Supporting Information

Selective Desaturation of Amides: A Direct Approach to Enamides

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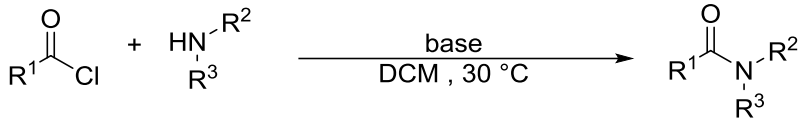
General remarks

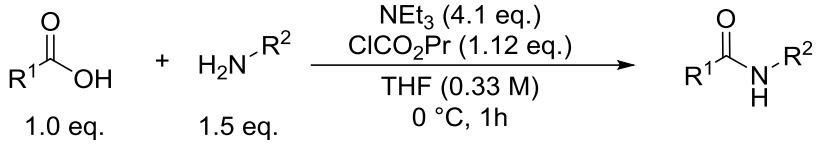
All manipulations were conducted with tubes. ^{1}H-NMR spectra were recorded on a Bruker AVANCE III-400 spectrometers. Chemical shifts are given in parts per million (ppm, δ), referenced to the solvent peak of CDCl3, defined at δ = 7.26 ppm (^{1}H NMR) and δ = 77.16 (^{13}C NMR). Coupling constants are quoted in Hz (*J*). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q) and quintet (quint) as they appeared in the spectrum. If the appearance of a signal differs from the expected splitting pattern, the observed pattern is designated as apparent (app). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) or broad (br). High Resolution Mass spectra were recorded using a Fourier Transform Ion Cyclotron Resonance Mass spectrometer (Waters Xevo G2 Q-TOF). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Preparation of substrates

Method A[1]:



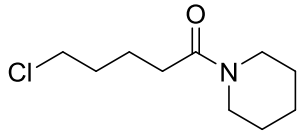
Method B[2]:



1a, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1u**, **1v, 1w, 1y, 1z, 1aa, 1ab, 1ac, 1ad, 1ae, 1af, 1ah, 1ai, 1aj** were prepared according Method A. **1s**, **1t**, and **1ag** were prepared according Method B.

Analytical data for products

5-Chloro-1-(piperidin-1-yl)pentan-1-one (**1r**)[3]



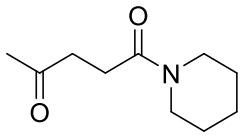
1r

Method A: A solution of Et_3N (1.52 g, 12.5 mmol) in DCM (20 mL) was added piperidine (1.02 g, 12 mmol) at room temperature. 5-Chloropentanoyl chloride (1.55 g, 10 mmol) was added in one portion with solution boiling. After allowing the reaction mixture to stir for 5 h at r.t., the precipitate formed was filtered off, the filtrate was concentrated, and isolated by column chromatography (silica gel, petroleum

ether/AcOEt), affording product **1r** as a colorless liquid in 92% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54-3.47 (m, 4H), 3.35 (t, *J* = 5.6 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.84-1.69 (m, 4H), 1.64-1.56 (m, 2H), 1.56-1.44 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 46.5, 44.6, 42.5, 32.3, 32.1, 26.4, 25.5, 24.4, 22.5.

HRMS *m/z* (ESI) calcd for $C_{10}H_{19}NOCl$ $[M+H]^+$ 204.1155, found: 204.1156.

1-(Piperidin-1-yl)pentane-1,4-dione (**1s**)[4]

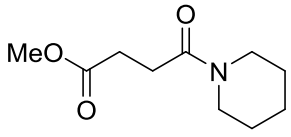


1s

Method B: A solution of 4-oxopentanoic acid (580.6 mg, 5.0 mmol) and triethylamine (632.2 mg, 6.25 mmol) in THF (10 mL) was cooled to 0 °C on an ice bath. Propyl chloroformate (643.4 mg, 5.25 mmol) was added dropwise to the cold solution. After allowing the reaction mixture to stir for 10 min at 0 °C, piperidine (510.9 mg, 6 mmol) was added and the reaction mixture was stirred for 60 min at 0 °C. The precipitate formed was filtered off, the filtrate was concentrated, and isolated by column chromatography (silica gel, petroleum ether/AcOEt), affording product **1s** as a colorless liquid in 86% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48-3.44 (m, 2H), 3.39-3.75 (m, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 2.52 (t, *J* = 6.4 Hz, 2H), 2.15 (s, 3H), 1.56-1.54 (m, 2H), 1.54-1.48 (m, 2H), 1.48-1.41 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 169.6, 46.3, 42.7, 38.0, 30.1, 26.9, 26.2, 25.4, 24.4.

HRMS *m/z* (ESI) calcd for $C_{10}H_{18}NO_2$ $[M+H]^+$ 184.1338, found: 184.1337.

Methyl 4-oxo-4-(piperidin-1-yl)butanoate (**1u**)



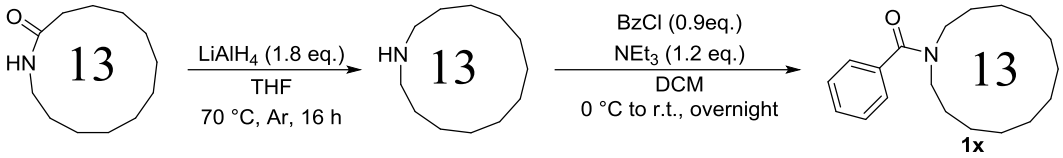
1u

Method A: A solution of Et_3N (1.52 g, 12.5 mmol) in DCM (20 mL) was added piperidine (1.02 g, 12 mmol) at room temperature. Methyl 4-chloro-4-oxobutanoate (1.50 g, 10 mmol) was added in one portion with solution boiling. After allowing the reaction mixture to stir for 5 h at r.t., the precipitate formed was filtered off, the filtrate was concentrated, and isolated by column chromatography (silica gel, petroleum ether/AcOEt), affording product **1u** as a colorless liquid in 90% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.54-3.50 (m, 2H), 3.42-3.37 (m, 2H), 2.66-2.57 (m, 4H), 1.65-1.58 (m, 2H), 1.58-1.47 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 169.2, 51.6, 46.3, 42.8, 29.2, 27.9, 26.3, 25.4,

24.5.

HRMS *m/z* (ESI) calcd for $C_{10}H_{18}NO_3$ $[M+H]^+$ 200.1287, found: 200.1285.

(azacyclotridecan-1-yl)(phenyl)methanone (**1x**)



1x

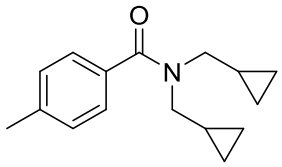
To the solution of azacyclotridecan-2-one (1.0 g, 5.07 mmol) in THF (25 mL) at r.t. under argon, $LiAlH_4$ (349 mg, 9.19 mmol) was added gradually and the reaction mixture was refluxed during 16 h. Then, a saturated solution of Na_2SO_4 was added gradually at 0 °C to neutralize the excess of $LiAlH_4$, followed diethyl ether/*n*-hexane 1:1 (50 mL) and excess of solid K_2CO_3 to absorb the whole aqueous phase. The organic phase was decanted and the precipitate was washed three times with diethyl ether/pentane 1:1. The solvent was removed under reduced pressure to give azacyclotridecane (0.90 g, 97%) as a colorless oil. And then, according to Method A, a solution of Et_3N (816 mg, 5.90 mmol) in DCM (10 mL) was added azacyclotridecane (0.90 g, 4.92 mmol) at room temperature. Benzoyl chloride (622 mg, 4.43 mmol) was added in one portion with solution boiling. After allowing the reaction mixture to stir for 5 h at r.t., the precipitate formed was filtered off, the filtrate was concentrated, and isolated by column chromatography (silica gel, petroleum ether/AcOEt), affording product **1x** as a colorless liquid in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 5H), 3.46 (t, *J* = 7.9 Hz, 2H), 3.17 (t, *J* = 7.5 Hz, 2H), 1.85-1.70 (m, 2H), 1.63-1.49 (m, *J* = 7.6 Hz, 2H), 1.46-1.31 (m, 14H), 1.25–1.13 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 137.5, 129.1, 128.4, 126.5, 50.7, 46.1, 26.8, 26.1, 25.5, 24.9, 24.5.

HRMS *m/z* (ESI) calcd for $C_{19}H_{29}NO_3$ $[M+H]^+$ 288.2327, found: 288.2322.

N,N-bis(cyclopropylmethyl)-4-methylbenzamide (**1ak**)



1ak

A solution of *N*-(cyclopropylmethyl)-4-methylbenzamide (567.9 mg, 3 mmol) in dry THF (30 mL) was added NaH (150 mg, 3.75 mmol, ca 60% dispersion in oil) at 0 °C under Ar atmosphere. After stirring for 1 h, (bromomethyl)cyclopropane (607.5 mg, 4.5 mmol) was added dropwise at 0 °C. The reaction mixture was allowed to warm to r.t., and after stirring for 5 h at r.t., the solution was concentrated, and isolated by column chromatography (silica gel, petroleum ether/AcOEt), affording desired product **1ak** as a colorless liquid in 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.62-

3.14 (m, 4H), 2.36 (s, 3H), 1.20-0.83 (m, 2H), 0.57-0.44 (m, 4H), 0.40-0 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 138.5, 133.9, 128.4, 126.3, 52.9, 48.1, 20.9, 9.5, 3.4.

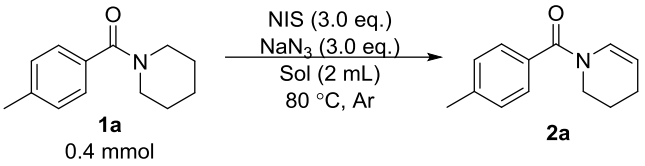
HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO$ $[M+H]^+$ 244.1701, found: 244.1698.

Optimization of reaction conditions

General procedures in Table S1

Piperidin-1-yl(p-tolyl)methanone **1a** (81.3 mg, 0.4 mmol), NIS (270.0 mg, 1.2 mmol) and NaN_3 (78.0 mg, 1.2 mmol) were added to a 20 mL tube with a magnetic stir bar. Then different solvent was added to the tube and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. After cooling to room temperature, the solution was concentrated affording rude product. And the yield of the desired compound **2a** was detected by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S1. Screening the solvent of the dehydrogenation of amides[a]



1a
0.4 mmol

2a

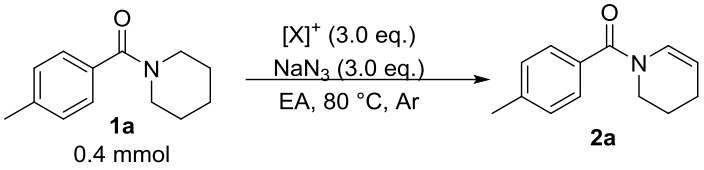
Entry	Sol	NMR Yield/%
1	EA	54
2	DCE	trace
3	MeCN	12
4	Tol	trace
5	PhCl	trace
6	dioxane	NR
7	EtOH	NR
8	CCl_4	trace
9	Acetone	8.5
10	$MeNO_2$	NR

[a]Reaction conditions: Piperidin-1-yl(p-tolyl)methanone (**1a**) (81.3 mg, 0.4 mmol), NIS (270.0 mg, 1.2 mmol) and NaN_3 (78.0 mg, 1.2 mmol) in solvent (2.0 mL) under Ar atmosphere stirring at 80 °C for 12 h. Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard.

General procedures in Table S2

Piperidin-1-yl(p-tolyl)methanone **1a** (81.3 mg, 0.4 mmol), oxidant (1.2 mmol) and NaN_3 (78.0 mg, 1.2 mmol) were added to a 20 mL tube with a magnetic stir bar. Then dry EA was added to the tube and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. After cooling to room temperature, the solution was concentrated affording rude product. And the yield of the desired compound **2a** was detected by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S2. Screening the oxidant of the dehydrogenation of amides[a]



1a
0.4 mmol

2a

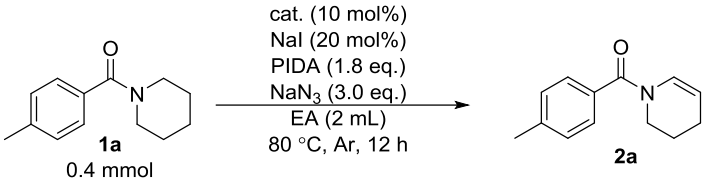
Entry	$[X]^+$/ 3.0 eq.	**2a** (%)
1	DIDMH	ND
2	I_2	ND
3	NBS	NR
4	Py•HBr_3	NR
5	DBDMH	ND
6	NCS	NR
7	DCDMH	NR
8	NFSI	NR
9	SelectFluor	NR
10	PIDA	23
11	PhIO	NR
12	$NaIO_4$	NR
13[b]	PIDA	NR

[a]Reaction conditions: Piperidin-1-yl(p-tolyl)methanone (**1a**) (81.3 mg, 0.4 mmol), oxidant (1.2 mmol) and NaN_3 (78.0 mg, 1.2 mmol) in dry EA (4.0 mL) under Ar atmosphere stirring at 80 °C for 12 h. Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard. [b] Under Air atmosphere.

General procedures in Table S3

Piperidin-1-yl(p-tolyl)methanone **1a** (81.3 mg, 0.4 mmol), NaI (12.0 mg, 0.08 mmol), PIDA (231.9 mg, 0.72 mmol), NaN_3 (78.0 mg, 1.2 mmol) and different catalysts were added to a 20 mL tube with a magnetic stir bar. Then dry EA was added to the tube and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. After cooling to room temperature, the solution was concentrated affording rude product. And the yield of the desired compound **2a** was detected by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S3. Screening the catalyst of the dehydrogenation of amides[a]



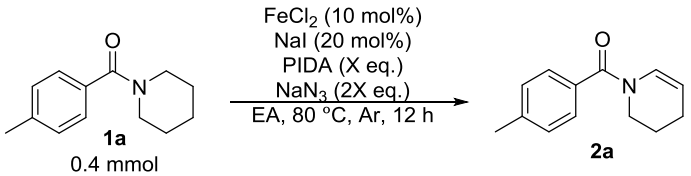
Entry	cat.	**2a** (%)	**1a** (%)
1	$FeCl_2$	61	29
2	$Fe(OAc)_2$	58	29
3	$Cu(OAc)_2$	42	33
4	$CuCl_2$	26	37
5	$MnBr_2$	31	52
6	--	47	29

[a] Reaction conditions: Piperidin-1-yl(p-tolyl)methanone (**1a**) (81.3 mg, 0.4 mmol), NaI (12.0 mg, 0.08 mmol), PIDA (231.9 mg, 0.72 mmol), NaN_3 (78.0 mg, 1.2 mmol) and different catalysts in dry EA (4.0 mL) under Ar atmosphere stirring at 80 °C for 12 h. Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard.

General procedures in Table S4

Piperidin-1-yl(p-tolyl)methanone **1a** (81.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (12.0 mg, 0.08 mmol), PIDA and NaN_3 were added to a 20 mL tube with a magnetic stir bar. Then dry EA was added to the tube and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. After cooling to room temperature, the solution was concentrated affording rude product. And the yield of the desired compound **2a** was detected by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S4. Screening the amount of PIDA and NaN_3 of the dehydrogenation of amides[a]



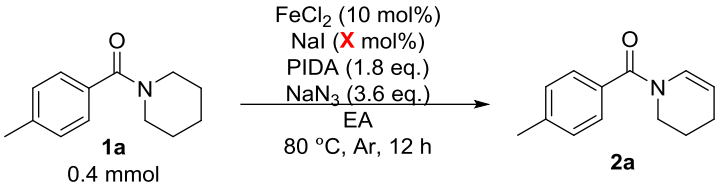
Entry	X	**2a** (%)
1	1.8	56
2	1.1	45
3	1.5	55
4	1.8	64
5	2.0	50
6	2.5	36
7	1.8, in air	24

[a]Reaction conditions: Piperidin-1-yl(p-tolyl)methanone (**1a**) (81.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (12.0 mg, 0.08 mmol), PIDA and NaN_3 was added as mentioned in above table in dry EA (4.0 mL) under Ar atmosphere stirring at 80 °C for 12 h. Determined by ^1H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard.

General procedures in Table S5

Piperidin-1-yl(p-tolyl)methanone **1a** (81.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI, PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) were added to a 20 mL tube with a magnetic stir bar. Then dry EA was added to the tube and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. After cooling to room temperature, the solution was concentrated affording rude product. And the yield of the desired compound **2a** was detected by ^1H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S5. Screening the amount of PIDA and NaN_3 of the dehydrogenation of amides[a]



Entry	X	yield of **2a** (%)
1	0	14
2	5	21
3	10	27
4	20	59
5	30	71 (64)
6	50	67
7	100	58

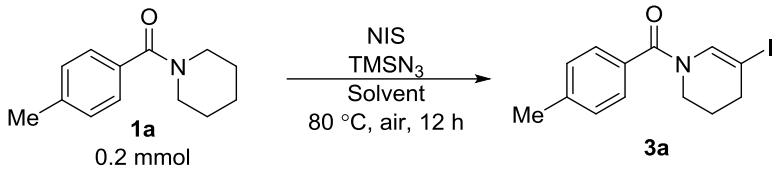
[a]Reaction conditions: Piperidin-1-yl(p-tolyl)methanone (**1a**) (81.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI, PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar atmosphere stirring at 80 °C for 12 h. Determined by ^1H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard. The numbers in parentheses are the isolated yields.

General procedures in Table S6

Piperidin-1-yl(p-tolyl)methanone **1a** (40.7 mg, 0.2 mmol), NIS and $TMSN_3$ were added to a 20 mL tube with a magnetic stir bar. Then solvent was added to the tube and the mixture was stirred at 80 °C for 12 h under Air atmosphere. After cooling to room temperature, the solution was concentrated affording rude product. And the yield of the desired compound **2a** was detected by ^1H NMR analysis with 1,1,2,2-tetrachloroethane

as internal standard.

Table S6. Optimization of the oxidative dehydrogenation *β*-iodination of amides[a]



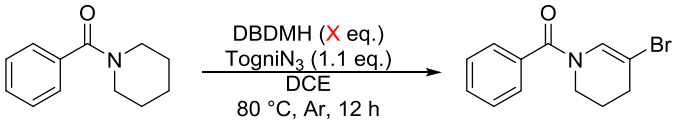
Entry	NIS/eq.	$TMSN_3$/eq.	Solvent	**3a** (%)
1	2.0	1.5	DCE	34
2	2.0	1.5	DCM	8
3	2.0	1.5	Tol	12
4	2.0	1.5	n-hexane	11
5	2.0	1.5	MeCN	32
6	2.0	1.5	PhCl	trace
7	2.0	1.5	CCl_4	53 (48)
8	1.0	1.0	CCl_4	38
9	1.5	1.5	CCl_4	51
10	2.0	2.0	CCl_4	62
11	2.2	2.2	CCl_4	63
12	2.5	2.5	CCl_4	68 (65)
13	3.0	3.0	CCl_4	69

[a]Reaction conditions: Piperidin-1-yl(p-tolyl)methanone (**1a**) (40.7 mg, 0.2 mmol), NIS and $TMSN_3$ in solvent (2.0 mL) under Air atmosphere stirring at 80 °C for 12 h. Determined by ^1H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard. The numbers in parentheses are the isolated yields.

General procedures in Table S7 – S8

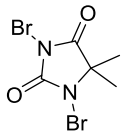
Phenyl(piperidin-1-yl)methanone **1b** (40.7 mg, 0.2 mmol), DBDMH and $TogniN_3$ were added to a 20 mL tube with a magnetic stir bar. Then DCE (2 mL) was added to the tube and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. After cooling to room temperature, the solution was concentrated affording rude product. And the yield of the desired compound **2a** was detected by ^1H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S7. Optimization of the oxidative dehydrogenation *β*-bromination of amides[a]

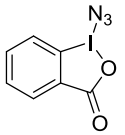


1b **3g**

Entry	X	TogniN$_3$/eq.	yield of 3g (%)
1	0.4	1.1	51
2	0.55	1.1	65 (57)
3	0.65	1.1	65
4	0.8	1.1	59
5	1.0	1.1	54
6	0.55	1.2	62
7	0.55	1.5	52
8	0.55	1.8	14



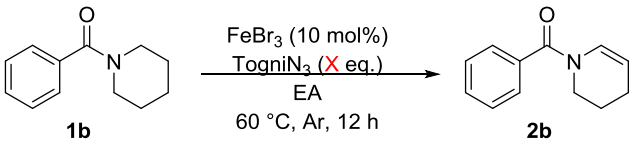
DBDMH



TogniN$_3$

[a]Reaction conditions: Phenyl(piperidin-1-yl)methanone **1b** (40.7 mg, 0.2 mmol), DBDMH and TogniN$_3$ in DEC (2.0 mL) under Ar atmosphere stirring at 80 °C for 12 h. Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard. The numbers in parentheses are the isolated yields.

Table S8. Optimization of the oxidative dehydrogenation of amides by TogniN$_3$[a]



1b **2b**

Entry	X	yield of **2b** (%)
1	0.8	33
2	1.2	48
3	1.5	55
4	2.0	59

[a]Reaction conditions: Phenyl(piperidin-1-yl)methanone **1b** (40.7 mg, 0.2 mmol), DBDMH and TogniN$_3$ in EA (2.0 mL) under Ar atmosphere stirring at 60 °C for 12 h. Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.19 mmol, 20 μL) as internal standard.

Coution:

The IN$_3$ solution generated in situ by NIS and TMSN$_3$ is a frequently used strategy in organic synthesis.[5] And we have not encountered any problems even on prolonged reflux under our reaction conditions.

The azidobenziodoxolone (TogniN$_3$) can be stored in refrigerator for several months without noticeable decomposition. Shocks of the compound are not recommended. This compound decomposes with explosion upheating to 138-140 ˚C.[6]

Variable temperature ^{1}H NMR analysis

It is interesting that rotamerism was observed form many products in this work. For example, the *N*-*β*-iodine enamide product **3a** display distinguishable rotameric ^{1}H NMR signals (263 K), and variable-temperature (263 K−313K) ^{1}H NMR spectroscopy revealed smooth coalescence of the rotameric (Figure S1).

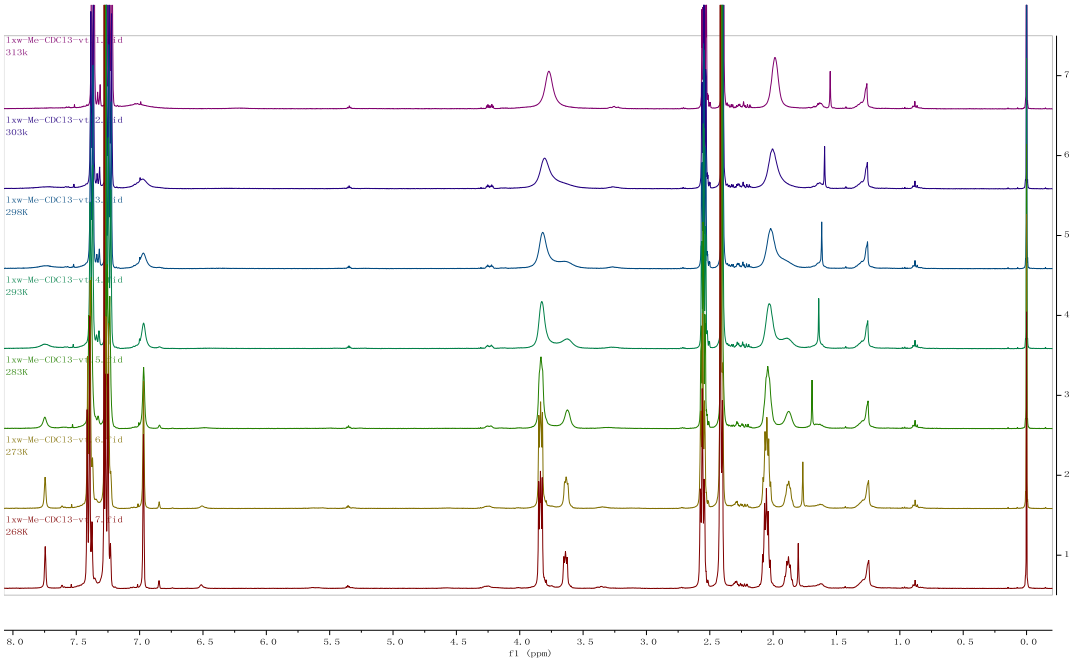


Figure S1. VT ^{1}H NMR spectra ($CDCl_3$) of **3a** showing the coalescence of *N*-*β*-iodine enamide rotamer peaks with increasing temperature.

Preliminary mechanistic studies

^{1}H NMR analysis

As shown in the Fig. S2, some *in situ* experiments were carried out and detected by ^{1}H-NMR analysis to gain additional insight of the mechanism of dehydrogenation *β*-halogenation process. In order to avoid the influence of deuterated reagent on the reaction system, specific standard solution or reaction solution was put into 5 mm NMR tube directly, the we use a 3 mm NMR tube containing 300 μL $CDCl_3$ and put this tube into the 5 mm NMR tube.

First of all, piperidin-1-yl(p-tolyl)methanone **1a**, intermediate **5** and product **3a** were dissolved in 300 μL CCl_4 separately, the ^{1}H NMR spectrums were obtained (Fig. S2a, b and c). The characteristic signal at 4.6 ppm is from hydrogen at N_3-α position of intermediate **5**, the characteristic signal at 2.7 ppm is from hydrogen at allylic position of product **3a**.

Then, eight reactions from 0.5 h to 7 h were carried out in parallel and finally stopped together. Piperidin-1-yl(p-tolyl)methanone **1a** (0.2 mmol), $TMSN_3$ (2.5 equiv.) and NIS (2.5 equiv.) were mixed in CCl_4, and the reaction was stirred at 80 °C for specified time. After the mixture was filtered, 300 μL filtrate was put into 5 mm NMR tube and conducted ^{1}H-NMR analysis according to the above method.

The ^{1}H NMR spectrum showed that the reaction system did not change

significantly before 1 hour (Fig. S2 d and e), and intermediates **5** gradually increased between 2 to 4 hours (Fig. S2 f, g and h). Then, the signal of intermediates **5** gradually weakened (Fig. S2 i and j). Finally, the product peak signal was obviously observed when the reaction time was 7 hours (Fig. S2 k).

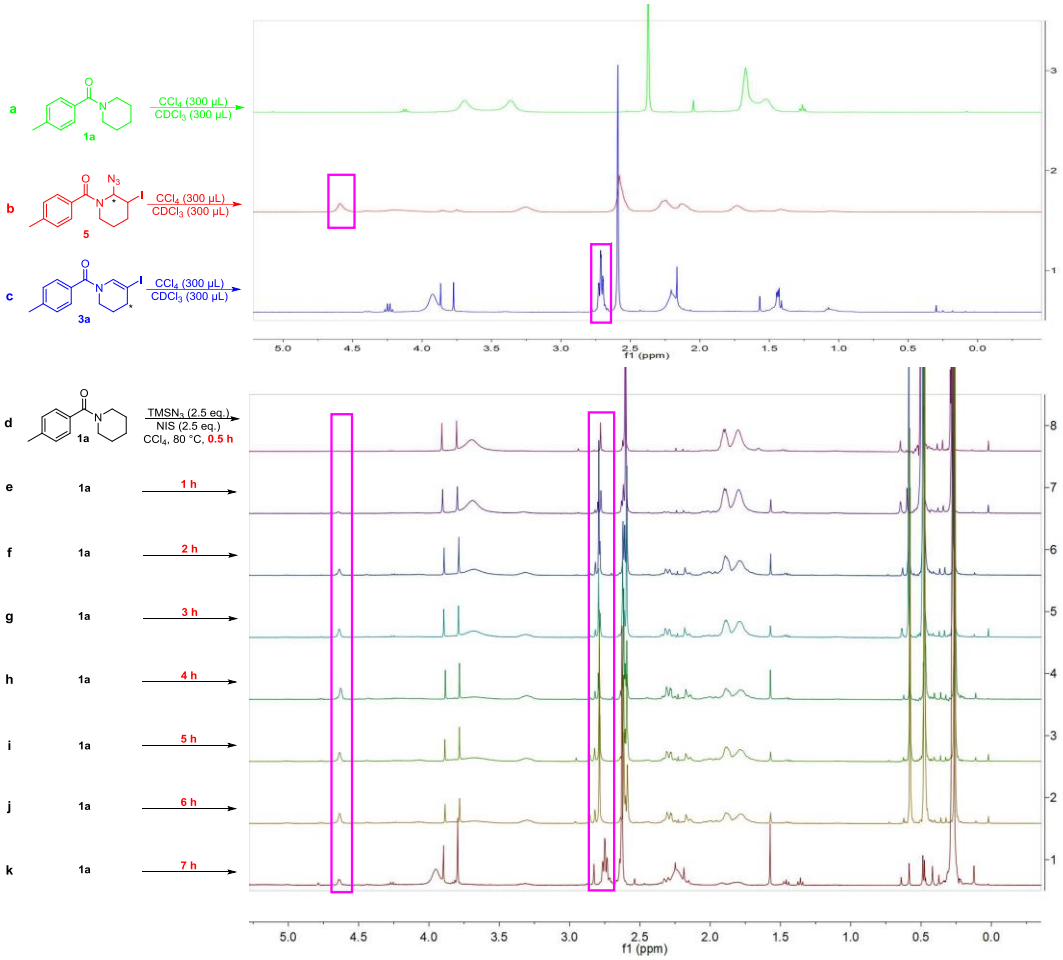
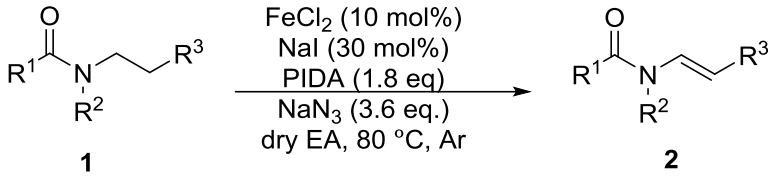


Figure S2. ^{1}H NMR analysis.

Experimental procedure and characterization data

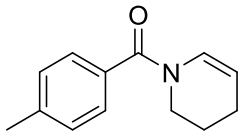
General procedures for the dehydrogenation of amides reaction



1 **2**

Amide **1** (0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) were added to a 20 mL tube with a magnetic stir bar. Then dry EA (4 mL) was added to the tube and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. After cooling to room temperature, the solution was concentrated and isolated by column chromatography (silica gel, petroleum ether/AcOEt), affording product **2**.

(3,4-Dihydropyridin-1(2H)-yl)(p-tolyl)methanone (**2a**)



2a

The reaction of phenyl(piperidin-1-yl)methanone **1b** (81.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 51.5 mg (64%) of **2a** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of 3.3:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 1H), 4.72 (app s, 1H), 3.80 (app s, 2H), 2.36 (s, 3H), 2.13-2.06 (m, 2H), 1.98-1.73 (m, 2H).

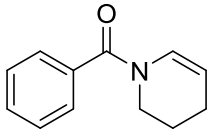
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 5.19 (app s, 1H), 3.56 (app s, 2H), 2.36 (s, 3H), 2.13-2.06 (m, 2H), 1.98-1.73 (m, 2H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 140.3, 132.1, 128.8, 128.2, 127.6, 107.1, 41.0, 21.8, 21.6, 21.3.

Minor isomer: **^{13}C NMR** could not be clearly identified.

HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO$ $[M+H]^+$ 202.1232, found: 202.1231.

(3,4-Dihydropyridin-1(2*H*)-yl)(phenyl)methanone (**2b**)[7]



2b

The reaction of phenyl(piperidin-1-yl)methanone **1b** (75.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3

(93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 43.5 mg (58%) of **2b** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of 3.5:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.43-7.36 (m, 3H), 6.43 (d, *J* = 8.4 Hz, 1H), 4.83 (app s, 1H), 3.86-3.78 (m, 2H), 2.14-2.08 (m, 2H), 1.98-1.89 (m, 2H).

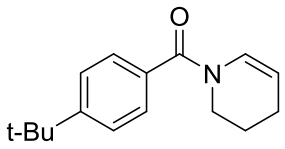
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.43-7.36 (m, 3H), 7.26 (app s, 1H), 5.22 (app s, 1H), 3.54 (app s, 2H), 2.14-2.08 (m, 2H), 1.83-1.72 (m, 2H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 135.1, 130.0, 128.2, 128.1, 127.4, 107.5, 41.0, 21.8, 21.6.

Minor isomer: **^{13}C NMR** could not be clearly identified.

MS (EI): m/z (%): 51.0 (22), 77.0 (65), 105.0 (100), 187.0 (M^+, 25).

(4-(*Tert*-butyl)phenyl)(3,4-dihydropyridin-1(2*H*)-yl)methanone (**2c**)



2c

The reaction of (4-(tert-butyl)phenyl)(piperidin-1-yl)methanone **1c** (98.2 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 60.2 mg (62%) of **2c** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of 3.3:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 4H), 6.49 (d, *J* = 8.4 Hz, 1H), 4.83-4.79 (m, 1H), 3.85-3.76 (m, 2H), 2.14-2.06 (m, 2H), 2.00-1.86 (m, 2H), 1.31 (s, 9H).

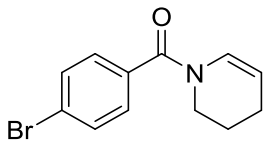
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 4H), 7.23 (app s, 1H), 5.19 (app s, 1H), 3.56 (app s, 2H), 2.14-2.06 (m, 2H), 1.86-1.71 (m, 2H), 1.31 (s, 9H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 153.4, 132.1, 128.0, 127.7, 125.1, 107.0, 41.0, 34.7, 31.1, 21.8, 21.6.

Minor isomer: **^{13}C NMR** could not be clearly identified.

HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO[M+H]^+$ 244.1701, found: 244.1699.

(4-Bromophenyl)(3,4-dihydropyridin-1(2*H*)-yl)methanone (**2d**)



2d

The reaction of (4-bromophenyl)(piperidin-1-yl)methanone **1d** (107.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded

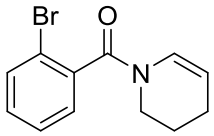
54.5 mg (51%) of **2d** as a white solid. The desired enamide was obtained as two rotamers in a ratio of around 3.4:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.37 (d, *J* = 8.0 Hz, 1H), 4.91-4.80 (m, 1H), 3.85-3.72 (m, 2H), 2.14-2.06 (m, 2H), 1.97-1.85 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 (app s, 1H), 5.23 (app s, 1H), 3.56-3.46 (m, 2H), 2.14-2.06 (m, 2H), 1.82-1.70 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 133.8, 131.5, 129.8, 127.0, 124.5, 108.1, 41.1, 21.8, 21.5.
Minor isomer: **^{13}C NMR** could not be clearly identified.

HRMS *m/z* (ESI) calcd for $C_{12}H_{13}NOBr$ $[M+H]^+$ 266.0181, found: 266.0179.

Melting Point: 46-48 ℃.

IR (neat) ν_{max}: 2925, 1625, 1591, 1410, 1376, 1258, 1070, 994.

(2-Bromophenyl)(3,4-dihydropyridin-1(2*H*)-yl)methanone (**2e**)

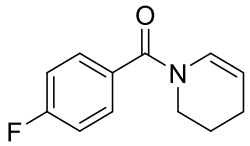


2e

The reaction of (2-bromophenyl)(piperidin-1-yl)methanone **1e** (107.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 66.9 mg (63%) of **2e** as a yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.3:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 1H), 7.42-7.25 (m, 3H), 6.11 (d, *J* = 8.4 Hz, 1H), 4.99-4.79 (m, 1H), 4.02-3.79 (m, 2H), 2.18-2.09 (m, 2H), 2.04-1.88 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 1H), 7.42-7.25 (m, 3H), 5.32-5.25 (m, 1H), 3.50-3.19 (m, 2H), 2.18-2.09 (m, 2H), 1.87-1.79 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 137.4, 132.8, 130.5, 128.3, 127.6, 125.9, 119.5, 109.0, 40.6, 21.9, 21.2.
Minor isomer: **^{13}C NMR** (100 MHz, CDCl3) δ 166.2, 137.9, 132.7, 130.4, 127.8, 127.7, 123.8, 119.2, 111.2, 45.1, 22.1, 22.1.

HRMS *m/z* (ESI) calcd for $C_{12}H_{13}NOBr$ $[M+H]^+$ 266.0181, found: 266.0175.

(3,4-Dihydropyridin-1(2*H*)-yl)(4-fluorophenyl)methanone (**2f**)[8]



2f

The reaction of (4-fluorophenyl)(piperidin-1-yl)methanone **1f** (82.9 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 45.1 mg (55%) of **2f** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 3.8:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.43 (m, 2H), 7.14-7.02 (m, 2H), 6.41 (d, J = 8.0 Hz, 1H), 4.91-4.81 (m, 1H), 3.87-3.69 (m, 2H), 2.16-2.04 (m, 2H), 2.01-1.85 (m, 2H).

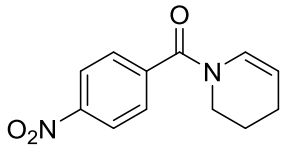
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.43 (m, 2H), 7.14-7.02 (m, 2H), 5.22 (app s, 1H), 3.54 (app s, 2H), 2.16-2.04 (m, 2H), 1.85-1.69 (m, 2H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 163.6 (d, ^1J = 250.6 Hz), 131.0, 130.5 (d, ^3J = 8.4 Hz), 129.8, 127.2, 115.3 (d, ^2J = 21.8 Hz), 107.9, 41.2, 21.8, 21.6.

Minor isomer: **^{13}C NMR** could not be clearly identified.

MS (EI): m/z (%): 75.0 (17), 95.0 (46), 123.0 (100), 205.1 (M^+, 21).

(3,4-Dihydropyridin-1(2*H*)-yl)(4-nitrophenyl)methanone (**2g**)



2g

The reaction of (4-nitrophenyl)(piperidin-1-yl)methanone **1g** (93.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 42.2 mg (45%) of **2g** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 3.2:1.

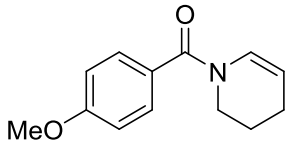
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32-8.24 (m, 2H), 7.69-7.59 (m, 2H), 6.32-6.25 (m, 1H), 5.00-4.89 (m, 1H), 3.89-3.77 (m, 2H), 2.18-2.10 (m, 2H), 2.01-1.90 (m, 2H).

Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32-8.24 (m, 2H), 7.69-7.59 (m, 2H), 5.35-5.22 (m, 1H), 3.55-3.45 (m, 2H), 2.18-2.10 (m, 2H), 1.85-1.77 (m, 2H).

Both rotamers are described together: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 148.5, 141.2, 129.1, 126.3, 123.6, 109.4, 41.1, 21.8, 21.4.

HRMS *m/z* (ESI) calcd for $C_{12}H_{13}N_2O_3$ $[M+H]^+$ 233.0926, found: 233.0926.

(3,4-Dihydropyridin-1(2H)-yl)(4-methoxyphenyl)methanone (**2h**)[8]



2h

The reaction of (4-methoxyphenyl)(piperidin-1-yl)methanone **1g** (87.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 31.6 mg (36%) of **2h** as a colorless liquid.

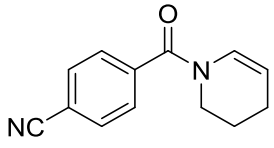
Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 6.90-6.87 (m, 2H), 6.93 and 6.50 (m, 1H), 5.25-4.76 (m, 1H), 3.82 (s, 3H), 3.83 and 3.77 (m, 2H), 2.14-2.06 (m, 2H), 2.02-1.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 130.3, 127.8, 127.7, 113.7, 113.5, 107.0, 55.3, 55.3, 41.2, 21.9.

MS (EI): m/z (%): 77.0 (20), 92.0 (17), 135.0 (100), 217.1 (M^+, 15).

4-(1,2,3,4-Tetrahydropyridine-1-carbonyl)benzonitrile (**2i**)



2i

The reaction of 4-(piperidine-1-carbonyl)benzonitrile **1i** (85.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 40.5 mg (48%) of **2i** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 3.0:1.

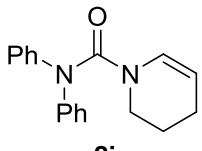
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.67 (m, 2H), 7.60-7.50 (m, 2H), 6.28 (d, J = 8.0 Hz, 1H), 4.99-4.86 (m, 1H), 3.86-73 (m, 2H), 2.16-2.08 (m, 2H), 1.99-1.90 (m, 2H).

Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.67 (m, 2H), 7.60-7.50 (m, 2H), 7.22 (d, J = 8.0 Hz, 1H), 5.34-5.16 (m, 1H), 3.57-3.42 (m, 2H), 2.16-2.08 (m, 2H), 1.85-1.75 (m, 2H).

Both rotamers are described together: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 139.3, 132.2, 128.7, 126.3, 124.1, 118.0, 113.8, 109.2, 41.1, 21.7, 21.4.

HRMS *m/z* (ESI) calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$ 213.1028, found: 213.1027.

N,N-diphenyl-3,4-dihydropyridine-1(2*H*)-carboxamide (**2j**)



2j

The reaction of N,N-diphenylpiperidine-1-carboxamide **1j** (112.2 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 51.2 mg (46%) of **2j** as a white solid. No rotameric effects were observed via NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 4H), 7.08-7.02 (m, 2H), 6.99-6.93 (m, 4H), 6.61-6.56 (m, 1H), 4.74-4.68 (m, 1H), 3.37-3.26 (m, 2H), 1.92-1.85 (m, 2H), 1.71-1.62 (m, 2H).

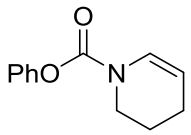
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 144.5, 129.2, 126.6, 125.2, 124.8, 106.7, 44.1, 21.63, 21.58.

HRMS *m/z* (ESI) calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$ 279.1497, found: 279.1497.

Melting Point: 64-65 ℃.

IR (neat) ν_{max}: 2929, 1674, 1590, 1493, 1403, 1366, 1355, 1296, 1260, 1233, 755, 696.

Phenyl 3,4-dihydropyridine-1(2*H*)-carboxylate (**2k**)[9]



2k

The reaction of phenyl piperidine-1-carboxylate **1k** (82.1 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 55.5 mg (68%) of **2k** as a white solid. The desired enamide was obtained as two rotamers in a ratio of around 1.5:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.24-7.19 (m, 1H), 7.16-7.12 (m, 2H), 7.00-6.94 (m, 1H), 5.04-4.97 (m, 1H), 3.84-3.78 (m, 2H), 2.14-2.08 (m, 2H), 1.96-1.88 (m, 2H).

Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.24-7.19 (m, 1H), 7.16-7.12 (m, 2H), 6.93-6.88 (m, 1H), 5.11-5.04 (m, 1H), 3.74-3.67 (m, 2H), 2.14-2.08 (m, 2H), 1.96-1.88 (m, 2H).

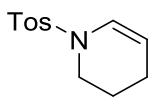
Both rotamers are described together: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 151.2, 129.3, 125.4, 125.2, 124.8, 121.7, 121.6, 107.9, 107.5, 43.0, 42.5, 21.7, 21.6, 21.4, 21.3.

MS (EI): m/z (%): 65.0 (32), 82.0 (85), 110.0 (100), 203.0 (M^+, 55).

Melting Point: 61-62 ℃.

IR (neat) ν_{max}: 2942, 1723, 1655, 1600, 1495, 1408, 1359, 1260, 1204, 1039, 750, 689.

1-Tosyl-1,2,3,4-tetrahydropyridine (**2l**)[10]

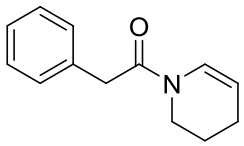


2l

The reaction of 1-tosylpiperidine **1l** (95.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44

mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 58.3 mg (55%) of **2l** as a white solid. No rotameric effects were observed via NMR spectroscopy.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.65-6.59 (m, 1H), 4.99-4.93 (m, 1H), 3.38-3.33 (m, 2H), 2.42 (s, 3H), 1.94-1.86 (m, 2H), 1.68-1.60 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 135.1, 129.7, 127.0, 125.0, 108.2, 43.8, 21.5, 20.90, 20.86.
MS (EI): m/z (%): 55.0 (82), 91.0 (100), 155.0 (24), 237.0 (M^+, 79).
Melting Point: 54-55 ℃.
IR (neat) ν_{max}: 2928, 2852, 1649, 1448, 1351, 1166, 1101, 931, 681, 550.

1-(3,4-dihydropyridin-1(2*H*)-yl)-2-phenylethan-1-one (**2m**)

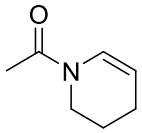


2m

The reaction of 2-phenyl-1-(piperidin-1-yl)ethan-1-one **1m** (81.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 35.9 mg (45%) of **2m** as a light red liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.4:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2H), 7.19-7.12 (m, 3H), 6.60-6.55 (m, 1H), 4.90-4.80 (m, 1H), 3.73-3.67 (m, 2H), 3.66-3.60 (m, 2H), 2.00-1.92 (m, 2H), 1.76-1.64 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2H), 7.19-7.12 (m, 3H), 6.60-6.55 (m, 1H), 5.02-4.95 (m, 1H), 3.73-3.67 (m, 2H), 3.47-3.41 (m, 2H), 2.00-1.92 (m, 2H), 1.76-1.64 (m, 2H).
Both rotamers are described together: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 134.5, 128.7, 128.5, 126.7, 125.3, 108.5, 41.1, 40.5, 21.7, 21.4.

HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO$ $[M+H]^+$ 202.1232, found: 202.1232.

1-(3,4-dihydropyridin-1(2*H*)-yl)ethan-1-one (**2n**)[11]

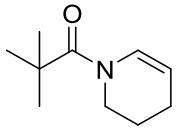


2n

The reaction of 1-(piperidin-1-yl)ethan-1-one **1n** (50.9 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 28.5 mg (57%) of **2n** as a colorless volatile liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.7:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.51 (d, *J* = 9.2Hz, 1H), 4.95-4.91 (m,

1H), 3.71-3.59 (m, 2H), 2.17-2.11 (m, 3H), 2.10-2.03 (m, 2H), 1.80-1.76 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.4 Hz, 1H), 5.08-4.96 (m, 1H), 3.56-3.54 (m, 2H), 2.17-2.11 (m, 3H), 2.10-2.03 (m, 2H), 1.89-1.80 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 125.7, 108.0, 40.0, 21.6, 21.36, 21.25.
Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 123.8, 108.3, 44.3, 22.0, 21.7, 21.40.
MS (EI): m/z (%): 68.0 (67), 82.0 (100), 125.0 (M^+, 50).

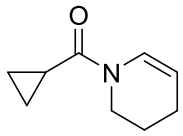
1-(3,4-Dihydropyridin-1(2*H*)-yl)-2,2-dimethylpropan-1-one (**2o**)



2o

The reaction of 2,2-dimethyl-1-(piperidin-1-yl)propan-1-one **1o** (67.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 33.3 mg (50%) of **2o** as a colorless liquid.
No rotameric effects were observed via NMR spectroscopy.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-6.94 (m, 1H), 4.93-4.86 (m, 1H), 3.71-3.65 (m, 2H), 2.09-2.02 (m, 2H), 1.86-1.78 (m, 2H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 126.9, 106.9, 42.5, 39.1, 28.3, 22.2, 22.0.
HRMS *m/z* (ESI) calcd for $C_{10}H_{18}NO$ $[M+H]^+$ 168.1388, found: 168.1388.

Cyclopropyl(3,4-dihydropyridin-1(2*H*)-yl)methanone (**2p**)



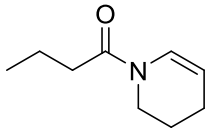
2p

The reaction of cyclopropyl(piperidin-1-yl)methanone **1p** (61.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 38.7 mg (64%) of **2p** as a colorless volatile liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.1:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 8.4 Hz, 1H), 5.01-4.87 (m, 1H), 3.69-3.55 (m, 2H), 2.09-2.00 (m, 2H), 1.81-1.68 (m, 3H), 1.00-0.90 (m, 2H), 0.79-0.70 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.8 Hz, 1H), 5.01-4.87 (m, 1H), 3.80-3.69 (m, 2H), 2.09-2.00 (m, 2H), 1.90-1.81 (m, 3H), 1.00-0.90 (m, 2H), 0.79-0.70 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 125.3, 107.8, 40.6, 21.8, 21.51, 11.0, 7.5.

Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 124.3, 107.6, 43.4, 22.1, 21.48, 11.1, 7.9.

HRMS *m/z* (ESI) calcd for $C_9H_{14}NO$ $[M+H]^+$ 152.1075, found: 152.1074.

1-(3,4-dihydropyridin-1(2*H*)-yl)butan-1-one (**2q**)



2q

The reaction of 1-(piperidin-1-yl)butan-1-one **1q** (62.1 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 31.3 mg (51%) of **2q** as a colorless volatile liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.9:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.58 (d, J = 8.3 Hz, 1H), 4.94-4.87 (m, 1H), 3.68-3.60 (m, 2H), 2.37-2.29 (m, 2H), 2.08-2.02 (m, 2H), 1.81-1.74 (m, 2H), 1.71-1.59 (m, 2H), 0.97-0.91 (m, 3H).

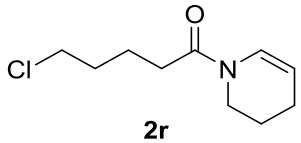
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ. 7.17 (d, J = 8.5 Hz, 1H), 5.05-4.98 (m, 1H), 3.58-3.51 (m, 2H), 2.37-2.29 (m, 2H), 2.08-2.02 (m, 2H), 1.87-1.81 (m, 2H), 1.71-1.59 (m, 2H), 0.97-0.91 (m, 3H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 125.3, 107.8, 40.1, 35.2, 22.2, 21.6, 18.4, 13.9.

Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 124.2, 108.1, 43.6, 35.5, 21.8, 18.3. One peak could not be detected presumably due to an overlapping with a peak of the major species.

HRMS *m/z* (ESI) calcd for $C_9H_{16}NO$ $[M+H]^+$ 154.1232, found: 154.1231.

5-Chloro-1-(3,4-dihydropyridin-1(2*H*)-yl)pentan-1-one (**2r**)



2r

The reaction of 5-chloro-1-(piperidin-1-yl)pentan-1-one **1r** (81.5 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 48.1 mg (60%) of **2r** as a yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.6:1.

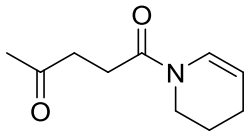
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.56 (d, J = 8.4 Hz, 1H), 4.93 (dt, J = 8.1, 3.9 Hz, 1H), 3.68-3.50 (m, 4H), 2.43-2.35 (m, 2H), 2.09-2.01 (m, 2H), 1.88-1.74 (m, 6H).

Minor isomer:-**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.6 Hz, 1H), 5.03 (dt, J = 8.1, 3.8 Hz, 1H), 3.68-3.50 (m, 4H), 2.43-2.35 (m, 2H), 2.09-2.01 (m, 2H), 1.88-1.74 (m,

6H).
Major isomer:-**^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 125.0, 108.2, 44.58, 40.2, 32.2, 32.01, 22.11, 21.8, 21.51.
Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 124.0, 108.4, 44.62, 43.5, 32.5, 31.99, 22.09, 22.0, 21.53.

HRMS *m/z* (ESI) calcd for $C_{10}H_{17}NOCl$ $[M+H]^+$ 202.0999, found: 202.0997.

1-(3,4-Dihydropyridin-1(2*H*)-yl)pentane-1,4-dione (**2s**)

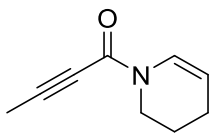


2s

The reaction of 1-(piperidin-1-yl)pentane-1,4-dione **1s** (73.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 42.4 mg (58%) of **2s** as a yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.3:1.
Major isomer:-**^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.61 (d, J = 8.4 Hz, 1H), 4.94 (dt, J = 8.1, 3.9 Hz, 1H), 3.65-3.60 (m, 2H), 2.79-2.72 (m, 2H), 2.67-2.59 (m, 2H), 2.19 (s, 3H), 2.07-2.01 (m, 2H), 1.81-1.73 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.5 Hz, 1H), 5.02 (dt, J = 8.2, 3.9 Hz, 1H), 3.60-3.56 (m, 2H), 2.79-2.72 (m, 2H), 2.67-2.59 (m, 2H), 2.19 (s, 3H), 2.07-2.01 (m, 2H), 1.88-1.81 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.52, 168.9, 124.9, 108.3, 40.3, 37.6, 30.0, 27.1, 21.8, 21.4.
Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.58, 168.8, 124.0, 108.4, 43.3, 37.7, 27.3, 21.9, 21.5. One peak could not be detected presumably due to an overlapping with a peak of the major species.

HRMS *m/z* (ESI) calcd for $C_{10}H_{16}NO_2$ $[M+H]^+$ 182.1181, found: 182.1182.

1-(3,4-Dihydropyridin-1(2*H*)-yl)but-2-yn-1-one (**2t**)



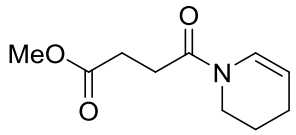
2t

The reaction of 1-(piperidin-1-yl)but-2-yn-1-one **1t** (60.5 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 42.8 mg (72%) of **2t** as a yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 1.9:1.
Major isomer:-**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (dt, J = 8.4, 2.0 Hz, 1H), 5.00 (dt, J

= 8.2, 4.0 Hz, 1H), 3.71-3.62 (m, 2H), 2.11-2.03 (m, 2H), 1.99 (s, 3H), 1.81-1.73 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (dt, *J* = 8.5, 2.1 Hz, 1H), 5.11 (dt, *J* = 8.2, 3.9 Hz, 1H), 3.82-3.75 (m, 2H), 2.11-2.03 (m, 2H), 1.99 (s, 3H), 1.87-1.81 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 126.2, 108.8, 90.47, 72.5, 40.2, 21.84, 21.0, 3.9.
Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ151.5, 123.2, 110.5, 90.49, 73.1, 45.0, 22.1, 21.80, 4.0.

HRMS *m/z* (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$ 150.0919, found: 150.0917.

Methyl 4-(3,4-dihydropyridin-1(2*H*)-yl)-4-oxobutanoate (**2u**)

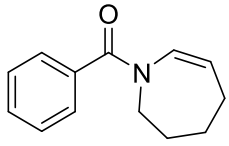


2u

The reaction of methyl 4-oxo-4-(piperidin-1-yl)butanoate **1u** (79.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 46.8 mg (59%) of **2u** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.1:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.59 (dt, *J* = 8.4, 2.0 Hz, 1H), 4.95 (dt, *J* = 8.1, 3.9 Hz, 1H), 3.66 (s, 3H), 3.65-3.62 (m, 2H), 2.70-2.61 (m, 4H), 2.08-2.02 (m, 2H), 1.81-1.70 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (dt, *J* = 8.6, 2.0 Hz, 1H), 5.03 (dt, *J* = 8.2, 3.9 Hz, 1H), 3.66 (s, 3H), 3.59-3.55 (m, 2H), 2.70-2.61 (m, 4H), 2.08-2.02 (m, 2H), 1.88-1.81 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 168.5, 124.7, 108.43, 51.7, 40.3, 28.7, 28.0, 21.8, 21.4.
Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 168.4, 124.0, 108.41, 51.7, 43.3, 28.8, 28.3, 21.9, 21.5. There is an overlapping peak at δ = 51.7 ppm.

HRMS *m/z* (ESI) calcd for $C_{10}H_{16}NO_3$ $[M+H]^+$ 198.1130, found: 198.1130.

Phenyl(2,3,4,5-tetrahydro-1*H*-azepin-1-yl)methanone (**2v**)[12]

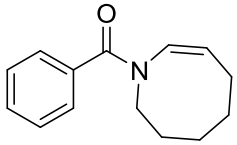


2v

The reaction of azepan-1-yl(phenyl)methanone **1v** (81.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 49.6 mg (57%)

of **2v** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 5.6:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.44 (m, 2H), 7.43-7.32 (m, 3H), 6.29-6.07 (m, 1H), 5.11-4.93 (m, 1H), 3.99-3.83 (m, 2H), 2.30-2.22 (m, 2H), 1.94-1.73 (m, 4H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.44 (m, 2H), 7.43-7.32 (m, 3H), 7.09-6.85 (m, 1H), 5.32-5.11 (m, 1H), 3.69-3.39 (m, 2H), 2.30-2.22 (m, 2H), 1.94-1.73 (m, 4H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 136.0, 132.8, 130.0, 128.2, 128.0, 116.6, 46.1, 27.8, 26.5, 24.7.
Minor isomer: ^{13}C NMR could not be clearly identified.
MS (EI): m/z (%): 77.0 (58), 105.0 (100), 201.1 (M^+, 22).

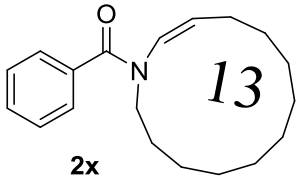
(Z)-phenyl(3,4,5,6-tetrahydroazocin-1(2H)-yl)methanone (**2w**)



2w

The reaction of azocan-1-yl(phenyl)methanone **1w** (86.8 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 44.8 mg (52%) of **2w** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 6.9:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.33 (m, 5H), 6.33-6.12 (m, 1H), 5.09-4.89 (m, 1H), 4.00-3.83 (m, 2H), 2.44-2.21 (m, 2H), 2.03-1.78 (m, 2H), 1.74-1.60 (m, 4H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.33 (m, 5H), 6.33-6.12 (m, 1H), 5.27-5.15 (m, 1H), 3.78-3.55 (m, 2H), 2.44-2.21 (m, 2H), 2.03-1.78 (m, 2H), 1.74-1.60 (m, 4H).
Both rotamers are described together: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 136.6, 131.1, 129.9, 129.7, 129.0, 128.2, 128.0, 126.8, 117.4, 45.4, 41.3, 29.6, 27.4, 26.7, 25.7, 25.4, 24.7, 24.3, 24.1.
HRMS *m/z* (ESI) calcd for $C_{14}H_{17}NO$ $[M+H]^+$ 216.1388, found: 216.1390.

(*Z*)-(azacyclotridec-2-en-1-yl)(phenyl)methanone (**2x**)

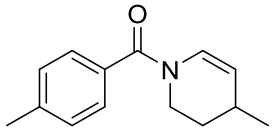


2x

The reaction of (azacyclotridecan-1-yl)(phenyl)methanone **1x** (114.8 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded

38.9 mg (34%) of **2x** as a colorless liquid. Both rotamers are described together:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.33 (m, 5H), 6.36-6.17 (m, 1H), 5.35-5.05 (m, 1H), 3.91-3.31 (m, 2H), 2.09-1.89 (m, 2H), 1.84-1.65 (m, 2H), 1.49-1.23 (m, 14H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 136.2, 130.1, 128.4, 127.3, 126.9, 116.1, 43.6, 29.6, 27.4, 26.6, 25.8, 25.5, 25.3, 24.4, 24.2.
HRMS *m/z* (ESI) calcd for $C_{19}H_{27}NO$ $[M+H]^+$ 286.2171, found: 286.2166.

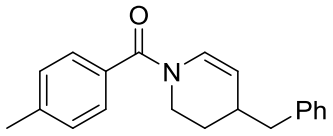
(4-Methyl-3,4-dihydropyridin-1(2*H*)-yl)(*p*-tolyl)methanone (**2y**)



2y

The reaction of methyl (4-methylpiperidin-1-yl)(p-tolyl)methanone **1y** (86.9 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 51.5 mg (60%) of **2y** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 1.6:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 1H), 4.80-4.65 (m, 1H), 3.72-3.48 (m, 2H), 2.40-2.32 (m, 4H), 2.08-1.98 (m, 1H), 1.63-1.38 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.12-4.80 (m, 1H), 4.08-3.95 (m, 2H), 2.40-2.32 (m, 4H), 1.98-1.83 (m, 1H), 1.63-1.38 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 140.3, 132.1, 128.9, 128.3, 126.5, 113.4, 39.8, 29.9, 27.3, 21.4, 21.2.
Minor isomer: ^{13}C NMR could not be clearly identified.
HRMS *m/z* (ESI) calcd for $C_{14}H_{18}NO$ $[M+H]^+$ 216.1388, found: 216.1386.

(4-Benzyl-3,4-dihydropyridin-1(2*H*)-yl)(*p*-tolyl)methanone (**2z**)



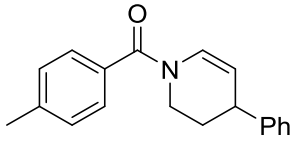
2z

The reaction of methyl (4-benzylpiperidin-1-yl)(*p*-tolyl)methanone **1z** (117.4 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 55.3 mg (57%) of **2z** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 1.4:1. Both rotamers are described together:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 2H), 7.34-7.28 (m, 2H), 7.25-7.16 (m, 5H), 6.55-6.45 (m, 1H), 5.18-4.68 (m, 1H), 4.16-3.62 (m, 1H), 3.62-3.45 (m, 1H), 2.75-2.66 (m, 1H), 2.66-2.50 (m, 2H), 2.39 (s, 3H), 2.03-1.90 (m, 1H), 1.72-1.50 (m, 1H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 140.4, 139.6, 131.9, 128.9, 128.8, 128.3, 127.2, 126.1, 110.9, 42.0, 39.8, 34.3, 27.5, 21.3.
Minor isomer: ^{13}C NMR could not be clearly identified.

HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO$ $[M+H]^+$ 292.1701, found: 292.1699.

(4-Phenyl-3,4-dihydropyridin-1(2*H*)-yl)(*p*-tolyl)methanone (**2aa**)

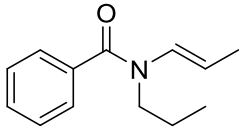


2aa

The reaction of (4-phenylpiperidin-1-yl)(*p*-tolyl)methanone **1aa** (111.8 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 59.7 mg (54%) of **2aa** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 1.6:1. Both rotamers are described together:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 2H), 7.27-7.21 (t, *J* = 7.5 Hz, 2H), 7.20-7.11 (m, 5H), 6.67-6.58 (m, 1H), 5.23-4.72 (m, 1H), 3.95-3.43 (m, 3H), 2.31 (s, 3H), 2.25-1.76 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 144.6, 140.6, 131.9, 128.9, 128.6, 128.4, 128.3, 127.5, 126.5, 109.6, 39.5, 38.5, 31.1, 21.4.
Minor isomer: ^{13}C NMR could not be clearly identified.

HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO$ $[M+H]^+$ 278.1545, found: 278.1543.

N-(prop-1-en-1-yl)-*N*-propylbenzamide (**2ab**)

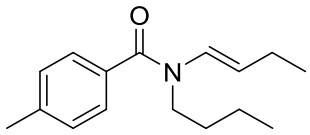


2ab

The reaction of *N,N*-dipropylbenzamide **1ab** (82.1 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 34.6 mg (43%) of **2ab** as a light yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.35 (m, 5H), 6.41-6.28 (m, 1H), 5.11-4.95 (m, 1H), 3.78-3.35 (m, 2H), 1.77-1.63 (m, 3H), 1.63-1.51 (m, 2H), 1.06-0.84 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 136.0, 129.7, 129.6, 128.6, 128.2, 127.8, 126.7, 105.9, 45.0, 20.1, 15.3, 11.2, 9.9.
No rotameric effects were observed via NMR spectroscopy.

HRMS *m/z* (ESI) calcd for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1388, found: 204.1390.

N-(but-1-en-1-yl)-*N*-butyl-4-methylbenzamide (**2ac**)



2ac

The reaction of *N,N*-dibutyl-4-methylbenzamide **1ac** (93.4 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 49.0 mg (50%) of **2ac** as a light yellow liquid.

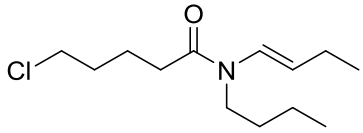
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2H), 7.21-7.16 (m, 2H), 6.47-6.32 (m, 1H), 5.11-4.99 (m, 1H), 3.81-3.65 (m, 2H), 2.37 (s, 3H), 2.03-1.89 (m, 2H), 1.67-1.56 (m, 2H), 1.44-1.28 (m, 2H), 1.01-0.84 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 140.0, 133.0, 128.8, 128.0, 126.8, 112.7, 43.3, 28.9, 23.5, 21.3, 20.2, 14.5, 13.8.

No rotameric effects were observed via NMR spectroscopy.

HRMS *m/z* (ESI) calcd for $C_{16}H_{24}NO$ $[M+H]^+$ 246.1858, found: 246.1855.

N-(but-1-en-1-yl)-*N*-butyl-5-chloropentanamide (**2ad**)



2ad

The reaction of *N,N*-dibutyl-5-chloropentanamide **1ad** (99.1 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 39.0 mg (40%) of **2ad** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 6.3:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.43 (d, J = 13.9 Hz, 1H), 5.16-5.05 (m, 1H), 3.63-3.42 (m, 4H), 2.49-2.39 (m, 2H), 2.14-2.05 (m, 2H), 1.91-1.76 (m, 4H), 1.62-1.45 (m, 2H), 1.38-1.27 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H), 0.98-0.90 (m, 3H).

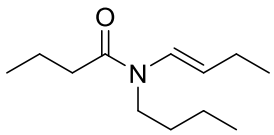
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, J = 14.7 Hz, 1H), 5.05-4.99 (m, 1H), 3.63-3.42 (m, 4H), 2.49-2.39 (m, 2H), 2.14-2.05 (m, 2H), 1.91-1.76 (m, 4H), 1.62-1.45 (m, 2H), 1.38-1.27 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H), 0.98-0.90 (m, 3H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 126.4, 115.4, 44.8, 43.2, 33.1, 32.2, 29.1, 23.9, 22.4, 20.4, 14.76, 14.0.

Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 125.1, 113.2, 44.9, 43.2, 32.9, 30.0, 29.4, 23.8, 22.6, 20.3, 14.80, 13.9. There is an overlapping peak at δ = 43.2 ppm.

HRMS *m/z* (ESI) calcd for $C_{13}H_{25}NOCl$ $[M+H]^+$ 246.1625, found: 246.1626.

N-(but-1-en-1-yl)-*N*-butylbutyramide (**2ae**)



2ae

The reaction of *N*,*N*-dibutylbutyramide **1ae** (79.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 47.9 mg (61%) of **2ae** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.8:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.48 (d, *J* = 14.0 Hz, 1H), 5.14-4.97 (m, 1H), 3.63-3.50 (m, 2H), 2.45-2.33 (m, 2H), 2.16-2.04 (m, 2H), 1.76-1.63 (m, 2H), 1.61-1.45 (m, 2H), 1.40-1.26 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00-0.90 (m, 6H).

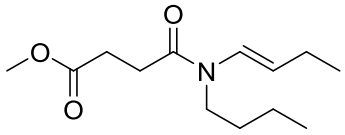
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 14.8 Hz, 1H), 5.14-4.97 (m, 1H), 3.50-3.41 (m, 2H), 2.45-2.33 (m, 2H), 2.16-2.04 (m, 2H), 1.76-1.63 (m, 2H), 1.61-1.45 (m, 2H), 1.40-1.26 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00-0.90 (m, 6H).

Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 126.5, 114.4, 42.8, 35.9, 28.9, 23.73, 20.21, 18.4, 14.6, 13.87, 13.8.

Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ171.0, 125.0, 112.6, 44.7, 35.6, 29.8, 23.65, 20.17, 18.6, 14.7, 13.92, 13.7.

HRMS *m/z* (ESI) calcd for $C_{12}H_{24}NO$ $[M+H]^+$ 198.1858, found: 198.1857.

Methyl 4-(but-1-en-1-yl(butyl)amino)-4-oxobutanoate (**2af**)



2af

The reaction of methyl 4-(dibutylamino)-4-oxobutanoate **1af** (97.3 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 41.0 mg (42%) of **2af** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.4:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.46 (d, *J* = 13.6 Hz, 1H), 5.19-5.00 (m, 1H), 3.70 (s, 3H), 3.62-3.53 (m, 2H), 2.77-2.64 (m, 4H), 2.14-2.04 (m, 2H), 1.67-1.45 (m, 2H), 1.40-1.29 (m, 2H), 1.07-0.98 (m, 3H), 0.98-0.89 (m, 3H).

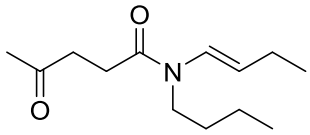
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 14.8 Hz, 1H) 5.19-5.00 (m, 1H), 3.70 (s, 3H), 3.53-3.45 (m, 2H), 2.77-2.64 (m, 4H), 2.14-2.04 (m, 2H), 1.67-1.45 (m, 2H), 1.40-1.29 (m, 2H), 1.07-0.98 (m, 3H), 0.98-0.89 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 169.5, 126.2, 115.9, 51.9, 43.4, 29.2, 29.1, 29.0, 23.9, 20.3, 14.7, 13.9.

Minor isomer: ^{13}C NMR could not be clearly identified.

HRMS *m/z* (ESI) calcd for $C_{13}H_{24}NO_3$ $[M+H]^+$ 242.1756, found: 242.1759.

N-(but-1-en-1-yl)-*N*-butyl-4-oxopentanamide (**2ag**)



2ag

The reaction of methyl *N*,*N*-dibutyl-4-oxopentanamide **1ag** (90.9 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 22.1 mg (25%) of **2ag** as a yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.9:1.

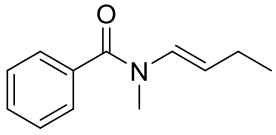
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.49 (d, *J* = 13.6 Hz, 1H), 5.16-5.05 (m, 1H), 3.60-3.50 (m, 2H), 2.83-2.75 (m, 2H), 2.73-2.66 (m, 2H), 2.23 (s, 3H), 2.13-2.04 (m, 2H), 1.65-1.46 (m, 2H), 1.37-1.27 (m, 2H), 1.06-0.98 (m, 3H), 0.97-0.89 (m, 3H).

Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 14.8 Hz, 1H), 5.05-4.98 (m, 1H), 3.50-3.44 (m, 2H), 2.83-2.75 (m, 2H), 2.73-2.66 (m, 2H), 2.23 (s, 3H), 2.13-2.04 (m, 2H), 1.65-1.46 (m, 2H), 1.37-1.27 (m, 2H), 1.06-0.98 (m, 3H), 0.97-0.89 (m, 3H).

Both rotamers are described together: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.6, 169.73, 169.68, 126.1, 125.0, 115.4, 113.0, 44.7, 43.2, 38.0, 37.9, 30.1, 29.6, 28.9, 27.8, 27.7, 23.7, 23.6, 20.2, 14.6, 13.8, 13.7.

HRMS *m/z* (ESI) calcd for $C_{13}H_{24}NO_2$ $[M+H]^+$ 226.1807, found: 226.1808.

(E)-N-(but-1-en-1-yl)-N-methylbenzamide (**2ah**)



2ah

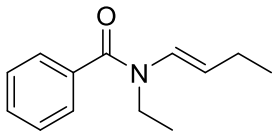
The reaction of methyl N-butyl-N-methylbenzamide **1ah** (76.4 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 22.7 mg (30%) of **2ah** as a yellow liquid. Both rotamers are described together:

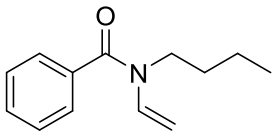
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.35 (m, 5H), 6.65-5.98 (m, 1H), 5.14 (m, 1H), 3.31-2.74 (m, 3H), 1.92-1.61 (m, 2H), 1.07-0.85 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 135.6, 130.1, 128.8, 128. 5, 127.2, 34.5, 18.6, 14.8, 13.7.

HRMS *m/z* (ESI) calcd for $C_{12}H_{15}NO$ $[M+H]^+$ 190.1232, found: 190.1235.

(*E*)-N-(but-1-en-1-yl)-N-ethylbenzamide (**2ai-1**) and N-butyl-N-vinylbenzamide (**2ai-2**)



2ai-1 and 

2ai-2

The reaction of methyl N-butyl-N-ethylbenzamide **1ai** (82.0 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 28.4 mg (35%) of **2ai-1** as a yellow liquid and 7.5 mg (9%) of **2aj-2** as a colorless liquid.

2ai-1: The desired enamide was obtained as two rotamers while the ratio could not be clearly identified. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.34 (m, 5H), 6.49-6.20 (m, 1H), 5.42-4.98 (m, 1H), 4.01-3.24 (m, 2H), 1.77-1.64 (m, 2H), 1.34-1.14 (m, 3H), 1.00-0.70 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 131.2, 129.7, 128.7, 128.4, 128.3, 126.9, 126.7, 35.1, 23.6, 18.8, 14.6, 13.5.

HRMS *m/z* (ESI) calcd for $C_{13}H_{17}NO$ $[M+H]^+$ 204.1388, found: 204.1390.

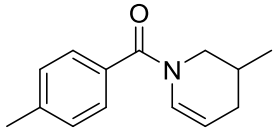
2ai-2: No rotameric effects were observed via NMR spectroscopy.

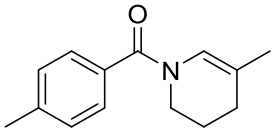
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.39 (m, 5H), 6.68 (br, s, 1H), 4.58-4.43 (d, *J* = 15.6 Hz, 1H), 4.25 (br, s, 1H), 3.88-3.64 (m, 2H), 1.77-1.59 (m, 2H), 1.48-1.33 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H),

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 135.8, 135.0, 130.2, 128.5, 128.0, 93.1, 42.5, 28.9, 20.5, 14.0.

HRMS *m/z* (ESI) calcd for $C_{13}H_{17}NO$ $[M+H]^+$ 204.1388, found: 204.1387.

(3-Methyl-3,4-dihydropyridin-1(2*H*)-yl)(*p*-tolyl)methanone (**2aj-1**) and (5-methyl-3,4-dihydropyridin-1(2*H*)-yl)(*p*-tolyl)methanone (**2aj-2**)



2aj-1 and 

2aj-2

The reaction of (3-methylpiperidin-1-yl)(*p*-tolyl)methanone **1aj** (86.9 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 °C for 12h, afforded 32.3 mg (38%) of **2aj-1** as a light yellow liquid and 27.9 mg (32%) of **2aj-2** as a colorless liquid.

2aj-1: The desired enamide was obtained as two rotamers while the ratio could not be clearly identified. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.23-7.18 (m, 2H), 6.50-6.42 (m, 1H), 5.21-4.77 (m, 1H), 4.24-3.54 (m, 1H), 3.08-2.96 (m, 1H), 2.38 (s, 3H), 2.23-2.13 (m, 1H), 2.08-1.97 (m, 1H), 1.80-1.70 (m, 1H), 1.13-0.84 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 140.5, 132.4, 129.0, 128.4, 127.4, 106.8, 47.4, 30.5, 27.3, 21.5, 19.0.

HRMS *m/z* (ESI) calcd for $C_{14}H_{18}NO$ $[M+H]^+$ 216.1388, found: 216.1388.

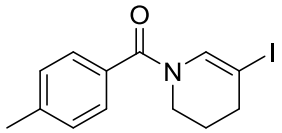
2aj-2: The desired enamide was obtained as two rotamers while the ratio could not be clearly identified. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 2H), 7.23-7.17 (m, 2H), 7.10-6.23 (m, 1H), 3.79-3.46 (m, 2H), 2.38 (s, 3H), 2.07-2.00 (m, 2H), 1.96-1.89 (m, 1H), 1.81-1.72 (m, 2H), 1.61-1.54 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 140.1, 132.4, 128.8, 128.3, 127.5, 122.5, 116.0, 40.6, 27.4, 21.7, 21.4, 20.8.

HRMS *m/z* (ESI) calcd for $C_{14}H_{18}NO$ $[M+H]^+$ 216.1388, found: 216.1383.

(5-Iodo-3,4-dihydropyridin-1(2*H*)-yl)(*p*-tolyl)methanone (**3a**)



3a

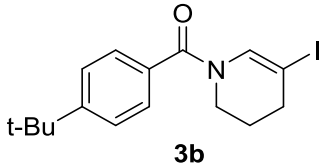
The reaction of piperidin-1-yl(*p*-tolyl)methanone **1a** (57.4 mg, 0.2 mmol), NIS (112.5 mg, 0.5 mmol) and $TMSN_3$ (57.6 mg, 0.5 mmol) in dry CCl_4 (2.0 mL) under Air at 80 °C for 7h, afforded 42.5 mg (65%) of **3a** as a light yellow liquid. The desired enamide was obtained as two rotamers while the ratio could not be clearly identified. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.03-6.90 (m, 1H), 3.87-3.53(m, 2H), 2.54 (td, J = 6.4, 1.8 Hz, 2H), 2.39 (s, 3H), 2.08-1.84 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 131.2, 129.1, 128.4, 39.8, 35.2, 21.4.

HRMS *m/z* (ESI) calcd for $C_{13}H_{15}NOI$ $[M+H]^+$ 328.0198, found: 328.0190.

(4-(*tert*-butyl)phenyl)(5-iodo-3,4-dihydropyridin-1(2*H*)-yl)methanone (**3b**)



3b

The reaction of (4-(*tert*-butyl)phenyl)(piperidin-1-yl)methanone **1c** (49.1 mg, 0.2 mmol), NIS (112.5 mg, 0.5 mmol) and $TMSN_3$ (57.6 mg, 0.5 mmol) in dry CCl_4 (2.0 mL) under Air at 80 °C for 7h, afforded 46.0 mg (62%) of **3b** as a white solid. The desired enamide was obtained as two rotamers while the ratio could not be clearly identified. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 4H), 7.07-6.94 (m, 1H), 3.89-3.57 (m, 2H), 2.54 (td, J = 6.3, 1.8 Hz, 2H), 2.07-1.86 (m, 2H), 1.33 (s, 9H).

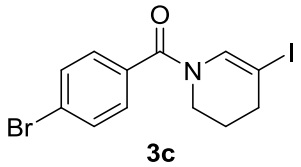
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.0, 133.5, 131.1, 128.2, 125.4, 125.2, 35.3, 34.9, 31.1. Minor isomer: ^{13}C NMR could not be clearly identified.

HRMS *m/z* (ESI) calcd for $C_{16}H_{21}NOI$ $[M+H]^+$ 370.0668, found: 370.0661.

Melting Point: 84-85 ℃.

IR (neat) ν_{max}: 2962, 1660, 1626, 1403, 1381, 1345, 1304, 1267, 1187, 1154, 989, 846, 732.

(4-Bromophenyl)(5-iodo-3,4-dihydropyridin-1(2*H*)-yl)methanone (**3c**)



3c

The reaction of (4-bromophenyl)(piperidin-1-yl)methanone **1d** (53.6 mg, 0.2 mmol), NIS (112.5 mg, 0.5 mmol) and $TMSN_3$ (57.6 mg, 0.5 mmol) in dry CCl_4 (2.0 mL) under Air at 80 °C for 7h, afforded 23.5 mg (30%) of **3c** as a white solid. The desired enamide was obtained as two rotamers in a ratio of around 2.8:1.

Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.92-6.82 (m, 1H), 3.88-3.67 (m, 2H), 2.55 (td, *J* = 6.3, 1.8 Hz, 2H), 2.09-1.95 (m, 2H).

Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.77-7.67 (m, 1H), 3.65-3.50 (m, 2H), 2.55 (td, *J* = 6.3, 1.8 Hz, 2H), 1.95-1.83 (m, 2H).

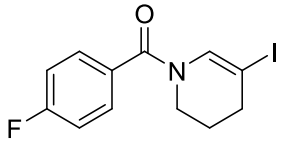
Both rotamers are described together: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 132.7, 131.6, 129.8, 125.1, 74.4, 39.8, 35.1, 31.7, 23.6.

HRMS *m/z* (ESI) calcd for $C_{12}H_{12}NOBrI$ $[M+H]^+$ 391.9147, found: 391.9138.

Melting Point: 103-104 °C.

IR (neat) ν_{max}: 2923, 1635, 1587, 1443, 1384, 1352, 1307, 1269, 1185, 1148, 1072, 1011, 986, 857, 755.

(4-Fluorophenyl)(5-iodo-3,4-dihydropyridin-1(2*H*)-yl)methanone (**3d**)



3d

The reaction of (4-fluorophenyl)(piperidin-1-yl)methanone **1f** (41.4 mg, 0.2 mmol), NIS (112.5 mg, 0.5 mmol) and $TMSN_3$ (57.6 mg, 0.5 mmol) in dry CCl_4 (2.0 mL) under Air at 80 °C for 7h, afforded 30.9 mg (47%) of **3d** as a white solid. The desired enamide was obtained as two rotamers while the ratio could not be clearly identified.

Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.46 (m, 2H), 7.16-7.09 (m, 2H), 6.96-6.85 (m, 1H), 3.89-3.54 (m, 2H), 2.55 (td, *J* = 6.3, 1.9 Hz, 2H), 2.08-1.84 (m, 2H).

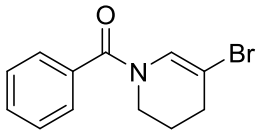
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 162.6, 133.1, 130.7, 130.2, 115.8, 115.5, 40.0, 35.2, 23.9.

HRMS *m/z* (ESI) calcd for $C_{12}H_{12}NOFI$ $[M+H]^+$ 331.9948, found: 331.9941.

Melting Point: 72-73 ℃.

IR (neat) ν_{max}: 2928, 1651, 1628, 1603, 1509, 1485, 1347, 1228, 1150, 846.

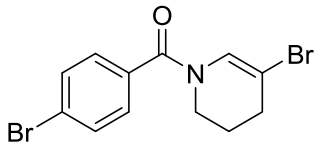
(5-Bromo-3,4-dihydropyridin-1(2*H*)-yl)(phenyl)methanone (**3e**)



3e

The reaction of phenyl(piperidin-1-yl)methanone **1b** (56.8 mg, 0.3 mmol), DBDMH (47.2 mg, 0.165 mmol) and $TogniN_3$ (95.4 mg, 0.33 mmol) in DCE (2.0 mL) under Ar at 80 □ for 12h, afforded 45.2 mg (57%) of **3e** as a colorless liquid. The desired enamide was obtained as two rotamers while the ratio could not be clearly identified.
Both rotamers are described together:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.37 (m, 5H), 6.78 (m, 1H), 3.84-3.47 (m, 2H), 2.49 (td, *J* = 6.3, 1.7 Hz, 2H), 2.07-1.82 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 134.2, 130.5, 128.4, 128.1, 39.9, 31.8, 22.7.
HRMS *m/z* (ESI) calcd for $C_{12}H_{13}NOBr$ $[M+H]^+$ 266.0181, found: 266.0177.

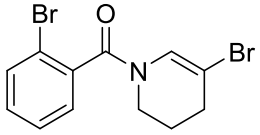
(5-Bromo-3,4-dihydropyridin-1(2*H*)-yl)(4-bromophenyl)methanone (**3f**)



3f

The reaction of (4-bromophenyl)(piperidin-1-yl)methanone **1d** (80.5 mg, 0.3 mmol), DBDMH (47.2 mg, 0.165 mmol) and $TogniN_3$ (95.4 mg, 0.33 mmol) in DCE (2.0 mL) under Ar at 80 °C for 12h, afforded 97.7 mg (47%) of **3f** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.5:1.
Both rotamers are described together:
^{1}H NMR (400 MHz, CDCl3) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.80-6.68 (m, 1H), 3.82-3.48 (m, 2H), 2.50 (td, *J* = 6.4, 1.6 Hz, 2H), 2.08-1.85 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 133.0, 131.7, 129.8, 127.5, 125.1, 104.1, 40.1, 31.8, 22.7.
Minor isomer: ^{13}C NMR could not be clearly identified.
HRMS *m/z* (ESI) calcd for $C_{12}H_{12}NOBr_2$ $[M+H]^+$ 343.9286, found: 343.9287.

(5-Bromo-3,4-dihydropyridin-1(2*H*)-yl)(2-bromophenyl)methanone (**3g**)

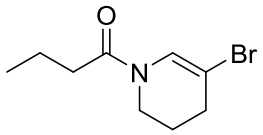


3g

The reaction of (2-bromophenyl)(piperidin-1-yl)methanone **1e** (80.5 mg, 0.3 mmol),

DBDMH (47.2 mg, 0.165 mmol) and TogniN$_3$ (95.4 mg, 0.33 mmol) in DCE (2.0 mL) under Ar at 80 °C for 12h, afforded 98.0 mg (47%) of **3g** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 1.4:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 1H), 7.43-7.36 (m, 1H), 7.33-7.25 (m, 2H), 6.45-6.42 (m, 1H), 3.99-3.3.74 (m, 2H), 2.55-2.49 (m, 2H), 2.10-1.99 (m, 2H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 1H), 7.43-7.36 (m, 1H), 7.33-7.25 (m, 2H), 7.72-7.68 (m, 1H), 3.47-3.17 (m, 2H), 2.55-2.49 (m, 2H), 1.99-1.88 (m, 2H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 136.4, 133.0, 131.0, 128.4, 127.8, 126.4, 119.5, 104.9, 39.4, 31.9, 22.3.
Minor isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 137.1, 132.7, 130.7, 128.4,127.8, 124.6, 119.0, 108.4, 43.9, 31.9, 23.3. There is an overlapping peak at δ = 128.4 ppm.
HRMS *m/z* (ESI) calcd for $C_{12}H_{12}NOBr_2$ $[M+H]^+$ 343.9286, found: 343.9288.

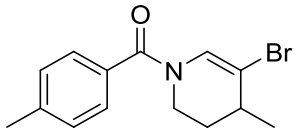
1-(5-Bromo-3,4-dihydropyridin-1(2*H*)-yl)butan-1-one (**3h**)



3h

The reaction of 1-(piperidin-1-yl)butan-1-one **1q** (46.6 mg, 0.3 mmol), DBDMH (47.2 mg, 0.165 mmol) and TogniN$_3$ (95.4 mg, 0.33 mmol) in DCE (2.0 mL) under Ar at 80 °C for 12h, afforded 57.9 mg (42%) of **3h** as colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 2.2:1.
Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (m, 1H), 3.73-3.57 (m, 2H), 2.47-2.41 (m, 2H), 2.37-2.28 (m, 2H), 1.92-1.84 (m, 2H), 1.70-1.60 (m, 2H), 0.98-0.91 (m, 3H).
Minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (m, 1H), 3.57-3.46 (m, 2H), 2.47-2.41 (m, 2H), 2.37-2.28 (m, 2H), 1.99-1.92 (m, 2H), 1.70-1.60 (m, 2H), 0.98-0.91 (m, 3H).
Major isomer: **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 126.1, 103.7, 38.8, 35.0, 31.7, 22.6, 18.2, 13.8.
Minor isomer: ^{13}C NMR could not be clearly identified.
HRMS *m/z* (ESI) calcd for $C_9H_{15}NOBr$ $[M+H]^+$ 232.0337, found: 232.0336.

(5-Bromo-4-methyl-3,4-dihydropyridin-1(2*H*)-yl)(*p*-tolyl)methanone (**3i**)



3i

The reaction of 1-(piperidin-1-yl)butan-1-one **1y** (65.2 mg, 0.3 mmol), DBDMH (47.2

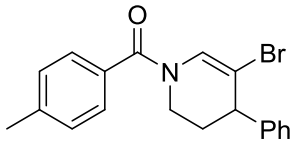
mg, 0.165 mmol) and TogniN_3 (95.4 mg, 0.33 mmol) in DCE (2.0 mL) under Ar at 80 °C for 12h, afforded 90.8 mg (51%) of **3i** as a colorless liquid. The desired enamide was obtained as two rotamers in a ratio of around 1.8:1. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.90-6.73 (m, 1H), 4.00-3.53 (m, 2H), 2.60-2.51 (m, 1H), 2.38 (s, 3H), 2.19-1.96 (m, 1H), 1.87-1.72 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 131.3, 129.0, 128.3, 34.7, 21.4, 20.1.

HRMS *m/z* (ESI) calcd for C14H17NOBr $[M+H]^+$ 294.0494, found: 294.0497.

(5-Bromo-4-phenyl-3,4-dihydropyridin-1(2*H*)-yl)(p-tolyl)methanone (**3j**)



3j

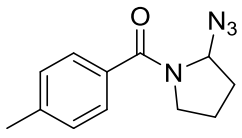
The reaction of (4-phenylpiperidin-1-yl)(p-tolyl)methanone **1aa** (83.8 mg, 0.3 mmol), DBDMH (47.2 mg, 0.165 mmol) and TogniN_3 (95.4 mg, 0.33 mmol) in DCE (2.0 mL) under Ar at 80 °C for 12h, afforded 88.9 mg (42%) of **3j** as a colorless liquid. No rotameric effects were observed via NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.29-7.23 (m, 2H), 7.22-7.10 (m, 5H), 7.10-7.00 (m, 1H), 4.00-3.84 (m, 1H), 3.70 (t, *J* = 5.2 Hz, 1H), 3.43-3.32 (m, 1H), 2.31 (s, 3H), 2.28-2.20 (m, 1H), 2.04-1.81 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.1, 131.1, 129.1, 128.5, 128.3, 127.9, 127.0, 46.5, 31.8, 21.4.

HRMS *m/z* (ESI) calcd for C19H19NOBr $[M+H]^+$ 356.0650, found: 356.0652.

(2-Azidopyrrolidin-1-yl)(*p*-tolyl)methanone (**4al)**



4al

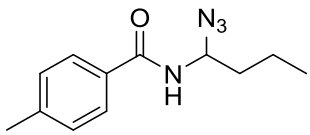
The reaction of pyrrolidin-1-yl(p-tolyl)methanone **1al** (75.7 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 ℃ for 12h, afforded 58.2 mg (63%) of **4al** as a light yellow liquid. The desired enamide was obtained as two rotamers in a ratio of around 1.9:1. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.94-5.14 (m, 1H), 3.70-3.67 (m, 2H), 2.36 (s, 3H), 2.11-1.81 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 140.6, 132.9, 128.9, 127.2, 126.8, 73.8, 49.2, 31.8, 23.9, 21.3.

HRMS *m/z* (ESI) calcd for $C_{12}H_{15}N_4O$ $[M+H]^+$ 231.1246, found: 231.1243.

N-(1-azidobutyl)-4-methylbenzamide (**4am**)



4am

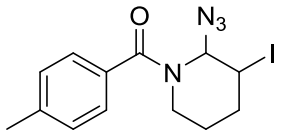
The reaction of N-butyl-4-methylbenzamide **1am** (76.5 mg, 0.4 mmol), $FeCl_2$ (5.1 mg, 0.04 mmol), NaI (18.0 mg, 0.12 mmol), PIDA (231.9 mg, 0.72 mmol) and NaN_3 (93.6 mg, 1.44 mmol) in dry EA (4.0 mL) under Ar at 80 ℃ for 12h, afforded 37.6 mg (40%) of **4am** as a light yellow solid. No rotameric effects were observed via NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.70-5.63 (m, 1H), 2.38 (s, 3H), 1.76-1.59 (m, 2H), 1.51-1.40 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 142.8, 130.4, 129.3, 127.1, 66.9, 36.7, 21.5, 18.4, 13.5.

HRMS *m/z* (ESI) calcd for $C_{12}H_{16}N_4ONa$ $[M+H]^+$ 255.1222, found: 255.1217.

(2-Azido-3-iodopiperidin-1-yl)(*p*-tolyl)methanone (**5**)



5

The reaction of piperidin-1-yl(*p*-tolyl)methanone **1a** (40.7 mg, 0.2 mmol), NIS (112.5 mg, 0.5 mmol) and $TMSN_3$ (57.6 mg, 0.5 mmol) in dry CCl_4 (2.0 mL) under Air at 80 °C for 4 h, afforded 42.2 mg (57%) of **5** as a white solid. No rotameric effects were observed via NMR spectroscopy.

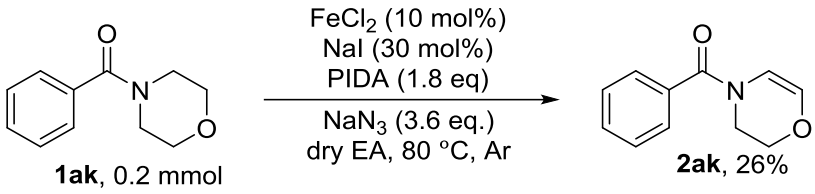
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.13 (brs, 1H), 4.43-4.35 (m, 1H), 4.01 (brs, 1H), 3.13-2.99 (m, 1H), 2.32 (s, 3H), 2.06-1.94 (m, 2H), 1.93-1.84 (m, 1H), 1.57-1.44 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 140.6, 131.5, 129.1, 127.4, 28.3, 28.1, 21.4, 20.8.

HRMS *m/z* (ESI) calcd for $C_{13}H_{16}N_4OI$ $[M+H]^+$ 371.0369, found: 371.0364.

Melting Point: 69-70 ℃.

IR (neat) ν_{max}:2918, 1629, 1568, 1447, 1392, 1348, 1306, 1264, 1183, 1149, 988, 828, 742.

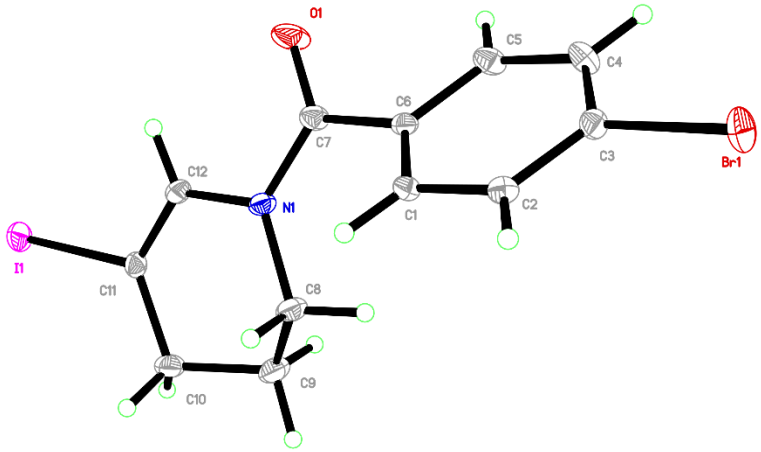


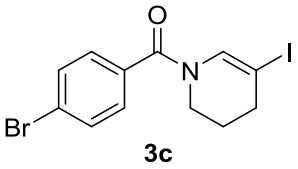
The reaction of morpholino(phenyl)methanone **1ak** (38.2 mg, 0.2 mmol), $FeCl_2$ (2.5 mg, 0.02 mmol), NaI (9.0 mg, 0.06 mmol), PIDA (116.0 mg, 0.36 mmol) and NaN_3 (46.8 mg, 0.72 mmol) in dry EA (2.0 mL) under Ar at 80 ℃ for 12h, afforded 9.8 mg (26%) of **2ak** as a yellow liquid. Both rotamers are described together:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.35 (m, 5H), 6.80-5.86 (m, 1H), 6.30-5.78 (m, 1H), 4.29-3.97 (m, 2H), 3.95-3.61 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 134.0, 132.7, 130.6, 129.2, 128.4, 128.3, 127.7, 107.6, 105.3, 65.0, 64.8, 45.9, 40.1. The spectral data are consistent with those reported in the literature. [5]

X-Ray Structure and Crystal Data of 3c





Item	Value
Molecular formula	$C_{12}H_{11}BrINO$
Formula weight	392.03
Crystal system	monoclinic
Space Group	C2/c
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b (Å)	6.2266(4)
c (Å)	20.7782(14)
α (°)	90
β (°)	102.111(2)
γ (°)	90
Volume (Å^3)	2503.4(3)
Z	8
T (K)	173(2)
ρ (g cm^{-1})	2.080
λ (Å)	0.71073
μ (mm^{-1})	5.729
# measured refl	8284

# unique refl	2194
R_{int}	0.0310
# parameters	145
$R(F^2)$, all refl	0.0253
$R_w(F^2)$, all refl	0.0612
Goodness of fit	1.117

References:

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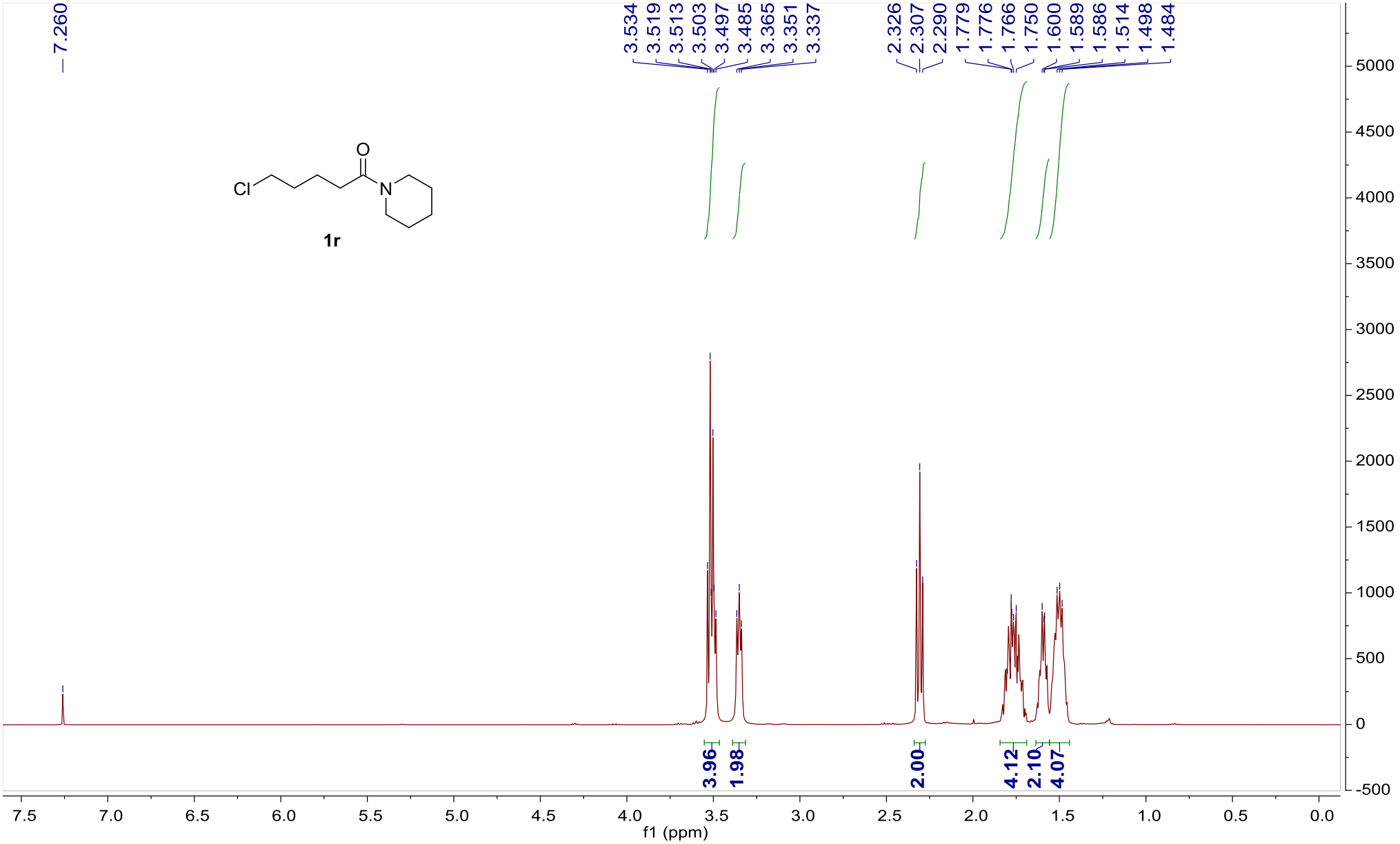
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1.600
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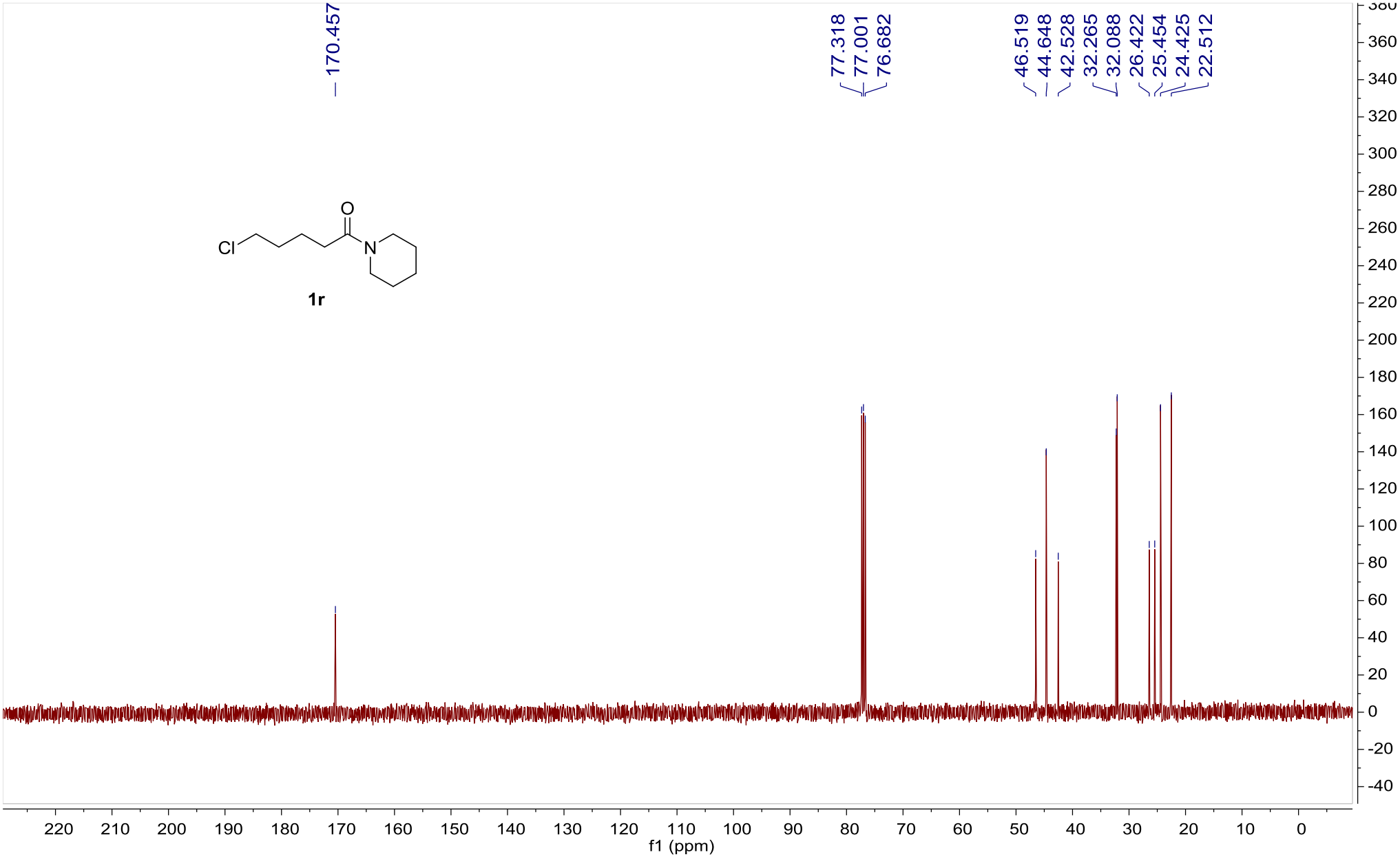
f1 (ppm)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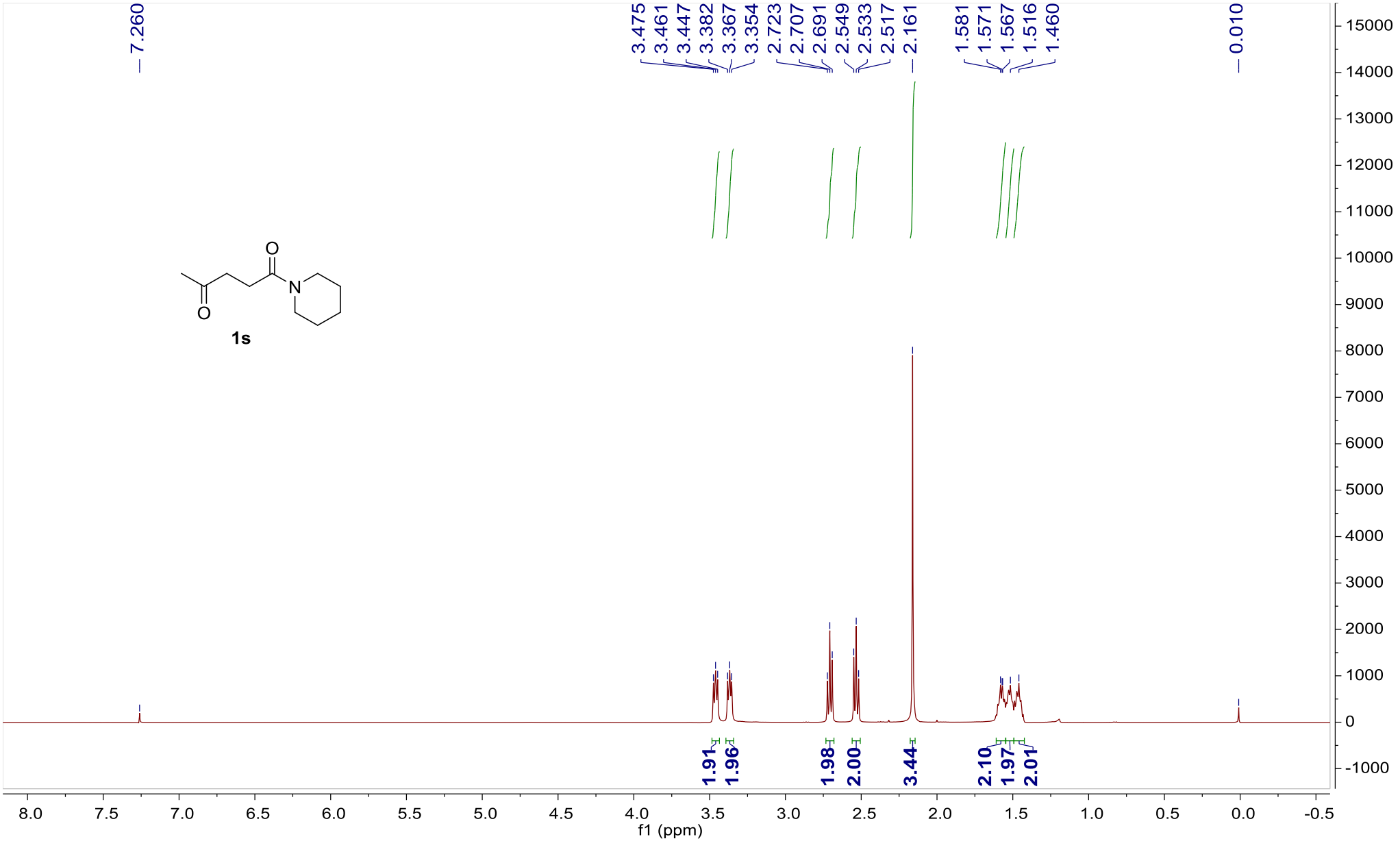
1r
f1 (ppm)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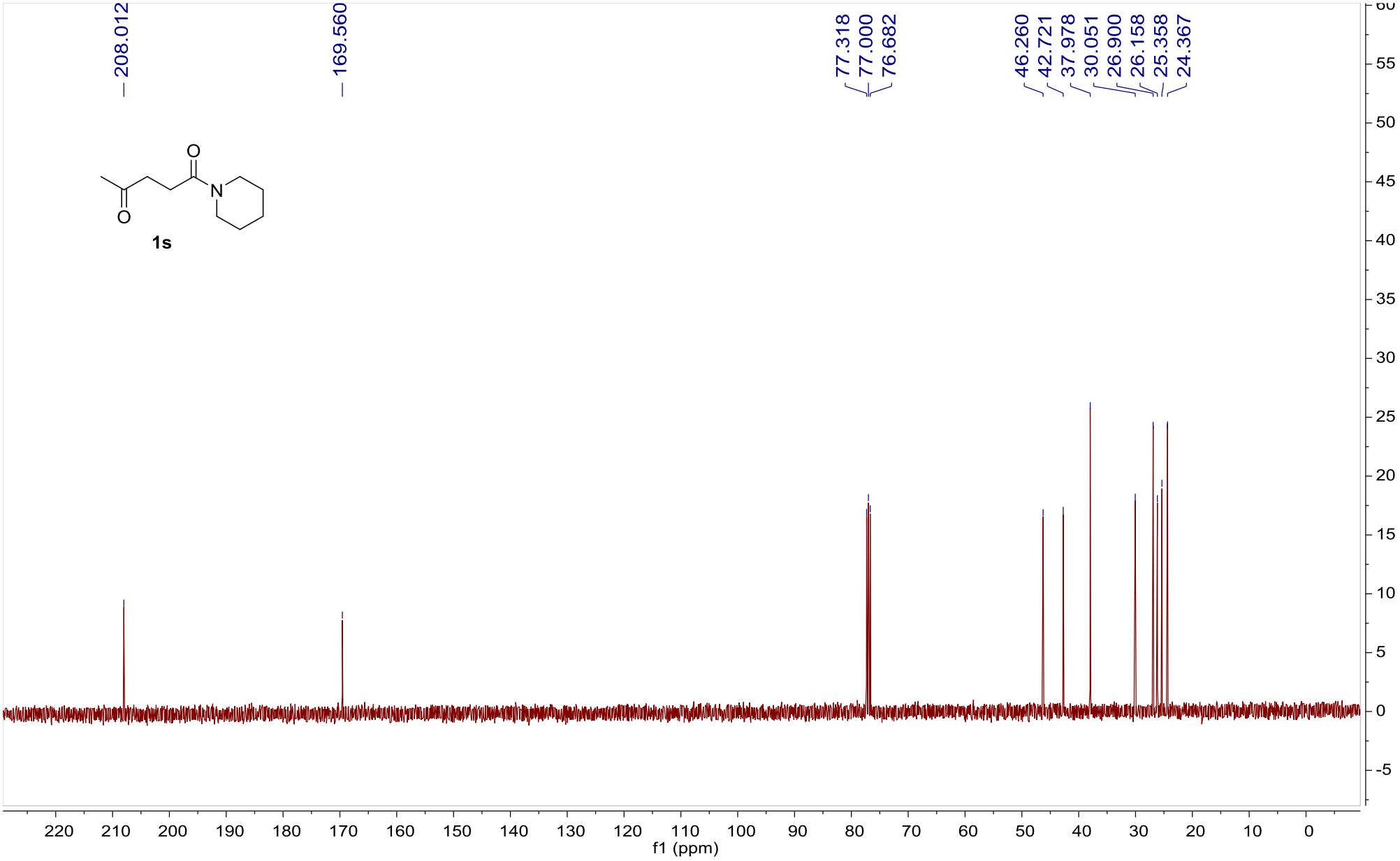
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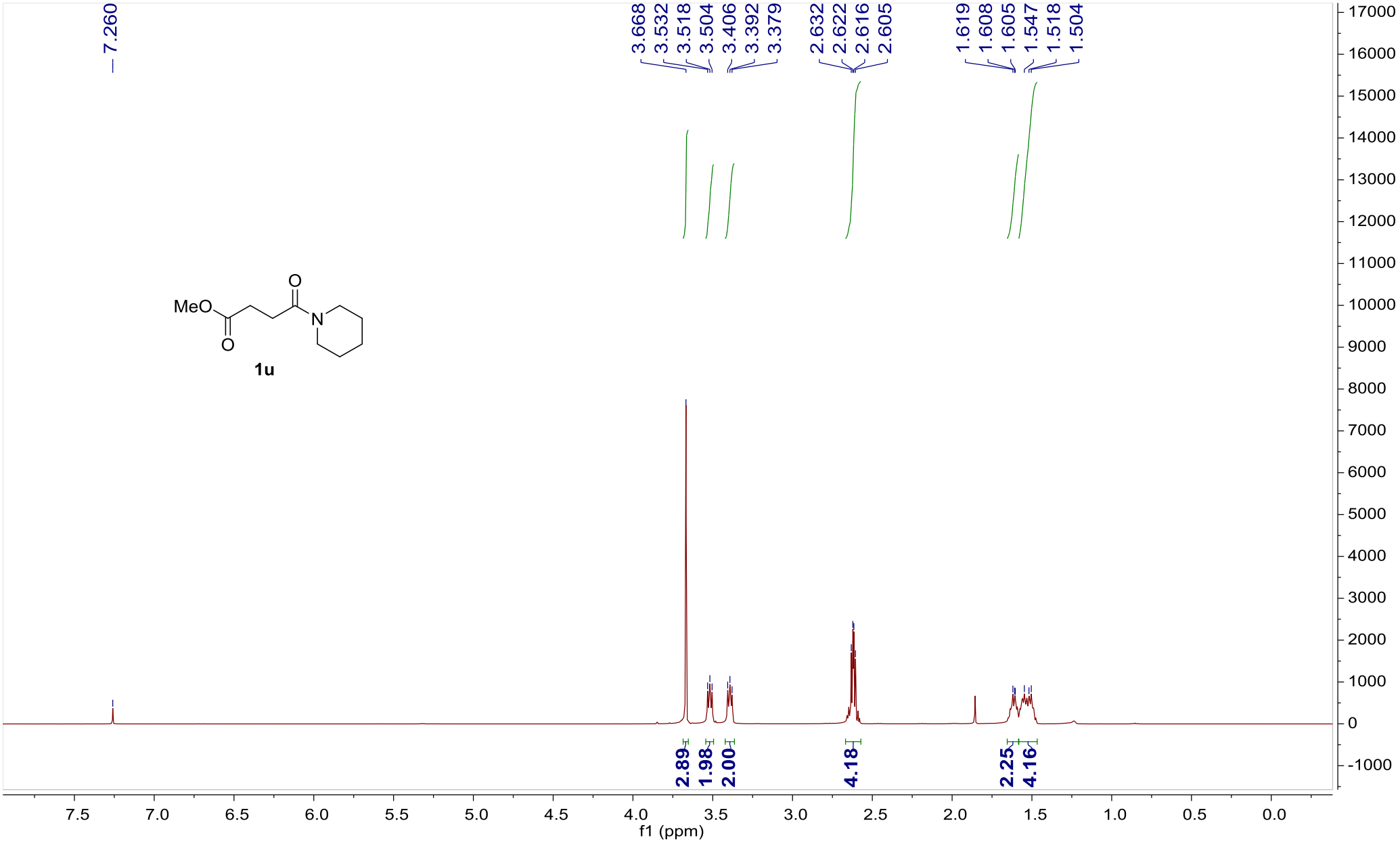
f1 (ppm)

=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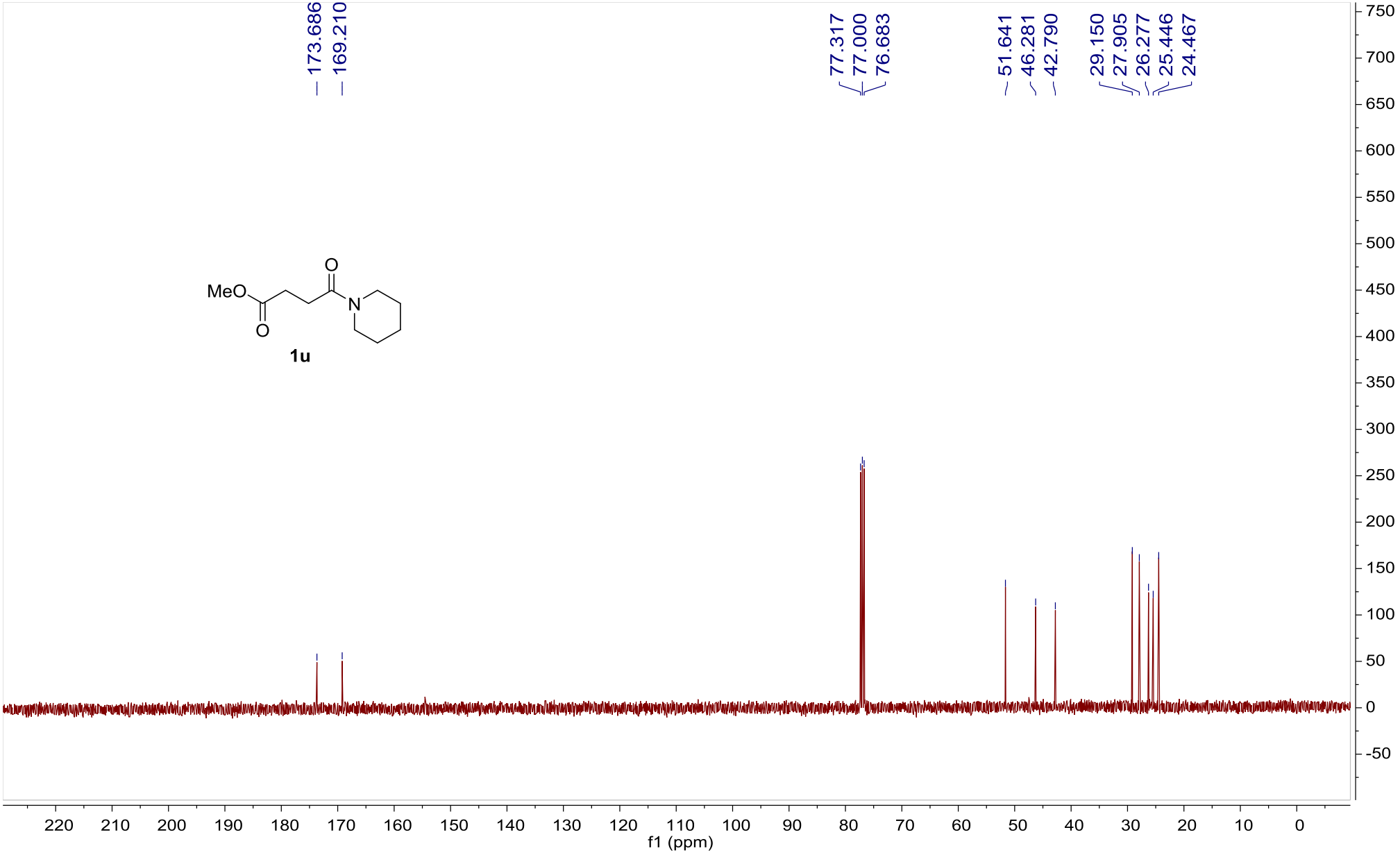
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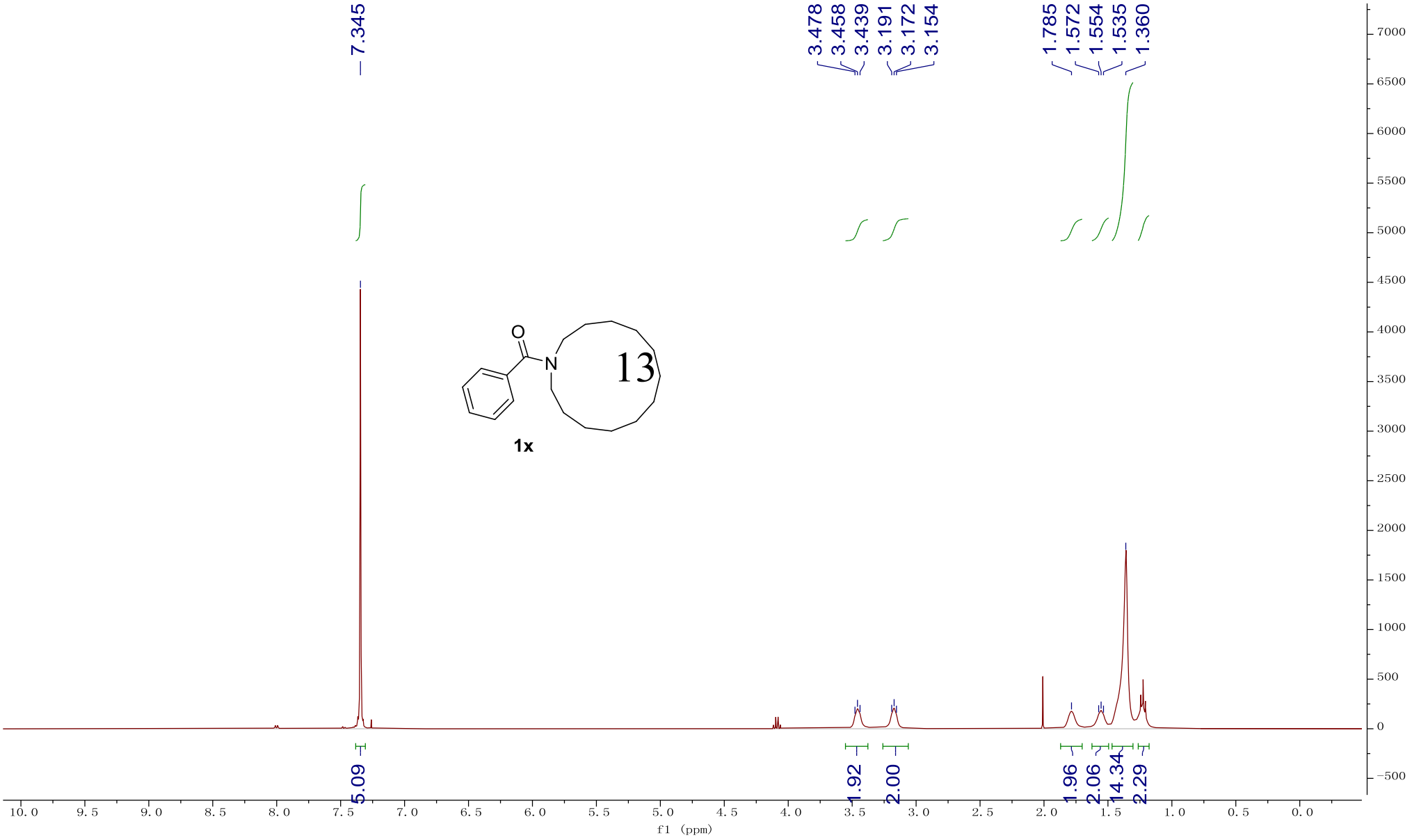
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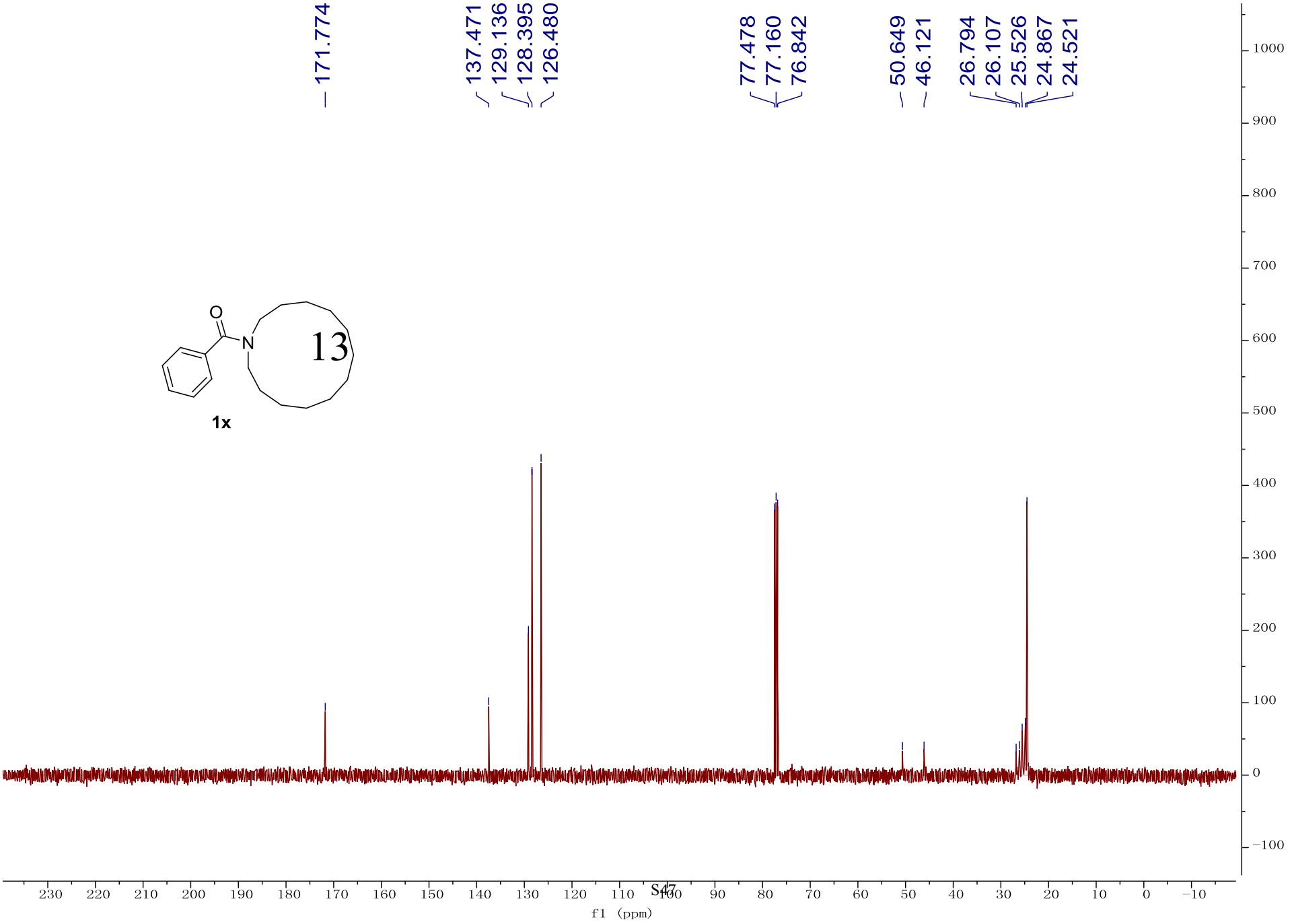
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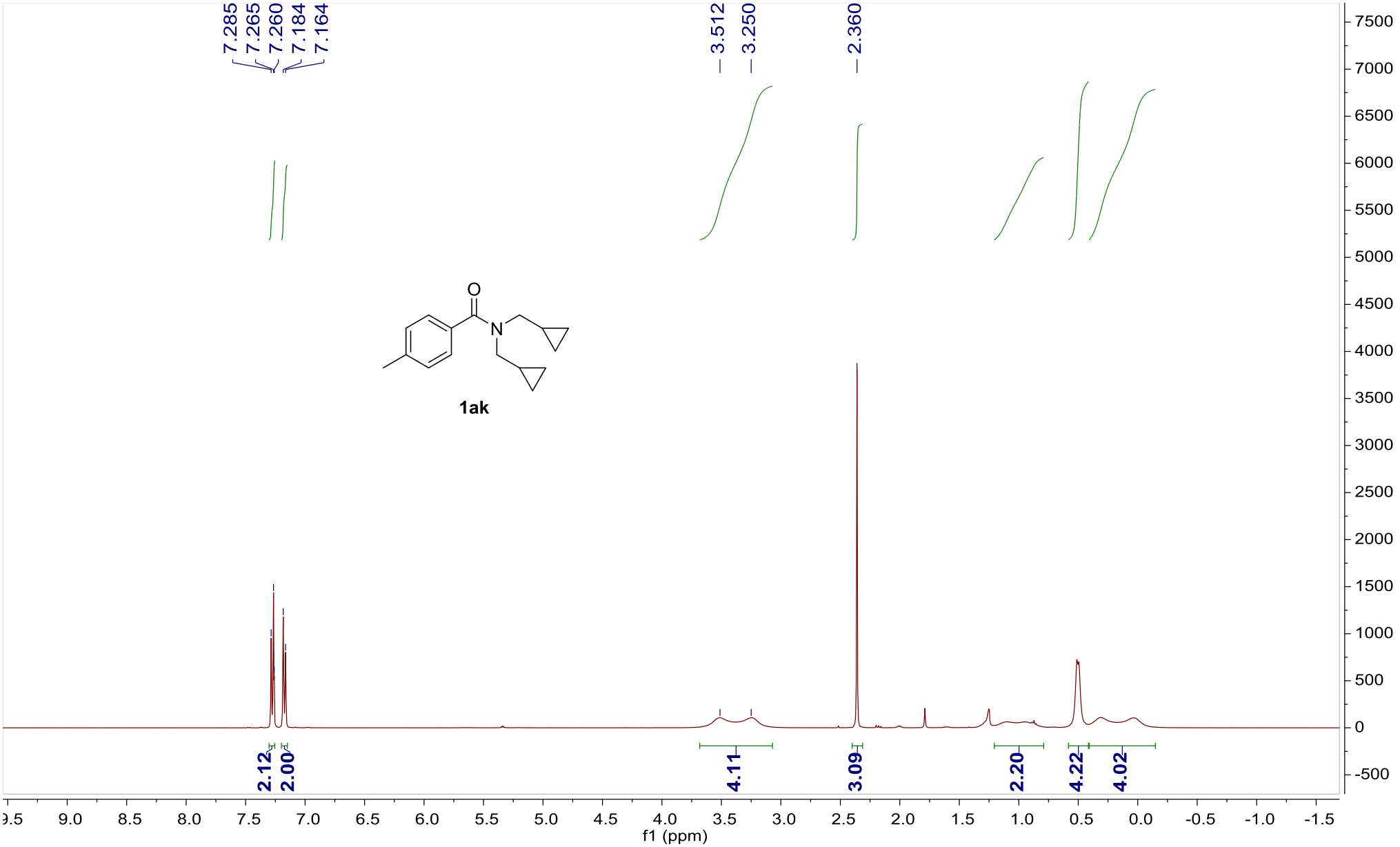
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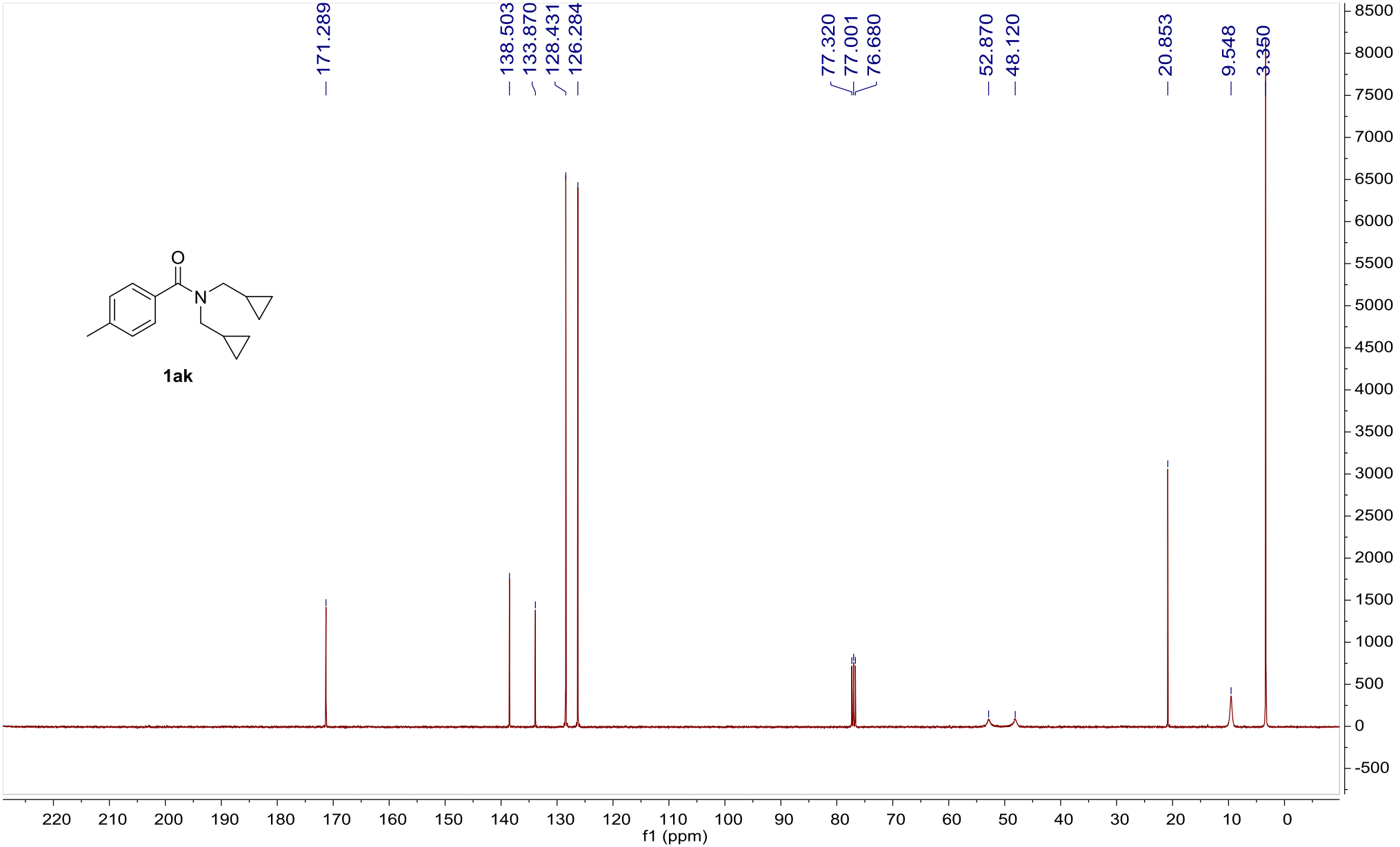
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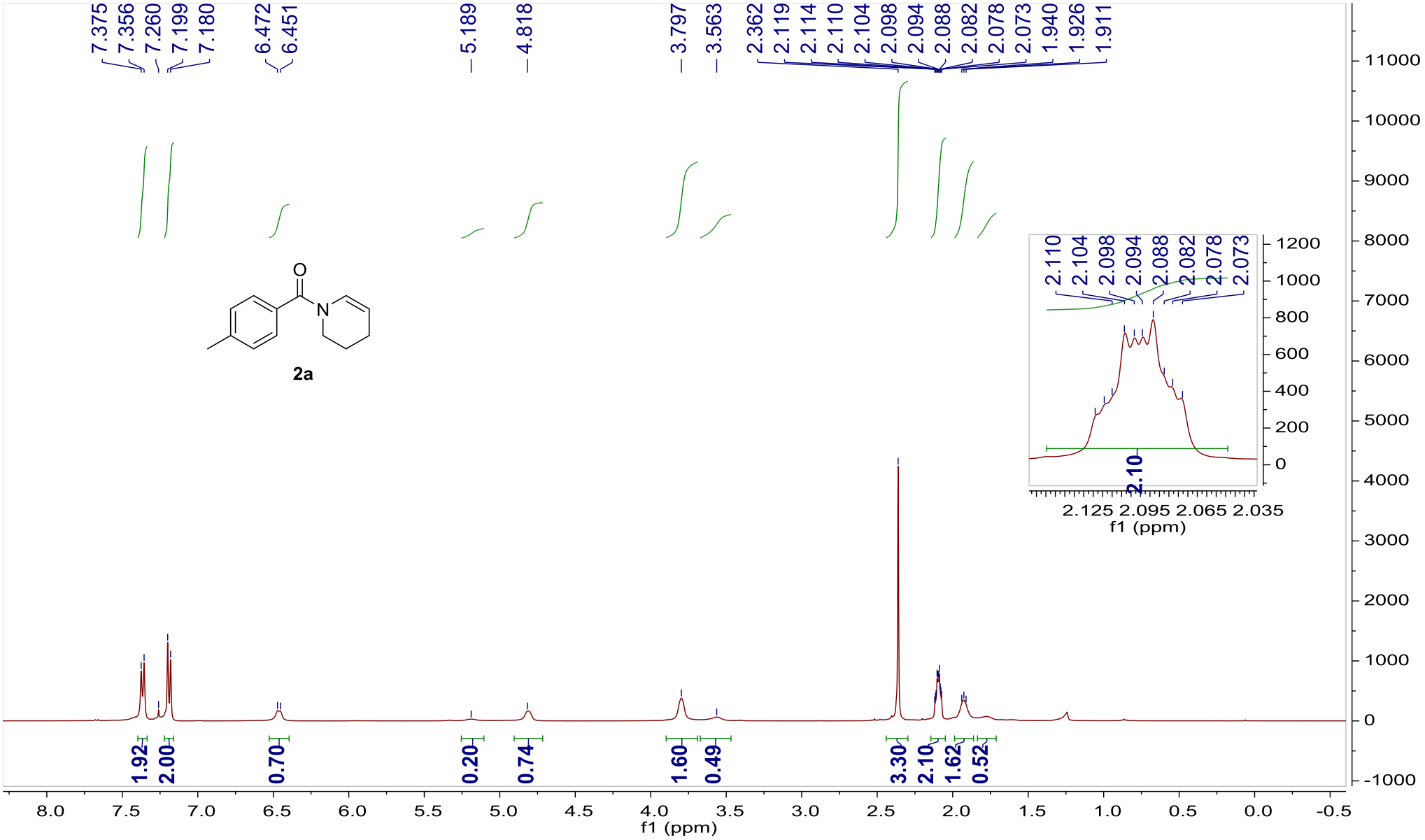
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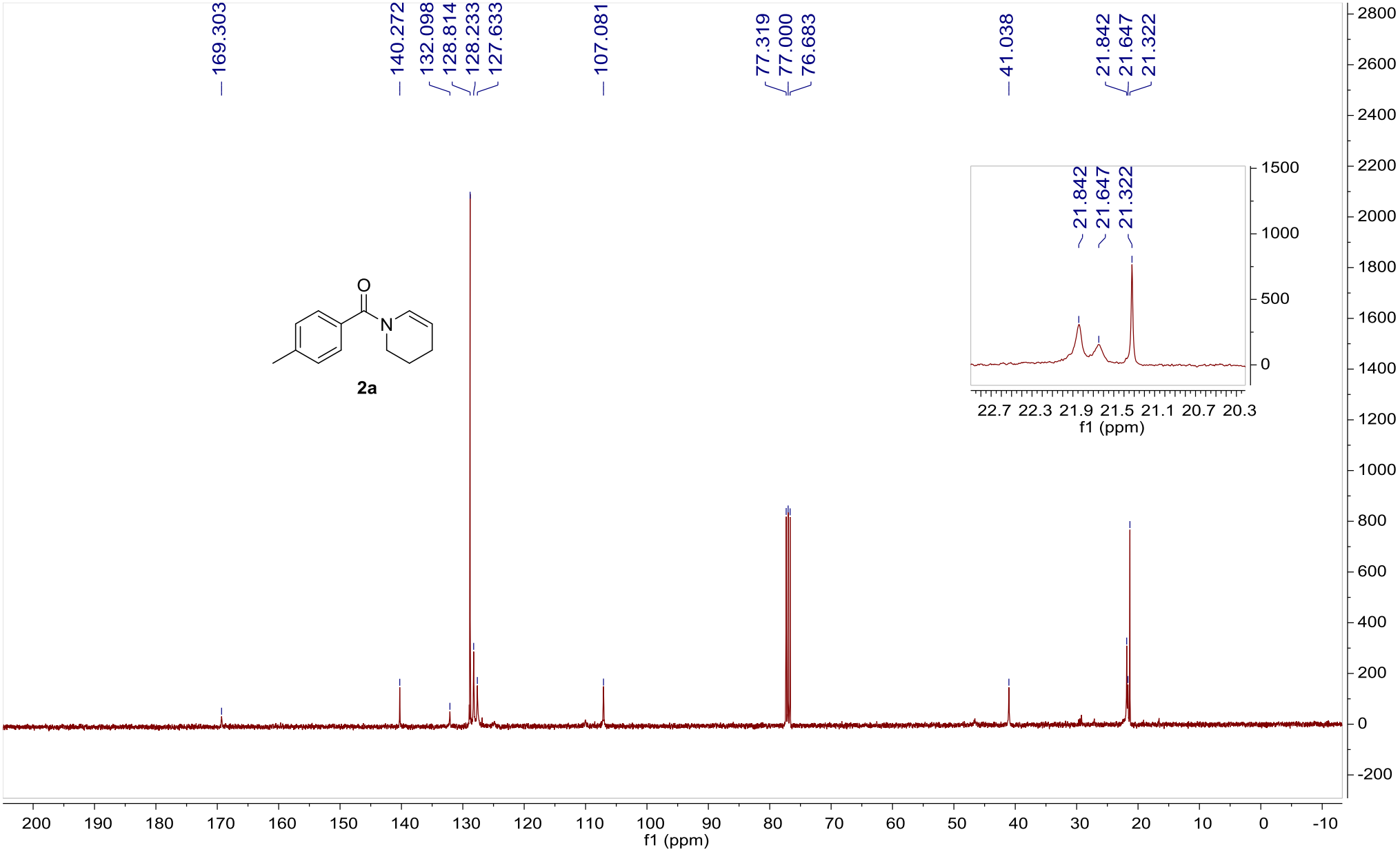
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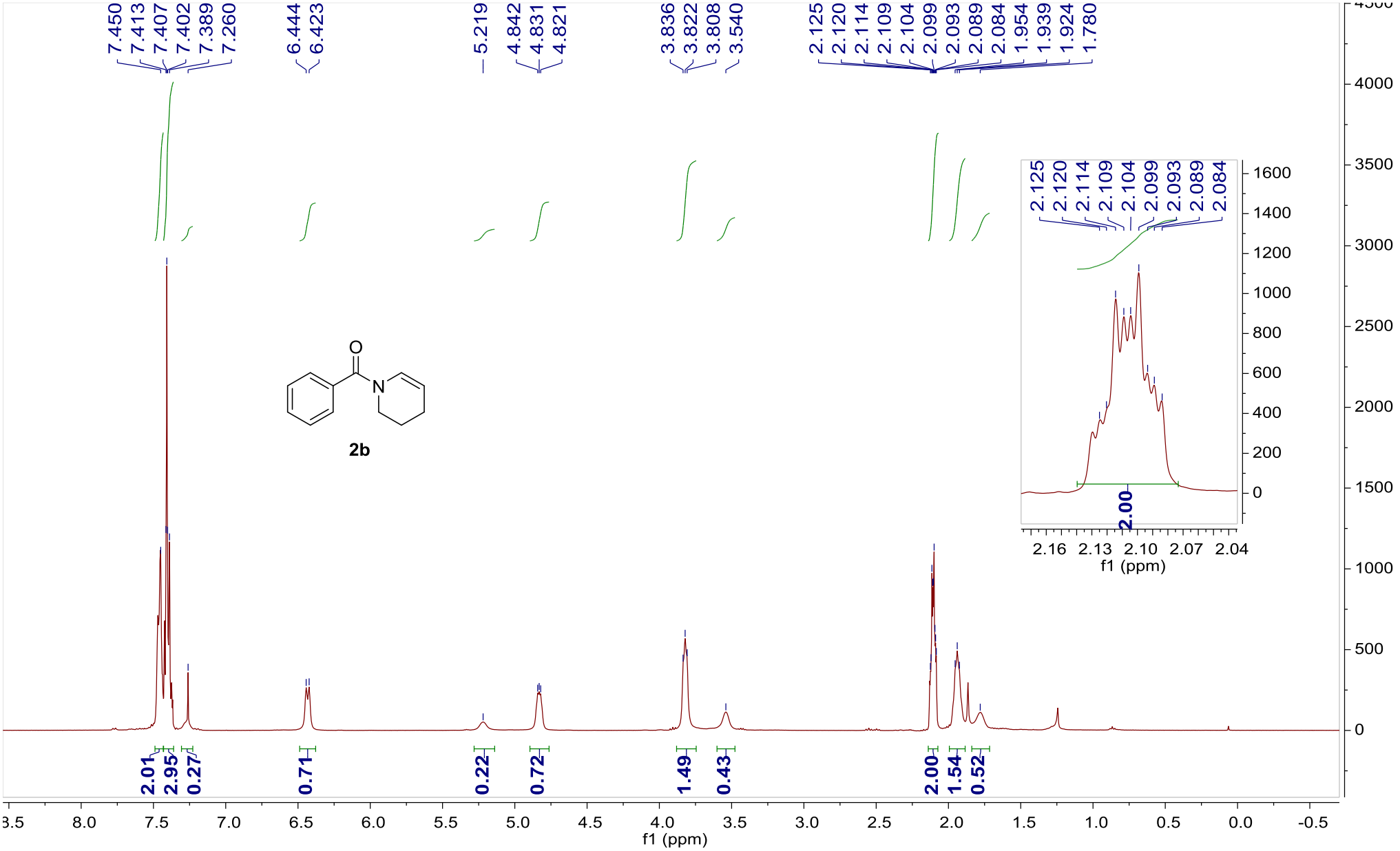
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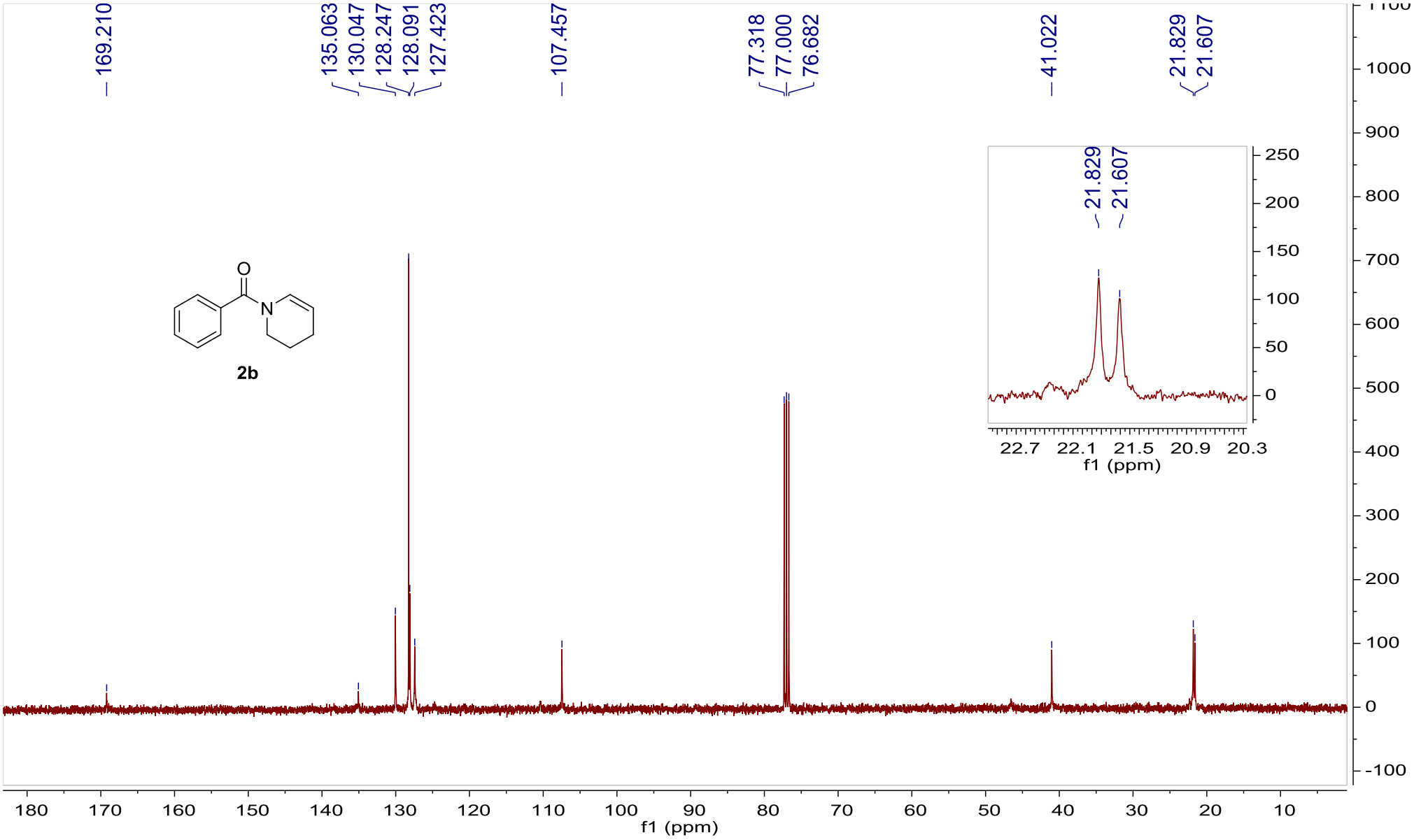
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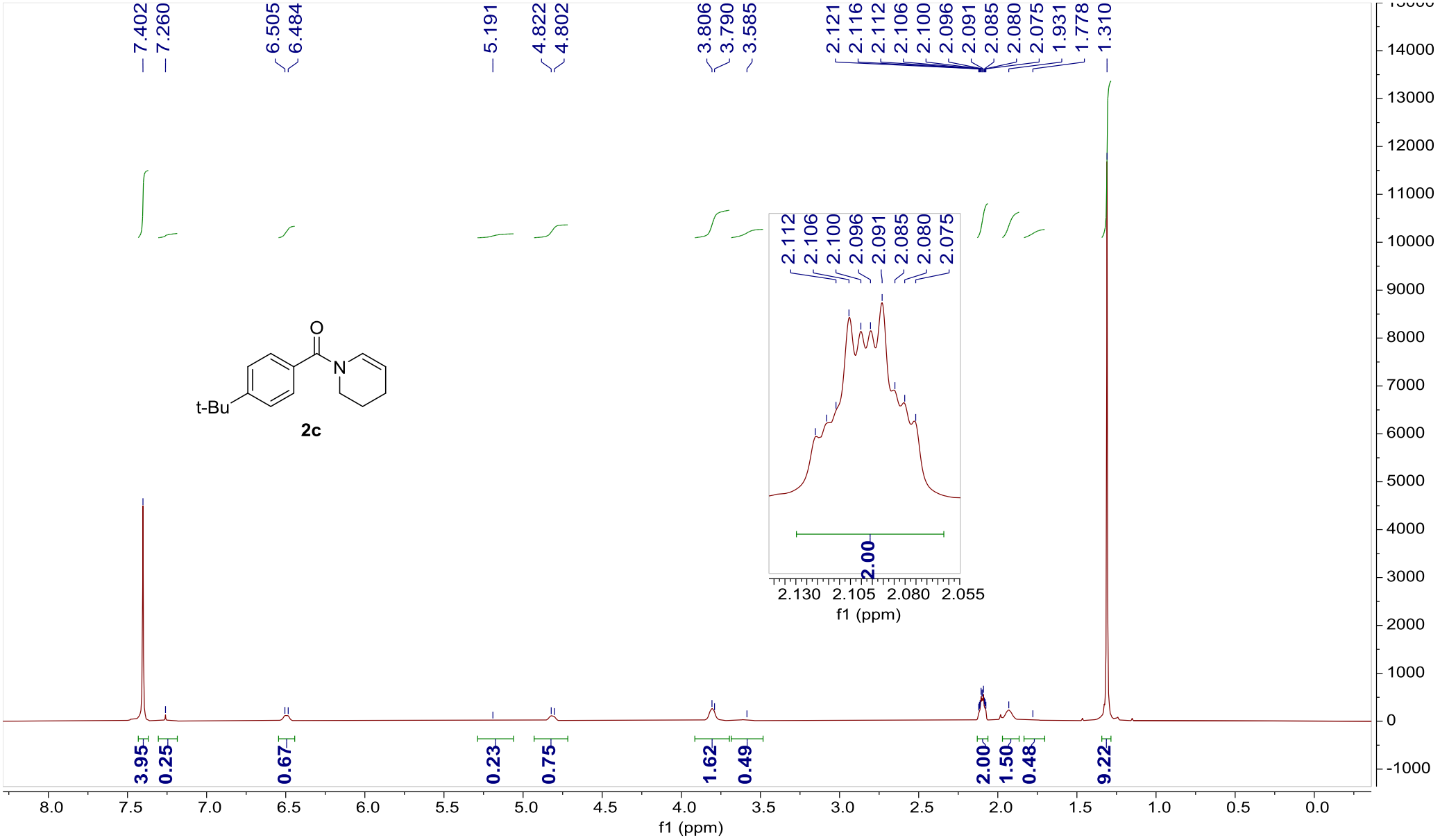
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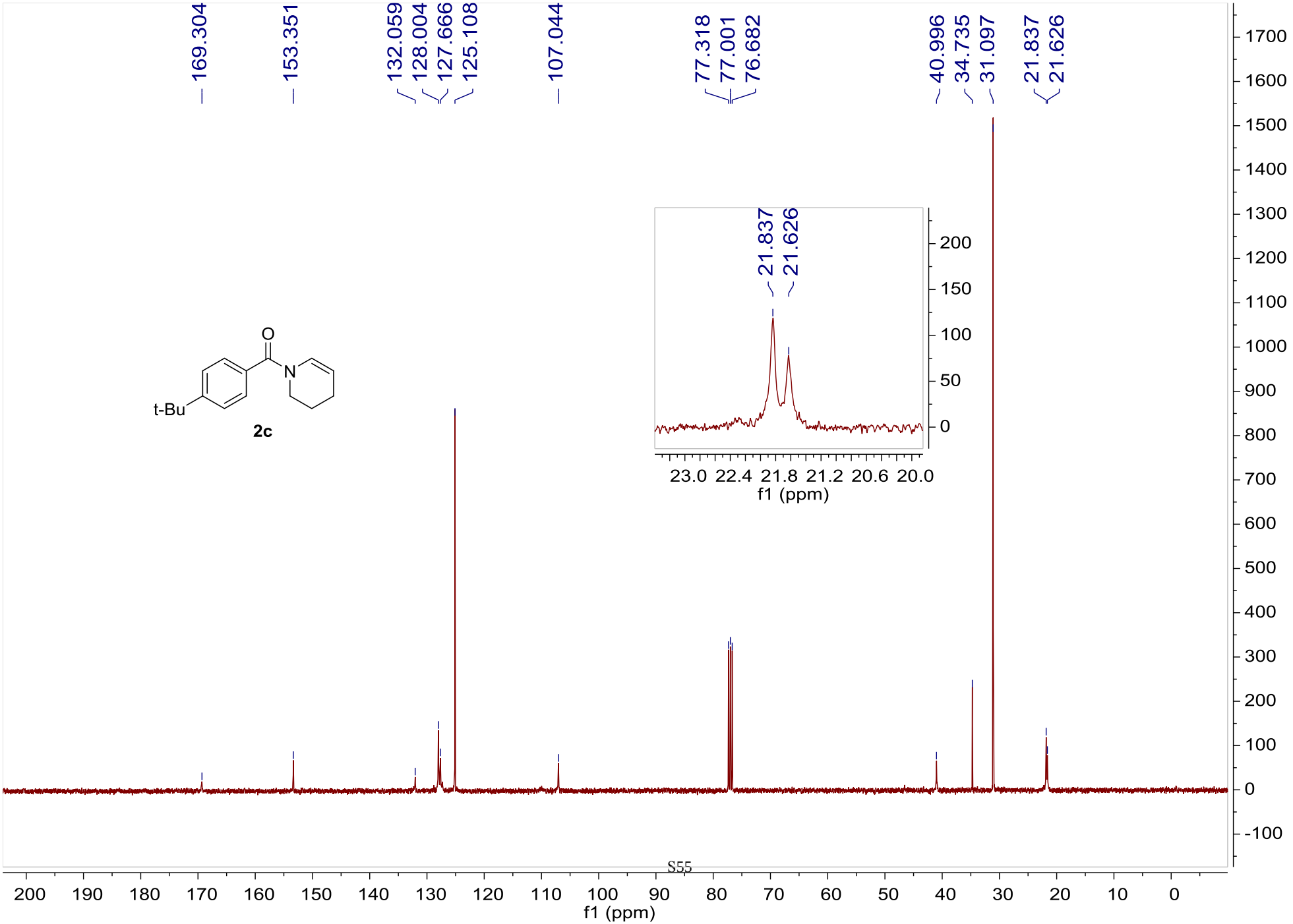
6.484
5.191
4.822
4.802
3.806
3.790
3.585
2.121
2.116
2.112
2.106
2.100
2.096
2.091
2.085
2.080
2.075
1.931
1.778
1.310
t-Bu
O
N
2c
2.00
2.130 2.105 2.080 2.055
f1 (ppm)
3.95
0.25
0.67
0.23
0.75
1.62
0.49
2.00
1.50
0.48
9.22
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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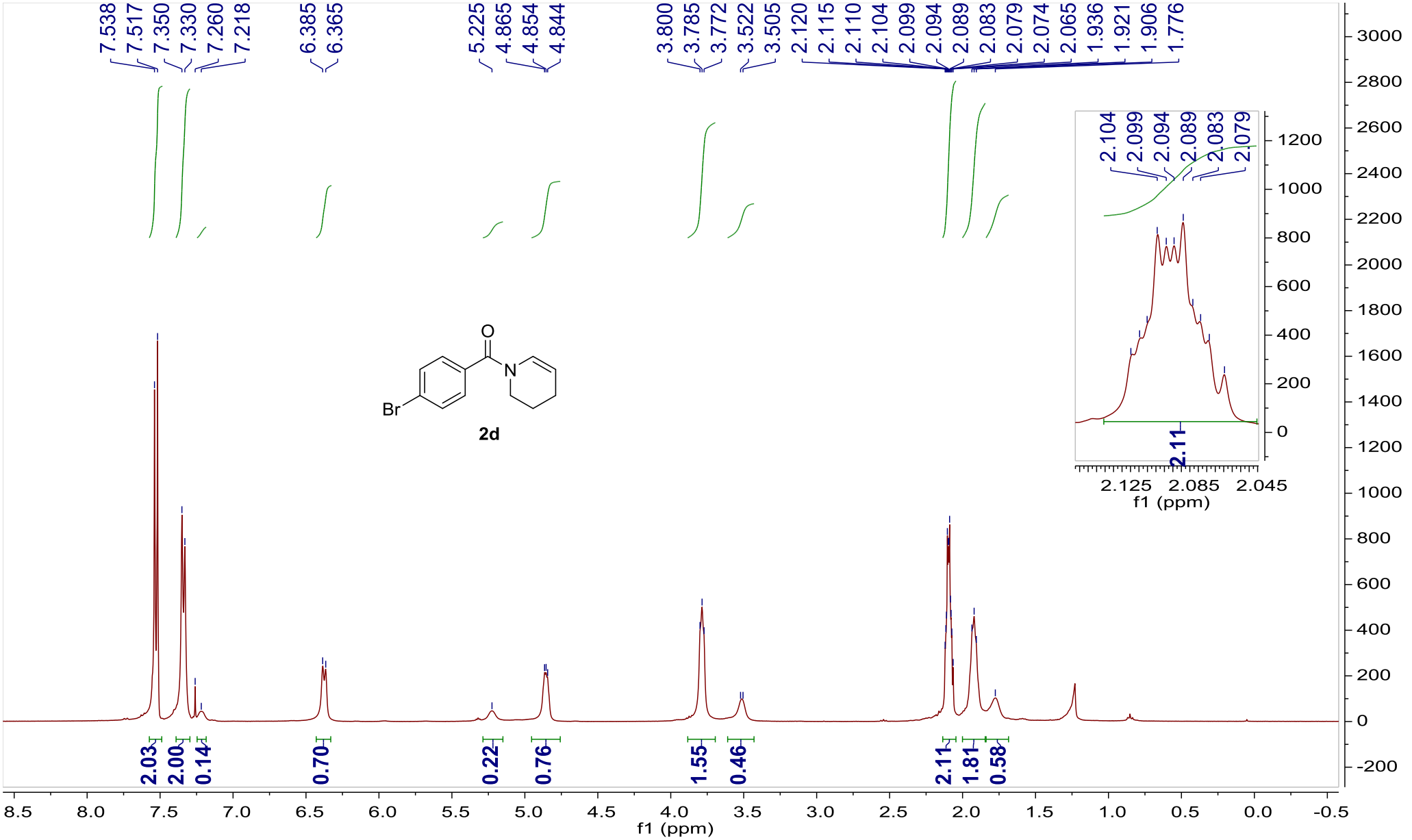
153.351
132.059
128.004
127.666
125.108
107.044
77.318
77.001
76.682
40.996
34.735
31.097
21.837
21.626
O
N
t-Bu
2c
f1 (ppm)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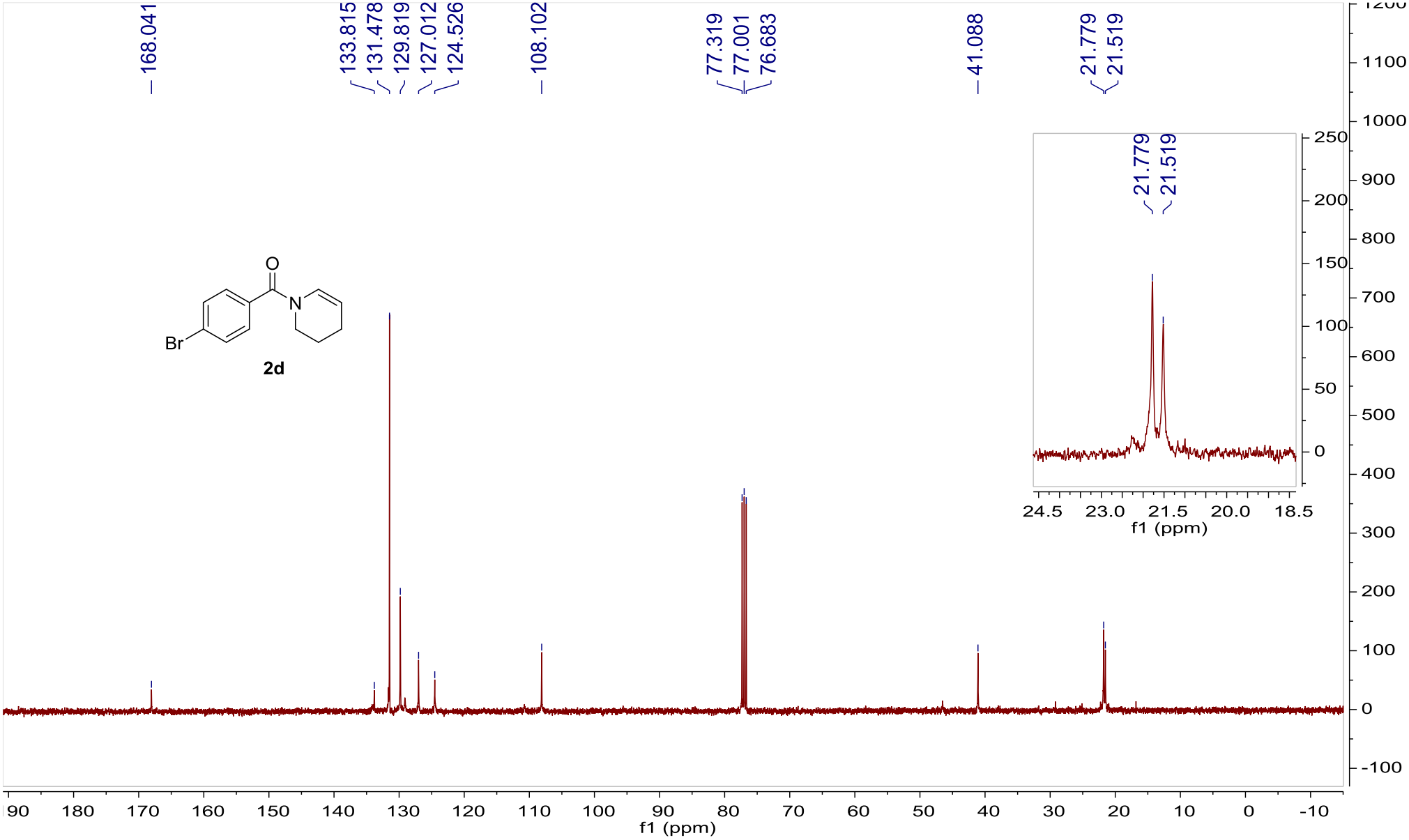
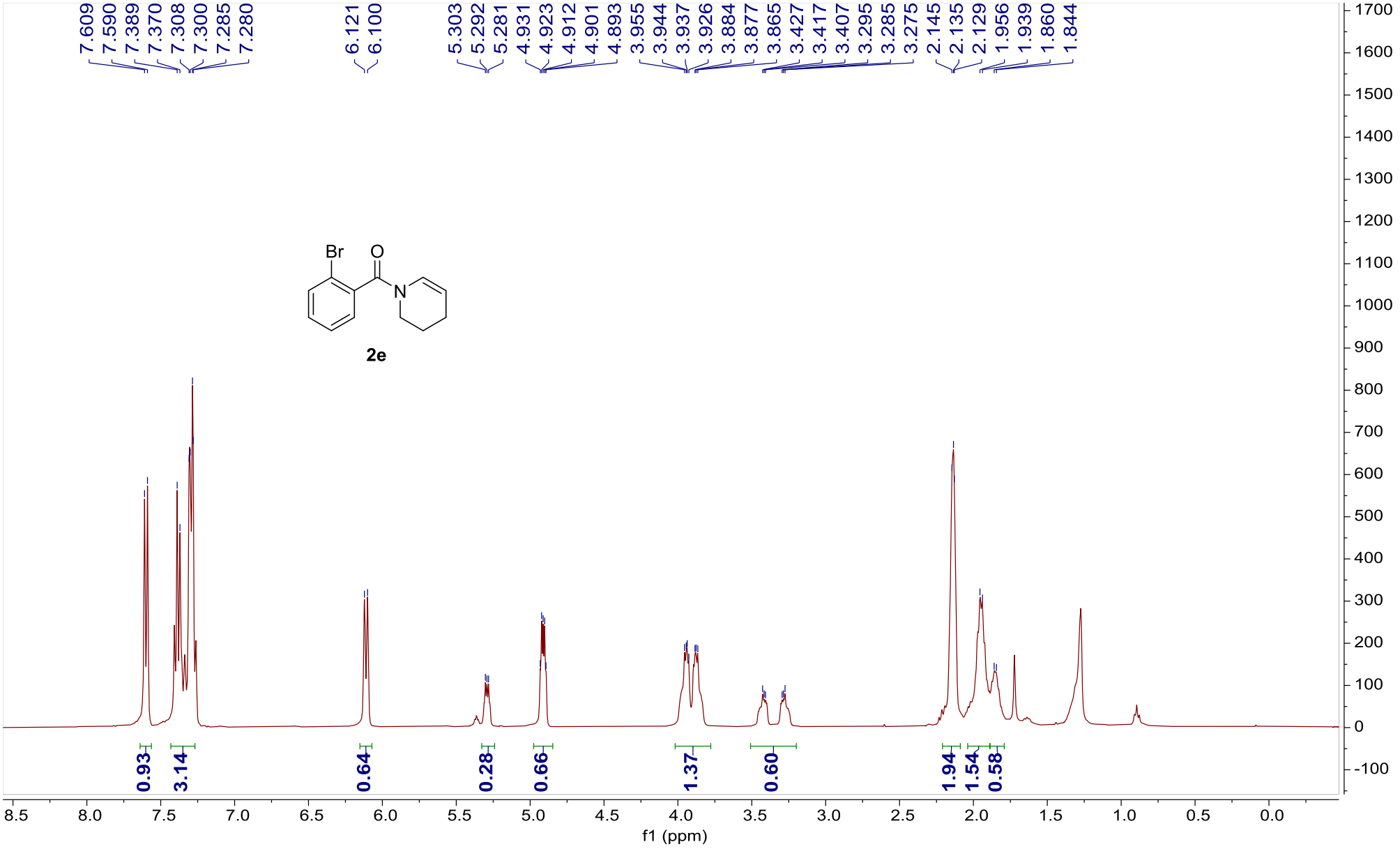
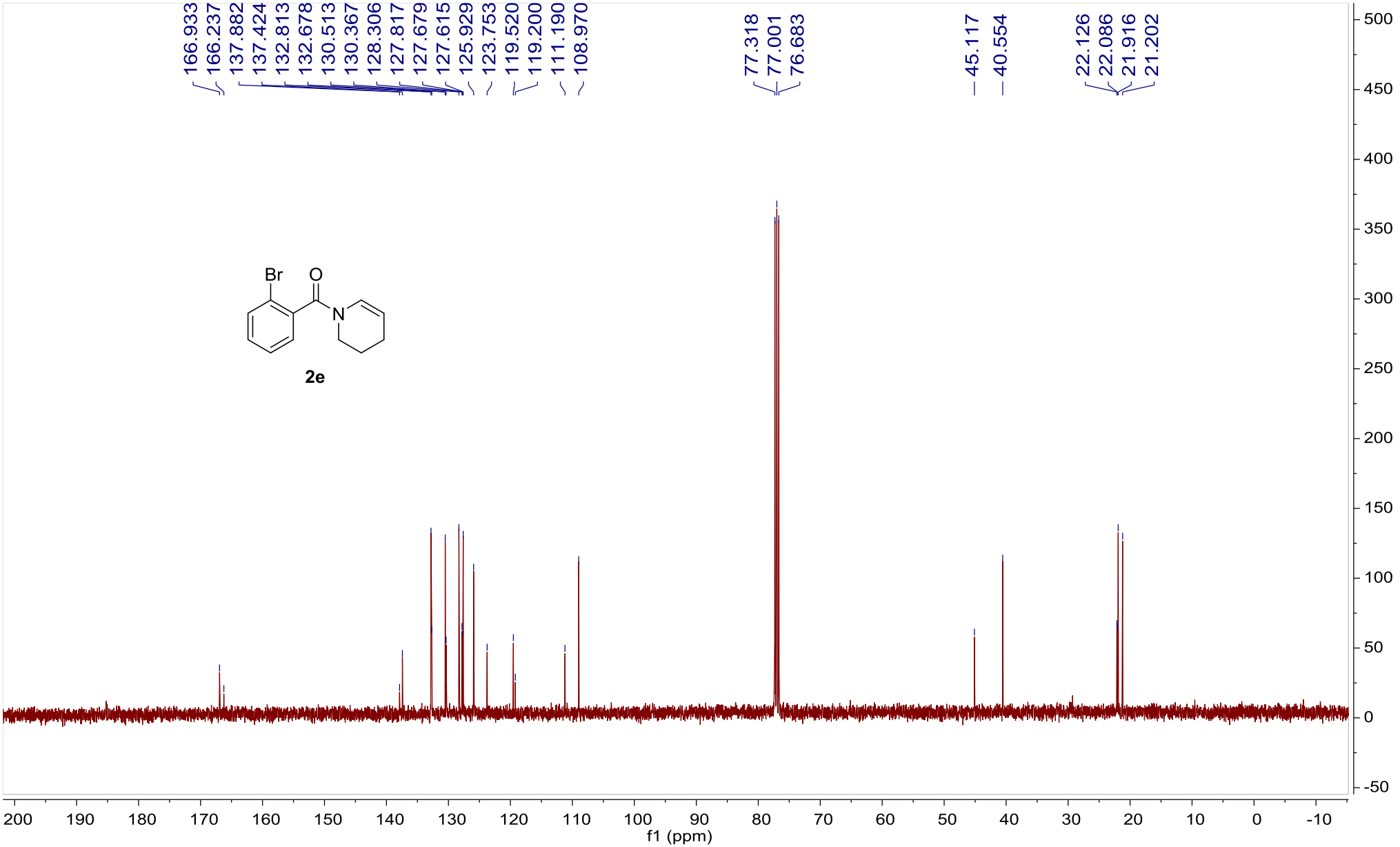
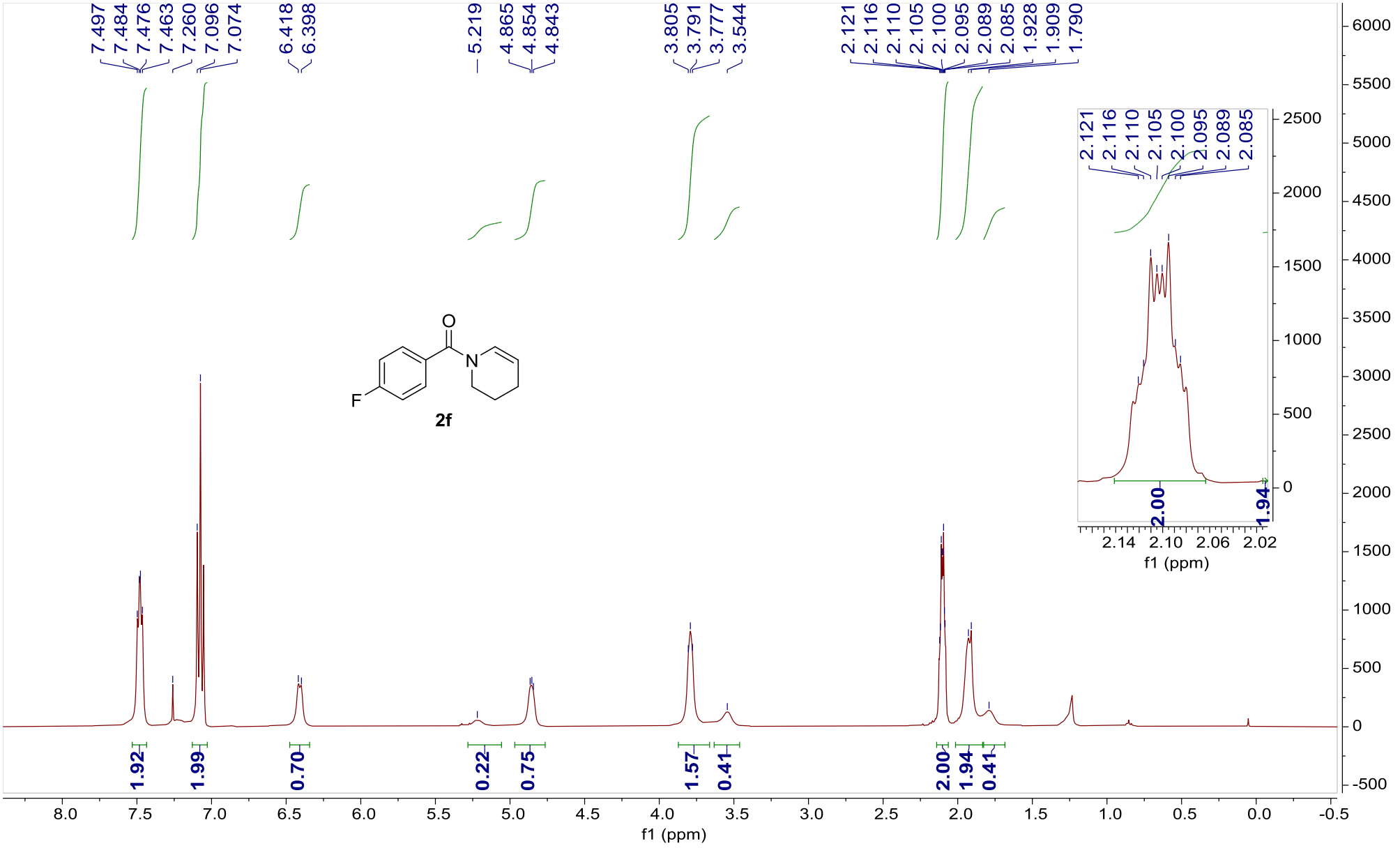
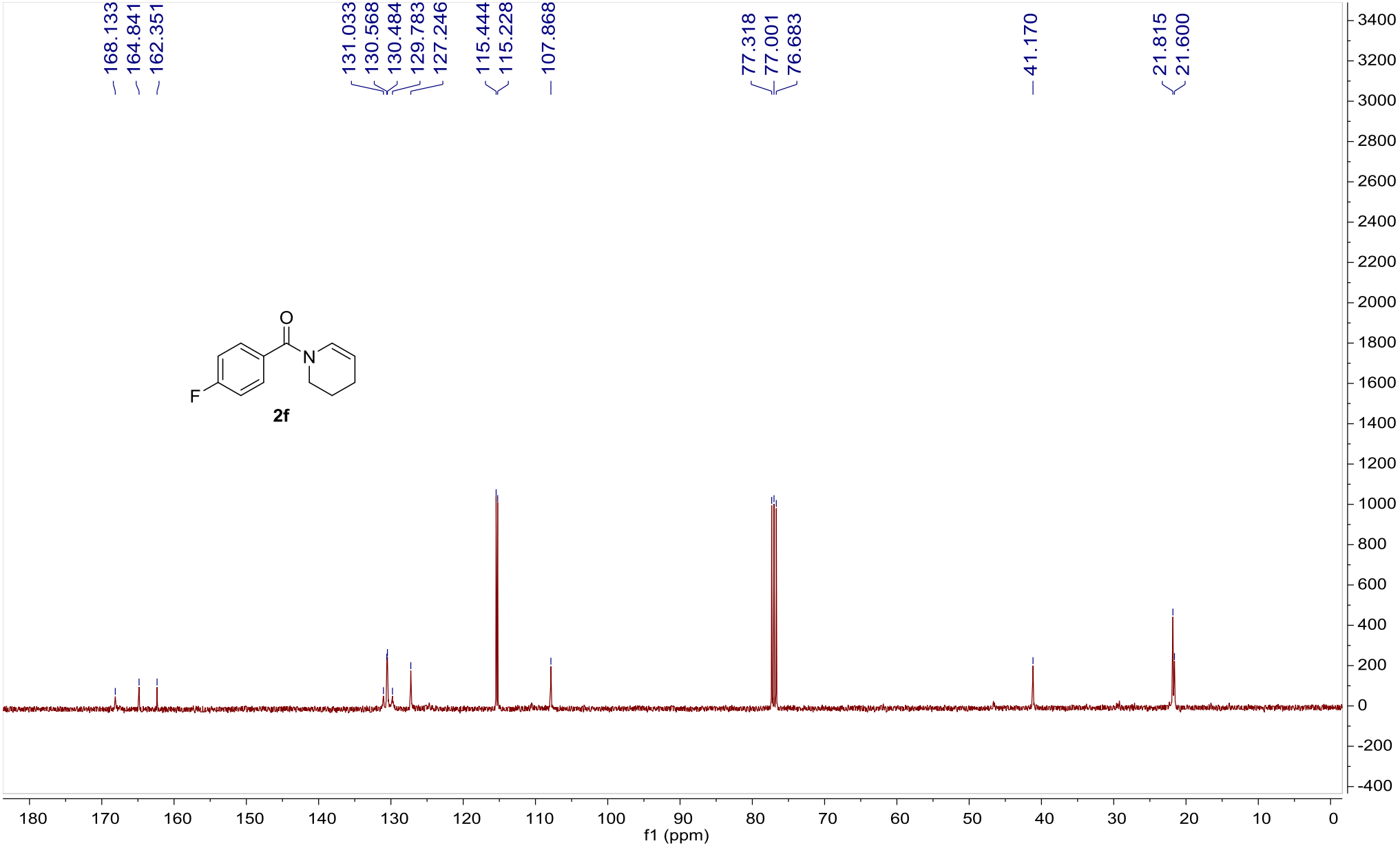
7.517
7.350
7.330
7.260
7.218
6.385
6.365
5.225
4.865
4.854
4.844
3.800
3.785
3.772
3.522
3.505
2.120
2.115
2.110
2.104
2.099
2.094
2.089
2.083
2.079
2.074
2.065
1.936
1.921
1.906
1.776
O
N
Br
2d
2.03
2.00
0.14
0.70
0.22
0.76
1.55
0.46
2.11
1.81
0.58
f1 (ppm)
2.11
2.125
2.085
2.045
f1 (ppm)

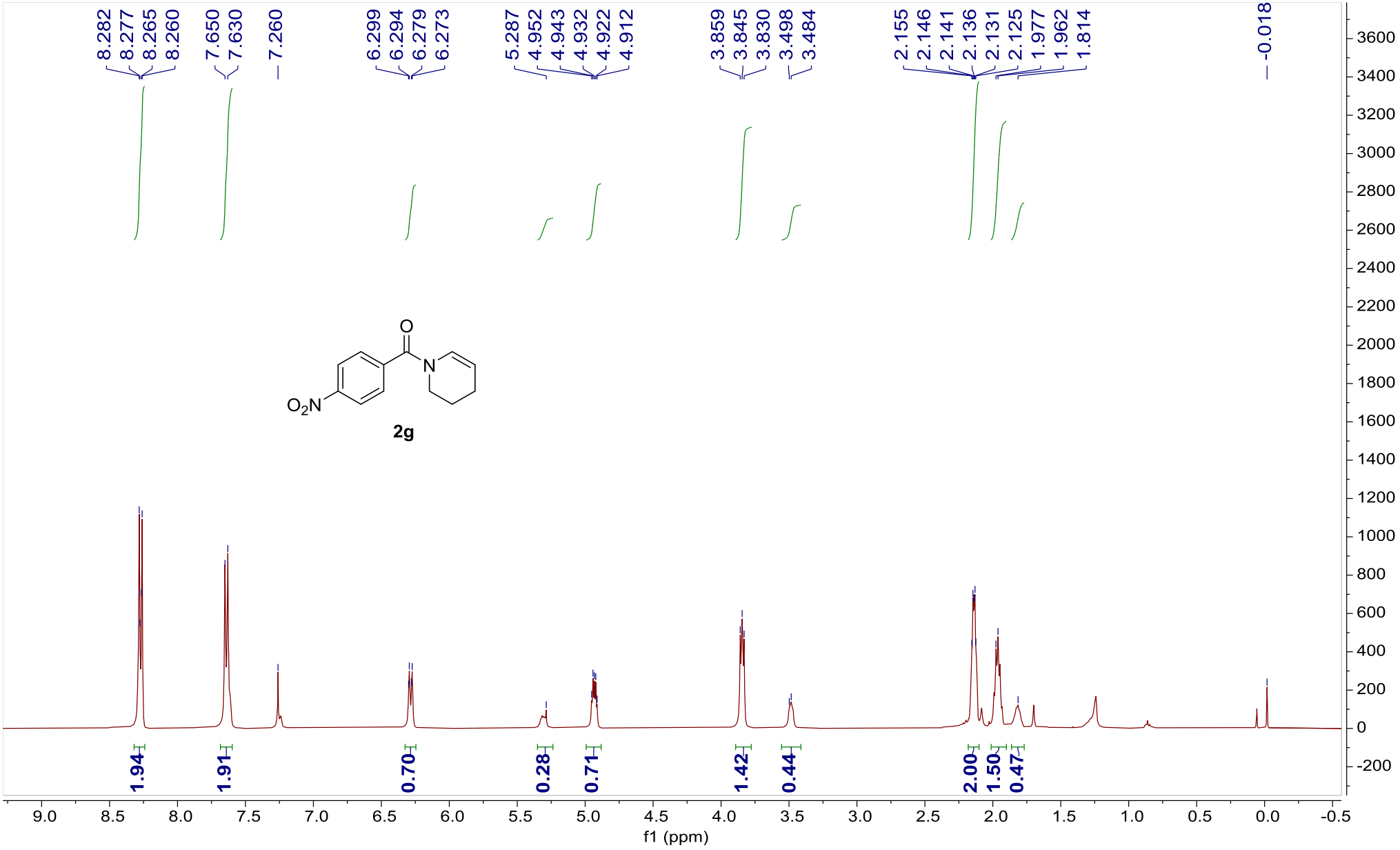

168.041
133.815
131.478
129.819
127.012
124.526
108.102
77.319
77.001
76.683
41.088
21.779
21.519
O
N
Br
2d
f1 (ppm)

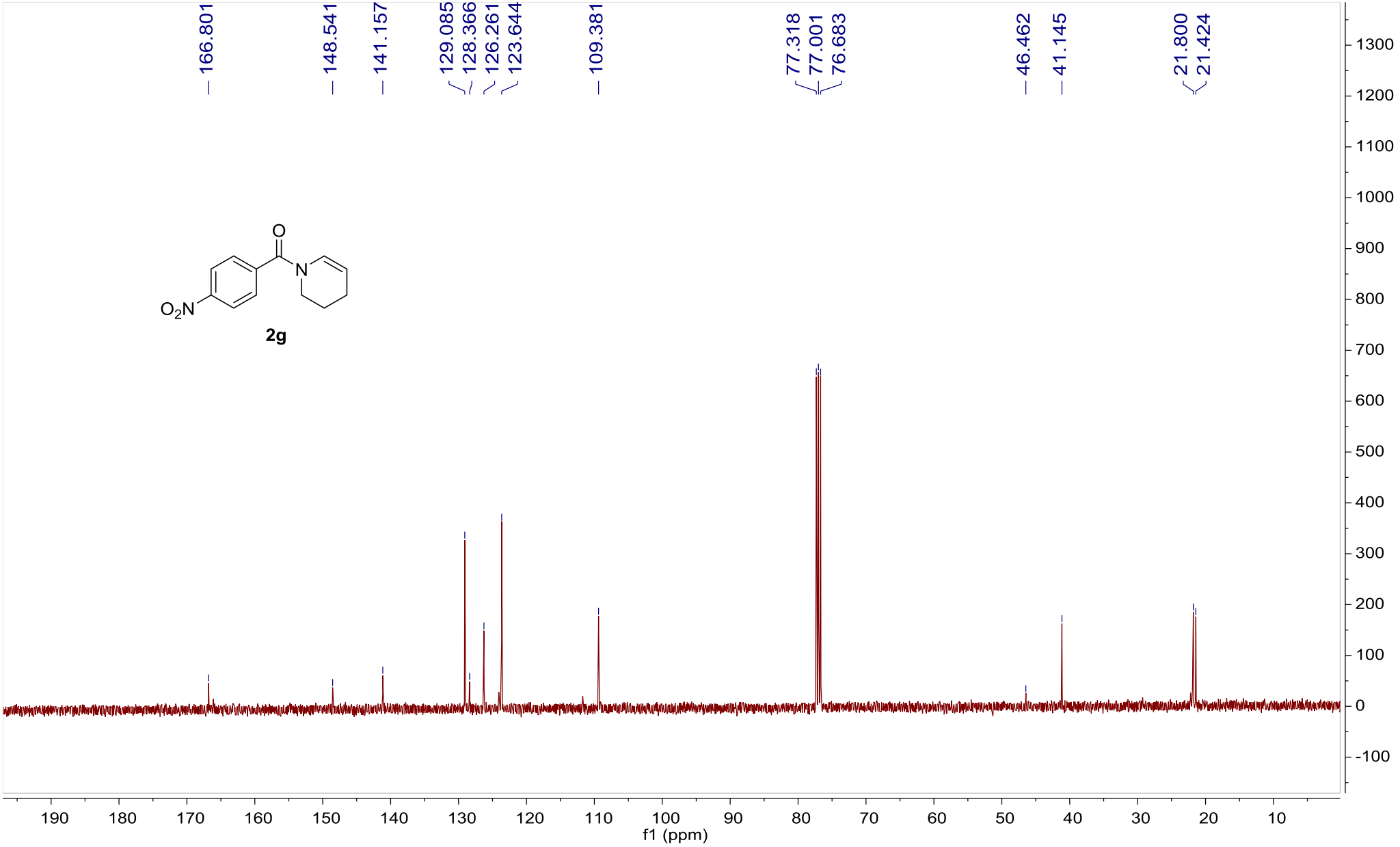

7.609
7.590
7.389
7.370
7.308
7.300
7.285
7.280
6.121
6.100
5.303
5.292
5.281
4.931
4.923
4.912
4.901
4.893
3.955
3.944
3.937
3.926
3.884
3.877
3.865
3.427
3.417
3.407
3.295
3.285
3.275
2.145
2.135
2.129
1.956
1.939
1.860
1.844
Br
O
N
2e
0.93
3.14
0.64
0.28
0.66
1.37
0.60
1.94
1.54
0.58
f1 (ppm)

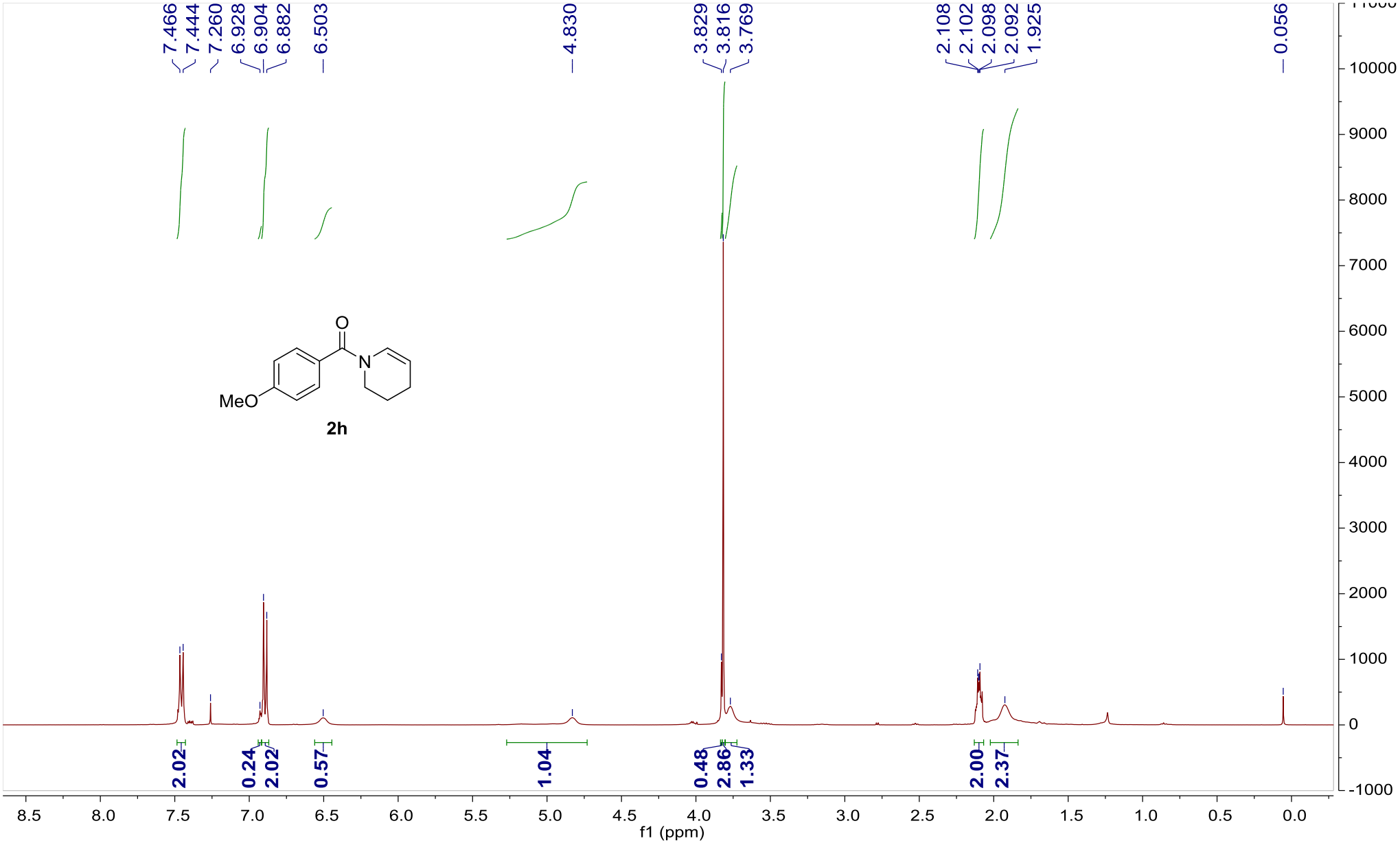

166.933
166.237
137.882
137.424
132.813
132.678
130.513
130.367
128.306
127.817
127.679
127.615
125.929
123.753
119.520
119.200
111.190
108.970
77.318
77.001
76.683
45.117
40.554
22.126
22.086
21.916
21.202
Br
O
N
2e
f1 (ppm)

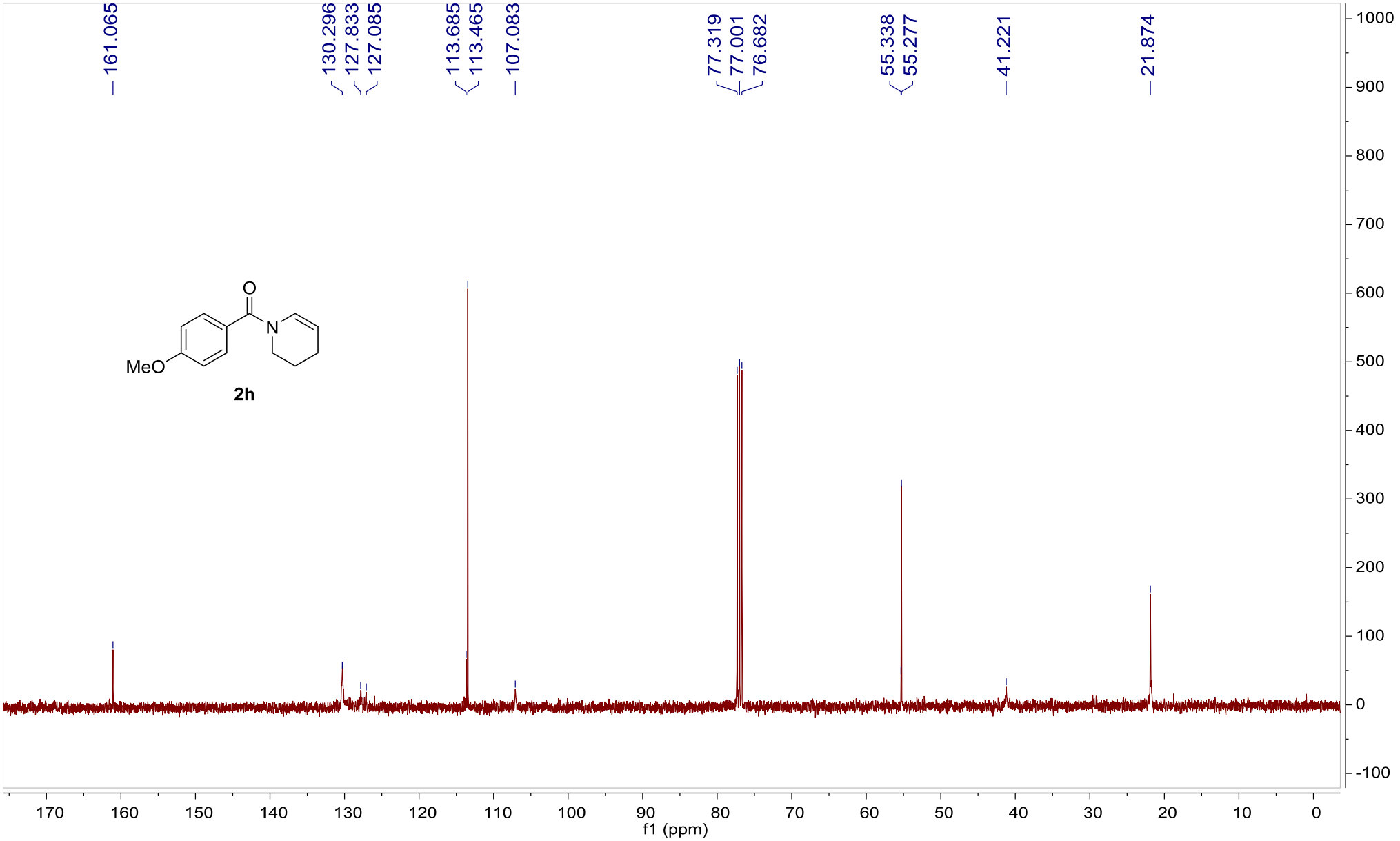

7.497
7.484
7.476
7.463
7.260
7.096
7.074
6.418
6.398
5.219
4.865
4.854
4.843
3.805
3.791
3.777
3.544
2.121
2.116
2.110
2.105
2.100
2.095
2.089
2.085
1.928
1.909
1.790
O
N
F
2f
1.92
1.99
0.70
0.22
0.75
1.57
0.41
2.00
1.94
0.41
f1 (ppm)
2.00
1.94
2.14 2.10 2.06 2.02
f1 (ppm)

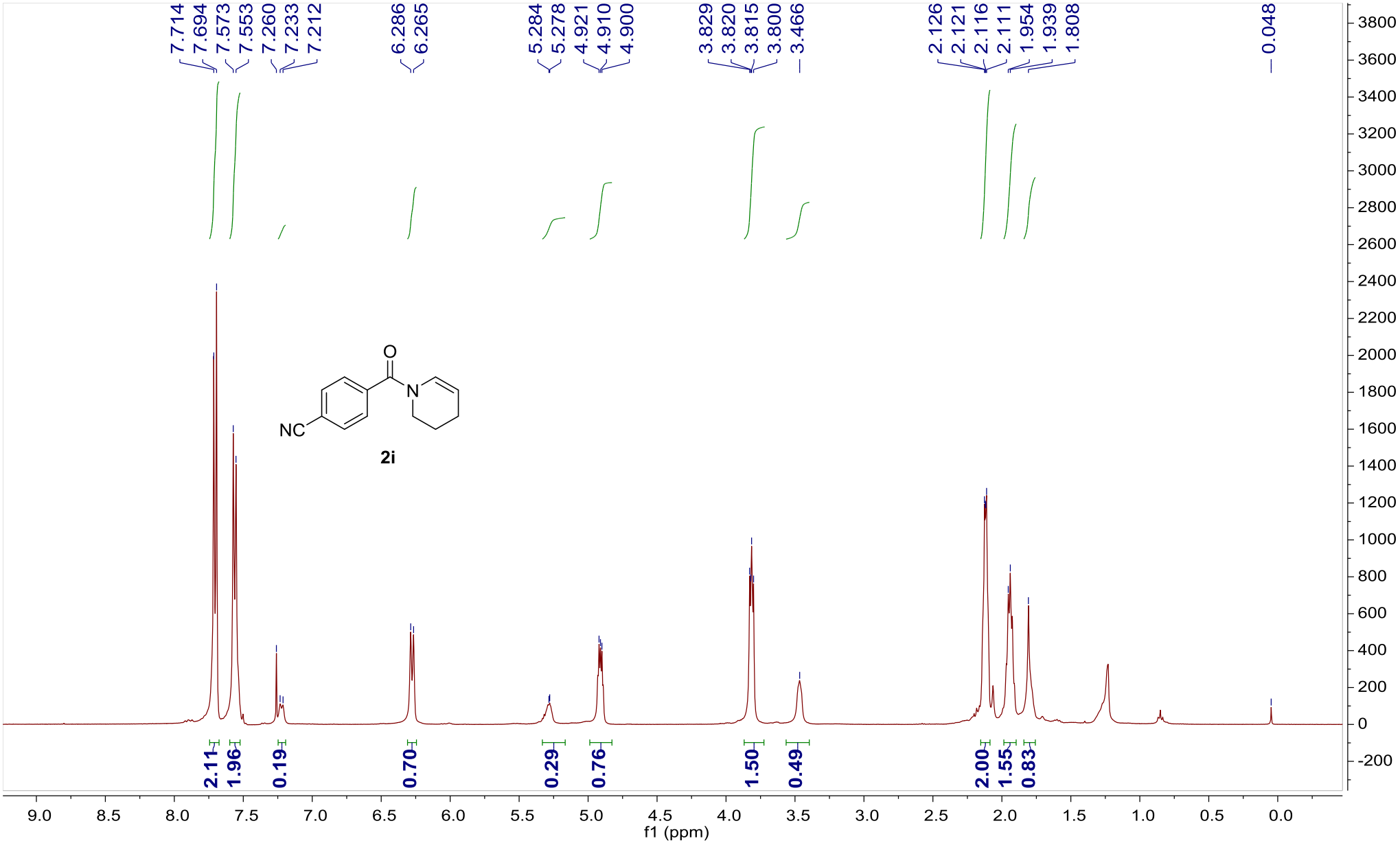

168.133
164.841
162.351
131.033
130.568
130.484
129.783
127.246
115.444
115.228
107.868
77.318
77.001
76.683
41.170
21.815
21.600
O
N
F
2f
f1 (ppm)

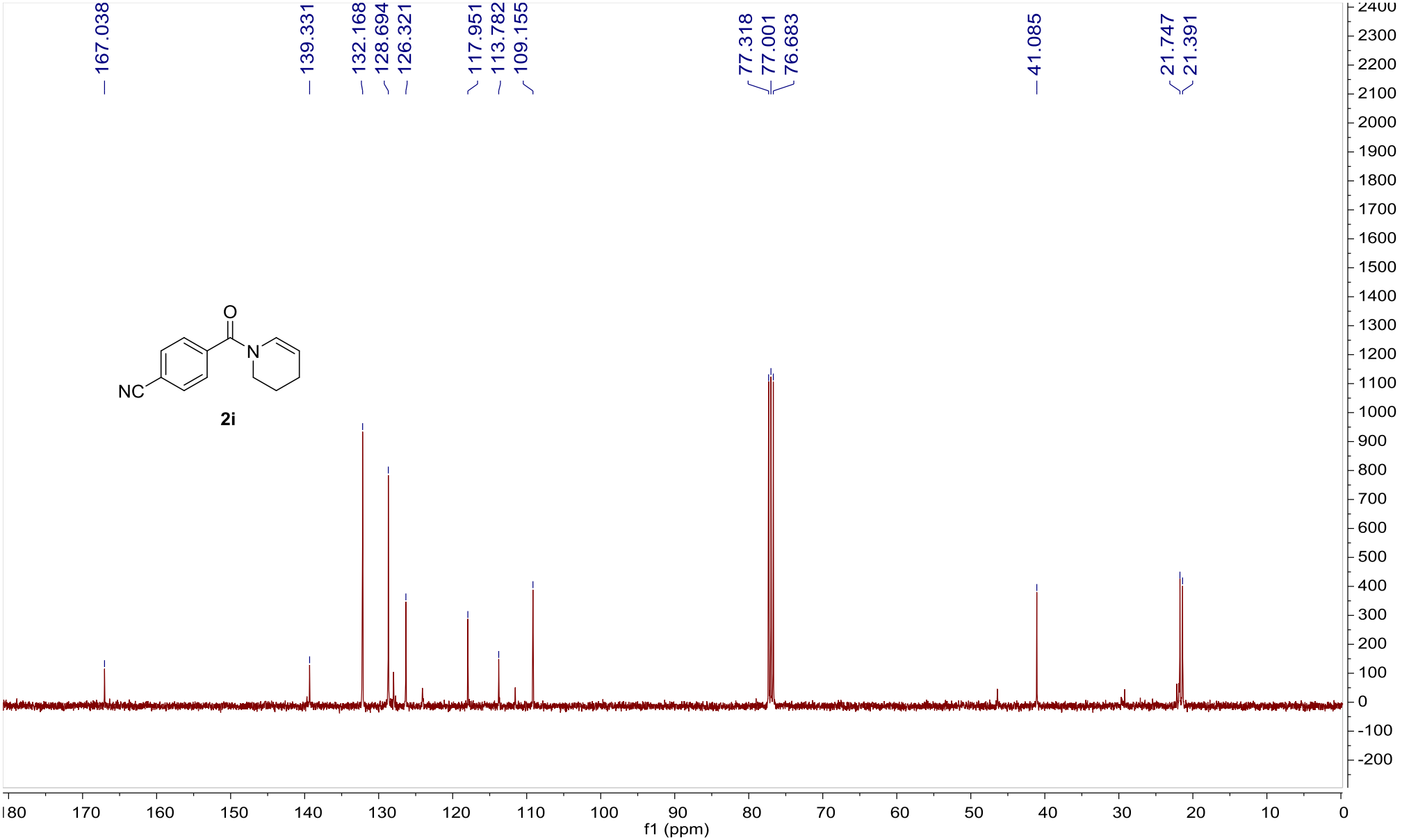

8.282
8.277
8.265
8.260
7.650
7.630
7.260
6.299
6.294
6.279
6.273
5.287
4.952
4.943
4.932
4.922
4.912
3.859
3.845
3.830
3.498
3.484
2.155
2.146
2.141
2.136
2.131
2.125
1.977
1.962
1.814
-0.018
O
N
O2N
2g
1.94
1.91
0.70
0.28
0.71
1.42
0.44
2.00
1.50
0.47
f1 (ppm)

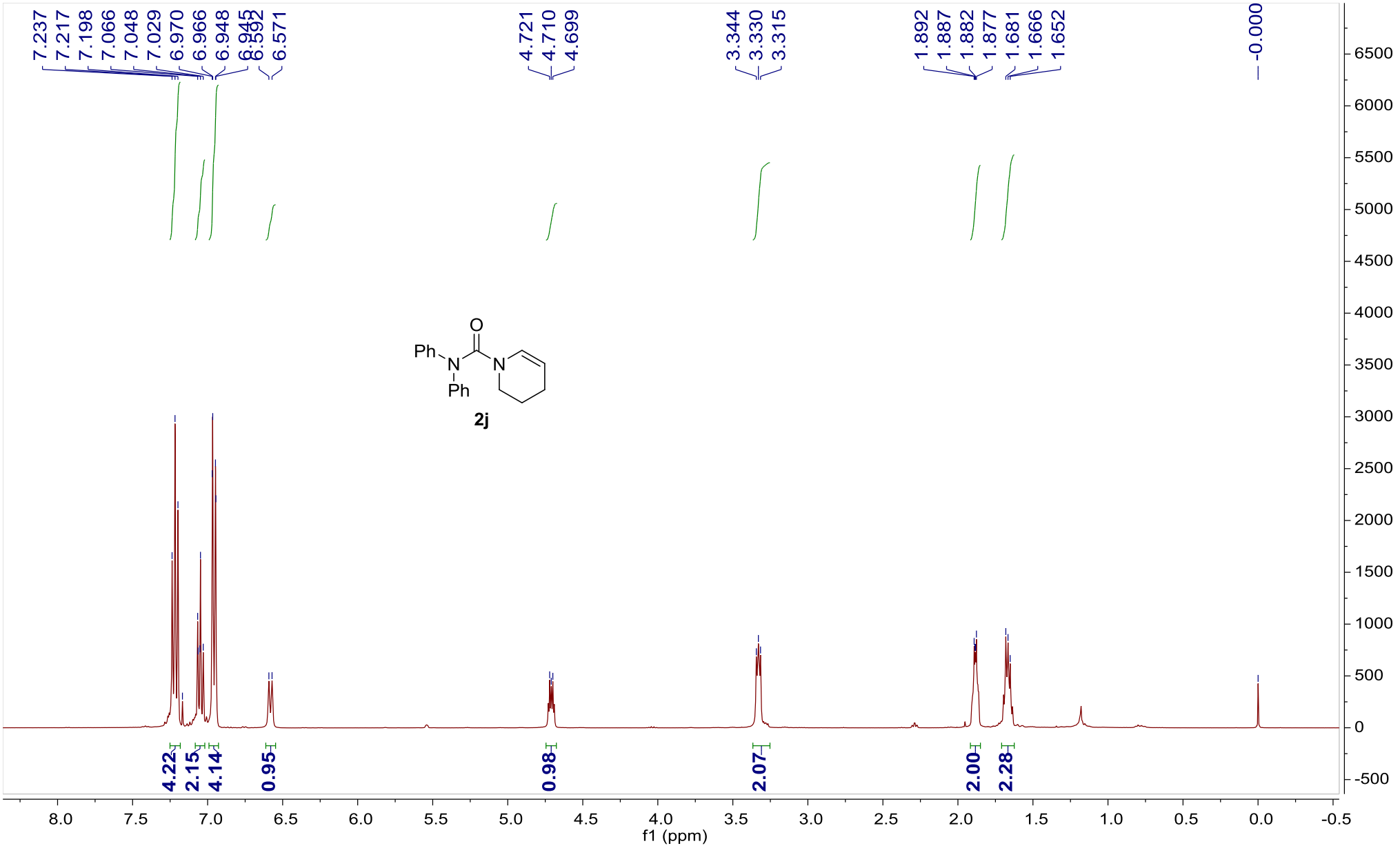

166.801
148.541
141.157
129.085
128.366
126.261
123.644
109.381
77.318
77.001
76.683
46.462
41.145
21.800
21.424
O
N
O2N
2g
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

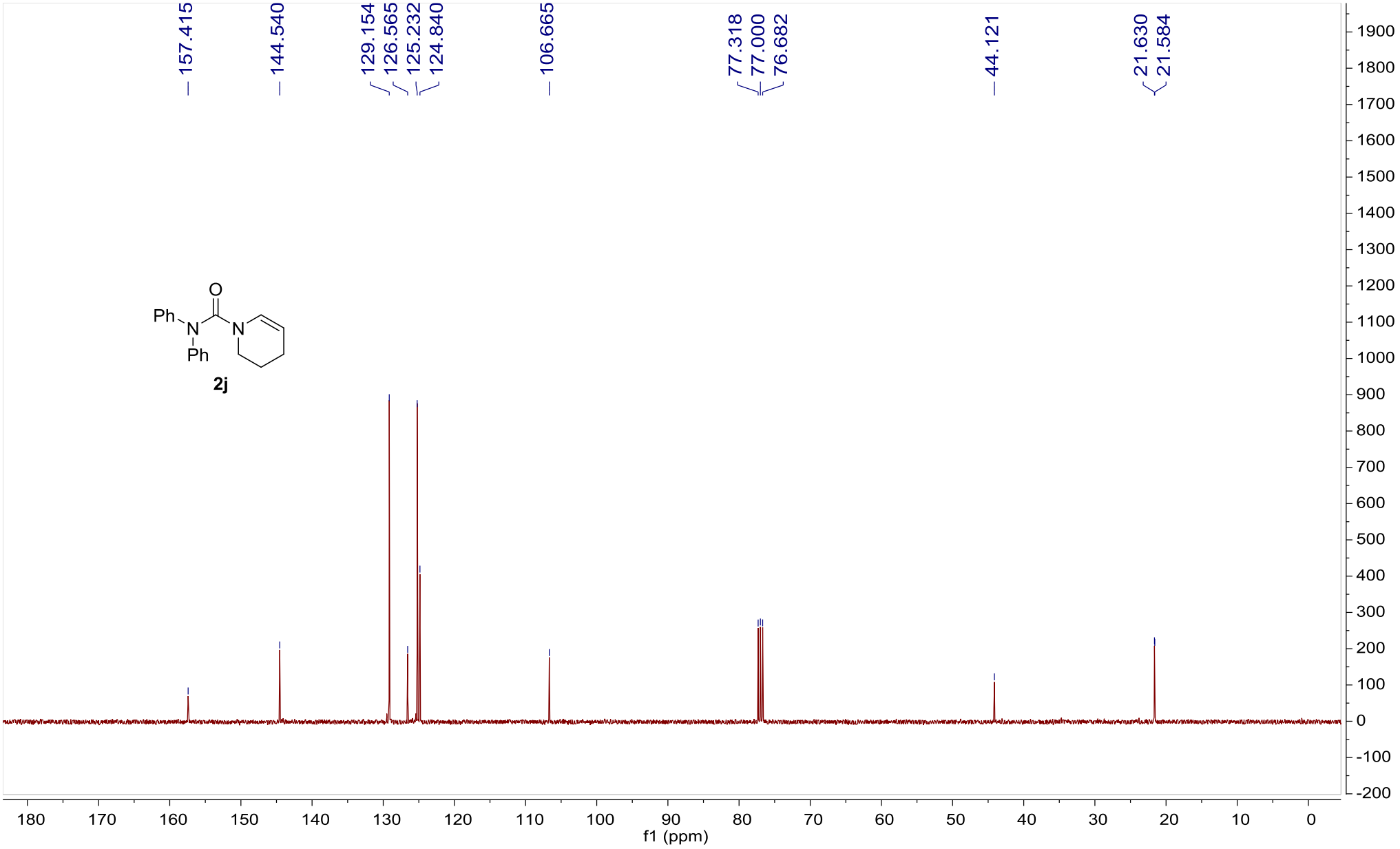

7.466
7.444
7.260
6.928
6.904
6.882
6.503
4.830
3.829
3.816
3.769
2.108
2.102
2.098
2.092
1.925
0.056
O
N
MeO
2h
2.02
0.24
2.02
0.57
1.04
0.48
2.86
1.33
2.00
2.37
f1 (ppm)

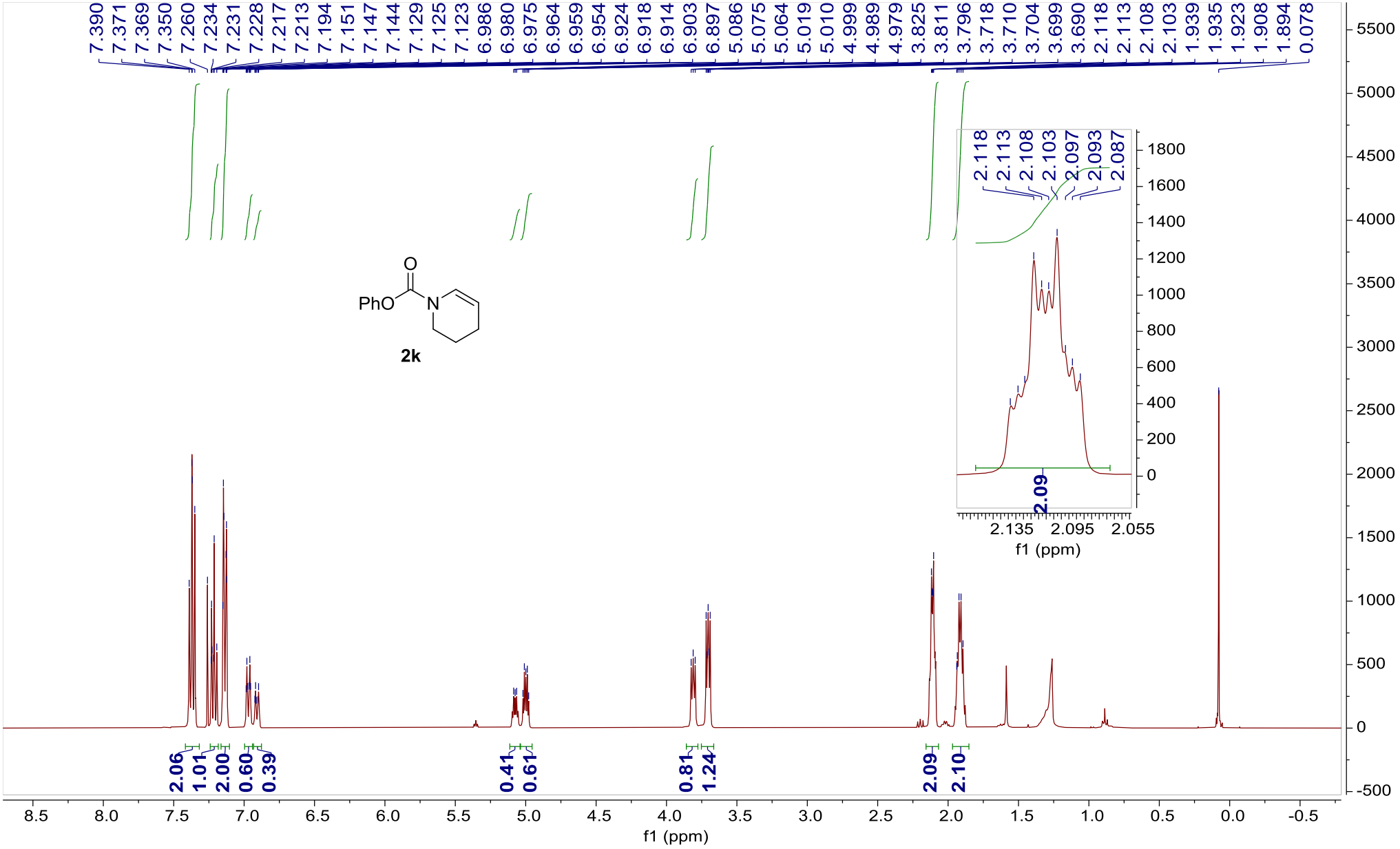

161.065
130.296
127.833
127.085
113.685
113.465
107.083
77.319
77.001
76.682
55.338
55.277
41.221
21.874
O
N
MeO
2h
1000
900
800
700
600
500
400
300
200
100
0
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

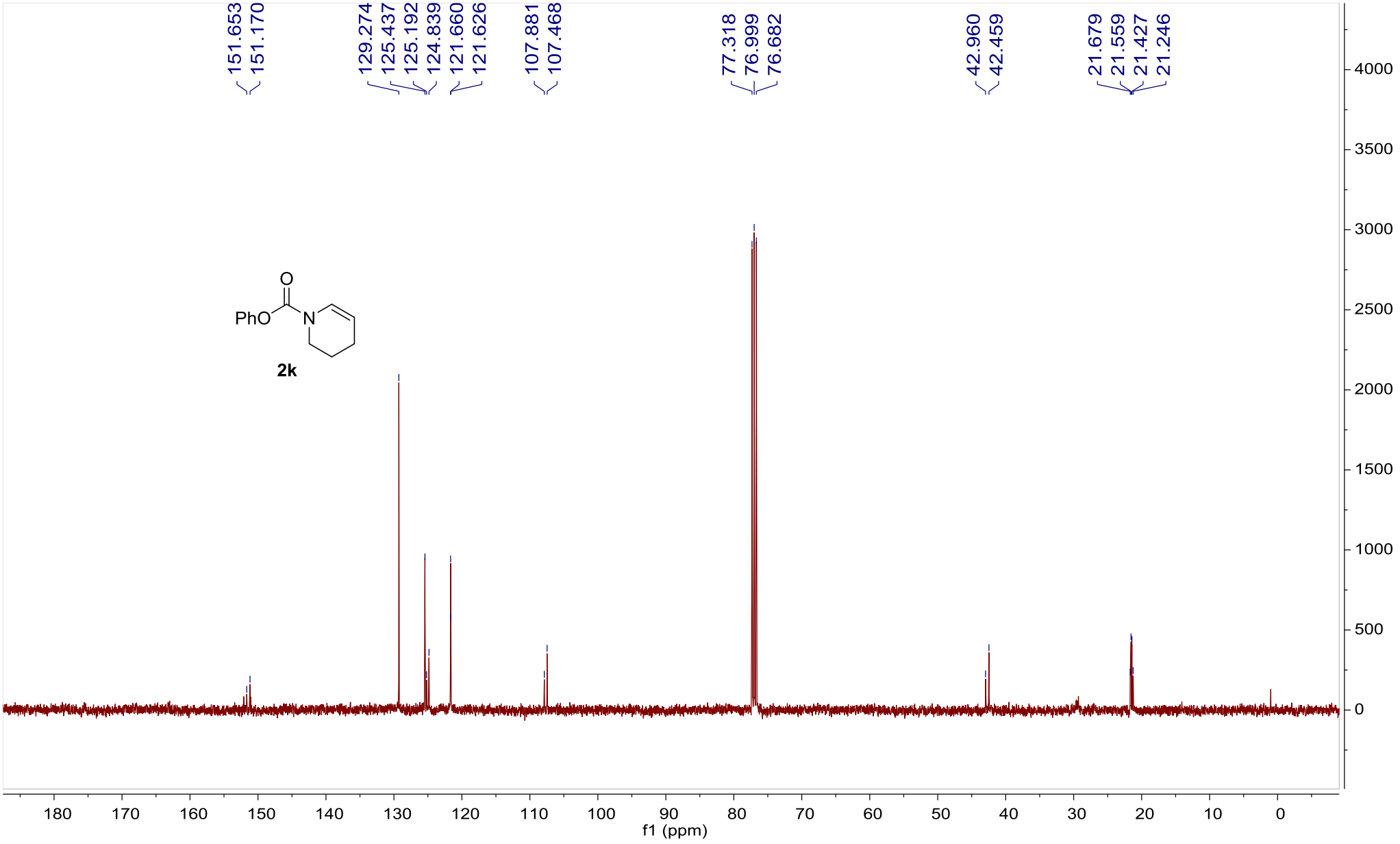

7.714
7.694
7.573
7.553
7.260
7.233
7.212
6.286
6.265
5.284
5.278
4.921
4.910
4.900
3.829
3.820
3.815
3.800
3.466
2.126
2.121
2.116
2.111
1.954
1.939
1.808
0.048
O
N
NC
2i
2.11
1.96
0.19
0.70
0.29
0.76
1.50
0.49
2.00
1.55
0.83
f1 (ppm)


167.038
139.331
132.168
128.694
126.321
117.951
113.782
109.155
77.318
77.001
76.683
41.085
21.747
21.391
O
N
NC
2i
f1 (ppm)


7.237
7.217
7.198
7.066
7.048
7.029
6.970
6.966
6.948
6.945
6.592
6.571
4.721
4.710
4.699
3.344
3.330
3.315
1.892
1.887
1.882
1.877
1.681
1.666
1.652
-0.000
Ph
N
O
N
Ph
2j
4.22
2.15
4.14
0.95
0.98
2.07
2.00
2.28
f1 (ppm)


157.415
144.540
129.154
126.565
125.232
124.840
106.665
77.318
77.000
76.682
44.121
21.630
21.584
Ph
N
O
N
Ph
2j
f1 (ppm)


7.390
7.371
7.369
7.350
7.260
7.234
7.231
7.228
7.217
7.213
7.194
7.151
7.147
7.144
7.129
7.125
7.123
6.986
6.980
6.975
6.964
6.959
6.954
6.924
6.918
6.914
6.903
6.897
5.086
5.075
5.064
5.019
5.010
4.999
4.989
4.979
3.825
3.811
3.796
3.718
3.710
3.704
3.699
3.690
2.118
2.113
2.108
2.103
2.097
2.093
2.087
0.078
PhO
O
N
2k
2.09
2.135
2.095
2.055
f1 (ppm)
2.06
1.01
2.00
0.60
0.39
0.41
0.61
0.81
1.24
2.09
2.10
f1 (ppm)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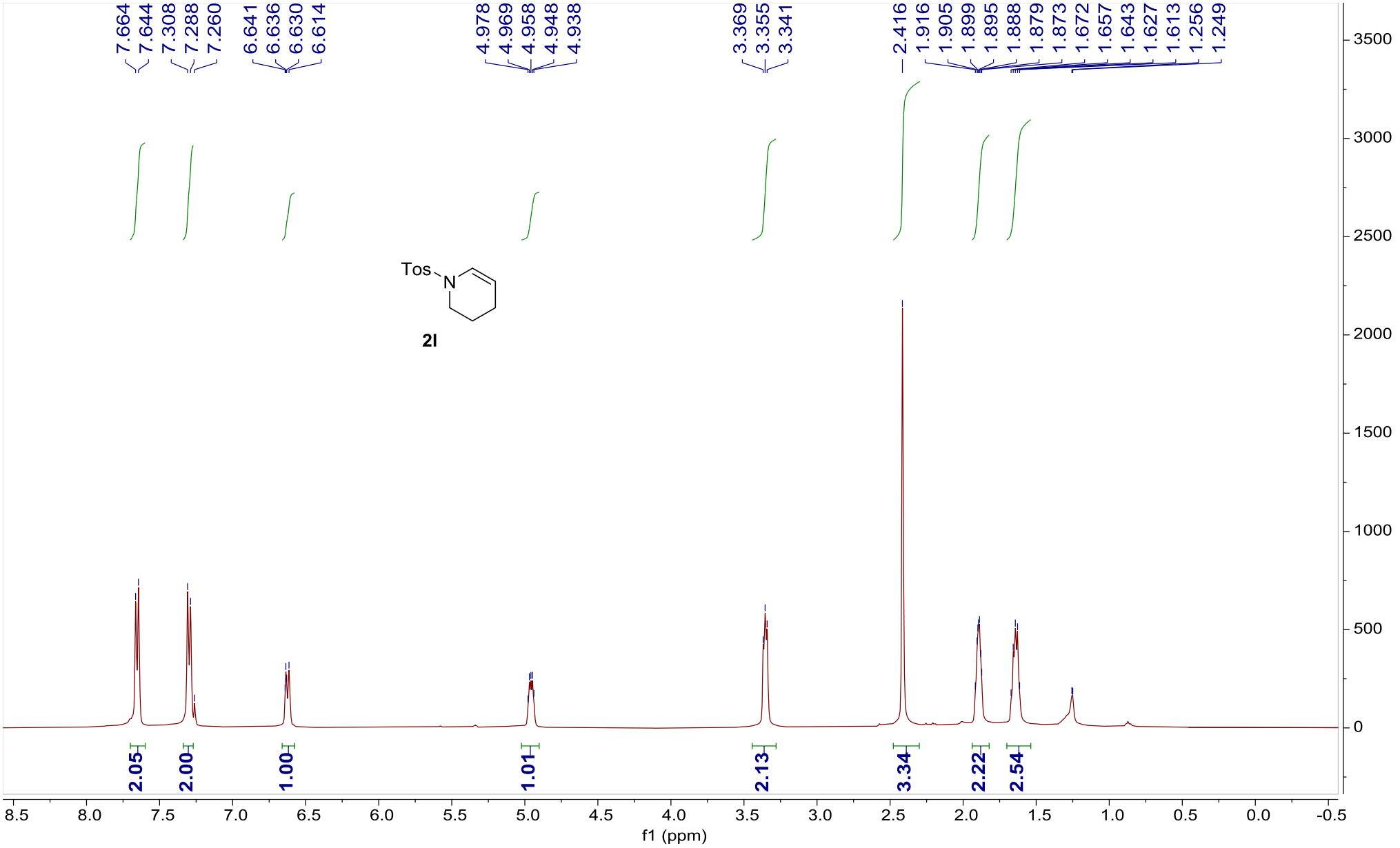
151.170
129.274
125.437
125.192
124.839
121.660
121.626
107.881
107.468
77.318
76.999
76.682
42.960
42.459
21.679
21.559
21.427
21.246
O
PhO
N
2k
4000
3500
3000
2500
2000
1500
1000
500
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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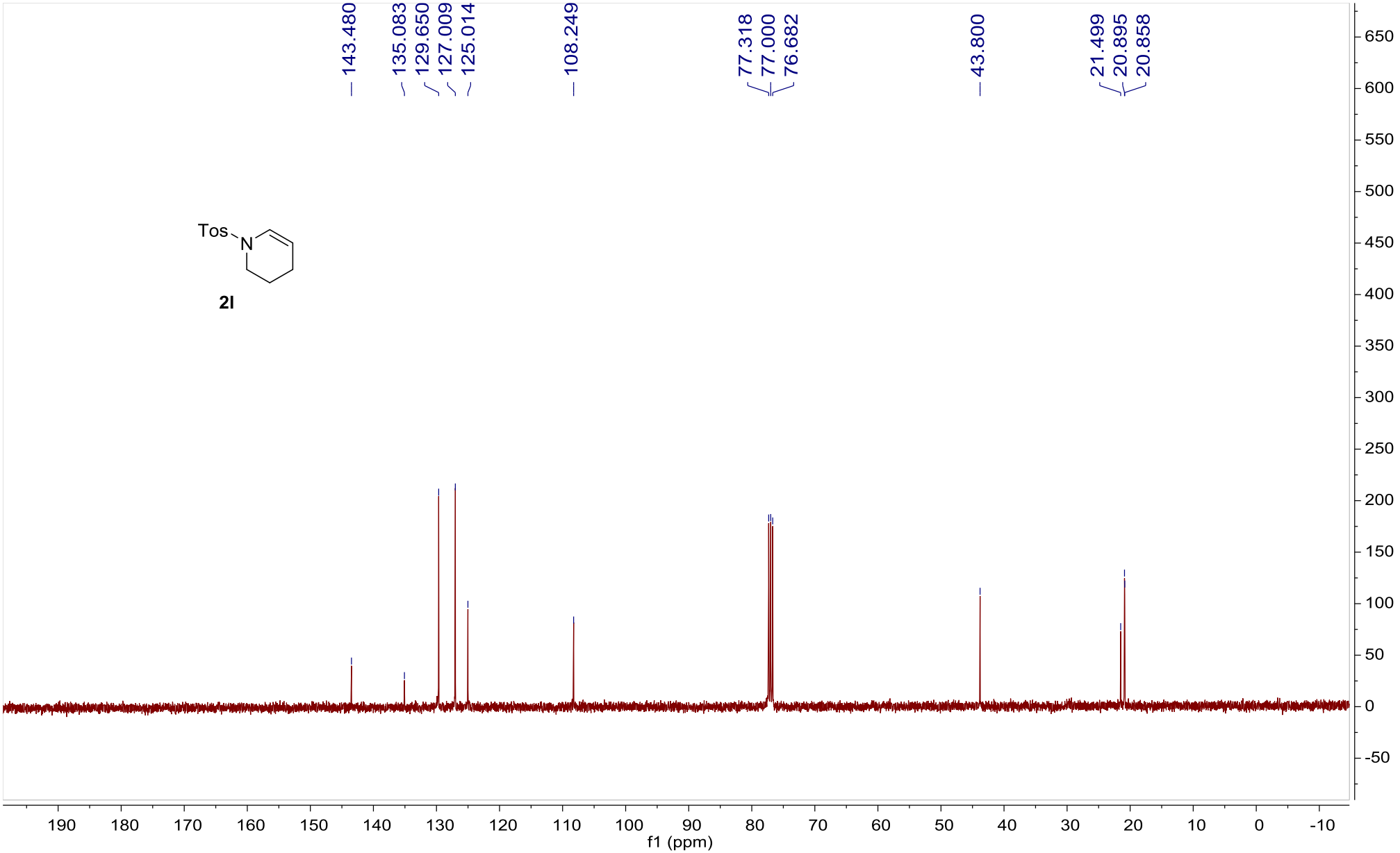
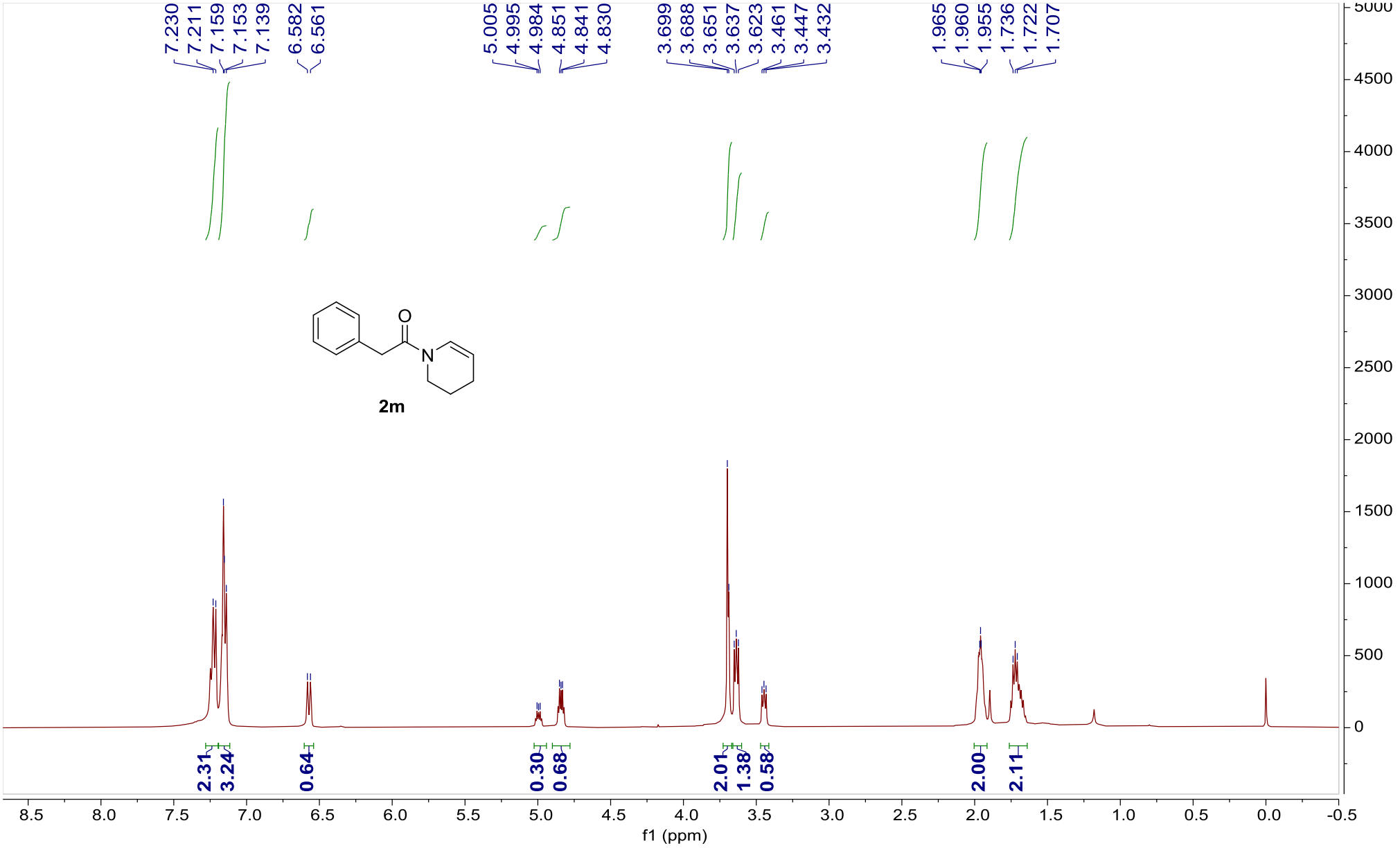
7.308
7.288
7.260
6.641
6.636
6.630
6.614
4.978
4.969
4.958
4.948
4.938
3.369
3.355
3.341
2.416
1.916
1.905
1.899
1.895
1.888
1.879
1.873
1.672
1.657
1.643
1.627
1.613
1.256
1.249
Tos
N
2l
2.05
2.00
1.00
1.01
2.13
3.34
2.22
2.54
f1 (ppm)


143.480
135.083
129.650
127.009
125.014
108.249
77.318
77.000
76.682
43.800
21.499
20.895
20.858
Tos
N
2l
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.211
7.159
7.153
7.139
6.582
6.561
5.005
4.995
4.984
4.851
4.841
4.830
3.699
3.688
3.651
3.637
3.623
3.461
3.447
3.432
1.965
1.960
1.955
1.736
1.722
1.707
O
N
2m
2.31
3.24
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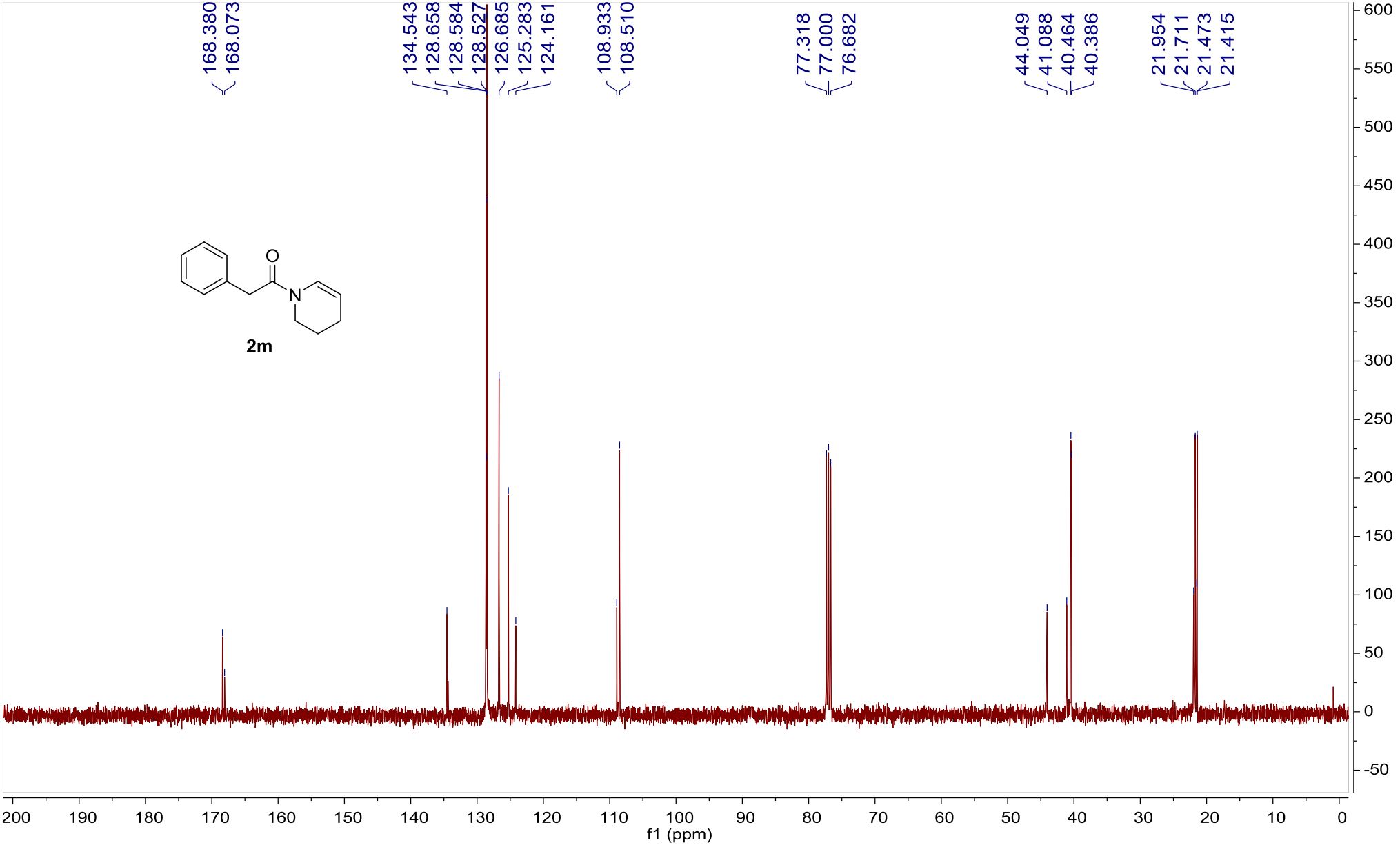
0.30
0.68
2.01
1.38
0.58
2.00
2.11
f1 (ppm)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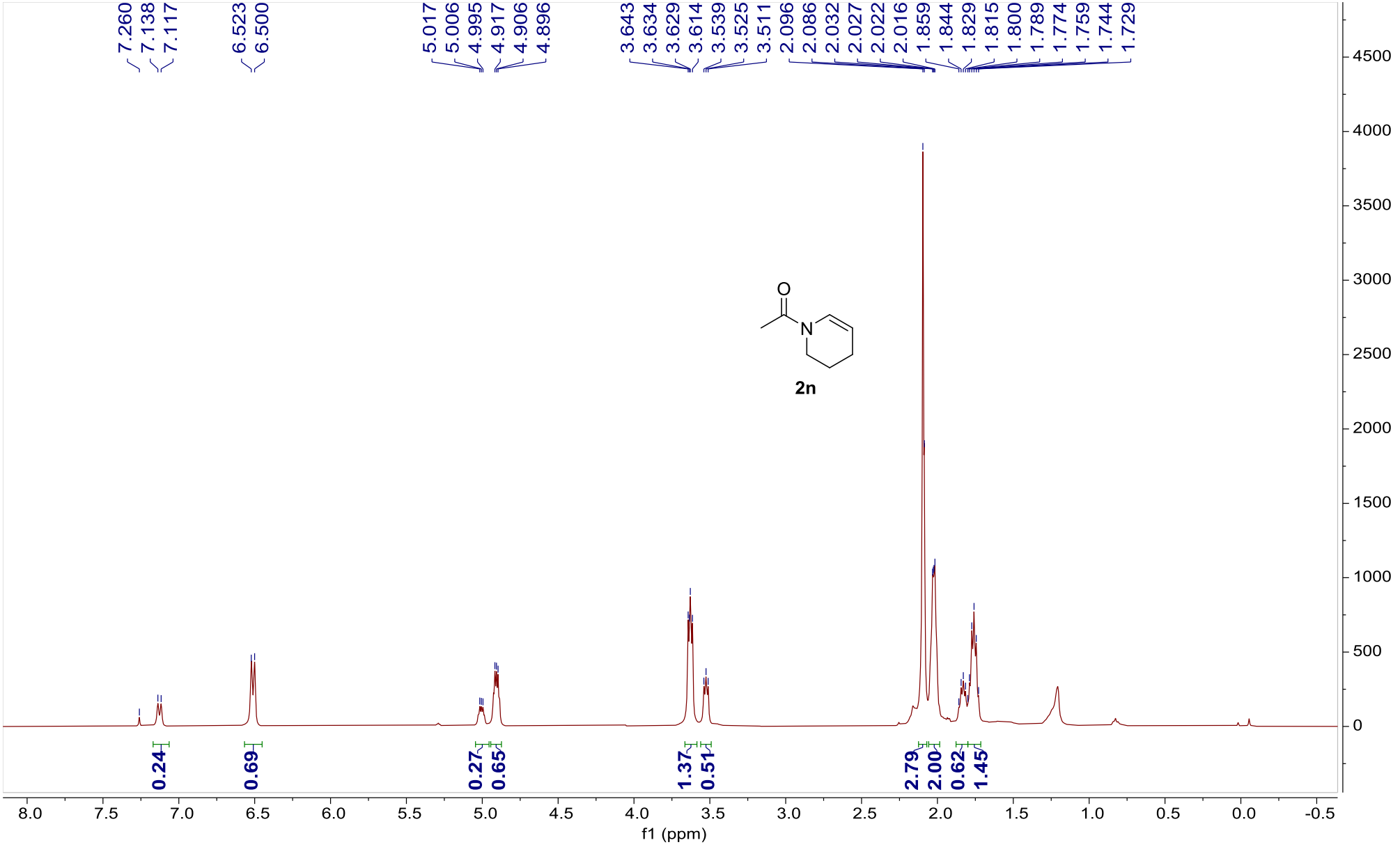
134.543
128.658
128.584
128.527
126.685
125.283
124.161
108.933
108.510
77.318
77.000
76.682
44.049
41.088
40.464
40.386
21.954
21.711
21.473
21.415
O
N
2m
f1 (ppm)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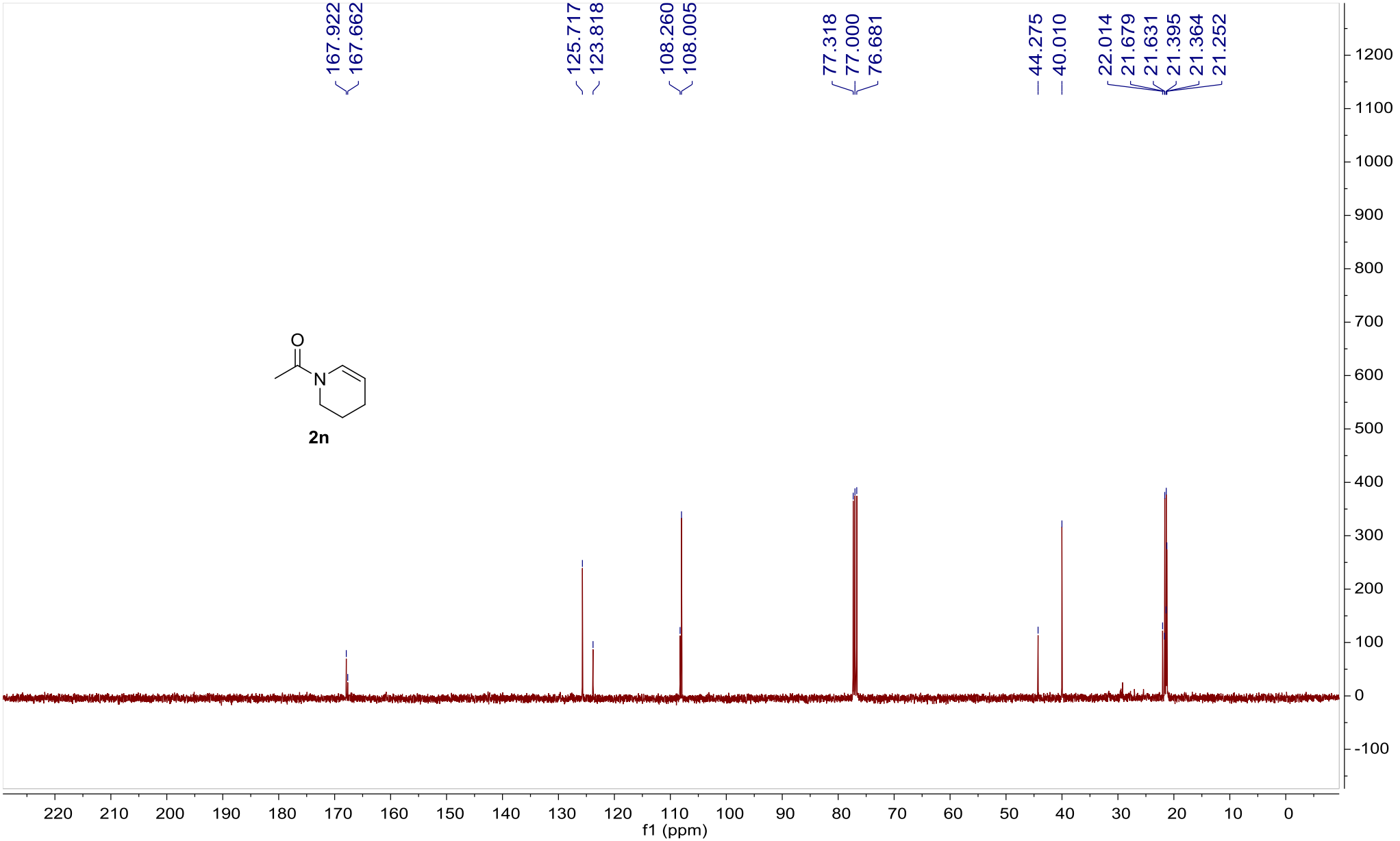
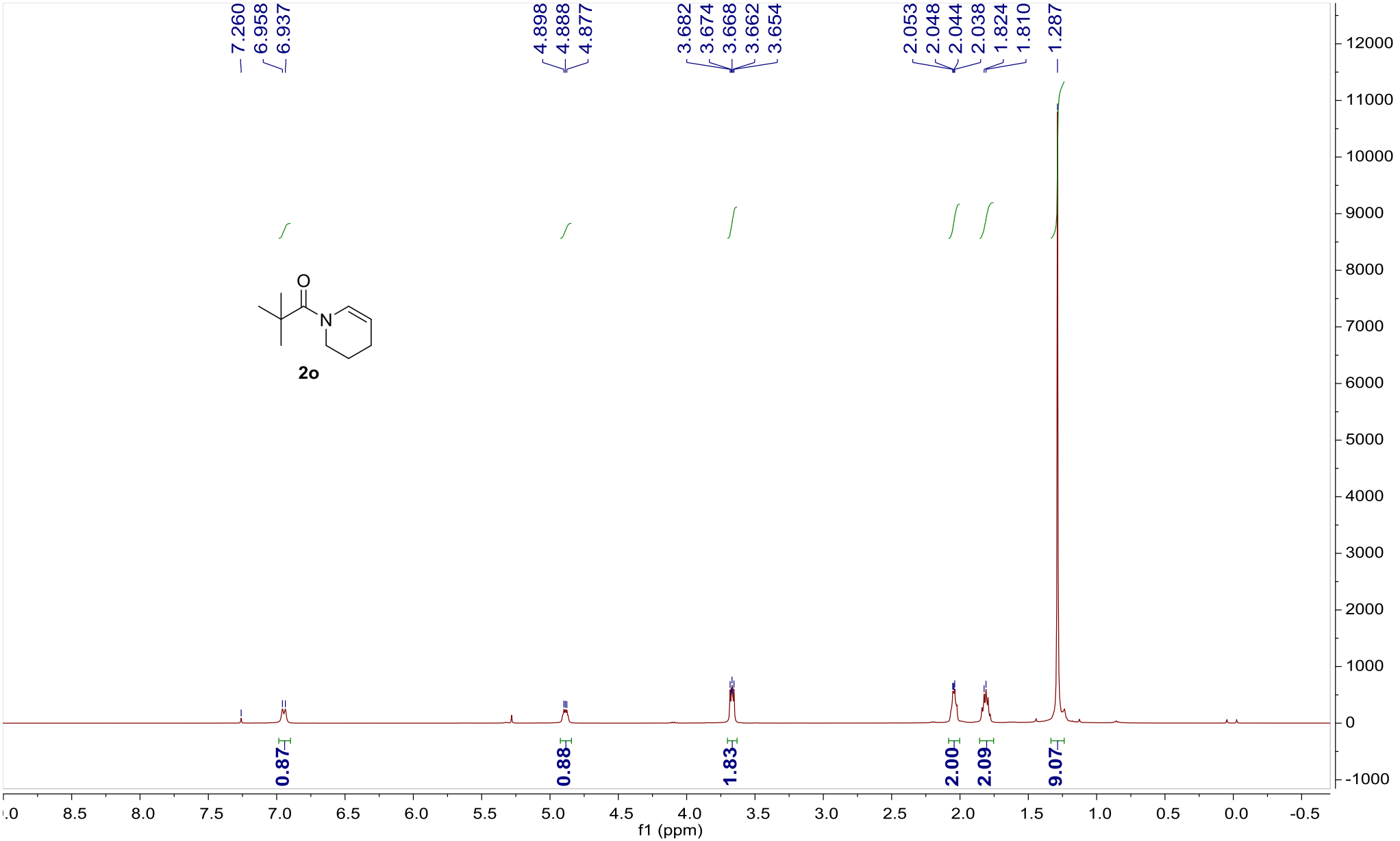
7.138
7.117
6.523
6.500
5.017
5.006
4.995
4.917
4.906
4.896
3.643
3.634
3.629
3.614
3.539
3.525
3.511
2.096
2.086
2.032
2.027
2.022
2.016
1.859
1.844
1.829
1.815
1.800
1.789
1.774
1.759
1.744
1.729
O
N
2n
0.24
0.69
0.27
0.65
1.37
0.51
2.79
2.00
0.62
1.45
f1 (ppm)


167.922
167.662
125.717
123.818
108.260
108.005
77.318
77.000
76.681
44.275
40.010
22.014
21.679
21.631
21.395
21.364
21.252
O
N
2n
f1 (ppm)


7.260
6.958
6.937
4.898
4.888
4.877
3.682
3.674
3.668
3.662
3.654
2.053
2.048
2.044
2.038
1.824
1.810
1.287
O
N
2o
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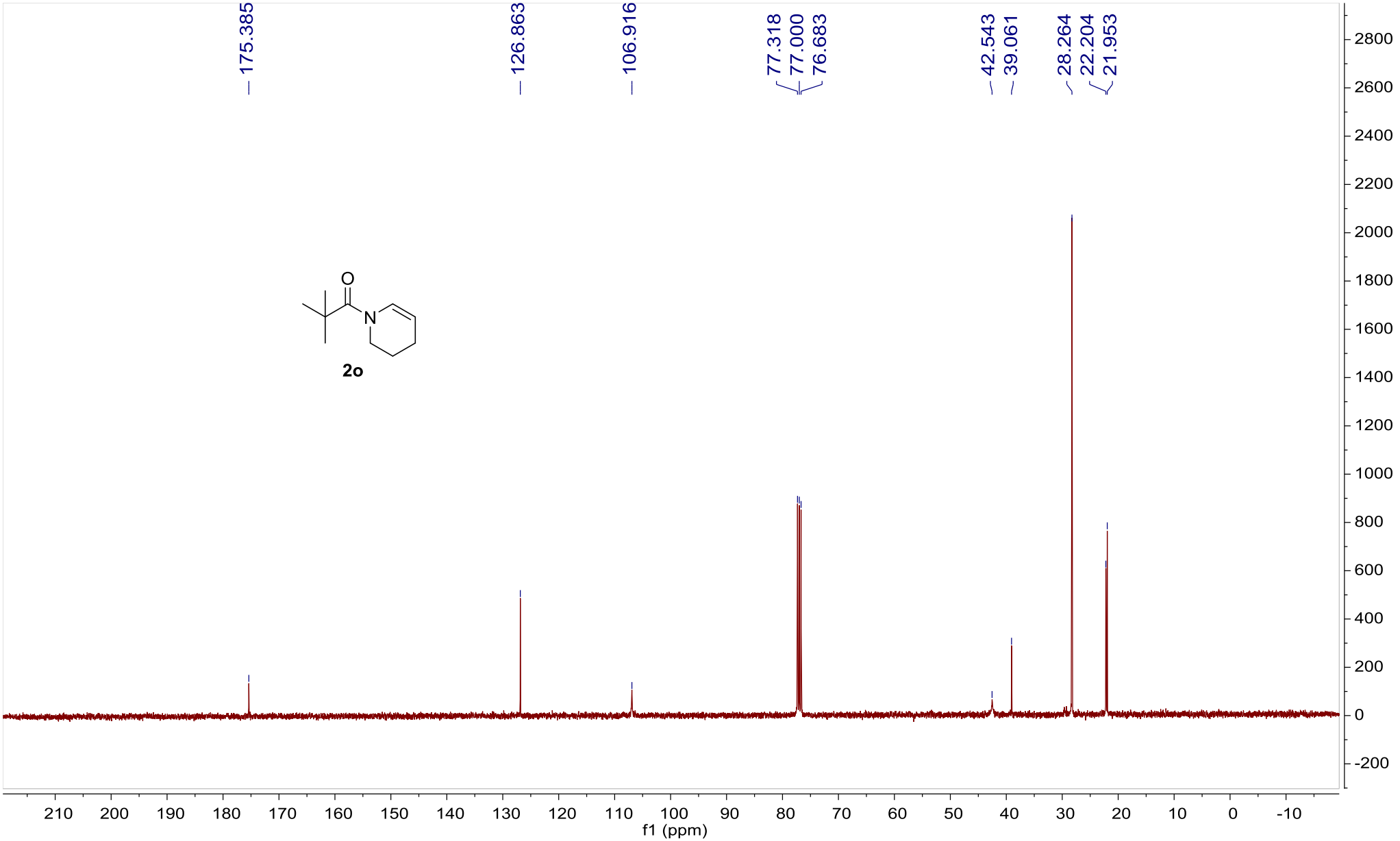
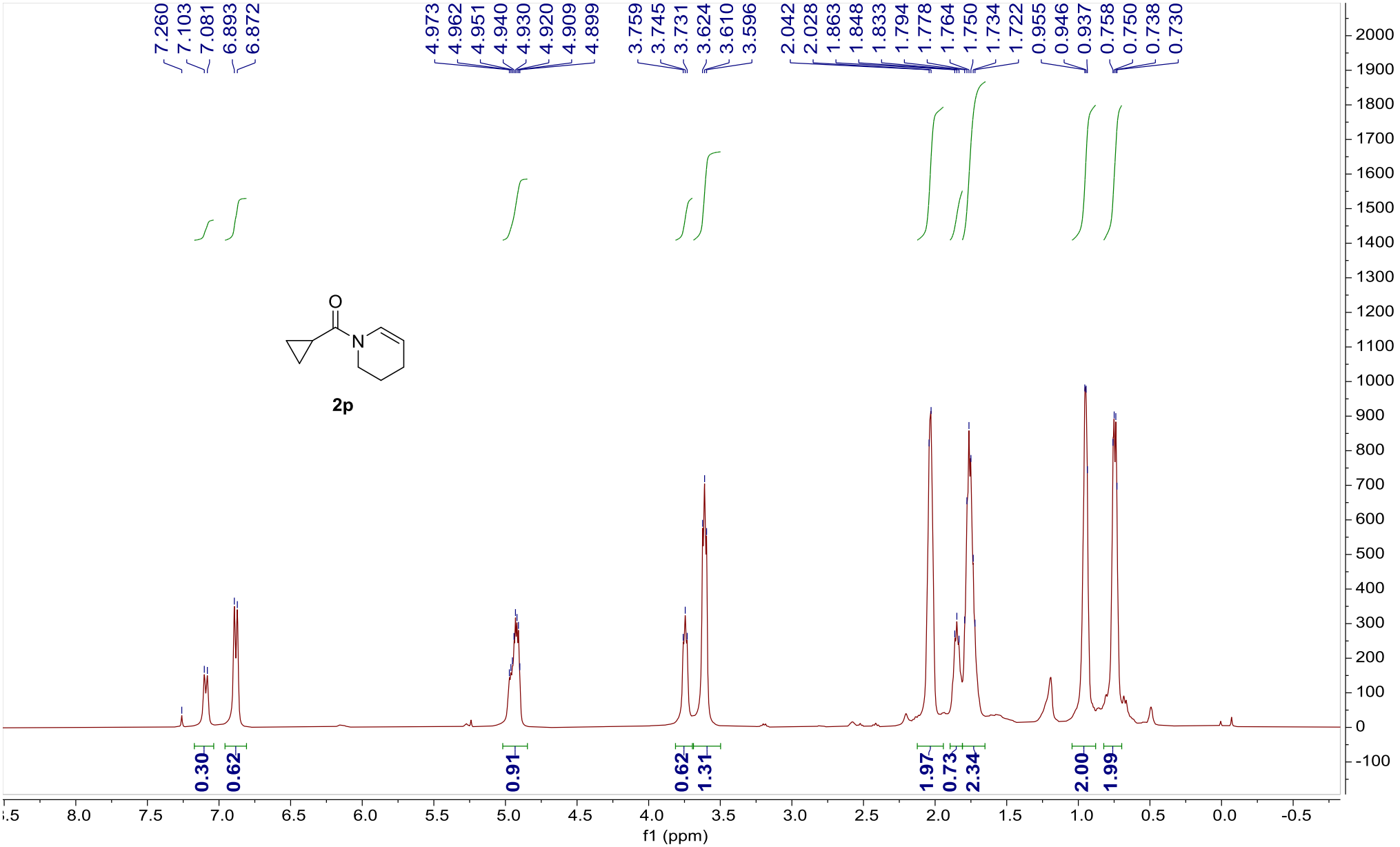
0.88
1.83
2.00
2.09
9.07
f1 (ppm)


175.385
126.863
106.916
77.318
77.000
76.683
42.543
39.061
28.264
22.204
21.953
O
N
2o
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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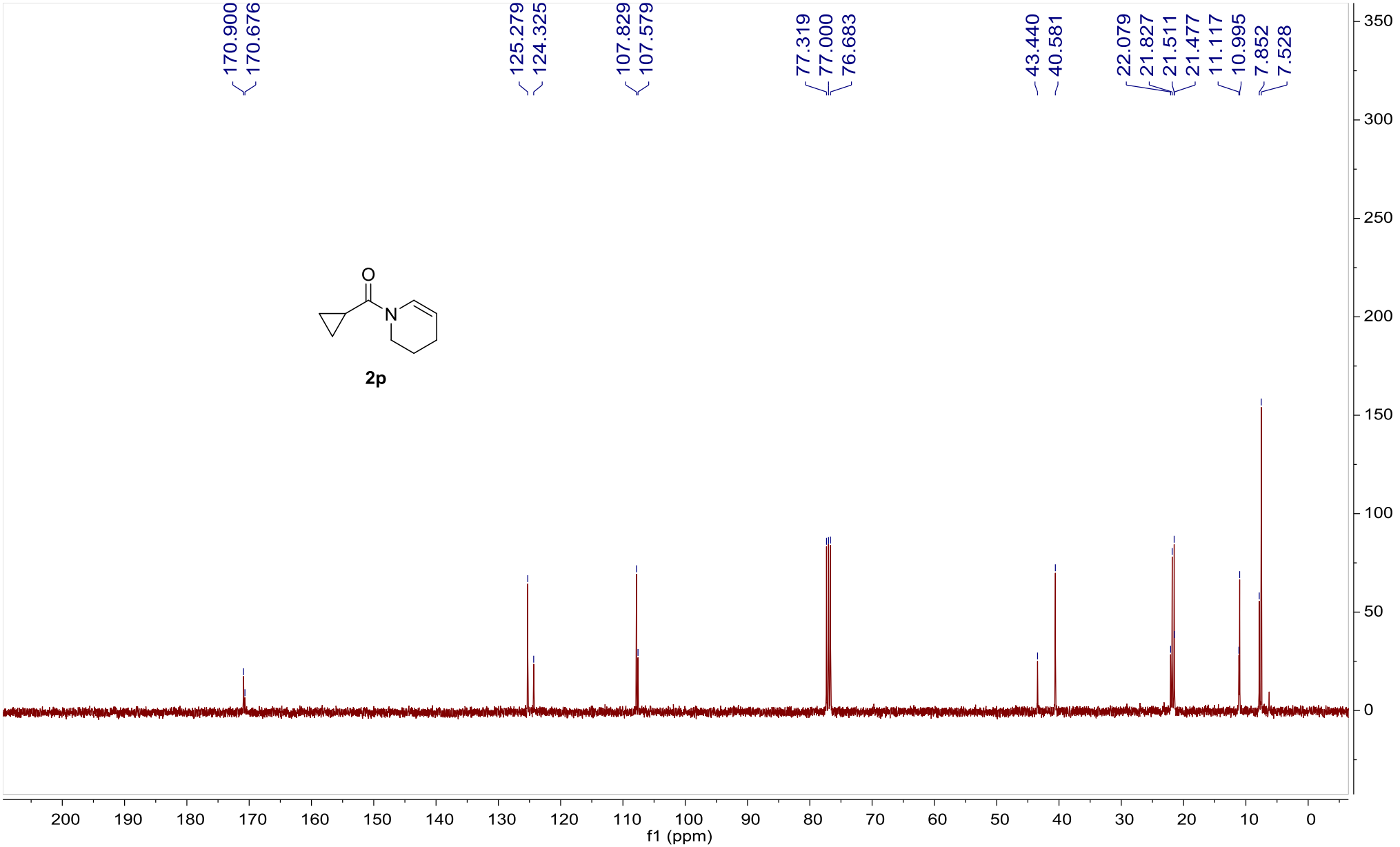
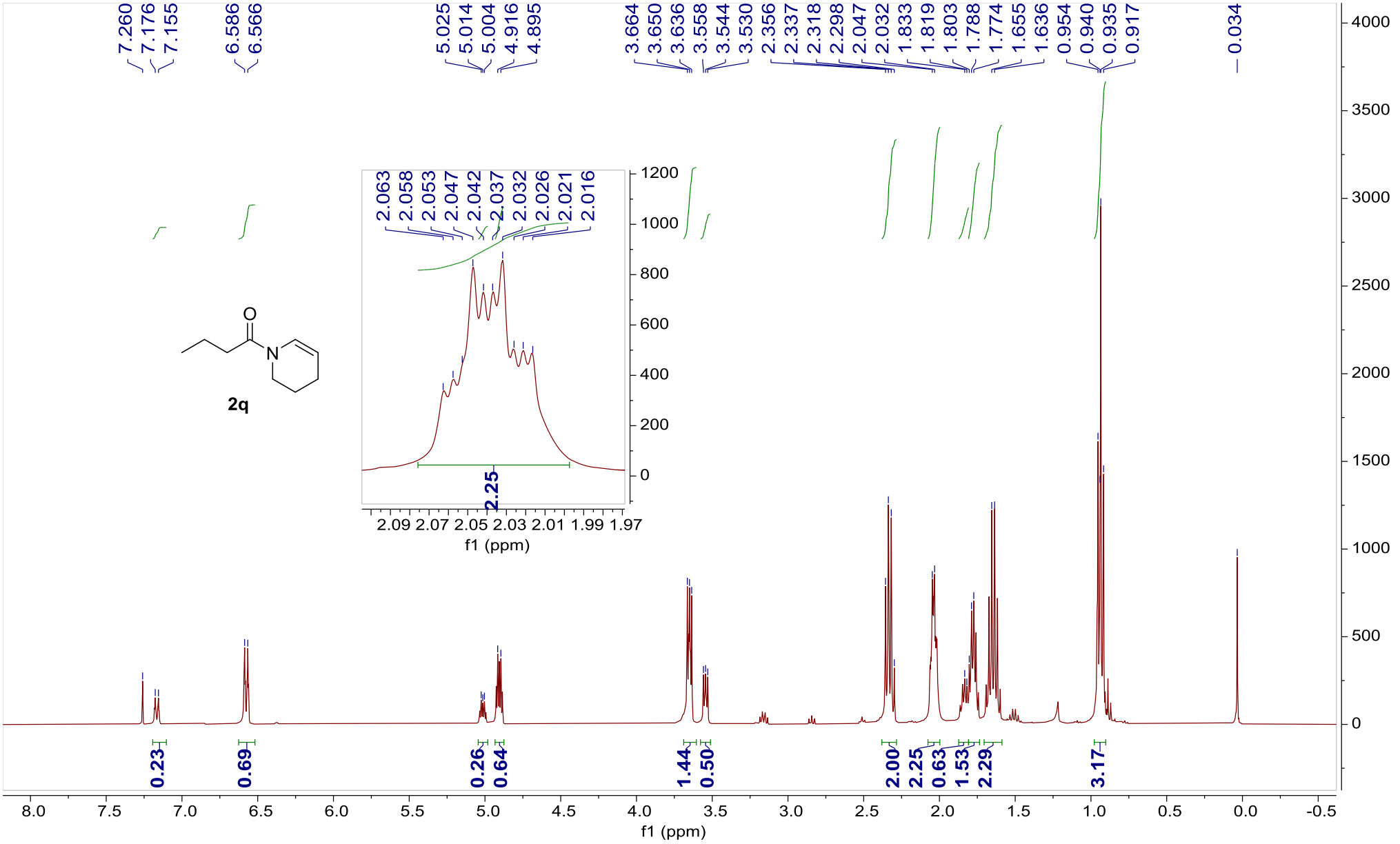
7.103
7.081
6.893
6.872
4.973
4.962
4.951
4.940
4.930
4.920
4.909
4.899
3.759
3.745
3.731
3.624
3.610
3.596
2.042
2.028
1.863
1.848
1.833
1.794
1.778
1.764
1.750
1.734
1.722
0.955
0.946
0.937
0.758
0.750
0.738
0.730
O
N
2p
0.30
0.62
0.91
0.62
1.31
1.97
0.73
2.34
2.00
1.99
f1 (ppm)


170.900
170.676
125.279
124.325
107.829
107.579
77.319
77.000
76.683
43.440
40.581
22.079
21.827
21.511
21.477
11.117
10.995
7.852
7.528
O
N
2p
f1 (ppm)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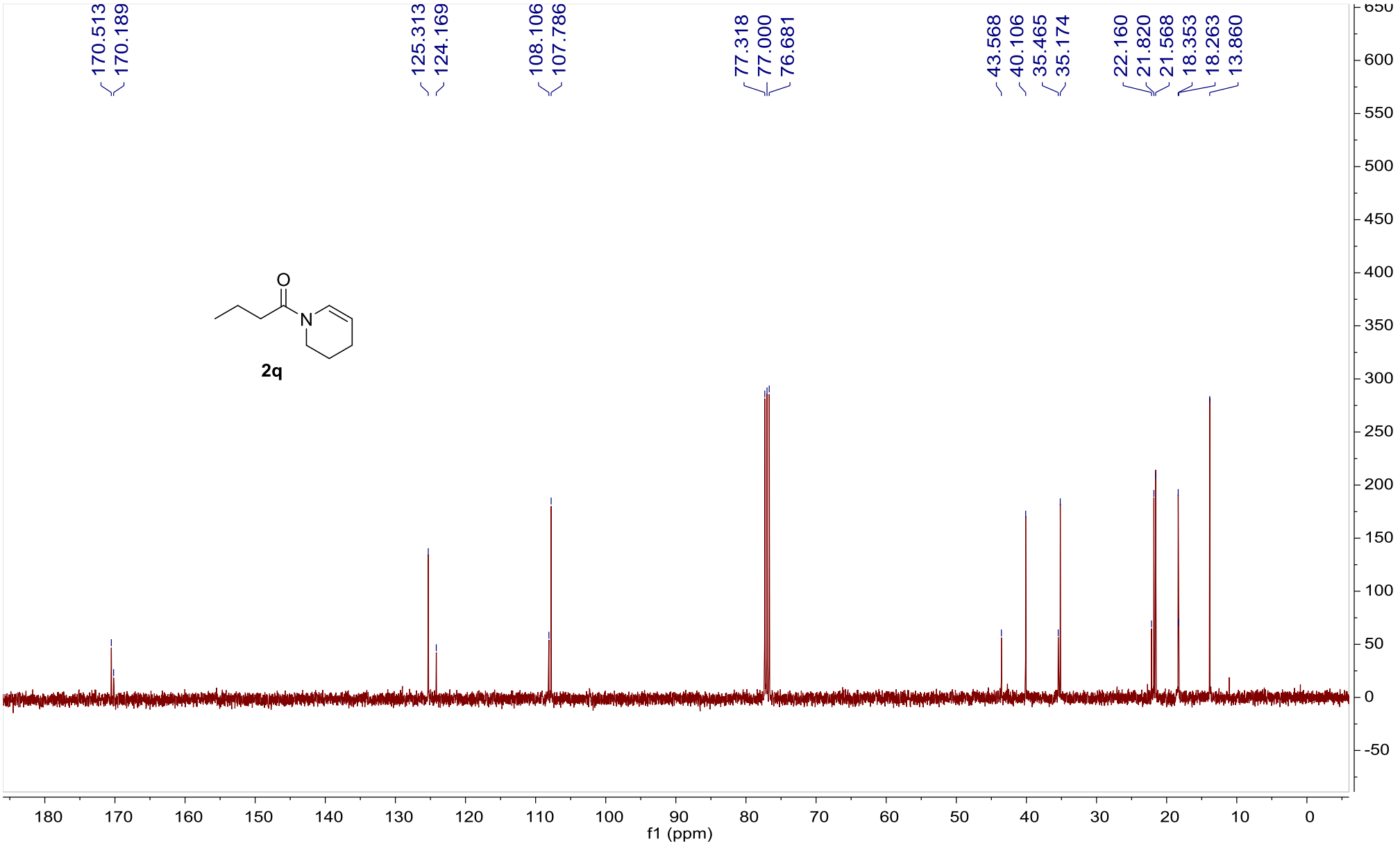
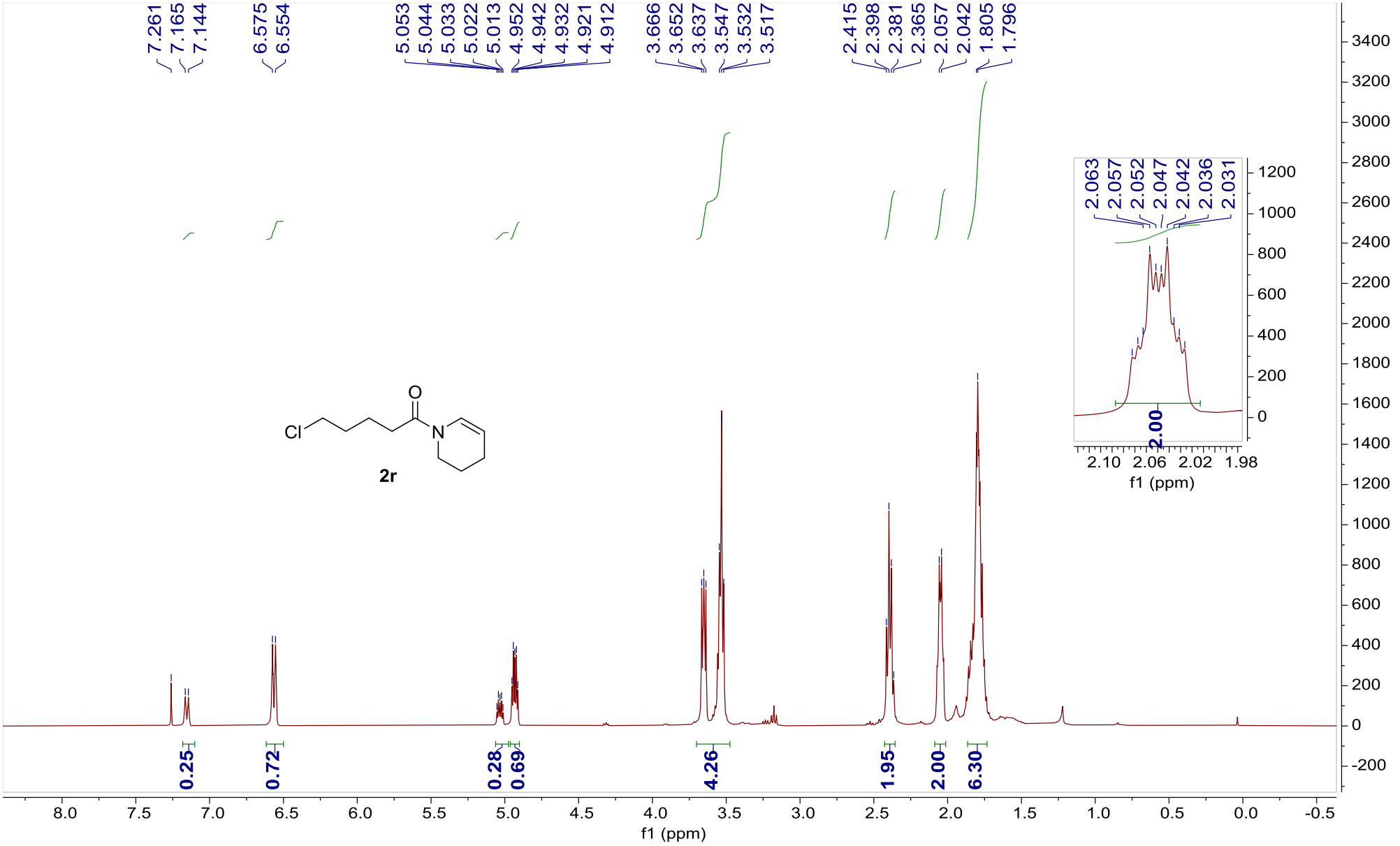
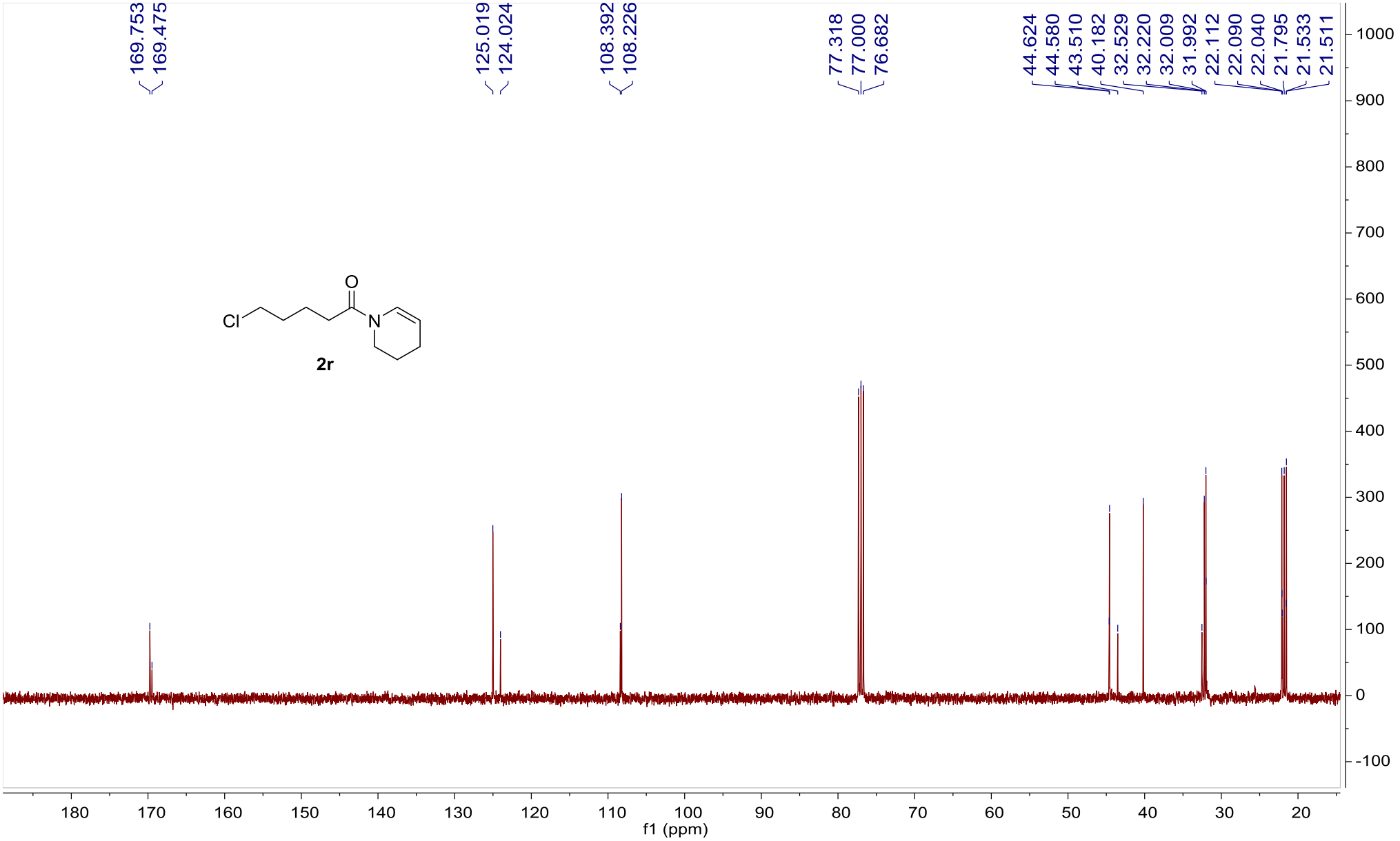
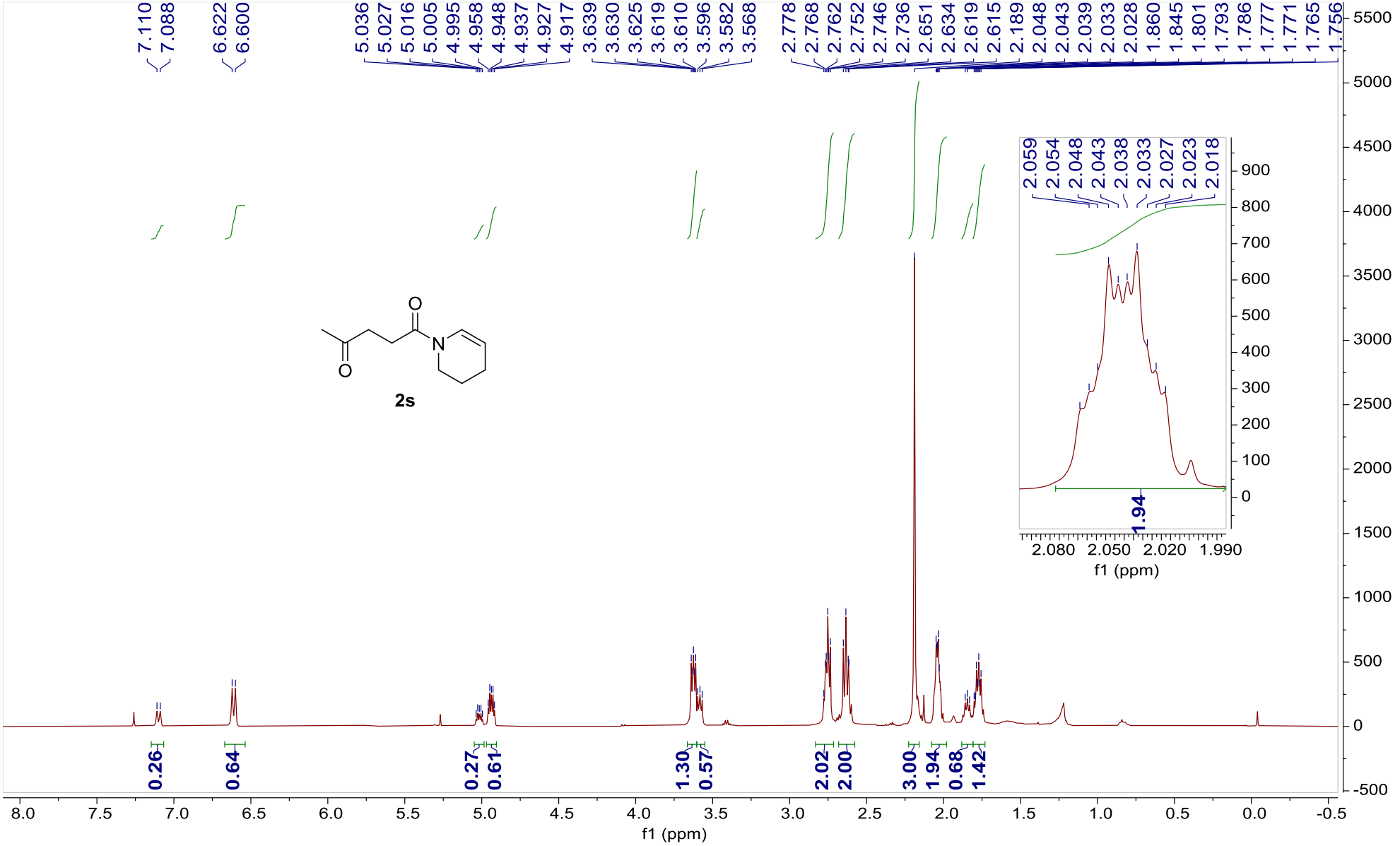
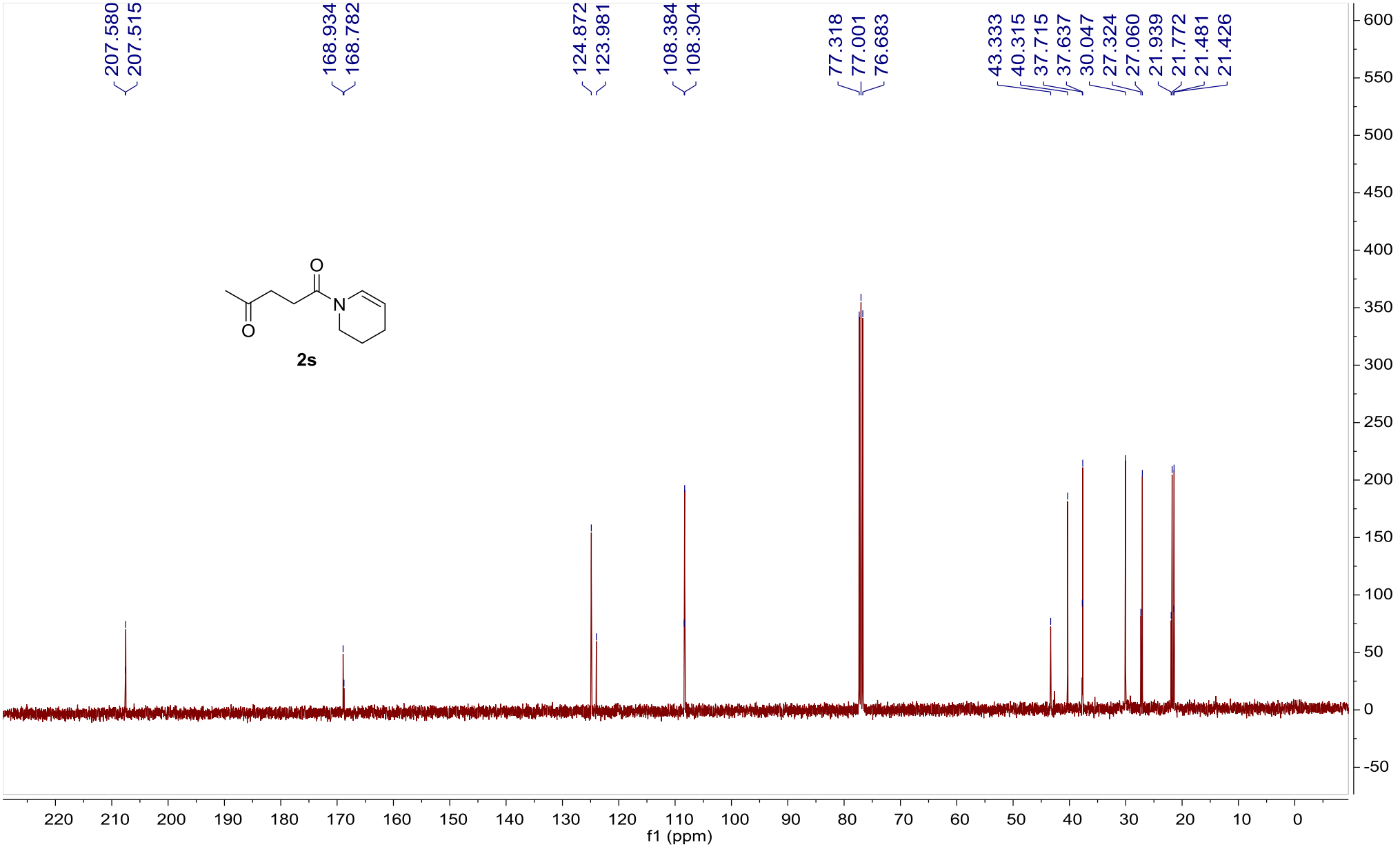
7.176
7.155
6.586
6.566
5.025
5.014
5.004
4.916
4.895
3.664
3.650
3.636
3.558
3.544
3.530
2.356
2.337
2.318
2.298
2.047
2.032
1.833
1.819
1.803
1.788
1.774
1.655
1.636
0.954
0.940
0.935
0.917
0.034
2.063
2.058
2.053
2.047
2.042
2.037
2.032
2.026
2.021
2.016
2.25
2.09 2.07 2.05 2.03 2.01 1.99 1.97
f1 (ppm)
O
N
2q
0.23
0.69
0.26
0.64
1.44
0.50
2.00
2.25
0.63
1.53
2.29
3.17
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

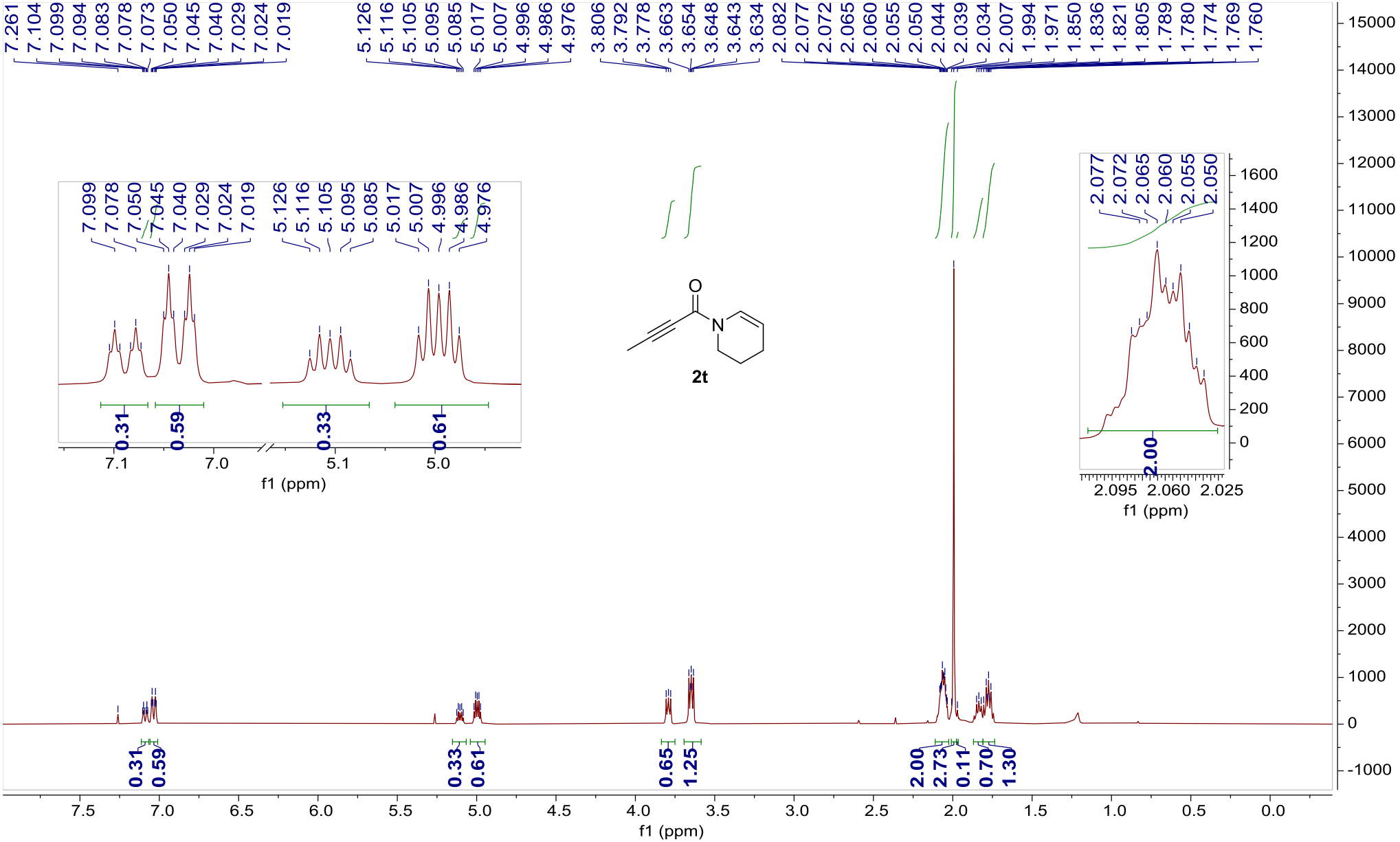

170.513
170.189
125.313
124.169
108.106
107.786
77.318
77.000
76.681
43.568
40.106
35.465
35.174
22.160
21.820
21.568
18.353
18.263
13.860
O
N
2q
f1 (ppm)

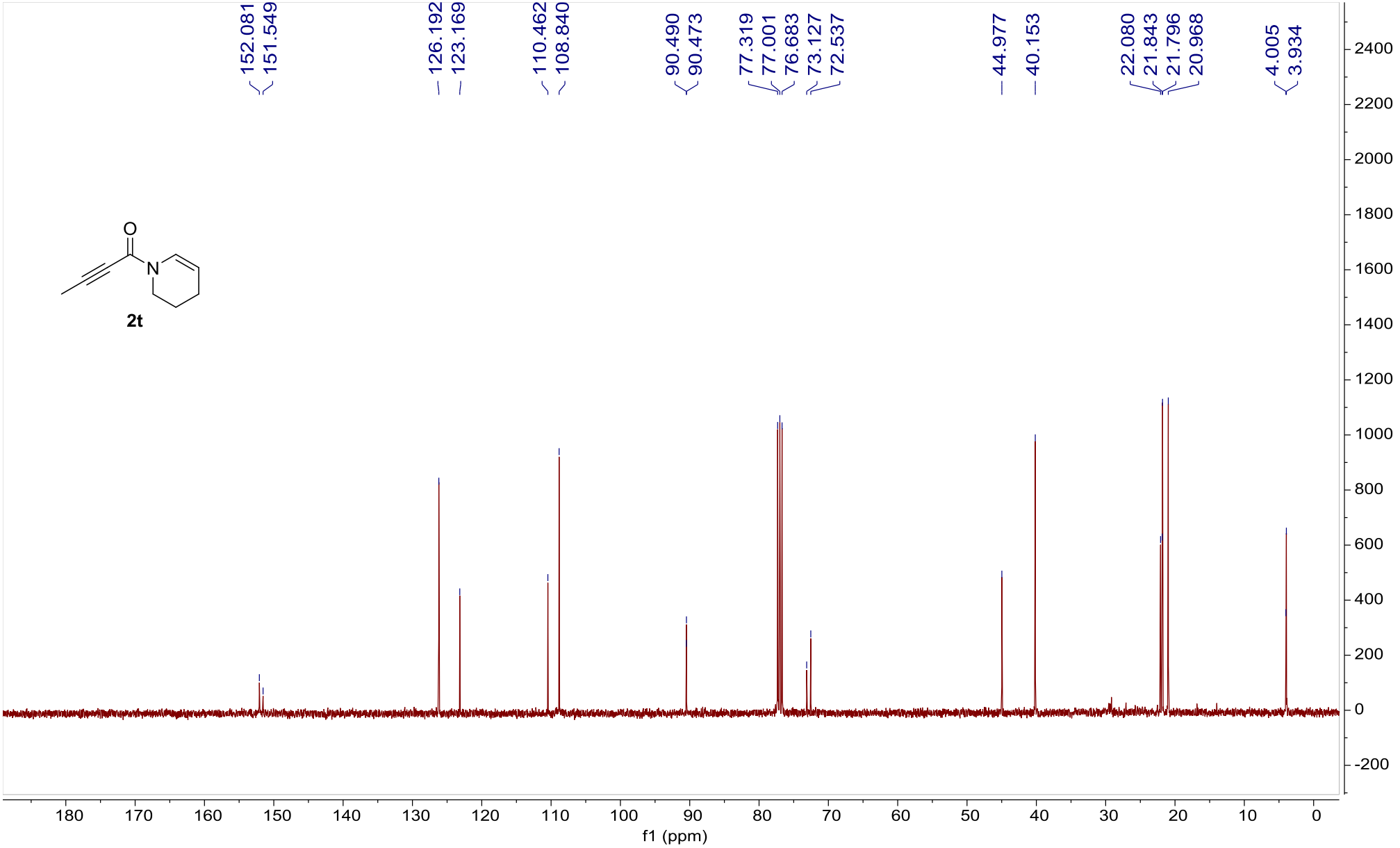

7.261
7.165
7.144
6.575
6.554
5.053
5.044
5.033
5.022
5.013
4.952
4.942
4.932
4.921
4.912
3.666
3.652
3.637
3.547
3.532
3.517
2.415
2.398
2.381
2.365
2.057
2.042
1.805
1.796
2.063
2.057
2.052
2.047
2.042
2.036
2.031
2.00
2.10 2.06 2.02 1.98
f1 (ppm)
Cl
N
O
2r
0.25
0.72
0.28
0.69
4.26
1.95
2.00
6.30
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

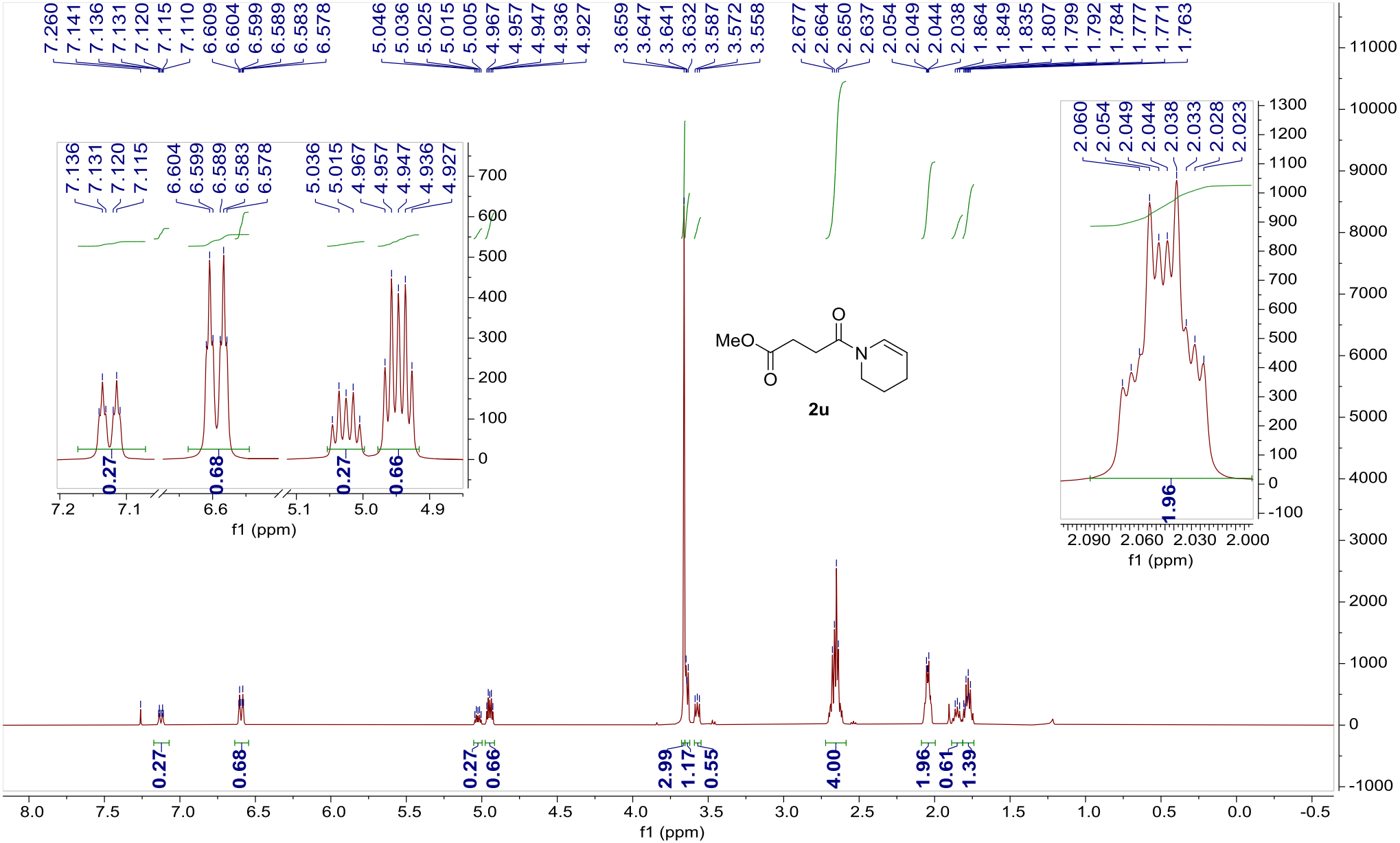

169.753
169.475
125.019
124.024
108.392
108.226
77.318
77.000
76.682
44.624
44.580
43.510
40.182
32.529
32.220
32.009
31.992
22.112
22.090
22.040
21.795
21.533
21.511
Cl
O
N
2r
f1 (ppm)

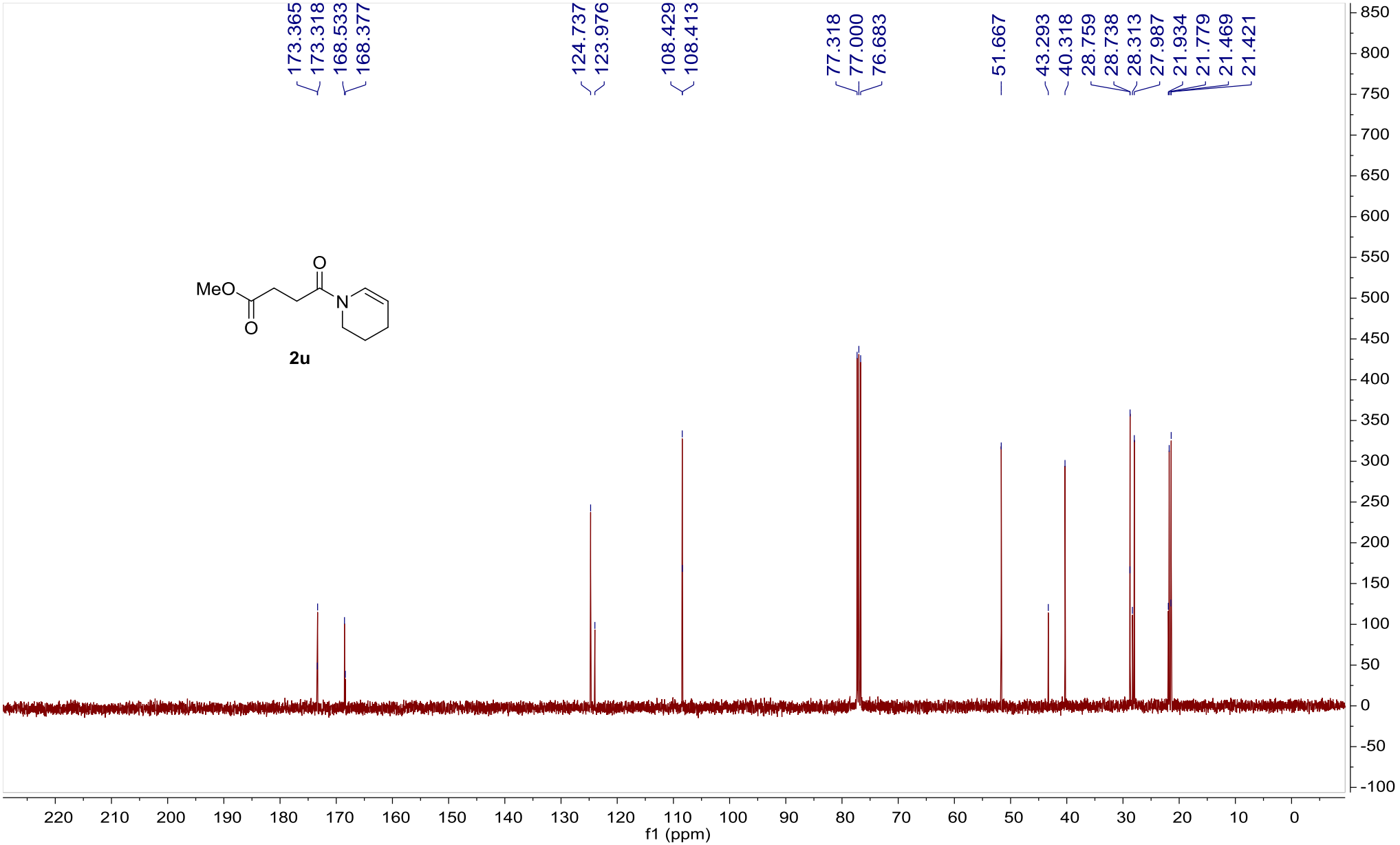

7.110
7.088
6.622
6.600
5.036
5.027
5.016
5.005
4.995
4.958
4.948
4.937
4.927
4.917
3.639
3.630
3.625
3.619
3.610
3.596
3.582
3.568
2.778
2.768
2.762
2.752
2.746
2.736
2.651
2.634
2.619
2.615
2.189
2.048
2.043
2.039
2.033
2.028
1.860
1.845
1.801
1.793
1.786
1.777
1.771
1.765
1.756
2.059
2.054
2.048
2.043
2.038
2.033
2.027
2.023
2.018
1.94
2.080 2.050 2.020 1.990
f1 (ppm)
O
O
N
2s
0.26
0.64
0.27
0.61
1.30
0.57
2.02
2.00
3.00
1.94
0.68
1.42
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

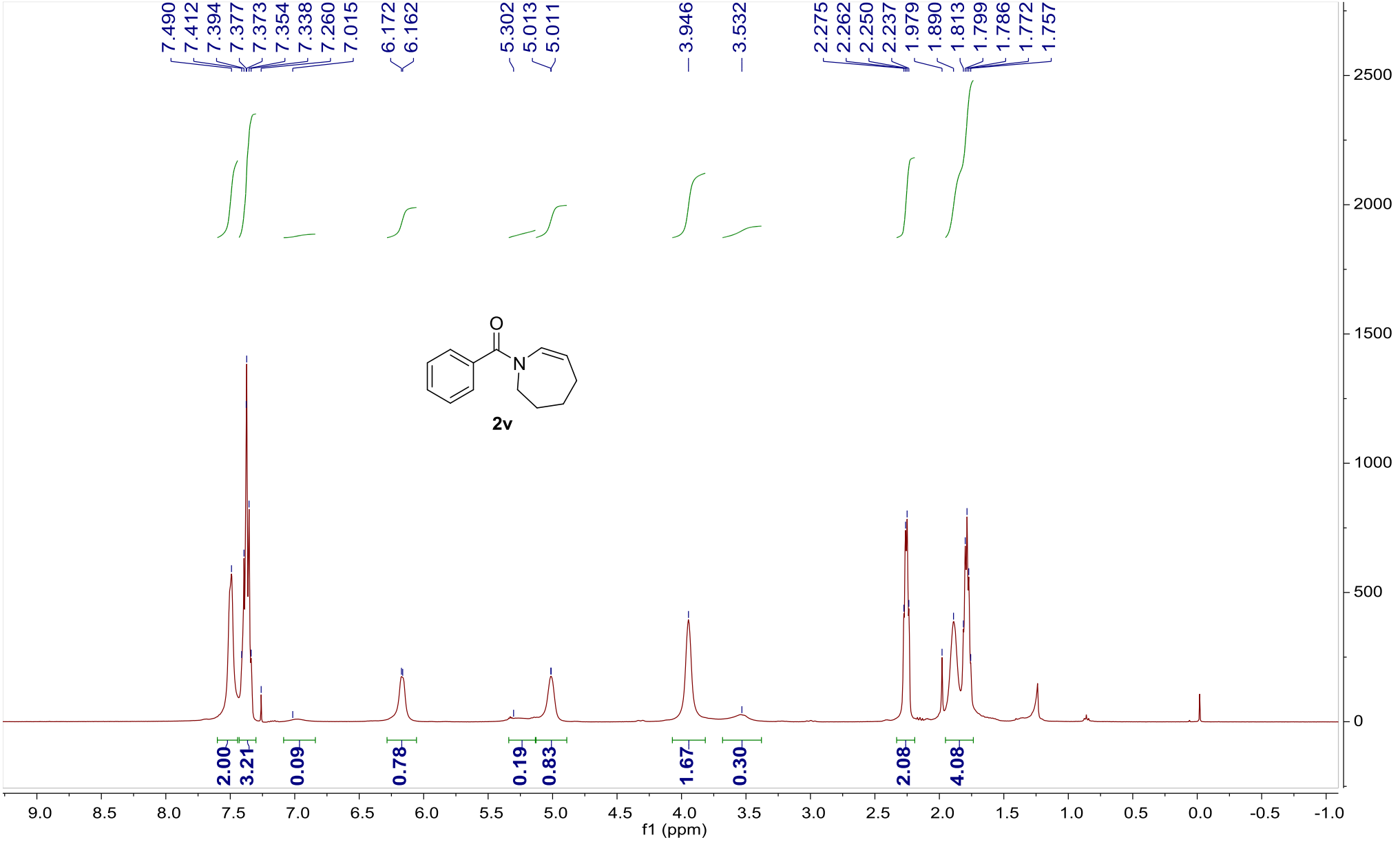

207.580
207.515
168.934
168.782
124.872
123.981
108.384
108.304
77.318
77.001
76.683
43.333
40.315
37.715
37.637
30.047
27.324
27.060
21.939
21.772
21.481
21.426
O
N
O
2s
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

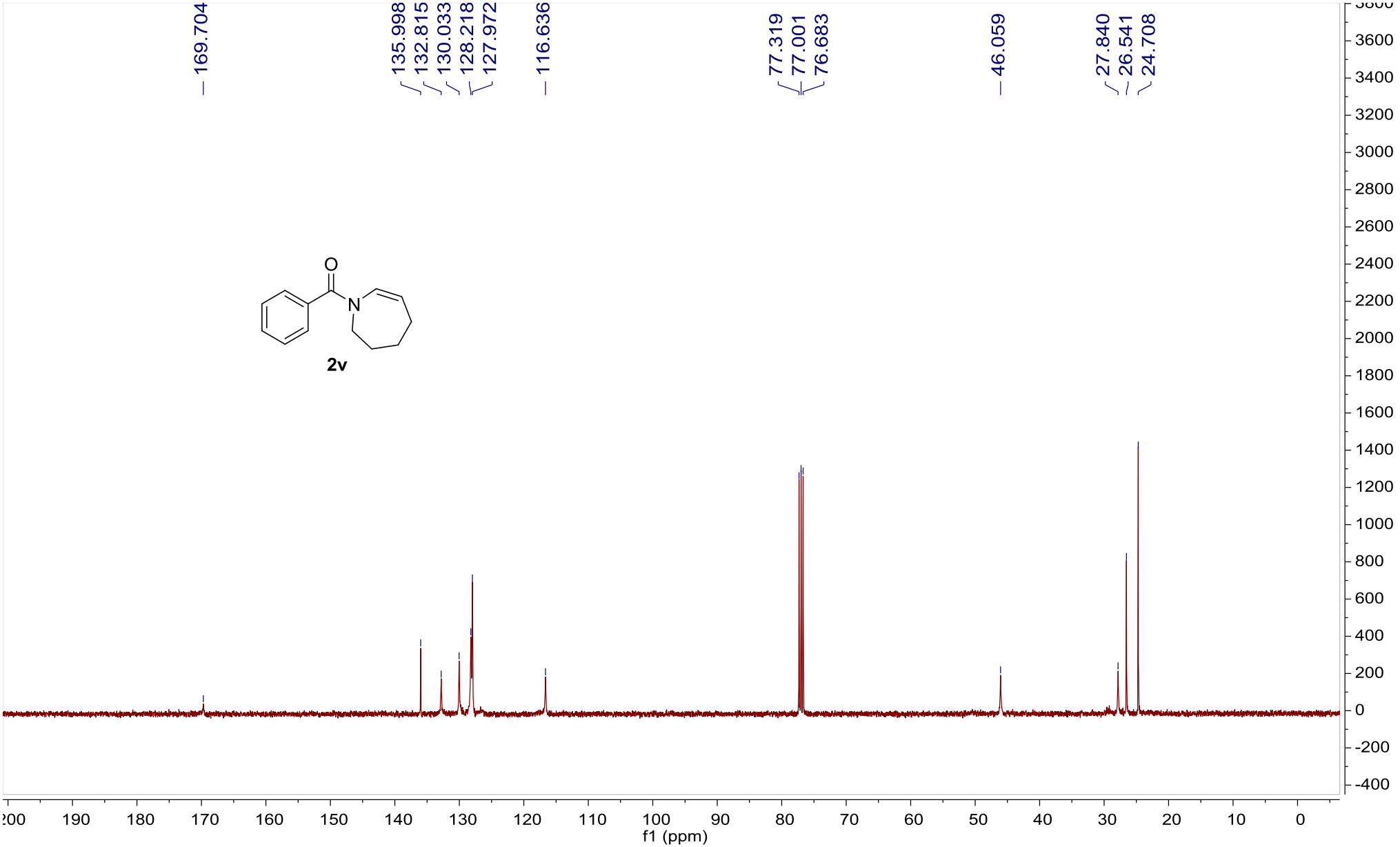

7.261 7.104 7.099 7.094 7.083 7.078 7.073 7.050 7.045 7.040 7.029 7.024 7.019
5.126 5.116 5.105 5.095 5.085 5.017 5.007 4.996 4.986 4.976
3.806 3.792 3.778 3.663 3.654 3.648 3.643 3.634
2.082 2.077 2.072 2.065 2.060 2.055 2.050 2.044 2.039 2.034 2.007 1.994 1.971 1.850 1.836 1.821 1.805 1.789 1.780 1.774 1.769 1.760
0.31 0.59 0.33 0.61 0.65 1.25 2.00 2.73 0.11 0.70 1.30
f1 (ppm)
2t

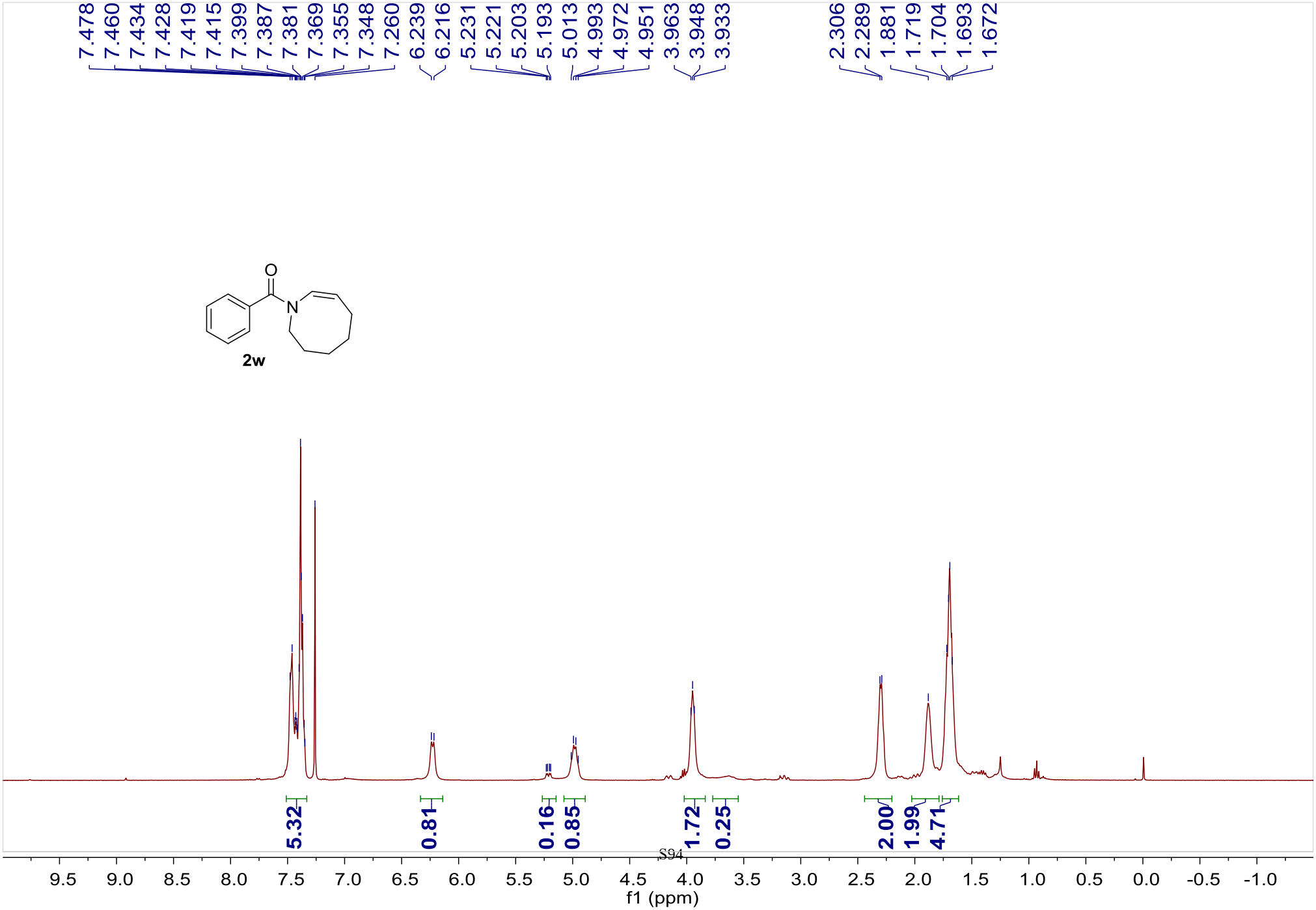

152.081
151.549
126.192
123.169
110.462
108.840
90.490
90.473
77.319
77.001
76.683
73.127
72.537
44.977
40.153
22.080
21.843
21.796
20.968
4.005
3.934
O
N
2t
f1 (ppm)

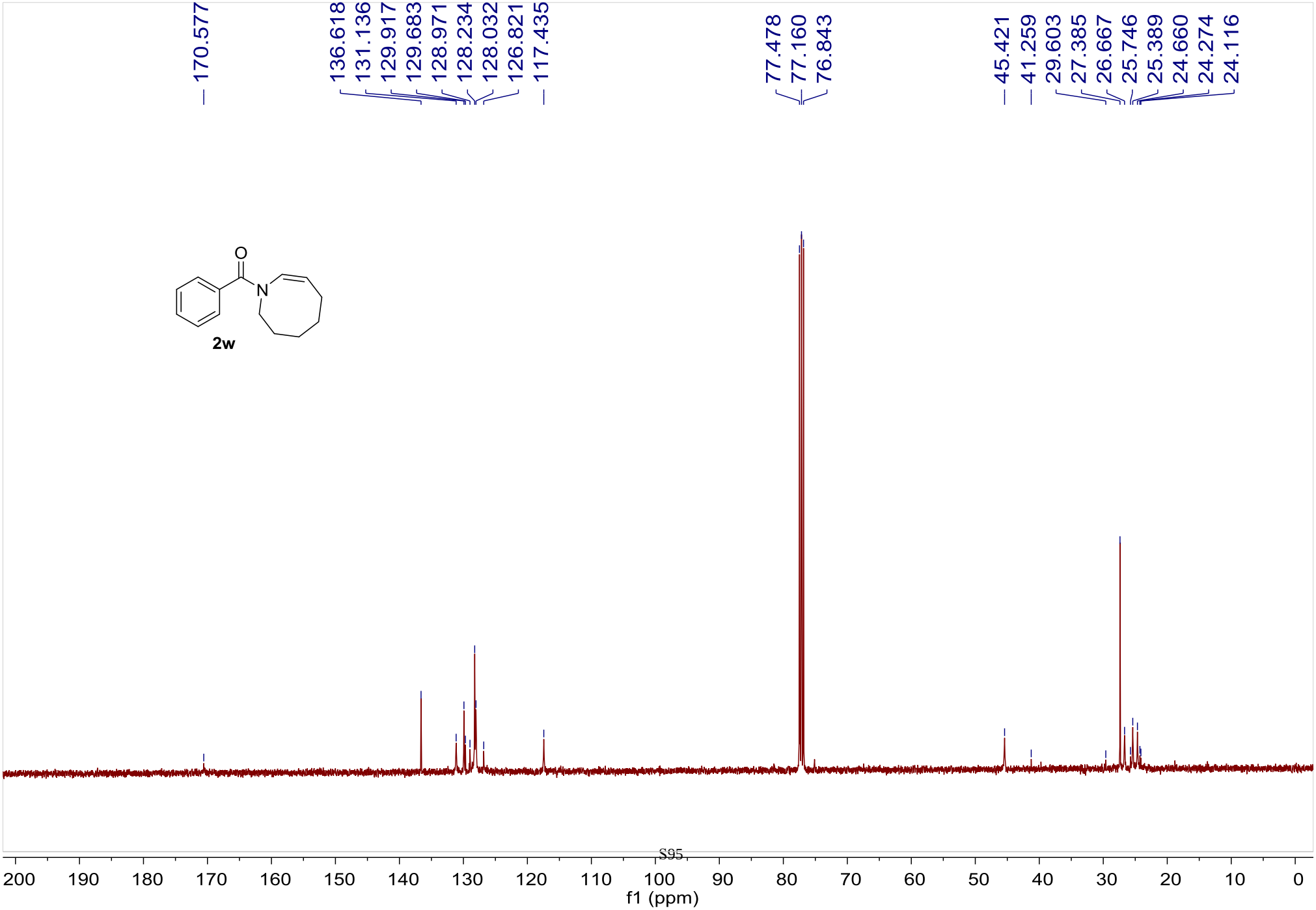

7.260 7.141 7.136 7.131 7.120 7.115 7.110 6.609 6.604 6.599 6.589 6.583 6.578
5.046 5.036 5.025 5.015 5.005 4.967 4.957 4.947 4.936 4.927
3.659 3.647 3.641 3.632 3.587 3.572 3.558
2.677 2.664 2.650 2.637 2.054 2.049 2.044 2.038 1.864 1.849 1.835 1.807 1.799 1.792 1.784 1.777 1.771 1.763
MeO
O
O
N
2u
0.27 0.68 0.27 0.66 2.99 1.17 0.55 4.00 1.96 0.61 1.39
f1 (ppm)
2.060 2.054 2.049 2.044 2.038 2.033 2.028 2.023
1.96
f1 (ppm)


173.365
173.318
168.533
168.377
124.737
123.976
108.429
108.413
77.318
77.000
76.683
51.667
43.293
40.318
28.759
28.738
28.313
27.987
21.934
21.779
21.469
21.421
MeO
O
O
N
2u
f1 (ppm)


7.490
7.412
7.394
7.377
7.373
7.354
7.338
7.260
7.015
6.172
6.162
5.302
5.013
5.011
3.946
3.532
2.275
2.262
2.250
2.237
1.979
1.890
1.813
1.799
1.786
1.772
1.757
O
N
2v
2.00
3.21
0.09
0.78
0.19
0.83
1.67
0.30
2.08
4.08
f1 (ppm)


169.704
135.998
132.815
130.033
128.218
127.972
116.636
77.319
77.001
76.683
46.059
27.840
26.541
24.708
O
N
2v
f1 (ppm)


7.478
7.460
7.434
7.428
7.419
7.415
7.399
7.387
7.381
7.369
7.355
7.348
7.260
6.239
6.216
5.231
5.221
5.203
5.193
5.013
4.993
4.972
4.951
3.963
3.948
3.933
2.306
2.289
1.881
1.719
1.704
1.693
1.672
O
N
2w
5.32
0.81
0.16
0.85
1.72
0.25
2.00
1.99
4.71
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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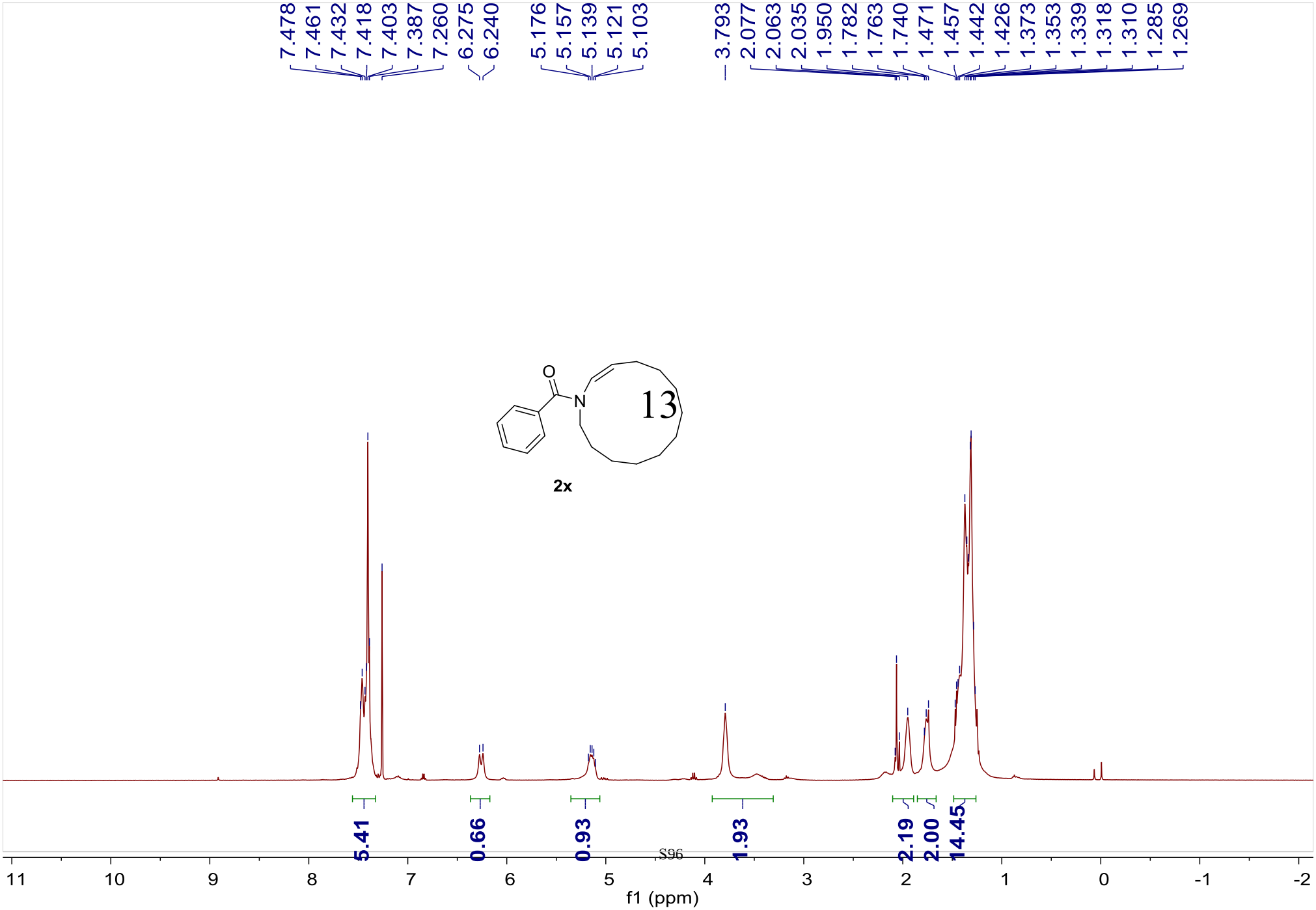
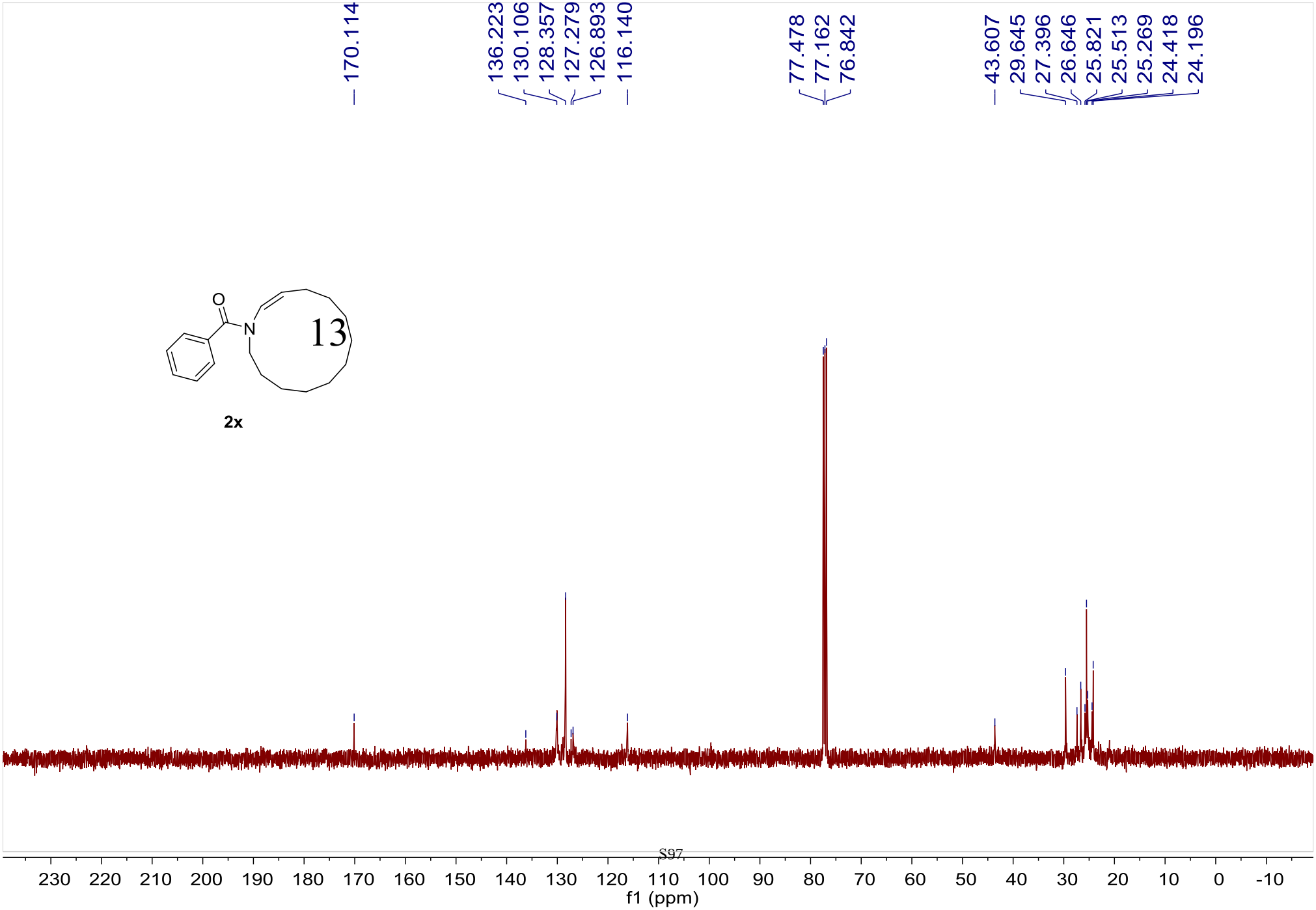
131.136
129.917
129.683
128.971
128.234
128.032
126.821
117.435
77.478
77.160
76.843
45.421
41.259
29.603
27.385
26.667
25.746
25.389
24.660
24.274
24.116
O
N
2w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.478
7.461
7.432
7.418
7.403
7.387
7.260
6.275
6.240
5.176
5.157
5.139
5.121
5.103
3.793
2.077
2.063
2.035
1.950
1.782
1.763
1.740
1.471
1.457
1.442
1.426
1.373
1.353
1.339
1.318
1.310
1.285
1.269
O
N
13
2x
5.41
0.66
0.93
1.93
2.19
2.00
14.45
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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136.223
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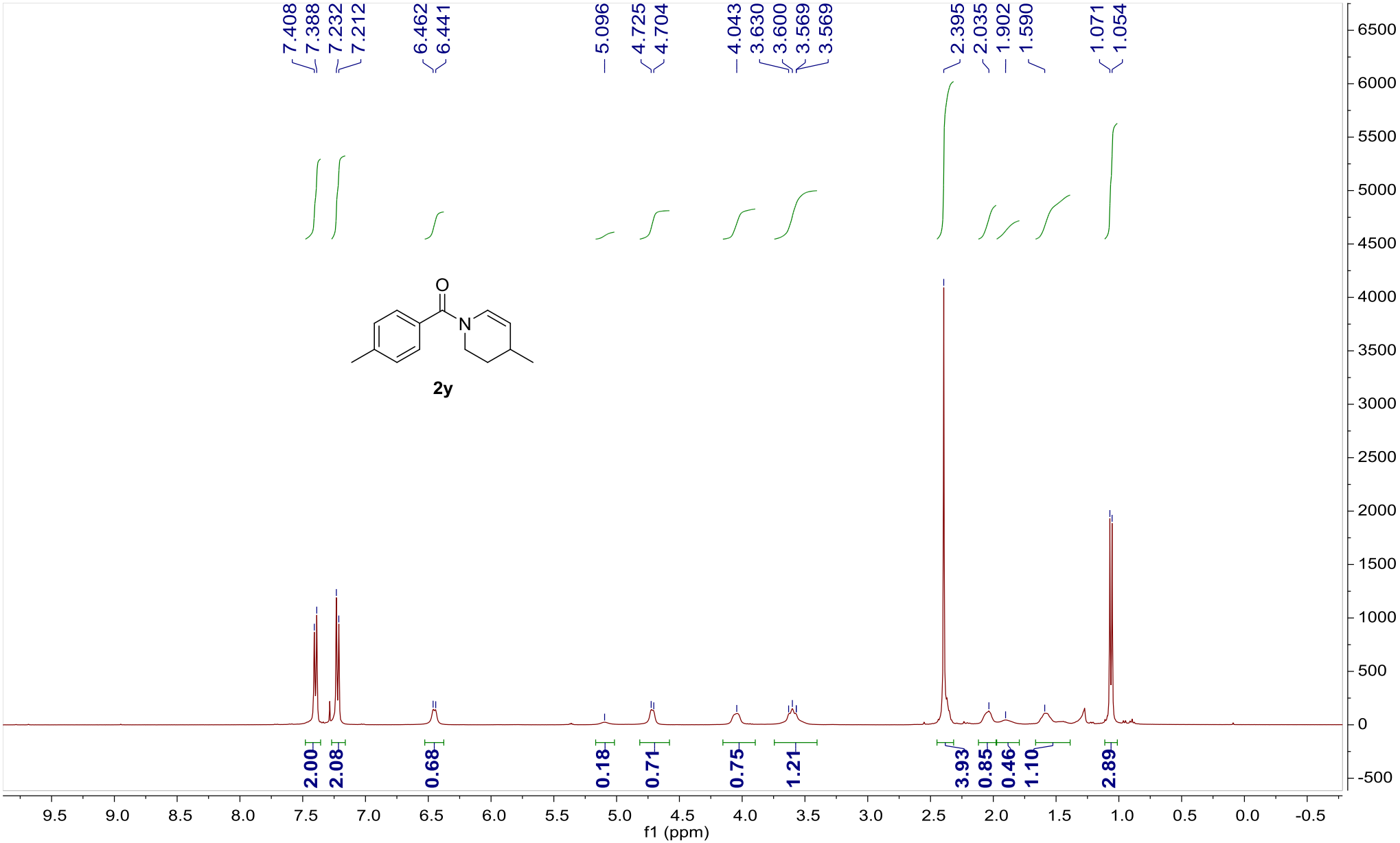
128.357
127.279
126.893
116.140
77.478
77.162
76.842
43.607
29.645
27.396
26.646
25.821
25.513
25.269
24.418
24.196
O
N
13
2x
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.388
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7.212
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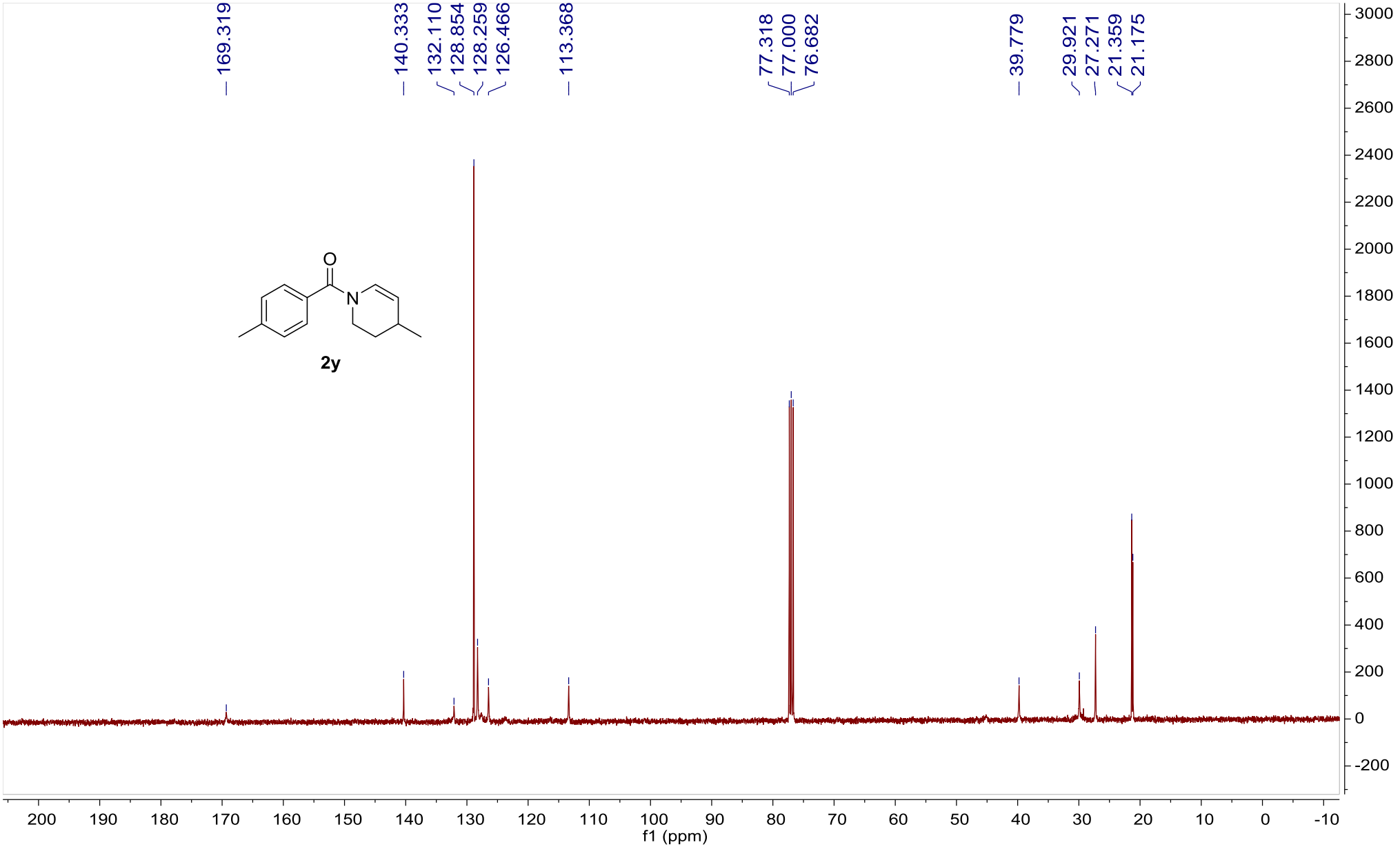
6.441
5.096
4.725
4.704
4.043
3.630
3.600
3.569
3.569
2.395
2.035
1.902
1.590
1.071
1.054
O
N
2y
2.00
2.08
0.68
0.18
0.71
0.75
1.21
3.93
0.85
0.46
1.10
2.89
f1 (ppm)


169.319
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128.854
128.259
126.466
113.368
77.318
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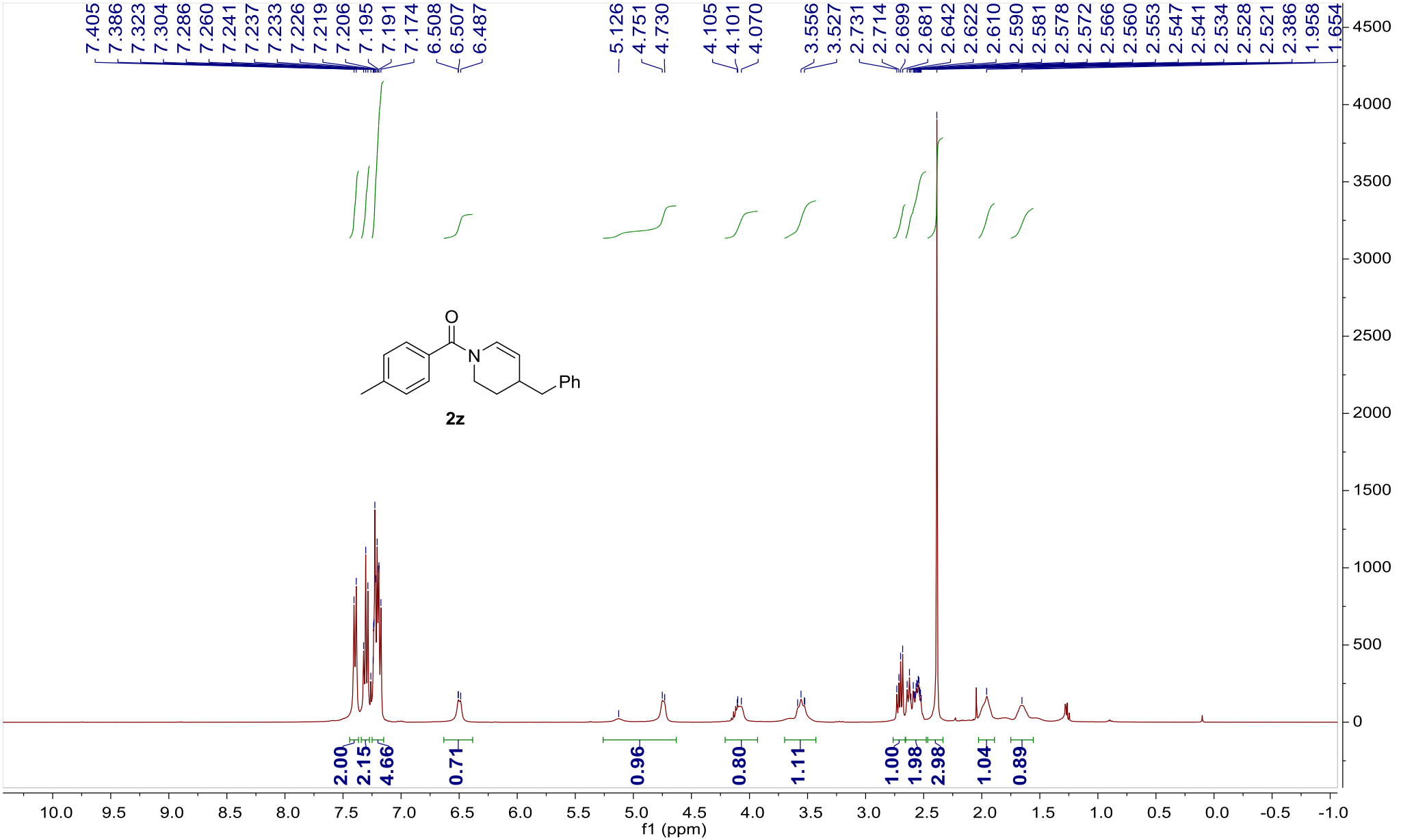
76.682
39.779
29.921
27.271
21.359
21.175
O
N
2y
f1 (ppm)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7.323
7.304
7.286
7.260
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7.237
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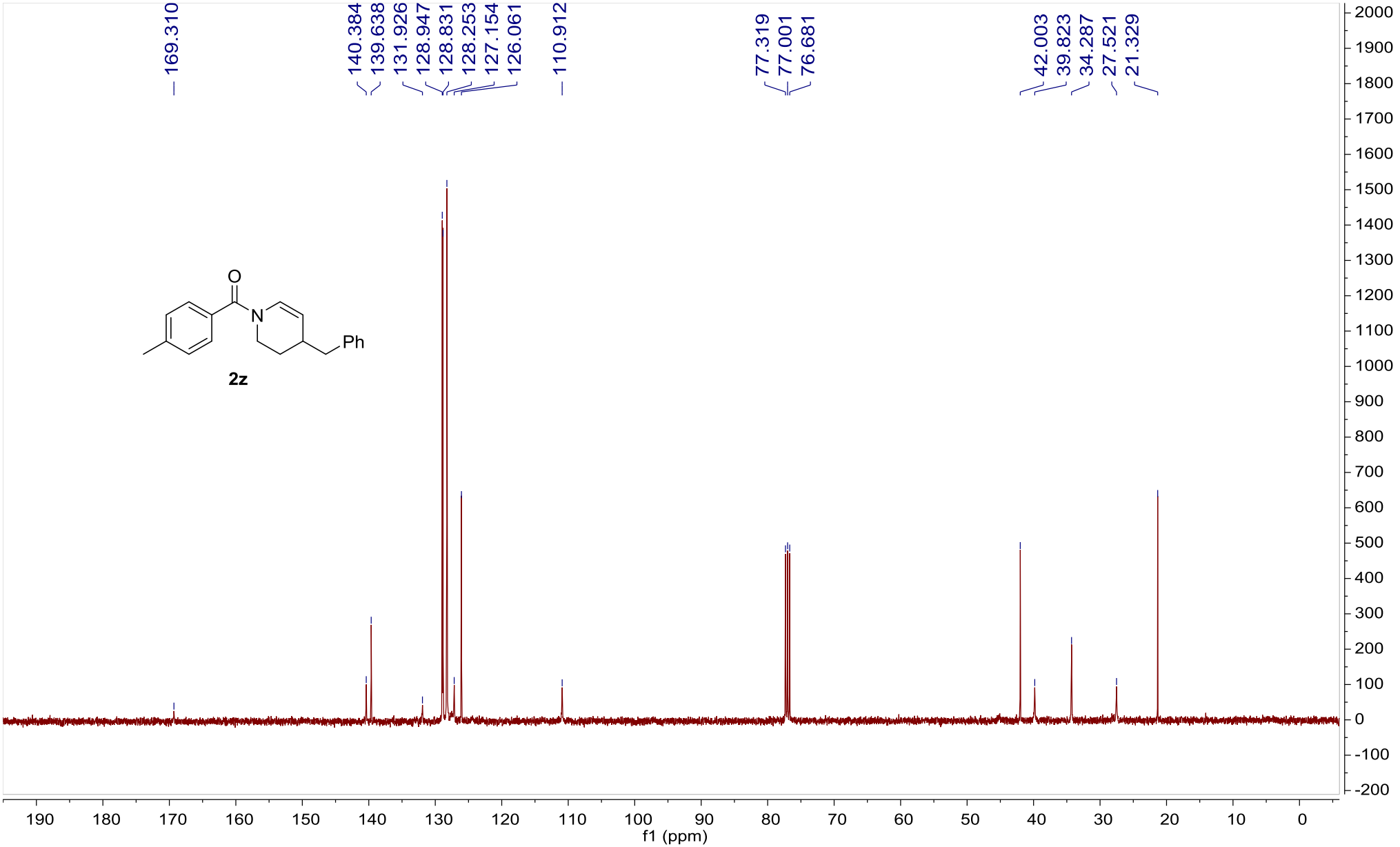
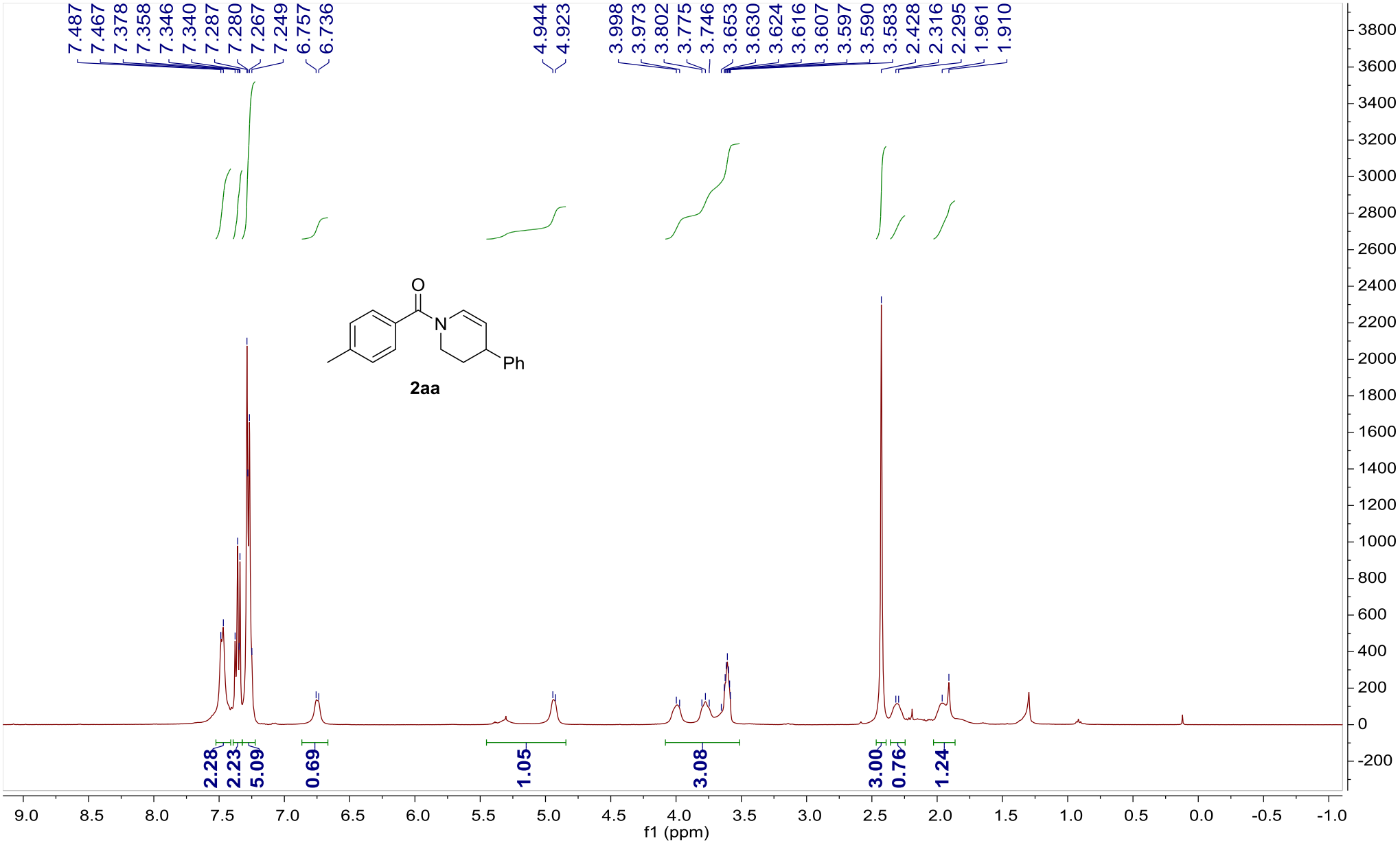
7.226
7.219
7.206
7.195
7.191
7.174
6.508
6.507
6.487
5.126
4.751
4.730
4.105
4.101
4.070
3.556
3.527
2.731
2.714
2.699
2.681
2.642
2.622
2.610
2.590
2.581
2.578
2.572
2.566
2.560
2.553
2.547
2.541
2.534
2.528
2.521
2.386
1.958
1.654
O
N
Ph
2z
2.00
2.15
4.66
0.71
0.96
0.80
1.11
1.00
1.98
2.98
1.04
0.89
f1 (ppm)


169.310
140.384
139.638
131.926
128.947
128.831
128.253
127.154
126.061
110.912
77.319
77.001
76.681
42.003
39.823
34.287
27.521
21.329
O
N
Ph
2z
f1 (ppm)


7.487
7.467
7.378
7.358
7.346
7.340
7.287
7.280
7.267
7.249
6.757
6.736
4.944
4.923
3.998
3.973
3.802
3.775
3.746
3.653
3.630
3.624
3.616
3.607
3.597
3.590
3.583
2.428
2.316
2.295
1.961
1.910
O
N
Ph
2aa
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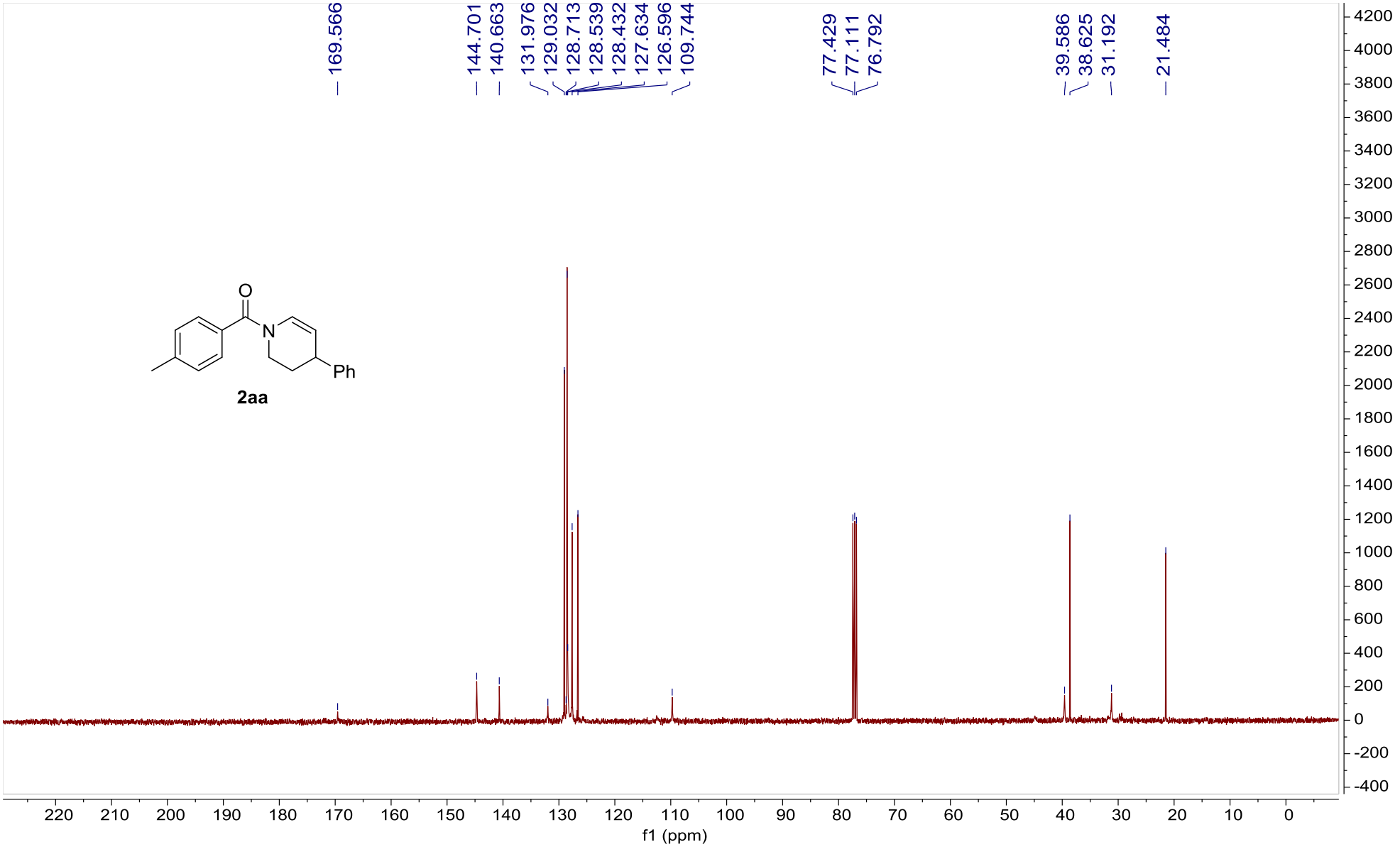
2.23
5.09
0.69
1.05
3.08
3.00
0.76
1.24
f1 (ppm)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128.713
128.539
128.432
127.634
126.596
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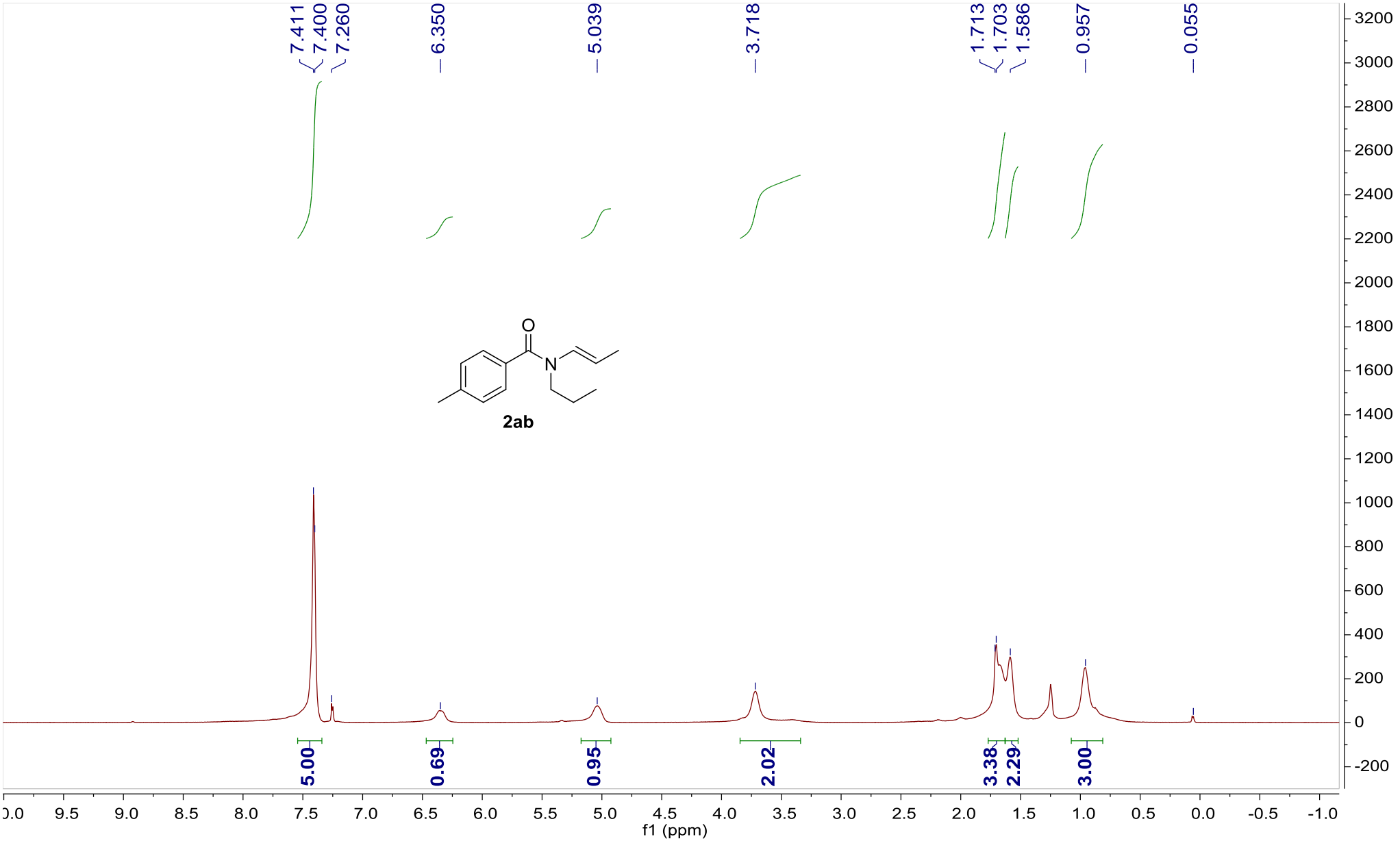
77.111
76.792
39.586
38.625
31.192
21.484
O
N
Ph
2aa
f1 (ppm)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7.400
7.260
6.350
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3.718
1.713
1.703
1.586
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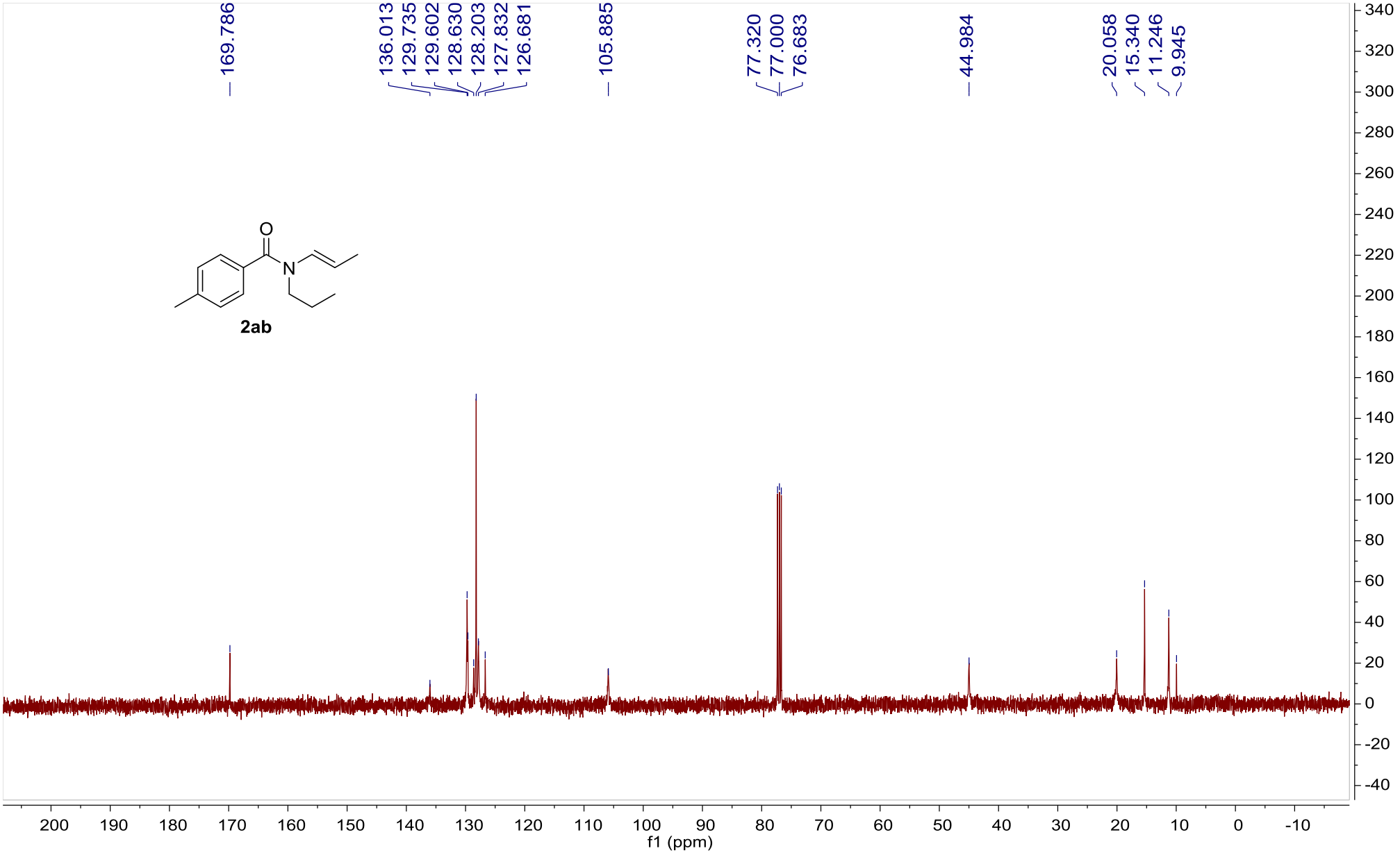
N
2ab
5.00
0.69
0.95
2.02
3.38
2.29
3.00
f1 (ppm)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128.203
127.832
126.681
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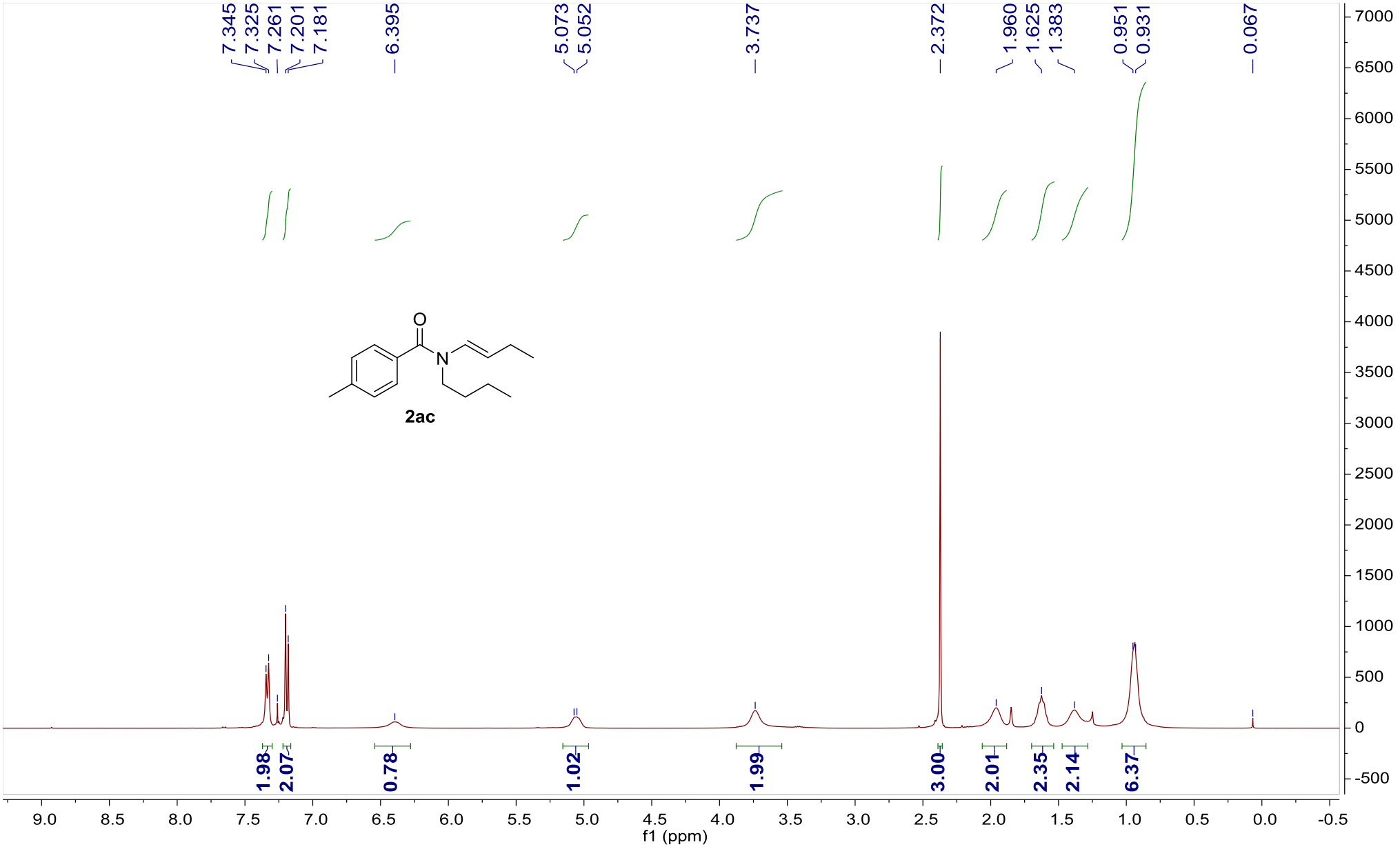
76.683
44.984
20.058
15.340
11.246
9.945
O
N
2ab
f1 (ppm)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7.261
7.201
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6.395
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5.052
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2.372
1.960
1.625
1.383
0.951
0.931
0.067
O
N
2ac
1.98
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0.78
1.02
1.99
3.00
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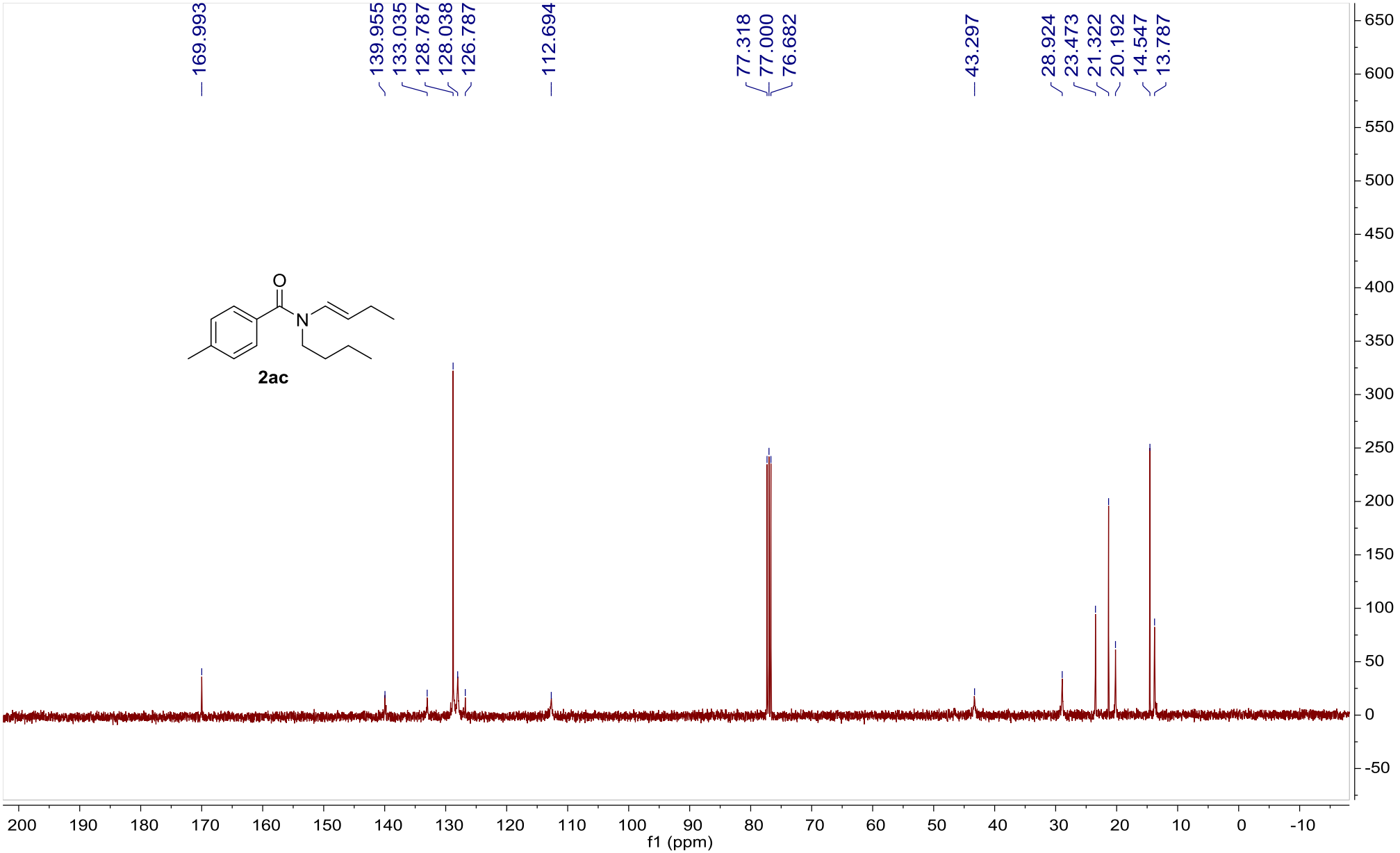
2.35
2.14
6.37
f1 (ppm)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77.318
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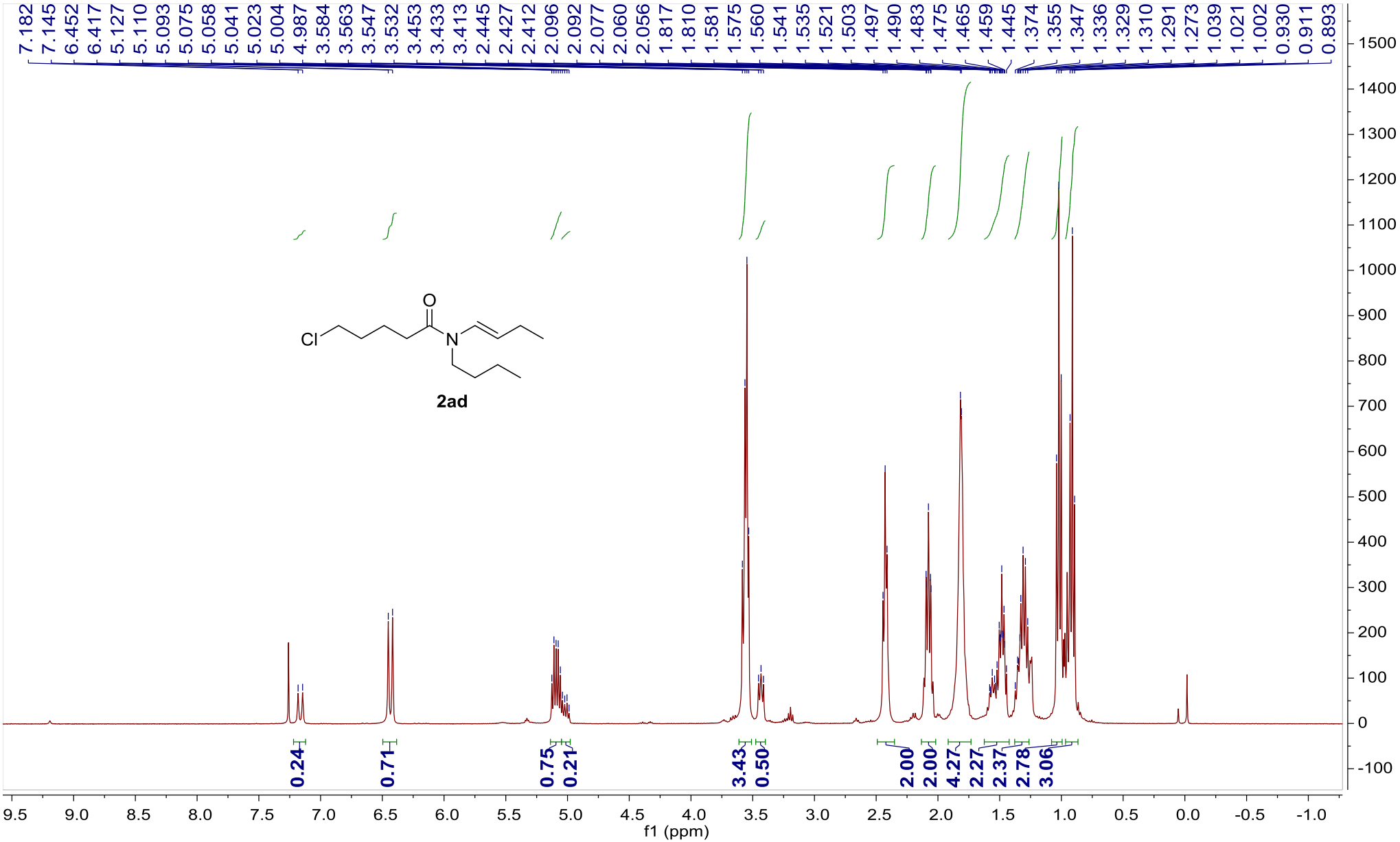
13.787
O
N
2ac
f1 (ppm)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6.452
6.417
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5.110
5.093
5.075
5.058
5.041
5.023
5.004
4.987
3.584
3.563
3.547
3.532
3.453
3.433
3.413
2.445
2.427
2.412
2.096
2.092
2.077
2.060
2.056
1.817
1.810
1.581
1.575
1.560
1.541
1.535
1.521
1.503
1.497
1.490
1.483
1.475
1.465
1.459
1.445
1.374
1.355
1.347
1.336
1.329
1.310
1.291
1.273
1.039
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1.002
0.930
0.911
0.893
Cl
O
N
2ad
0.24
0.71
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0.21
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0.50
2.00
2.00
4.27
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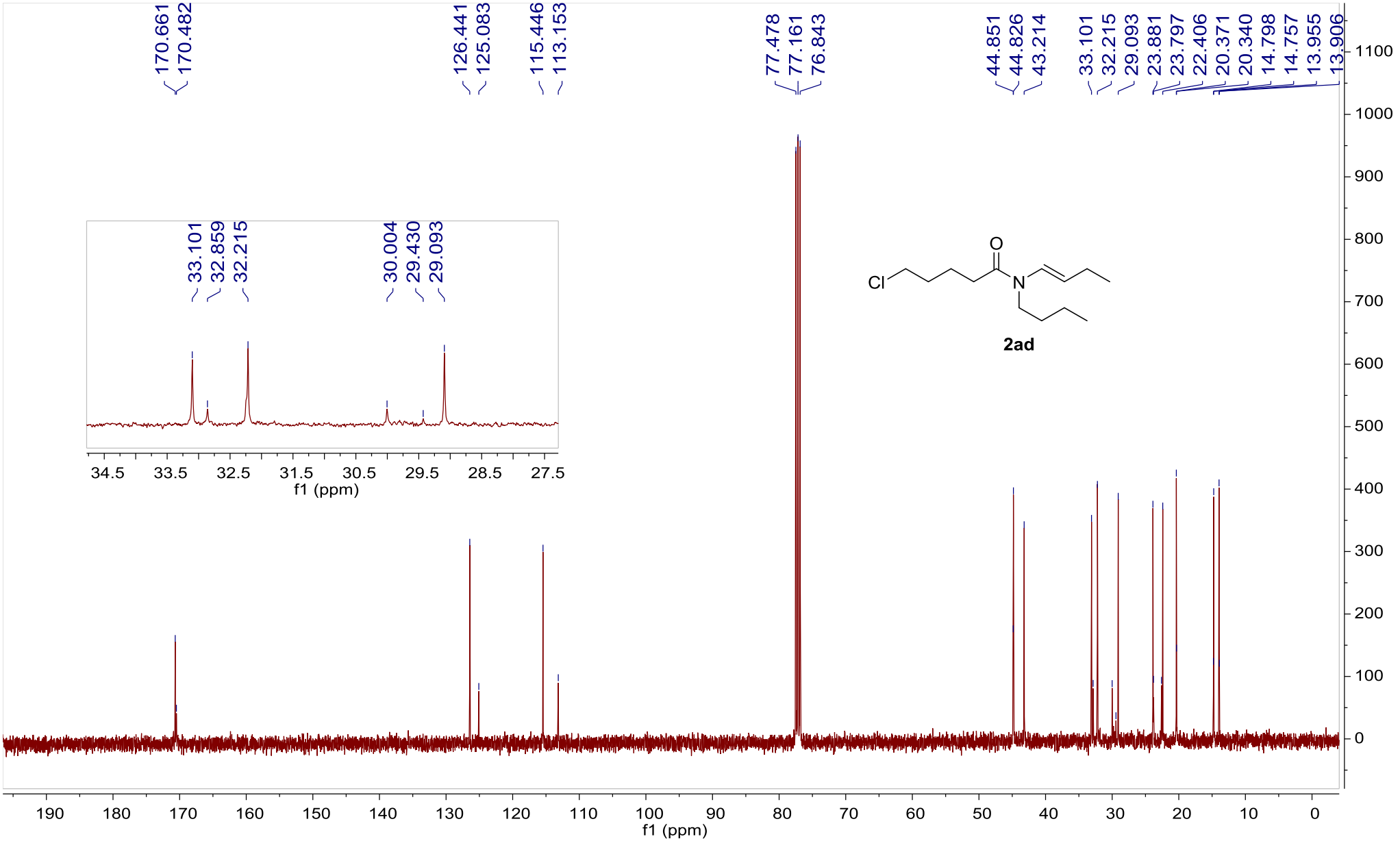
2.37
2.78
3.06
f1 (ppm)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44.826
43.214
33.101
32.215
29.093
23.881
23.797
22.406
20.371
20.340
14.798
14.757
13.955
13.906
33.101
32.859
32.215
30.004
29.430
29.093
34.5
33.5
32.5
31.5
30.5
29.5
28.5
27.5
f1 (ppm)
Cl
O
N
2ad
1100
1000
900
800
700
600
500
400
300
200
100
0
190
180
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160
150
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130
120
110
100
90
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30
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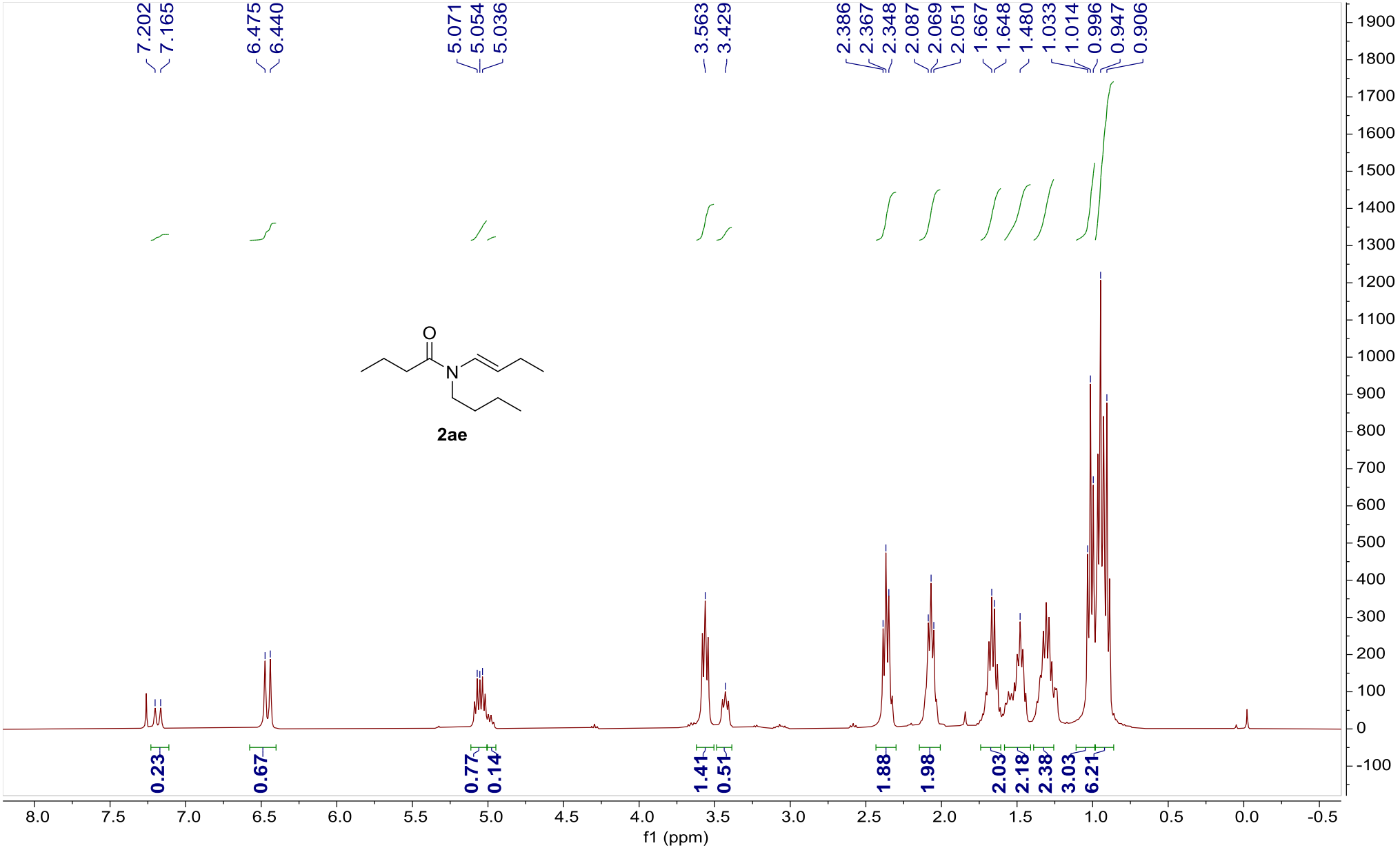
0
f1 (ppm)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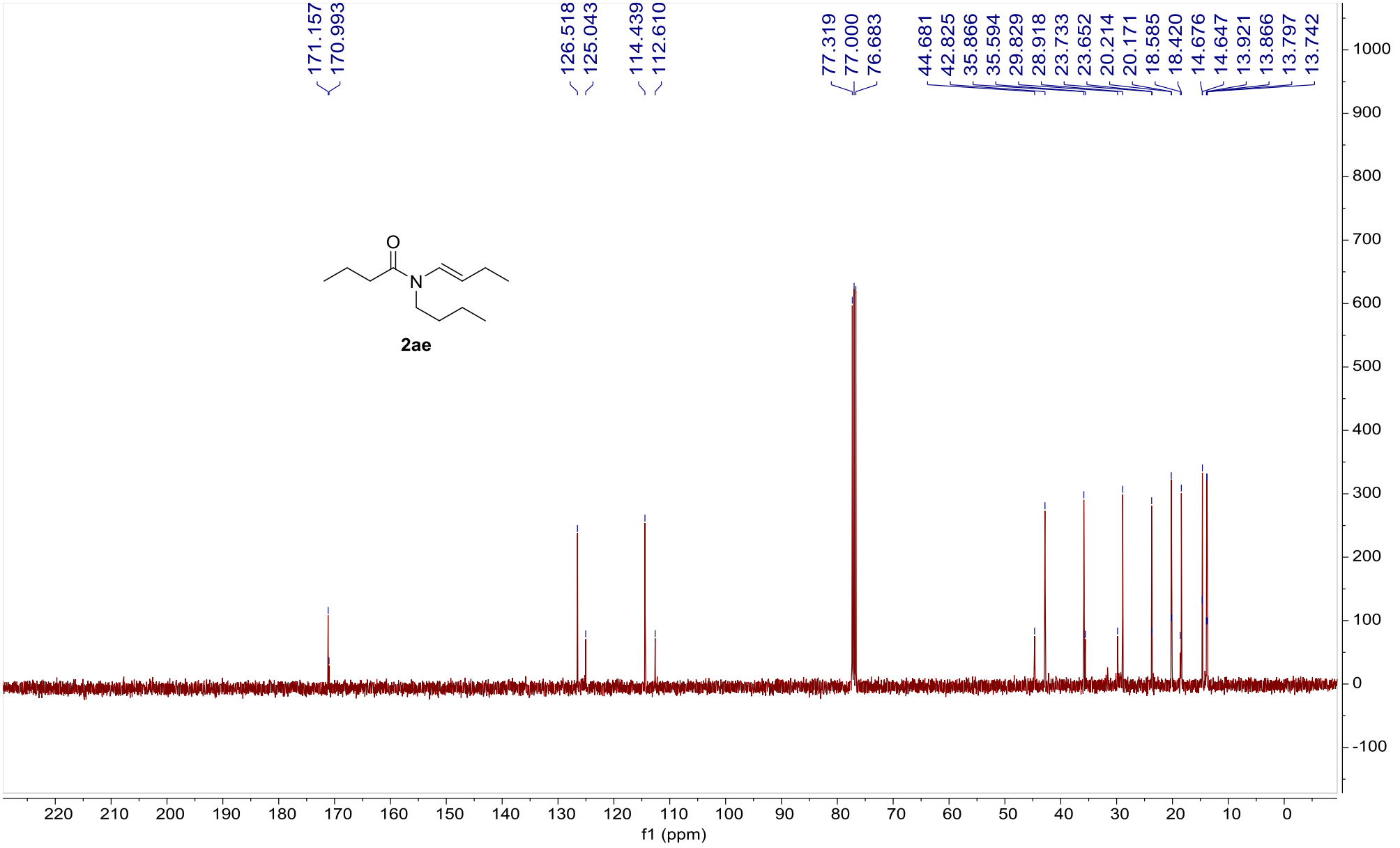
7.165
6.475
6.440
5.071
5.054
5.036
3.563
3.429
2.386
2.367
2.348
2.087
2.069
2.051
1.667
1.648
1.480
1.033
1.014
0.996
0.947
0.906
O
N
2ae
0.23
0.67
0.77
0.14
1.41
0.51
1.88
1.98
2.03
2.18
2.38
3.03
6.21
f1 (ppm)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170.993
126.518
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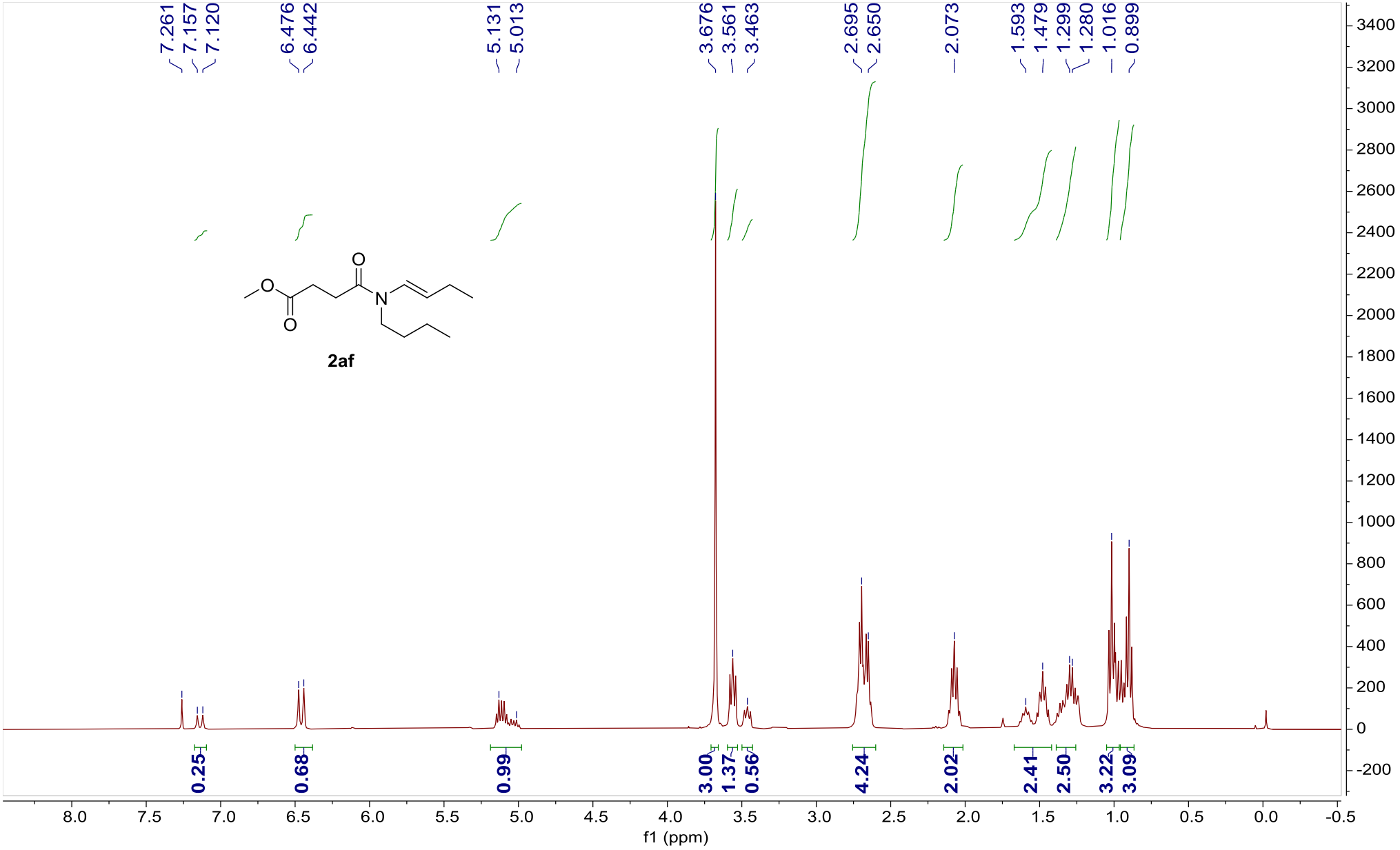
114.439
112.610
77.319
77.000
76.683
44.681
42.825
35.866
35.594
29.829
28.918
23.733
23.652
20.214
20.171
18.585
18.420
14.676
14.647
13.921
13.866
13.797
13.742
O
N
2ae
f1 (ppm)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7.157
7.120
6.476
6.442
5.131
5.013
3.676
3.561
3.463
2.695
2.650
2.073
1.593
1.479
1.299
1.280
1.016
0.899
O
O
O
N
2af
0.25
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1.37
0.56
4.24
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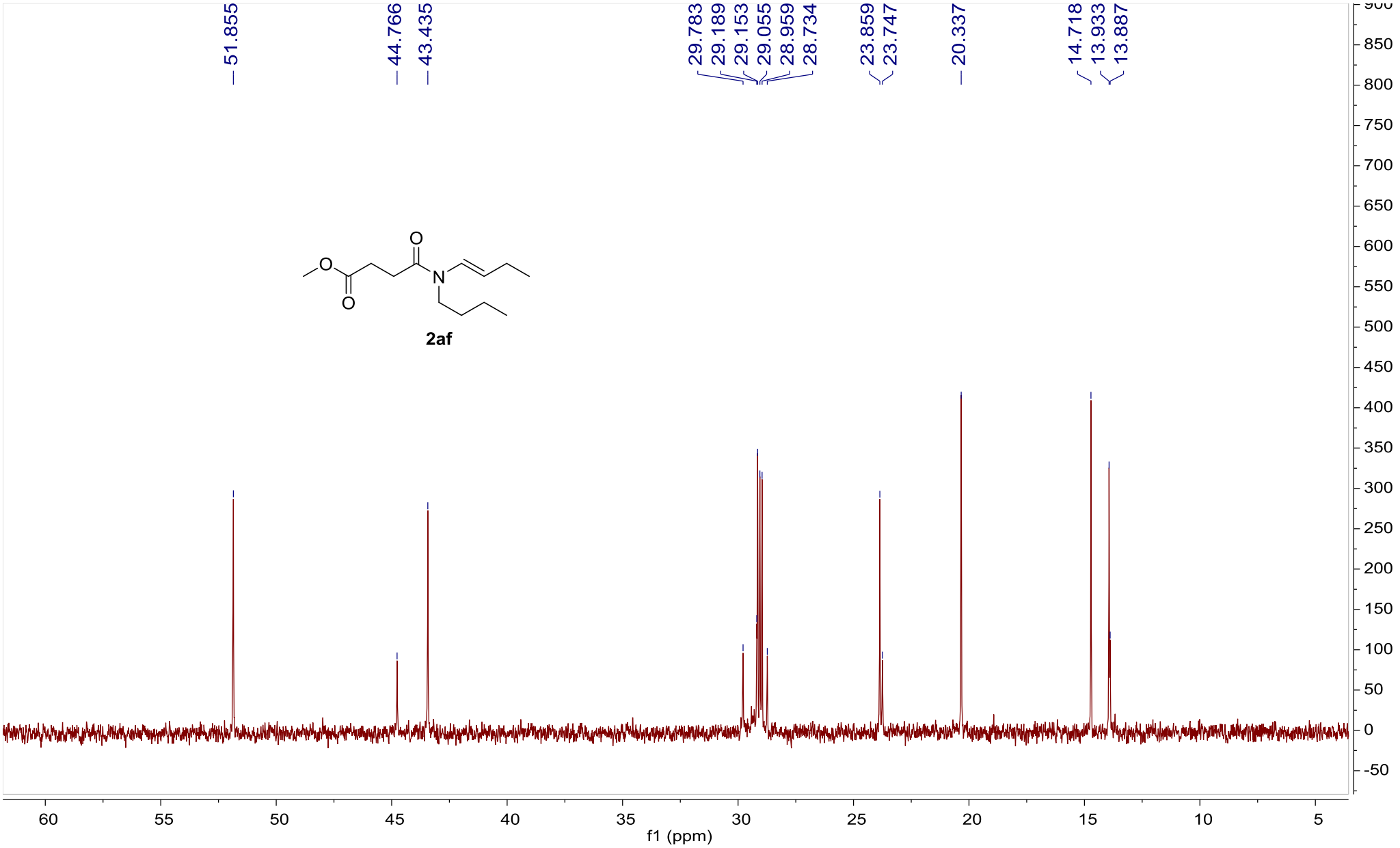
2.41
2.50
3.22
3.09
f1 (ppm)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44.766
43.435
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29.189
29.153
29.055
28.959
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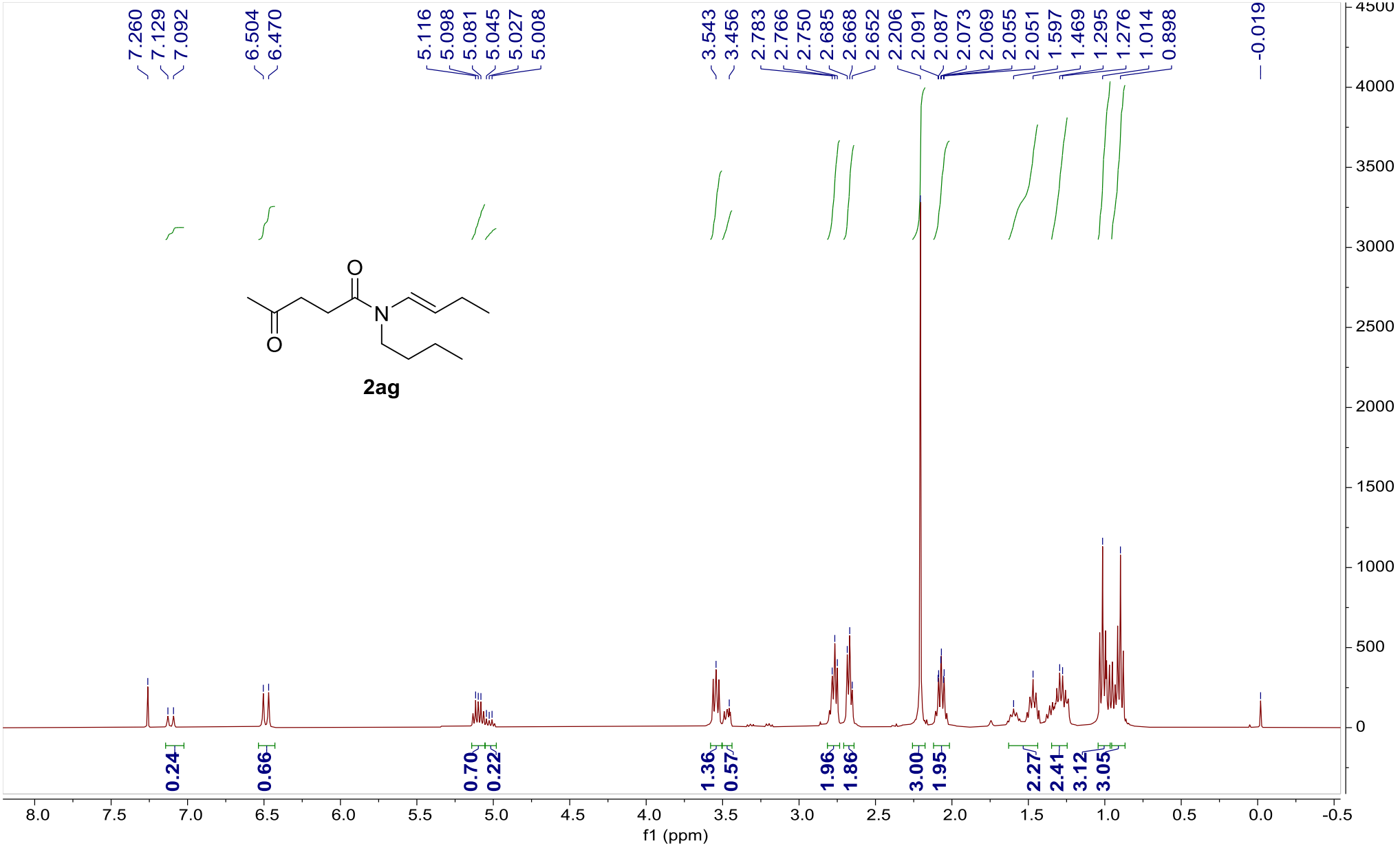
23.747
20.337
14.718
13.933
13.887
O
O
O
N
2af
f1 (ppm)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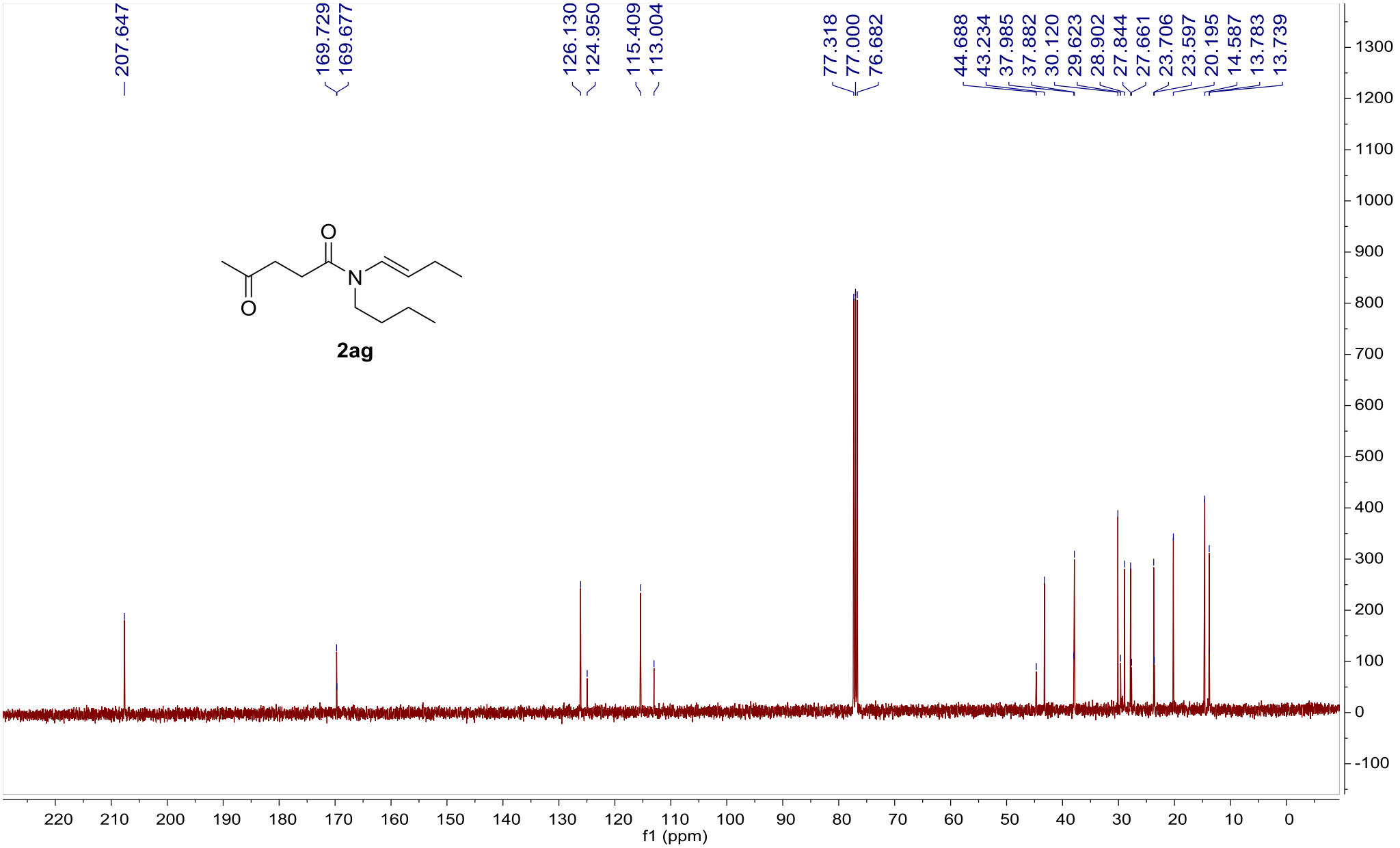
7.129
7.092
6.504
6.470
5.116
5.098
5.081
5.045
5.027
5.008
3.543
3.456
2.783
2.766
2.750
2.685
2.668
2.652
2.206
2.091
2.087
2.073
2.069
2.055
2.051
1.597
1.469
1.295
1.276
1.014
0.898
-0.019
O
O
N
2ag
0.24
0.66
0.70
0.22
1.36
0.57
1.96
1.86
3.00
1.95
2.27
2.41
3.12
3.05
f1 (ppm)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169.677
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115.409
113.004
77.318
77.000
76.682
44.688
43.234
37.985
37.882
30.120
29.623
28.902
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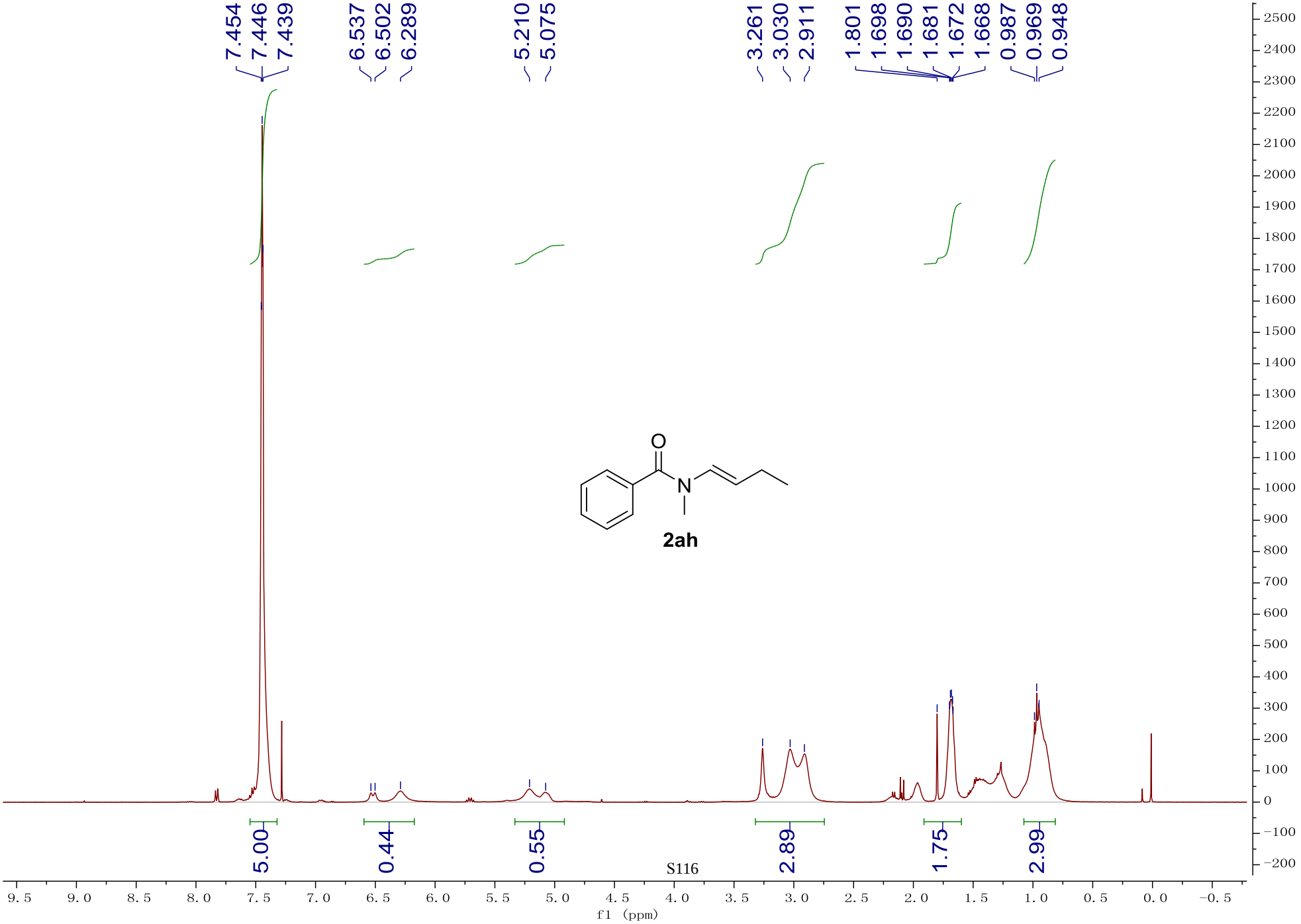
23.597
20.195
14.587
13.783
13.739
O
O
N
2ag
f1 (ppm)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7.446
7.439
6.537
6.502
6.289
5.210
5.075
3.261
3.030
2.911
1.801
1.698
1.690
1.681
1.672
1.668
0.987
0.969
0.948
O
N
2ah
5.00
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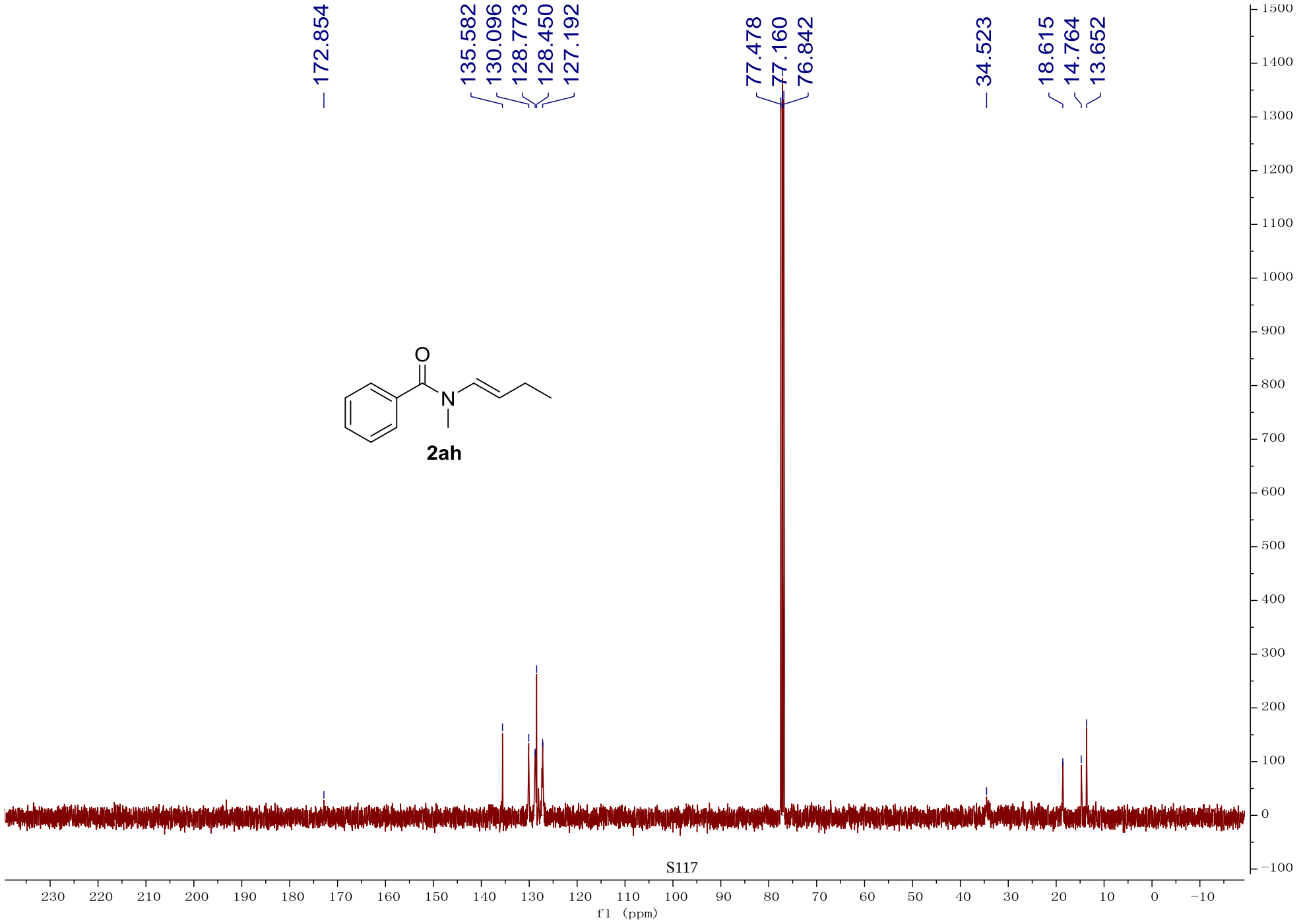
0.55
2.89
1.75
2.99
f1 (ppm)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130.096
128.773
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77.160
76.842
34.523
18.615
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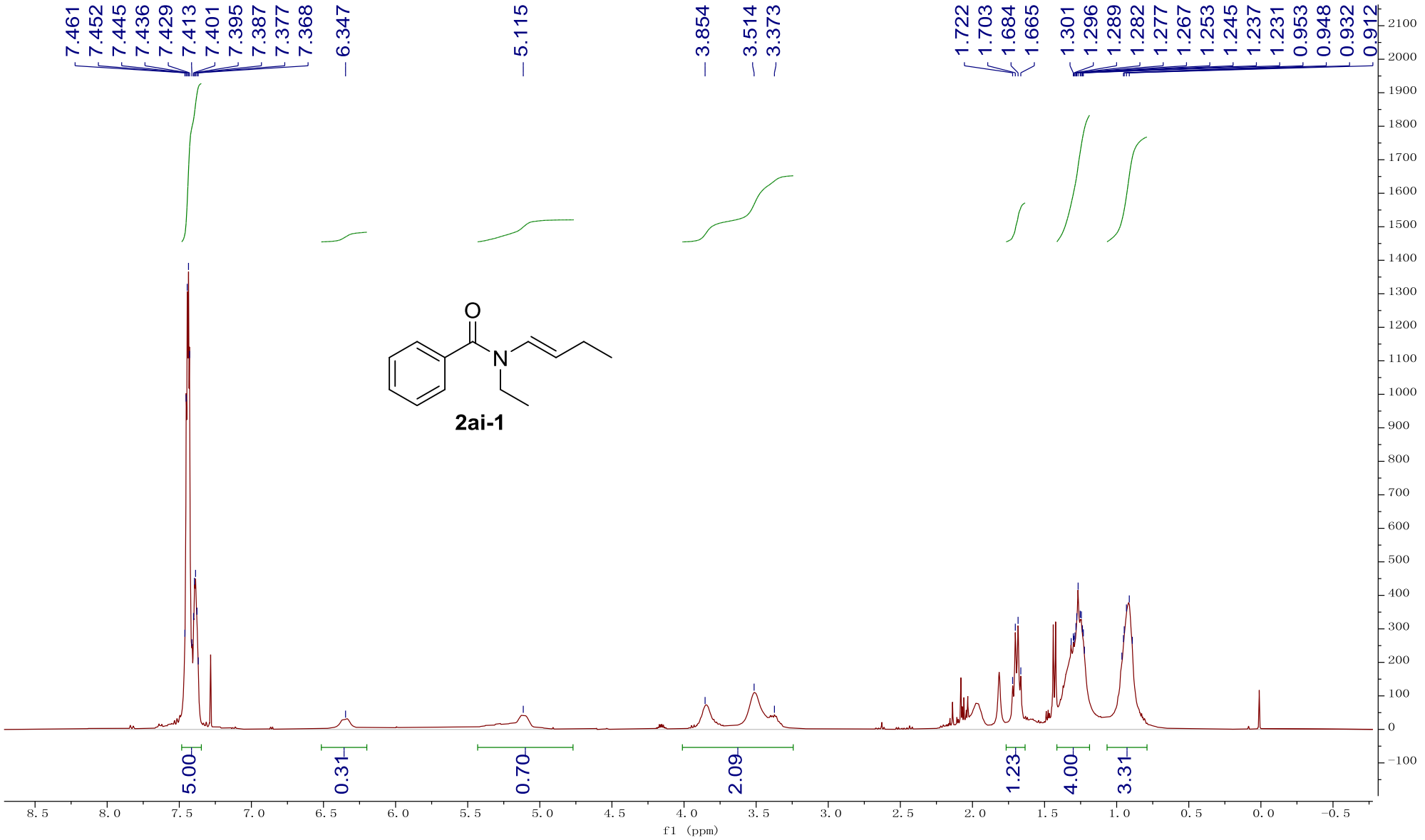
O
N
2ah
f1 (ppm)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7.436
7.429
7.413
7.401
7.395
7.387
7.377
7.368
6.347
5.115
3.854
3.514
3.373
1.722
1.703
1.684
1.665
1.301
1.296
1.289
1.282
1.277
1.267
1.253
1.245
1.237
1.231
0.953
0.948
0.932
0.912
O
N
2ai-1
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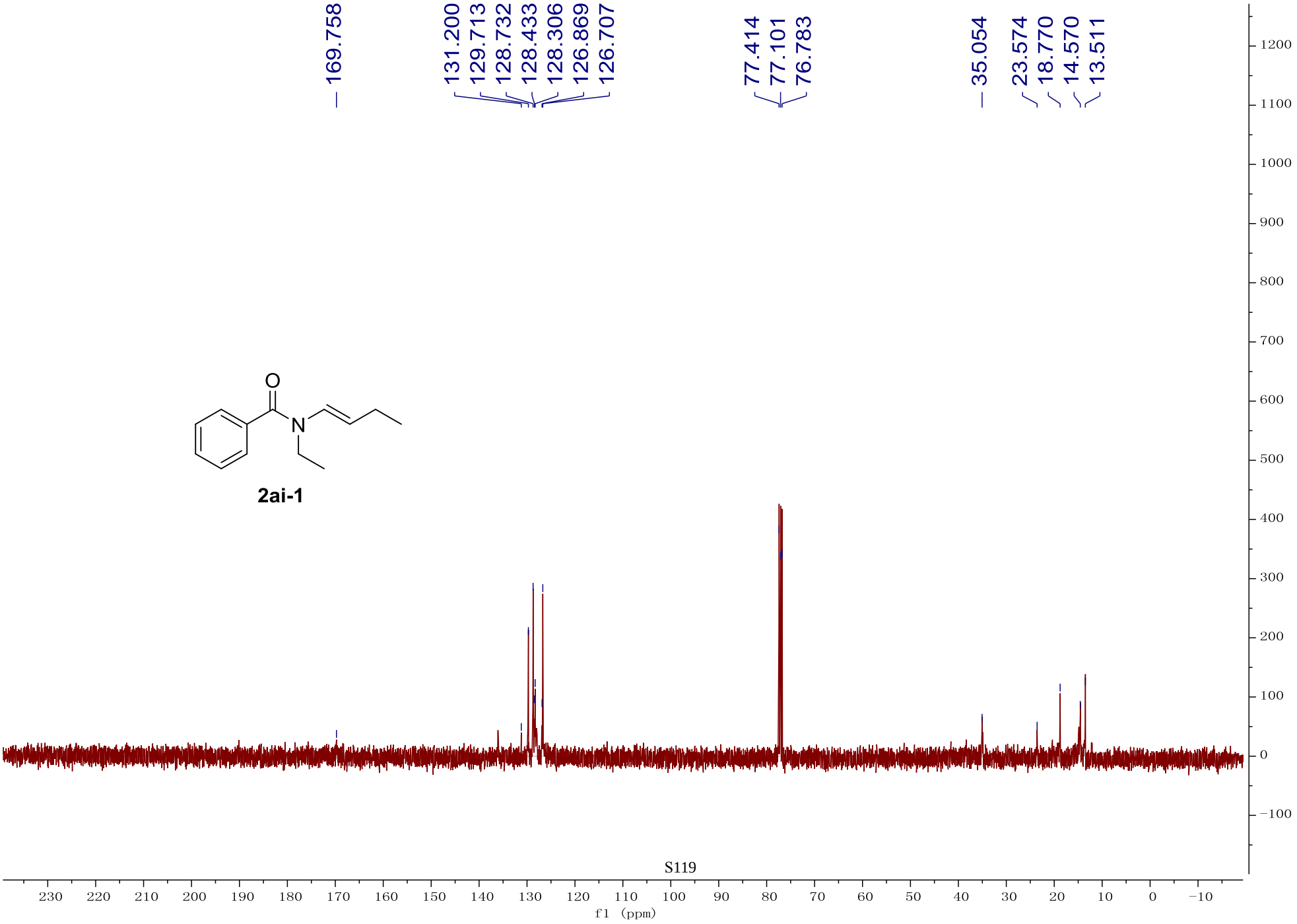
1.23
4.00
3.31
f1 (ppm)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126.707
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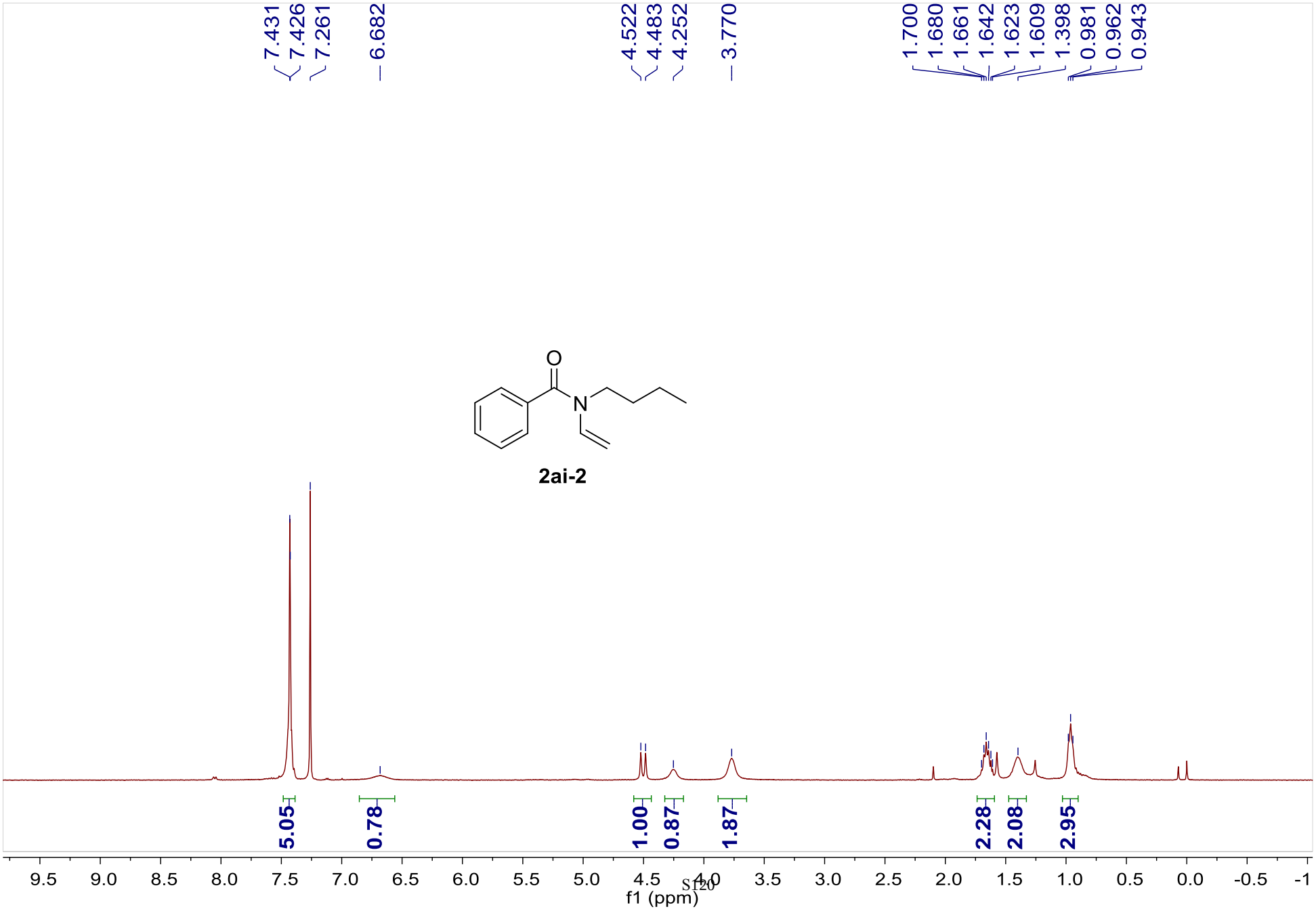
77.101
76.783
35.054
23.574
18.770
14.570
13.511
O
N
2ai-1
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.261
6.682
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4.483
4.252
3.770
1.700
1.680
1.661
1.642
1.623
1.609
1.398
0.981
0.962
0.943
O
N
2ai-2
5.05
0.78
1.00
0.87
1.87
2.28
2.08
2.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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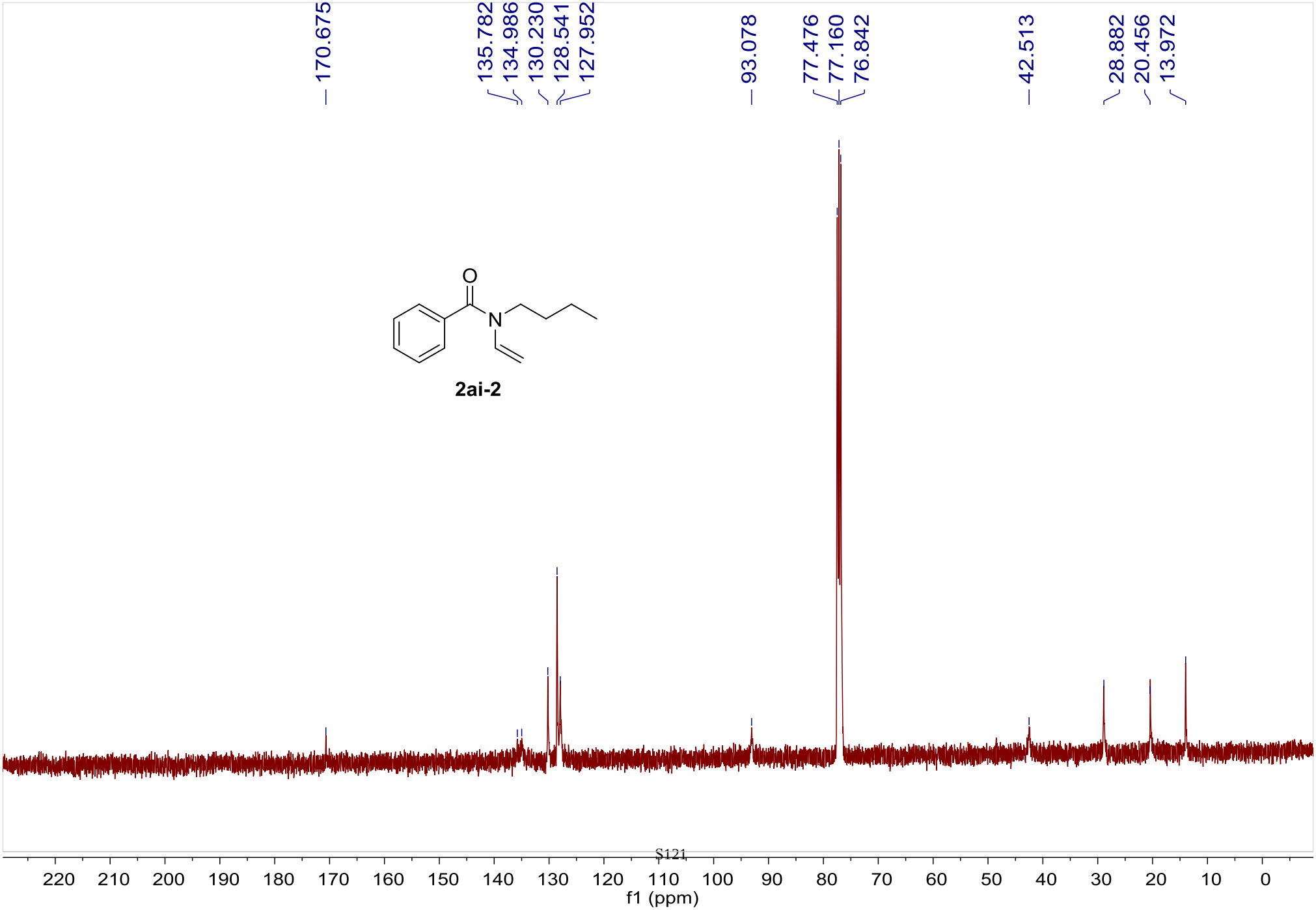
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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134.986
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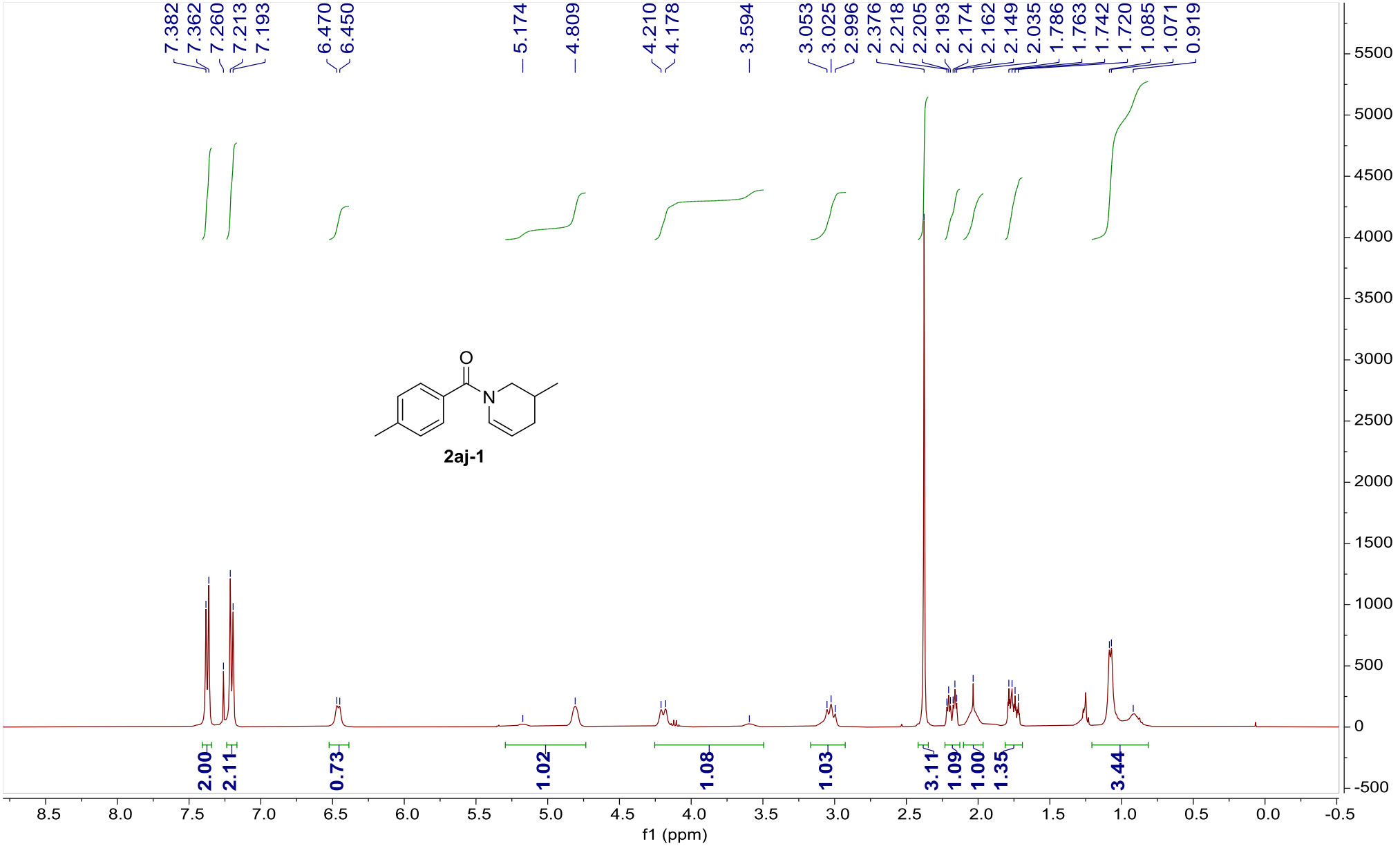
128.541
127.952
93.078
77.476
77.160
76.842
42.513
28.882
20.456
13.972
O
N
2ai-2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.213
7.193
6.470
6.450
5.174
4.809
4.210
4.178
3.594
3.053
3.025
2.996
2.376
2.218
2.205
2.193
2.174
2.162
2.149
2.035
1.786
1.763
1.742
1.720
1.085
1.071
0.919
O
N
2aj-1
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1.02
1.08
1.03
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1.09
1.00
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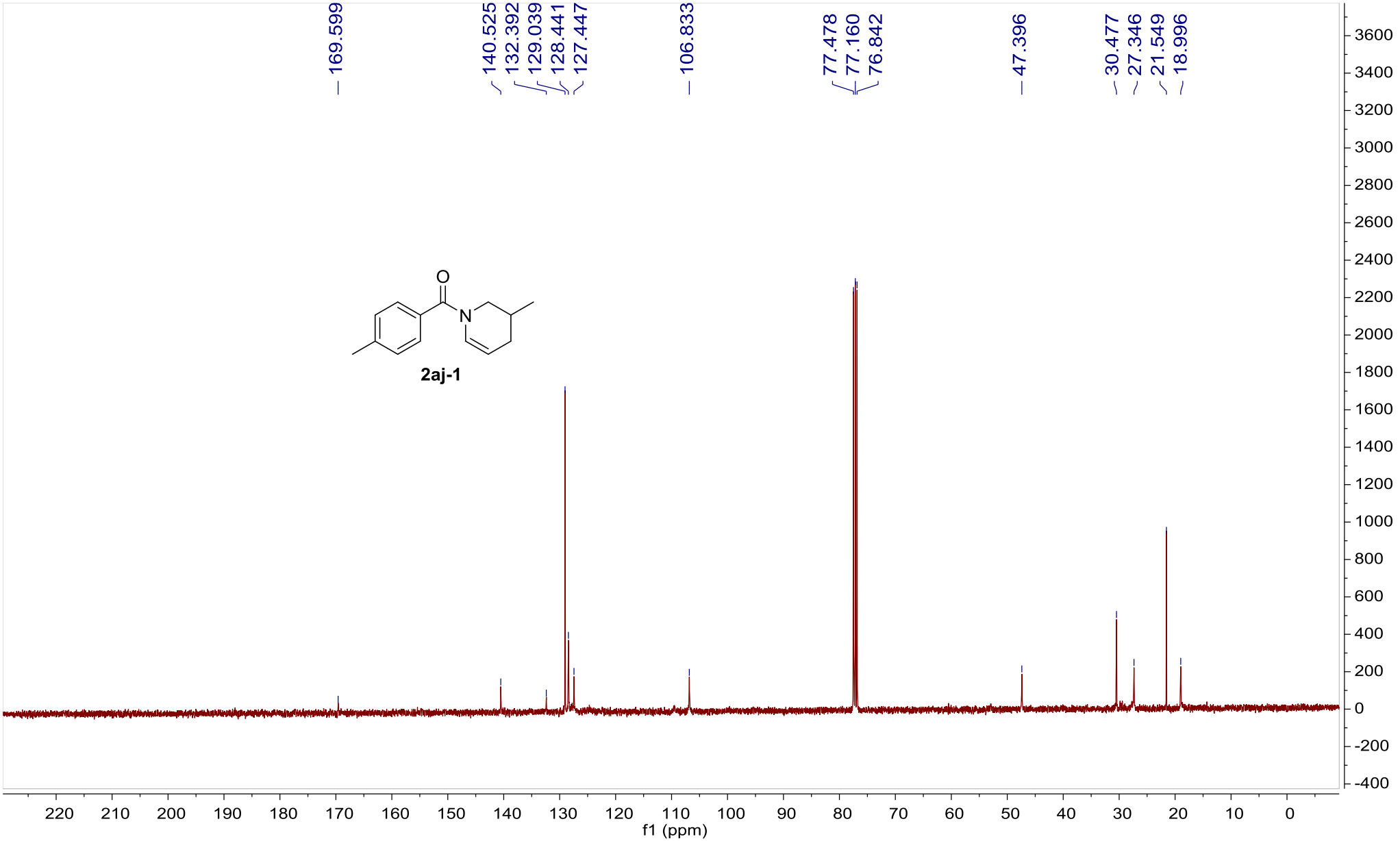
3.44
f1 (ppm)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129.039
128.441
127.447
106.833
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76.842
47.396
30.477
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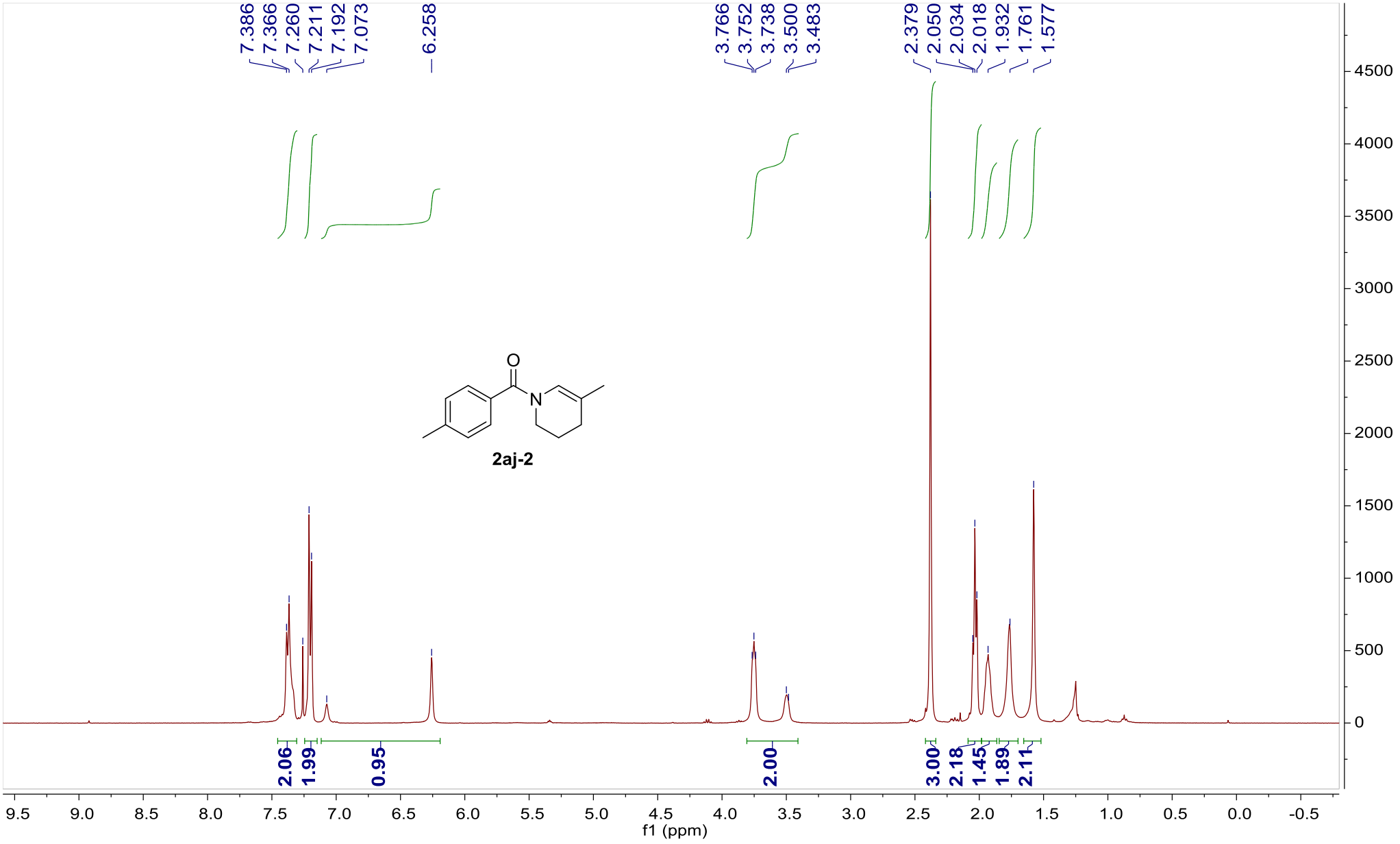
21.549
18.996
O
N
2aj-1
f1 (ppm)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7.211
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7.073
6.258
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3.738
3.500
3.483
2.379
2.050
2.034
2.018
1.932
1.761
1.577
O
N
2aj-2
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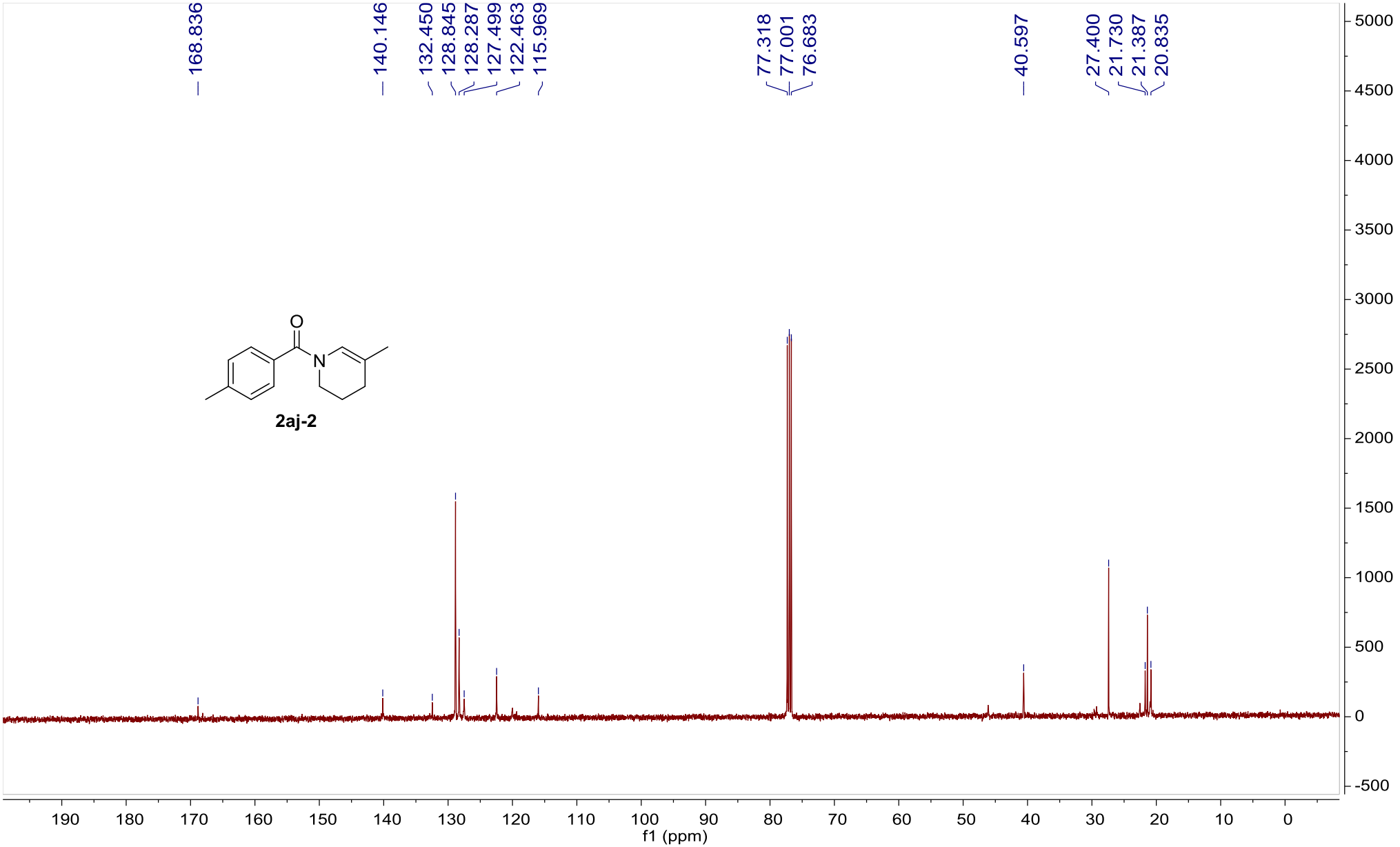
2.11
f1 (ppm)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122.463
115.969
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77.001
76.683
40.597
27.400
21.730
21.387
20.835
O
N
2aj-2
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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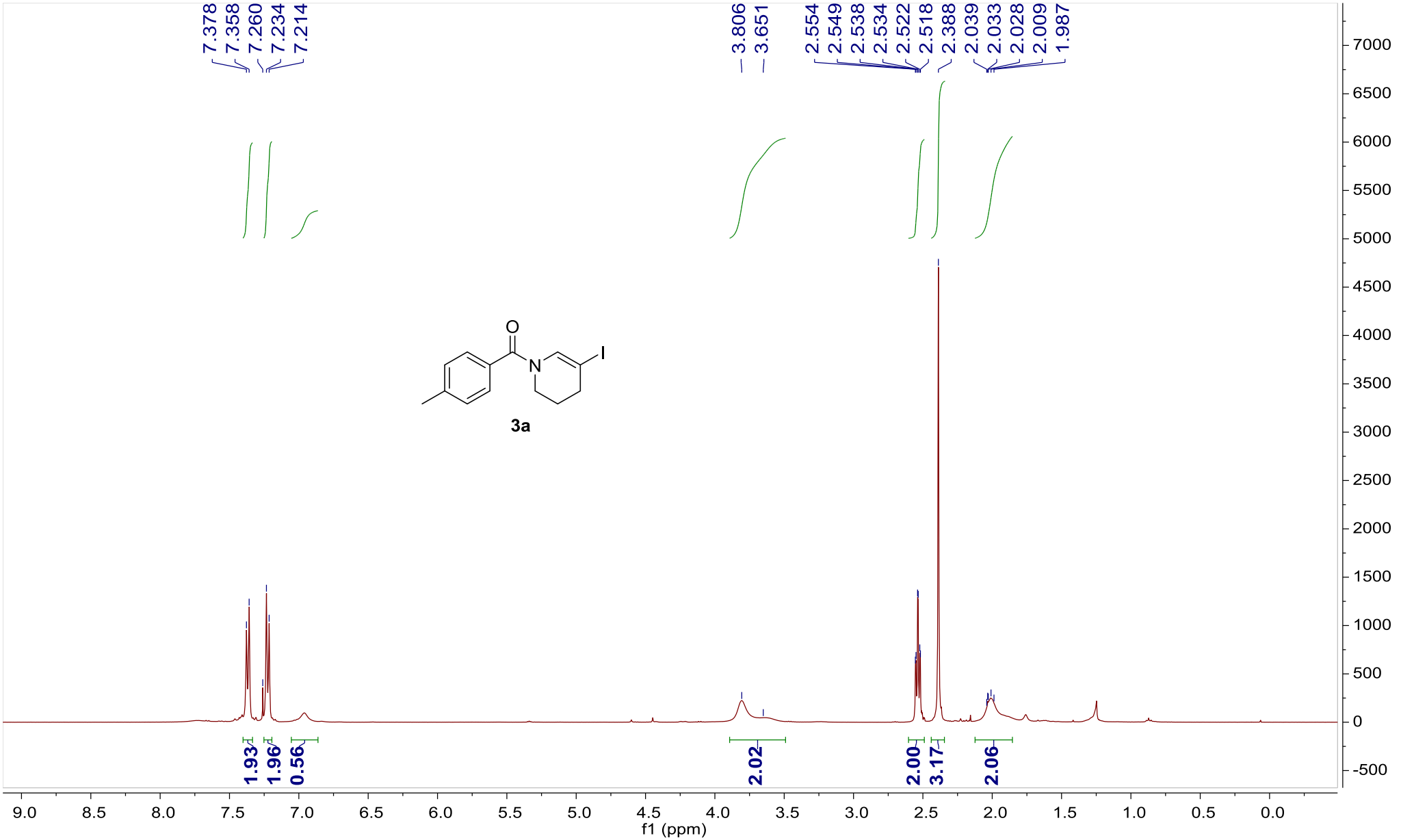
f1 (ppm)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2.534
2.522
2.518
2.388
2.039
2.033
2.028
2.009
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N
I
3a
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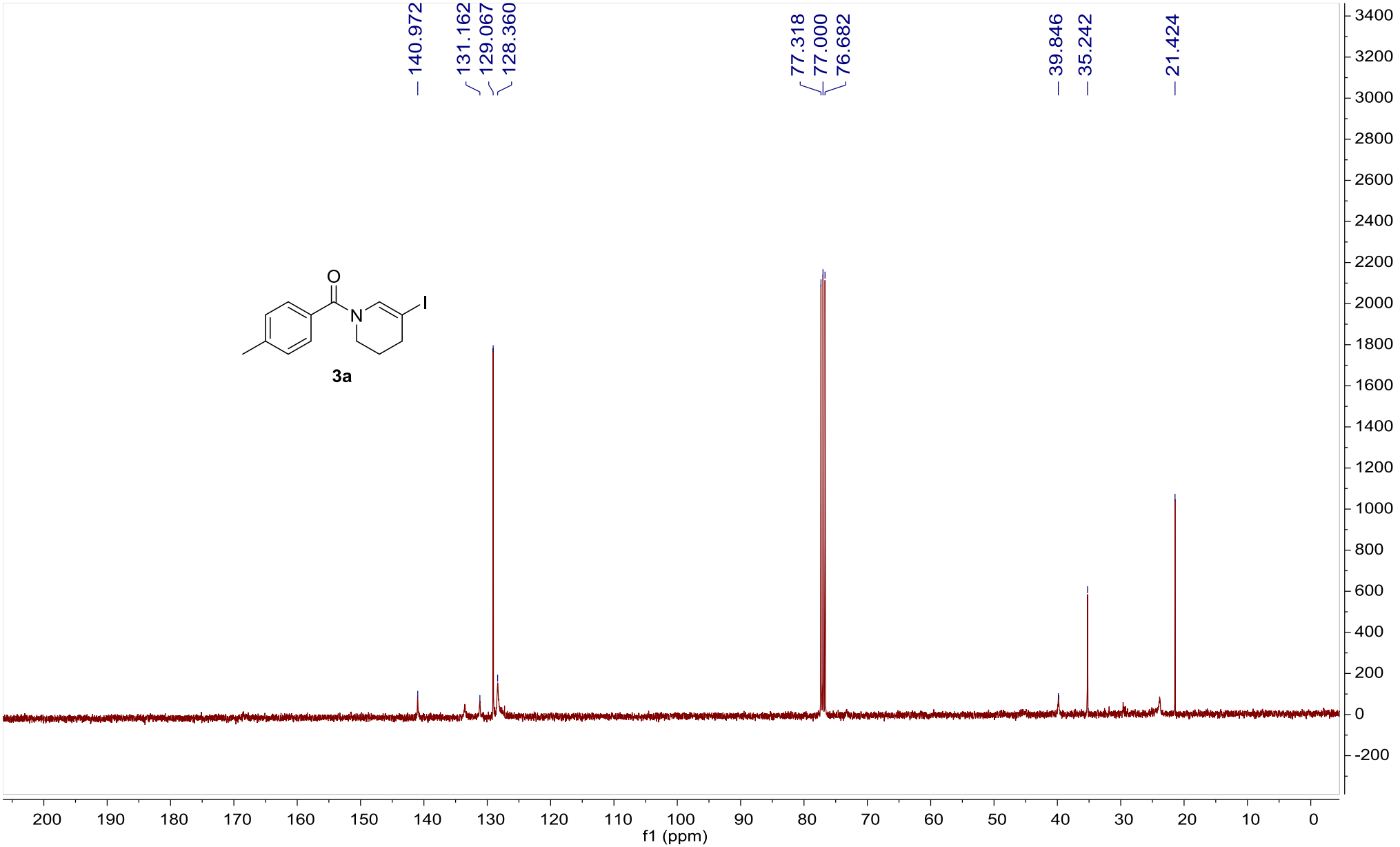
2.00
3.17
2.06
f1 (ppm)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39.846
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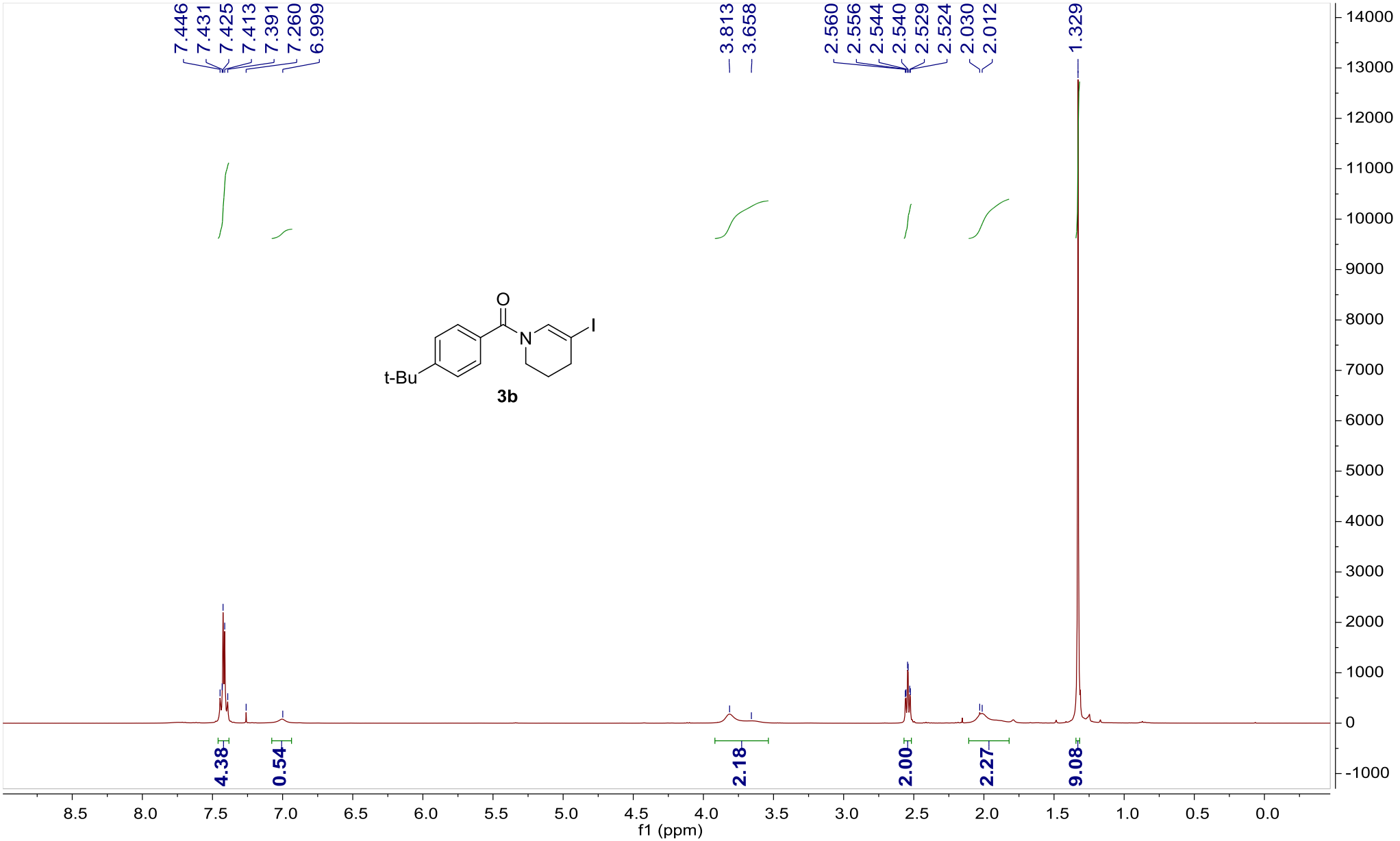
21.424
O
N
I
3a
f1 (ppm)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2.556
2.544
2.540
2.529
2.524
2.030
2.012
1.329
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I
t-Bu
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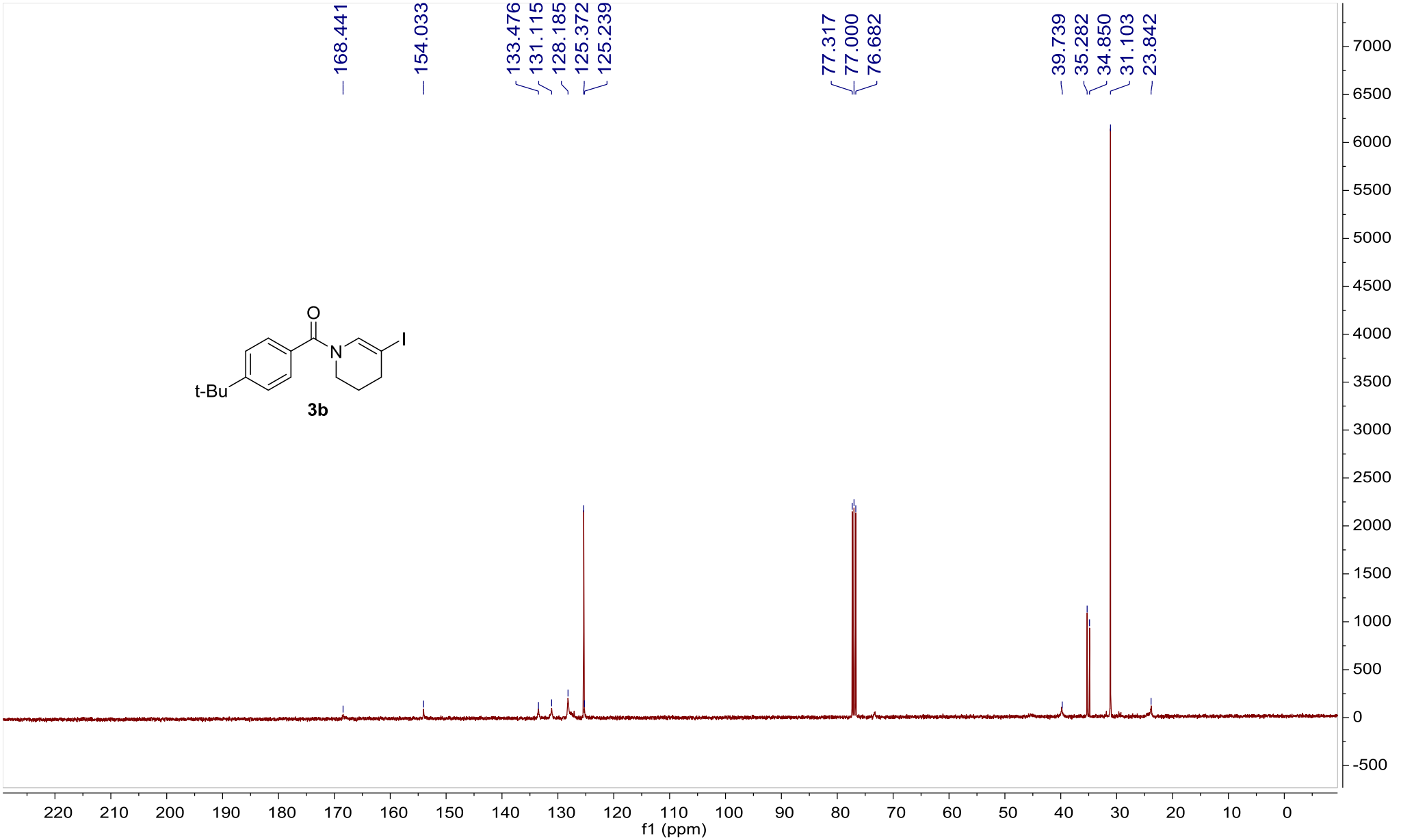
9.08
f1 (ppm)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77.317
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76.682
39.739
35.282
34.850
31.103
23.842
O
N
I
t-Bu
3b
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
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50
40
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20
10
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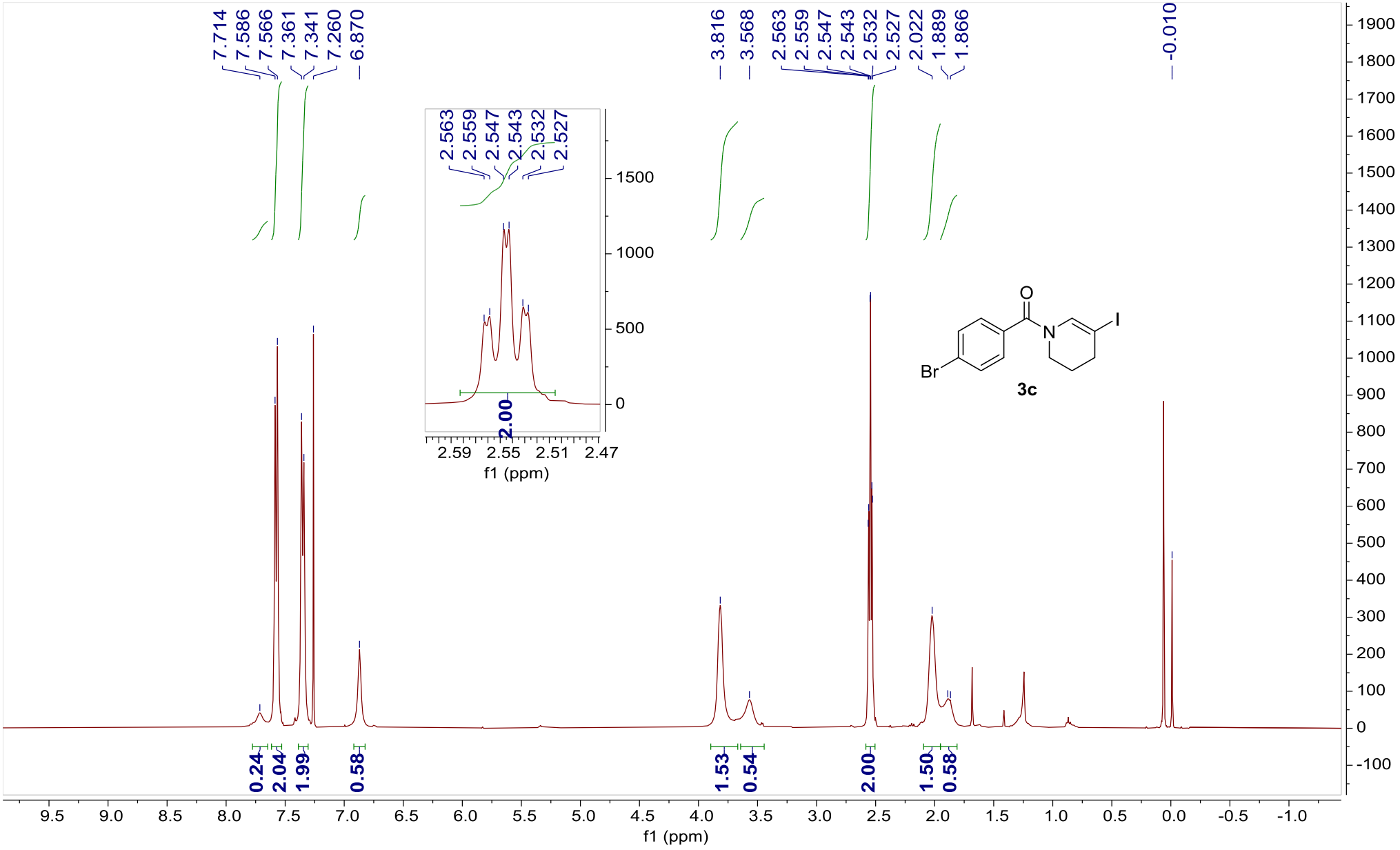
f1 (ppm)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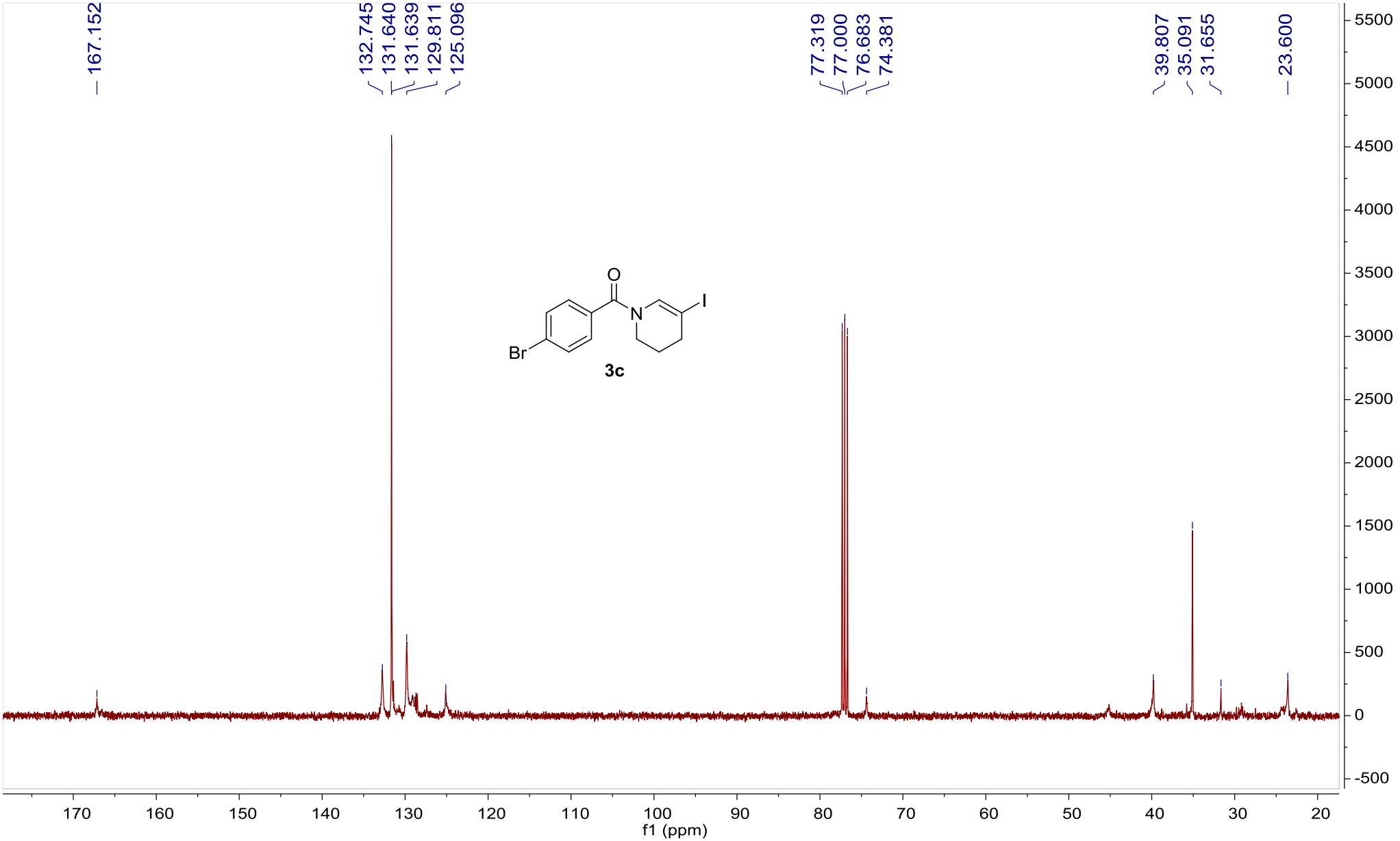
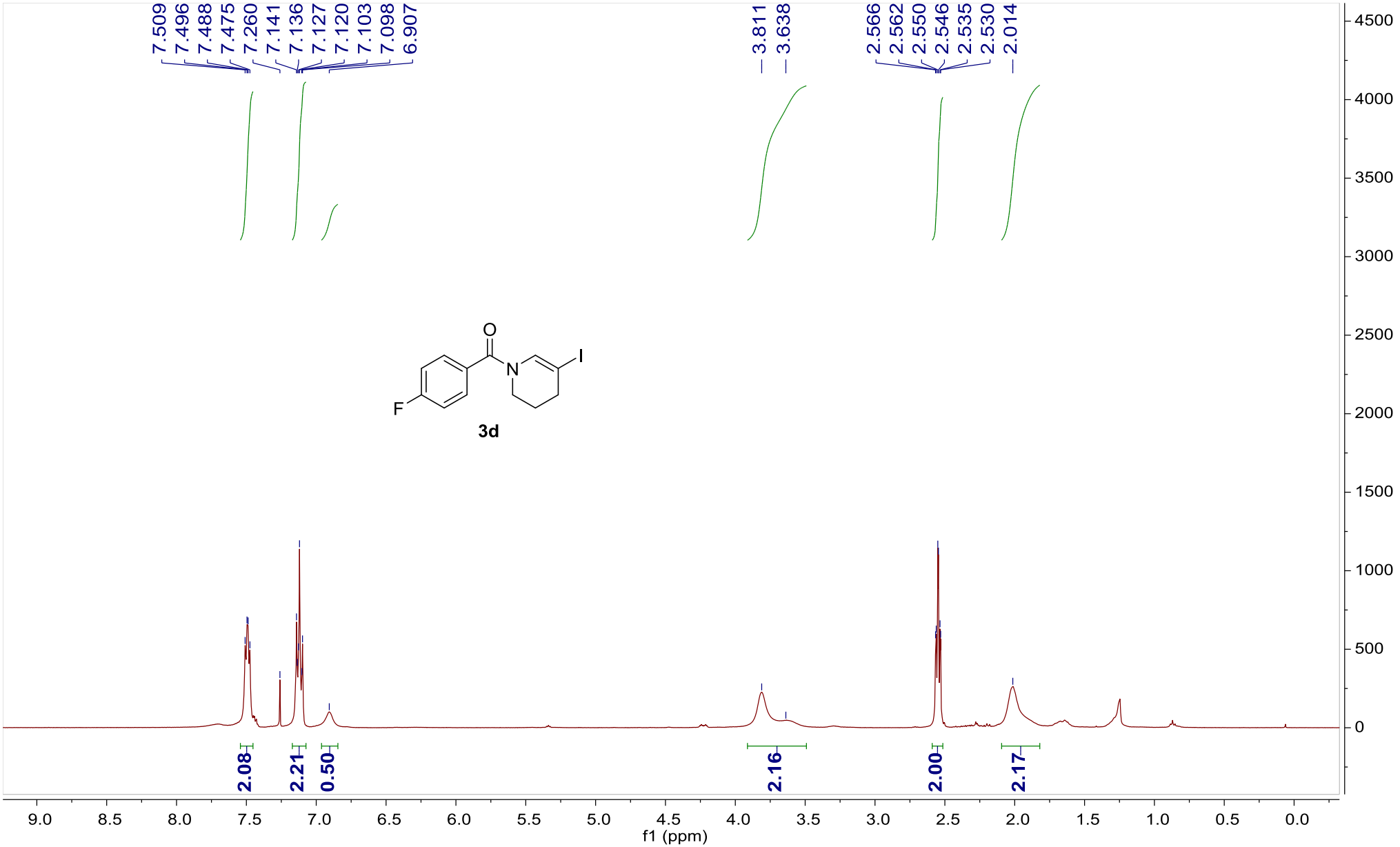
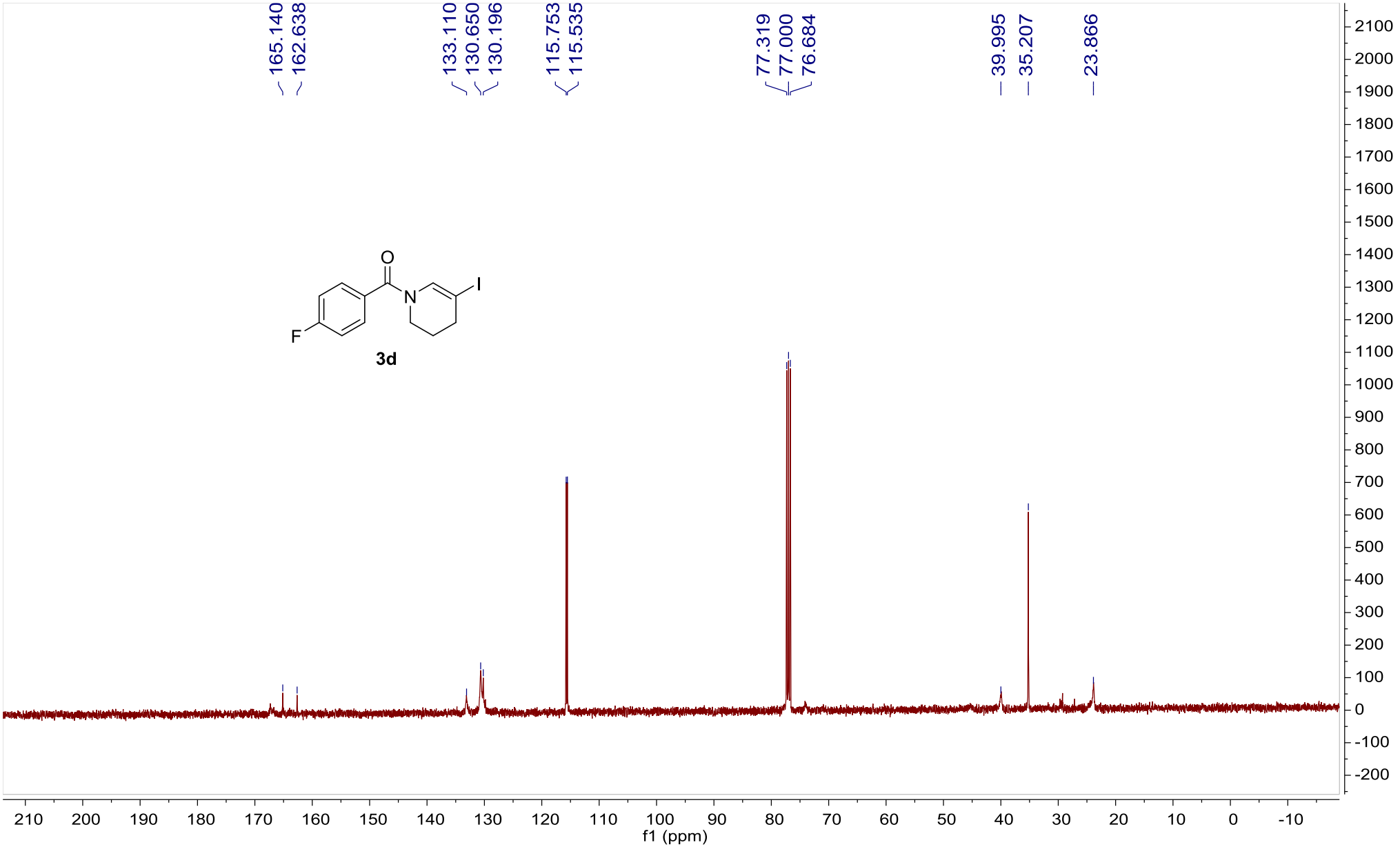
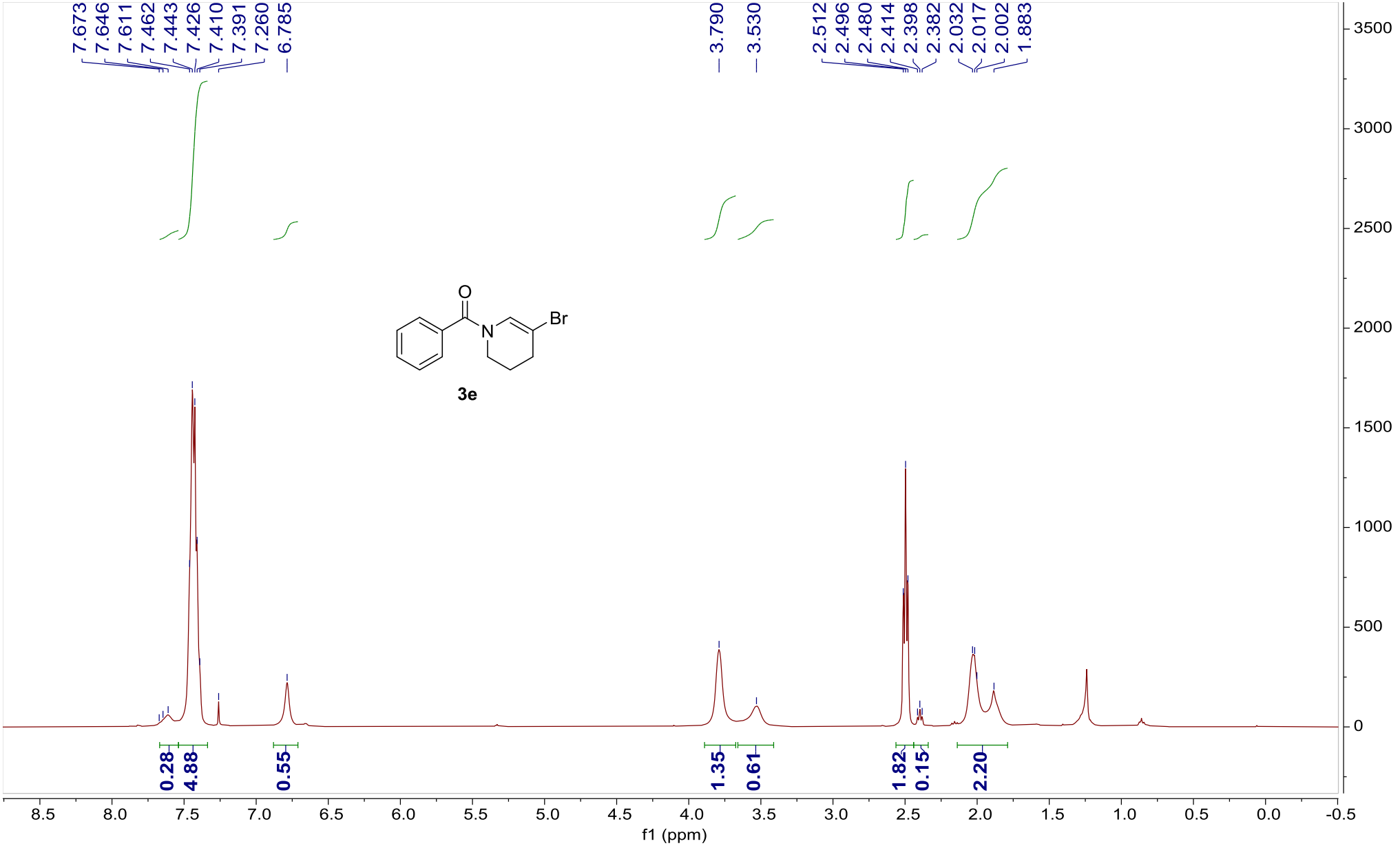
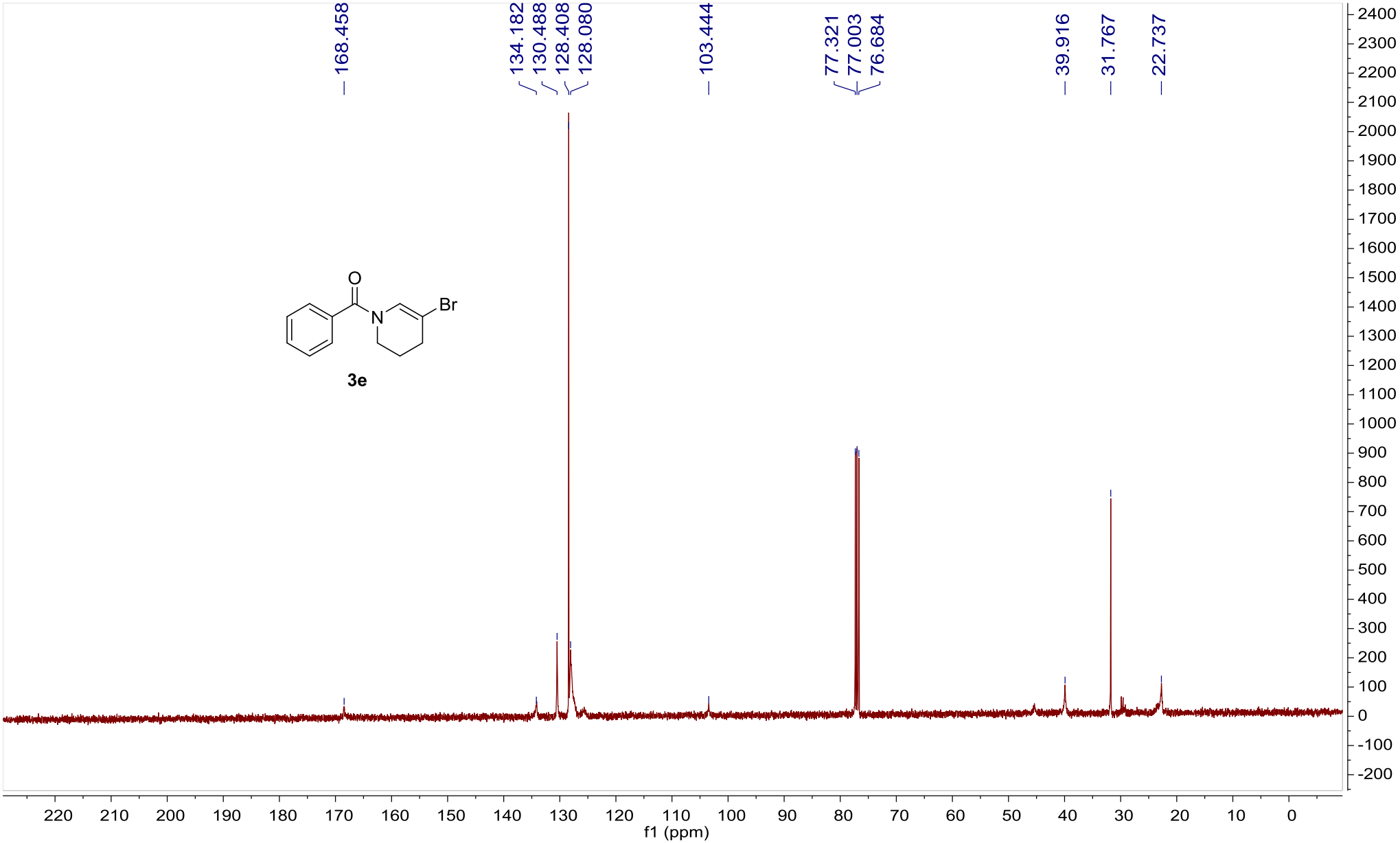
7.566
7.361
7.341
7.260
6.870
3.816
3.568
2.563
2.559
2.547
2.543
2.532
2.527
2.022
1.889
1.866
-0.010
0.24
2.04
1.99
0.58
1.53
0.54
2.00
1.50
0.58
f1 (ppm)
O
N
I
Br
3c


167.152
132.745
131.640
131.639
129.811
125.096
77.319
77.000
76.683
74.381
39.807
35.091
31.655
23.600
O
N
I
Br
3c
f1 (ppm)


7.509
7.496
7.488
7.475
7.260
7.141
7.136
7.127
7.120
7.103
7.098
6.907
3.811
3.638
2.566
2.562
2.550
2.546
2.535
2.530
2.014
O
N
I
F
3d
2.08
2.21
0.50
2.16
2.00
2.17
f1 (ppm)


165.140
162.638
133.110
130.650
130.196
115.753
115.535
77.319
77.000
76.684
39.995
35.207
23.866
O
N
I
F
3d
f1 (ppm)


7.673
7.646
7.611
7.462
7.443
7.426
7.410
7.391
7.260
6.785
3.790
3.530
2.512
2.496
2.480
2.414
2.398
2.382
2.032
2.017
2.002
1.883
O
N
Br
3e
0.28
4.88
0.55
1.35
0.61
1.82
0.15
2.20
f1 (ppm)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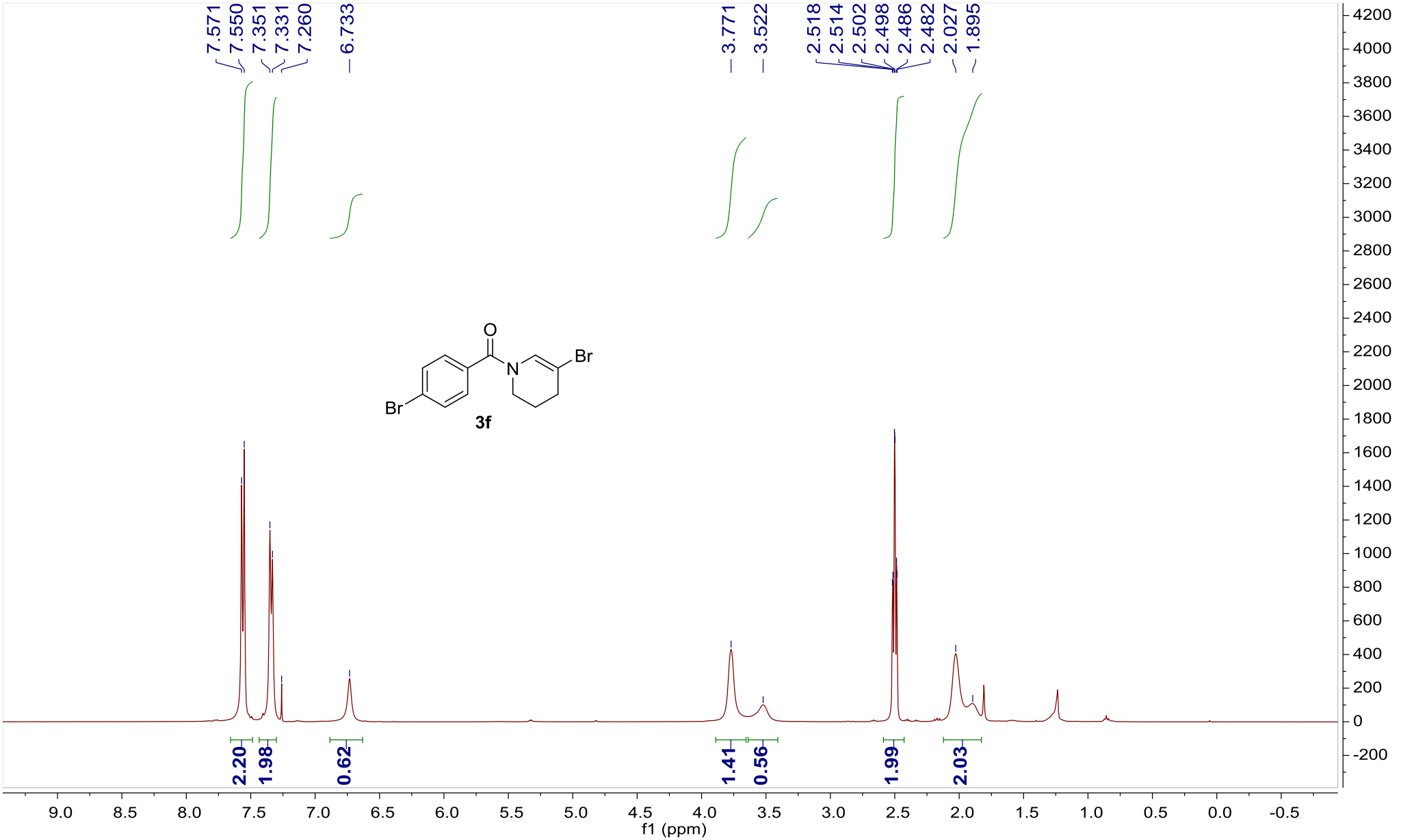
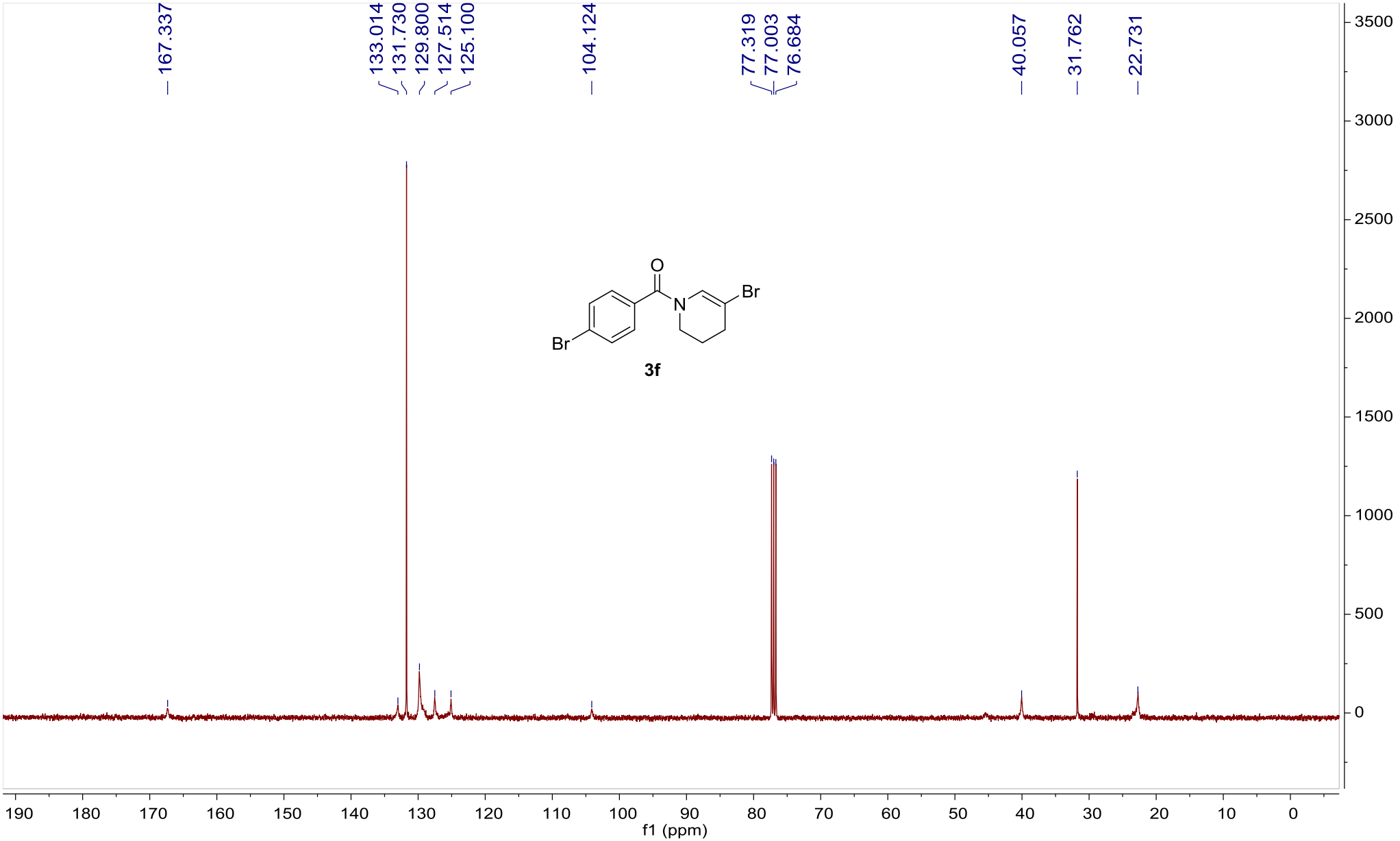
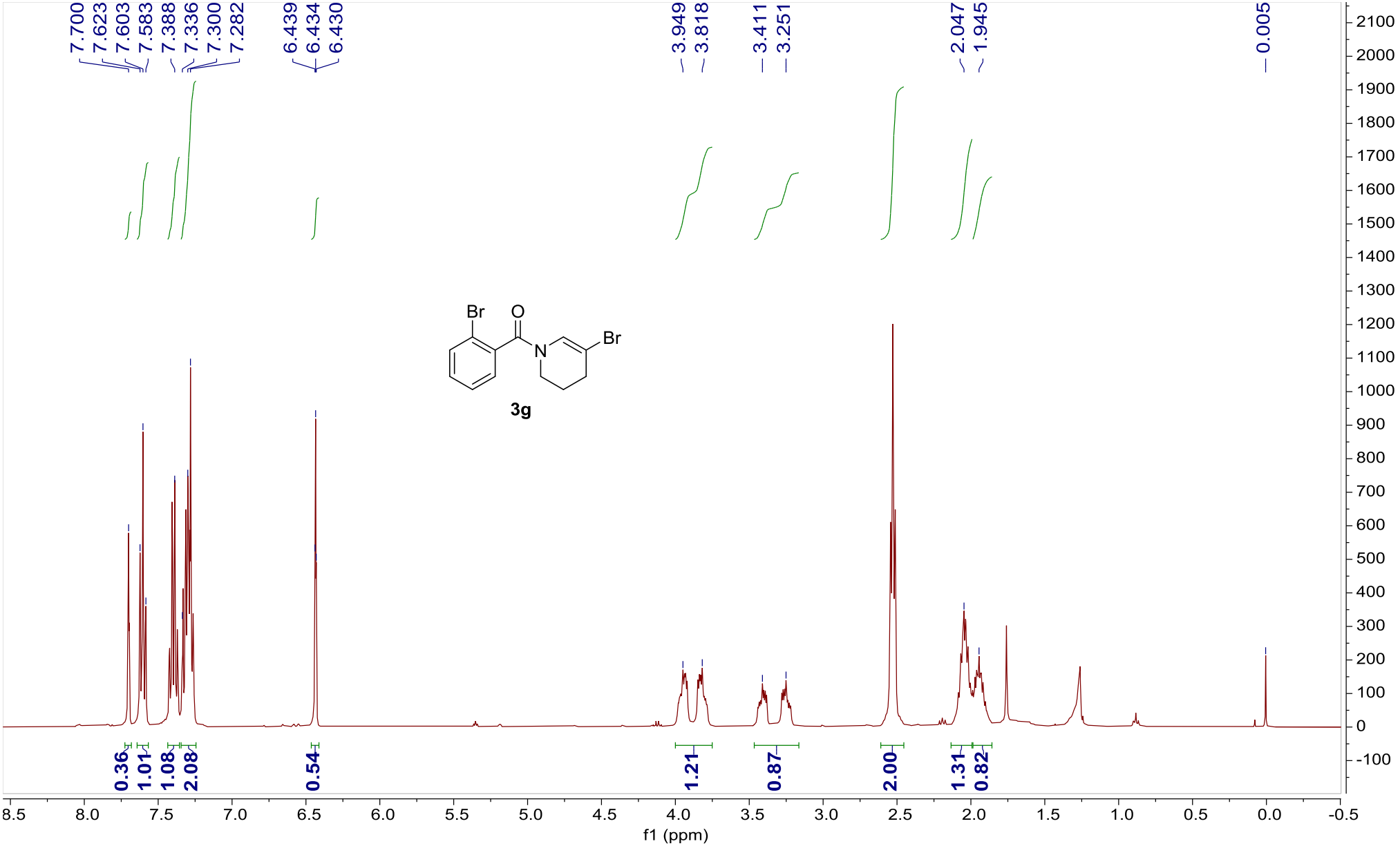
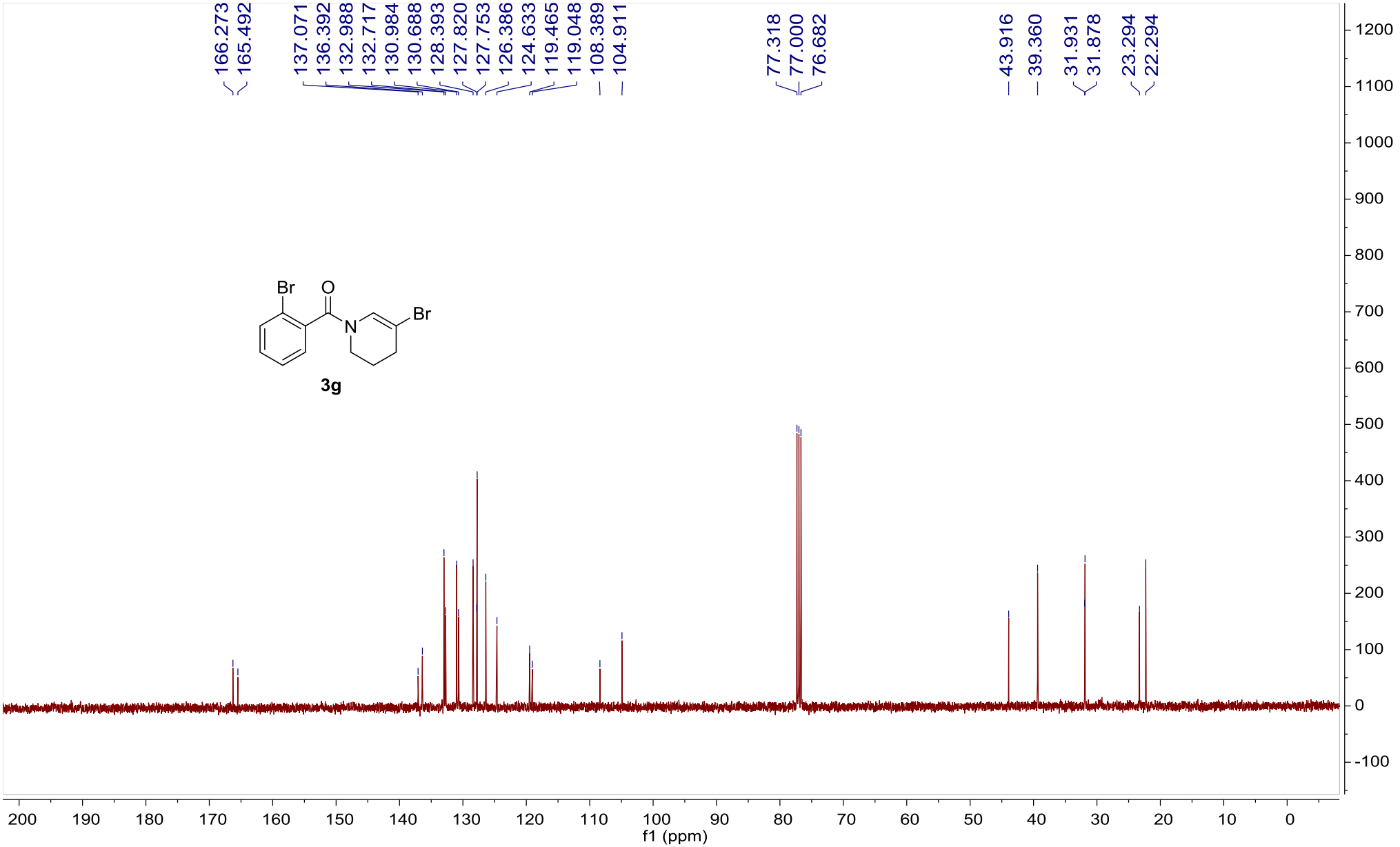
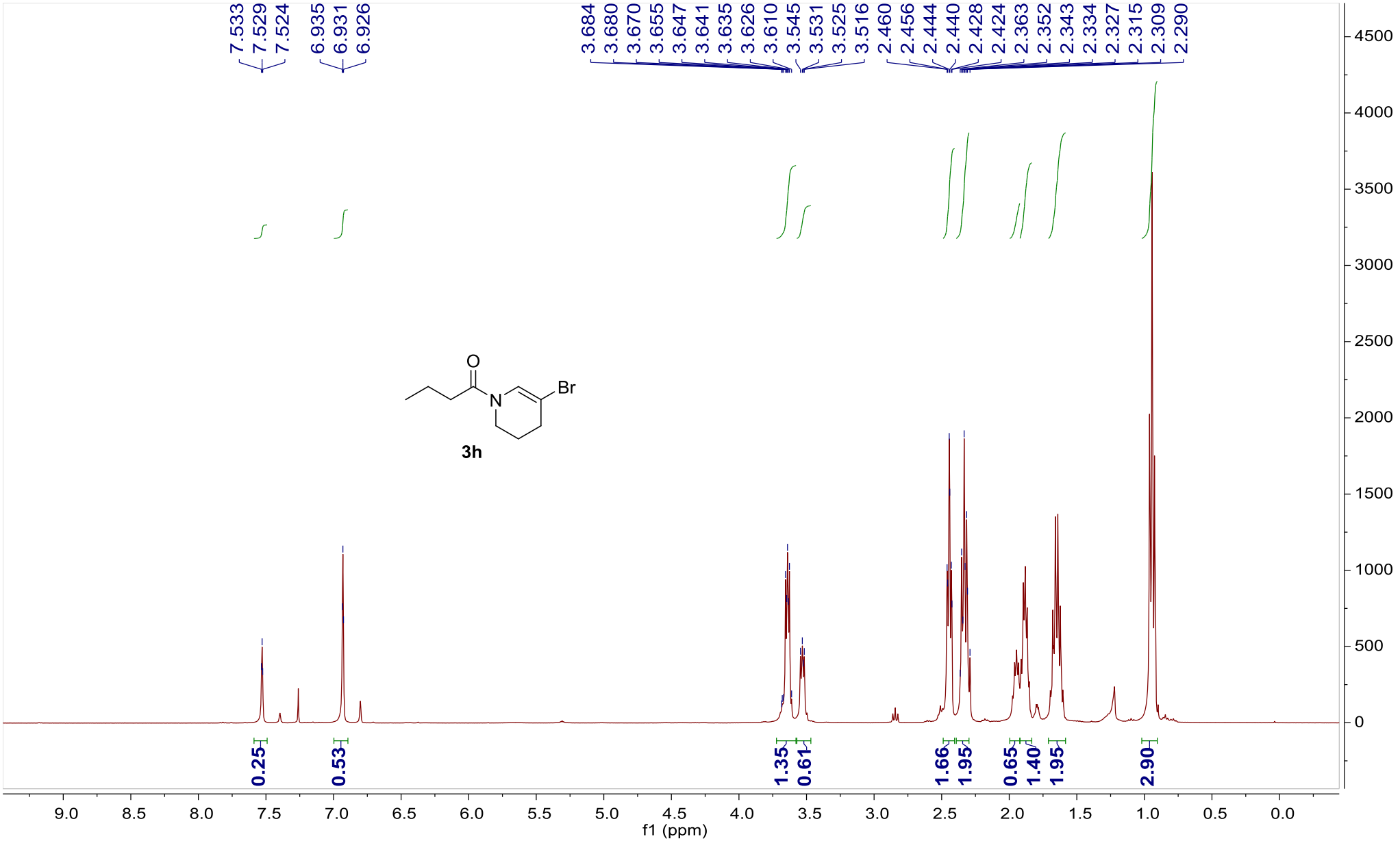
134.182
130.488
128.408
128.080
103.444
77.321
77.003
76.684
39.916
31.767
22.737
O
N
Br
3e
f1 (ppm)

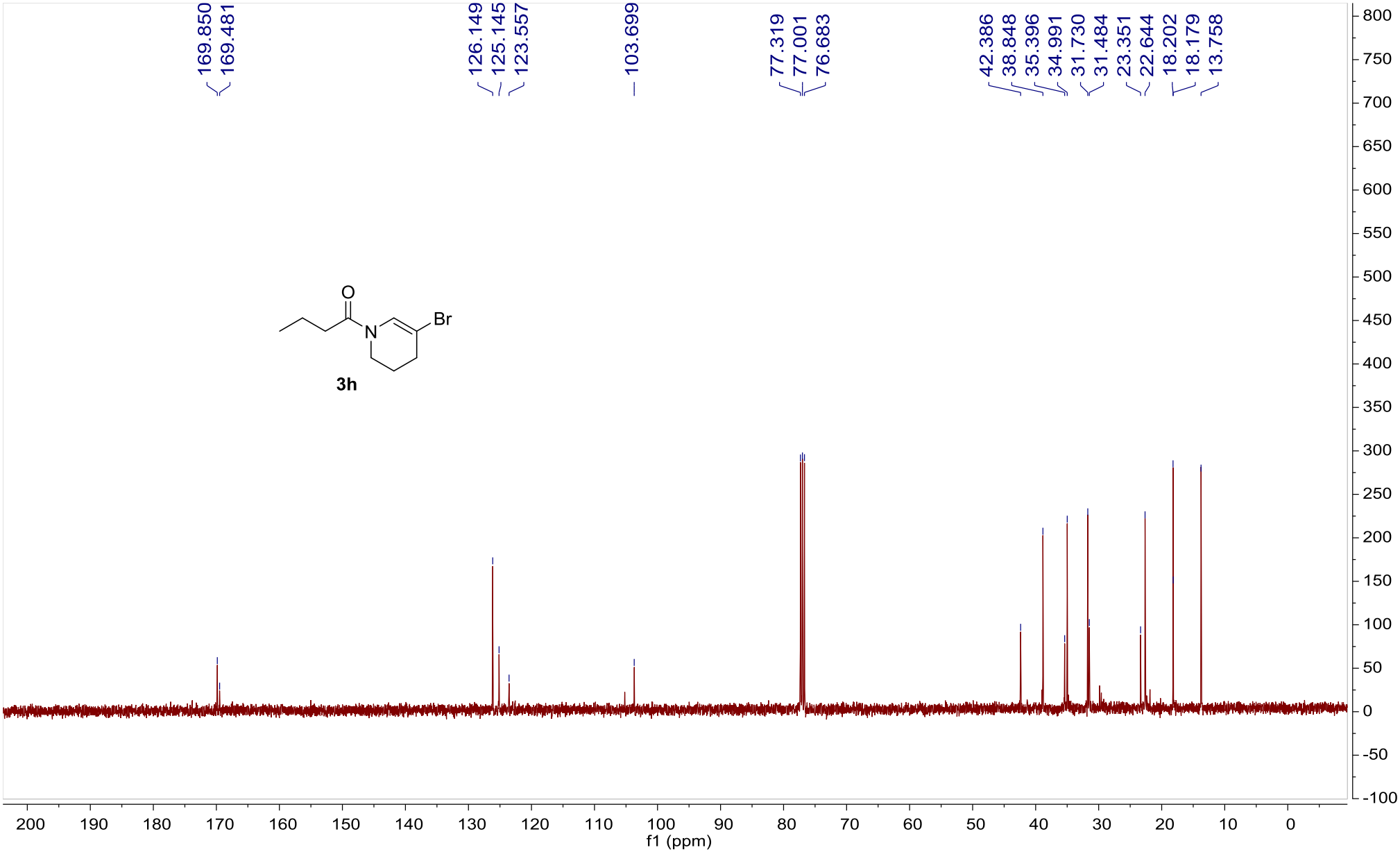

7.571
7.550
7.351
7.331
7.260
6.733
3.771
3.522
2.518
2.514
2.502
2.498
2.486
2.482
2.027
1.895
O
N
Br
Br
3f
2.20
1.98
0.62
1.41
0.56
1.99
2.03
f1 (ppm)

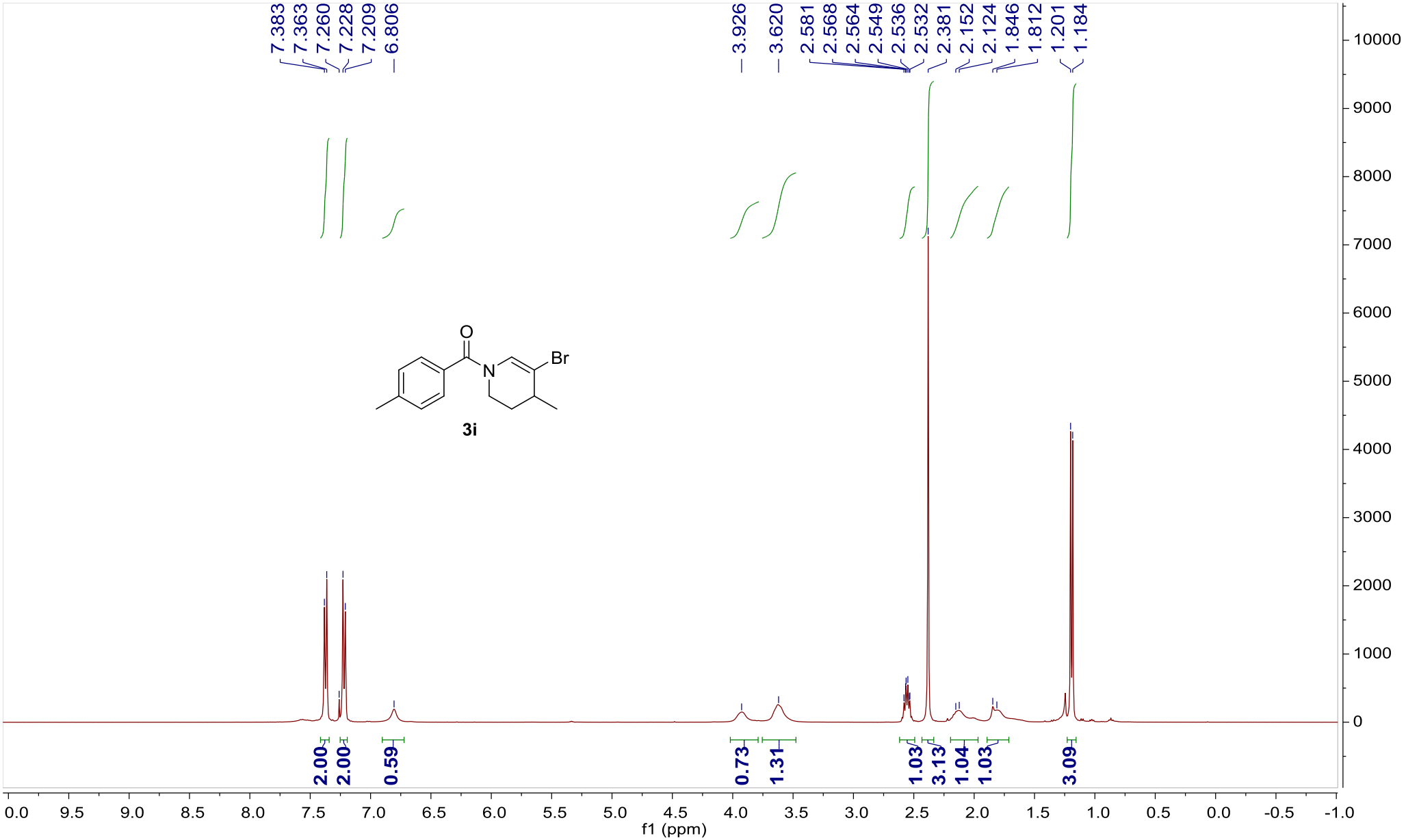

167.337
133.014
131.730
129.800
127.514
125.100
104.124
77.319
77.003
76.684
40.057
31.762
22.731
O
N
Br
Br
3f
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

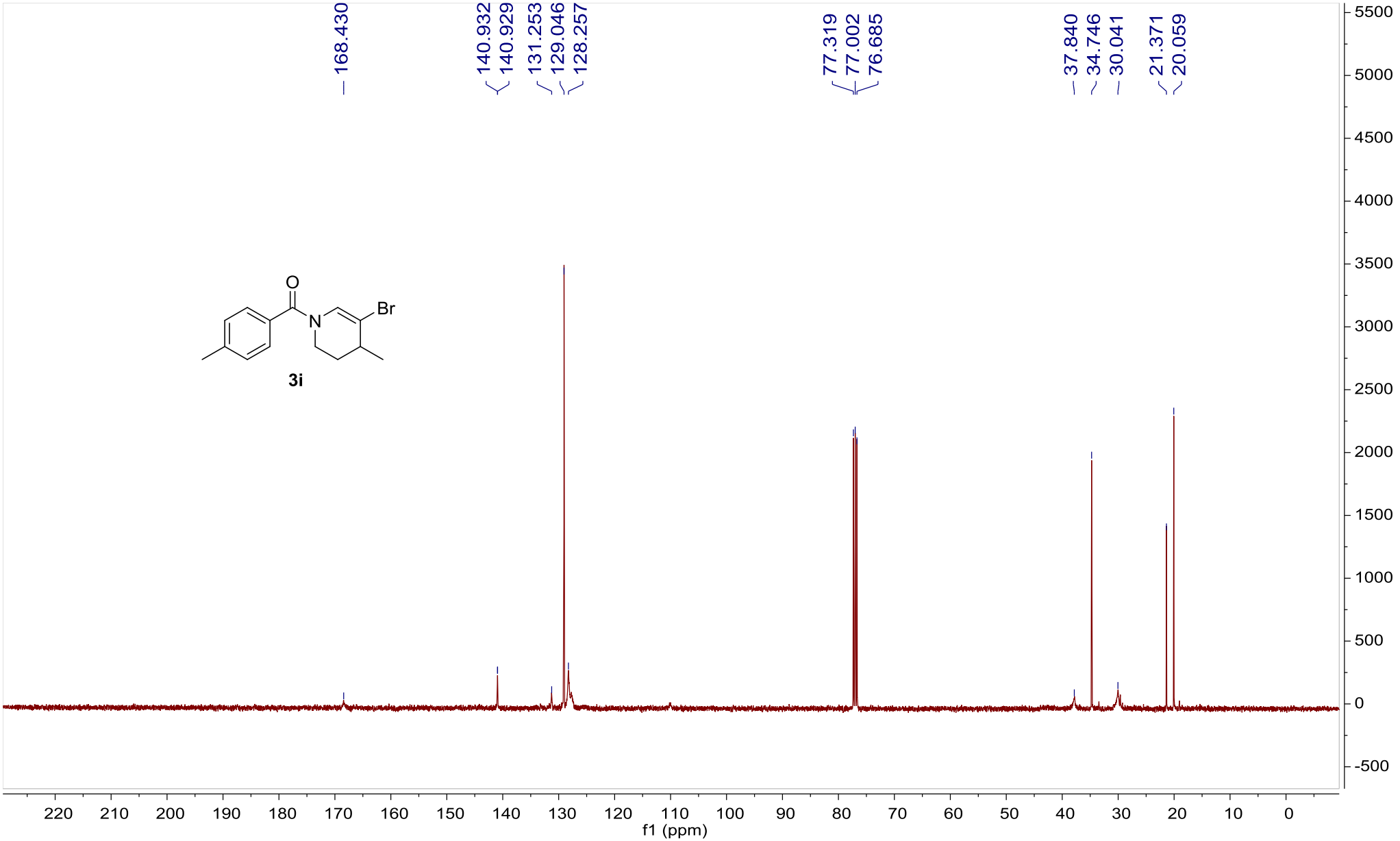

7.700
7.623
7.603
7.583
7.388
7.336
7.300
7.282
6.439
6.434
6.430
3.949
3.818
3.411
3.251
2.047
1.945
0.005
Br
O
N
Br
3g
0.36
1.01
1.08
2.08
0.54
1.21
0.87
2.00
1.31
0.82
f1 (ppm)

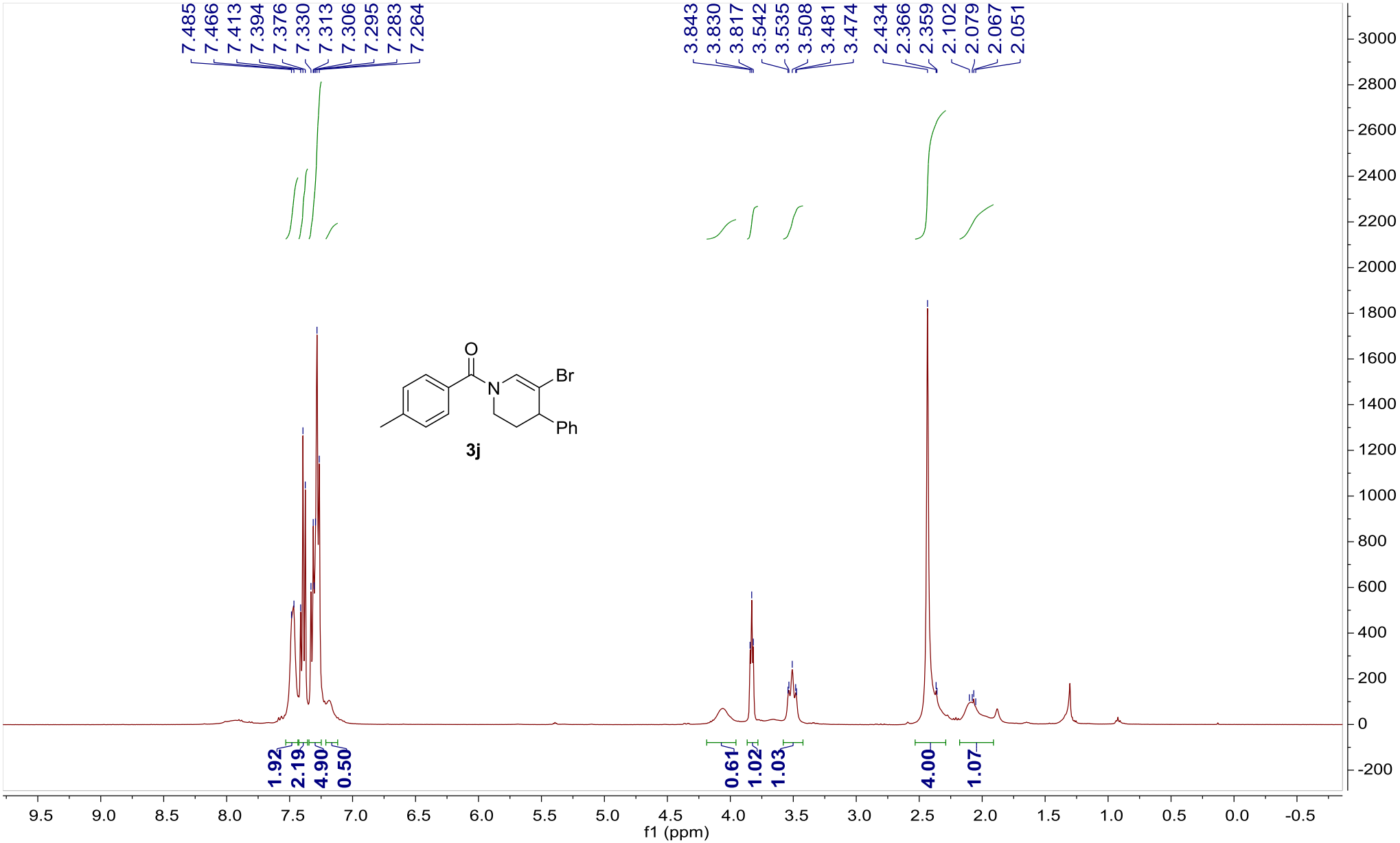

166.273
165.492
137.071
136.392
132.988
132.717
130.984
130.688
128.393
127.820
127.753
126.386
124.633
119.465
119.048
108.389
104.911
77.318
77.000
76.682
43.916
39.360
31.931
31.878
23.294
22.294
Br
O
N
Br
3g
f1 (ppm)

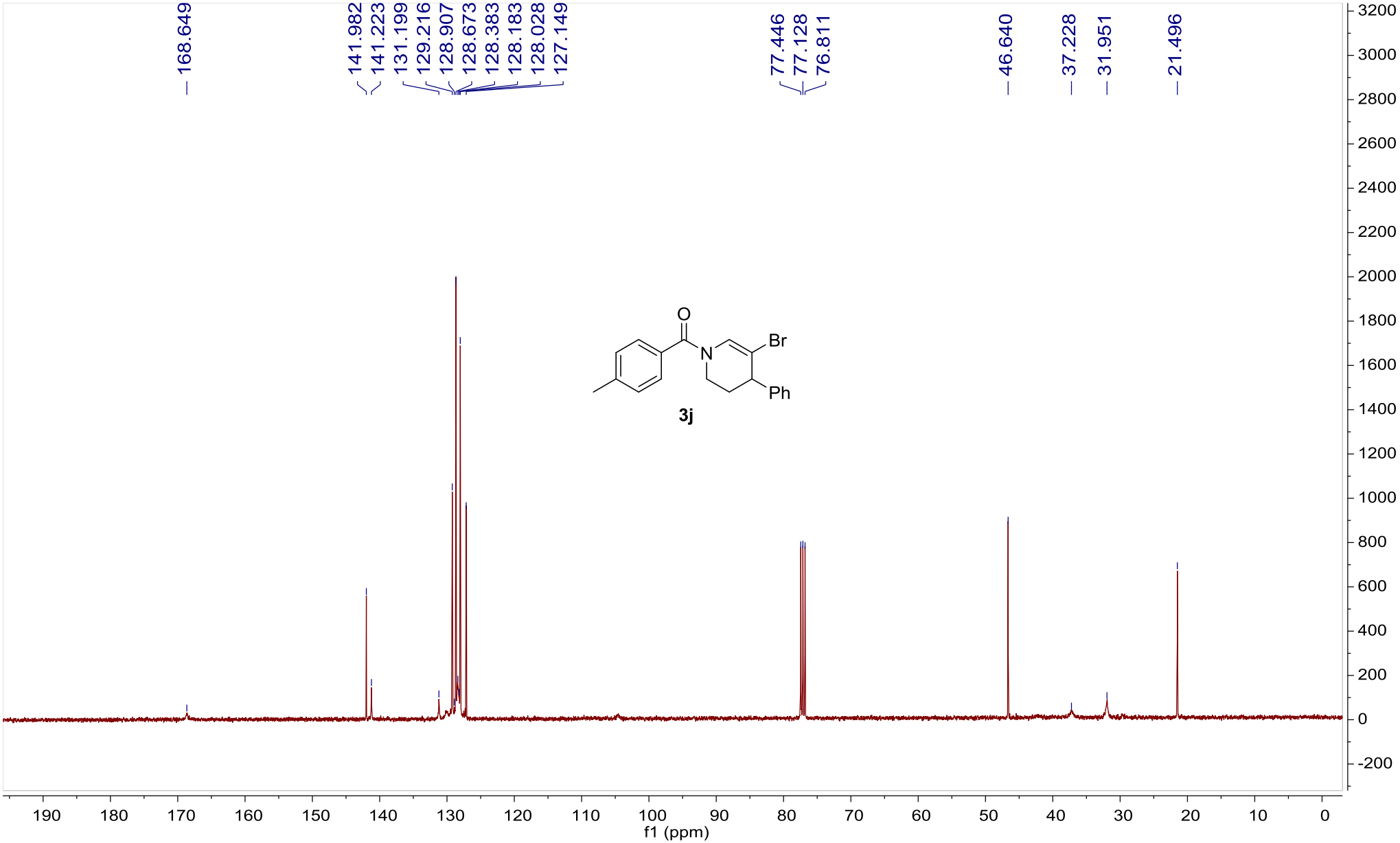

7.533
7.529
7.524
6.935
6.931
6.926
3.684
3.680
3.670
3.655
3.647
3.641
3.635
3.626
3.610
3.545
3.531
3.525
3.516
2.460
2.456
2.444
2.440
2.428
2.424
2.363
2.352
2.343
2.334
2.327
2.315
2.309
2.290
O
N
Br
3h
0.25
0.53
1.35
0.61
1.66
1.95
0.65
1.40
1.95
2.90
f1 (ppm)

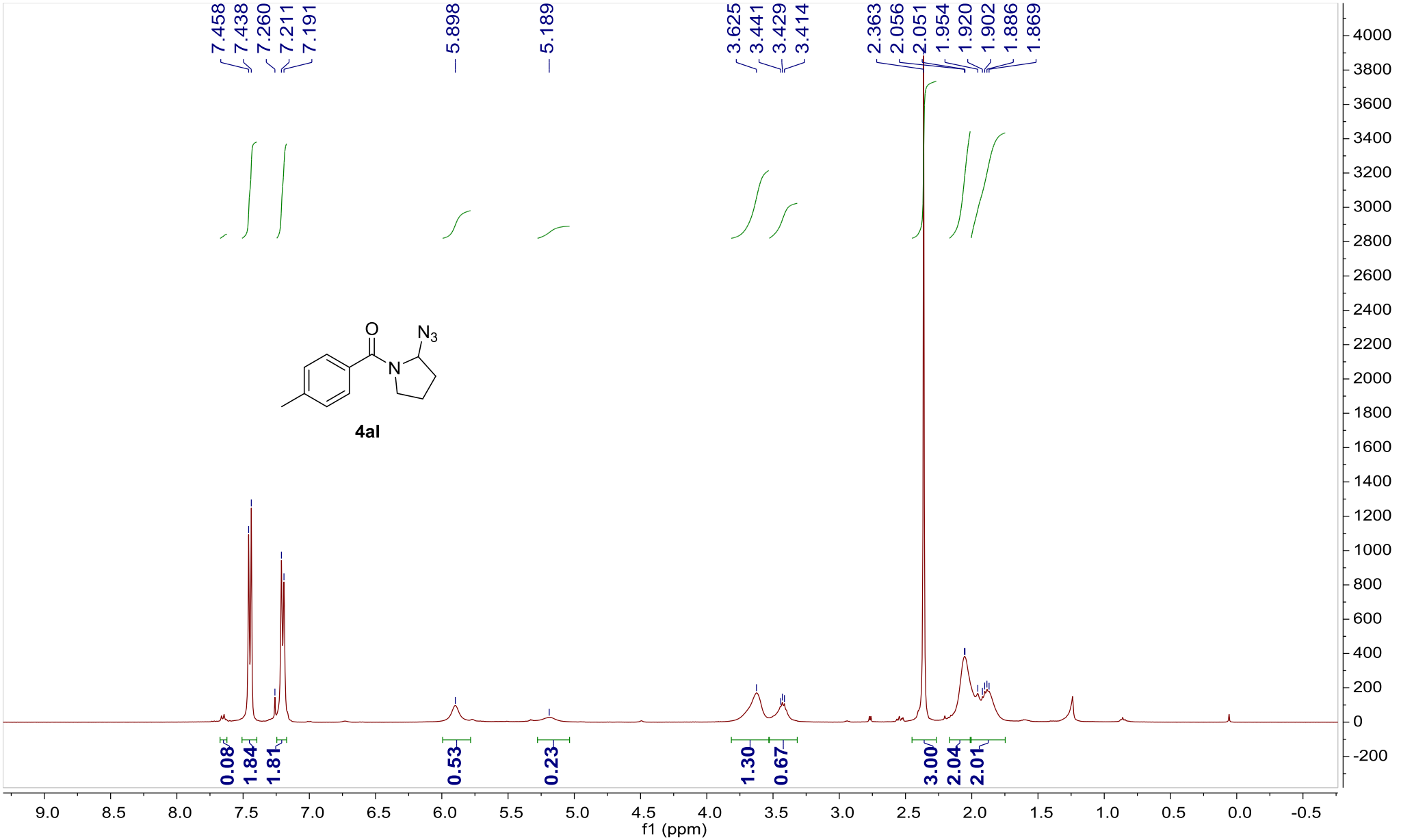

169.850
169.481
126.149
125.145
123.557
103.699
77.319
77.001
76.683
42.386
38.848
35.396
34.991
31.730
31.484
23.351
22.644
18.202
18.179
13.758
O
N
Br
3h
f1 (ppm)

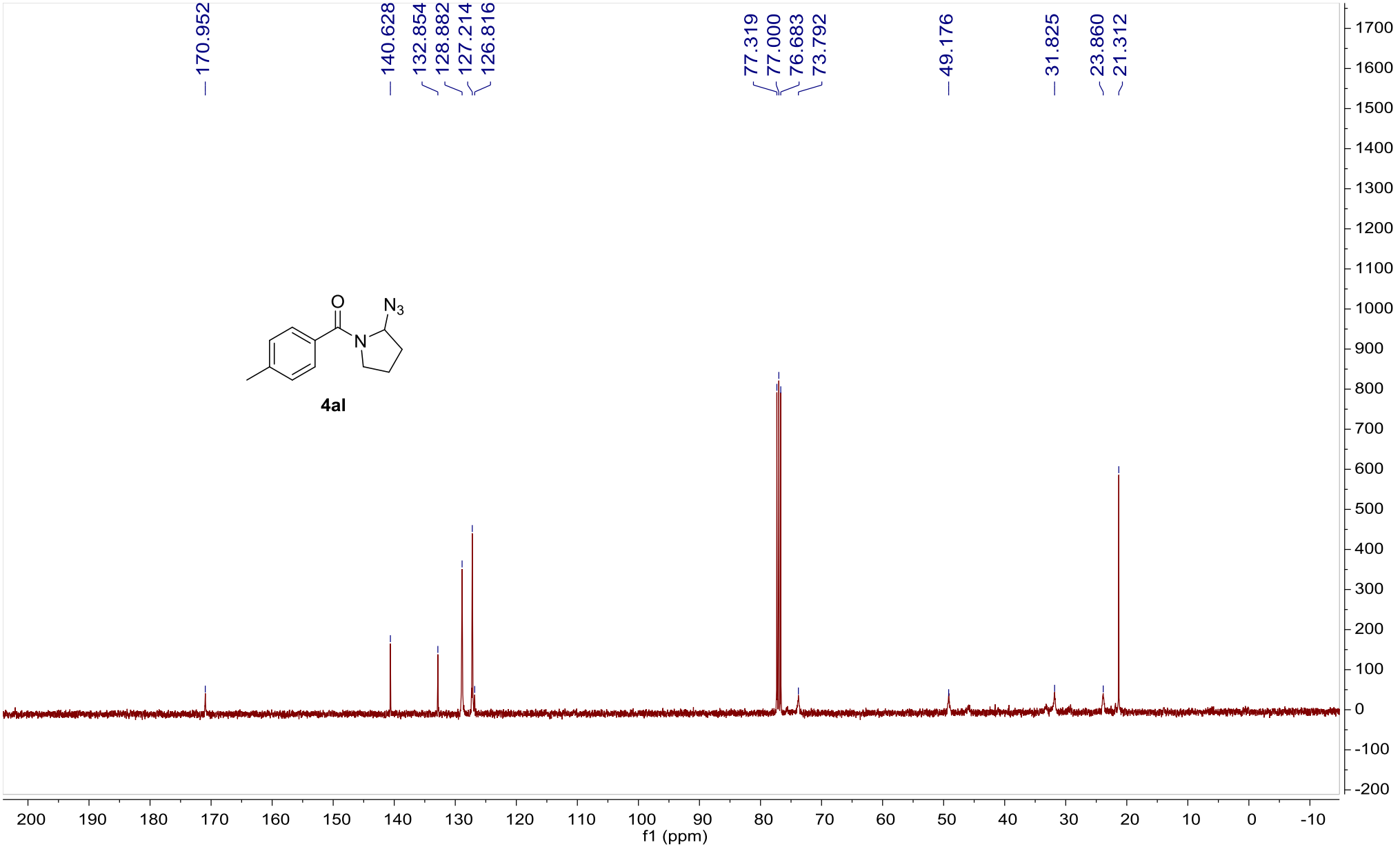

7.383
7.363
7.260
7.228
7.209
6.806
3.926
3.620
2.581
2.568
2.564
2.549
2.536
2.532
2.381
2.152
2.124
1.846
1.812
1.201
1.184
O
N
Br
3i
2.00
2.00
0.59
0.73
1.31
1.03
3.13
1.04
1.03
3.09
f1 (ppm)

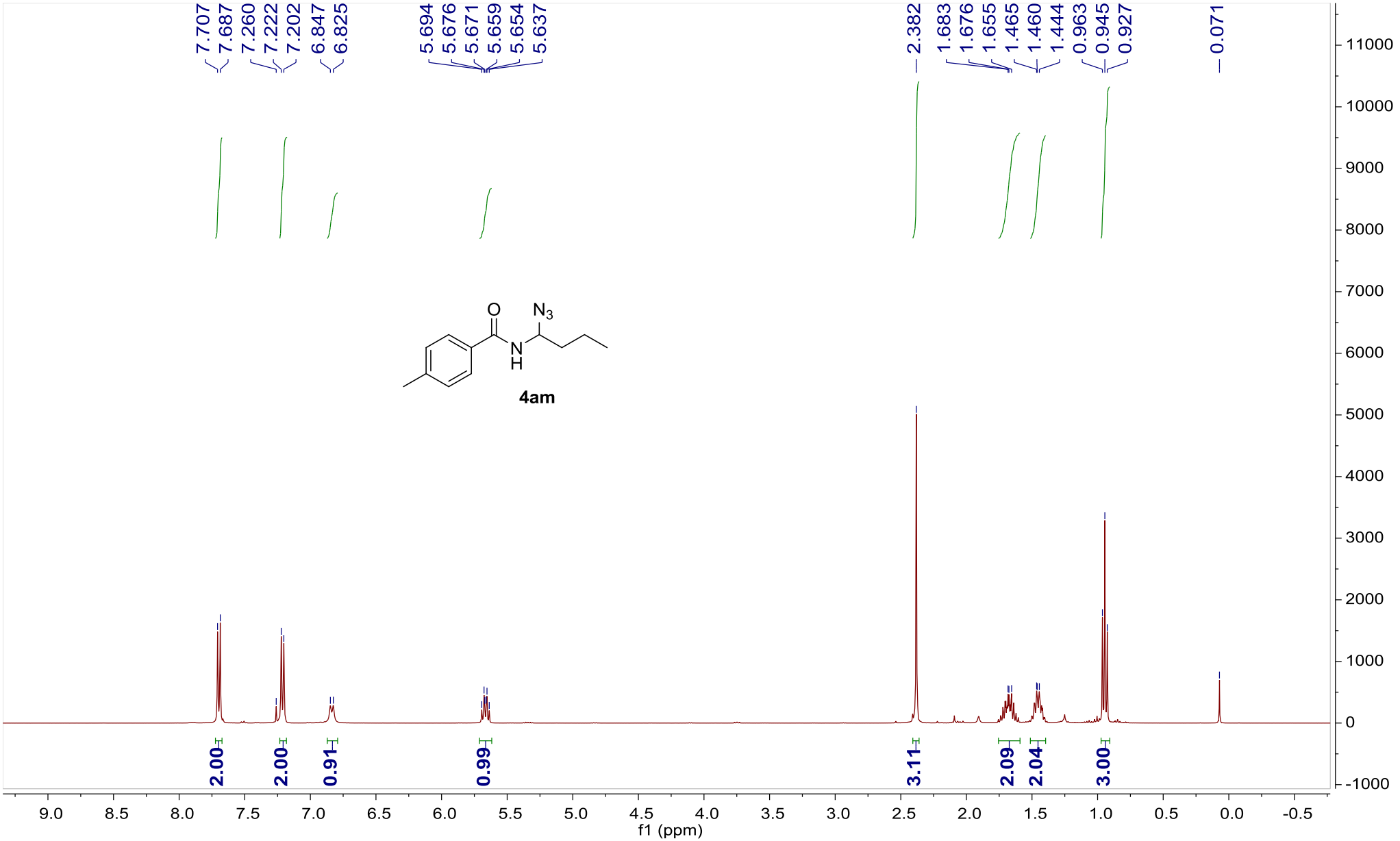

168.430
140.932
140.929
131.253
129.046
128.257
77.319
77.002
76.685
37.840
34.746
30.041
21.371
20.059
O
N
Br
3i
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

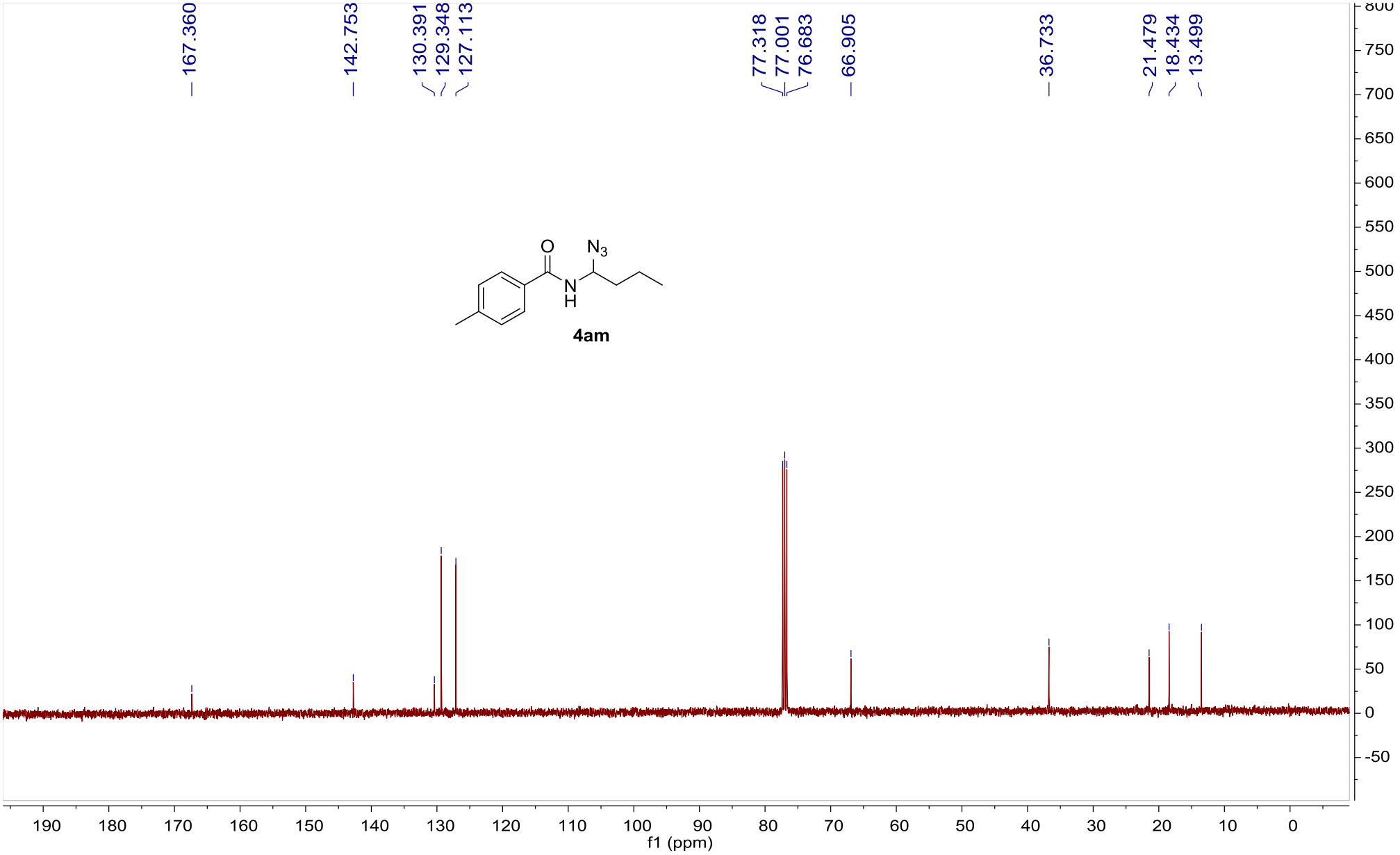

7.485
7.466
7.413
7.394
7.376
7.330
7.313
7.306
7.295
7.283
7.264
3.843
3.830
3.817
3.542
3.535
3.508
3.481
3.474
2.434
2.366
2.359
2.102
2.079
2.067
2.051
O
N
Br
Ph
3j
1.92
2.19
4.90
0.50
0.61
1.02
1.03
4.00
1.07
f1 (ppm)


168.649
141.982
141.223
131.199
129.216
128.907
128.673
128.383
128.183
128.028
127.149
77.446
77.128
76.811
46.640
37.228
31.951
21.496
O
N
Br
Ph
3j
f1 (ppm)


7.458
7.438
7.260
7.211
7.191
5.898
5.189
3.625
3.441
3.429
3.414
2.363
2.056
2.051
1.954
1.920
1.902
1.886
1.869
O
N3
N
4al
0.08
1.84
1.81
0.53
0.23
1.30
0.67
3.00
2.04
2.01
f1 (ppm)


170.952
140.628
132.854
128.882
127.214
126.816
77.319
77.000
76.683
73.792
49.176
31.825
23.860
21.312
O
N3
N
4al
f1 (ppm)


7.707
7.687
7.260
7.222
7.202
6.847
6.825
5.694
5.676
5.671
5.659
5.654
5.637
2.382
1.683
1.676
1.655
1.465
1.460
1.444
0.963
0.945
0.927
0.071
O
N3
N
H
4am
2.00
2.00
0.91
0.99
3.11
2.09
2.04
3.00
f1 (ppm)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129.348
127.113
77.318
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76.683
66.905
36.733
21.479
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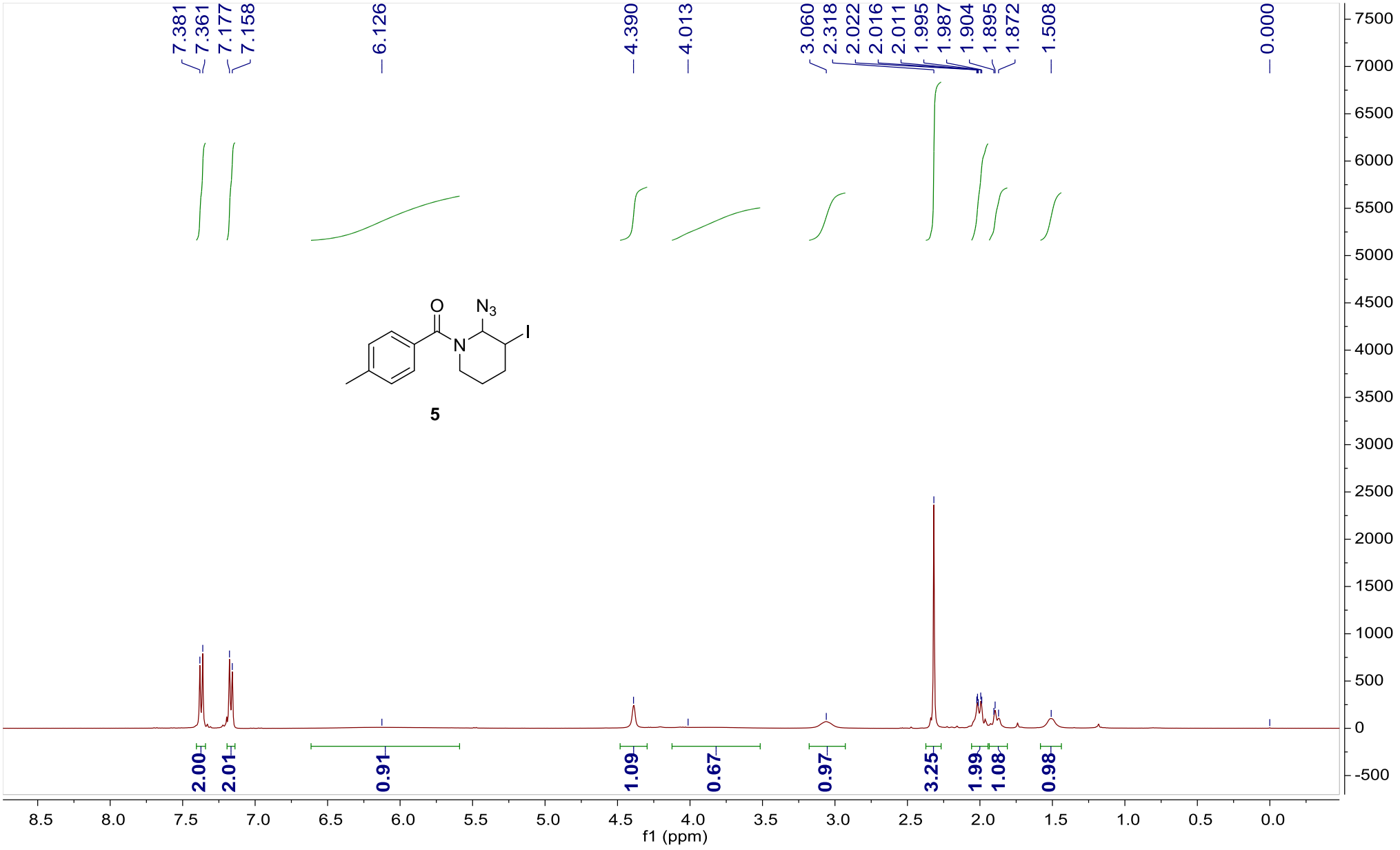
13.499
O
N3
N
H
4am
f1 (ppm)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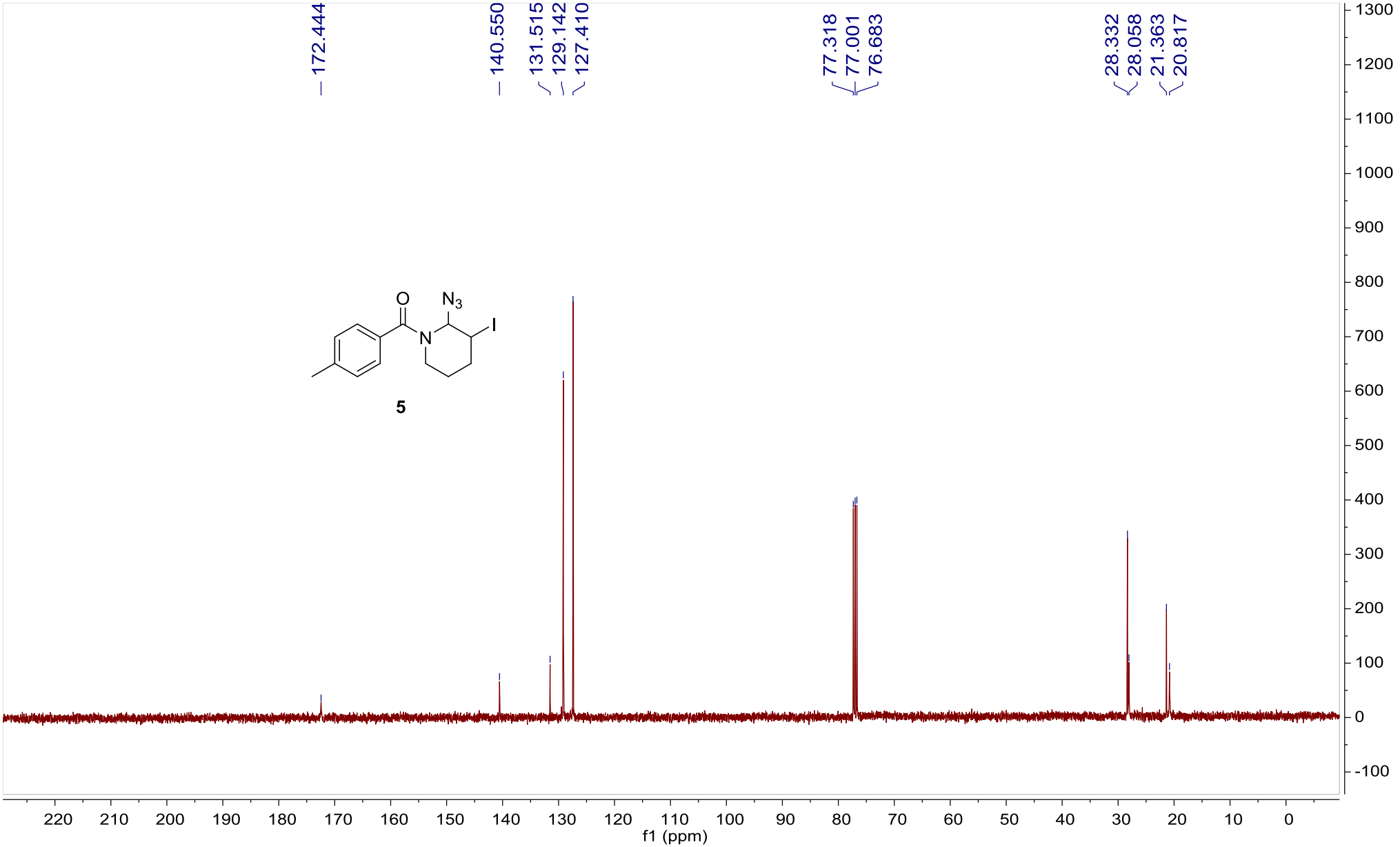
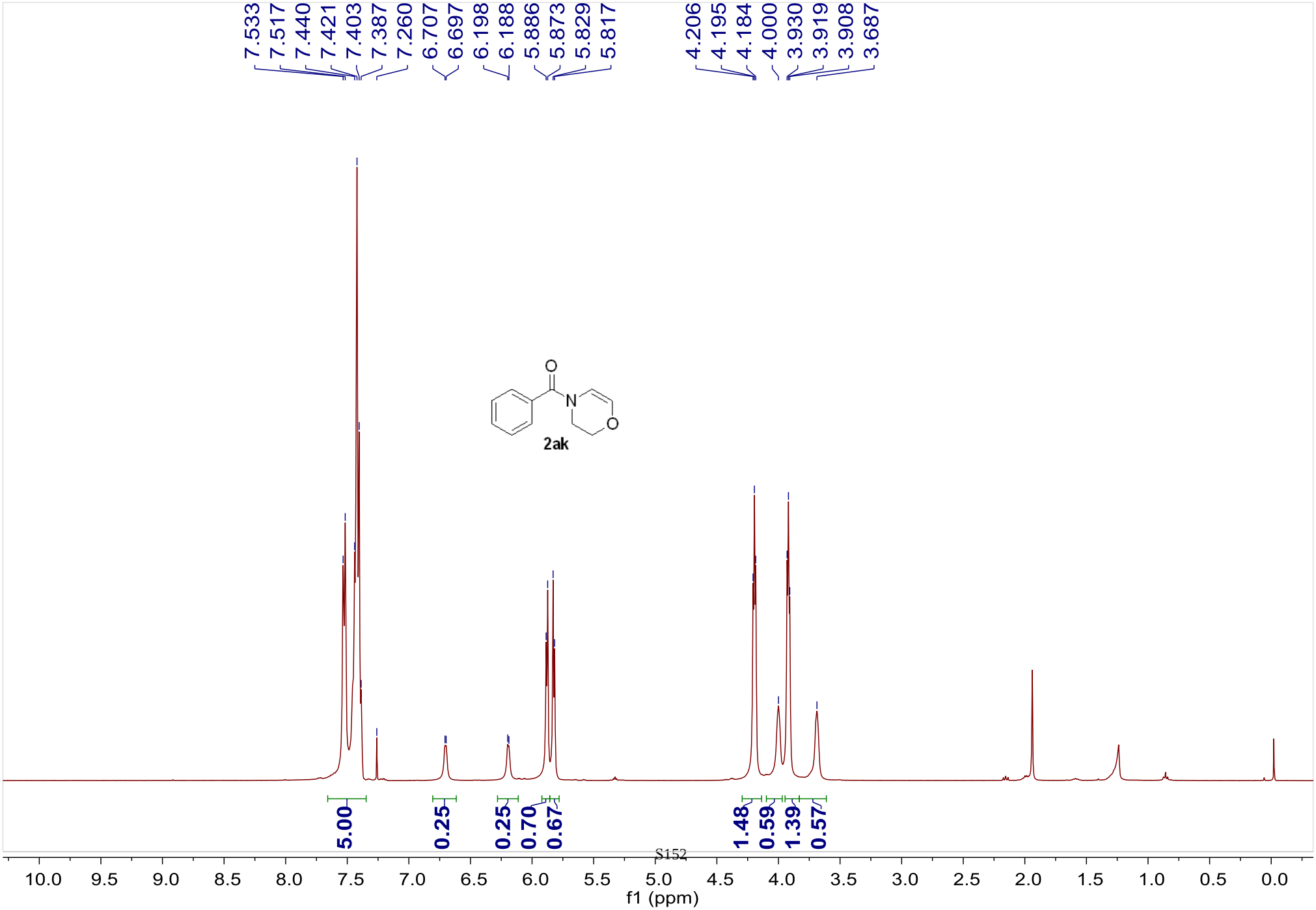
7.361
7.177
7.158
6.126
4.390
4.013
3.060
2.318
2.022
2.016
2.011
1.995
1.987
1.904
1.895
1.872
1.508
0.000
O
N3
N
I
5
2.00
2.01
0.91
1.09
0.67
0.97
3.25
1.99
1.08
0.98
f1 (ppm)


172.444
140.550
131.515
129.142
127.410
77.318
77.001
76.683
28.332
28.058
21.363
20.817
O
N3
N
I
5
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.517
7.440
7.421
7.403
7.387
7.260
6.707
6.697
6.198
6.188
5.886
5.873
5.829
5.817
4.206
4.195
4.184
4.000
3.930
3.919
3.908
3.687
O
N
O
2ak
5.00
0.25
0.25
0.70
0.67
1.48
0.59
1.39
0.57
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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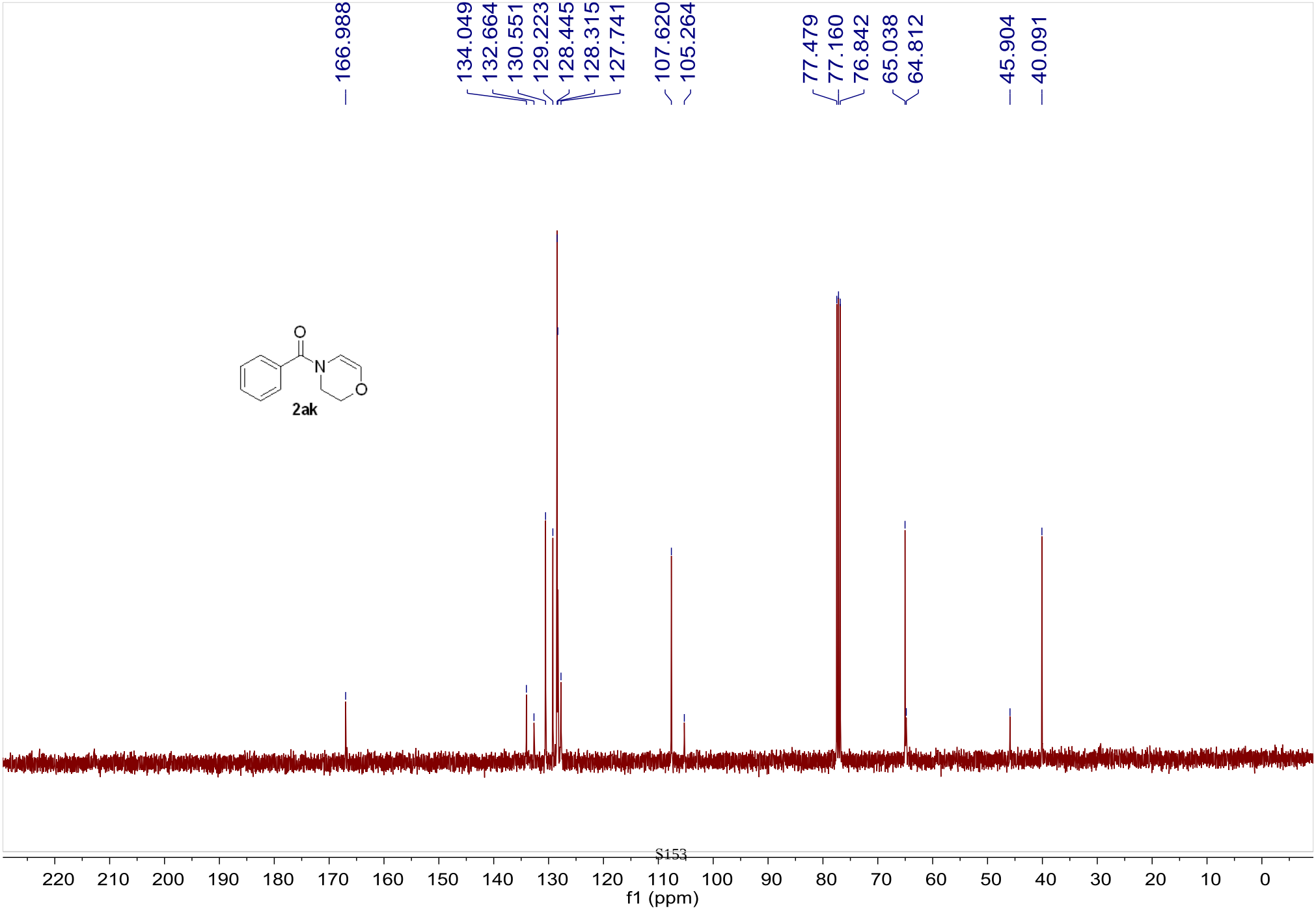
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.049
132.664
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129.223
128.445
128.315
127.741
107.620
105.264
77.479
77.160
76.842
65.038
64.812
45.904
40.091
O
N
O
2ak
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)