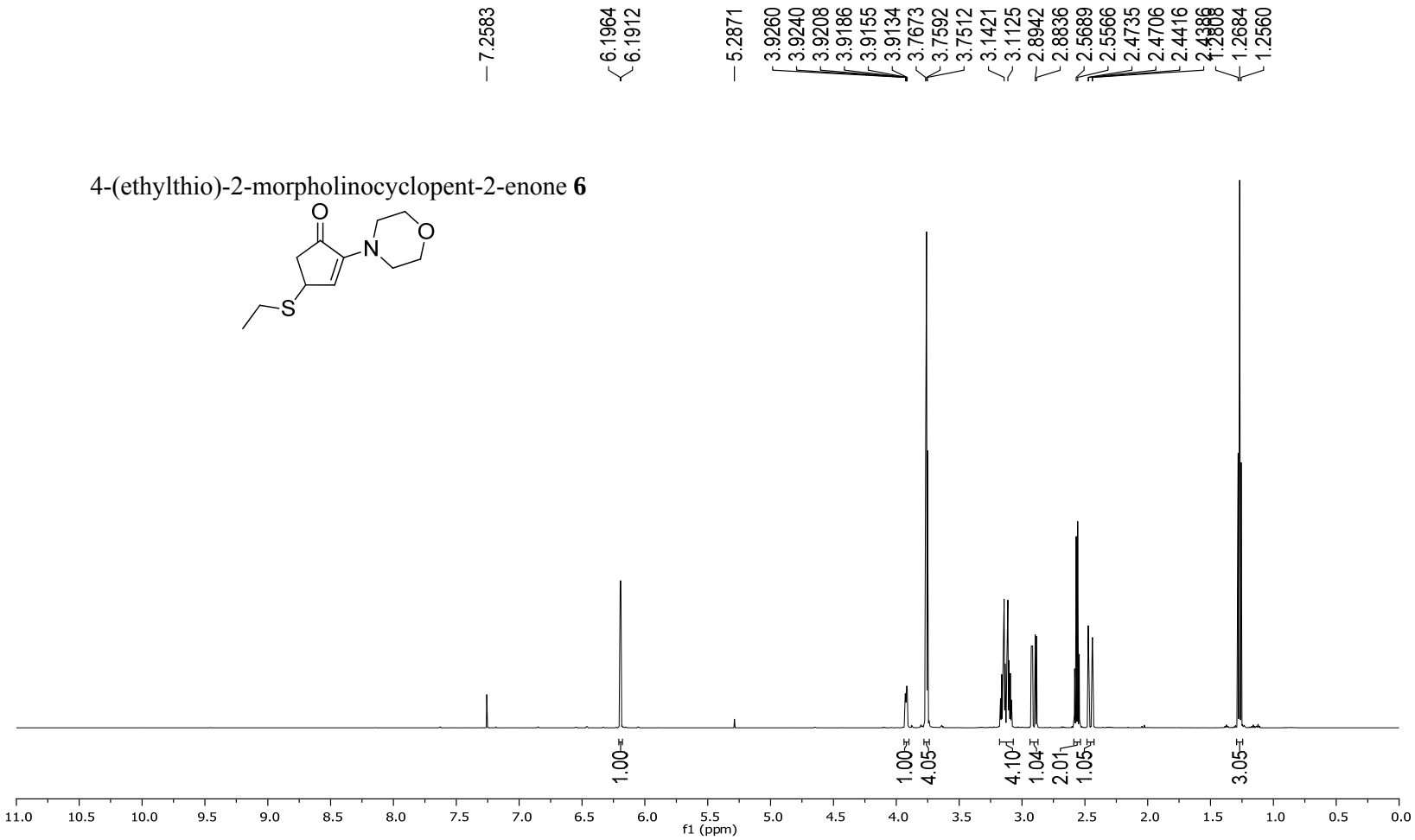


Figure S18 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **6**.

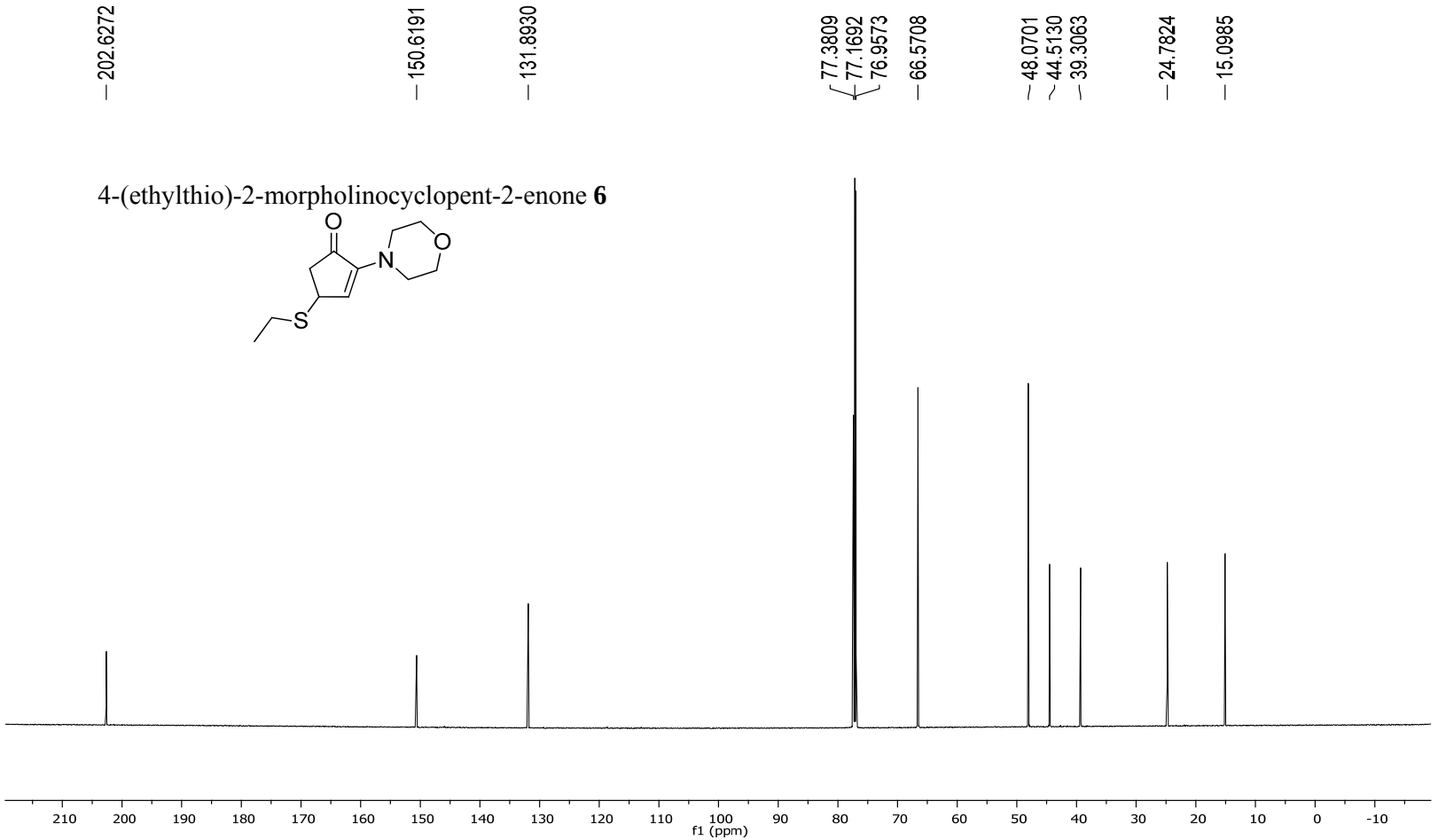


Figure S19 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **6**.

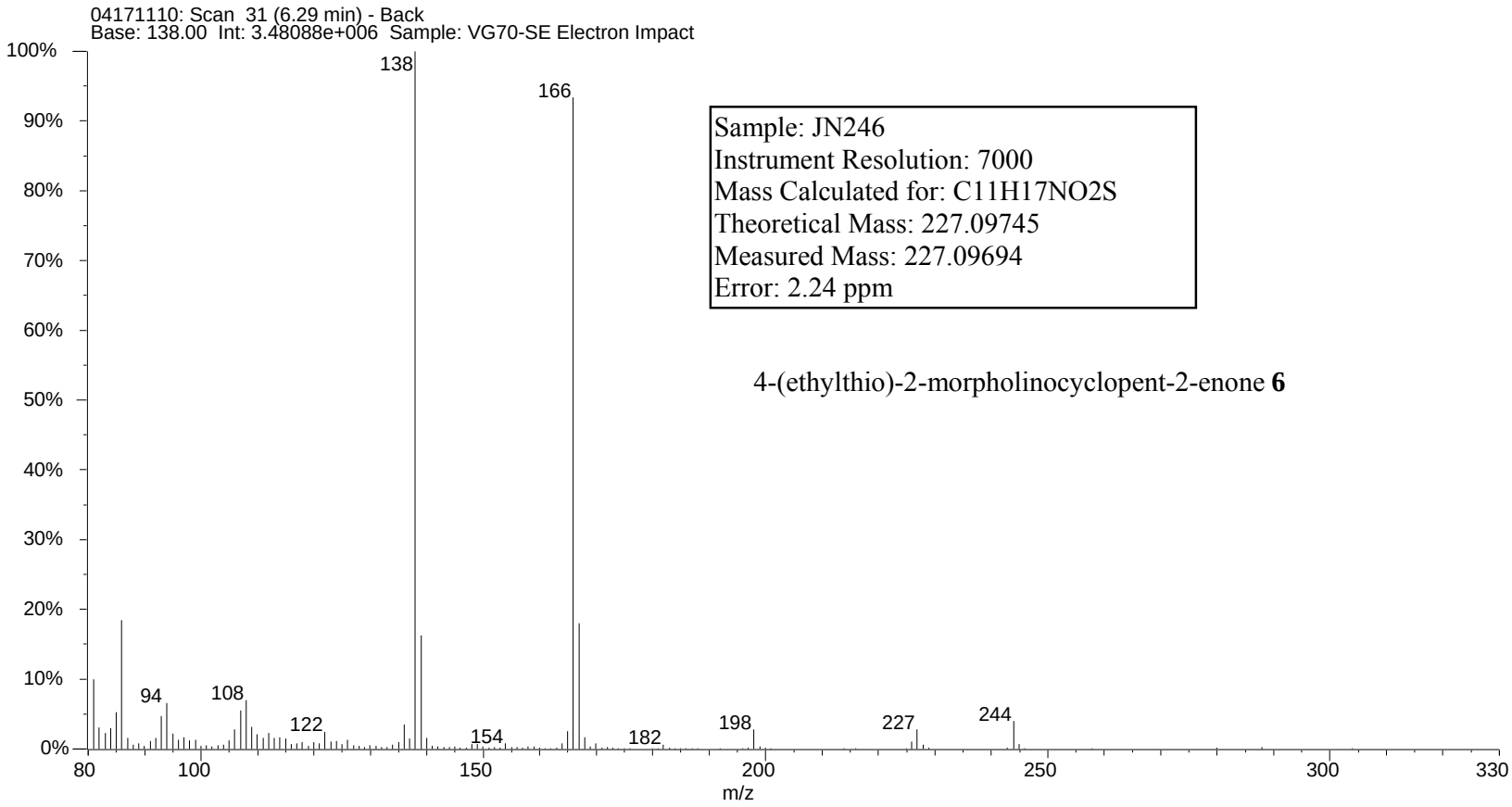


Figure S20 – EI mass spectra for exact mass measurement of isolated enone **6**.

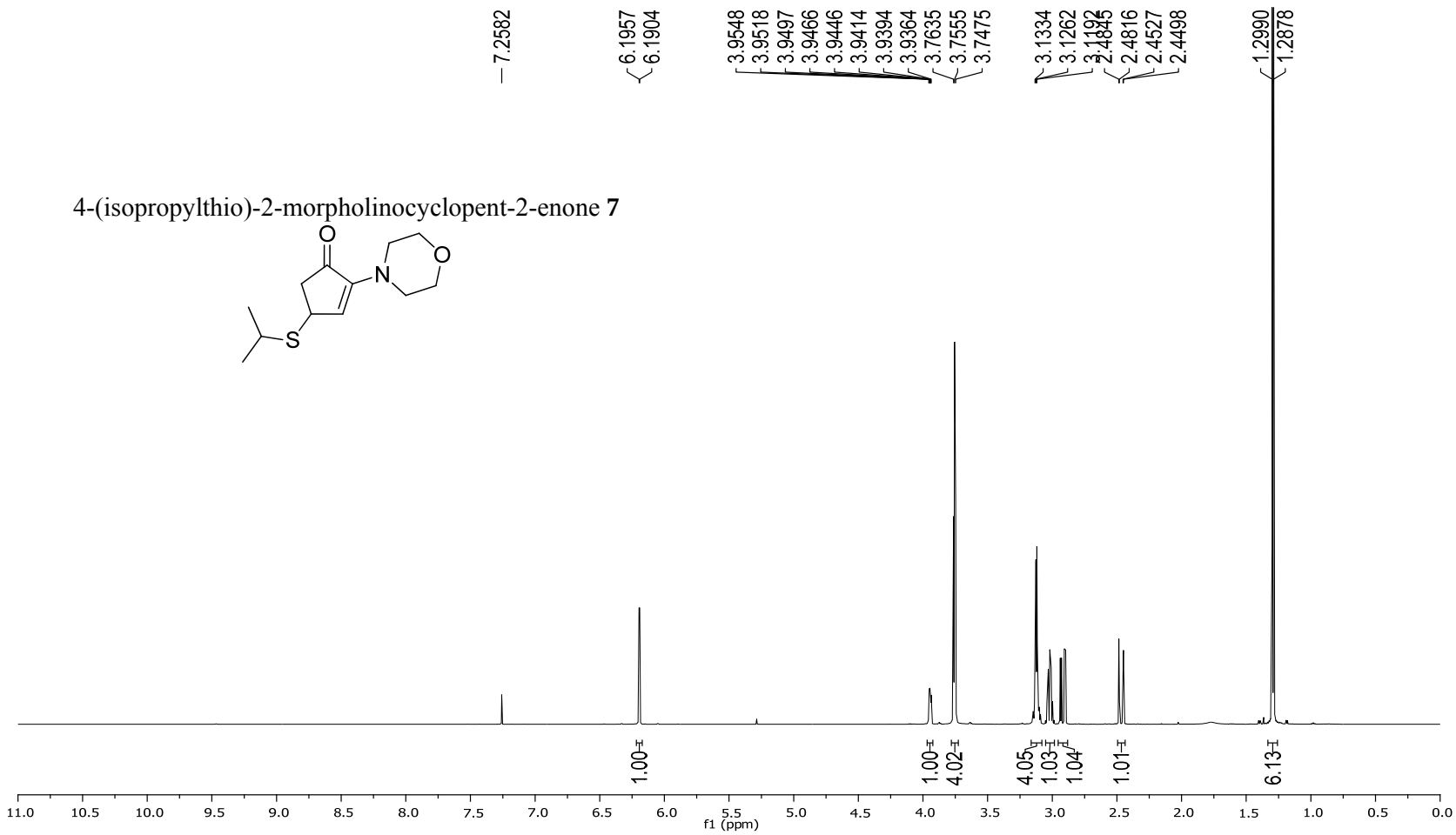


Figure S21 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **7**.

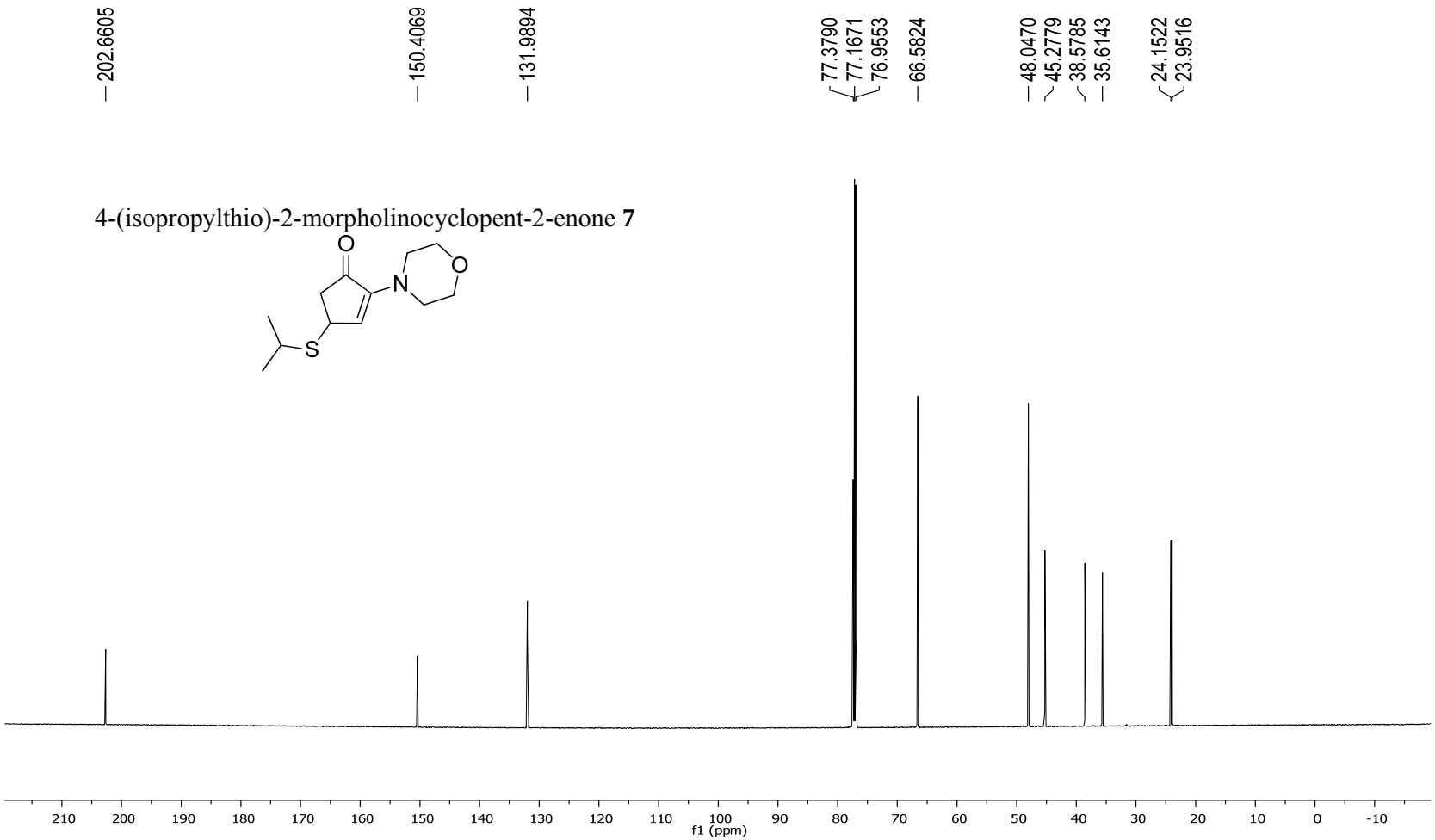


Figure S22 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **7**.

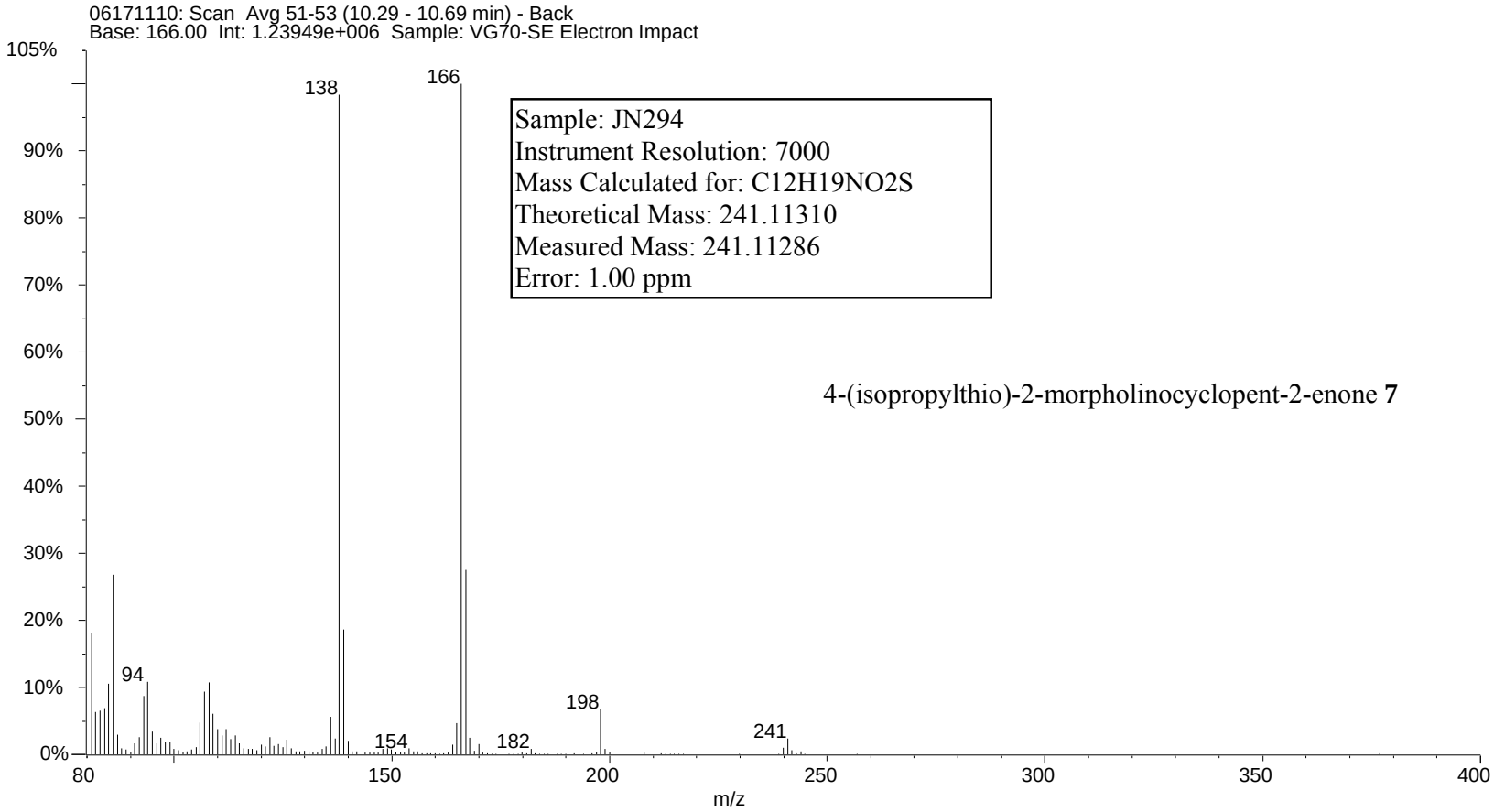


Figure S23 – EI mass spectra for exact mass measurement of isolated enone **7**.

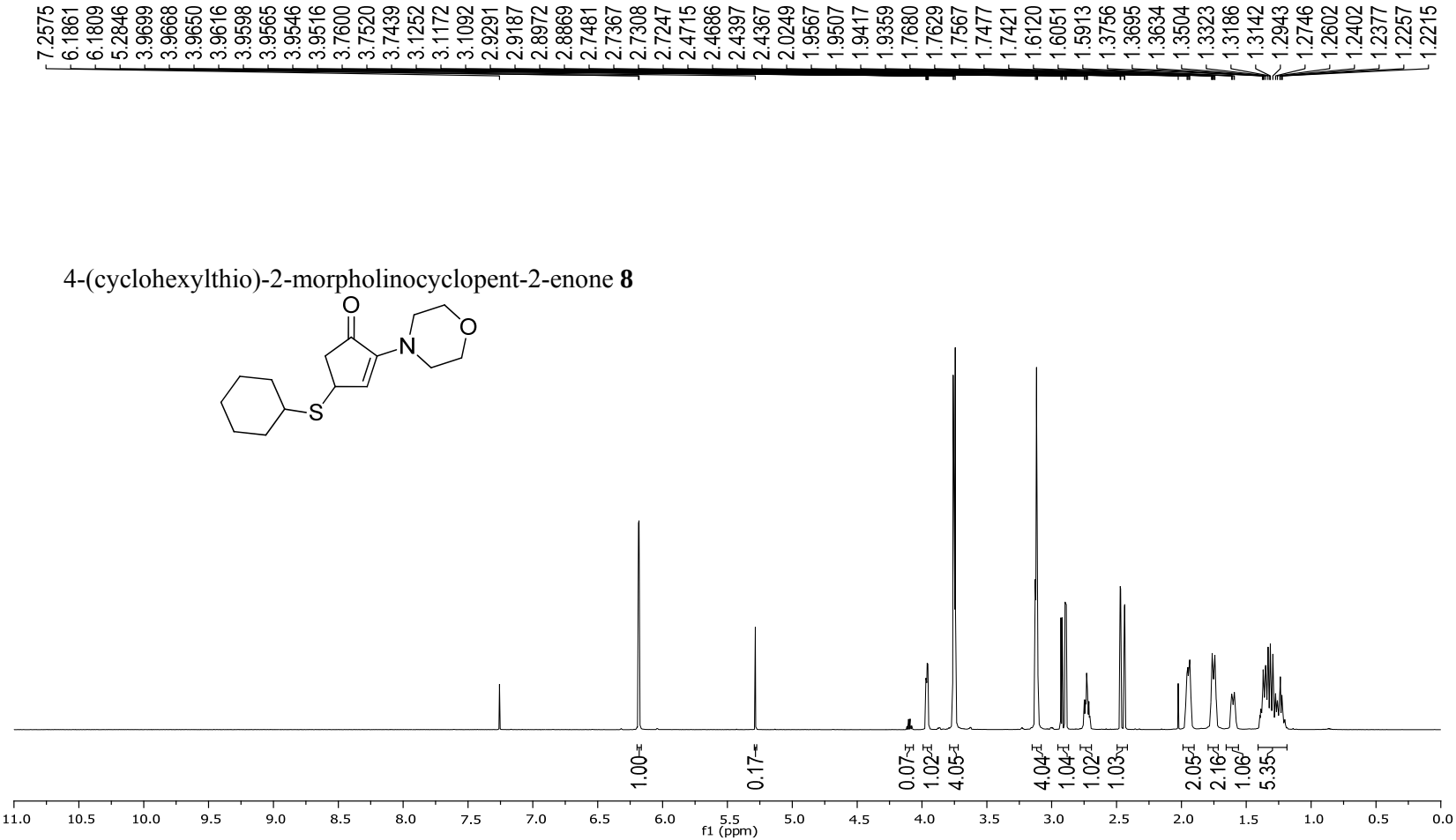


Figure S24 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **8**.

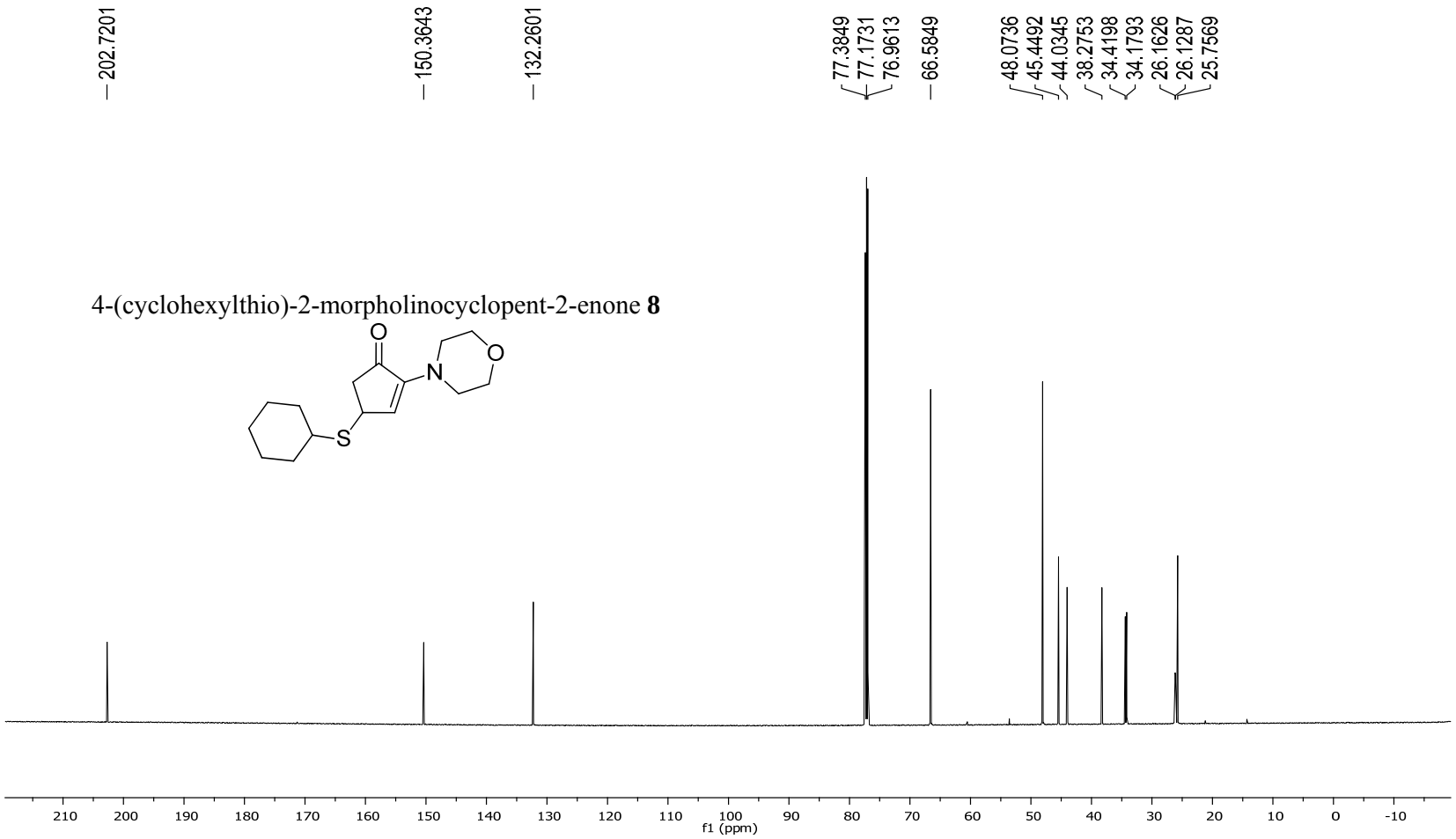


Figure S25 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **8**.

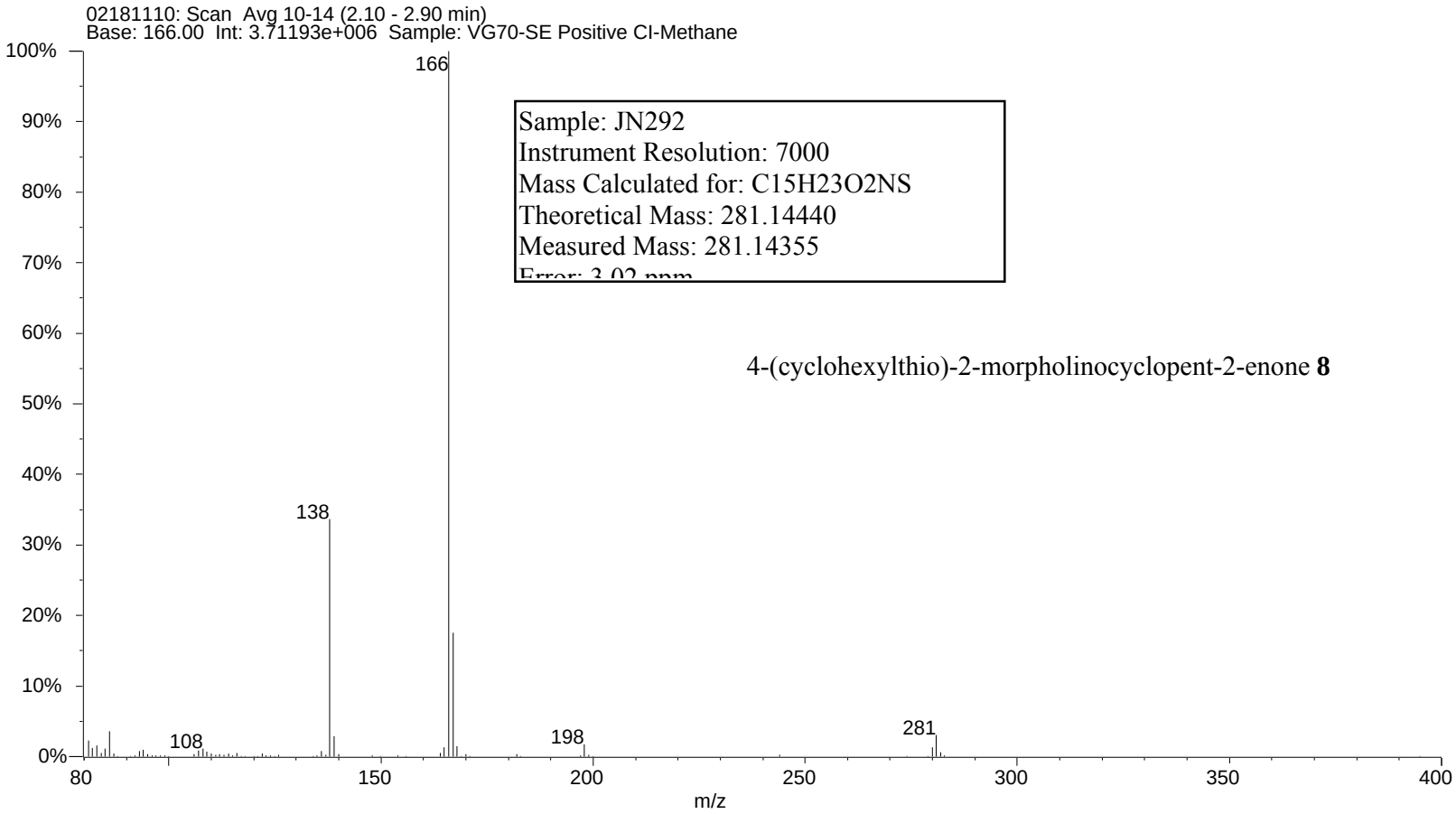


Figure S26 – EI mass spectra for exact mass measurement of isolated enone **8**.

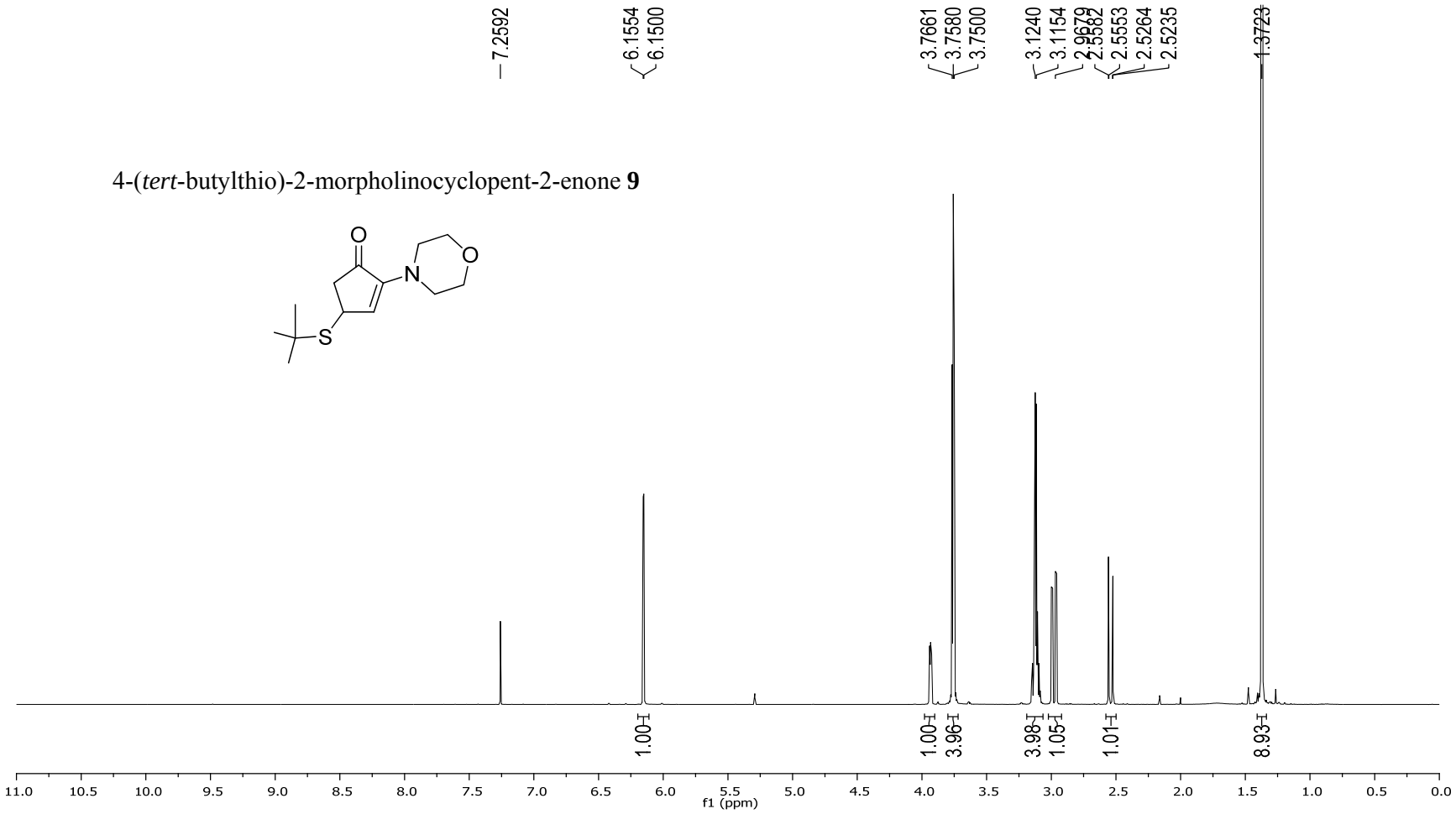


Figure S27 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **9**.

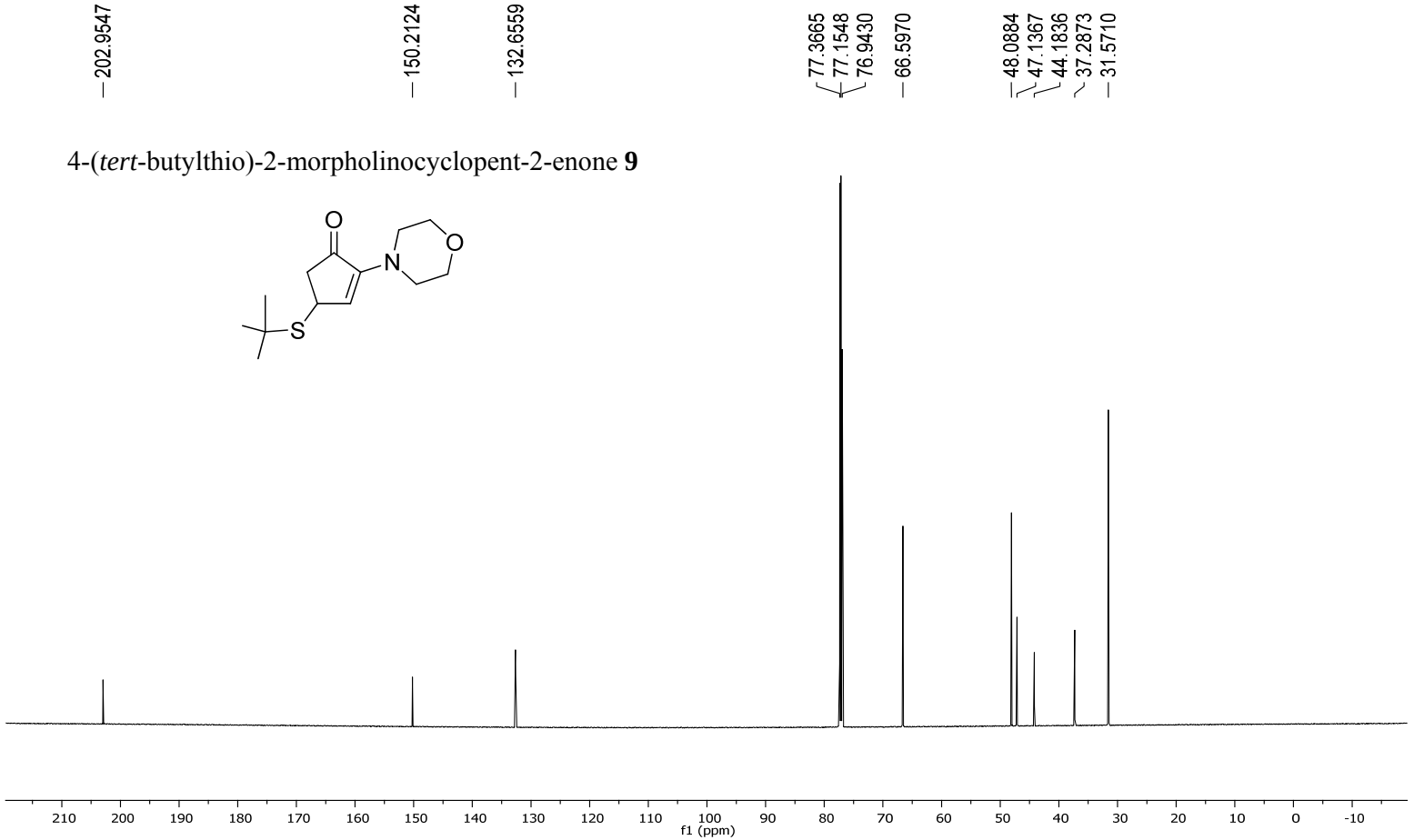


Figure S28 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **9**.

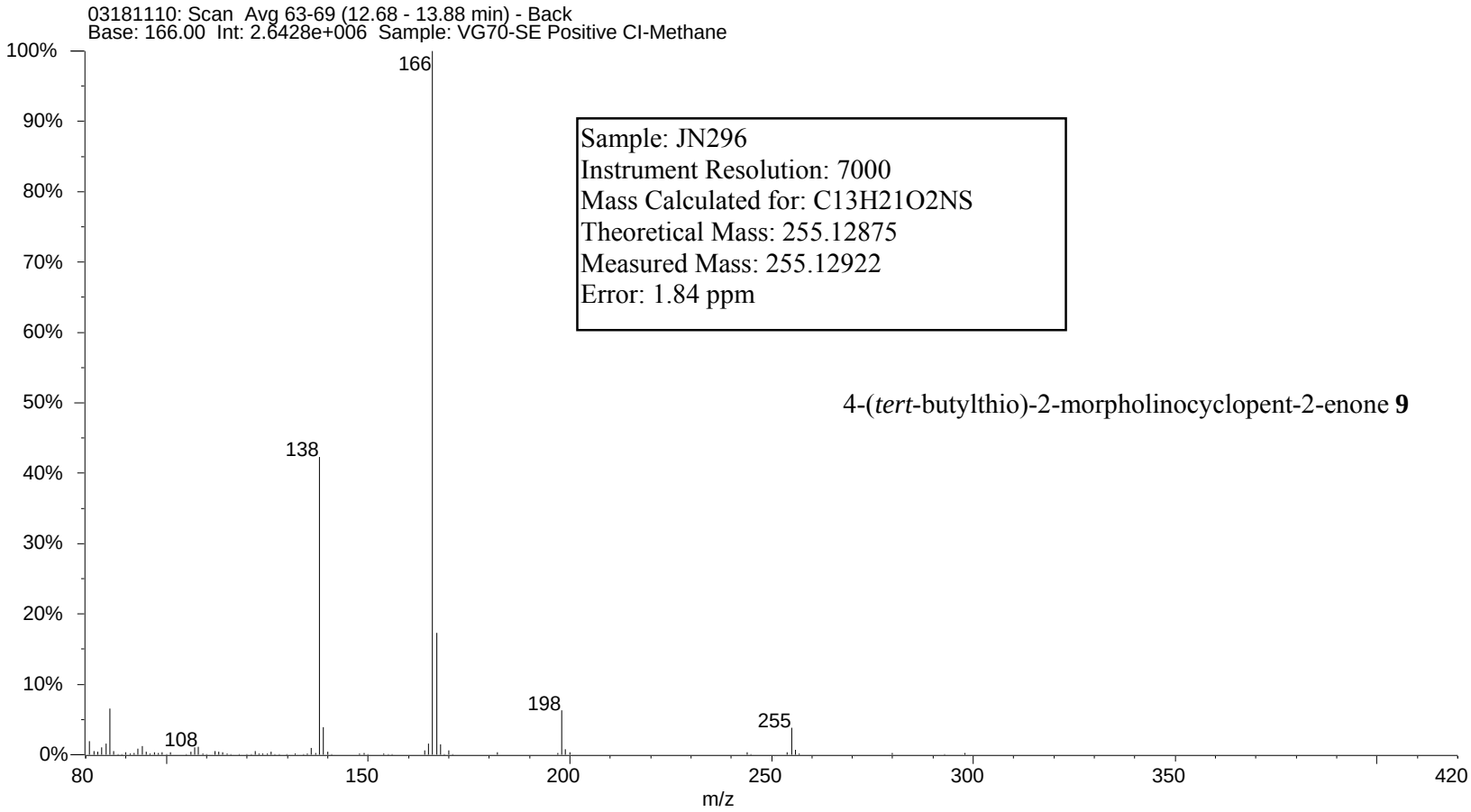


Figure S29 – EI mass spectra for exact mass measurement of isolated enone **9**.

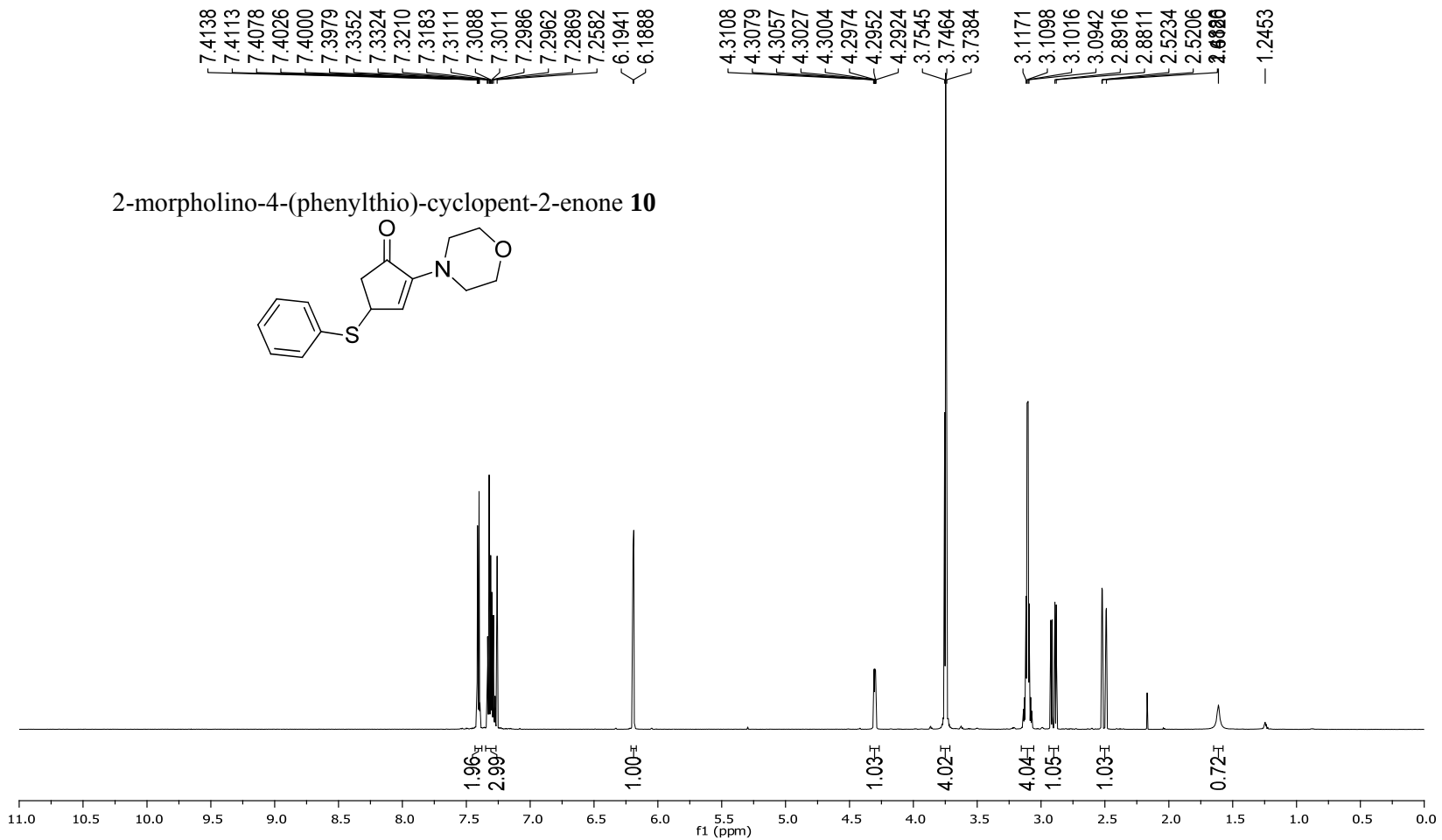


Figure S30 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **10**.

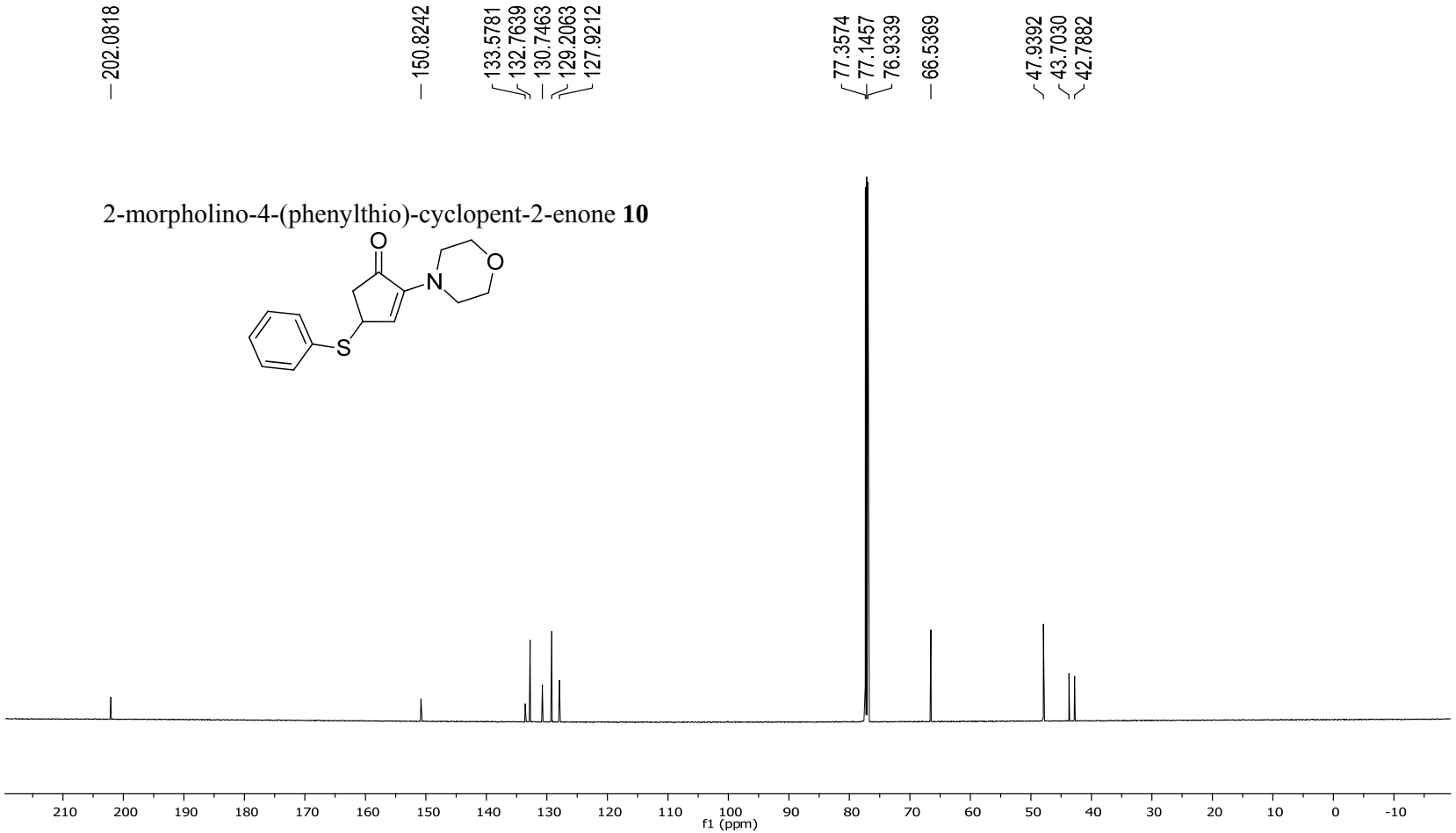


Figure S31 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **10**.

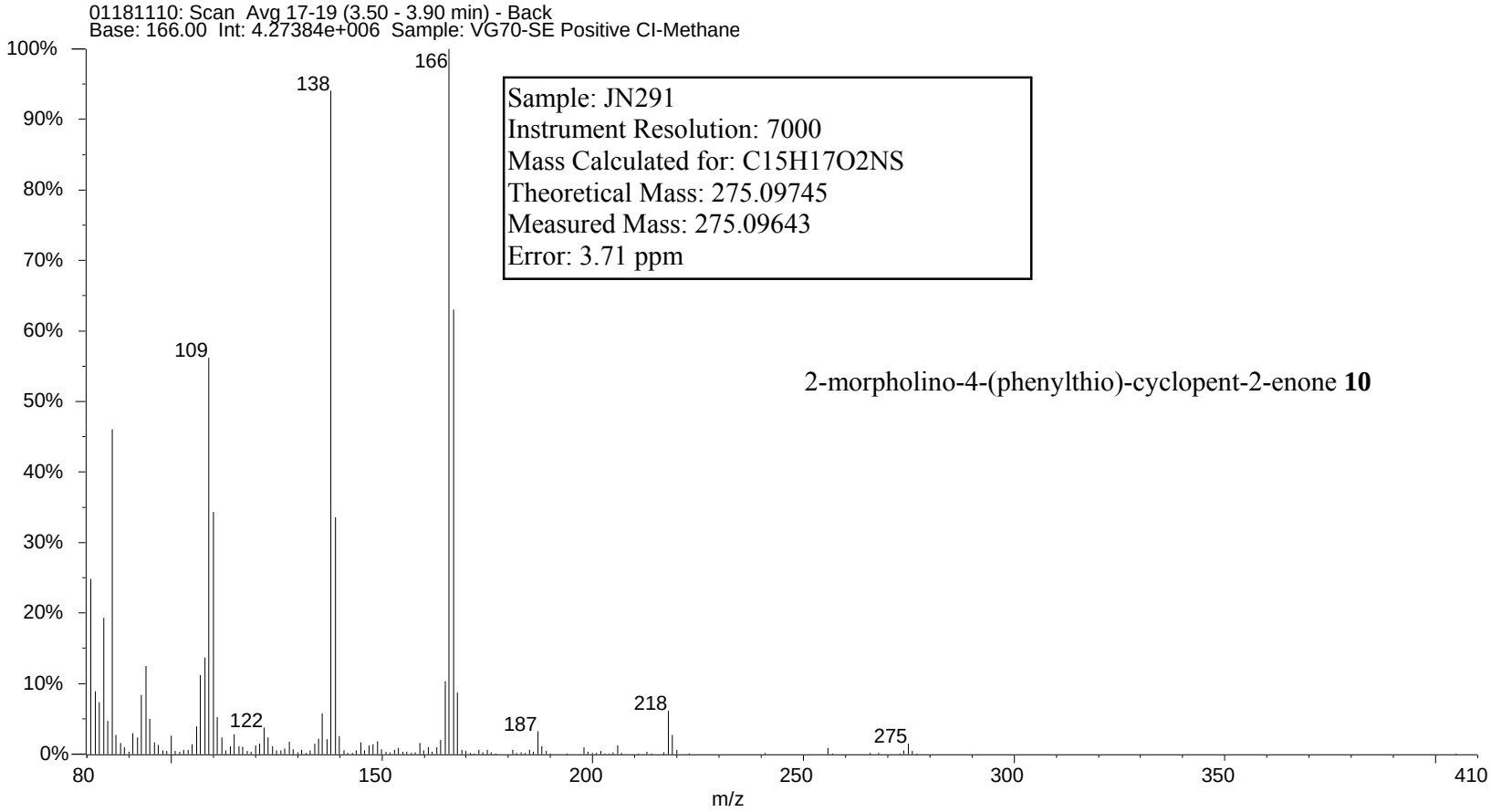


Figure S32 – EI mass spectra for exact mass measurement of isolated enone **10**.

4-(benzylthio)-2-morpholinocyclopent-2-enone **11**

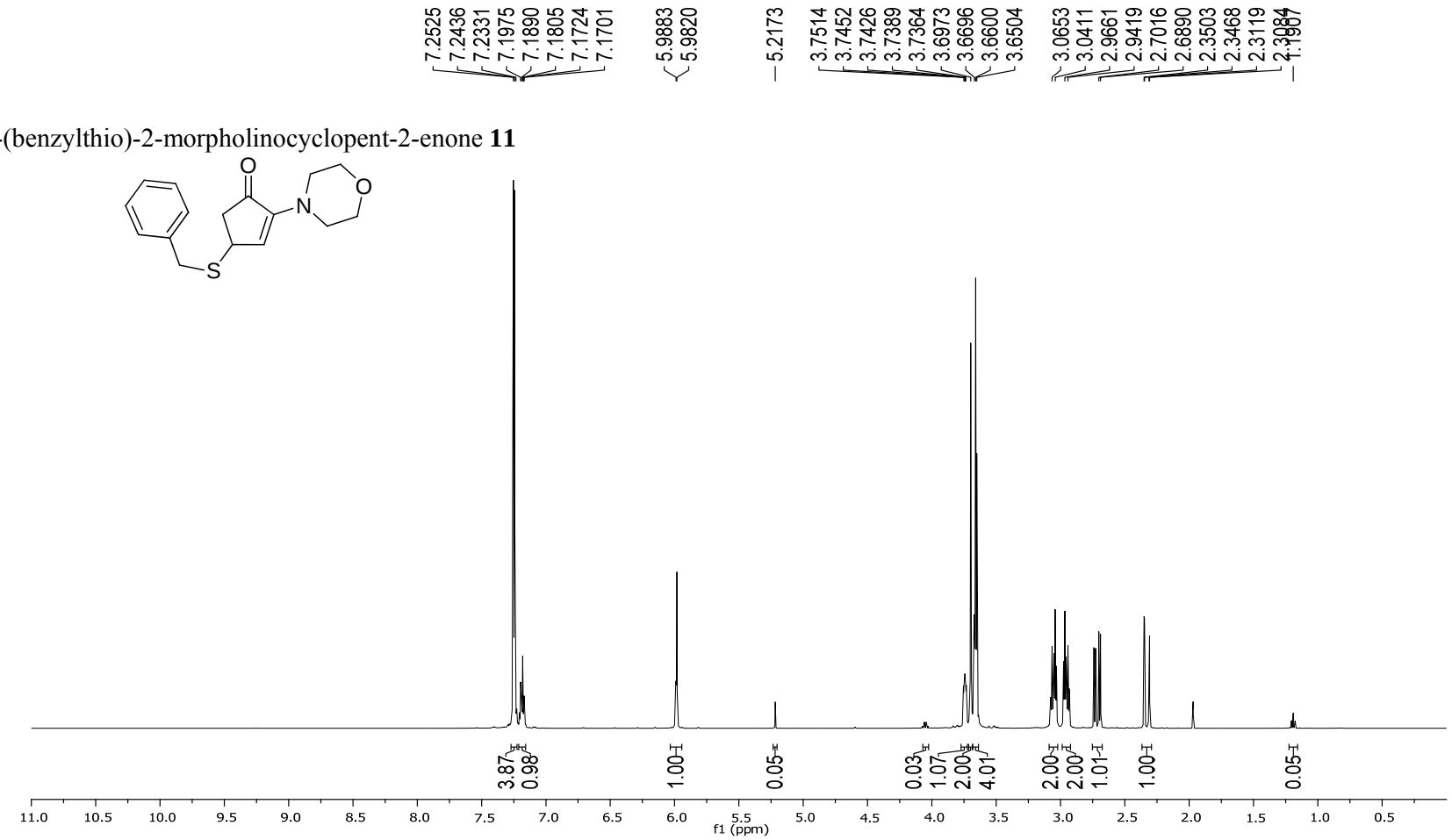
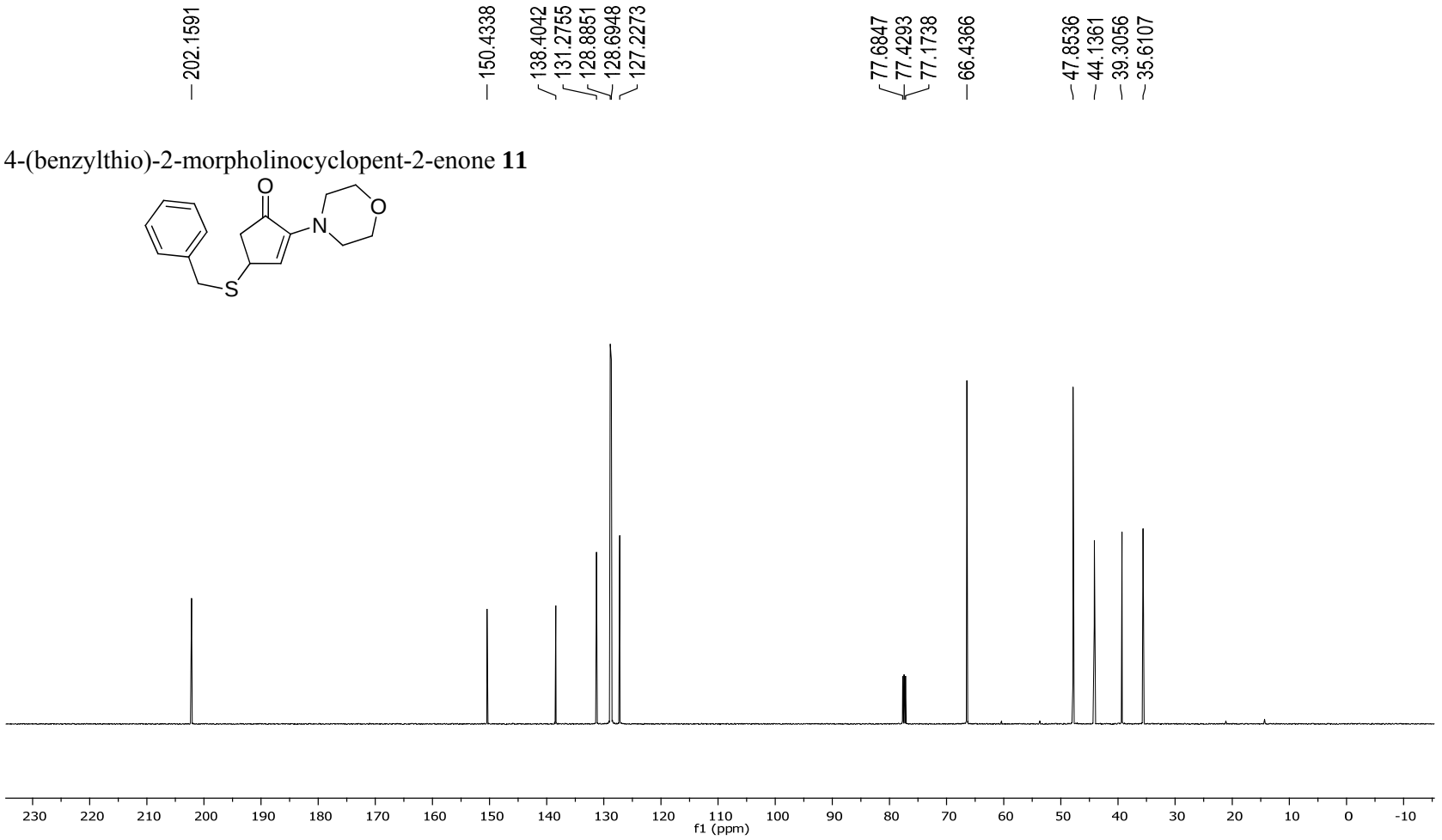


Figure S33 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **11**.



4-(benzylthio)-2-morpholinocyclopent-2-enone **11**

Figure S34 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **11**.

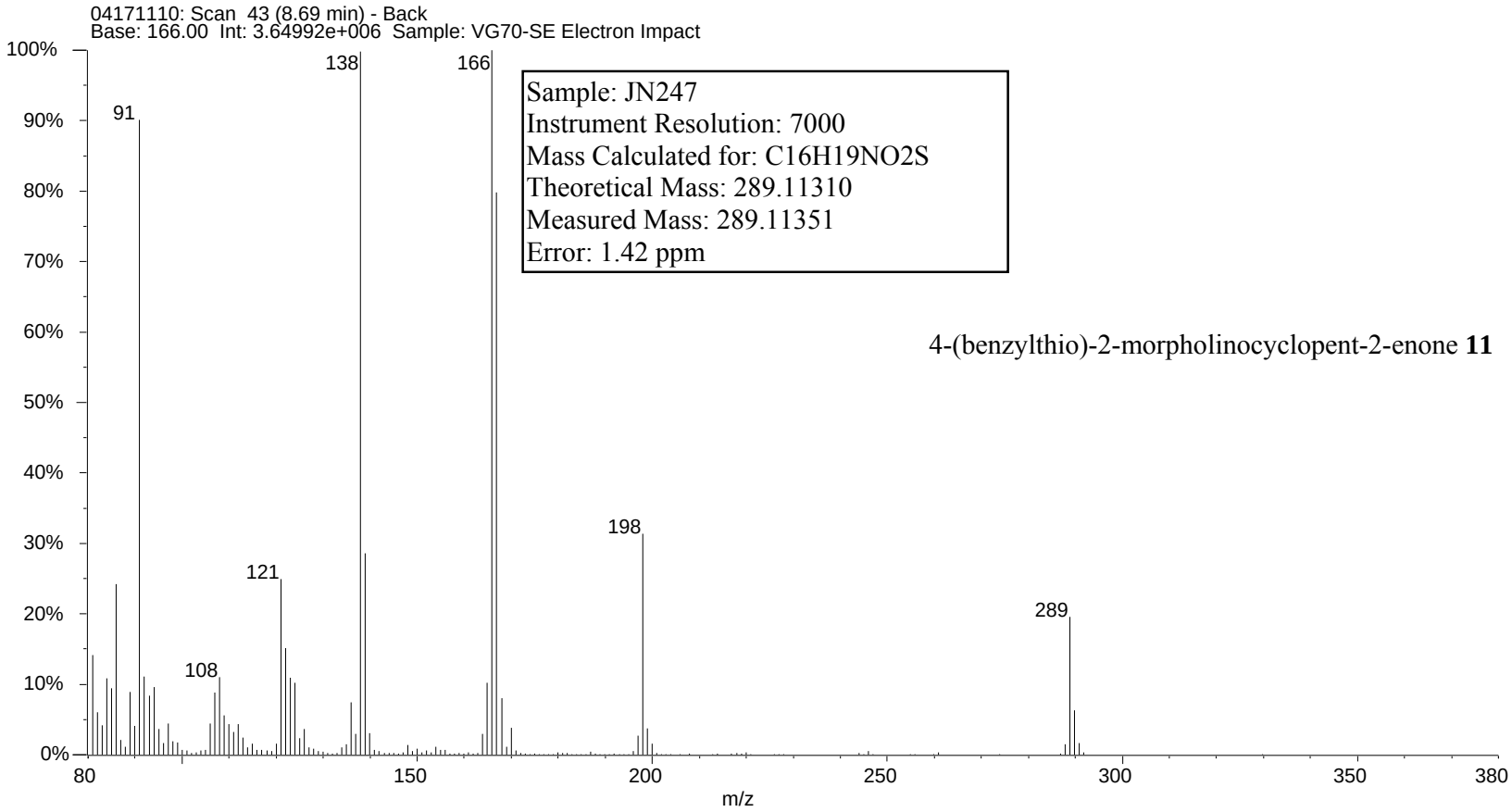


Figure S35 – EI mass spectra for exact mass measurement of isolated enone **11**.

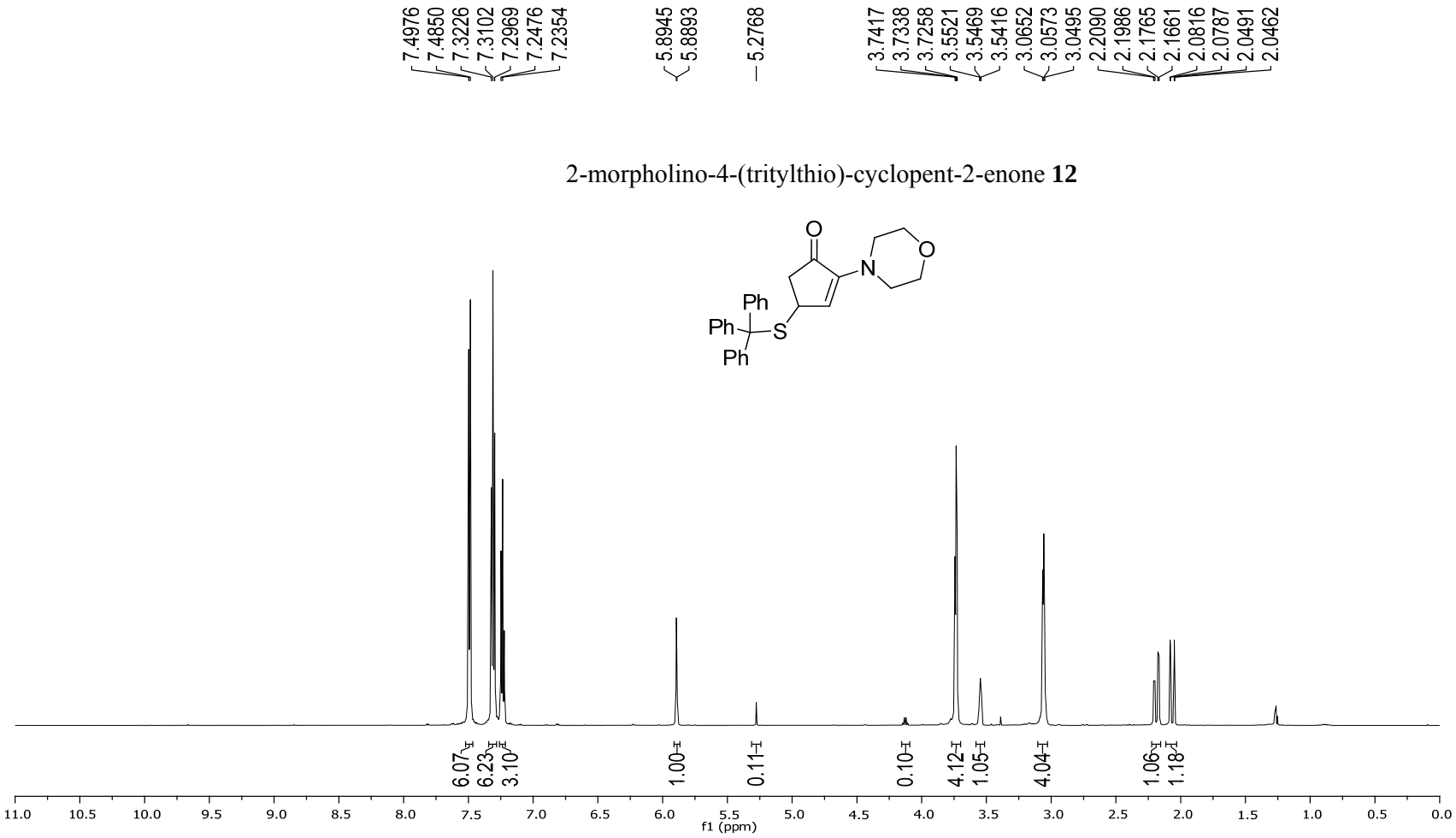


Figure S36 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **12**.

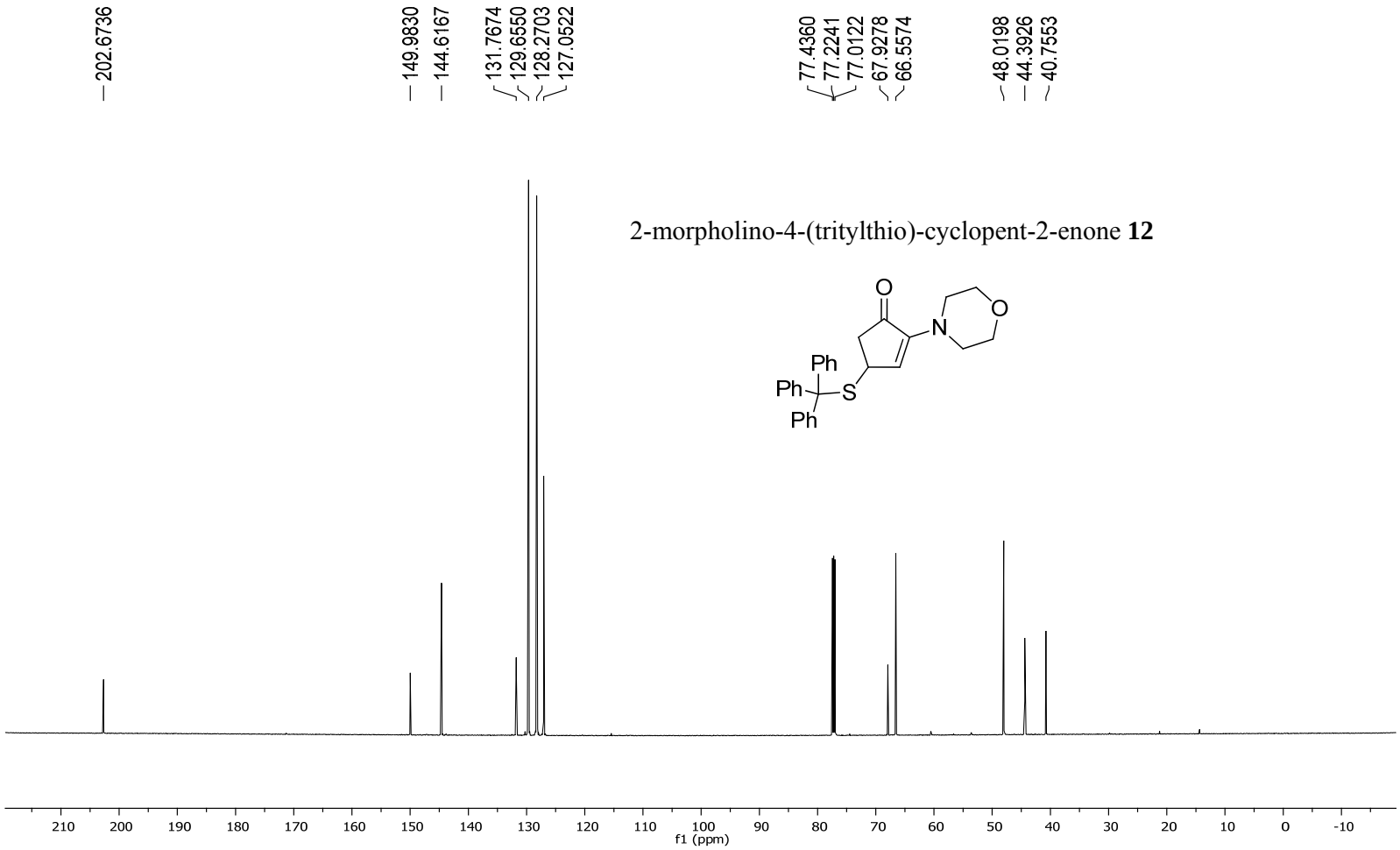


Figure S37 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **12**.

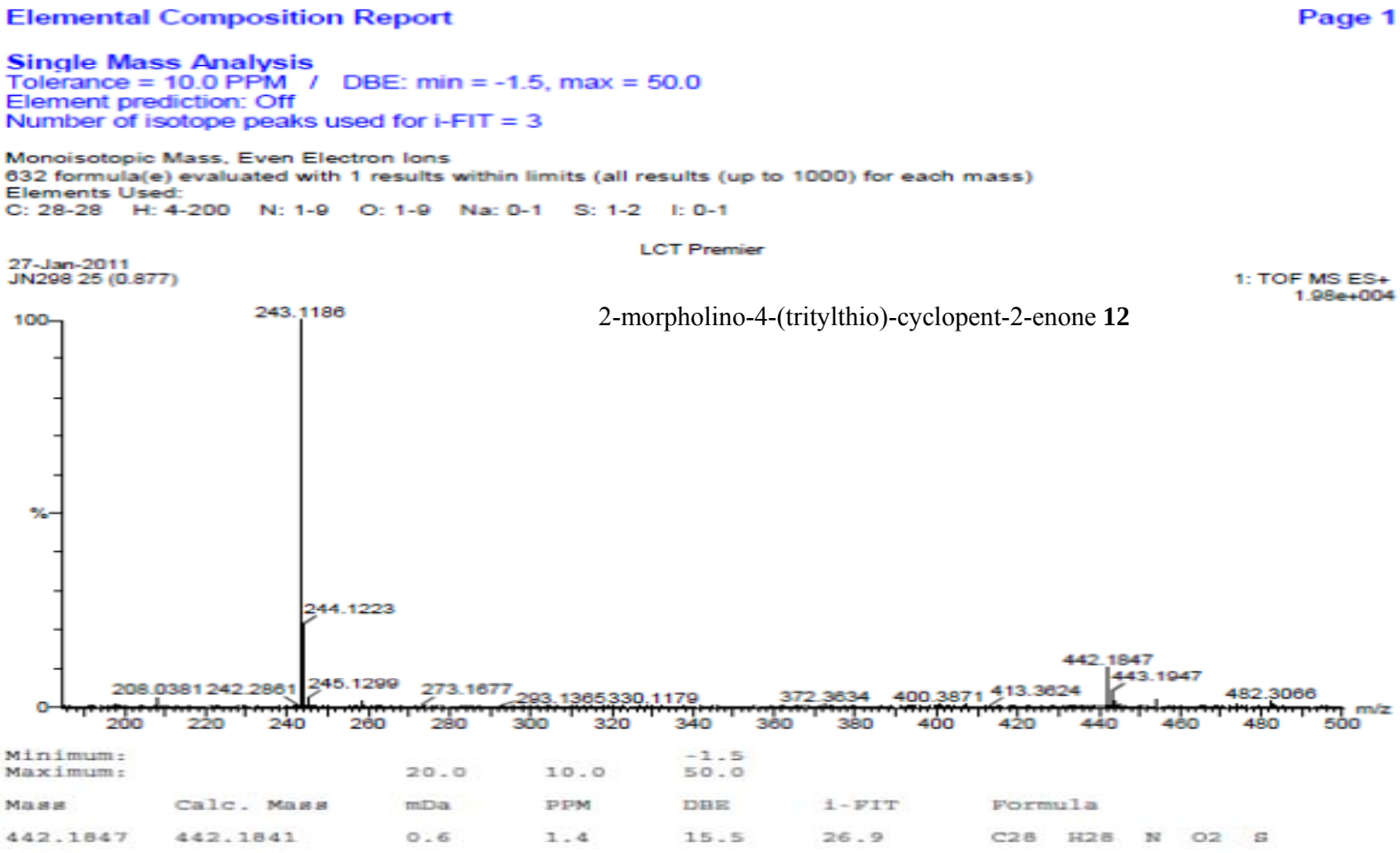


Figure S38 – EI mass spectra for exact mass measurement of isolated enone **12**.

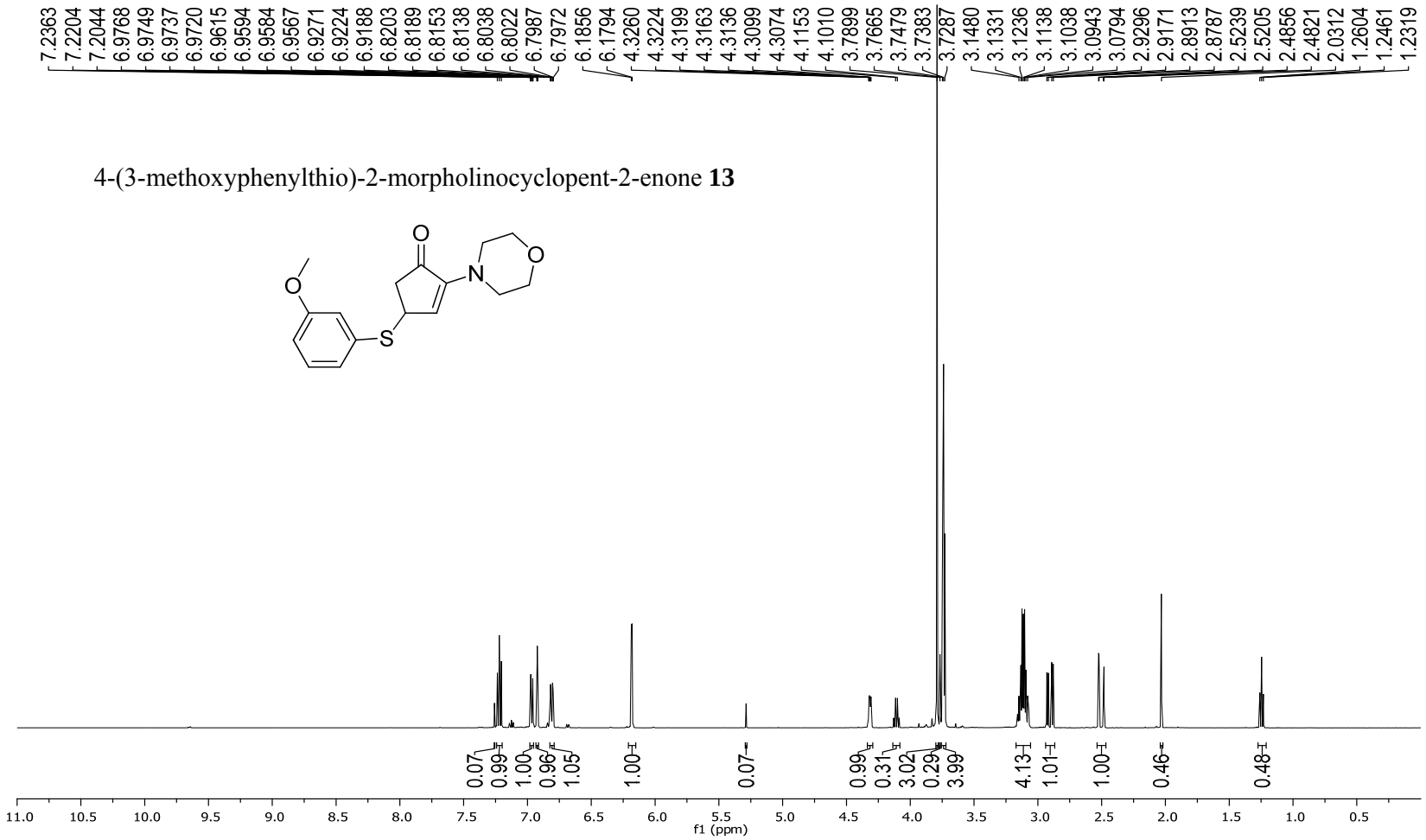
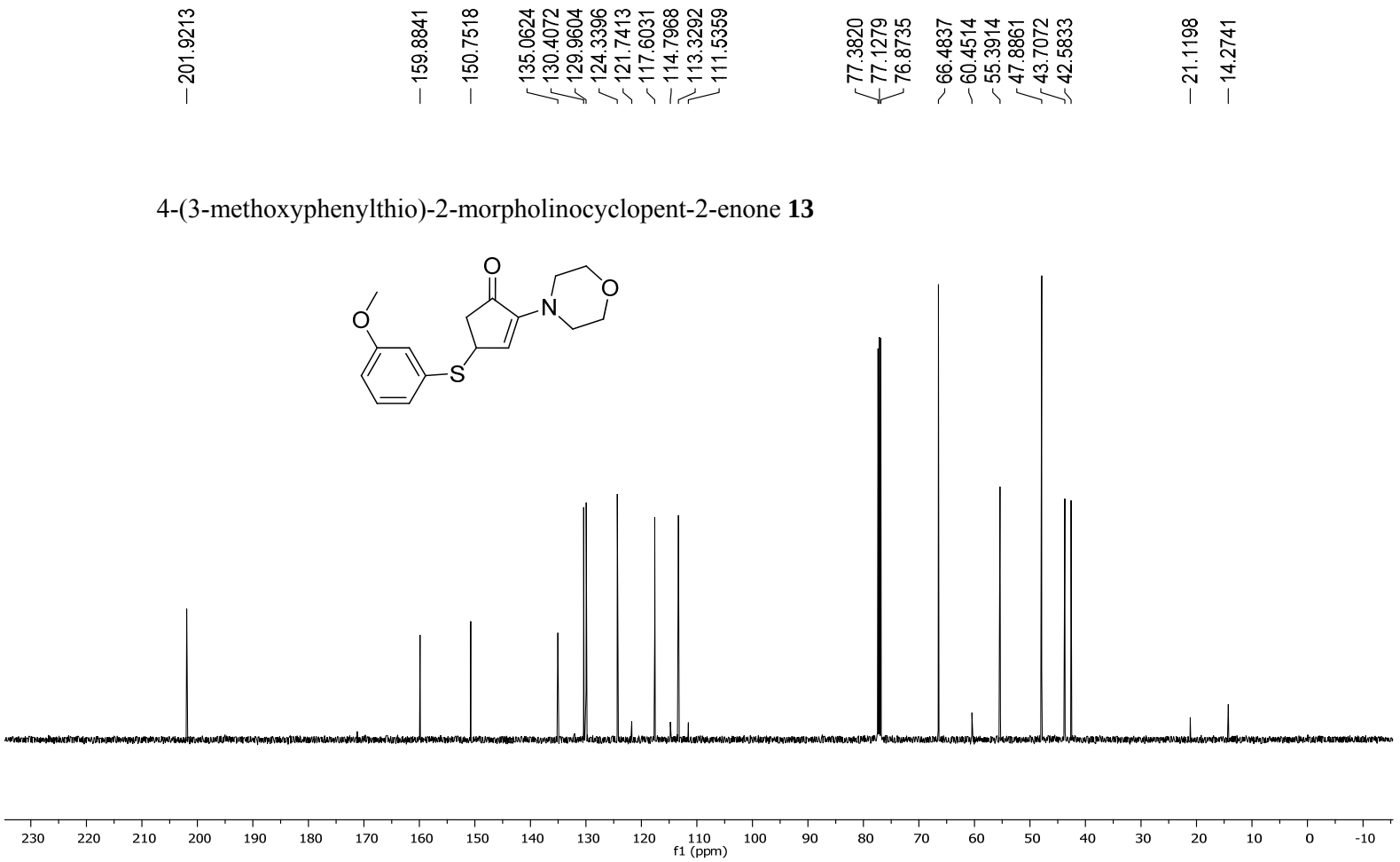
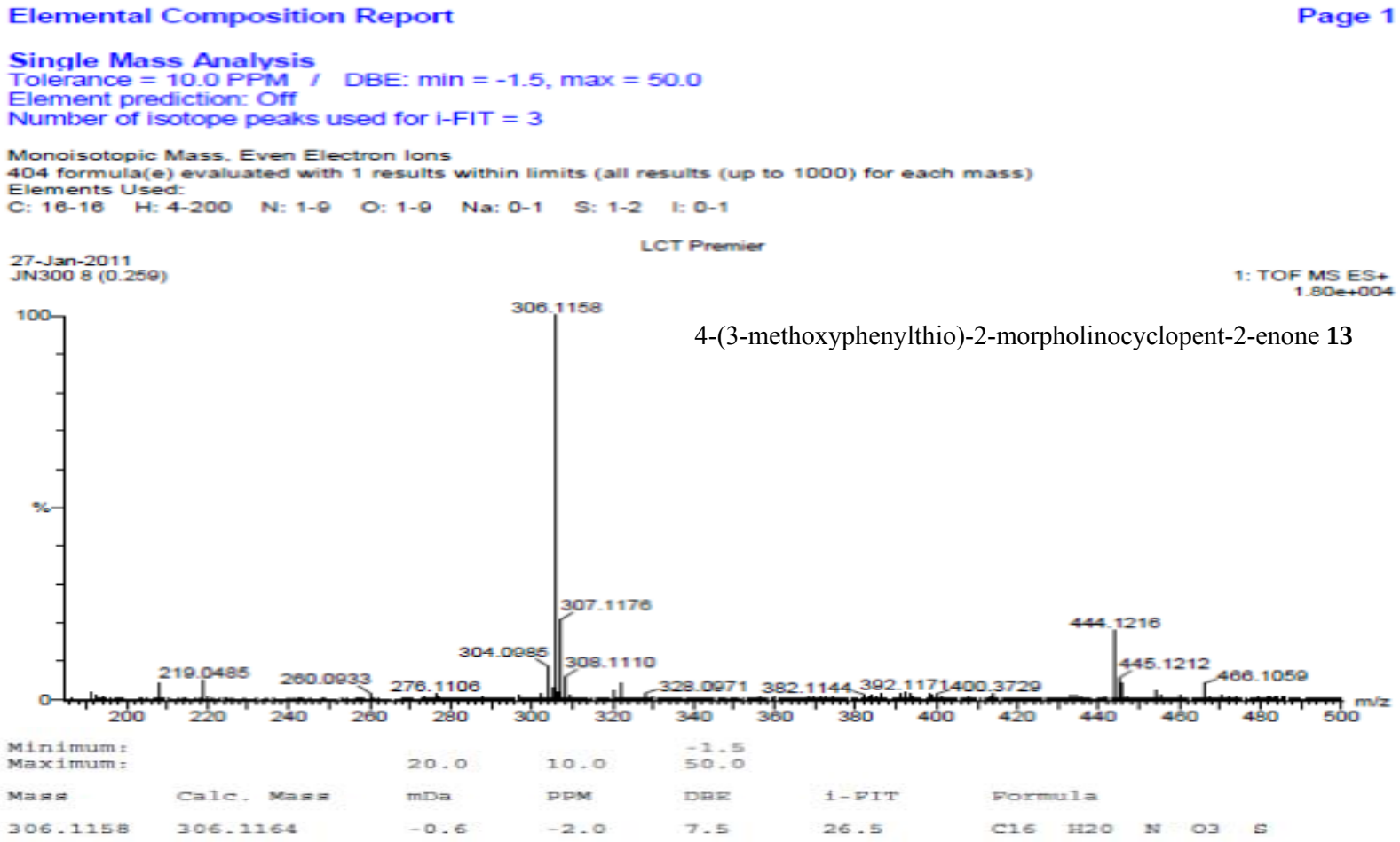


Figure S39 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **13**.



4-(3-methoxyphenylthio)-2-morpholinocyclopent-2-enone **13**

Figure S40 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **13**.



4-(3-methoxyphenylthio)-2-morpholinocyclopent-2-enone **13**

Figure S41 – EI mass spectra for exact mass measurement of isolated enone **13**.

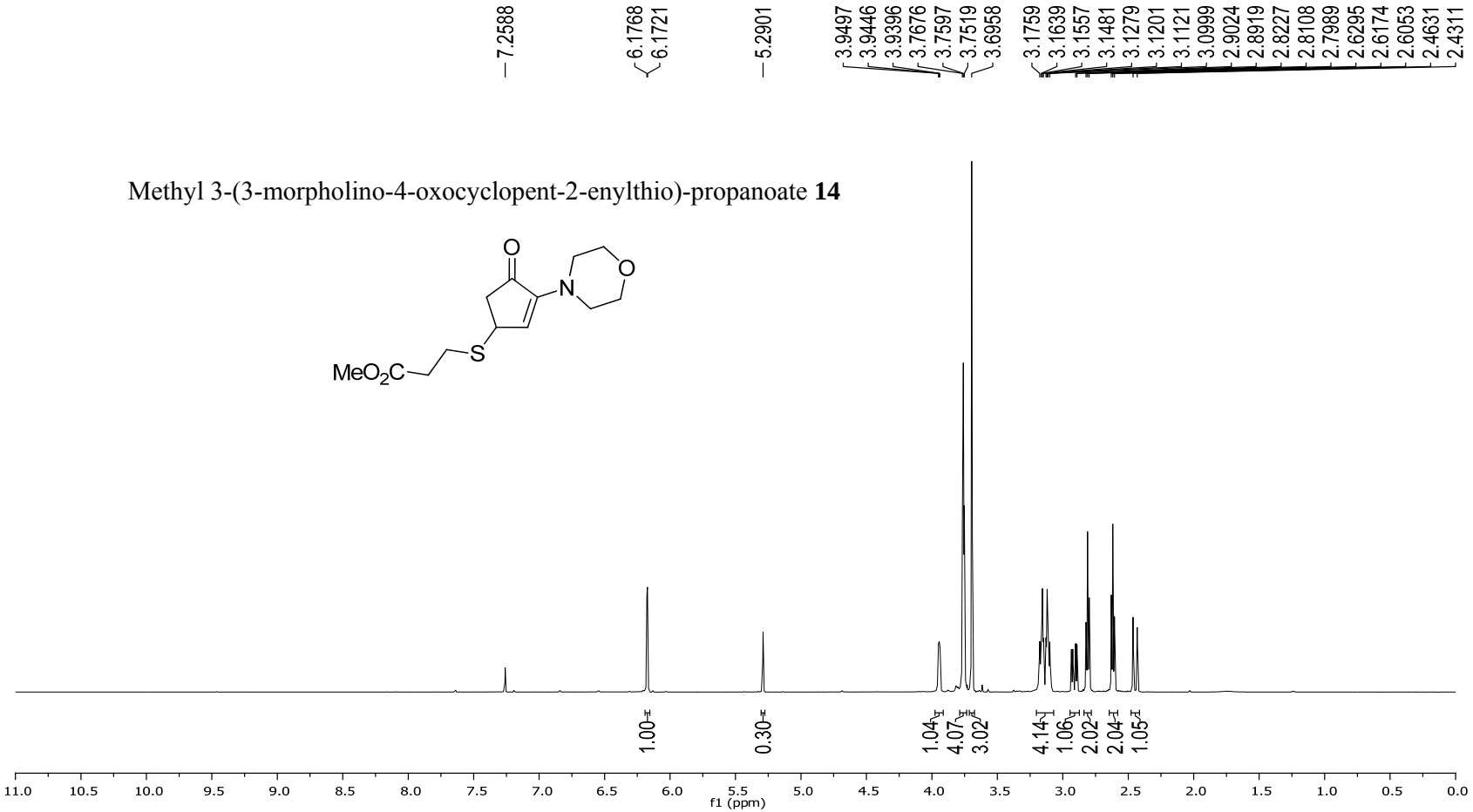


Figure S42 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **14**.

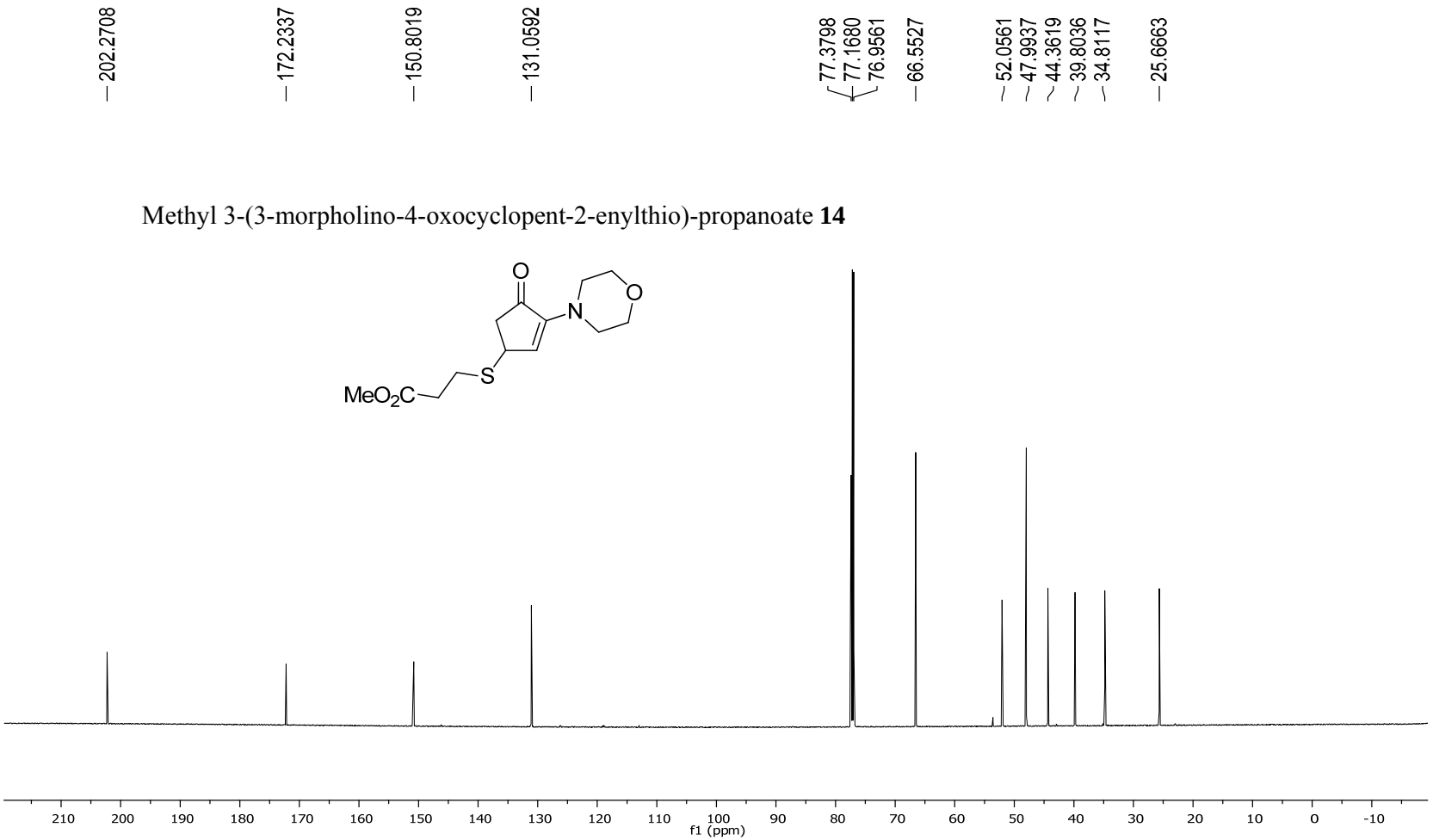


Figure S43 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **14**.

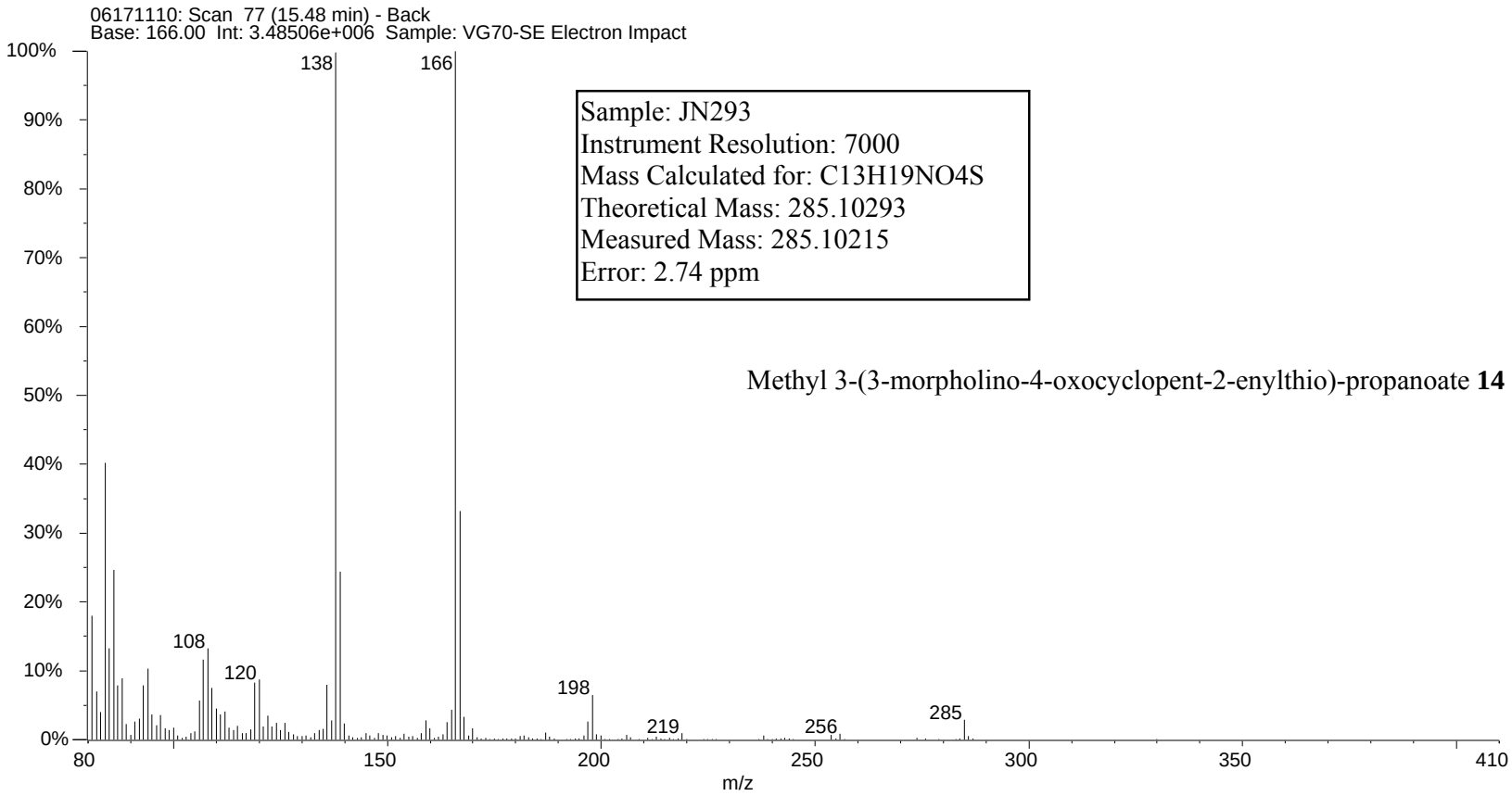


Figure S44 – EI mass spectra for exact mass measurement of isolated enone **14**.

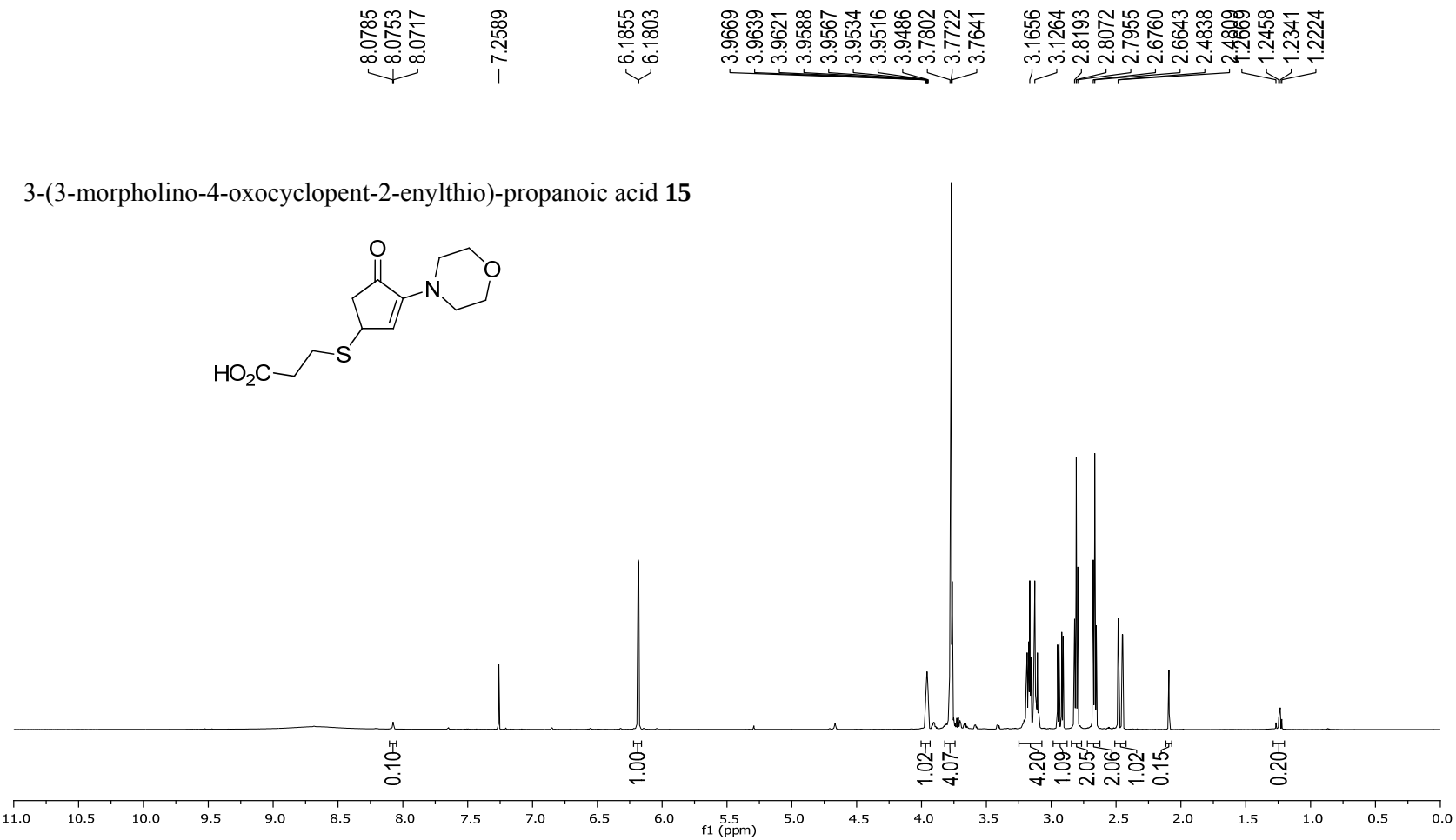


Figure S45 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **15**.

3-(3-morpholino-4-oxocyclopent-2-enylthio)-propanoic acid **15**

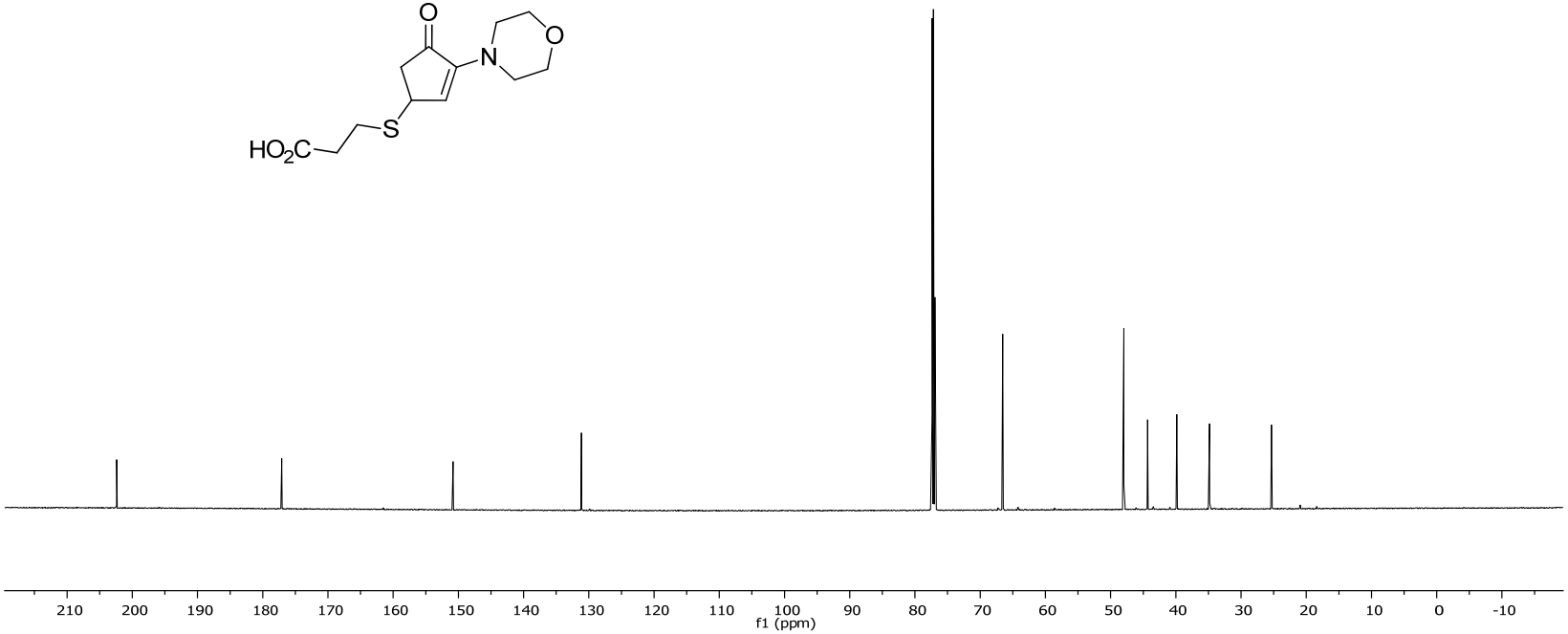


Figure S46 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **15**.

Elemental Composition Report Page 1

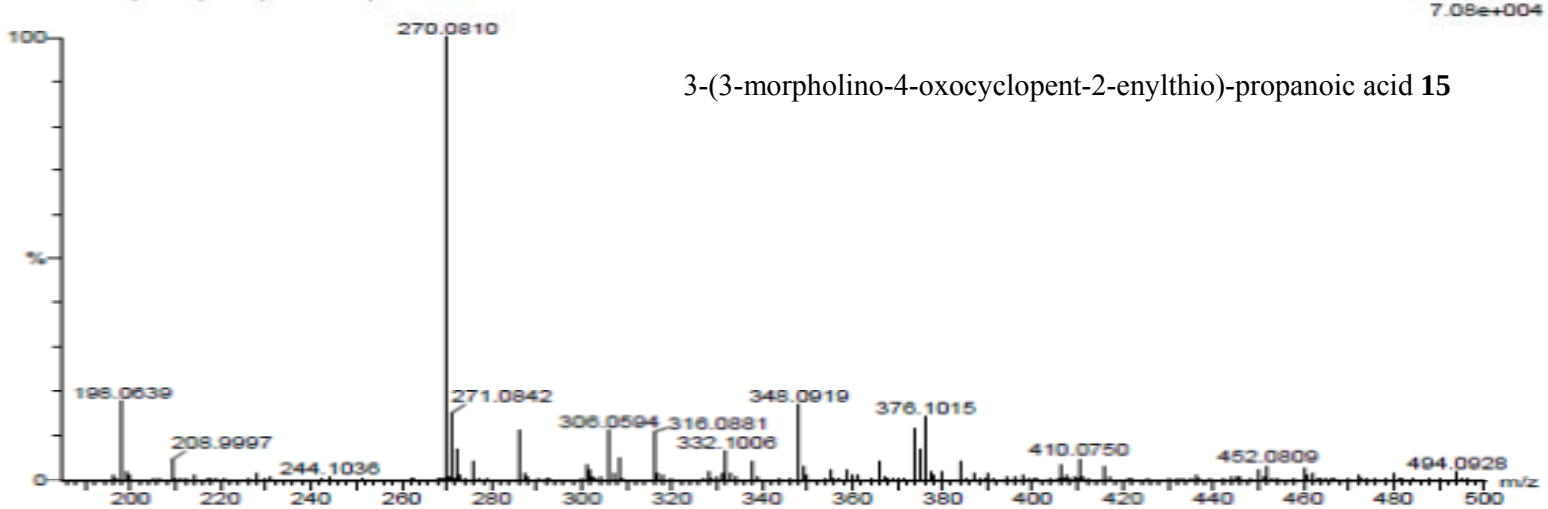
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
309 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 12-12 H: 4-200 N: 1-9 O: 1-9 Na: 0-1 S: 1-2 I: 0-1

LCT Premier

27-Jan-2011
JN299A 13 (0.471) Cm (12:16-2:5)

2: TOF MS ES-
7.08e+004



3-(3-morpholino-4-oxocyclopent-2-enylthio)-propanoic acid **15**

Minimum:				-1.5		
Maximum:		20.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
270.0810	270.0800	1.0	3.7	5.5	25.3	C12 H16 N O4 S

Figure S47 – EI mass spectra for exact mass measurement of isolated enone **15**.

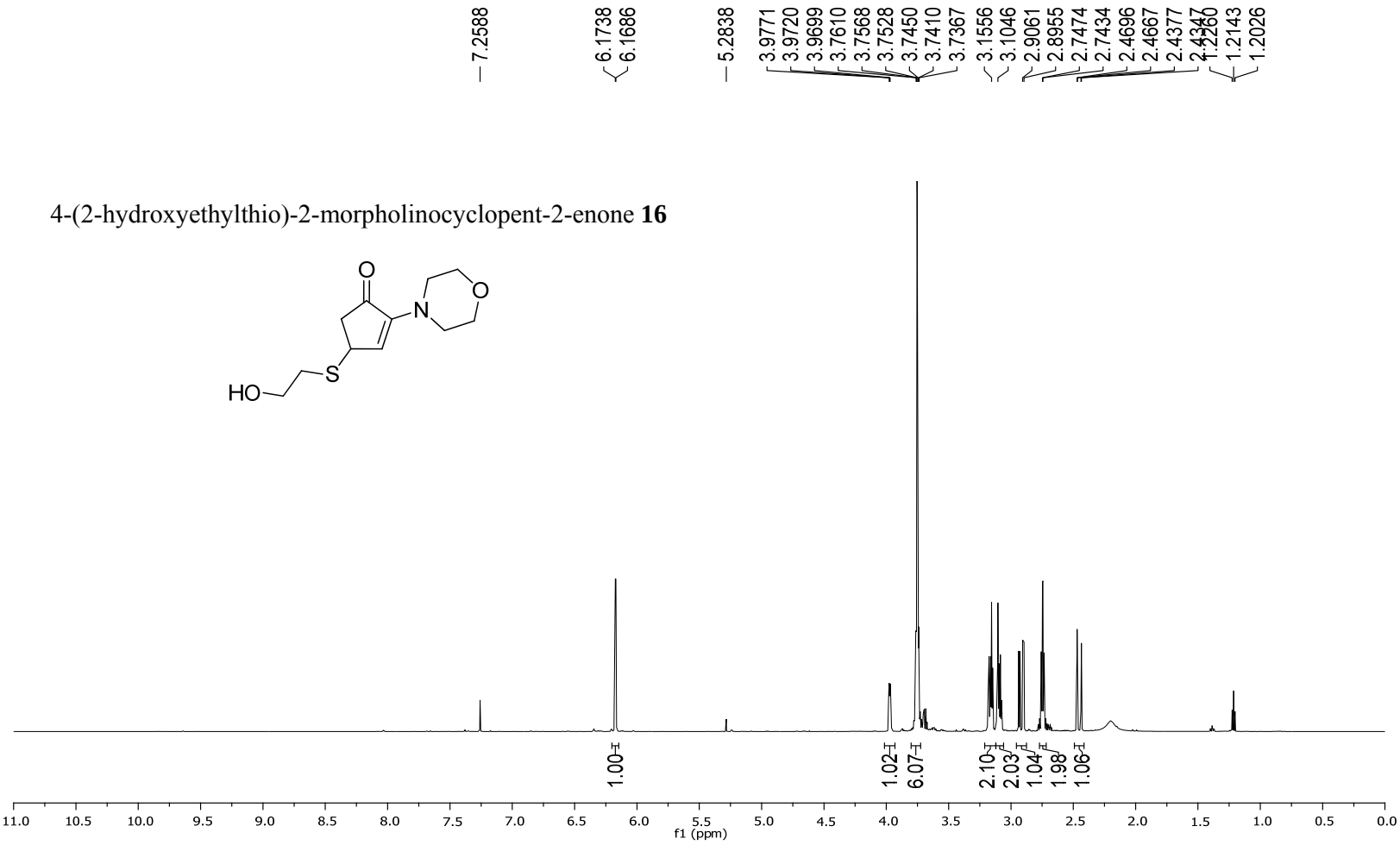


Figure S48 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **16**.

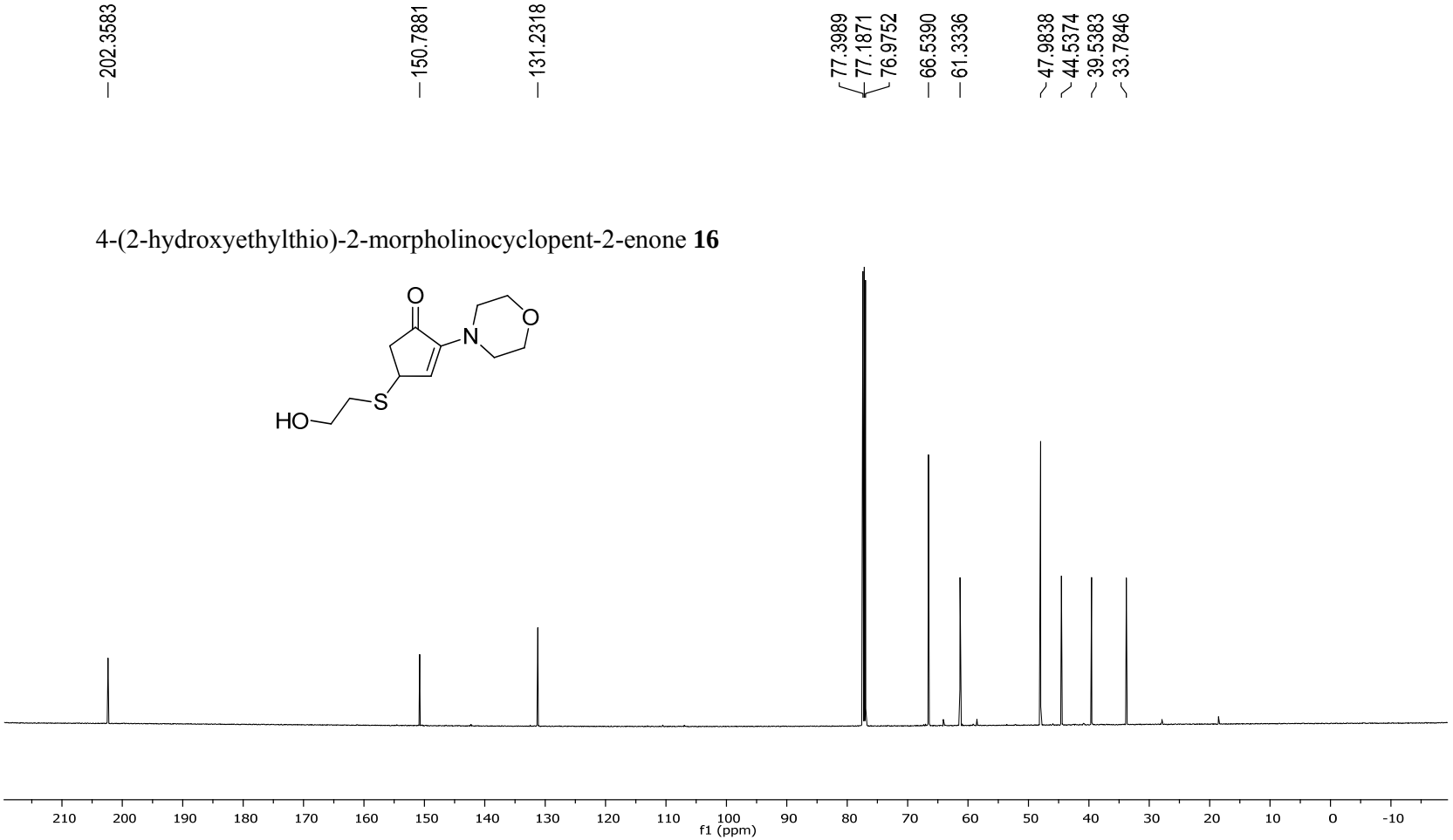


Figure S49 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **16**.

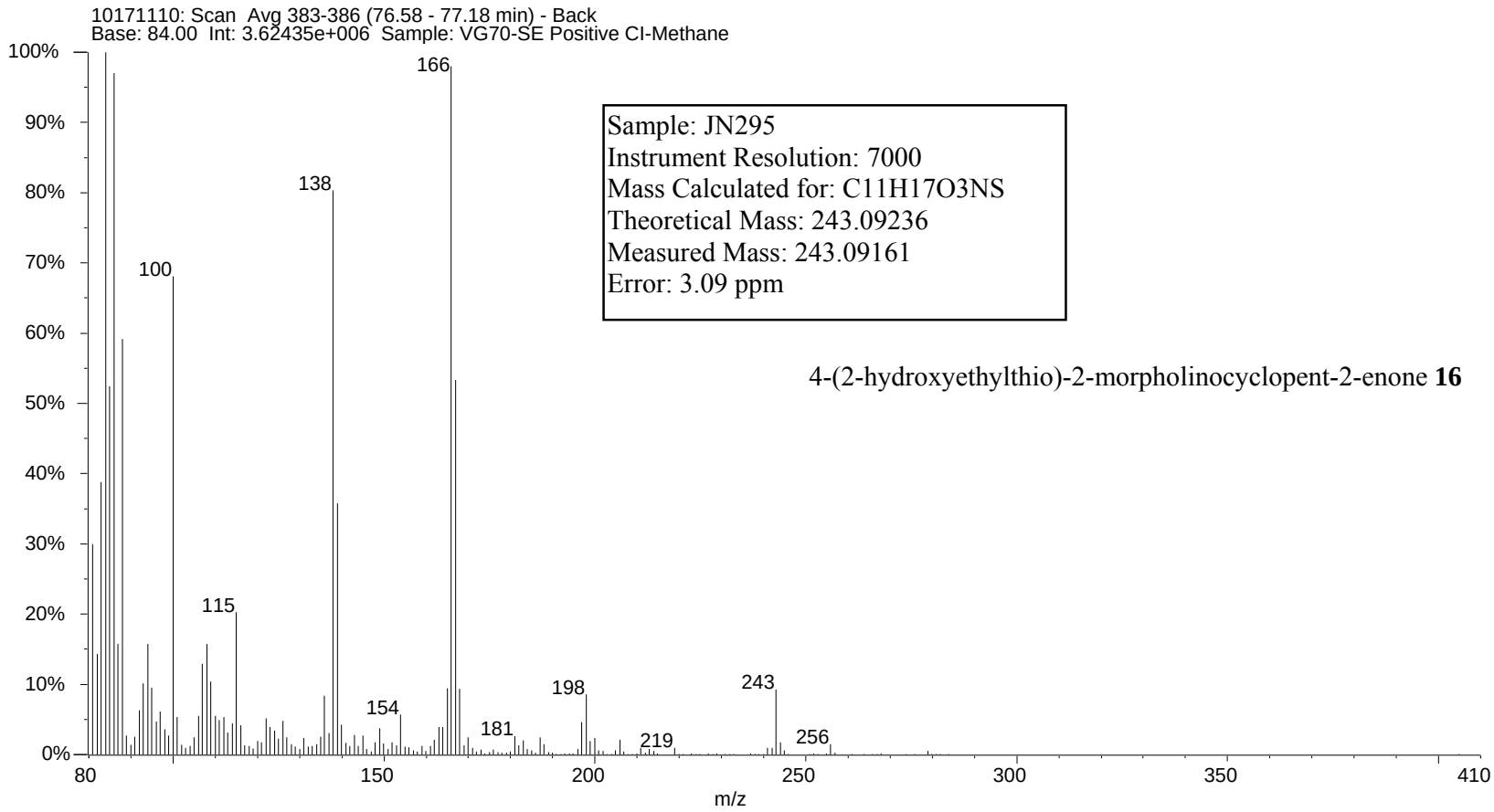


Figure S50 – EI mass spectra for exact mass measurement of isolated enone **16**.

4-(2-(diethylamino)ethylthio)-2-morpholinocyclopent-2-enone **17**

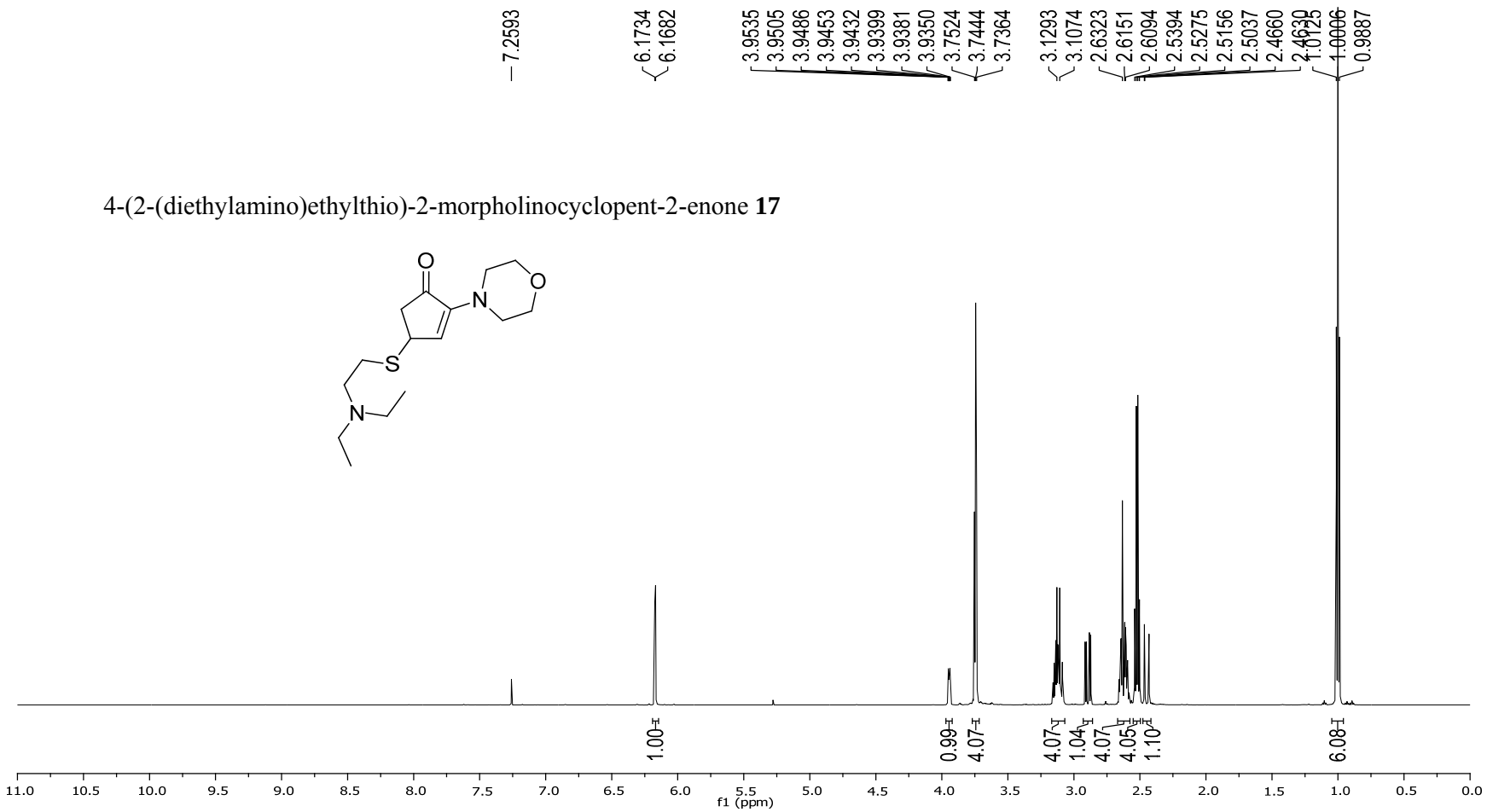


Figure S51 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **17**.

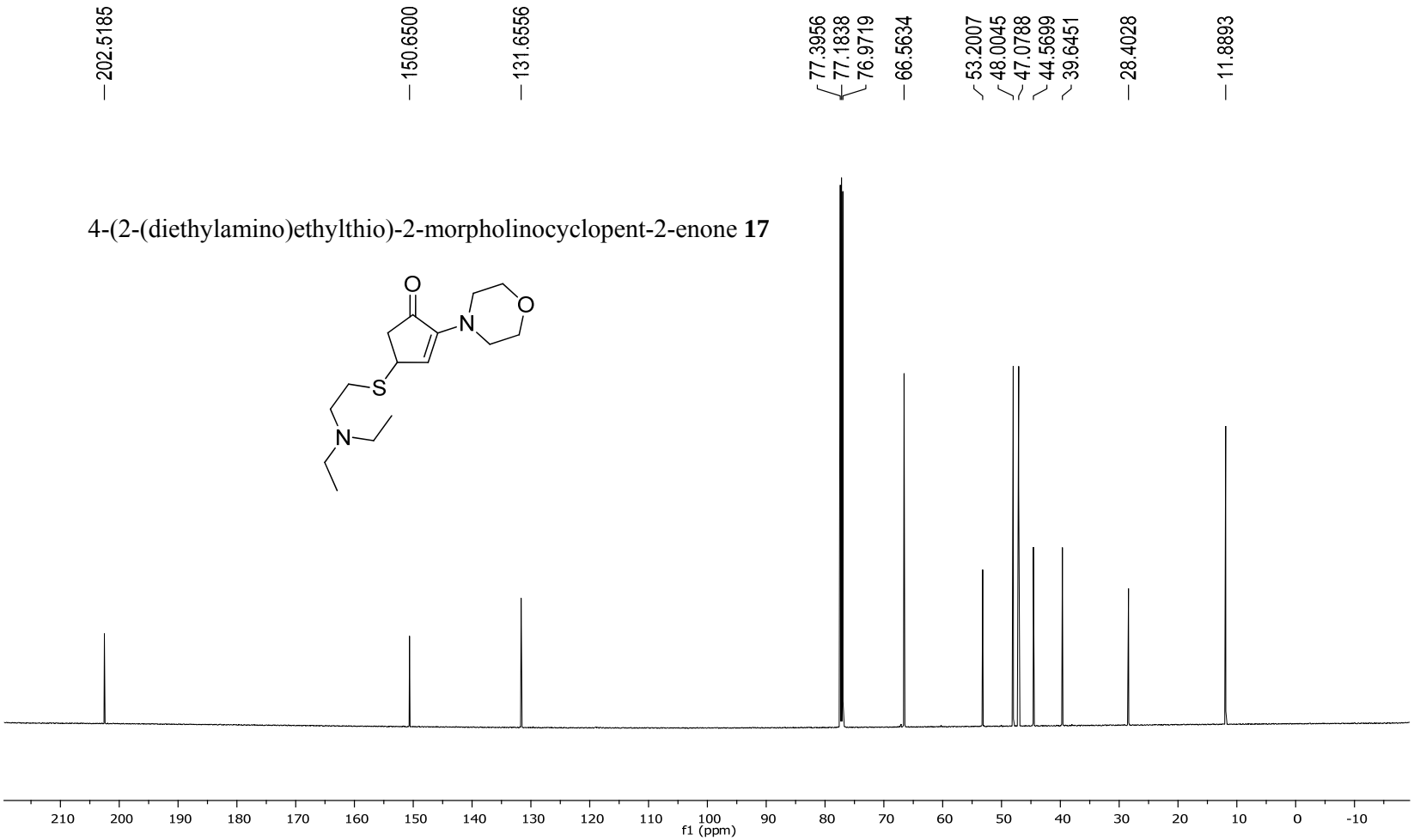


Figure S52 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **17**.

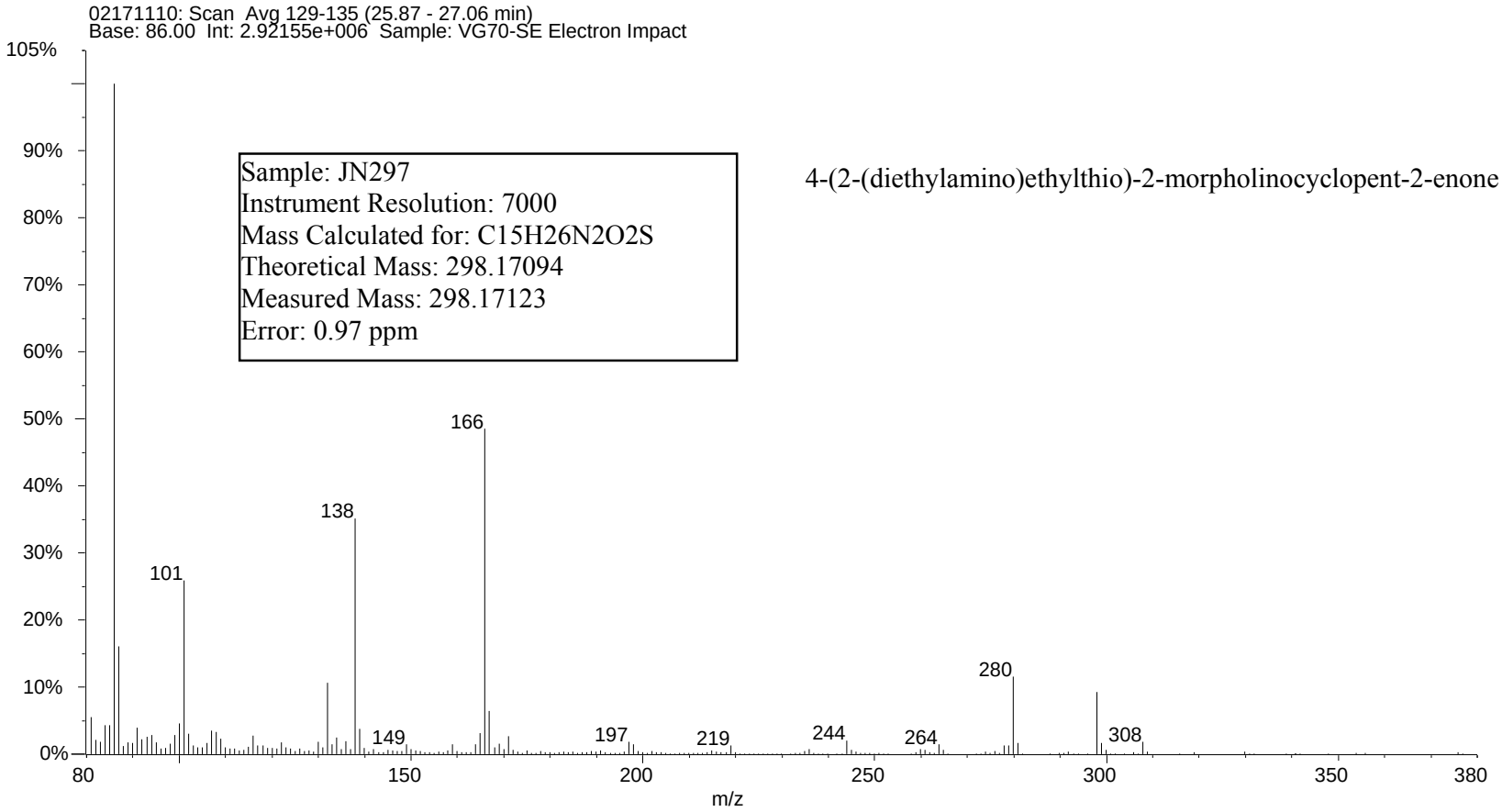


Figure S53 – EI mass spectra for exact mass measurement of isolated enone **17**.

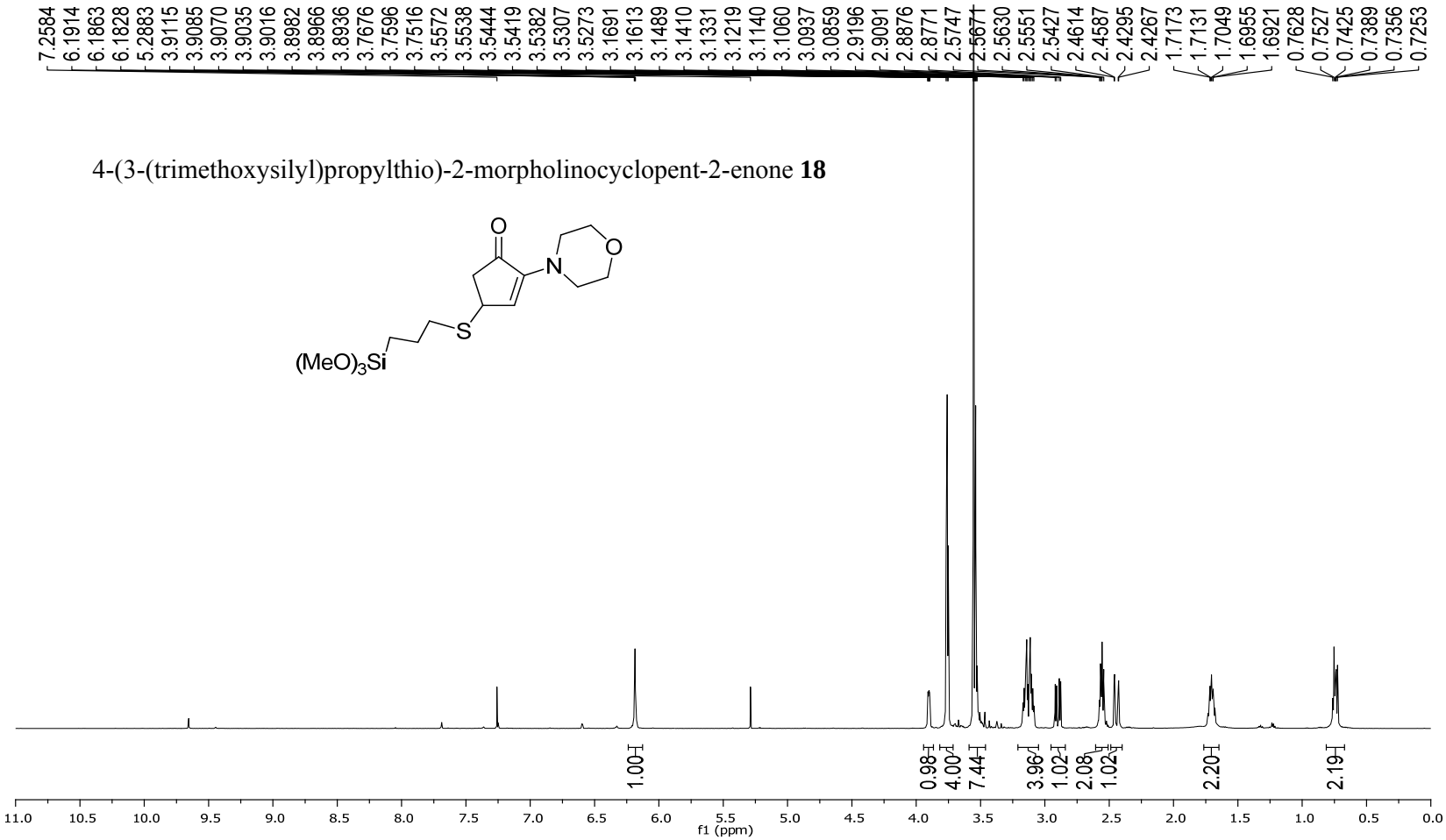


Figure S54 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **18**.

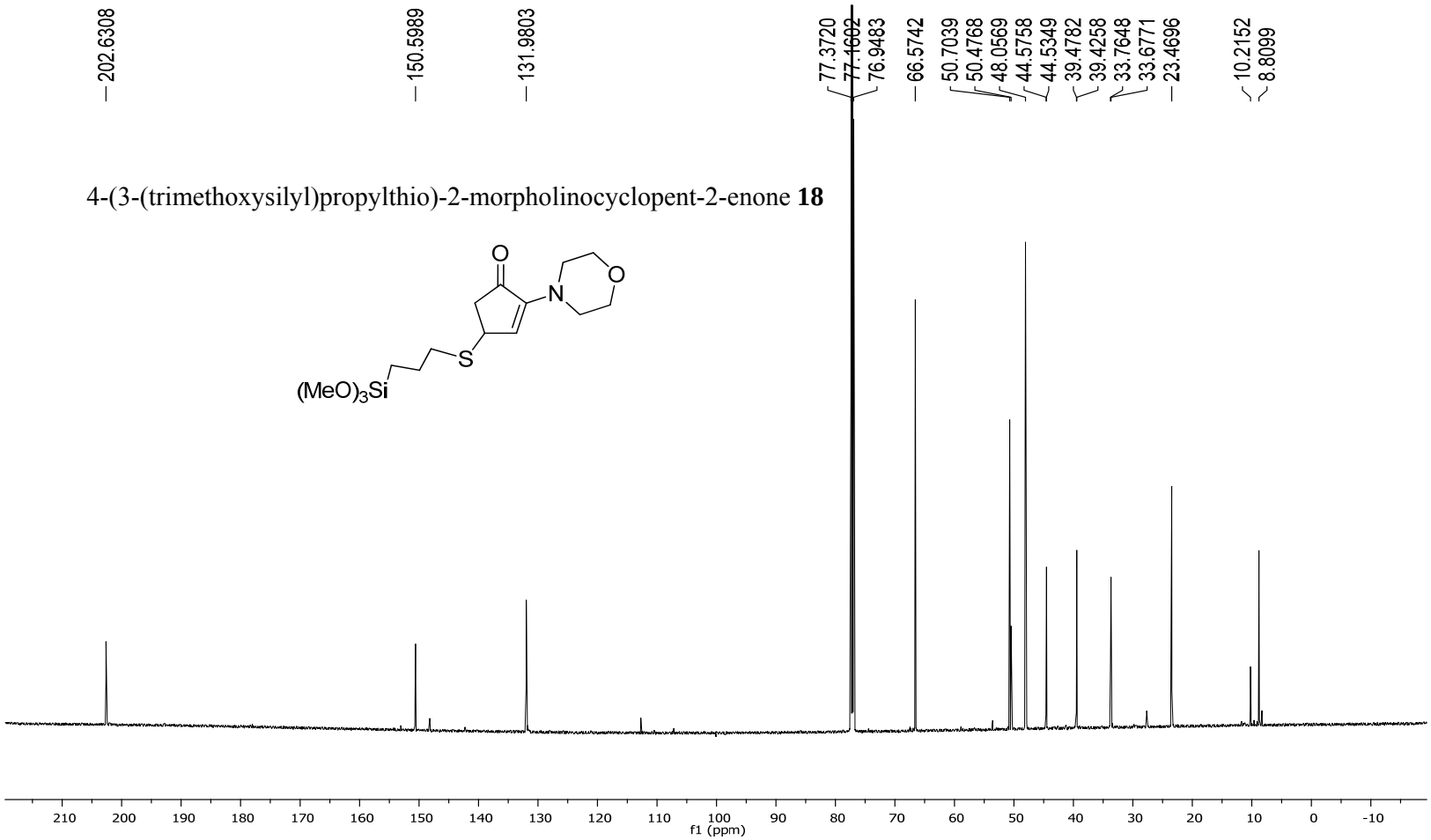


Figure S55 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **18**.

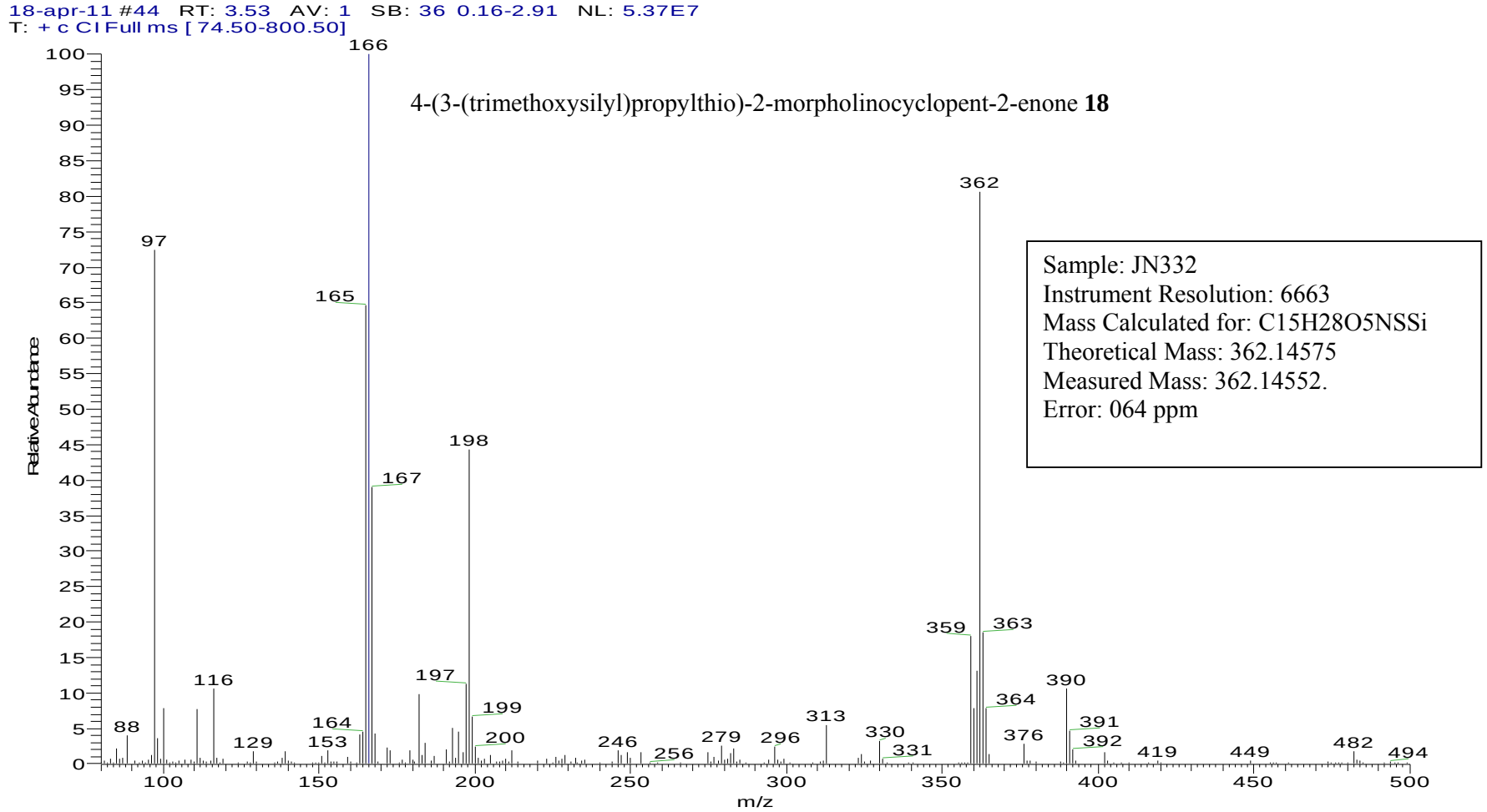


Figure S56 – EI mass spectra for exact mass measurement of isolated enone **18**.

2-morpholino-4-(propylamino)-cyclopent-2-enone **19**

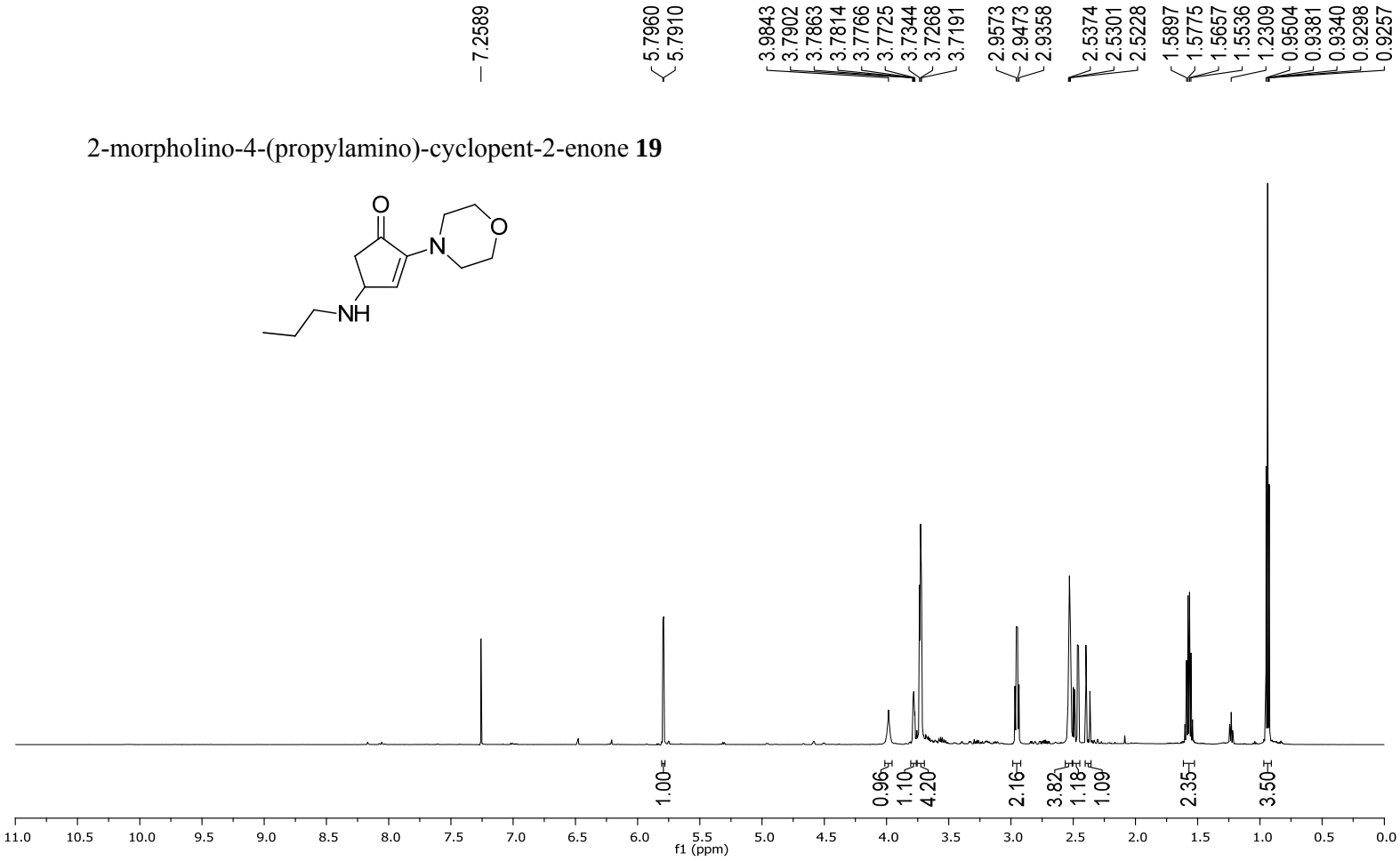


Figure S57 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **19**.

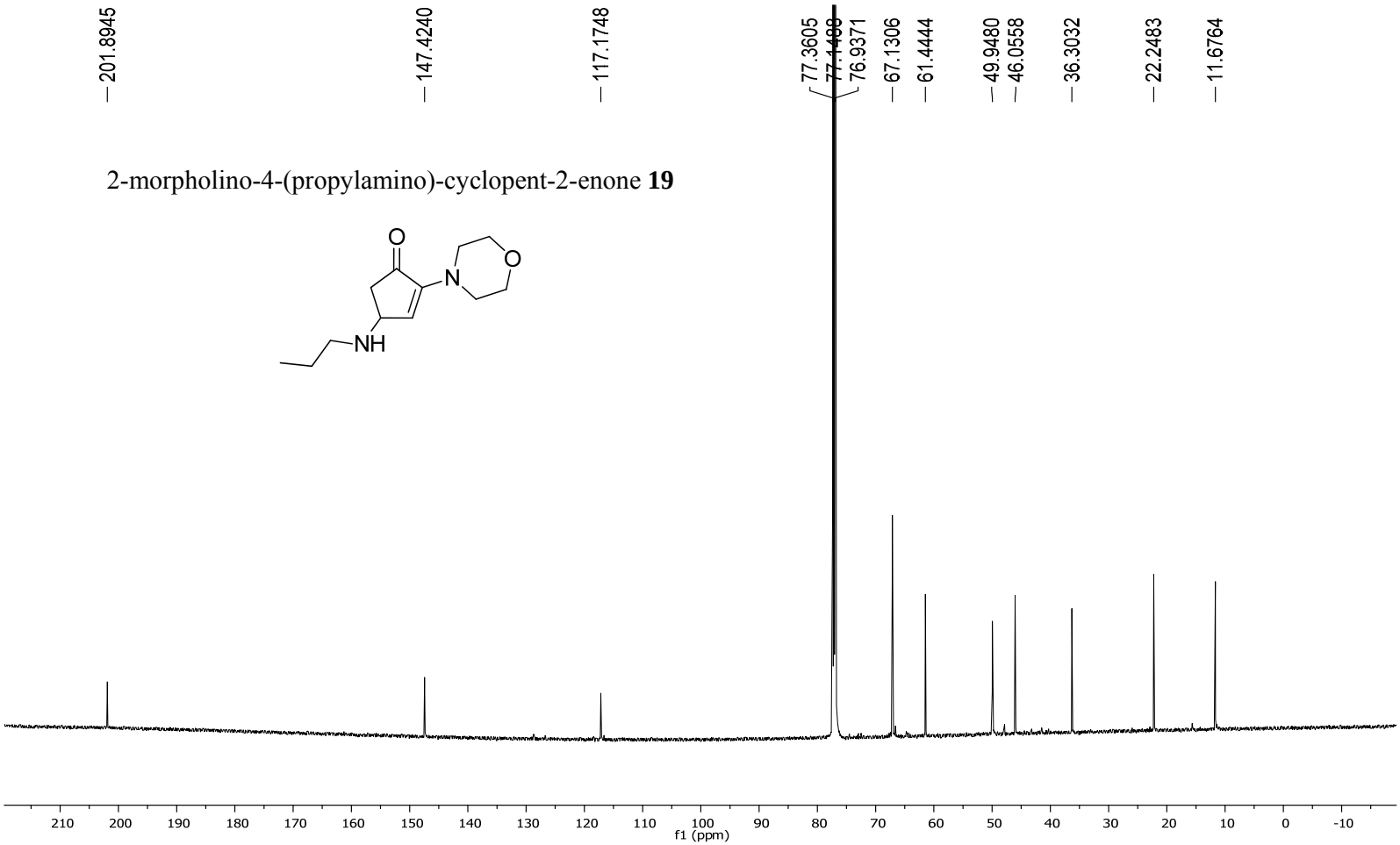


Figure S58 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **19**.

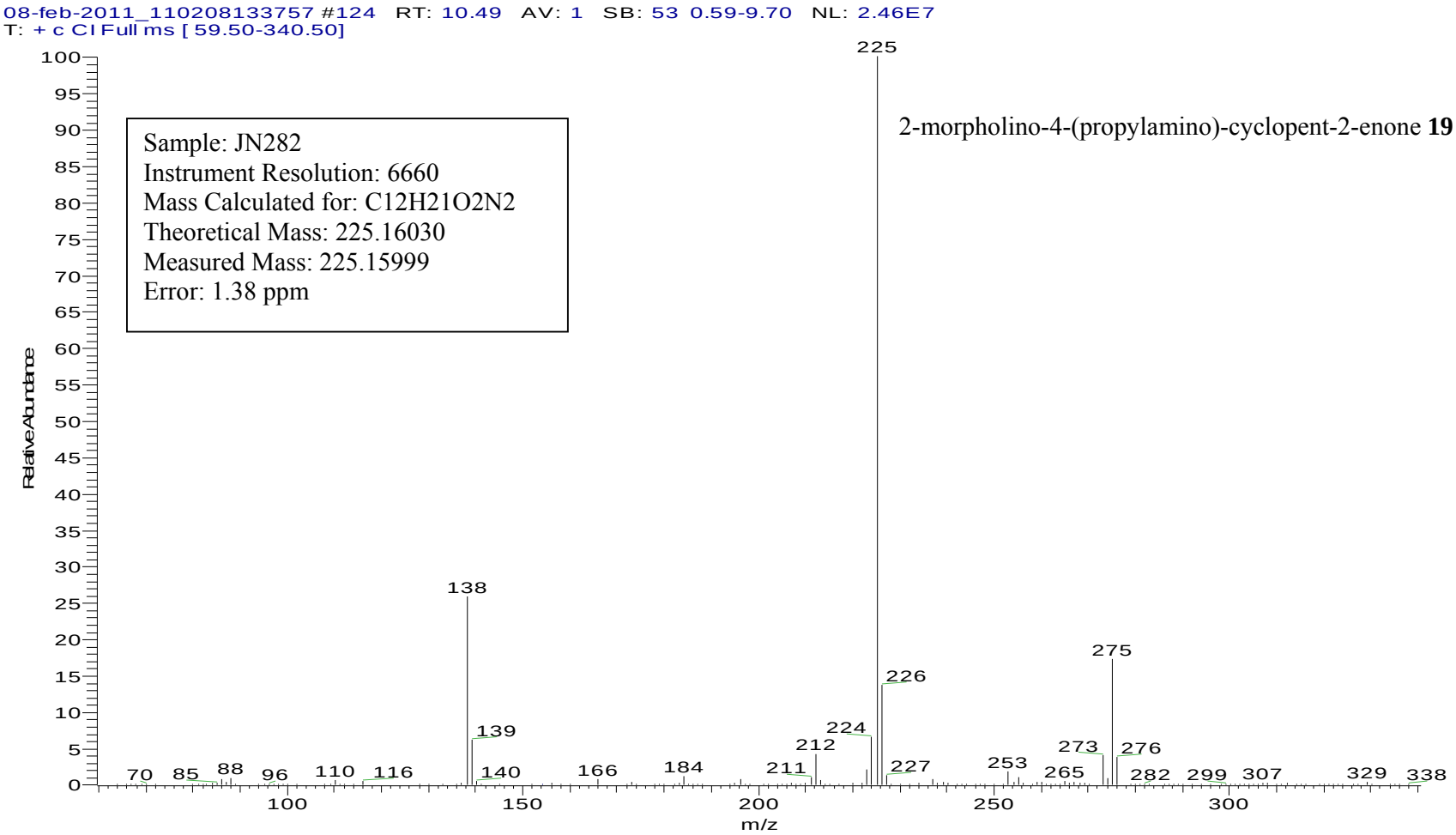


Figure S59 – EI mass spectra for exact mass measurement of isolated enone **19**.

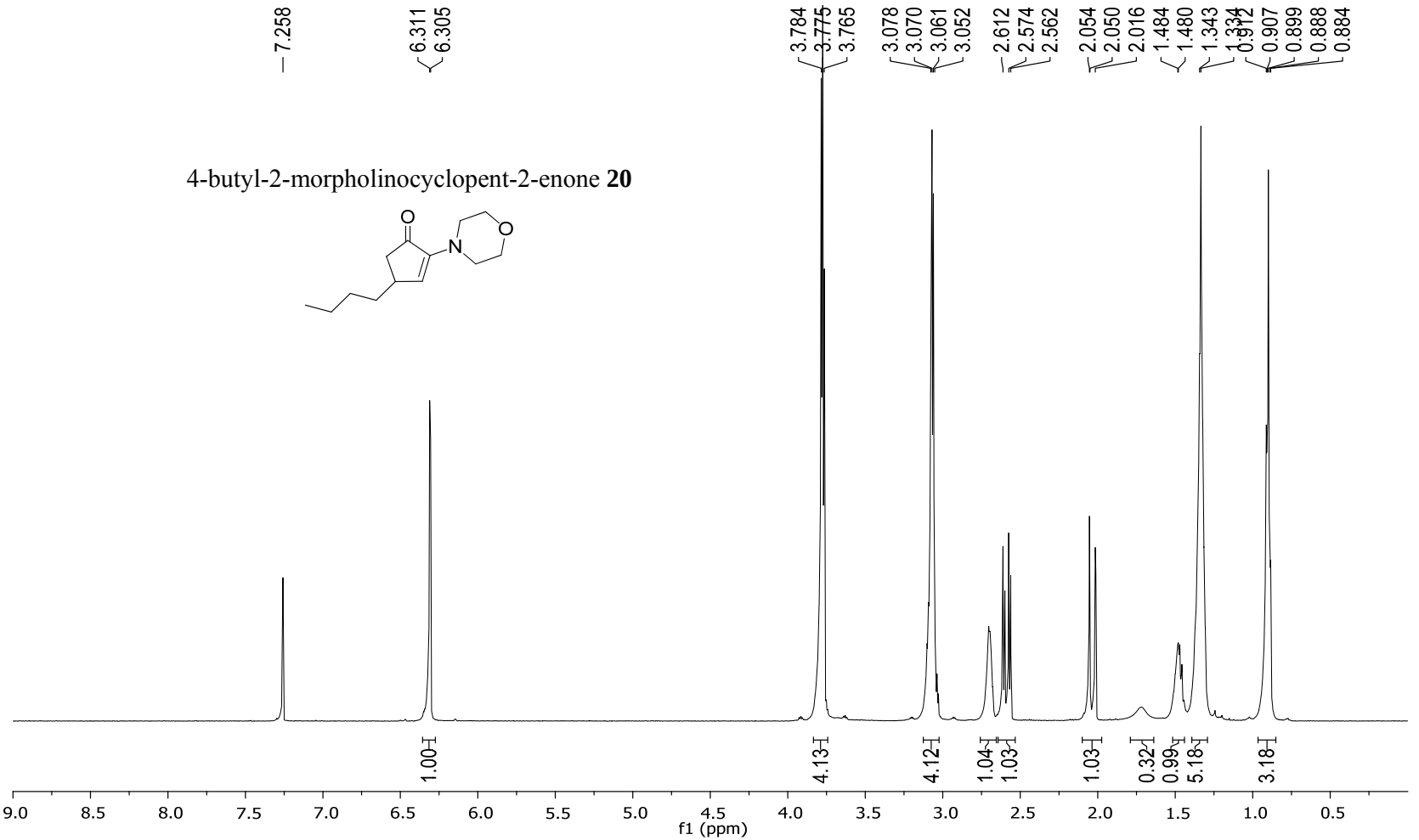


Figure S60 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated compound **20**.

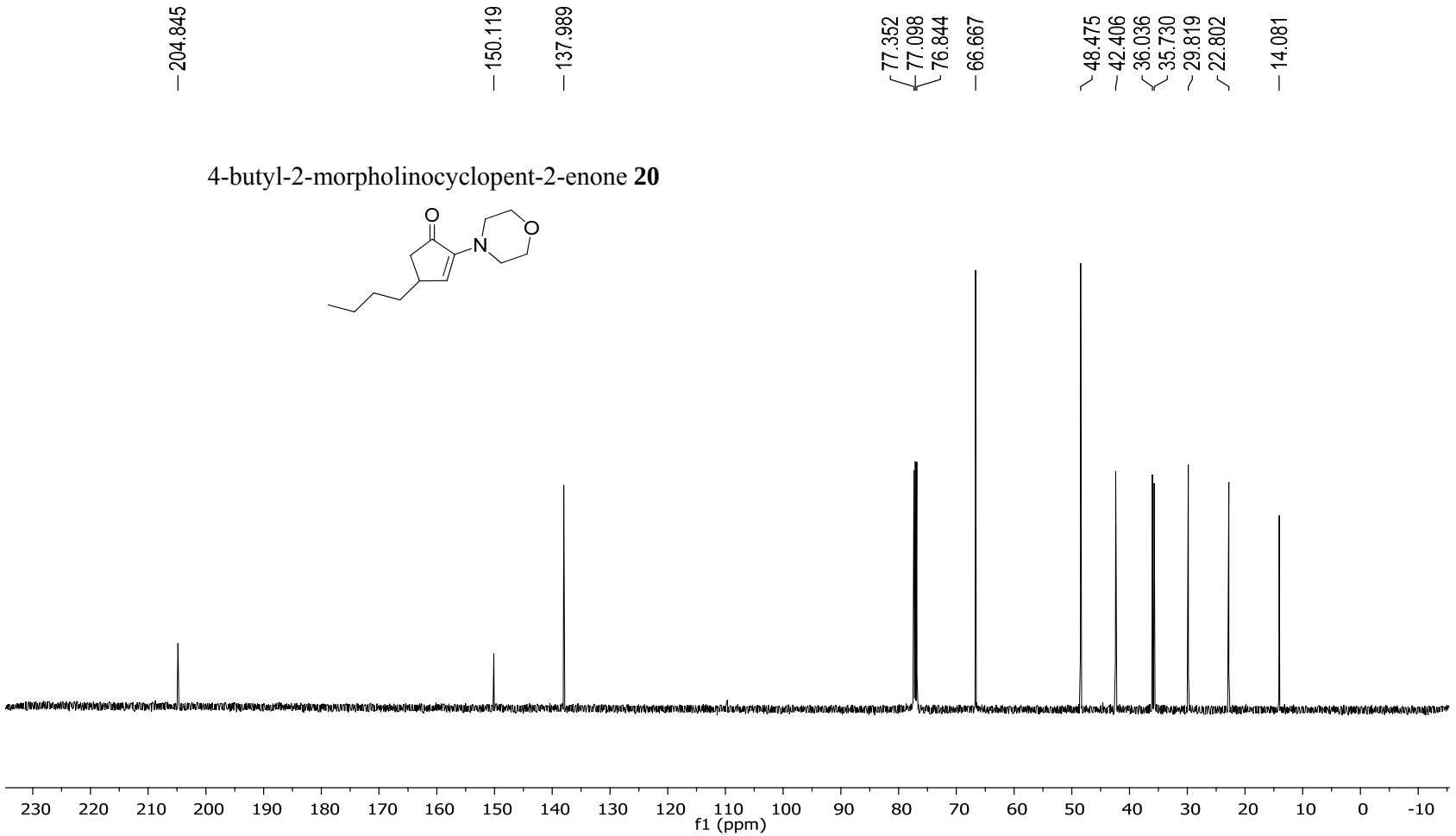


Figure S61 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated compound **20**.

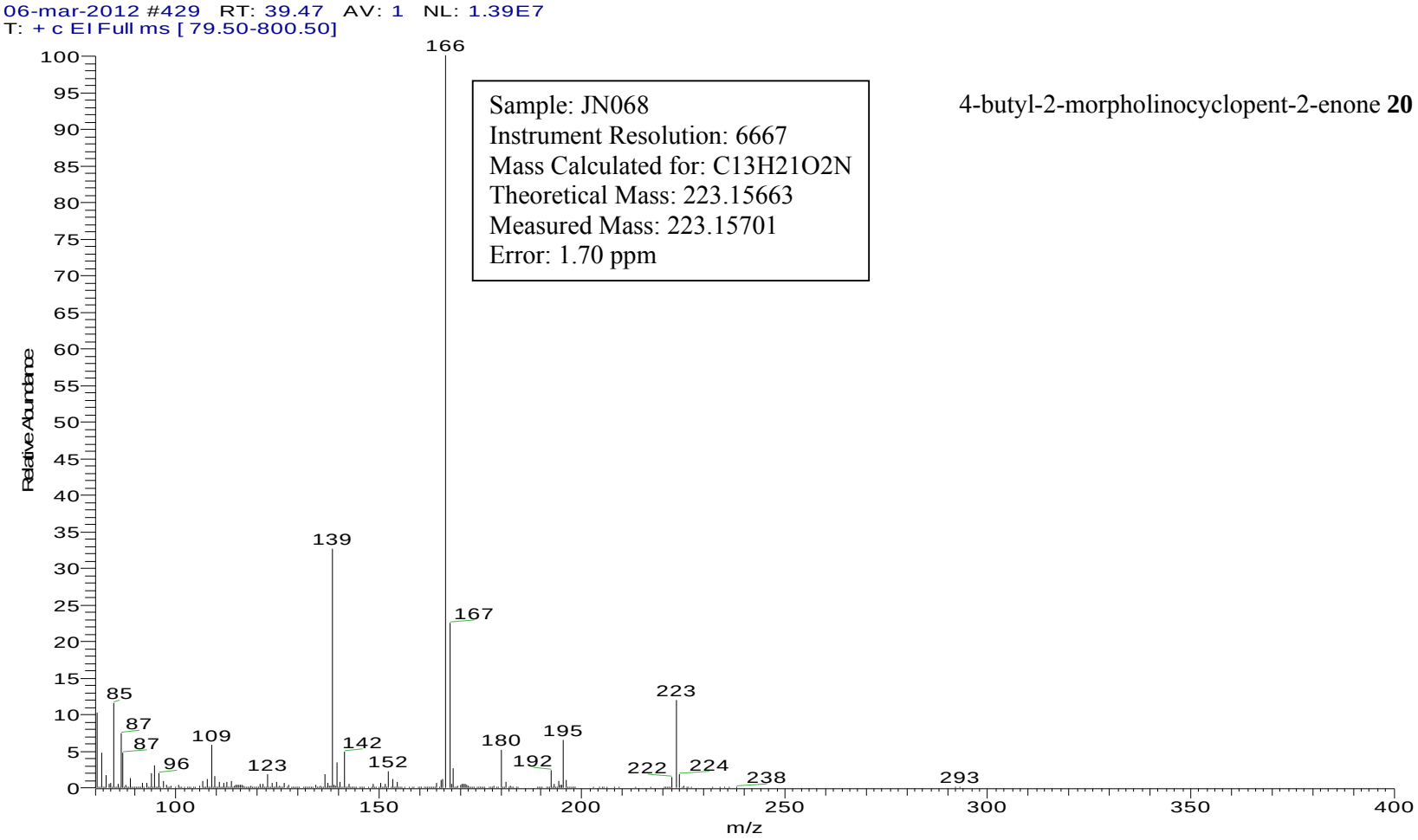


Figure S62 – EI mass spectra for exact mass measurement of isolated compound **20**.

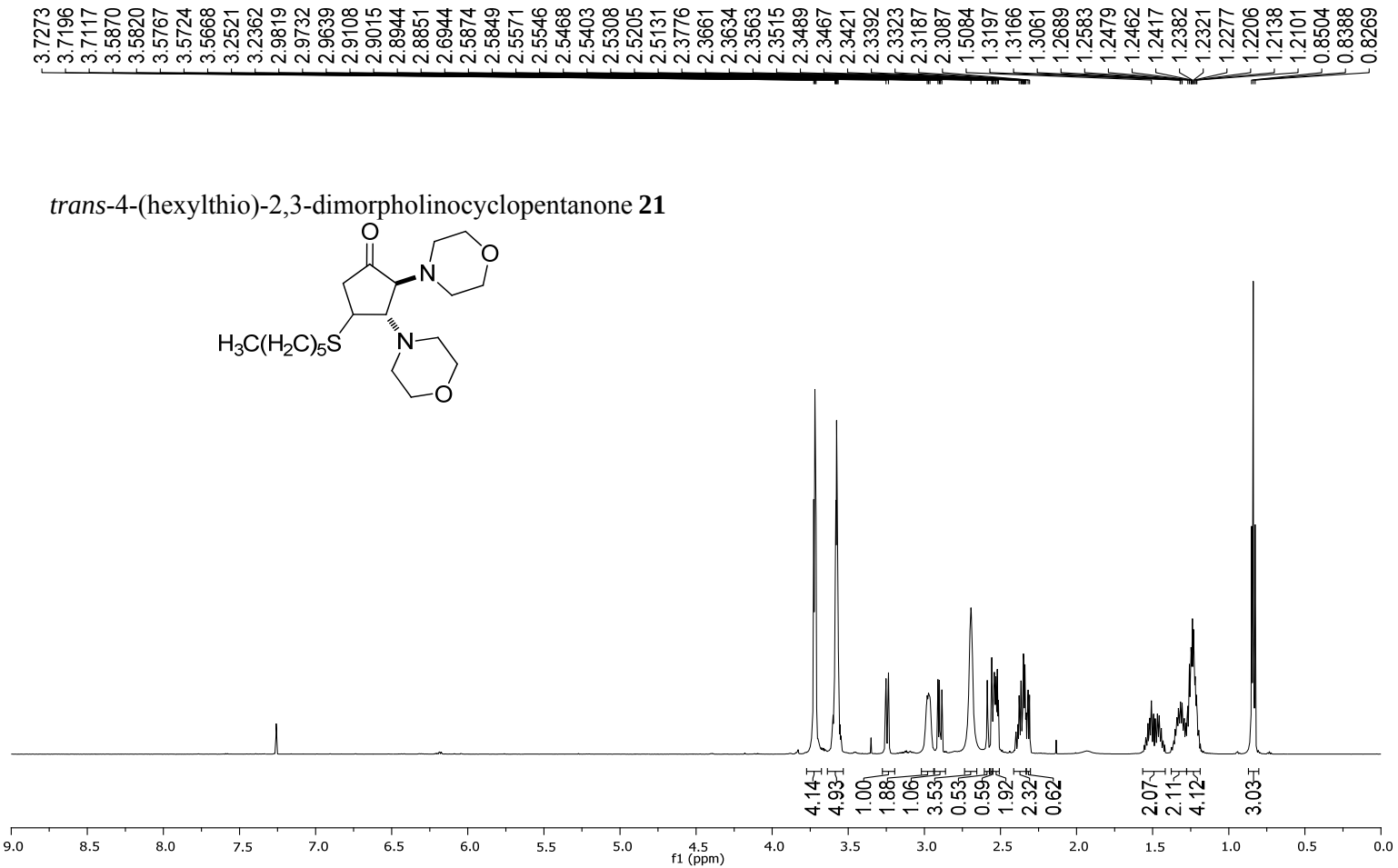


Figure S63 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated compound **21**.

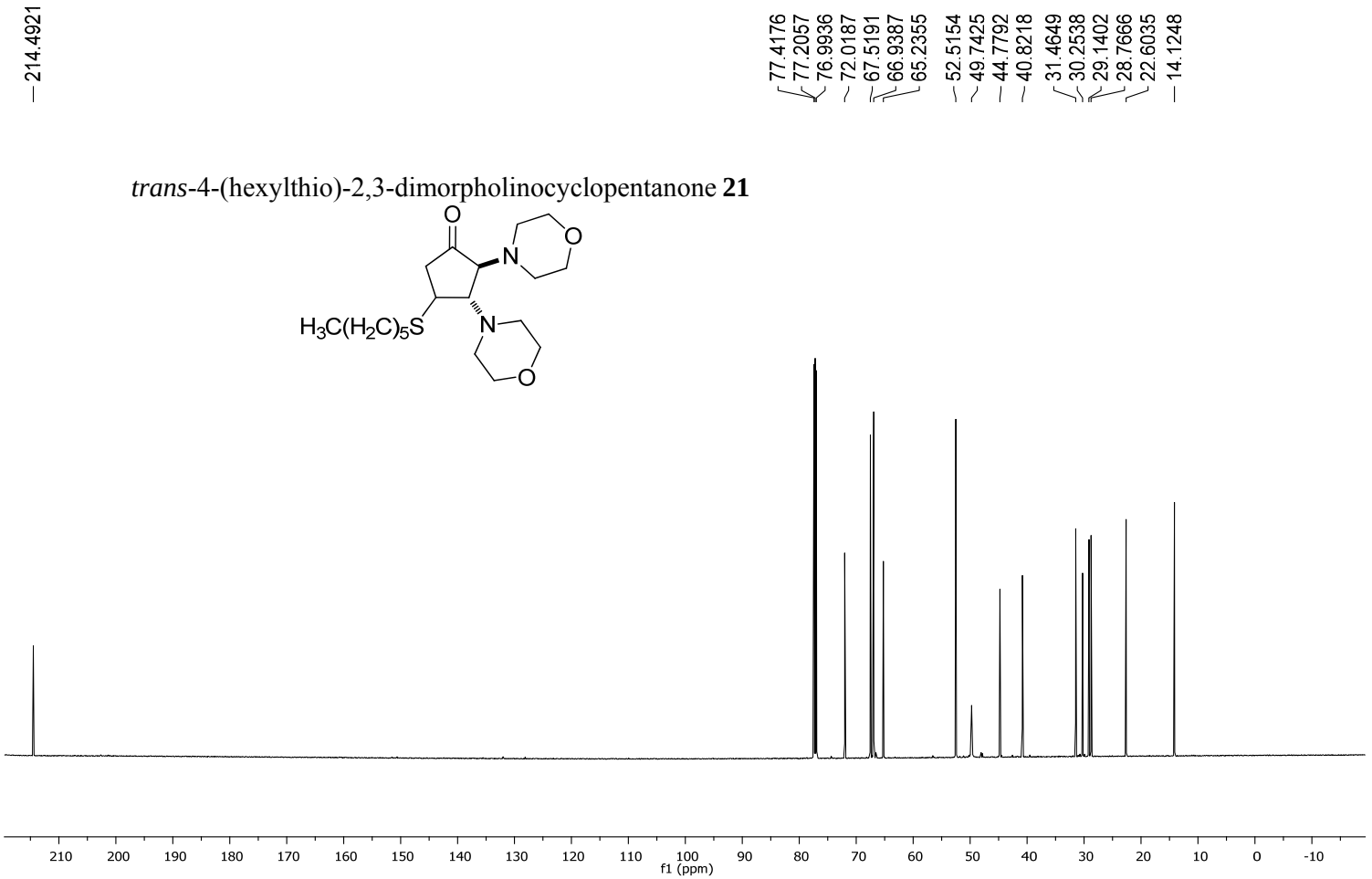


Figure S64 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated compound **21**.

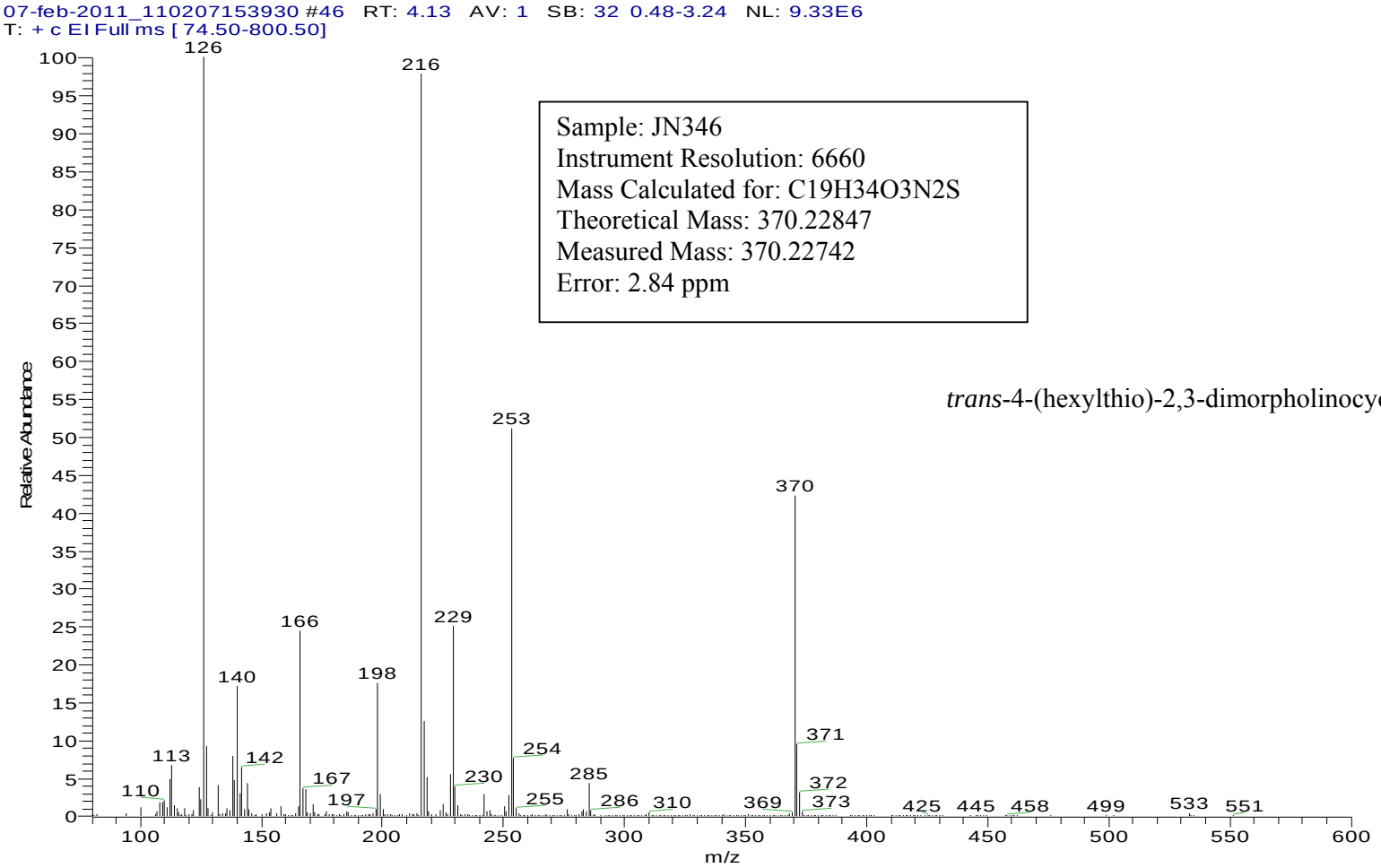


Figure S65 – EI mass spectra for exact mass measurement of isolated compound **21**.

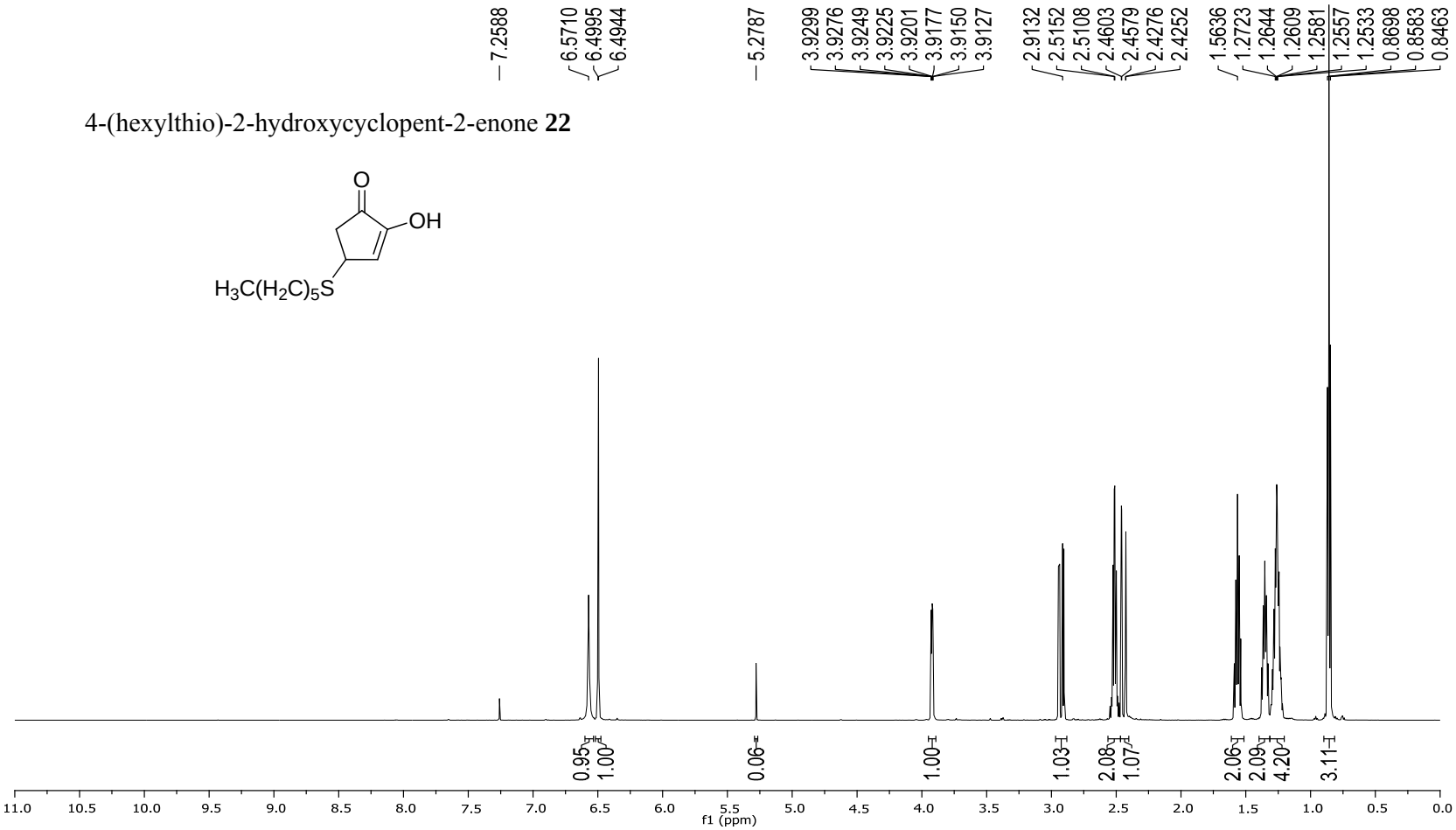


Figure S66 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **22**.

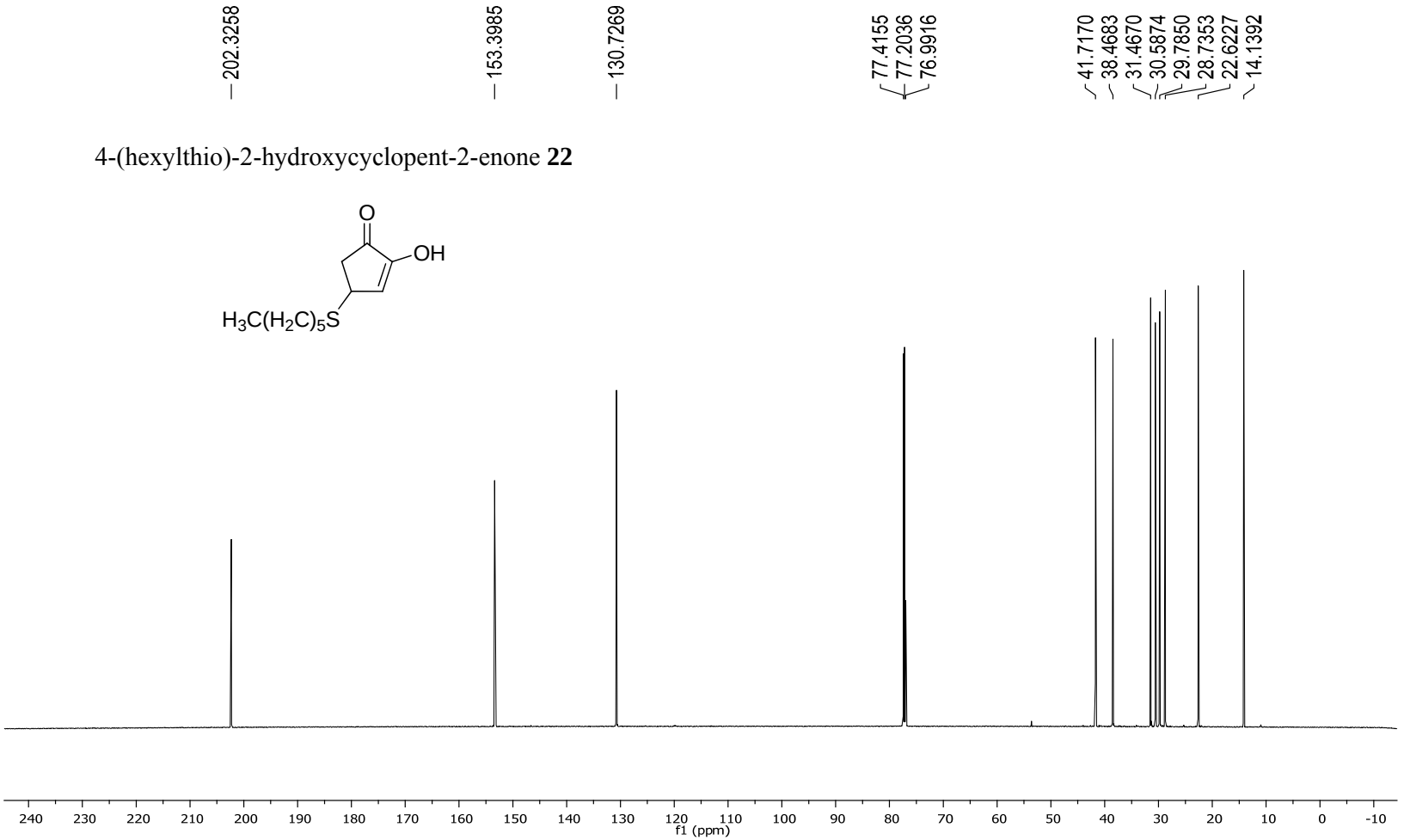


Figure S67 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **22**.

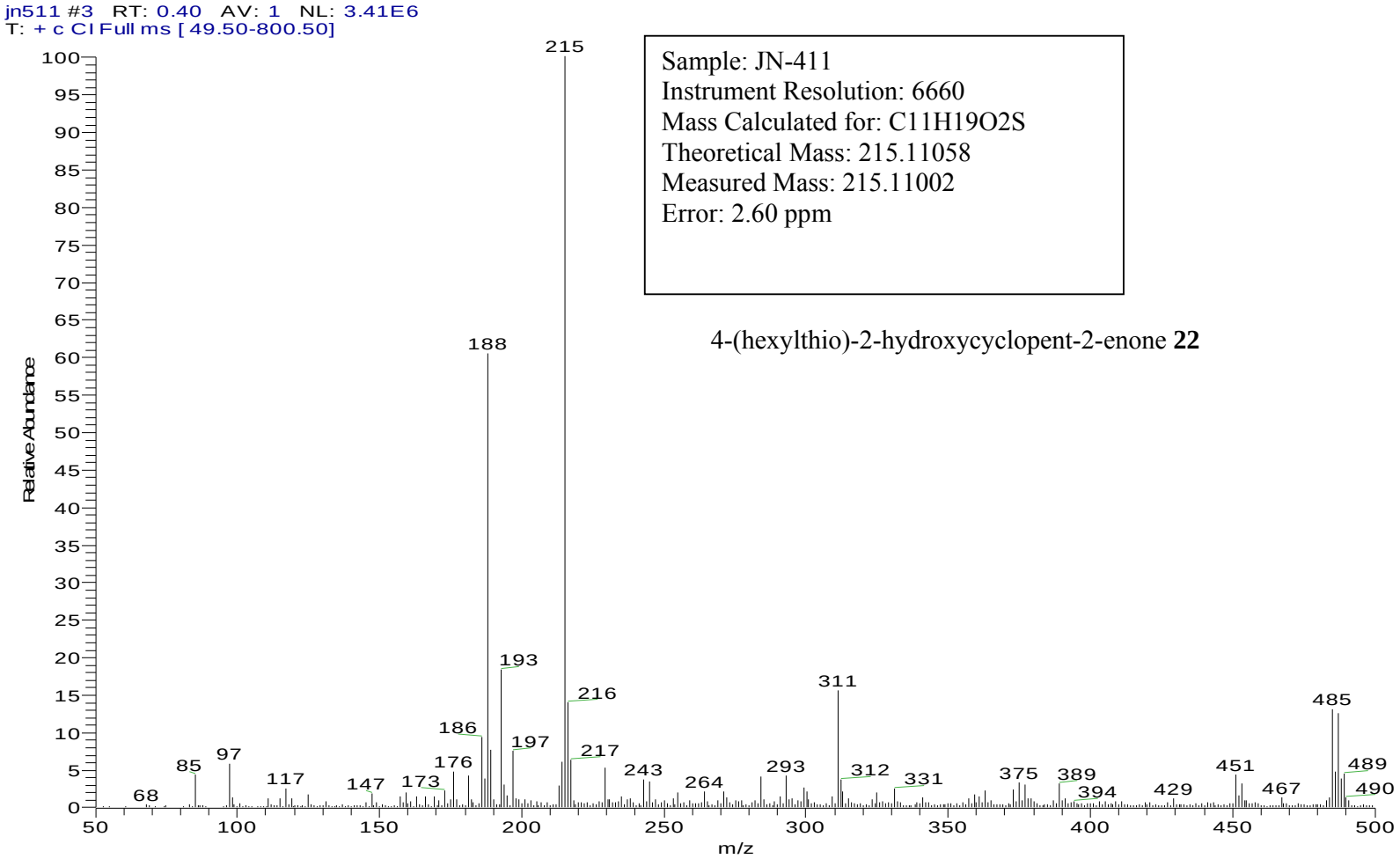


Figure S68 – EI mass spectra for exact mass measurement of isolated enone **22**.

4-(ethylthio)-2-hydroxycyclopent-2-enone **23**

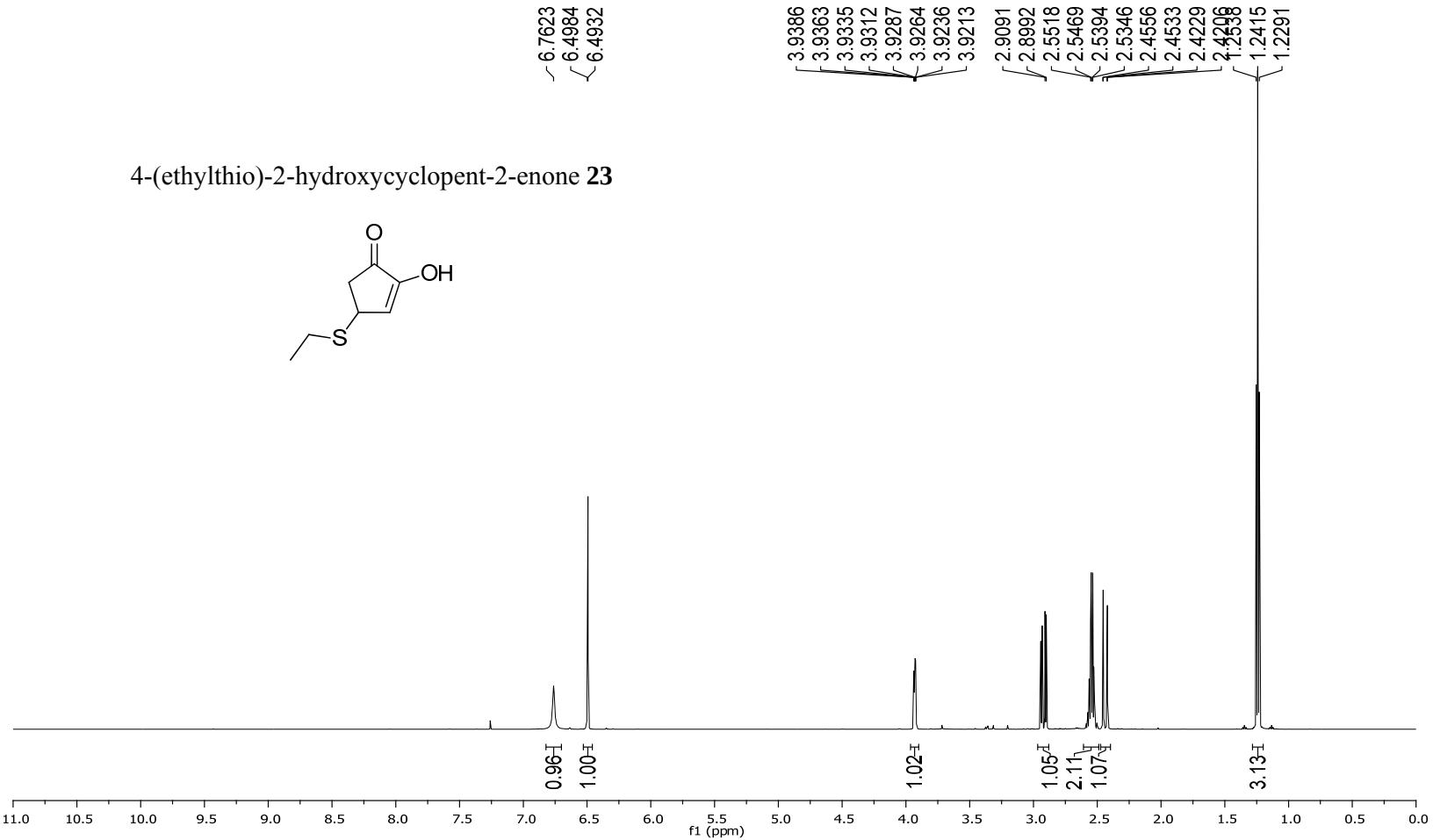


Figure S69 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **23**.

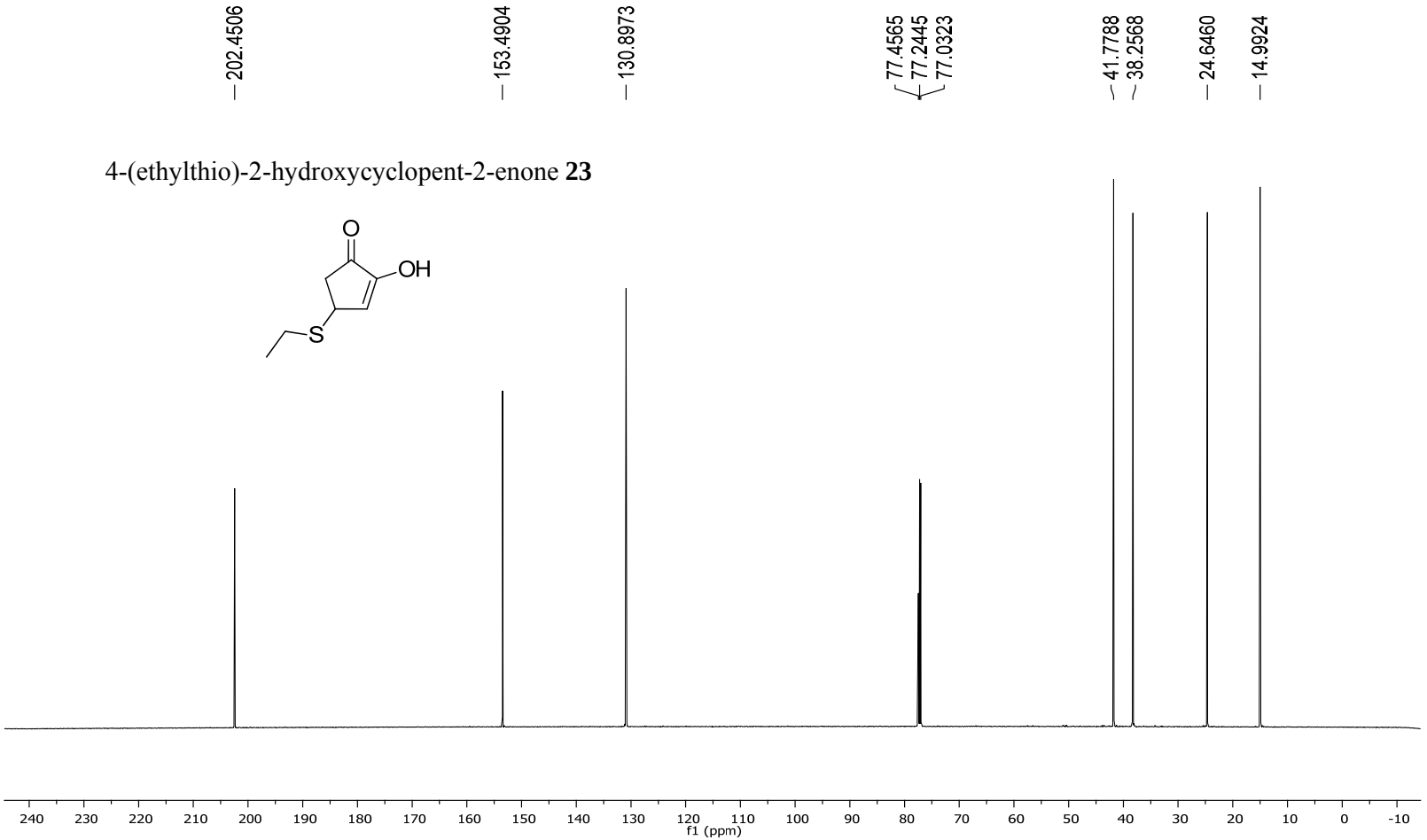
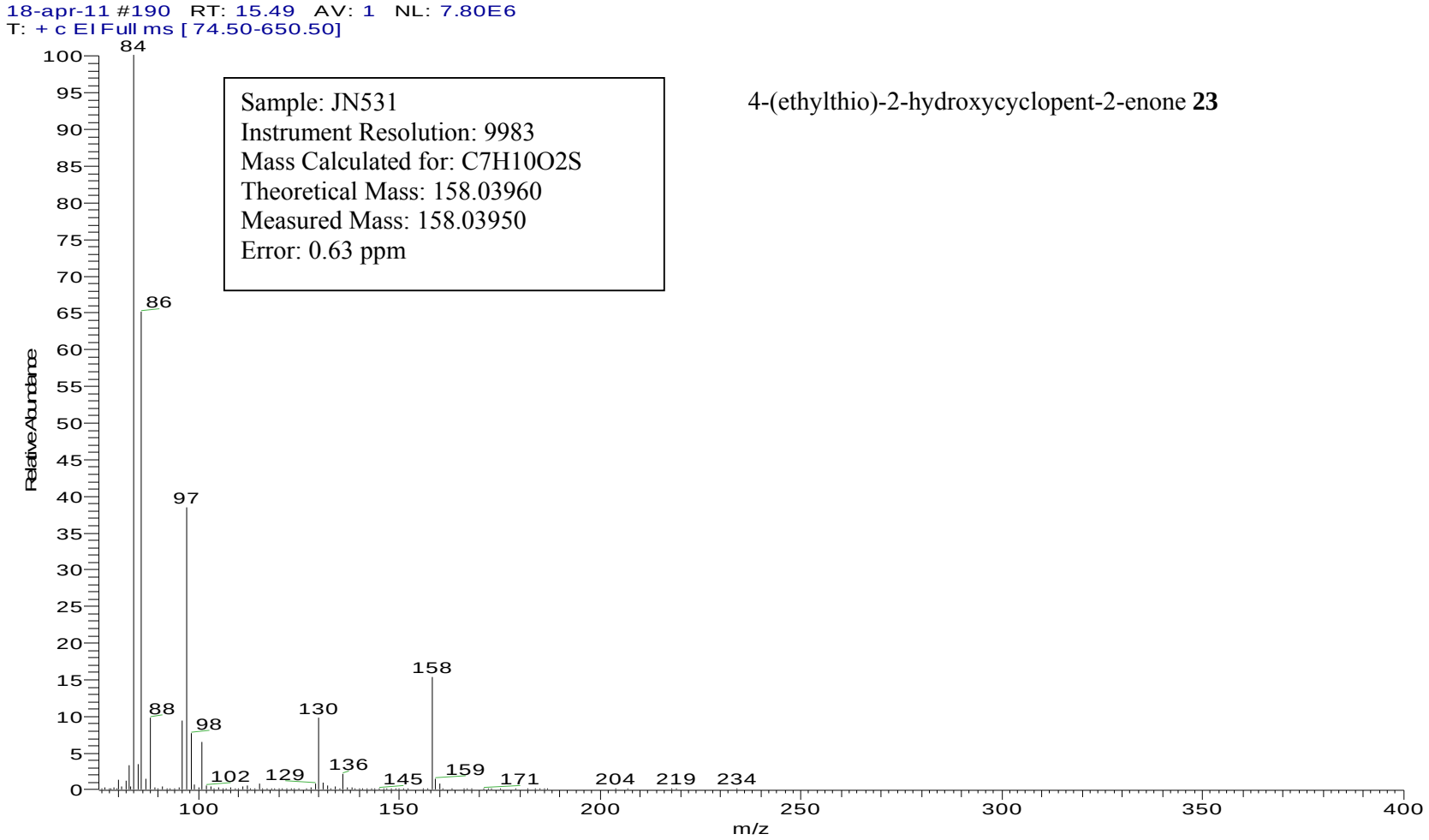


Figure S70 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **23**.



4-(ethylthio)-2-hydroxycyclopent-2-enone **23**

Figure S71 – EI mass spectra for exact mass measurement of isolated enone **23**.

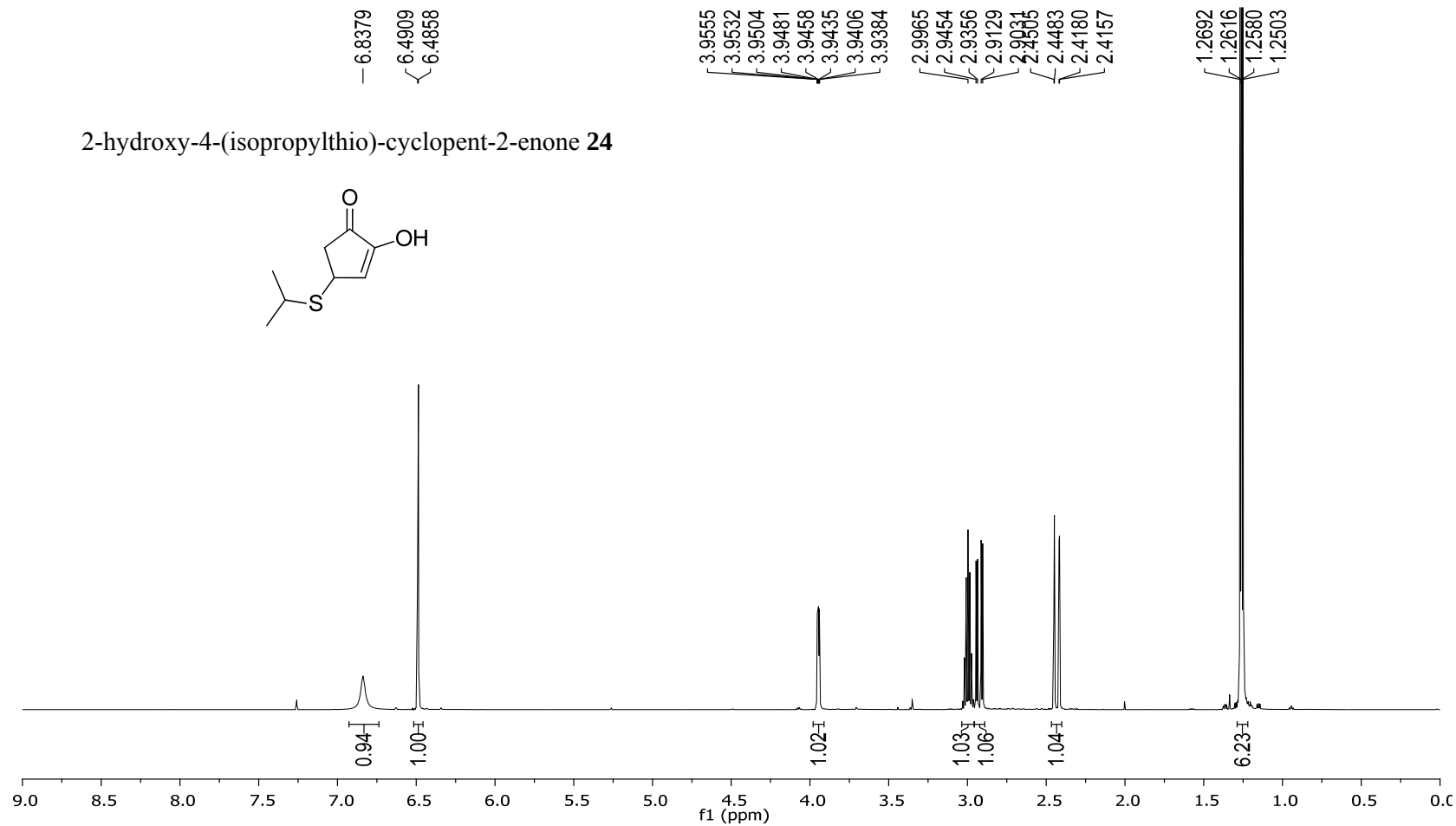


Figure S72 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **24**.

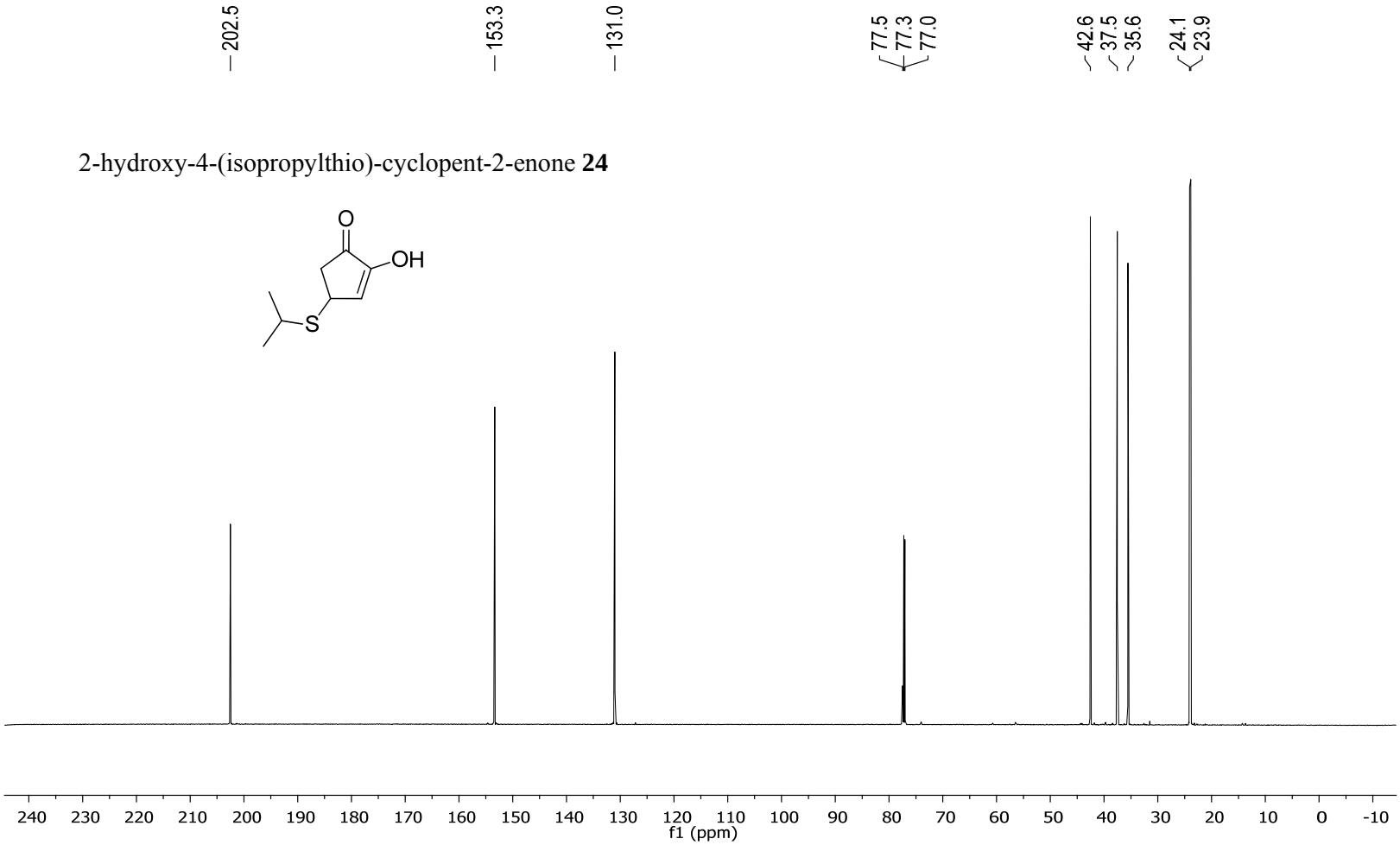


Figure S73 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **24**.

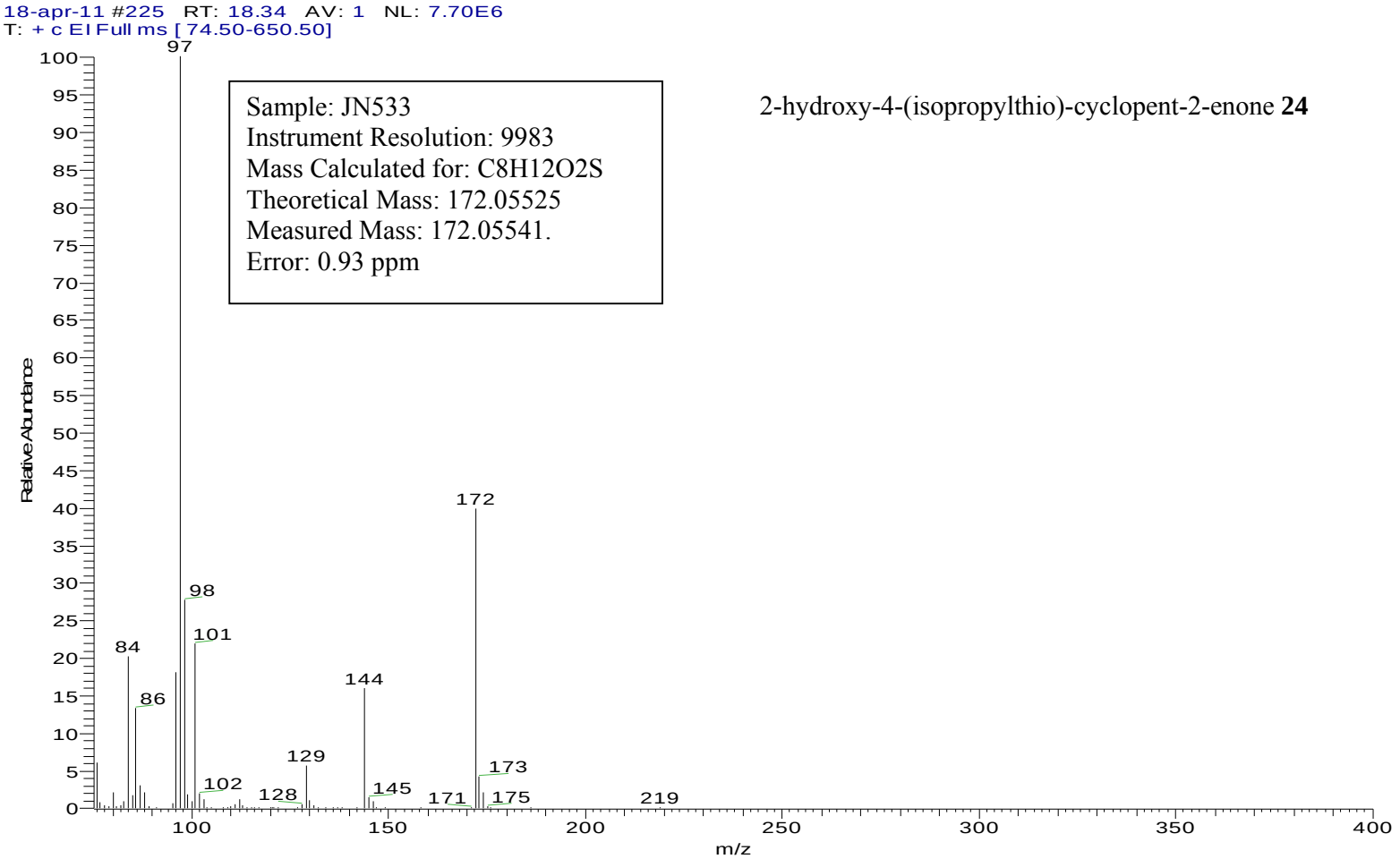
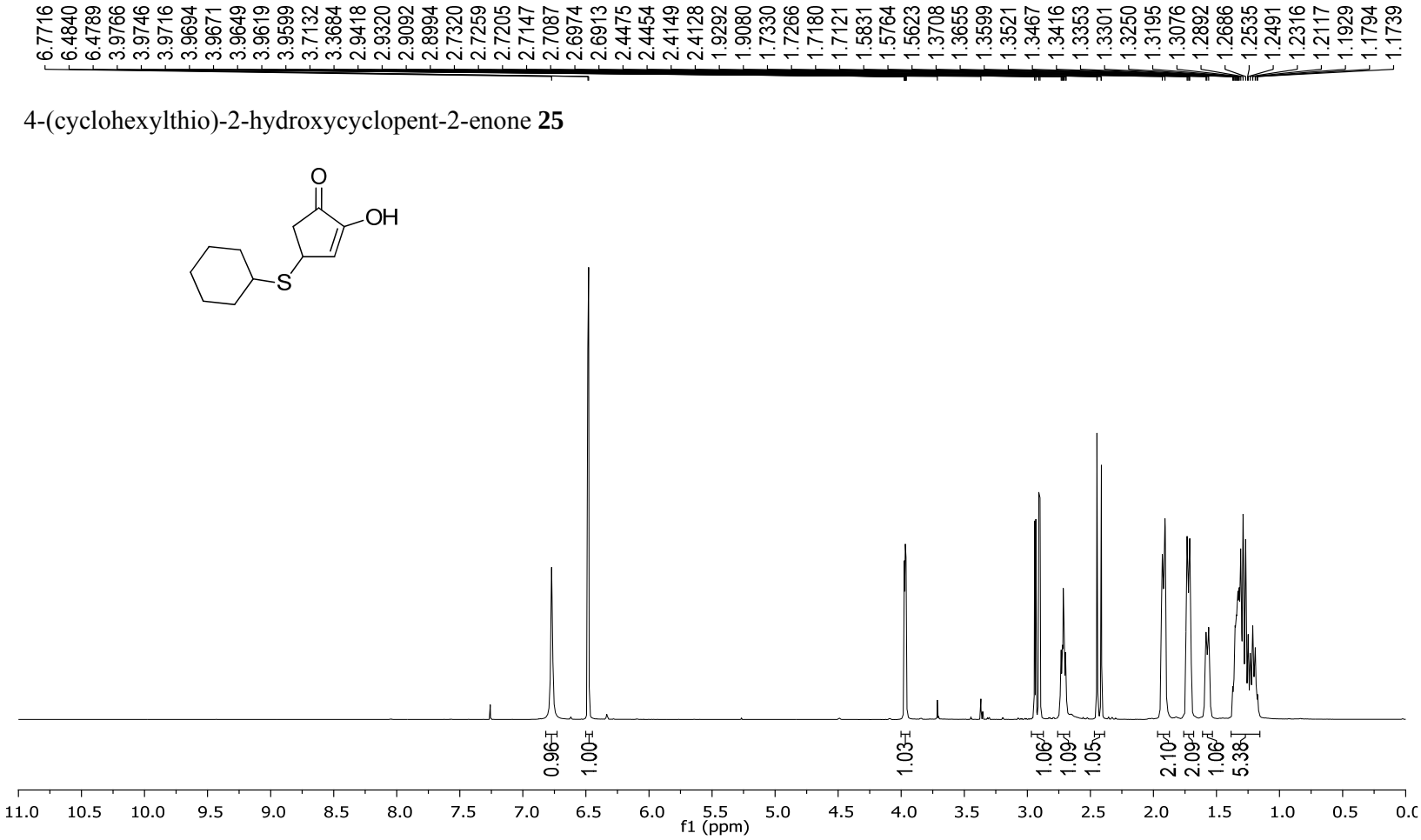


Figure S74 – EI mass spectra for exact mass measurement of isolated enone **24**.



4-(cyclohexylthio)-2-hydroxycyclopent-2-enone **25**

Figure S75 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **25**.

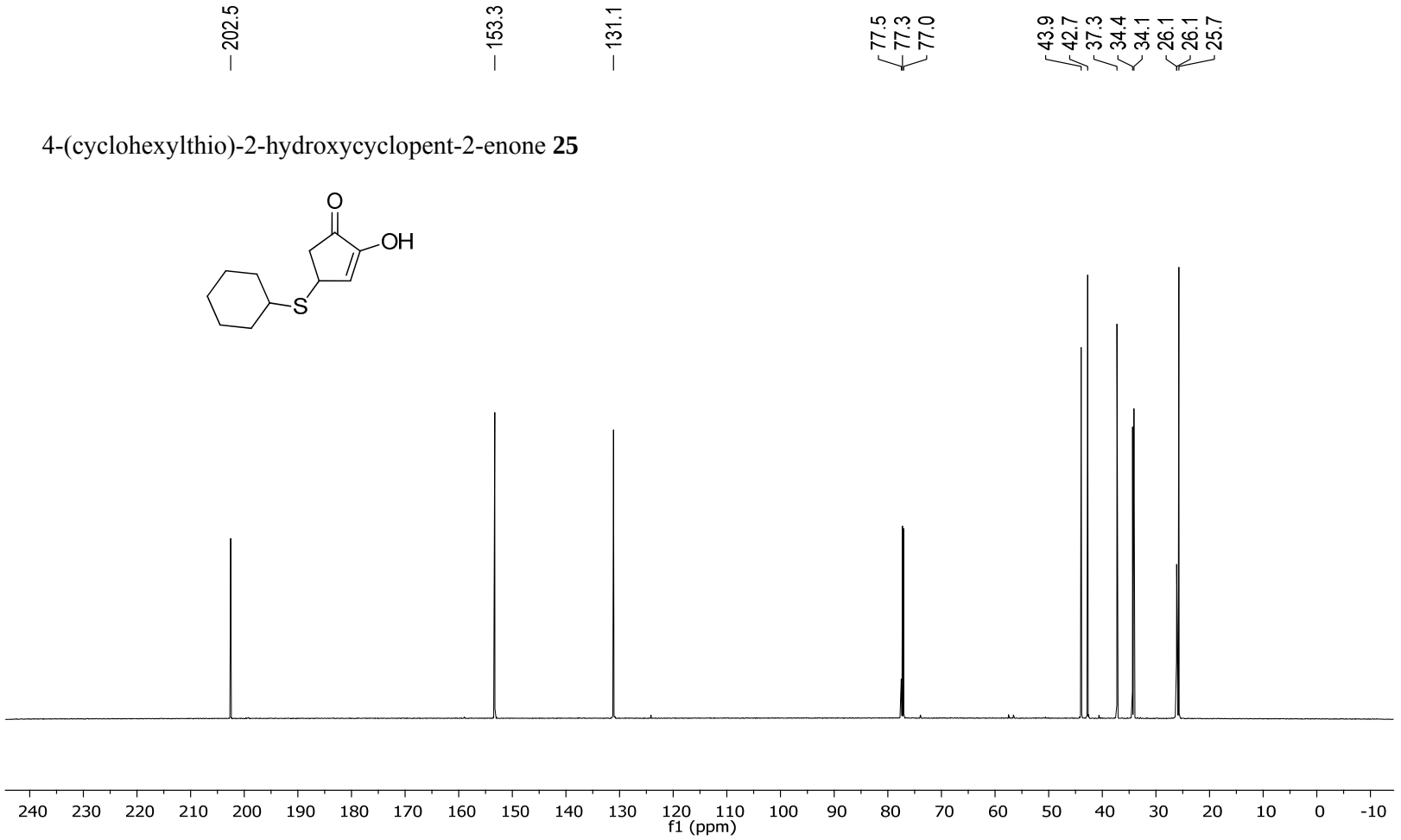


Figure S76 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **25**.

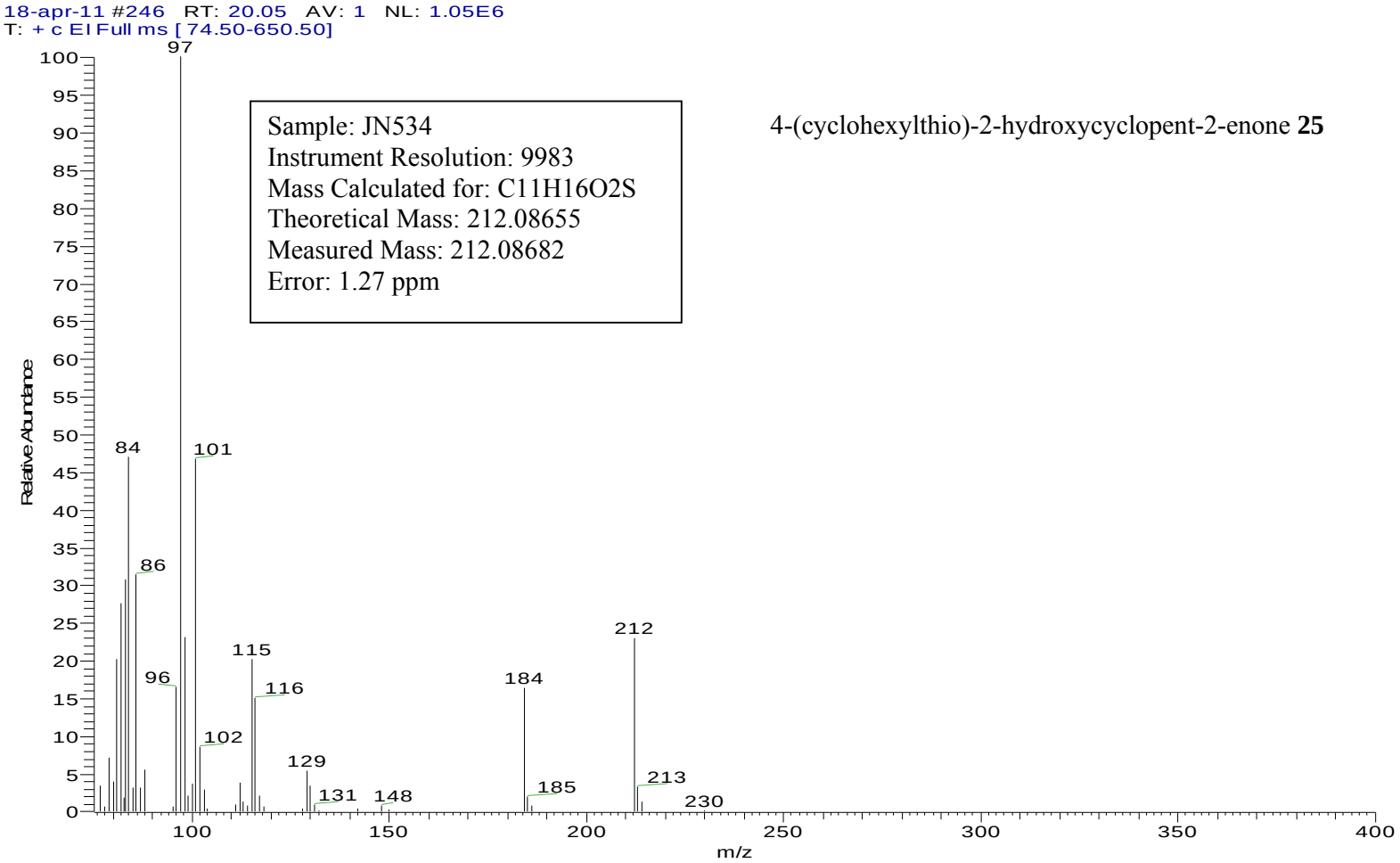


Figure S77 – EI mass spectra for exact mass measurement of isolated enone **25**.

4-(*tert*-butylthio)-2-hydroxycyclopent-2-enone **26**

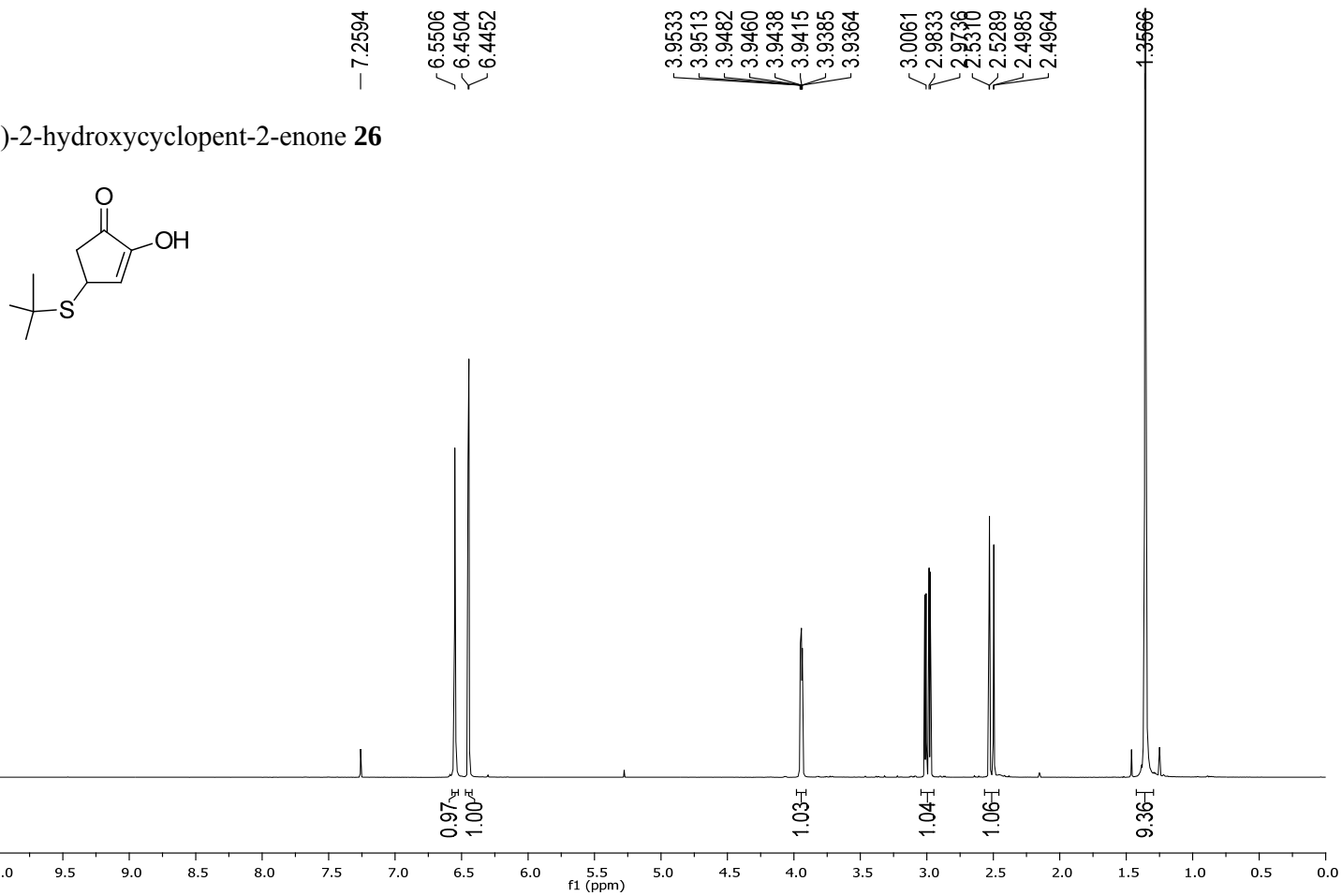


Figure S78 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **26**.

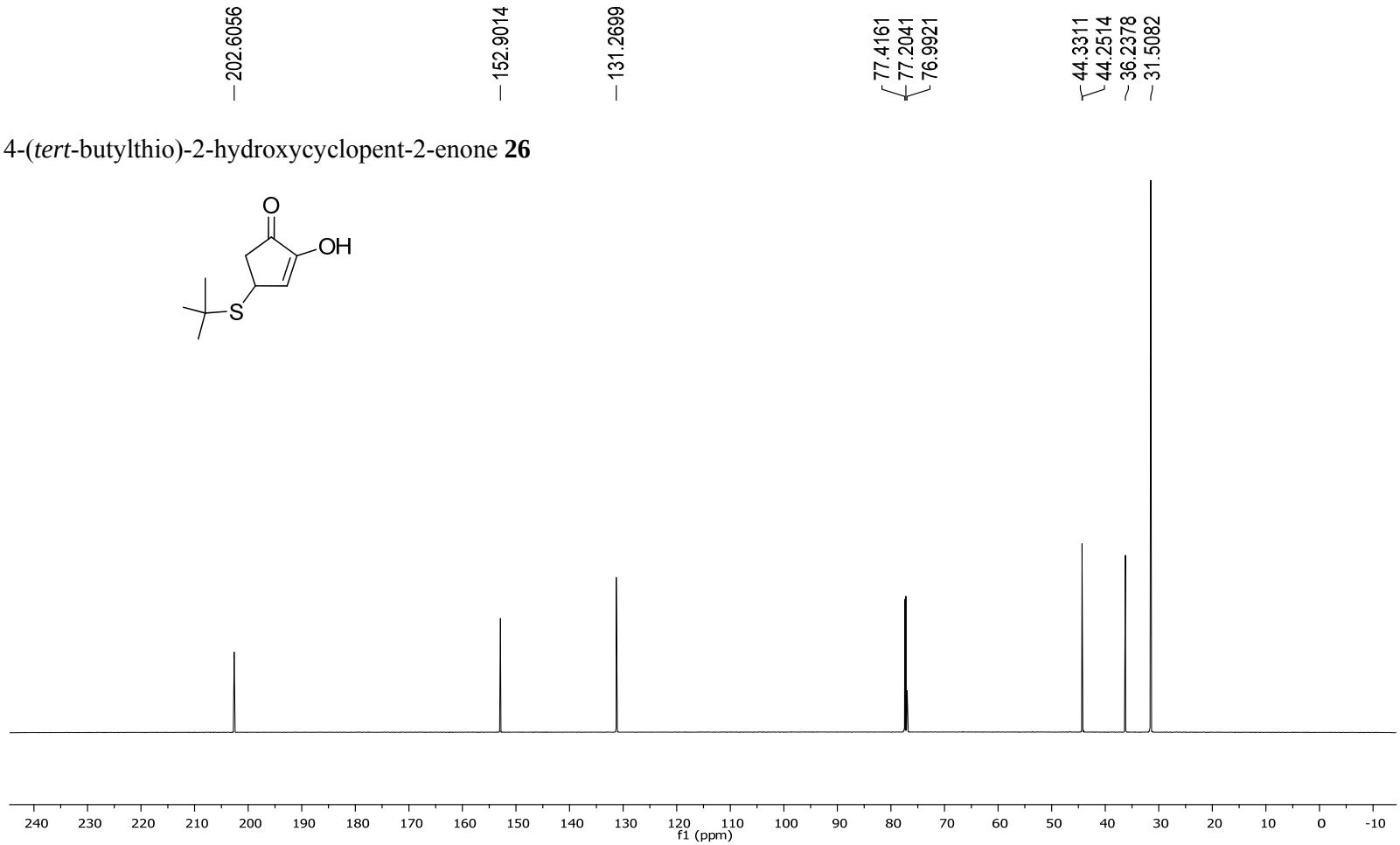
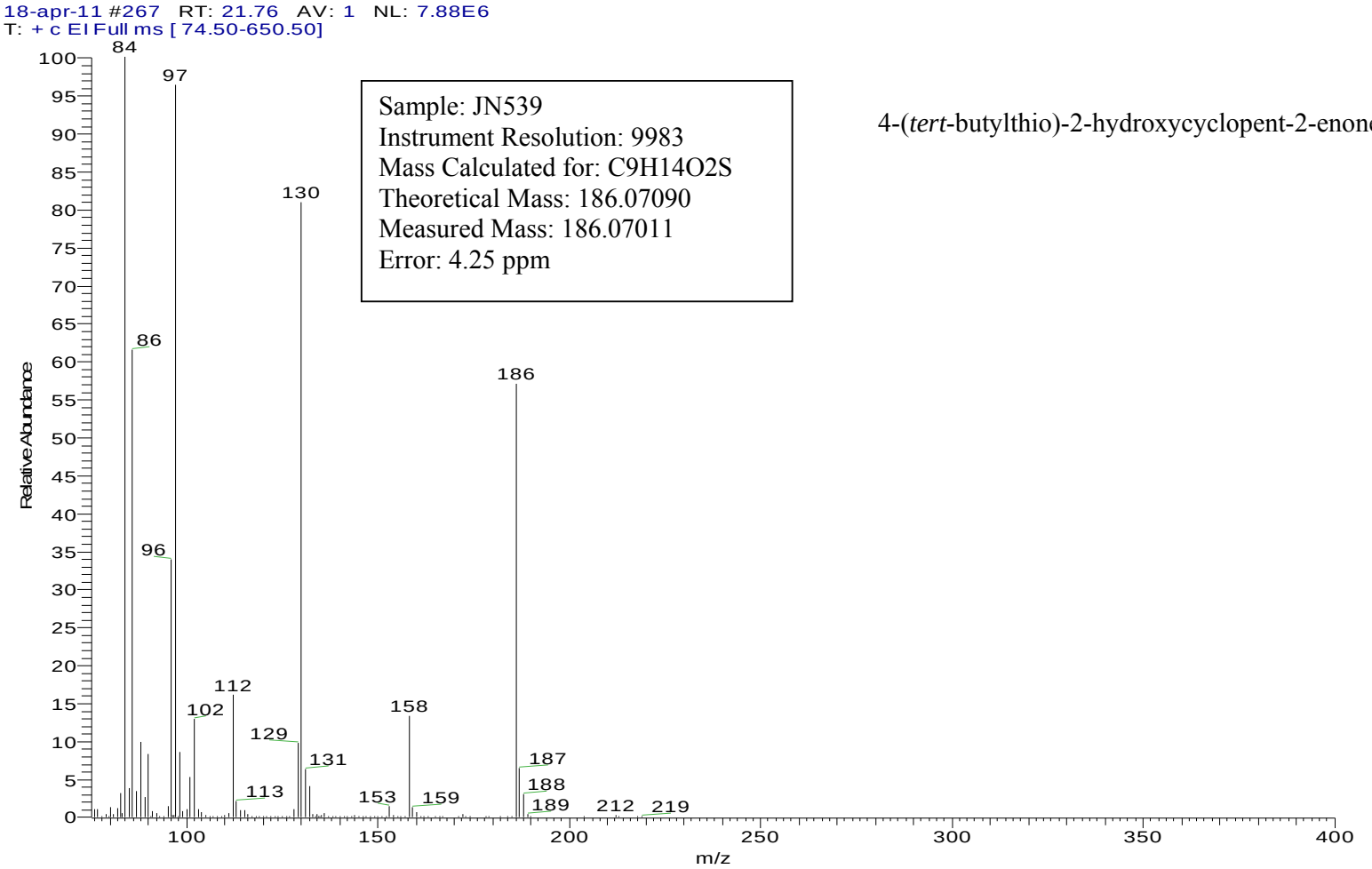
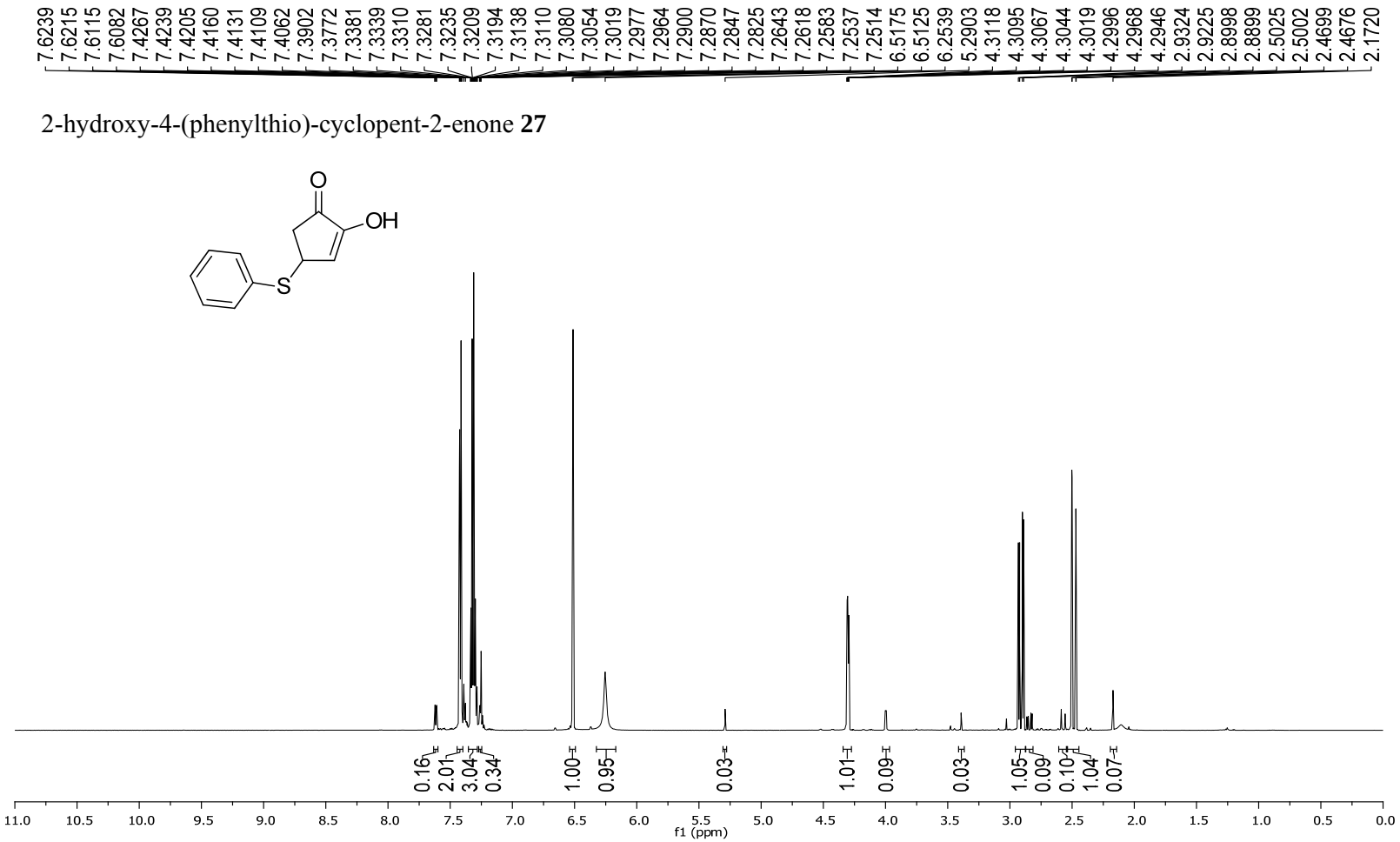


Figure S79 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **26**.



4-(*tert*-butylthio)-2-hydroxycyclopent-2-enone **26**

Figure S80 – EI mass spectra for exact mass measurement of isolated enone **26**.



2-hydroxy-4-(phenylthio)-cyclopent-2-enone **27**

Figure S81 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **27**.

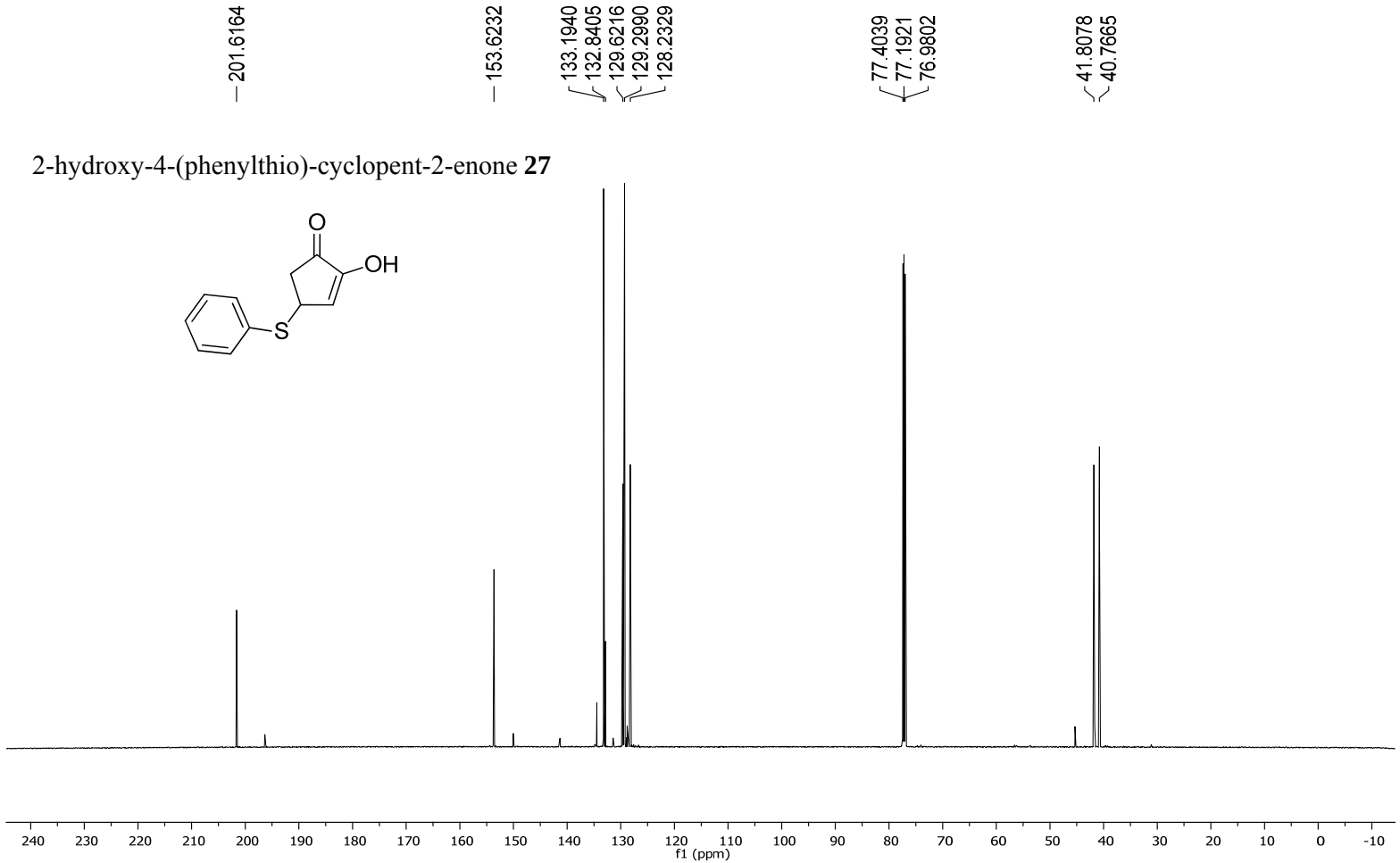


Figure S82 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **27**.

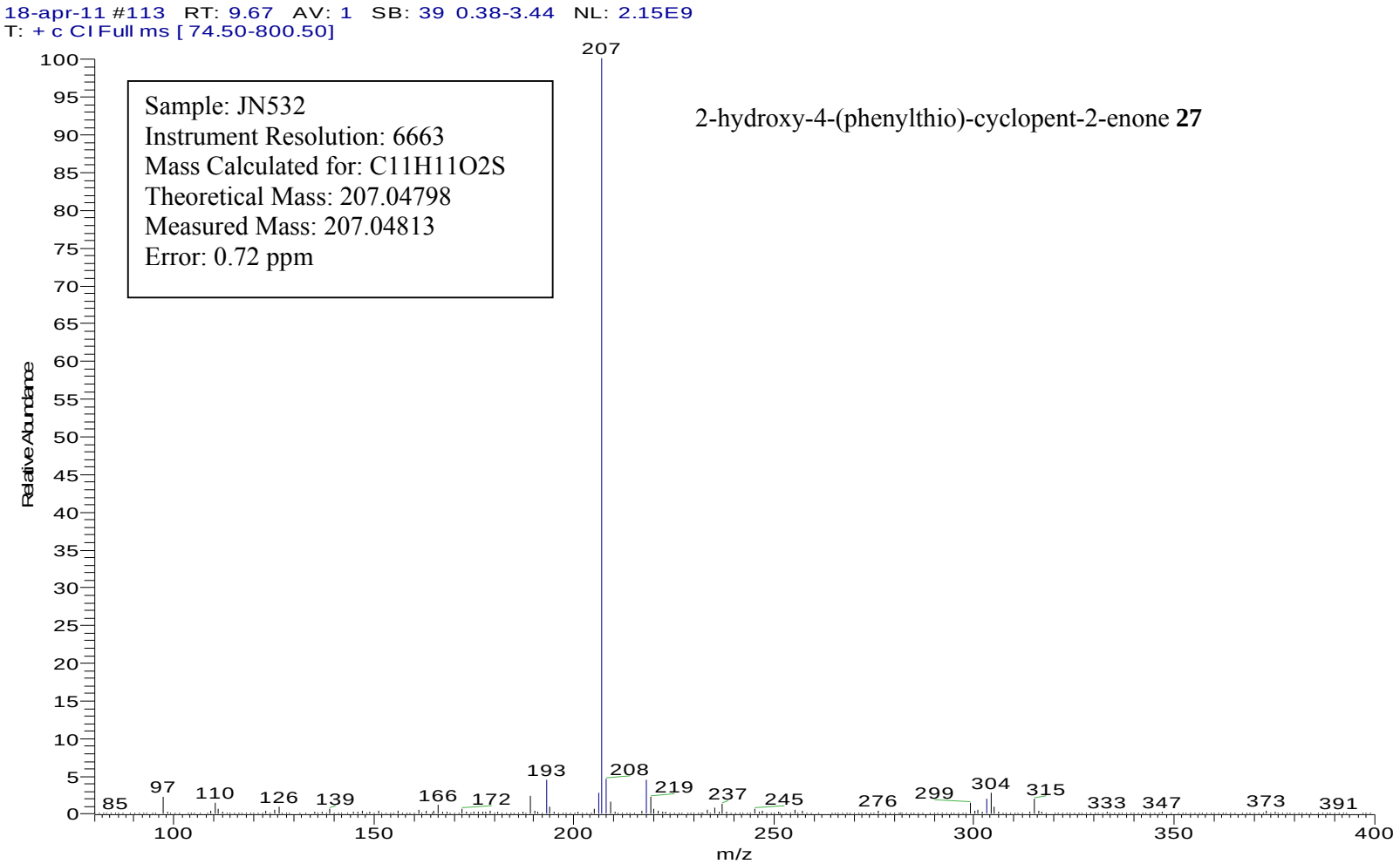


Figure S83 – EI mass spectra for exact mass measurement of isolated enone **27**.

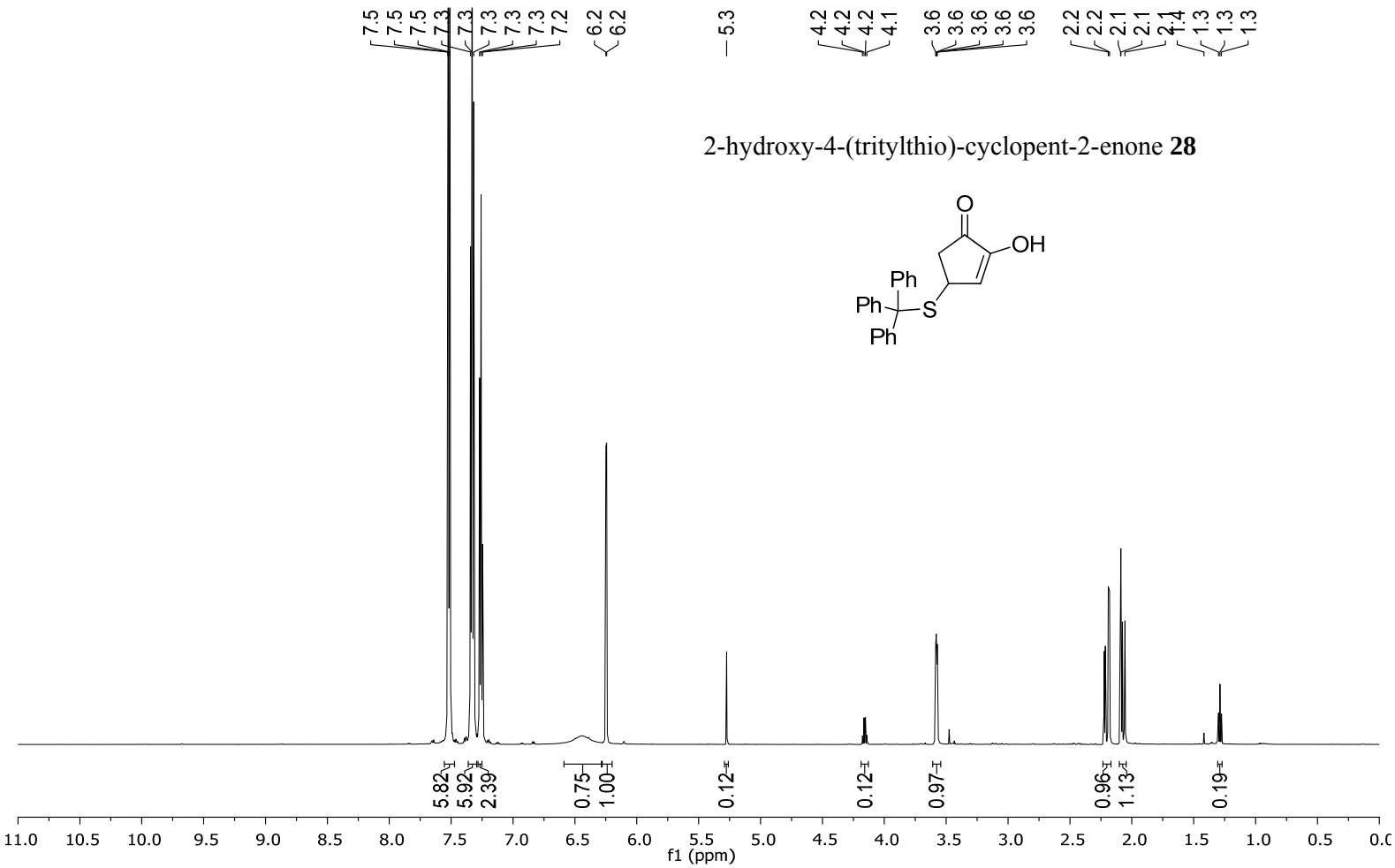


Figure S84 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **28**.

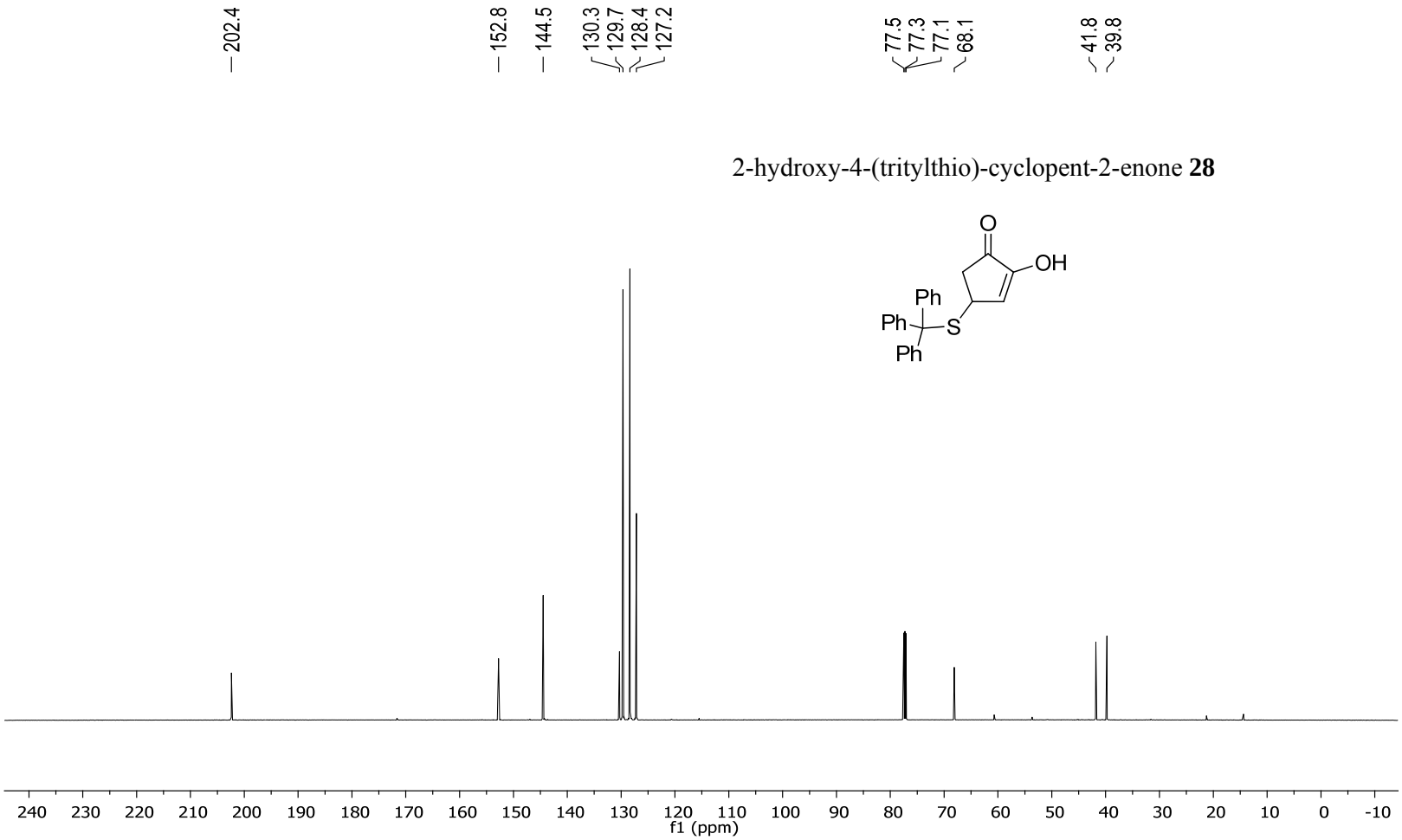


Figure S85 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **28**.

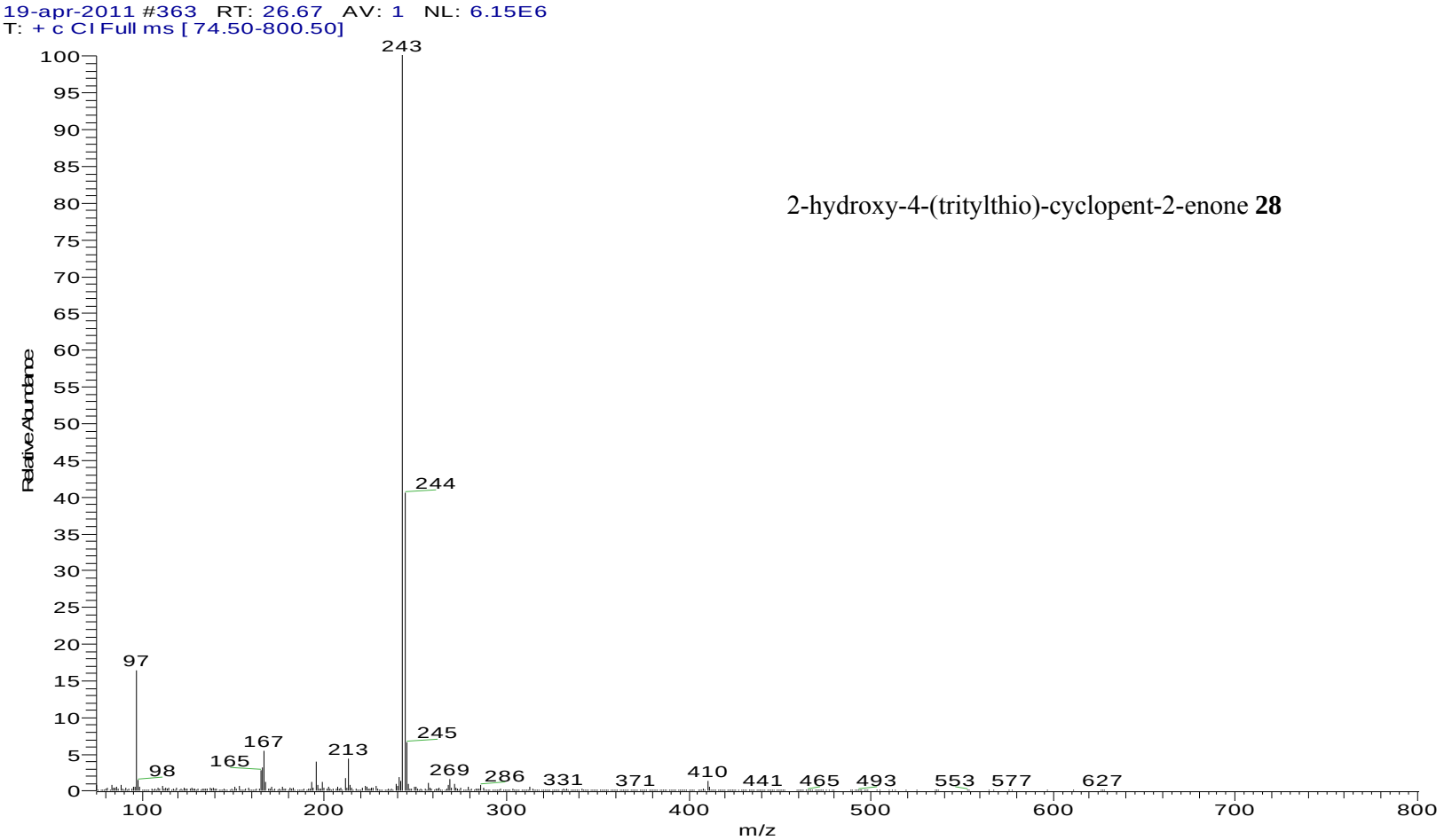


Figure S86 – EI mass spectra for exact mass measurement of isolated enone **28**.

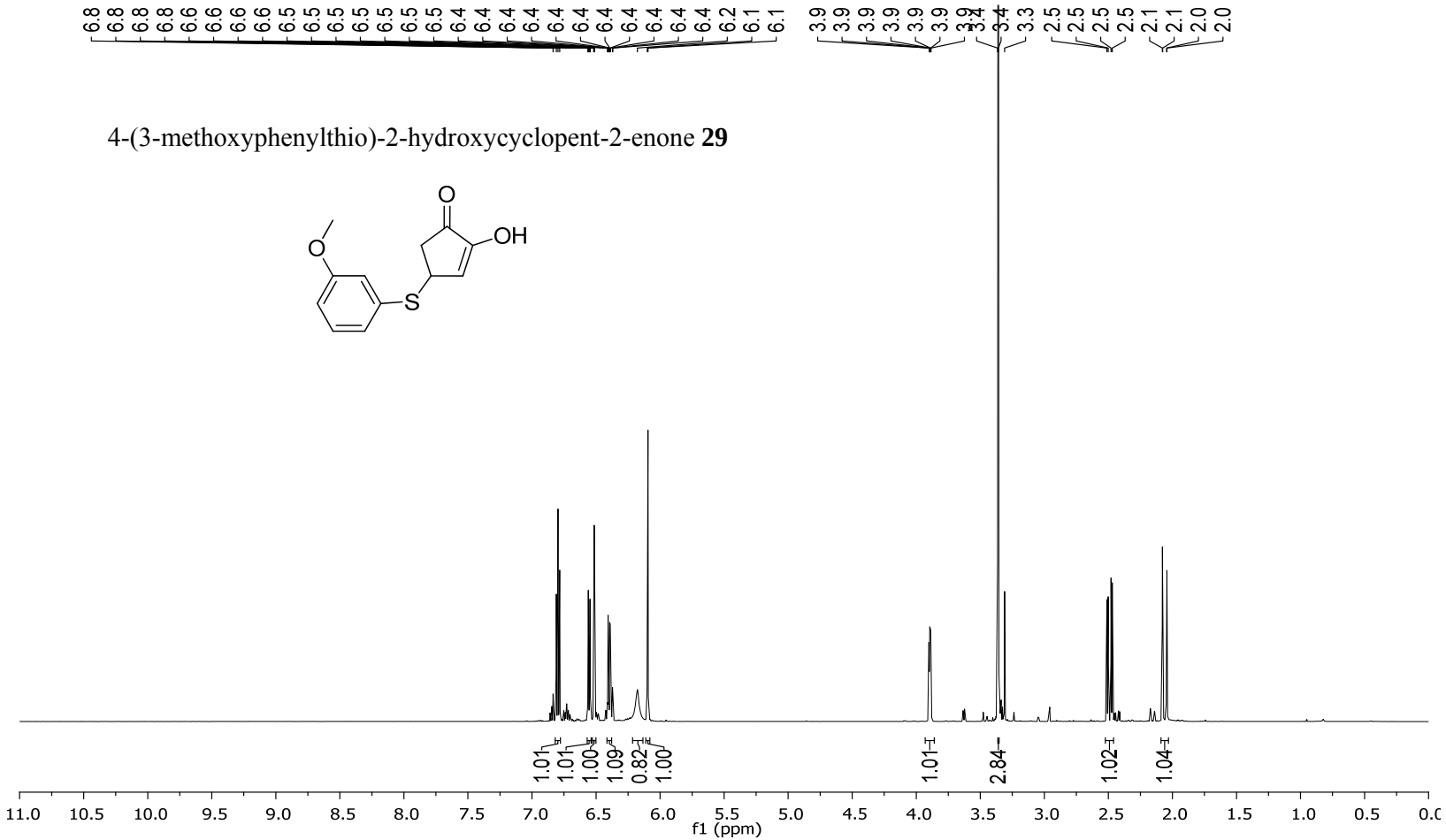


Figure S87 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **29**.

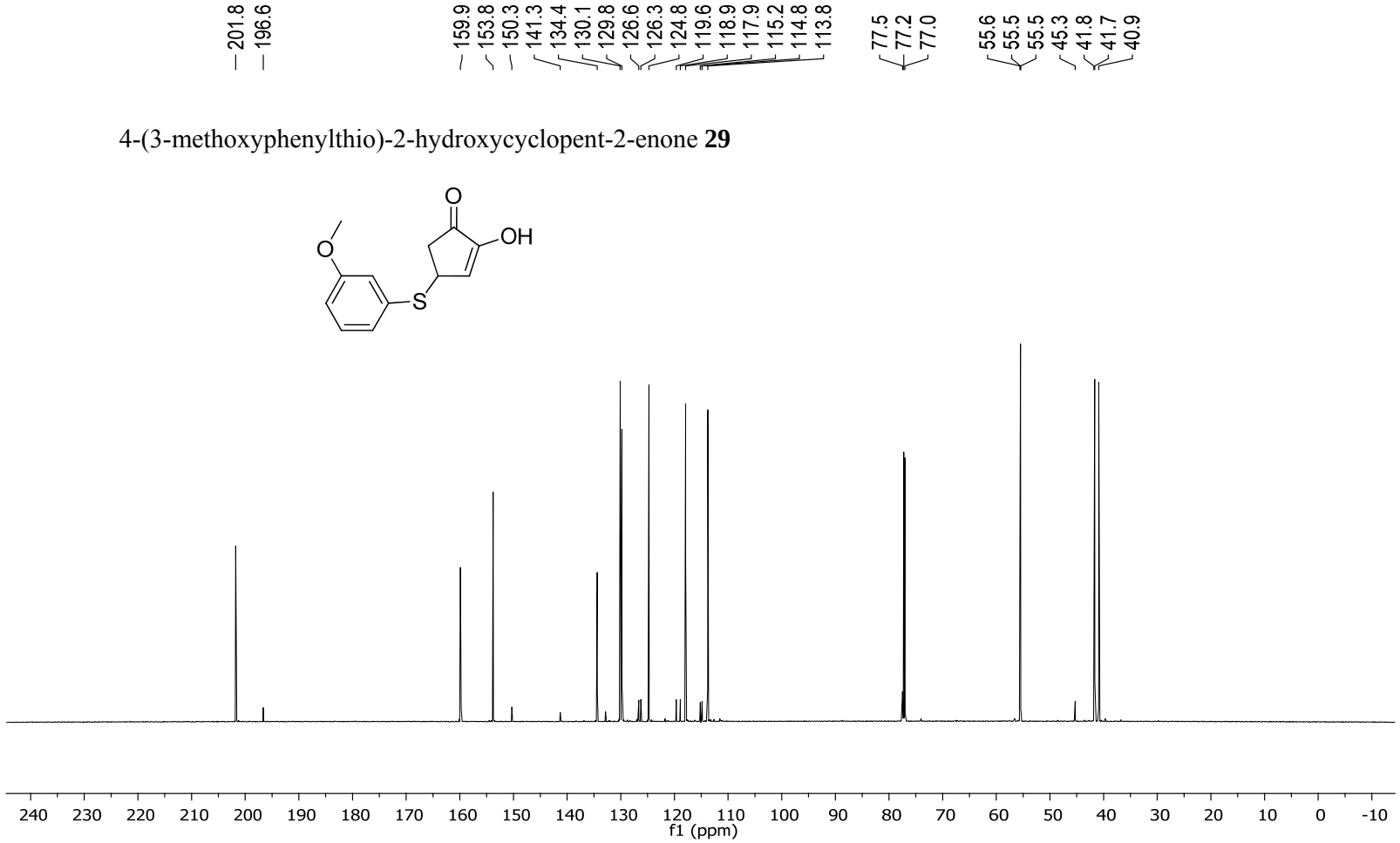


Figure S88 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **29**.

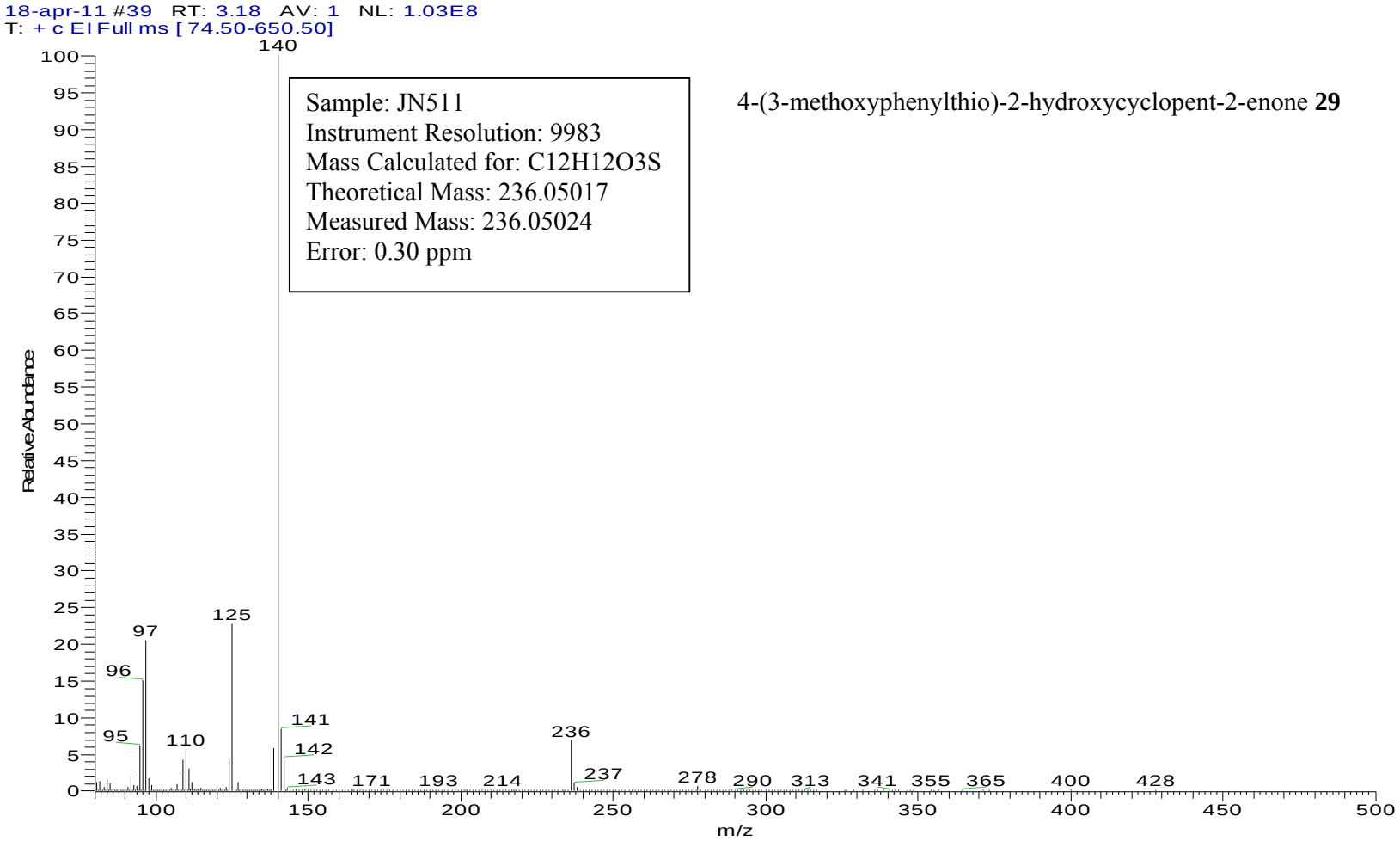


Figure S89 – EI mass spectra for exact mass measurement of isolated enone **29**.

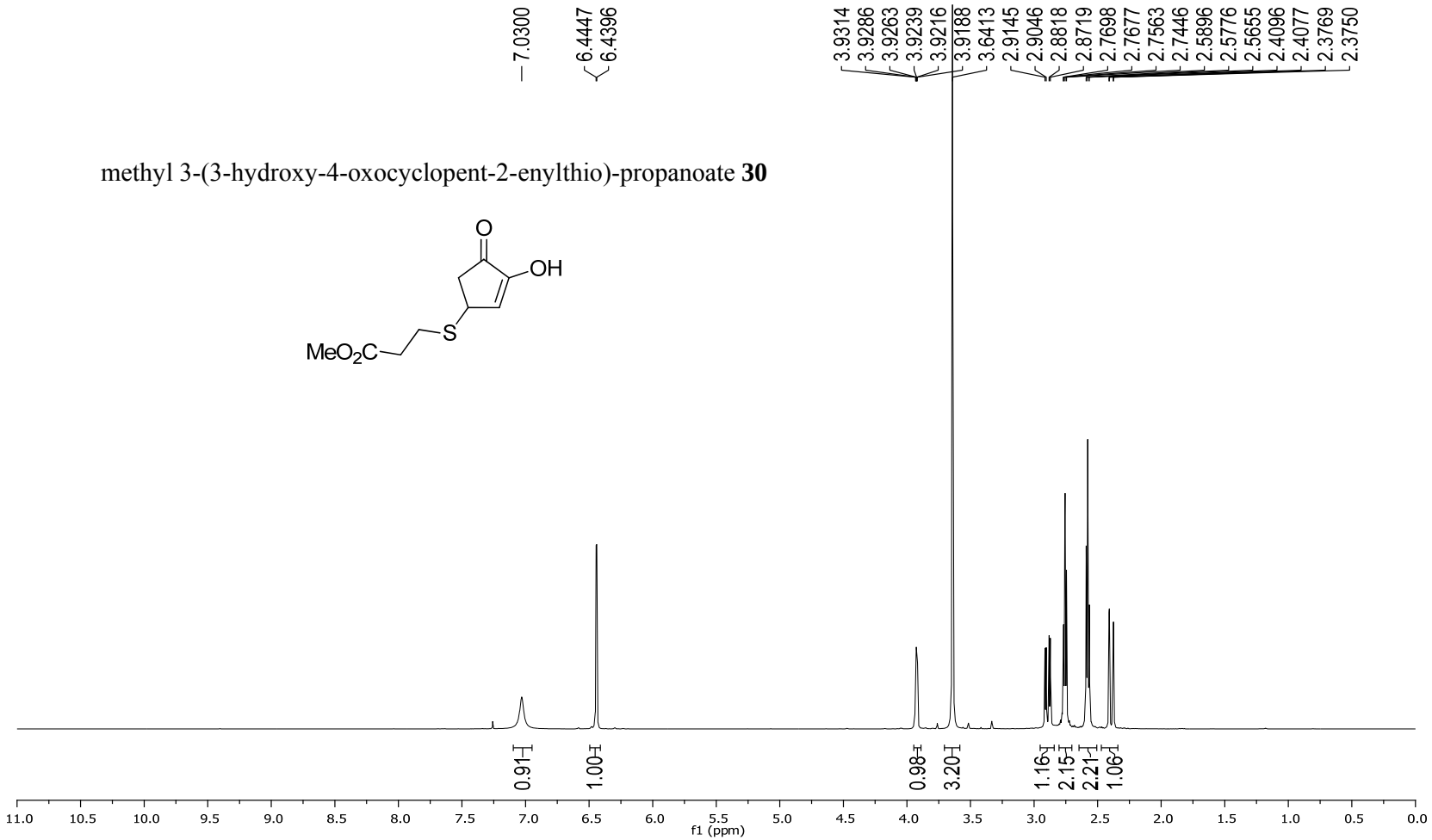
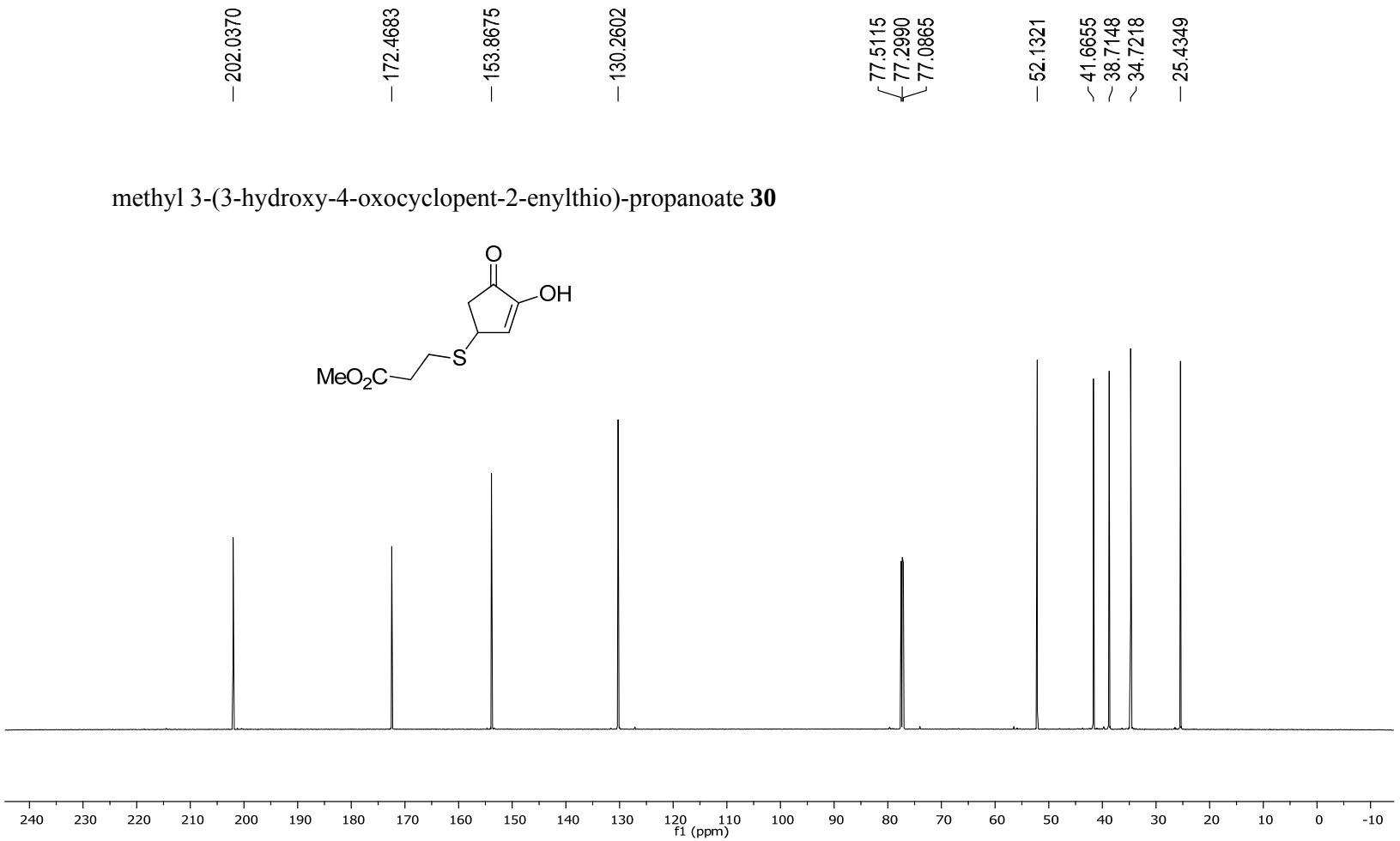
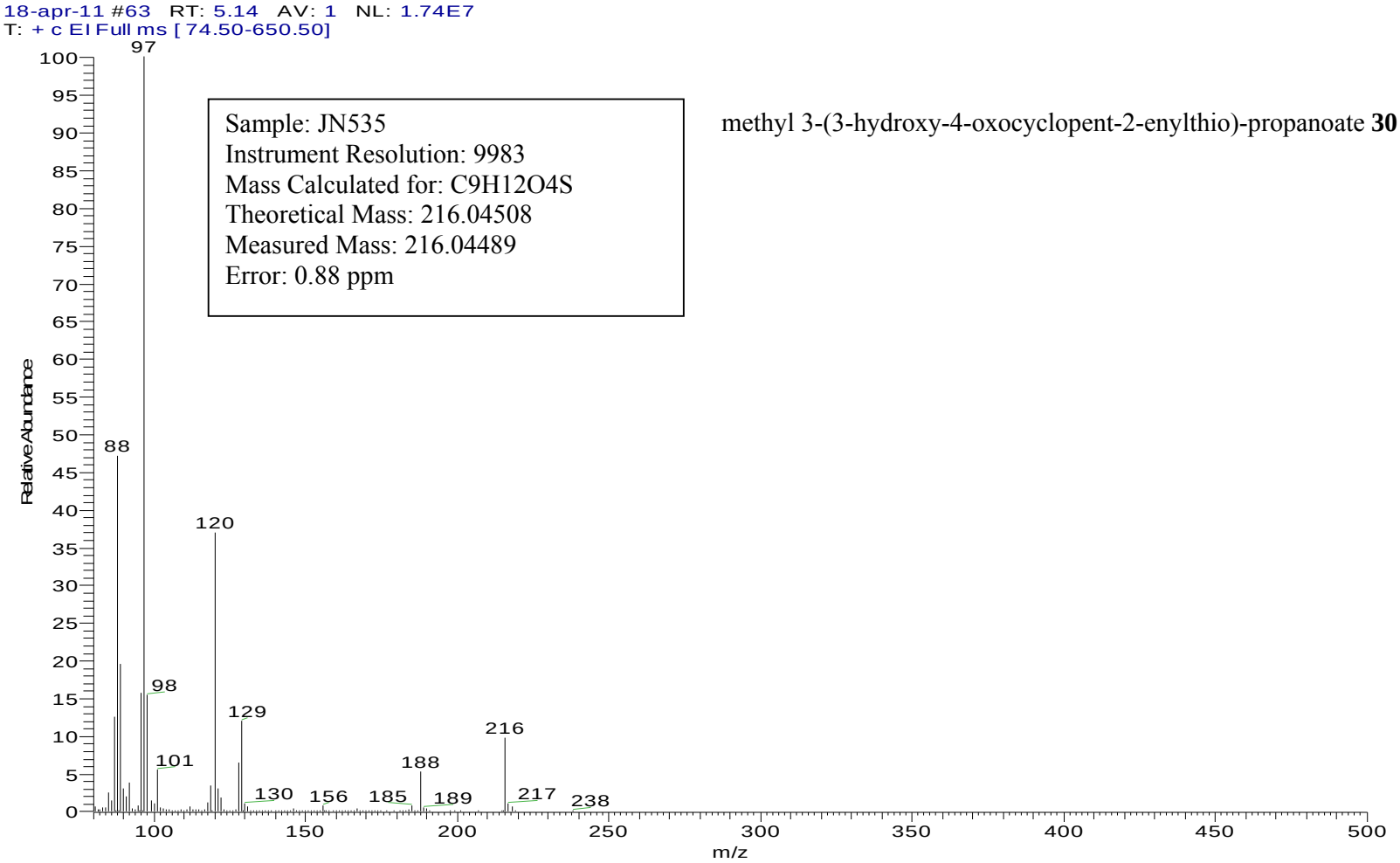


Figure S90 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **30**.



methyl 3-(3-hydroxy-4-oxocyclopent-2-enylthio)-propanoate **30**

Figure S91 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **30**.



methyl 3-(3-hydroxy-4-oxocyclopent-2-enylthio)-propanoate **30**

Figure S92 – EI mass spectra for exact mass measurement of isolated enone **30**.

4-(2-hydroxyethylthio)-2-hydroxycyclopent-2-enone **31**

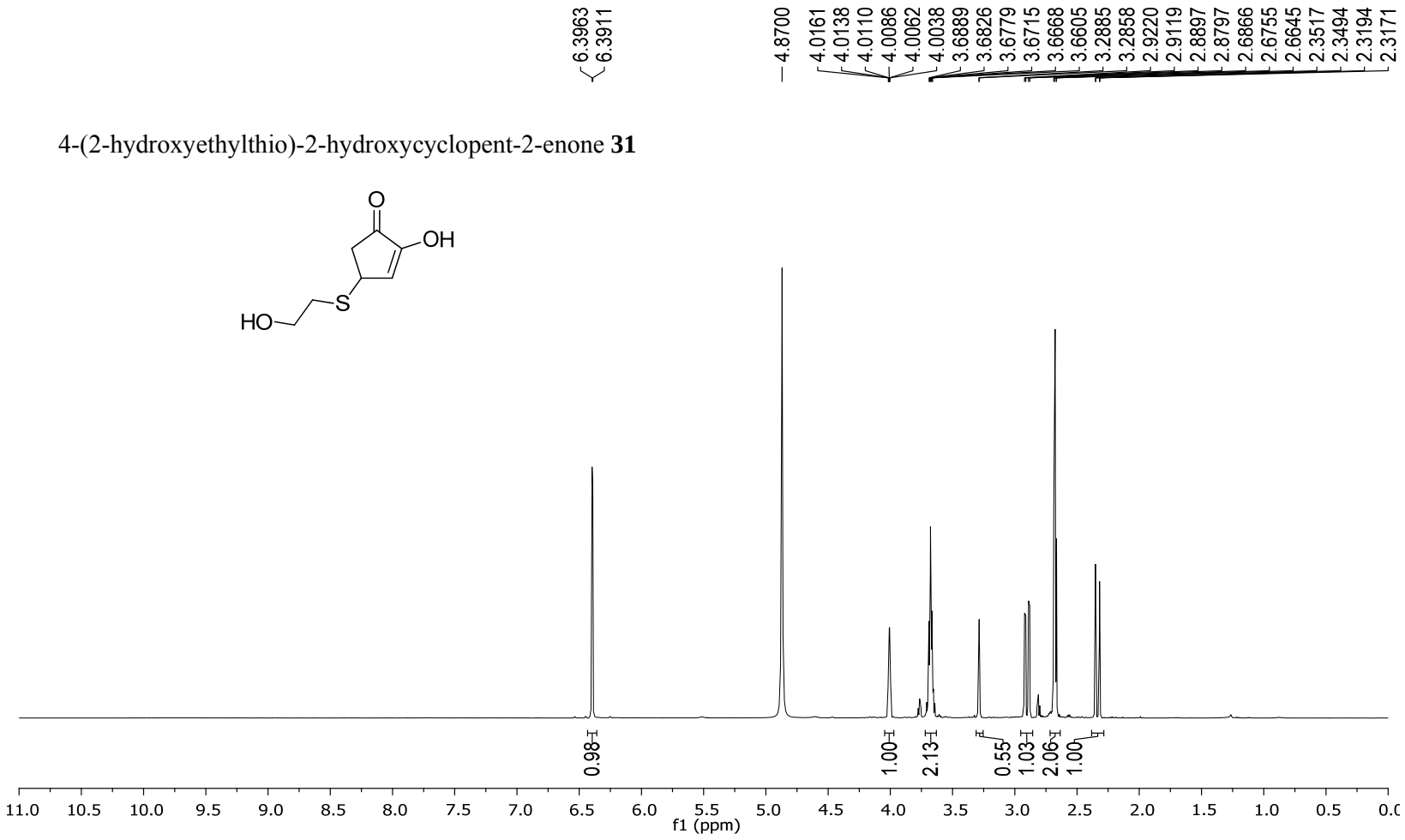


Figure S93 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **31**.

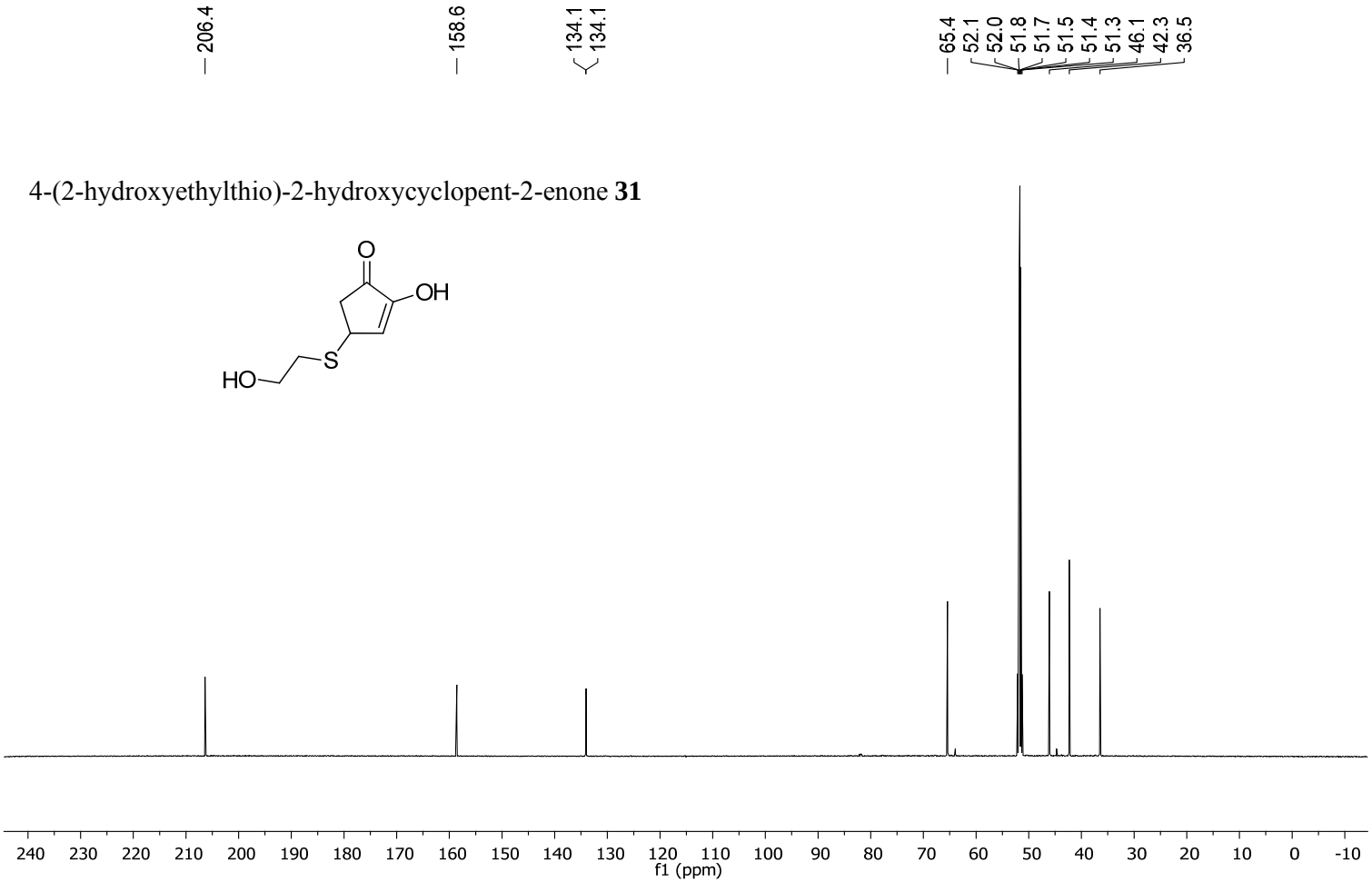
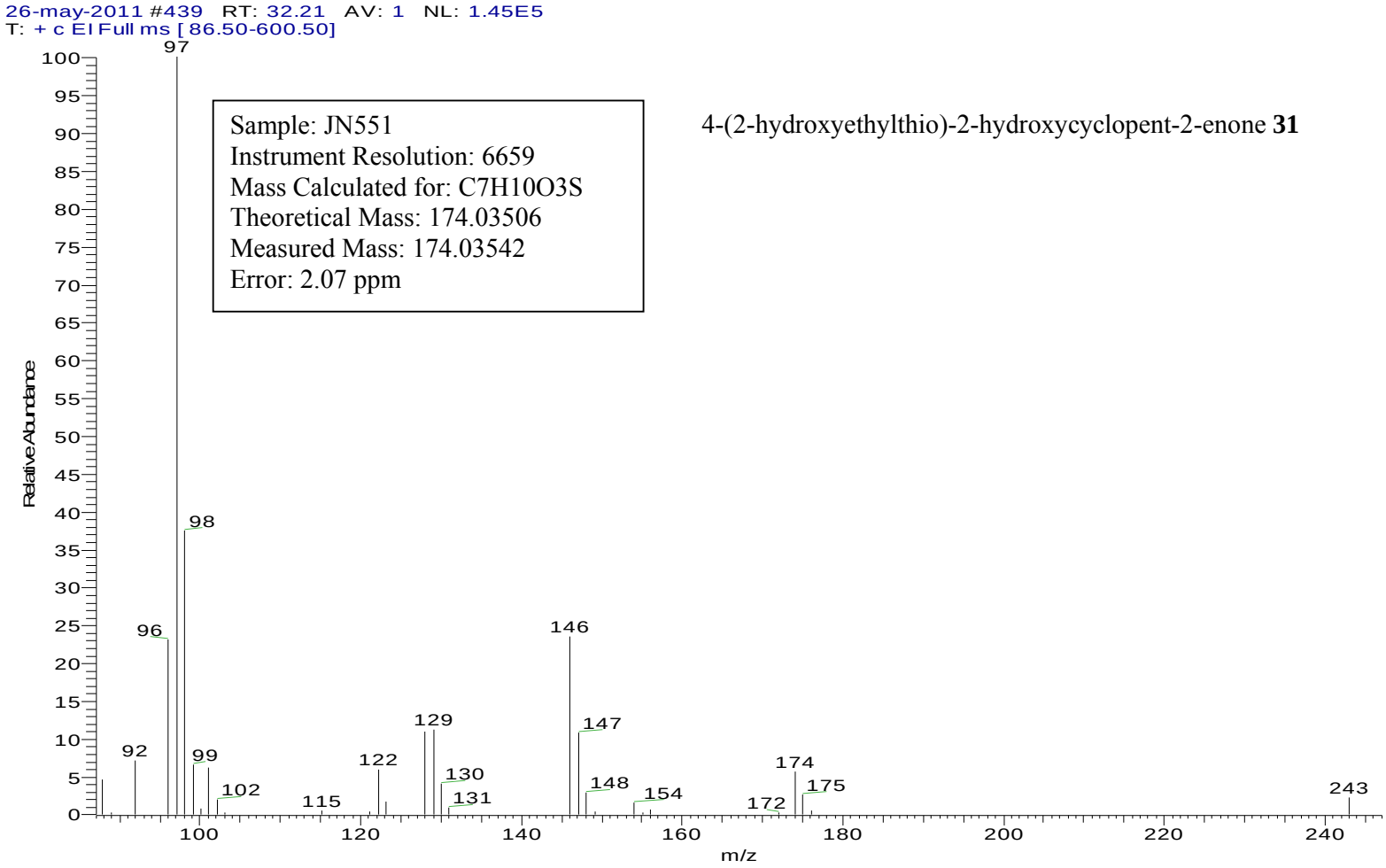


Figure S94 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **31**.



4-(2-hydroxyethylthio)-2-hydroxycyclopent-2-enone **31**

Figure S95 – EI mass spectra for exact mass measurement of isolated enone **31**.

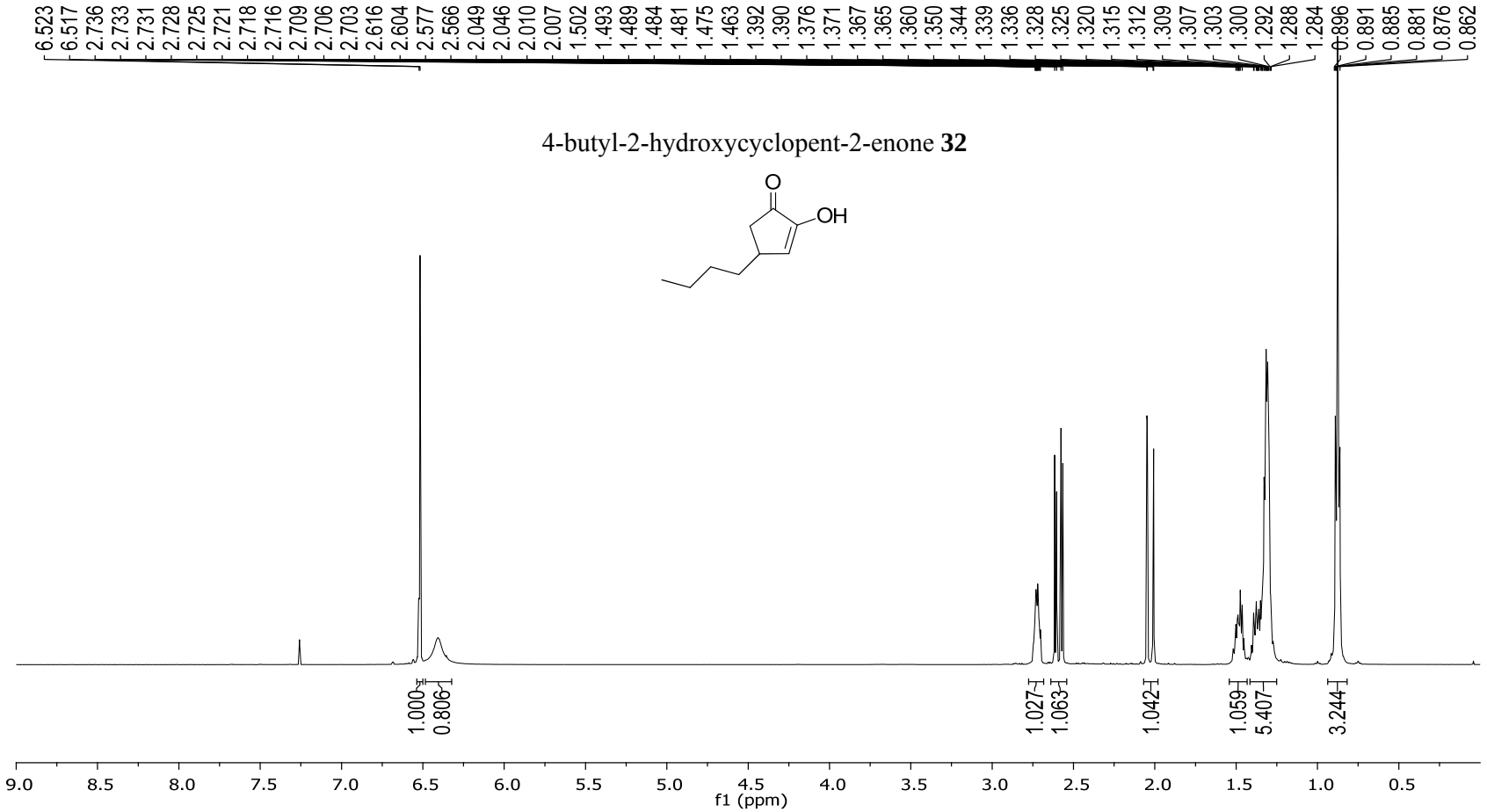


Figure S96 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated compound **32**.

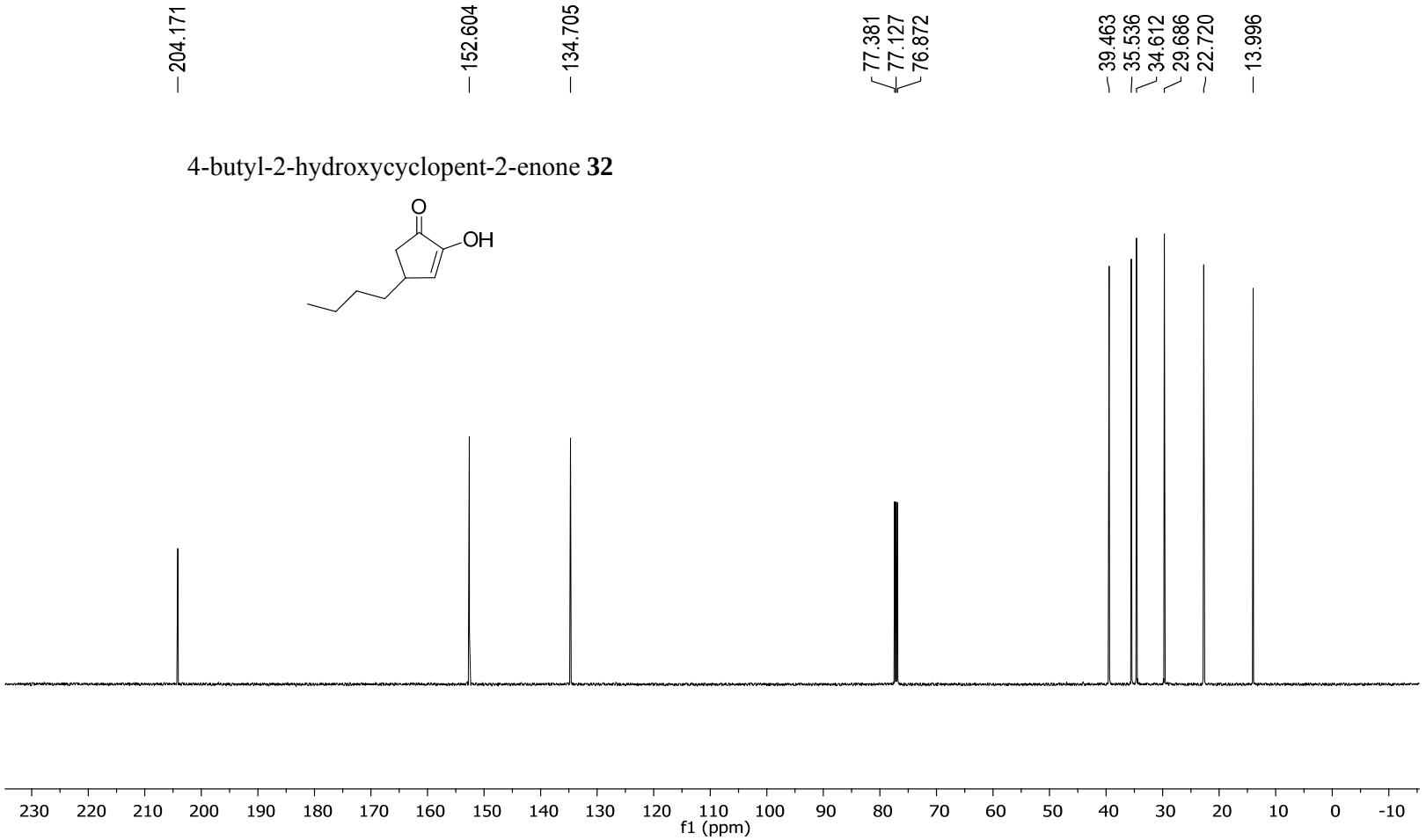


Figure S97 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated compound **32**.

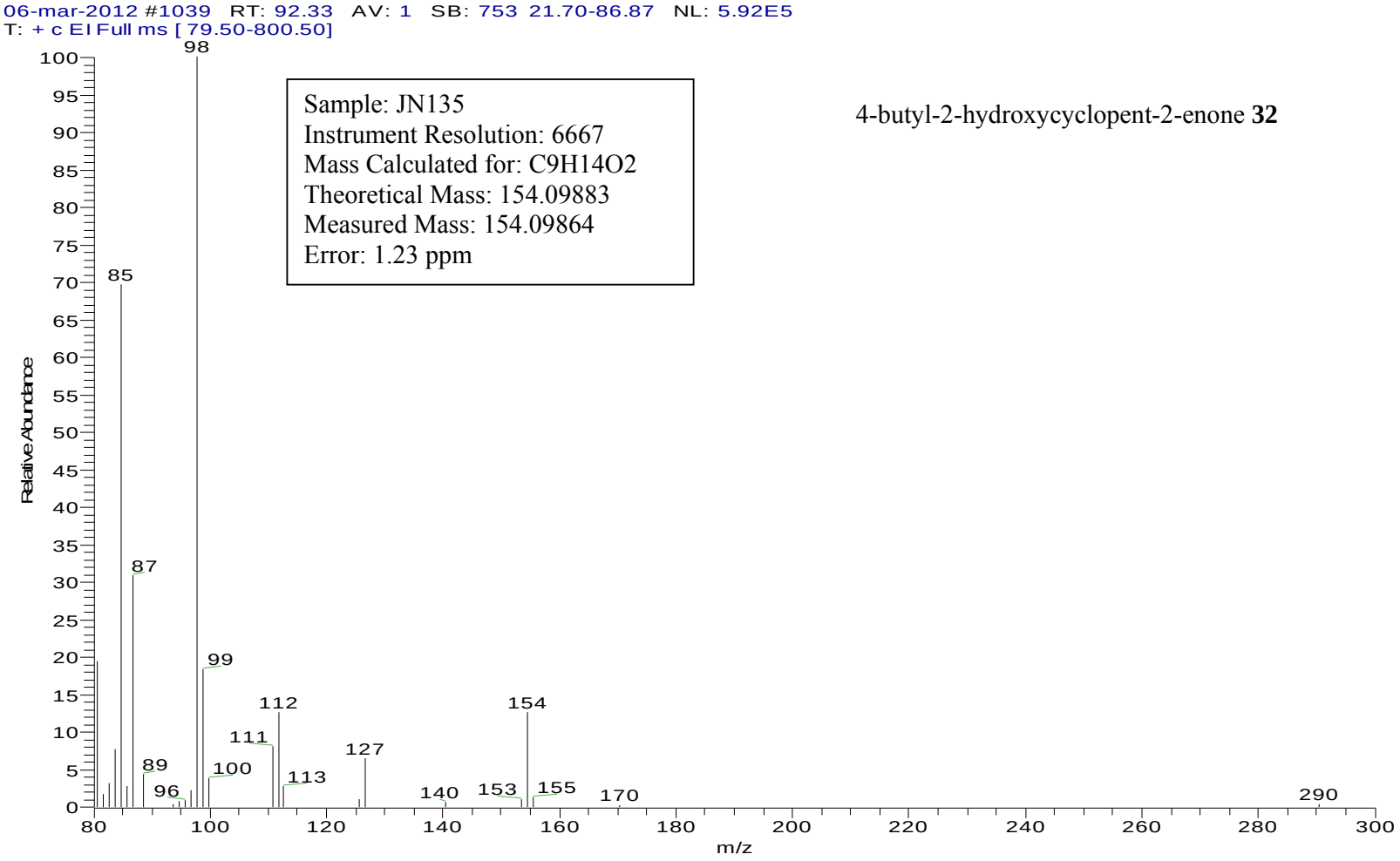


Figure S98 – EI mass spectra for exact mass measurement of isolated compound **32**.

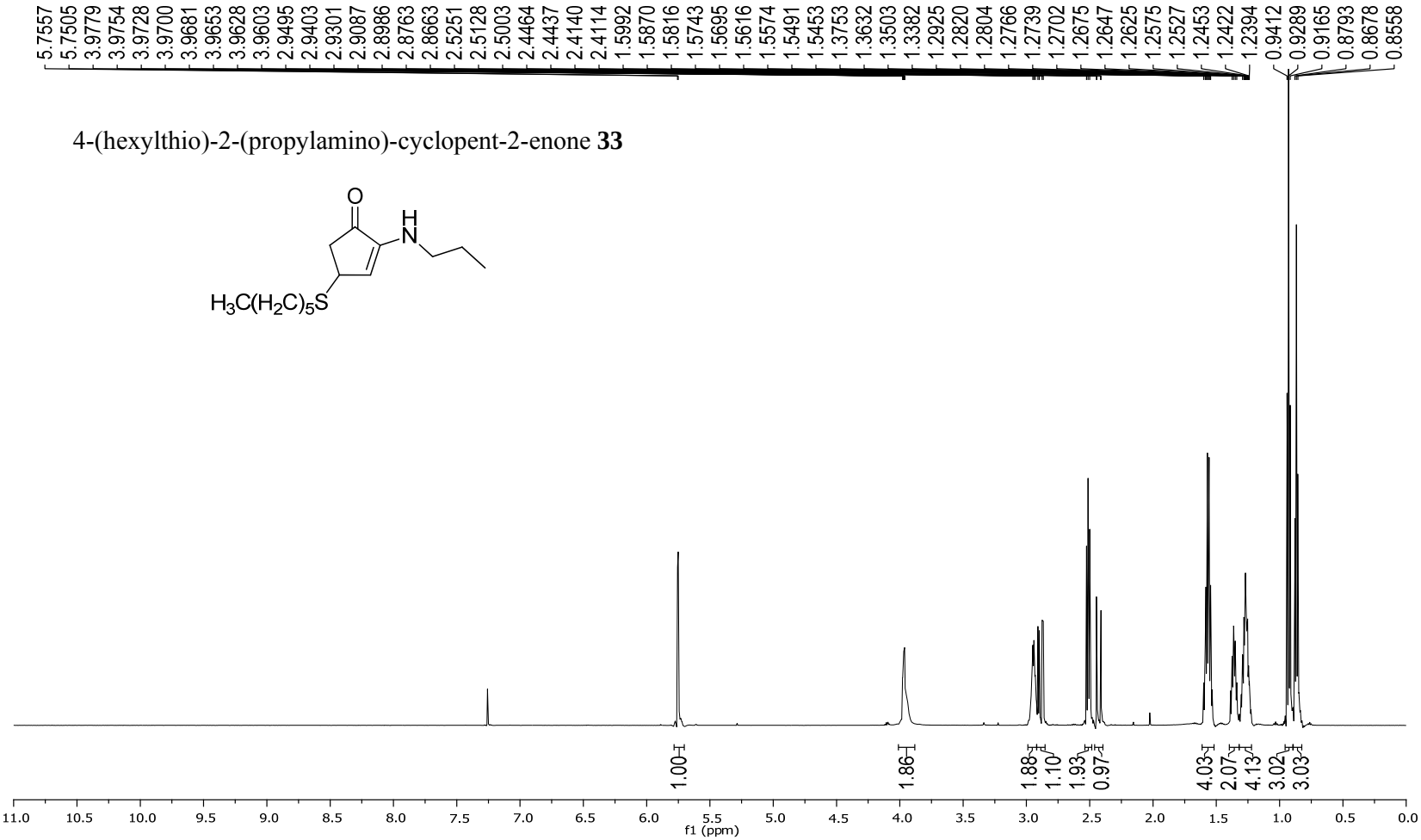


Figure S99 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **33**.

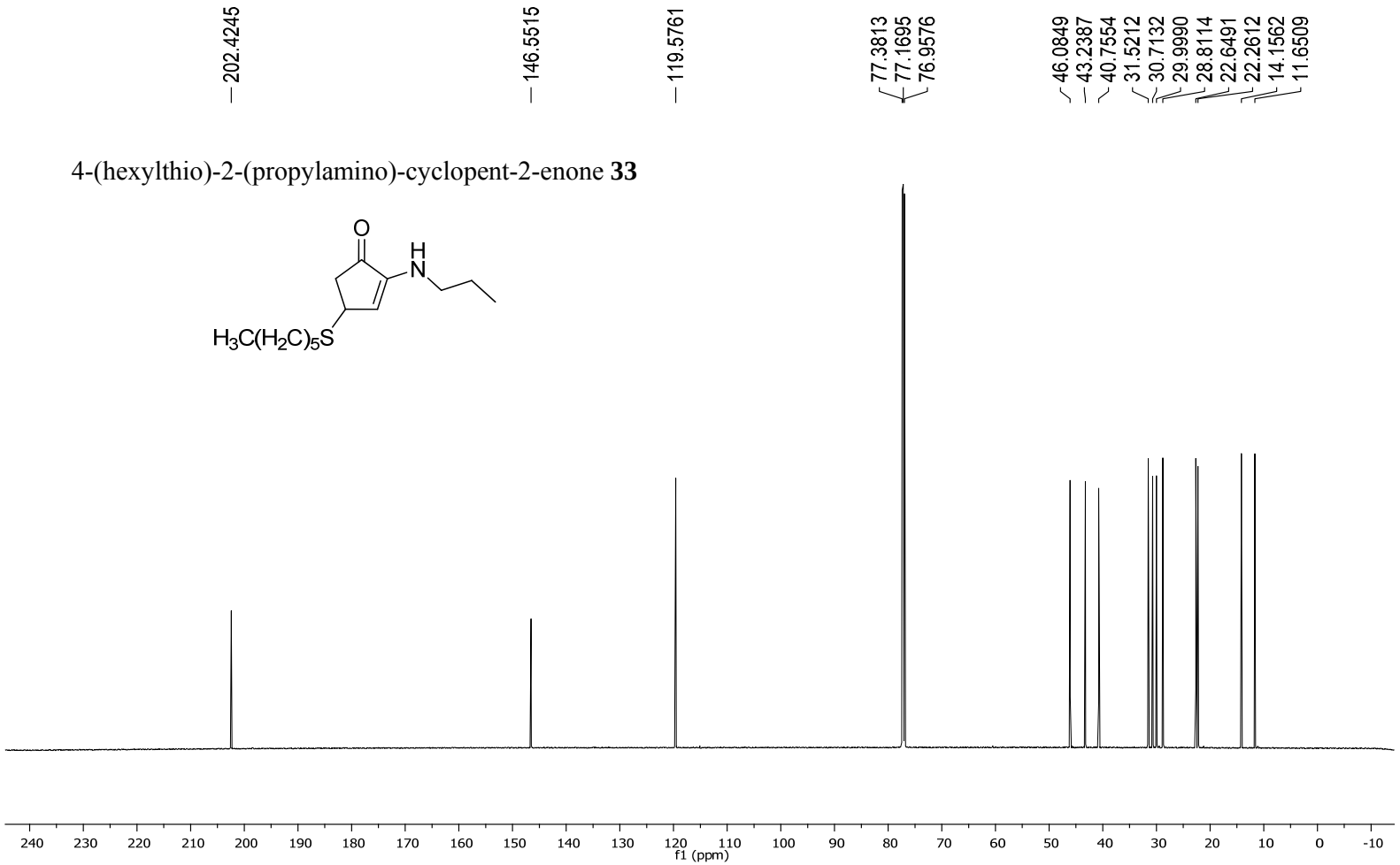


Figure S100 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **33**.

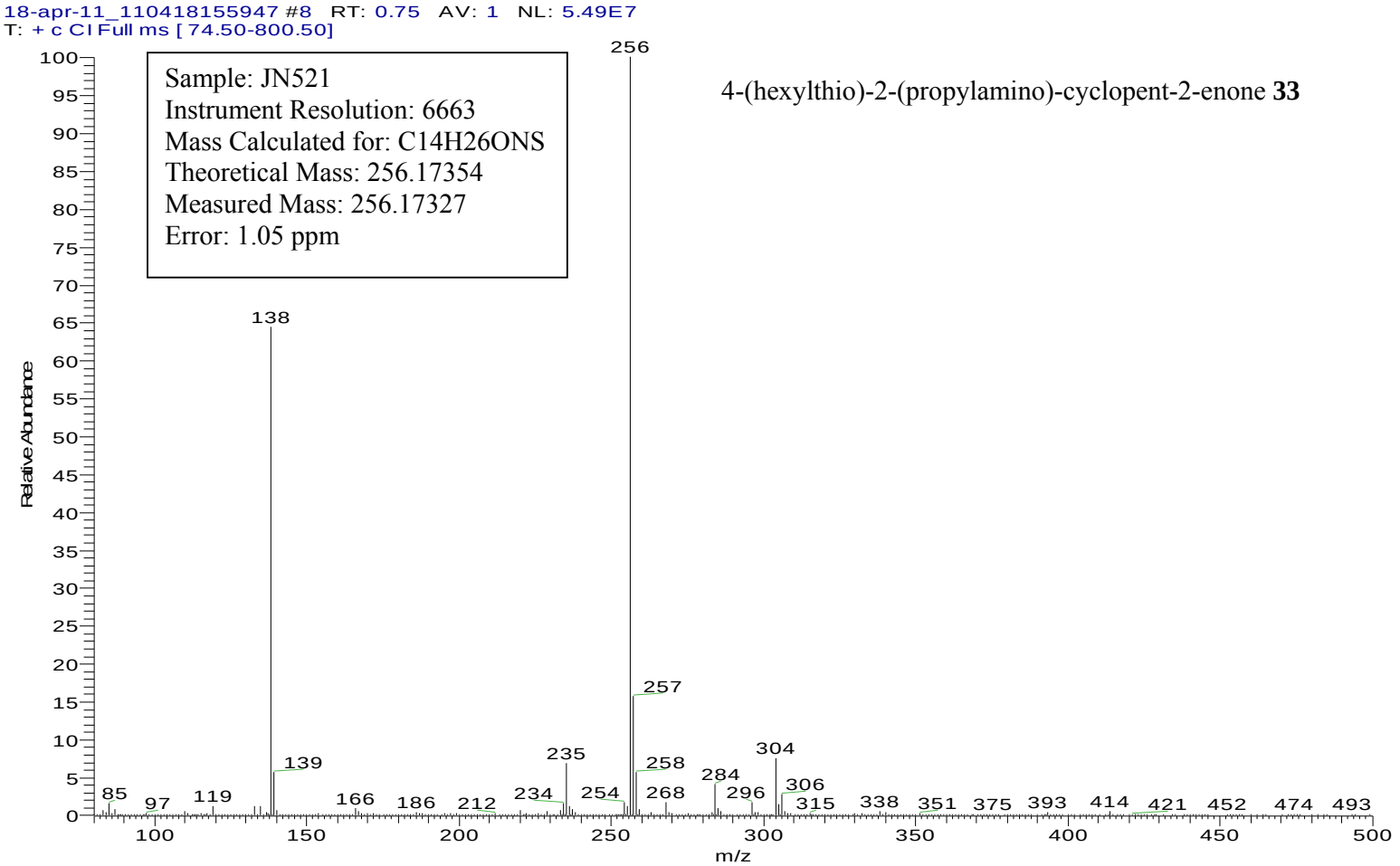


Figure S101 – EI mass spectra for exact mass measurement of isolated enone **33**.

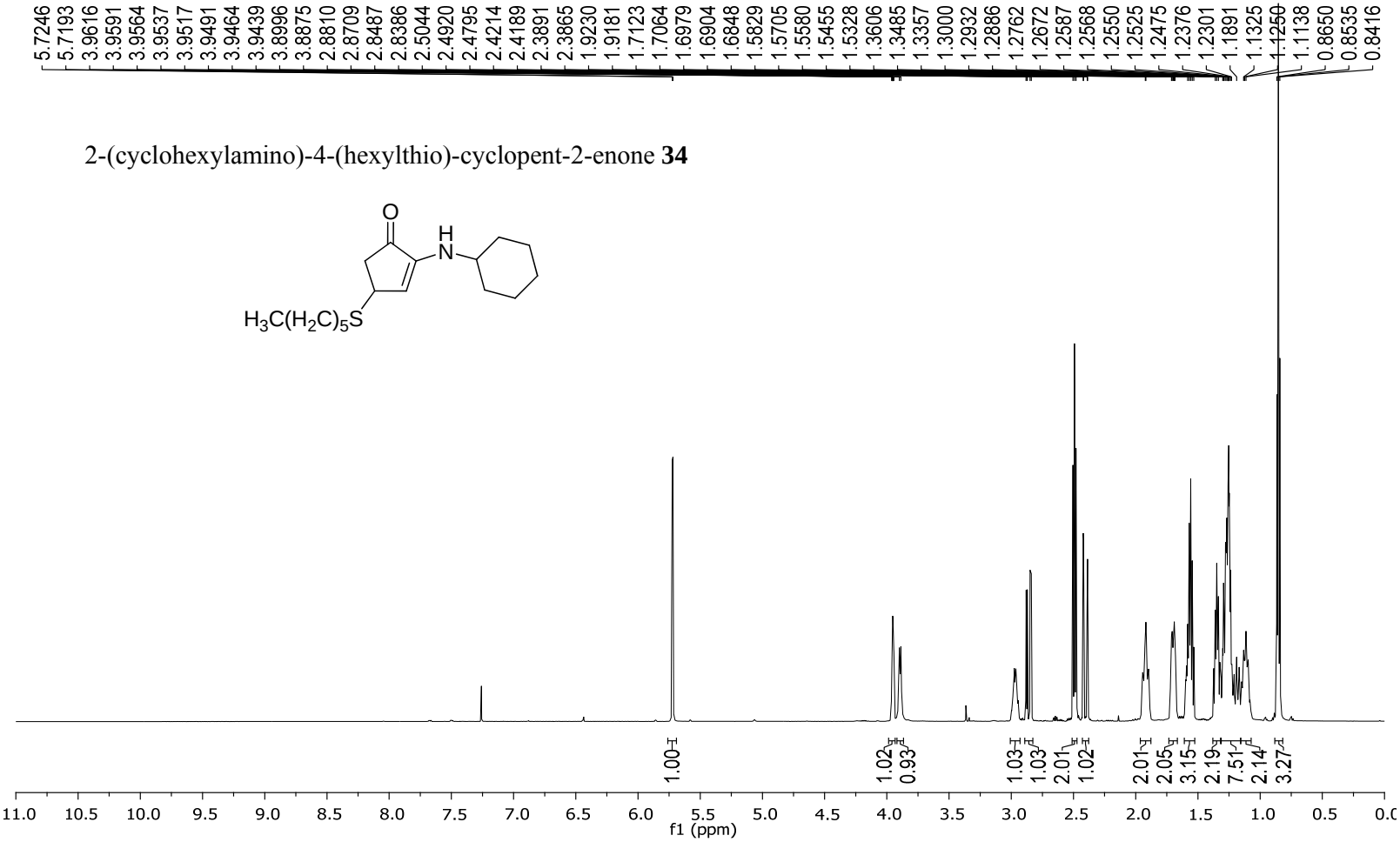


Figure S102 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **34**.

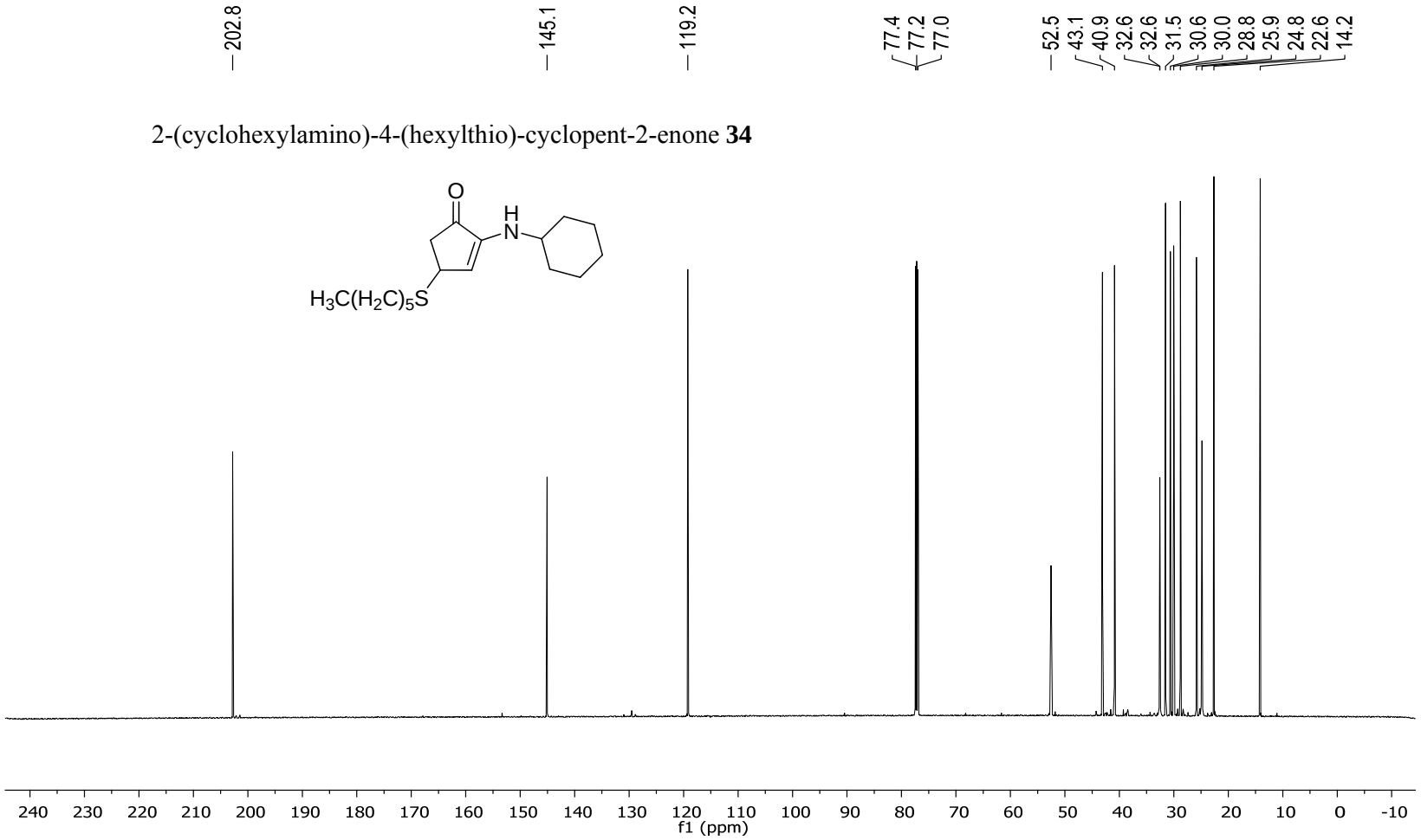


Figure S103 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **34**.

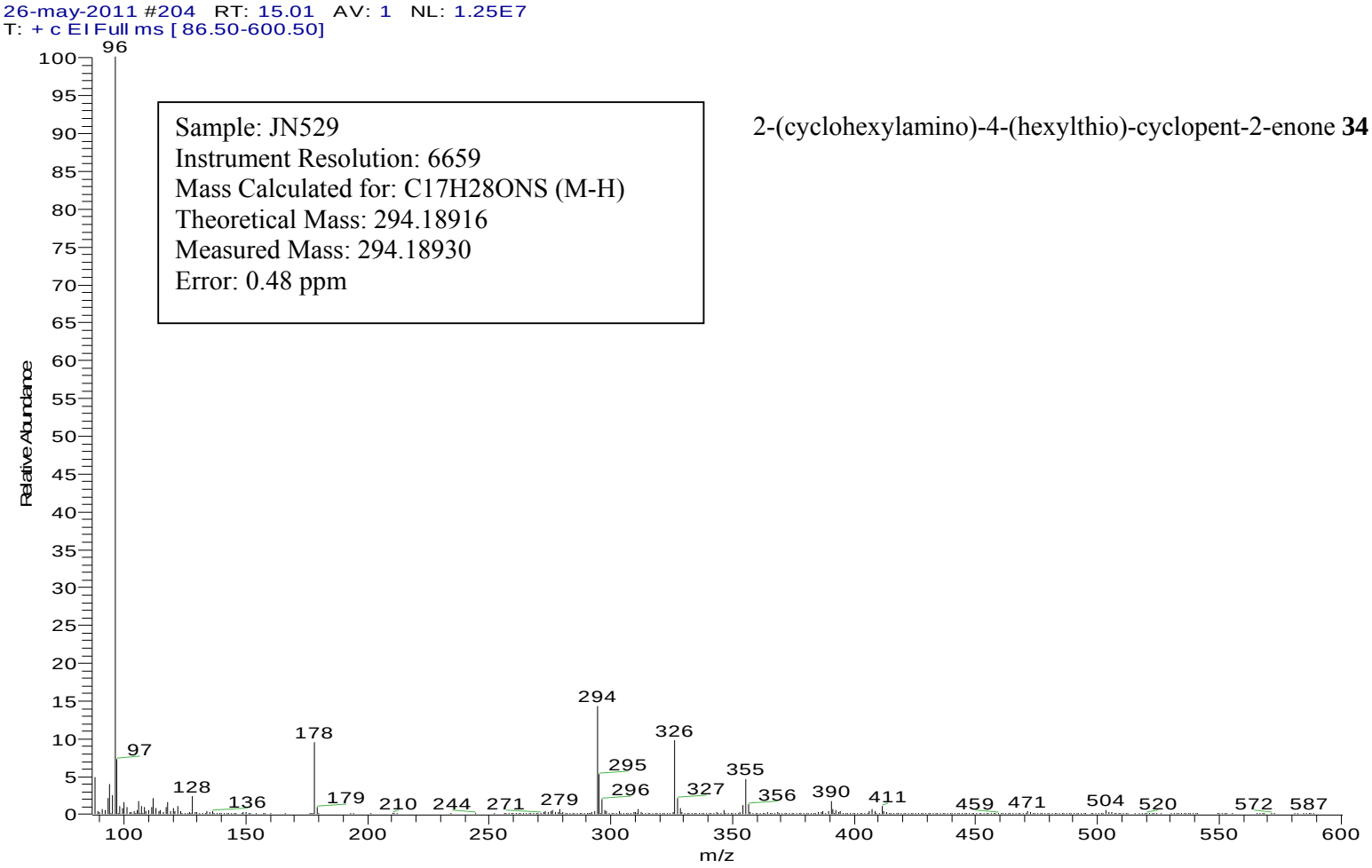


Figure S104 – EI mass spectra for exact mass measurement of isolated enone **34**.

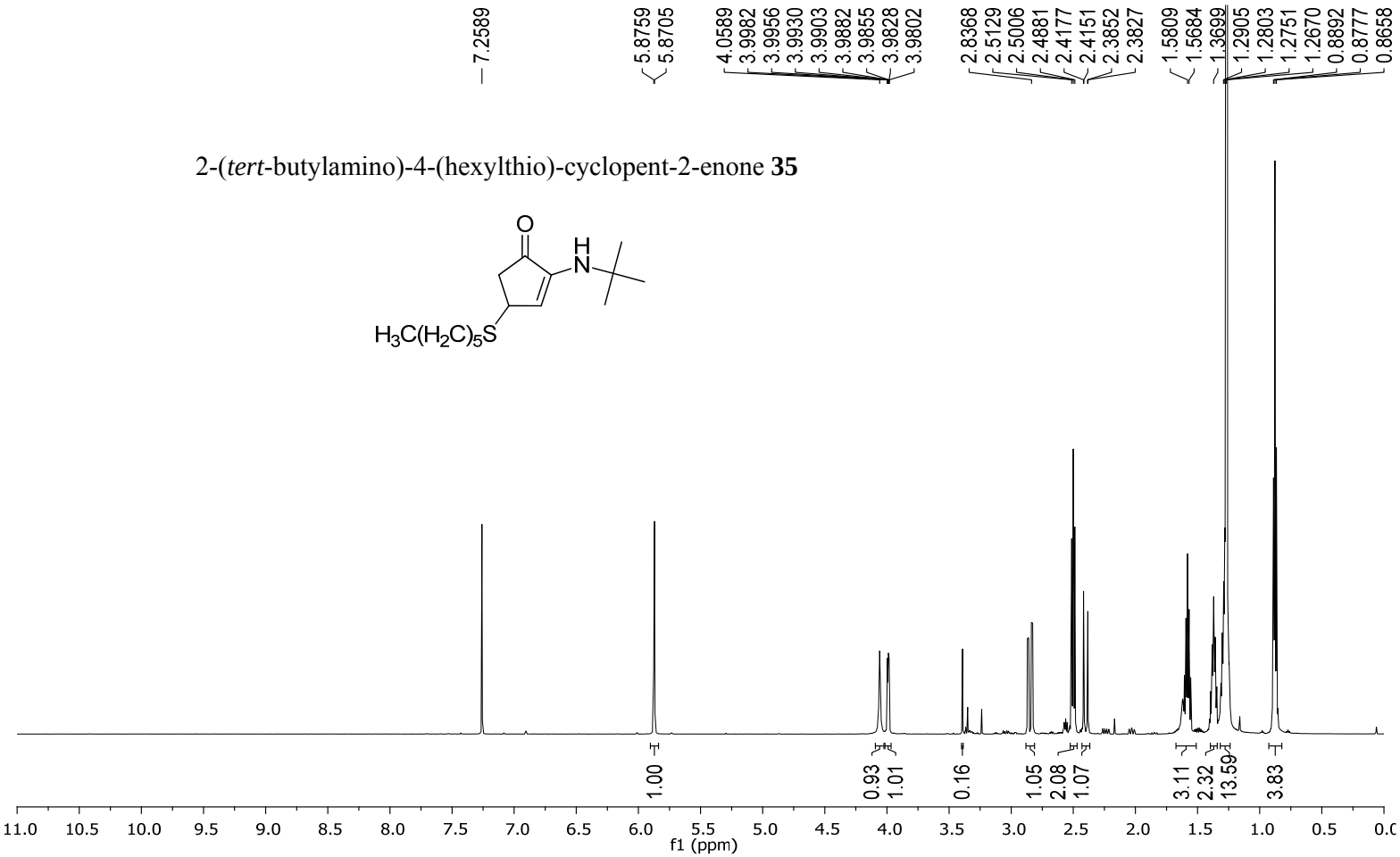


Figure S105 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **35**.

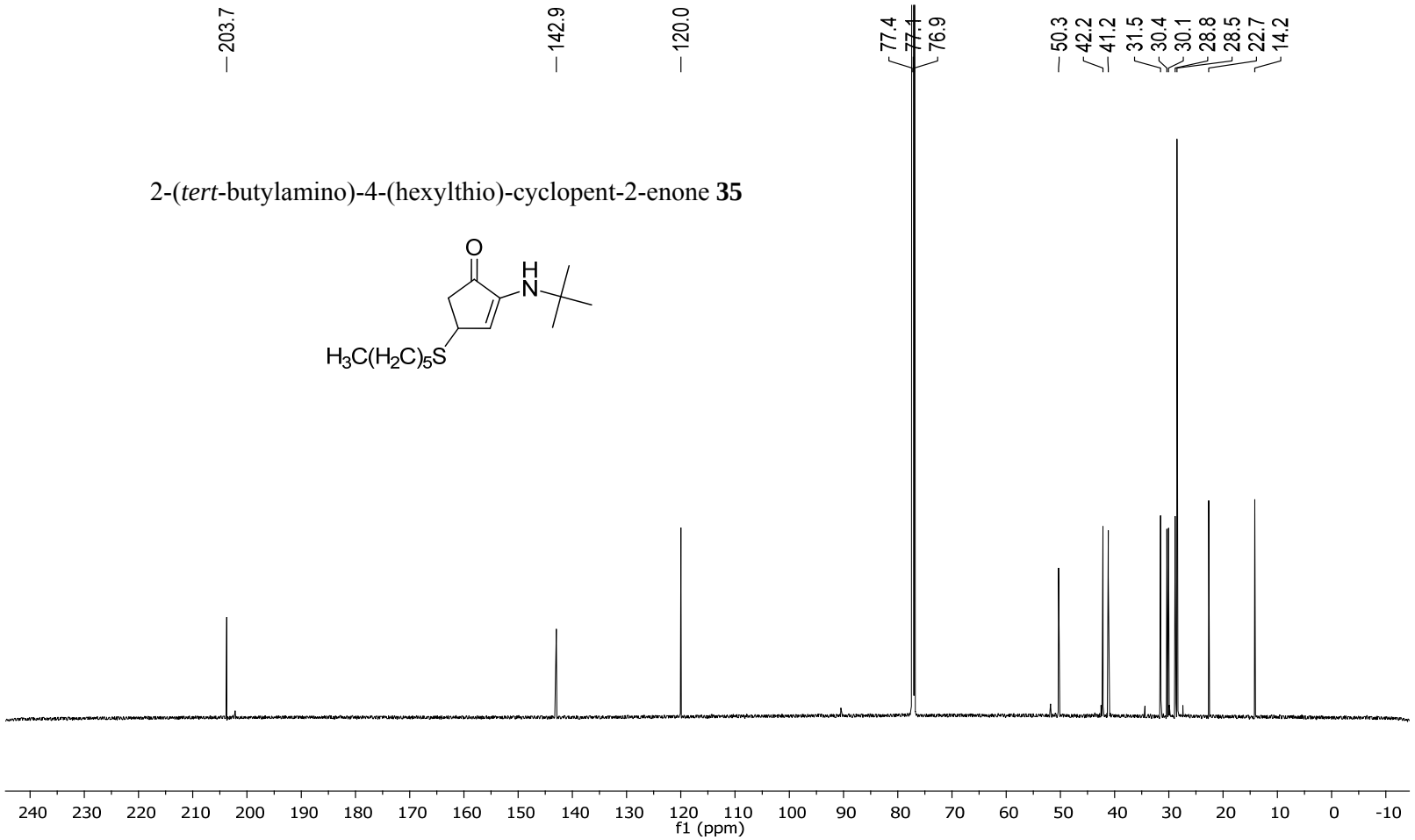
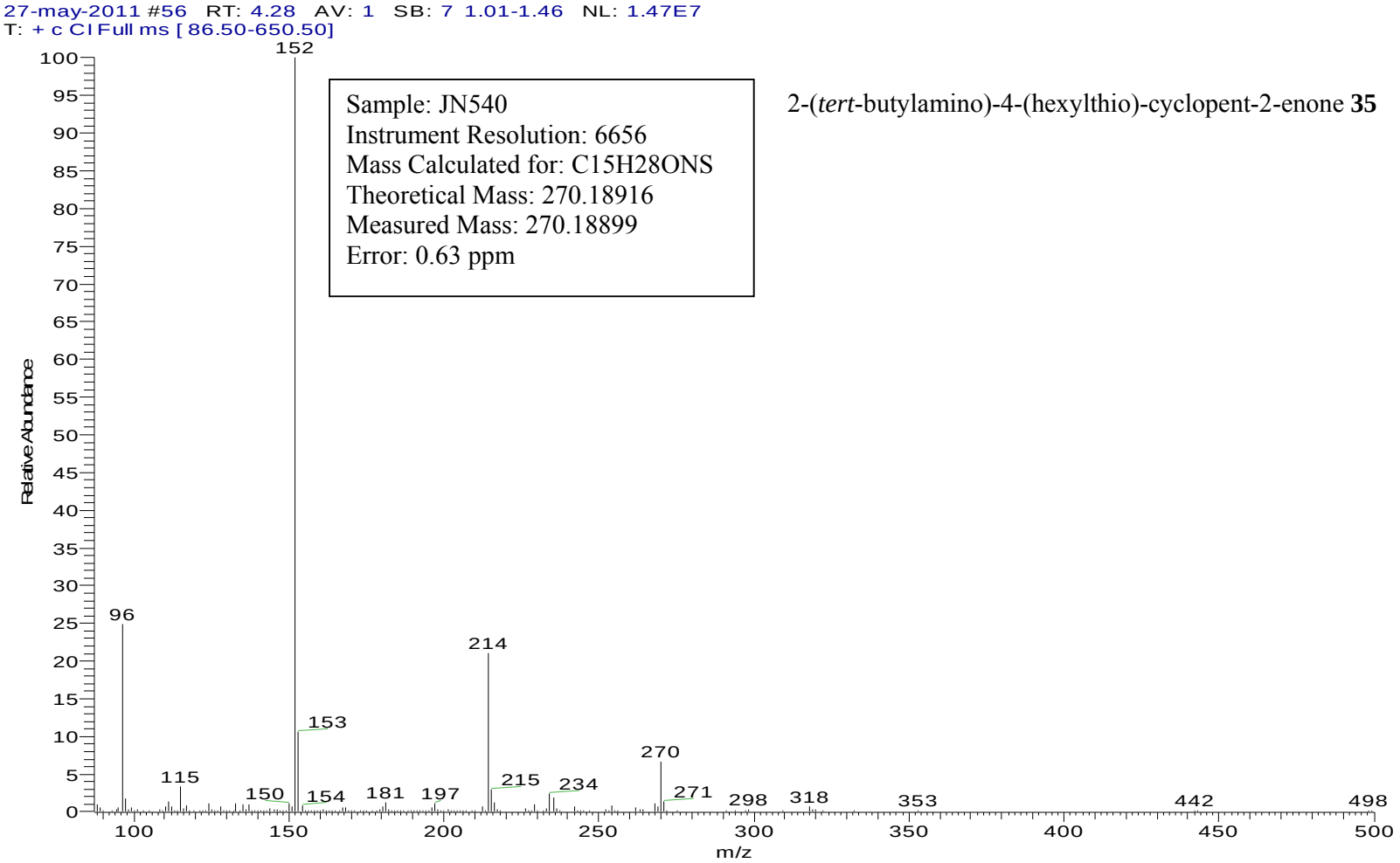


Figure S106 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **35**.



2-(*tert*-butylamino)-4-(hexylthio)-cyclopent-2-enone **35**

Figure S107 – EI mass spectra for exact mass measurement of isolated enone **35**.

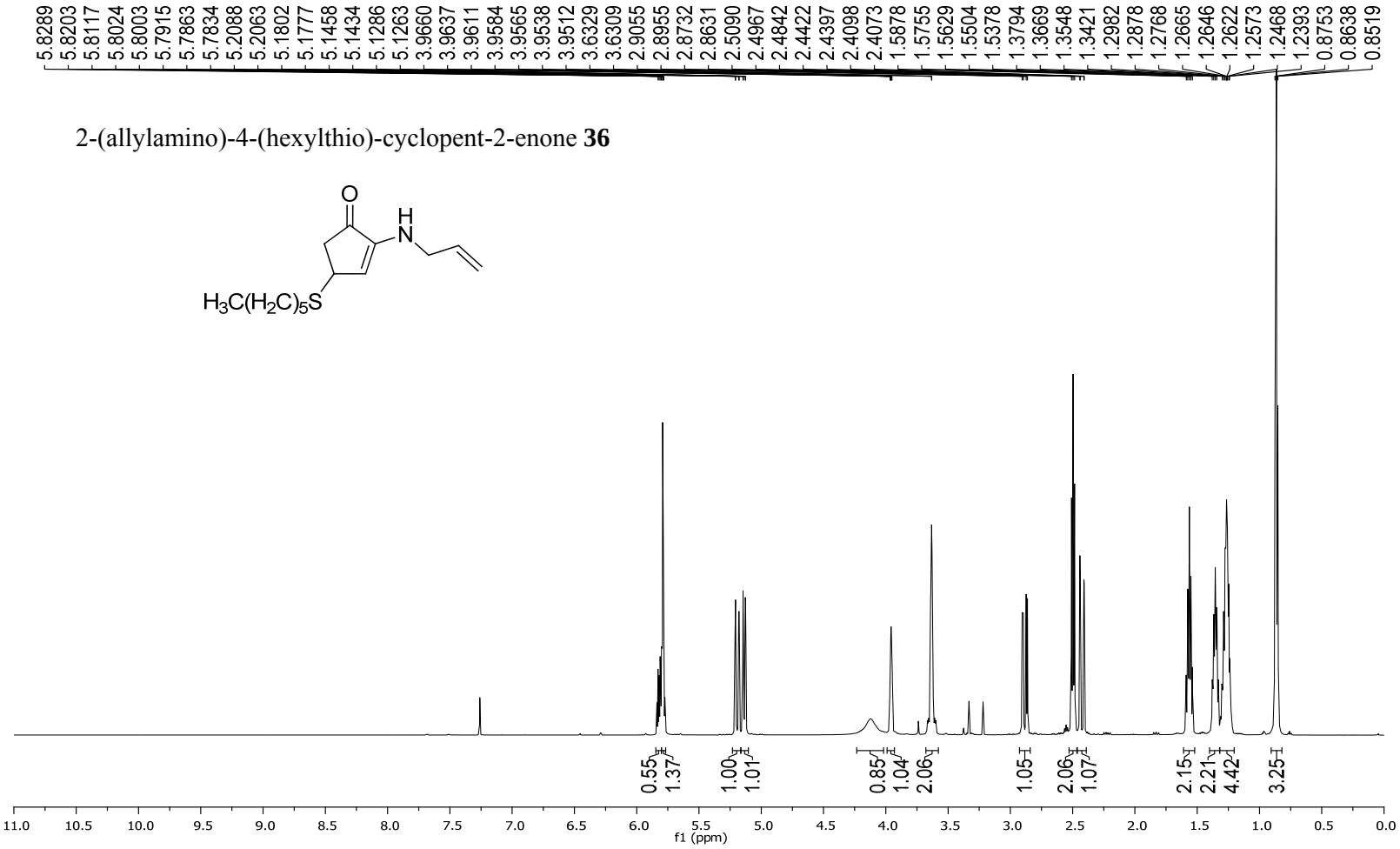


Figure S108 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **36**.

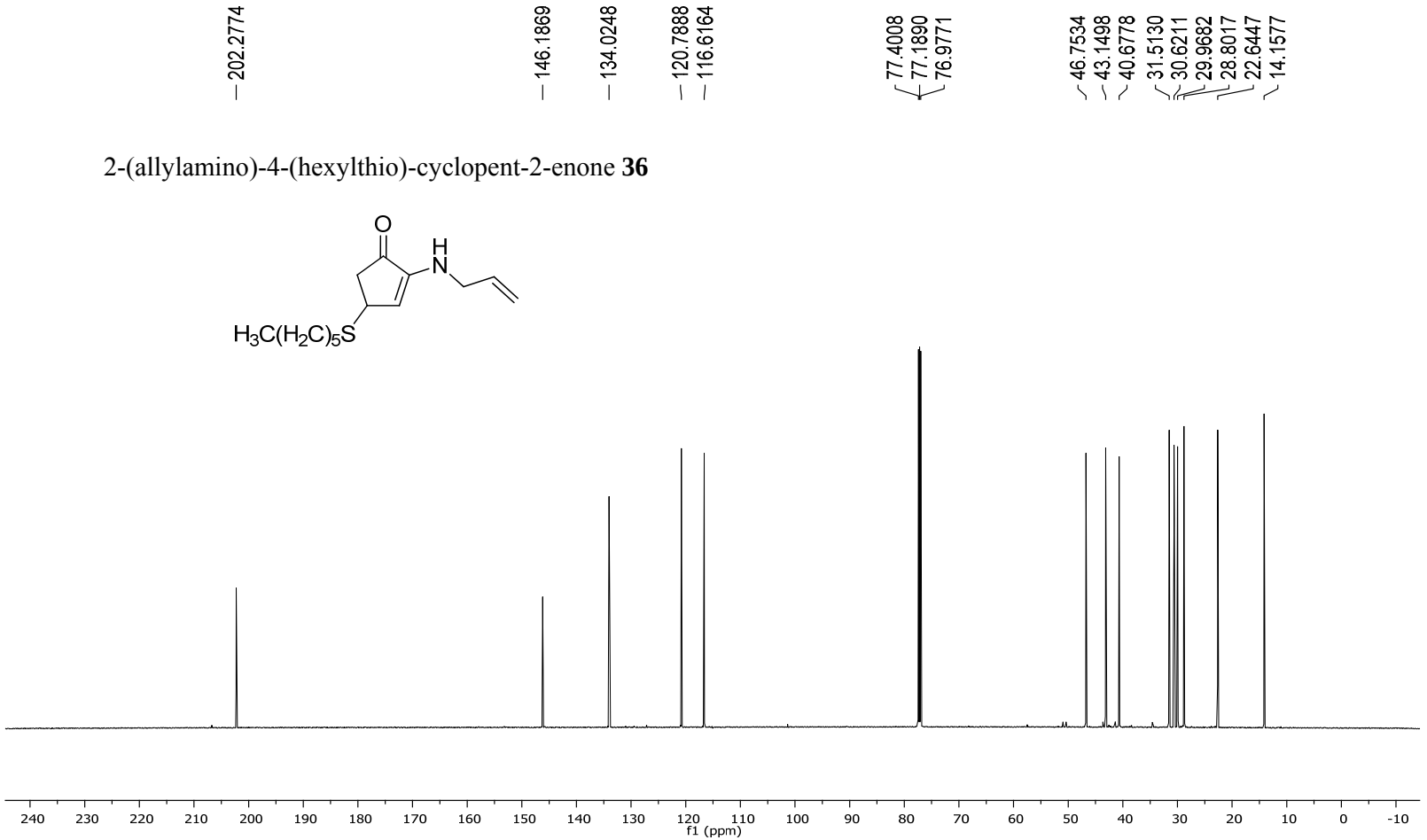
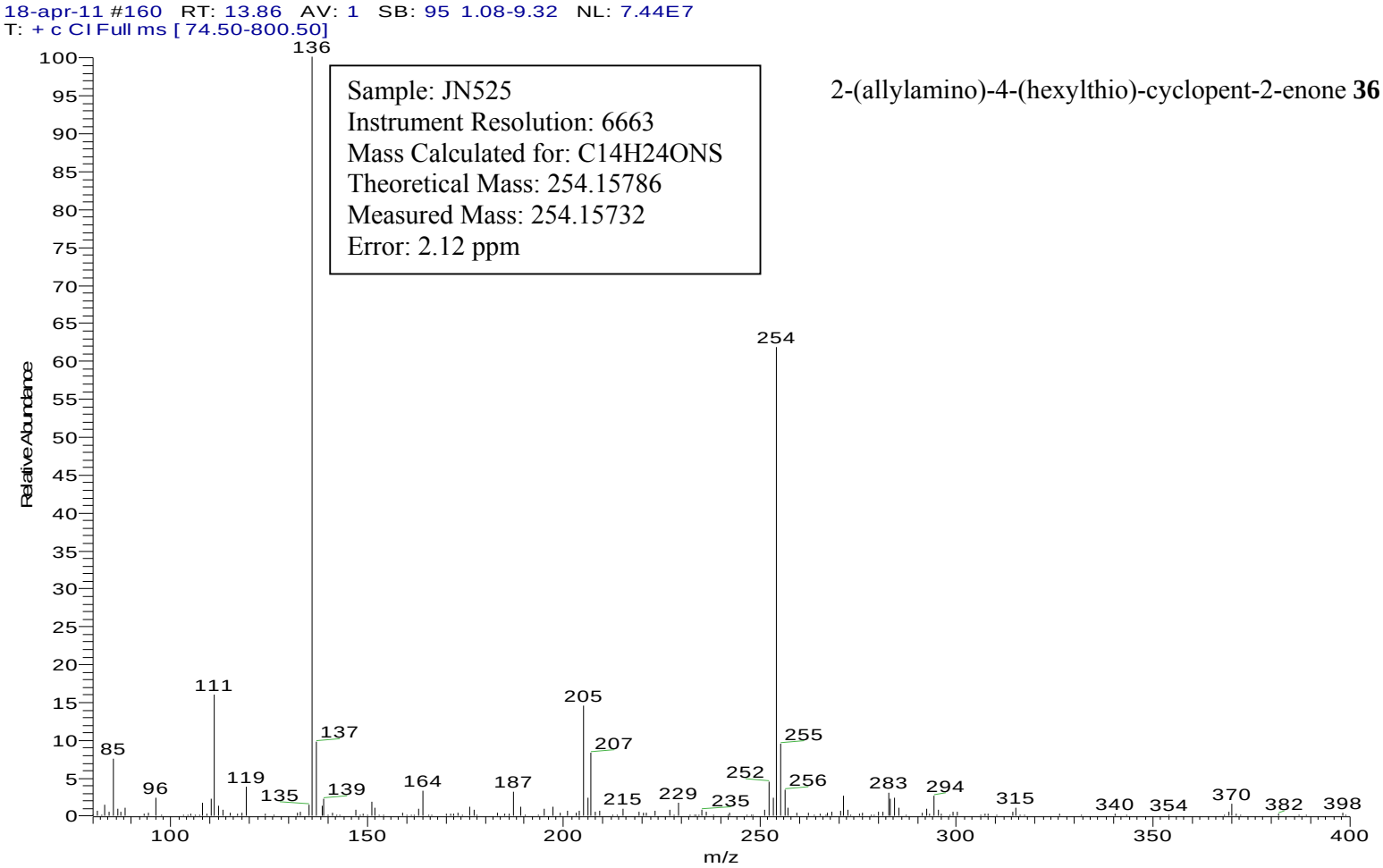


Figure S109 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **36**.



2-(allylamino)-4-(hexylthio)-cyclopent-2-enone **36**

Figure S110 – EI mass spectra for exact mass measurement of isolated enone **36**.

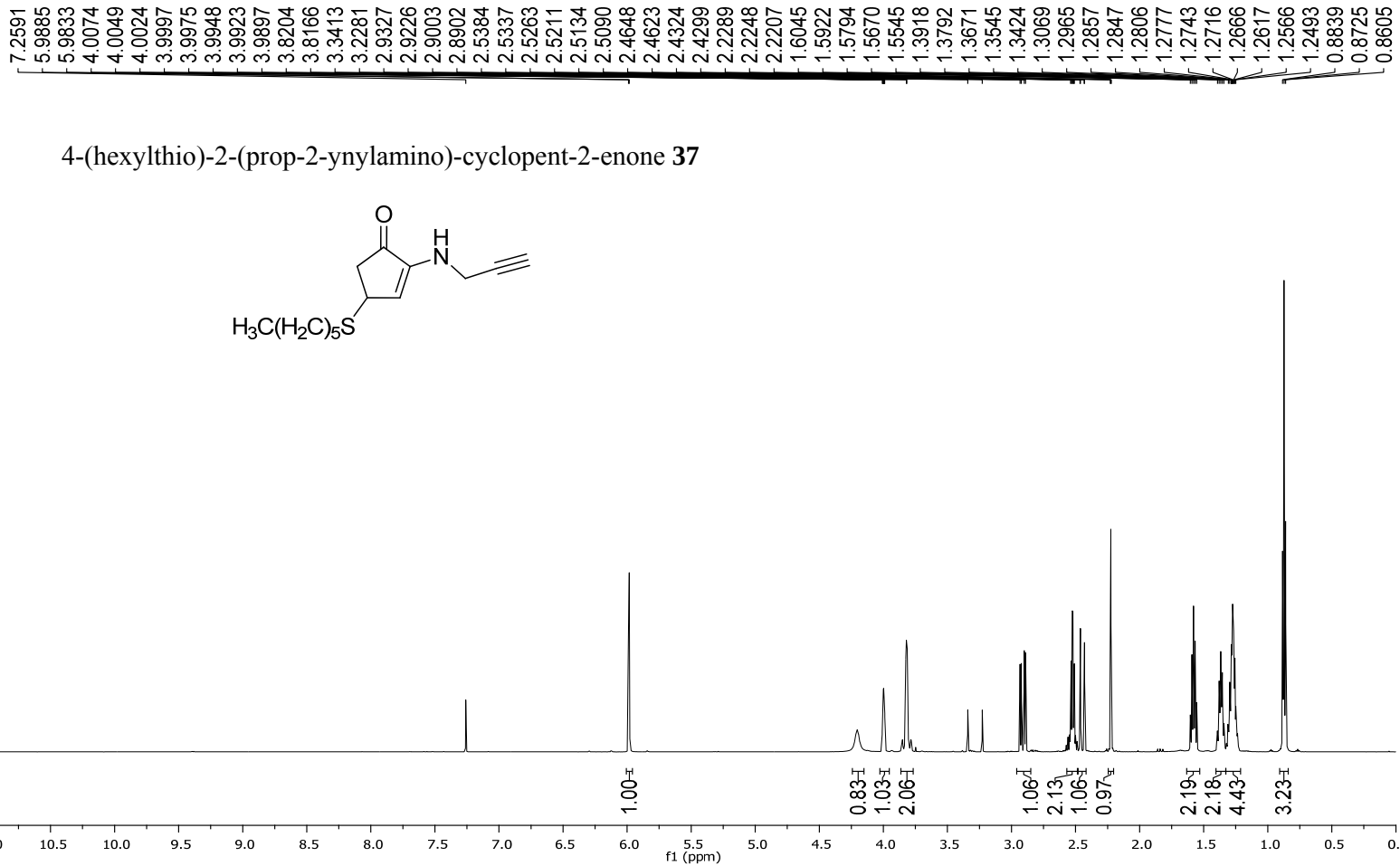


Figure S111 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **37**.

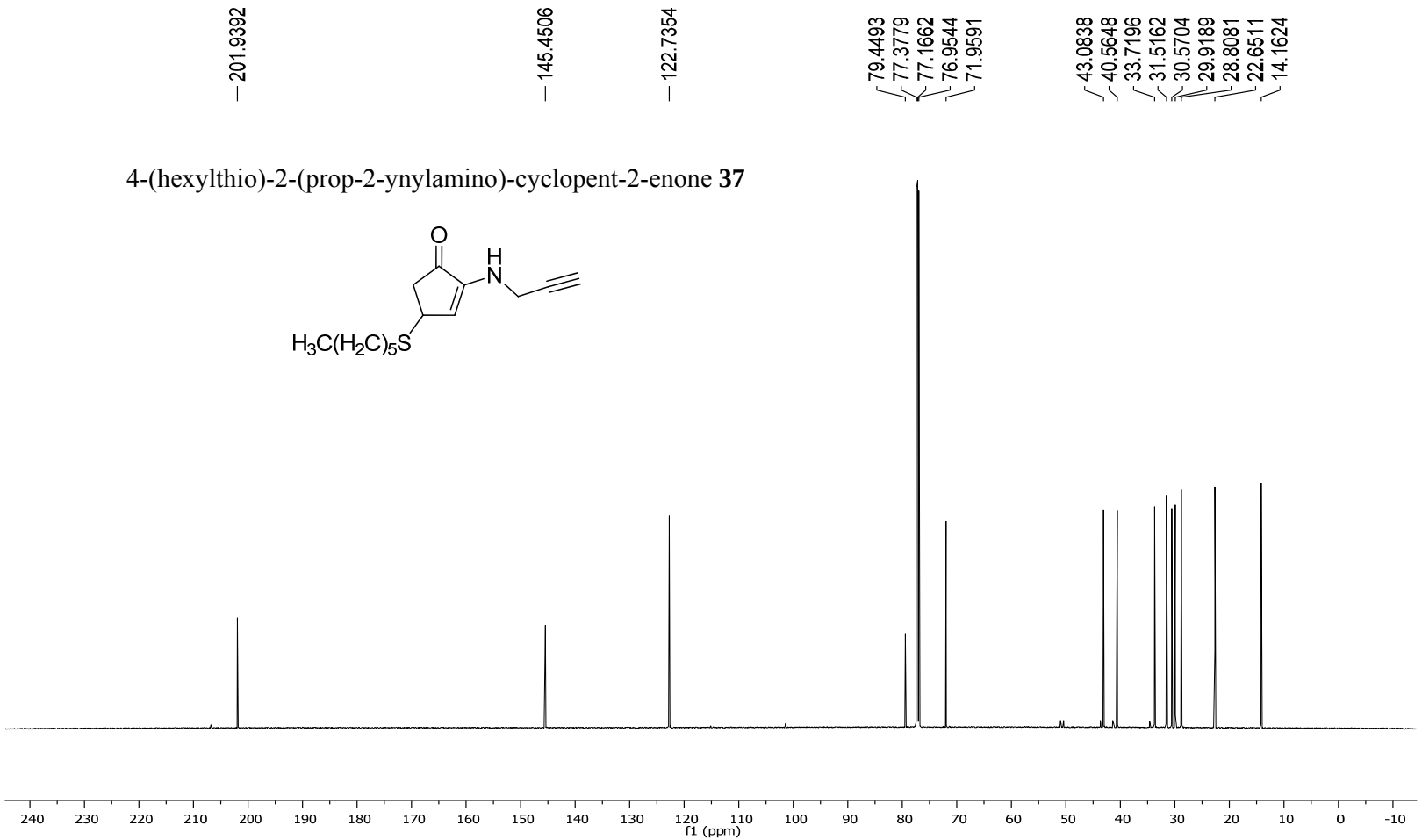
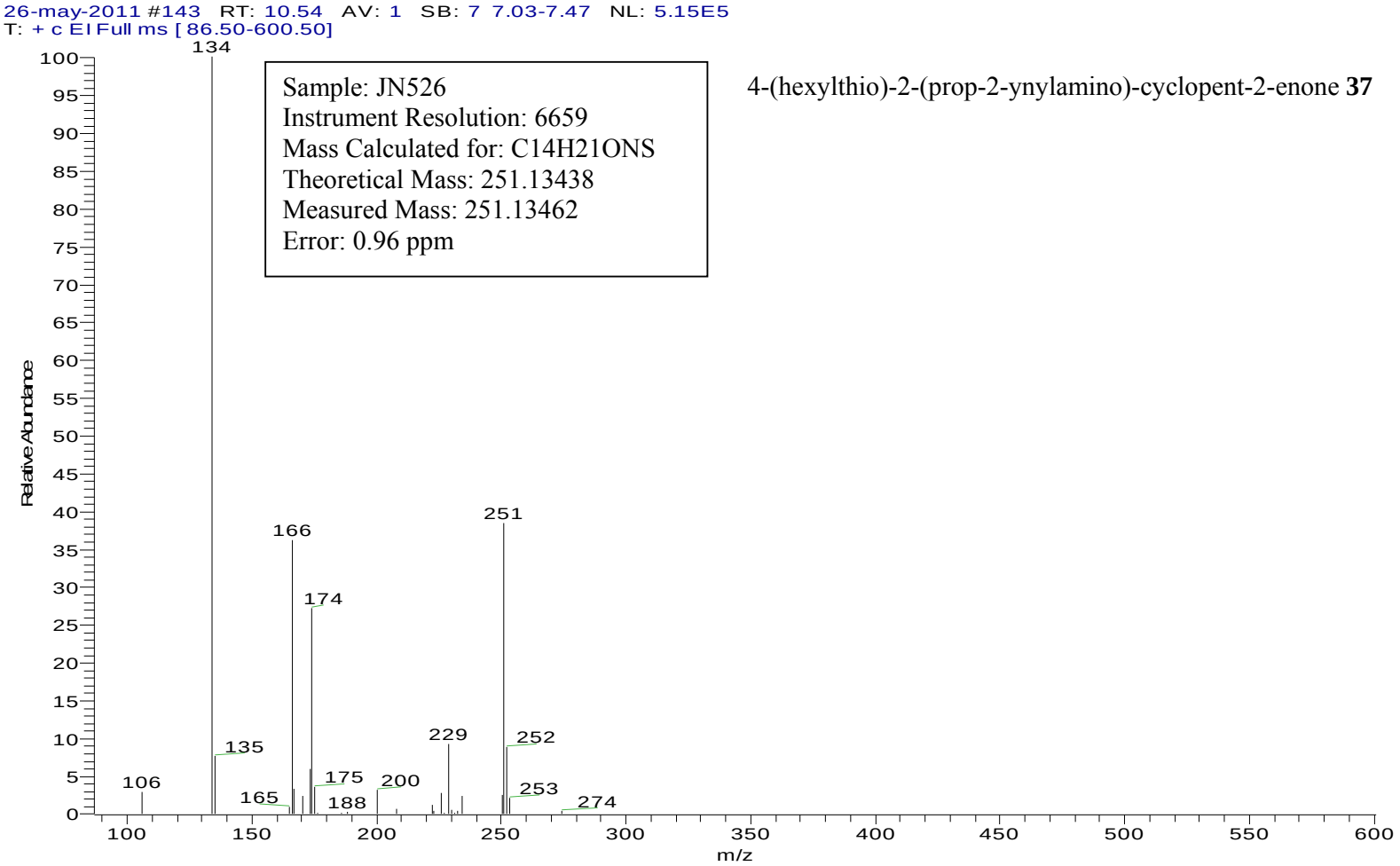


Figure S112 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **37**.



4-(hexylthio)-2-(prop-2-ynylamino)-cyclopent-2-enone **37**

Figure S113 – EI mass spectra for exact mass measurement of isolated enone **37**.

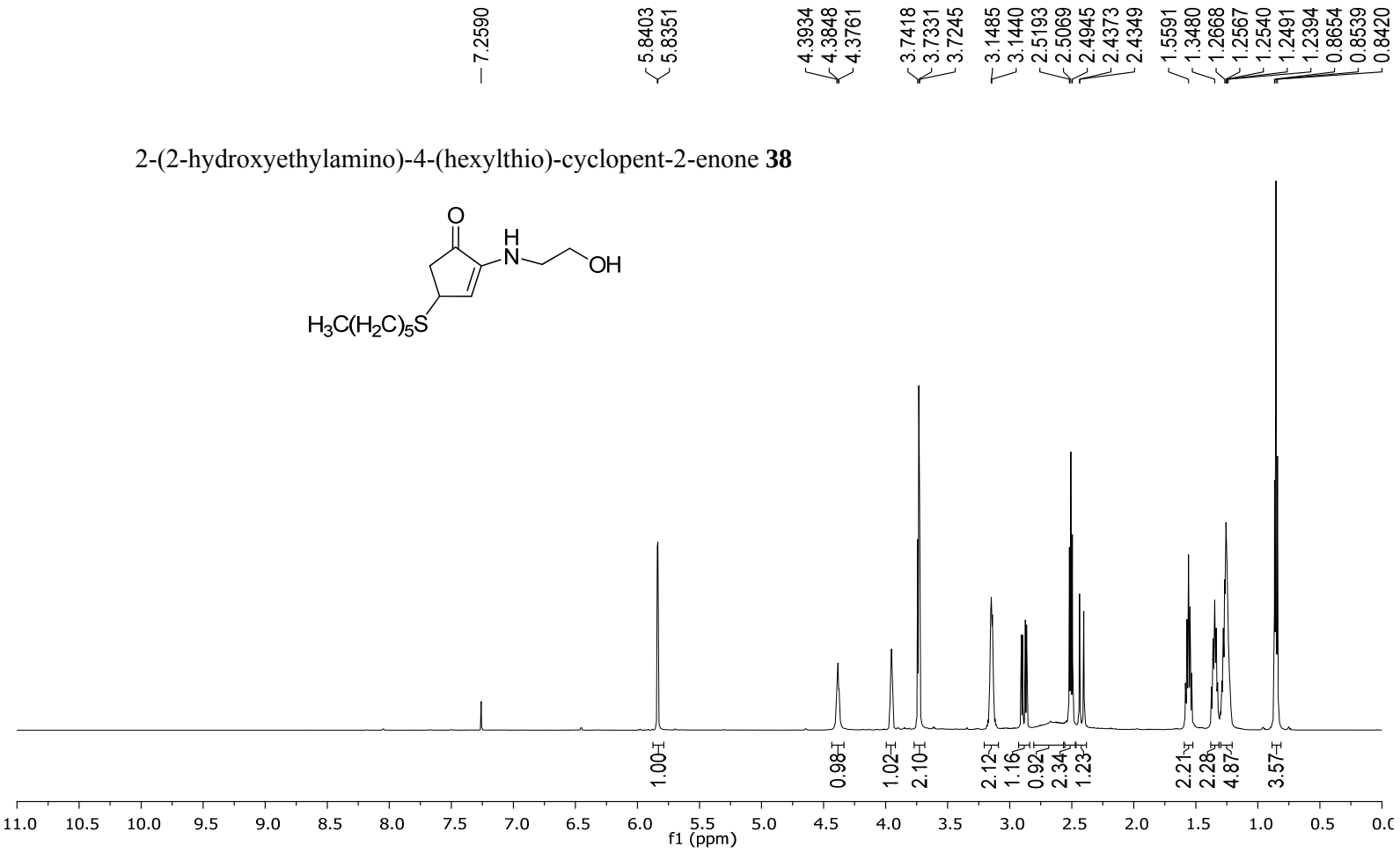


Figure S114 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **38**.

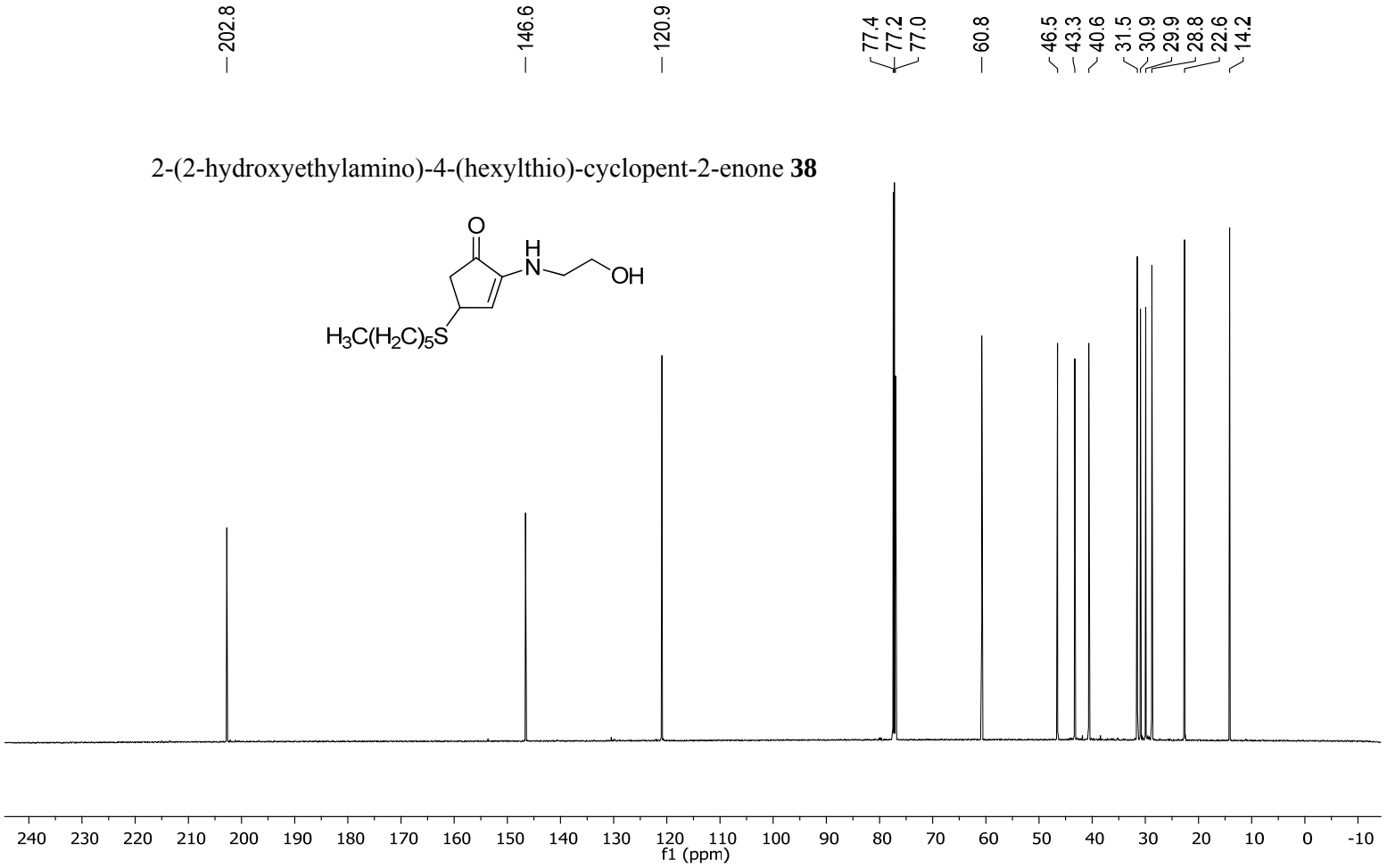


Figure S115 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **38**.

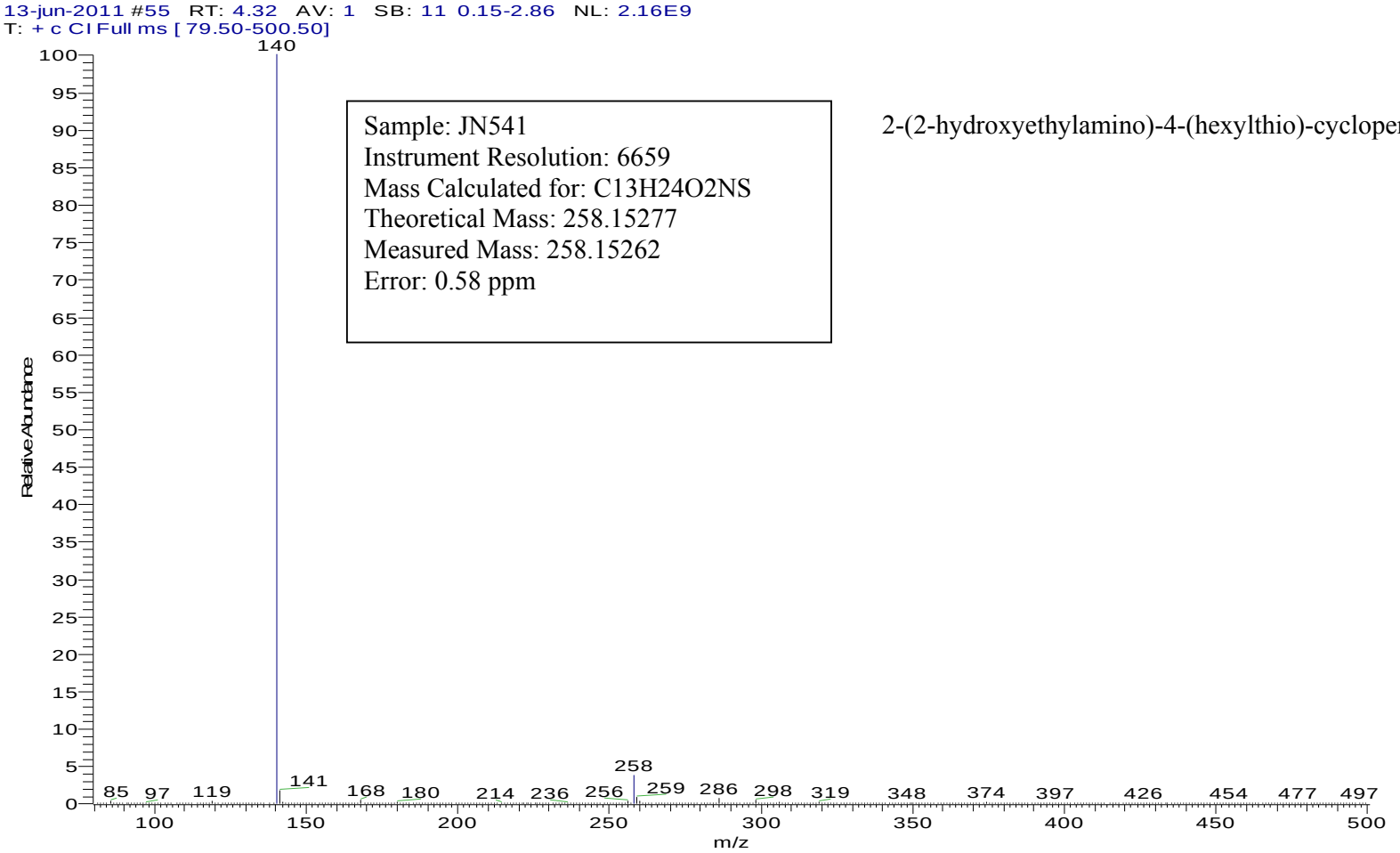


Figure S116 – EI mass spectra for exact mass measurement of isolated enone **38**.

4-(hexylthio)-2-(phenylamino)-cyclopent-2-enone **39**

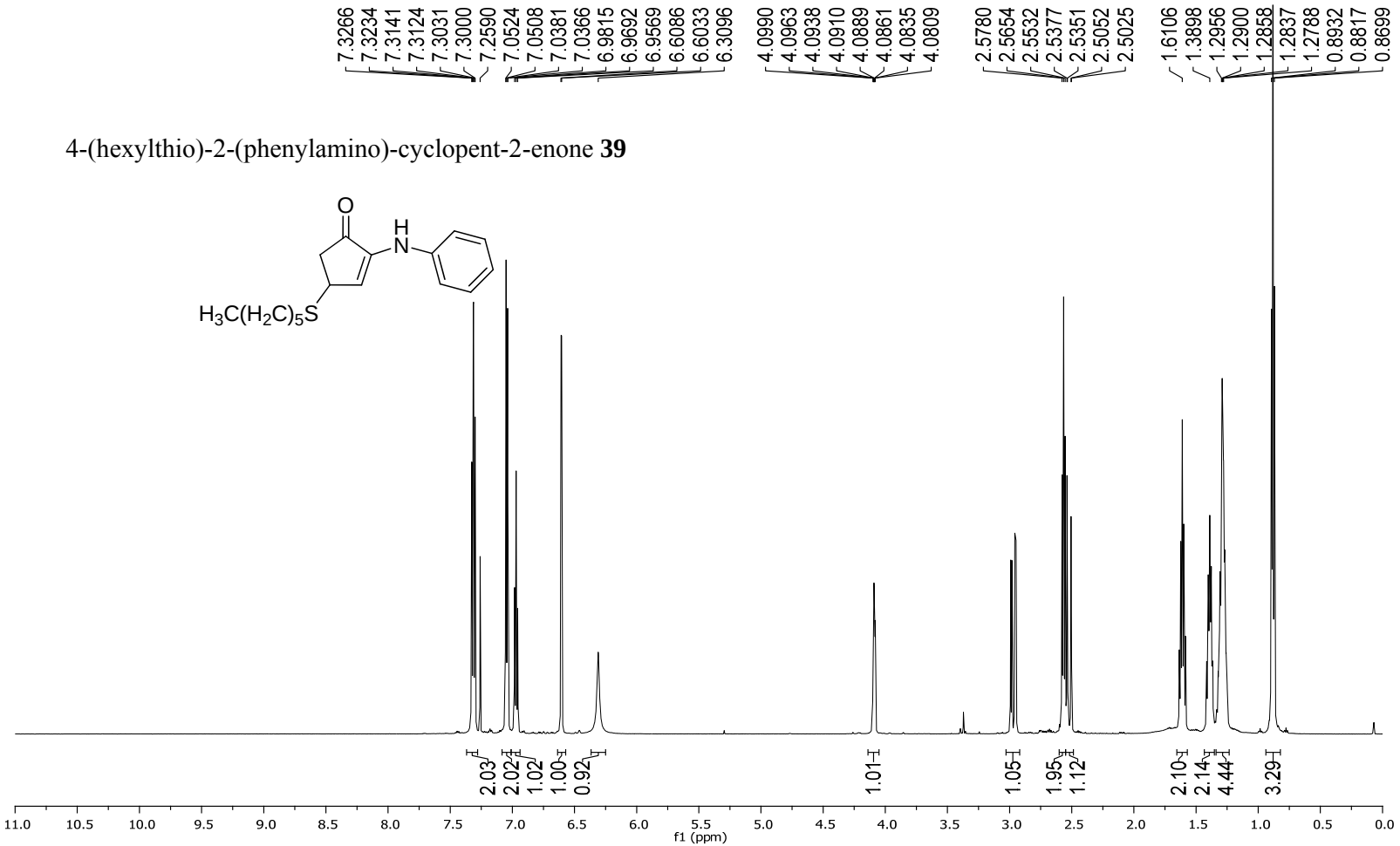


Figure S117 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **39**.

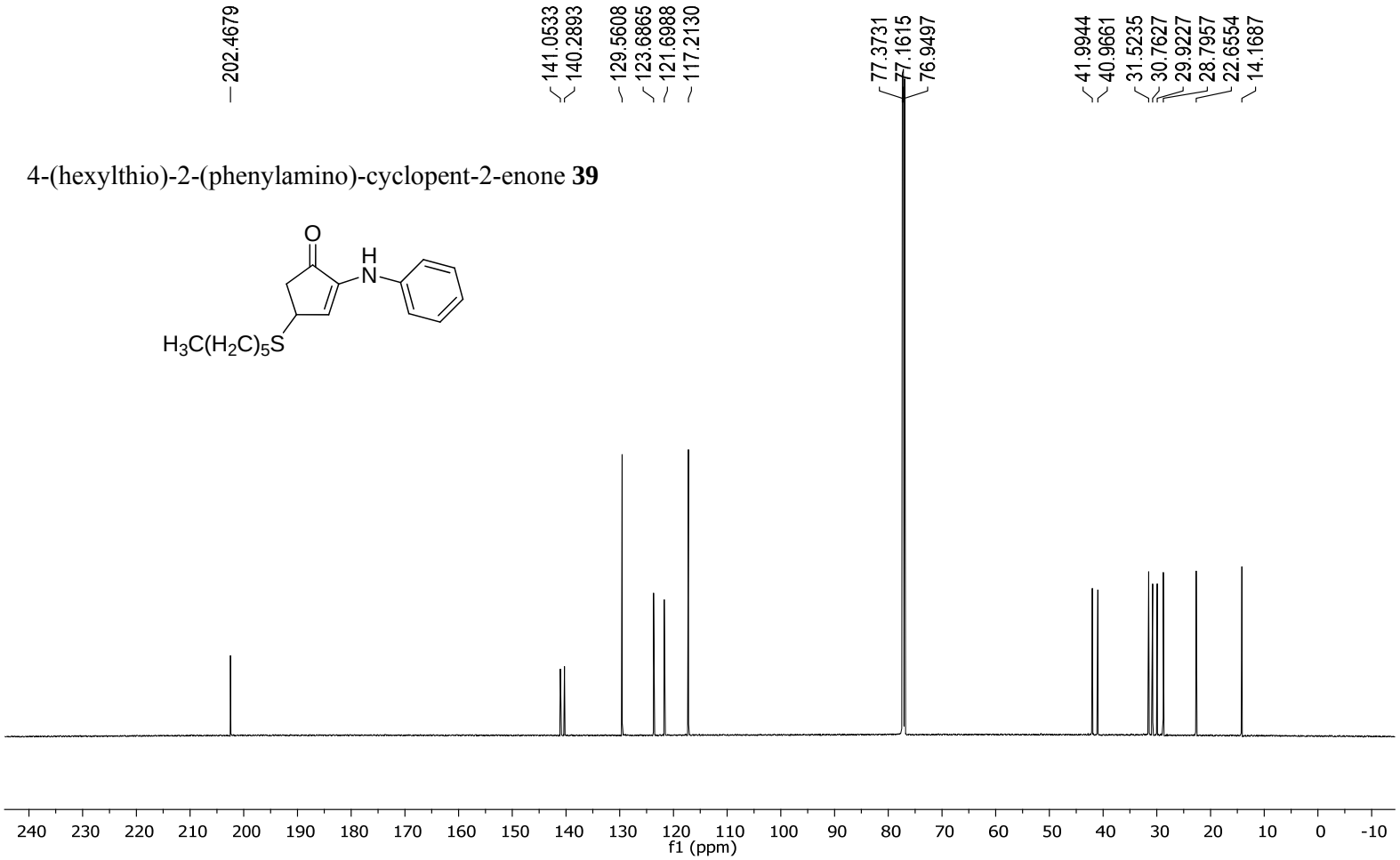
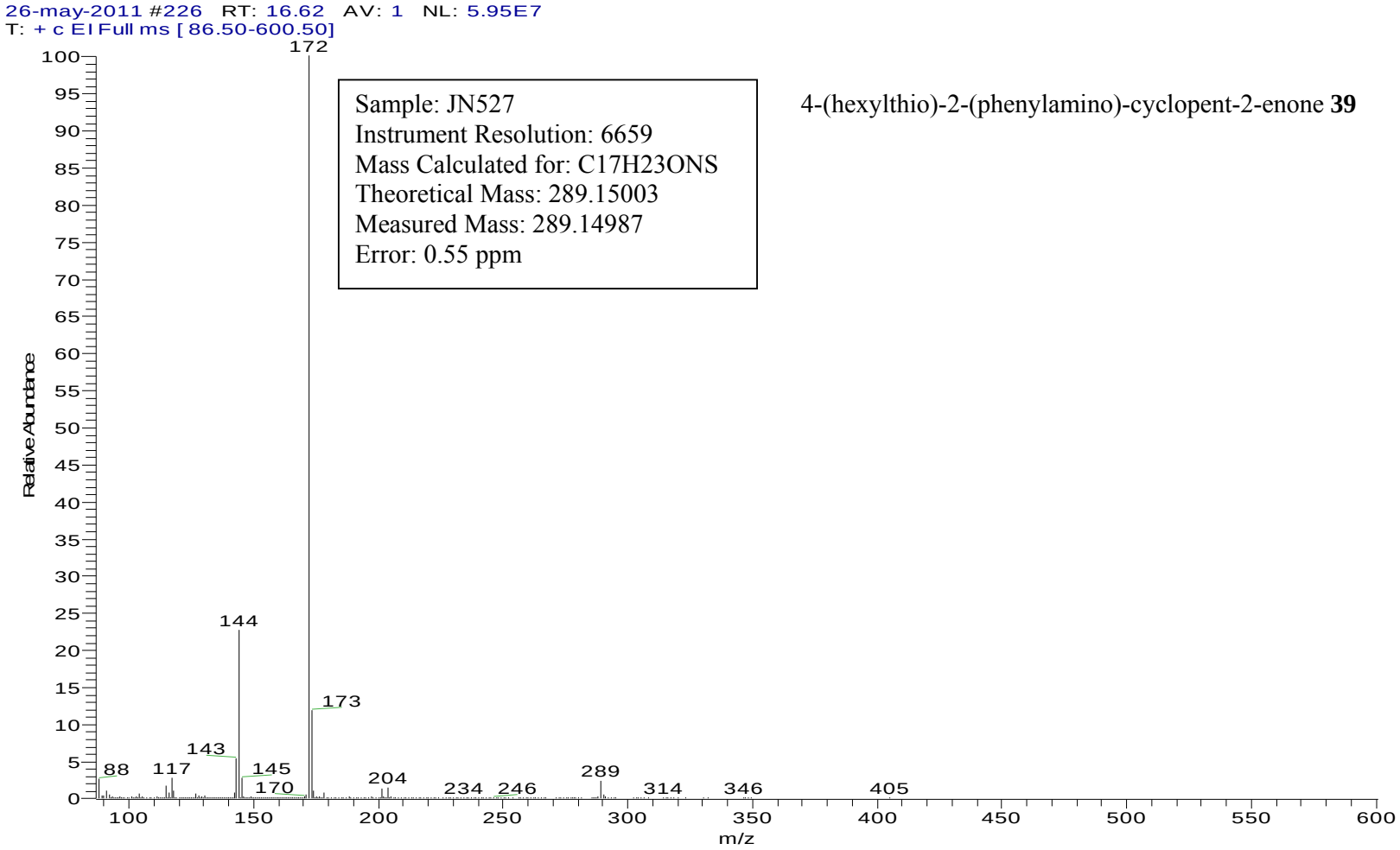


Figure S118 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **39**.



4-(hexylthio)-2-(phenylamino)-cyclopent-2-enone **39**

Figure S119 – EI mass spectra for exact mass measurement of isolated enone **39**.

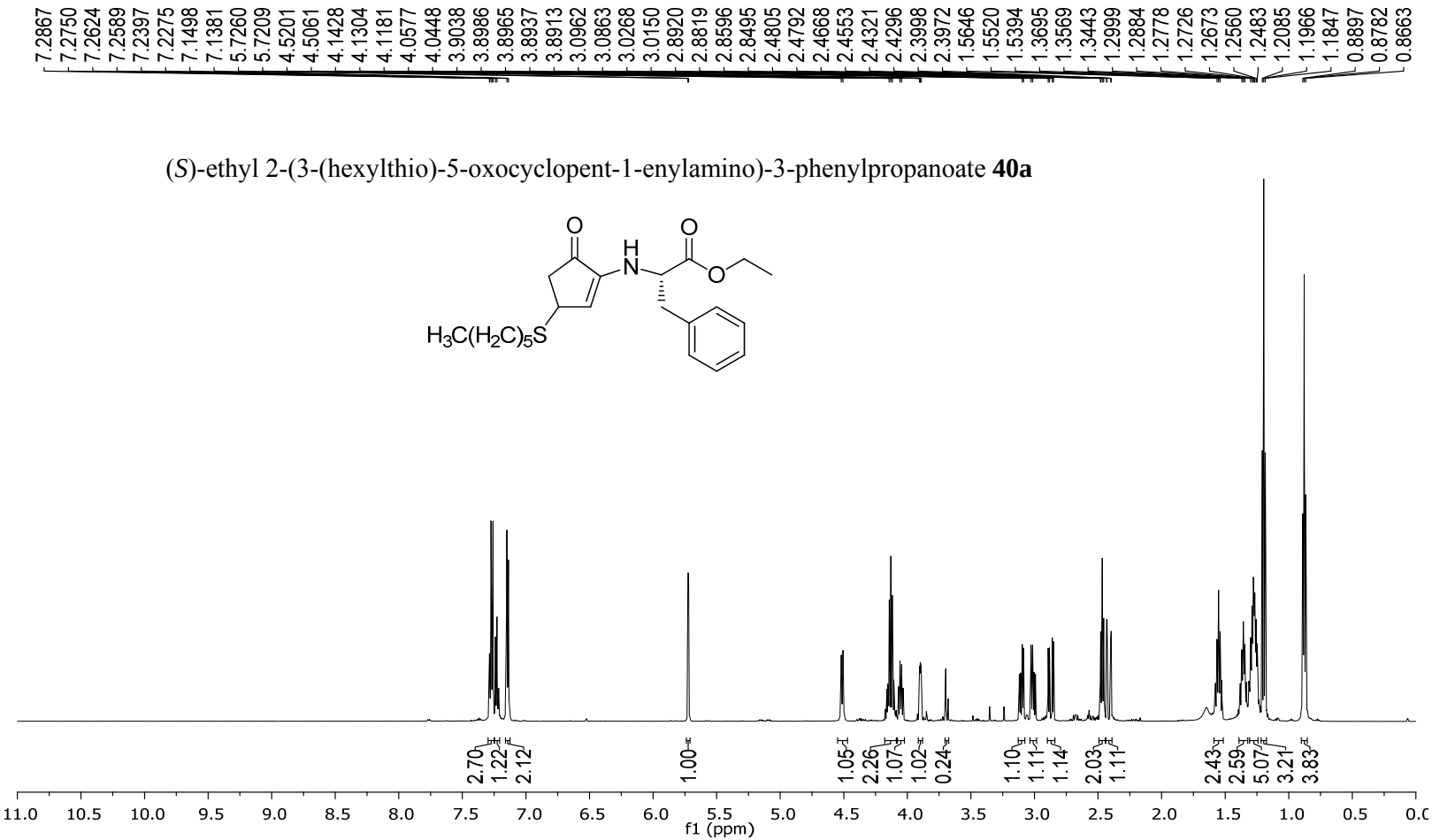


Figure S120 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **40a**.

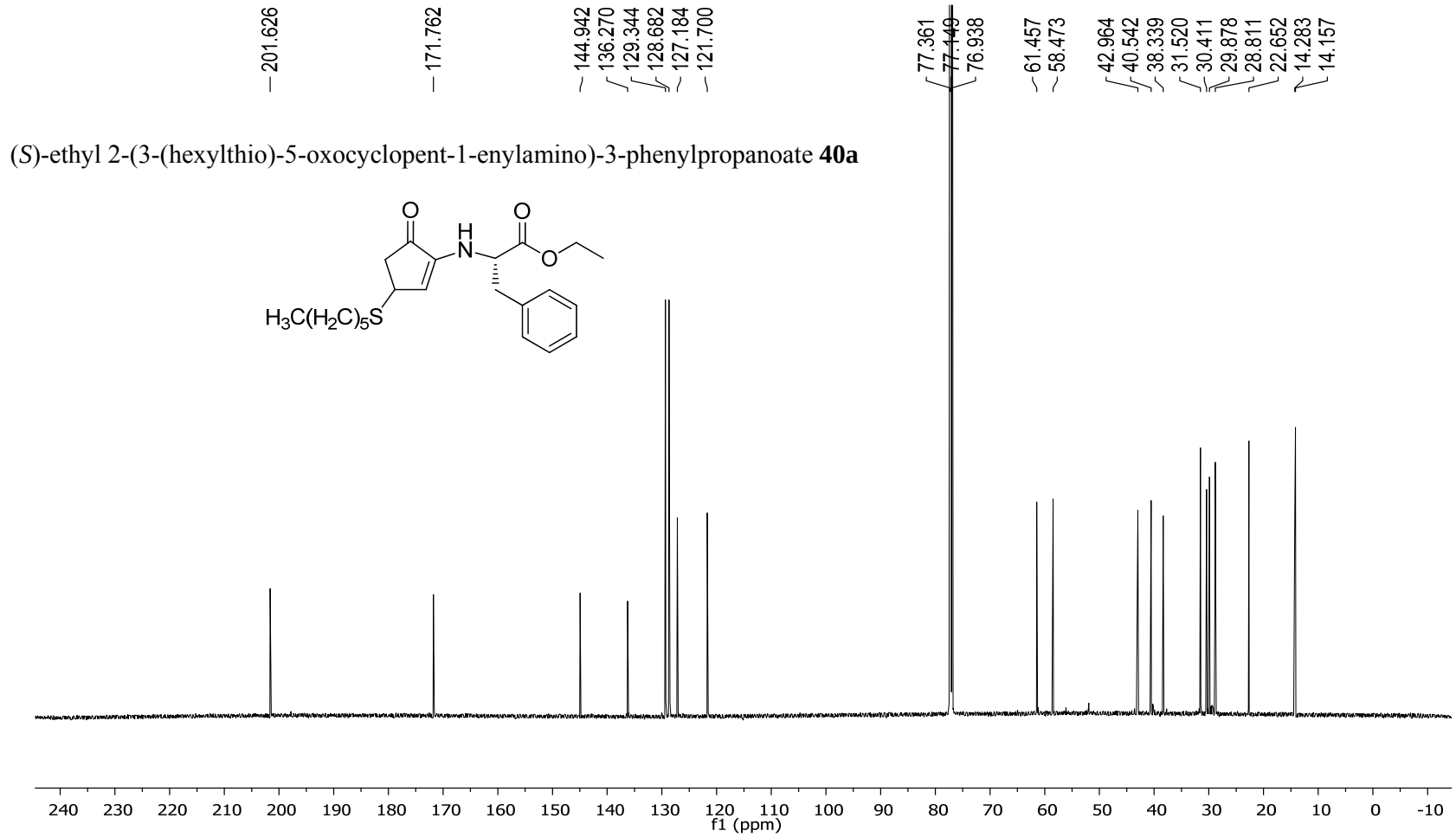


Figure S121 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **40a**.

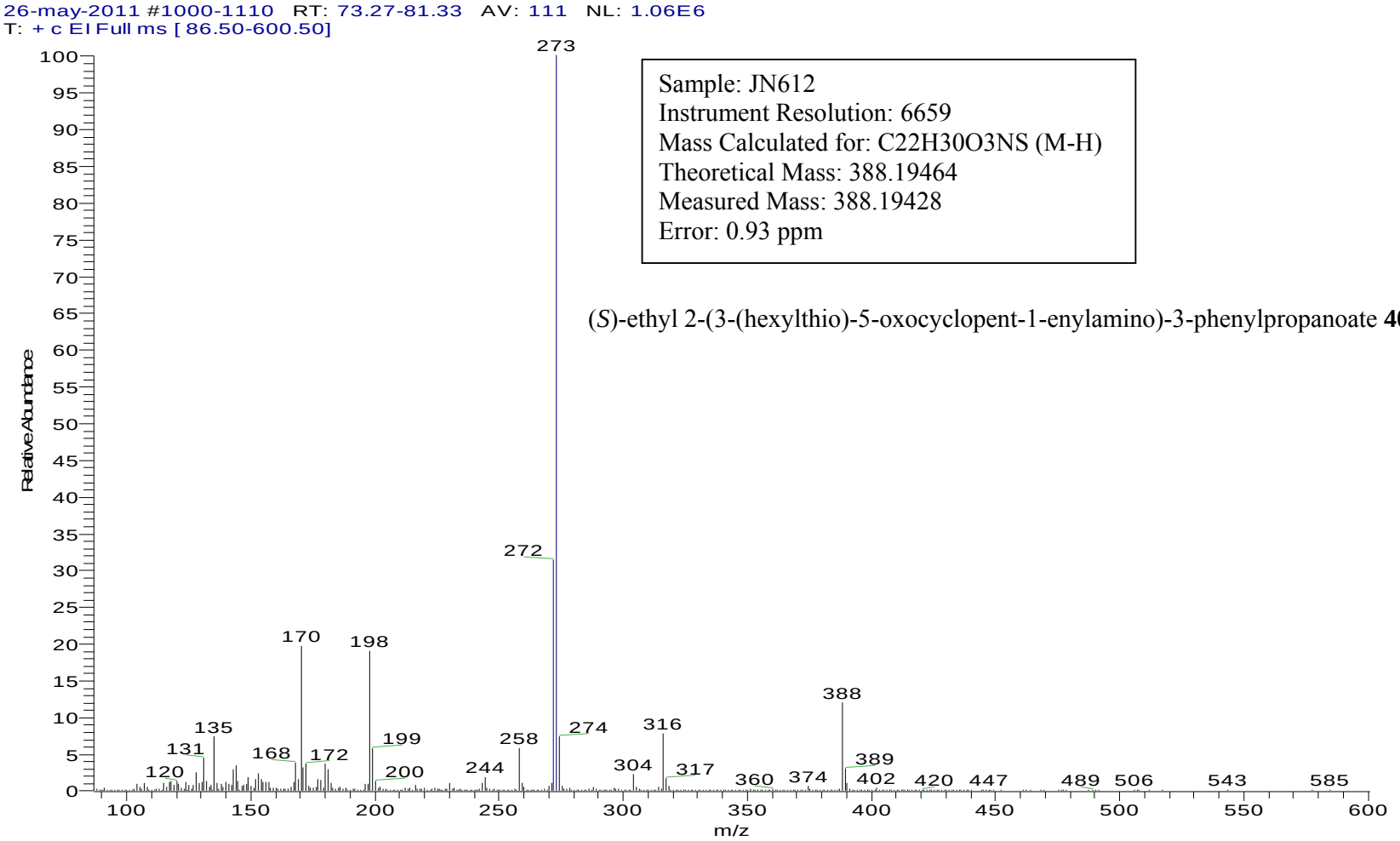


Figure S122 – EI mass spectra for exact mass measurement of isolated enone **40a**.

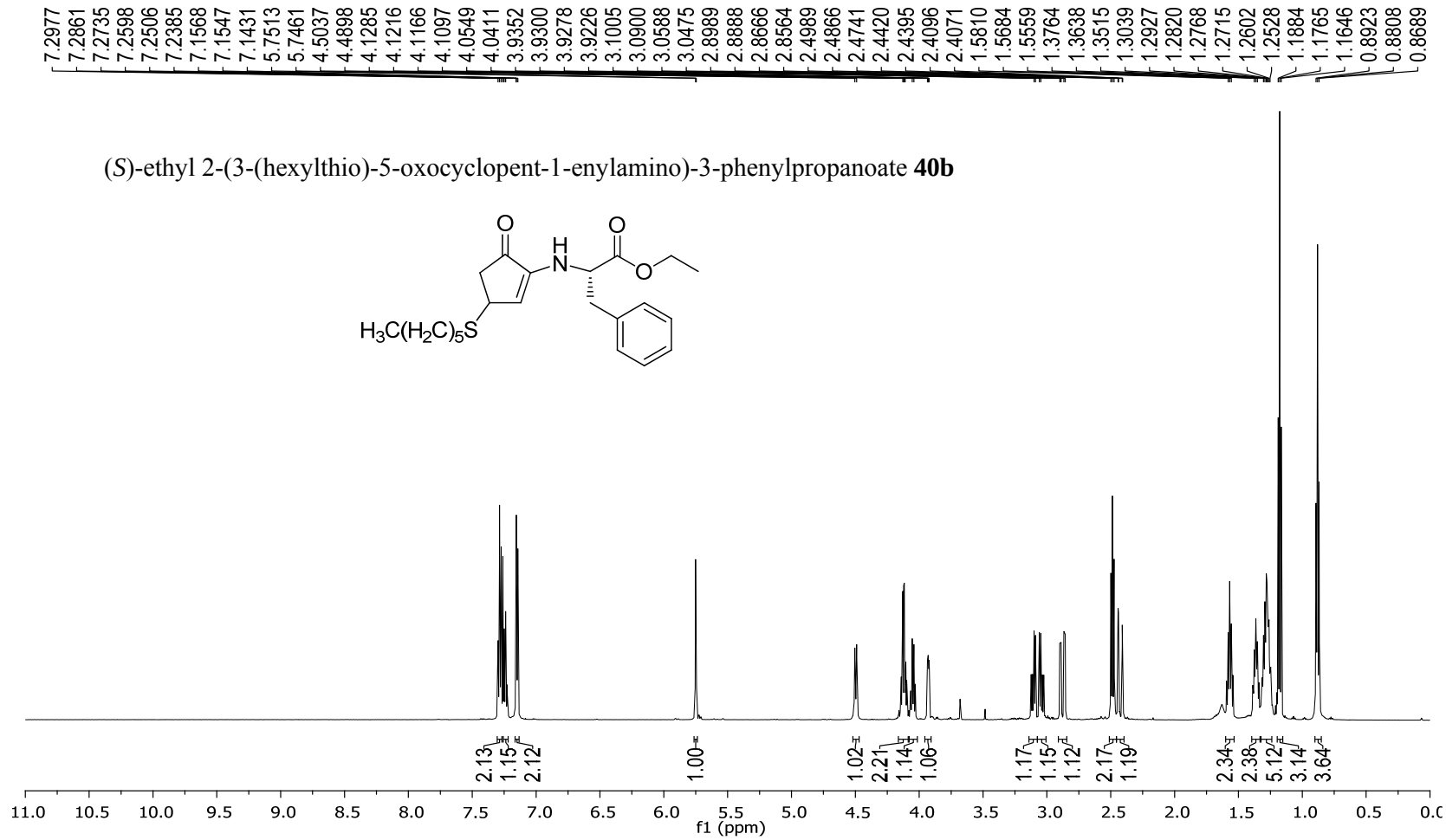


Figure S123 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated enone **40b**.

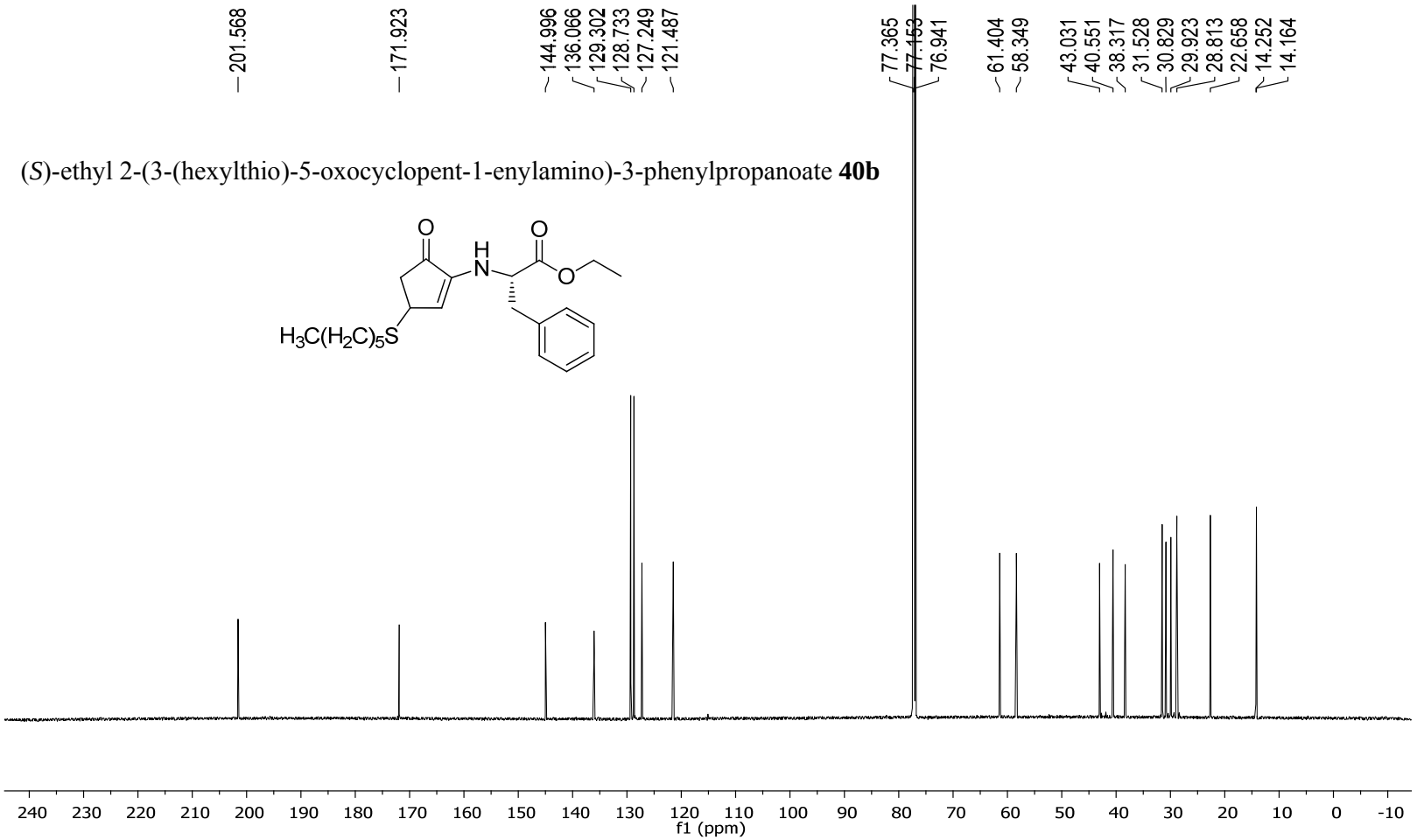


Figure S124 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated enone **40b**.

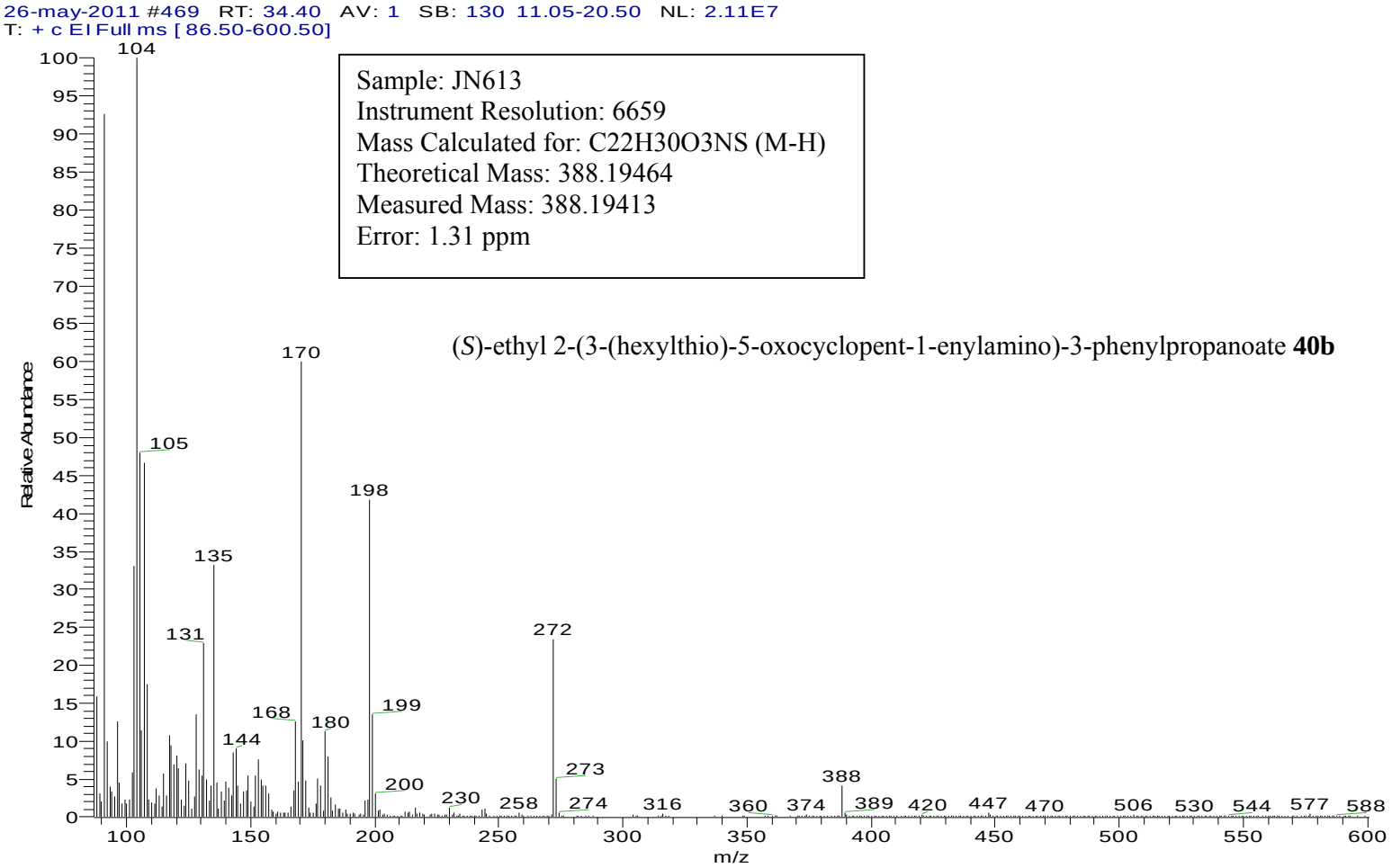


Figure S125 – EI mass spectra for exact mass measurement of isolated enone **40b**.

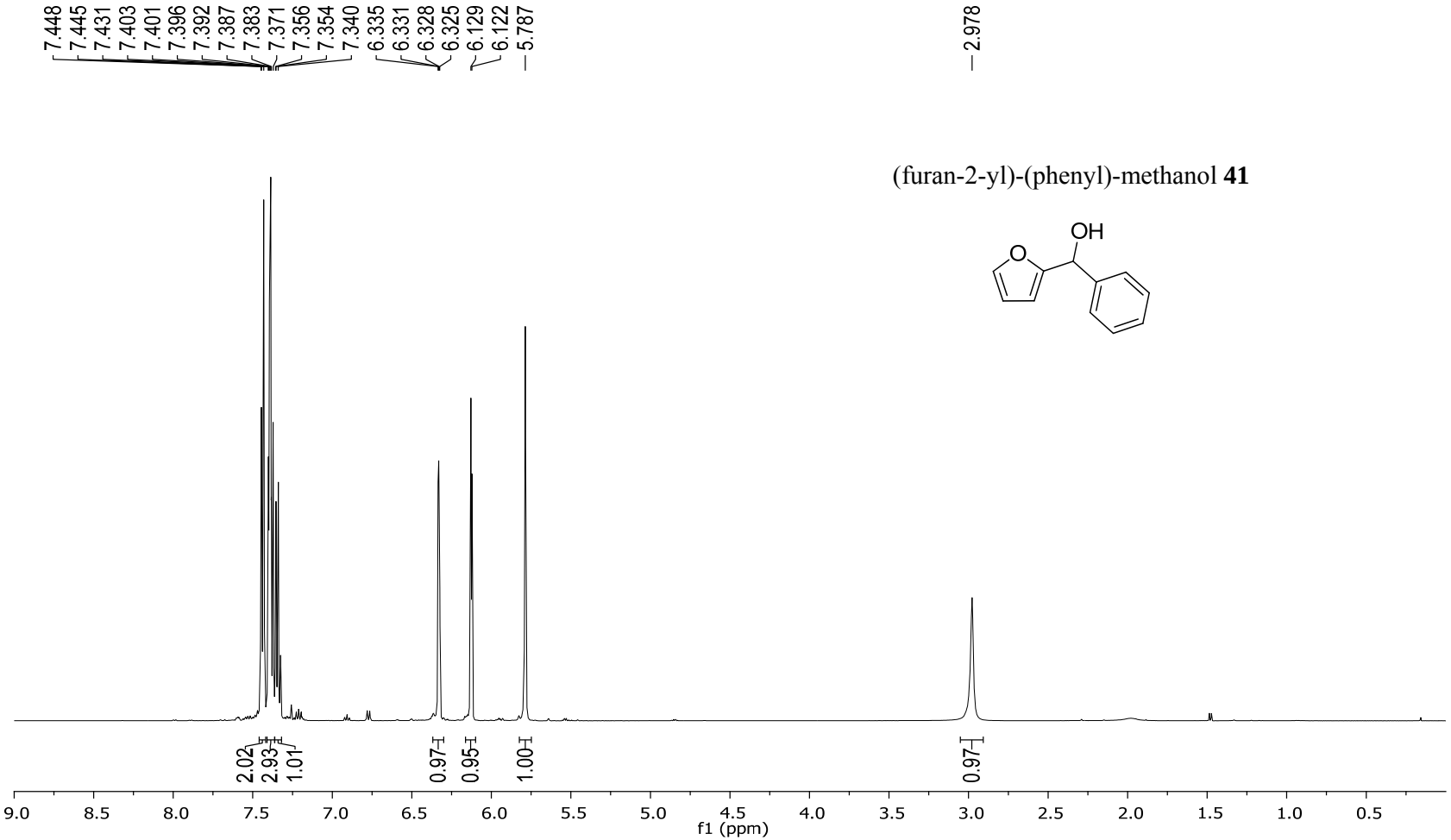


Figure S126 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated compound **41**.

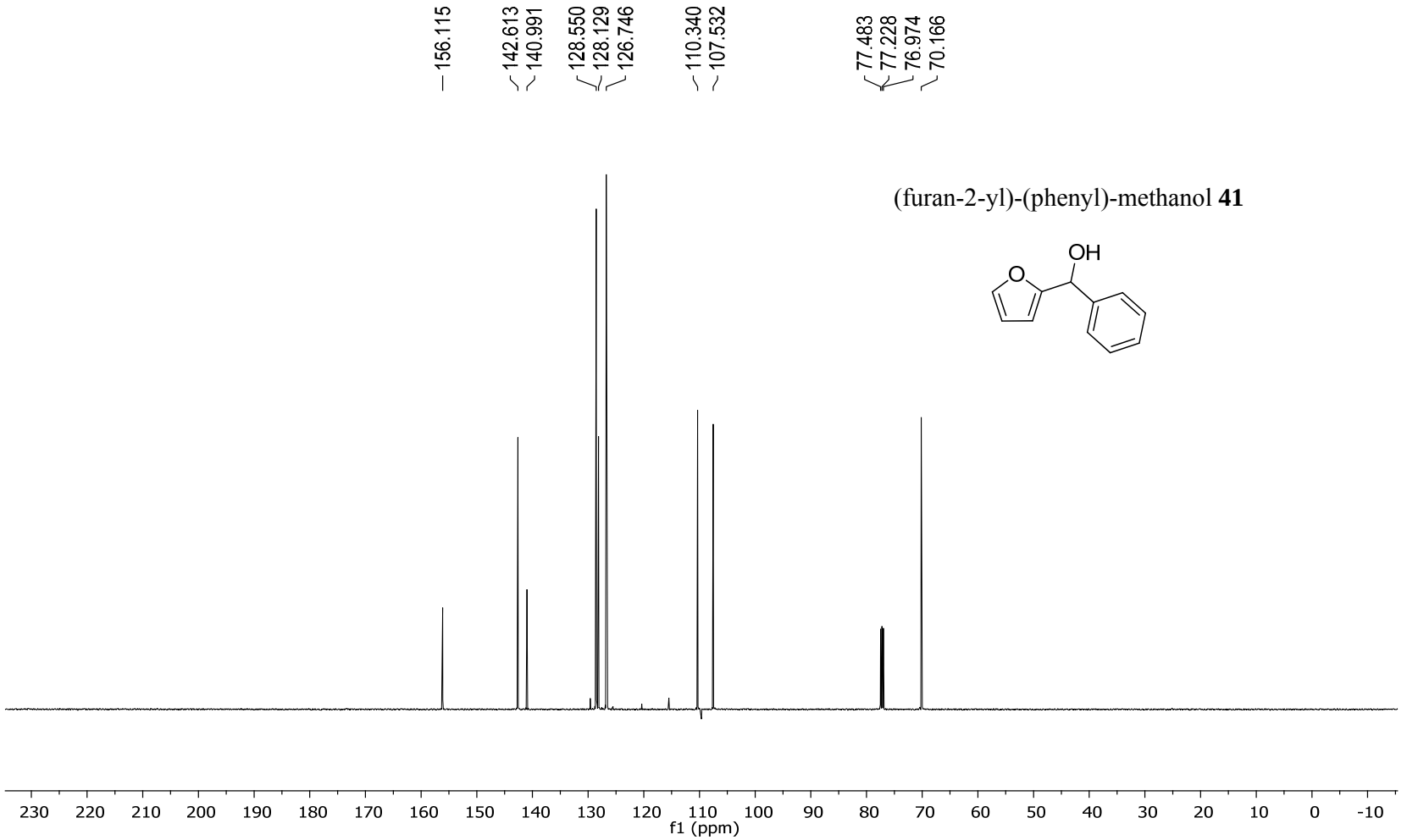


Figure S127 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated compound **41**.

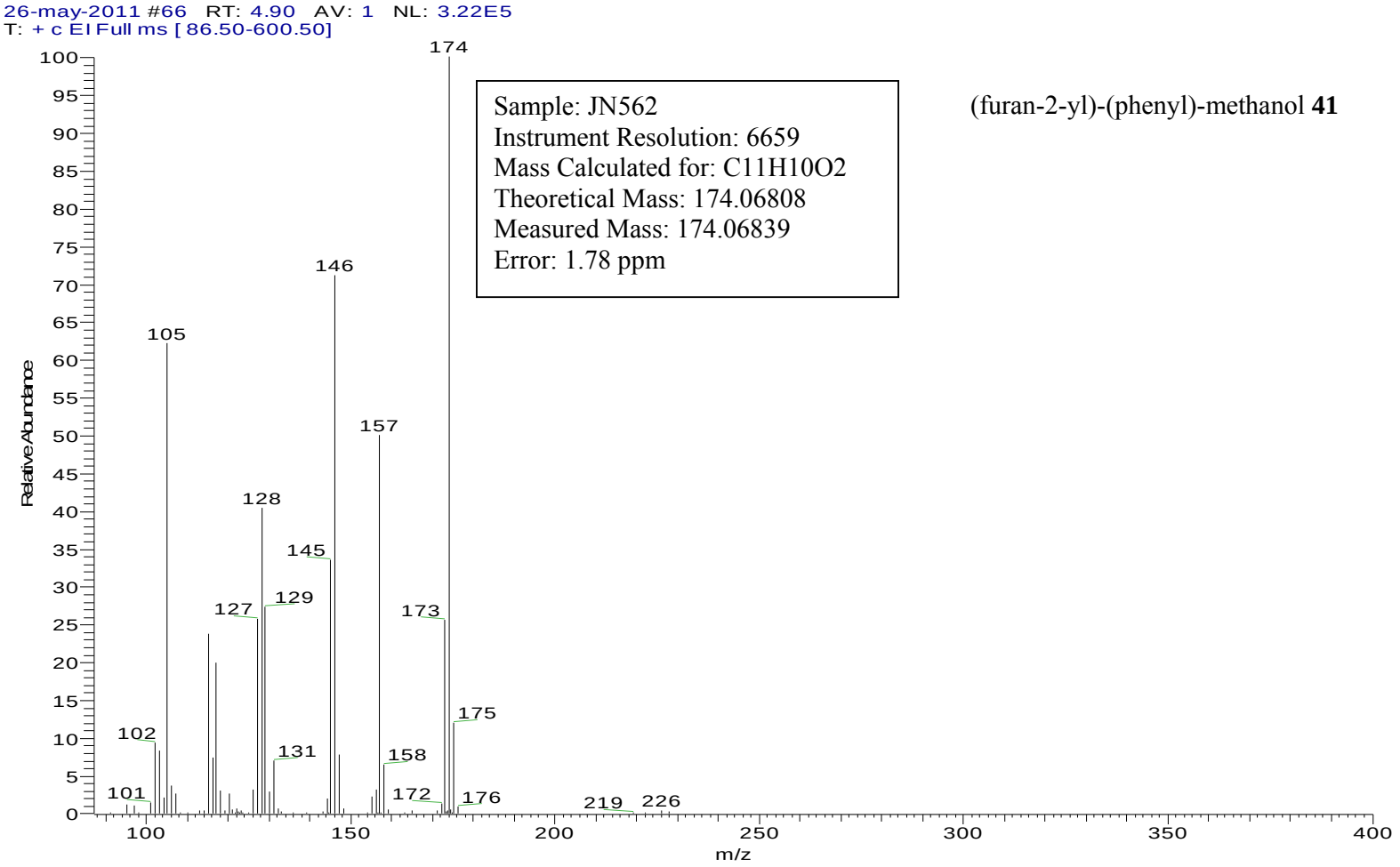
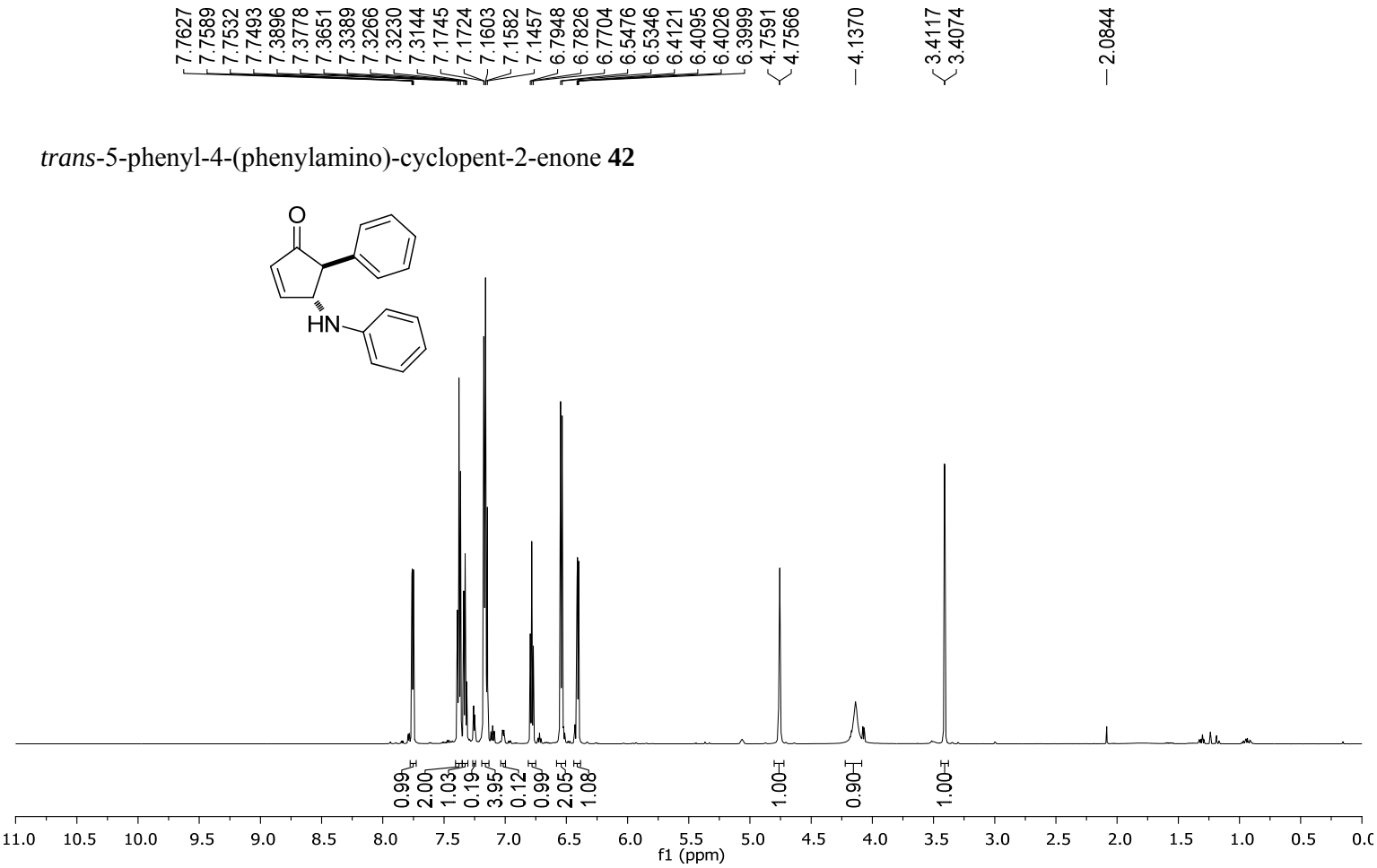
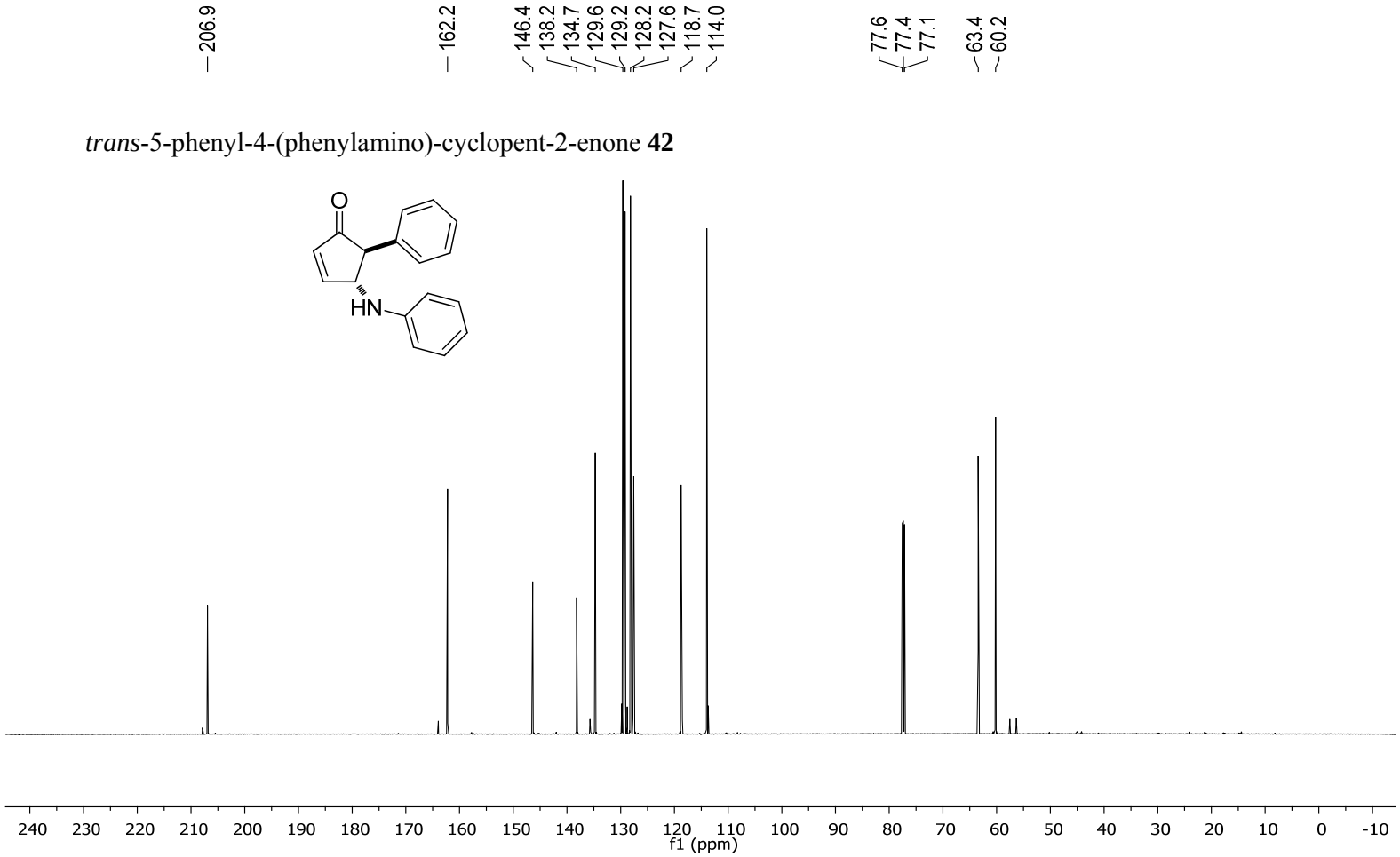


Figure S128 – EI mass spectra for exact mass measurement of isolated compound **41**.



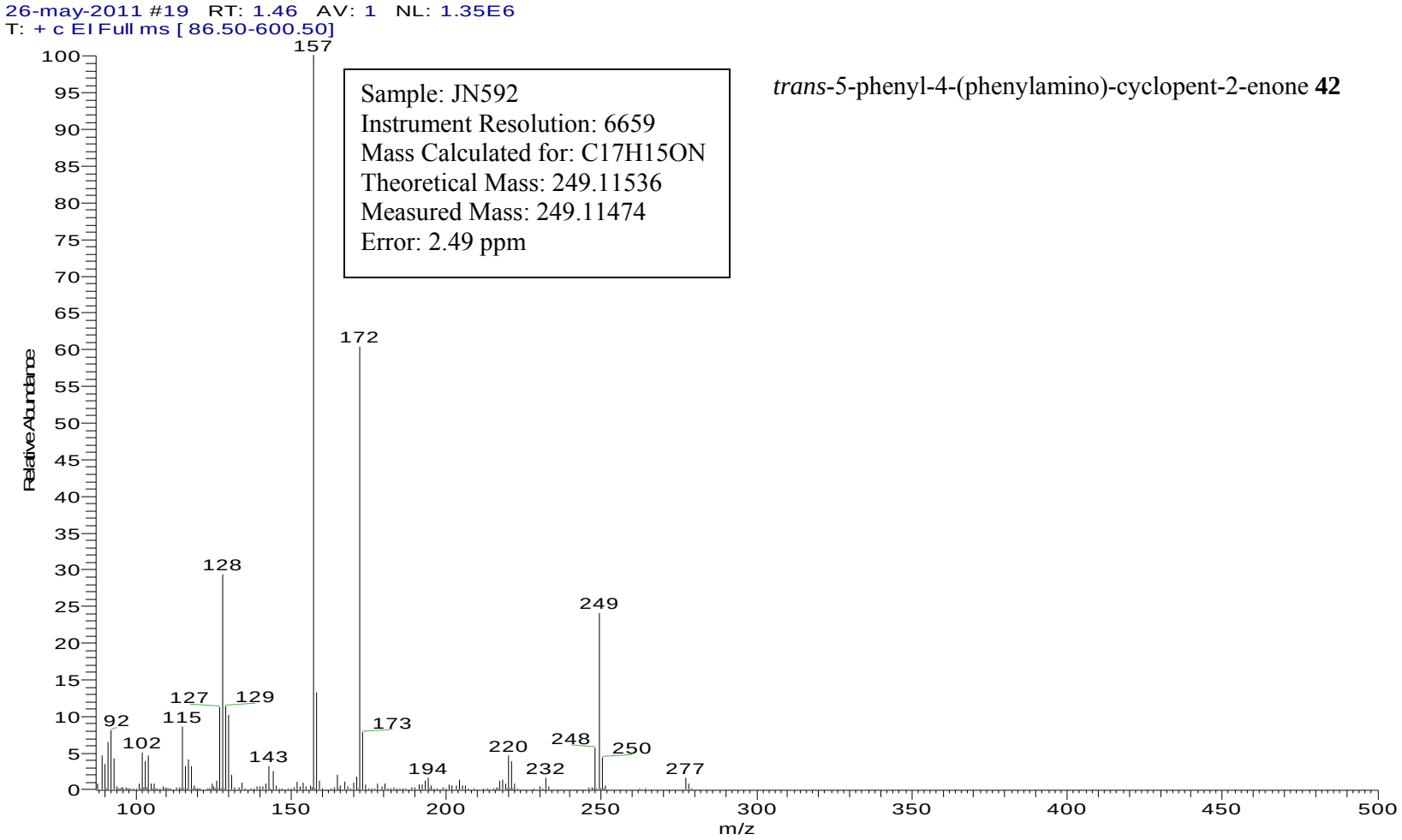
trans-5-phenyl-4-(phenylamino)-cyclopent-2-enone **42**

Figure S129 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated compound **42**.



trans-5-phenyl-4-(phenylamino)-cyclopent-2-enone **42**

Figure S130 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated compound **42**.



trans-5-phenyl-4-(phenylamino)-cyclopent-2-enone **42**

Figure S131 – EI mass spectra for exact mass measurement of isolated compound **42**.

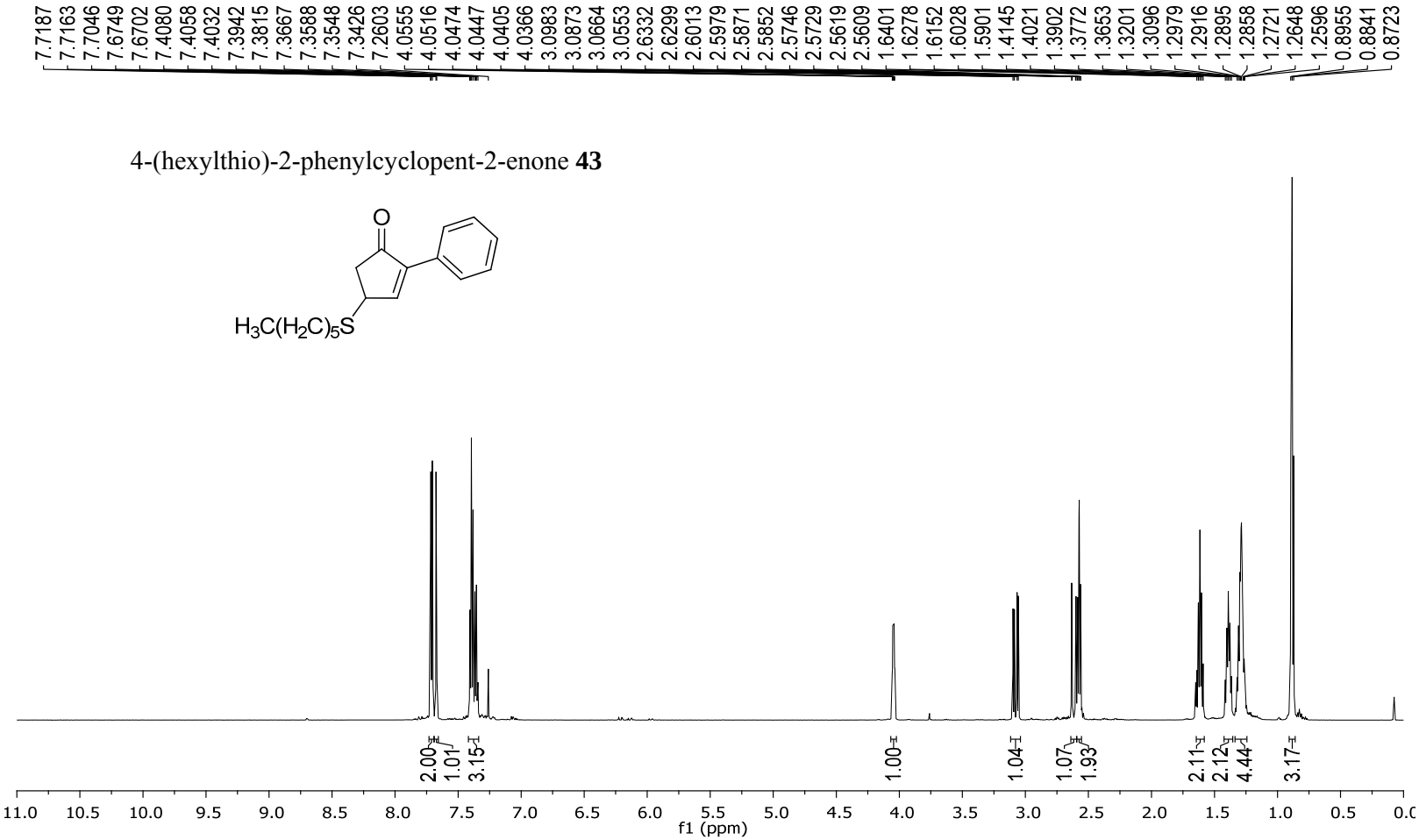


Figure S132 – ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of isolated compound **43**.

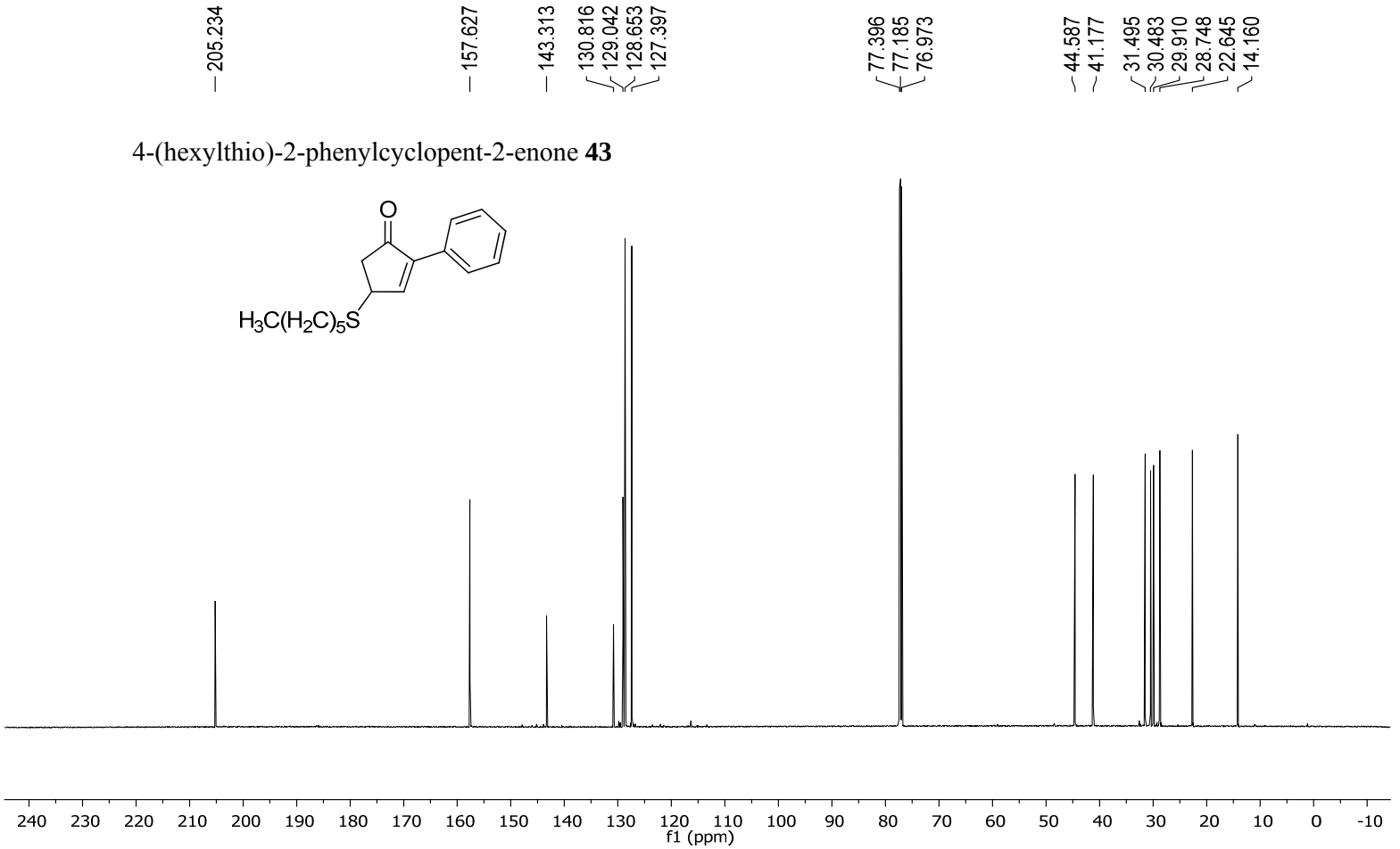


Figure S133 – ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of isolated compound **43**.

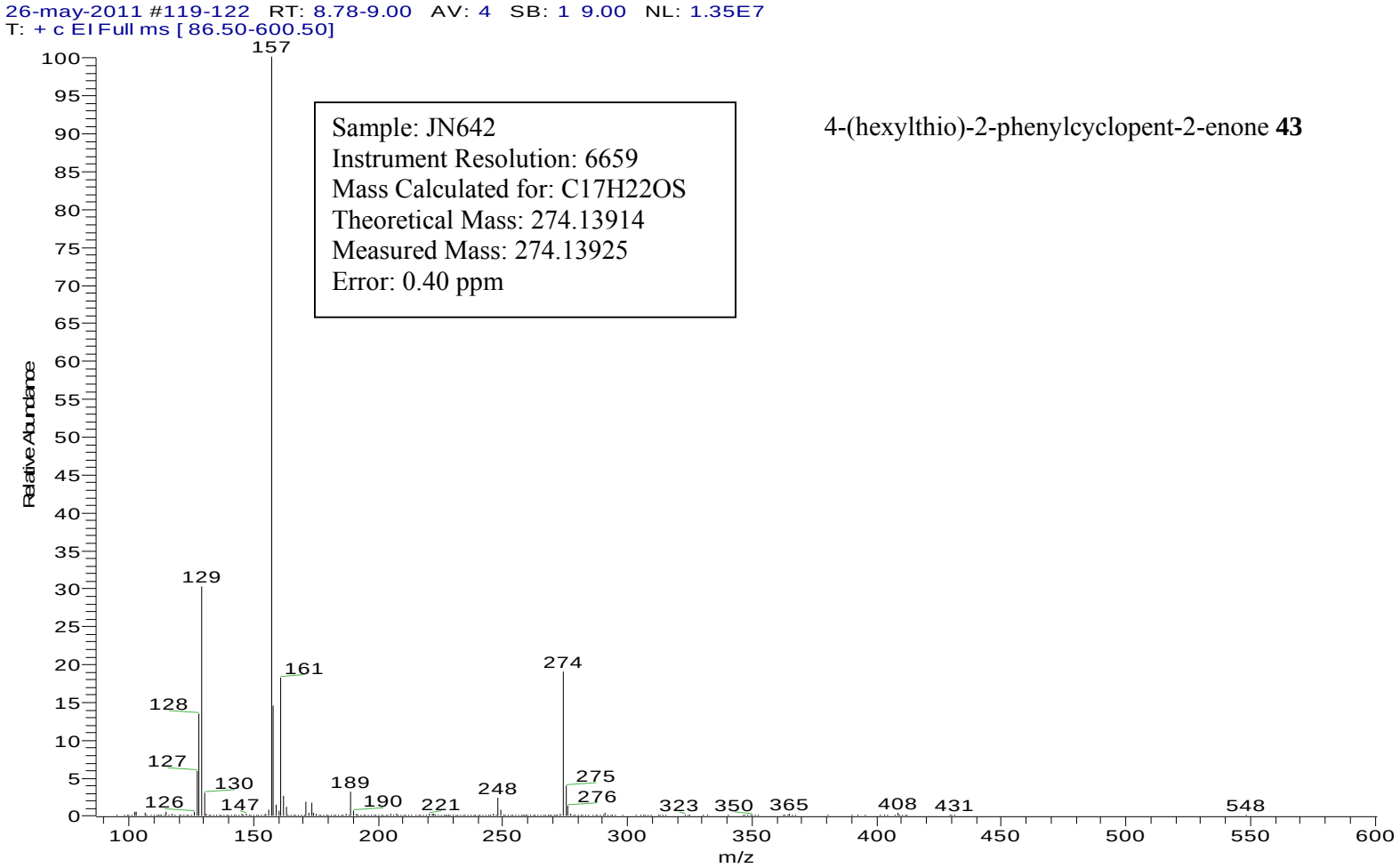


Figure S134 – EI mass spectra for exact mass measurement of isolated compound **43**.

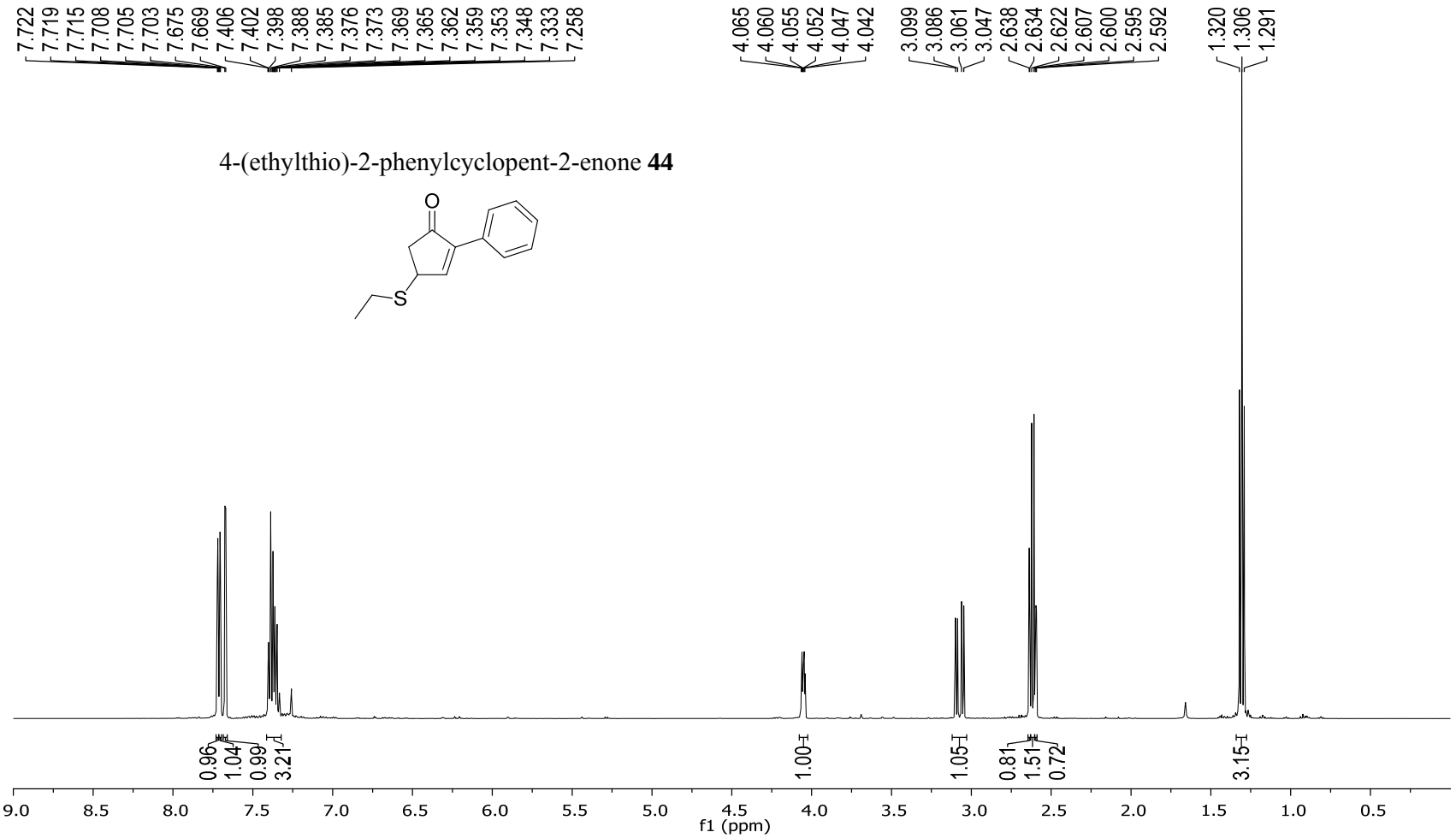


Figure S135 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated compound **44**.

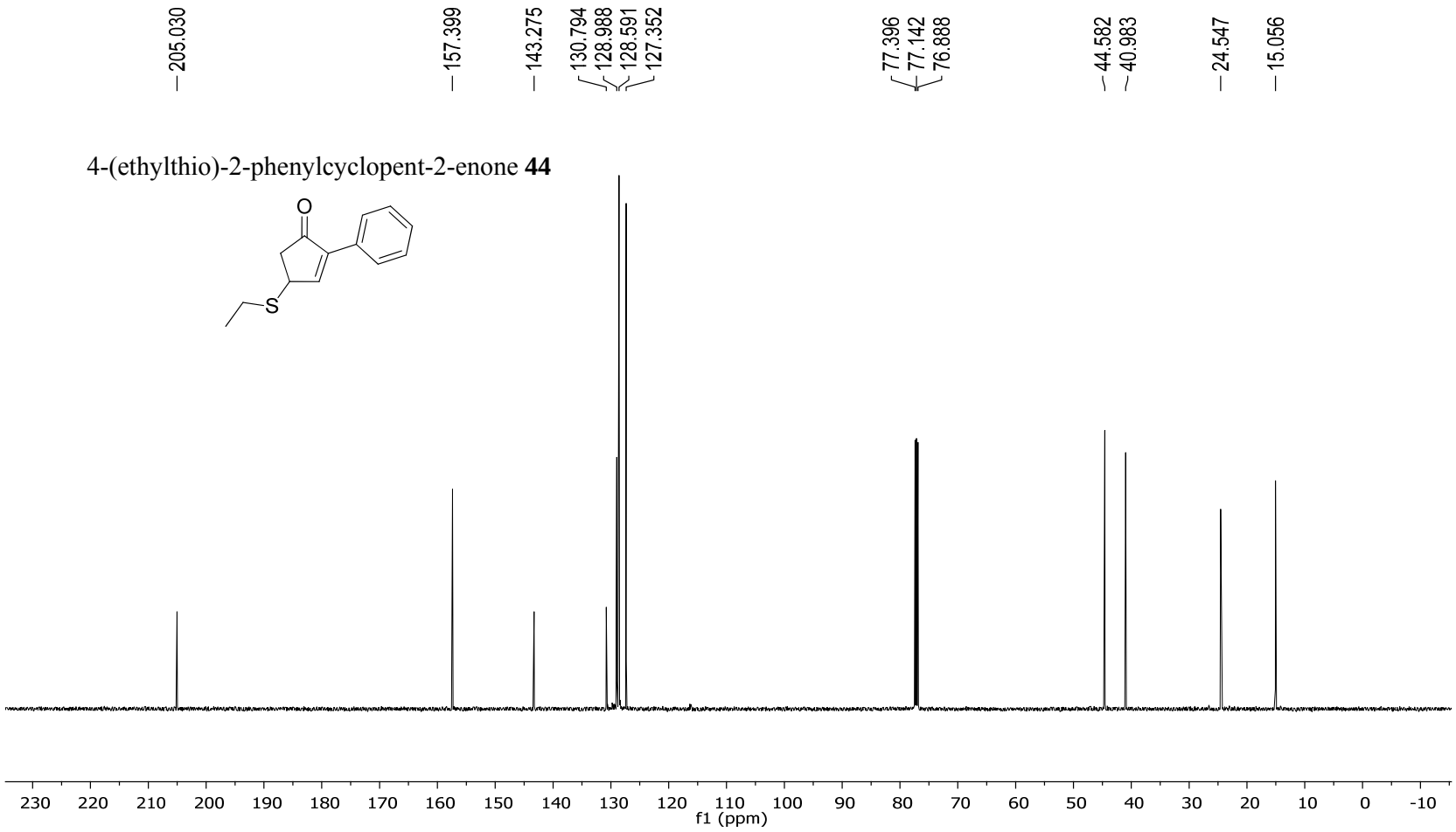


Figure S136 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated compound **44**.

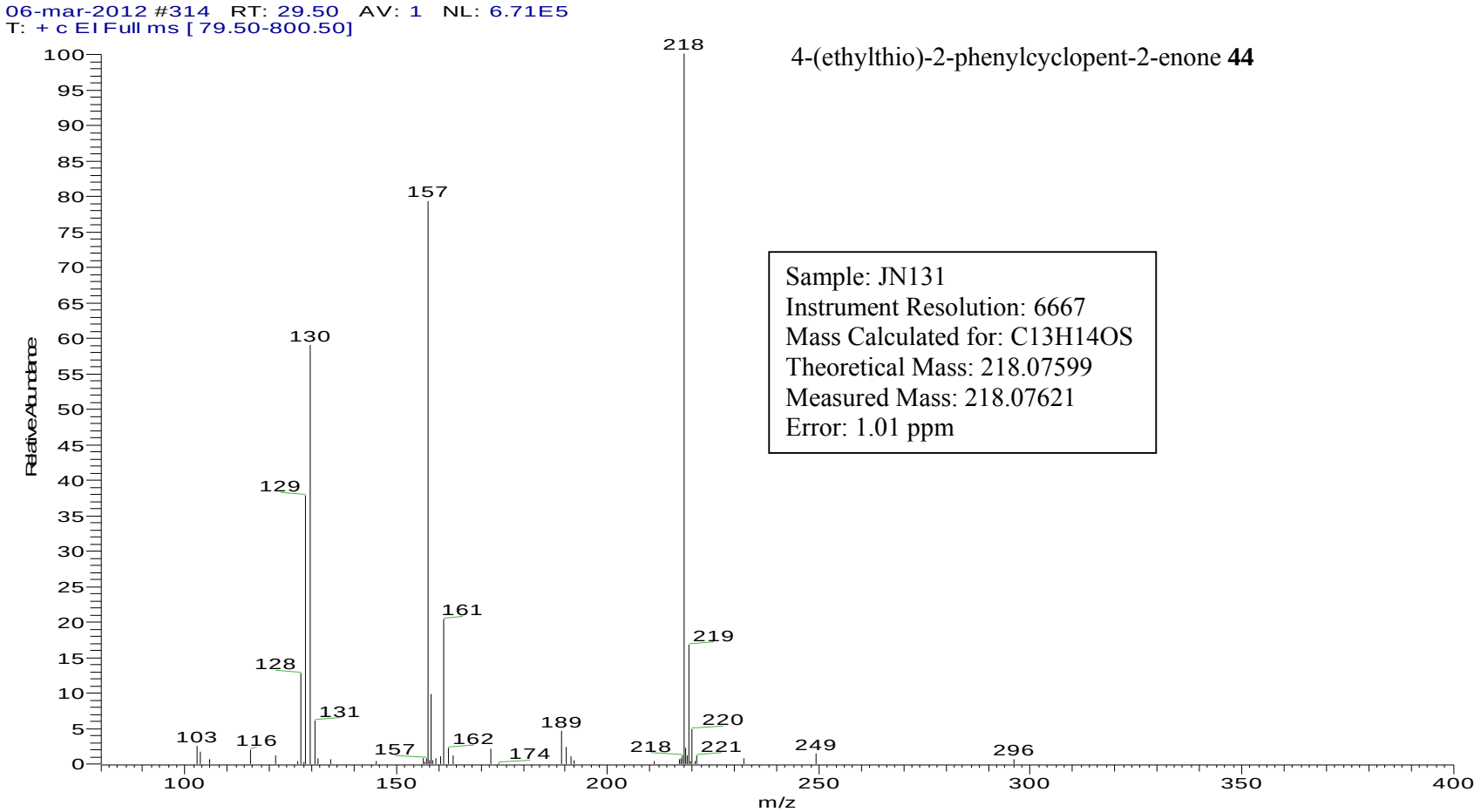


Figure S137 – EI mass spectra for exact mass measurement of isolated compound **44**.

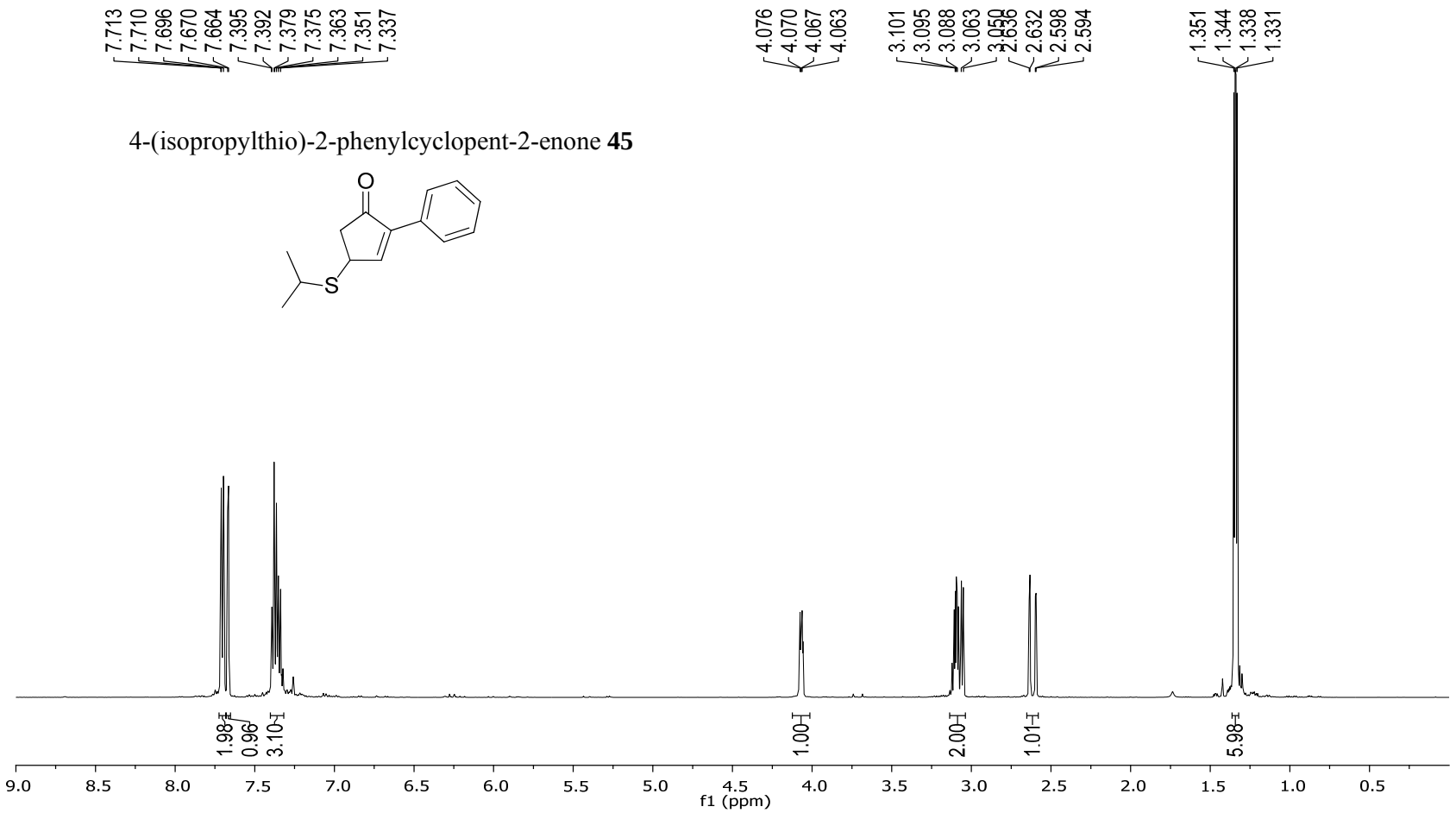


Figure S138 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated compound **45**

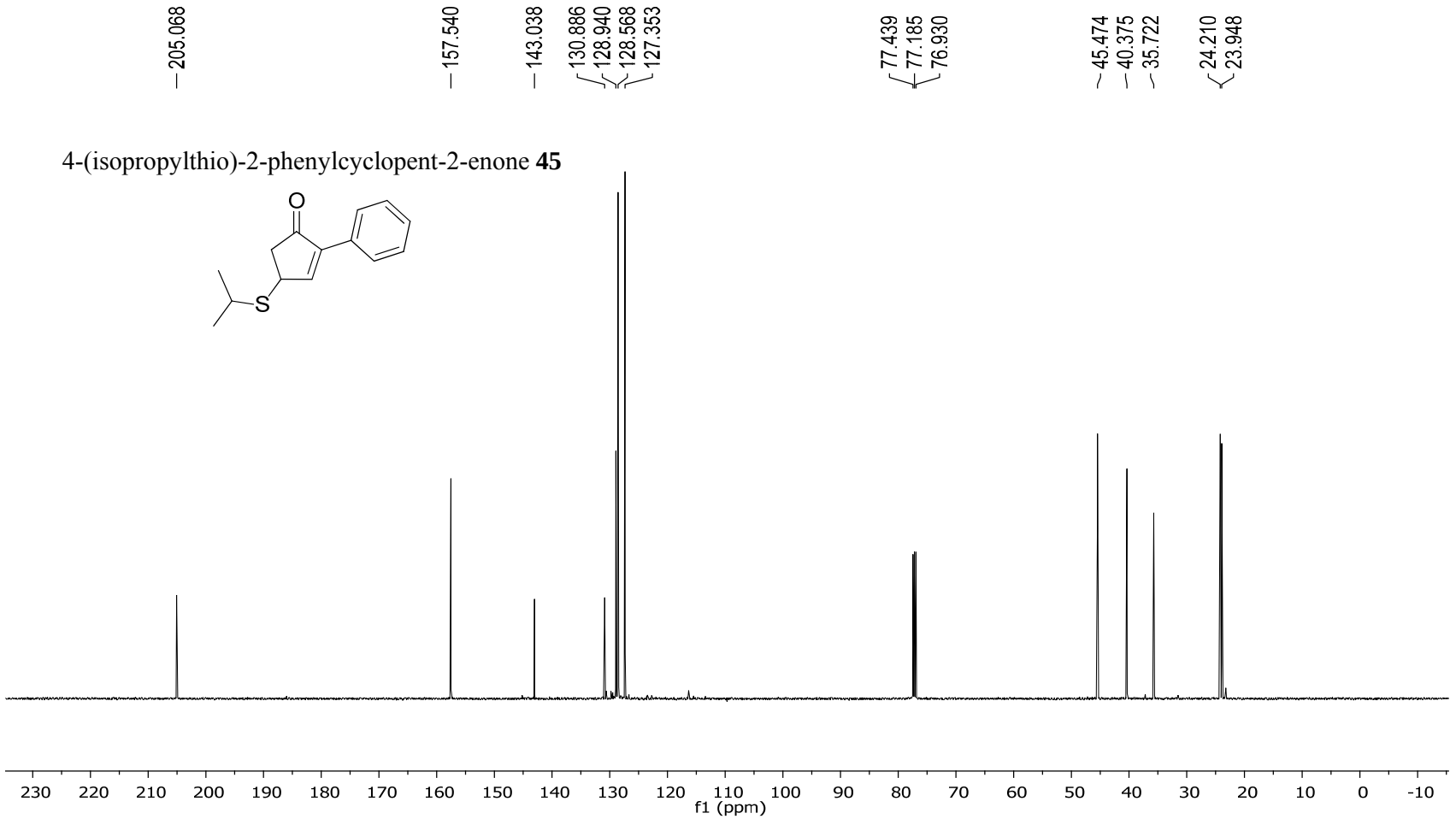


Figure S139 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated compound **45**.

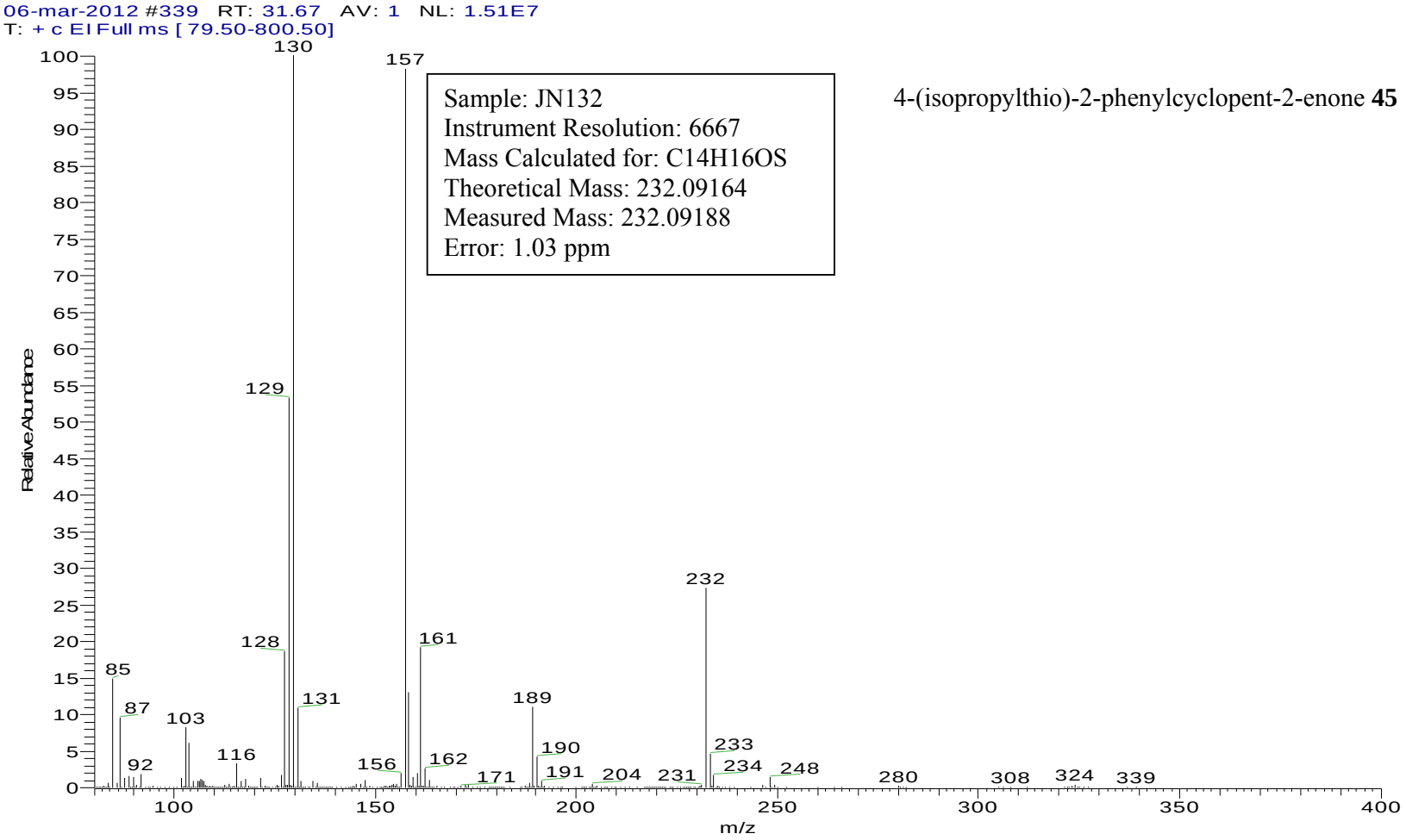


Figure S140 – EI mass spectra for exact mass measurement of isolated compound **45**.

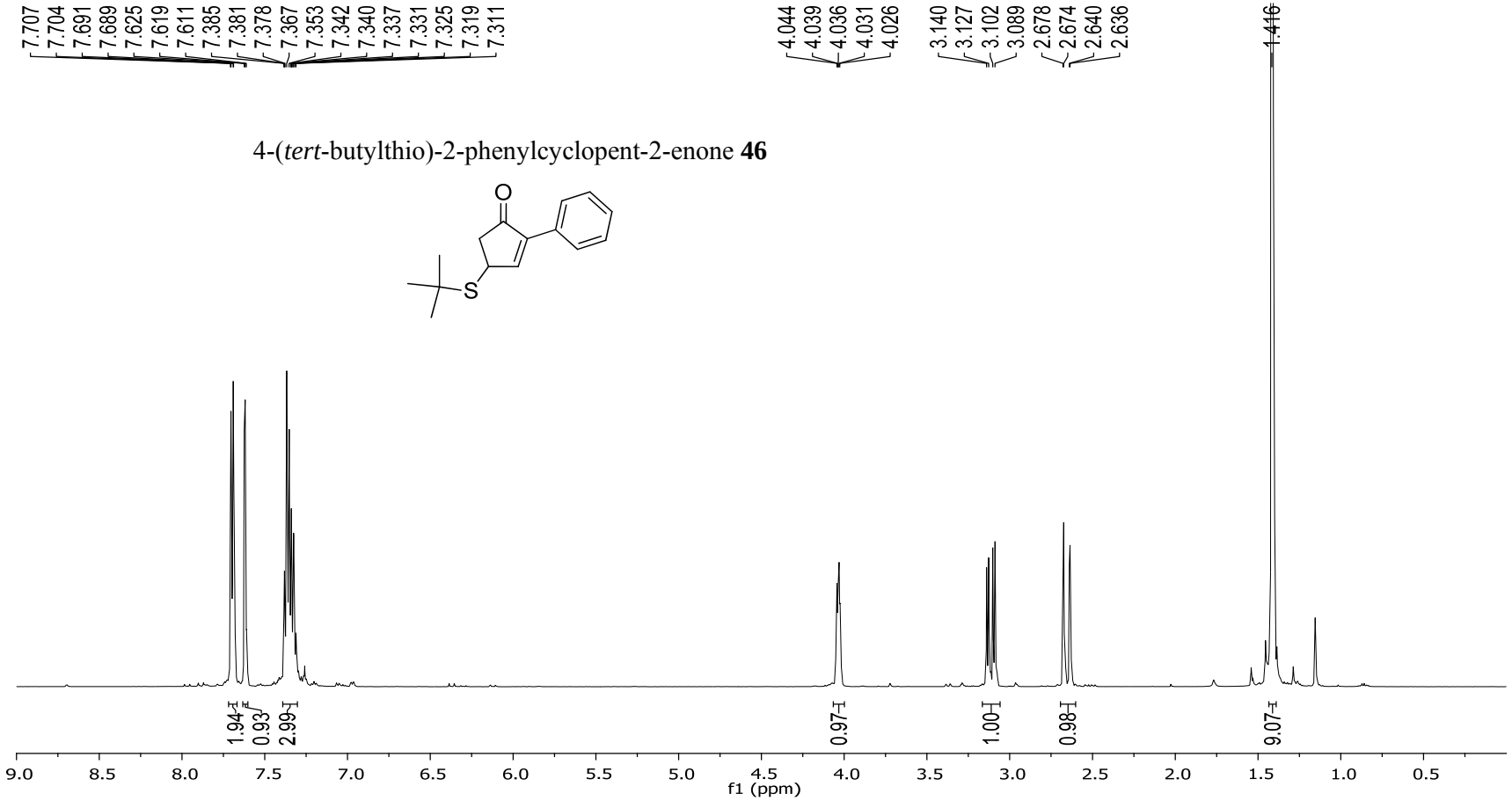


Figure S141 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated compound **46**.

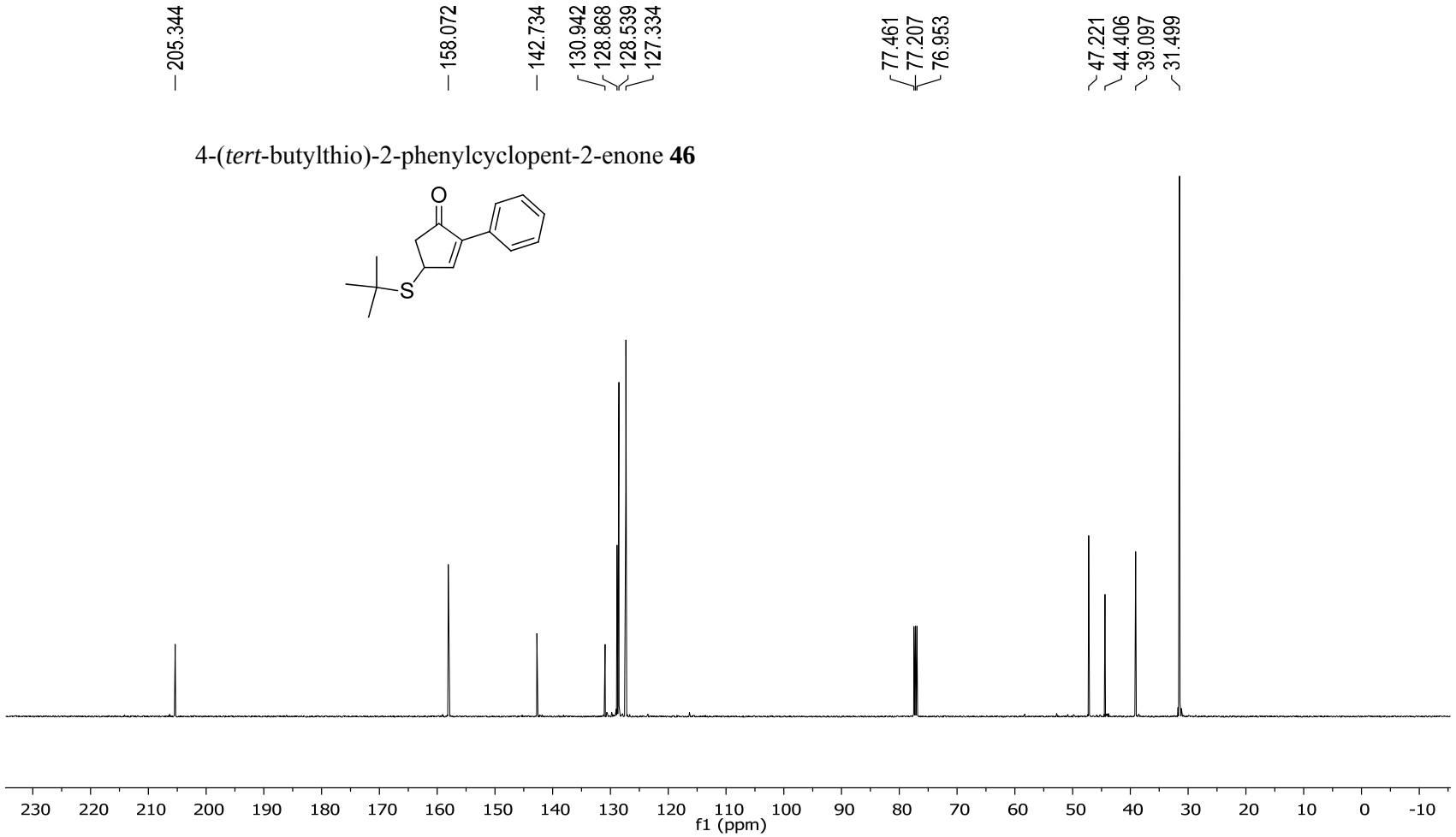
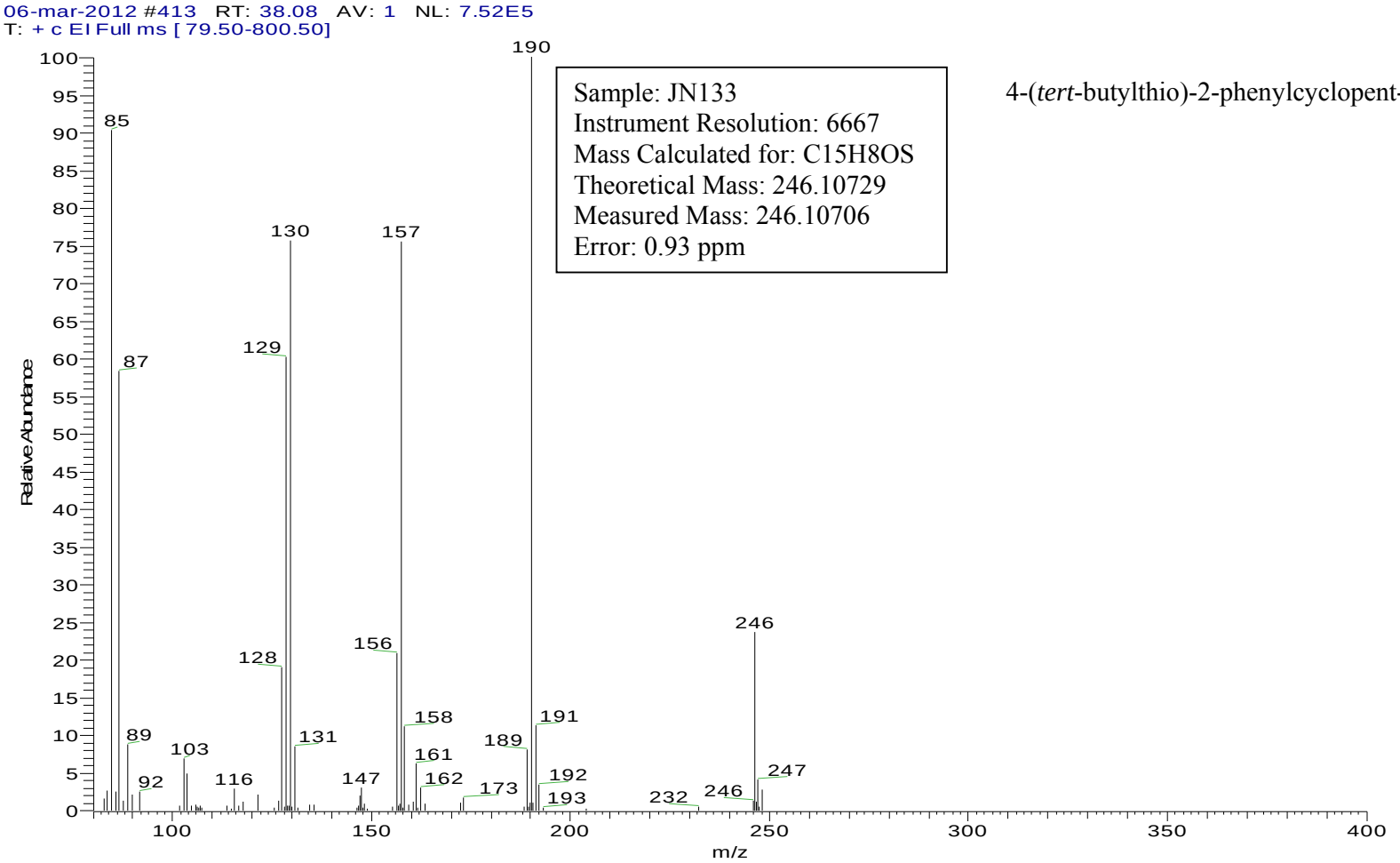


Figure S142 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated compound **46**.



4-(*tert*-butylthio)-2-phenylcyclopent-2-enone **46**

Figure S143 – EI mass spectra for exact mass measurement of isolated compound **46**.

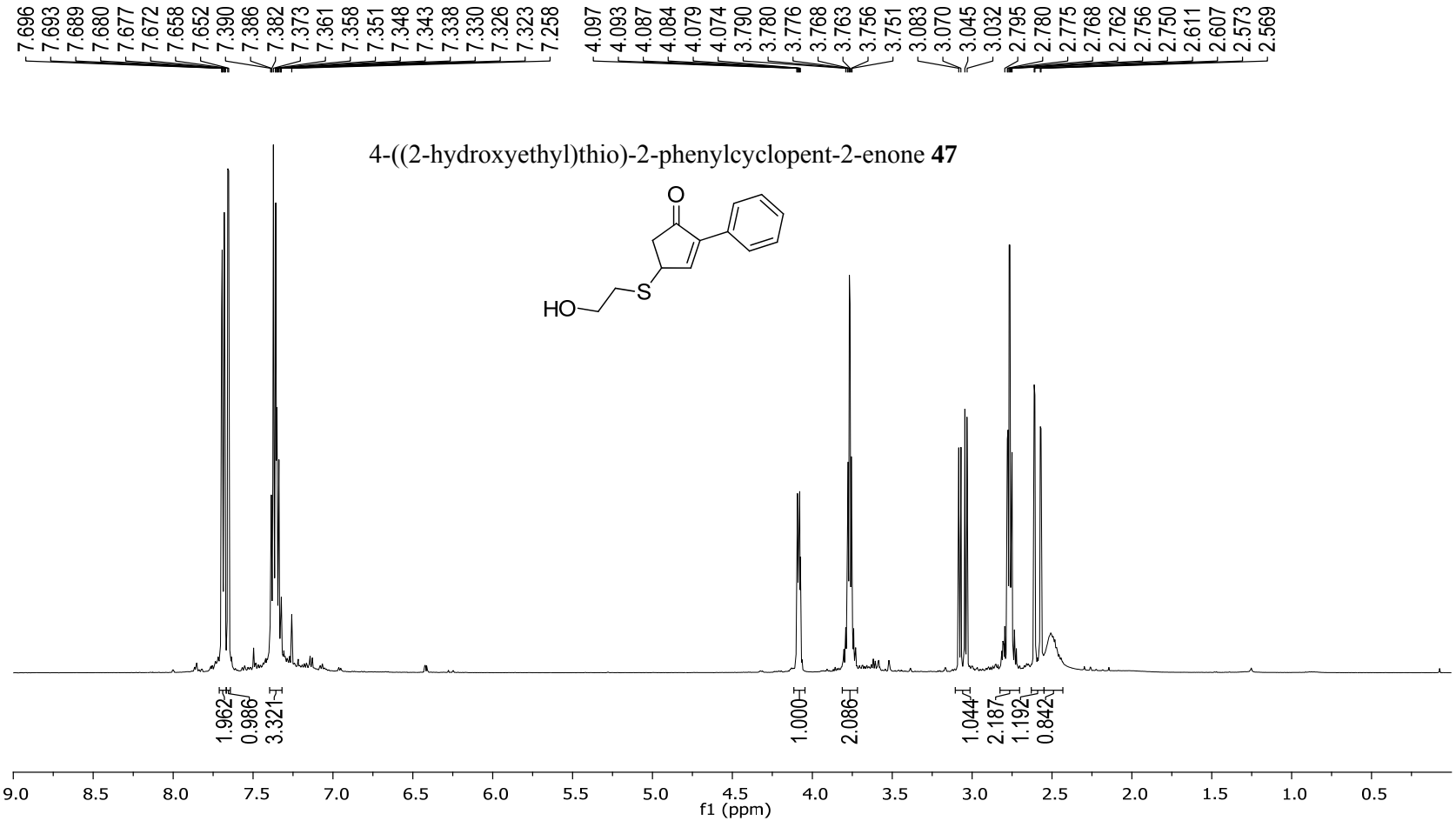


Figure S144 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated compound **47**.

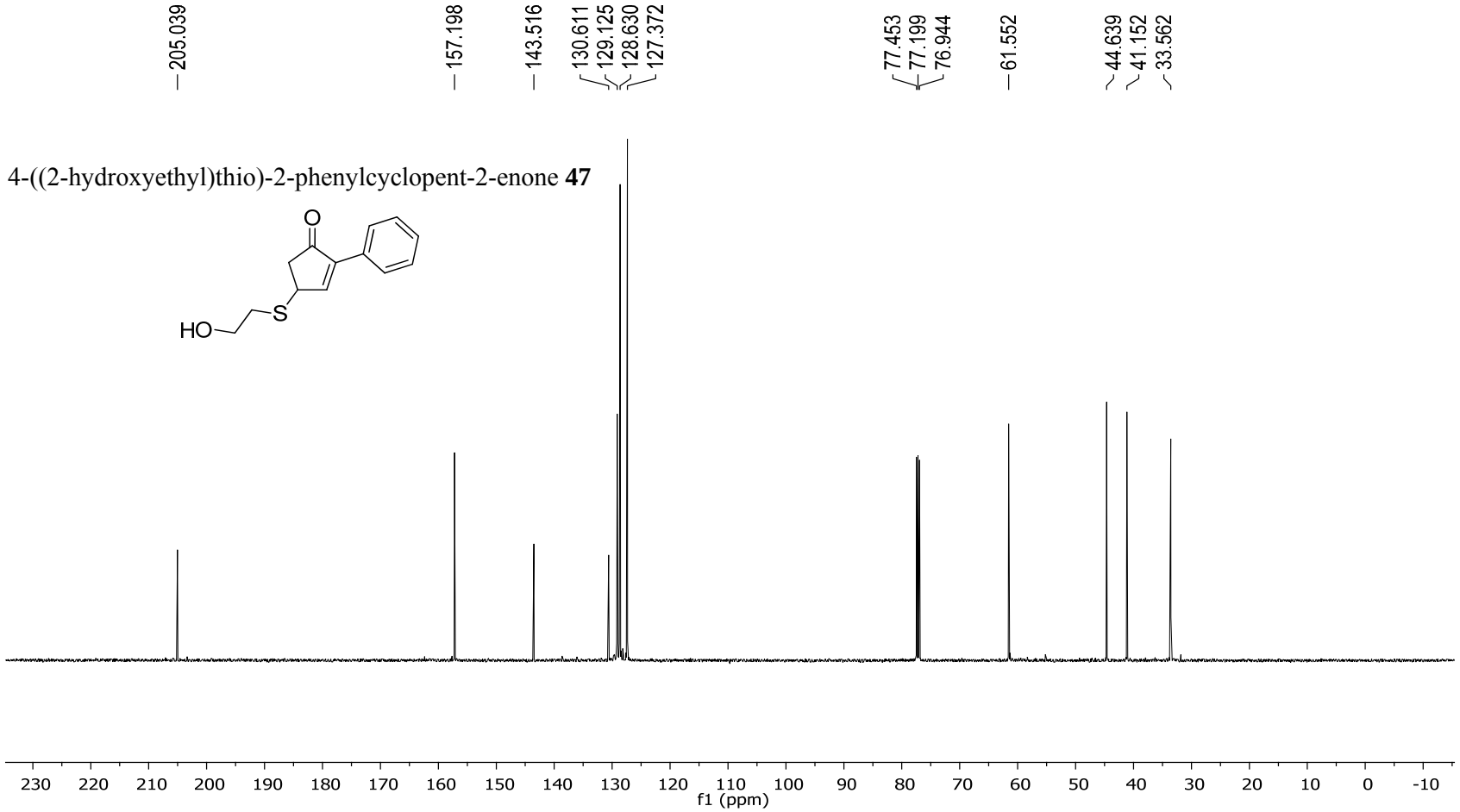
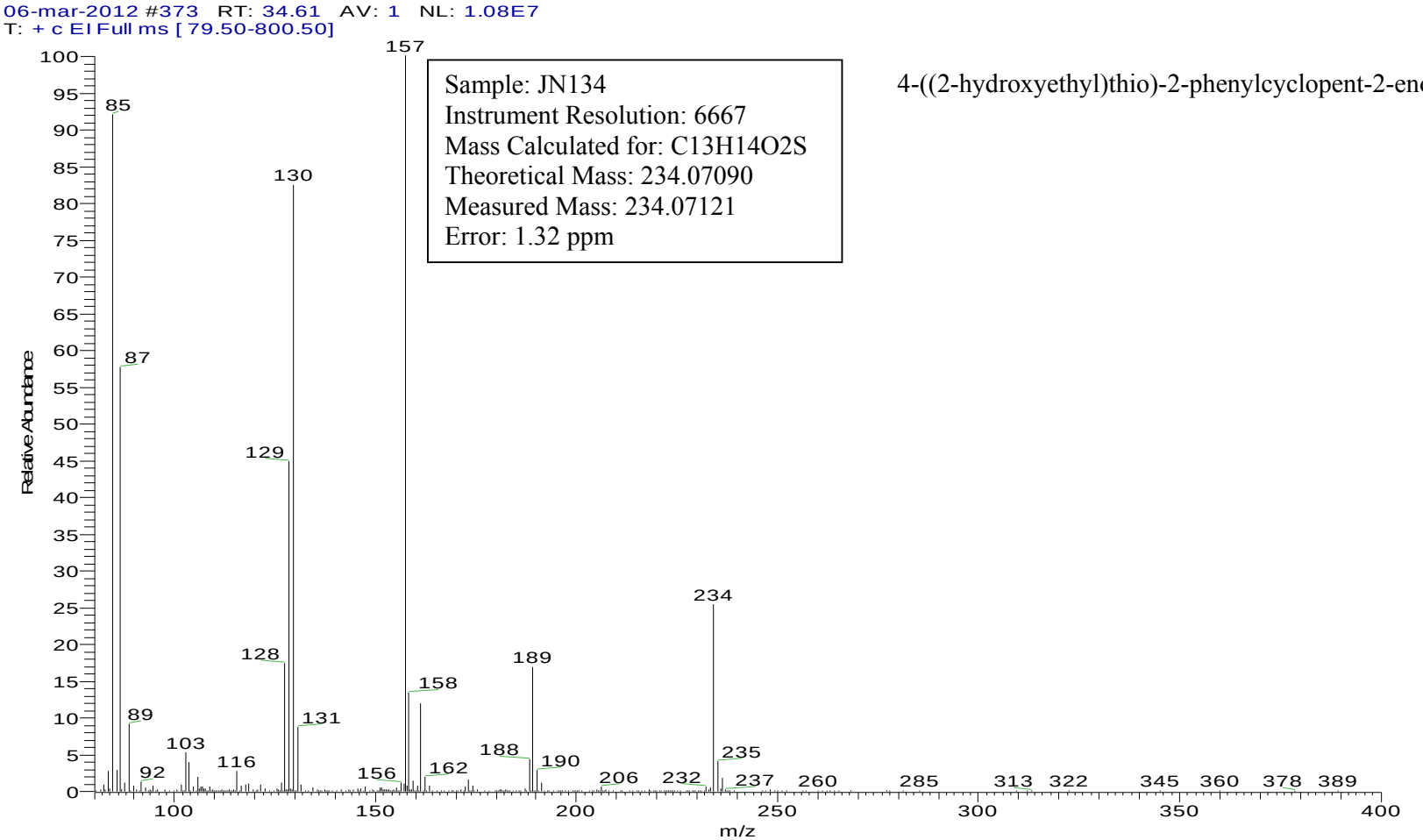


Figure S145 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated compound **47**.



4-((2-hydroxyethyl)thio)-2-phenylcyclopent-2-enone **47**

Figure S146 – EI mass spectra for exact mass measurement of isolated compound **47**.

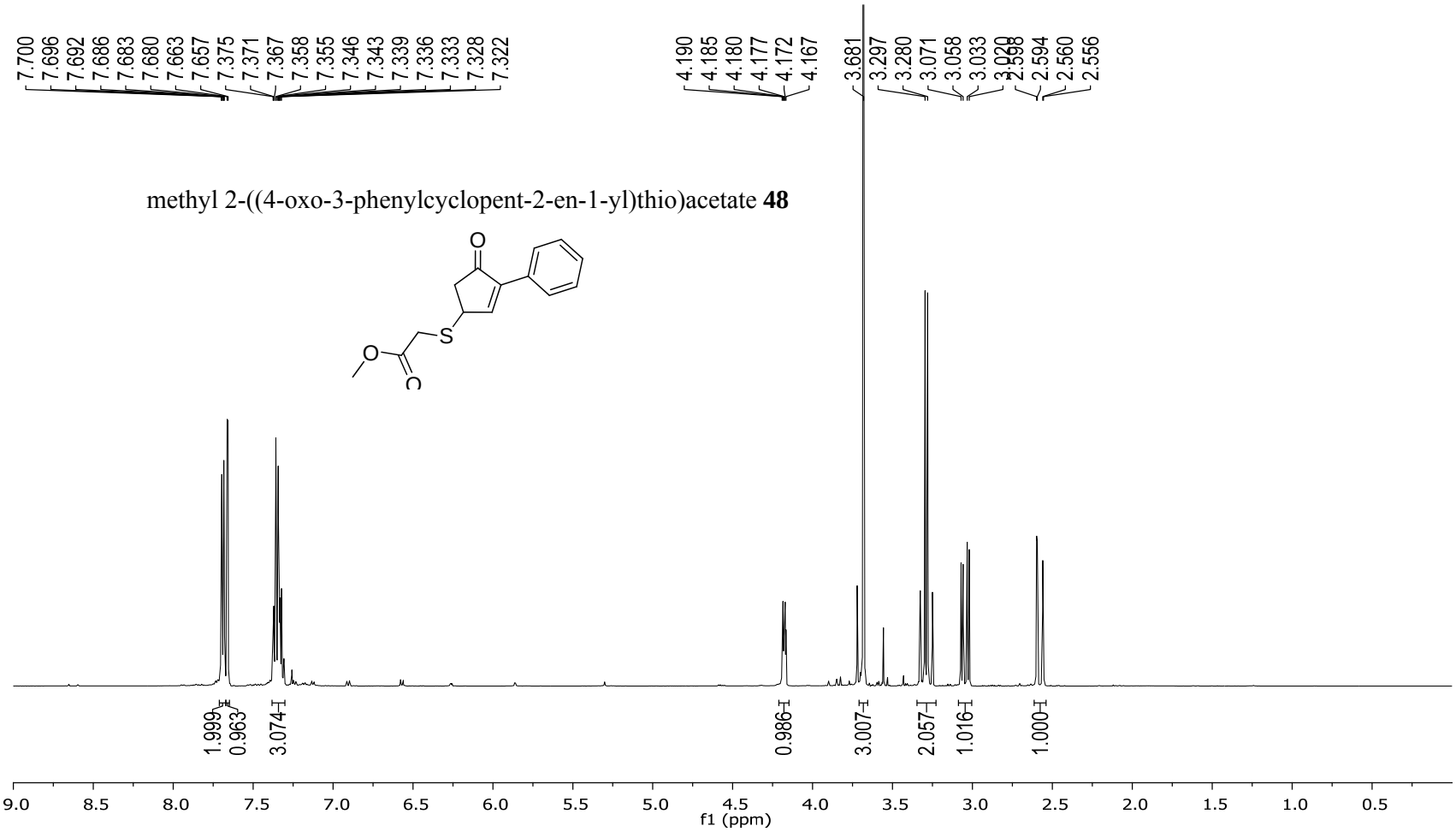


Figure S147 – ^{1}H NMR spectra at 500 MHz in $CDCl_3$ of isolated compound **48**.

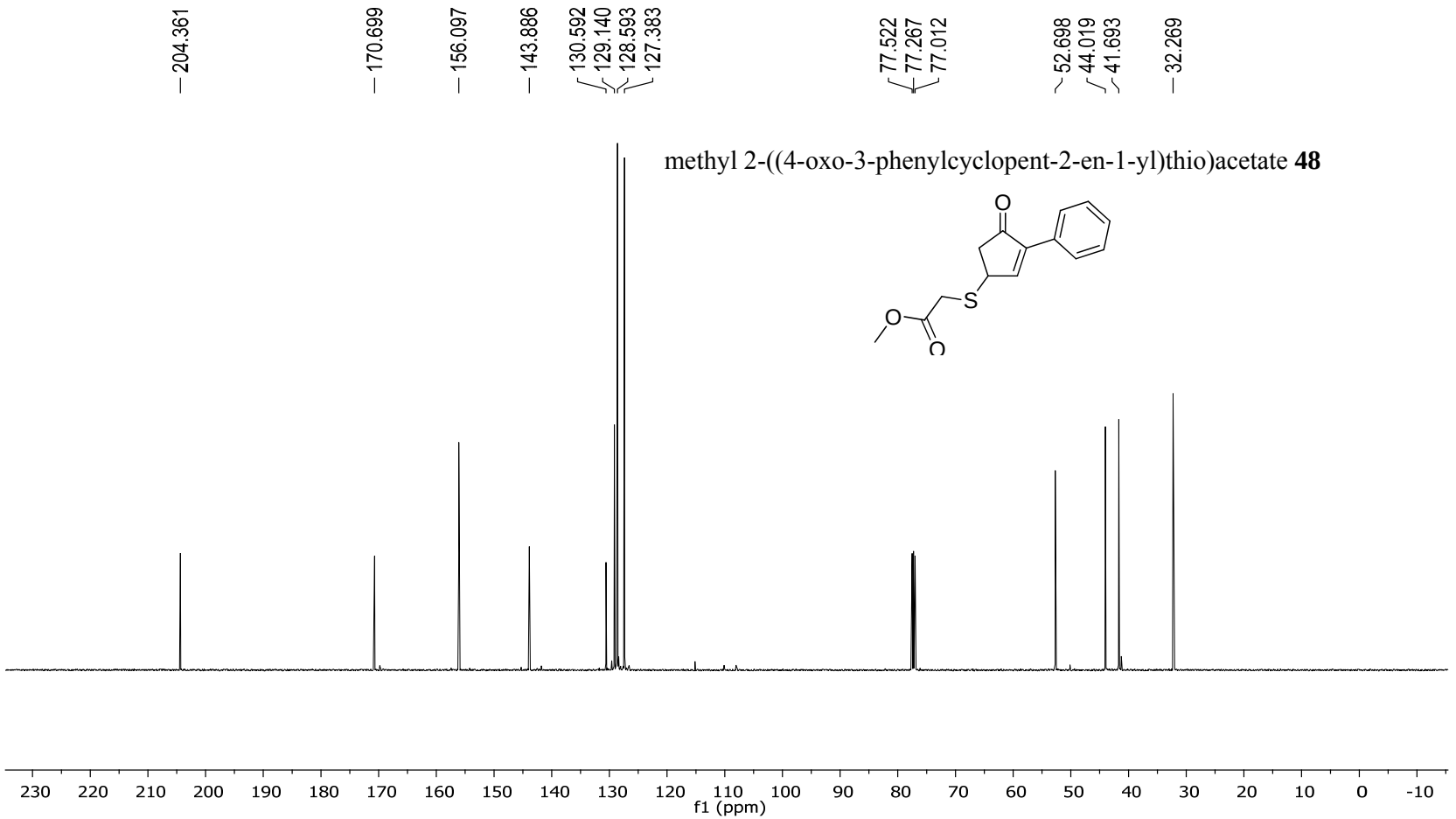
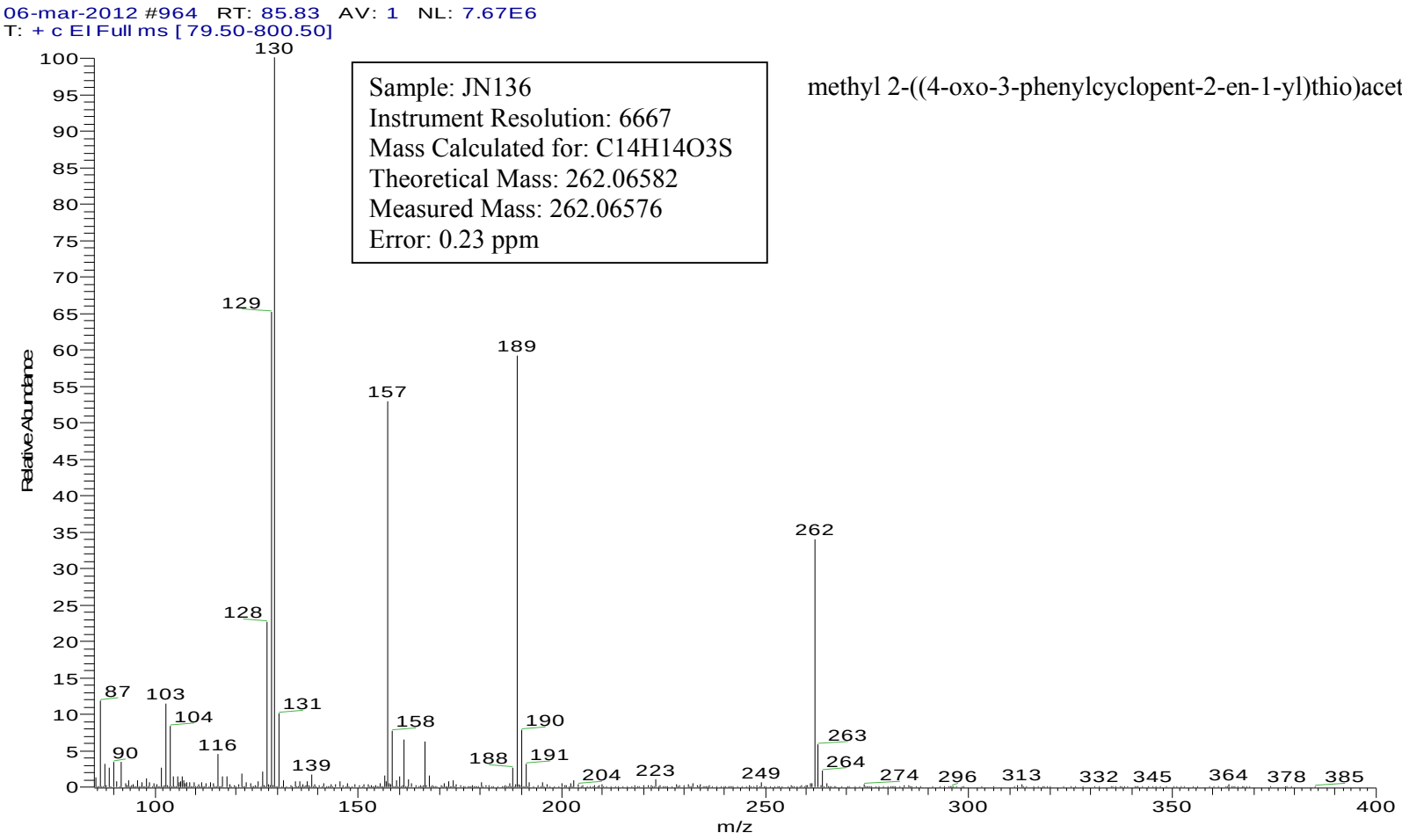


Figure S148 – ^{13}C NMR spectra at 125 MHz in $CDCl_3$ of isolated compound **48**.



methyl 2-((4-oxo-3-phenylcyclopent-2-en-1-yl)thio)acetate **48**

Figure S149 – EI mass spectra for exact mass measurement of isolated compound **48**.

References

1. S. W. Li, R. A. Batey, *Chem. Commun.*, 2007, 3759-3761.
2. A. G. Csaky, M. Mba, J. Plumet, *Synlett*, 2003, 2092-2094.
3. G. K. Veits, D. R. Wenz, J. R. de Alaniz, *Angew. Chem., Int. Ed. Engl.*, 2010, **49**, 9484-9487.