Replacing conventional carbon nucleophiles with electrophiles:nickel-catalyzed reductive alkylation of aryl bromides and chlorides

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Supporting Information

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1. Chemicals

$NiI_2 \cdot xH_2O$ (x = 3.5 by elemental analysis) and anhydrous sodium iodide were purchased from Strem and used as received. It is important to note that the stoichiometry of NiI_2 hydrate is variable. We found that *excess nickel is not detrimental to the isolated yield of product*, but we obtained lower yields in reactions employing excess ligands. Therefore, we employed slight excess (0.107 equiv [Ni] to 0.100 mol% [ligands] or 0.054 equiv [Ni] to 0.050% [ligands]) in our reactions to account for the variable nickel stoichiometry.

4,4'-Dimethoxy-2, 2'-bipyridine, 1,10-phenanthroline, zinc dust (<10 mircon), ethyl 4-bromobutyrate, 4-bromo-N,N-dimethyl aniline, 4-bromoaniline, 1,4-dibromobenzene, 4-bromoanisole, 4-bromophenol, 2-bromotoluene, bromobenzene, 1-bromo-4-fluorobenzene, 4-bromobenzotrifluroide, 4-bromophenylboronic acid, 4-bromobenzonitrile, 4'-bromoacetophenone, 3-bromoanisole, chlorobenzene, 1-chloronaphthalene (tech. grade), methyl 4-chlorobenzoate, 4-chlorobenzonitrile, 3-bromopropyl amine hydrobromide, 2-ethylhexyl bromide, 2-bromomethyl-1,3-dioxolane, 2-chloro-6-methylpyridine, anhydrous pyridine, *p*-toluenesulfonyl chloride, acetyl chloride, 2-bromo-1-butene, cyclopentyl bromide, cycloheptyl bromide, 2-bromoheptane, benzyl alcohol, 4-bromobutyric acid, *n*-butyl lithium (1.6 M in hexanes), dichlorodimethylsilane, were purchased from Aldrich and used as received.

5-Bromo-2-methyl-2-pentene, (*E*)-2-bromo-2-butene, and (*Z*)-2-bromo-2-butene were purchased from Aldrich and filtered through a short basic alumina pad (1.5 cm) in a pipette packed with glass wool prior to use.

2-Bromoethanol and 4-chlorobenzotrifluoride were purchased from TCI and used as recieved.

2-Chloro-5-(trifluoromethyl)benzonitrile, 4-chlorophenyl methyl sulfone were purchased from Acros and used as recieved.

Ethyl 3-bromobenzoate, 4'-chloroacetophenone, and 3-bromopropylboronic acid pinacol ester, 2-bromo-1-butene were purchased from Alfa Asear and used as received.

Tert-butyl-dimethylchlorosilane was purchased for Gelest and used as received.

1-Bromo-2-methylpropene was purchased from Synthonix and used as received.

Octylbenzene [2189-60-8],[1] 3-bromopropyl-carbamic acid tert-butyl ester [83948-53-2],[2] (3-bromopropyl)carbamic acid benzyl ester [39945-54-5],[3] p-bromophenylboronic pinacol ester [68716-49-4],[4] (2-bromoethoxy)(tert-butyl)dimethylsilane [86864-60-0],[5] N-acetyl-5-bromoindole [61995-52-6],[6] (4-bromophenyl)trimethylstannane [937-11-1],[7] 4-bromophenyl 4-methylbenzenesulfonate [6324-15-8],[8] 4-acetoxybromobenzene [1927-95-3],[9] 4-bromophenyl trifluoromethanesulfonate [66107-30-0],[10] 1-bromo-4-N-(p-toluenesulfonamido)benzene [32857-48-0],[11] benzyl 4-bromobutanoate [126430-46-4],[12] were synthesized according to the literature procedures and spectral data were in agreement with the reported values.

Solvents. DMPU (1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, absolute, over molecular sieve (H_2O ≤0.03%), ≥99.0% (GC) was purchased from Aldrich or AK Scientific, and in most cases was used as received. Although sequential drying of DMPU over 4 Å molecular sieves before use could reduce water content to as low as 16 ppm, successful reactions were observed in DMPU containing as much as 1000 ppm water. The solvent can be stored on the bench over molecular sieves (4 Å) for extended periods of time (weeks) without detrimental effects on the yield of the cross-coupling reaction.

One lot received from Aldrich was a pale yellow color instead of a colorless liquid. Reactions run using this yellow DMPU resulted in lower yields. Impure DMPU can be purified by short path distillation from calcium hydride, followed by drying over molecular sieves (4 Å). The resulting material is colorless, dry (typically <100 ppm H_2O by Karl-Fischer titration, Metrohm), and provides the expected yields.

All other dry solvents were prepared from ACS grade, inhibitor free solvents by passage through activated alumina and molecular sieves in a Vacuum Atmospheres solvent purification system. Water content was routinely measured using Karl-Fisher titration (Metrohm) and was less than 50 ppm in all cases.

Zinc. While we obtained good yields with a variety of zinc sources, one lot of zinc dust (< 10 um) purchased from Aldrich resulted in long induction periods and reaction times (> 48 h) for the catalytic cross coupling reactions. Additionally, zinc dust (< 10 um) that had remained on the bench and exposed to air in chemical inventory for extended periods for time (months to years) also resulted in long induction periods and reaction times. However, the problem of inactive zinc could be remedied by (1) careful activation with acid (listed directly below) or (2) the addition of

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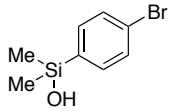
[1] Everson, D. A.; Shrestha, R.; Weix, D. J., *J. Am. Chem. Soc.* **2010**, *132*, 920-921.
[2] Georgiades, S. N.; Clardy, J., *Org. Lett.* **2005**, *7*, 4091-4094.
[3] Robarge, M. J.; Husbands, S. M.; Kieltyka, A.; Brodbeck, R.; Thurkauf, A.; Newman, A. H., *J. Med. Chem.* **2001**, *44*, 3175-3186.
[4] Koolmeister, T.; Södergren, M.; Scobie, M., *Tetrahedron Lett.* **2002**, *43*, 5965-5968.
[5] Kuwabe, S.-i.; Torraca, K. E.; Buchwald, S. L., *J. Am. Chem. Soc.* **2001**, *123*, 12202-12206.
[6] Phipps, R. J.; Grimster, N. P.; Gaunt, M. J., *J. Am. Chem. Soc.* **2008**, *130*, 8172-8174.
[7] Deushi, T.; Takahashi, Y.; Ishiwata, H.; Okuno, Y.; Oda, T.; Shiratsuchi, M.; Yamamoto, K. (Kowa Co. Japan). Azoxy Compund. US Patent 5,541,169, July 30, 1996.
[8] Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001** , *3*, 3049-3052
[9] Johnson, A. T.; Wang, L.; Standeven, A. M.; Escobar, M.; Chandraratna, R. A. S. *Bioorg. Med. Chem.* **1999**, *7*, 1321-1338.
[10] Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478-5486.
[11] McKeown, S. C.; Hall, A.; Blunt, R.; Brown, S. H.; Chessell, I. P.; Chowdhury, A.; Giblin, G. M. P.; Healy, M. P.; Johnson, M. R.; Lorthioir, O.; Michel, A. D.; et al. *Bioorg. Med. Chem.* **2007**, *17*, 1750-1754.
[12] Notre, J. L.; Mele, D. V.; Frost, C. G. *Adv. Synth. Catal.* **2007**, *349*, 432-440.

catalytic amounts of TMSCl and 1,2-dibromoethane directly to the reaction mixture (detailed on page S-9).

Zinc activation with acid. Zinc dust (120 g) was washed with 2% aqueous HCl (300 mL) for 1 min in a 400 mL beaker. It is important that the zinc not be exposed to the acidic solution for more than ~1 min. We found that longer exposure times resulted in zinc dust that was too active, which resulted in diminished yields of cross-coupled product and increased amounts of hydrodehalogenation. The zinc was collected by vacuum filtration and washed with water (3 × 200 mL), ethanol (200 mL), and ether (200 mL). Any clumps of zinc were lightly broken-up by crushing in a mortar and pestle (grinding also appeared to make the zinc too reactive). The zinc was dried in an oven for 30 min at 150 °C.



p-Bromphenyl-dimethylsilanol [18246-02-1][13] was prepared in analogy to a published procedure.[14] A 100 mL round bottom flask equipped with a teflon coated magnetic stir bar was flame dried and cooled under argon. 1,4-dibromobenzene (1.5 g, 6.5 mmol) was dissolved in dry ether (50 mL). Under an argon atomosphere at room temperature *n*-butyllithium (1.6M in hexanes, 4.0 mL, 6.5 mmol) was added slowly over the course of 5 minutes to generate the monoanion. A separate 2-neck 100 mL round bottom flask equipped with a teflon coated magnetic stir bar, a septum on one neck and a reflux condenser on the other neck was flame dried and cooled under argon. The two-neck flask was then charged with dichlorodimethylsilane (719 µL, 7.8 mmol) and dry ether (5 mL). Next, the reaction solution was slowly transferred over 30 minutes by cannula to the two-neck round bottom flask, causing a white precipitate to form. After the addition was complete the septum on the 2-neck flask was replaced with a glass stopper and the reaction mixture was head to 50 °C for 18 h. After allowing the reaction to cool to room temperature saturated ammonium chloride (20 mL) was added causing the white precipitate to dissolve after stirring. The contents of the flask were transferred to a separtory funnel; the organics were collected and washed with saturated ammonium chloride (20 mL), water (20 mL), and brine (20 mL) before drying over $MgSO_4$, filtering and concentrating. The crude material was purified by chromatography on silica gel (8:2 hexanes: ethyl acetate, R_f = 0.35, stains with $KMnO_4$) to give 464 mg of faintly yellow oil (31%).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 2.33 (s, 1H), 0.38 (s, 6H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 138.0, 134.8, 131.2, 124.6, 0.1.

GC-MS *m/z* (% relative intensity, ion): 231.95 (17.48, M^+), 216.85 (99.35, M^+-CH_3), 214.90 (100.00, M^+-CH_3), 77.00 (18.17, M^+-C_2H_7BrOSi).

[13] Aoki, Toshiki; Watanabe, Jun; Ishimoto, Yoshiyuki; Oikawa, Eizo; Hayakawa, Yoshio; Nishida, Masakazu *J. Fluorine Chem.*, **1992**, *59*, 285-288.
[14] Aoki, T.; Watanabe, J.; Ishimoto, Y.; Oikawa, E.; Hayakawa, Y.; Nishida, M. *J. Fluorine Chem.* **1992**, *59*, 285-288.

2. **Analytical Methods**

NMR chemical shifts are reported in ppm and referenced to the residual solvent peak $CDCl_3$ (δ = 7.26 ppm ^1H or δ = 77.16 ppm ^{13}C) as an internal standard or trifluorotoluene (δ = 0.000 ppm) as an external standard (^{13g}). NMR spectra were recorded on Bruker model Avance NMR spectrometer operating at 400.13 MHz or 500.13 MHz proton NMR frequency, and data analysis was performed using the iNMR software package (version 4.0.4). In the ^{13}C spectra of boron containing compounds (**3ag-ah**) the resonance corresponding to the carbon attached to boron was not observed.[15] The 1H NMR spectrum of **3o** and the 1H and 13C NMR spectra of **3al** contain peaks corresponding to long chain aliphatic hydrocarbons (grease).[16]

GC analyses of crude reaction mixtures were performed on an Agilent 7890A GC equipped with dual DB-5 columns (20 m x 180 μm x 0.18 μm), dual FID detectors and using hydrogen as the carrier gas. The analysis method used in all cases was 1 μL inj. of sample, inj. temp of 300 ºC, 100:1 split ratio, initial inlet pressure was 20.3 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. Initial oven temperature of 50 ºC was held for 0.46 min followed by a temperature ramp up to 300 ºC at 65 ºC/min and finally the temperature was held at 300 ºC for 0.69 min. Total run time was ~ 5 min. FID temperature was 325 ºC.

GC analyses of crude reaction mixtures for competition experiments were performed on an Agilent 7890A GC equipped with dual DB-5 columns (20 m x 180 μm x 0.18 μm), dual FID detectors and using hydrogen as the carrier gas. The analysis method used for experiments employing 4-fluorobromobenzene, 3-bromoanisole, ethyl-3-bromobenzoate, 4-fluorobenzotrifluoride and 4'-bromoacetophenone was 1 μL inj. of sample, inj. temp of 300 ºC, 100:1 split ratio, initial inlet pressure was 20.3 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. Initial oven temperature of 50 ºC was held for 1.0 min followed by a temperature ramp up to 300 ºC at 30 ºC/min and finally the temperature was held at 300 ºC for 0.69 min. Total run time was ~ 9.5 min. FID temperature was 325 ºC. The competition experiment employing 4-bromoanisole used the same GC analysis used for evaluating crude reaction mixtures (described above).

GC/MS analyses were performed on a Shimadzu GCMS-QP2010 equipped with an RTX-XLB column (30 m x 0.25 mm x 0.28 μm) with a quadrupole mass analyzer using helium as the carrier gas. The analysis method used in all cases was 5 μL inj. of sample, inj. temp of 225 ºC, 25:1 split ratio, initial inlet pressure was 7.8 psi, but varied as the column flow was held constant at 1.0 mL/min for the duration of the run, the interface temperature was held at 250 ºC, and the ion source (EI, 30 eV) was held at 250 ºC. Initial oven temperature was held at 50 ºC for 3 min with the detector off followed by a temperature ramp, with the detector on, to 280 ºC at 40 ºC/min, and finally the temperature was held at 280 ºC for 3 min. Total run time was 11.75 min. For compounds **3aa** and **3ad** the method was modified to hold the final temperature of 280 °C for 8 min.

[15] Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130,* 7534-7535.
[16] Gottlieb, H. E.; Vadim, K.; Nudelman, A. *J. Org. Chem.*, ***1997,*** 62*,* 7512-7515.

Chromatography was performed on silica gel (EMD, silica gel 60, particle size 0.040-0.063 mm) using standard flash techniques. Products were visualized by one of the following methods: UV stain, ninhydrin stain, $KMnO_4$ stain, iodine stain, or by GC.

3. General Procedures for Reductive Cross-Coupling Reactions

Optimization and Control Reactions.

Reactions were set upon the bench-top without any precautions to exclude air or moisture. To a 1-dram vial containing a teflon-coated stir-bar was added the required amount of appropriate catalyst and ligand(s) followed by DMPU (2 mL), pyridine, organohalide(s) (0.500 mmol each), Zn^0 dust (>10 μm, 2.00 equiv), and dodecane (10.0 μL internal standard). The reaction vials were capped with a PTFE-faced silicone septum, and heated in a reaction block on the bench-top. After 15-41 h reaction time, 10-50 μL aliquots of reaction mixture were removed with a 50 μL gas-tight syringe and quenched with 10-50 μL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether or ethyl acetate (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield or percent conversion based on unreacted starting material was calculated.

GC response factor for 1-bromooctane (2) and 1-phenyloctane (3)

The GC response factor for **3** was determined by making standard solutions of **3** with the internal standard dodecane in volumetric flasks using ether as the solvent. The response factor (R_f) was calculated from equation (1):

$$R_f = (\text{analyte signal})([\text{dodecane}]) / ([\text{analyte}])(\text{dodecane signal}) \quad (1)$$

Analyte	[Analyte] mM	Analyte Signal (pA*s)	[dodecane]	Dodecane signal (pA*s)	Response factor (R_f)	Average
1-phenyloctane (**3**)	0.00124	542.2475	0.00174	44.90781	1.141	1.183
	0.00994	379.89758	0.00120	43.59599	1.050	
	0.00752	316.98511	0.00110	37.45347	1.235	
	0.00500	72.07383	0.00113	13.80404	1.177	
	0.00248	48.28048	0.00122	18.07833	1.310	
1-bromooctane (**2**)	0.01125	245.24623	0.00132	47.55844	0.605	0.627
	0.00843	189.69733	0.00132	46.93354	0.633	
	0.00562	125.32188	0.00132	45.38866	0.649	
	0.00281	60.75986	0.00132	45.94073	0.621	

General procedure for preparative reactions.

Reactions run with un-activated zinc.

<u>On the bench-top with no precaution to exclude air or moisture</u> $NiI_2 \cdot xH_2O$ (x = 3.5, MW = 375.56 determined by elemental analysis, 15.1-30.2 mg, 0.040-0.080 mmol, 0.053-0.107 equiv) 4,4'-dimethoxy-2, 2'-bipyridine (for electron rich aryl halides, 8.1-16.2 mg, 0.0375-0.0750 mmol, 0.050-0.100 equiv) or 1,10-phenanthroline (for electron poor aryl halides, 6.8-13.6 mg, 0.0377-0.0750 mmol, 0.050-0.100 equiv), sodium iodide (28.5 mg, 0.190 mmol, 0.250 equiv), and solid substrates (0.75 mmol, 1.00 equiv) were weighed on weigh paper and

transferred to a 1 dram vial equipped with a magnetic stir bar. Solvent, DMPU (1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3.0 mL), pyridine (3-6 μL, 0.039-0.0775 mmol, 0.052-0.103 equiv), liquid reagents, and zinc dust (>10 μm, 98 mg, 1.50 mmol, 2.00 equiv) were added. The reaction vials were capped with a PTFE-faced silicone septum, and the generally green solution was stirred at room temperature for approximately 5 min. before heating to 60 or 80 °C in a reaction block on the bench-top.

The reaction progress was followed by GC analysis. At appropriate times 10 μL aliquots of reaction mixture were removed with a 10 μL gas-tight syringe and quenched with 50 μL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether or ethyl acetate (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography.

The reactions generally turn from green to black when complete (Figure S1). Upon completion (judged as <1 Area % of starting materials remaining by GC analysis) the entire reaction mixture was loaded onto a silica gel column for purification. The reaction vial was rinsed with ether and dichloromethane (1 mL each), which were also loaded on the column.

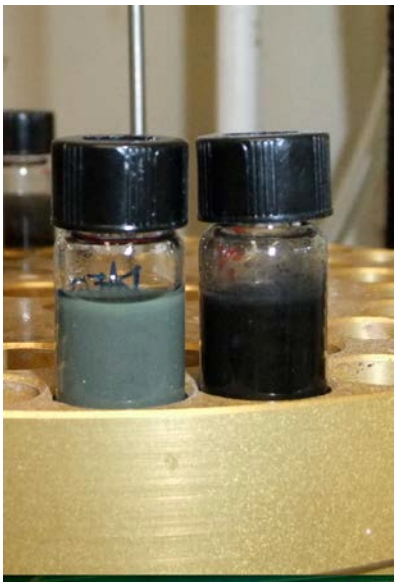


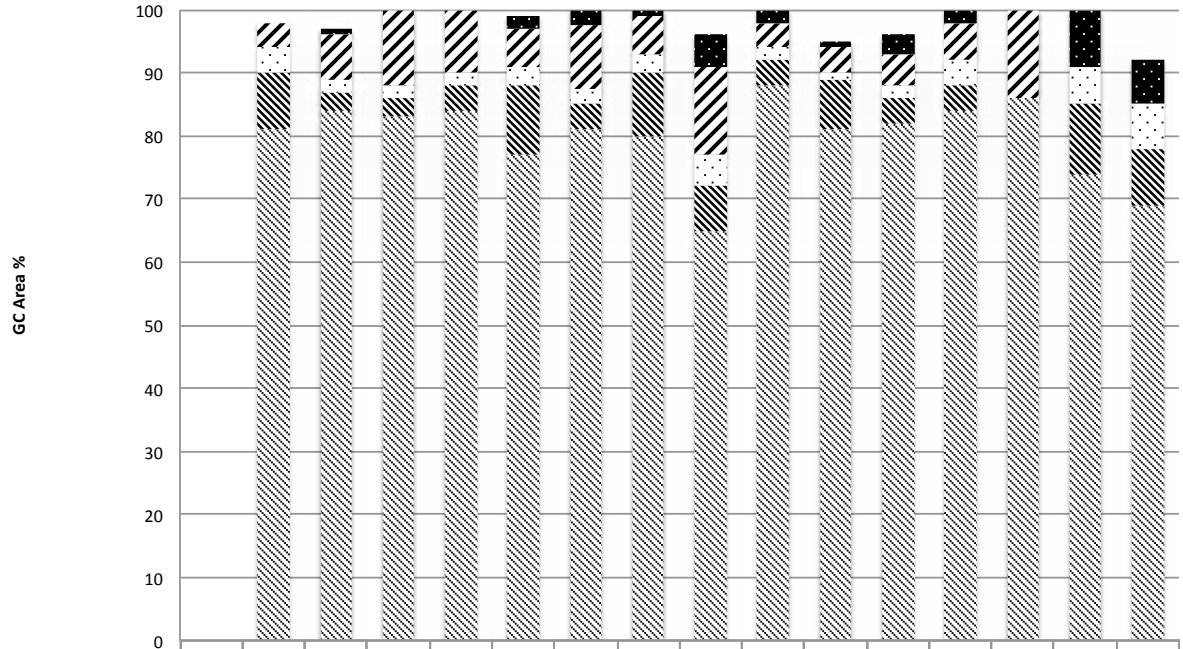
Figure S1: Reactions color change from gray-green (active reaction on the left) to black (complete reaction on the right), which reliably marks the end-point (complete consumption of both starting materials) of the reaction.

Reactions run with activated zinc.

The general procedure above for reactions run with un-activated zinc was followed except chlorotrimethylsilane and 1,2-dibromoethane (6 μL each) were added sequentially as the last two reagents to the reaction vial. The reactions progressed normally and were followed in the same manner. The reaction color change from gray green to black occurred generally in 2-4 h compared 12-24 h for reactions run with un-activated zinc.

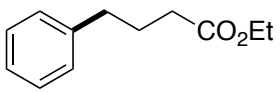
4. Selectivity Data for the Reactions in Schemes 2-4

Chart S1: GC Product Distribution Data for Scheme 2, Compounds 3b-3e

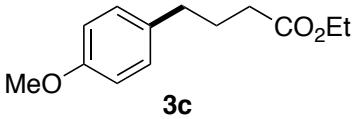


		3b	3b	3b	3b	3c	3c	3c	3c	3d	3d	3d	3d	3d	3e	3e
	Ligand	6	6	6	7	6	6	6	7	7	7	7	7	6	6	6
	Entry	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Alkyl Dimer (A%)	0	0	1	0	0	2	2.5	1	5	2	1	3	2	0	9	7
Aryl Dimer (A%)	0	4	7	12	10	6	10	6	14	4	4	5	6	14	0	0
Reduced Alkyl (A%)	0	4	2	2	2	3	2.5	3	5	2	1	2	4	0	6	7
Reduced Arene (A%)	0	9	3	3	4	11	4	10	7	4	8	4	4	0	11	9
Product (A%)	0	81	84	83	84	77	81	80	65	88	81	82	84	86	74	69

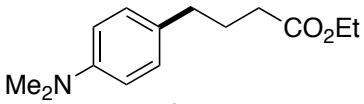
Area percent determined by GC from crude reaction mixtures. In cases were the A% is 0, a peak of <0.5 A% is present or no peak is observed and the retention time of the compound is known. Excpetions are the aryl dimer peak for **3e**, in which there is no assignable peak and retention time of the compound is unknown. Superscripts correspond to footnotes for the respective scheme in the manuscript.



3b
5 mol % **6**, 76%
7 mol % **6**, 86%

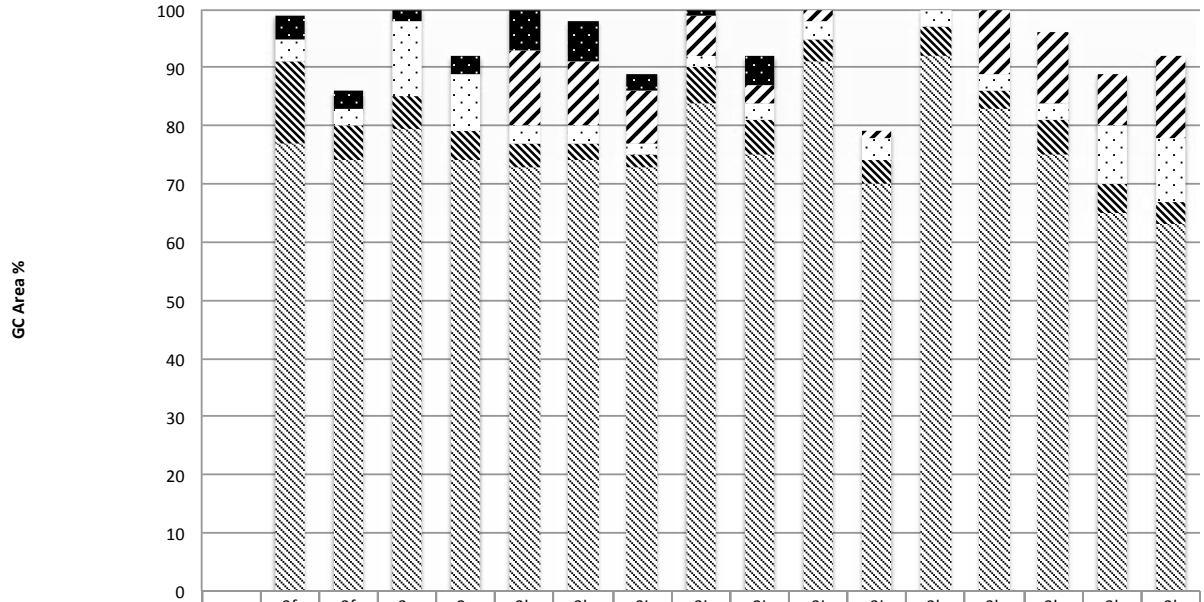


3c
5 mol % **6**, 70%
7 mol % **6**, 73%
10 mol % **6**, 73%



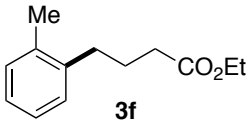
3e
5 mol % **6**, 72%[b]

Chart S2: GC Product Distribution Data for Scheme 2, Compounds 3f-3l

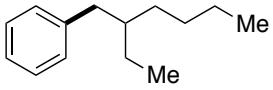


		3f	3f	3g	3g	3h	3h	3i	3i	3i	3j	3j	3k	3k	3k	3l	3l
	Ligand	6	6	6	6	7	7	7	7	6	7	7	6	6	6	6	6
	Entry	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Alkyl Dimer (A%)		4	3	2	3	7	7	3	1	5	0	0	0	0	0	0	0
Aryl Dimer (A%)		0	0	0	0	13	11	9	7	3	2	1	0	11	12	9	14
Reduced Alkyl (A%)		4	3	13	10	3	3	2	2	3	3	4	3	3	3	10	11
Reduced Arene (A%)		14	6	5.5	5	4	3	2	6	6	4	4	5	3	6	5	4
Product (A%)		77	74	79.5	74	73	74	73	84	75	91	70	92	83	75	65	63

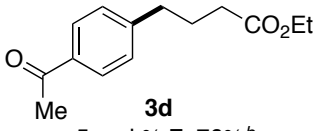
Area percent determined by GC from crude reaction mixtures. In cases were the A% is 0, a peak of <0.5 A% is present or no peak is observed and the retention time of the compound is known. The product and aryl dimer peaks co-elute for **3g**, and the reported area percent for product includes both compounds. Superscripts correspond to footnotes for the respective scheme in the manuscript.



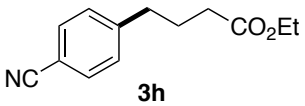
3f
5 mol % **6**, 78%
10 mol % **6**, 88%



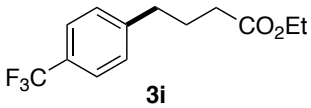
3g
5 mol % **6**, 66%
10 mol % **6**, 60%



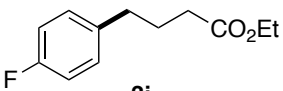
3d
5 mol % **7**, 76%[b]
10 mol % **7**, 83%[b]



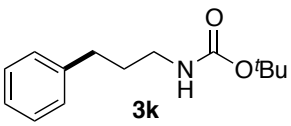
3h
5 mol % **7**, 68%[b]



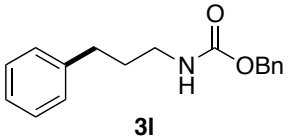
3i
5 mol % **7**, 72%[b]



3j
5 mol % **7**, 79%[b]

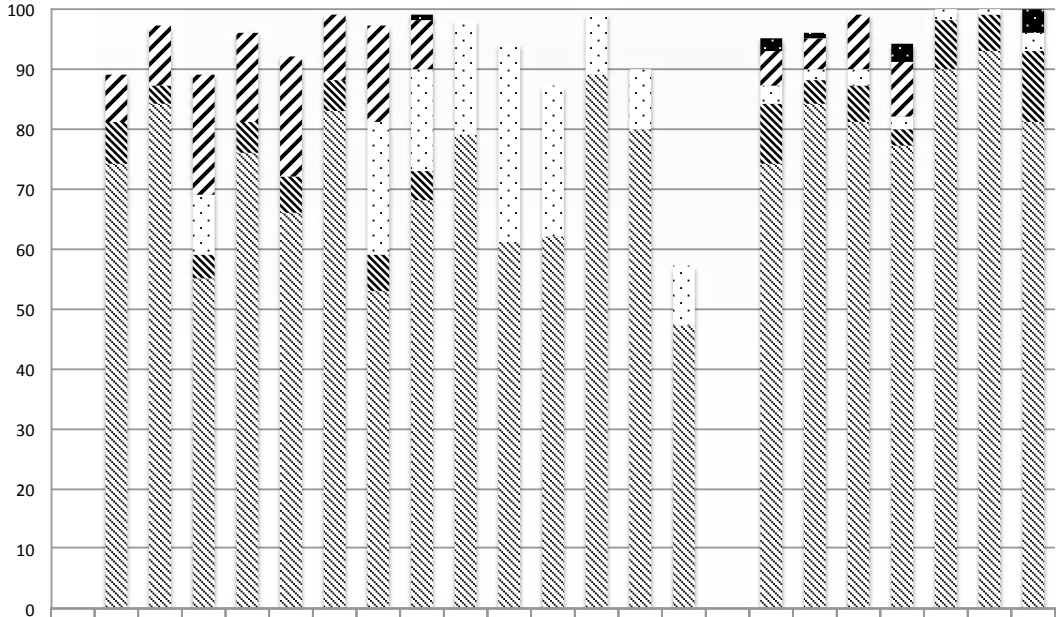


3k
5 mol % **6**, 79%[b]



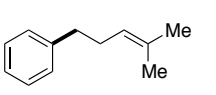
3l
5 mol % **6**, 60%
10 mol % **6**, 70%

Chart S3: GC Product Distribution Data for Scheme 2, Compounds 3m-3v

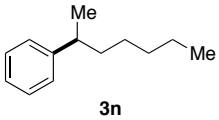


		3m	3m	3n	3n	3o	3o	3p	3p	3q	3r	3r	3s	3s	3t	3t	3u	3u	3u	3u	3v	3v	3v
	Ligand	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	7	7	6	6	7	7	6
	Entry	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53
Alkyl Dimer (A%)	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	2	1	0	3	0	0	4
Aryl Dimer (A%)	0	8	10	20	15	20	11	16	8	0	0	0	0	0	0	0	6	5	9	9	0	0	0
Reduced Alkyl (A%)	0	0	0	10	0	0	0	22	17	19	33	25	10	10	10	0	3	2	3	2	2	1	3
Reduced Arene (A%)	0	7	3	4	5	6	5	6	5	0	0	0	0	0	0	0	10	4	6	3	8	6	12
Product (A%)	0	74	84	55	76	66	83	53	68	79	61	62	89	80	47	0	74	84	81	77	90	93	81

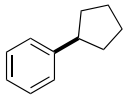
Area percent determined by GC from crude reaction mixtures. In cases were the A% is 0, a peak of <0.5 A% is present or no peak is observed and the retention time of the compound is known. Excpetions are the reduced alkyl for **3m** and **3o**, the reduced aryl, aryl dimer, and alkyl dimer for **3q-s**, in which there is no assignable peak and retention time of the compounds is unknown. Additionally, there is no data available for one run of product **3t**. Superscripts correspond to footnotes for the respective scheme in the manuscript.



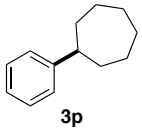
3m
5 mol % **6**, 53%[c]



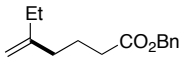
3n
5 mol % **6**, 57%
5 mol % **6**, 61%[c, d]



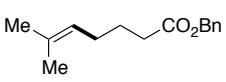
3o
5 mol % **6**, 56%
5 mol % **6**, 63%[c]



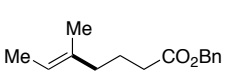
3p
5 mol % **6**, 56%
5 mol % **6**, 63%[c]



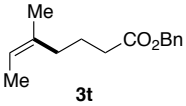
3q
5 mol % **6**, 66%[d]



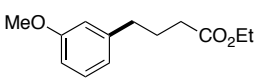
3r
5 mol % **6**, 53%[b, d]



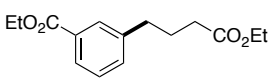
3s
5 mol % **6**, 76%[b, f]
91:11 (*E*):(*Z*)[b, g]



3t
5 mol % **6**, 58%[b, f]
71:29 (*Z*):(*E*)[b, g]

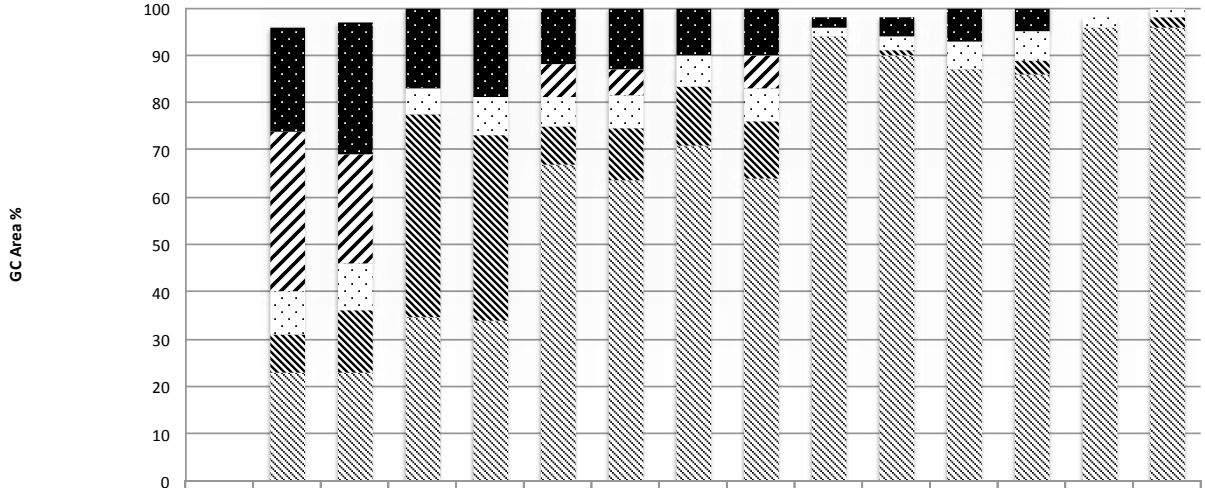


3u
5 mol % **6**, 74%[b]
5 mol % **7**, 75%[b]



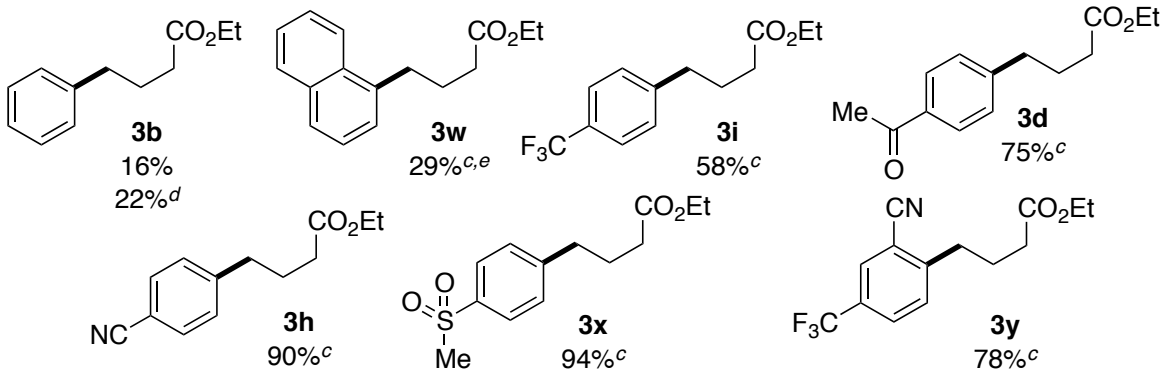
3v
5 mol % **7**, 82%[b]
5 mol % **6**, 68%

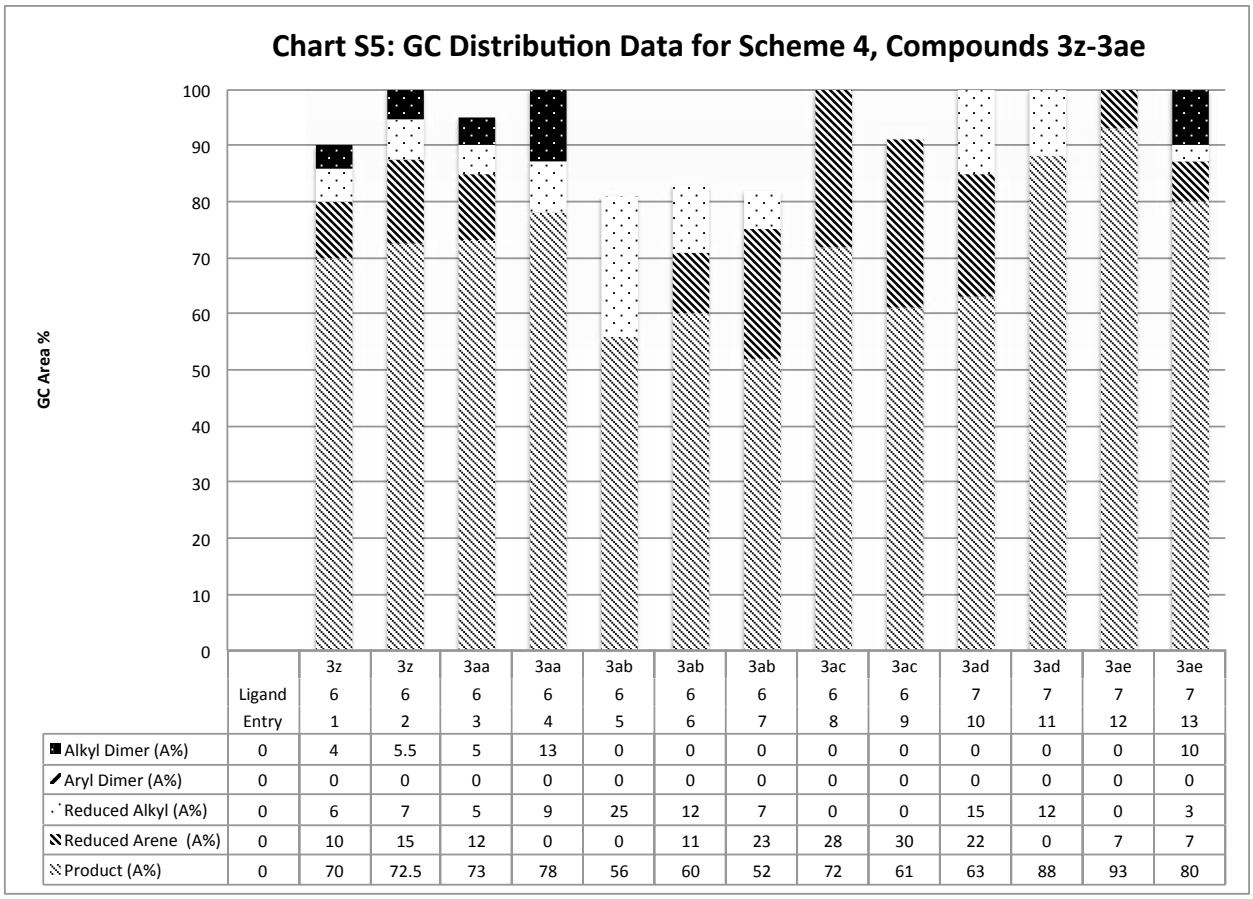
Chart S4: GC Product Distribution Data for Scheme 3



		3b	3b	3w	3w	3i	3i	3d	3d	3h	3h	3x	3x	3y	3y
	Ligand	6	6	6	6	6	6	6	6	6	6	6	6	6	6
	Entry	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Alkyl Dimer (A%)	0	22	28	17	19	12	13	10	10	2	4	7	5	0	0
Aryl Dimer (A%)	0	34	23	0	0	7	5.5	0	7	0	0	0	0	0	0
Reduced Alkyl A%)	0	9	10	5.5	8	6	7	6.5	7	2	3	6	6	2	2
Reduced Arene (A%)	0	8	13	43	39	8	11	12.5	12	0	1	0	3	0	2
Product (A%)	0	23	23	34.5	34	67	63.5	71	64	94	90	87	86	96	96

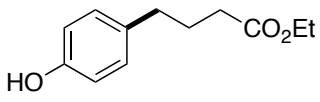
Area percent determined by GC from crude reaction mixtures. In cases were the A% is 0, a peak of <0.5 A% is present or no peak is observed and the retention time of the compound is known. Excpetions are the aryl dimer for **3w** and **3x**, in which there is no assignable peak and retention time of the compounds is unknown. Superscripts correspond to footnotes for the respective scheme in the manuscript.



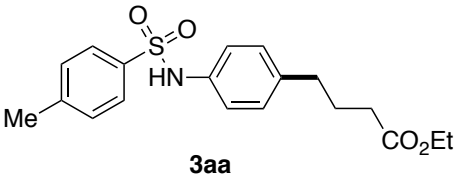


		3z	3z	3aa	3aa	3ab	3ab	3ab	3ac	3ac	3ad	3ad	3ae	3ae
Ligand	6	6	6	6	6	6	6	6	6	7	7	7	7
Entry	1	2	3	4	5	6	7	8	9	10	11	12	13
Alkyl Dimer (A%)	0	4	5.5	5	13	0	0	0	0	0	0	0	0	10
Aryl Dimer (A%)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Reduced Alkyl (A%)	0	6	7	5	9	25	12	7	0	0	15	12	0	3
Reduced Arene (A%)	0	10	15	12	0	0	11	23	28	30	22	0	7	7
Product (A%)	0	70	72.5	73	78	56	60	52	72	61	63	88	93	80

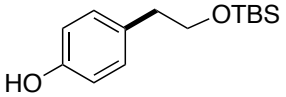
Area percent determined by GC from crude reaction mixtures. In cases were the A% is 0, a peak of <0.5 A% is present or no peak is observed and the retention time of the compound is known. Excpetions are the aryl dimer for **3aa**, **3ac-ae** in which there is no assignable peak and retention time of the compounds is unknown. Superscripts correspond to footnotes for the respective scheme in the manuscript.



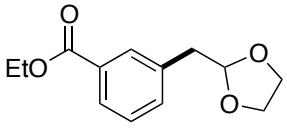
3z
5 mol % **6**, 74%[c]



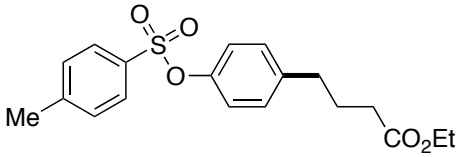
3aa
5 mol % **6**, 96%[c]



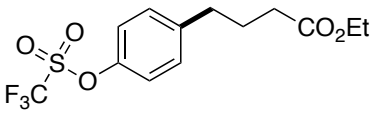
3ab
5 mol % **6**, 76%[c, e]
5 mol % **6**, 65%[f]



3ac
5 mol % **7**, 60%[c, d]

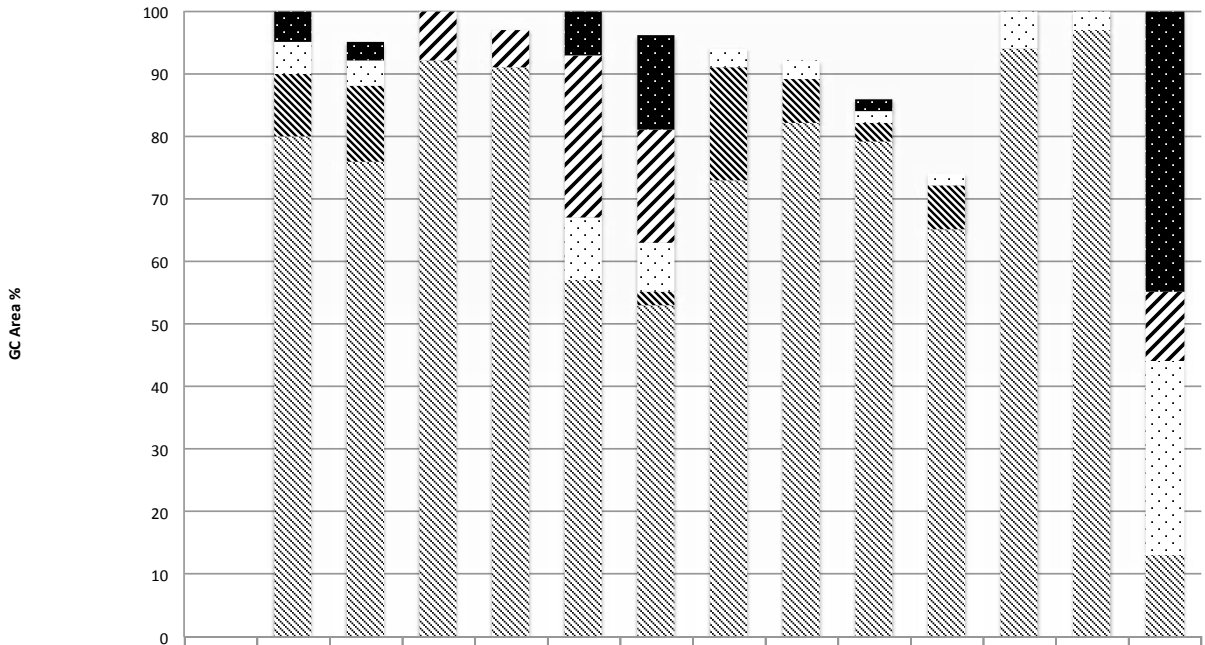


3ad
5 mol % **7**, 76%[c]



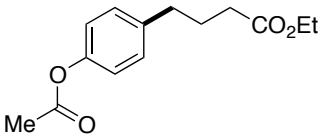
3ae
5 mol % **7**, 74%[c]

Chart S6: GC Distribution Data for Scheme 4, Compounds 3af-3al

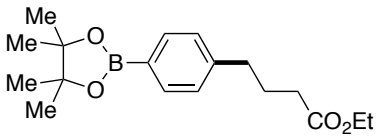


		3af	3af	3ag	3ag	3ah	3ah	3ai	3ai	3aj	3aj	3ak	3ak	3al
	Ligand	7	7	7	7	6	6	6	6	6	6	6	6	7
	Entry	14	15	16	17	18	19	20	21	22	23	24	25	26
Alkyl Dimer (A%)	0	5	3	0	0	7	15	0	0	2	0	0	0	45
Aryl Dimer (A%)	0	0	0	8	6	26	18	0	0	0	0	0	0	11
Reduced Alkyl (A%)	0	5	4	0	0	10	8	3	3	2	2	6	3	31
Reduced Arene (A%)	0	10	12	0	0	0	2	18	7	3	7	0	0	0
Product (A%)	0	80	76	92	91	57	53	73	82	79	65	94	97	13

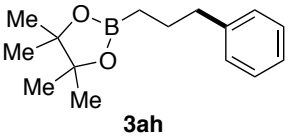
Area percent determined by GC from crude reaction mixtures. In cases were the A% is 0, a peak of <0.5 A% is present or no peak is observed and the retention time of the compound is known. Excpetions are the aryl dimer for **3af-ag** and **3ai-ak** in which there is no assignable peak and retention time of the compounds is unknown. Superscripts correspond to footnotes for the respective scheme in the manuscript.



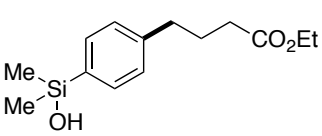
3af
5 mol % **7**, 64%[c]



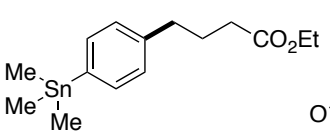
3ag
5 mol % **7**, 76%[c]



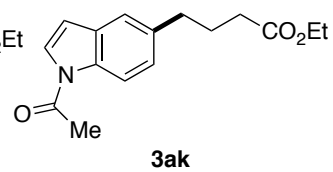
3ah
5 mol %, 48%
5 mol %, 41%[e]



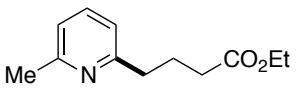
3ai
5 mol % **6**, 67%[c]



3aj
5 mol % **6**, 74%[c]



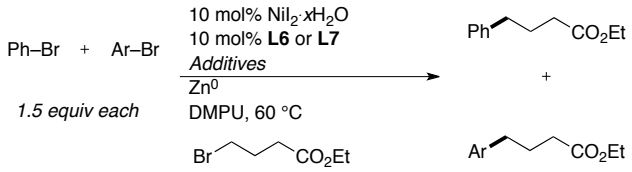
3ak
5 mol % **6**, 81%[c]



3al
5 mol % **7**, 26%

5. Hammett Study

Reaction set-up and data collection.



The general procedure was followed except for the use of two different aryl bromides (0.375 mmol, 1.50 equiv each) and ethyl 4-bromobutyrate (0.25 mmol, 1.00 equiv), dodecane (10 µL, 0.044 mmol as internal standard), and the sequential addition of 1,2-dibromoethane (0.07 mmol, 0.28 equiv) and chlorotrimethylsilane (0.034 mmol, 0.136 equiv) as the last two reagents to activate the zinc. The reactions were heated at 60 °C, and the reaction progress were followed by GC analysis until complete consumption of alkyl bromide. At appropriate times 25 µL aliquots of reaction mixture were removed with a 100 µL gas-tight syringe and quenched with 25 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography.

Determination of k_{rel} for six aryl bromides

The k_{rel} values were obtained by fitting the data to equation (2):

$$\ln([ArBr]_0/[ArBr]) = k_{rel}\ln([PhBr]_0/[PhBr]). \quad (2)$$

Chart S7: k_{rel} for 4-bromoanisole

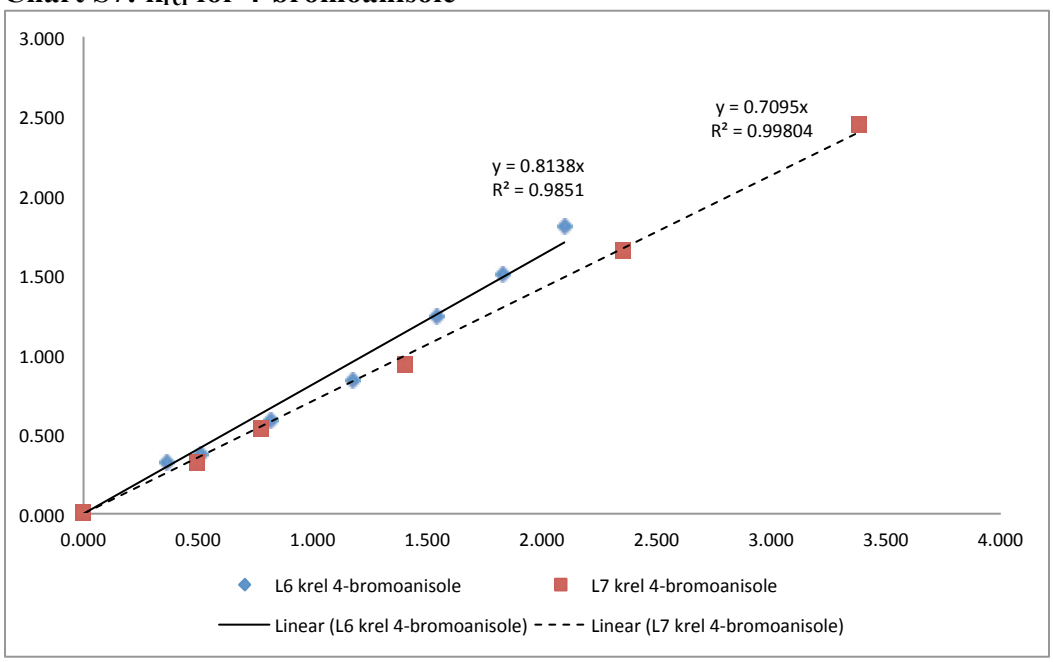


Chart S8: k_{rel} for 4-fluorobromobenzene

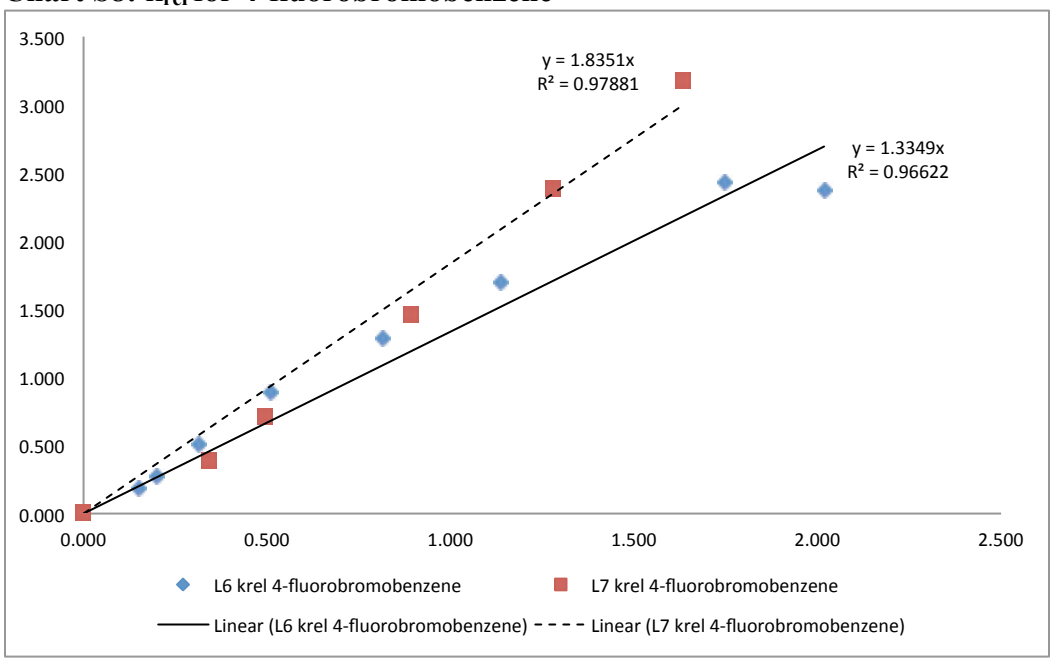


Chart S9: k_{rel} for 3-bromoanisole

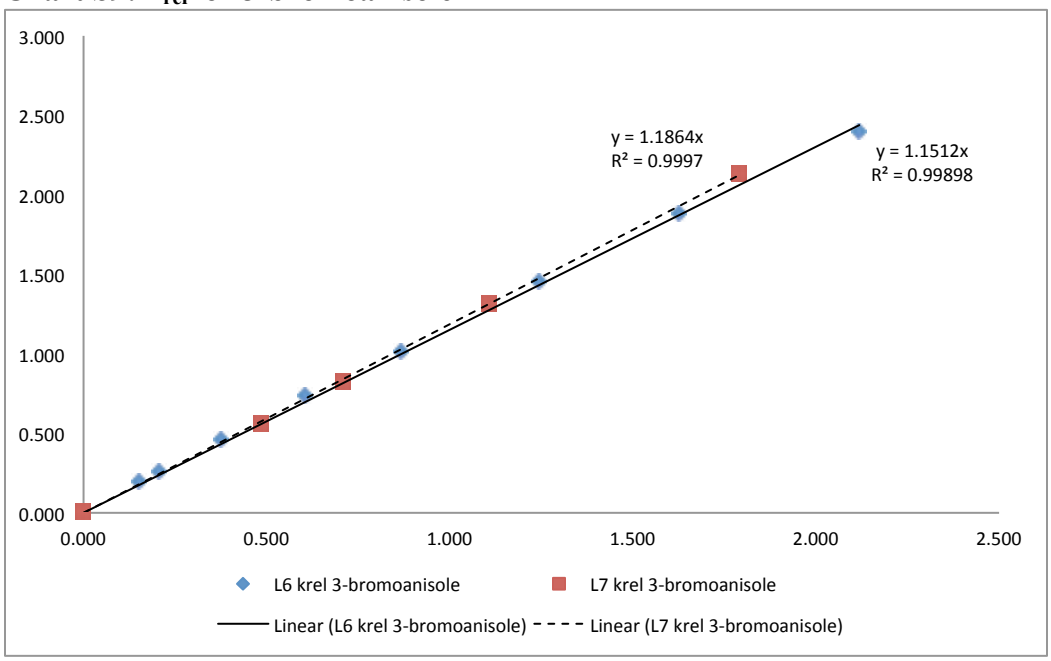


Chart S10: k_{rel} for ethyl 3-bromobenzoate

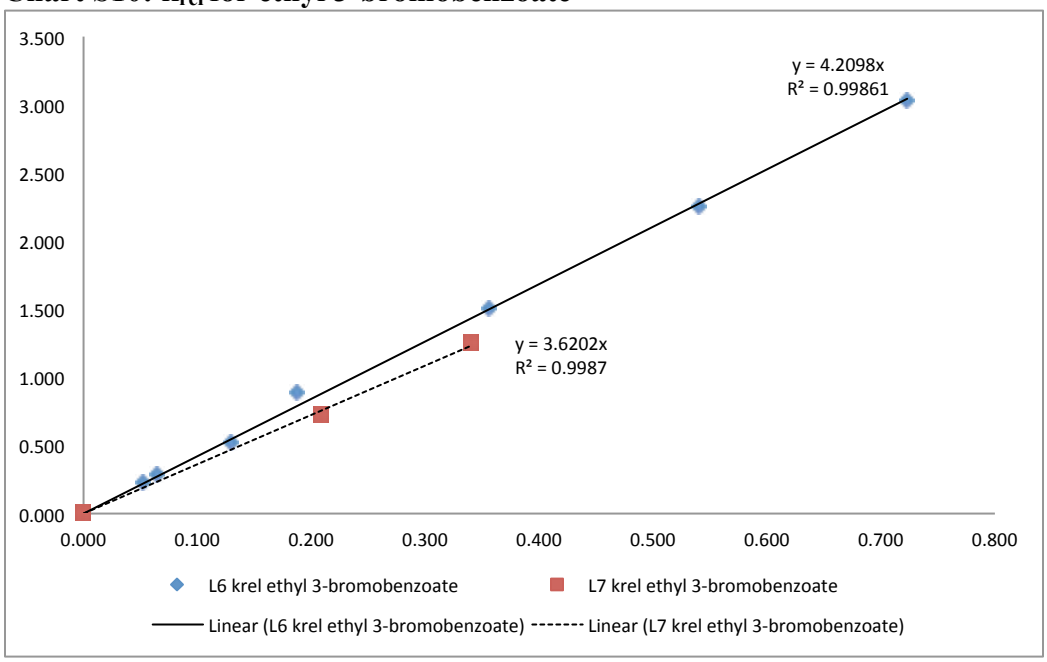


Chart S11: k_{rel} for 4-bromobenzotrifluoride

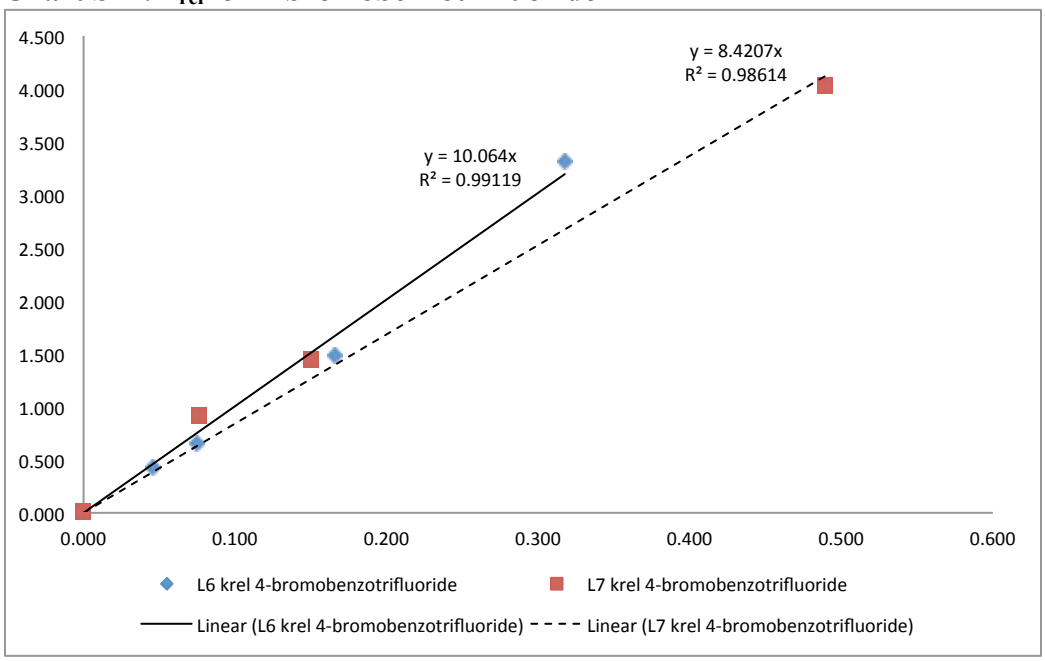
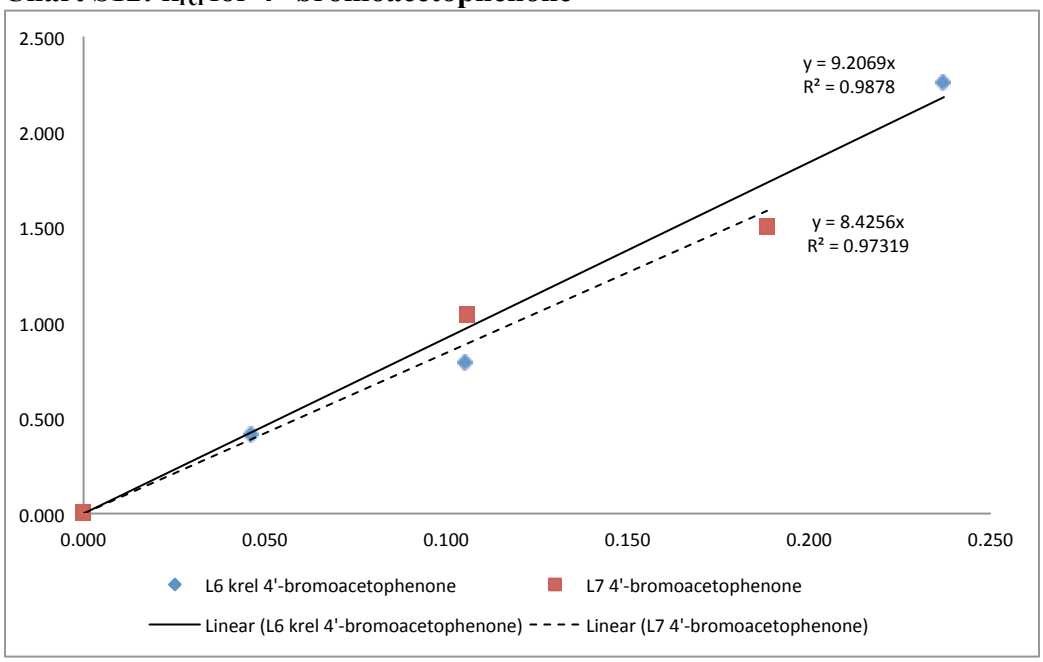


Chart S12: k_{rel} for 4'-bromoacetophenone



GC response factors for aryl bromides used in Hammett study

The GC response factors for the aryl bromides used in the Hammett study were determined by making standard solutions of each aryl bromide with the internal standard in 100.00 mL volumetric flasks using hexanes as the solvent. The response factor (R_f) was calculated from equation (1).

Analyte	[Analyte] mM	Analyte Signal (pA*s)	[dodecane]	Dodecane signal (pA*s)	Response factor (R_f)	Average
bromobenzene (**1a**)	0.01125	68.61488	0.00132	15.07314	0.534	0.487
	0.00843	94.05482	0.00132	34.61944	0.425	
	0.00562	112.93882	0.00132	52.16728	0.508	
	0.00281	54.63529	0.00132	53.29126	0.482	
4-bromoanisole	0.01125	200.53317	0.00132	47.86666	0.492	0.514
	0.00843	118.33664	0.00132	34.9503	0.530	
	0.00562	84.66516	0.00132	37.89532	0.525	
	0.00281	26.36431	0.00132	24.29691	0.510	
3-bromoanisole	0.01125	213.93135	0.00132	43.73502	0.574	0.484
	0.00843	157.93858	0.00132	50.56739	0.489	
	0.00562	111.9446	0.00132	57.44534	0.458	
	0.00281	52.17599	0.00132	59.2877	0.413	
4-fluoro-bromobenzene	0.01125	207.32381	0.00132	47.41028	0.513	0.501
	0.00843	149.09506	0.00132	47.09661	0.496	
	0.00562	59.11299	0.00132	27.11171	0.512	
	0.00281	42.78619	0.00132	41.64735	0.483	
4-bromobenzotrifluoride	0.01125	63.57201	0.00132	18.31174	0.407	0.377
	0.00843	21.69062	0.00132	7.7937	0.436	

	0.00562	22.27199	0.00132	20.03488	0.261	
	0.00281	40.76057	0.00132	47.37431	0.404	
4'-bromoacetophenone	0.01125	258.54169	0.00132	49.48981	0.613	0.603
	0.00843	194.25781	0.00132	50.27432	0.605	
	0.00562	127.78354	0.00132	49.64022	0.605	
	0.00281	62.00702	0.00132	49.46333	0.589	
ethyl 3-bromobenzoate	0.01125	309.31046	0.00132	49.48981	0.613	0.648
	0.00843	203.75116	0.00132	50.27432	0.605	
	0.00562	134.89	0.00132	49.64022	0.605	
	0.00281	61.72871	0.00132	49.46333	0.589	

Chart S13: Ligand 6: Log(k_{rel}) versus σ(•)

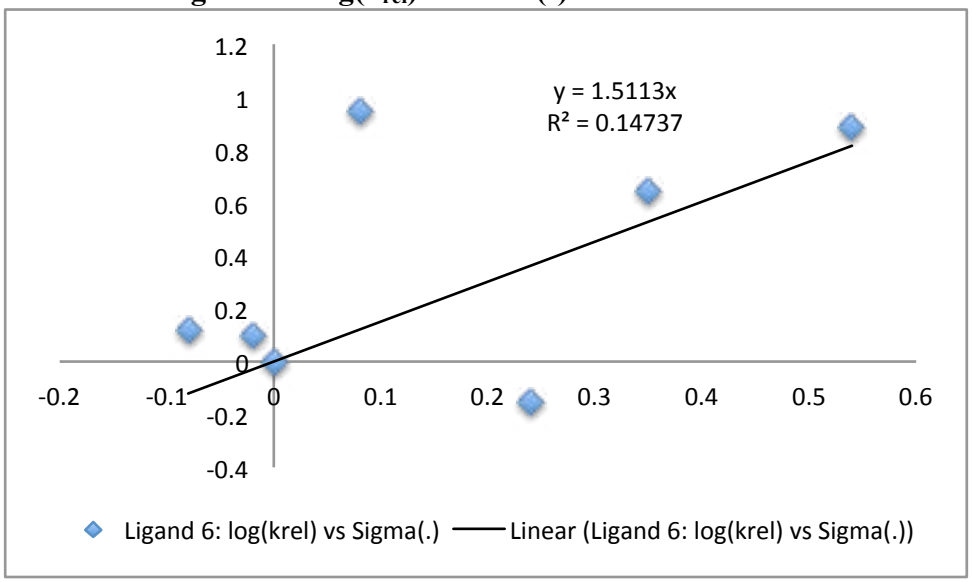
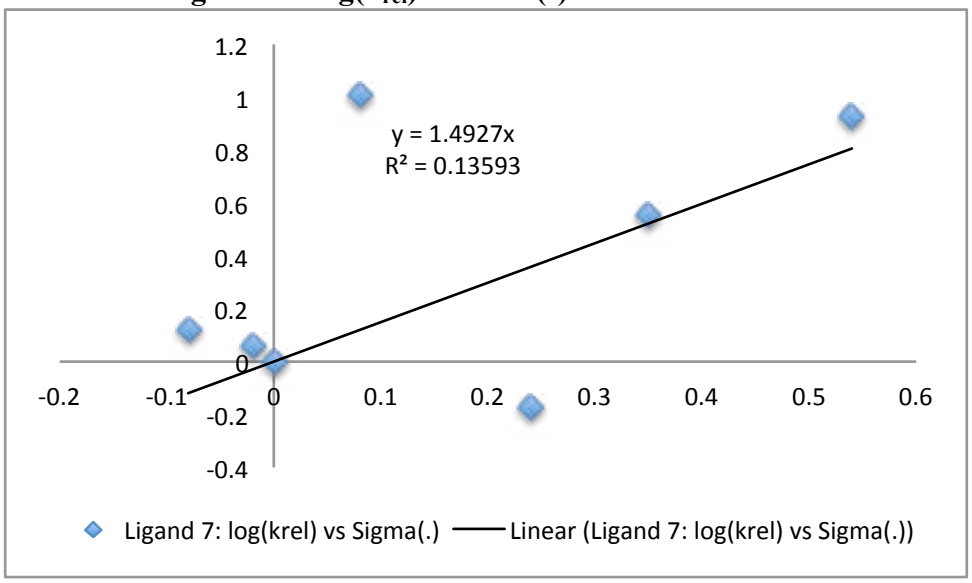


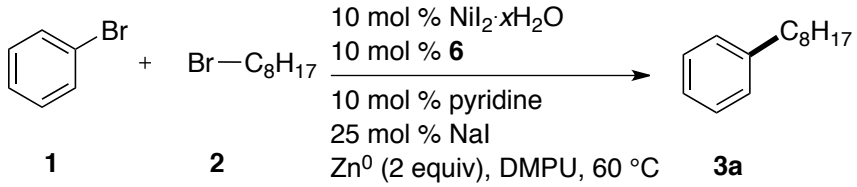
Chart S14: Ligand 7: Log(k_{rel}) versus σ(•)



As mentioned in the main text the plot of k_{rel} versus σ(•) was not linear.

6. Substrates, catalyst, and reducing agent effect on rate

Reaction set-up and data collection using un-activated zinc



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

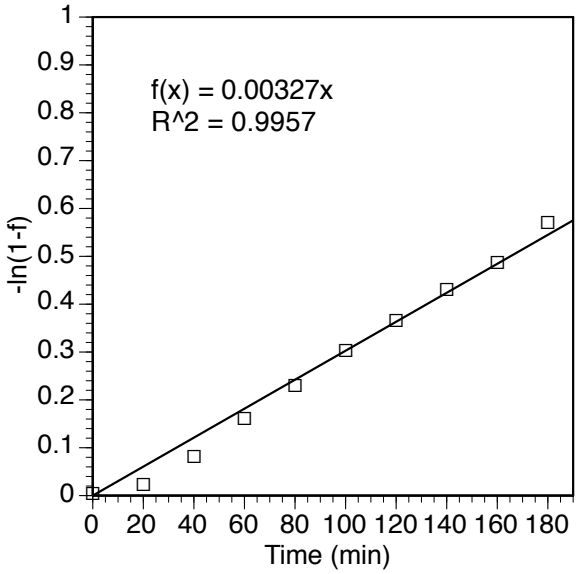
Standard reaction with un-activated zinc

A 10 mL Schlenk flask was charged with bromobenzene (**1**) (112 µL, 1.00 mmol), 1-bromooctane (**2**) (172 µL, 1.00 mmol), $NiI_2{\cdot}xH_2O$ (40.2 mg, 0.108 mmol), 4,4'-dimethyoxy-2, 2'-bipyridine (**6**) (21.6 mg, 0.10 mmol), pyridine (4 µL, 0.10 mmol), sodium iodide (38 mg, 0.25 mmol), zinc dust (>10 µm, 130 mg, 2.00 mmol), DMPU (4.0 mL) and dodecane (10 µL, 0.044 mmol as internal standard). The vessel was capped with a septum and the headspace was flushed with Ar gas for 10 seconds. The reaction was heated at 60 °C under positive Ar gas pressure, and the reaction progress were followed by GC analysis. At appropriate times 50 µL aliquots of reaction mixture were removed with a 100 µL gas-tight syringe and quenched with 50 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography. Formation of **3a** was followed with time and plotted using equation (3).

$$-\ln(1-f) = mt \qquad (3)$$

Where f is the fraction of product formed as a function of time and t is time (min).

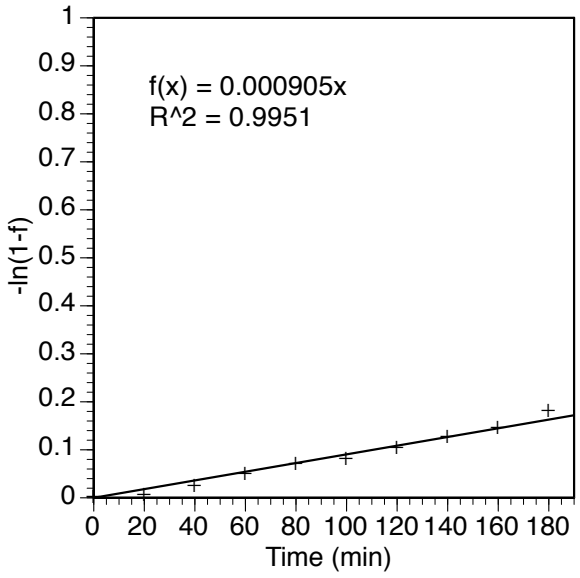
Chart S15: Standard reaction with un-activated zinc



Effect of doubling the amount of bromobenzene (1) with un-activated zinc

The general procedure for the standard reaction was followed except with excess bromobenzene (**1a**) (224 μL, 2.00 mmol).

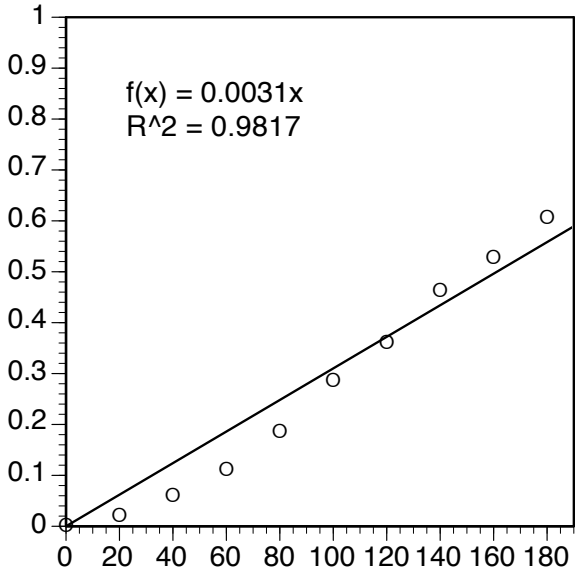
Chart S16: Effect of doubling the amount of bromobenzene (1) with un-activated zinc



Effect of doubling the amount of 1-bromooctane (2) with un-activated zinc

The general procedure for the standard reaction was followed except with excess 1-bromooctane (**2**) (344 μL, 2.00 mmol).

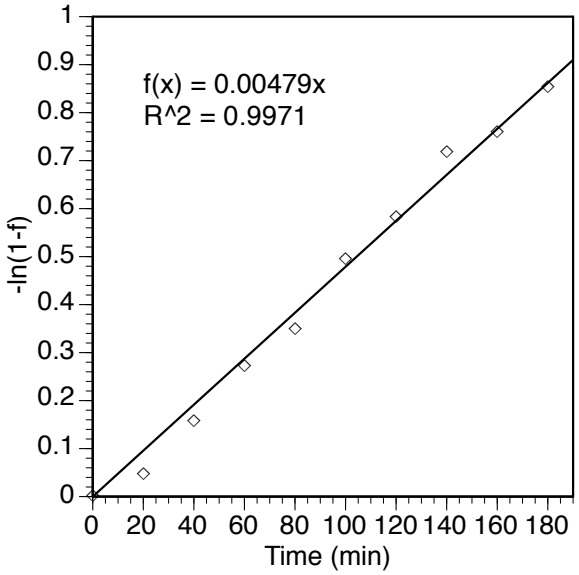
Chart S17: Effect of doubling the amount of 1-bromooctane (2) with un-activated zinc



Effect of doubling the amount of 6/Ni/pyridine with un-activated zinc

The general procedure for the standard reaction was followed except with 20 mol% catalyst loading using $NiI_2 \cdot xH_2O$ (80.4 mg, 0.216 mmol), 4,4'-dimethyoxy-2, 2'-bipyridine (**6**) (43.2 mg, 0.20 mmol), pyridine (8 μL, 0.10 mmol).

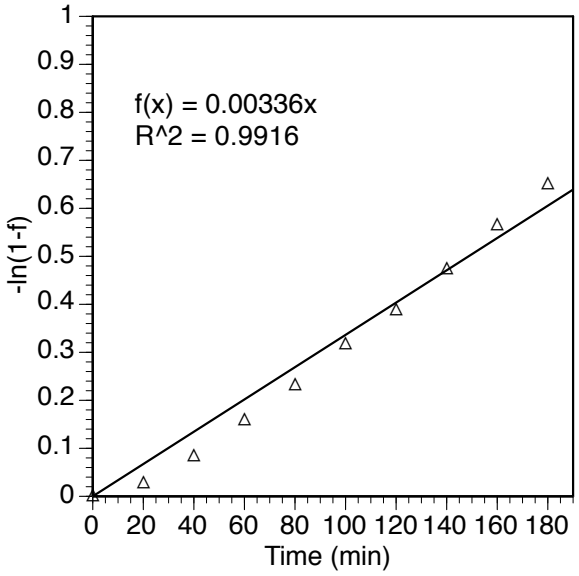
Chart S18: Effect of doubling the amount of 6/Ni/pyridine with un-activated zinc



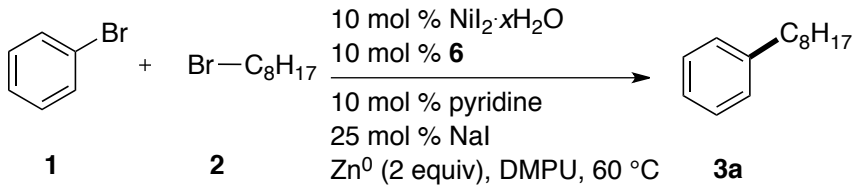
Effect of doubling the amount of un-activated zinc

The general procedure for the standard reaction was followed except with 4 equiv Zn dust (>10 μm, 260 mg, 4.00 mmol)

Chart S19: Effect of doubling the amount of un-activated zinc



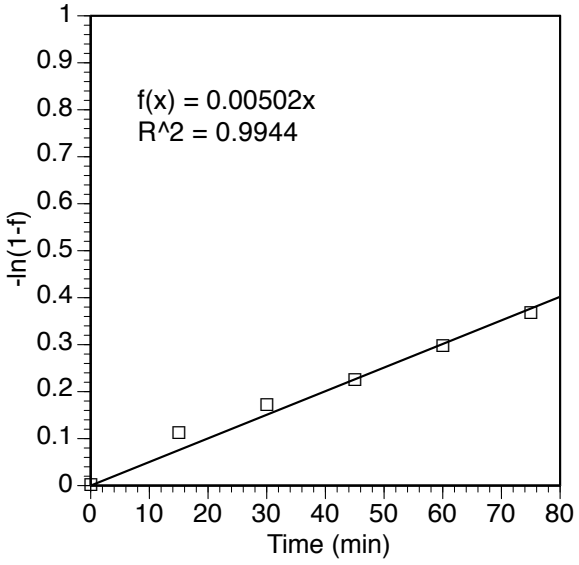
Reaction set-up and data collection using activated zinc



Standard reaction with activated zinc

The general procedure was followed with bromobenzene (**1**) (56 μL, 0.50 mmol), 1-bromooctane (**2**) (86 μL, 0.50 mmol), $NiI_2 \cdot xH_2O$ (20.1 mg, 0.054 mmol), 4,4'-dimethyoxy-2, 2'-bipyridine (**6**) (10.8 mg, 0.05 mmol), pyridine (2 μL, 0.05 mmol), sodium iodide (19 mg, 0.125 mmol), zinc dust (>10 μm, 65 mg, 1.00 mmol), DMPU (2.0 mL) and dodecane (10 μL, 0.044 mmol as internal standard). Chlorotrimethylsilane and 1,2-dibromoethane (6 mL each) were sequentially added as the last two reagents. The reaction was heated at 60 °C, and the reaction progress were followed by GC analysis. At appropriate times 25 μL aliquots of reaction mixture were removed with a 100 μL gas-tight syringe and quenched with 25 μL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography. Formation of **3a** was followed with time and plotted using equation (3).

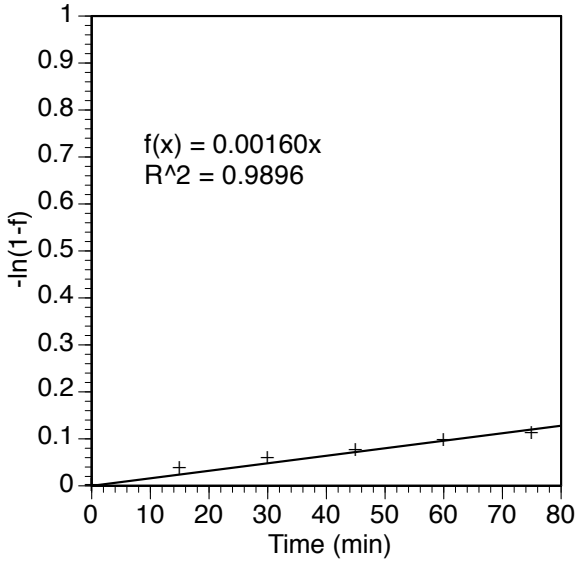
Chart S20: Standard reaction with activated zinc



Effect of doubling the amount of bromobenzene (1) with activated zinc

The general procedure for the standard reaction was followed except with excess bromobenzene (**1a**) (112 μL, 1.00 mmol).

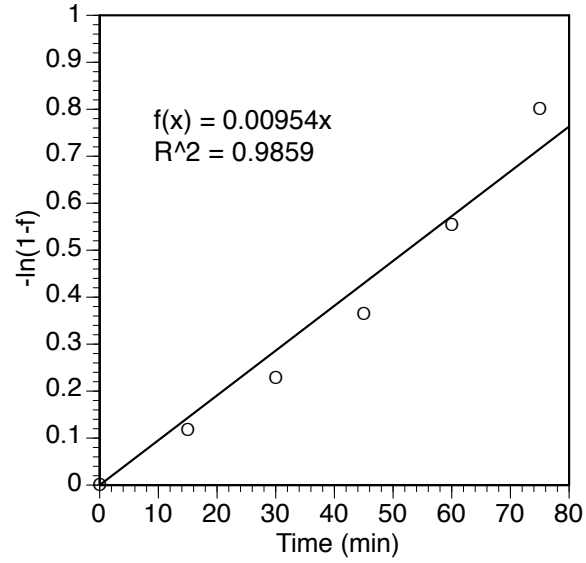
Chart S21: Effect of doubling the amount of bromobenzene (1) with activated zinc



Effect of doubling the amount of 1-bromooctane (2) with activated zinc

The general procedure for the standard reaction was followed except with excess 1-bromooctane (**2**) (172 μL, 1.00 mmol).

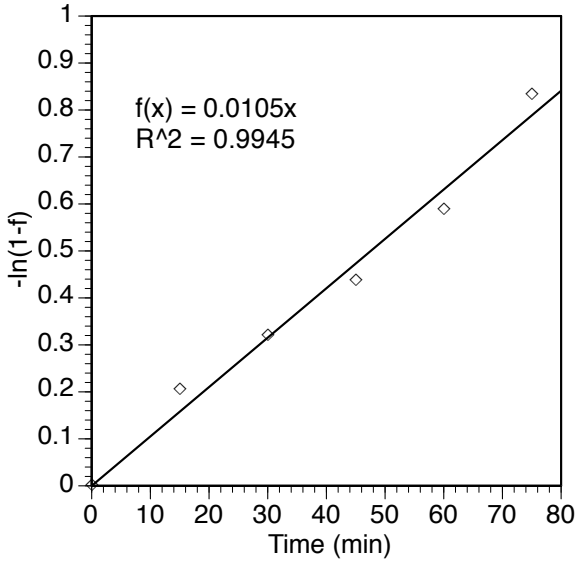
Chart S22: Effect of doubling the amount of 1-bromooctane (2) with activated zinc



Effect of doubling the amount of 6/Ni/pyridine with activated zinc

The general procedure for the standard reaction was followed except with 20 mol% catalyst loading using $NiI_2{\cdot}xH_2O$ (40.2 mg, 0.108 mmol), 4,4'-dimethyoxy-2, 2'-bipyridine (**6**) (21.6 mg, 0.10 mmol), pyridine (4 μL, 0.10 mmol).

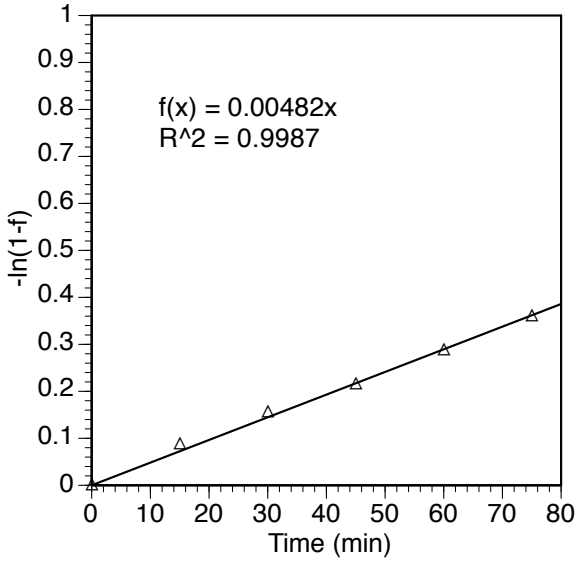
Chart S23: Effect of doubling the amount of 6/Ni/pyridine with activated zinc



Effect of doubling the amount of activated zinc

The general procedure for the standard reaction was followed except with 4 equiv Zn dust (>10 μm, 130 mg, 2.00 mmol).

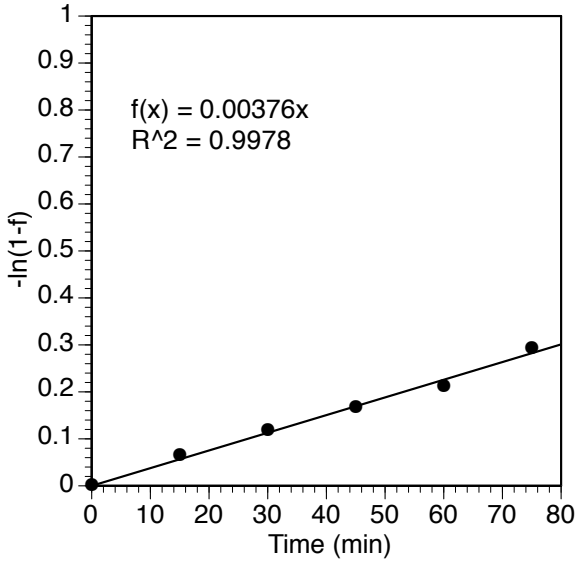
Chart S24: Effect of doubling the amount of activated zinc



Effect of spiking 1 equiv benzene into the standard reaction with activated zinc

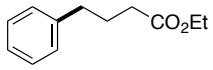
The general procedure was followed for the standard reaction except with the addition of benzene (1 equiv 42 μL).

Chart S25: Effect of spiking 1 equiv benzene into the standard reaction with activated zinc



7. Procedures and Compound Characterization

Compounds in Scheme 2:Aryl and alkyl bromides

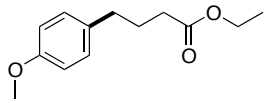


ethyl 4-phenylbutanoate (3b) [CAS:10031-93-3].[17] The general procedure was followed with bromobenzene (80 µL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 14-41 h. The product was isolated by chromatography (95:5 hexanes: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 124 mg (86%, 11 mol% catalyst, 21 h). Second run 109 mg (76%, 5 mol% catalyst, 41 h). Third run 124 mg (86%, 7 mol% catalyst, 24 h). With 1,10-phenanthroline: 104 mg (72%, 11 mol% catalyst, 14.5 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.37-7.24 (m, 5H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.03 (quintet, *J* = 7.5 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.5, 141.5, 128.57, 128.45, 126.0, 60.3, 35.2, 33.8, 26.6, 14.3.

GC-MS *m/z* (% relative intensity, ion): 192.05 (21.91, M^+), 147.05 (57.00, M^+-C_2H_5O), 105.00 (24.23, M^+-$C_4H_7O_2$), 91.00 (100.00, M^+-C_7H_7).



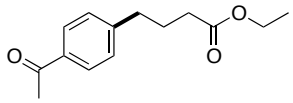
[17] Kurono, Nobuhito.; Sugita, K.; Takasugi, S.; Tokuda, M. *Tetrahedron*, **1999**, *55*, 6097.

ethyl 4-(4-methoxyphenyl)butanoate (3c) [CAS:4586-89-4].[18] The general procedure was followed with 4-bromoanisole (94 µL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 13-21 h. The product was isolated by chromatography (9:1 pentane: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 121 mg (73%, 11 mol% catalyst, 13 h). Second run 121 mg (73%, 7 mol% catalyst, 19 h). Third run 117 mg (70%, 5 mol% catalyst, 21 h). With 1,10-phenanthroline: 102 mg (61%, 11 mol% catalyst, 15 h), isolated by chromatography (95:5 pentane: ether).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.09 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 2.59 (t, J = 7.6 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.92 (quintet, J = 7.5 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.7, 158.0, 133.6, 129.5, 113.9, 60.4, 55.4, 34.4, 33.8, 26.9, 14.4.

GC-MS *m/z* (% relative intensity, ion): 222.05 (25.27, M^+), 177.05 (17.70, M^+-C_2H_5O), 134.05 (100.00, M^+-$C_4H_8O_2$), 121.00 (77.81, M^+-C_8H_9O).



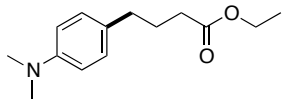
ethyl 4-(4-acetylphenyl)butanoate (3d) [CAS:71665-59-3].[19] The general procedure was followed with 4'-bromoacetophenone (149 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 12-25 h. The product was isolated by chromatography (8:2 pentane: ether) as colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 123 mg (70%, 11 mol% catalyst, 21 h). With 1,10-phenanthroline: first run 148 mg (84%, 11 mol% catalyst, 25 h), isolated by chromatography (85:15 pentane: ether). Second run 143 mg (81%, 11 mol% catalyst, 12 h), isolated by chromatography (7:3 hexanes: ether). Third run 133 mg (76%, 5 mol% catalyst, 19 h), isolated by chromatography (5:1 hexanes: ether). Fourth run 133 mg (76%, 5 mol% catalyst, 19 h), isolated by chromatography (7:3 hexanes: ether).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.89 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.2 3H), 4.13 (q, J = 7.1 Hz, 2H), 2.71 (t, J = 7.6 Hz, 2H), 2.58 (s, 3H), 2.32 (t, J = 7.4 Hz, 2H), 1.97 (quintet, J = 7.5 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 197.9, 173.3, 147.4, 135.4, 128.81, 128.70, 60.5, 35.2, 33.7, 26.7, 26.3, 14.4.

GC-MS *m/z* (% relative intensity, ion): 234.05 (36.10, M^+), 219.00 (10.98, M^+-CH_3), 147.05 (100.00, M^+-$C_4H_7O_2$), 131.05 (38.08, M^+-$C_5H_{11}O_2$), 90.00 (26.55, M^+-$C_7H_{12}O_3$).

[18] Cahiez, G.; Foulgoc, L.; Moyeux, A. *Angew. Chem., Int. Ed.*, **2009**, *48*, 2969-2972.
[19] Sase, S.; Jaric, M.; Metzger, A.; Malakhov, V.; Knochel, P. *J. Org. Chem.*, **2008**, *73*, 7380-7382.

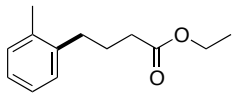


ethyl 4-(4-(dimethylamino)phenyl)butanoate (3e). The general procedure was followed with 4-bromo-N,N-dimethylaniline (150 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 16-23 h. The product was isolated by chromatography (95:5 hexanes: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 122 mg (69%, 5 mol% catalyst, 23 h). Second run 131 mg (74%, 5 mol% catalyst, 19 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.08 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 2.93 (s, 6H), 2.59 (t, J = 7.5 Hz, 2H), 2.33 (t, J = 7.4 Hz, 2H), 1.95 (dt, J = 9.4, 5.5 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.8, 149.3, 129.7, 129.2, 113.1, 60.3, 41.0, 34.2, 33.9, 27.0, 14.4.

GC-MS *m/z* (% relative intensity, ion): 235.10 (25.35, M^+), 190.05 (6.72, M^+-C_2H_5O), 134.10 (100.00, M^+-$C_5H_9O_2$).

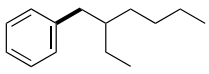


ethyl 4-(*o*-tolyl)butanoate (3f) [CAS:105986-51-4].[20] The general procedure was followed with 2-bromotoluene (90 μL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 23-24 h. The product was isolated by chromatography (pentane) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 137 mg (88%, 11 mol% catalyst, 24 h). Second run 121 mg (78%, 5 mol% catalyst, 19 h), isolated by chromatography (95:5 pentane: ether).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.15-7.10 (m, 5H), 4.14 (q, J = 7.1 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H), 2.37 (t, J = 7.4 Hz, 3H), 2.32 (s, 3H), 1.92 (dt, J = 15.3, 7.6 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.6, 139.8, 136.1, 130.4, 129.1, 126.23, 126.06, 60.4, 34.1, 32.7, 25.5, 19.4, 14.4.

GC-MS *m/z* (% relative intensity, ion): 206.15 (11.02, M^+), 161.10 (18.29, M^+-C_2H_5O), 88.10 (25.46, M^+-C_9H_{11}), 118.10 (46.98, M^+-$C_4H_7O_2$), 105.05 (100.00, M^+-$C5H_9O_2$).



(2-ethylhexyl)benzene (3g) [CAS:5617-39-0].[21] The general procedure was followed with bromobenzene (80 μL, 0.75 mmol, 1.00 equiv) and 2-ethylhexyl bromide (133 μL, 0.75 mmol,

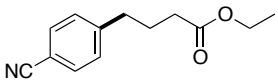
[20] Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Tetrahedron Lett.*, **1986**, *27*, 955-958.
[21] (a) Fessard, T. C.; Motoyoshi, H.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2078; (b) Toussaint, H. *J. Am .Chem. Soc.* **1940**, *62*, 1145.

1.00 equiv) at 60 °C for 23-38 h. The product was isolated by chromatography (pentane) as colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 94 mg (66%, 5 mol% catalyst, 38 h). Second run 86 mg (60%, 11 mol% catalyst, 23 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.34-7.20 (m, 5H), 2.64-2.56 (m, 2H), 1.64 (m, 1H), 1.35 (m, 8H), 0.94 (m, 6H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 141.9, 129.2, 128.1, 125.5, 41.2, 40.2, 32.4, 28.9, 25.5, 23.1, 14.2, 10.8.

GC-MS *m/z* (% relative intensity, ion): 190.10 (22.83, M^+), 98.10 (16.38, M^+-C_7H_8), 92.05 (100.00, M^+-C_7H_6), 91.00 (89.47, M^+-C_7H_7), 57.05 (M^+-C_4H_9).

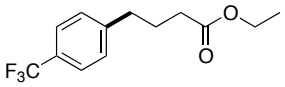


ethyl 4-(4-cyanophenyl)butanoate (3h) [CAS:131379-33-4].[22] The general procedure was followed with 4-bromobenzonitrile (137 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 18-19 h. The product was isolated by chromatography (8:2 pentane: ether) as colorless oil. With 1,10-phenanthroline: first run 113 mg (69%, 5 mol% catalyst, 18 h). Second run 107 mg (66%, 5 mol% catalyst, 18 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.96 (quintet, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.2, 147.2, 132.4, 129.4, 119.1, 110.1, 60.6, 35.3, 33.5, 26.1, 14.4.

GC-MS *m/z* (% relative intensity, ion): 217.00 (14.63, M^+), 172.05 (34.76, M^+-C_3H_5O), 130.05 (60.09, M^+-$C_4H_7O_2$), 116.00 (100.00, M^+-$C_5H_9O_2$).



ethyl 4-(4-(trifluoromethyl)phenyl)butanoate (3i) [CAS:1235271-20-1].[22] The general procedure was followed with 4-bromobenzotrifluroide (104 μL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 19-20 h. The product was isolated by chromatography (95:5 pentane: ether) as yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 120 mg (61%, 5 mol% catalyst, 20 h). With 1,10-phenanthroline: first run 135 mg (69%, 5 mol% catalyst, 20 h). Second run 144 mg (74%, 5 mol% catalyst, 19 h).

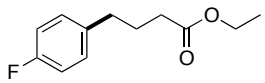
^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.95 (quintet, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

[22] Amatore, M.; Gosmini, C. *Chem.-Eur. J.*, **2010**, *16*, 5848-5852.

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.3, 145.7, 128.9, 128.5 (q, *J*= 33.4 Hz), 125.4 (q, *J*= 3.8 Hz), 124.5 (q, *J*= 271.8 Hz), 60.5, 35.0, 33.6, 26.3, 14.3.

^{19}F-NMR (376 MHz; $CDCl_3$): δ 0.5.

GC-MS *m/z* (% relative intensity, ion): 215.00 (23.28, M^+-C_2H_5O), 172.00 (22.10, M^+-$C_4H_8O_2$), 159.00 (72.48, M^+-$C_5H_9O_2$), 88.00 (100.00, M^+-$C_{3i8}F_3$), 70.00 (29.55, M^+-$C_{12}H_{15}O_2$).



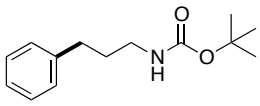
ethyl 4-(4-fluorophenyl)butanoate (3j) [CAS:1693-05-6].[23] The general procedure was followed with 1-bromo-4-fluorobenzene (82 µL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 16-20 h. The product was isolated by chromatography (95:5 pentane: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 114 mg (72%, 5 mol% catalyst, 20 h). With 1,10-phenanthroline: first run 124 mg (79%, 5 mol% catalyst, 19 h). Second run 123 mg (78%, 5 mol% catalyst, 16 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.13 (td, *J* = 6.0, 2.4 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.93 (quintet, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.5, 161.4 (d, *J*= 243.1 Hz), 137.1 (d, *J*= 2.6 Hz), 129.9 (d, *J*= 7.9 Hz), 115.2 (d, *J*= 21.4 Hz), 60.4, 34.4, 33.6, 26.7, 14.3.

^{19}F-NMR (376 MHz; C_6D_6): δ -118.0.

GC-MS *m/z* (% relative intensity, ion): 210.05 (18.12, M^+), 165.05 (46.57, M^+-C_2H_5O), 122.00 (60.77, M^+-$C_4H_8O_2$), 109.00 (100.00, M^+-$C_5H_9O_2$).



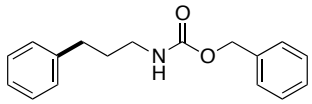
***tert*-butyl (3-phenylpropyl)carbamate (3k) [CAS:147410-39-7].**[24] The general procedure was followed with bromobenzene (80 µL, 0.75 mmol, 1.00 equiv) and *tert*-butyl (3-bromopropyl)carbamate (179 mg, 0.75 mmol, 1.00 equiv) at 60 °C for 13-17 h. The product was isolated by chromatography (9:1 hexanes: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 140 mg (79%, 5 mol% catalyst, 20 h). Second run 138 mg (78%, 5 mol% catalyst, 17 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.31-7.19 (m, 5H), 4.54 (s, 1H), 3.18 (d, *J* = 6.0 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.83 (quintet, *J* = 7.4 Hz, 2H), 1.47 (s, 3i).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 156.1, 141.7, 128.52, 128.47, 126.0, 79.2, 40.4, 33.3, 31.9, 28.5.

[23] Kitazawa, N.; Ueno, K.; Takahashi, K.; Kimura, T.; Sasaki, A.; Kawano, K.; Okabe, T.; Komatsu, M.; Matsunaga, M.; Kubota, A.; Eisai Co., Ltd. Indoles. US2002/19531, May 18, 2001.
[24] Maddani, Mahagundappa R.; Moorthy, Saravana K.; Prabhu, Kandikere R. *Tetrahedron*, **2010**, *66*, 329-333.

GC-MS *m/z* (% relative intensity, ion): 179.05 (28.56, M^+-C_4H_9), 118.05 (100.00, M^+-$C_5H_{11}NO_2$), 91.00 (36.09, M^+-$C_7H_{14}NO_2$).

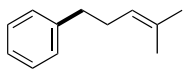


benzyl (3-phenylpropyl)carbamate (3l) [CAS:302569-84-2].[25] The general procedure was followed with bromobenzene (80 µL, 0.75 mmol, 1.00 equiv) and benzyl (3-bromopropyl)carbamate (204 mg, 0.75 mmol, 1.00 equiv) at 60 °C for 5-17 h. The product was isolated by chromatography (75:25 hexanes: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 121 mg (60%, 5 mol% catalyst, 17 h). Second run 141 mg (70%, 11 mol% catalyst, 5 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.39-7.20 (m, 10H), 5.14 (s, 2H), 4.99 (s, 1H), 3.25 (d, *J* = 6.3 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.86 (t, *J* = 7.1 Hz, 2H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 176.5, 156.5, 141.4, 136.7, 128.52, 128.45, 128.37, 128.1, 126.0, 66.6, 40.7, 33.0, 31.6.

GC-MS *m/z* (% relative intensity, ion): 178.10 (36.72, M^+-C_7H_7), 117.05 (25.22, M^+-$C_{12}H_{10}$), 91.00 (100.00, M^+-$C_{10}H_{12}NO_2$), 77.00 (11.62, M^+-$C_5H_9NO_2$).

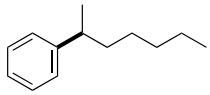


(4-methylpent-3-en-1-yl)benzene (3m) [CAS:33501-90-5].[26] The general procedure was followed with bromobenzene (80 µL, 0.75 mmol, 1.00 equiv) and 5-bromo-2-methyl-2-pentene (100 µL, 0.75 mmol, 1.00 equiv, filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool prior to use to remove yellow coloration) at 60 °C for 20-25 h. The product was isolated by chromatography (hexanes) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 60 mg (50%, 5 mol% catalyst, 20 h), further purified by preparative TLC (hexanes). Second run 68 mg (56%, 5 mol% catalyst, 25 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.32-7.19 (m, 5H), 5.21 (ddd, *J* = 7.0, 5.8, 1.2 Hz, 1H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.33 (q, *J* = 7.5 Hz, 2H), 1.72 (s, 3H), 1.60 (s, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 142.6, 132.2, 128.6, 128.4, 125.8, 123.9, 36.3, 30.2, 25.8, 17.8.

GC-MS *m/z* (% relative intensity, ion): 160.10 (48.52, M^+), 104.00 (11.23, M^+-C_4H_7), 91.00 (73.07, M^+-C_5H_9), 69.05 (100.00, M^+-C_7H_7).



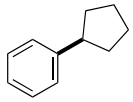
[25] Yang, B-L.; Tian, S-K. *Eur. J. Org. Chem.* **2007**, *28*, 4646.
[26] Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12160.

heptan-2-ylbenzene (3n) [CAS:2132-84-5].[27] The general procedure was followed with bromobenzene (80 μL, 0.75 mmol, 1.00 equiv) and 2-bromohepatane (148 μL, 0.94 mmol, 1.25 equiv, technical grade, 89:11 2-bromoheptane:3-bromoheptane) at 60 °C for 17-23 h. The product was isolated by chromatography (pentane) as a 6.3:1 mixture of **3n**:heptan-3-ylbenzene as colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 75 mg (57% isolated as a 87:13 ratio of **3n**:heptan-3-ylbenzene, 5 mol% catalyst, 23 h). Second run with 2-bromoheptane (177 μL, 1.125 mmol, 1.50 equiv) 81 mg (61% isolated as a 79:21 ratio of **3n**:heptan-3-ylbenzene, 5 mol% catalyst, 25 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.31-7.17 (m, 5H), 2.67 (sextet, J = 7.1 Hz, 1H), 1.59-1.52 (m, 2H), 1.25 (m, 3i), 0.85 (t, J = 6.8 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 148.1, 128.4, 127.1, 125.9, 40.1, 38.6, 32.1, 27.5, 22.7, 22.5, 14.2.

GC-MS *m/z* (% relative intensity, ion): 176.10 (15.86, M^+), 105.05 (100.00, M^+-C_5H_{11}), 91.05 (19.36, M^+-C_6H_{14}), 77.05 (12.47, M^+-C_7H_{15}).

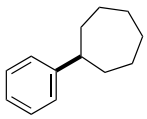


cyclopentylbenzene (3o) [CAS:700-88-9].[28] The general procedure was followed with bromobenzene (80 μL, 0.75 mmol, 1.00 equiv) and cyclopentyl bromide (101 μL, 0.94 mmol, 1.25 equiv) at 60 °C for 17-23 h. The product was isolated by chromatography (pentane) as colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 62 mg (56%, 5 mol% catalyst, 23 h). Second run with cyclopentyl bromide (121 μL, 1.125 mmol, 1.50 equiv) 69 mg (63%, 5 mol% catalyst, 25 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.31-7.16 (m, 5H), 3.03-2.96 (m, 1H), 2.08-2.06 (m, 2H), 1.83-1.80 (m, 2H), 1.71-1.58 (m, 4H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 146.7, 128.4, 127.2, 125.8, 46.1, 34.8, 25.7.

GC-MS *m/z* (% relative intensity, ion): 146.10 (67.78, M^+), 117.05 (100.00, M^+-C_2H_4), 104.00 (67.78, M^+-C_3H_6), 91.05 (52.29, M^+-C_4H_8), 77.05 (26.40, M^+-C_5H_9).



phenylcycloheptane (3p) [CAS:4401-18-7].[29] The general procedure was followed with bromobenzene (80 μL, 0.75 mmol, 1.00 equiv) and cycloheptyl bromide (129 μL, 0.94 mmol, 1.25 equiv) at 60 °C for 17-23 h. The product was isolated by chromatography (pentane) as colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 74 mg (57%, 5 mol% catalyst, 23

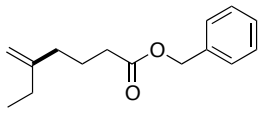
[27] Hobbs, C.; Hammann, W. *J. Org. Chem.* **1970**, *35* 4188-4191.
[28] Clive, D. L. J.; Pham, M. P. *J. Org. Chem.*, **2009**, *74*, 1685-1690.
[29] Kawamura, S.; Ishizuka, K.; Takaya, H.; Nakamura, M. *Chem. Commun.*, **2010**, *46*, 6054-6056.

h). Second run with cycloheptyl bromide (155 μL, 1.125 mmol, 1.50 equiv) 81 mg (61%, 5 mol% catalyst, 25 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.30-7.14 (m, 5H), 2.66 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.92 (dq, *J* = 10.0, 3.3 Hz, 2H), 1.82-1.77 (m, 2H), 1.73-1.53 (m, 8H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 150.2, 128.4, 126.8, 125.6, 47.2, 37.0, 28.1, 27.4.

GC-MS *m/z* (% relative intensity, ion): 174.10 (36.12, M^+), 117.10 (56.38, M^+-C_4H_8), 104.00 (100.00, M^+-C_5H_{10}), 91.00 (71.15, M^+-C_6H_{12}), 77.05 (13.31, M^+-C_7H_{13}).

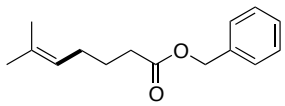


benzyl 5-methyleneheptanoate (3q). The general procedure was followed with 2-bromo-1-butene (77 μL, 0.75 mmol, 1.00 equiv) and benzyl 4-bromobutanoate (193 mg, 0.75 mmol, 1.00 equiv) at 60 °C for 25 h. The product was isolated by chromatography (95:5 hexanes: ether) as a 74:26 mixture of product:benzylbutyrate.[30] These products proved challenging to separate by chromatography and the yield for product was calculated from the NMR ratio with MW data. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 146 mg, which corresponds to a 66% yield of **3q**, 5 mol% catalyst. Characterization data are for **3q** only.

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.36-7.31 (m, 5H), 5.12 (s, 2H), 4.73 (s, 1H), 4.69 (s, 1H), 2.36 (t, *J* = 7.6 Hz, 2H), 2.07-1.98 (m, 4H), 1.79 (quintet, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.6, 150.4, 136.2, 128.7, 128.3, 108.6, 66.2, 35.6, 33.9, 28.7, 23.1, 12.4.

GC-MS *m/z* (% relative intensity, ion): 141.10 (24.32, M^+-C_7H_7), 95.05 (20.10, M^+-$C_8H_7O_2$), 91.00 (100.00, M^+-$C_8H_{13}O_2$), 55.00 (16.39, M^+-$C_{11}H_{13}O_2$).



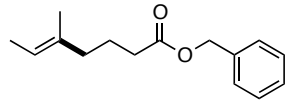
benzyl 6-methylhept-5-enoate (3r) [CAS:108957-11-5]. The general procedure was followed with 2-bromo-1-propene (67 μL, 0.75 mmol, 1.00 equiv) and benzyl 4-bromobutanoate (193 mg, 0.75 mmol, 1.00 equiv) at 60 °C for 18-25 h. The product was isolated by chromatography (95:5 hexanes: ether) as yellow oil, which was contaminated with benzyl butyrate.[30] Yields quoted in the text exclude the weight of the contaminant. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 117 mg of a 71:29 ratio of **3r**:benzyl butyrate, which corresponds to a 51% yield of **3r**, (5 mol% catalyst, 25 h). Second run, 112 mg of 82:18 ratio of **3r**:benzyl butyrate, which corresponds to a 55% yield of **3r**, (5 mol% catalyst, 18 h). Characterization data are for **3r** only.

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.36 (m, 5H), 5.12-5.08 (m, 3H), 2.35 (tt, *J* = 7.3, 3.8 Hz, 2H), 2.02 (q, *J* = 7.2 Hz, 2H), 1.71-1.66 (m, 5H), 1.58 (s, 3H).

[30] Poeylaut-Palena, A. A.; Testero, S. A.; Mata, E. G., *Chem. Commun.* **2010**, *46*, 6054-6056.

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.7, 136.3, 132.7, 128.7, 128.32, 128.29, 123.6, 66.2, 33.9, 27.5, 25.8, 25.2, 17.8.

GC-MS *m/z* (% relative intensity, ion): 141.10 (79.93, M^+-C_7H_7), 99.05 (12.44, M^+-$C_{10}H_{14}$), 91.00 (100.00, M^+-$C_8H_{13}O_2$), 69.05 (12.87, M^+-$C_{10}H_{11}O_2$).

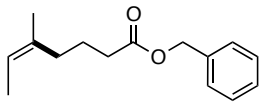


(*E*)-benzyl 5-methylhept-5-enoate (3s). The general procedure was followed with (*E*)-2-bromo-2-butene (76 μL, 0.75 mmol, 1.00 equiv) and benzyl 4-bromobutanoate (198.2 mg, 0.75 mmol, 1.00 equiv) at 60 °C for 22-26 h. The product was isolated by chromatography (95:5 hexanes:ether) as yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 125 mg (72%, 5 mol% catalyst, 26 h) isolated as a 93:7 ratio of **3s**:**3t**. Second run 137 mg (79%, 5 mol% catalyst, 22 h) isolated as a 89:11 ratio of **3s**:**3t**. Reported chemical shifts are for the major isomer (**3s**) only.

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.37-7.33 (m, 5H), 5.21 (q, *J* = 6.2 Hz, 1H), 5.13 (s, 2H), 2.34 (dt, *J* = 12.6, 6.7 Hz, 2H), 2.02 (t, *J* = 7.3 Hz, 2H), 1.77 (quintet, *J* = 7.4 Hz, 2H), 1.59-1.53 (m, 6H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.7, 136.3, 134.7, 128.6, 128.28, 128.25, 119.5, 66.2, 39.0, 33.8, 23.2, 15.5, 13.4.

GC-MS *m/z* (% relative intensity, ion): 141.10 (52.43, M^+-C_7H_7), 97.05 (2.55, M^+ -$C_8H_7O_2$), 91.00 (100.00, M^+ -$C_6H_{13}O_2$).

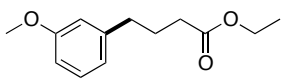


(*Z*)-benzyl 5-methylhept-5-enoate (3t). The general procedure was followed with (*Z*)-2-bromo-2-butene (76 μL, 0.75 mmol, 1.00 equiv, 88:12 ratio of *Z*:*E* isomers by ^{1}H NMR analysis) and benzyl 4-bromobutanoate (198.2 mg, 0.75 mmol, 1.00 equiv) at 60 °C for 20 h. The product was isolated by chromatography (95:5 hexanes:ether) as yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 85 mg (49%, 5 mol% catalyst, 20 h) isolated as a 68:32 ratio of **3t**:**3s**. Second run 115 mg (66%, 5 mol% catalyst, 20 h) isolated as a 73:27 ratio of **3t**:**3s**. Reported chemical shifts are for the major isomer (**3t**) only.

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.37-7.33 (m, 5H), 5.24 (q, *J* = 6.7 Hz, 1H), 5.12 (s, 3H), 2.34 (dt, *J* = 13.5, 7.0 Hz, 3H), 2.07 (t, *J* = 7.5 Hz, 2H), 1.78-1.71 (m, 3H), 1.69-1.66 (m, 3H), 1.58-1.52 (m, 5H), 0.96 (t, *J* = 7.4 Hz, 1H), 0.89 (t, *J* = 6.9 Hz, 1H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.7, 136.2, 134.9, 128.7, 128.39, 128.32, 128.29, 120.1, 66.3, 33.9, 30.6, 23.28, 23.16, 23.00, 13.4.

GC-MS *m/z* (% relative intensity, ion): 141.10 (51.58, M^+-C_7H_7), 97.10 (2.52, M^+ -$C_8H_7O_2$), 91.00 (100.00, M^+ -$C_6H_{13}O_2$).

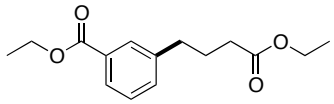


ethyl 4-(3-methoxyphenyl)butanoate (3u) [CAS:57816-01-0].[31] The general procedure was followed with 3-bromoanisole (95 μL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 19-25 h. The product was isolated by chromatography (9:1 hexanes: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 115 mg (69%, 5 mol% catalyst, 25 h). Second run 130 mg (78%, 5 mol% catalyst, 19 h). With 1,10-phenanthroline: first run 116 mg (69%, 5 mol% catalyst, 25 h). Second run 134 mg (81%, 5 mol% catalyst, 19 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.22-7.19 (m, 1H), 6.76 (dd, *J* = 17.1, 6.8 Hz, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.96 (quintet, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.5, 159.7, 143.1, 129.4, 121.0, 114.3, 111.3, 60.3, 55.2, 35.2, 33.7, 26.5, 14.3.

GC-MS *m/z* (% relative intensity, ion): 222.05 (29.39, M^+), 177.05 (24.70, M^+-C_2H_5O), 135.10 (33.51, M^+-$C_4H_7O_2$), 134.05 (100.00, M^+-C_4H_8O2), 121.05 (30.30, M^+-$C_5H_9O_2$).



ethyl 3-(4-ethoxy-4-oxobutyl)benzoate (3v) [CAS:364359-10-4].[32] The general procedure was followed with ethyl-3-bromobenzoate (120 μL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 15-20 h. The product was isolated by chromatography (9:1 pentane: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 136 mg (68%, 5 mol% catalyst, 20 h). With 1,10-phenanthroline: first run 159 mg (80%, 5 mol% catalyst, 17 h). Second run 167 mg (84%, 5 mol% catalyst, 15 h).

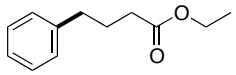
^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.88 (dd, *J* = 7.8, 2.8 Hz, 2H), 7.38-7.34 (m, 2H), 4.40-4.35 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.32 (dd, *J* = 9.9, 5.0 Hz, 2H), 2.01-1.95 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.4, 166.8, 141.8, 133.1, 130.7, 129.6, 128.5, 127.4, 61.0, 60.4, 35.0, 33.7, 26.5, 14.47, 14.36.

GC-MS *m/z* (% relative intensity, ion): 264.10 (24.98, M^+), 219.00 (48.48, M^+-C_2H_5O), 190.05 (100.00, M^+-$C_3H_6O_2$), 177.05 (73.39, M^+-$C_4H_2O_2$), 163.05 (29.30, M^+-C_5H_{3p2}), 91.00 (78.92, M^+-$C_8H_{14}O_4$).

[31] Wilhelm, T.; Lautens, M. *Org. Lett.*, **2005**, *7*, 4053-4056.
[32] Dohle, W.; Lindsay, D. M.; Knochel, P. *Org. Lett.*, **2001**, *3*, 2871-2874.

Compounds in Scheme 3:Aryl Chlorides

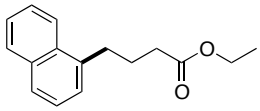


ethyl 4-phenylbutanoate (3b) [CAS:10031-93-3].[17] The general procedure was followed, omitting sodium iodide, with chlorobenzene (76 µL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 80 °C for 19-22 h. The product was isolated by chromatography (95:5 hexanes: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 23 mg (16%, 5 mol% catalyst, 22 h). Second run with ethyl 4-bromobutanoate (135 µL, 0.94 mmol, 1.25 equiv) 31 mg (22%, 5 mol% catalyst, 19 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.28-7.18 (m, 5H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.96 (quintet, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.6, 141.6, 128.64, 128.52, 126.1, 60.4, 35.3, 33.9, 26.7, 14.4.

GC-MS *m/z* (% relative intensity, ion): 192.00 (16.22, M^+), 147.05 (47.84, M^+-C_2H_5O), 105.00 (23.77, M^+-$C_4H_7O_2$), 91.00 (100.00, M^+-$C_5H_9O_2$).



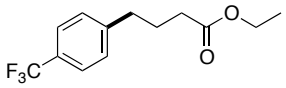
ethyl 4-(naphthalen-1-yl)butanoate (3w) [CAS:6326-89-2].[33] The general procedure was followed, omitting sodium iodide, with 1-chloronaphthalene (102 µL, 0.75 mmol, 1.00 equiv, technical grade 1-chloronaphthalene (87:13 1-chloronaphthalene:2-chloronaphthalene) and ethyl 4-bromobutanoate (135 µL, 0.94 mmol, 1.25 equiv) at 80 °C for 19-23 h. The product was isolated by chromatography (95:5 hexanes: ether) as yellow oil, which was a mixture of 1- and 2-alkylated naphthalenes. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 50 mg (28%, 5 mol% catalyst, 23 h). Second run 53 mg (29%, 5 mol% catalyst, 19 h). Characterization data are for 1-alkylated product **3w** only.

^{1}H-NMR (500 MHz; $CDCl_3$): δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.53-7.47 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 6.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.13 (t, *J* = 7.7 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 2.10 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.6, 137.7, 134.1, 132.0, 128.9, 127.0, 126.3, 126.0, 125.6, 123.9, 60.5, 34.2, 32.5, 26.0, 14.4.

GC-MS *m/z* (% relative intensity, ion): 242.05 (29.68, M^+), 154.05 (100.00, M^+-$C_4H_8O_2$), 141.00 (55.69, M^+-$C_5H_9O_2$), 115.00 (33.21, M^+-$C_{10}H_7$).

[33] Dutta, A. K.; Ryan, W.; Thomas, B. F.; Singer, M.; Compton, D. R.; et al. *Bioorg. Med. Chem.*, **1997**, *5*, 1591-1600.



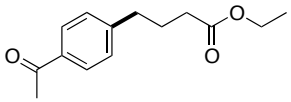
ethyl 4-(4-(trifluoromethyl)phenyl)butanoate (3i) [CAS:1235271-20-1].[22] The general procedure was followed, omitting sodium iodide, with 4-chlorobenzotrifluoride (100 µL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (135 µL, 0.94 mmol, 1.25 equiv) at 80 °C for 18-19 h. The product was isolated by chromatography (95:5 hexanes: ether) as colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 109 mg (56%, 5 mol% catalyst, 18 h). Second run 115 mg (59%, 5 mol% catalyst, 19 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.97 (quintet, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.3, 145.7, 128.9, 128.5 (q, *J*= 33.3 Hz), 125.4 (q, *J*= 3.8 Hz), 124.5 (q, *J*= 271.9 Hz), 60.5, 35.0, 33.6, 26.3, 14.3.

^{19}F-NMR (376 MHz; $CDCl_3$): δ 0.5.

GC-MS *m/z* (% relative intensity, ion): 260.05 (7.36, M^+), 215.00 (17.04, M^+-C_2H_5O), 159.00 (57.74, M^+-$C_5H_9O_2$), 88.00 (M+H –$C_9H_8F_3$).

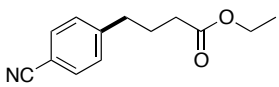


ethyl 4-(4-acetylphenyl)butanoate (3d) [CAS:71665-59-3].[19] The general procedure was followed, omitting sodium iodide, with 4'-chloroacetophenone (97 µL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (135 µL, 0.94 mmol, 1.25 equiv) at 80 °C for 18-20 h. The product was isolated by chromatography (7:3 hexanes: ether) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 132 mg (75%, 5 mol% catalyst, 18 h). Second run 132 mg (75%, 5 mol% catalyst, 20 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.58 (s, 3H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.97 (quintet, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 197.9, 173.3, 147.4, 135.4, 128.82, 128.71, 60.5, 35.2, 33.7, 26.7, 26.3, 14.4.

GC-MS *m/z* (% relative intensity, ion): 234.05 (34.83, M^+), 21900 (10.38, M^+-CH_3), 147.05 (100.00, M^+-$C_4H_7O_2$), 146.05 (15.73, M^+-$C_4H_8O_2$), 118.00 (15.48, M^+-$C_6H_{12}O_2$).



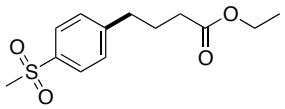
ethyl 4-(4-cyanophenyl)butanoate (3h) [CAS:131379-33-4].[22] The general procedure was followed, omitting sodium iodide, with 4-chlorobenzonitrile (103 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (135 µL, 0.94 mmol, 1.25 equiv) at 80 °C for 19-23 h. The product

was isolated by chromatography (8:2 hexanes: ether) as yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 144 mg (88%, 5 mol% catalyst, 23 h). Second run 149 mg (92%, 5 mol% catalyst, 19 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.95 (quintet, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.1, 147.2, 132.4, 129.4, 119.1, 110.1, 60.5, 35.3, 33.5, 26.1, 14.4.

GC-MS *m/z* (% relative intensity, ion): 216.95 (19.84, M^+-H), 172.00 (44.22, M^+-C_2H_5O), 130.05 (63.60, M^+-$C_4H_7O_2$), 116.00 (100.00, M^+-$C_5H_9O_2$), 88.00 (95.52, M^+-C_9H_8N).

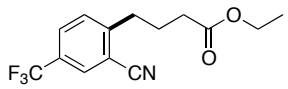


ethyl 4-(4-(methylsulfonyl)phenyl)butanoate (3x). The general procedure was followed, omitting sodium iodide, with 4-chloropehnyl-methylsulfone (143 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (135 µL, 0.94 mmol, 1.25 equiv) at 80 °C for 18 h. The product was isolated by chromatography (1:1 hexanes: ether) as yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 190 mg (94%, 5 mol% catalyst, 18 h). Second run 192 mg (94%, 5 mol% catalyst, 18 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.02 (s, 3H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.96 (quintet, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.1, 148.2, 138.3, 129.5, 127.6, 60.5, 44.6, 35.0, 33.5, 26.1, 14.3.

GC-MS *m/z* (% relative intensity, ion): 270.10 (12.17, M^+), 183.00 (100.00, M^+-$C_4H_7O_2$), 147.05 (20.00, M^+-$C_3H_8O_3S$), 90.00 (30.34, M^+-$C_6H_{12}O_4S$).



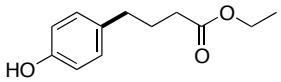
ethyl 4-(2-cyano-4-(trifluoromethyl)phenyl)butanoate (3y). The general procedure was followed, omitting sodium iodide, with 2-chloro-5-(trifluoromethyl)benzonitirle (154 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (135 µL, 0.94 mmol, 1.25 equiv) at 80 °C for 18 h. The product was isolated by chromatography (7:3 hexanes: ether) as yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 170 mg (80%, 5 mol% catalyst, 18 h). Second run 162mg (76%, 5 mol% catalyst, 18 h).
^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.87 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.02 (quintet, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 172.8, 149.6, 130.5, 129.7 (dd, J_1 = 37.50 Hz, J_2 = 3.43 Hz), 123.1 (q, J = 272.31), 116.6, 113.5, 33.8, 33.5, 25.7, 14.3.

^{19}F-NMR (376 MHz; CDCl3): δ-0.1.

GC-MS *m/z* (% relative intensity, ion): 285.1 (6.58, M^+), 240.00 (16.97, M^+-C_2H_5O), 198.00 (12.97, M^+-$C_4H_7O_2$), 184.00 (43.54, M^+-$C_5H_9O_2$), 88.05 (M+H –$C_{10}H_7F_3N$).

Compounds in Scheme 4.

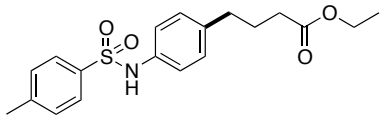


ethyl 4-(4-hydroxyphenyl)butanoate (3z) [CAS:62889-58-1].[34] The general procedure was followed with 4-bromophenol (130 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 16 h. The product was isolated by chromatography (7:3 pentane: ether) mixed fractions were further purified by preparative TLC (7:3 pentane: ether, 1500 µm) as yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 116 mg (74%, 5 mol% catalyst, 16 h). Second run 115 mg (74%, 5 mol% catalyst, 16 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.02 (d, J = 8.4 Hz, 2H), 6.77-6.75 (m, 2H), 5.43 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 2.31 (t, J = 7.5 Hz, 2H), 1.91 (t, J = 7.5 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 174.1, 154.0, 133.6, 129.7, 115.3, 60.6, 34.4, 33.8, 26.9, 14.4.

GC-MS *m/z* (% relative intensity, ion): 208.05 (17.05, M^+), 163.05 (21.21, M^+-C_2H_5O), 121.05 (13.04, M^+-$C_4H_7O_2$), 120.00 (100.00, M^+-$C_4H_8O_2$), 107.00 (55.63, M^+-$C_5H_9O_2$).



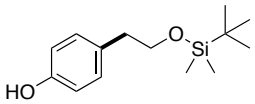
ethyl 4-(4-(4-methylphenylsulfonamido)phenyl)butanoate (3aa) [CAS:1138239-43-6].[35] The general procedure was followed with *N*- (4-bromophenyl)-4-methylbenzenesulfonamide (245 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 16-23 h. The product was isolated by chromatography (75:25 hexanes: ethyl acetate) mixed fractions were further purified by preparative TLC (75:25 hexanes: ethyl acetate, 1500 µm) as viscous colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 221 mg (93%, 5 mol% catalyst, 23 h). Second run 233 mg (98%, 5 mol% catalyst, 16 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.62 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 6.34 (s, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 2.38 (s, 3H), 2.27 (t, J = 7.4 Hz, 2H), 1.89 (quintet, J = 7.5 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

[34] Yi, C.S. Martinelli, L. C.; Blanton, C. D. *J. Org. Chem.*, **1978**, *43*, 405-409.
[35] Manolikakes, G.; Mayr, H.; Knochel, P.; Dong, Z.; Li, J. *Chem.-Eur. J.*, **2009**, *15*, 1324-1328.

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.4, 148.0, 145.4, 140.6, 132.6, 129.81, 129.62, 128.6, 122.3, 60.4, 34.6, 33.6, 26.4, 21.8, 14.3.

GC-MS *m/z* (% relative intensity, ion): 362.15 (18.42, M+H), 317.15 (12.56, M+H –C_2H_5O), 274.10 (33.32, M^+ $C_4H_7O_2$), 207.1 (10.34, M^+-$C_7H_7O_2$), 155.05 (43.92, M^+-$C_{12}H_{16}NO_2$), 91.05 (100.00, M^+-$C_{12}H_{16}NO_4S$).



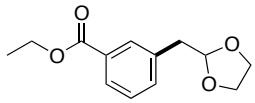
4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)phenol (3ab) [CAS:96013-76-2].[36] The general procedure was followed with 4-bromophenol (130 mg, 0.75 mmol, 1.00 equiv) and (2-bromoethoxy)(*tert*-butyl)dimethylsilane (225 mg, 0.94 mmol, 1.25 equiv) at 60 °C for 18-19 h. The product was isolated by chromatography (8:2 hexanes: acetone) as white solid. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 148 mg (78%, 5 mol% catalyst, 16 h). Second run 138 mg (73%, 5 mol% catalyst, 16 h).

Procedure for the reaction run with activated zinc.
The general procedure was followed with 4-bromophenol (130 mg, 0.75 mmol, 1.00 equiv) and (2-bromoethoxy)(tert-butyl)dimethylsilane (225 mg, 0.94 mmol, 1.25 equiv), with the sequential addition of 1,2-dibromoethane (6 µL) and chlorotrimethylsilane (6 µL) as the last two reagents. The reaction was heated at 60 °C for 3.5 h. The product was isolated by chromatography (8:2 hexanes: acetone) mixed fractions were further purified by preparative TLC (8:2 hexanes: acetone, 1500 µm) as white solid. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 123 mg (65%, 5 mol% catalyst, 16 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 5.47 (s, 1H), 3.78 (t, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 7.1 Hz, 2H), 0.89 (s, 3i), 0.01 (s, 5H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 154.2, 130.4, 115.3, 65.0, 38.8, 26.1, 18.5, -5.2.

GC-MS *m/z* (% relative intensity, ion): 195.00 (100.00, M^+-C_4H_{10}), 177.05 (48.69, M^+-$C_4H_{11}O$), 121.05 (23.43, M^+-$C_6H_{15}OSi$).



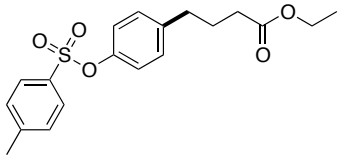
ethyl 3-((1,3-dioxolan-2-yl)methyl)benzoate (3ac) [CAS:898776-72-2]. The general procedure was followed with ethyl-3-bromobenzoate (120 µL, 0.75 mmol, 1.00 equiv) and 2-bromomethyl-1,3-dioxolane (97.3 µL, 0.75 mmol, 1.00 equiv) using sodium iodide (112 mg, 0.75 mmol, 1.00 equiv) at 80 °C for 19-23 h. The product was isolated by chromatography (9:1 hexanes: acetone) as yellow oil. With 1,10-phenanthroline: first run 116 mg (66%, 5 mol% catalyst, 19 h). Second run 94 mg (53%, 5 mol% catalyst, 23 h).

[36] Shah, S. T. A.; Singh, S.; Guiry, P. J. *J. Org. Chem.*, **2009**, *74*, 2179-2182.

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.95-7.91 (m, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 5.09 (t, *J* = 4.7 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.95-3.83 (m, 4H), 3.02 (d, *J* = 4.7 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 166.7, 136.5, 134.4, 130.9, 130.7, 128.4, 128.0, 104.4, 65.2, 61.0, 40.6, 14.5.

GC-MS *m/z* (% relative intensity, ion): 191.00 (8.06, M^+-C_2H_5O), 119.00 (5.53, M^+-$C_5H_{10}O_3$), 73.05 (100.00, M^+-$C_{10}H_{11}O_2$).

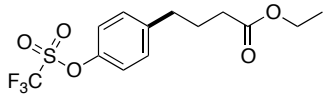


ethyl 4-(4-(tosyloxy)phenyl)butanoate (3ad). The general procedure was followed with 4-bromophenyl 4-methylbenzenesulfonate (245 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 16 h. The product was isolated by chromatography (9:1 hexanes: ethyl acetate) as colorless oil. With 1, 10-phenanthroline: first run 206 mg (76%, 5 mol% catalyst, 16 h). Second run 207 mg (76%, 5 mol% catalyst, 16 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.90 (quintet, *J* = 7.6 Hz, 2H), 1.27-1.23 (m, 4H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.3, 147.9, 145.3, 140.6, 132.5, 129.78, 129.58, 128.5, 122.3, 60.4, 34.5, 33.6, 26.4, 21.7, 14.3.

GC-MS *m/z* (% relative intensity, ion): 362.15 (19.43, M^+), 317.15 (12.75, M^+-C_2H_5O), 274.10 (34.05, M^+-$C_4H_7O_2$), 155.00 (45.43, M^+-$C_{12}H_{15}O_3$), 91.05 (100.00, M^+-$C_{12}H_{15}O_5S$).



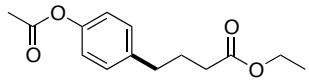
ethyl 4-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)butanoate (3ae). The general procedure was followed with 4-bromophenyl trifluoromethanesulfonate (229 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 16-17 h. The product was isolated by chromatography (9:1 hexanes: ethyl acetate) as colorless oil. With 1, 10-phenanthroline: first run 182 mg (71%, 5 mol% catalyst, 17 h). Second run 195 mg (76%, 5 mol% catalyst, 16 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.25 (d, *J* = 6.8 Hz, 3H), 7.19 (d, *J* = 8.6 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.95 (quintet, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.2, 148.0, 142.2, 130.3, 121.3, 118.9 (q, *J* = 321 Hz, $–CF_3$) 60.5, 34.5, 33.6, 26.4, 14.3.

^{19}F-NMR (376 MHz; $CDCl_3$): δ-10.0.

GC-MS *m/z* (% relative intensity, ion): 340.20 (6.09, M^+), 295.15 (16.31, M^+-C_2H_5O), 252.05 (12.95, M^+-$C_4H_7O_2$), 239.10 (5.56, M^+-$C_5H_9O_2$), 106.10 (20.69, M^+-$C_6H_9F_3O_4S$), 88.10 (100.00, M^+-$C_9H_8F_3O_3S$).

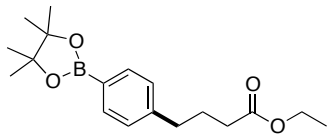


ethyl 4-(4-acetoxyphenyl)butanoate (3af) [CAS:155589-46-1].[37] The general procedure was followed with 4-bromophenyl acetate (161 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 17-23 h. The product was isolated by chromatography (8:2 hexanes: ethyl acetate) mixed fractions were further purified by preparative TLC (8:2 hexanes: ethyl acetate, 1500 μm) as colorless oil. With 1, 10-phenanthroline: first run 126 mg (67%, 5 mol% catalyst, 17 h). Second run 115 mg (61%, 5 mol% catalyst, 23 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.18 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.33-2.28 (m, 5H), 1.95 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.5, 169.7, 149.0, 139.1, 129.5, 121.5, 60.4, 34.6, 33.7, 26.6, 21.2, 14.4.

GC-MS *m/z* (% relative intensity, ion): 250.05 (2.14, M^+), 208.05 (30.05, M^+-C_2H_3O), 205.05 (7.63, M^+-C_2H_5O), 163.05 (12.44, M^+-$C_4H_7O_2$), 120.00 (100.00, M^+-$C_6H_{10}O_3$).



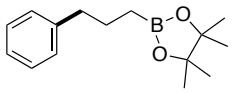
ethyl 4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanoate (3ag). The general procedure was followed with 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (212 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 19-20 h. The product was isolated by chromatography (75:25 hexanes: ether) as faintly yellow oil. With 1, 10-phenanthroline: first run 188 mg (79%, 5 mol% catalyst, 20 h). Second run 175 mg (73%, 5 mol% catalyst, 19 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.95 (quintet, *J* = 7.5 Hz, 2H), 1.34 (s, 3ae), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.5, 144.9, 135.0, 128.0, 83.7, 60.3, 35.4, 33.7, 26.4, 24.9, 14.3.

[37] Klement. I.; Knochel, P.; Chau, K.; Cahiez, G. *Tetrahedron Lett.*, **1994**, *35*, 1177-1180.

GC-MS *m/z* (% relative intensity, ion): 318.20 (51.36, M^+), 273.15 (17.57, M^+-C_2H_5O), 217.00 (19.45, M^+-$C_5H_9O_2$), 189.00 (16.20, M^+-$C_8H_{17}O$), 117.05 (100.00, M^+-$C_{11}H_{19}O_3$), 101.05 (78.86, M^+-$C_{13}H_{18}BO_2$).

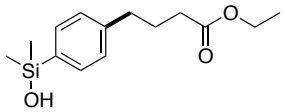


4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (3ah) [CAS:329685-40-7].[38] The general procedure was followed with 3-bromopropylboronic acid pinacol ester (158.6 µL, 0.75 mmol, 1.00 equiv) and bromobenzene (80 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 15 h. The product was isolated by chromatography (95:5 hexanes: ether) as pale yellow oil. Mixed fractions were further purified by preparative TLC (1500 µm thickness, 95:5 hexanes: ether). With 4,4'-dimethoxy-2, 2'-bipyridine: first run 89 mg (48%, 11 mol% catalyst, 15 h), second run 141 mg (70%, 11 mol% catalyst, 5 h). The general procedure was followed with 3-bromopropylboronic acid pinacol ester (158.6 µL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (134.5 µL, 0.94 mmol, 1.25 equiv) at 60 °C for 15 h, second run 77 mg (41%, 11 mol% catalyst, 16 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.29-7.16 (m, 5H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.75 (quintet, *J* = 7.8 Hz, 2H), 1.26 (s, 3ae), 0.85 (t, *J* = 7.8 Hz, 2H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 142.8, 128.7, 128.3, 125.7, 83.0, 38.7, 26.2, 25.0.

GC-MS *m/z* (% relative intensity, ion): 127.10 (25.61, $M^{+\cdot}C_{3i11}$), 119.05 (17.87, M^+-C6H_{12}BO2), 117.10 (19.21, $M^{+\cdot}C_9H_{11}B$), 91.05 (76.83, M^+-$C_8H_{16}BO_2$), 85.05 (100.00, M^+-$C_9H_{15}BO_2$).



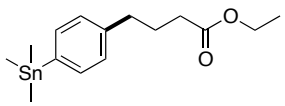
ethyl 4-(4-(hydroxydimethylsilyl)phenyl)butanoate (3ai). The general procedure was followed with (4-bromophenyl)dimethylsilanol (173.4 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 18 h. The product was isolated by chromatography (8:2 hexanes: ethyl acetate) mixed fractions were further purified by preparative TLC (8:2 hexanes: ethyl acetate, 1500 µm) as colorless oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 122 mg (61%, 5 mol% catalyst, 18 h). Second run 146 mg (73%, 5 mol% catalyst, 18 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.96 (quintet, *J* = 7.5 Hz, 2H), 1.76 (s, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 6H).

^{13}C-NMR (101 MHz; $CDCl_3$): δ 173.7, 143.0, 136.6, 133.3, 128.2, 60.5, 35.2, 33.8, 26.5, 14.3, 0.1.

[38] Lata, C. J.; Crudden, C. M. *J. Am. Chem. Soc.*, **2010**, *132*, 131-137.

GC-MS *m/z* (% relative intensity, ion): 265.15 (1.10, M^+-H), 221.05 (18.94, M^+-C_2H_5O), 178.10 (21.33, M^+-$C_4H_7O_2$), 150.00 (40.10, M^+-$C_6H_{12}O_2$), 147.05 (13.11, M^+-$C_4H_{12}O_2Si$), 105.00 (100.00, M^+-$C_6H_{14}O_3Si$).

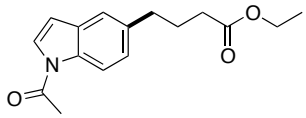


ethyl 4-(4-(trimethylstannyl)phenyl)butanoate (3aj). The general procedure was followed with (4-bromophenyl)trimethylstannane (239.9 mg, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 16 h. The product was isolated by chromatography (9:1 hexanes: ethyl acetate) as pale yellow oil. With 4,4'-dimethoxy-2, 2'-bipyridine: first run 233 mg (87%, 5 mol% catalyst, 16 h), second run 160 mg (60%, 5 mol% catalyst, 16 h).

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.48-7.35 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.95 (quintet, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.34-0.20 (m, 3i).

^{13}C-NMR (101 MHz; $CDCl_3$): δ 173.5, 141.6, 139.2, 136.0, 128.4, 60.3, 35.2, 33.8, 26.6, 14.4,-9.5.

GC-MS *m/z* (% relative intensity, ion): 341.05 (100.00, M^+-CH_3), 164.95 (47.72, M^+-$C_{312}H_{16}O_2$), 147.00 (28.34, M^+-$C_5H_{14}Sn$), 105.05 (90.23, M^+-$C_7H_{16}SnO_2$).

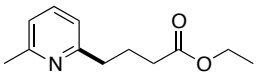


ethyl 4-(1-acetyl-1*H*-indol-5-yl)butanoate (3ak). The general procedure was followed with N-acetyl-5-bromoindole (176.3 mg, 0.74 mmol, 0.987 equiv) and ethyl 4-bromobutanoate (107 µL, 0.75 mmol, 1.00 equiv) at 60 °C for 19 h. The product was isolated by chromatography (6:4 pentane: ether) as a pale yellow oil. Mixed fractions were further purified by preparative TLC silica plates (1500 µm thickness, 6:4 pentane: ether). With 4,4'-dimethoxy-2, 2'-bipyridine: first run 160 mg (79%, 5 mol% catalyst, 19 h), second run 168 mg (78%, 5 mol% catalyst, 19 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 8.33 (d, *J* = 6.9 Hz, 1H), 7.39-7.36 (m, 2H), 7.17 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.58 (d, *J* = 3.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.61 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.99 (quintet, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.6, 168.6, 137.0, 134.2, 130.8, 125.9, 125.5, 120.5, 116.4, 109.1, 60.4, 35.1, 33.7, 27.0, 24.0, 14.4.

GC-MS *m/z* (% relative intensity, ion): 273.10 (35.93, M^+), 231.05 (13.40, M^+-C_2H_3O), 186.05 (13.82, M^+-$C_4H_7O_2$), 130.05 (100.00, M^+-$C_7H_{12}O_3$).

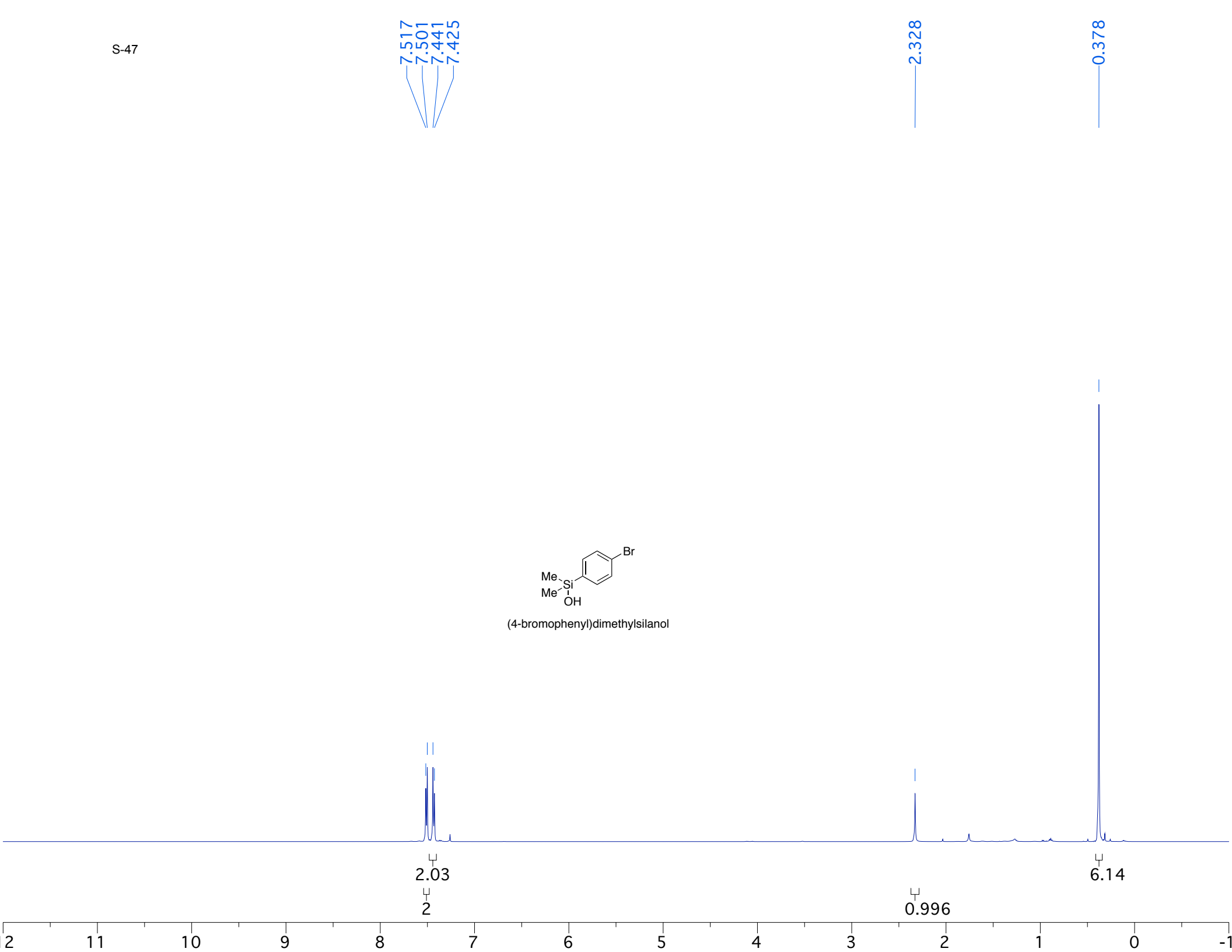


ethyl 4-(6-methylpyridin-2-yl)butanoate (3al) [CAS:100370-10-3]. The general procedure was followed with 2-chloro-6-methylpyridine (85.5 μL, 0.75 mmol, 1.00 equiv) and ethyl 4-bromobutanoate (107 μL, 0.75 mmol, 1.00 equiv) at 60 °C for 17 h. The product was isolated by chromatography (75:25 hexanes: ethyl acetate) as a pale yellow oil. With 1,10-phenanthroline: 40 mg (26%, 5 mol% catalyst, 17 h).

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.48 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.3 Hz, 2H), 4.12 (q, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.53 (s, 3H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.08-2.02 (m, 3H), 1.25 (t, *J* = 6.9 Hz, 3H).

^{13}C-NMR (126 MHz; $CDCl_3$): δ 173.6, 158.0, 136.7, 120.8, 119.8, 60.4, 37.7, 33.9, 25.3, 24.6, 14.4.

GC-MS *m/z* (% relative intensity, ion): 207.25 (3.21, M^+), 162.15 (20.29, M^+-C_2H_5O), 134.20 (42.21, M^+-$C_3H_5O_2$), 120.05 (45.55, M^+-$C_4H_7O_2$), 107.05 (100.00, M^+-$C_5H_9O_2$).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Si
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6.14
2
0.996
12
11
10
9
8
7
6
5
4
3
2
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0
-1

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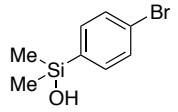
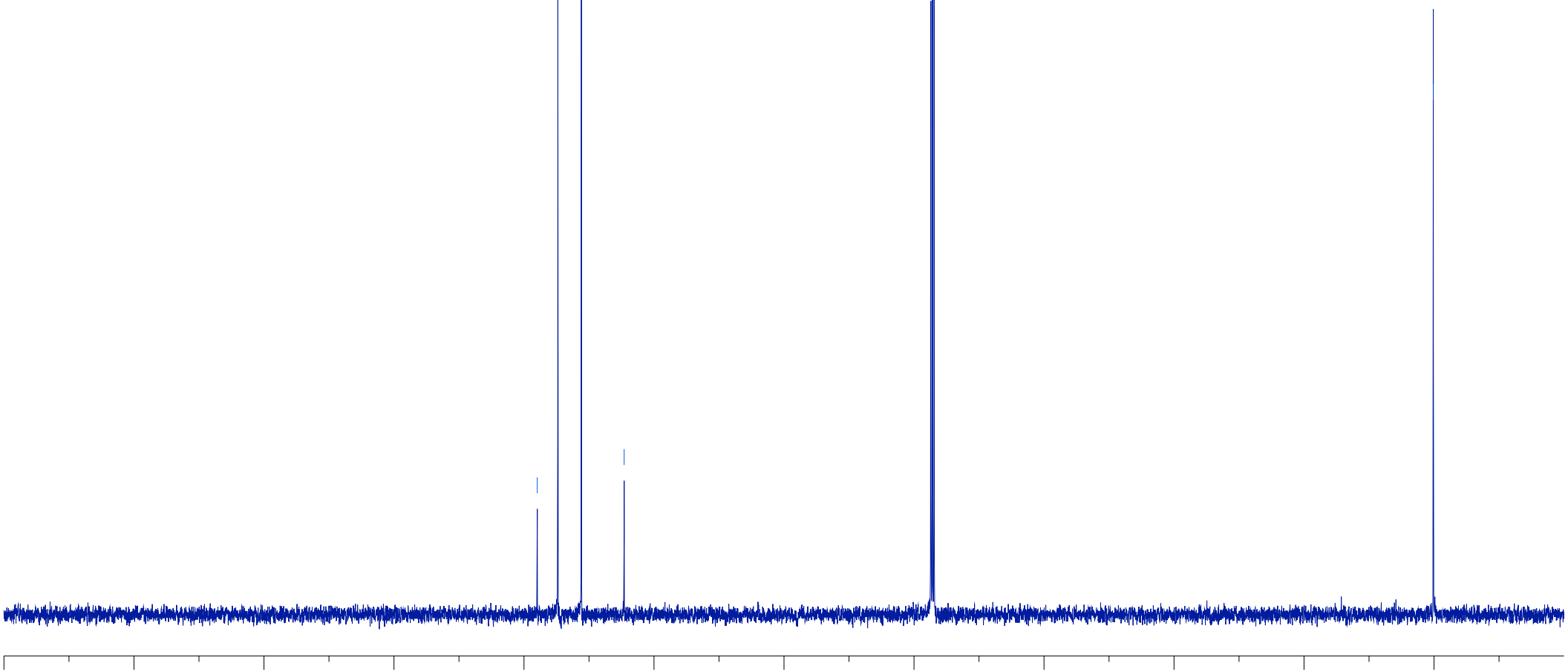
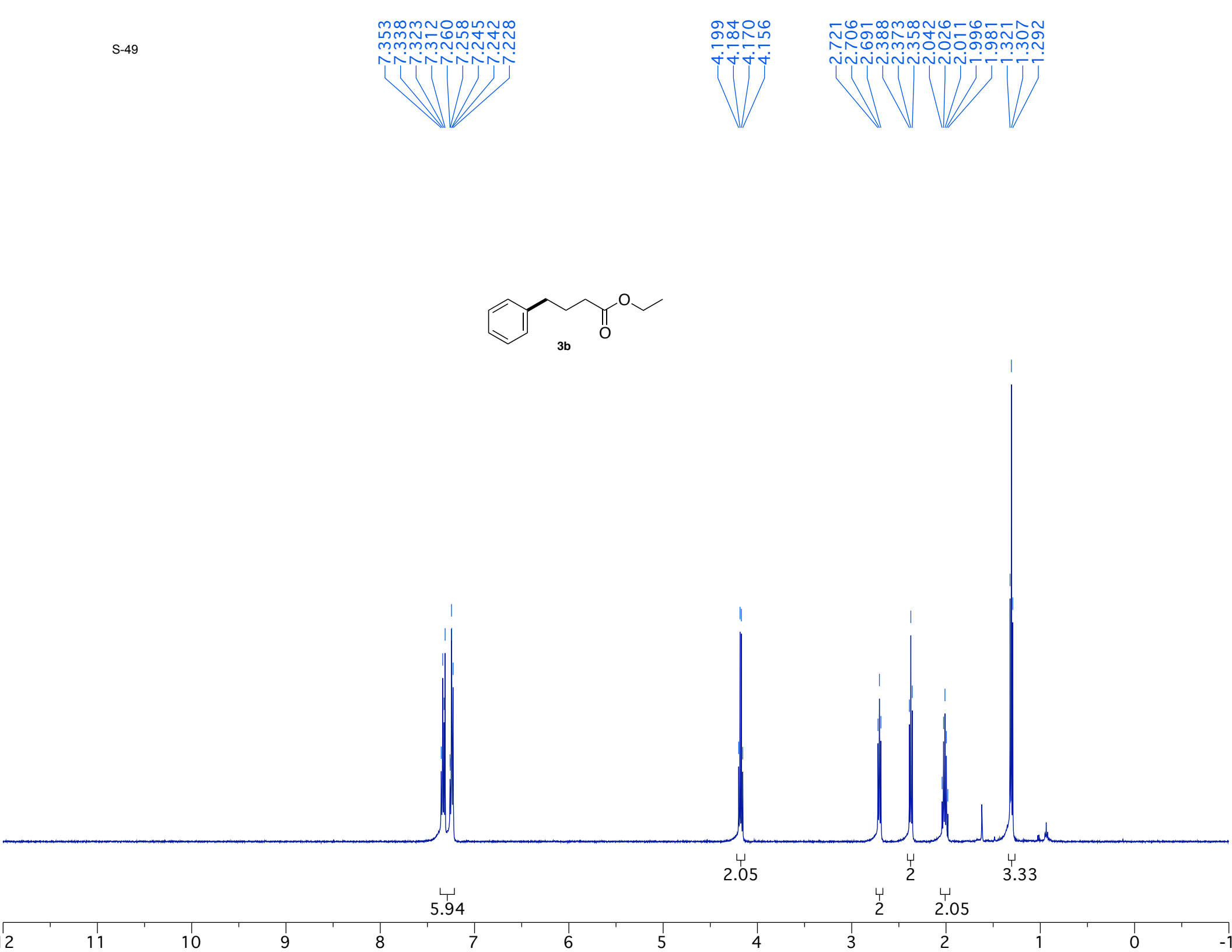


(4-bromophenyl)dimethylsilanol

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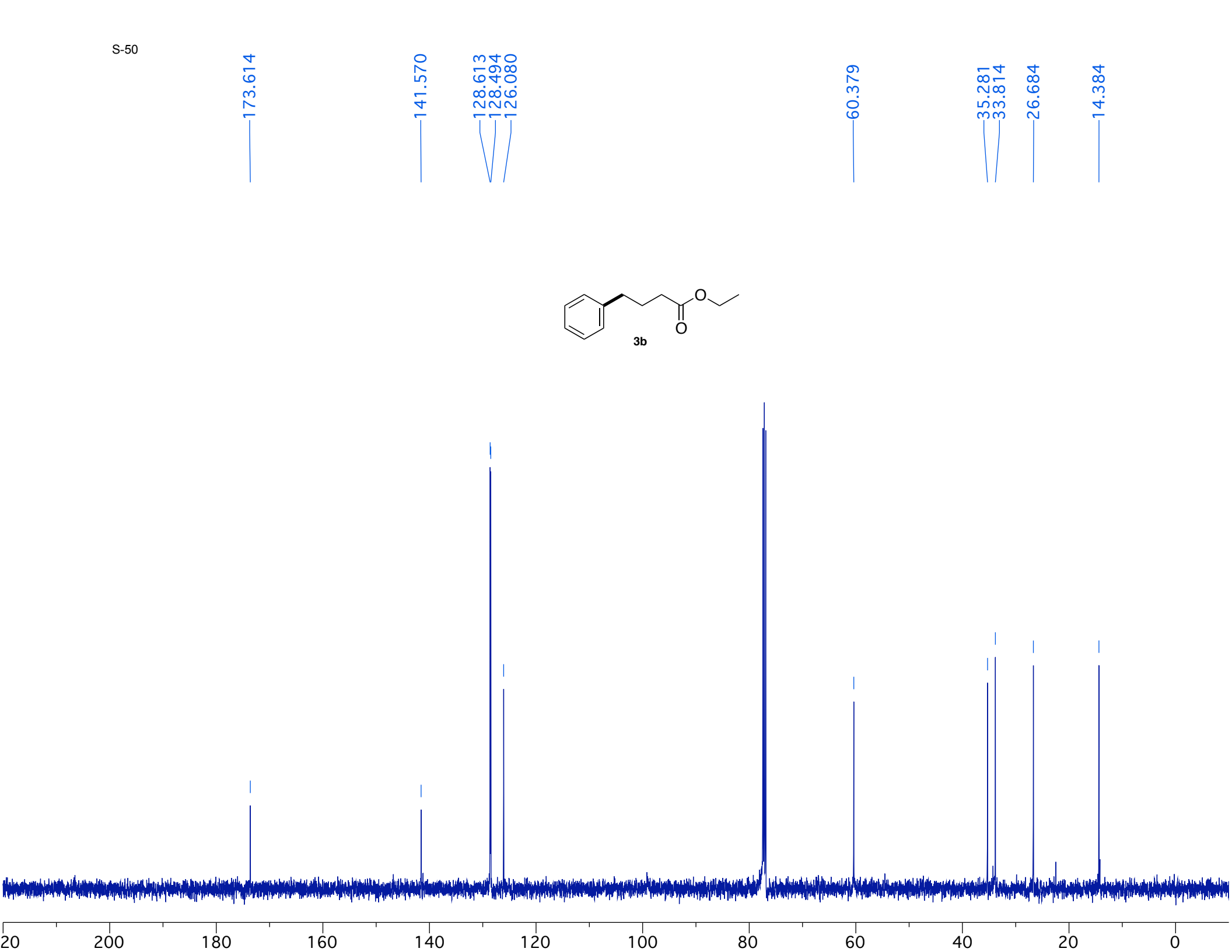
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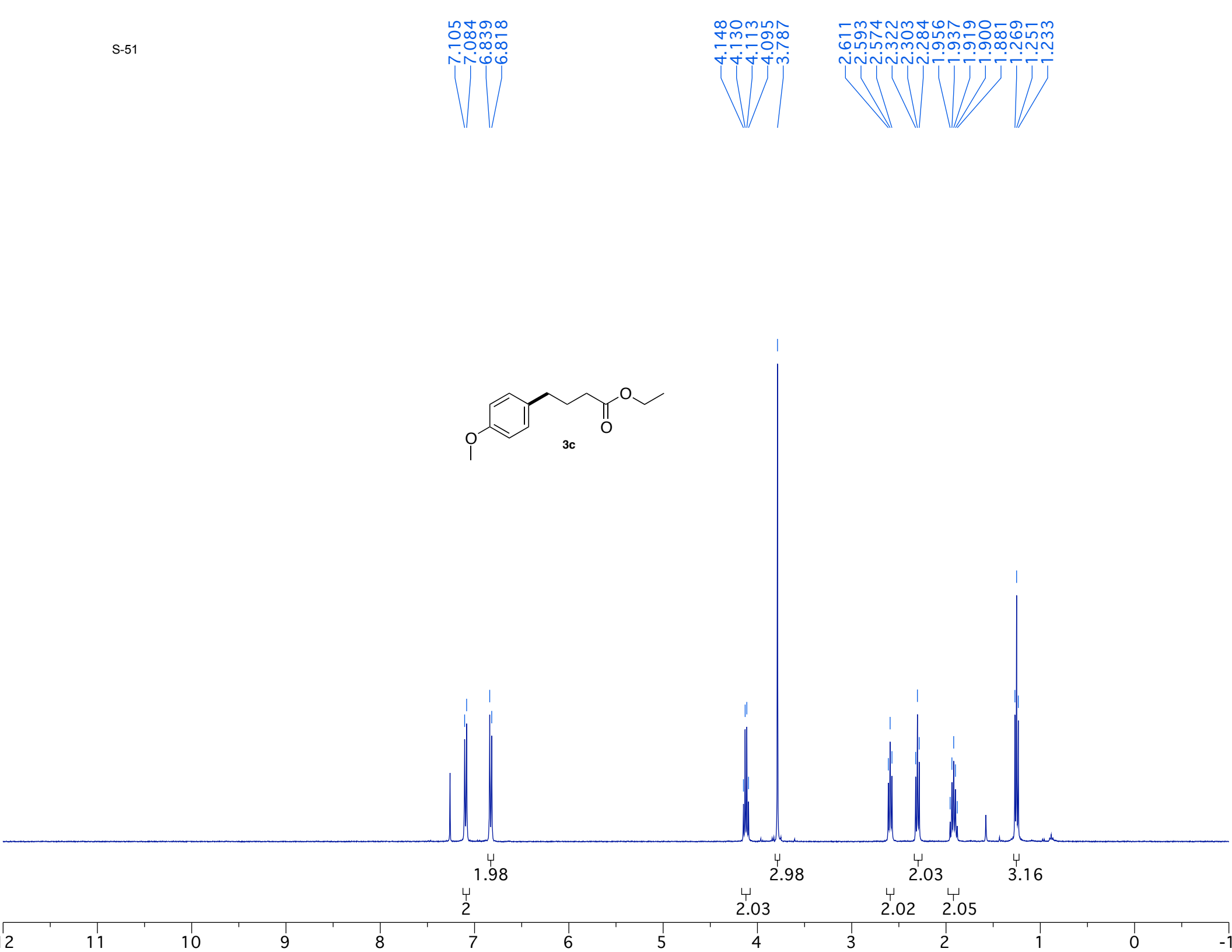
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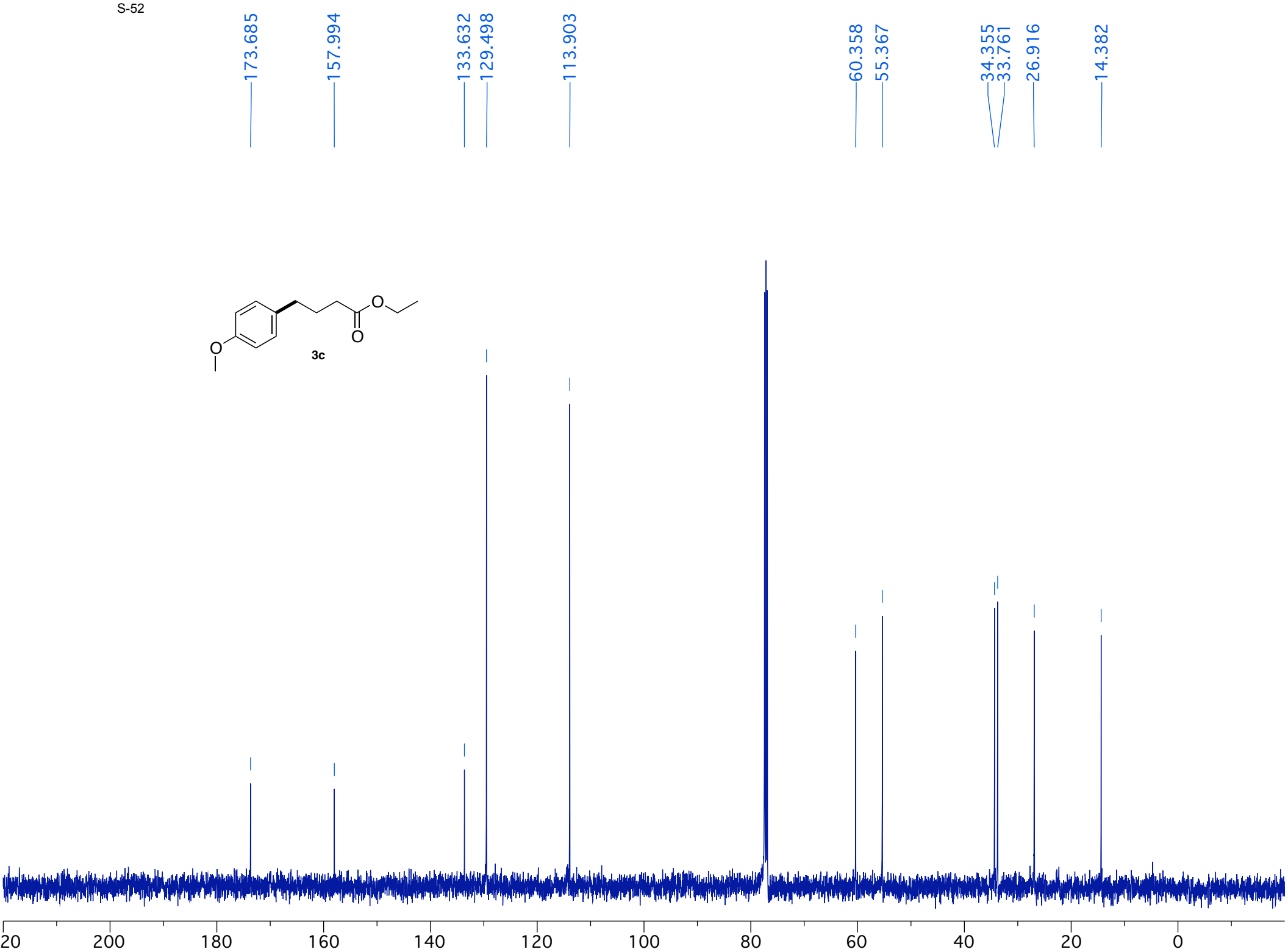
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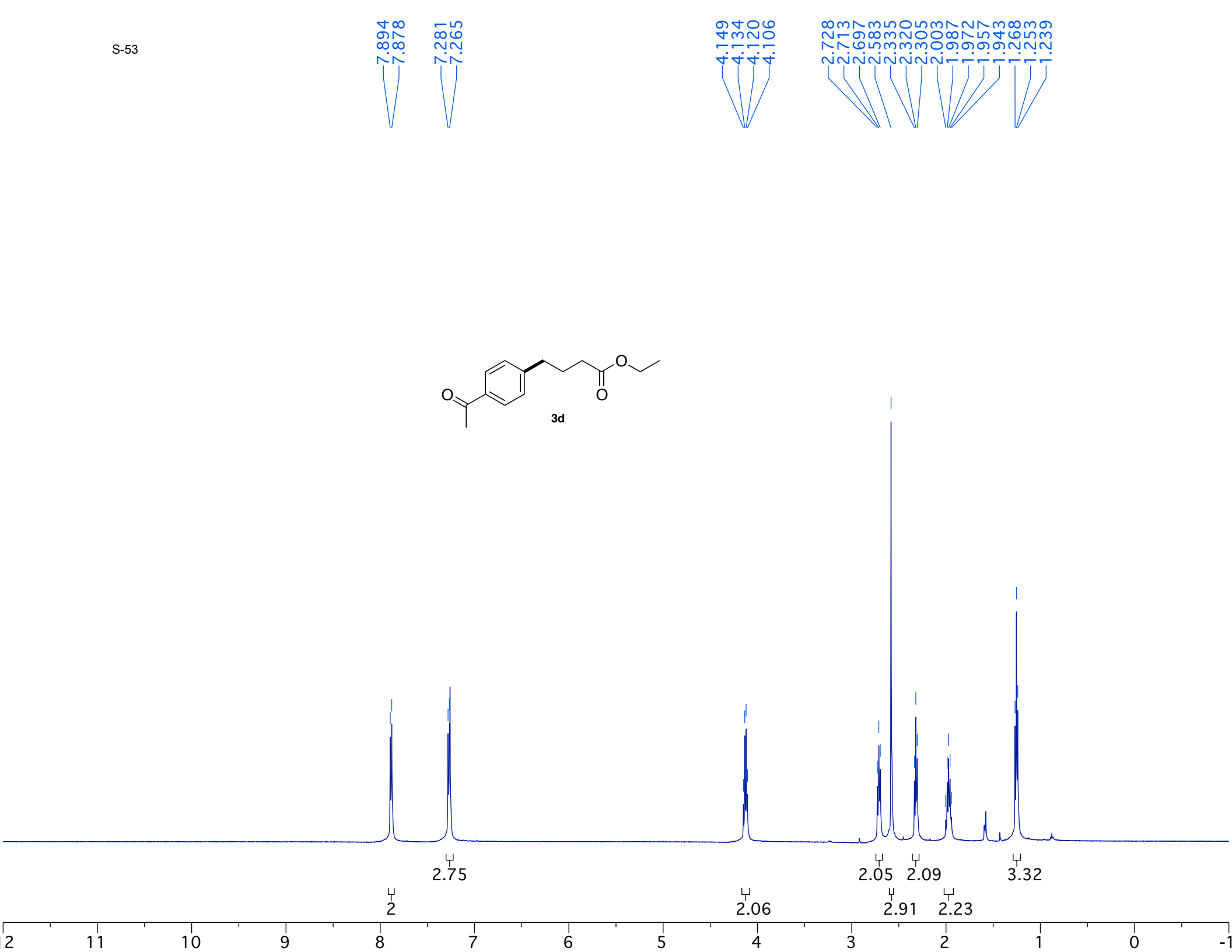
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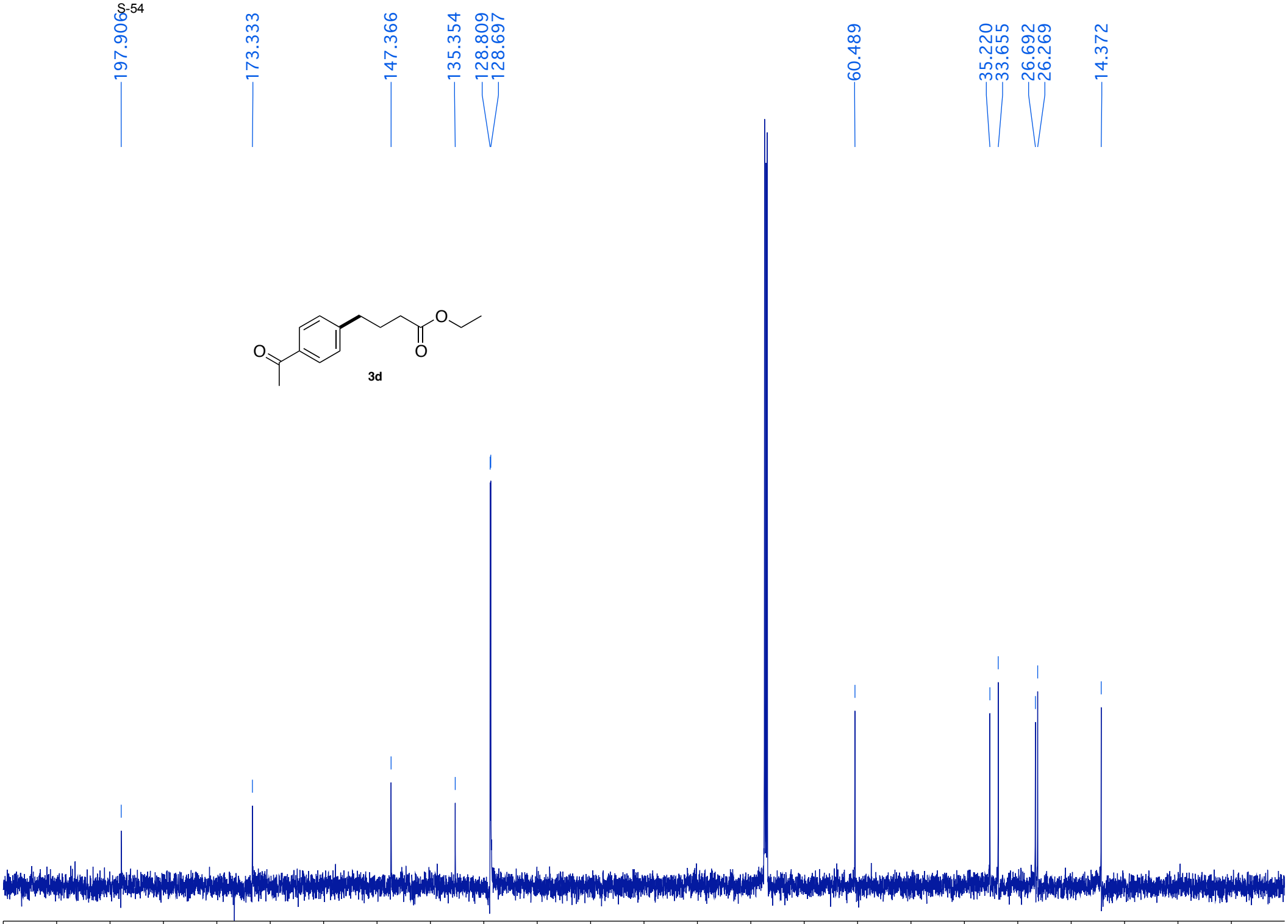
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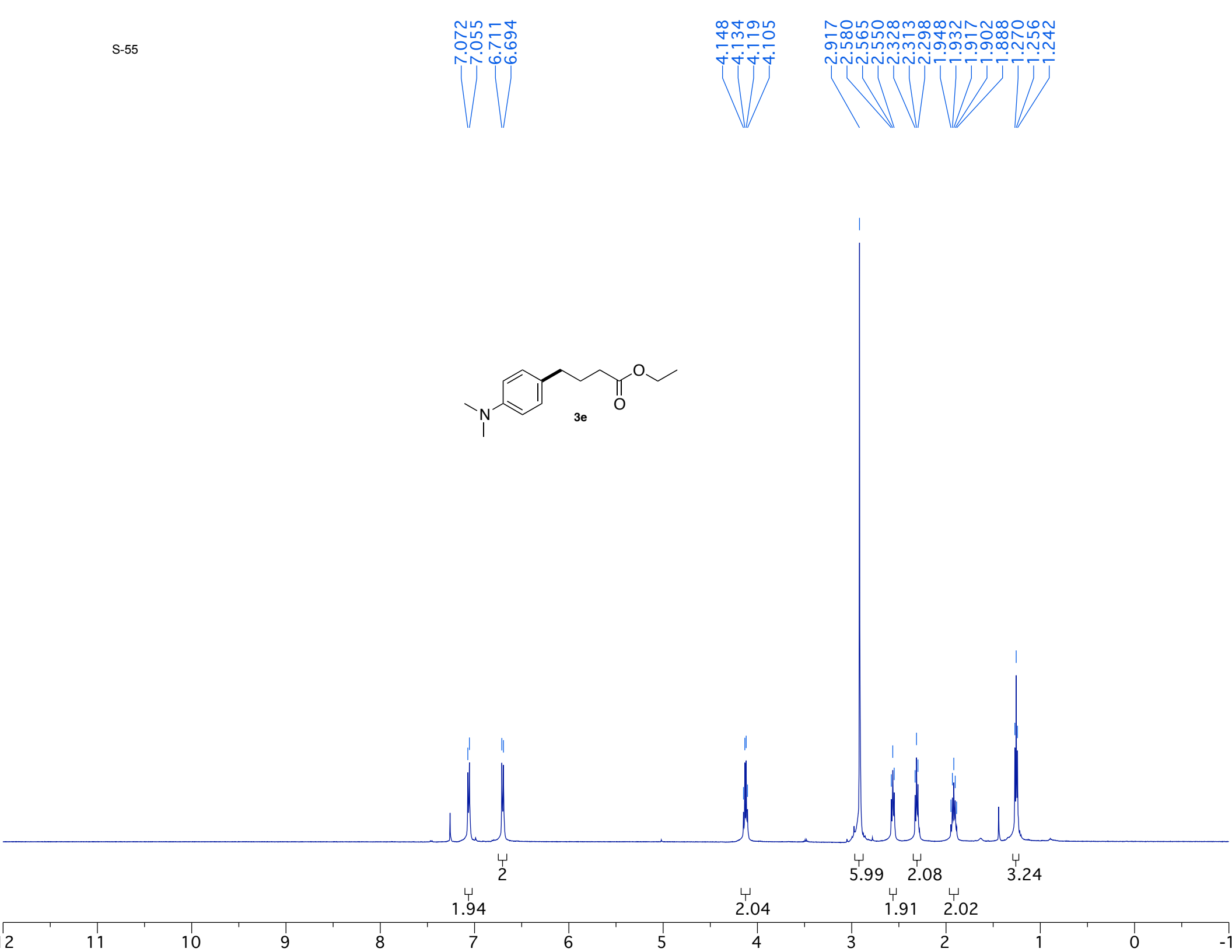
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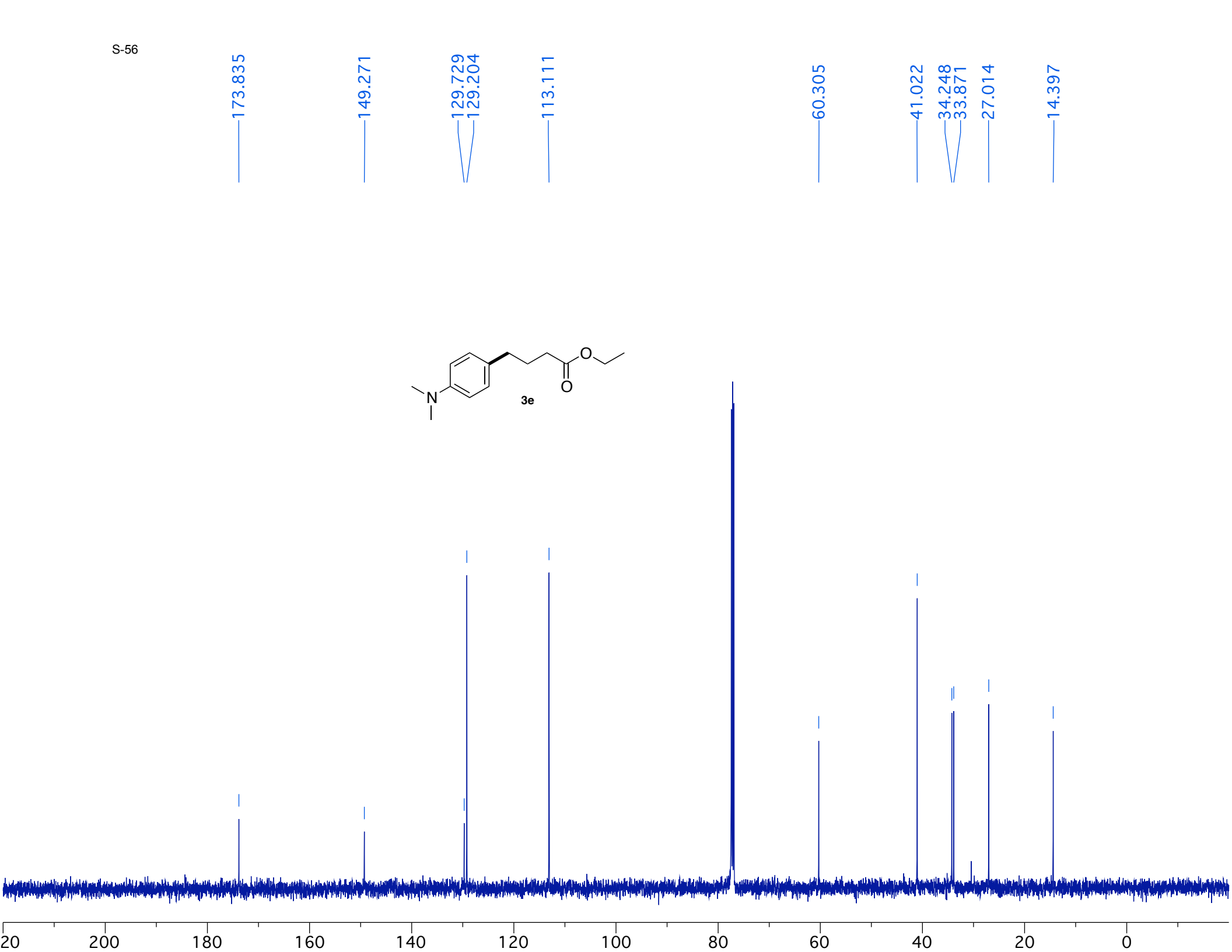
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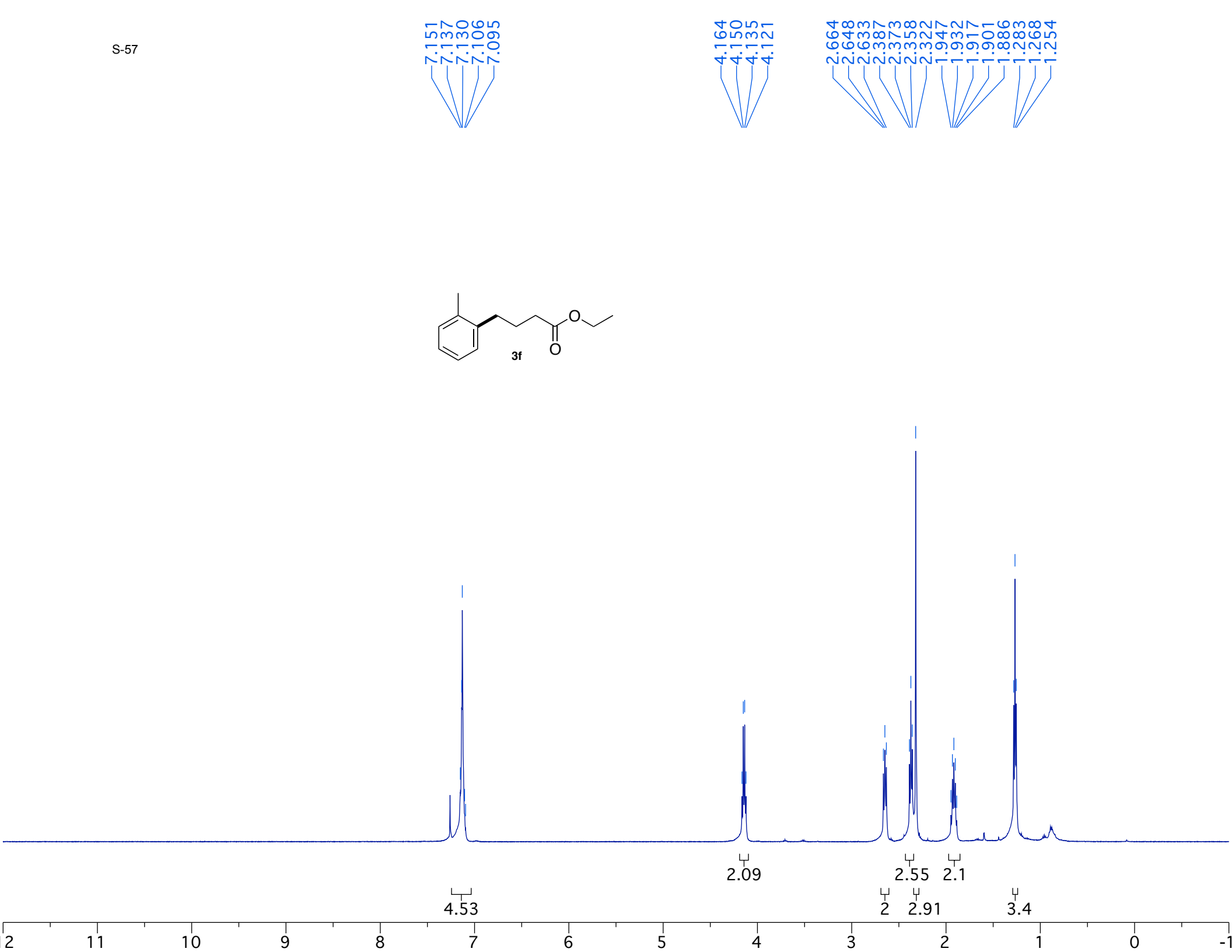
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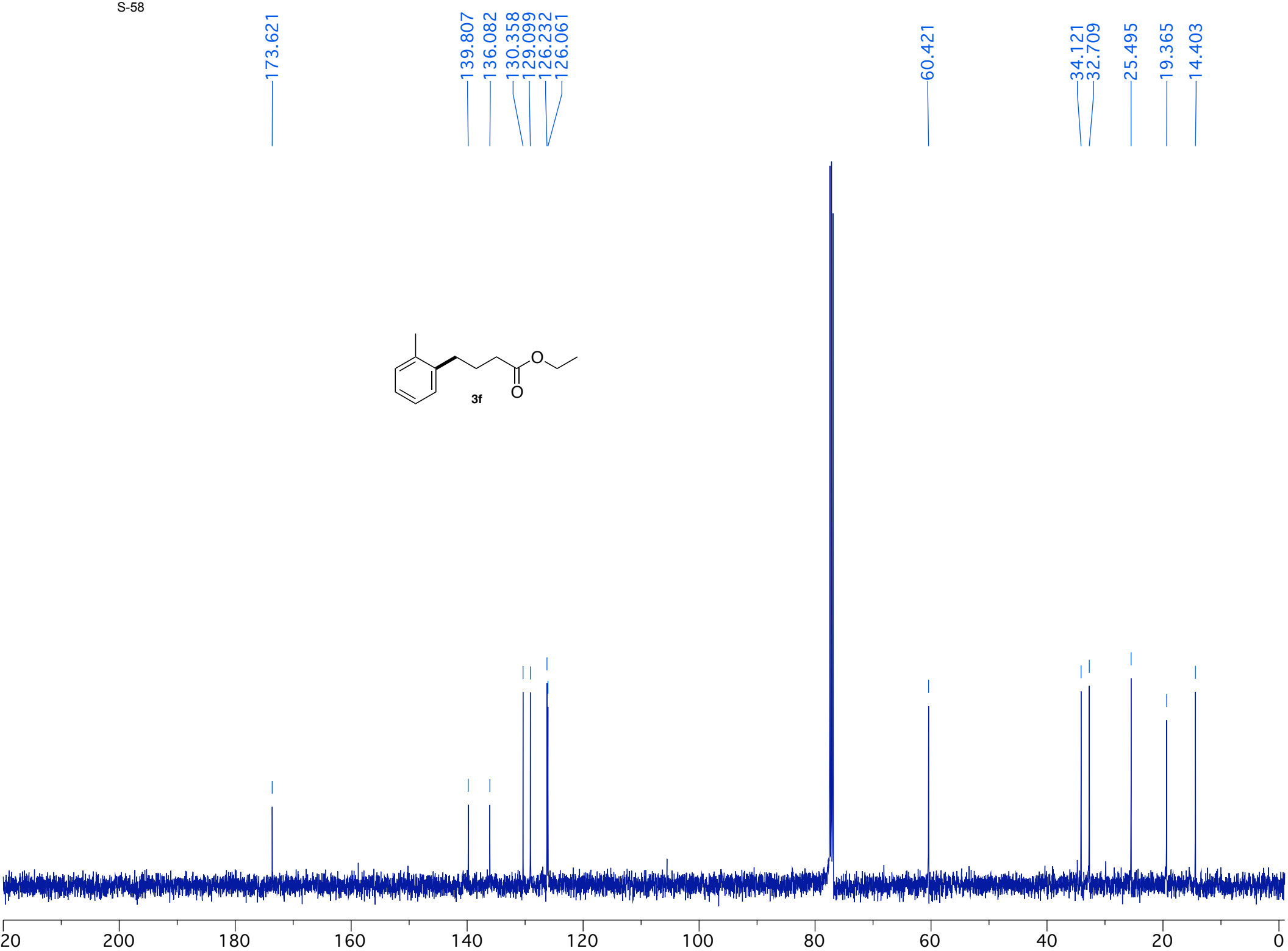
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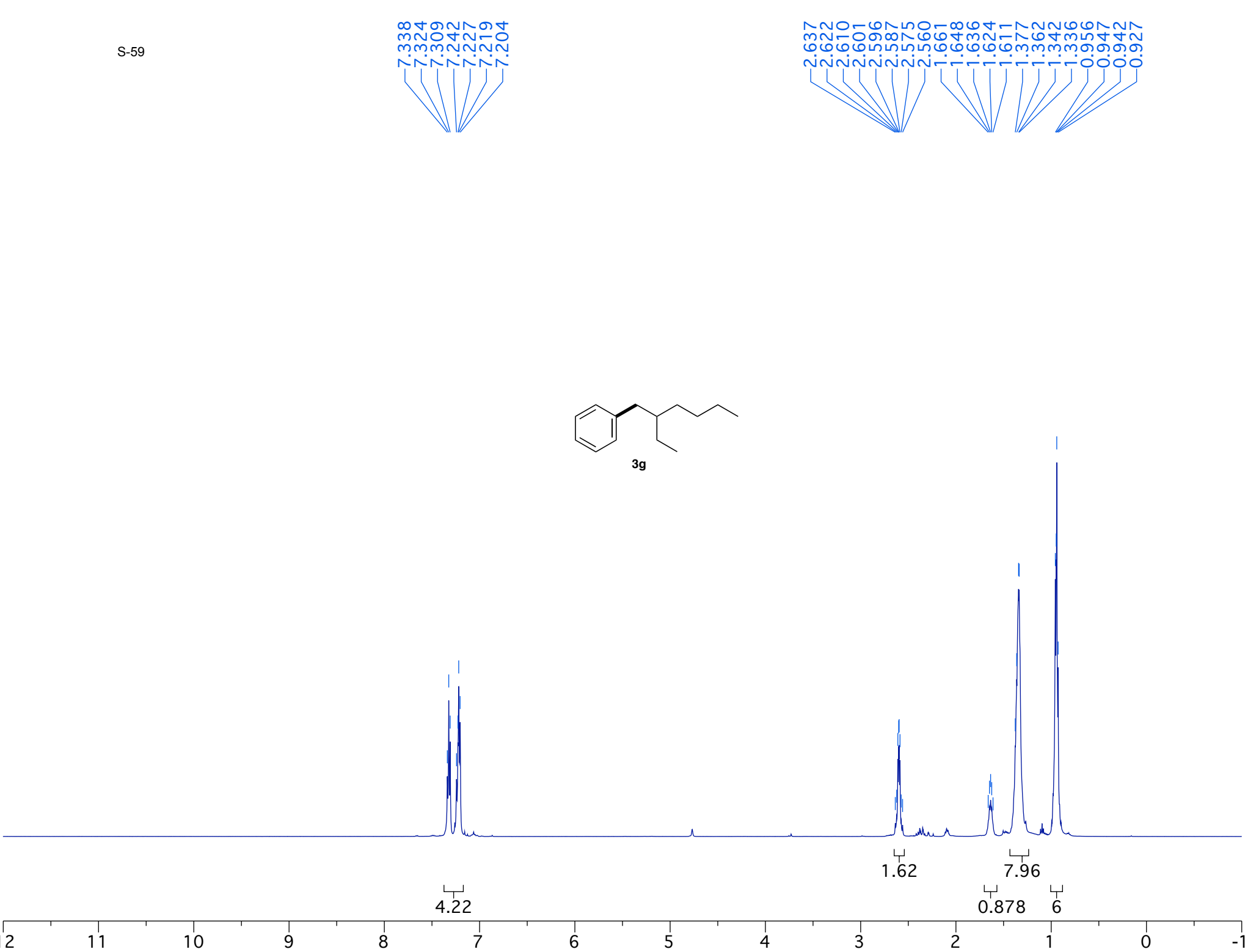
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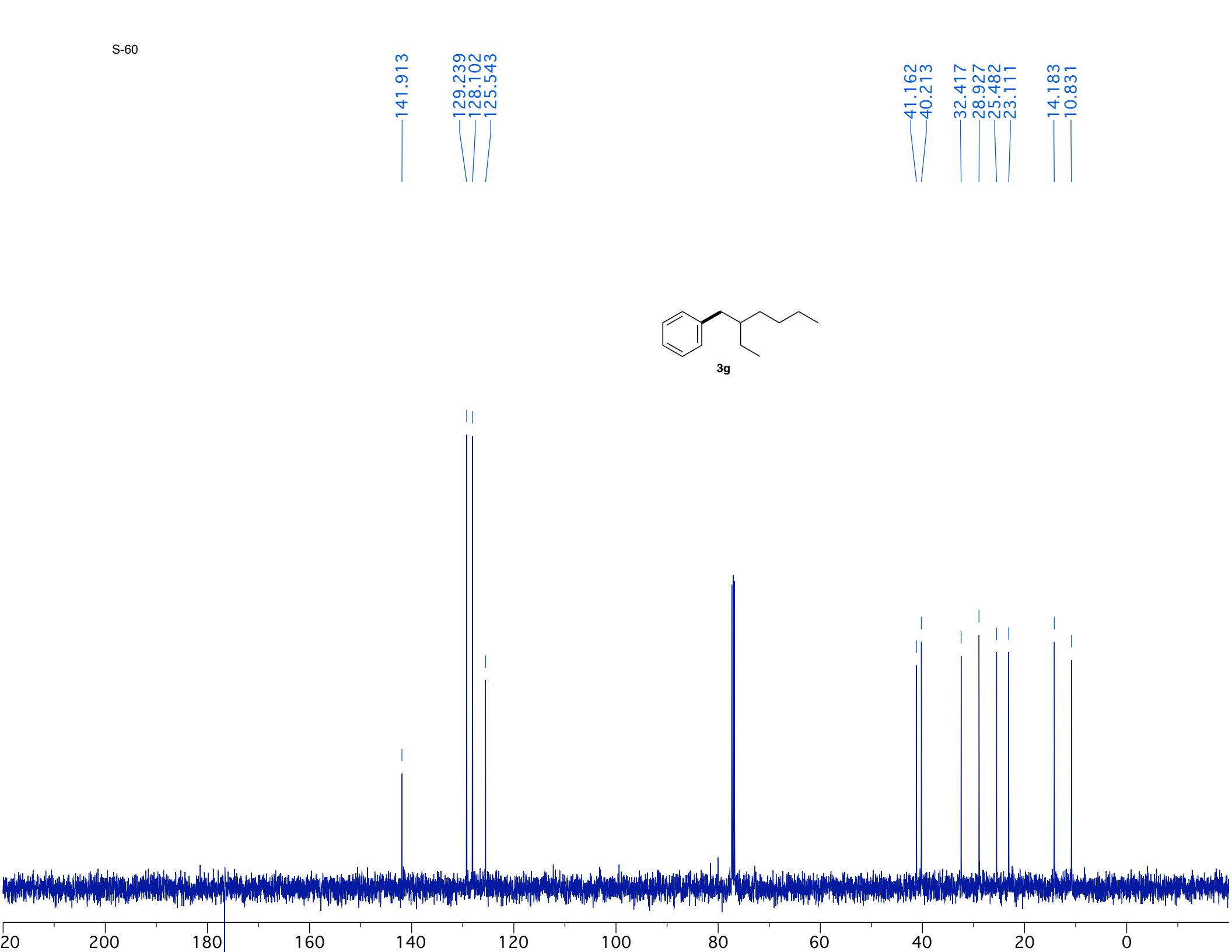
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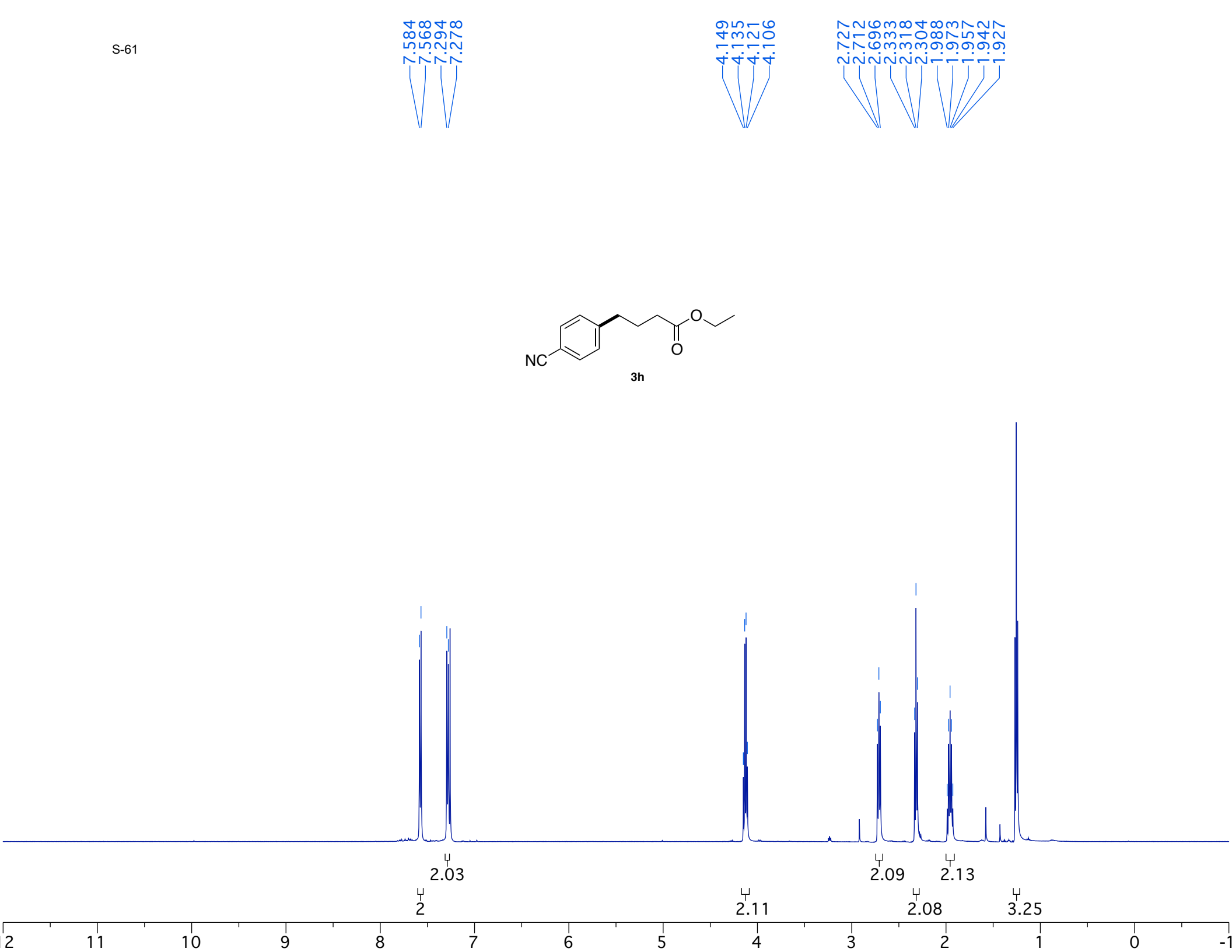
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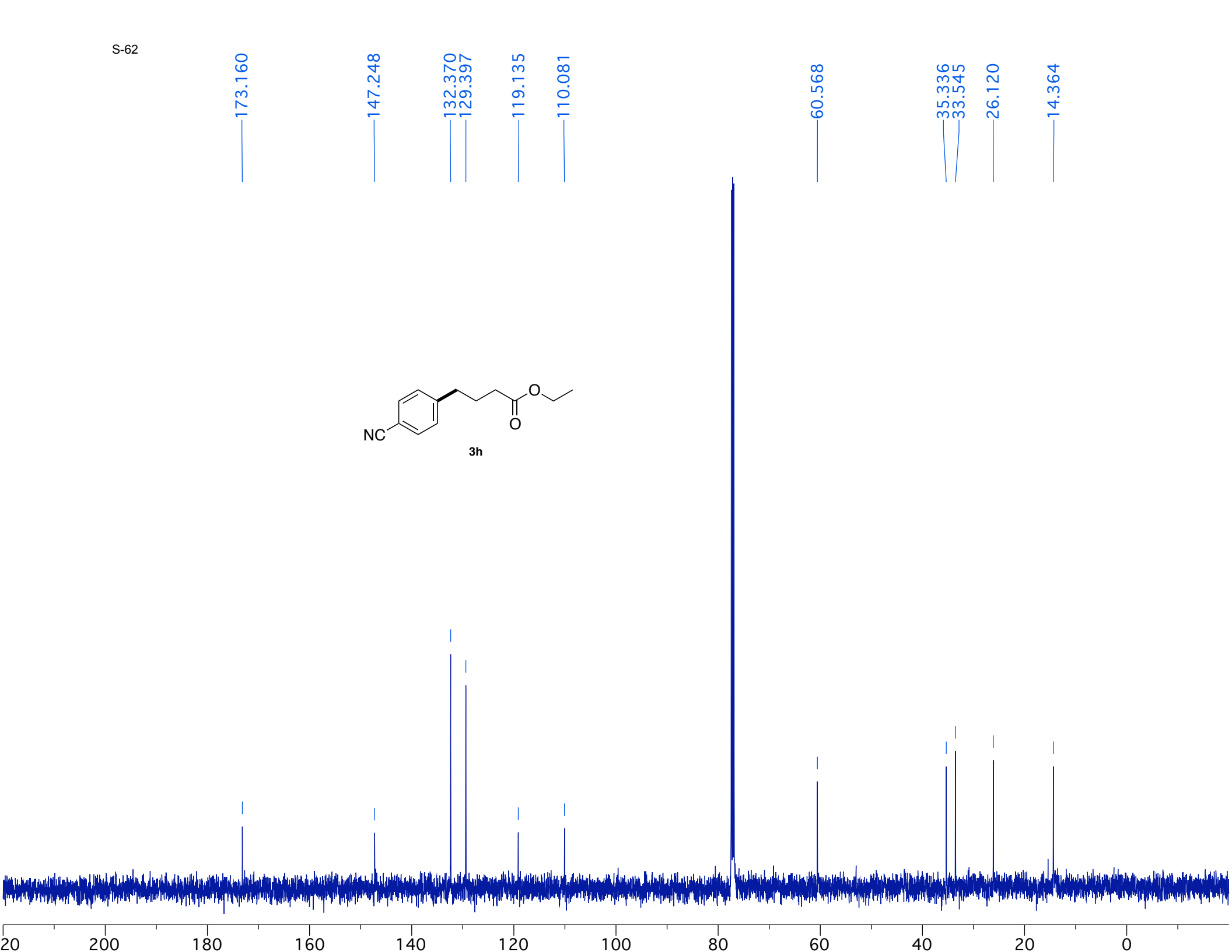
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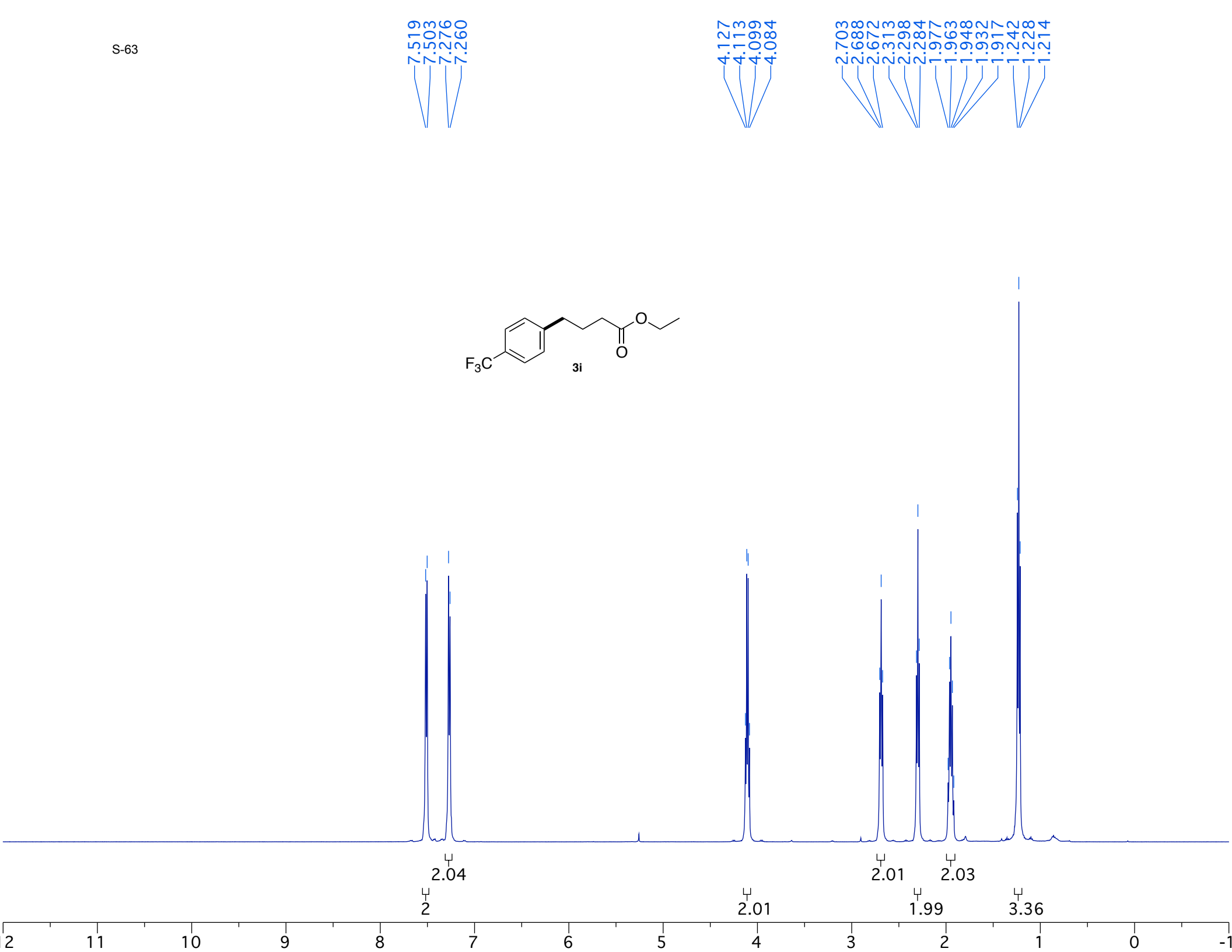
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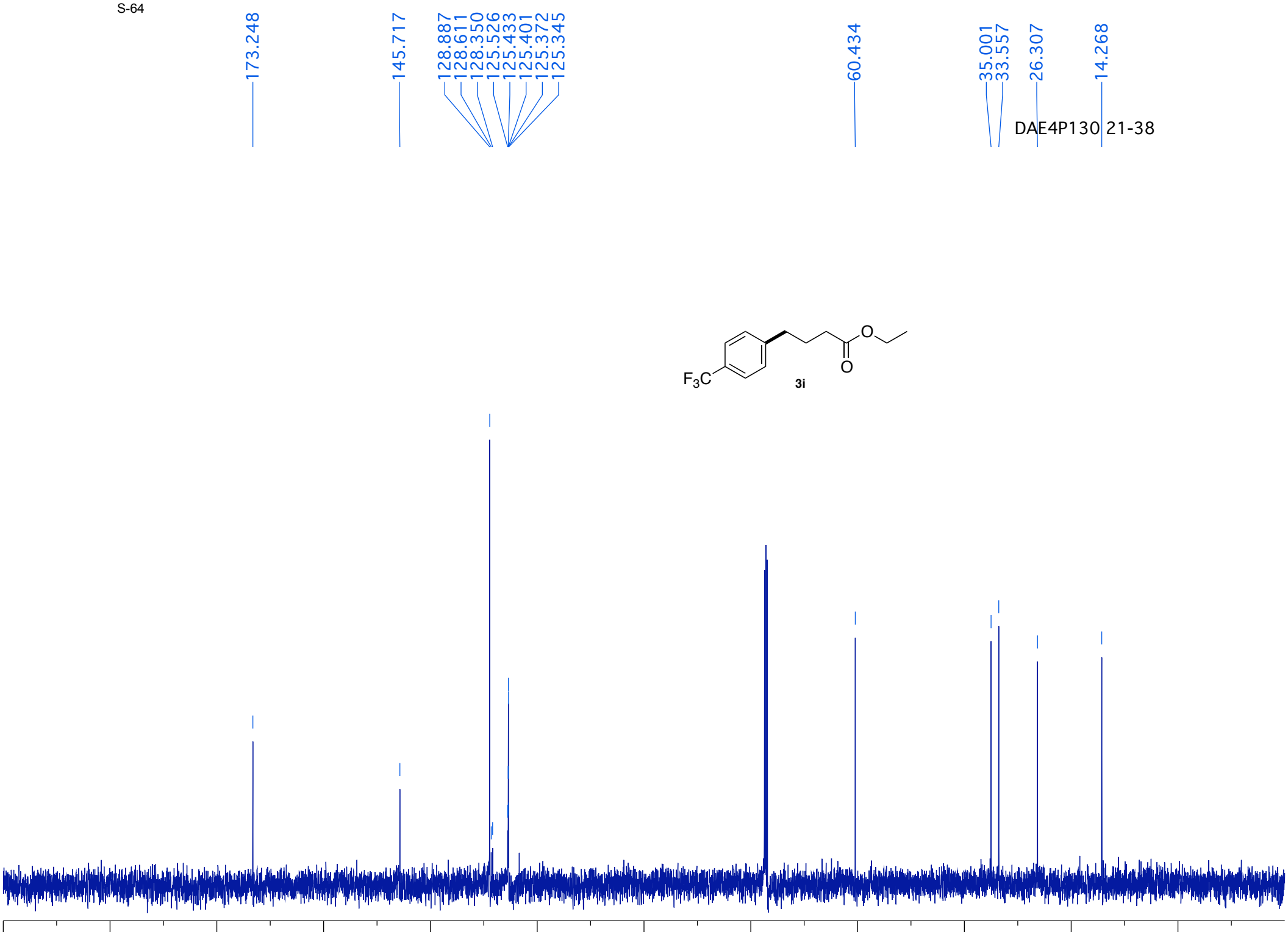
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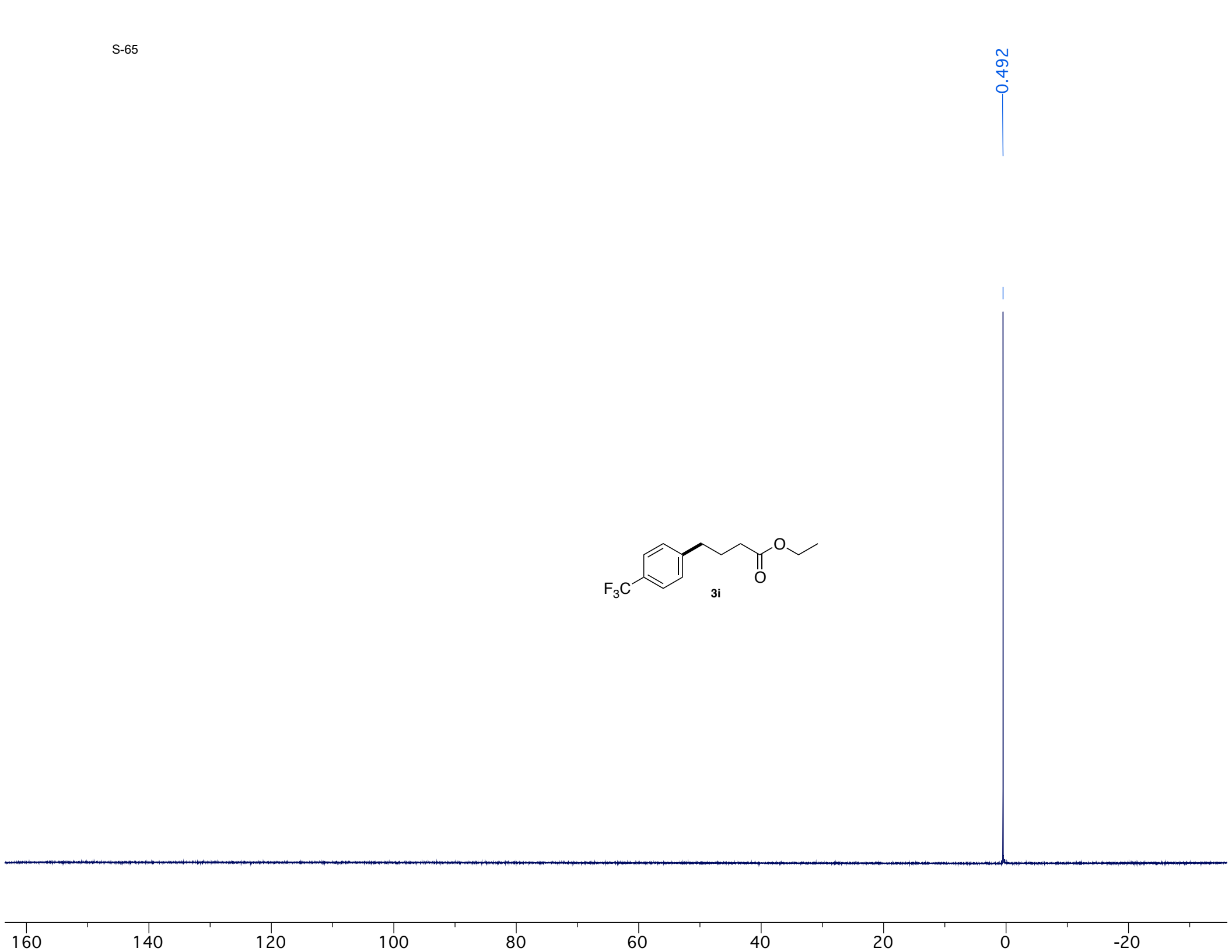
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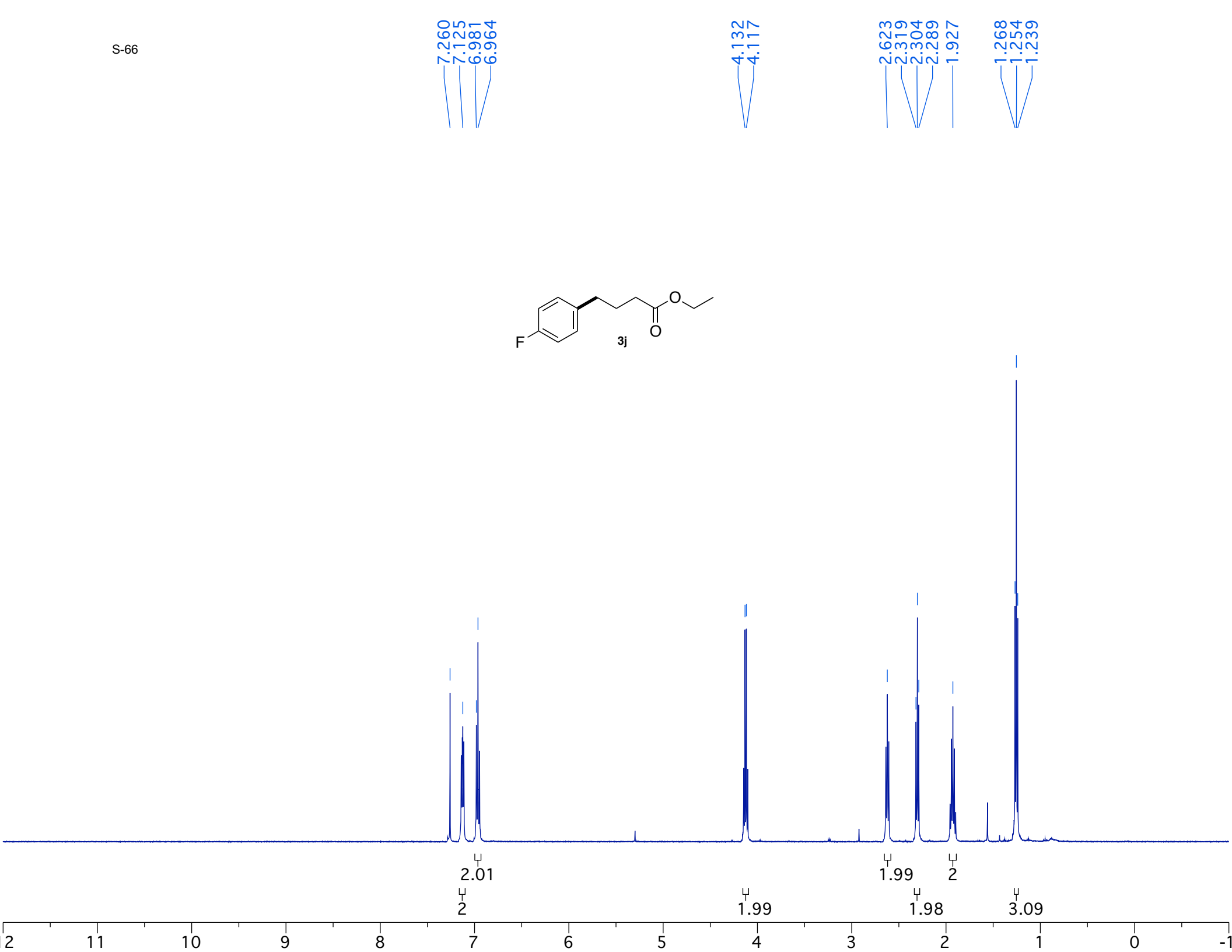
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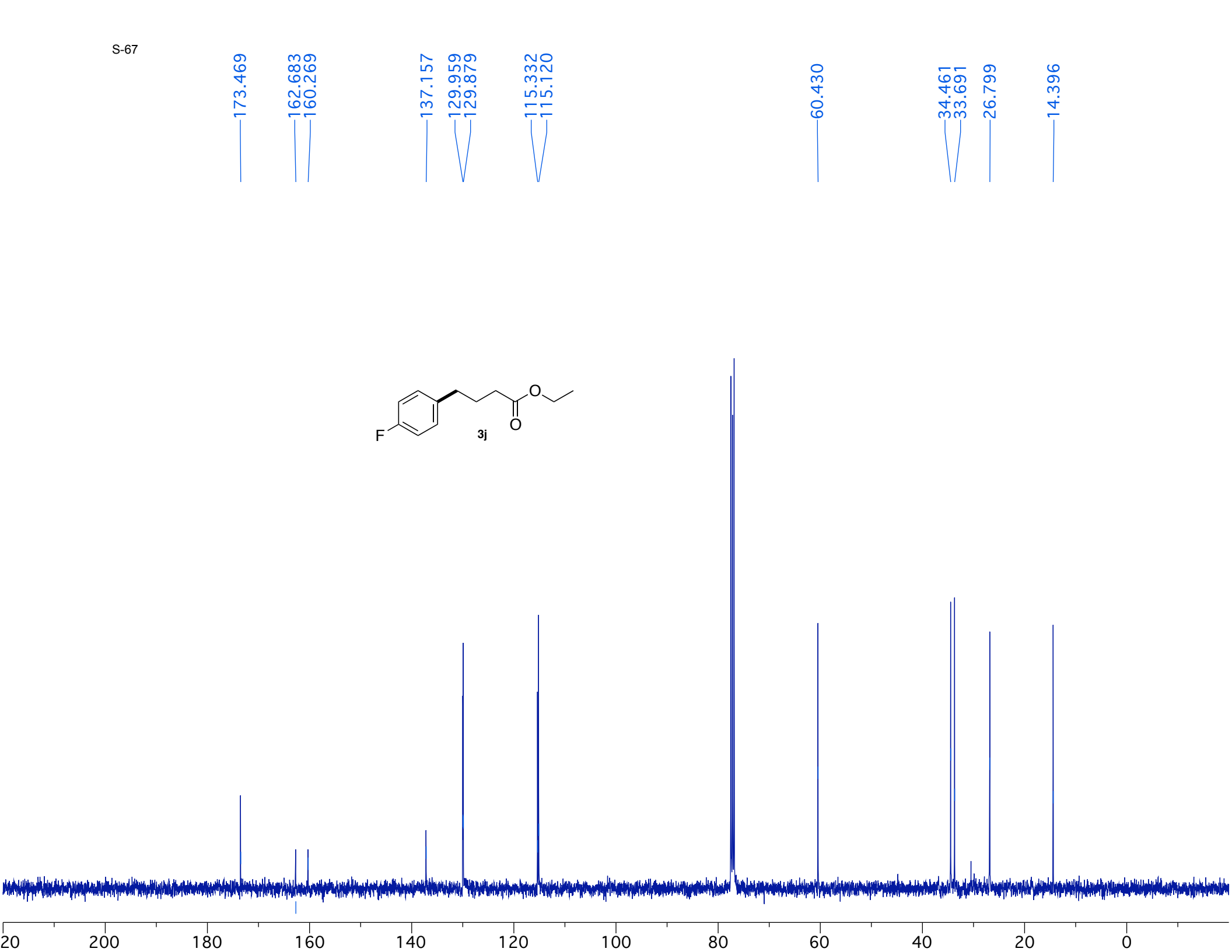
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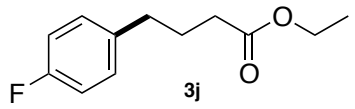

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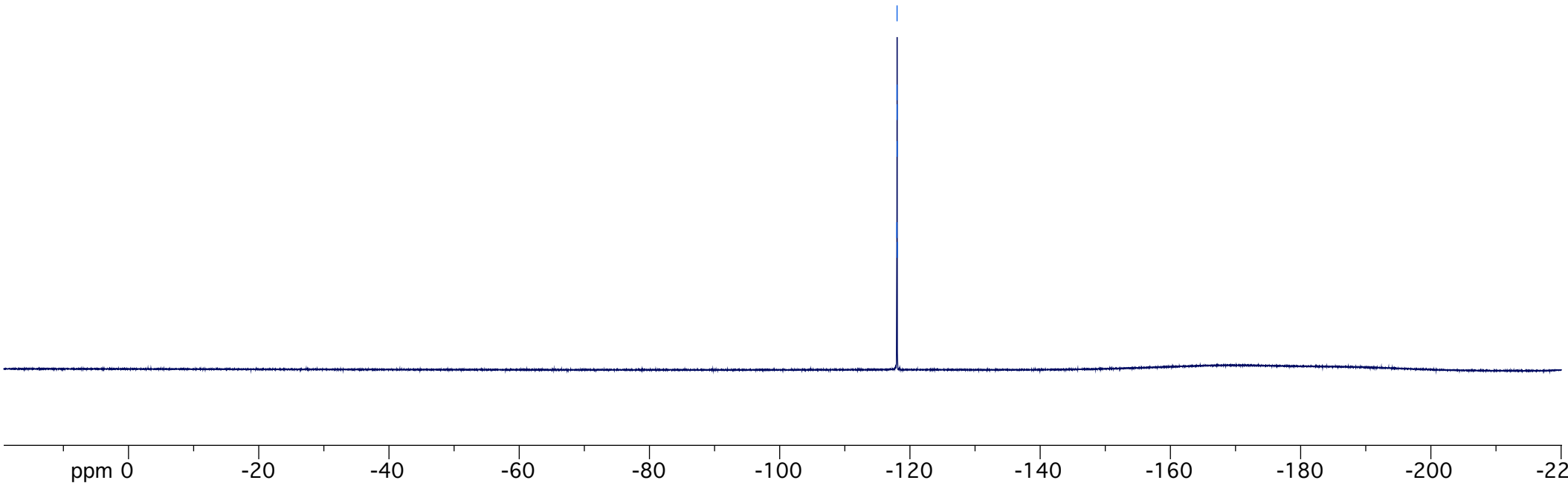

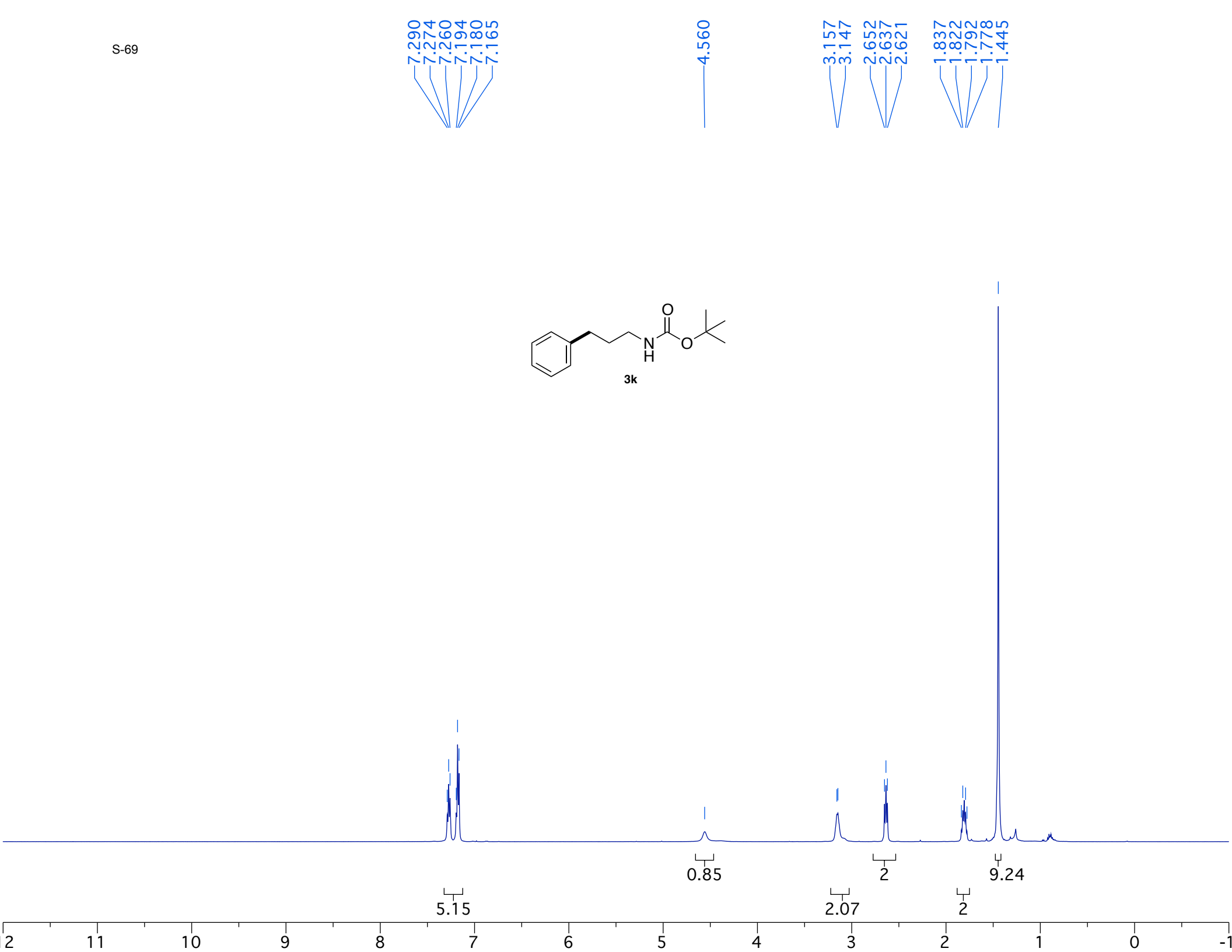
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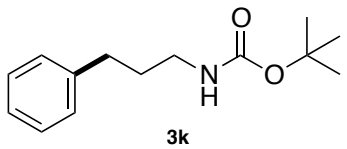

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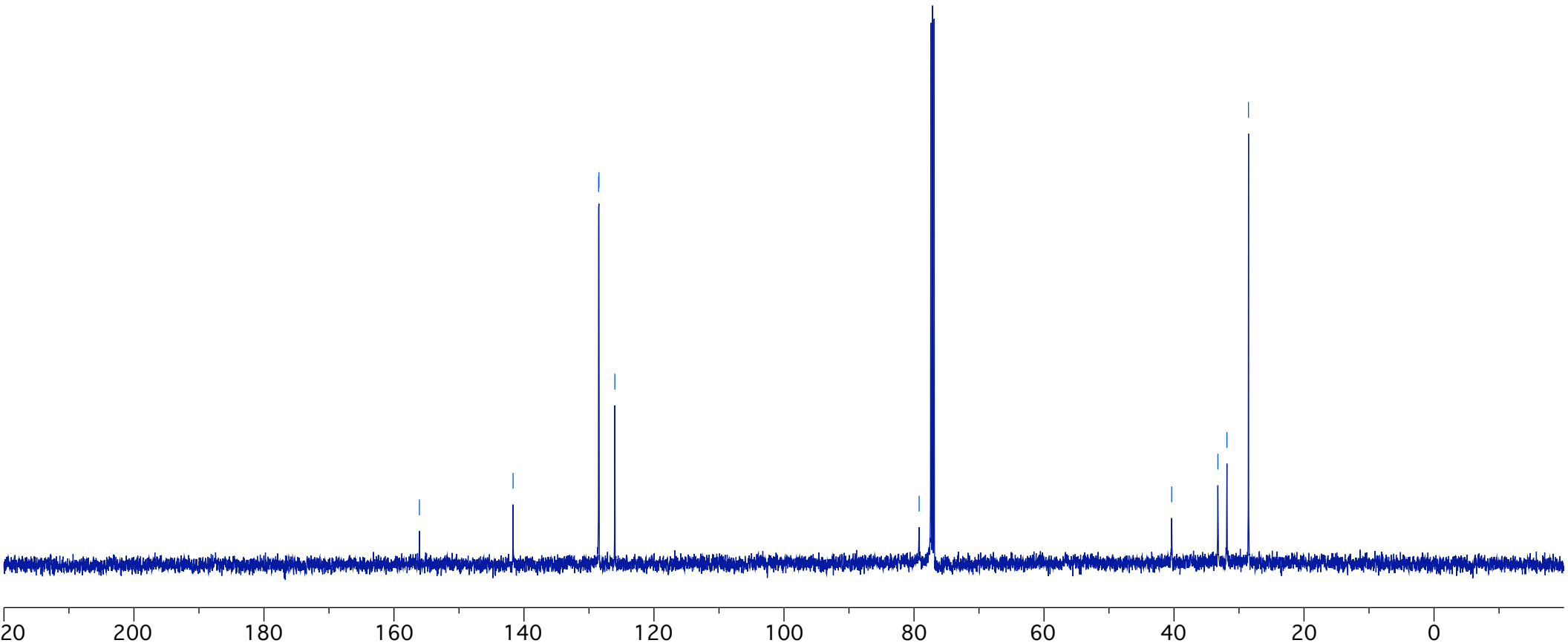

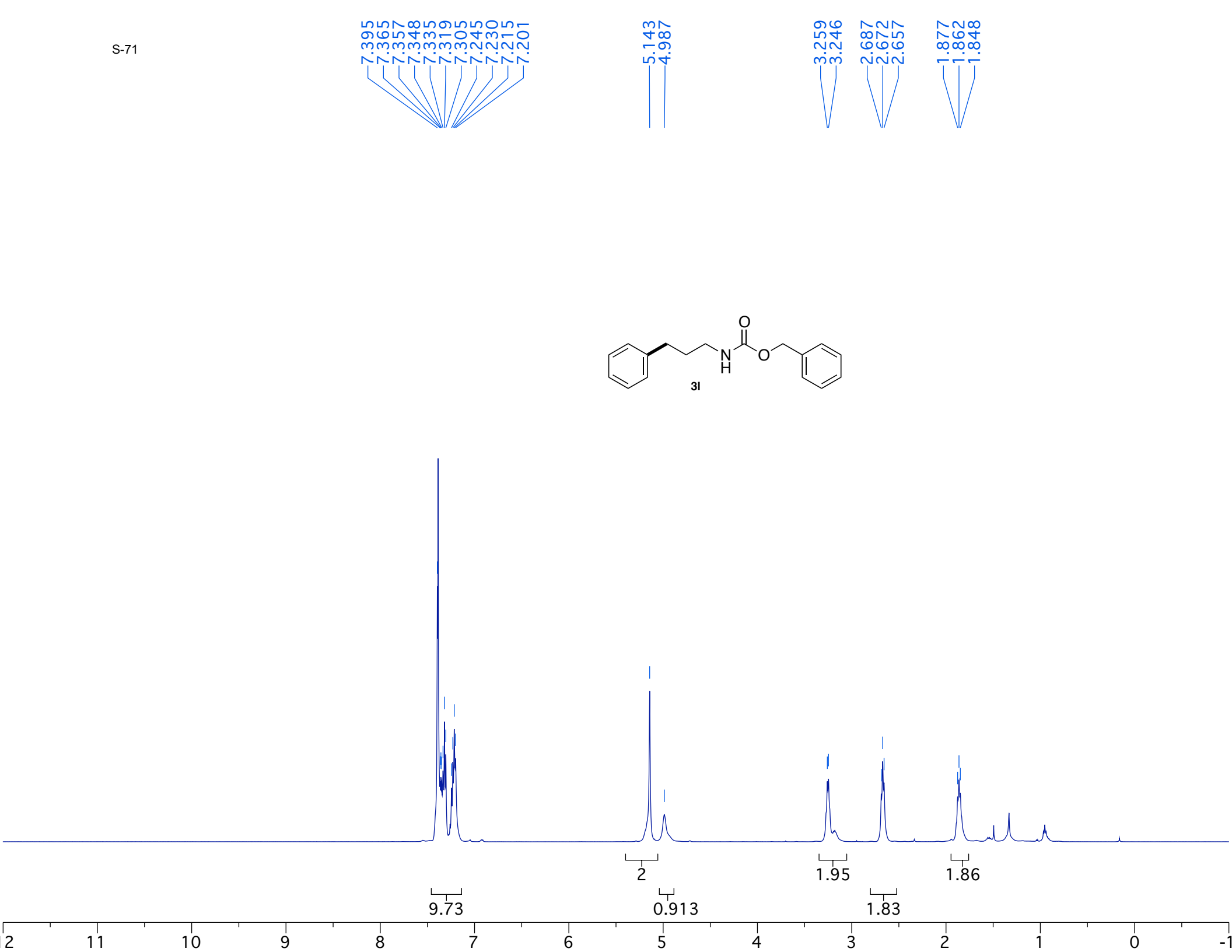
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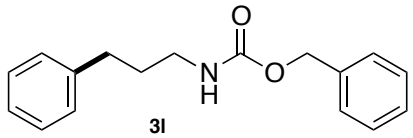

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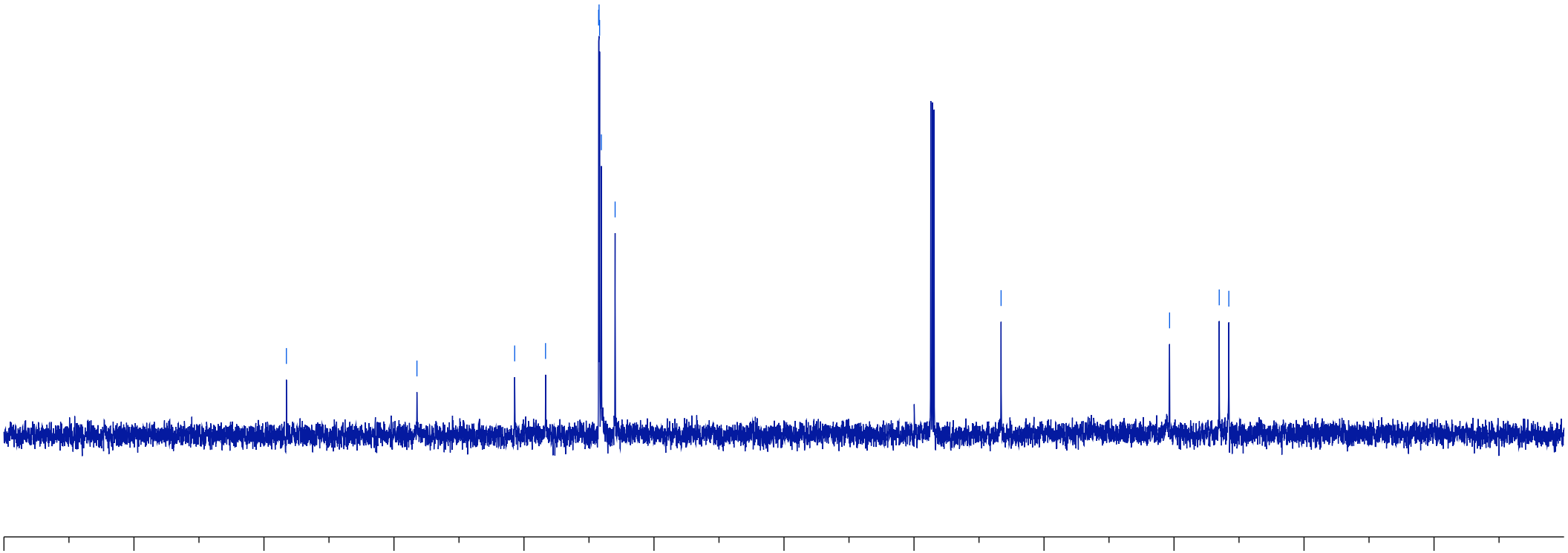

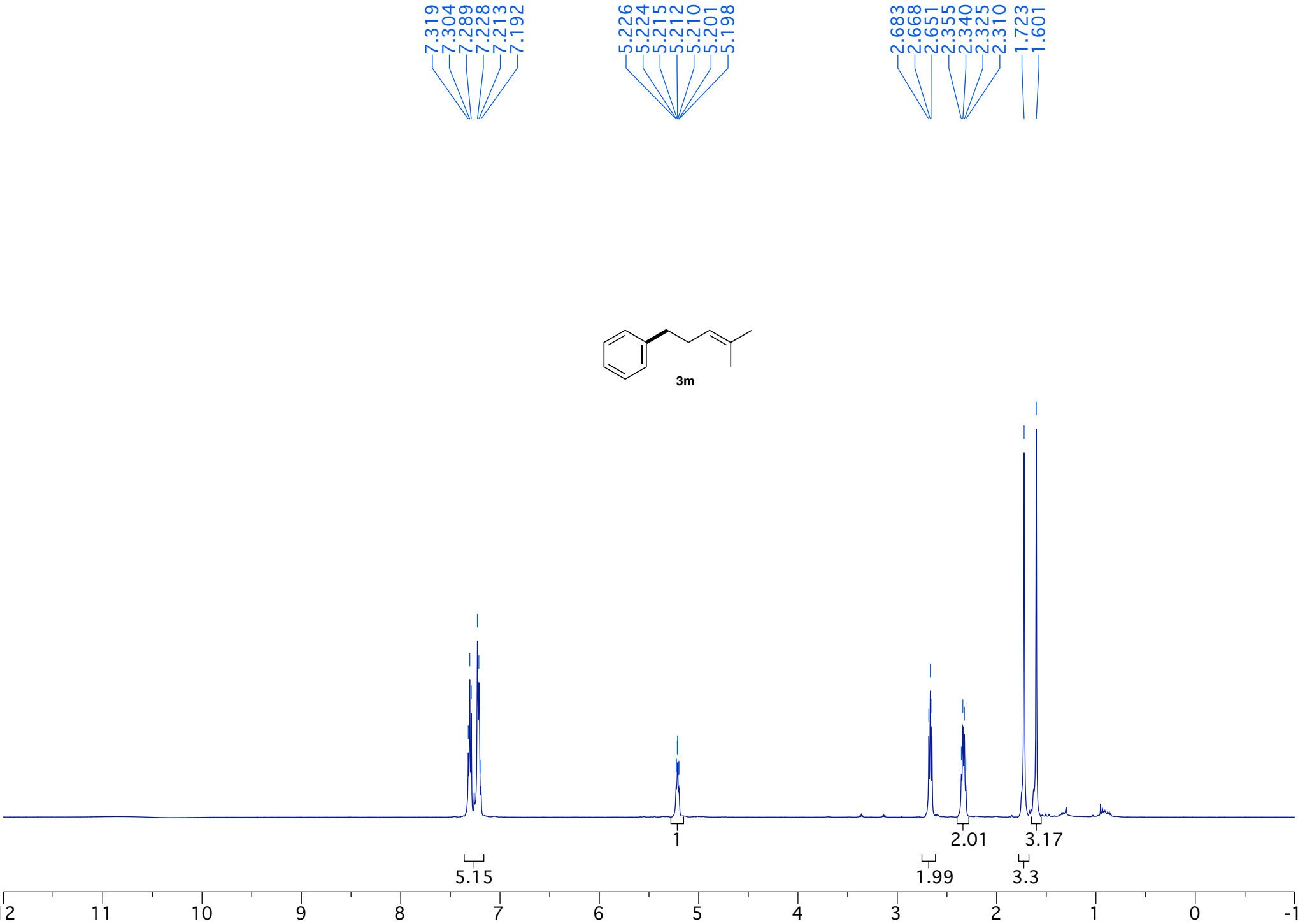
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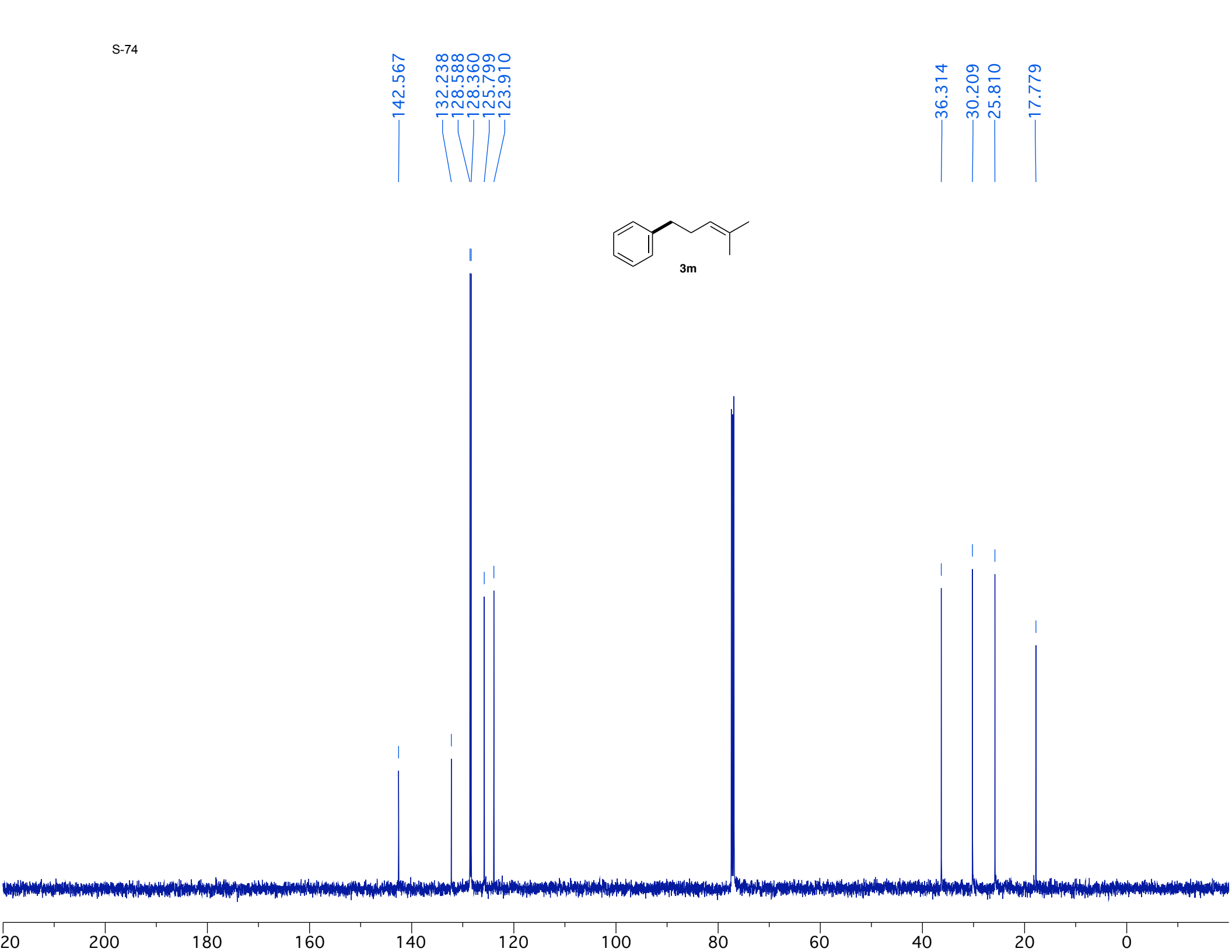
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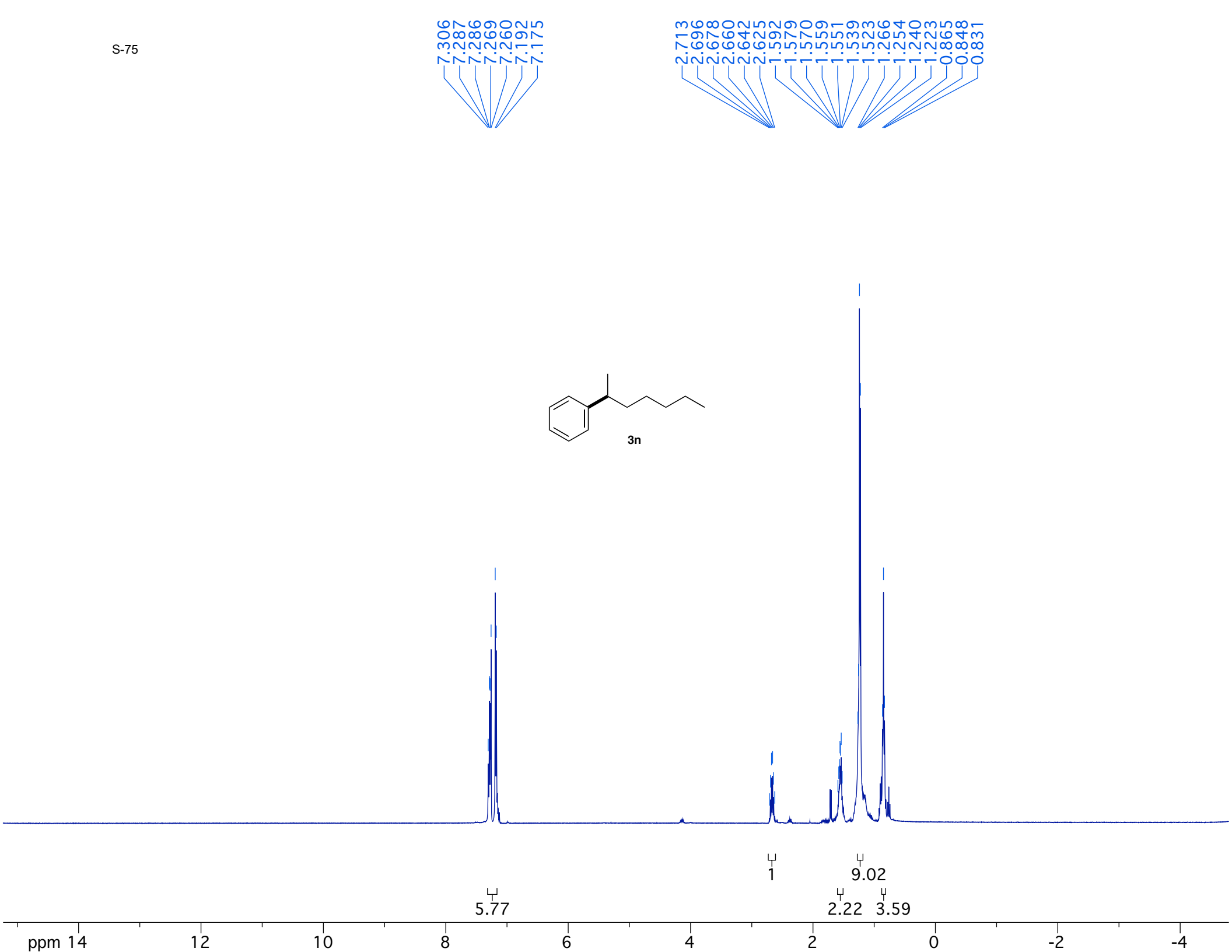
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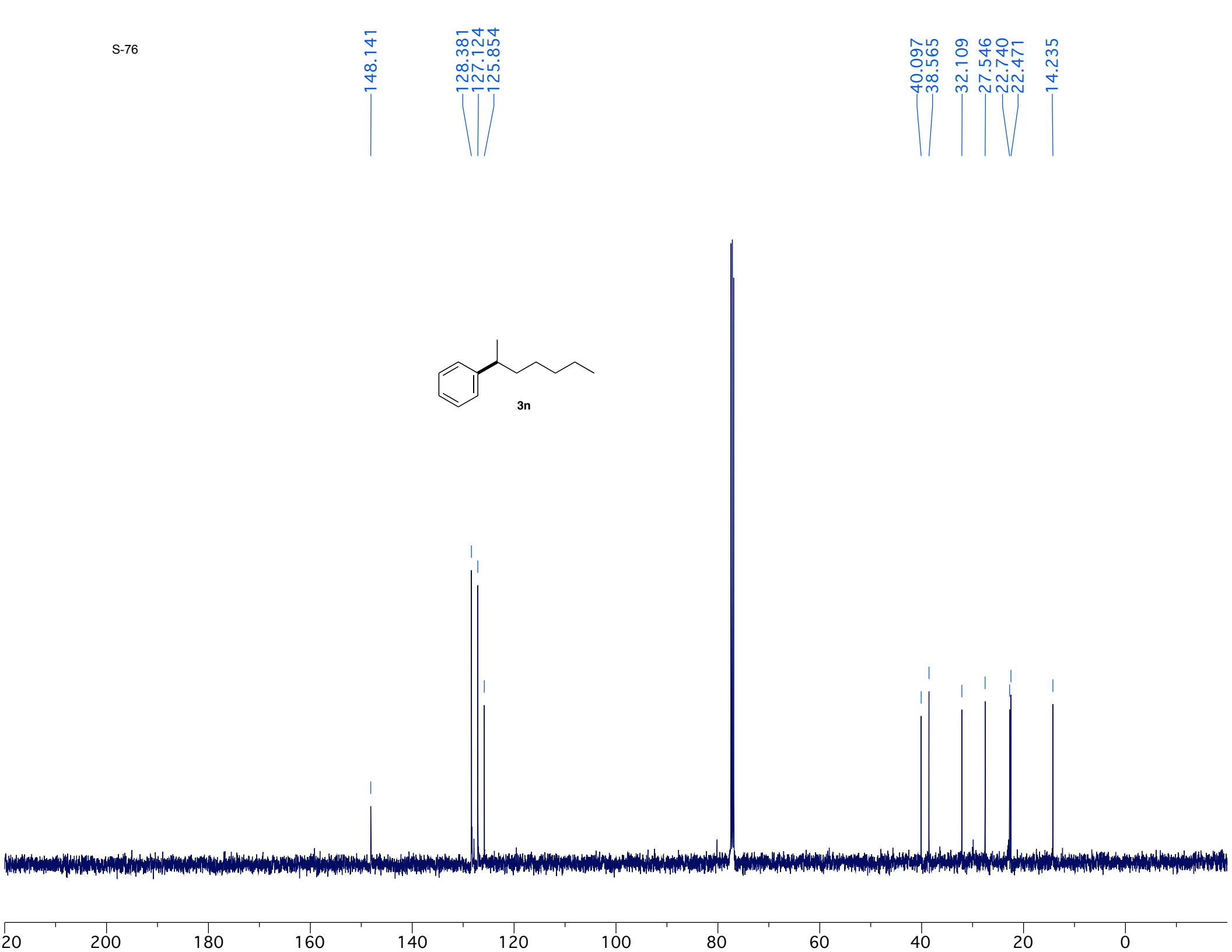
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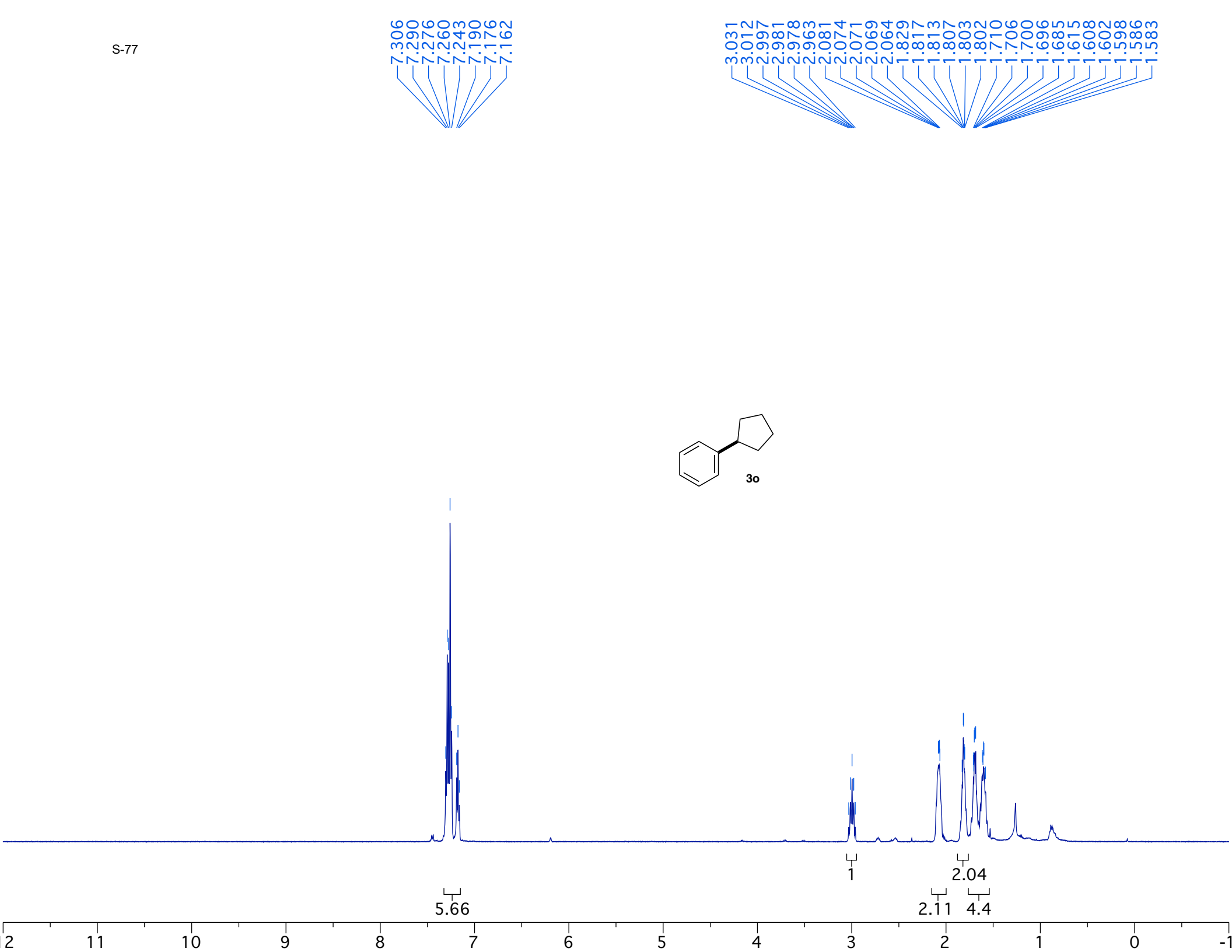
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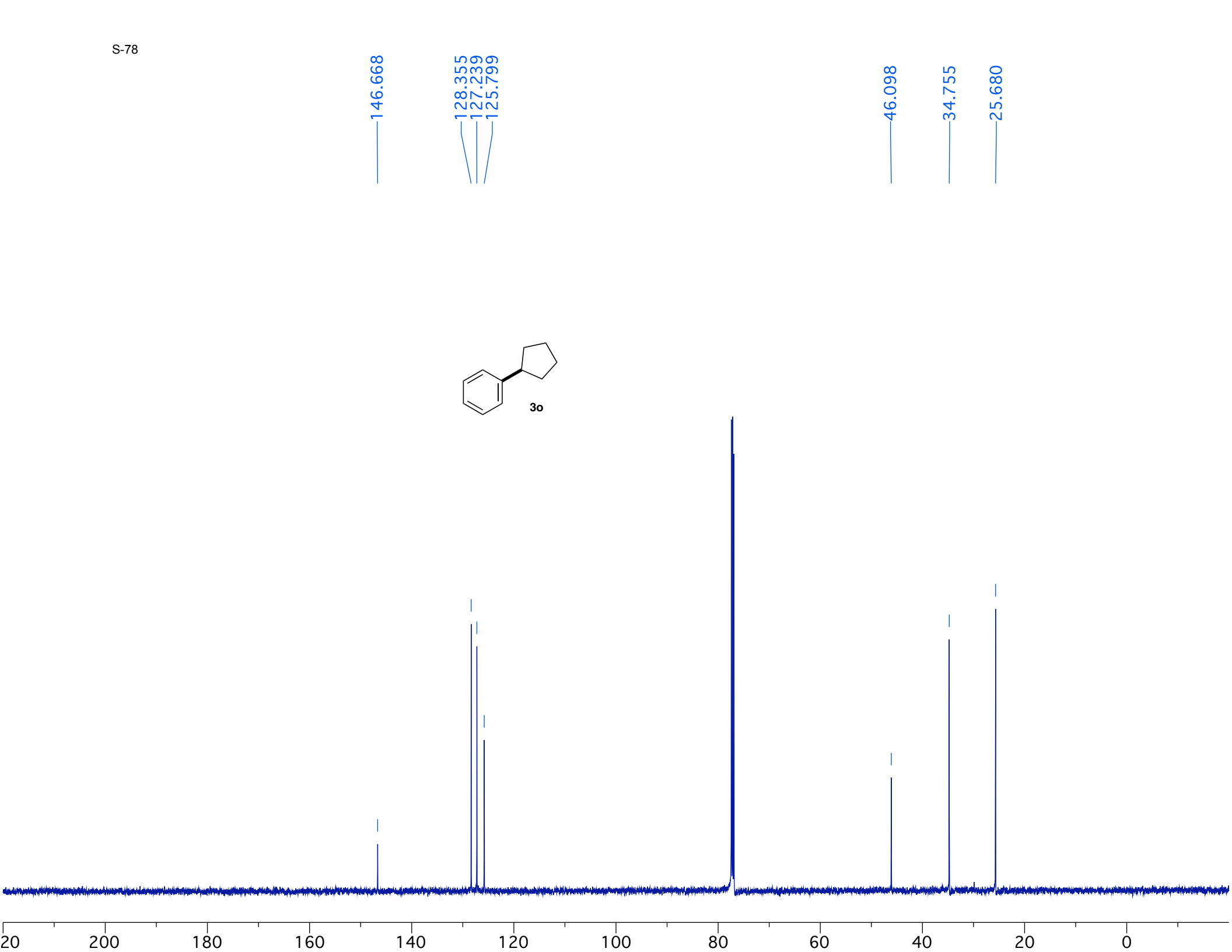
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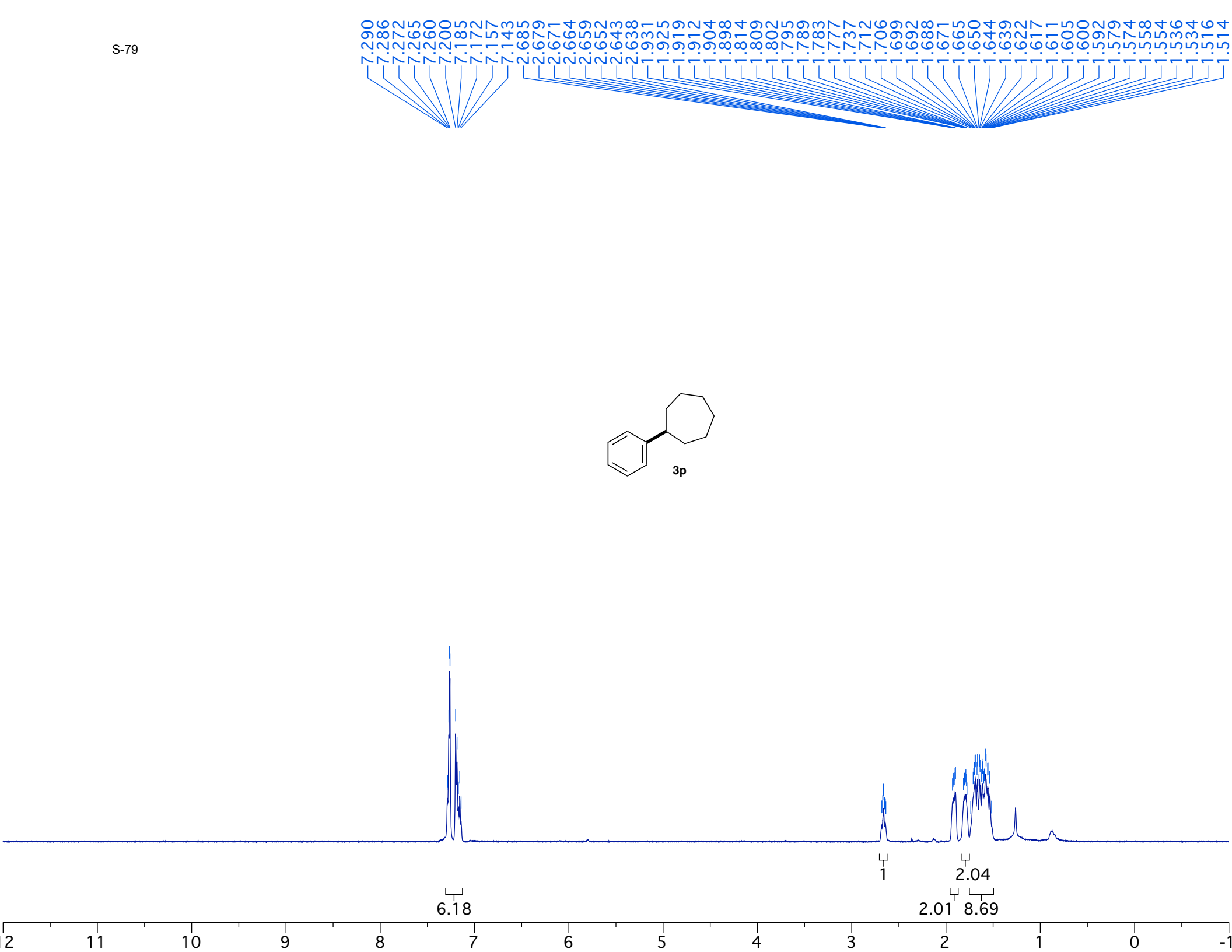
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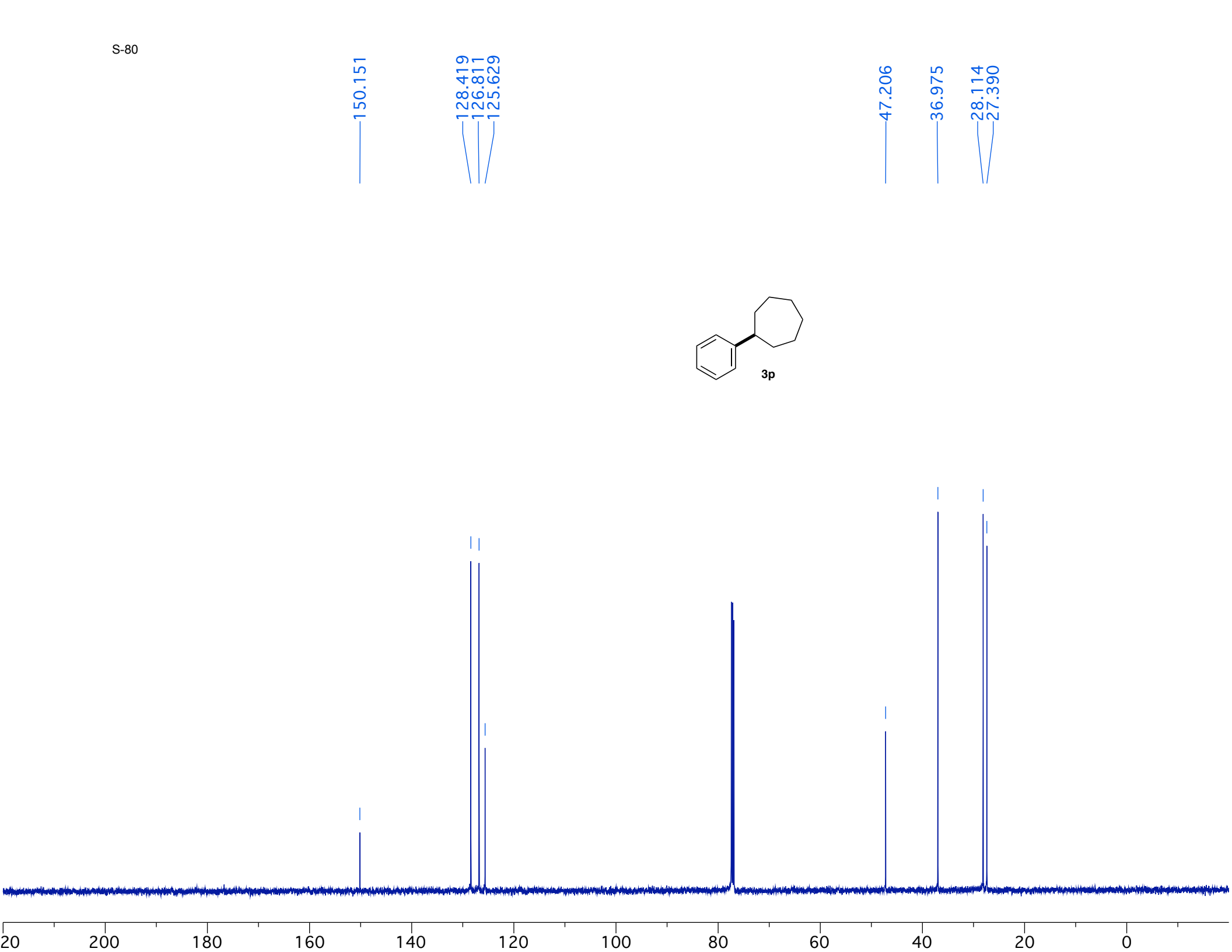
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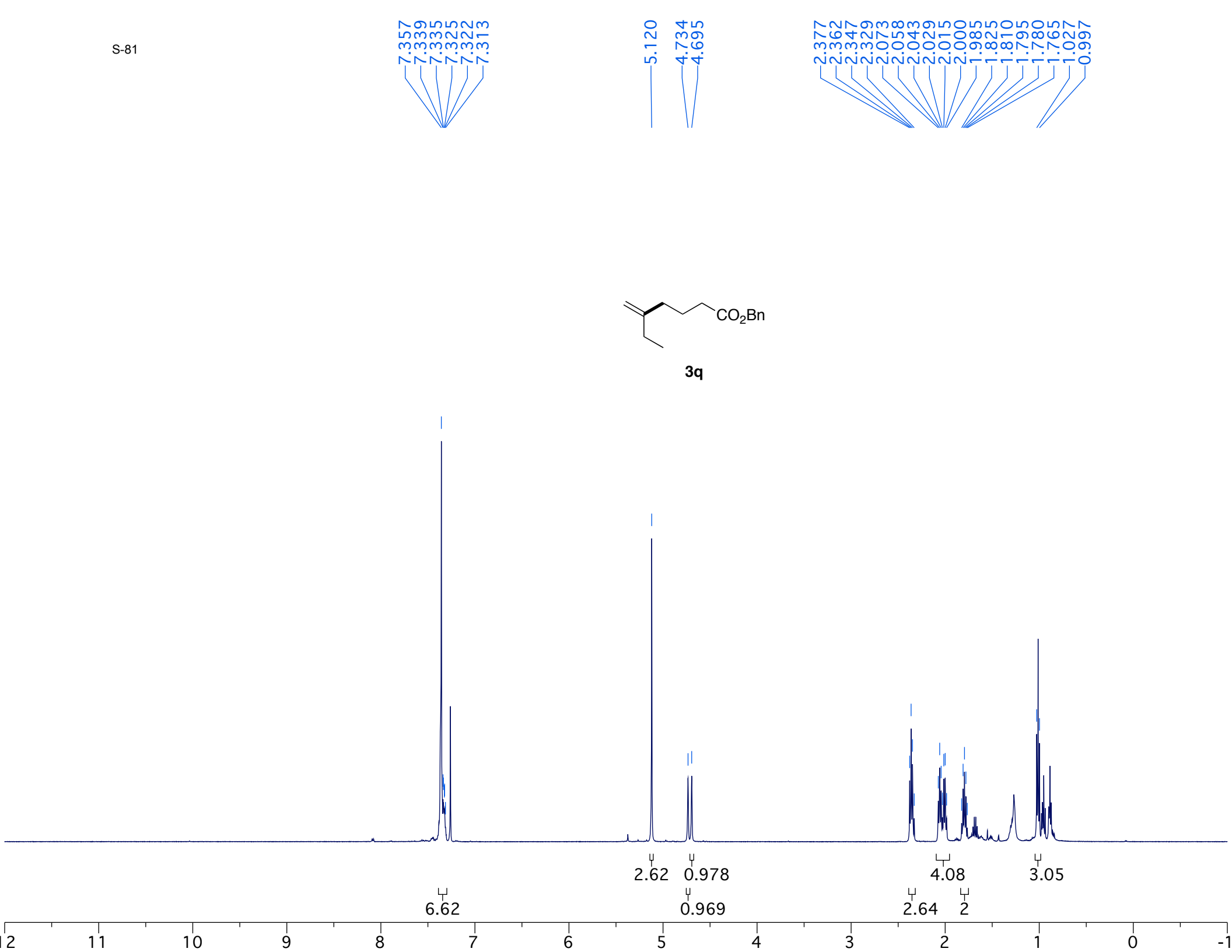
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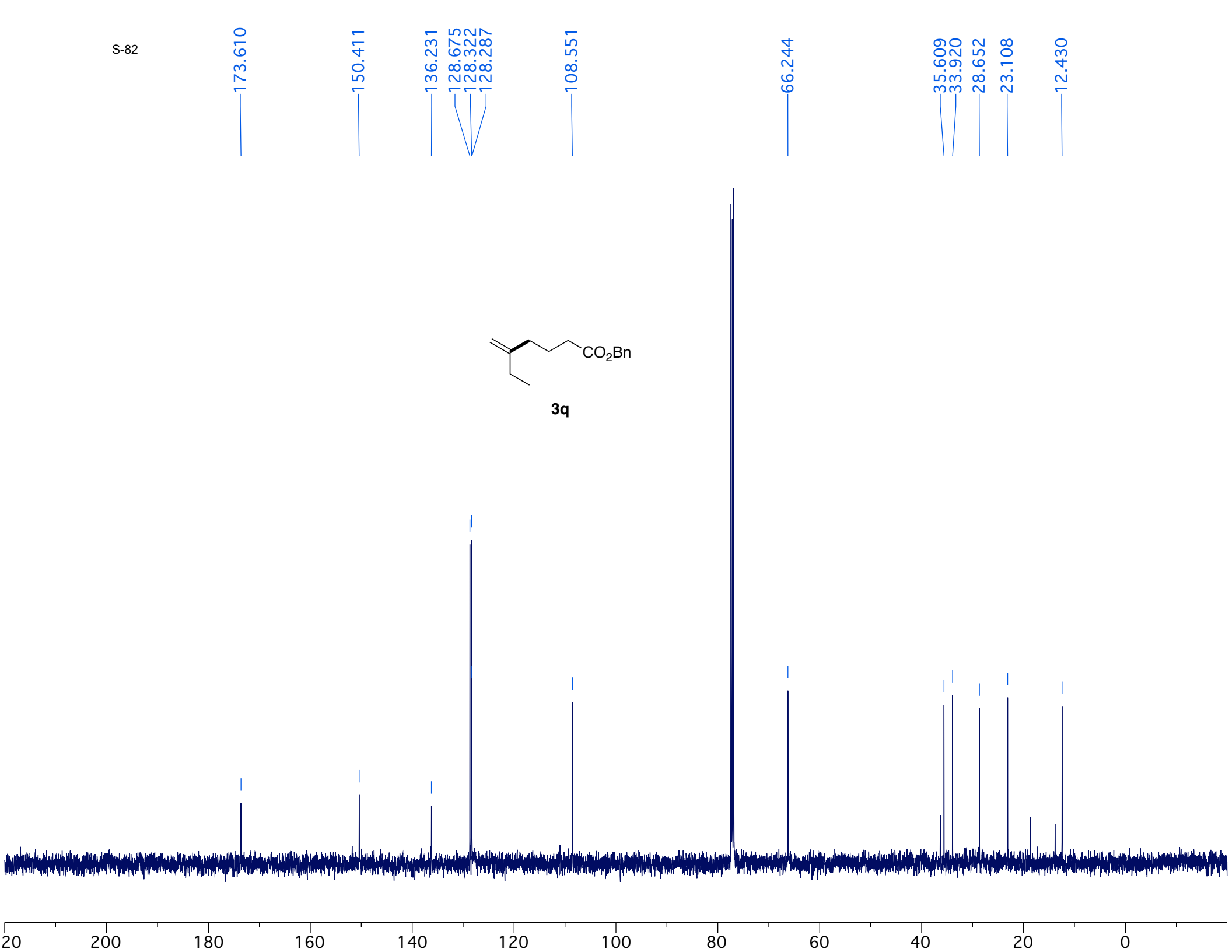
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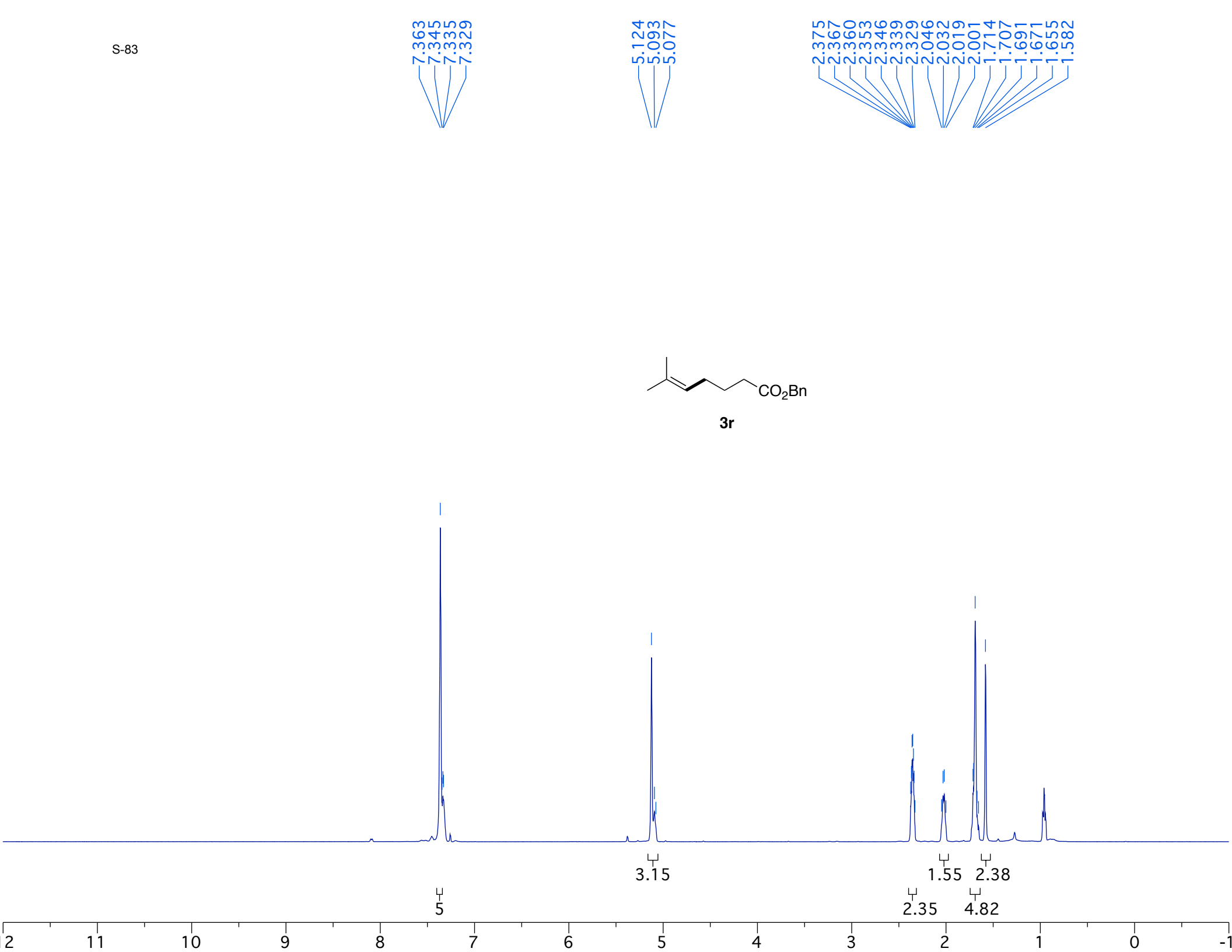
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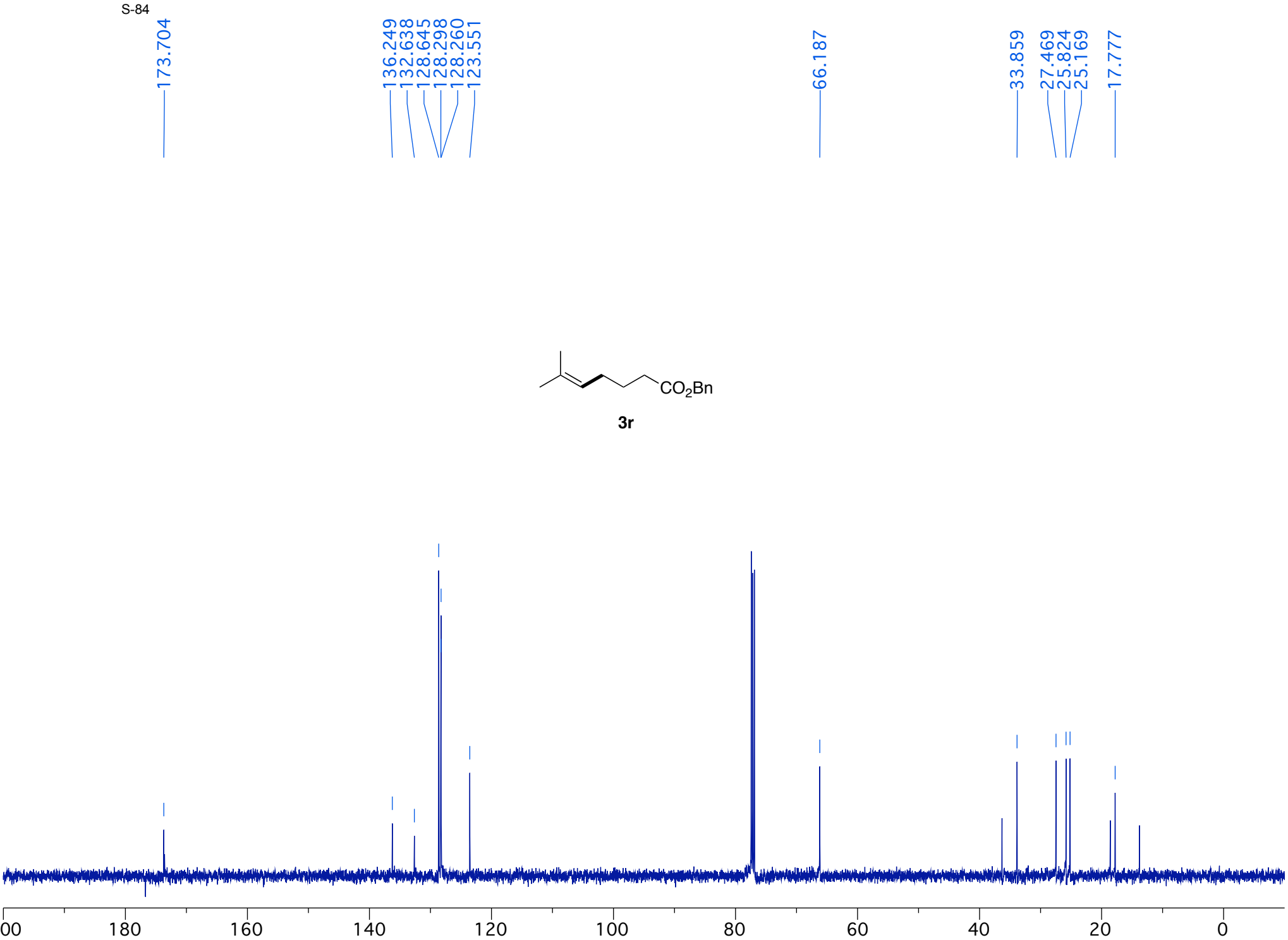
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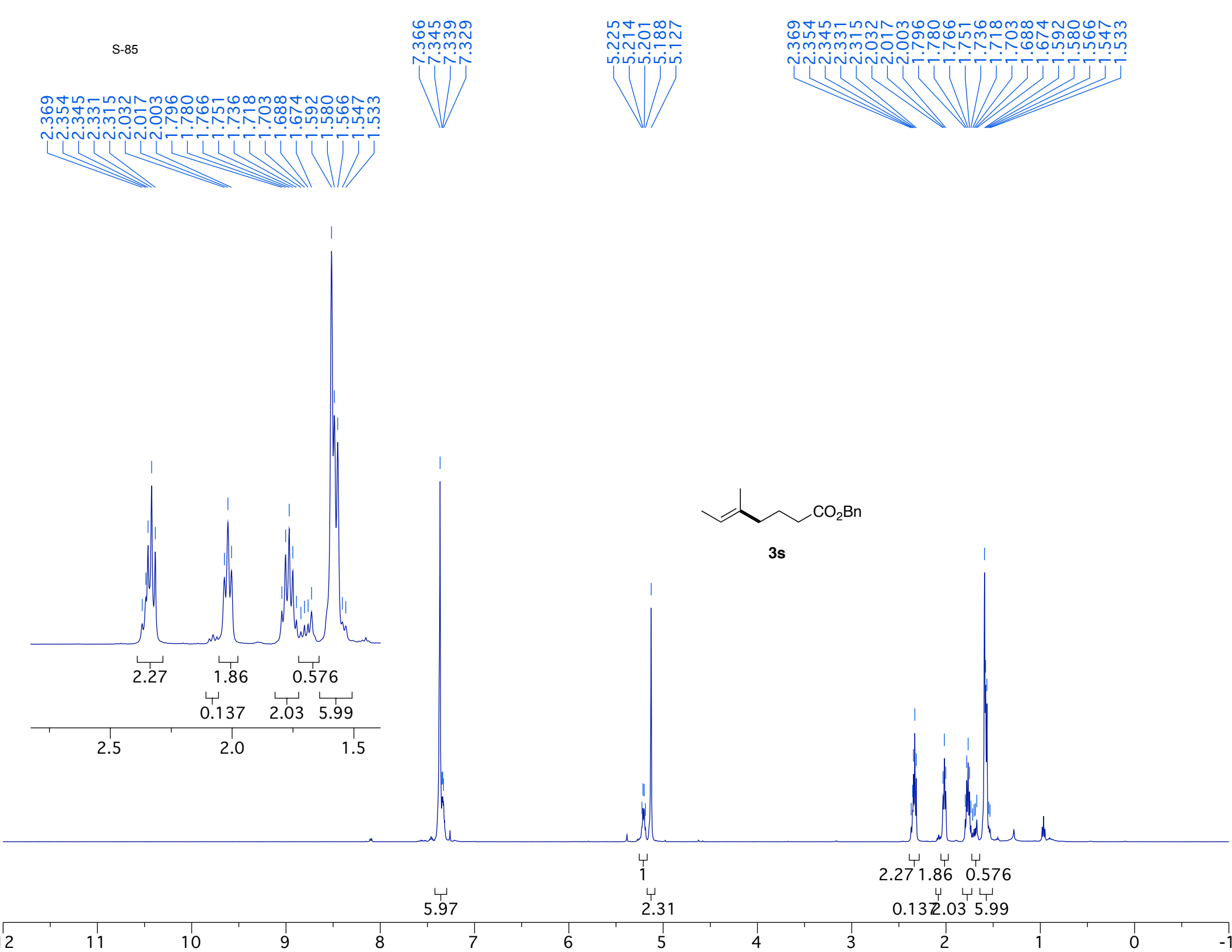
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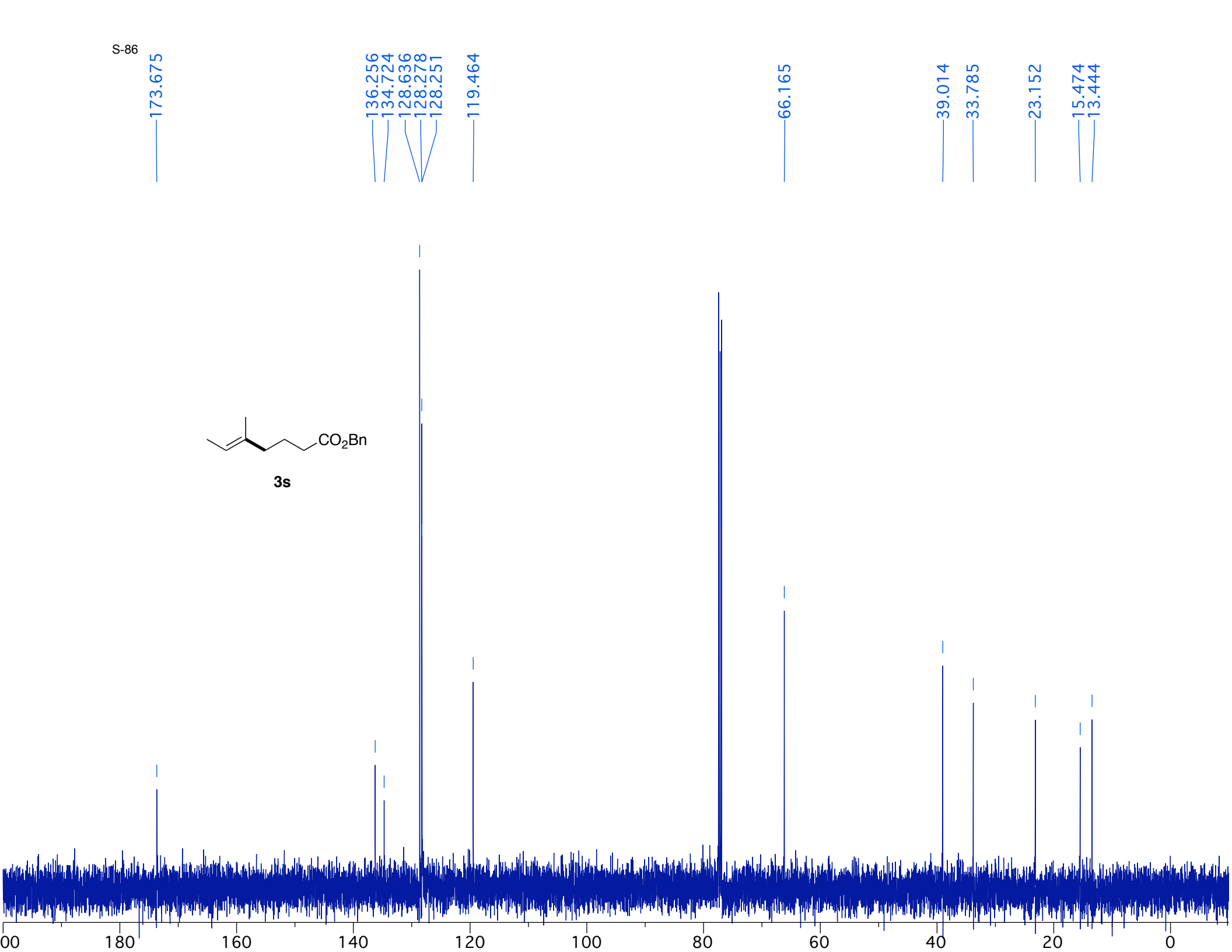
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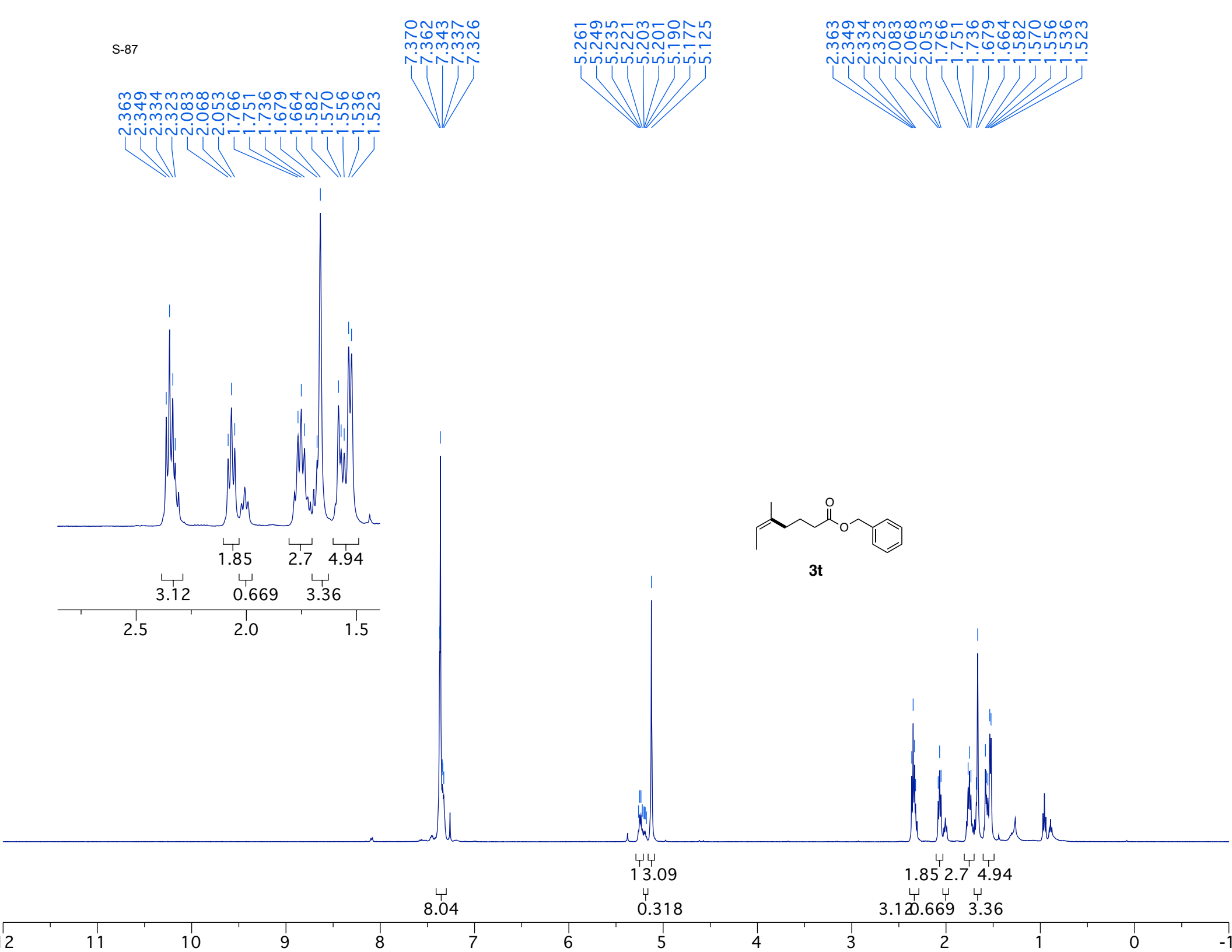
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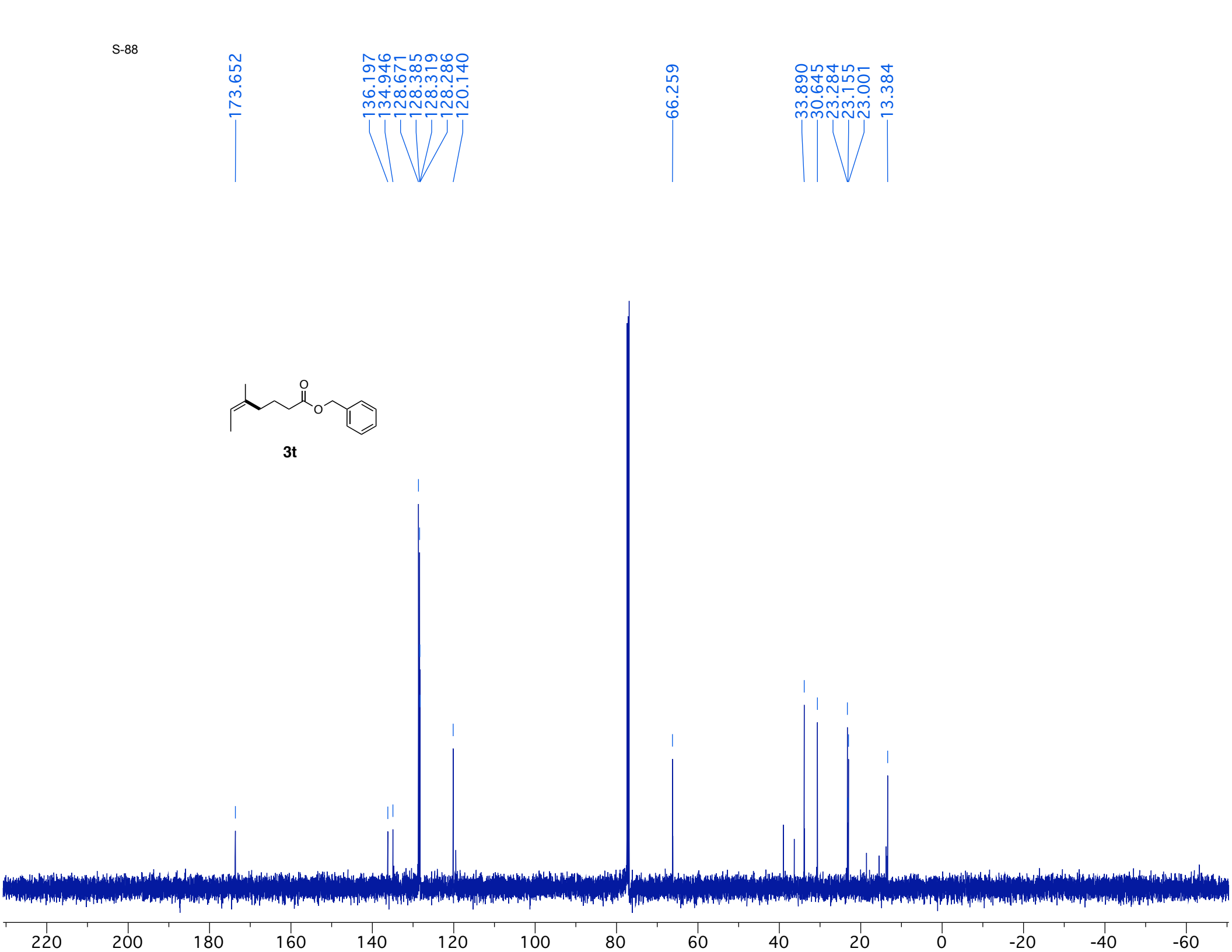
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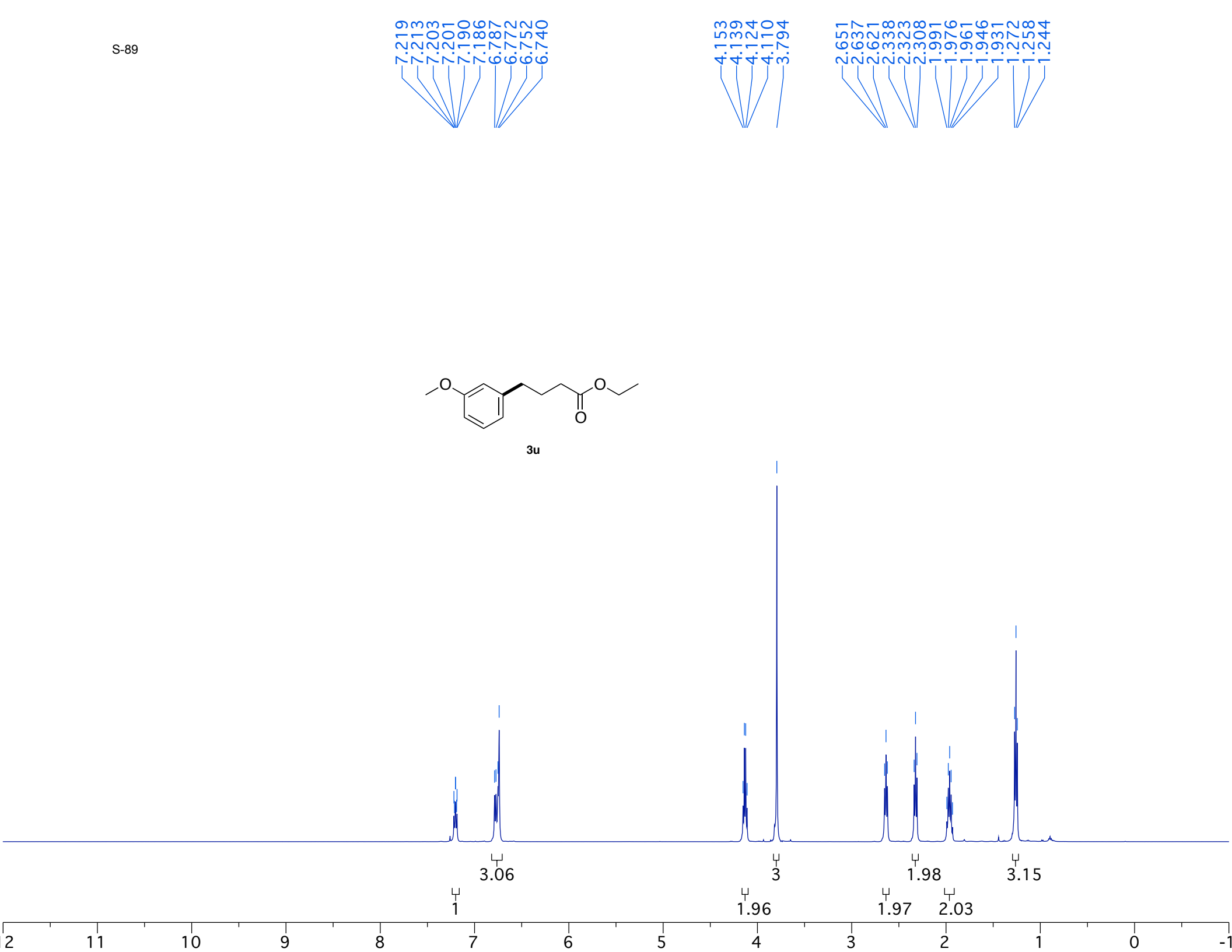
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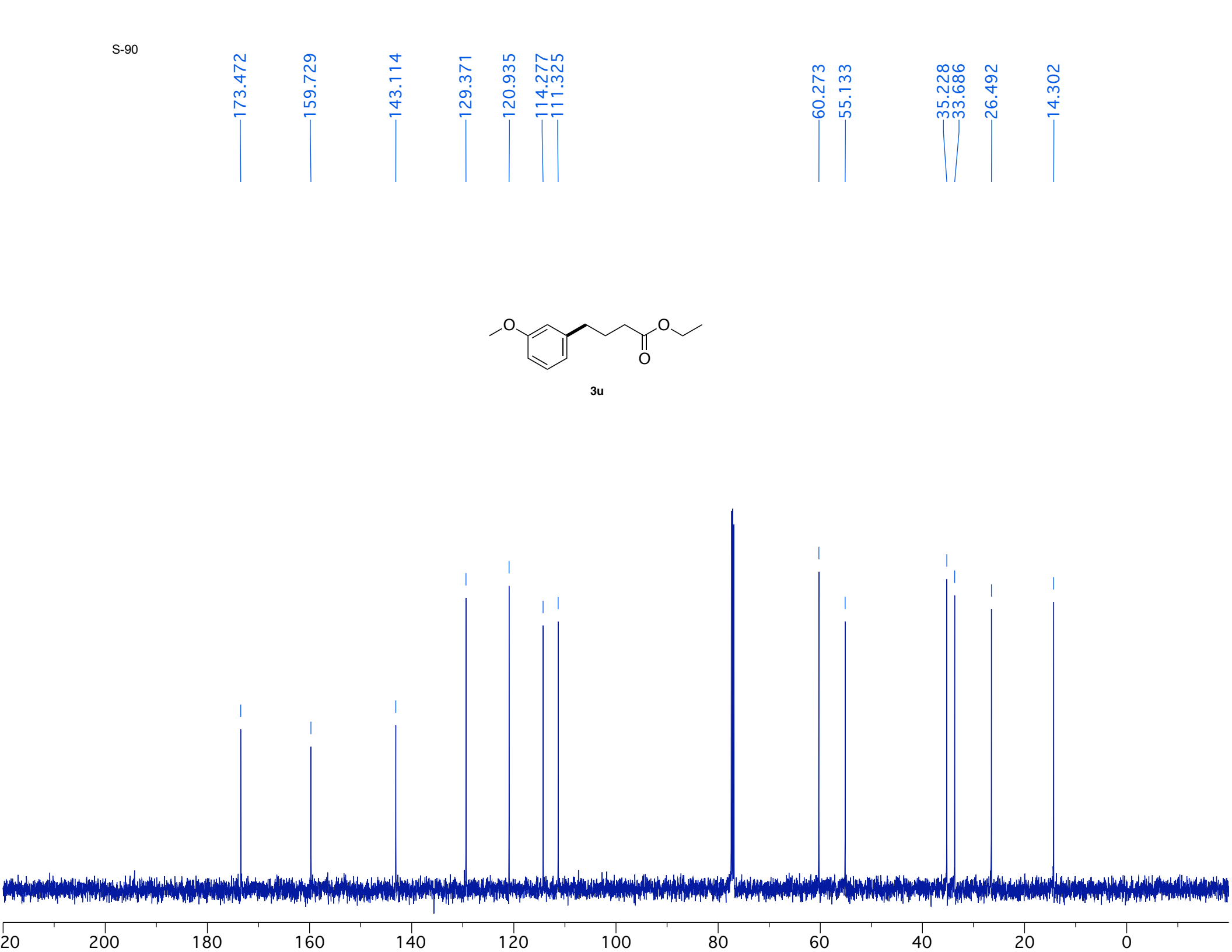
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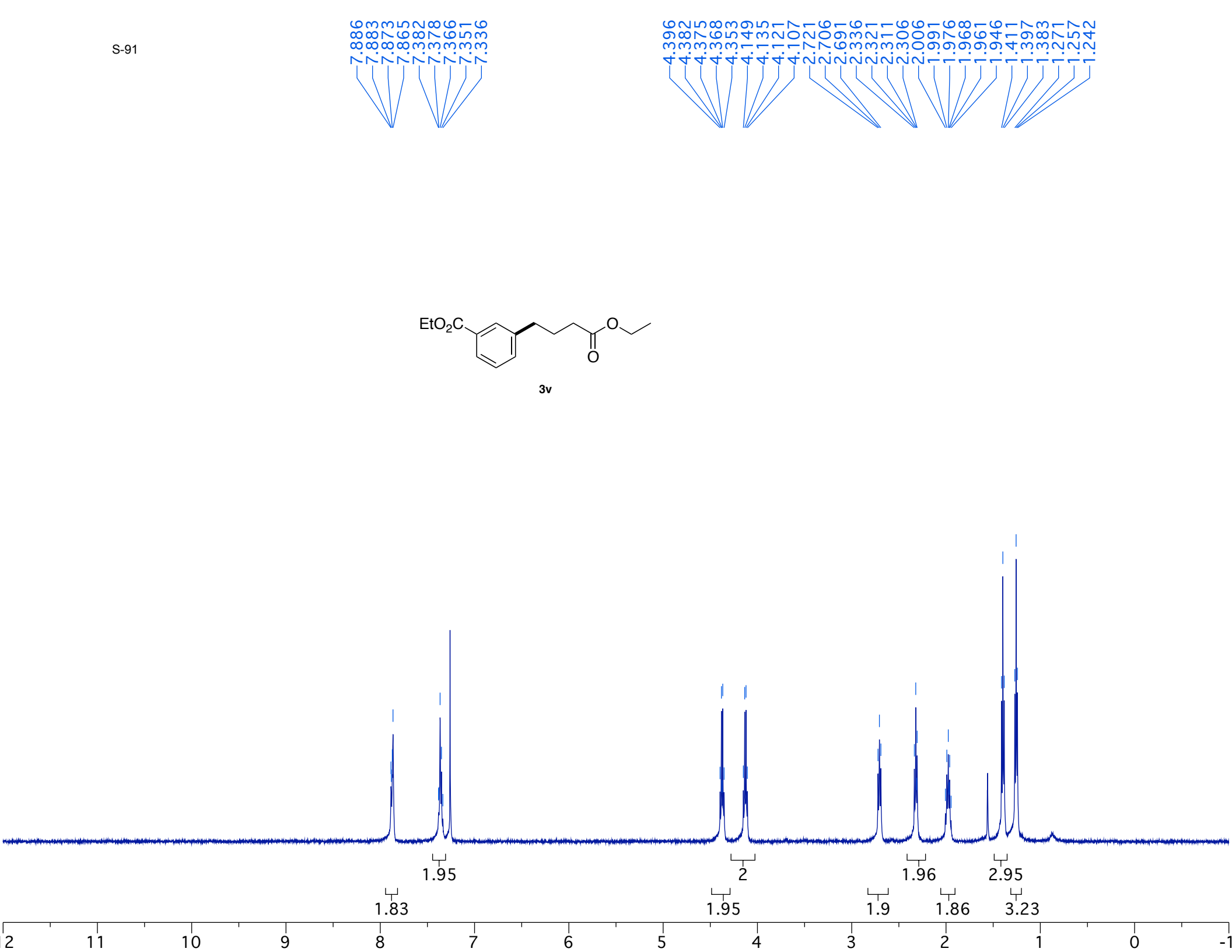
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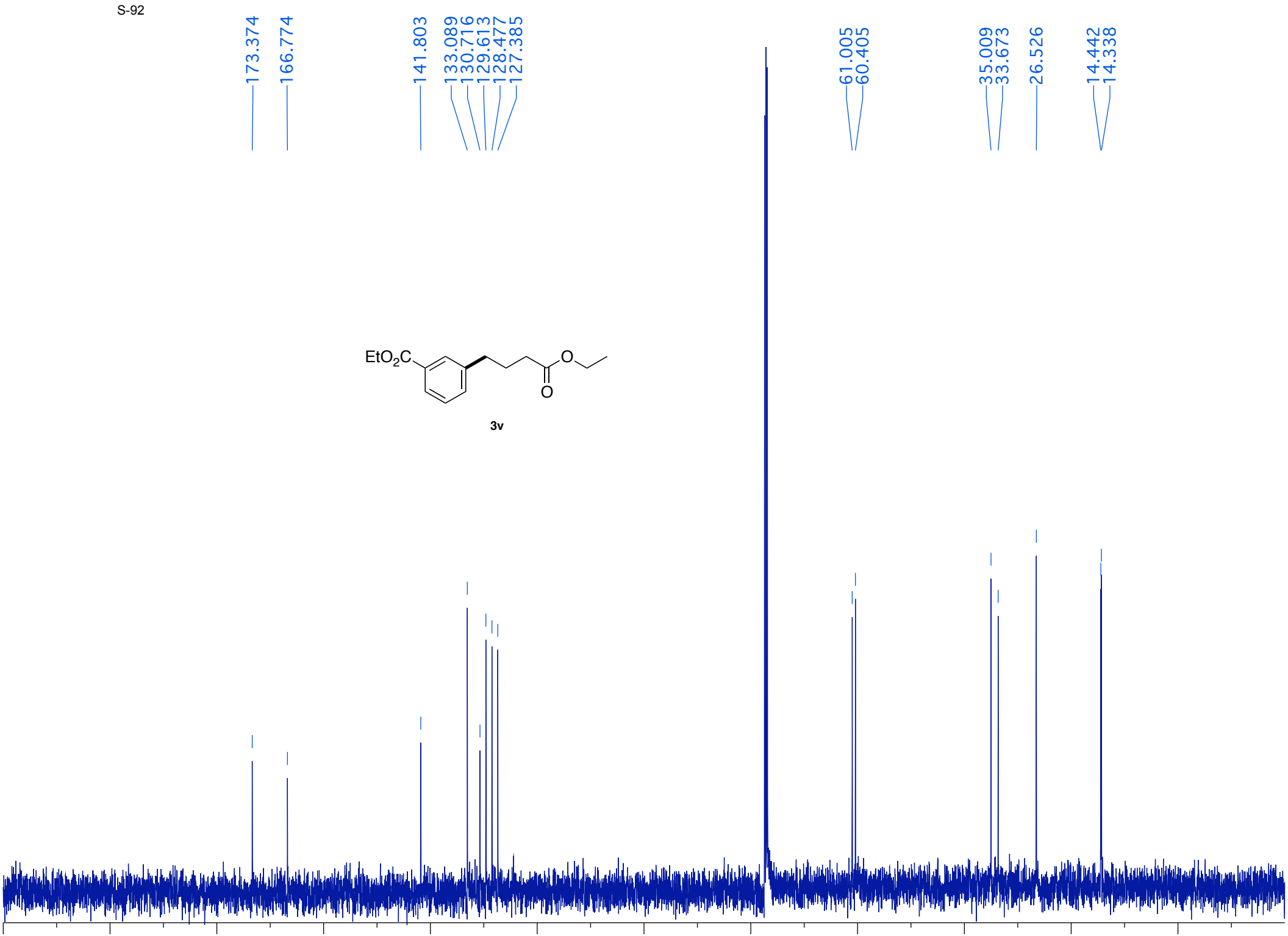
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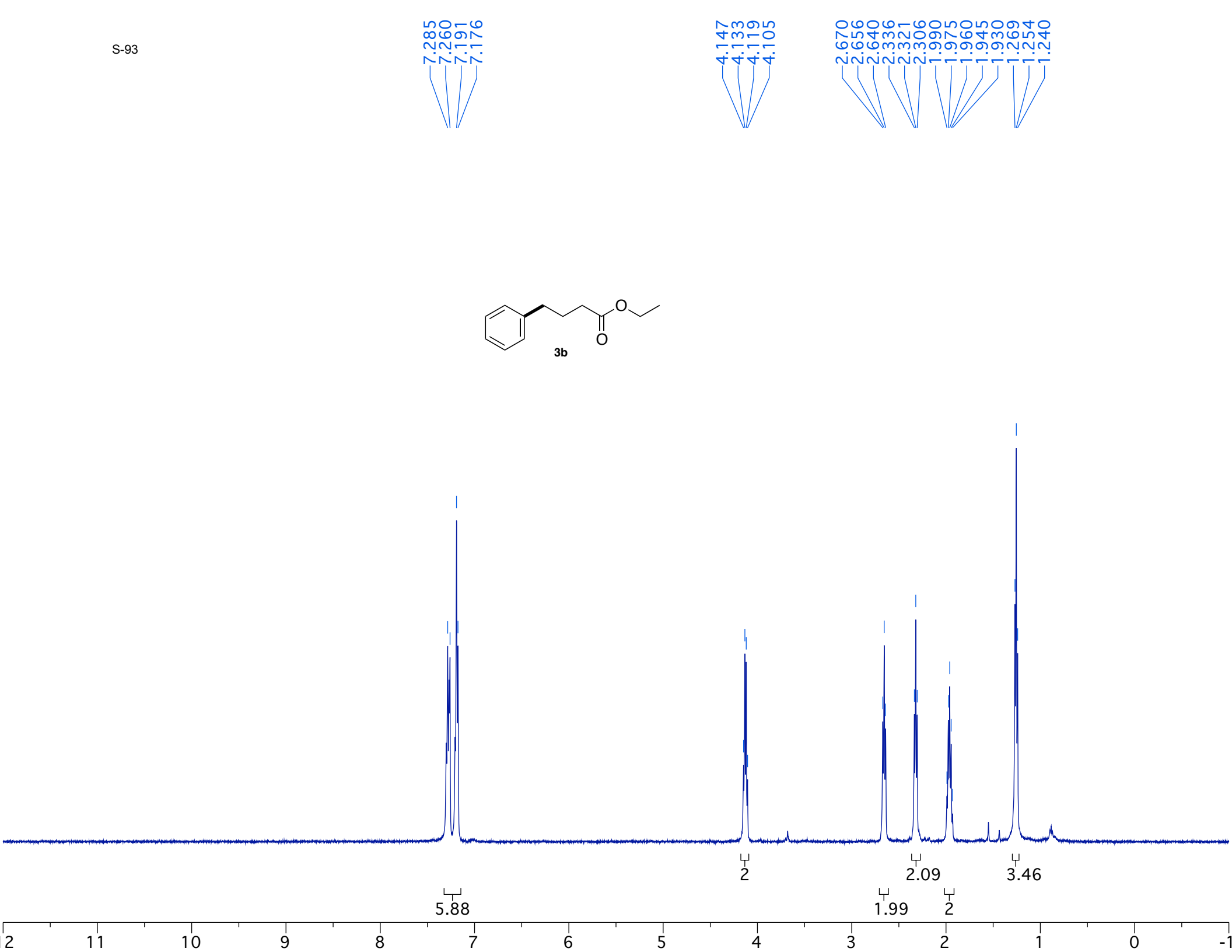
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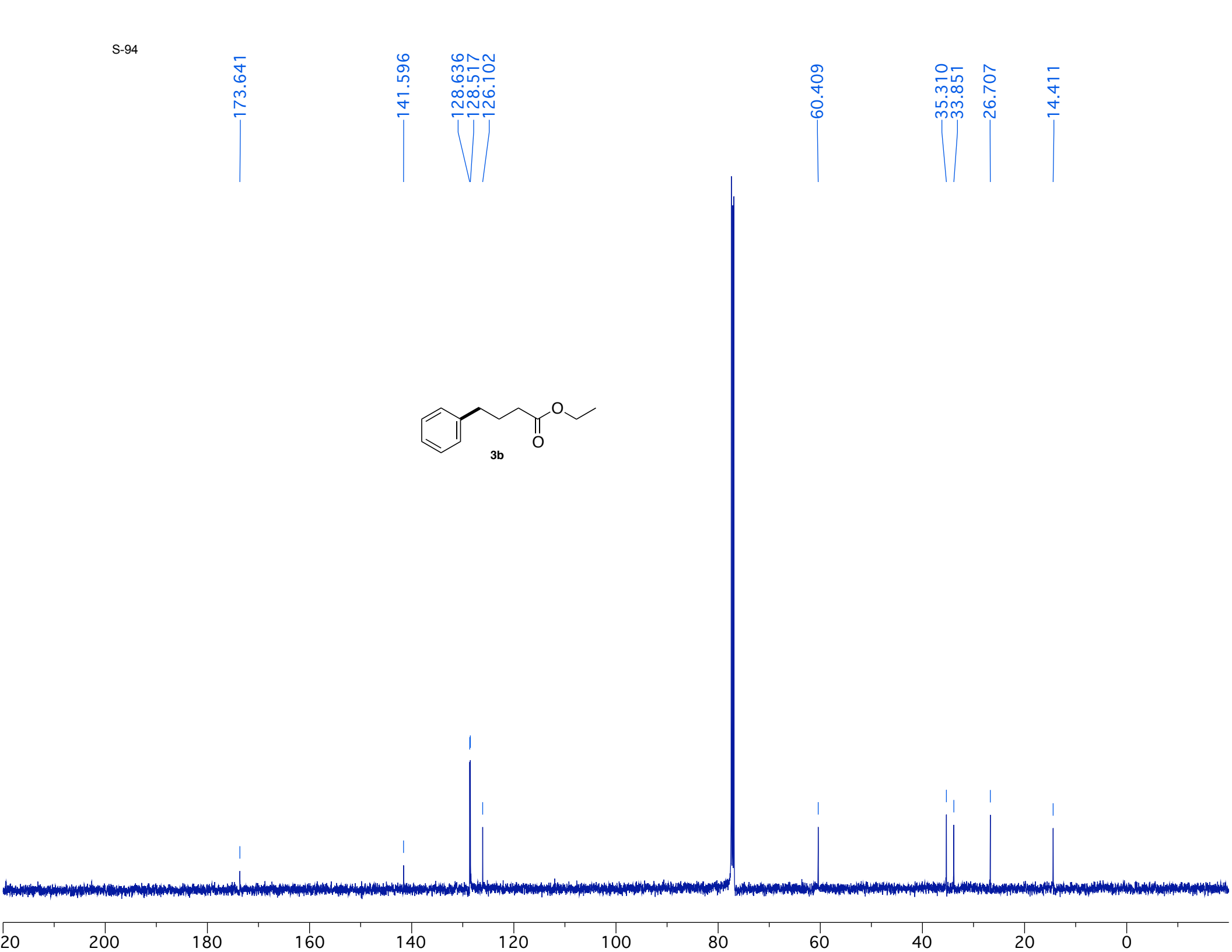
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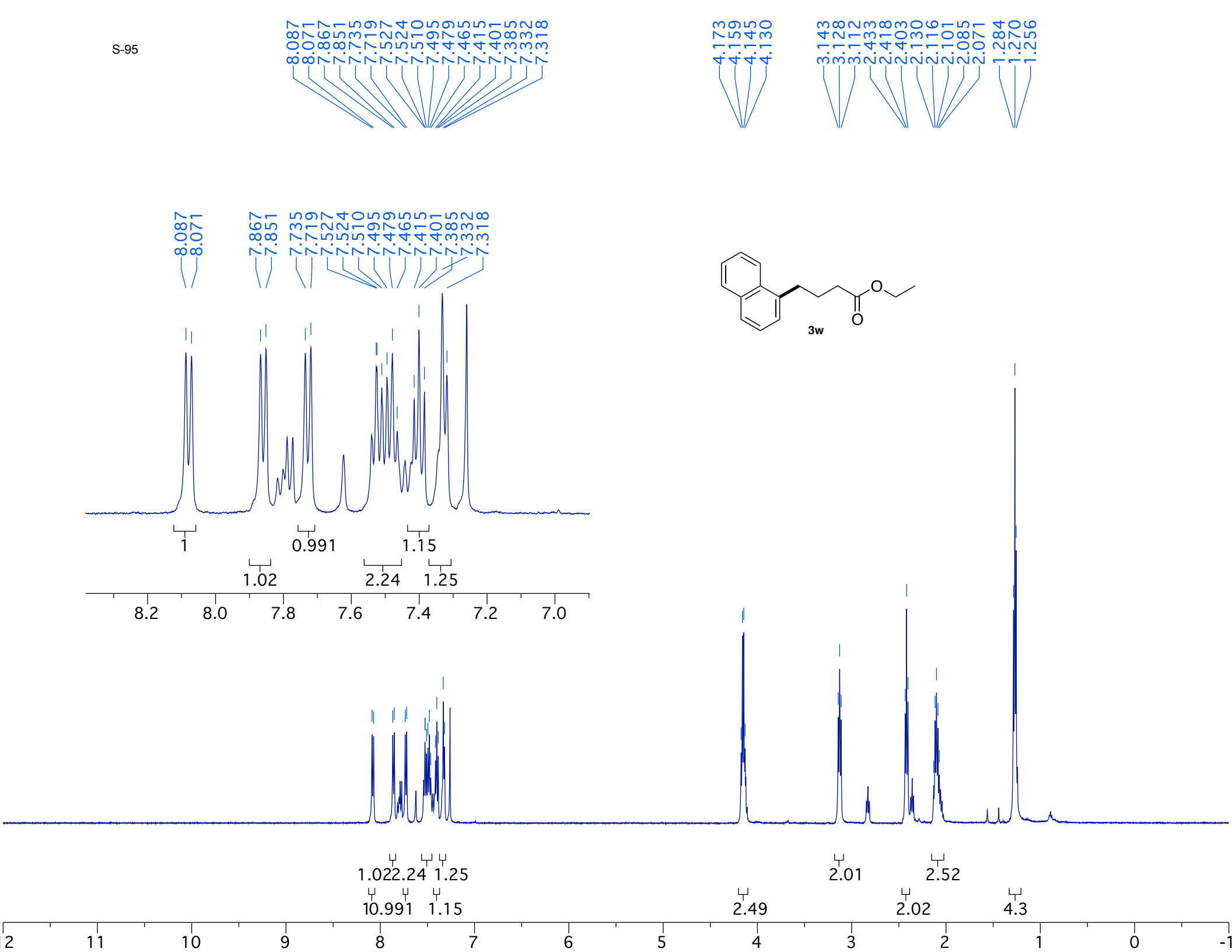
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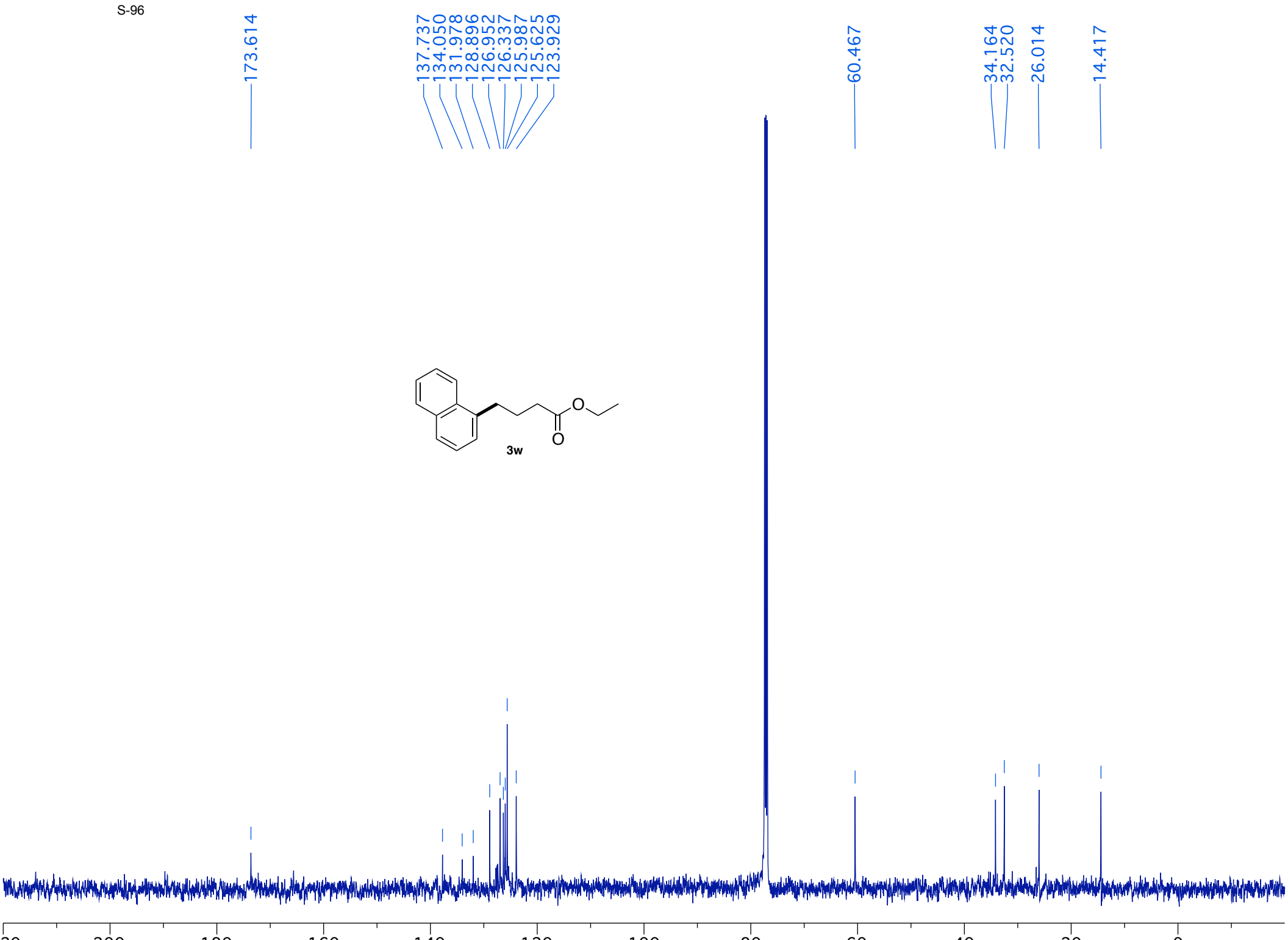
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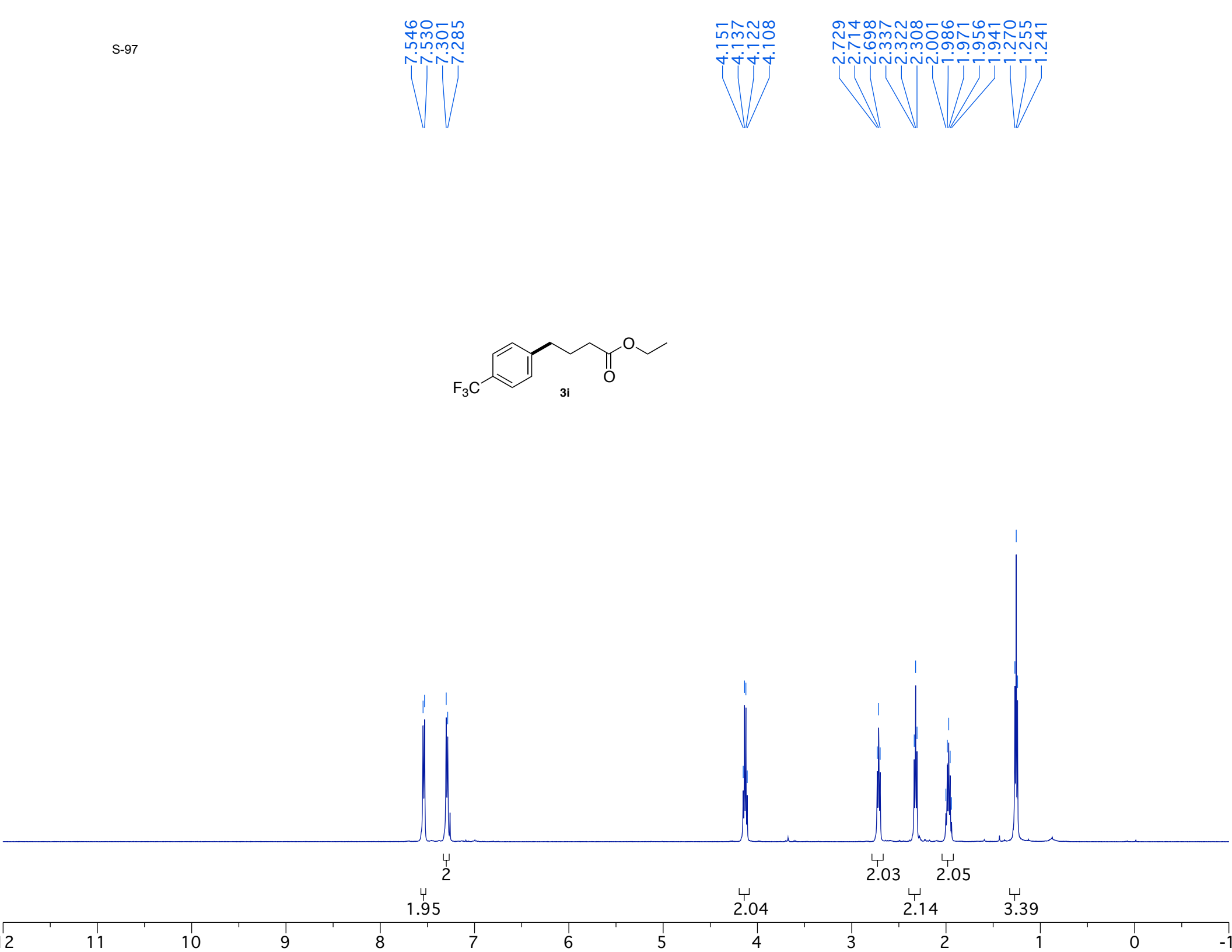
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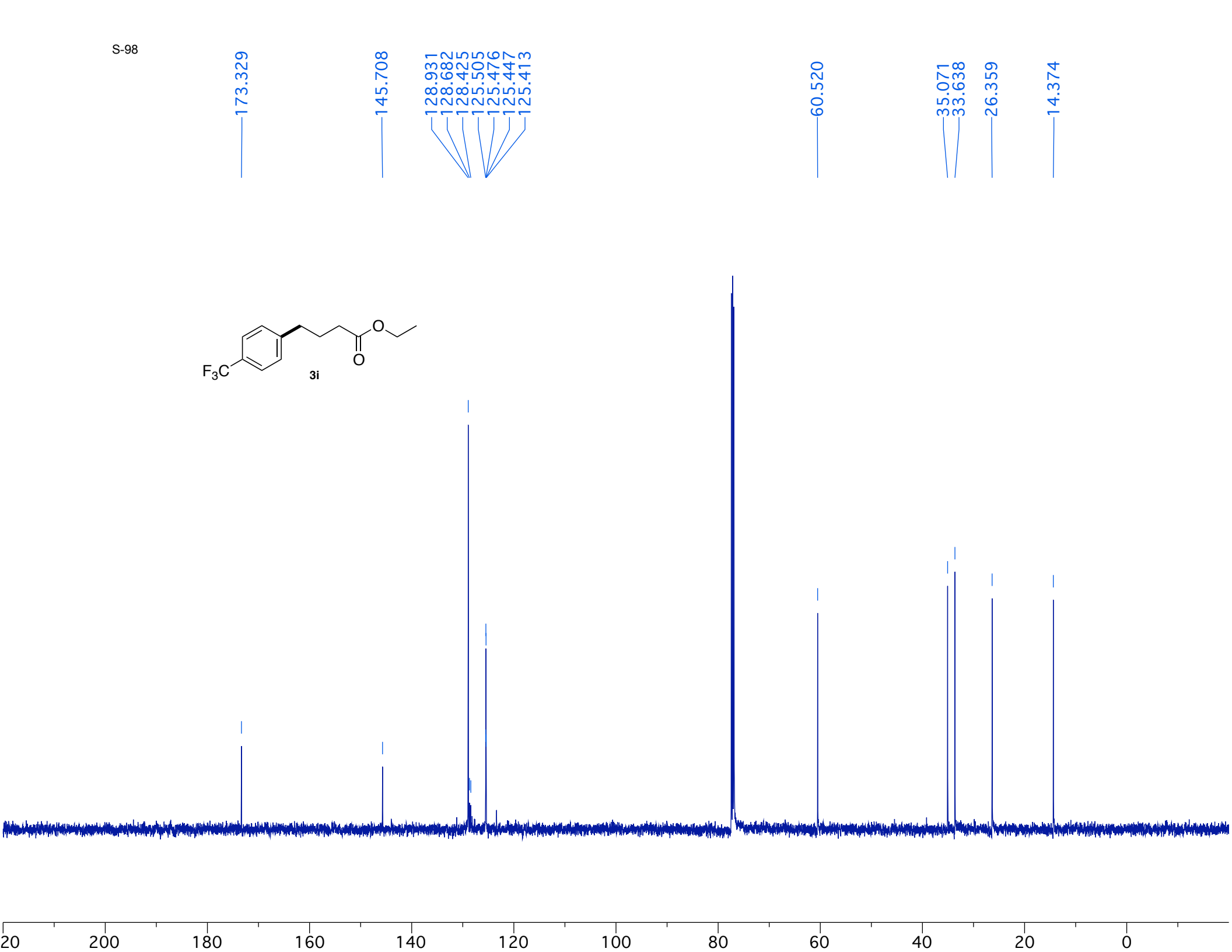
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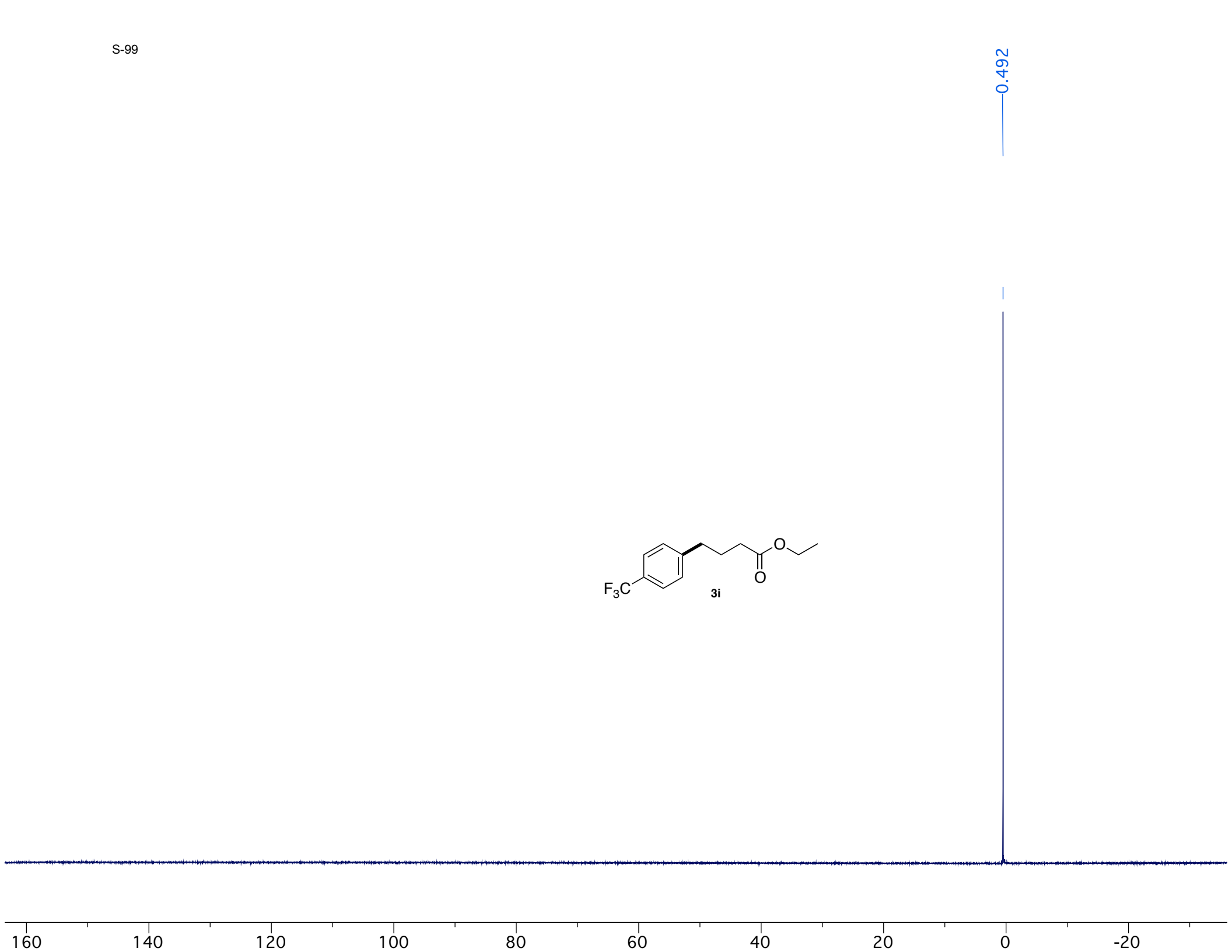
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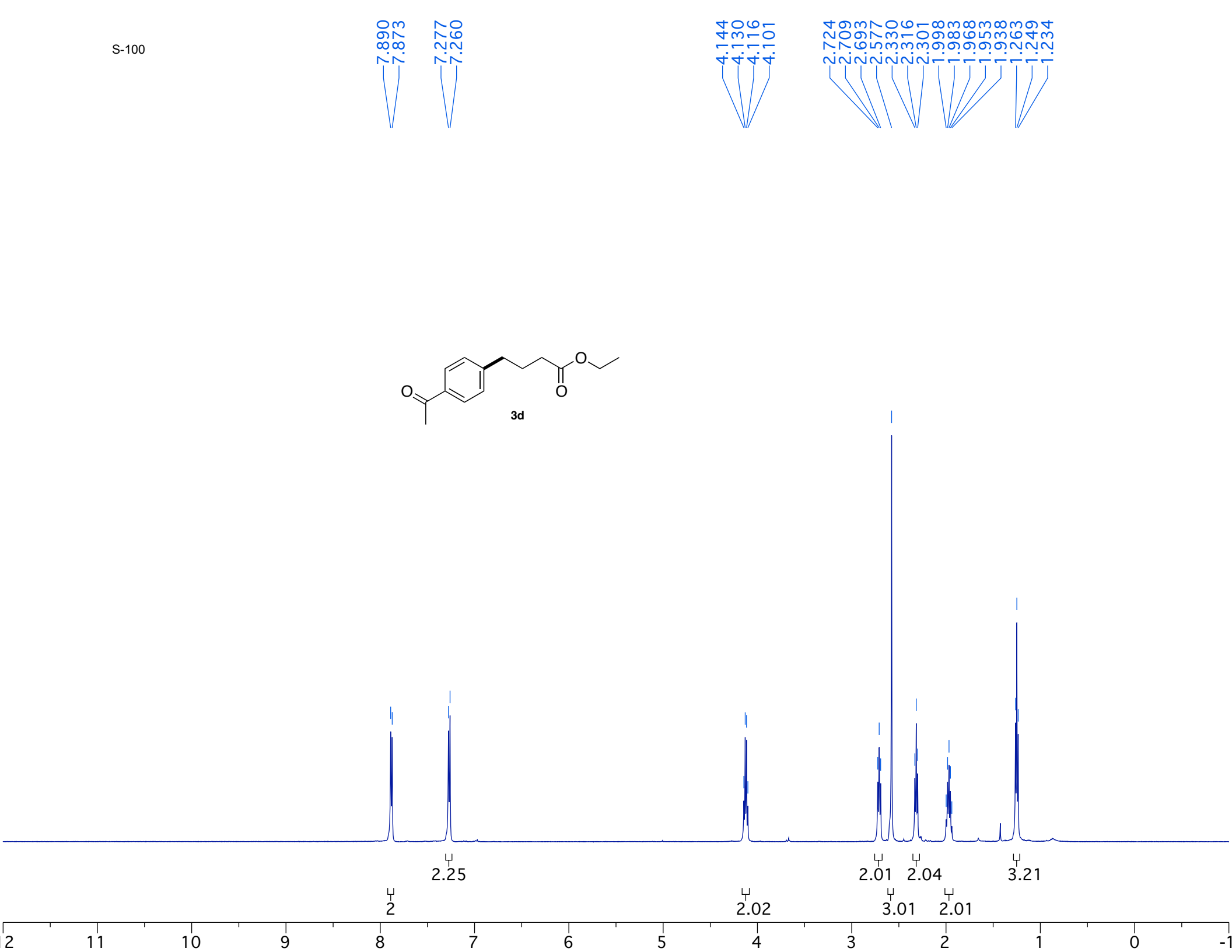
S-100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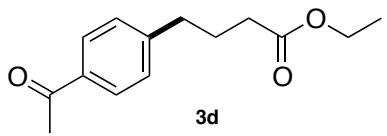

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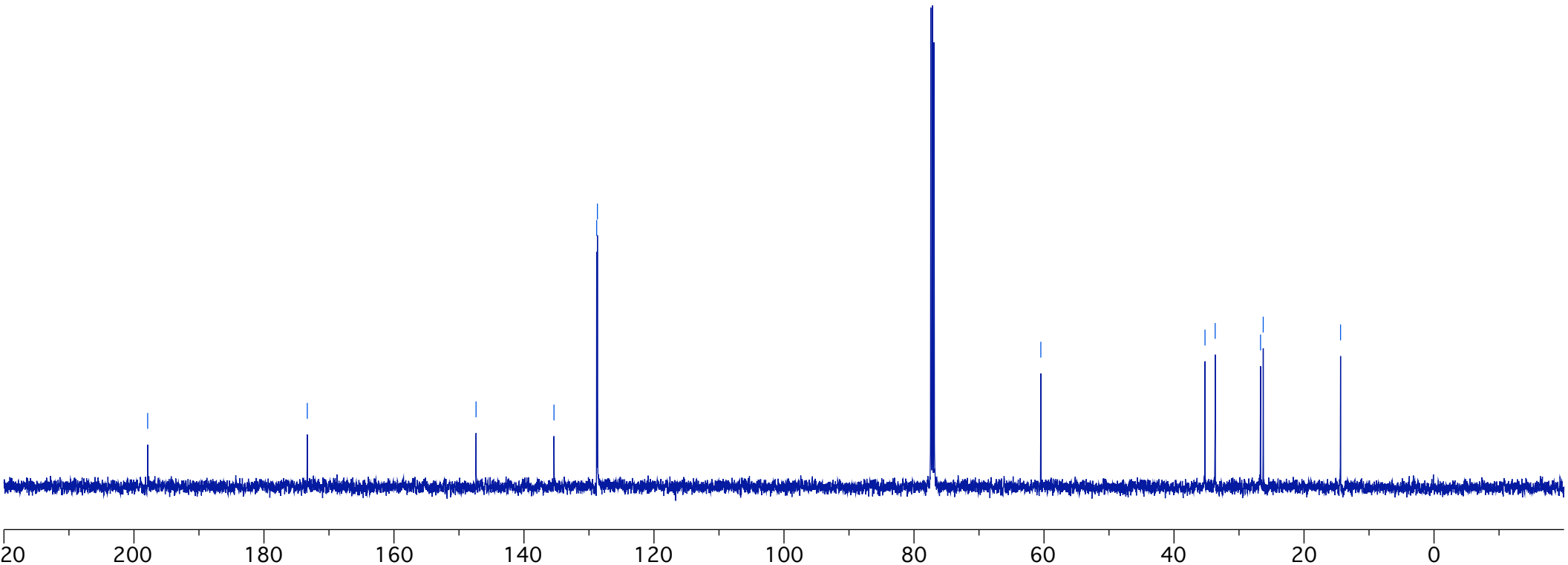

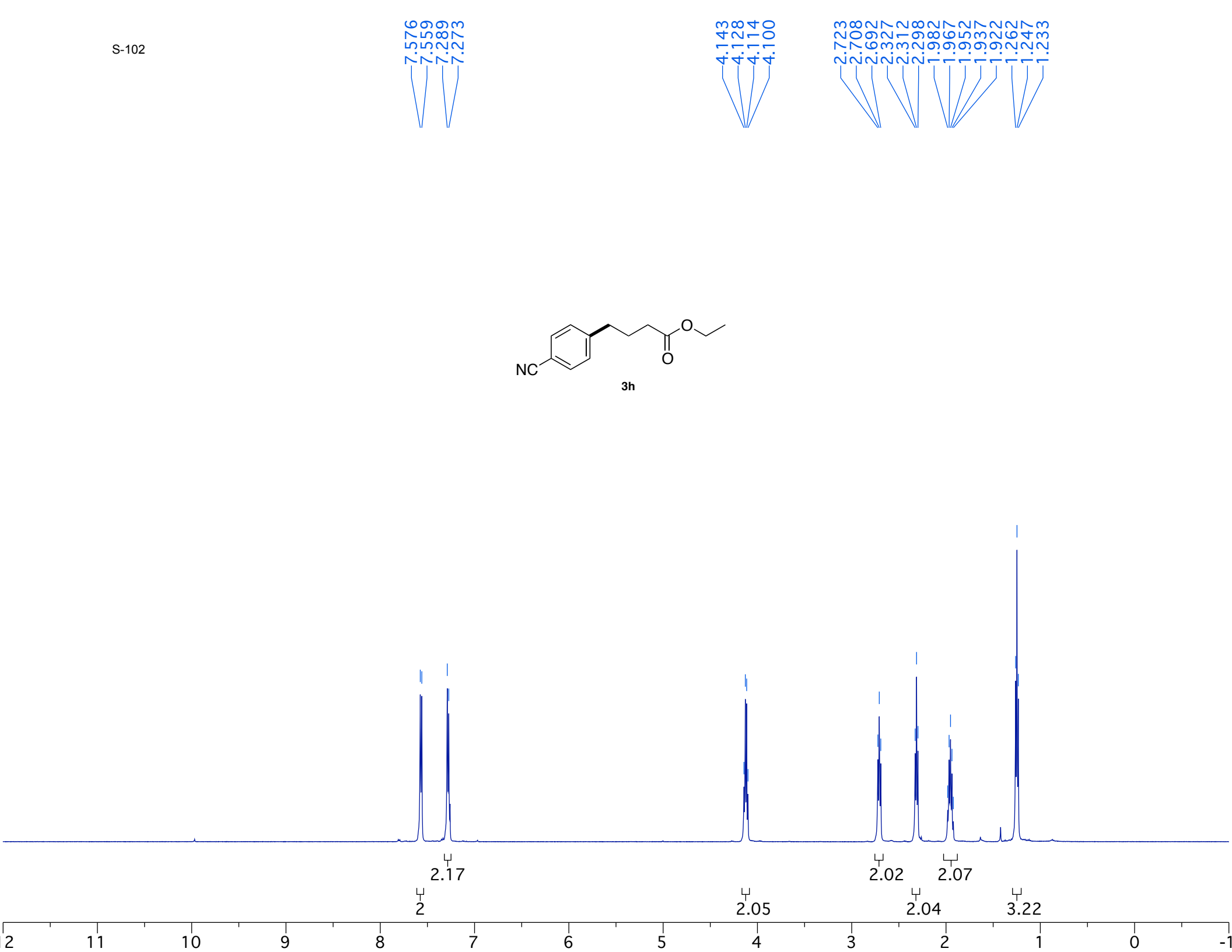
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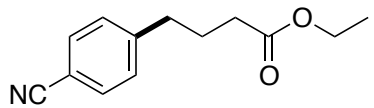

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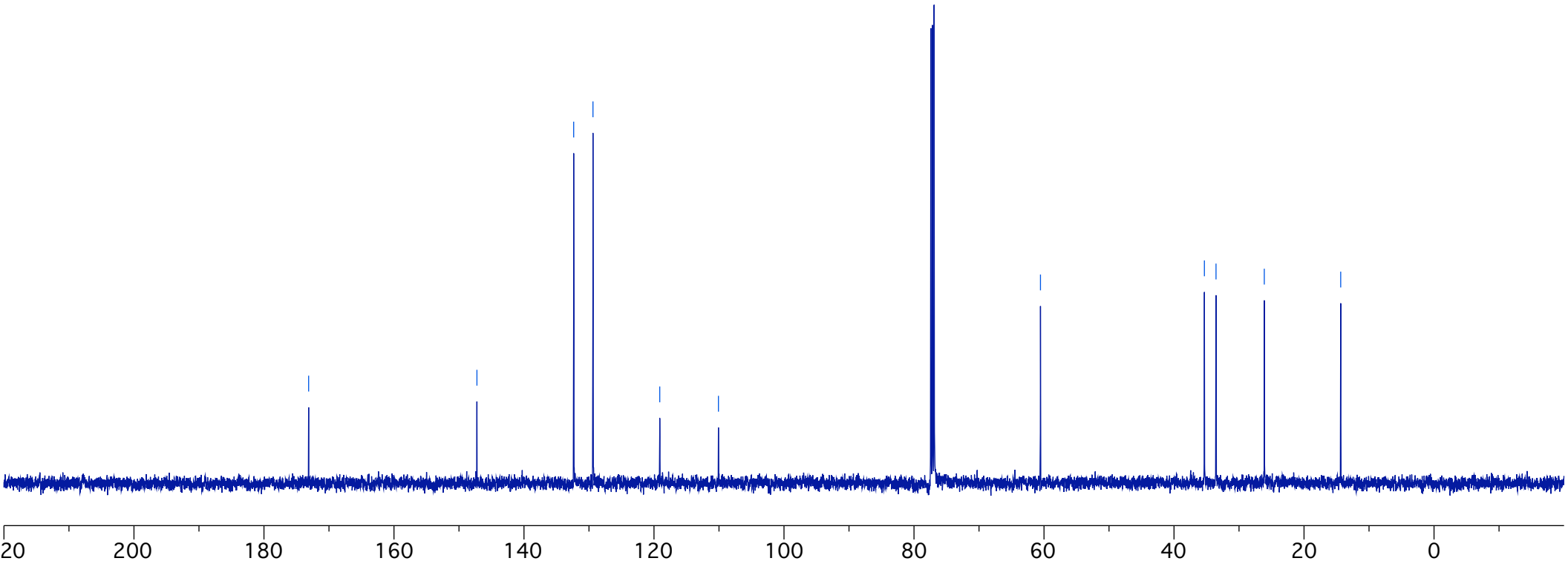

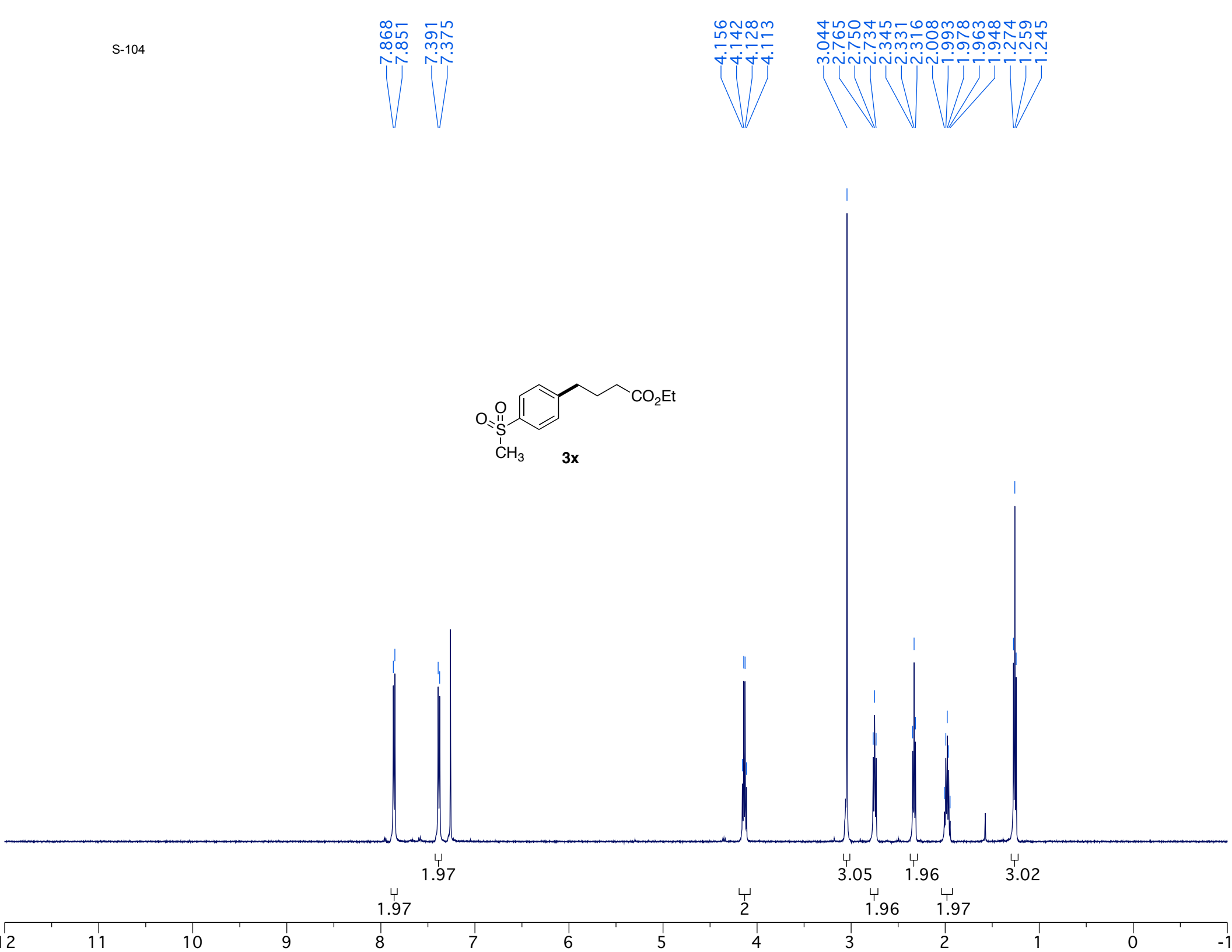
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1.948
1.274
1.259
1.245
CO2Et
O
O
S
CH3
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1.96
3.02
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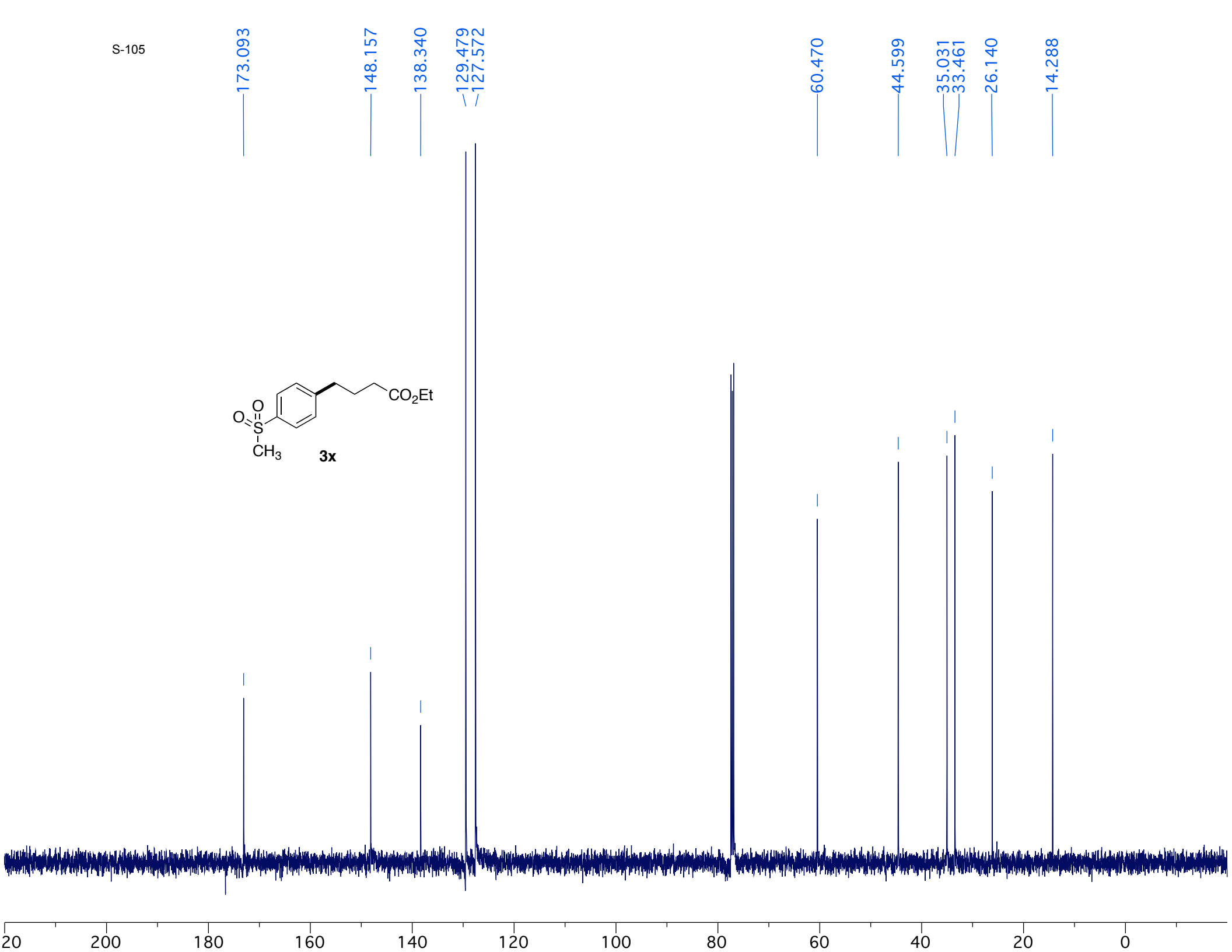
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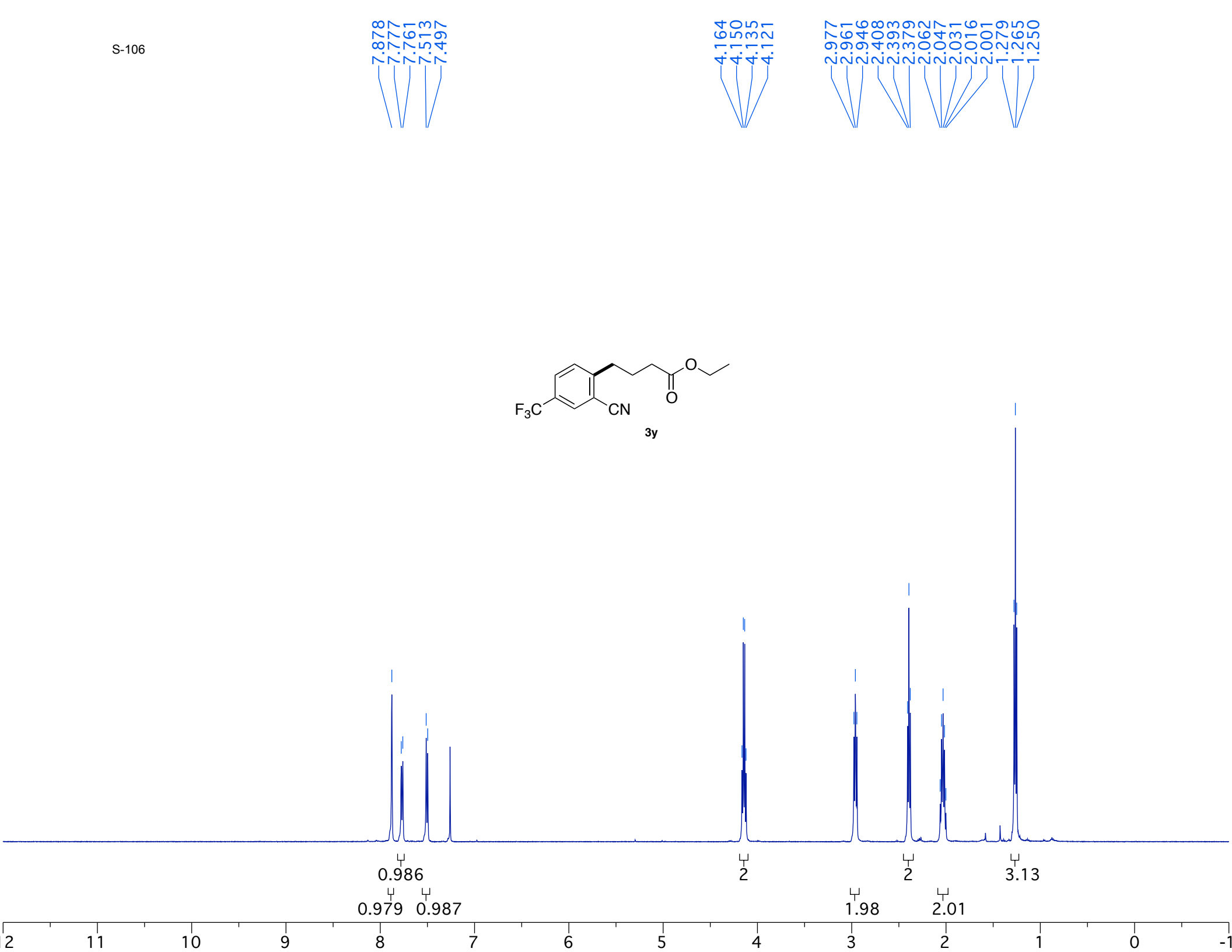
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1.265
1.250
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O
F3C
CN
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DAE5P020 15-30

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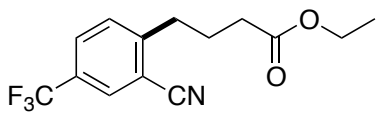

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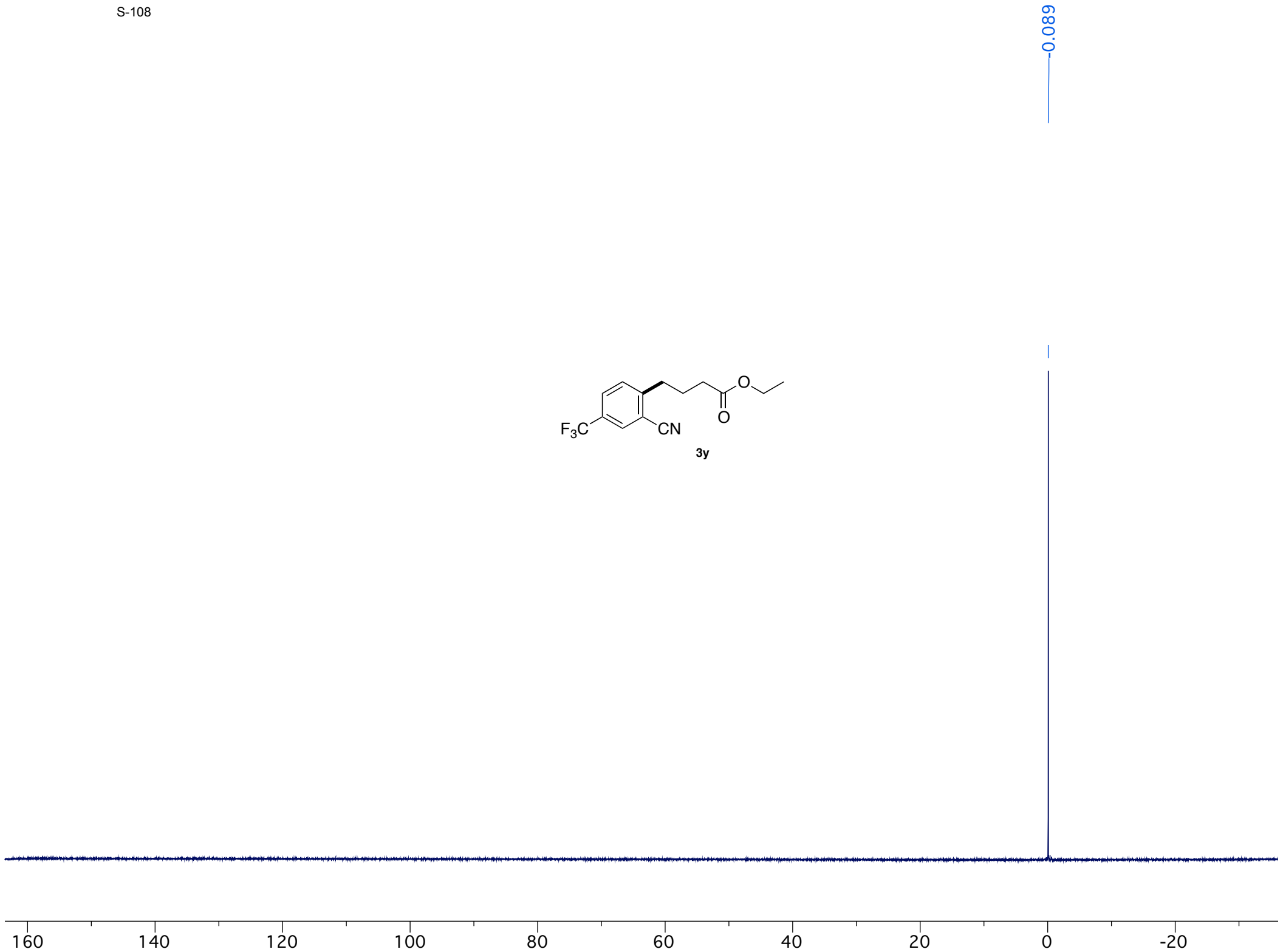
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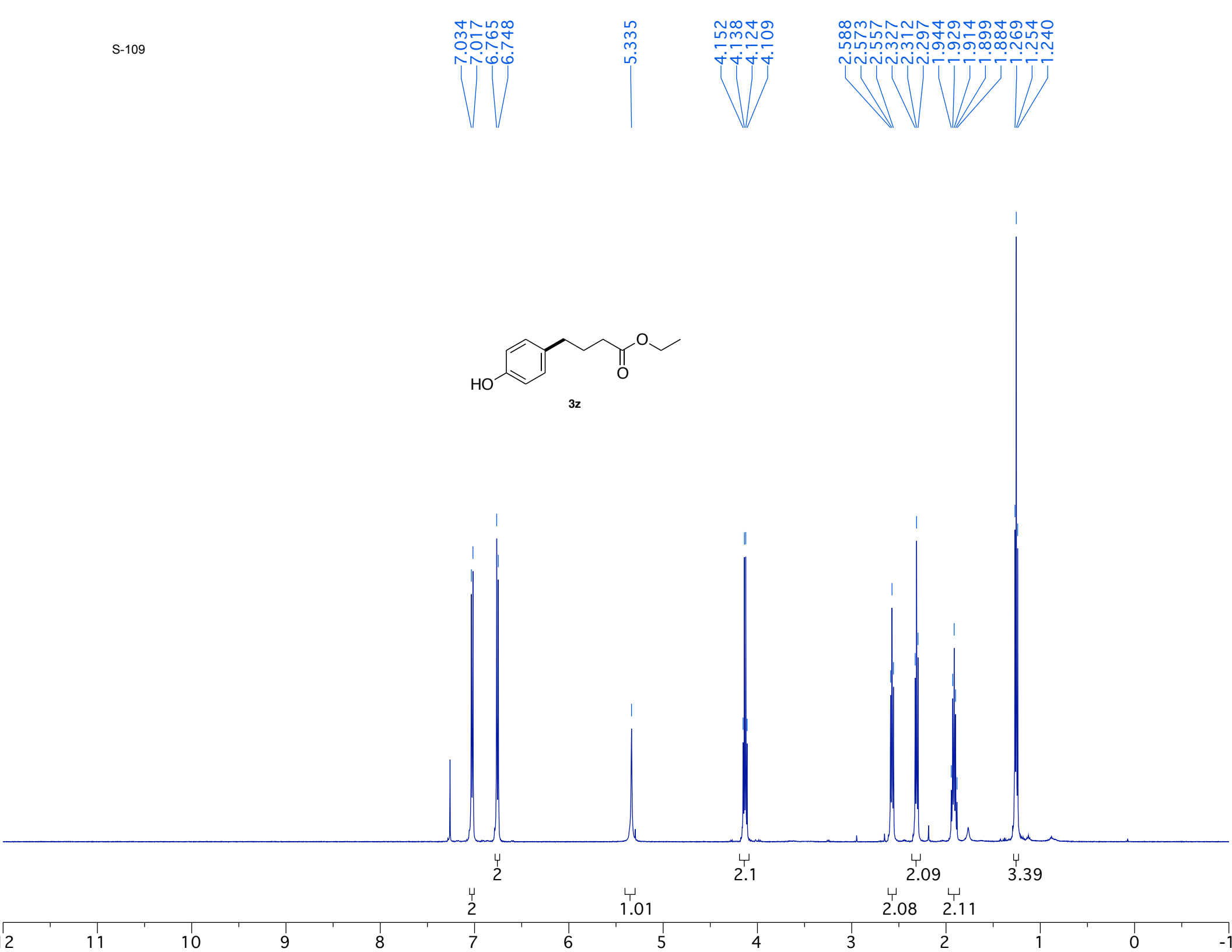
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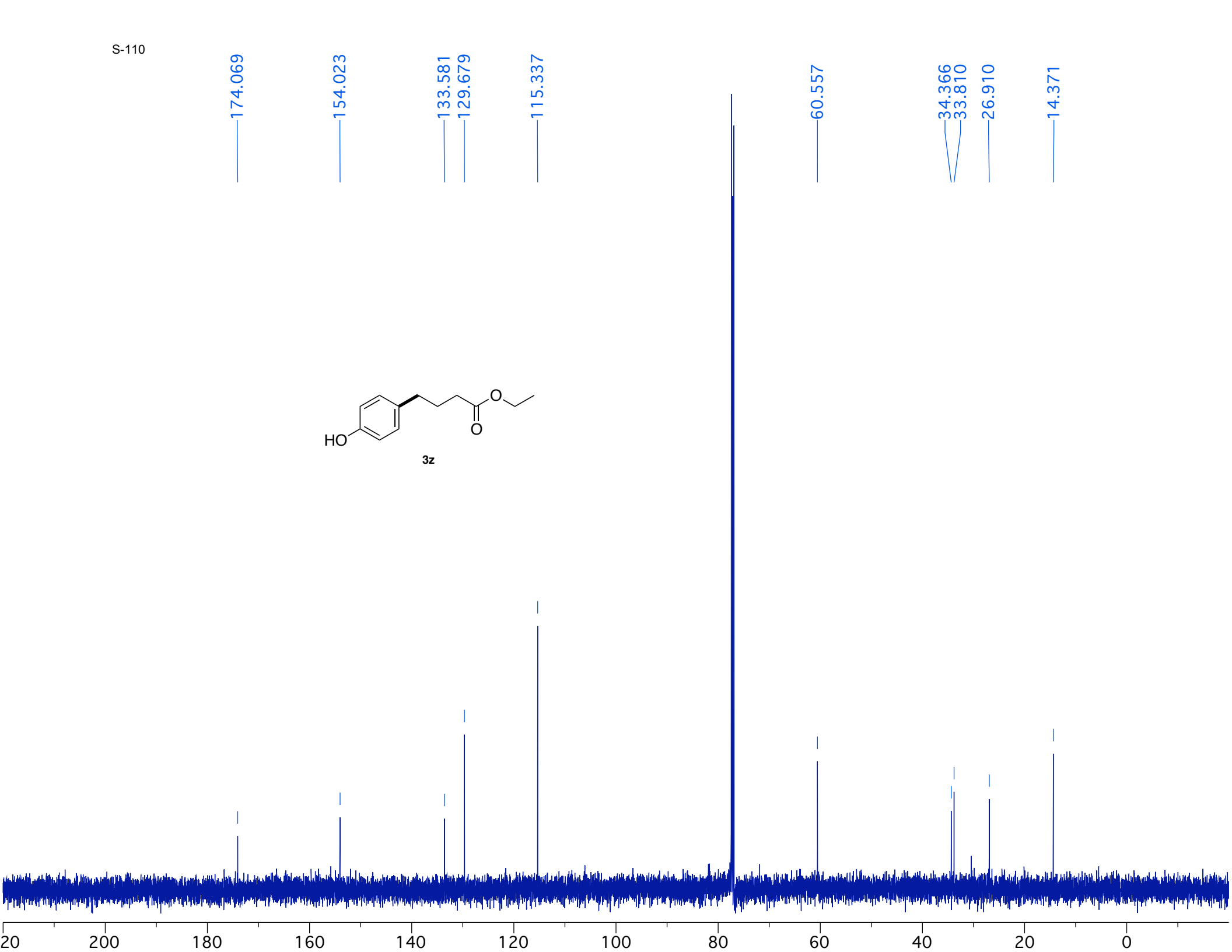
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33.810
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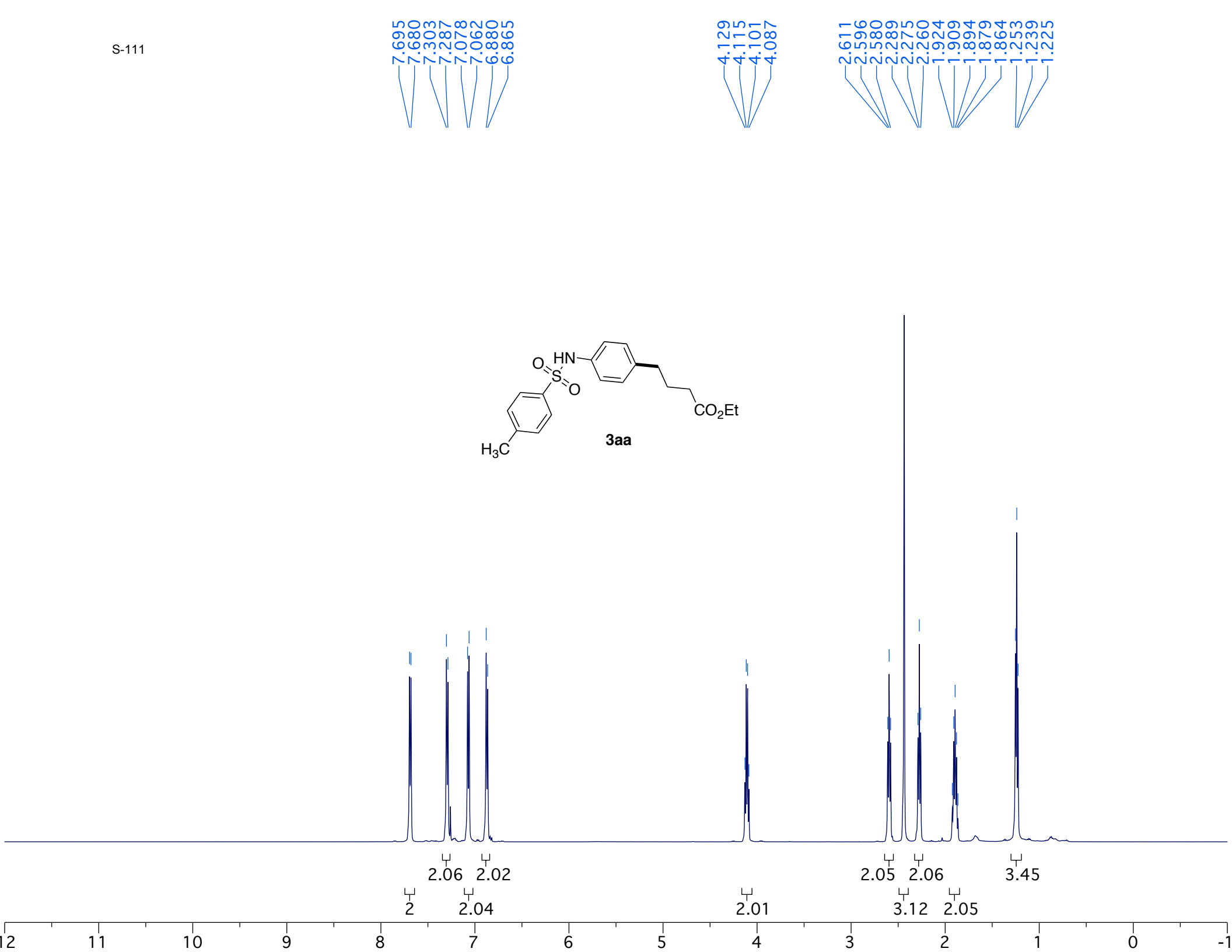
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O
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2.02
2.05
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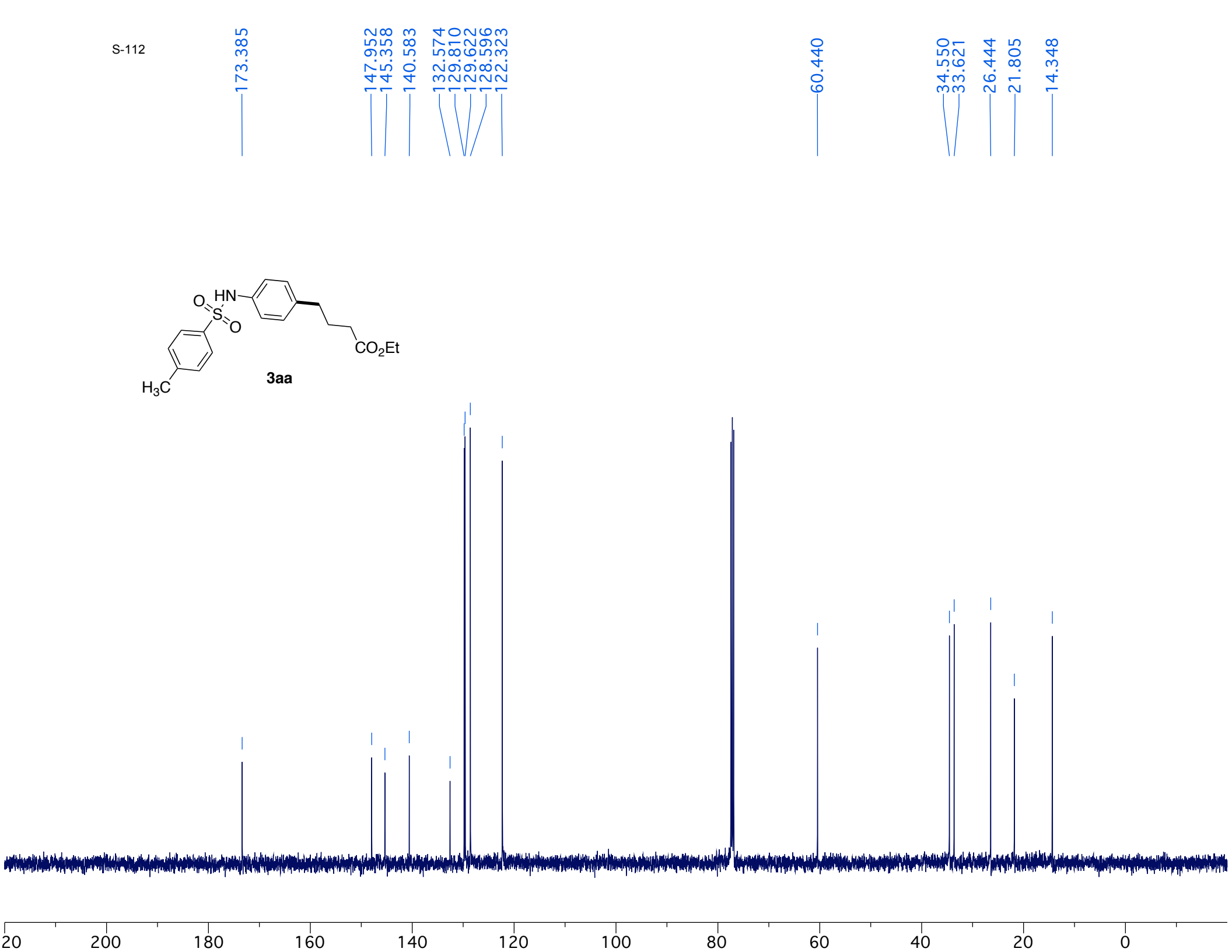
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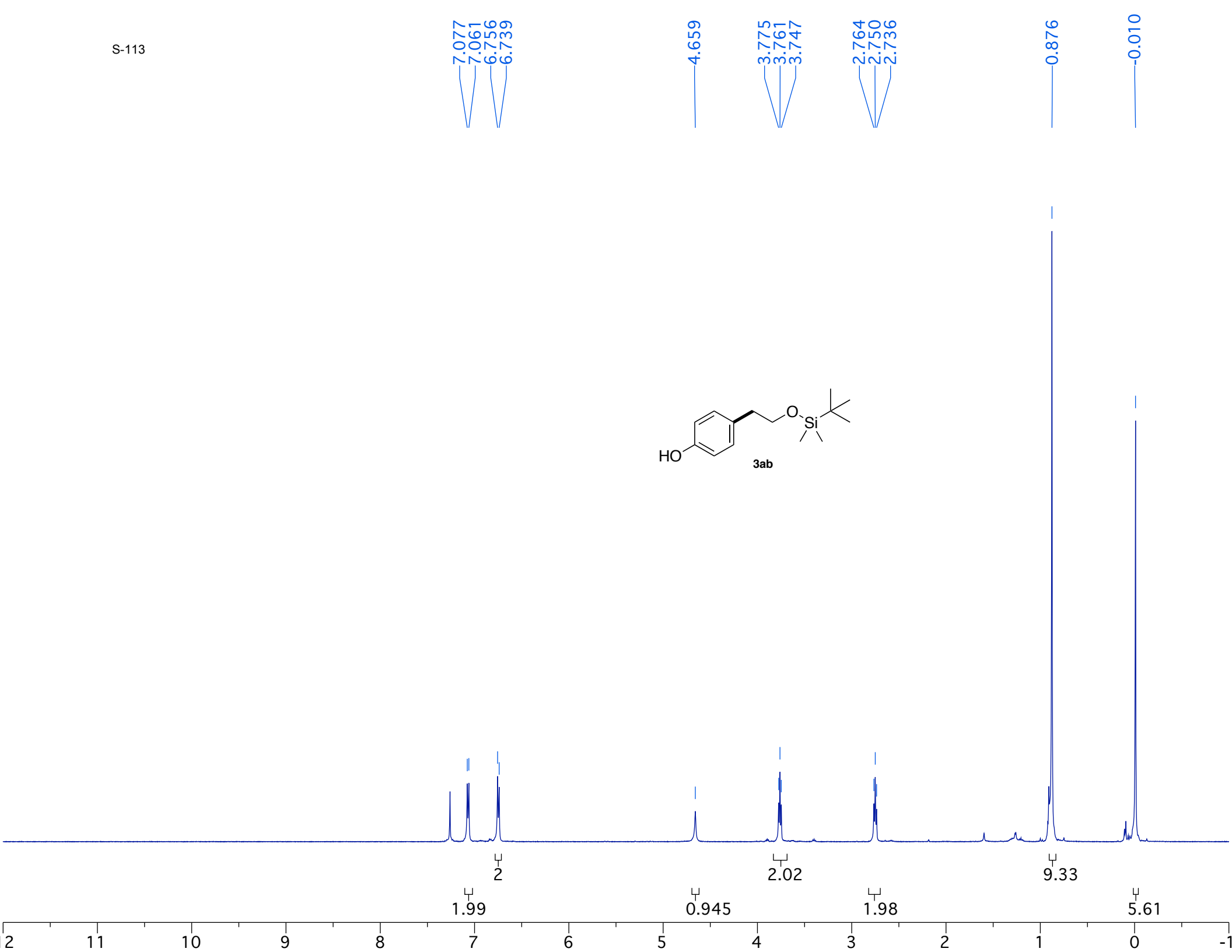
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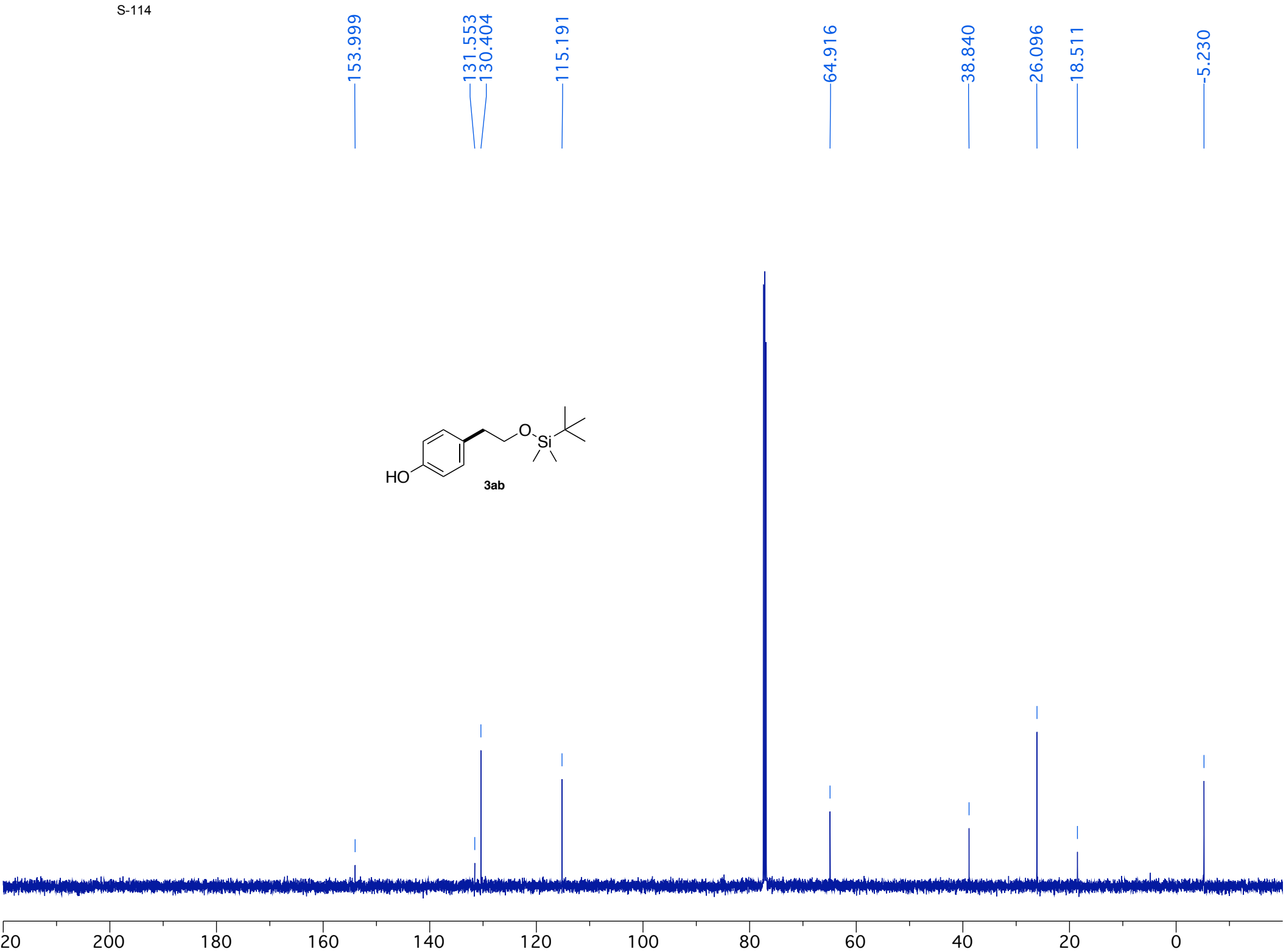
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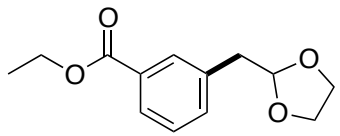

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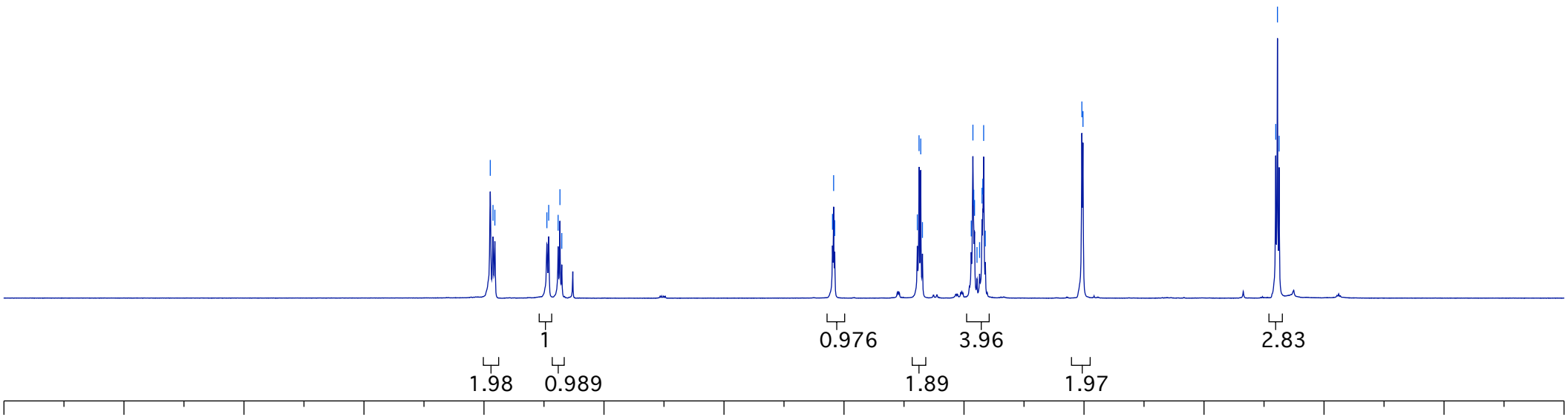

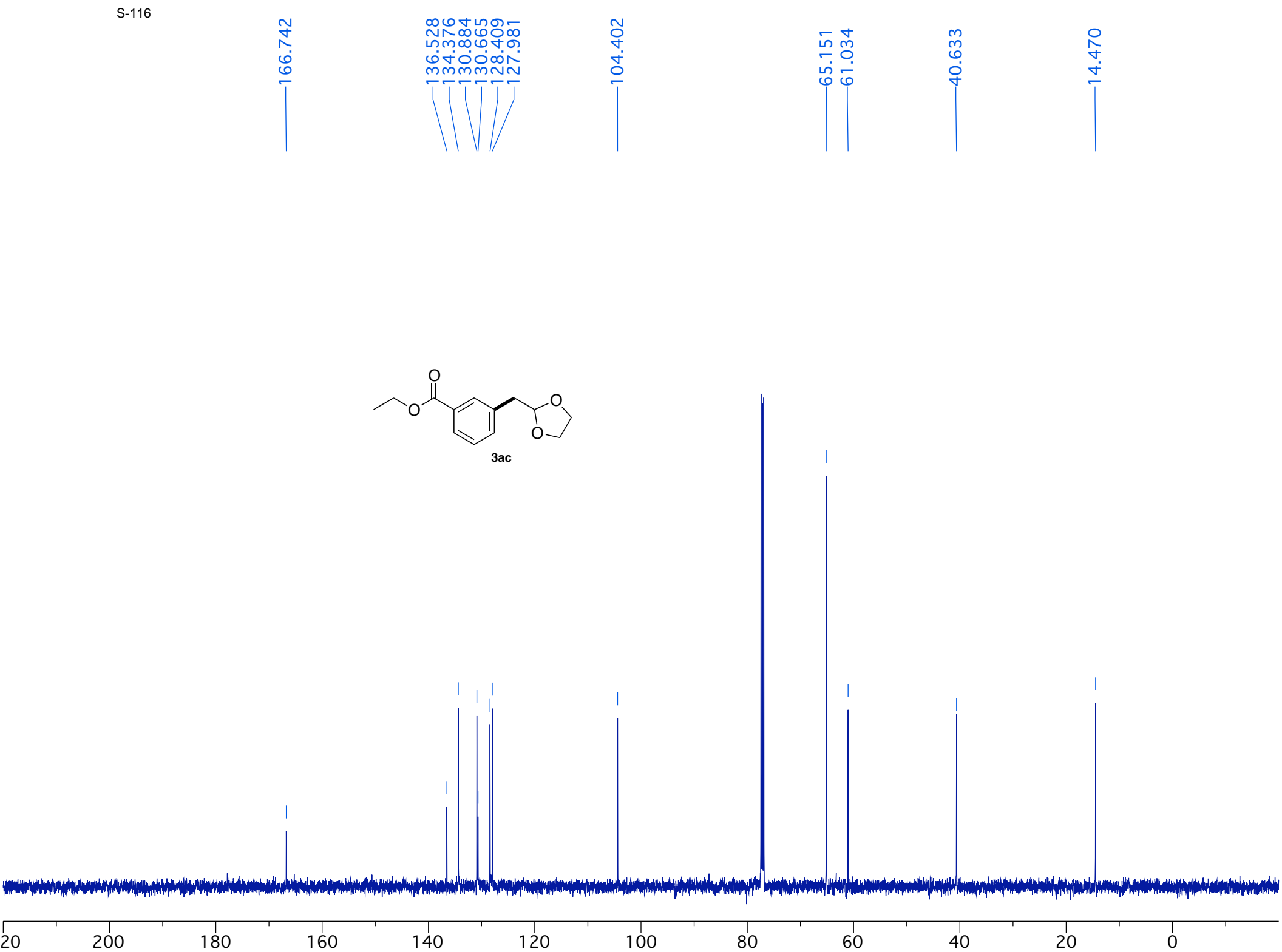
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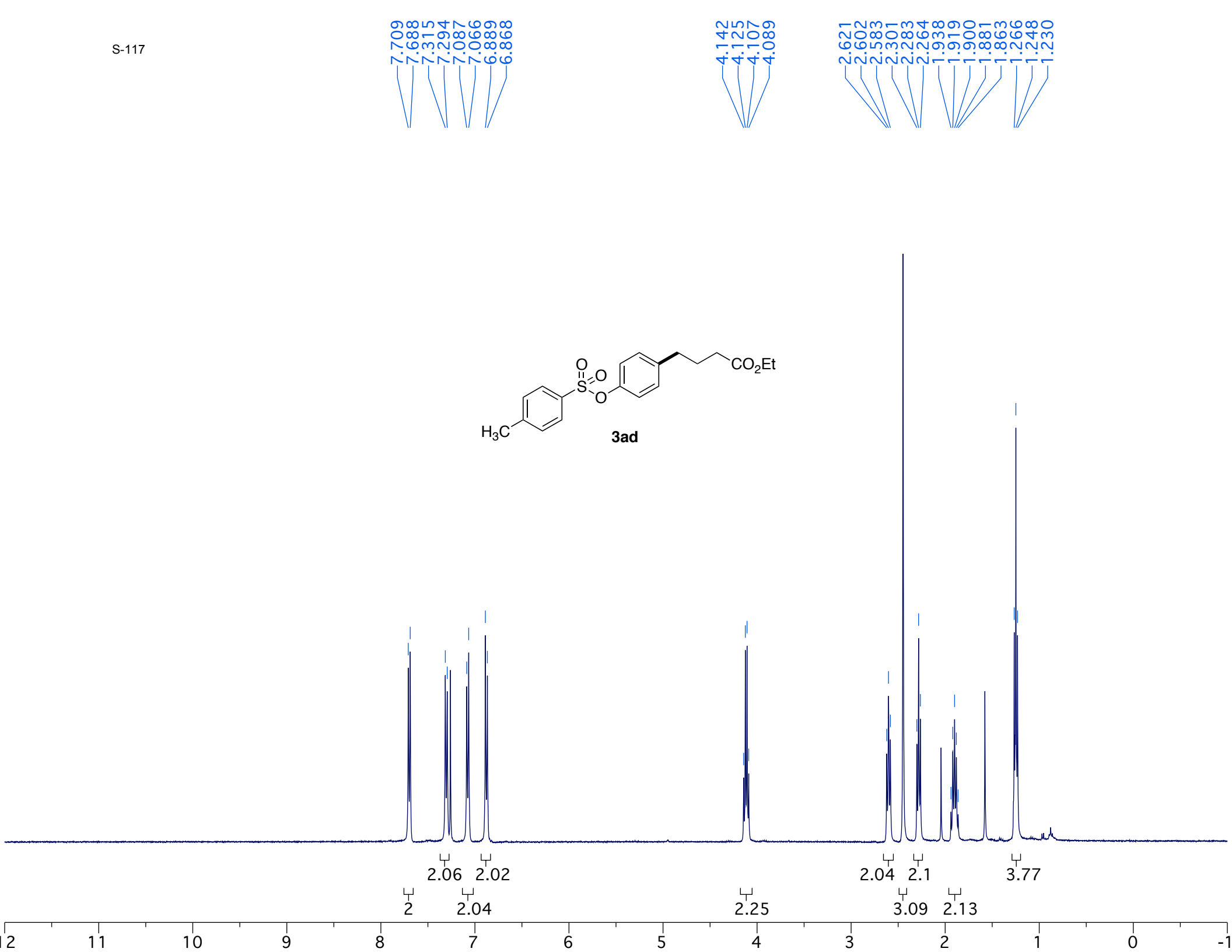
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1.919
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1.863
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1.248
1.230
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S
O
CO2Et
H3C
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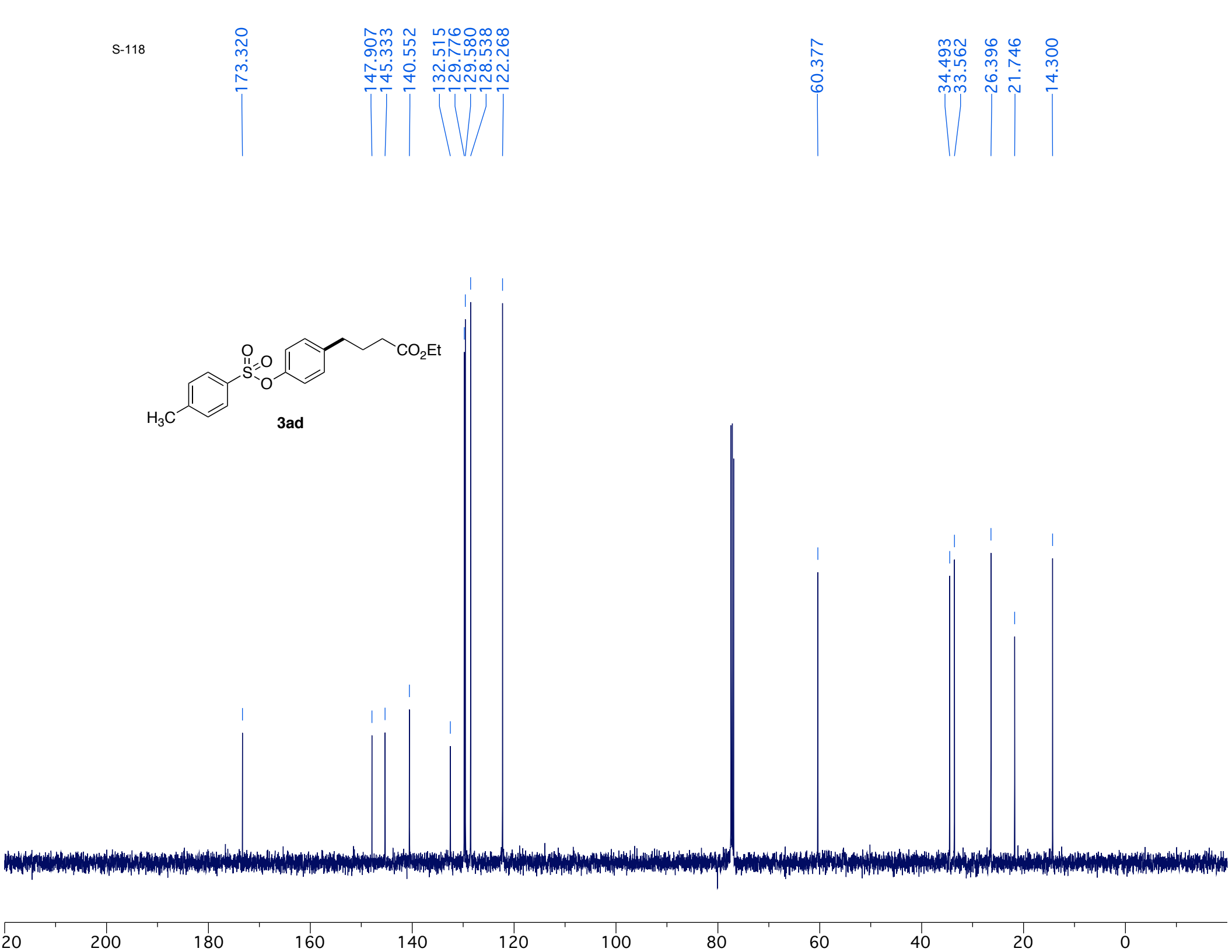
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O
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40
20
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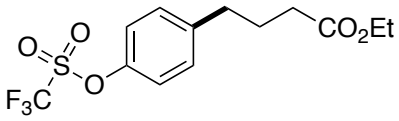

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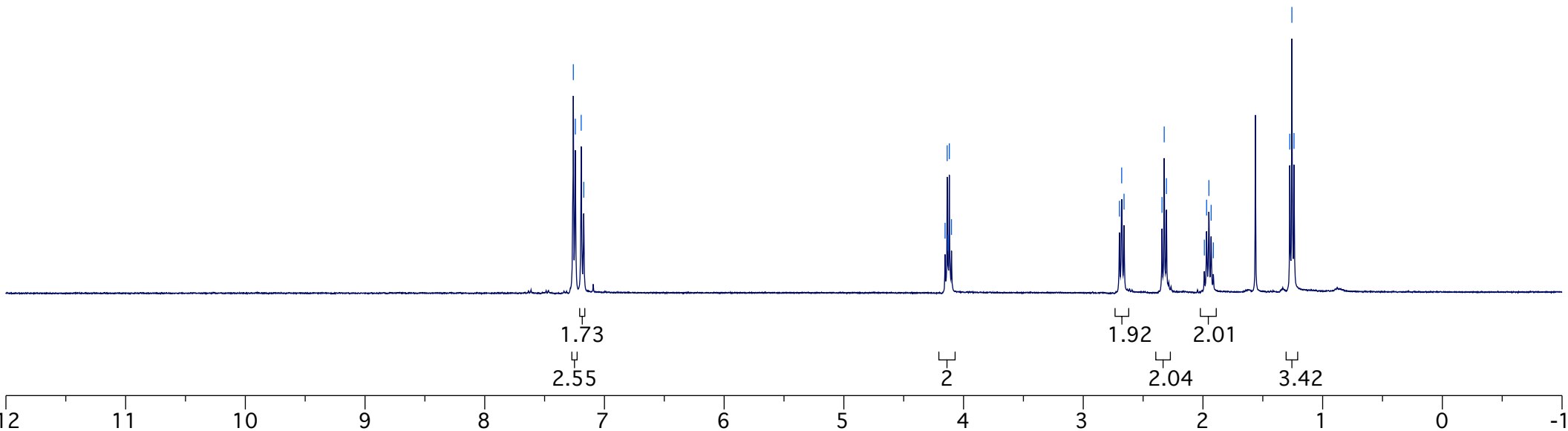

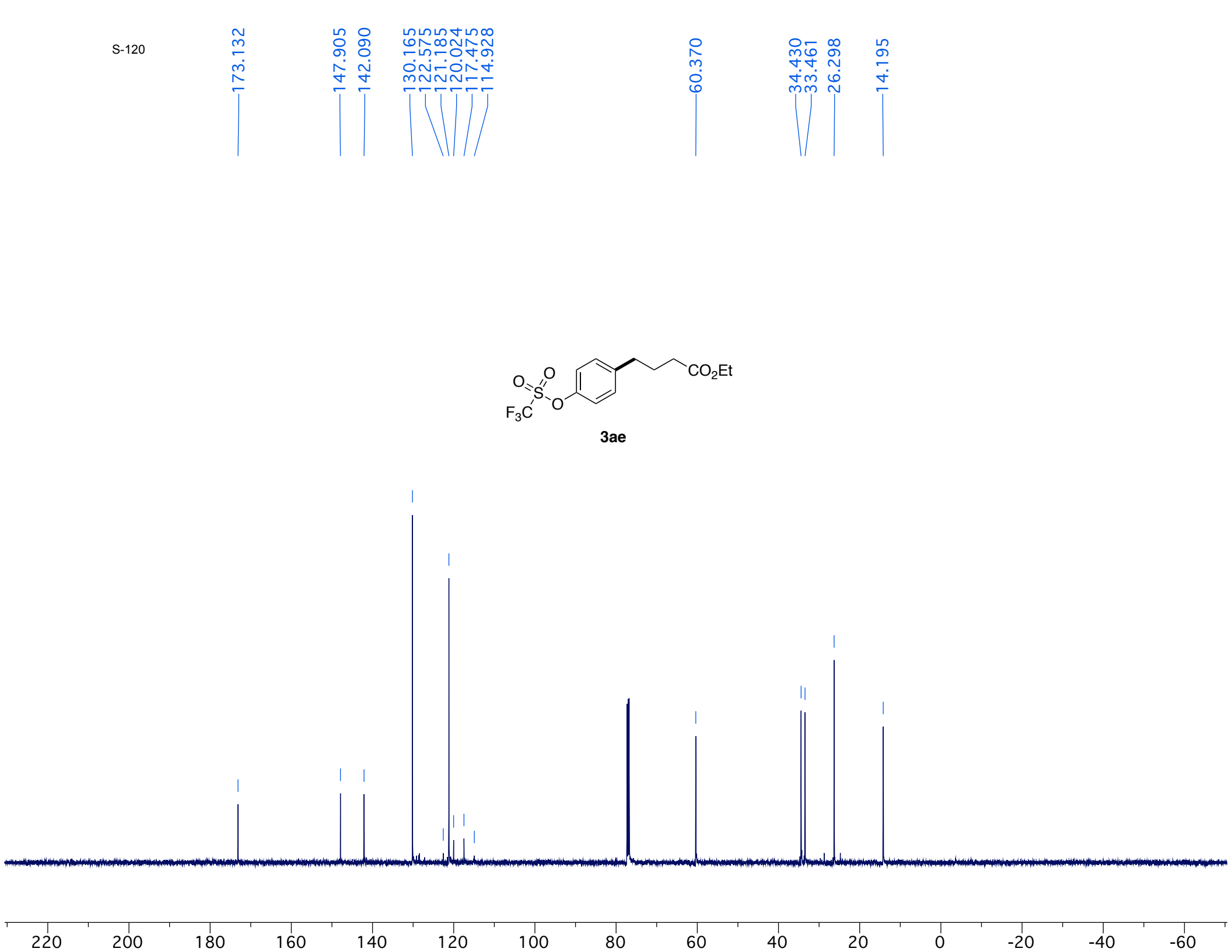
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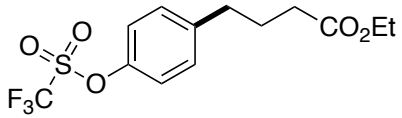

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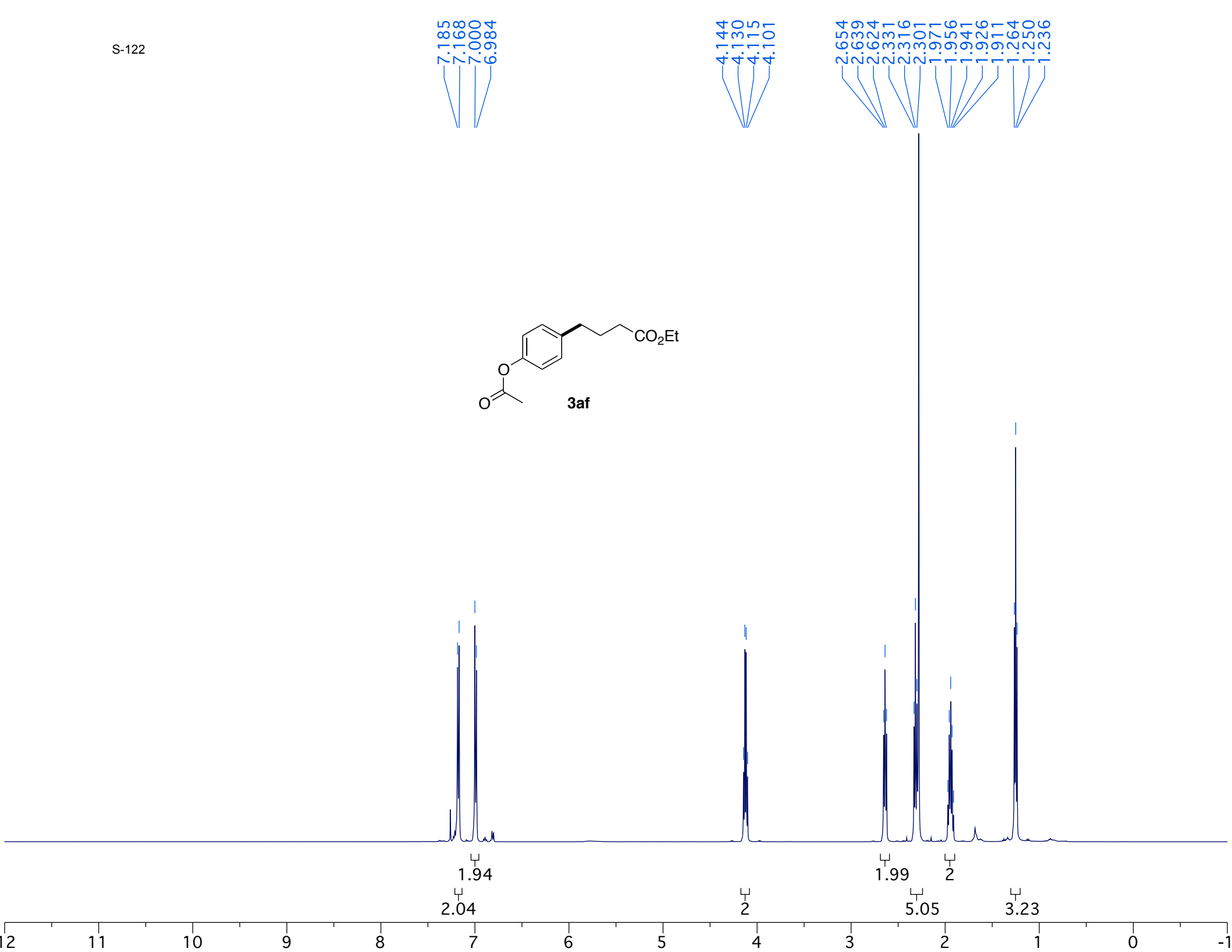
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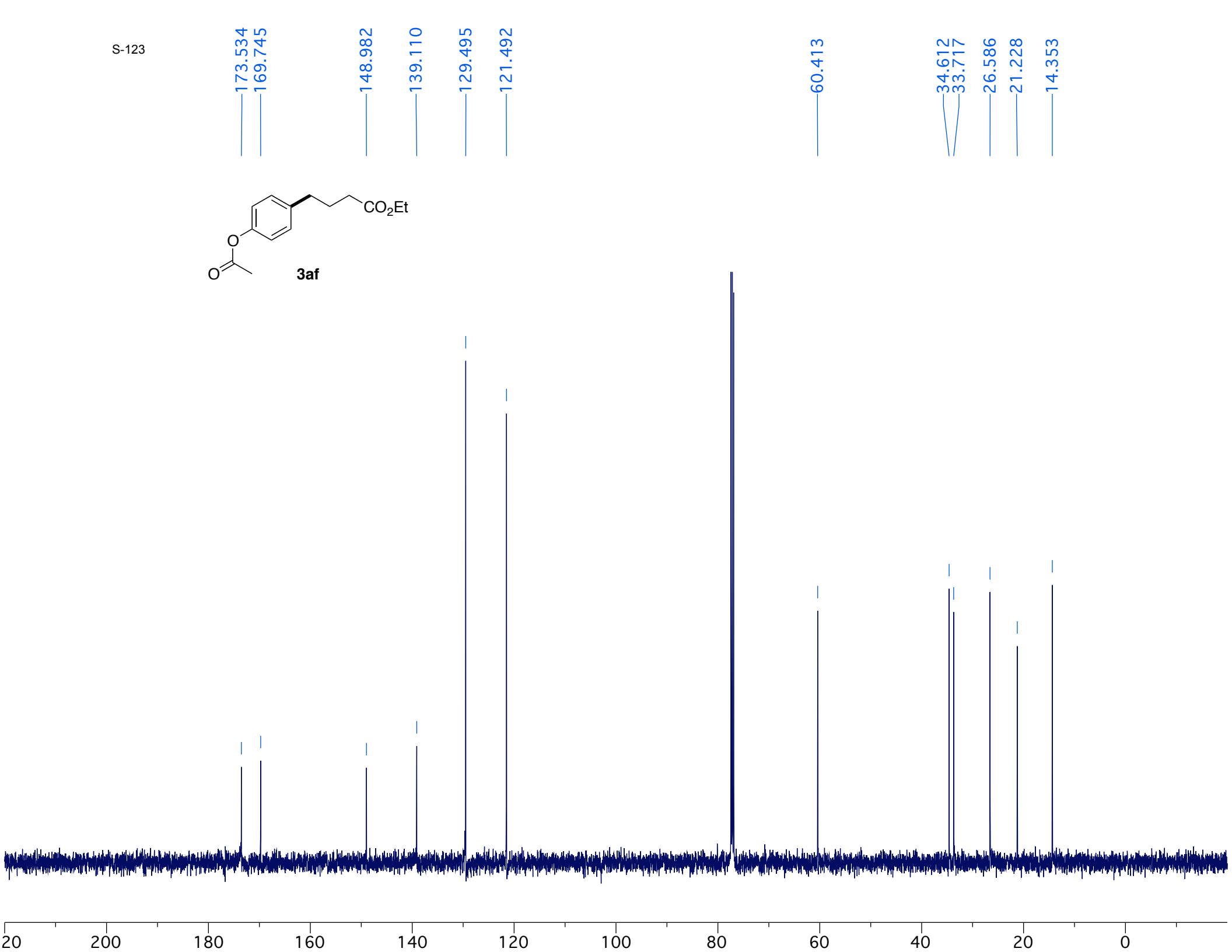
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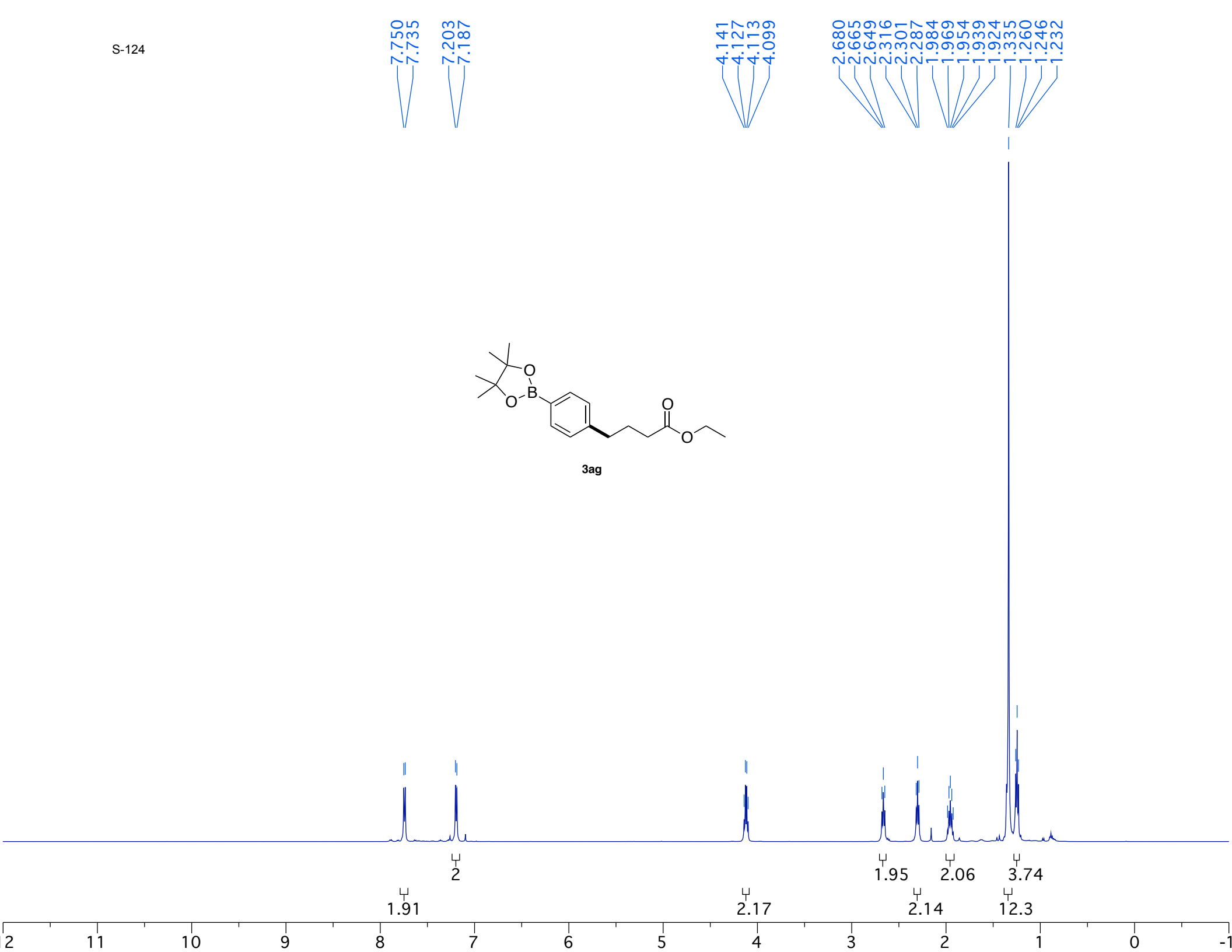
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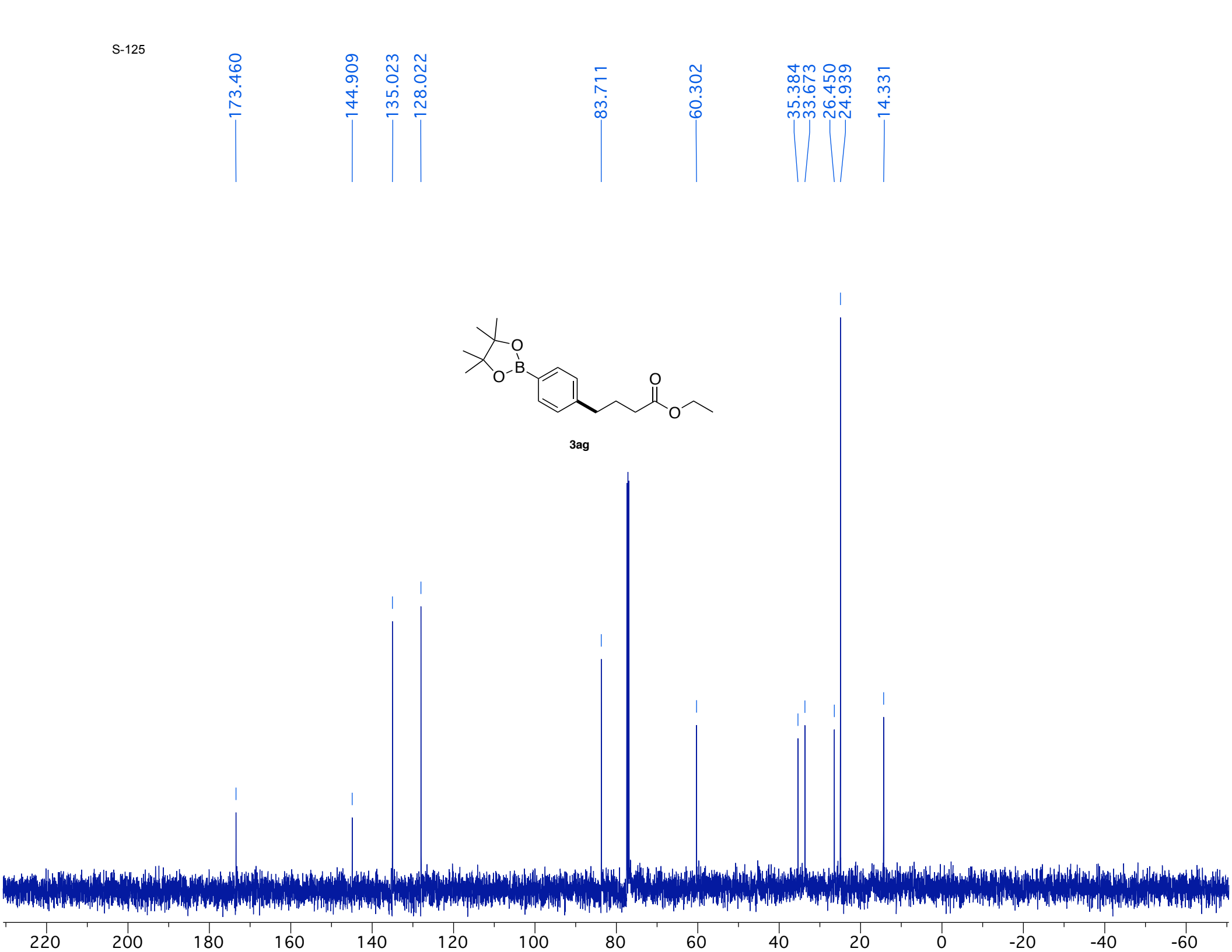
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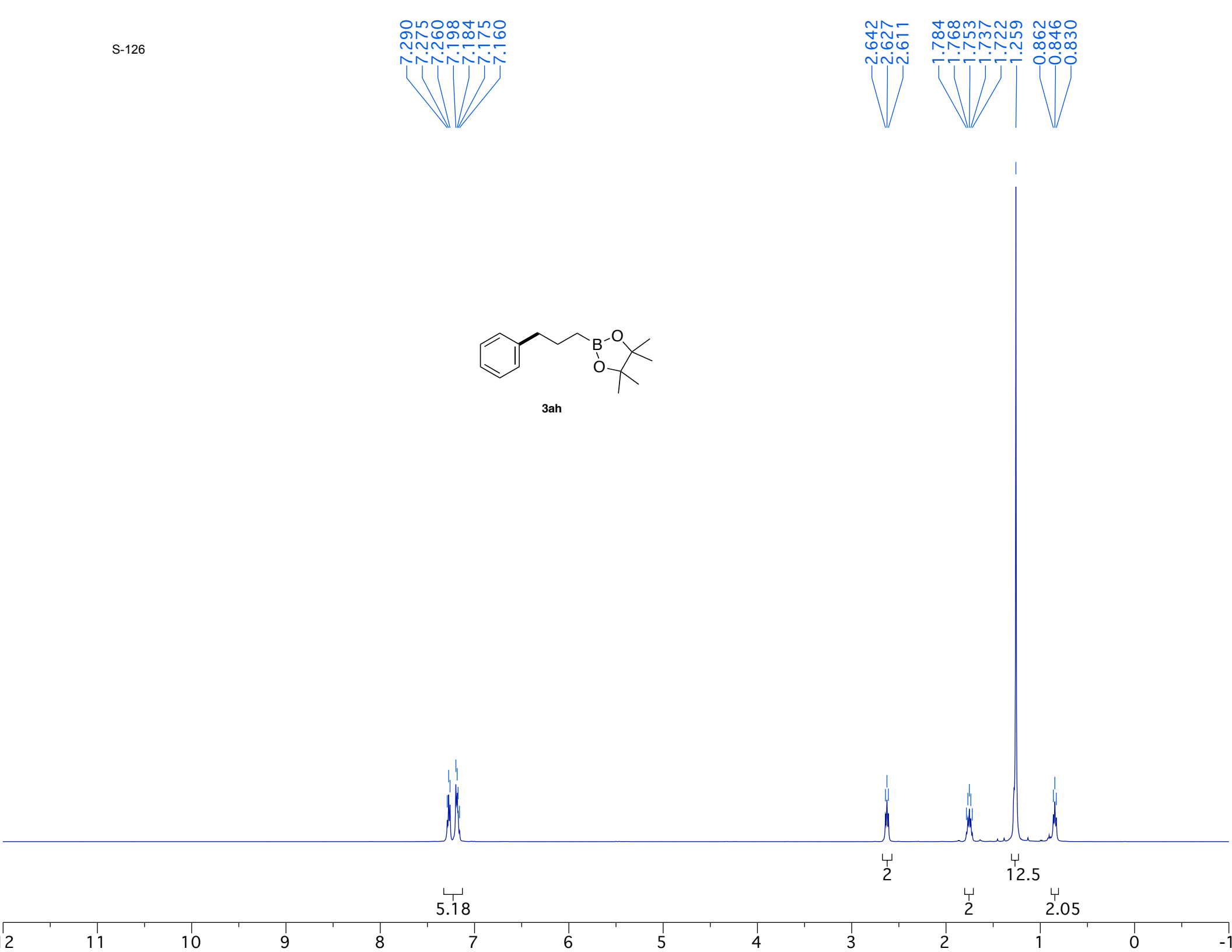
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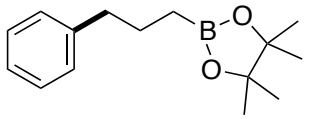

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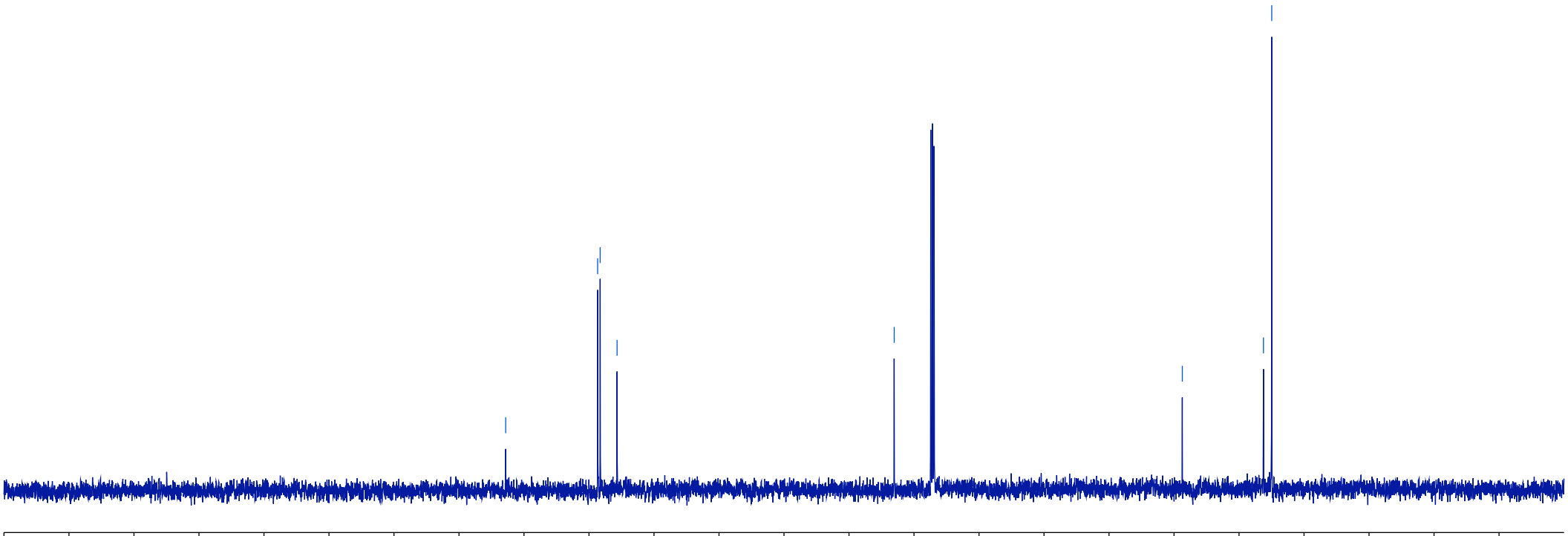

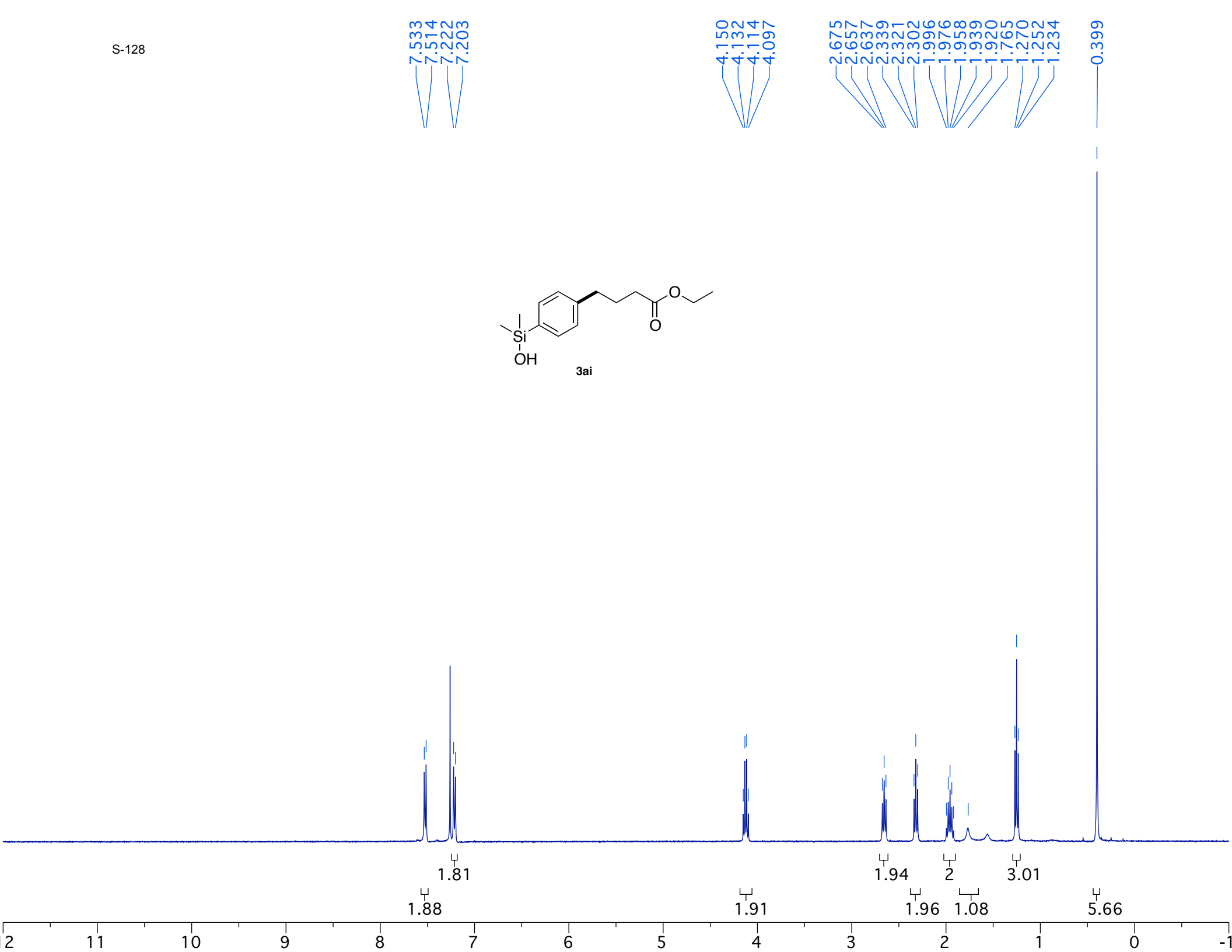
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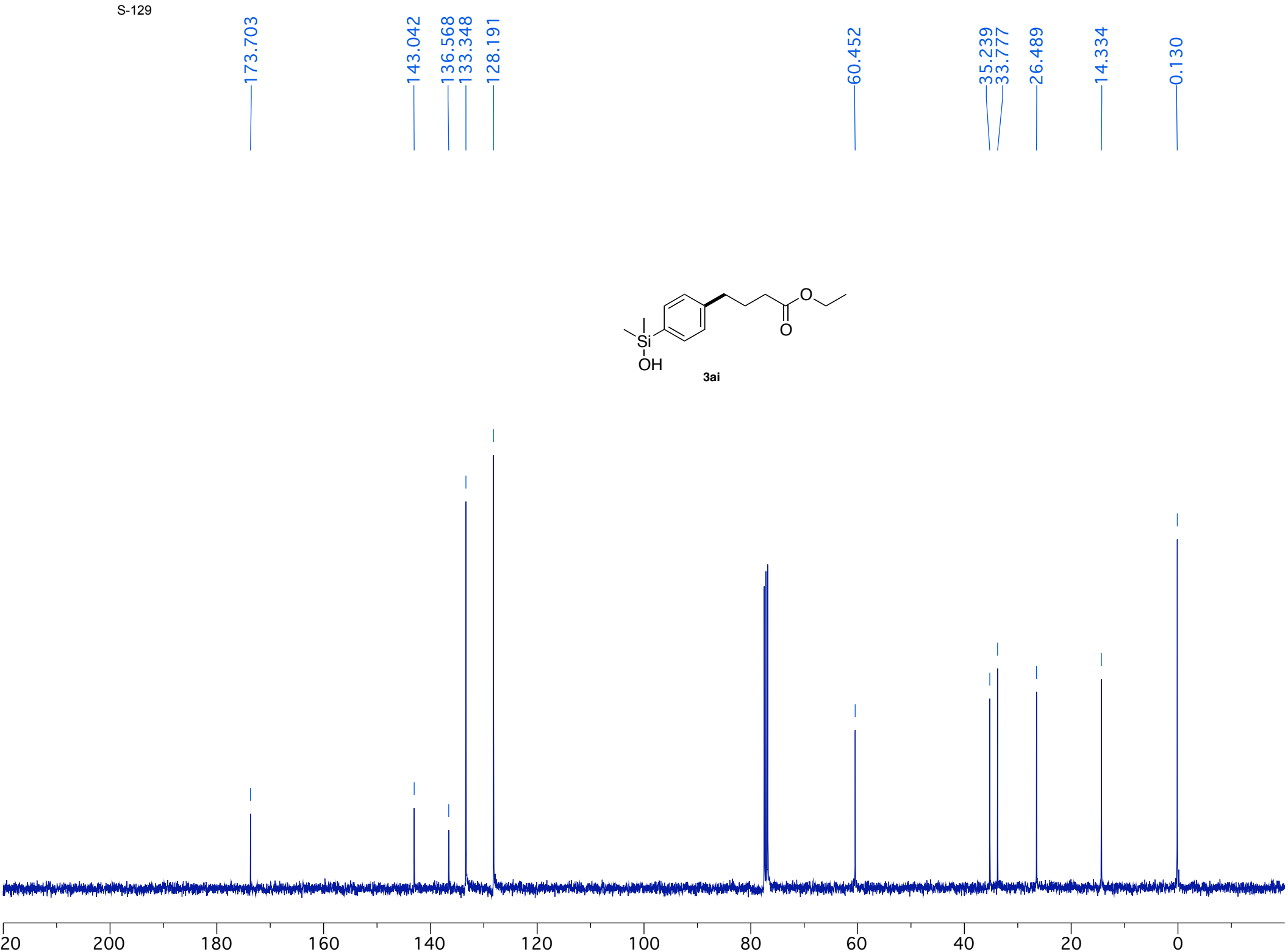
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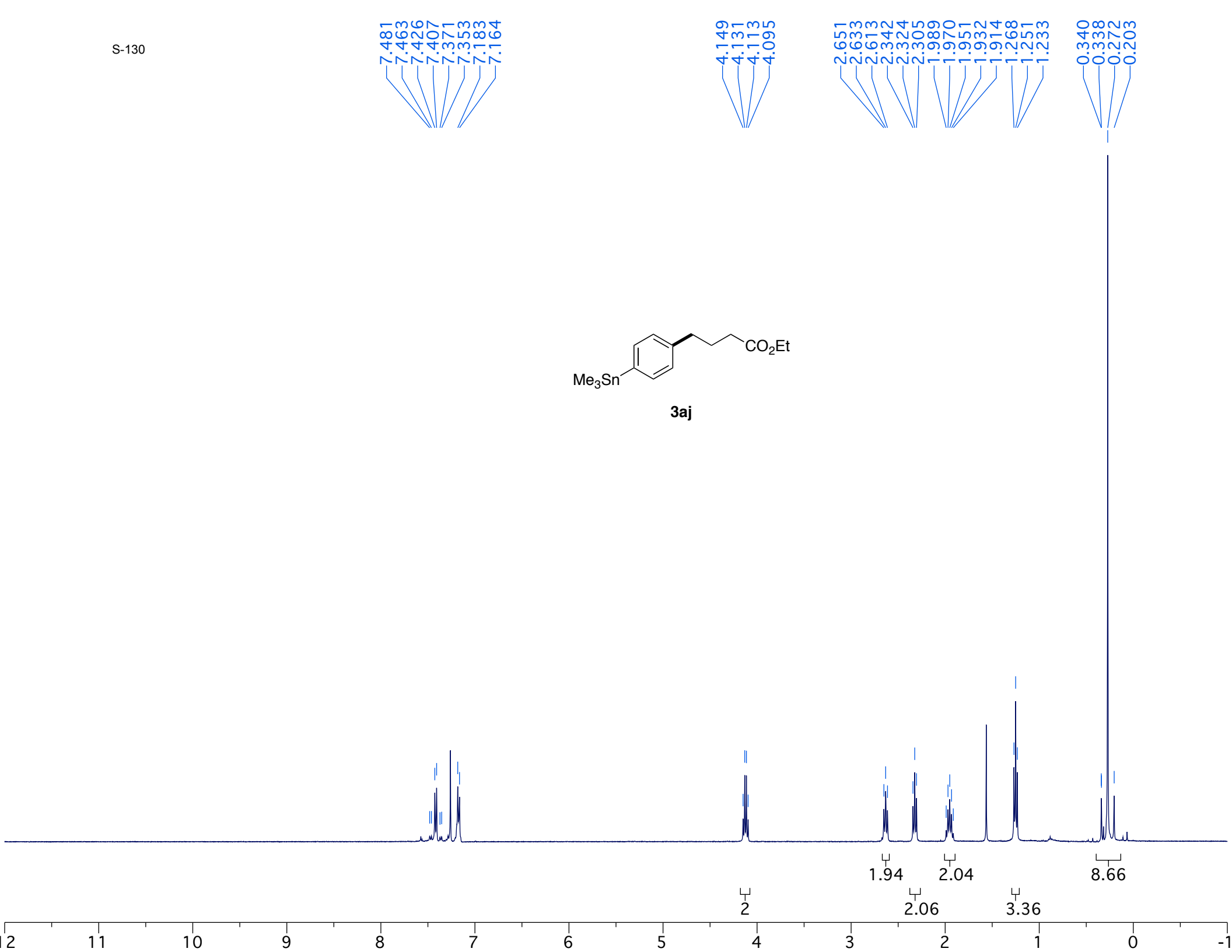
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Me3Sn
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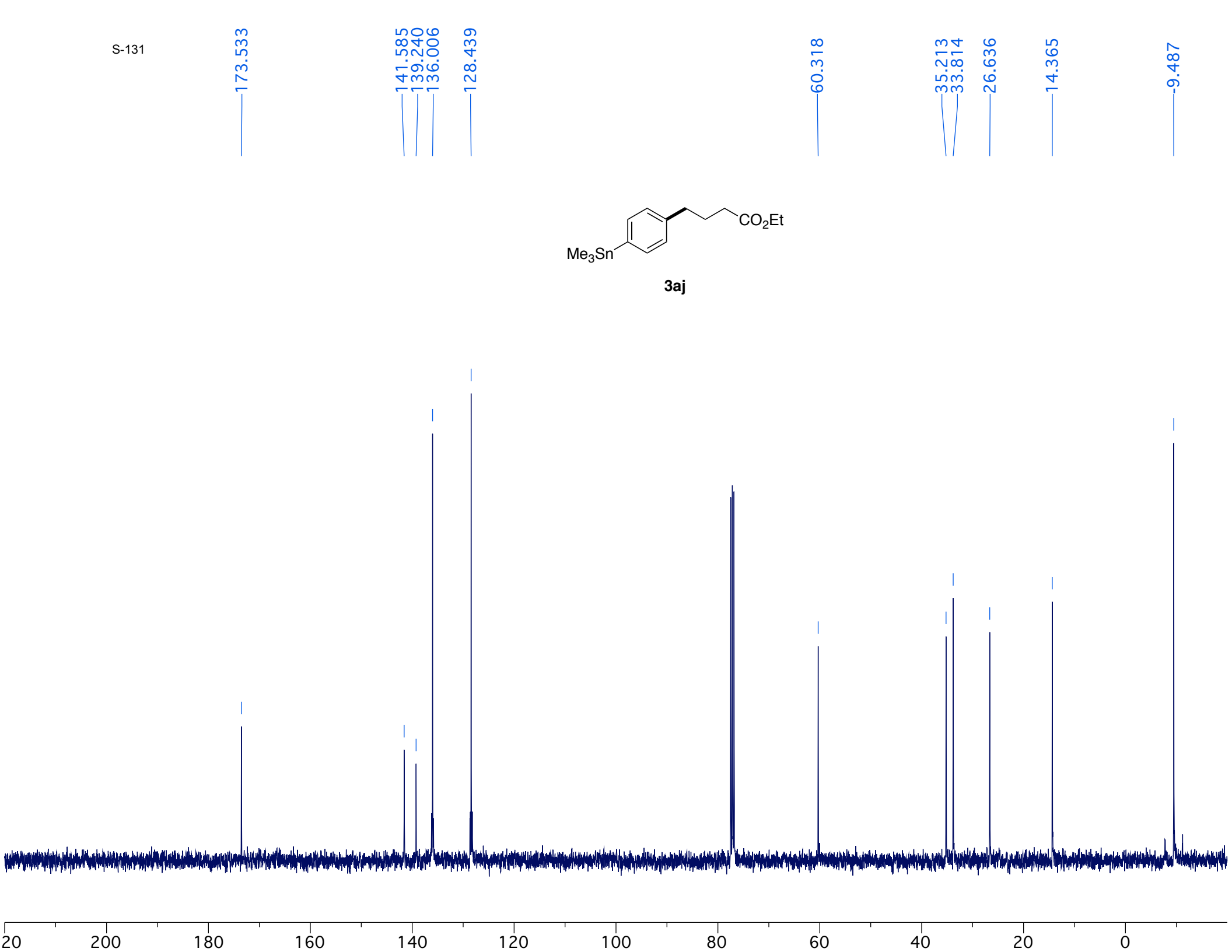
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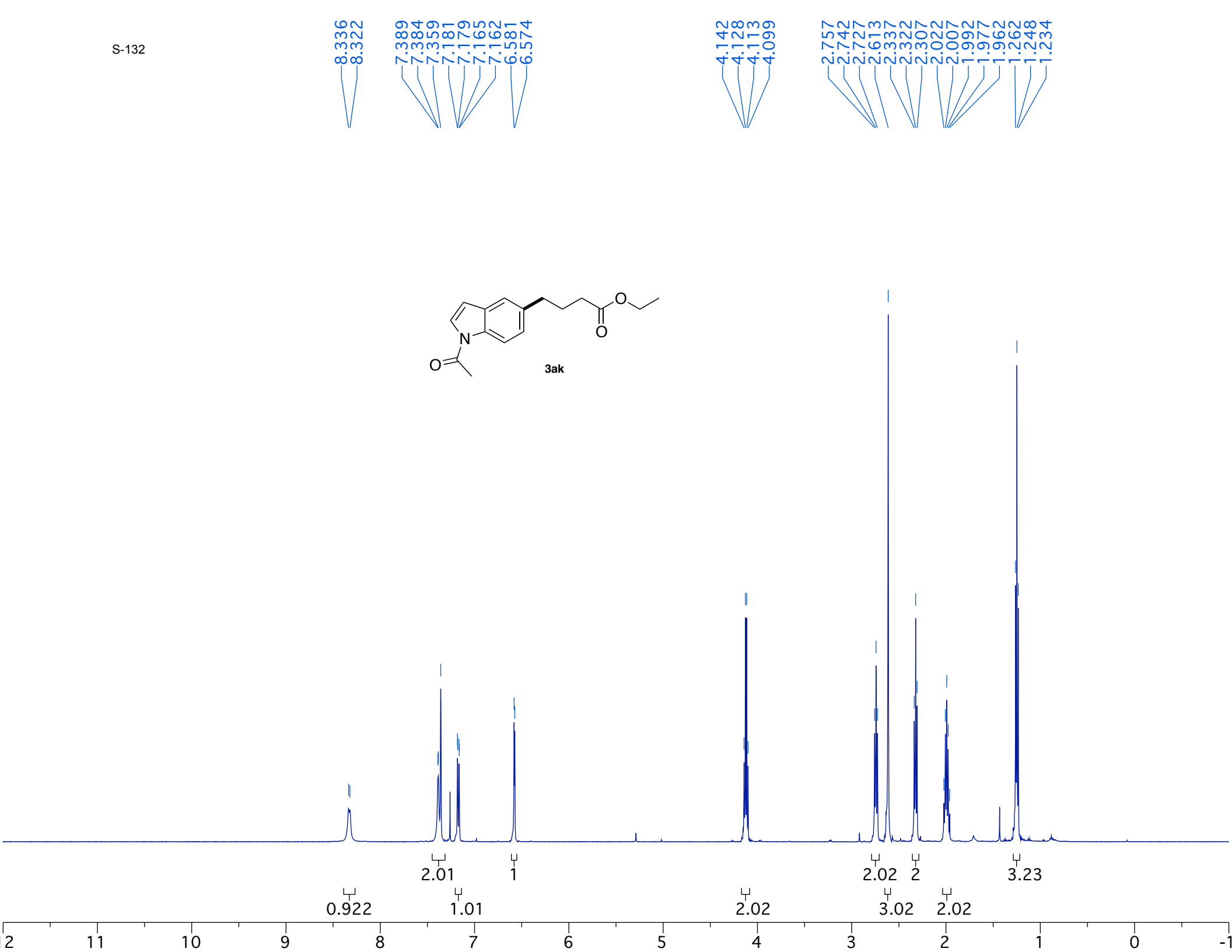
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1.234
O
O
N
O
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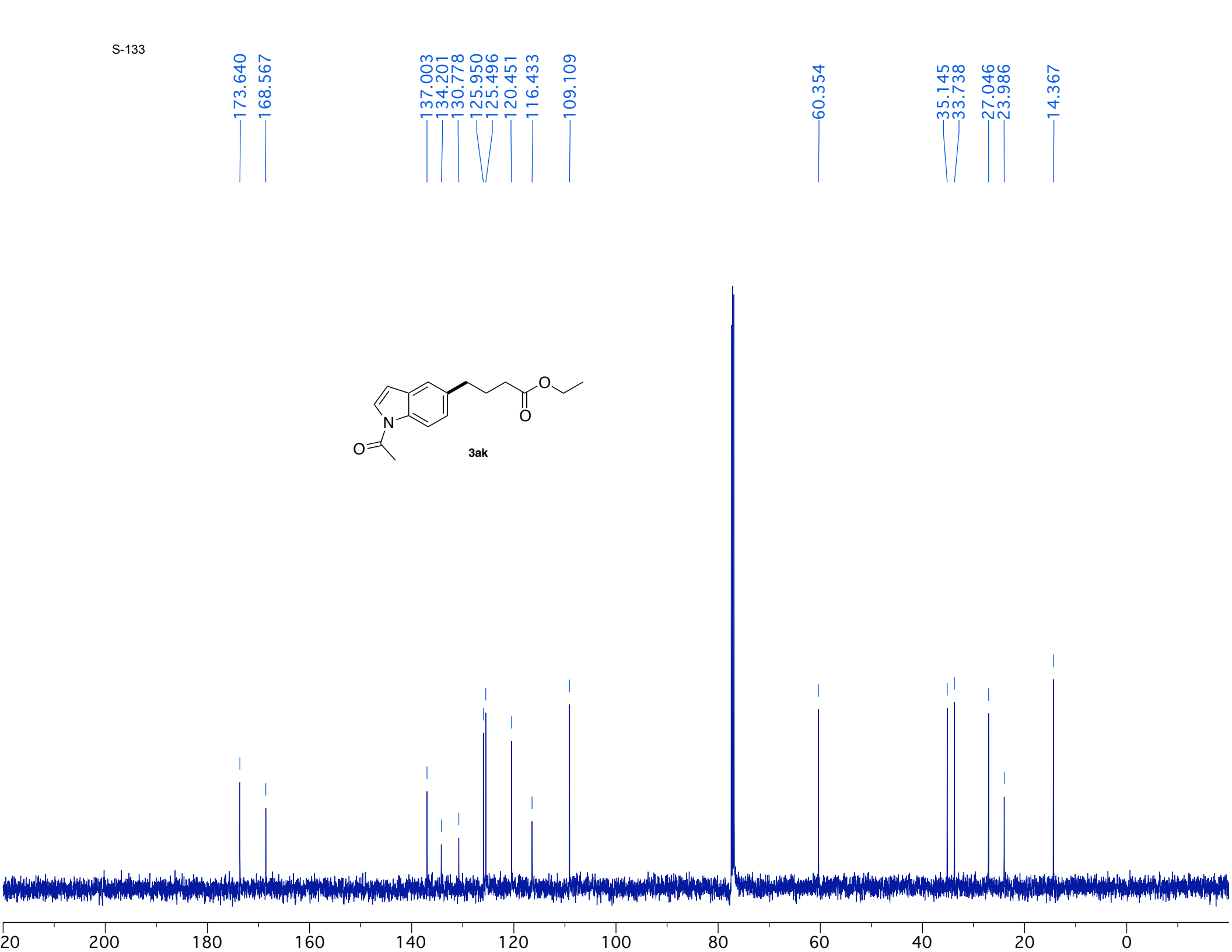
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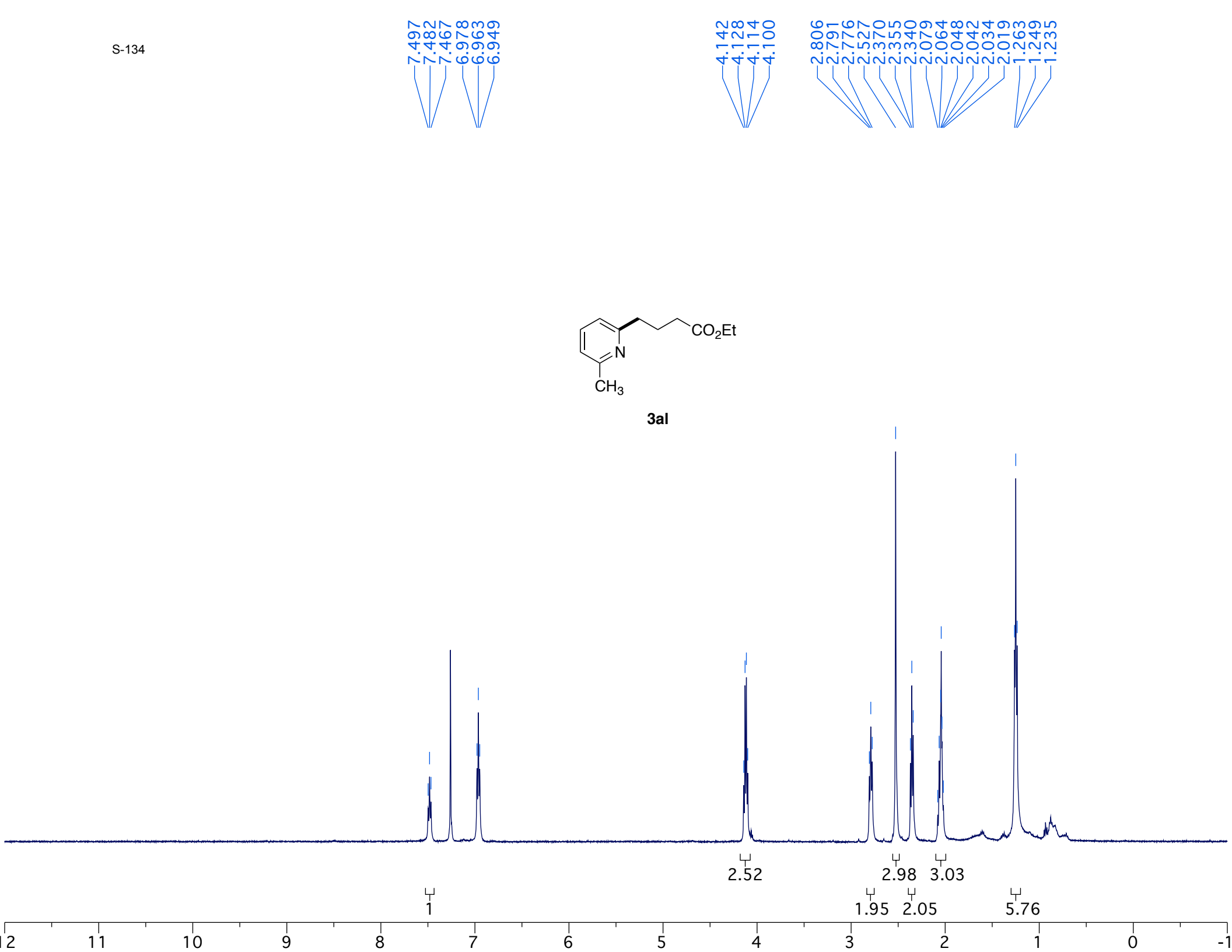
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CO2Et
N
CH3
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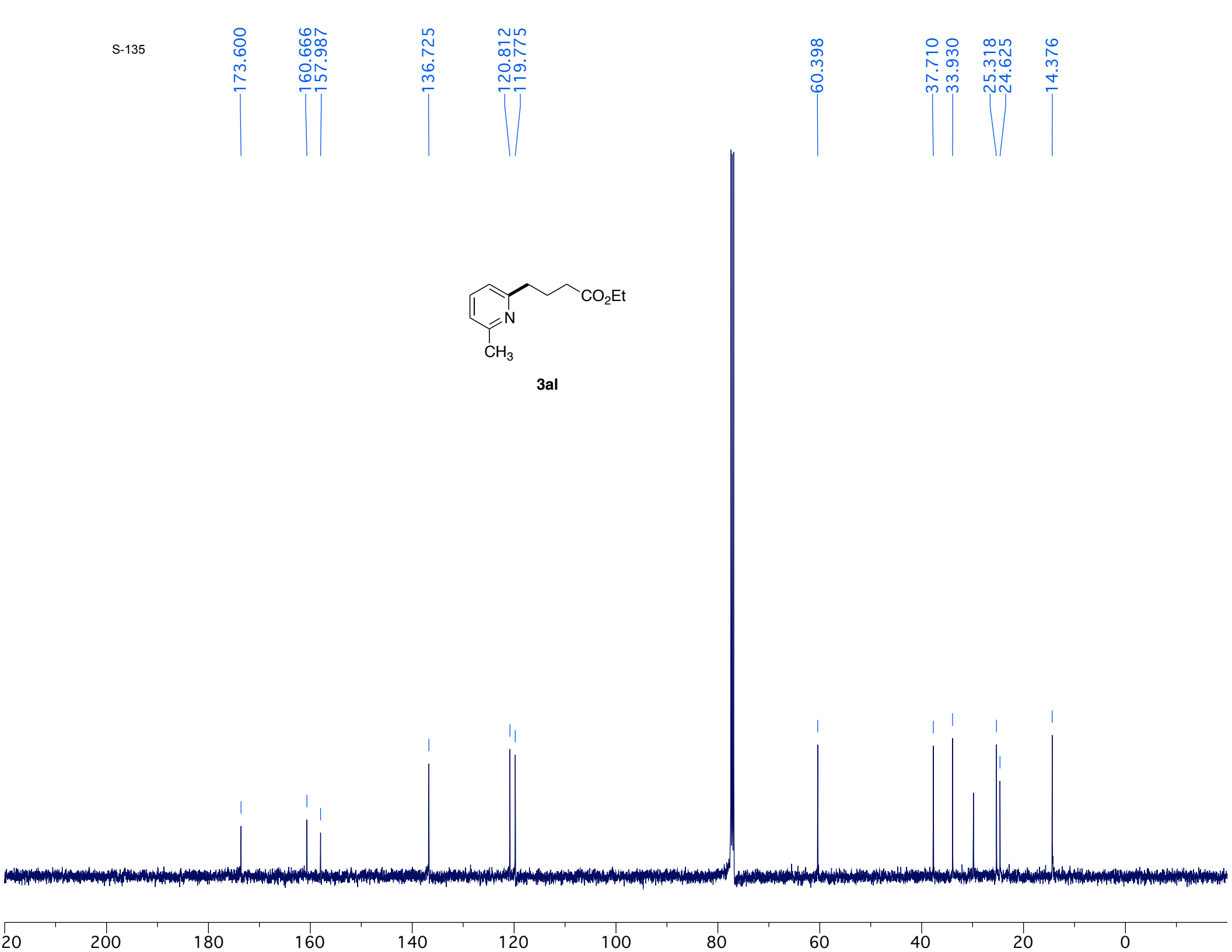
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0