Electronic Supplementary Information

N-Chloroamines as substrates for metal-free photochemical atom-transfer radical addition reactions in continuous flow

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1. General information

1.1. Materials and methods

All materials were purchased from commercial sources (TCI, Sigma-Aldrich or VWR) and used without further purification.

GC-FID: chromatography was performed using a Shimadzu GC FID 230 gas chromatograph with a flame ionization detector (FID). Helium, used as the carrier gas (40 cm sec-1 linear velocity), goes through a RTX-5MS column (30 m × 0.25 mm ID × 0.25 µm). The injector temperature is set to 280 °C. After 1 min at 50 °C, the column temperature is increased by 25 °C min^{-1} to 300 °C, then held for 4 min at 300 °C. The gases used in the detector for flame ionization are hydrogen and synthetic air (5.0 quality).

NMR spectra: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz instrument at 300 MHz, 282 MHz and 75 MHz, respectively. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, dd, t, q, and m are used to indicate singlet, doublet, doublet of doublets, triplet, quadruplet, and multiplet, respectively. The prefix br denotes a broad peak.

UV/vis spectra: UV/vis spectra were recorded using a fiber-coupled Avantes Starline AvaSpec-2048 spectrometer and were processed using Avasoft 8.7 software. Inline UV/vis data was recorded using a flow-through cuvette (Hellma, Article # 176-762-85-40, Suprasil quartz, 0.15 mm path length)

Flash column chromatography: automated flash column chromatography was performed on a Biotage Isolera system using columns packed with KP-SIL, 60 Å (32-63 µm particle size) silica.

High-resolution mass spectrometry (HRMS) measurements were carried out with an Agilent 6230 TOF mass spectrometer, after separation of the compounds with an Agilent 1260 Infinity Series HPLC-system. The injection volume was set to 0.5 µL and the flow rate to 0.3 mL/min of a mixture of 40% H_2O (0.1% 5 M ammonium formate) and 60% MeCN/H_2O (5:1 +0.1% 5 M ammonium formate). The HRMS module comprises an electrospray ionization source (Dual AJS ESI) and uses nitrogen as the nebulizer (15 psig) and the drying gas (5 L/min). ESI experiments were performed using the positive ionization mode (Gas Temp. = 300 °C, Fragmentor = 150 V, Skimmer

= 65 V, OCT 1 RF Vpp = 750 V, Vcap = 1400, Nozzle Voltage = 2000 V, Reference Masses = 121.050873 and 922.009798, Acquisition = 100-1,100 m/z, 1 spectra/s).

1.2. Batch reaction setup

Batch screening reactions were carried out in sealed microwave vials (Biotage, 0.5-2 mL volume, part# 352016), equipped with a magnetic stirrer and irradiated by a 50 W (input power) LED chip at a distance of 7 cm (Fig. S1).

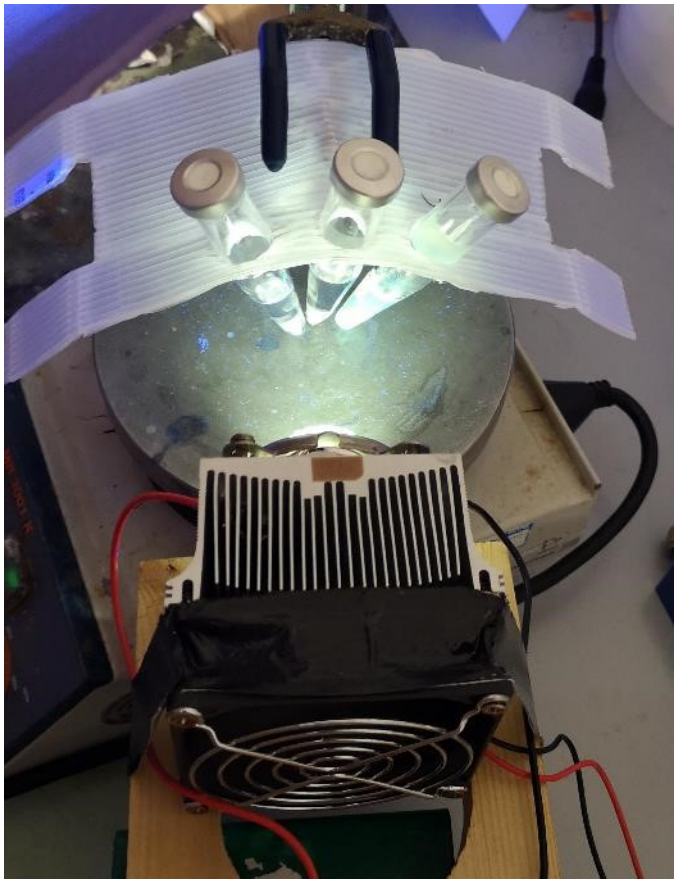


Fig. S1. Photograph of batch setup used for reaction screening.

1.3. Flow reactor setup

Flow reactions were conducted in a commercial continuous flow reactor: Corning Advanced-Flow Lab Photo Reactor (**Fig. S2**).

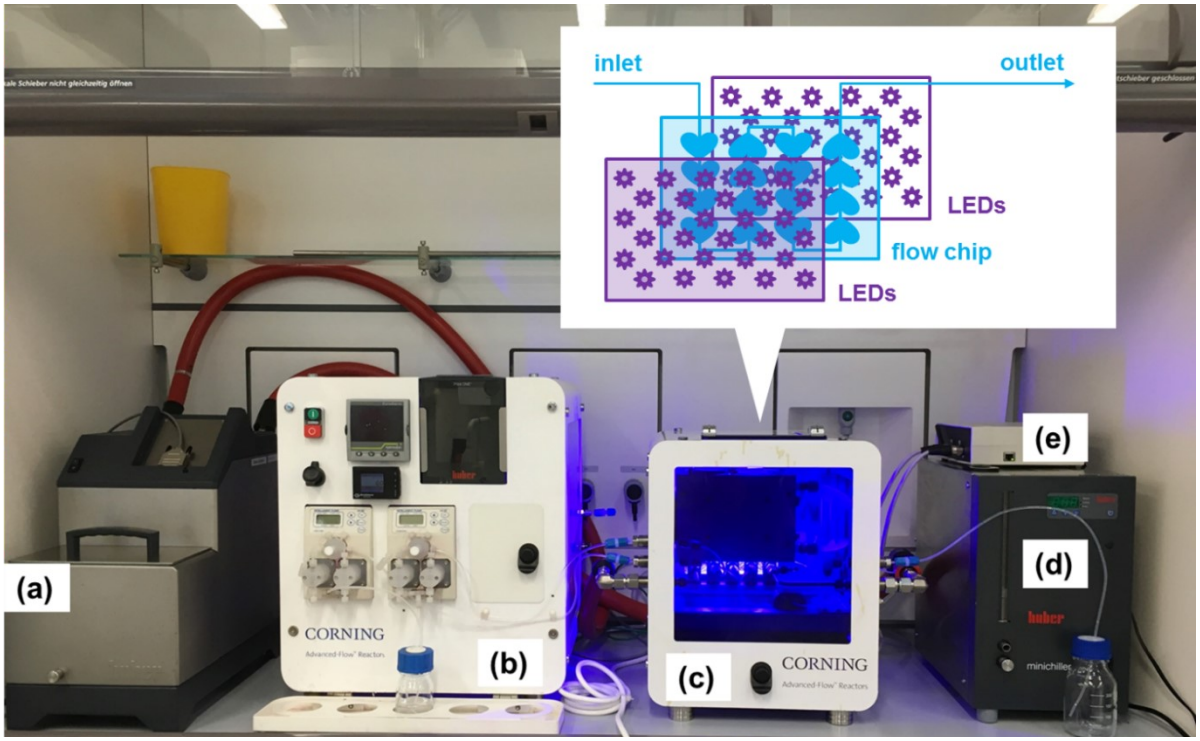


Fig. S2. Photograph of commercial photoreactor setup: a) temperature control for reaction plate; b) control module, containing pumps, mass flow controller, Huber controller and data logger; c) fluidic module housing, with tinted plastic panels for light containment; d) temperature control for LED panels; e) wireless receiver for LED control.

Reactor module (G1LF fluidic module): The flow photoreactor used in this work consisted of a compact glass fluidic module (155 × 125 × 8 mm size, 0.4 mm channel depth, 2.77 mL internal volume), encased within a high capacity heat exchange channel (20 mL volume).

Light source: LED panels were mounted on both sides of the fluidic module (40 mm from the center of the process stream). Each LED panel was equipped with 20 LEDs of 6 different wavelengths (120 LEDs in total) and a heat exchanger (T = 15 °C). The LED wavelength and intensity was controlled externally using a web-based interface, connected wirelessly to a router. This study utilized 405 nm LEDs; see details on LED power and emission spectra below, Table S1 and Fig. S2.

Table S1. Power of LEDs used in flow reactions in this study.

Peak wavelength (nm)	Total radiant flux (W)	Photon flux (mmol h^{-1})[a]
365	43.6	477
385	53.6	619
405	56.8	690
450	47.6	650
540	18.8	299
610	29.3	536

[a]Photon flux is calculated based on the radiant flux specified in the respective LED data sheet.

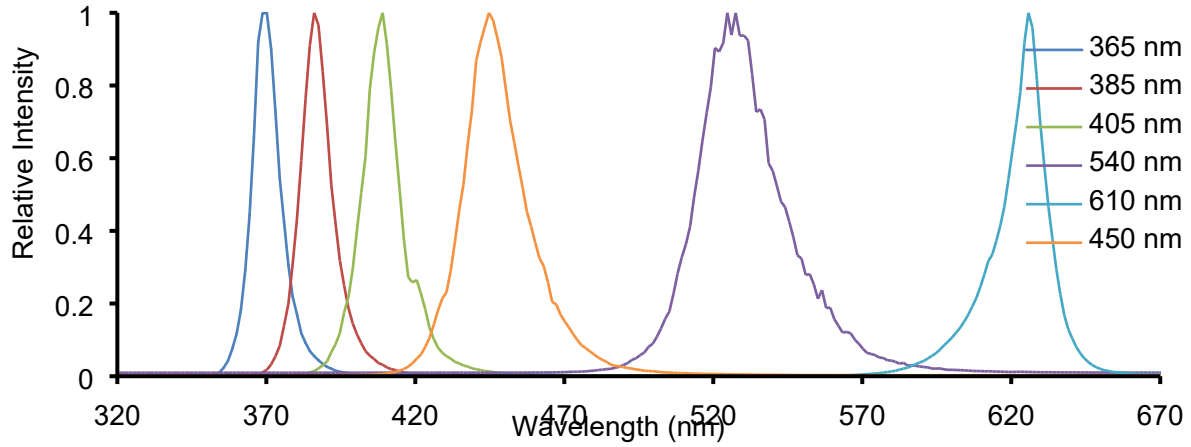


Fig. S3. Emission spectra of LEDs used in this study.

Temperature control: Thermal regulation of the LED panels was carried out using a Huber Minichiller 280 filled with 30% ethylene glycol in water. Thermal regulation of the glass fluidic module was carried out using a Huber Ministat 230 filled with silicon oil (–20 °C to 195 °C).

Pumps: The amine and NaOCl solutions were delivered using FLOM UI 22-110DC HPLC pumps (0.01-10 mL/min; wetted parts: PTFE, PCTFE, FFKM and ruby). The olefin and H_2SO_4 solutions were delivered using Syrris Asia pumps (wetted parts: PTFE, glass).

General connections: Connection between the pumps, fluidic module input and output was achieved using 1/8” (outer diameter, 1.6 mm inner diameter) PFA tubing (Swagelok), using metal-free connectors (Swagelok MS-GC-2 swaging system). Other

connections used 1/16” (outer diameter, 0.8 mm inner diameter) PFA tubing, with 1/4” PTFE or PEEK finger tight fittings.

Sample loop: Optimization experiments were conducted using two Upchurch 6-way switching valves to inject the amine and NaOCl streams (part # V-450, https://www.idex-hs.com/store/injection-valve-2-postion-6-port-040-black.html), with 5 or 10 mL sample loops (made from 1/16” outer diameter, 0.8 mm inner diameter PFA tubing) installed.

1.4. *N*-Chloroamine formation and membrane separator setup

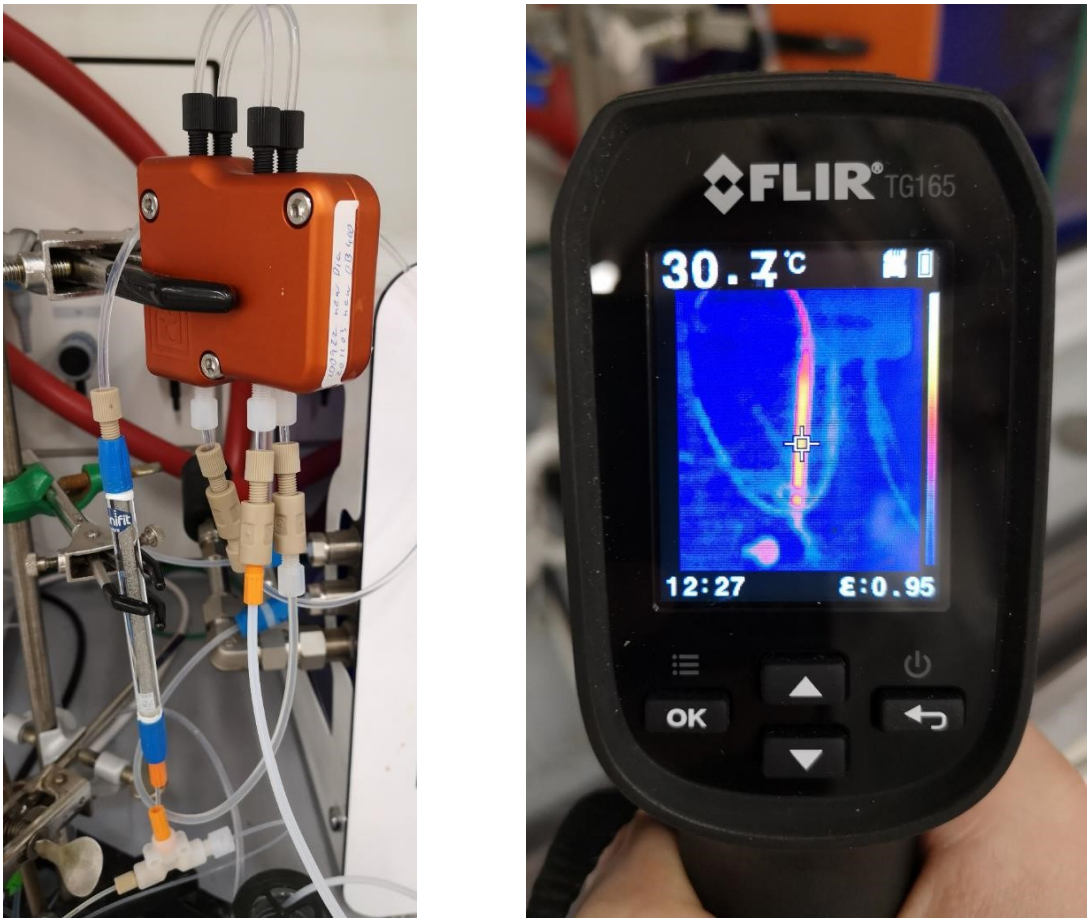


Fig. S4. Left: photograph of the packed Omnifit column used to form the *N*-chloroamine, followed by the membrane separator. Right: thermal imaging camera (FLIR TG165) used to roughly assess the temperature within the Omnifit column, which shows a mild exotherm (~30 °C).

1.5. General procedure 1, for optimization experiments in batch

A 4 mL microwave vial equipped with a stirring bar was charged with *N*-chloropiperidine **3** (83 µL, 0.75 mmol). 1 mL of a solution containing allylbenzene **2** (59.1 mg, 0.5 mmol) and biphenyl (internal standard) in MeCN was added. After sparging with an argon balloon, H_2SO_4 (95%, 42.1 µL, 0.75 mmol) was added, the vial was closed with a crimp cap and irradiated for 15 min using a 365 nm LED (50 W input power). Prior to analysis by GC-FID, 10 µL of the sample mixture was diluted with MeCN and passed through $NaHCO_3$ to neutralize the acid.

1.6. General procedure 2, for experiments in flow

Sample loops (5 mL for optimization experiments, 10 mL for isolation experiments) were used to introduce the amine and bleach solutions into the reactor. These streams were pumped using FLOM UI 22-110DC HPLC pumps. The olefin solution and sulfuric acid were pumped directly using syringe pumps (Syrris Asia).

The amine solutions were prepared by dissolving the corresponding amine in a volumetric flask in toluene (technical grade) to give a 2 M solution.

The bleach solution was prepared by dissolving $NaOCl \cdot 5H_2O$ in deionized water in a volumetric flask to give a 2.2 M solution.

The olefin solutions were prepared by dissolving the olefin (optional: biphenyl as internal standard and/or photosensitizer) in a volumetric flask in MeCN to provide either a 0.8 or 0.7 M solution of the olefin.

All solutions were degassed by sparging with an argon balloon. The reactor was turned on (LEDs, pump and thermostats) and the system was given ~10 min to equilibrate. The sample loops were charged with the amine and the bleach solutions and injected into the reactor. To account for any dilution effects at the edges of the injected sample, only the central fraction (~1 mL for optimization, 2.0 or 3.0 minutes = 5.54 mL or 8.31 mL for isolation) was collected.

Prior to analysis by GC-FID, 10 µL of the sample mixture was diluted with MeCN and passed through $NaHCO_3$ to neutralize the acid.

For isolation, the collected liquid was dry loaded onto silica by evaporation of solvent under reduced pressure, in the presence of silica. The apolar compounds were removed by washing with cyclohexane (25-50 mL), followed by 1:1 cyclohexane:EtOAc (100-250 mL). The product was eluted using EtOAc + 5% Et_3N (100-200 mL), then obtained after evaporation of the solvent. Any additional purification (if required) is detailed for the specific substrate.

Table S2. Example flow rates used for experiments detailed in the manuscript, with either 1.1 or 1.5 equiv. chloramine

Flow conditions	Flow rate (mL min^{-1})			
	2 M Amine in PhMe	2.2 M NaOCl in H_2O	Olefin in MeCN	95% H_2SO_4
A "1.5 equiv. chloramine"	1.04	1.04	1.73 (0.8 M)	0.115
B "1.1 equiv. chloramine"	0.762	0.762	2.01 (0.7 M)	0.085

2. Additional reaction data

2.1. GC-FID calibration

The model reaction product **4** was found to have a non-linear response versus Ph_2 across the examined ratios. Therefore, two different calibrations were used:

a) in cases of area ratio ($4/Ph_2$) > 3 (“high yield”)

b) in cases of area ratio ($4/Ph_2$) < 3 (“low yield”).

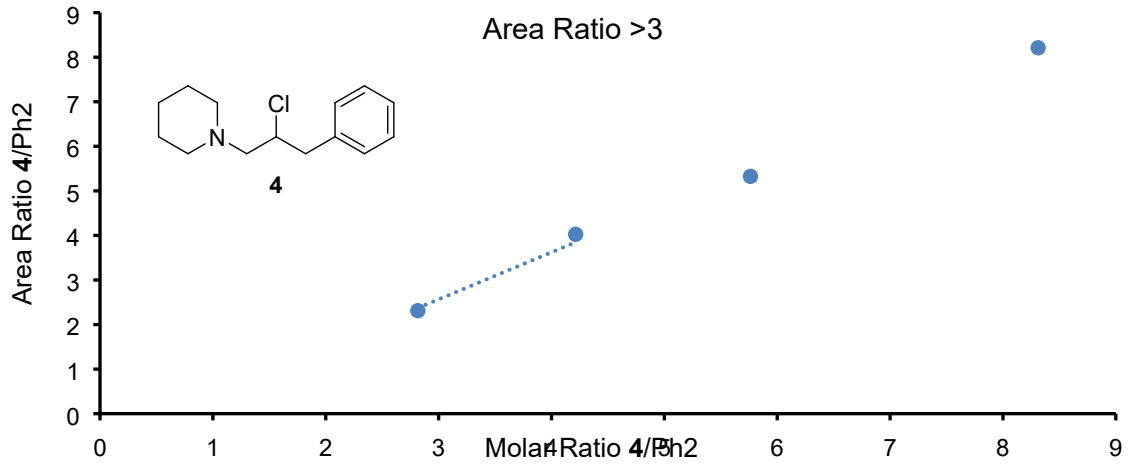


Fig. S5. Calibration of product **4** (1-(2-chloro-3-phenylpropyl)piperidine) against Ph_2 as internal standard, for “high yield” conditions.

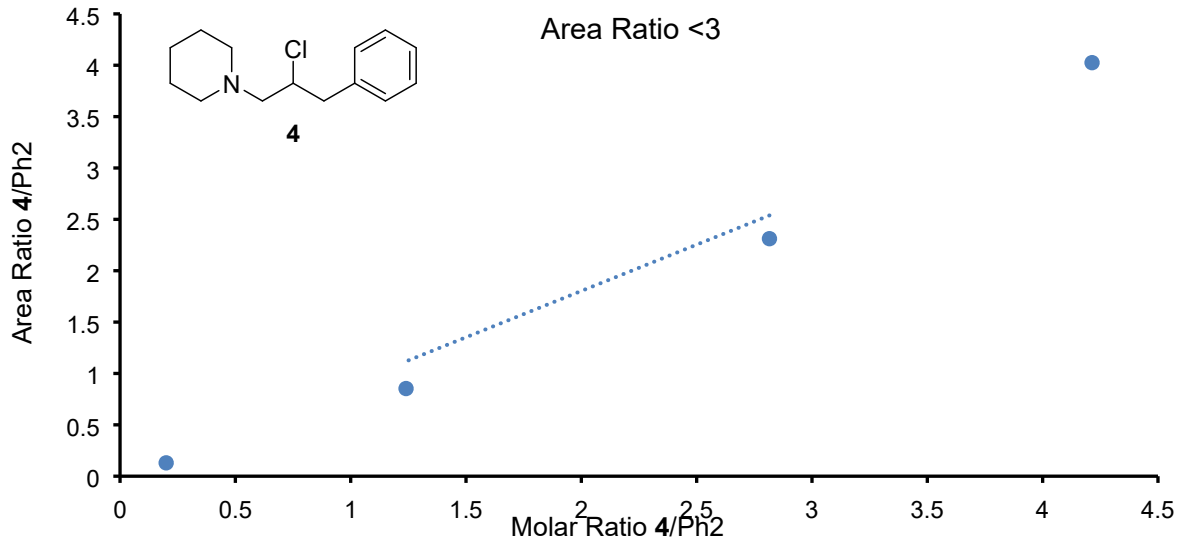


Fig. S6. Calibration of product **4** (1-(2-chloro-3-phenylpropyl)piperidine) against Ph_2 as internal standard, for “low yield” conditions.

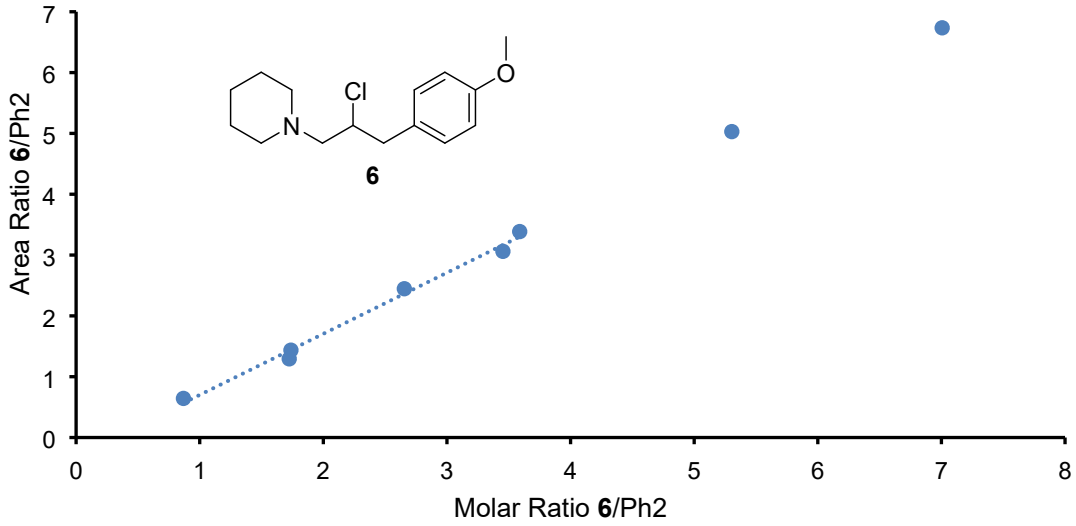


Fig. S7. Calibration of product **6** (1-(2-chloro-3-(4-methoxyphenyl)propyl)piperidine) against Ph_2 as internal standard.

2.2. UV/vis data

2.2.1. Offline analysis of N-chloropiperidine 3

Isolated *N*-chloropiperidine **3** was analyzed using a standard cuvette (1 cm path length). This was performed in the presence and absence of H_2SO_4 (equimolar concentration), which showed no notable difference.

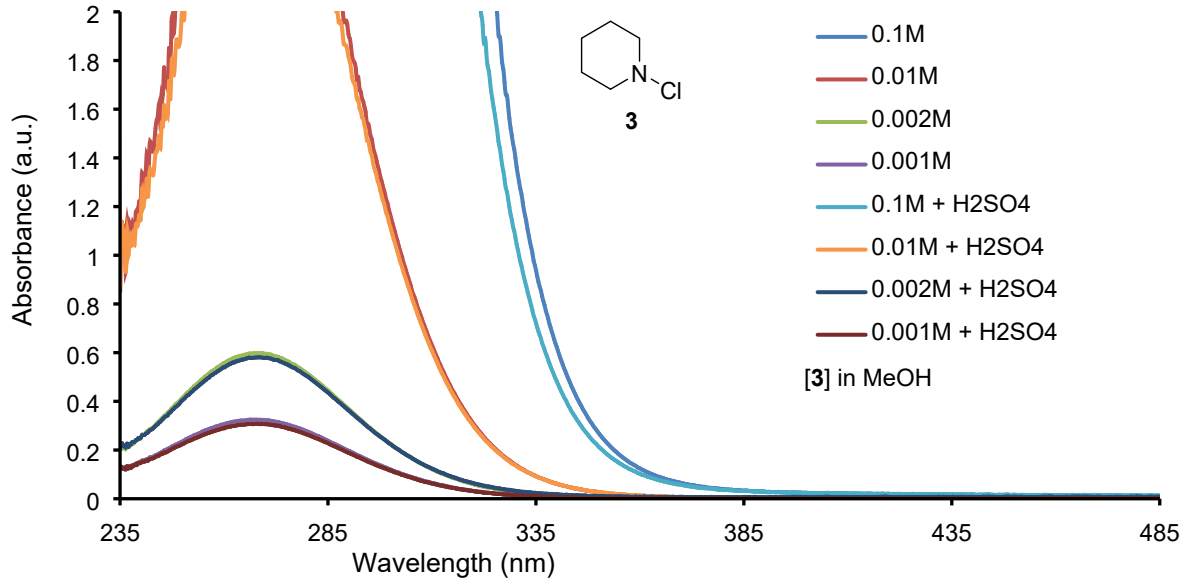


Fig. S8. UV/Vis data for N-chloropiperidine **3**, using a standard 1 cm cuvette. "+ H2SO4" indicates an equimolar concentration of H_2SO_4 was added.

λ_{max} = 271 nm

Absorption (271 nm, 0.002 M) = 0.519 → ε_{271nm}= 260 L mol^{-1} cm^{-1}

Absorption (271 nm, 0.001 M) = 0.247 → ε_{271nm}= 247 L mol^{-1} cm^{-1}

Average ε_{271nm}= 2.5 × 10^2 L mol^{-1} cm^{-1}

Absorption (365 nm, 0.1 M) = 0.0864 → ε_{365nm}= 0.86 L mol^{-1} cm^{-1}

2.2.2. Online calibration of N-chloropiperidine 3

Different concentration solutions of N-chloropiperidine **3** were measured in stopped flow mode, in a flow cuvette with a 1.5 mm path length. ε_{360nm}= 2.3 L mol^{-1} cm^{-1}

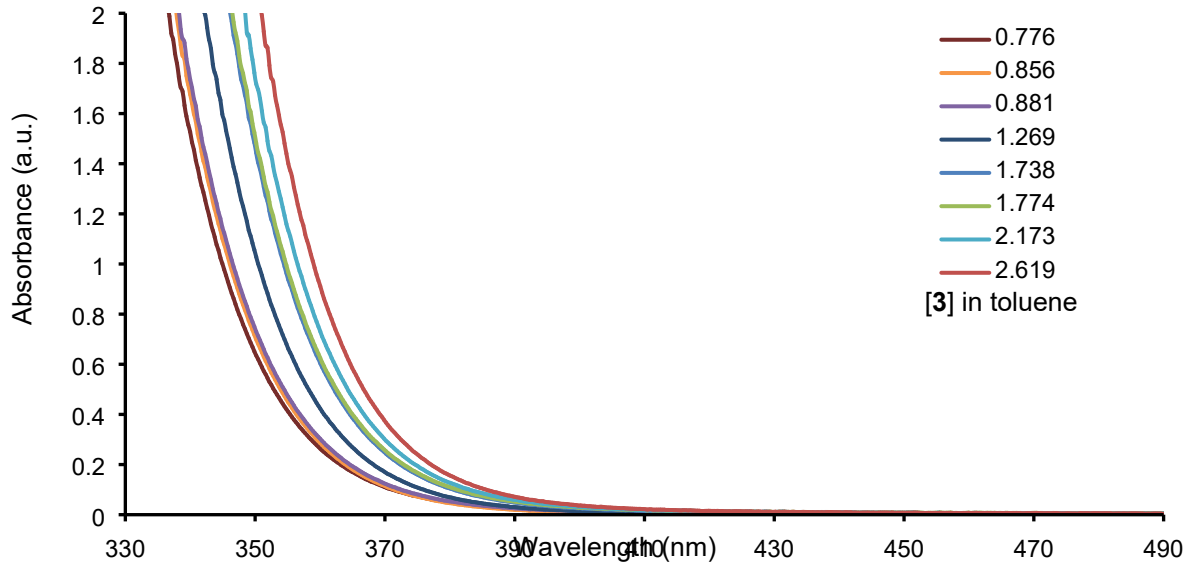


Fig. S9. Measurement of known concentrations of *N*-chloropiperidine **3** using a flow cuvette (1.5 mm path length)

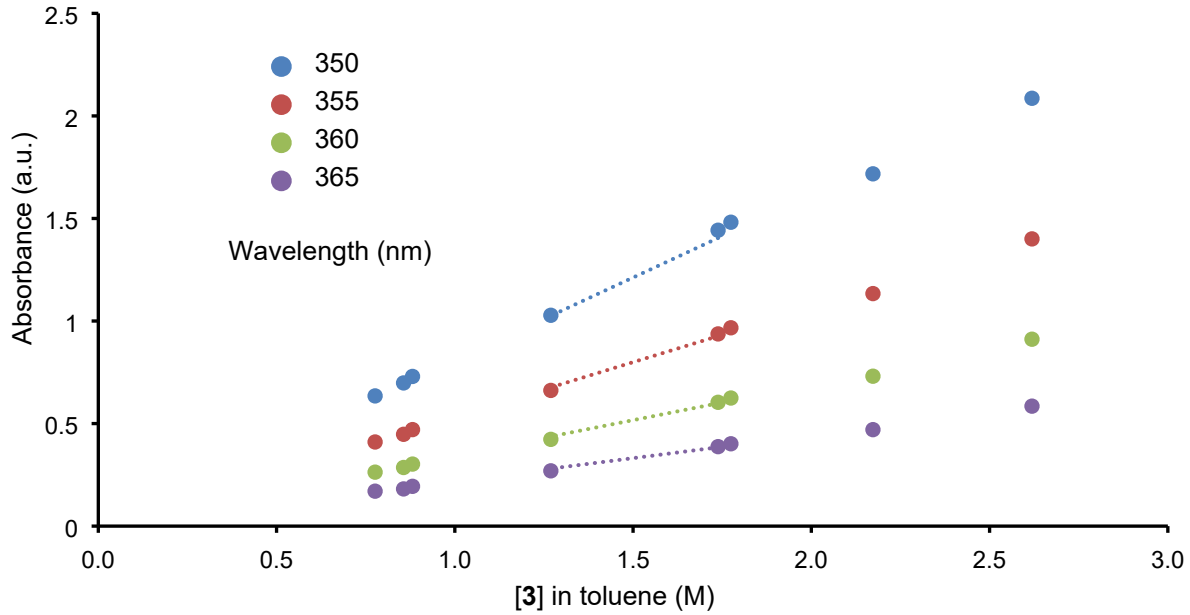


Fig. S10. Calibration curves for quantification of *N*-chloropiperidine **3** in toluene. The absorbance at 360 nm was deemed to be most suitable, so was used for online analysis.

2.2.3. Online analysis of other amine substrates

During substrate scope experiments, the UV/vis spectra of various *N*-chloroamines in solution were measured, without isolation of the *N*-chloroamines. This data was used to determine the applicability of the non-sensitized reaction conditions to these different substrates. The theoretical concentration of *N*-chloroamine in toluene was 2 M, and spectra were measured in a flow cuvette with 1.5 mm path length.

The resulting differences in absorbance provide a good justification for the use of a triplet sensitizer for different amine substrates. For example, *N*-chloroazepane shows significantly higher absorbance, which resulted in poor selectivity in the absence of a sensitizer (see section below: “2.4.4. Reaction of azepane under different conditions”).

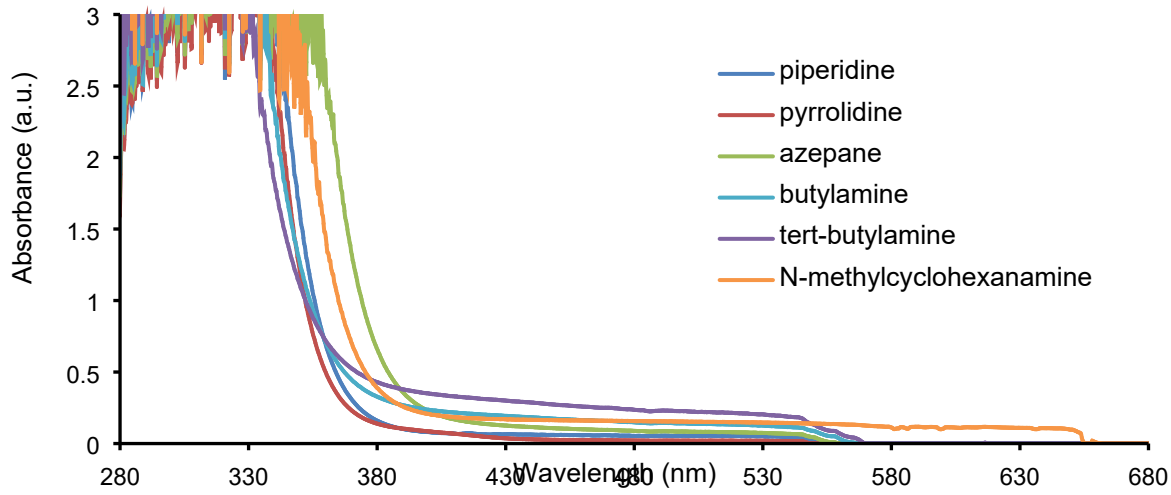


Fig. S11. UV/vis spectra of different *N*-chloroamines in toluene, after formation and membrane separation.

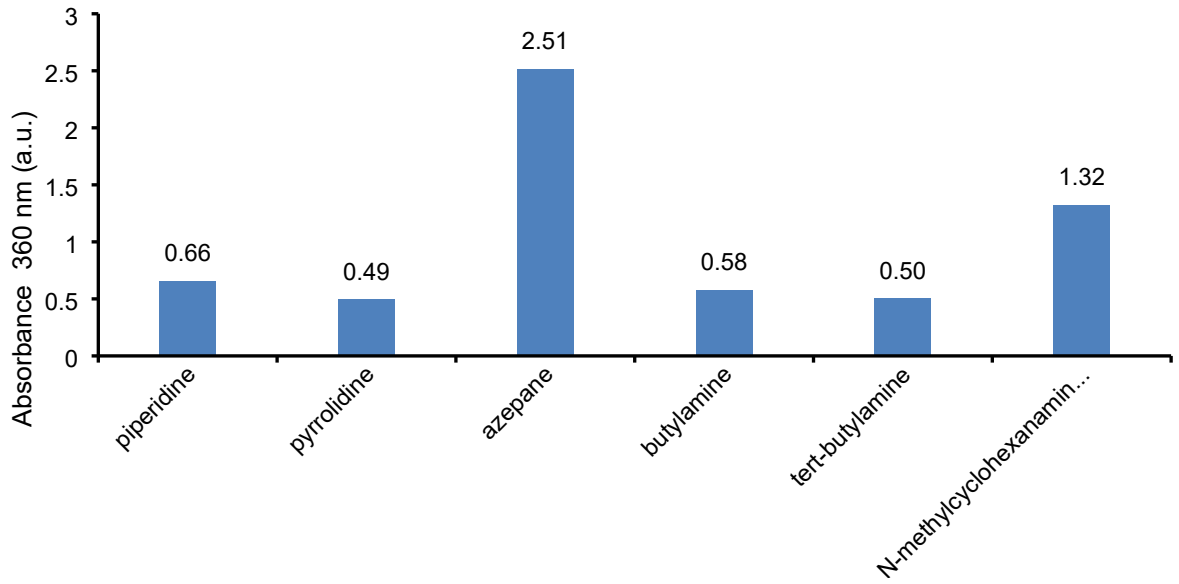
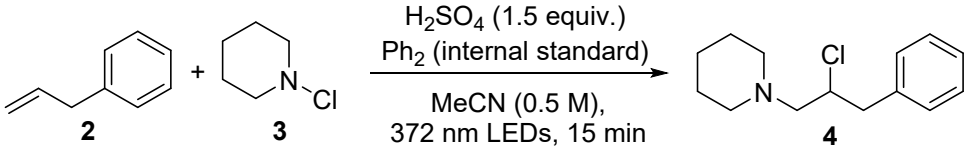


Fig. S12. Summarized absorbance of different *N*-chloroamine substrates at 360 nm. Absorbance averaged between 355-365 nm, with a baseline (average 495-505 nm) subtracted

2.3. Initial batch optimization data

Table S3. Details of batch optimization experiments.



2 0.5 mmol + **3** 1.5 equiv. → **4**

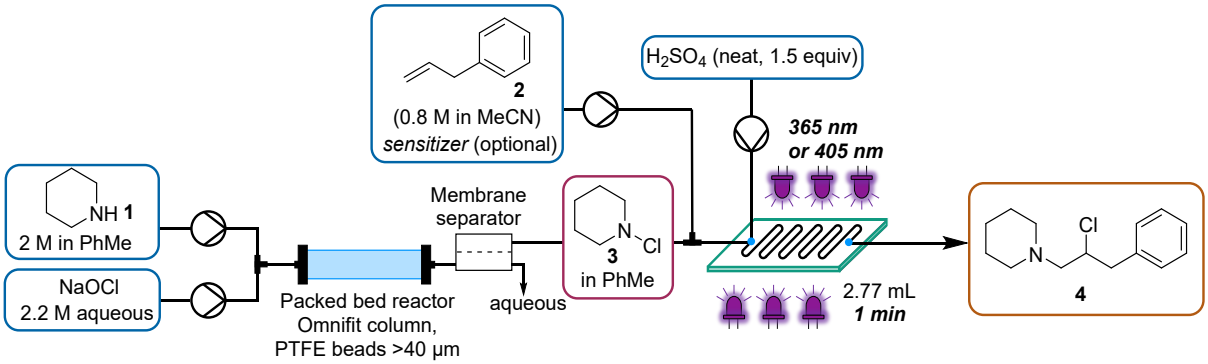
Entry	Deviation from standard conditions	Yield 4 (%)	Conversion[a] (%)	Selectivity[a] (%)
1	No deviation	64[b]	>99	64[b]
2	MeOH as solvent	48	>99	48
3	0.1 M concentration	15	39	39
4	0.1 M in MeOH	34	81	43
5	1 equiv. chloropiperidine **3** and H_2SO_4, 1.5 equiv. allylbenzene **2**	68	>99 (0.90)[c]	68 (76)[d]
6	1 equiv. chloropiperidine **3** and H_2SO_4, 1.5 equiv. allylbenzene **2**, MeOH as solvent	52	>99 (0.84)[c]	52 (61)[d]
7	3 equiv. H_2SO_4	82	>99	82
8	0.75 equiv. H_2SO_4	34	75	45
9	0.3 equiv. H_2SO_4	13	33	40
10	No acid	0	6	0
11	$HClO_4$ instead of H_2SO_4	41	84	49
12	TFA instead of H_2SO_4	16	61	26
13	1.2 equiv. chloramine	65	>99	65
14	1.0 equiv. chloramine	62	90	62
15	No degassing	28	83	33
16	Anhydrous MeCN	65	>99	65
17	Solvent: 70%[e] MeCN 30%[e] water	61	91	69
18	Solvent: 70%[e] MeCN 30%[e] toluene	54	>99	54
19	No irradiation, 20 °C, 1 h (21 h)	4 (14)	14 (>99)	32 (14)
20	No irradiation, 45 °C, 0.5 h	7	94	8
21	No irradiation, 70 °C, 0.6 h	18	>99	18
22	405 nm irradiation	72	>99	72
23[f]	450 nm irradiation	17 - 63	59 - >99	29 - 63

[a]Based on limiting starting material measured by GC-FID analysis, calibrated versus biphenyl as internal standard. [b]Average result of 4 reactions. [c]Value in parentheses shows the number of equivalents of allylbenzene **2** consumed. [d]Value in parentheses shows the selectivity based on consumed allylbenzene **2**. [e]Solvent mixture percentages by volume. [f]Results were highly irreproducible, differences thought to be caused by slight changes in LED distance and angle.

2.4. Additional flow data

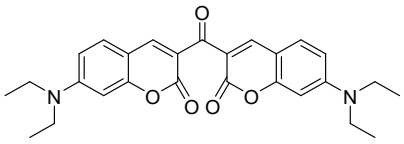
2.4.1. Four-feed flow reaction setup

Following optimization in flow (manuscript **Table 1**, entries 11 and 12) a four-feed setup was utilized for all experiments. This allowed the olefin/sensitizer solution to be separated from the acid stream, avoiding compatibility issues and improving photoreaction selectivity.



Scheme S1. Schematic representation of the four-feed flow setup used for flow experiments after initial optimization.

2.4.2. Ketocoumarin triplet sensitizer



5

The ketocoumarin sensitizer **5** used in manuscript **Table 2**, entry 5 was synthesized according to a published procedure.[1]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.16 (s, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 6.59 (dd, *J* = 8.9, 2.5 Hz, 2H), 6.47 (d, *J* = 2.4 Hz, 2H), 3.43 (q, *J* = 7.1 Hz, 8H), 1.22 (t, *J* = 7.1 Hz, 12H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 188.6, 160.4, 158.2, 152.3, 145.8, 131.1, 120.3, 109.4, 108.4, 97.2, 45.1, 12.5.

The characterization data is in agreement with previous reports.[1]

2.4.3. Incompatible reaction substrates

During the investigation of the reaction substrate scope, a small number of substrates (both amines and olefins) were found to be incompatible. These are summarized below. Unsuccessful amine substrates were found to be incompatible with the NaOCl reaction – this is thought to be due to over-oxidation in most cases.

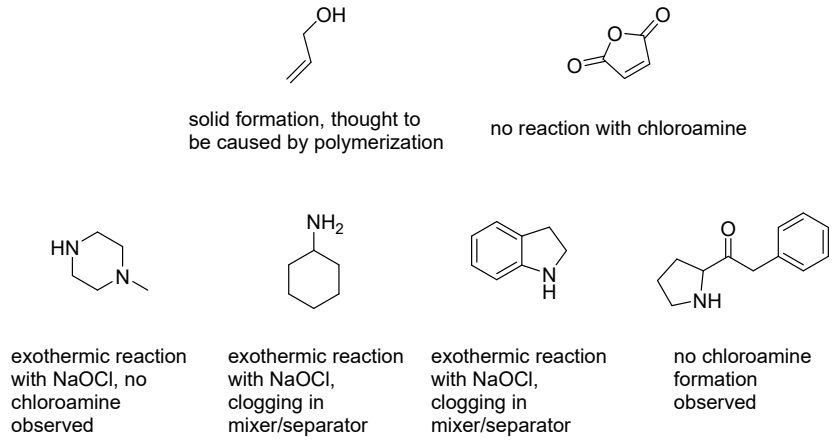


Fig. S13. Summary of substrates which were unsuccessful under the applied reaction conditions, with a summary of observed reaction/reason for incompatibility.

2.4.4. Reaction of azepane under different conditions

Table S4. Comparison of reaction performance with azepane, under different reaction conditions.

Entry	Equiv. Chloramine	Sensitizer 9-fluorenone	Irradiation	Temperature	Stand. ratio product to IS[a]
1	1.5	No	365 nm	20 °C	21
2	1.5	5 mol%	405 nm	20 °C	8
3	1.1	No	365 nm	7 °C	10
4	1.1	5 mol%	405 nm	7 °C	72
5	1.5	5 mol%	405 nm	7 °C	72[b]

[a]Results are estimated based on ratio product/Ph_2, using entry 5 (72% isolated yield) as a comparison. [b]72% isolated yield

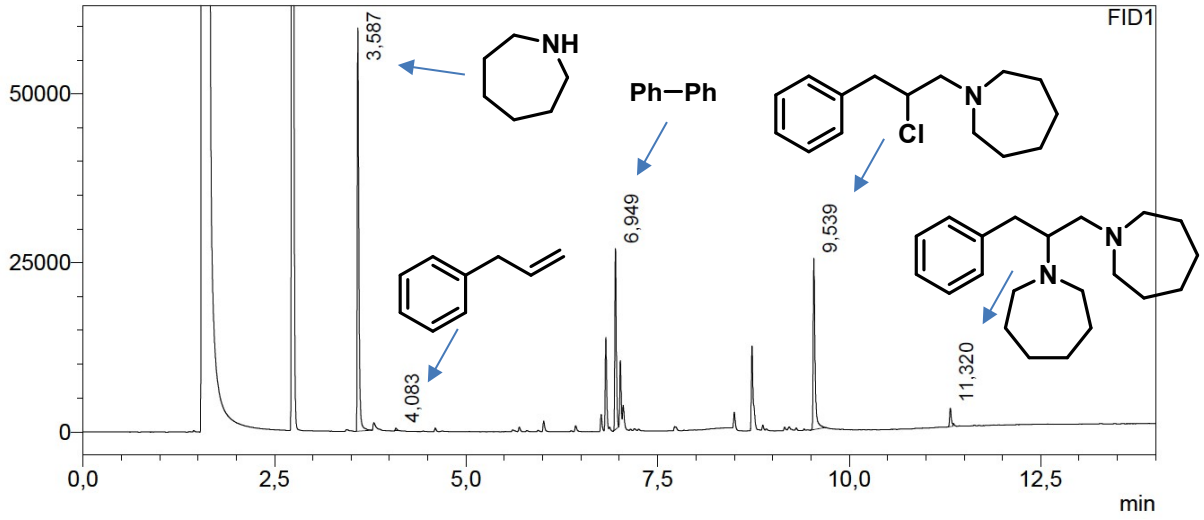


Fig. S14. GC trace of result from **Table S4** Entry 1: 1.5 equiv amine, 20 °C, 365 nm no sensitizer.

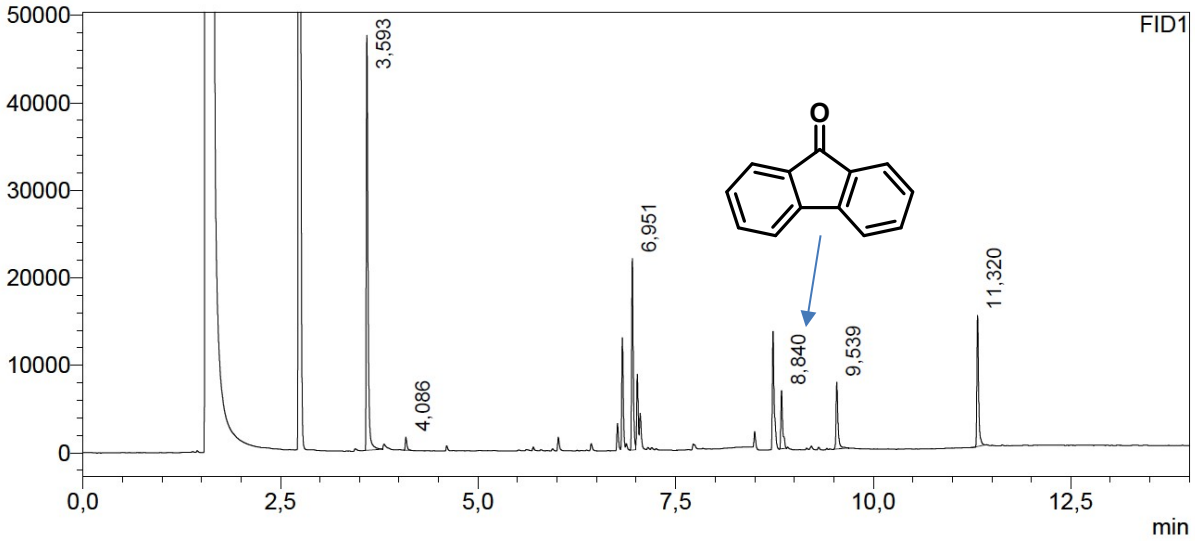


Fig. S15. GC trace of result from **Table S4** Entry 2: 1.5 equiv amine, 20 °C, 405 nm, 5mol% 9-fluorenone.

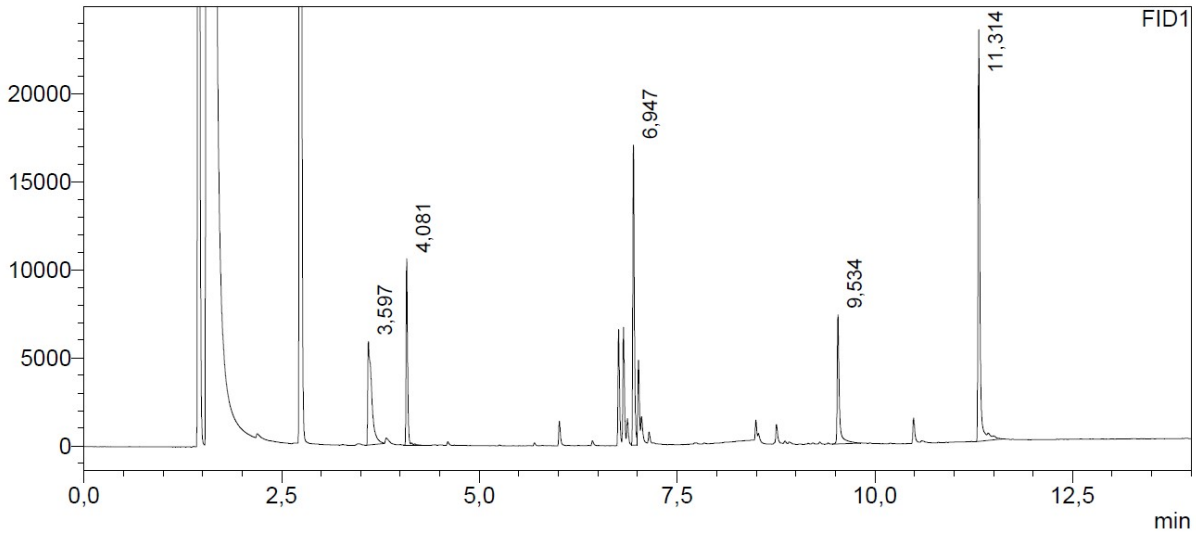


Fig. S16. GC trace of result from **Table S4** Entry 3: 1.1 equiv amine, 7 °C, 365 nm no sensitizer.

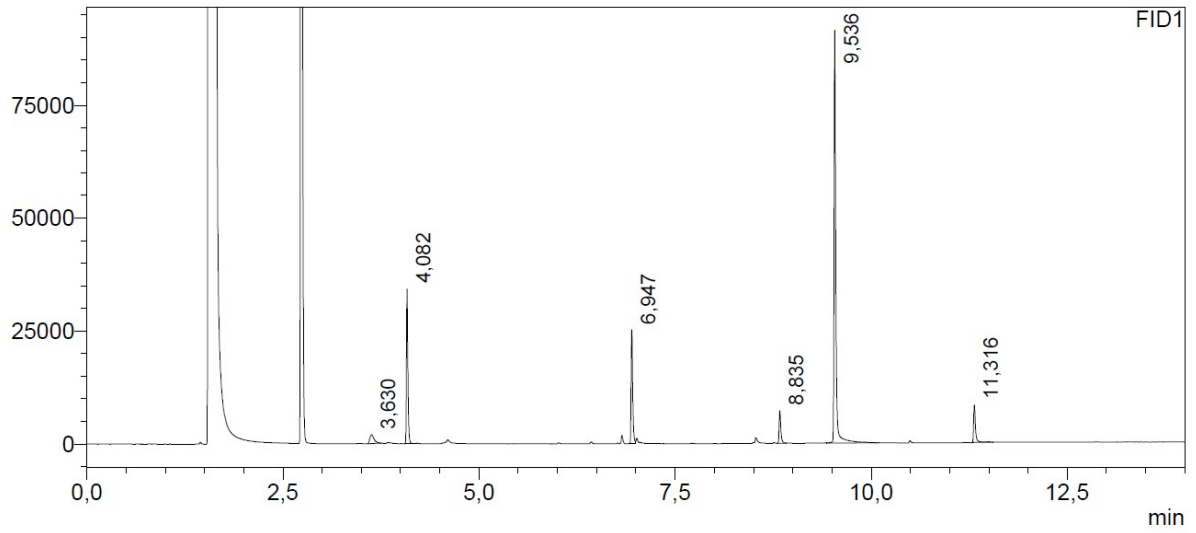


Fig. S17. GC trace of result from **Table S4** Entry 4: 1.1 equiv amine, 7 °C, 405 nm, 5 mol% 9-fluorenone.

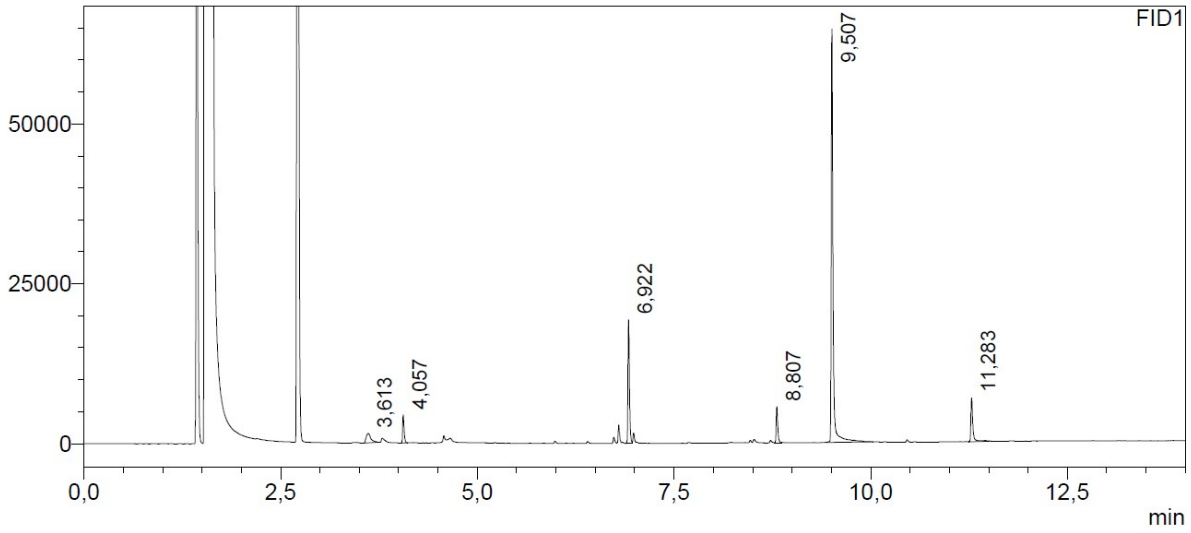


Fig. S18. GC trace of result from **Table S4** Entry 5: 1.5 equiv amine, 7 °C, 405 nm, 5 mol% 9-fluorenone.

2.4.5. Extended operation experiment results

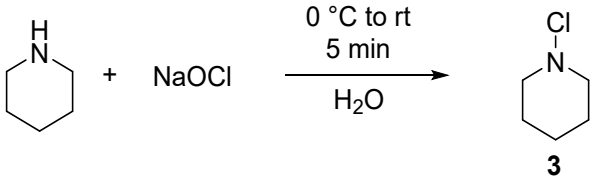
Table S5. Tabulated data from extended operation experiment (manuscript Fig. 2).

Time (min)	[3] (M)[a]	6 (%)[b]
8	1.92	91.4
23	1.92	90.9
38	1.92	93.5
53	1.92	92.0
68	1.92	92.7
83	1.92	90.9
98	1.91	94.3
113	1.91	96.0
128	1.91	95.7
143	1.91	94.9
158	1.91	94.6
173	1.91	93.2
188	1.91	96.2
203	1.91	92.2
218	1.91	93.0
233	1.91	96.6
248	1.90	97.3
263	1.90	95.1

[a]Concentration determined by calibrated inline UV/vis analysis. [b]Yield determined by GC-FID analysis versus Ph_2 as internal standard.

3. Compound isolation and characterization

N-Chloropiperidine 3:



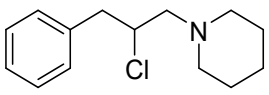
3

A 100 mL round bottomed flask, equipped with a magnetic stirrer, was charged with $NaOCl.5H_2O$ (3.6 g, 22 mmol, 1.1 equiv.) and water (10 mL) to provide a 2 M solution. This solution was cooled in an ice bath. Piperidine (2 mL, 20 mmol) was added. The immediate chloramine formation was observed by the formation of a second phase. The ice bath was removed, then the solution was allowed to warm to rt and diethyl ether (20 mL) was added. After phase separation, the aqueous phase was extracted with diethyl ether (2 × 10 mL). After drying the combined organic phases over Na_2SO_4 and filtering, the diethyl ether was removed under reduced pressure (30 °C, 150 mbar) and the product was obtained as a pale yellow oil (2.3 g, 96% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75-2.50 (br s, 4H), 1.70 (p, *J* = 5.7 Hz, 4H), 1.65-1.25 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.0, 27.7, 23.1;

The characterization data is in agreement with previous reports.[S2]

1-(2-chloro-3-phenylpropyl)piperidine 4:

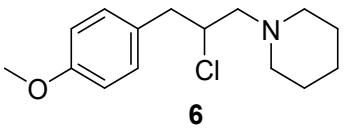


4

Following General Procedure 2-A with a set temperature of 20 °C (measured T = 21 °C), the desired product **4** (631.0 mg, 96%) was obtained as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.22 (m, 5H), 4.19 (tdd, *J* = 7.9, 6.4, 4.3 Hz, 1H), 3.29 (dd, *J* = 14.3, 4.3 Hz, 1H), 2.92 (dd, *J* = 14.3, 8.2 Hz, 1H), 2.63 (dd, *J* = 13.1, 6.4 Hz, 1H), 2.54 (dd, *J* = 13.1, 7.5 Hz, 1H), 2.48-2.37 (m, 4H), 1.59 (p, J = 5.5 Hz, 4H), 1.47-1.39 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 129.7, 128.4, 126.7, 65.2, 60.4, 55.1, 42.4, 26.1, 24.4; HRMS (ESI, positive mode) calculated for $C_{14}H_{20}N[^{35}Cl]$ $(M+H)^+$: 238.1357, found: 238.1355.

1-(2-chloro-3-(4-methoxyphenyl)propyl)piperidine 6:

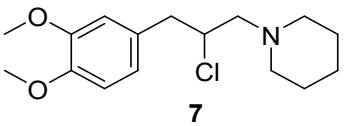


6

Following General Procedure 2-B with a set temperature of 0 °C (measured T = 6 °C), the desired product **6** (1.03 g, 91%) was obtained as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.20-4.10 (m, 1H), 3.80 (s, 3H), 3.20 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.88 (dd, *J* = 14.3, 8.0 Hz, 1H), 2.60 (dd, *J* = 13.1, 6.4 Hz, 1H), 2.52 (dd, *J* = 13.1, 7.3 Hz, 1H), 2.47-2.36 (m, 4H), 1.62-1.55 (m, 4H), 1.46-1.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 130.7, 130.1, 113.8, 65.1, 60.7, 55.4, 55.0, 41.5, 26.1, 24.4; HRMS (ESI, positive mode) calculated for $C_{15}H_{22}NO[^{35}Cl]$ $(M+H)^+$: 268.1463, found: 268.1465.

1-(2-chloro-3-(3,4-dimethoxyphenyl)propyl)piperidine 7:

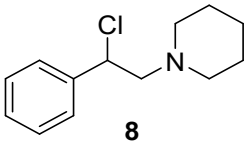


7

Following General Procedure 2-B with a set temperature of 0 °C (measured T = 6 °C), the desired product **7** (730 mg, 58%) was obtained as an olive/brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83-6.77 (m, 3H), 4.22-4.10 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.18 (dd, *J* = 14.3, 4.5 Hz, 1H), 2.90 (dd, *J* = 14.3, 7.7 Hz, 1H), 2.63-2.50 (m, 2H), 2.48-2.37 (m, 4H), 1.62-1.55 (m, 4H), 1.46-1.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 147.9, 130.5, 121.8, 113.0, 111.0, 64.9, 60.5, 55.97, 55.95, 55.1, 41.8, 26.1, 24.4; HRMS (ESI, positive mode) calculated for $C_{16}H_{24}NO_2[^{35}Cl]$ $(M+H)^+$: 298.1568, found: 298.1576.

1-(2-chloro-2-phenylethyl)piperidine 8:



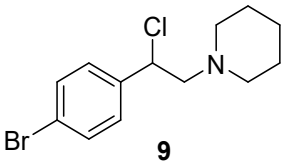
8

Following General Procedure 2-A with a set temperature of 20 °C (measured T = 21 °C), the desired product **8** (850 mg, 91%) was obtained as a dark green/brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.29 (m, 5H), 4.98 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.00 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.79 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.45 (t, *J* = 5.3 Hz, 4H), 1.59-1.50 (m, 4H), 1.44-1.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 128.6, 128.4, 127.4, 67.1, 60.6, 54.8, 26.0, 24.3; HRMS (ESI, positive mode) calculated for $C_{13}H_{18}N[^{35}Cl]$ $(M+H)^+$: 224.1201, found: 224.1204.

The characterization data is in agreement with previous reports.[S3]

1-(2-(4-bromophenyl)-2-chloroethyl)piperidine 9:

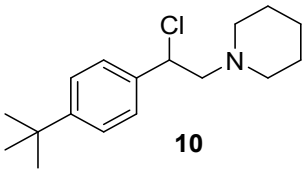


9

Following General Procedure 2-A with a set temperature of 20 °C (measured T = 21 °C), the desired product **9** (1.11 g, 88%) was obtained as a brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.91 (t, *J* = 7.1 Hz, 1H), 2.94 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.76 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.49-2.35 (m, 4H), 1.57-1.47 (m, 4H), 1.43-1.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 131.6, 129.1, 122.1, 66.7, 59.5, 54.8, 25.9, 24.1; HRMS (ESI, positive mode) calculated for $C_{14}H_{20}N[^{35}Cl][^{81}Br]$ $(M+H)^+$: 304.0291, found: 304.0290.

1-(2-(4-(*tert*-butyl)phenyl)-2-chloroethyl)piperidine 10:

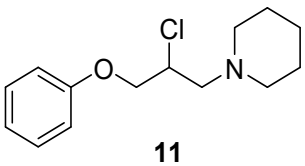


10

Following General Procedure 2-B with a set temperature of 0 °C (measured T = 5 °C), a partially solid mixture was obtained. Petrol was added to this mixture and cooled in the fridge overnight. A pale red solid was removed by filtration, and after removal of the petrol under reduced pressure, the desired product **10** (360 mg, 46%) was obtained as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.31 (m, 4H), 5.00 (dd, *J* = 8.5, 5.4 Hz, 1H), 3.02 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.78 (dd, *J* = 13.6, 5.4 Hz, 1H), 2.48 (t, *J* = 5.5 Hz, 4H), 1.63-1.52 (m, 4H), 1.47-1.63 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 137.9, 126.98, 125.5, 67.0, 60.5, 54.8, 34.6, 31.4, 25.9, 24.3; HRMS (ESI, positive mode) calculated for $C_{17}H_{26}N[^{35}Cl]$ $(M+H)^+$: 280.1827, found: 280.1827.

1-(2-chloro-3-phenoxypropyl)piperidine 11:

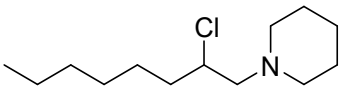


11

Following General Procedure 2-B with a set temperature of 20 °C (measured T = 21 °C), the desired product **11** (860 mg, 82%) was obtained as a green/blue oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.26 (m, 2H), 7.00-6.86 (m, 3H), 4.36-4.13 (m, 3H), 2.79 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.69 (dd, *J* = 13.4, 5.9 Hz, 1H), 2.54-2.39 (m, 4H), 1.60-1.53 (m, 4H), 1.46-1.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 129.6, 121.3, 114.9, 70.6, 62.5, 56.8, 55.3, 26.1, 24.3; HRMS (ESI, positive mode) calculated for $C_{14}H_{20}NO[^{35}Cl]$ $(M+H)^+$: 254.1306, found: 254.1307.

1-(2-chlorooctyl)piperidine 12:

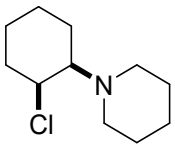


12

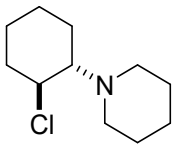
Following General Procedure 2-A with a set temperature of 20 °C (measured T = 21 °C), the desired product **12** (915.1 mg, 95%) was obtained as a dark yellow/orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (dtd, *J* = 8.8, 6.7, 3.6 Hz, 1H), 2.61 (dd, *J* = 13.1, 6.9 Hz, 1H), 2.48 (dd, *J* = 13.1, 6.7 Hz, 1H), 2.44-2.38 (m, 4H), 1.93-1.82 (m, 1H), 1.66-1.49 (m, 6H), 1.45-1.26 (m, 9H), 0.91-0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.3, 60.6, 55.2, 36.6, 31.9, 29.0, 26.4, 26.1, 24.4, 22.7, 14.2.; HRMS (ESI, positive mode) calculated for $C_{13}H_{26}N[^{35}Cl]$ $(M+H)^+$: 232.1827, found: 232.1829.

syn-1-(2-chlorocyclohexyl)piperidine 13 and *anti*-1-(2-chlorocyclohexyl)piperidine 13:



***syn*-13**



***anti*-13**

Following General Procedure 2-A with a set temperature of 2 °C (measured T = 7 °C), a mixture of syn-**13** and anti-**13** was obtained (696 mg, 83%). After separation by column chromatography (5-50% EtOAc+1% Et_3N in cyclohexane) the desired products *syn*-**13** (280 mg, 33%) and *anti*-**13** (229 mg, 27%) were obtained as yellow oils.

Data for *syn*-**13**

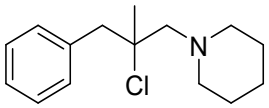
R_f 0.3 [40-60 petroleum ether:EtOAc:Et_3N=1:1:1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60-4.58 (m, 1H), 2.65-2.53 (m, 4H), 2.34-2.28 (m, 1H), 2.06-2.00 (m, 1H), 1.87-1.66 (m, 5H), 1.65-1.52 (m, 4H), 1.50-1.39 (m, 3H), 1.34-1.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.9, 61.1, 50.9, 34.3, 26.4, 25.6, 24.8, 24.3, 19.9; HRMS (ESI, positive mode) calculated for $C_{11}H_{20}N[^{35}Cl]$ $(M+H)^+$: 202.1357, found: 202.1359.

The characterization data is in agreement with previous reports.[S4]

Data for *anti*-**13**

R_f 0.6 [40-60 petroleum ether:EtOAc:Et_3N=1:1:1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (td, *J* = 10.6, 4.3 Hz, 1H), 2.69-2.57 (m, 2H), 2.55-2.37 (m, 3H), 2.32-2.22 (m, 1H),1.92 (br s, 1H), 1.78-1.49 (m, 7H), 1.43 (q, *J* = 5.7 Hz, 2H) 1.29-1.16 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.9, 61.7, 49.8, 37.8, 26.8, 26.3, 26.2, 25.2, 25.1; HRMS (ESI, positive mode) calculated for $C_{11}H_{20}N[^{35}Cl]$ $(M+H)^+$: 202.1357, found: 202.1360.

1-(2-chloro-2-methyl-3-phenylpropyl)piperidine 14:

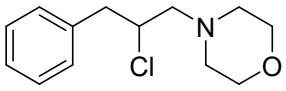


14

Following General Procedure 2-B with a set temperature of 0 °C (measured T = 6 °C), the desired product **14** (775 mg, 77%) was obtained as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.25 (m, 5H), 3.09 (q, *J* = 13.7 Hz, 2H), 2.62-2.58 (m, 6H), 1.62-1.54 (m, 4H), 1.44-1.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 131.3, 127.9, 126.7, 74.6, 70.3, 57.0, 47.5, 27.5, 26.5, 24.2; HRMS (ESI, positive mode) calculated for $C_{15}H_{22}[^{35}Cl]N$ $(M+H)^+$: 252.1514, found: 252.1509.

4-(2-chloro-3-phenylpropyl)morpholine 15:



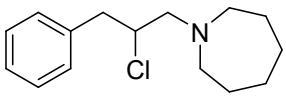
15

Following General Procedure 2-A with a set temperature of 20 °C (measured T = 21 °C), the desired product **15** (913 mg, 92%) was obtained as a dark yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.22 (m, 5H), 4.25-4.15 (m, 1H), 3.74-3.71 (m, 4H), 3.26 (dd, *J* = 14.2, 4.7 Hz, 1H), 2.96 (dd, *J* = 14.3, 8.0 Hz, 1H), 2.68 (dd, *J* = 13.2, 6.7 Hz, 1H), 2.59 (dd, *J* = 13.2, 6.9 Hz, 1H), 2.52-2.49 (m, 4H); ^{13}C NMR (75 MHz, CDCl3) δ 137.8, 129.7, 128.5, 126.89, 67.1, 64.7, 59.6, 54.0, 42.4; HRMS (ESI, positive mode) calculated for $C_{13}H_{18}[^{35}Cl]NO$ $(M+H)^+$: 240.1150, found: 240.1151.

The characterization data is in agreement with previous reports.[S5]

1-(2-chloro-3-phenylpropyl)azepane 16:

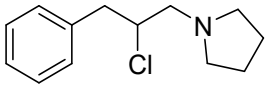


16

Following General Procedure 2-A adding 5 mol% 9-fluorenone to the olefin solution and irradiating at 405 nm with a set temperature of 0 °C (measured T = 7 °C), the desired product **16** (752 mg, 72%) was obtained as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.21 (m, 5H), 4.12-4.03 (m, 1H), 3.35 (dd, *J* = 14.2, 4.0 Hz, 1H), 2.90-2.82 (m, 2H), 2.73-2.66 (m, 5H), 1.66 -1.54 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 129.7, 128.4, 126.7, 64.0, 61.8, 55.9, 42.2, 28.7, 27.3; HRMS (ESI, positive mode) calculated for $C_{15}H_{22}[^{35}Cl]N$ $(M+H)^+$: 252.1514, found: 252.1515.

1-(2-chloro-3-phenylpropyl)pyrrolidine 17:

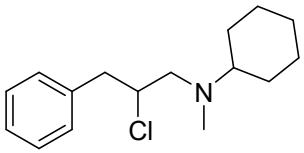


17

Following General Procedure 2-A adding 5 mol% 9-fluorenone to the olefin solution and irradiating at 405 nm with a set temperature of 0 °C (measured T = 7 °C), the desired product **17** (533 mg, 57%) was obtained as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.22 (m, 5H), 4.21-4.12 (m, 1H), 3.25 (dd, *J* = 14.2, 4.8 Hz, 1H), 2.95 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.76 (dd, *J* = 6.8, 1.8 Hz, 2H), 2.60-2.55 (m, 4H), 1.82-1.77 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 129.7, 128.4, 126.8, 62.7, 61.6, 54.5, 42.6, 23.7; HRMS (ESI, positive mode) calculated for $C_{13}H_{18}[^{35}Cl]N$ $(M+H)^+$: 224.1201, found: 224.1200.

N-(2-chloro-3-phenylpropyl)-*N*-methylcyclohexanamine 18:

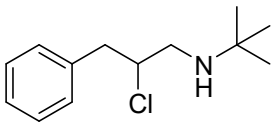


18

Following General Procedure 2-A adding 5mol% 9-fluorenone to the olefin solution and irradiating at 405 nm with a set temperature of 0 °C (measured T = 7 °C), the desired product **18** (752 mg, 68%) was obtained as an orange-red oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.21 (m, 5H), 4.12-4.03 (m, 1H), 3.35 (dd, *J* = 14.3, 4.0 Hz, 1H), 2.84-2.63 (m, 3H), 2.45-2.34 (m, 1H), 2.32 (s, 3H), 1.82-1.72 (m, 4H), 1.65-1.61 (m, 1H), 1.30-1.04 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 129.5, 128.4, 126. 7, 63.7, 62.3, 60.5, 42.4, 38.9, 28.89, 28.85, 26.5, 26.19, 26.17; HRMS (ESI, positive mode) calculated for $C_{16}H_{24}[^{35}Cl]N$ $(M+H)^+$: 266.1670, found: 266.1672.

N-(*tert*-butyl)-2-chloro-3-phenylpropan-1-amine 19:



19

Following General Procedure 2-A adding 5mol% 9-fluorenone to the olefin solution and irradiating at 405 nm with a set temperature of 0 °C (measured T = 7 °C) crude product (504 mg, 54% yield) with a purity of 90 % (GC-FID area) was obtained as an orange oil. After purification by column chromatography (2-25% EtOAc+1% Et_3N in cyclohexane) the desired product **19** (335 mg, 36%) was obtained as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.23 (m, 5H), 4.28-4.19 (m, 1H), 3.19 (dd, *J* = 14.0, 6.2 Hz, 1H), 3.06 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.90 (dd, *J* = 12.2, 3.9 Hz, 1H), 2.80 (dd, *J* = 12.2, 7.8 Hz, 1H), 1.51 (br s, 1H), 1.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 129.4, 128.6, 126.9, 64.8, 50.4, 48.8, 42.9, 29.2; HRMS (ESI, positive mode) calculated for $C_{13}H_{20}[^{35}Cl]N$ $(M+H)^+$: 226.1357, found: 226.1359.

4. DFT Calculations

Calculations were carried out on a desktop computer (AMD Ryzen 9 3950X processor, 32 GB RAM). All density functional theory (DFT) calculations[S6] were carried out using the Gaussian09 software package.[S7] Solvation was modelled implicitly, using a conductor-like polarizable continuum model (CPCM)[S8] with acetonitrile (ε = 36.6) assigned as the solvent. All structures were found as energy minima, with frequency calculations performed, to verify zero imaginary frequencies. All transition states had a negative frequency and were verified using an intrinsic reaction coordinate (IRC) calculation. CYLview20 was used for the visualization of structures and plotting energy level diagrams.

Quoted triplet energies were approximated by simply subtracting the ground state singlet energy (multiplicity 1) from the ground state triplet energy (multiplicity 3). CAM-B3LYP was used for these ground state triplet calculations, due to the better stability of the triplet state molecule.

Details of all optimized structures and transition states are presented below.

4.1. Additional calculations

4.1.1. Involvement of Cl_2 homolysis

As discussed in the manuscript, it is also possible for the radical chain reaction to be initiated by the homolysis of Cl_2. The performed calculations imply that this route to forming aminium radicals has an energy barrier of not insignificant magnitude. Paired with the fact that Cl_2 is likely only present in trace quantities, this pathway is likely not responsible for the observed reaction.

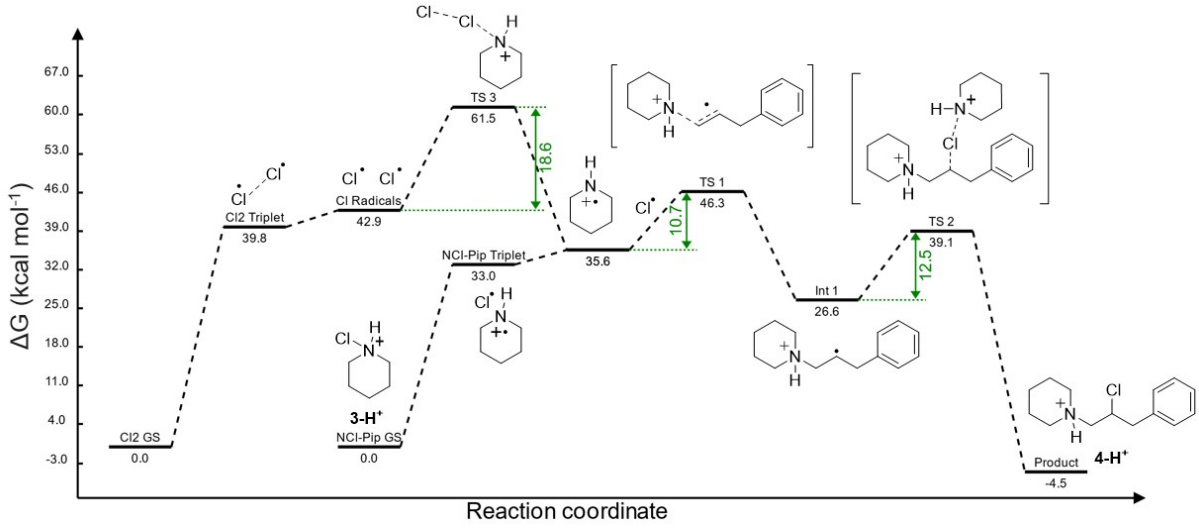


Fig. S19. Modified reaction pathway calculation, showing homolysis of Cl_2 as an alternative possible route of initiation.

4.1.2. Reaction with maleic anhydride

Maleic anhydride was tested as an olefin substrate, but was found to be unreactive. The energy barrier to this radical addition was calculated to be 23.5 kcal mol^{-1} and the resulting radical species (Int2) is not stabilized compared to the starting piperidinium radical.

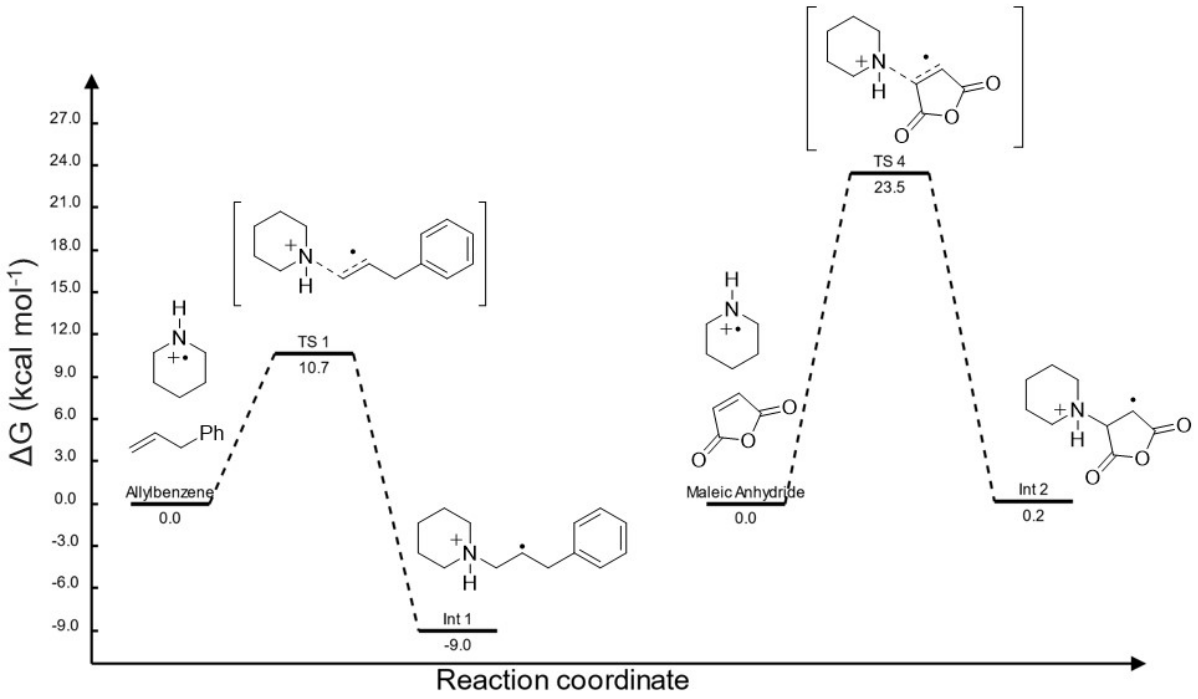
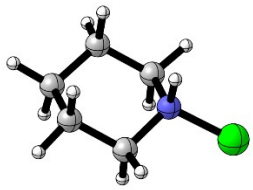


Fig. S20. Comparison of aminium radical addition to allylbenzene **2** versus maleic anhydride (incompatible substrate).

4.2. All structures and intermediates

N-Chloropiperidinium Cation Ground State



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Sum of electronic and thermal Energies=              -711.677538
Sum of electronic and thermal Enthalpies=            -711.676594
Sum of electronic and thermal Free Energies=         -711.714899
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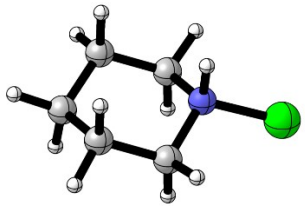
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.058778	1.255799	-0.189245
2	6	0	-1.526833	1.250880	0.211542
3	6	0	-2.238760	0.000000	-0.297584
4	6	0	-1.526834	-1.250879	0.211546
5	6	0	-0.058782	-1.255798	-0.189247
6	7	0	0.602190	-0.000001	0.327417
7	17	0	2.308155	-0.000001	-0.052277
8	1	0	0.559338	-0.000001	1.353425
9	1	0	0.074414	1.233114	-1.271687
10	1	0	0.490339	2.094661	0.233628
11	1	0	-1.611443	1.324077	1.300356
12	1	0	-1.968442	2.158312	-0.203898
13	1	0	-3.276644	0.000001	0.036450
14	1	0	-2.246453	-0.000001	-1.391955
15	1	0	-1.611446	-1.324071	1.300361
16	1	0	-1.968449	-2.158312	-0.203886
17	1	0	0.490343	-2.094660	0.233613
18	1	0	0.074400	-1.233111	-1.271692

N-Chloropiperidinium Cation Ground State (CAM-B3LYP)



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Sum of electronic and thermal Energies=              -711.682909
Sum of electronic and thermal Enthalpies=            -711.681965
Sum of electronic and thermal Free Energies=         -711.720280
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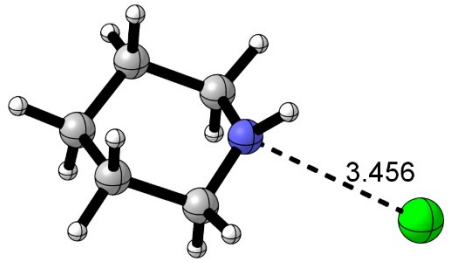
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.060294	-1.256250	-0.187700
2	6	0	1.528286	-1.252168	0.207095
3	6	0	2.243427	0.000000	-0.290506
4	6	0	1.528286	1.252167	0.207095
5	6	0	0.060294	1.256250	-0.187700
6	7	0	-0.600748	0.000000	0.324461
7	17	0	-2.315146	0.000000	-0.051680
8	1	0	-0.563643	0.000000	1.348346
9	1	0	-0.076434	-1.245255	-1.268324
10	1	0	-0.484473	-2.094679	0.239361
11	1	0	1.618378	-1.338377	1.293910
12	1	0	1.969986	-2.155780	-0.216173
13	1	0	3.277267	0.000000	0.055975
14	1	0	2.270655	0.000000	-1.384251
15	1	0	1.618378	1.338377	1.293910
16	1	0	1.969986	2.155780	-0.216173
17	1	0	-0.484473	2.094679	0.239361
18	1	0	-0.076435	1.245255	-1.268324

N-Chloropiperidinium Triplet State (CAM-B3LYP)

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Sum of electronic and zero-point Energies=           -711.630397
Sum of electronic and thermal Energies=              -711.621959
Sum of electronic and thermal Enthalpies=            -711.621015
Sum of electronic and thermal Free Energies=         -711.667734
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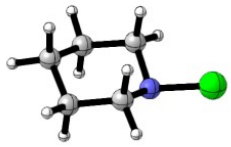
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.407092	-1.236193	0.019778
2	6	0	1.960817	-1.260203	0.103137
3	6	0	2.547697	-0.000004	-0.520093
4	6	0	1.960824	1.260199	0.103135
5	6	0	0.407099	1.236197	0.019777
6	7	0	-0.041298	0.000004	0.582176
7	17	0	-3.420318	0.000000	-0.145473
8	1	0	-0.482902	0.000005	1.499687
9	1	0	0.110601	-1.257233	-1.032714
10	1	0	-0.044918	-2.066491	0.554608
11	1	0	2.252776	-1.349167	1.151487
12	1	0	2.290338	-2.161876	-0.413628
13	1	0	3.630659	-0.000007	-0.376822
14	1	0	2.367924	-0.000005	-1.598961
15	1	0	2.252784	1.349163	1.151485
16	1	0	2.290350	2.161869	-0.413632
17	1	0	-0.044906	2.066498	0.554605
18	1	0	0.110607	1.257237	-1.032715

N-Chloropiperidine Ground State (CAM-B3LYP)



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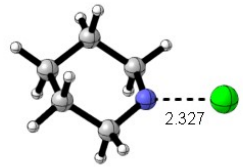
Sum of electronic and thermal Enthalpies= -711.268679
Sum of electronic and thermal Free Energies= -711.307045

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.029258	1.215002	0.178088
2	6	0	1.502456	1.251391	-0.216045
3	6	0	2.231008	0.000000	0.265984
4	6	0	1.502456	-1.251391	-0.216045
5	6	0	0.029258	-1.215002	0.178088
6	7	0	-0.578227	0.000000	-0.379106
7	17	0	-2.303961	0.000000	0.020332
8	1	0	-0.499222	2.077232	-0.228132
9	1	0	-0.071905	1.233257	1.273081
10	1	0	1.578486	1.331206	-1.304528
11	1	0	1.950374	2.153674	0.206749
12	1	0	3.264429	0.000000	-0.087569
13	1	0	2.268420	0.000000	1.360912
14	1	0	1.578486	-1.331206	-1.304528
15	1	0	1.950374	-2.153674	0.206749
16	1	0	-0.499222	-2.077232	-0.228132
17	1	0	-0.071905	-1.233257	1.273081

N-Chloropiperidine Triplet State (CAM-B3LYP)

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Sum of electronic and thermal Enthalpies=            -711.227949
Sum of electronic and thermal Free Energies=         -711.271157
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Standard orientation:

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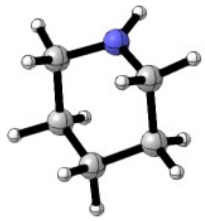
1	6	0	-0.558081	0.059443	1.237648
2	6	0	-0.558081	-1.479629	1.254614
3	6	0	-1.223633	-2.037043	0.000000
4	6	0	-0.558081	-1.479629	-1.254614
5	6	0	-0.558081	0.059443	-1.237648
6	7	0	-0.038338	0.549802	0.000000
7	17	0	1.692761	2.105075	0.000000
8	1	0	0.025113	0.477164	2.057237
9	1	0	-1.589821	0.429132	1.329458
10	1	0	0.474962	-1.831510	1.319474
11	1	0	-1.071476	-1.808083	2.159891
12	1	0	-1.163023	-3.127327	0.000000
13	1	0	-2.287379	-1.776479	0.000000
14	1	0	0.474962	-1.831510	-1.319474
15	1	0	-1.071476	-1.808083	-2.159891
16	1	0	0.025113	0.477164	-2.057237
17	1	0	-1.589821	0.429132	-1.329458

N-Chloropiperidinium Radical Cation



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Standard orientation:

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1	6	0	1.234151	-0.773460	0.239964
2	6	0	1.258376	0.712501	-0.242165
3	6	0	-0.000363	1.431745	0.227313
4	6	0	-1.258791	0.711861	-0.242015
5	6	0	-1.233759	-0.774131	0.239796
6	7	0	0.000410	-1.338783	-0.210776
7	1	0	0.000677	-1.938720	-1.034996
8	1	0	2.069108	-1.343869	-0.157458
9	1	0	1.237563	-0.785246	1.333428
10	1	0	2.165392	1.157522	0.168294
11	1	0	1.332892	0.724022	-1.331685
12	1	0	-0.000675	2.449481	-0.170768
13	1	0	-0.000310	1.508373	1.318718
14	1	0	-2.165931	1.156399	0.168699
15	1	0	-1.333512	0.723557	-1.331516
16	1	0	-2.068330	-1.344920	-0.157905
17	1	0	-1.237425	-0.786214	1.333265

Chlorine Radical

```
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Standard orientation:

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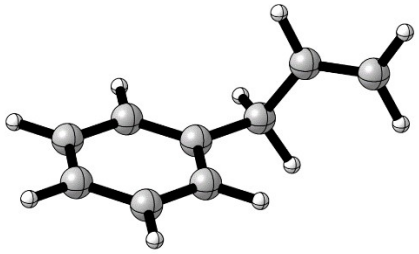
Allylbenzene



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Sum of electronic and thermal Enthalpies= -348.715864
Sum of electronic and thermal Free Energies= -348.759118

Standard orientation:

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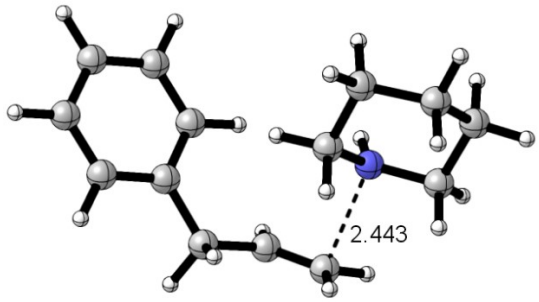
3	6	0	-2.258620	-0.907225	-0.275923
4	6	0	-0.947666	-1.274941	0.023660
5	6	0	0.009334	-0.309705	0.333945
6	6	0	-0.369900	1.035355	0.335966
7	6	0	1.443248	-0.691307	0.640465
8	6	0	2.370302	-0.291800	-0.476303
9	1	0	2.172817	-0.749715	-1.443880
10	6	0	3.368772	0.576588	-0.350463
11	1	0	-1.956444	2.454134	0.052813
12	1	0	-3.646155	0.721063	-0.497468
13	1	0	-2.991043	-1.670465	-0.512782
14	1	0	-0.666992	-2.323412	0.019785
15	1	0	0.370393	1.794779	0.569626
16	1	0	1.765941	-0.209204	1.567675
17	1	0	1.498416	-1.773153	0.793167
18	1	0	4.001285	0.838045	-1.190977
19	1	0	3.583377	1.052235	0.601933

TS1 (Piperidinium Radical Cation and Allylbenzene to Intermediate 1)



Opt=QST3 freq M062X/6-311++G(d,p) FormCheck
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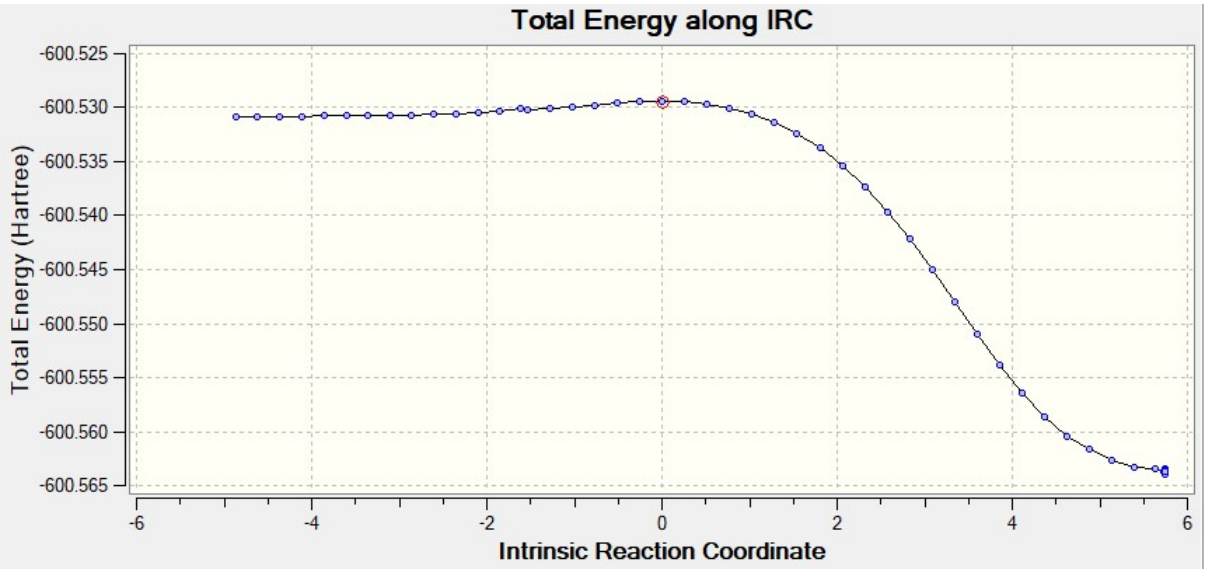
Charge = 1 Multiplicity = 2

Imaginary Freq. (cm^{-1}): -226.6690
Sum of electronic and zero-point Energies= -600.206106
Sum of electronic and thermal Energies= -600.191480
Sum of electronic and thermal Enthalpies= -600.190536
Sum of electronic and thermal Free Energies= -600.250941

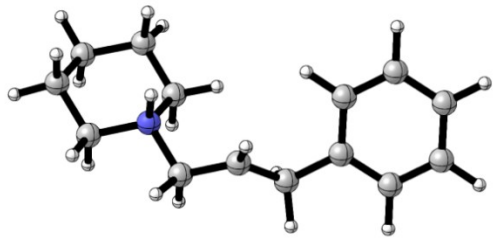
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.021925	-0.951003	-0.674905
2	6	0	-3.760189	-1.638761	0.509369
3	6	0	-2.732086	-1.207106	1.337823
4	6	0	-1.966496	-0.095415	0.985803
5	6	0	-2.217909	0.597199	-0.198064
6	6	0	-3.257845	0.155911	-1.022078
7	6	0	-1.396118	1.793537	-0.644132
8	6	0	-0.406137	2.301790	0.351178
9	6	0	0.881284	2.572217	0.059748
10	7	0	1.868783	0.368418	0.425768
11	6	0	1.347035	-0.493616	-0.615925
12	6	0	2.105384	-1.839243	-0.556935
13	6	0	3.610892	-1.603021	-0.642028
14	6	0	4.073282	-0.646402	0.453498
15	6	0	3.284093	0.680931	0.374748
16	1	0	1.468584	0.253373	1.355404
17	1	0	-4.823246	-1.277784	-1.327305
18	1	0	-4.354819	-2.502684	0.781636
19	1	0	-2.519975	-1.731930	2.261894
20	1	0	-1.173395	0.224214	1.653476
21	1	0	-3.466493	0.687406	-1.945198
22	1	0	-0.888463	1.561441	-1.586178
23	1	0	-2.090530	2.613669	-0.870266
24	1	0	-0.765075	2.480102	1.362221
25	1	0	1.253289	2.480409	-0.956130
26	1	0	1.539100	3.020092	0.795370
27	1	0	1.534463	-0.007298	-1.576864
28	1	0	0.275732	-0.626420	-0.470236
29	1	0	1.849578	-2.351643	0.374765
30	1	0	1.745030	-2.451926	-1.385160
31	1	0	4.138086	-2.554577	-0.546305
32	1	0	3.863903	-1.188267	-1.623332

33	1	0	3.923129	-1.091821	1.440807
34	1	0	5.131997	-0.399852	0.355766
35	1	0	3.533409	1.348972	1.196610
36	1	0	3.484616	1.173498	-0.579948



Int1 (1-(3-phenylpropyl)piperidinium Radical Cation)



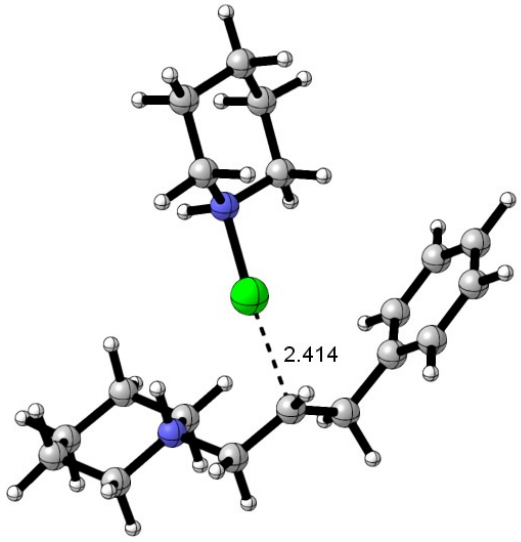
Opt Freq M062X/6-311++G(d,p) FormCheck scrf=(CPCM,solvent=Acetonitrile)
Charge = 1 Multiplicity = 2

Sum of electronic and zero-point Energies= -600.238518
Sum of electronic and thermal Energies= -600.224368
Sum of electronic and thermal Enthalpies= -600.223424
Sum of electronic and thermal Free Energies= -600.282298

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.929594	-0.159454	0.338633
2	6	0	-4.847170	1.071414	-0.305866
3	6	0	-3.601960	1.566003	-0.684873
4	6	0	-2.448398	0.834087	-0.419680
5	6	0	-2.520547	-0.401688	0.227851
6	6	0	-3.773564	-0.889597	0.600526
7	6	0	-1.268040	-1.185390	0.551386
8	6	0	-0.250208	-1.194364	-0.539074
9	6	0	1.145223	-1.636474	-0.288061
10	7	0	2.144650	-0.496692	-0.396369
11	6	0	1.905132	0.560723	0.645421
12	6	0	2.890300	1.708521	0.486342
13	6	0	4.332466	1.210397	0.548141
14	6	0	4.554601	0.125316	-0.503404
15	6	0	3.557119	-1.010652	-0.338400
16	1	0	2.007190	-0.060949	-1.314541
17	1	0	-5.894339	-0.554672	0.634828
18	1	0	-5.745960	1.639454	-0.514852
19	1	0	-3.527431	2.522787	-1.188702
20	1	0	-1.483258	1.228034	-0.722473
21	1	0	-3.845747	-1.850555	1.099413
22	1	0	-0.815981	-0.788461	1.471113
23	1	0	-1.547542	-2.219594	0.800024
24	1	0	-0.561769	-1.040043	-1.566001
25	1	0	1.274717	-2.048097	0.714894
26	1	0	1.472808	-2.378461	-1.018912
27	1	0	2.022145	0.062690	1.611016
28	1	0	0.873526	0.893100	0.536424
29	1	0	2.706725	2.215553	-0.466877
30	1	0	2.687464	2.431826	1.277731
31	1	0	5.024499	2.037782	0.386356
32	1	0	4.536767	0.802739	1.543772
33	1	0	4.460228	0.548734	-1.508903
34	1	0	5.556587	-0.300037	-0.426797
35	1	0	3.654958	-1.761703	-1.121302
36	1	0	3.659696	-1.496348	0.634723

TS2 (Intermediate 1 and *N*-chloropiperidinium cation to Product)



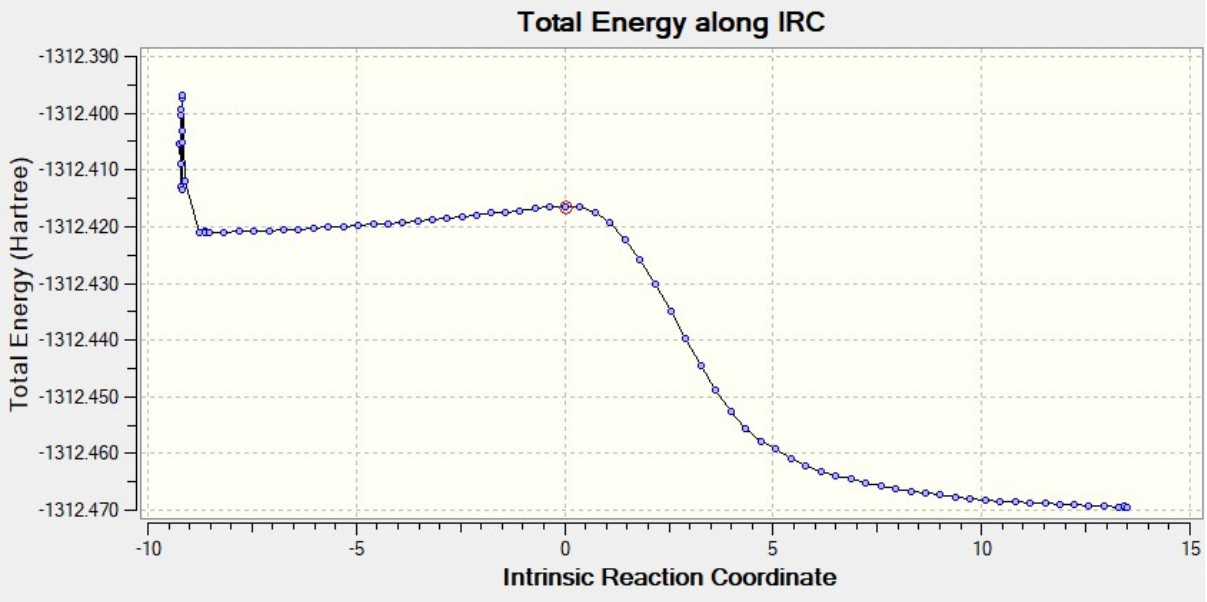
opt=qst3 Freq M062X/6-311++G(d,p) FormCheck
scrf=(CPCM,solvent=Acetonitrile)
Charge = 2 Multiplicity = 2

Imaginary Freq. (cm^{-1}): -269.1948
Sum of electronic and zero-point Energies= -1311.922500
Sum of electronic and thermal Energies= -1311.900701
Sum of electronic and thermal Enthalpies= -1311.899757
Sum of electronic and thermal Free Energies= -1311.977225

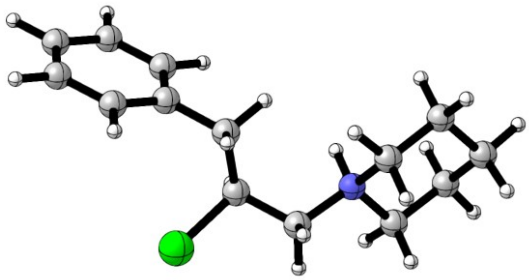
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.246375	-2.953398	-0.742519
2	6	0	-3.802413	-2.518882	0.458738
3	6	0	-2.969455	-2.167959	1.516631
4	6	0	-1.586309	-2.240960	1.370178
5	6	0	-1.024317	-2.668341	0.168564
6	6	0	-1.864839	-3.031405	-0.884478
7	6	0	0.476831	-2.697267	-0.002036
8	6	0	0.988960	-1.771857	-1.058007
9	6	0	2.468011	-1.509122	-1.186455
10	7	0	2.980687	-0.284860	-0.475984
11	6	0	2.812435	-0.342280	1.020154
12	6	0	3.300559	0.950297	1.656243
13	6	0	4.757936	1.231800	1.299067
14	6	0	4.929875	1.245783	-0.218103
15	6	0	4.426133	-0.043971	-0.843609
16	1	0	2.442740	0.521023	-0.814660
17	1	0	-3.888492	-3.237903	-1.567723
18	1	0	-4.878636	-2.460237	0.570236
19	1	0	-3.393635	-1.831059	2.455614
20	1	0	-0.940213	-1.954538	2.194010
21	1	0	-1.440308	-3.380659	-1.820882
22	1	0	0.979906	-2.533695	0.953176
23	1	0	0.789426	-3.703250	-0.331532
24	1	0	0.441001	-1.760239	-1.994437
25	1	0	3.033368	-2.350886	-0.776232

26	1	0	2.734007	-1.381736	-2.234317
27	1	0	3.390549	-1.206827	1.354734
28	1	0	1.757813	-0.510449	1.226883
29	1	0	2.661917	1.777654	1.326533
30	1	0	3.168119	0.855209	2.735097
31	1	0	5.070313	2.187820	1.720803
32	1	0	5.397920	0.457757	1.734590
33	1	0	4.392025	2.094573	-0.653063
34	1	0	5.979209	1.356419	-0.496167
35	1	0	4.475672	-0.018196	-1.931099
36	1	0	4.977991	-0.913852	-0.480625
37	6	0	-1.539988	2.592853	-1.331921
38	6	0	-2.355855	3.819234	-0.930512
39	6	0	-3.582572	3.414247	-0.116590
40	6	0	-3.155467	2.613253	1.111341
41	6	0	-2.328821	1.393040	0.712921
42	7	0	-1.162141	1.834013	-0.105630
43	17	0	-0.157731	0.301826	-0.595965
44	1	0	-0.501698	2.371803	0.463750
45	1	0	-2.127063	1.907286	-1.945566
46	1	0	-0.619688	2.852674	-1.851729
47	1	0	-1.727083	4.505211	-0.354746
48	1	0	-2.637449	4.333765	-1.850899
49	1	0	-4.137253	4.301619	0.190849
50	1	0	-4.250787	2.808345	-0.736826
51	1	0	-2.571956	3.241907	1.790804
52	1	0	-4.018611	2.247639	1.670567
53	1	0	-1.935443	0.853420	1.573100
54	1	0	-2.898017	0.703885	0.084828



Product (1-(2-chloro-3-phenylpropyl)piperidinium cation)



Opt Freq M062X/6-311++G(d,p) FormCheck scrf=(CPCM,solvent=Acetonitrile)
Charge = 1 Multiplicity = 1

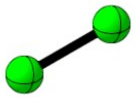
Sum of electronic and zero-point Energies= -1060.494304
Sum of electronic and thermal Energies= -1060.479420
Sum of electronic and thermal Enthalpies= -1060.478476
Sum of electronic and thermal Free Energies= -1060.537972

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.707325	-1.795731	-1.076889
2	6	0	4.816573	-1.267367	-0.421305
3	6	0	4.636761	-0.357621	0.616593
4	6	0	3.352706	0.025376	0.995119
5	6	0	2.237327	-0.495939	0.340709
6	6	0	2.425536	-1.411852	-0.695973
7	6	0	0.842367	-0.064123	0.722587
8	6	0	0.251933	0.950215	-0.254868
9	6	0	-1.182636	1.365312	0.055129
10	7	0	-2.151482	0.216432	-0.096588
11	6	0	-2.636936	-0.301018	1.237274
12	6	0	-3.552194	-1.499082	1.047957
13	6	0	-4.740278	-1.145534	0.155836
14	6	0	-4.246056	-0.591664	-1.178907
15	6	0	-3.319139	0.594724	-0.978216
16	17	0	1.216266	2.474717	-0.223632
17	1	0	-1.673775	-0.558536	-0.570454
18	1	0	3.839727	-2.511560	-1.879593
19	1	0	5.815517	-1.567248	-0.715077
20	1	0	5.495736	0.055096	1.132528
21	1	0	3.215047	0.737126	1.802228
22	1	0	1.563132	-1.833783	-1.203704
23	1	0	0.197216	-0.949804	0.731434
24	1	0	0.828421	0.363383	1.728801
25	1	0	0.325750	0.588205	-1.282085
26	1	0	-1.266762	1.741551	1.074951
27	1	0	-1.494606	2.148051	-0.633532
28	1	0	-3.160384	0.536465	1.703101
29	1	0	-1.755830	-0.538901	1.831664
30	1	0	-2.983929	-2.328958	0.614438
31	1	0	-3.882225	-1.820137	2.037185
32	1	0	-5.359884	-2.027370	-0.011062
33	1	0	-5.362839	-0.397146	0.656538
34	1	0	-3.720175	-1.371709	-1.739754
35	1	0	-5.078287	-0.257951	-1.800675
36	1	0	-2.899023	0.951020	-1.917951

37	1	0	-3.818709	1.422821	-0.471395

Chlorine Ground State



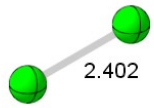
```
Opt Freq M062X/6-311++G(d,p) FormCheck scrf=(CPCM,solvent=Acetonitrile)
Charge =  0 Multiplicity = 1

Sum of electronic and zero-point Energies=           -920.345287
Sum of electronic and thermal Energies=              -920.342744
Sum of electronic and thermal Enthalpies=            -920.341800
Sum of electronic and thermal Free Energies=         -920.367103
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	0.000000	0.000000	1.011121
2	17	0	0.000000	0.000000	-1.011121

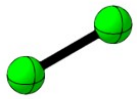
Chlorine Triplet State




```
Opt Freq M062X/6-311++G(d,p) FormCheck scrf=(CPCM,solvent=Acetonitrile)
Charge = 0 Multiplicity = 3

Sum of electronic and zero-point Energies=           -920.272547
Sum of electronic and thermal Energies=              -920.269822
Sum of electronic and thermal Enthalpies=            -920.268877
Sum of electronic and thermal Free Energies=         -920.295856
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1         17           0        0.000000    0.000000    1.201028
      2         17           0        0.000000    0.000000   -1.201028
 ---------------------------------------------------------------------
```

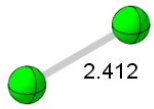
Chlorine Ground State (CAM-B3LYP)



```
Opt Freq CAM-B3LYP/6-311++G(d,p) FormCheck scrf=(CPCM,solvent=Acetonitrile)
Charge = 0 Multiplicity = 1

Sum of electronic and zero-point Energies=           -920.405416
Sum of electronic and thermal Energies=              -920.402863
Sum of electronic and thermal Enthalpies=            -920.401919
Sum of electronic and thermal Free Energies=         -920.427243
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1         17           0        0.000000    0.000000    1.014725
      2         17           0        0.000000    0.000000   -1.014725
 ---------------------------------------------------------------------
```

Chlorine Triplet State (CAM-B3LYP)



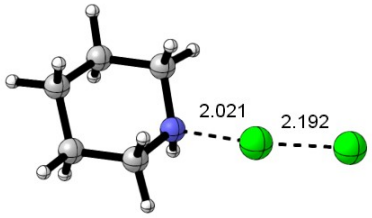

```
Opt Freq CAM-B3LYP/6-311++G(d,p) FormCheck scrf=(CPCM,solvent=Acetonitrile)
Charge = 0 Multiplicity = 3

Sum of electronic and zero-point Energies=           -920.340500
Sum of electronic and thermal Energies=              -920.337763
Sum of electronic and thermal Enthalpies=            -920.336819
Sum of electronic and thermal Free Energies=         -920.363828
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	0.000000	0.000000	1.206016
2	17	0	0.000000	0.000000	-1.206016

TS3 (Chlorine Radical and N-chloropiperidinium cation to Chlorine and Piperidinium Radical Cation)

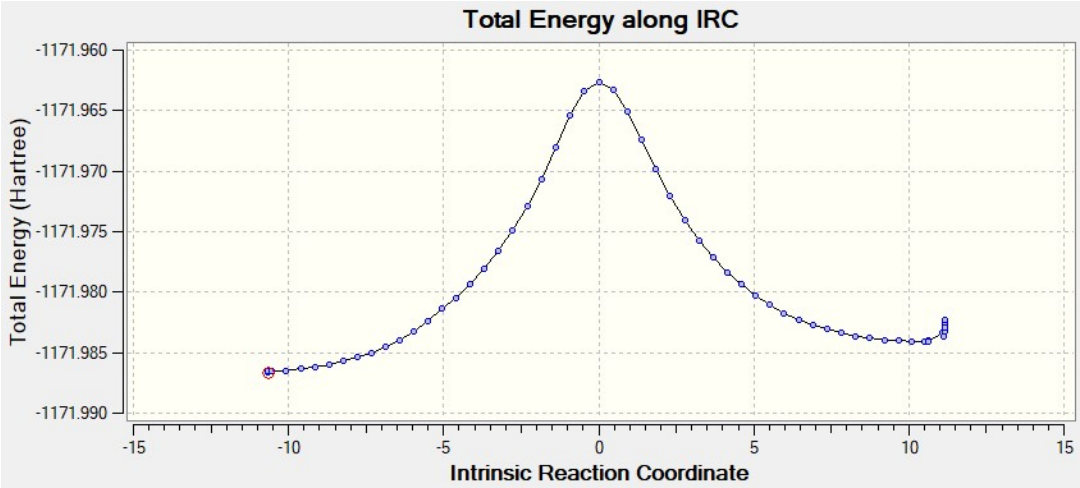



```
Opt=(qst3,Vtight) Freq M062X/6-311++G(d,p) FormCheck
scrf=(CPCM,solvent=Acetonitrile)
Charge = 1 Multiplicity = 2

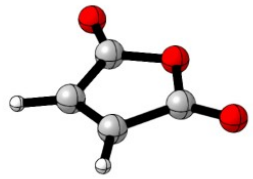
Imaginary Freq. (cm-1): -465.3713 and -32.3968
Sum of electronic and zero-point Energies=          -1171.800158
Sum of electronic and thermal Energies=             -1171.792235
Sum of electronic and thermal Enthalpies=           -1171.791291
Sum of electronic and thermal Free Energies=        -1171.834609
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.948581	1.220426	-0.181707
2	6	0	2.432862	1.345470	0.200342
3	6	0	3.223247	0.140608	-0.298714
4	6	0	2.621191	-1.151197	0.241300
5	6	0	1.132466	-1.262640	-0.144462
6	7	0	0.446308	-0.056990	0.356825
7	1	0	0.370264	-0.047985	1.378642
8	1	0	0.348467	2.025246	0.237591
9	1	0	0.823440	1.181954	-1.264682
10	1	0	2.790972	2.277002	-0.241590
11	1	0	2.520966	1.441796	1.286150
12	1	0	4.262700	0.222868	0.024367
13	1	0	3.221481	0.121944	-1.392630
14	1	0	3.109784	-2.035485	-0.171996
15	1	0	2.713465	-1.198978	1.329668
16	1	0	0.663017	-2.136685	0.302926
17	1	0	1.011218	-1.276663	-1.228927
18	17	0	-1.494671	-0.279909	-0.160568
19	17	0	-3.629447	0.166257	0.063048


Total Energy along IRC
Total Energy (Hartree)
-1171.960
-1171.965
-1171.970
-1171.975
-1171.980
-1171.985
-1171.990
-15
-10
-5
0
5
10
15
Intrinsic Reaction Coordinate

Maleic Anhydride



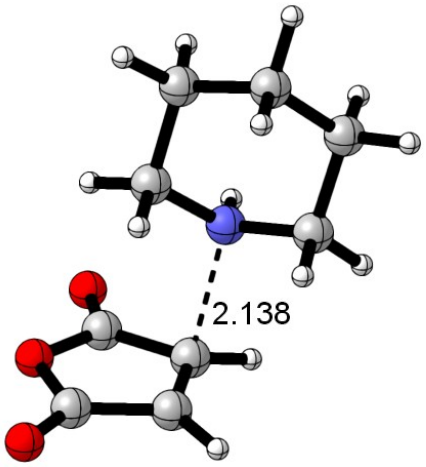
Opt Freq M062X/6-311++G(d,p) FormCheck scrf=(CPCM,solvent=Acetonitrile)
Charge = 0 Multiplicity = 1

Sum of electronic and zero-point Energies= -379.213445
Sum of electronic and thermal Energies= -379.208283
Sum of electronic and thermal Enthalpies= -379.207339
Sum of electronic and thermal Free Energies= -379.242523

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.663767	1.261092	-0.000062
2	6	0	-0.663767	1.261094	0.000067
3	6	0	-1.120678	-0.155925	-0.000838
4	8	0	0.000003	-0.962522	0.000009
5	6	0	1.120670	-0.155933	0.000719
6	8	0	2.218788	-0.608791	-0.000237
7	8	0	-2.218786	-0.608796	0.000301
8	1	0	1.355634	2.089445	-0.000096
9	1	0	-1.355631	2.089449	0.000203

TS4 (Maleic Anhydride and Piperidinium Radical Cation to Intermediate 2)

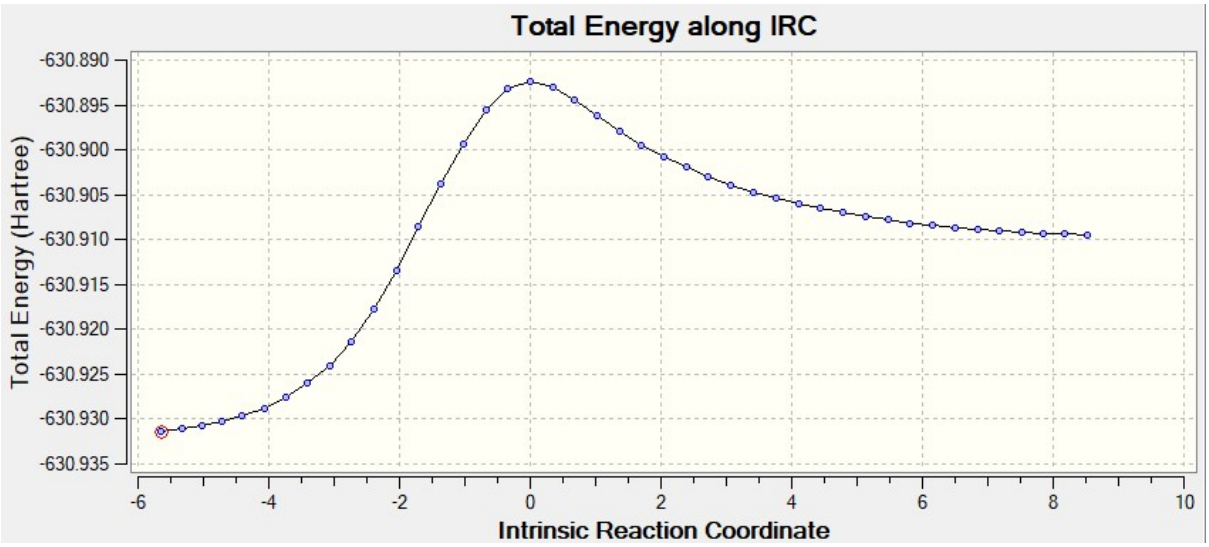



```
Opt=QST3 freq M062X/6-311++G(d,p) FormCheck
scrf=(CPCM,solvent=Acetonitrile)
Charge =  1 Multiplicity = 2

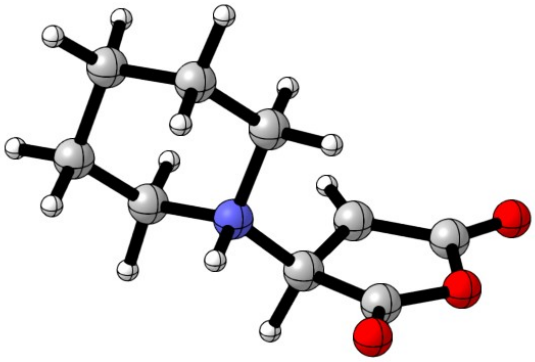
Imaginary Freq. (cm-1): -575.3901
Sum of electronic and zero-point Energies=           -630.674762
Sum of electronic and thermal Energies=              -630.663284
Sum of electronic and thermal Enthalpies=            -630.662340
Sum of electronic and thermal Free Energies=         -630.713872
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.319820	-1.019986	-0.077096
2	6	0	1.540143	-0.804767	1.167039
3	6	0	1.121357	0.495099	1.177259
4	6	0	1.764182	1.164652	-0.003492
5	8	0	2.404996	0.198531	-0.737447
6	8	0	2.824675	-2.003251	-0.504499
7	8	0	1.724942	2.302966	-0.331532
8	7	0	-0.857504	0.525975	0.368372
9	6	0	-0.869988	-0.014568	-0.989697
10	6	0	-2.313790	0.064377	-1.528762
11	6	0	-3.272631	-0.657438	-0.588201
12	6	0	-3.171202	-0.082576	0.820842
13	6	0	-1.717353	-0.159953	1.332221
14	1	0	-0.935356	1.546592	0.402124
15	1	0	1.379308	-1.583452	1.897732
16	1	0	0.779889	1.062238	2.032242
17	1	0	-0.545762	-1.056629	-0.938890
18	1	0	-0.190781	0.564186	-1.615607
19	1	0	-2.597205	1.114657	-1.637311
20	1	0	-2.301825	-0.381996	-2.524579
21	1	0	-4.294901	-0.551133	-0.956380
22	1	0	-3.041450	-1.727060	-0.571036
23	1	0	-3.504430	0.958578	0.836560
24	1	0	-3.784606	-0.638185	1.532380
25	1	0	-1.608664	0.315792	2.305594
26	1	0	-1.391817	-1.200412	1.385702


Total Energy along IRC
Total Energy (Hartree)
-630.890
-630.895
-630.900
-630.905
-630.910
-630.915
-630.920
-630.925
-630.930
-630.935
-6
-4
-2
0
2
4
6
8
10
Intrinsic Reaction Coordinate

Int2 (1-(2,5-dioxotetrahydrofuran-3-yl)piperidinium Radical Cation)



Opt=Tight Freq M062X/6-311++G(d,p) FormCheck
scrf=(CPCM,solvent=Acetonitrile)
Charge = 1 Multiplicity = 2

Sum of electronic and zero-point Energies= -630.712989
Sum of electronic and thermal Energies= -630.701882
Sum of electronic and thermal Enthalpies= -630.700938
Sum of electronic and thermal Free Energies= -630.750986

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.627660	-0.792793	0.240956
2	6	0	-1.346328	-1.206155	-0.298645
3	6	0	-0.671528	-0.003513	-0.840355
4	6	0	-1.560982	1.134674	-0.322933
5	8	0	-2.698232	0.611923	0.185789
6	8	0	-3.531105	-1.428352	0.681179
7	8	0	-1.305541	2.292750	-0.345647
8	7	0	0.747819	0.225987	-0.442627
9	6	0	0.957741	0.153763	1.054386
10	6	0	2.396174	0.504507	1.397049
11	6	0	3.379260	-0.407539	0.665902
12	6	0	3.129632	-0.350813	-0.839715
13	6	0	1.690620	-0.704022	-1.174931
14	1	0	0.970470	1.186565	-0.738202
15	1	0	-1.047830	-2.238944	-0.390806
16	1	0	-0.707527	0.010896	-1.937170
17	1	0	0.711228	-0.869746	1.345685
18	1	0	0.249717	0.843270	1.515221
19	1	0	2.585320	1.552523	1.143313
20	1	0	2.502662	0.413263	2.479031
21	1	0	4.403052	-0.103913	0.886257
22	1	0	3.260284	-1.436216	1.020260
23	1	0	3.354936	0.648463	-1.226102
24	1	0	3.770521	-1.053427	-1.374230
25	1	0	1.474411	-0.599749	-2.237351
26	1	0	1.435480	-1.714123	-0.848368

5. References

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S2 T. J. Barker and E. R. Jarvo, *J. Am. Chem. Soc.*, 2009, **131**, 15598–15599.

S3 S. R. Anderson, J. T. Ayers, K. M. DeVries, F. Ito, D. Mendenhall and B. C. Vanderplas, *Tetrahedron Asymmetry*, 1999, **10**, 2655–2663.

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S5 E. Falk, S. Makai, T. Delcaillau, L. Gürtler and B. Morandi, *Angew. Chem. Int. Ed.*, 2020, **59**, 21064–21071.

S6 W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley, Weinheim, 2001.

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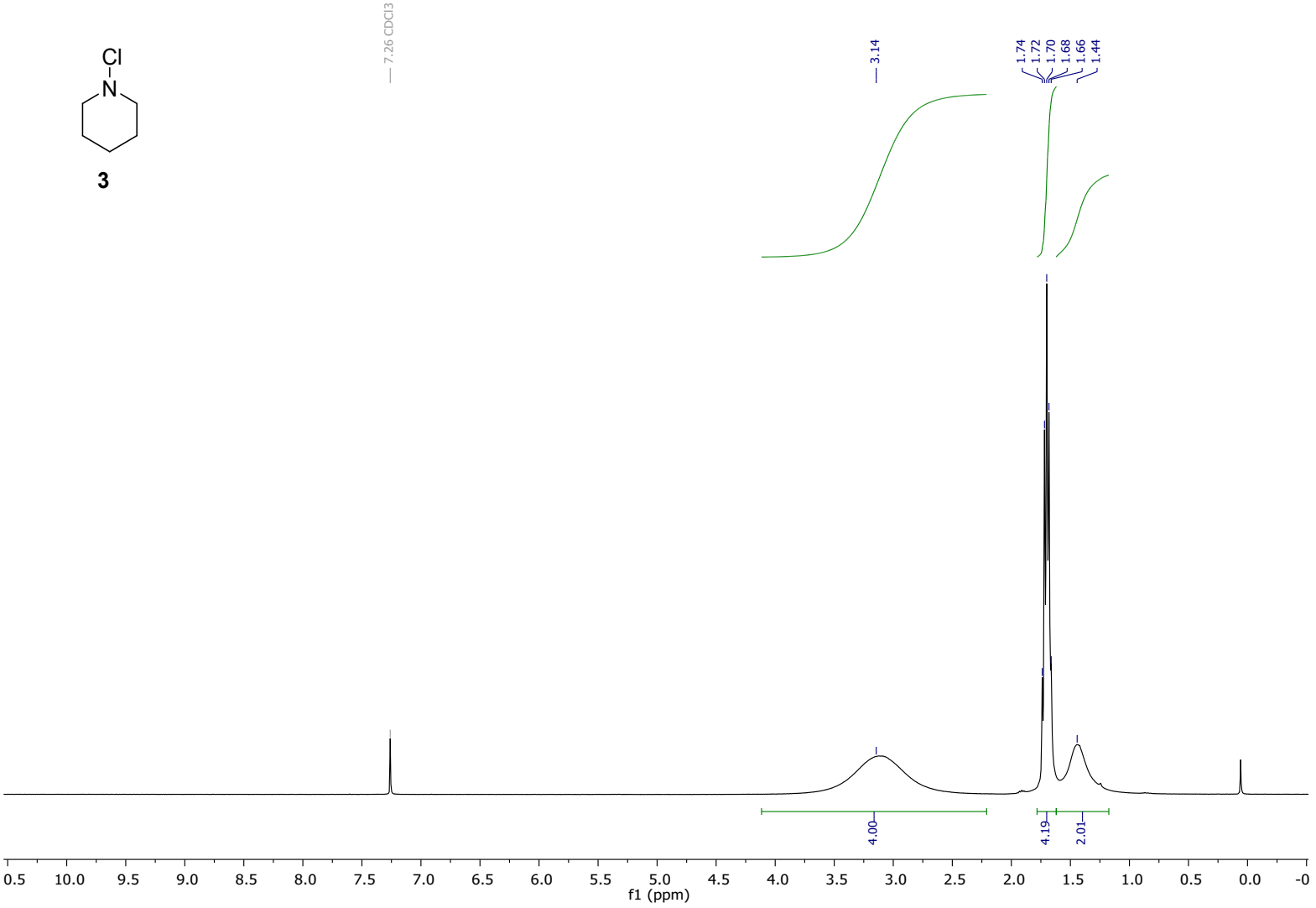
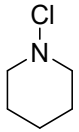
S8 M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681.

6. NMR Spectra

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N

3

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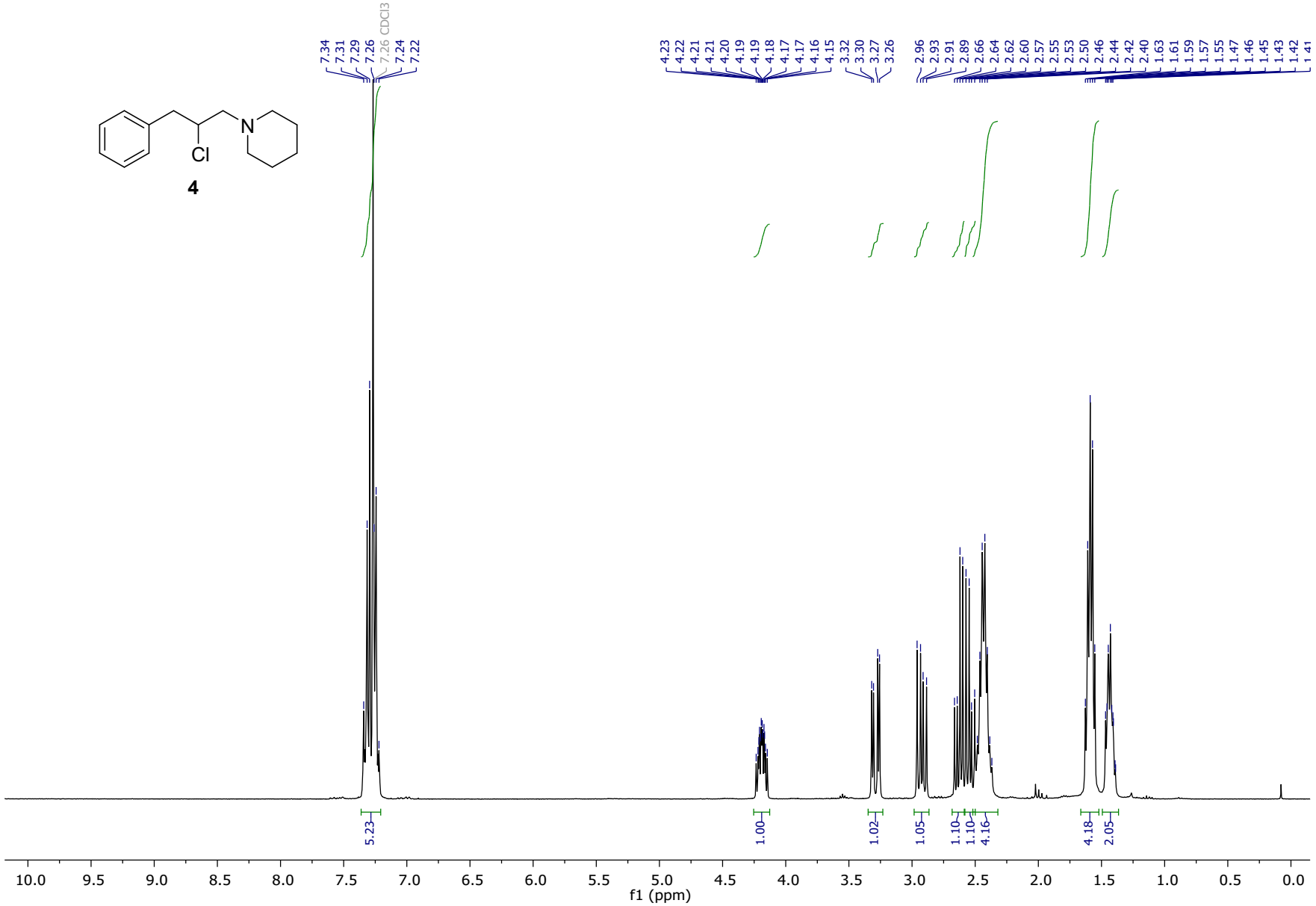
27.7
23.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.31
7.29
7.26
7.26 CDCl3
7.24
7.22
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.18
4.17
4.17
4.16
4.15
3.32
3.30
3.27
3.26
2.96
2.93
2.91
2.89
2.66
2.64
2.62
2.60
2.57
2.55
2.53
2.50
2.46
2.44
2.42
2.40
1.63
1.61
1.59
1.57
1.55
1.47
1.46
1.45
1.43
1.42
1.41
Cl
N
4
5.23
1.00
1.02
1.05
1.10
1.10
4.16
4.18
2.05
10.0
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
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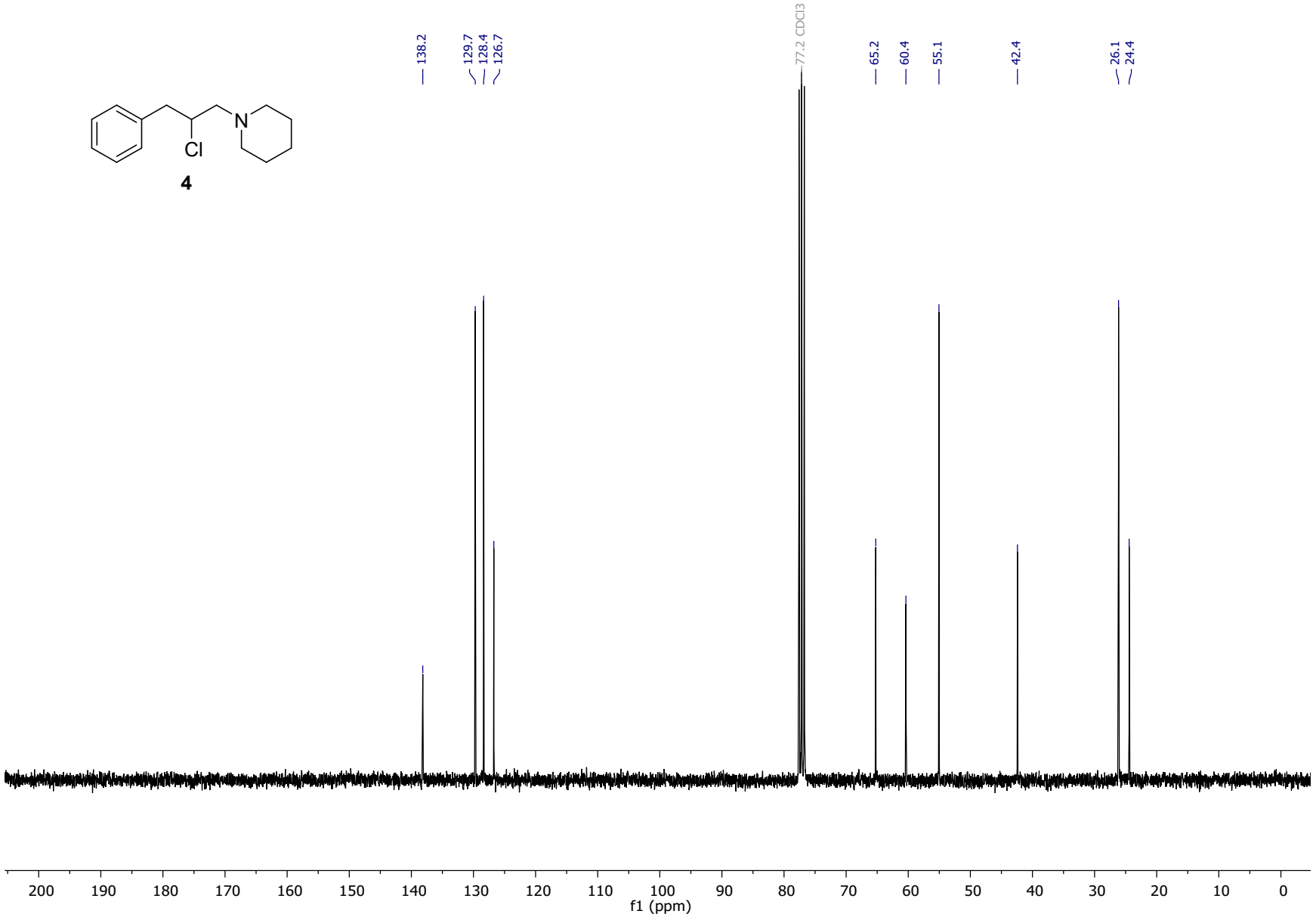
f1 (ppm)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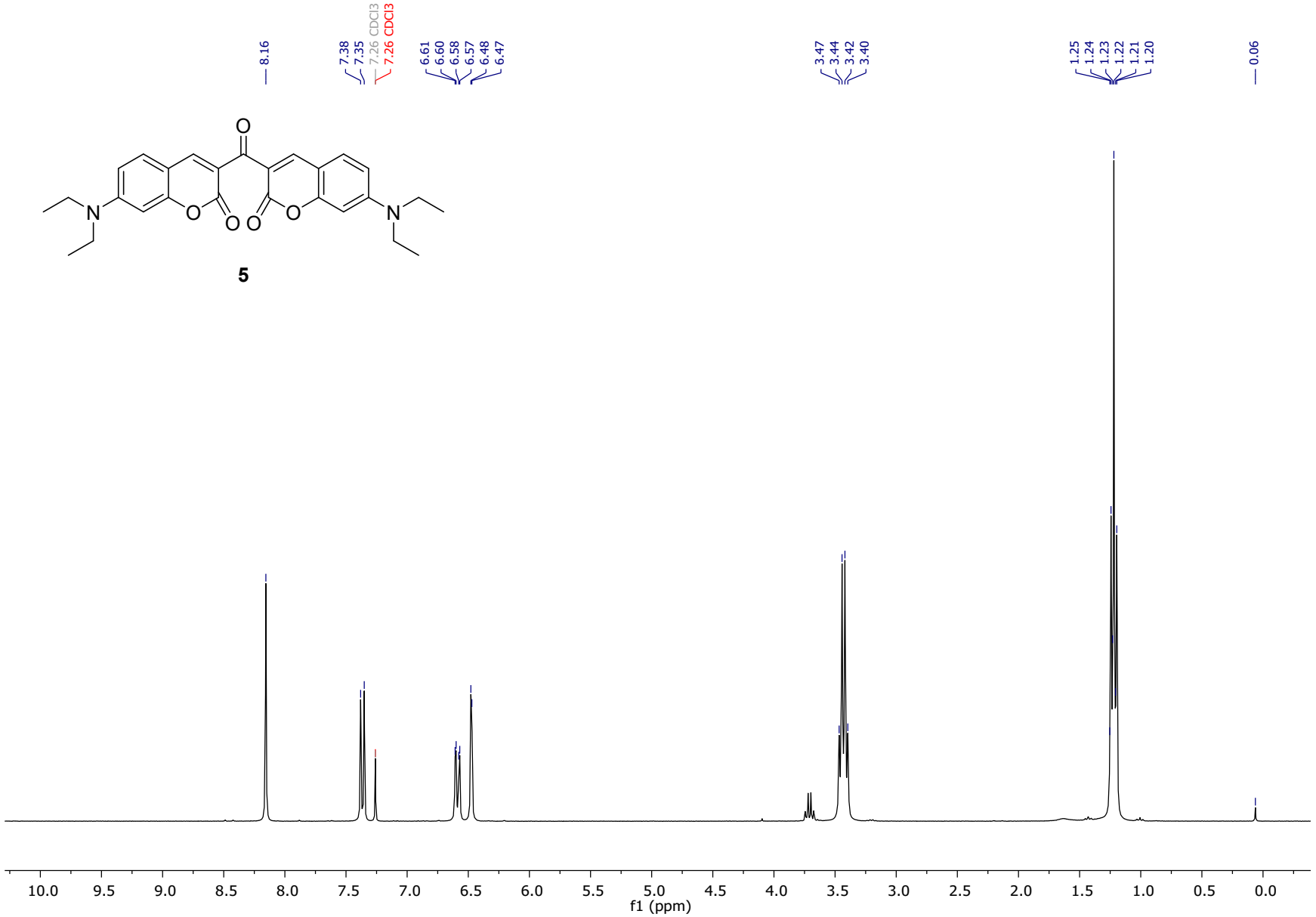
129.7
128.4
126.7
77.2 CDCl3
65.2
60.4
55.1
42.4
26.1
24.4
N
Cl
4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.38
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7.26 CDCl3
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6.60
6.58
6.57
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3.47
3.44
3.42
3.40
1.25
1.24
1.23
1.22
1.21
1.20
0.06
O
O
O
O
O
N
N
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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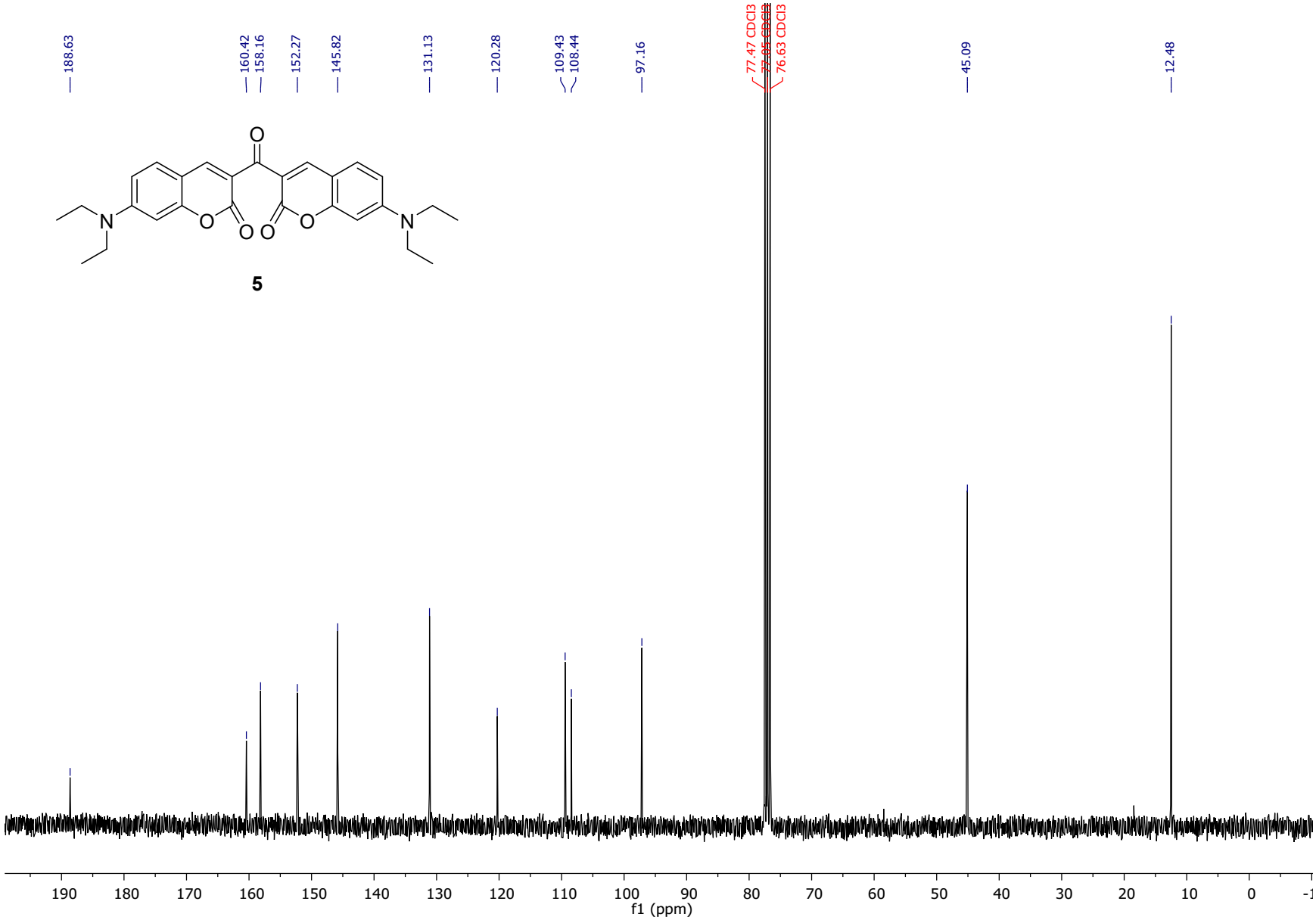
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5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152.27
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131.13
120.28
109.43
108.44
97.16
77.47 CDCl3
76.63 CDCl3
45.09
12.48
O
N
O
O
O
O
N
5
190
180
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130
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90
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50
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30
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10
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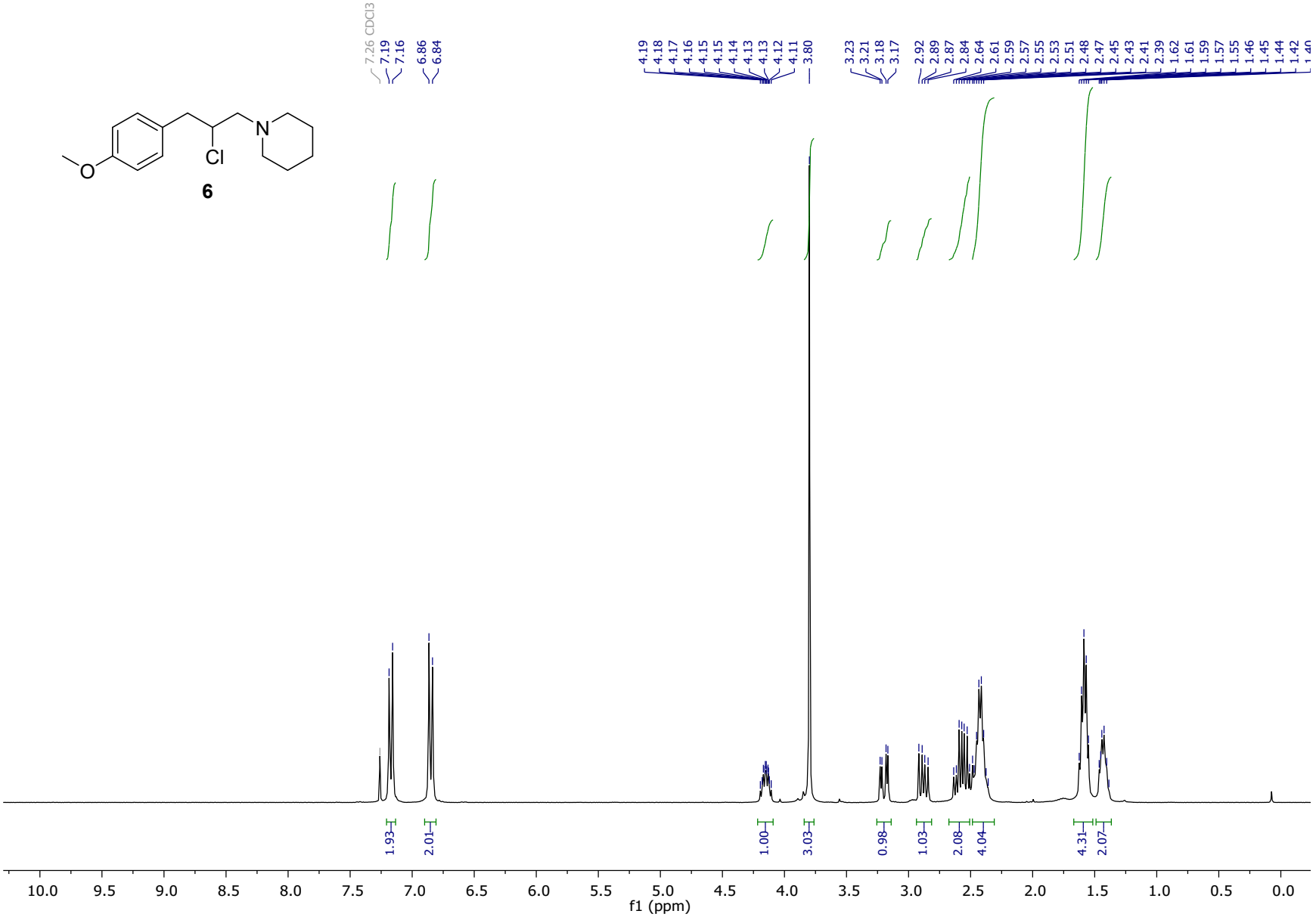
f1 (ppm)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4.14
4.13
4.13
4.12
4.11
3.80
3.23
3.21
3.18
3.17
2.92
2.89
2.87
2.84
2.64
2.61
2.59
2.57
2.55
2.53
2.51
2.48
2.47
2.45
2.43
2.41
2.39
1.62
1.61
1.59
1.57
1.55
1.46
1.45
1.44
1.42
N
Cl
O
6
1.93
2.01
1.00
3.03
0.98
1.03
2.08
4.04
4.31
2.07
10.0
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
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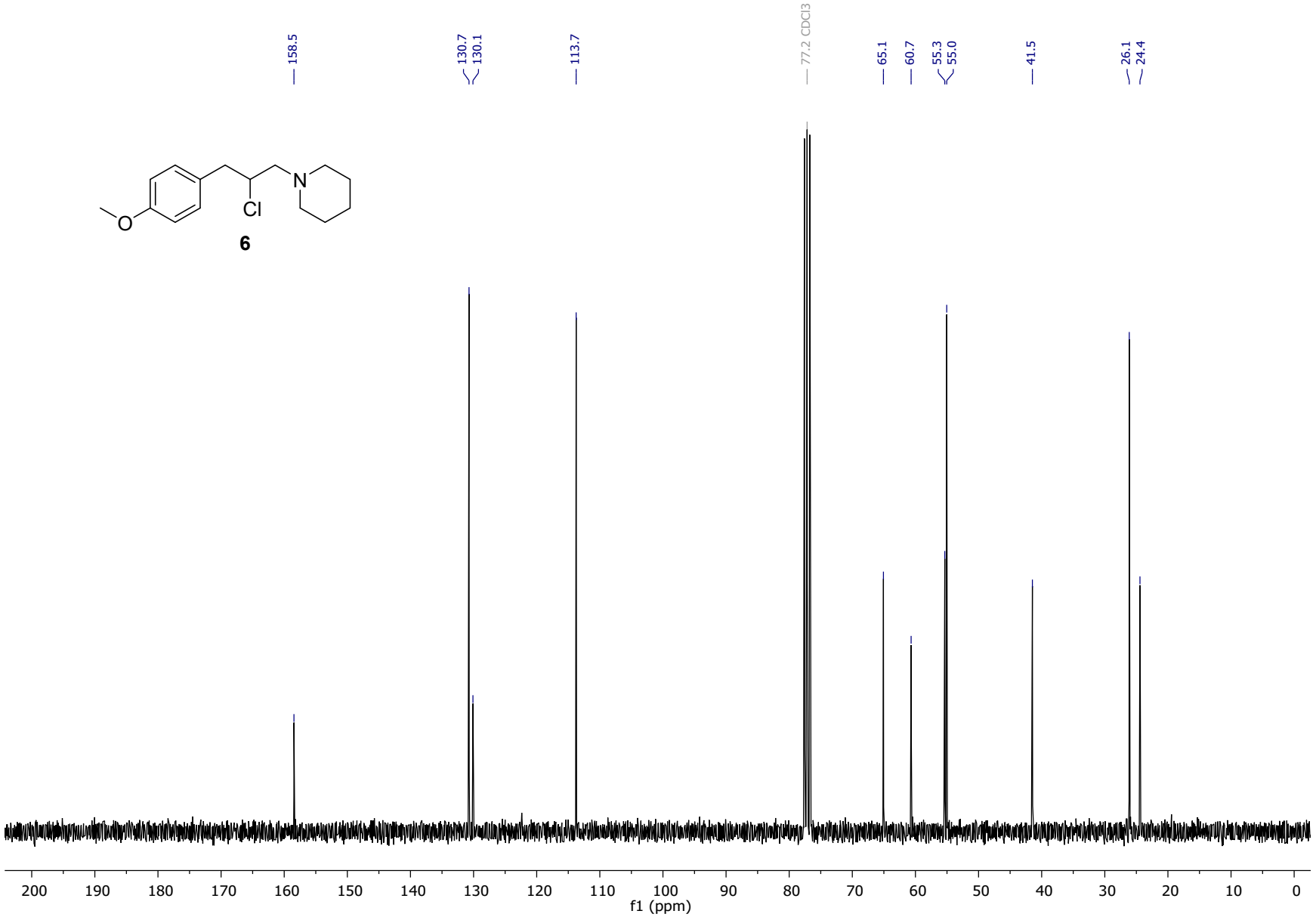
0.0
f1 (ppm)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24.4
N
Cl
O
6
200
190
180
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130
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70
60
50
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30
20
10
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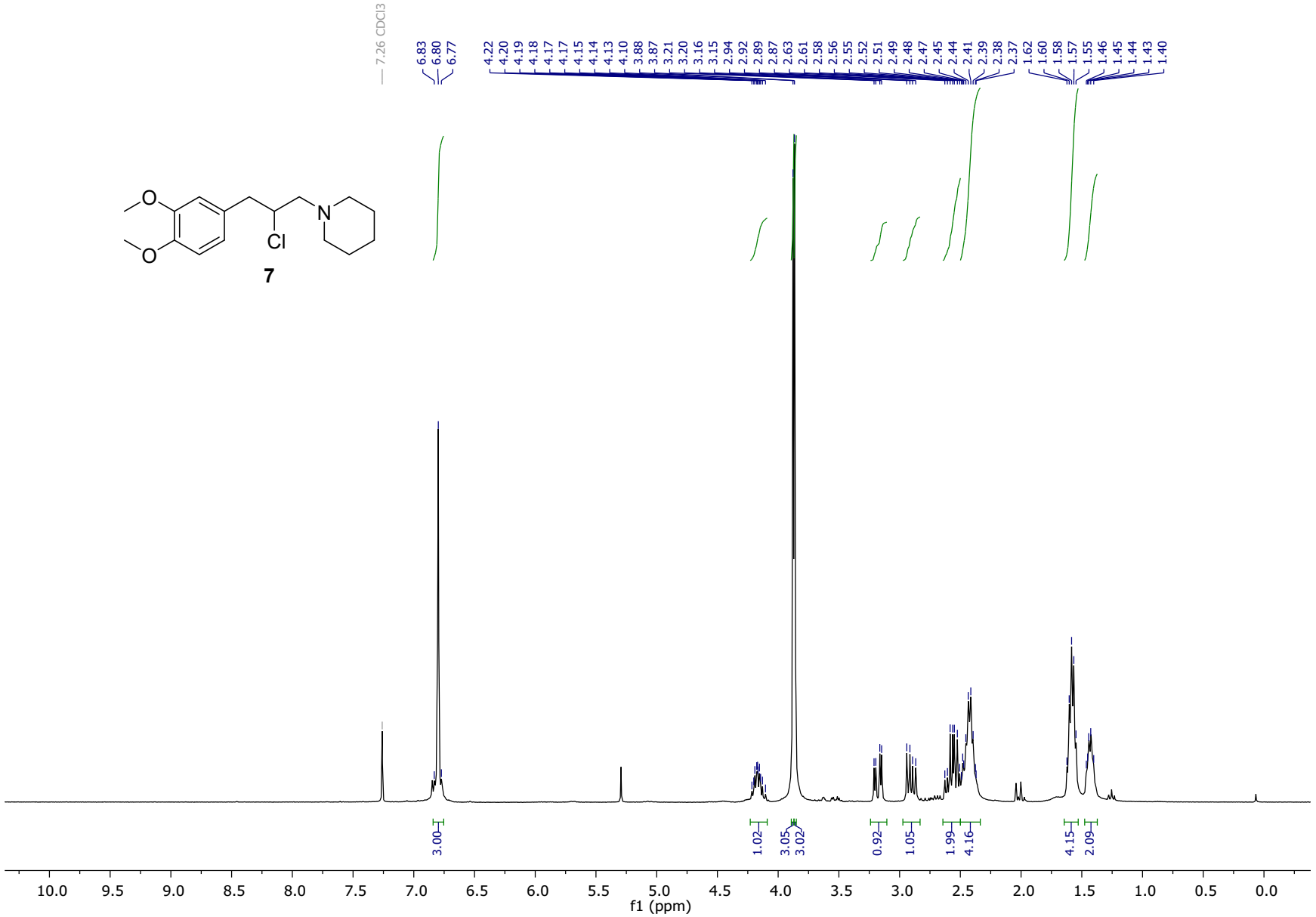
f1 (ppm)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4.14
4.13
4.10
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3.21
3.20
3.16
3.15
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2.44
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2.39
2.38
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1.60
1.58
1.57
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1.46
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1.44
1.43
1.40
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O
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3.02
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1.99
4.16
4.15
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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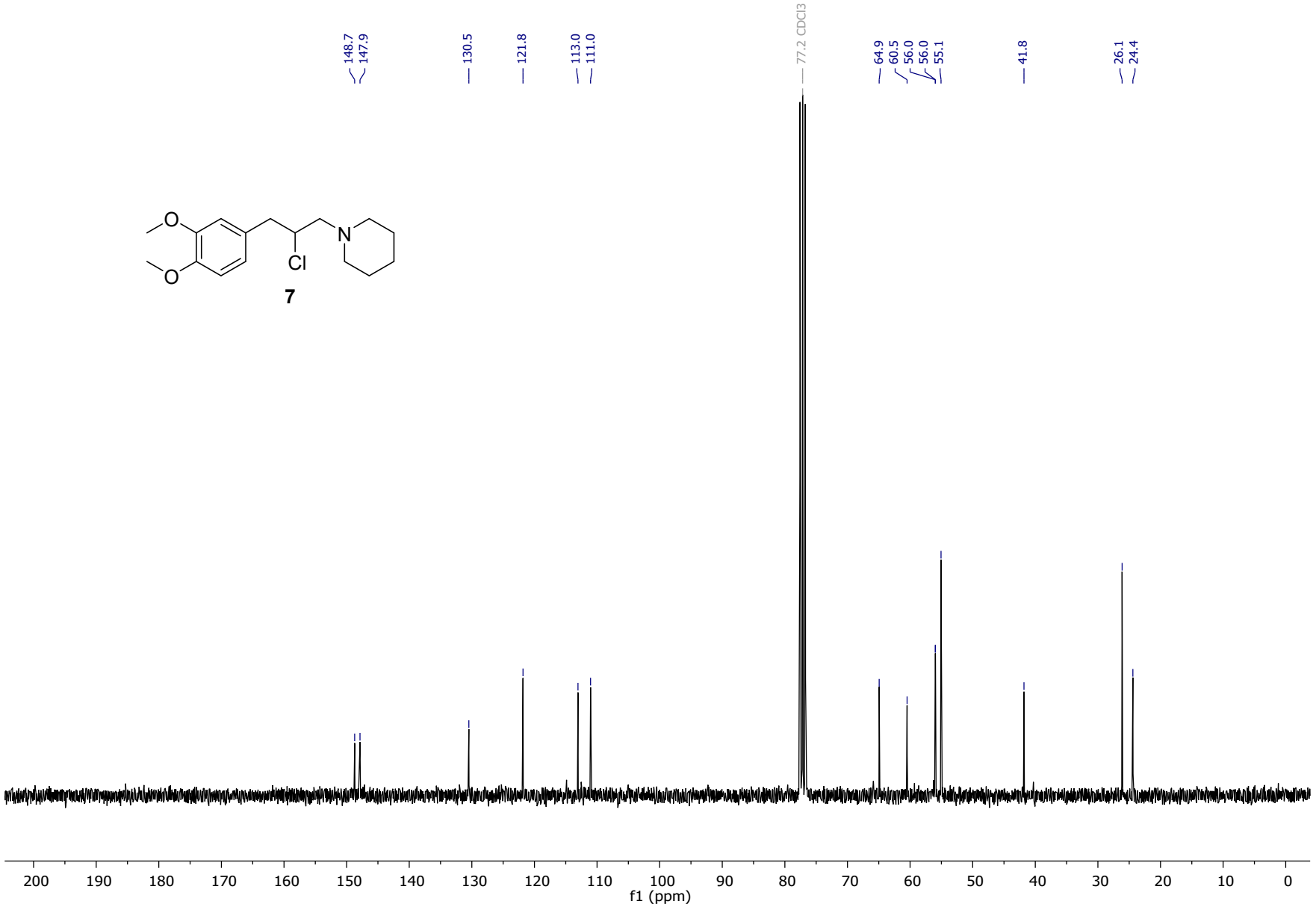
f1 (ppm)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56.0
55.1
41.8
26.1
24.4
O
O
Cl
N
7
200
190
180
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160
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130
120
110
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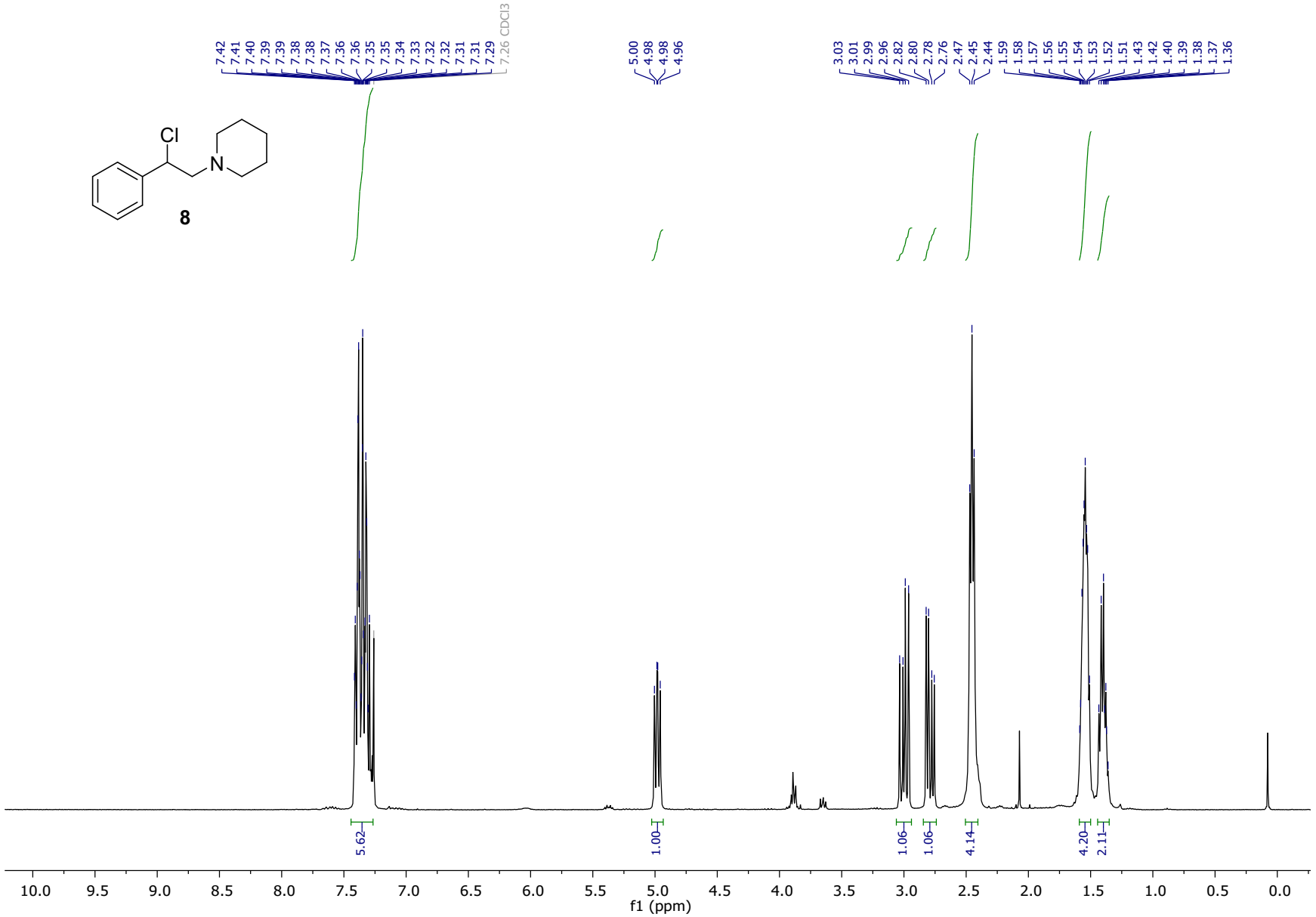
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.33
7.32
7.32
7.31
7.31
7.29
7.26 CDCl3
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6.5
6.0
5.5
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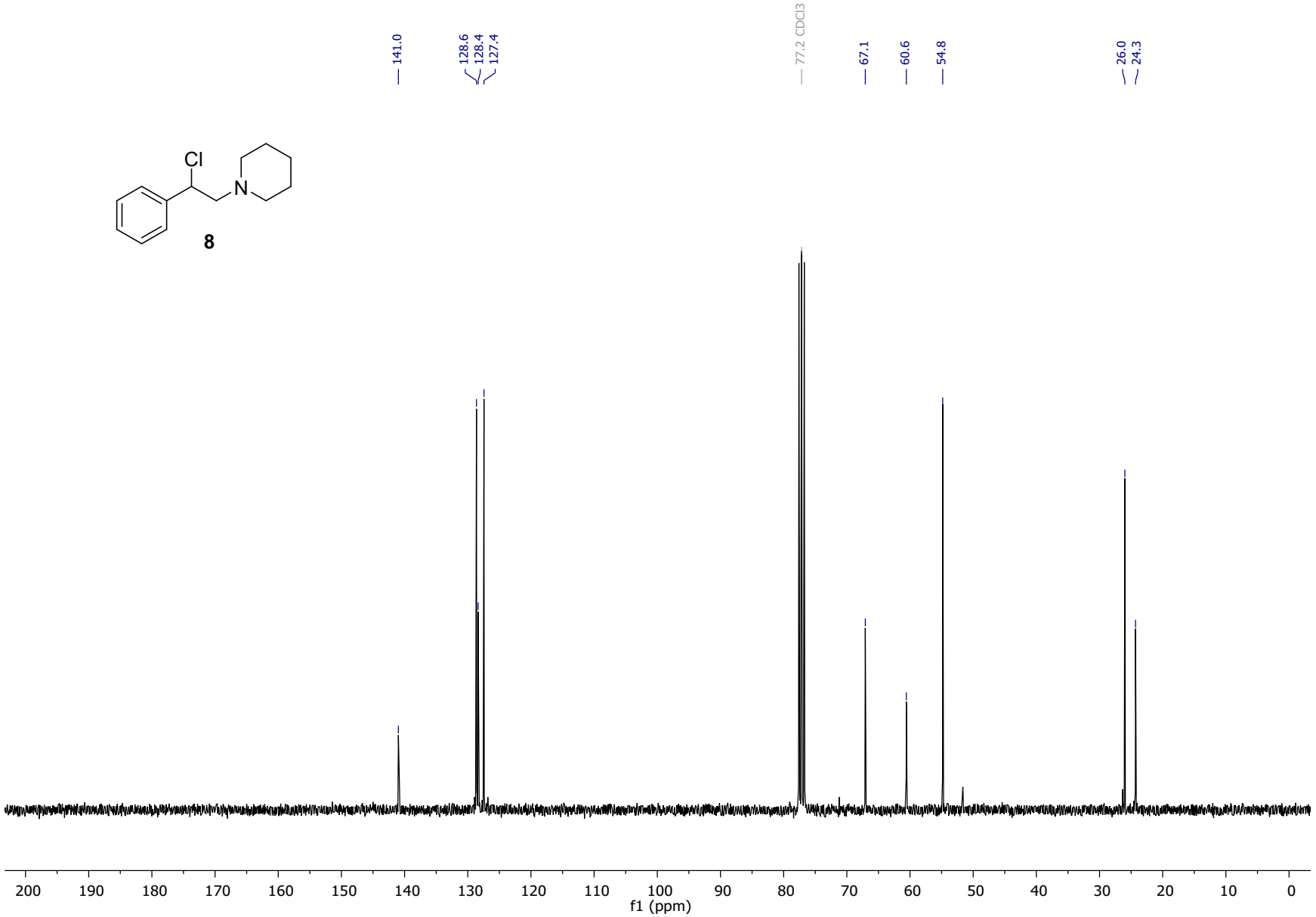
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180
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130
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50
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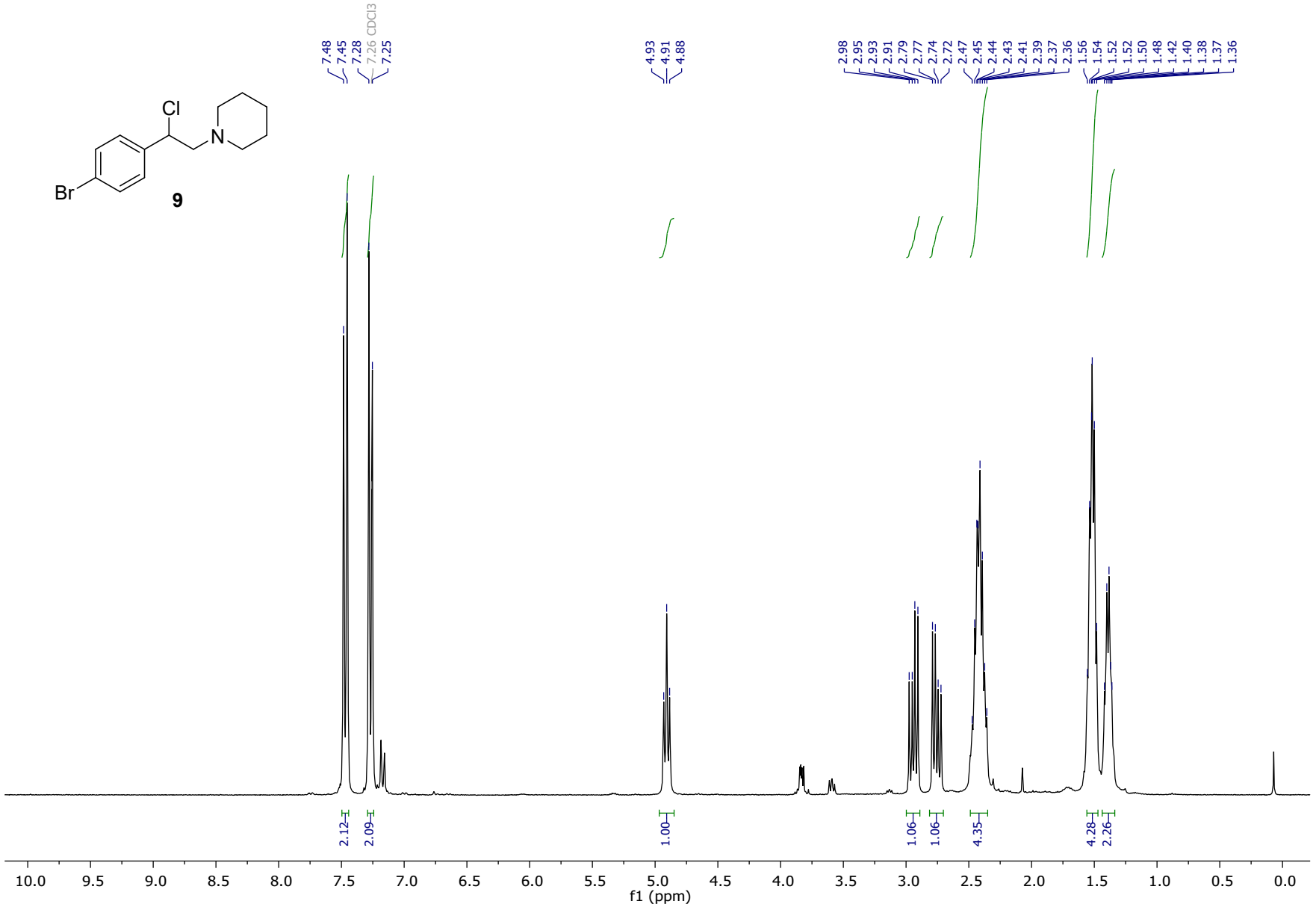
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2.93
2.91
2.79
2.77
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2.47
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2.44
2.43
2.41
2.39
2.37
2.36
1.56
1.54
1.52
1.52
1.50
1.48
1.42
1.40
1.38
1.37
1.36
2.12
2.09
1.00
1.06
1.06
4.35
4.28
2.26
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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
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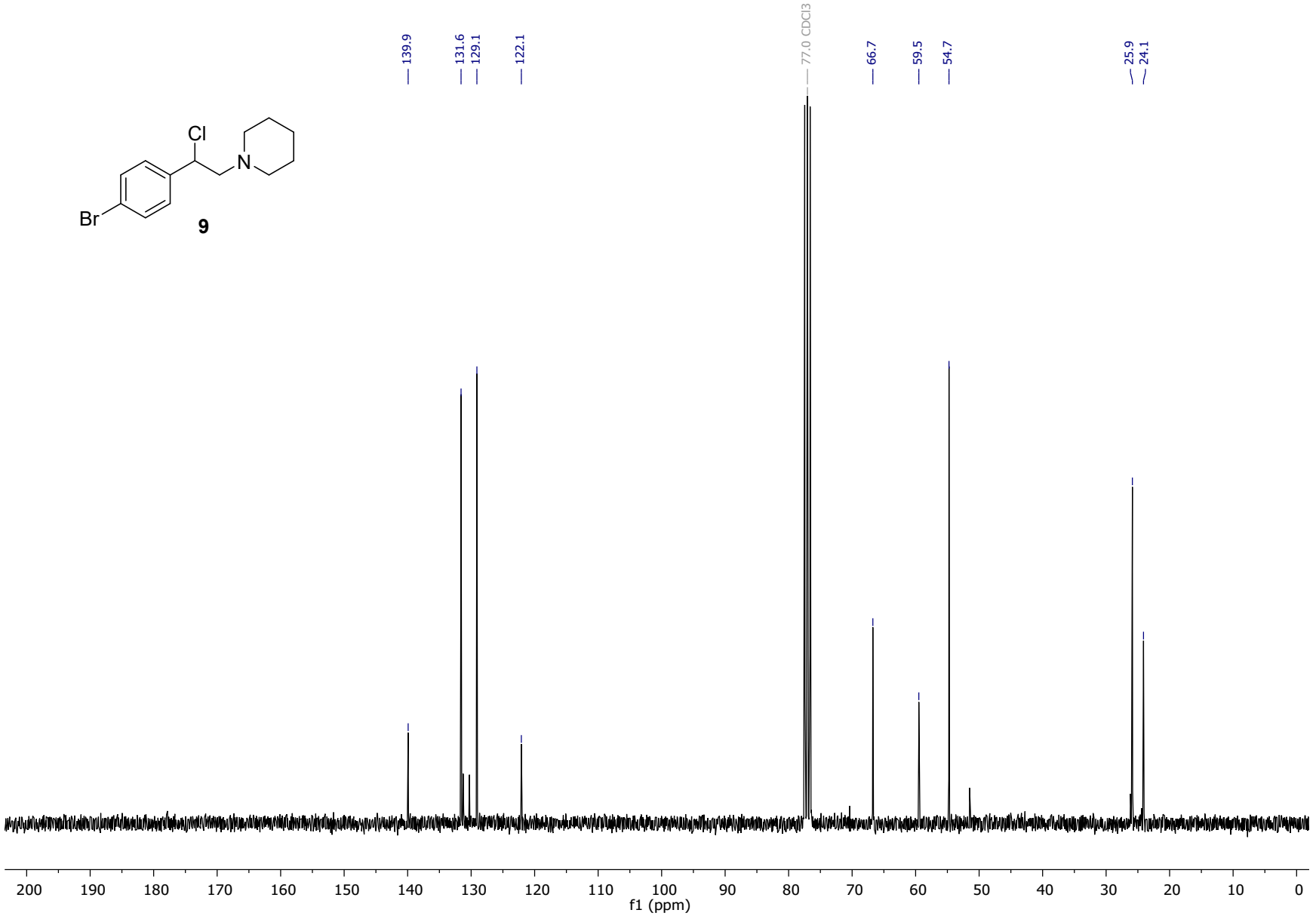
f1 (ppm)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59.5
54.7
25.9
24.1
Cl
N
Br
9
200
190
180
170
160
150
140
130
120
110
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80
70
60
50
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30
20
10
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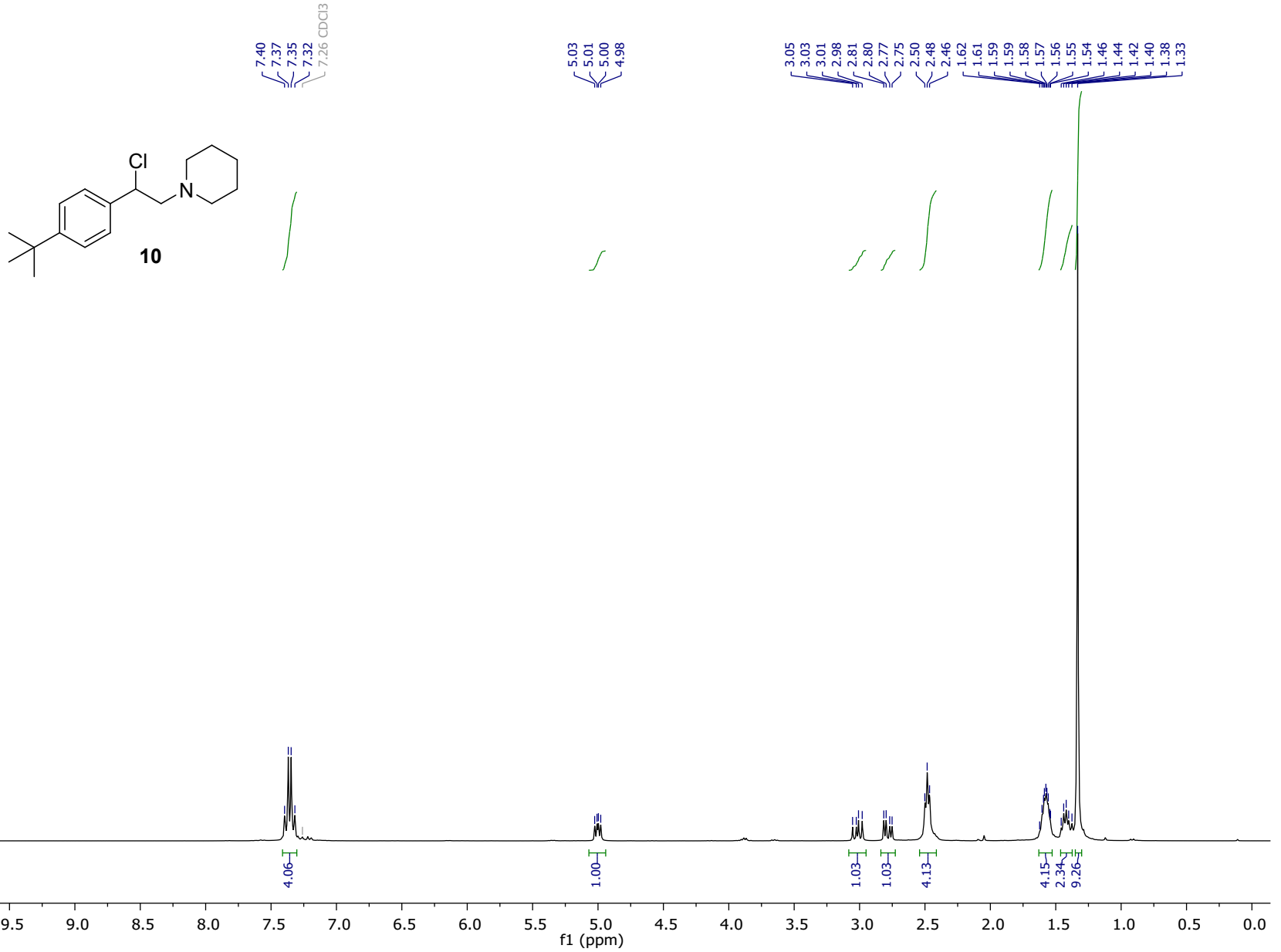
f1 (ppm)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1.38
1.33
Cl
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10
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1.03
1.03
4.13
4.15
2.34
9.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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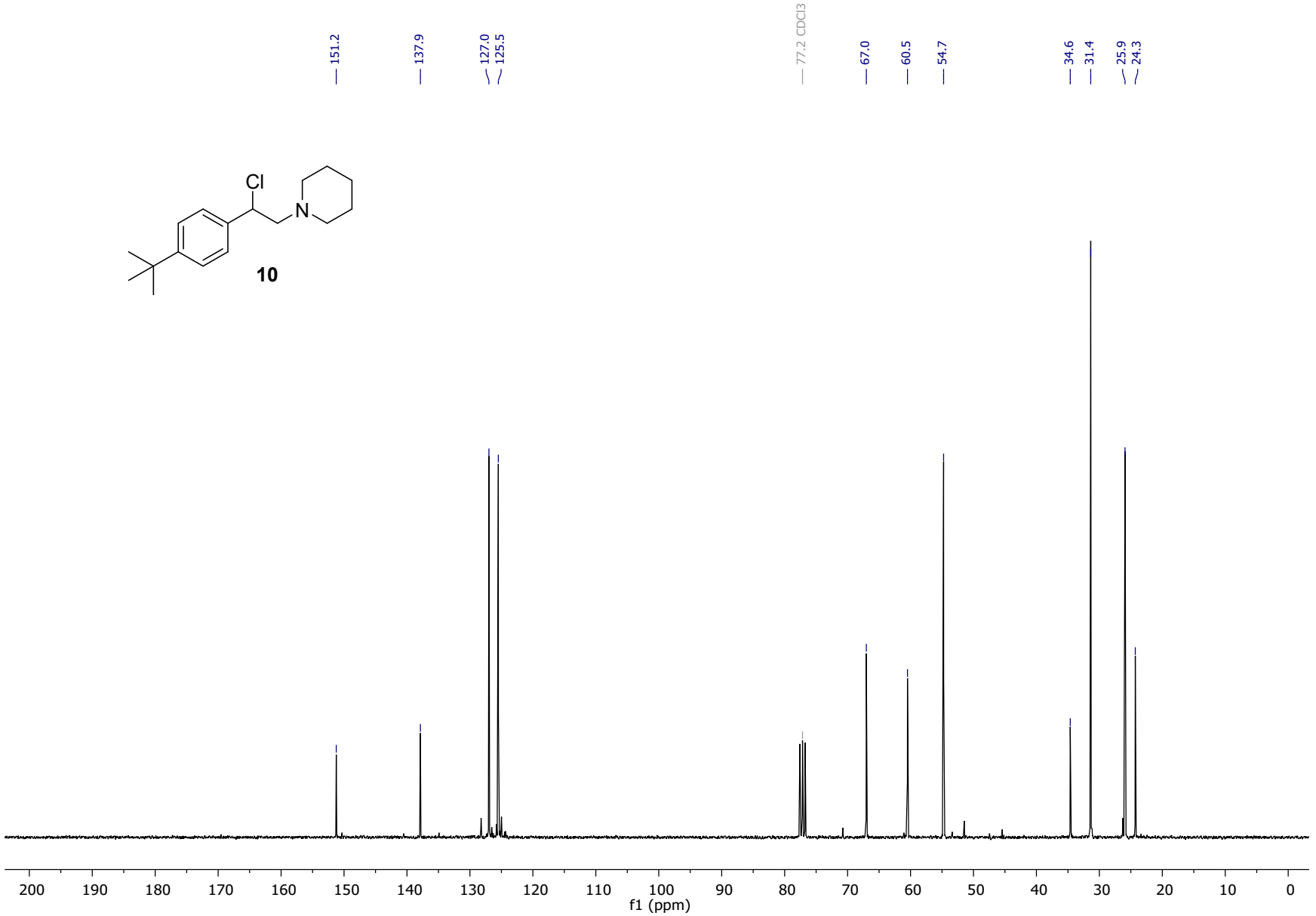
f1 (ppm)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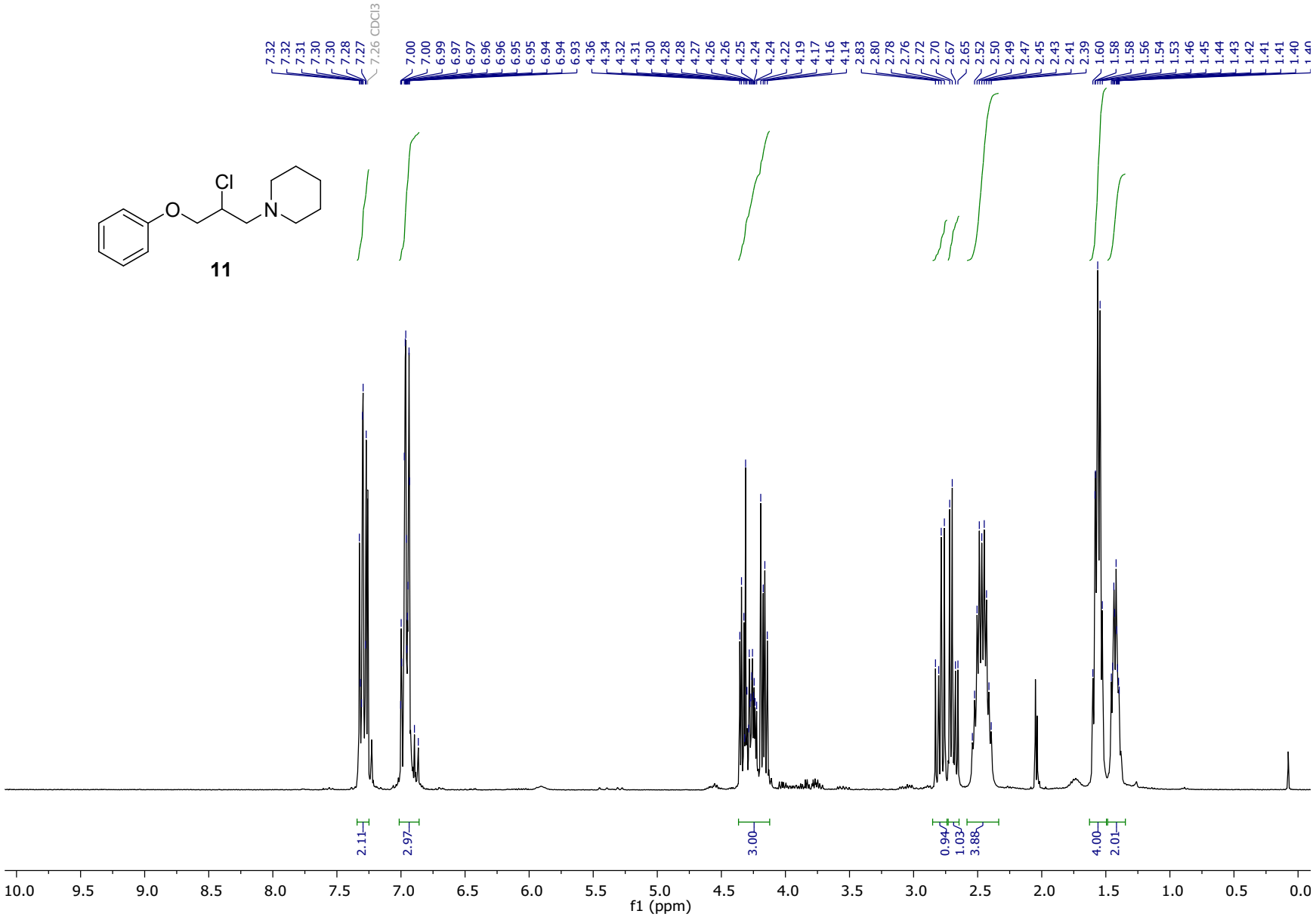
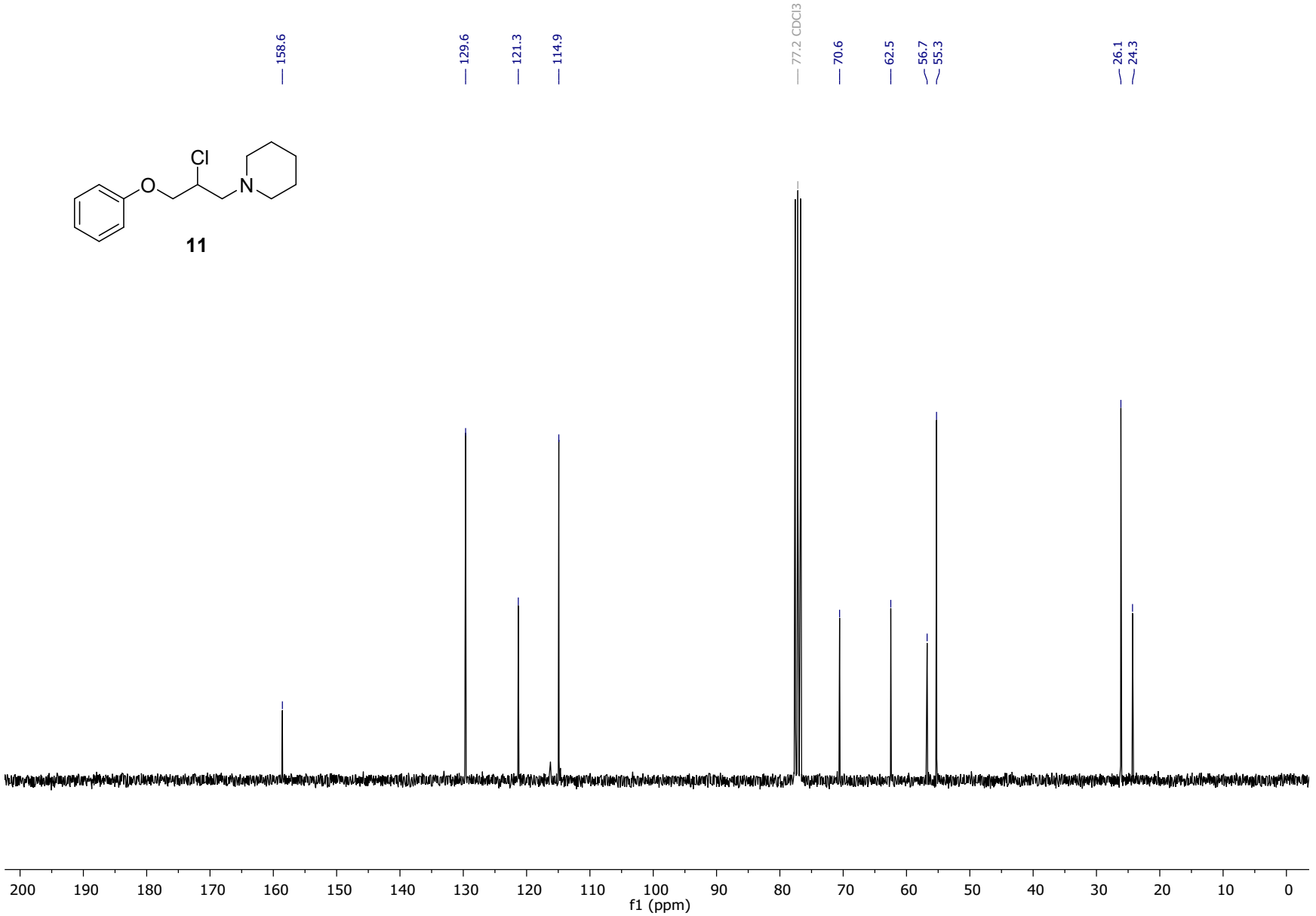
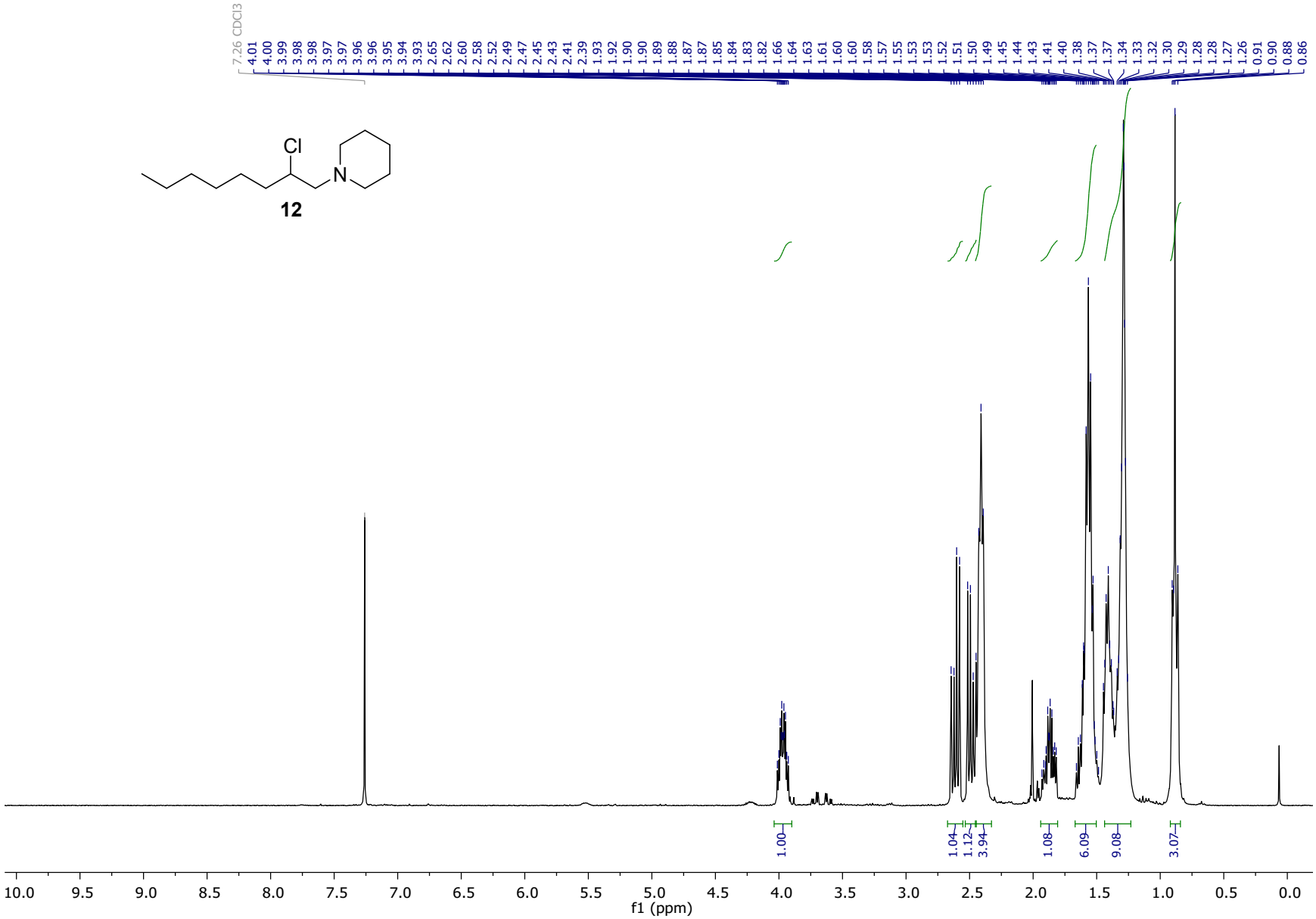
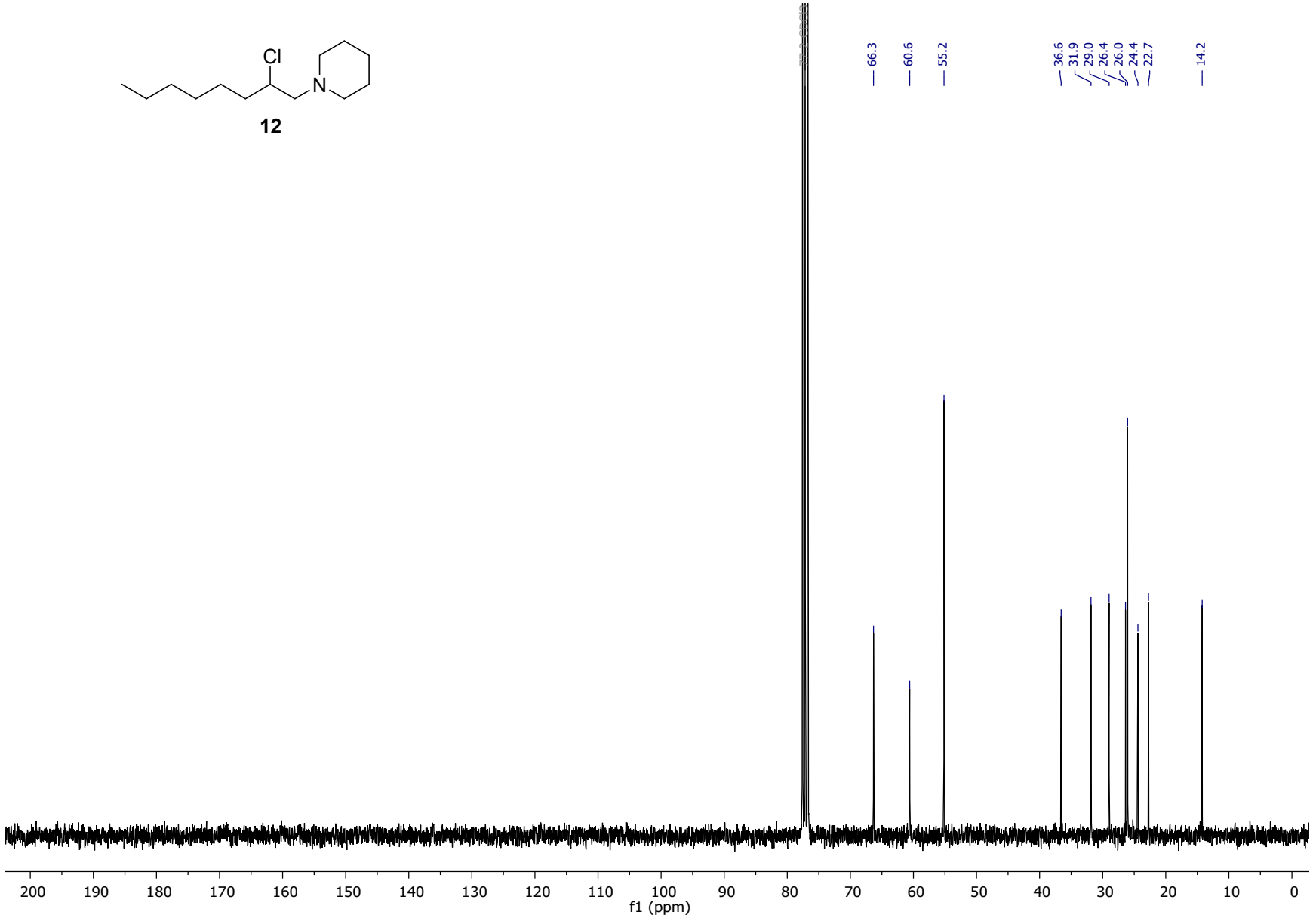
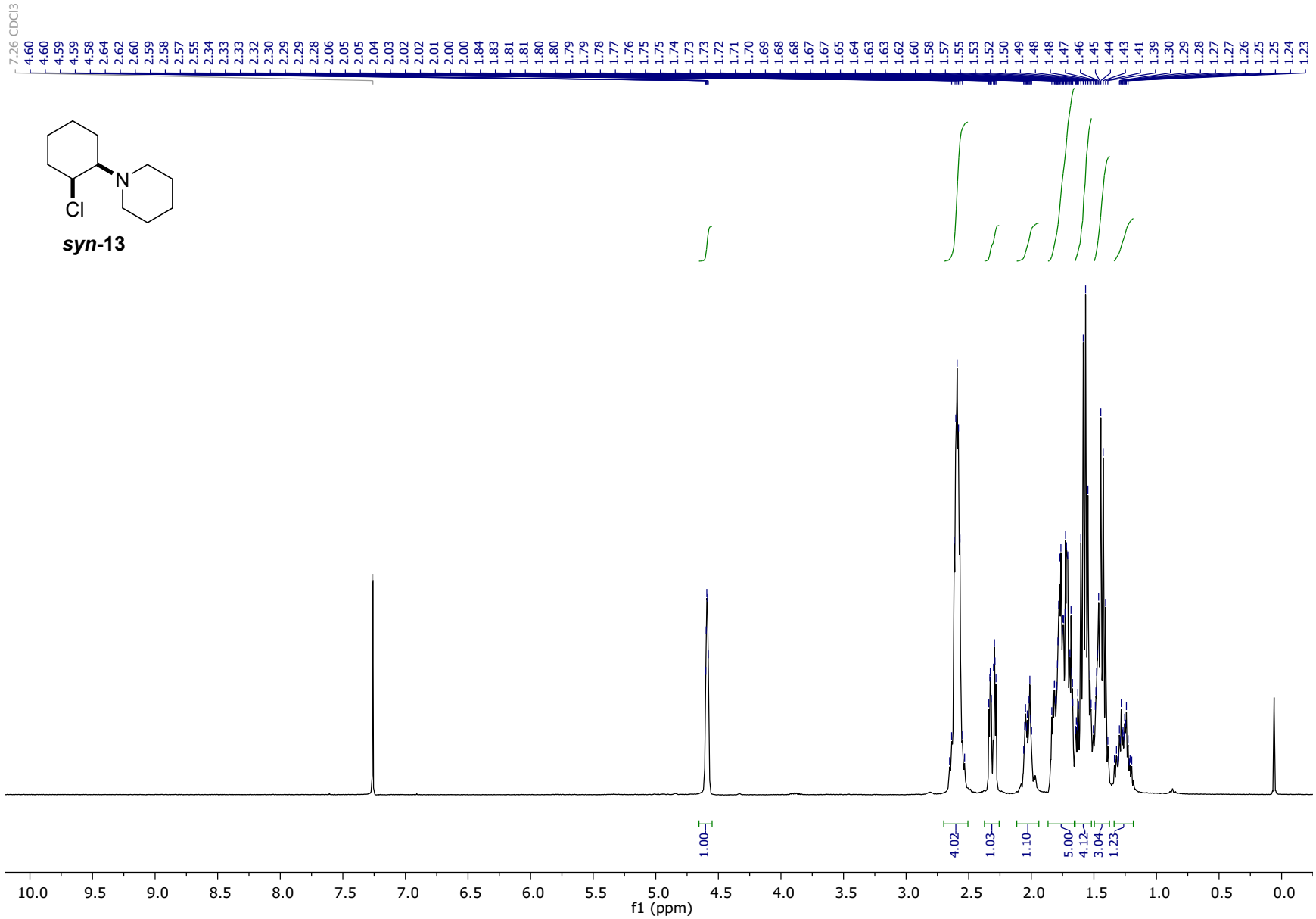
60.5
54.7
34.6
31.4
25.9
24.3
Cl
N
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
O
N
11
7.26 CDCl3
2.11
2.97
3.00
0.94
1.03
3.88
4.00
2.01
f1 (ppm)

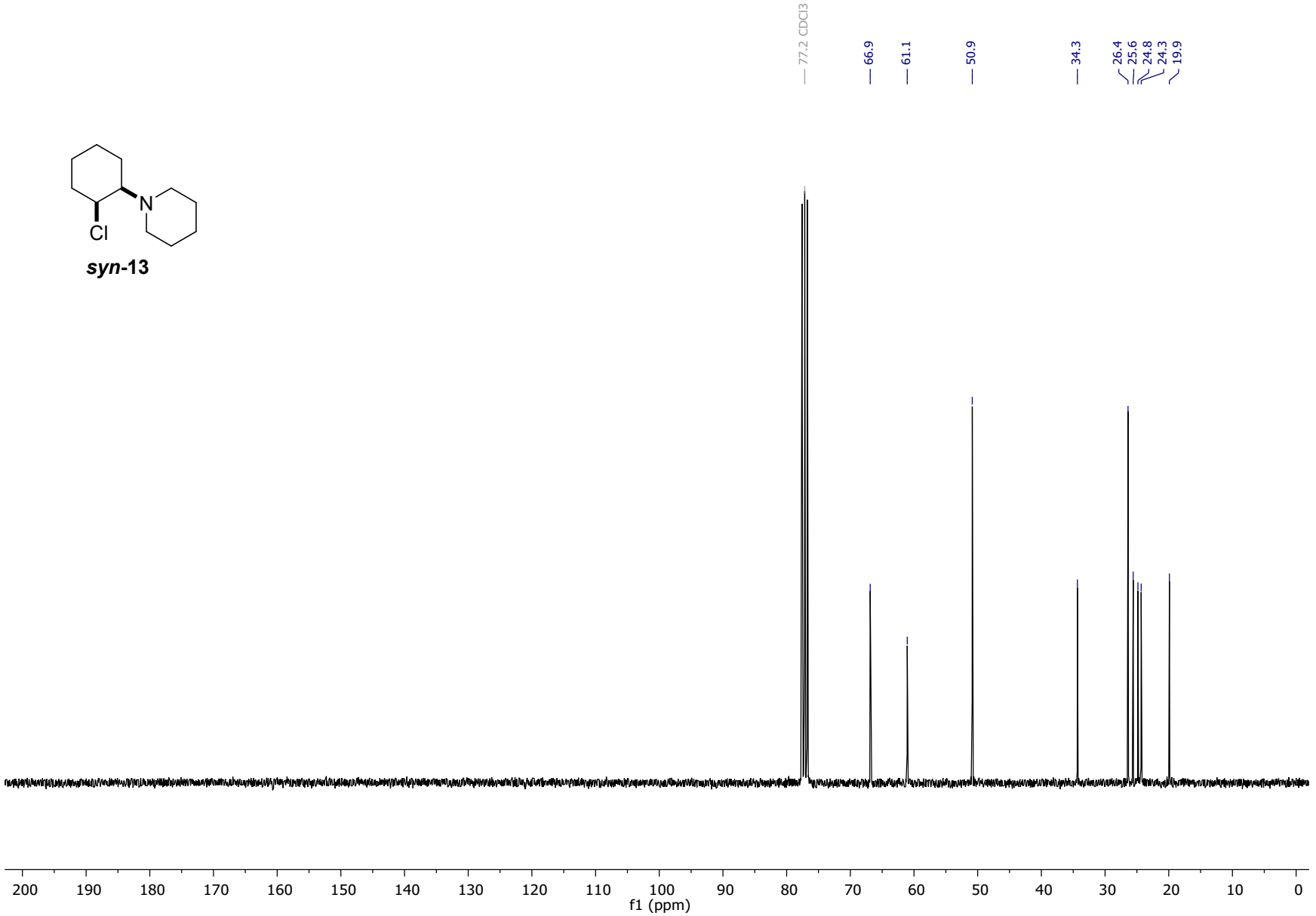

158.6
129.6
121.3
114.9
77.2 CDCl3
70.6
62.5
56.7
55.3
26.1
24.3
Cl
O
N
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

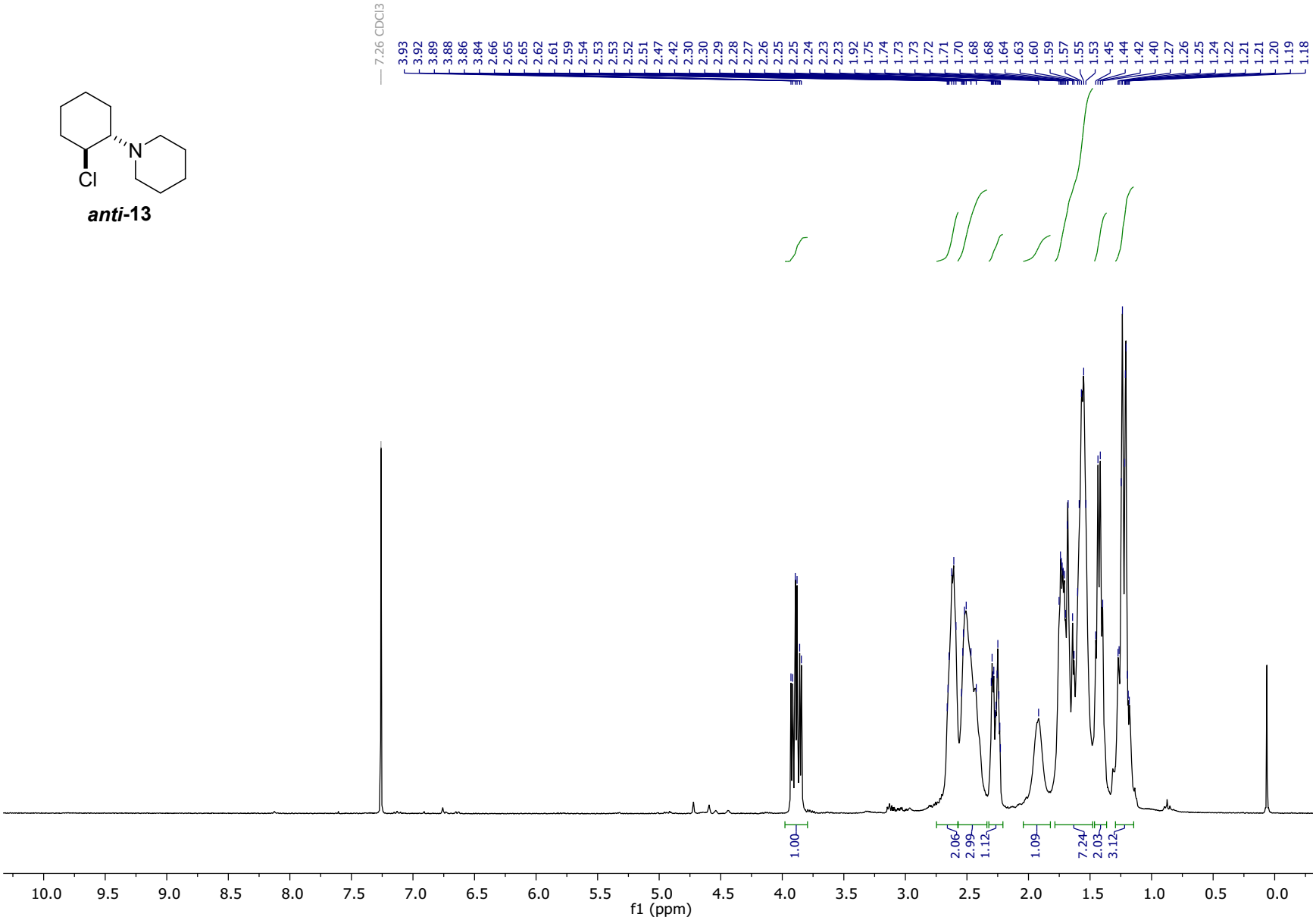

7.26 CDCl3
4.01 4.00 3.99 3.98 3.98 3.97 3.97 3.96 3.96 3.95 3.94 3.93 2.65 2.62 2.60 2.58 2.52 2.49 2.47 2.45 2.43 2.41 2.39 1.93 1.92 1.90 1.90 1.89 1.88 1.87 1.87 1.85 1.84 1.83 1.82 1.66 1.64 1.63 1.61 1.60 1.60 1.58 1.57 1.55 1.53 1.53 1.52 1.51 1.50 1.49 1.45 1.44 1.43 1.41 1.40 1.38 1.37 1.37 1.34 1.33 1.32 1.30 1.29 1.28 1.28 1.27 1.26 0.91 0.90 0.88 0.86
Cl
N
12
1.00
1.04
1.12
3.94
1.08
6.09
9.08
3.07
10.0 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
f1 (ppm)

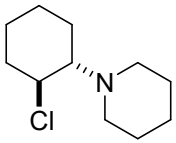

Cl
N
12
66.3
60.6
55.2
36.6
31.9
29.0
26.4
26.0
24.4
22.7
14.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
4.60 4.59 4.59 4.58 2.64 2.62 2.60 2.59 2.58 2.57 2.55 2.34 2.33 2.33 2.32 2.30 2.29 2.29 2.28 2.06 2.05 2.05 2.04 2.03 2.02 2.02 2.01 2.00 2.00 1.84 1.83 1.81 1.81 1.80 1.80 1.79 1.79 1.78 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.72 1.71 1.70 1.69 1.68 1.68 1.67 1.67 1.65 1.64 1.63 1.63 1.62 1.60 1.58 1.57 1.55 1.53 1.52 1.50 1.49 1.48 1.48 1.47 1.46 1.45 1.44 1.43 1.41 1.39 1.30 1.29 1.28 1.27 1.27 1.26 1.25 1.25 1.24 1.23
N
Cl
1.00
4.02
1.03
1.10
5.00
4.12
3.04
1.23
10.0 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
f1 (ppm)

***syn*-13**

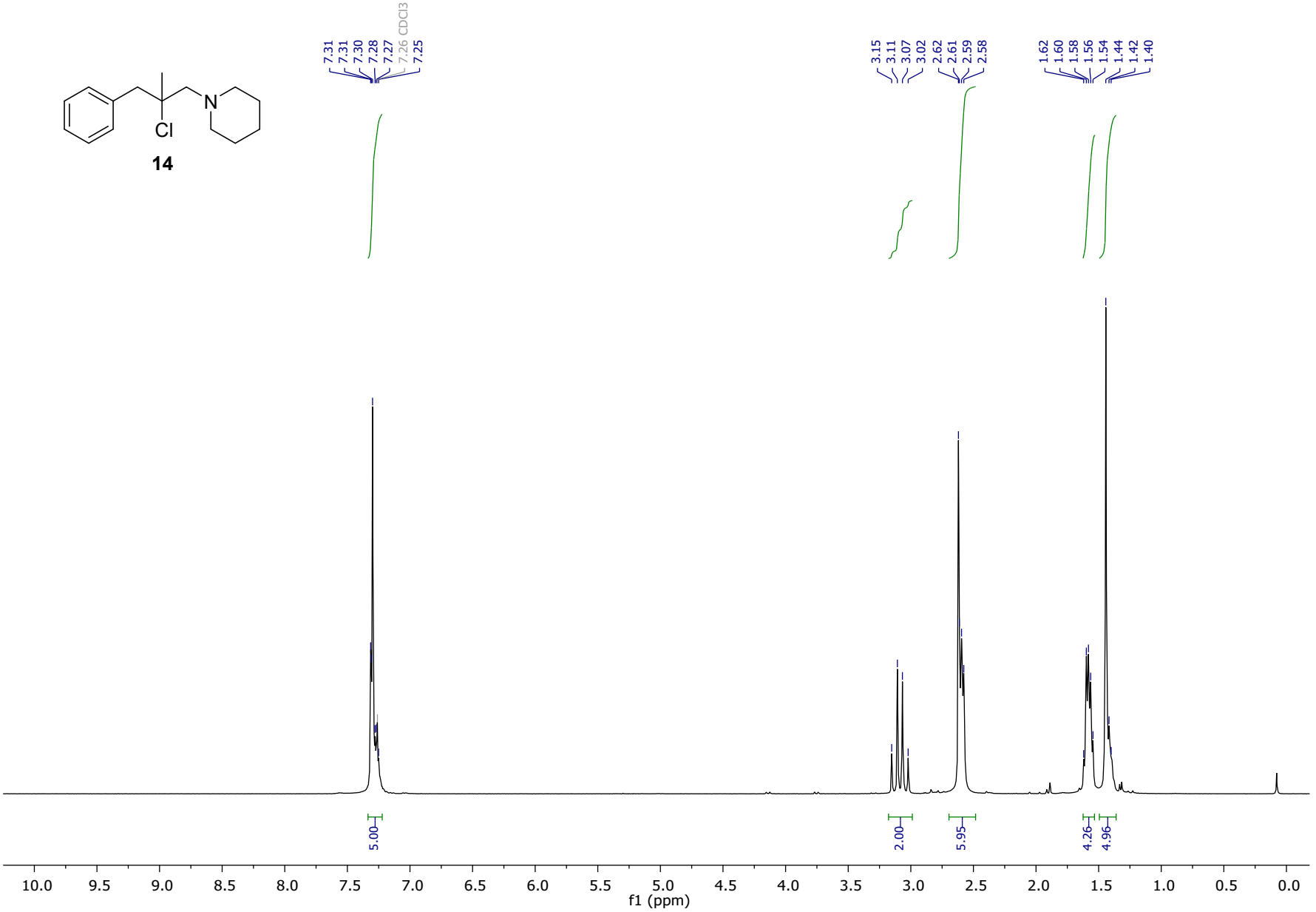

77.2 CDCl3
66.9
61.1
50.9
34.3
26.4
25.6
24.8
24.3
19.9
N
Cl
syn-13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

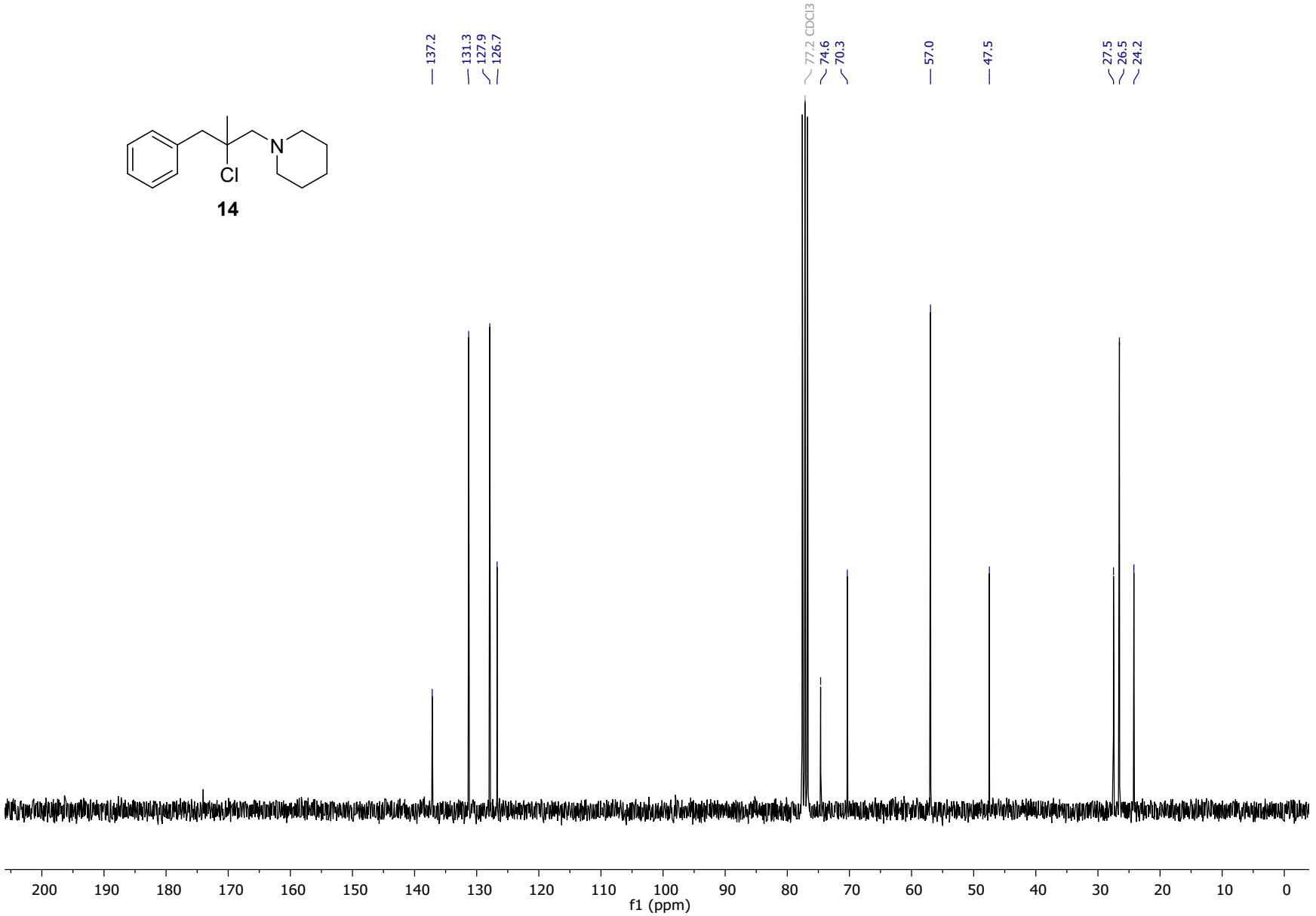

Cl
N
anti-13
7.26 CDCl3
3.93 3.92 3.89 3.88 3.86 3.84 2.66 2.65 2.65 2.62 2.61 2.59 2.54 2.53 2.53 2.52 2.51 2.47 2.42 2.30 2.30 2.29 2.28 2.27 2.26 2.25 2.25 2.24 2.23 2.23 1.92 1.75 1.74 1.73 1.73 1.72 1.71 1.70 1.68 1.68 1.64 1.63 1.60 1.59 1.57 1.55 1.53 1.45 1.44 1.42 1.40 1.27 1.26 1.25 1.24 1.22 1.21 1.21 1.20 1.19 1.18
1.00
2.06
2.99
1.12
1.09
7.24
2.03
3.12
10.0 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
f1 (ppm)

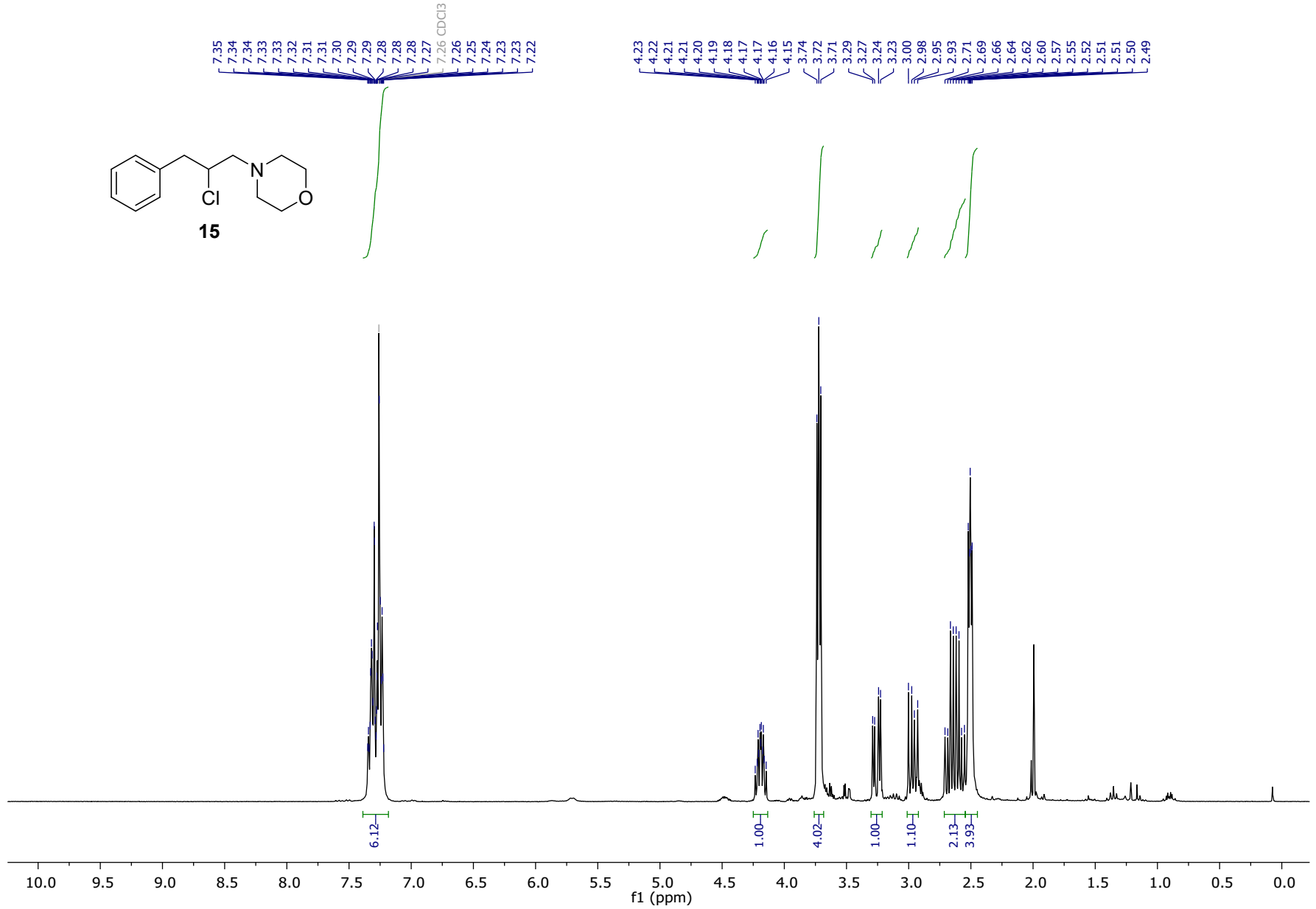

N
Cl

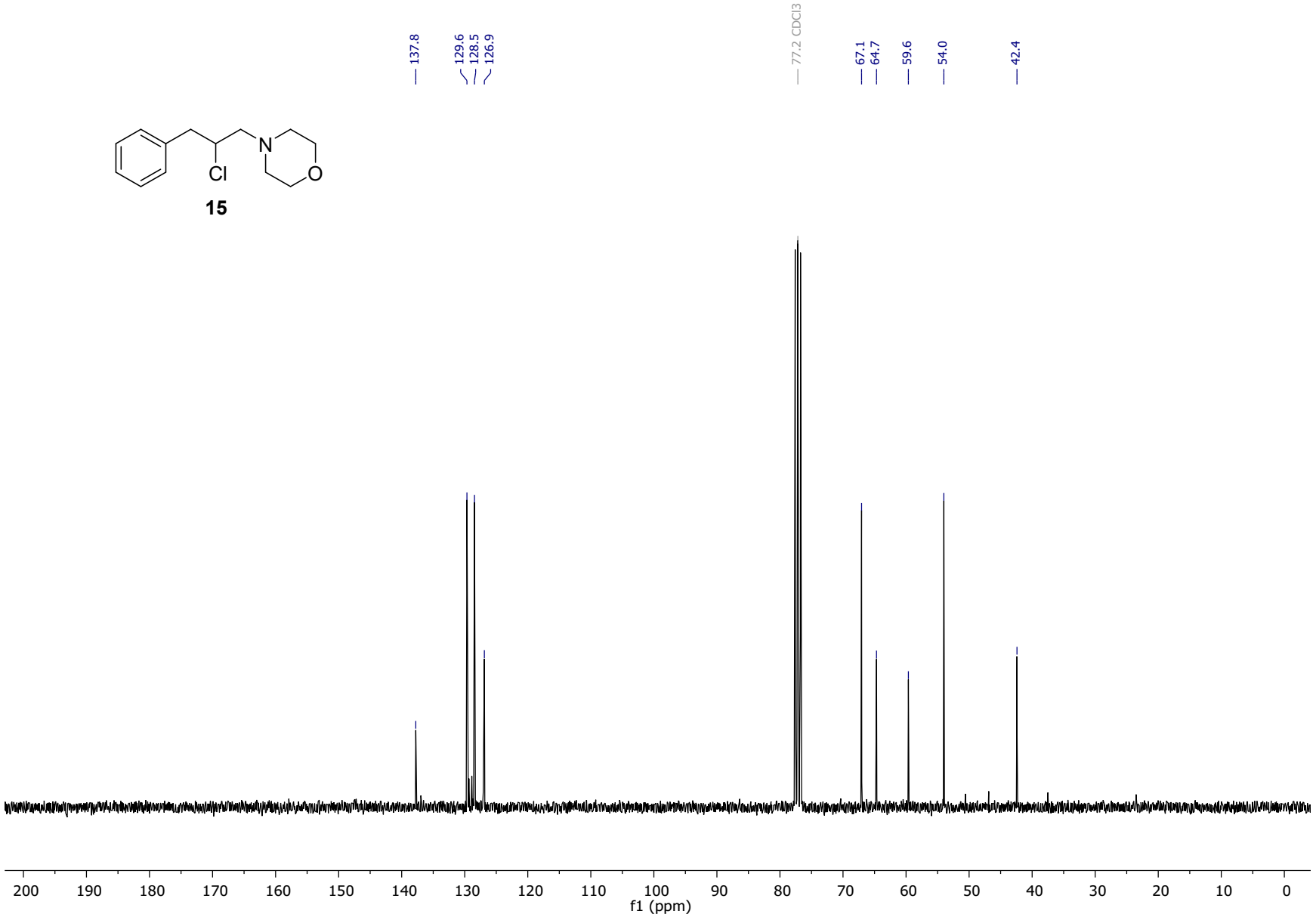
***anti*-13**

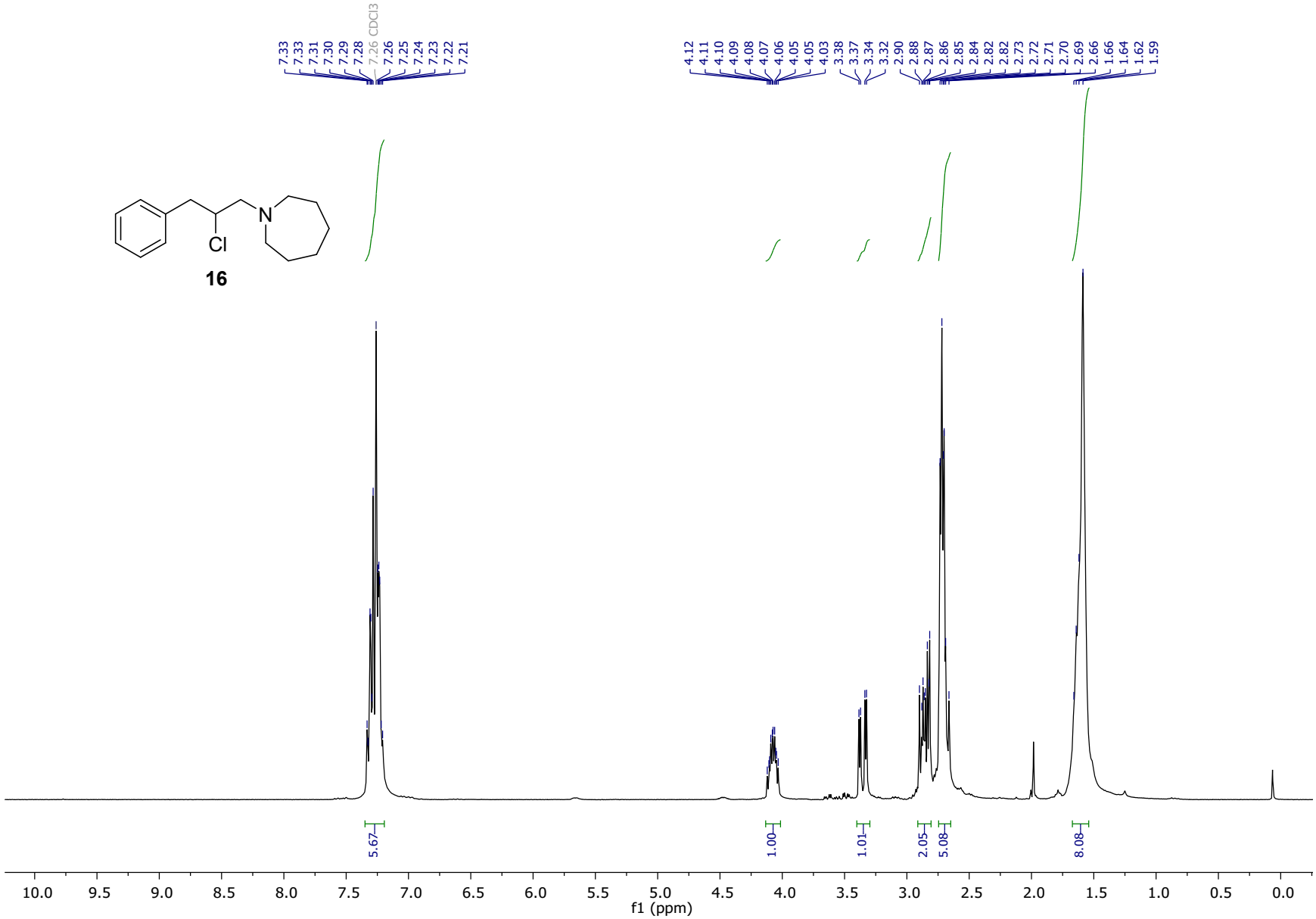
77.2 CDCl3
69.9
61.7
49.8
37.7
26.8
26.3
26.2
25.2
25.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

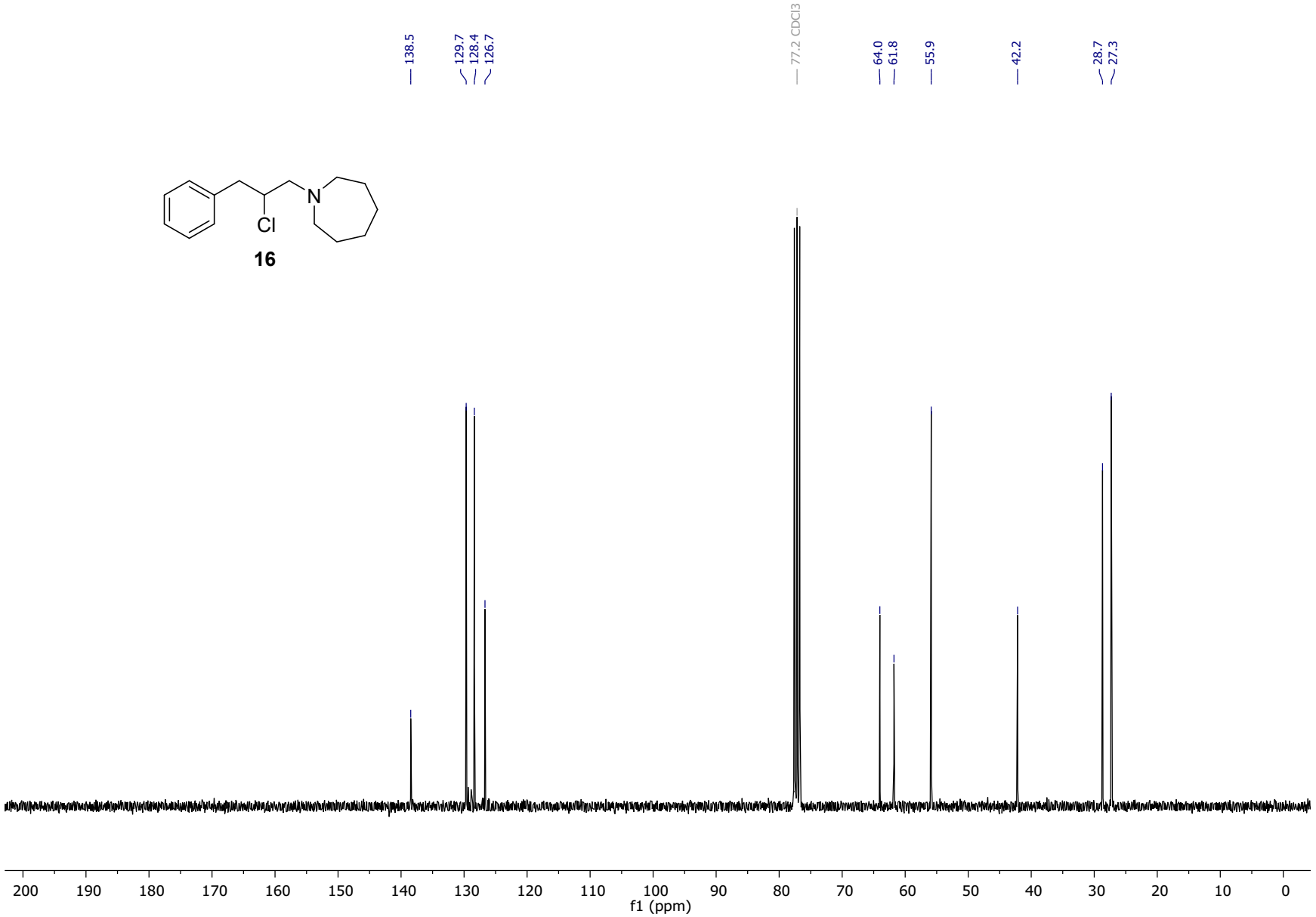

Cl
N
14
7.31
7.31
7.30
7.28
7.27
7.26 CDCl3
7.25
3.15
3.11
3.07
3.02
2.62
2.61
2.59
2.58
1.62
1.60
1.58
1.56
1.54
1.44
1.42
1.40
5.00
2.00
5.95
4.26
4.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

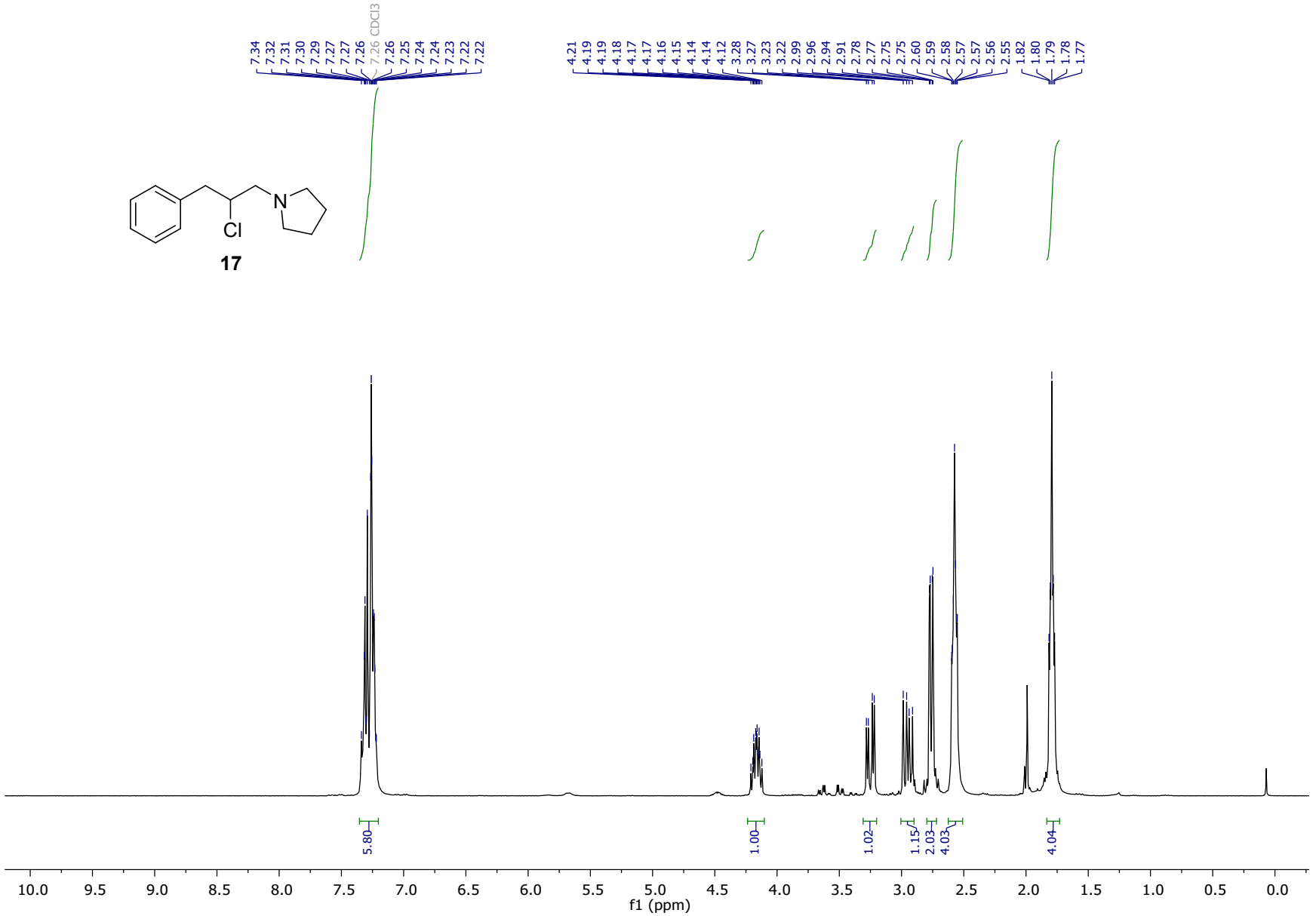

137.2
131.3
127.9
126.7
77.2 CDCl3
74.6
70.3
57.0
47.5
27.5
26.5
24.2
N
Cl
14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

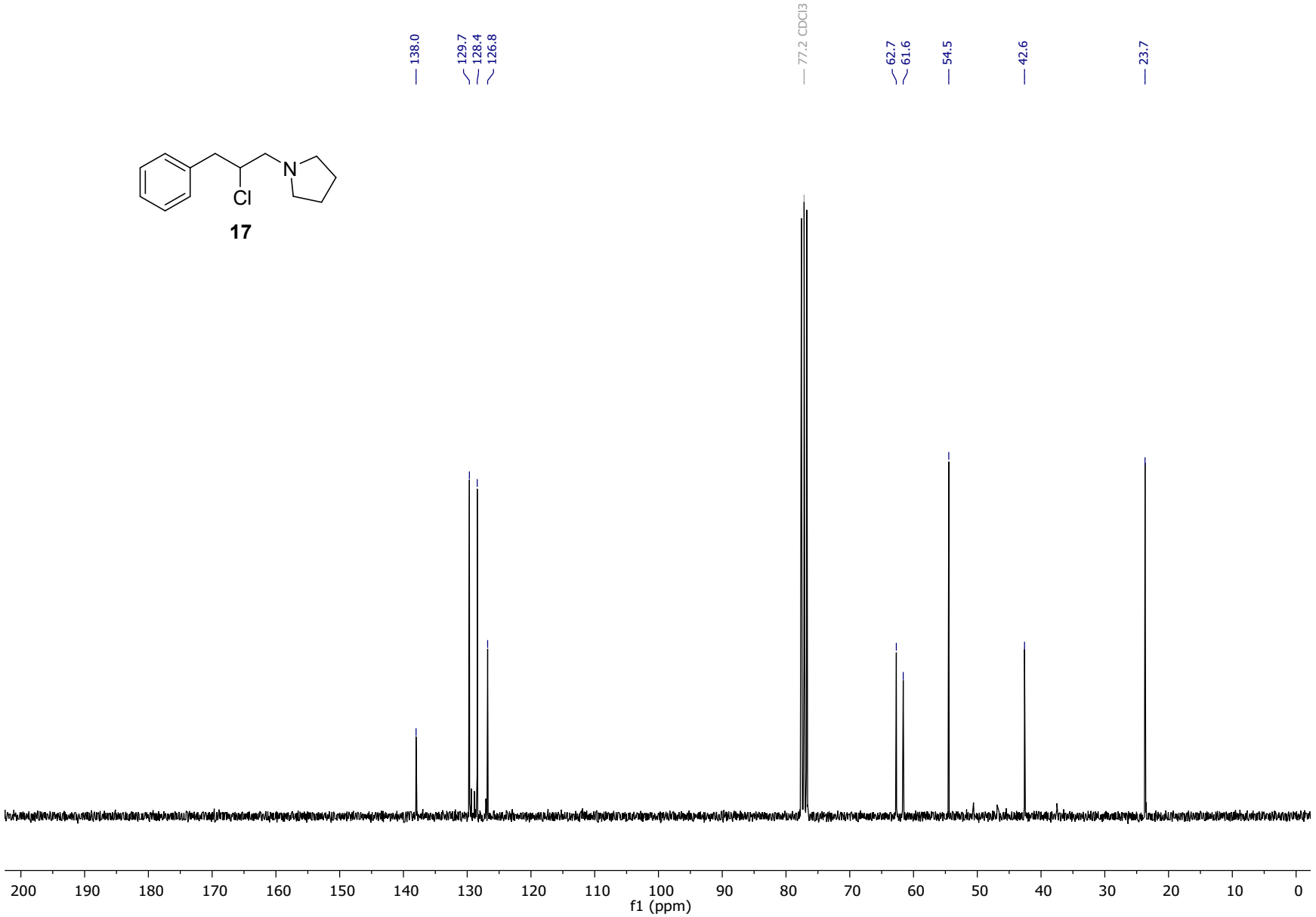

7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.26 CDCl3 7.25 7.24 7.23 7.23 7.22
4.23 4.22 4.21 4.21 4.20 4.19 4.18 4.17 4.17 4.16 4.15 3.74 3.72 3.71 3.29 3.27 3.24 3.23 3.00 2.98 2.95 2.93 2.71 2.69 2.66 2.64 2.62 2.60 2.57 2.55 2.52 2.51 2.51 2.50 2.49
Cl
N
O
15
6.12
1.00
4.02
1.00
1.10
2.13
3.93
10.0 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
f1 (ppm)

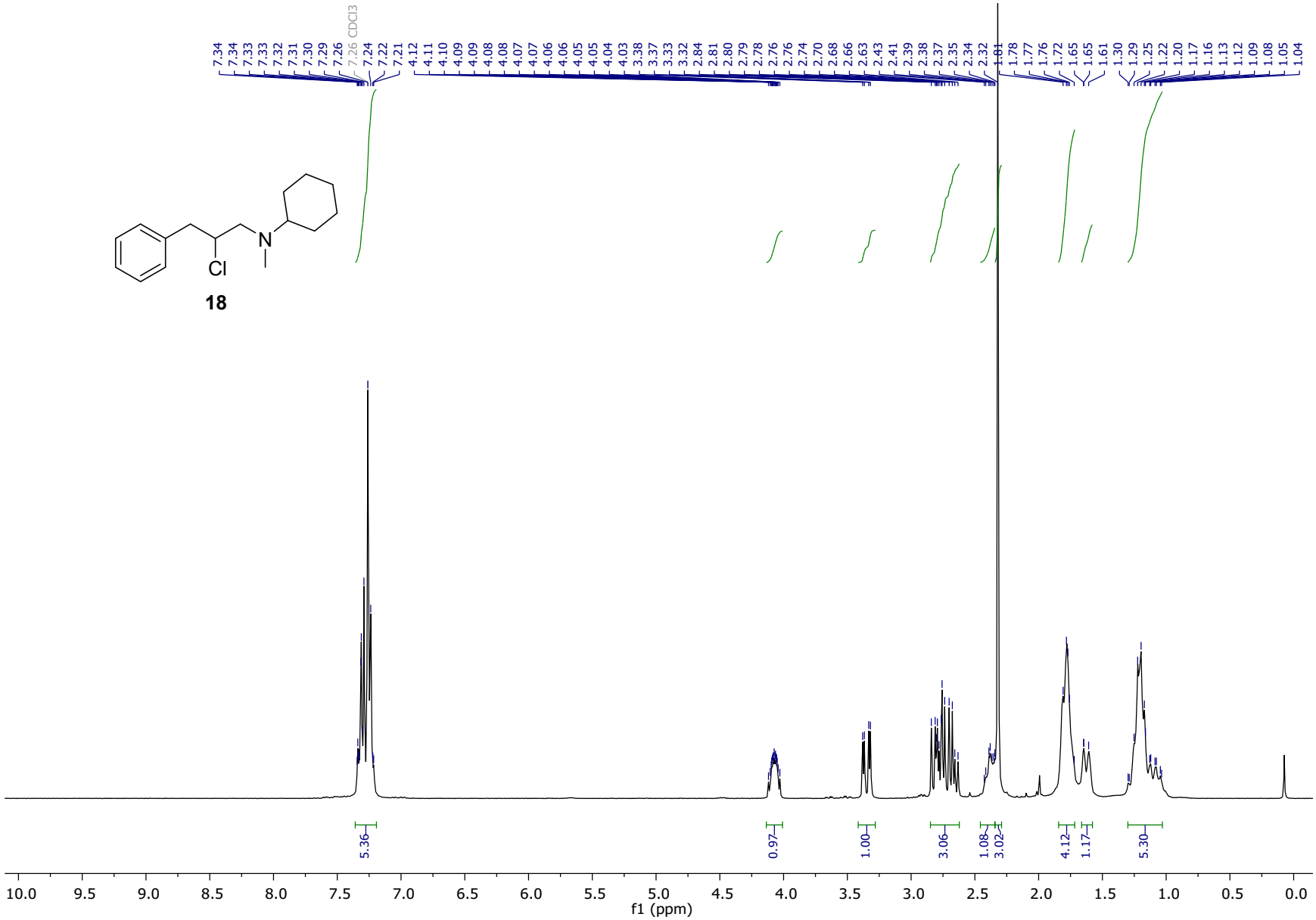

137.8
129.6
128.5
126.9
77.2 CDCl3
67.1
64.7
59.6
54.0
42.4
Cl
N
O
15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

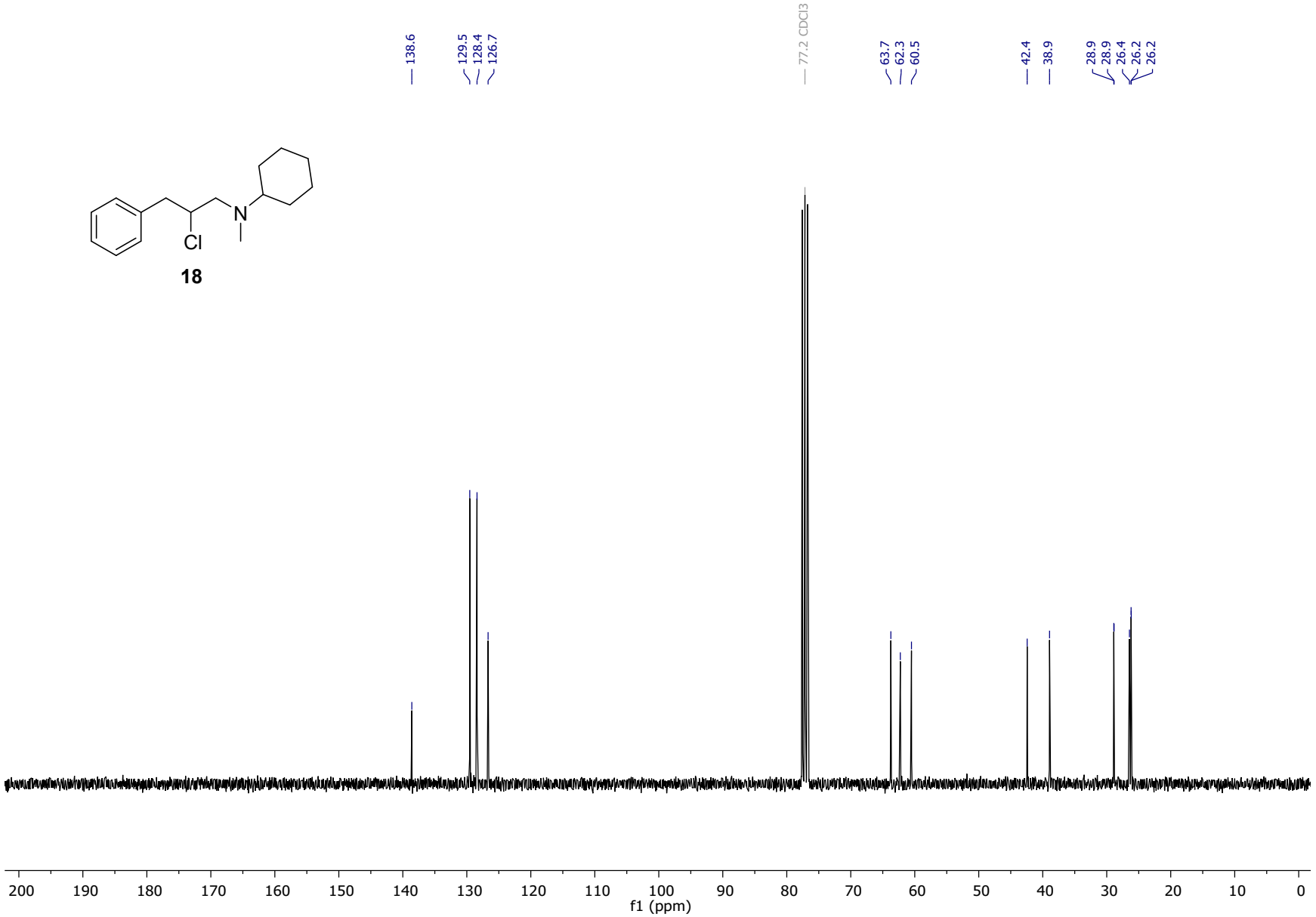

7.33
7.33
7.31
7.30
7.29
7.28
7.26 CDCl3
7.26
7.25
7.24
7.23
7.22
7.21
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.05
4.05
4.03
3.38
3.37
3.34
3.32
2.90
2.88
2.87
2.86
2.85
2.84
2.82
2.82
2.73
2.72
2.71
2.70
2.69
2.66
1.66
1.64
1.62
1.59
N
Cl
16
5.67
1.00
1.01
2.05
5.08
8.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
f1 (ppm)

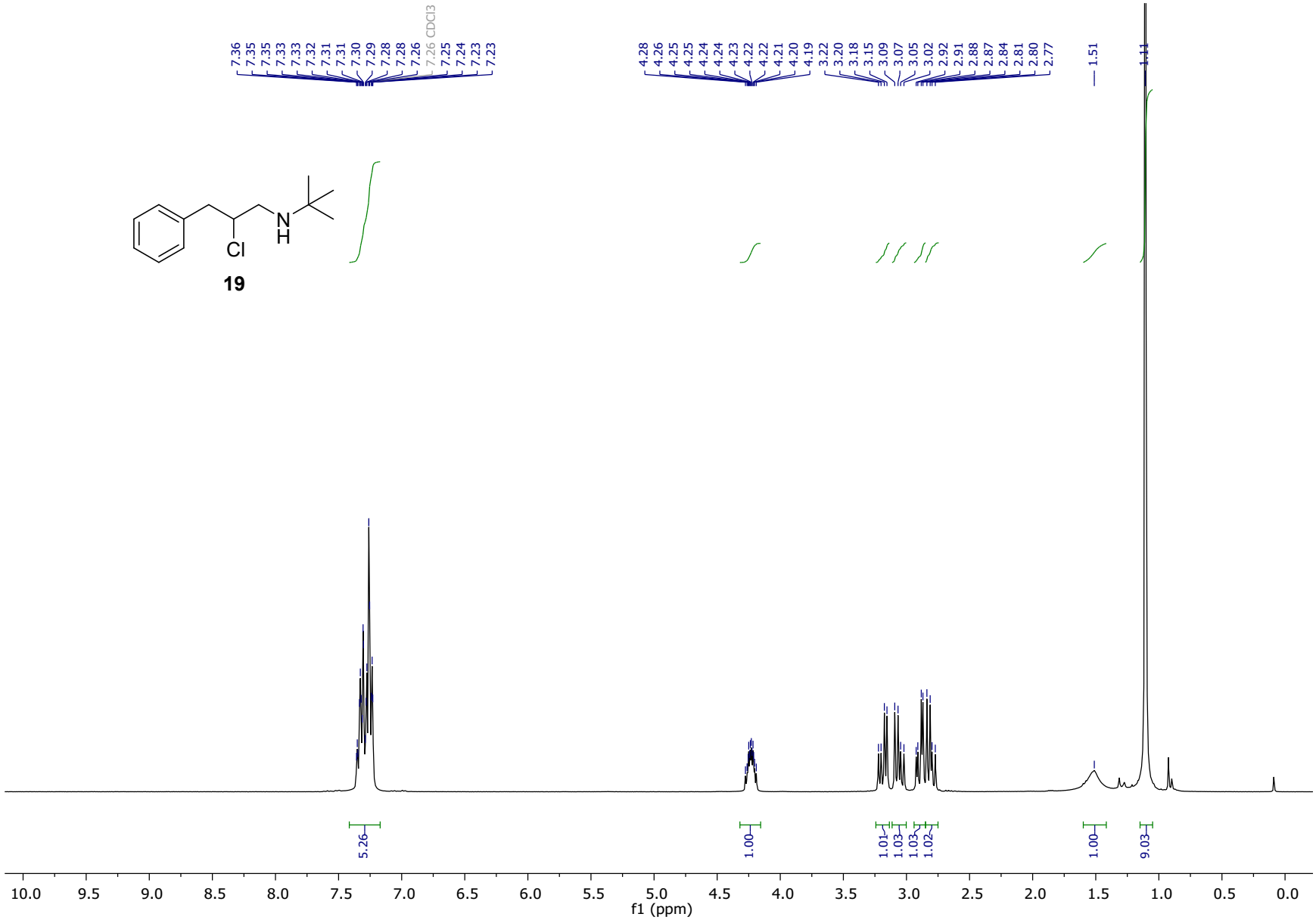

138.5
129.7
128.4
126.7
77.2 CDCl3
64.0
61.8
55.9
42.2
28.7
27.3
N
Cl
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

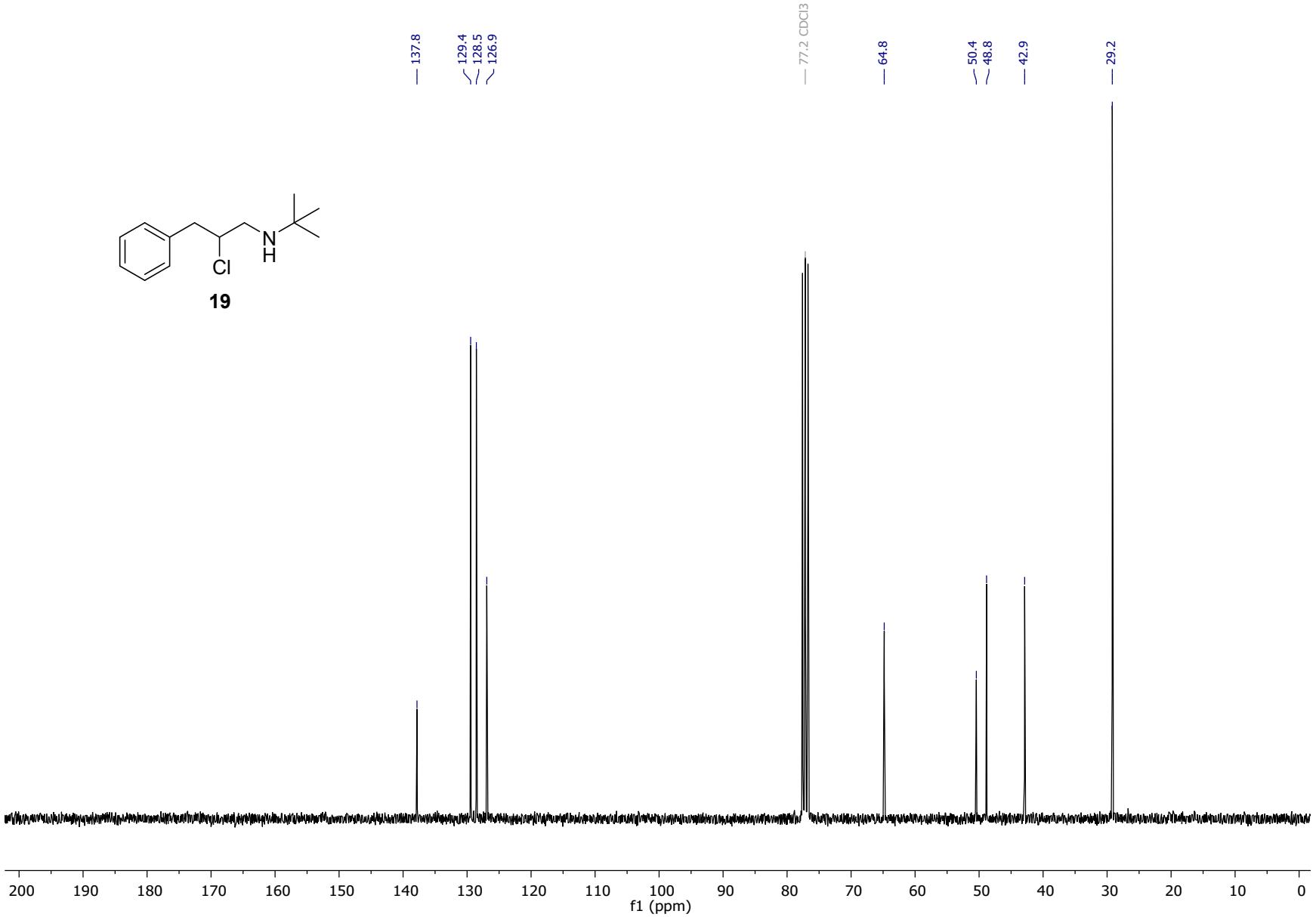

7.34
7.32
7.31
7.30
7.29
7.27
7.27
7.26
7.26 CDCl3
7.26
7.25
7.24
7.24
7.23
7.22
7.22
4.21
4.19
4.19
4.18
4.17
4.17
4.16
4.15
4.14
4.14
4.12
3.28
3.27
3.23
3.22
2.99
2.96
2.94
2.91
2.78
2.77
2.75
2.75
2.60
2.59
2.58
2.57
2.57
2.56
2.55
1.82
1.80
1.79
1.78
1.77
N
Cl
17
5.80
1.00
1.02
1.15
2.03
4.03
4.04
10.0
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
f1 (ppm)


138.0
129.7
128.4
126.8
77.2 CDCl3
62.7
61.6
54.5
42.6
23.7
N
Cl
17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

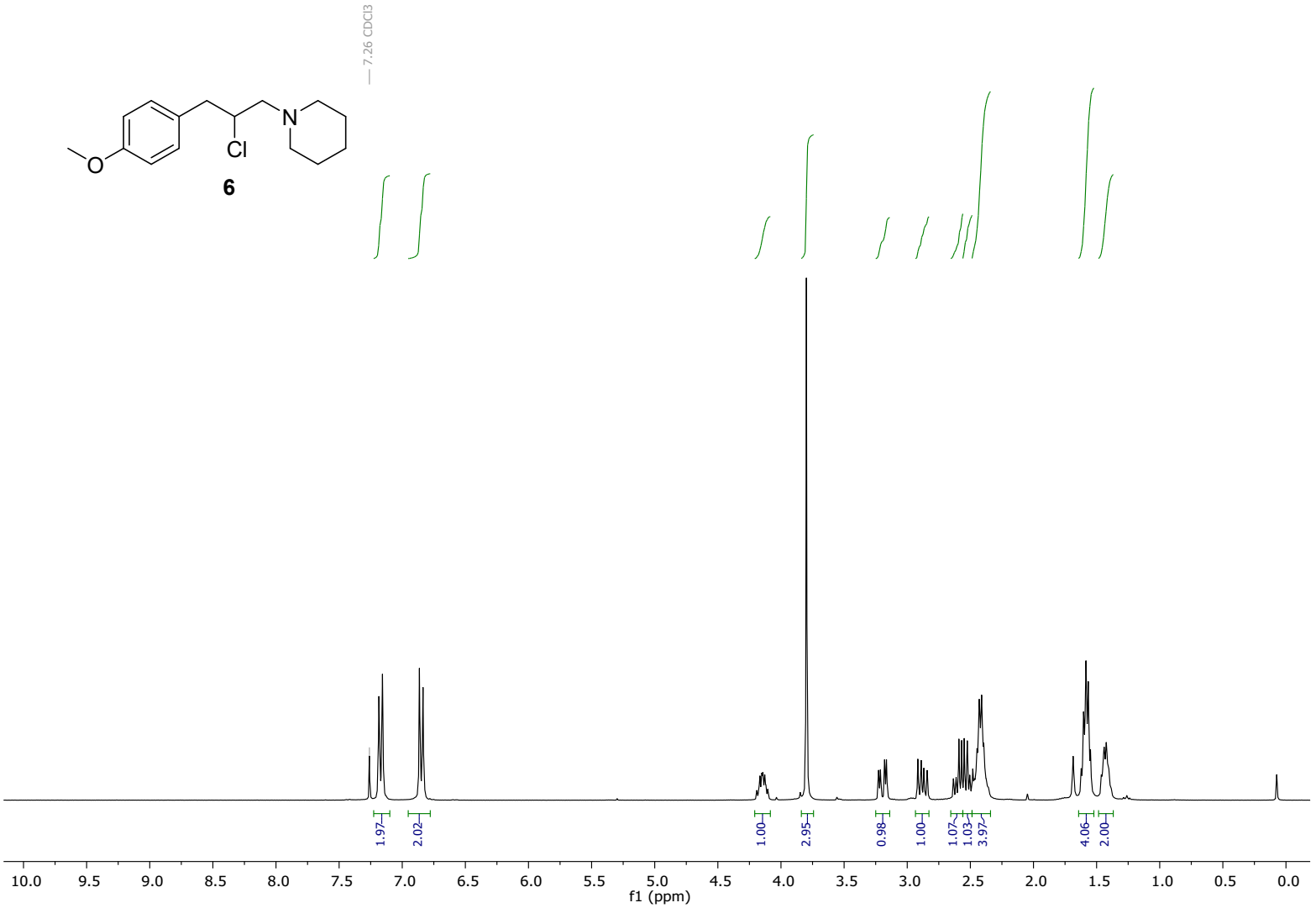

7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.26
7.26 CDCl3
7.24
7.22
7.21
4.12
4.11
4.10
4.09
4.09
4.08
4.08
4.07
4.07
4.06
4.06
4.05
4.05
4.04
4.03
3.38
3.37
3.33
3.32
2.84
2.81
2.80
2.79
2.78
2.76
2.76
2.74
2.70
2.68
2.66
2.63
2.43
2.41
2.39
2.38
2.37
2.35
2.34
2.32
1.81
1.78
1.77
1.76
1.72
1.65
1.65
1.61
1.30
1.29
1.25
1.22
1.20
1.17
1.16
1.13
1.12
1.09
1.08
1.05
1.04
N
Cl
18
5.36
0.97
1.00
3.06
1.08
3.02
4.12
1.17
5.30
10.0
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
f1 (ppm)


138.6
129.5
128.4
126.7
77.2 CDCl3
63.7
62.3
60.5
42.4
38.9
28.9
28.9
26.4
26.2
26.2
N
Cl
18
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

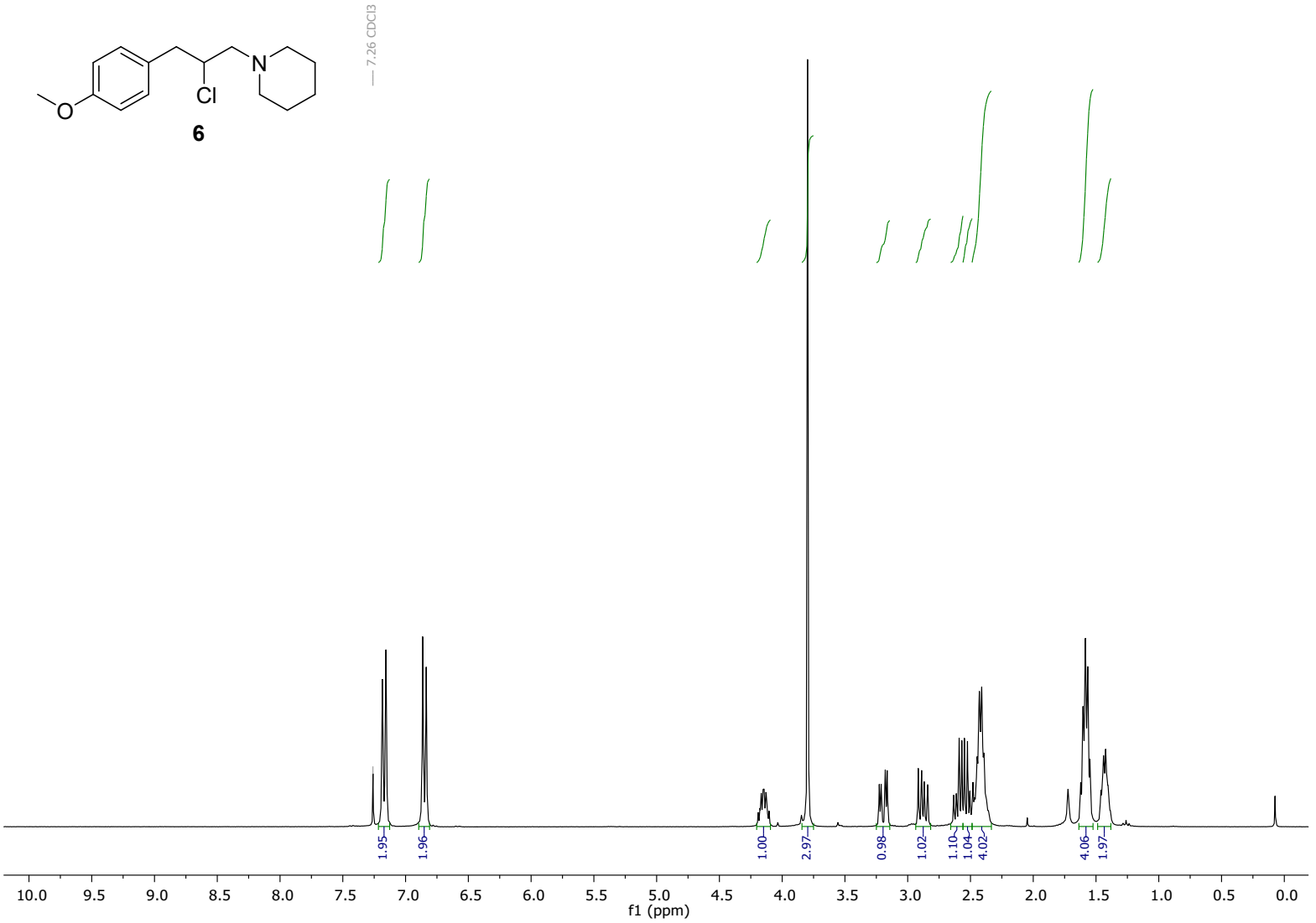

7.36
7.35
7.35
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.26
7.26 CDCl3
7.25
7.24
7.23
7.23
4.28
4.26
4.25
4.25
4.24
4.24
4.23
4.22
4.22
4.21
4.20
4.19
3.22
3.20
3.18
3.15
3.09
3.07
3.05
3.02
2.92
2.91
2.88
2.87
2.84
2.81
2.80
2.77
1.51
1.11
N
H
Cl
19
5.26
1.00
1.01
1.03
1.03
1.02
1.00
9.03
10.0
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
f1 (ppm)


137.8
129.4
128.5
126.9
77.2 CDCl3
64.8
50.4
48.8
42.9
29.2
N
H
Cl
19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

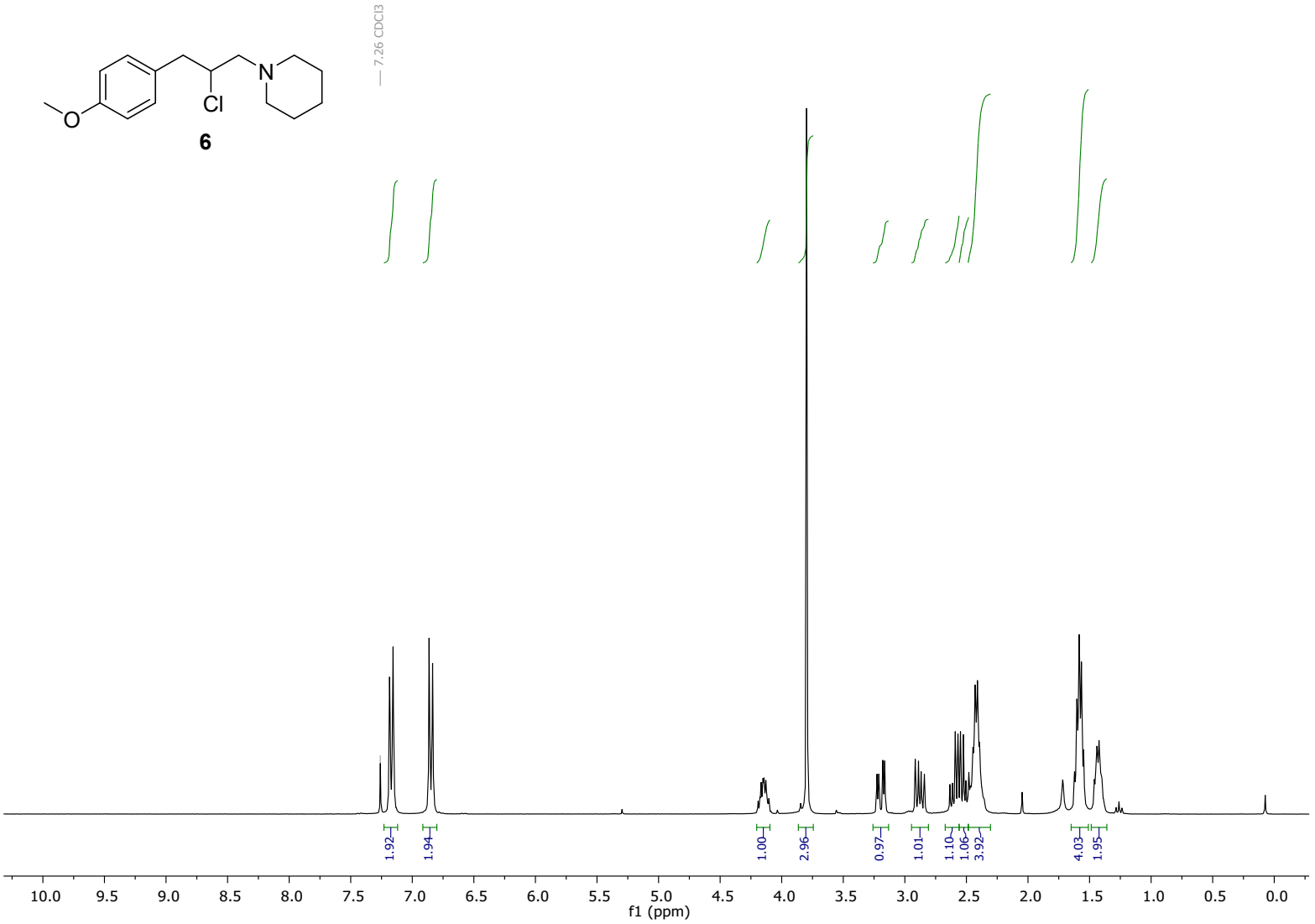
Isolated product **6** from extended operation experiment: fraction 2, 91% yield, 5.15 g



Isolated product **6** from extended operation experiment: fraction 9, 92% yield, 5.20 g



Isolated product **6** from extended operation experiment: fraction 17, 91% yield, 5.14 g



6