Preparation of thioamides from alkyl bromides, nitriles, and hydrogen sulfide through a thio-Ritter-type reaction

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1. General Information

NMR spectra were obtained from Bruker Avance III 400 MHz NMR Spectrometer, Varian INOVA 600MHz spectrometer or Bruker Avance NOE 600 MHz NMR Spectrometer, and spectral data are reported in ppm relative to tetramethylsilane (TMS, 0.00 ppm), $CHCl_3$ (7.26 ppm) or CH_3CN (1.96 ppm) as internal standard. The following abbreviations were used to indicate the multiplicity in NMR spectra: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; dt = doublet of triplets; td = triplet of doublets; ddd = doublet of doublet of doublets; m = multiplet. Electron ionization mass spectra (EI-MS) were measured on a Shimadzu GCMSQP2010SE spectrometer by direct inlet at 70 eV and the corresponding signals were given in m/z with relative intensity (%) in brackets. High-resolution mass spectra (HRMS) were obtained on a Thermo Scientfic Orbitrap Elite Mass Spectrometer or Agilent 6530 accurate-Mass Q-TOF spectrometer. Infrared (IR) spectra were measured on Nicolet Nexus 670 FT-IR spectrometer. Melting points were determined on a microscopic apparatus and were uncorrected. X-ray data collections were performed in ROD, Synergy Custom system, HyPix diffractometer. Enantiomeric excesses (ee) values were determined by UPC^2 equipped with Waters 2998 Photodiode Array Detector. Optical rotation was measured in $CHCl_3$ on IP-digi300/8 Polarimeter.

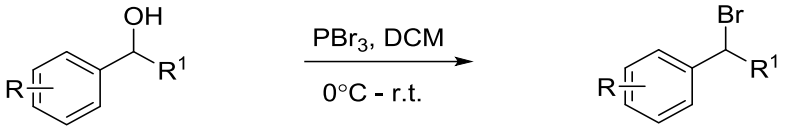
All reactions were monitored by thin-layer chromatography (TLC), and the spots were visualized with UV light (254 nm) or phosphomolybdic acid in ethanol (10%). The products were purified by flash column chromatography on silica gel (200-300 mesh).

Unless otherwise mentioned, all reactions were performed under an atmosphere of argon using anhydrous solvents in an oven-dried tube. Acetonitrile was purchased from Innochem Comp. (extra dry over molecular sieves) and used as received. Other nitriles were dried over 3Å MS for 3 days. Nitromethane was dried over $CaSO_4$ for 3 days and then distilled under an atmosphere of argon and stored with $MgSO_4$ for no more than a week. Benzyl bromide was purified by distillation under an atmosphere of argon. Nitronium salts were commercially available and dried under vacuum at 60 ℃ for 8 h before used. Among them, NO_2BF_4 is a white and stable crystal, and moisture usually caused slightly hydrolyzed.[1] H_2S was purchased from Hebei QiMing Company and directly used.

2. Preparation of substrates

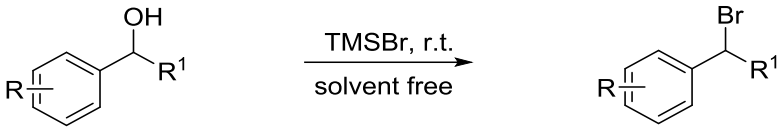
Unless otherwise noted, commercial substrates were purchased and directly used. Substrates **1t**, **1v**, and **1w** were synthesized according to the Method A[2], and substrates **1ap** and **1as** were prepared according to the Method B[3]. The ^{1}H NMR spectra data of substrates **1t**[4], **1v**[5], and **1w**[4]are in accordance with the literature.

Method A:



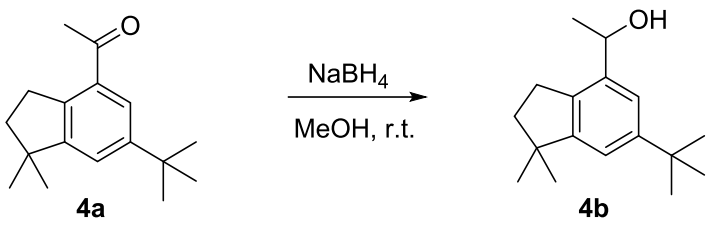
Under an argon atmosphere, to a solution of alcohol (5 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise PBr_3 (2.5 mmol) at 0 ℃. The reaction mixture was stirred at 0 ℃ and was allowed to warm-up to room temperature. Cold water was added after the starting material disappeared (monitored by TLC). The mixture was extracted with EtOAc (3 × 50 mL), and the combined organic layer was washed successively with a saturated solution of $NaHCO_3$ (3 × 50 mL) and H_2O (3 × 50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired bromide.

Method B:



Under an argon atmosphere, to a 25 mL over-dried round bottom vessel equipped with a magnetic stir-bar were added alcohol (5 mmol) and TMSBr (725.9 uL, 5.5 mmol). The reaction mixture was stirred at room temperature until the starting material disappeared (monitored by TLC). Volatile product $(TMS)_2O$ was removed under reduced pressure, and the expected bromide was obtained, which was directly used without further purification.

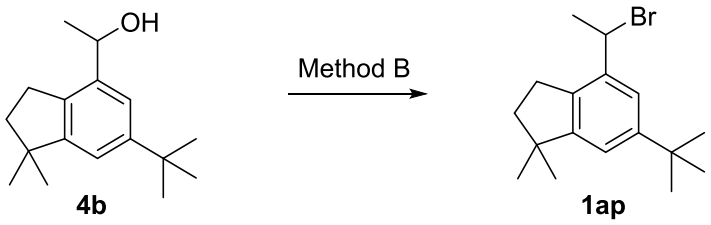
Syntheses of alcohol 4b：



Under an argon atmosphere, to a solution of celestolide **4a** (1.22 g, 5 mmol) in MeOH (10 mL) was added $NaBH_4$ (94.6 mg, 2.5 mmol) in three portions, and the reaction mixture was stirred at room temperature until the starting material disappeared (monitored by TLC). The reaction was quenched by addition of cold water. The mixture was extracted with EtOAc (3 × 50 mL), and the combined organic phase was washed successively with water (3 × 50 mL) and brine (3 × 50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired alcohol **4b** (1.05g, 85%). White solid, m.p. = 111.9-113.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 1.6 Hz, 1 H), 7.13 (d, J = 1.2 Hz, 1 H), 5.02 (q, J = 6.4 Hz, 1 H), 2.92-2.86 (m, 2 H), 1.97 (t, J = 7.2 Hz, 2 H), 1.89 (s, 1 H), 1.52 (d, J = 6.4 Hz, 3 H), 1.37 (s, 9 H), 1.29 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.9, 150.5, 140.8, 136.6, 119.5, 118.1, 68.7, 43.9, 41.6, 35.0, 31.8, 28.90, 28.86, 27.9, 23.9. **HRMS** (ESI) *m/z* calculated for $C_{17}H_{26}ONa$ $[M+Na]^+$ 269.1876, found 269.1875. **MS** (EI) *m/z* (%): 246 (18), 231 (100), 228 (72), 213 (76), 129 (45), 115 (28). **IR** (KBr plate): 3335, 2955, 2864, 1460, 1363, 1068, 1030, 877 cm^{-1}.

Syntheses of compound 1ap：



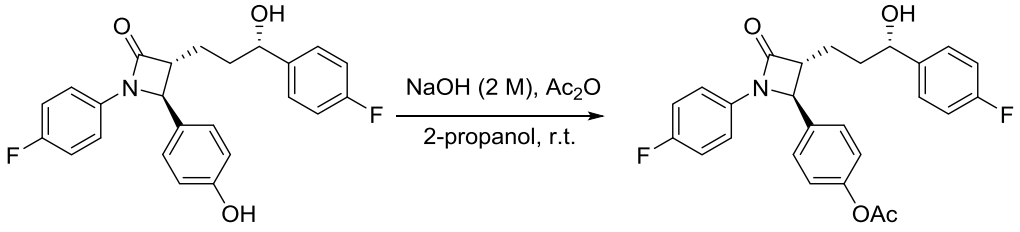
Compound **1ap** was prepared according to the Method B.

Under an argon atmosphere, to a 25 mL over-dried round bottom vessel equipped with a magnetic stir-bar were added alcohol **4b** (1.23 g, 5 mmol) and TMSBr (725.9 uL, 5.5 mmol). The reaction mixture was stirred at room temperature until the starting material disappeared (monitored by

TLC). Volatile product $(TMS)_2O$ was removed under reduced pressure, and the expected compound **1ap** (1.42 g, 92%) was obtained, which was directly used without further purification. White solid, m.p. = 48.4-50.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1 H), 7.14 (d, J = 0.4 Hz, 1 H), 5.35 (q, J = 6.8 Hz, 1 H), 3.03-2.85 (m, 2 H), 2.11 (d, J = 7.2 Hz, 3 H), 2.01-1.96 (m, 2 H), 1.37 (d, J = 0.8 Hz, 9 H), 1.291 (s, 3 H), 1.285 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.1, 150.5, 137.9, 137.8, 120.9, 119.3, 48.3, 44.2, 41.4, 35.0, 31.7, 28.91, 28.85, 27.9, 25.9. **MS** (EI) *m/z* (%): 310 (1), 308 (1), 229 (100), 228 (48), 213 (32), 129 (25), 115 (5). **IR** (KBr plate): 2955, 2863, 1458, 1362, 1105, 876, 617 cm^{-1}.

Syntheses of compound 5b[6]:



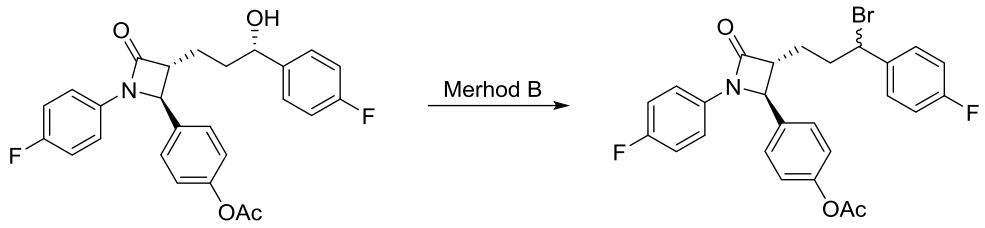
5a **5b**

To a solution of zetimibe **5a** (5.53 g, 13.5 mmol) in 2-propanol (70 mL) were added aq. NaOH (2 mol/L, 15 mL) and Ac_2O (3.0 mL, 32 mmol), the solution was stirred for 5 h at room temperature. After reaction completion, a saturated solution of $NaHCO_3$ (200 mL) was added to quench the reaction at 0℃. The mixture was extracted with EtOAc (3 × 50 mL), and the combined organic layer was washed consecutively with sat. aq. $NaHCO_3$ (3 × 50 mL) and H_2O (3 × 50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate to afford the compound **5b** (5.61 g, 92%). White crystal, m.p. = 140.7-141.5 °C.

^{1}H NMR (400 Mz, $CDCl_3$): δ 7.30 (d, J = 8.4 Hz, 2 H), 7.24 (dd, J = 5.6 Hz, J = 8.8 Hz, 2 H), 7.22-7.17 (m, 2 H), 7.08 (d, J = 8.8 Hz, 2 H), 6.96 (t, J = 8.8 Hz, 2 H), 6.89 (t, J = 8.8 Hz, 2 H), 4.64 (t, J = 6.0 Hz, 1 H), 4.61 (d, J = 2.0 Hz, 1 H), 3.22 (s, 1 H), 3.03 (t, J = 6.0 Hz, 1 H), 2.26 (s, 3 H), 1.95-1.82 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.4, 167.5, 162.0 (d, J = 244.0 Hz), 159.0 (d, J = 242.0 Hz), 150.7, 140.2 (d, J = 3.0 Hz), 135.0, 133.6 (d, J = 2.0 Hz), 127.4 (d, J = 8.0 Hz), 126.9, 122.5, 118.4 (d, J = 8.0 Hz), 115.9 (d, J = 23.0 Hz), 115.2 (d, J = 21.0 Hz), 72.8,

60.7, 60.3, 36.5, 24.9, 21.0. **HRMS** (ESI) *m/z* calculated for $C_{26}H_{23}F_2NO_4Na$ $[M+Na]^+$ 474.1487, found 474.1487. **MS** (EI) *m/z* (%): 451 (6), 341 (7), 272 (44), 254 (39), 215 (29), 134 (100). **IR** (KBr plate): 3463, 3072, 2985, 2938, 2863, 1748, 1510, 1427, 1387, 1221, 1198, 1046, 1016, 836 cm^{-1}.

Syntheses of compound 1as：



5b **1as**

Compound **1as** was prepared according to the Method B.

Under an argon atmosphere, to a 25 mL over-dried round bottom vessel equipped with a magnetic stir-bar were added compound **5b** (2.26 g, 5 mmol) and TMSBr (725.9 uL, 5.5 mmol) The reaction mixture was stirred at room temperature until the starting material disappeared (monitored by TLC). Volatile product $(TMS)_2O$ was removed under reduced pressure, and two inseparable bromide **1as** (2.44 g, 95%, yellow solid) was obtained, which was directly used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.32 (m, 4 H), 7.24-7.21 (m, 2 H), 7.14-7.11 (m, 2 H), 7.04-6.99 (m, 2 H), 6.96-6.92 (m, 2 H), 4.95-4.90 (m, 1 H), 4.67 (d, *J* = 2.4 Hz, 0.5 H), 4.64 (d, *J* = 2.0 Hz, 0.5 H), 3.13-3.07 (m, 1 H), 2.54-2.46 (m, 0.5 H), 2.40-2.34 (m, 1 H), 2.31 (s, 3 H), 2.26-2.11 (m, 1.5 H), 1.99-1.85 (m, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.5, 166.8, 166.7, 163.8, 161.4, 160.5, 158.0, 151.1, 151.0, 137.64, 137.55, 135.0, 133.8, 129.18, 129.15, 129.10, 129.06, 127.09, 127.04, 122.8, 118.6, 118.5, 116.2, 116.03, 115.97, 115.8, 60.88, 60.85, 60.04, 59.97, 53.9, 53.7, 37.7, 37.6, 27.9, 27.5, 21.3. **HRMS** (ESI) *m/z* calculated for $C_{26}H_{22}BrF_2NO_3Na$ $[M+Na]^+$ 536.0643 and 538.0623, found 536.0636 and 538.0627, respectively. **MS** (EI) *m/z* (%): 515 (1), 513 (1), 296 (19), 254 (100), 296 (19), 214 (32), 135 (64); **IR** (KBr plate): 3077, 2983, 2932, 2875, 1740, 1604, 1510, 1277, 1045, 1015, 835 cm^{-1}.

3. Experimental details and characterization data

3.1 General procedure

3.1.1 General procedure A

In an argon-filled glove box, to a 10 mL over-dried reaction tube equipped with a magnetic stir-bar were sequentially added NO_2BF_4 (0.6 mmol, 79.7 mg) and acetonitrile (1.0 mL). After removal from the glove box, the reaction tube was placed in a preheated oil bath at corresponding reaction temperature T_1, and bromide (0.4 mmol) was then added under an argon atmosphere. After stirred for 30 min (the colour of reaction mixture was gradually changed to brownish-yellow from nearly colorless), the reaction mixture was purged with continuous H_2S for 1 min (**Caution！The process must be run in an efficient fume hood with appropriate personal protection**) at the corresponding reaction temperature T_2 and stirred for another 20 min at this temperature, in which some light yellow solid was observed. The mixture was then filtered with celite using ethyl acetate as the eluent, and the filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the thioamide.

3.1.2 General procedure B

In an argon-filled glove box, to a 10 mL over-dried reaction tube equipped with a magnetic stir-bar were sequentially added NO_2BF_4 (0.6 mmol, 79.7 mg), nitrile (2.0 mmol) and CH_3NO_2 (1.0 mL). After removal from the glove box, the rection tube was placed in a preheated oil bath at corresponding reaction temperature T_1, and bromide (0.4 mmol) was then added under an argon atmosphere. After stirred for 30 min (the colour of reaction mixture was gradually changed to brownish-yellow from nearly colorless), the reaction mixture was purged with continuous H_2S for 1 min (**Caution！The process must be run in an efficient fume hood with appropriate personal protection.**) at corresponding reaction temperature T_2 and stirred for another 20 min at this temperature, in which some light yellow solid was observed. The mixture was then filtered with celite using ethyl acetate as the eluent, and the filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the thioamide.

3.2 The details for the optimal reaction conditions

3.2.1 The details for the optimal reaction conditions

Initially, we selected benzyl bromide (**1a**) and acetonitrile (**2a**) as reaction partners to yield a nitrilium ion intermediate, and hydrogen sulfide as a nucleophile to trap the resulting intermediate. The investigation details were listed in Table S1. When the mixture of benzyl bromide and NO_2BF_4 in acetonitrile was stirred at room temperature for 30 min under an argon atmosphere, hydrogen sulfide was then inleted into the reaction mixture for 1 min. The mixture was stirred for another 20 min and then filtered, the desired *N*-benzylethanethioamide (**3a**) was isolated in 55% yield (Table S1, entry 1). Encouraged by this preliminary result, the reaction temperatures were first screened. Pleasingly, an excellent yield of 88% was obtained when the reaction was performed at 45℃ (upon addition of the benzyl bromide) and -15 ºC (upon introduction of hydrogen sulfide), respectively (Table S1, entries 2-14). Subsequently, a series of sulfur-based nucleophiles were examined to improve reaction results, however, they generally gave poor results or inhibited the reaction (Table S1, entries 15-24). Next, screening of several nitronium salts revealed that just $NOBF_4$ gave the similar reaction results (Table S1, entries 25-29). Since $NOBF_4$ is more easily hydrolyzed in comparison to NO_2BF_4, NO_2BF_4 was finally chosen. Then, the equivalent amount of NO_2BF_4 was varied, but no obvious improvement was observed (Table S1, entries 30-34). Finally, the concentration of the model reaction was also investigated and was found to have marginal effect on reaction outcomes (Table S1, entries 35 and 36).

From the above experimental results, the reaction parameters listed in entry 9 (Table S1) were selected as the optimal reaction conditions.

Table S1 The details for the optimal reaction conditions[a]

1a **2a** **3a**

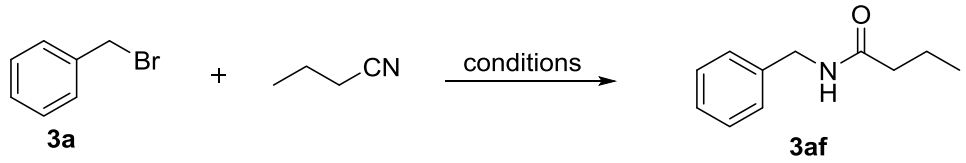
Entry	T_1	T_2	Nitronium salts (equiv)	Sulfur sources	Yield (%)[b]
1	20℃	20℃	NO_2BF_4 (1.5)	H_2S	55
2	35℃	**35℃**	NO_2BF_4 (1.5)	H_2S	47
3	35℃	**R.T.**	NO_2BF_4 (1.5)	H_2S	66
4	35℃	**0℃**	NO_2BF_4 (1.5)	H_2S	77
5	**35℃**	**-15**	NO_2BF_4 (1.5)	H_2S	86
6	**20℃**	-15℃	NO_2BF_4 (1.5)	H_2S	73
7	**30℃**	-15℃	NO_2BF_4 (1.5)	H_2S	84
8	**40℃**	-15℃	NO_2BF_4 (1.5)	H_2S	85
9	**45℃**	-15℃	NO_2BF_4 (1.5)	H_2S	88
10	**50℃**	-15℃	NO_2BF_4 (1.5)	H_2S	80
11	45℃	**-35**	NO_2BF_4 (1.5)	H_2S	76
12	45℃	**-25**	NO_2BF_4 (1.5)	H_2S	88
13	45℃	**0℃**	NO_2BF_4 (1.5)	H_2S	74
14	45℃	**20℃**	NO_2BF_4 (1.5)	H_2S	73
15	45℃	-15℃	NO_2BF_4 (1.5)	**Na_2S[c]**	34
16	45℃	-15℃	NO_2BF_4 (1.5)	**NaSH[c]**	24
17	45℃	-15℃	NO_2BF_4 (1.5)	**K_2S[c]**	0
18	45℃	-15℃	NO_2BF_4 (1.5)	**FeS[c]**	0
19	45℃	-15℃	NO_2BF_4 (1.5)	**Ag_2S[c]**	0
20	45℃	-15℃	NO_2BF_4 (1.5)	**Cu_2S[c]**	0
21	45℃	-15℃	NO_2BF_4 (1.5)	**S_8[c]**	0
22	45℃	-15℃	NO_2BF_4 (1.5)	**P_2S_5[c]**	0
23	45℃	-15℃	NO_2BF_4 (1.5)	**NH_2CSNH_2[c]**	15
24	45℃	-15℃	NO_2BF_4 (1.5)	**Lawesson' reagent[c]**	0
25	45℃	-15℃	**$NOSbF_6$ (1.5)**	H_2S	33
26	45℃	-15℃	**NO_2SbF_6 (1.5)**	H_2S	0
27	45℃	-15℃	**$NOPF_6$ (1.5)**	H_2S	75
28	45℃	-15℃	**NO_2PF_6 (1.5)**	H_2S	0
29	45℃	-15℃	**$NOBF_4$ (1.5)**	H_2S	88
30	45℃	-15℃	**NO_2BF_4 (1.0)**	H_2S	56
31	45℃	-15℃	**NO_2BF_4 (1.1)**	H_2S	82
32	45℃	-15℃	**NO_2BF_4 (1.3)**	H_2S	85
33	45℃	-15℃	**NO_2BF_4 (1.8)**	H_2S	88
34	45℃	-15℃	**NO_2BF_4 (2.0)**	H_2S	88
35	45℃	-15℃	NO_2BF_4 (1.5)	H_2S	88[d]
36	45℃	-15℃	NO_2BF_4 (1.5)	H_2S	70[e]

a) Reaction was performed using benzyl bromide (0.4 mmol) and nitronium salts (0.6 mmol, 1.5 equiv) in 1.0 mL CH_3CN at the noted temperature (T_1) under an argon and then stirred for 30 min minutes, followed by the introduction of H_2S at the second noted temperature (T_2) at which point the resulting reaction mixture was stirred for another 20 minutes; b) isolated yield; c) S source (10.0 eq) was added. d) Reaction was performed in 1.5 mL CH_3CN. e) Reaction was performed in 2.0 mL CH_3CN.

3.2.2 The details for the optimal reaction conditions using butyronitrile as a substrate

As low yield of product **3af** was observed when butyronitrile was used to replace acetonitrile under the aboved-mentional optimal reaction conditions. Therefore, a reoptimization of the reaction conditions was performed (Table S2). After screening the various reaction conditions, the reaction parameters listed in entry 3 (Table S2) were selected as the slightly adjusted reaction conditions for further investigation.

Table S2 The details for the optimal reaction conditions using butyronitrile[a]

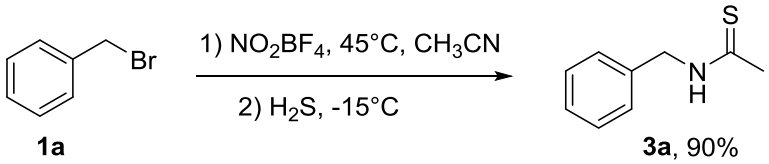


3a **3af**

Entry	Solvent (1 mL)	T_1	T_2	Nitronium salts (eq.)	Butyronitrile	Yield (%)[b]
1	$CH_3CH_2CH_2CN$	45℃	-15℃	NO_2BF_4 (2.0)	28.7 eq.	34
2	CH_3NO_2	**r.t.**	-15℃	NO_2BF_4 (2.0)	5.0 eq.	44
3	CH_3NO_2	**45℃**	-15℃	NO_2BF_4 (2.0)	5.0 eq.	57
4	CH_3NO_2	**60℃**	-15℃	NO_2BF_4 (2.0)	5.0 eq.	22
5	CH_3NO_2	**90℃**	-15℃	NO_2BF_4 (2.0)	5.0 eq.	trace
6	CH_3NO_2	45℃	**-35℃**	NO_2BF_4 (2.0)	5.0 eq.	39
7	CH_3NO_2	45℃	**0℃**	NO_2BF_4 (2.0)	5.0 eq.	50
8	CH_3NO_2	45℃	-15℃	NO_2BF_4 (2.0)	**2.0 eq.**	30
9	CH_3NO_2	45℃	-15℃	NO_2BF_4 (2.0)	**10.0 eq.**	54
10	CH_3NO_2[c]	45℃	-15℃	NO_2BF_4 (2.0)	**14.4 eq**	56

a) Reaction was performed using benzyl bromide (0.4 mmol) and nitronium salts (0.6 mmol, 1.5 equiv) in 1.0 mL CH_3CN at the noted temperature (T_1) under an argon and then stirred for 30 min minutes, followed by the introduction of H_2S at the second noted temperature (T_2) at which point the resulting reaction mixture was stirred for another 20 minutes; b) isolated yield; c) 0.5 mL CH_3NO_2 was used.

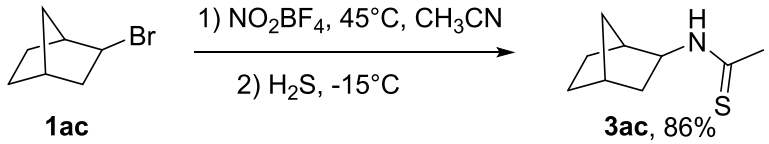
3.3 Synthesis of products 3a、3ac and 3af on 1g-scale



1a **3a**, 90%

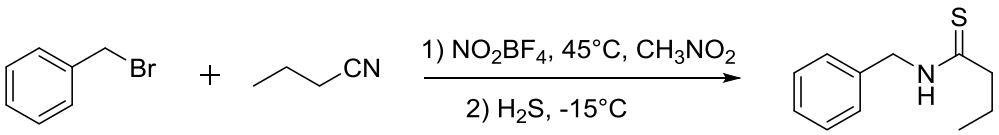
In an argon-filled glove box, to a 50 mL over-dried round bottom vessel equipped with a magnetic stir-bar were sequentially added NO_2BF_4 (8.78 mmol, 1.17 g) and acetonitrile (15.0 mL). After removal from the glove box, the rection vessel was placed in a preheated oil bath at 45 ^oC, and

benzyl bromide (5.85 mmol, 1 g) was then added under an argon atmosphere. After stirred for 30 min, the reaction mixture was purged with continuous H_2S for 1 min (**Caution! The process must be run in an efficient fume hood with appropriate personal protection**.) at -15 °C and stirred for 20 min at -15 °C. The mixture was then filtered with celite using ethyl acetate as the eluent, and the filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **3a** (870.0 mg, 90%).



1ac **3ac**, 86%

In an argon-filled glove box, to a 50 mL over-dried round bottom vessel equipped with a magnetic stir-bar were sequentially added NO_2BF_4 (8.57 mmol, 1.14 g) and acetonitrile (15.0 mL). After removal from the glove box, the rection vessel was placed in a preheated oil bath at 45 °C, and *exo*-2-bromonorbornane (5.71 mmol, 1 g) was then added under an argon atmosphere. After stirred for 30 min, the reaction mixture was purged with continuous H_2S for 1 min (**Caution! The process must be run in an efficient fume hood with appropriate personal protection.**) at -15 °C and stirred for 20 min at -15 °C. The mixture was then filtered with celite using ethyl acetate as the eluent, and the filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **3ac** (836.4 mg, 86%).



1a **2af** **3af**, 61%

In an argon-filled glove box, to a 50 mL over-dried round bottom vessel equipped with a magnetic stir-bar were sequentially added NO_2BF_4 (8.78 mmol, 1.17 g), butyronitrile (29.3 mmol, 2.02 g) and CH_3NO_2 (15.0 mL). After removal from the glove box, the rection vessel was placed in a preheated oil bath at 45 °C, and benzyl bromide (5.85 mmol, 1 g) was then added under an argon atmosphere. After stirred for 30 min, the reaction mixture was purged with continuous H_2S for 1 min (**Caution! The process must be run in an efficient fume hood with appropriate personal protection.**) at -15 °C and stirred for 20 min at -15 °C. The mixture was then filtered with celite

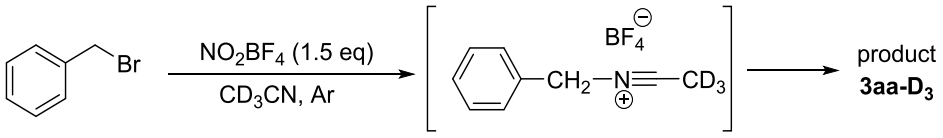
using ethyl acetate as the eluent, and the filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **3af** (684.2 mg, 61%).

3.4 Some control experiments

3.4.1 The NMR experiments in situ

The general procedure is as follows:

In an argon-filled glove box, to a dry NMR tube were sequentially added NO_2BF_4 (0.3 mmol, 39.8 mg), CD_3CN (0.5 mL) and benzyl bromide (0.2 mmol, 34.2 mg) at room temperature and the NMR tube was swayed at the same temperature (Scheme S1). The NMR spectra were recorded during consecutive 2 h.



Scheme S1 NMR experiments *in situ*

3.4.1.1 ^{1}H NMR spectra in situ

The representative ^{1}H NMR spectra in situ at different reaction time was showed in Figure S1.

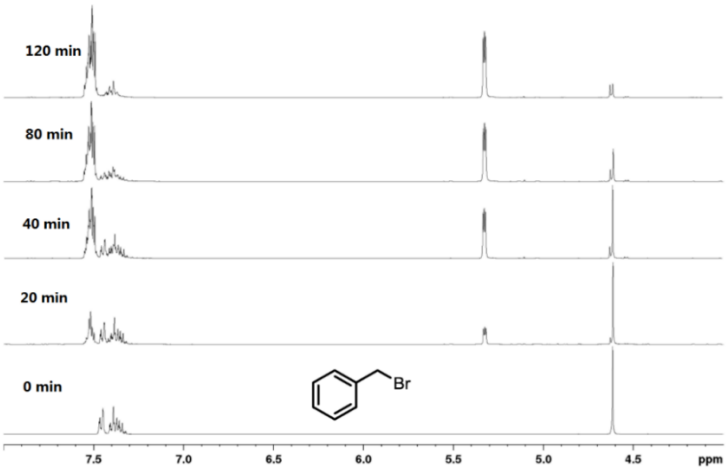


Figure S1 The ^{1}HNMR spectra of reaction mixture in CD_3CN.

3.4.1.2 ^{13}CNMR spectra of reaction intermediate

When the model reaction was performed in CD_3CN for 2 h, the ^{13}C NMR spectra of the reaction system were recorded (Figure S2). The corresponding data are listed: ^{13}C NMR (100 MHz, CD_3CN): δ 134.3 (s), 130.5 (s), 129.9 (s), 129.4 (s), 110.4 (t, J = 45.0 Hz), 49.8 (t, J = 6.0 Hz), 4.04 (sep, J = 22.0 Hz).

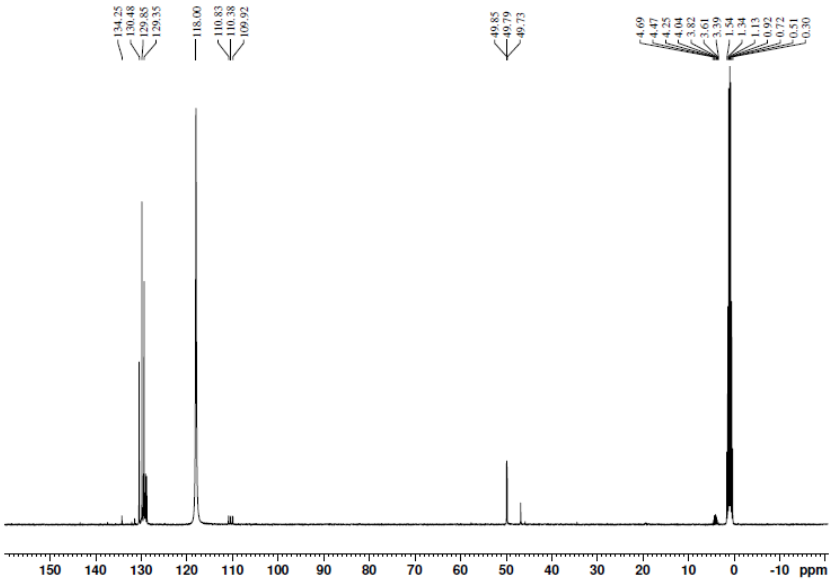
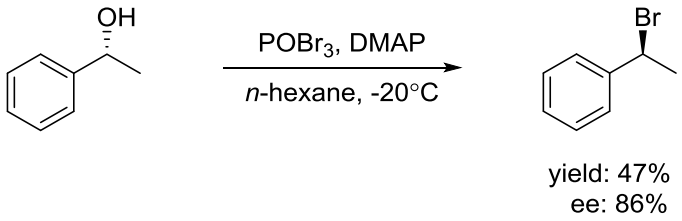


Figure S2 The ^{13}C NMR spectra of reaction intermediate.

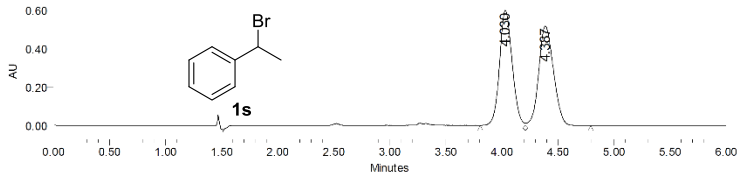
3.4.2 Carbocation intermediate experiment

(*S*)-(1-Bromoethyl)benzene were prepared according to the literature[4][7].



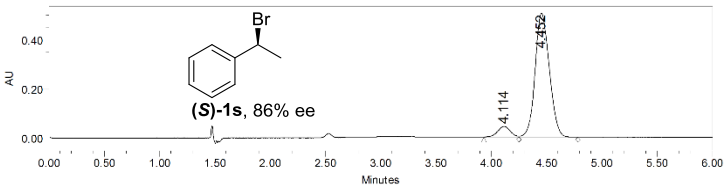
To a solution of (*R*)-1-phenylethan-1-ol (10 mmol, 1.22 g) in dry *n*-hexane (30 mL) was added DMAP (20 mmol, 2.44 g) at -20 ℃. A solution of phosphorous oxybromide (7 mmol, 2.0 g) in dry hexane (20 mL) was then added dropwise at -20 ℃. After 30 min, the reaction mixture was slowly poured into 100 mL ice-water. The organic phase was washed with water (30 mL × 3) and saturated aqueous solution Na_2CO_3 (30 mL × 3), dried over Na_2SO_4 and concentrated to afford the (*S*)-(1-bromoethyl)benzene as colourless oil, which was directly used for next step without further

purification (870 mg, 47%, 86% ee). $[\alpha]_D^{27.5}$: -31.3° (c = 1, $CHCl_3$). Enantiomeric excess was determined by UPC[2] (Chiralpak IG-3 column, CO_2/Methanol = 99.9/0.1, flow rate: 0.5 mL/min, 40 °C, λ = 220 nm), t_R = 4.030 min (*R*)-isomer, 4.387 min (*S*)-isomer (Figure S3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2 H), 7.37-7.26 (m, 3 H), 5.22 (q, *J* = 6.8 Hz, 1 H), 2.06 (d, *J* = 6.8 Hz, 3 H).



peak information:

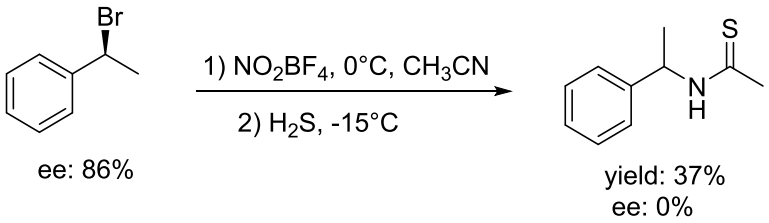
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.030	4663294	49.86	596751
2	4.387	4689114	50.14	515952



peak information:

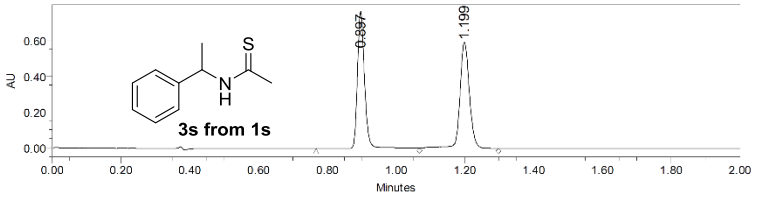
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.114	337272	6.95	43140
2	4.452	4518577	93.05	505522

Figure S3 The UPC spectra of bromide **1s** and chiral bromide (*S*)-**1s**.



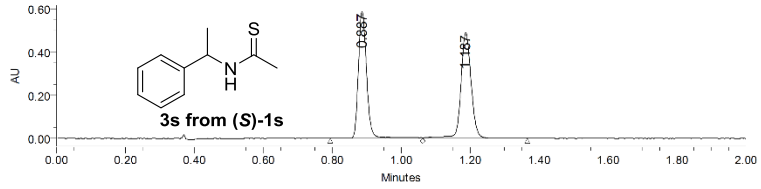
In an argon-filled glove box, to a 10 mL over-dried reaction tube equipped with a magnetic stir-bar were sequentially added NO_2BF_4 (0.6 mmol, 79.7 mg) and acetonitrile (1.0 mL). After removal from the glove box, the rection tube was placed in an ice water bath, and the synthetic chiral (*S*)-(1-bromoethyl)benzene (0.4 mmol, 74.0 mg, 86% ee) was then added under an argon atmosphere. After stirred for 30 min, the reaction mixture was purged with continuous H_2S for 1 min (**Caution！The process must be run in an efficient fume hood with appropriate personal protection.**) at -15 ℃ and stirred for 20 min at -15 ℃. The mixture was then filtered with celite using ethyl acetate as the eluent, and the filtrate was concentrated in vacuo. The crude product was

purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the racemic product **3s** (26.9 mg, 37%, 0% ee). Enantiomeric excess was determined by UPC^2 (Chiralpak AD-3 column, CO_2/Methanol = 90/10, flow rate: 2.0 mL/min, 40 ^oC, λ = 265 nm), t_R = 0.897 min, 1.199 min (Figure S4).



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	0.897	1109722	49.26	764797
2	1.199	1143206	50.74	592836



peak information:

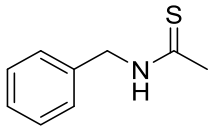
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	0.887	983679	49.34	588755
2	1.187	1009813	50.66	489783

Figure S4 The spectra of product **3s** derived from two different starting materials.

3.5 Characterization data of products

A pair of thioamide isomers were observed in the NMR spectrum due to the atropisomer[8][9] in some cases, and the NMR data of the major isomer was provided.

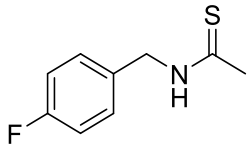
***N*-Benzylethanethioamide (3a)**[10]



Prepared according to the general procedure A; 58.2 mg, 88% yield. White crystal, m.p. = 66.6-67.8 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 5 H), 4.80 (d, J = 5.2 Hz, 2 H), 2.57 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.0, 136.2, 129.1, 128.5, 128.3, 50.8, 34.3. **MS** (EI) *m/z* (%): 165 (52), 132 (21), 105 (32), 91 (100). **IR** (KBr plate): 3220, 3069, 2923, 1551, 1393, 1341, 1165, 1071, 940, 694 cm^{-1}.

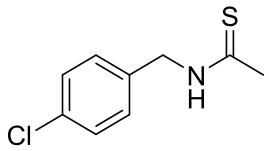
***N*-(4-Fluorobenzyl)ethanethioamide (3b)**



Prepared according to the general procedure A; 56.5 mg, 77% yield; White crystal, m.p. = 67.1-68.6 ^{o}C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1 H), 7.31-7.28 (m, 2 H), 7.03 (t, J = 8.4 Hz, 2 H), 4.77 (d, J = 5.2 Hz, 2 H), 2.55 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.1, 162.6 (d, J = 246.0 Hz), 132.0 (d, J = 3.0 Hz), 130.2 (d, J = 8.0 Hz), 115.9 (d, J = 21.0 Hz), 49.8, 34.2. **HRMS** (ESI) *m/z* calculated for $C_9H_{11}FNS$ $[M+H]^+$ 184.0591, found 184.0598. **MS** (EI) *m/z* (%):184 (4), 183 (37), 124 (19), 109 (100), 59 (17). **IR** (KBr plate): 3224, 3070, 1555, 1509, 1227, 1168, 1079, 827, 729 cm^{-1}.

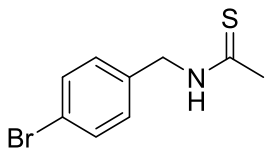
***N*-(4-Chlorobenzyl)ethanethioamide (3c)**



Prepared according to the general procedure A; 57.0 mg, 71 % yield. Yellow crystal, m.p. = 69.3-70.6 ^{o}C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (s, 1 H), 7.34-7.32 (m, 2 H), 7.27 (d, J = 8.4 Hz, 2 H), 4.80 (d, J = 5.4 Hz, 2 H), 2.58 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.4, 134.7, 134.2, 129.8, 129.2, 49.8, 34.3. **HRMS** (ESI) *m/z* calculated for $C_9H_{11}ClNS$ $[M+H]^+$ 200.0295 and 202.0266, found 200.0293 and 202.0262, respectively. **MS** (EI) *m/z* (%): 201 (16), 199 (40), 142 (8), 140 (28), 127 (33), 125 (100), 89 (26). **IR** (KBr plate): 3227, 3065, 2927, 1596, 1376, 1336, 1169, 1117, 1092, 927, 814, 695 cm^{-1}.

***N*-(4-Bromobenzyl)ethanethioamide (3d)**

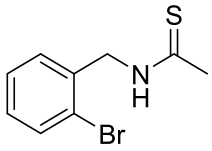


Prepared according to the general procedure A; 79.6 mg, 82% yield. White crystal, m.p. = 85.2-86.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1 H), 7.49- 7.45 (m, 2 H), 7.20 (d, J = 8.4 Hz, 2 H), 4.77

(d, J = 5.2 Hz, 2 H), 2.57 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.4, 135.2, 132.1, 130.1, 122.2, 49.8, 34.2. **HRMS** (ESI) *m/z* calculated for $C_9H_{11}BrNS$ $[M+H]^+$ 243.9790 and 245.9770, found 243.9801 and 245.9779, respectively. **MS** (EI) *m/z* (%): 245 (85), 243 (81), 186 (25), 184 (30), 171 (94), 169 (100). **IR** (KBr plate): 3216, 3044, 2924, 1536, 1487, 1383, 1332, 1167, 1104, 1072, 1012, 798 cm^{-1}.

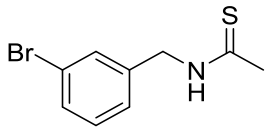
***N*-(2-Bromobenzyl)ethanethioamide (3e)**



Prepared according to the general procedure A; 57.5 mg, 59% yield. Yellow crystal, m.p. = 56.1-57.7 ^oC.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (s, 1 H), 7.57 (dd, J = 1.2 Hz, J = 7.8 Hz, 1 H), 7.44 (dd, J = 1.8 Hz, J = 7.8 Hz, 1 H), 7.29 (td, J = 1.2 Hz, J = 7.2 Hz, 1 H), 7.19 (td, J = 1.8 Hz, J = 7.8 Hz, 1 H), 4.91 (d, J =5.4 Hz, 2 H), 2.56 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.2, 135.4, 133.1, 131.4, 130.0, 127.9, 124.2, 50.4, 34.2. **HRMS** (ESI) *m/z* calculated for $C_9H_{11}BrNS$ $[M+H]^+$ 243.9790 and 245.9770, found 243.9790 and 245.9765, respectively. **MS** (EI) *m/z* (%): 245 (1), 243 (1), 171 (8), 169 (8), 165 (10), 164 (100). **IR** (KBr plate): 3219, 3051, 2925, 1532, 1386, 1334, 1172, 1121, 1076, 1027, 927, 752 cm^{-1}.

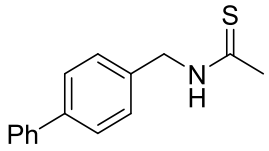
***N*-(3-Bromobenzyl)ethanethioamide (3f)**



Prepared according to the general procedure A; 49.1 mg, 50% yield. Yellow crystal, m.p. = 86.9-87.6 ^oC.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (s, 1 H), 7.39-7.37 (m, 2 H), 7.20-7.15 (m, 2 H), 4.73 (d, J = 5.4 Hz, 2 H), 2.51 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.5, 138.4, 131.32, 131.29, 130.6, 127.0, 122.9, 49.7, 34.2. **HRMS** (ESI) *m/z* calculated for $C_9H_{11}BrNS$ $[M+H]^+$ 243.9790 and 245.9770, found 243.9788 and 245.9766, respectively. **MS** (EI) *m/z* (%): 245 (100), 243 (98), 212 (22), 210 (25), 186 (30), 184 (35), 171 (61), 169 (66). **IR** (KBr plate): 3217, 3050, 2925, 1571, 1385, 1327, 1169, 1093, 943, 683 cm^{-1}.

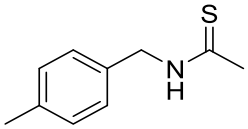
***N*-([1,1'-Biphenyl]-4-ylmethyl)ethanethioamide (3g)**



Prepared according to the general procedure A; 45.7 mg, 47% yield. Yellow crystal, m.p. = 104.6-106.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61-7.57 (m, 4 H), 7.47-7.41 (m, 4 H), 7.38-7.37 (m, 1 H), 4.87 (d, J = 5.4 Hz, 2 H), 2.62 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.1, 141.4, 140.6, 135.2, 129.03, 129.01, 127.9, 127.7, 127.2, 50.5, 34.4. **HRMS** (ESI) *m/z* calculated for $C_{15}H_{16}NS$ $[M+H]^+$ 242.0998, found 242.0997. **MS** (EI) *m/z* (%): 241 (35), 182 (5), 167 (100), 165 (30), 153 (8). **IR** (KBr plate): 3188, 3030, 2997, 2924, 1537, 1385, 1332, 1176, 1113, 1072, 1008, 760, 737, 698 cm^{-1}.

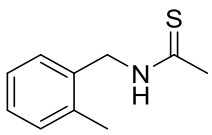
***N*-(4-Methylbenzyl)ethanethioamide (3h)**



Prepared according to the general procedure A; 55.3 mg, 77% yield. Yellow crystal, m.p. = 52.8-53.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 (s, 1 H), 7.21 (d, J = 7.8 Hz, 2 H), 7.16 (d, J = 7.8 Hz, 2 H), 4.74 (d, J = 5.4 Hz, 2 H), 2.55 (s, 3 H), 2.34 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 200.7, 138.1, 133.1, 129.7, 128.5, 50.5, 34.2, 21.2. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{14}NS$ $[M+H]^+$ 180.0841, found 180.0839. **MS** (EI) *m/z* (%): 179 (31), 120 (19), 105 (100), 91 (17). **IR** (KBr plate): 3220, 3049, 3023, 2922, 1535, 1385, 1333, 1166, 1113, 1071, 924, 808, 700 cm^{-1}.

***N*-(2-Methylbenzyl)ethanethioamide (3i)**

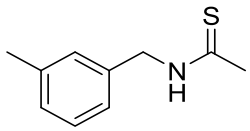


Prepared according to the general procedure A; 58.5 mg, 82% yield. Yellow crystal, m.p. = 57.3-58.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.18 (m, 5 H), 4.76 (d, J = 4.8 Hz, 2 H), 2.55 (s, 3 H), 2.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.6, 137.1, 134.1, 130.9, 129.6, 128.6, 126.5, 49.1, 34.1,

19.2. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{14}NS$ $[M+H]^+$ 180.0841, found 180.0850. **MS** (EI) *m/z* (%): 179 (83), 164 (9), 105 (100), 91 (18). **IR** (KBr plate): 3218, 3021, 2924, 1531, 1389, 1331, 1169, 1071, 924, 745 cm^{-1}.

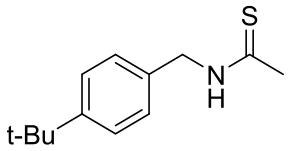
***N*-(3-Methylbenzyl)ethanethioamide (3j)**



Prepared according to the general procedure A; 51.5 mg, 72% yield. Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1 H), 7.27-7.24 (m, 1 H), 7.15-7.11 (m, 3 H), 4.76 (d, *J* = 5.2 Hz, 2 H), 2.57 (s, 3 H), 2.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.8, 138.9, 136.0, 129.2, 129.04, 128.95, 125.5, 50.8, 34.2, 21.5. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{14}NS$ $[M+H]^+$ 180.0841, found 180.0850. **MS** (EI) *m/z* (%): 179 (86), 146 (36), 120 (28), 105 (100), 91 (12). **IR** (KBr plate): 3220, 3026, 2921, 1534, 1491, 1331, 1168, 1072, 942, 693 cm^{-1}.

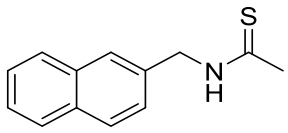
***N*-(4-(Tert-butyl)benzyl)ethanethioamide (3k)**



Prepared according to the general procedure A; 74.6 mg, 84% yield. White crystal, m.p. = 99.6-100.8 ºC.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 H z, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 4.76 (d, *J* = 4.8 Hz, 2 H), 2.56 (s, 3 H), 1.32 (s, 9 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 200.7, 151.5, 133.1, 128.4, 126.0, 50.5, 34.7, 34.2, 31.4. **HRMS** (ESI) *m/z* calculated for $C_{13}H_{20}NS$ $[M+H]^+$ 222.1311, found 222.1320. **MS** (EI) *m/z* (%): 221 (78), 162 (19), 147 (100), 132 (52), 117 (29). **IR** (KBr plate): 3217, 2962, 2868, 1536, 1388, 1333, 1166, 1109, 1071, 1019, 927, 690 cm^{-1}.

***N*-(Naphthalen-2-ylmethyl)ethanethioamide (3l)**

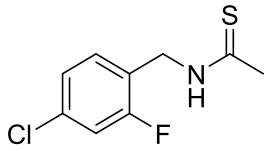


Prepared according to the general procedure A; 56.7 mg, 66% yield. Yellow crystal, m.p. = 97.6-98.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.81 (m, 3 H), 7.76 (s, 1 H), 7.51-7.48 (m, 2 H), 7.42 (dd, *J* =

1.6 Hz, *J* = 8.4 Hz, 1 H), 4.96 (d, *J* = 5.2 Hz, 2 H), 2.59 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 201.0, 133.5, 133.4, 133.1, 128.9, 127.9, 127.8, 127.4, 126.6, 126.4, 126.1, 50.8, 34.2. **HRMS** (ESI) *m/z* calculated for $C_{13}H_{14}NS$ $[M+H]^+$216.0841, found 216.0842. **MS** (EI) *m/z* (%): 215 (33), 182 (25), 156 (9), 141 (100), 127 (8). **IR** (KBr plate): 3219, 3051, 2965, 2923, 1531, 1392, 1362, 1323, 1167, 1125, 1074, 1019, 818, 741 cm^{-1}.

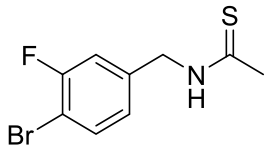
***N*-(4-Chloro-2-fluorobenzyl)ethanethioamide (3m)**



Prepared according to the general procedure A; 44.2 mg, 51% yield. Yellow crystal, m.p. = 58.0-59.3 ºC.

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.64 (s, 1 H), 7.35 (t, *J* = 8.4 Hz, 1 H), 7.10 (t, *J* = 7.8 Hz, 2 H), 4.84 (d, *J* = 5.4 Hz, 2 H), 2.55 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): *δ* 201.6, 160.9 (d, *J* = 247.5 Hz), 135.0 (d, *J* = 10.5 Hz), 131.8 (d, *J* = 4.5 Hz), 124.8 (d, *J* = 3.0 Hz), 121.9 (d, *J* = 15.0 Hz), 116.5 (d, *J* = 24.0 Hz), 43.6 (d, *J* = 1.5 Hz), 34.2. **HRMS** (ESI) *m/z* calculated for $C_9H_{10}ClFNS$ $[M+H]^+$ 218.0201 and 220.0172, found 218.0200 and 220.0170, respectively. **MS** (EI) *m/z* (%): 219 (15), 217 (39), 160 (11), 158 (36), 145 (22), 143 (100). **IR** (KBr plate): 3220, 3048, 2932, 1612, 1535, 1489, 1336, 1170, 1119, 1078, 931, 896, 687 cm^{-1}.

***N*-(4-Bromo-3-fluorobenzyl)ethanethioamide (3n)**

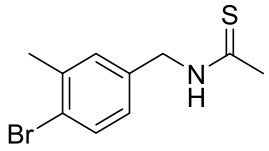


Prepared according to the general procedure A; 60.3 mg, 57% yield. Yellow crystal, m.p. = 106.1-107.3 ºC.

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.60 (s, 1 H), 7.51 (t, *J* = 7.8 Hz, 1 H), 7.09 (dd, *J* = 1.8 Hz, *J* = 9.0 Hz, 1 H), 7.00 (dd, *J* = 1.2 Hz, *J* = 8.4 Hz, 1 H), 4.80 (d, *J* = 5.4 Hz. 2 H), 2.58 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): *δ* 201.8, 159.2 (d, *J* = 246.0 Hz), 138.0 (d, *J* = 7.5 Hz), 134.0, 125.1 (d, *J* = 3.0 Hz), 116.3 (d, *J* = 22.5 Hz), 108.6 (d, *J* = 21.0 Hz), 49.2, 34.2. **HRMS** (ESI) *m/z* calculated for $C_9H_{10}BrFNS$ $[M+H]^+$ 261.9696 and 263.9675, found 261.9695 and 263.9674, respectively. **MS** (EI) *m/z* (%): 263 (93), 261 (100), 204 (29), 202 (42), 189 (73), 187 (78), 149 (46), 108 (68), 107

(66). **IR** (KBr plate): 3212, 3063, 3012, 2964, 1561, 1486, 1428, 1338, 1171, 1080, 1041, 817, 759, 704 cm^{-1}.

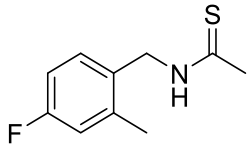
***N*-(4-Bromo-3-methylbenzyl)ethanethioamide (3o)**



Prepared according to the general procedure A; 46.8 mg, 45% yield. Yellow crystal, m.p. = 82.4-84.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (s, 1 H), 7.48 (d, J = 7.8 Hz, 1 H), 7.18 (d, J = 1.2 Hz, 1 H), 7.00 (dd, J = 1.8 Hz, J = 7.8 Hz, 1 H), 4.72 (d, J = 5.4 Hz, 2 H), 2.55 (s, 3 H), 2.37 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.1, 138.6, 135.4, 132.8, 130.8, 127.3, 124.6, 49.8, 34.2, 23.0. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{13}BrNS$ $[M+H]^+$ 257.9947 and 259.9926, found 257.9946 and 259.9924, respectively. **MS** (EI) *m/z* (%): 259 (80), 257 (80), 200 (20), 198 (24), 185 (90), 183 (100), 145 (50), 103 (56). **IR** (KBr plate): 3218, 3044, 3012, 2923, 1534, 1477, 1380, 1329, 1169, 1075, 1028, 941, 696 cm^{-1}.

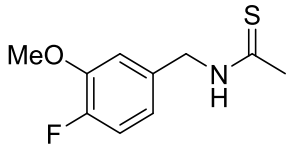
***N*-(4-Fluoro-2-methylbenzyl)ethanethioamide (3p)**



Prepared according to the general procedure A; 67.3 mg, 85% yield. White crystal, m.p. = 67.1-68.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (s, 1 H), 7.19 (dd, J = 6.0 Hz, J = 8.4 Hz, 1 H), 6.90-6.83 (m, 2 H), 4.69 (d, J = 4.8 Hz, 2 H), 2.52 (s, 3 H), 2.29 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 200.7, 162.5 (d, J = 244.5), 139.5 (d, J = 7.5 Hz), 131.1 (d, J = 9.0 Hz), 129.8 (d, J = 3.0 Hz), 117.5 (d, J = 21.0 Hz), 113.0 (d, J = 21.0 Hz), 48.2, 33.9, 19.3. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{13}FNS$ $[M+H]^+$ 198.0747, found 198.0746. **MS** (EI) *m/z* (%): 198 (6), 197 (48), 138 (10), 123 (100), 122 (57), 109 (11). **IR** (KBr plate): 3217, 3033, 2984, 2925, 1532, 1500, 1388, 1329, 1254, 1170, 1101, 1068, 1005, 961, 699 cm^{-1}.

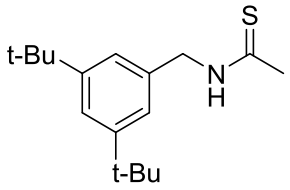
***N*-(4-Fluoro-3-methoxybenzyl)ethanethioamide (3q)**



Prepared according to the general procedure A; 44.6 mg, 52% yield. Yellow crystal, m.p. = 92.5-93.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.00 (dd, J = 8.4 Hz, J = 10.8 Hz, 1 H), 6.94 (dd, J = 1.8 Hz, J = 7.8 Hz, 1 H). 6.83-6.81 (m, 1 H), 4.73 (d, J = 5.4 Hz, 2 H), 3.84 (s. 3 H), 2.55 (s, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.0, 152.1 (d, J = 244.5 Hz), 147.8 (d, J = 12.0 Hz), 132.5 (d, J = 3.0 Hz), 120.8 (d, J = 7.5 Hz), 116.3 (d, J = 18.0 Hz), 113.8, 56.3, 50.2, 34.1. **HRMS** (ESI) *m/z* calculated for $C_{12}H_{13}FNOS$ $[M+H]^+$ 214.0696, found 214.0694. **MS** (EI) *m/z* (%): 213 (45), 154 (21), 139 (100), 125 (6). **IR** (KBr plate): 3243, 3066, 3008, 2982, 2950, 2926, 1611, 1520, 1465, 1418, 1383, 1337, 1282, 1118, 1090, 1028, 851, 694 cm^{-1}.

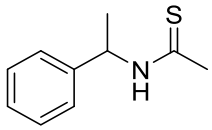
***N*-(3,5-Di-*tert*-butylbenzyl)ethanethioamide (3r)**



Prepared according to the general procedure A; 90.9 mg, 82% yield. White crystal, m.p. = 131.6-132.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 (s, 1 H), 7.42 (s, 1 H), 7.19 (d, J = 1.8 Hz, 2 H), 4.76 (d, J = 4.8 Hz, 2 H), 2.57 (s, 3 H), 1.34 (s, 18 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 200.4, 151.7, 135.2, 123.0, 122.5, 51.7, 35.0, 34.1, 31.5. **HRMS** (ESI) *m/z* calculated for $C_{17}H_{27}NSNa$ $[M+Na]^+$ 300.1756, found 300.1768. **MS** (EI) *m/z* (%): 278 (20), 277 (100), 262 (7), 203 (95), 187 (31), 57 (43). **IR** (KBr plate): 3238, 3055, 2964, 2866, 1599, 1545, 1390, 1363, 1172, 1077, 945, 712 cm^{-1}.

***N*-(1-Phenylethyl)ethanethioamide (3s)**[11]

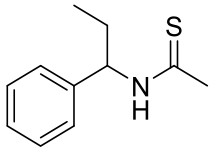


Prepared according to the general procedure A; 52.9 mg, 74% yield. Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (s, 1 H), 7.38-7.34 (m, 4 H), 7.32-7.28 (m, 1 H), 5.76-5.71

(m, 1 H), 2.53 (s, 3 H), 1.60 (d, J = 7.2 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 199.6, 141.3, 128.9, 128.0, 126.7, 54.9, 34.5, 20.0. **MS** (EI) *m/z* (%): 179 (44), 146 (61), 120 (11), 105 (100), 104 (58), 77 (28). **IR** (KBr plate): 3219. 3030, 2974, 1531, 1453, 1385, 1217, 1181, 1091, 761, 698 cm^{-1}.

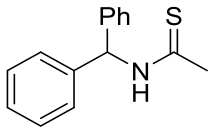
***N*-(1-Phenylpropyl)ethanethioamide (3t)**



Prepared according to the general procedure A; 56.0 mg, 72% yield. Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 (s, 1 H), 7.28-7.24 (m, 4 H), 7.24-7.19 (m, 1 H), 5.42 (dd, J = 7.8 Hz, J = 15.6 Hz, 1 H), 2.44 (s, 3 H), 1.99-1.93 (m, 1 H), 1.86-1.78 (m, 1 H), 0.83 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 199.9, 140.1, 128.8, 127.8, 127.2, 61.1, 34.4, 27.9, 10.7. **HRMS** (ESI) *m/z* calculated for $C_{11}H_{16}NS$ $[M+H]^+$ 194.0998, found 194.0997. **MS** (EI) *m/z* (%): 193 (22), 134 (5), 119 (41), 118 (100), 117 (61). **IR** (KBr plate): 3220, 3030, 2966, 2933, 1532, 1457, 1386, 1207, 1100, 1052, 752, 699 cm^{-1}.

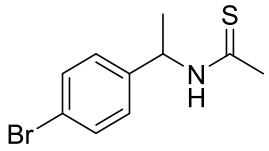
***N*-Benzhydrylethanethioamide (3u)**



Prepared according to the general procedure A; 44.5 mg, 46% yield. White crystal, m.p. = 127.0-128.2 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1 H), 7.37-7.27 (m, 6 H), 7.24-7.21 (m, 4 H), 6.84 (d, J = 8.0 Hz, 1 H), 2.56 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.4, 139.9, 128.9,127.9, 127.8, 63.1, 34.3. **HRMS** (ESI) *m/z* calculated for $C_{15}H_{15}NSNa$ $[M+Na]^+$ 264.0817, found 264.0817. **MS** (EI) *m/z* (%): 241 (40), 208 (32), 167 (100), 164 (9), 152 (33). **IR** (KBr plate): 3219, 3060, 2915, 1520, 1376, 1173, 1084, 1061, 744, 698 cm^{-1}.

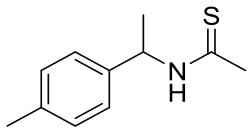
***N*-(1-(4-Bromophenyl)ethyl)ethanethioamide (3v)**



Prepared according to the general procedure A; 81.3 mg, 79% yield. Yellow crystal, m.p. = 80.0-80.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.20 (d, J = 8.4 Hz, 2 H), 5.67-5.60 (m, 1 H), 2.49 (s, 3 H), 1.54 (d, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.9, 140.3, 131.8, 128.3, 121.6, 54.3, 34.2, 20.3. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{13}BrNS$ $[M+H]^+$ 257.9947 and 259.9926, found 257.9946 and 269.9925, respectively. **MS** (EI) *m/z* (%): 259 (37), 257 (33), 185 (42), 184 (34), 183 (43), 182 (32), 104 (100). **IR** (KBr plate): 3217, 3028, 2975, 2928, 1530, 1489, 1455, 1383, 1218, 1094, 1073, 1009, 826, 728 cm^{-1}.

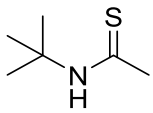
***N*-(1-(*p*-Tolyl)ethyl)ethanethioamide (3w)**



Prepared according to the general procedure A; 34.5 mg, 45% yield. Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1 H), 7.25 (d, J = 7.6 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 5.74-5.66 (m, 1 H), 2.54 (s, 3 H), 2.34 (s, 3 H), 1.59 (d, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 138.4, 137.8, 129.6, 126.7, 54.7, 34.7, 21.2, 19.9. **HRMS** (ESI) *m/z* calculated for $C_{11}H_{16}NS$ $[M+H]^+$194.0998, found 194.0997. **MS** (EI) *m/z* (%): 193 (26), 160 (27), 134 (4), 119 (100). **IR** (KBr plate):3219, 3026, 2974, 2924, 1531, 1453, 1384, 1179, 1094, 1020, 817, 719 cm^{-1}.

***N*-(tert-Butyl)ethanethioamide (3x)** [11]

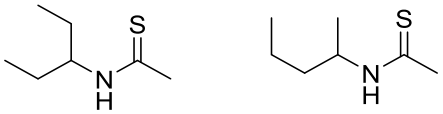


Prepared according to the general procedure A; 11.9 mg, 23% yield. White crystal, m.p. = 81.8-83.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.02 (s, 1 H), 2.51 (s, 3 H), 1.55 (s, 9 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 199.9, 56.0, 37.6, 27.8. **MS** (EI) *m/z* (%): 131 (100). **IR** (KBr plate): 3231, 3046, 2966,

2928, 1540, 1363, 1140, 1021, 738, 703 cm^{-1}.

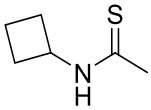
***N*-(Pentan-3-yl)ethanethioamide and *N*-(pentan-2-yl)ethanethioamide (3y)**



Prepared according to the general procedure A; 25.0 mg, 43% yield. Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 1.5 H), 4.62-4.51 (m, 0.6 H), 4.48-4.39 (m, 1 H), 2.55 (s, 3 H), 2.52 (s, 1.8 H), 1.71-1.61 (m, 2.9 H), 1.60-1.44 (m, 3.6 H), 1.40-1.31 (m, 1.5 H), 1.21 (d, J = 6.4 Hz, 2 H), 0.92 (t, J = 7.6 Hz, 8 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.4, 199.5, 58.5, 51.7, 38.1, 34.8, 28.0, 26.2, 19.4, 19.3, 14.0, 10.2. **HRMS** (ESI) *m/z* calculated for $C_7H_{16}NS$ $[M+H]^+$ 146.0998, found 146.0998; **MS** (EI) *m/z* (%): 145 (100). **IR** (KBr plate): 3224, 3044, 2965, 2933, 2876, 1655, 1539, 1461, 1391, 1193, 1152, 1111, 1018, 792, 709 cm^{-1}.

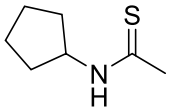
***N*-Cyclobutylethanethioamide (3z)** [11]



Prepared according to the general procedure A. 23.4 mg, 45% yield; Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (s, 1 H), 4.81-4.75 (m, 1 H), 2.51 (s, 3 H), 2.50-2.45 (m, 2 H), 1.98-1.91 (m, 2 H), 1.82-1.79 (m, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 199.7, 50.7, 34.3, 30.0, 15.7. **HRMS** (ESI) *m/z* calculated for $C_6H_{12}NS$ $[M+H]^+$ 130.0685, found 130.0685. **MS** (EI) *m/z* (%): 129 (38), 100 (100), 114 (4). **IR** (KBr plate): 3221, 3035, 2983, 2943, 1654, 1536, 1389, 1338, 1121, 1001, 719, 655 cm^{-1}.

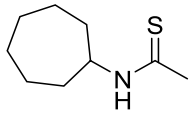
***N*-Cyclopentylethanethioamide (3aa)**



Prepared according to the general procedure A; 36.1 mg, 63% yield. Yellow crystal, m.p. = 32.0-33.0 ^oC.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (s, 1 H), 4.71-4.65 (m, 1 H), 2.50 (s, 3 H), 2.13-2.08 (m, 2 H), 1.72-1.66 (m, 2 H), 1.65-1.60 (m, 2 H), 1.51-1.46 (m, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 199.8, 57.7, 34.5, 32.2, 24.1. **HRMS** (ESI) *m/z* calculated for $C_7H_{13}NSNa$ $[M+Na]^+$ 166.0661, found 166.0660. **MS** (EI) *m/z* (%): 143 (100), 84 (9), 76 (68), 69 (7), 59 (24). **IR** (KBr plate): 3225, 3036, 2960, 2869, 1536, 1456. 1390, 1346, 1143, 1095, 723 cm^{-1}.

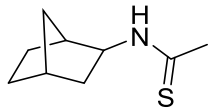
***N*-Cycloheptylethanethioamide (3ab)**



Prepared according to the general procedure A; 31.1 mg, 45% yield. Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (s, 1 H), 4.44-4.41 (m, 1 H), 2.48 (s, 3 H), 2.03-1.99 (m, 2 H), 1.63-1.57 (m. 4 H), 1.52-1.47 (m, 6 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 198.4, 56.9, 34.5, 33.6, 28.0, 24.2. **HRMS** (ESI) *m/z* calculated for $C_9H_{18}NS$ $[M+H]^+$172.1154, found 172.1154. **MS** (EI) *m/z* (%): 171 (54), 138 (100), 112 (56). **IR** (KBr plate): 3221, 3036, 2928, 2855, 1534, 1461, 1391, 1368, 1155, 1069, 715 cm^{-1}.

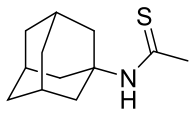
***N*-((1*S**, 4*R**)-Bicyclo[2.2.1]heptan-2-yl)ethanethioamide (3ac)**



Prepared according to the general procedure A; 51.9 mg, 77% yield. White crystal, m.p. = 101.1-102.1 ^oC.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (s, 1 H), 4.14 (dd, J = 7.8 Hz, J = 10.8 Hz, 1 H), 2.49 (s, 3 H), 2.37 (d, J = 3.6 Hz, 1 H), 2.31 (s, 1 H), 1.90-1.86 (m, 1 H), 1.54-1.44 (m, 2 H), 1.34-1.23 (m, 4 H), 1.16-1.12 (m, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 199.2, 59.4, 41.6, 39.8, 36.2, 35.9, 34.4, 28.1, 26.5. **HRMS** (ESI) *m/z* calculated for $C_9H_{16}NS$ $[M+H]^+$170.0998, found 170.0996. **MS** (EI) *m/z* (%): 169 (100), 136 (38), 113 (67), 110 (11), 95 (30). **IR** (KBr plate): 3214, 3039, 2956, 2873, 1537, 1454, 1370, 1347, 1304, 1137, 1096, 718 cm^{-1}.

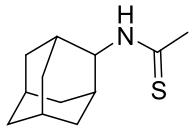
***N*-((3*S**, 5*S**, 7*S**)-Adamantan-1-yl)ethanethioamide (3ad)** [11]



Prepared according to the general procedure A; 55.2 mg, 66% yield. White crystal, m.p. = 192.6-193.5^oC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 1 H), 2.49 (s, 3 H), 2.28 (d, J = 1.6 Hz, 6 H), 2.10 (s, 3 H), 1.68 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.3, 56.7, 40.1, 37.8, 36.3, 29.5. **MS** (EI) *m/z* (%): 209 (55), 208 (64), 194 (8), 150 (3), 135 (100). **IR** (KBr plate): 3308, 2908, 2895, 1525, 1406, 1393, 1090, 670, 639 cm^{-1}.

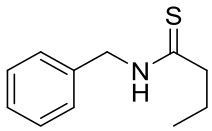
***N*-(1*R**, 3*R**, 5*R**, 7*R**)-Adamantan-2-yl)ethanethioamide (3ae)**



Prepared according to the general procedure A; 64.3 mg, 77% yield. White crystal, m.p. = 93.2-94.5 ^{o}C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (s, 1 H), 4.49 (t, J = 4.2 Hz, 1 H), 2.54 (s, 3 H), 2.10 (d, J = 1.8 Hz, 2 H), 1.85 (d, J =2.4 Hz, 2 H), 1.81 (s, 4 H), 1.75-1.72 (m, 4 H), 1.68-1.66 (m, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 199.4, 59.6, 37.3, 36.8, 34.9, 32.2, 30.5, 27.0. **HRMS** (ESI) *m/z* calculated for $C_{12}H_{20}NS$ $[M+H]^+$ 210.1311, found 210.1309. **MS** (EI) *m/z* (%): 209 (100), 176 (86), 150 (64), 135 (78). **IR** (KBr plate): 3300, 2910, 2855, 1529, 1456, 1387, 1102, 1065, 1035, 820, 729, 665 cm^{-1}.

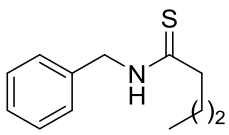
***N*-Benzylbutanethioamide (3af)**



Prepared according to the general procedure B; 44.2 mg, 57% yield. Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (s, 1 H), 7.38-7.35 (m, 2 H), 7.33-7.31 (m, 3 H), 4.82 (d, J = 4.8 Hz, 2 H), 2.64 (t, J = 7.2 Hz, 2 H), 1.85-1.79 (m, 2 H), 0.95 (t. J = 7.8 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 205.6, 136.3, 129.1, 128.4, 128.2, 50.4, 49.1, 22.9, 13.5. **HRMS** (ESI) *m/z* calculated for $C_{11}H_{16}NS$ $[M+H]^+$ 194.0998, found 194.0997. **MS** (EI) *m/z* (%):193 (100), 149 (53), 123 (59), 106 (59); **IR** (KBr plate): 3226, 3032, 2962, 2931, 2872, 1532, 1454, 1404, 1167, 1075, 1027, 738, 697 cm^{-1}.

***N*-Benzylpentanethioamide (3ag)**

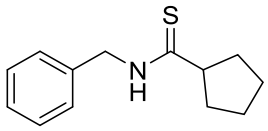


Prepared according to the general procedure B; 42.5 mg, 51% yield; Yellow crystal, m.p. = 50.9-52.4 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.31 (m, 5 H), 4.82 (d, J = 4.8 Hz, 2 H), 2.67 (t, J = 8.0 Hz, 2 H), 1.81-1.73 (m, 2 H), 1.41-1.32 (m, 2 H), 0.92 (t, J = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz,

$CDCl_3$): δ 205.9, 136.3 129.1, 128.4, 128.3, 50.5, 47.1, 31.6, 22.2, 13.9. **HRMS** (ESI) *m/z* calculated for $C_{12}H_{18}NS$ $[M+H]^+$ 208.1154, found 208.1154. **MS** (EI) *m/z* (%): 207 (81), 165 (73), 149 (48), 106 (100). **IR** (KBr plate): 3219, 3056, 2957, 2930, 2871, 1534, 1457, 1319, 1165, 1076, 733, 696 cm^{-1}.

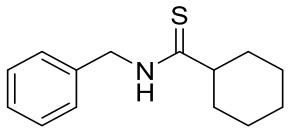
***N*-Benzylcyclopentanecarbothioamide (3ah)**



Prepared according to the general procedure B; 44.4 mg, 51% yield. Yellow crystal, m.p. = 38.6-39.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.31 (m, 5 H), 4.84 (d, J = 5.2 Hz, 2 H), 2.94-2.86 (m, 1 H), 2.00-1.93 (m, 4 H), 1.87-1.77 (m, 2 H), 1.66-1.55 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 210.2, 136.5, 129.1, 128.4, 128.2, 55.3, 50.3, 34.2, 25.9. **HRMS** (ESI) *m/z* calculated for $C_{13}H_{18}NS$ $[M+H]^+$ 220.1154, found 220.1153. **MS** (EI) *m/z* (%): 219 (100), 149 (30), 113 (19), 106 (60). **IR** (KBr plate): 3237, 3031, 2955, 2867, 1527, 1451, 1402, 1321, 1131, 1076, 1028, 732, 696, 617 cm^{-1}.

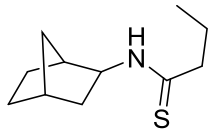
***N*-Benzylcyclohexanecarbothioamide (3ai)**



Prepared according to the general procedure B; 36.3 mg, 39% yield. Yellow crystal, m.p. = 54.4-55.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.30 (m, 5 H), 4.83 (d, J = 5.2 Hz, 2 H), 2.55-2.48 (m, 1 H), 1.93 -1.90 (m, 2 H), 1.84-1.80 (m, 2 H), 1.71-1.66 (m, 1 H), 1.63-1.56 (m, 2 H), 1.35-1.19 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 210.4, 136.5, 129.1, 128.4, 128.3, 55.2, 50.1, 33.1, 26.1, 25.7. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{20}NS$ $[M+H]^+$ 234.1311, found 234.1309; **MS** (EI) *m/z* (%): 233 (100), 178 (66), 149 (57), 127 (19),106 (58). **IR** (KBr plate): 3233, 3031, 2929, 2853, 1525, 1451, 1416, 1107, 1028, 697, 617 cm^{-1}.

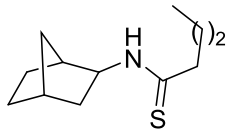
***N*-((1*R**, 4*S**)-Bicyclo[2.2.1]heptan-2-yl)butanethioamide (3aj)**



Prepared according to the general procedure B; 59.2 mg, 75% yield. Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (s, 1 H), 4.18-4.15 (m, 1 H), 2.55 (t, J = 7.8 Hz, 2 H), 2.37 (d, J = 3.6 Hz, 1 H), 2.31 (s, 1 H), 1.91-1.87 (m, 1 H), 1.77-1.74 (m, 2 H), 1.53-1.46 (m, 2 H), 1.33-1.23 (m, 4 H), 1.16-1.13 (m, 1 H), 0.91 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.8, 59.0, 49.2, 41.6, 40.0, 36.2, 35.9, 28.1, 26.5, 22.9, 13.3. **HRMS** (ESI) *m/z* calculated for $C_{11}H_{20}NS$ $[M+H]^+$ 198.1311, found 198.1300. **MS** (EI) *m/z* (%): 198 (18), 197 (100), 196 (31), 154 (10), 141 (52), 110 (11), 95 (28). **IR** (KBr plate):3242. 3027, 2958, 2872, 1525, 1454, 1410, 1348, 1193, 1138, 1100, 1076, 752, 702 cm^{-1}.

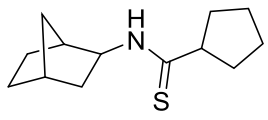
***N*-((1*R**,4*S**)-Bicyclo[2.2.1]heptan-2-yl)pentanethioamide (3ak)**



Prepared according to the general procedure B; 60.9 mg, 72% yield. Colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (s, 1 H), 4.17-4.14 (m, 1 H), 2.58 (t, J = 7.8 Hz, 2 H), 2.37 (d, J = 4.2 Hz, 1 H), 2.31 (s, 1 H), 1.90-1.86 (m, 1 H), 1.72-1.67 (m, 2 H), 1.55-1.43 (m, 2 H), 1.34-1.23 (m, 6 H), 1.16-1.12 (m, 1 H), 0.89 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.0, 59.0, 47.2, 41.6, 39.9, 36.2, 35.9, 31.7, 28.1, 26.5, 22.1, 13.9. **HRMS** (ESI) *m/z* calculated for $C_{12}H_{22}NS$ $[M+H]^+$ 212.1467, found 212.1456. **MS** (EI) *m/z* (%): 212 (21), 211 (100), 136 (86), 116 (5), 110 (12), 95 (52). **IR** (KBr plate): 3241, 3025, 2956, 2872, 1525, 1455, 1409, 1349, 1138, 1081, 1045, 739, 706 cm^{-1}.

***N*-((1*R**, 4*S**)-Bicyclo[2.2.1]heptan-2-yl)cyclopentanecarbothioamide (3al)**

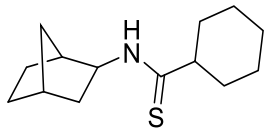


Prepared according to the general procedure B; 64.3 mg, 72% yield. Yellow crystal, m.p. = 92.2-93.9 ^{o}C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.07 (s, 1 H), 4.24-4.21 (m, 1 H), 2.85-2.79 (m, 1 H), 2.39 (d, J =

4.2 Hz, 1 H), 2.34 (s, 1 H), 1.95-1.90 (m, 5 H), 1.83-1.78 (m, 2 H), 1.64-1.46 (m, 4 H), 1.33-1.26 (m, 4 H), 1.19-1.16 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.4, 58.8, 55.4, 41.7, 40.3, 36.3, 36.0, 34.2, 34.1, 28.2, 26.5, 25.9. **HRMS** (ESI) *m/z* calculated for $C_{13}H_{22}NS$ $[M+H]^+$ 224.1467, found 224.1453. **MS** (EI) *m/z* (%): 224 (19), 223 (100), 222 (31), 167 (53), 128 (4), 113 (12), 110 (24), 95 (51). **IR** (KBr plate): 3261, 2955, 2870, 1517, 1451, 1422, 1325, 1222, 1126, 1107, 703 cm^{-1}.

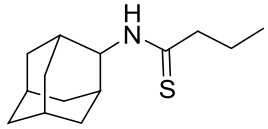
***N*-((1*R**, 4*S**)-Bicyclo[2.2.1]heptan-2-yl)cyclohexanecarbothioamide (3am)**



Prepared according to the general procedure B; 69.3 mg, 73% yield. Yellow crystal, m.p. = 95.5-97.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 1 H), 4.23-4.18 (m, 1 H), 2.45-2.33 (m, 3 H), 1.95-1.78 (m, 5 H), 1.69-1.67 (m, 1 H), 1.61-1.45 (m, 4 H), 1.33-1.14 (m, 8 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.6, 58.5, 55.1, 41.7, 40.2, 36.3, 36.0, 33.04, 32.95, 28.2, 26.5, 26.1, 25.7. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{24}NS$ $[M+H]^+$ 238.1624, found 238.1609. **MS** (EI) *m/z* (%): 238 (20), 237 (100), 236 (33), 181 (43), 110 (29), 95 (68). **IR** (KBr plate): 3202, 3021, 2930, 2869, 2854, 1524, 1452, 1412, 1340, 1291, 1195, 1128, 1102, 713 cm^{-1}.

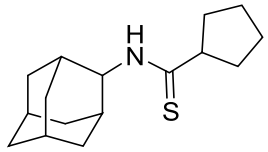
***N*-((1*R**, 3*R**, 5*R**,7*R**)-Adamantan-2-yl)butanethioamide (3an)**



Prepared according to the general procedure B; 69.3mg, 73% yield. White crystal, m.p. = 89.4-91.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1 H), 4.56-4.52 (m, 1 H), 2.62 (t, *J* = 7.2 Hz, 2 H), 2.12 (s, 2 H), 1.87-1.71 (m, 14 H), 0.93 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.9, 59.1, 49.8, 37.4, 36.9, 32.4, 30.6, 27.08, 27.06, 22.9, 13.3. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{24}NS$ $[M+H]^+$ 238.1624, found 238.1611. **MS** (EI) *m/z* (%): 237 (100), 236 (94), 208 (43), 194 (28), 150 (25), 135 (55). **IR** (KBr plate): 3274, 2964, 2908, 2852, 1523, 1453, 1414, 1318, 1164, 1102, 769, 738 cm^{-1}.

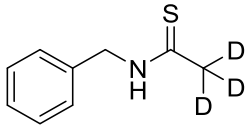
***N*-((1*R**, 3*R**, 5*R** ,7*R**)-Adamantan-2-yl)cyclopentanecarbothioamide (3ao)**



Prepared according to the general procedure B; 68.5 mg, 65% yield. Yellow crystal, m.p. = 82.8-84.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1 H), 4.59-4.56 (m, 1 H), 2.96-2.87 (m, 1 H), 2.14 (s, 2 H), 1.97-1.59 (m, 20 H);**^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.2, 58.7, 55.8, 37.4, 36.9, 34.0, 32.5, 30.6, 27.13, 27.12, 25.9. **HRMS** (ESI) *m/z* calculated for $C_{16}H_{26}NS$ $[M+H]^+$ 264.1780, found 264.1760. **MS** (EI) *m/z* (%): 263 (100), 262 (76), 194 (25), 150 (50), 135 (78). **IR** (KBr plate): 3301, 2909, 2853, 1511, 1452, 1418, 1376, 1322, 1269, 1136, 1101, 738 cm^{-1}.

***N*-Benzylethanethioamide-d_3 (3a-D_3)**

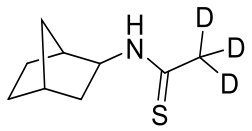


Prepared according to the general procedure B; 45.8 mg, 68% yield. White crystal,

m.p. = 59.5-60.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (s, 1 H), 7.48-7.32 (m, 5 H), 4.80 (d, J = 5.4 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 200.9, 136.1, 129.0, 128.5, 128.3, 50.7, 33.8-33.0 (m). **HRMS** (ESI) *m/z* calculated for $C_9H_9D_3NS$ $[M+H]^+$ 169.0873, found 169.0872. **MS** (EI) m/z (%): 168 (100), 135 (82), 106 (72). **IR** (KBr plate): 3219, 3066, 2921, 1553, 1403, 1343, 1173, 1004, 967, 736 cm^{-1}.

***N*-((1*S**, 4*R**)-Bicyclo[2.2.1]heptan-2-yl)ethanethioamide-d_3 (3ac-D_3)**



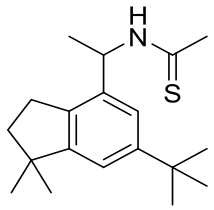
Prepared according to the general procedure B; 53.1 mg, 77% yield. White crystal,

m.p. = 93.6-94.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 1 H), 4.15-4.11 (m, 1 H), 2.37-2.30 (m, 2 H), 1.89-1.84 (m, 1 H), 1.56-1.42 (m, 2 H), 1.35-1.22 (m, 4 H), 1.16-1.11 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.1, 59.4, 41.5, 39.7, 36.2, 35.9, 34.0-33.2 (m), 28.1, 26.5. **HRMS** (ESI) *m/z*

calculated for $C_9H_{13}D_3NS$ $[M+H]^+$ 173.1186, found 173.1185. **MS** (EI) *m/z* (%): 172 (65), 110 (5), 95 (13), 77 (16), 62 (100). **IR** (KBr plate): 3206, 3035, 2873, 1535, 1410, 1346, 1303, 1195, 684 cm^{-1}.

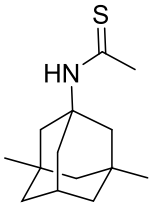
***N*-(1-(6-(*tert*-Butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethyl)ethanethioamide (3ap)**



Prepared according to the general procedure A; 61.8 mg, 51% yield. White crystal, m.p. = 128.5-192.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s,1 H), 7.21 (d, J = 1.6 Hz, 1 H), 7.16 (d, J = 1.6 Hz, 1 H), 5.81-5.74 (m, 1 H), 2.86 (td, J = 2.8 Hz, J = 7.2 Hz, 2 H), 2.53 (s, 3 H), 1.93 (t, J = 7.2 Hz, 2 H), 1.62 (d, J = 6.8 Hz, 3 H), 1.35 (s, 9 H), 1.27 (s, 3 H), 1.26 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.0, 153.5, 150.7, 139.3, 135.8, 120.2, 118.9, 53.2, 44.3, 41.4, 35.1, 34.6, 31.8, 28.9, 28.8, 28.4, 18.5. **HRMS** (ESI) *m/z* calculated for $C_{19}H_{30}NS$ $[M+H]^+$ 304.2093, found 304.2092. **MS** (EI) *m/z* (%): 303 (9), 229 (88), 228 (100), 213 (91), 129 (43), 115 (29). **IR** (KBr plate): 3217, 2955, 2864, 1531, 1458, 1384, 1254, 1175, 1103, 1042, 748, 720 cm^{-1}.

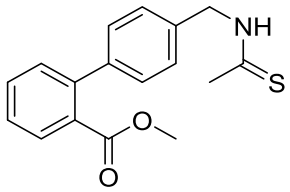
***N*-((1*R**, 3*R**, 5*S**, 7*R**)-3,5-Dimethyladamantan-1-yl)ethanethioamide (3aq)**



Prepared according to the general procedure A; 67.9 mg, 72% yield. Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (s, 1 H), 2.46 (s, 3 H), 2.16-2.13 (m, 1 H), 2.12 (s, 2 H), 1.90 (dd, J = 12.4 Hz, J = 28.4 Hz, 4 H), 1.38-1.25 (m, 4 H), 1.18-1.10 (m, 2 H), 0.83 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.3, 58.3, 50.6, 45.9, 42.6, 38.5, 37.7, 32.6, 30.1, 30.0. **HRMS** (ESI) *m/z* calculated for $C_{14}H_{24}NS$ $[M+H]^+$ 238.1624, found 238.1623. **MS** (EI) *m/z* (%): 237 (30), 236 (40), 213 (16), 163 (58), 107 (100). **IR** (KBr plate): 3253, 3037, 2945, 2903, 2862, 2842, 1535, 1454, 1393, 1161, 1142, 1069, 1040, 690 cm^{-1}.

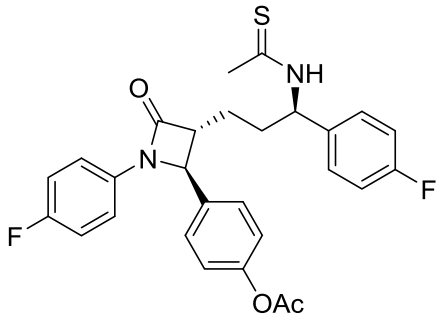
Methyl 4'-(ethanethioamidomethyl)-[1,1'-biphenyl]-2-carboxylate (3ar)

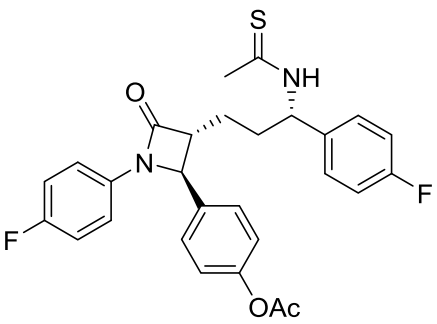


Prepared according to the general procedure A; 93.6 mg, 78% yield. Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, J = 0.8 Hz, J = 7.6 Hz, 1 H), 7.84 (s, 1 H), 7.54 (td, J = 1.2 Hz, J = 7.6 Hz, 1 H), 7.42 (td, J = 1.2 Hz, J = 7.6 Hz, 1 H), 7.35-7.31 (m, 3 H), 7.29-7.27 (m, 2 H), 4.84 (d, J = 5.6 Hz, 2 H), 3.67 (s, 3 H), 2.57 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.1, 168.8, 142.2, 141.2, 135.1, 131.6, 131.0, 130.3, 130.0, 128.9, 128.1, 127.5, 52.2, 50.3, 34.1. **HRMS** (ESI) *m/z* calculated for $C_{17}H_{17}NO_2SNa$ $[M+Na]^+$ 322.0872, found 322.0871. **MS** (EI) *m/z* (%): 299 (84), 240 (8), 234 (25), 225 (100), 165 (53), 152 (25). **IR** (KBr plate): 3310, 3231, 3027, 2997, 2948, 1718, 1537, 1387, 1286, 1253, 1128, 1090, 1048, 765, 712 cm^{-1}.

4-((2*S*,3*R*)-3-((*R*)-3-Ethanethioamido-3-(4-fluorophenyl)propyl)-1-(4-fluorophenyl)-4-oxoazetidin-2-yl)phenyl acetate and 4-((2*S*,3*R*)-3-((*S*)-3-Ethanethioamido-(4-fluorophenyl)propyl)-3- 1-(4-fluorophenyl)-4-oxoazetidin-2-yl)phenyl acetate (3as)



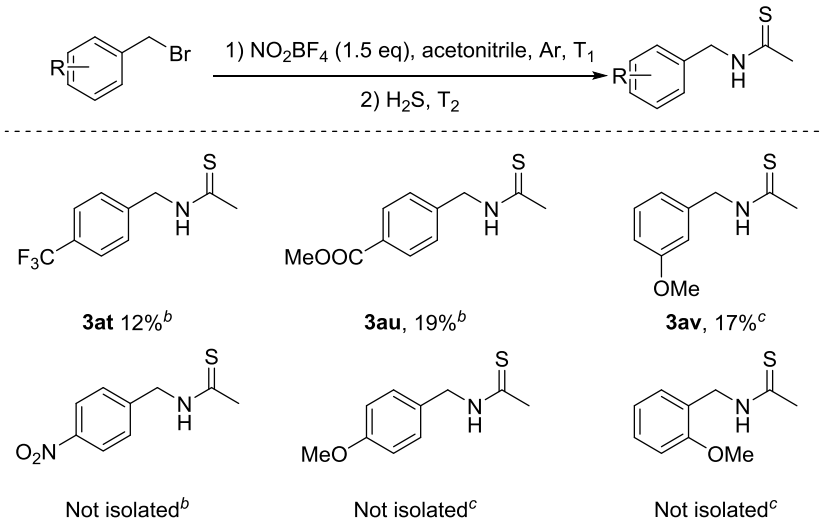


Prepared according to general procedure A; 105.0 mg, 52% yield. Yellow crystal, m.p. = 82.0-83.5 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.0 Hz, 1 H), 8.21 (d, J = 8.4 Hz, 0.9 H), 7.34-7.27 (m, 8 H), 7.22-7.17 (m, 4 H), 7.10 (s, 2 H), 7.08 (s, 1.8 H), 7.02-6.98 (m, 4 H), 6.94-6.89 (m, 4 H), 5.64 (dd, J = 8.0 Hz, J = 14.0 Hz 0.9 H), 5.54 (dd, J = 7.6 Hz, J = 15.2 Hz, 1 H), 4.65 (d , J = 2.0 Hz, 0.9 H), 4.63 (d, J = 2.0 Hz, 1 H), 3.08-3.04 (m, 2 H), 2.48 (s, 3 H), 2.45 (s, 2.8 H), 2.30 (s, 3 H), 2.29 (s, 2.7 H), 2.24-1.76 (m, 8 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.5, 200.2, 169.6, 169.5, 167.2, 167.1, 163.51, 163.46, 161.1, 161.0, 160.4, 157.9, 150.9, 135.88, 135.85, 135.5, 135.4, 134.8, 134.7, 133.5, 129.0, 128.9, 128.8, 128.7, 127.0, 122.62, 122.59, 118.54, 118.46, 116.1,

115.92, 115.87, 115.71, 115.65, 60.9, 60.6, 60.2, 60.1, 58.9, 58.6, 34.1, 32.5, 32.1, 25.58, 25.55, 21.1. **HRMS** (ESI) *m/z* calculated for $C_{28}H_{26}F_2N_2O_3SNa$ $[M+Na]^+$ 531.1524, found 531.1523. **MS** (EI) *m/z* (%): 509 (11), 508 (36), 474 (19), 296 (16), 254 (96), 194 (51), 135 (100). **IR** (KBr plate): 3302, 3047, 2985, 2936, 1743, 1510, 1372, 1223, 1198, 1102, 1046, 1015, 836 cm^{-1}.

Some additional substrates and the corresponding characterization data[a]

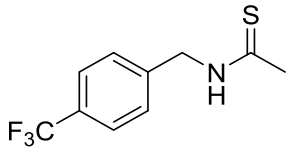


3at 12%[b] **3au**, 19%[b] **3av**, 17%[c]

Not isolated[b] Not isolated[c] Not isolated[c]

a) Reaction was performed using benzyl bromide (0.4 mmol) and NO_2BF_4 (0.6 mmol, 1.5 equiv) in 1.0 mL CH_3CN at the noted temperature (T_1) under an argon and then stirred for 30 minutes, followed by the introduction of H_2S at the second noted temperature (T_2) at which point the resulting reaction mixture was stirred for another 20 minutes; b) T_1 = 90℃, T_2 = -15℃; c) T_1 = 0℃, T_2 = -15℃.

***N*-(4-(Trifluoromethyl)benzyl)ethanethioamide (3at)**

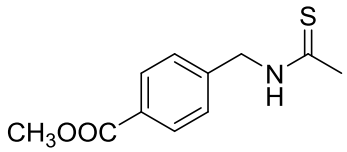


Prepared according to the general procedure A; 11.6 mg, 12% yield. White crystal, m.p. = 84.6-85.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 2 H), 7.60 (s, 1 H), 7.44 (d, J = 8.0 Hz, 2 H), 4.90 (d, J = 5.6 Hz, 2 H), 2.59 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.8, 140.2, 130.4 (q, J = 33.0 Hz), 128.6, 125.9 (q, J = 4.0 Hz), 124.0 (q, J = 270.0 Hz). 49.7, 34.2. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{11}F_3NS$ $[M+H]^+$ 234.0559, found 234.0558. **MS** (EI) *m/z* (%): 234 (12), 233

(68), 174 (46), 159 (100), 145 (11). **IR** (KBr plate): 3222, 3048, 2928, 1537, 1387, 1326, 1166, 1124, 1067, 1019, 931, 692 cm^{-1}.

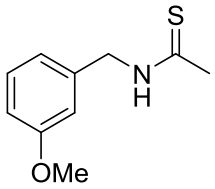
***N*-4-(Ethanethioamidomethyl)phenyl acetate (3au)**



Prepared according to the general procedure A; 17.0 mg, 19% yield. Yellow crystal, m.p. = 73.3-74.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.0 Hz, 2 H), 7.74 (s 1 H), 7.36 (d, J = 8.4 Hz, 2 H), 4.89 (d, J = 5.2 Hz, 2 H), 3.89 (s, 3 H), 2.60 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.7, 166.9, 141.4, 130.2, 129.8, 128.2, 52.4, 50.0, 34.2. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{14}NO_2S$ $[M+H]^+$ 224.0740, found 224.0738. **MS** (EI) *m/z* (%): 223 (100), 164 (67), 149 (89), 121 (74), 105 (18). **IR** (KBr plate): 3209, 3041 ,3005, 2952, 1722, 1540, 1436, 1388, 1284, 1177, 1110, 1020, 934, 759, 693 cm^{-1}.

***N*-(3-Methoxybenzyl)ethanethioamide (3av)**



Prepared according to the general procedure A; 13.0 mg, 17% yield. Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1 H), 7.30-7.27 (m, 1 H), 6.92-6.85 (m, 3 H), 4.77 (d, J = 5.2 Hz, 2 H), 3.81 (s, 3 H), 2.58 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.9, 160.0, 137.6, 130.1, 120.6, 114.1, 113.6, 55.4, 50.7, 34.2. **HRMS** (ESI) *m/z* calculated for $C_{10}H_{14}NOS$ $[M+H]^+$ 196.0791, found 196.0799. **MS** (EI) *m/z* (%): 195 (73), 162 (45), 136 (20), 122 (12), 121 (100). **IR** (KBr plate): 3221, 3049, 2933, 1601, 1534, 1490, 1331, 1292, 1166, 1047, 785, 691 cm^{-1}.

3.6 X-Ray crystallography data of products 3ac, 3al, and 3am.

3.6.1 X-Ray Crystal Structure data of product **3ac** (CCDC number 2168879).

The crystal of product **3ac** for X-ray diffraction study has been obtained through the dissolving of compound in petroleum ether and dichloromethane (Vpetroleum ether/Vdichloromethane = 2:1), followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in ROD, Synergy Custom system, HyPix diffractometer (Figure S5).

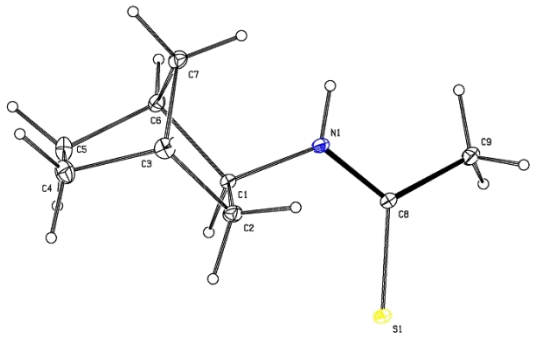


Figure S5. X-Ray coordinate of product **3ac**, ORTEP drawing of product **3ac** showing ellipsoids at the 10% contour probability level.

Crystal data and structure refinement for product **3ac**

Identification code	tangshizhong1_0425_auto
Empirical formula	$C_9H_{15}NS$
Formula weight	169.28
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.6856(3)
b/Å	9.2050(2)
c/Å	10.7124(2)
α/°	90
β/°	118.687(3)
γ/°	90
Volume/Å^3	924.35(4)
Z	4
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	2.580
F(000)	368.0
Crystal size/mm^3	0.28 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.61 to 155.064
Index ranges	$-13 \le h \le 13$, $-11 \le k \le 11$, $-13 \le l \le 13$
Reflections collected	8401
Independent reflections	1878 [R_{int} = 0.0312, R_{sigma} = 0.0226]
Data/restraints/parameters	1878/0/165
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.0997
Final R indexes [all data]	R_1 = 0.0415, wR_2 = 0.1007
Largest diff. peak/hole / e Å^{-3}	0.21/-0.17

3.6.2 X-Ray Crystal Structure data of product **3al** (CCDC number 2168880).

The crystal of product **3al** for X-ray diffraction study has been obtained through the dissolving of compound in petroleum ether and dichloromethane (Vpetroleum ether/Vdichloromethane = 2:1), followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in ROD, Synergy Custom system, HyPix diffractometer (Figure S6).

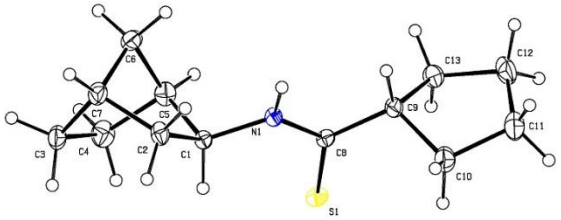


Figure S6. X-Ray coordinate of product **3al**, ORTEP drawing of product **3al** showing ellipsoids at the 30% contour probability level.

Crystal data and structure refinement for product 3al

Identification code	tangshizhong2_0425_auto
Empirical formula	$C_{13}H_{21}NS$
Formula weight	223.37
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.16255(17)
b/Å	10.98512(17)
c/Å	10.23216(13)
α/°	90
β/°	94.9987(13)
γ/°	90
Volume/Å^3	1249.92(3)
Z	4
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	2.024
F(000)	488.0
Crystal size/mm^3	0.25 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.95 to 155.132
Index ranges	-14 ≤ h ≤ 14, -13 ≤ k ≤ 13, -10 ≤ l ≤ 12
Reflections collected	8622
Independent reflections	2508 [R_{int} = 0.0342, R_{sigma} = 0.0312]
Data/restraints/parameters	2508/0/136
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1359
Final R indexes [all data]	R_1 = 0.0520, wR_2 = 0.1377
Largest diff. peak/hole / e Å^{-3}	0.63/-0.38

3.6.3 X-Ray Crystal Structure data of product **3am** (CCDC number 2168881).

The crystal of product **3am** for X-ray diffraction study has been obtained through the dissolving of compound in petroleum ether and dichloromethane (Vpetroleum ether/Vdichloromethane = 2:1), followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in ROD, Synergy Custom system, HyPix diffractometer (Figure S7).

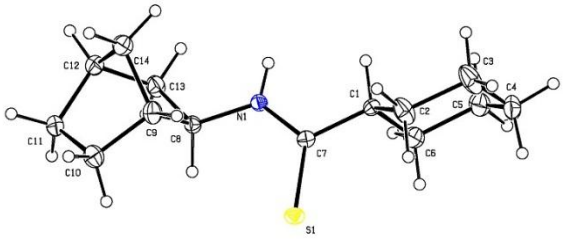


Figure S7. X-Ray coordinate of product **3am**, ORTEP drawing of product **3am** showing ellipsoids at the 30% contour probability level.

Crystal data and structure refinement for product 3am

Identification code	tangshizhong3_0425_auto
Empirical formula	$C_{14}H_{23}NS$
Formula weight	237.39
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.57483(18)
b/Å	11.2206(2)
c/Å	10.30302(15)
α/°	90
β/°	93.9195(14)
γ/°	90
Volume/Å^3	1334.99(4)
Z	4
ρ_{calc}g/cm^3	1.181
μ/mm^{-1}	1.923
F(000)	520.0
Crystal size/mm^3	0.28 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.656 to 153.976
Index ranges	$-14 \le h \le 14$, $-13 \le k \le 13$, $-8 \le l \le 12$
Reflections collected	9526
Independent reflections	2659 [R_{int} = 0.0414, R_{sigma} = 0.0369]
Data/restraints/parameters	2659/0/145
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0469, wR_2 = 0.1292
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1318
Largest diff. peak/hole / e Å^{-3}	0.48/-0.28

4. References

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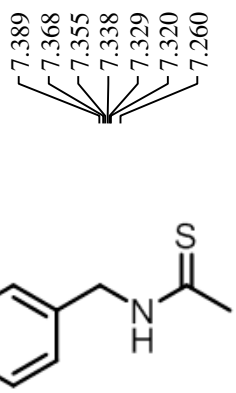
5. Copies of ^{1}H and ^{13}C NMR spectra of products


S
N
H

3a

7.389
7.368
7.355
7.338
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7.260
4.811
4.798
4.506
4.491
2.573
2.540
-0.003
9
8
7
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5
4
3
2
1
0
-1
ppm
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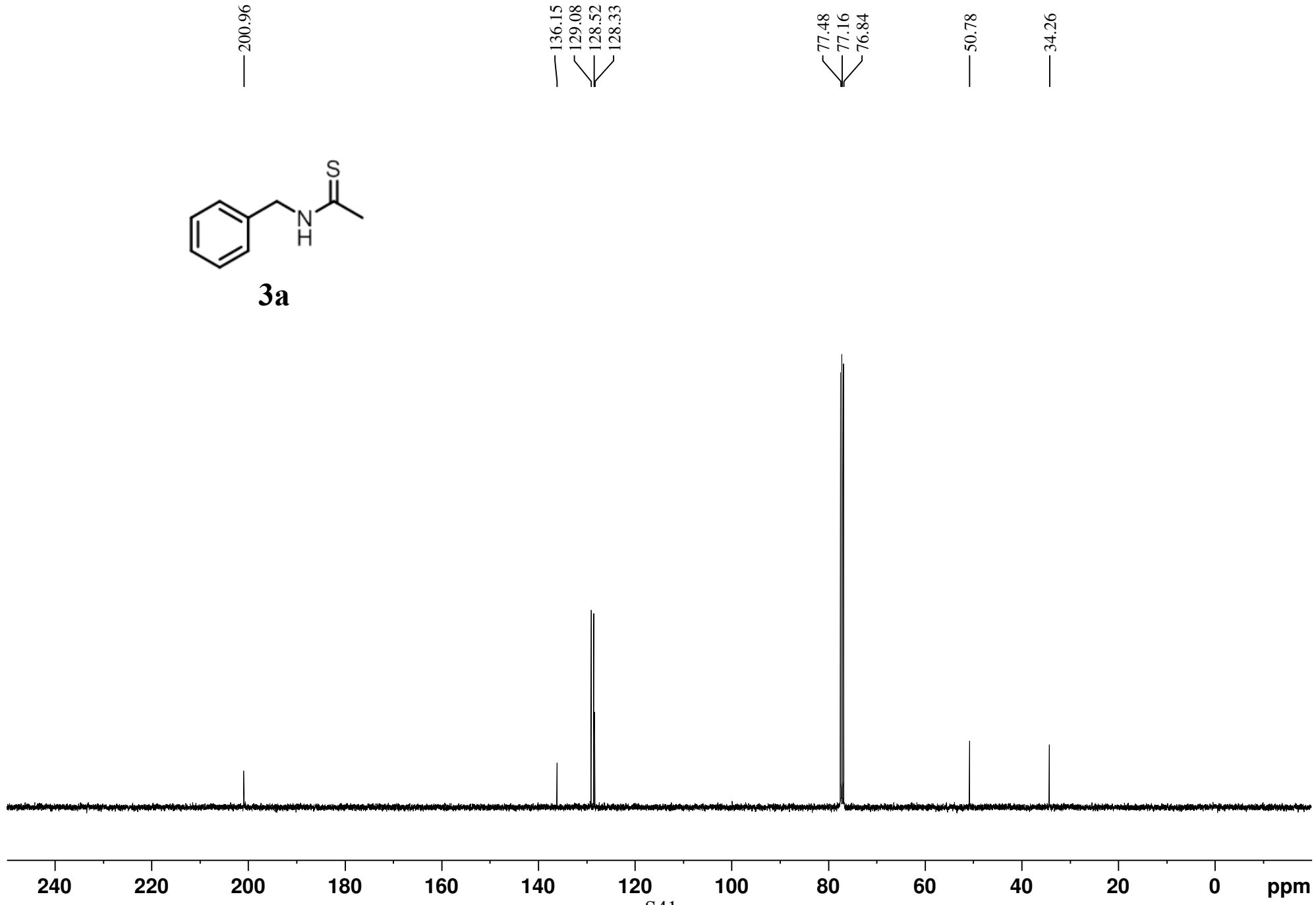
2.03
0.07
3.00
0.11


200.96
136.15
129.08
128.52
128.33
77.48
77.16
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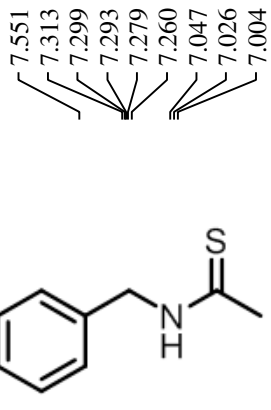
50.78
34.26
S
N
H
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3a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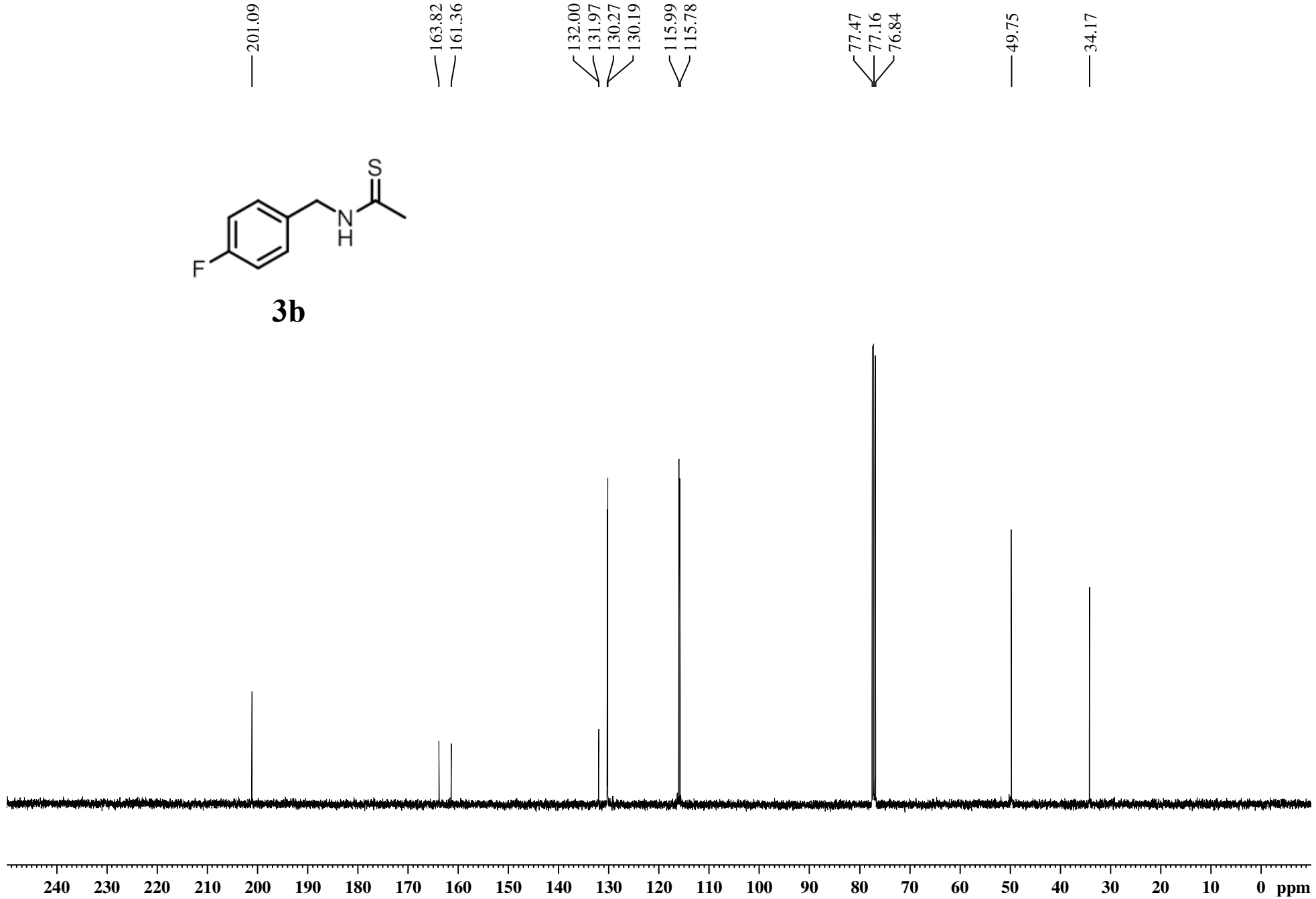
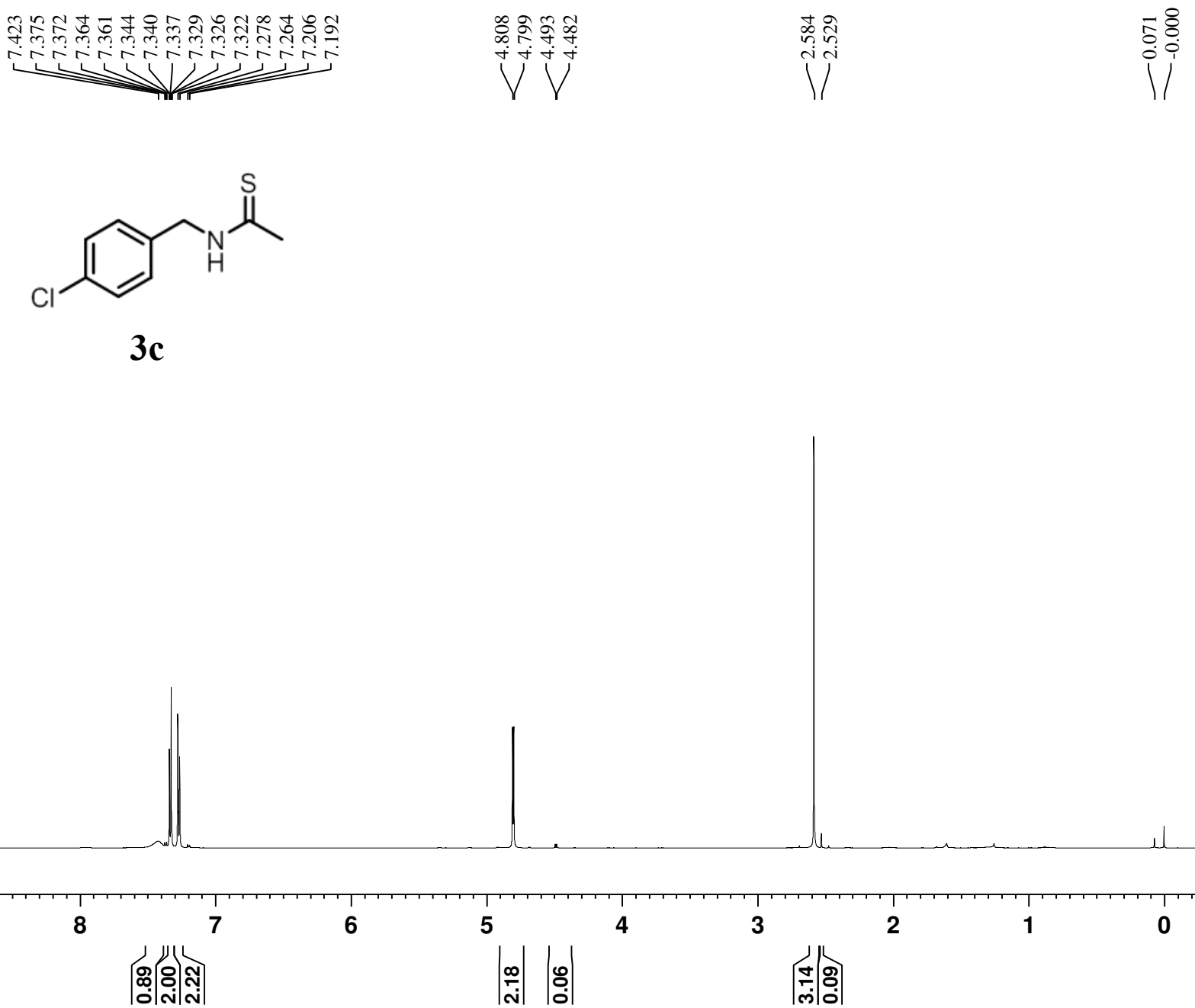
7.313
7.299
7.293
7.279
7.260
7.047
7.026
7.004
4.777
4.764
4.473
4.458
2.550
2.508
0.060
-0.015
S
N
H
F
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.04
2.02
2.05
0.06
3.02
0.10

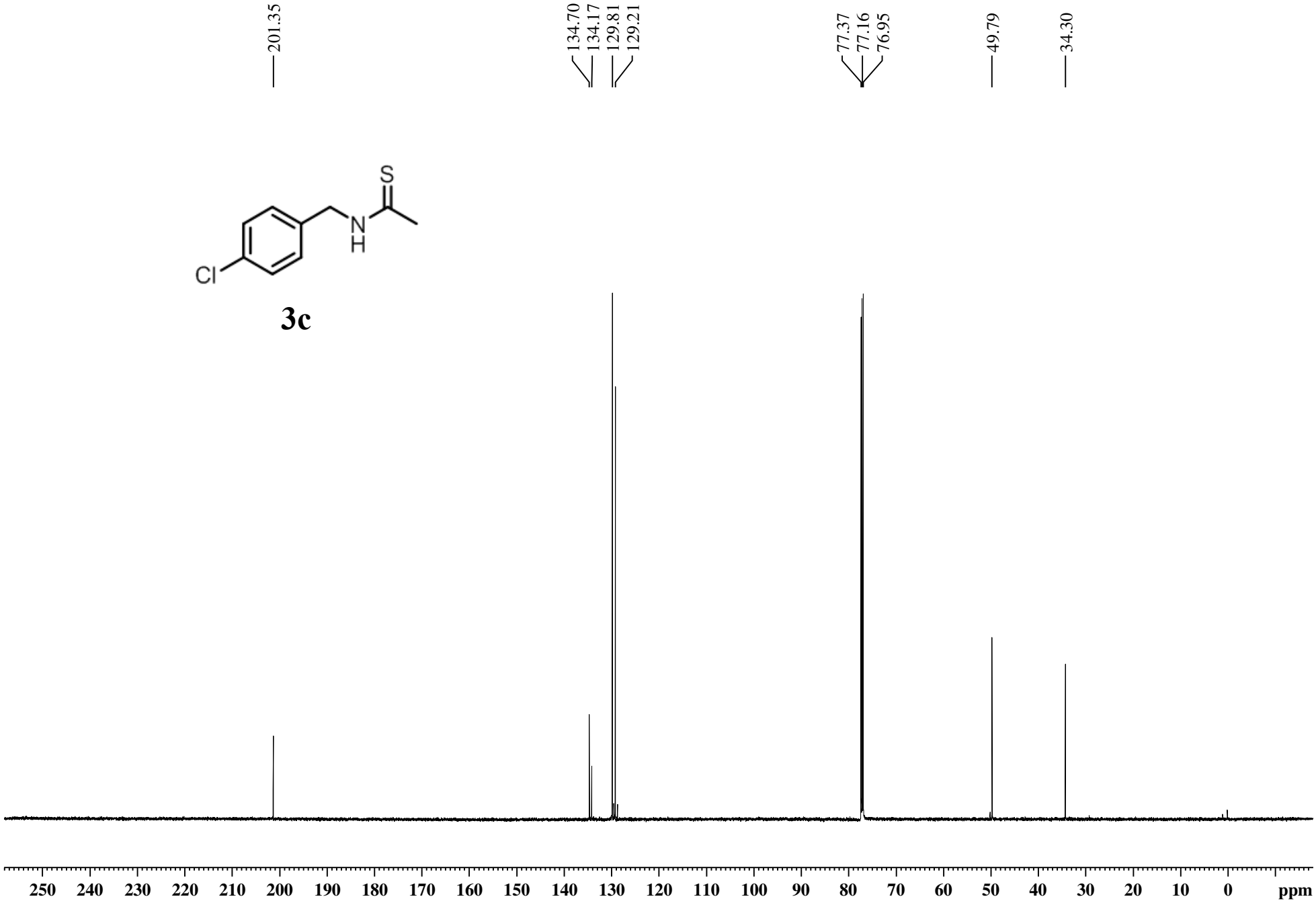
3b


201.09
163.82
161.36
132.00
131.97
130.27
130.19
115.99
115.78
77.47
77.16
76.84
49.75
34.17
S
N
H
F
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3b


7.423
7.375
7.372
7.364
7.361
7.344
7.340
7.337
7.329
7.326
7.322
7.278
7.264
7.206
7.192
4.808
4.799
4.493
4.482
2.584
2.529
0.071
-0.000
S
N
H
Cl
9
8
7
6
5
4
3
2
1
0
ppm
0.89
2.00
2.22
2.18
0.06
3.14
0.09

3c


201.35
134.70
134.17
129.81
129.21
77.37
77.16
76.95
49.79
34.30
S
N
H
Cl
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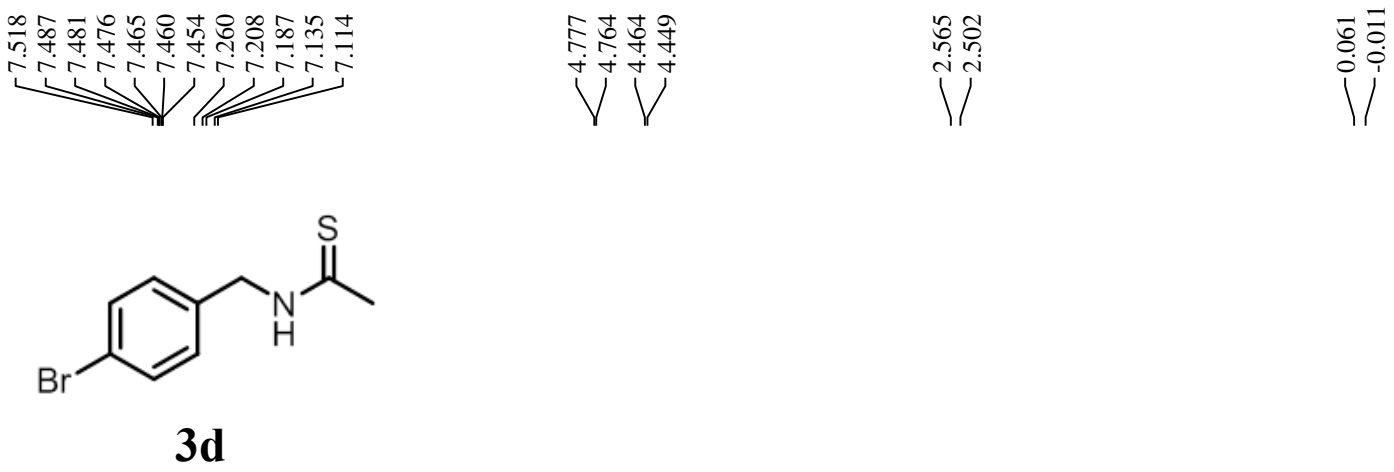
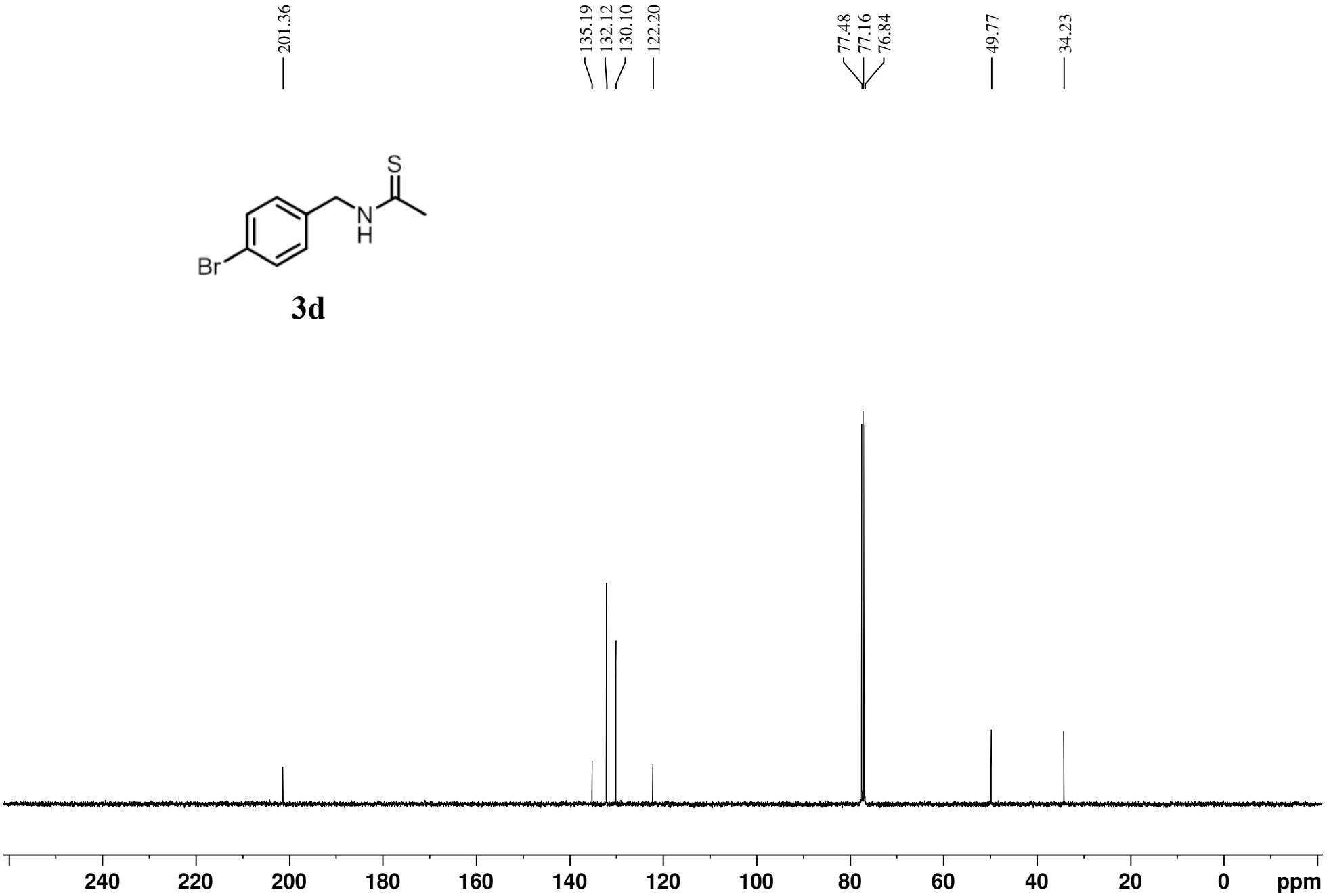
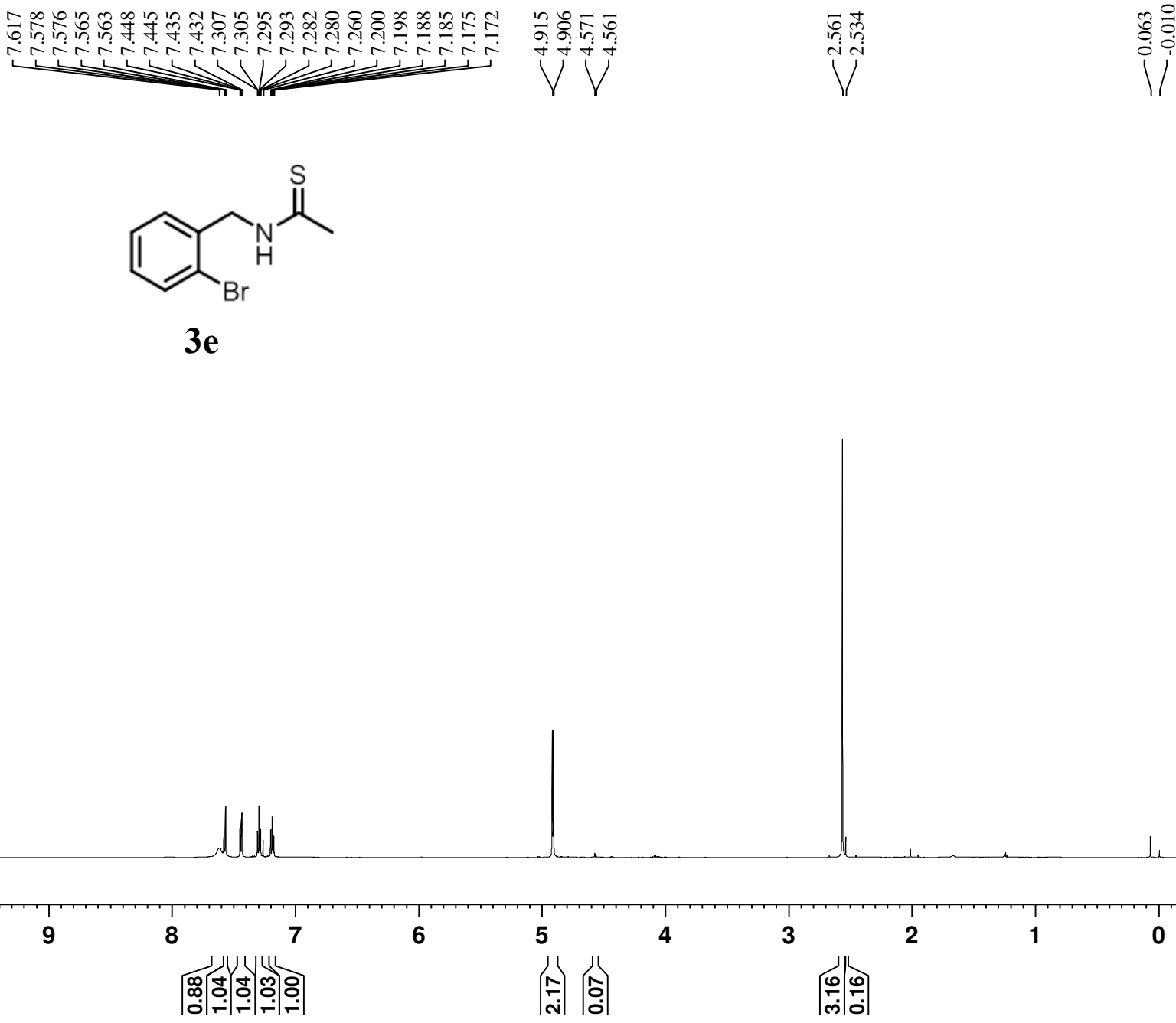
3c

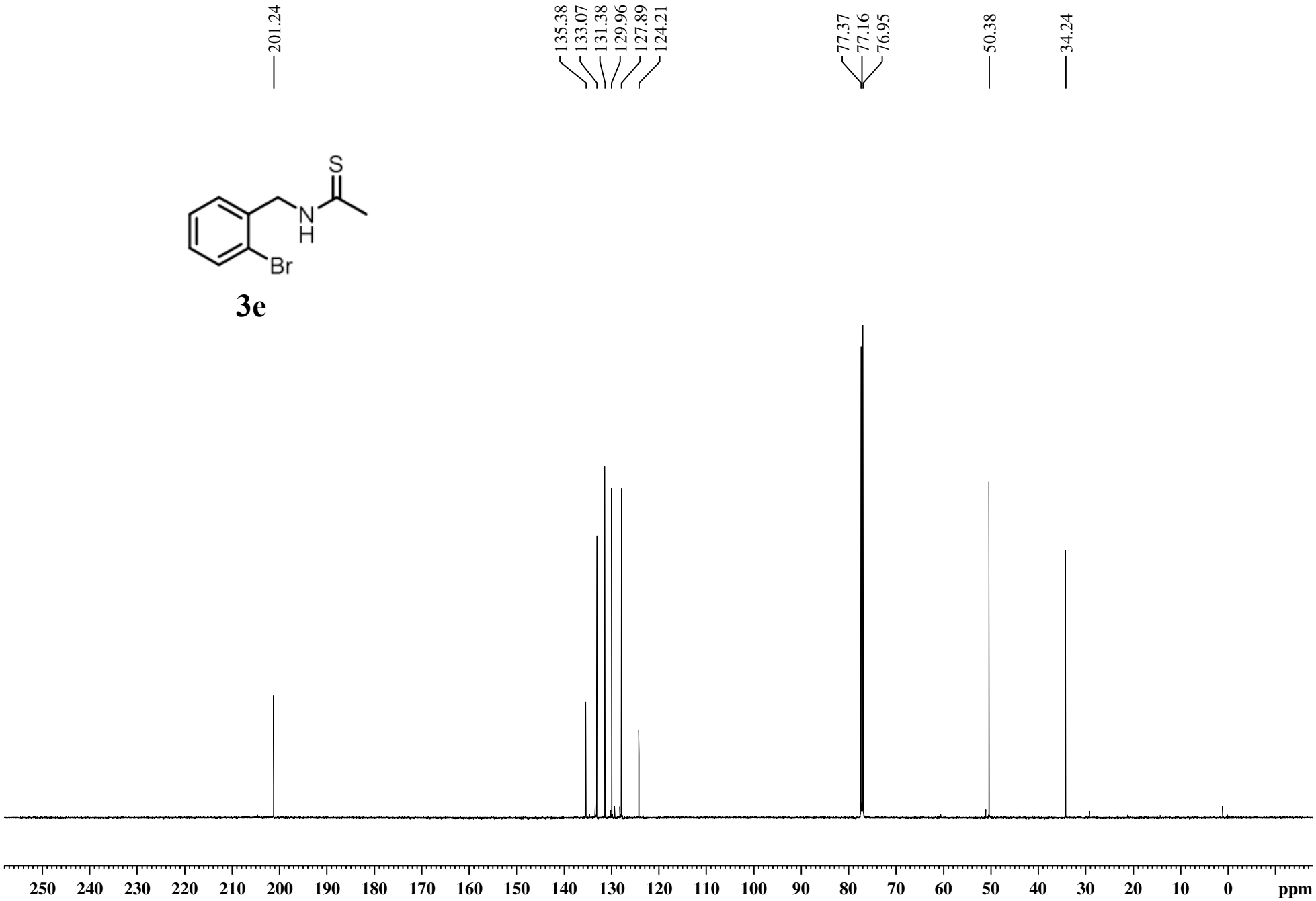

7.518
7.487
7.481
7.476
7.465
7.460
7.454
7.260
7.208
7.187
7.135
7.114
4.777
4.764
4.464
4.449
2.565
2.502
0.061
-0.011
S
N
H
Br
3d
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.76
2.09
2.00
0.07
2.03
0.05
3.03
0.09


201.36
135.19
132.12
130.10
122.20
77.48
77.16
76.84
49.77
34.23
S
N
H
Br
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

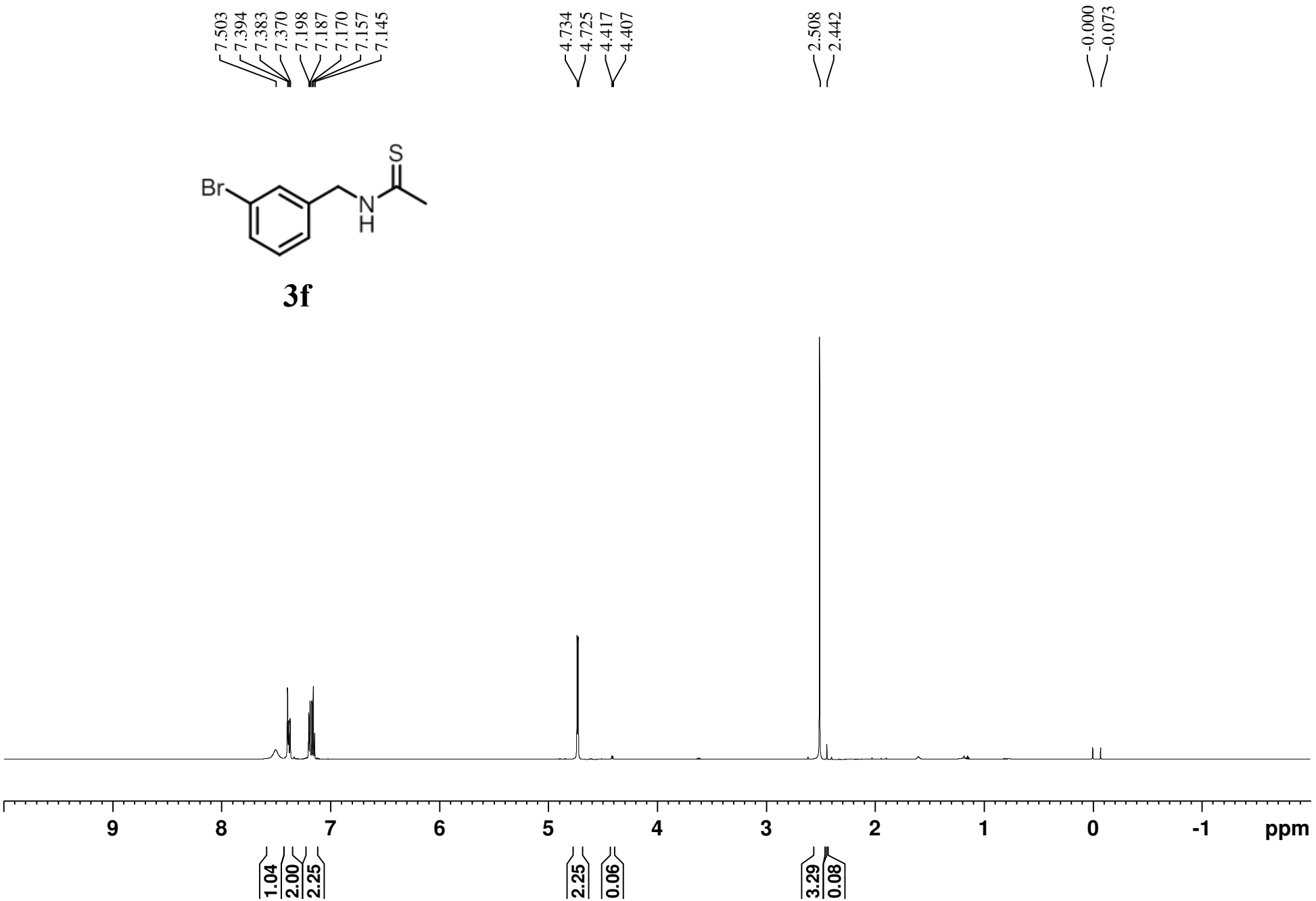
3d


7.617
7.578
7.576
7.565
7.563
7.448
7.445
7.435
7.432
7.307
7.305
7.295
7.293
7.282
7.280
7.260
7.200
7.198
7.188
7.185
7.175
7.172
4.915
4.906
4.571
4.561
2.561
2.534
0.063
-0.010
S
N
H
Br
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.88
1.04
1.04
1.03
1.00
2.17
0.07
3.16
0.16

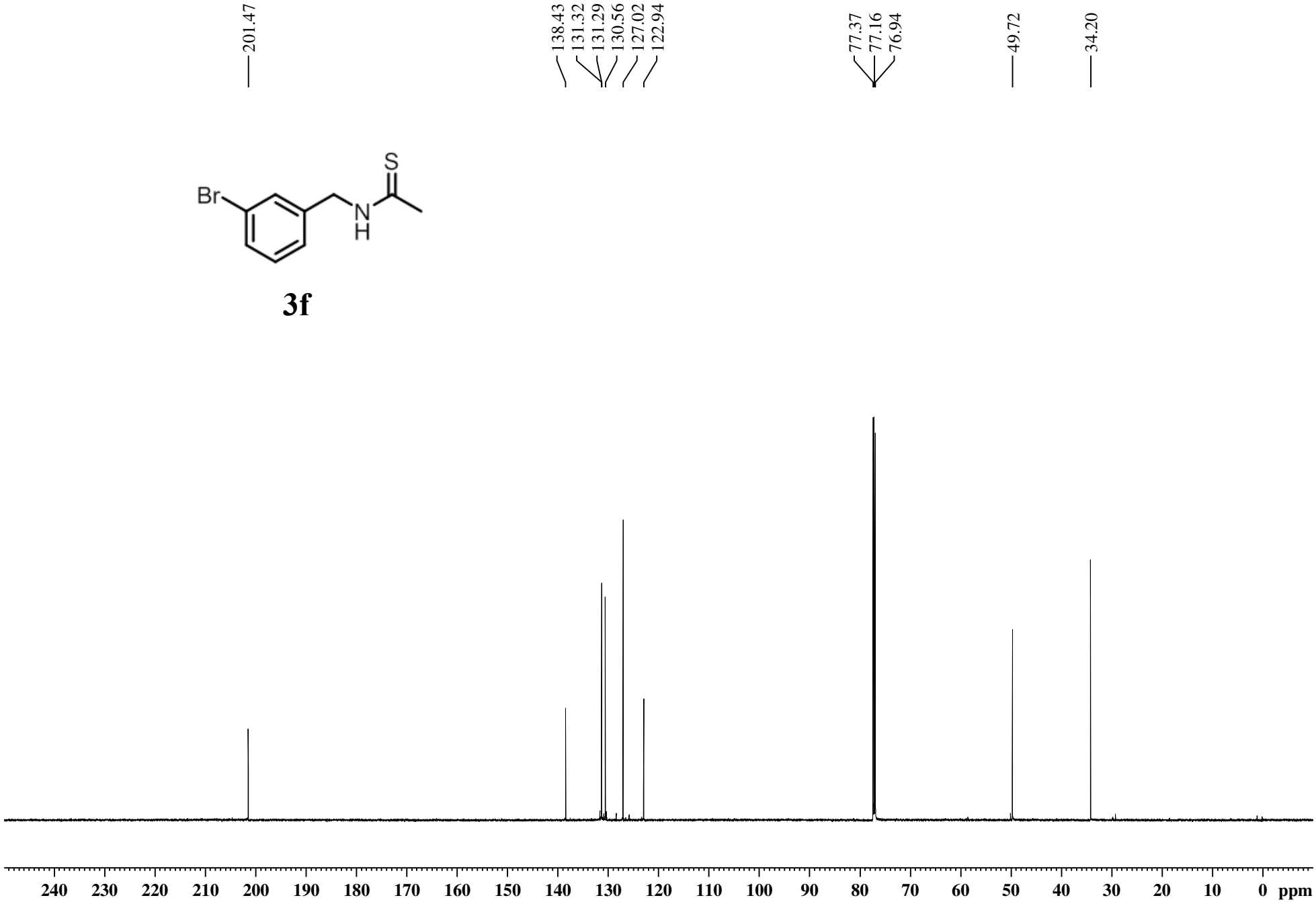
3e


201.24
135.38
133.07
131.38
129.96
127.89
124.21
77.37
77.16
76.95
50.38
34.24
S
N
H
Br
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

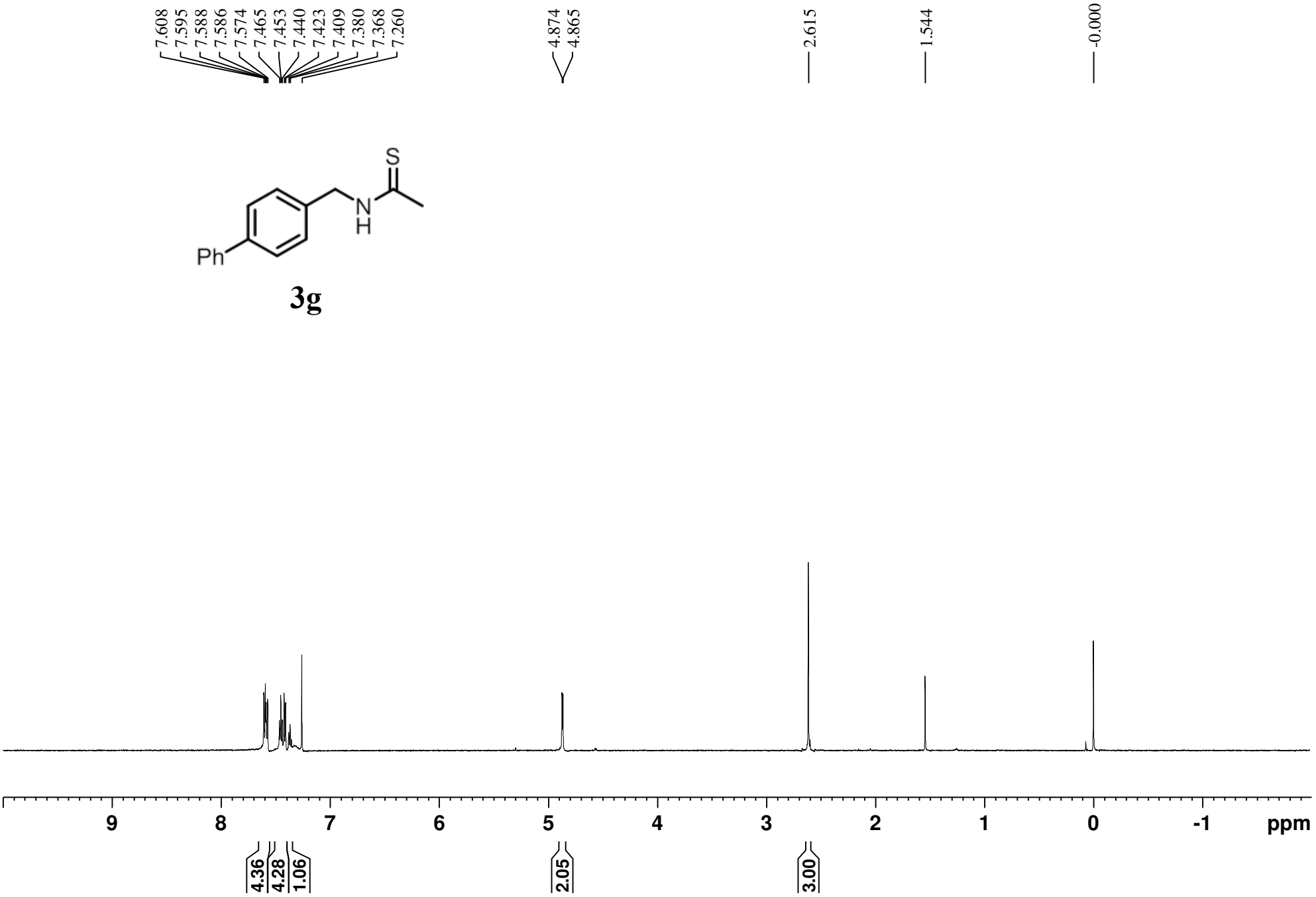
3e


7.503
7.394
7.383
7.370
7.198
7.187
7.170
7.157
7.145
4.734
4.725
4.417
4.407
2.508
2.442
-0.000
-0.073
Br
N
H
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.04
2.00
2.25
2.25
0.06
3.29
0.08

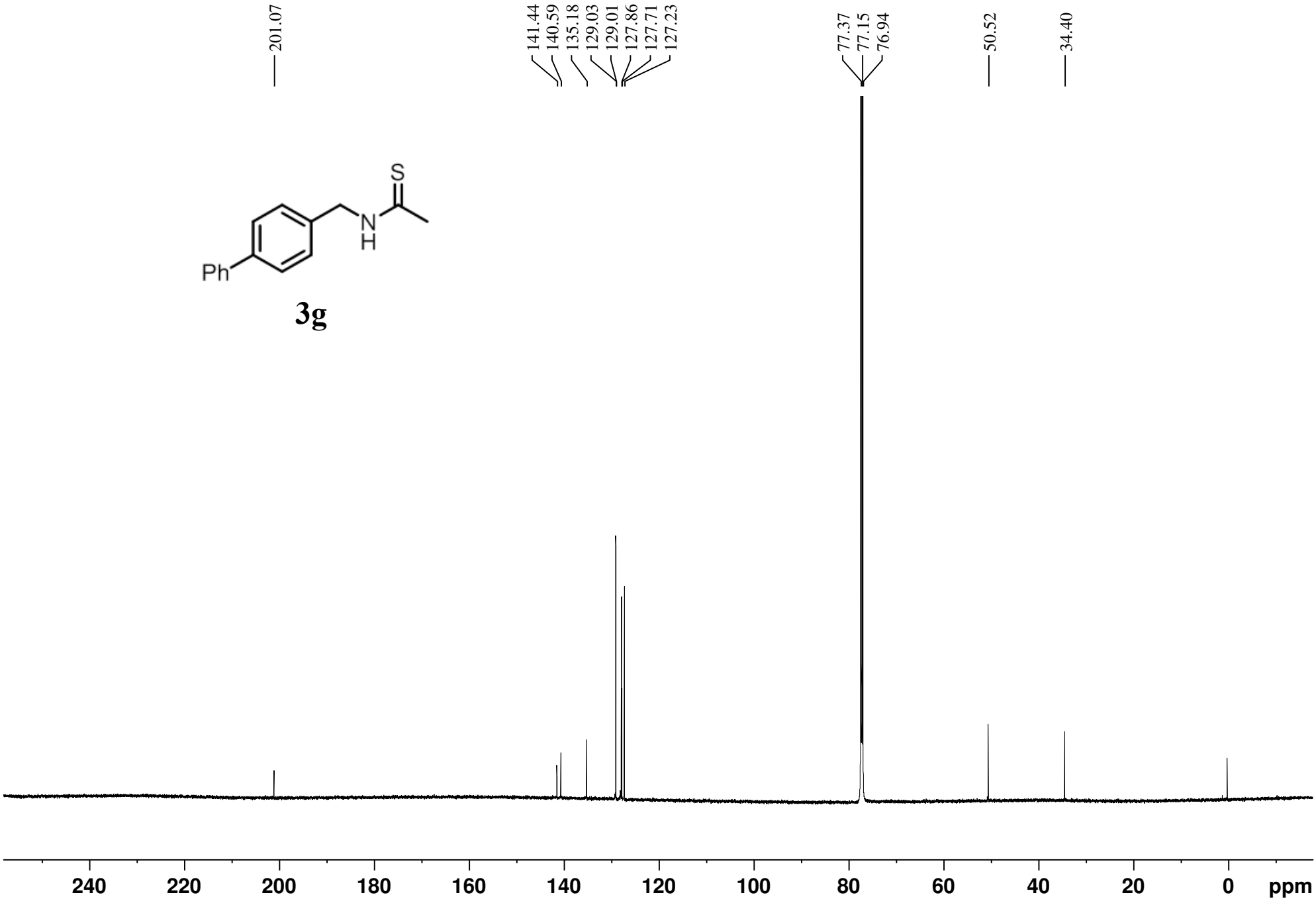
3f


201.47
138.43
131.32
131.29
130.56
127.02
122.94
77.37
77.16
76.94
49.72
34.20
Br
N
H
S
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

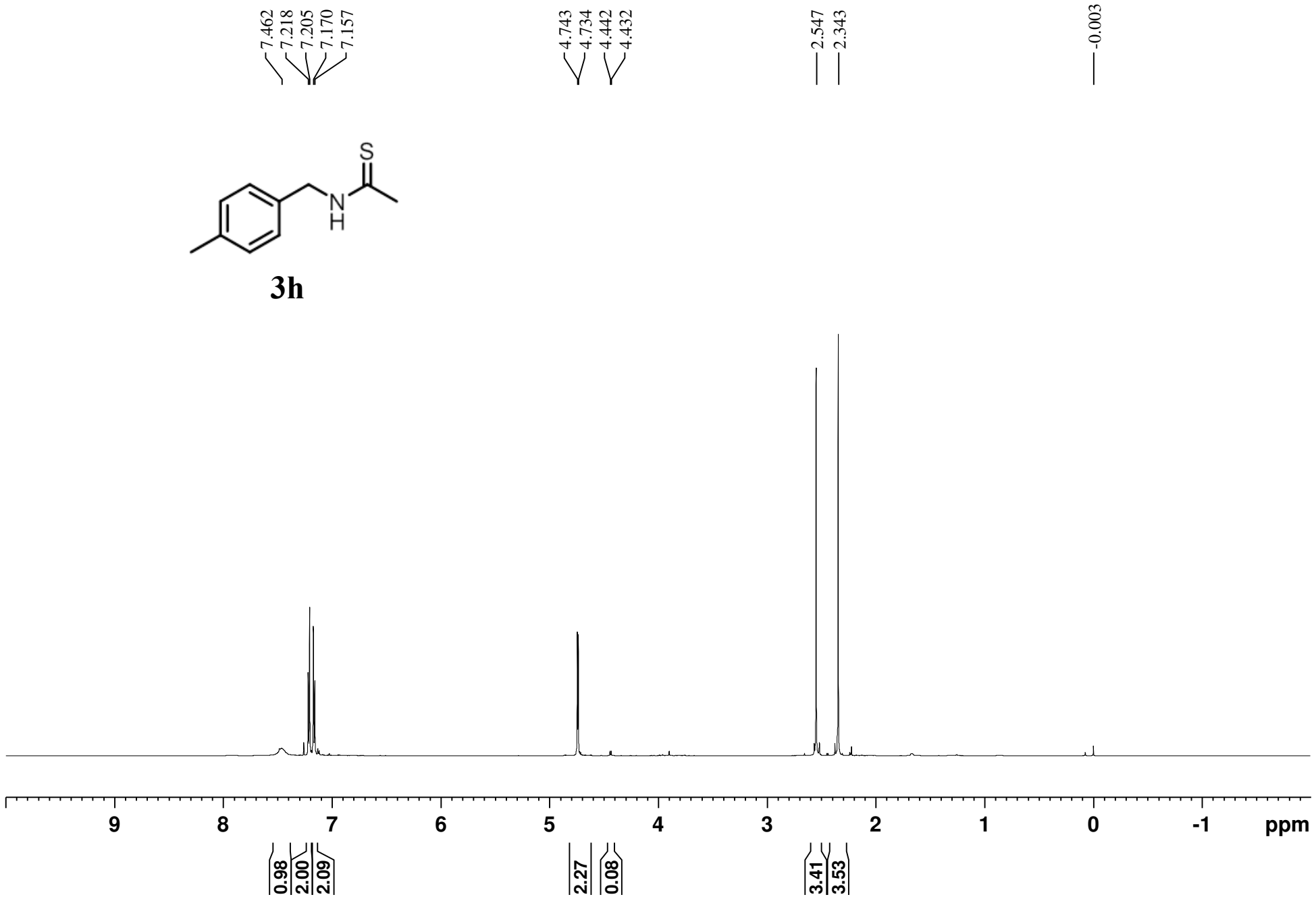
3f


7.608
7.595
7.588
7.586
7.574
7.465
7.453
7.440
7.423
7.409
7.380
7.368
7.260
4.874
4.865
2.615
1.544
-0.000
S
N
H
Ph
9
8
7
6
5
4
3
2
1
0
-1
ppm
4.36
4.28
1.06
2.05
3.00

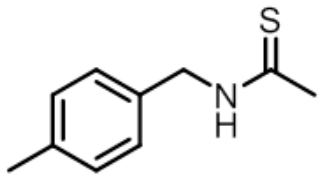
3g


201.07
141.44
140.59
135.18
129.03
129.01
127.86
127.71
127.23
77.37
77.15
76.94
50.52
34.40
S
N
H
Ph
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3g

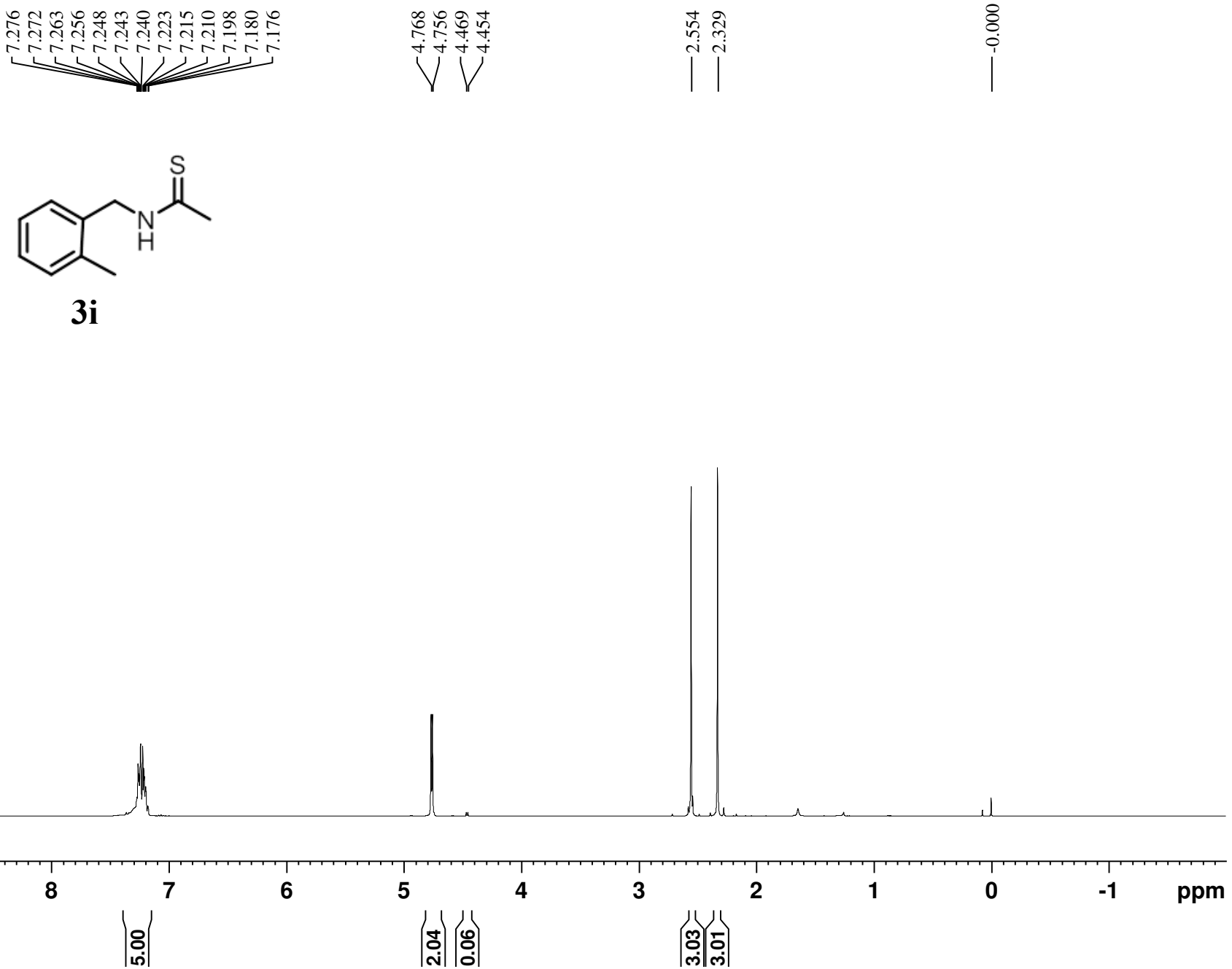

7.462
7.218
7.205
7.170
7.157
4.743
4.734
4.442
4.432
2.547
2.343
-0.003
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
2.00
2.09
2.27
0.08
3.41
3.53

3h

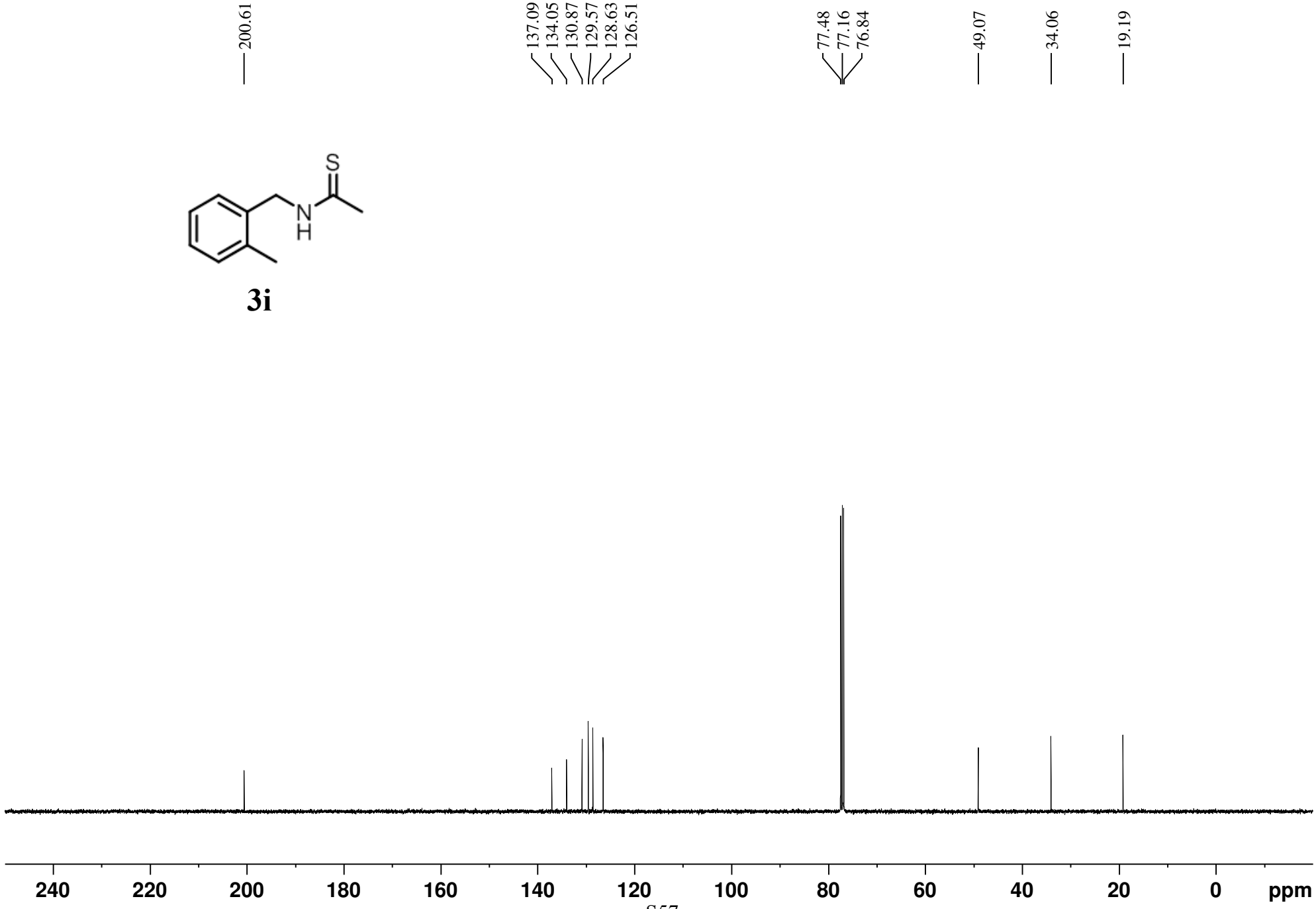

S
N
H

3h

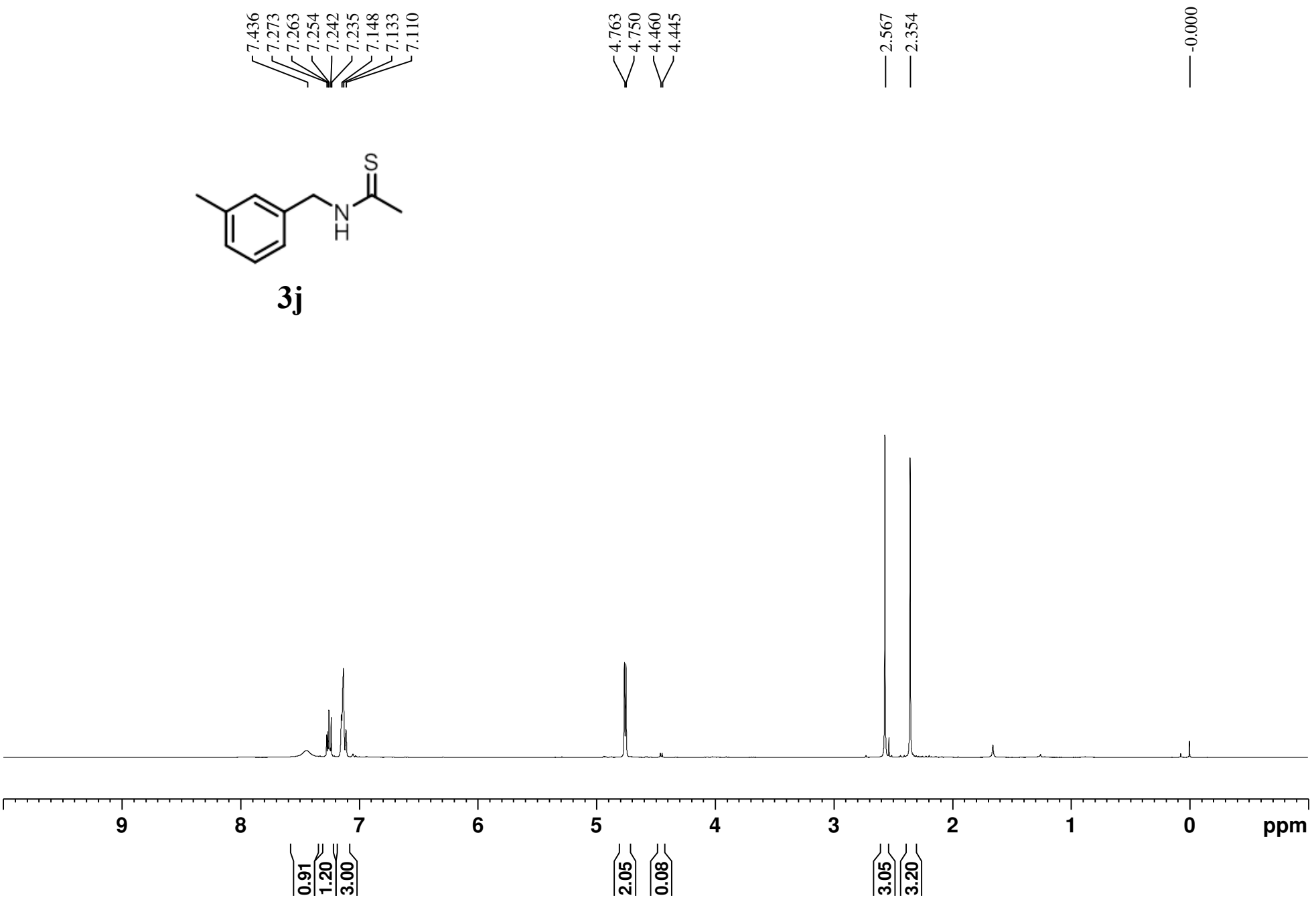
200.67
138.09
133.05
129.67
128.46
77.37
77.16
76.95
50.51
34.18
21.22
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.276
7.272
7.263
7.256
7.248
7.243
7.240
7.223
7.215
7.210
7.198
7.180
7.176
4.768
4.756
4.469
4.454
2.554
2.329
-0.000
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
5.00
2.04
0.06
3.03
3.01

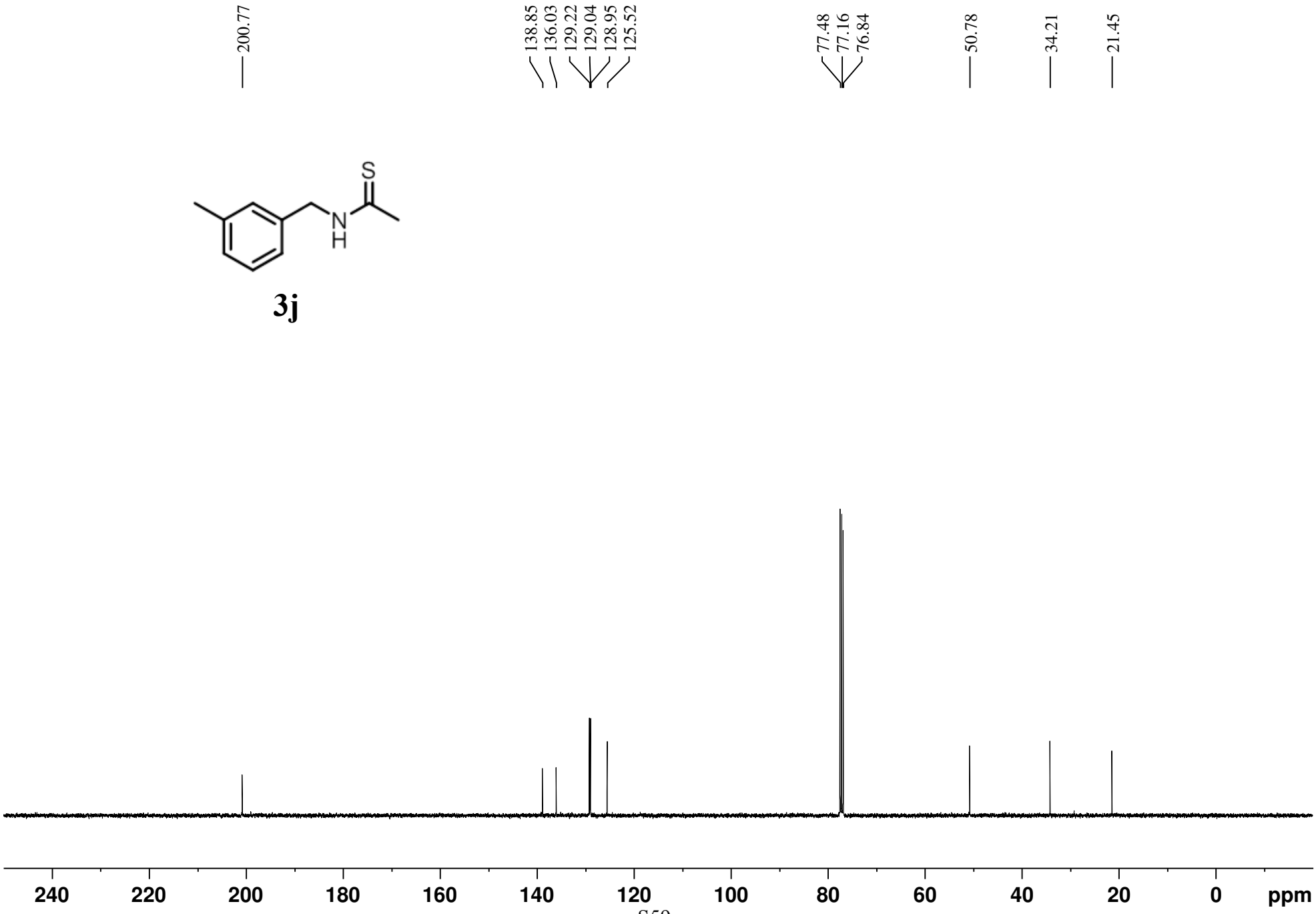
3i


200.61
137.09
134.05
130.87
129.57
128.63
126.51
77.48
77.16
76.84
49.07
34.06
19.19
S
N
H
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

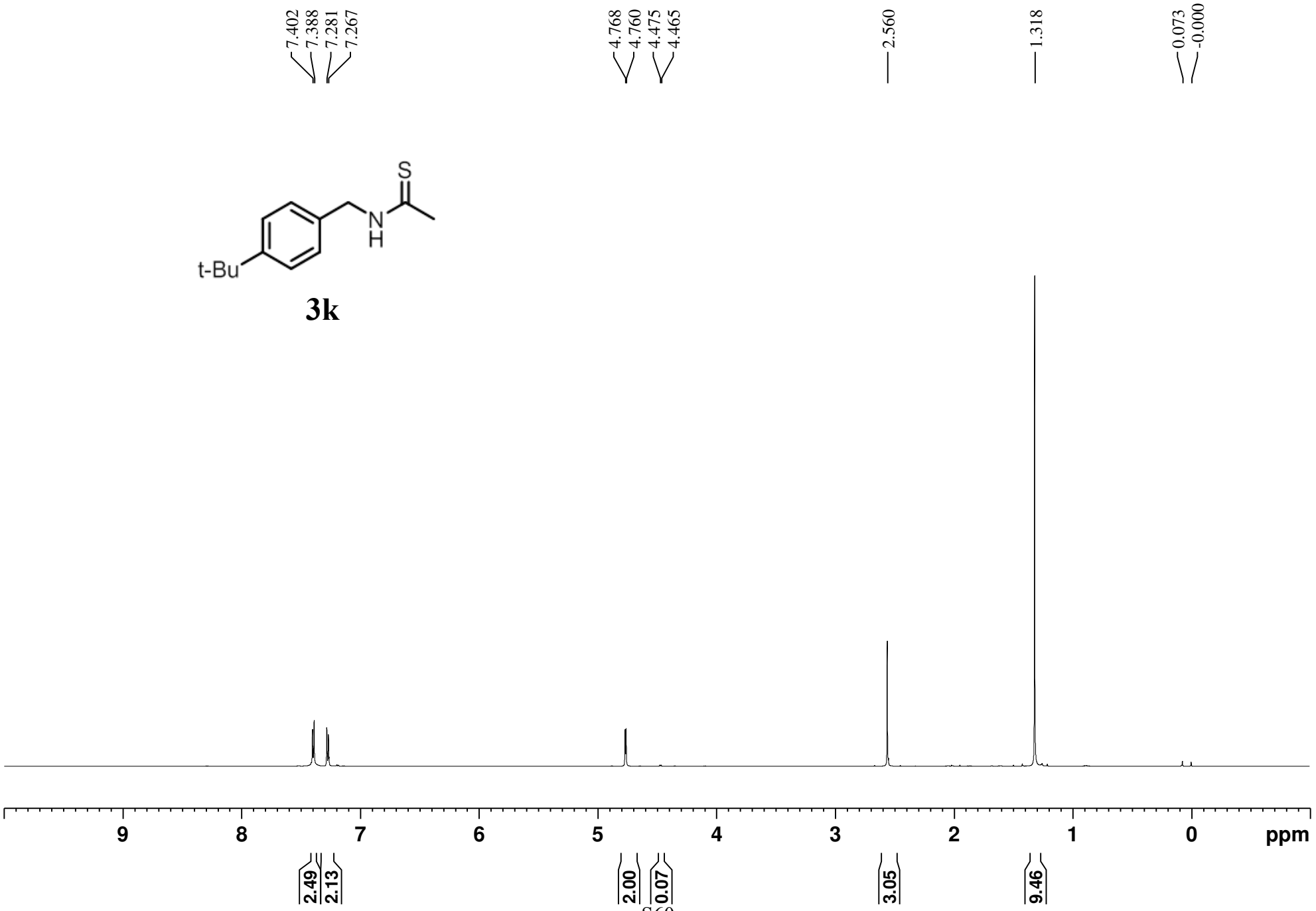
3i


7.436
7.273
7.263
7.254
7.242
7.235
7.148
7.133
7.110
4.763
4.750
4.460
4.445
2.567
2.354
-0.000
S
N
H
9
8
7
6
5
4
3
2
1
0
ppm
0.91
1.20
3.00
2.05
0.08
3.05
3.20

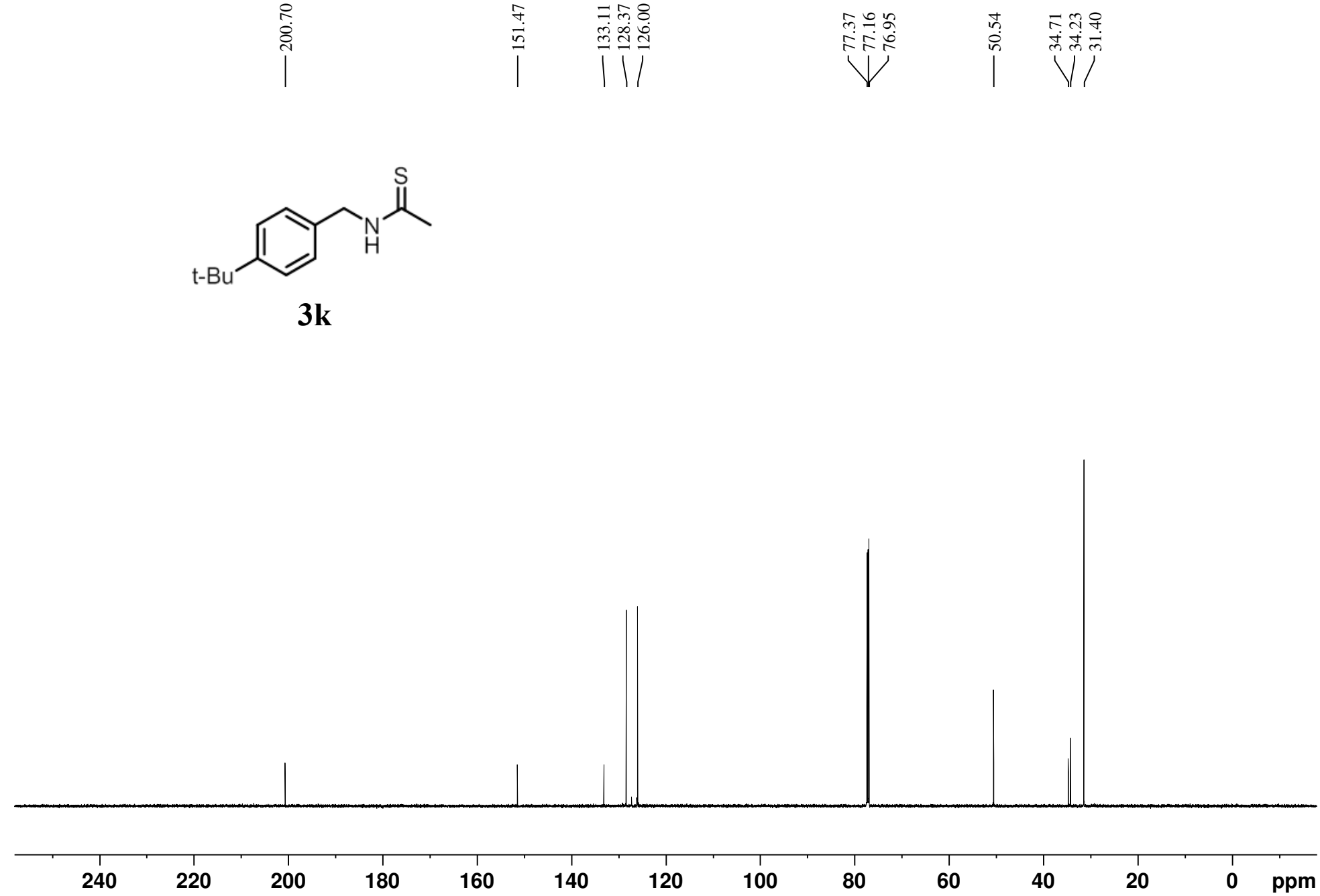
3j


200.77
138.85
136.03
129.22
129.04
128.95
125.52
77.48
77.16
76.84
50.78
34.21
21.45
S
N
H
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

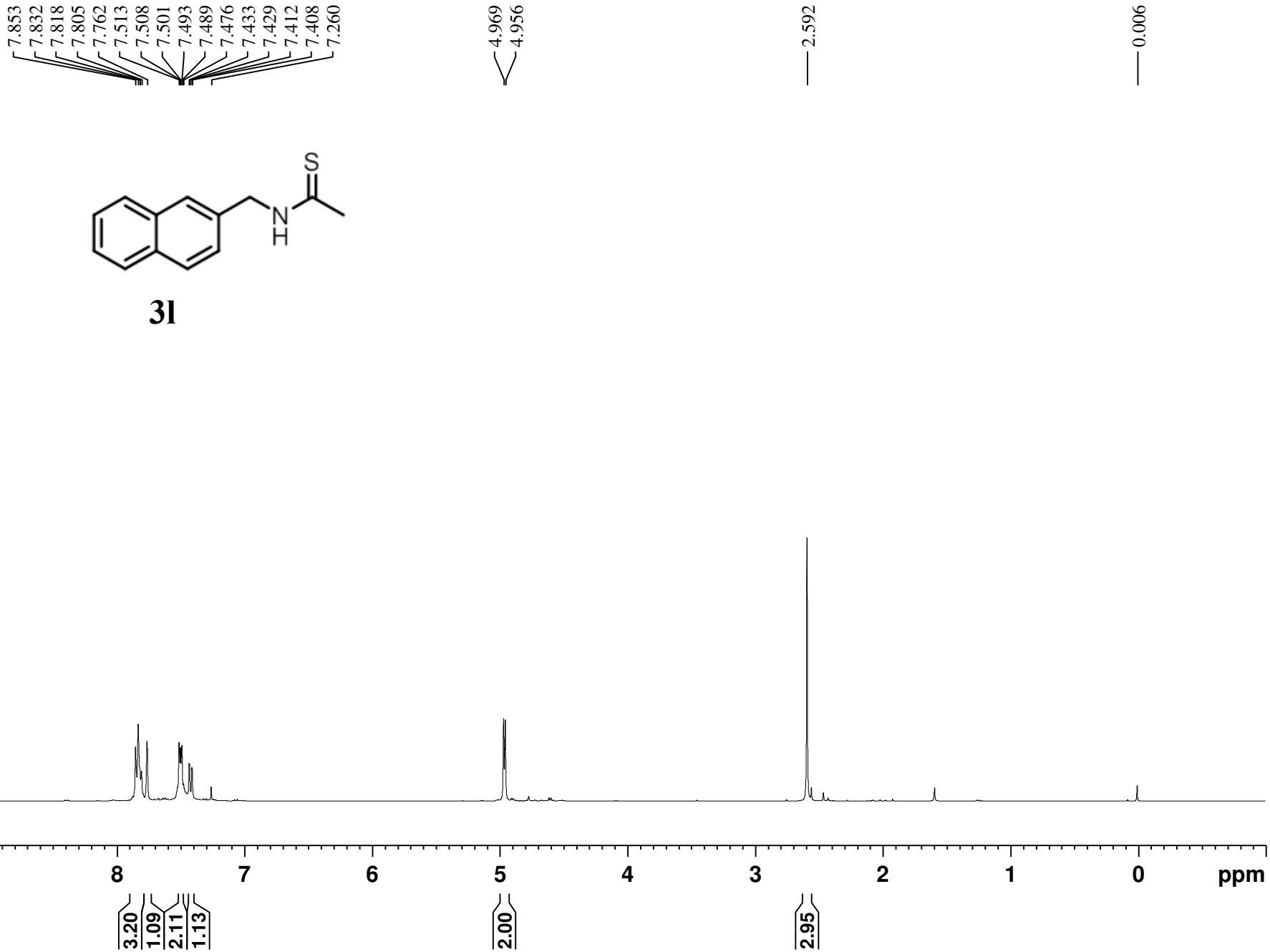
3j


7.402
7.388
7.281
7.267
4.768
4.760
4.475
4.465
2.560
1.318
0.073
-0.000
S
N
H
t-Bu
9
8
7
6
5
4
3
2
1
0
ppm
2.49
2.13
2.00
0.07
3.05
9.46

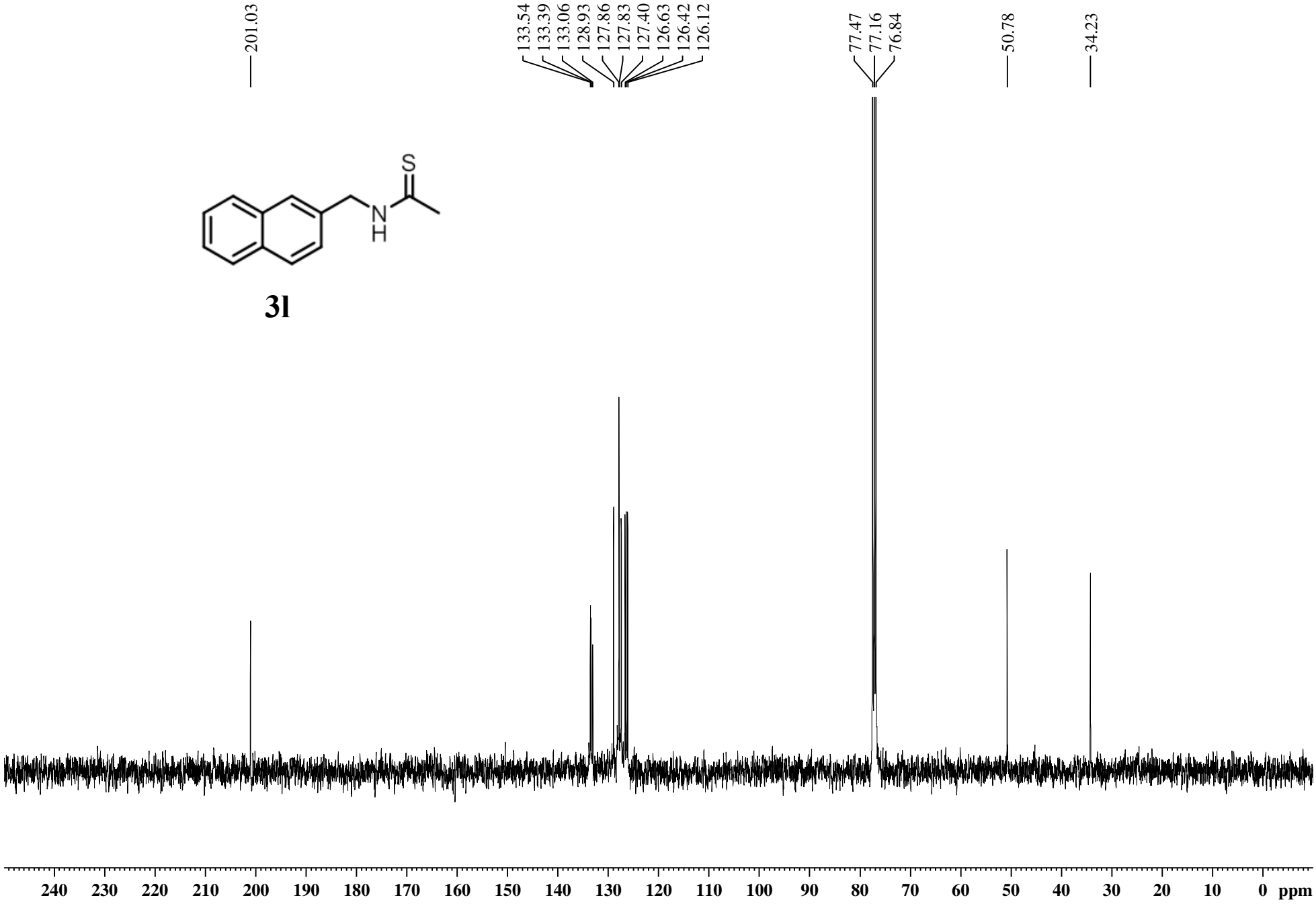
3k


200.70
151.47
133.11
128.37
126.00
77.37
77.16
76.95
50.54
34.71
34.23
31.40
S
N
H
t-Bu
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

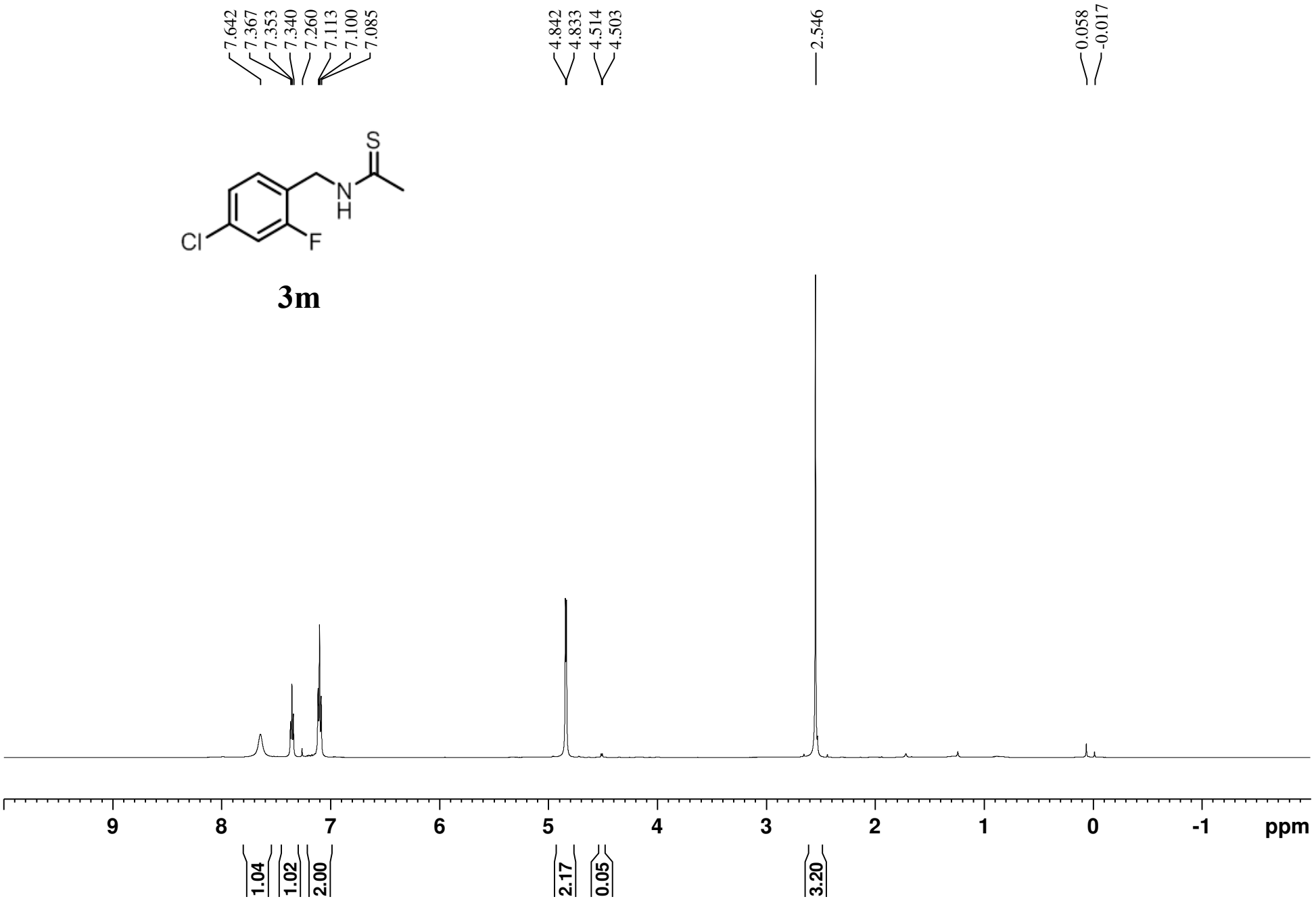
3k


7.853
7.832
7.818
7.805
7.762
7.513
7.508
7.501
7.493
7.489
7.476
7.433
7.429
7.412
7.408
7.260
4.969
4.956
2.592
0.006
S
N
H
9
8
7
6
5
4
3
2
1
0
ppm
3.20
1.09
2.11
1.13
2.00
2.95

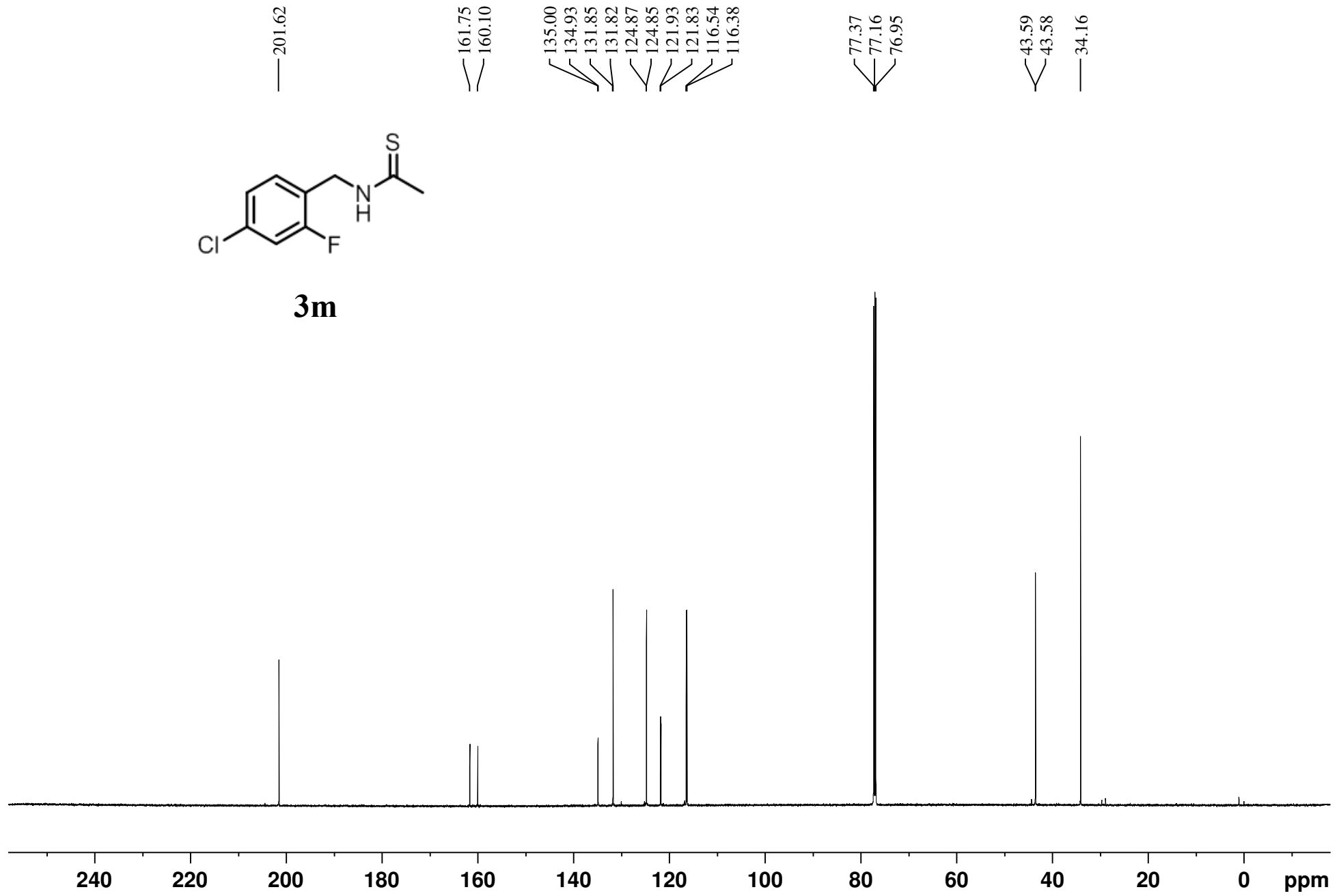
3l


201.03
133.54
133.39
133.06
128.93
127.86
127.83
127.40
126.63
126.42
126.12
77.47
77.16
76.84
50.78
34.23
S
N
H
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

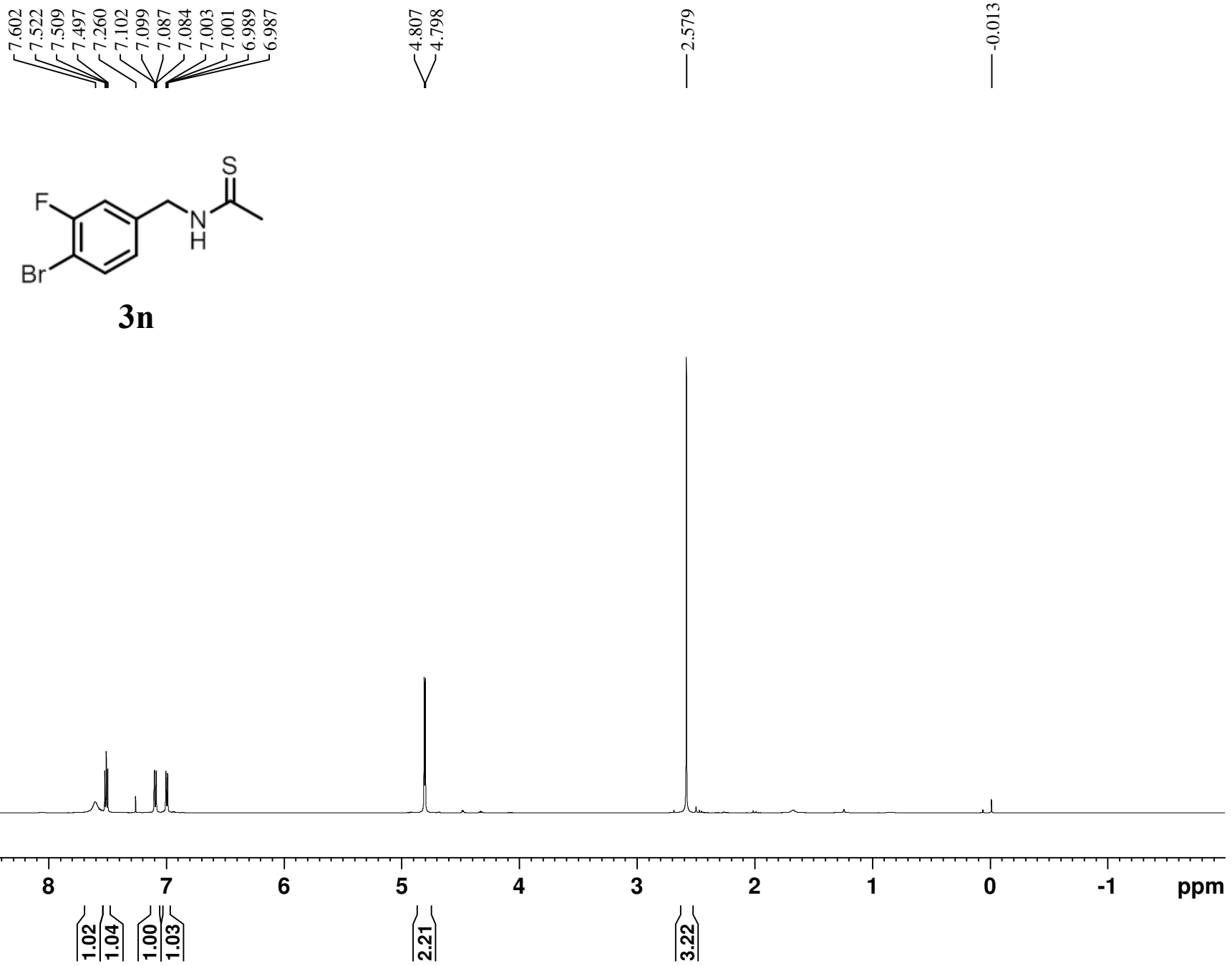
3l


7.642
7.367
7.353
7.340
7.260
7.113
7.100
7.085
4.842
4.833
4.514
4.503
2.546
0.058
-0.017
S
N
H
Cl
F
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.04
1.02
2.00
2.17
0.05
3.20

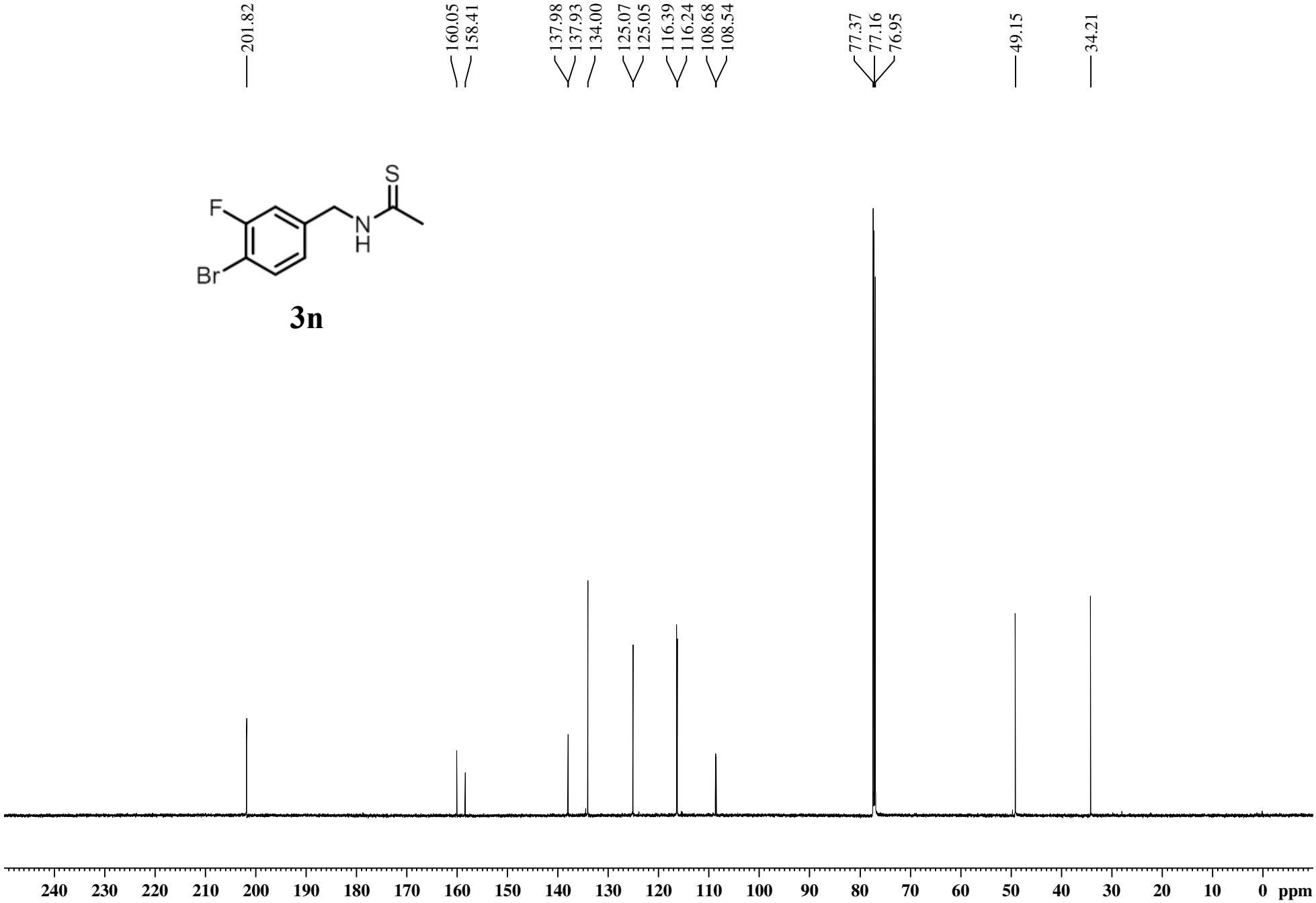
3m


201.62
161.75
160.10
135.00
134.93
131.85
131.82
124.87
124.85
121.93
121.83
116.54
116.38
77.37
77.16
76.95
43.59
43.58
34.16
S
N
H
Cl
F
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

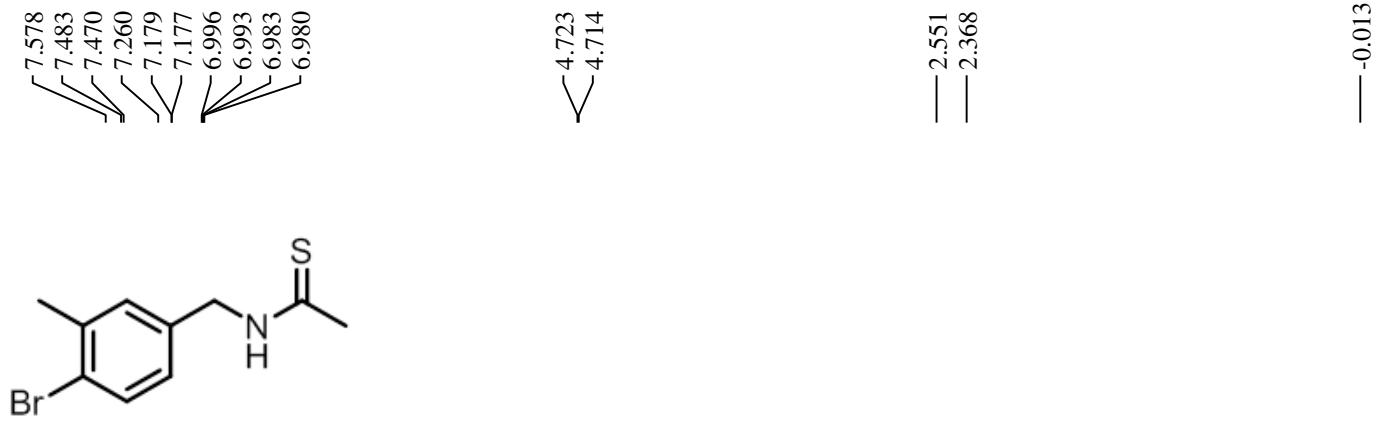
3m


7.602
7.522
7.509
7.497
7.260
7.102
7.099
7.087
7.084
7.003
7.001
6.989
6.987
4.807
4.798
2.579
-0.013
F
Br
N
H
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.04
1.00
1.03
2.21
3.22

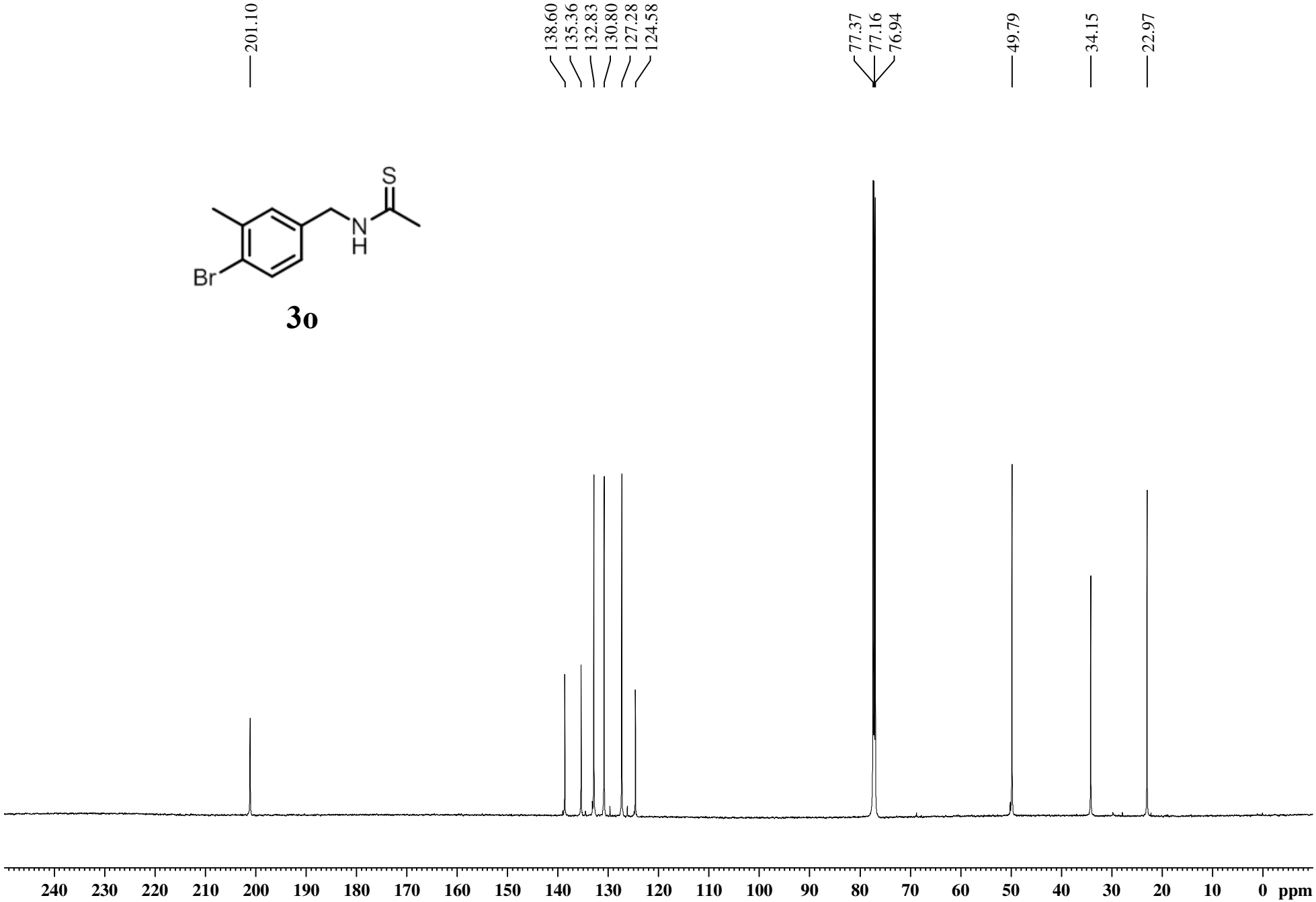
3n


201.82
160.05
158.41
137.98
137.93
134.00
125.07
125.05
116.39
116.24
108.68
108.54
77.37
77.16
76.95
49.15
34.21
F
Br
N
H
S
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

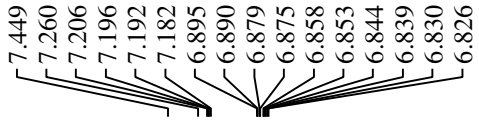
3n

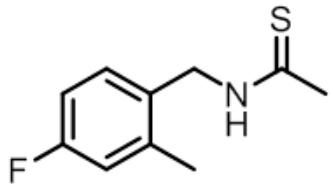

7.578
7.483
7.470
7.260
7.179
7.177
6.996
6.993
6.983
6.980
4.723
4.714
2.551
2.368
-0.013
S
N
H
Br
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
1.00
1.02
1.00
2.10
3.13
3.14

3o

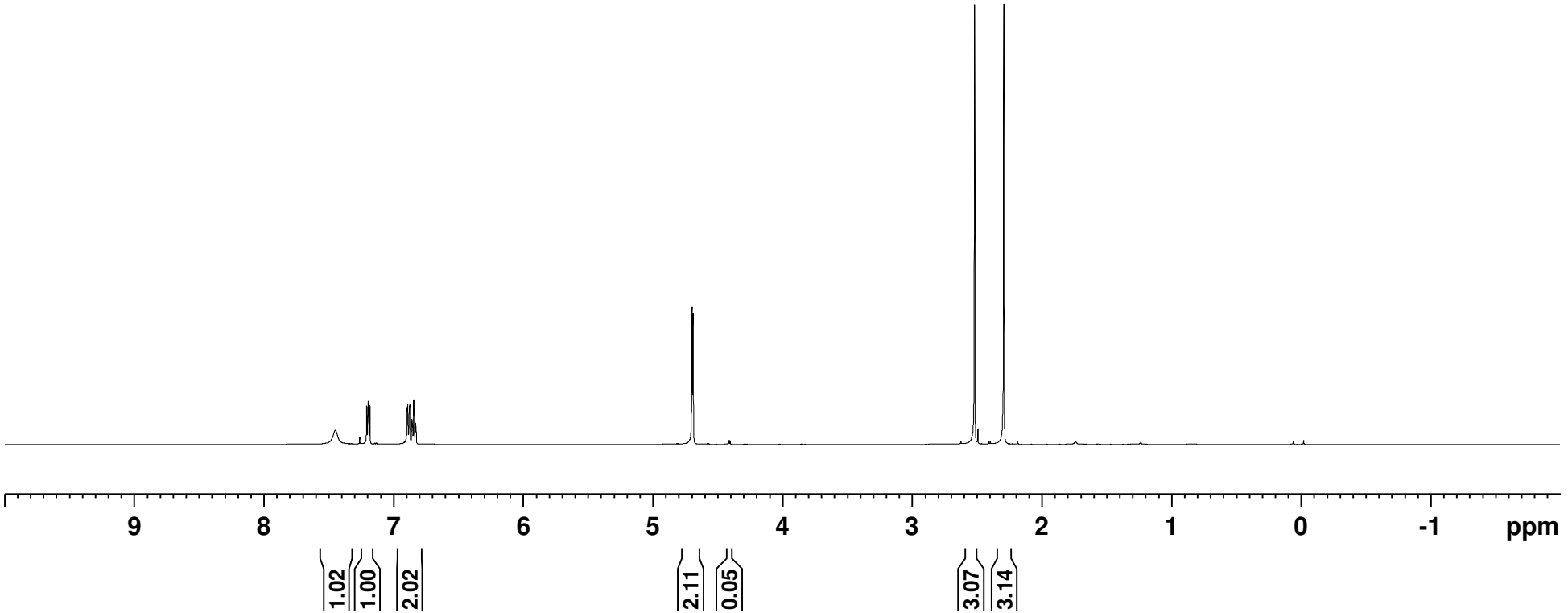

201.10
138.60
135.36
132.83
130.80
127.28
124.58
77.37
77.16
76.94
49.79
34.15
22.97
S
N
H
Br
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

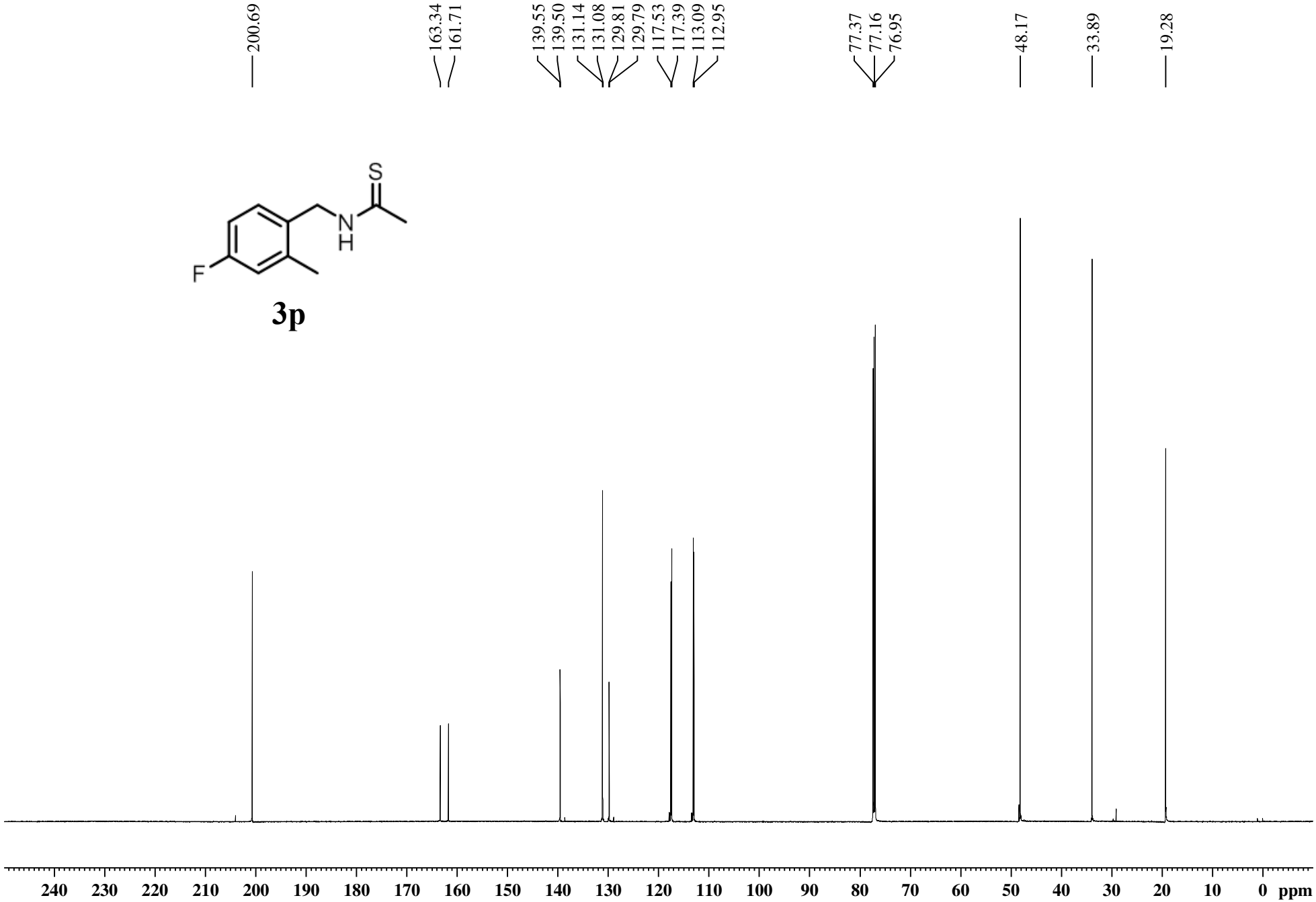
3o


7.449
7.260
7.206
7.196
7.192
7.182
6.895
6.890
6.879
6.875
6.858
6.853
6.844
6.839
6.830
6.826
4.697
4.689
4.414
4.404
2.517
2.291

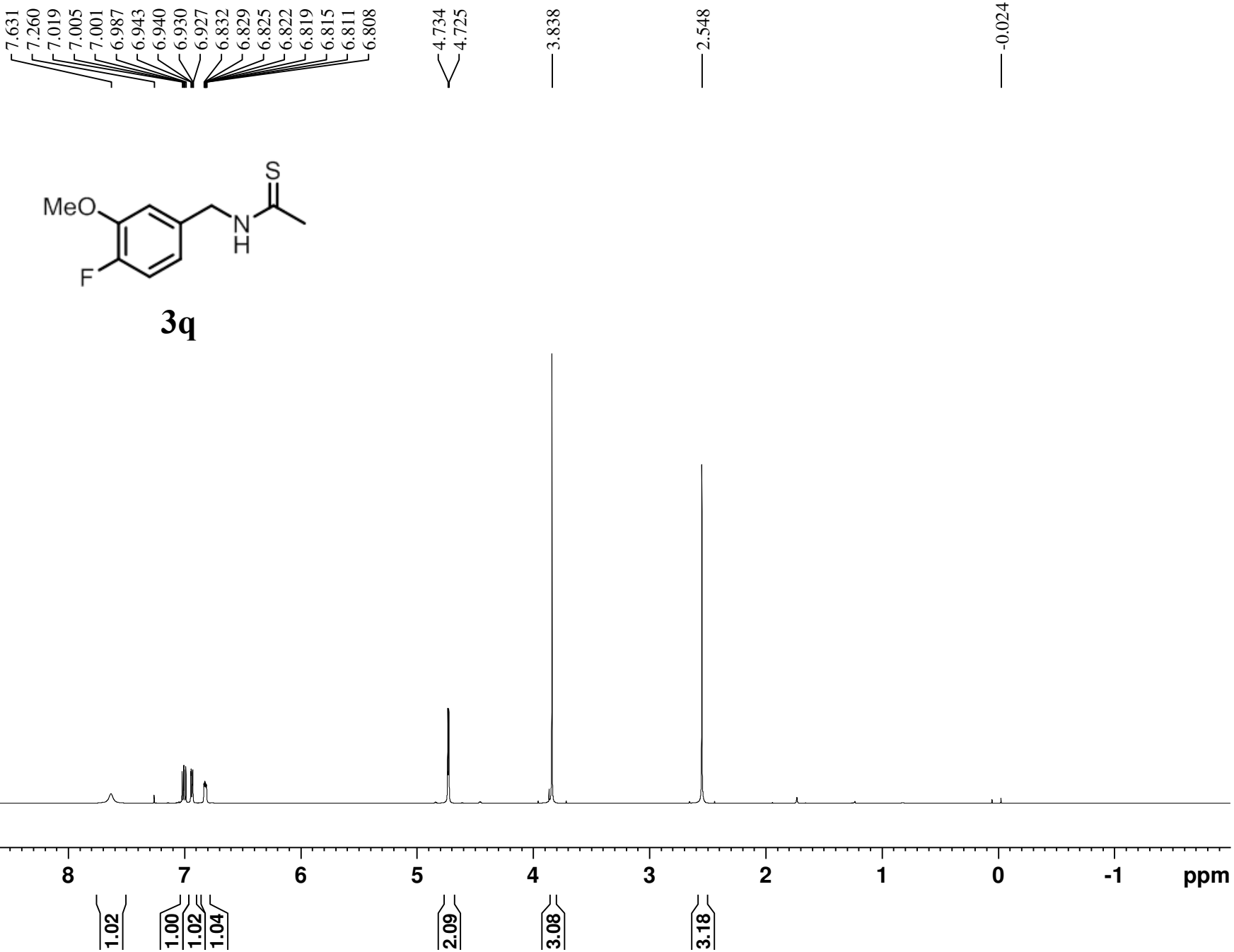

S
N
H
F

3p

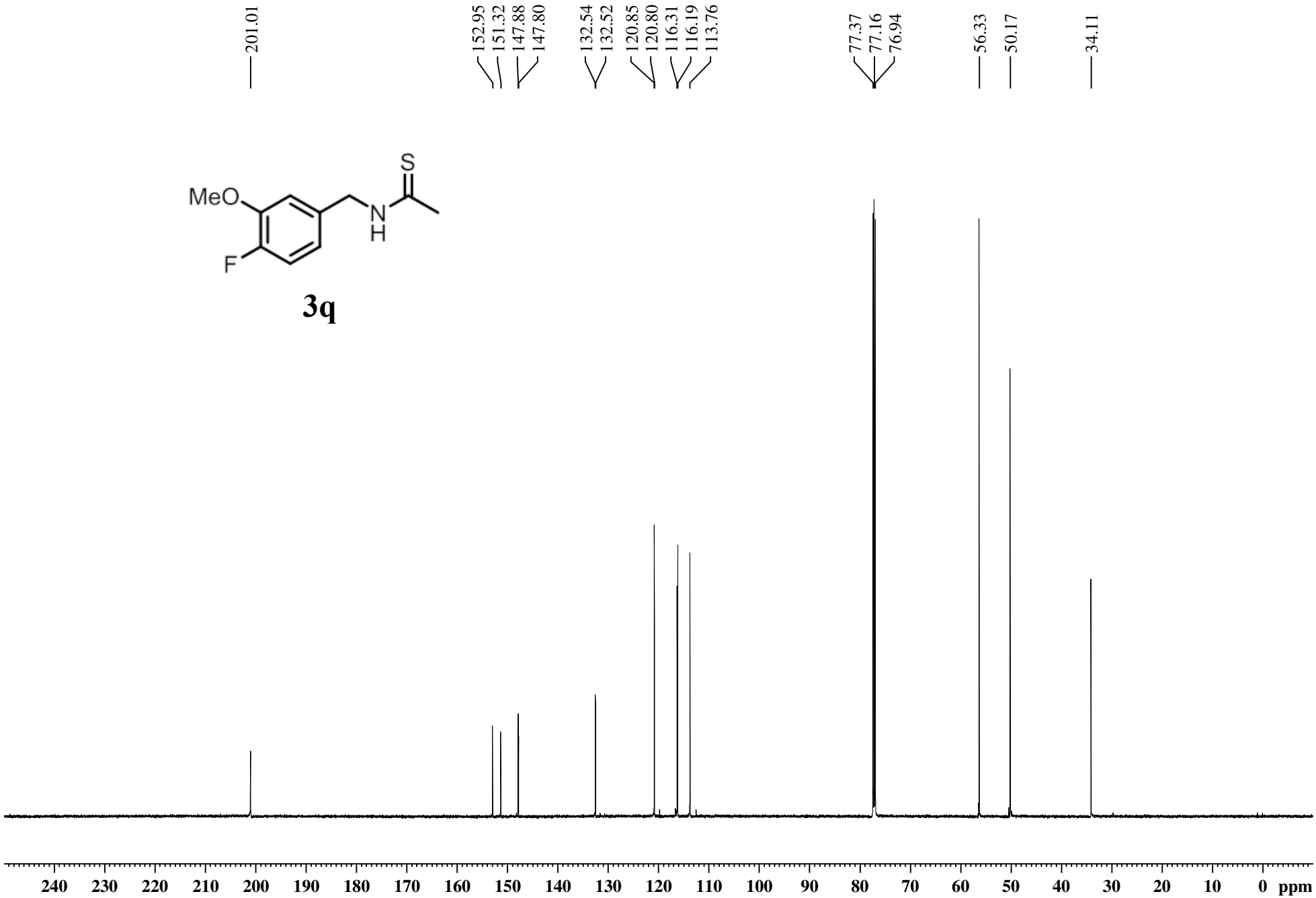

9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.00
2.02
2.11
0.05
3.07
3.14


200.69
163.34
161.71
139.55
139.50
131.14
131.08
129.81
129.79
117.53
117.39
113.09
112.95
77.37
77.16
76.95
48.17
33.89
19.28
S
N
H
F
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

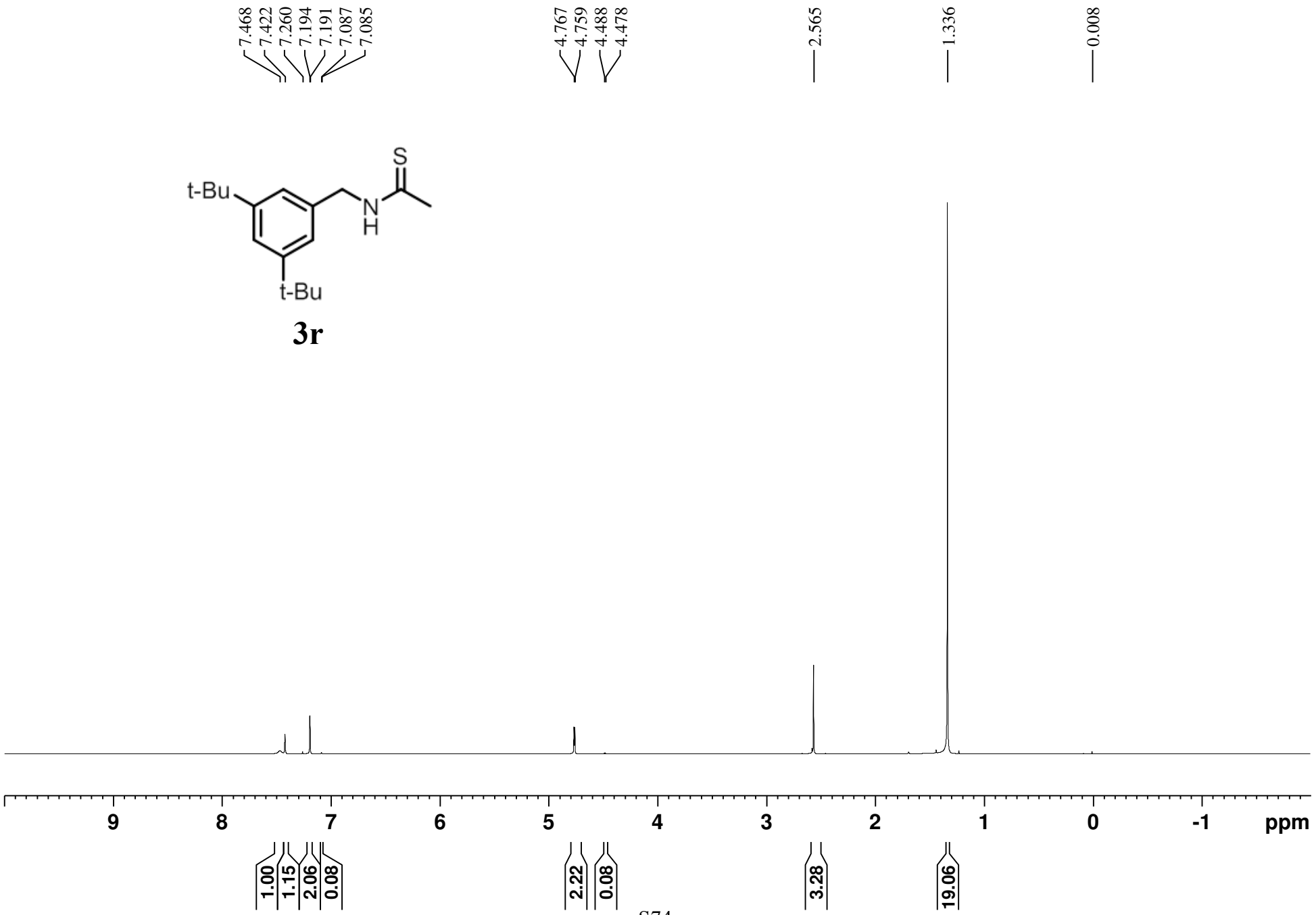
3p


7.631
7.260
7.019
7.005
7.001
6.987
6.943
6.940
6.930
6.927
6.832
6.829
6.825
6.822
6.819
6.815
6.811
6.808
4.734
4.725
3.838
2.548
-0.024
MeO
F
N
H
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.00
1.02
1.04
2.09
3.08
3.18

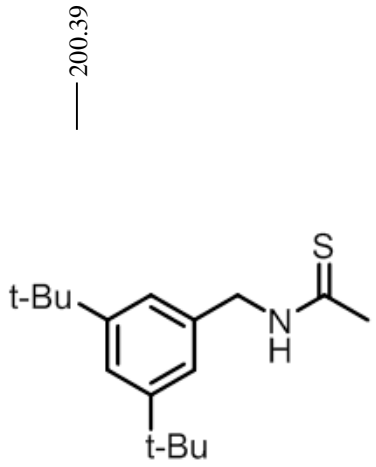
3q


201.01
152.95
151.32
147.88
147.80
132.54
132.52
120.85
120.80
116.31
116.19
113.76
77.37
77.16
76.94
56.33
50.17
34.11
MeO
F
N
H
S
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3q

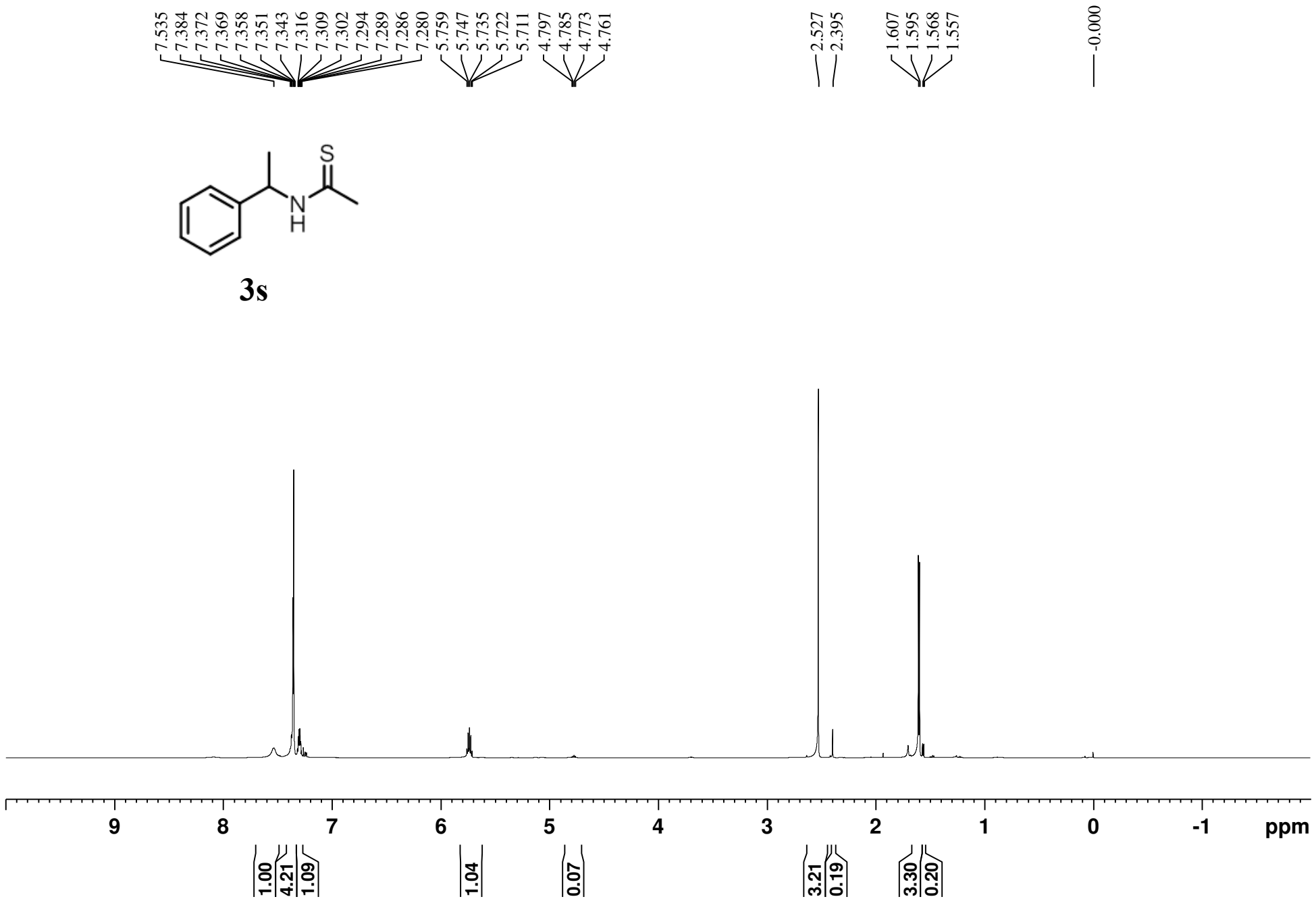

7.468
7.422
7.260
7.194
7.191
7.087
7.085
4.767
4.759
4.488
4.478
2.565
1.336
0.008
t-Bu
t-Bu
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.15
2.06
0.08
2.22
0.08
3.28
19.06

3r

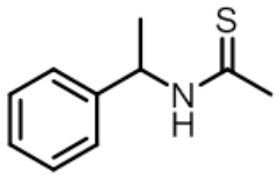

t-Bu
t-Bu
S
N
H

3r

200.39
151.74
135.18
123.02
122.46
77.37
77.16
76.95
51.70
34.95
34.14
31.50
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

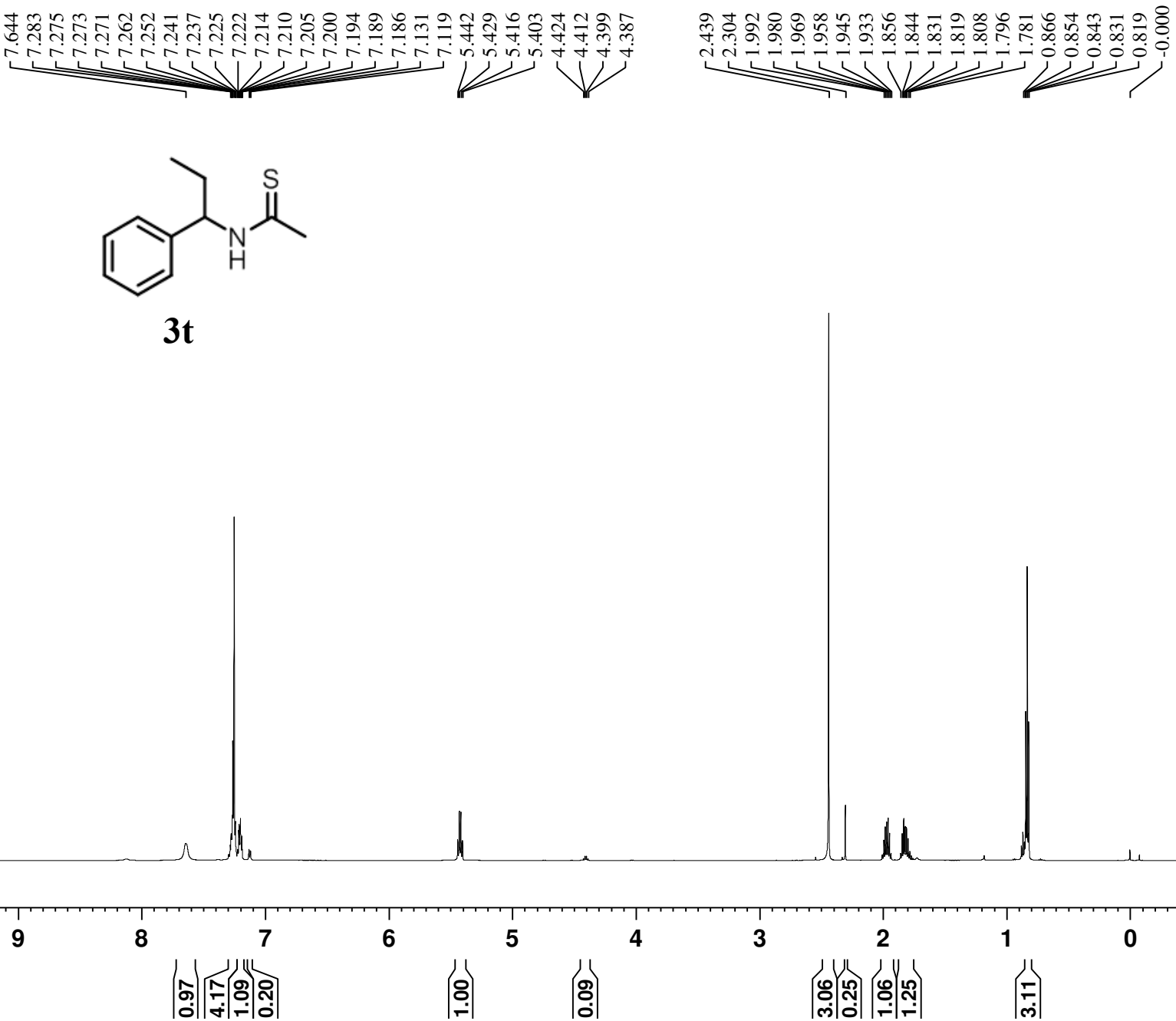

7.535
7.384
7.372
7.369
7.358
7.351
7.343
7.316
7.309
7.302
7.294
7.289
7.286
7.280
5.759
5.747
5.735
5.722
5.711
4.797
4.785
4.773
4.761
2.527
2.395
1.607
1.595
1.568
1.557
-0.000
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
4.21
1.09
1.04
0.07
3.21
0.19
3.30
0.20

3s

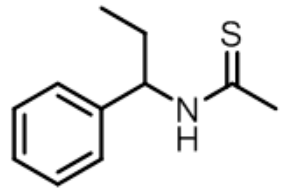

S
N
H

3s

199.63
141.29
128.91
127.96
126.67
77.37
77.16
76.95
54.90
34.54
20.01
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

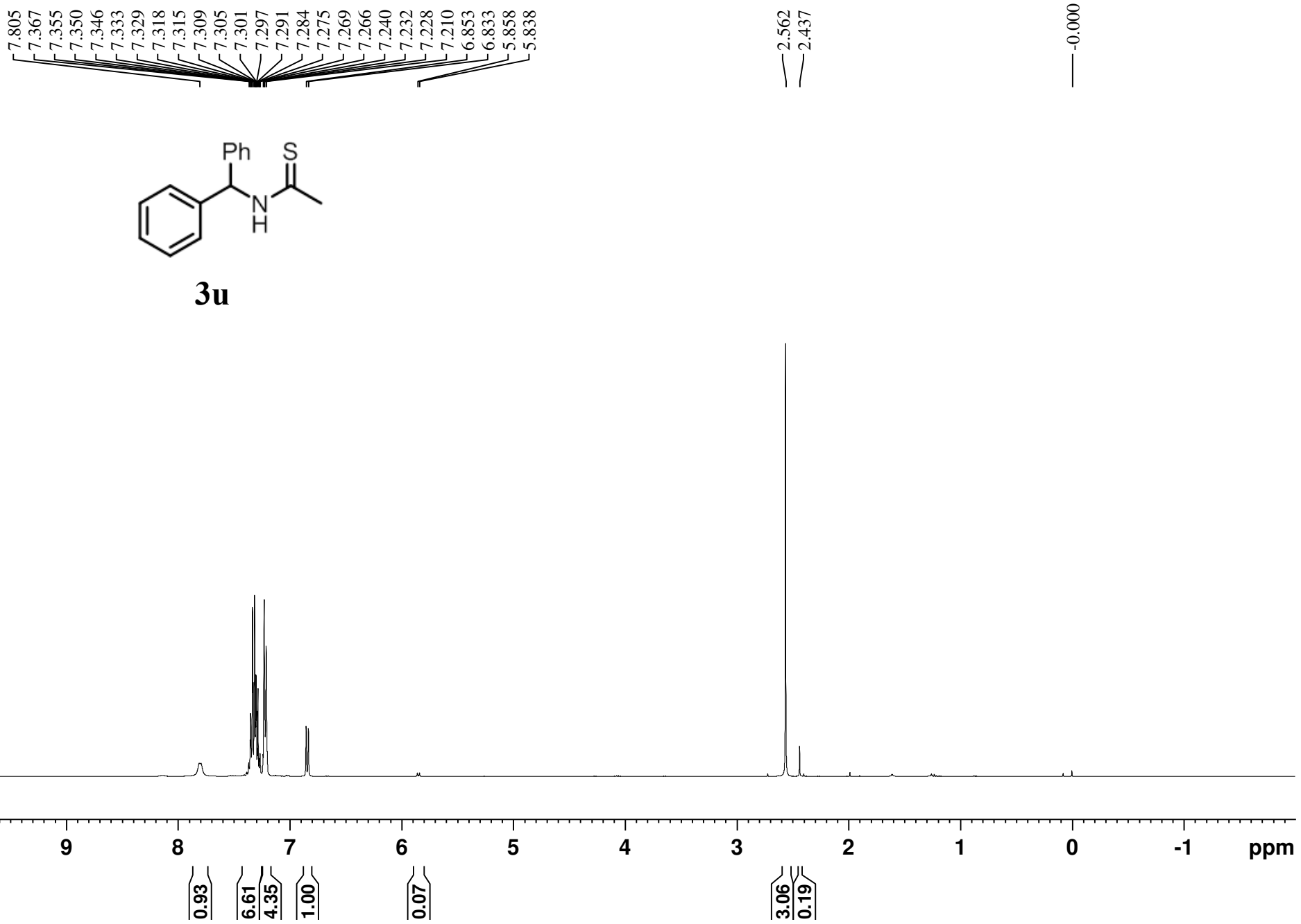

7.644
7.283
7.275
7.273
7.271
7.262
7.252
7.241
7.237
7.225
7.222
7.214
7.210
7.205
7.200
7.194
7.189
7.186
7.131
7.119
5.442
5.429
5.416
5.403
4.424
4.412
4.399
4.387
2.439
2.304
1.992
1.980
1.969
1.958
1.945
1.933
1.856
1.844
1.831
1.819
1.808
1.796
1.781
0.866
0.854
0.843
0.831
0.819
-0.000
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
4.17
1.09
0.20
1.00
0.09
3.06
0.25
1.06
1.25
3.11

3t

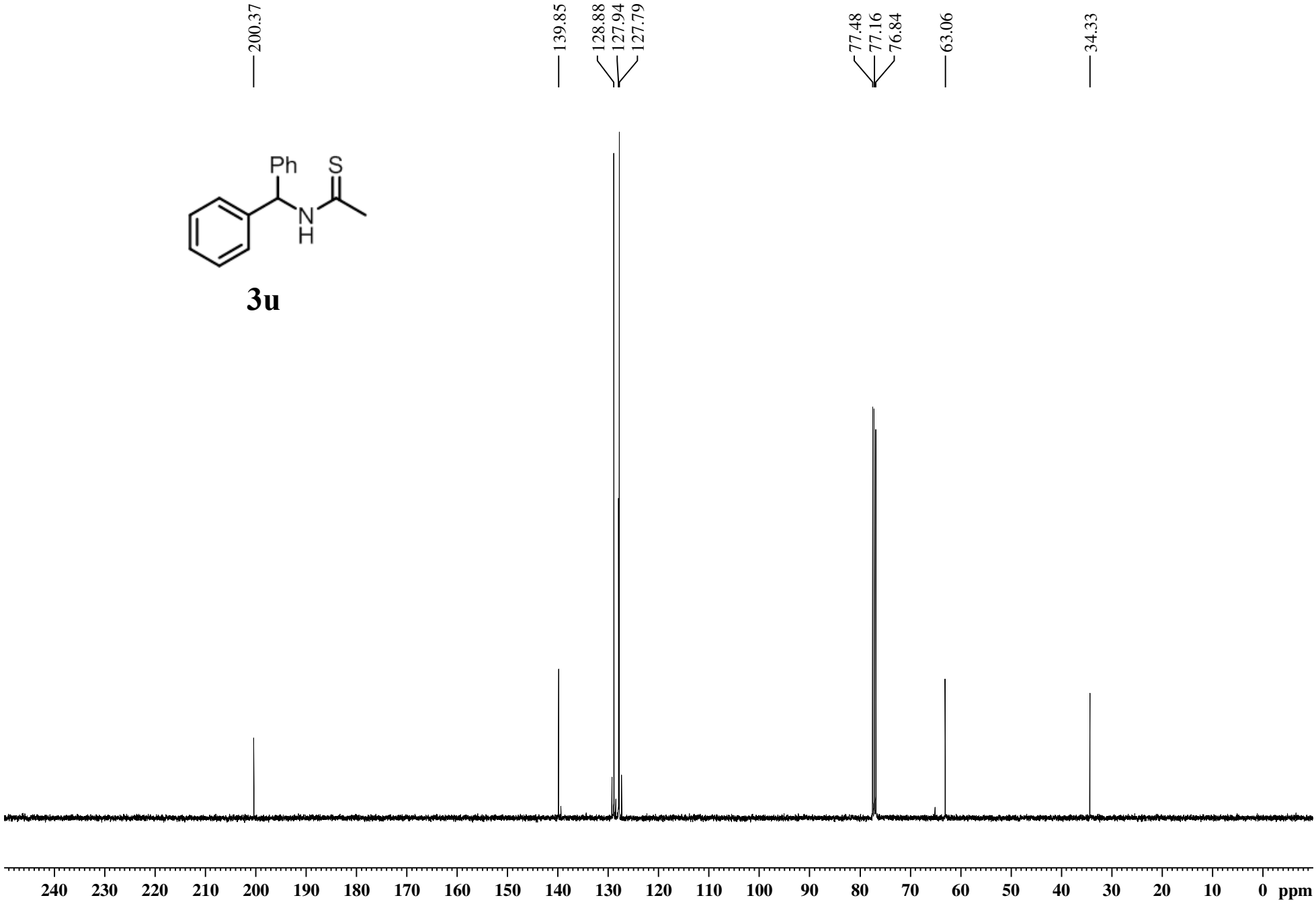

S
N
H

3t

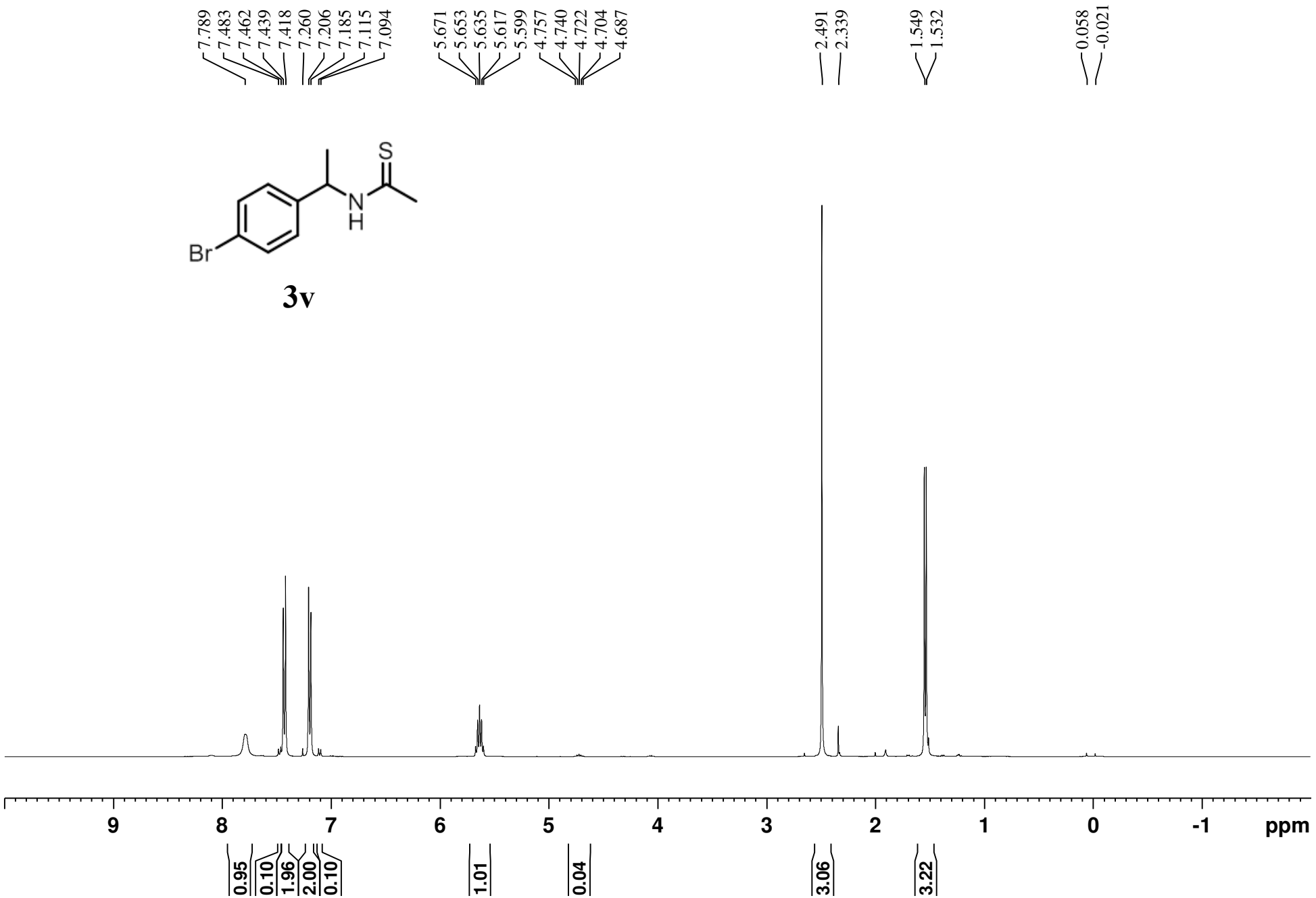
199.93
140.10
128.78
127.83
127.18
77.37
77.16
76.95
61.12
34.43
27.93
10.68
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.805
7.367
7.355
7.350
7.346
7.333
7.329
7.318
7.315
7.309
7.305
7.301
7.297
7.291
7.284
7.275
7.269
7.266
7.240
7.232
7.228
7.210
6.853
6.833
5.858
5.838
2.562
2.437
-0.000
Ph
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.93
6.61
4.35
1.00
0.07
3.06
0.19

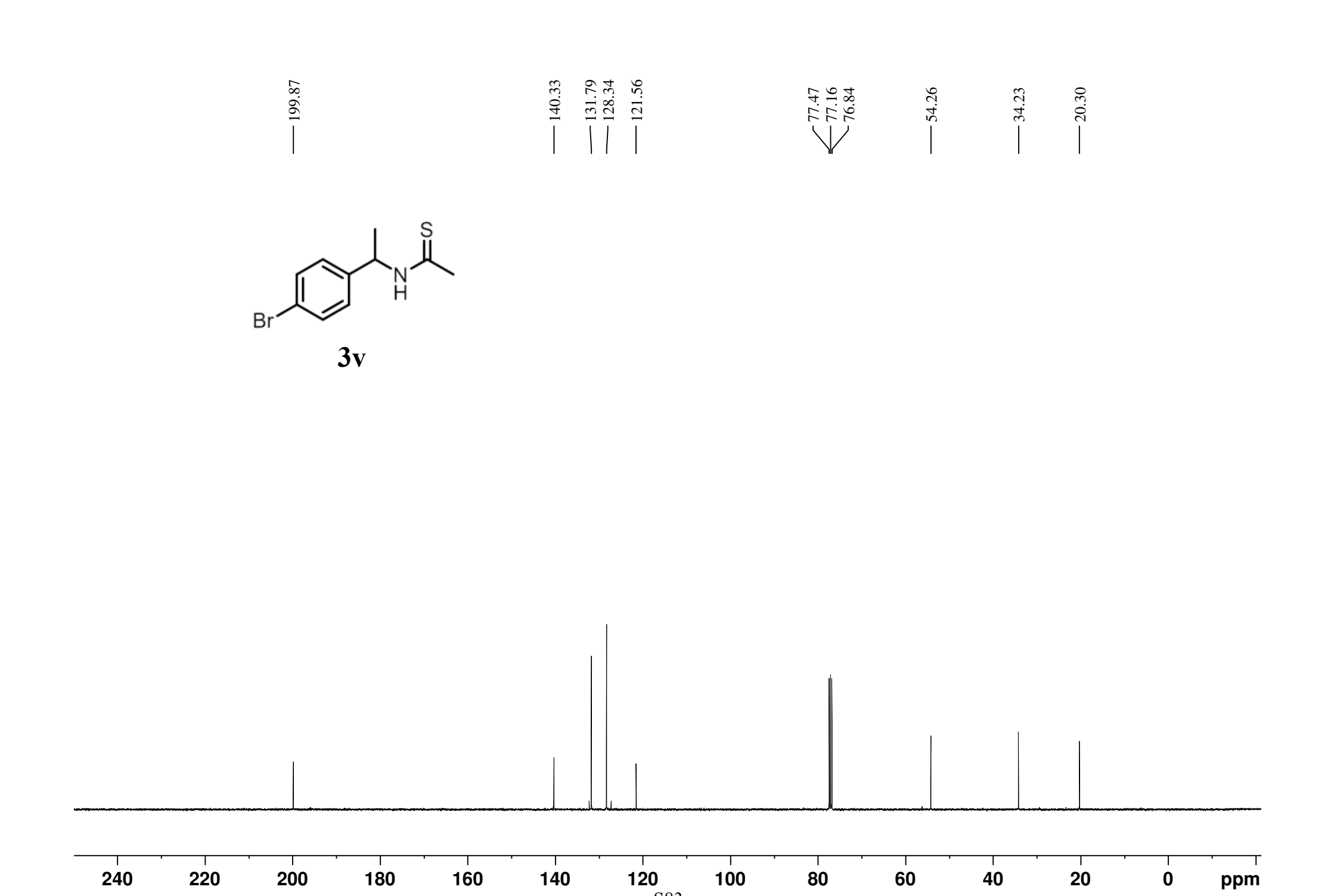
3u


200.37
139.85
128.88
127.94
127.79
77.48
77.16
76.84
63.06
34.33
Ph
S
N
H
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

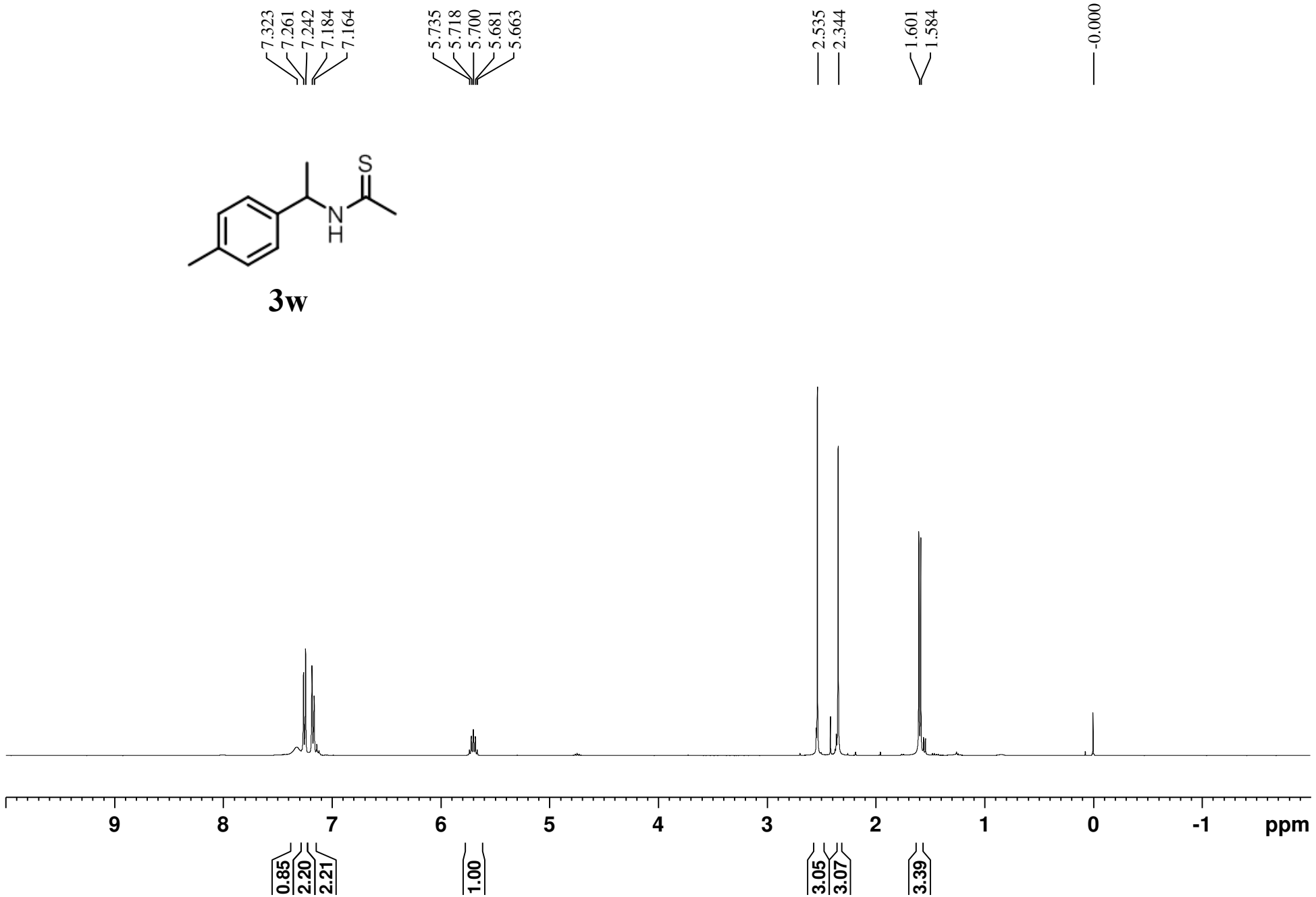
3u

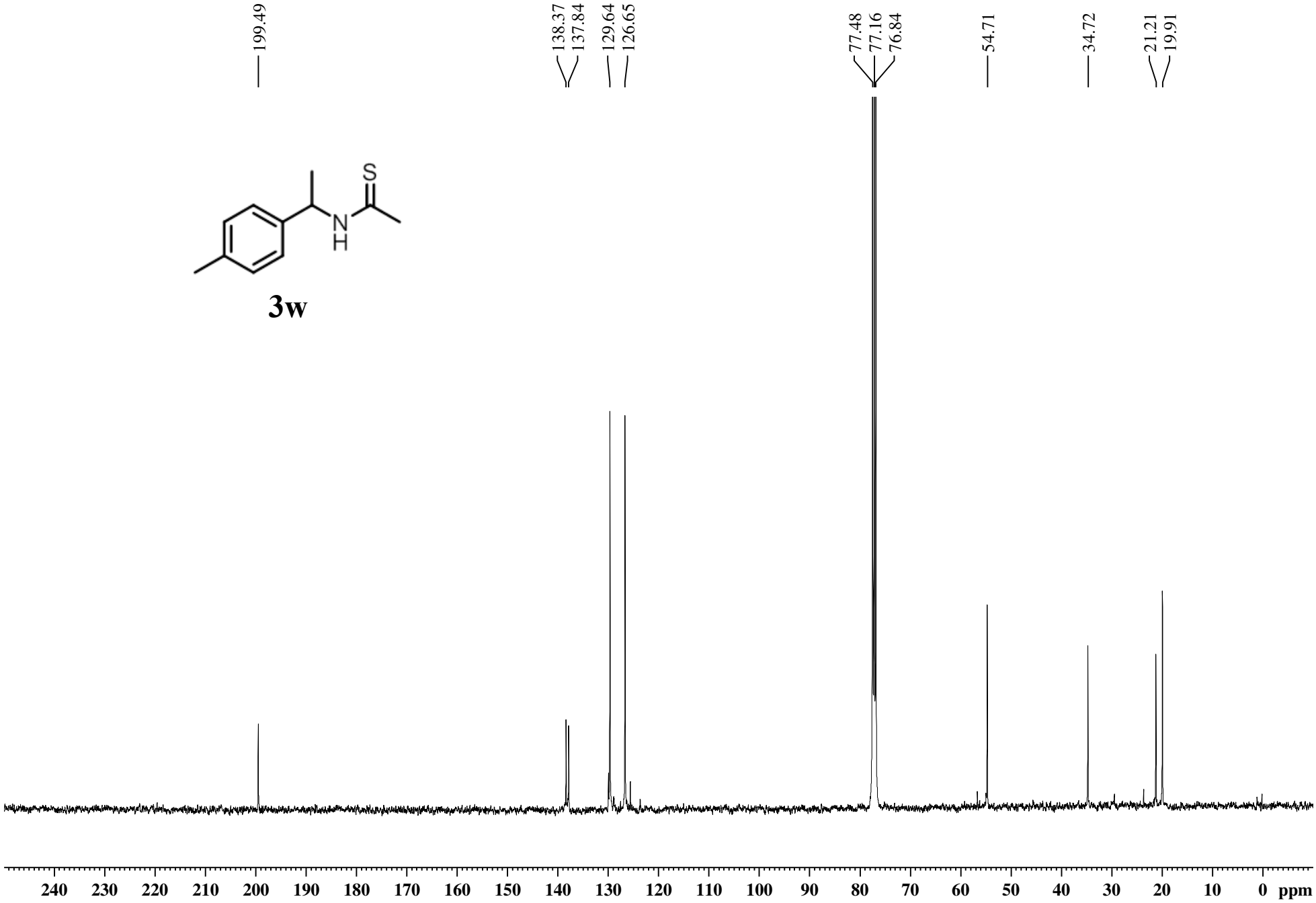

7.789
7.483
7.462
7.439
7.418
7.260
7.206
7.185
7.115
7.094
5.671
5.653
5.635
5.617
5.599
4.757
4.740
4.722
4.704
4.687
2.491
2.339
1.549
1.532
0.058
-0.021
S
N
H
Br
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
0.10
1.96
2.00
0.10
1.01
0.04
3.06
3.22

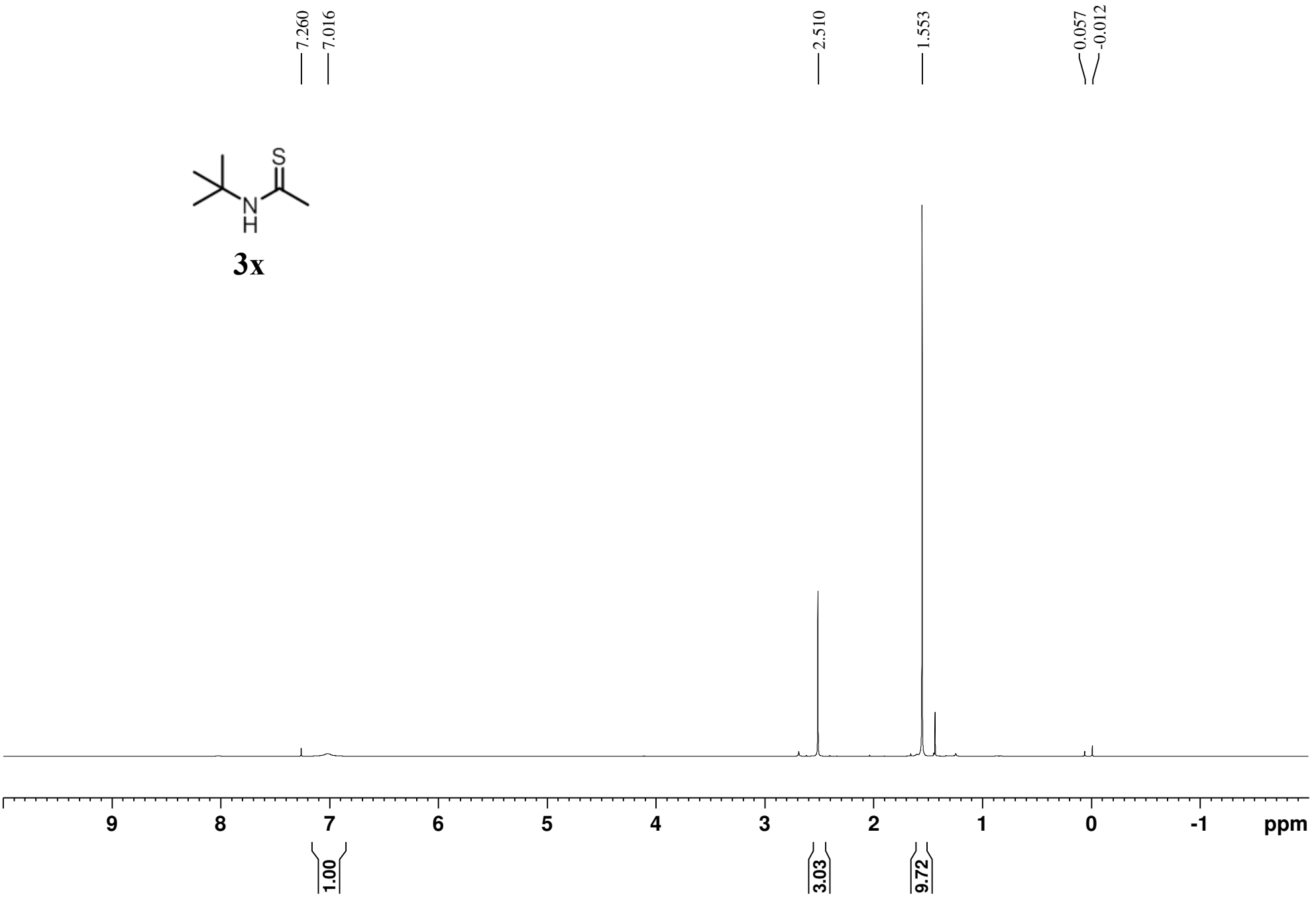
3v

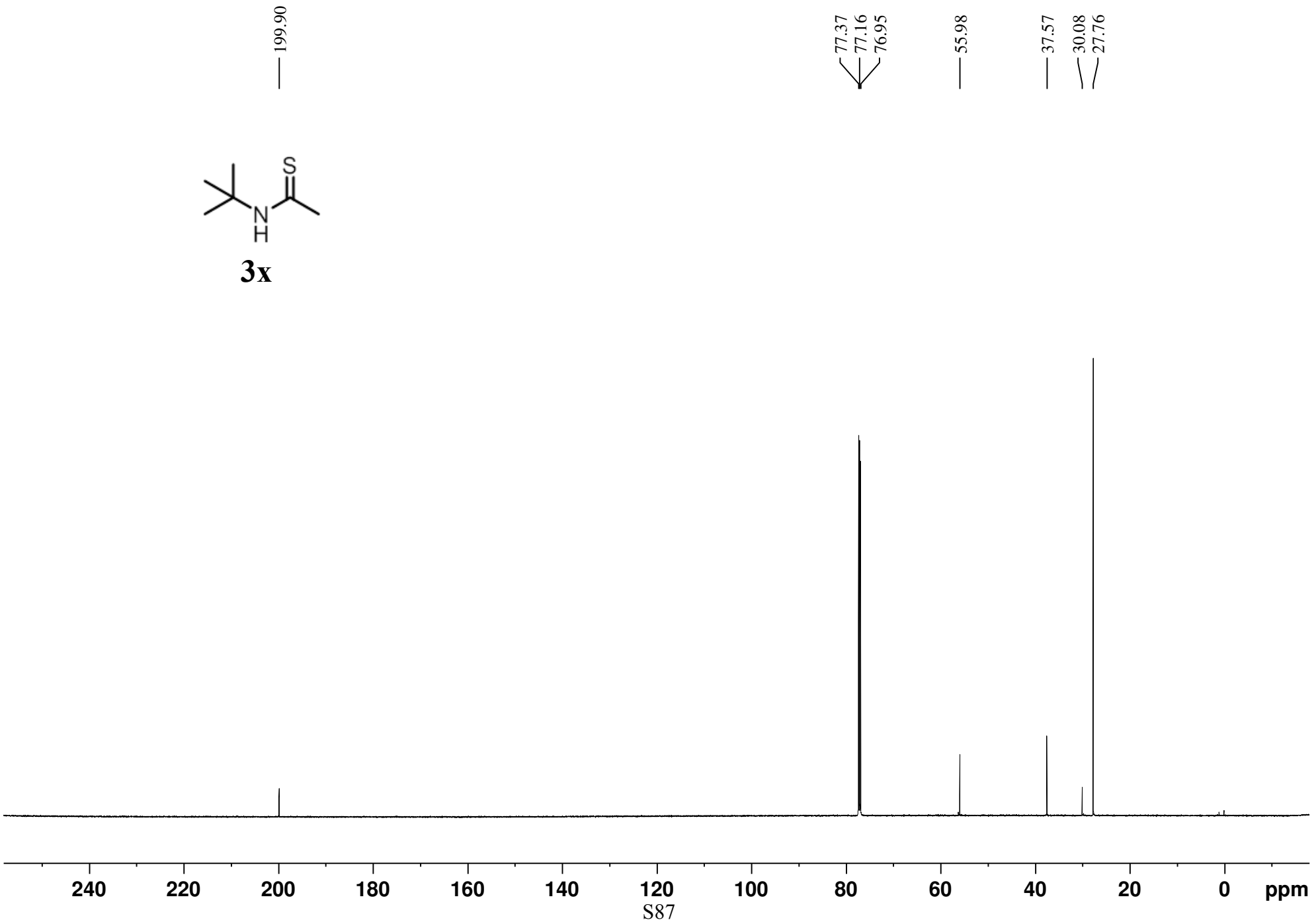

199.87
140.33
131.79
128.34
121.56
77.47
77.16
76.84
54.26
34.23
20.30
S
N
H
Br
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3v

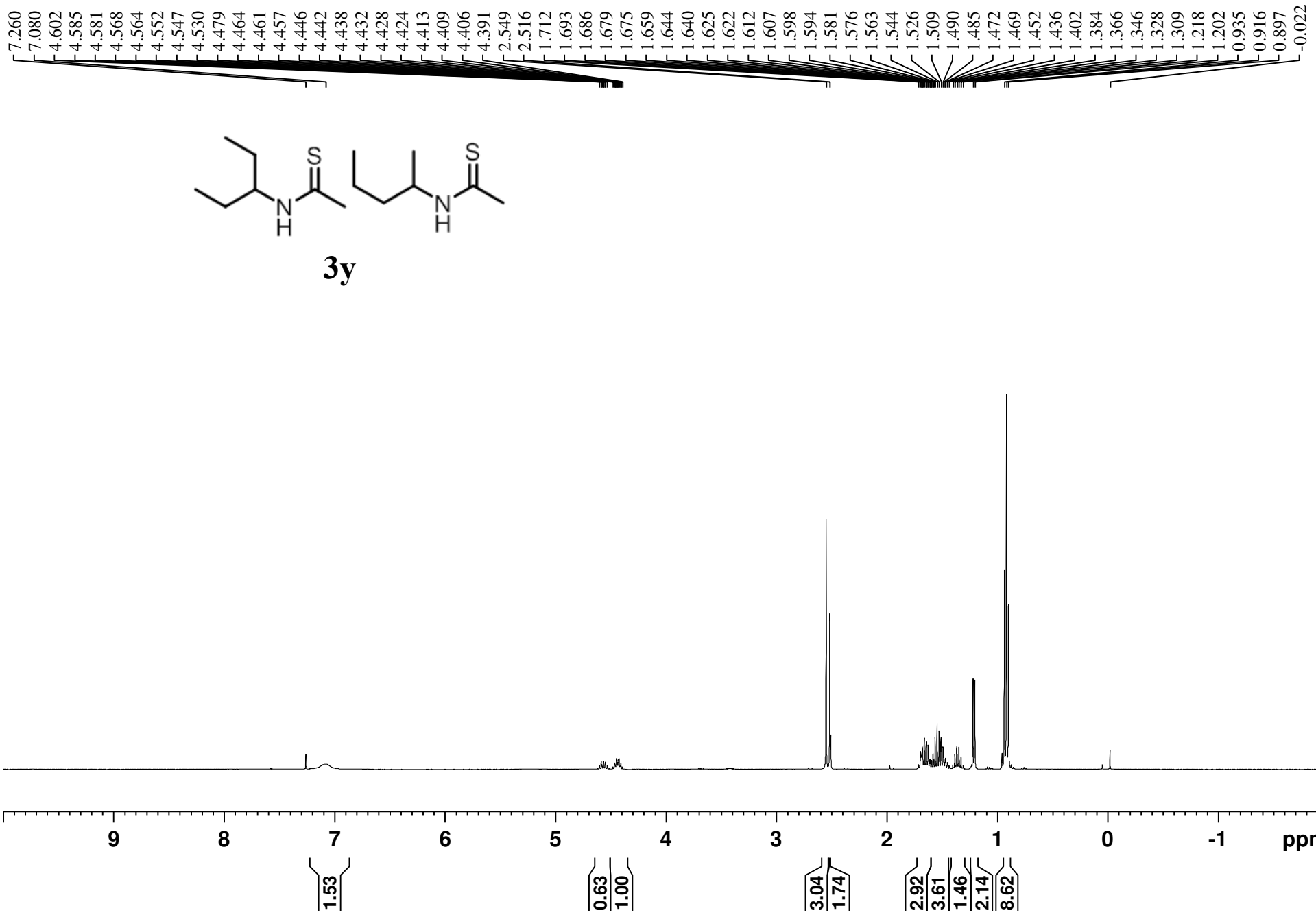

7.323
7.261
7.242
7.184
7.164
5.735
5.718
5.700
5.681
5.663
2.535
2.344
1.601
1.584
-0.000
S
N
H
3w
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.85
2.20
2.21
1.00
3.05
3.07
3.39


199.49
138.37
137.84
129.64
126.65
77.48
77.16
76.84
54.71
34.72
21.21
19.91
S
N
H
3w
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

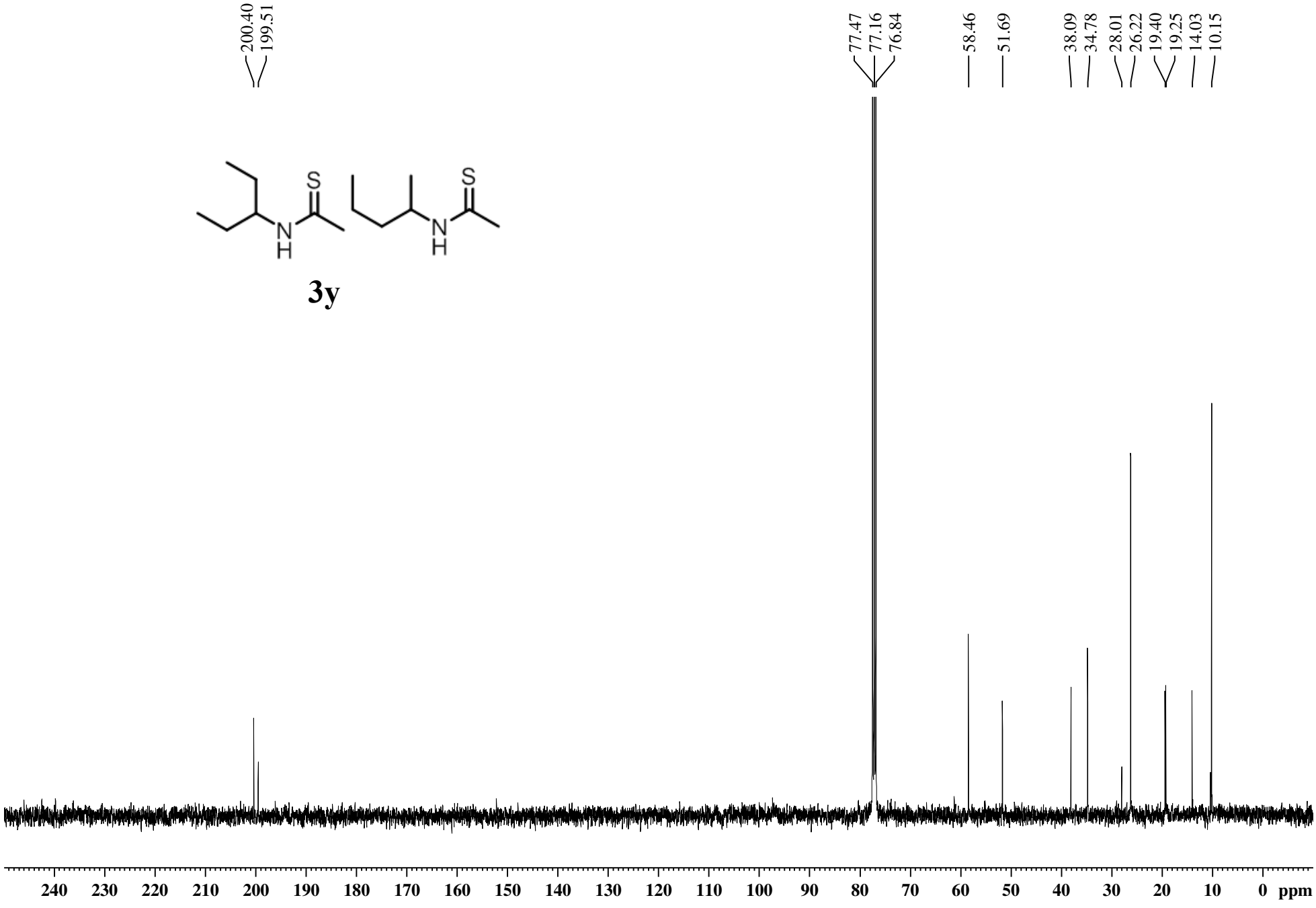

7.260
7.016
2.510
1.553
0.057
-0.012
S
N
H
3x
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
3.03
9.72


199.90
77.37
77.16
76.95
55.98
37.57
30.08
27.76
S
N
H
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

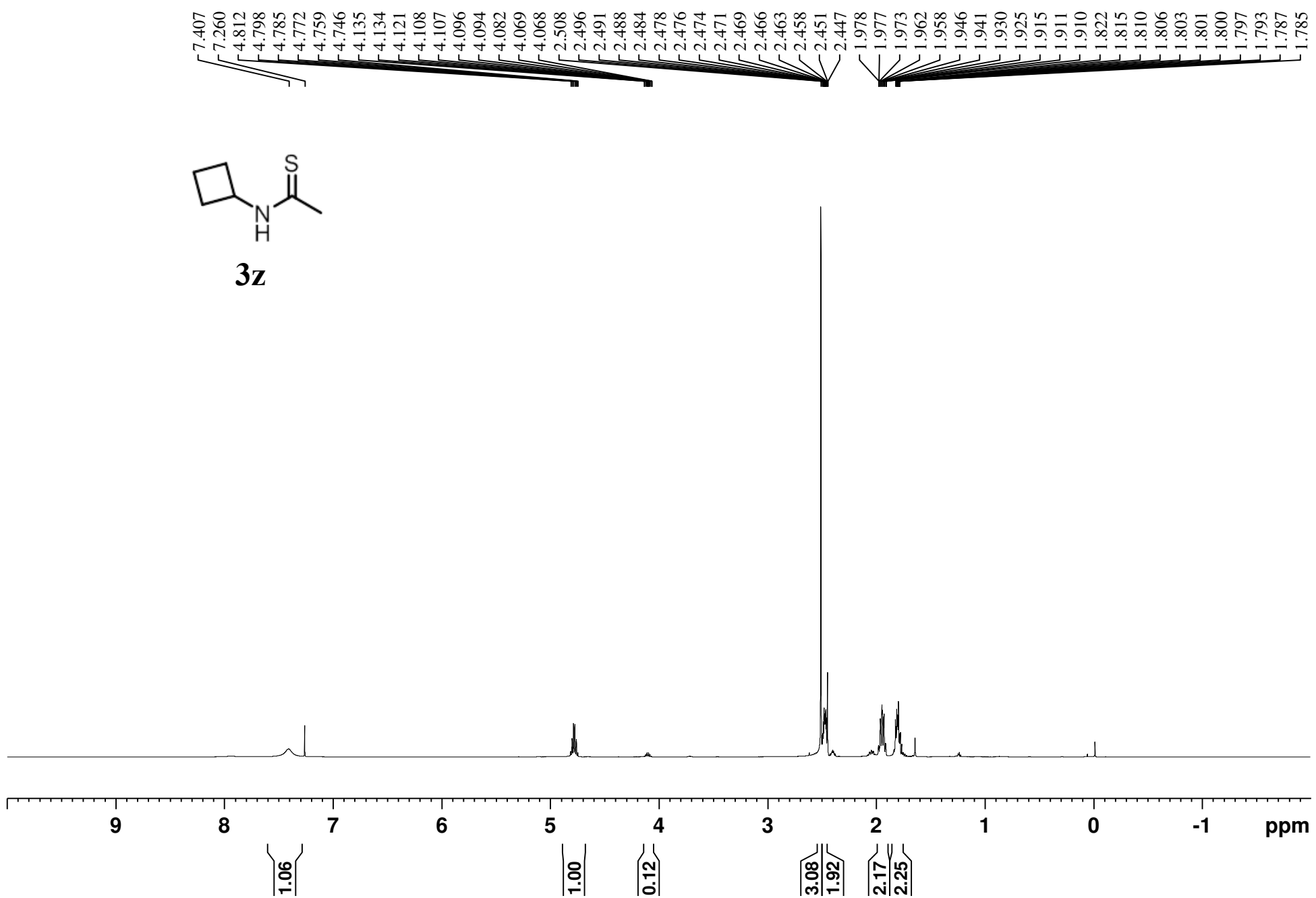
3x


7.260
7.080
4.602
4.585
4.581
4.568
4.564
4.552
4.547
4.530
4.479
4.464
4.461
4.457
4.446
4.442
4.438
4.432
4.428
4.424
4.413
4.409
4.406
4.391
2.549
2.516
1.712
1.693
1.686
1.679
1.675
1.659
1.644
1.640
1.625
1.622
1.612
1.607
1.598
1.594
1.581
1.576
1.563
1.544
1.526
1.509
1.490
1.485
1.472
1.469
1.452
1.436
1.402
1.384
1.366
1.346
1.328
1.309
1.218
1.202
0.935
0.916
0.897
-0.022
S
N
H
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.53
0.63
1.00
3.04
1.74
2.92
3.61
1.46
2.14
8.62

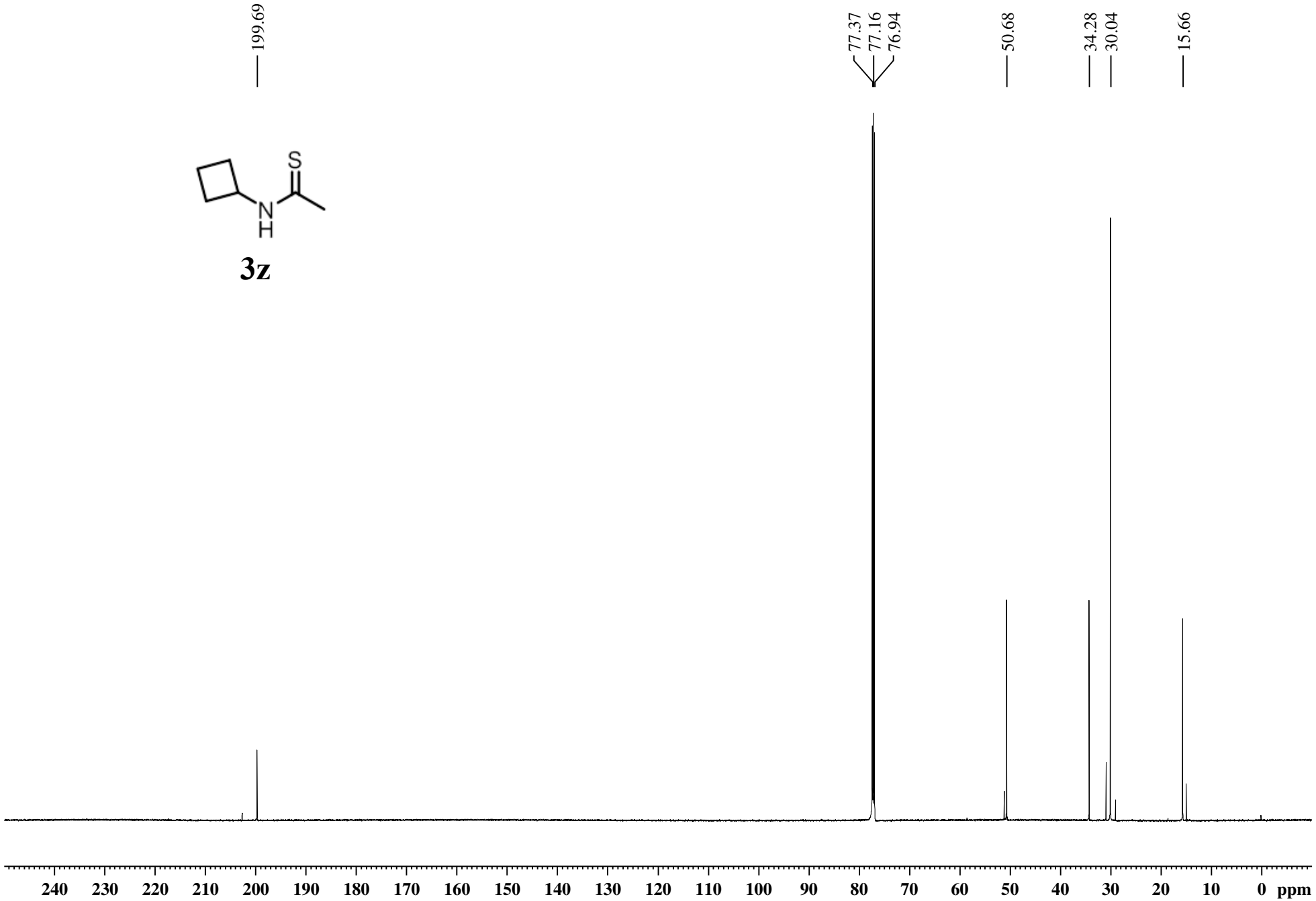
3y


200.40
199.51
77.47
77.16
76.84
58.46
51.69
38.09
34.78
28.01
26.22
19.40
19.25
14.03
10.15
S
N
H
S
N
H
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

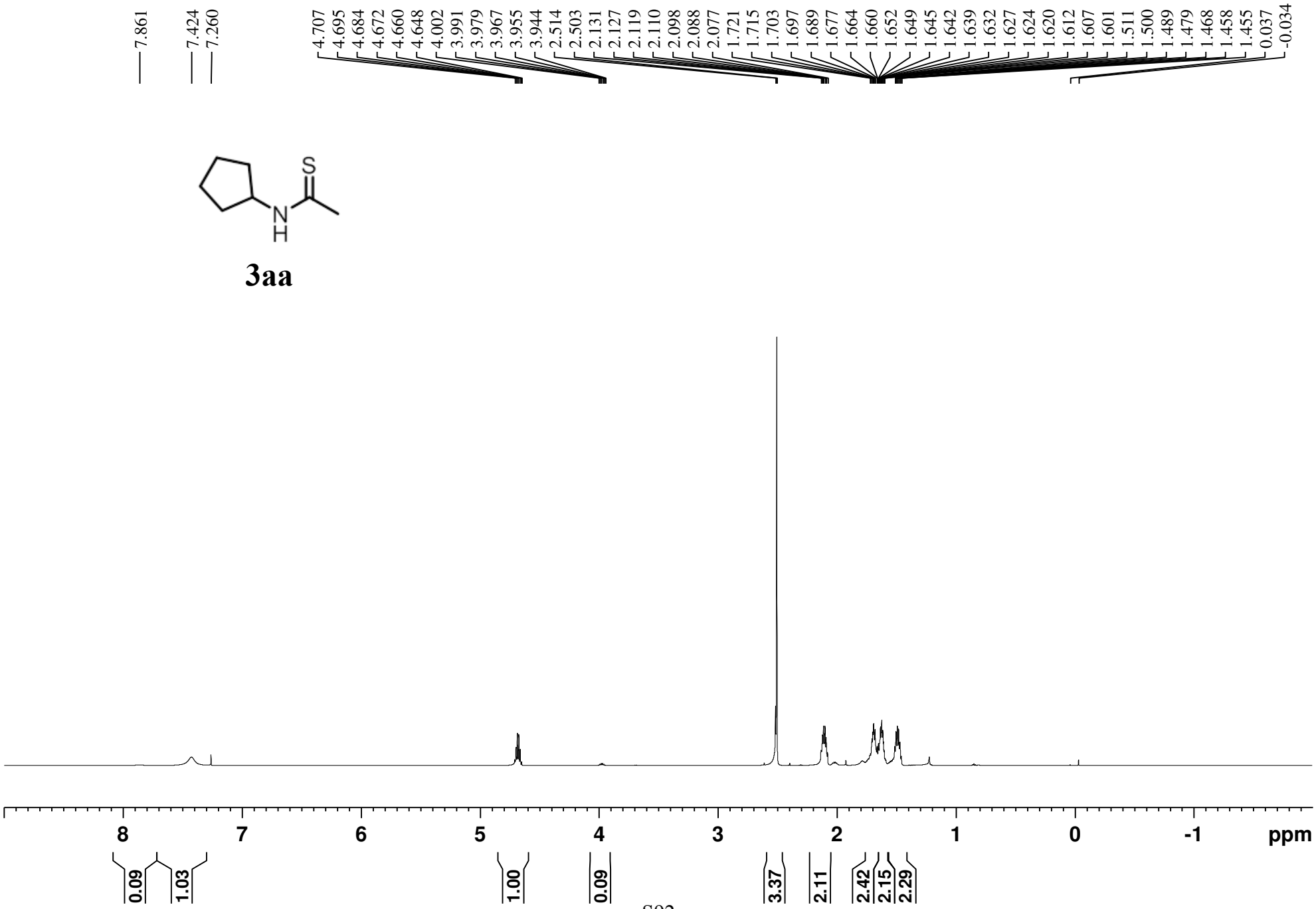
3y


7.407
7.260
4.812
4.798
4.785
4.772
4.759
4.746
4.135
4.134
4.121
4.108
4.107
4.096
4.094
4.082
4.069
4.068
2.508
2.496
2.491
2.488
2.484
2.478
2.476
2.474
2.471
2.469
2.466
2.463
2.458
2.451
2.447
1.978
1.977
1.973
1.962
1.958
1.946
1.941
1.930
1.925
1.915
1.911
1.910
1.822
1.815
1.810
1.806
1.803
1.801
1.800
1.797
1.793
1.787
1.785
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.06
1.00
0.12
3.08
1.92
2.17
2.25

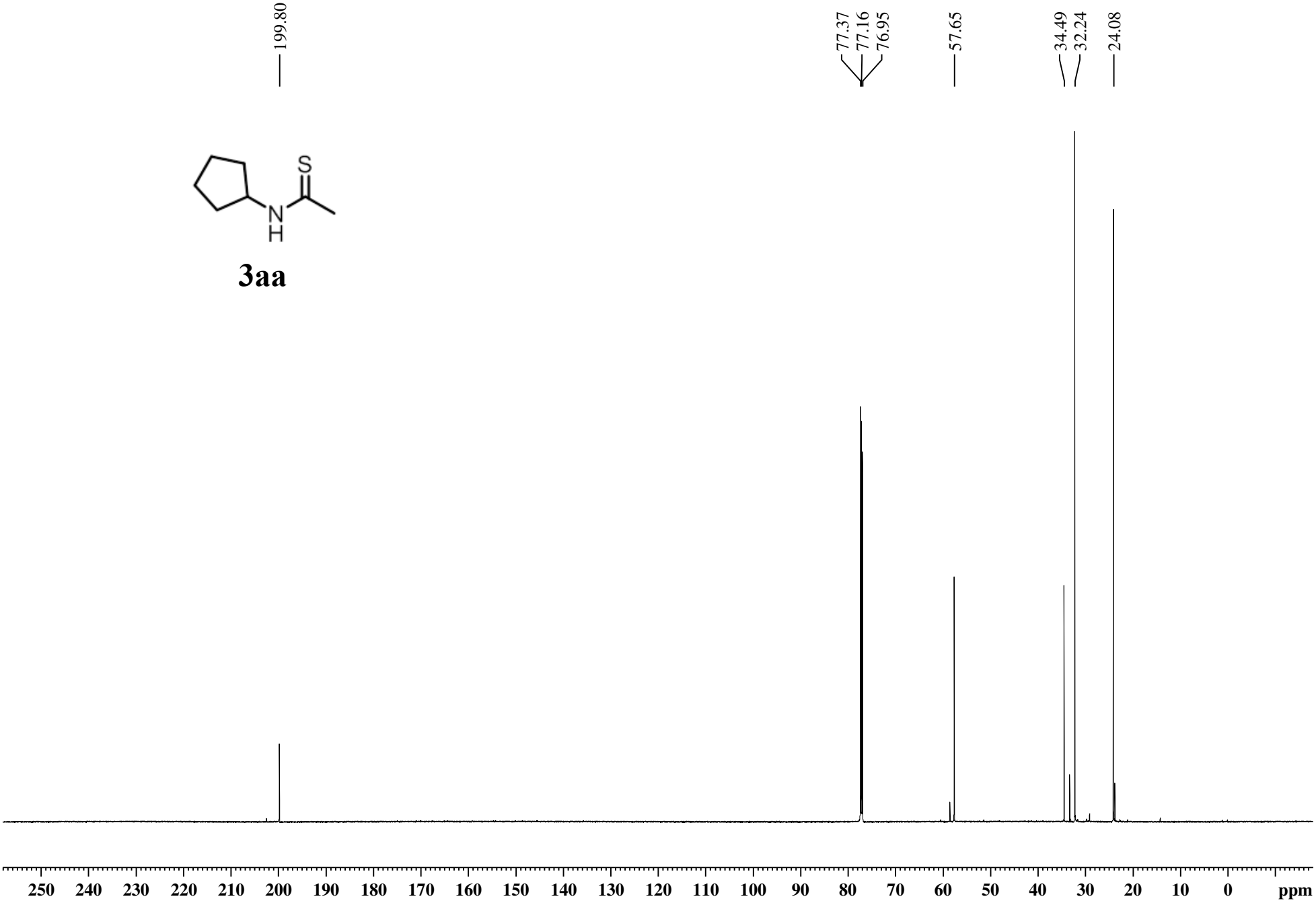
3z


199.69
77.37
77.16
76.94
50.68
34.28
30.04
15.66
S
N
H
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

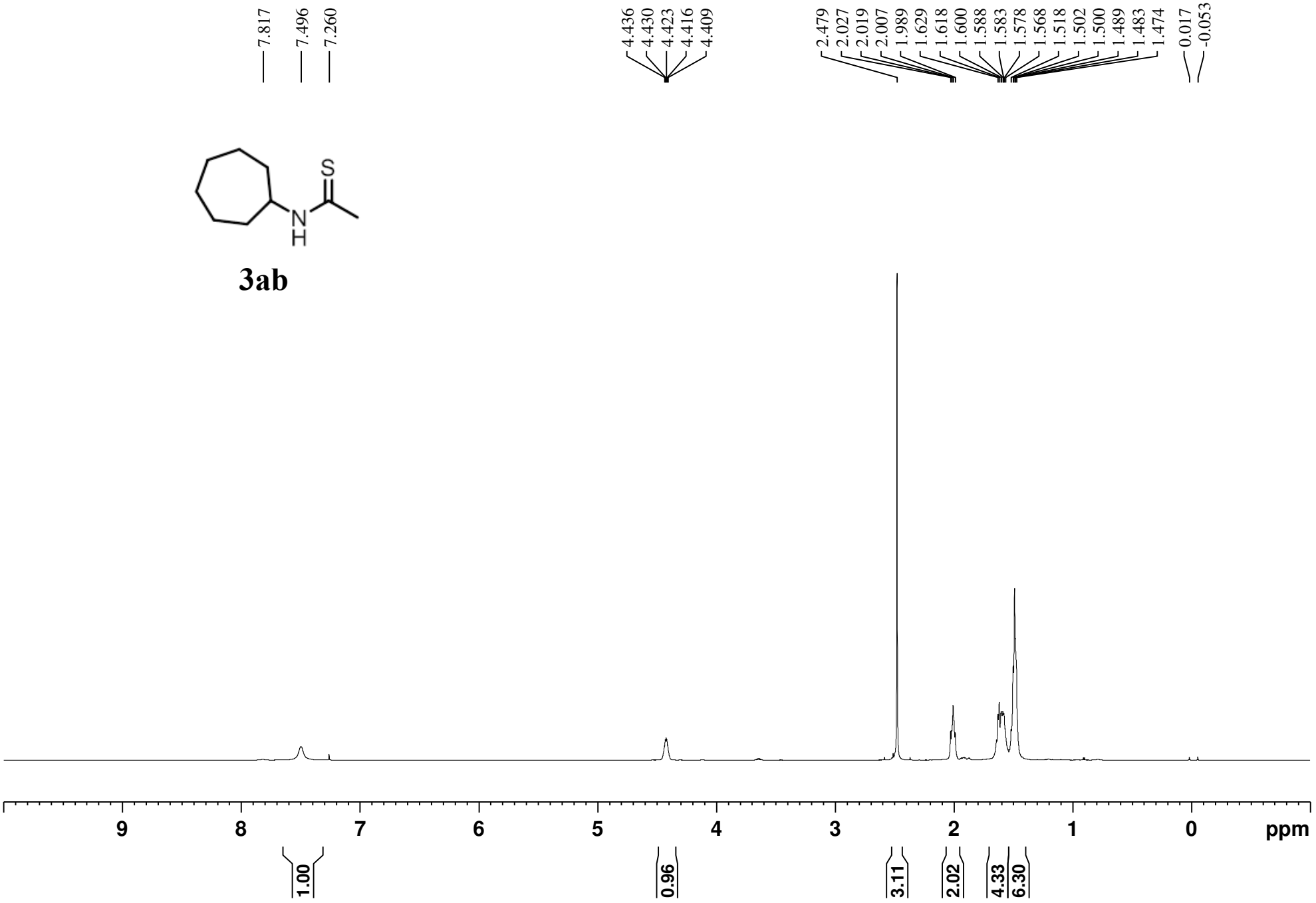
3z

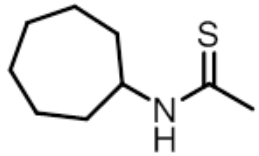

7.861
7.424
7.260
4.707
4.695
4.684
4.672
4.660
4.648
4.002
3.991
3.979
3.967
3.955
3.944
2.514
2.503
2.131
2.127
2.119
2.110
2.098
2.088
2.077
1.721
1.715
1.703
1.697
1.689
1.677
1.664
1.660
1.652
1.649
1.645
1.642
1.639
1.632
1.627
1.624
1.620
1.612
1.607
1.601
1.511
1.500
1.489
1.479
1.468
1.458
1.455
0.037
-0.034
S
N
H
8
7
6
5
4
3
2
1
0
-1
ppm
0.09
1.03
1.00
0.09
3.37
2.11
2.42
2.15
2.29

3aa


199.80
77.37
77.16
76.95
57.65
34.49
32.24
24.08
S
N
H
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

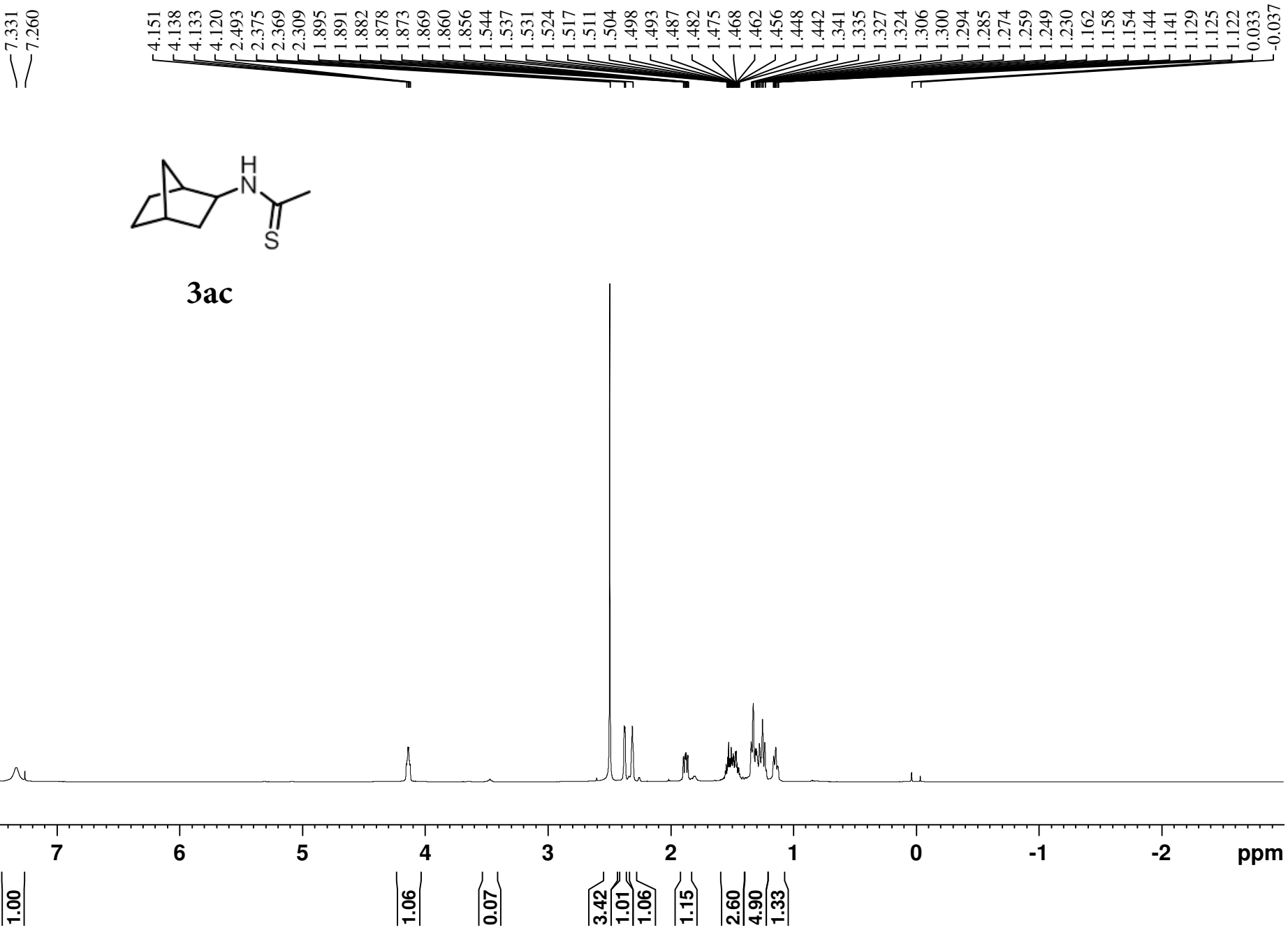
3aa


7.817
7.496
7.260
4.436
4.430
4.423
4.416
4.409
2.479
2.027
2.019
2.007
1.989
1.629
1.618
1.600
1.588
1.583
1.578
1.568
1.518
1.502
1.500
1.489
1.483
1.474
0.017
-0.053
S
N
H
3ab
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.96
3.11
2.02
4.33
6.30


S
N
H

3ab

198.35
77.37
77.16
76.95
56.91
34.47
33.64
28.02
24.23
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.331
7.260
4.151
4.138
4.133
4.120
2.493
2.375
2.369
2.309
1.895
1.891
1.882
1.878
1.873
1.869
1.860
1.856
1.544
1.537
1.531
1.524
1.517
1.511
1.504
1.498
1.493
1.487
1.482
1.475
1.468
1.462
1.456
1.448
1.442
1.341
1.335
1.327
1.324
1.306
1.300
1.294
1.285
1.274
1.259
1.249
1.230
1.162
1.158
1.154
1.144
1.141
1.129
1.125
1.122
0.033
-0.037
H
N
S
3ac
7
6
5
4
3
2
1
0
-1
-2
ppm
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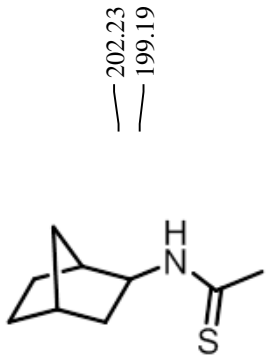
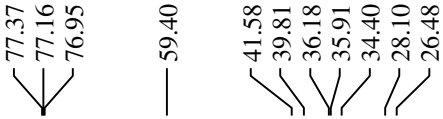
1.06
0.07
3.42
1.01
1.06
1.15
2.60
4.90
1.33


202.23
199.19
H
N
S

3ac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77.16
76.95
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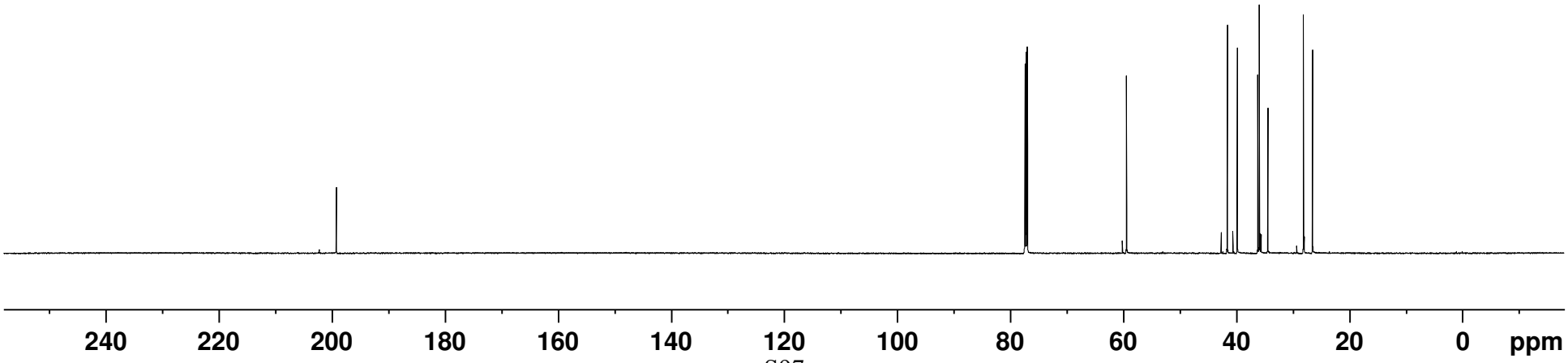
41.58
39.81
36.18
35.91
34.40
28.10
26.48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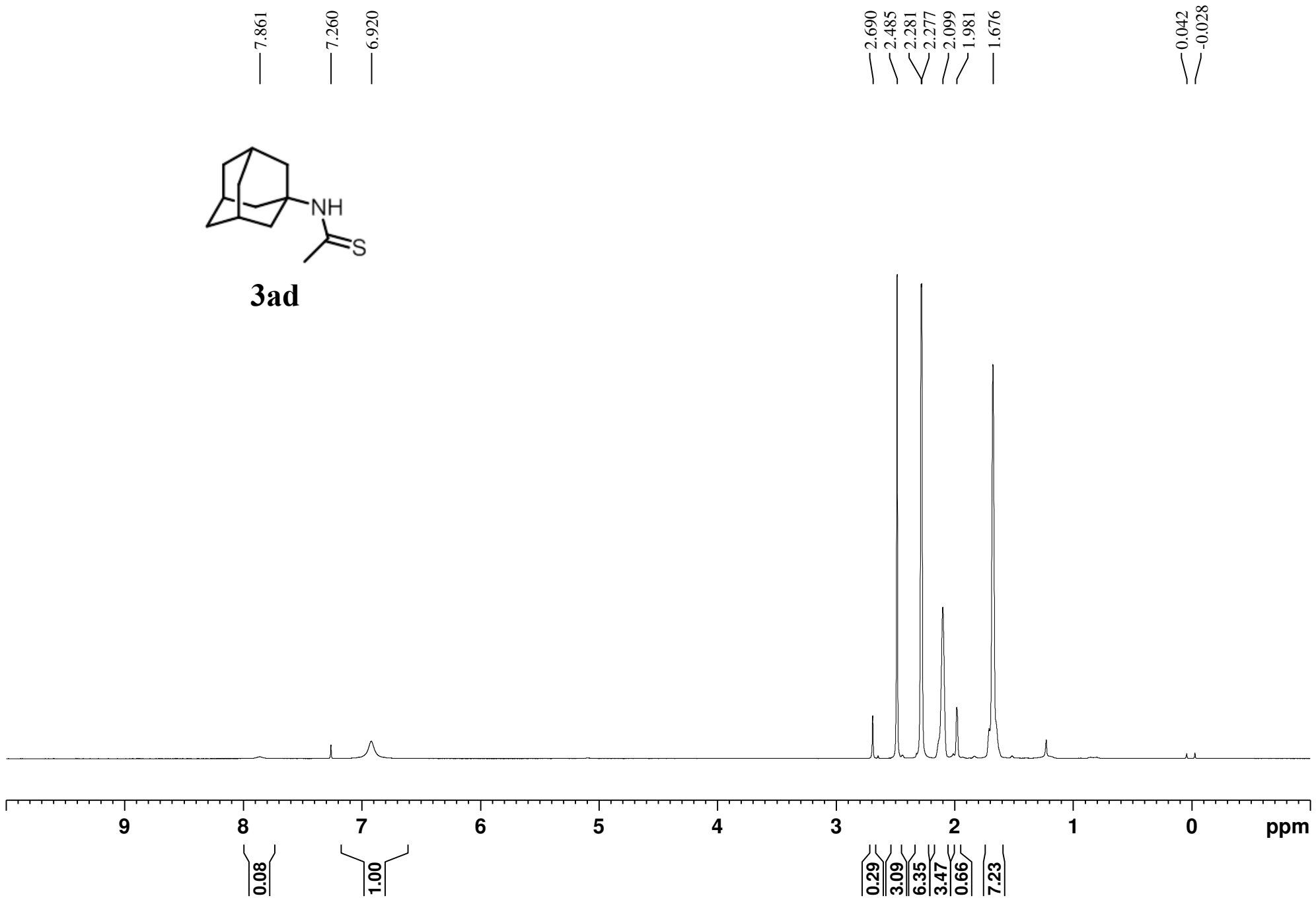
180
160
140
120
100
80
60
40
20
0
ppm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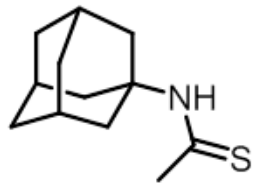
2.281
2.277
2.099
1.981
1.676
0.042
-0.028
NH
S
3ad
9
8
7
6
5
4
3
2
1
0
ppm
0.08
1.00
0.29
3.09
6.35
3.47
0.66
7.23


NH
S

3ad

199.28
77.48
77.16
76.84
56.74
40.08
37.79
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29.51
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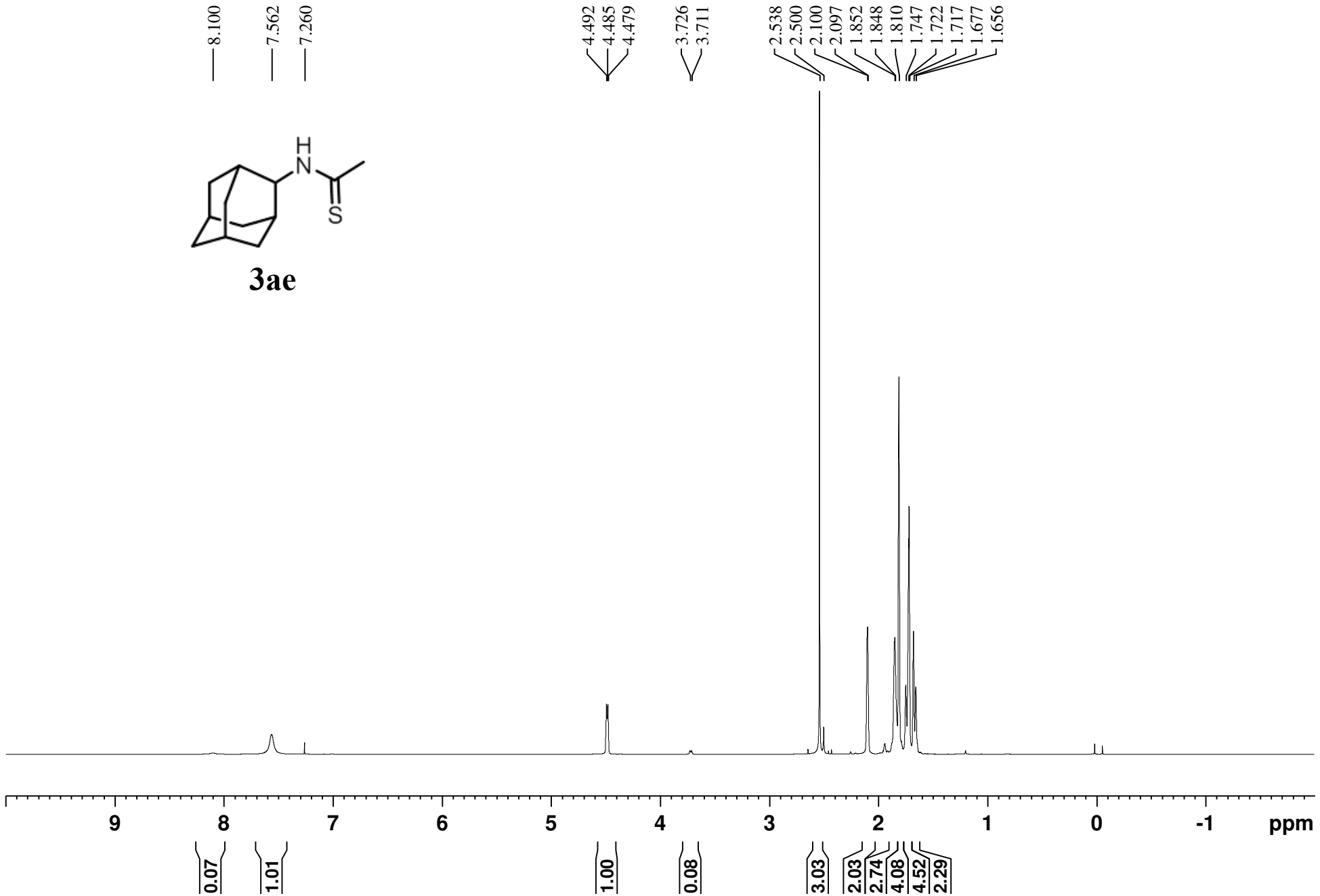
200
180
160
140
120
100
80
60
40
20
0
ppm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7.562
7.260
4.492
4.485
4.479
3.726
3.711
2.538
2.500
2.100
2.097
1.852
1.848
1.810
1.747
1.722
1.717
1.677
1.656
H
N
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
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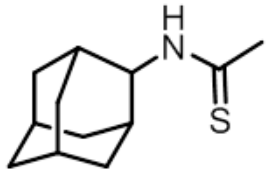
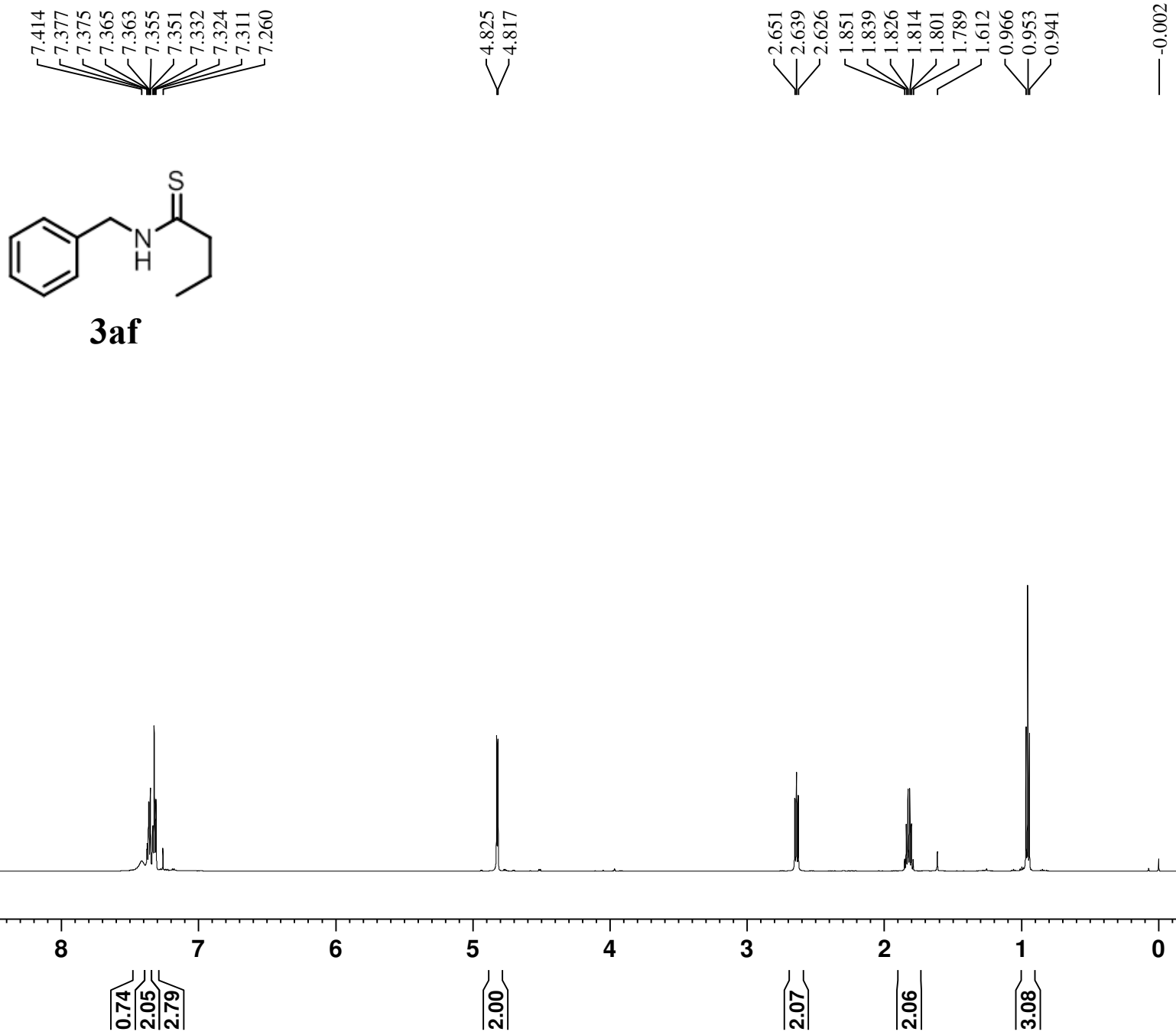
1.01
1.00
0.08
3.03
2.03
2.74
4.08
4.52
2.29

3ae


H
N
S

3ae

199.36
77.37
77.16
76.94
59.59
37.30
36.84
34.85
32.24
30.52
27.00
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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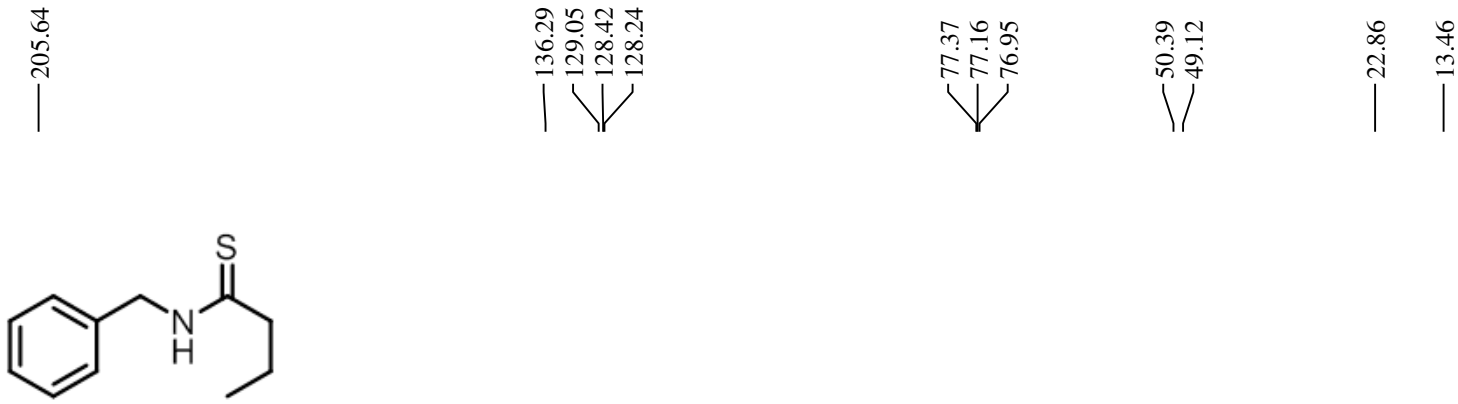
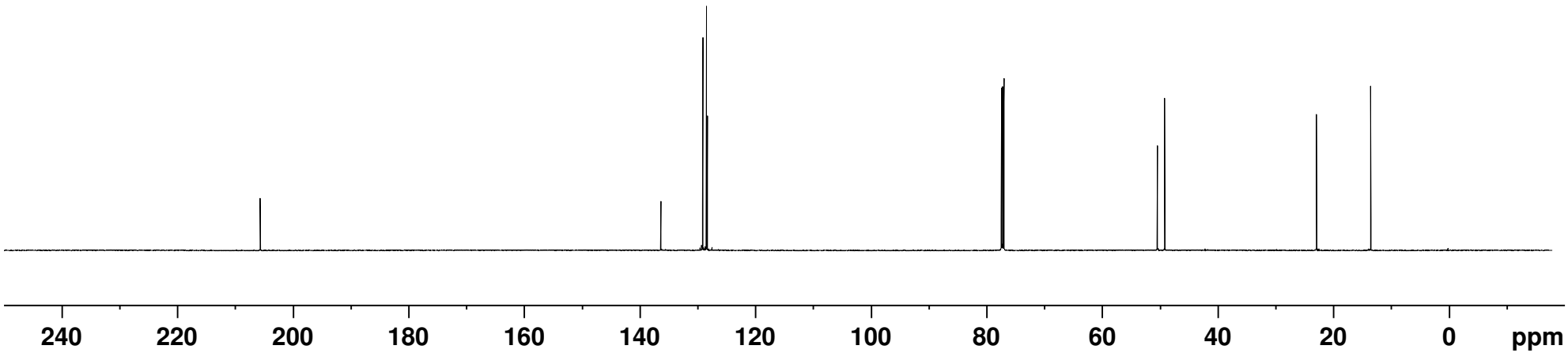
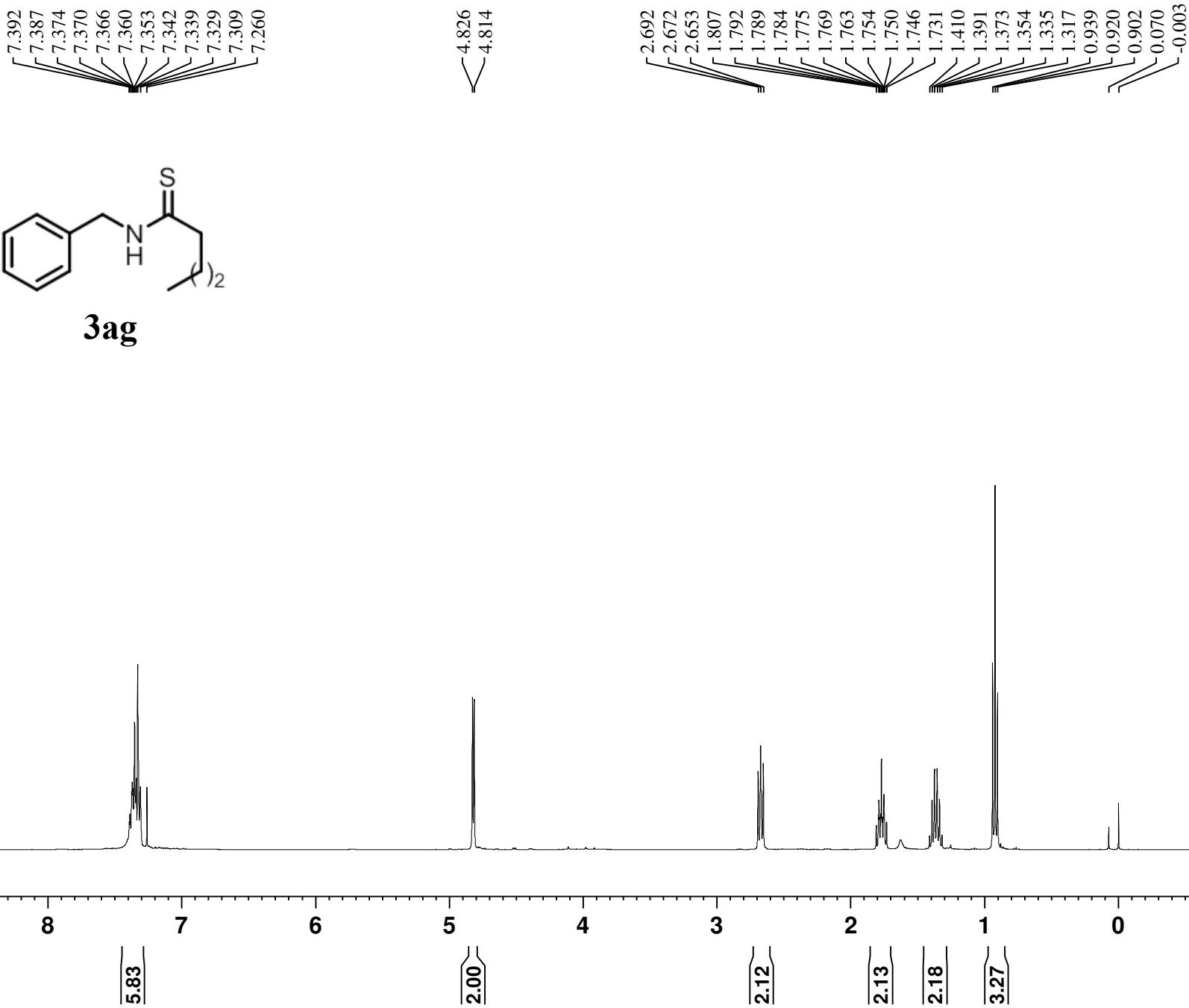
7.377
7.375
7.365
7.363
7.355
7.351
7.332
7.324
7.311
7.260
4.825
4.817
2.651
2.639
2.626
1.851
1.839
1.826
1.814
1.801
1.789
1.612
0.966
0.953
0.941
-0.002
S
N
H
9
8
7
6
5
4
3
2
1
0
ppm
0.74
2.05
2.79
2.00
2.07
2.06
3.08

3af


205.64
136.29
129.05
128.42
128.24
77.37
77.16
76.95
50.39
49.12
22.86
13.46
S
N
H

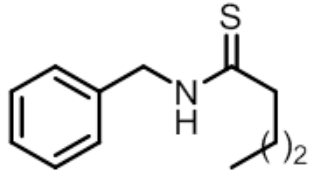
3af


240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

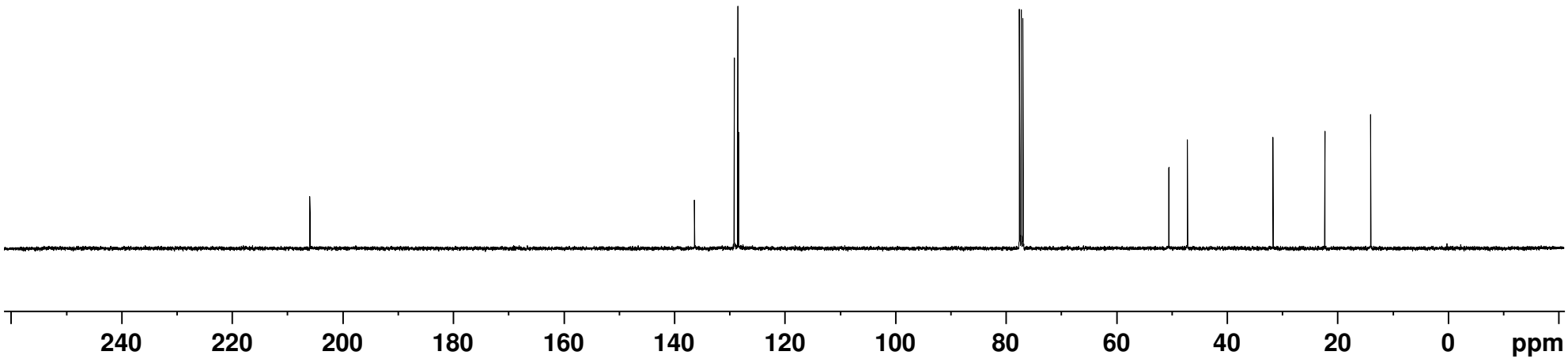

7.392
7.387
7.374
7.370
7.366
7.360
7.353
7.342
7.339
7.329
7.309
7.260
4.826
4.814
2.692
2.672
2.653
1.807
1.792
1.789
1.784
1.775
1.769
1.763
1.754
1.750
1.746
1.731
1.410
1.391
1.373
1.354
1.335
1.317
0.939
0.920
0.902
0.070
-0.003
S
N
H
)2
9
8
7
6
5
4
3
2
1
0
ppm
5.83
2.00
2.12
2.13
2.18
3.27

3ag


205.87
136.32
129.08
128.44
128.27
77.48
77.16
76.84
50.45
47.09
31.61
22.22
13.92


S
N
H
)2

3ag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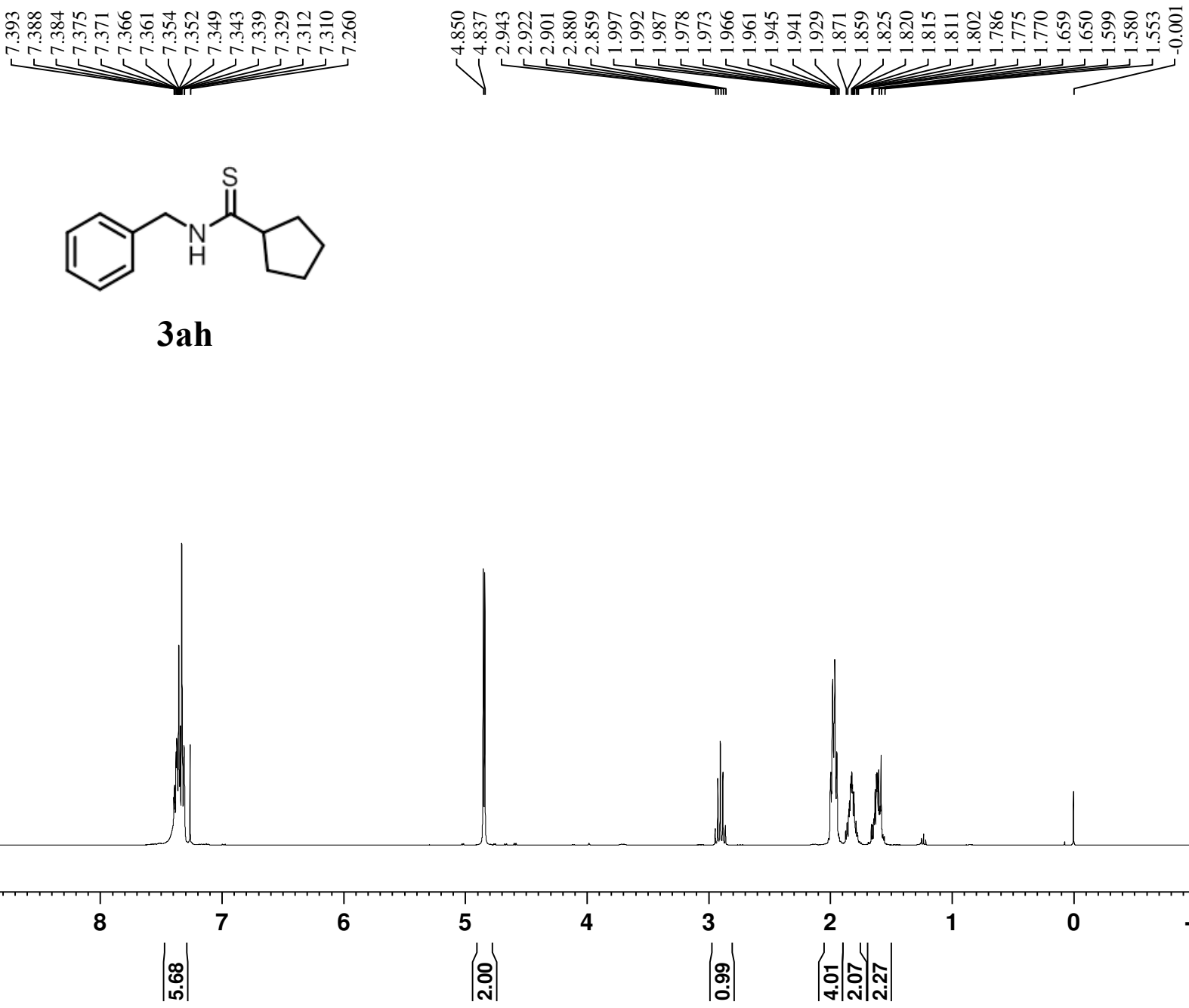
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.388
7.384
7.375
7.371
7.366
7.361
7.354
7.352
7.349
7.343
7.339
7.329
7.312
7.310
7.260
4.850
4.837
2.943
2.922
2.901
2.880
2.859
1.997
1.992
1.987
1.978
1.973
1.966
1.961
1.945
1.941
1.929
1.871
1.859
1.825
1.820
1.815
1.811
1.802
1.786
1.775
1.770
1.659
1.650
1.599
1.580
1.553
-0.001
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
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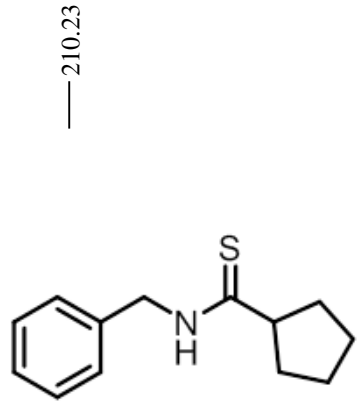
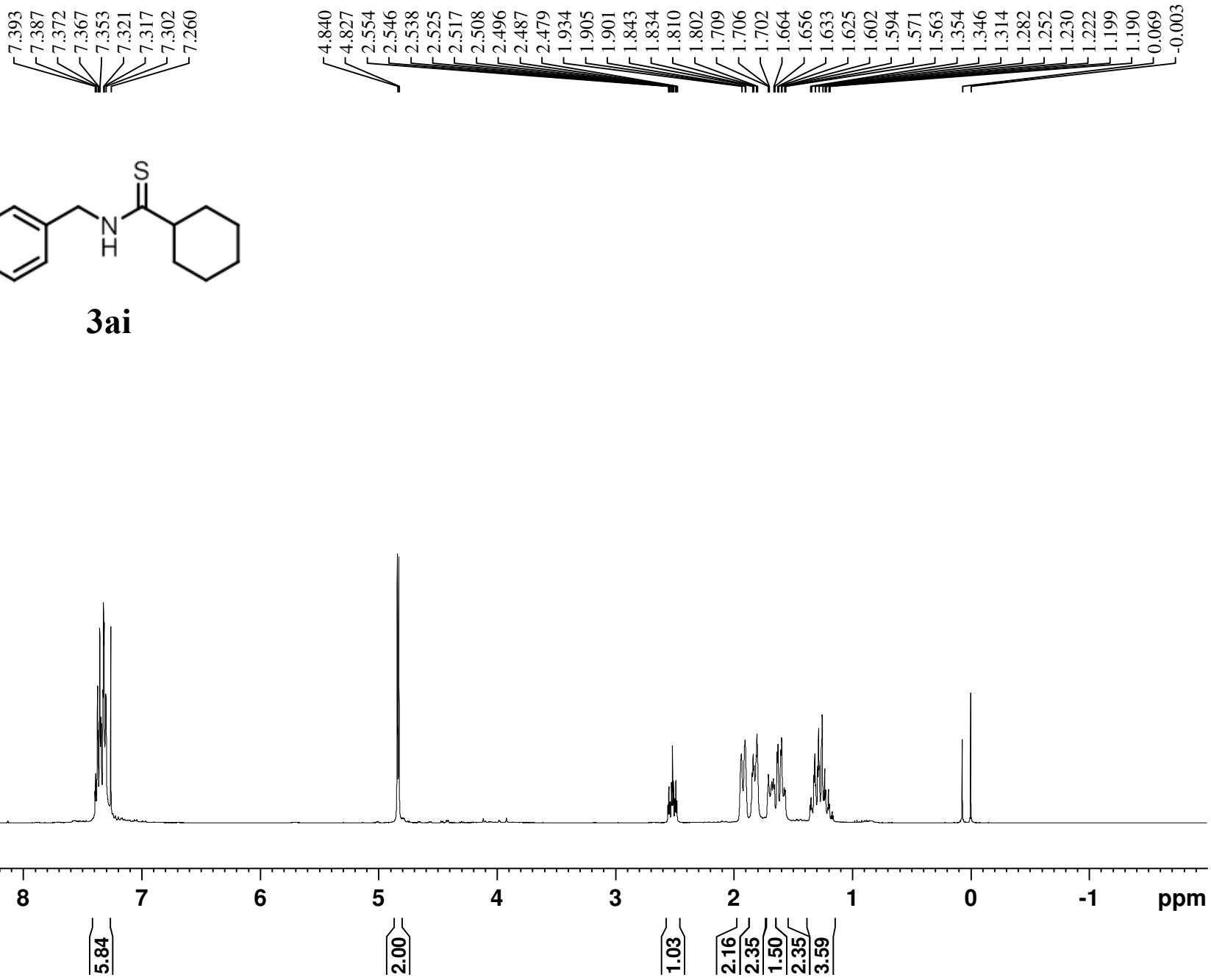
2.00
0.99
4.01
2.07
2.27

3ah


S
N
H

3ah

210.23
136.45
129.08
128.41
128.23
77.48
77.16
76.84
55.30
50.31
34.19
25.93
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.372
7.367
7.353
7.321
7.317
7.302
7.260
4.840
4.827
2.554
2.546
2.538
2.525
2.517
2.508
2.496
2.487
2.479
1.934
1.905
1.901
1.843
1.834
1.810
1.802
1.709
1.706
1.702
1.664
1.656
1.633
1.625
1.602
1.594
1.571
1.563
1.354
1.346
1.314
1.282
1.252
1.230
1.222
1.199
1.190
0.069
-0.003
S
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm
5.84
2.00
1.03
2.16
2.35
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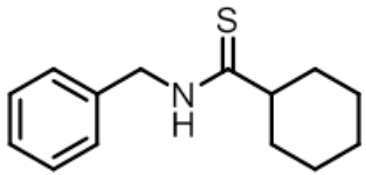
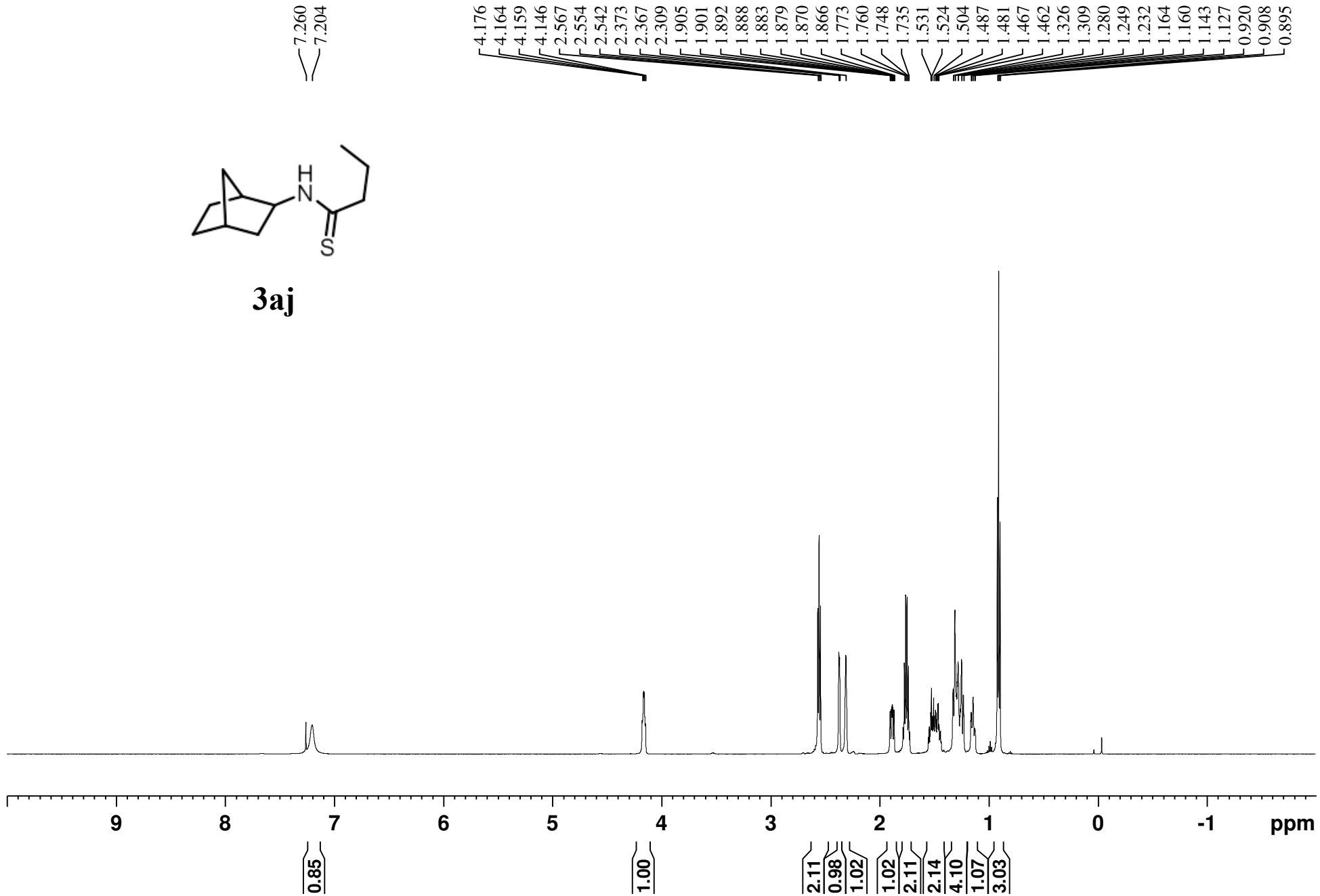
2.35
3.59

3ai


S
N
H

3ai

210.44
136.47
129.11
128.40
128.25
77.48
77.16
76.84
55.15
50.11
33.05
26.08
25.72
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.204
4.176
4.164
4.159
4.146
2.567
2.554
2.542
2.373
2.367
2.309
1.905
1.901
1.892
1.888
1.883
1.879
1.870
1.866
1.773
1.760
1.748
1.735
1.531
1.524
1.504
1.487
1.481
1.467
1.462
1.326
1.309
1.280
1.249
1.232
1.164
1.160
1.143
1.127
0.920
0.908
0.895
H
N
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.85
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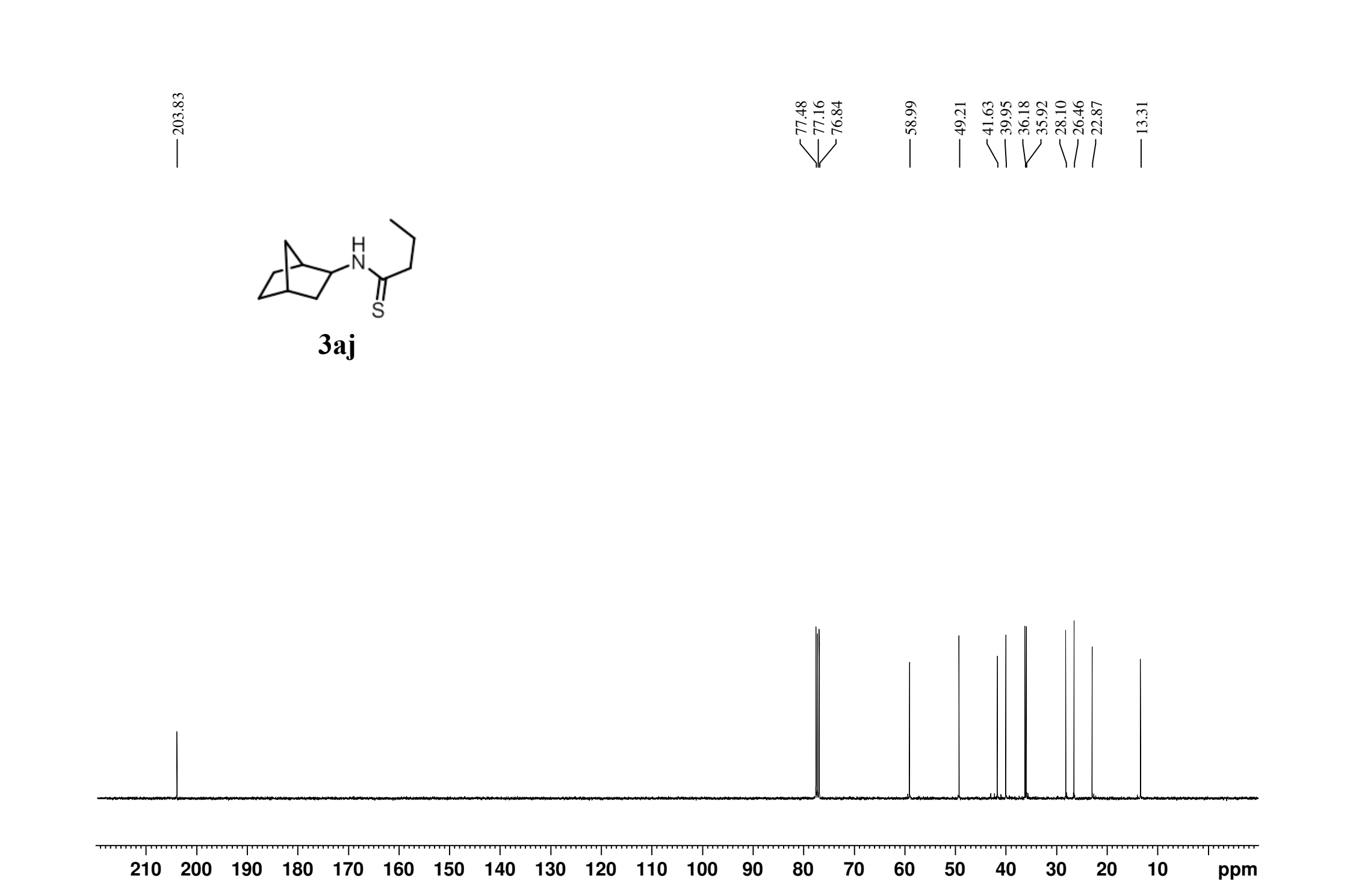
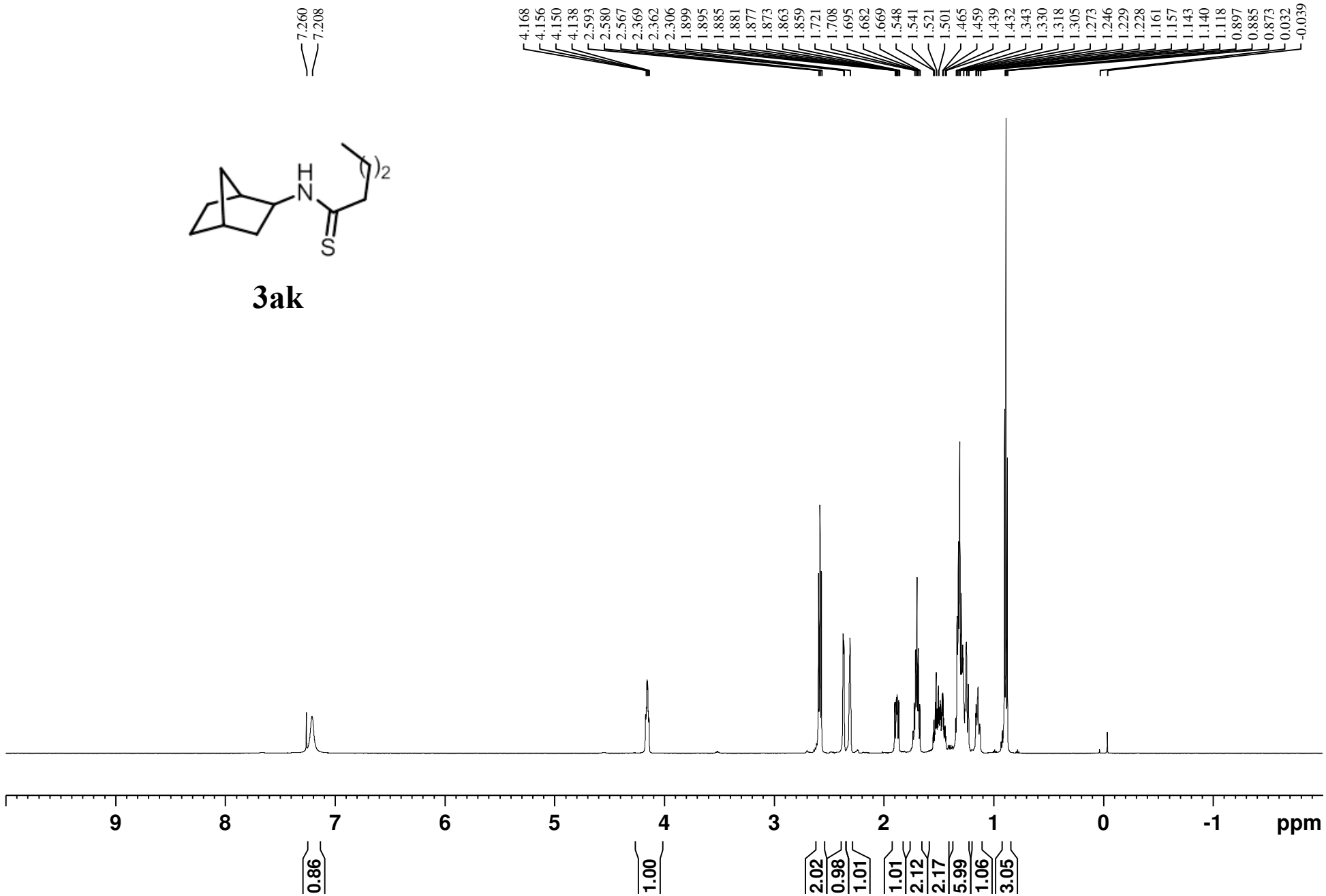
2.11
0.98
1.02
1.02
2.11
2.14
4.10
1.07
3.03

3aj


203.83
77.48
77.16
76.84
58.99
49.21
41.63
39.95
36.18
35.92
28.10
26.46
22.87
13.31
H
N
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3aj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7.208
4.168
4.156
4.150
4.138
2.593
2.580
2.567
2.369
2.362
2.306
1.899
1.895
1.885
1.881
1.877
1.873
1.863
1.859
1.721
1.708
1.695
1.682
1.669
1.548
1.541
1.521
1.501
1.465
1.459
1.439
1.432
1.343
1.330
1.318
1.305
1.273
1.246
1.229
1.228
1.161
1.157
1.143
1.140
1.118
0.897
0.885
0.873
0.032
-0.039
H
N
S
)2
9
8
7
6
5
4
3
2
1
0
-1
ppm
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2.02
0.98
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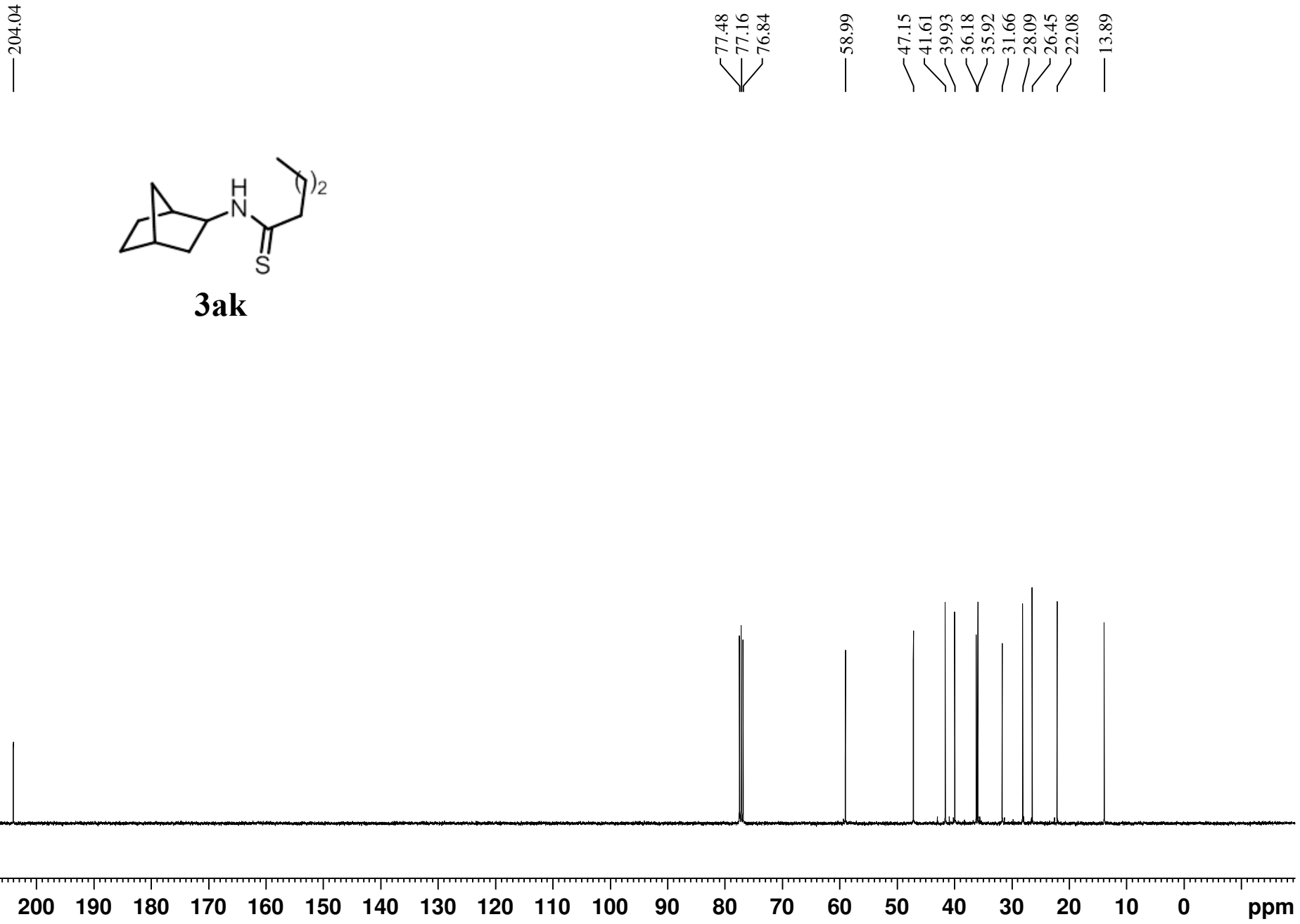
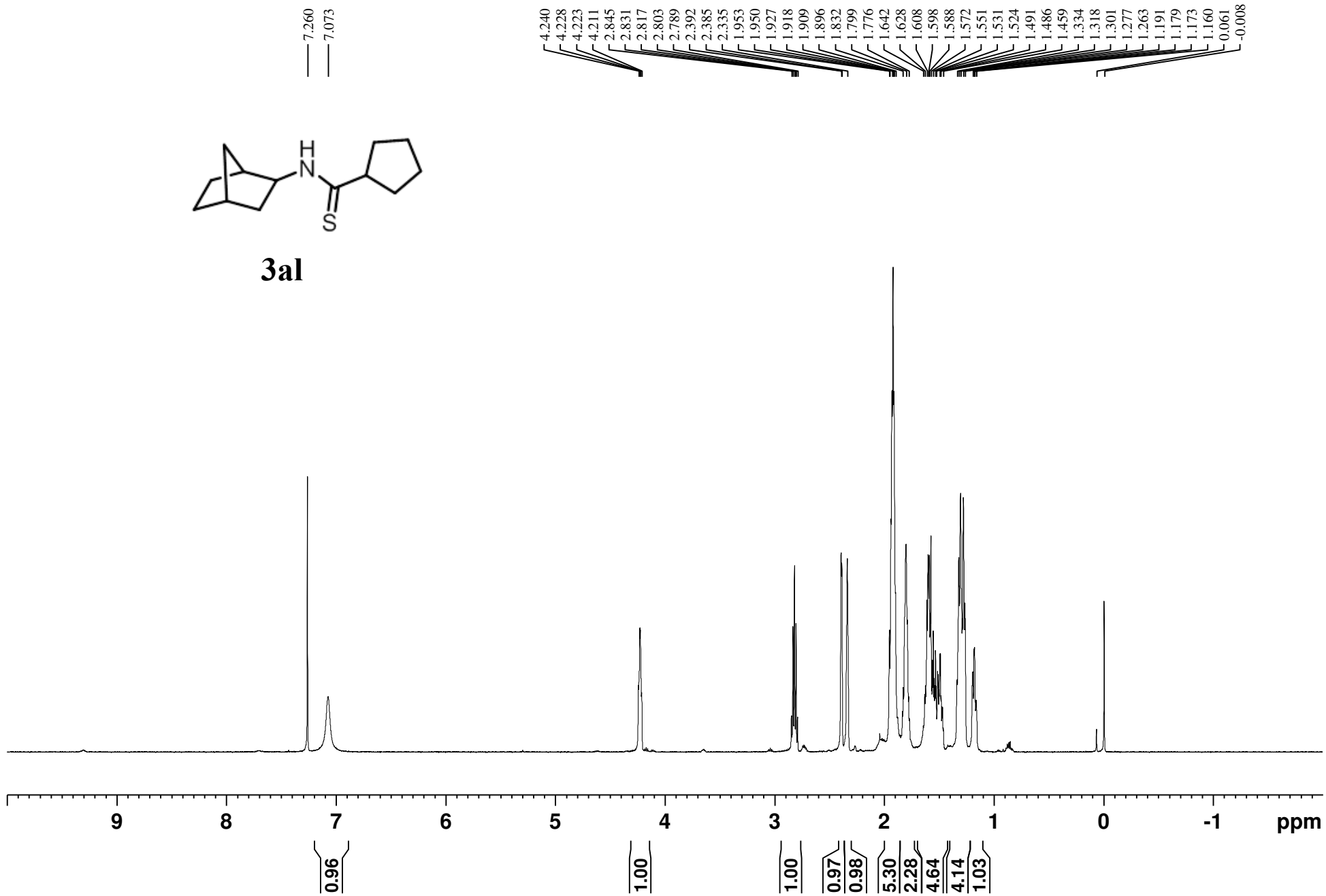
1.01
2.12
2.17
5.99
1.06
3.05

3ak


204.04
77.48
77.16
76.84
58.99
47.15
41.61
39.93
36.18
35.92
31.66
28.09
26.45
22.08
13.89
H
N
S
)2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3ak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7.073
4.240
4.228
4.223
4.211
2.845
2.831
2.817
2.803
2.789
2.392
2.385
2.335
1.953
1.950
1.927
1.918
1.909
1.896
1.832
1.799
1.776
1.642
1.628
1.608
1.598
1.588
1.572
1.551
1.531
1.524
1.491
1.486
1.459
1.334
1.318
1.301
1.277
1.263
1.191
1.179
1.173
1.160
0.061
-0.008
H
N
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
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1.00
1.00
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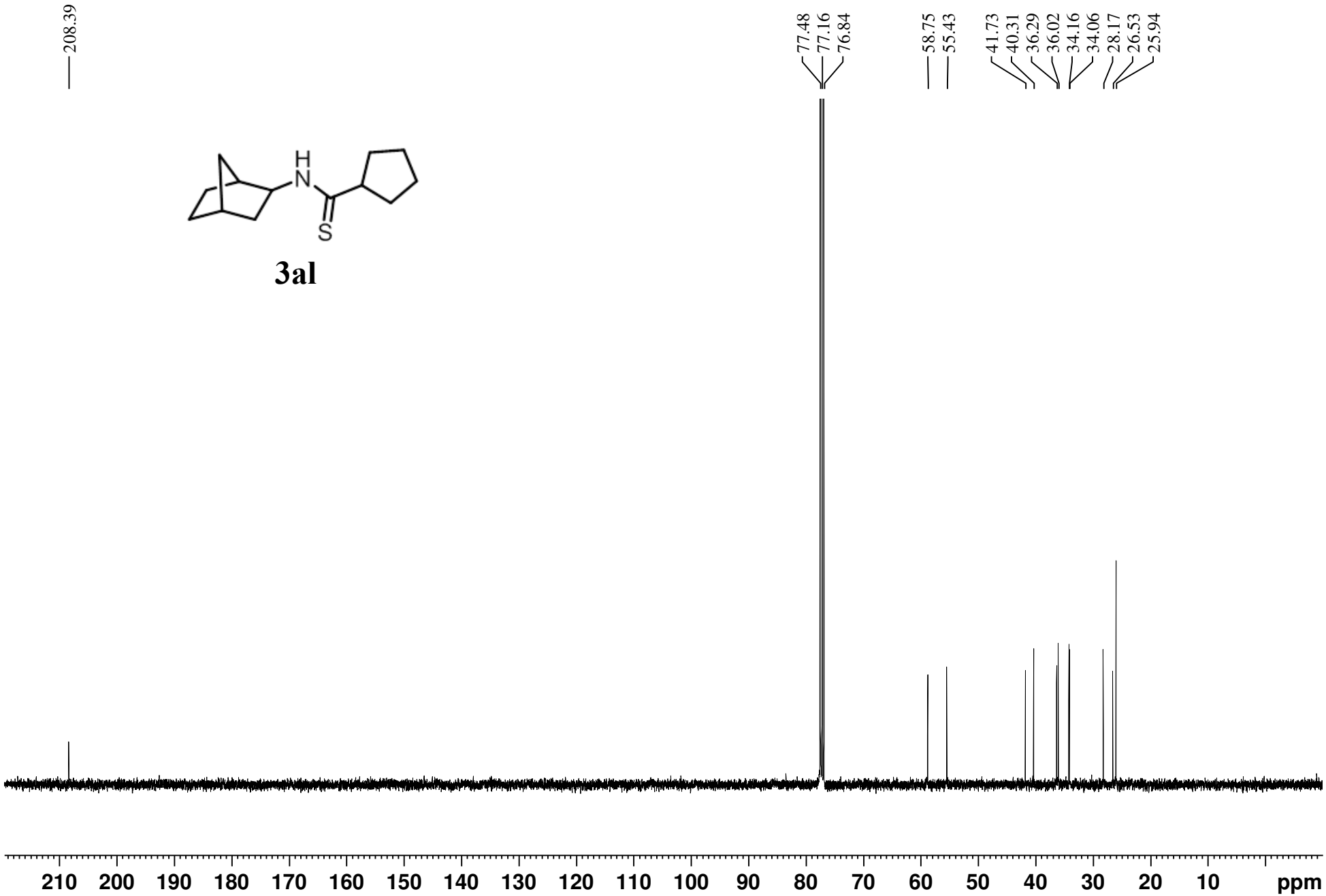
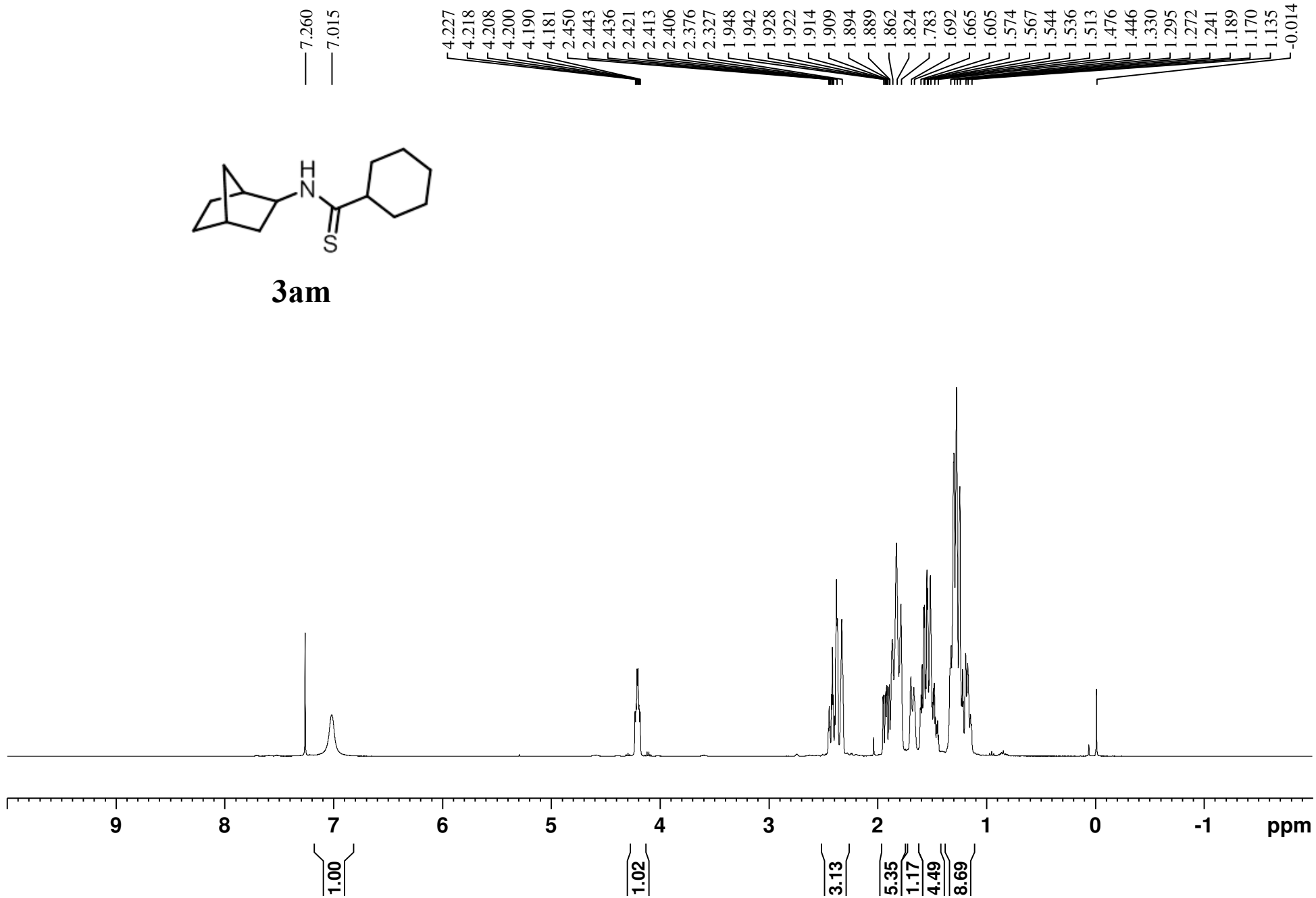
0.98
5.30
2.28
4.64
4.14
1.03

3al


208.39
77.48
77.16
76.84
58.75
55.43
41.73
40.31
36.29
36.02
34.16
34.06
28.17
26.53
25.94
H
N
S
3al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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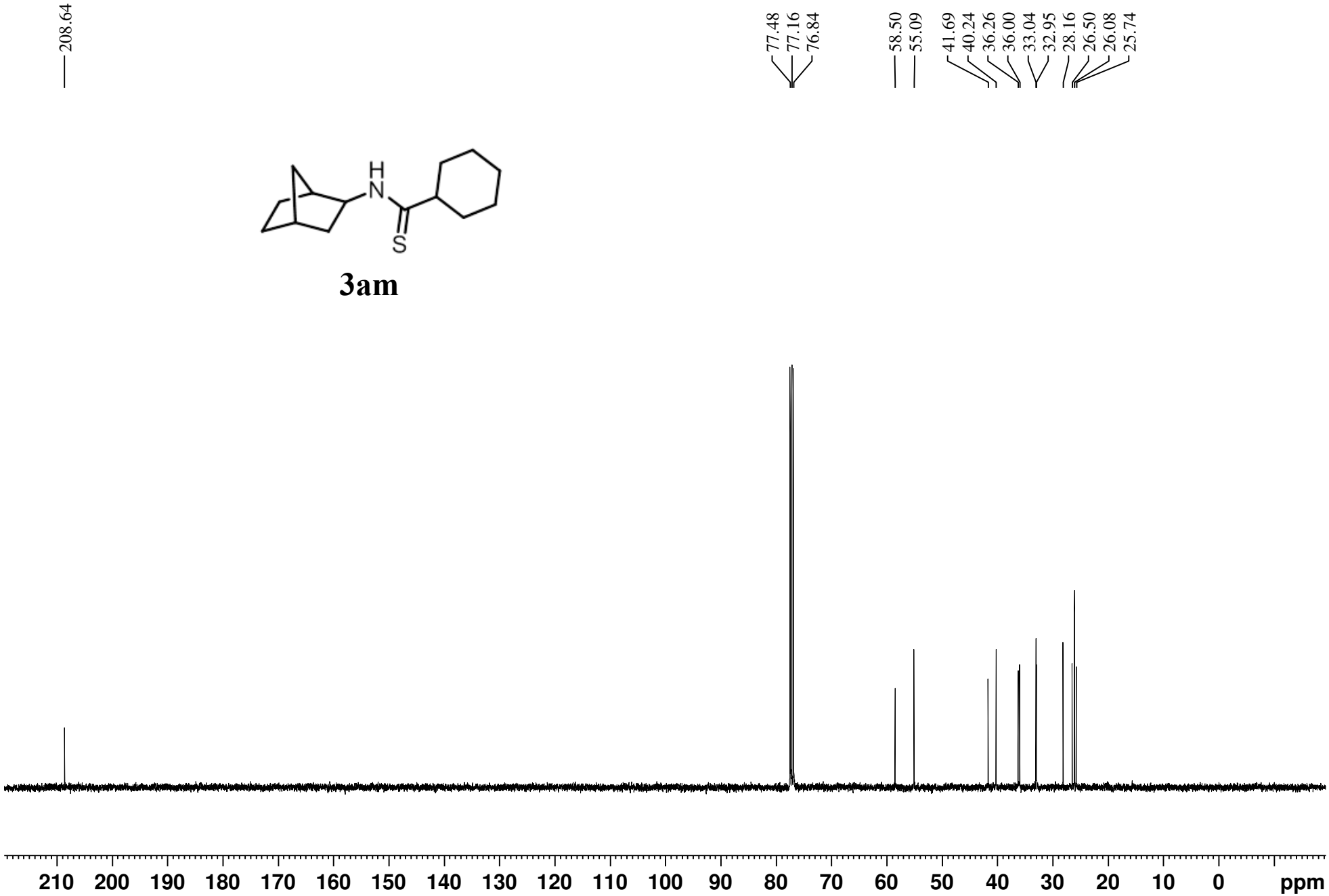
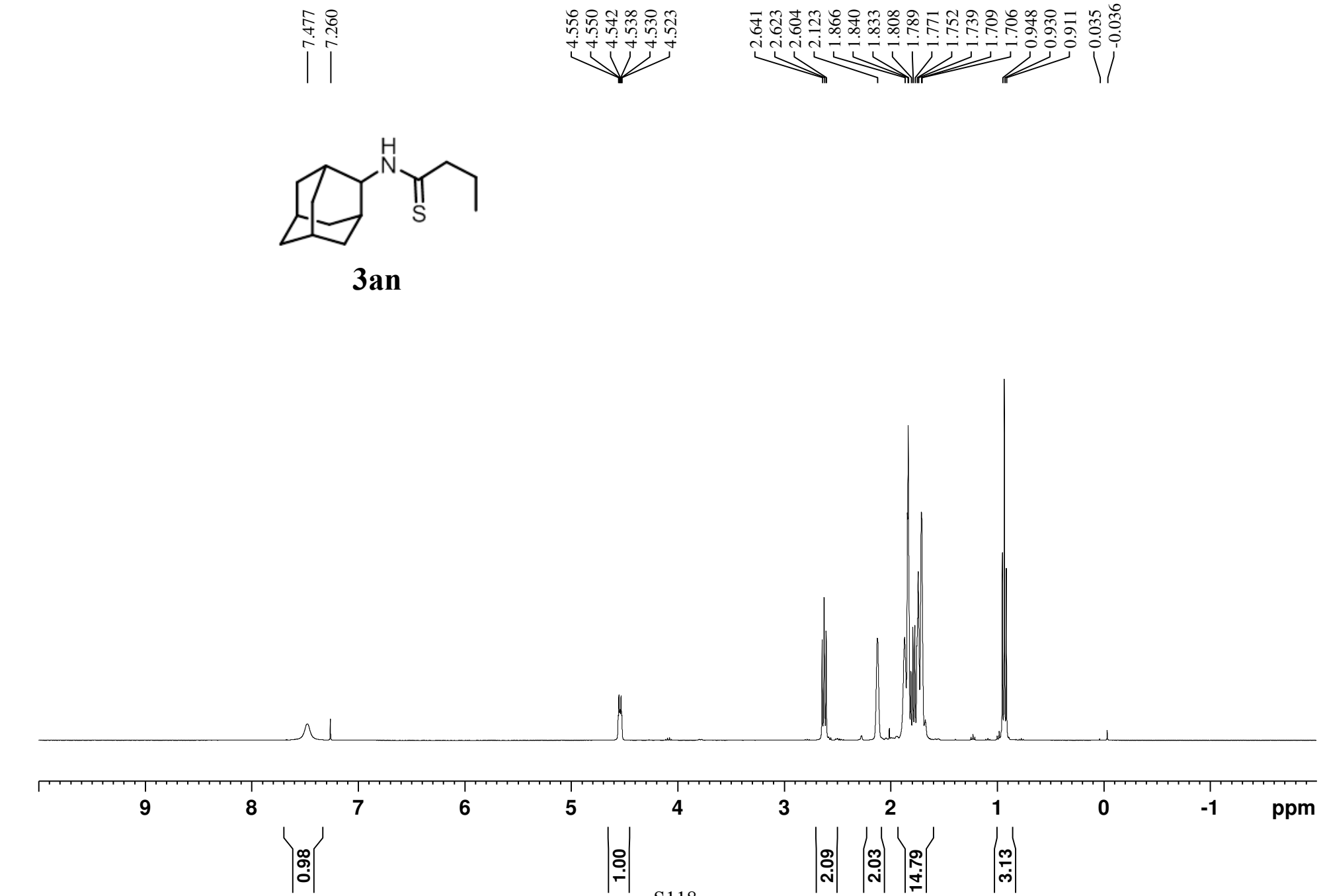
7.015
4.227
4.218
4.208
4.200
4.190
4.181
2.450
2.443
2.436
2.421
2.413
2.406
2.376
2.327
1.948
1.942
1.928
1.922
1.914
1.909
1.894
1.889
1.862
1.824
1.783
1.692
1.665
1.605
1.574
1.567
1.544
1.536
1.513
1.476
1.446
1.330
1.295
1.272
1.241
1.189
1.170
1.135
-0.014
H
N
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.02
3.13
5.35
1.17
4.49
8.69

3am


208.64
77.48
77.16
76.84
58.50
55.09
41.69
40.24
36.26
36.00
33.04
32.95
28.16
26.50
26.08
25.74
H
N
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3am

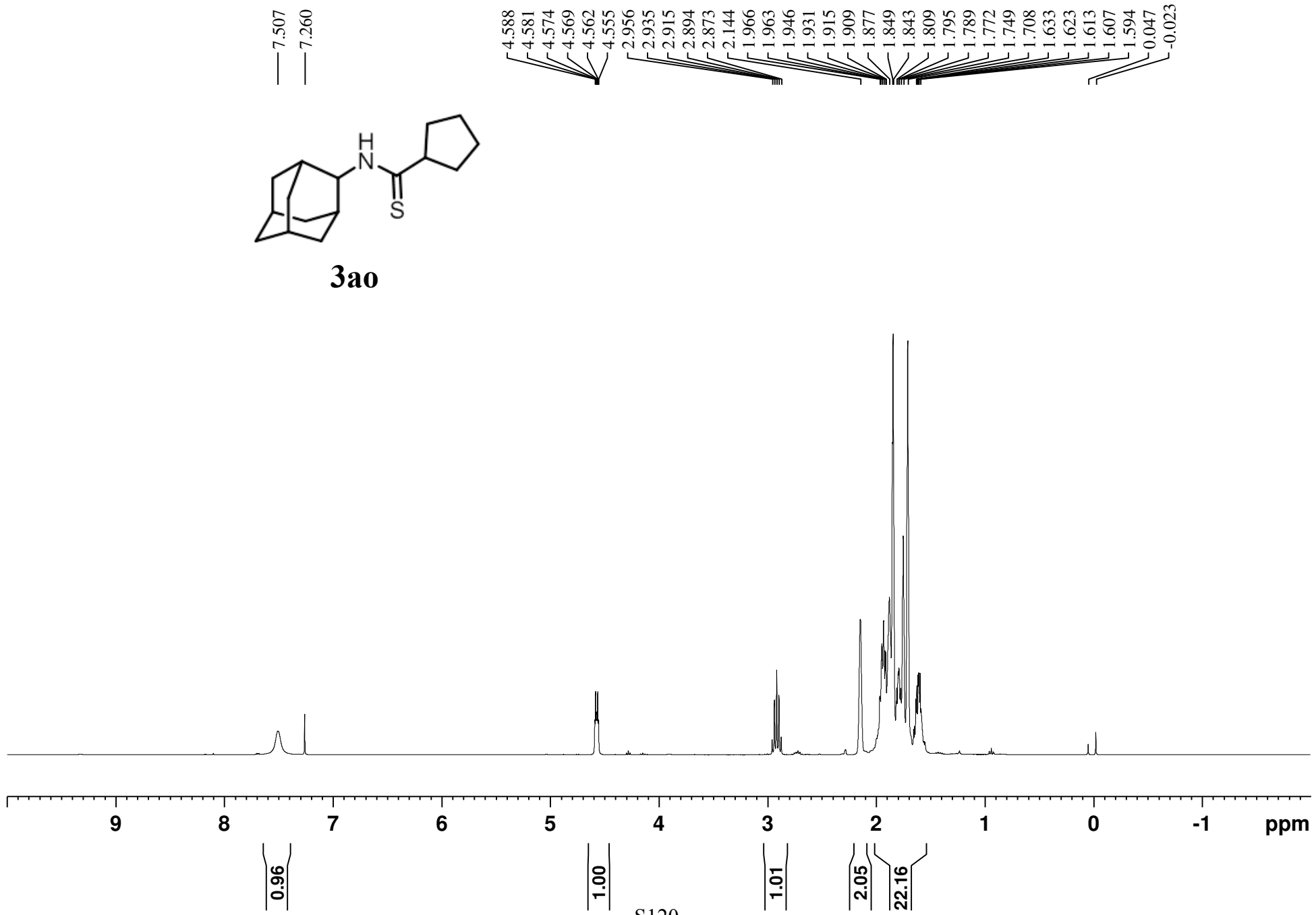

7.477
7.260
4.556
4.550
4.542
4.538
4.530
4.523
2.641
2.623
2.604
2.123
1.866
1.840
1.833
1.808
1.789
1.771
1.752
1.739
1.709
1.706
0.948
0.930
0.911
0.035
-0.036
H
N
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
1.00
2.09
2.03
14.79
3.13

3an


H
N
S

3an

203.90
77.37
77.16
76.94
59.07
49.79
37.39
36.89
32.39
30.61
27.08
27.06
22.85
13.30
200
180
160
140
120
100
80
60
40
20
0
ppm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7.260
4.588
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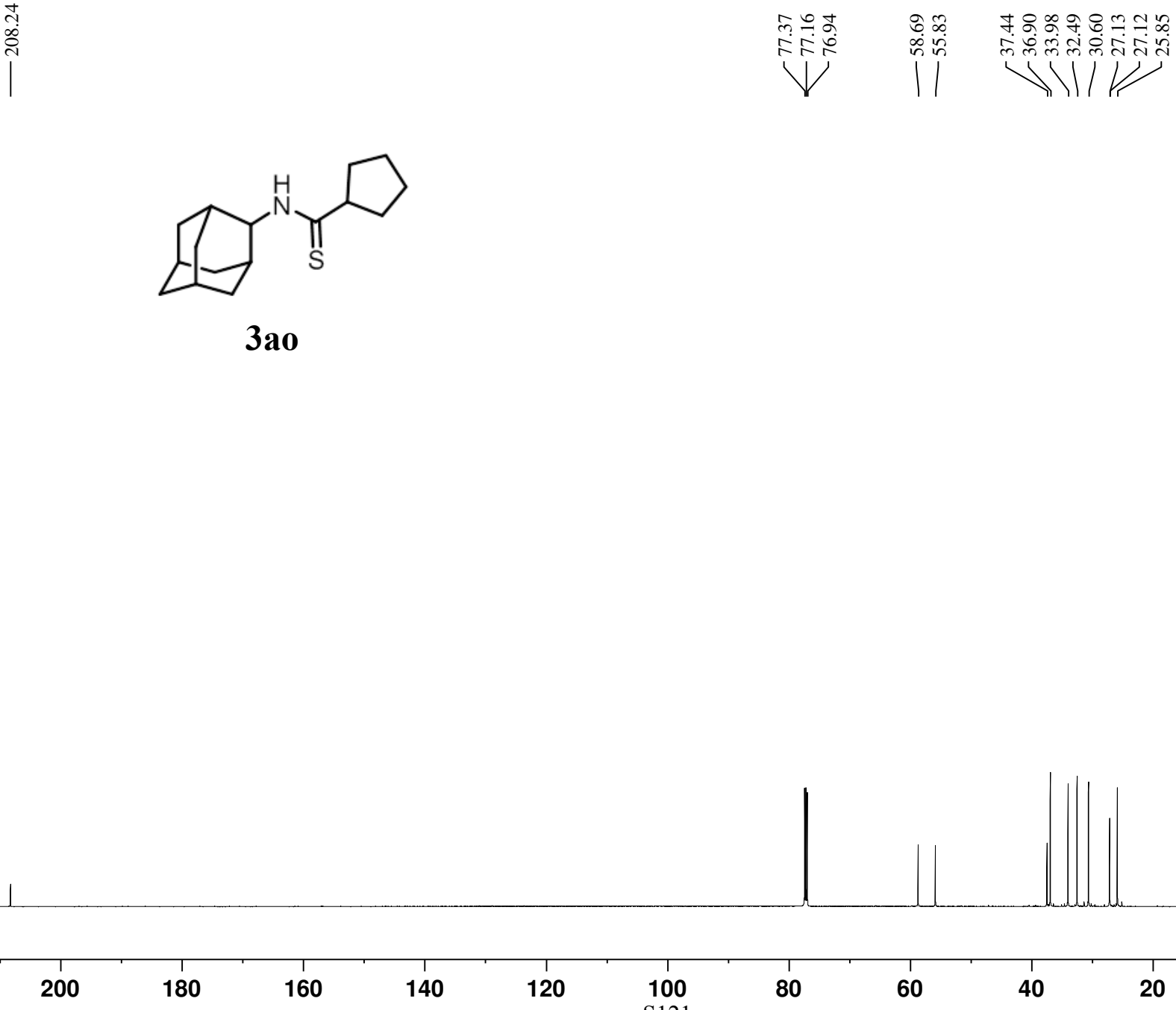
4.562
4.555
2.956
2.935
2.915
2.894
2.873
2.144
1.966
1.963
1.946
1.931
1.915
1.909
1.877
1.849
1.843
1.809
1.795
1.789
1.772
1.749
1.708
1.633
1.623
1.613
1.607
1.594
0.047
-0.023
H
N
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.96
1.00
1.01
2.05
22.16

3ao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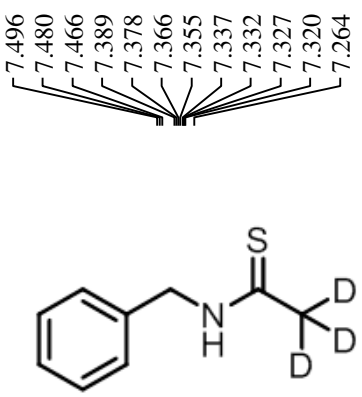
77.37
77.16
76.94
58.69
55.83
37.44
36.90
33.98
32.49
30.60
27.13
27.12
25.85
H
N
S
200
180
160
140
120
100
80
60
40
20
0
ppm

3ao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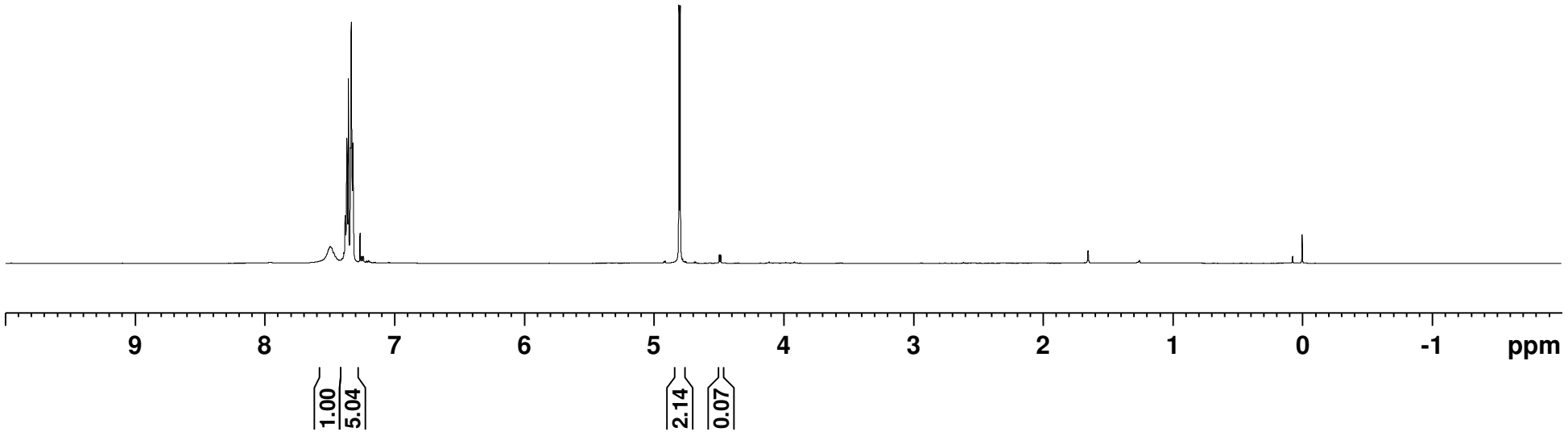
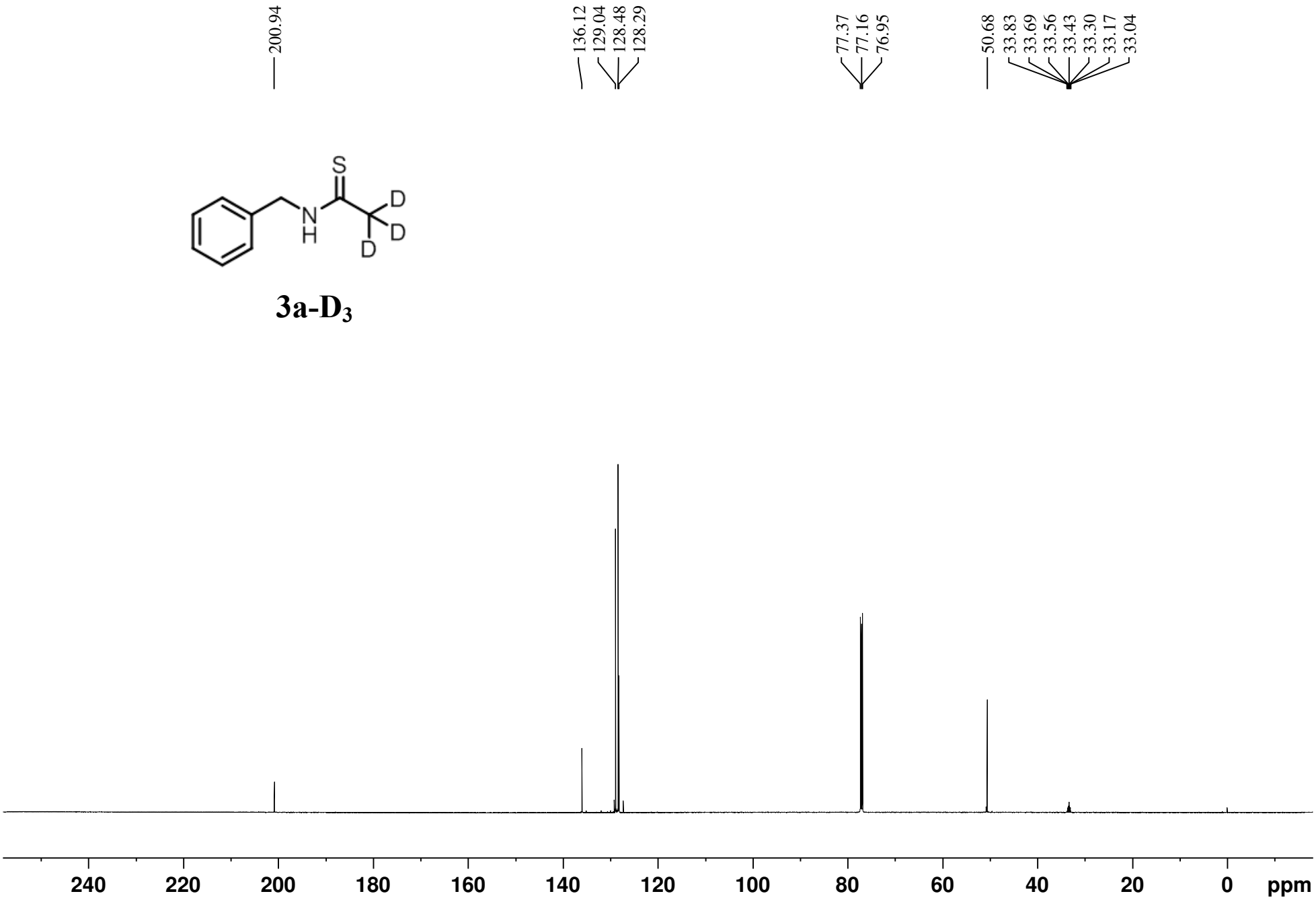
7.480
7.466
7.389
7.378
7.366
7.355
7.337
7.332
7.327
7.320
7.264
4.805
4.796
4.494
4.484
-0.000
S
N
H
D
D
D

3a-D_3


9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
5.04
2.14
0.07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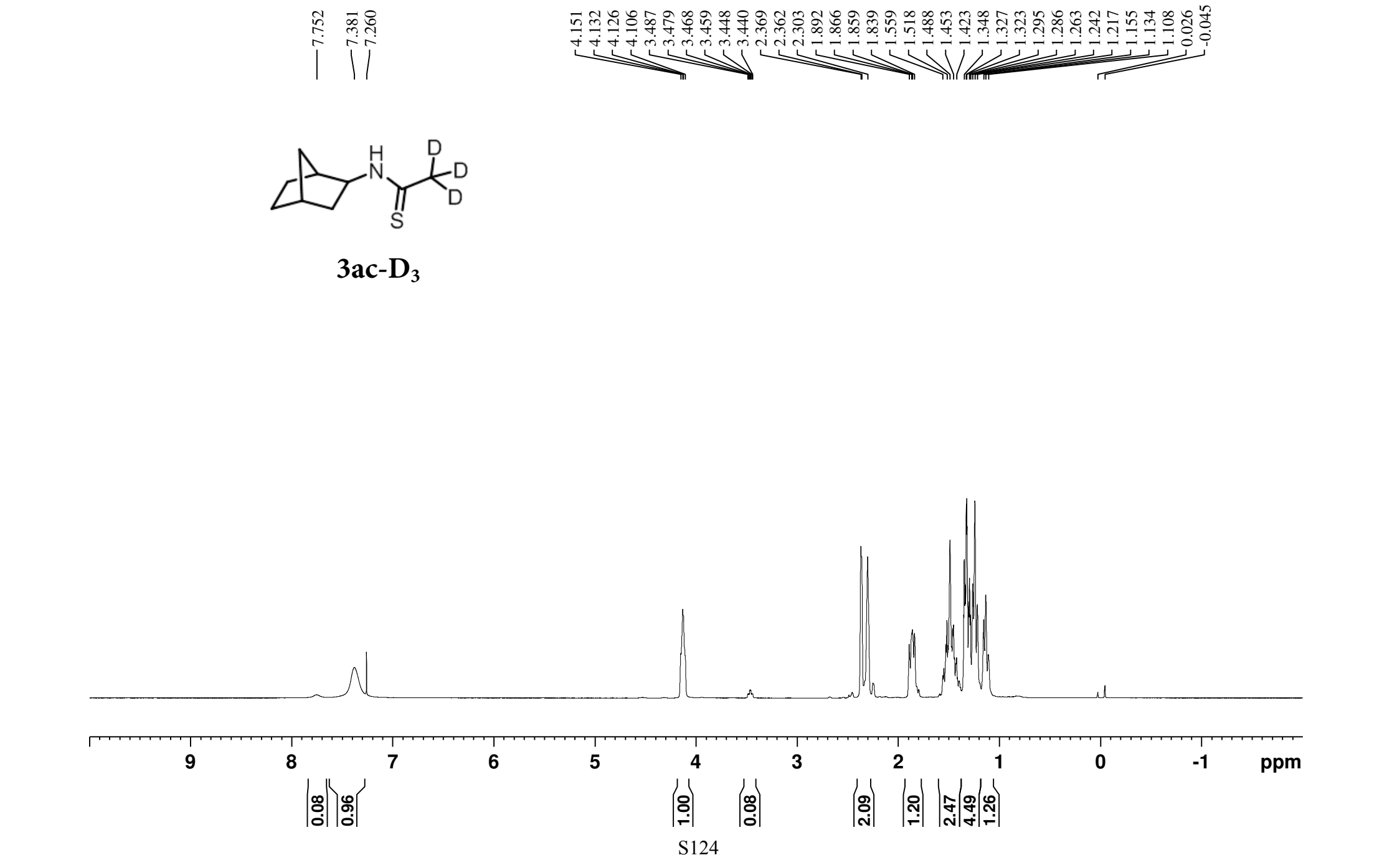
136.12
129.04
128.48
128.29
77.37
77.16
76.95
50.68
33.83
33.69
33.56
33.43
33.30
33.17
33.04
S
N
H
D
D
D
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3a-D_3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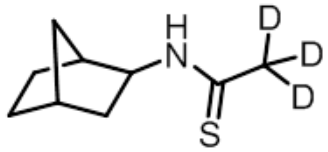
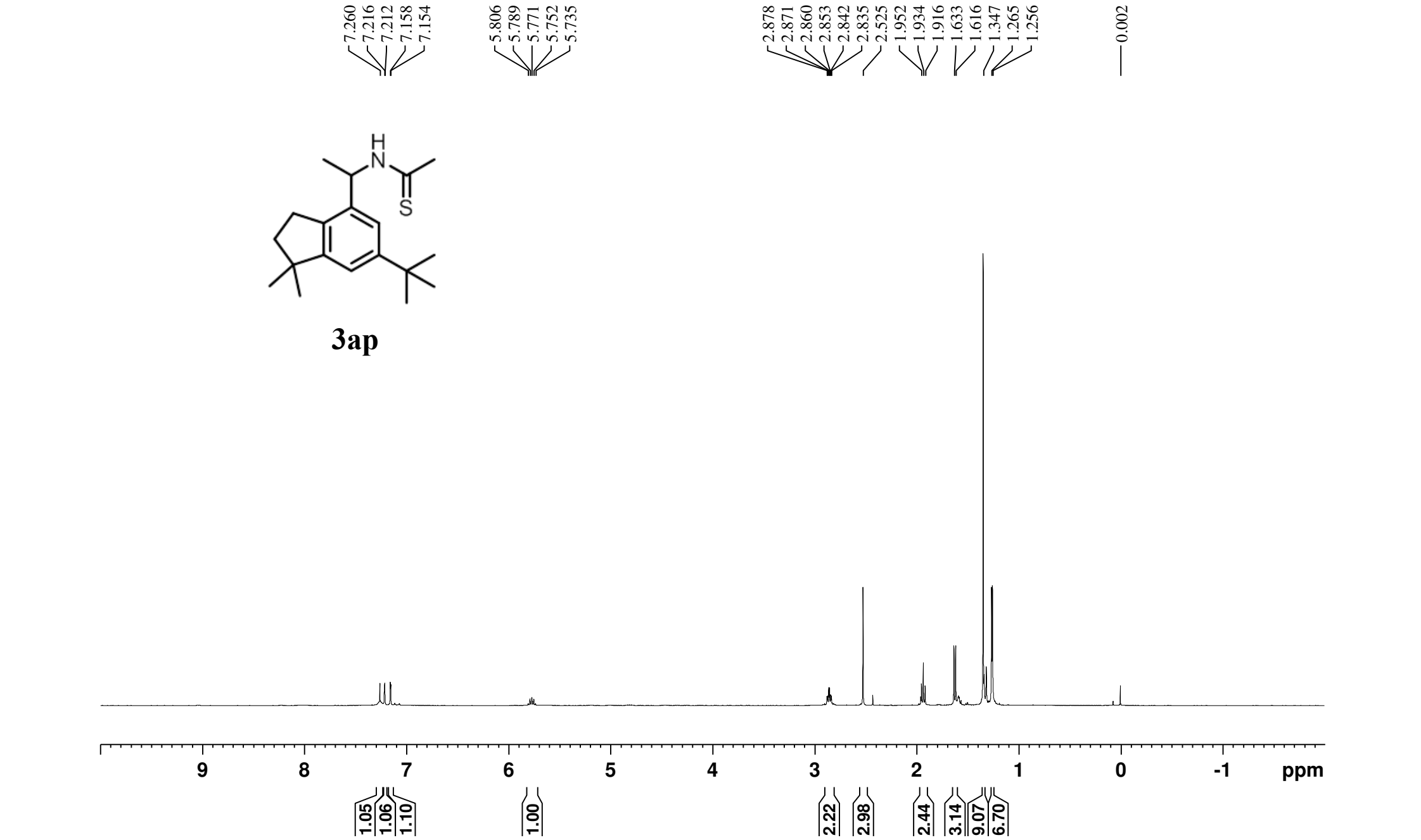
7.381
7.260
4.151
4.132
4.126
4.106
3.487
3.479
3.468
3.459
3.448
3.440
2.369
2.362
2.303
1.892
1.866
1.859
1.839
1.559
1.518
1.488
1.453
1.423
1.348
1.327
1.323
1.295
1.286
1.263
1.242
1.217
1.155
1.134
1.108
0.026
-0.045
H
N
D
D
D
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.08
0.96
1.00
0.08
2.09
1.20
2.47
4.49
1.26

3ac-D_3


H
N
D
D
D
S

3ac-D_3

199.14
77.47
77.16
76.84
59.37
41.54
39.72
36.15
35.87
33.95
33.75
33.55
33.36
33.16
28.07
26.45
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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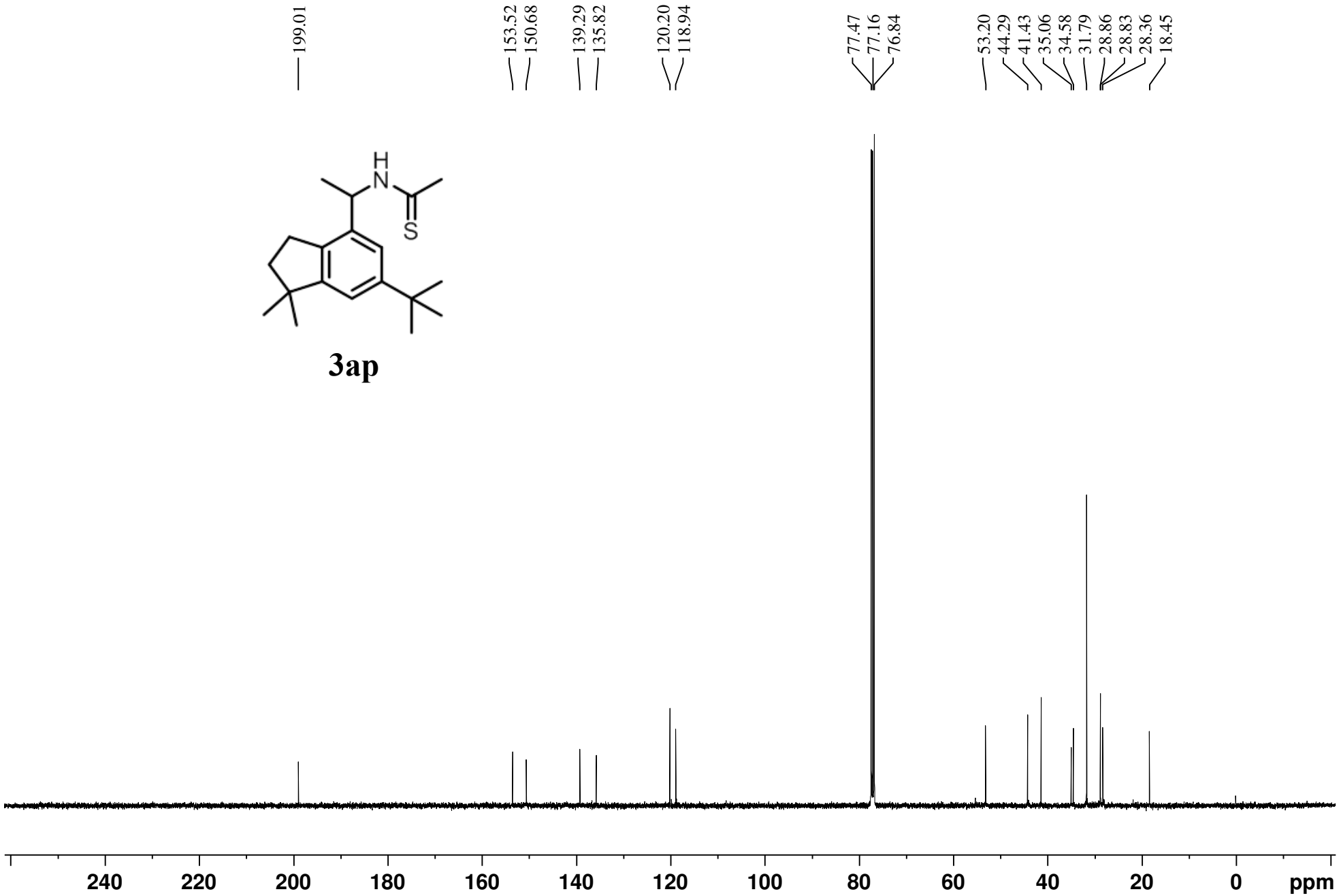
7.216
7.212
7.158
7.154
5.806
5.789
5.771
5.752
5.735
2.878
2.871
2.860
2.853
2.842
2.835
2.525
1.952
1.934
1.916
1.633
1.616
1.347
1.265
1.256
0.002
H
N
S
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.05
1.06
1.10
1.00
2.22
2.98
2.44
3.14
9.07
6.70

3ap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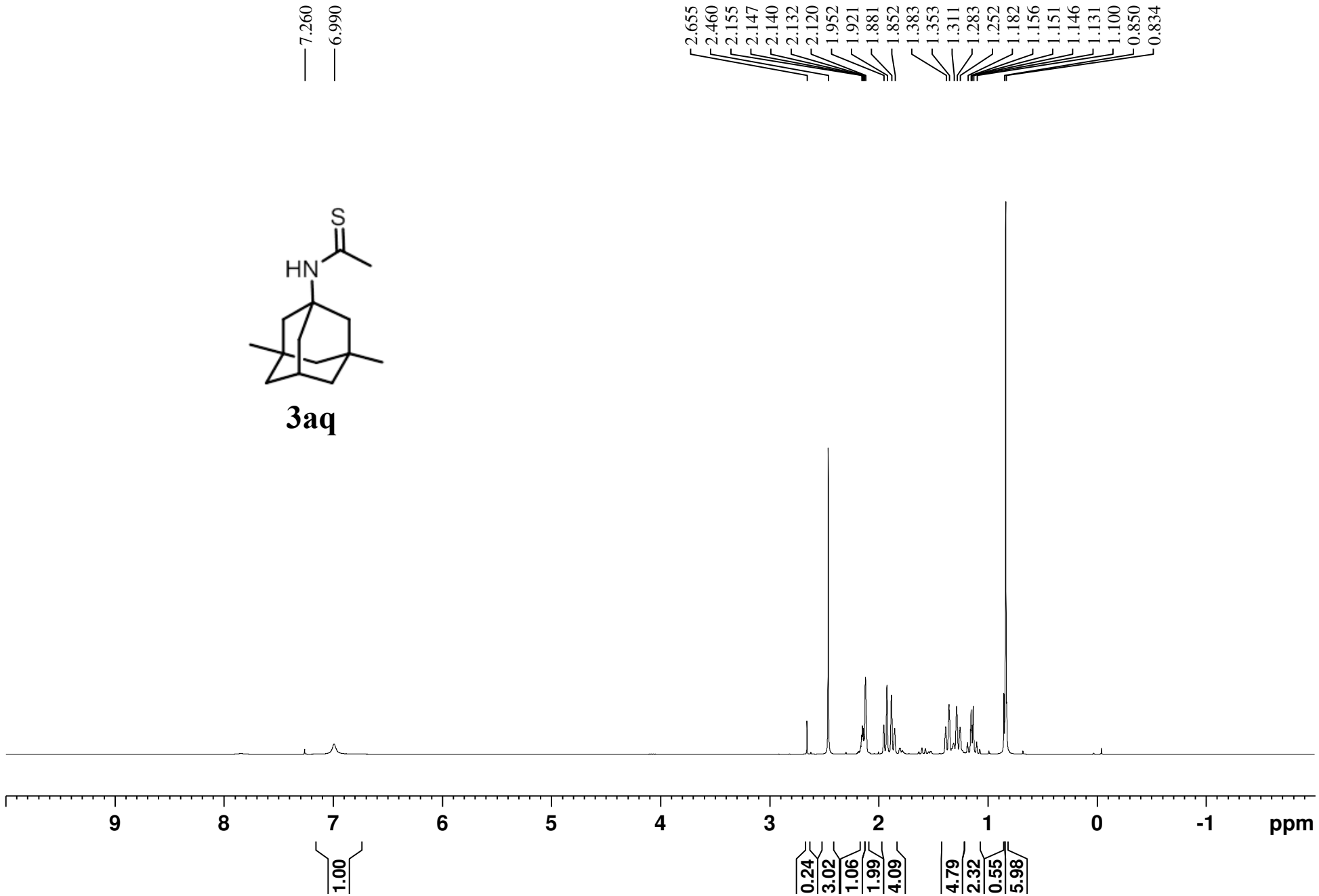
153.52
150.68
139.29
135.82
120.20
118.94
77.47
77.16
76.84
53.20
44.29
41.43
35.06
34.58
31.79
28.86
28.83
28.36
18.45
H
N
S
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3ap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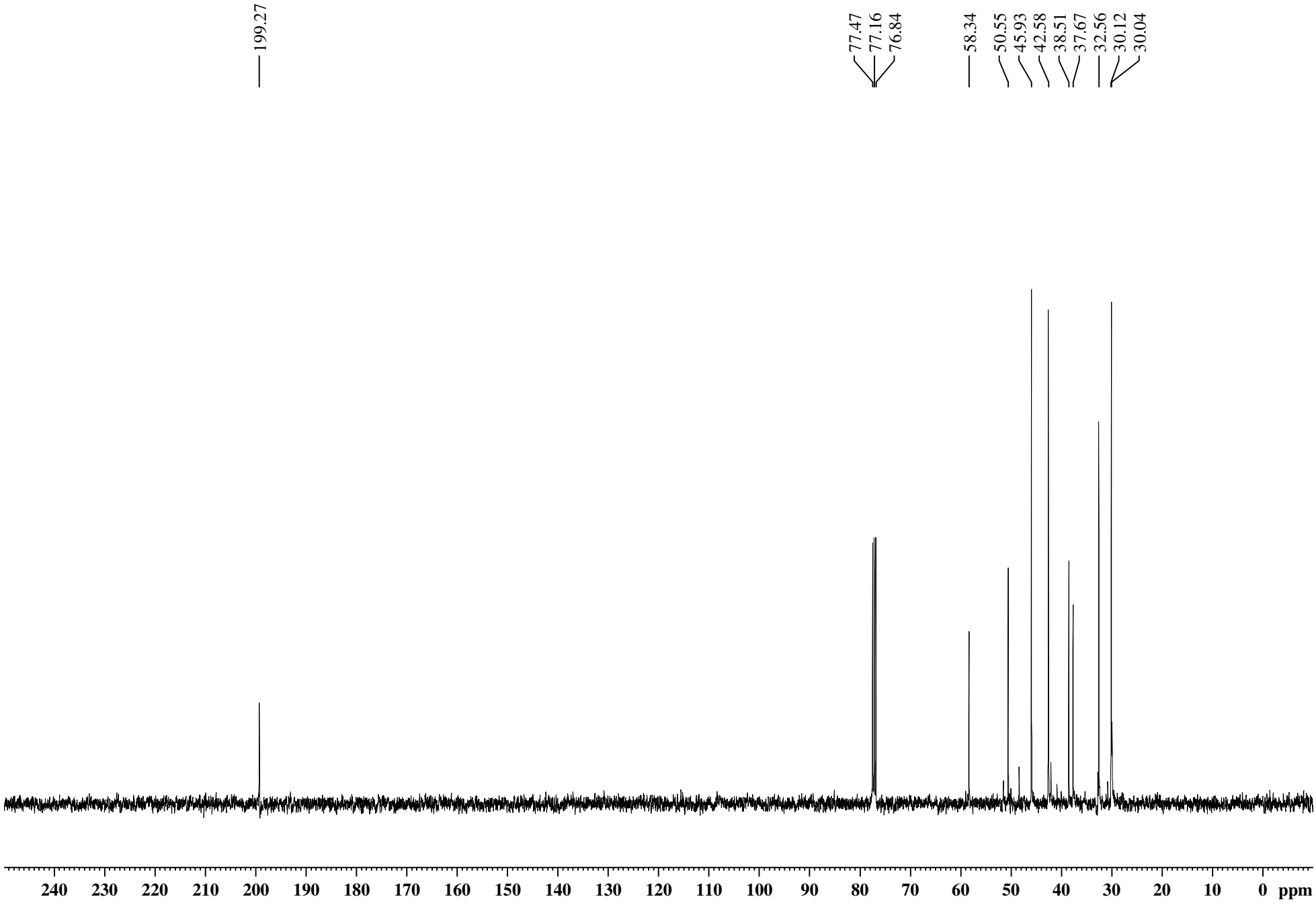
6.990
2.655
2.460
2.155
2.147
2.140
2.132
2.120
1.952
1.921
1.881
1.852
1.383
1.353
1.311
1.283
1.252
1.182
1.156
1.151
1.146
1.131
1.100
0.850
0.834
S
HN
3aq
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
0.24
3.02
1.06
1.99
4.09
4.79
2.32
0.55
5.98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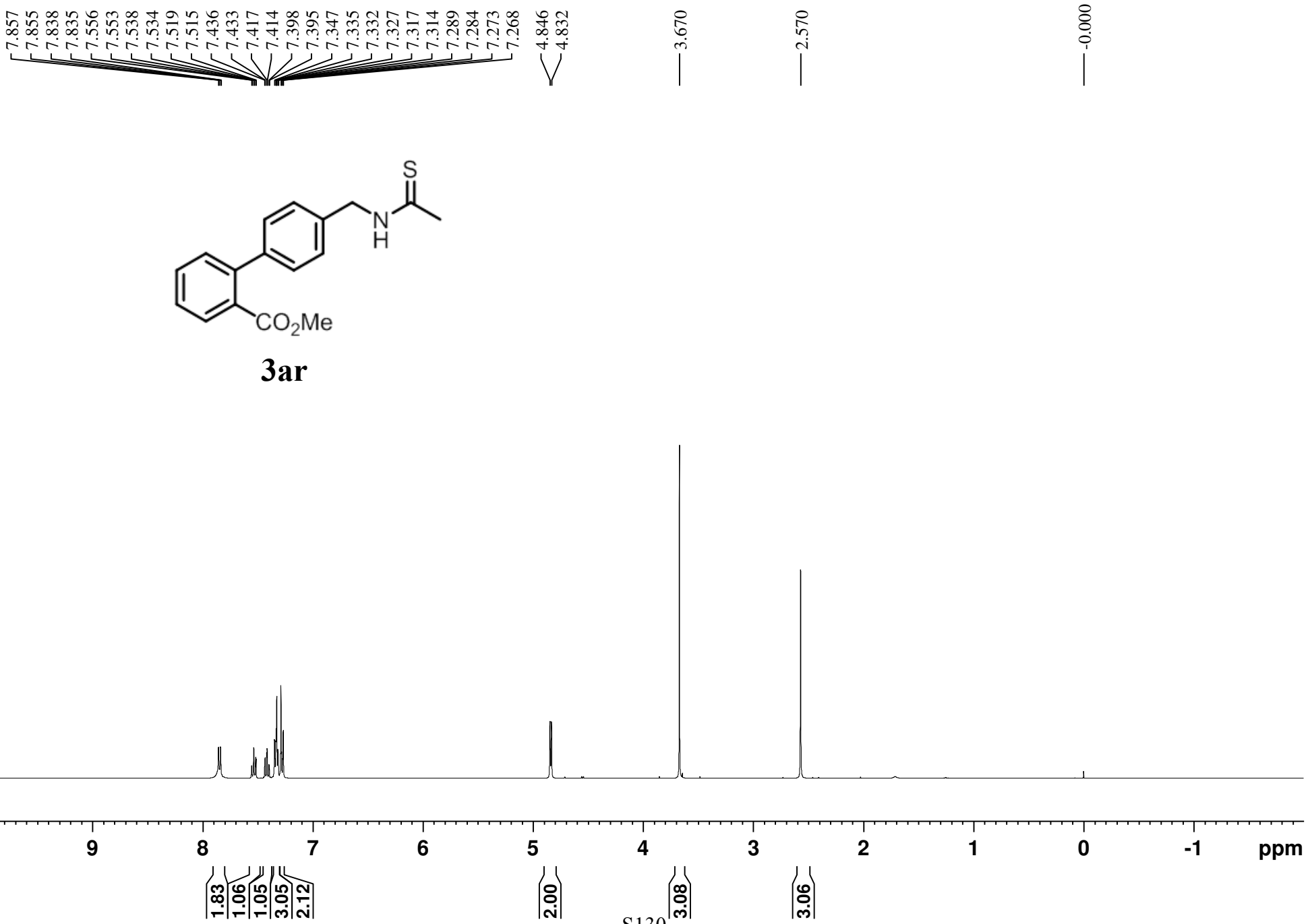
77.47
77.16
76.84
58.34
50.55
45.93
42.58
38.51
37.67
32.56
30.12
30.04
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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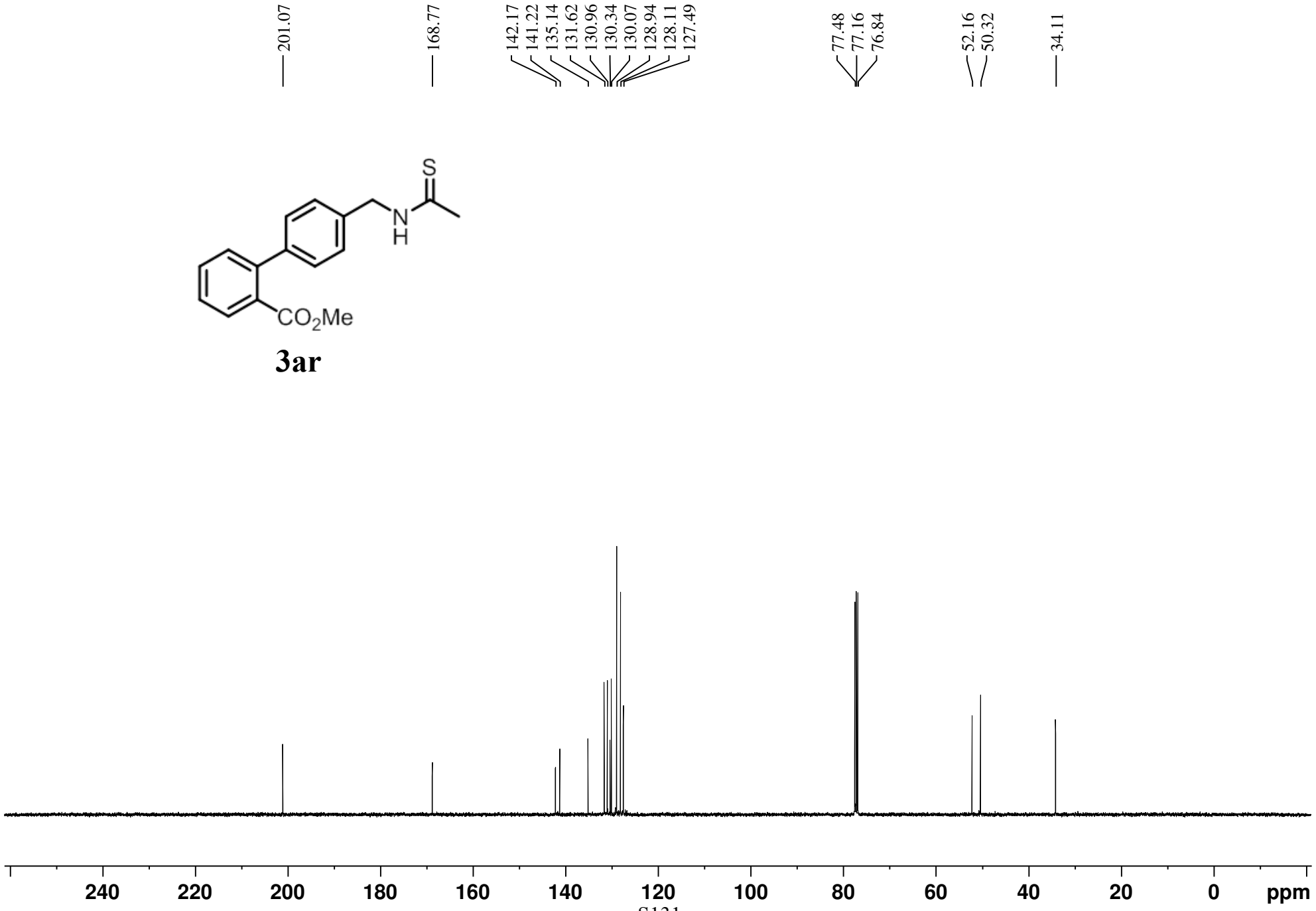
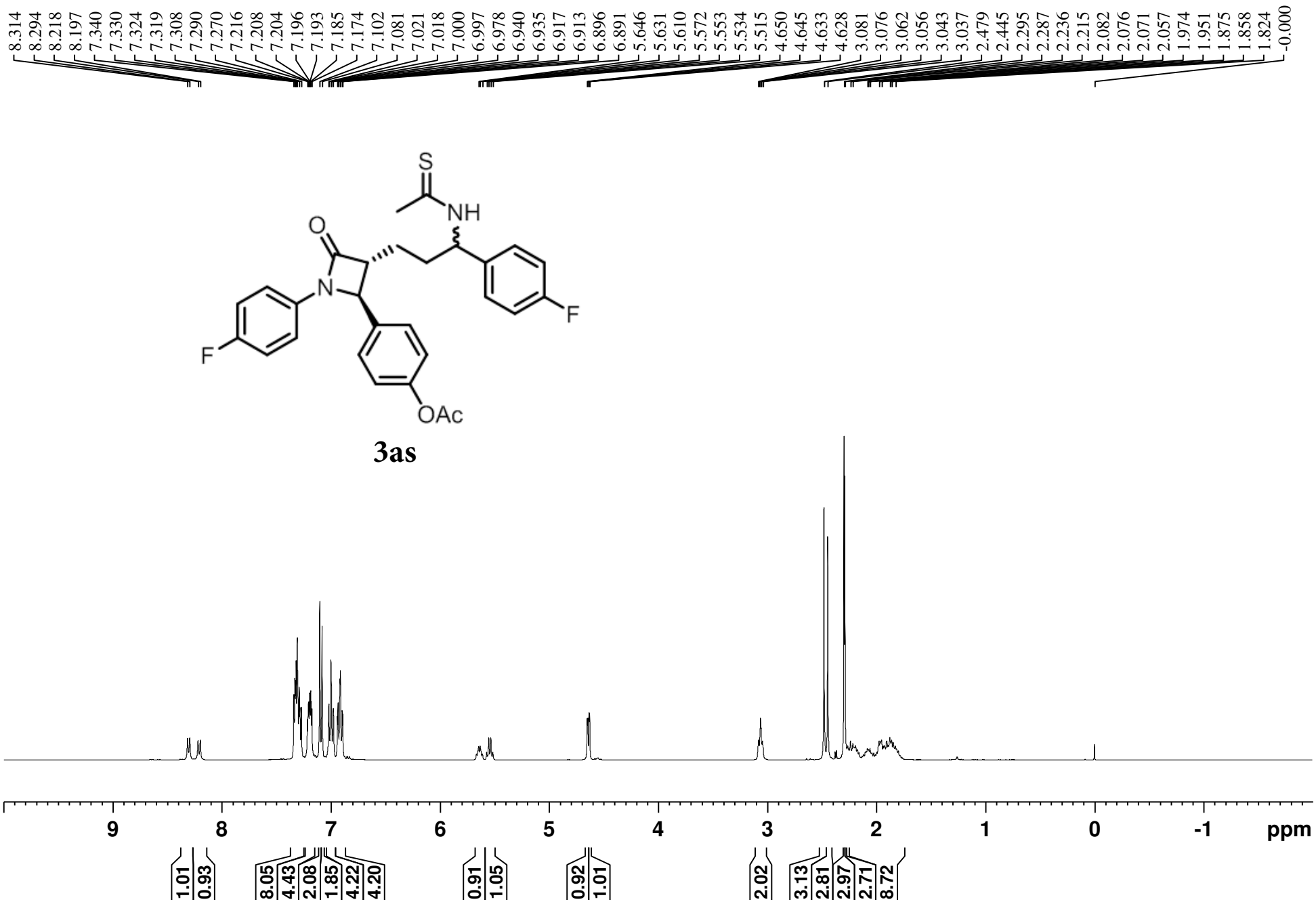
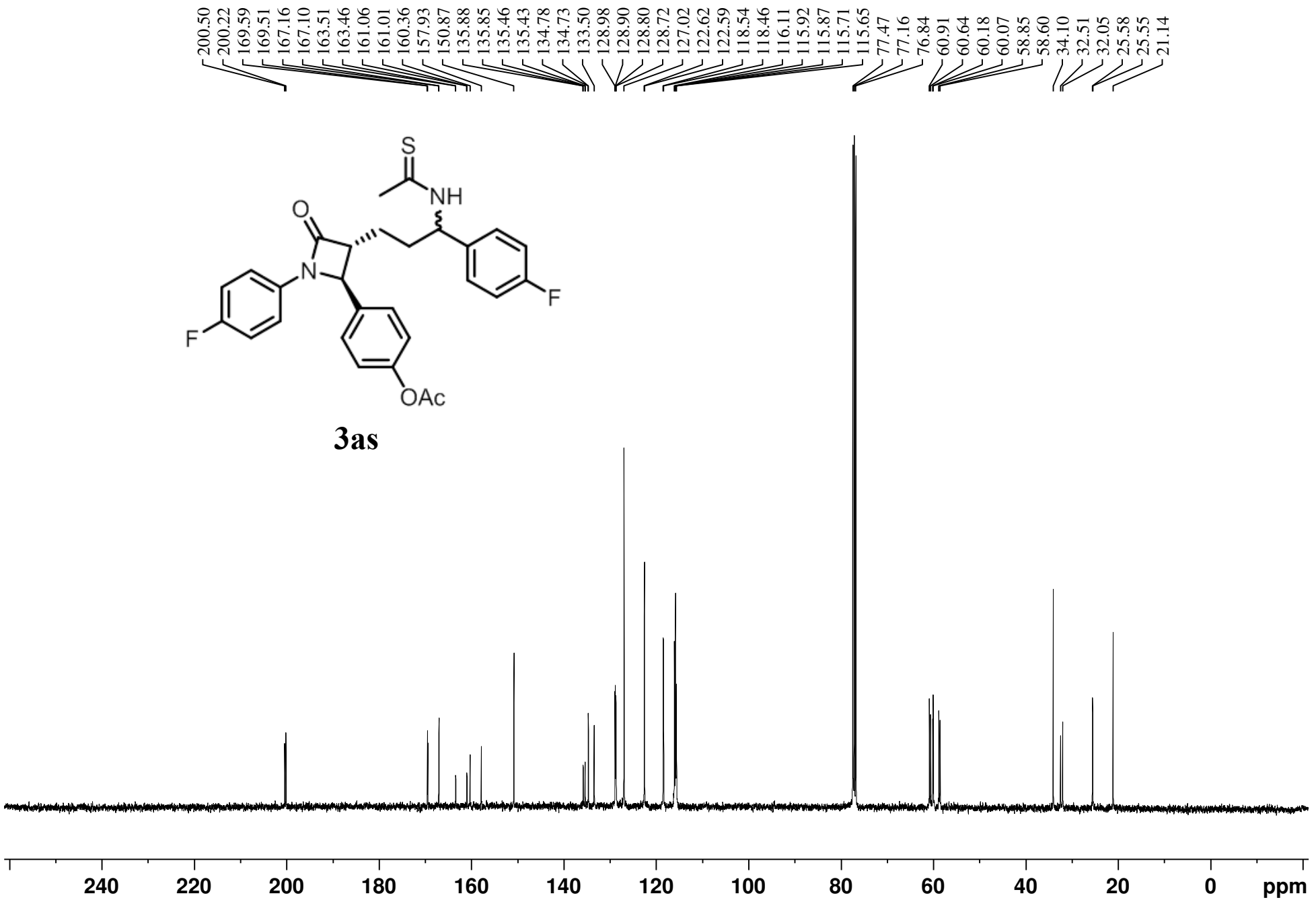
7.855
7.838
7.835
7.556
7.553
7.538
7.534
7.519
7.515
7.436
7.433
7.417
7.414
7.398
7.395
7.347
7.335
7.332
7.327
7.317
7.314
7.289
7.284
7.273
7.268
4.846
4.832
3.670
2.570
-0.000
S
N
H
CO2Me
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.83
1.06
1.05
3.05
2.12
2.00
3.08
3.06

3ar

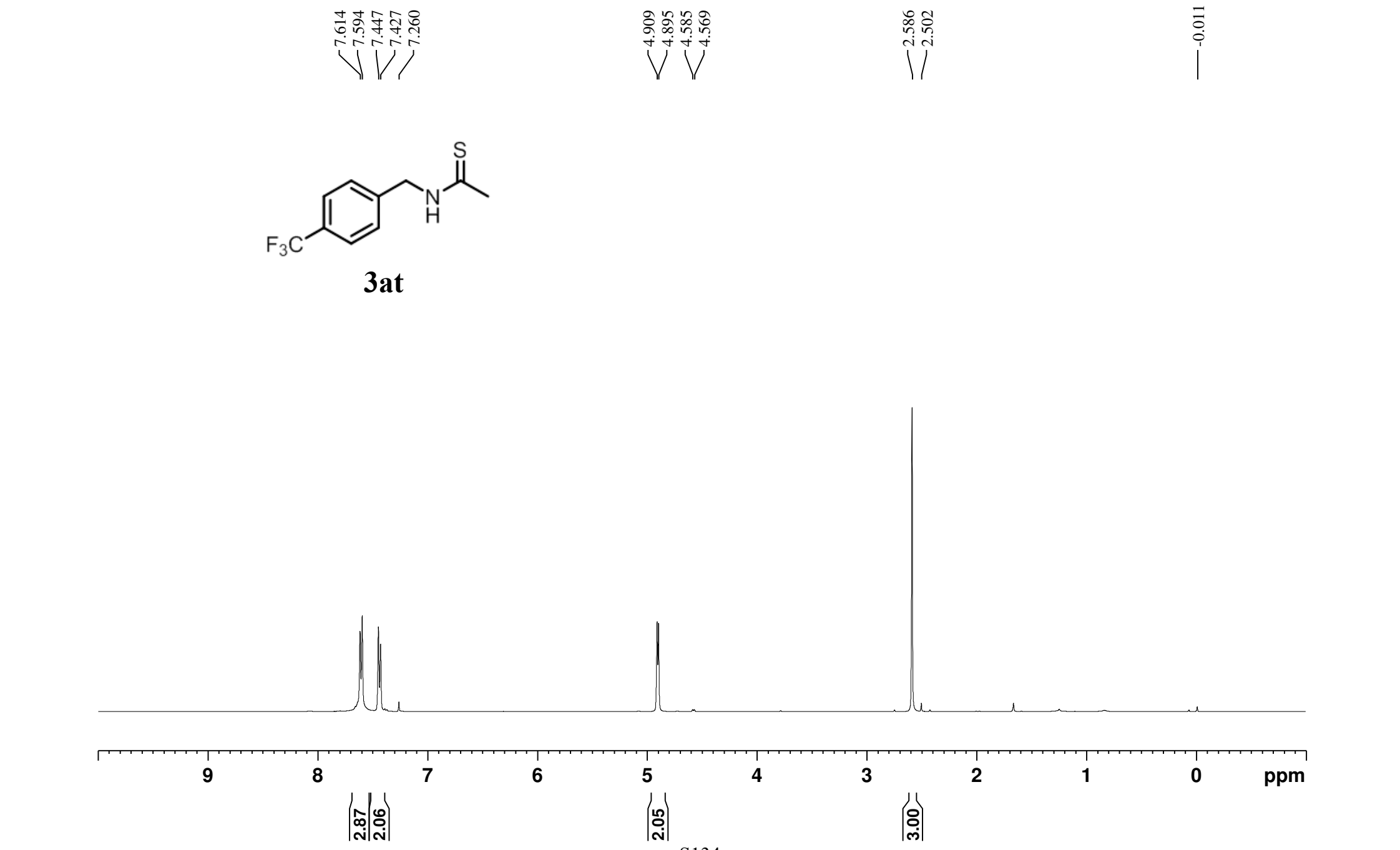

201.07
168.77
142.17
141.22
135.14
131.62
130.96
130.34
130.07
128.94
128.11
127.49
77.48
77.16
76.84
52.16
50.32
34.11
S
N
H
CO2Me
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3ar

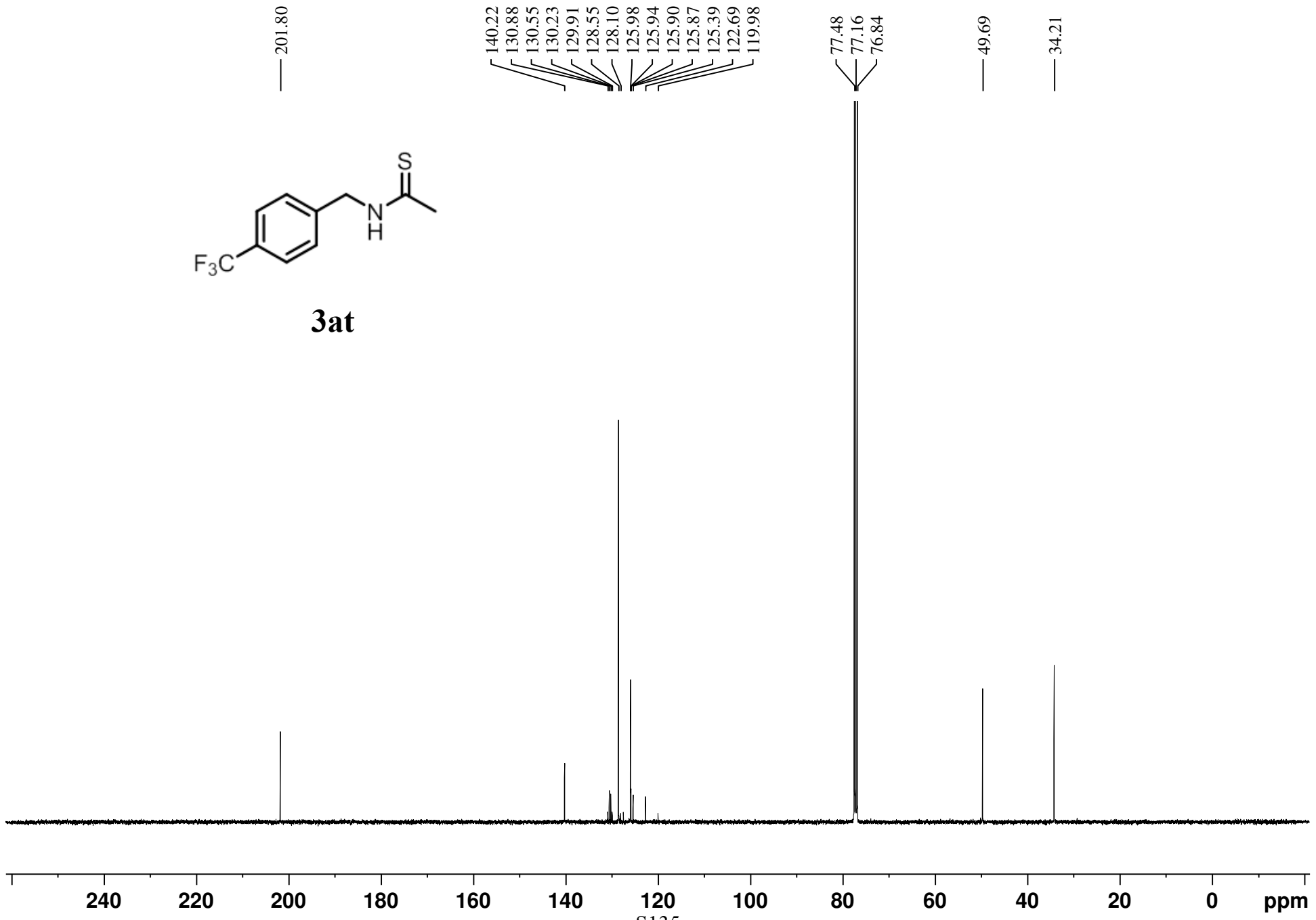

8.314
8.294
8.218
8.197
7.340
7.330
7.324
7.319
7.308
7.290
7.270
7.216
7.208
7.204
7.196
7.193
7.185
7.174
7.102
7.081
7.021
7.018
7.000
6.997
6.978
6.940
6.935
6.917
6.913
6.896
6.891
5.646
5.631
5.610
5.572
5.553
5.534
5.515
4.650
4.645
4.633
4.628
3.081
3.076
3.062
3.056
3.043
3.037
2.479
2.445
2.295
2.287
2.236
2.215
2.082
2.076
2.071
2.057
1.974
1.951
1.875
1.858
1.824
-0.000
S
NH
O
N
F
F
OAc
3as
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.01
0.93
8.05
4.43
2.08
1.85
4.22
4.20
0.91
1.05
0.92
1.01
2.02
3.13
2.81
2.97
2.71
8.72


200.50
200.22
169.59
169.51
167.16
167.10
163.51
163.46
161.06
161.01
160.36
157.93
150.87
135.88
135.85
135.46
135.43
134.78
134.73
133.50
128.98
128.90
128.80
128.72
127.02
122.62
122.59
118.54
118.46
116.11
115.92
115.87
115.71
115.65
77.47
77.16
76.84
60.91
60.64
60.18
60.07
58.85
58.60
34.10
32.51
32.05
25.58
25.55
21.14
S
NH
O
N
F
F
OAc
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

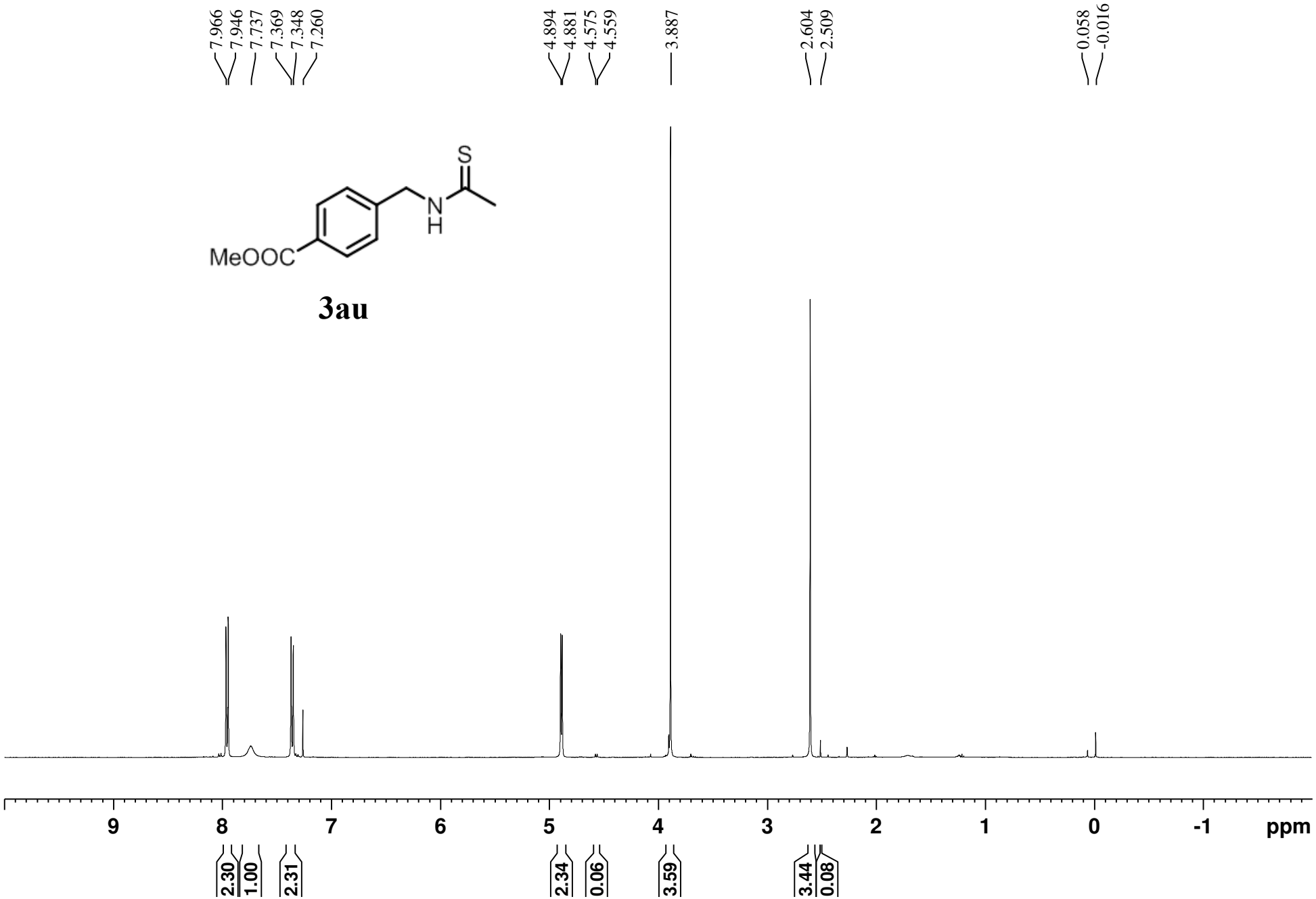
3as


7.614
7.594
7.447
7.427
7.260
4.909
4.895
4.585
4.569
2.586
2.502
-0.011
S
N
H
F3C
9
8
7
6
5
4
3
2
1
0
ppm
2.87
2.06
2.05
3.00

3at


201.80
140.22
130.88
130.55
130.23
129.91
128.55
128.10
125.98
125.94
125.90
125.87
125.39
122.69
119.98
77.48
77.16
76.84
49.69
34.21
S
N
H
F3C
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3at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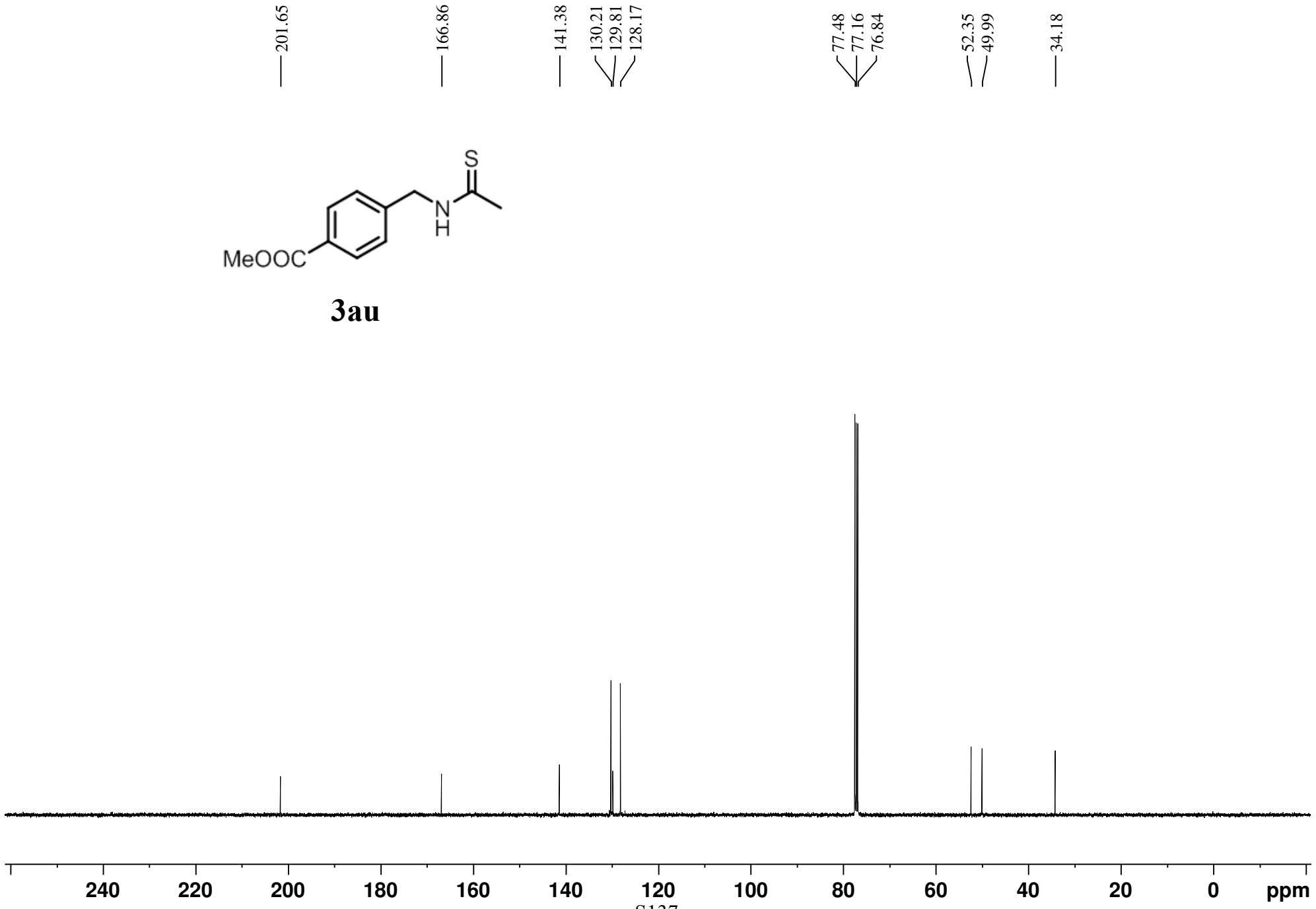
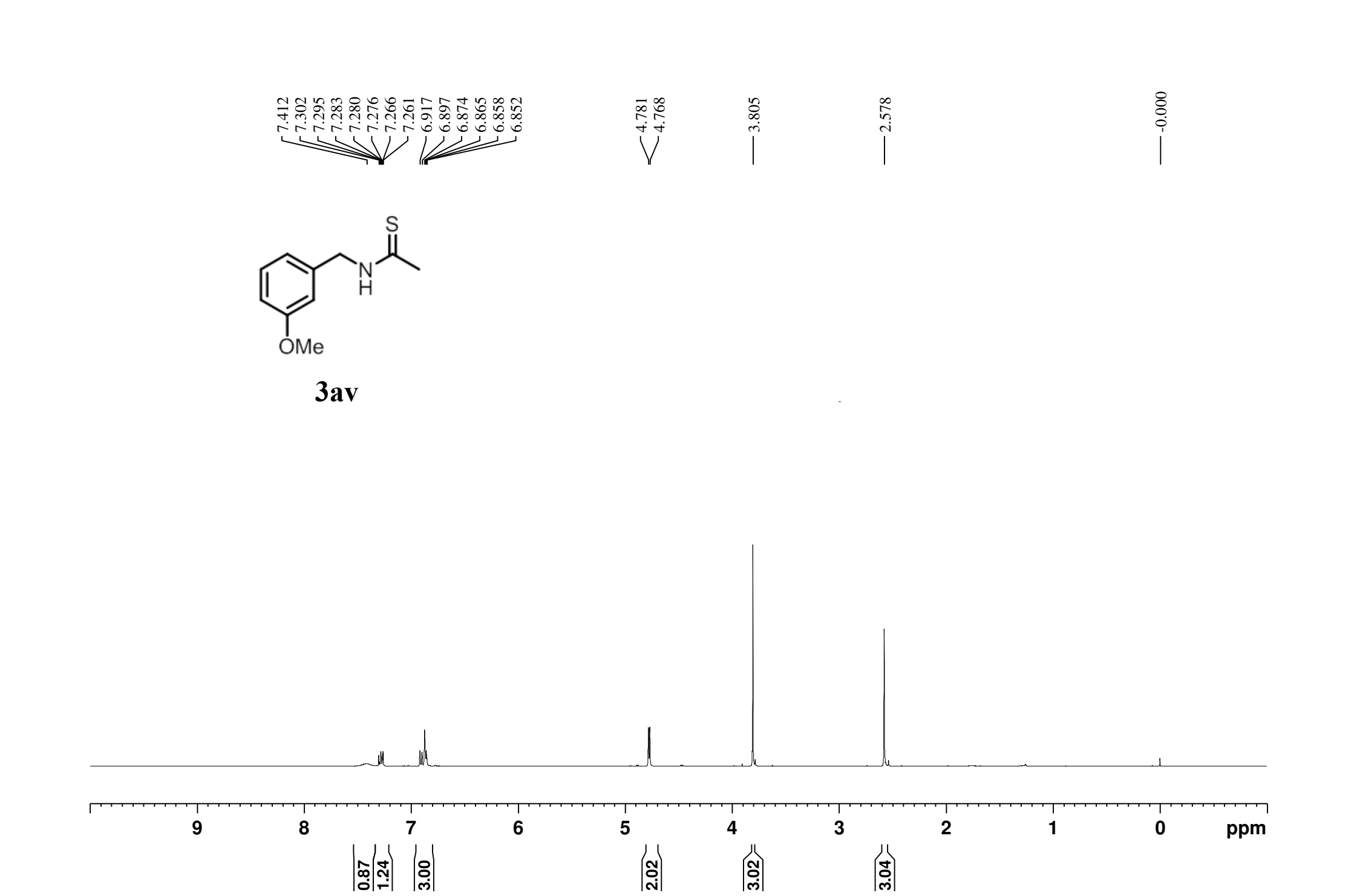
7.946
7.737
7.369
7.348
7.260
4.894
4.881
4.575
4.559
3.887
2.604
2.509
0.058
-0.016
S
N
H
MeOOC
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.30
1.00
2.31
2.34
0.06
3.59
3.44
0.08

3au


201.65
166.86
141.38
130.21
129.81
128.17
77.48
77.16
76.84
52.35
49.99
34.18
S
N
H
MeOOC
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3au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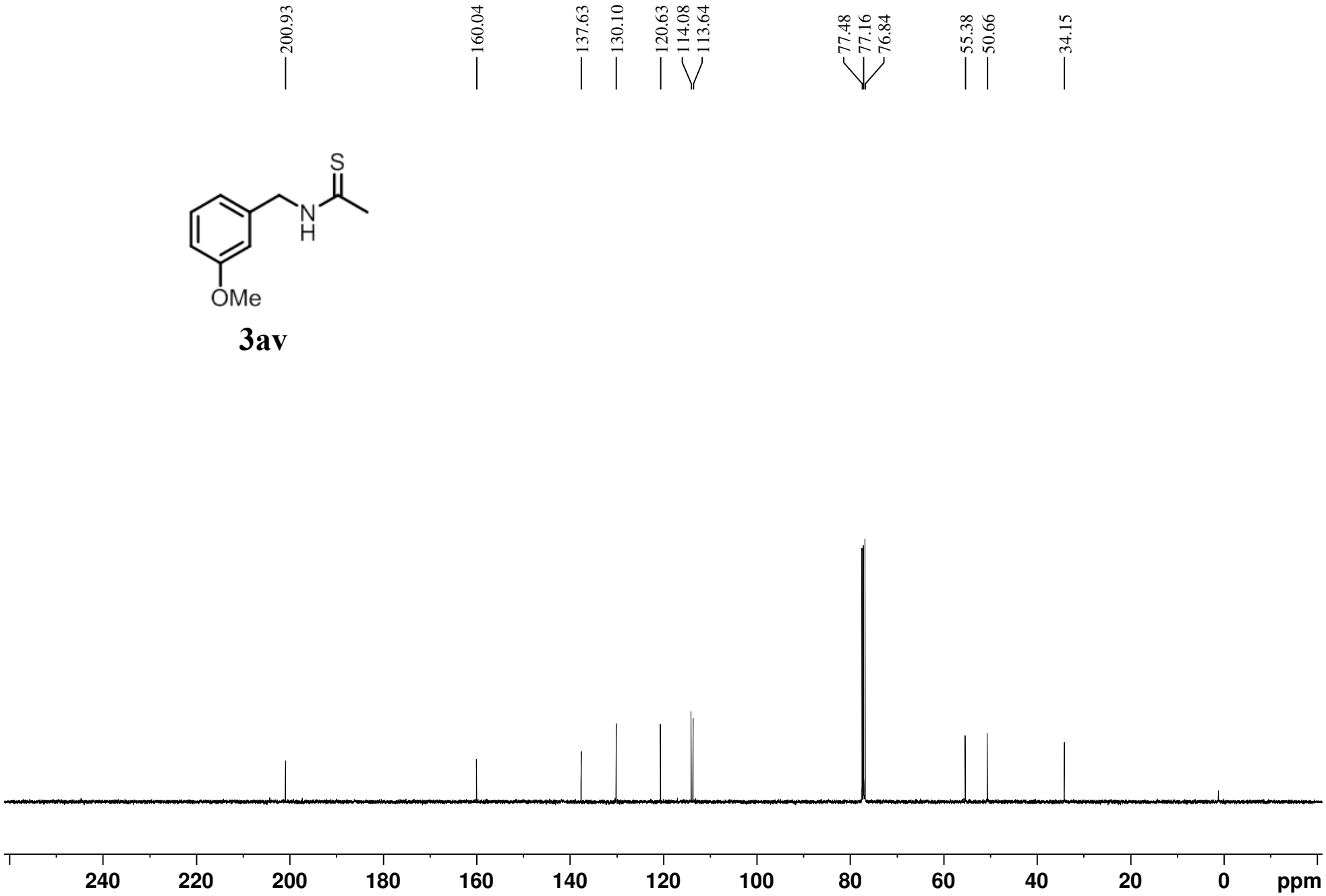
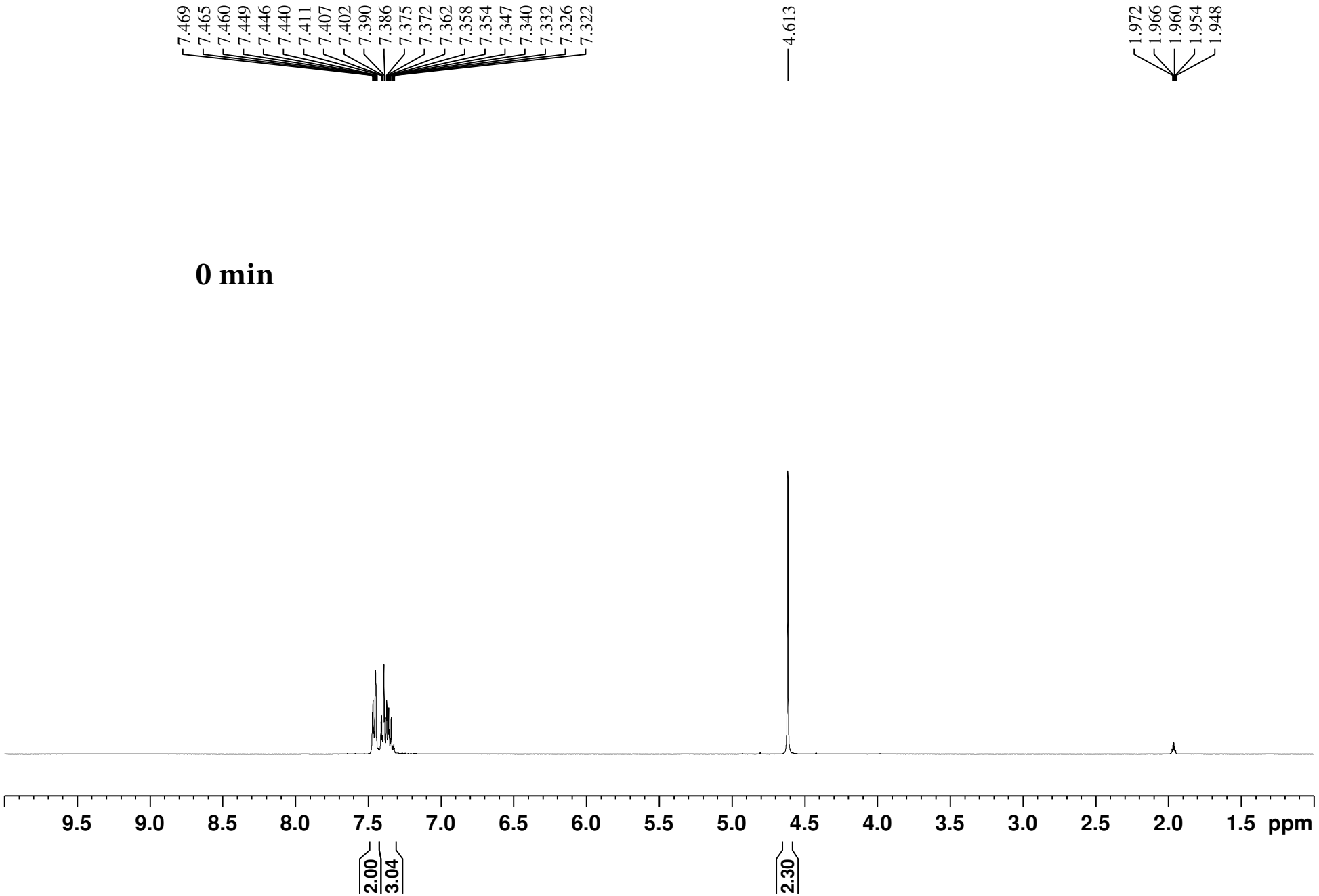
7.280
7.276
7.266
7.261
6.917
6.897
6.874
6.865
6.858
6.852
4.781
4.768
3.805
2.578
-0.000
S
N
H
OMe
9
8
7
6
5
4
3
2
1
0
ppm
0.87
1.24
3.00
2.02
3.02
3.04

3av


200.93
160.04
137.63
130.10
120.63
114.08
113.64
77.48
77.16
76.84
55.38
50.66
34.15
S
N
H
OMe
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3av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7.460
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7.446
7.440
7.411
7.407
7.402
7.390
7.386
7.375
7.372
7.362
7.358
7.354
7.347
7.340
7.332
7.326
7.322
4.613
1.972
1.966
1.960
1.954
1.948
0 min
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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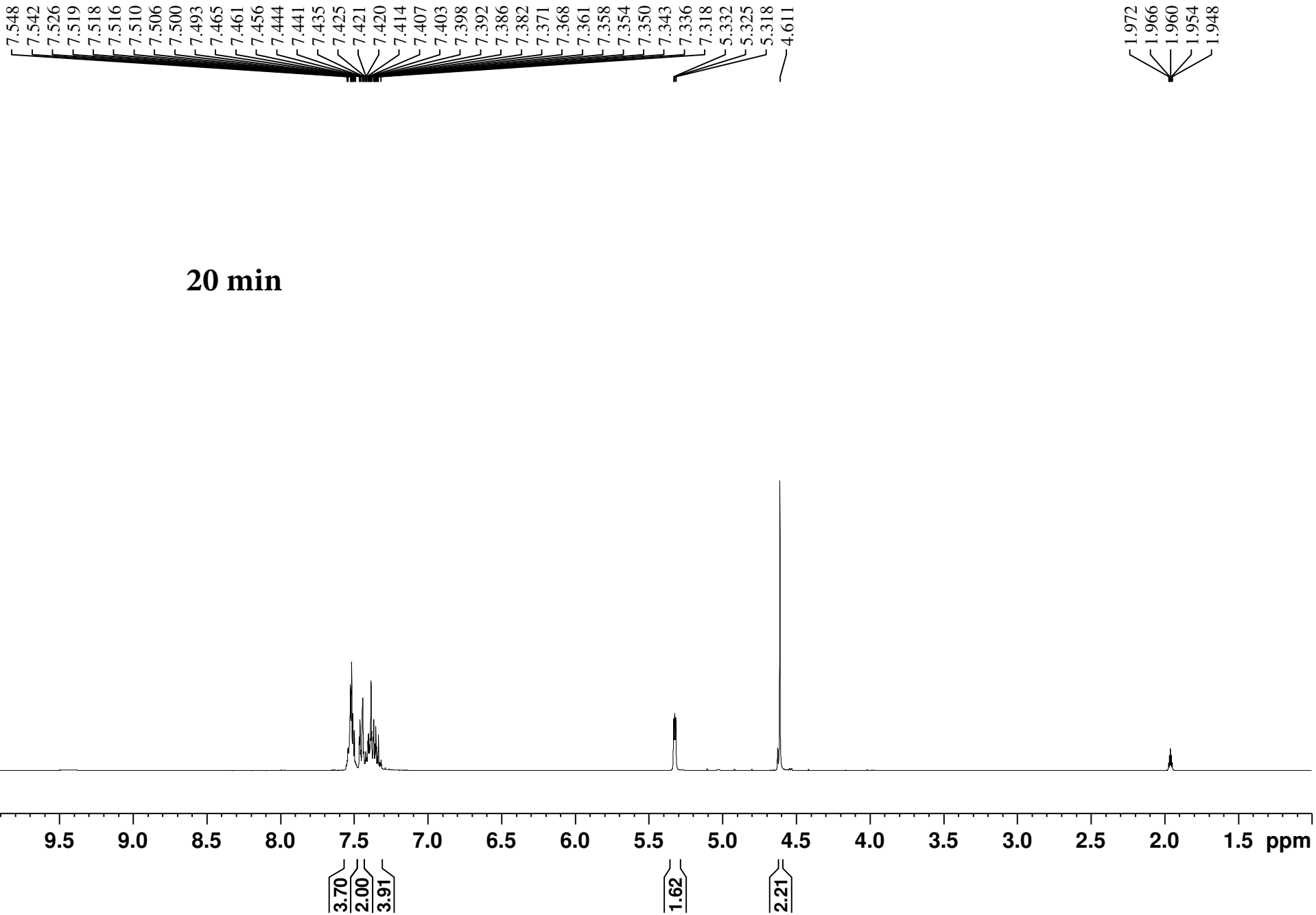
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.00
3.04
2.30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7.519
7.518
7.516
7.510
7.506
7.500
7.493
7.465
7.461
7.456
7.444
7.441
7.435
7.425
7.421
7.420
7.414
7.407
7.403
7.398
7.392
7.386
7.382
7.371
7.368
7.361
7.358
7.354
7.350
7.343
7.336
7.318
5.332
5.325
5.318
4.611
1.972
1.966
1.960
1.954
1.948
20 min
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
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1.5
ppm
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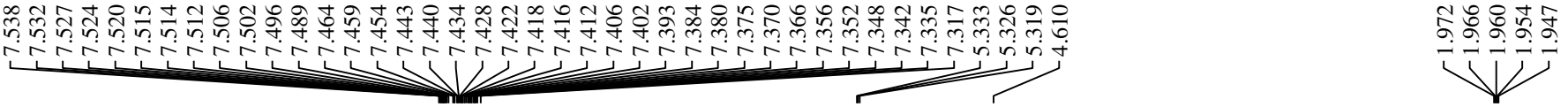
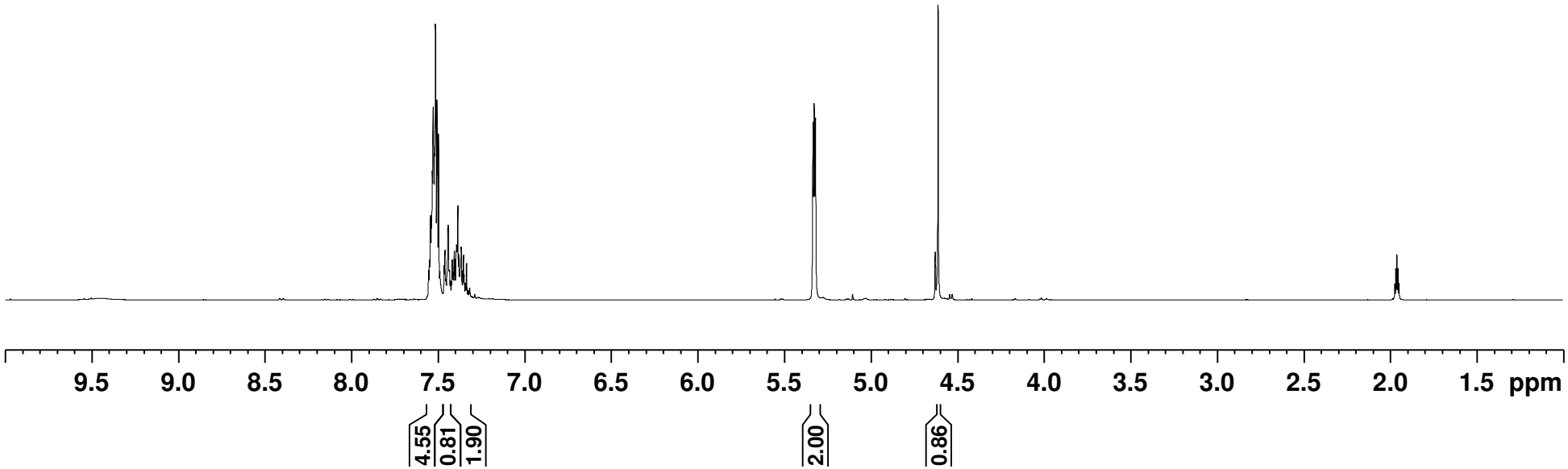
1.62
2.21


7.538
7.532
7.527
7.524
7.520
7.515
7.514
7.512
7.506
7.502
7.496
7.489
7.464
7.459
7.454
7.443
7.440
7.434
7.428
7.422
7.418
7.416
7.412
7.406
7.402
7.393
7.384
7.380
7.375
7.370
7.366
7.356
7.352
7.348
7.342
7.335
7.317
5.333
5.326
5.319
4.610
1.972
1.966
1.960
1.954
1.947

40 min


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
1.5
ppm
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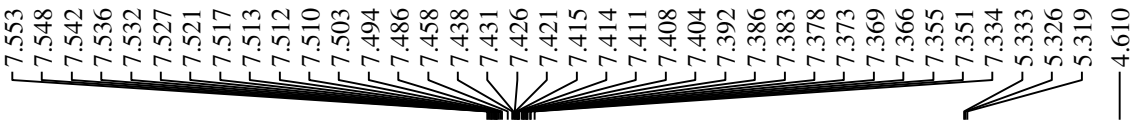
2.00
0.86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7.548
7.542
7.536
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7.527
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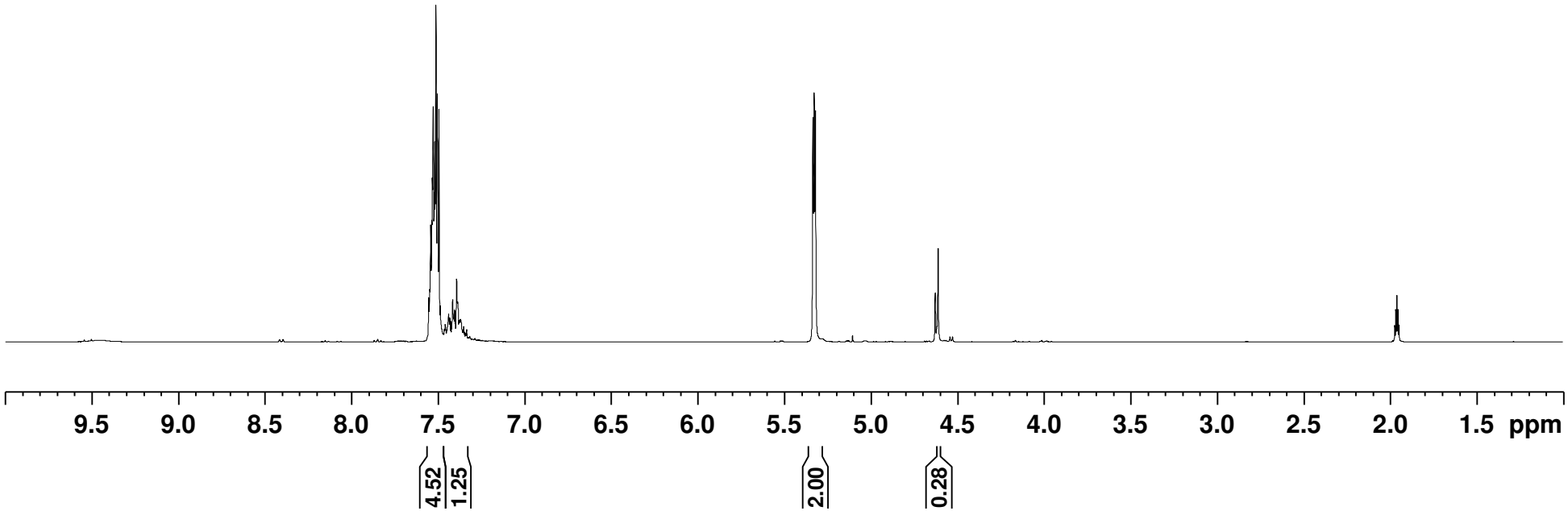
7.517
7.513
7.512
7.510
7.503
7.494
7.486
7.458
7.438
7.431
7.426
7.421
7.415
7.414
7.411
7.408
7.404
7.392
7.386
7.383
7.378
7.373
7.369
7.366
7.355
7.351
7.334
5.333
5.326
5.319
4.610
1.972
1.966
1.960
1.954
1.948

80 min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3.5
3.0
2.5
2.0
1.5
ppm
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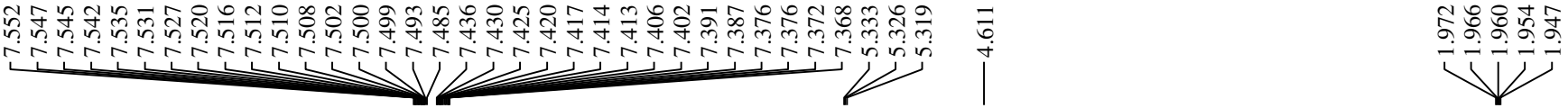
1.25
2.00
0.28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7.547
7.545
7.542
7.535
7.531
7.527
7.520
7.516
7.512
7.510
7.508
7.502
7.500
7.499
7.493
7.485
7.436
7.430
7.425
7.420
7.417
7.414
7.413
7.406
7.402
7.391
7.387
7.376
7.376
7.372
7.368
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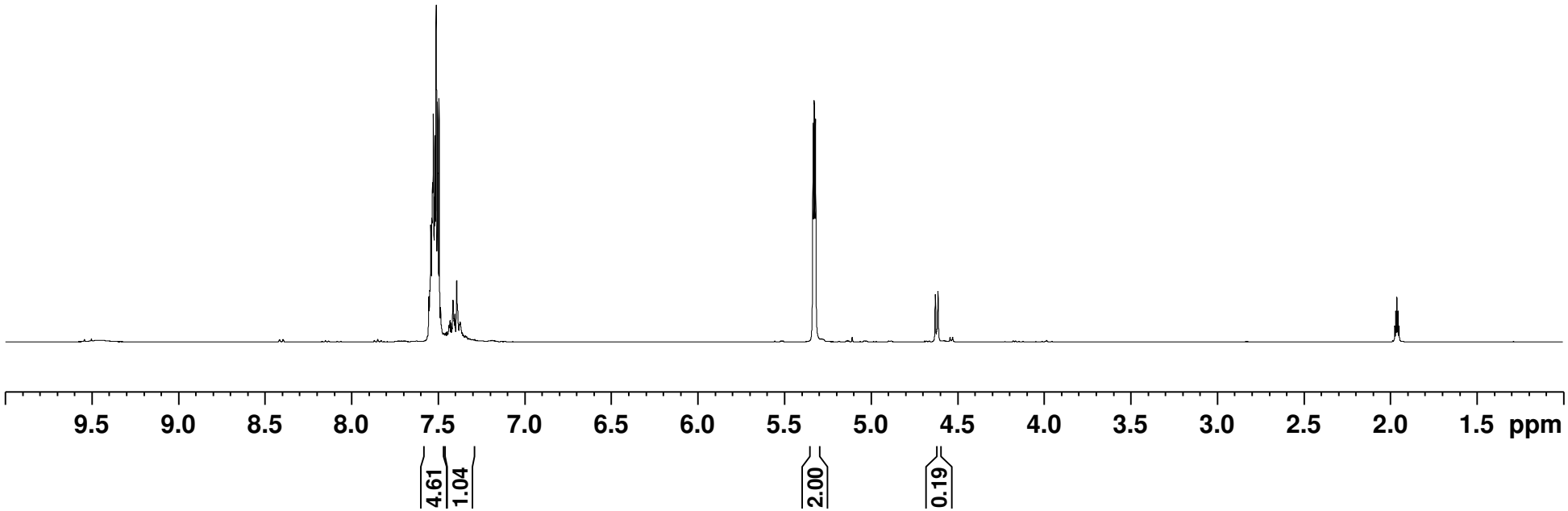
5.326
5.319
4.611
1.972
1.966
1.960
1.954
1.947

120 min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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
ppm
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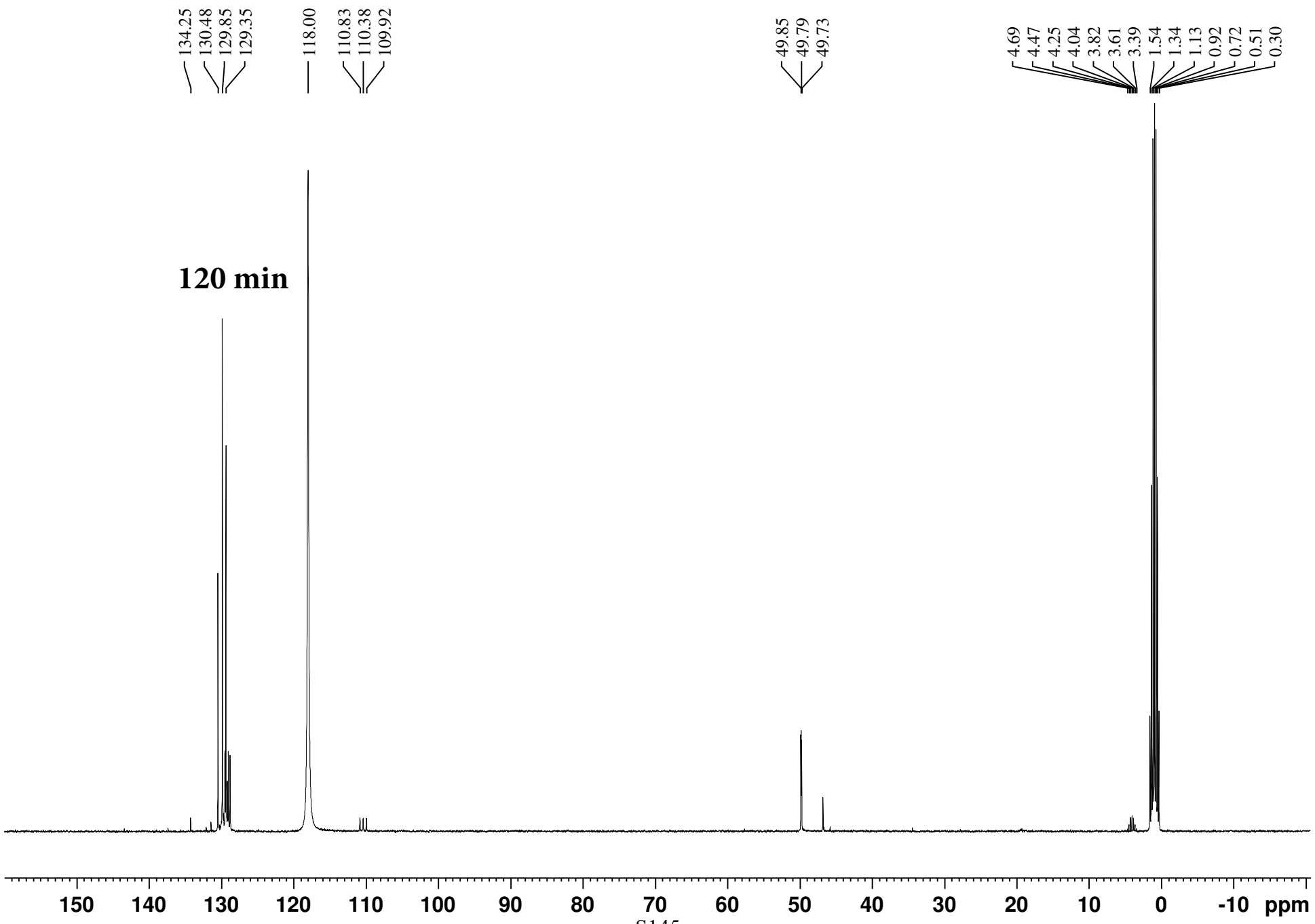
1.04
2.00
0.19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130.48
129.85
129.35
118.00
110.83
110.38
109.92
49.85
49.79
49.73
4.69
4.47
4.25
4.04
3.82
3.61
3.39
1.54
1.34
1.13
0.92
0.72
0.51
0.30
120 min
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm