Supplementary Information

Straightforward access to *α*-thiocyanoketones and thiazoles from sulfoxonium ylides

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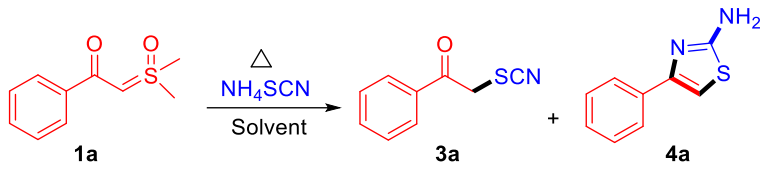
1. General information: All the chemicals and solvents were used as received without further purification from Merck, Spectrochem and TCI. Organic extracts were dried over anhydrous sodium sulphate. Progress of the reactions was monitored by TLC using precoated aluminium plates of Merck Kieselgel 60 F254. An oil bath was used for heating. Organic extracts were dried over anhydrous sodium sulphate. Column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate/n-hexane. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) on JEOL ECS and Brucker operating at 500/126 MHz 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: Optimization[a]

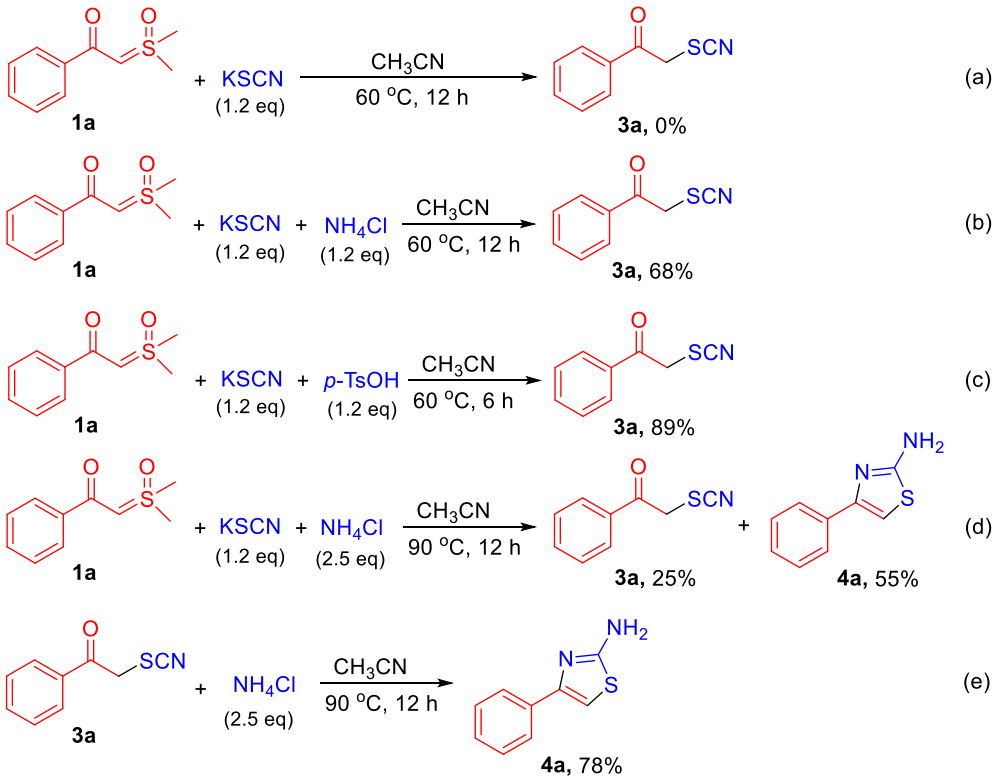


entry	solvent	additive (*x* equiv)	temp. (°C)	time (h)	Yield[b] of 3a (%)	Yield[b] of 4a (%)
1	THF	---	rt	36	30	0
2	THF	---	60	18	41	20
3	DCM	---	60	18	25	30
4	DMSO	---	60	18	Trace	---
5	toluene	---	60	14	45	24
6	CH_3CN	---	60	14	65	22
7	CH_3CN	---	90	14	33	54
8	MeOH	---	60	24	Trace	---
9	H_2O	---	60	24	0	---
10	CH_3CN	HFIP (1.0 eq)	60	14	72	0
11	CH_3CN	BzOH (1.0 eq)	60	14	30	0
12	CH_3CN	TfOH (1.0 eq)	60	8	52	0
13	CH_3CN	TFA (1.0 eq)	60	8	45	0
14	CH_3CN	*p*-TsOH (1.0 eq)	60	4	94	0
15	CH_3CN	*p*-TsOH (0.5 eq)	60	8	71	---
16	CH_3CN	*p*-TsOH (0.8 eq)	60	8	85	---
17	CH_3CN	*p*-TsOH (1.5 eq)	60	4	94	---
18	CH_3CN[c]	---	90	10	0	92
19	CH_3CN[d]	---	90	12	0	92
20	CH_3CN[d]	---	110	10	0	93

[a]General conditions: *β*-Ketosulfoxonium ylides **1a** (1.0 mmol), and NH_4SCN **2** (1.25 mmol), with (*x* mmol) or without additive in 10 mL of solvent at a specified temp. in a closed vessel for a specified time, except otherwise noted. [b]Isolated yield. [c]NH_4SCN **2** (5.0 mmol) used. [d]Reactions performed in a sealed tube with NH_4SCN **2** (2.5 mmol).

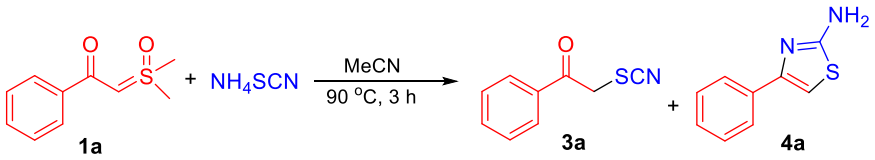
3. Control experiments

A series of control experiments employing another SCN^- salts was conducted to elucidate the reaction mechanism underlying the synthesis of *α*-thiocyanoketones **3** and 2-aminothiazoles **4** (Scheme S1). The reaction of sulfoxonium ylide **1a** with KSCN under standard conditions proved ineffectual in generating *α*-thiocyanoketone **3a**. However, when compound **1a** was subjected to the reaction with KSCN in the presence of NH_4Cl, α-thiocyanoketone **3a** was obtained with a yield of 68%. Similarly, when compound **1a** was subjected to treatment with KSCN in the presence of *p*-TsOH, *α*-thiocyanoketone **3a** was obtained with a yield of 89% (Scheme S1, eqs. a-c). These outcomes provide evidence in the support of the hypothesis that sulfoxonium ylide **1a** acts as a proton abstractor, resulting in the formation of intermediate **I**, which subsequently engages in an intermolecular nucleophilic substitution reaction with the thiocyanate anion, resulting in the formation of α-thiocyanoketone **3a**. Subsequently, upon conducting the reaction of sulfoxonium ylide **1a** with KSCN in the presence of 2.5 equivalents of NH_4Cl at 90°C, both 2-aminothiazole **4a** and *α*-thiocyanoketone **3a** were formed. Interestingly, when *α*-thiocyanoketone **3a** was subjected to treatment with NH_4Cl, 2-aminothiazole **4a** was obtained with a yield of 78% (Scheme S1, eqs. d-e). These findings further support that the emitted ammonia reacts with the intermediate **3a** and results in the formation of product **4a** *via* the intermediates **II** and **III**.

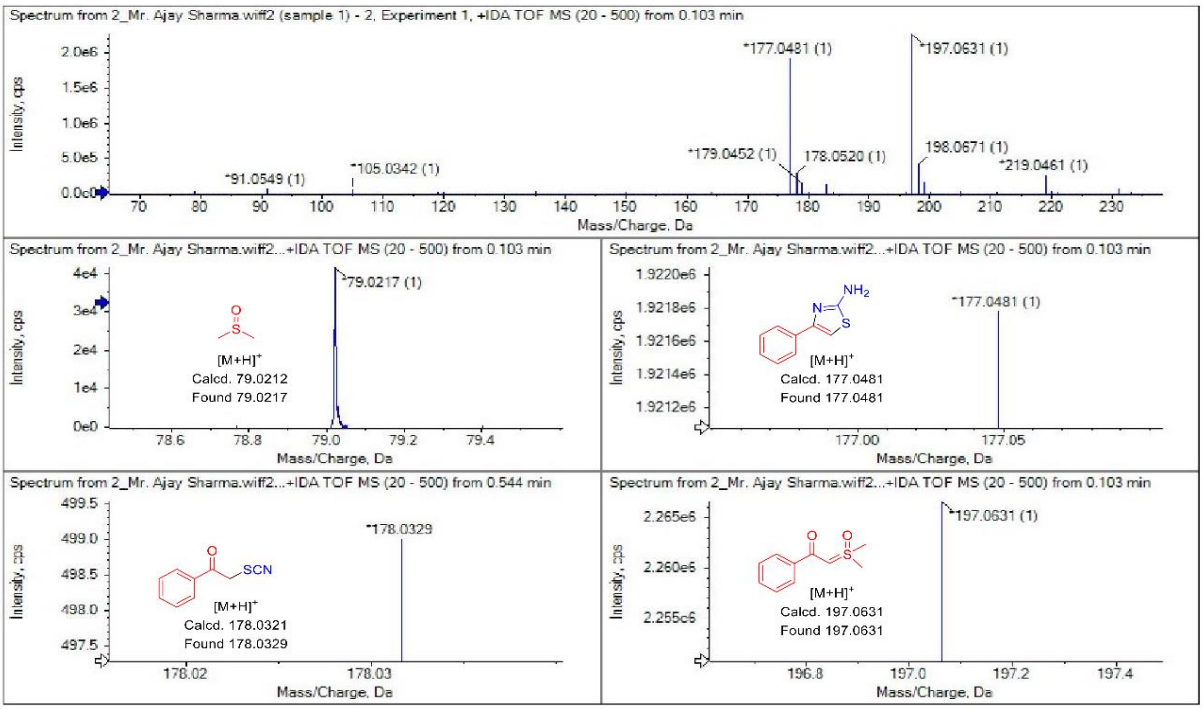


Scheme S1: Control experiments

Additionally, in a different experiment, sulfoxonium ylide **1a** was treated with 2.5 eq. of NH_4SCN at 90°C for 3 hours, and the crude reaction mixture was analysed using High-Resolution Mass Spectrometry (HRMS) (Scheme S2). Sulfoxonium ylide **1a**, α-thiocyanoketone **3a**, 2-aminothiazole **4a**, and DMSO (which was liberated from sulfoxonium ylide **1a** during the process) peaks were all successfully identified by the HRMS analysis.



Scheme S2: Control experiment 2.



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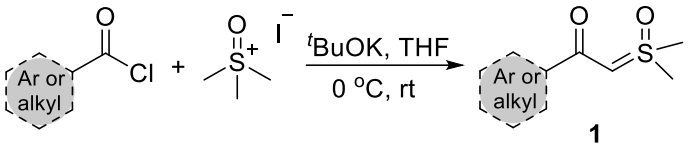
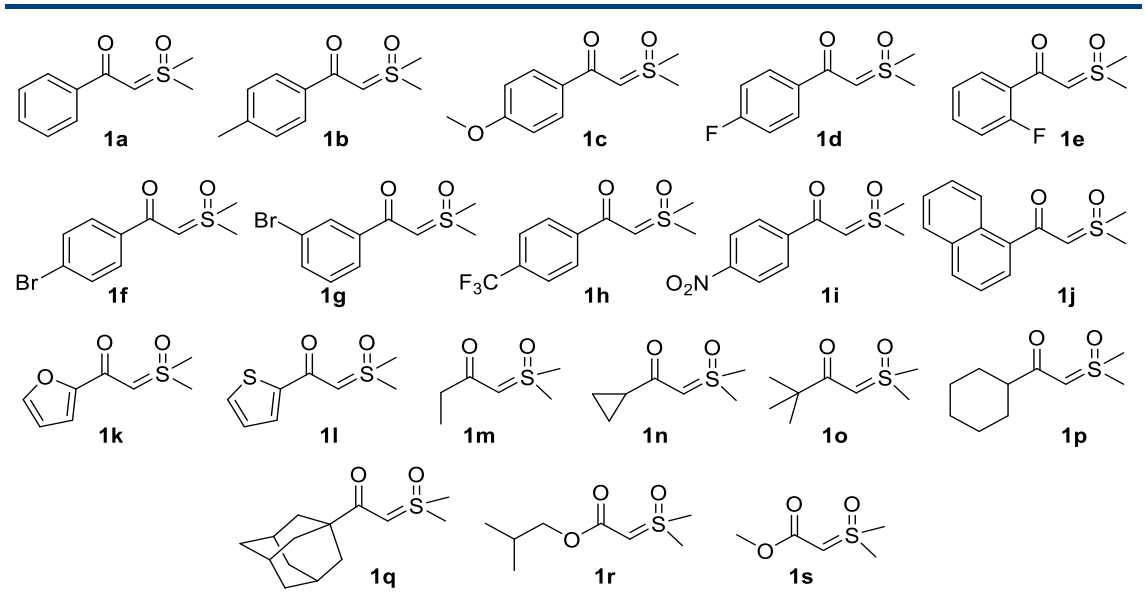
4. Experimental Section:

4.1 Preparation of sulfoxonium ylides, 1



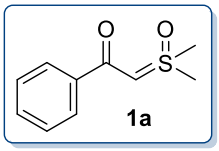
β-Ketosulfoxonium ylides **1** were synthesized according to the known literature procedure[1d] Briefly, to a stirred solution of KO*t*Bu (19.0 mmol, 3.8 equiv.) in anhydrous THF (25 mL) was added trimethylsulfoxonium iodide (16.0 mmol, 3.2 equiv.) at room temperature. The resulting solution was heated on an oil bath to reflux for 2 hours. Further, the reaction mixture was cooled to 0 °C, followed by dropwise addition of acyl chlorides (5.0 mmol, 1.0 equiv.) in THF (5 mL) solvent. The reaction was allowed to bring at room temperature and stirred for additional 3 hours. After completion of reaction as monitored by TLC, the solvent was evaporated and water (15 mL) and EtOAc (15 mL) were added to the resulting slurry. The organic layer was separated and the aqueous layer was washed with ethyl acetate (2 x 25 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 ylides as solid in the stated yields (R_f = 0.4, EtOAc/MeOH, 95:5). All the Spectroscopic data were consistent with previous reports.[1]

4.2 Structures of *β*-ketosulfoxonium ylides 1 used in the study:



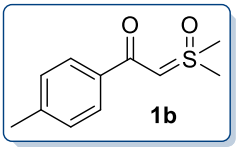
4.3 Characterization of Compounds, 1

2-(Dimethyl(oxo)-λ⁶-sulfaneylidene)-1-phenylethan-1-one, 1a[1a]



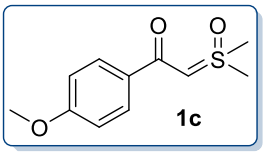
White solid (754 mg, 77%); mp 117–119 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 5.6 Hz, 2H), 7.46–7.27 (m, 3H), 5.06 (s, 1H), 3.47 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 182.3, 138.9, 130.7, 128.1, 126.5, 69.2, 42.0.

2-(Dimethyl(oxo)-λ⁶-sulfanylidene)-1-(*p*-tolyl)ethan-1-one, 1b[1a]



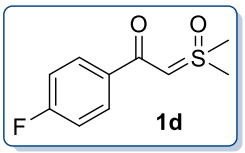
White solid (871 mg, 83%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 4.88 (s, 1H), 3.42 (s, 6H), 2.30 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 182.4, 141.0, 136.3, 128.9, 126.6, 68.1, 42.6, 21.5.

2-(Dimethyl(oxo)-λ⁶-sulfanylidene)-1-(4-methoxyphenyl)ethan-1-one, 1c[1a]



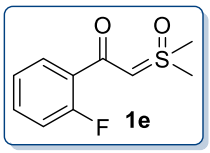
White solid (915 mg, 81%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 4.93 (s, 1H), 3.83 (s, 3H), 3.49 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 181.9, 161.8, 131.6, 128.4, 113.4, 67.5, 55.4, 42.6.

2-(Dimethyl(oxo)-λ⁶-sulfanylidene)-1-(4-fluorophenyl)ethan-1-one, 1d[1a]



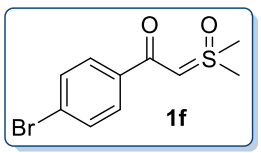
White solid (909 mg, 85%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.88–7.72 (t, *J* = 8.1 Hz, 2H), 7.05 (t, *J* = 8.1 Hz, 2H), 4.93 (s, 1H), 3.51 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 181.2, 164.6 (d, *J* = 250.5 Hz) 135.3, 128.9 (d, *J* = 8.6 Hz), 115.2 (d, *J* = 21.7 Hz), 68.3, 42.7.

2-(Dimethyl(oxo)-λ⁶-sulfanylidene)-1-(2-fluorophenyl)ethan-1-one, 1e[1d]



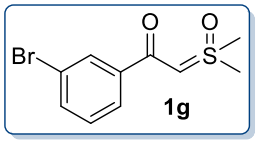
White solid (835 mg, 78%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.89 (t, *J* = 7.7 Hz, 1H), 7.36 (dd, *J* = 11.6, 5.9 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.07–7.00 (m, 1H), 5.20 (s, 1H), 3.51 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 177.5 (d, *J* = 2.3 Hz), 160.6 (d, *J* = 251.0 Hz), 131.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 2.5 Hz), 126.8 (d, *J* = 13.4 Hz), 124.0 (d, *J* = 3.2 Hz), 115.9 (d, *J* = 24.2 Hz), 74.2 (d, *J* = 12.5 Hz), 42.0.

1-(4-Bromophenyl)-2-(dimethyl(oxo)-λ⁶-sulfanylidene)ethan-1-one, 1f[1d]



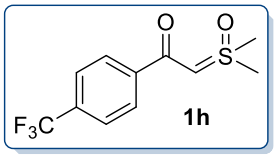
White solid (1.13 g, 83%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 4.99 (s, 1H), 3.50 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 181.0, 137.8, 131.4, 128.2, 125.2, 68.9, 42.3.

1-(3-Bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one, 1g[1b]



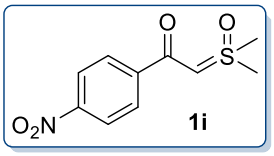
White solid (1.14 g, 84%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.92 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 5.01 (s, 1H), 3.50 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 180.5, 141.0, 133.5, 129.82, 129.80 125.2, 122.4, 69.4, 42.2.

2-(Dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one, 1h[1d]



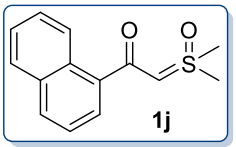
White solid (1.12 g, 85%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 5.02 (s, 1H), 3.53 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 180.7, 142.3, 132.4 (q, *J* = 32.5 Hz), 127.04 (s), 125.3, (d, *J* = 3.9 Hz), 124.1 (q, *J* = 271.9 Hz), 69.6, 42.5.

2-(Dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-nitrophenyl)ethan-1-one, 1i[1d]



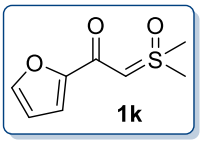
Brown solid (903 mg, 75%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ: 8.19 (d, *J* = 8.9 Hz, 2H), 7.95 (d, *J* = 9.1 Hz, 2H), 5.74 (s, 1H), 3.56 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ: 177.5, 148.3, 145.1, 127.5, 123.3, 74.4, 40.4.

2-(Dimethyl(oxo)-λ^6-sulfanylidene)-1-(naphthalen-1-yl)ethan-1-one, 1j[1d]



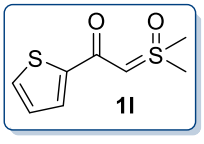
White solid (972 mg, 79%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.51–7.43 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 4.83 (s, 1H), 3.48 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 186.2, 139.2, 133.8, 130.3, 129.7, 128.2, 126.4, 126.0, 125.9, 125.1, 124.8, 72.7, 42.1.

2-(Dimethyl(oxo)-λ^6-sulfanylidene)-1-(furan-2-yl)ethan-1-one, 1k[1a]



White solid (688 mg, 74%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.41 (s, 1H), 6.92 (s, 1H), 6.44 (s, 1H), 5.03 (s, 1H), 3.51 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 175.7, 145.7, 129.2, 127.7, 127.1, 67.3, 42.9.

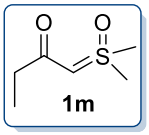
2-(Dimethyl(oxo)-λ^6-sulfanylidene)-1-(thiophen-2-yl)ethan-1-one, 1l[1d]



Grey solid (777 mg, 77%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 3.3 Hz, 1H), 7.33 (d, *J* = 4.9 Hz, 1H), 6.99–6.94 (m, 1H), 4.82 (s, 1H) 3.43 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 175.8, 145.8, 129.1, 127.6, 127.1, 67.4, 42.9.

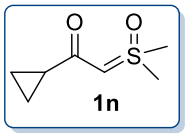
1-(Dimethyl(oxo)-λ^6-sulfanylidene)butan-2-one, 1m[1e]

Brown oil (562 mg, 76%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.43 (s, 1H), 3.41 (s, 6H), 2.19 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 192.1, 68.9, 42.1, 33.9, 10.2.



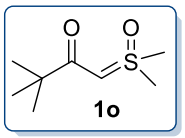
1-Cyclopropyl-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one, 1n[1e]

White solid (640 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.59 (s, 1H), 3.40 (s, 6H), 1.57 (s, 1H), 0.88 (s, 2H), 0.65 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 190.0, 68.9, 42.1, 18.7, 7.4.



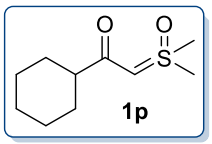
1-(Dimethyl(oxo)-λ^6-sulfanylidene)-3,3-dimethylbutan-2-one, 1o[1e]

White solid (722 mg, 82%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 4.48 (s, 1H), 3.39 (s, 6H), 1.11 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 197.8, 66.6, 42.2, 40.8, 27.8.



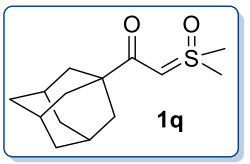
1-Cyclohexyl-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one, 1p[1d]

White solid (818 mg, 81%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.37 (s, 1H), 3.39 (s, 6H), 2.05 (t, *J* = 11.6 Hz, 1H), 1.82 (d, *J* = 12.7 Hz, 2H), 1.76 (d, *J* = 12.5 Hz, 2H), 1.65 (d, *J* = 12.1 Hz, 1H), 1.37–1.13 (m, 5H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 194.9, 67.7, 49.1, 42.4, 30.1, 26.14, 26.10.



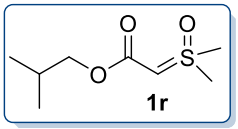
1-((3r,5r,7r)-Adamantan-1-yl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one, 1q[1c]

White solid (1.05 g, 83%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.42 (s, 1H), 3.38 (s, 6H), 2.01 (s, 3H), 1.79 (s, 6H), 1.70 (q, *J* = 12.1 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 197.5, 66.5, 42.9, 42.5, 39.7, 36.9, 28.5.



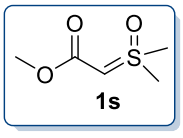
Isobutyl 2-(dimethyl(oxo)-λ^6-sulfanylidene)acetate1r[1e]

White solid (825 mg, 86%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 3.97 (s, 1H), 3.82 (d, *J* = 5.9 Hz, 2H), 3.39 (s, 6H), 1.90 (s, 1H), 0.93 (d, *J* = 6.6 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.4, 69.1, 55.4, 42.4, 28.1, 19.3.



Methyl 2-(dimethyl(oxo)-λ^6-sulfanylidene)acetate, 1s[1e]

White solid (585 mg, 78%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.05 (s, 1H), 3.59 (s, 3H), 3.40 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.6, 55.5, 49.8, 41.6.

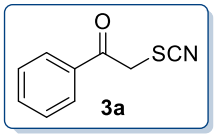


4.4 General procedure for the synthesis of compound, 3

To a stirred solution of sulfoxonium ylides **1** (0.50 mmol, 1.0 equiv.) in CH_3CN (5 mL) were added ammonium thiocyanate **2** (0.62 mmol, 1.25 equiv.) and *p*-TsOH (0.50 mmol, 1.0 equiv.), and the reaction mixture was heated at 60 °C (oil bath) for 4 hours. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature, quenched with sat. $NaHCO_3$ solution and the crude product was extracted with DCM (3 x 7 mL). The organic extract was dried over anhydrous Na_2SO_4, concentrated in *vacuo* and the crude products were purified by column chromatography (silica gel, 100-200 mesh) which afforded the desired *α*-thiocyanoketone products **3** in good to high yields.

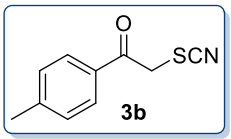
4.5 Characterization of Compounds, 3

1-Phenyl-2-thiocyanatoethan-1-one, 3a[2b]



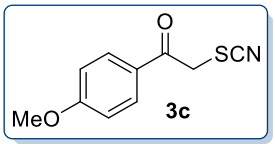
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (83 mg, 94%); mp: 70–72 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.93 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 4.74 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 191.0, 134.8, 134.0, 129.2, 128.5, 112.0, 43.0.

2-Thiocyanato-1-(*p*-tolyl)ethan-1-one, 3b[2b]



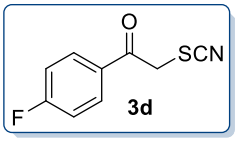
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (91 mg, 96%); mp: 97–99 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 2.45 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 190.5, 146.2, 131.6, 130.0, 128.7, 112.1, 43.2, 22.0.

1-(4-Methoxyphenyl)-2-thiocyanatoethan-1-one, 3c[2c]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (98 mg, 95%); mp: 103–105 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.63 (s, 2H), 3.83 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 189.3, 164.9, 131.0, 127.0, 114.5, 112.3, 55.8, 43.0.

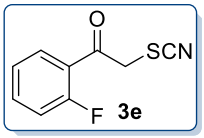
1-(4-Fluorophenyl)-2-thiocyanatoethan-1-one, 3d[2b]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (89 mg, 92%); mp: 98–100 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 8.00–7.97 (m, 2H), 7.21 (t, *J* = 8.5 Hz, 2H), 4.72 (s,

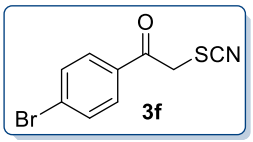
2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 189.4, 166.8 (d, *J* = 257.8 Hz), 131.4 (d, *J* = 9.3 Hz), 130.6, 116.6 (d, *J* = 22.4 Hz), 111.8, 42.8; **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ: –101.24.

1-(2-Fluorophenyl)-2-thiocyanatoethan-1-one, 3e[2e]



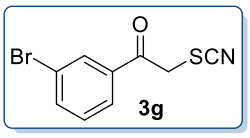
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Yellow solid (86 mg, 89%); mp: 96–98 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.99 (dd, *J* = 7.9, 5.9 Hz, 1H), 7.69–7.63 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 11.5, 8.4 Hz, 1H), 4.66 (d, *J* = 2.6 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 188.7 (s), 162.5 (d, *J* = 254.9 Hz), 136.8 (d, *J* = 9.4 Hz), 131.2, 125.3 (d, *J* = 2.5 Hz), 122.4 (d, *J* = 12.0 Hz), 117.0 (d, *J* = 23.4 Hz), 111.8, 46.4 (d, *J* = 10.7 Hz); **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ: –107.51.

1-(4-Bromophenyl)-2-thiocyanatoethan-1-one, 3f[2b]



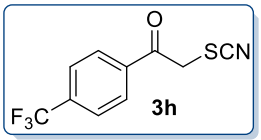
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (116 mg, 92%); mp: 87–89 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 4.69 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 190.0, 132.8, 132.7, 130.5, 130.0, 111.7, 42.7.

1-(3-Bromophenyl)-2-thiocyanatoethan-1-one, 3g[2b]



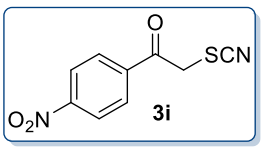
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (115 mg, 91%); mp: 102–104 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 1.7 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 4.69 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 189.7, 137.8, 135.7, 131.6, 130.9, 127.1, 123.6, 111.5, 42.7.

2-Thiocyanato-1-(4-(trifluoromethyl)phenyl)ethan-1-one, 3h[2b]



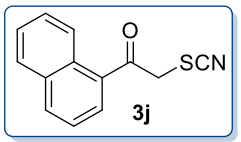
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (110 mg, 90%); mp: 78–80 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 4.73 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 190.1, 136.8, 136.1 (q, *J* = 32.9 Hz),129.0, 126.4 (d, *J* = 3.8 Hz), 123.37 (q, *J* = 273.2 Hz),111.4, 42.6; ; **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ: –63.28.

1-(4-Nitrophenyl)-2-thiocyanatoethan-1-one, 3i[2f]



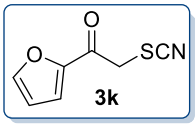
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Orange solid (83 mg, 75%); mp: 85–87 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ: 8.38 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ: 191.6, 150.4, 139.0, 130.0, 124.0, 112.6, 41.7.

1-(Naphthalen-1-yl)-2-thiocyanatoethan-1-one, 3j[2b]



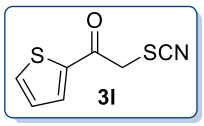
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (104 mg, 92%); mp: 102–104 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 8.80 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 7.1 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 4.84 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 193.5, 135.4, 134.2, 131.2, 130.4, 129.9, 129.3, 128.9, 127.3, 125.7, 124.4, 112.0, 45.1.

1-(Furan-2-yl)-2-thiocyanatoethan-1-one, 3k[2b]



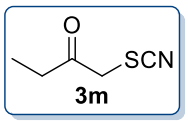
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (73 mg, 88%); mp: 69–71 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.80–7.78 (m, 2H), 7.22–7.21 (m, 1H), 4.57 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 183.4, 140.6, 136.3, 133.8, 128.9, 111.6, 41.8.

2-Thiocyanato-1-(thiophen-2-yl)ethan-1-one, 3l[2b]



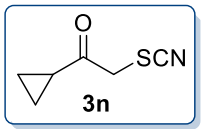
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); White solid (79 mg, 87%); mp: 71–73 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.80–7.78 (m, 2H), 7.22–7.21 (m, 1H), 4.57 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 183.4, 140.6, 136.3, 133.8, 128.9, 111.6, 41.8.

1-Thiocyanatobutan-2-one, 3m[2d]



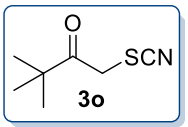
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); Colorless liquid (51 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.04 (s, 2H), 2.62 (q, *J* = 7.3 Hz, 2H), 1.15 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 201.8, 111.6, 43.7, 35.0, 7.8.

1-Cyclopropyl-2-thiocyanatoethan-1-one, 3n[2f]



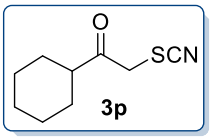
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); Colorless liquid (57 mg, 81%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.19 (s, 2H), 2.10–2.04 (m, 1H), 1.22–1.19 (m, 2H), 1.12–1.08 (m, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 201.3, 111.6, 44.6, 20.0, 12.8.

3,3-Dimethyl-1-thiocyanatobutan-2-one, 3o[2f]



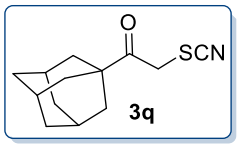
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.5/9.5); Colorless liquid (64 mg, 82%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.32 (s, 2H), 1.23 (s, 9H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 207.1, 112.2, 44.4, 42.1, 26.5.

1-Cyclohexyl-2-thiocyanatoethan-1-one, 3p[2d]



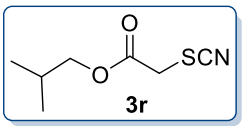
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); Colorless liquid (72 mg, 79%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.15 (s, 2H), 2.51 (tt, *J* = 11.3, 3.5 Hz, 1H), 1.90 (dd, *J* = 13.2, 2.9 Hz, 2H), 1.84–1.79 (m, 2H), 1.72–1.67 (m, 1H), 1.44–1.37 (m, 2H), 1.35–1.27 (m, 2H), 1.26–1.20 (m, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 204.4, 111.9, 49.8, 43.4, 25.6, 25.5.

1-((3r,5r,7r)-Adamantan-1-yl)-2-thiocyanatoethan-1-one, 3q



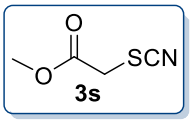
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.7/9.3); White solid (89 mg, 76%); mp: 102–104 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.30 (s, 2H), 2.09 (s, 3H), 1.85 (d, *J* = 2.5 Hz, 6H), 1.79–1.76 (m, 4H), 1.71–1.69 (m, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 206.7, 112.4, 46.7, 42.3, 40.4, 38.4, 36.5, 36.3, 28.2, 27.8; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{13}H_{18}NOS$ 236.1104; Found 236.1106.

Isobutyl 2-thiocyanatoacetate, 3r



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); Colorless liquid (70 mg, 82%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 4.01 (d, *J* = 6.6 Hz, 2H), 3.79 (s, 2H), 2.00 (tp, *J* = 13.4, 6.7 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 166.3, 110.9, 72.9, 35.1, 27.7, 19.0; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_7H_{12}NO_2S$ 174.0573; Found 174.0567.

Methyl 2-thiocyanatoacetate, 3s[2a]



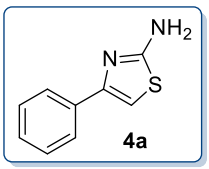
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 0.3/9.7); Colorless liquid (52 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 3.84 (s, 3H), 3.79 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 166.8, 110.8, 53.6, 34.9.

4.6 General procedure for the synthesis of compound, 4

To a stirred solution of sulfoxonium ylides **1** (0.50 mmol, 1.0 equiv.) in CH_3CN (5 mL) was added ammonium thiocyanate **2** (1.25 mmol, 2.50 equiv.) in a sealed tube, and the reaction mixture was heated at 110 °C (oil bath) for 10 hours. After completion of reaction as monitored by TLC, the reaction mixture was cooled to room temperature, diluted with water and the crude product was extracted with DCM (3 x 7 mL). The organic extract was dried over anhydrous Na_2SO_4, concentrated in *vacuo* and then the crude products were purified by column chromatography (silica gel, 100-200 mesh) which afforded the desired products **4** in good to high yields.

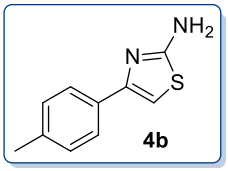
4.7 Characterization of Compounds, 4

4-Phenylthiazol-2-amine, 4a[3a]



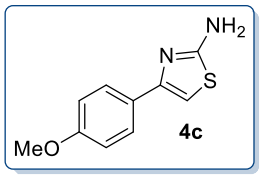
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (81 mg, 93%); mp: 150–152 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.72 (s, 1H), 5.21 (brs, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.5, 151.3, 134.7, 128.7, 127.9, 126.1, 102.9.

4-(*p*-Tolyl)thiazol-2-amine, 4b[3a]



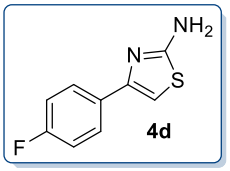
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (89 mg, 94%); mp: 151–153 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.66 (s, 1H), 5.17 (brs, 1H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.4, 151.4, 137.7, 132.0, 129.4, 126.0, 102.1, 21.4.

4-(4-Methoxyphenyl)thiazol-2-amine, 4c[3a]



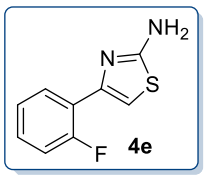
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (95 mg, 93%); mp: 180-182 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 8.8 Hz, 2H), 7.00 (s, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.81 (s, 1H), 3.76 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ: 168.1, 158.5, 149.6, 127.8, 126.8, 113.8, 99.3, 55.0.

4-(4-Fluorophenyl)thiazol-2-amine, 4d[3a]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (87 mg, 90%); mp: 103–105 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.76–7.70 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.63 (s, 1H), 5.29 (brs, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 167.7, 162.6 (d, *J* = 246.4 Hz), 150.4, 131.1 (d, *J* = 2.6 Hz), 127.8 (d, *J* = 7.9 Hz), 115.6 (d, *J* = 21.4 Hz), 102.4; **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ: –114.18.

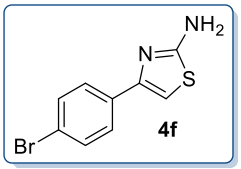
4-(2-Fluorophenyl)thiazol-2-amine, 4e[3c]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Yellow solid (79 mg, 82%); mp: 107–109 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 8.01 (t, *J* = 8.0 Hz, 1H), 7.26–7.22 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.10 (dd, *J* = 11.6, 8.2 Hz, 1H), 7.02 (s, 1H), 5.24 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 166.5, 160.3 (d, *J* = 250.3 Hz), 144.8, 129.8, 128.8 (d, *J* = 8.6 Hz), 124.4 (d, *J* = 2.9 Hz),

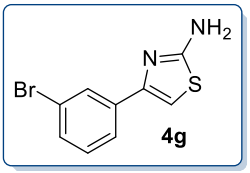
122.5 (d, *J* = 11.5 Hz), 116.0 (d, *J* = 23.1 Hz), 108.0 (d, *J* = 15.0 Hz); **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ: –114.07.

4-(4-Bromophenyl)thiazol-2-amine, 4f[3a]



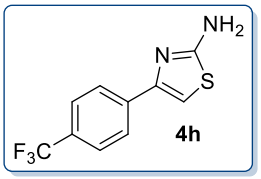
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (112 mg, 89%); mp: 172–174 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ: 7.74 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 2H), 7.08 (s, 1H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ: 168.3, 148.5, 134.0, 131.4, 127.5, 120.1, 102.4.

4-(3-Bromophenyl)thiazol-2-amine, 4g[3a]



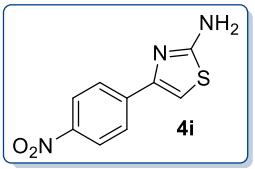
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (111 mg, 88%); mp: 130–132 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.93 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.26–7.22 (m 1H), 6.74 (s, 1H), 5.18 (brs, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 167.5, 149.9, 136.7, 130.7, 130.2, 129.2, 124.6, 122.9, 104.0.

4-(4-(Trifluoromethyl)phenyl)thiazol-2-amine, 4h[3b]



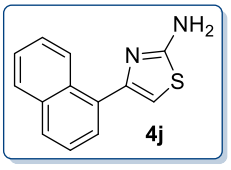
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (107 mg, 88%); mp: 185–187 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ: 8.00 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.24 (s, 1H), 7.16 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ: 168.5, 148.3, 138.6, 127.18 (q, *J* = 31.6 Hz), 126.0, 125.4 (d, *J* = 3.1 Hz), 123.3, 121.1, 104.3; **^{19}F{^{1}H} NMR** (471 MHz, DMSO-d_6) δ: –60.75.

4-(4-Nitrophenyl)thiazol-2-amine, 4i[3f]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); Red solid (77 mg, 70%); mp: 190–192 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ: 8.24 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.42 (s, 1H), 7.23 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ: 168.6, 147.8, 145.9, 140.9 126.3, 124.0, 106.6.

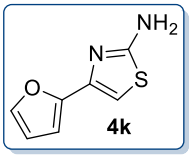
4-(Naphthalen-1-yl)thiazol-2-amine, 4j[3b]



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (96 mg, 85%); mp: 152–154 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ: 8.47 (d, *J* = 8.7 Hz, 1H), 7.97–7.92 (m, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.52–7.49 (dd, *J* = 8.5, 5.7 Hz, 3H),

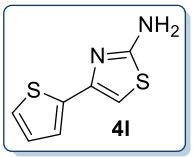
7.13 (s, 2H), 6.77 (s, 1H); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ: 168.0, 150.1, 133.52, 133.50, 130.7, 128.1, 127.9, 126.6, 126.2, 125.9, 125.8, 125.4, 105.0.

4-(Furan-2-yl)thiazol-2-amine, 4k[3b]



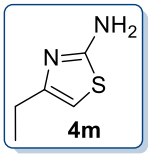
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (69 mg, 84%); mp: 125–126 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 3.4 Hz, 1H), 7.21 (d, *J* = 4.9 Hz, 1H), 7.05–6.99 (m, 1H), 6.60 (s, 1H), 5.43 (brs, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.7, 145.7, 138.7, 127.7, 124.7, 123.5, 101.5.

4-(Thiophen-2-yl)thiazol-2-amine, 4l[3a]



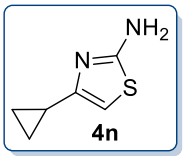
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (74 mg, 82%); mp: 135–137 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 3.5 Hz, 1H), 7.22 (d, *J* = 4.2 Hz, 1H), 7.03–7.02 (m, 1H), 6.60 (s, 1H), 5.29 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.6, 145.6, 138.6, 127.8, 124.7, 123.6, 101.6.

4-Ethylthiazol-2-amine, 4m[3d]



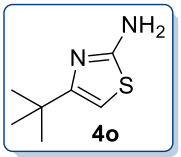
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Colorless liquid (49 mg, 78%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.08 (s, 1H), 5.11 (brs, 2H), 2.57 (qd, *J* = 7.5, 1.0 Hz, 4H), 1.22 (t, *J* = 7.5 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.5, 154.8, 101.5, 24.9, 13.0.

4-Cyclopropylthiazol-2-amine, 4n[3e]



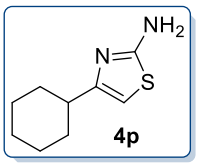
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Colorless liquid (56 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.05 (s, 1H), 5.16 (brs, 2H), 1.84–1.79 (m, 1H), 0.83–0.80 (m, 2H), 0.77–0.74 (m, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.5, 154.6, 100.2, 12.4, 7.1.

4-(*tert*-Butyl)thiazol-2-amine, 4o[3b]



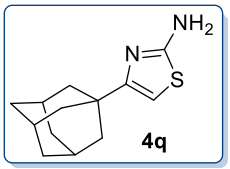
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Colorless liquid (50 mg, 65%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.09 (s, 1H), 5.09 (brs, 2H), 1.26 (s, 9H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.1, 162.5, 100.0, 34.6, 29.8.

4-Cyclohexylthiazol-2-amine, 4p



Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); White solid (63 mg, 70%); mp: 152–154 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.05 (s, 1H), 5.10 (brs, 2H), 2.49 (s, 1H), 1.99 (d, *J* = 7.3 Hz, 2H), 1.79 (d, *J* = 4.4 Hz, 2H), 1.70 (d, *J* = 12.6 Hz, 1H), 1.40–1.29 (m, 4H), 1.26–1.20 (m, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 167.2, 158.8, 100.6, 40.7, 32.7, 26.5, 26.3; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_9H_{15}N_2S$ 183.0950; Found 183.0953.

4-((3r,5r,7r)-Adamantan-1-yl)thiazol-2-amine, 4q



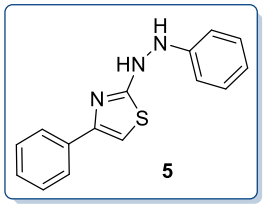
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.5/8.5); Colorless liquid (72 mg, 62%); **^{1}H NMR** (600 MHz, DMSO-d_6) δ: 6.76 (s, 2H), 5.99 (s, 1H), 1.98 (s, 3H), 1.80 (s, 6H), 1.72–1.65 (m, 6H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ: 167.7, 161.8, 97.3, 41.5, 36.5, 35.9, 27.9; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{13}H_{19}N_2S$ 235.1263; Found 235.1253.

4.8 General procedure for the synthesis of compound, 5, 6, and 7

To a stirred solution of sulfoxonium ylide **1** (1.0 mmol, 1.0 equiv.) in CH_3CN (10 mL) were added ammonium thiocyanate **2** (1.25 mmol, 1.25 equiv.) and amines (phenylhydrazine, *p*-toluidine, or pyrrolidine, 2.0 mmol, 2.0 equiv.), (2.0 mmol, 2.0 equiv.) in 25 mL round bottom flask, and the reaction mixture was heated at 90 °C (oil bath) for 8 hours. After completion of reaction as monitored by TLC, the reaction mixture was cooled to room temperature, diluted with water and extracted with DCM (3 x 10 mL). The organic extract was dried over anhydrous Na_2SO_4, concentrated in *vacuo* and then the crude products were purified by column chromatography (silica gel, 100-200 mesh) which afforded the desired products **5, 6,** and **7** in good yields.

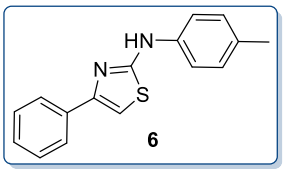
4.9 Characterization of Compounds, 5, 6, and 7

4-Phenyl-2-(2-phenylhydrazinyl)thiazole, 5[4]



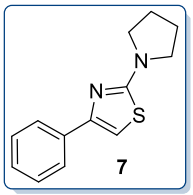
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 2.0/8.0); Red solid (176 mg, 66%); mp: 208–210 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ: 9.47 (s, 1H), 8.31 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.15 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ: 174.6, 150.9, 148.5, 134.9, 128.9, 128.5, 127.4, 125.5, 119.3, 112.3, 102.4.

4-Phenyl-*N*-(*p*-tolyl)thiazol-2-amine, 6[5]



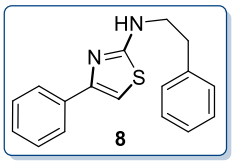
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Brown solid (207 mg, 78%); mp: 152–154 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ: 10.15 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.29 (s, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 2.26 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ: 163.3, 150.0, 138.8, 134.6, 130.0, 129.4, 128.6, 127.5, 125.6, 117.0, 102.5, 20.4.

4-Phenyl-2-(pyrrolidin-1-yl)thiazole, 7[2a]



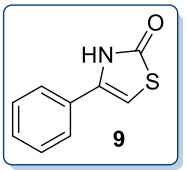
Purified by column chromatography (silica gel 100-200 mesh, ethyl acetate/hexane, v/v = 1.0/9.0); Colourless liquid (186 mg, 81%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.28–7.24 (m, 1H), 6.66 (s, 1H), 3.53–3.50 (m, 4H), 2.06–2.01 (m, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 167.5, 152.3, 135.5, 128.5, 127.5, 126.2, 100.3, 49.6, 25.4.

4.10 Synthesis of Fanetizole, 8[6]



To a stirred solution of sulfoxonium ylide **1** (1.50 g, 7.65 mmol, 1.0 equiv.) in CH_3CN (30 mL) were added ammonium thiocyanate **2** (727 mg, 9.56 mmol, 1.25 equiv.) and phenethylamine (1.85 g, 15.30 mmol, 2.0 equiv), and the reaction mixture was heated at 90 °C (oil bath) for 8 hours. After completion of reaction as monitored by TLC, the reaction mixture was cooled to room temperature, diluted with water and extracted with DCM (3 x 25 mL). The organic extract was dried over anhydrous Na_2SO_4, concentrated in *vacuo* and then purified by silica gel column chromatography using EtOAc/hexane (1:9, v/v) as eluent to afford the Fanetizole **8** (1.77 g, 83%) as a white solid. mp: 165–168 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 7.2 Hz, 2H), 7.41–7.17 (m, 8H), 6.70 (s, 1H), 5.37 (s, 1H), 3.56 (t, *J* = 5.8 Hz, 2H), 2.97 (t, *J* = 6.5 Hz, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ: 169.4, 151.8, 138.6, 135.1, 128.95, 128.90, 128.7, 127.8, 126.8, 126.2, 101.0, 47.3, 35.6.

4.11 Synthesis of 4-phenylthiazol-2(3*H*)-one, 9[2a]



To a stirred solution of sulfoxonium ylide **1** (1.0 mmol, 1.0 equiv.) in H_2O (10 mL) were added ammonium thiocyanate **2** (1.25 mmol, 1.25 equiv.) and HCl (38% aq, 3 mL) in a 25 mL round bottom flask, and the reaction mixture was heated at 110 °C (oil bath) for 7 hours. After completion of reaction as monitored by TLC, the reaction mixture was cooled to ambient temperature, and poured into cold water, resulting in precipitation. The precipitate was separated by filtration and washed with hexane to give product **9** (155 mg, 88%) as a white solid. mp: 64–66 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ: 11.77 (s, 1H), 7.65 (d, *J* = 7.4 Hz, 2H),

7.53–7.25 (m, 3H), 6.80 (s, 1H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, DMSO-d_6) δ: 173.0, 133.9, 129.7, 128.8, 128.5, 124.9, 98.1.

5. References:

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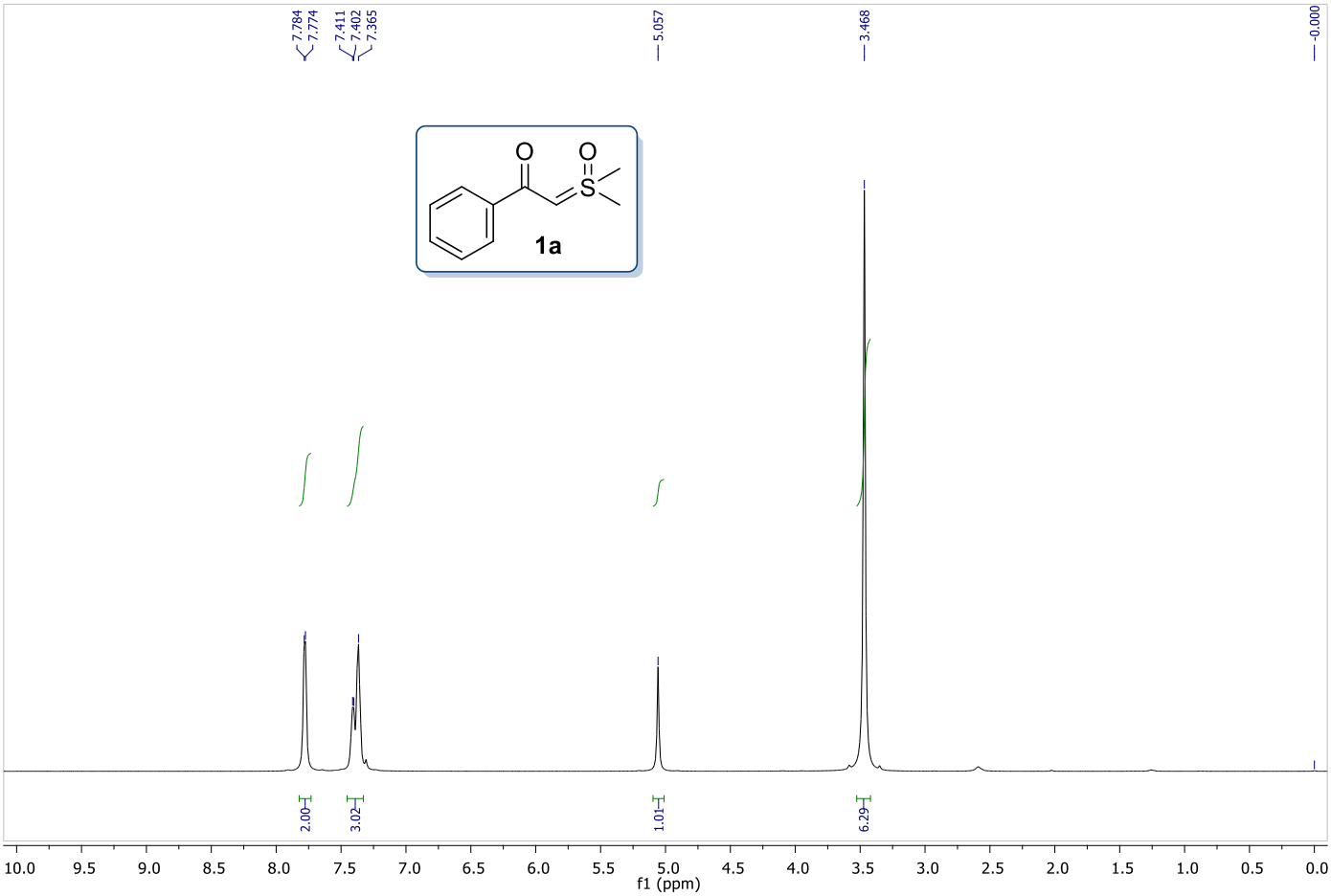
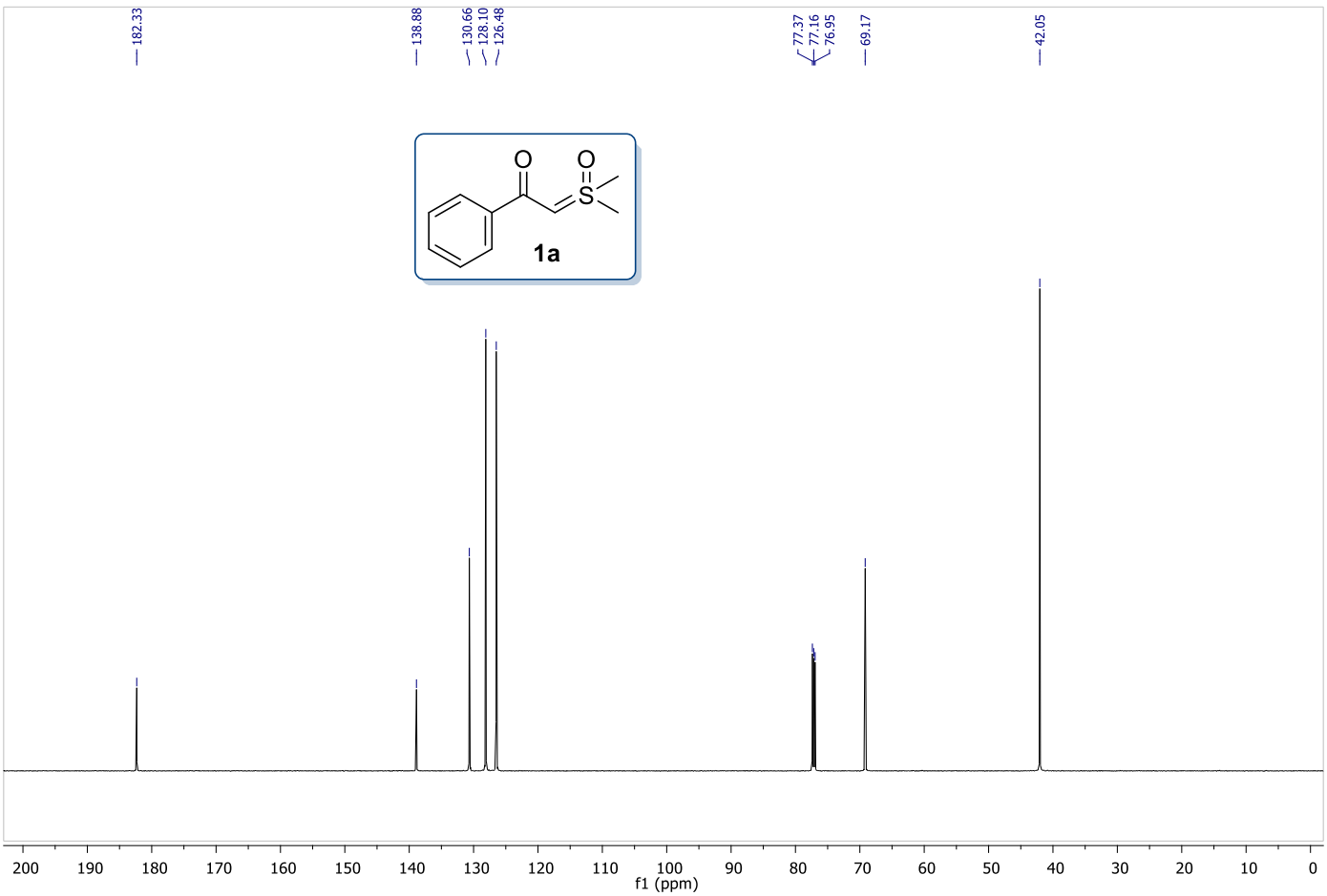
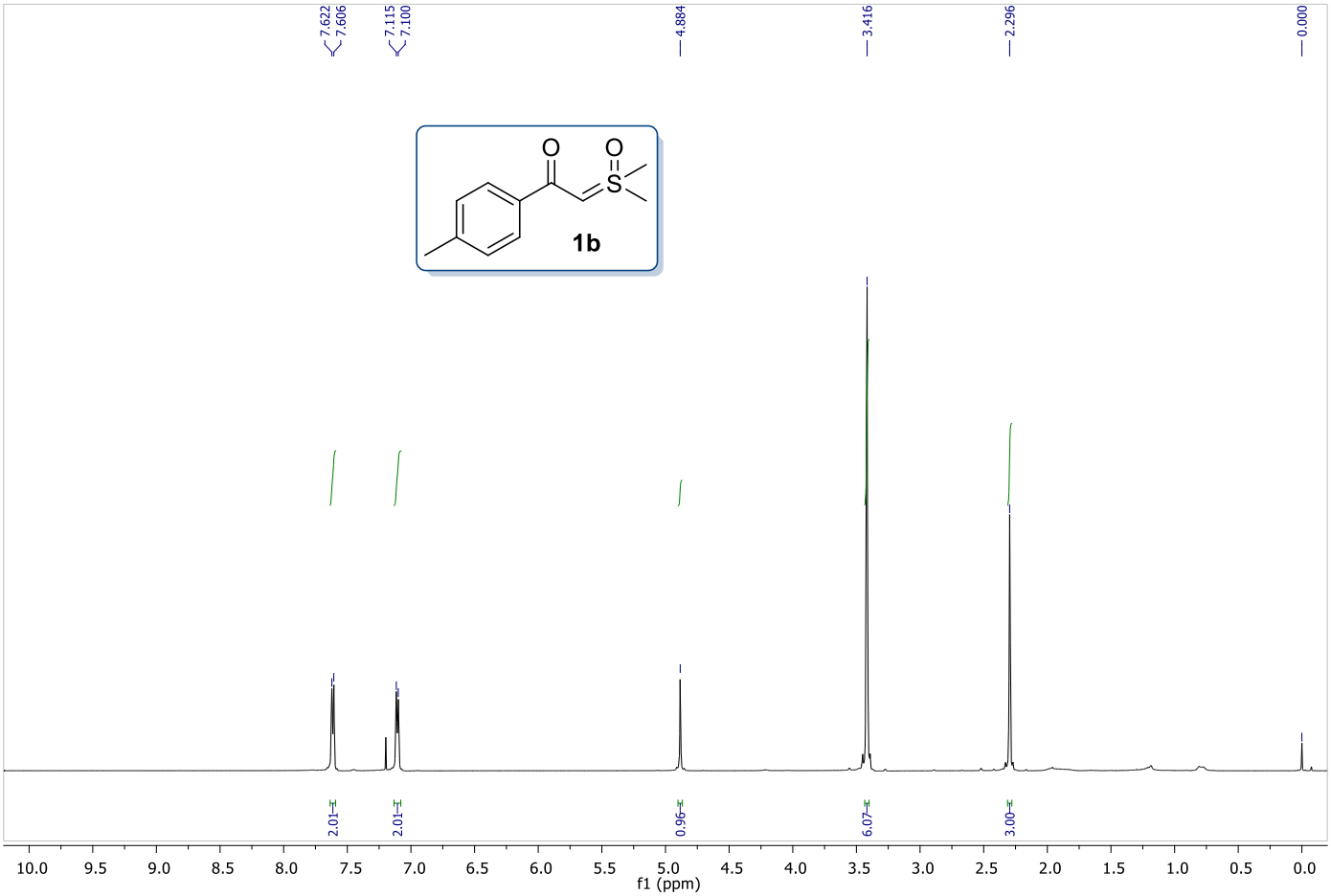
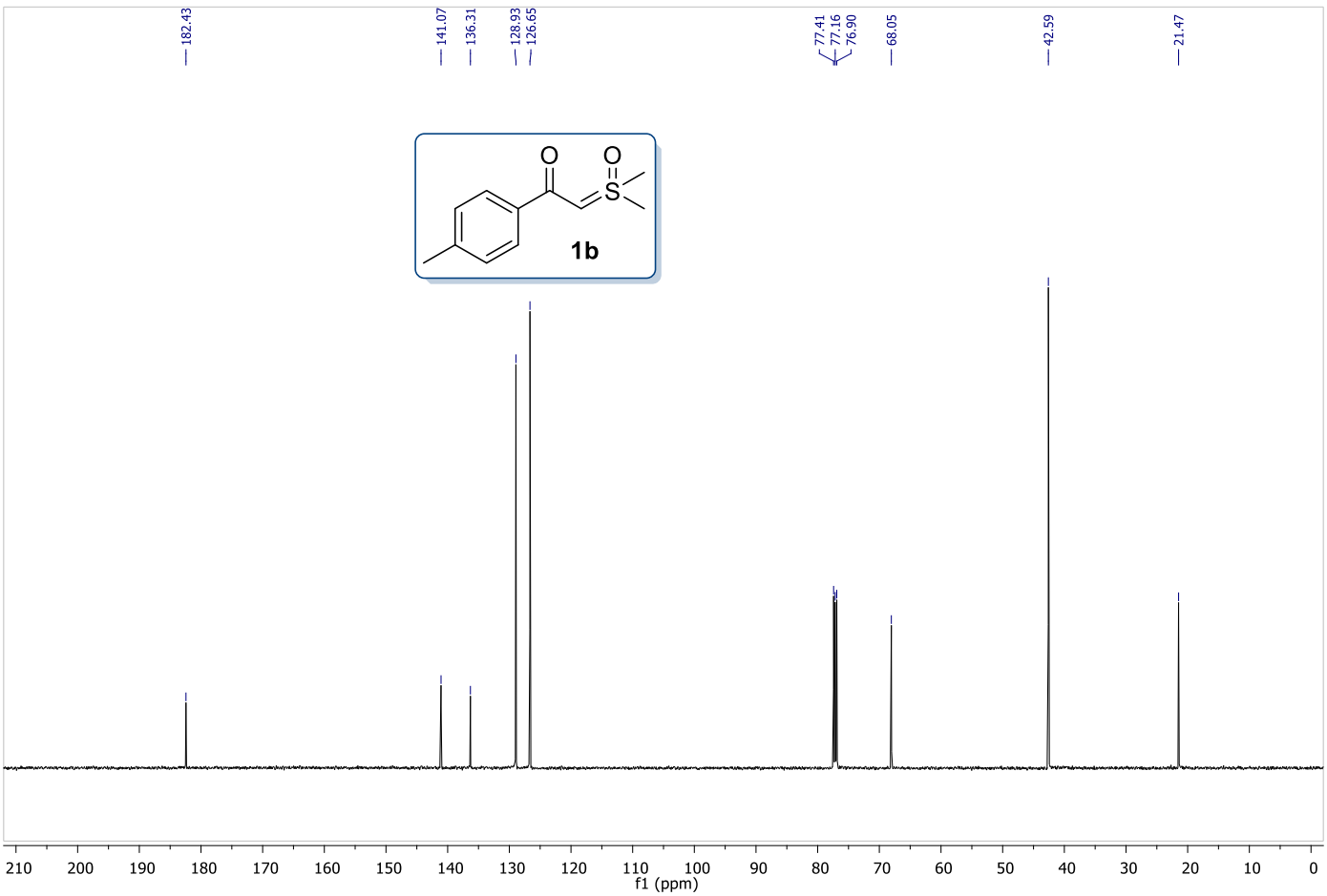
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **1a**





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





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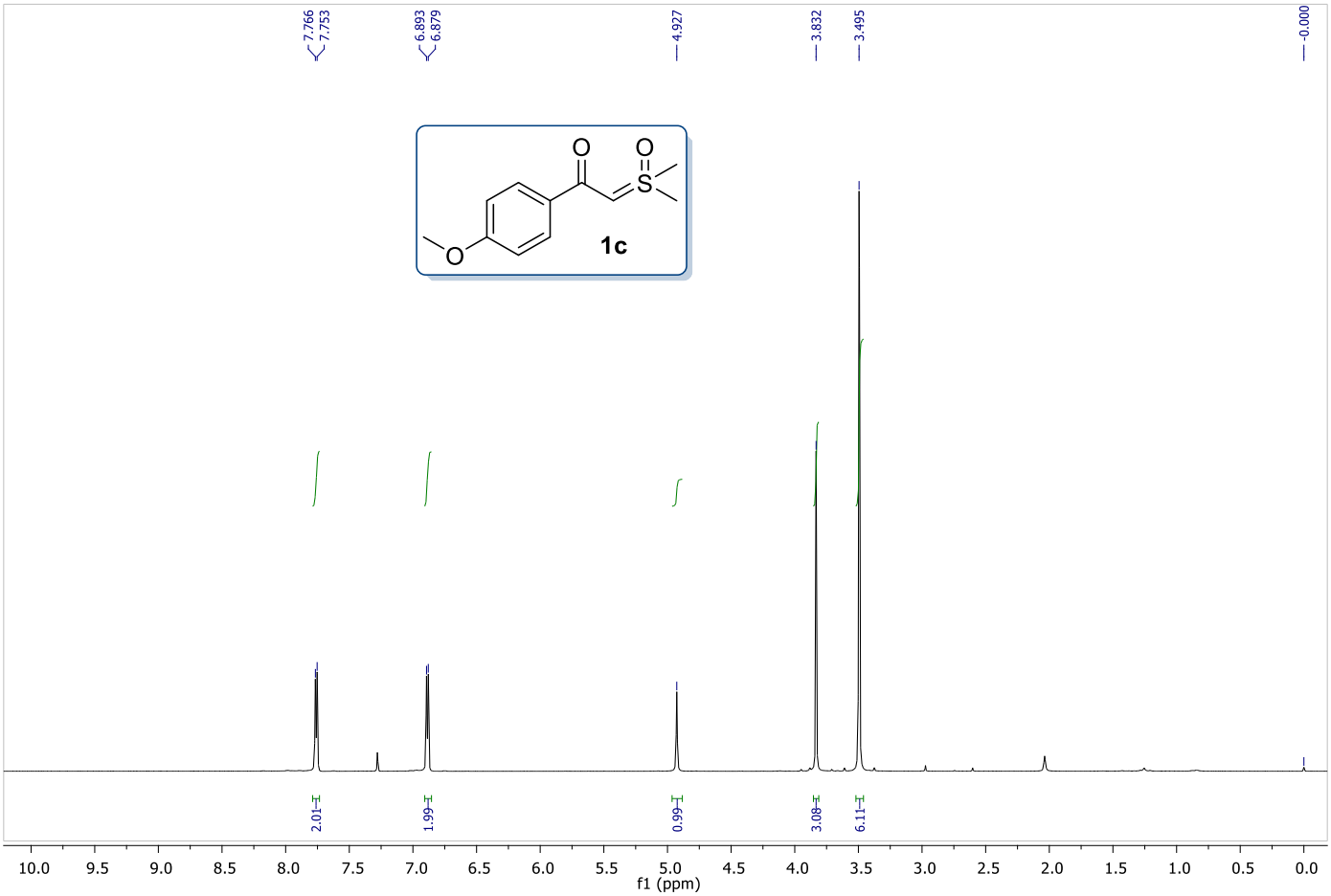

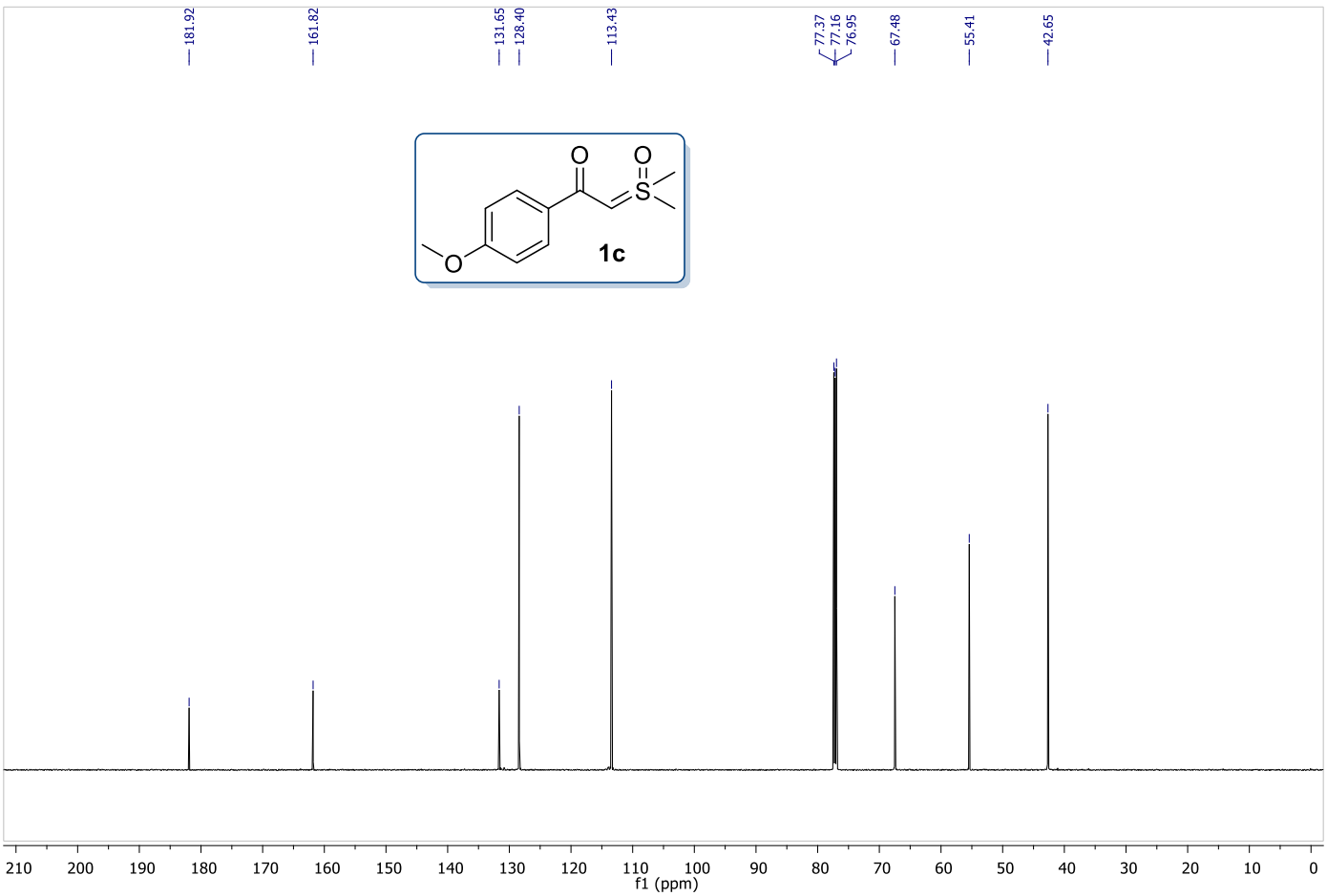

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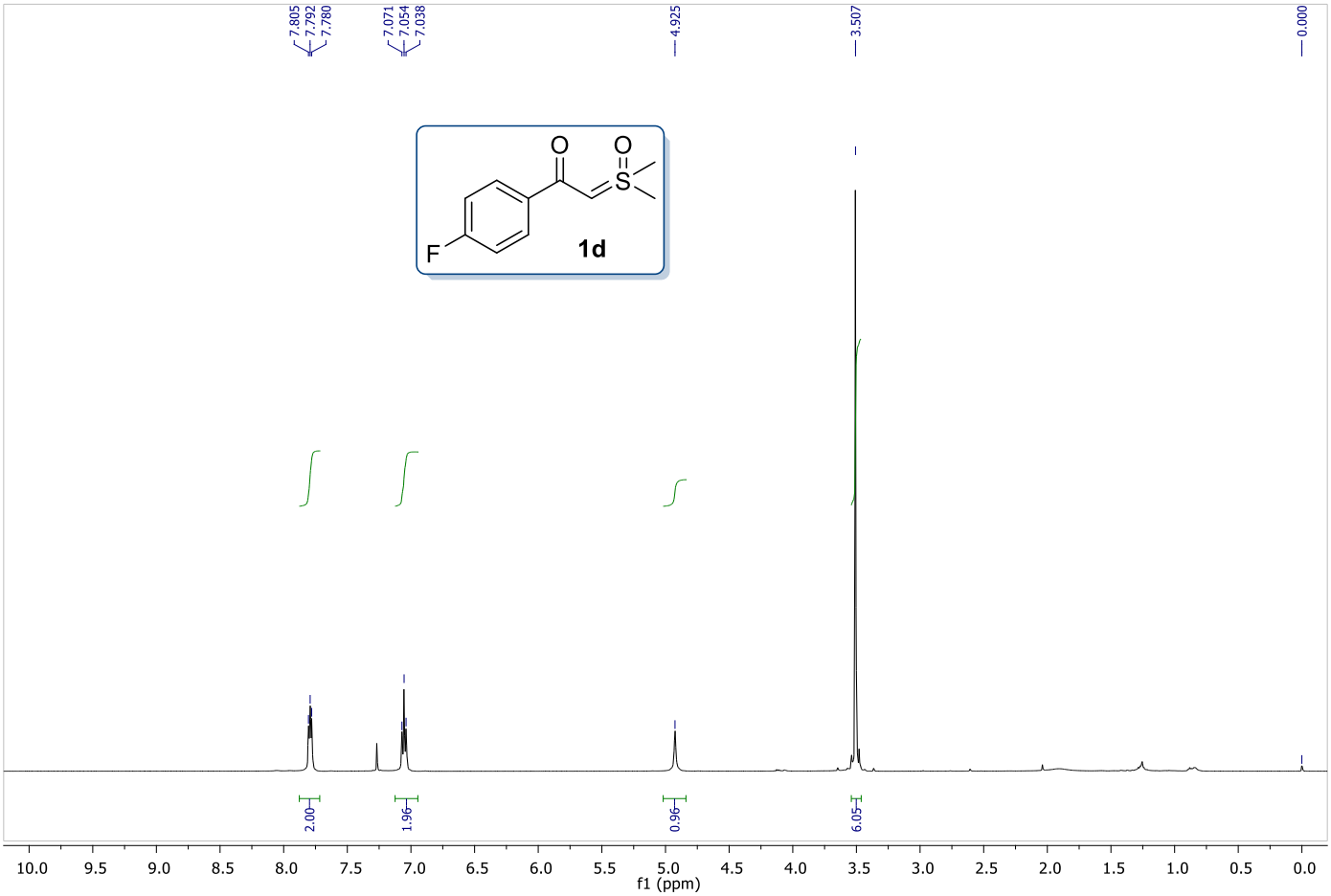

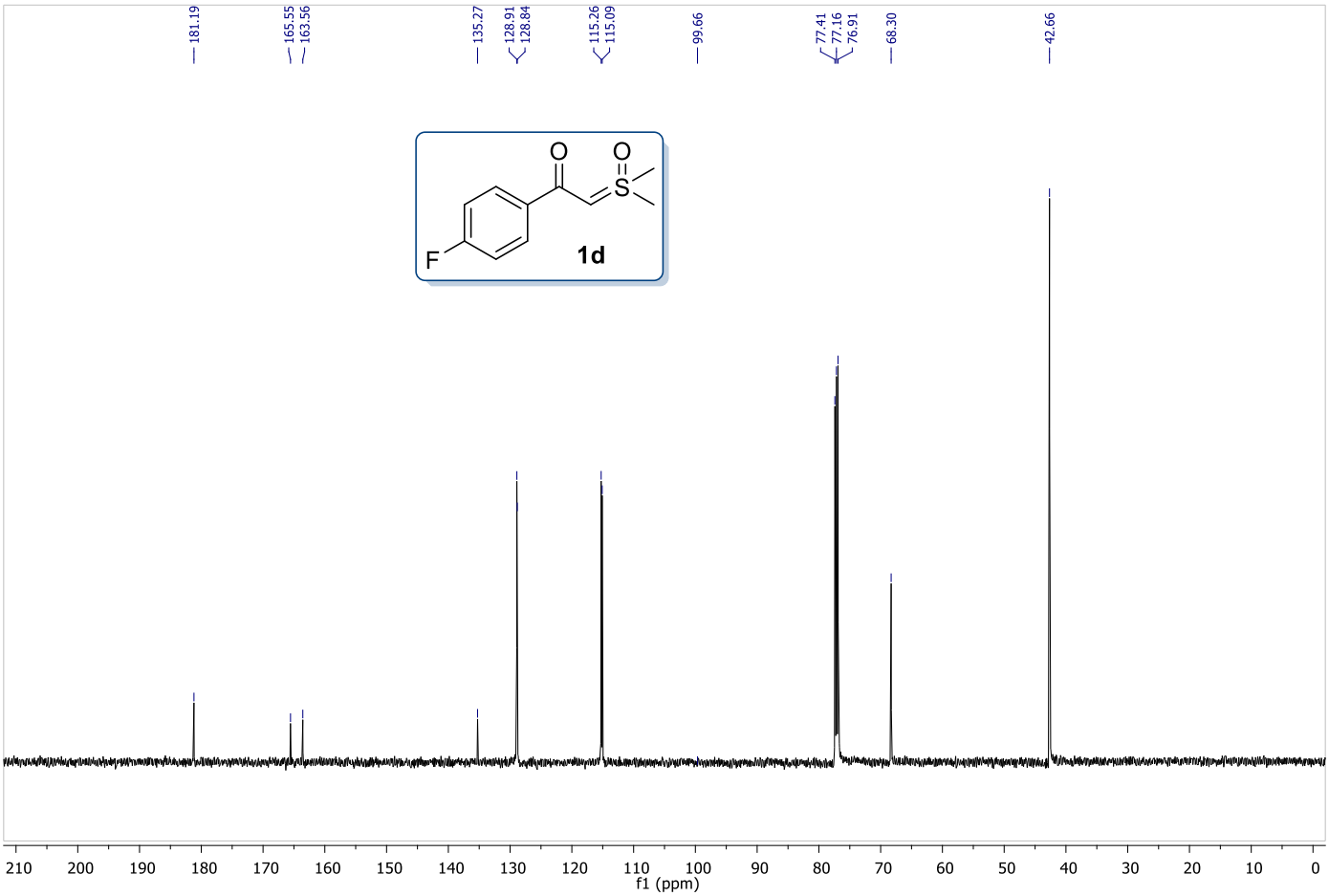

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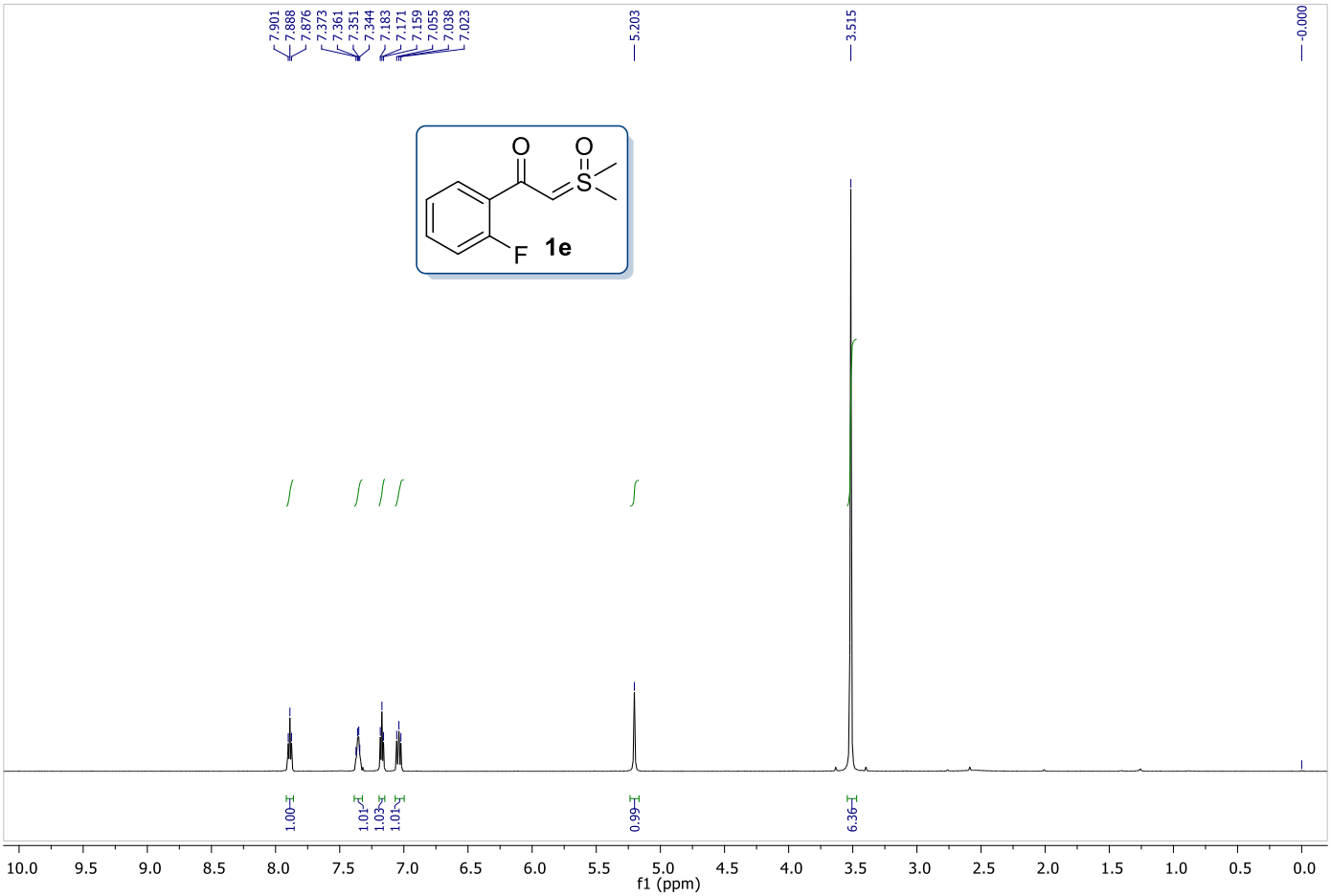

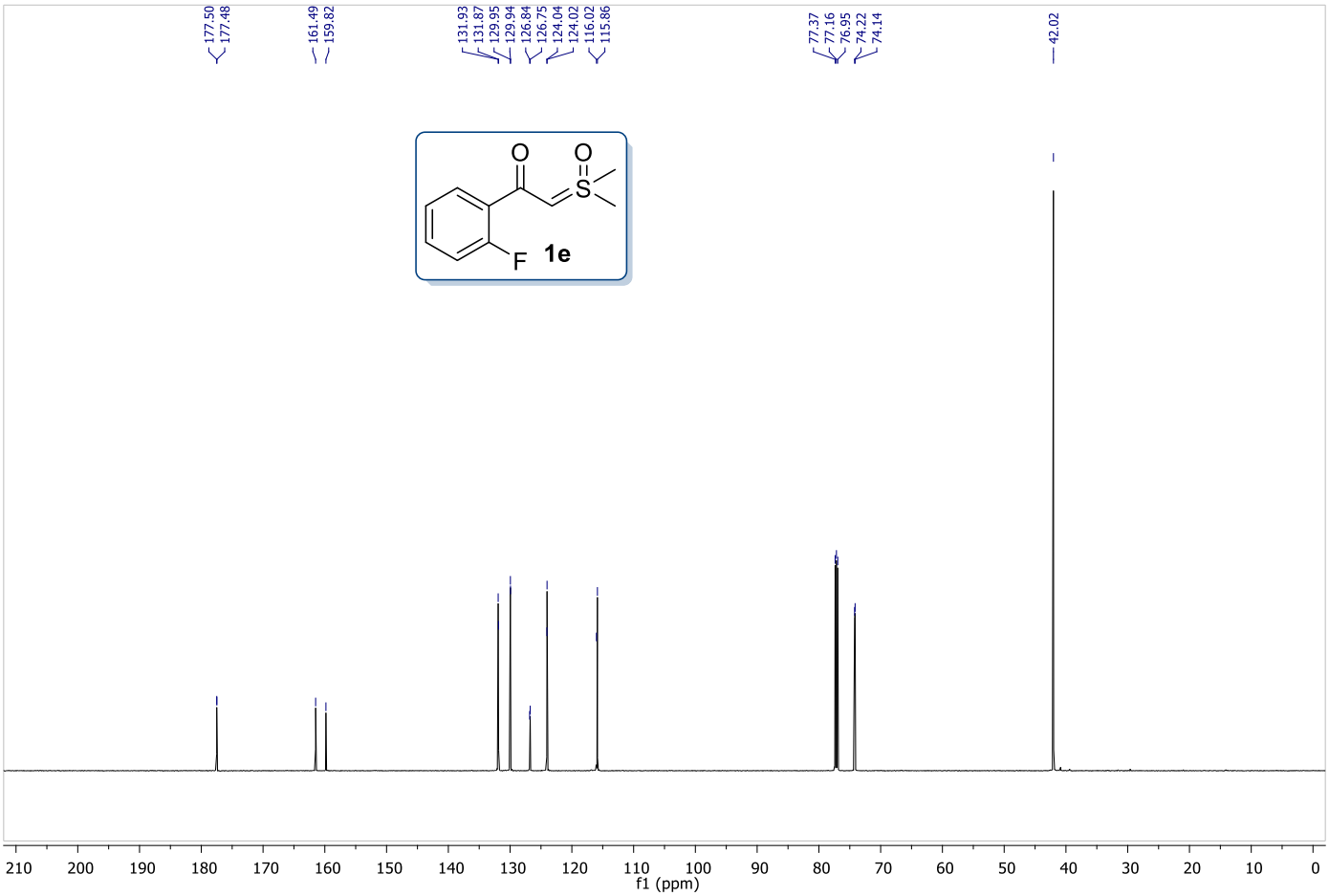

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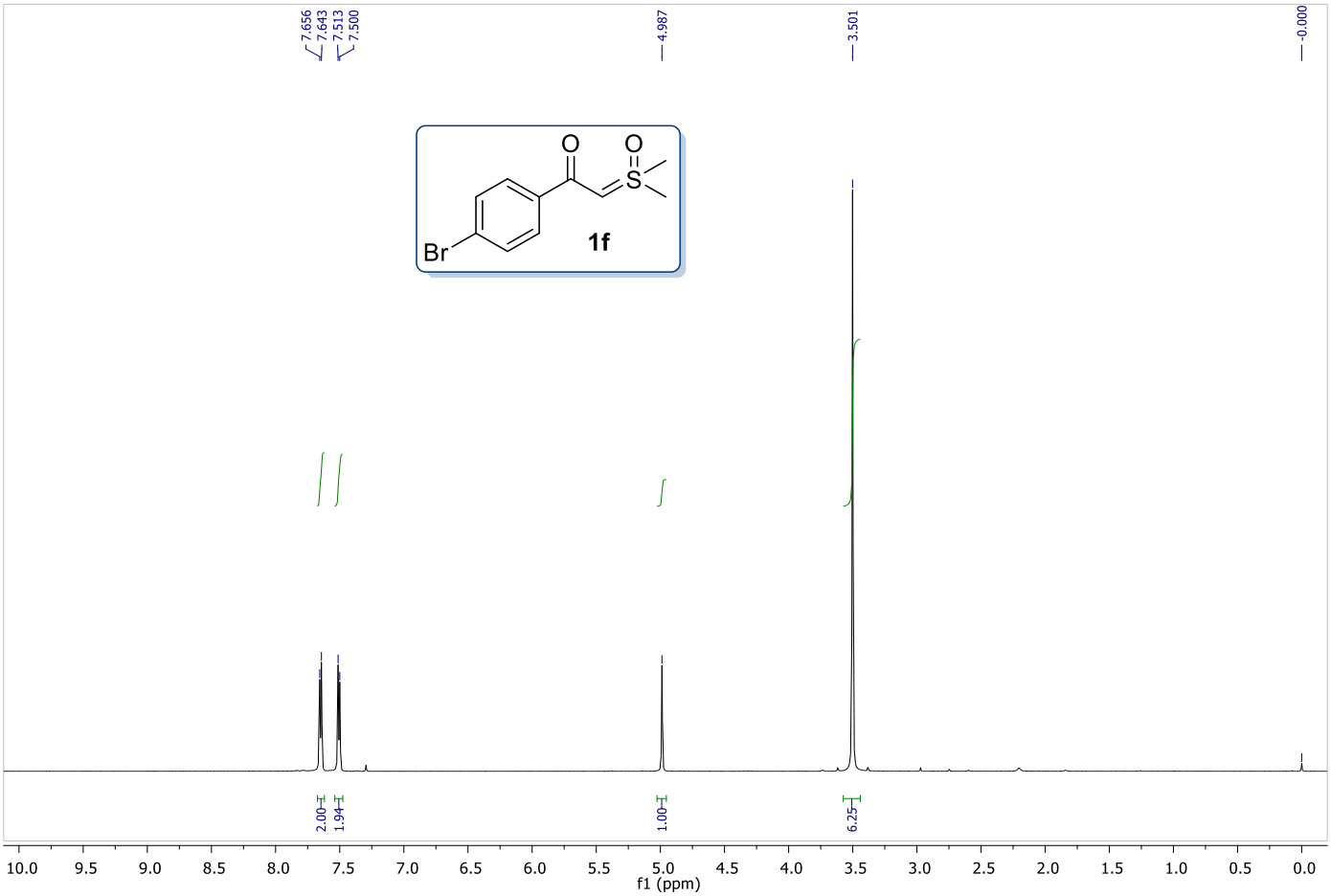

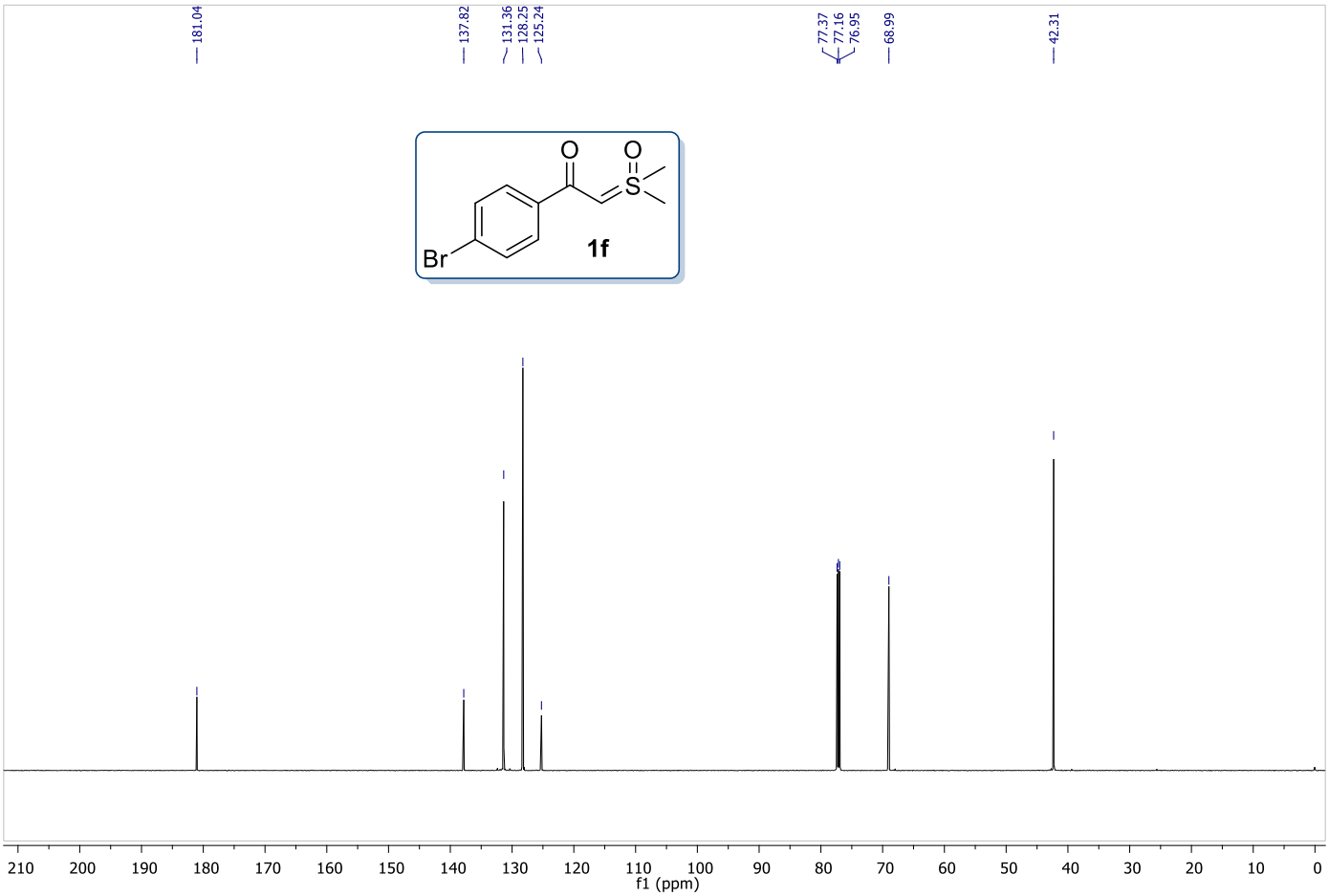

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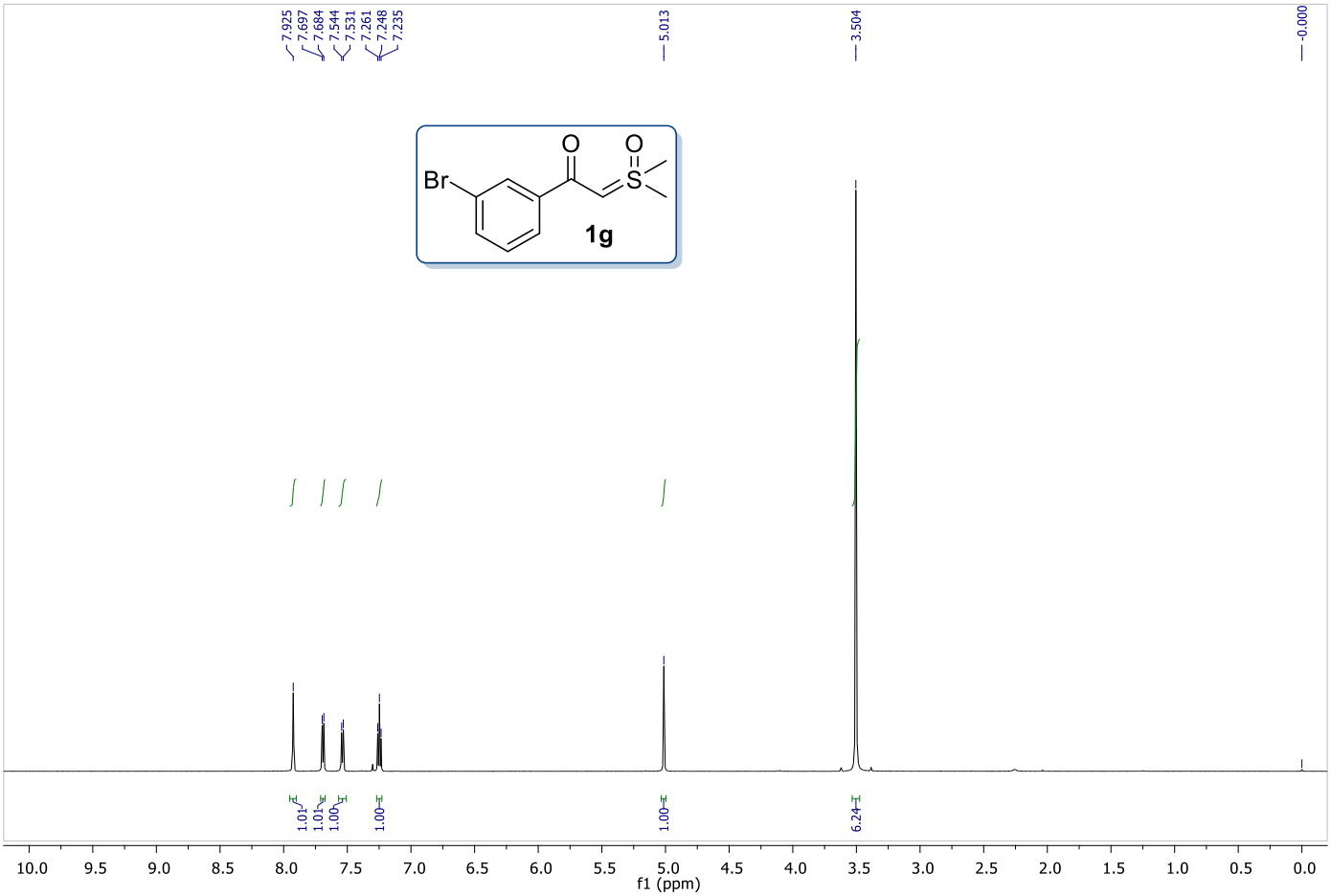

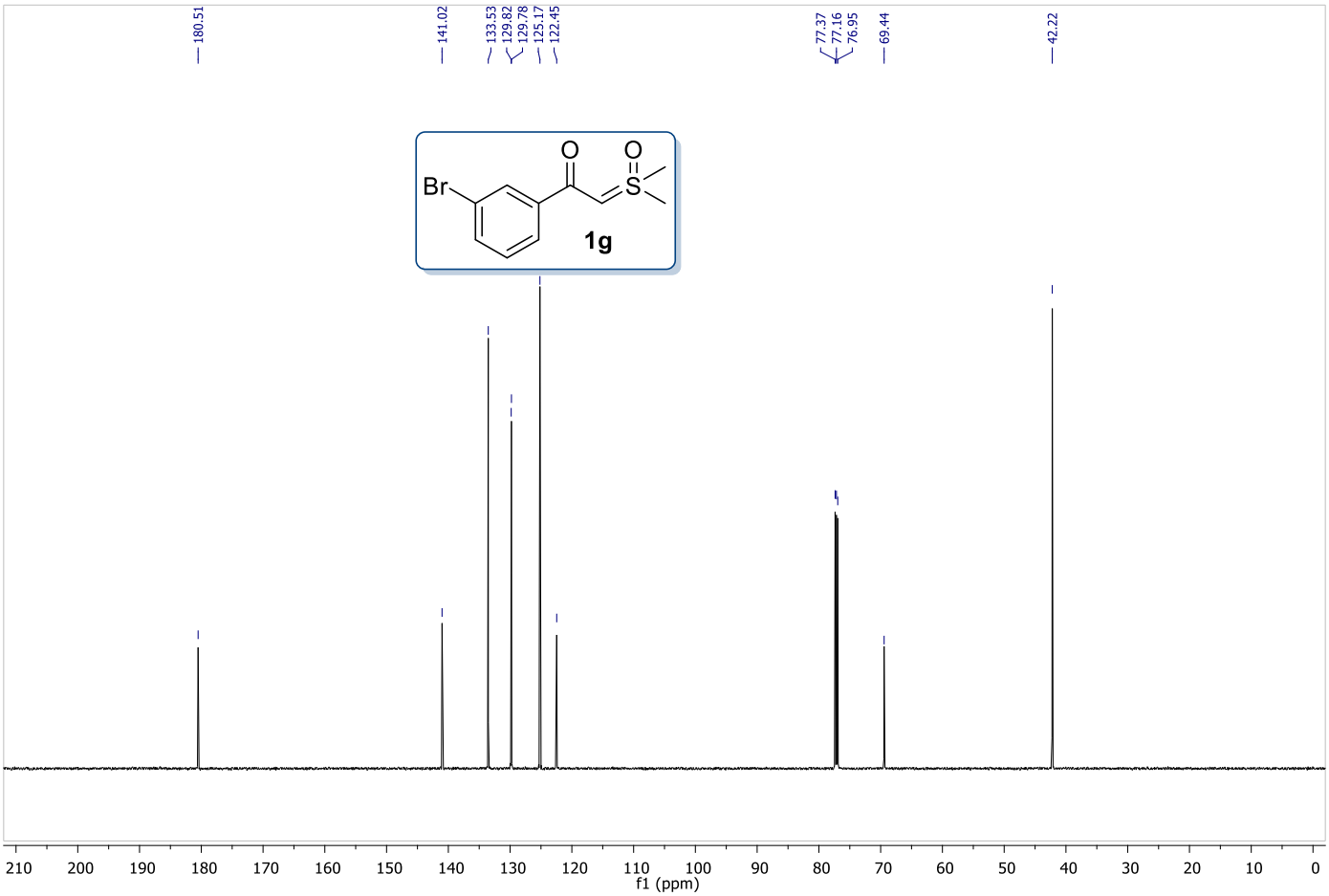

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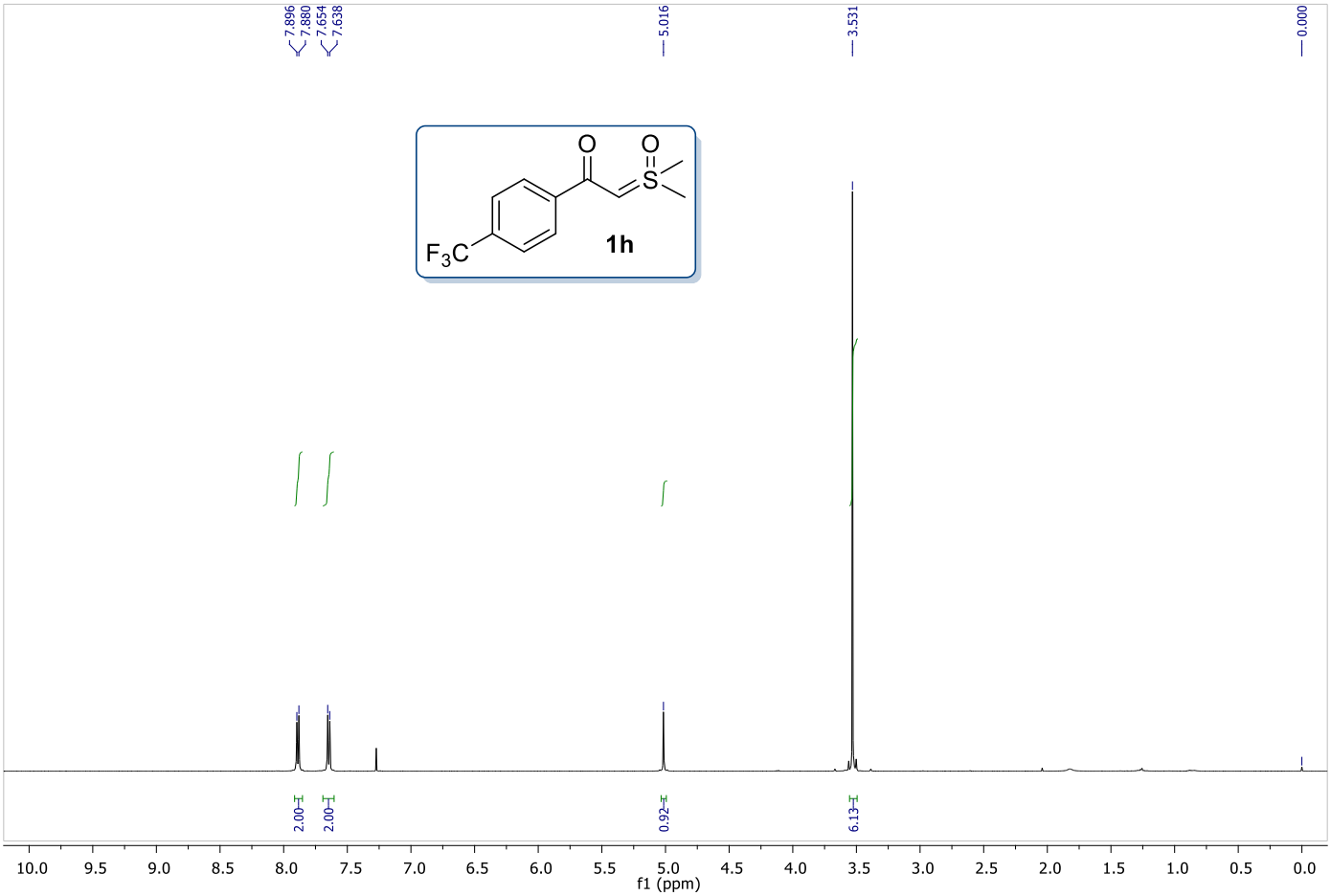

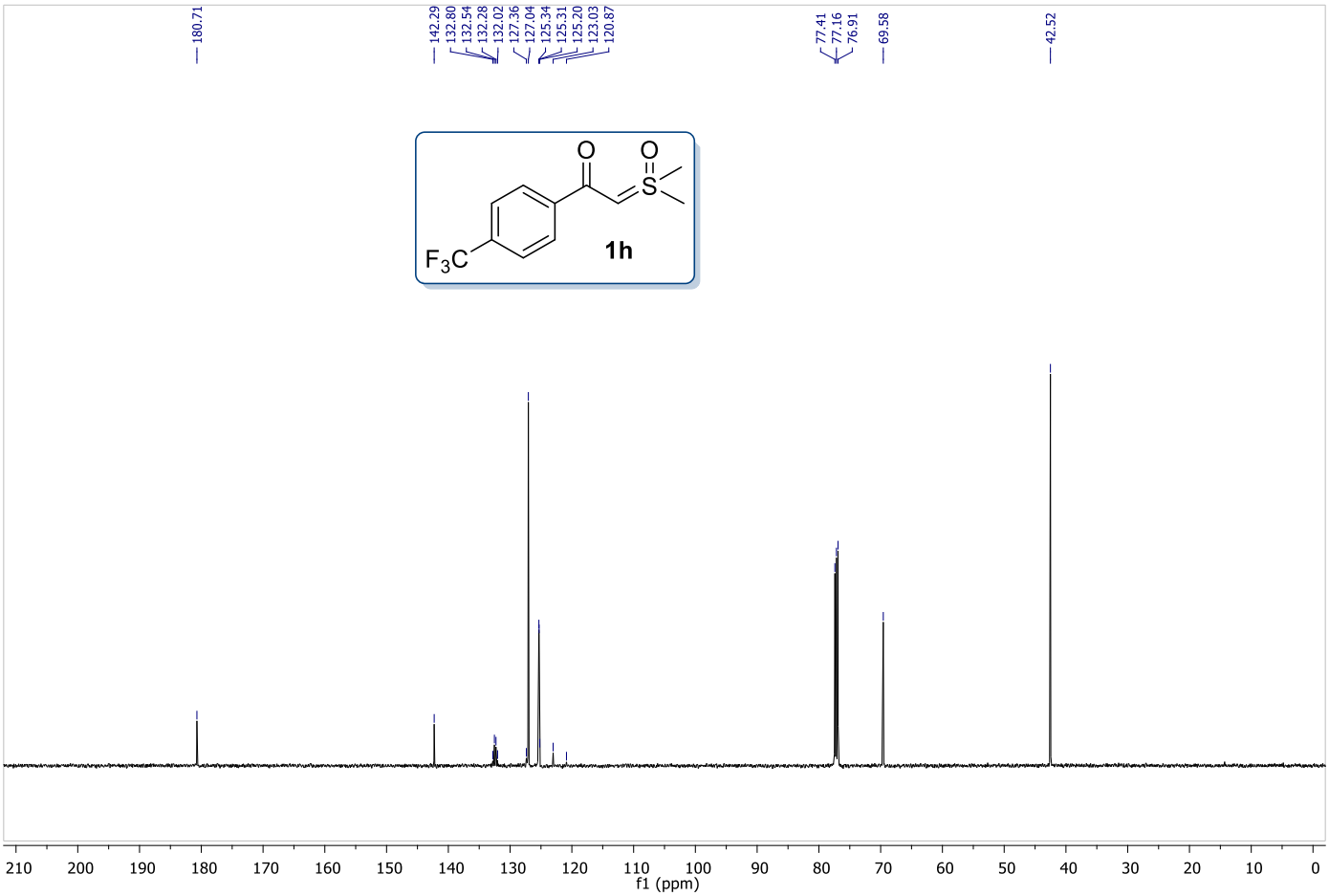

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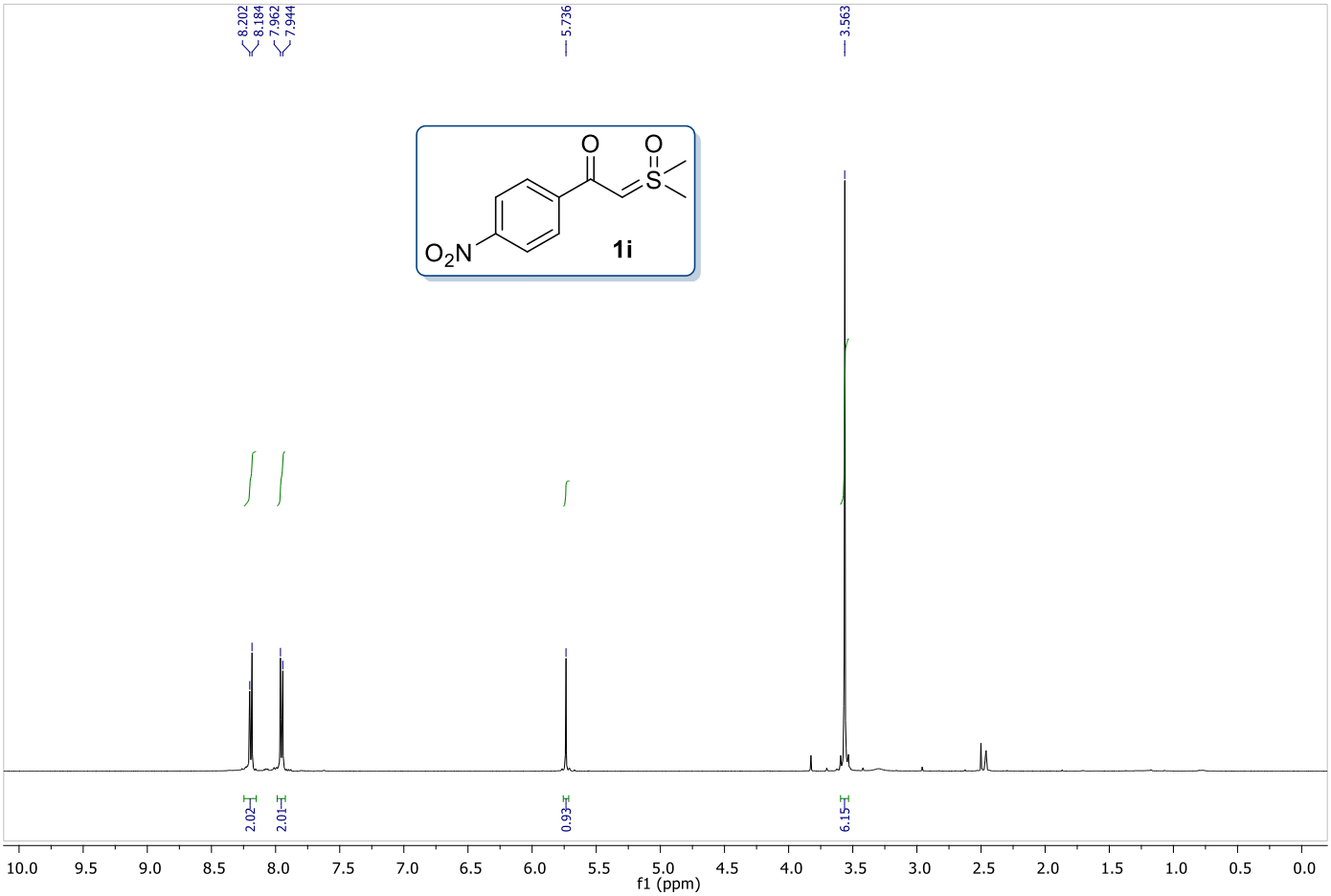

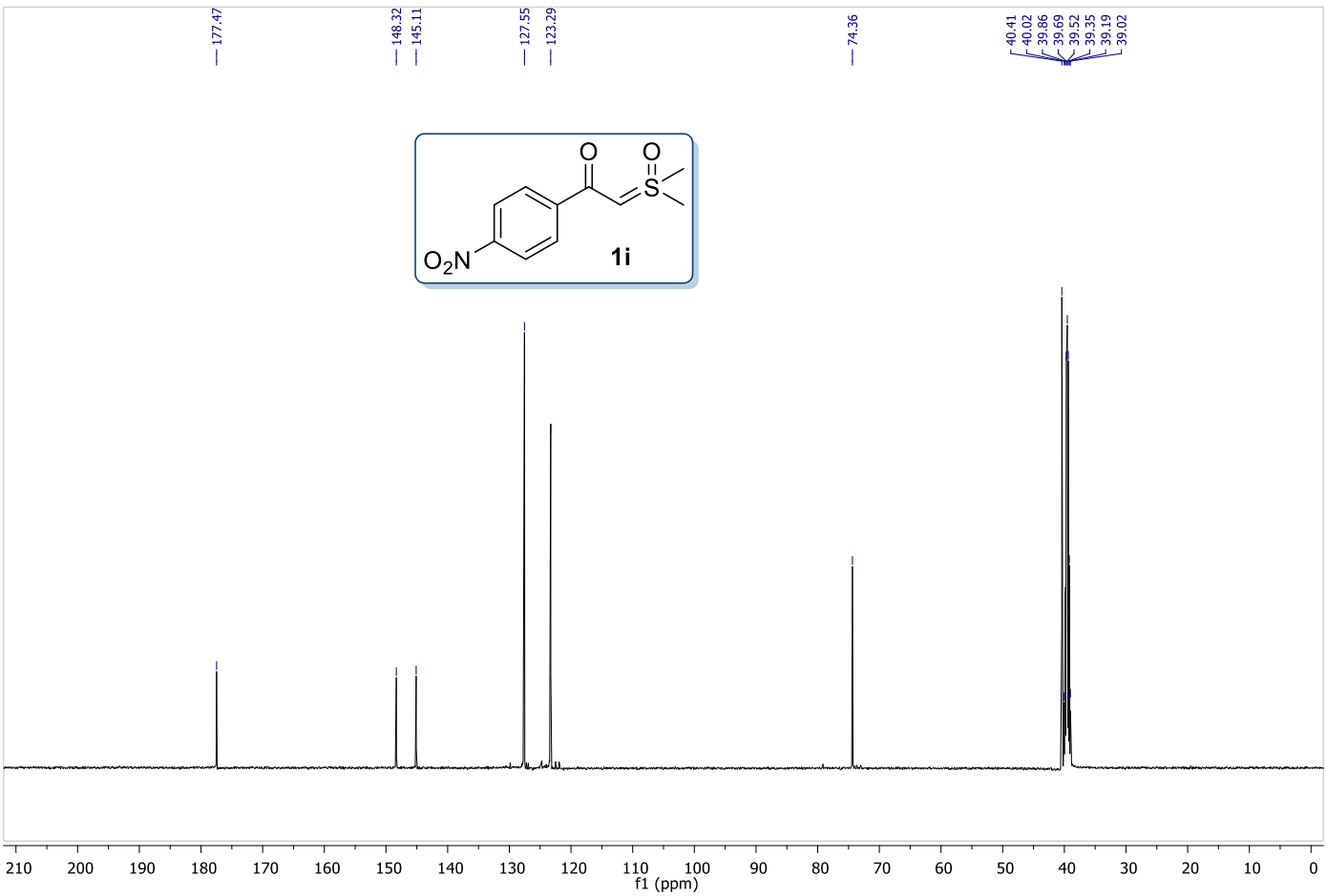

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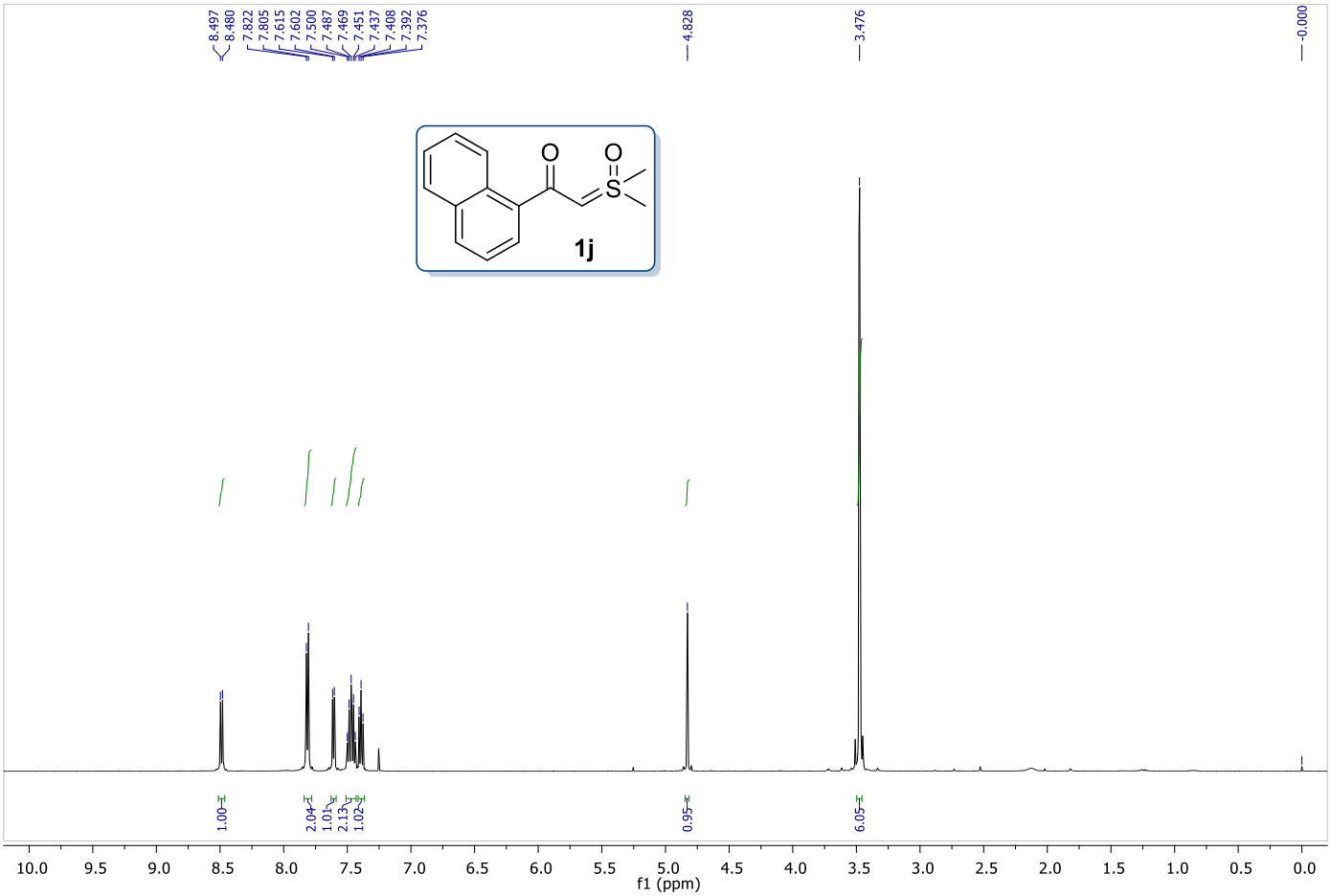

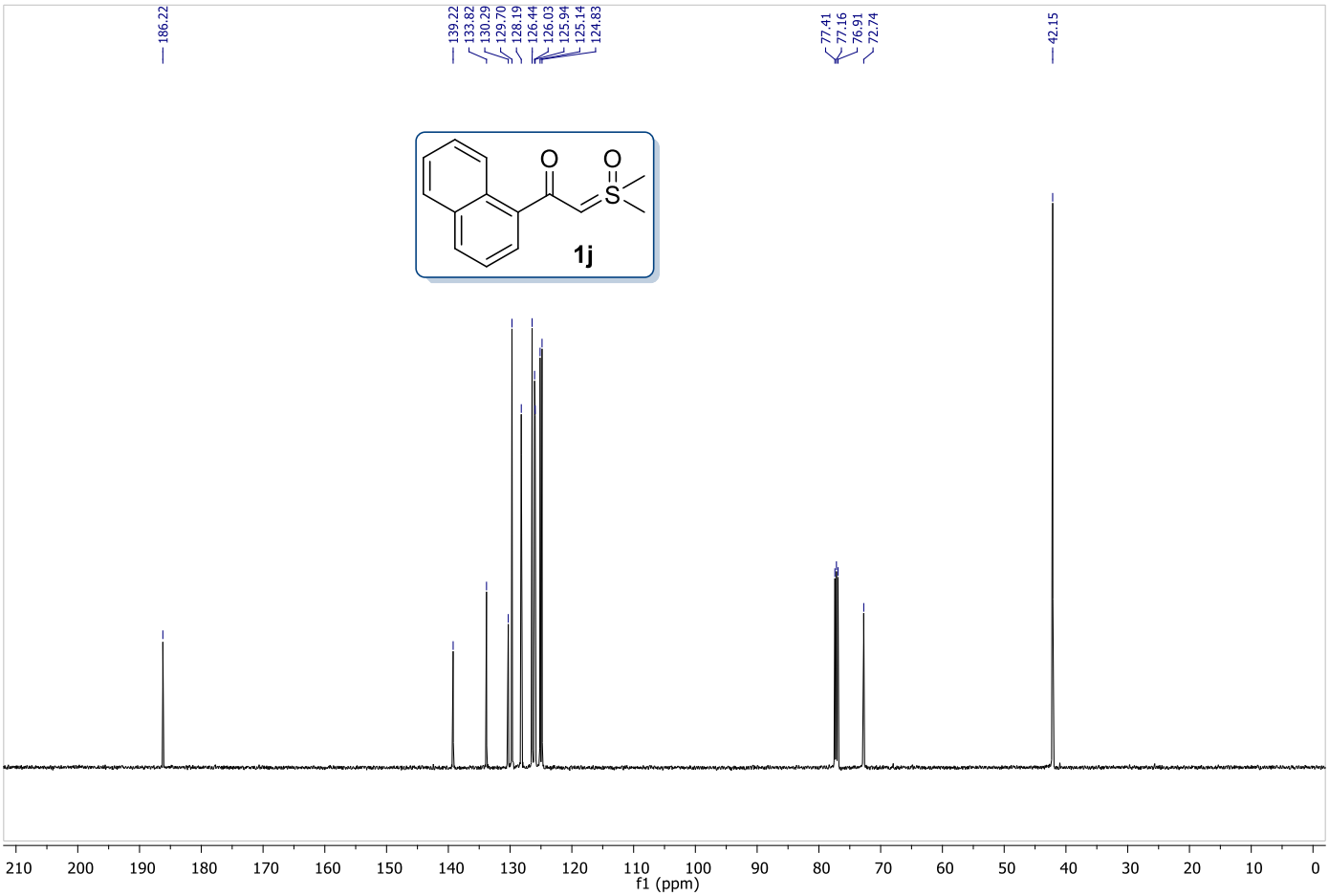

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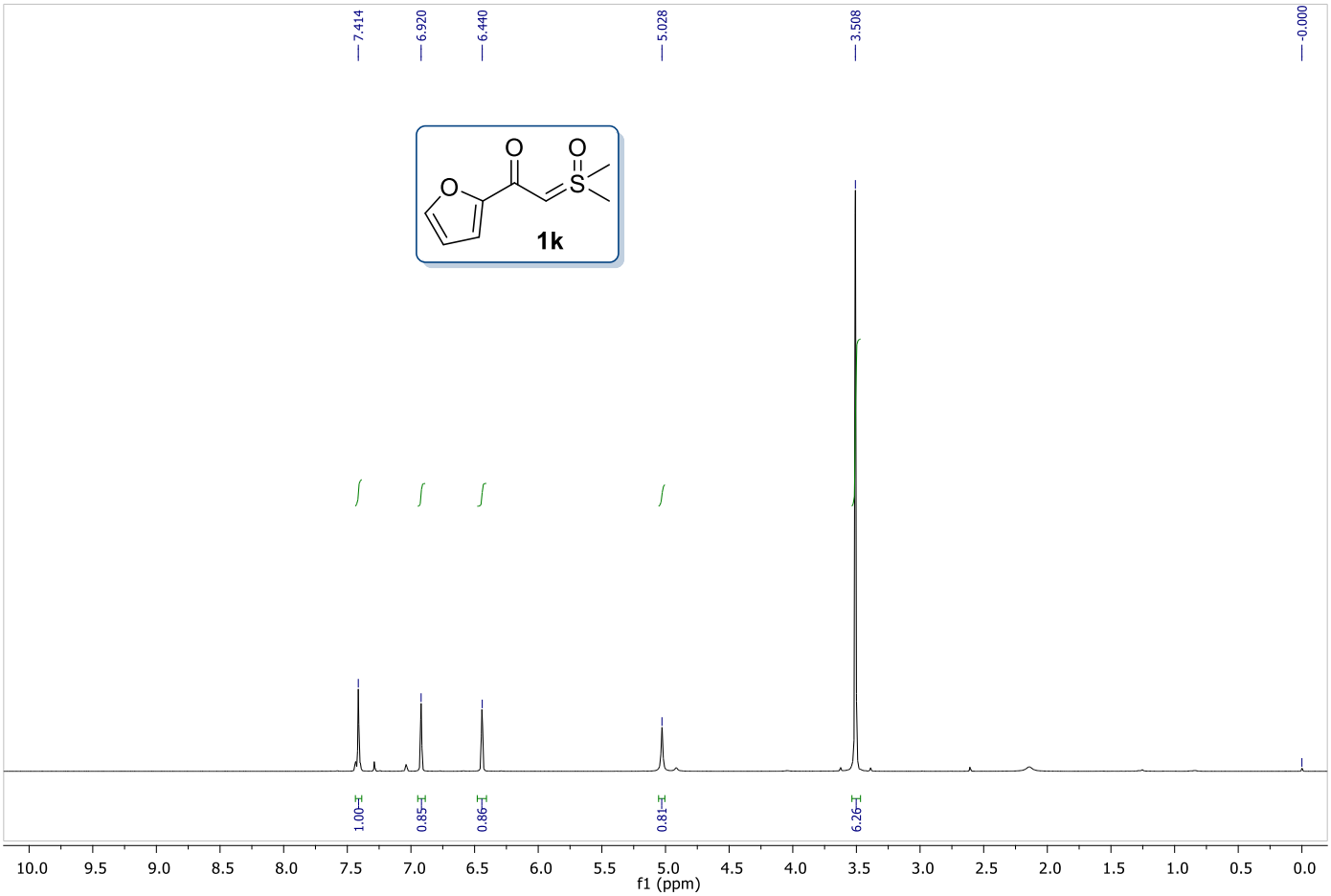

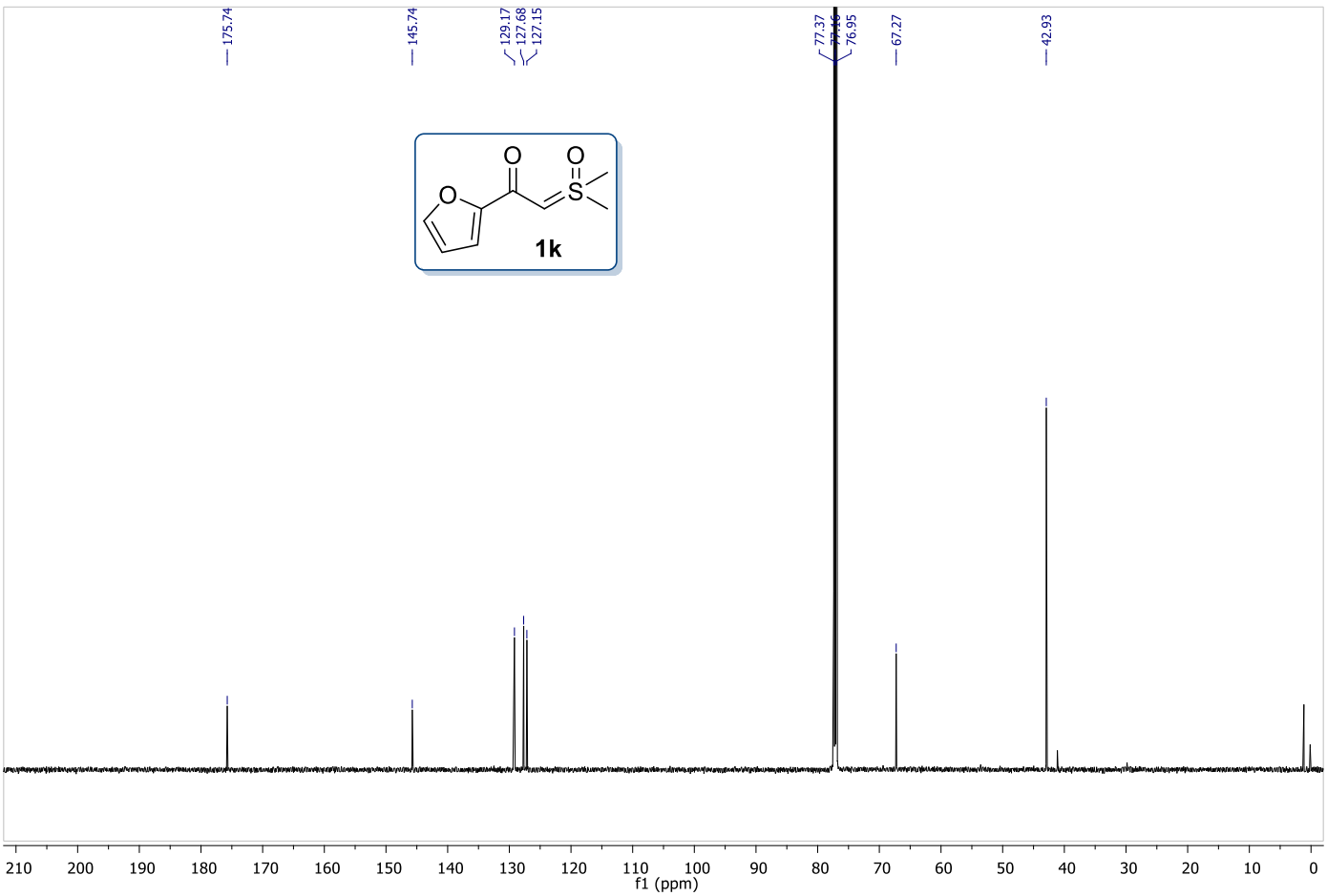

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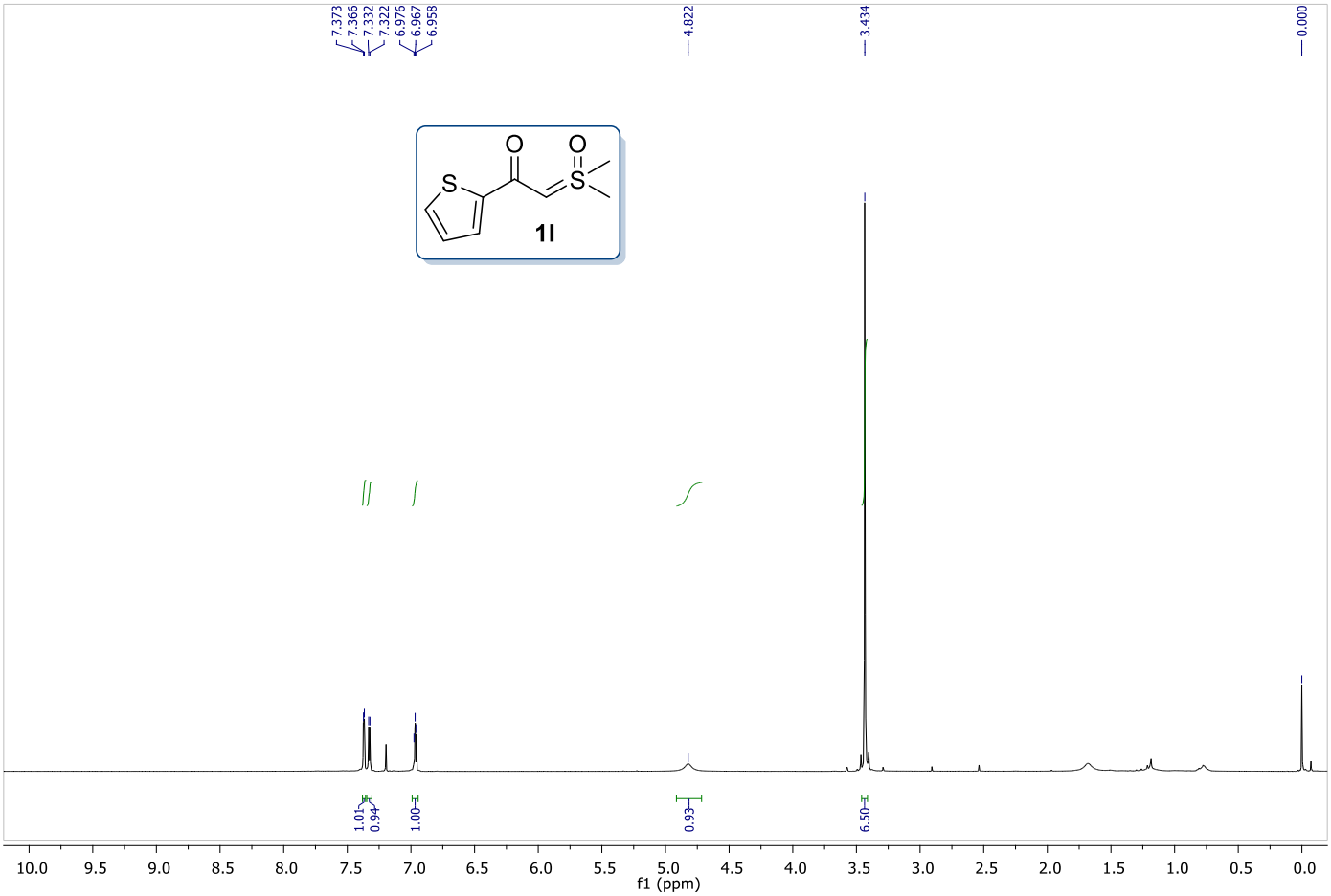

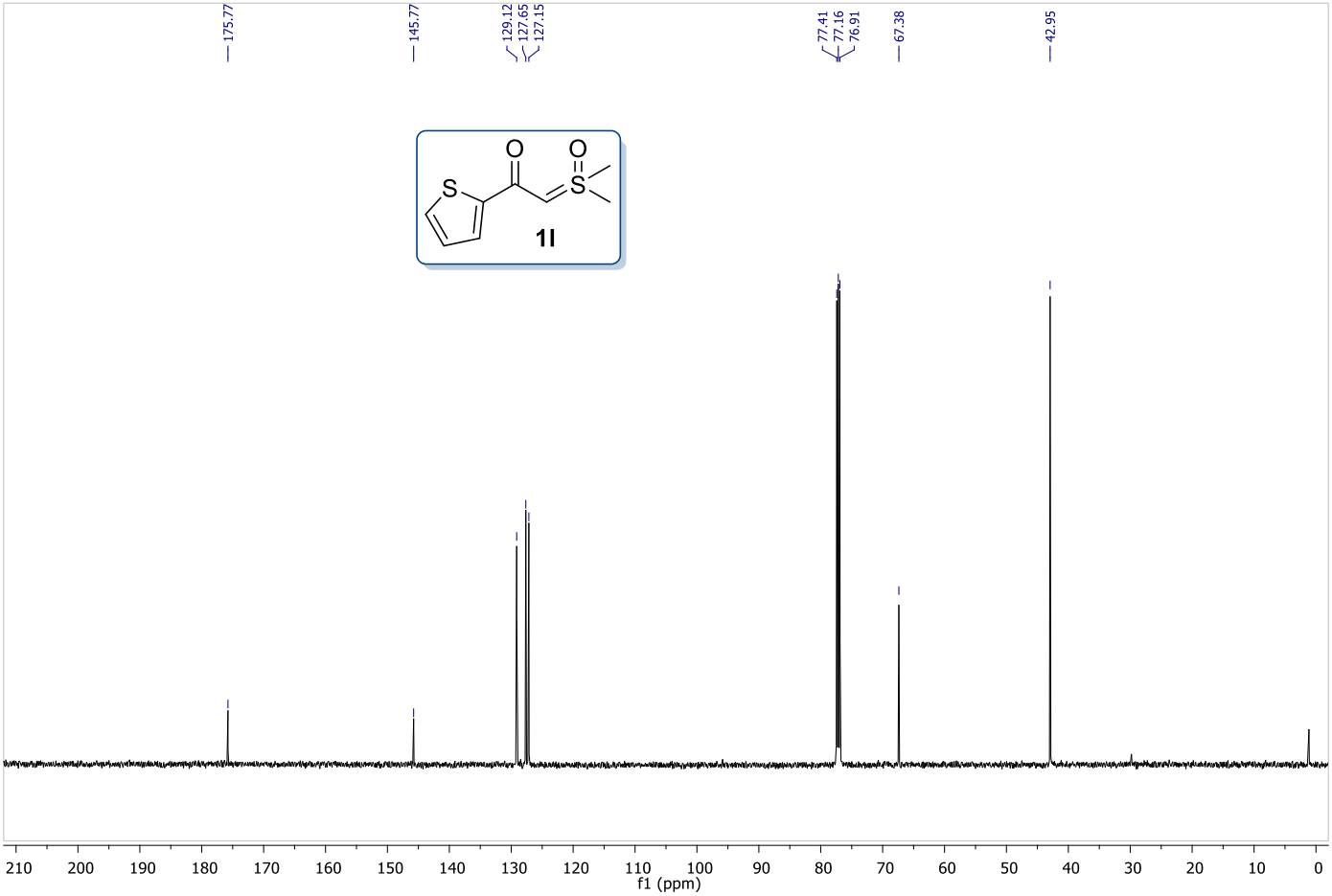

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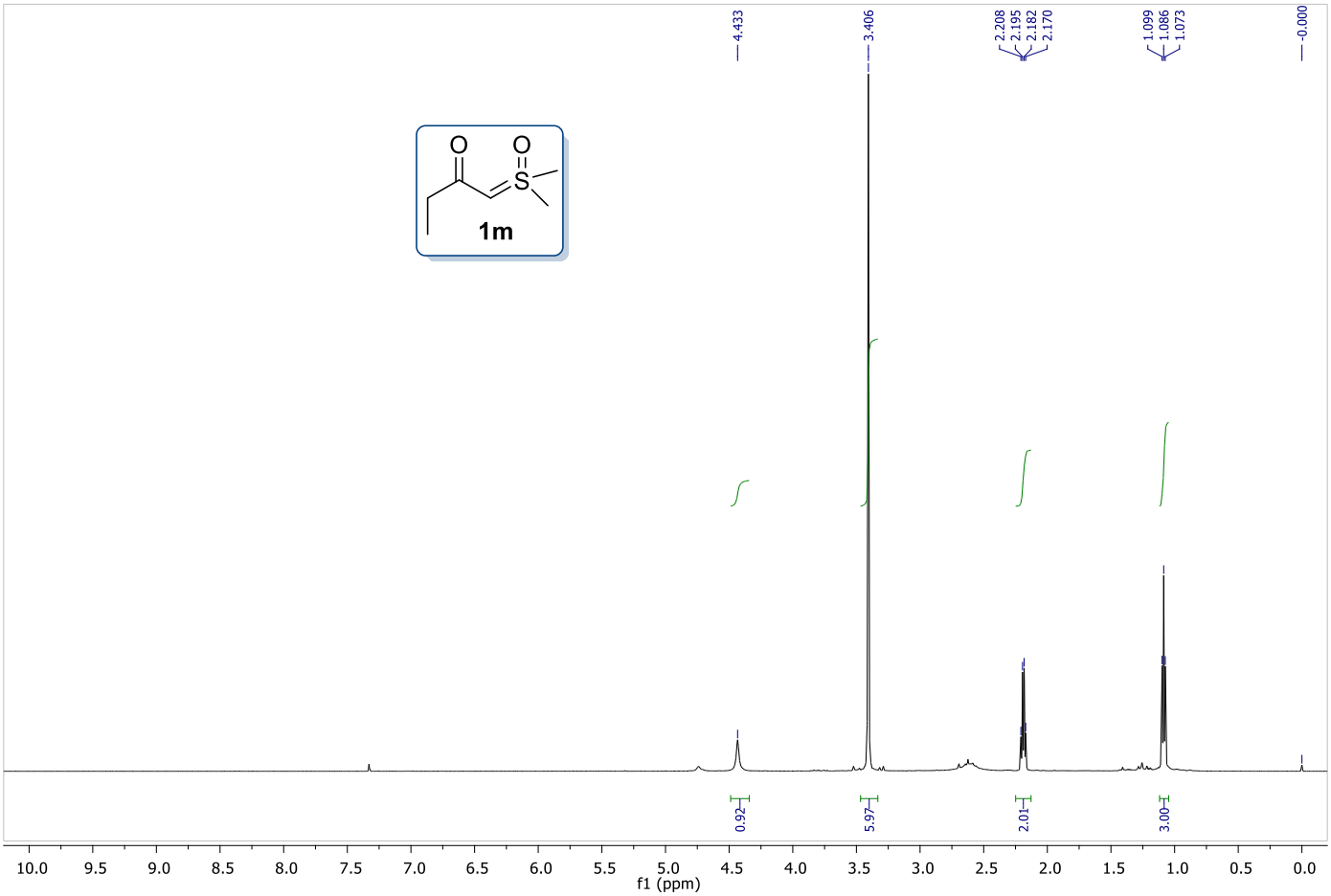

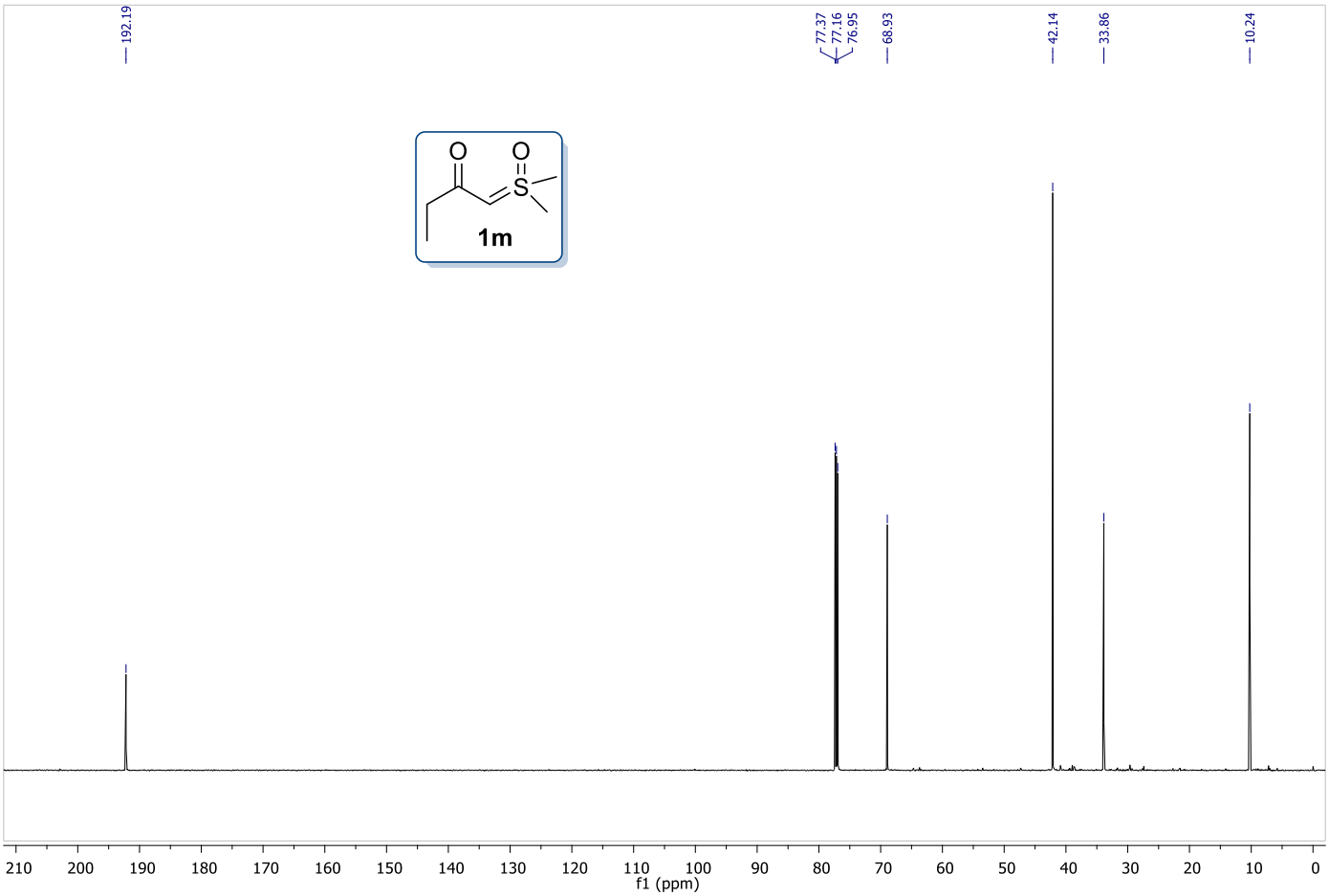

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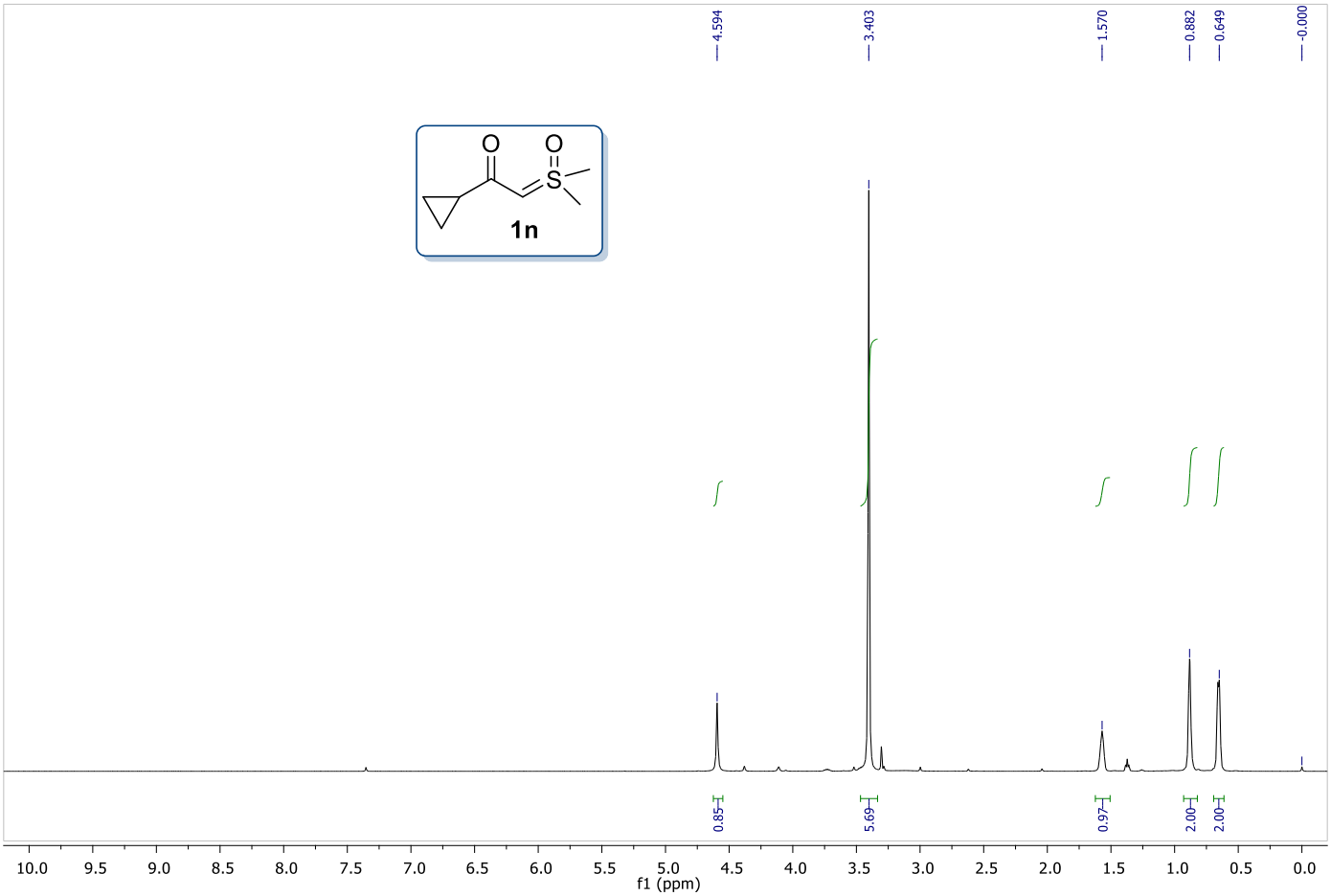

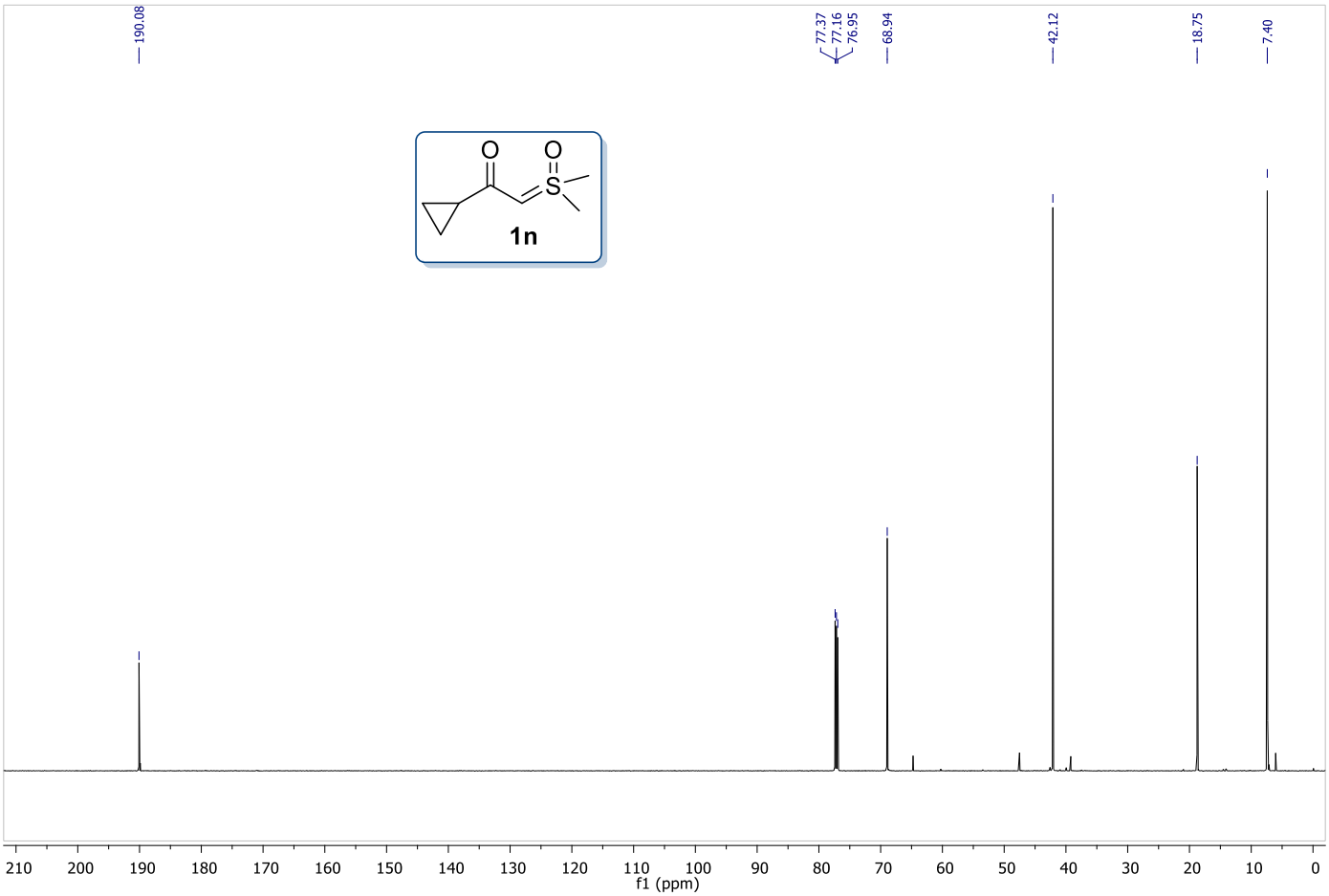

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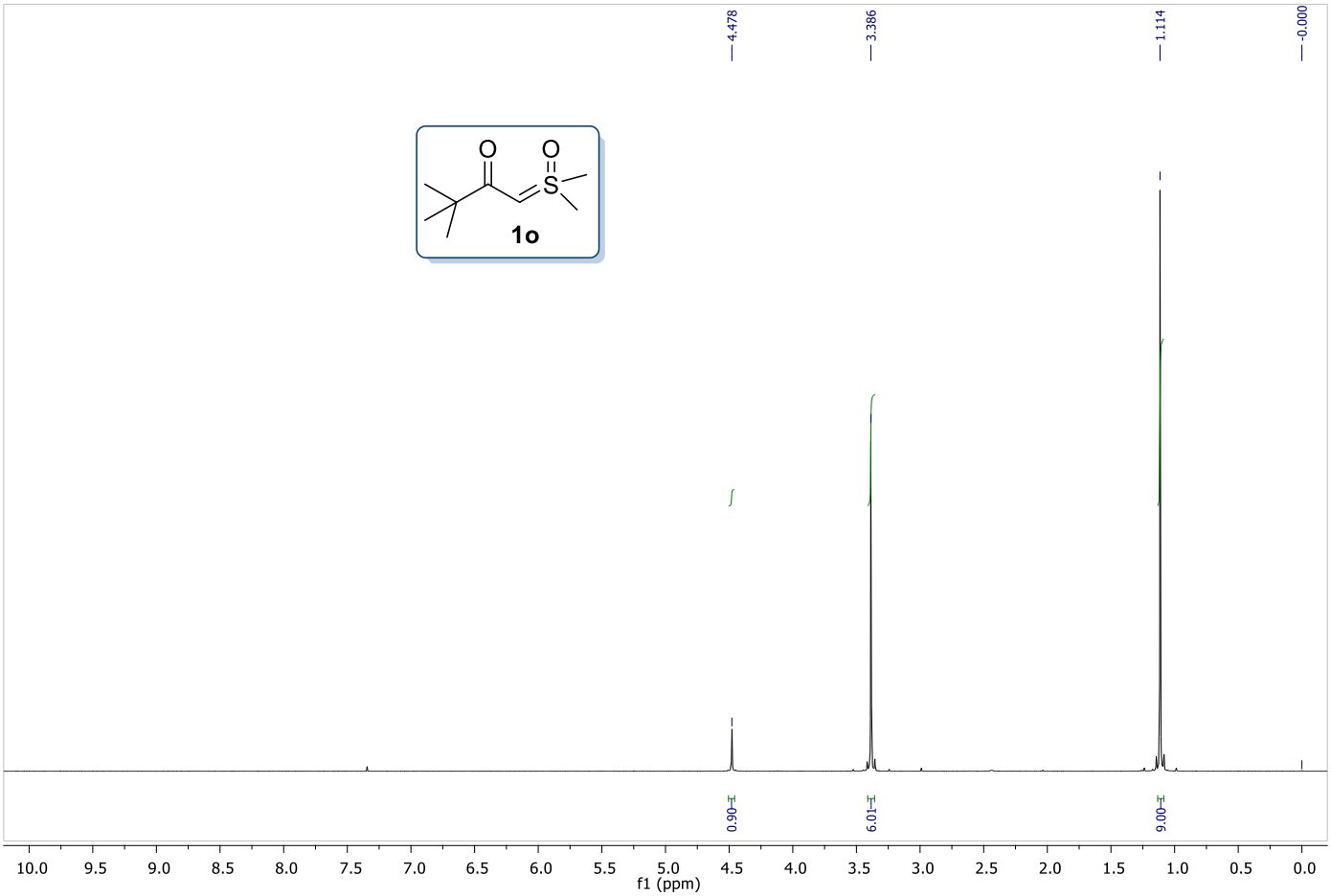

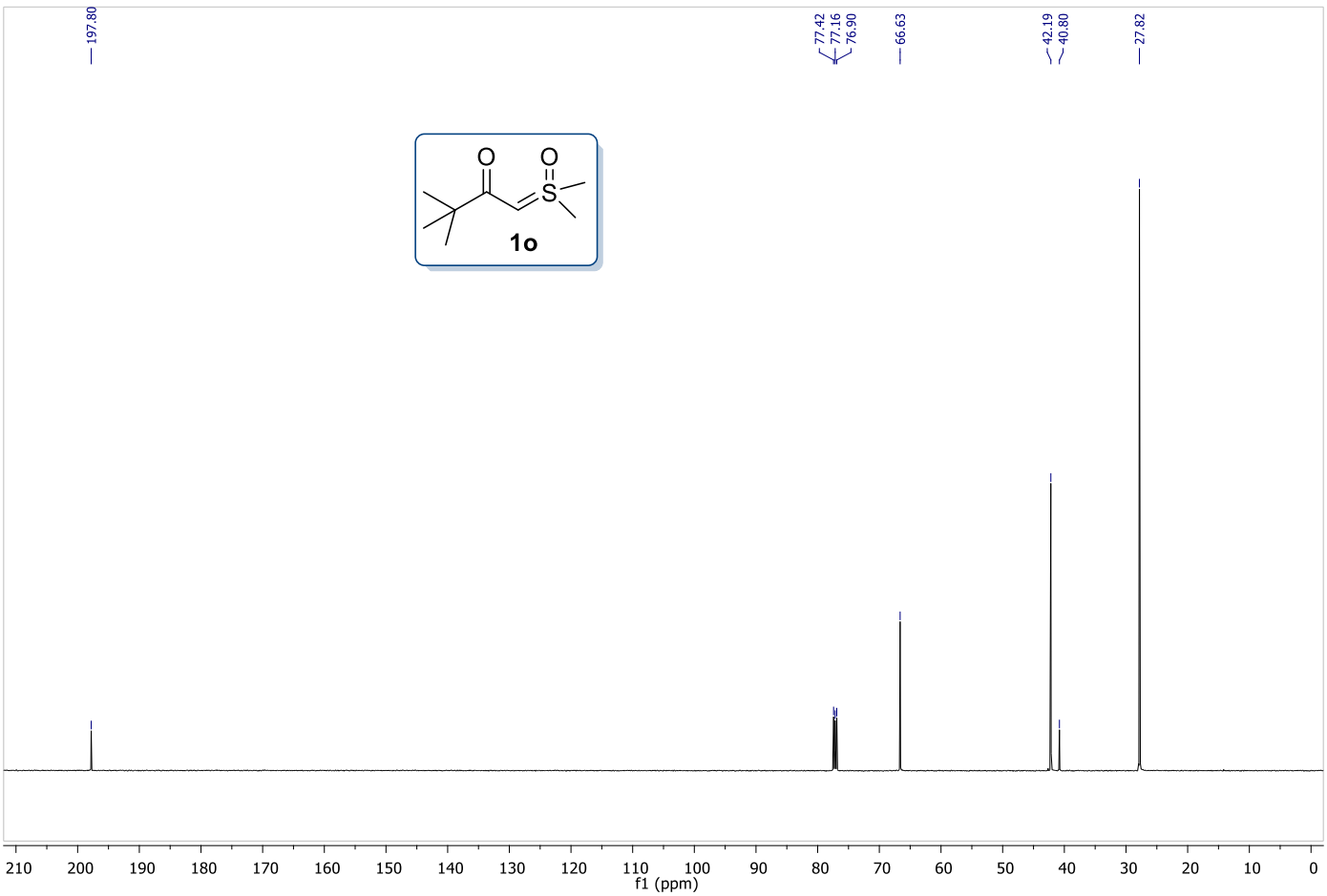

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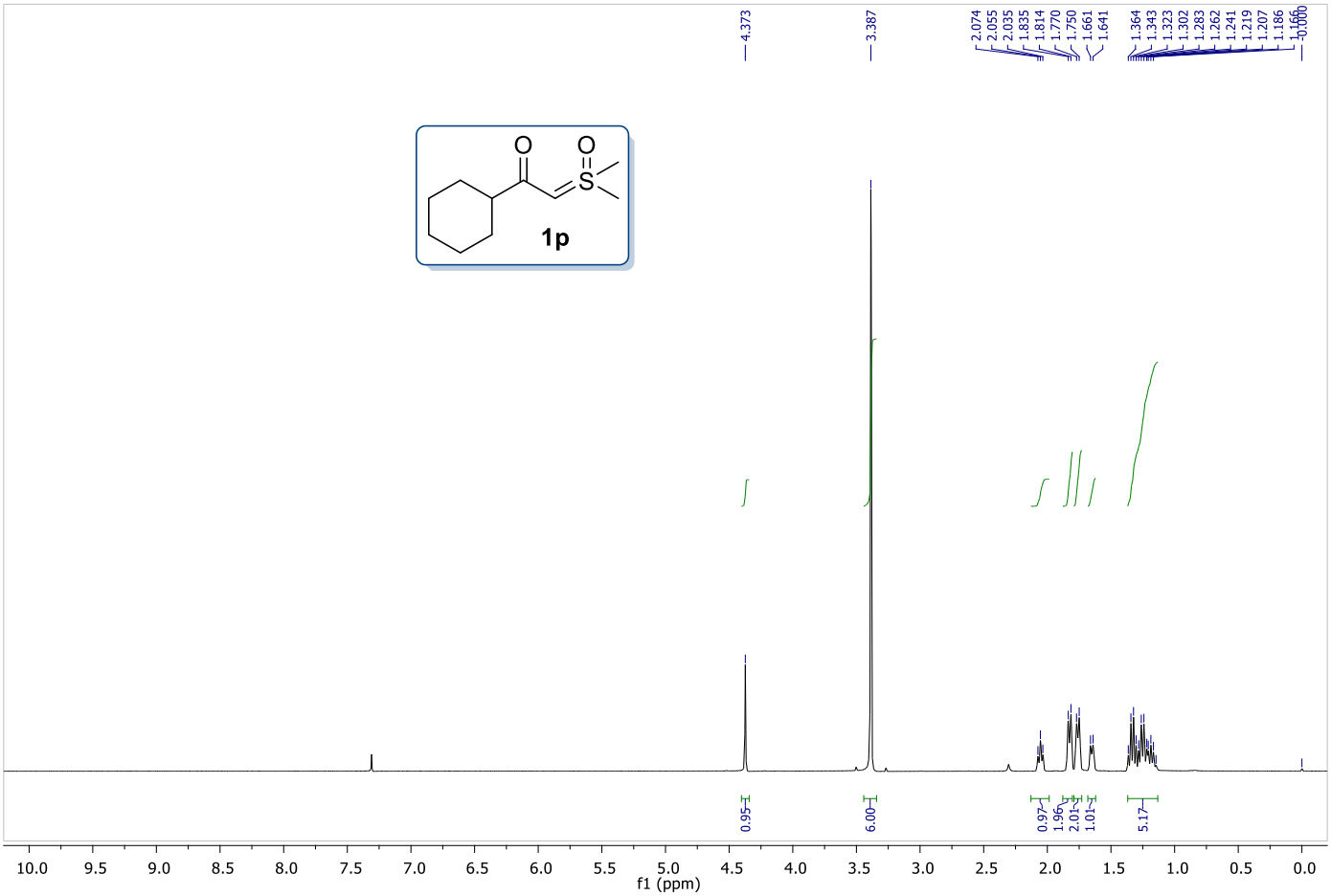

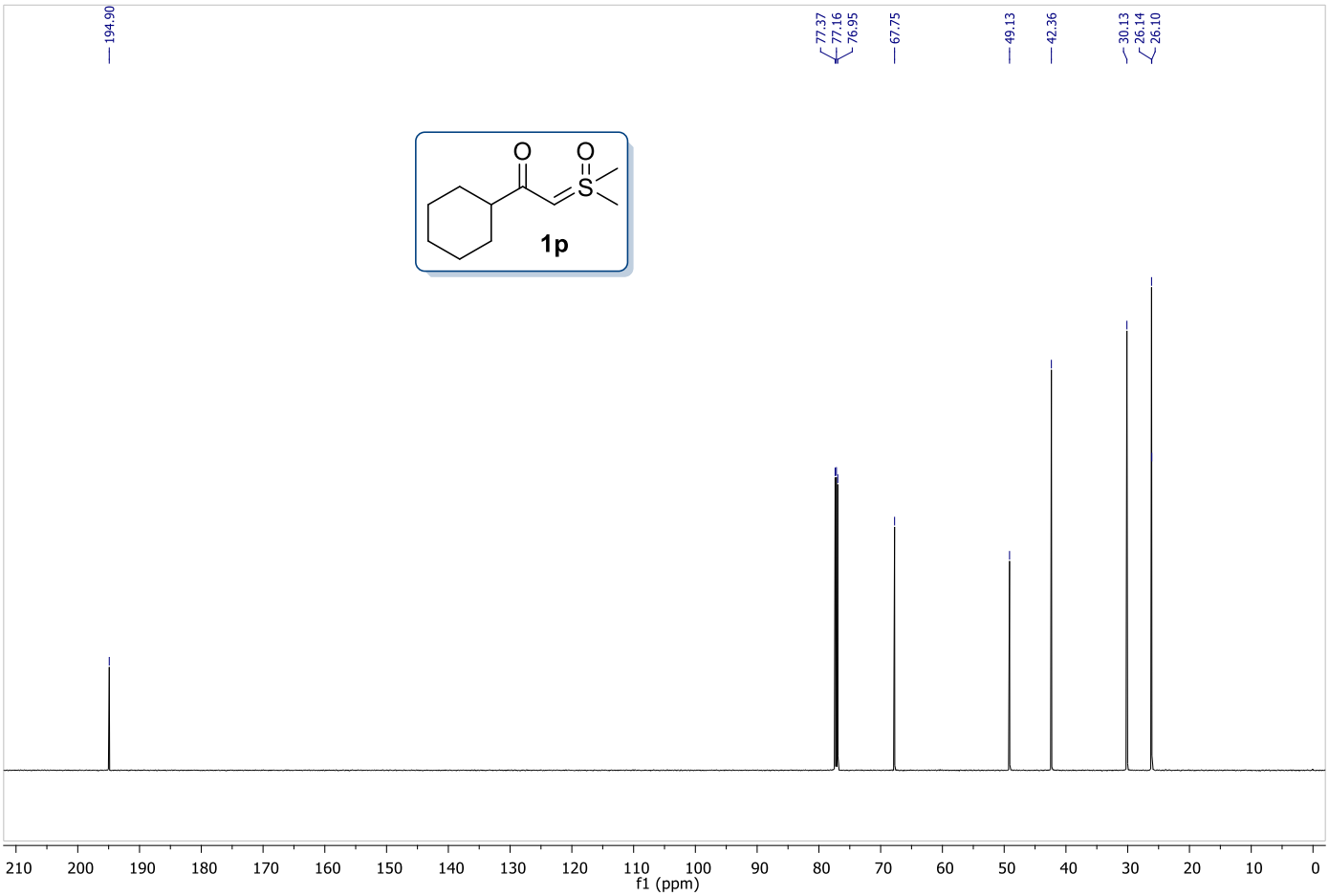

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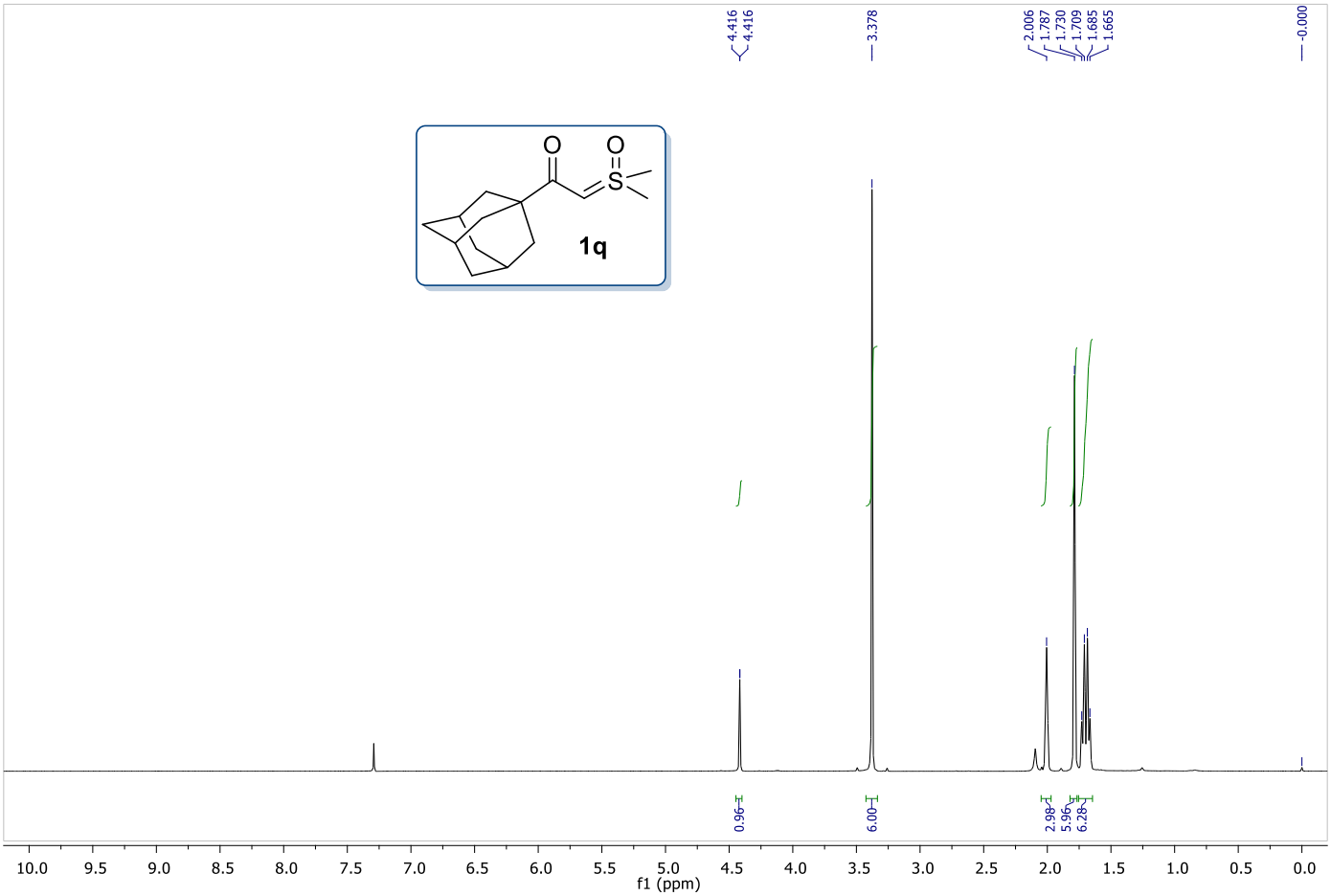

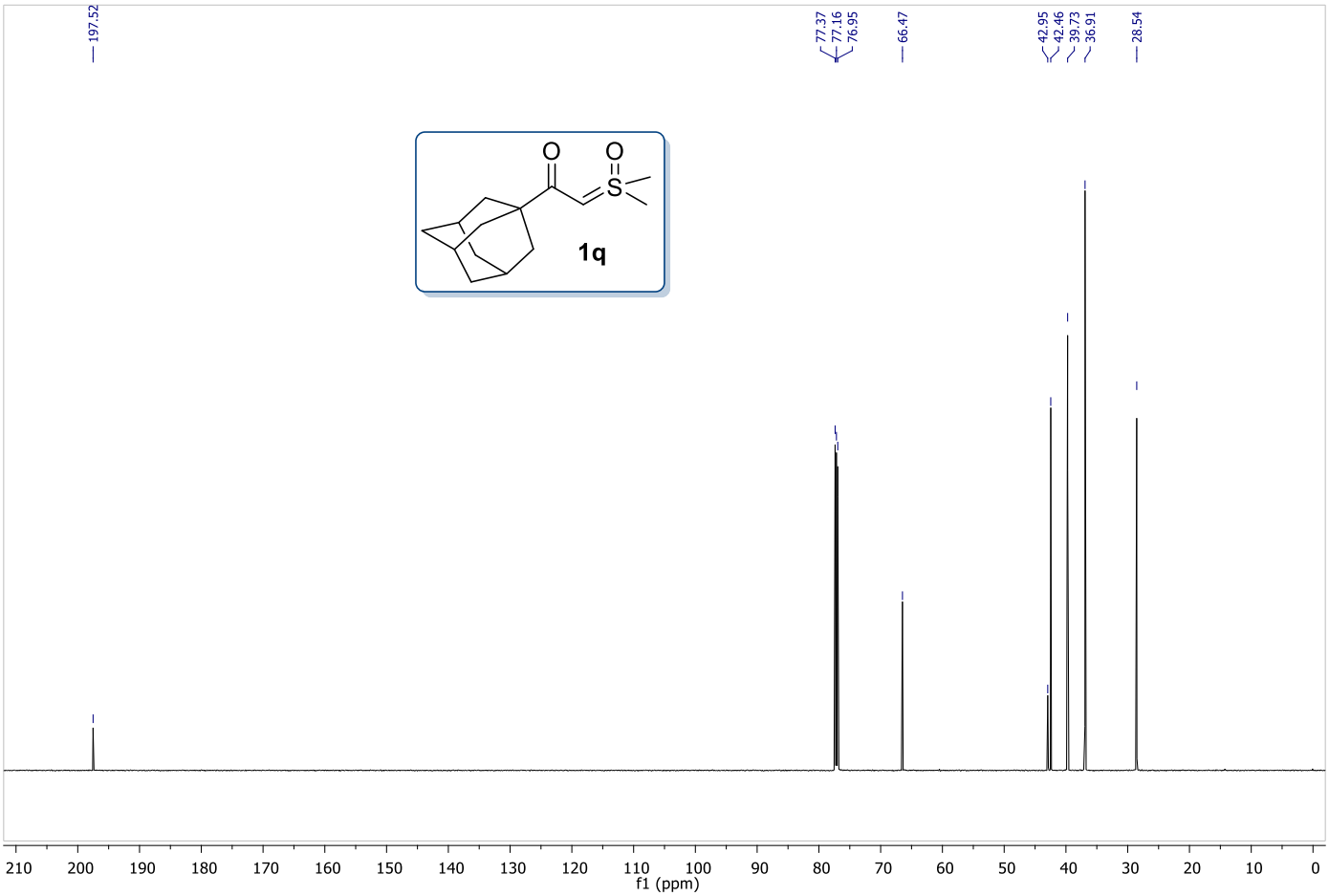

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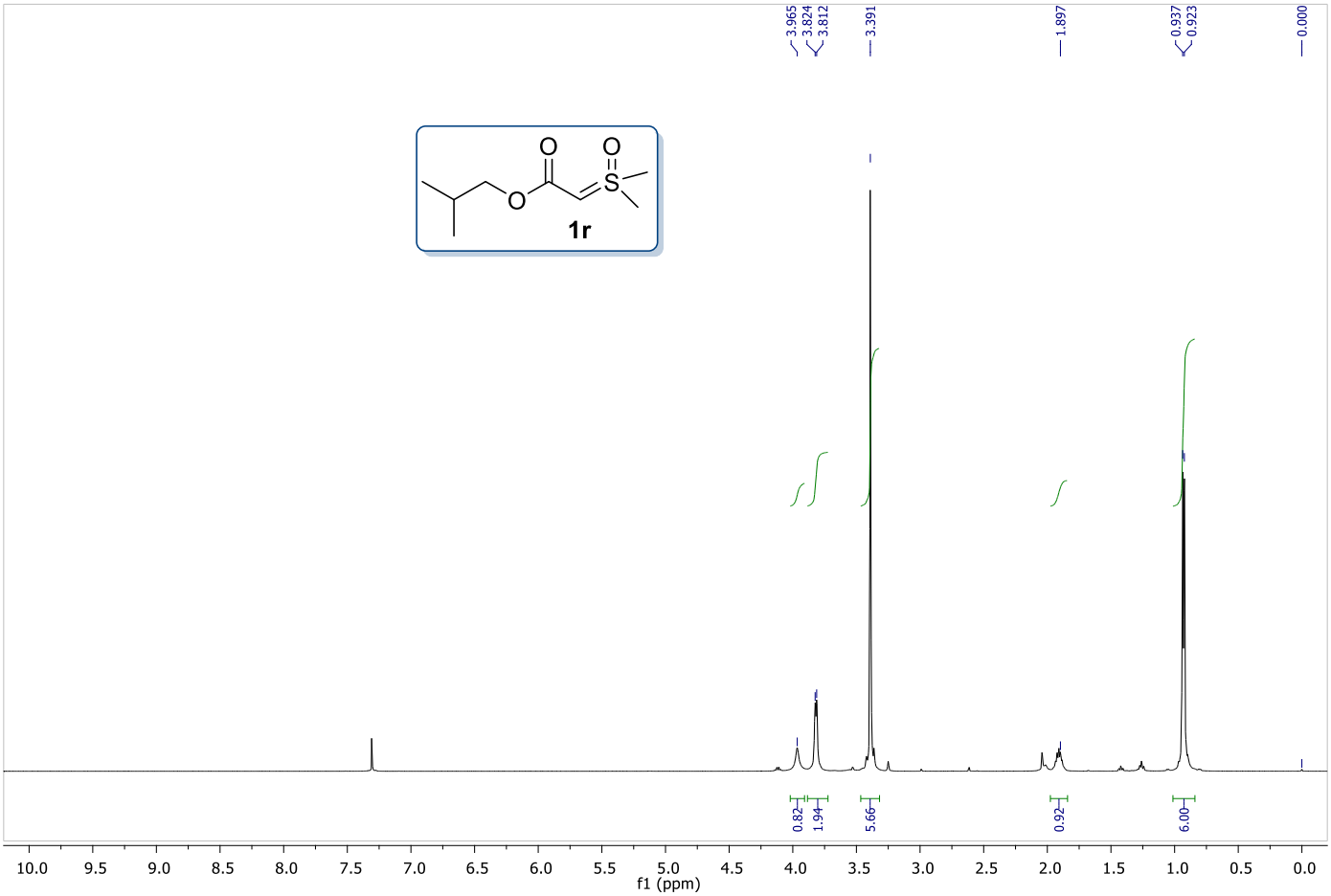

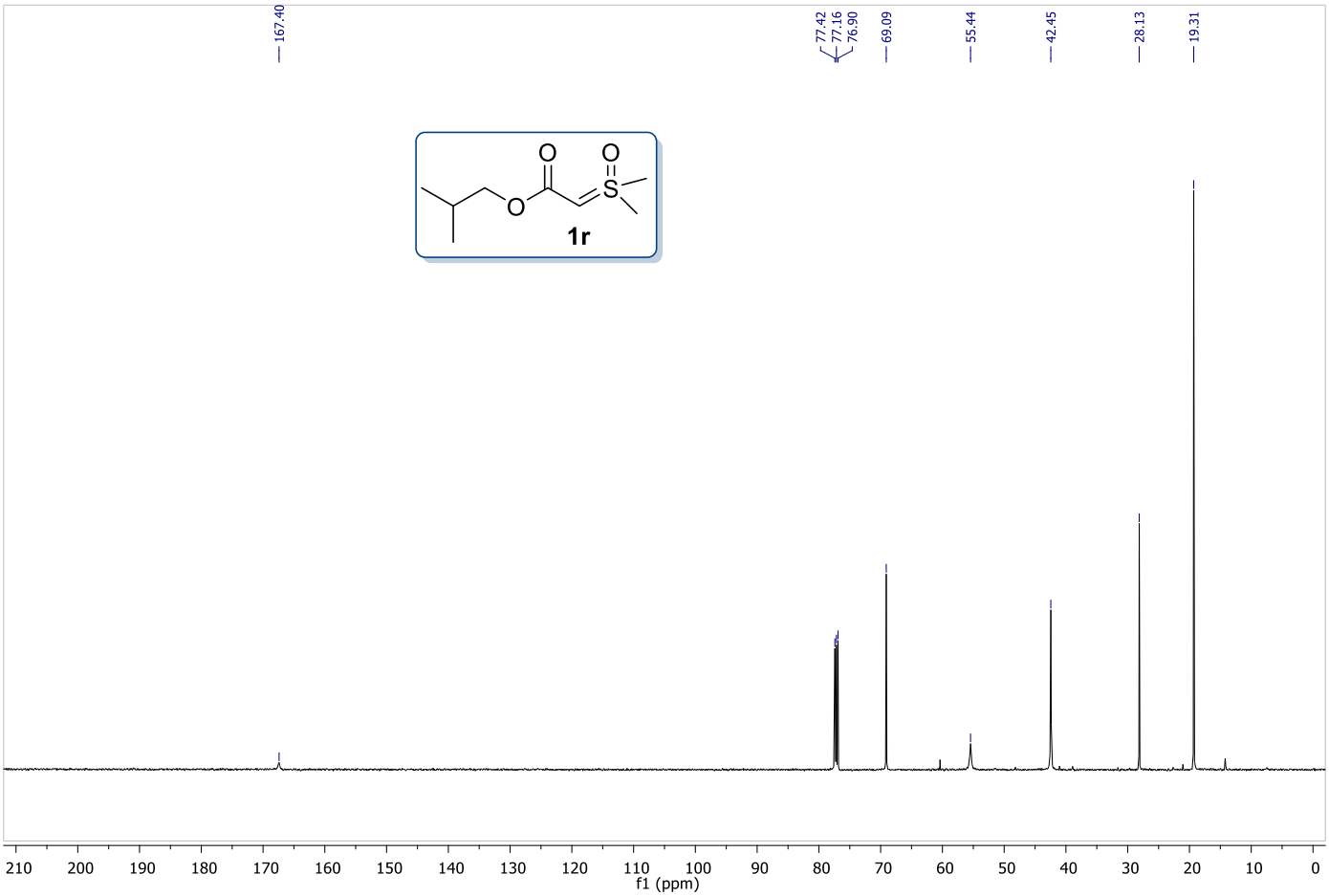

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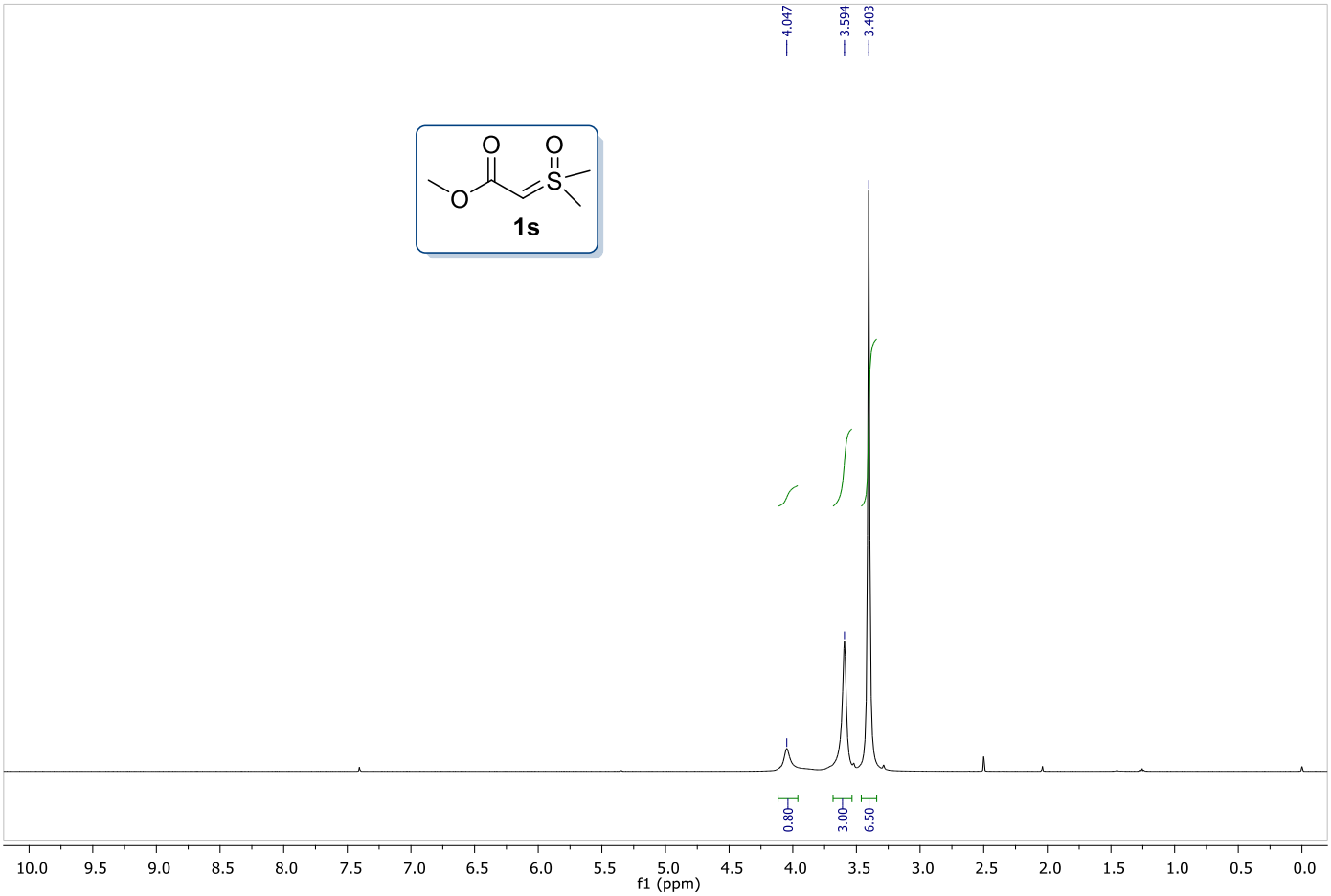

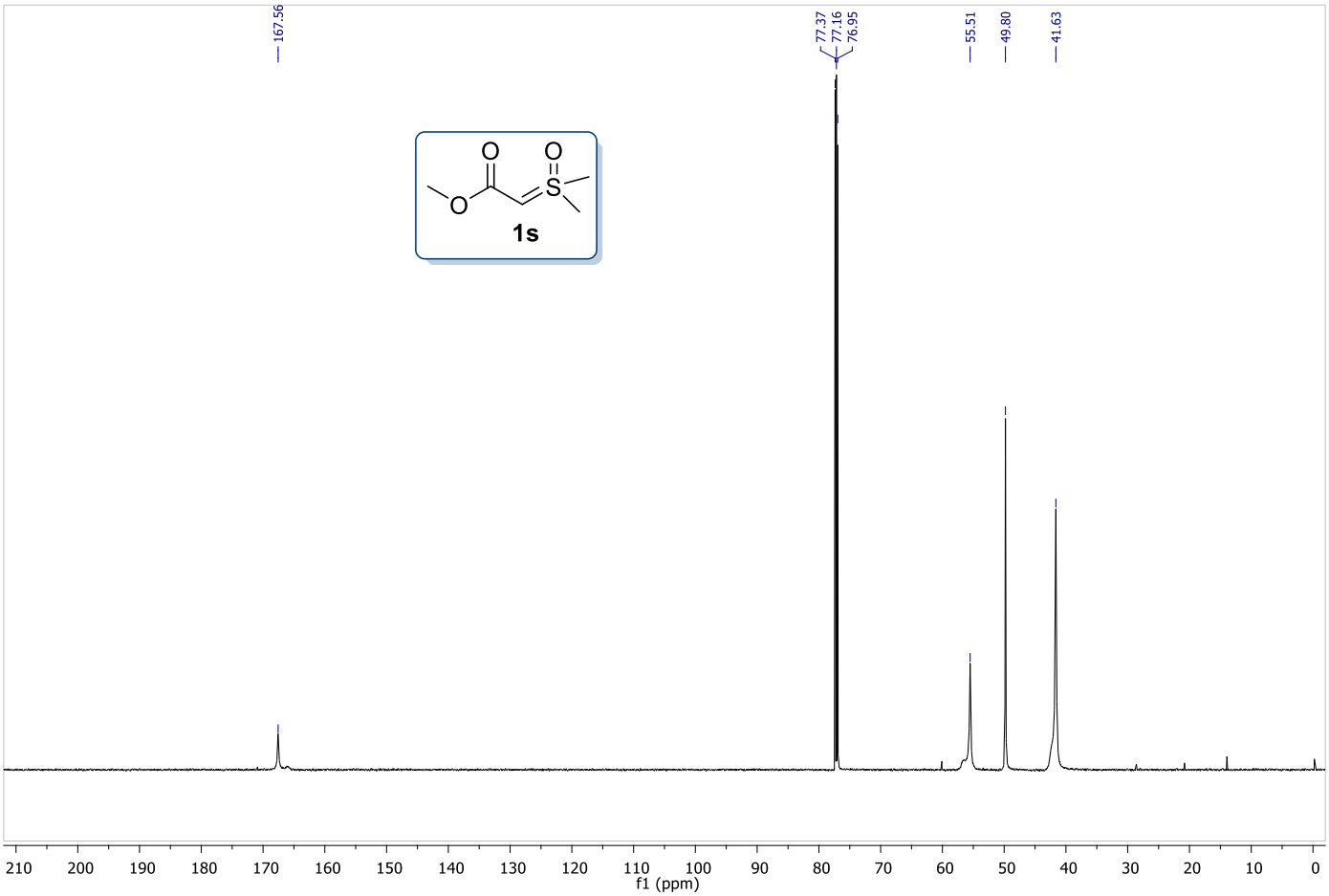

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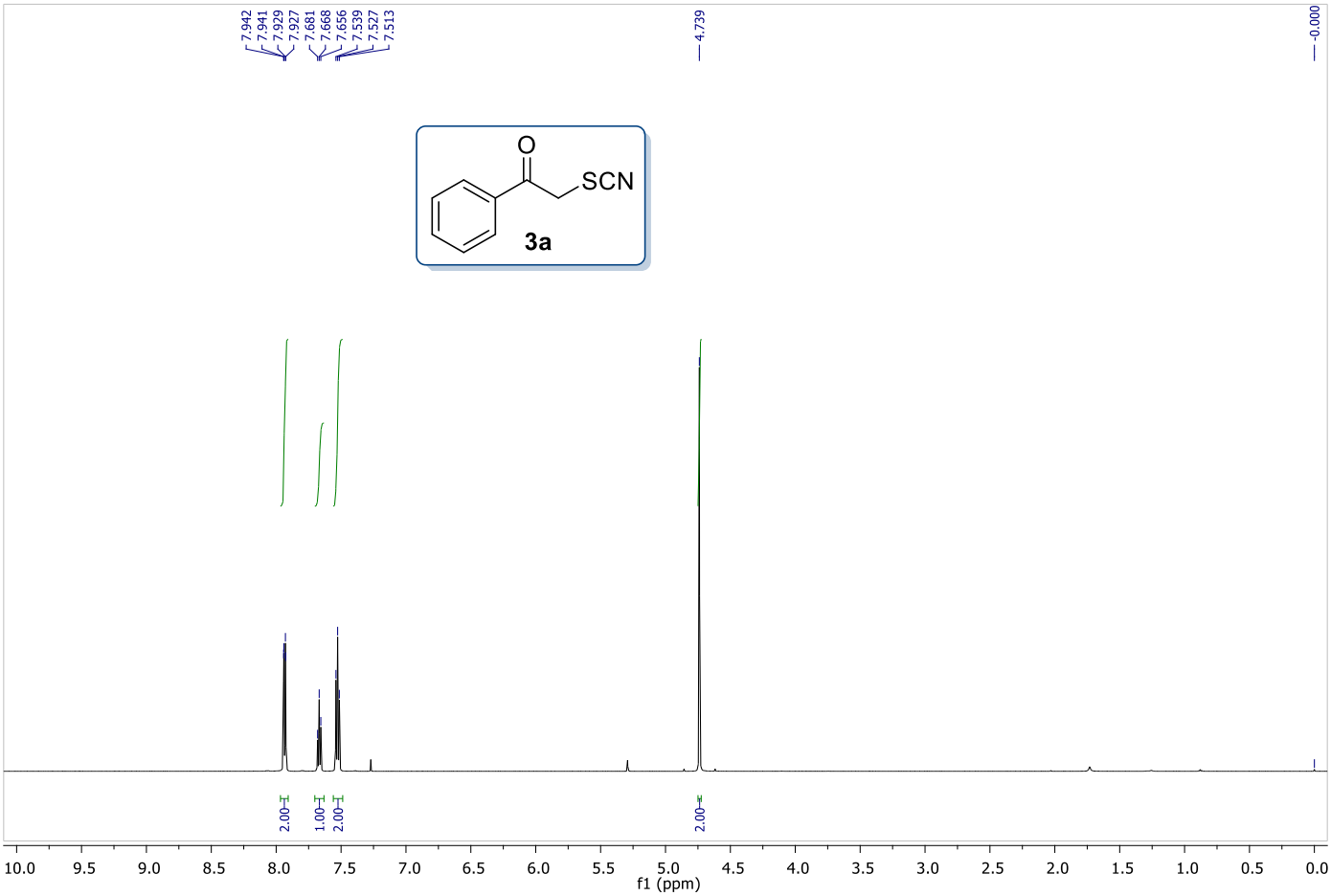
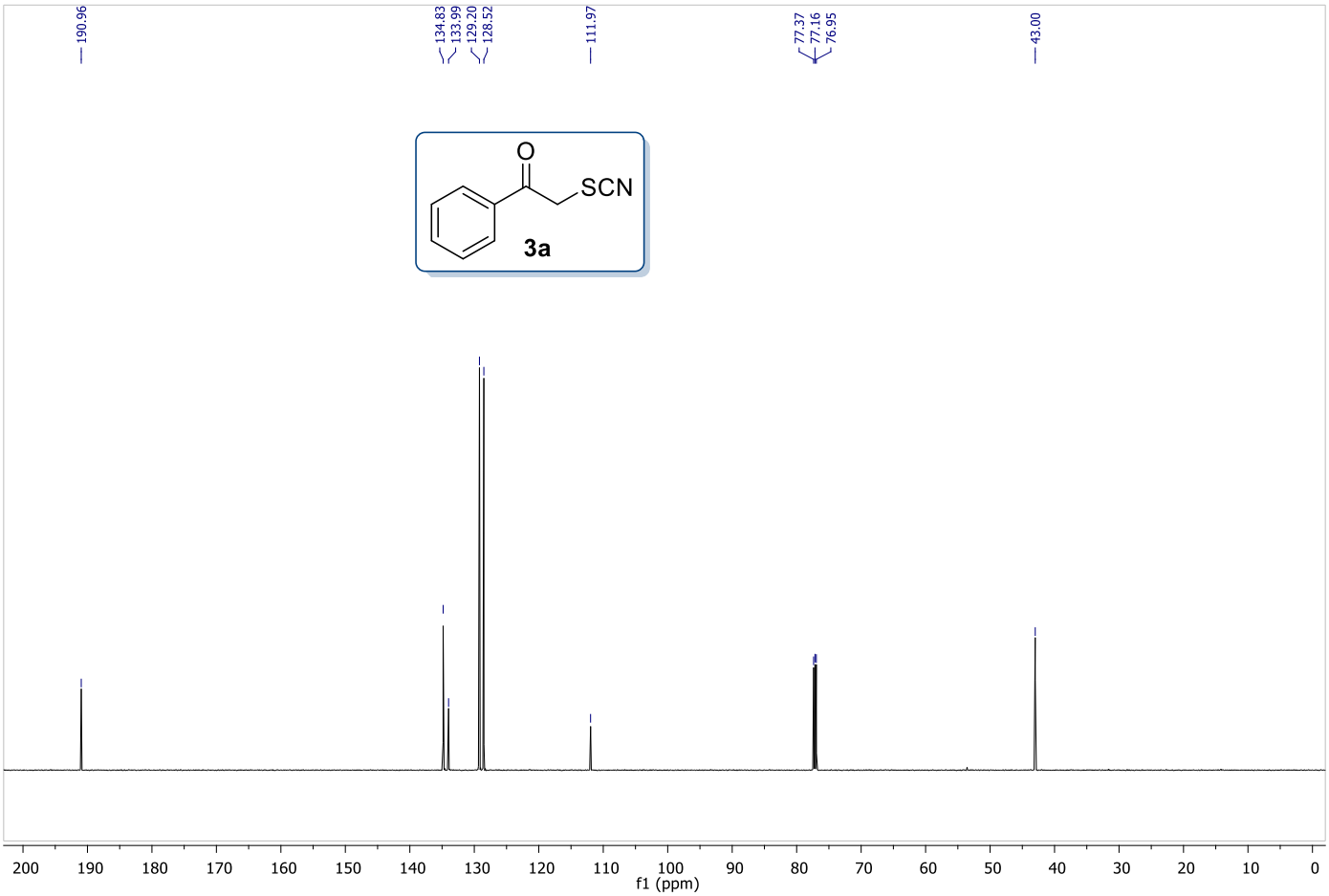
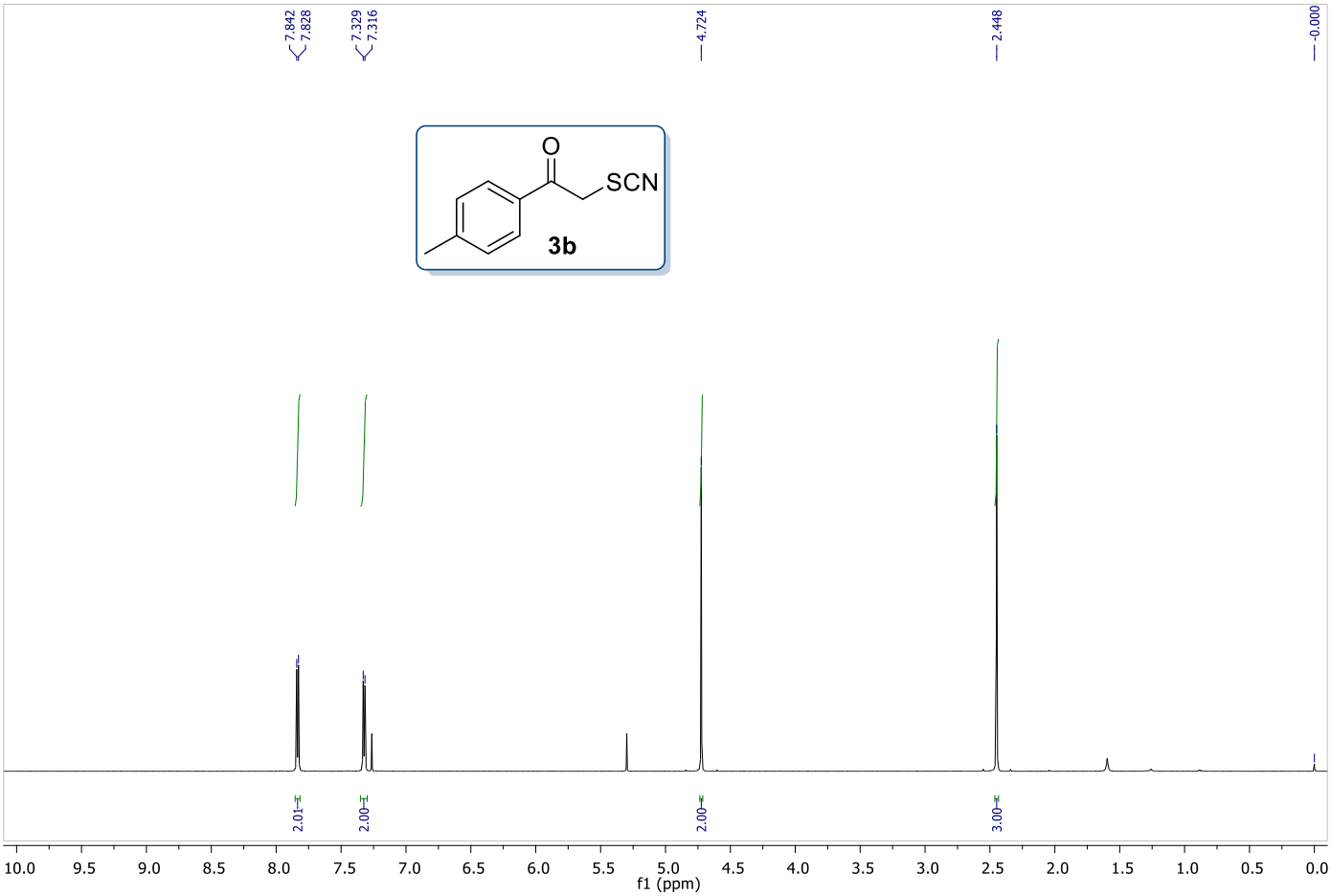
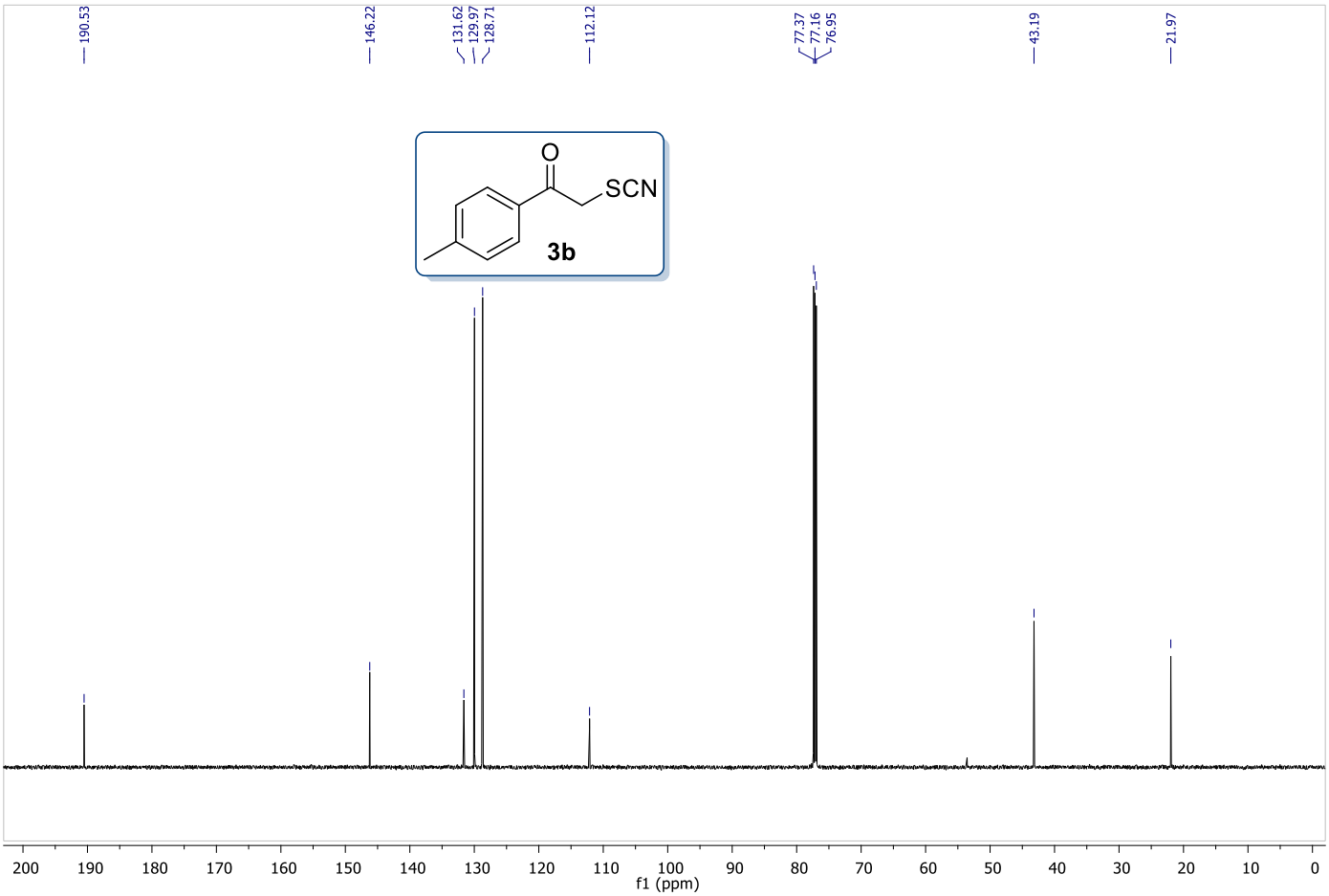


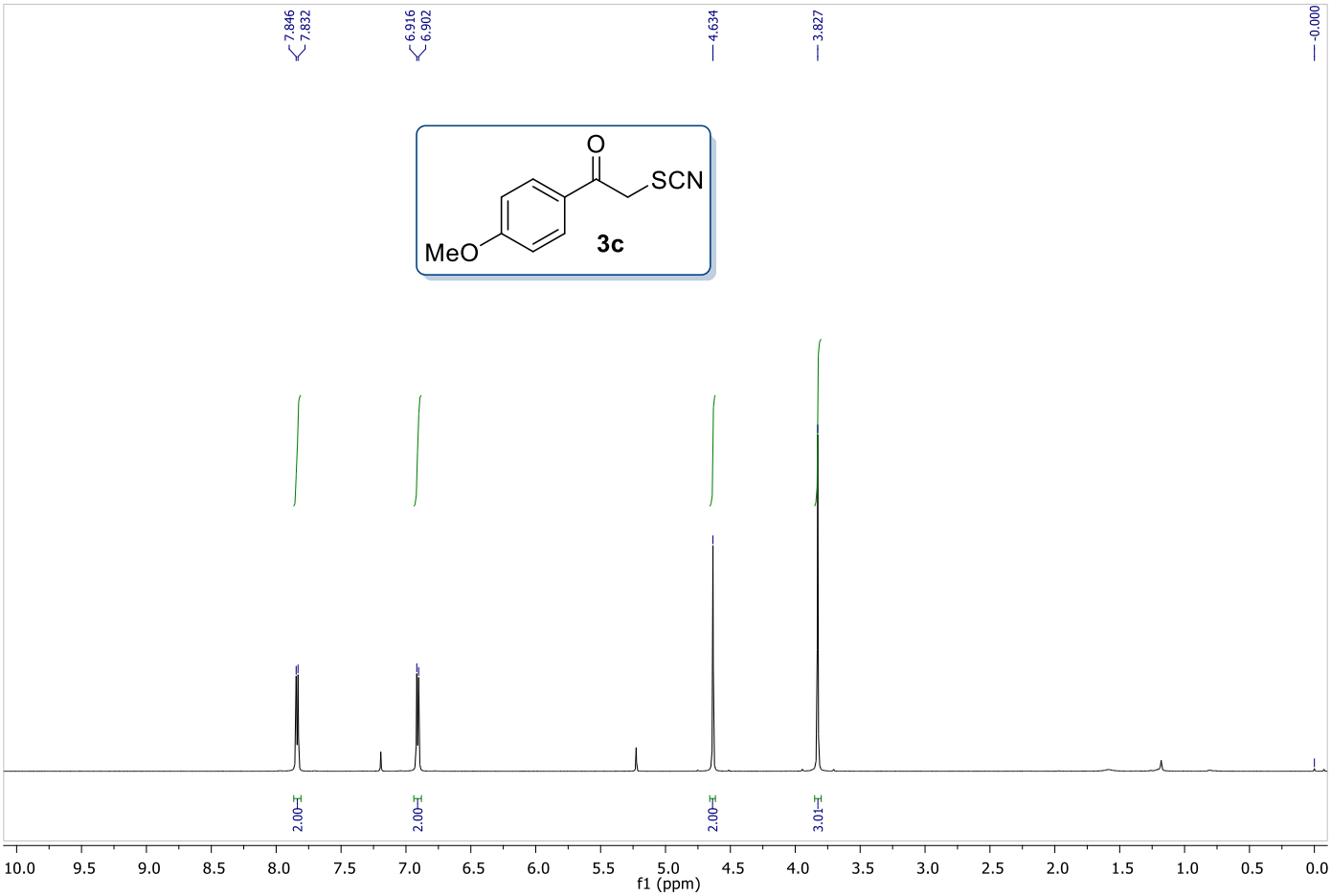


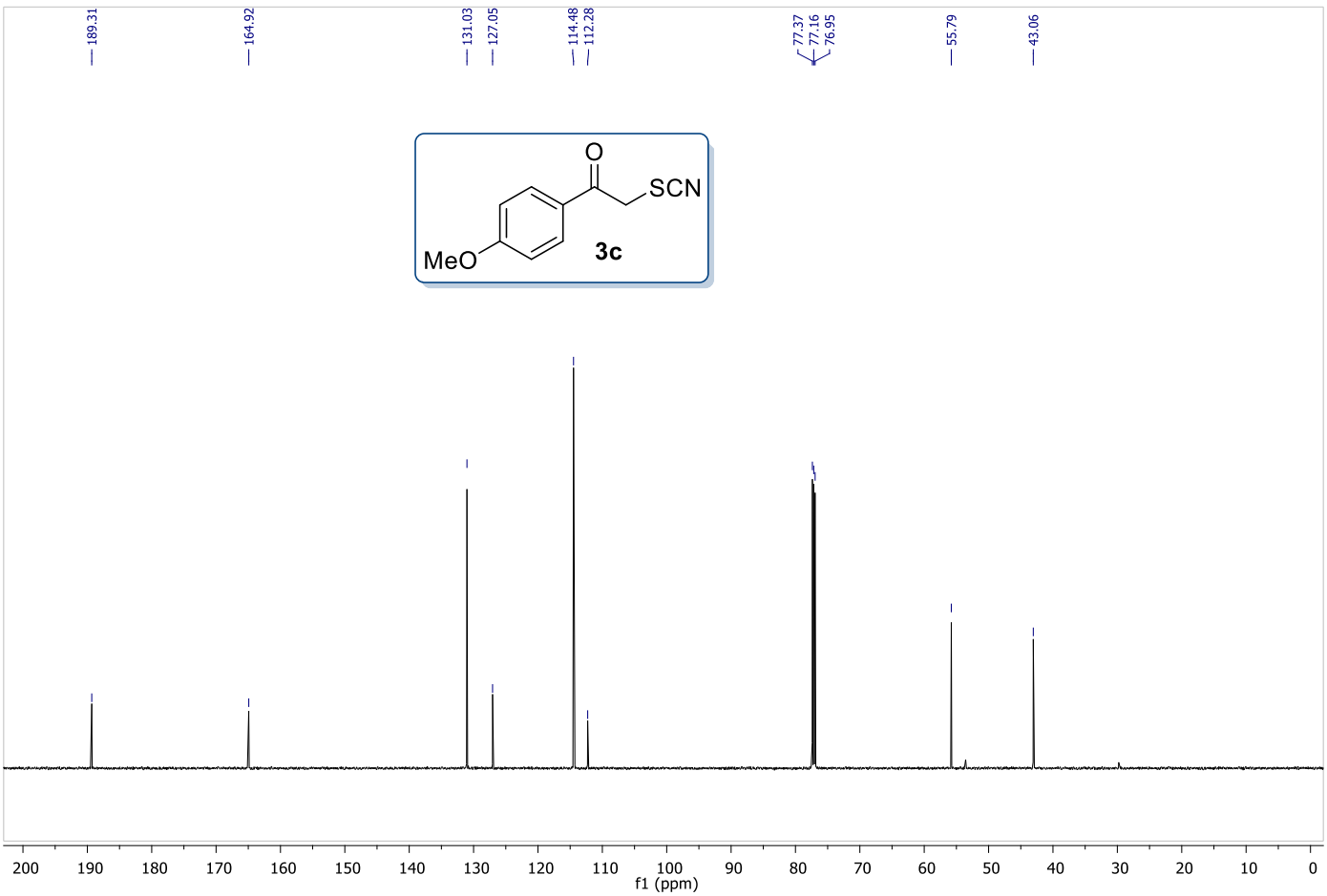
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3b**



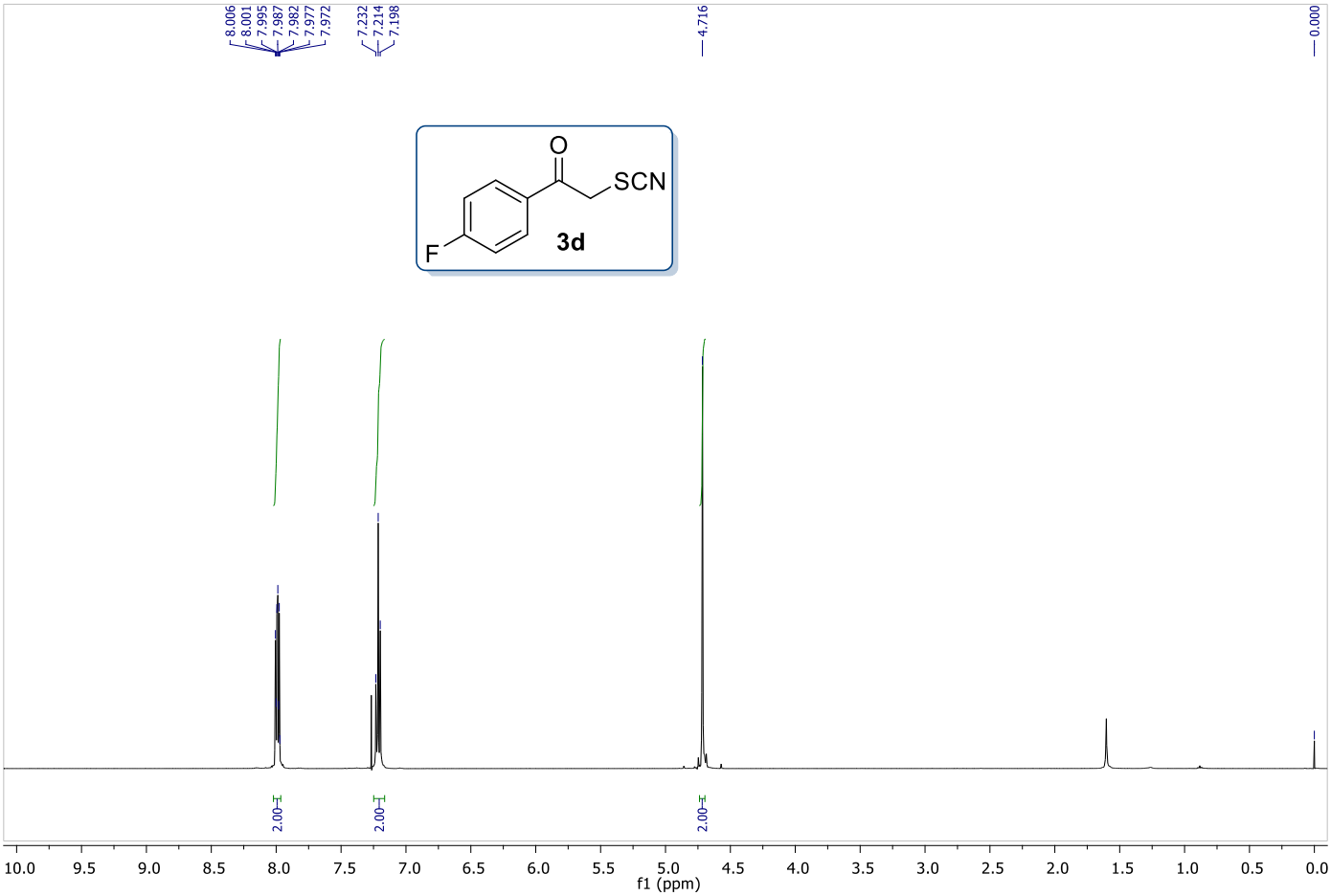


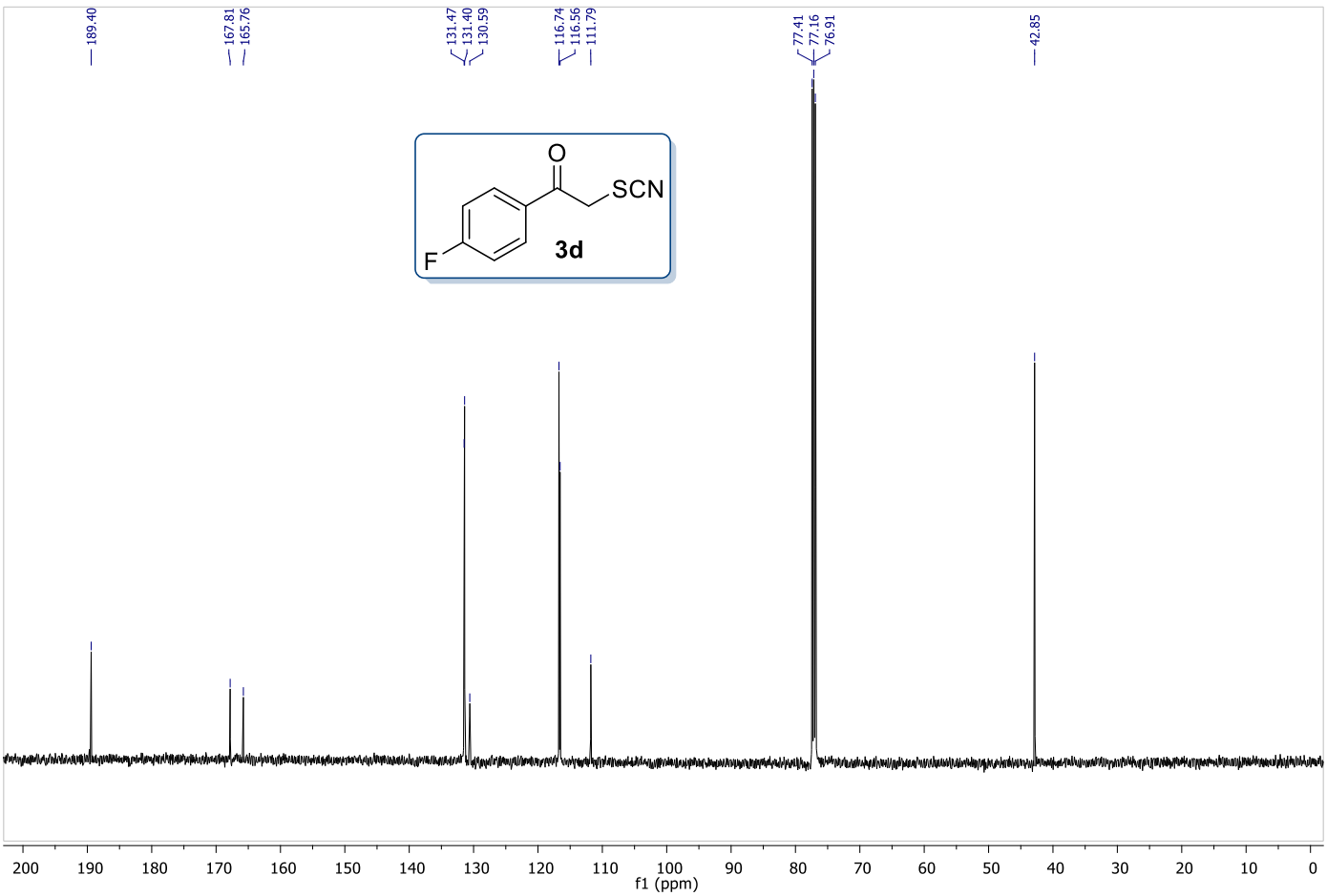
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3c**



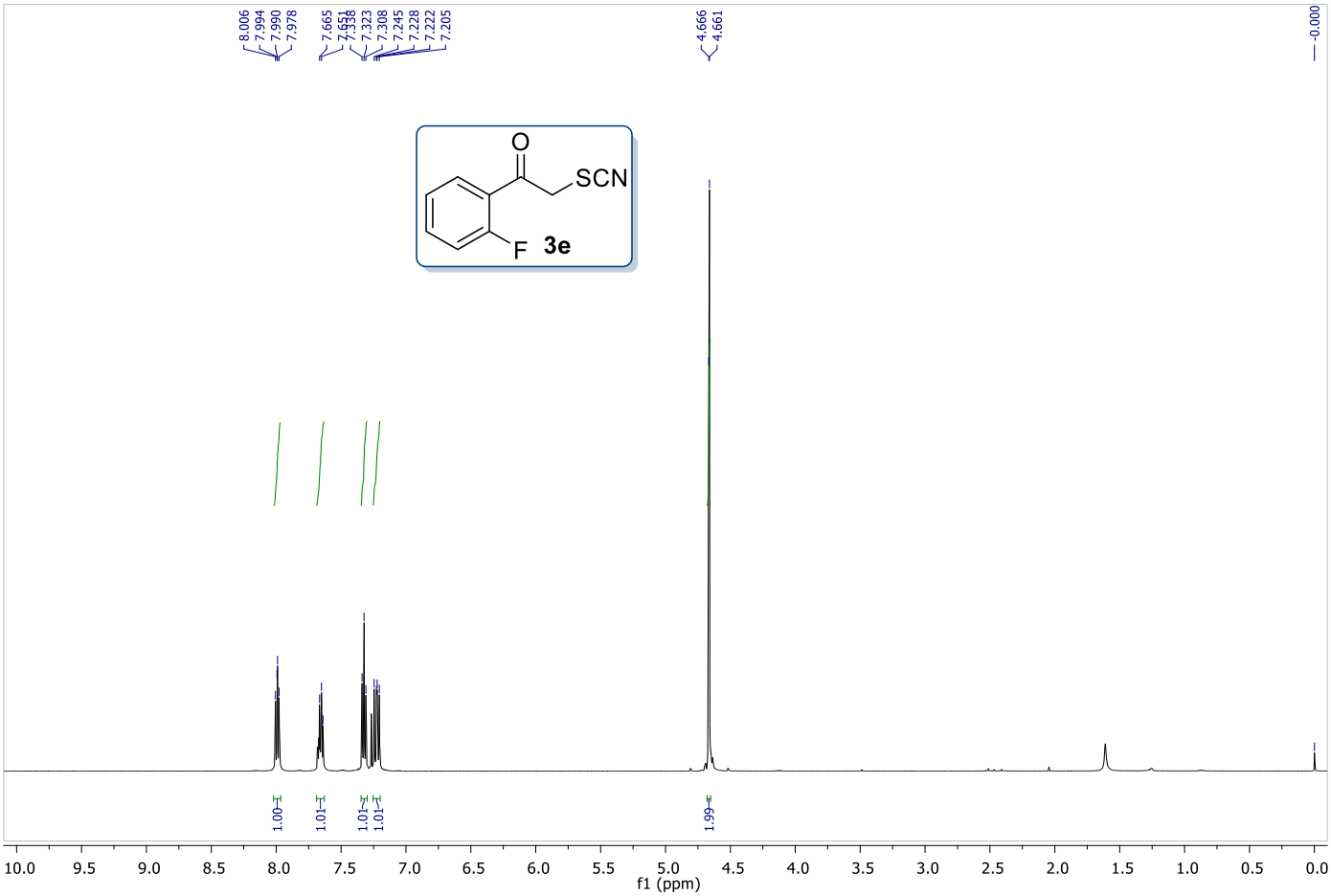


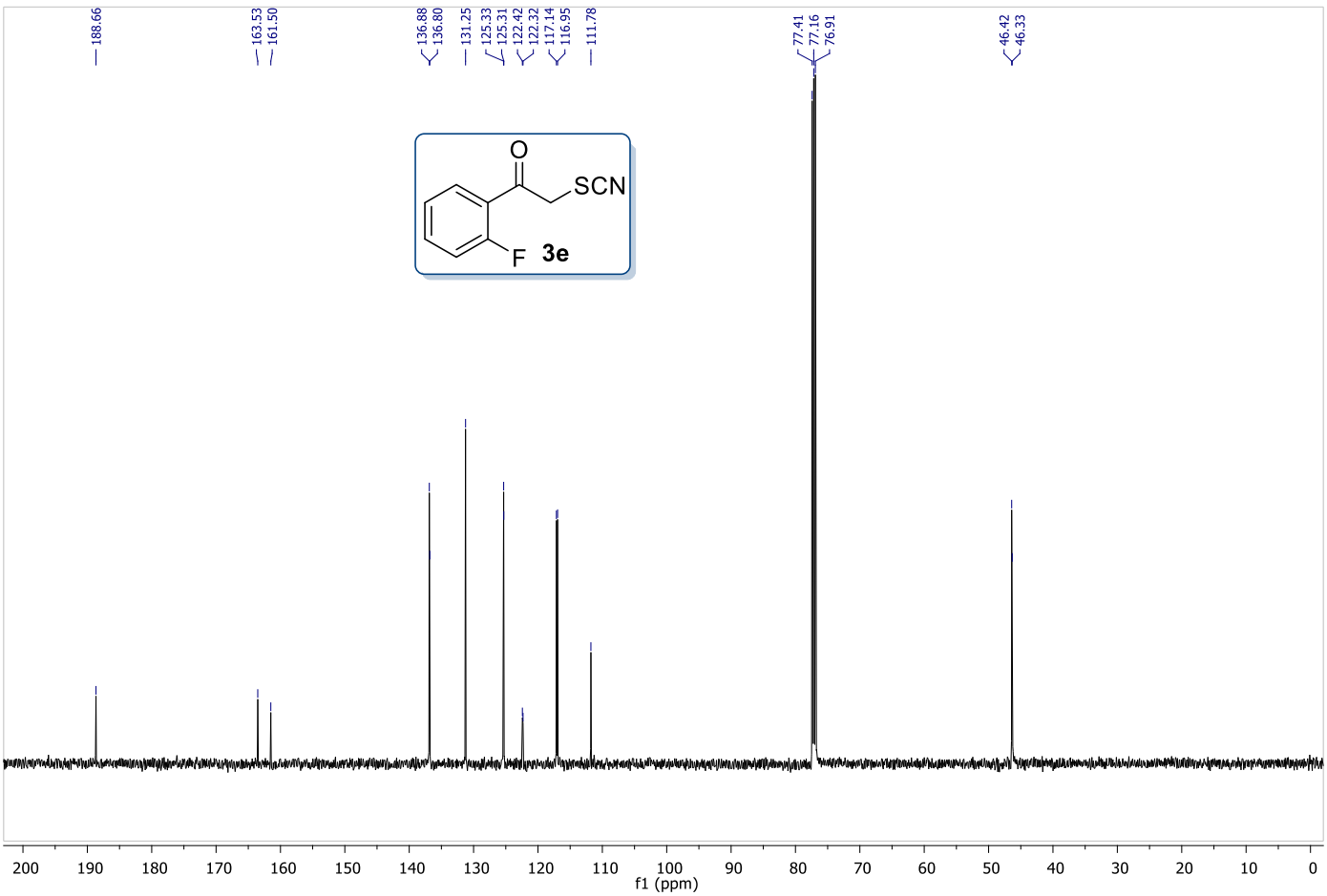
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3d**



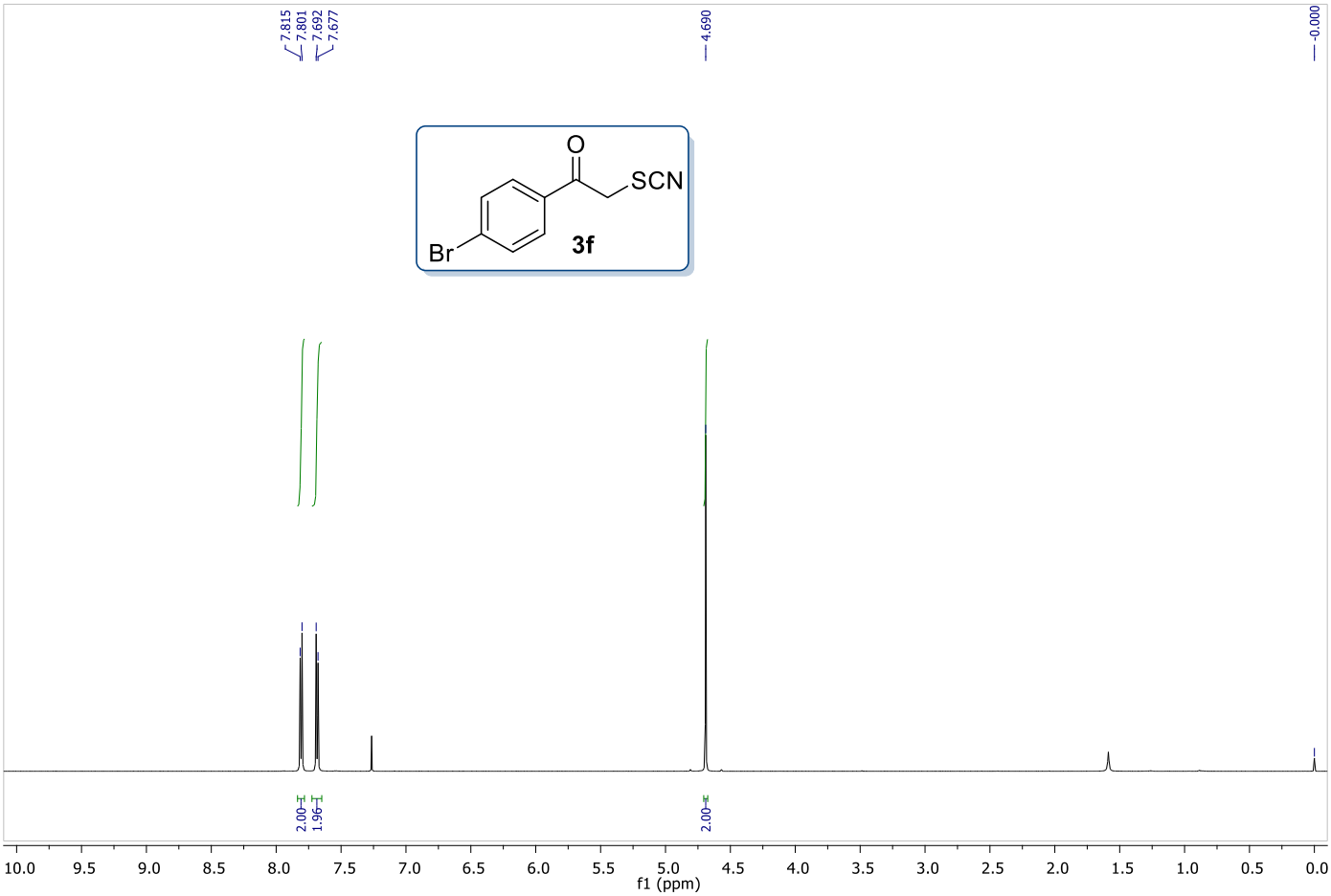


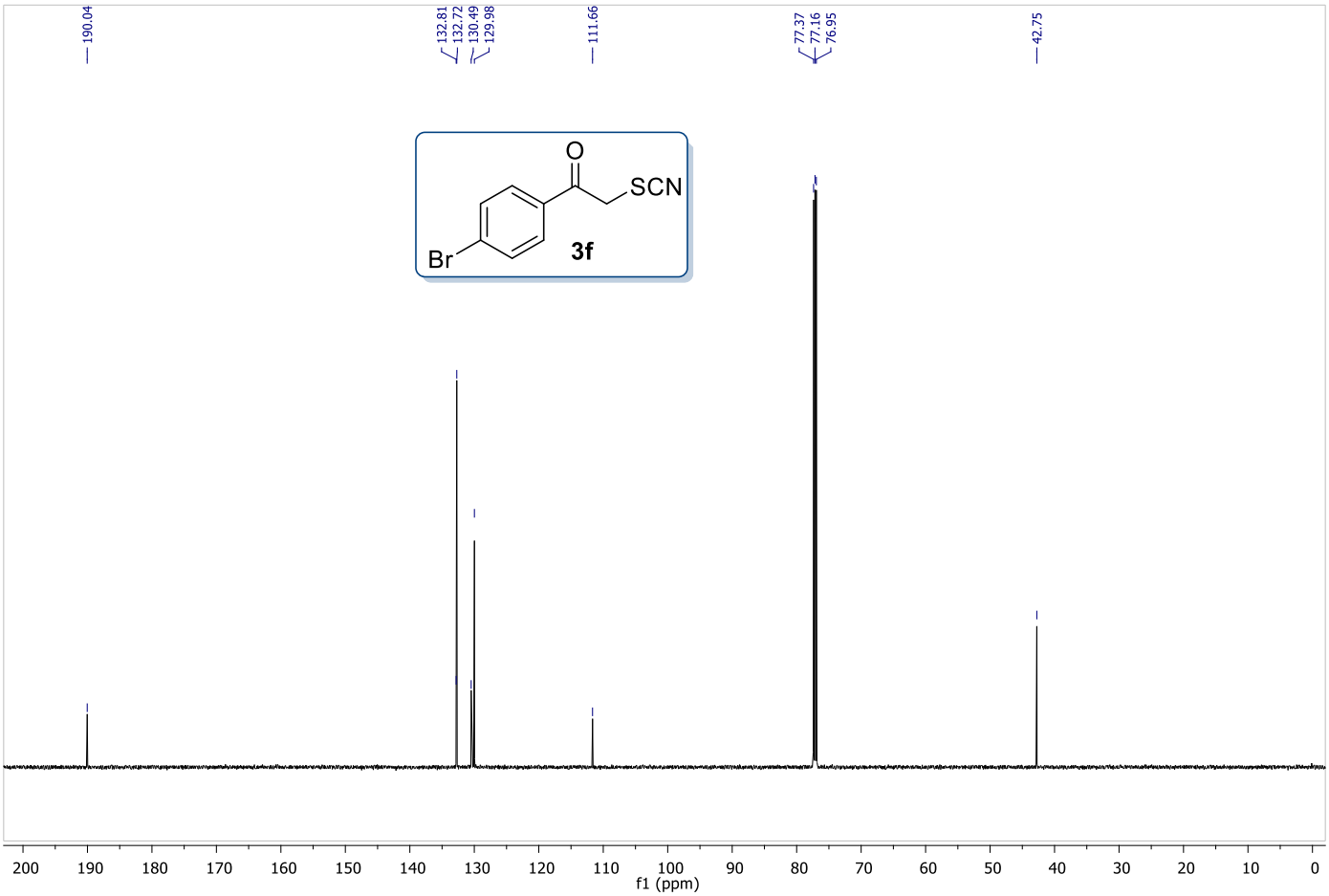
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3e**



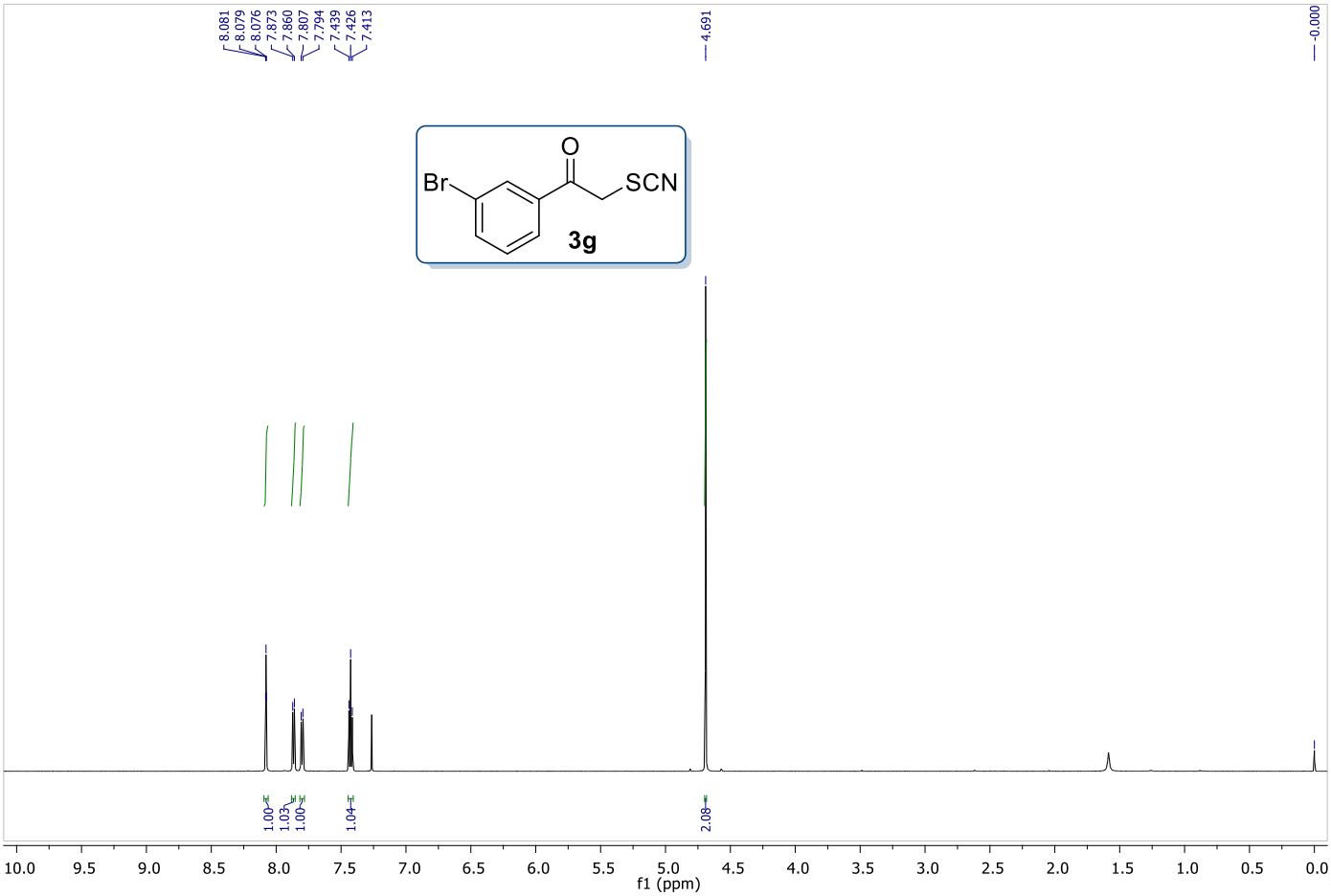


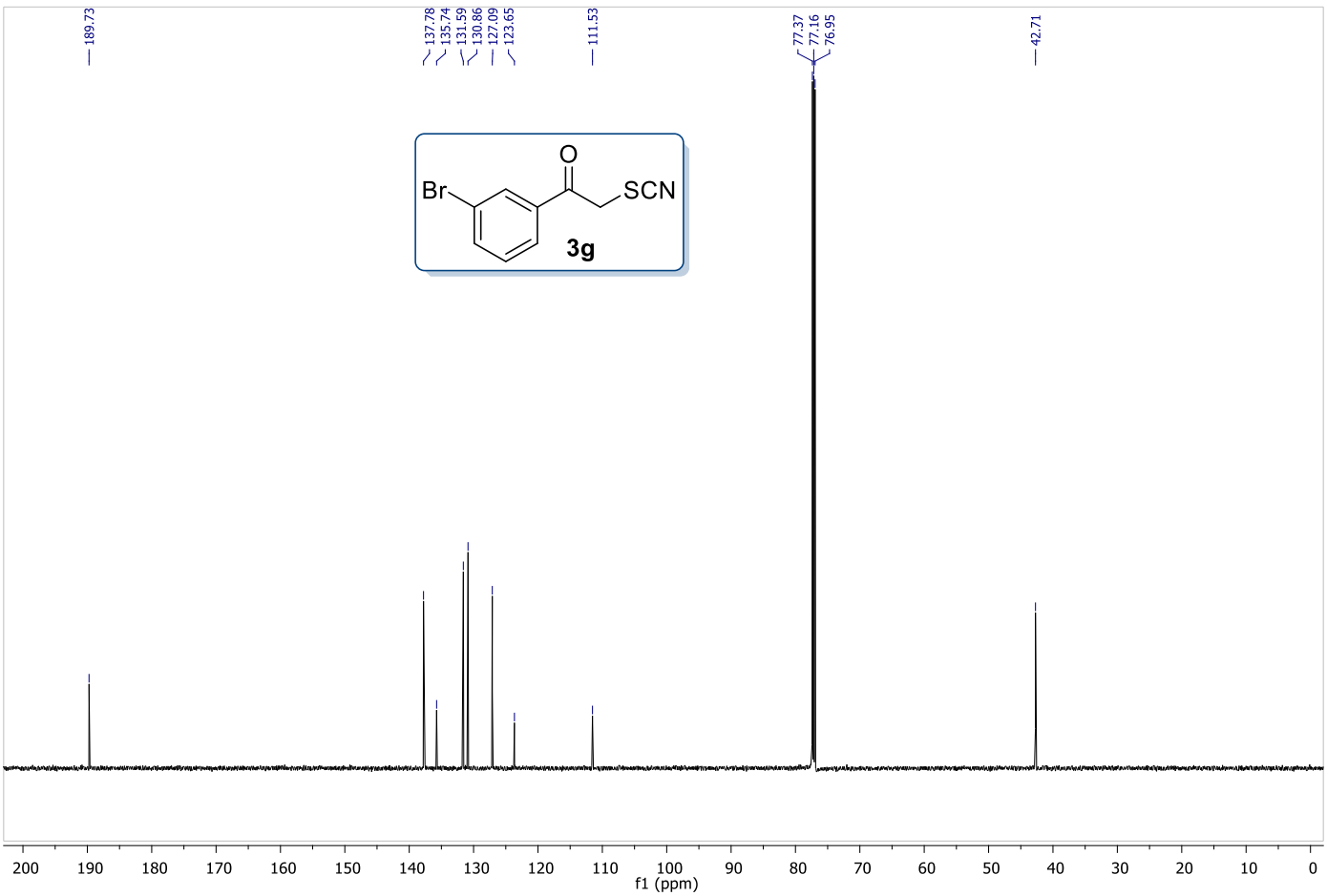
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3f**



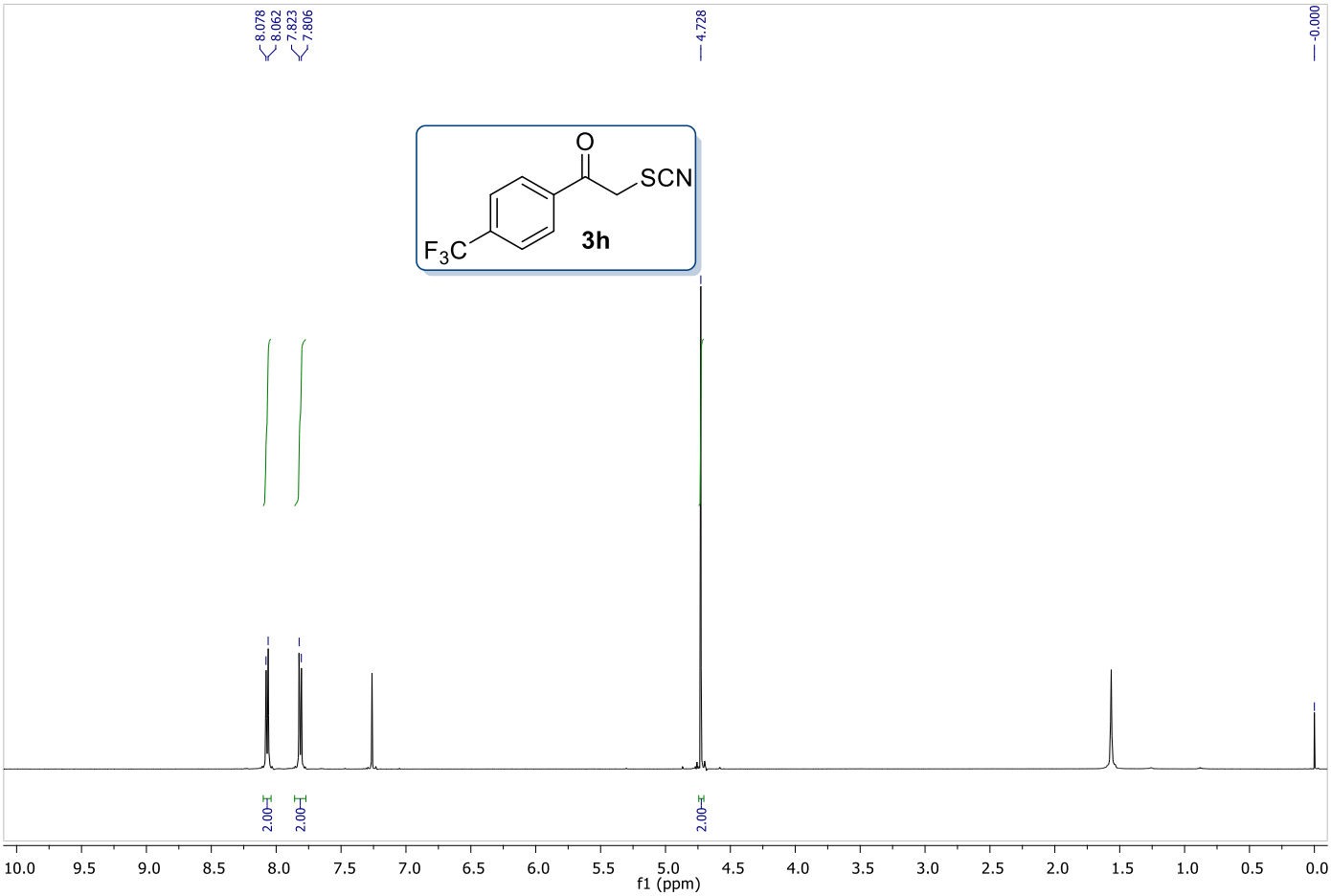


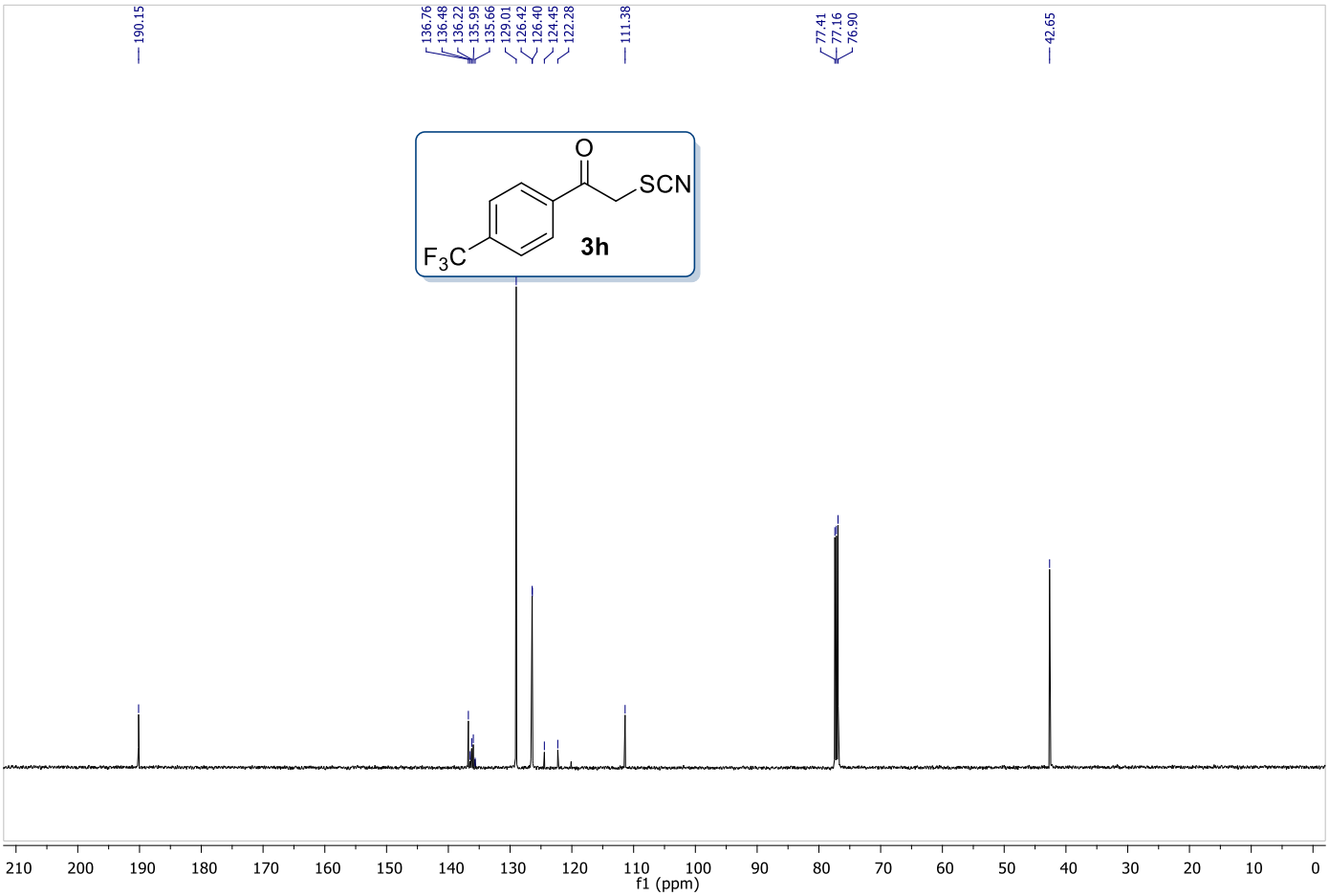
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3g**



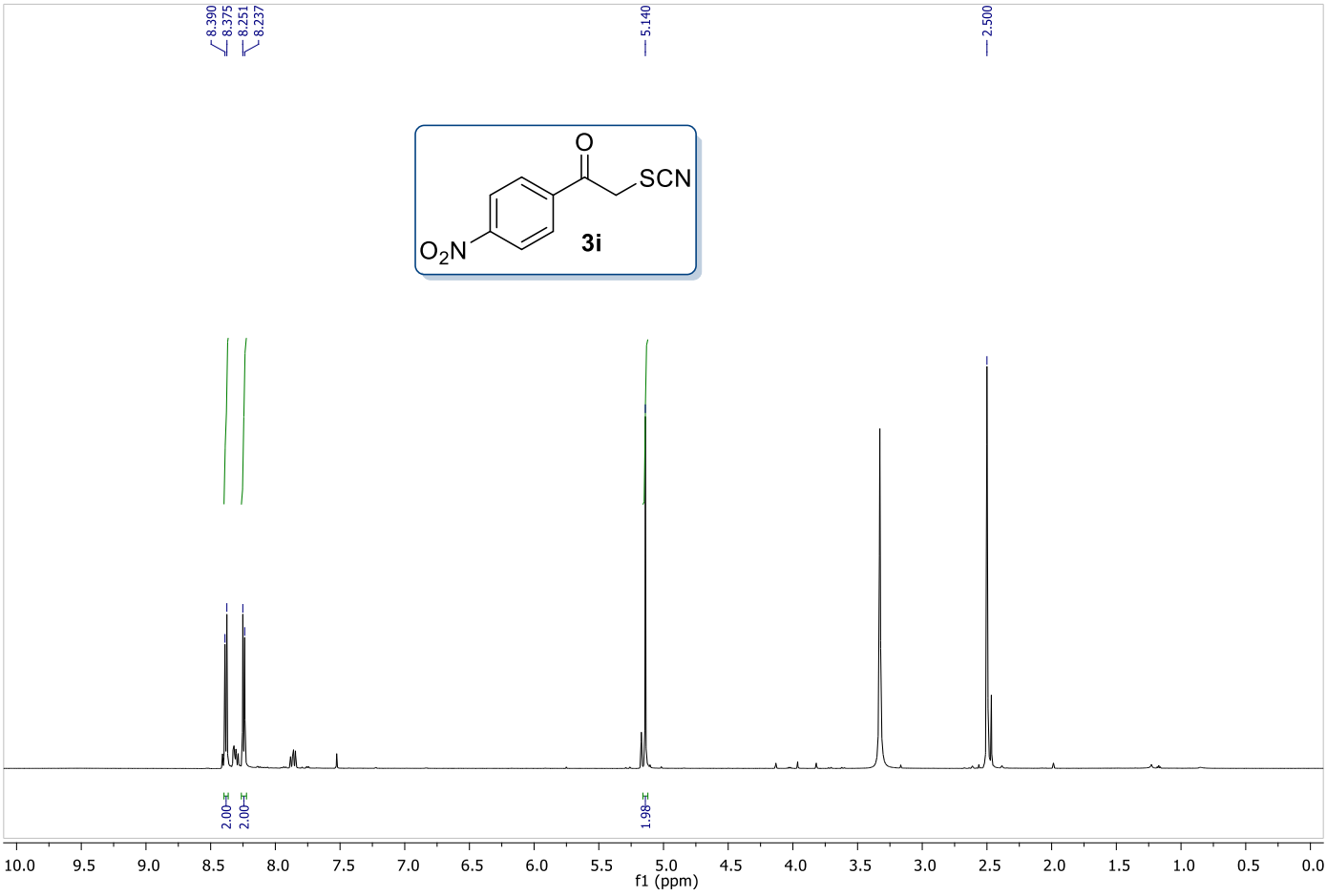


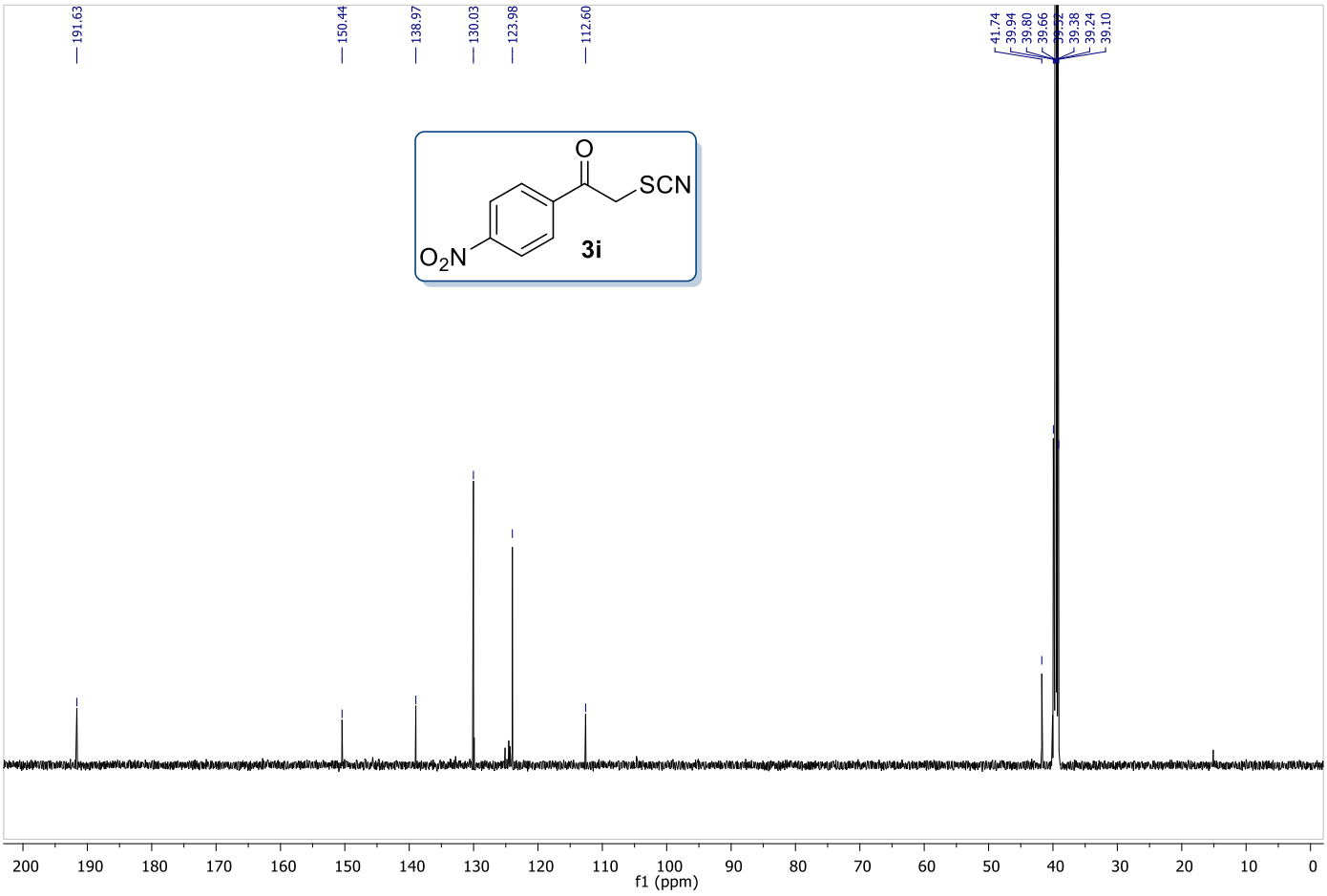
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3h**



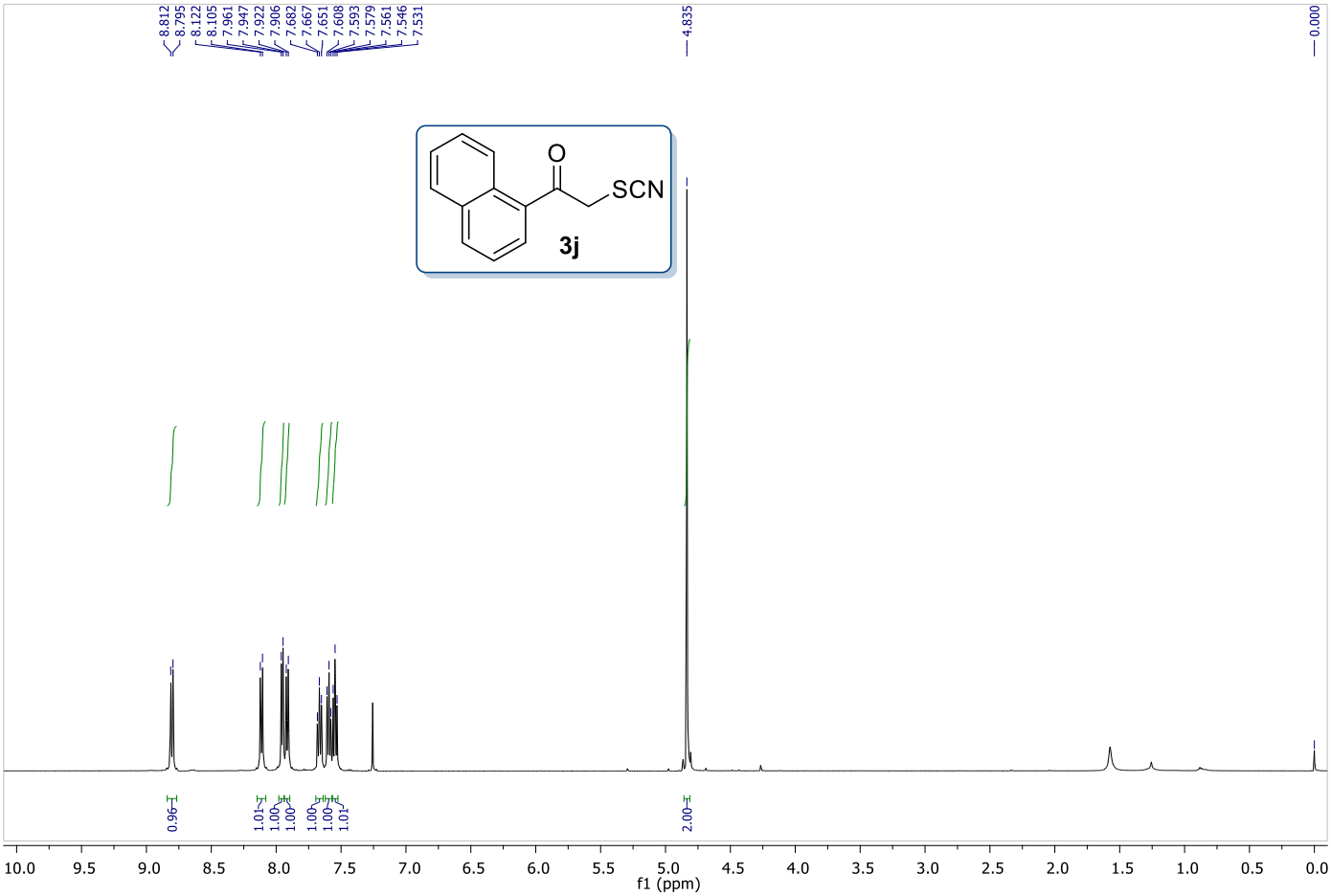


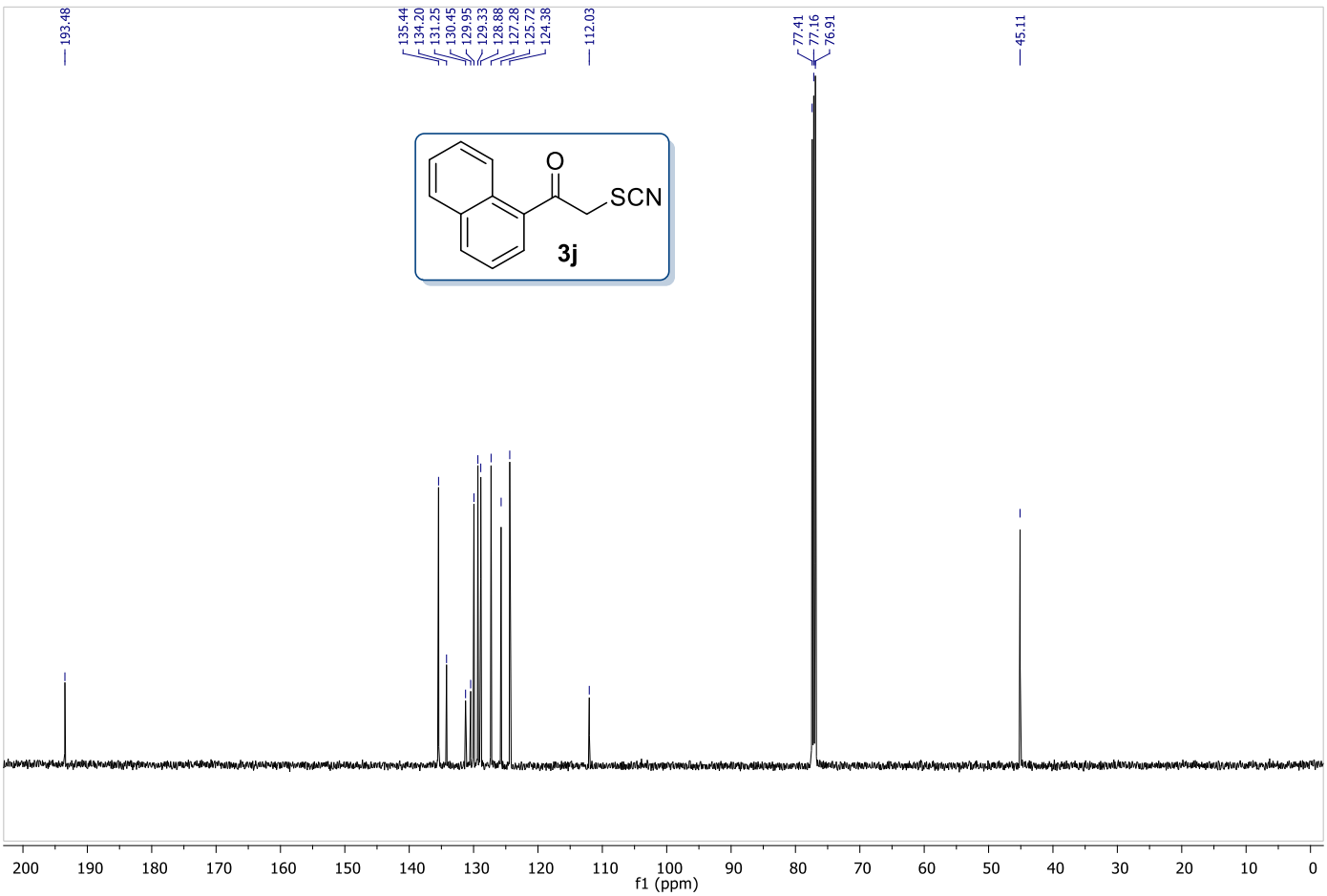
^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6), **3i**



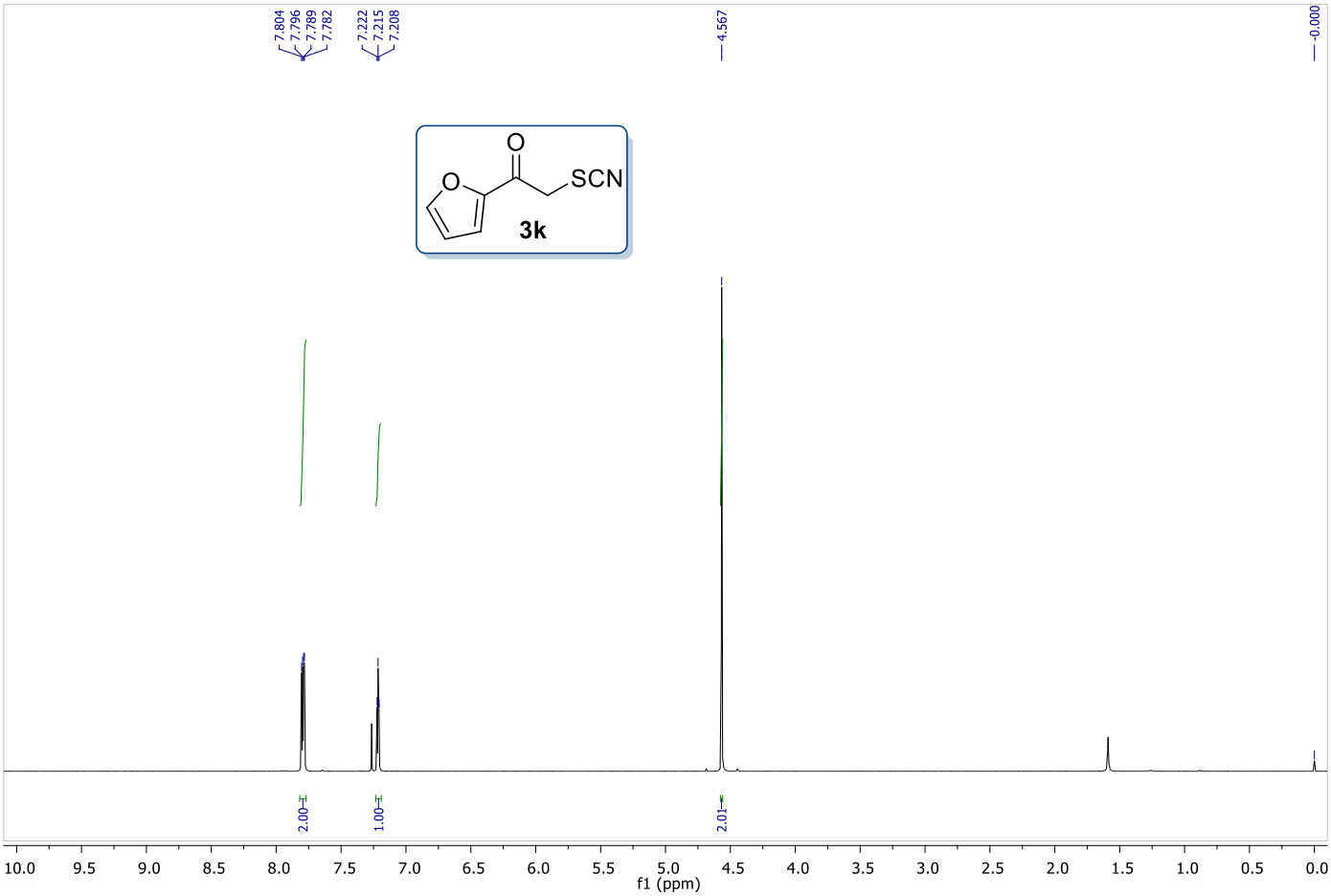


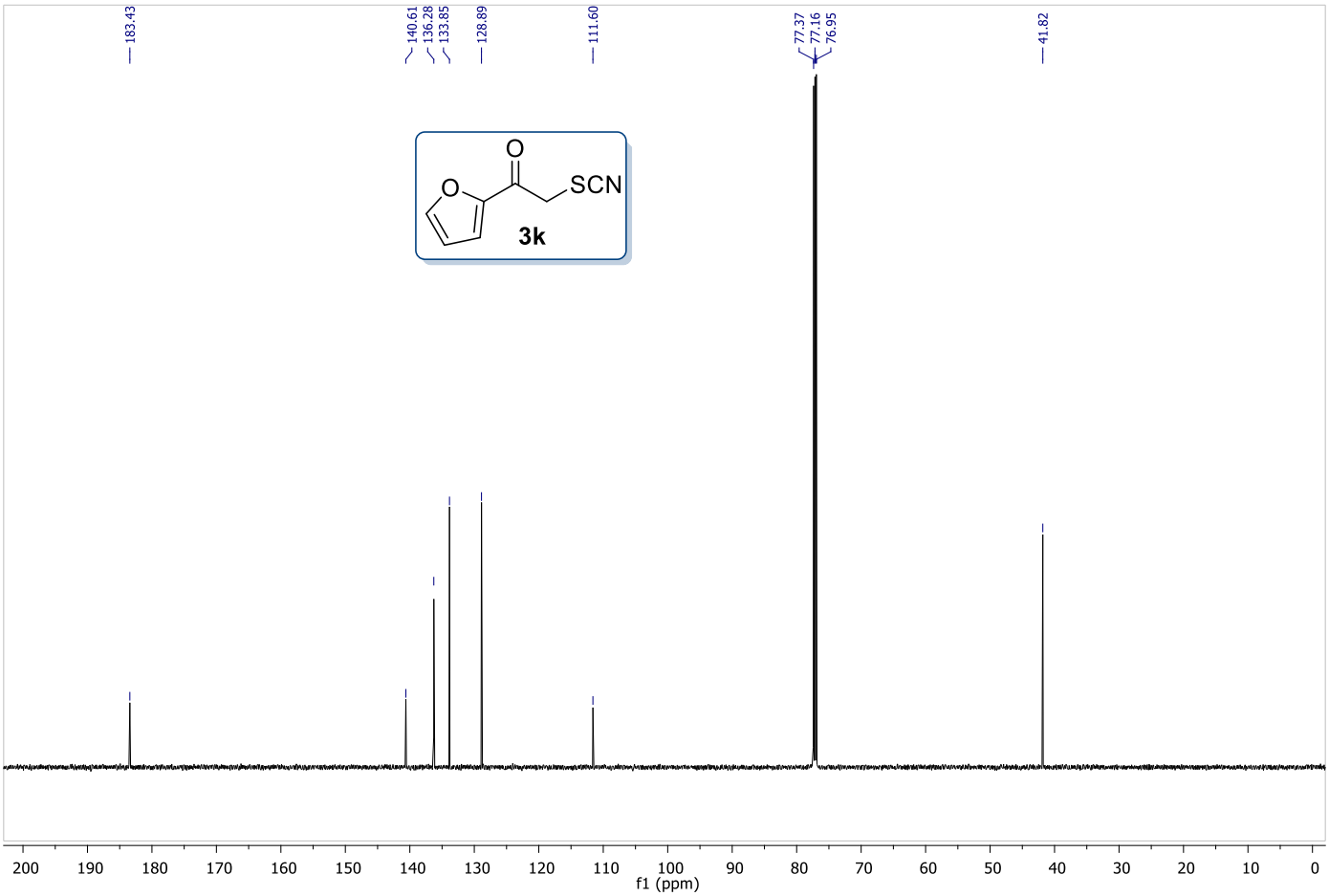
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **3j**



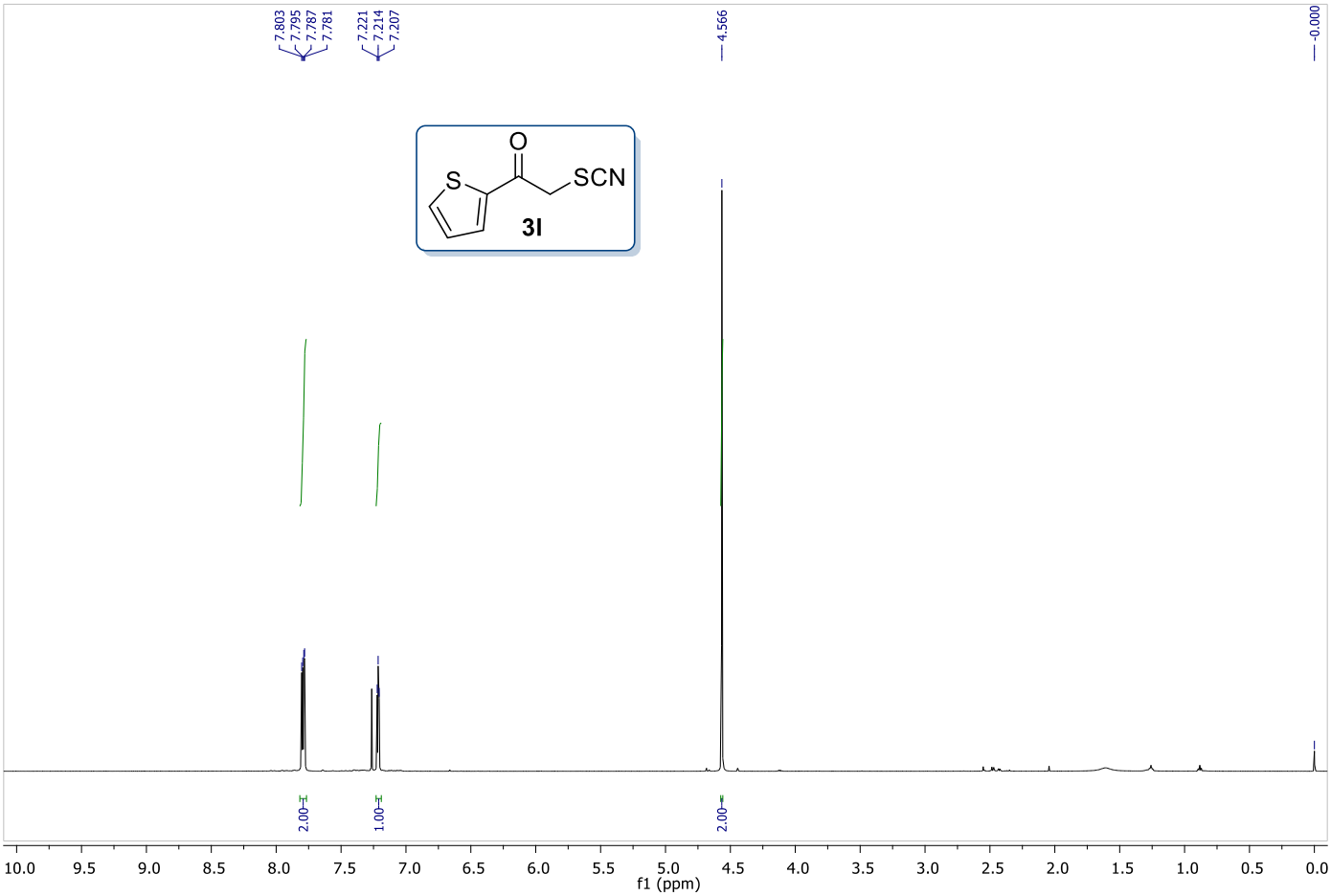


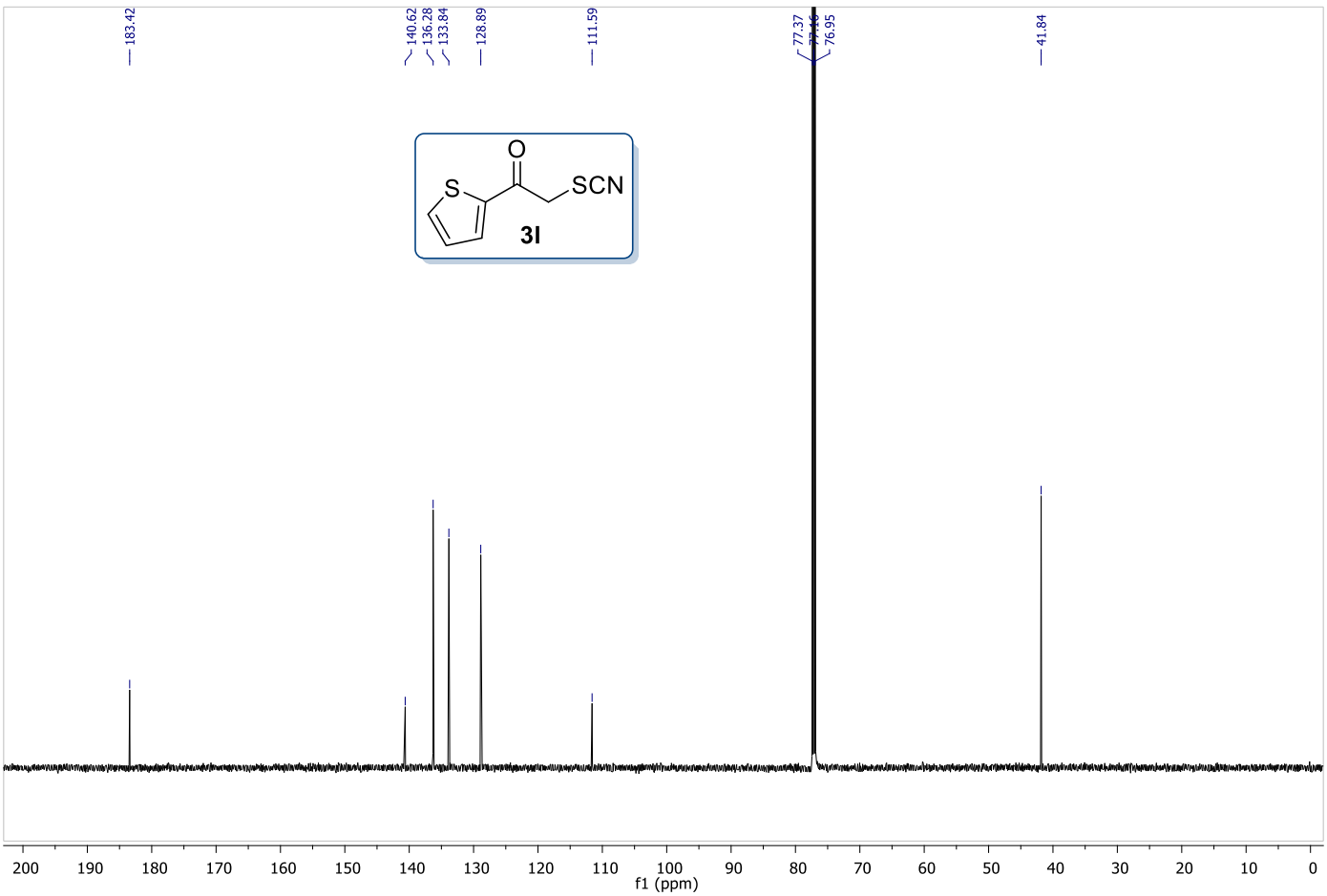
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3k**



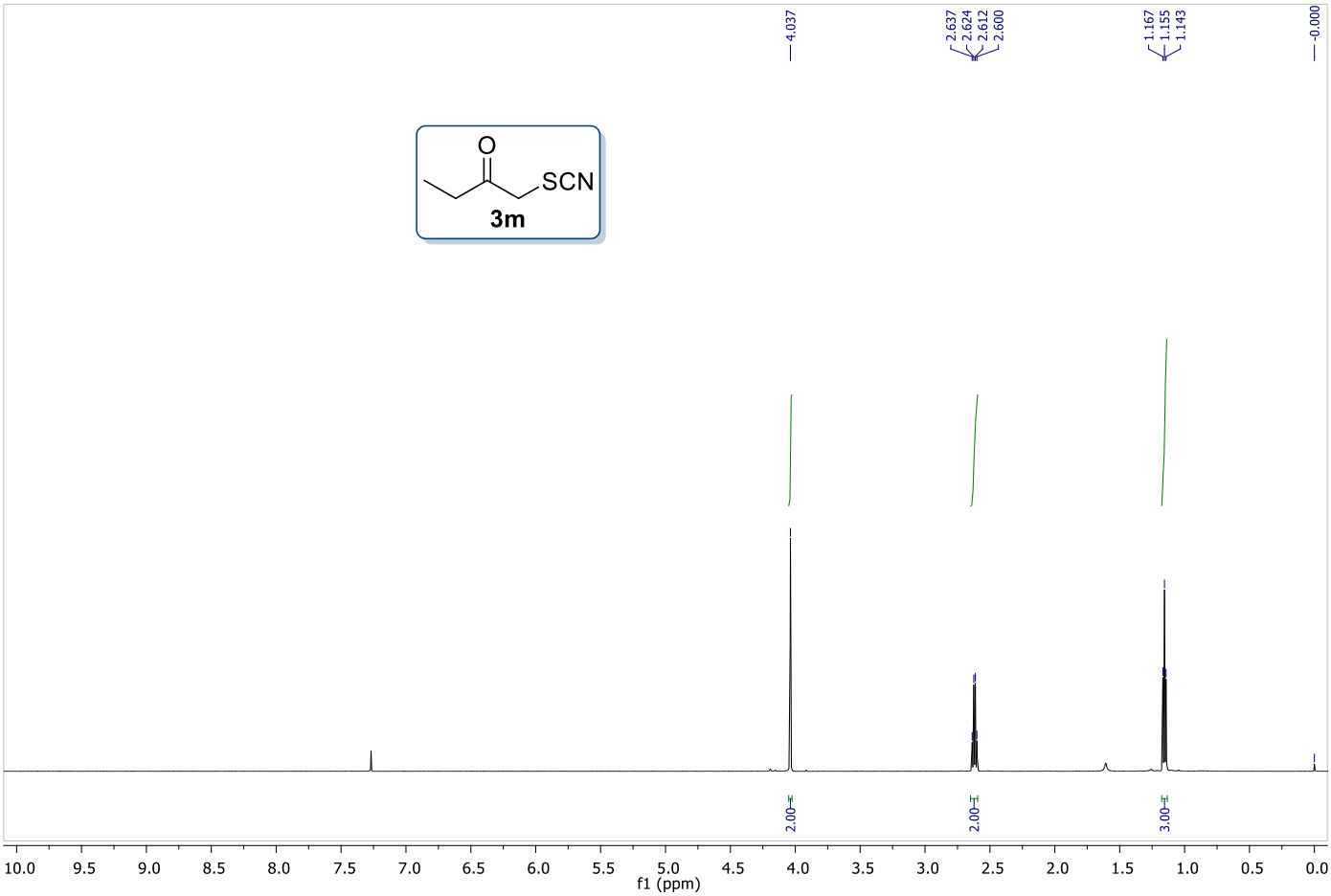


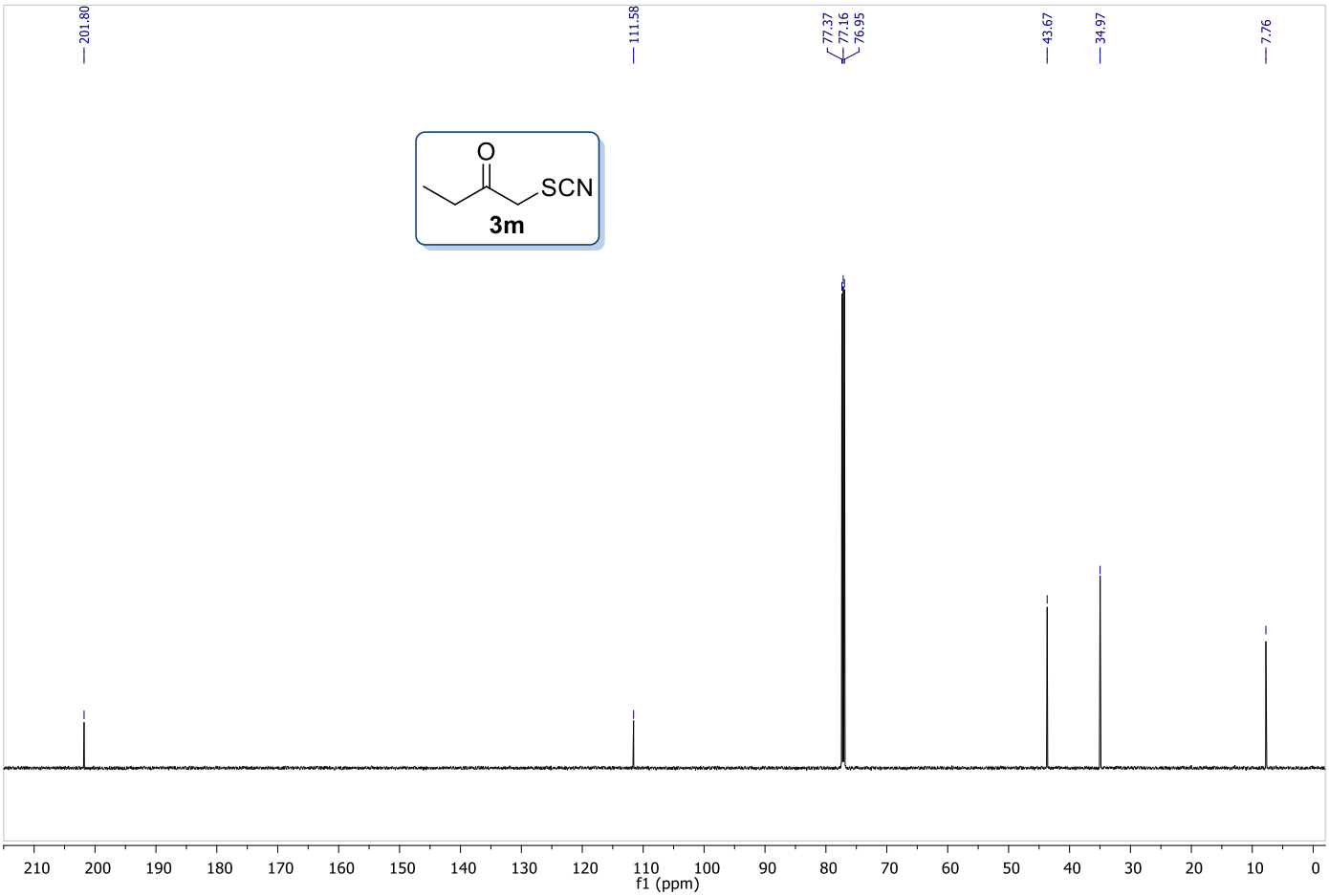
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3l**



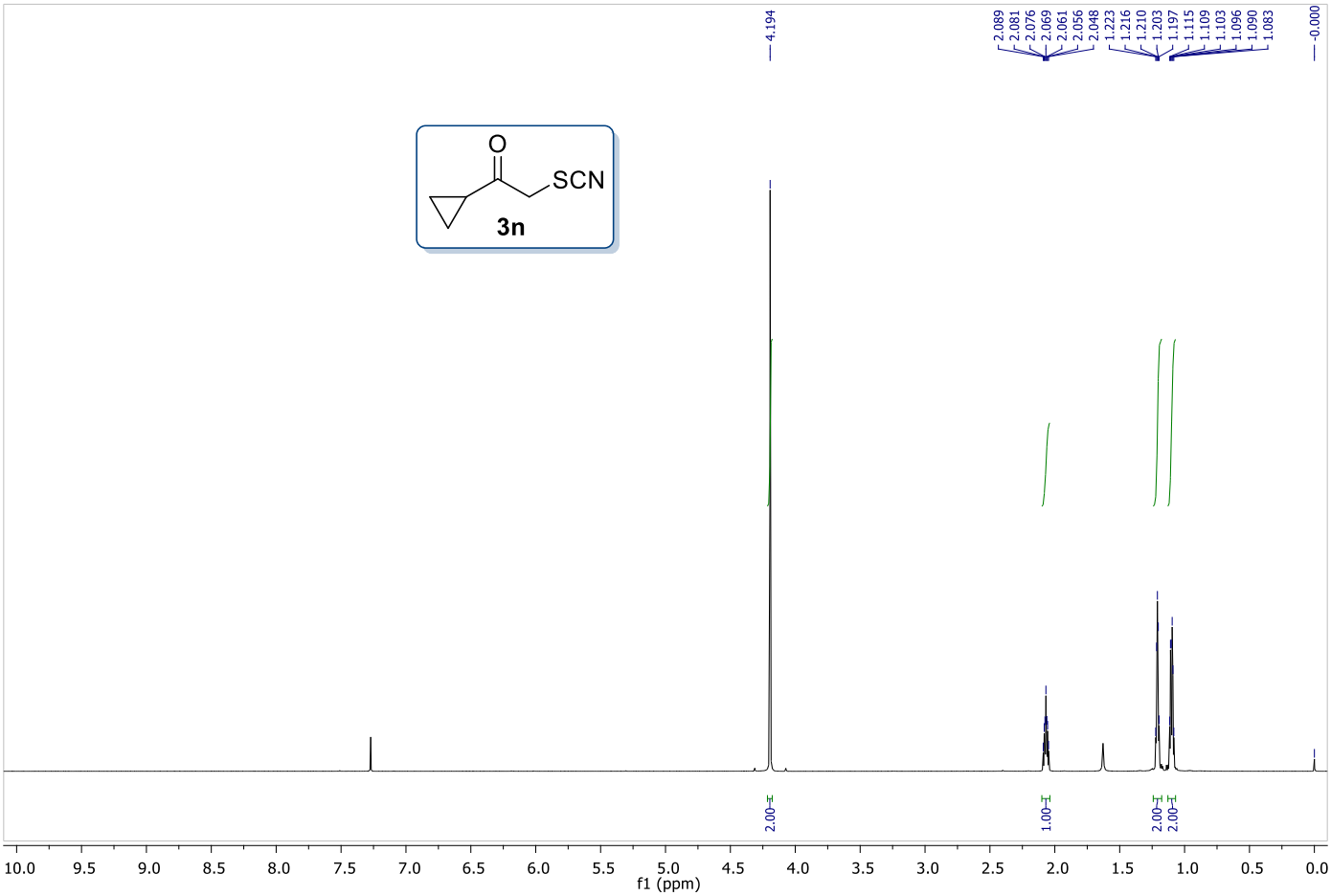


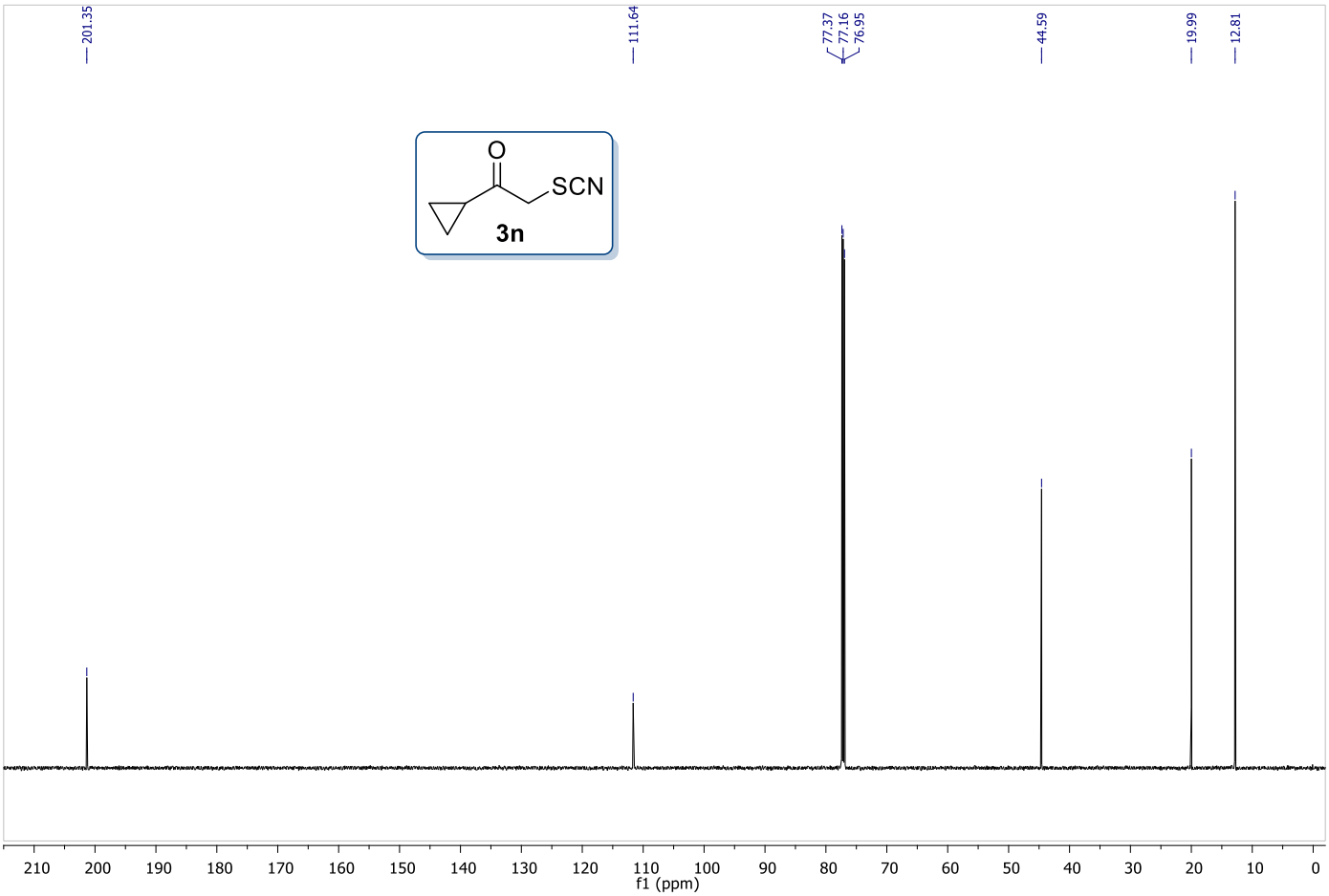
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3m**



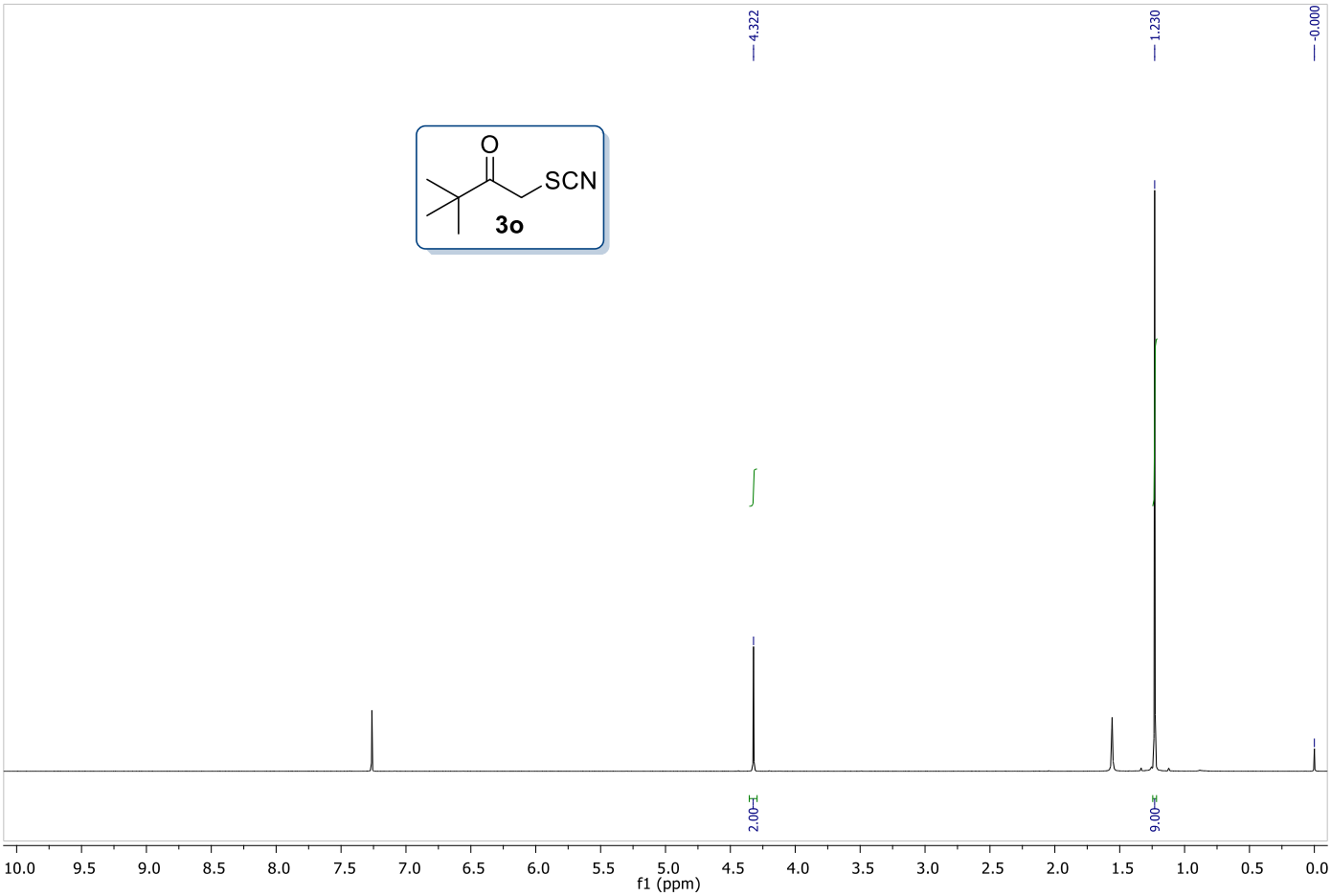


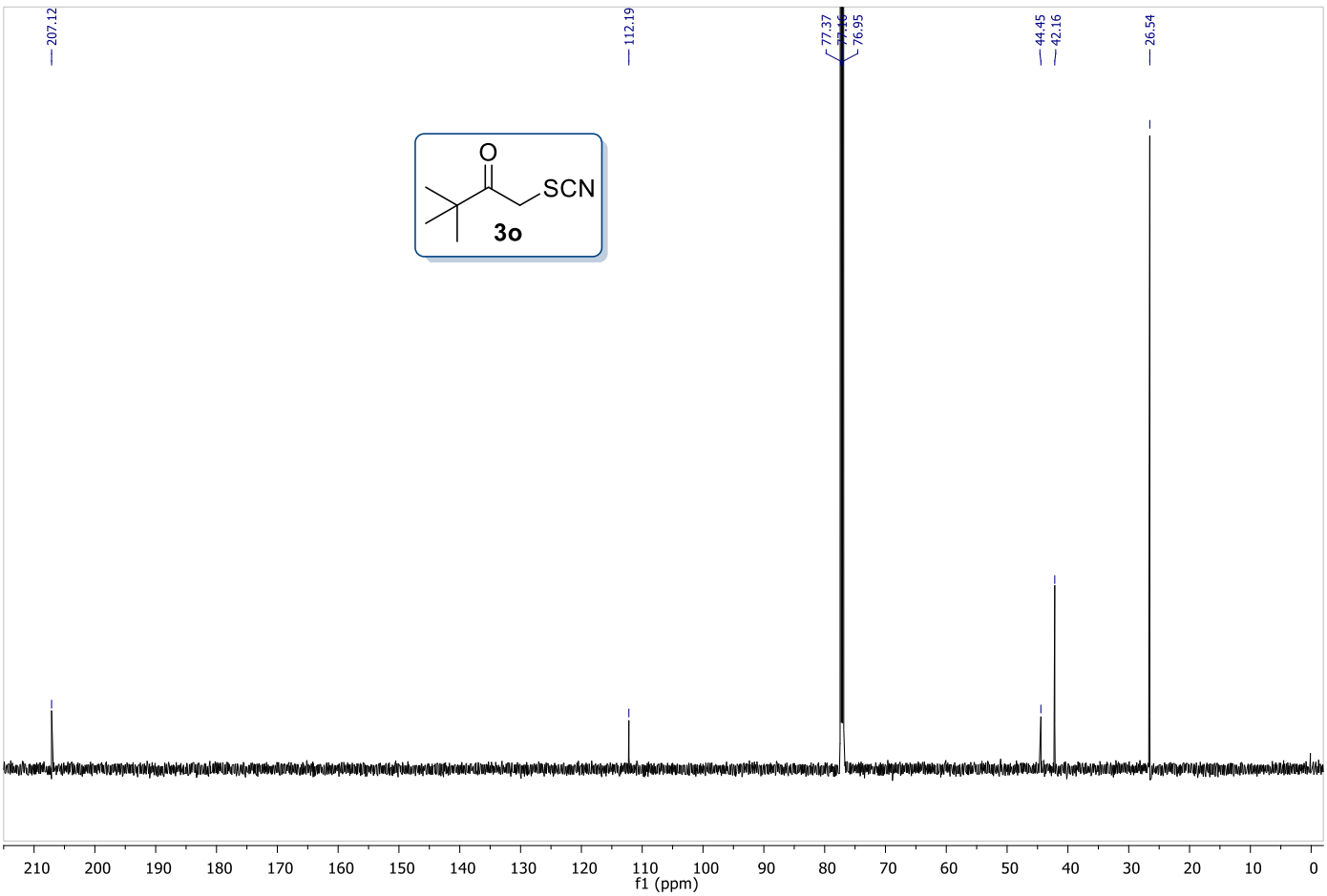
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3n**



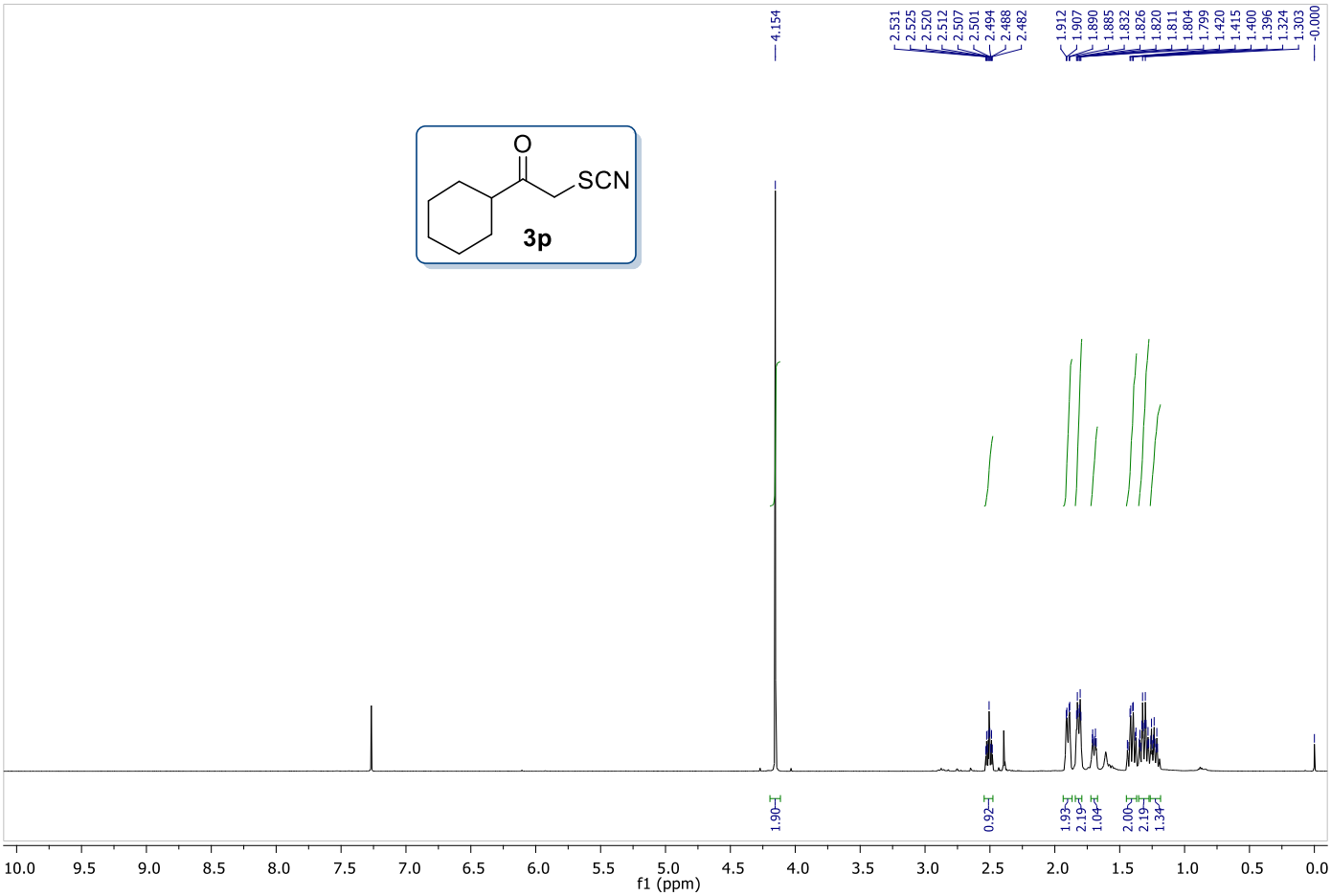


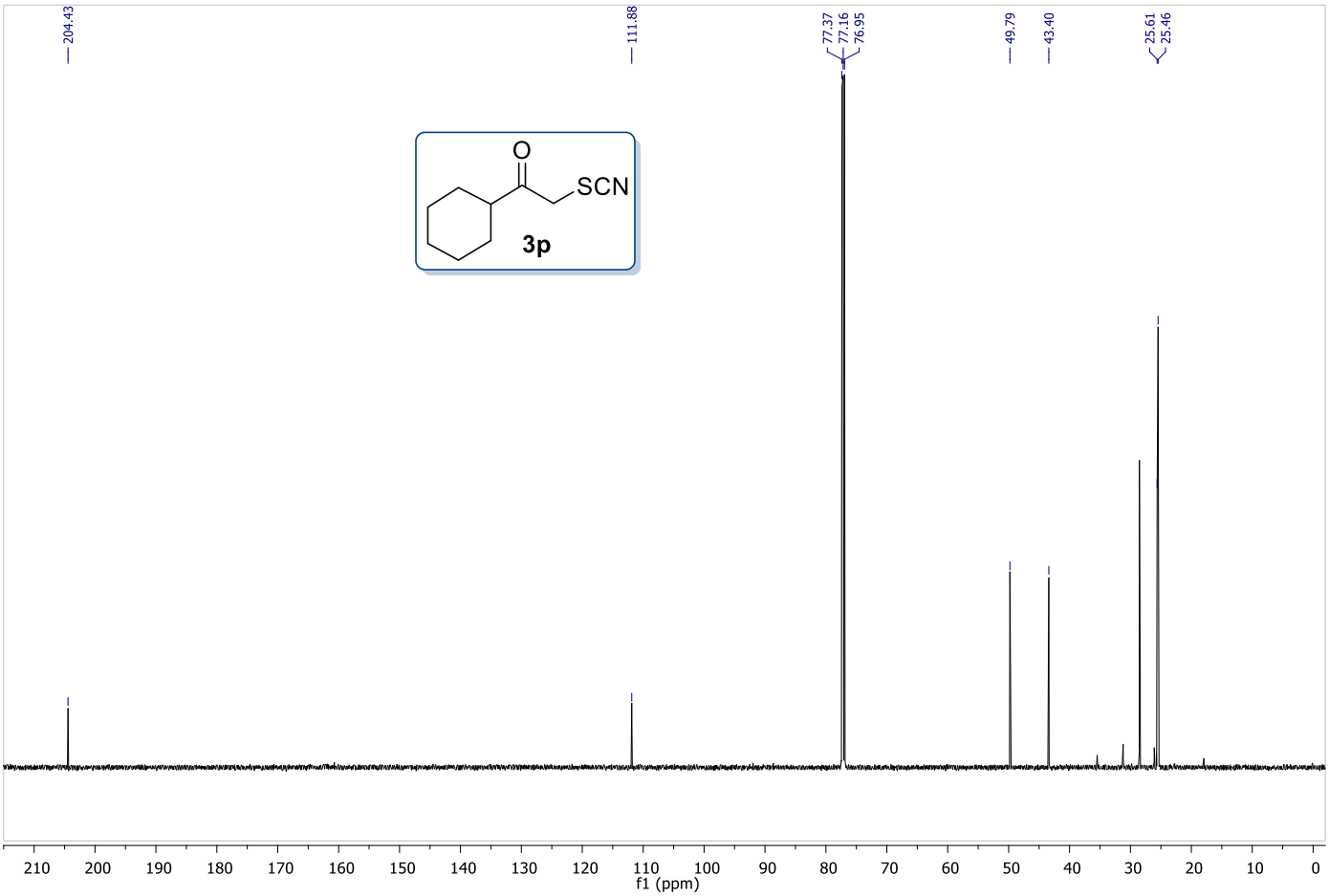
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3o**



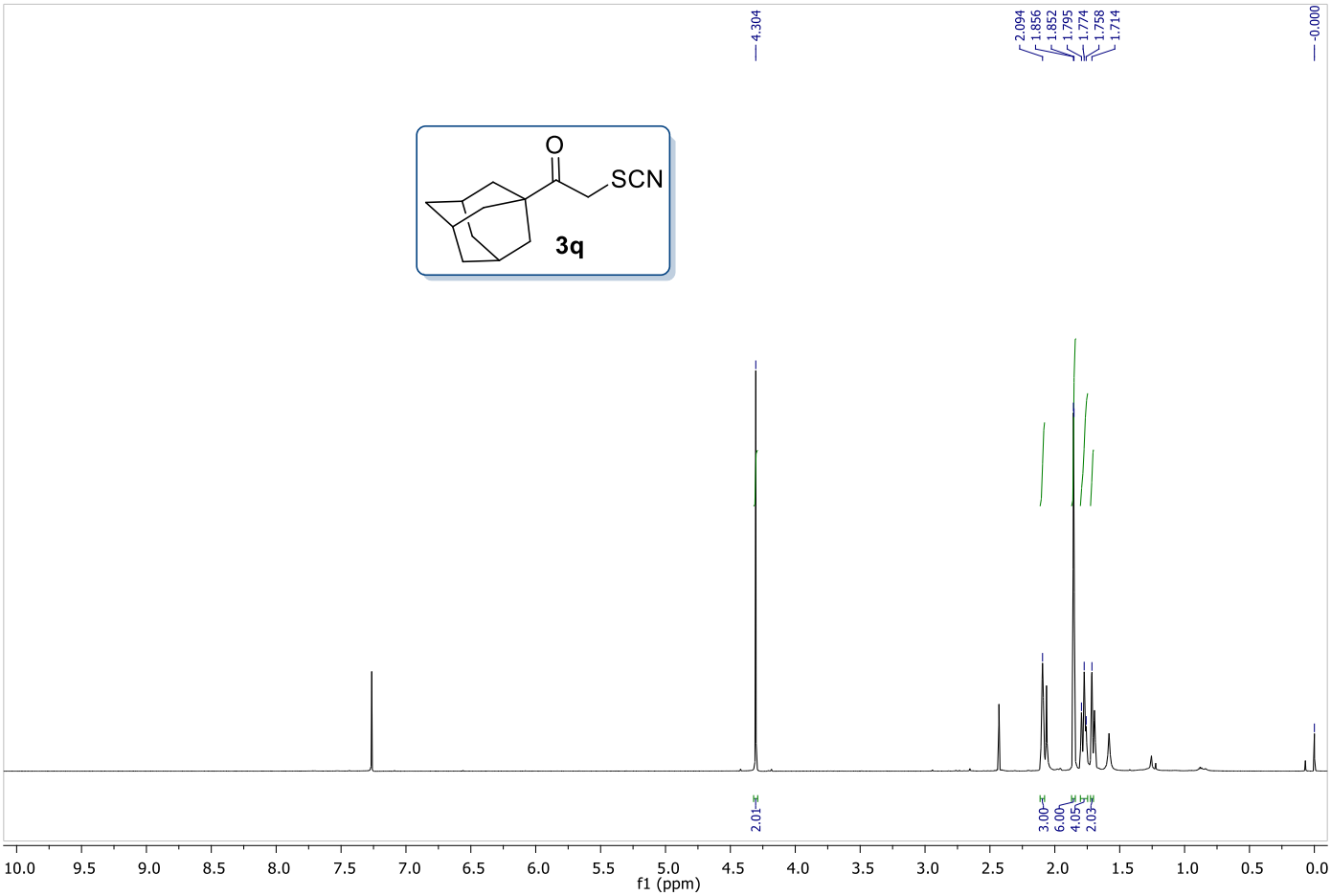


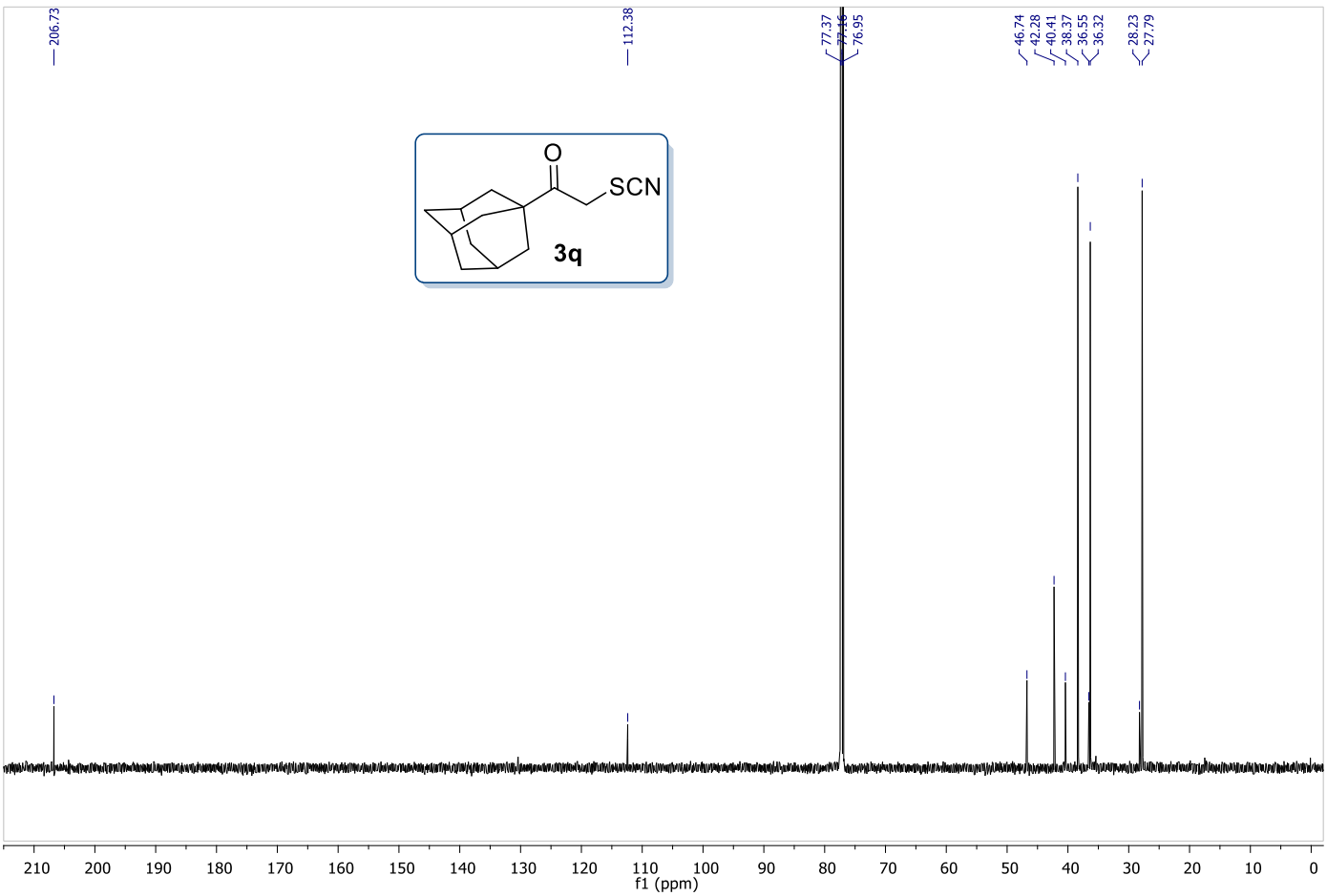
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3p**



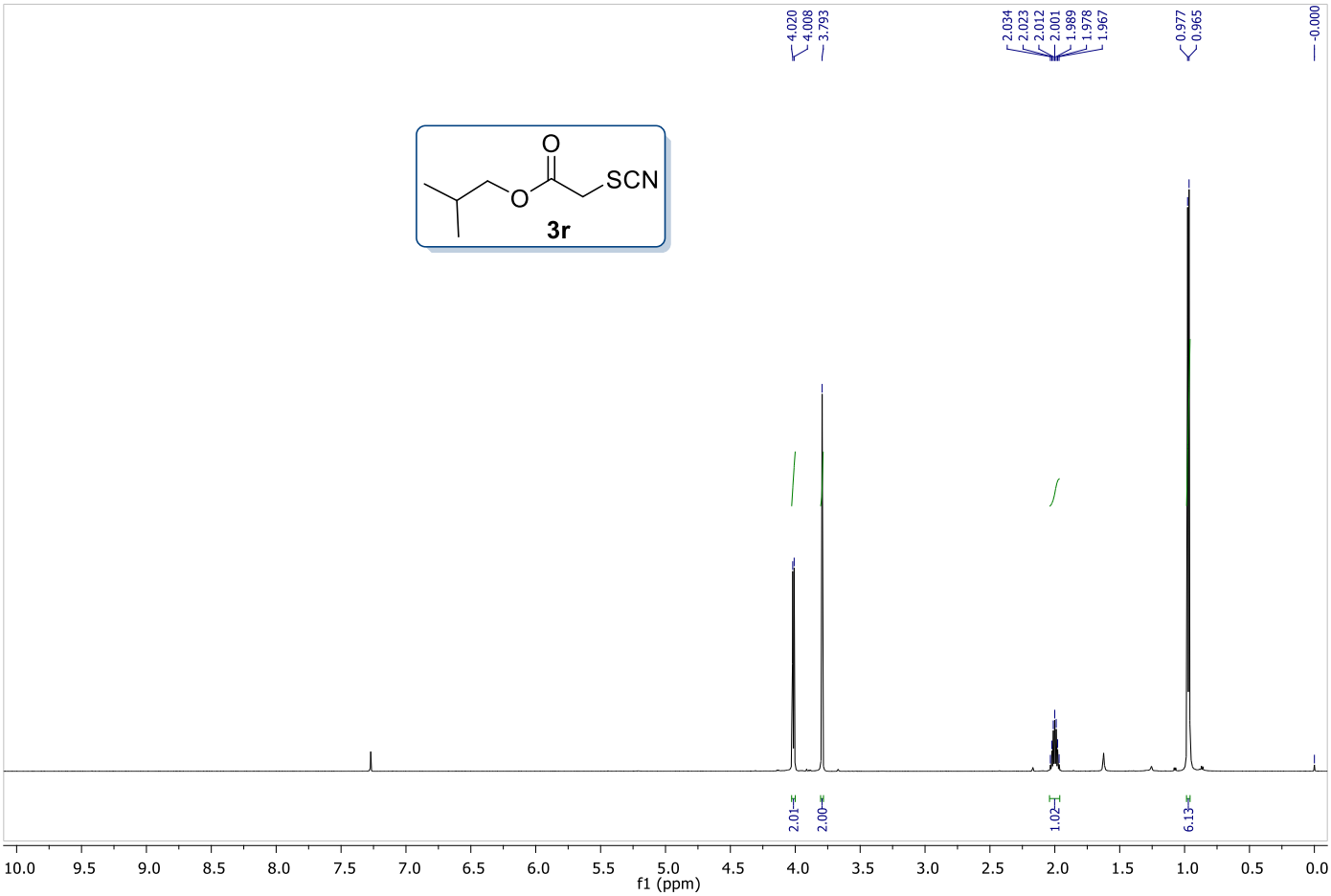


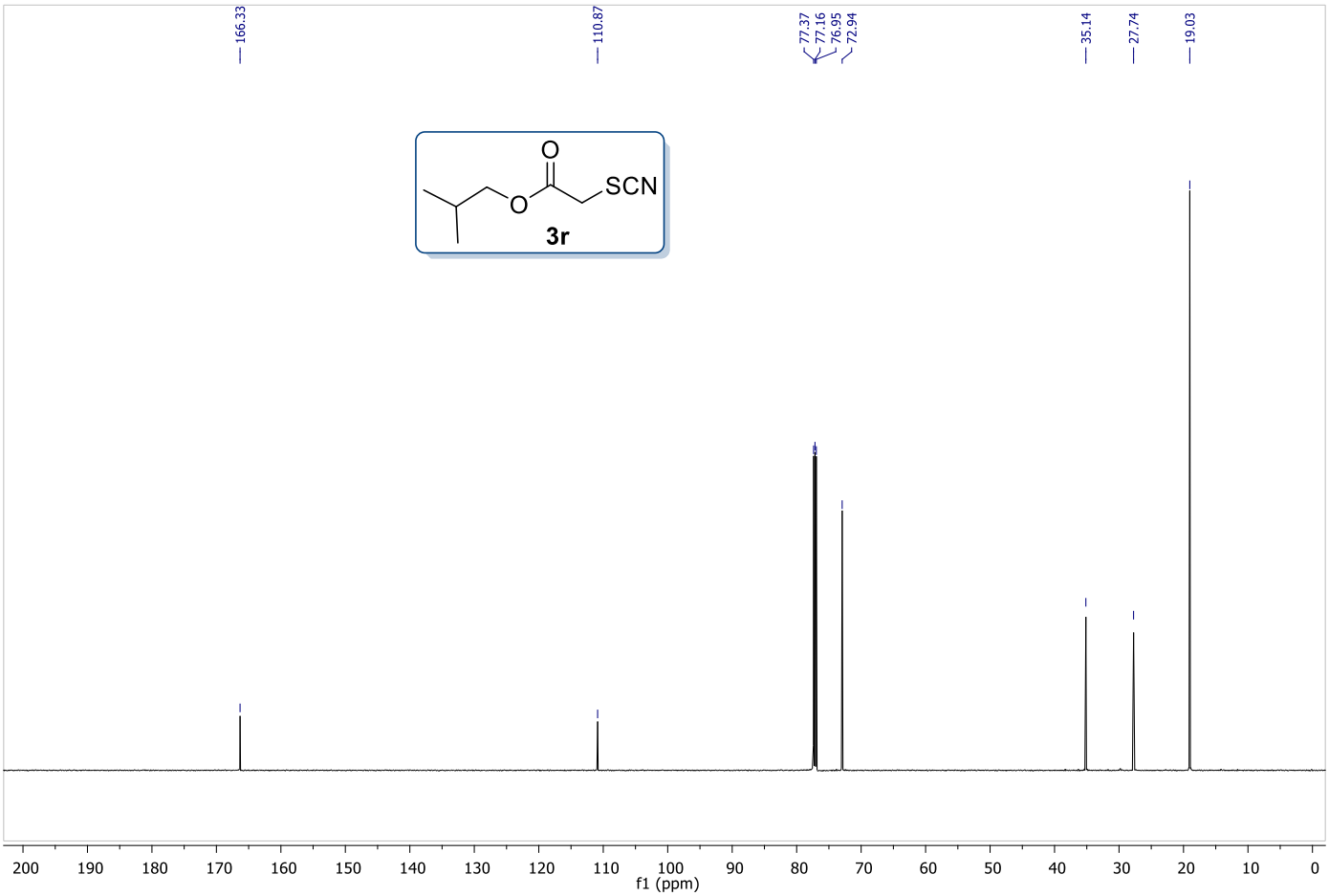
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3q**





^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **3r**





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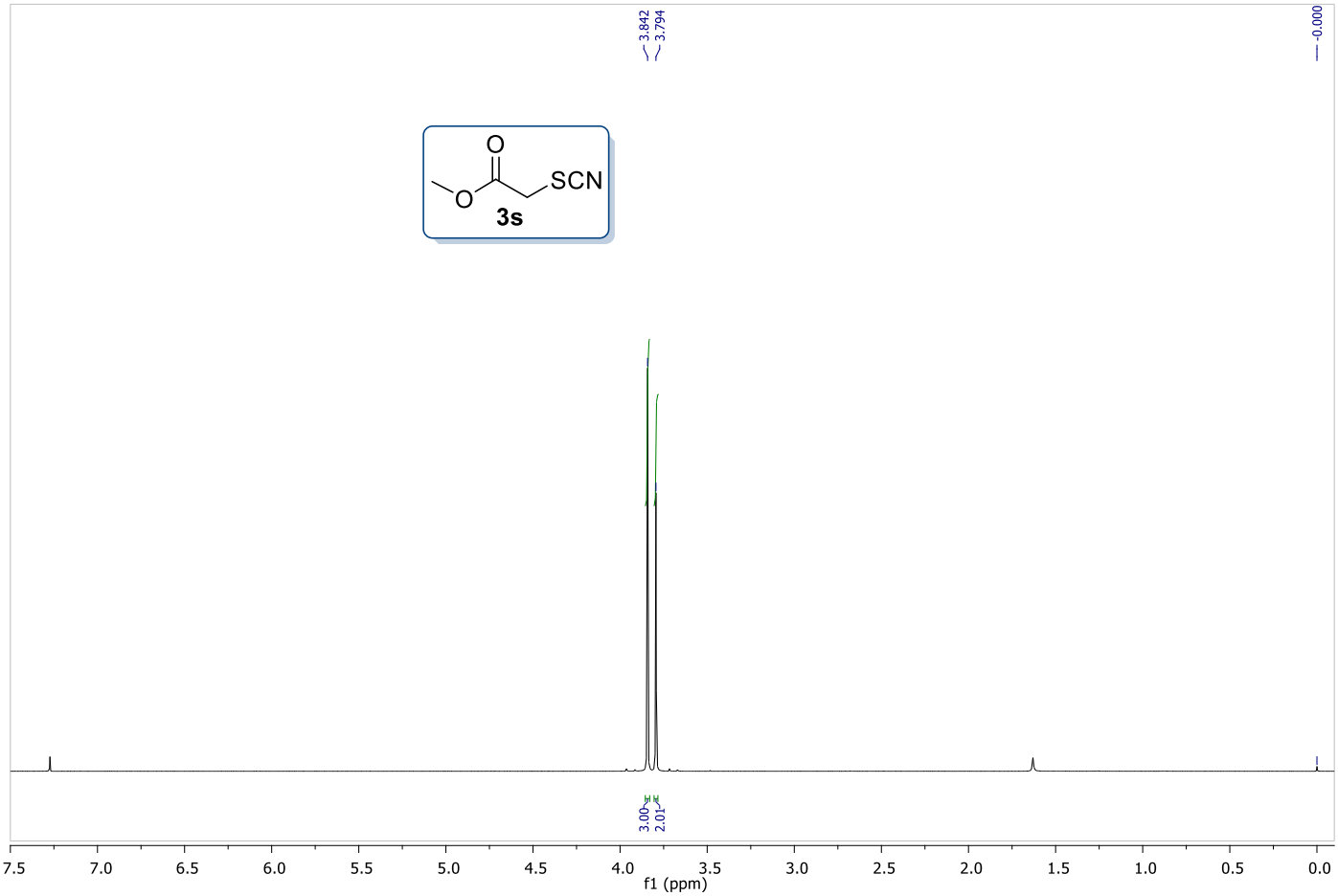
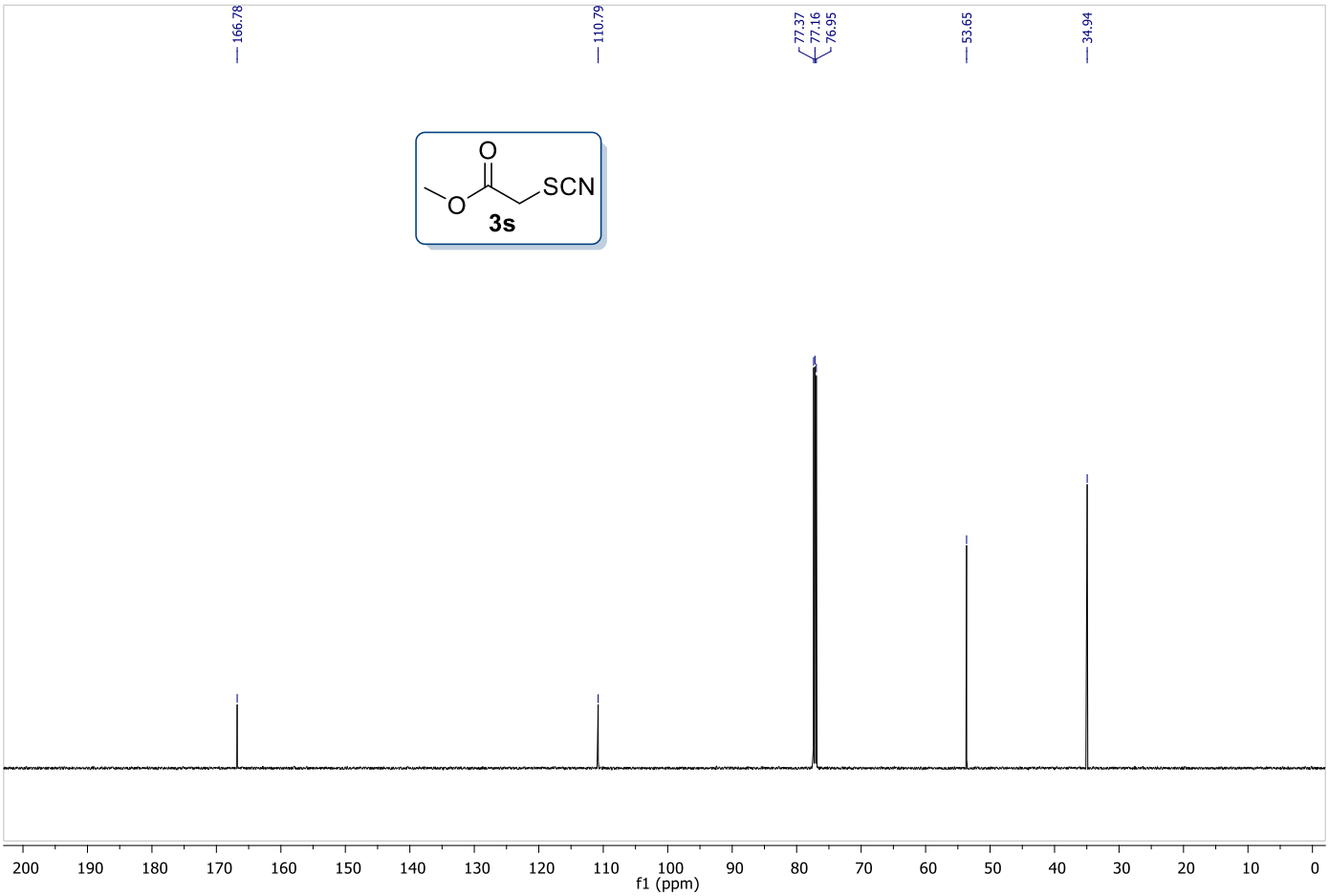
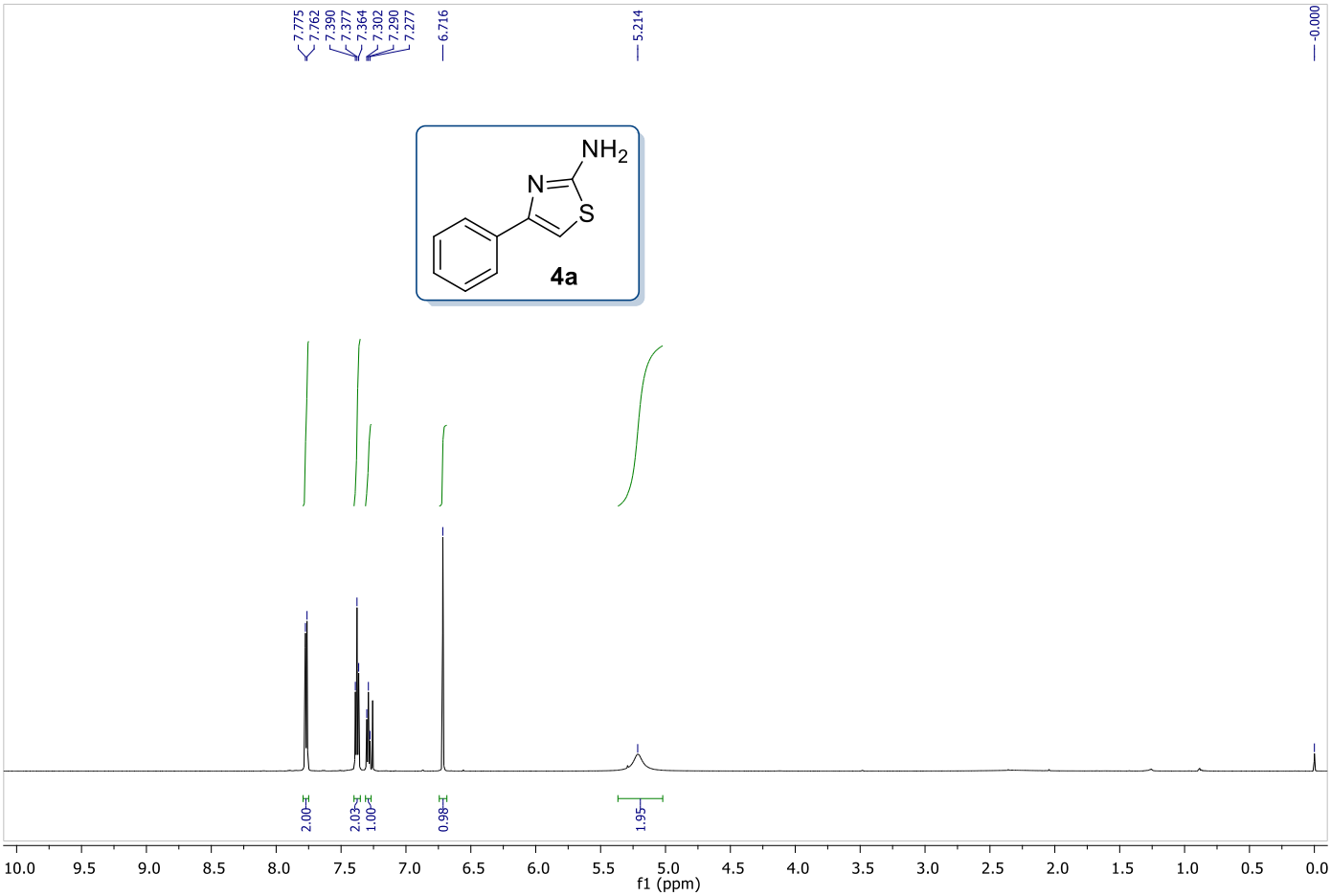
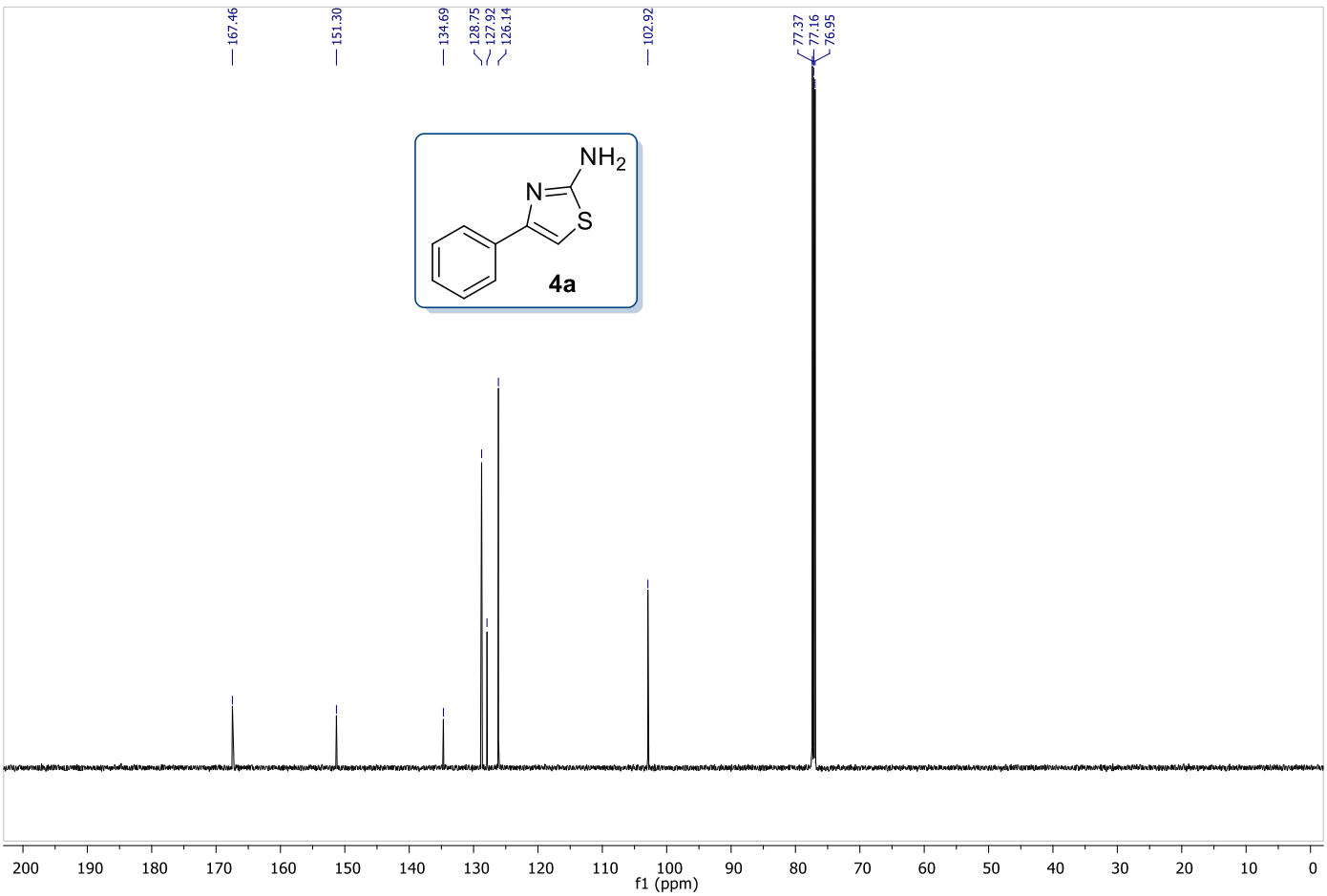


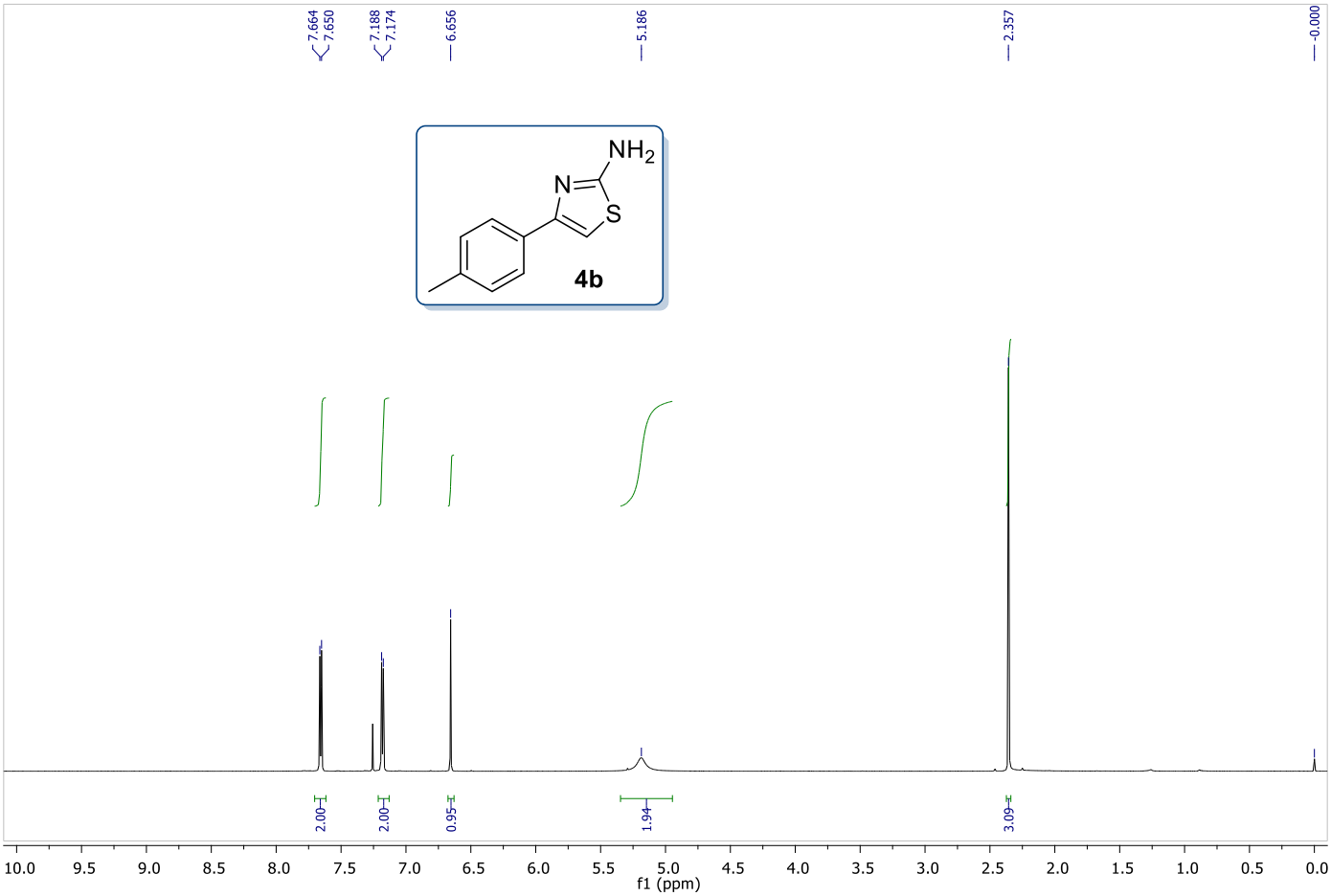


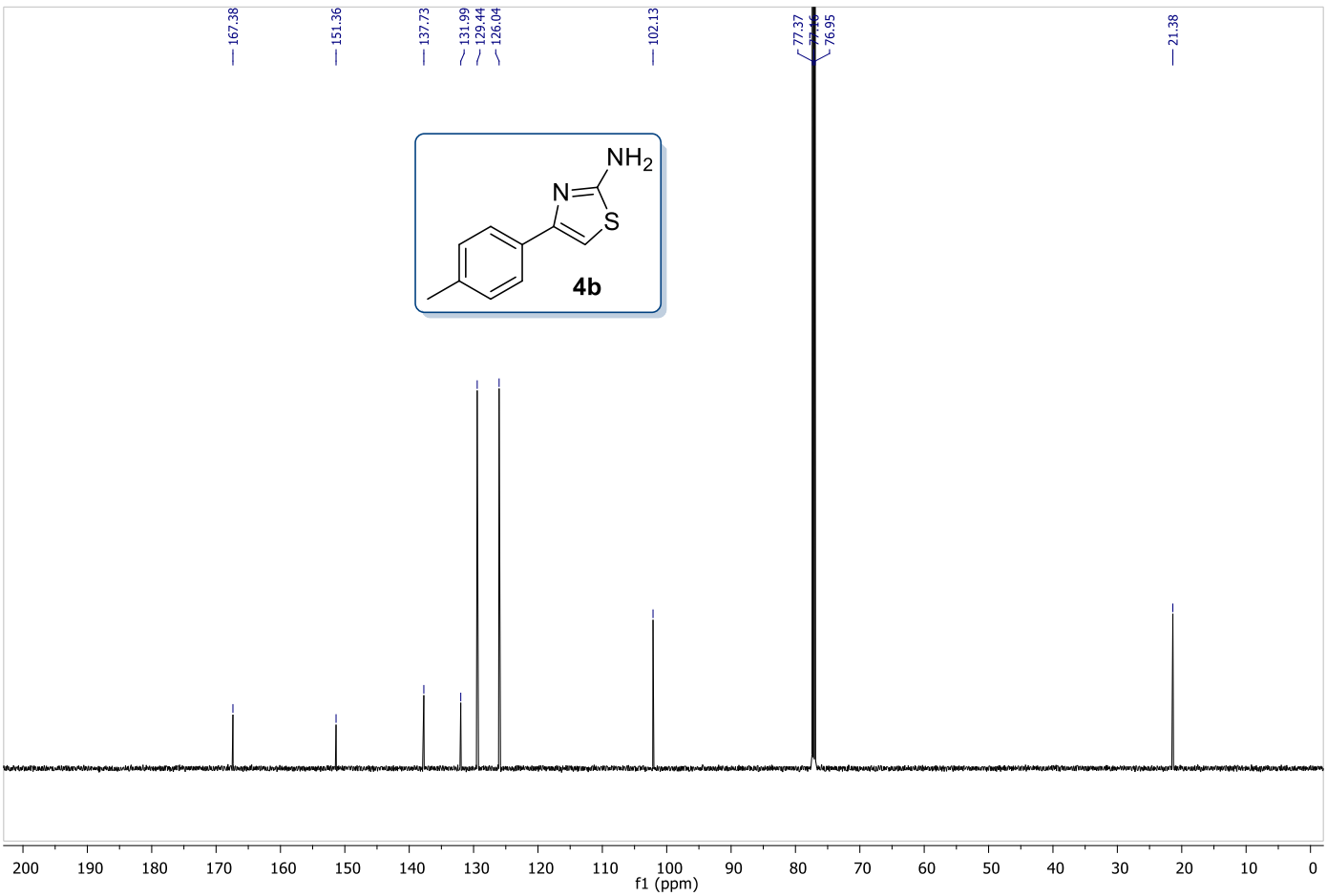
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4a**



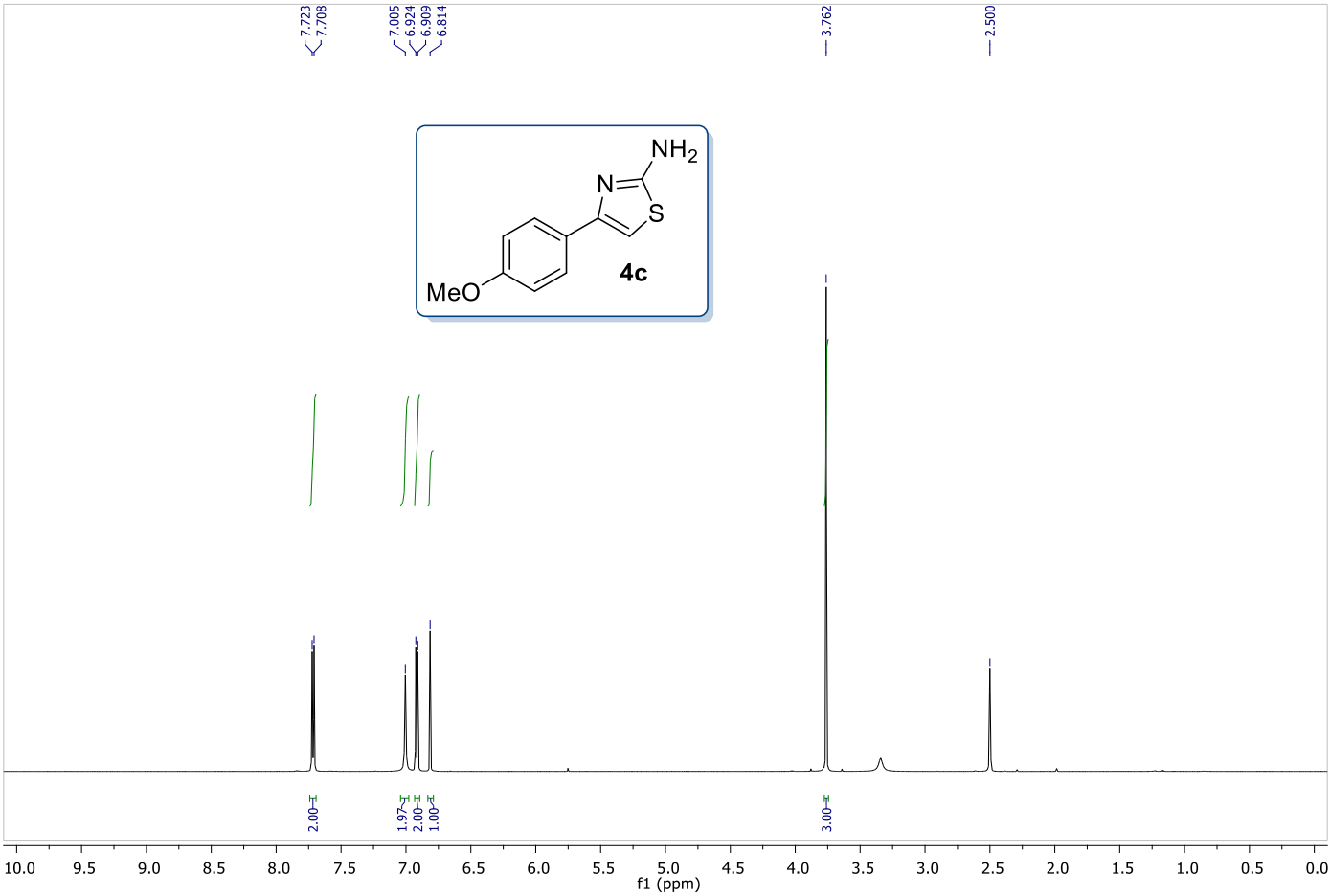


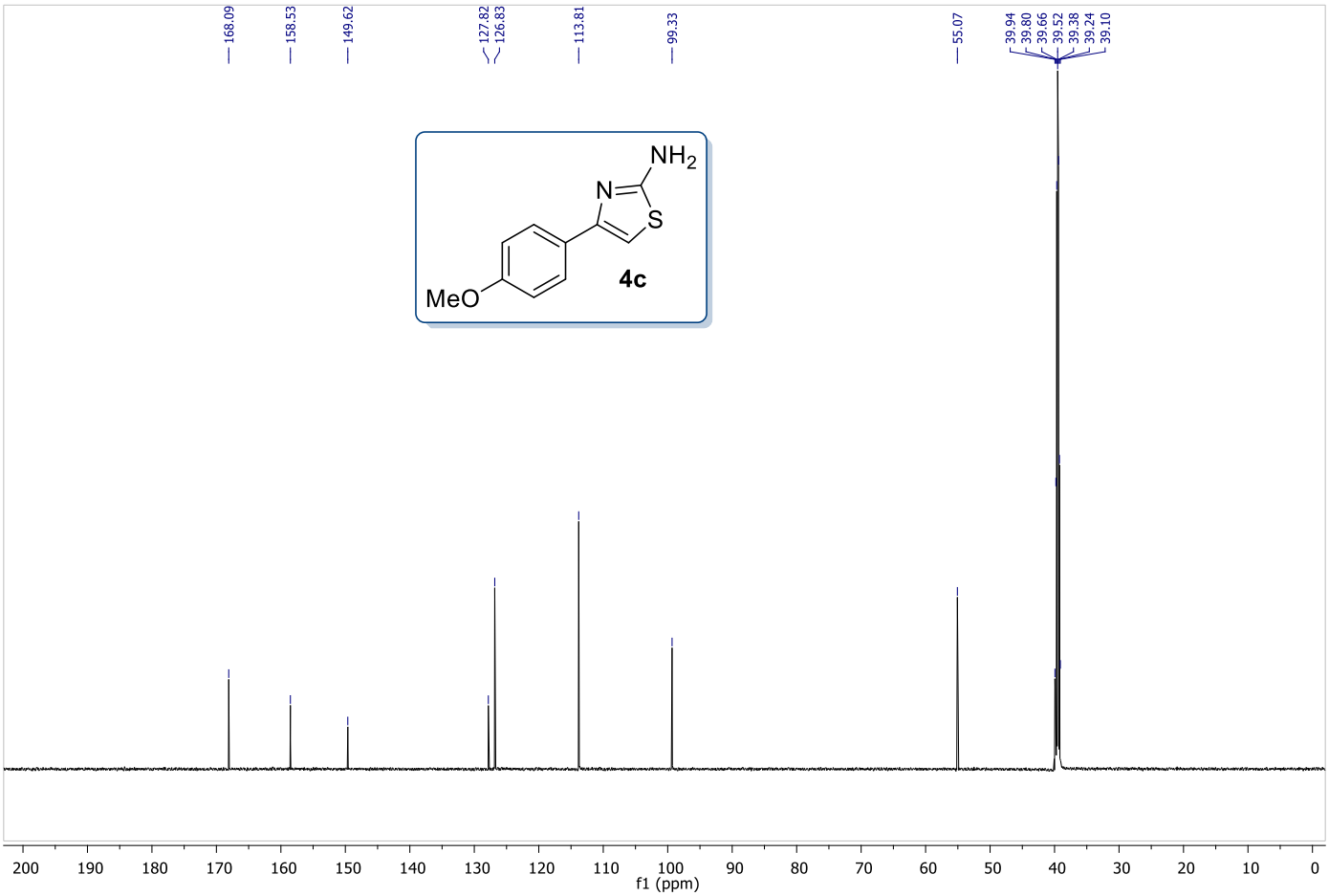
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4b**



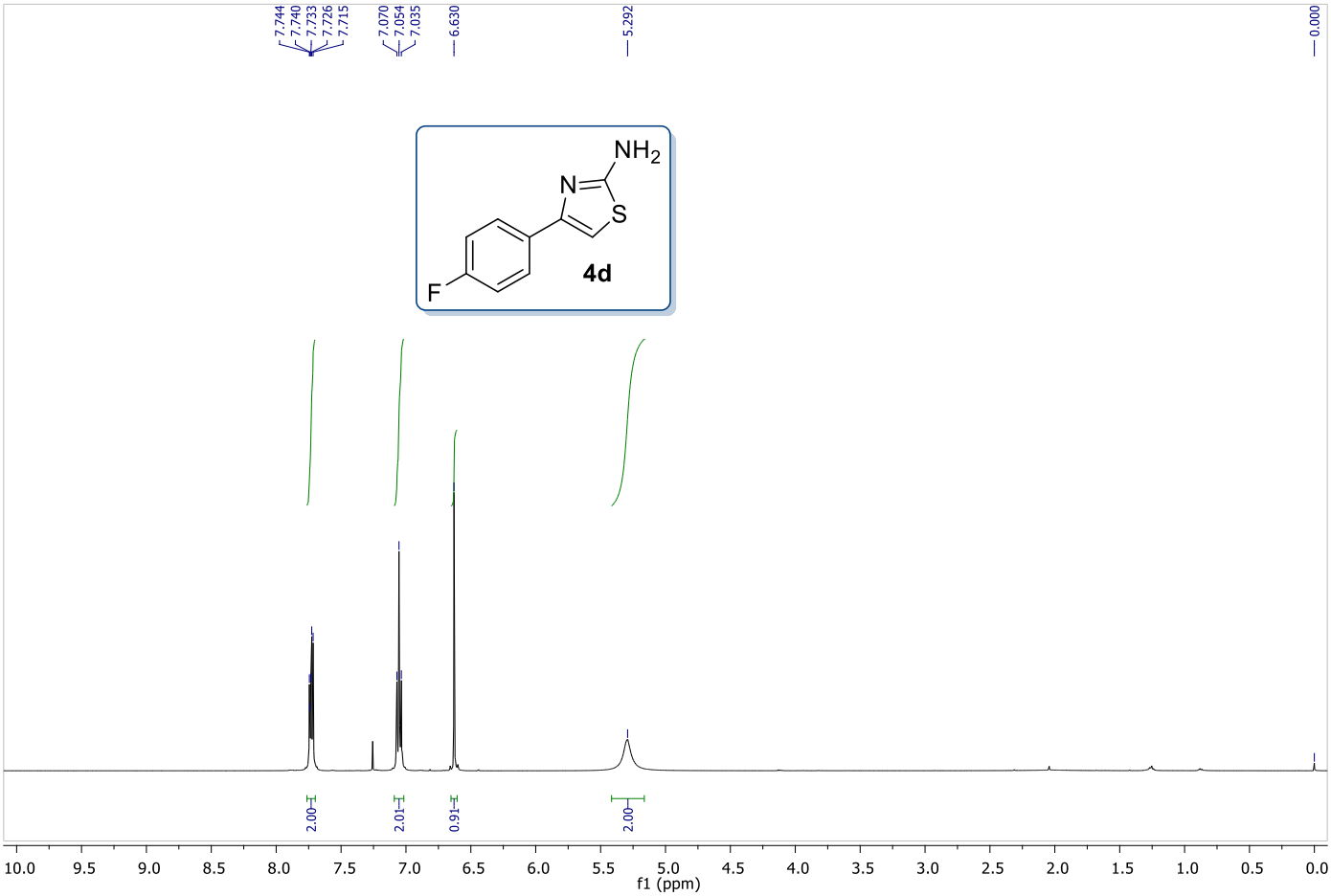


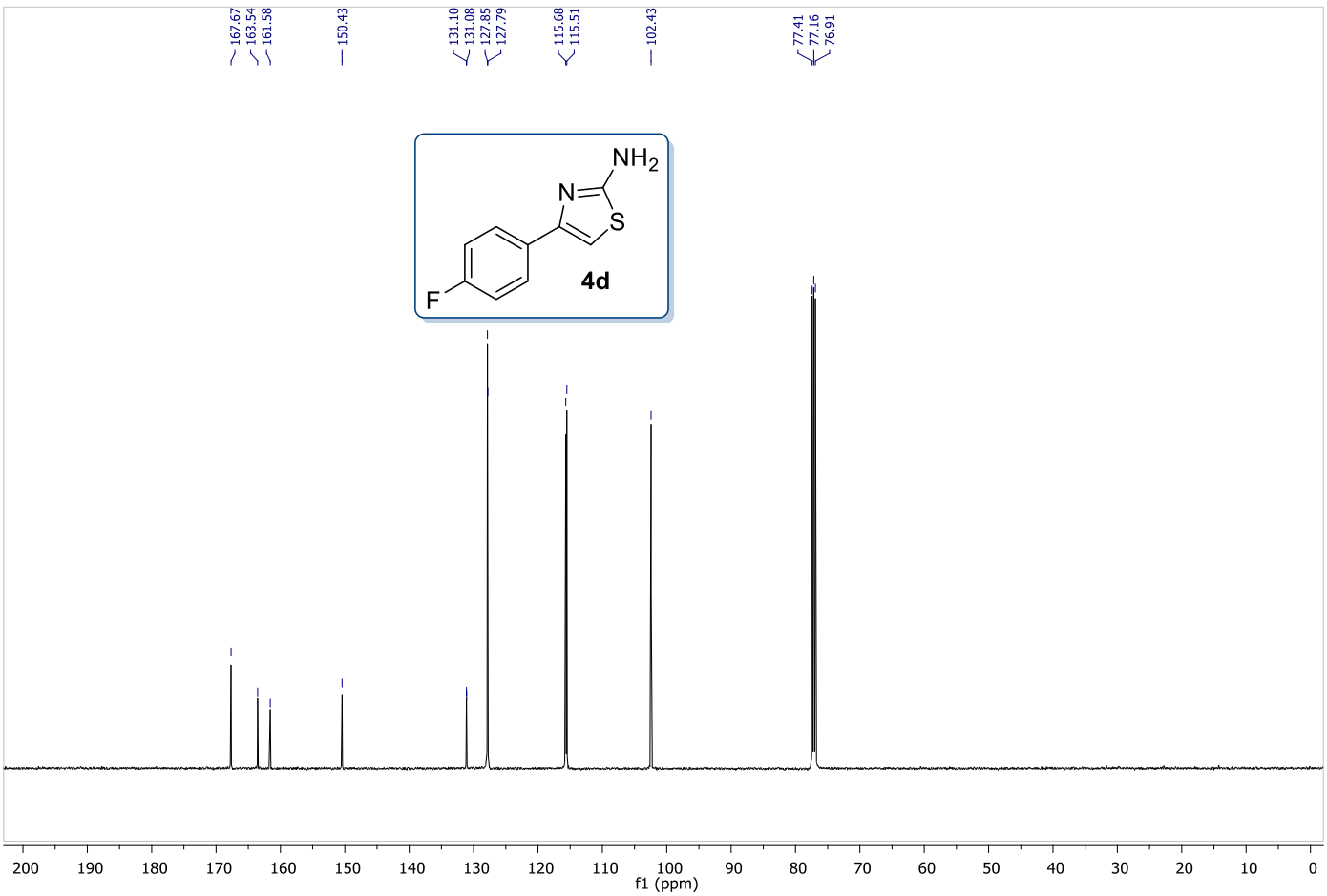
^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6), **4c**



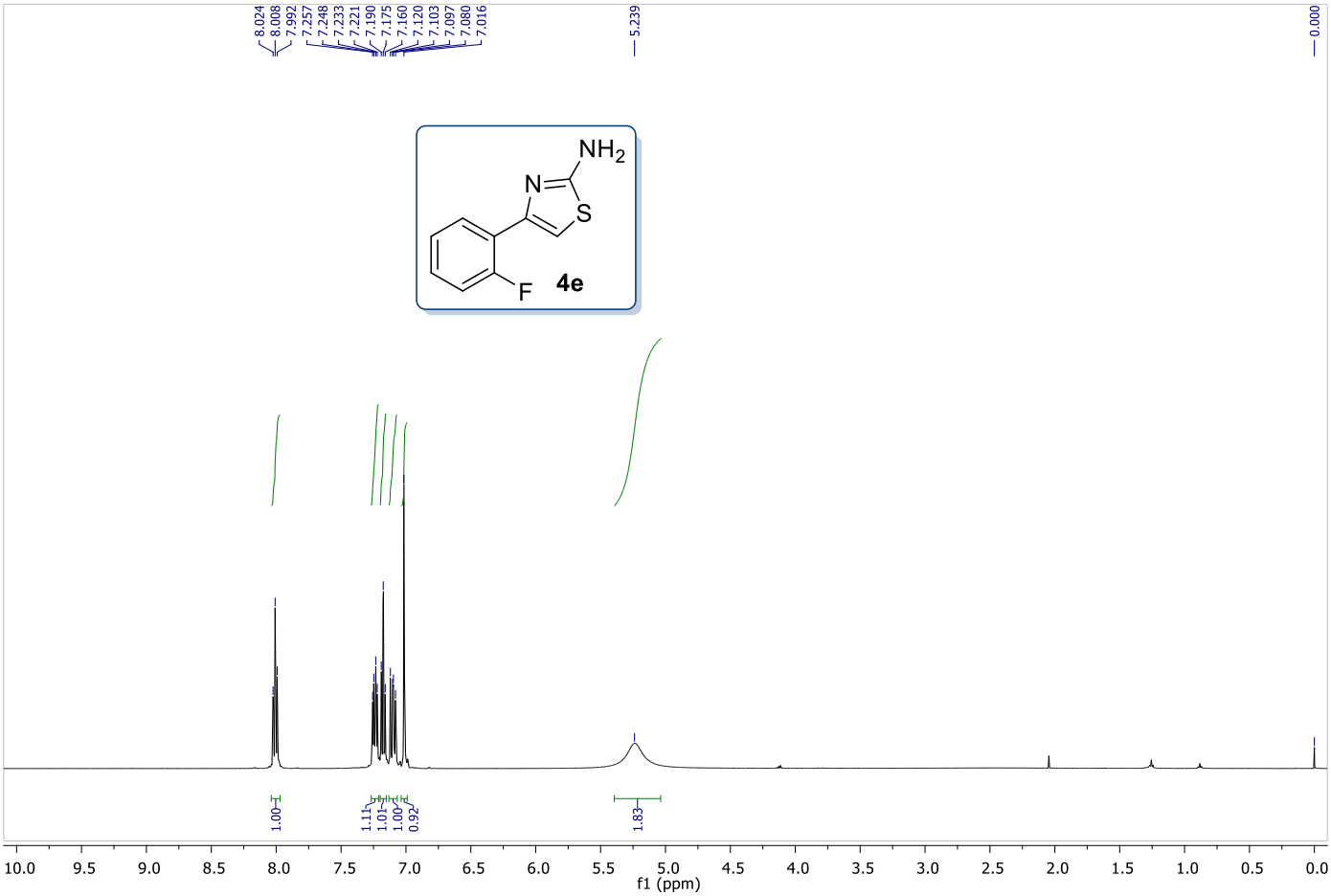


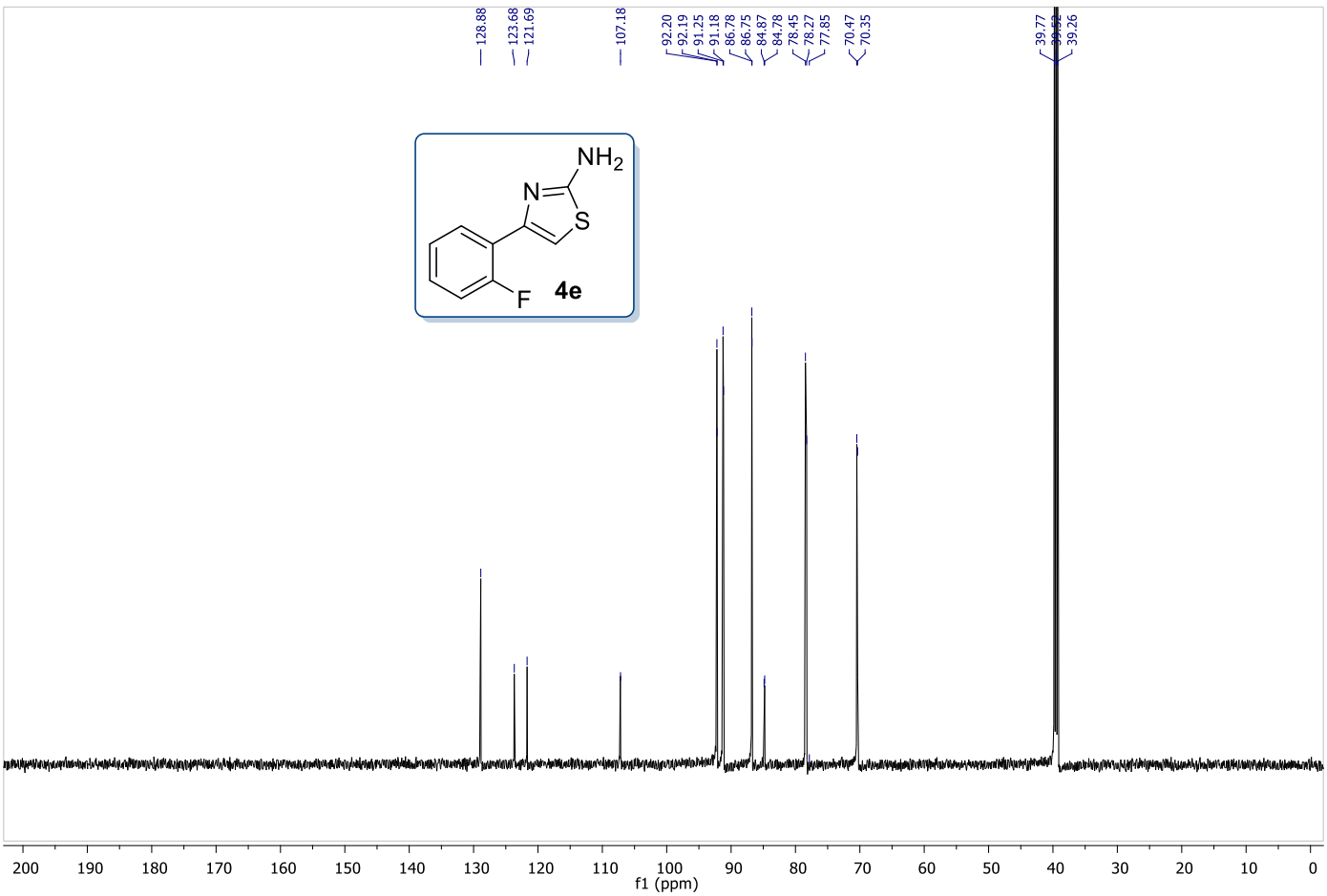
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **4d**



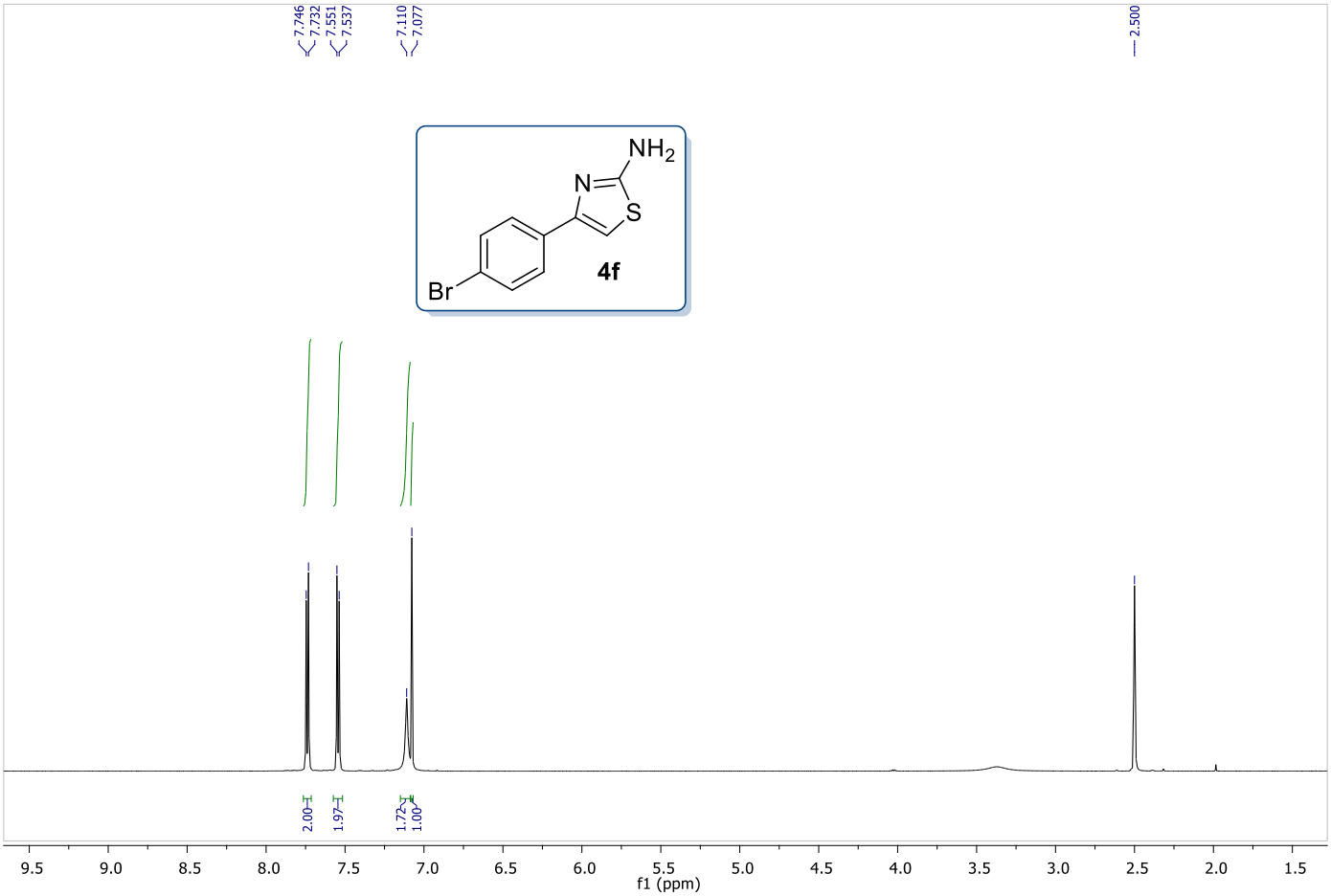


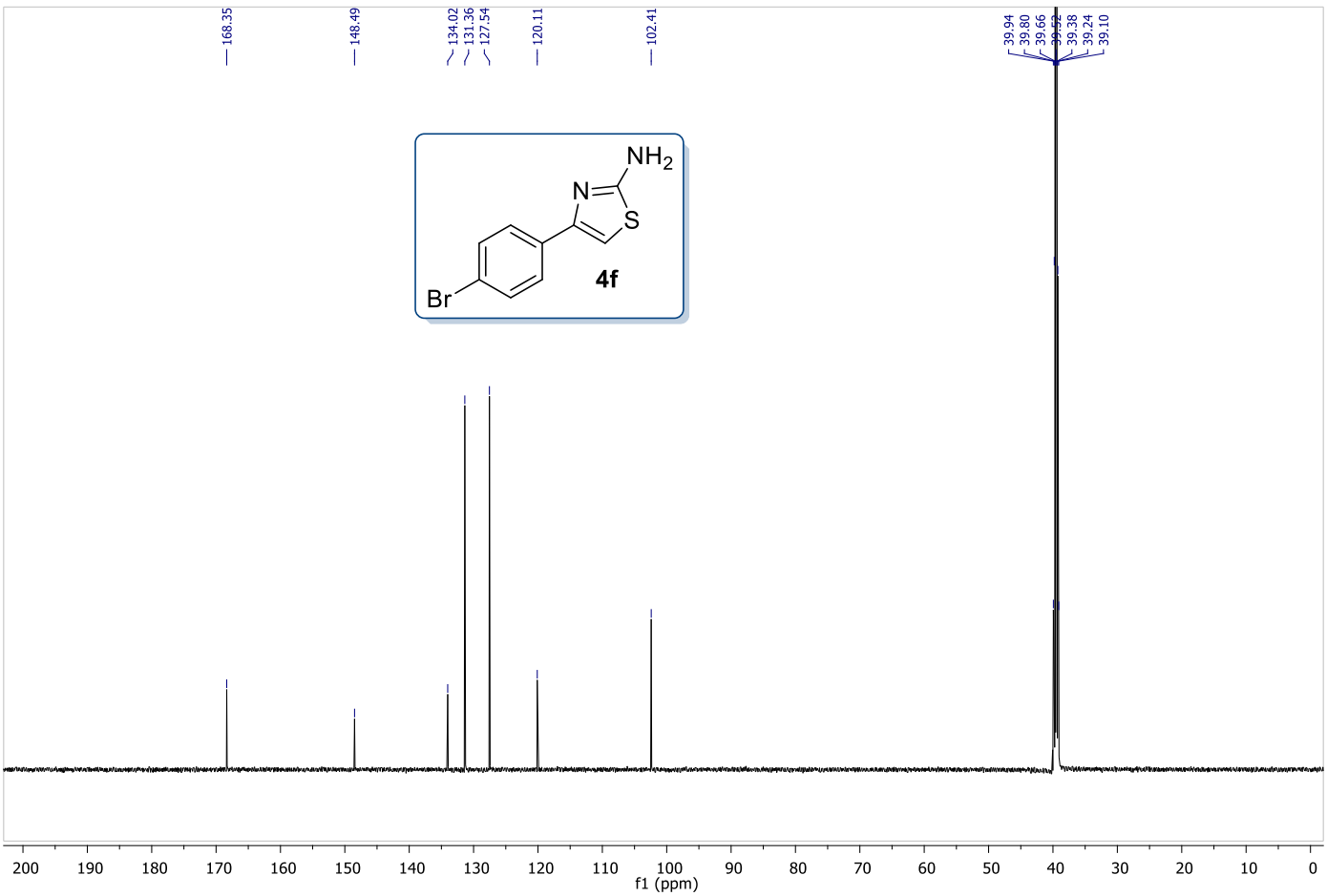
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **4e**



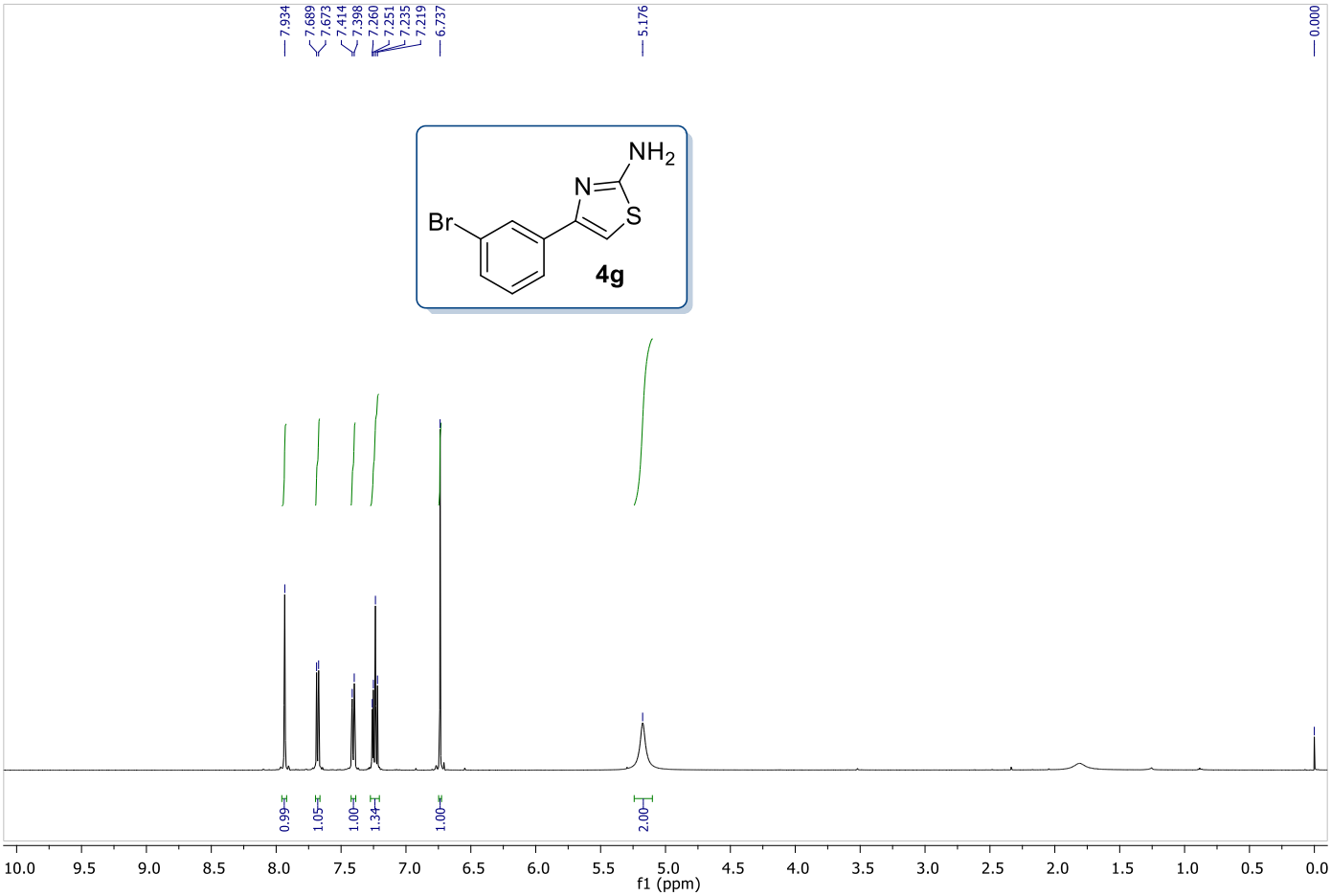


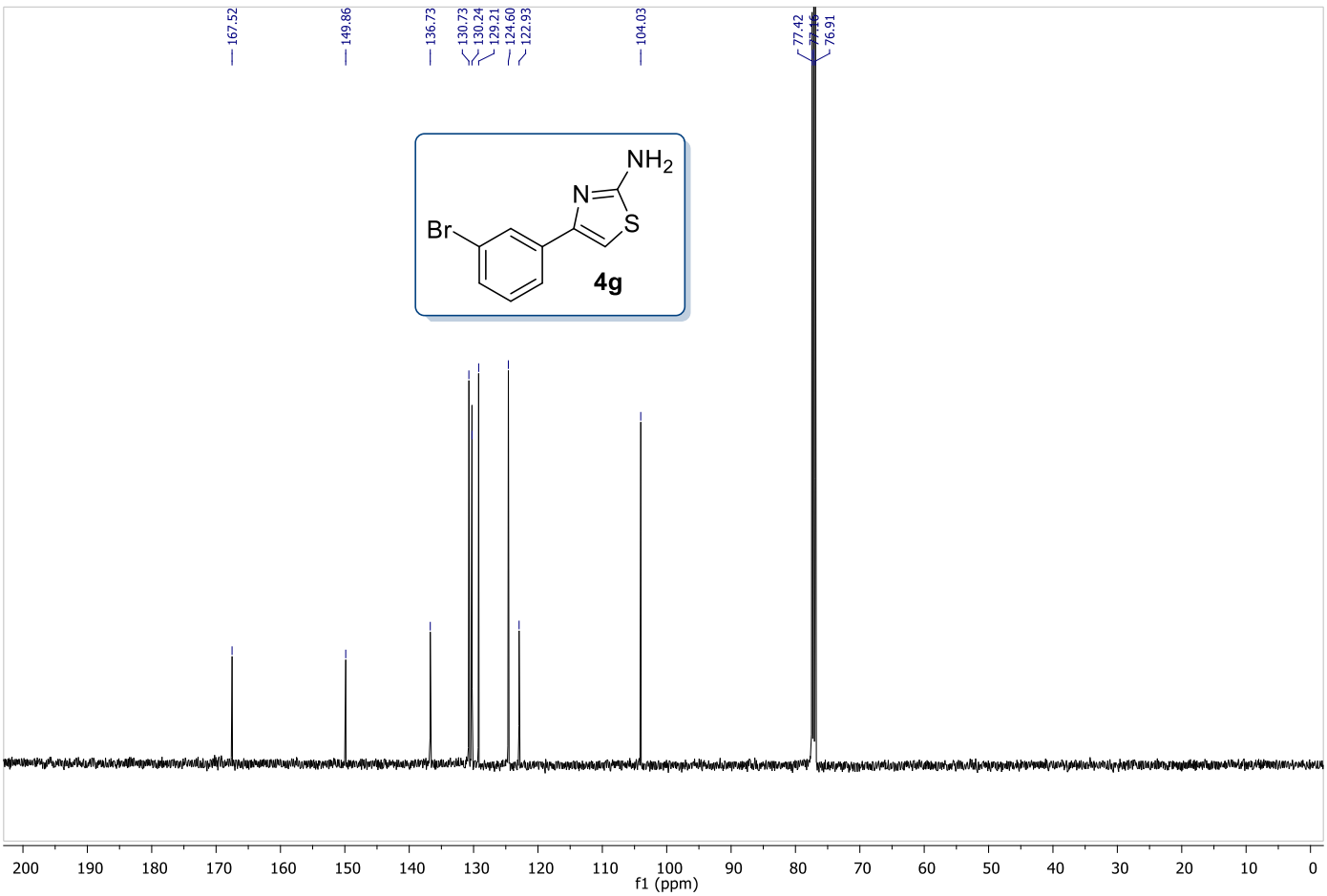
^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6), **4f**



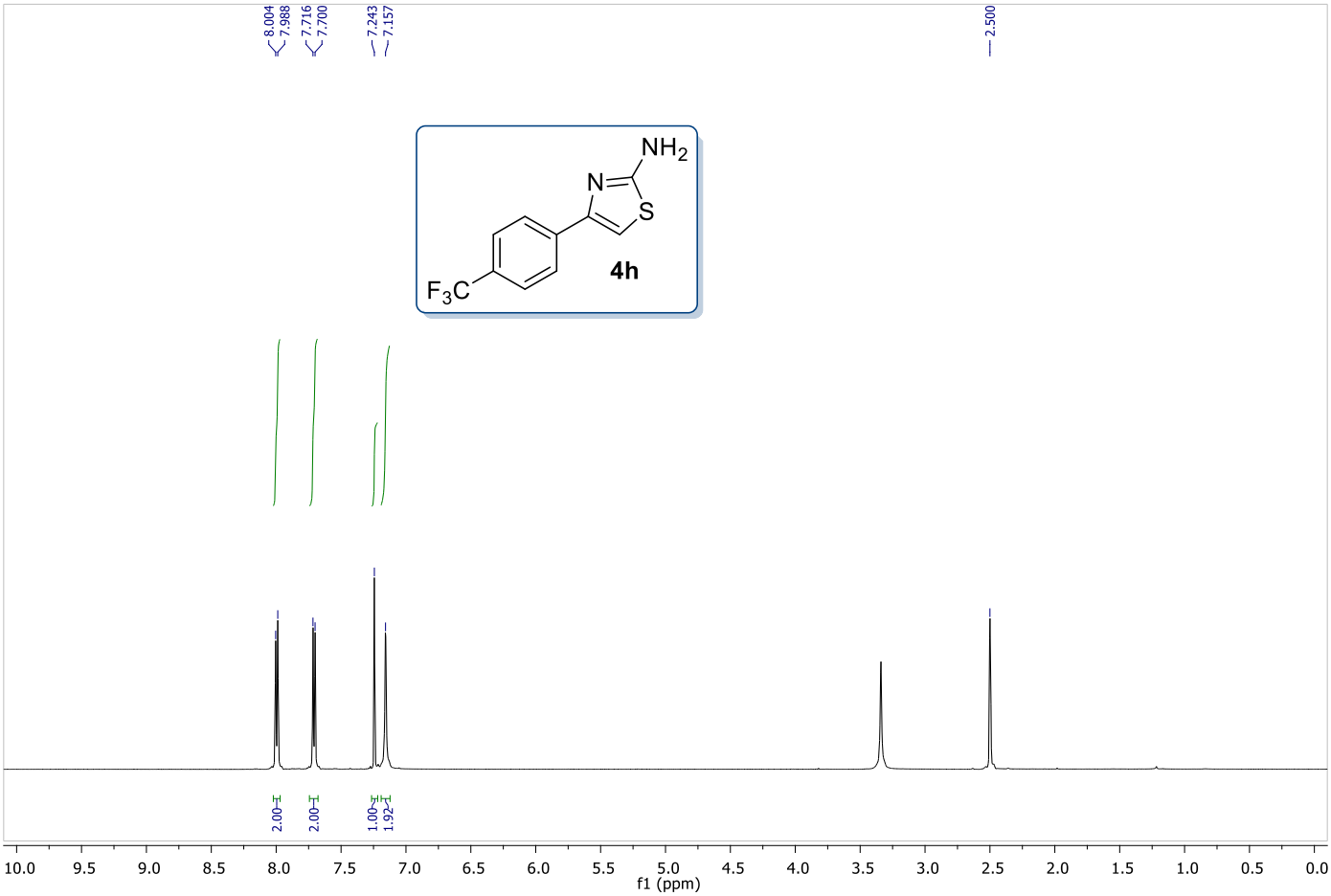


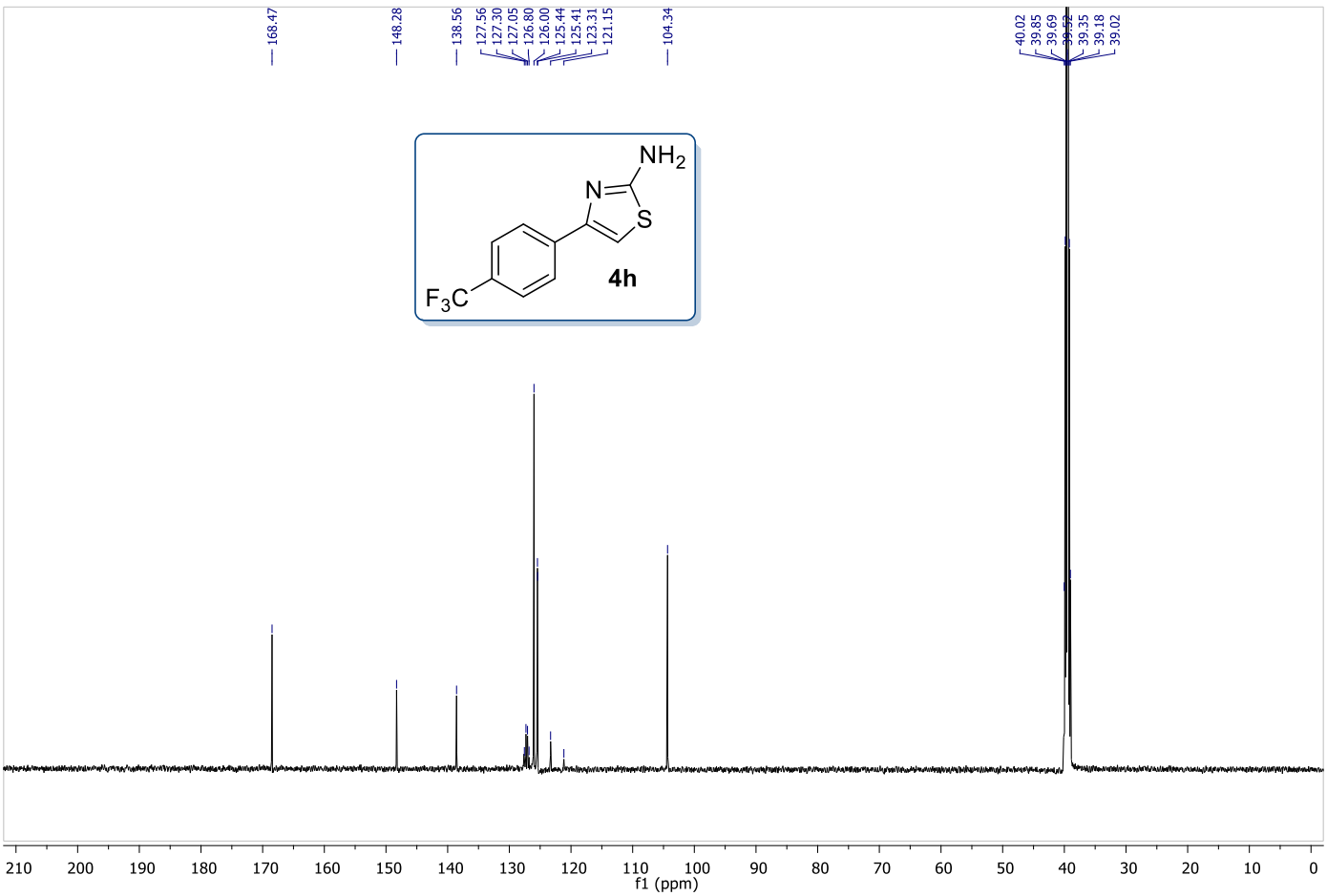
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), **4g**



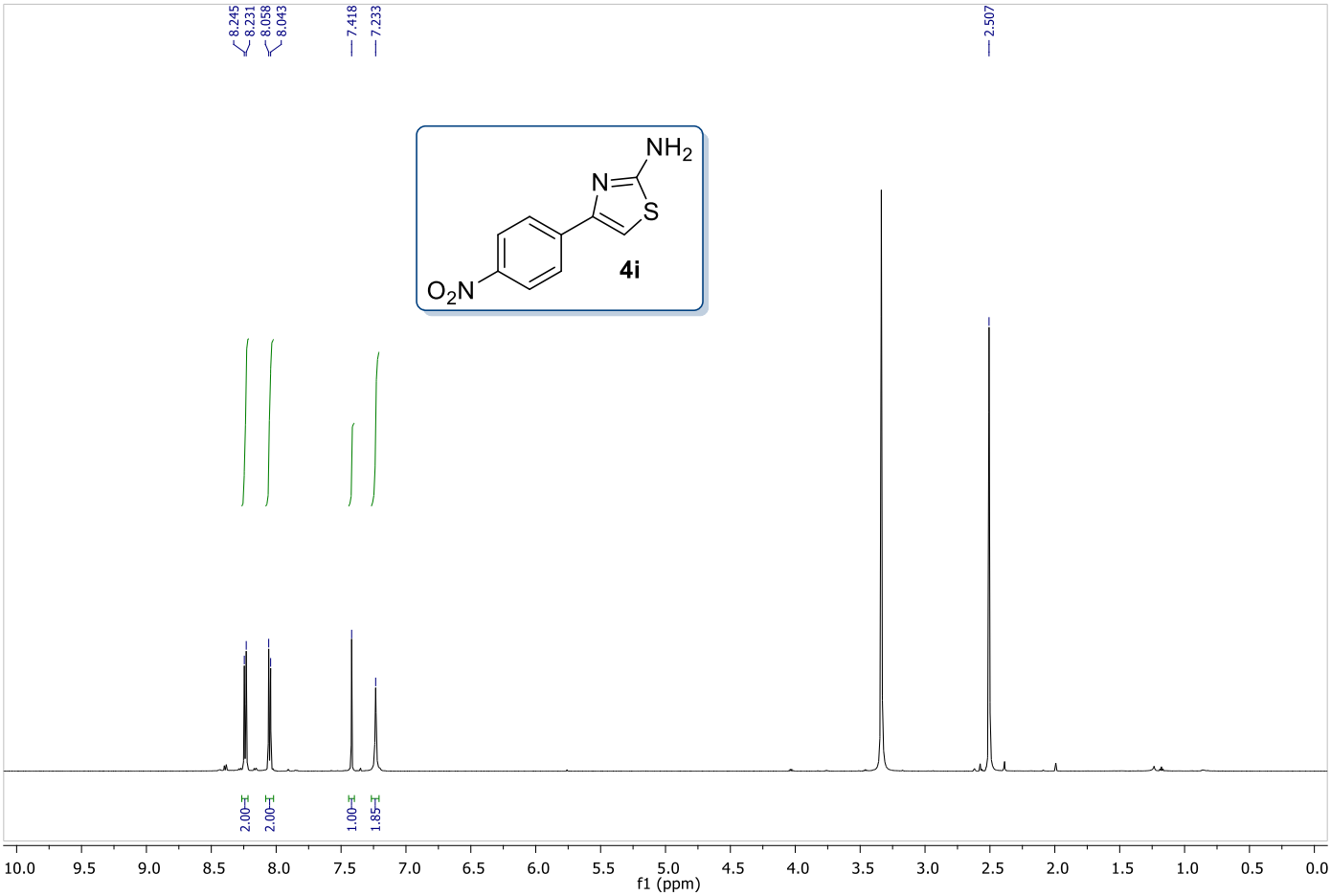


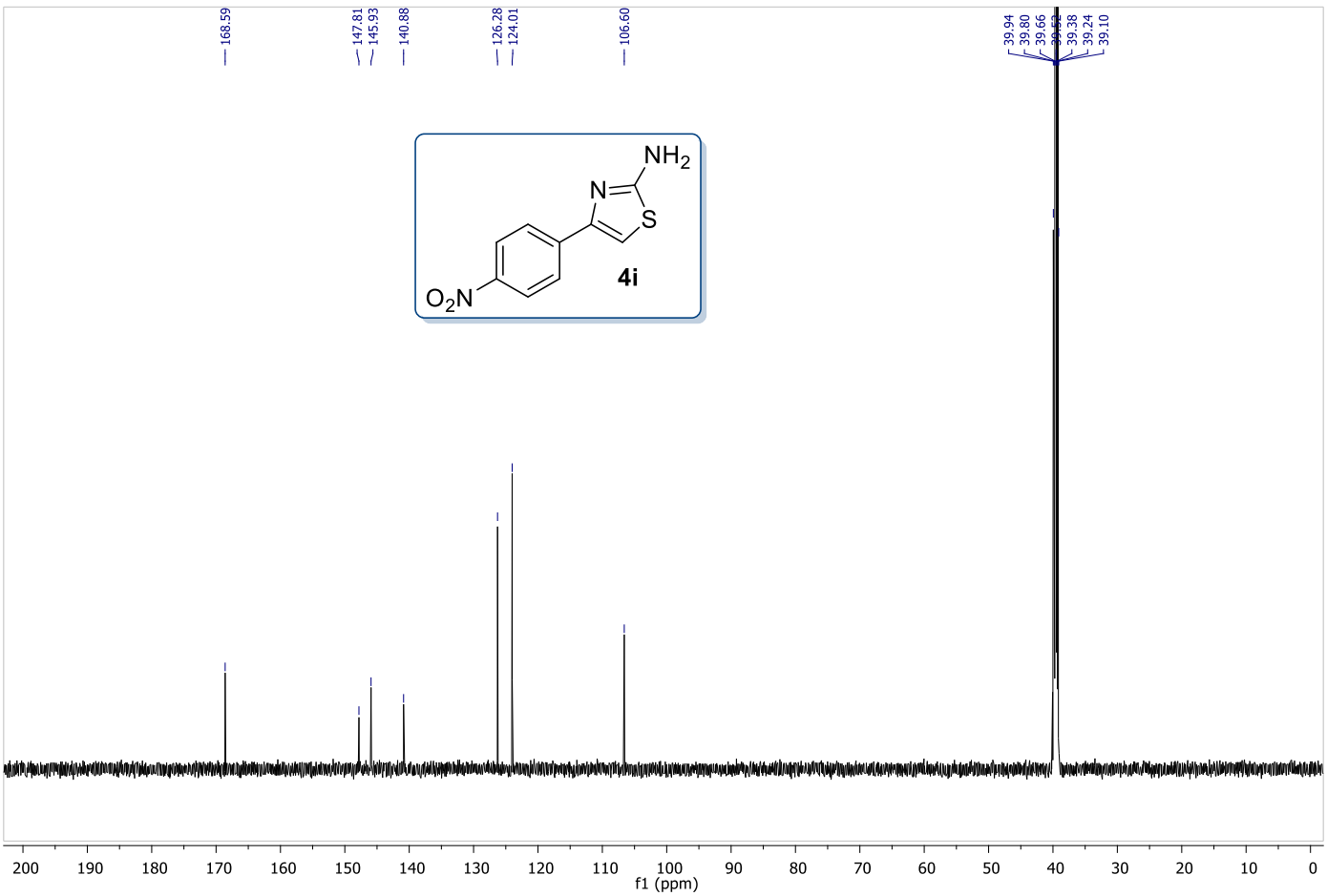
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6), **4h**



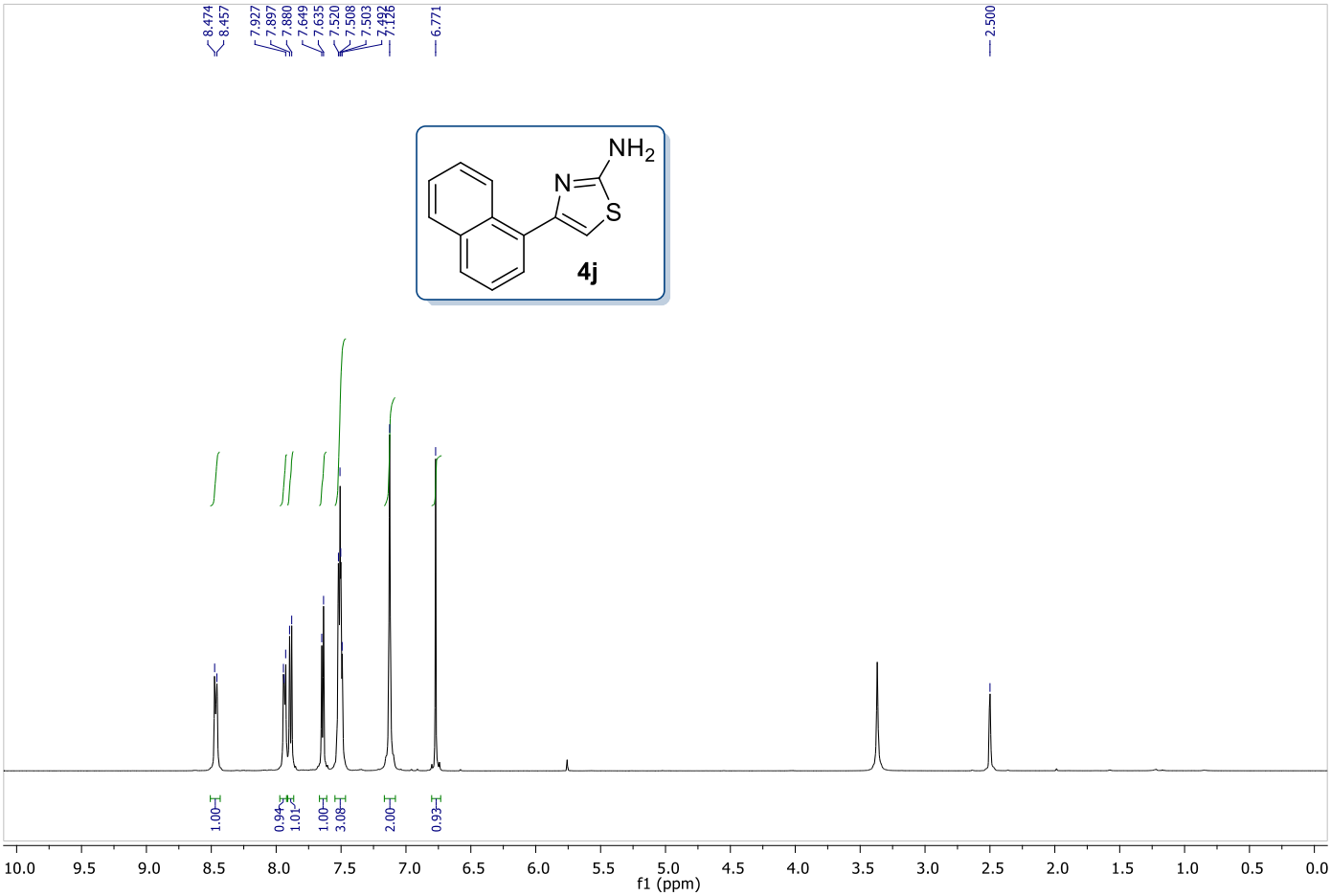


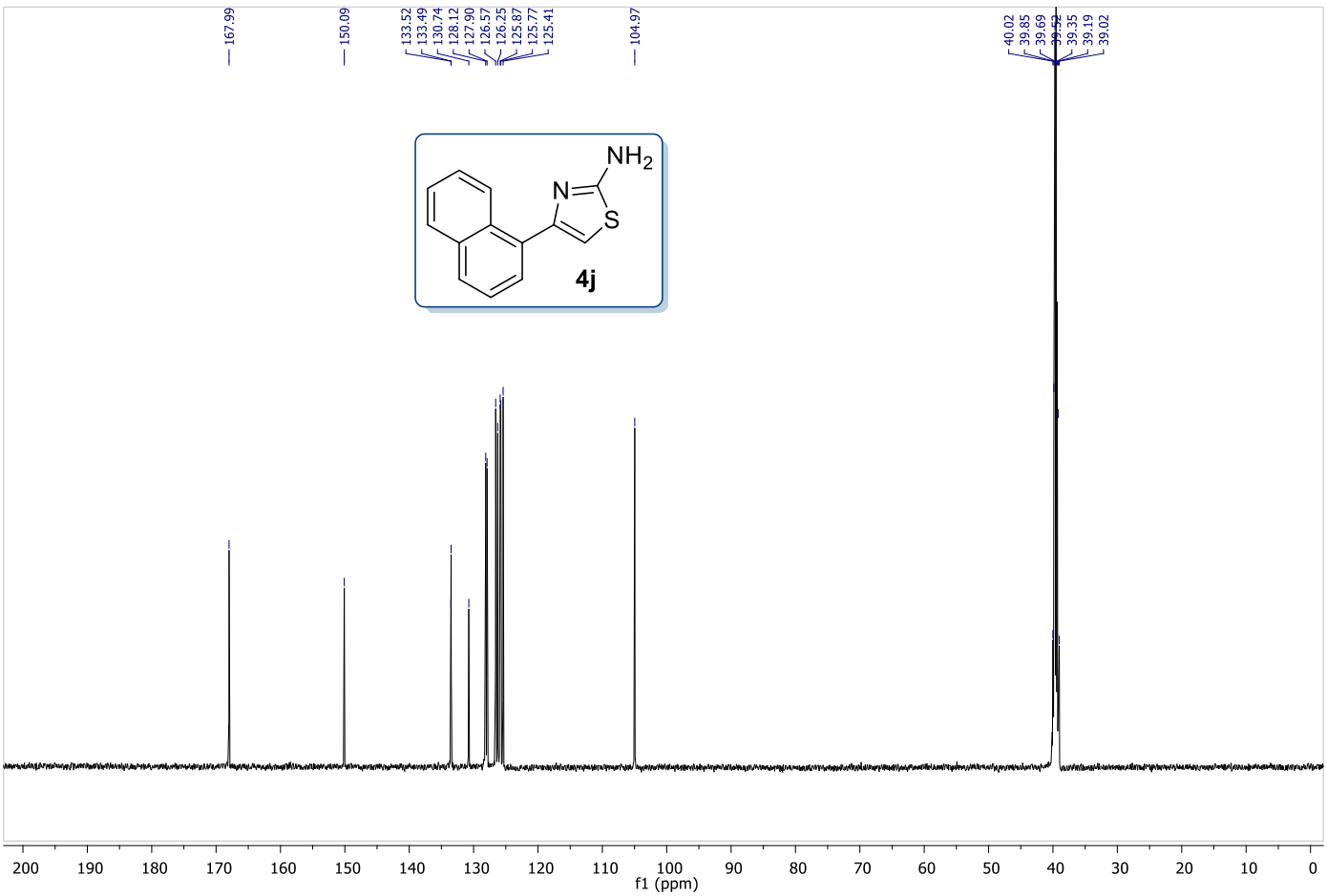
^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6), **4i**



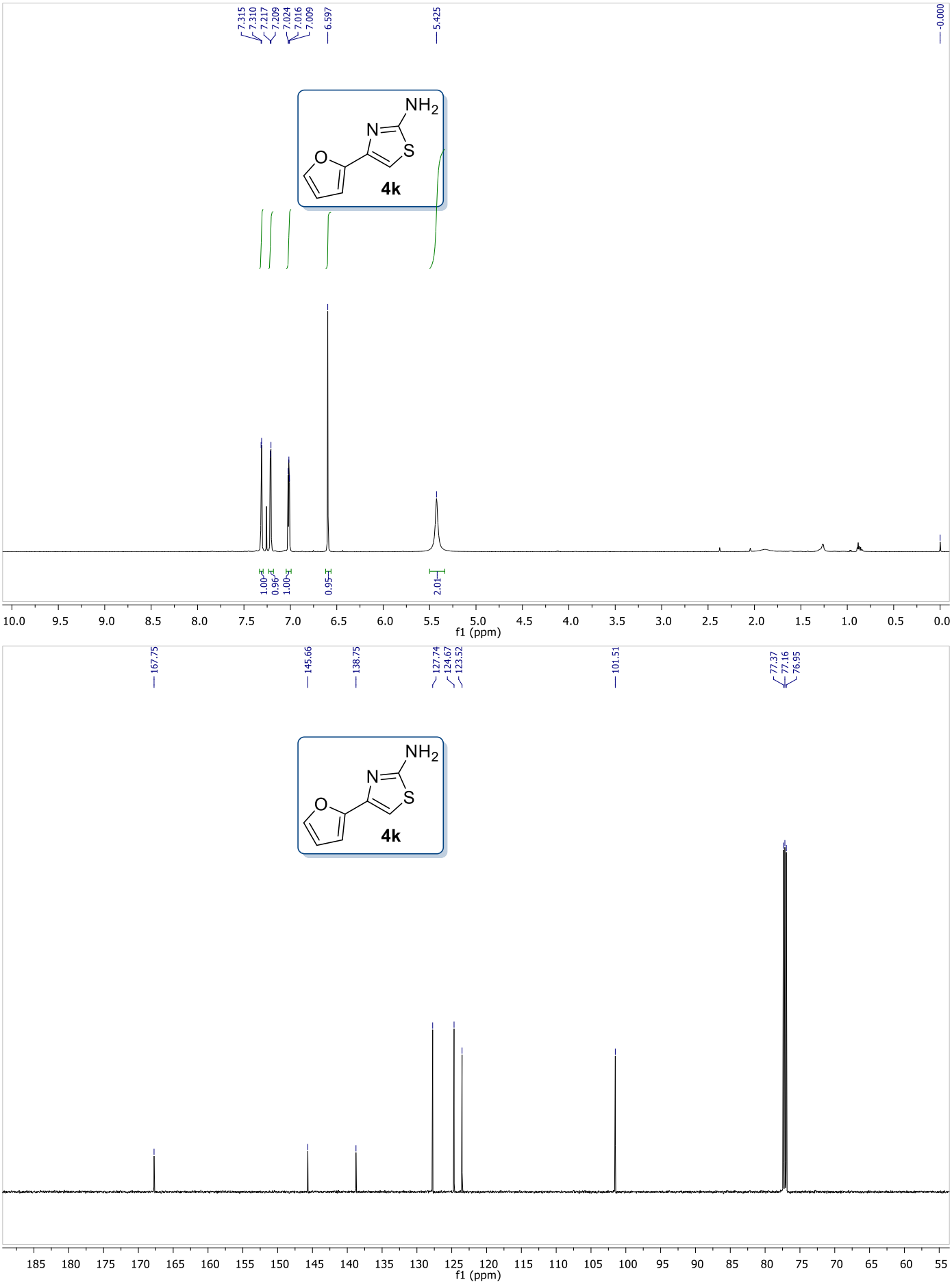


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6), **4j**

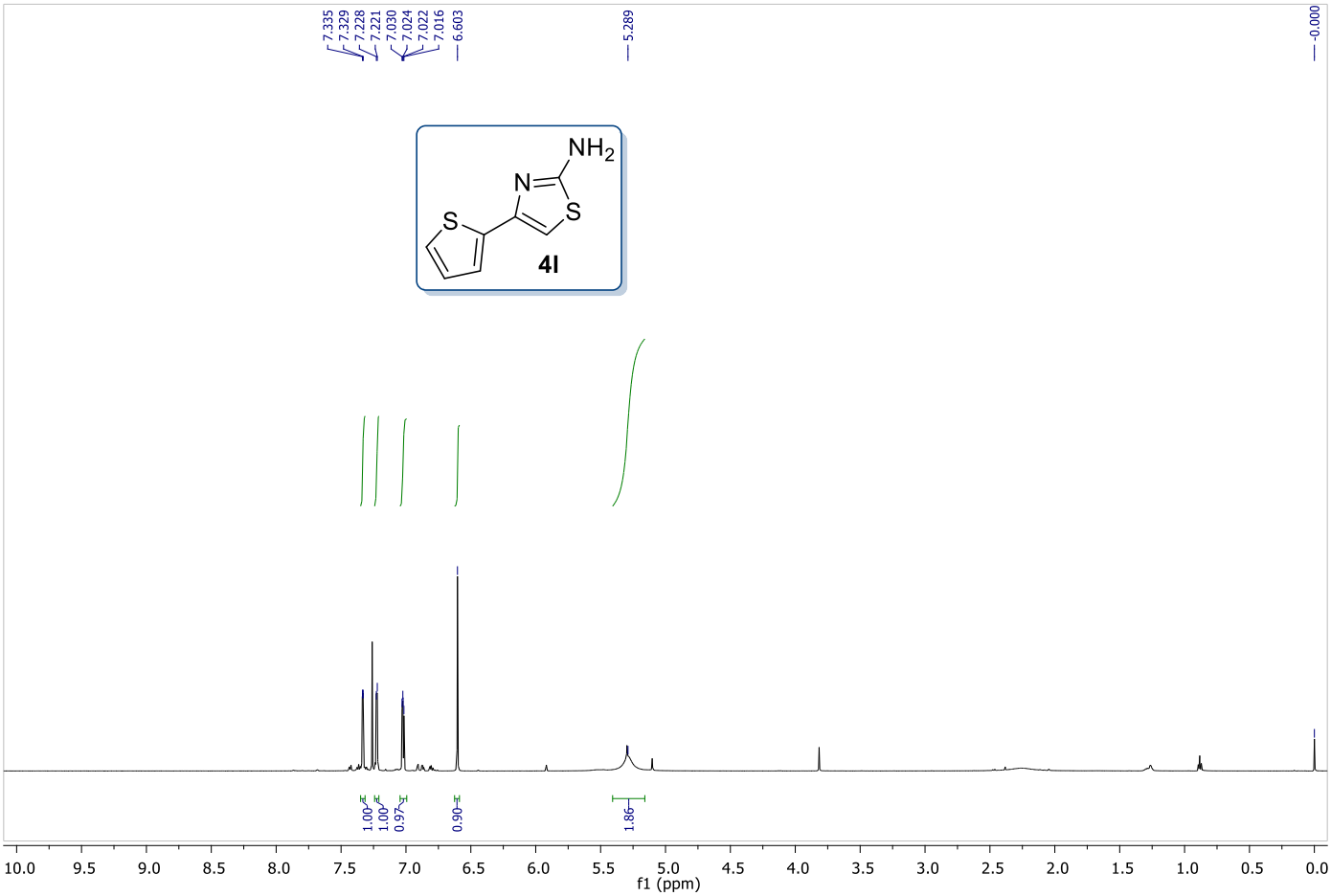


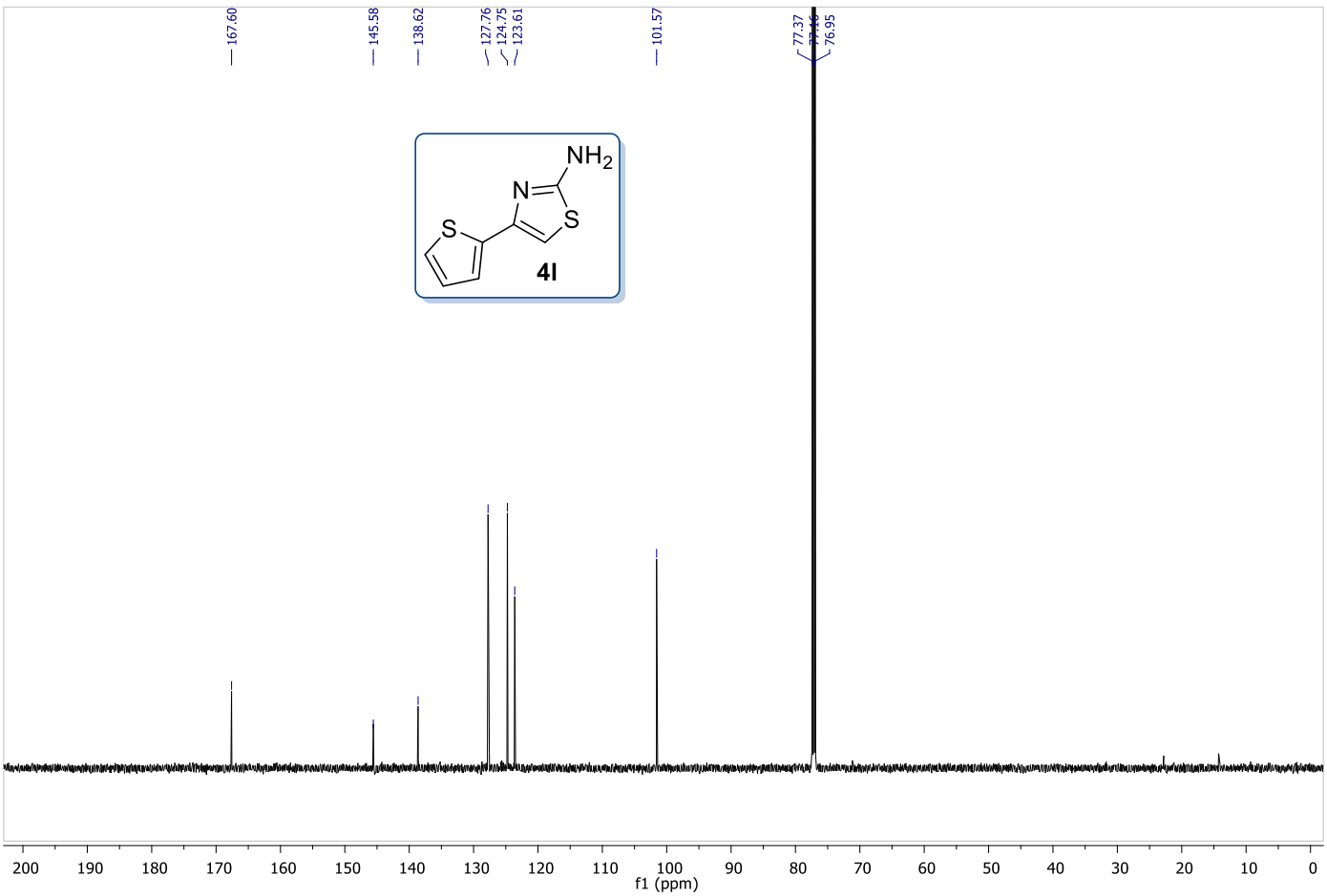


^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4k**

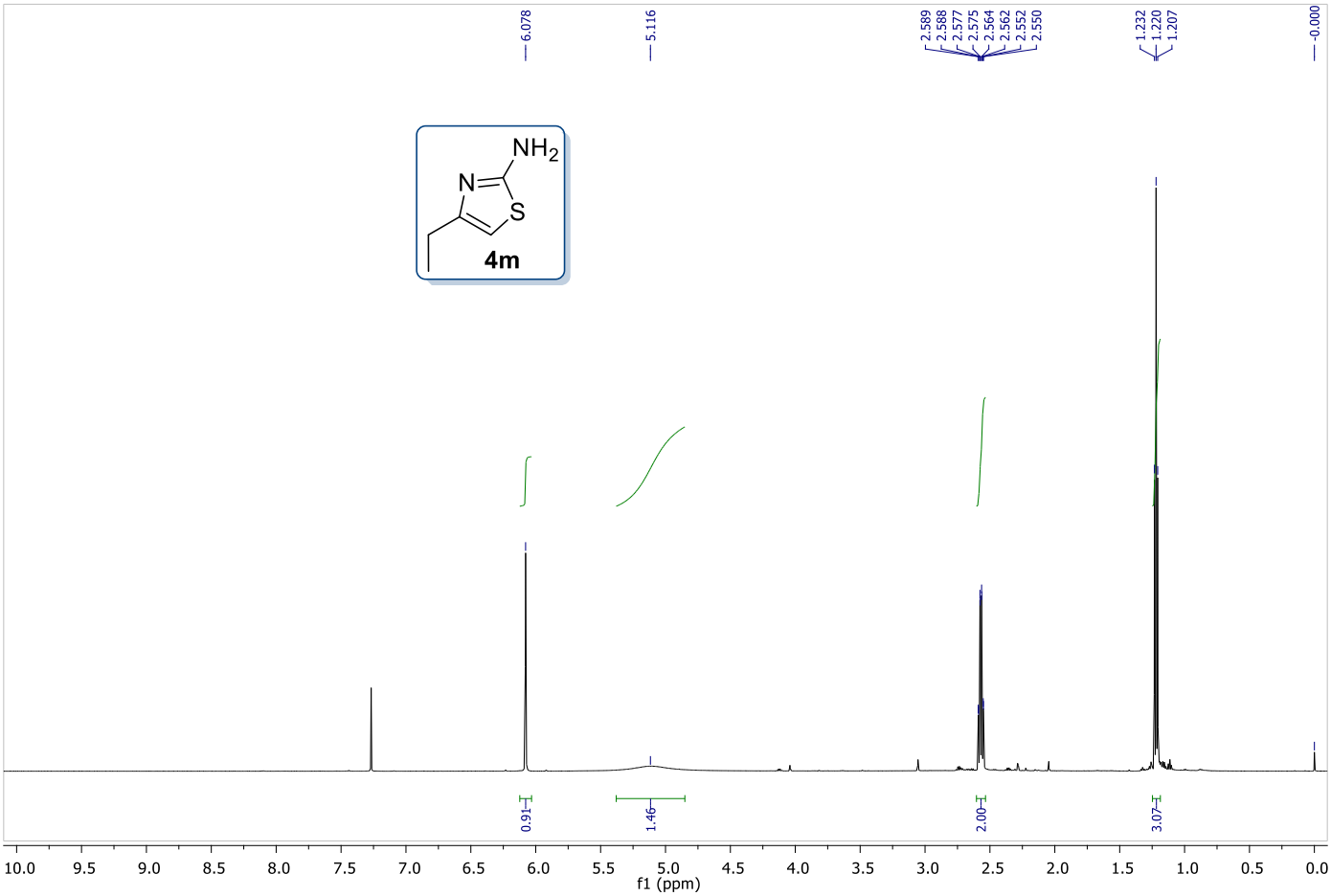


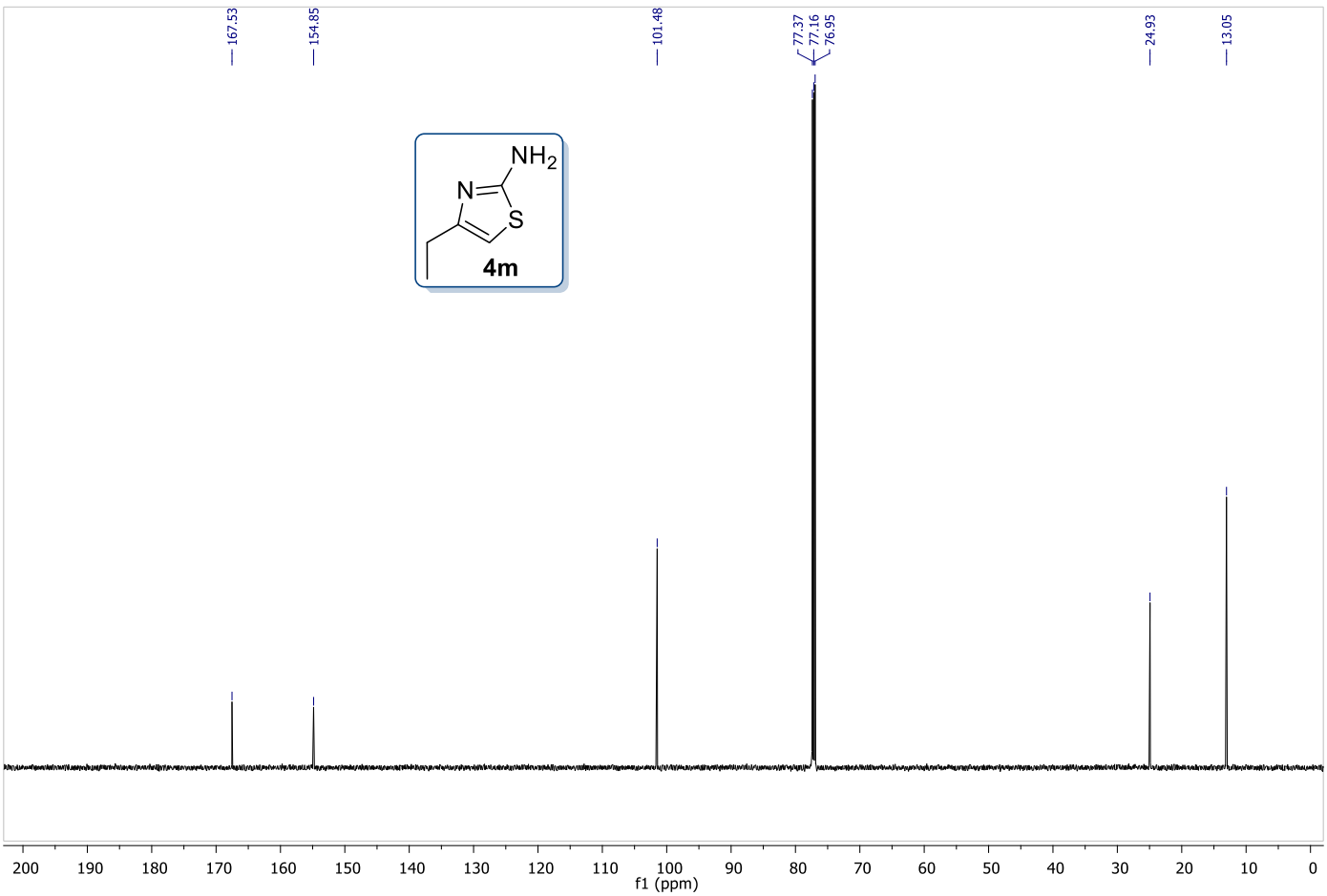
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4l**



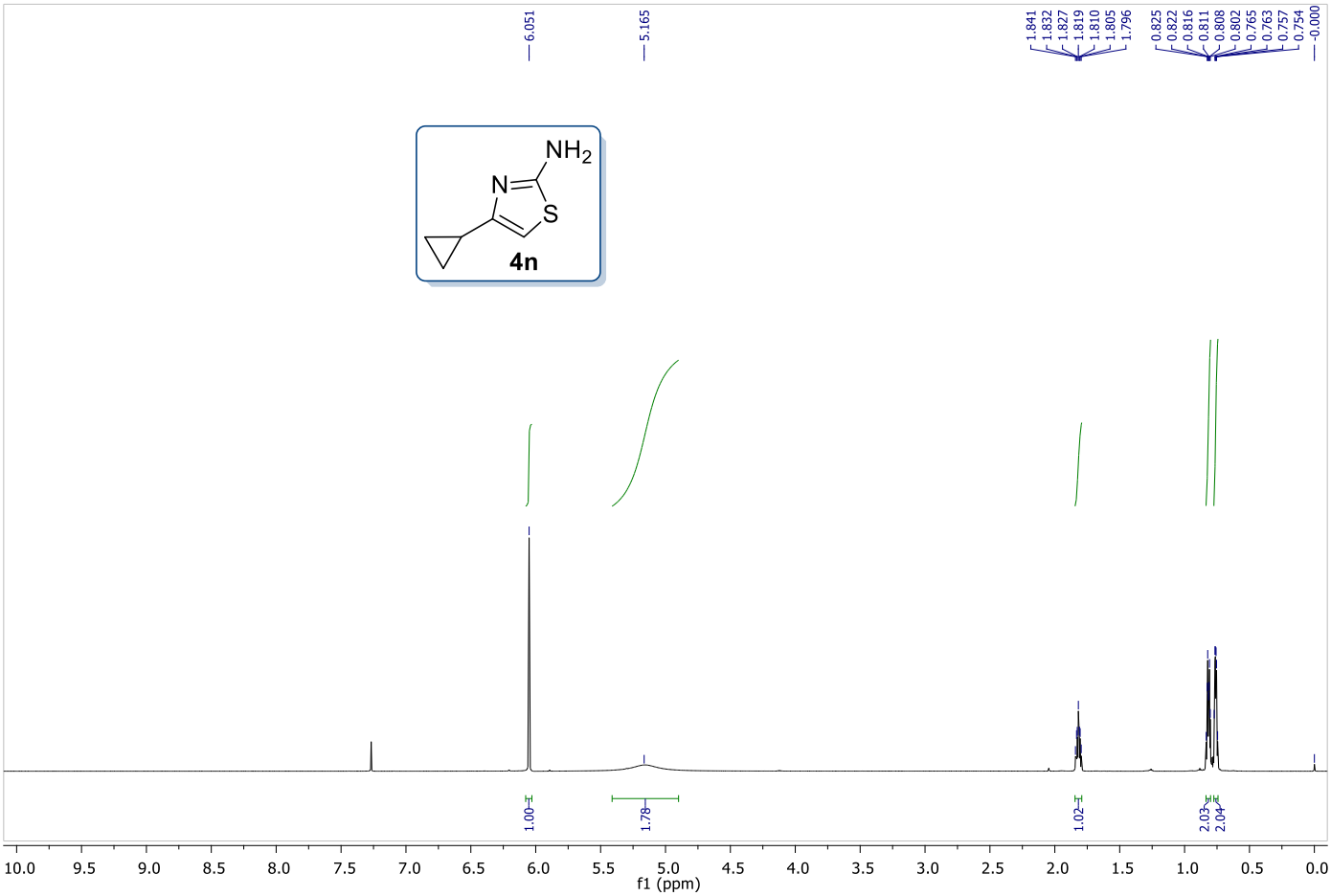


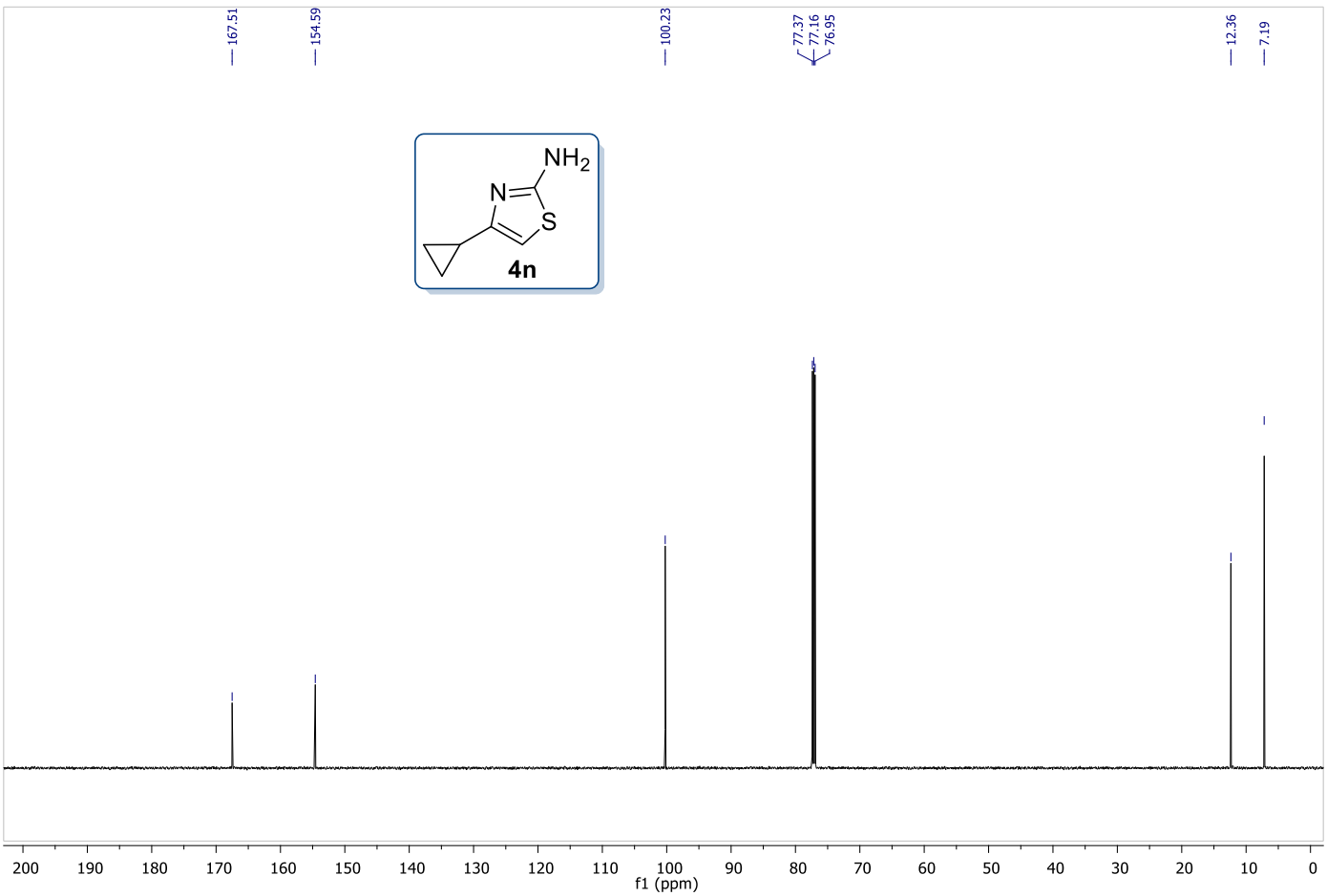
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4m**



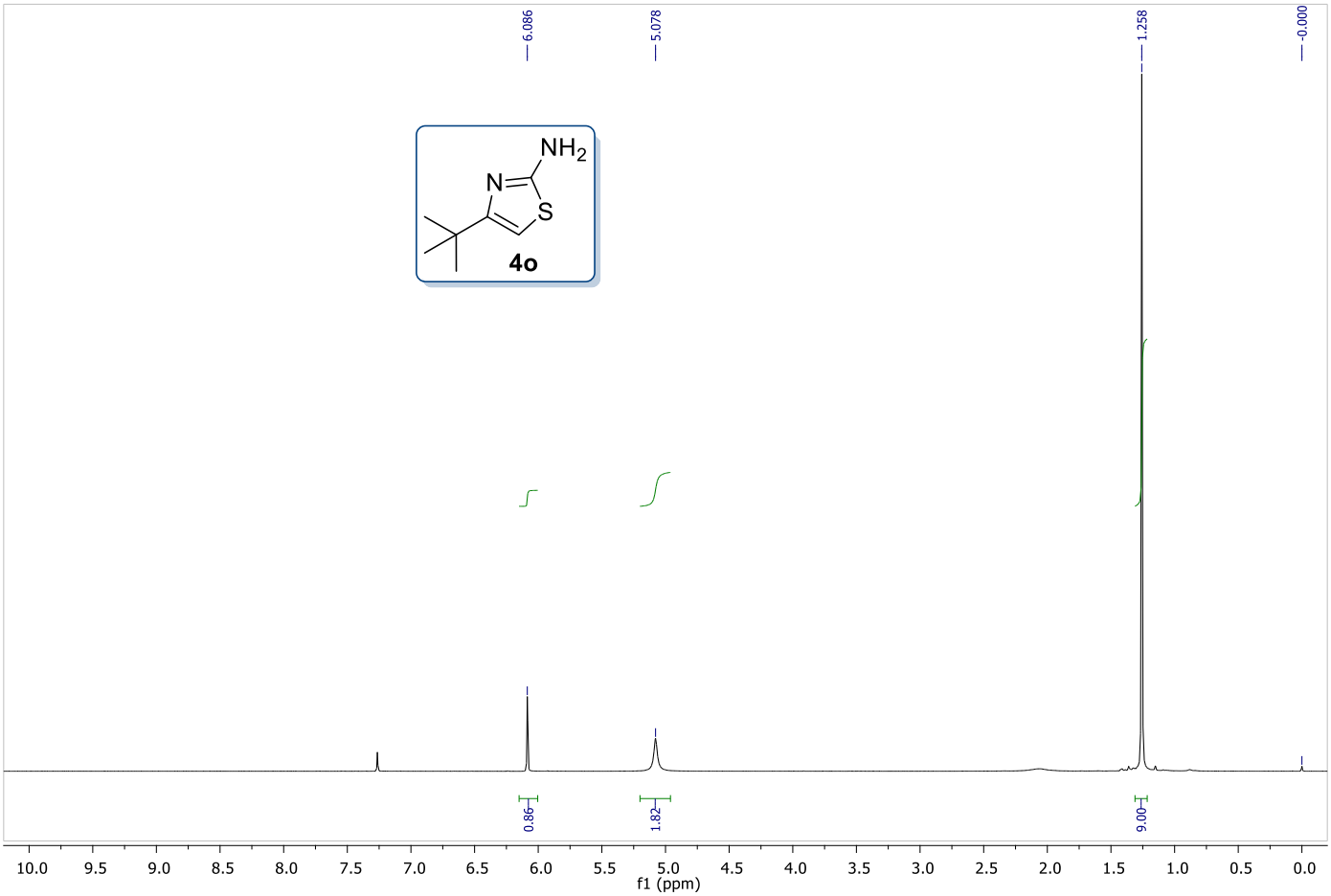


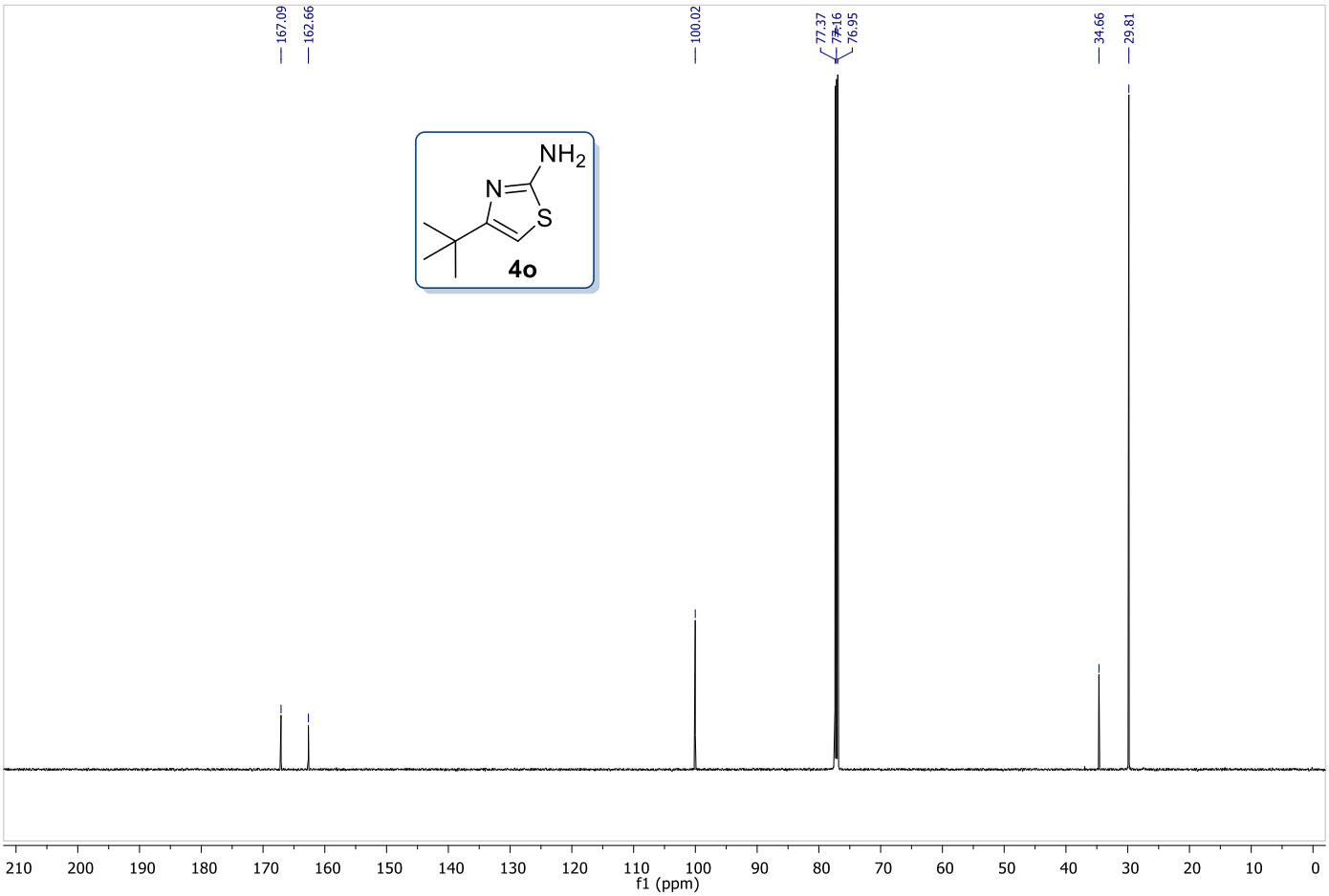
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4n**



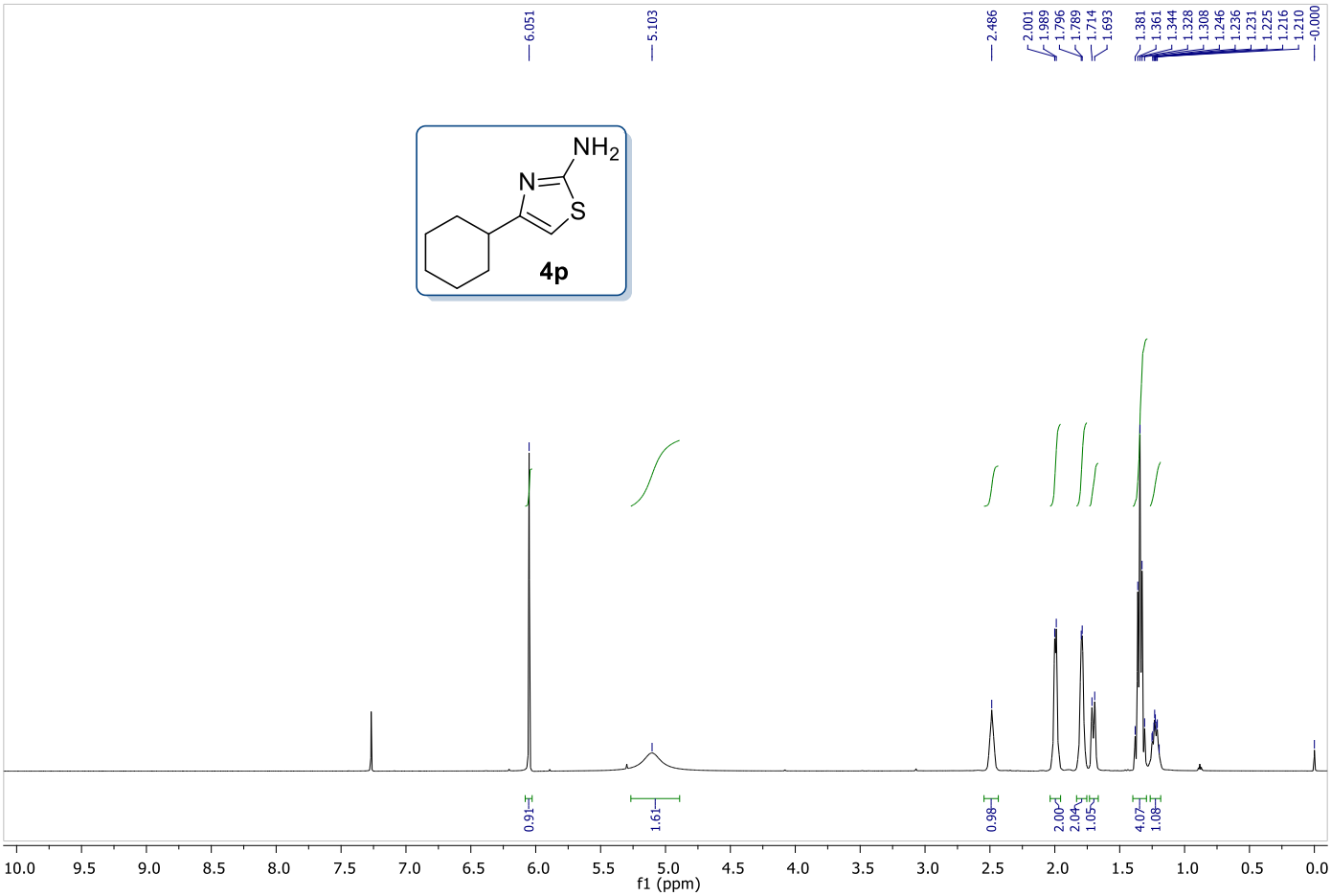


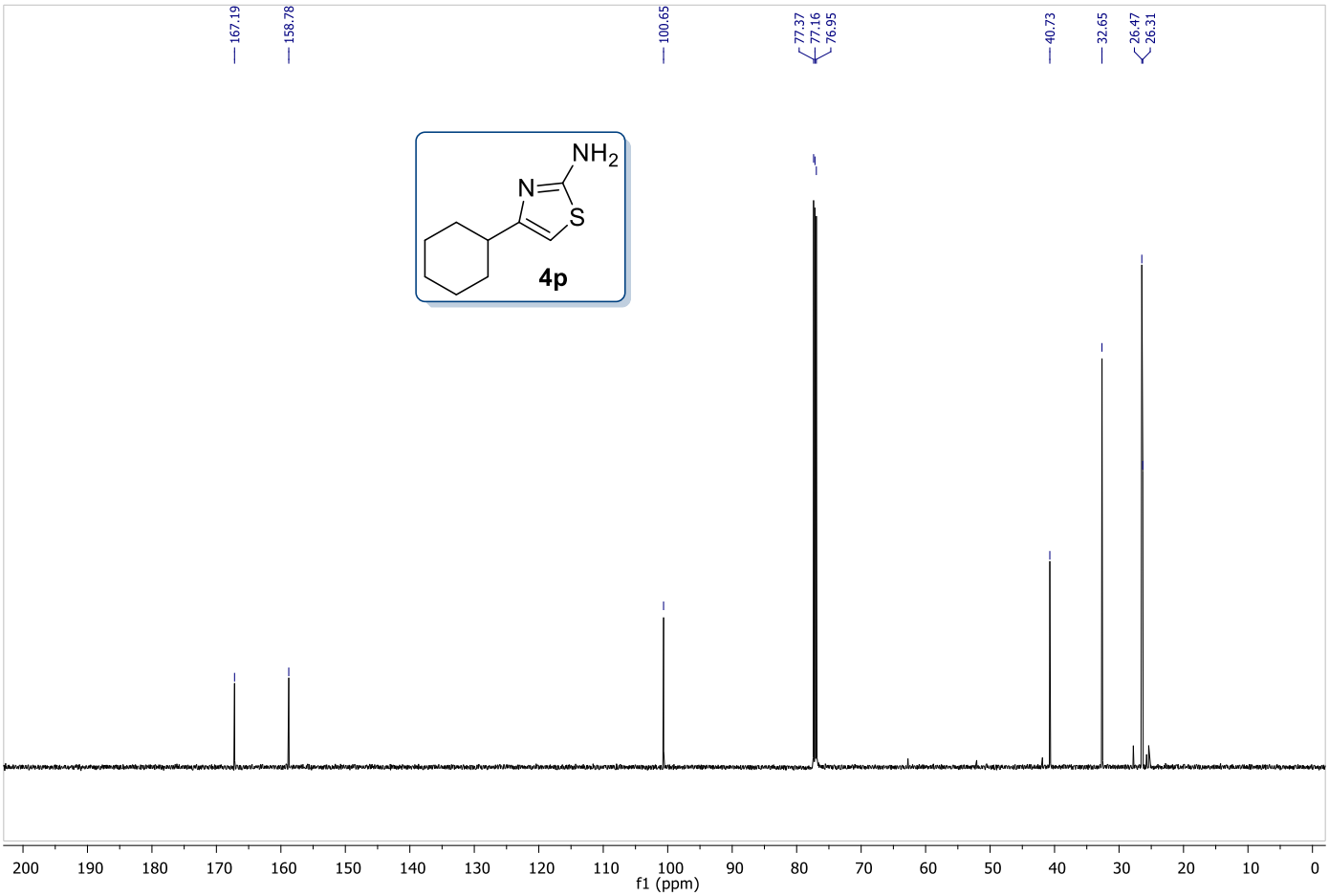
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4o**



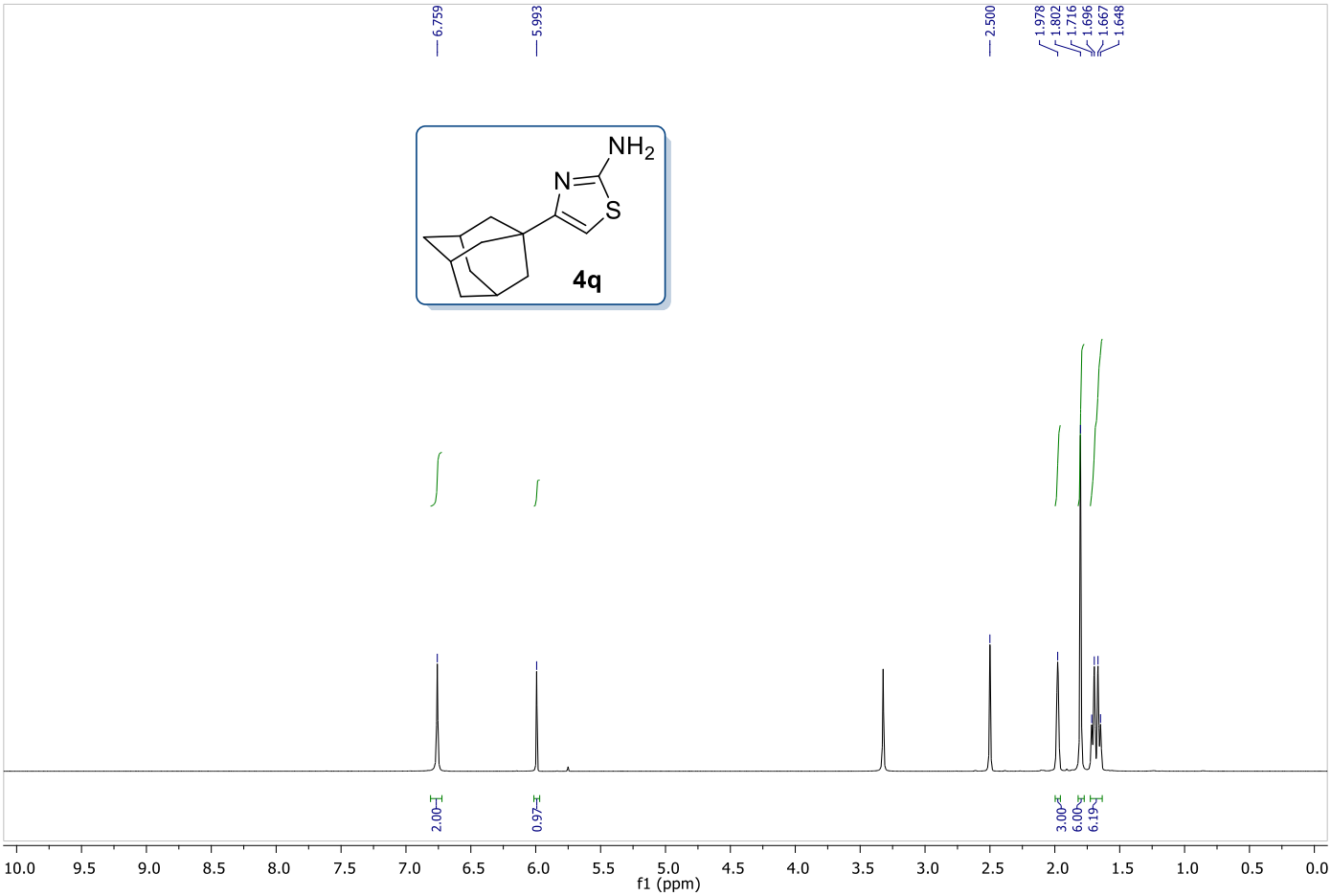


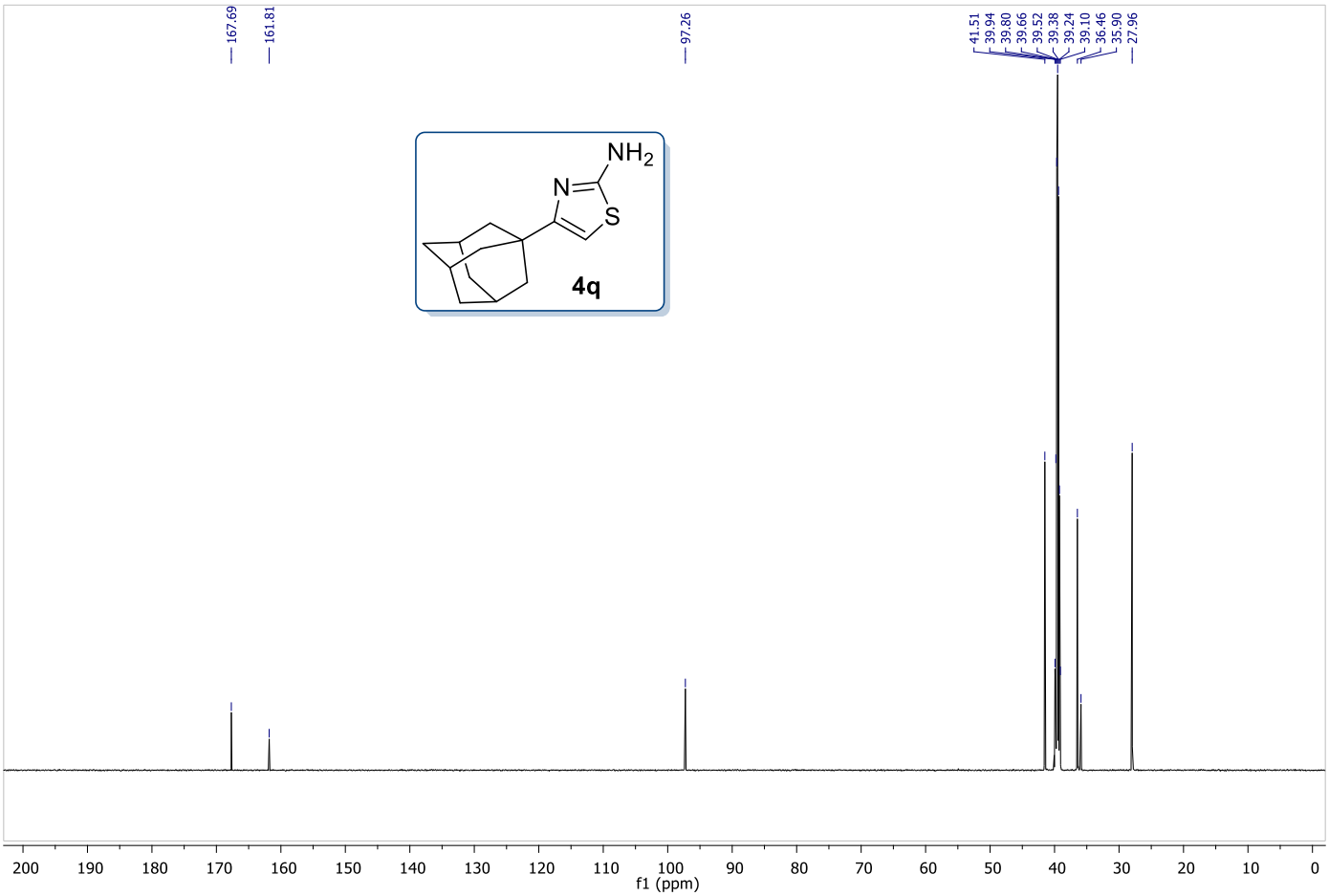
^{1}H NMR (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), **4p**



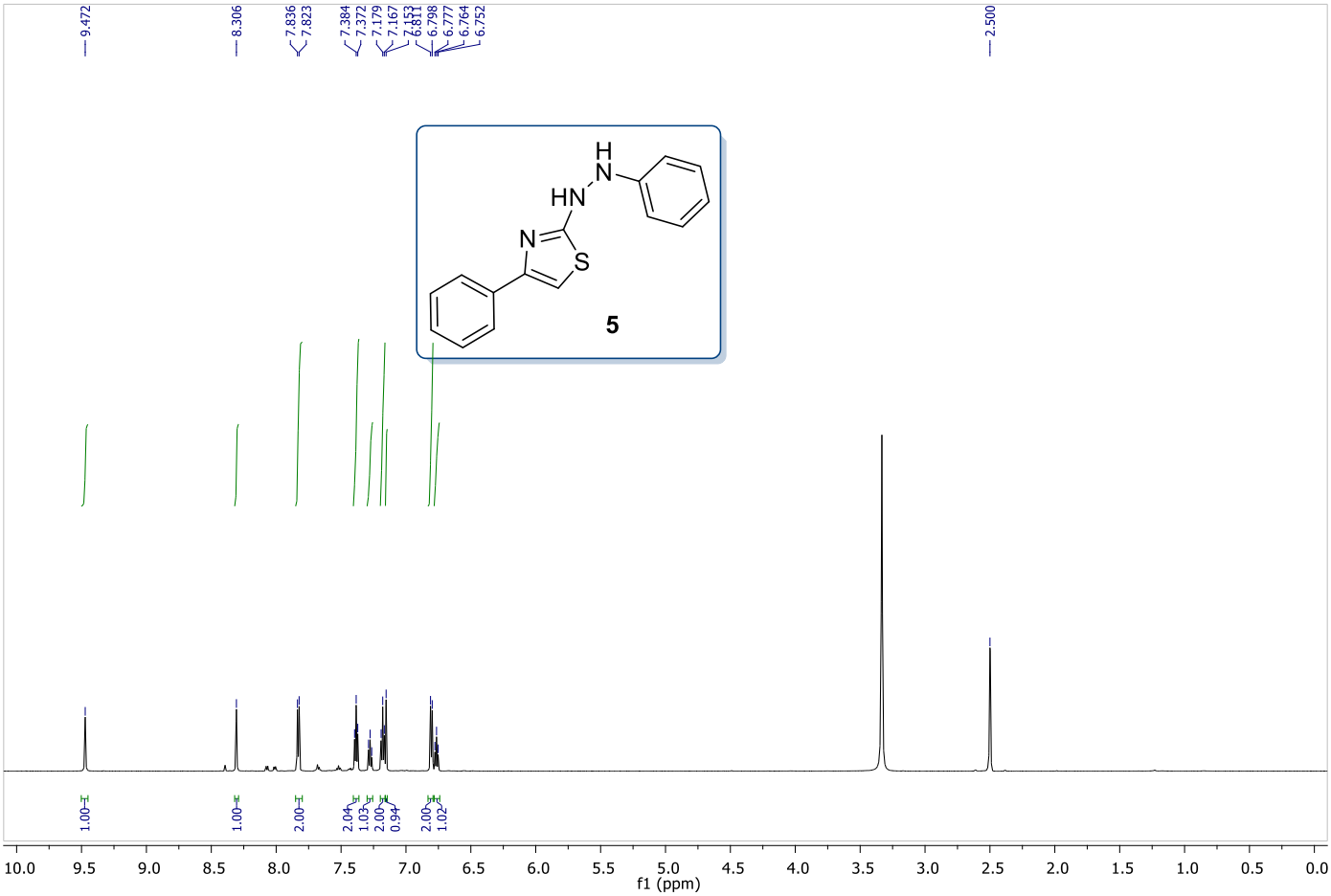


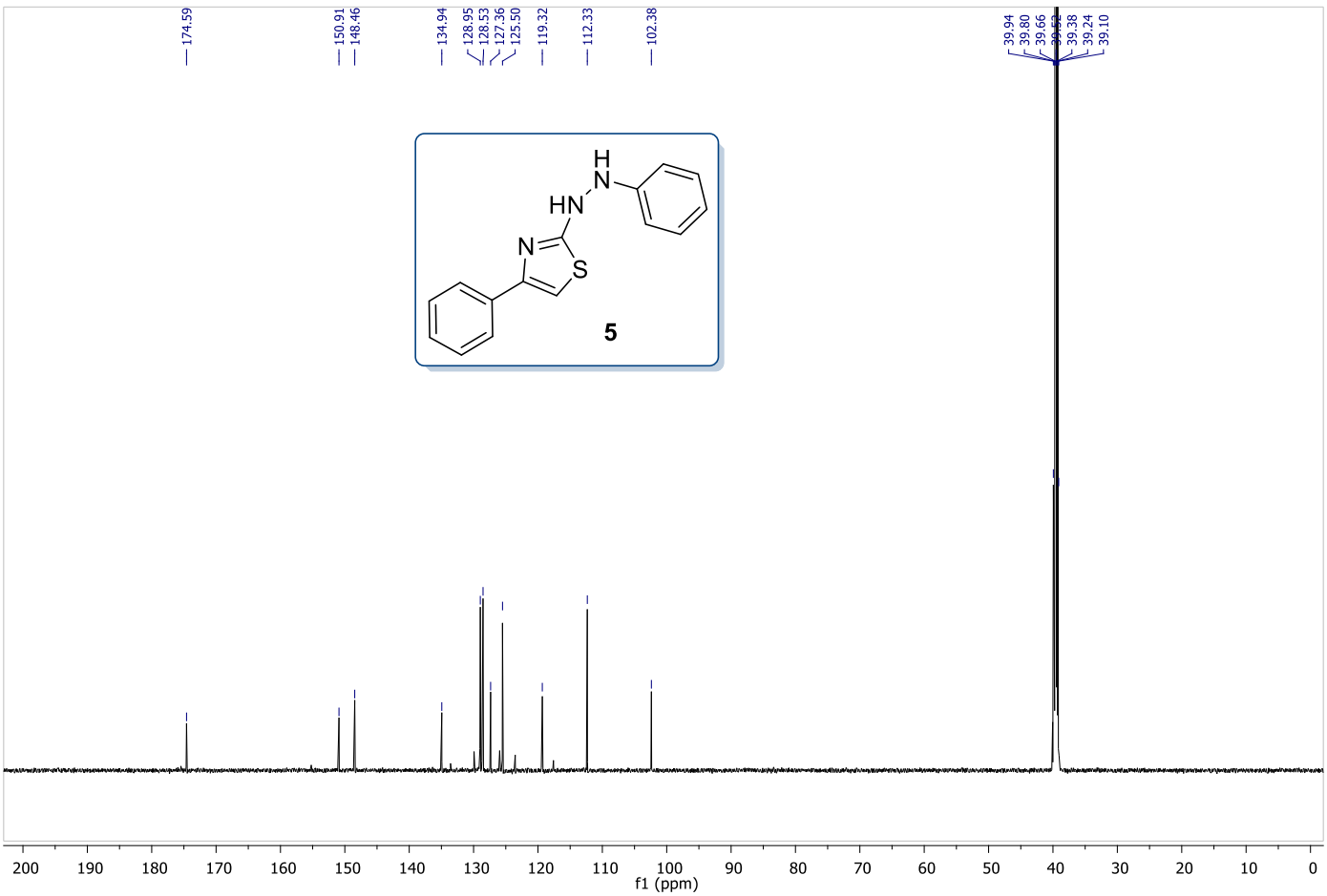
^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6), **4q**



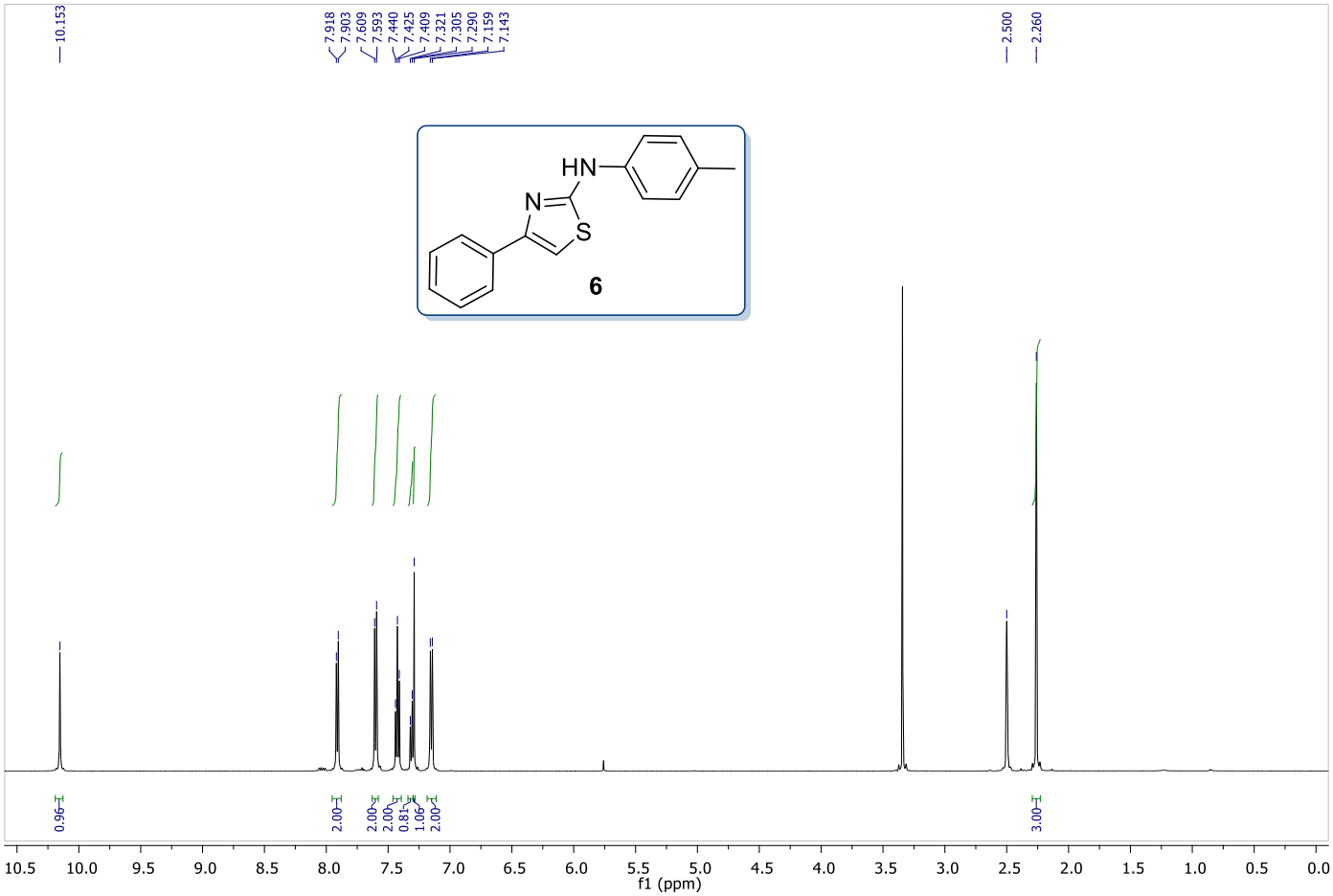


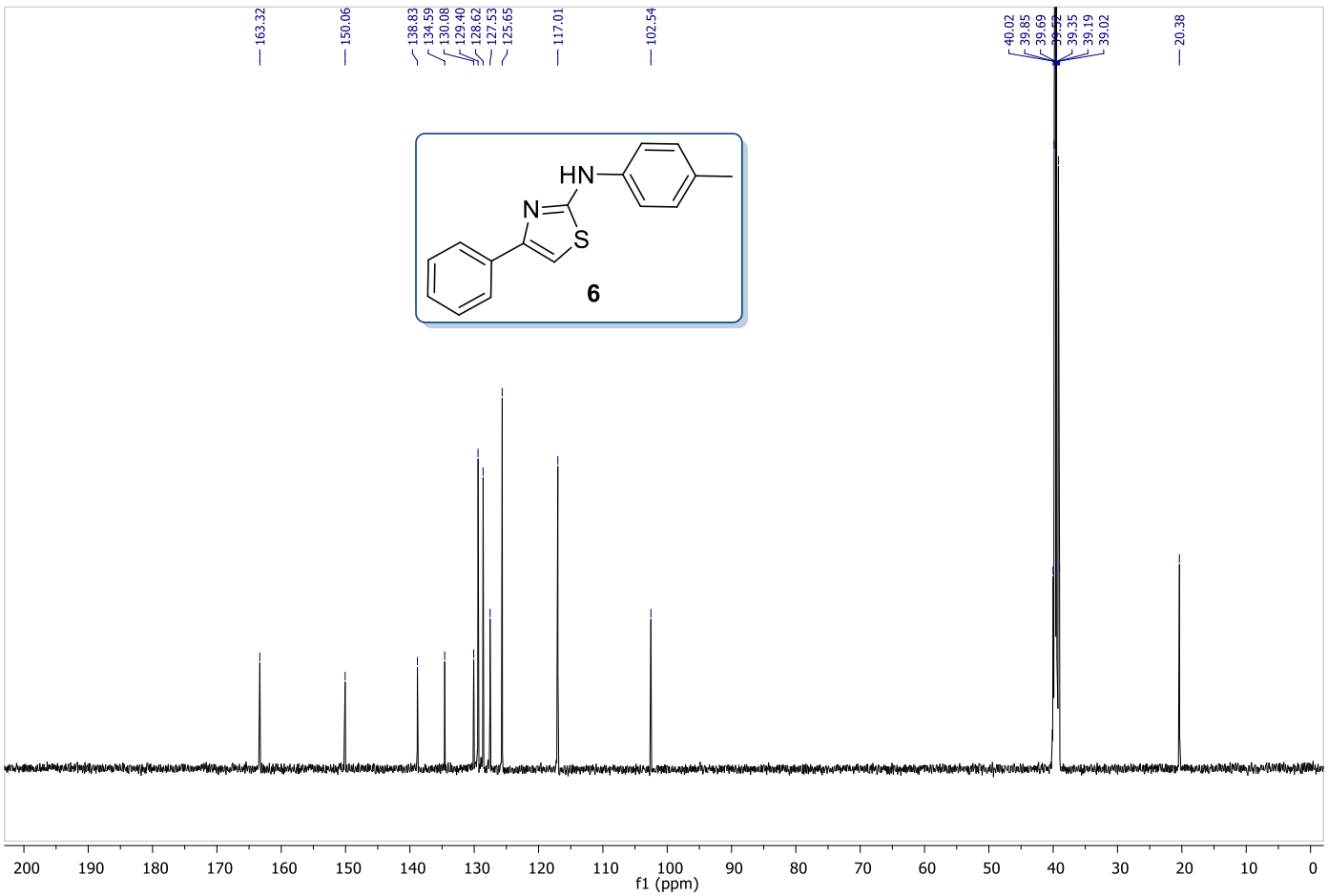
^{1}H NMR (600 MHz, DMSO-d$_6$) and ^{13}C{^{1}H} NMR (151 MHz, DMSO-d$_6$), **5**



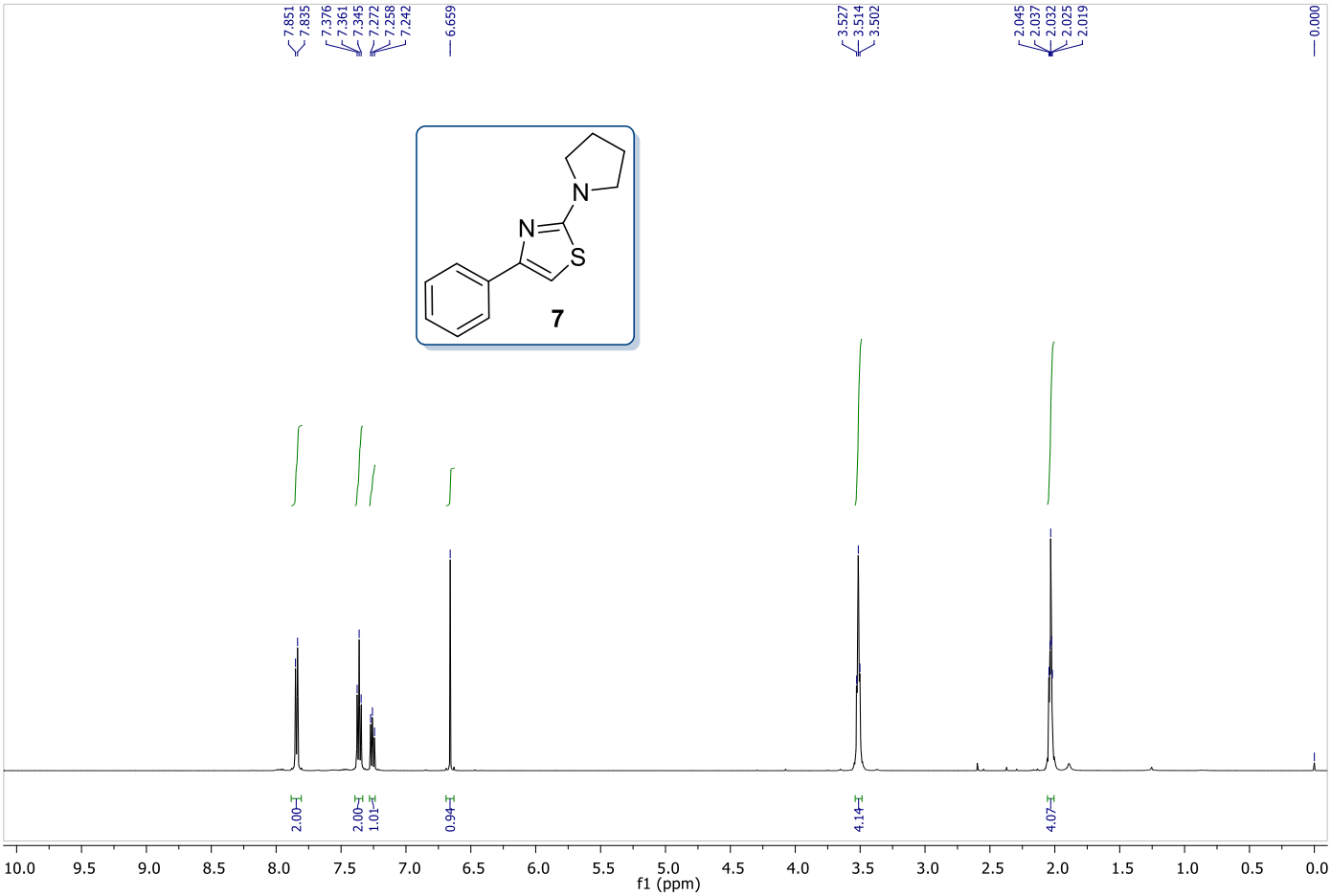


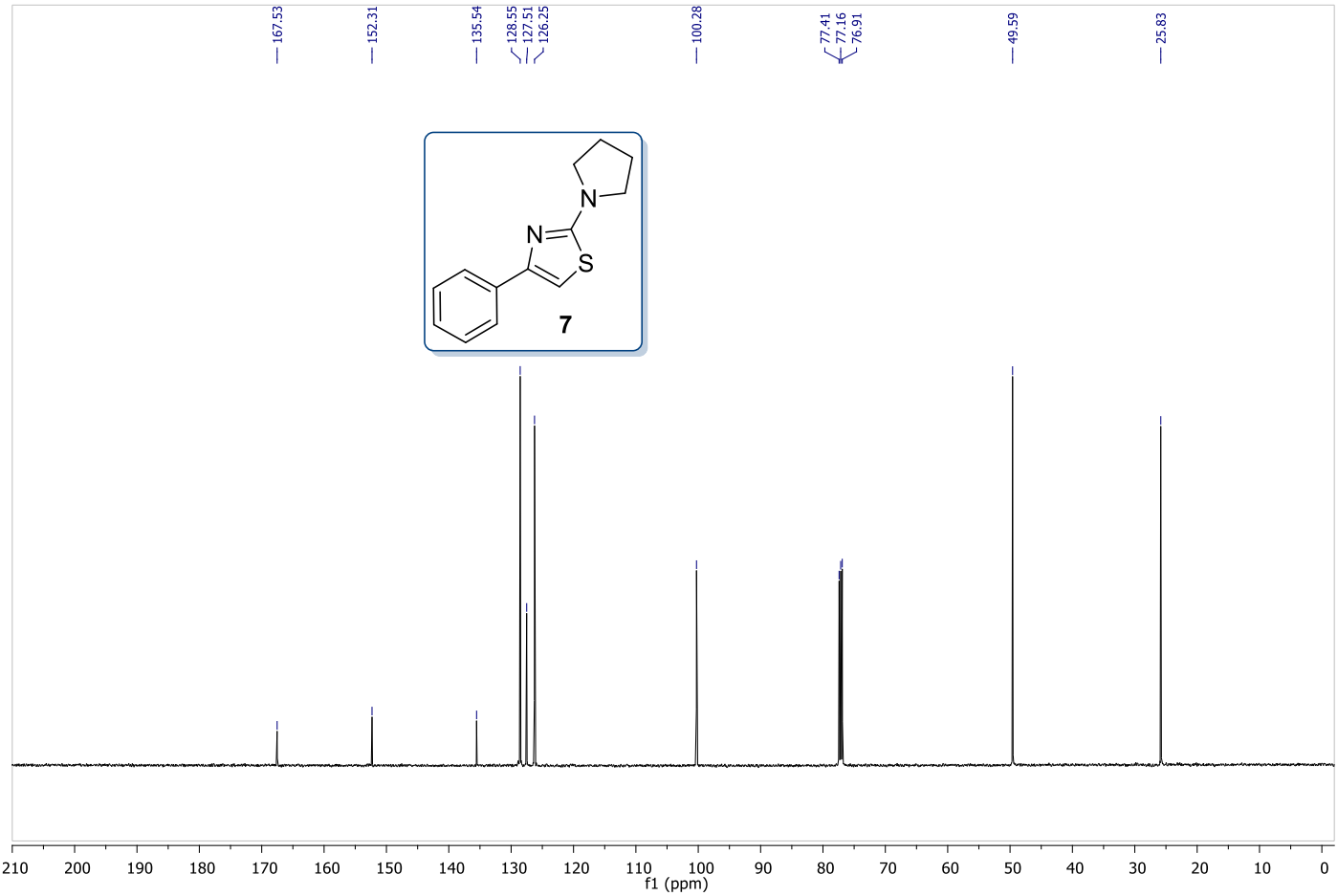
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6), **6**



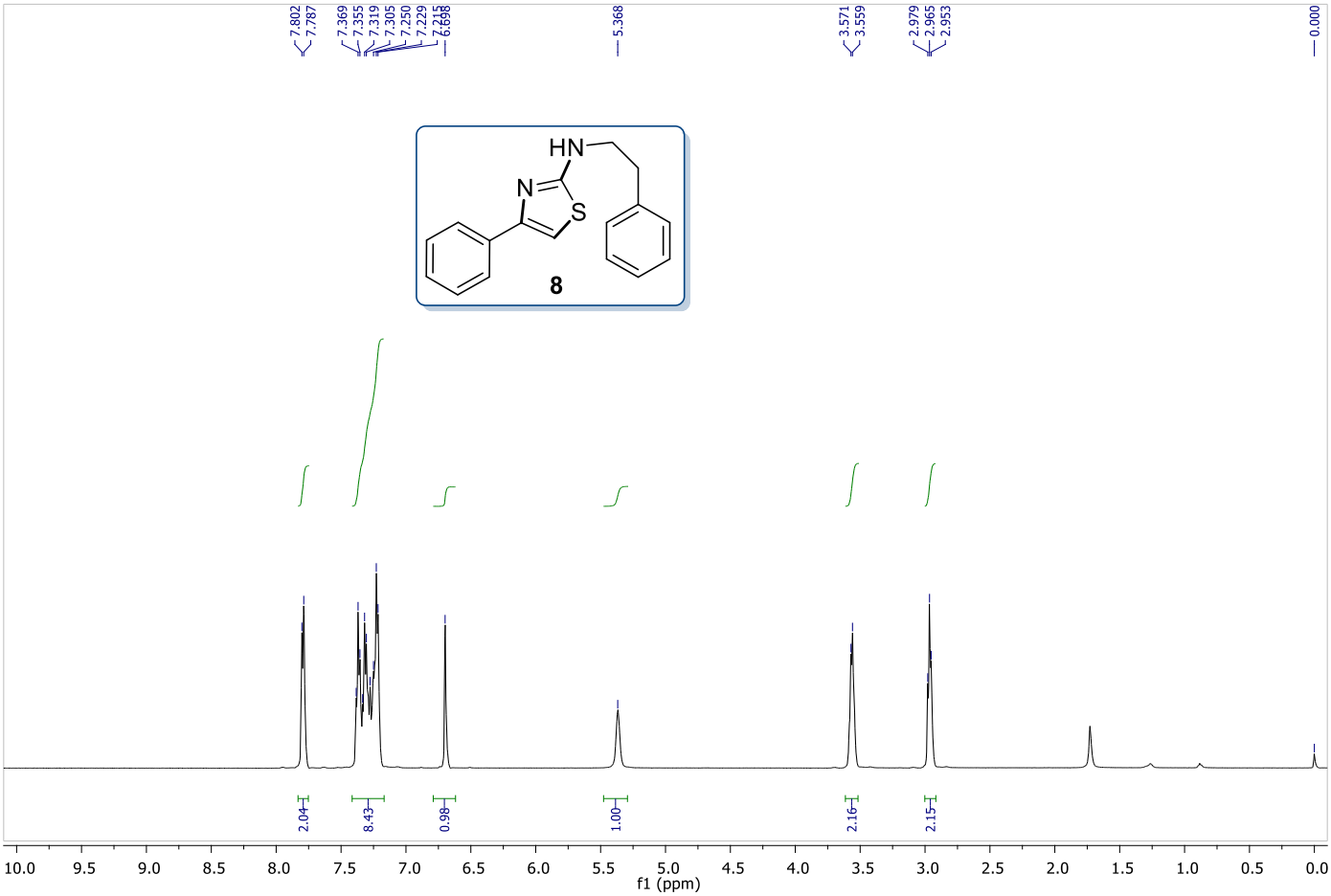


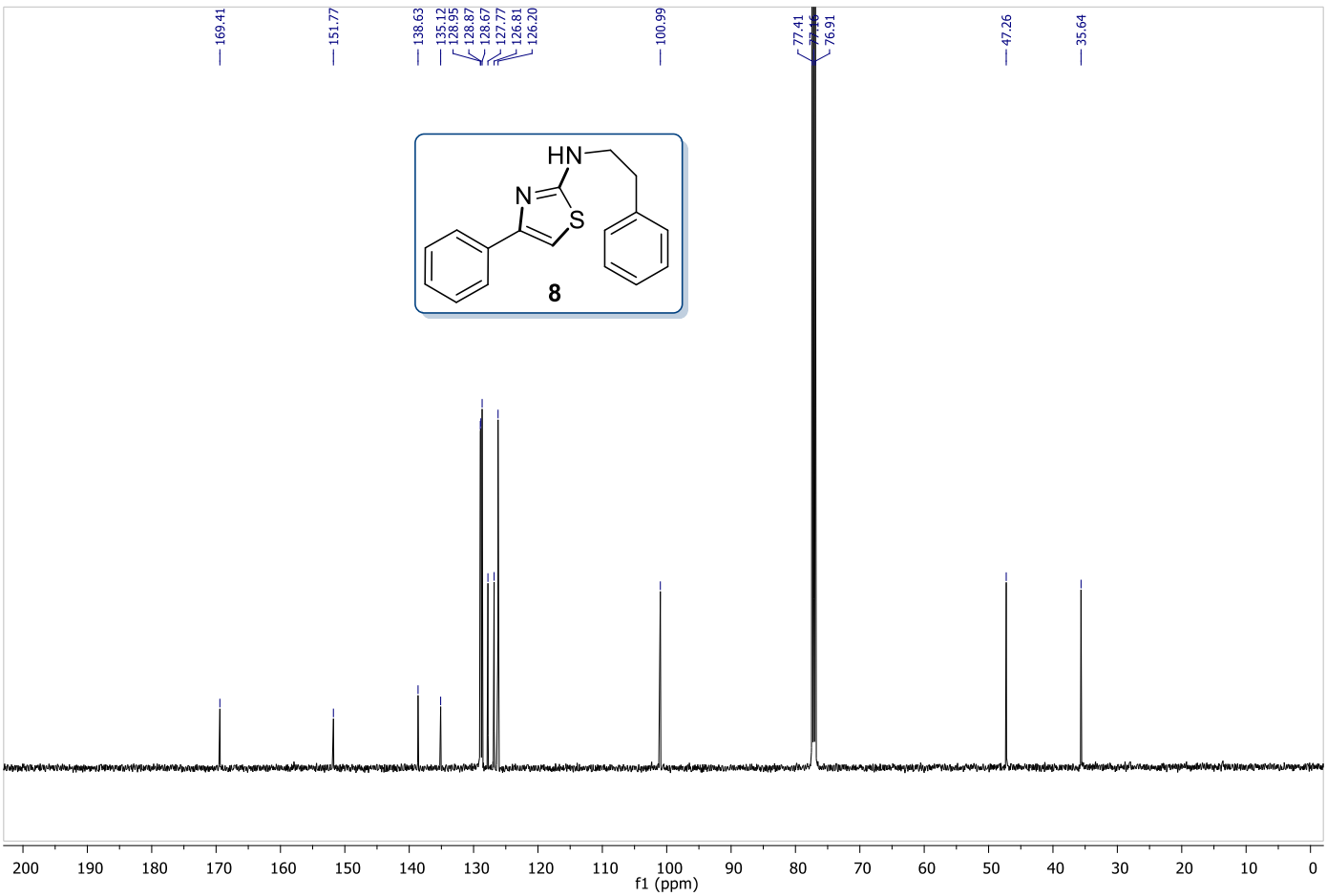
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **7**



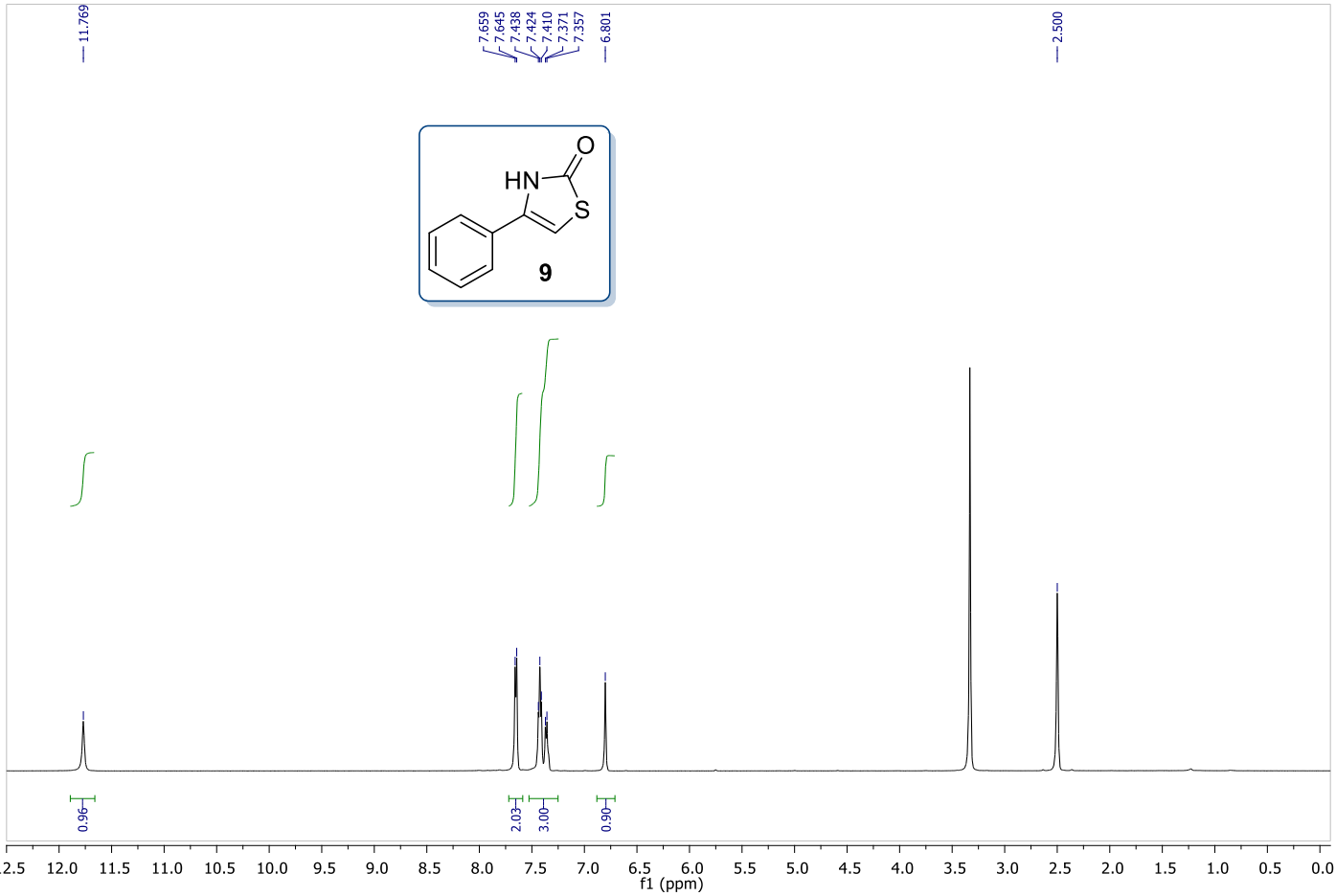


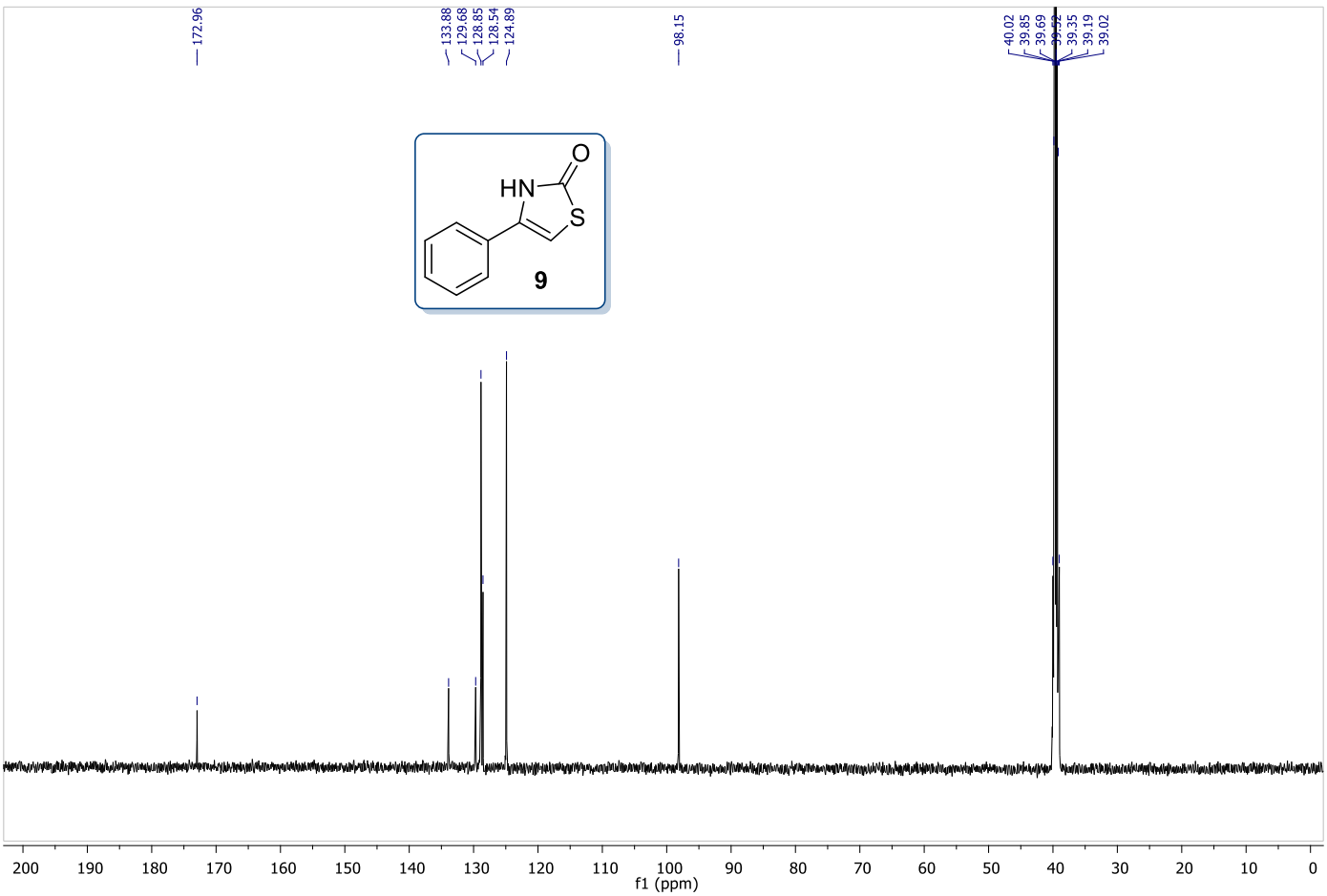
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), **8**



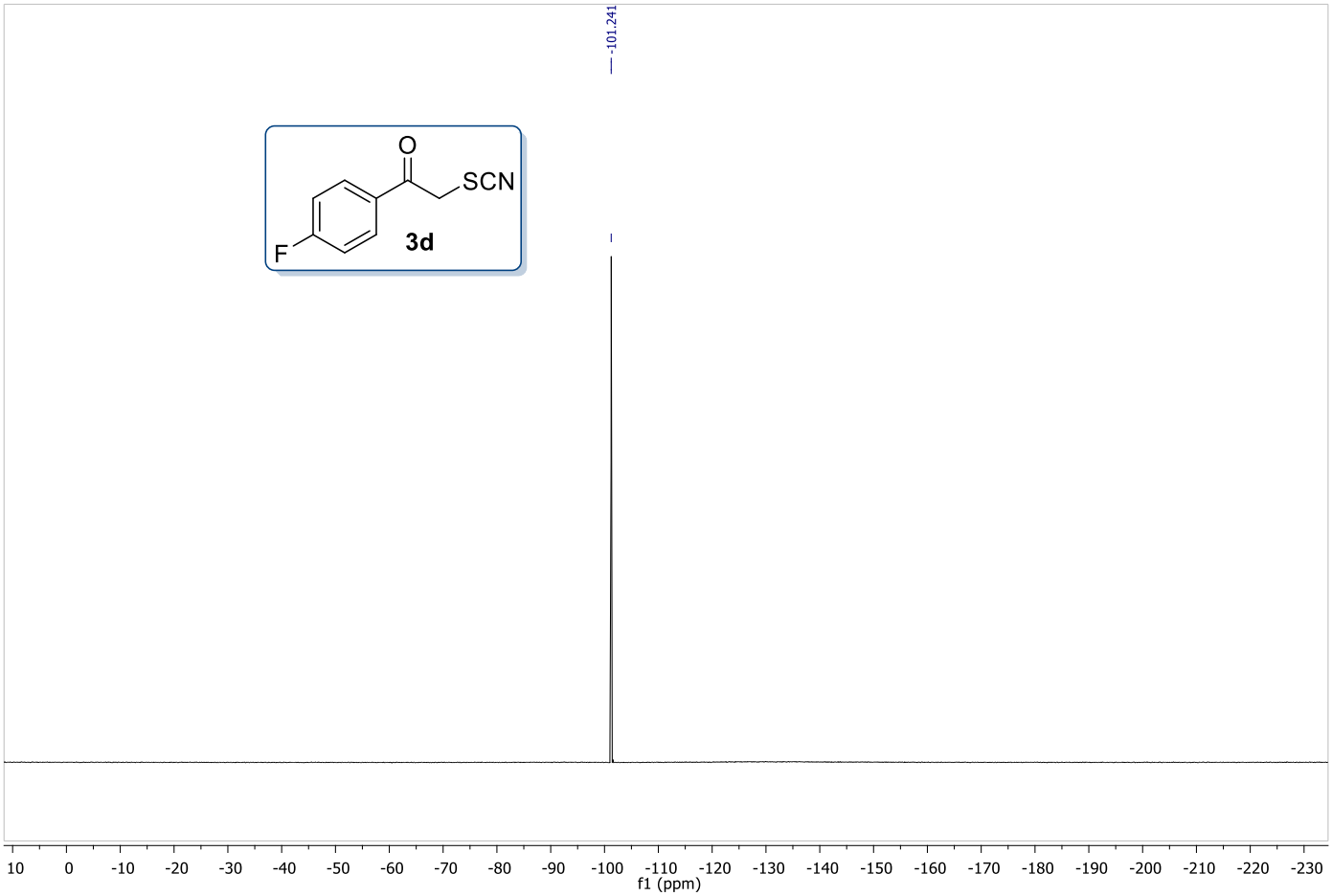


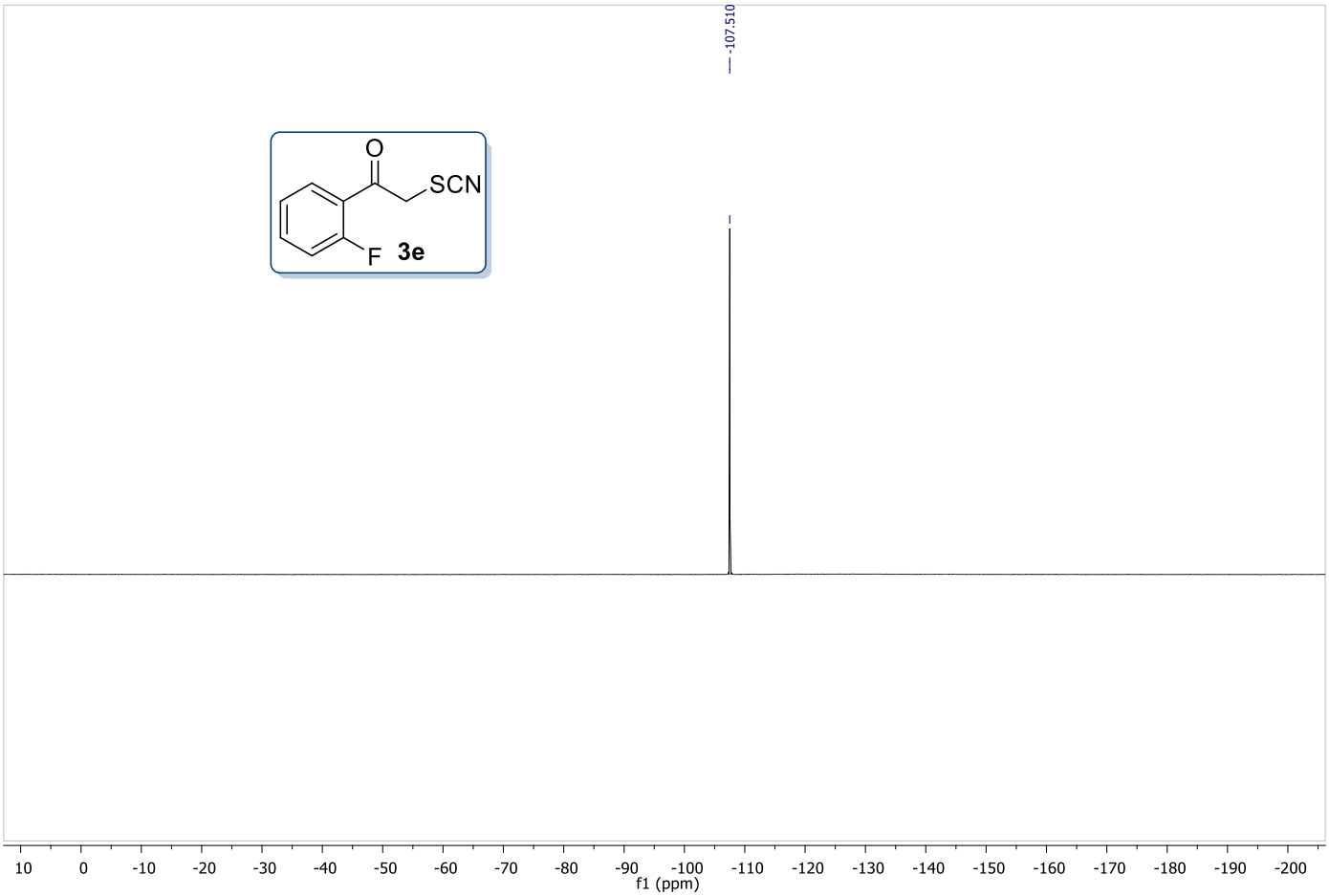
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6), **9**



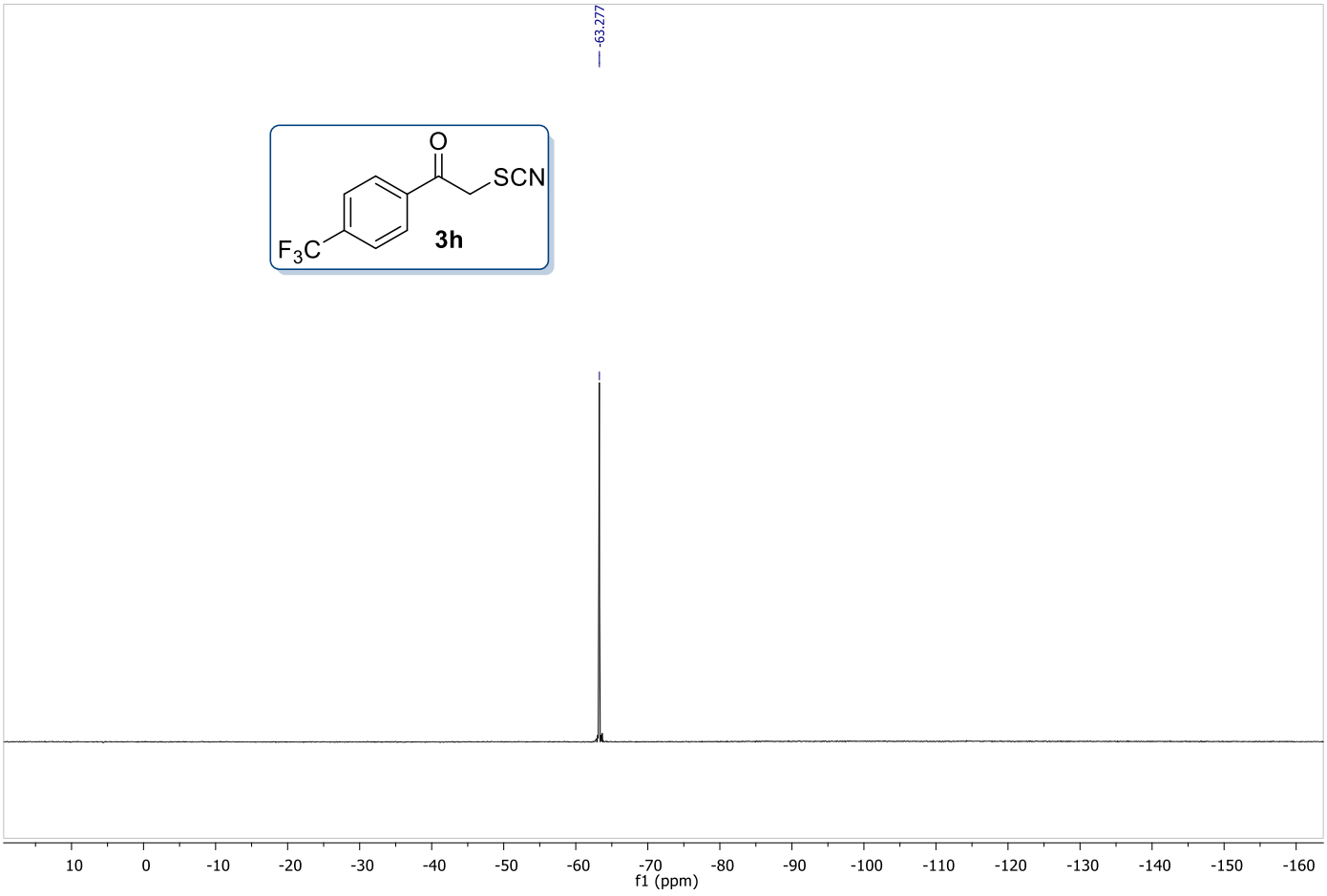


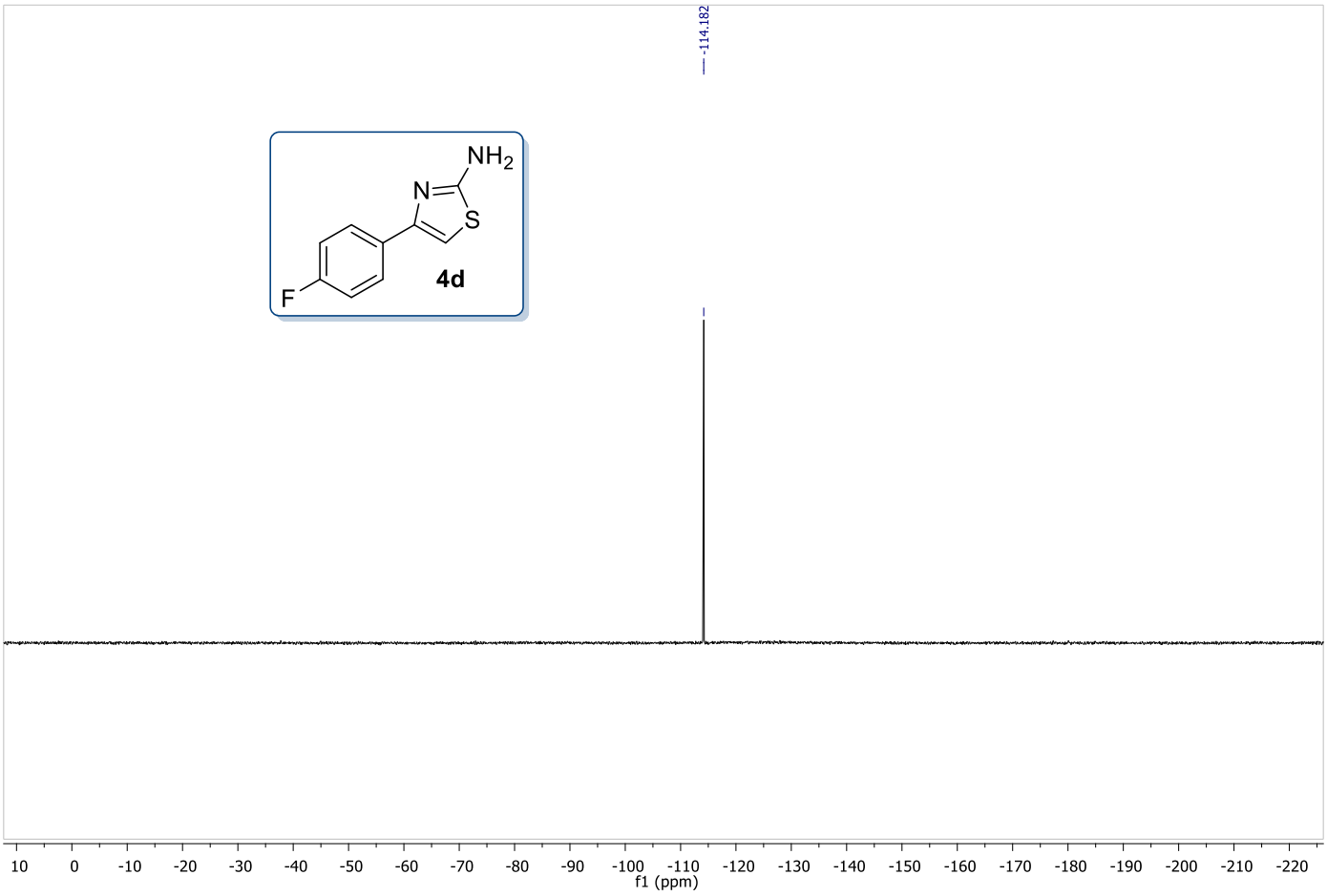
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), **3d** and **3e**





$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), **3h** and **4d**





$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), **4e** and $^{19}F\{^{1}H\}$ NMR (471 MHz, DMSO-d_6), **4h**