Supplementary Information

Catalyst- and additive-free syntheses of rhodanine and S-alkyl dithiocarbamate derivatives from sulfoxonium ylides

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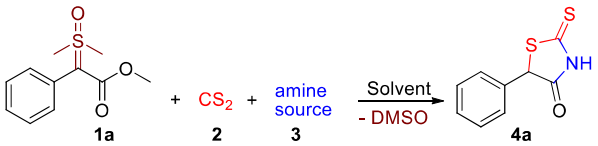
1. General information: All the chemicals and solvents were used as received without further purification. Organic extracts were dried over anhydrous Na_2SO_4. Progress of the reactions was monitored by TLC using precoated aluminium plates of Merck Kieselgel 60 F254. Column chromatography was performed on silica gel (100-200 mesh) using a mixture of n-hexane/ethyl acetate. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) on JEOL ECS and Brucker operating at 500/126 and 600/151 MHz, respectively. Chemical shifts are reported in δ (ppm), referenced to TMS and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet) etc. The coupling constants *J*, are reported in Hertz (Hz). Mass spectra were recorded on SCIEX X500R QTOF (TOF-MS).

2. Table S1. Synthesis of rhodanines: Optimization[a]



entry	amines	solvent	temp (°C)	time (h)	yield[b] of 4a (%)
1[c]	$NH_3.H_2O$	MeCN	rt	4	43
2[c]	$NH_3.H_2O$	DMF	rt	4	36
3[c]	$NH_3.H_2O$	DMSO	rt	4	27
4[c]	$NH_3.H_2O$	Toluene	rt	4	38
5[c]	$NH_3.H_2O$	CH_2Cl_2	rt	4	32
6[c]	$NH_3.H_2O$	THF	rt	4	62
7[c]	$NH_3.H_2O$	H_2O	rt	12	0
8[c]	$NH_3.H_2O$	H_2O	100	12	0
9[c]	$NH_3.H_2O$	MeOH	rt	4	58
10[d]	NH_3.MeOH	MeOH	rt	2	89
11	NH_4Cl	MeOH	rt	12	NR
12	$HCOONH_4$	MeOH	rt	5	30
13	CH_3COONH_4	MeOH	rt	4	61
14	CH_3COONH_4	THF	rt	4	55
15	$(NH_4)_2SO_4$	MeOH	rt	12	0

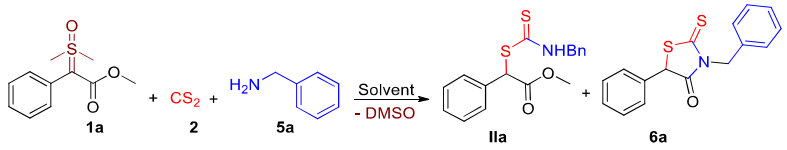
[a]General conditions: Except where otherwise noted, all reactions were conducted using **1a** (0.50 mmol), **2** (1.0 mmol), and amine **3** (0.75 mmol) in 3 mL of solvent at given temp. in a sealed tube.

[b]Isolated yield.

[c]25% aq. NH_3 (0.50 mL, 0.75 mmol) was used.

[d]2.0 M NH_3.MeOH (0.40 mL, 0.75 mmol) was used.

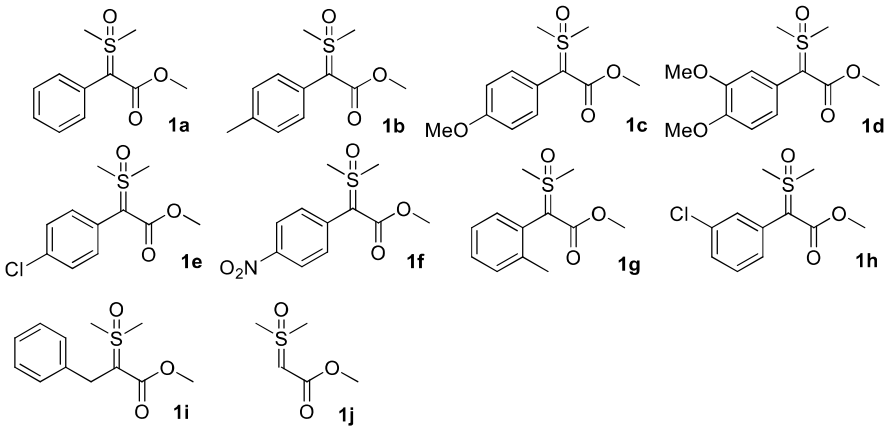
3. Table S2. Synthesis of intermediate IIa: Optimization[a]



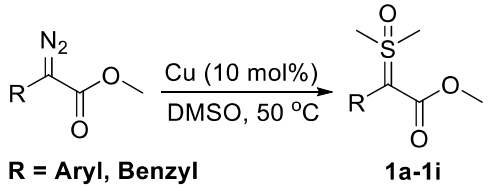
entry	solvent	temp (°C)	time (h)	yield[b] of IIa (%)	yield[b] of 6a (%)
1	MeOH	rt	1.5 h	N.D.[c]	92
2	MeOH	0 °C	5 h	12	68
3[f]	MeOH	-10 °C	12 h	Trace	Trace
4[f]	MeOH	-20 °C	12 h	N.R.[d]	N.R.
5[f]	THF	0 °C	4 h	Trace	47
6[f]	Toluene	0 °C	5 h	18	42
7[f]	Toluene	-5 °C	6 h	24	Trace
8[f]	DCM	0 °C	4 h	N.D.	N.I.[e]
9[f]	$CHCl_3$	0 °C	4 h	N.D.	N.I.
10	CH_3CN	0 °C	4 h	N.D.	N.I.

[a]Except where otherwise noted, all reactions were conducted using **1a** (1.0 mmol), **2** (1.50 mmol), and benzyl amine **5a** (1.20 mmol) in 5 mL of solvent, used new glassware (25 mL round bottom flask) and stir-bar. The reaction mixture was stirred at given temp for given time.
[b]Isolated yield.
[c]Not detected.
[d]No reaction.
[e]Not isolated.
[f]Sulfoxonium ylide recovered.

4. Structures of *α*-ester sulfoxonium ylides used in this study:

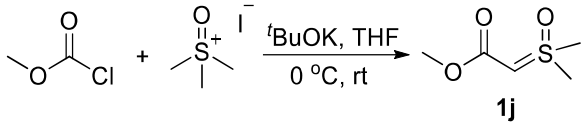


5. General procedure for preparation of *α*-ester sulfoxonium ylides 1a-1i:



All the *α*-ester sulfoxonium ylides were synthesized from *α*-diazoesters[1] according to the known literature procedure.[2c] Briefly, to a stirred solution of corresponding *α*-diazoesters (10.0 mmol, 1 equiv.) in 7 mL DMSO was added 10 mol% copper powder at 50 °C. The reaction mixture was stirred for 24 h at the same temperature. After completion of the reaction, the reaction was cooled to r.t., diluted with EtOAc (20 mL) and the organic phase was washed with ice cold water (3 x 30 mL) until there was no more DMSO in the organic phase (analysis by TLC). The organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and crude material was purified by crystallization in the minimal amount of hot EtOAc (5-10 mL), followed by slow addition of 20 mL of hexane, which was filtered through a Buchner funnel under vacuum to afford the corresponding *α*-ester sulfoxonium ylides as solid in the stated yields (**1a-1i**). Spectroscopic data was consistent with previous reports.[2]

6. Procedure for preparation of *α*-ester sulfoxonium ylides 1j:



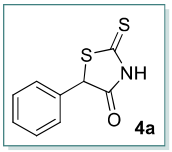
Sulfoxonium ylide **1j** was synthesized according to the known literature procedure.[3] Briefly, to a stirred solution of potassium *tert*-butoxide (4.50 g, 40.0 mmol, 3.80 equiv.) in anhydrous THF (20 mL) was added trimethylsulfoxonium iodide (7.40 g, 33.86 mmol, 3.20 equiv.) at room temperature. The resulting solution was heated to reflux for 2 h. Further, the reaction mixture was cooled to 0 °C, followed by dropwise addition of methyl chloroformate (1.0 g, 10.5 mmol, 1.0 equiv.) in THF (15 mL) solvent. The reaction was allowed to bring at room temperature and stirred for additional 3h. After completion of reaction as monitored by TLC, the solvent was evaporated after that water (30 mL) and EtOAc (30 mL) were added to the resulting slurry. The organic layer was separated and the aqueous layer was washed with ethyl acetate (2 x 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The crude product was purified by EtOAc/diethyl ether with constant stirring, resulting in precipitation of pure ylide, which was filtered through a Buchner funnel under vacuum and washed with cold EtOAc/diethylether to afford the corresponding sulfoxonium ylide **1j** (1.20 g, 78%) as solid compound. Spectroscopic data was consistent with previous reports.[3]

7. General procedure for the synthesis of compounds, 4

To a stirred solution of methanolic NH_3 **3** (0.40 mL, 0.75 mmol, 1.5 equiv., 2.0 M in MeOH) in MeOH (3 mL) in a sealed tube were added CS_2 **2** (1.0 mmol, 2 equiv.) and α-ester sulfoxonium ylide **1** (0.5 mmol, 1 equiv.) at room temperature, and the reaction mixture was stirred for 2 h. After completion of reaction as monitored by TLC, the solvent was evaporated under reduce pressure and extracted with EtOAc (3 x 7 mL). The organic extract was dried over anhydrous Na_2SO_4 and removed solvent under reduced pressure. The crude product **4** was purified by column chromatography (silica gel, 100-200 mesh; ethyl acetate/hexane 1.5/8.5) which afforded the desired products **4** in good to excellent yields.

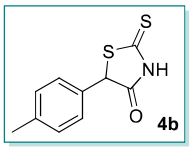
8. Characterization of Compounds, 4

5-Phenyl-2-thioxothiazolidin-4-one, 4a



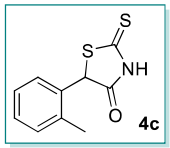
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (93 mg, 89%); mp: 154-156 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.41 (brs, 1H), 7.43 - 7.40 (m, 2H), 7.38 - 7.36 (m, 3H), 5.91 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ: 203.1, 177.3, 134.8, 129.1, 128.7, 128.6, 57.4.; HRMS (ESI$^+$) *m/z* $C_9H_7NOS_2$ $[M + H]^+$ calcd. 210.0042, found 210.0043.

2-Thioxo-5-(p-tolyl)thiazolidin-4-one, 4b



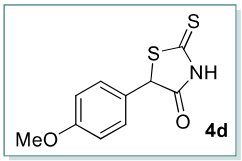
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (100 mg, 90%); mp: 135-137 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.36 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 5.87 (s, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 203.0, 177.4, 138.2, 131.8, 129.6, 128.4, 57.1 20.7.; HRMS (ESI$^+$) *m/z* $C_{10}H_9NOS_2$ $[M + H]^+$ calcd. 224.0199, found 224.0206.

2-Thioxo-5-(o-tolyl)thiazolidin-4-one, 4c



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (95 mg, 86%); mp: 139-141 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.45 (s, 1H), 7.29 - 7.23 (m, 4H), 6.14 (s, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 203.0, 177.4, 137.0, 132.8, 131.0, 129.0, 128.8, 126.7, 55.5, 18.95 (s).; HRMS (ESI$^+$) *m/z* $C_{10}H_9NOS_2$ $[M + H]^+$ calcd. 224.0199, found 224.0205.

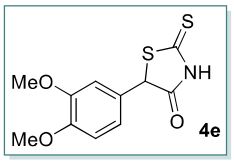
5-(4-Methoxyphenyl)-2-thioxothiazolidin-4-one, 4d



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); White solid (109 mg, 92%); mp: 109-111 ºC;

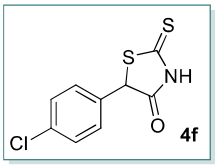
^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.35 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 5.86 (s, 1H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 203.1, 177.5, 159.5, 129.9, 126.5, 114.5, 57.0, 55.2; HRMS (ESI$^+$) *m/z* $C_{10}H_9NO_2S_2$ $[M + H]^+$ calcd. 240.0148, found 240.0161.

5-(3,4-Dimethoxyphenyl)-2-thioxothiazolidin-4-one, 4e



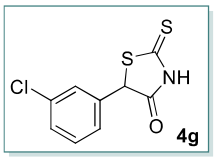
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.5/7.5); White solid (122 mg, 91%); mp: 115-118 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.33 (s, 1H), 6.98 - 6.93 (m, 2H), 6.89 - 6.88 (m, 1H), 5.85 (s, 1H), 3.75 (brs, 6H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 203.0, 177.3, 149.1, 148.9, 126.6, 121.0, 112.1, 112.0 57.3, 55.6, 556.5; HRMS (ESI$^+$) *m/z* $C_{11}H_{11}NO_3S_2$ $[M + H]^+$ calcd. 270.0253, found 270.0248.

5-(4-Chlorophenyl)-2-thioxothiazolidin-4-one, 4f



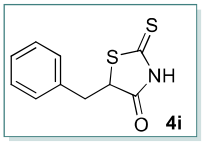
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (103 mg, 85%); mp: 130-132 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.43 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 9.1 Hz, 2H), 5.95 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 203.4, 177.6, 134.3, 133.9, 131.0, 129.6, 57.1.; HRMS (ESI$^+$) *m/z* $C_9H_6ClNOS_2$ $[M + H]^+$ calcd. 243.9652, found 243.9661.

5-(3-Chlorophenyl)-2-thioxothiazolidin-4-one, 4g



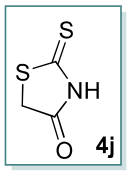
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (100 mg, 83%); mp: 132-135 ºC; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.44 (s, 1H), 7.48 (s, 1H), 7.45 (d, *J* = 4.9 Hz, 2H), 7.36 - 7.35 (m, 1H), 5.94 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 202.8, 176.8, 137.0, 133.5, 131.0, 128.7, 128.6, 127.2, 56.7.; HRMS (ESI$^+$) *m/z* $C_9H_6ClNOS_2$ $[M + H]^+$ calcd. 243.9652, found 243.9655.

5-Benzyl-2-thioxothiazolidin-4-one, 4i[4]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (90 mg, 81%); mp: 120-122 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.17 (brs, 1H), 7.33 - 7.30 (m, 2H), 7.26 - 7.23 (m, 3H), 5.03 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.37 (dd, *J* = 14.1, 4.7 Hz, 1H), 3.17 (dd, *J* = 14.0, 8.9 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 203.3, 178.0, 136.6, 129.1, 128.5, 127.1, 55.7, 36.5.; HRMS (ESI$^+$) *m/z* $C_{10}H_9NOS_2$ $[M + H]^+$ calcd. 224.0199, found 224.0204.

2-Thioxothiazolidin-4-one, 4j[5]



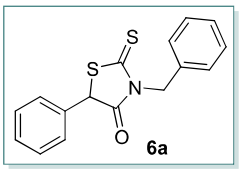
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.5/7.5); Red solid (51mg, 78%); mp: 145-147 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.13 (s, 1H), 4.26 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 205.3, 176.7, 39.2.

9. General procedure for the synthesis of compounds, 6

To a stirred solution of CS_2 **2** (0.75 mmol, 1.50 equiv.) in MeOH (3 mL) were added corresponding 1° amines **5** (0.6 mmol, 1.2 equiv.) and α-ester sulfoxonium ylide **1** (0.5 mmol, 1.0 equiv.) at room temperature, and the reaction mixture was stirred for 1.5 h. After completion of reaction as monitored by TLC, the solvent was evaporated under reduce pressure and extracted with EtOAc (3 x 10 mL). The organic extract was dried over anhydrous Na_2SO_4 and removed solvent under reduced pressure. The crude product **6** was purified by column chromatography (silica gel, 100-200 mesh; ethyl acetate/hexane 1.0/9.0) which afforded the desired products in good to excellent yields.

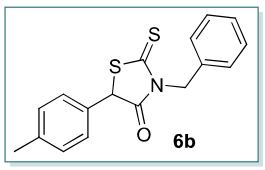
10. Characterization of Compounds, 6

3-Benzyl-5-phenyl-2-thioxothiazolidin-4-one, 6a[6]



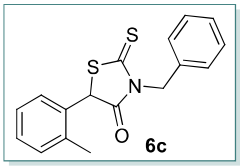
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); White solid (139 mg, 93%); mp: 88-90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 - 7.39 (m, 2H), 7.36 - 7.35 (m, 3H), 7.33 - 7.26 (m, 5H), 5.28 - 5.25 (m, 2H), 5.18 - 5.15 (m, 1H); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ: 199.9, 175.1, 134.9, 133.9, 129.4, 129.3, 129.0, 128.7, 128.4, 128.3, 54.4, 48.0.; HRMS (ESI$^+$) *m/z* $C_{16}H_{13}NOS_2$ $[M + H]^+$ calcd. 300.0512, found 300.0501.

3-Benzyl-2-thioxo-5-(p-tolyl)thiazolidin-4-one, 6b



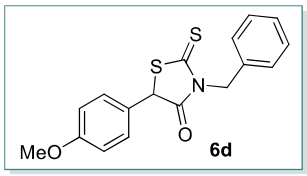
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); White solid (140 mg, 90%); mp: 95-98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 6.1 Hz, 2H), 7.32 - 7.27 (m, 3H), 7.16 (s, 4H), 5.26 (d, *J* = 13.9 Hz, 1H), 5.22 (s, 1H), 5.17 (d, *J* = 13.9 Hz, 1H), 2.34 (s, 3H): ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 200.1, 175.3, 139.4, 135.0, 130.9, 130.1, 129.0, 128.7, 128.3, 54.3, 48.0, 21.3.; HRMS (ESI$^+$) *m/z* $C_{17}H_{15}NOS_2$ $[M + H]^+$ calcd. 314.0668, found 314.0671.

3-Benzyl-2-thioxo-5-(o-tolyl)thiazolidin-4-one, 6c Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); White solid (142 mg, 91%); mp: 109-112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 7.4 Hz, 2H), 7.32 - 7.27 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.18 - 7.13 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 5.48 (s, 1H), 5.27 - 5.20 (m, 2H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR



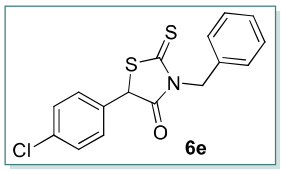
(126 MHz, $CDCl_3$) δ: 200.0, 175.2, 137.0, 134.8, 132.3, 131.4, 129.27, 129.20, 128.7, 128.6, 128.3, 127.0, 52.0, 48.0, 19.6.; HRMS (ESI^+) *m/z* $C_{17}H_{15}NOS_2$ $[M + H]^+$ calcd. 314.0668, found 314.0676.

3-Benzyl-5-(4-methoxyphenyl)-2-thioxothiazolidin-4-one, 6d



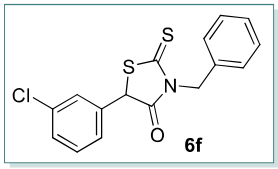
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (151 mg, 92%); mp: 110-113 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 - 7.27 (m, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.26 (d, *J* = 13.8 Hz, 1H), 5.21 (s, 1H), 5.16 (d, *J* = 14.2 Hz, 1H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 195.3, 170.6, 155.5, 130.2, 124.8, 124.2, 123.9, 123.5, 120.8, 110.0, 50.7, 49.3, 43.2; HRMS (ESI^+) *m/z* $C_{17}H_{15}NO_2S_2$ $[M + H]^+$ calcd. 330.0617, found 330.0627.

3-Benzyl-5-(4-chlorophenyl)-2-thioxothiazolidin-4-one, 6e



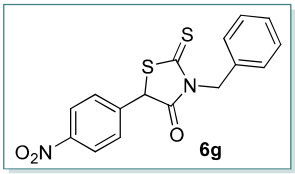
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Colorless oil (144 mg, 87%); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.41 - 7.39 (m, 2H), 7.35 - 7.29 (m, 5H), 7.24 - 7.22 (m, 2H), 5.26 (d, *J* = 14.1 Hz, 1H), 5.24 (s, 1H), 5.17 (d, *J* = 14.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 199.3, 174.8, 135.5, 134.8, 132.4, 129.7, 129.8, 129.0, 128.8, 128.4, 53.8, 48.1.; HRMS (ESI^+) *m/z* $C_{16}H_{12}ClNOS_2$ $[M + H]^+$ calcd. 334.0124, found 334.0135.

3-Benzyl-5-(3-chlorophenyl)-2-thioxothiazolidin-4-one, 6f



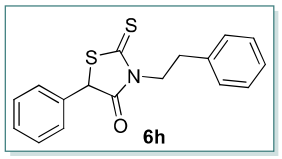
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Colorless oil (142 mg, 86%); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.0 Hz, 2H), 7.34 - 7.28 (m, 6H), 7.17 (d, *J* = 7.9 Hz, 1H), 5.26 (d, *J* = 14.4 Hz, 1H), 5.21 (s, 1H), 5.16 (d, *J* = 14.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 199.2, 174.6, 135.8, 135.4, 134.7, 130.7, 129.6, 129.0, 128.8, 128.5, 126.6, 53.8, 48.1.; HRMS (ESI^+) *m/z* $C_{16}H_{12}ClNOS_2$ $[M + H]^+$ calcd. 334.0124, found 334.0128.

3-Benzyl-5-(4-nitrophenyl)-2-thioxothiazolidin-4-one, 6g



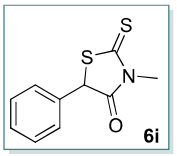
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Colorless oil (122 mg, 71%); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.25 - 8.21 (m, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 6.6 Hz, 2H), 7.32 (d, *J* = 6.6 Hz, 3H), 5.38 (s, 1H), 5.28 (d, *J* = 14.3 Hz, 1H), 5.20 (d, *J* = 14.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 198.3, 174.25, 148.8, 136.0, 134.5, 134.4, 130.6, 129.0, 128.9, 128.5, 124.3, 123.6, 53.5, 48.3.; HRMS (ESI^+) *m/z* $C_{16}H_{12}N_2O_3S_2$ $[M + H]^+$ calcd. 345.0364, found 345.0383.

3-Phenethyl-5-phenyl-2-thioxothiazolidin-4-one, 6h



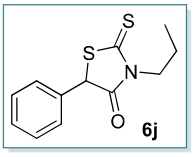
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); White solid (139 mg, 89%); mp: 108-110 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36 - 7.35 (m, 3H), 7.30 - 7.19 (m, 7H), 5.19 (s, 1H), 4.31 - 4.23 (m, 2H), 3.03 - 2.99 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 200.0, 174.9, 137.3, 133.8, 129.4, 129.2, 129.1, 128.8, 128.4, 127.0, 54.4, 46.0, 32.8.; HRMS (ESI$^+$) *m/z* $C_{17}H_{15}NOS_2$ $[M + H]^+$ calcd. 314.0668, found 314.0661.

3-Methyl-5-phenyl-2-thioxothiazolidin-4-one, 6i[7]



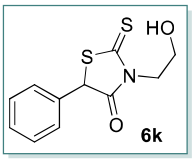
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); White solid (100 mg, 90%); mp: 105-107 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 - 7.34 (m, 5H), 5.28 (s, 1H), 3.44 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 200.3, 175.0, 133.7, 129.4, 129.3, 128.4, 54.8, 31.8.; HRMS (ESI$^+$) *m/z* $C_{10}H_9NOS_2$ $[M + H]^+$ calcd. 224.0199, found 224.0201.

5-Phenyl-3-propyl-2-thioxothiazolidin-4-one, 6j



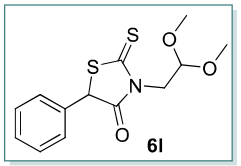
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); White solid (109 mg, 87%); mp:112-114 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 - 7.31 (m, 5H), 5.23 (s, 1H), 4.00 (t, *J* = 15 Hz, 2H), 1.70 (tq, *J* = 14.6, 7.3 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 200.2, 175.1, 134.0, 129.4, 129.2, 128.3, 54.4, 46.5, 20.3, 11.2.; HRMS (ESI$^+$) *m/z* $C_{12}H_{13}NOS_2$ $[M + H]^+$ calcd. 252.0512, found 252.0506.

3-(2-Hydroxyethyl)-5-phenyl-2-thioxothiazolidin-4-one, 6k



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 3.0/7.0); White solid (103 mg, 82%); mp: 125-127 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 - 7.32 (m, 5H), 5.28 (s, 1H), 4.27 - 4.19 (m, 2H), 3.87 (q, *J* = 5.6 Hz, 2H), 2.20 (t, *J* = 5.9 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 200.9, 175.9, 133.8, 129.4, 129.3, 128.4, 59.6, 54.5, 46.8.; HRMS (ESI$^+$) *m/z* $C_{11}H_{11}NO_2S_2$ $[M + H]^+$ calcd. 254.0306, found 254.0305.

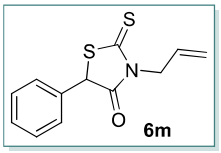
3-(2,2-Dimethoxyethyl)-5-phenyl-2-thioxothiazolidin-4-one, 6l



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (130 mg, 88%); mp: 120-122 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 - 7.32 (m, 5H), 5.26 (s, 1H), 4.91 (t, *J* = 5.9 Hz, 1H), 4.23 - 4.16 (m, 2H), 3.38 (s, 3H), 3.34 (s, 3H); ^{13}C{^{1}H} NMR (126

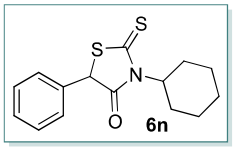
MHz, $CDCl_3$) δ: 200.3, 174.9, 134.2, 129.4, 129.3, 128.4, 99.2, 54.4, 53.9, 53.8, 45.0.; HRMS (ESI^+) *m/z* $C_{13}H_{15}NO_3S_2$ $[M + H]^+$ calcd. 298.0566, found 298.0575.

3-Allyl-5-phenyl-2-thioxothiazolidin-4-one, 6m



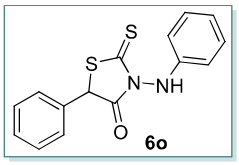
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Yellow liquid (110 mg, 89%); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40 - 7.31 (m, 5H), 5.89 - 5.77 (m, 1H), 5.28 - 5.21 (m, 3H), 4.63 (d, *J* = 5.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 199.5, 174.6, 133.8, 129.45, 129.40, 129.2, 128.3,119.6, 54.4, 46.7.; HRMS (ESI^+) *m/z* $C_{12}H_{11}NOS_2$ $[M + H]^+$ calcd. 250.0355, found 250.0354.

3-Cyclohexyl-5-phenyl-2-thioxothiazolidin-4-one, 6n



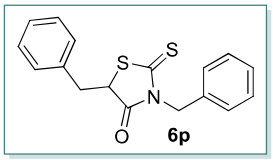
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); White solid (107 mg, 74%); mp: 133-135 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.41 - 7.29 (m, 5H), 5.05 (s, 1H), 4.93 (tt, *J* = 12.6, 8.3, 3.6 Hz, 1H), 2.35 - 2.23 (m, 2H), 1.87 - 1.82 (m, 2H), 1.72 - 1.62 (m, 3H), 1.36 (qt, *J* = 13.1, 3.3 Hz, 2H), 1.20 (ddt, *J* = 19.9, 13.3, 3.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 201.3, 175.5, 134.6, 129.5, 129.2, 128.3, 58.7, 52.5, 27.8, 27.7, 26.1, 26.0, 25.1.; HRMS (ESI^+) *m/z* $C_{15}H_{17}NOS_2$ $[M + H]^+$ calcd. 292.0825, found 292.0830.

5-Phenyl-3-(phenylamino)-2-thioxothiazolidin-4-one, 6o



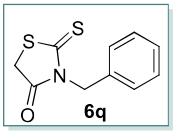
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.5/7.5); Red solid (114 mg, 76%); mp: 80-82 ºC; ^1H NMR (500 MHz, DMSO-d_6) δ: 9.05 (s, 1H), 7.48 - 7.41 (m, 5H), 7.21 (t, *J* = 7.4 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 2H), 6.07 (s, 1H);$^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ: 199.4, 173.3, 145.7, 134.9, 129.8, 129.6, 129.5, 129.2, 120.8, 113.0, 51.5.; HRMS (ESI^+) *m/z* $C_{15}H_{12}N_2OS_2$ $[M + H]^+$ calcd. 301.0464, found 301.0461.

3,5-Dibenzyl-2-thioxothiazolidin-4-one, 6p



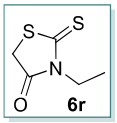
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Colorless oil (129 mg, 83%); ^1H NMR (600 MHz, $CDCl_3$) δ: 7.29 - 7.25 (m, 8H), 7.17 - 7.16 (m, 2H), 5.16 - 5.10 (m, 2H), 4.46 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.50 (dd, *J* = 14.1, 4.0 Hz, 1H), 3.12 (dd, *J* = 14.1, 9.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 200.2, 175.9, 135.6, 134.8, 129.3, 129.0, 128.7, 128.1, 127.8, 52.7, 47.7, 38.3.; HRMS (ESI^+) *m/z* $C_{17}H_{15}NOS_2$ $[M + H]^+$ calcd. 314.0668, found 314.0664.

3-Benzyl-2-thioxothiazolidin-4-one, 6q[8]



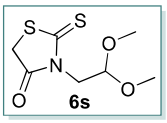
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Yellow solid (100 mg, 90%); mp: 84-86 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.46 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.35 - 7.29 (m, 3H), 5.20 (s, 2H), 3.97 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 201.1, 173.9, 134.8, 129.1, 128.6, 128.3, 47.7, 35.5.; HRMS (ESI^+) *m/z* $C_{10}H_9NOS_2$ $[M + H]^+$ calcd. 224.0201, found 224.0211.

3-Ethyl-2-thioxothiazolidin-4-one, 6r[8]



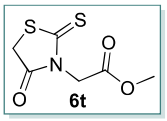
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Yellow liquid (70 mg, 87%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.06 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 201.1, 173.8, 40.0, 35.5, 12.1.; HRMS (ESI^+) *m/z* $C_5H_7NOS_2$ $[M + H]^+$ calcd. 162.0042, found 162.0048.

3-(2,2-Dimethoxyethyl)-2-thioxothiazolidin-4-one, 6s



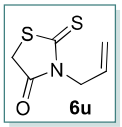
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Yellow liquid (97 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.85 (t, *J* = 5.7 Hz, 1H), 4.14 (d, *J* = 5.7 Hz, 2H), 4.01 (s, 2H), 3.37 (s, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 201.6, 173.7, 99.3, 53.9, 45.0, 35.5.; HRMS (ESI^+) *m/z* $C_7H_{11}NO_3S_2$ $[M + H]^+$ calcd. 222.0253, found 222.057.

Methyl 2-(4-oxo-2-thioxothiazolidin-3-yl)acetate, 6t[9]



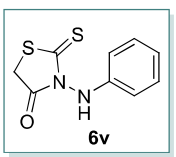
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Yellow liquid (90 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.73 (s, 2H), 4.09 (s, 2H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 200.6, 173.1, 166.4, 52.9, 44.8, 35.7.

3-Allyl-2-thioxothiazolidin-4-one, 6u[8]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Yellow liquid (74 mg, 86%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.84 -5.76 (m, 1H), 5.26 (dd, *J* = 19.9, 13.7 Hz, 2H), 4.61 (d, *J* = 6.3 Hz, 2H), 4.00 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 200.8, 173.6, 129.5, 119.7, 46.6, 35.5.; HRMS (ESI^+) *m/z* $C_6H_7NOS_2$ $[M + H]^+$ calcd. 174.0042, found 174.0047.

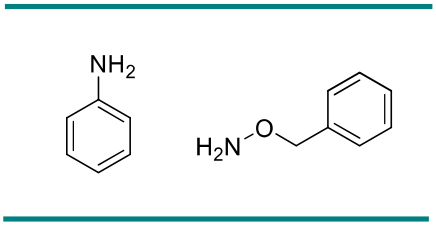
3-(Phenylamino)-2-thioxothiazolidin-4-one, 6v



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.5/7.5); Red solid (89 mg, 80%); mp: 131-133 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.26 (t, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.80 (m, 3H), 4.04 (s, 2H);

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 197.7, 170.3, 144.1, 129.5, 123.3, 115.4 32.7.; HRMS (ESI^+) *m/z* $C_9H_8N_2OS_2$ $[M + H]^+$ calcd. 225.0151, found 225.0149.

11. Unsuccessful examples of primary amines:

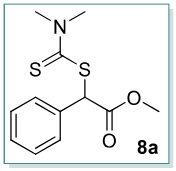


12. General procedure for synthesis of compounds, 8

To a stirred solution of CS_2 (0.75 mmol, 1.5 equiv.) in MeOH (3 mL) were added corresponding 2° amines **7** (0.6 mmol, 1.2 equiv.) and *α*-ester sulfoxonium ylide **1** (0.5 mmol, 1.0 equiv.) at room temperature, and the reaction mixture was stirred for 1.5 h. After completion of reaction as monitored by TLC, the solvent was evaporated under reduce pressure and extracted with EtOAc (3 x 10 mL). The organic extract was dried over anhydrous Na_2SO_4 and removed solvent under reduced pressure. The crude product was purified by column chromatography (silica gel, 100-200 mesh; ethyl acetate/hexane 0.5/9.5) which afforded the desired product **8** in good to excellent yields.

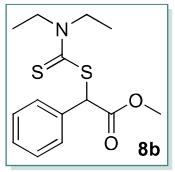
13. Characterization of Compounds, 8

Methyl 2-((dimethylcarbamothioyl)thio)-2-phenylacetate, 8a



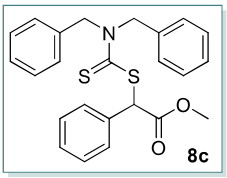
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Light yellow solid (117 mg, 87%); mp: 90-92 °C; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.0 Hz, 2H), 7.36 - 7.33 (m, 3H), 5.76 (s, 1H), 3.76 (s, 3H), 3.51 (s, 3H), 3.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ: 194.9, 170.7, 133.7, 129.0, 128.9, 128.8, 59.4, 53.1, 45.3, 41.7.; HRMS (ESI^+) *m/z* $C_{12}H_{15}NO_2S_2$ $[M + H]^+$ calcd. 270.0617, found 270.0616.

Methyl 2-((diethylcarbamothioyl)thio)-2-phenylacetate, 8b[10]



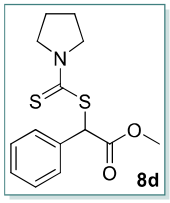
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Light yellow solid (126 mg, 85%); mp: 93-95 °C; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.0 Hz, 2H), 7.35 - 7.33 (m, 3H), 5.79 (s, 1H), 3.99 (dd, *J* = 12.9, 6.1 Hz, 2H), 3.76 (brs, 4H), 3.70 - 3.64 (m, 1H), 1.30 - 1.25 (m, 6H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ: 193.4, 170.8, 133.9, 129.08, 129.04, 128.8, 59.0, 53.1, 49.6, 47.1, 12.7, 11.7.

Methyl 2-((dibenzylcarbamothioyl)thio)-2-phenylacetate, 8c



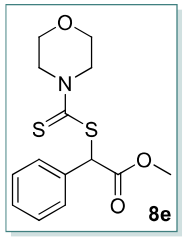
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Light yellow liquid (155 mg, 74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 7.7 Hz, 2H), 7.34 - 7.31 (brs, 9H), 7.22 - 7.20 (m, 4H), 5.87 (s, 1H), 5.29 (d, *J* = 14.8 Hz, 1H), 5.21 (d, *J* = 14.9 Hz, 1H), 4.88 (q, *J* = 16.4 Hz, 2H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 197.4, 170.5, 135.4, 134.4, 133.5, 129.13, 129.11, 128.9, 128.8, 128.2, 128.1, 128.0, 127.5, 59.8, 55.9, 54.4, 53.2; HRMS (ESI$^+$) *m/z* $C_{24}H_{23}NO_2S_2$ $[M + H]^+$ calcd. 422.1243, found 422.1224.

Methyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, 8d[10]



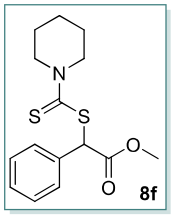
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Light yellow solid (112 mg, 76%); mp: 104-105 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.41 - 7.34 (m, 5H), 5.75 (s, 1H), 3.76 - 3.71 (m, 2H), 3.65 - 3.53 (m, 5H), 2.03 - 1.96 (m, 2H), 1.92 - 1.88 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ:188.3, 169.7, 133.9, 129.0, 128.6, 128.5, 57.3, 55.0, 52.8, 50.6, 25.7, 23.7.; HRMS (ESI$^+$) *m/z* $C_{14}H_{17}NO_2S_2$ $[M + H]^+$ calcd. 296.0774, found 296.0767.

Methyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate, 8e[10]



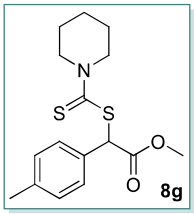
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); White solid (146 mg, 94%); mp: 110-112 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 8.1 Hz, 2H), 7.38 - 7.31 (m, 3H), 5.80 (s, 1H), 4.25 (brs, 2H), 3.89 (brs, 2H), 3.73 (brs, 7H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 195.0, 170.4, 133.4, 129.0, 128.9, 128.8, 66.1, 58.7, 53.1, 50.8.

Methyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate, 8f[10]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); White solid (146 mg, 95%); mp: 103-105 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 10.3 Hz, 2H), 7.37 - 7.30 (m, 3H), 5.82 (s, 1H), 4.35 (brs, 1H), 4.10 (brs, 1H), 3.90 (brs, 1H), 3.76 (brs, 4H), 1.69 (brs, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 193.4, 170.8, 133.9,129.08, 129.04, 128.8, 59.0, 53.1, 52.8, 51.7, 26.1, 25.5, 24.3.

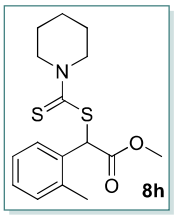
Methyl 2-((piperidine-1-carbonothioyl)thio)-2-(p-tolyl)acetate, 8g



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); White solid (145 mg, 90%); mp: 114-116 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.76 (s, 1H), 4.35 (brs, 1H), 4.09 (brs, 1H), 3.90 (brs, 1H), 3.75 (br, 4H), 2.33 (s, 3H), 1.69 (brs, 6H);

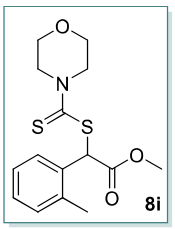
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 193.5, 170.9, 138.7, 130.7, 129.8, 128.9, 58.7, 53.1, 52.71, 51.70, 26.1, 25.5, 24.2, 21.3.; HRMS (ESI^+) *m/z* $C_{16}H_{21}NO_2S_2$ $[M + H]^+$ calcd. 324.1087, found 324.1085.

Methyl 2-((piperidine-1-carbonothioyl)thio)-2-(o-tolyl)acetate, 8h



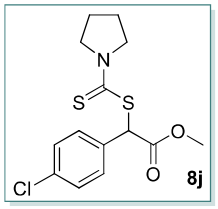
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); White solid (143 mg, 89%); mp: 115-118 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 7.6 Hz, 1H), 7.22 (s, 2H), 7.16 (s, 1H), 6.02 (s, 1H), 4.34 (brs, 1H), 4.14 (brs, 1H), 3.88 (brs, 1H), 3.82 (s, 1H), 3.76 (s, 3H), 2.47 (s, 3H), 1.70 (s, 6H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ: 193.7, 171.1, 137.2, 132.0, 131.0, 128.8, 128.5, 126.5, 56.0, 53.1, 52.9, 51.7, 26.1, 25.4, 24.2, 19.8.; HRMS (ESI^+) *m/z* $C_{16}H_{21}NO_2S_2$ $[M + H]^+$ calcd. 324.1087, found 324.1088.

Methyl 2-((morpholine-4-carbonothioyl)thio)-2-(o-tolyl)acetate, 8i



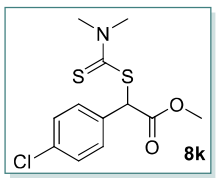
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); White solid (147 mg, 91%); mp: 108-110 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.32 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 2H), 7.17 (m, 1H), 6.01 (s, 1H), 4.29 (brs, 2H), 3.93 (brs, 2H), 3.76 (s, 7H), 2.47 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ: 195.6, 170.9, 137.1, 131.6, 131.1, 129.0, 128.5, 126.6, 66.4, 66.1, 55.8, 53.2, 51.1, 50.6, 19.8.; HRMS (ESI^+) *m/z* $C_{15}H_{19}NO_3S_2$ $[M + H]^+$ calcd. 326.0879, found 326.0877.

Methyl 2-(4-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate, 8j



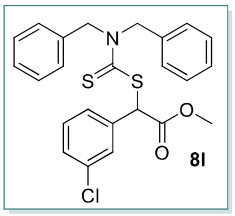
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Light yellow solid (123 mg, 75%); mp: 103-105 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.89 (s, 1H), 3.93 - 3.85 (m, 2H), 3.76 (s, 3H), 3.71 - 3.67 (m, 1H), 3.60 - 3.56 (m, 1H), 2.07 - 2.06 (m, 2H), 1.98 - 1.95 (m, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ: 189.8, 170.5, 134.7, 133.1, 130.3, 129.2, 57.5, 55.2, 53.3, 50.7, 26.3, 24.4.; HRMS (ESI^+) *m/z* $C_{14}H_{16}ClNO_2S_2$ $[M + H]^+$ calcd. 330.0384, found 330.0375.

Methyl 2-(4-chlorophenyl)-2-((dimethylcarbamothioyl)thio)acetate, 8k



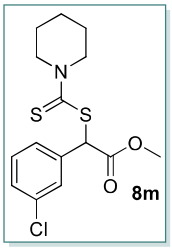
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (133 mg, 88%); mp: 110-113 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.78 (s, 1H), 3.75 (s, 3H), 3.51 (s, 3H), 3.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ: 194.3, 170.3, 134.8, 132.7, 130.3, 129.2, 58.6, 53.3, 45.4, 41.7.; HRMS (ESI^+) *m/z* $C_{12}H_{14}ClNO_2S_2$ $[M + H]^+$ calcd. 304.0227, found 304.0224.

Methyl 2-(3-chlorophenyl)-2-((dibenzylcarbamothioyl)thio)acetate, 8l



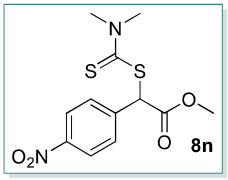
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Light yellow liquid (166 mg, 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.47 (s, 1H), 7.35 - 7.20 (m, 13H), 5.88 (s, 1H), 5.30 (d, *J* = 14.9 Hz, 1H), 5.20 (d, *J* = 15.1 Hz, 1H), 4.92 - 4.84 (m, 2H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ: 196.7, 170.0, 135.8, 135.2, 134.9, 134.2, 130.3, 129.2, 129.1, 129.0, 128.0, 128.3, 128.1, 128.0, 59.1, 56.1, 54.4, 53.4.; HRMS (ESI^{+}) *m/z* $C_{24}H_{22}ClNO_2S_2$ $[M + H]^{+}$ calcd. 456.0855, found 456.0842.

Methyl 2-(3-chlorophenyl)-2-((piperidine-1-carbonothioyl)thio)acetate, 8m



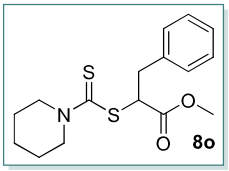
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (147 mg, 86%); mp: 120-122 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (s, 1H), 7.34 (dd, *J* = 6.7, 2.2 Hz, 1H), 7.30 - 7.27 (m, 2H), 5.85 (s, 1H), 4.31 (brs, 1H), 4.14 (brs, 1H), 3.87 (brs, 2H), 3.76 (s, 3H), 1.70 (brs, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 192.6, 170.3, 136.2, 134.8, 130.1, 129.0, 128.9, 127.2, 58.3, 53.3, 53.0, 51.7, 26.1, 25.4, 24.2.; HRMS (ESI^{+}) *m/z* $C_{15}H_{18}ClNO_2S_2$ $[M + H]^{+}$ calcd. 344.0540, found 344.0539.

Methyl 2-((dimethylcarbamothioyl)thio)-2-(4-nitrophenyl)acetate, 8n



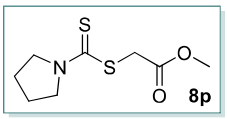
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (113 mg, 72%); mp: 110-113 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 2.4 Hz, 1H), 8.19 (t, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 6.05 (s, 1H), 3.78 (s, 3H), 3.53 (s, 3H), 3.39 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 193.4, 169.7, 148.5, 137.2, 135.2, 130.1, 129.8, 124.1, 124.0, 123.6, 58.6, 58.5, 53.5, 45.8, 41.7.; HRMS (ESI^{+}) *m/z* $C_{12}H_{14}N_2O_4S_2$ $[M + H]^{+}$ calcd. 315.0468, found 315.0469.

Methyl 3-phenyl-2-((piperidine-1-carbonothioyl)thio)propanoate, 8o



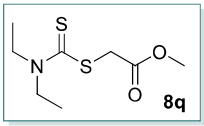
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (122 mg, 76%); mp: 97-99 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 5.8 Hz, 1H), 5.54 (dd, *J* = 10.0, 5.1 Hz, 1H), 4.31 (brs, 1H), 4.20 (brs, 1H), 3.82 (brs, 2H), 3.58 (s, 3H), 3.47 (dd, *J* = 15.9, 4.8 Hz, 1H), 3.03 (m, 1H), 1.68 (brs, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 193.6, 171.1, 139.2, 128.7, 128.4, 127.9, 52.7, 51.8, 51.5, 40.9, 26.1, 25.0, 24.4.; HRMS (ESI^{+}) *m/z* $C_{16}H_{21}NO_2S_2$ $[M + H]^{+}$ calcd. 324.1087, found 324.1084.

Methyl 2-((pyrrolidine-1-carbonothioyl)thio)acetate, 8p[11]



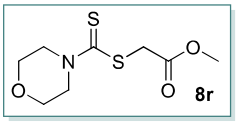
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (86 mg, 79%); mp: 87-89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.19 (s, 2H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 3.71 (t, *J* = 6.9 Hz, 2H), 2.10 (p, *J* = 6.8 Hz, 2H), 1.99 (p, *J* = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ: 190.8, 169.4, 55.5, 52.9, 50.8, 38.4, 26.2, 24.4.

Methyl 2-((diethylcarbamothioyl)thio)acetate, 8q[11]



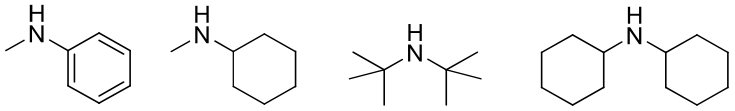
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Light yellow liquid (95 mg, 87%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.17 (s, 2H), 4.02 (q, *J* = 7.0 Hz, 2H), 3.80 - 3.76 (m, 5H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ: 193.8, 169.4, 52.9, 50.1, 47.1, 39.0, 12.7, 11.6.

Methyl 2-((morpholine-4-carbonothioyl)thio)acetate, 8r



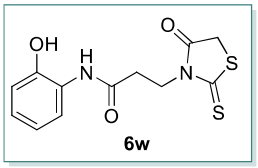
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); White solid (105 mg, 90%); mp: 95-96 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.31 (brs, 2H), 4.19 (s, 2H), 3.98 (s, 2H), 3.77 (s, 7H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ: 195.6, 169.0, 66.2, 52.9, 51.7, 50.6, 38.7.; HRMS (ESI$^+$) *m/z* $C_8H_{13}NO_3S_2$ $[M + H]^+$ calcd. 236.0410, found 236.416.

14. Unsuccessful examples of secondary amines:



15. Synthesis of FE15:

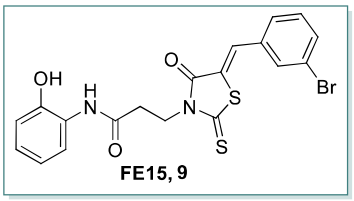
N-(2-Hydroxyphenyl)-3-(4-oxo-2-thioxothiazolidin-3-yl)propanamide, 6w[12]



To a stirred solution of CS_2 **2** (0.60 mL, 10.0 mmol, 1.50 equiv.) in MeOH (20 mL) were added amine **5w** (1.44 g, 8.0 mmol, 1.20 equiv.) and *α*-ester sulfoxonium ylide **1j** (1.0 g, 6.66 mmol, 1.0 equiv.) at room temperature, and the reaction mixture was stirred for 2 h. After completion of reaction as monitored by TLC, the solvent was evaporated under reduce pressure and extracted with EtOAc (3 x 20 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, concentrated in *vacuo*

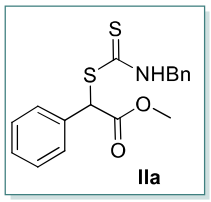
and then purified by silica gel column chromatography using EtOAc/hexane (4:6, v/v) as eluent to afford the rhodanine derivative, **6w** (1.50 g, 78%) as a yellow solid. mp: 165-168 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.65 (s, 1H), 9.36 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 4.25 (s, 2H), 4.15 (t, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ: 202.9, 174.2, 168.7, 148.3, 125.9, 124.9, 123.0, 118.9, 115.7, 40.5, 35.9, 32.7.

(*Z*)-3-(5-(3-bromobenzylidene)-4-oxo-2-thioxothiazolidin-3-yl)-*N*-(2hydroxyphenyl)propaneide (FE15), 9[12]



To a stirred solution of rhodanine derivative **6w** (1.40 g, 4.70 mmol, 1.0 equiv.) in dry toluene (25 mL) were added NH_4OAc (542 mg, 7.05 mmol, 1.50 equiv.) and 3-Bromobenzaldehyde (1.0 g, 5.64 mmol, 1.20 equiv.) at 100 ºC. The reaction mixture was stirred for 4 h at the same temperature. After completion of the reaction, the reaction was cooled to r.t. and the yellow precipitate was filtered through a Buchner funnel under vacuum, washed with EtOH and hexane to afford the FE15, **9** (1.80 g, 84%) as a yellow solid. mp: 218-220 ºC ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.66 (s, 1H), 9.40 (s, 1H), 7.83 (s, 1H), 7.77 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 4.32 (t, *J* = 6.9 Hz, 2H), 2.81 (t, *J* = 6.9 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, DMSO-d6) δ: 192.8, 168.6, 166.6, 148.1, 135.3, 133.4, 133.3, 131.4, 130.9, 128.6, 125.9, 124.8, 124.1, 122.9, 122.6, 118.9, 115.7, 39.9, 32.9.

16. Characterization of intermediate, IIa



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Colorless oil (105 mg, 32%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.85 (brs, 1H), 7.40 - 7.31 (m, 14H), 4.82 - 4.72 (m, 3H), 3.67 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 190.2, 170.7, 135.6, 133.9, 129.4, 129.0, 128.5, 128.3, 60.1, 53.5, 50.4.; HRMS (ESI^{+}) *m/z* $C_{17}H_{17}NO_2S_2$ $[M + H]^{+}$ calcd. 332.0774, found 332.0775.

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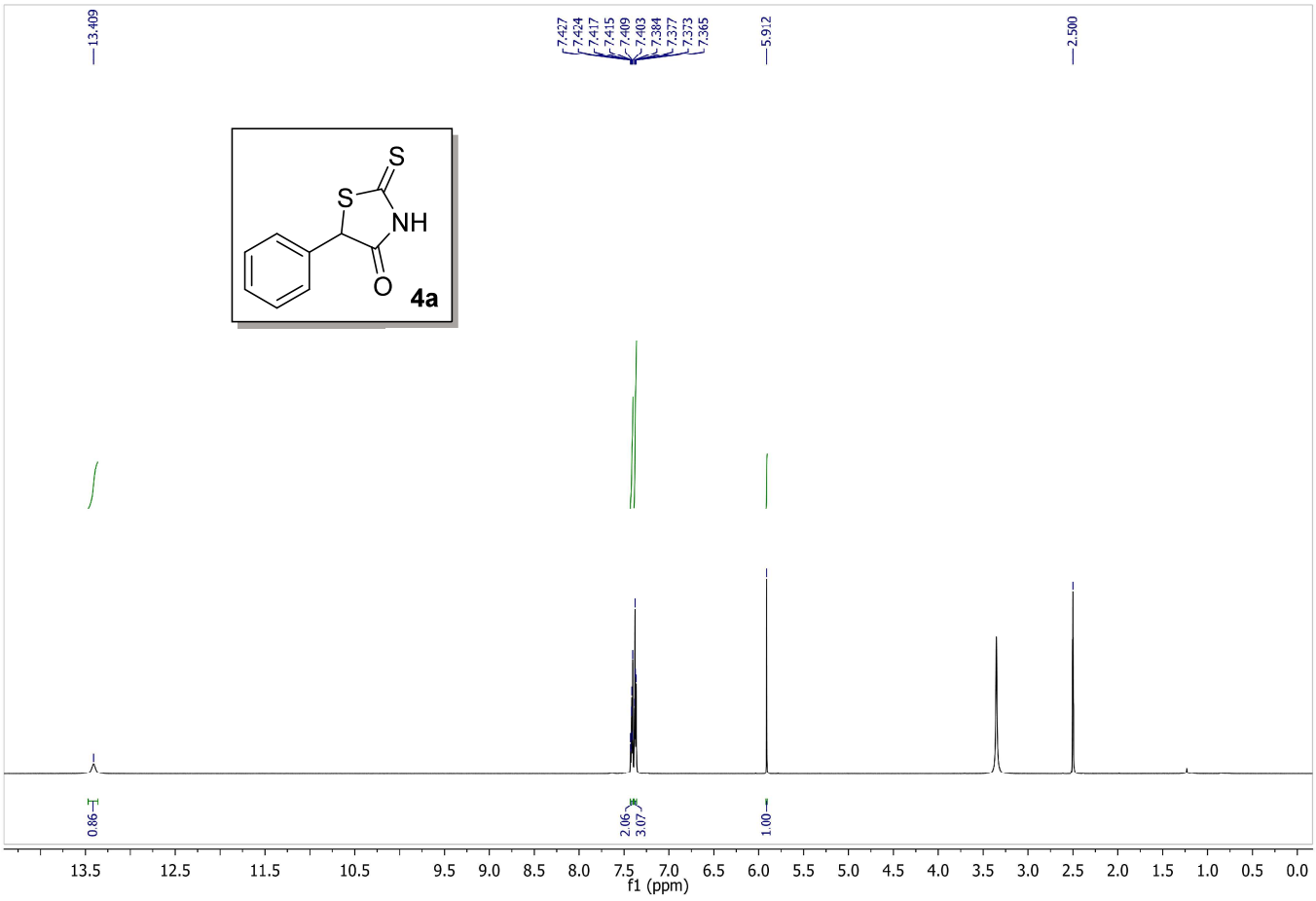
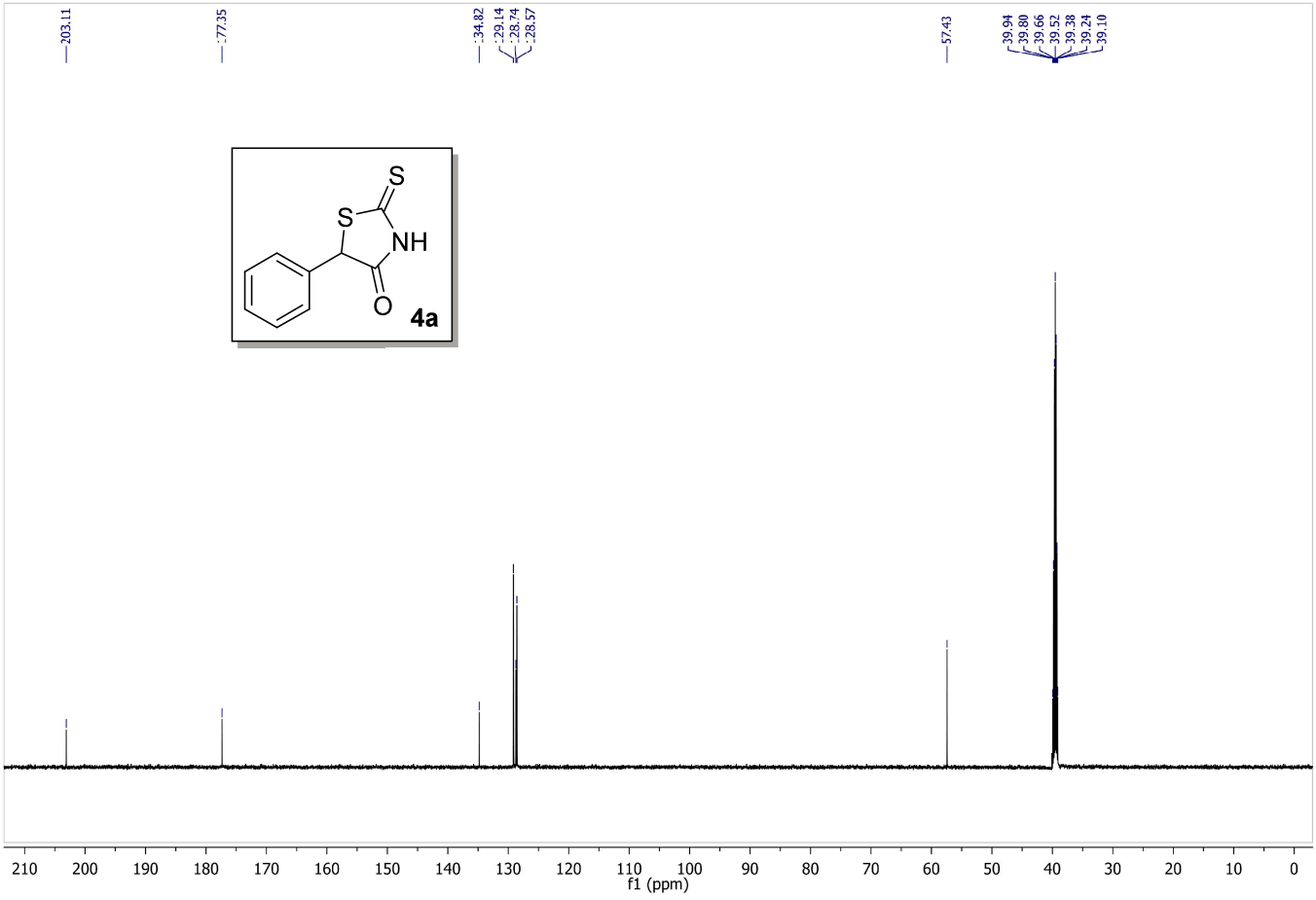
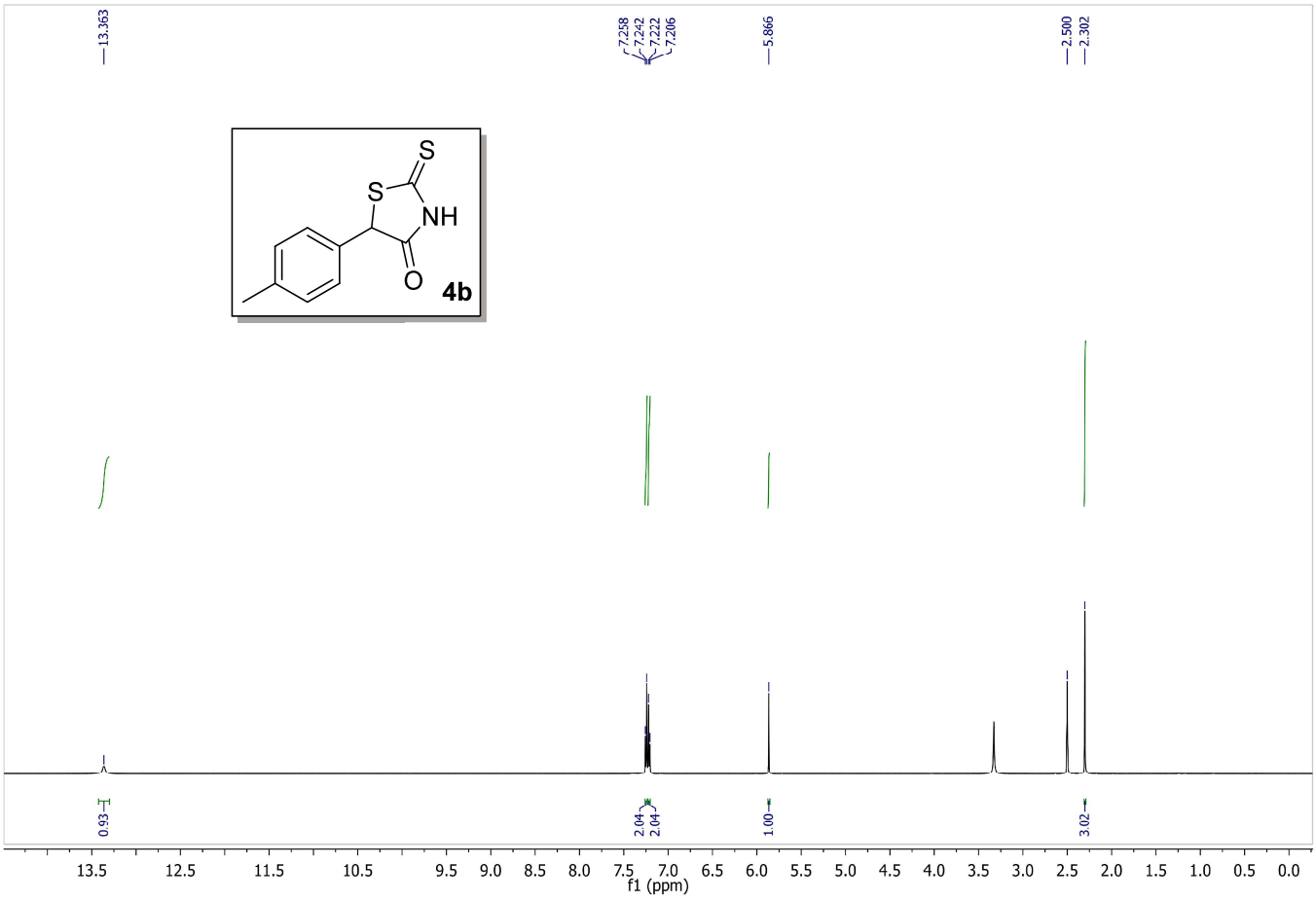
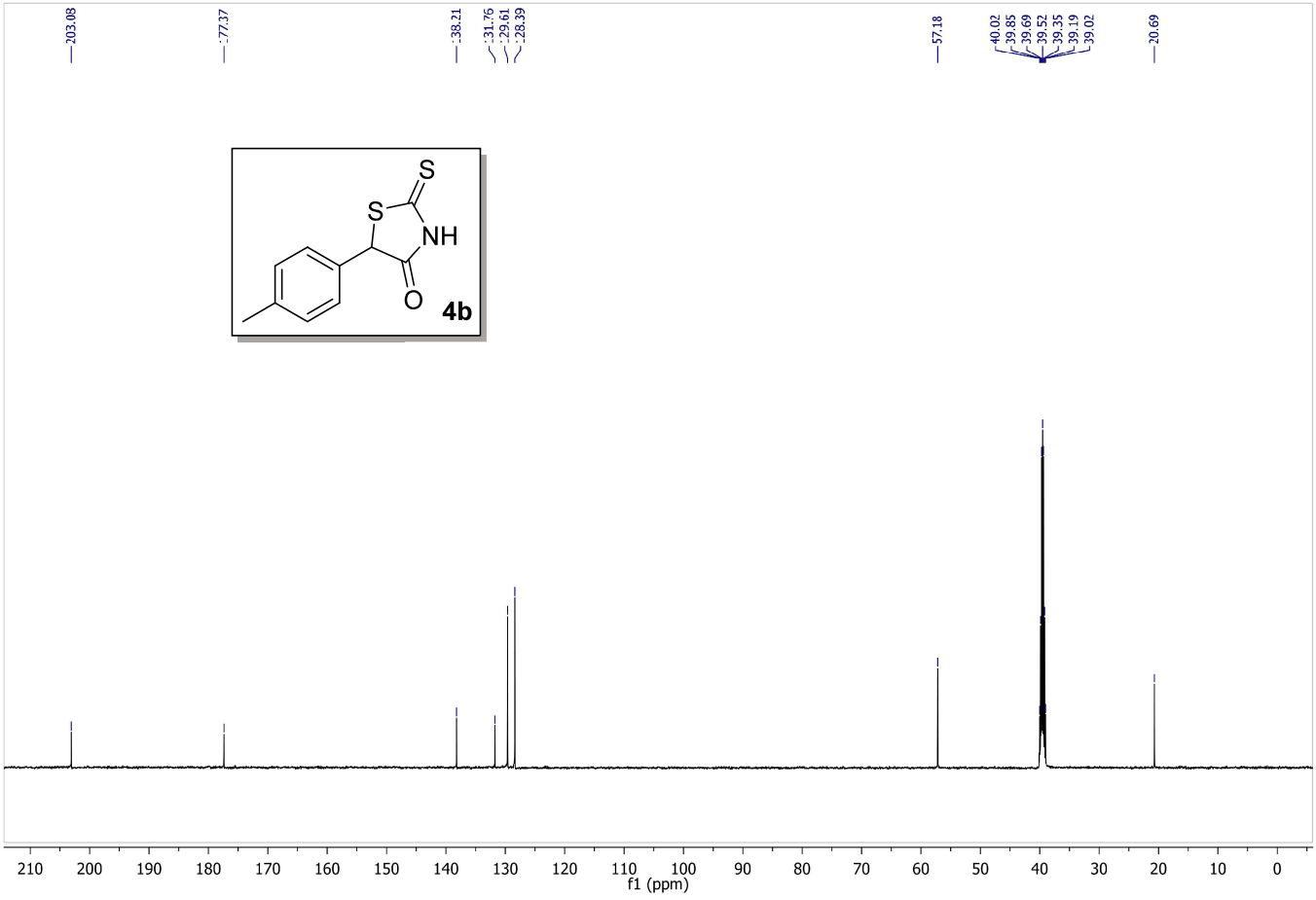
^{1}H NMR (600 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d6), **4a**





^{1}H NMR (500 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6), **4b**





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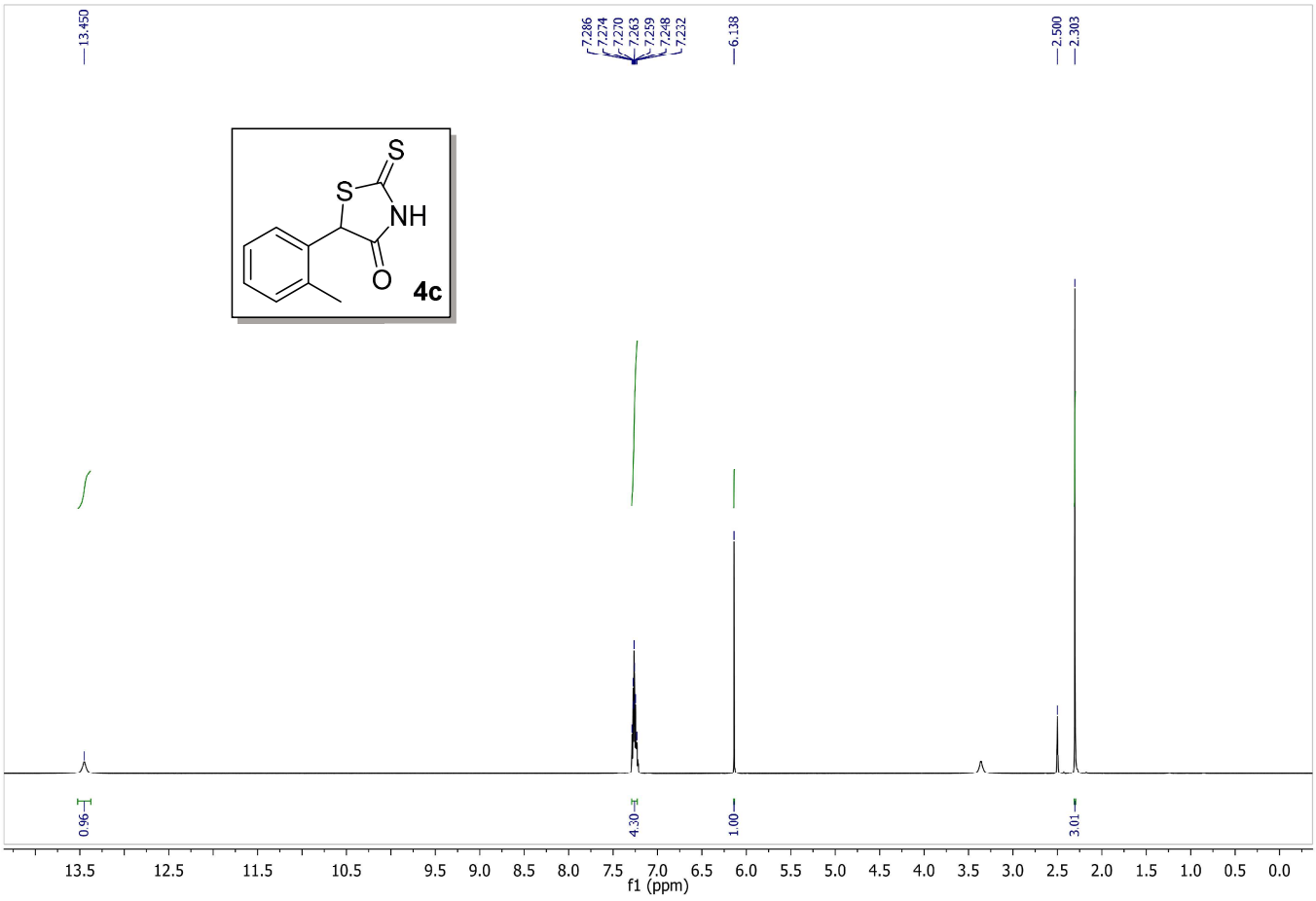
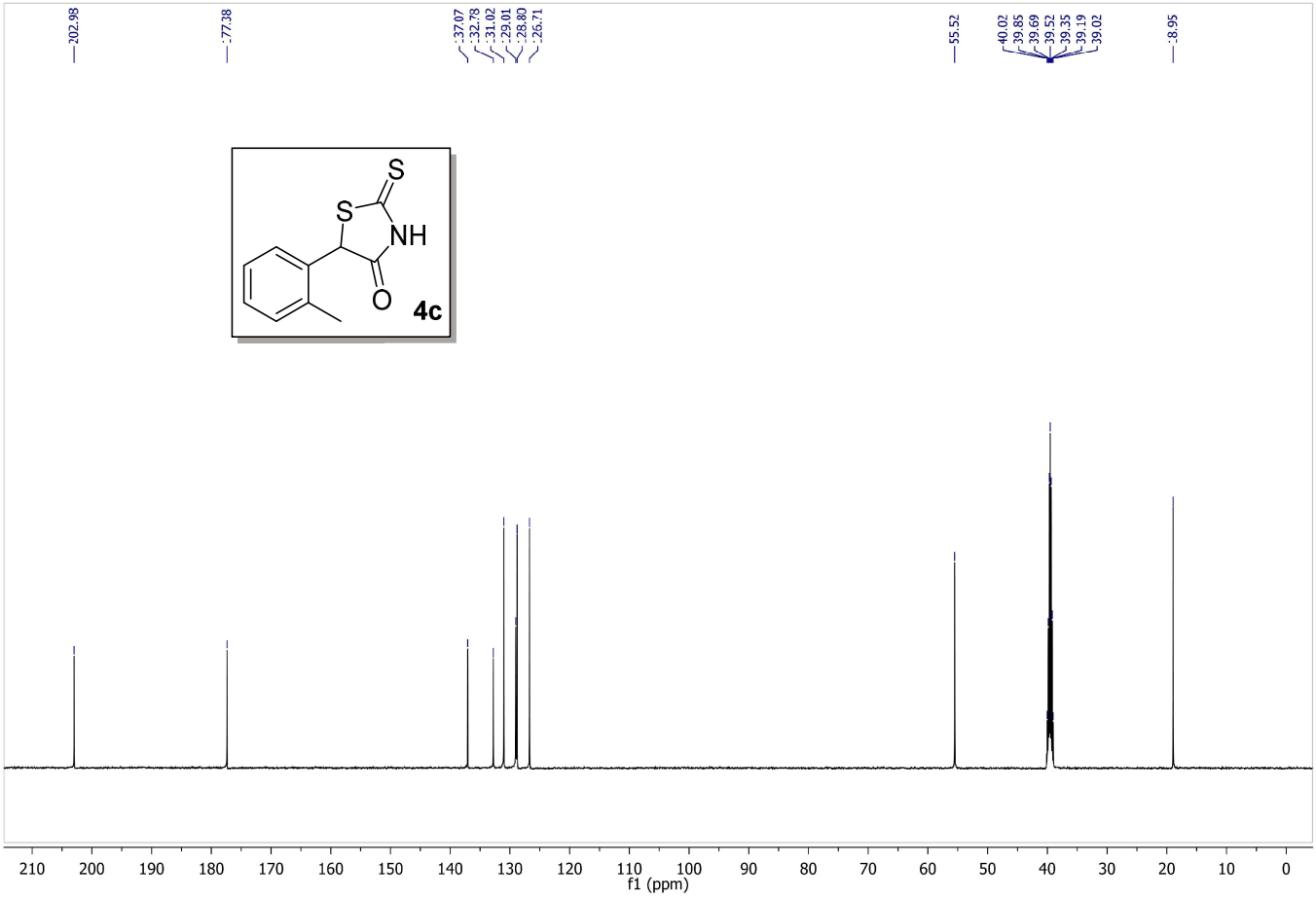
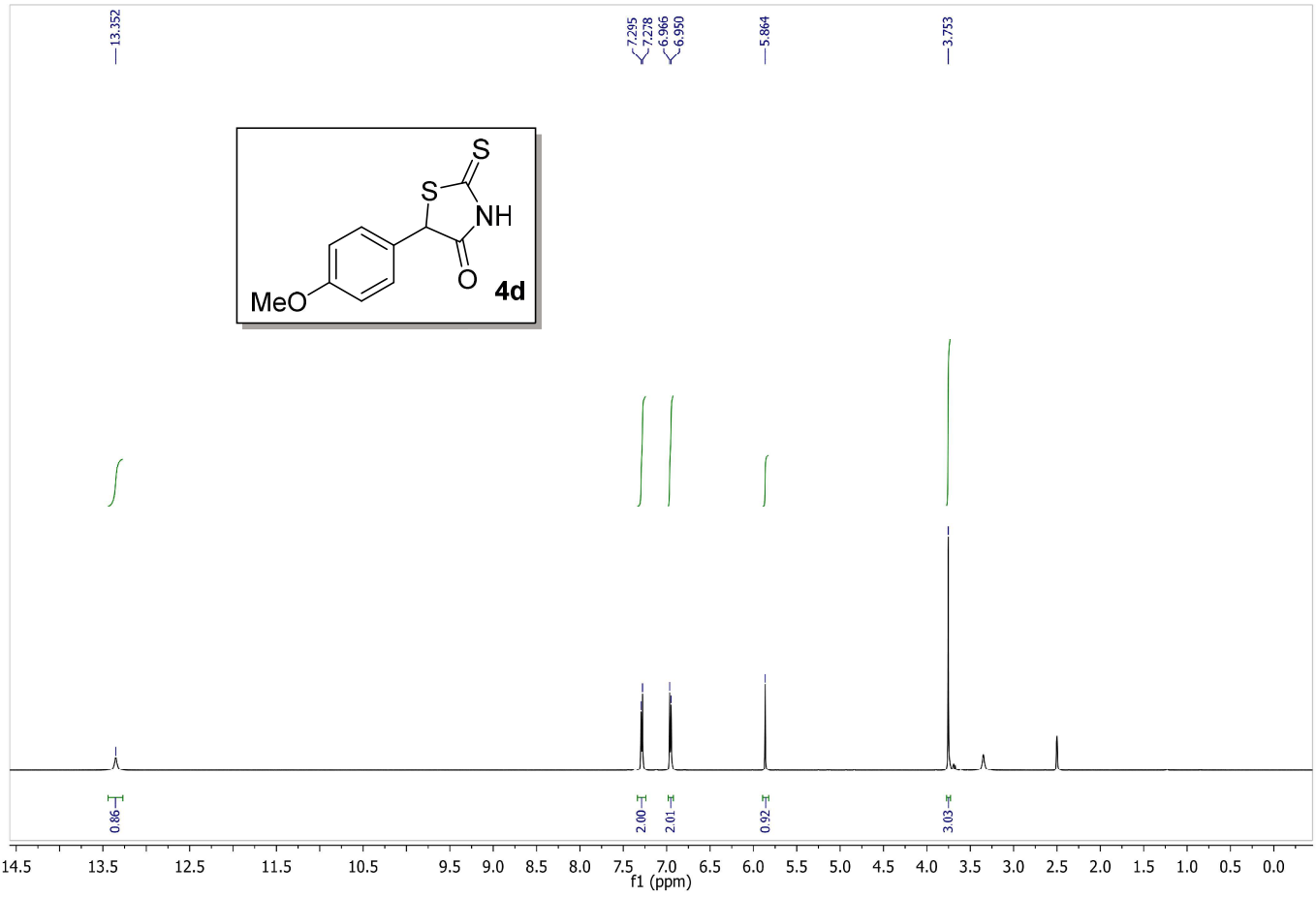
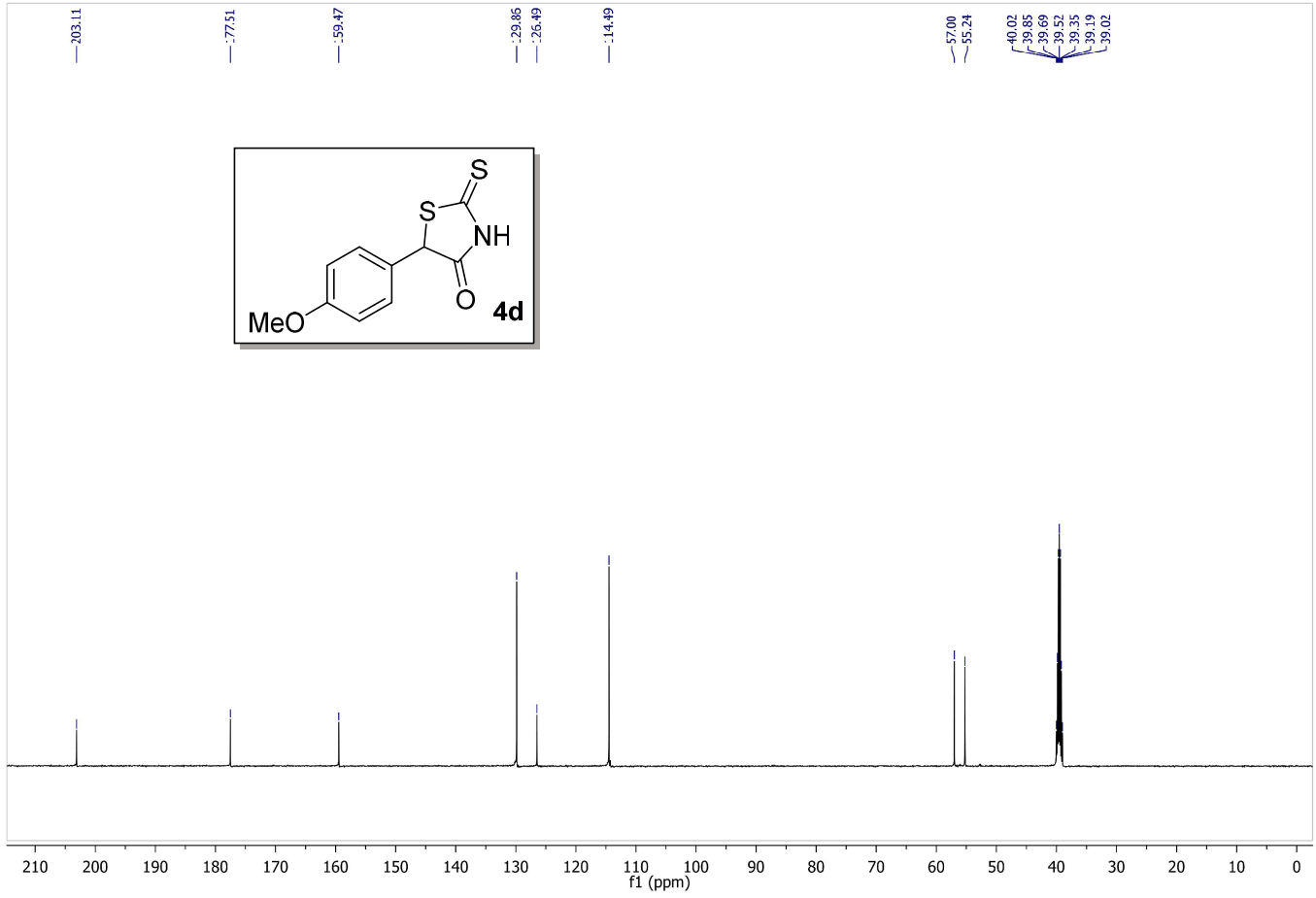




^{1}H NMR (500 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6), **4d**





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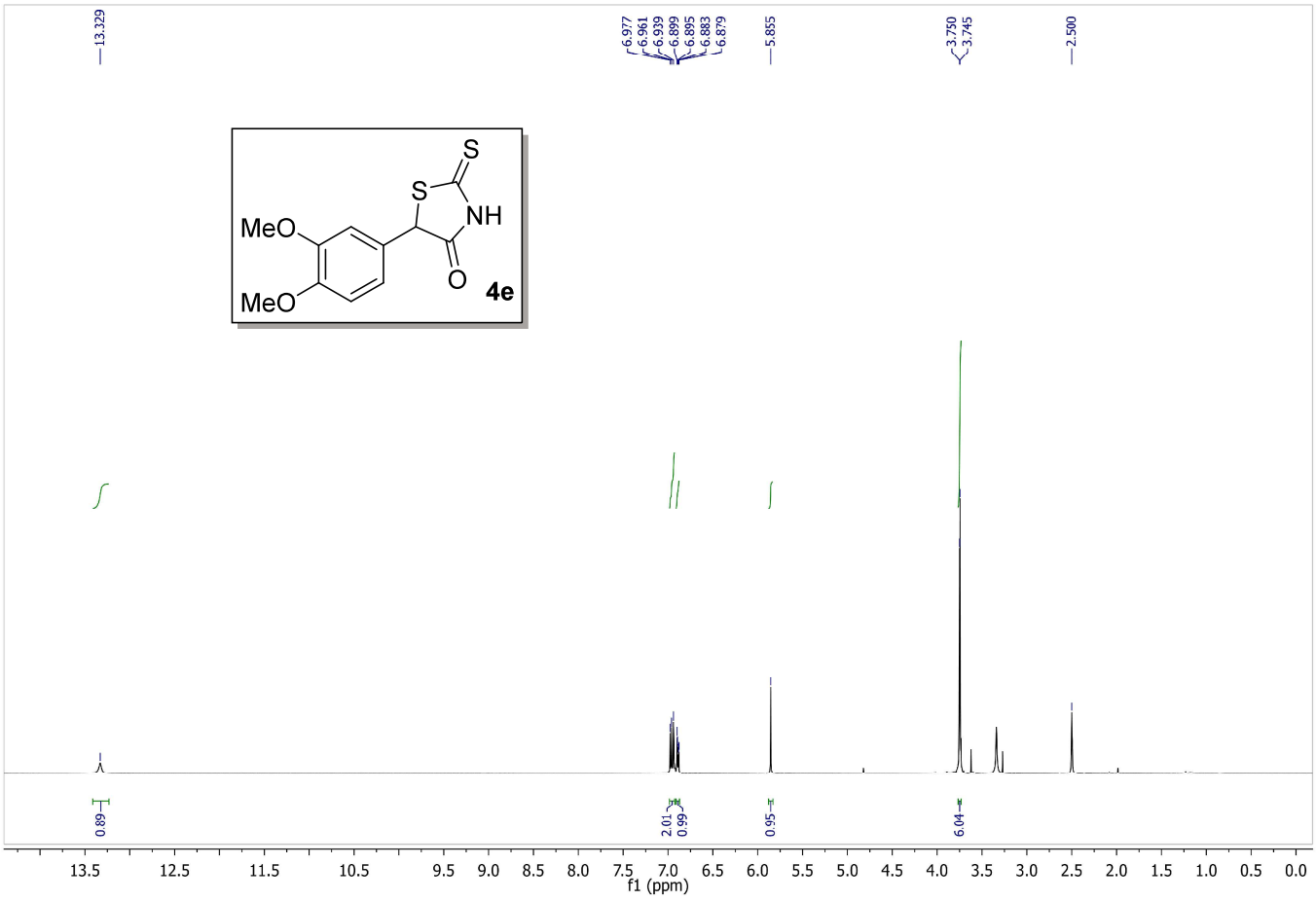
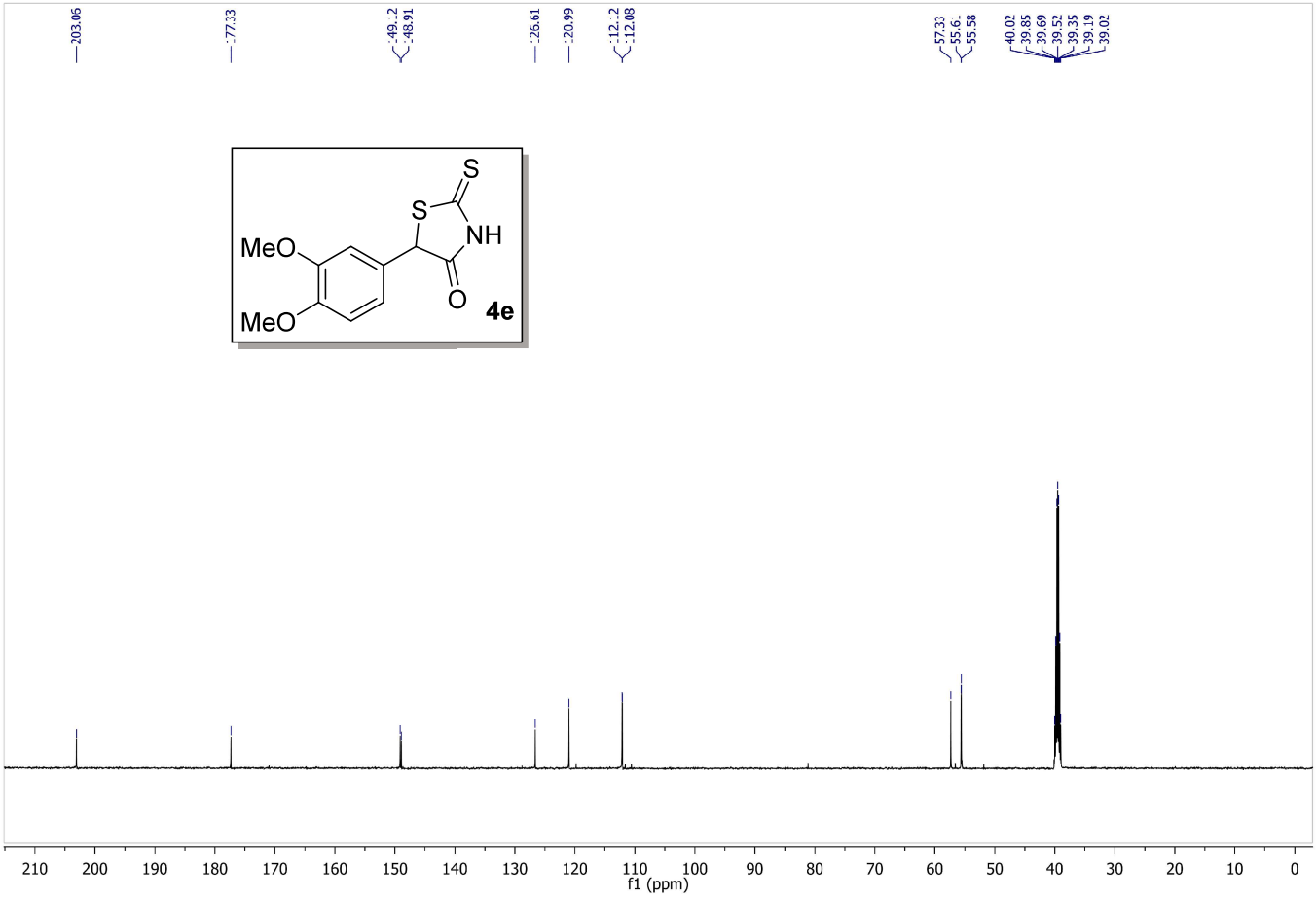
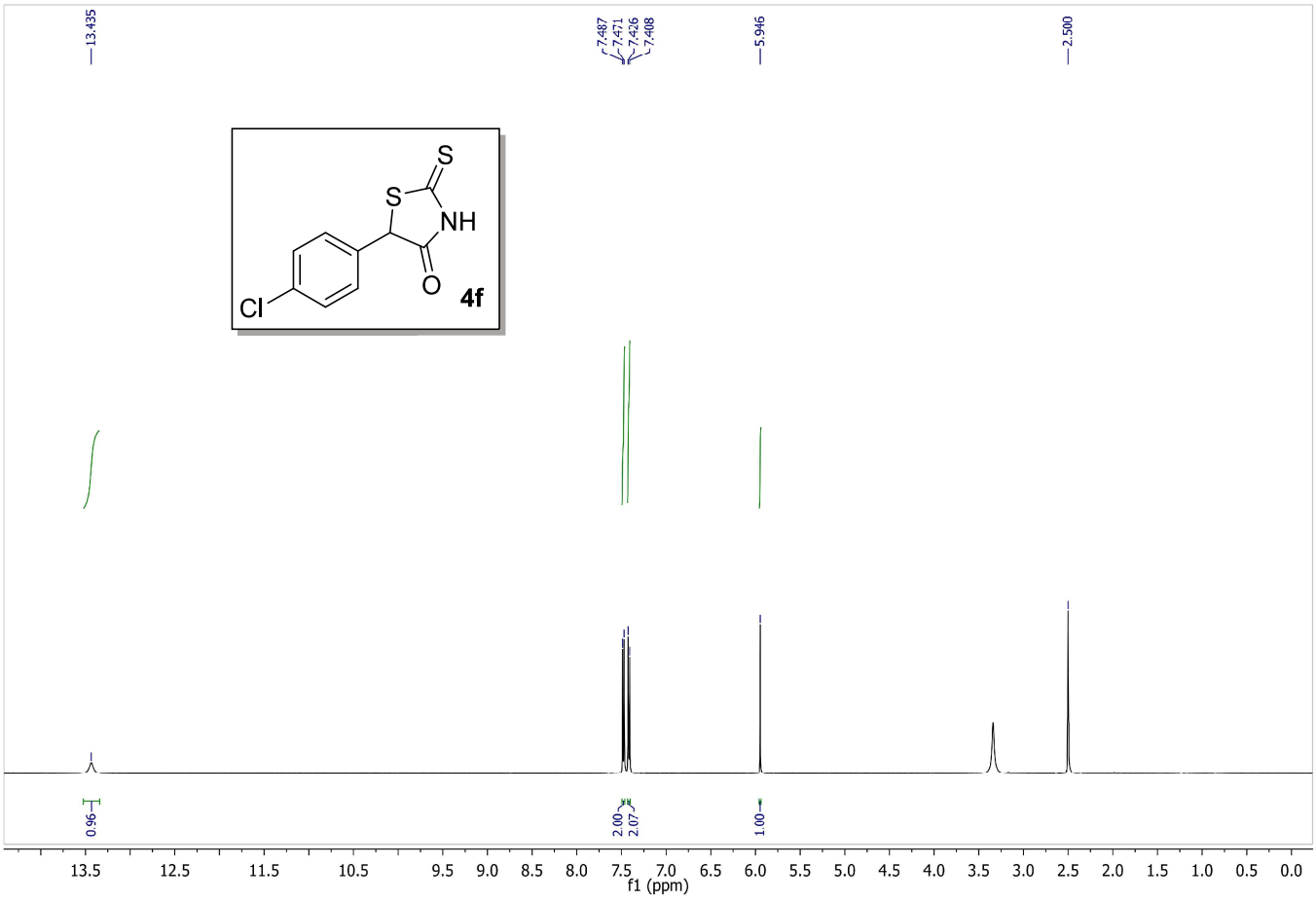
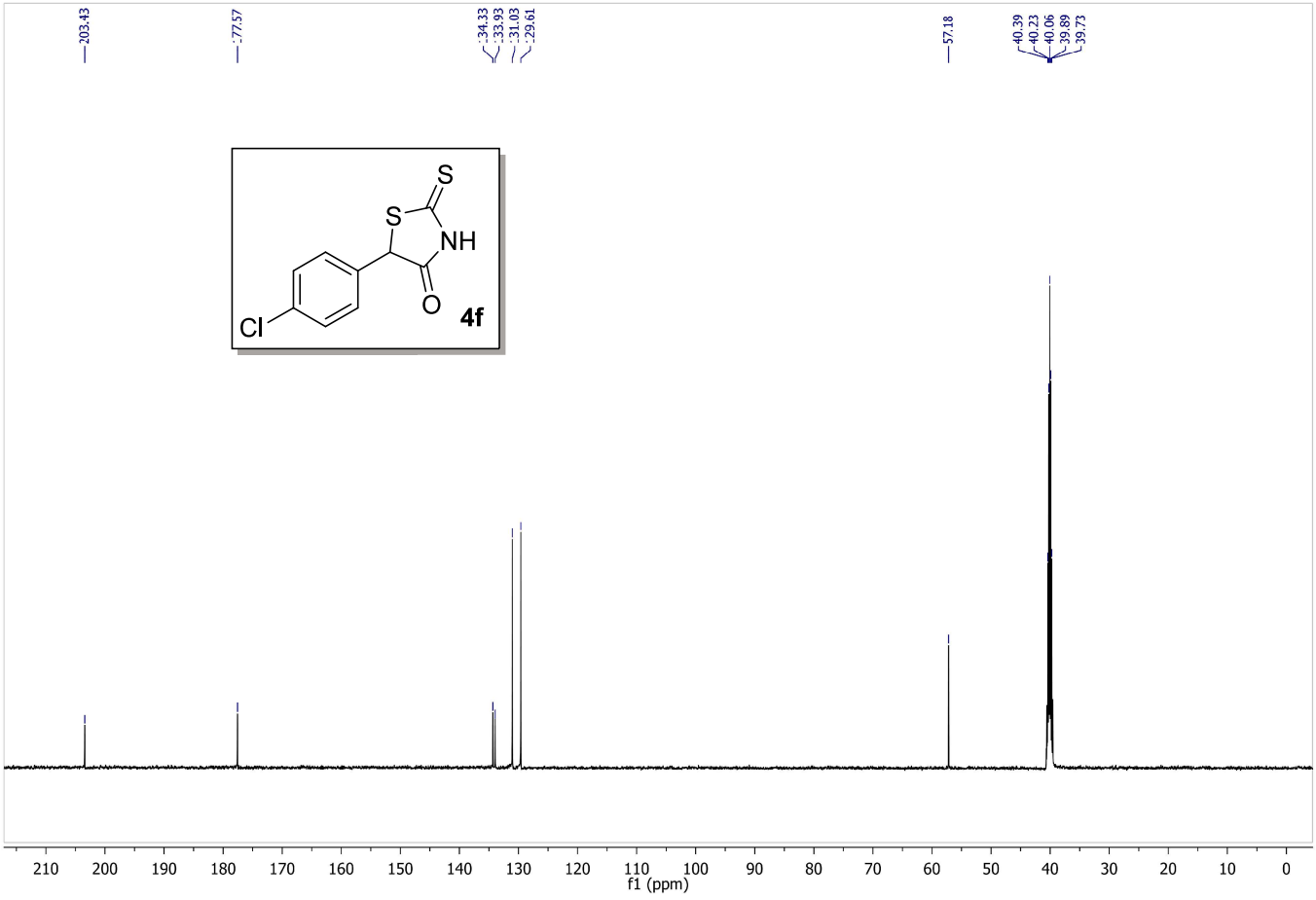




^{1}H NMR (500 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6), **4f**





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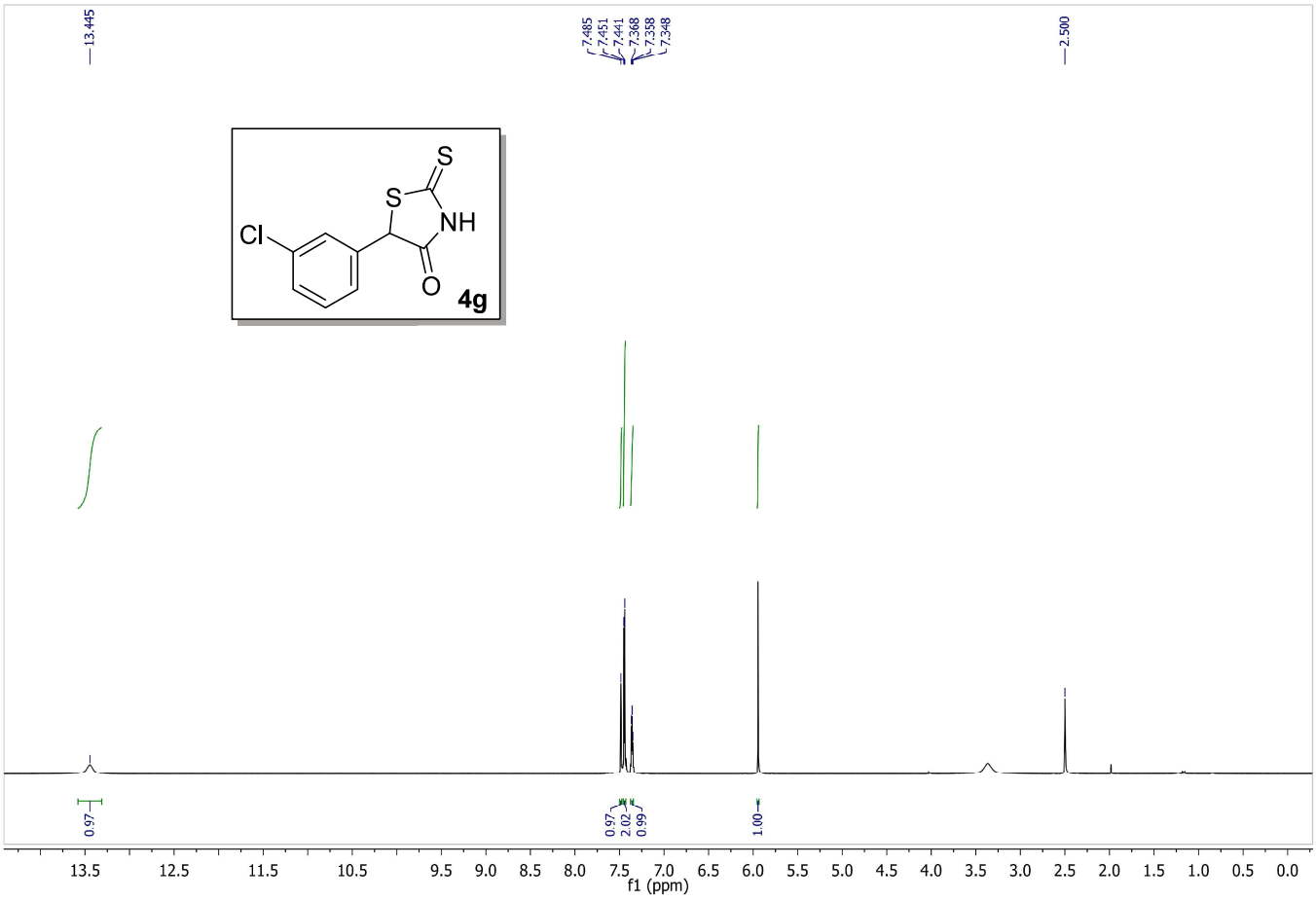

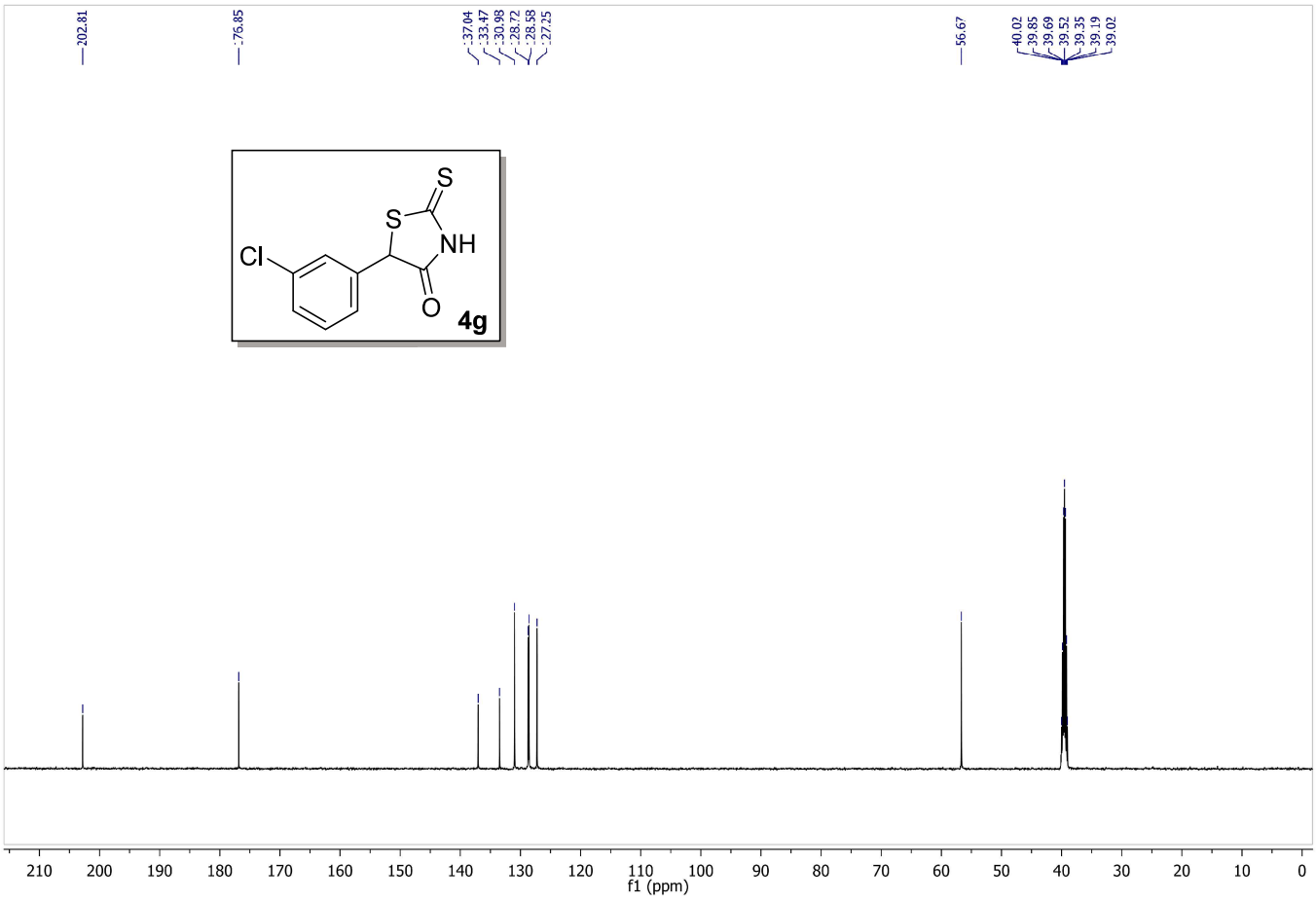

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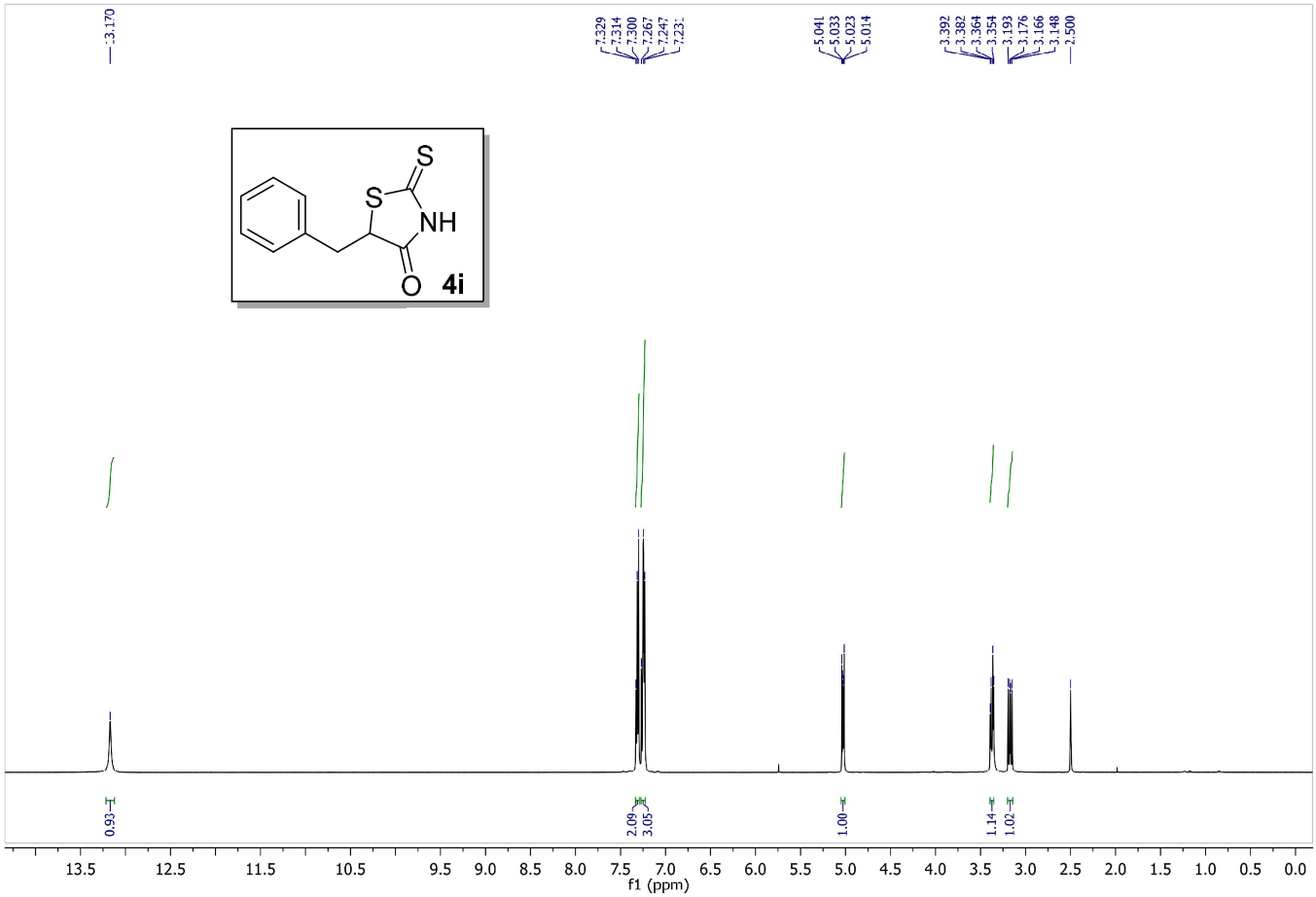
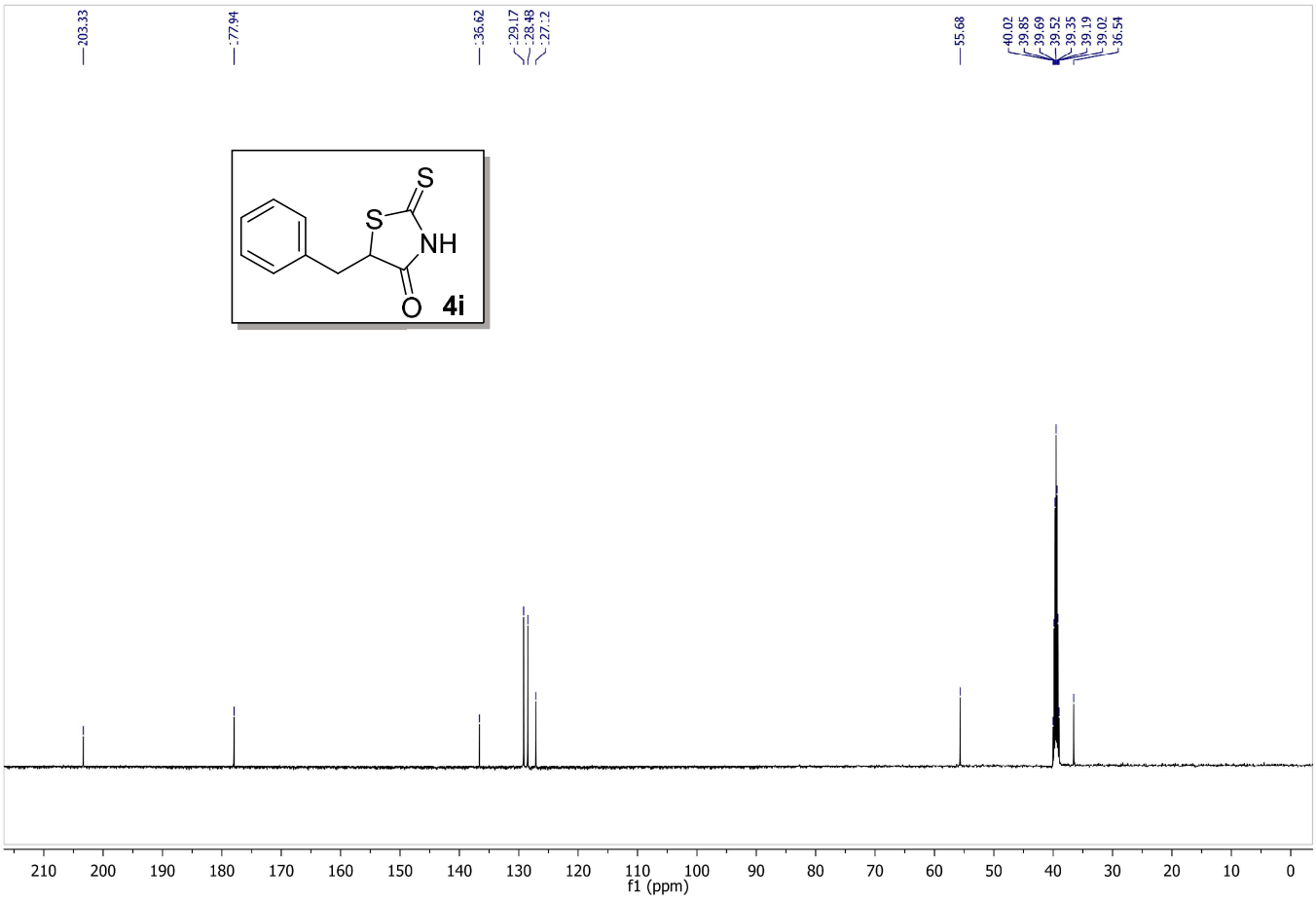
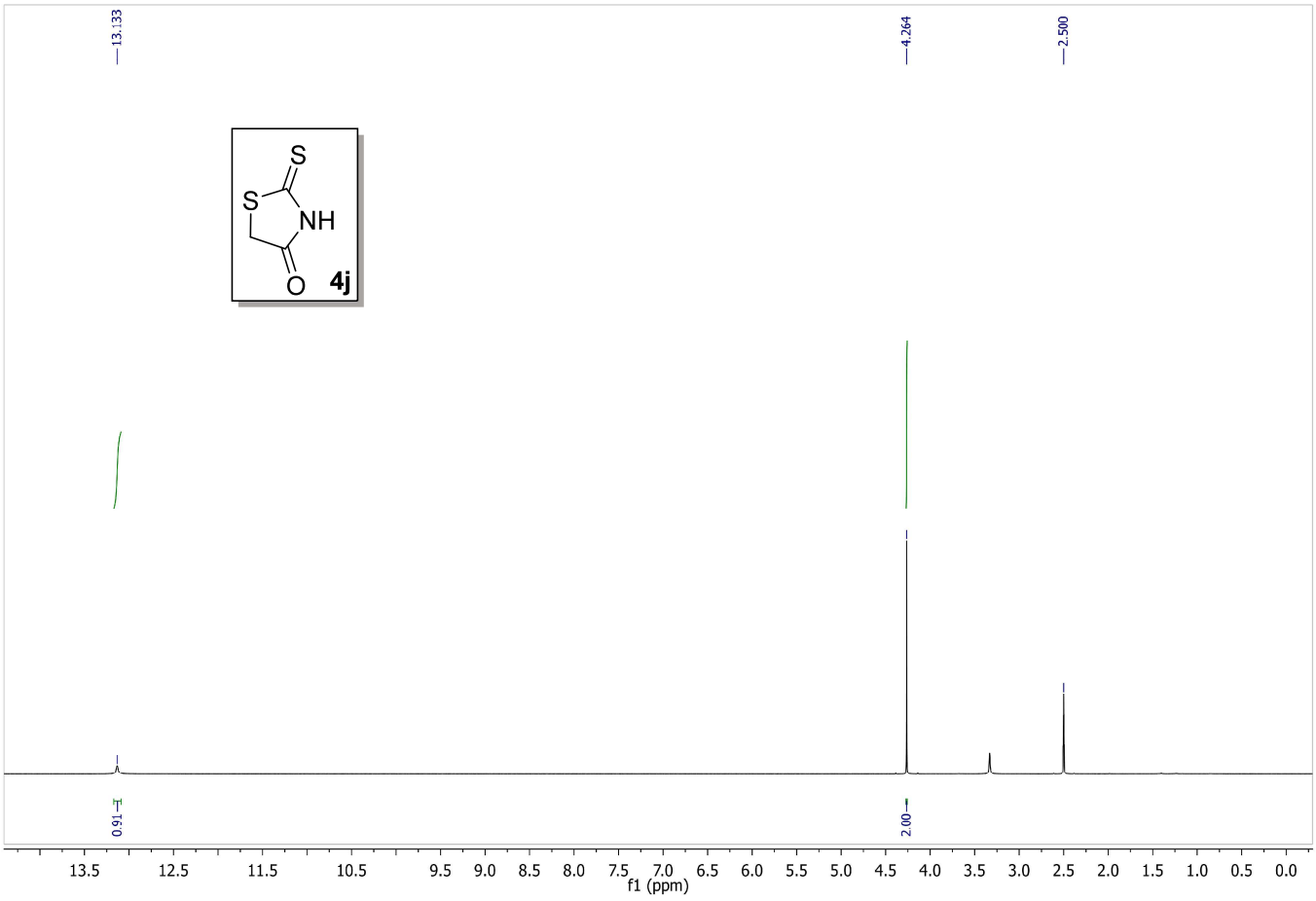
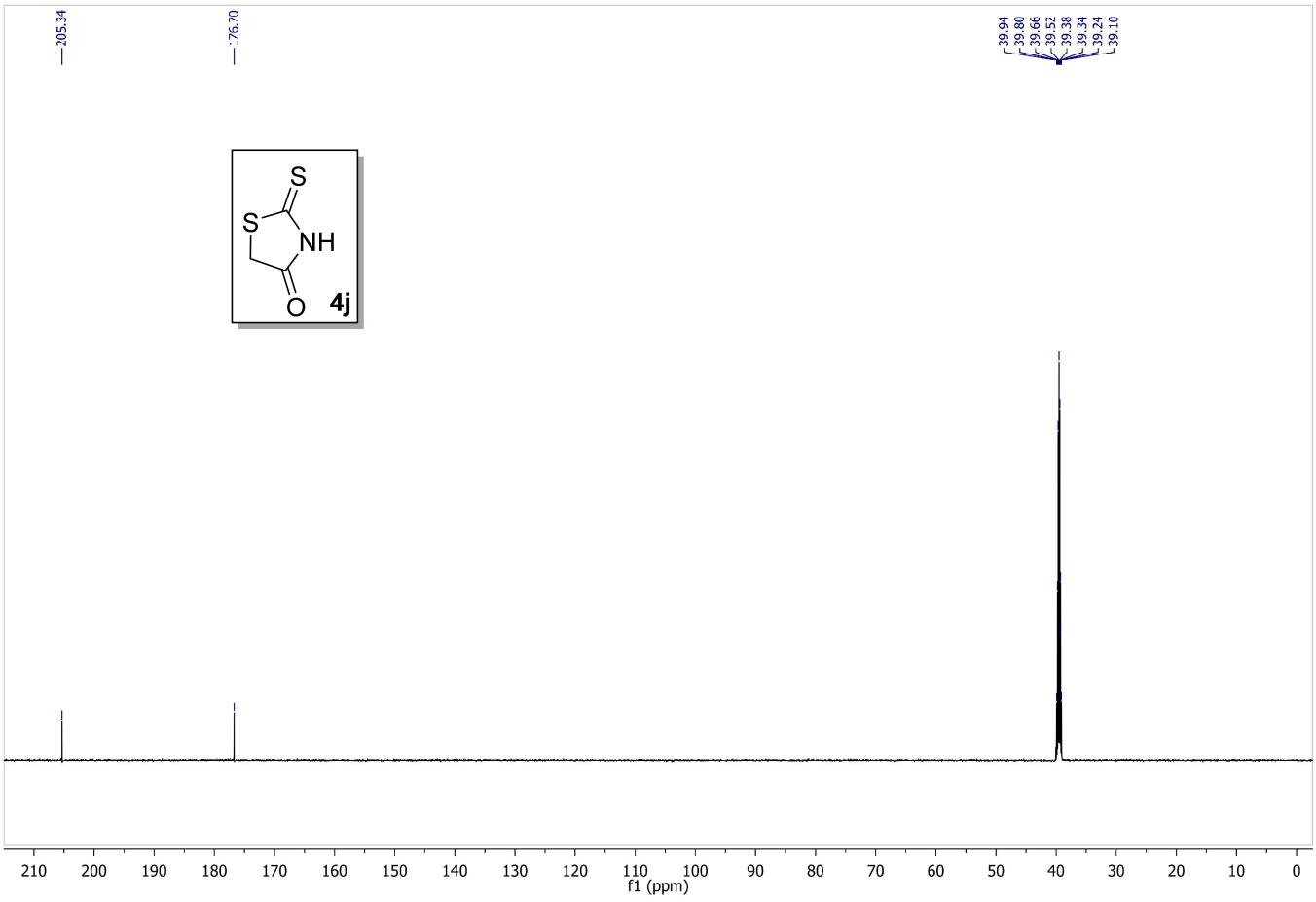


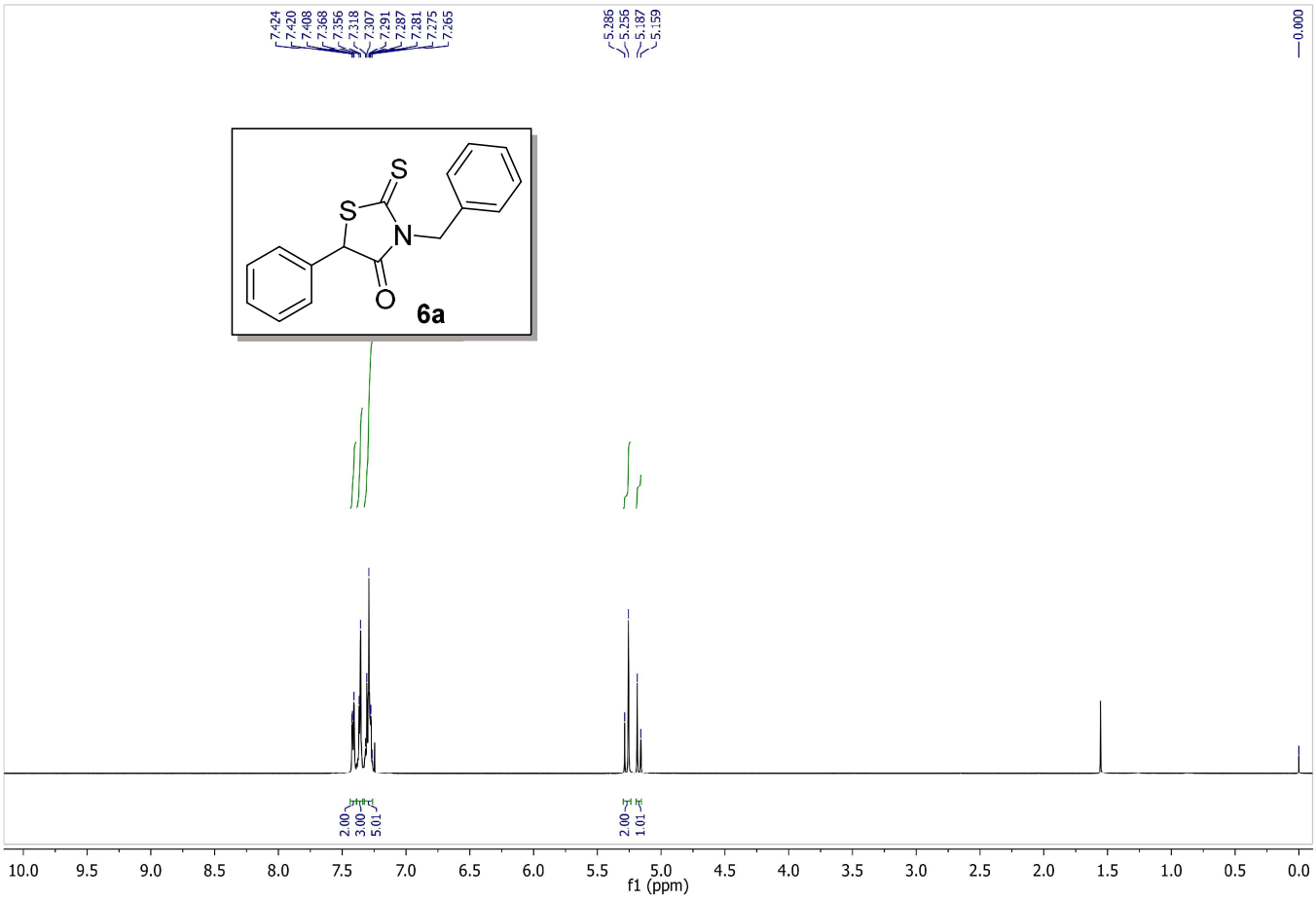


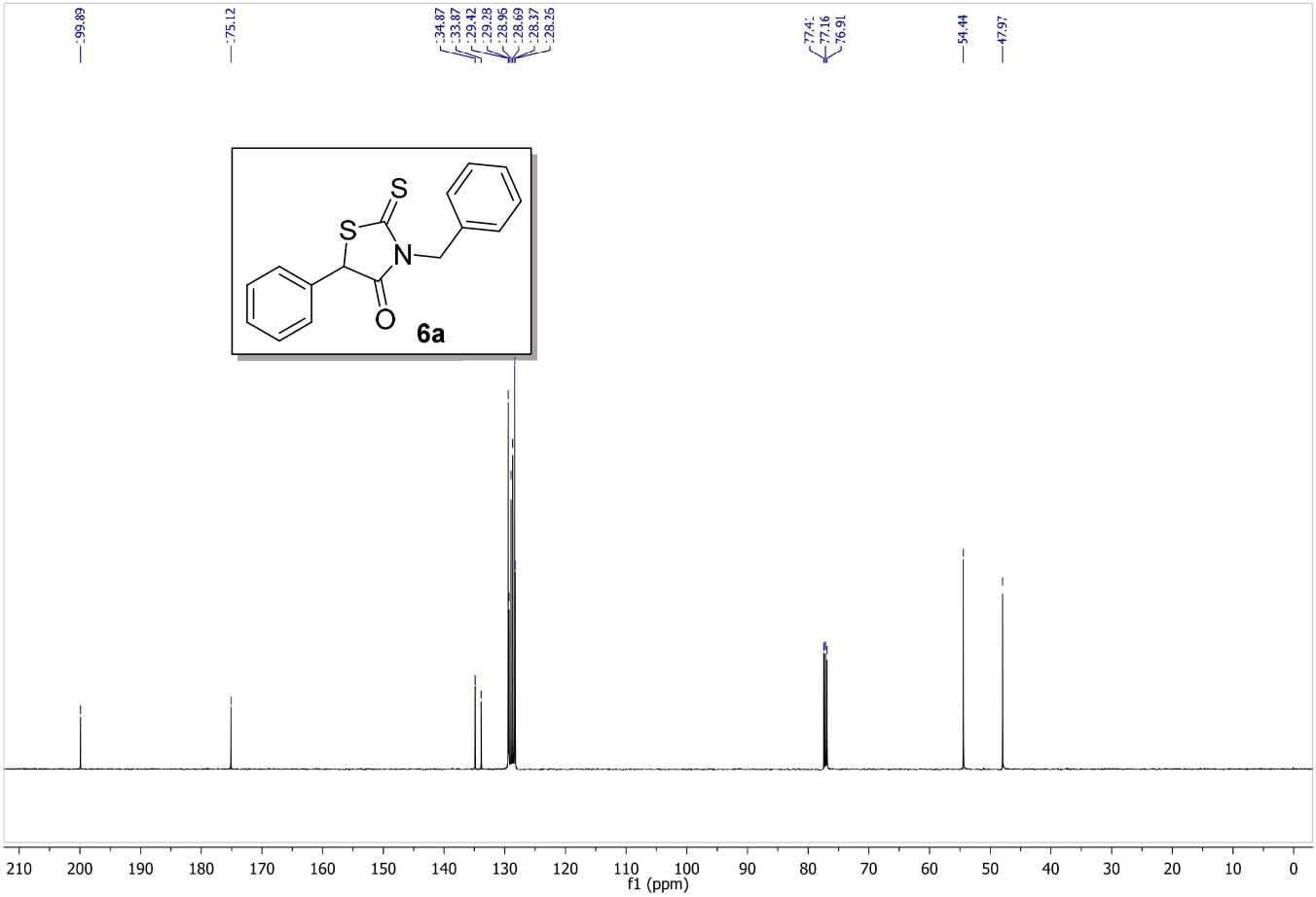
^{1}H NMR (600 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6), **4j**



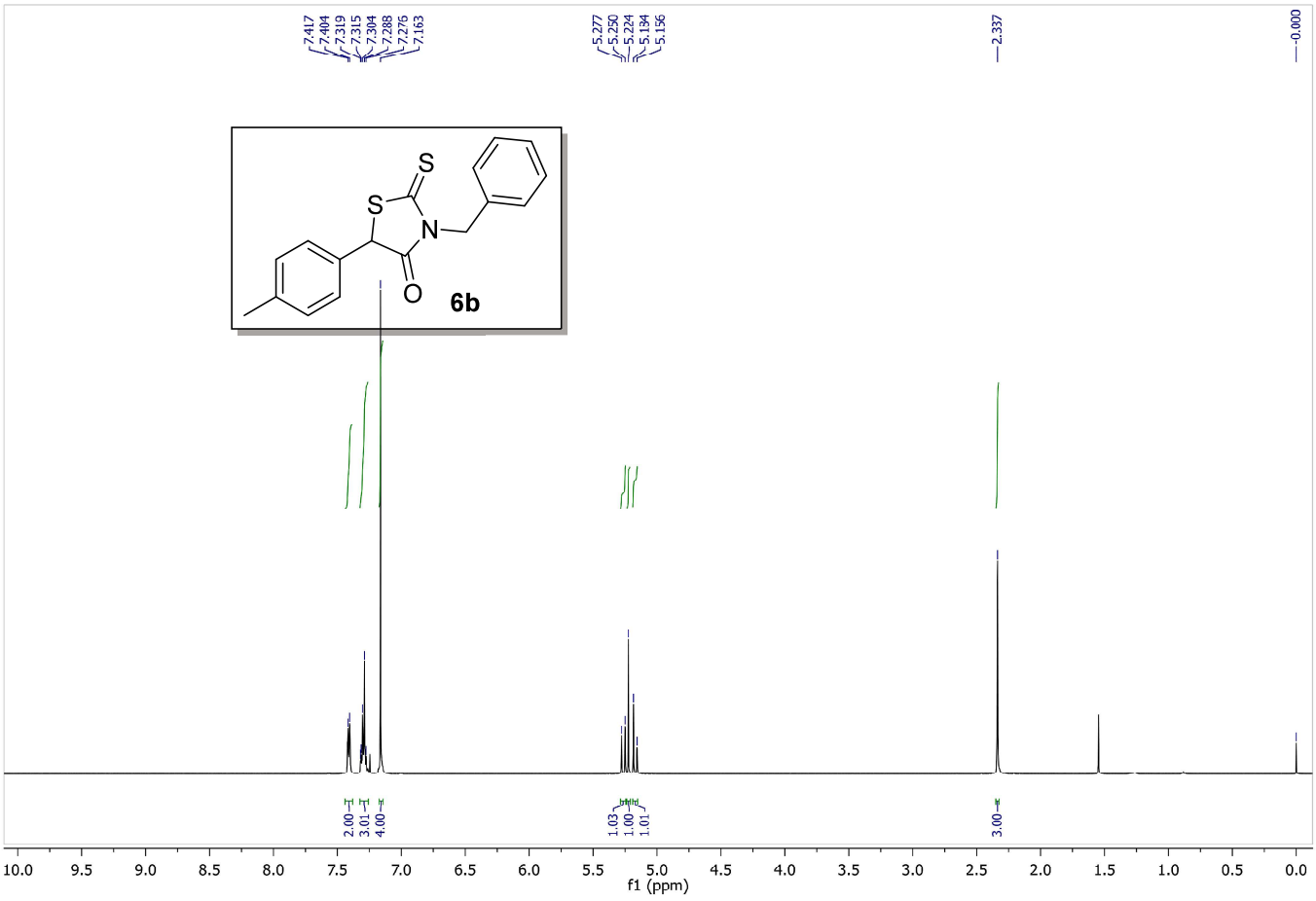


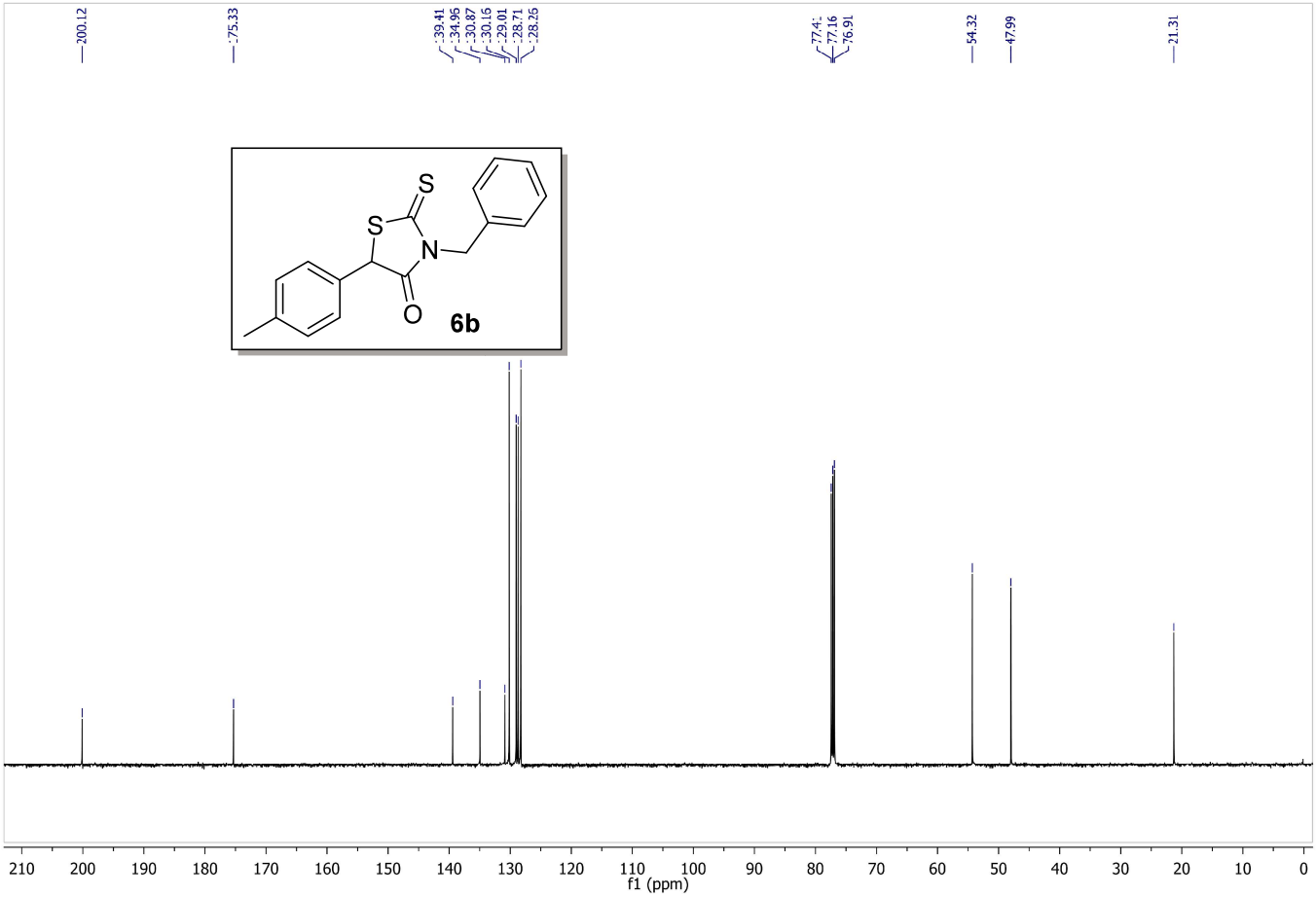
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6a**





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **6b**





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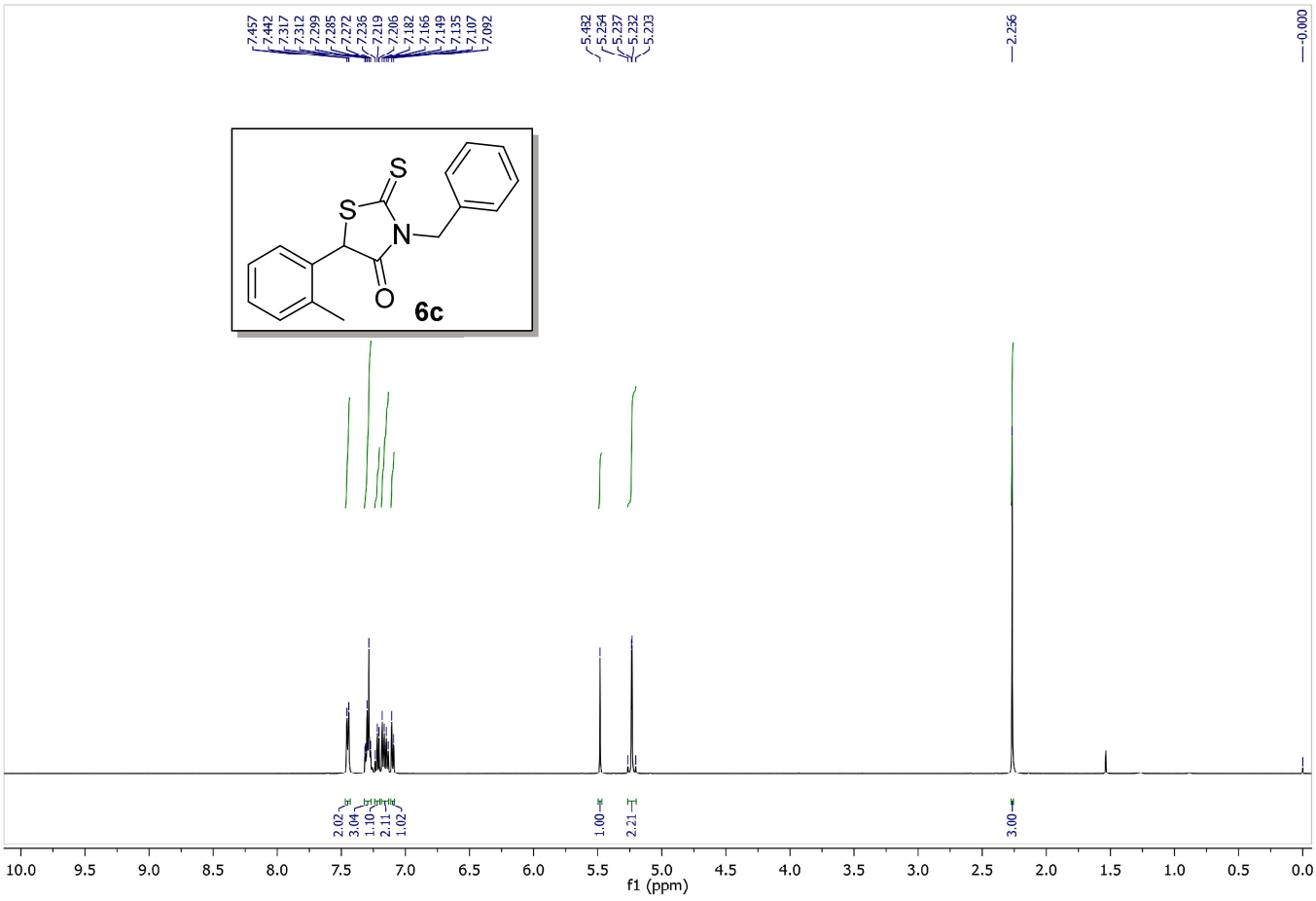
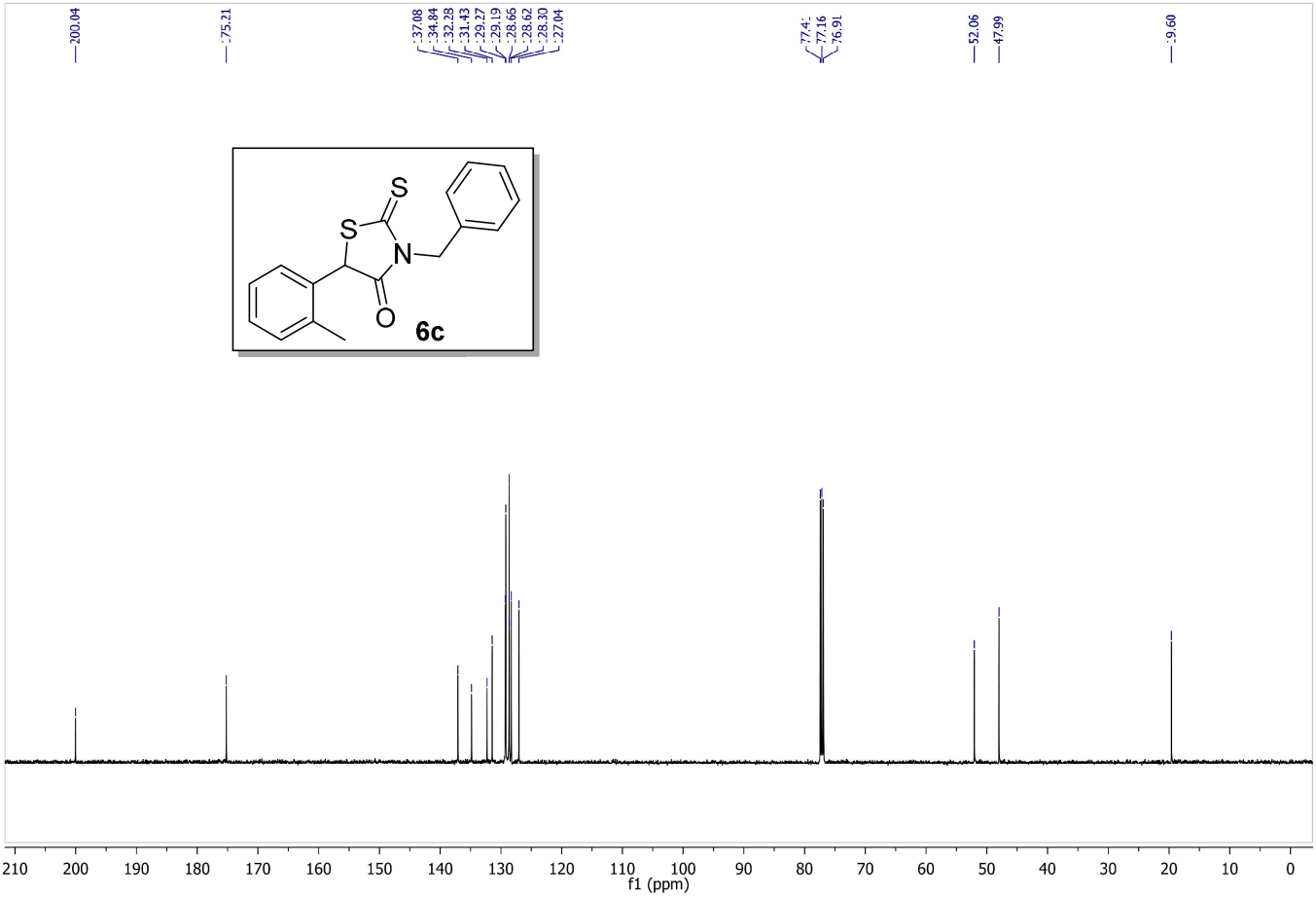
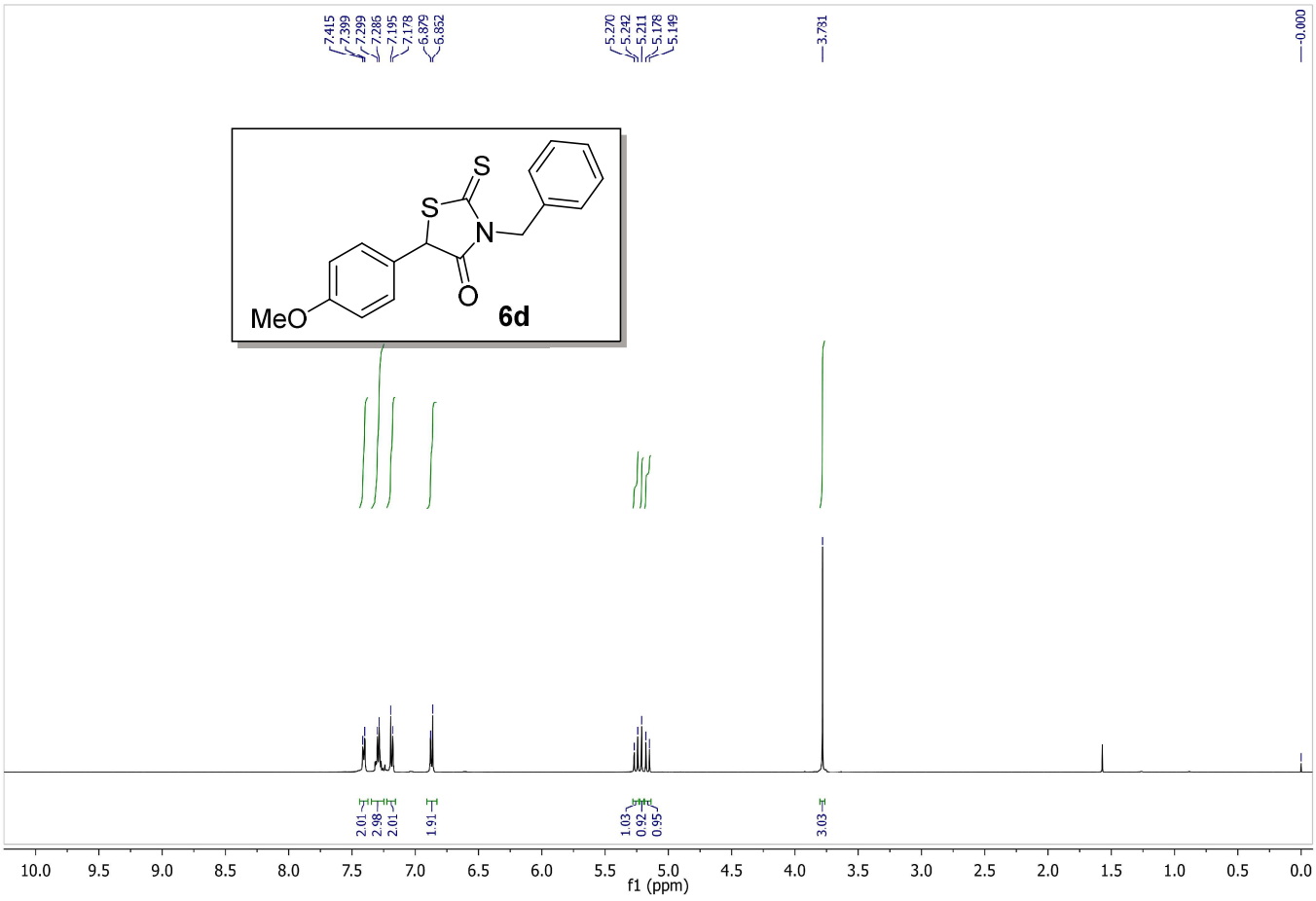
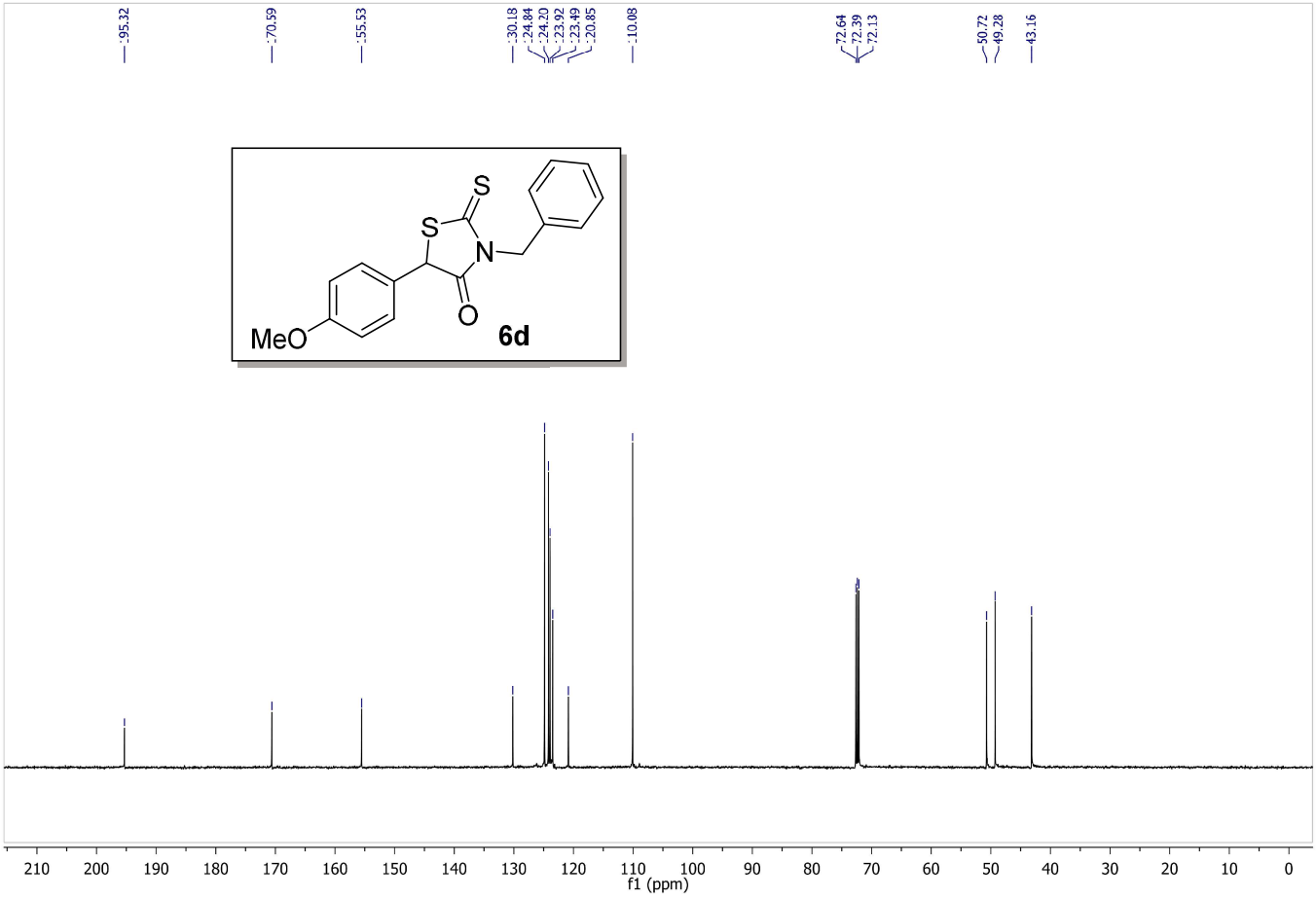




^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6d**





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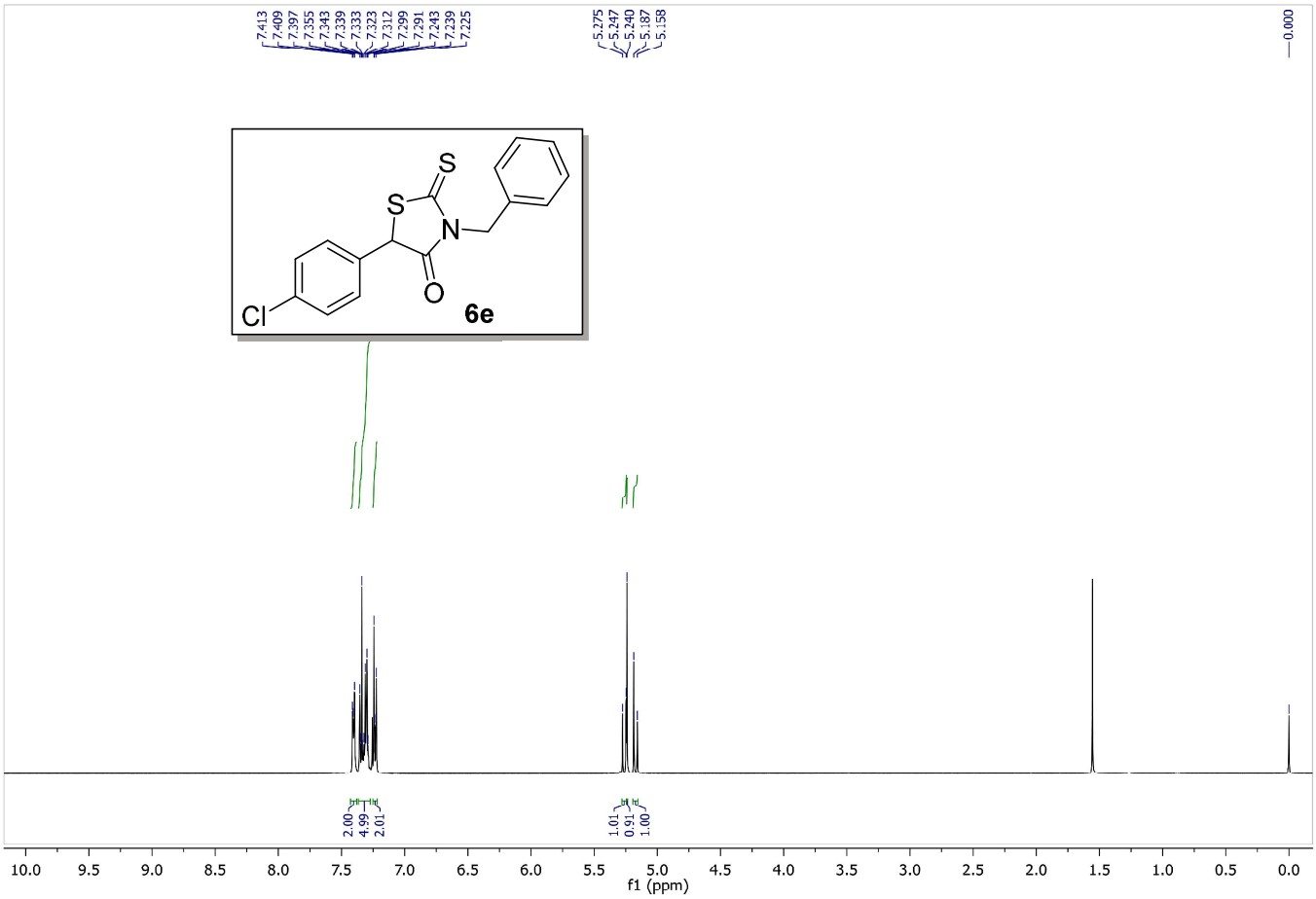
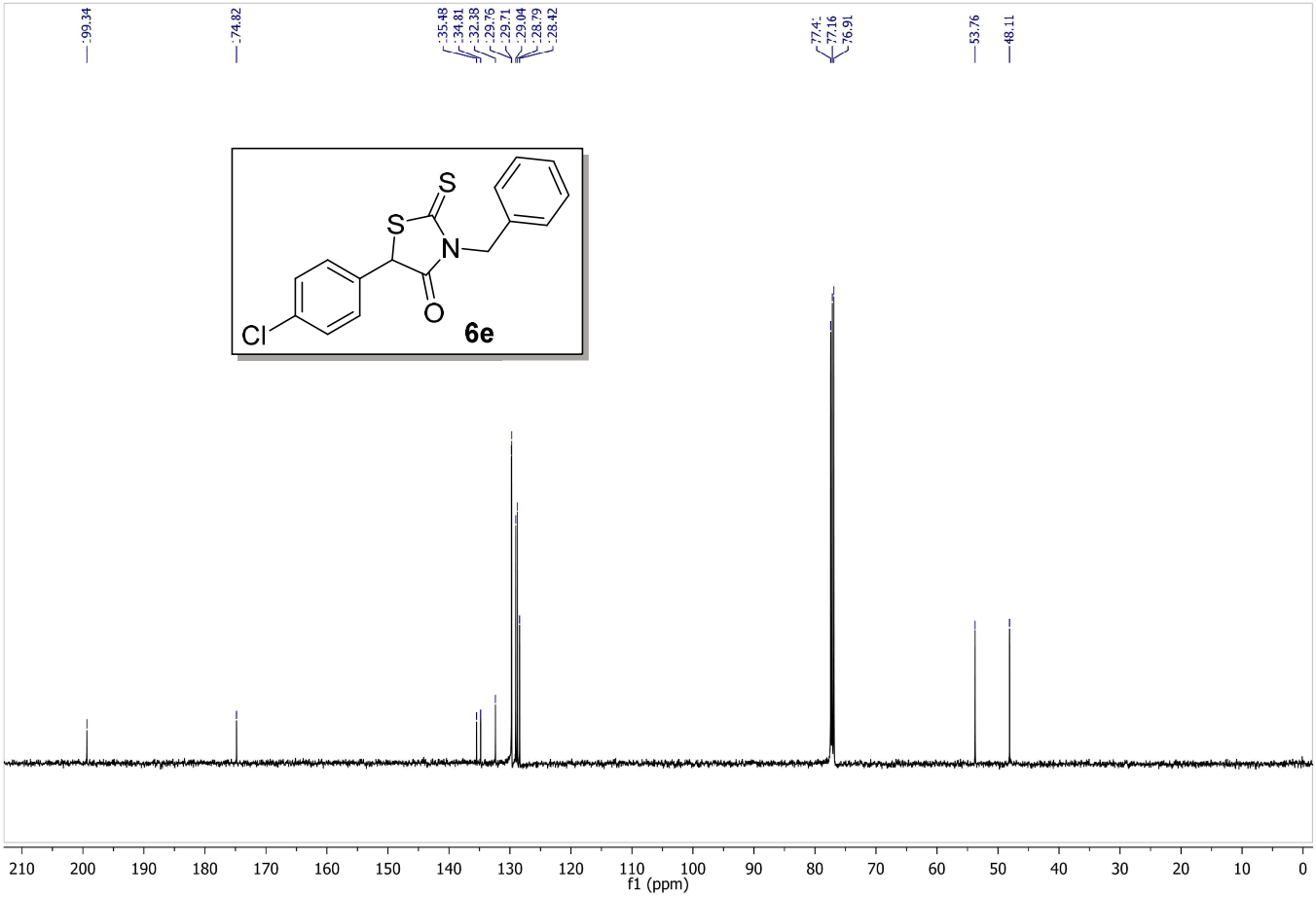
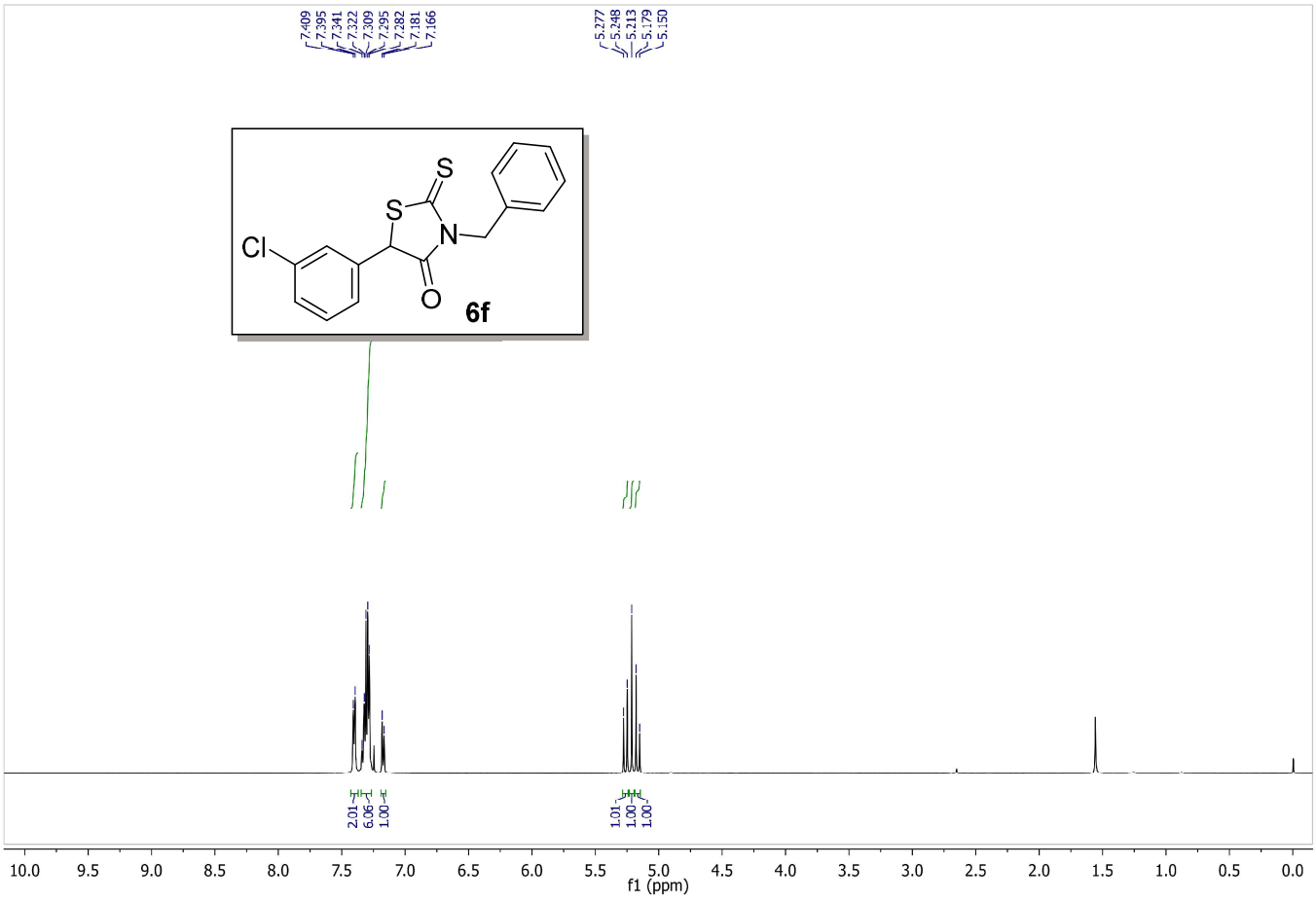
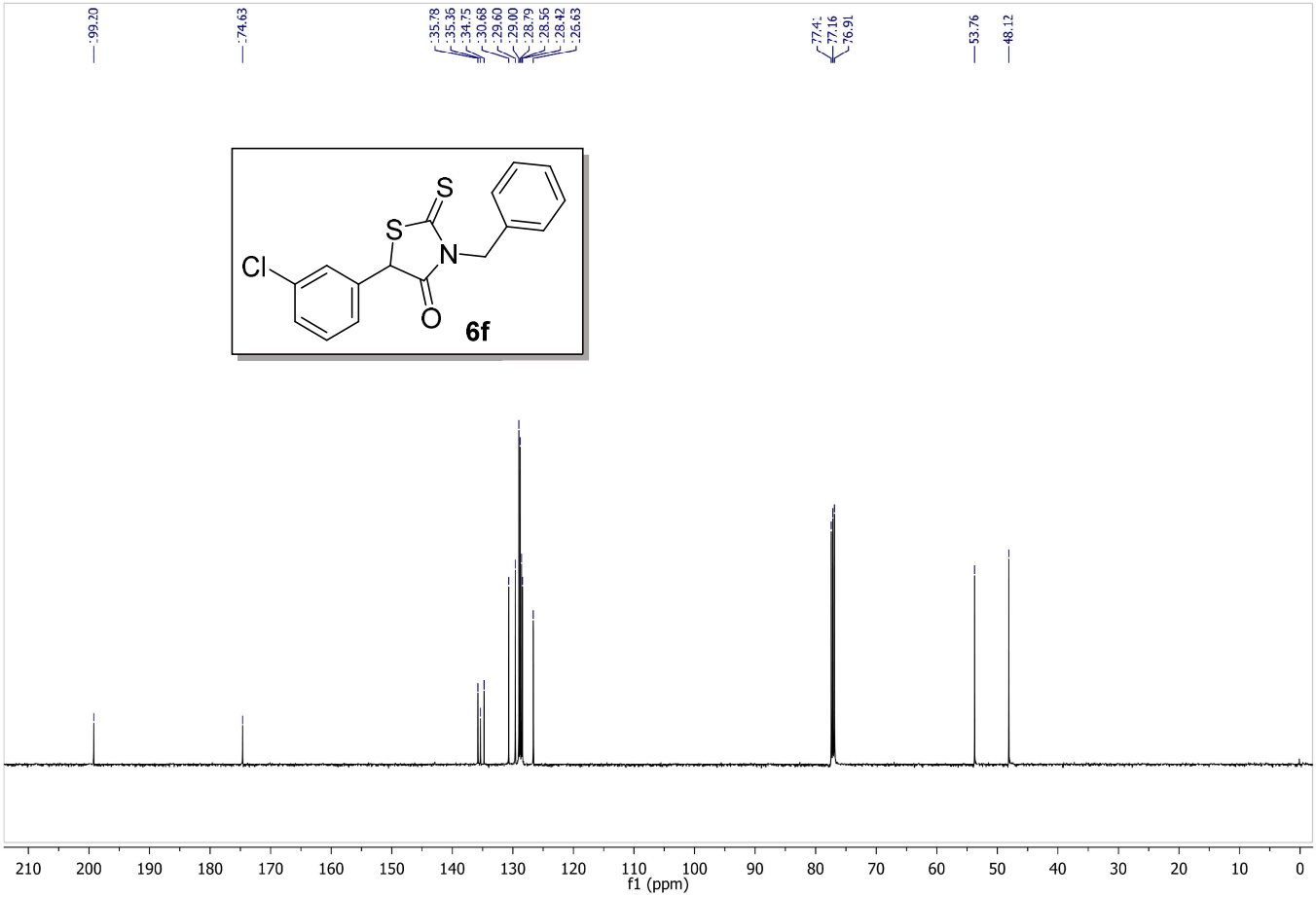


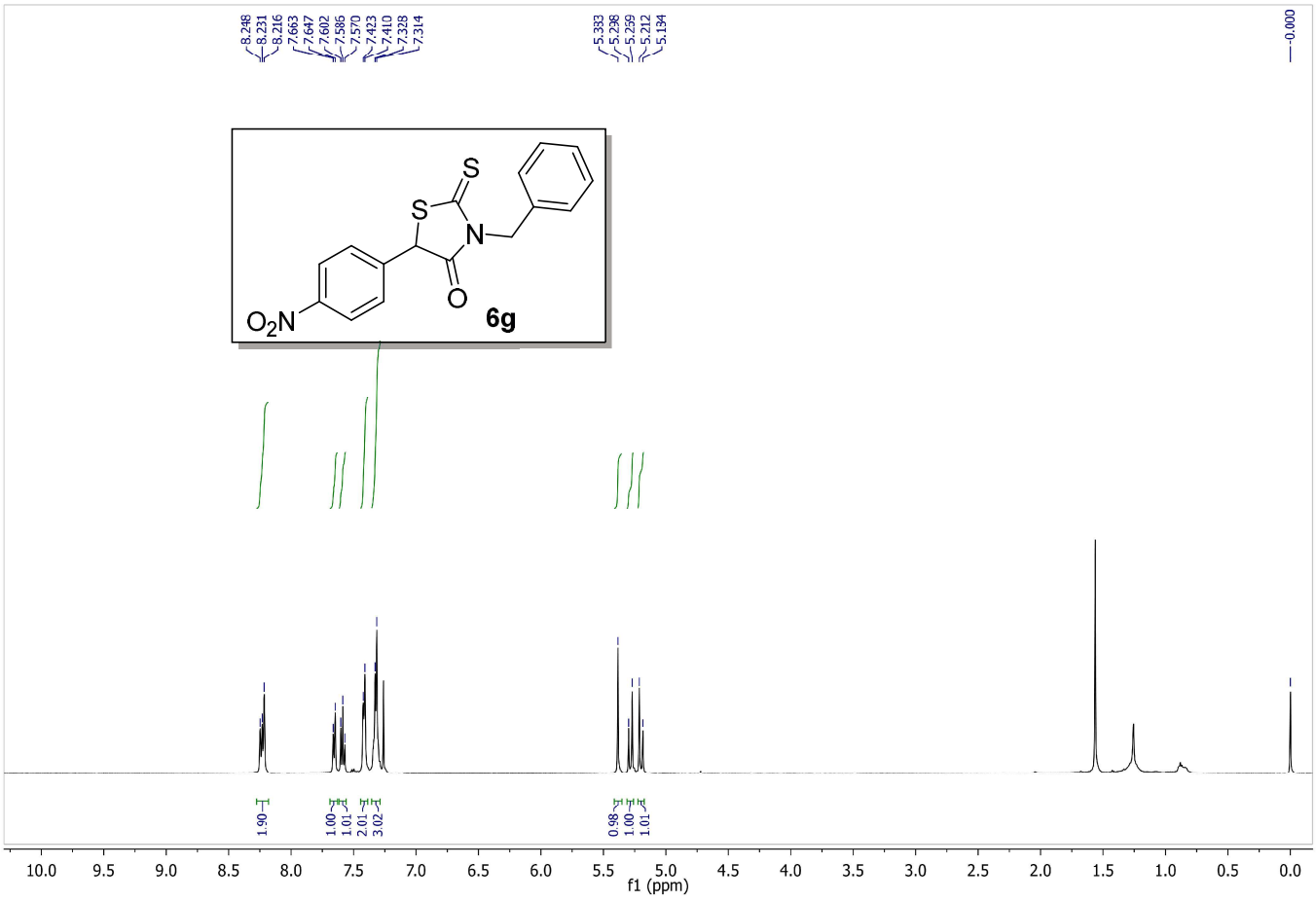


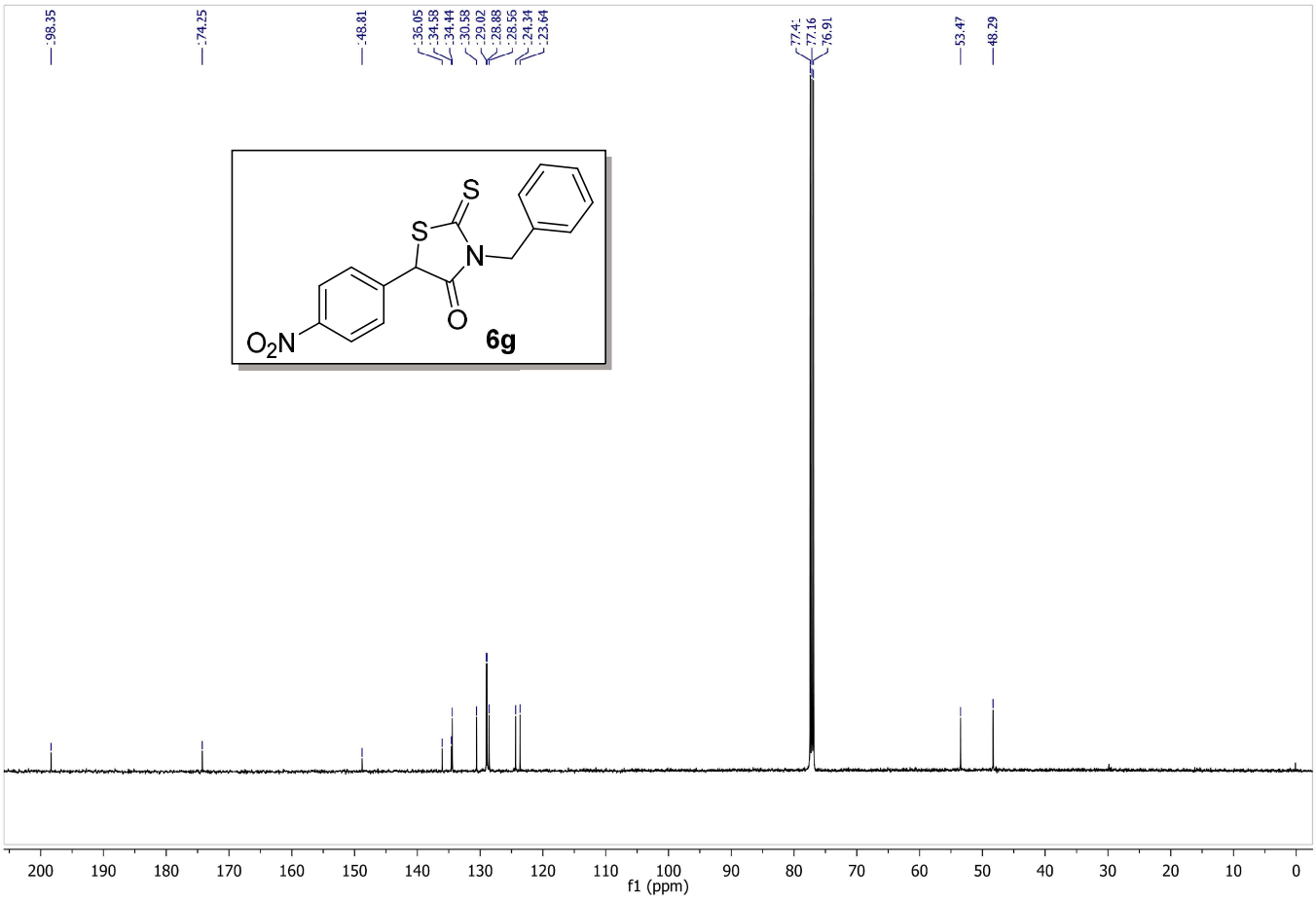
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6f**



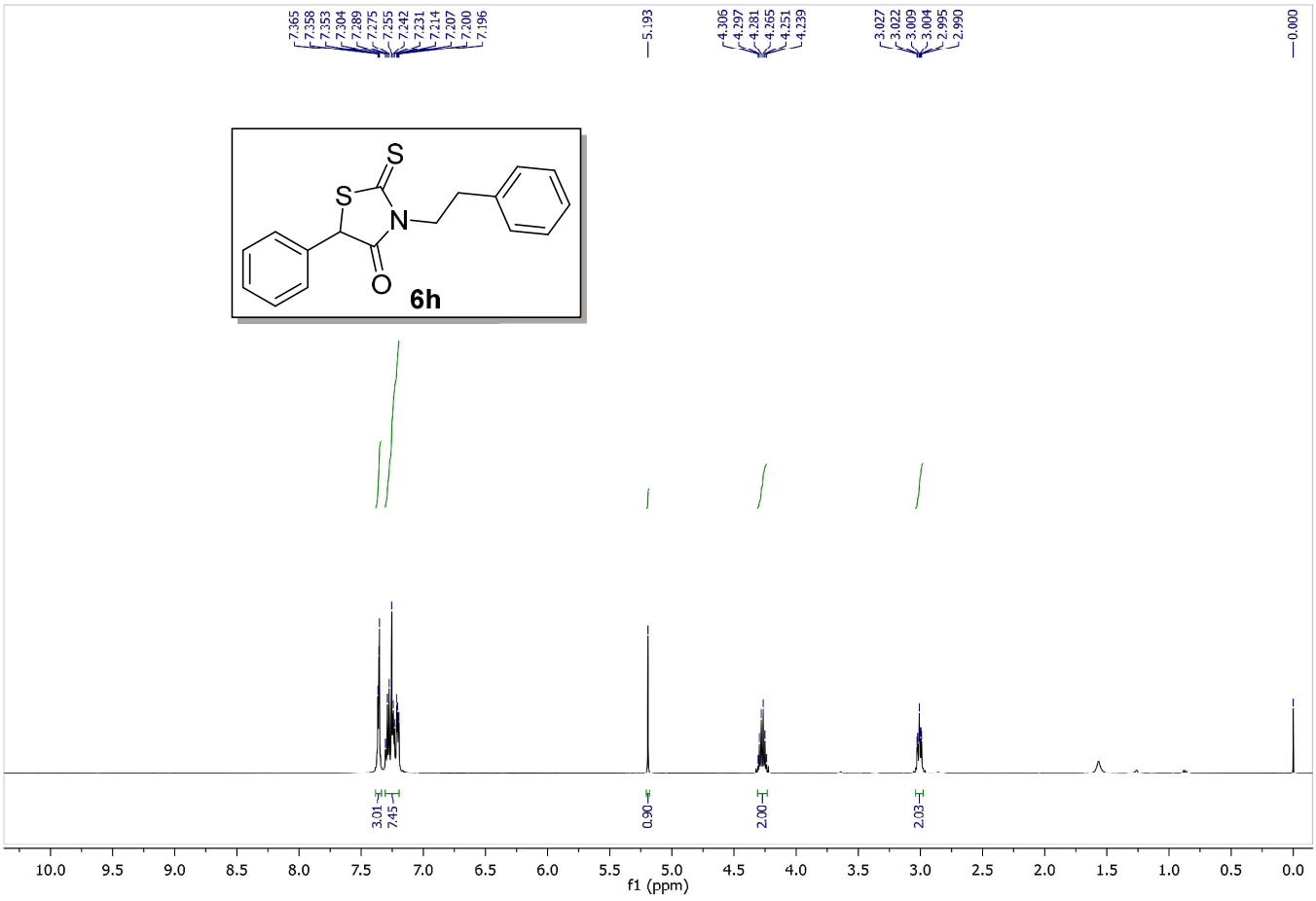


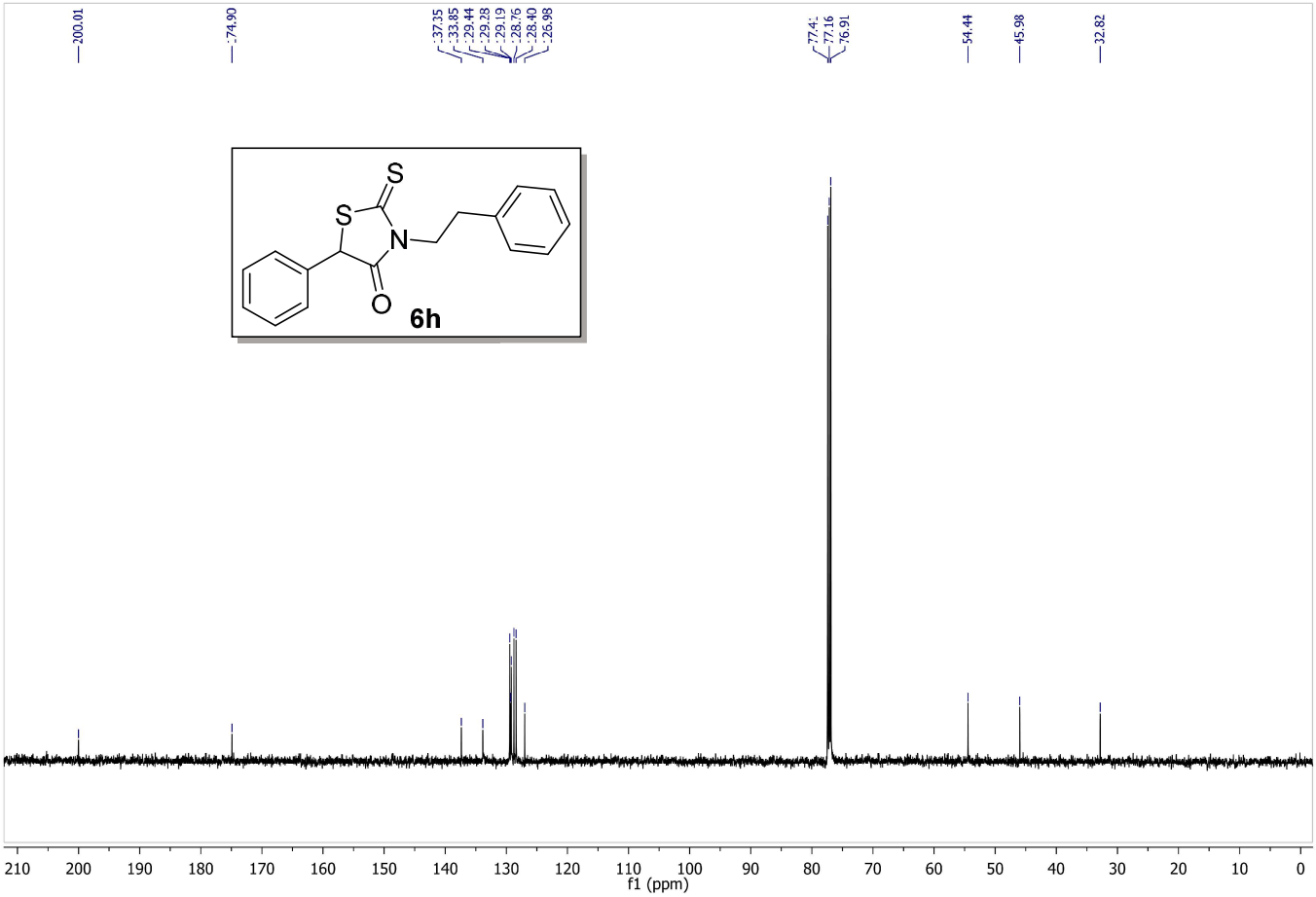
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **6g**



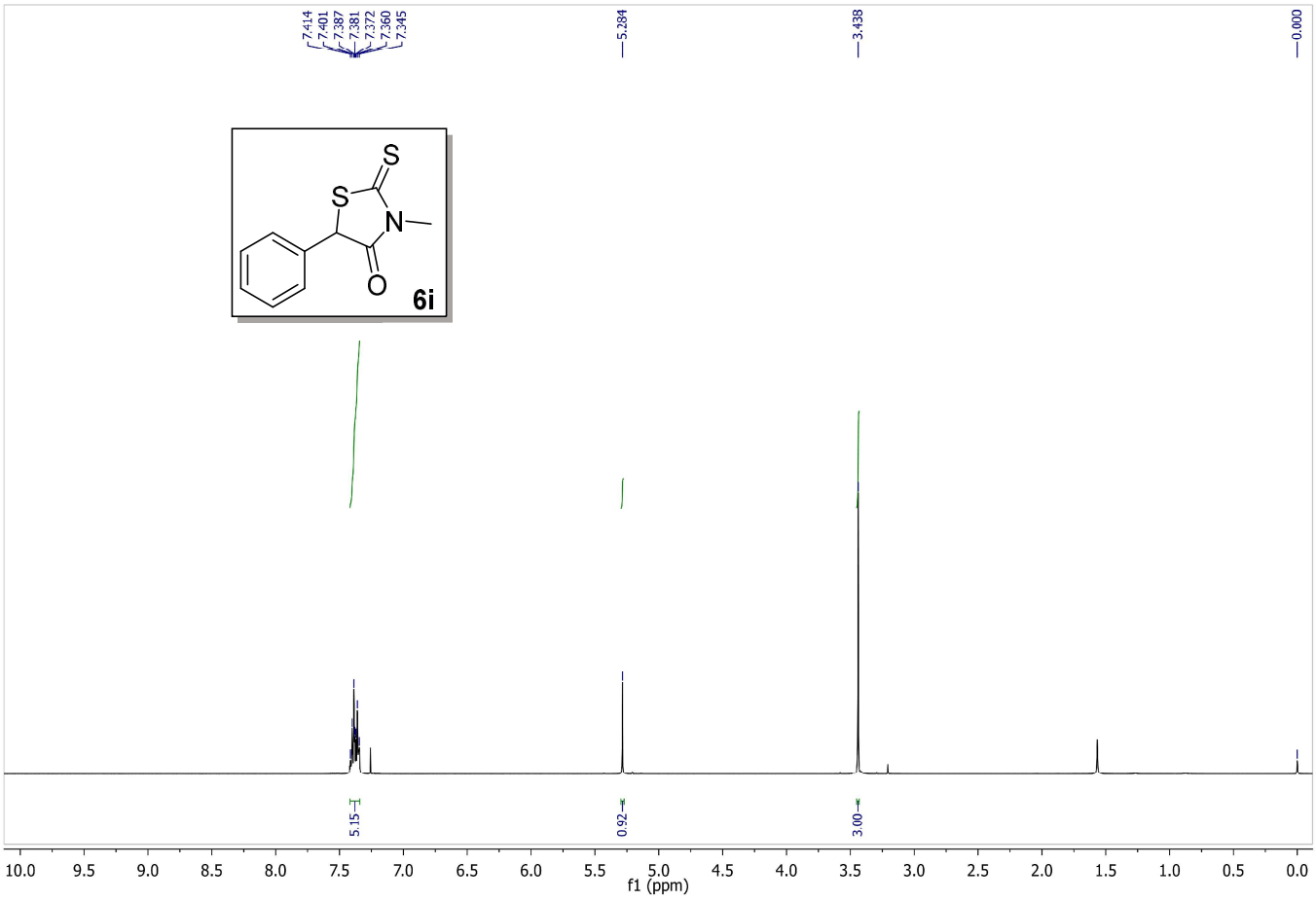


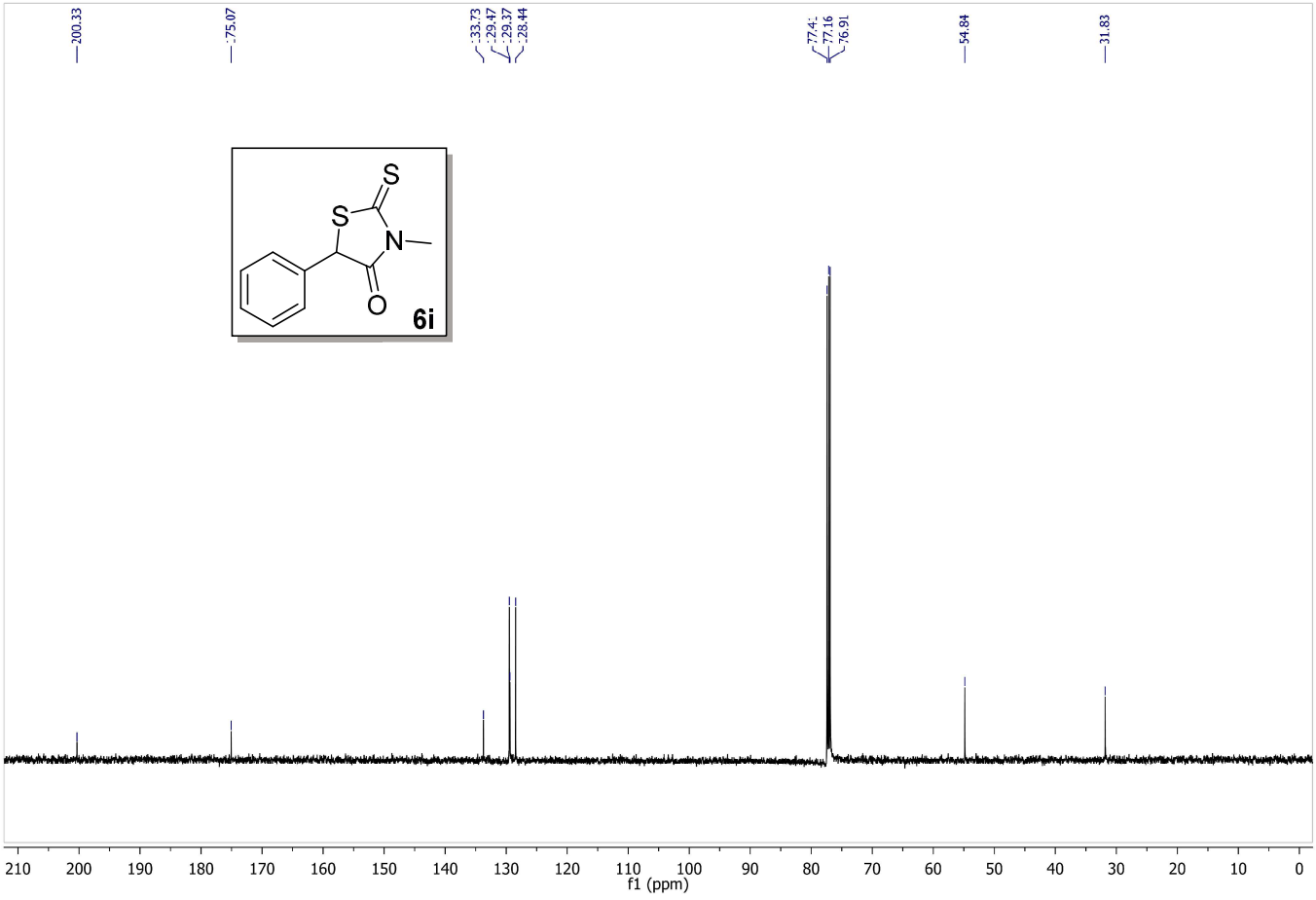
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6h**



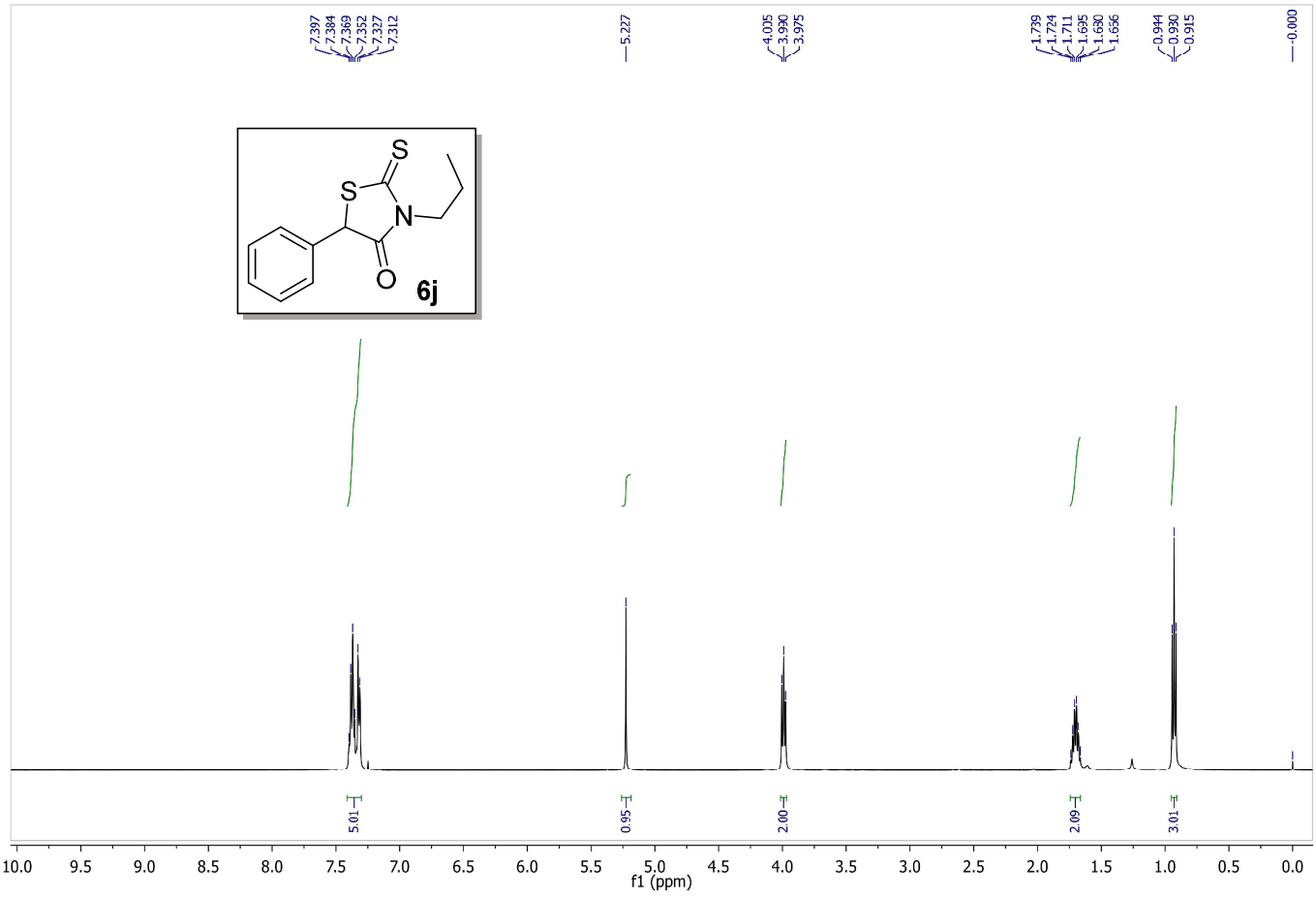


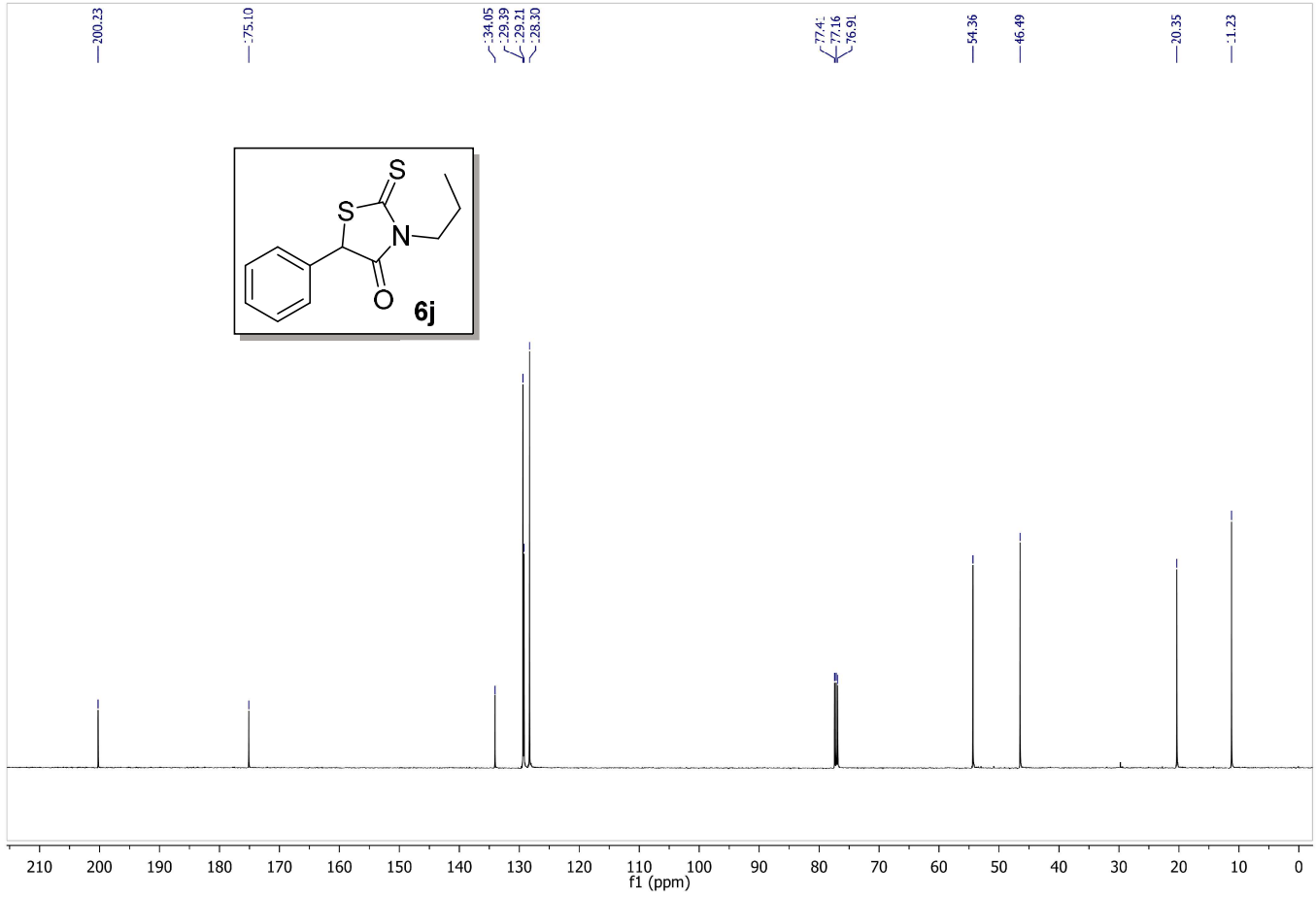
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6i**



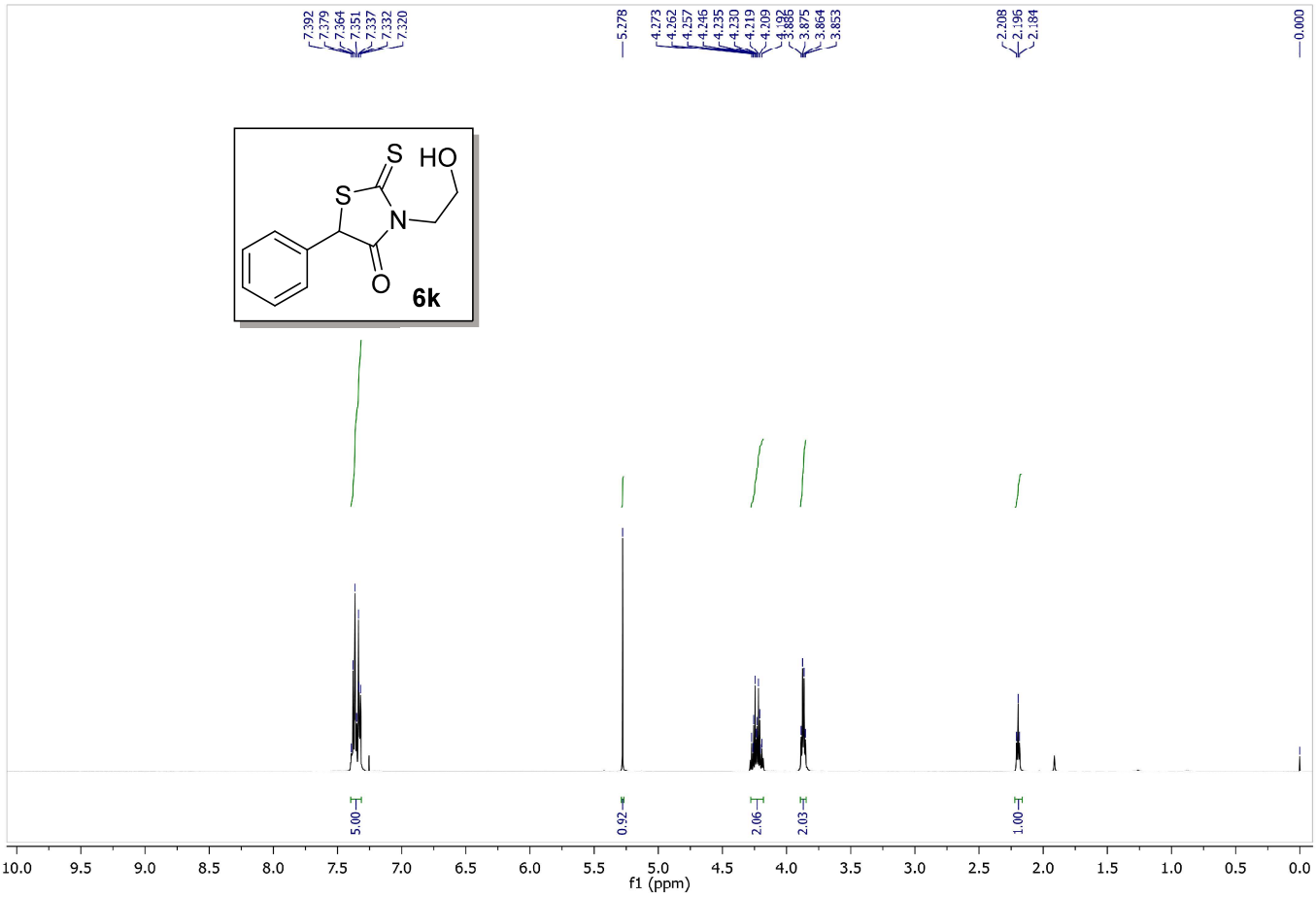


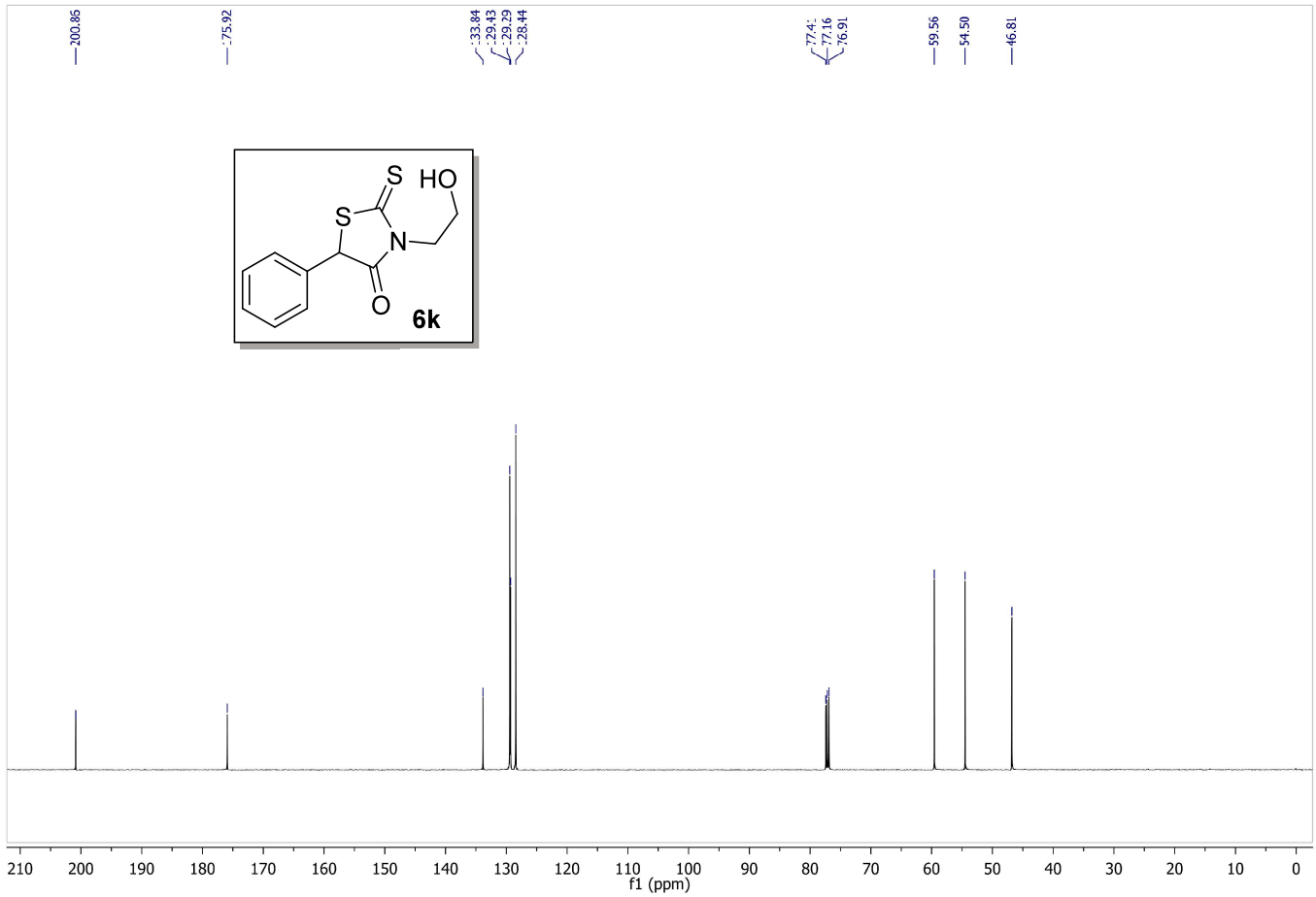
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6j**



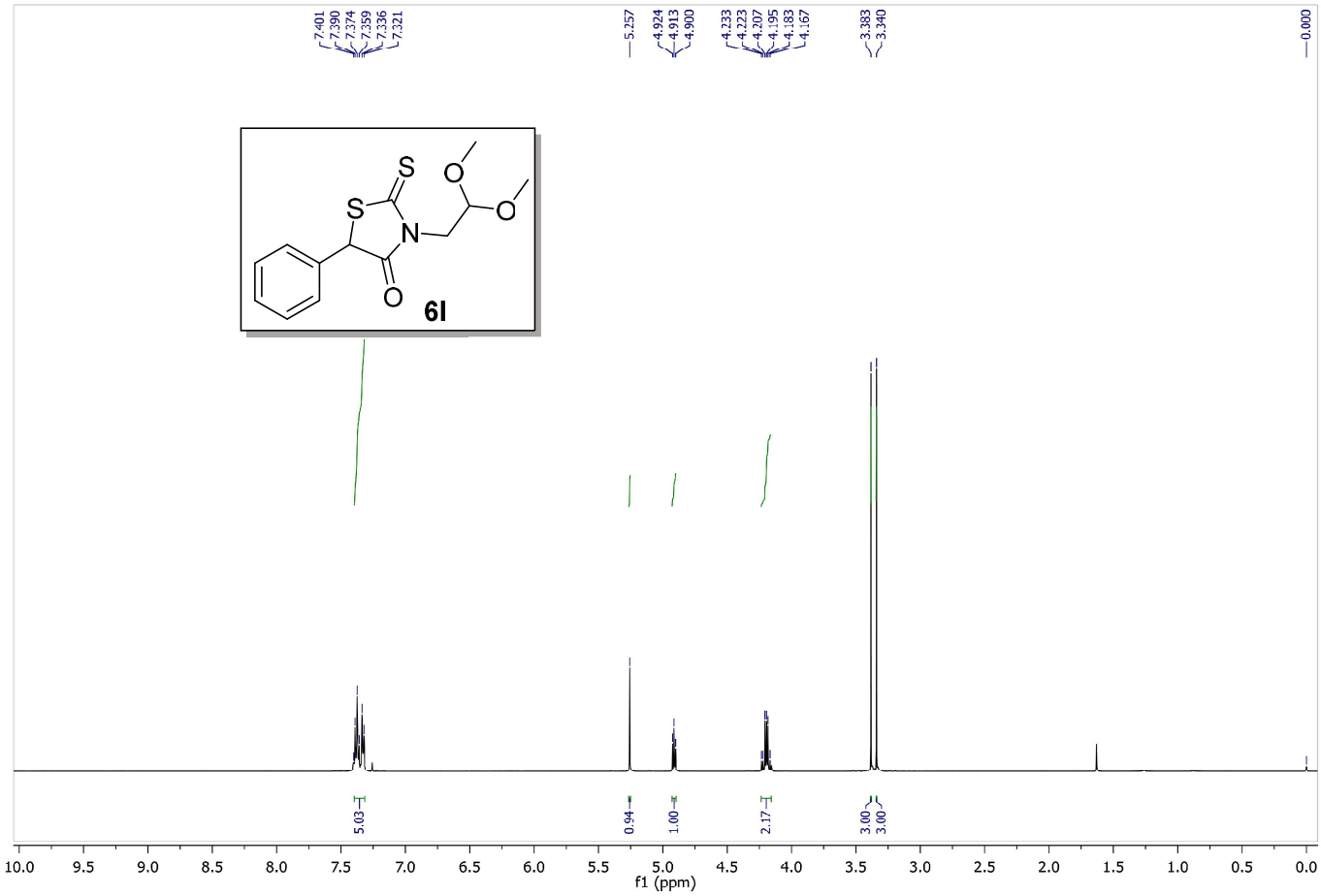


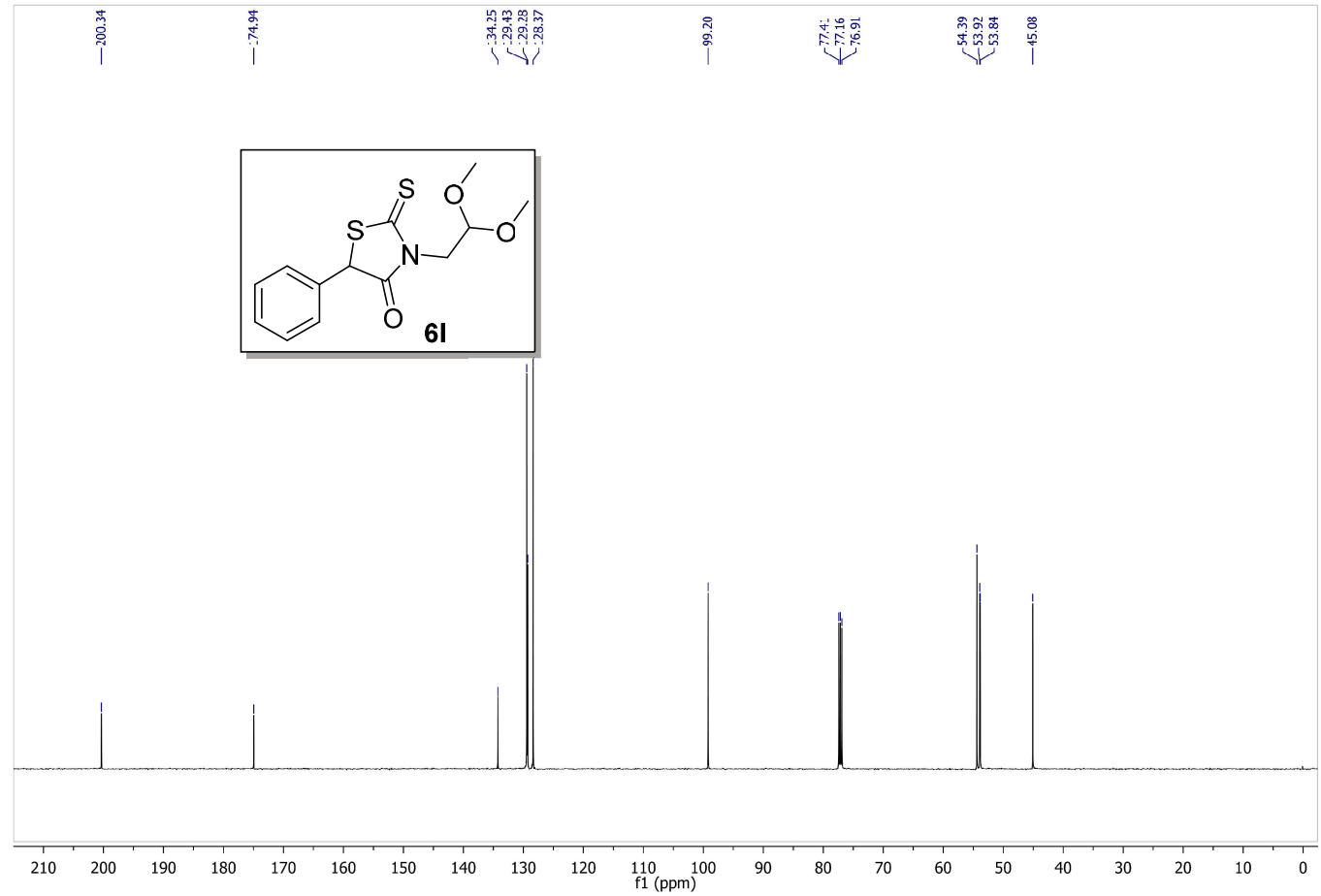
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **6k**



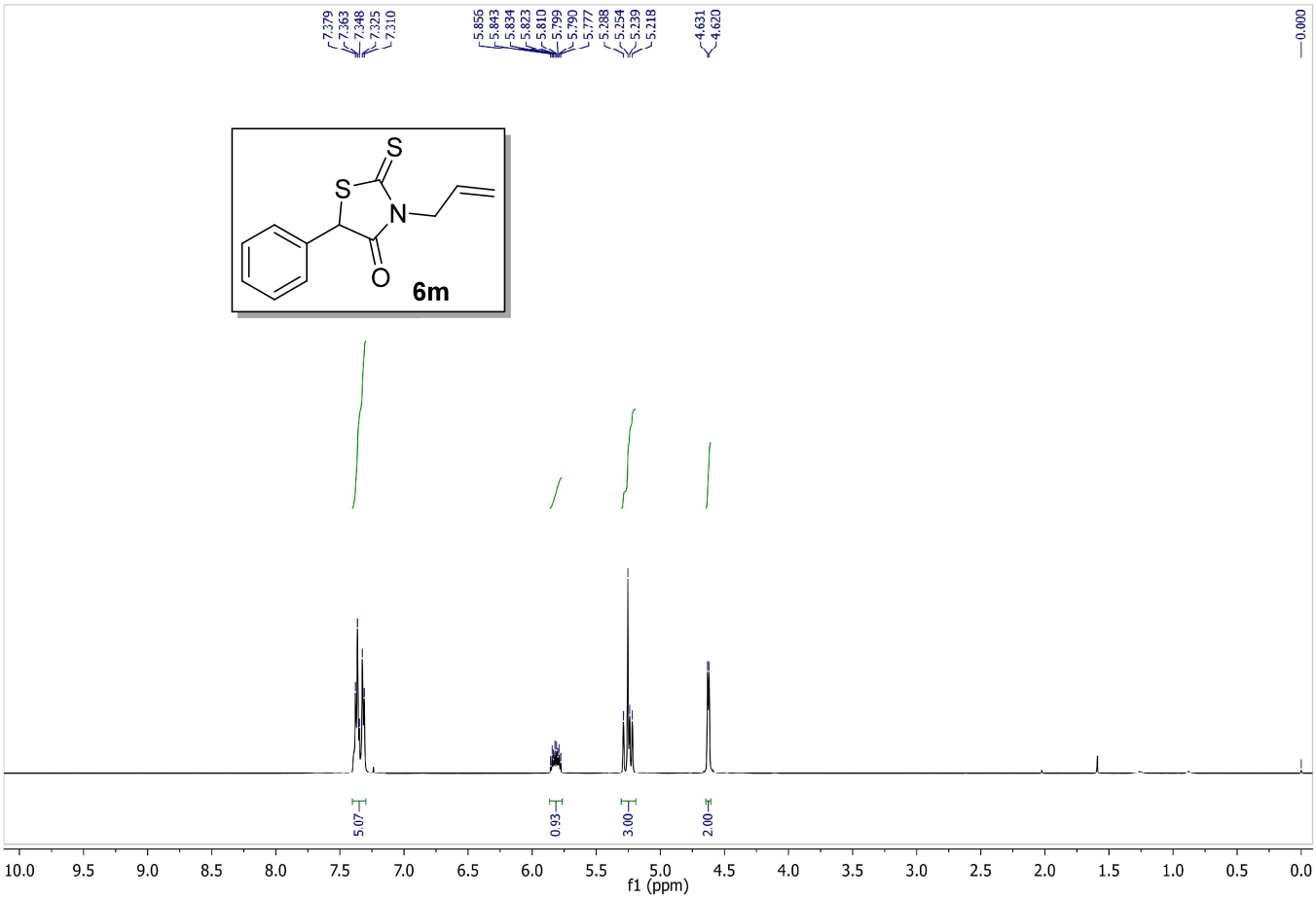


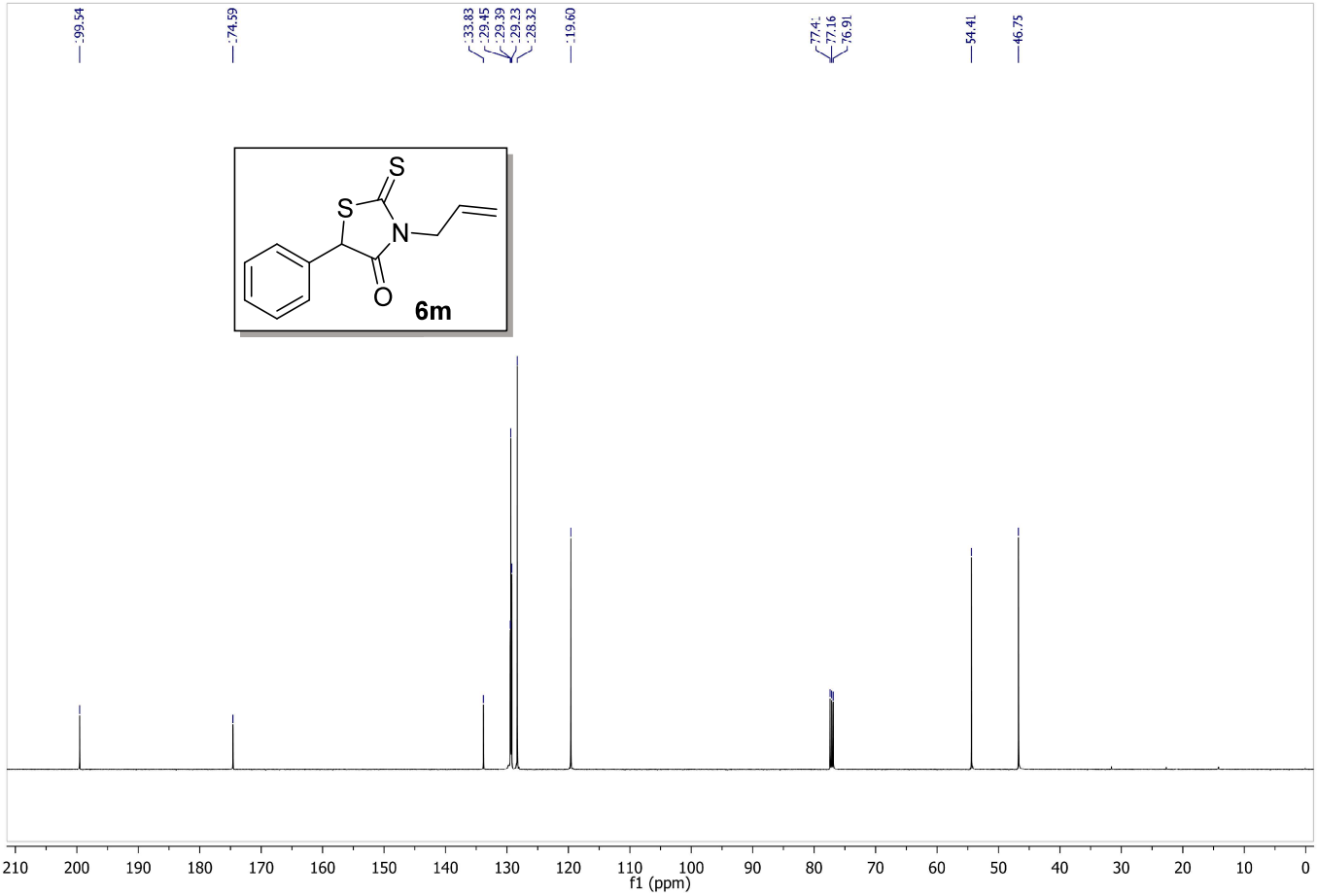
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6l**



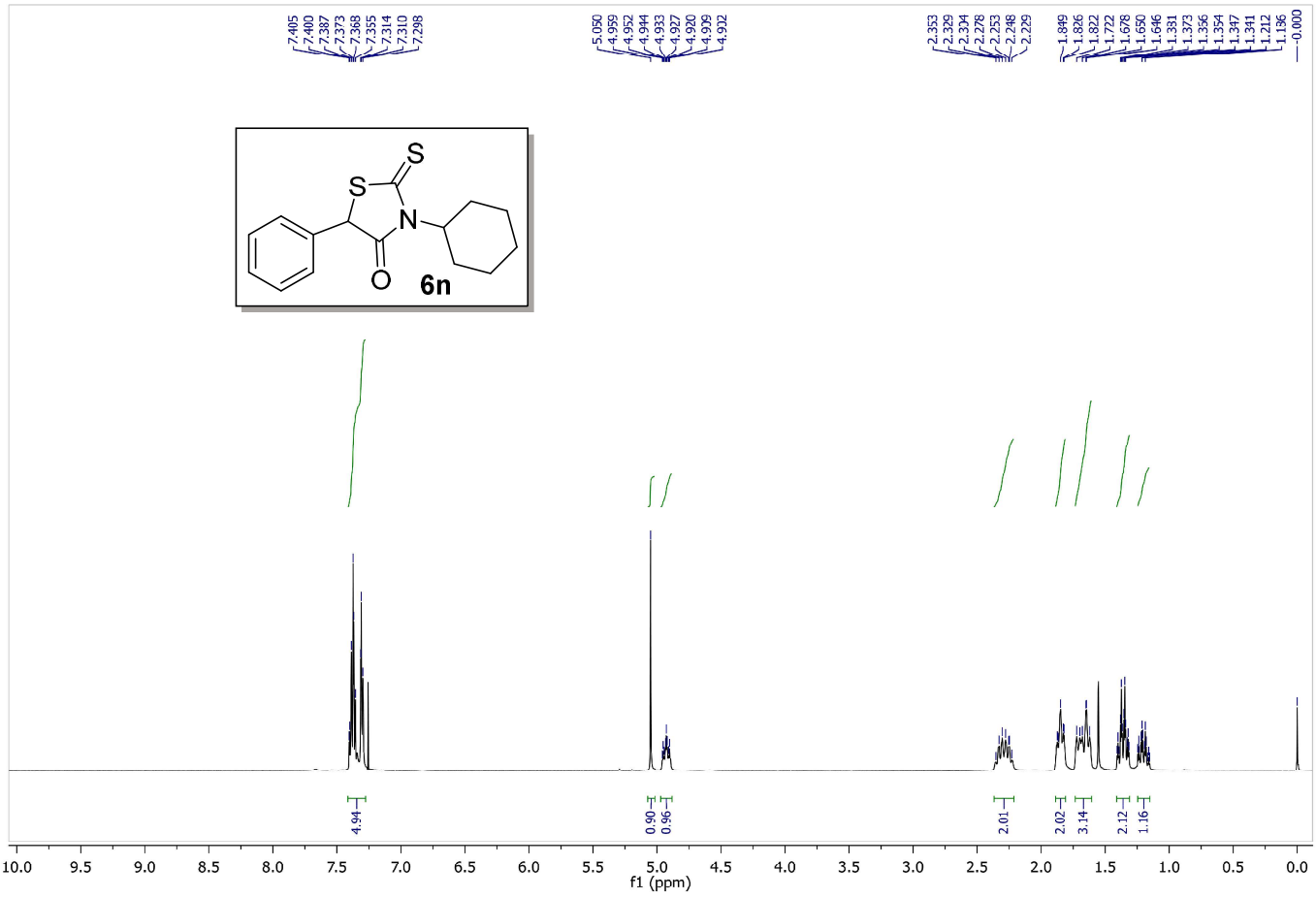


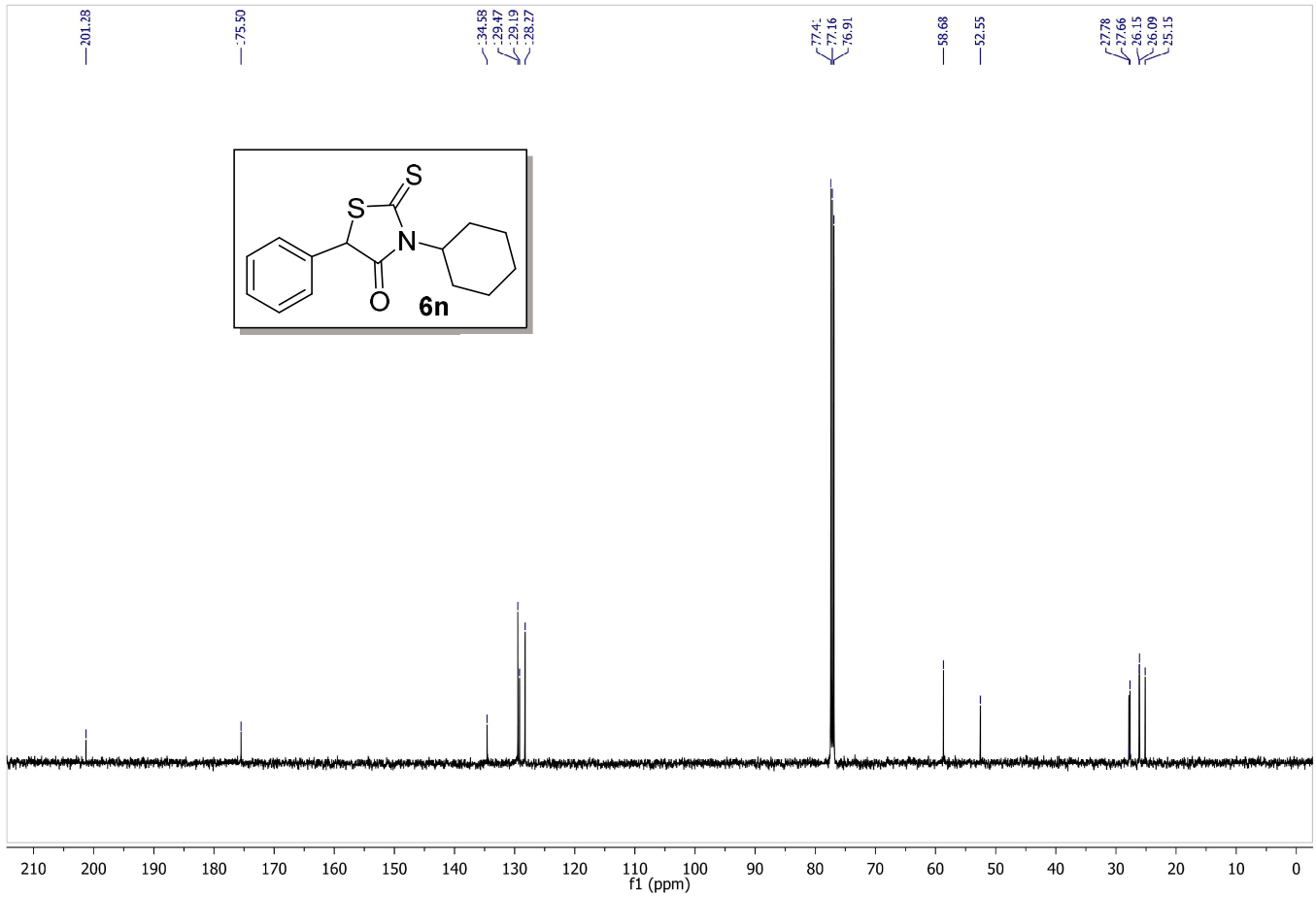
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6m**



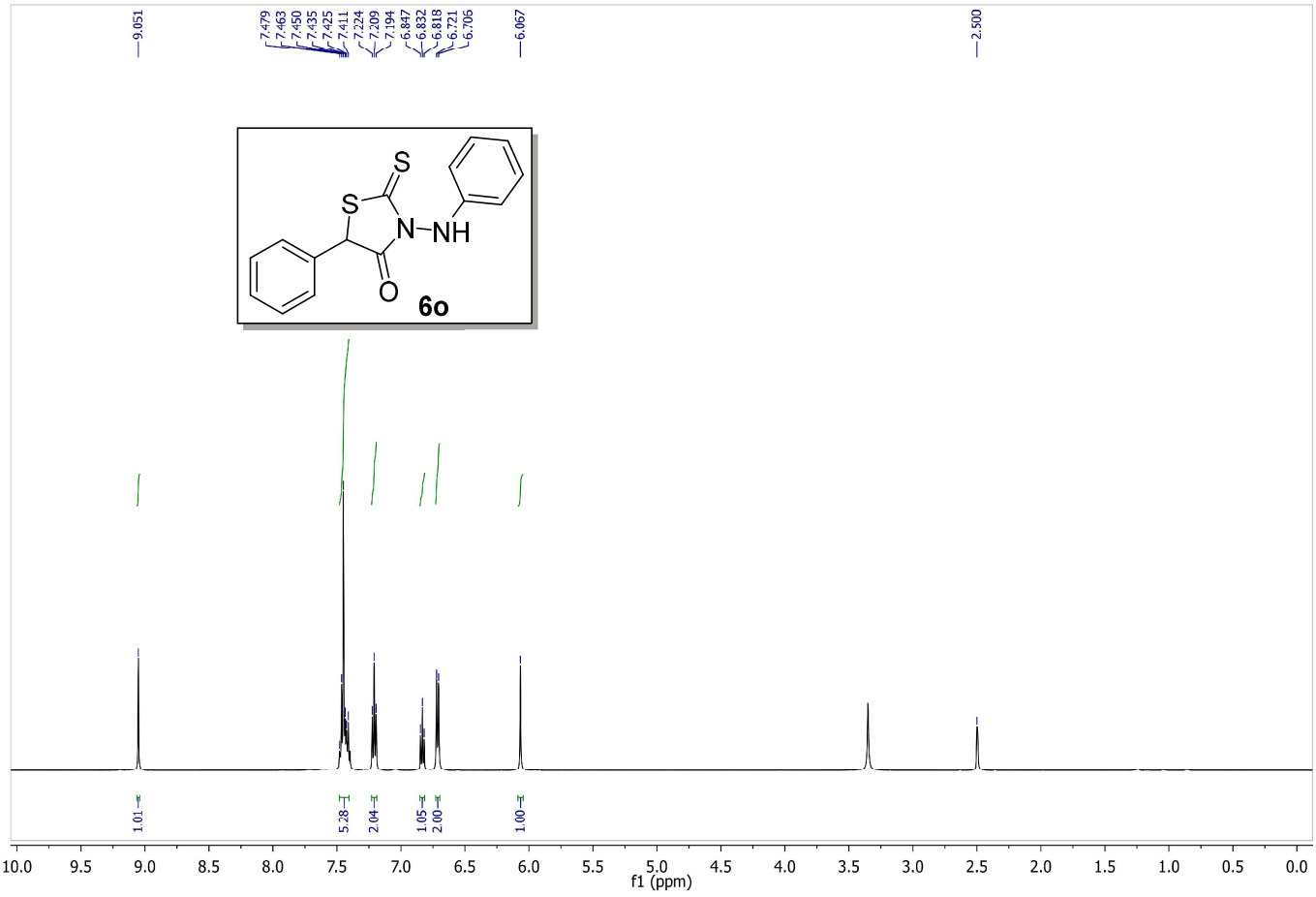


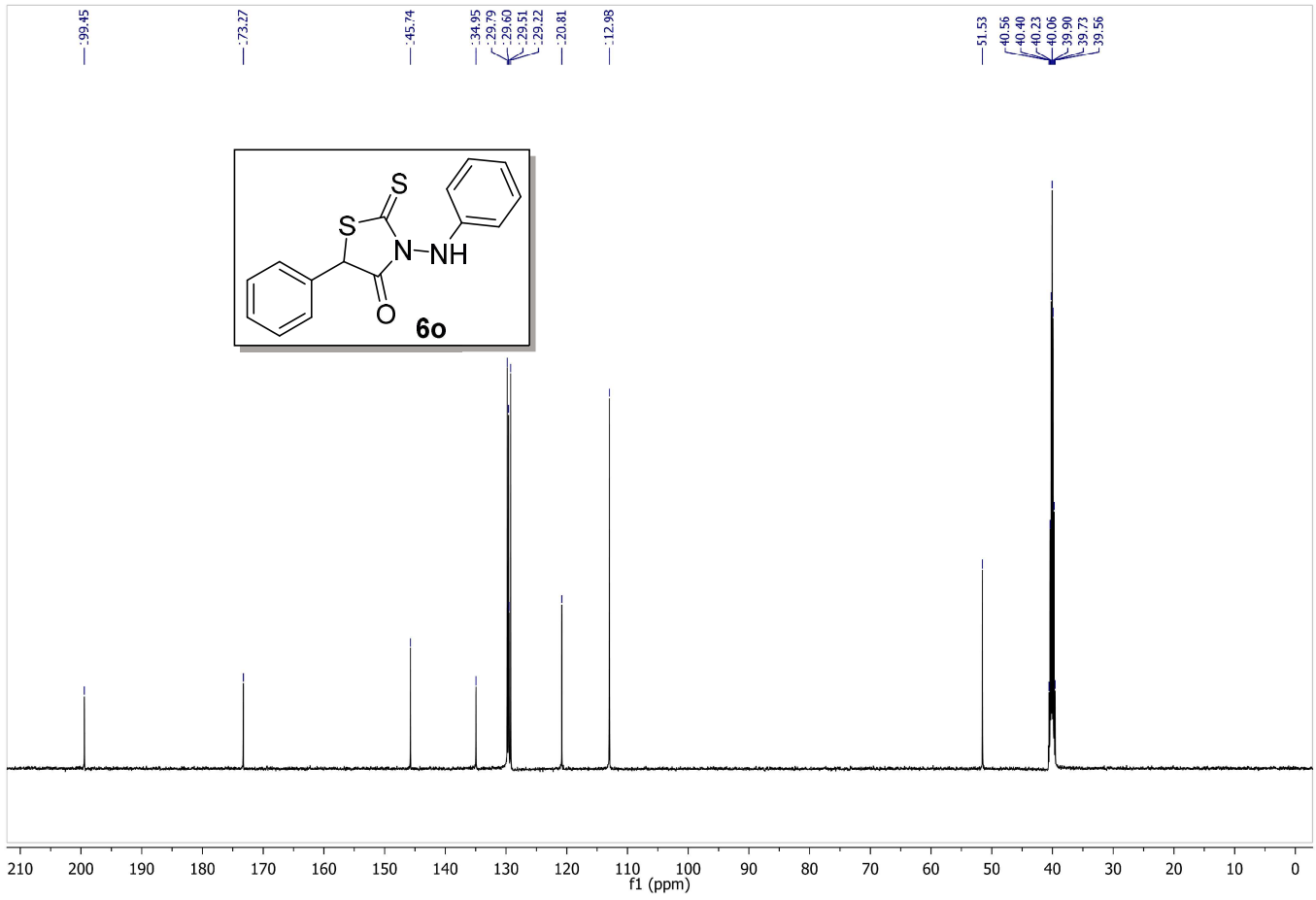
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6n**



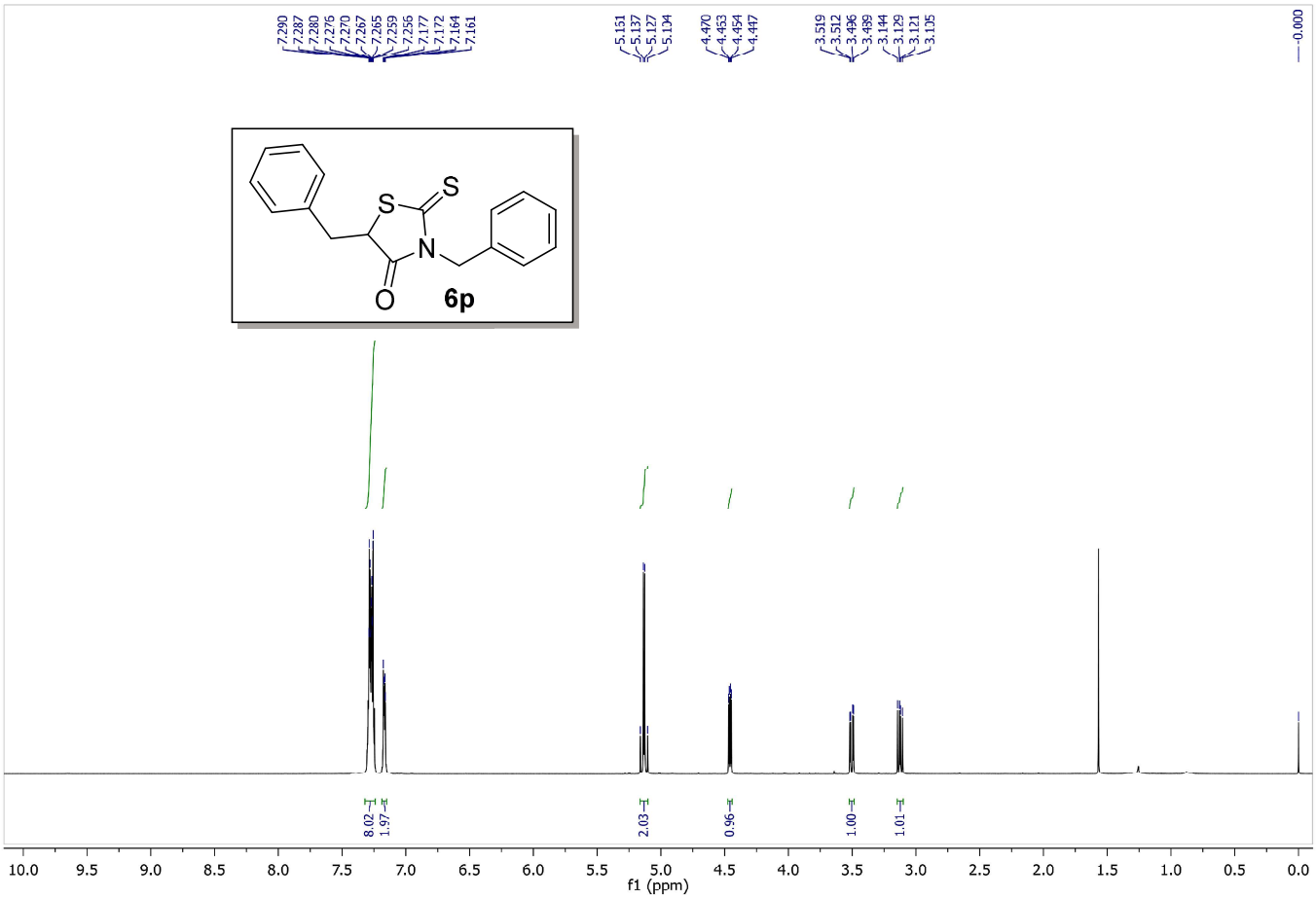


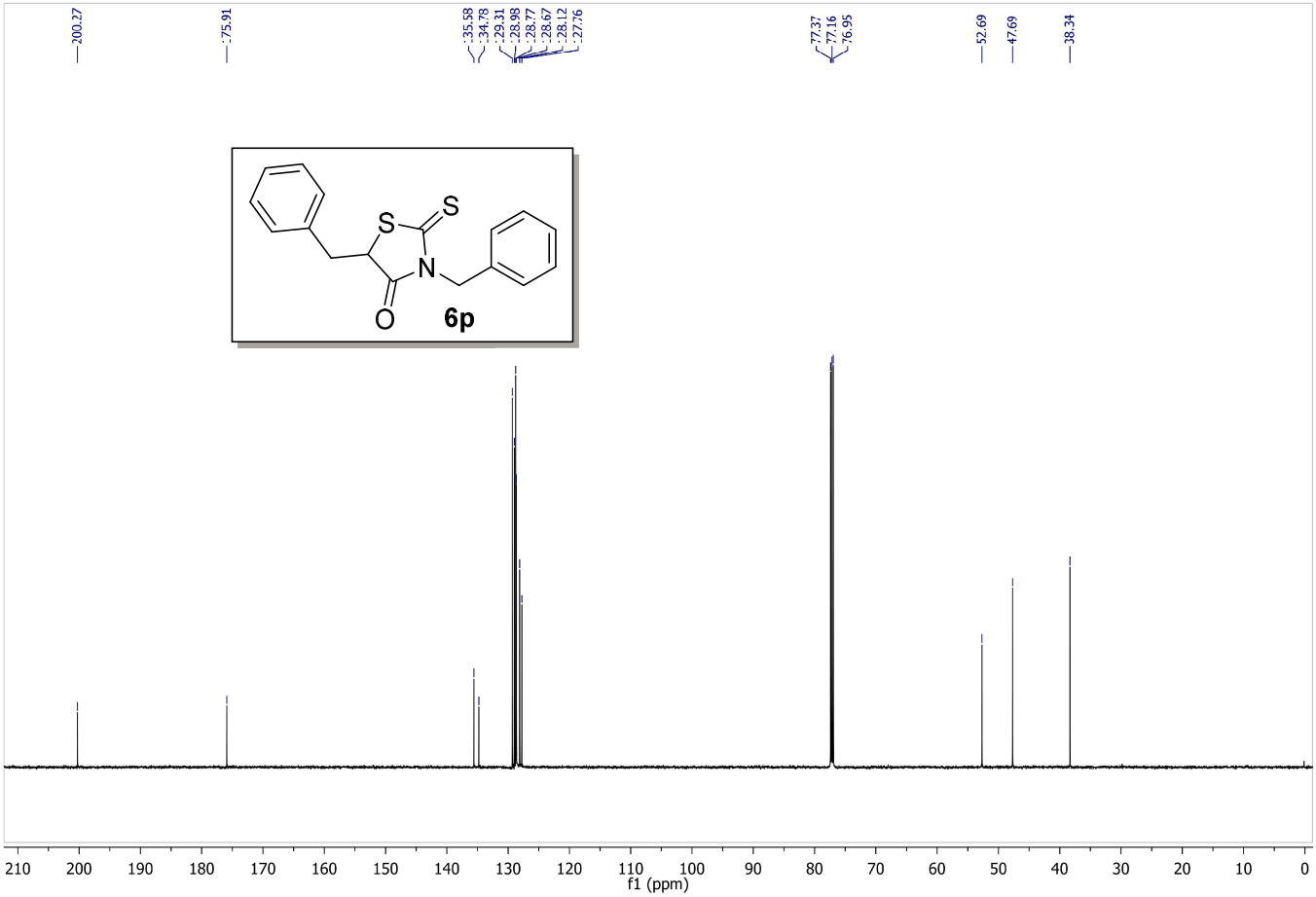
^{1}H NMR (500 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6), **6o**



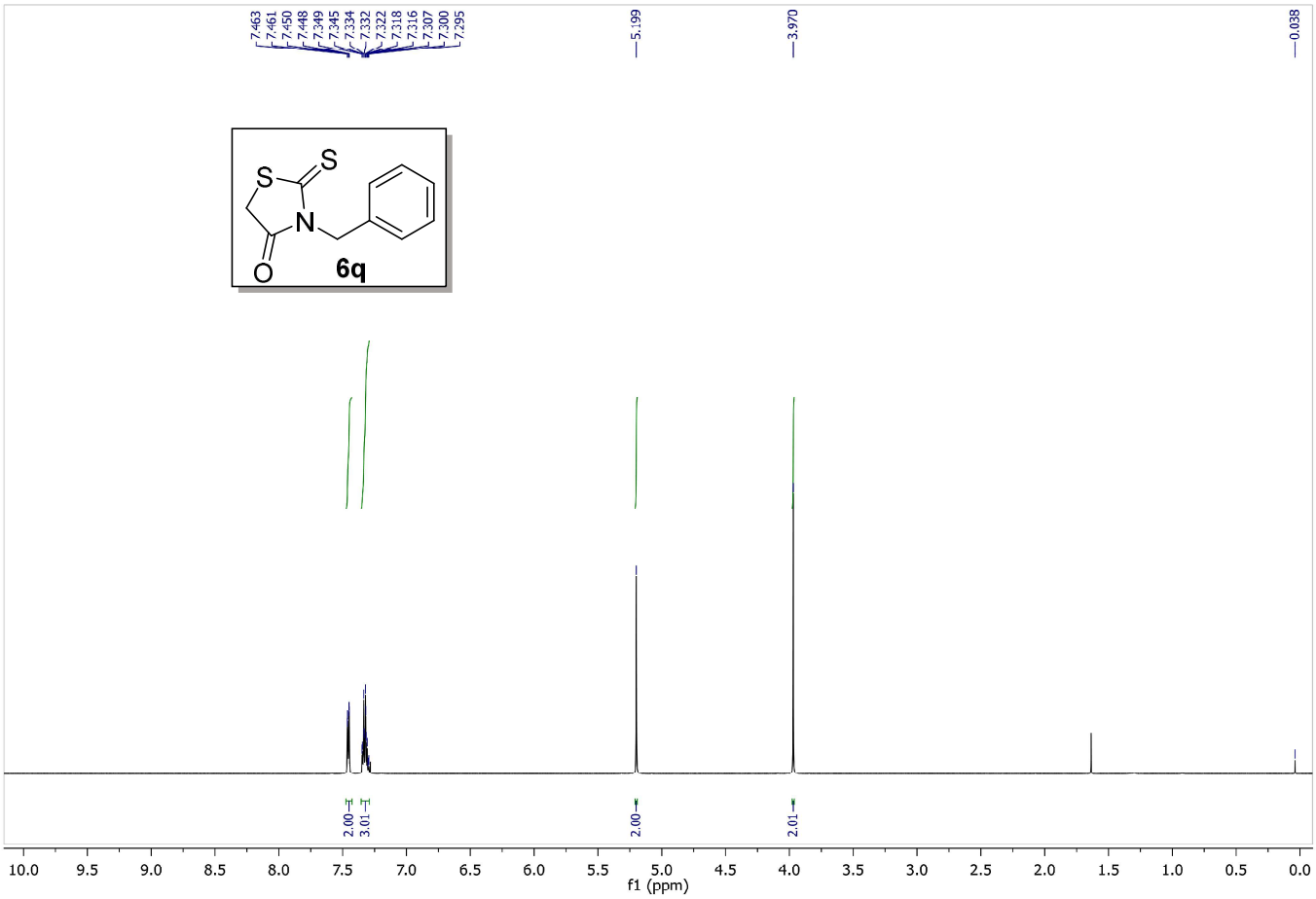


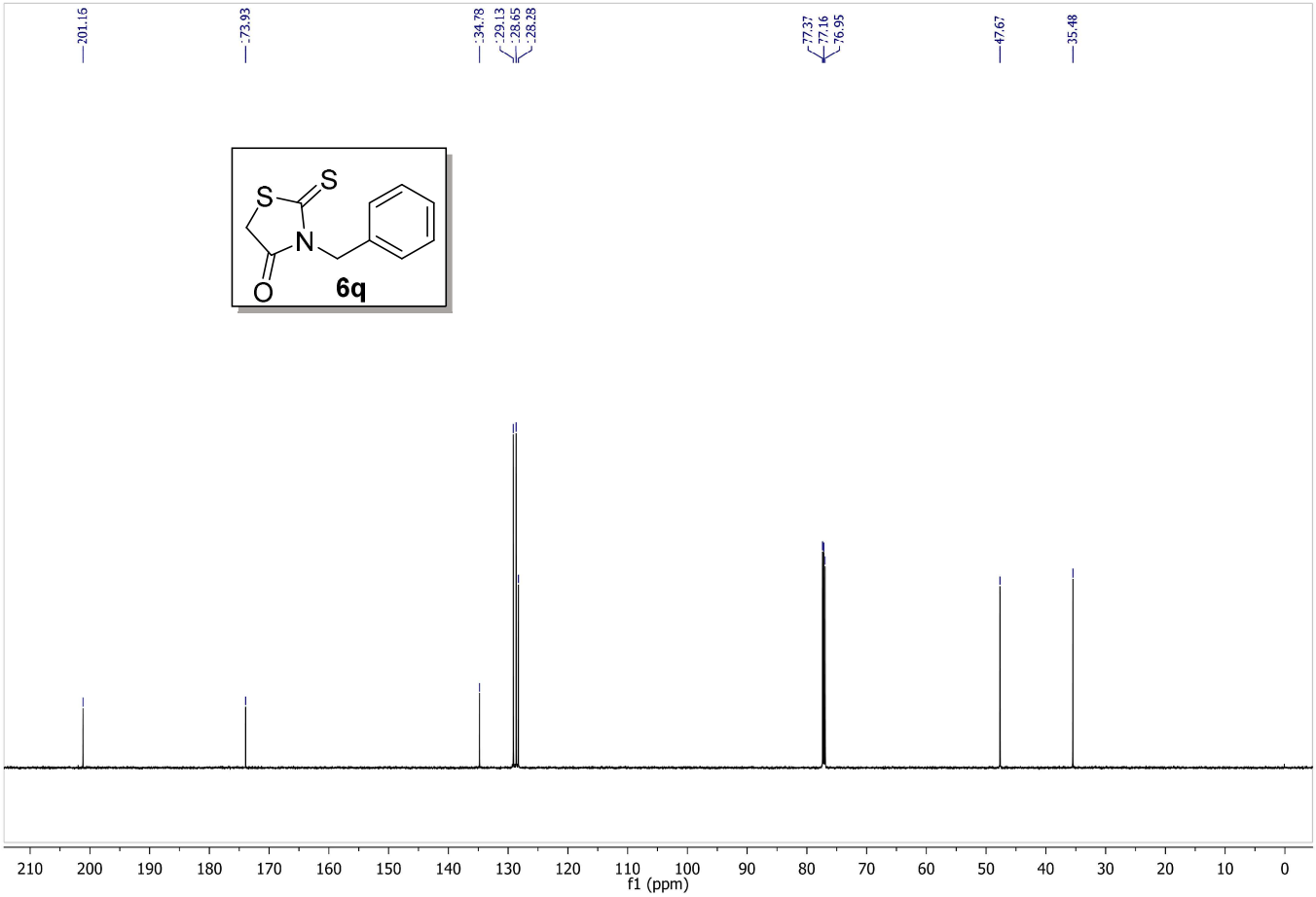
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **6p**



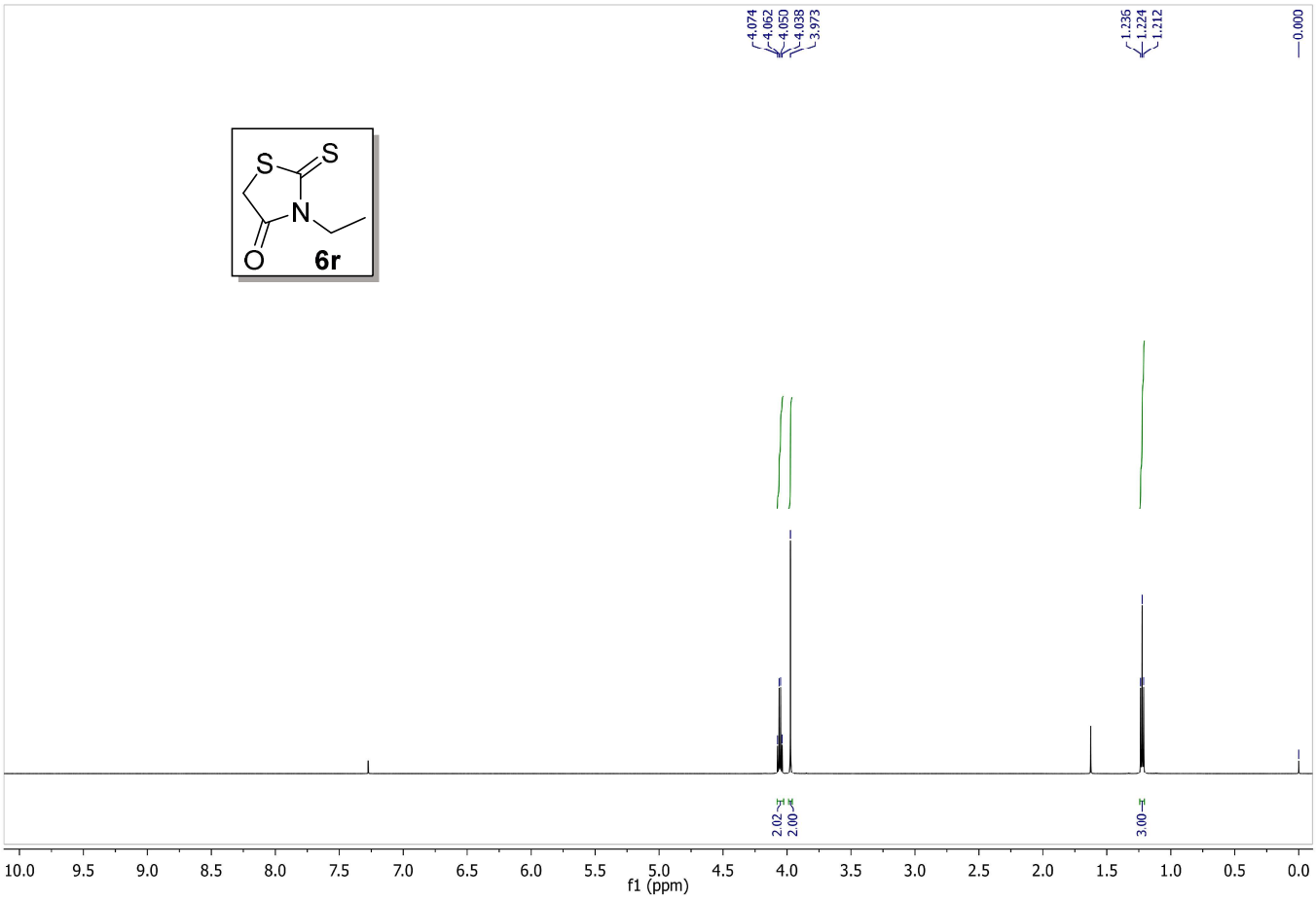


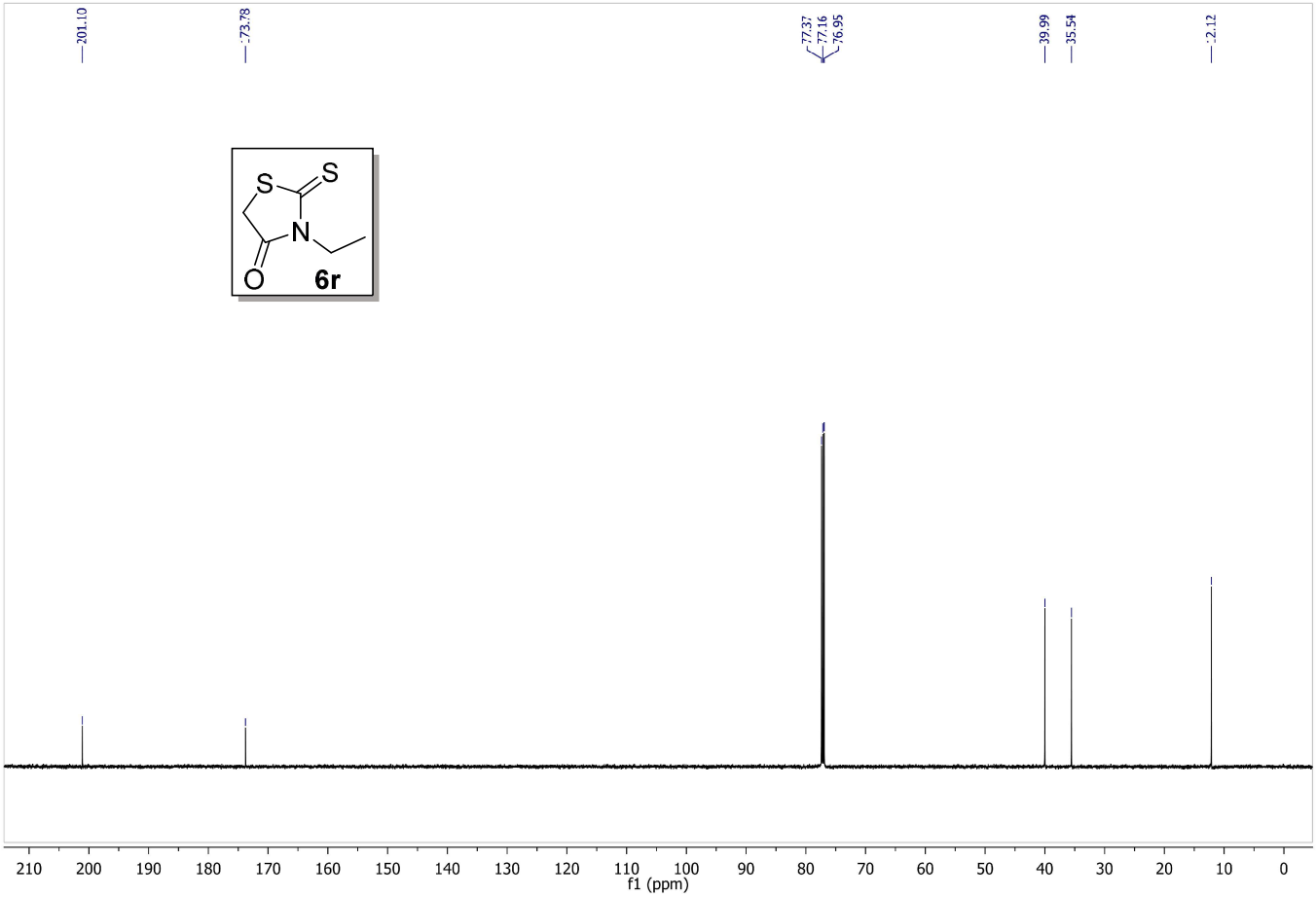
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **6q**



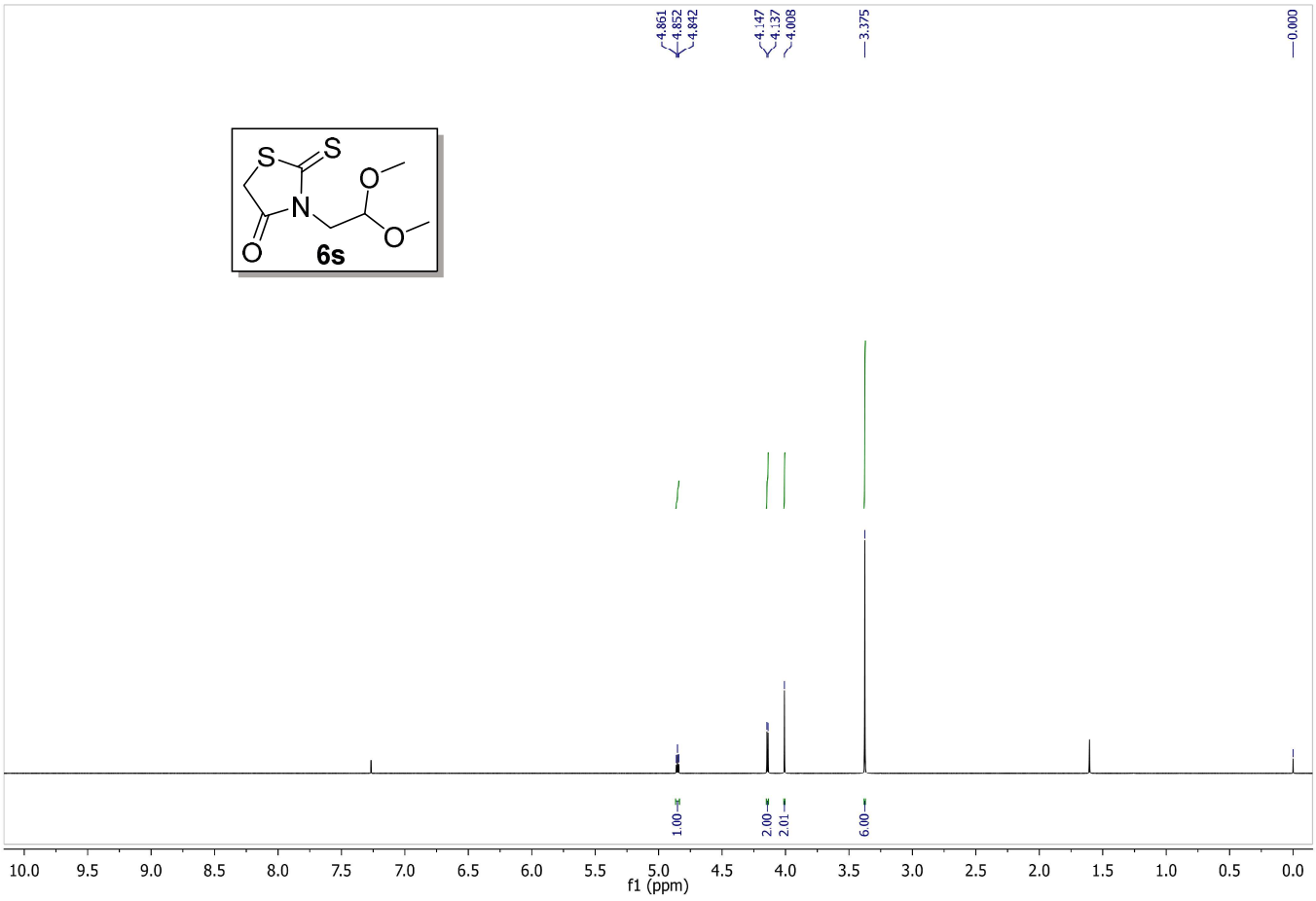


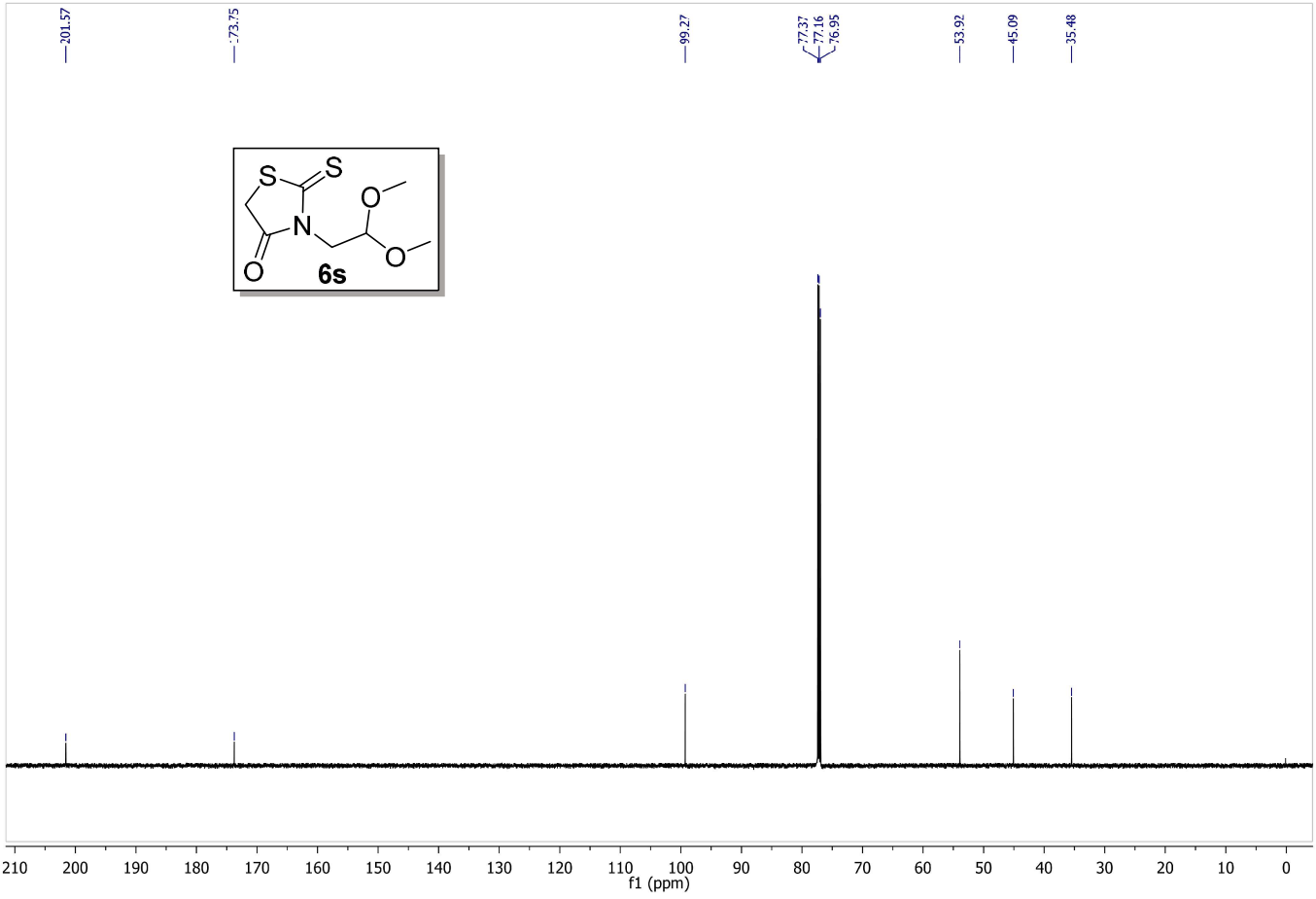
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **6r**



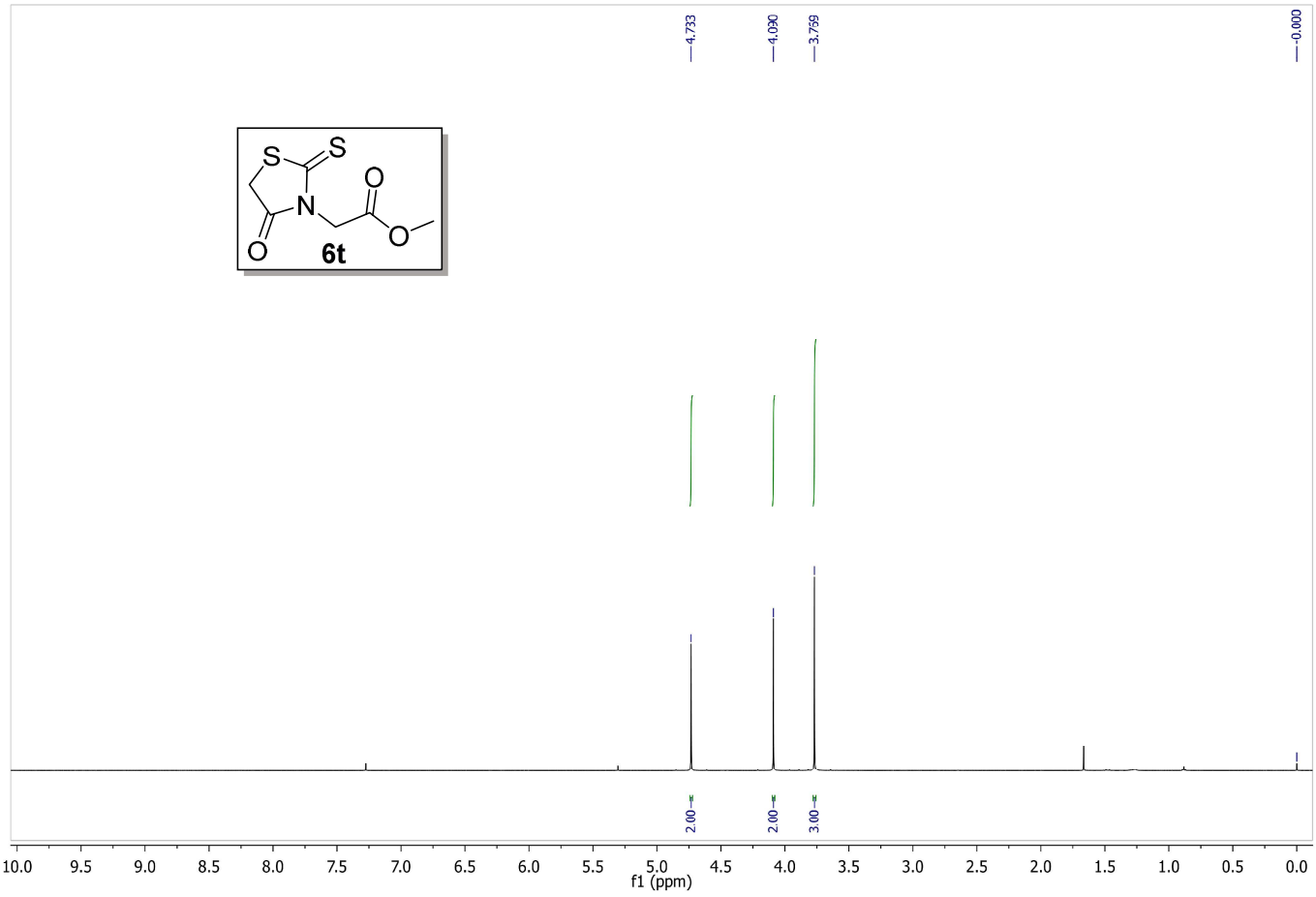


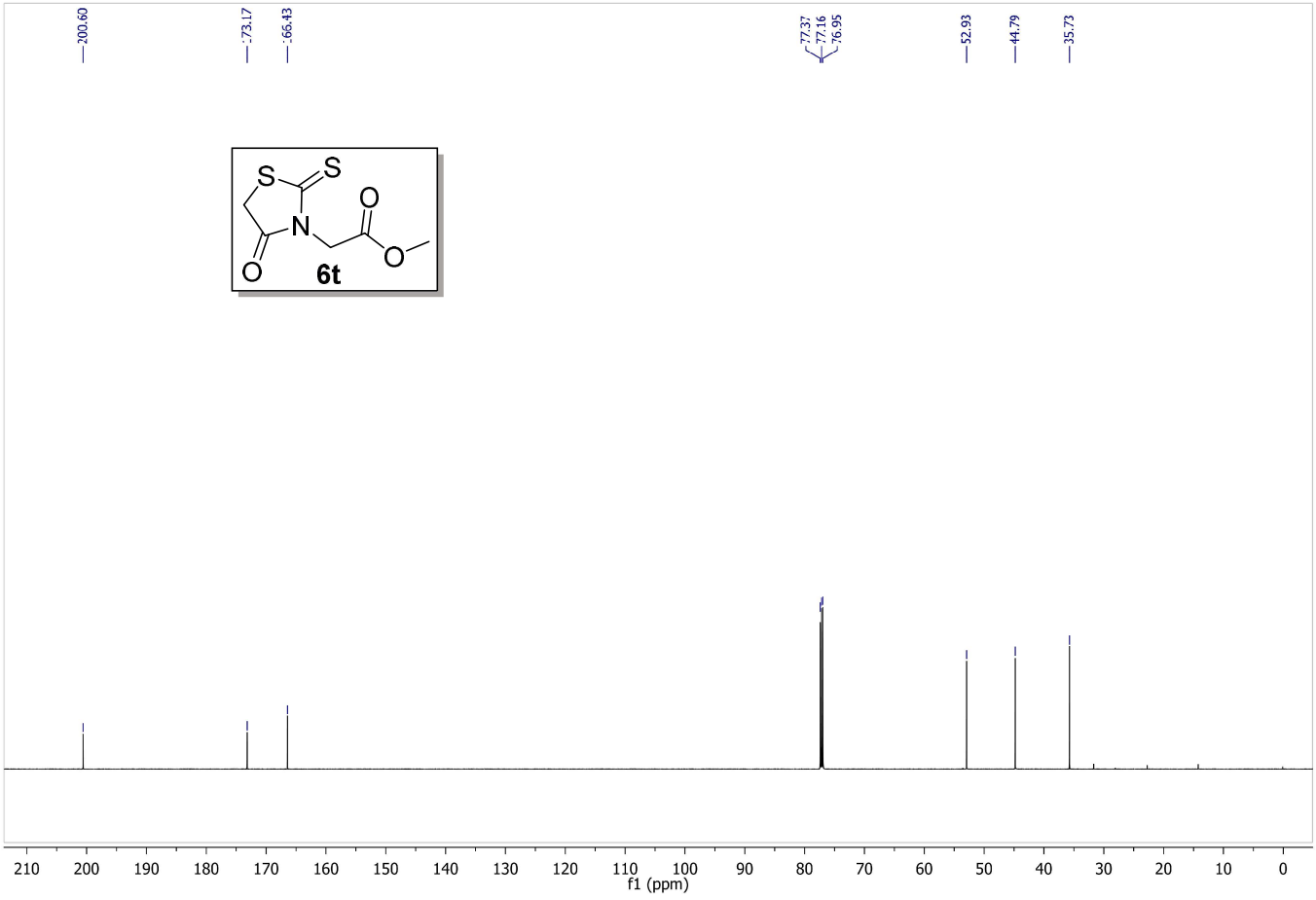
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **6s**



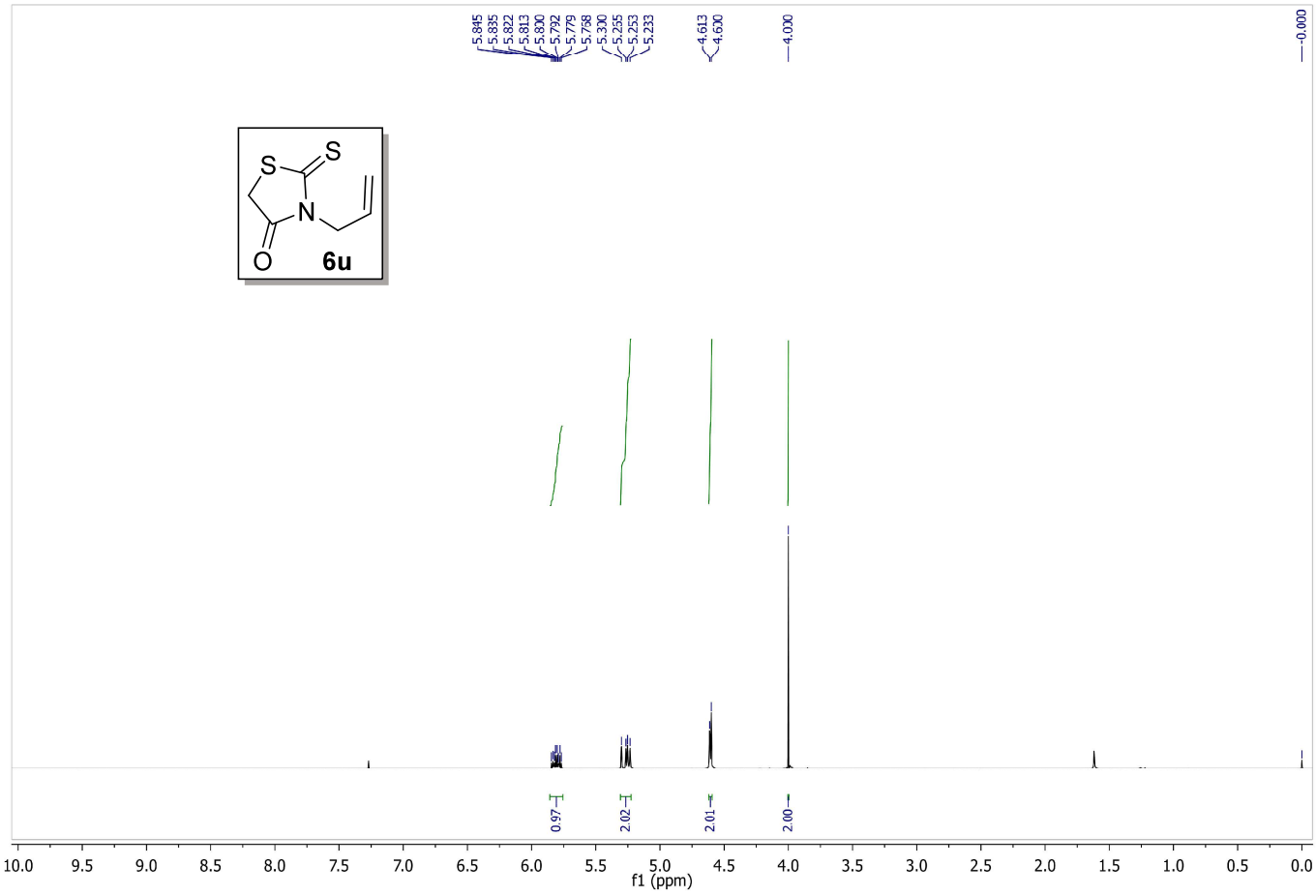


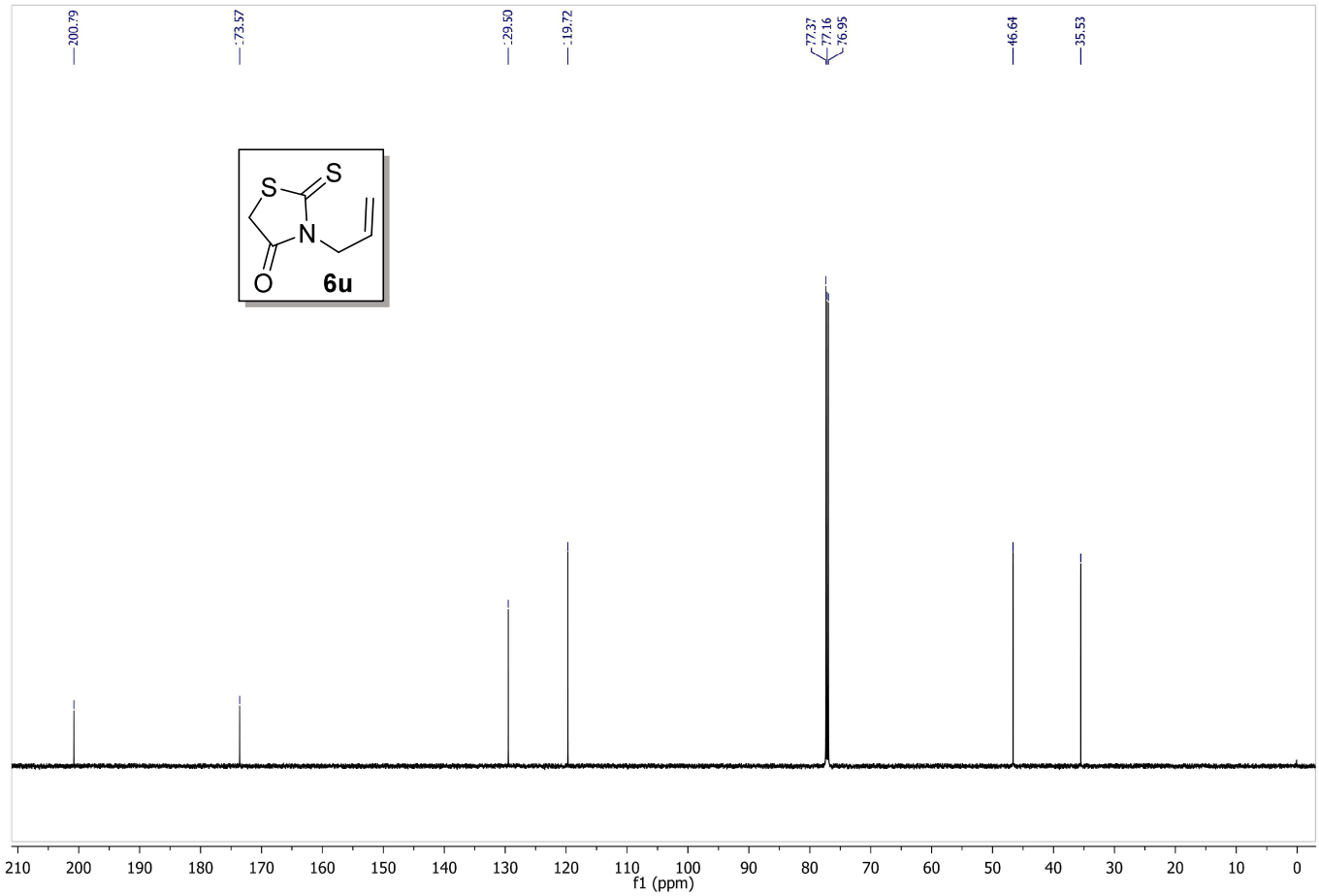
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **6t**



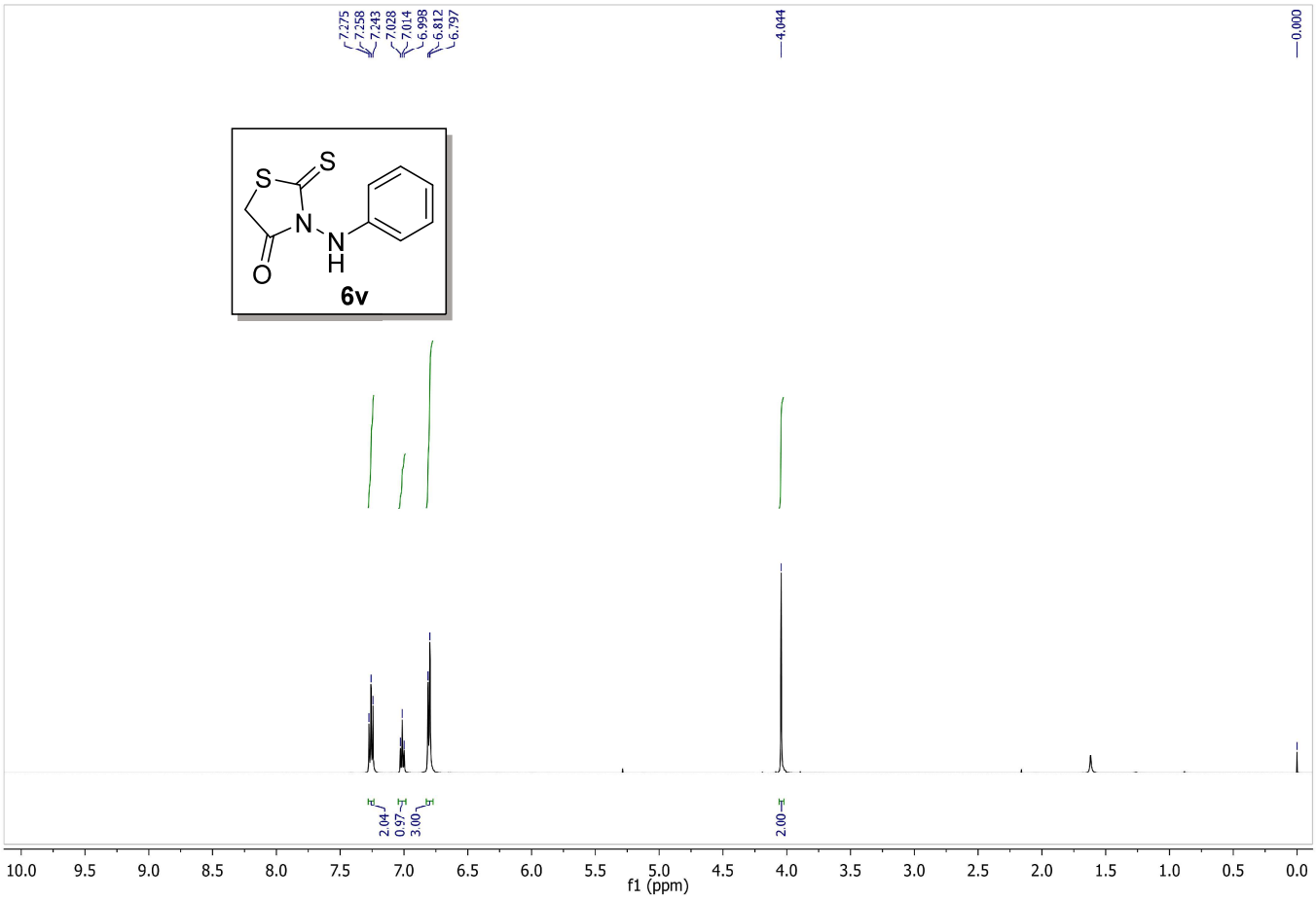


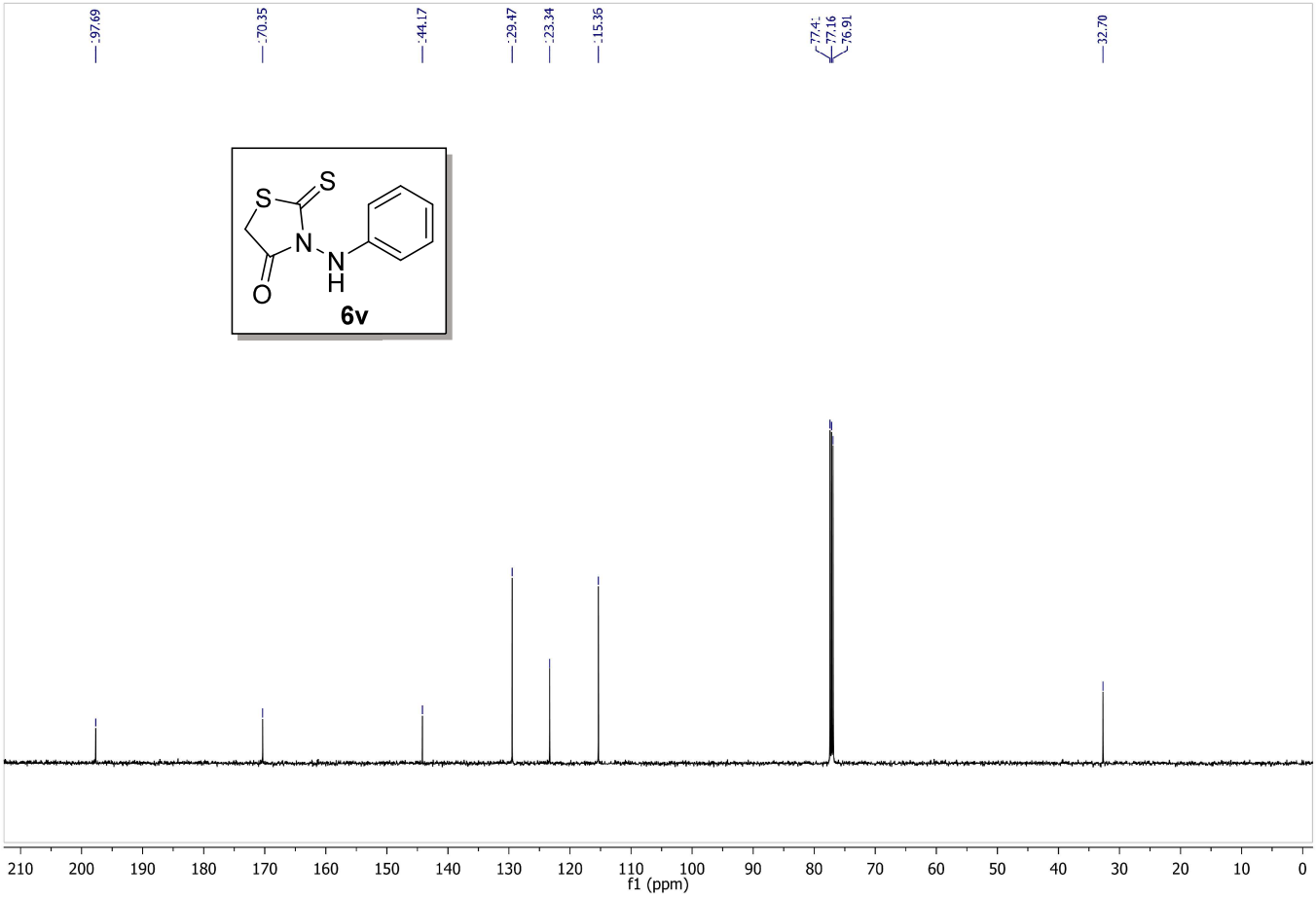
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **6u**



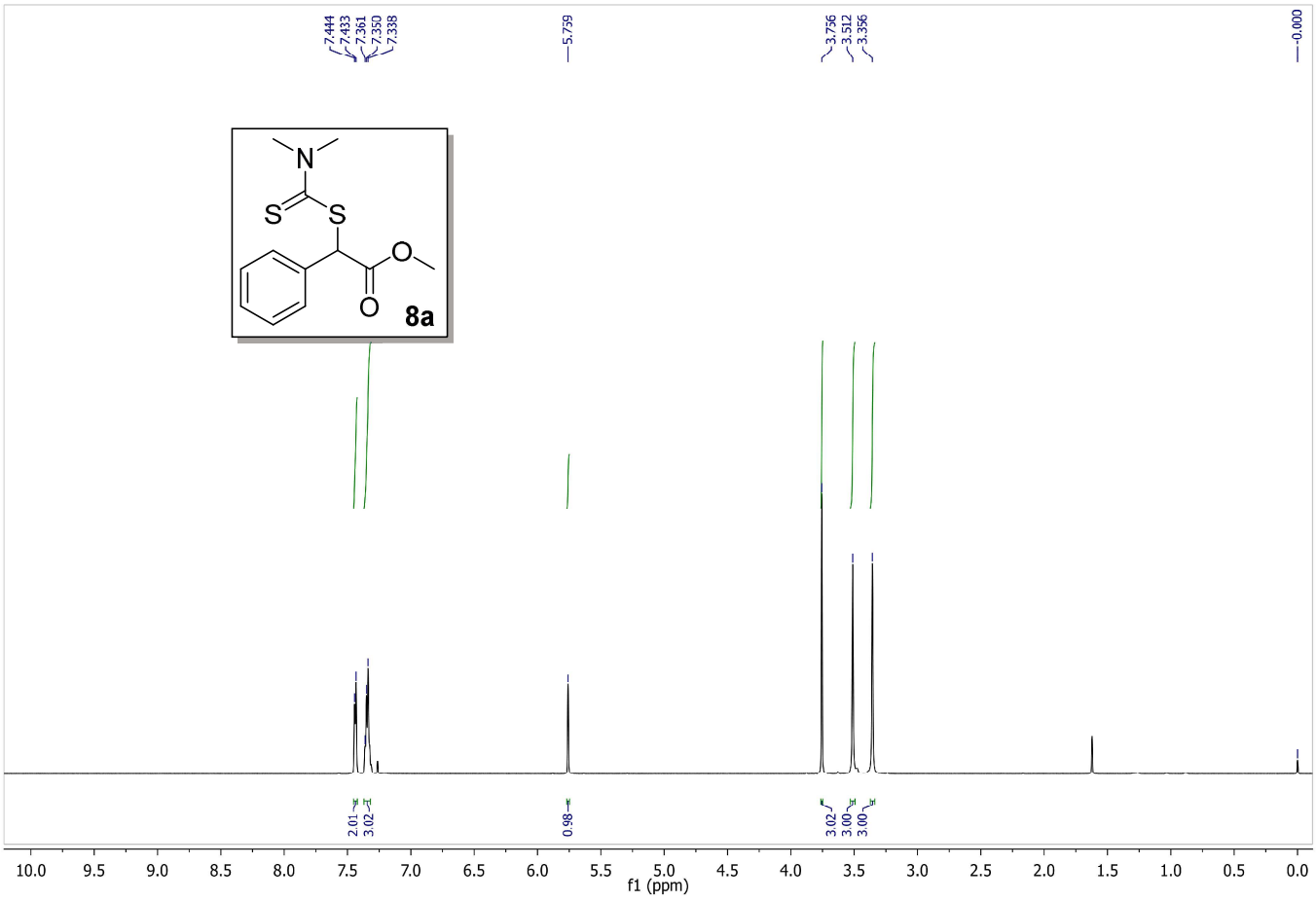


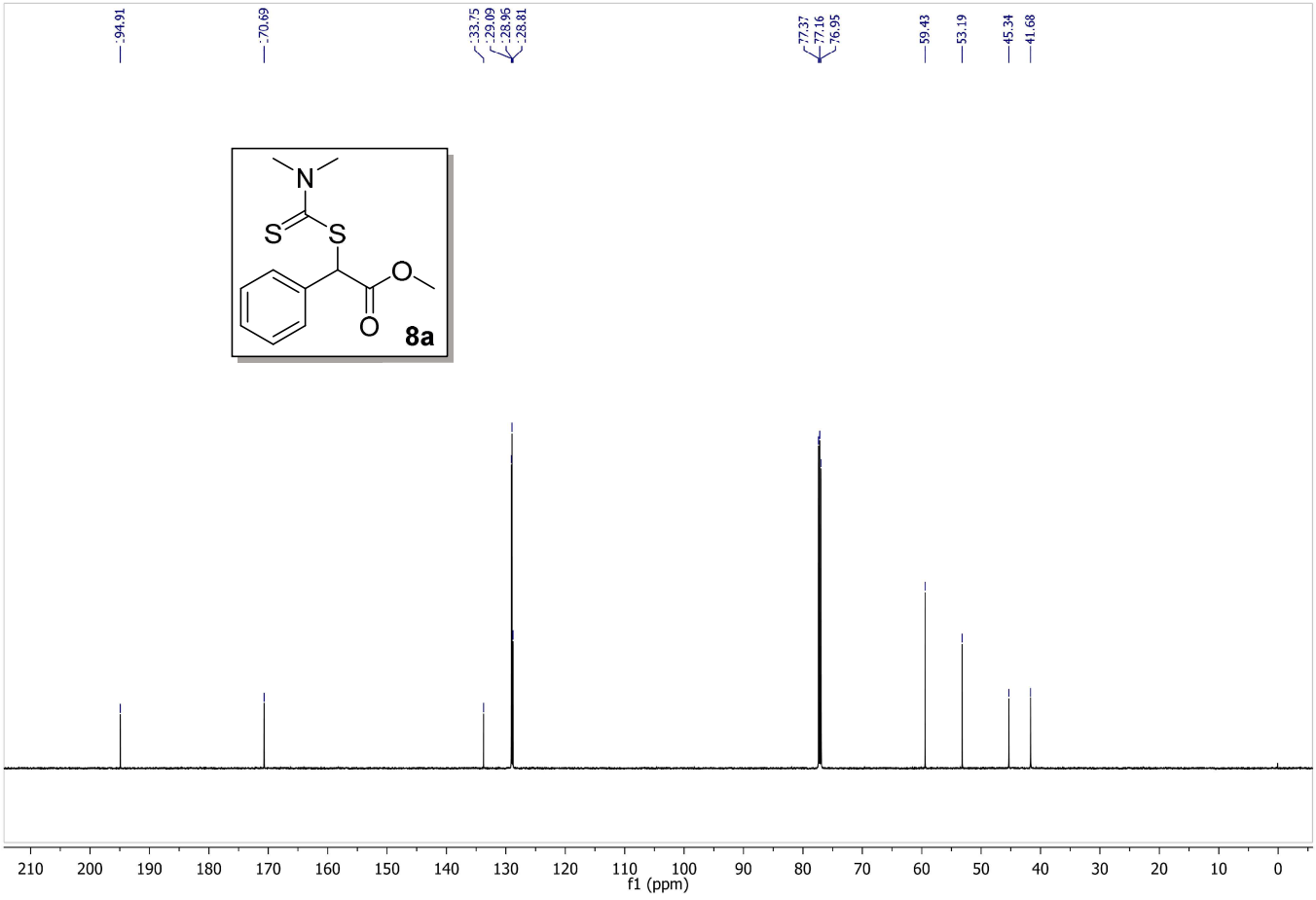
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **6v**



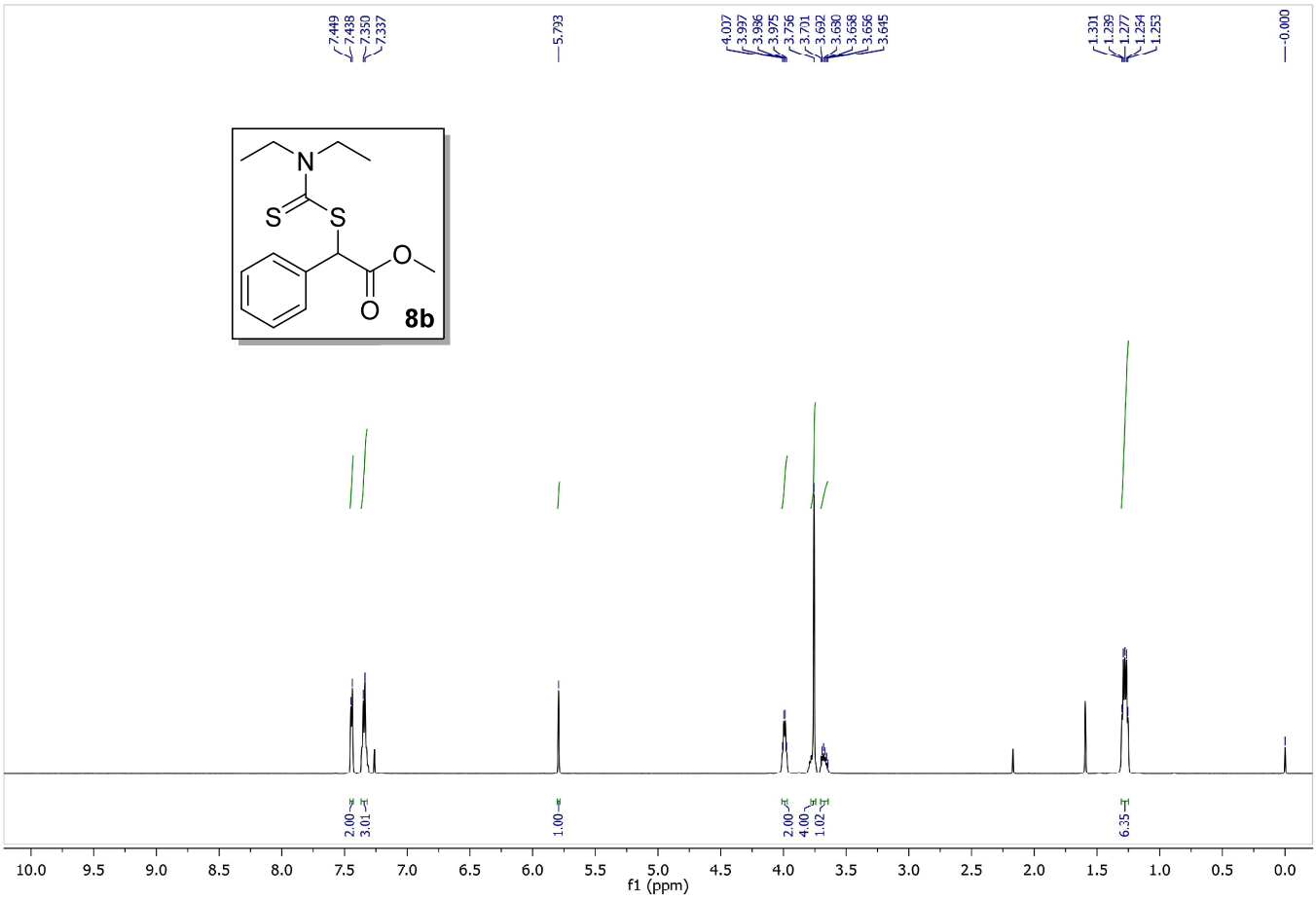


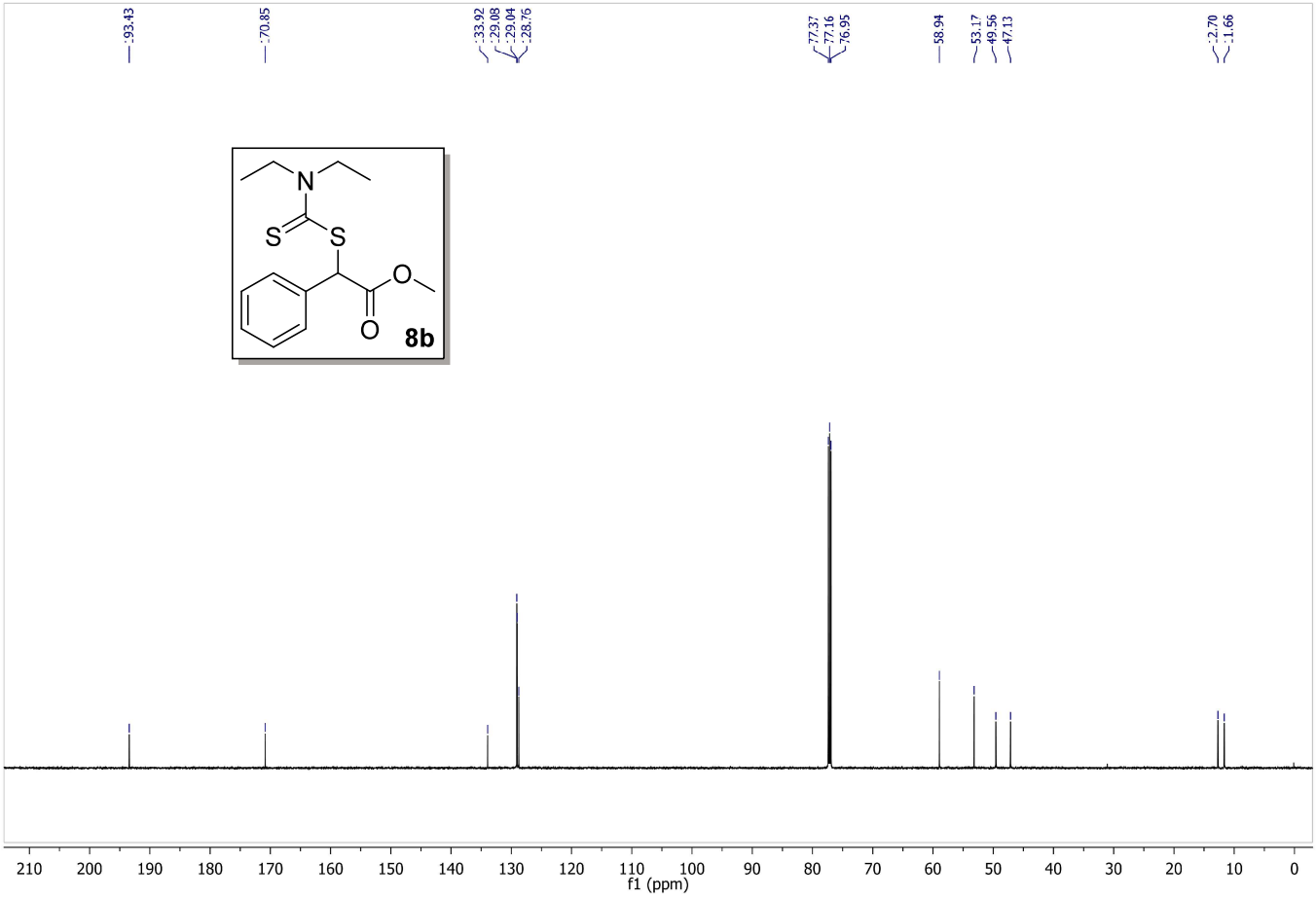
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), **8a**



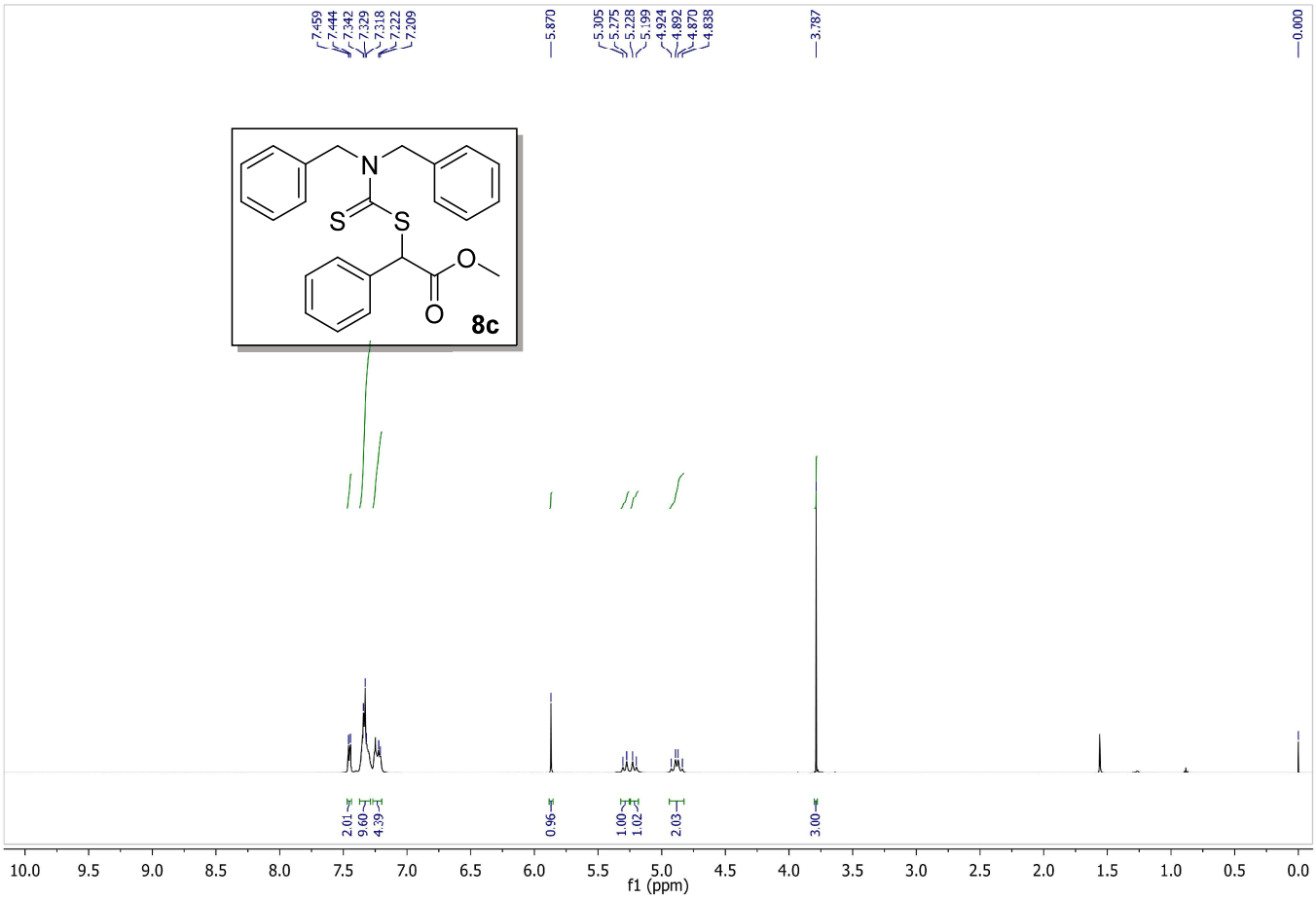


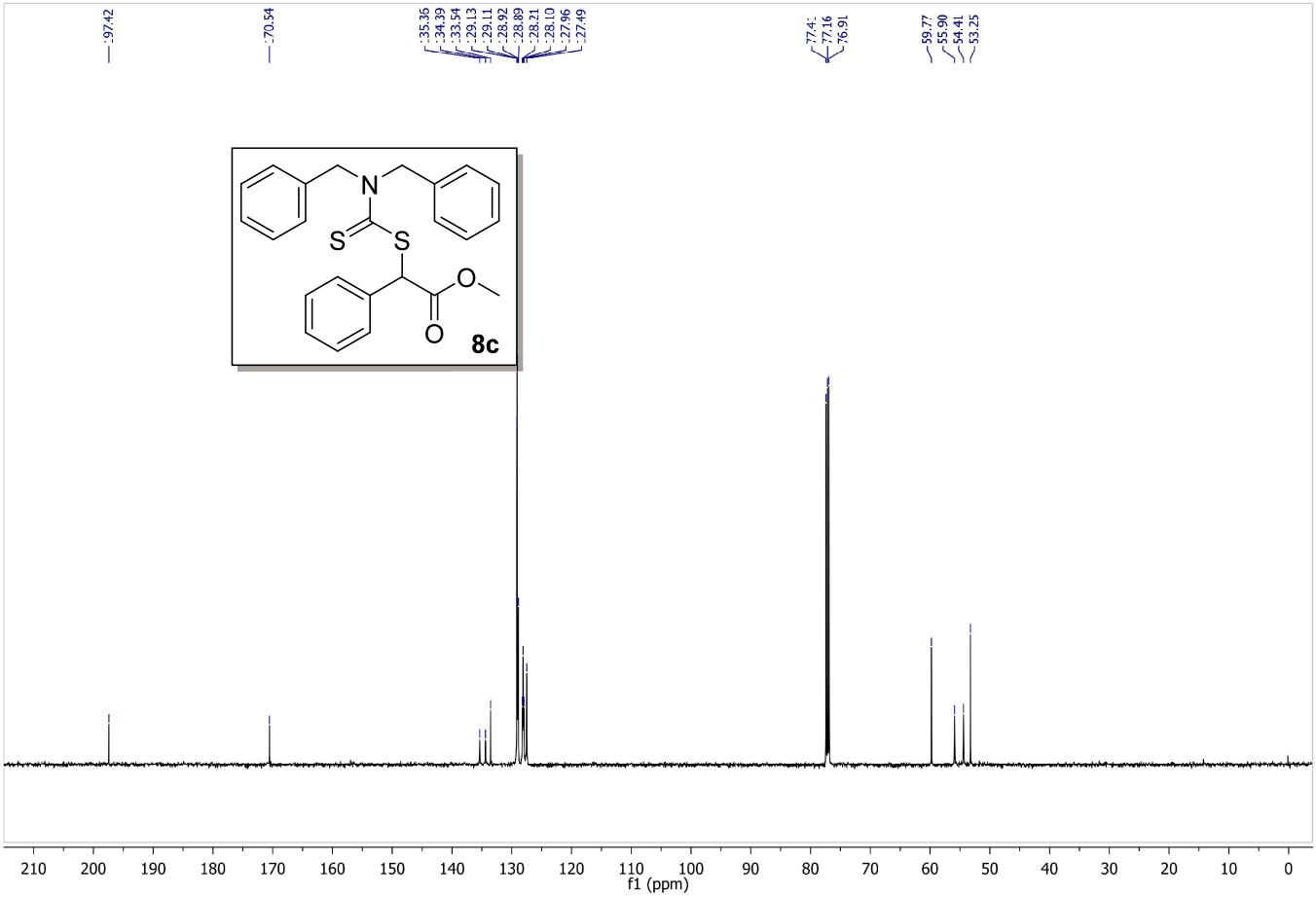
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), **8b**



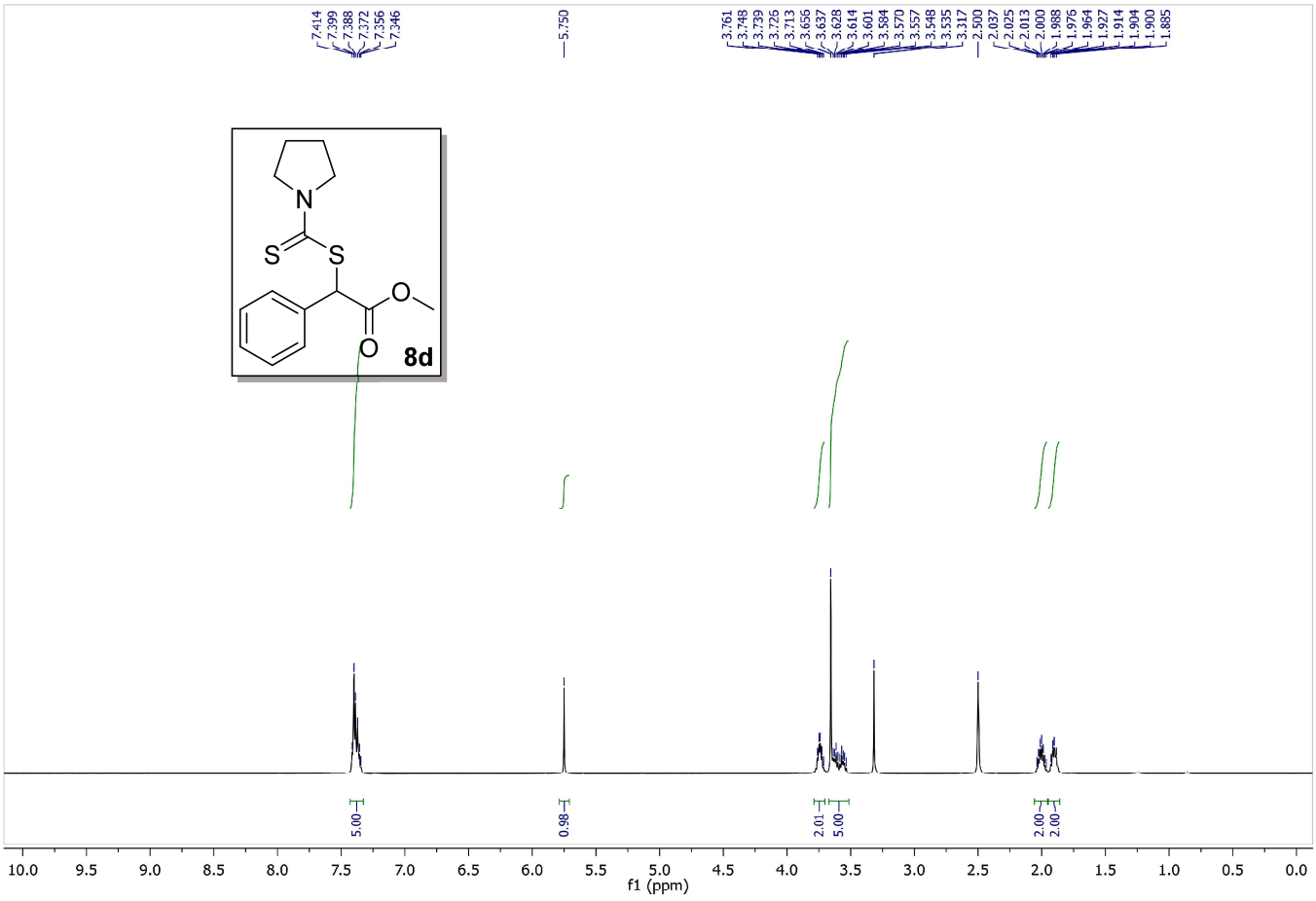


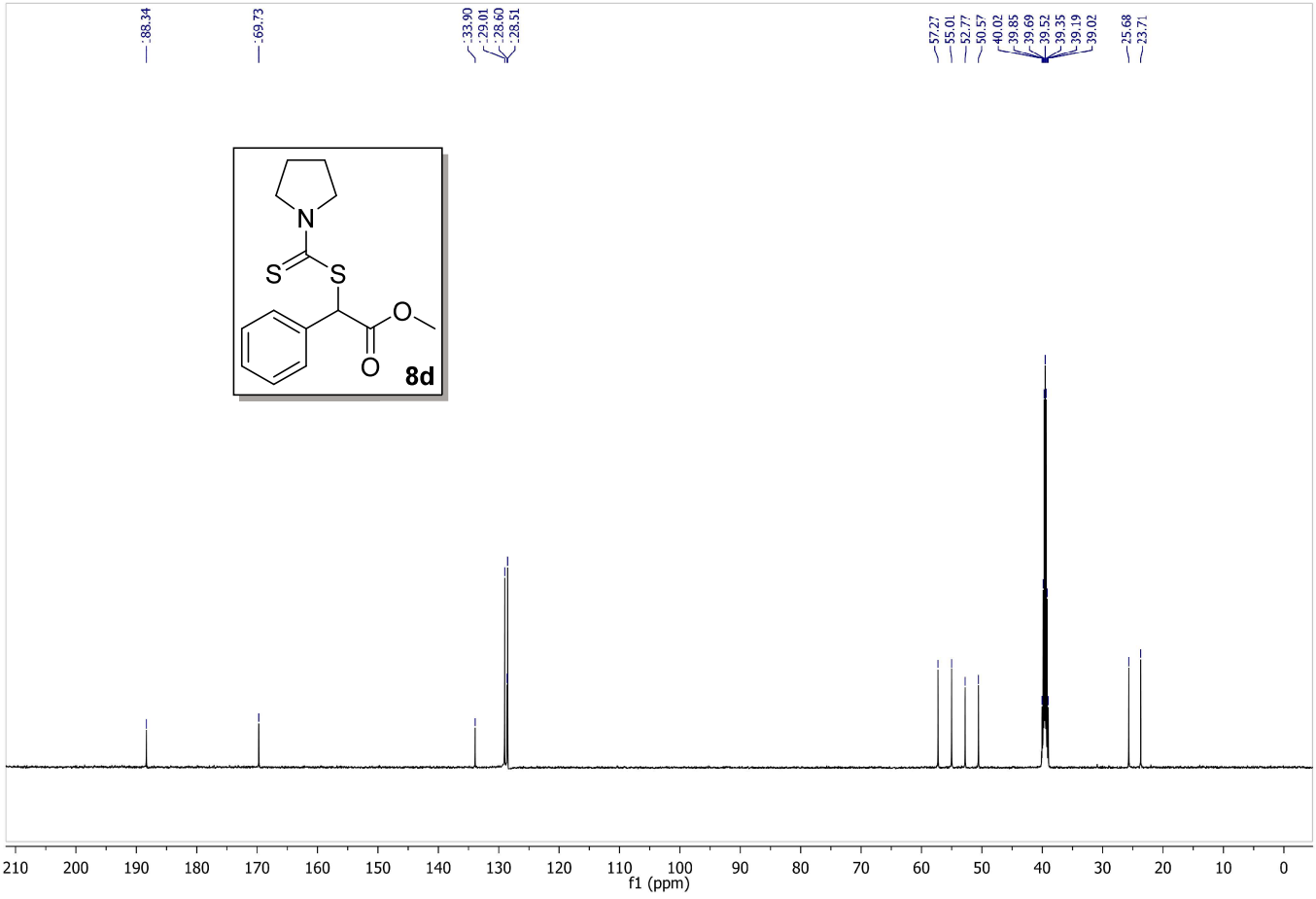
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **8c**



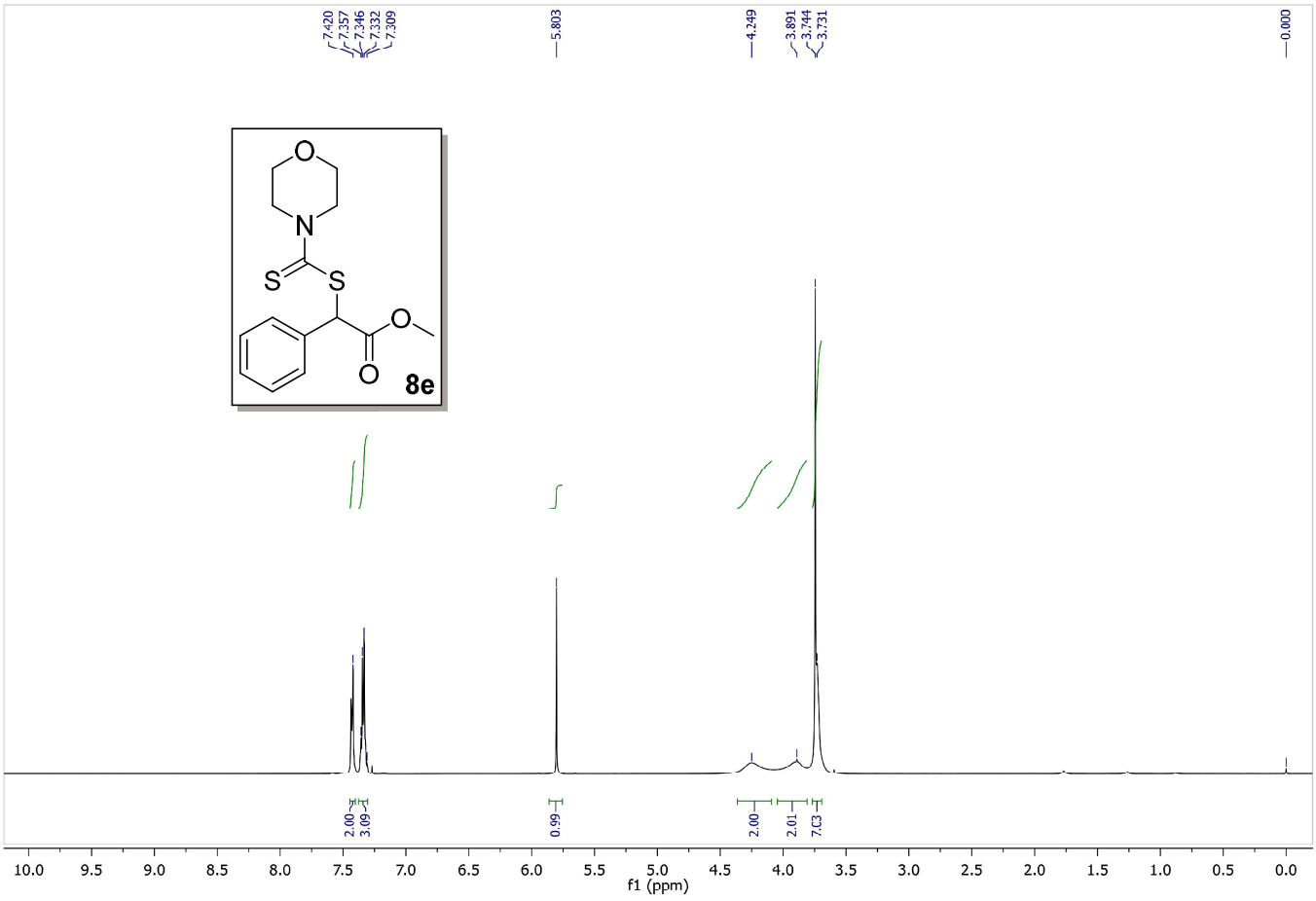


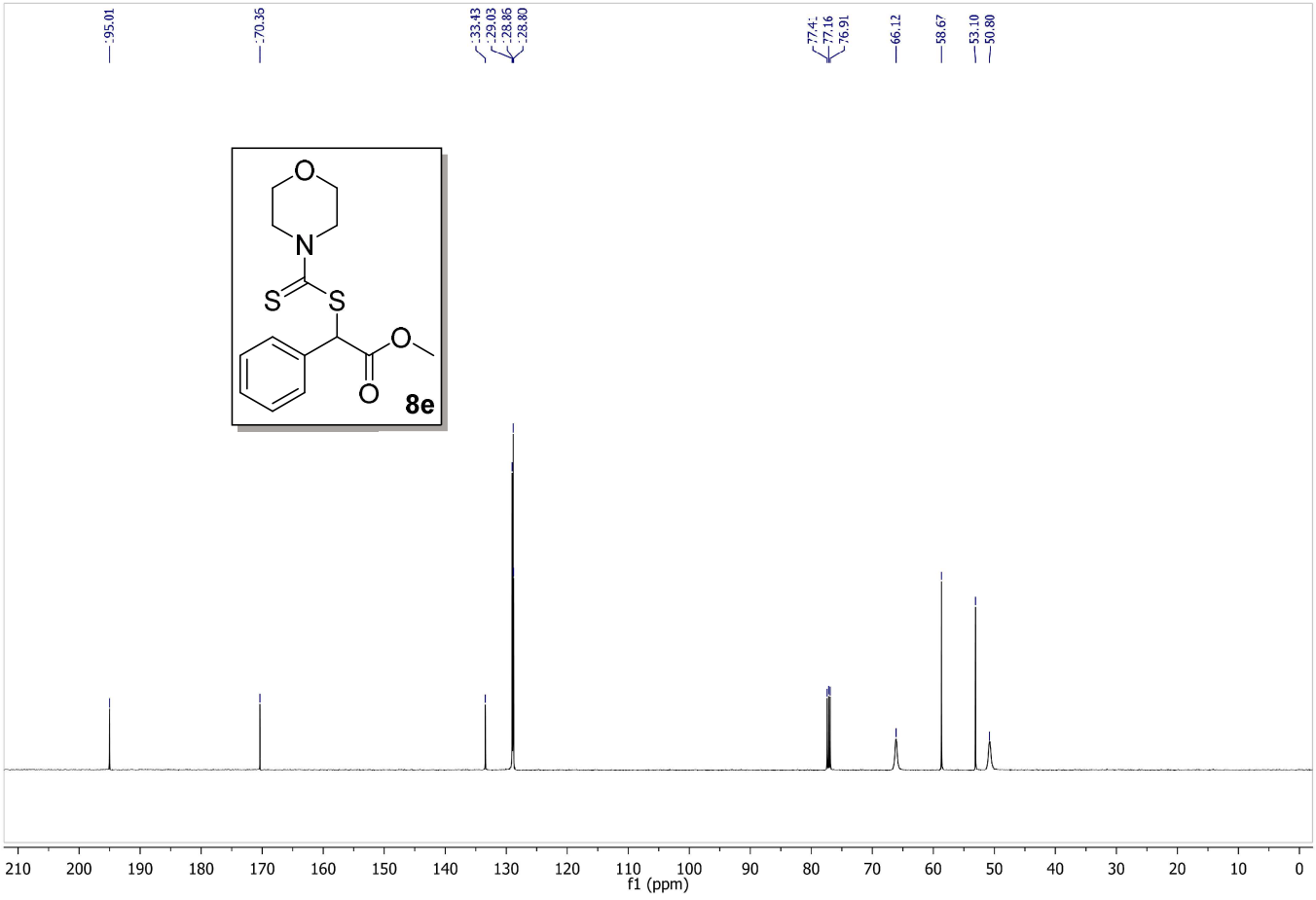
^{1}H NMR (500 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6), **8d**



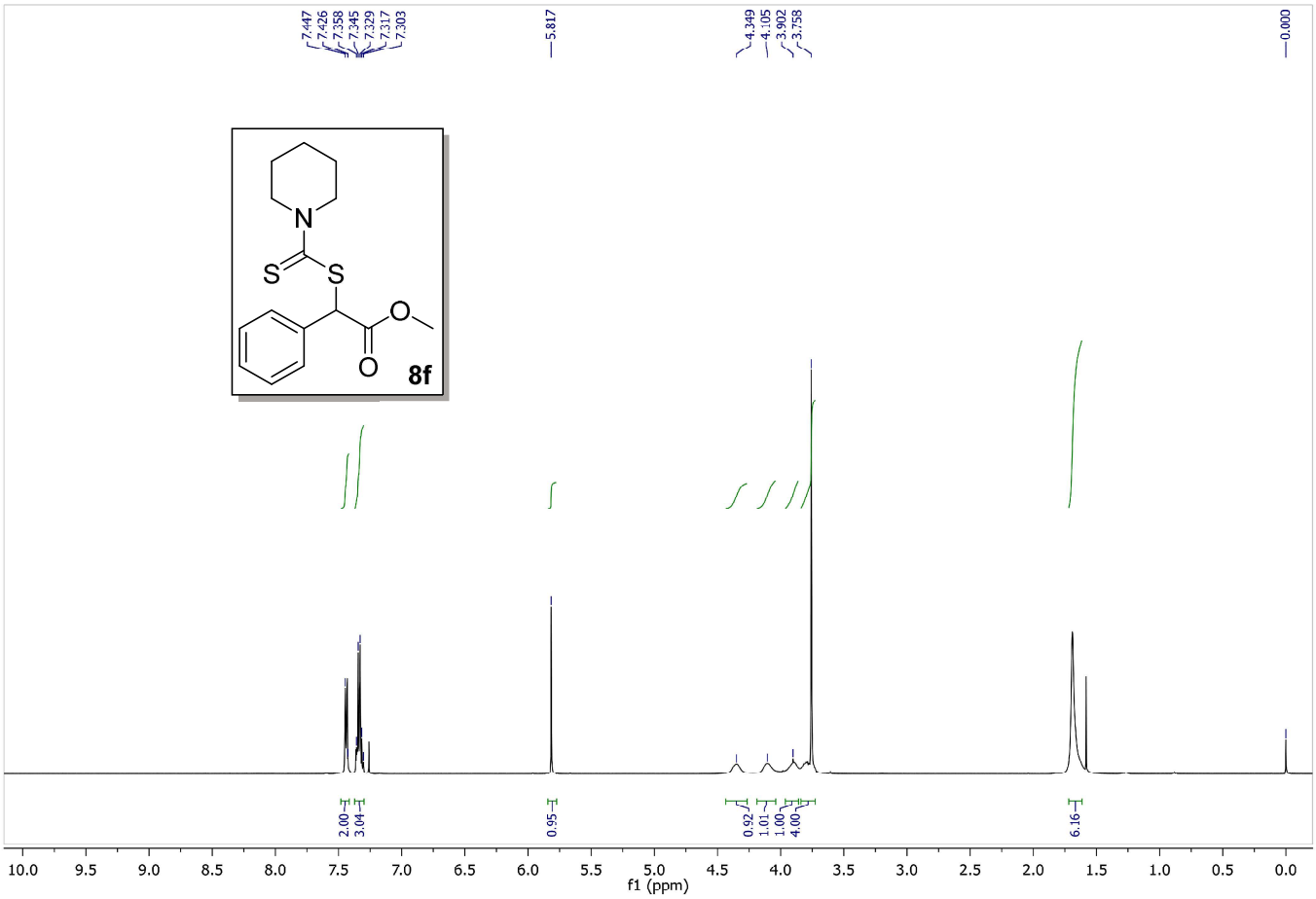


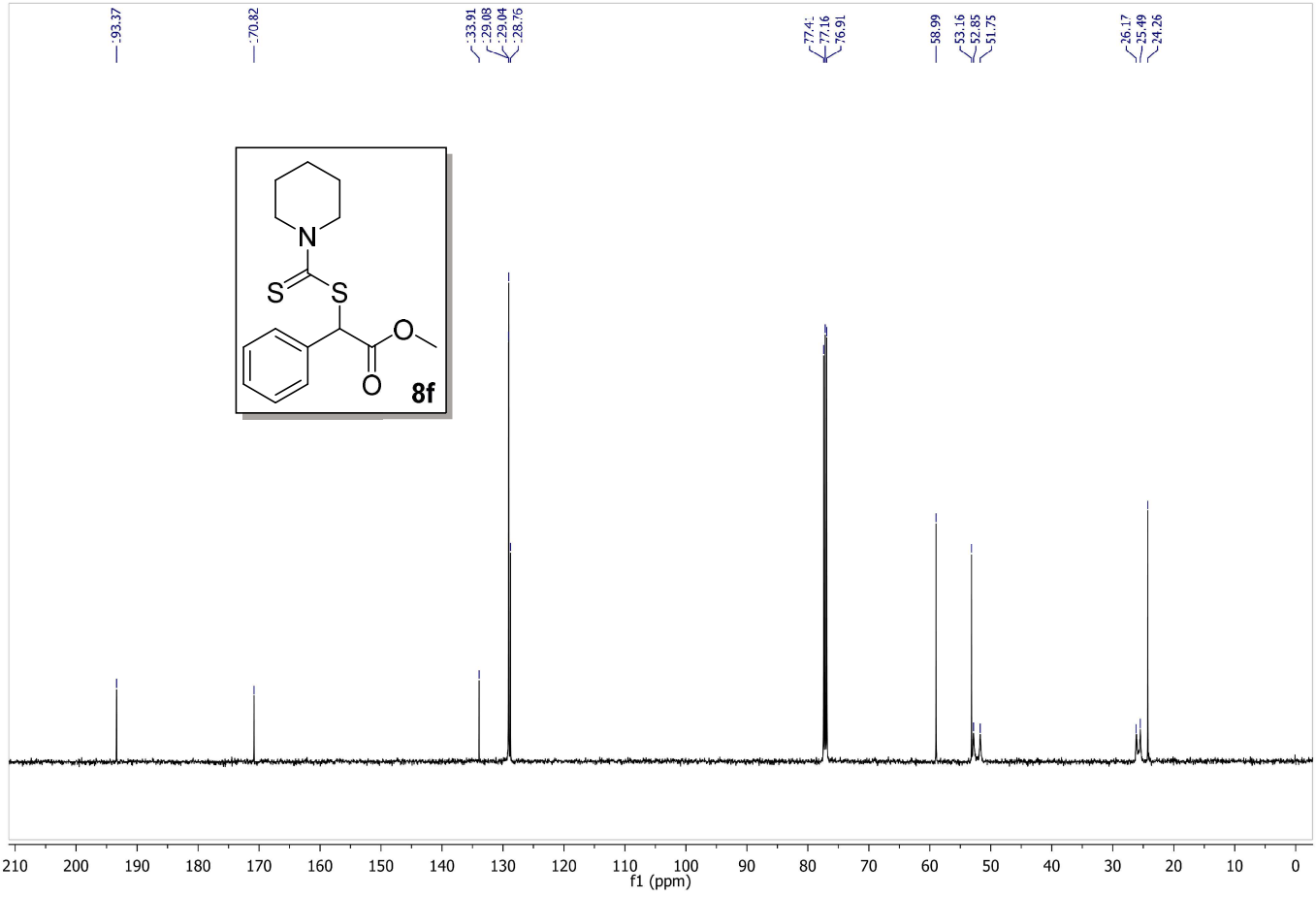
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **8e**



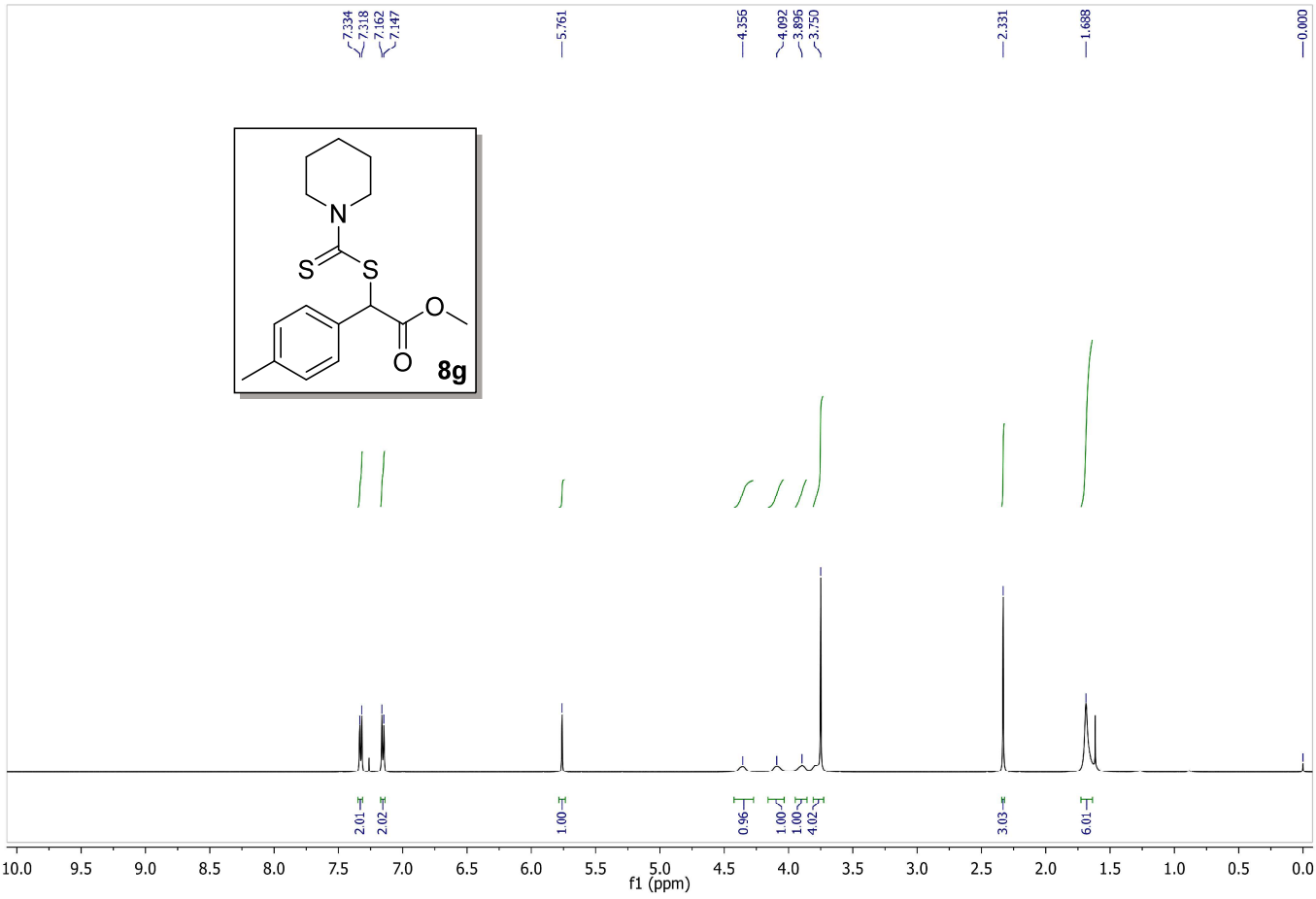


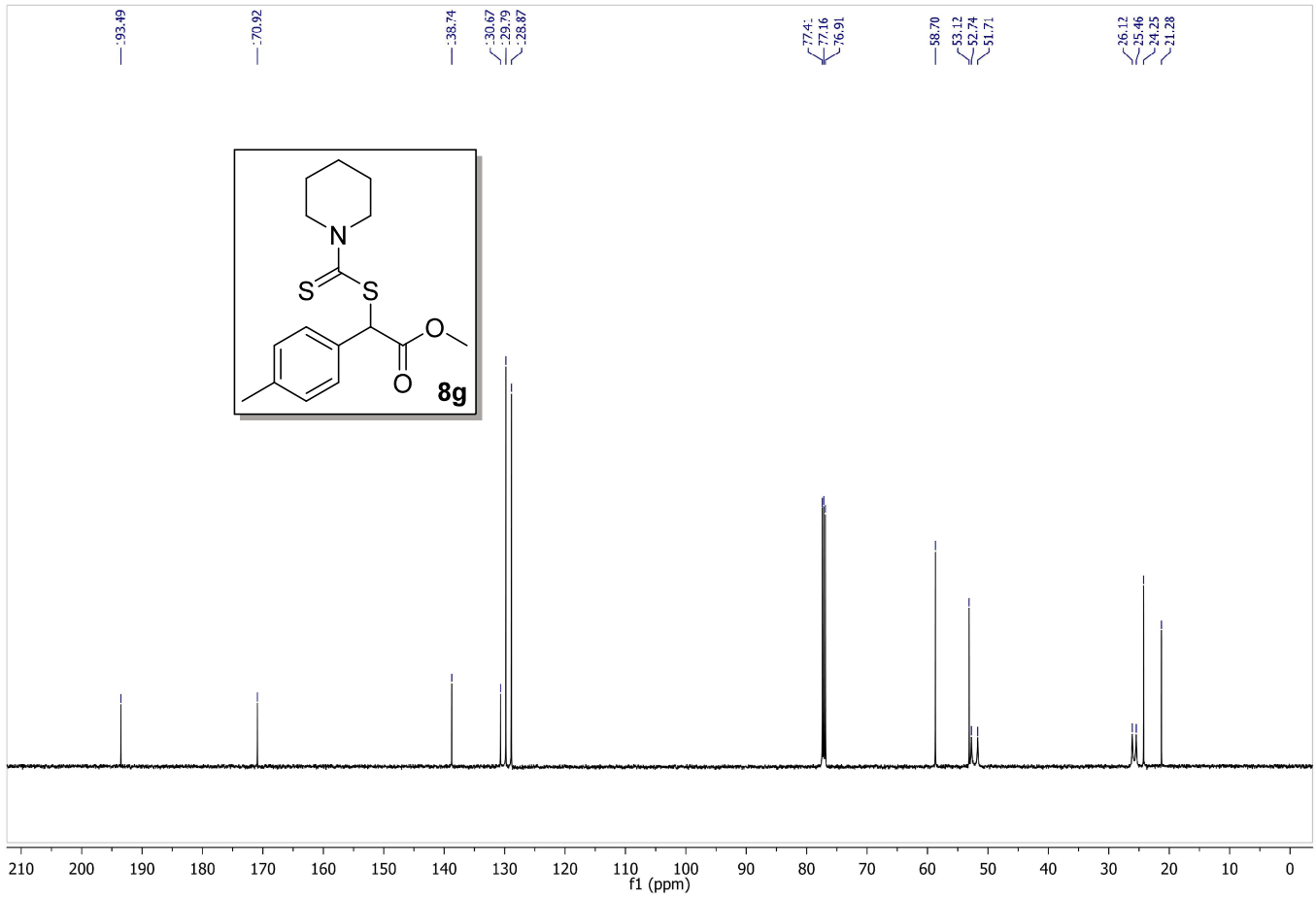
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **8f**



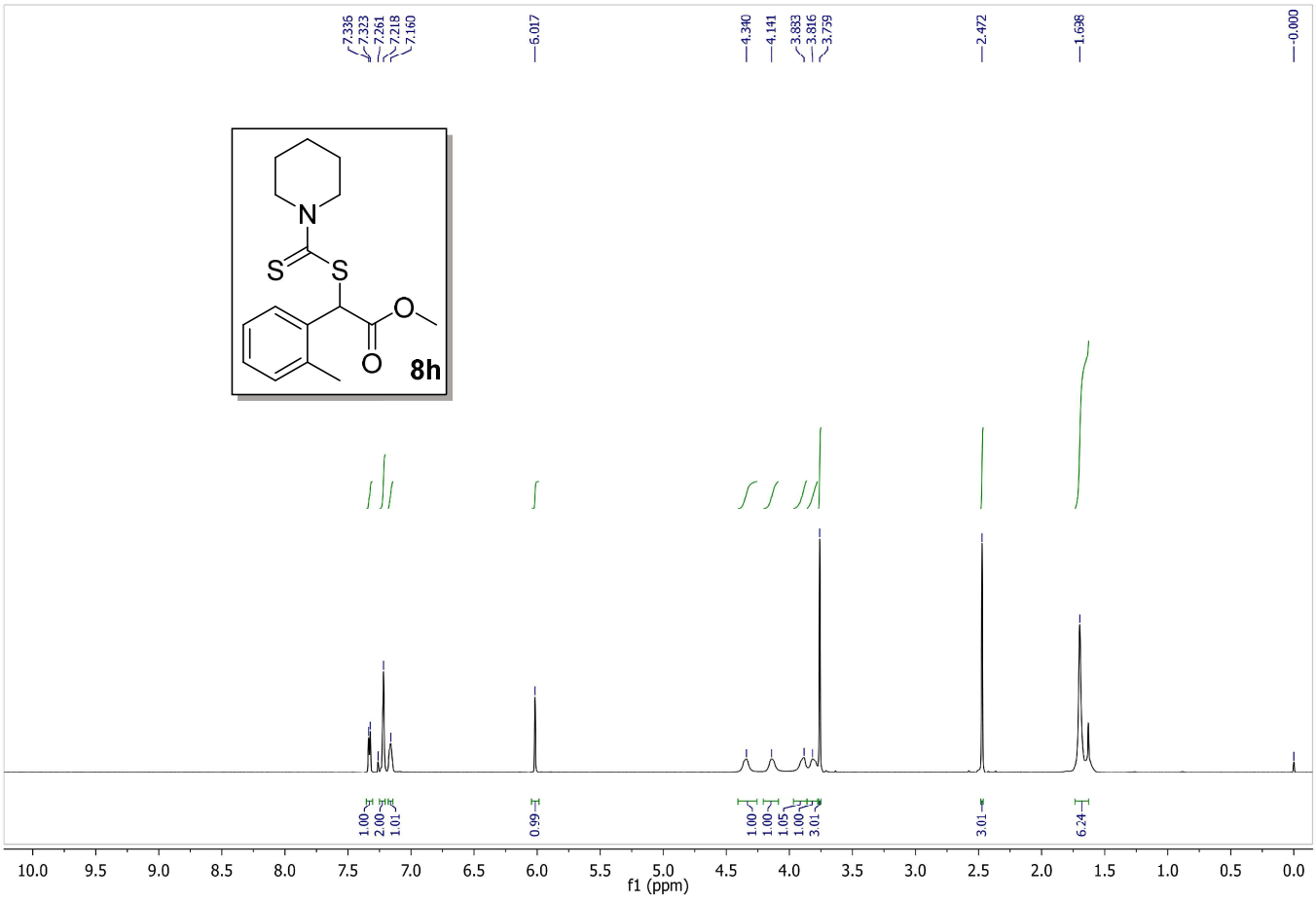


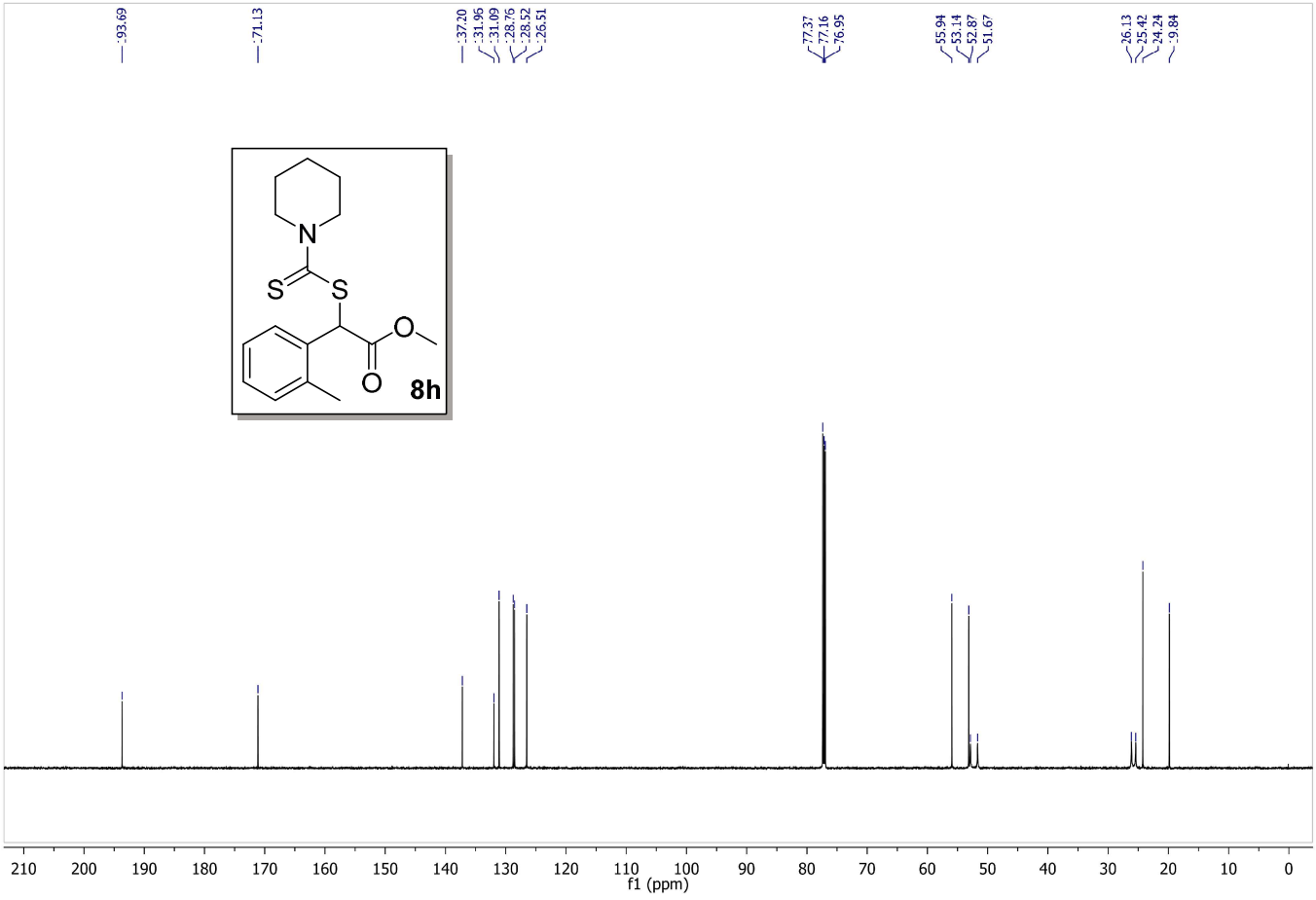
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **8g**



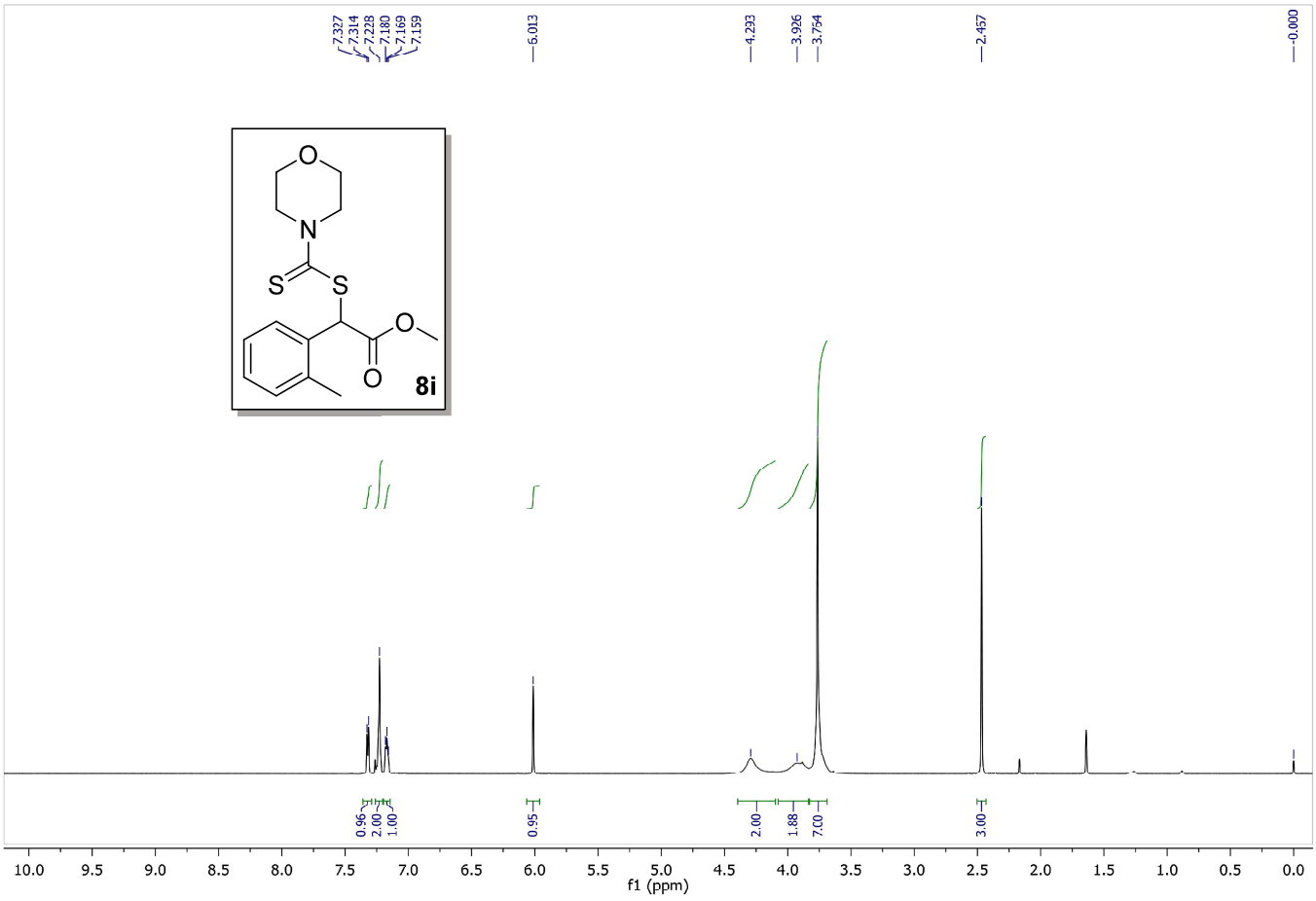


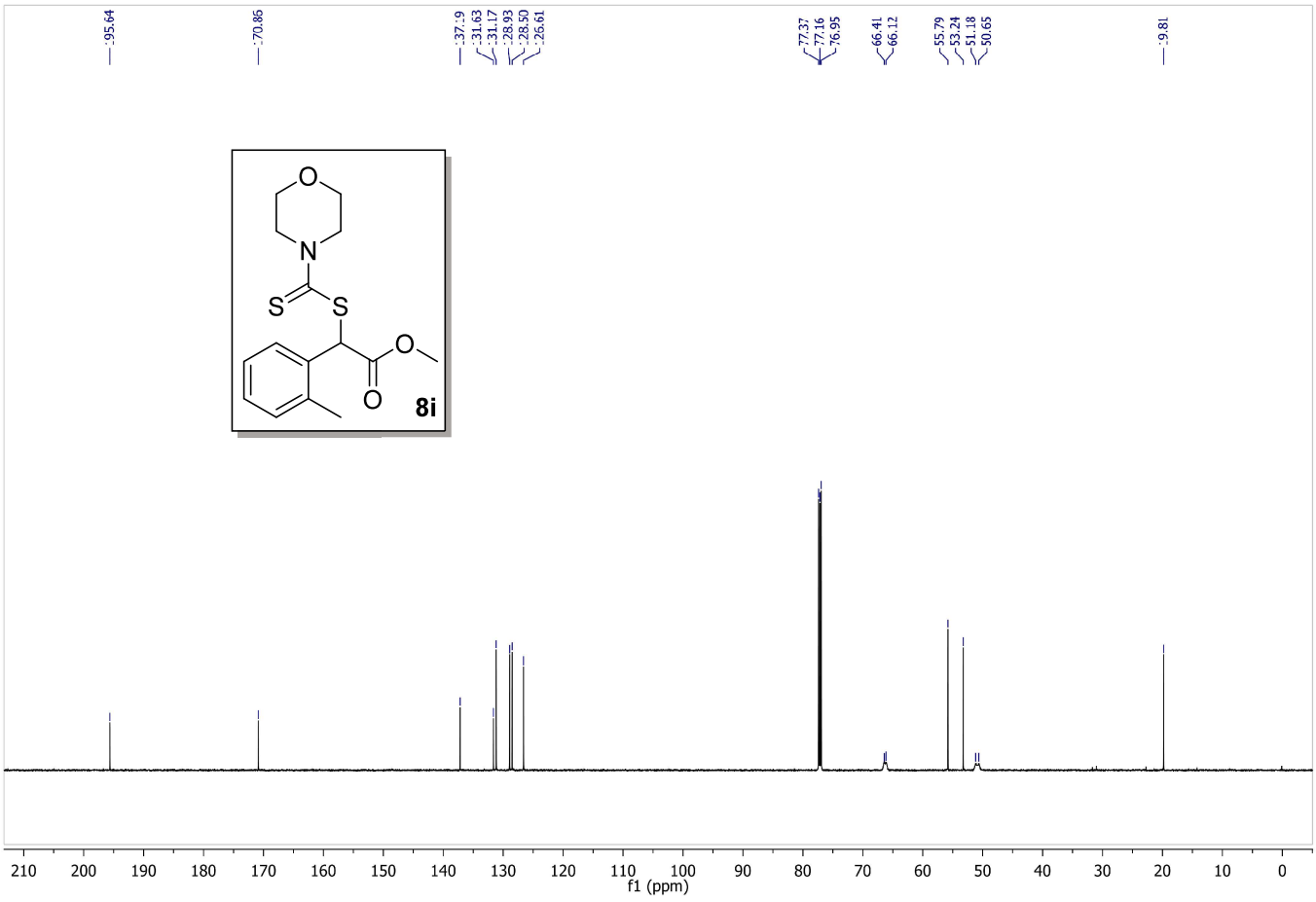
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), **8h**



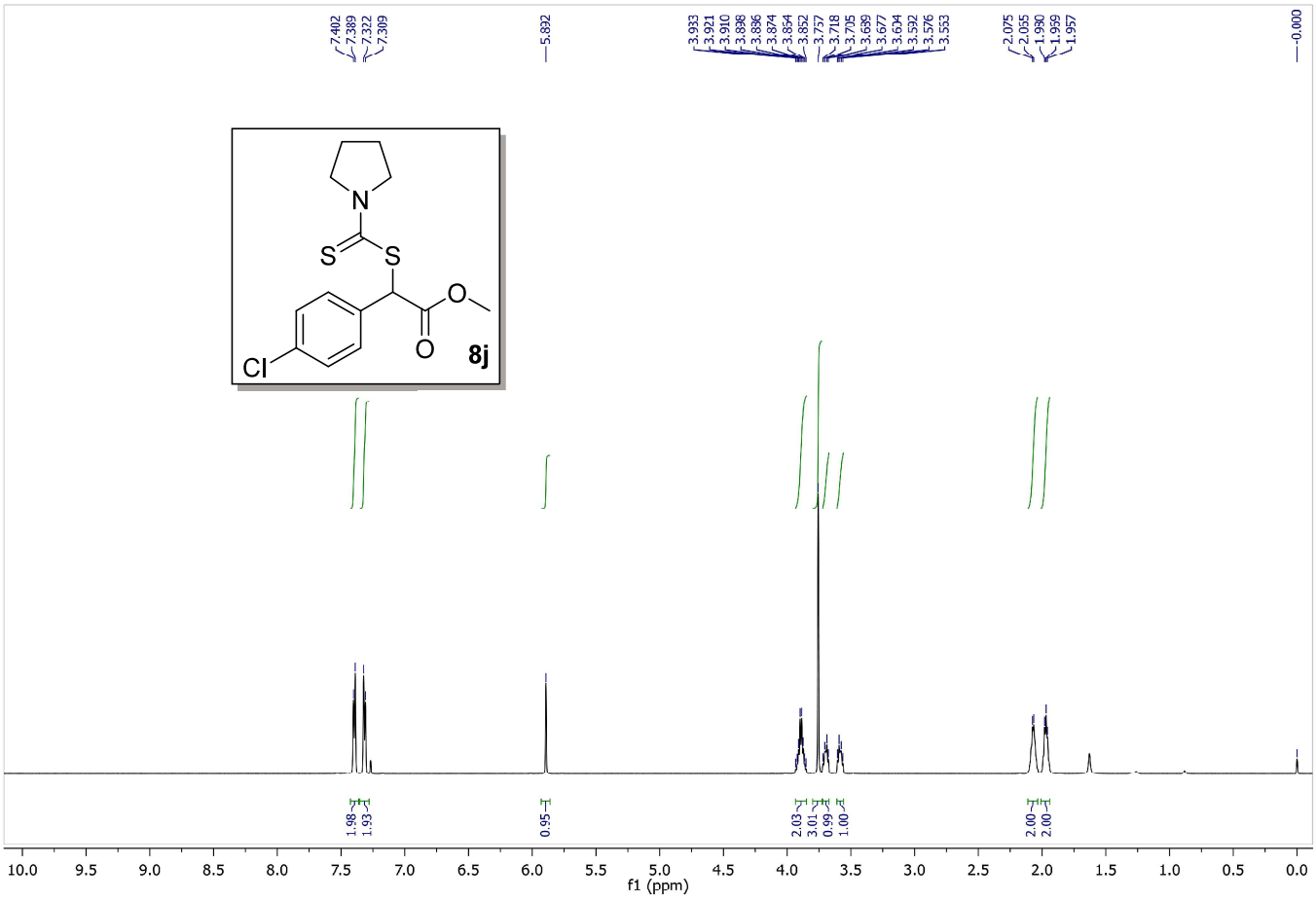


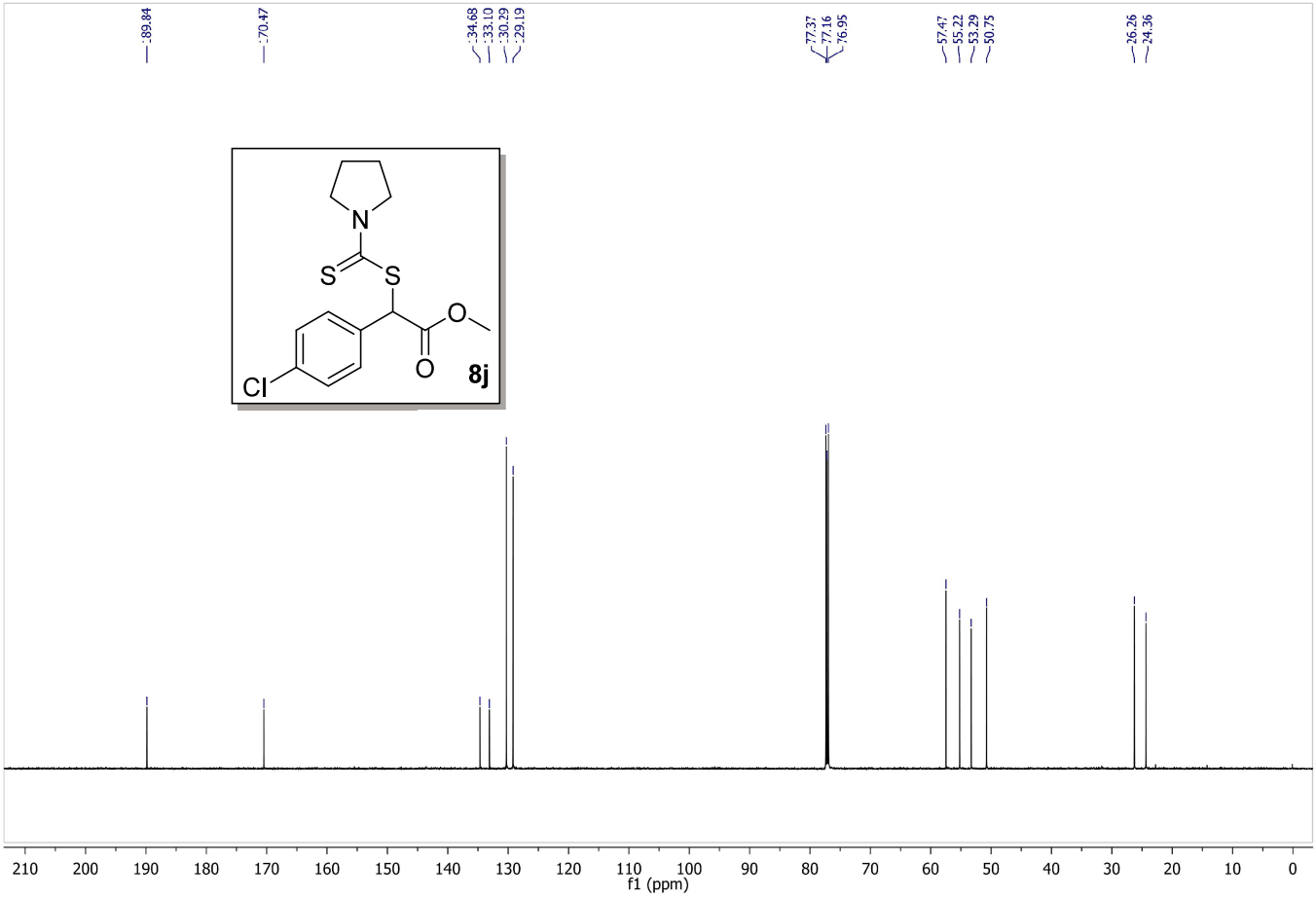
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **8i**



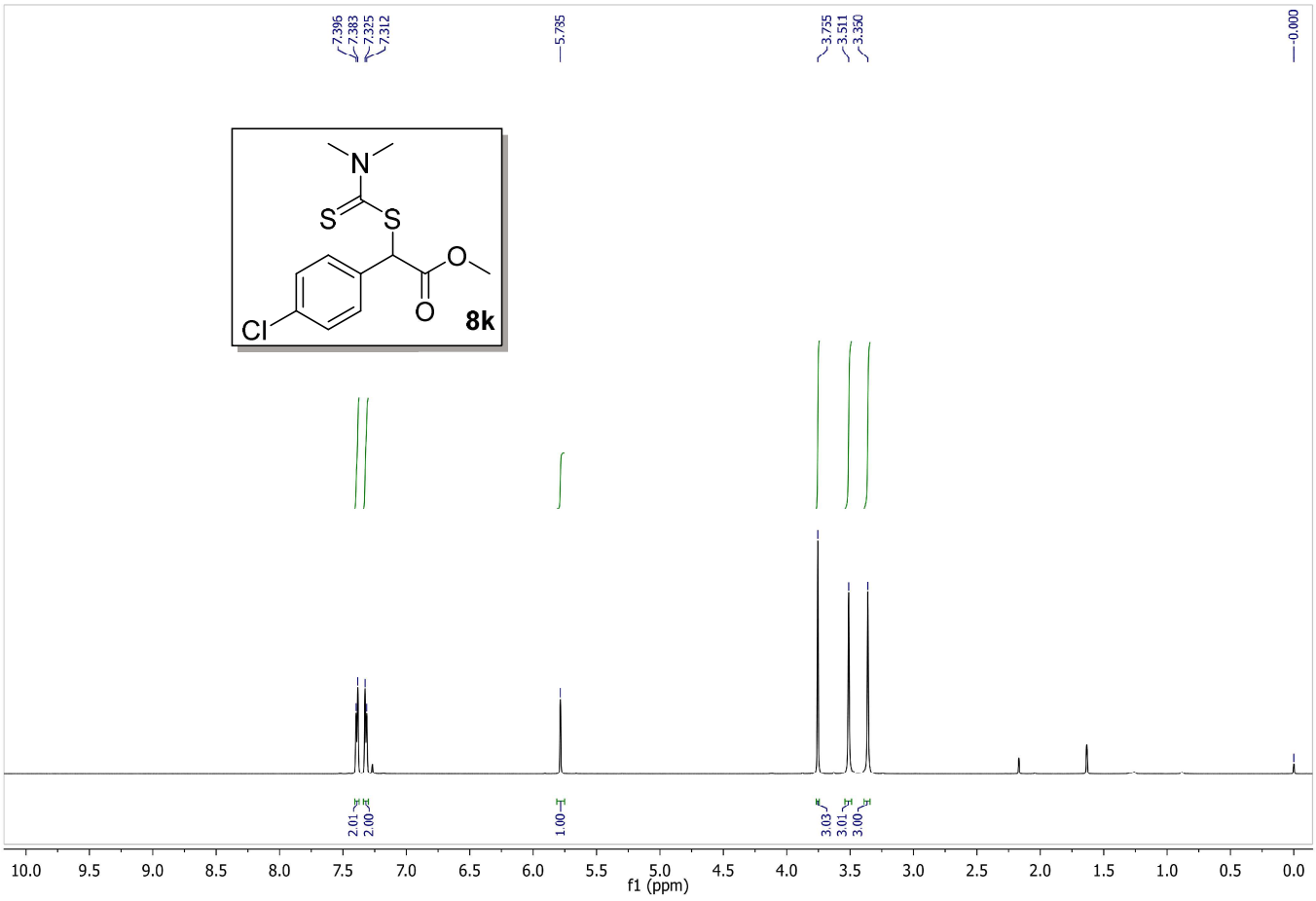


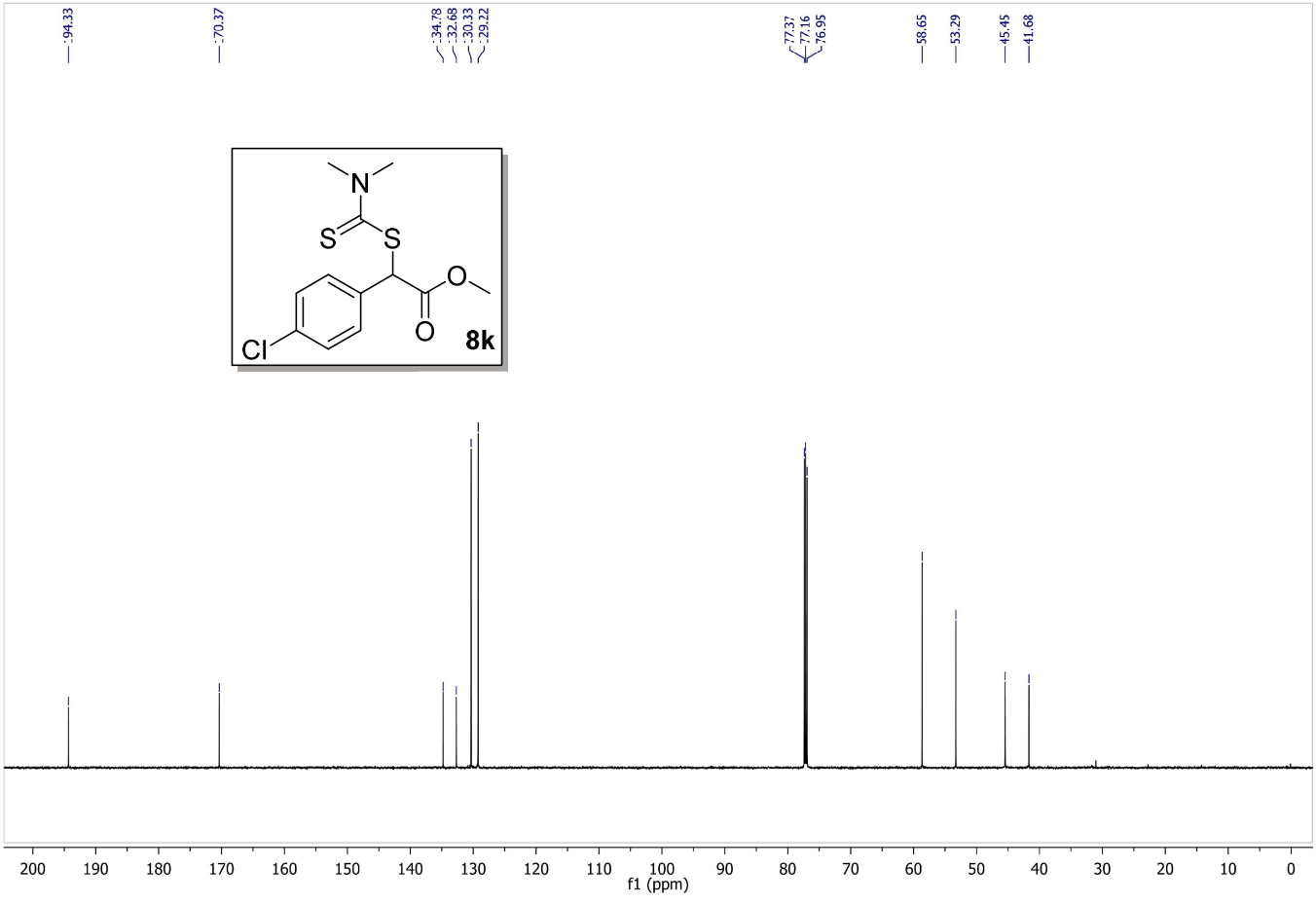
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), **8j**



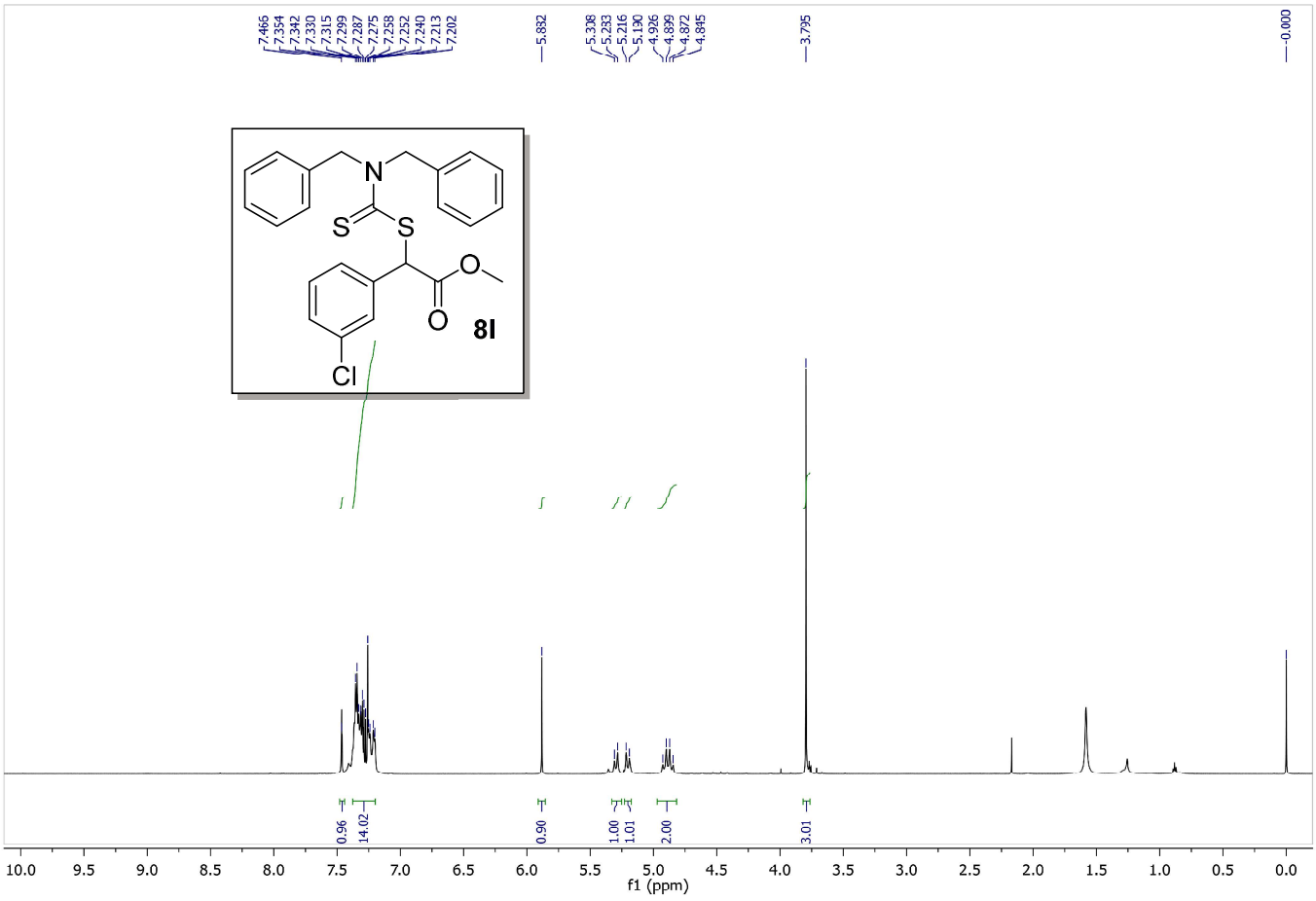


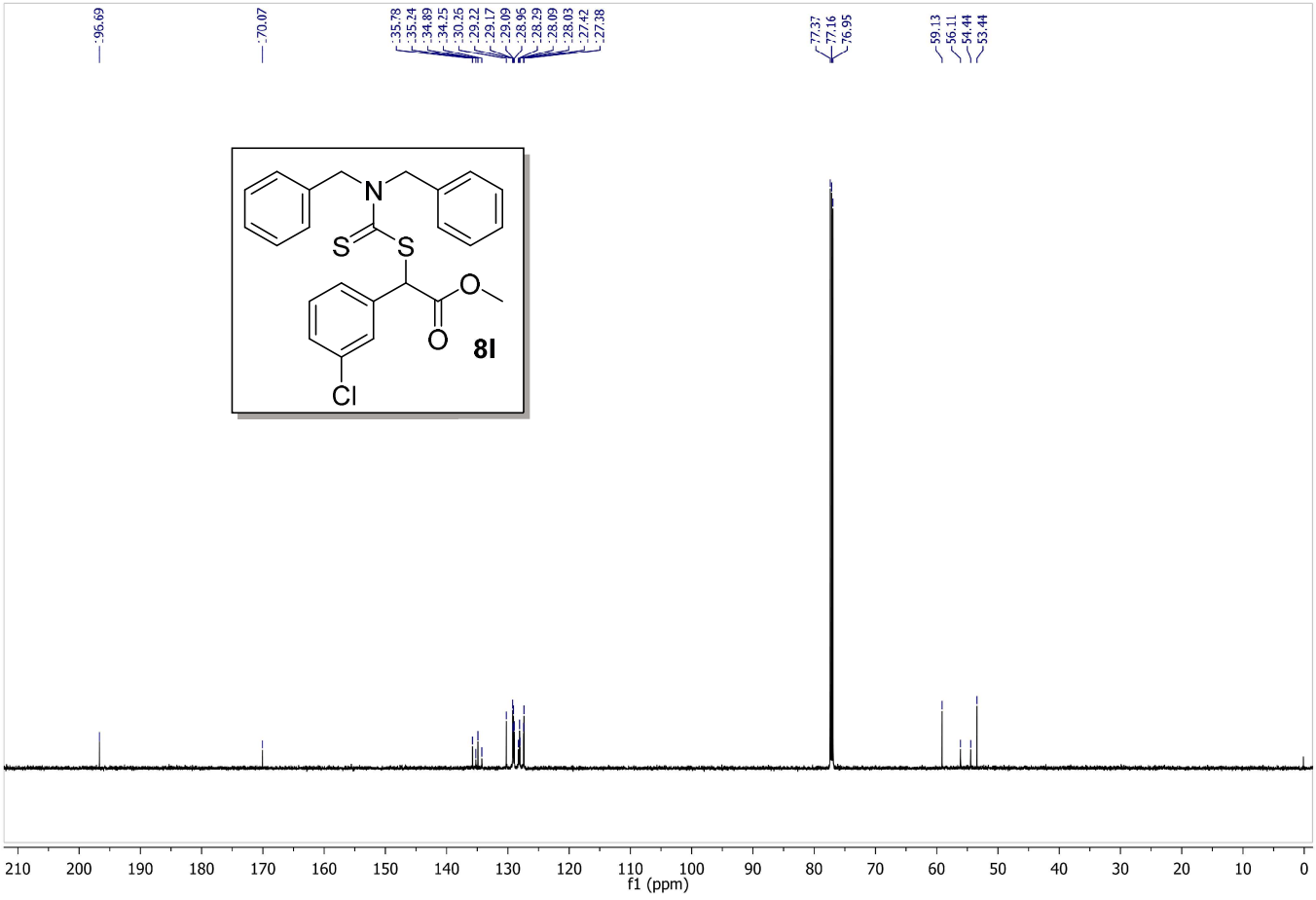
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **8k**



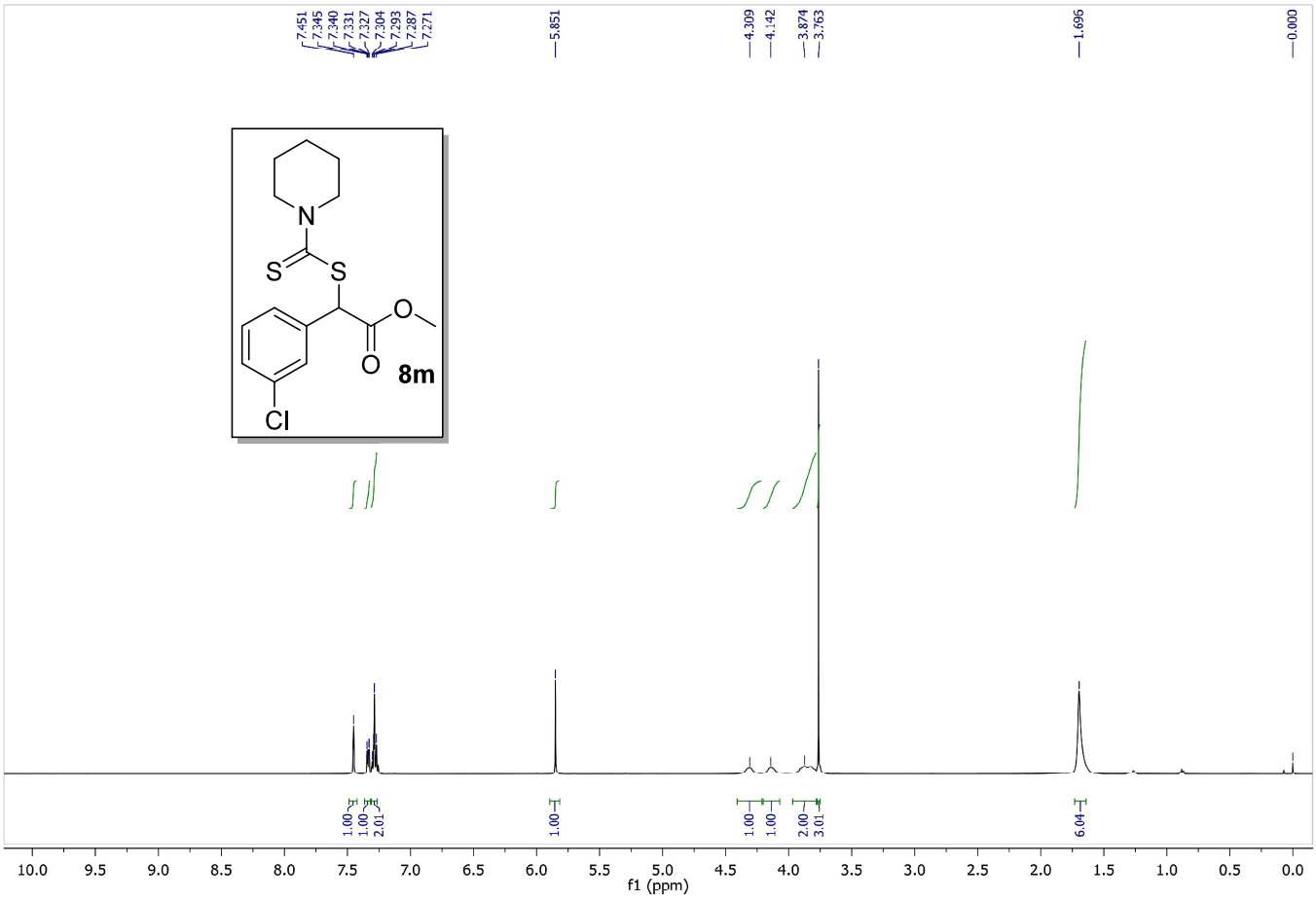


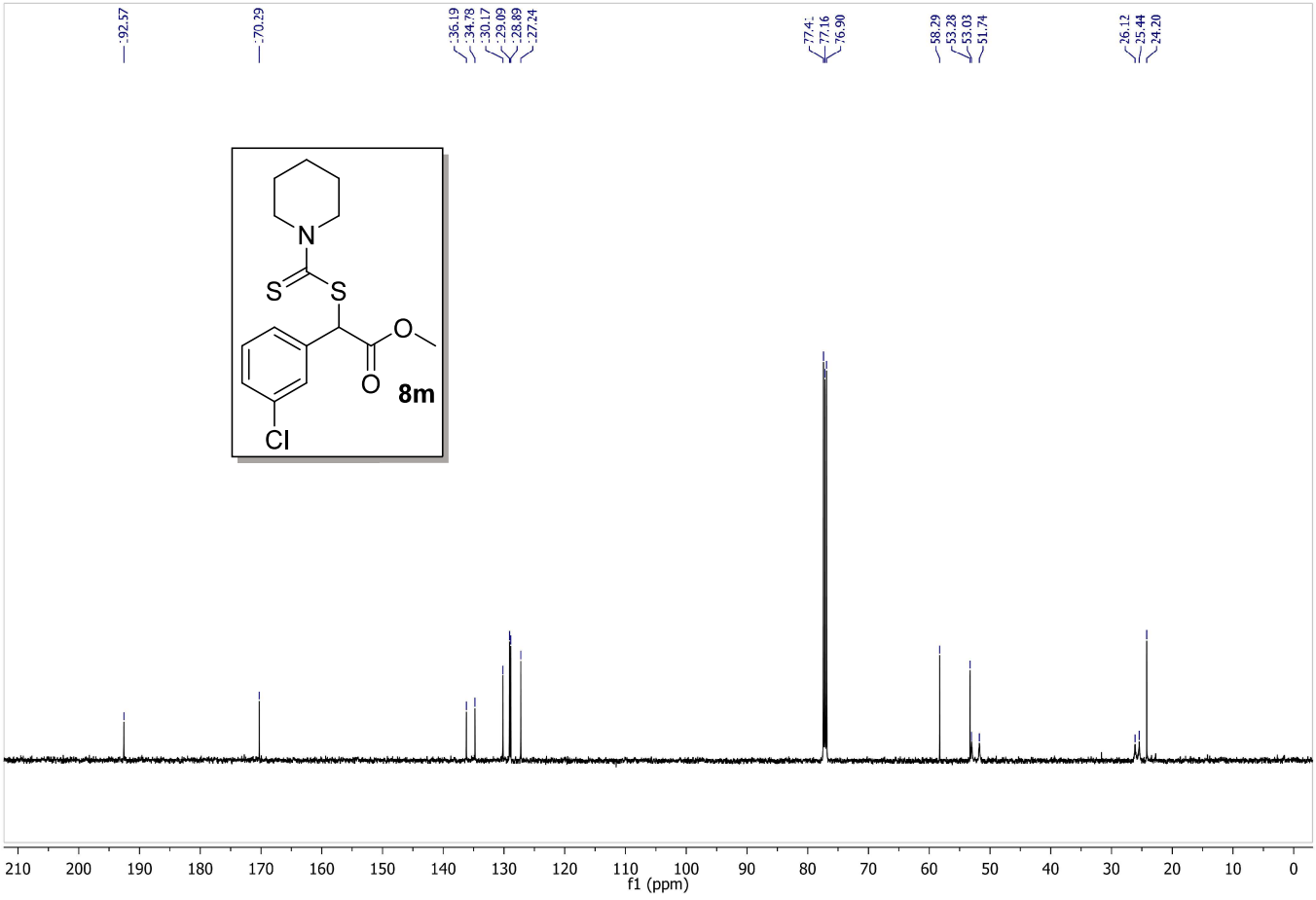
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **8l**



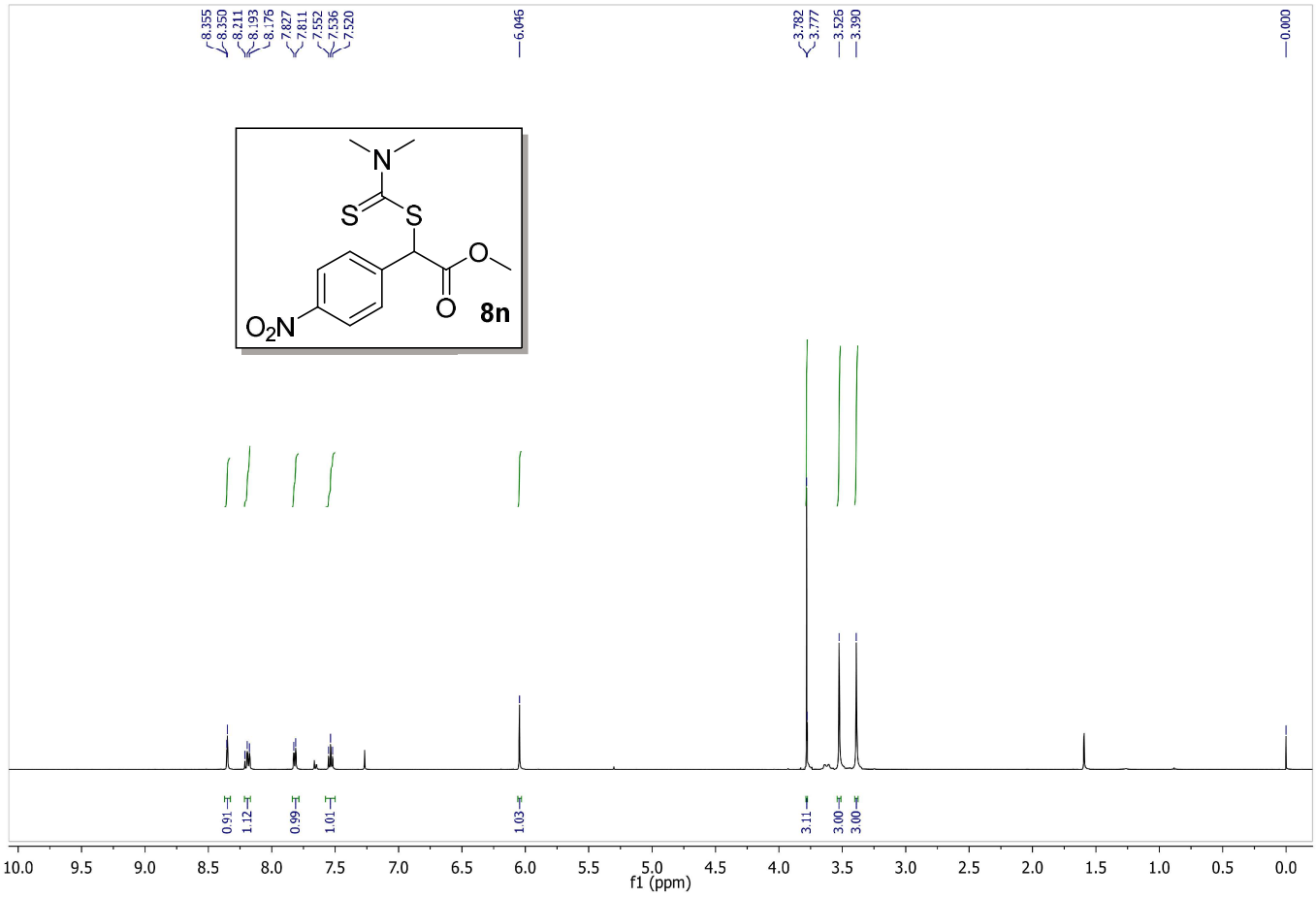


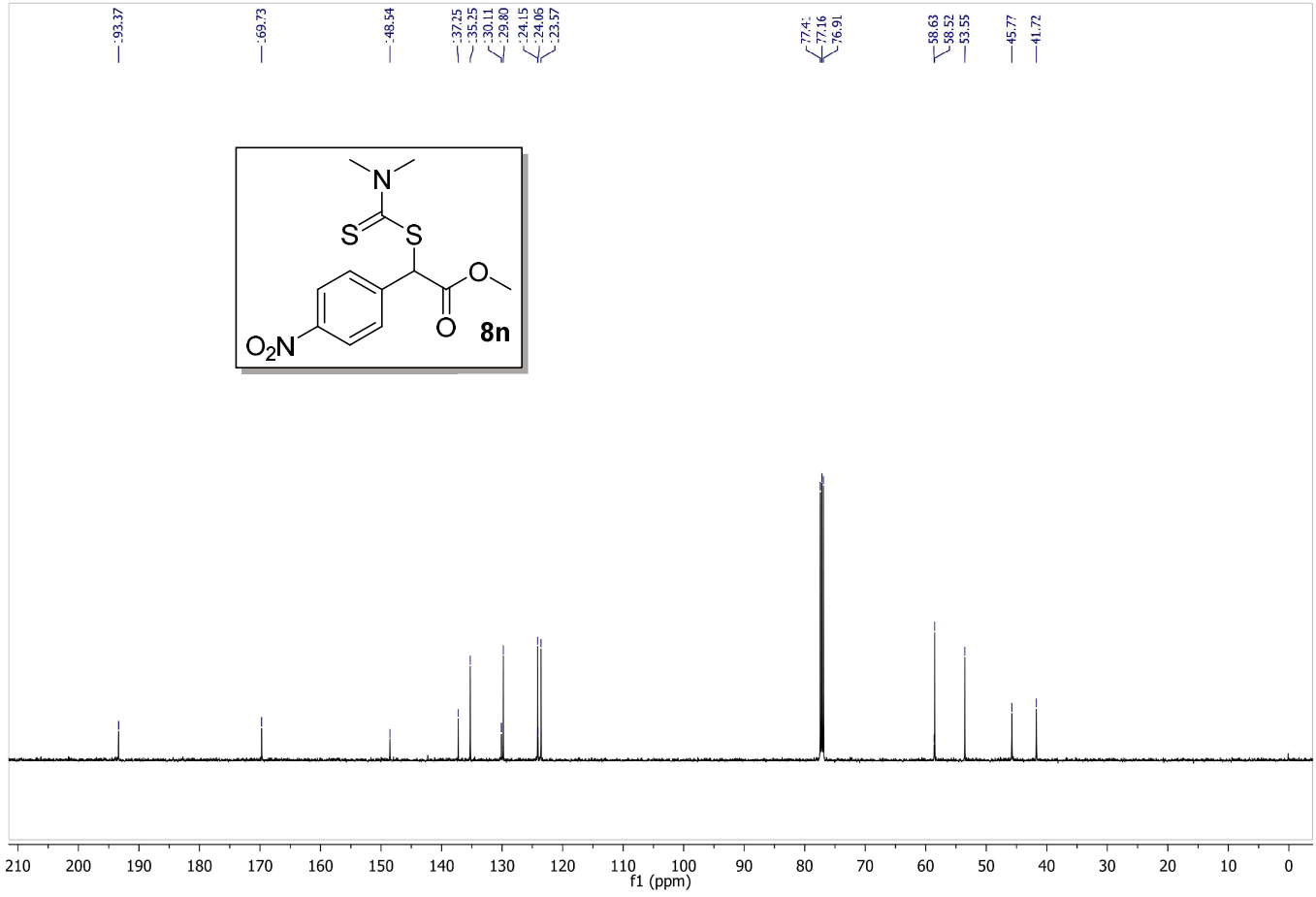
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **8m**



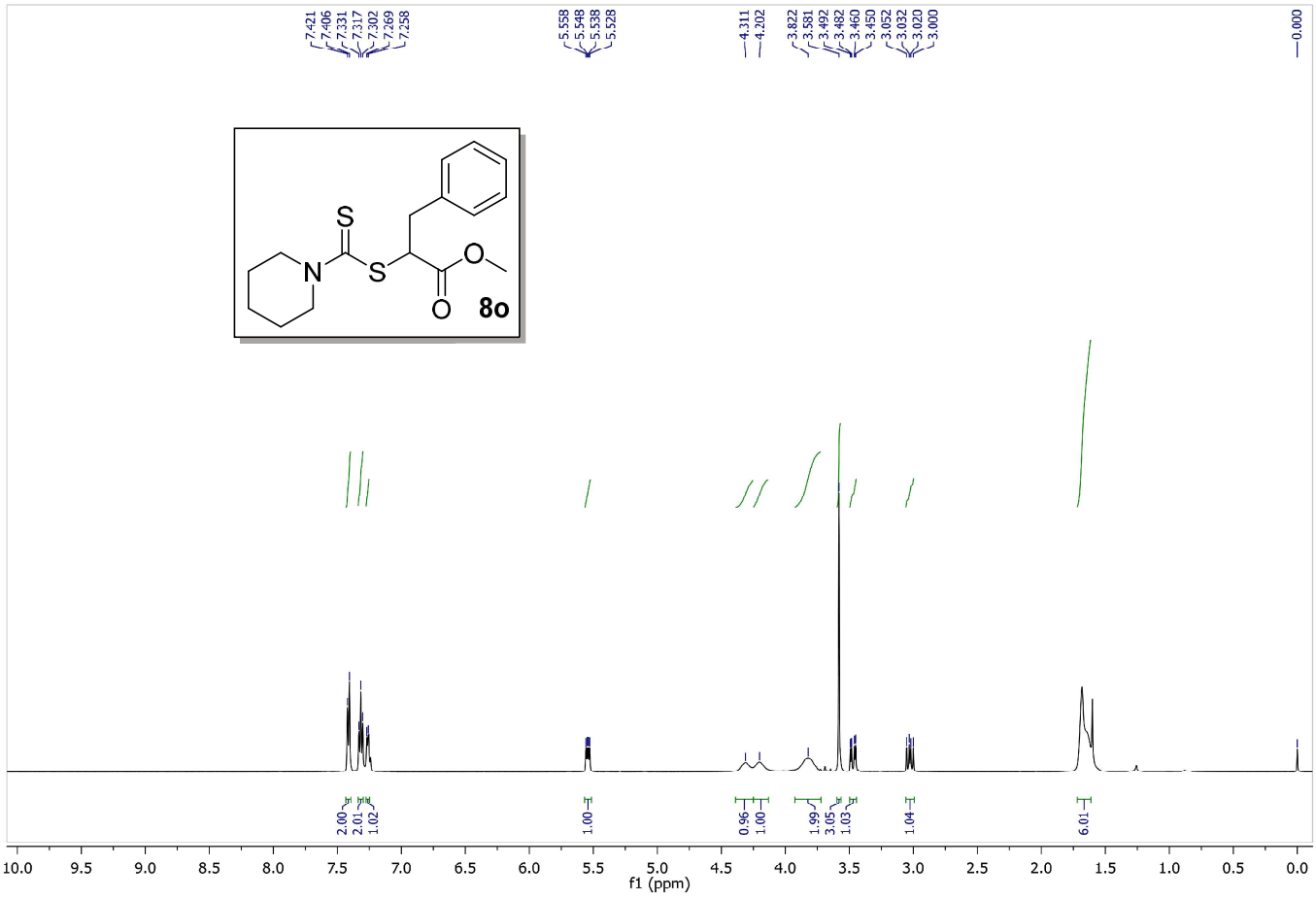


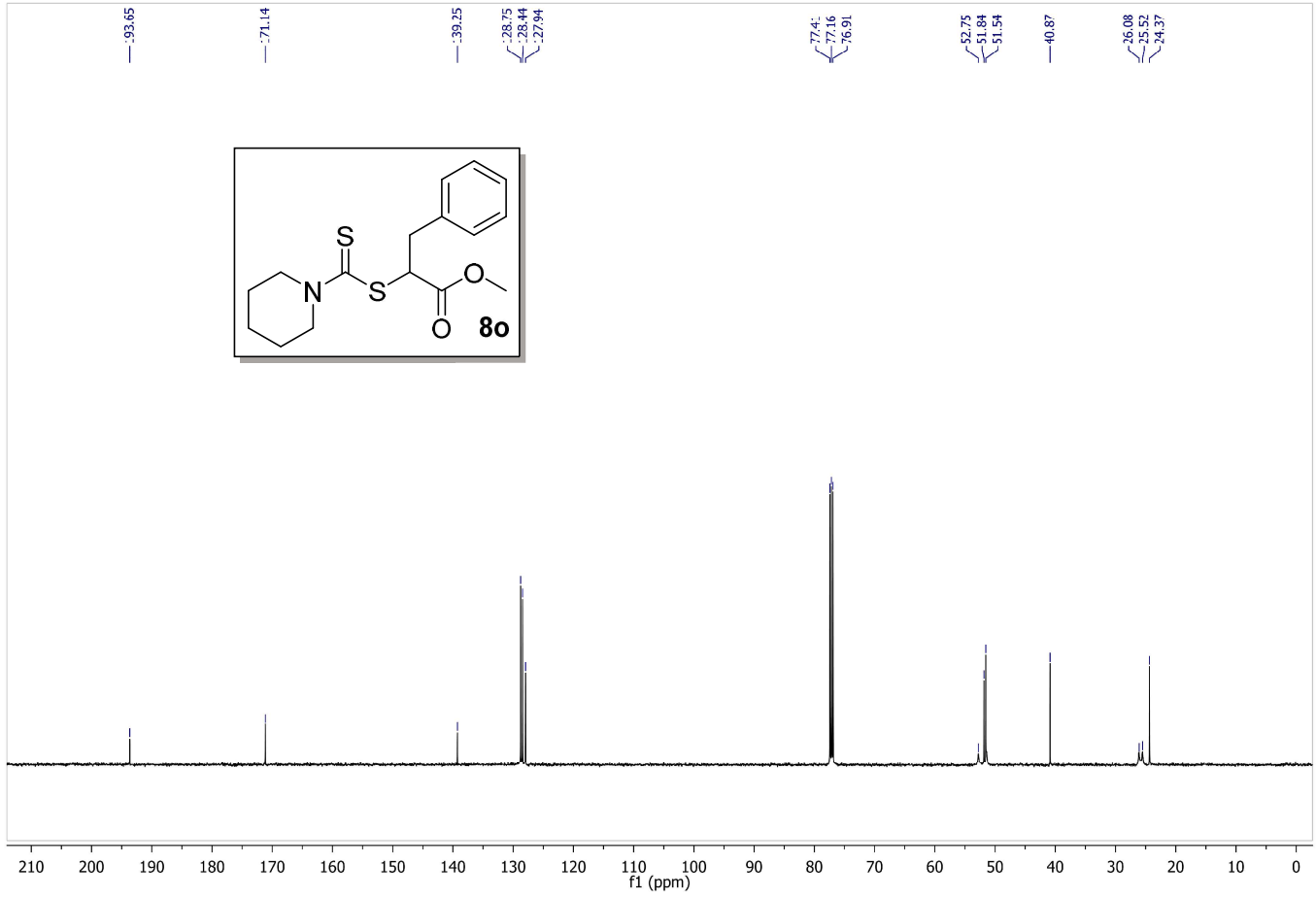
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **8n**



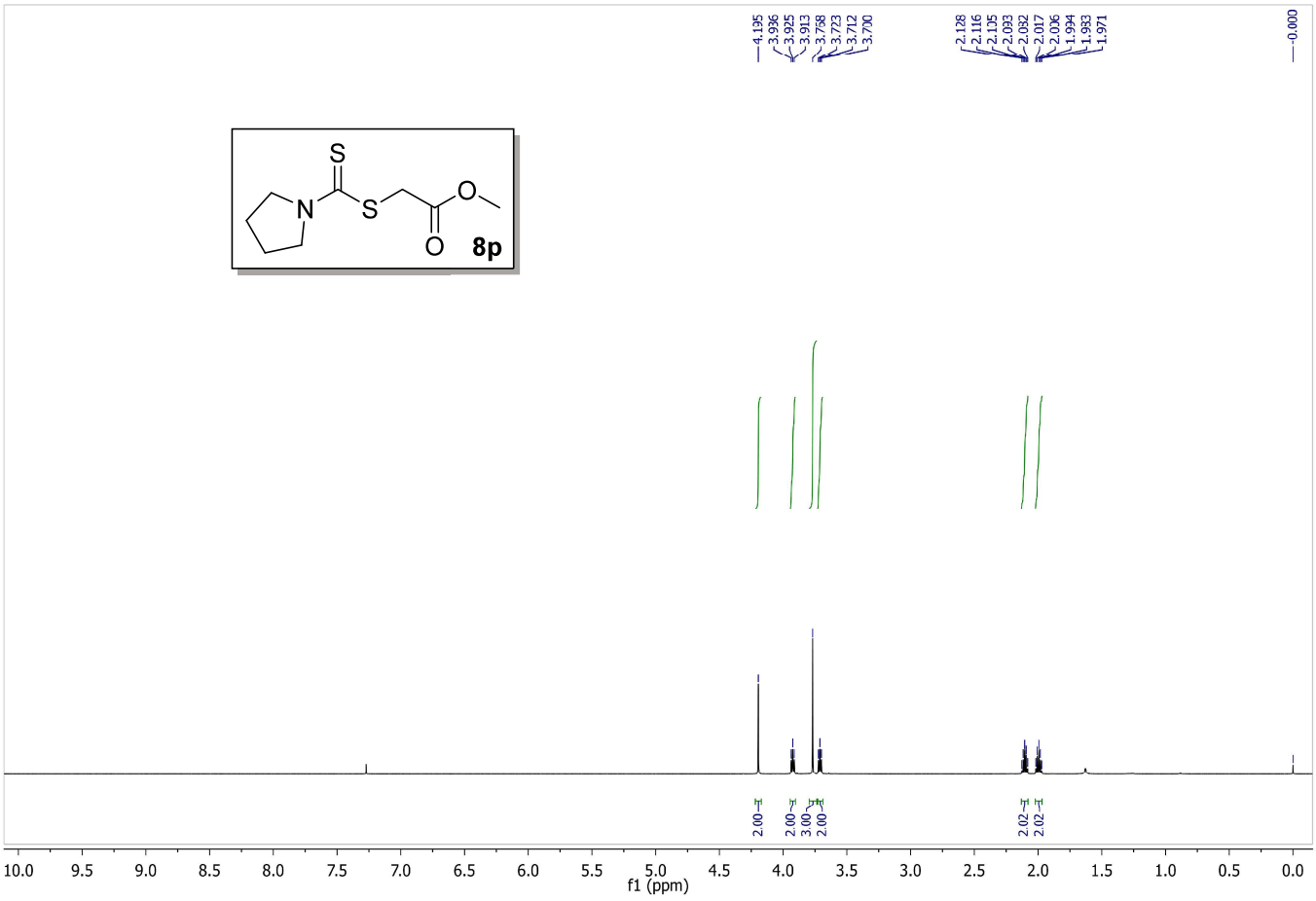


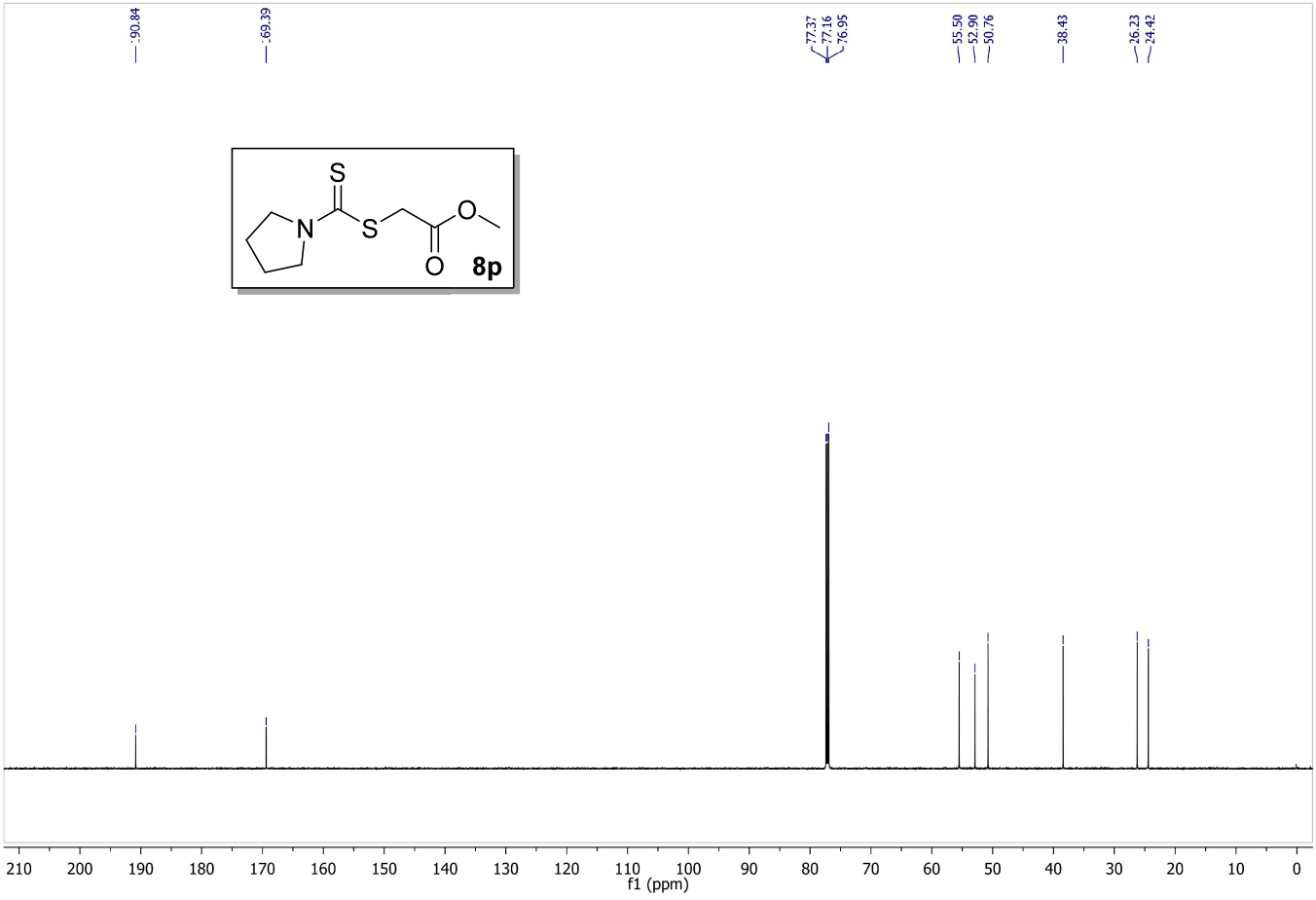
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **8o**



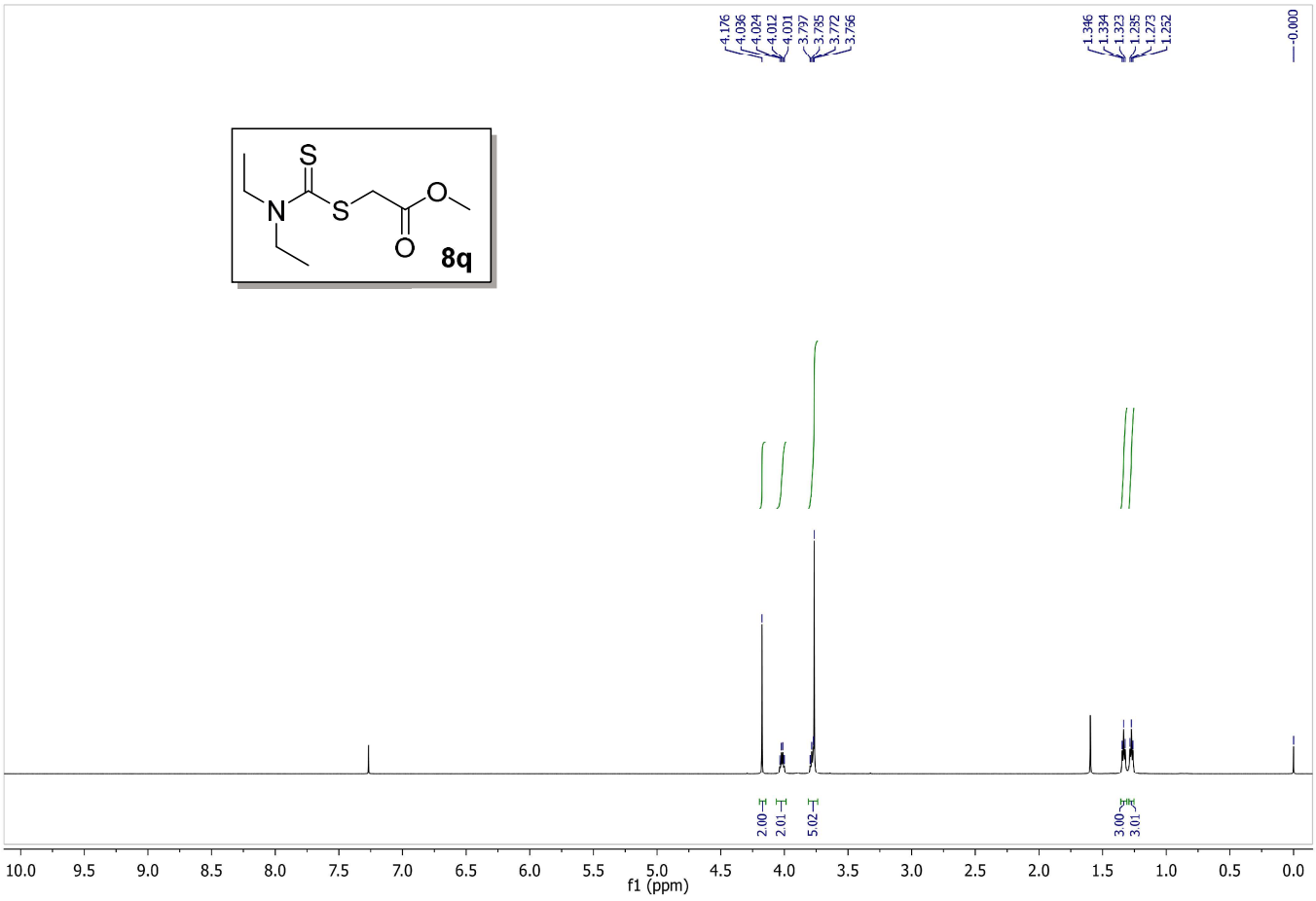


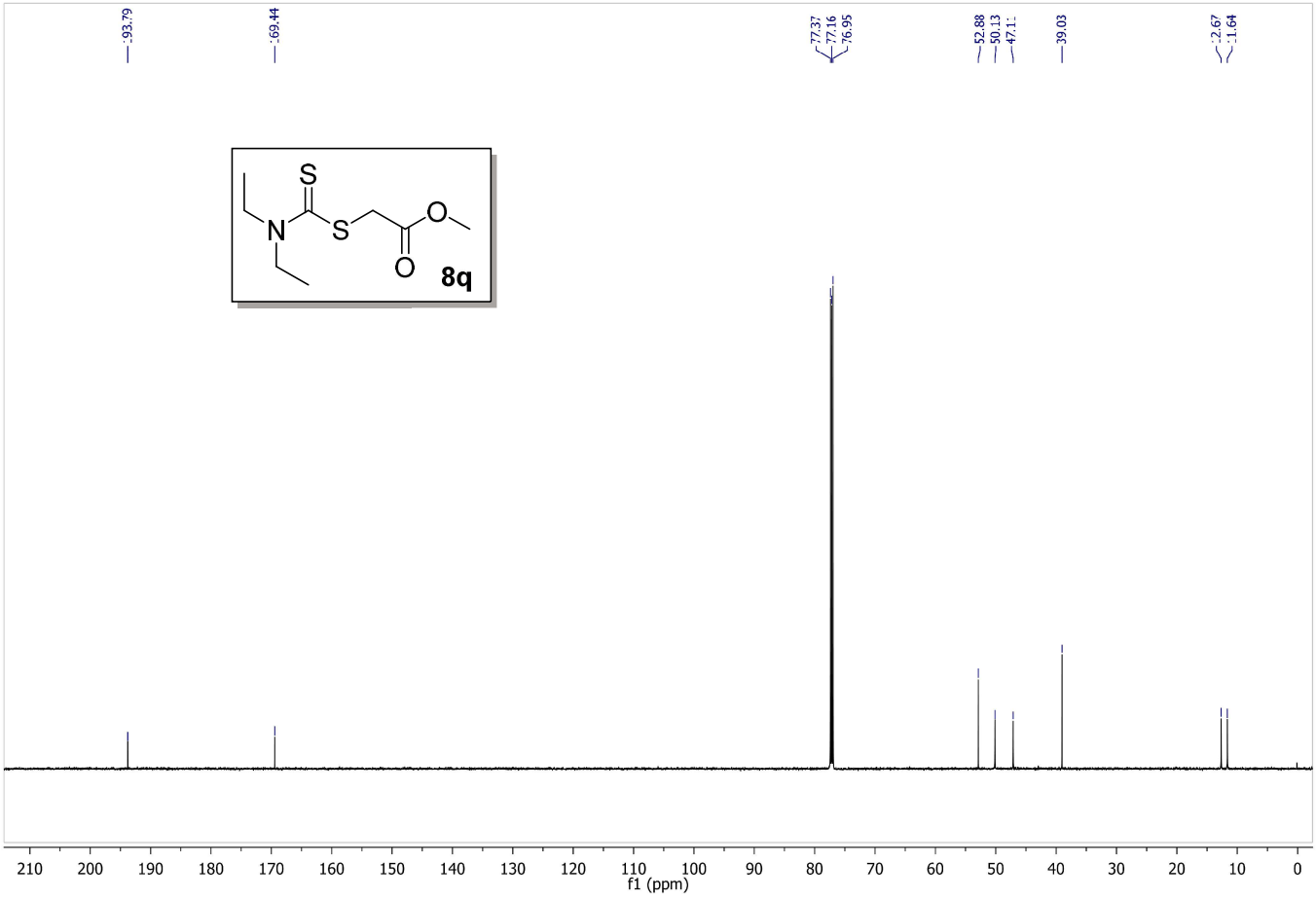
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **8p**



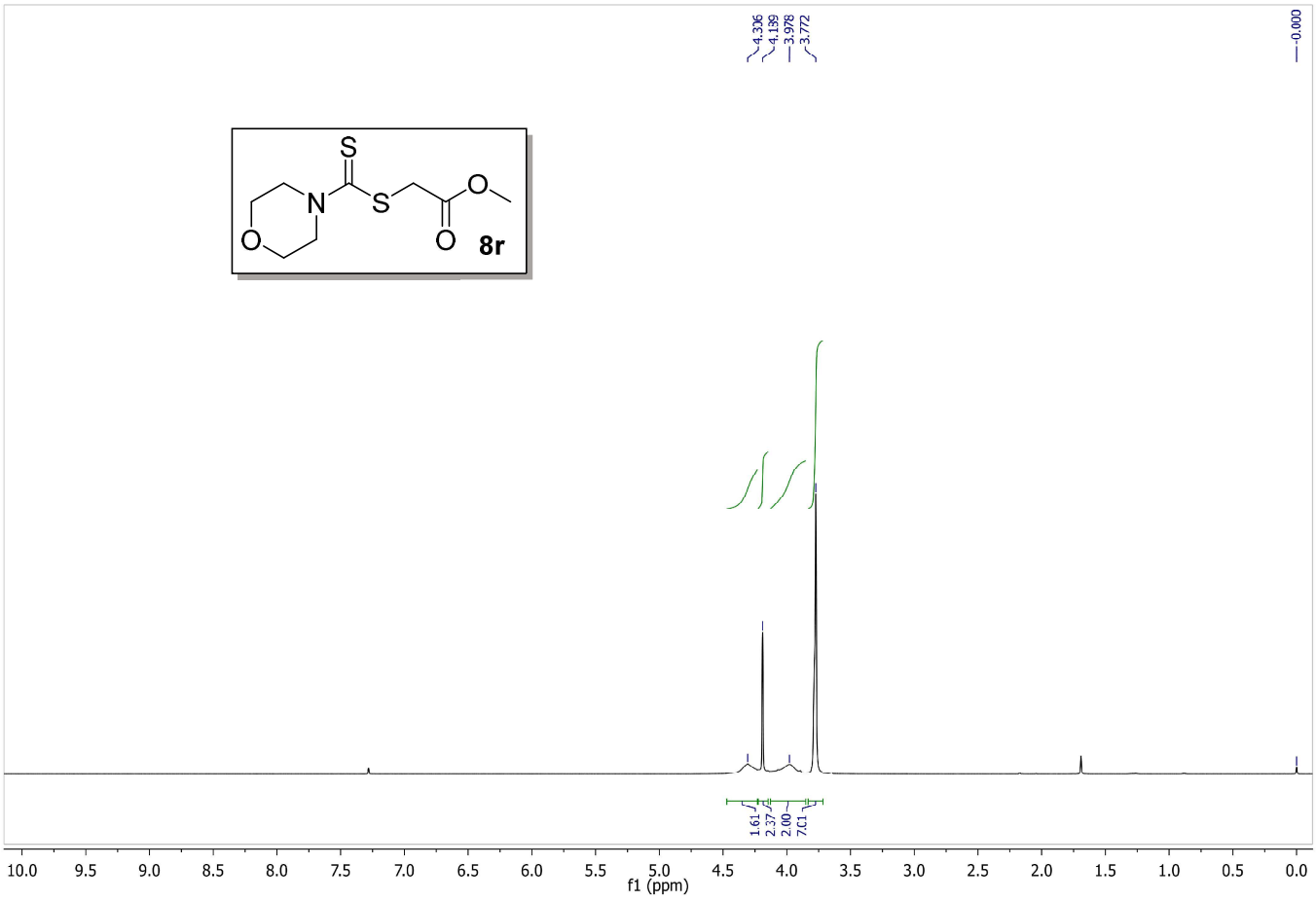


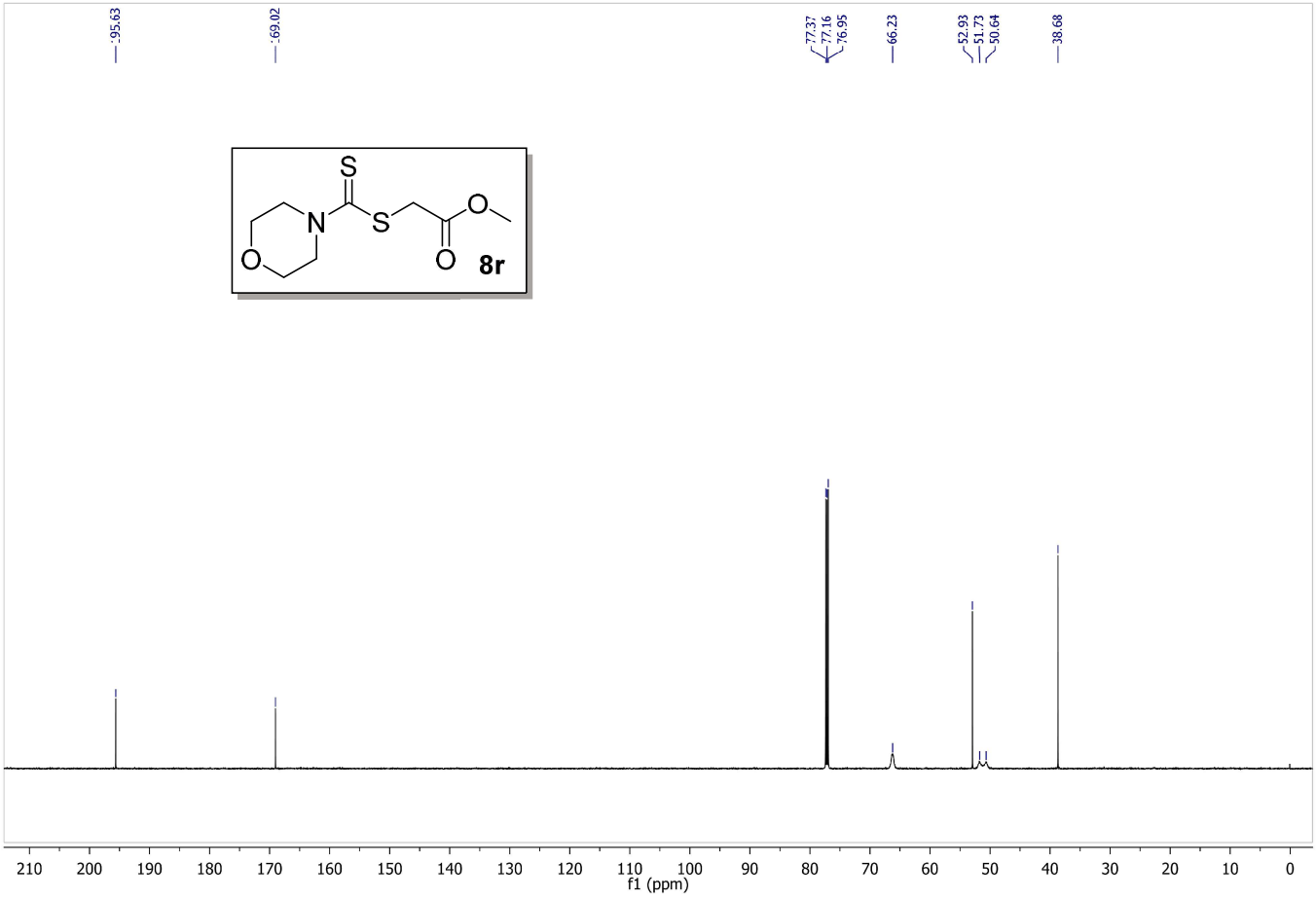
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **8q**



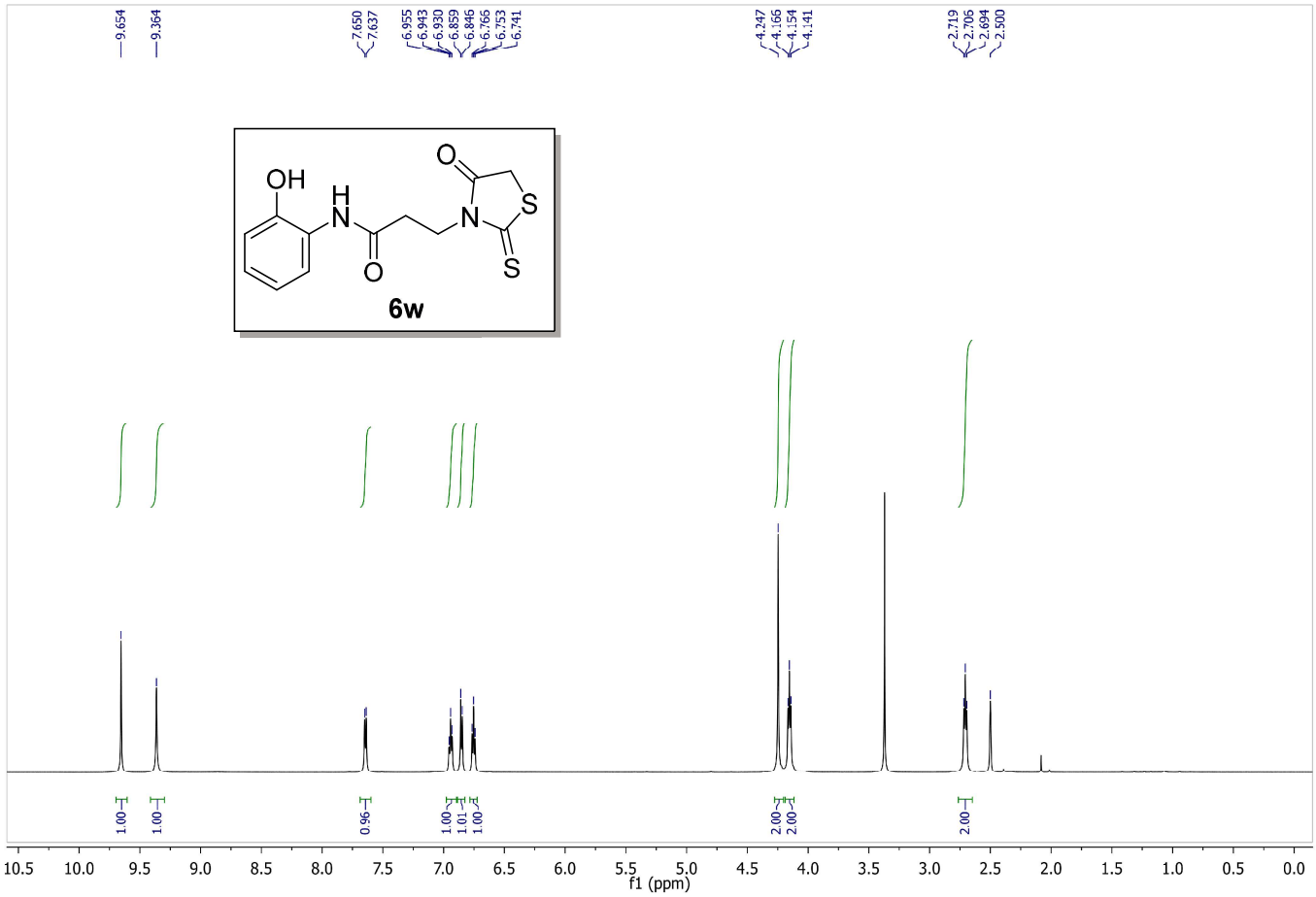


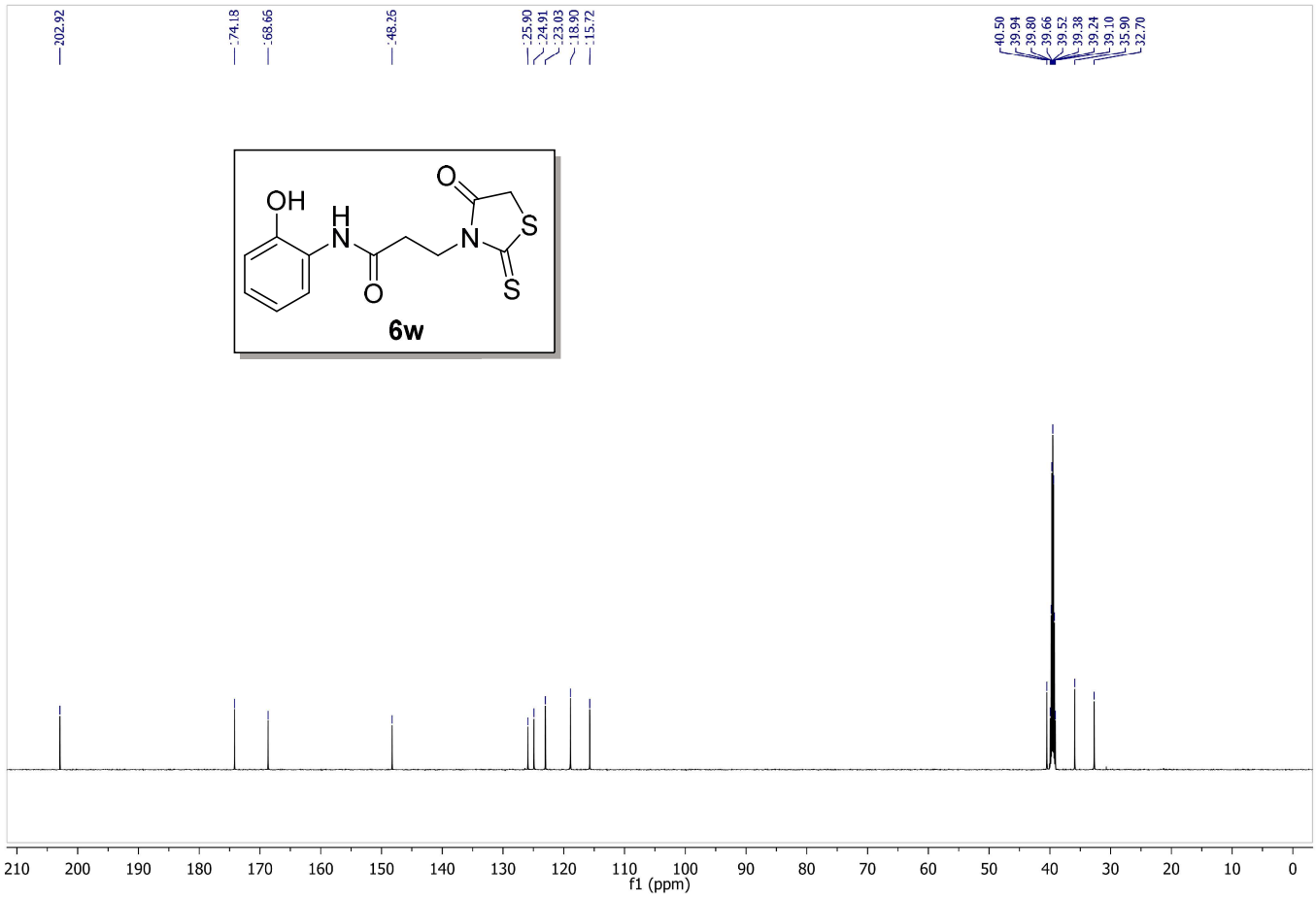
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **8r**



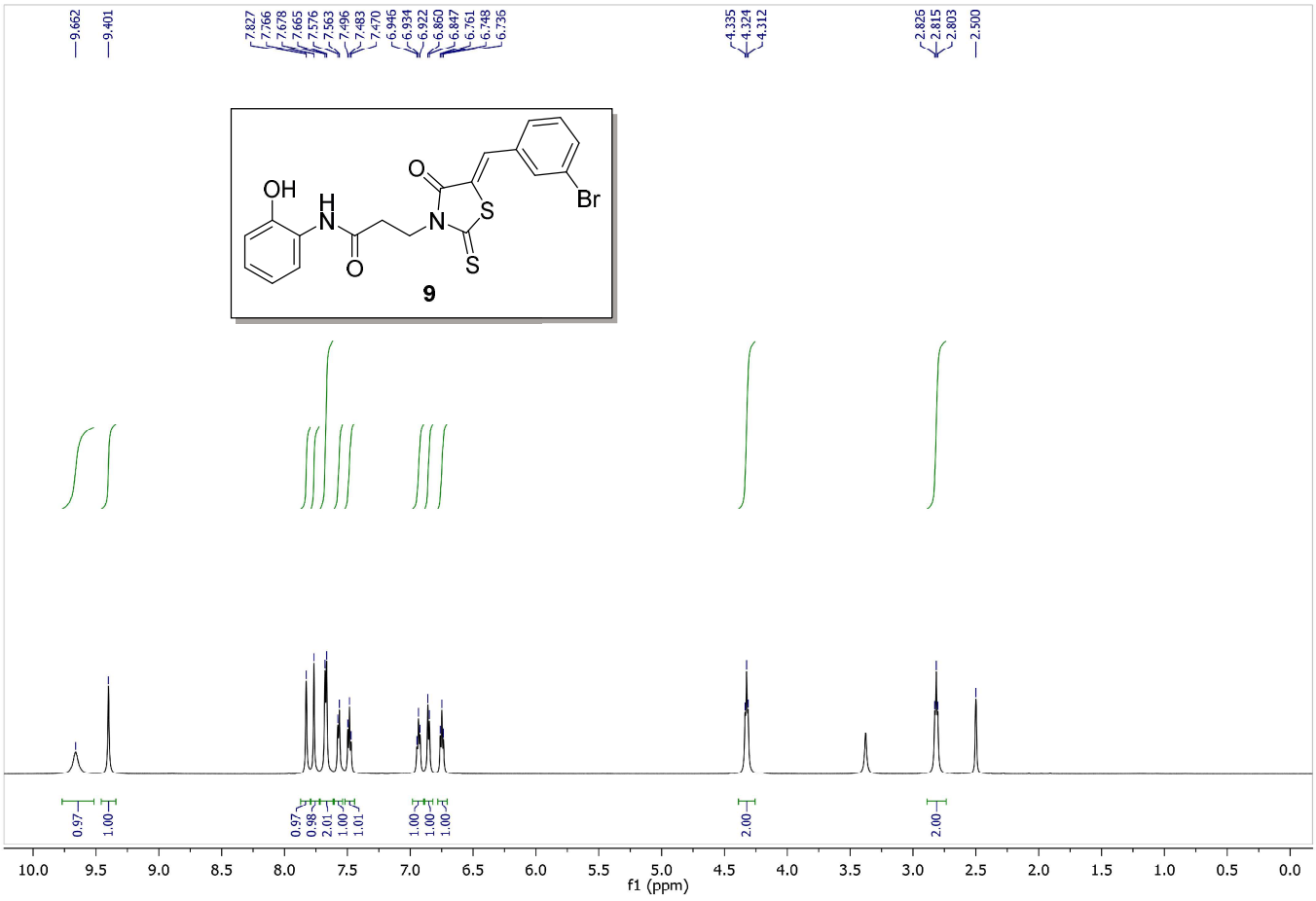


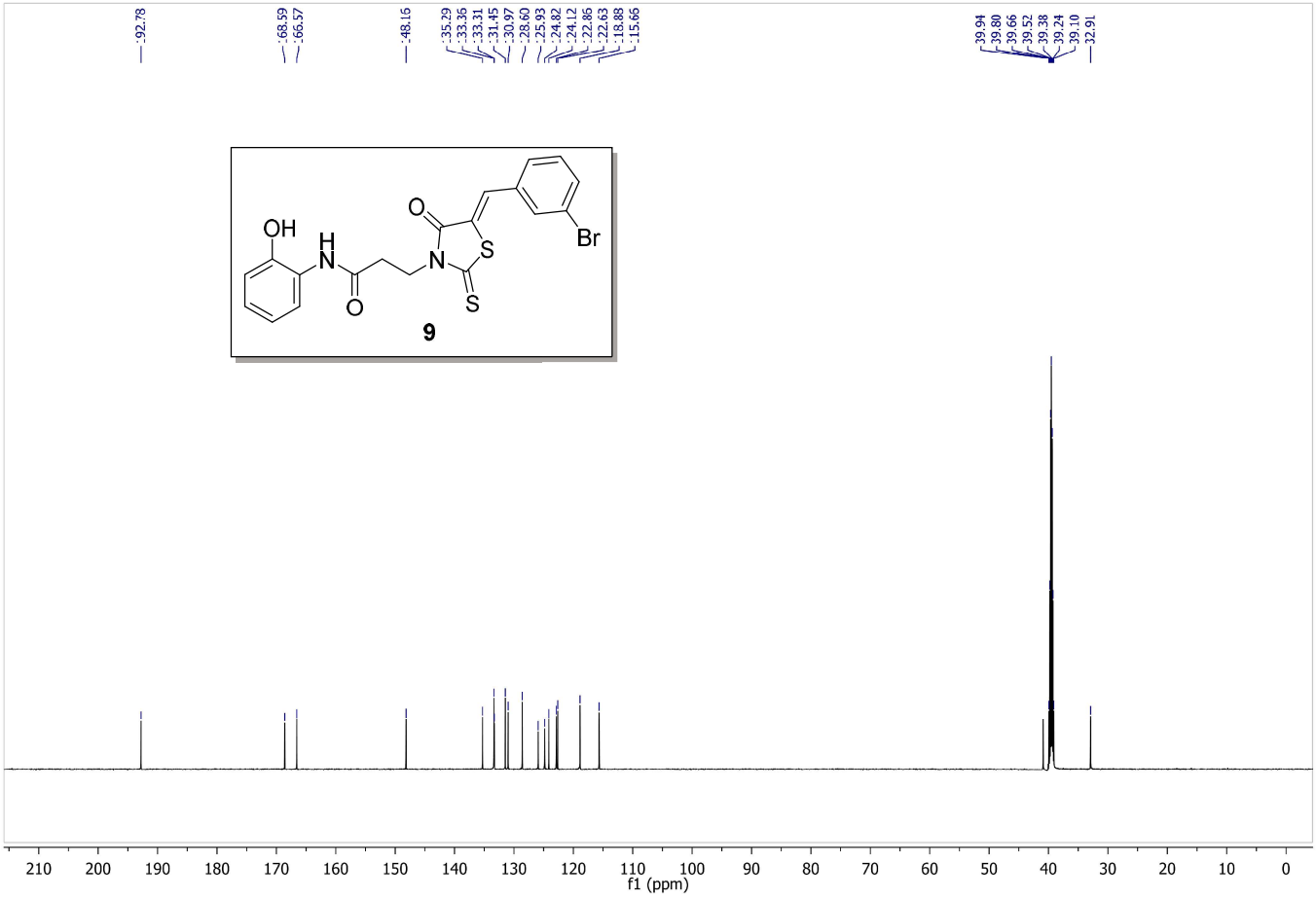
^{1}H NMR (600 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d6), **6w**





^{1}H NMR (600 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d6), **9**





^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **IIa**