Dual Photoredox/Nickel-Promoted Alkylation of Heteroaryl Halides with Redox-Active Esters

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Supporting Information

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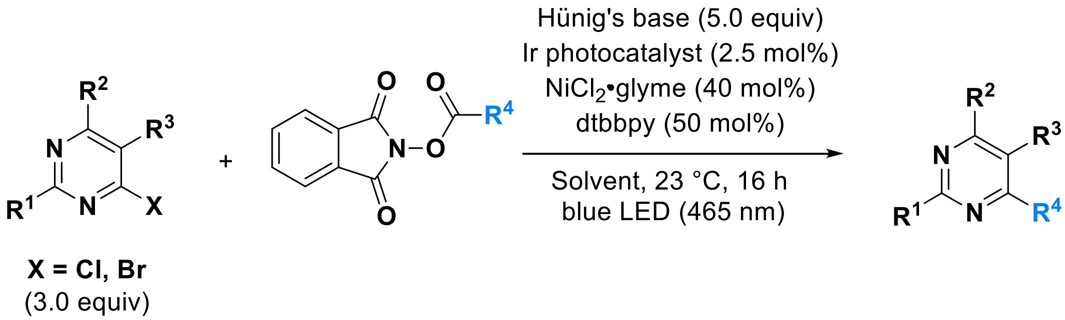
General Procedures

Procedure for Alkylation of Halogenated Pyrimidines with Redox-Active Esters

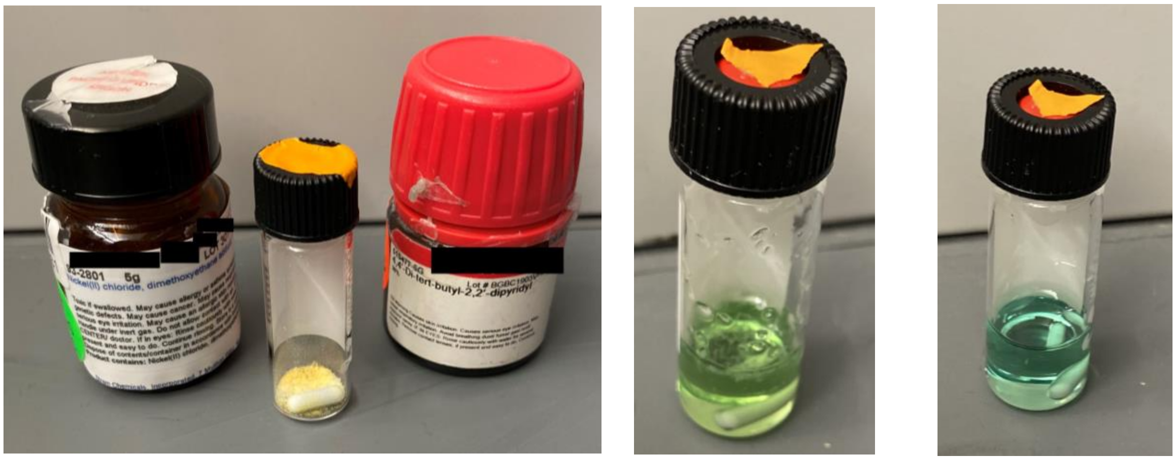
Scheme S1. Photochemical/Ni-Promoted Alkylation of Heteroaryl Pyrimidines with Redox-Active Esters.



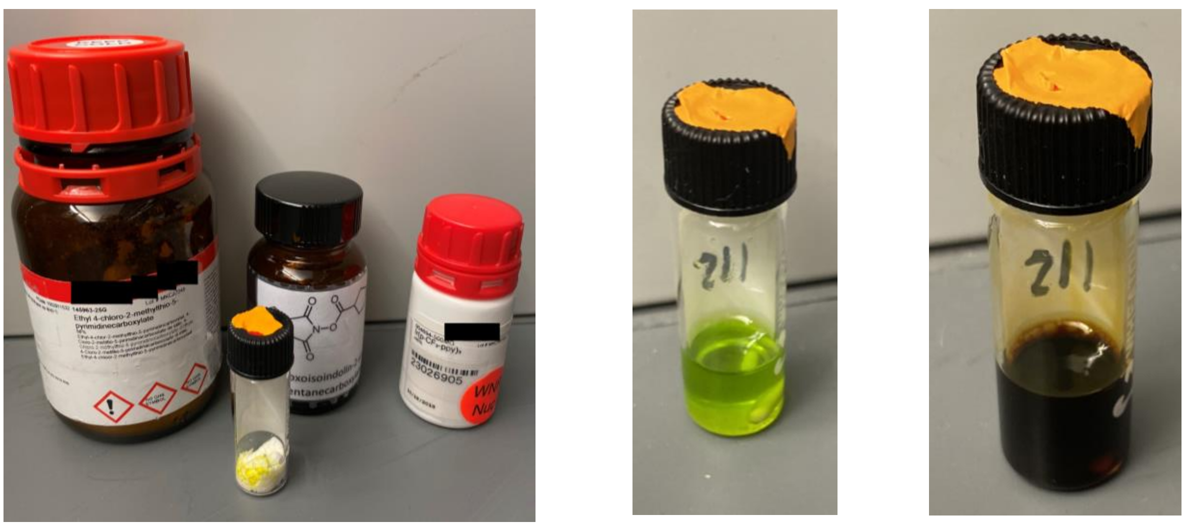
Vial 1[1]: To a 1 dram vial purged and backfilled with N_2 (3X) and equipped with a magnetic stir bar, 4,4'-di-*tert*-butyl-2,2'-bipyridine (0.1 mmol, 50 mol%) and Nickel(II) chloride ethylene glycol dimethyl ether complex (0.08 mmol, 40 mol%) were dissolved in the corresponding solvent (1.33 mL, 0.15 M). The vial was sealed and heated to 30 ˚C with vigorous stirring for 15 minutes. The solution was removed from heat and stirred for an additional 15 minutes at 23 °C.

Vial 2: To a 1 dram vial equipped with a magnetic stir bar was added pyrimidine (0.6 mmol, 3.0 equiv), redox-active ester (0.2 mmol, 1.0 equiv), and the corresponding Ir photocatalyst (0.005 mmol, 2.5 mol%). The vial was evacuated and backfilled with N_2 (3X). The solution from Vial 1 was added to Vial 2. Hünig's base (1.0 mmol, 5.0 equiv) was added and the reaction was exposed to blue LED (465 nm) while stirring with overhead fan for 16 hours. After the reaction time, the solution was poured into H_2O (15 mL) and extracted with EtOAc (3 X 15 mL). The combined organic layers were washed with one portion of brine (25 mL) and dried over anhydrous Na_2SO_4. The crude material was concentrated *in vacuo* and purified by column chromatography to provide the desired product.

Figure S1. Guide for Ir/Ni-Promoted Cross-Coupling of Pyrimidine 1 with Redox-Active Ester 2



Left: Reagents in Vial 1. Center: Vial 1 dissolved in DMSO. Right: Vial 1 after 30 minute stirring.



Left: Reagents in Vial 2. Center: After Vial 1 is combined with Vial 2. Right: After overnight exposure to blue LED.

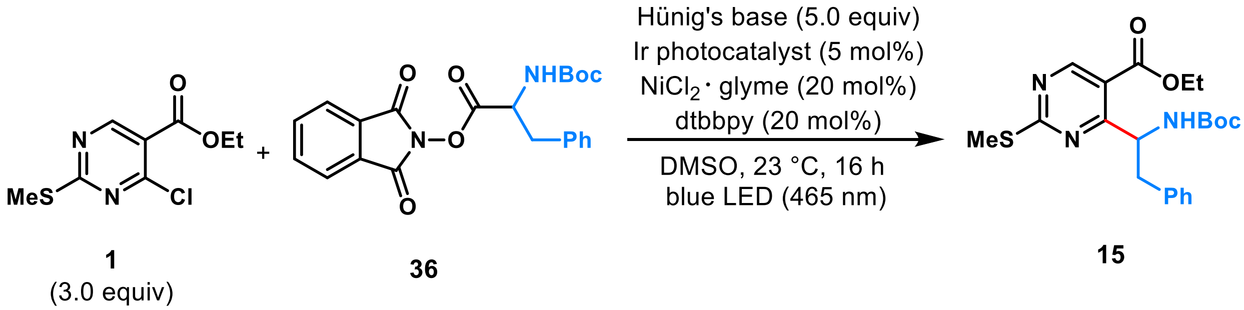
Reaction Optimization and Scope Evaluation using High Throughput Experimentation Conducted at the Discovery Process Research HTE Lab

General Information. High-throughput Experimentation Screening was accomplished in a Vacuum Atmospheres glovebox with oxygen typically <5 ppm. The experimental design was accomplished using Library Studio (Unchained Labs). Screening reactions were carried out in 1 mL vials (30 mm height × 8 mm diameter) in “Para-dox” standard 96-position photoredox aluminum reaction blocks (Analytical-sales). Liquid chemicals were dosed using multi-channel or single-channel pipettors. Solid chemicals were dosed manually as solutions or slurries in appropriate solvents. Undesired additional solvent was removed using a Speedvac system located inside the glovebox. The reactions were stirred at 23 °C over Lumidox 96-well Blue LED array (analytical-sales) on an aluminum block with a tumble-stirrer (V&P Scientific) using 1.98 mm diameter × 4.80 mm length parylene stir bars. The tumble stirring mechanism helped to insure uniform stirring throughout the 96-well plate. Results of the screening were analyzed by Waters UPLC with addition of an internal standard. The UPLC areas of product over internal standard are shown in the tables below. Note that area ratios are pertinent only to the corresponding specific screening and are not quantitatively compared with different screening.

Screening of Ir Photocatalyst.

Procedure of High-Throughput Experimentation: In the glovebox, to a “Para-dox” standard 96-position photoredox aluminum reaction block containing 1 mL reaction vials pre-plated with photocatalysts (0.05 equiv) and equipped with Teflon-coated magnetic stir bar was added sequentially: solution of pre-mixed $NiCl_2$·glyme (0.2 equiv) and dtbbpy (0.2 equiv) dissolved in DMSO and solution of pyrimidine (3.0 equiv), redox-active ester (1.0 equiv), Hünig’s base(5.0 equiv). The plate was sealed, moved out of glovebox, and was stirred over blue LED lights at 23 °C. After 16 hours, the reactions were opened to air and diluted with 500 μL of a MeCN solution of 4,4’-Di-tert-butylbiphenyl. After stirring for 15 min, the vials were centrifuged with Genevac and 50 μL aliquots were taken from the reaction vials and dosed into a 96 well UPLC collection plate. These aliquots were further diluted by addition of 600 μL of MeCN. The reactions were analyzed by UPLC. Area ratio of product over internal standard was further converted to assay yield using calibration curve generated from product standard.

Table S1. High-Throughput Experimentation Results for Photochemical/Ni-Promoted Cross-Coupling of Pyrimidine 1 and Redox-Active Ester 36.

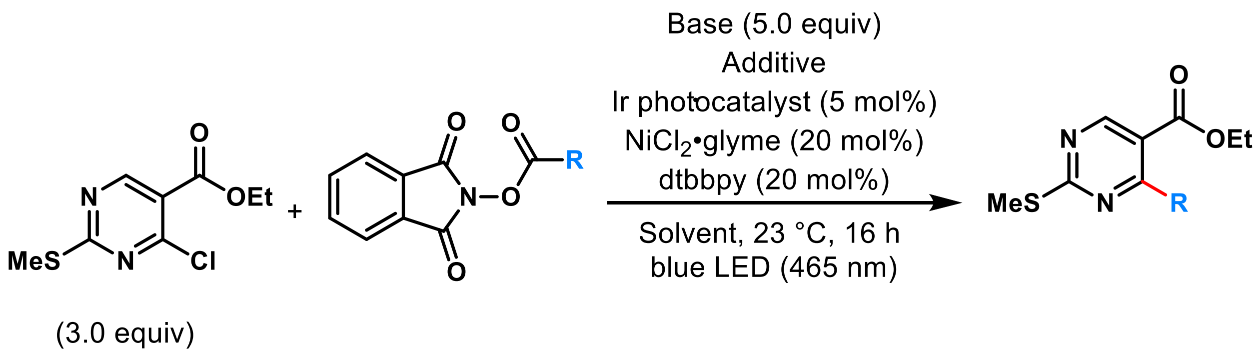


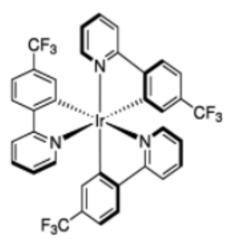
Photocatalyst	Pdt/IS Area Ratio	Assay Yield
[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine]bis[3,5-difluoro-2-(5-methyl-2-pyridinyl)phenyl] iridium	0.39	39.44
[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine]bis[3,5-difluoro-2-(2-pyridinyl-κN)phenyl-κC]iridium	0.33	32.74
[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine]bis[3,5-difluoro-2-(5-fluoro-2-pyridinyl)phenyl]iridium	0.33	32.78
Tris[(2-(2-pyridinyl-kN)-5-(trifluoromethyl)phenyl-kC]iridium(III)	0.48	47.83
[4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine]bis[5-fluoro-2-(5-methyl-2-pyridinyl)phenyl-]iridium	0.41	40.99
(2,2'-Bipyridine)bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl][phenyl-kC]iridium(III)	0.44	43.97
10-Phenylphenothiazine	0.18	17.62
4,4'-Bis(t-butyl-2,2'-bipyridine]bis[5-methyl-2-(4-methyl-2-pyridinyl-kN)phenyl-kC]iridium	0.44	44.48
[Ir(dtbbpy)(ppy)2]PF6	0.40	40.05
(4,4'-Di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III)	0.38	38.06
9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium	0.00	0.00
Eosin Y	0.27	27.21
[Ru(phen)3]Cl2	0.00	0.00
[Ru(dmbpy)3](PF6)2	0.26	25.55
Ru(p-CF3-bpy)3 (BF4)2	0.36	36.22
Tris[4,4'-bis(t-butyl)-2,2'-bipyridine]ruthenium(II) hexafluorophosphate	0.30	30.24
[Ru(bpz)3][PF6]2	0.00	0.00
[Ru(bpm)3][Cl]2	0.02	1.84
Ru(BPY)3	0.31	31.26
Ru(bpy)3(PF6)2	0.38	38.04
Tris(1,10-phenanthroline)ruthenium(II) chloride hydrate	0.21	20.46
9-Mesityl-2,7-dimethyl-10-phenylacridinium tetrafluoroborate	0.00	0.00
10-Methyl-9-(2,4,6-trimethylphenyl)acridinium perchlorate	0.00	0.00
4,4’-Bis(N-carbazolyl)-1,1’-biphenyl	0.26	25.57

Substrate Evaluation.

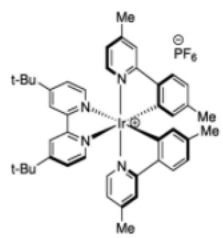
Procedure of High-Throughput Experimentation: To a "Para-dox" standard 96-position photoredox aluminum reaction block containing 1 mL reaction vials equipped with Teflon-coated magnetic stir bar was added solution of photocatalyst (0.05 equiv) in THF or MeOH, the solvents were then removed via Genevac. To certain vials (shown in Tables below), Tetrabutylammonium iodide (1 equiv) was added as a slurry in THF, which were then removed via Genevac. In the glovebox, to the 96 well plate was added sequentially, (1) solution of pre-mixed $NiCl_2 \cdot$glyme (0.2 equiv) and dtbbpy (0.2 equiv) dissolved in DMSO or Dioxane, (2) solution of pyrimidine (3.0 equiv) dissolved in DMSO or Dioxane, (3) solution of redox-active ester (1.0 equiv), Hünig's base (5.0 equiv) dissolved in DMSO or Dioxane. The plate was sealed, moved out of glovebox, and was stirred over blue LED lights at 23 °C. After 16 hours, the reactions were opened to air and diluted with 500 μL of a MeCN solution of 4,4'-Di-tert-butylbiphenyl. After stirring for 15 min, the vials were centrifuged with Genevac and 50 μL aliquots were taken from the reaction vials and dosed into a 96 well UPLC collection plate. These aliquots were further diluted by addition of 600 μL of MeCN. The reactions were analyzed by UPLC. Area ratio of product over internal standard were used to evaluate the reaction conditions for each substrate.

Scheme S2. High-Throughput Experimentation for Photochemical/Ni-Promoted Cross-Coupling of Heteroaryl Halides and Redox-Active Esters.

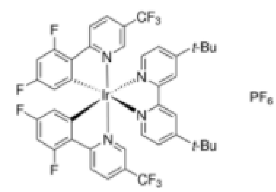




PC1

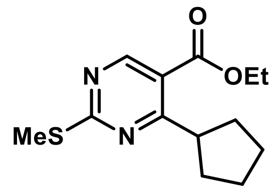


PC2



PC3

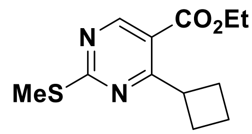
Table S2. Results of High-Throughput Experimentation for Product 3.



3

Solvent	Photocatalyst CAS#	Base	Ratio
DMSO	PC1 500295-52-3	DIPEA	0.60
DMSO	PC2 1607469-49-7	DIPEA	0.52
DMSO	PC3 870987-63-6	DIPEA	0.34
DMSO	PC1 500295-52-3	DIPEA+TBAI	0.41
DMSO	PC2 1607469-49-7	DIPEA+TBAI	0.42
DMSO	PC3 870987-63-6	DIPEA+TBAI	0.27
Dioxane	PC1 500295-52-3	DIPEA	0.25
Dioxane	PC2 1607469-49-7	DIPEA	0.45
Dioxane	PC3 870987-63-6	DIPEA	0.05
Dioxane	PC1 500295-52-3	DIPEA+TBAI	0.18
Dioxane	PC2 1607469-49-7	DIPEA+TBAI	0.14
Dioxane	PC3 870987-63-6	DIPEA+TBAI	0.00

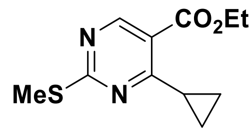
Table S3. Results of High-Throughput Experimentation for Product 6.



6

Solvent	Photocatalyst CAS#	Ratio
DMSO	PC1 500295-52-3	0.29
DMSO	PC2 1607469-49-7	0.24
DMSO	PC3 870987-63-6	0.17
DMSO	PC4 676525-77-2	0.27
DMSO	PC5 60804-74-2	0.00
DMSO	PC 6 808142-88-3	0.21
Dioxane	PC1 500295-52-3	0.35
Dioxane	PC2 1607469-49-7	0.40
Dioxane	PC3 870987-63-6	0.64
Dioxane	PC4 676525-77-2	0.78
Dioxane	PC5 60804-74-2	0.00
Dioxane	PC 6 808142-88-3	0.53

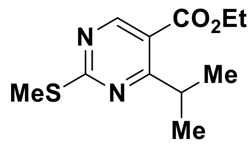
Table S4. Results of High-Throughput Experimentation for Product 7.



7

Solvent	Photocatalyst CAS#	Ratio
DMSO	PC1 500295-52-3	0.59
DMSO	PC2 1607469-49-7	0.61
DMSO	PC3 870987-63-6	0.56
DMSO	PC4 676525-77-2	0.64
DMSO	PC5 60804-74-2	0.40
DMSO	PC 6 808142-88-3	0.58
Dioxane	PC1 500295-52-3	0.07
Dioxane	PC2 1607469-49-7	0.05
Dioxane	PC3 870987-63-6	0.05
Dioxane	PC4 676525-77-2	0.05
Dioxane	PC5 60804-74-2	0.17
Dioxane	PC 6 808142-88-3	0.06

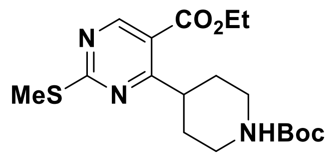
Table S5. Results of High-Throughput Experimentation for Product 8.



8

Solvent	Photocatalyst CAS#	Base	Ratio
DMSO	PC1 500295-52-3	DIPEA	0.43
DMSO	PC2 1607469-49-7	DIPEA	0.30
DMSO	PC3 870987-63-6	DIPEA	0.22
DMSO	PC1 500295-52-3	DIPEA+TBAI	0.37
DMSO	PC2 1607469-49-7	DIPEA+TBAI	0.25
DMSO	PC3 870987-63-6	DIPEA+TBAI	0.18
Dioxane	PC1 500295-52-3	DIPEA	0.33
Dioxane	PC2 1607469-49-7	DIPEA	0.74
Dioxane	PC3 870987-63-6	DIPEA	0.07
Dioxane	PC1 500295-52-3	DIPEA+TBAI	0.29
Dioxane	PC2 1607469-49-7	DIPEA+TBAI	0.31
Dioxane	PC3 870987-63-6	DIPEA+TBAI	0.02

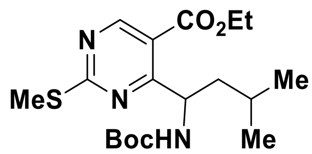
Table S6. Results of High-Throughput Experimentation for Product 12.



12

Solvent	Photocatalyst CAS#	Ratio
DMSO	PC1 500295-52-3	0.33
DMSO	PC2 1607469-49-7	0.26
DMSO	PC3 870987-63-6	0.24
DMSO	PC4 676525-77-2	0.25
DMSO	PC5 60804-74-2	0.00
DMSO	PC 6 808142-88-3	0.25
Dioxane	PC1 500295-52-3	0.39
Dioxane	PC2 1607469-49-7	0.70
Dioxane	PC3 870987-63-6	0.87
Dioxane	PC4 676525-77-2	0.61
Dioxane	PC5 60804-74-2	0.00
Dioxane	PC 6 808142-88-3	0.67

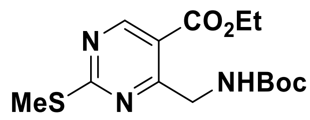
Table S7. Results of High-Throughput Experimentation for Product 14.



14

Solvent	Photocatalyst CAS#	Ratio
DMSO	PC1 500295-52-3	0.29
DMSO	PC2 1607469-49-7	0.34
DMSO	PC3 870987-63-6	0.32
DMSO	PC4 676525-77-2	0.37
DMSO	PC5 60804-74-2	0.05
DMSO	PC 6 808142-88-3	0.35
Dioxane	PC1 500295-52-3	0.06
Dioxane	PC2 1607469-49-7	0.47
Dioxane	PC3 870987-63-6	0.67
Dioxane	PC4 676525-77-2	0.20
Dioxane	PC5 60804-74-2	0.00
Dioxane	PC 6 808142-88-3	0.47

Table S8. Results of High-Throughput Experimentation for Product 16.

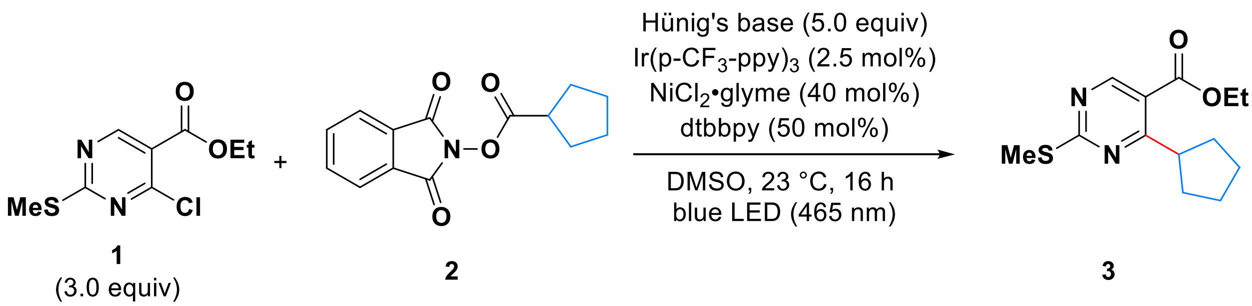


16

Solvent	Photocatalyst CAS#	Ratio
DMSO	PC1 500295-52-3	0.46
DMSO	PC2 1607469-49-7	0.41
DMSO	PC3 870987-63-6	0.40
DMSO	PC4 676525-77-2	0.44
DMSO	PC5 60804-74-2	0.19
DMSO	PC 6 808142-88-3	0.43
Dioxane	PC1 500295-52-3	0.42
Dioxane	PC2 1607469-49-7	0.40
Dioxane	PC3 870987-63-6	0.75
Dioxane	PC4 676525-77-2	0.54
Dioxane	PC5 60804-74-2	0.07
Dioxane	PC 6 808142-88-3	0.51

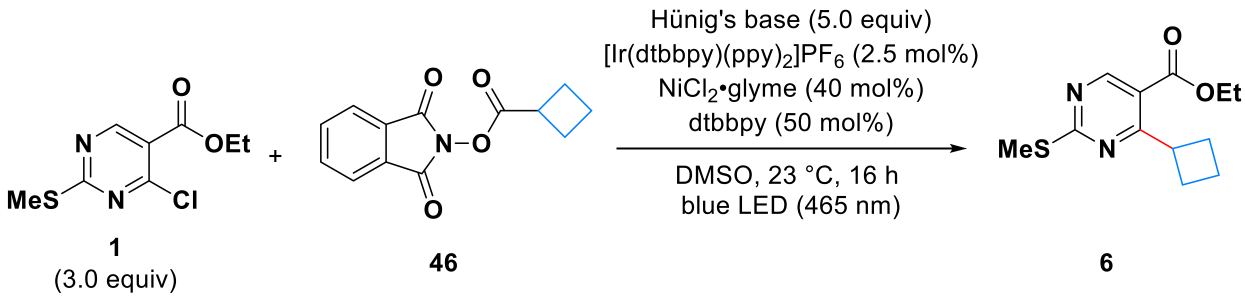
Optimization of Reaction Conditions for Alkylation of Halogenated Pyrimidines with Redox-Active Esters

Table S9: Optimization of Reaction Conditions for Alkylation of Pyrimidine 1 with Cyclopentane Redox-Active Ester 2



entry	deviation from above	yield
1	1.0 equiv **1**, 1.5 equiv **2**, 20 mol% Ni, 25 mol% Ligand, $(Ir[df(CF_3)ppy]_2(dtbpy))PF_6$ photocatalyst	20%
2	1.0 equiv **1**, 1.5 equiv **2**, 2 mol% Ir, 20 mol% Ni, 25 mol% Ligand	27%
3	1.0 equiv **1**, 1.5 equiv **2**, 1 mol% Ir, 20 mol% Ni, 25 mol% Ligand	22%
4	1.0 equiv **1**,1.5 equiv **2**, 5 mol% Ir, 20 mol% Ni, 25 mol% Ligand	40%
5	1.0 equiv **1**, 3.0 equiv **2**, 20 mol% Ni, 25 mol% Ligand	11%
6	20 mol% Ni, 25 mol% Ligand	58%
7	5 mol% Ir, 20 mol% Ni, 25 mol% Ligand	53%
8	1 mol% Ir, 20 mol% Ni, 25 mol% Ligand	44%
9	20 mol% Ni, 25 mol% Ligand, 1,4-Cyclohexadiene instead of Hünig's base	7%
10	20 mol% Ni, 25 mol% Ligand, NEt_3 instead of Hünig's base	48%
11	20 mol% Ni, 25 mol% Ligand, Hantzsch ester instead of Hünig's base	11%
12	20 mol% Ni, 25 mol% Ligand, 1,4-Cyclohexadiene (1.25 equiv)	60%
13	20 mol% Ni, 25 mol% Ligand, NEt_3 (1.25 equiv)	45%
14	20 mol% Ni, 25 mol% Ligand, Hantzsch ester (1.25 equiv)	48%
15	20 mol% Ni, 25 mol% Ligand, 8.0 equivalents Hünig's base	15%
16	8.0 equivalents Hünig's base	28%
17	Zn (3.0 equiv) instead of Hünig's Base	22%
18	Zn (3.0 equiv) and LiCl (3.0 equiv) instead of Hünig's Base	17%
19	No Ni, Ligand	6%
20	No Ir, 20 mol% Ni, 25 mol% Ligand	<5%
21	No Hünig's base, 20 mol% Ni, 25 mol% Ligand	15%
22	5 mol% Ir	64%
23	1 hour reaction time	16%
24	5 hour reaction time	45%
25	1,4-dioxane instead of DMSO	40%
26	No blue LED	0%
27	None	70%

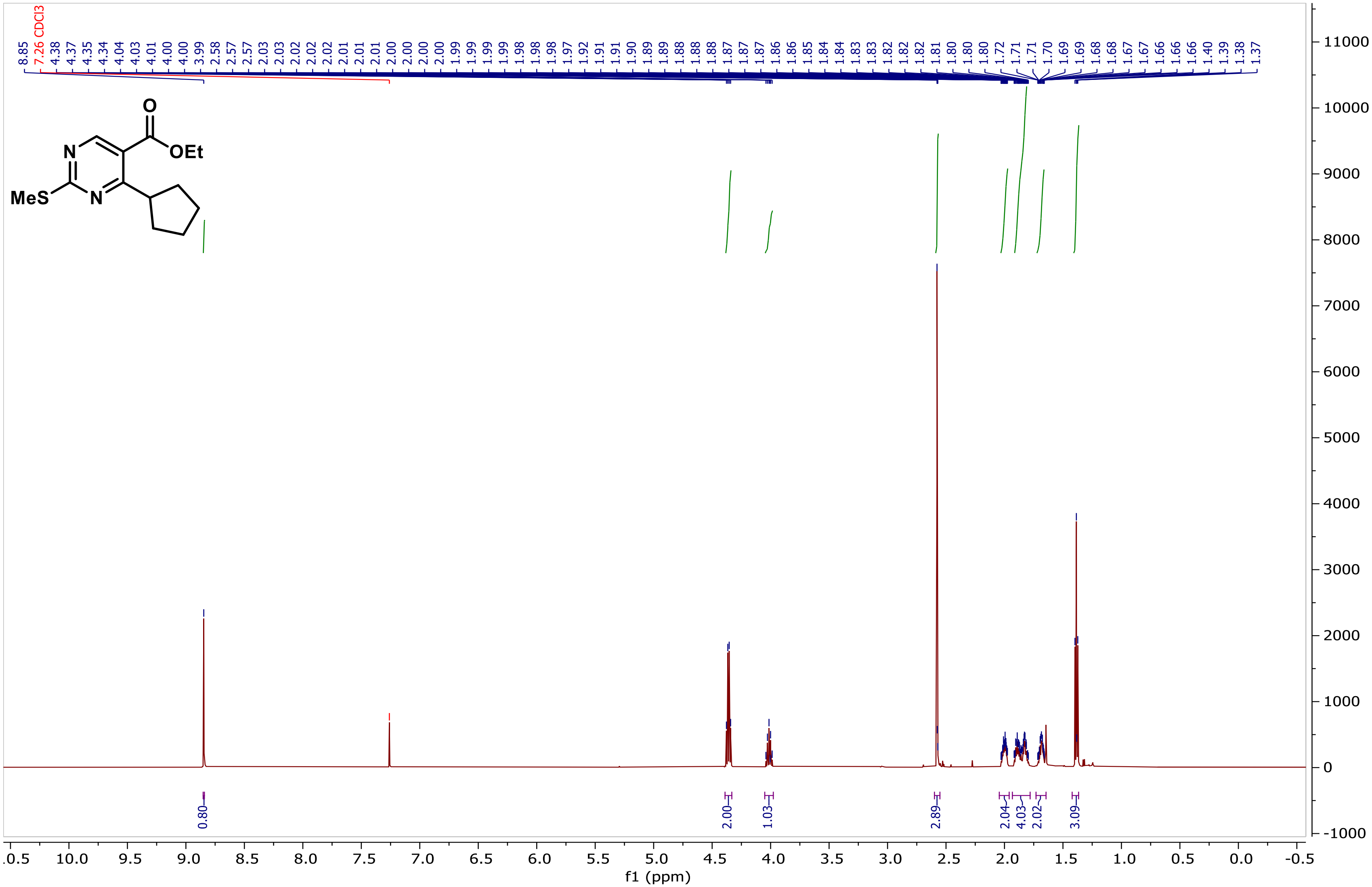
Table S10: Optimization of Reaction Conditions for Alkylation of Pyrimidine 1 with Cyclobutane Redox-Active Ester 46



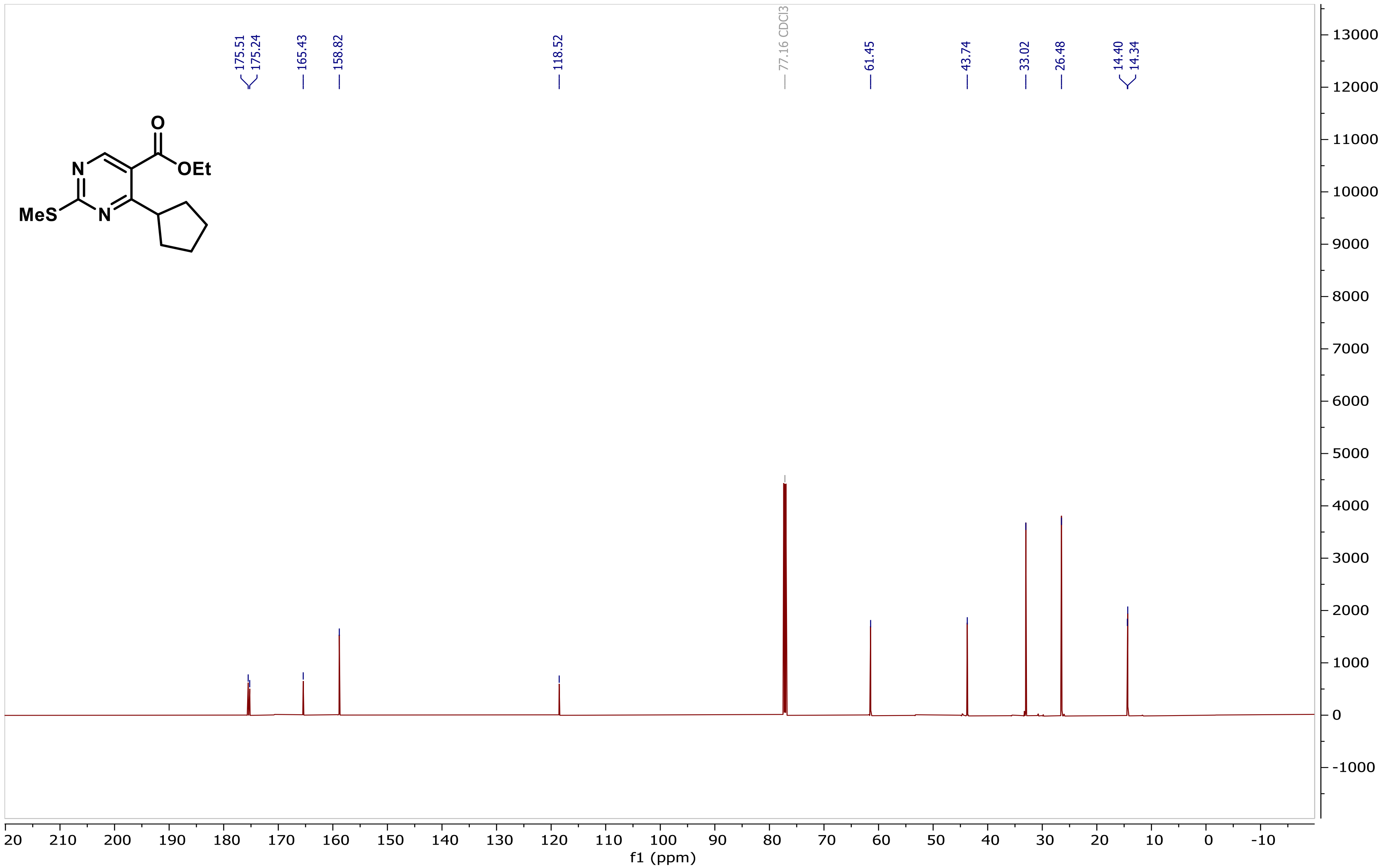
entry	deviation from above	yield
1	1.0 equiv **1**, 1.5 equiv **46**, 20 mol% Ni, 25 mol% Ligand	12%
2	20 mol% Ni, 25 mol% Ligand	36%
3	DMSO instead of 1,4-dioxane	47%
4	None	58%

NMR Characterization

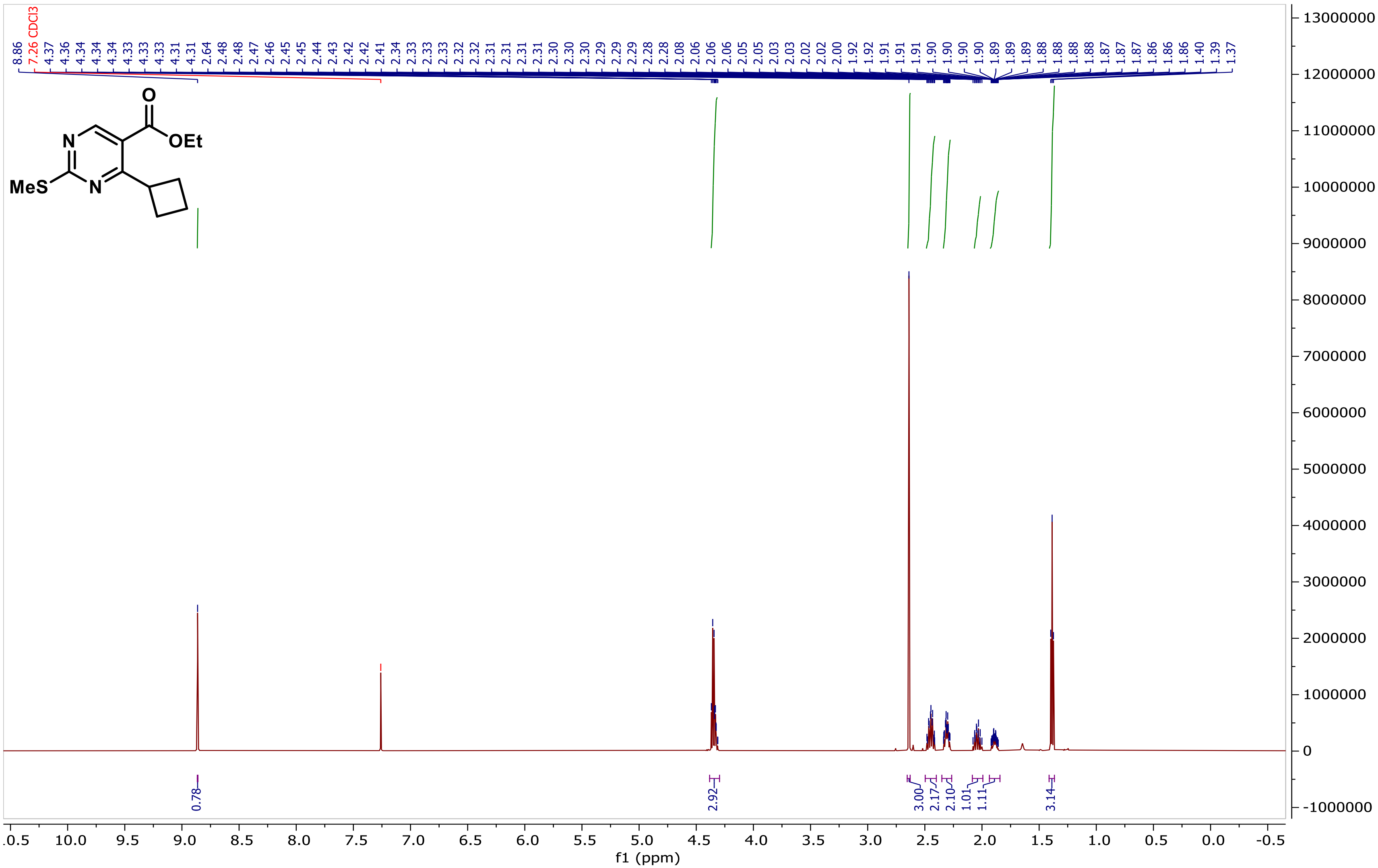
Compound 3, ^1H NMR ($CDCl_3$, 600 MHz)



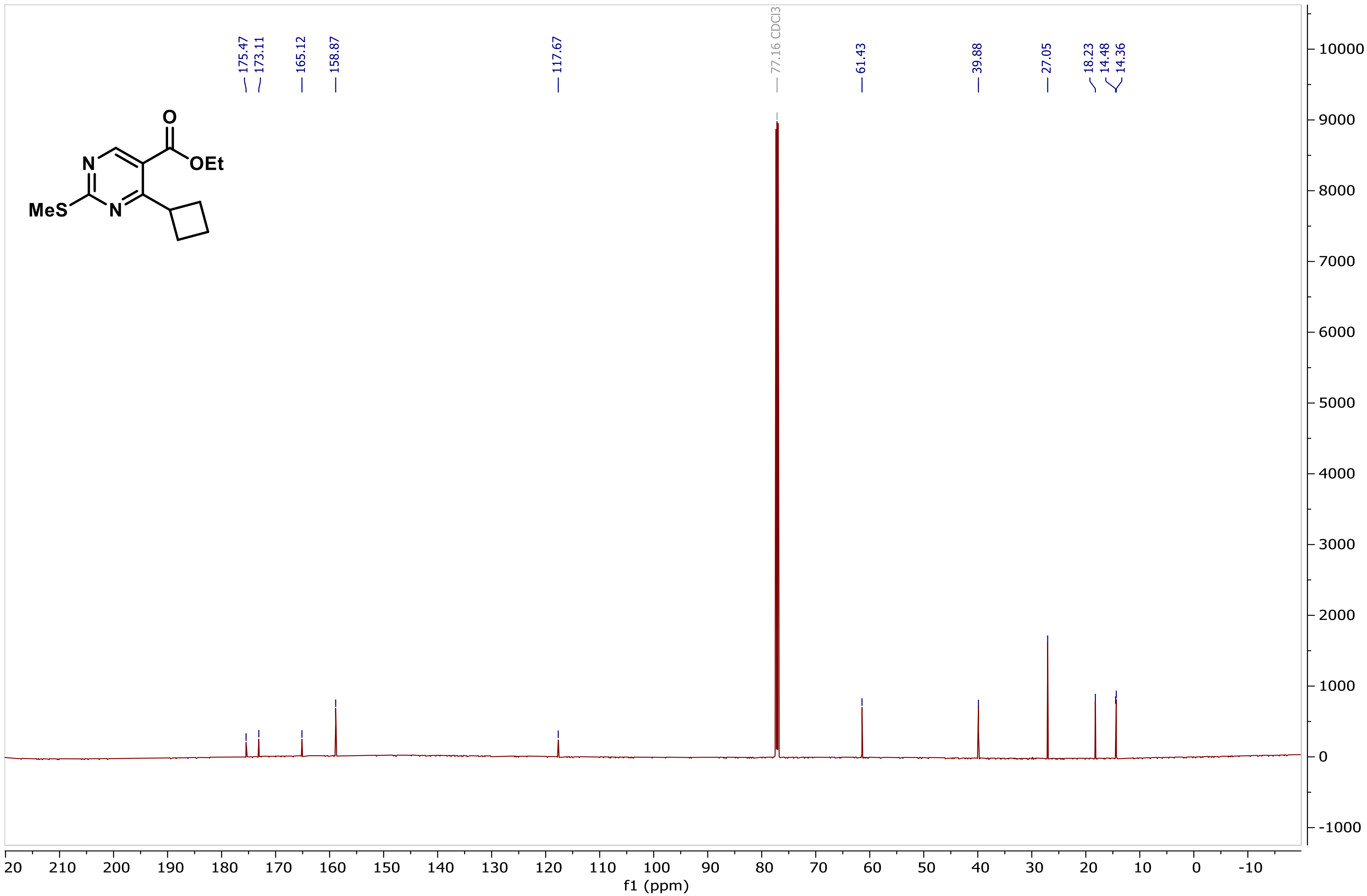
Compound 3, ^{13}C {^{1}H} NMR ($CDCl_3$, 151 MHz)



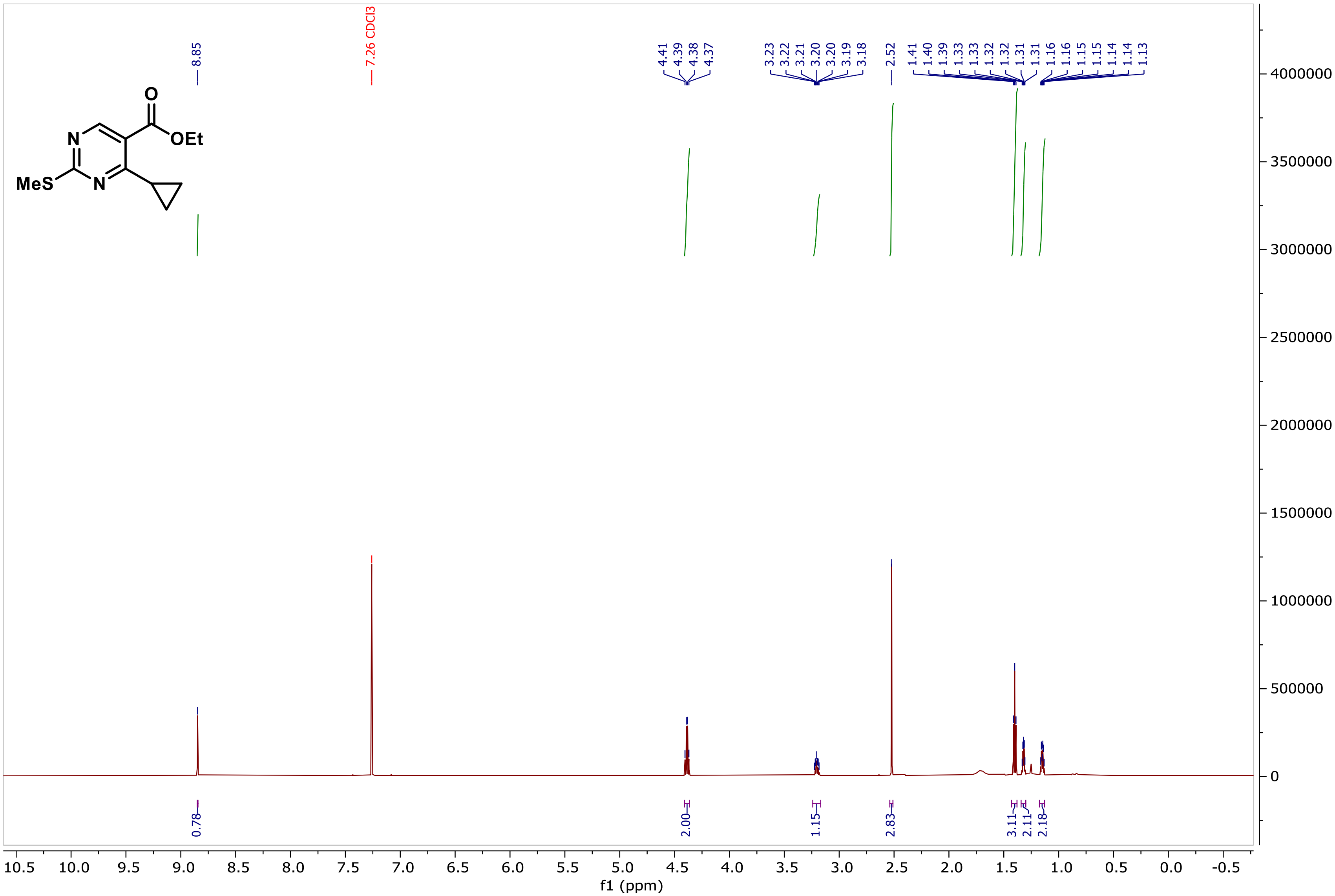
Compound 6, ^1H NMR ($CDCl_3$, 600 MHz)



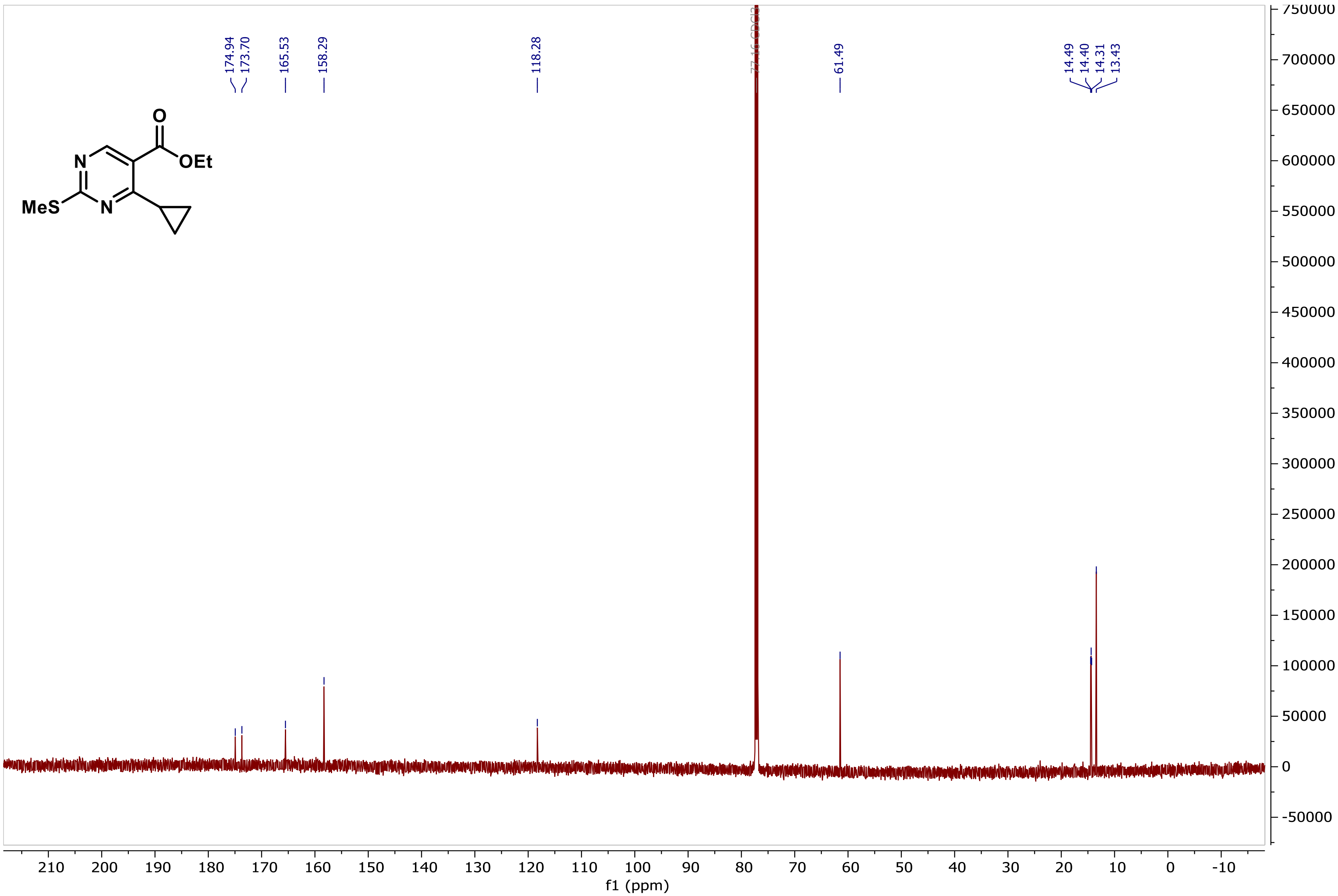
Compound 6, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



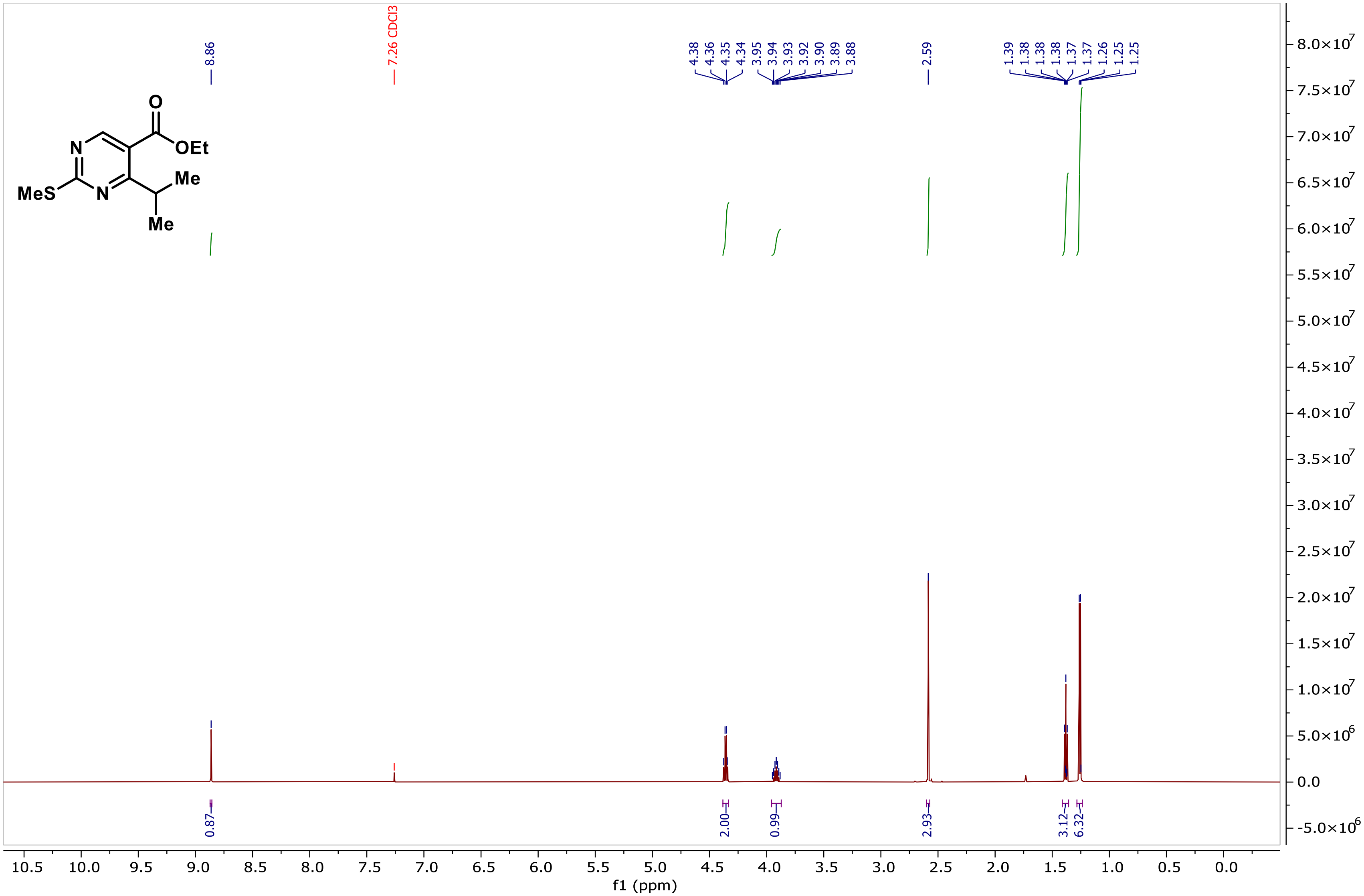
Compound 7, ^1H NMR ($CDCl_3$, 600 MHz)



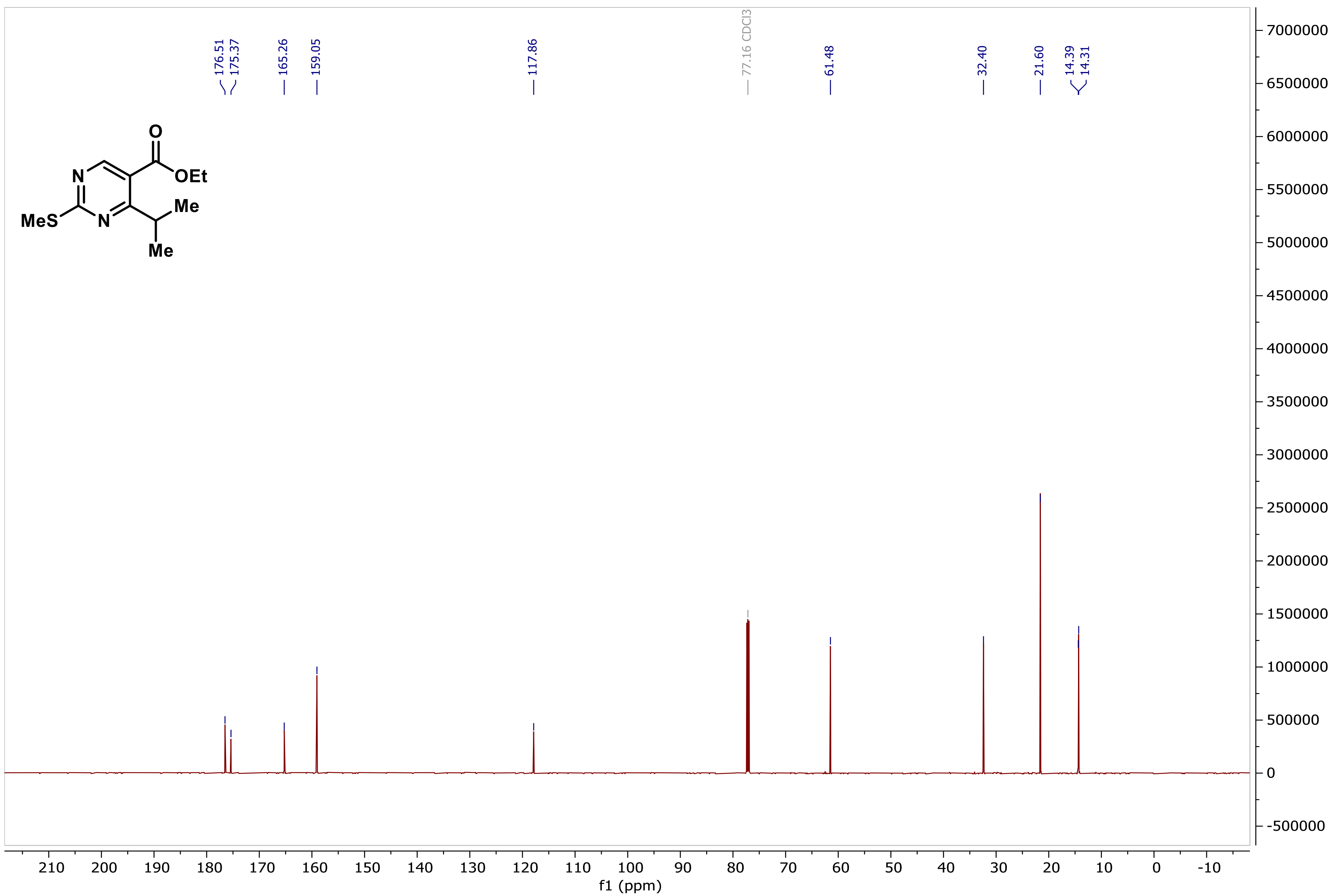
Compound 7, ^{13}C {^{1}H} NMR ($CDCl_3$, 151 MHz)



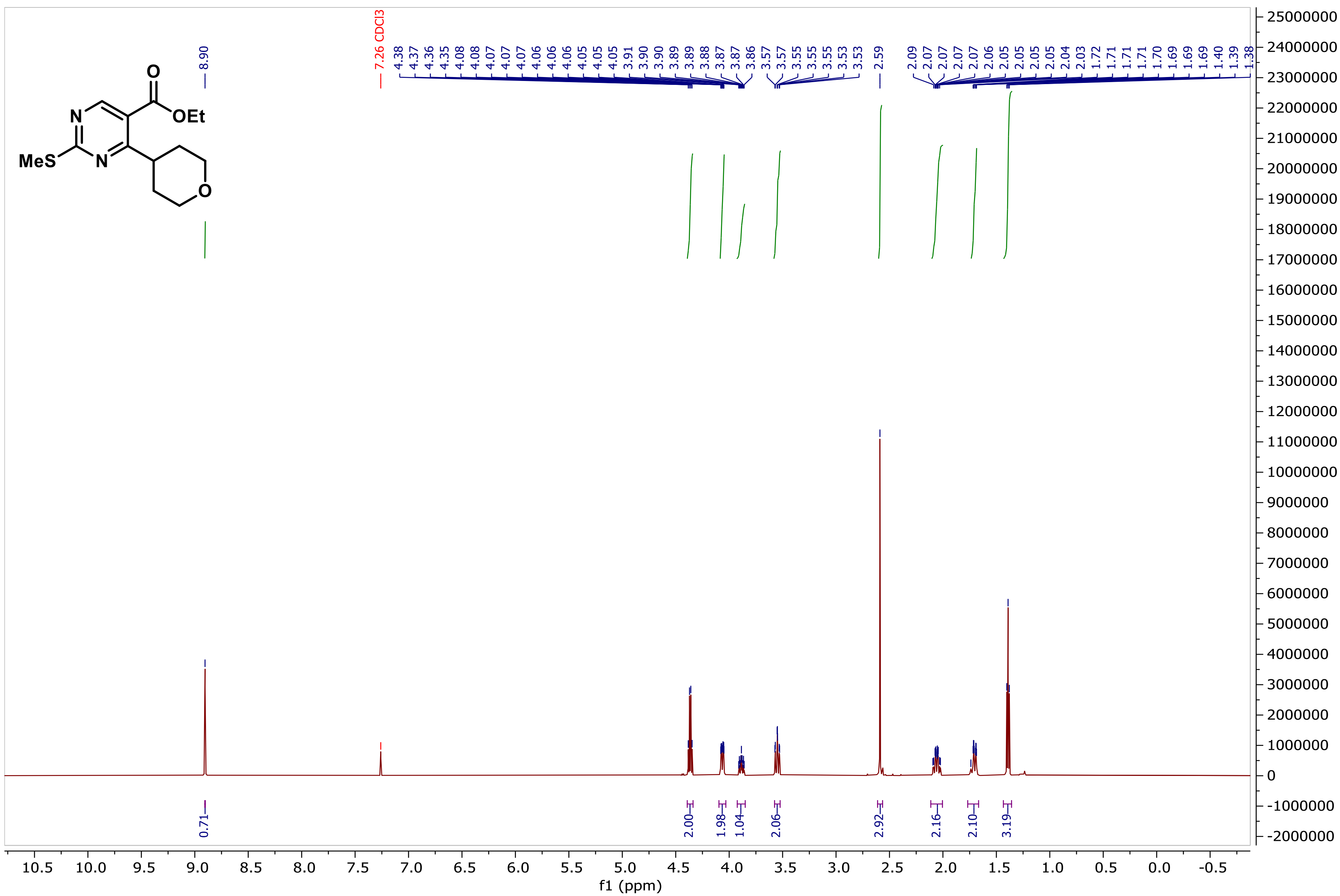
Compound 8, ^{1}H NMR ($CDCl_3$, 600 MHz)



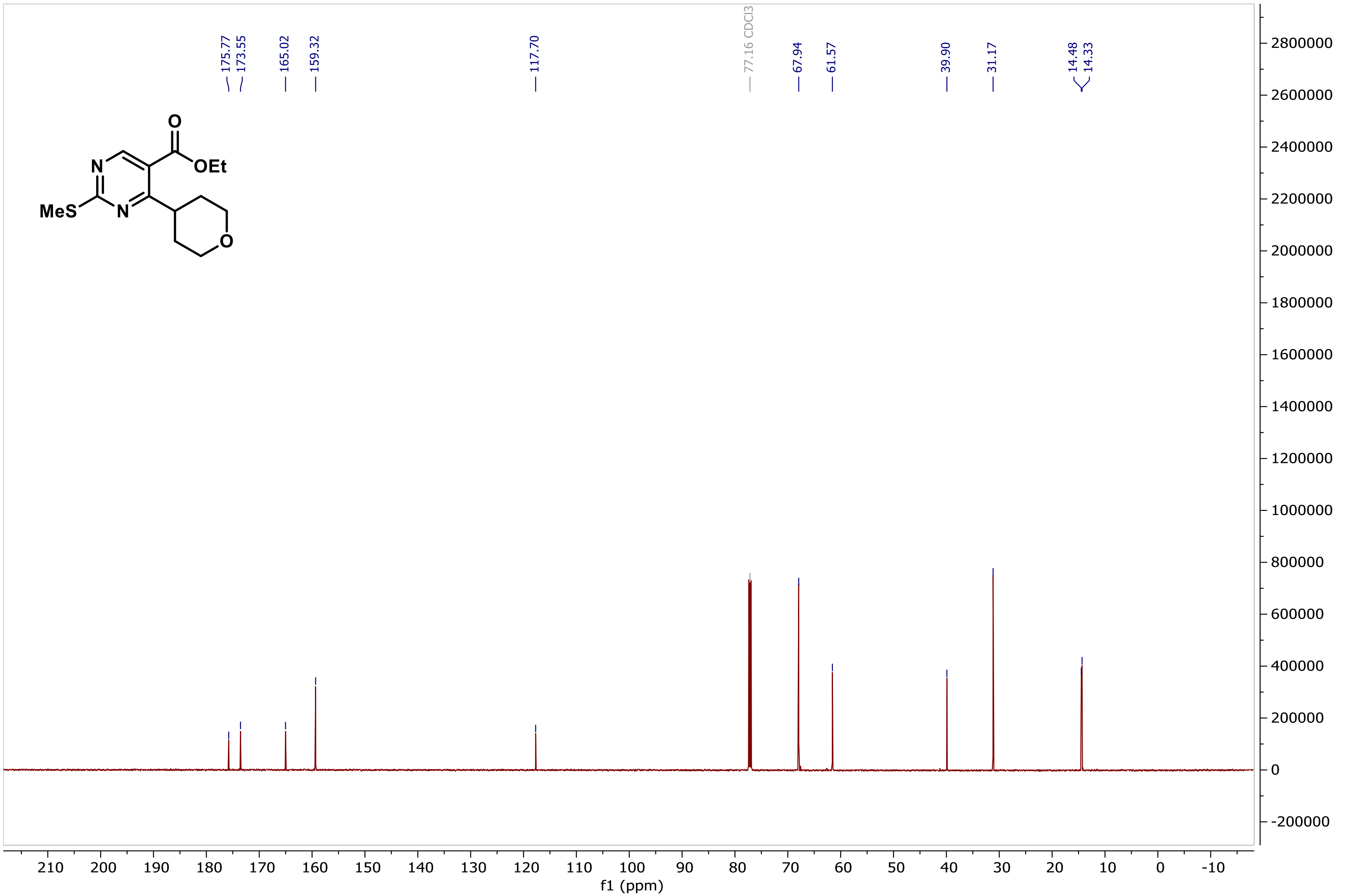
Compound 8, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



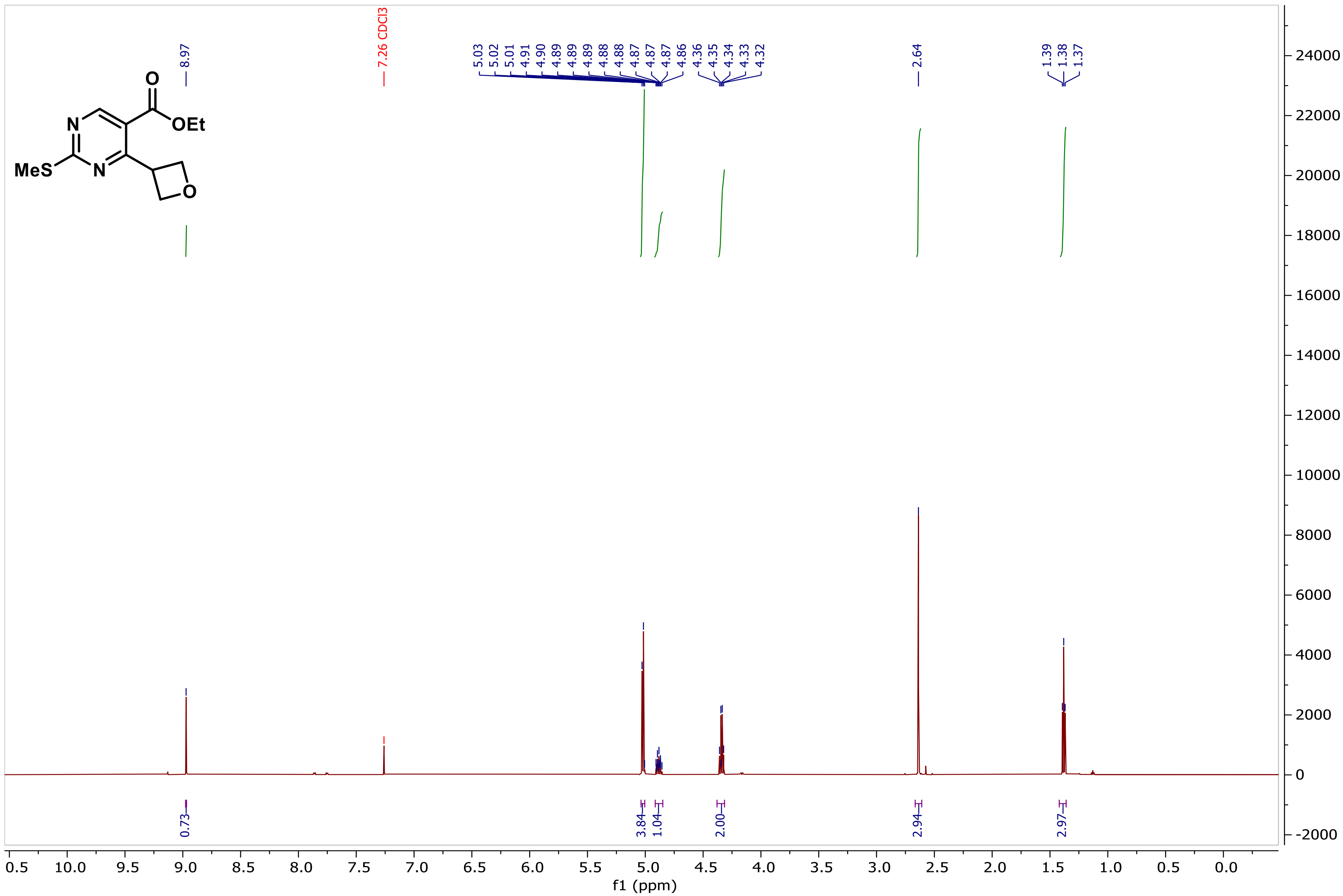
Compound 9, ^{1}H NMR ($CDCl_3$, 600 MHz)



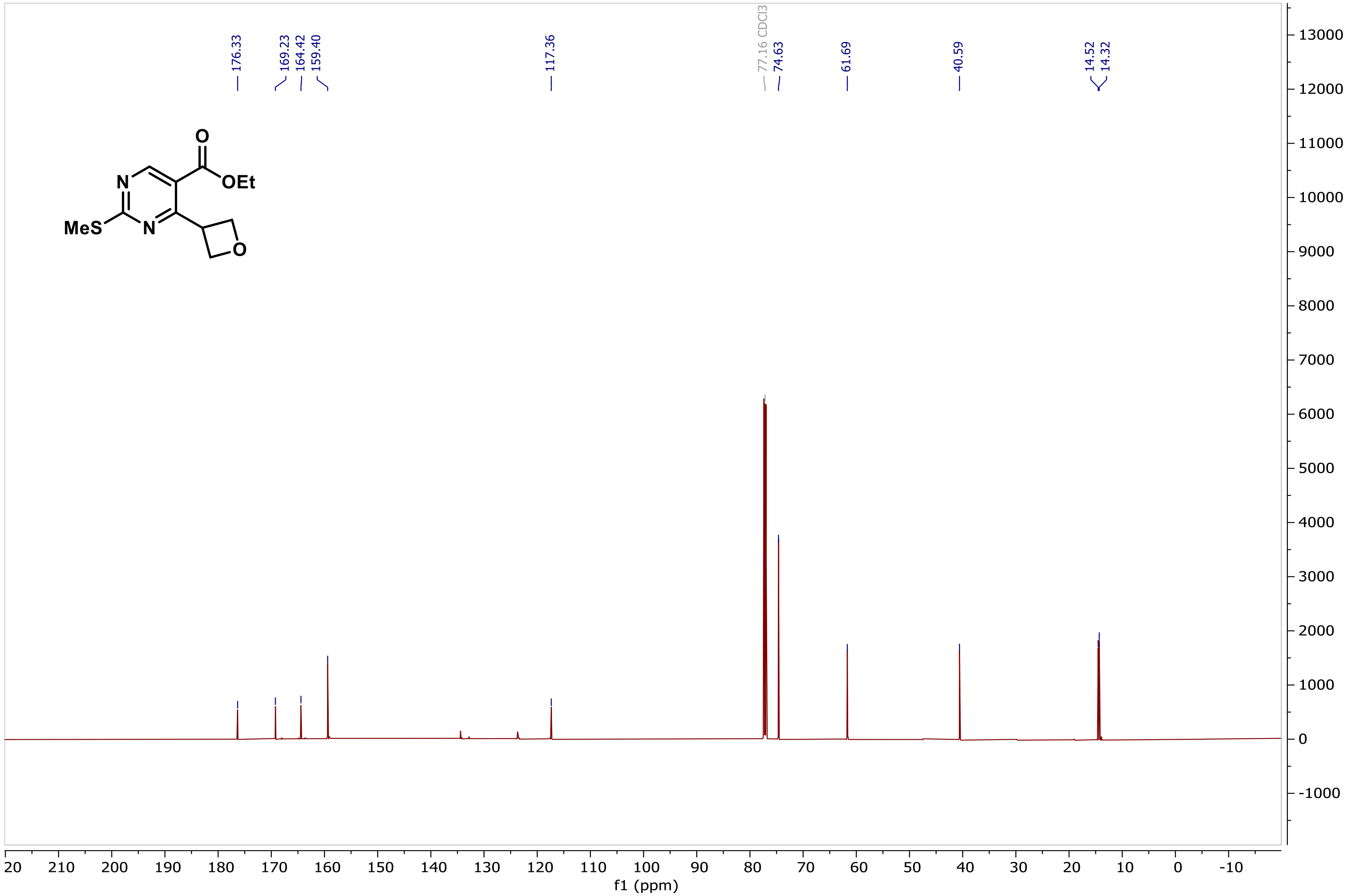
Compound 9, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



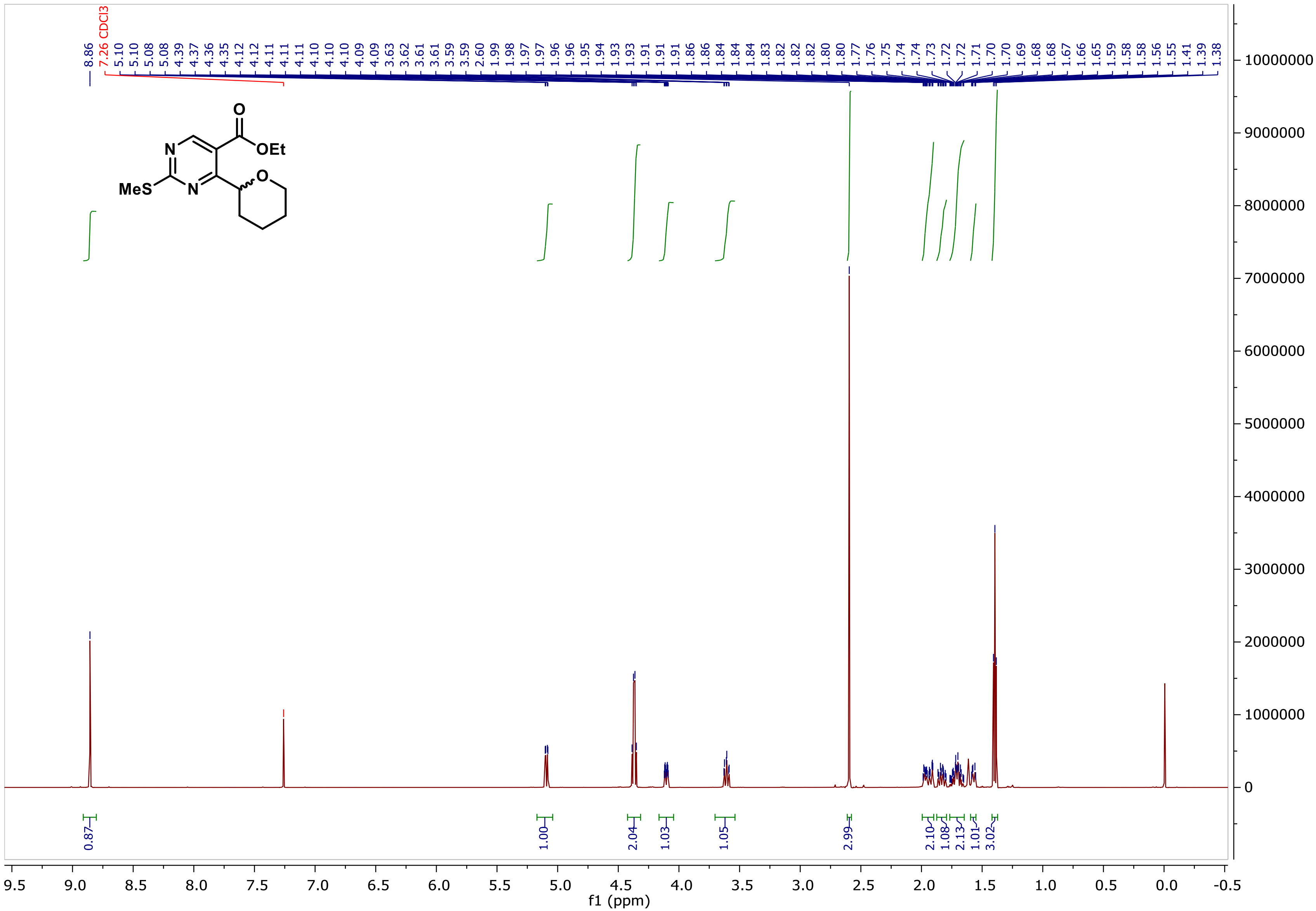
Compound 10, ^{1}H NMR ($CDCl_3$, 600 MHz)



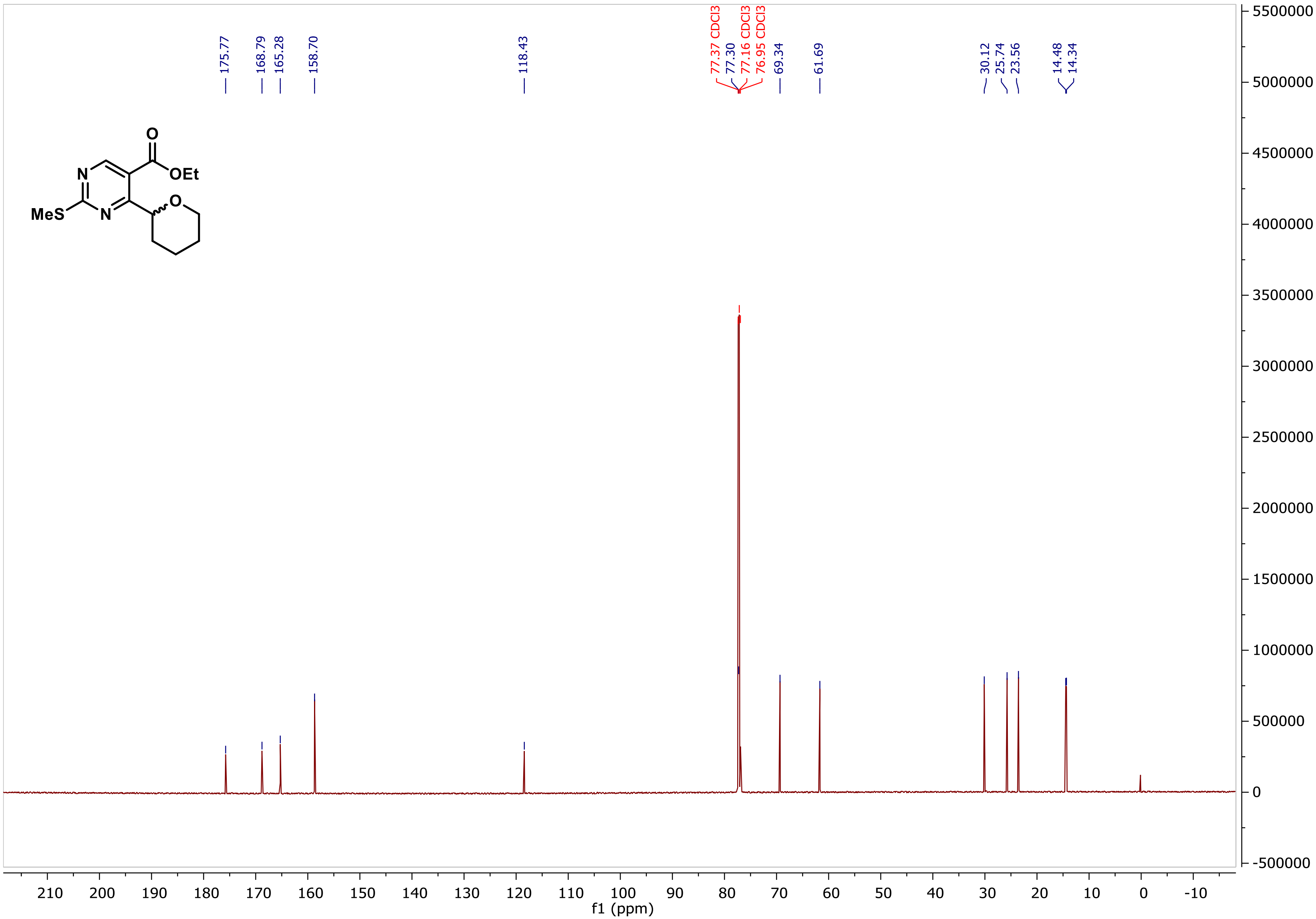
Compound 10, $^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



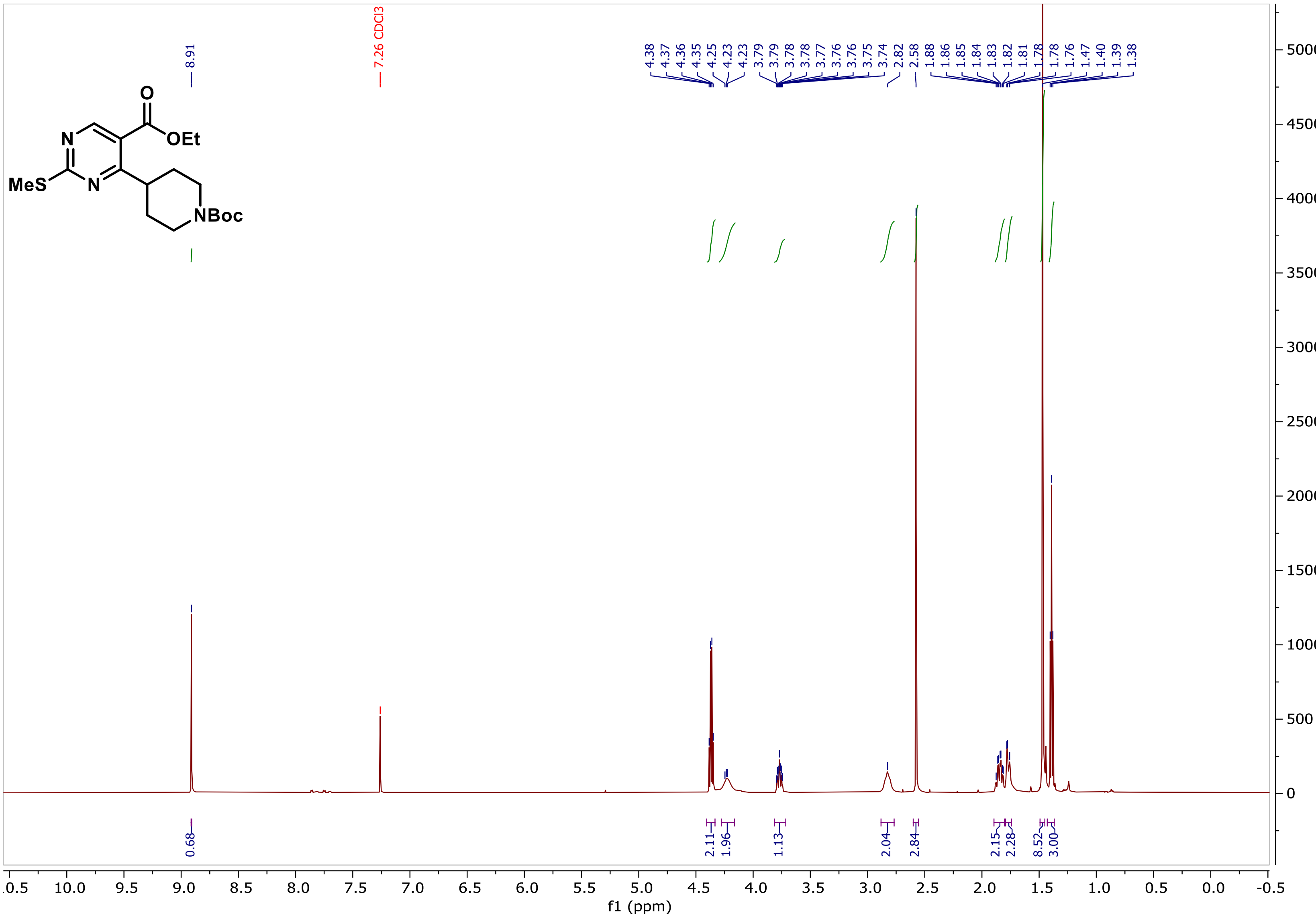
Compound 11, ^{1}H NMR ($CDCl_3$, 600 MHz)



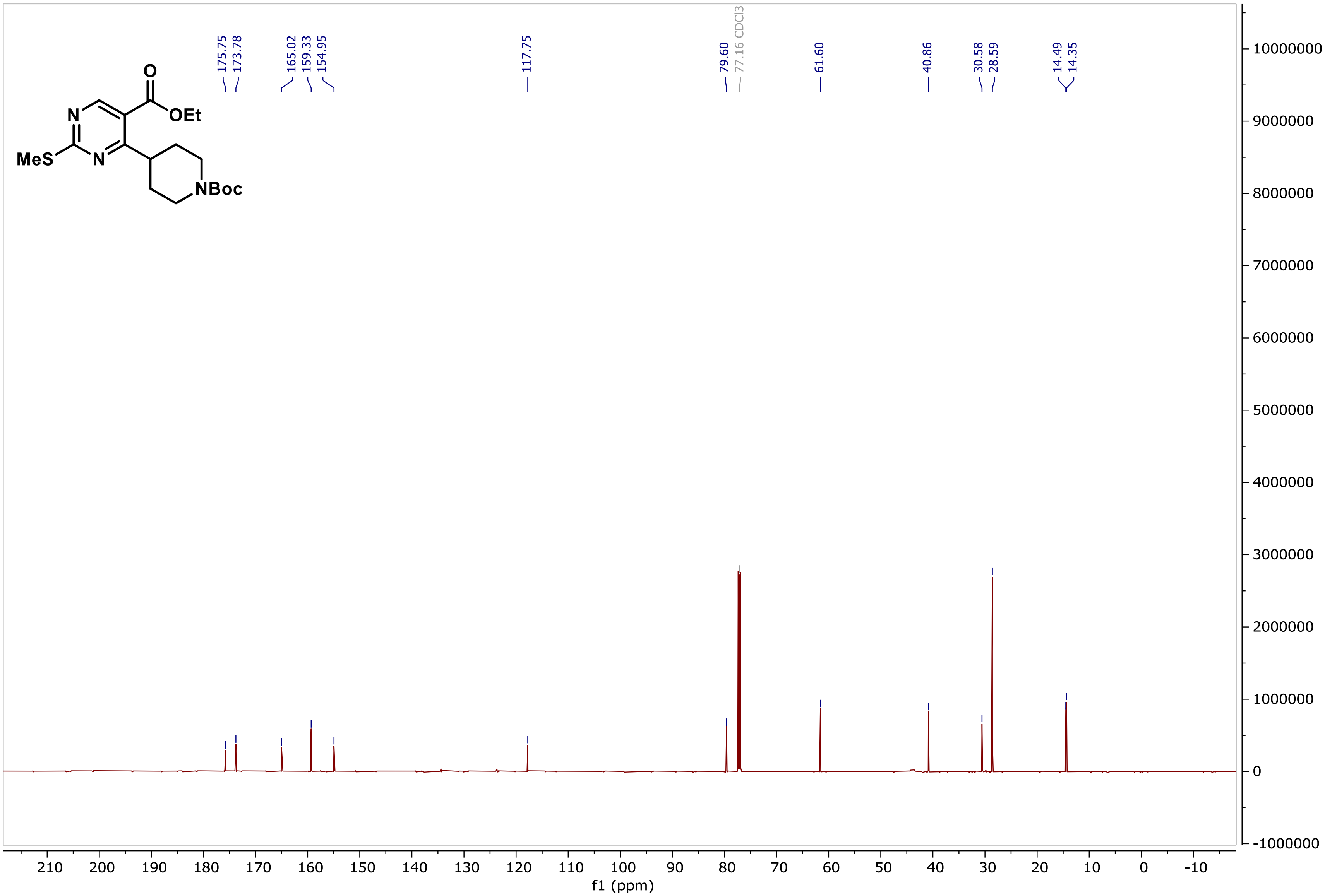
Compound 11, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



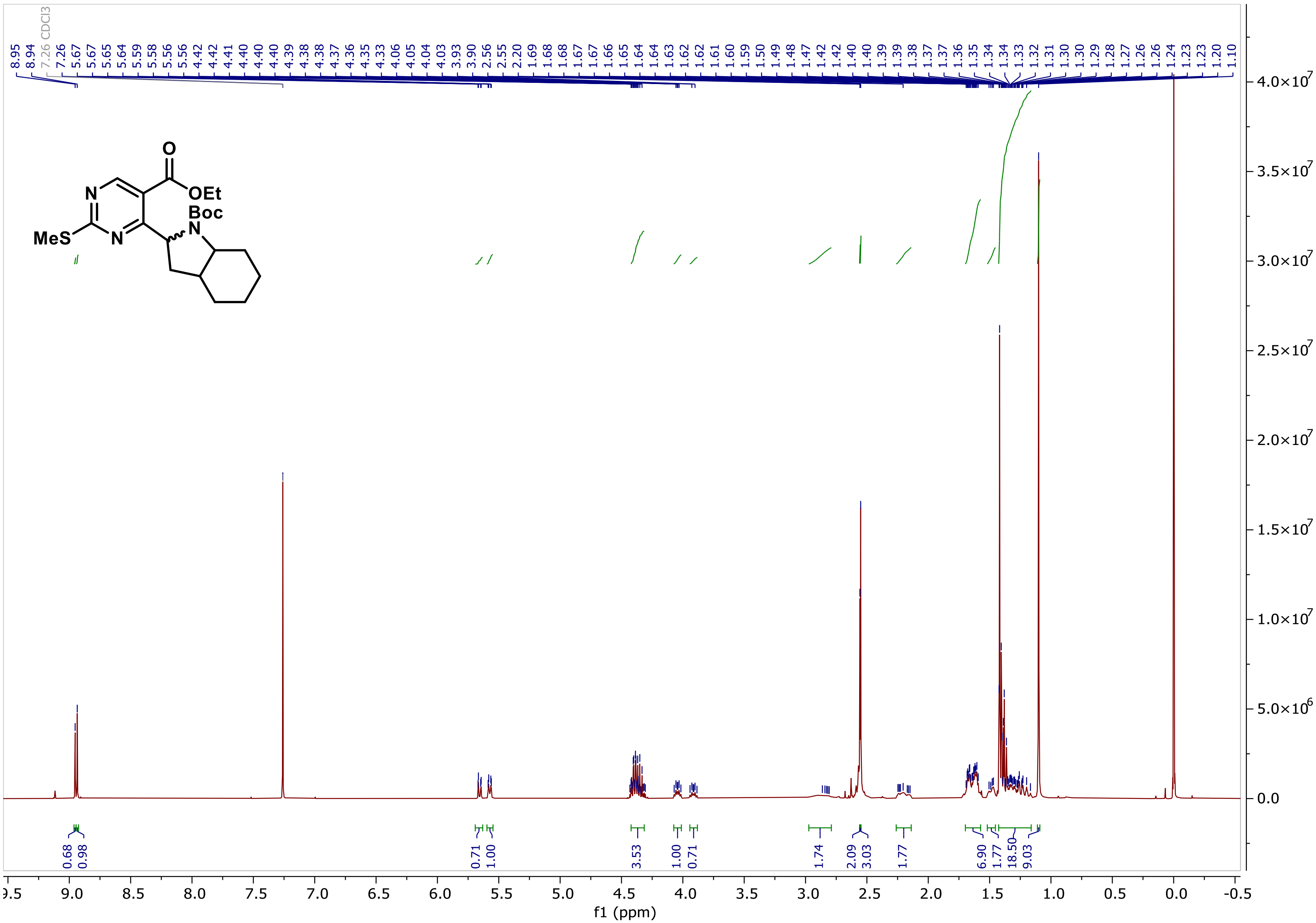
Compound 12, ^{1}H NMR ($CDCl_3$, 600 MHz)



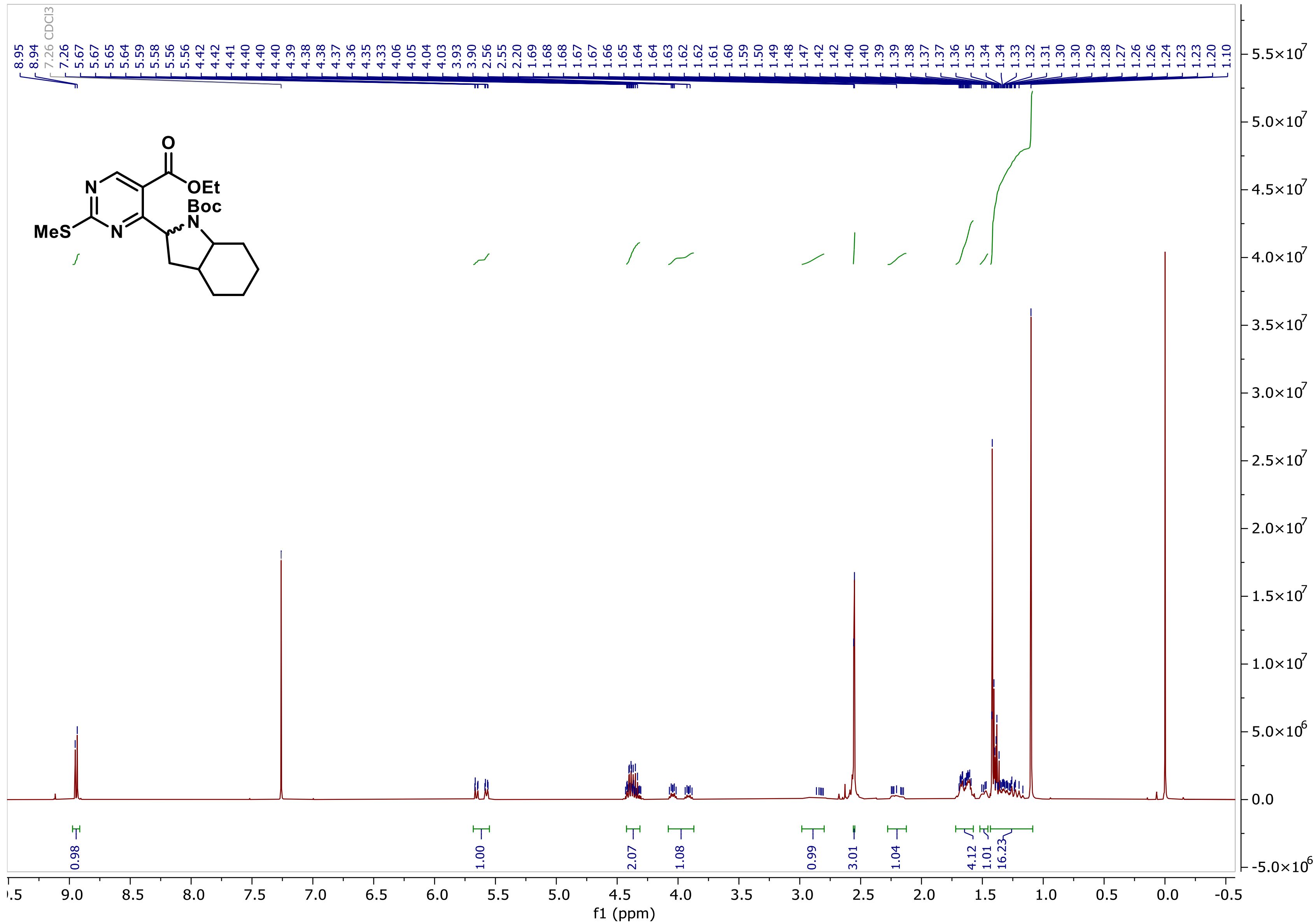
Compound 12, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



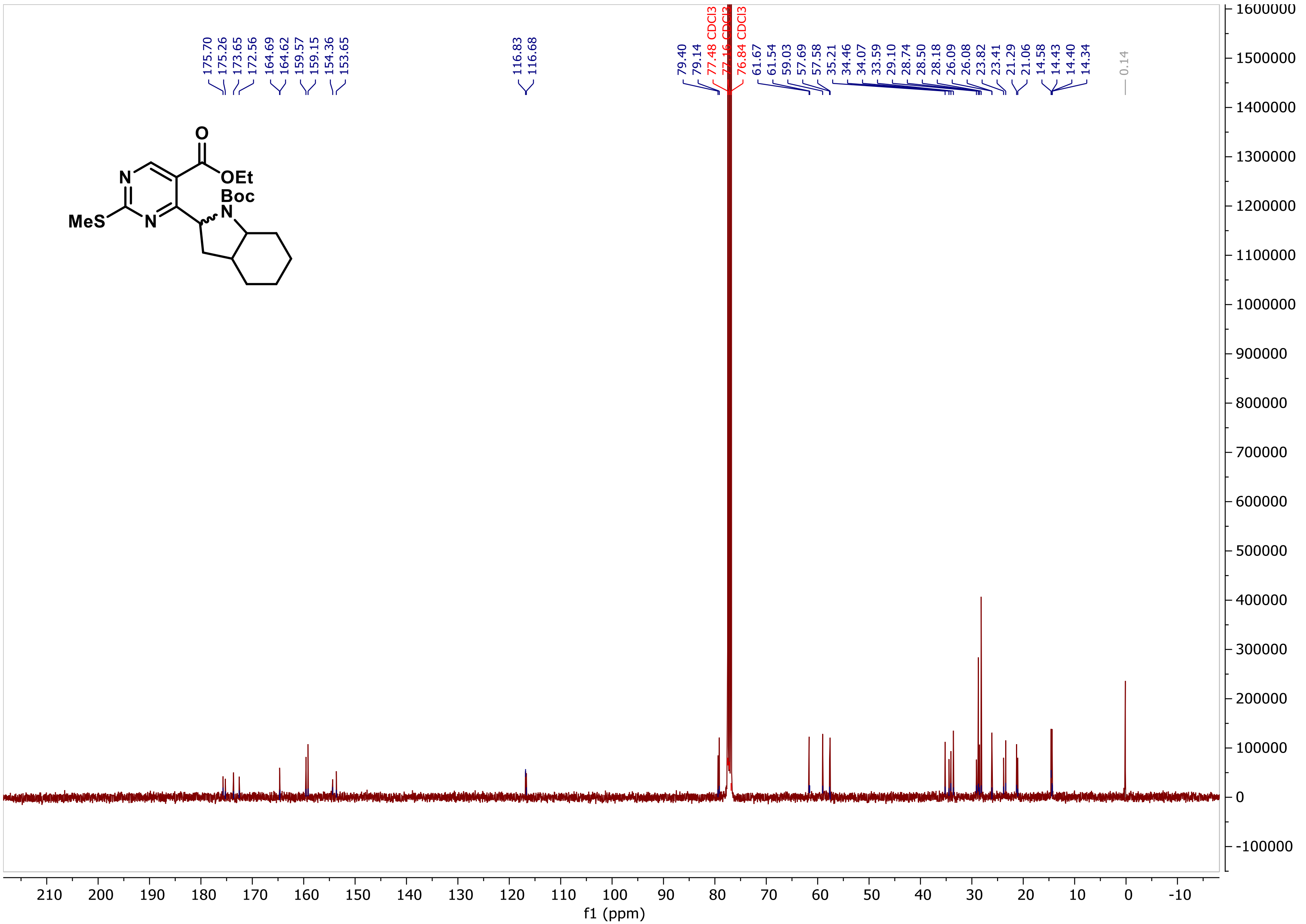
Compound 13, ^{1}H NMR ($CDCl_3$, 400 MHz)



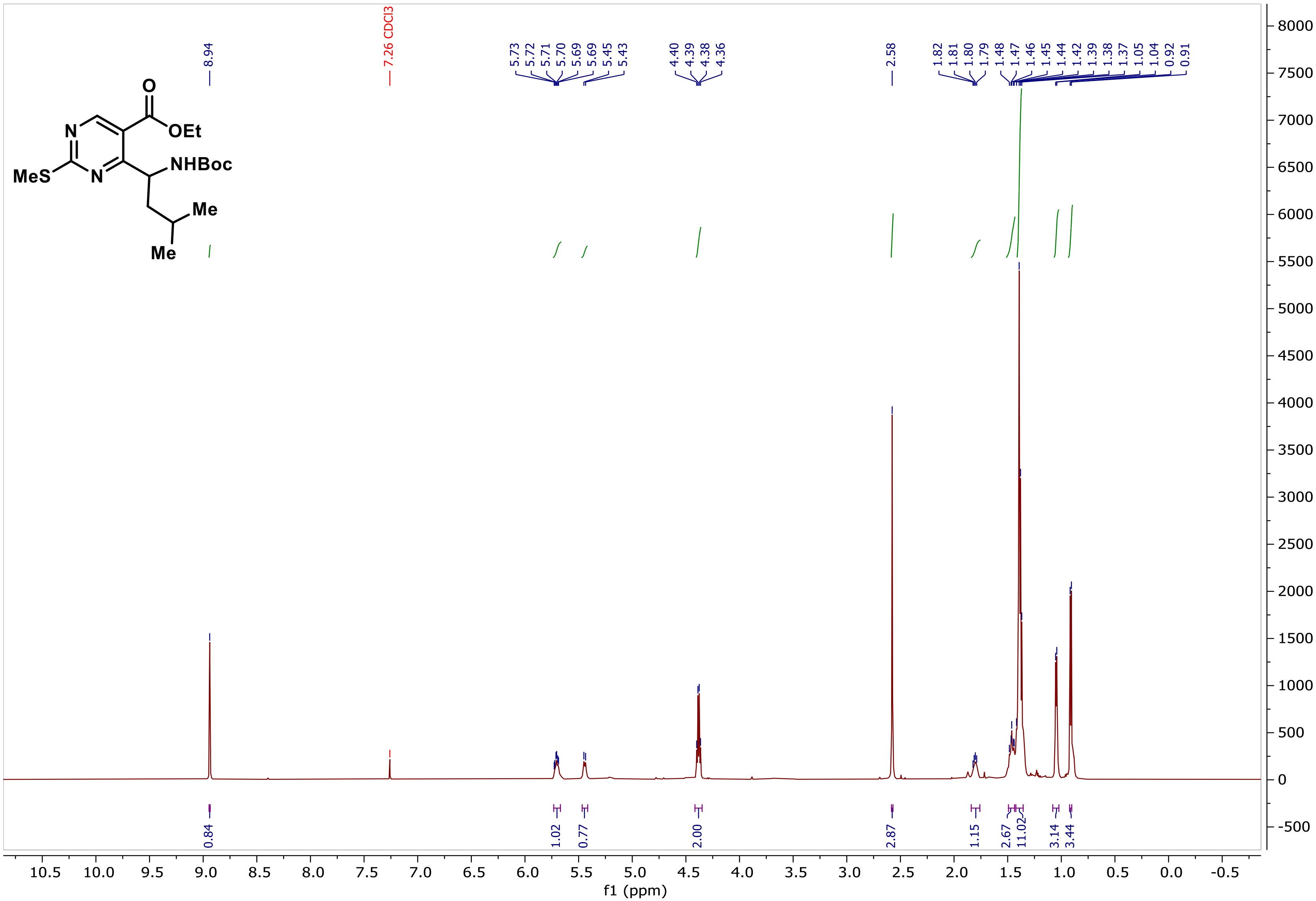
Integration for Diastereomers (combined)



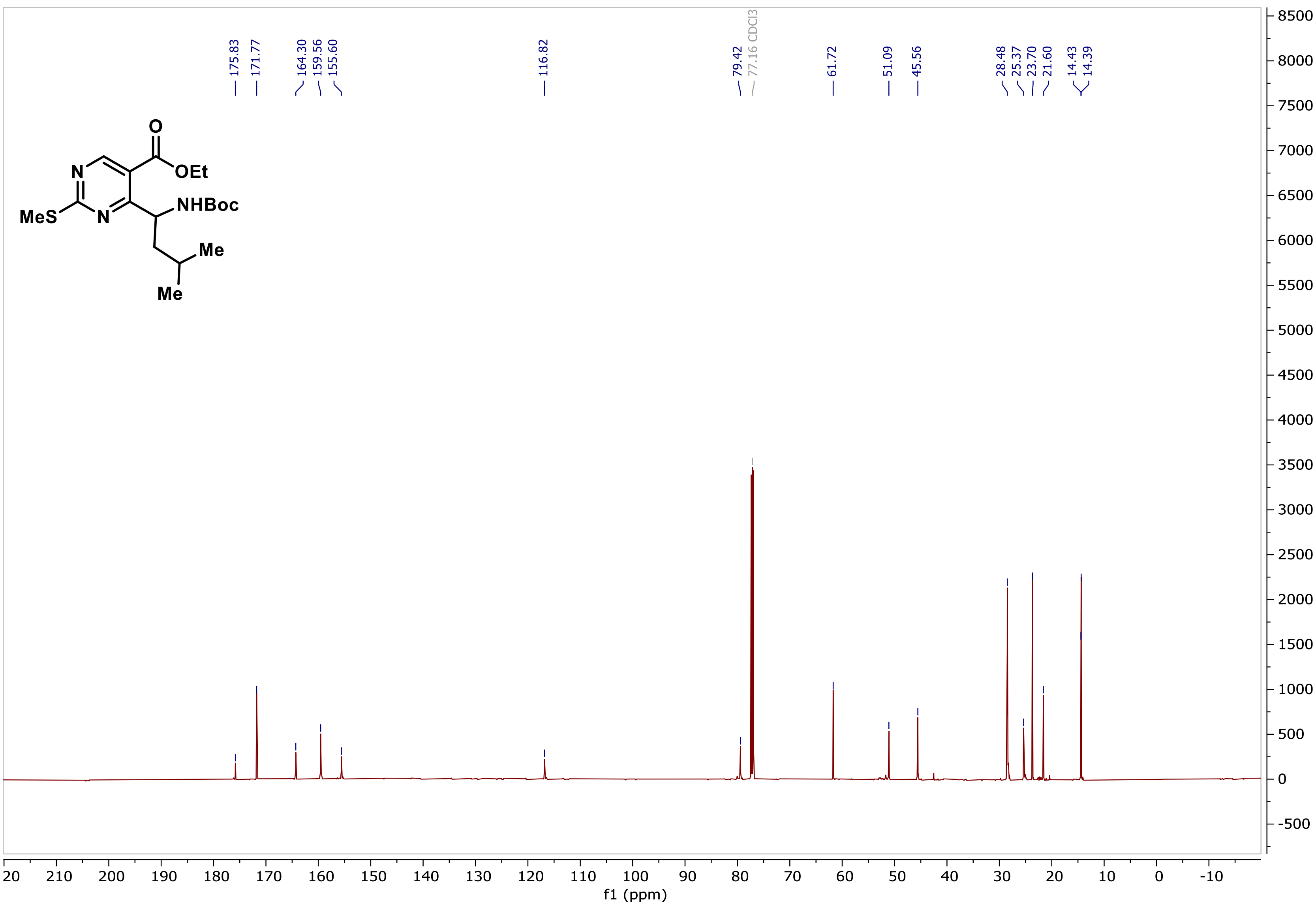
Compound 13, $^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



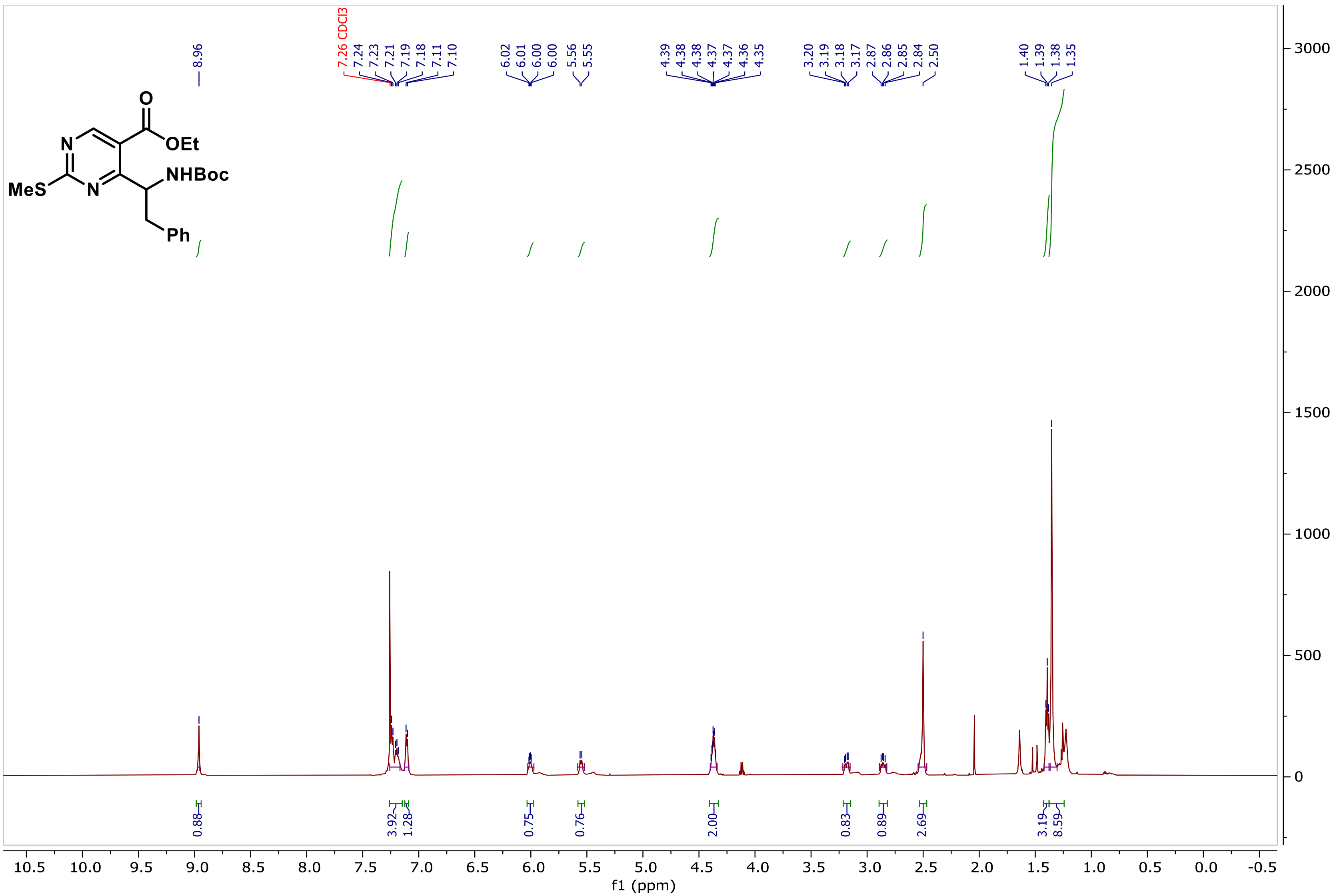
Compound 14, ^{1}H NMR ($CDCl_3$, 600 MHz)



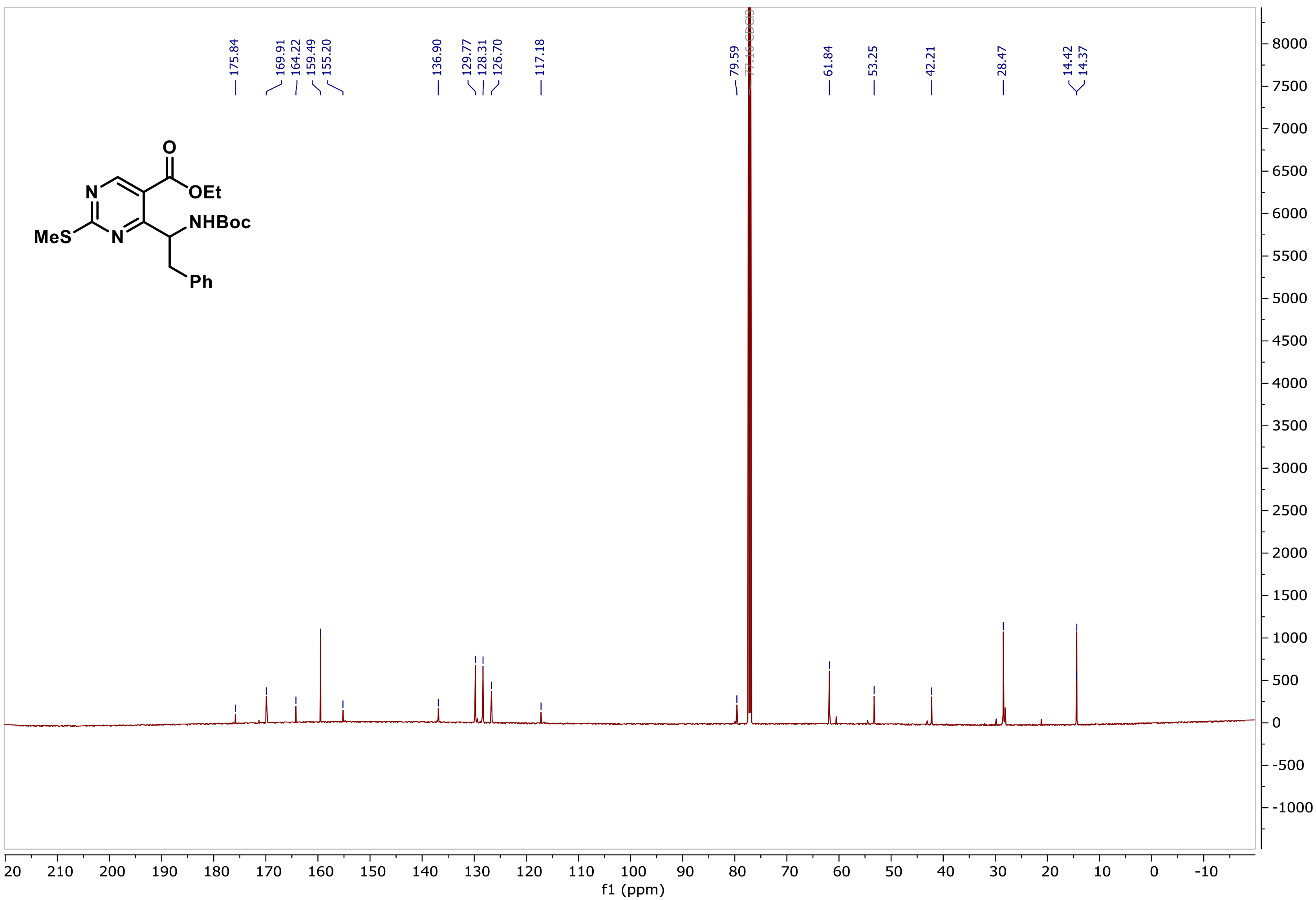
Compound 14, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



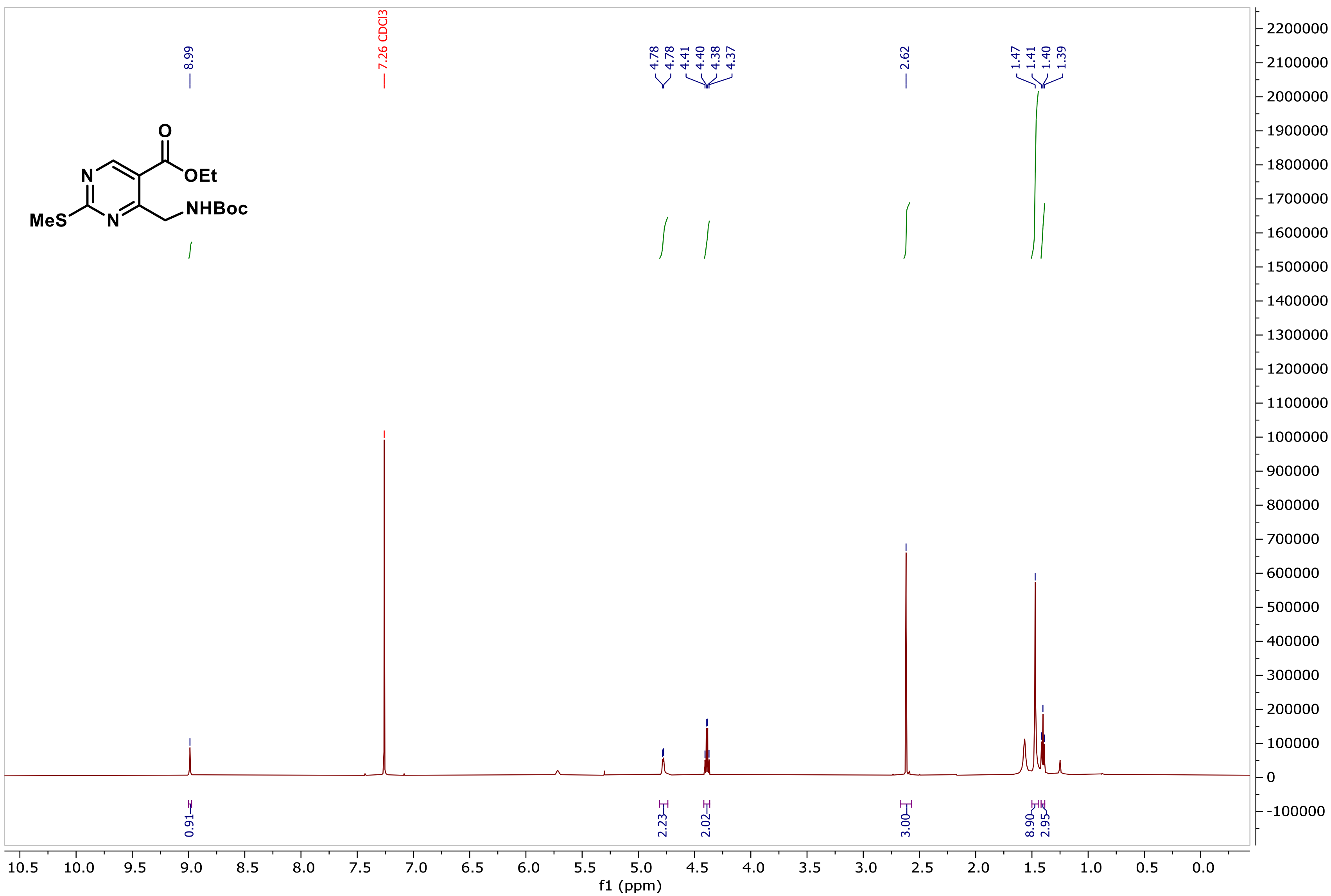
Compound 15, ^{1}H NMR ($CDCl_3$, 600 MHz)



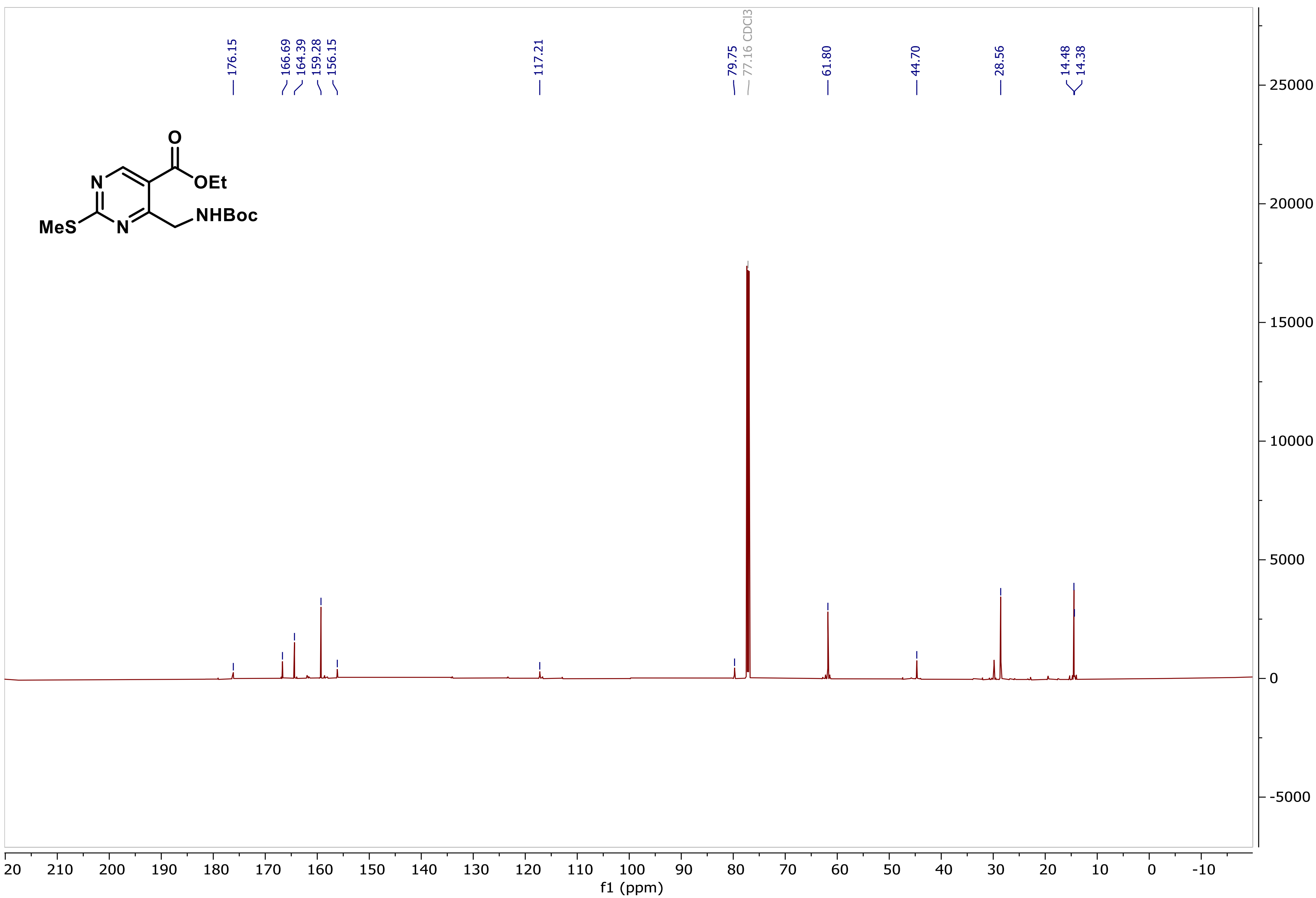
Compound 15, $^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



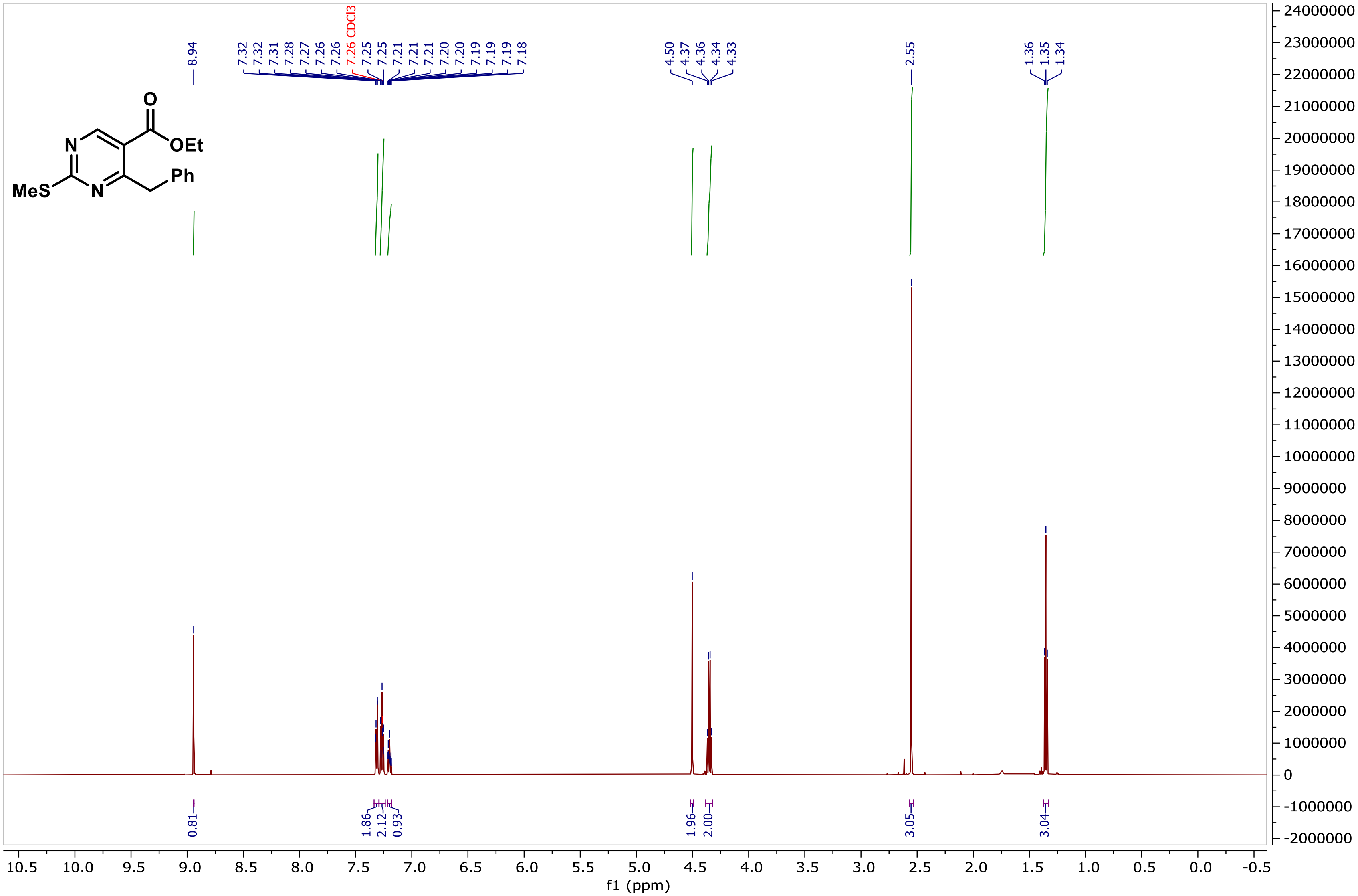
Compound 16, ^1H NMR ($CDCl_3$, 600 MHz)



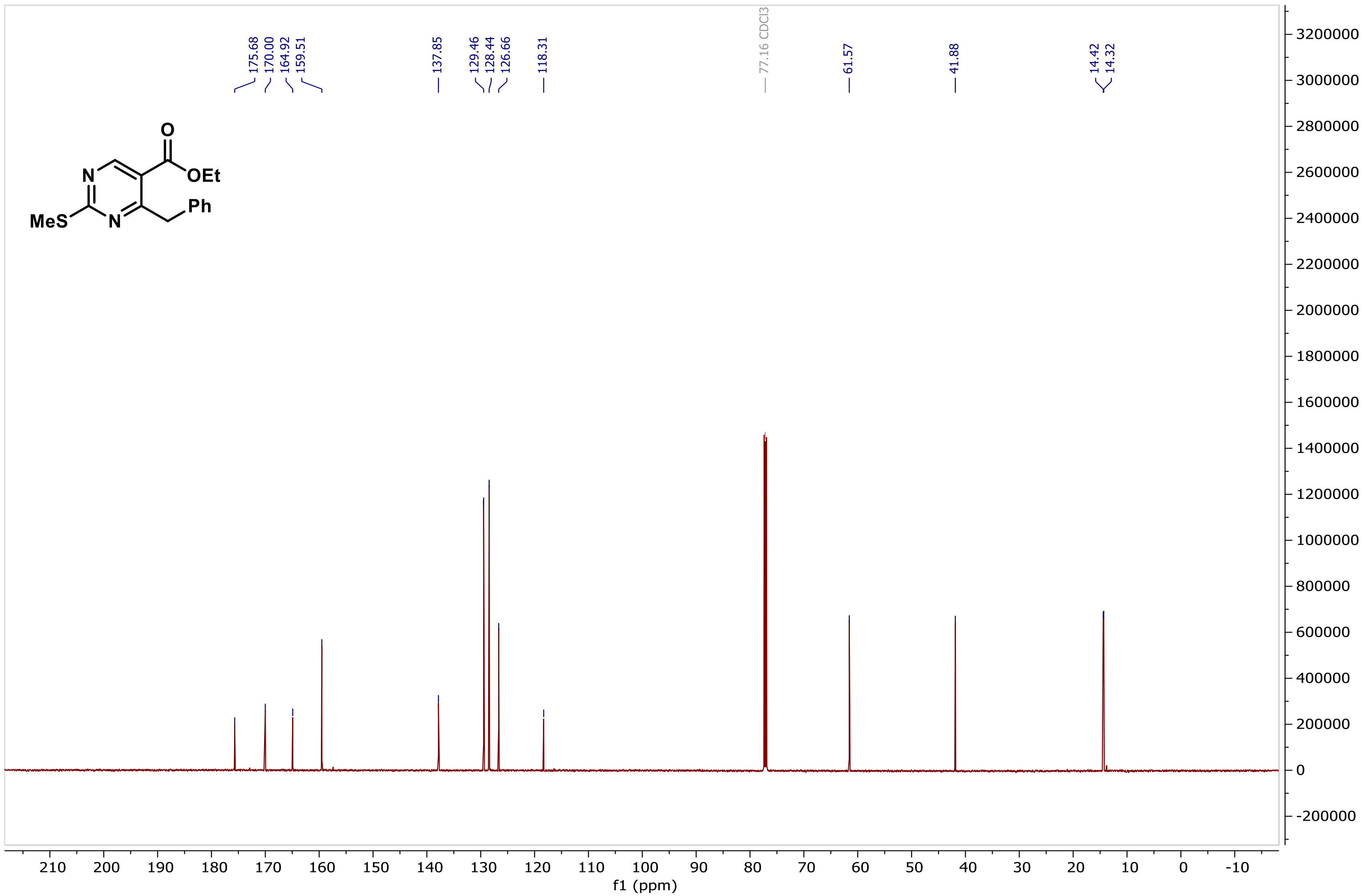
Compound 16, $^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



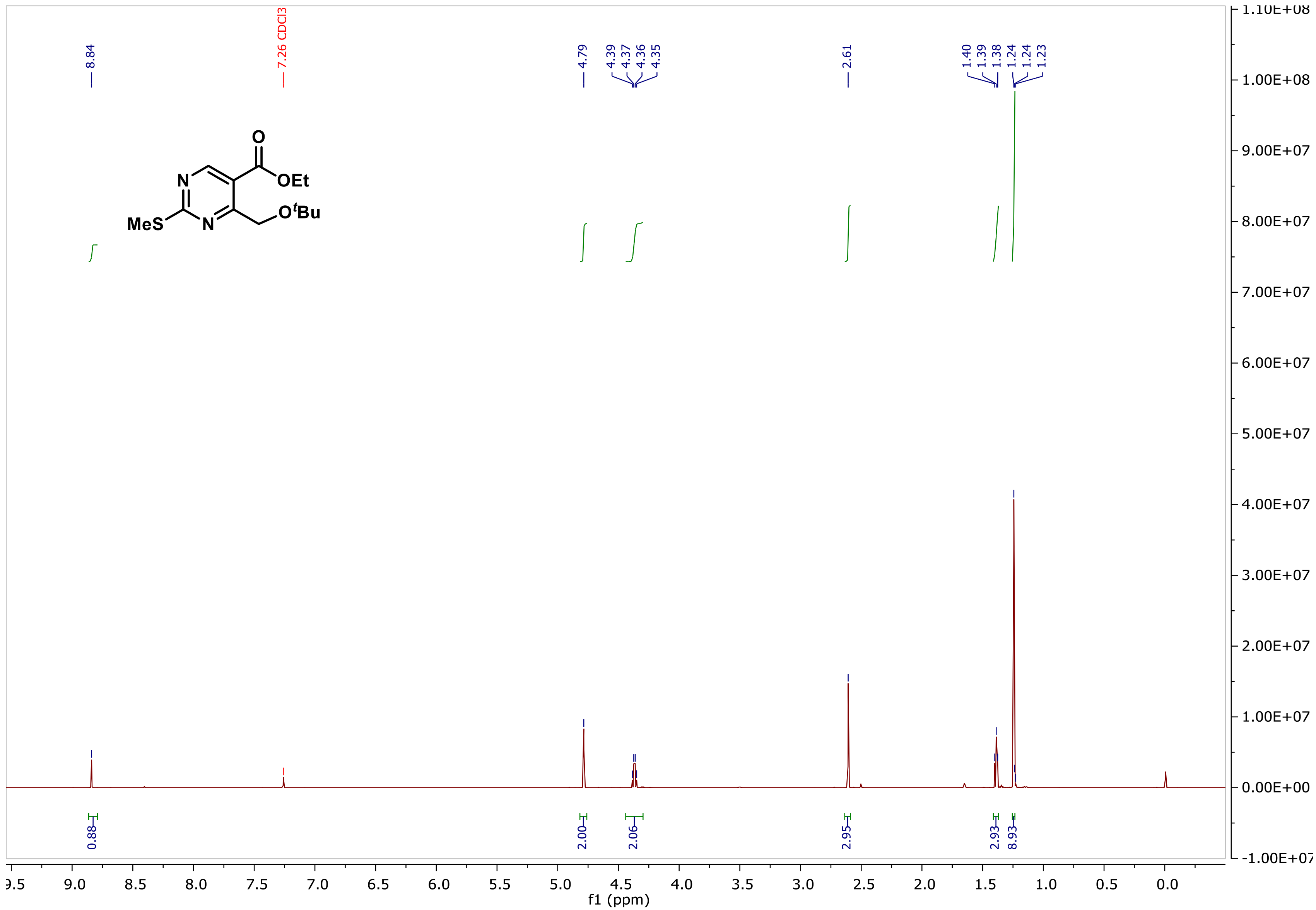
Compound 17, ^{1}H NMR ($CDCl_3$, 600 MHz)



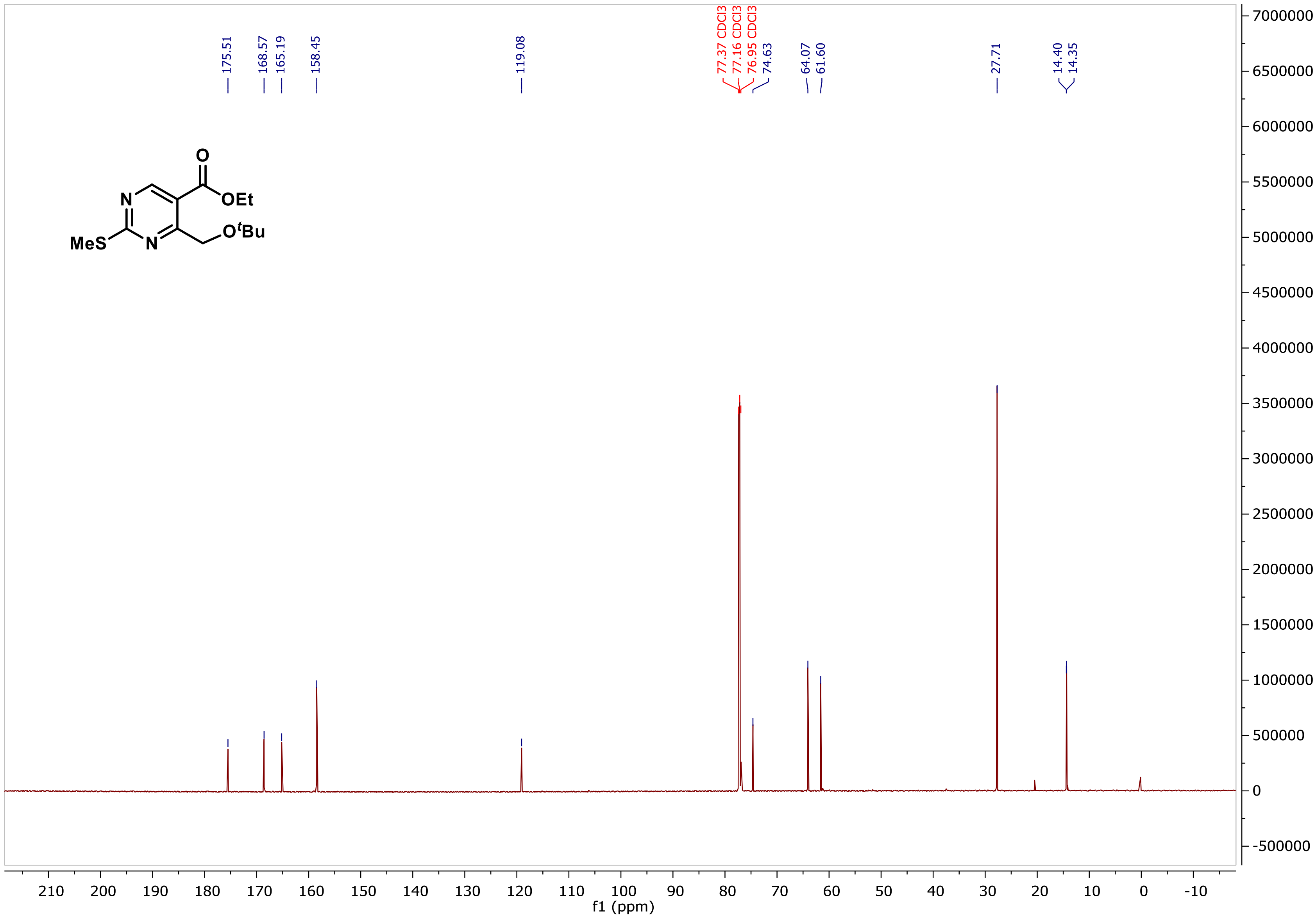
Compound 17, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



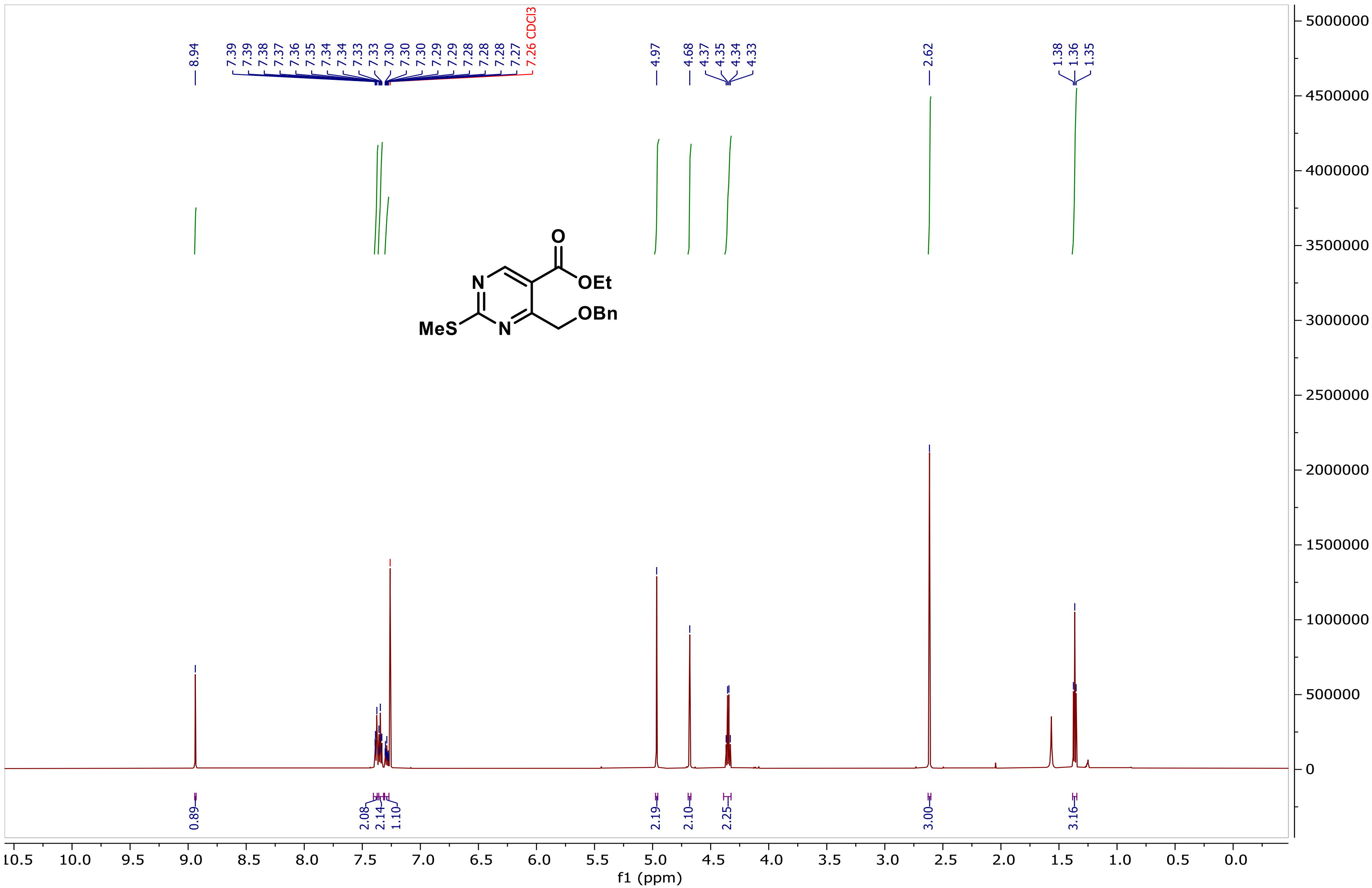
Compound 18, ^{1}H NMR ($CDCl_3$, 600 MHz)



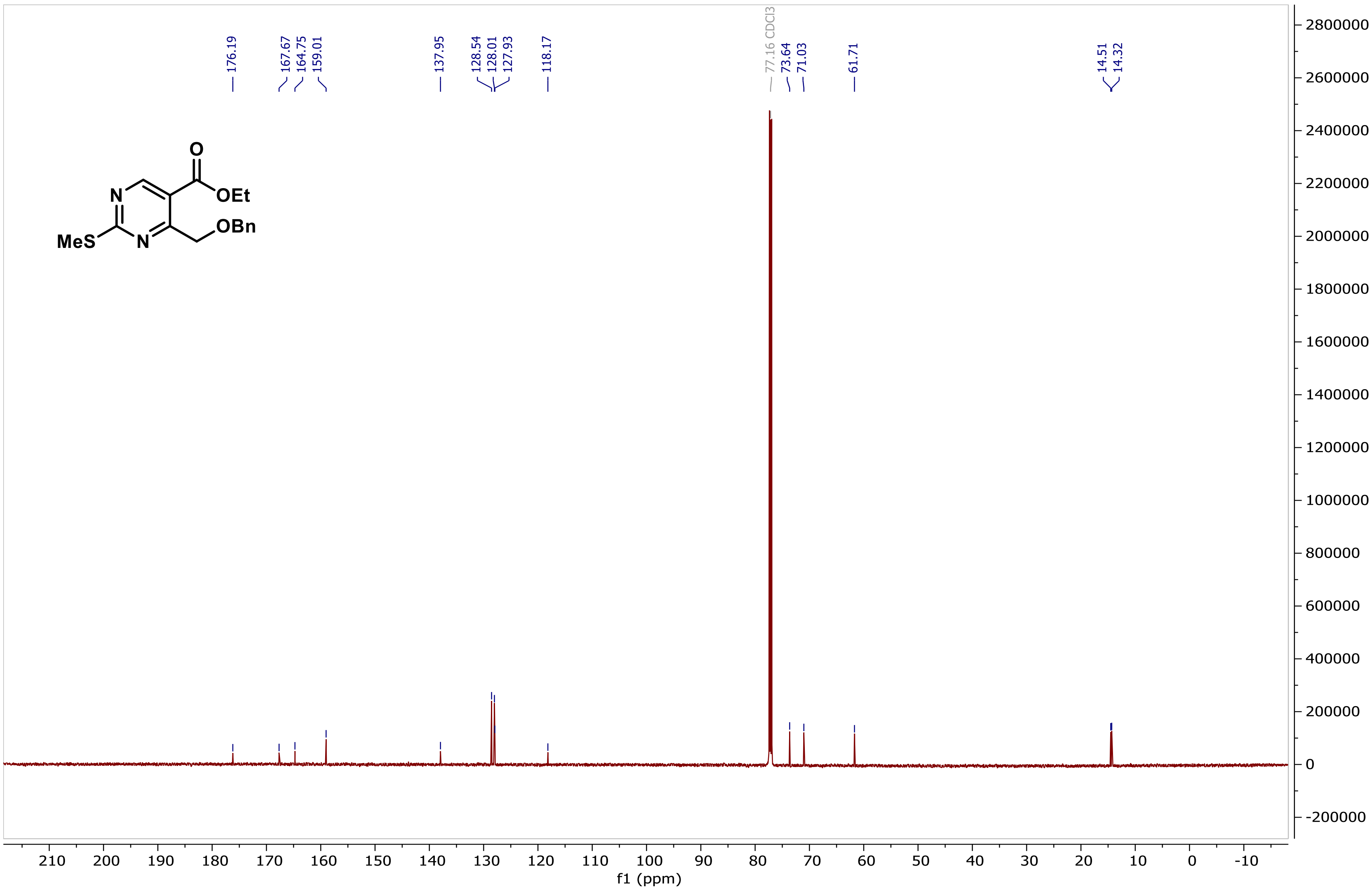
Compound 18, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



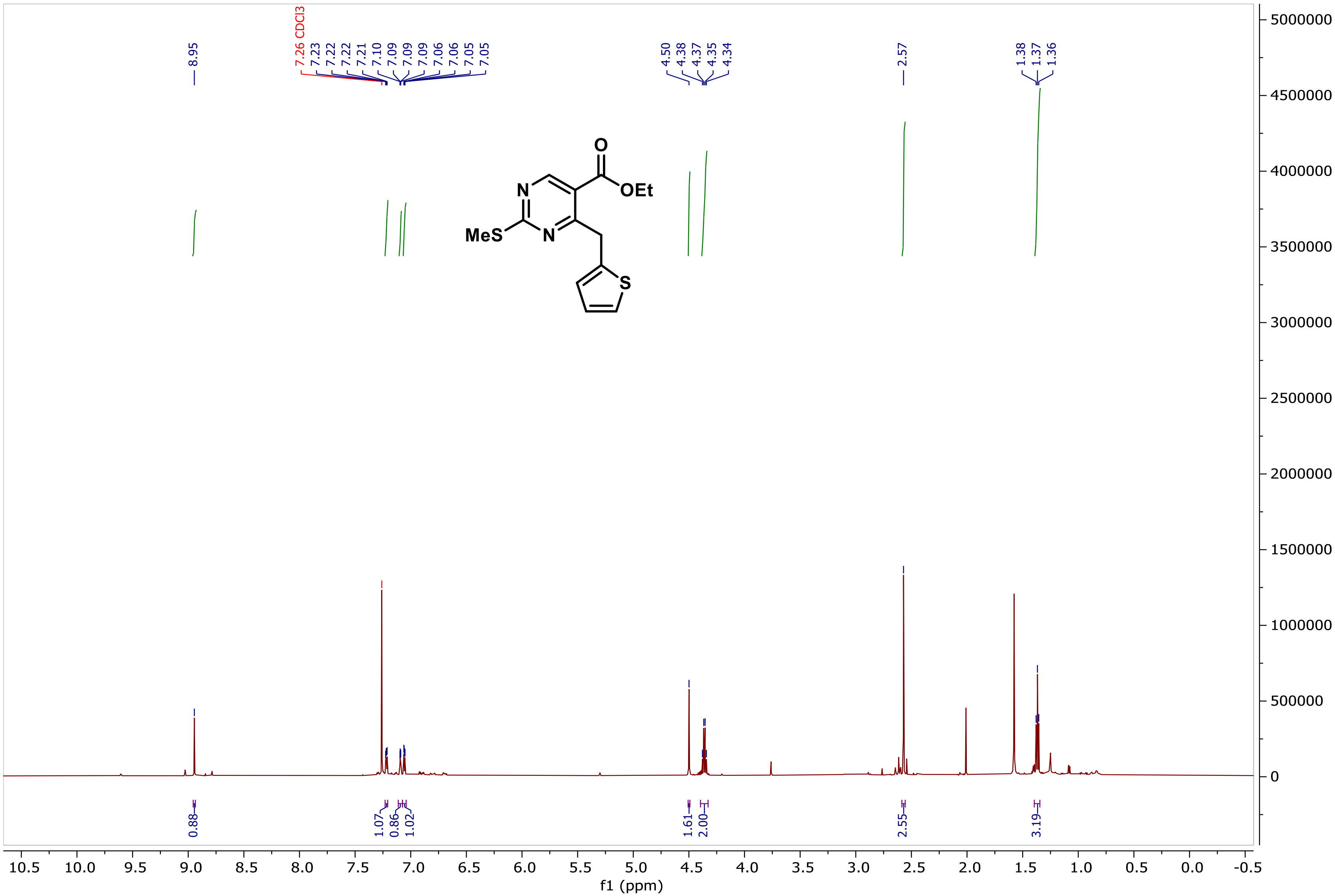
Compound 19, ^{1}H NMR ($CDCl_3$, 600 MHz)



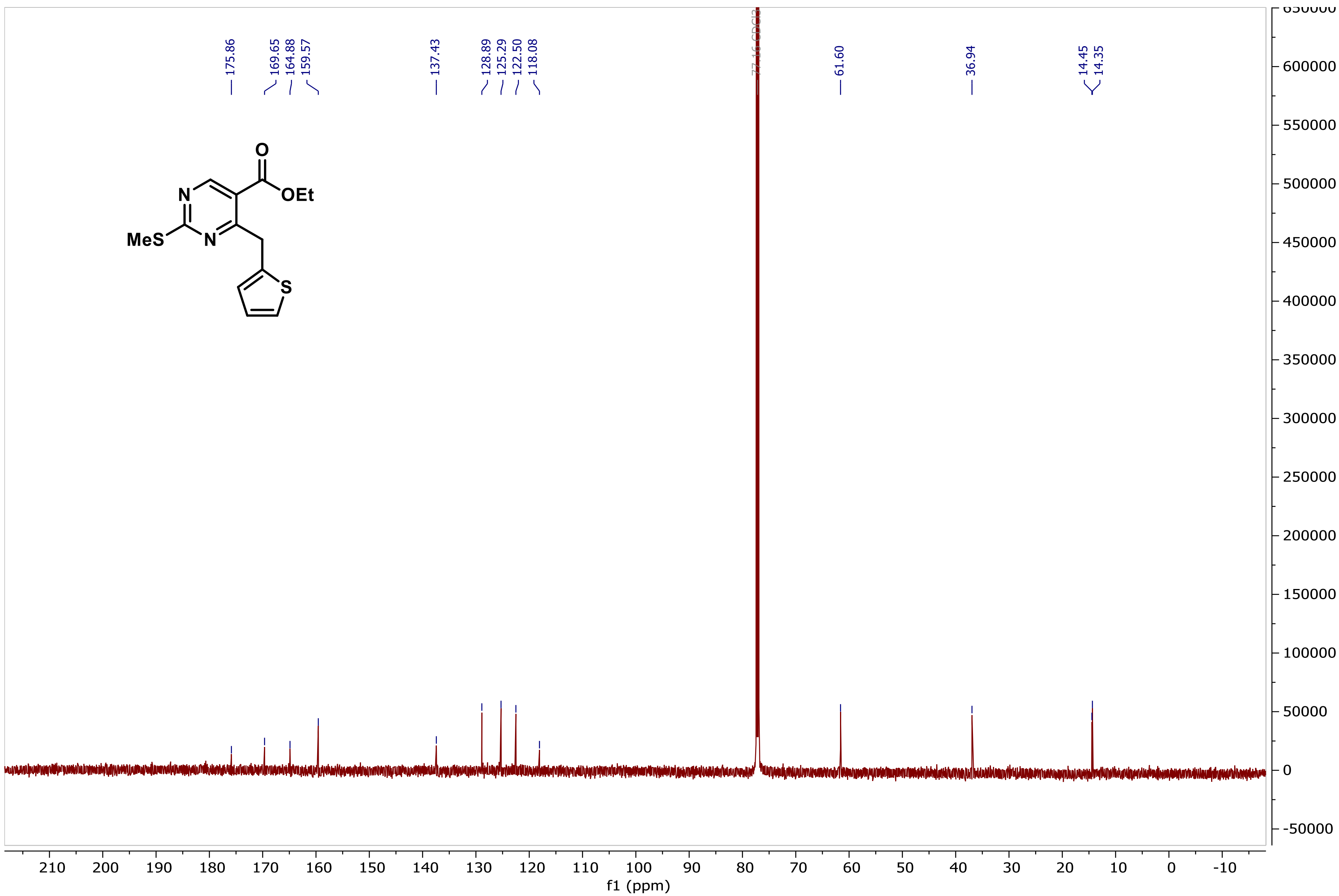
Compound 19, $^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



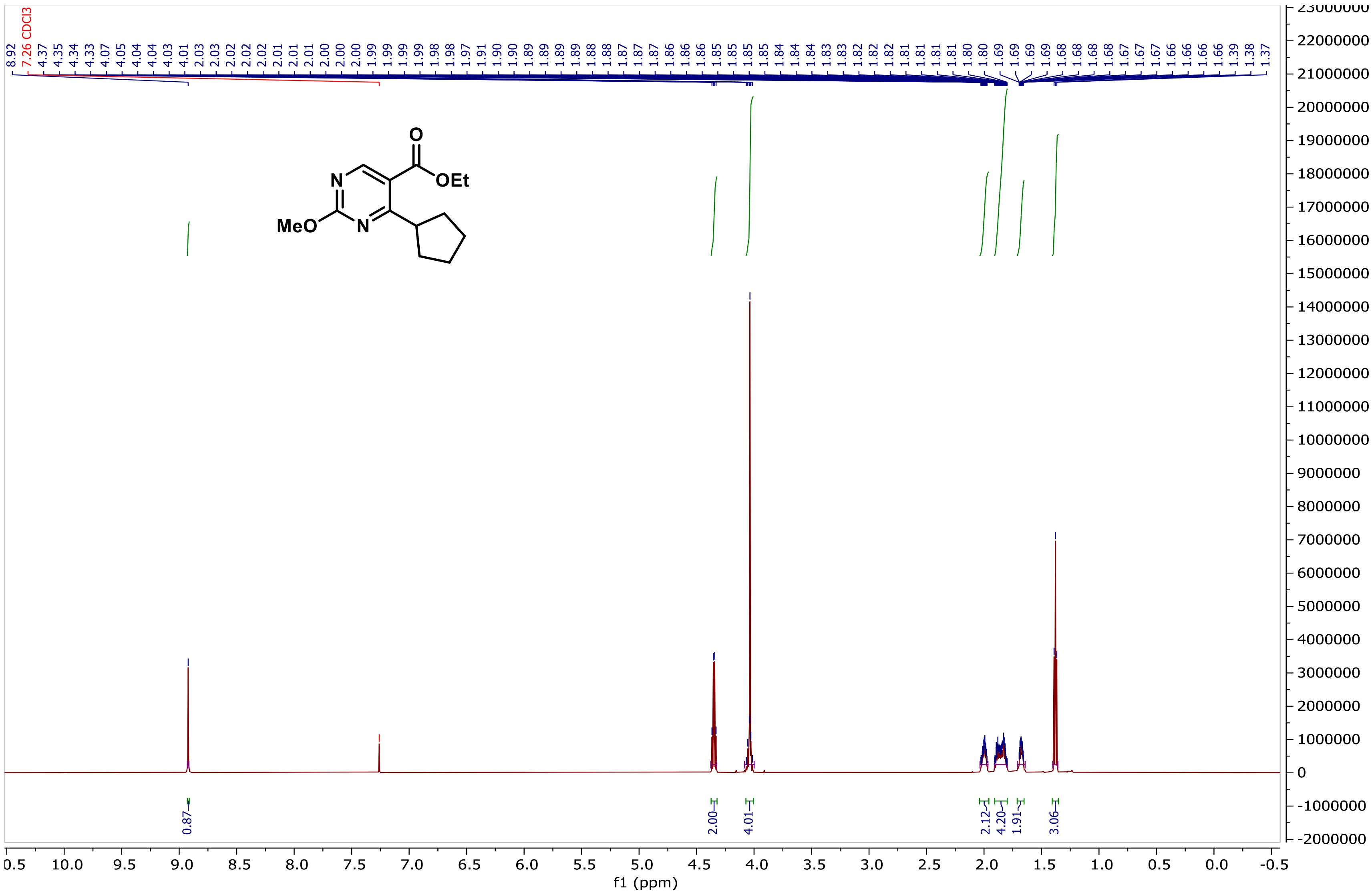
Compound 20, ^{1}H NMR ($CDCl_3$, 600 MHz)



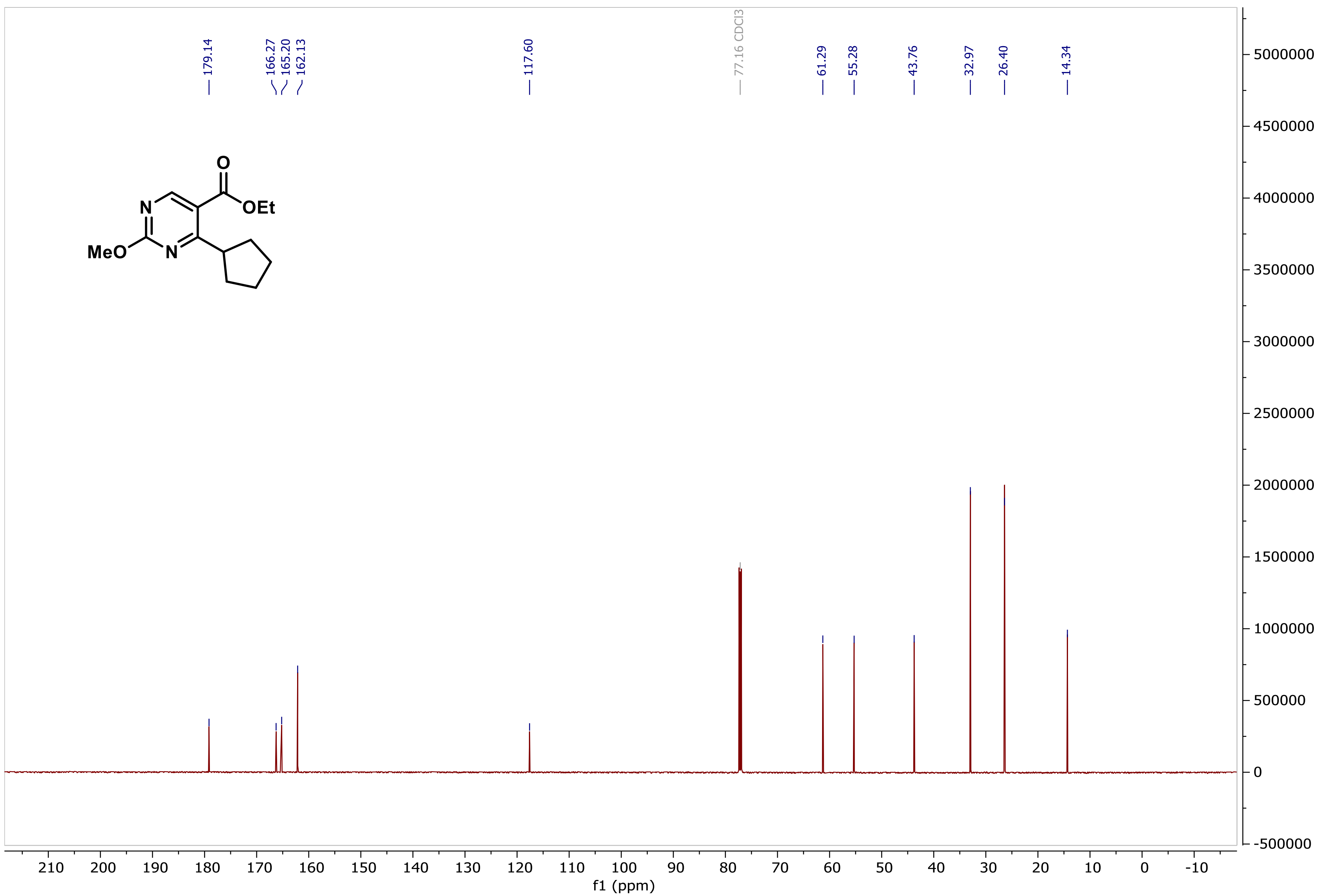
Compound 20, $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, 151 MHz)



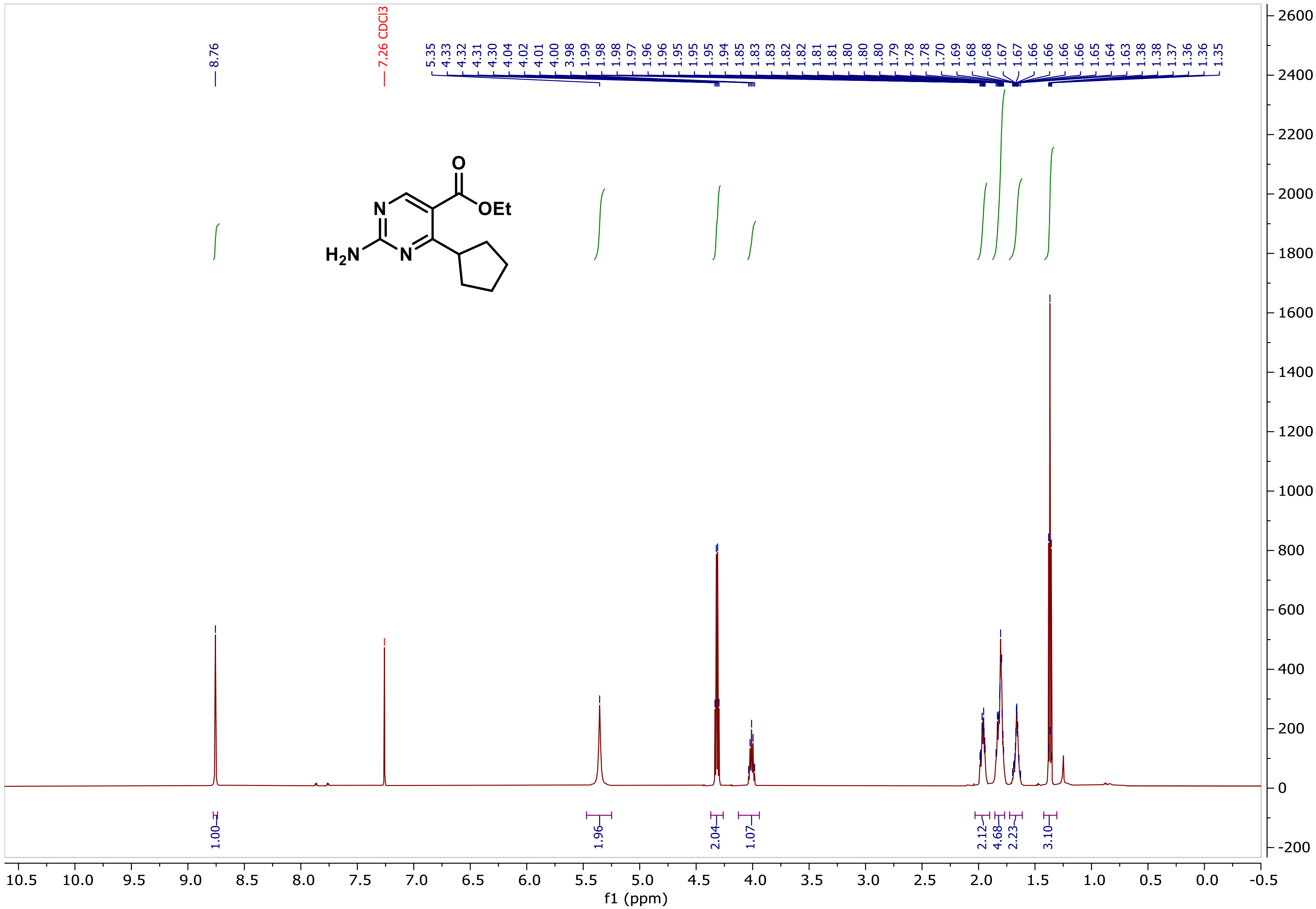
Compound 23, ^{1}H NMR ($CDCl_3$, 600 MHz)



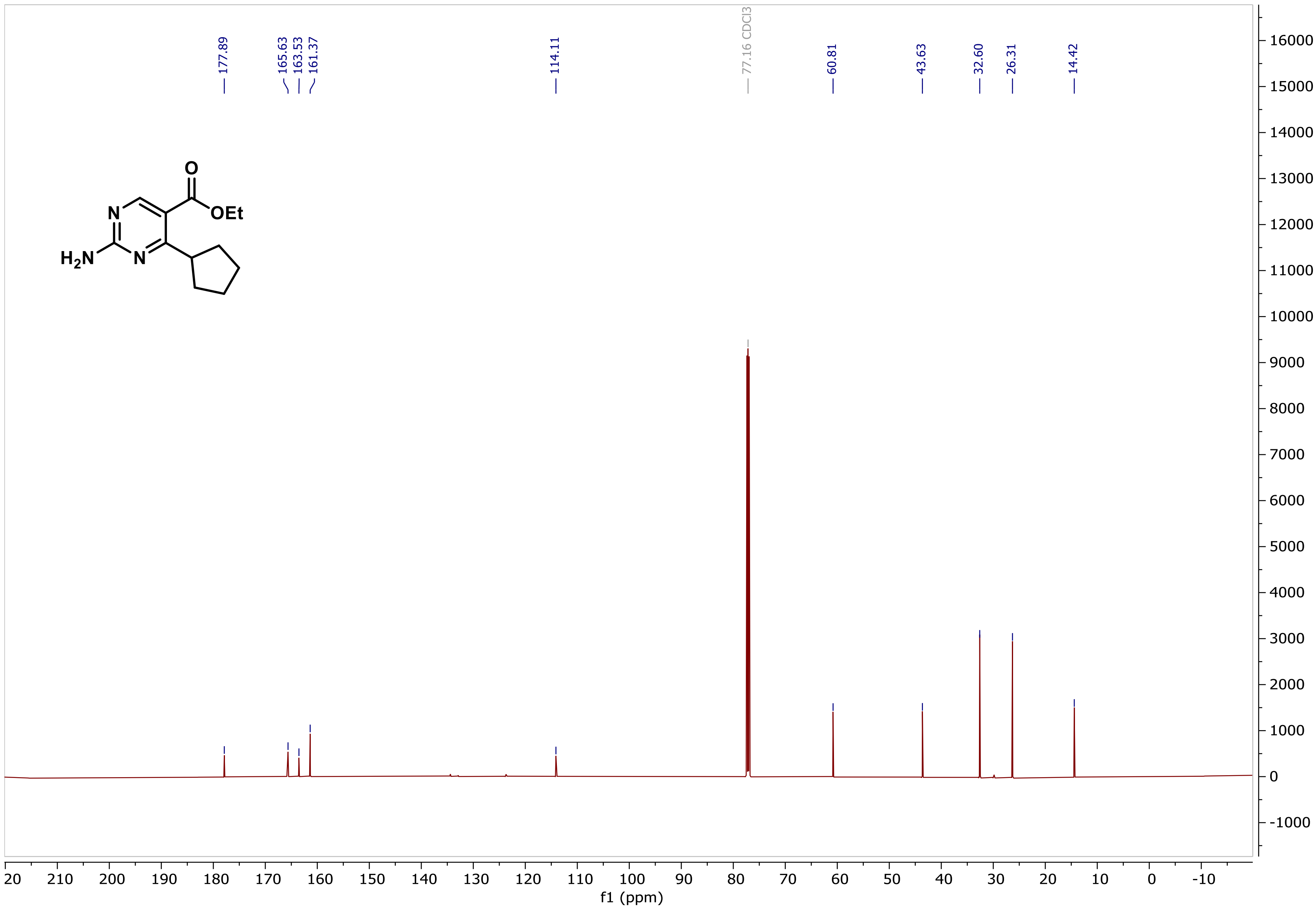
Compound 23, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



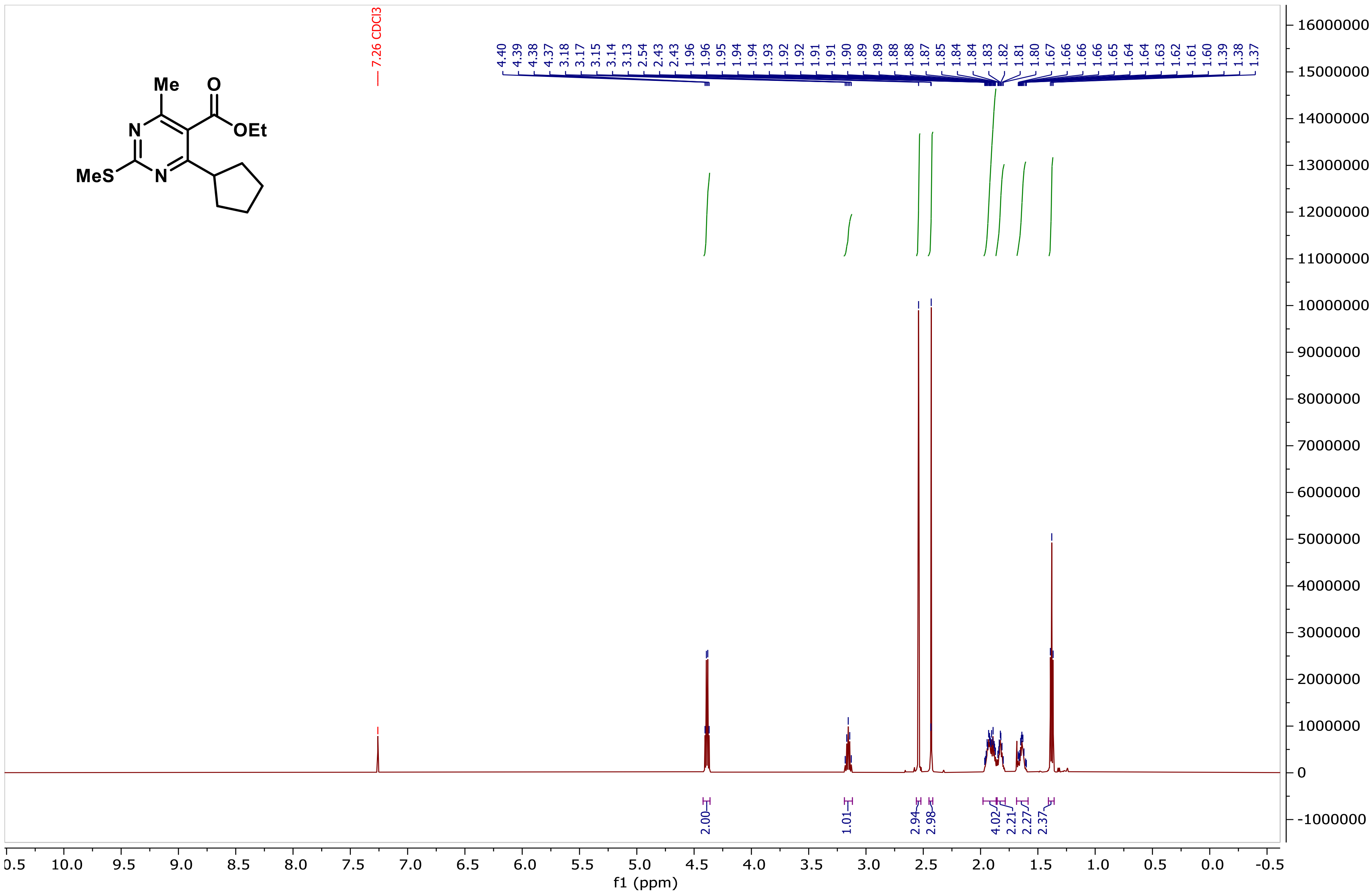
Compound 24, ^{1}H NMR ($CDCl_3$, 600 MHz)



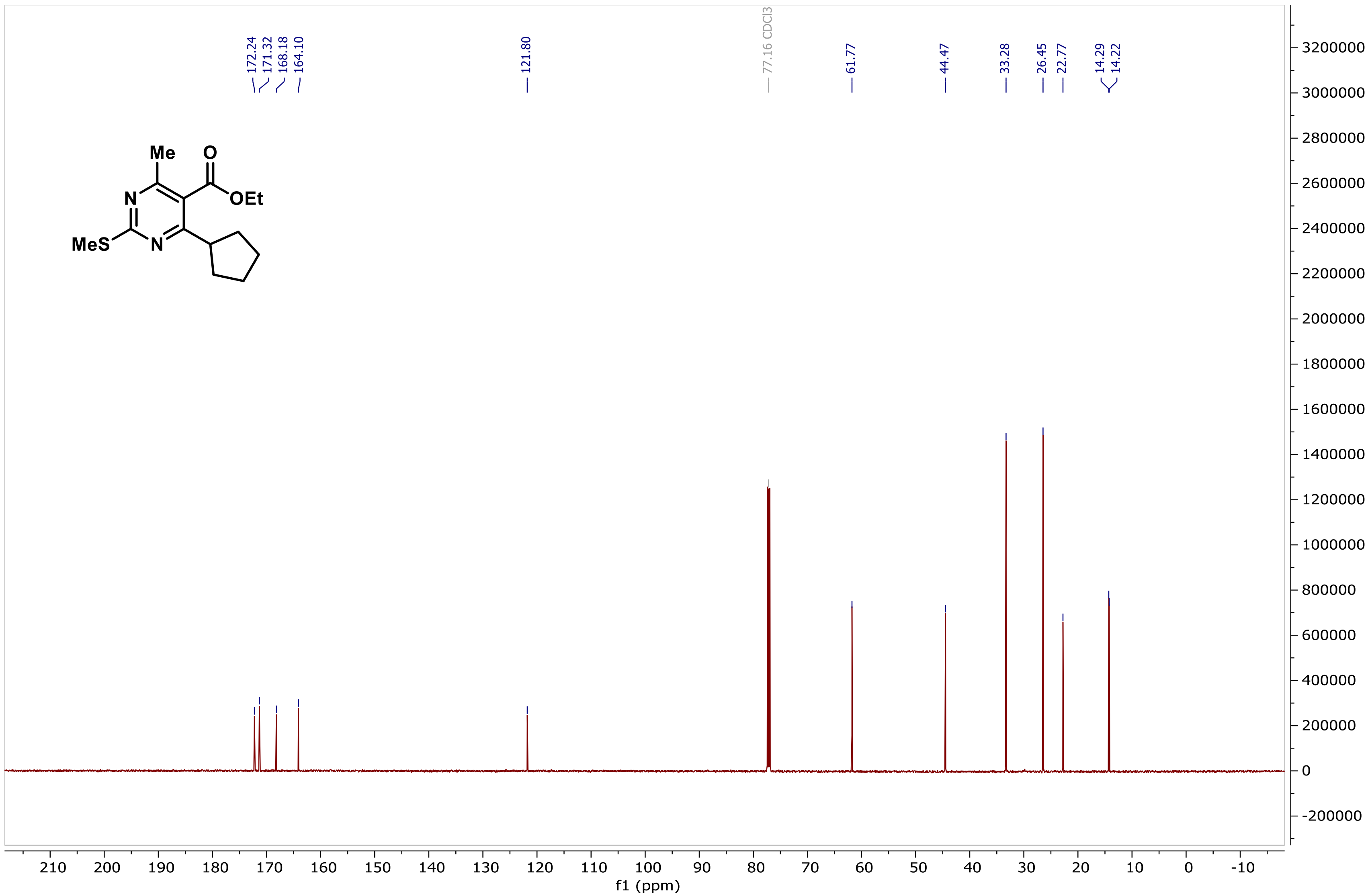
Compound 24, $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, 151 MHz)



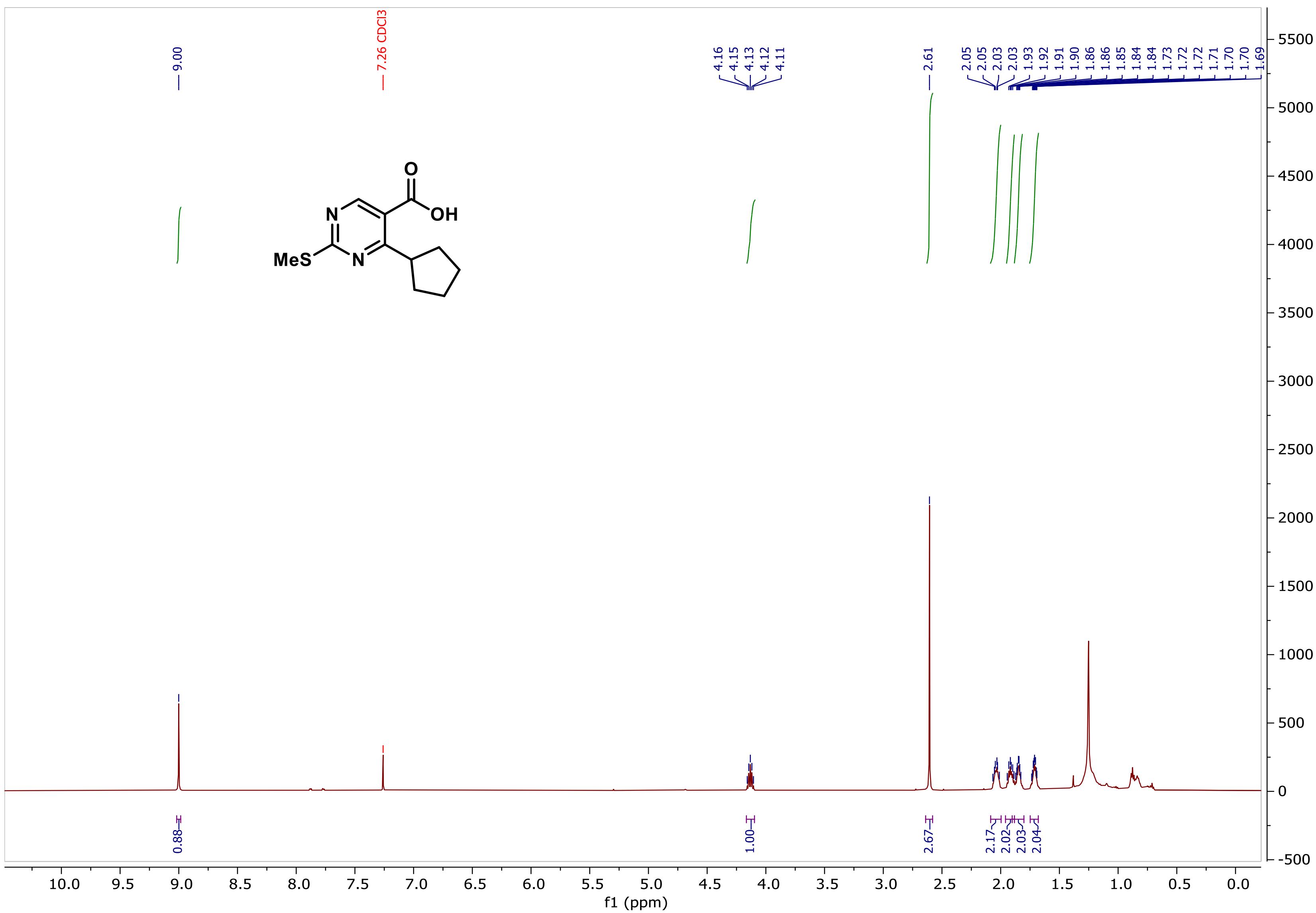
Compound 25, ^{1}H NMR ($CDCl_3$, 600 MHz)



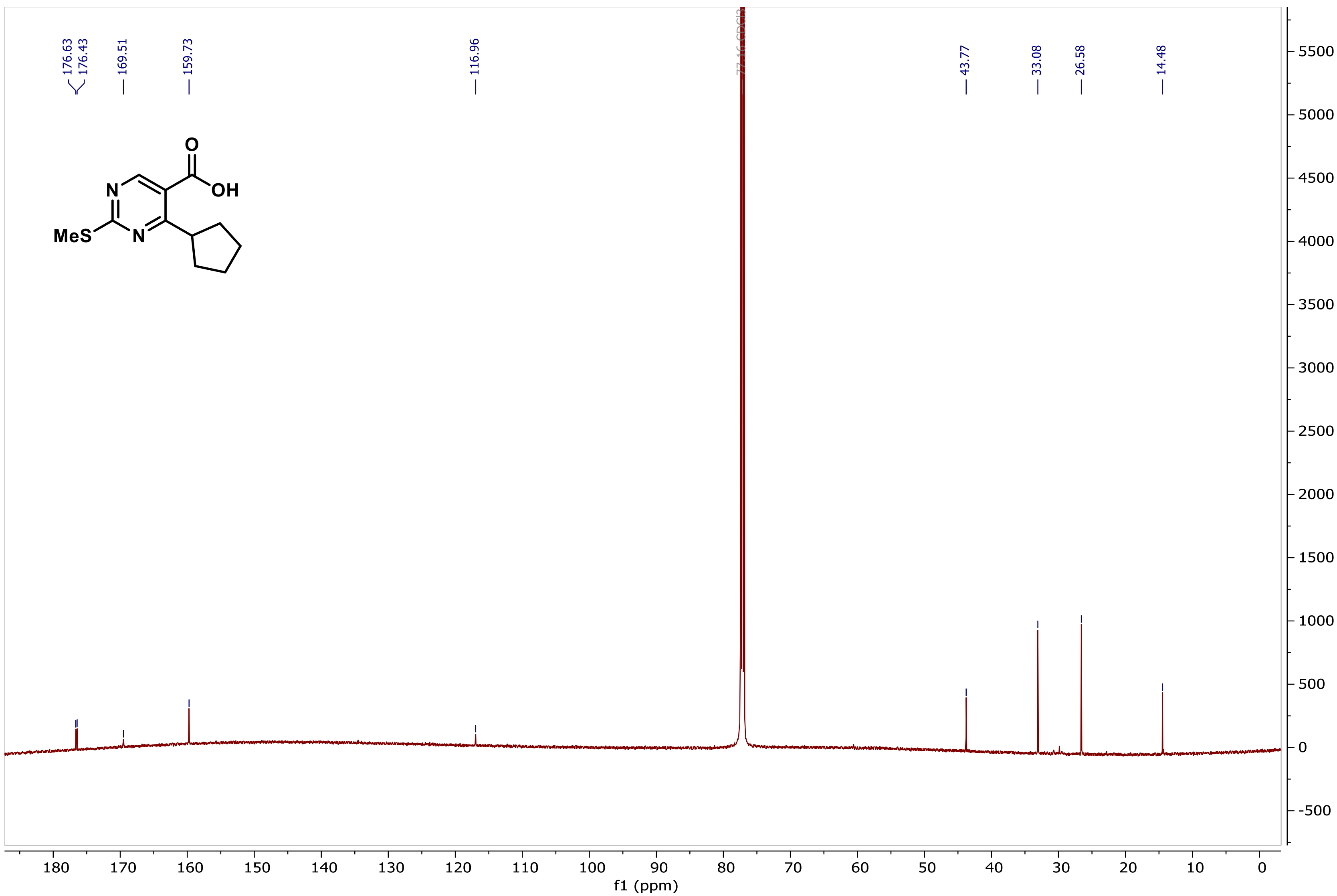
Compound 25, $^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



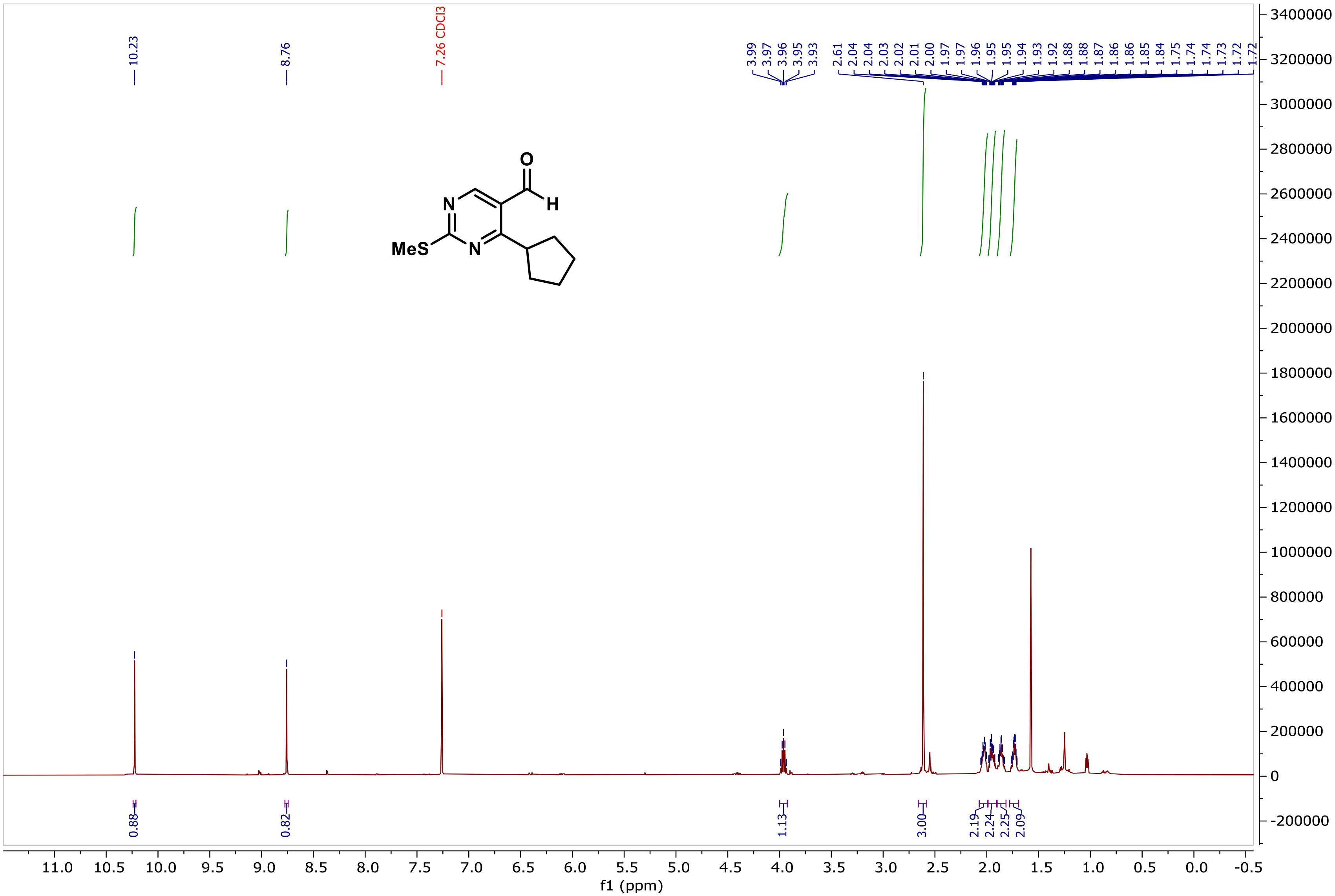
Compound 26, ^{1}H NMR ($CDCl_3$, 600 MHz)



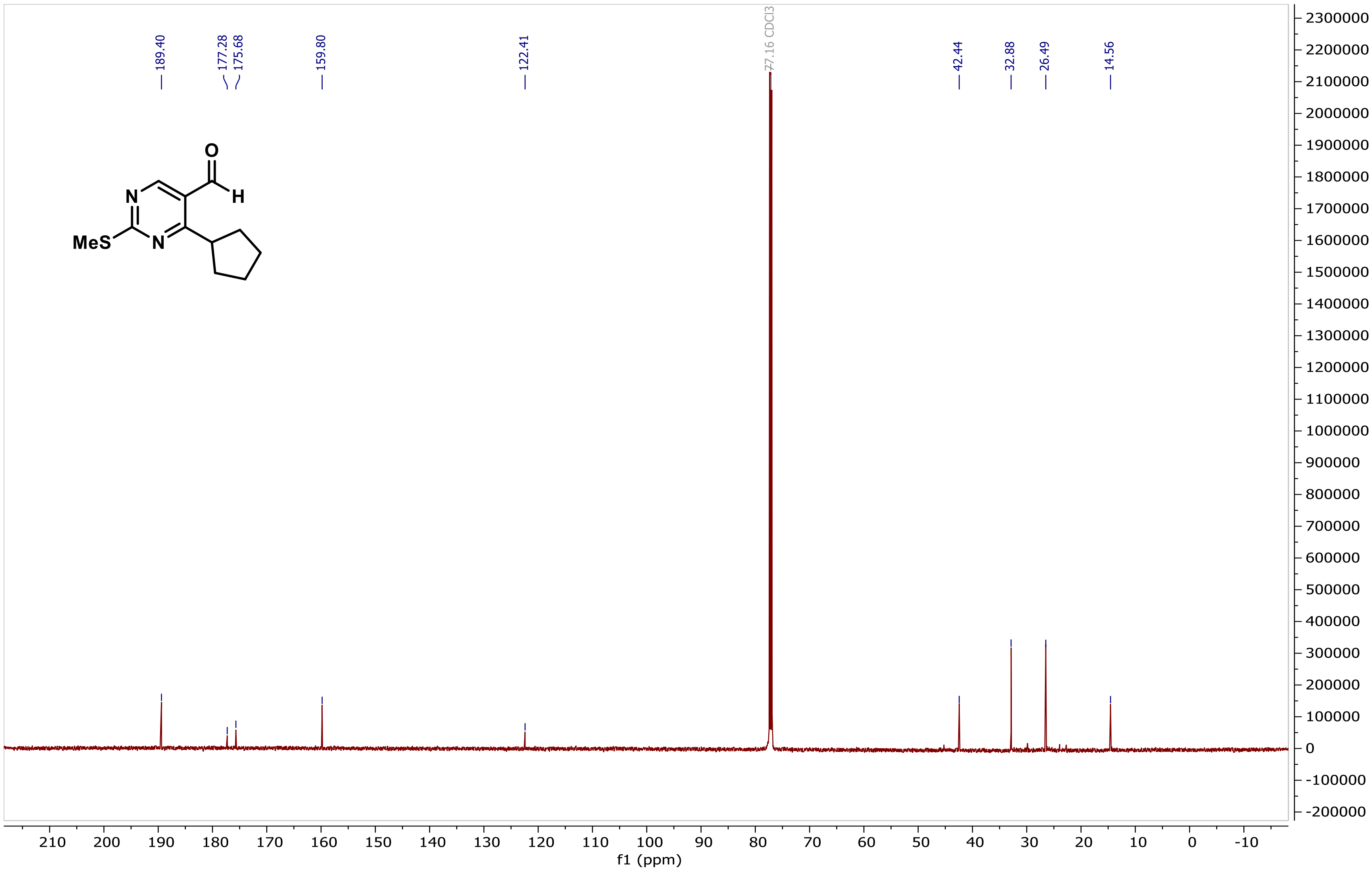
Compound 26, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



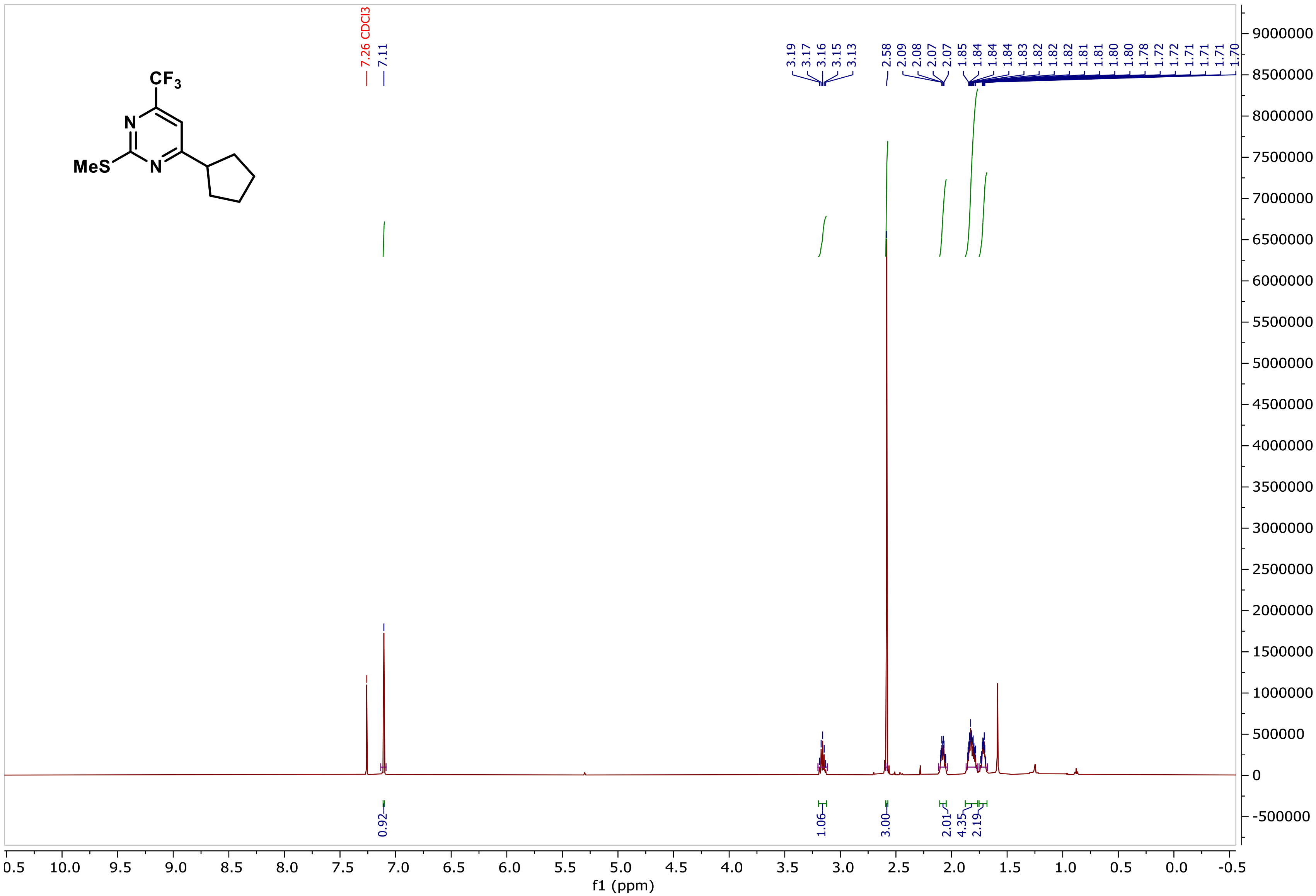
Compound 27, ^{1}H NMR ($CDCl_3$, 600 MHz)



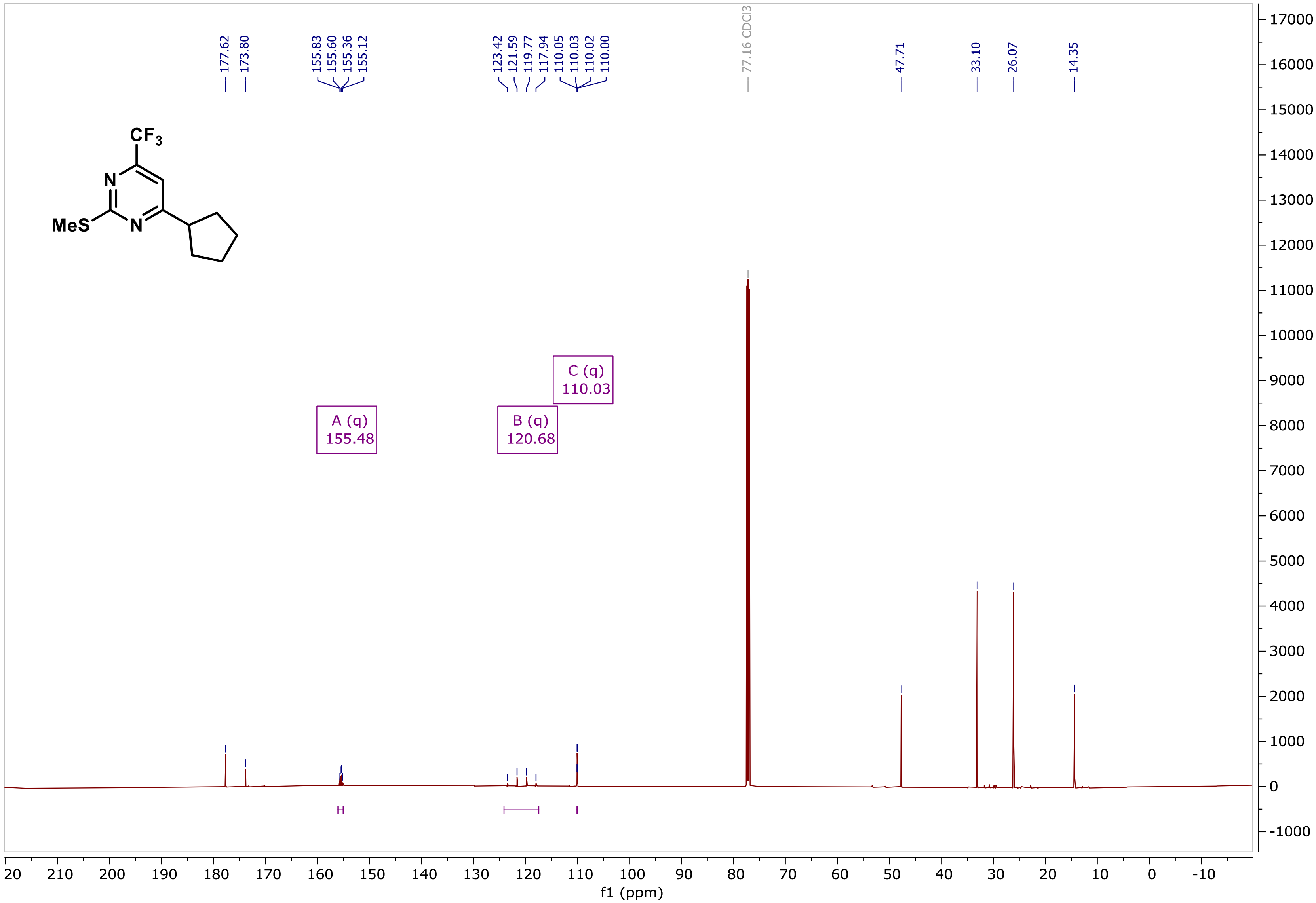
Compound 27, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



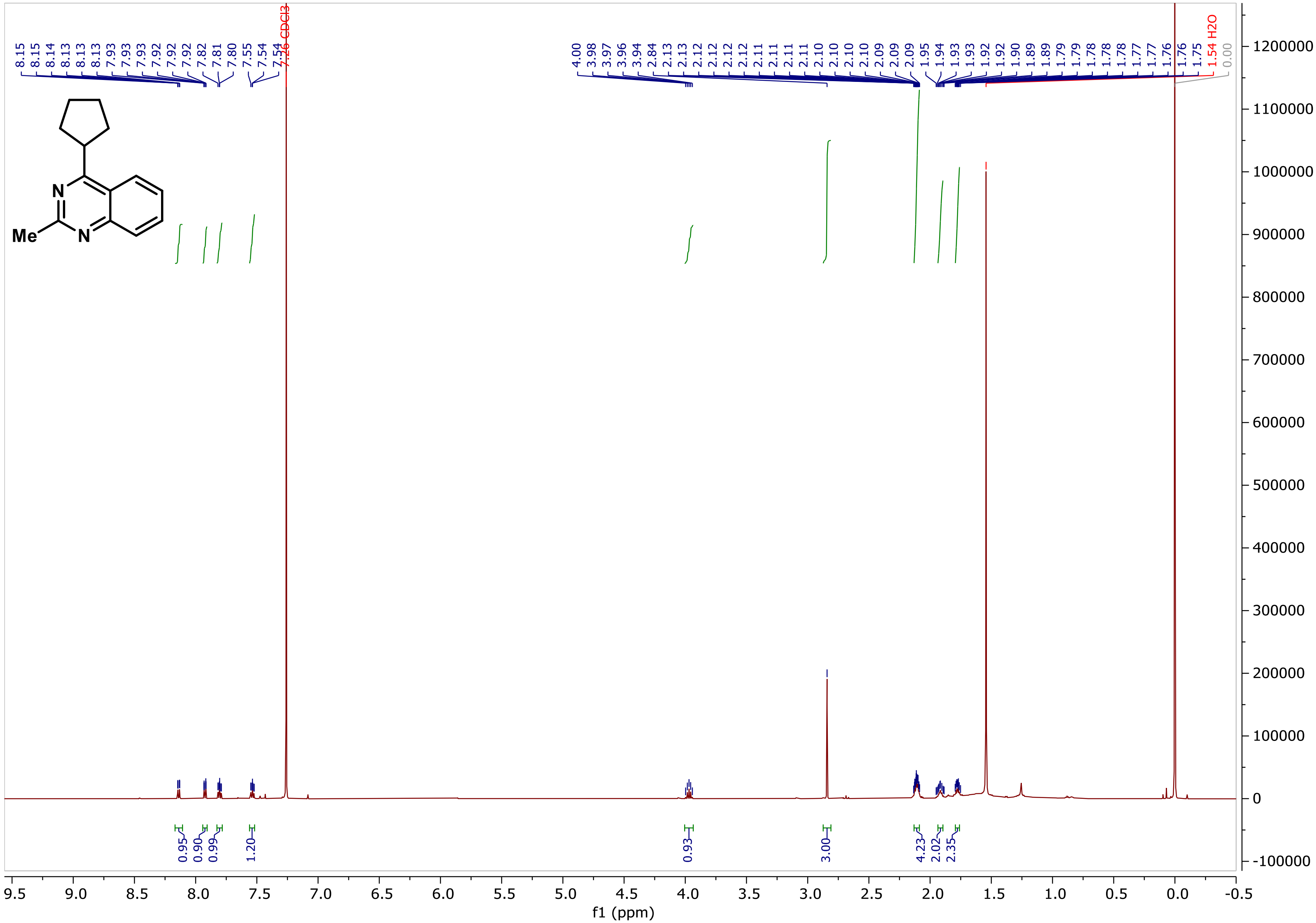
Compound 28, ^{1}H NMR ($CDCl_3$, 600 MHz)



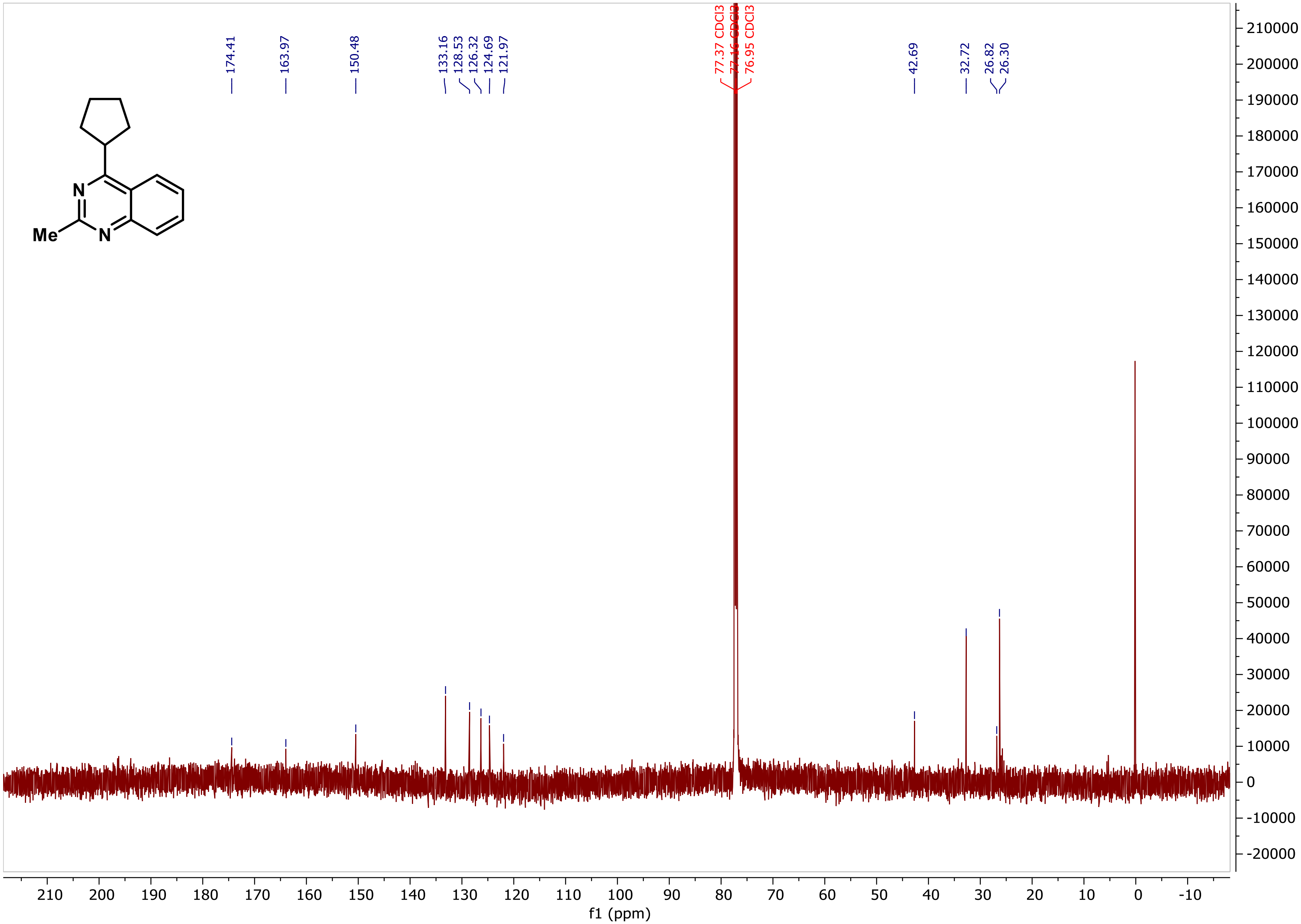
Compound 28, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



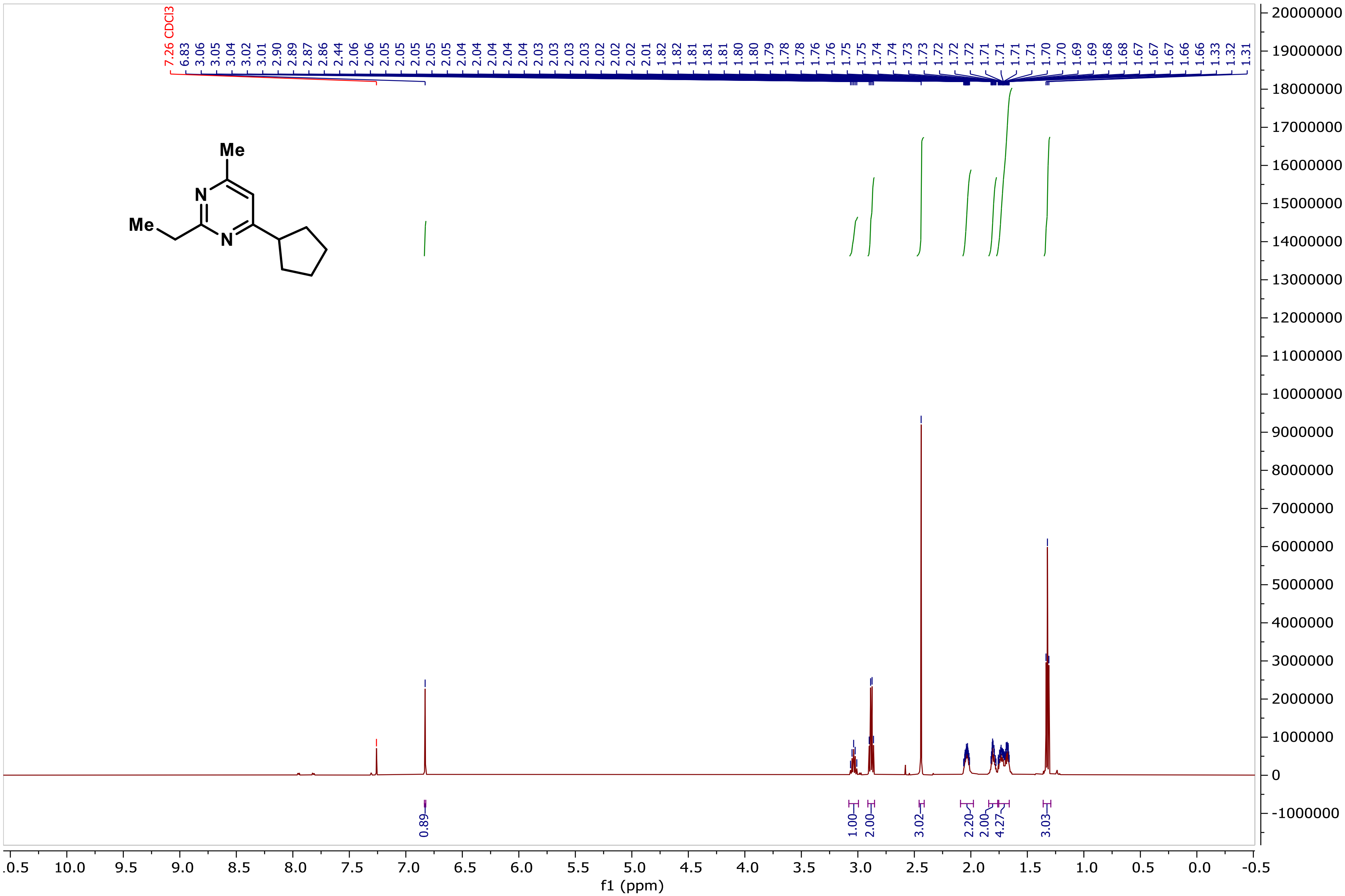
Compound 29, ^{1}H NMR ($CDCl_3$, 600 MHz)



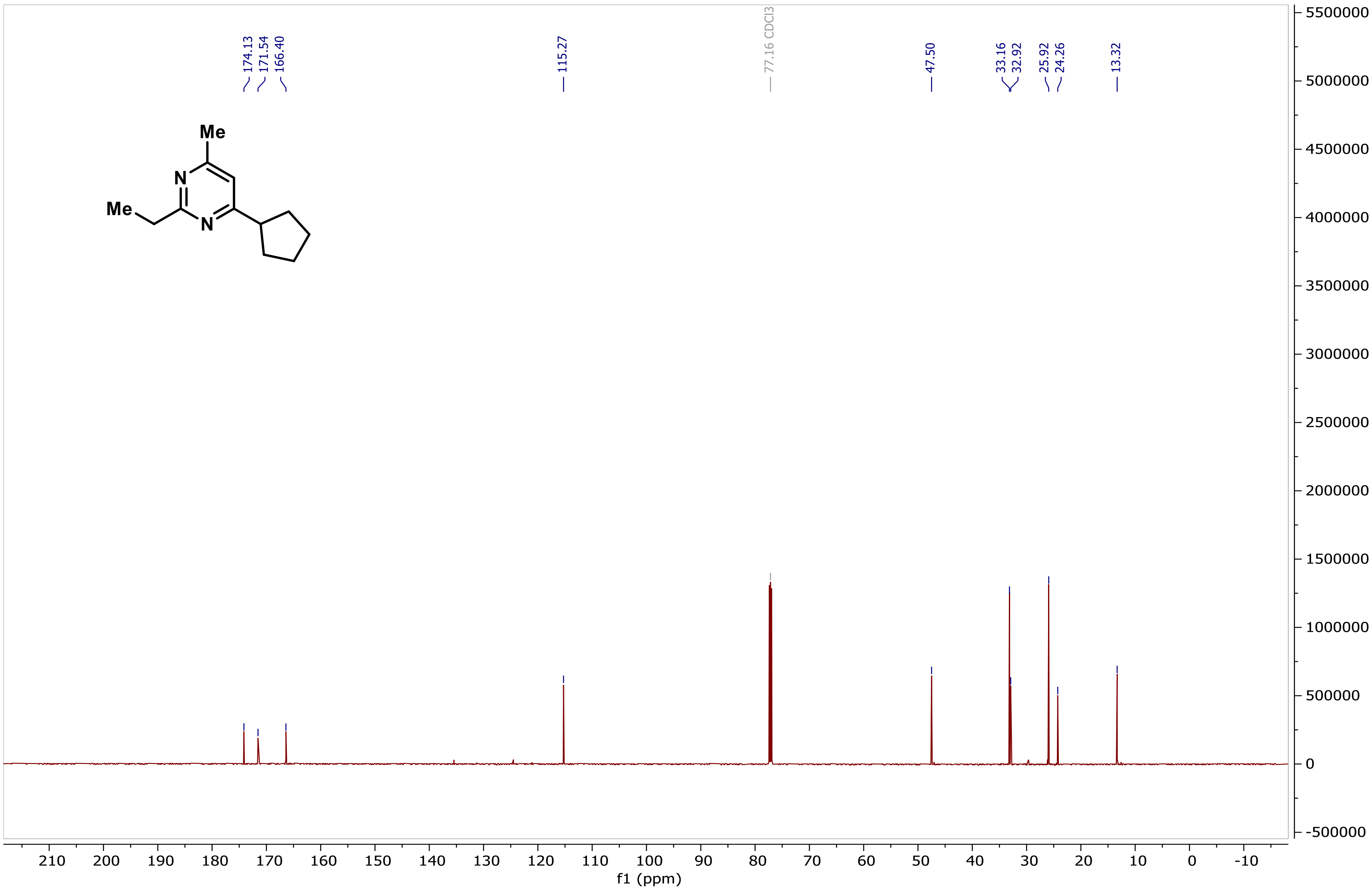
Compound 29, $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, 151 MHz)



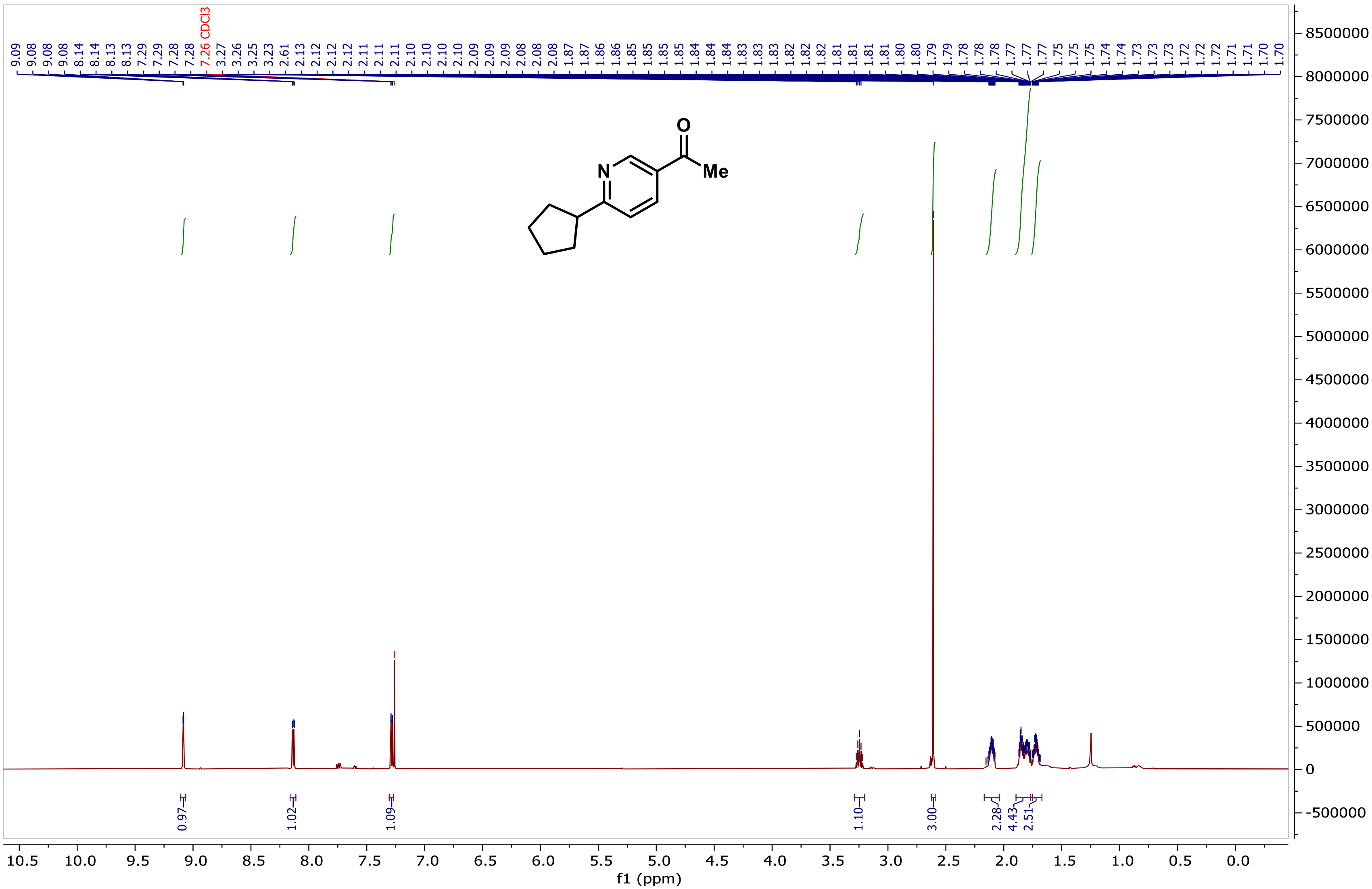
Compound 31, ^{1}H NMR ($CDCl_3$, 600 MHz)



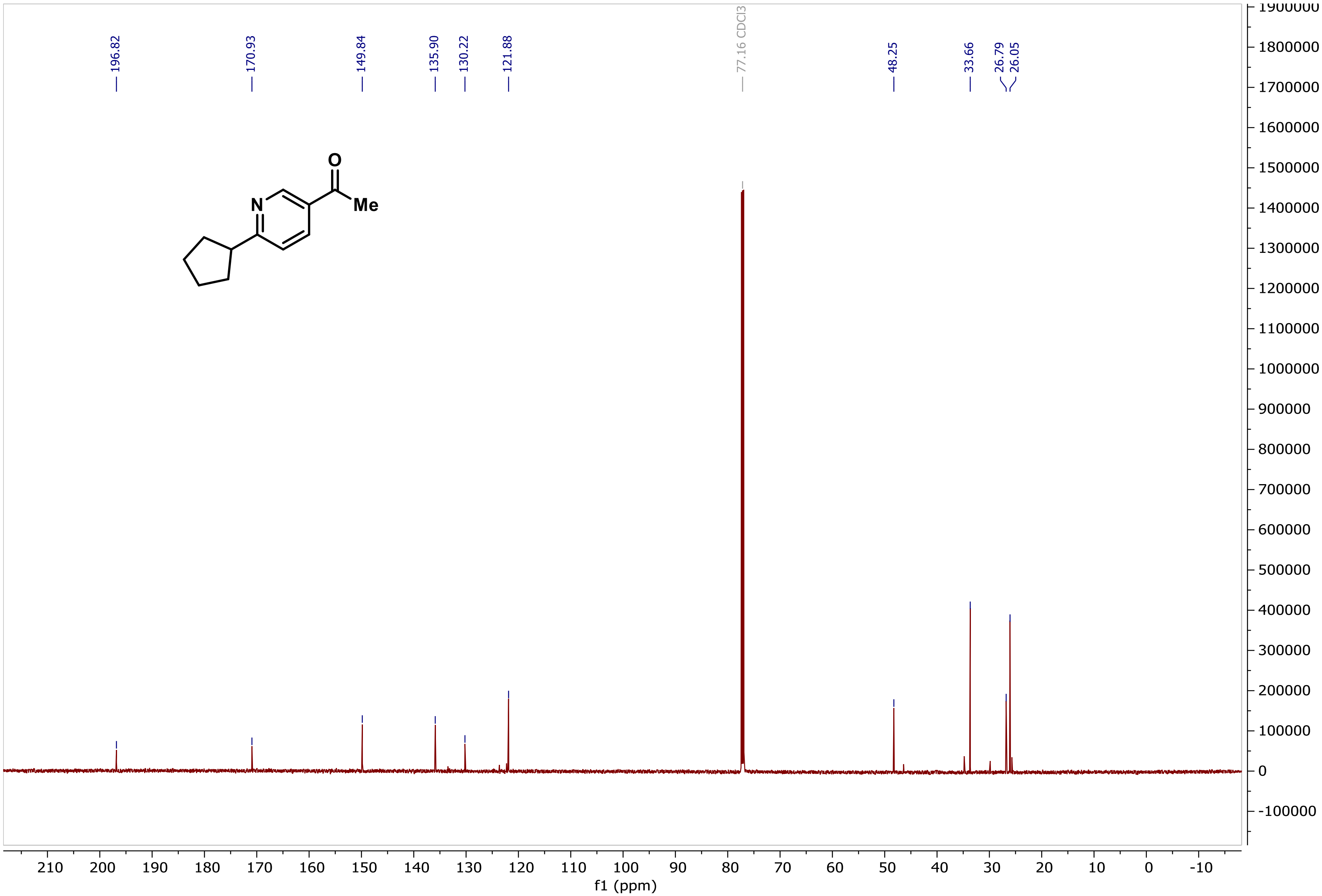
Compound 31, $^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



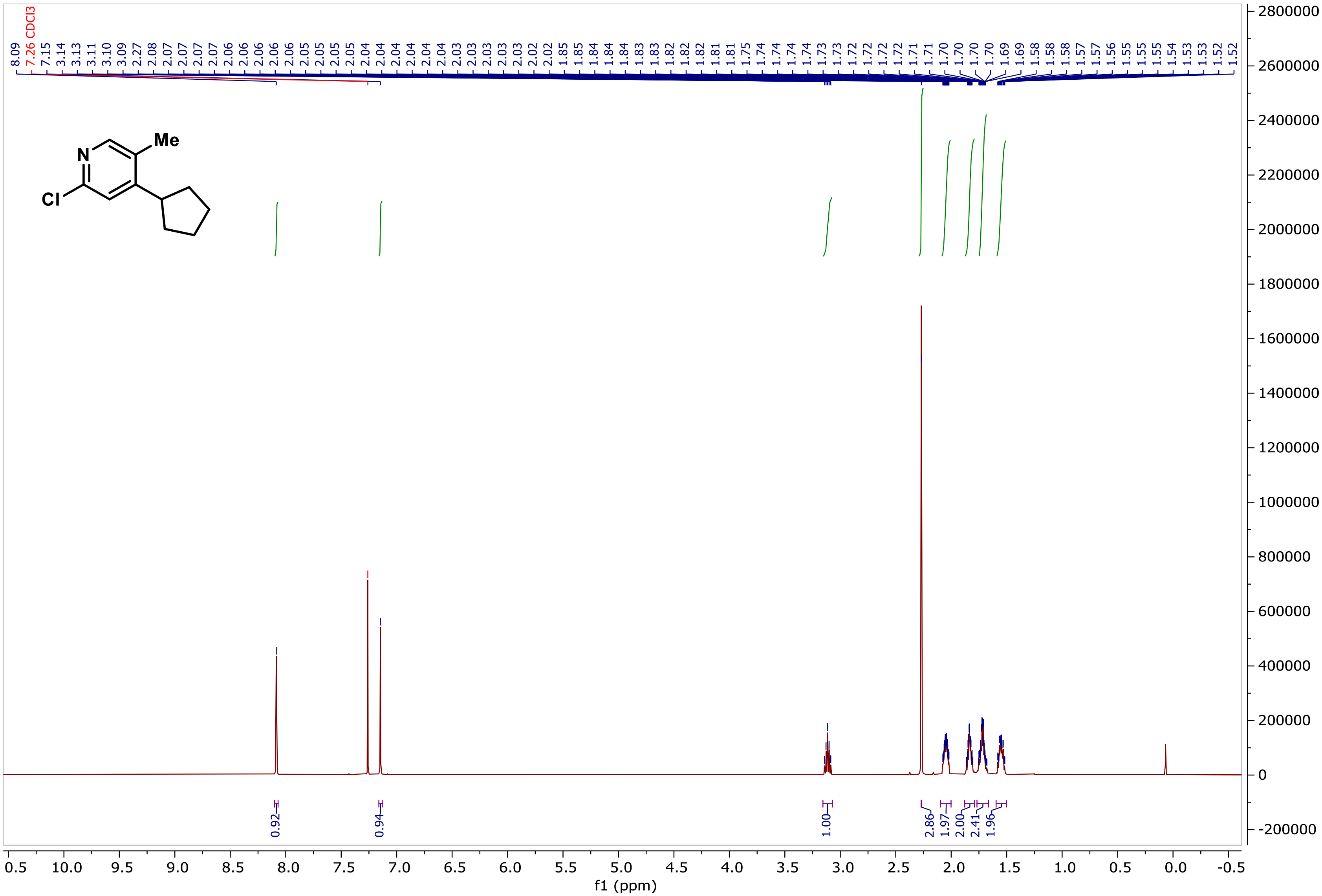
Compound 32, ^{1}H NMR ($CDCl_3$, 600 MHz)



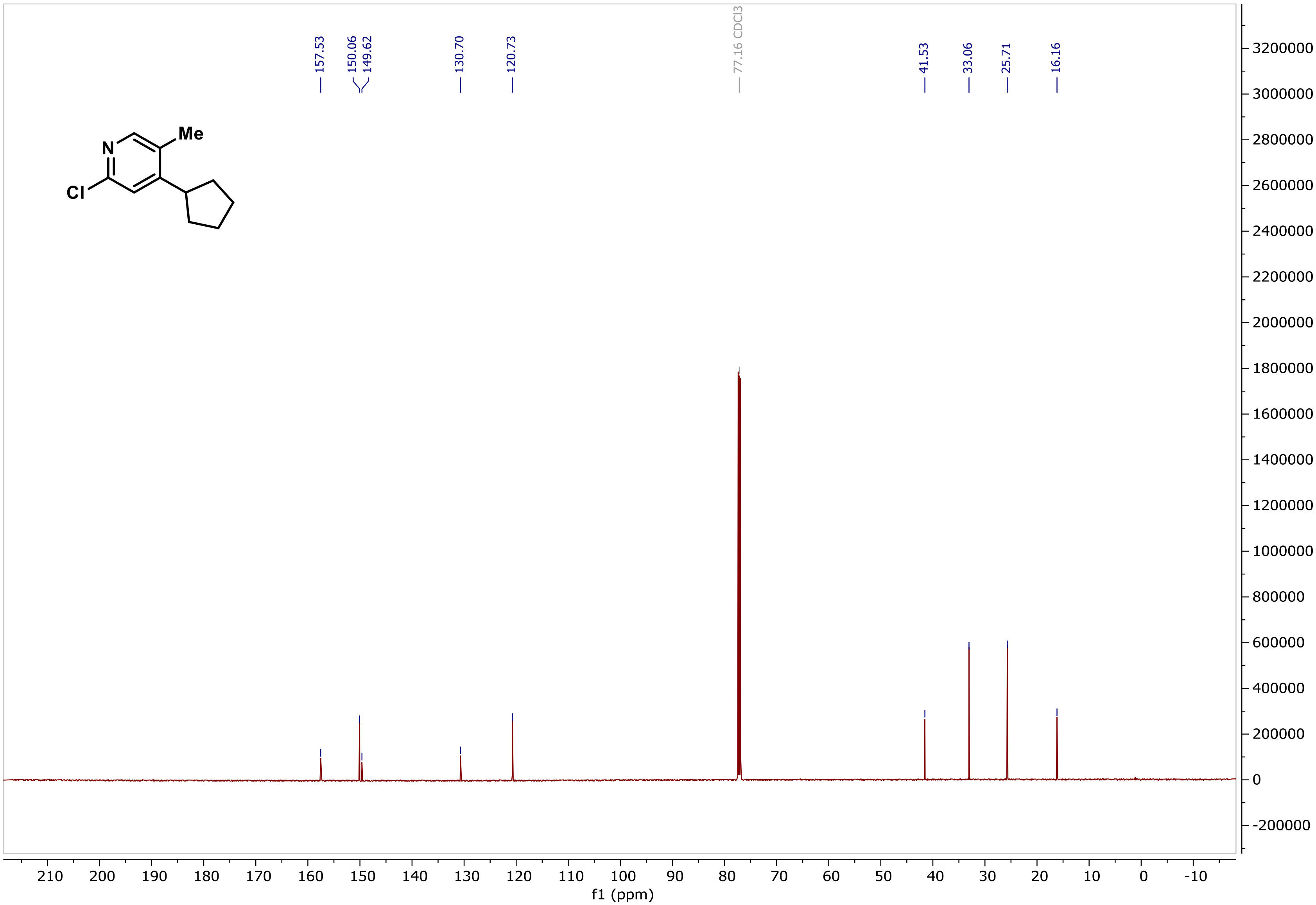
Compound 32, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



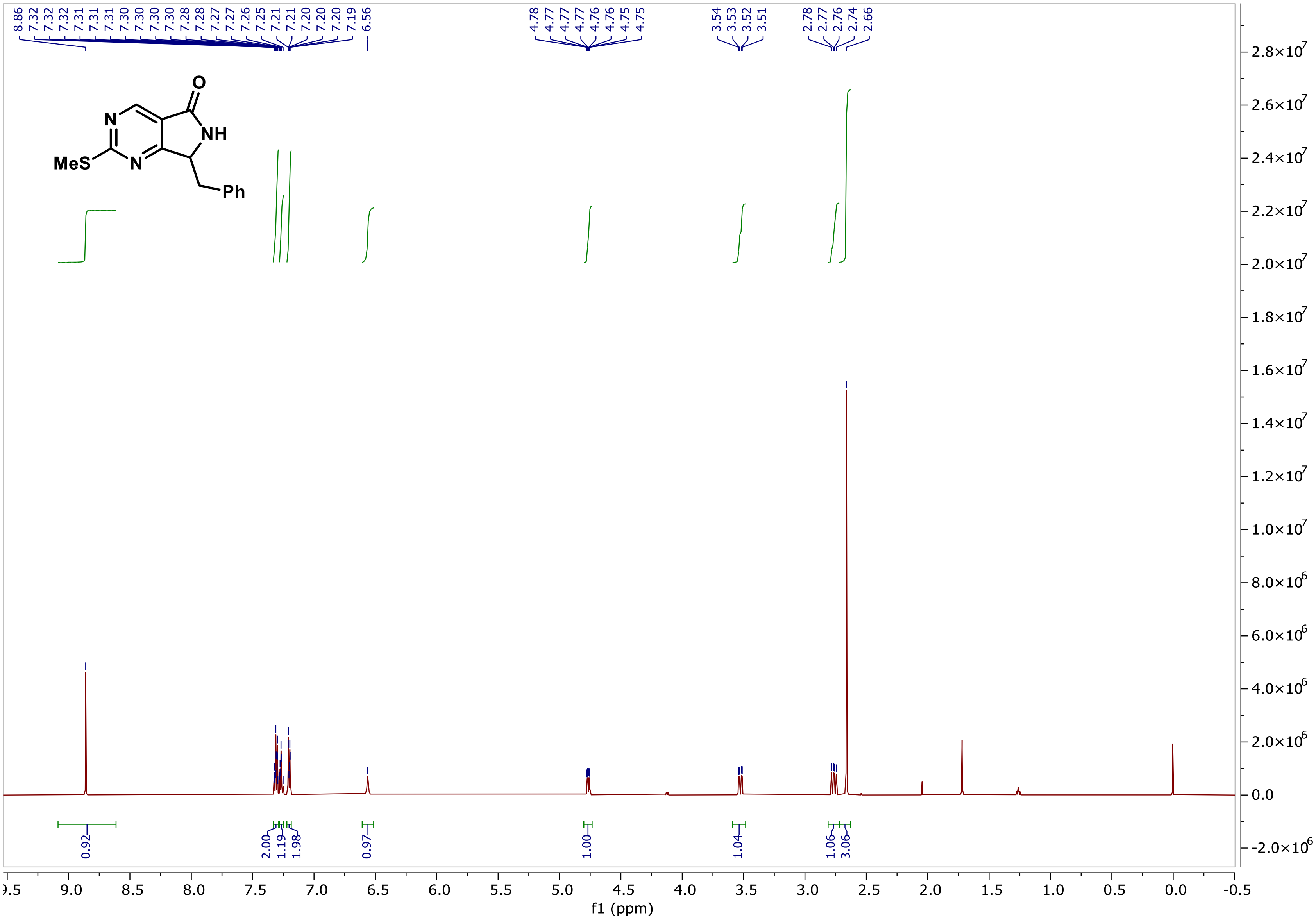
Compound 33, ^{1}H NMR ($CDCl_3$, 600 MHz)



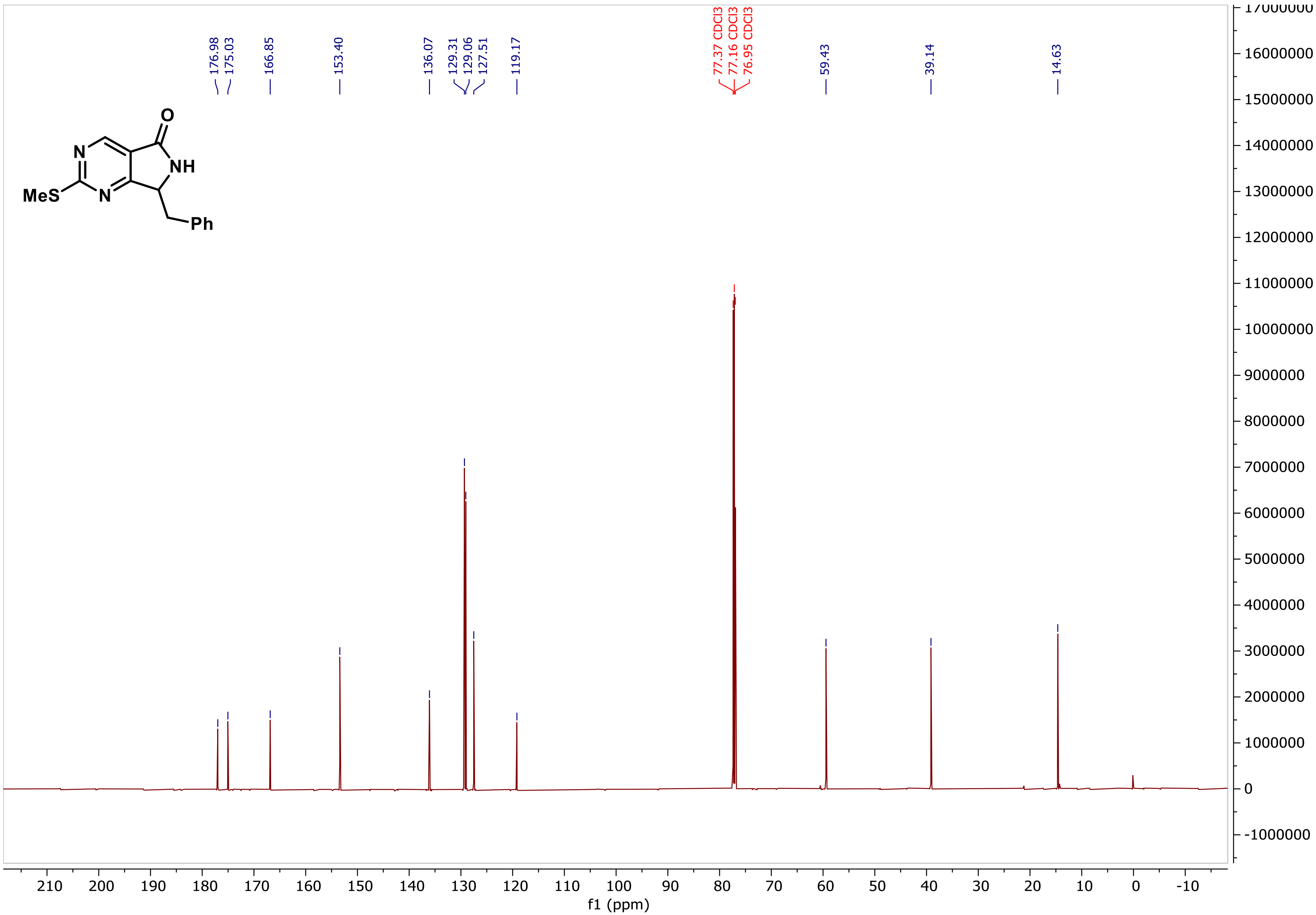
Compound 33, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



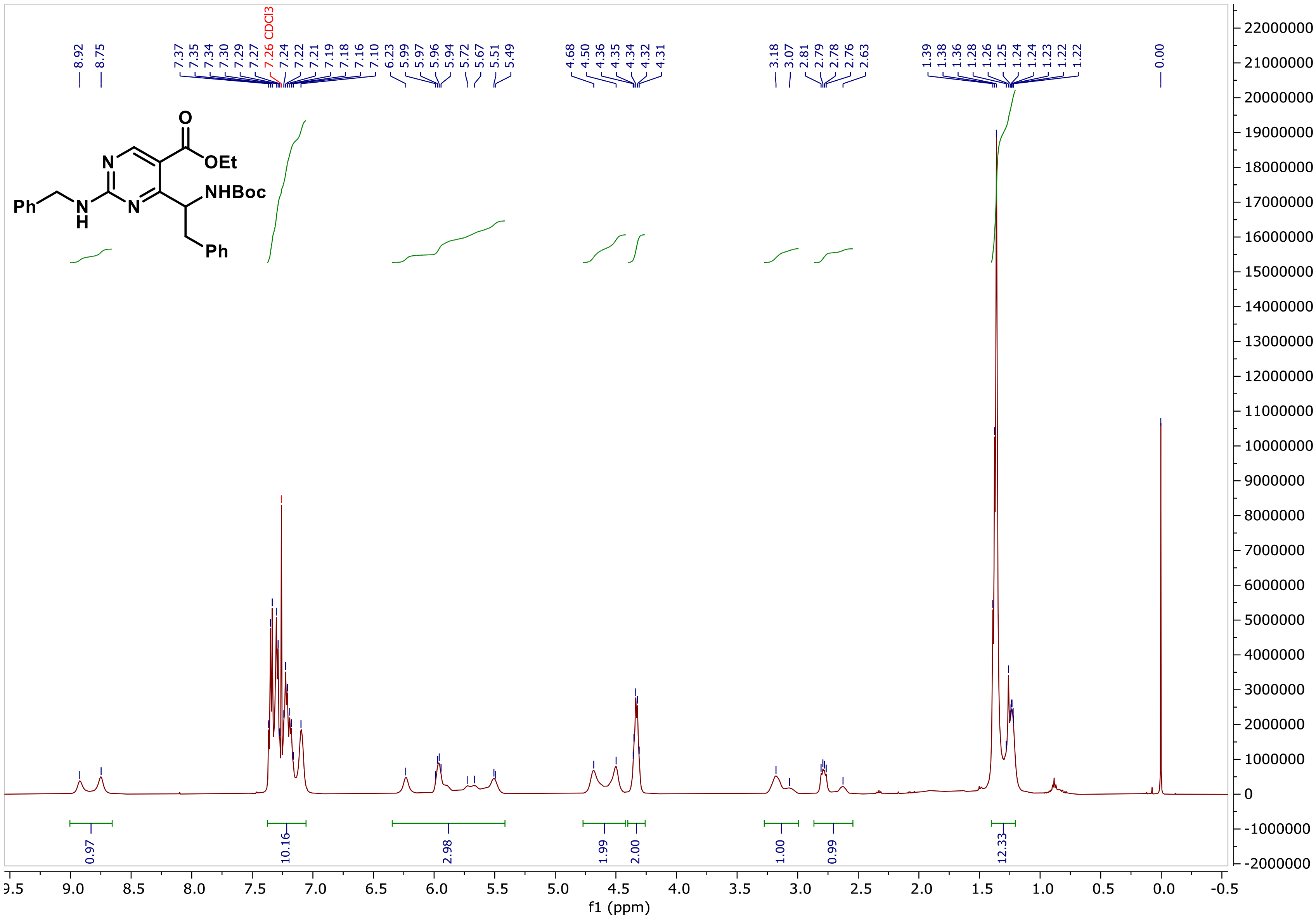
Compound 34, ^1H NMR ($CDCl_3$, 600 MHz)



Compound 34, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



Compound 35, ^{1}H NMR ($CDCl_3$, 500 MHz)



Compound 35, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz)