Supplementary Information (SI) for Green Chemistry.

Supporting Information

The Low-Temperature Selective Oxidation of Alcohols and a One-Pot Oxidative Esterification Using an IBS(III/V)/Oxone Catalysis

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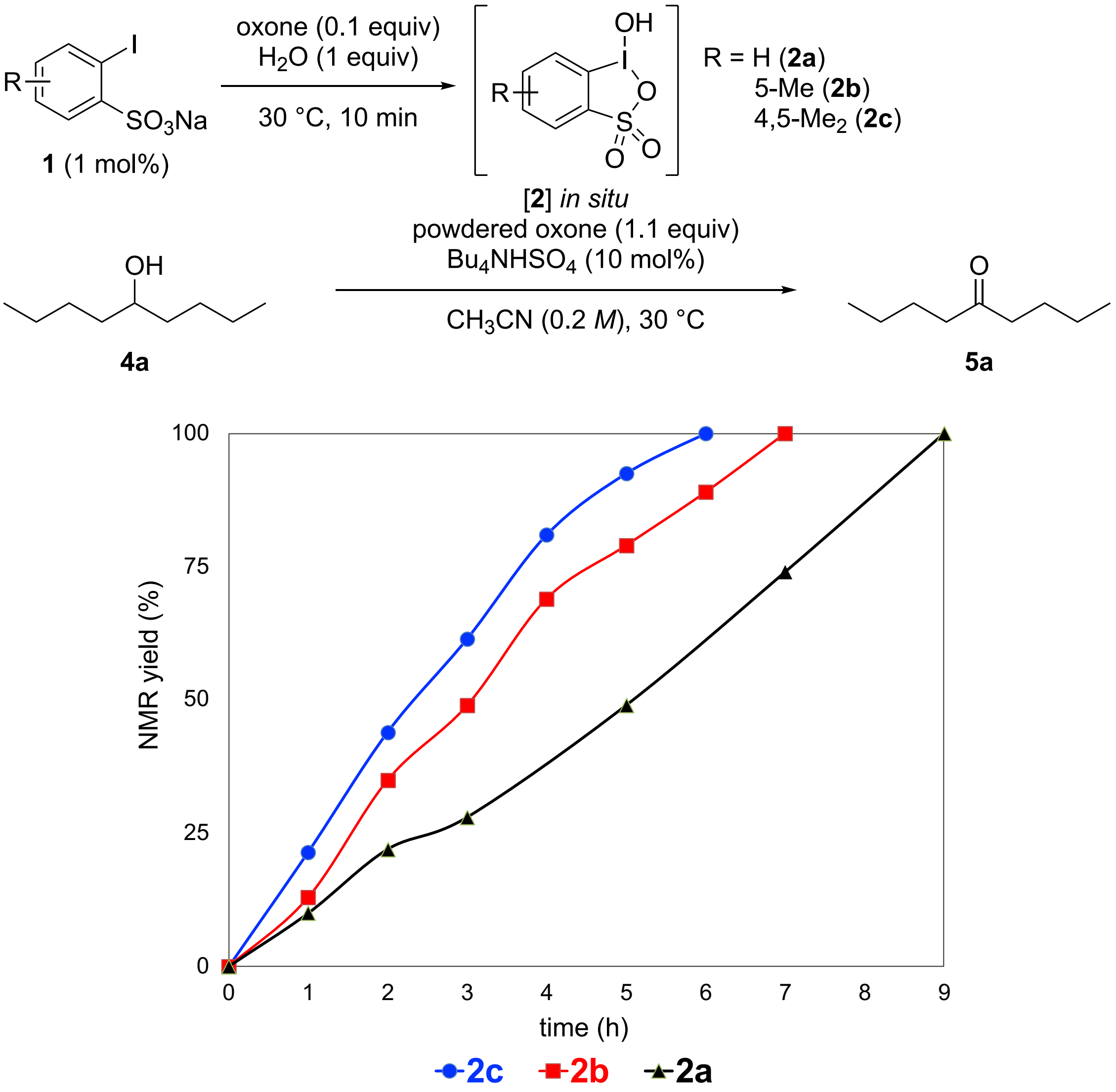
Materials and Methods

Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm from the solvent resonance (CD_3CN: 1.94 ppm) or Me_4Si resonance (0.00 ppm; $CDCl_3$) as internal standard. Data were recorded as follows: the chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; quin = quintet; sept = septet; m = multiplet; brs = broad singlet), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometer at ambient temperature. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$: 77.00 ppm, CD_3CN: 1.32 ppm). Chemical shifts were recorded in ppm from the solvent resonance employed as the external standard ($CFCl_3$ at 0 ppm). High-resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Center, Nagoya University [JEOL JMS-700 (FAB). HRMS were obtained by fast atom bombardment (FAB) using a double-focusing magnetic sector mass spectrometer. Elemental analyses were performed on a Yanaco MT-6 analyzer. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm or silica gel 60 NH_2 F_{254}s 0.20 mm) were used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385). An oil bath was used for reactions that required heating.

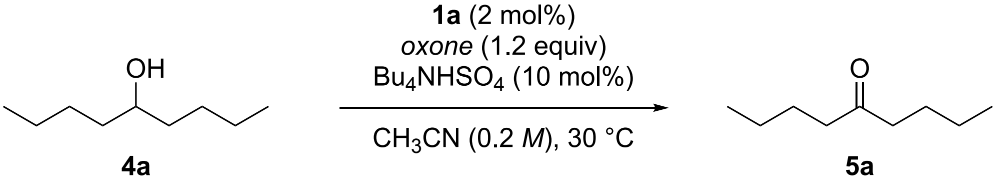
In experiments that required dry solvents, toluene, benzene, diethyl ether (Et_2O), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) and dichloromethane (CH_2Cl_2) were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. as the “anhydrous” and stored over 4A molecular sieves. Other solvents were purchased from Aldrich Chemical Co., Inc., FUJIFILM Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry Co., Ltd. and used without further purification. Oxone ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) and peracetic acid (9% acetic acid solution) were purchased from Aldrich Chemical Co., Inc. and used without further purification. Powdered oxone was prepared according to the known procedure.[1] Other commercially available simple chemicals were analytical-grade and used without further purification.

Additional Information

Scheme S1. Comparison of IBS(III) Species 2a–2c in Method C



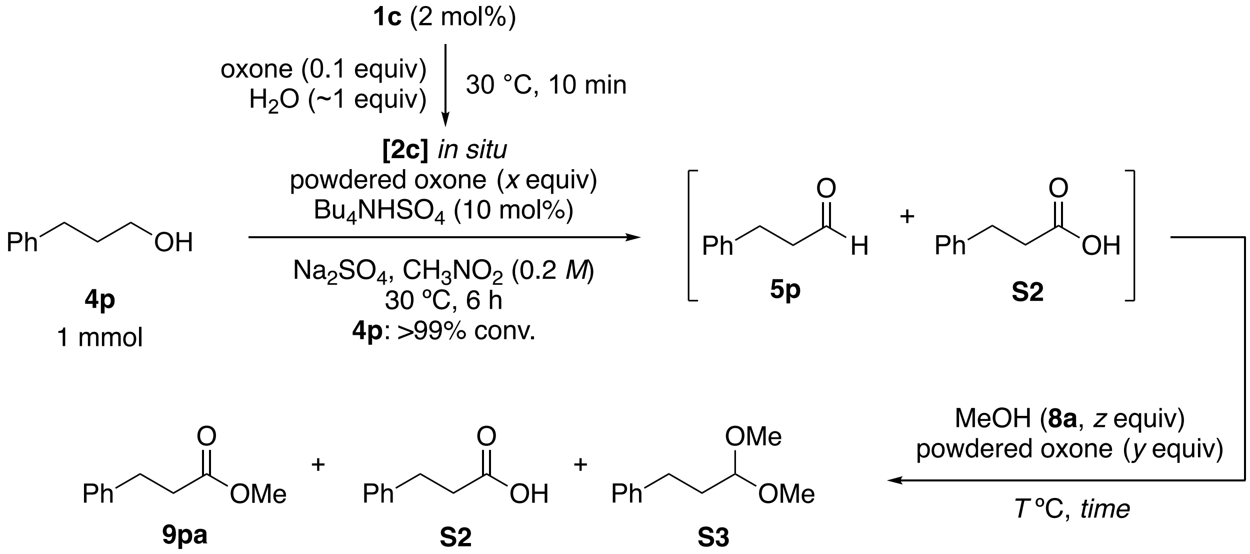
Scheme S2. Effect of “Buffered” Oxone on the Oxidation Reaction



oxone:	powdered oxone	10 h, >95%
	“buffered” oxone	11 h, 73–77%

$$\text{powdered oxone (1.2 equiv)} \xrightarrow[\text{Na}_2\text{SO}_4\text{ (1g), CH}_3\text{CN, RT, 24}\ \textit{premixing}]{\text{K}_2\text{CO}_3\text{ (0.3 or 0.6 equiv)}} \text{“buffered” oxone}$$

Table S1. Optimization of Reaction Conditions for Oxidative Esterification



Entry	Oxone (equiv)		**8a** (equiv)	T (°C)	*Time* (h)	Yield (%)[a]		
	x	y	z			**9pa**	**S2**	**S3**
1	2.4	0	2	30	24	44	18	32
2	2.4	0	2	50	18	51	15	34
3	3.6	0	2	30	18	80	5	12
4	1.6	2.0	2	30	14	66	9	25
5	1.6	2.0	10	30	18	60	10	30
6	1.6	2.0	20	30	18	75	6	19
7	1.6	2.0	30	30	18	90	2	7
8	1.6	2.0	40	30	18	90	3	7
9	1.6	2.0	30	30	24	95 (92)[b]	5	–

[a] ^{1}H NMR analysis. [b] Isolated yield.

EcoScale Calculation

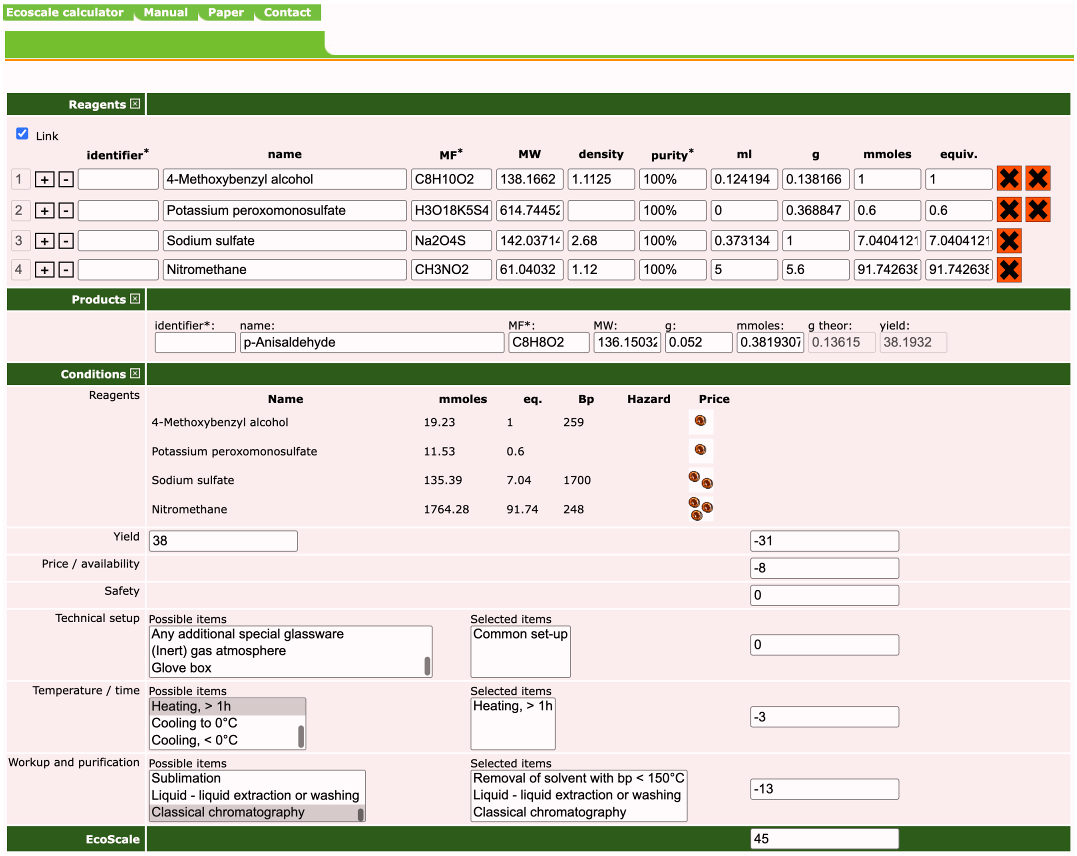
EcoScale scores were calculated for representative reactions to provide a quantitative assessment of the greenness of the methods. The calculations were performed for a 1 mmol scale reaction using the online EcoScale Calculator (available at https://ecoscale.cheminfo.org/calculator), which is based on the work of Van Aken et al.[2]

Table S2. Comparison of The EcoScale for Our Previous and Present Works[a]

	Previous work[1a]	This work
Oxidation of **4b** to **5b**	45	76
Oxidation of **4c** to **5c**	19.5	68

[a] The catalysts employed (e.g., **1a**, **1c**, **2c**) are not commercially listed in the EcoScale calculator database. However, as they are readily synthesized in high yields from inexpensive precursors and common reagents,[1a] the price penalty for these catalysts was considered to be zero in our EcoScale calculations.

Previous method: Oxidation of **4b** to **5b**



Reagents

☑ Link

		identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.	
1	+ -		4-Methoxybenzyl alcohol	C8H10O2	138.1662	1.1125	100%	0.124194	0.138166	1	1	☒ ☒
2	+ -		Potassium peroxomonosulfate	H3O18K5S4	614.74452		100%	0	0.368847	0.6	0.6	☒ ☒
3	+ -		Sodium sulfate	Na2O4S	142.03714	2.68	100%	0.373134	1	7.0404121	7.0404121	☒
4	+ -		Nitromethane	CH3NO2	61.04032	1.12	100%	5	5.6	91.742638	91.742638	☒

Products

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	p-Anisaldehyde	C8H8O2	136.15032	0.052	0.3819307	0.13615	38.1932

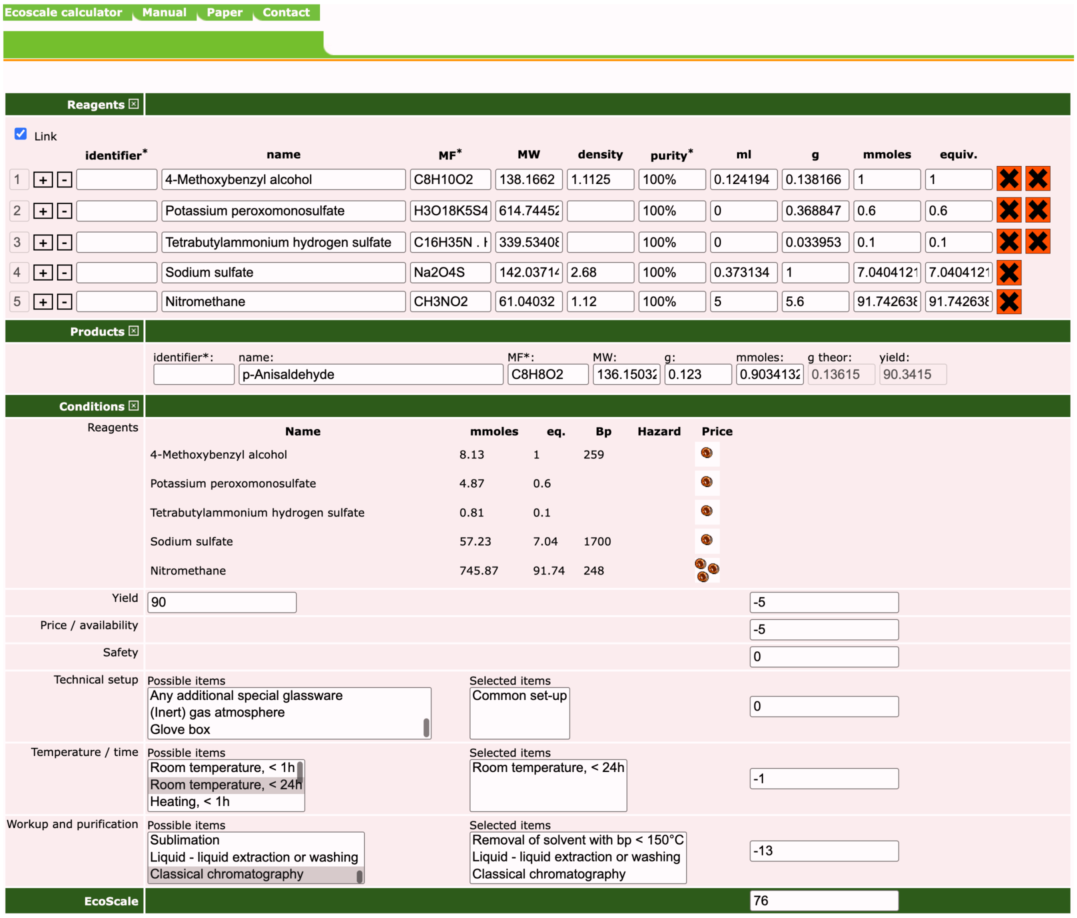
Conditions

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
4-Methoxybenzyl alcohol	19.23	1	259		●
Potassium peroxomonosulfate	11.53	0.6			●
Sodium sulfate	135.39	7.04	1700		●●
Nitromethane	1764.28	91.74	248		●●●

	Possible items	Selected items	Score
Yield	38		-31
Price / availability			-8
Safety			0
Technical setup	Any additional special glassware (Inert) gas atmosphere Glove box	Common set-up	0
Temperature / time	Heating, > 1h Cooling to 0°C Cooling, < 0°C	Heating, > 1h	-3
Workup and purification	Sublimation Liquid - liquid extraction or washing Classical chromatography	Removal of solvent with bp < 150°C Liquid - liquid extraction or washing Classical chromatography	-13
EcoScale			45

Current method: Oxidation of **4b** to **5b**



Reagents

☑ Link

		identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.	
1	+ -		4-Methoxybenzyl alcohol	C8H10O2	138.1662	1.1125	100%	0.124194	0.138166	1	1	☒ ☒
2	+ -		Potassium peroxomonosulfate	H3O18K5S4	614.74452		100%	0	0.368847	0.6	0.6	☒ ☒
3	+ -		Tetrabutylammonium hydrogen sulfate	C16H35N . H	339.53408		100%	0	0.033953	0.1	0.1	☒ ☒
4	+ -		Sodium sulfate	Na2O4S	142.03714	2.68	100%	0.373134	1	7.0404121	7.0404121	☒
5	+ -		Nitromethane	CH3NO2	61.04032	1.12	100%	5	5.6	91.742638	91.742638	☒

Products

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	p-Anisaldehyde	C8H8O2	136.15032	0.123	0.9034132	0.13615	90.3415

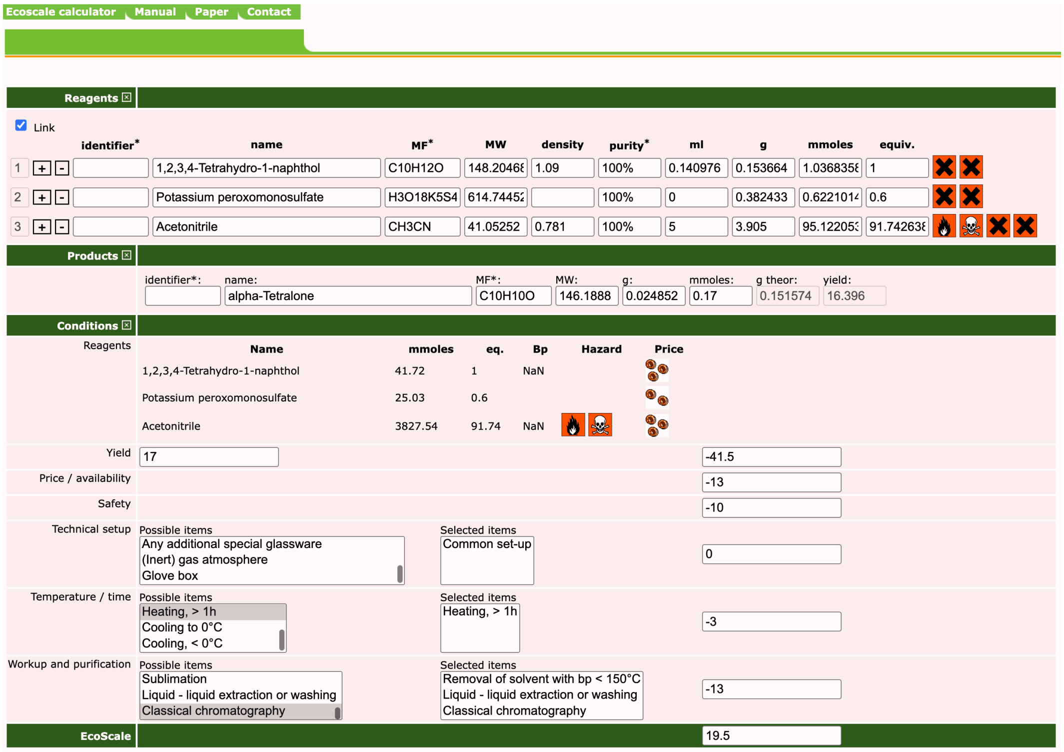
Conditions

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
4-Methoxybenzyl alcohol	8.13	1	259		●
Potassium peroxomonosulfate	4.87	0.6			●
Tetrabutylammonium hydrogen sulfate	0.81	0.1			●
Sodium sulfate	57.23	7.04	1700		●
Nitromethane	745.87	91.74	248		●●●

	Possible items	Selected items	Score
Yield	90		-5
Price / availability			-5
Safety			0
Technical setup	Any additional special glassware (Inert) gas atmosphere Glove box	Common set-up	0
Temperature / time	Room temperature, < 1h Room temperature, < 24h Heating, < 1h	Room temperature, < 24h	-1
Workup and purification	Sublimation Liquid - liquid extraction or washing Classical chromatography	Removal of solvent with bp < 150°C Liquid - liquid extraction or washing Classical chromatography	-13
EcoScale			76

Previous method: Oxidation of **4c** to **5c**



Reagents ☒

☑ Link

		identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.	
1	+ -		1,2,3,4-Tetrahydro-1-naphthol	C10H12O	148.2046	1.09	100%	0.140976	0.153664	1.036835	1	✖ ✖
2	+ -		Potassium peroxomonosulfate	H3O18K5S4	614.7445		100%	0	0.382433	0.622101	0.6	✖ ✖
3	+ -		Acetonitrile	CH3CN	41.05252	0.781	100%	5	3.905	95.12205	91.74263	🔥 ☠ ✖ ✖

Products ☒

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	alpha-Tetralone	C10H10O	146.1888	0.024852	0.17	0.151574	16.396

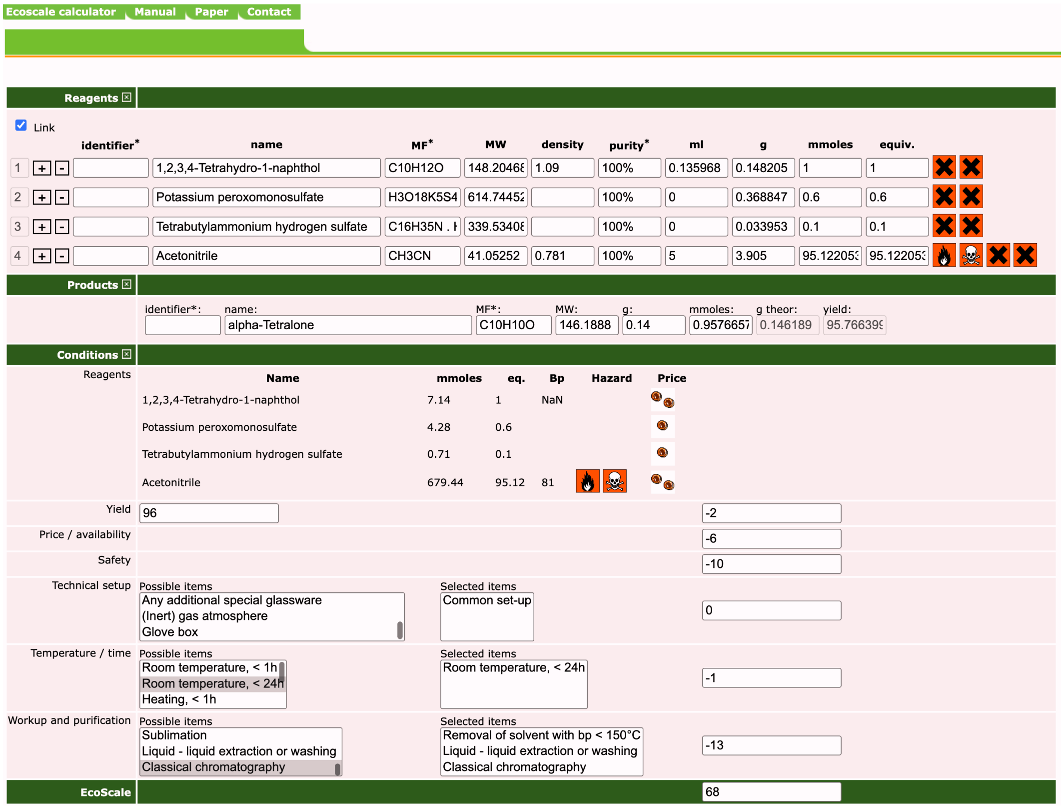
Conditions ☒

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
1,2,3,4-Tetrahydro-1-naphthol	41.72	1	NaN		●●●
Potassium peroxomonosulfate	25.03	0.6			●●
Acetonitrile	3827.54	91.74	NaN	🔥 ☠	●●●

Yield	17		-41.5
Price / availability			-13
Safety			-10
Technical setup	Possible items Any additional special glassware (Inert) gas atmosphere Glove box	Selected items Common set-up	0
Temperature / time	Possible items Heating, > 1h Cooling to 0°C Cooling, < 0°C	Selected items Heating, > 1h	-3
Workup and purification	Possible items Sublimation Liquid - liquid extraction or washing Classical chromatography	Selected items Removal of solvent with bp < 150°C Liquid - liquid extraction or washing Classical chromatography	-13
EcoScale			19.5

Current method: Oxidation of **4c** to **5c**



Reagents ☒

☑ Link

		identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.	
1	+ -		1,2,3,4-Tetrahydro-1-naphthol	C10H12O	148.2046	1.09	100%	0.135968	0.148205	1	1	✖ ✖
2	+ -		Potassium peroxomonosulfate	H3O18K5S4	614.7445		100%	0	0.368847	0.6	0.6	✖ ✖
3	+ -		Tetrabutylammonium hydrogen sulfate	C16H35N .	339.5340		100%	0	0.033953	0.1	0.1	✖ ✖
4	+ -		Acetonitrile	CH3CN	41.05252	0.781	100%	5	3.905	95.12205	95.12205	🔥 ☠ ✖ ✖

Products ☒

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	alpha-Tetralone	C10H10O	146.1888	0.14	0.957665	0.146189	95.76639

Conditions ☒

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
1,2,3,4-Tetrahydro-1-naphthol	7.14	1	NaN		●●
Potassium peroxomonosulfate	4.28	0.6			●
Tetrabutylammonium hydrogen sulfate	0.71	0.1			●
Acetonitrile	679.44	95.12	81	🔥 ☠	●●

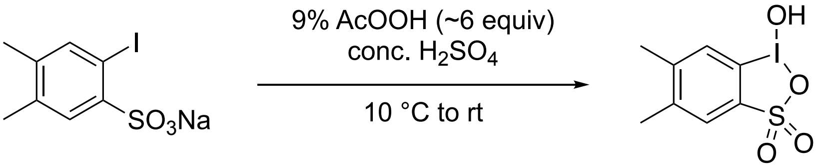
Yield	96		-2
Price / availability			-6
Safety			-10
Technical setup	Possible items Any additional special glassware (Inert) gas atmosphere Glove box	Selected items Common set-up	0
Temperature / time	Possible items Room temperature, < 1h Room temperature, < 24h Heating, < 1h	Selected items Room temperature, < 24h	-1
Workup and purification	Possible items Sublimation Liquid - liquid extraction or washing Classical chromatography	Selected items Removal of solvent with bp < 150°C Liquid - liquid extraction or washing Classical chromatography	-13
EcoScale			68

Catalysts and Substrates

Pre-IBSs **1a**–**1c** were prepared according to the known procedures.[2] **1a** and **1b** (as their potassium salts) are also commercially available from Junsei Chemical or Sigma-Aldrich.

Alcohols **4a**–**4j**, **4l**–**4u**, and **6** were purchased from Aldrich Chemical Co., Inc., FUJIFILM Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry Co., Ltd. and used without further purification. **1k**[3] is a known compound and was prepared by following the literature procedures.

Synthesis of IBS(III) 2c



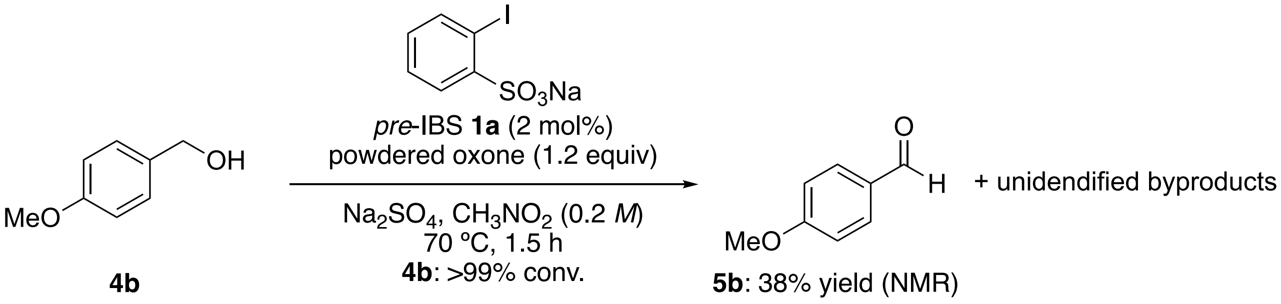
1c **2c**

Procedure adapted from literature.[4] To a stirred mixture of **1c** (as 1.5 hydrate, 1.60 g, 4.43 mmol) and concentrated H_2SO_4 (0.600 mL), maintained at ~10 °C under a nitrogen atmosphere, was added peroxyacetic acid (9 wt% acetic acid solution, 22.0 mL) dropwise. The mixture was stirred at 10 °C and then allowed to stir overnight at room temperature. Diethyl ether (20 mL) was added to the mixture to precipitate solids, which were collected by filtration and washed with cold diethyl ether and cold water. The resulting solid was suspended in acetonitrile (20.0 mL) and water (10.0 mL), and the mixture was heated to 70 °C until most of the solids dissolved. The hot mixture was filtered, allowed to cool to room temperature, and then kept overnight to allow crystallization. The precipitated solid was filtrated and washed with cold diethyl ether to afford **2c** (0.609 g, 1.86 mmol). The filtrate was concentrated to one-third of its original volume to give a second crop of solid (0.416 g, 1.27 mmol). Combined yield: 3.13 mmol, 71%.

1-Hydroxy-5,6-dimethyl-1*H*-1λ^3-benzo[*d*][1,2,3]iodaoxathiole 3,3-dioxide (2c):[1] White powder. **^{1}H NMR** (CD_3CN, 400 MHz) δ 2.23 (s, 3H), 2.24 (s, 3H), 7.78 (s, 1H), 7.82 (s, 1H); **^{13}C NMR** (CD_3CN, 100 MHz) δ 19.4, 20.6, 109.6, 126.5, 130.0, 138.0, 142.8, 145.8. Anal. Calcd for C8H9IO4S: C, 29.28; H, 2.76. Found: C, 29.18; H, 2.69.

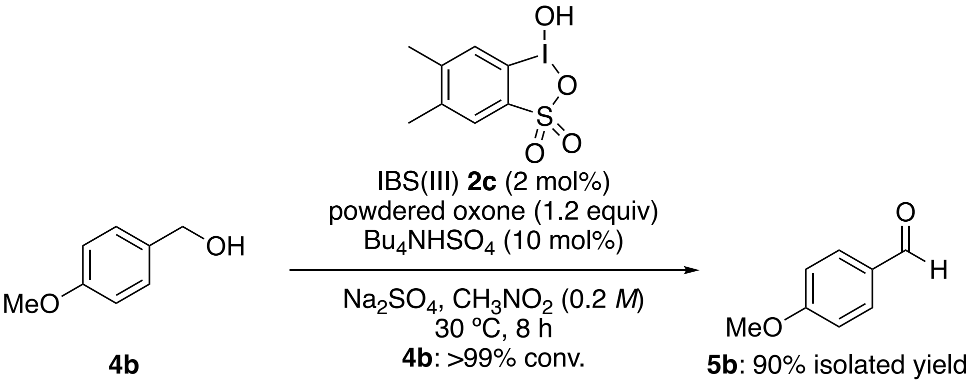
Representative Procedures for Oxidation of Primary Alcohols to Aldehydes

Previous Method (Method A):



To a rigorously stirring mixture of powdered oxone (0.369 g, 1.20 mmol, 1.2 equiv), **1a** (as a monohydrate, 0.00650 g, 0.0200 mmol, 2 mol%), biphenyl (0.0771 g, 0.500 mmol, as an internal standard) and anhydrous Na_2SO_4 (1.00 g, pre-dried under vacuum with a heat gun) in CH_3NO_2 (5.00 mL, 0.200 *M*) was added **4b** (0.138 g, 1.00 mmol) at room temperature under a nitrogen atmosphere. The reaction mixture was then heated to 70 °C and monitored by TLC and ^1H NMR analysis. Upon completion, the mixture was cooled to room temperature, filtered through a tightly packed celite plug, and washed thoroughly with diethyl ether. The combined filtrates were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The yield of the **5b** was determined to be 38% by ^1H NMR analysis of the crude using biphenyl as a calibrated internal standard. Multiple unidentified byproducts were observed, indicating competing side reactions under the reaction conditions.

Current Method (Method B):

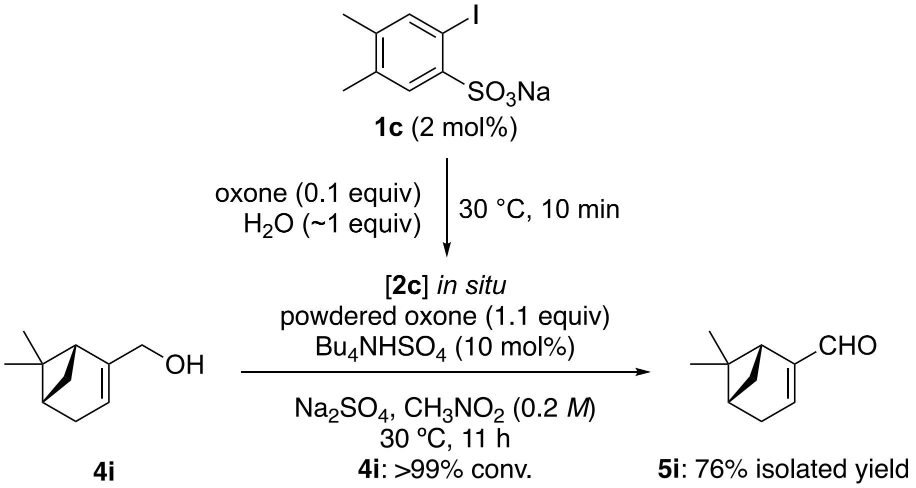


To a rigorously stirring mixture of powdered oxone (0.369 g,1.20 mmol), **2c** (0.00660 g, 0.0200 mmol, 2 mol%), Bu_4NHSO_4 (0.0340 g, 0.100 mmol, 10 mol%) and anhydrous Na_2SO_4 (1.00 g, pre-dried under vacuum with a heat gun) in CH_3NO_2 (5.00 mL, 0.200 *M*) was added **4b** (0.138 g, 1.00 mmol) at 30 °C using a thermostated bath under a nitrogen atmosphere. The reaction progress was monitored by TLC analysis. Upon completion, the mixture was filtered through a tightly packed celite plug and washed thoroughly with diethyl ether. The combined filtrates were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure.

The crude product was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 10:1) to afford product **5b** (0.123 g, 0.903 mmol, 90% yield) in analytically pure form.

4-Methoxybenzaldehyde (5b): This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. Colorless oil; **TLC,** R_f = 0.23 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.90 (s, 3H), 7.01 (td, *J* = 2.3, 9.6 Hz, 2H), 7.85 (td, *J* = 2.3, 9.2 Hz, 2H), 9.89 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 55.4, 114.1, 129.7, 131.8, 164.4, 190.6.

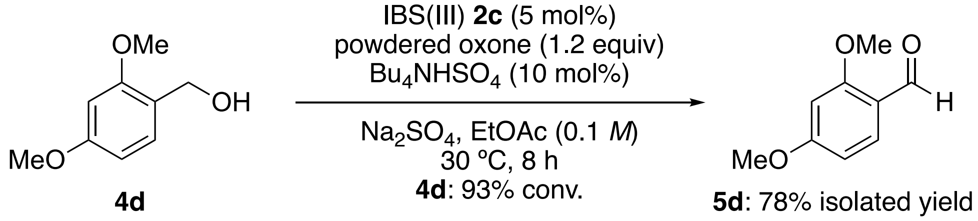
Current Method (Method C):



A mixture of **1c** (as 1.5 hydrate, 0.00720 g, 0.0200 mmol, 2 mol%), oxone (0.0307 g, 0.100 mmol), and H_2O (ca. 20 μL) was stirred at 30 °C for 10 min. To this stirring mixture were added powdered oxone (0.338 g, 1.10 mmol), Bu_4NHSO_4 (0.0340 g, 0.100 mmol, 10 mol%), anhydrous Na_2SO_4 (1.00 g, pre-dried under vacuum with a heat gun), CH_3NO_2 (5.00 mL, 0.200 *M*), and **4i** (0.152 g, 1.00 mmol) at 30 °C using a thermostated bath under a nitrogen atmosphere. The reaction progress was monitored by TLC analysis. Upon completion, the mixture was filtered through a tightly packed celite plug and washed with diethyl ether. The combined organic layers were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (eluent: hexane–EtOAc = 10:1) to yield **5i** (0.114 g, 0.761 mmol, 76% yield) in analytically pure form.

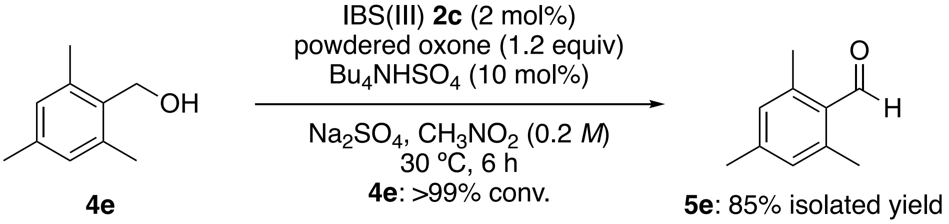
cf. Method A, 8 h: **4i**, >99% conv.; **5i**, 25% NMR yield (multiple unidentified byproducts were observed).

(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde (5i): This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 30:1). Colorless oil; **TLC,** R_f = 0.48 (hexane–EtOAc = 10:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.75 (s, 3H), 1.06 (d, *J* = 9.6 Hz, 1H), 1.34 (s, 3H), 2.18–2.22 (m, 1H), 2.49 (td, *J* = 4.6, 9.6 Hz, 1H), 2.57 (td, *J* = 3.0, 10.1 Hz, 2H), 2.87 (t, *J* = 5.5 Hz, 1H), 6.72 (sept, *J* = 1.5 Hz, 1H), 9.44 (s 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.9, 25.6, 31.0, 33.0, 37.5, 38.0, 40.6, 147.9, 151.4, 191.3.



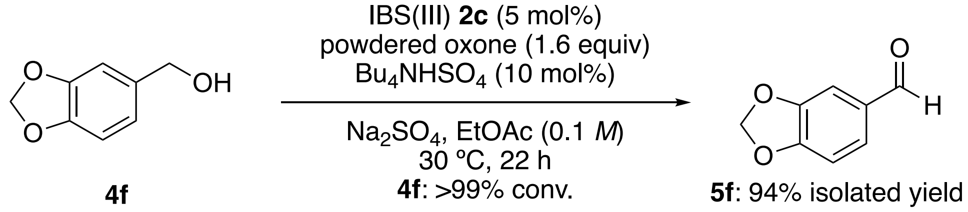
cf. Method A [**1a** (5 mol%), EtOAc (0.1 *M*)], 3 h: **4d**, 90% conv.; **5d**, 2% NMR yield (multiple unidentified byproducts were observed).

2,4-Dimethoxybenzaldehyde (5d): Method B, 78% yield (0.130 g, 0.783 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 10:1). Colorless oil; **TLC,** R_f = 0.25 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.88 (s, 3H), 3.91 (s, 3H), 6.45 (d, *J* = 1.8 Hz, 1H), 6.56 (dd, *J* = 1.8, 8.7 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 10.30 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 55.5, 55.6, 97.8, 105.7, 118.9, 130.6, 163.5, 166.1, 188.3.



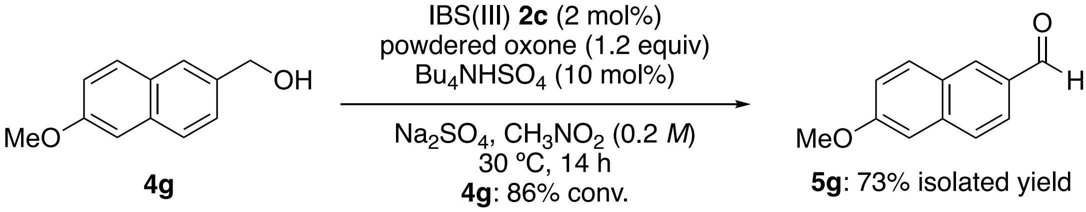
cf. Method A, 2 h: **4e**, >99% conv.; **5e**, 10% NMR yield. Dibenzyl ether, a dehydrative dimerization byproduct, was obtained as a main byproduct in 70% yield.

2,4,6-Trimethylbenzaldehyde (5e): Method B, 85% yield (0.126 g, 0.853 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 10:1). Colorless oil; **TLC,** R_f = 0.55 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.32 (s 3H), 2.59 (s 6H), 6.91 (s, 2H), 10.57 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.5, 21.4, 129.9, 130.5, 141.4, 143.8, 192.9.



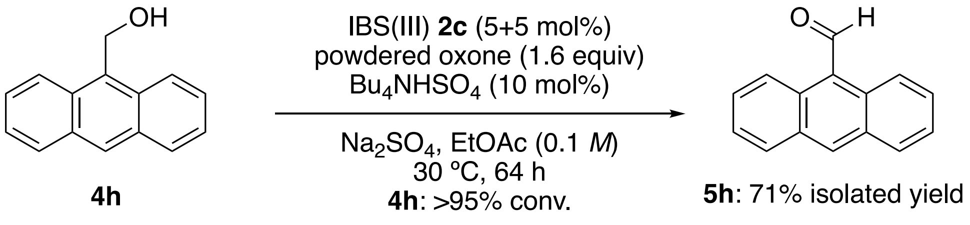
cf. Method A [**1a** (5 mol%), oxone (1.6 equiv), EtOAc (0.1 *M*)], 14 h: **4f**, 93% conv.; **5f**, 14% NMR yield (multiple unidentified byproducts were observed).

Benzo[*d*][1,3]dioxole-5-carbaldehyde (5f): Method B, 94% yield (0.141 g, 0.939 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 10:1). Colorless oil; **TLC,** R_f = 0.34 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.09 (s, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 1.4 Hz, 1H), 7.43 (dd, *J* = 1.4, 7.8 Hz, 1H), 9.82 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 102.1, 106.9, 108.3, 128.7, 131.8, 148.7, 153.1, 190.3.



cf. Method A, 7 h: **4f**, >95% conv.; **5g**, 11% NMR yield (multiple unidentified byproducts were observed).

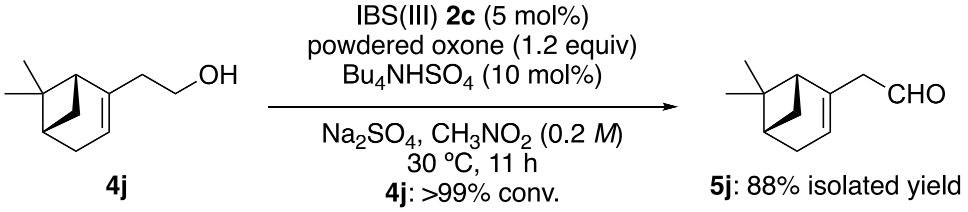
6-Methoxy-2-naphthaldehyde (5g): Method B, 73% yield (0.135 g, 0.726 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 20:1). Pale yellow oil; **TLC,** R_f = 0.23 (hexane–EtOAc = 10:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.97 (s, 3H), 7.19 (d, *J* = 2.3 Hz, 1H), 7.24 (dd, *J* = 2.3, 9.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.93 (dd, *J* = 1.4, 8.7 Hz, 1H), 8.26 (s, 1H), 10.10 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 55.4, 106.0, 119.8, 123.5, 127.6, 127.8, 131.0, 132.2, 134.2, 138.1, 160.1, 191.9.



cf. Method A [**1a** (10 mol%), oxone (1.6 equiv), EtOAc (0.1 *M*)], 24 h: **4h**, >99% conv.; **5h**, 17%

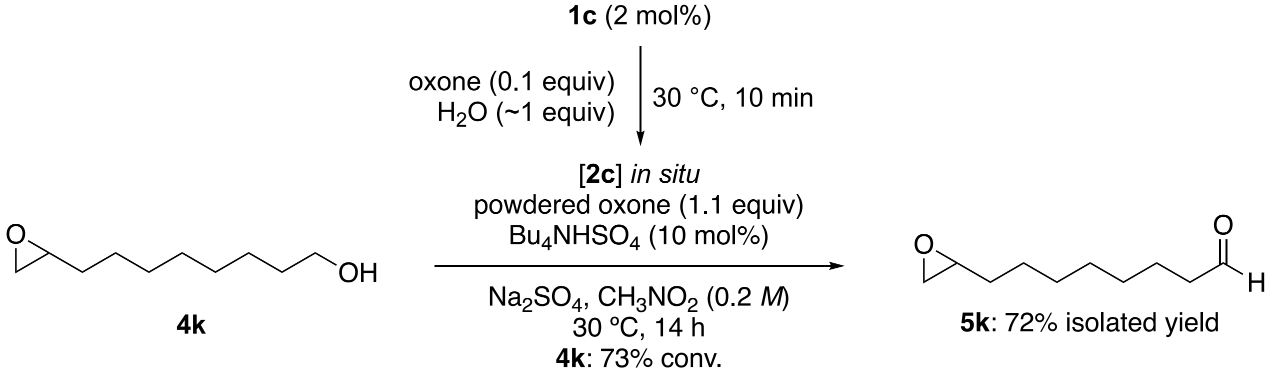
NMR yield (multiple unidentified byproducts were observed).

Anthracene-9-carbaldehyde (5h): Method B (after 16 h, **2c** (5 mol%) was further added), 71% yield (0.146 g, 0.707 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O = 50:1). Yellow solid; **TLC,** *R*f = 0.37 (hexane–EtOAc = 10:1); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.55–7.59 (m, 2H), 7.68–7.72 (m, 2H), 8.09 (d, *J* = 8.7 Hz, 2H), 8.73 (s, 1H), 9.01 (d, *J* = 9.2 Hz, 2H), 11.56 (s, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 123.5, 124.6, 125.7, 129.1, 129.3, 131.0, 132.1, 135.2, 193.0.



cf. Method A [**1a** (5 mol%)], 3 h: **4j**, >99% conv.; **5j**, 6% NMR yield (multiple unidentified byproducts were observed).

2-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)acetaldehyde (5j): Method B, 88% yield (0.145 g, 0.881 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O = 30:1). Yellow oil; **TLC,** *R*f = 0.63 (hexane–EtOAc = 10:1); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 0.86 (s, 3H), 1.22 (d, *J* = 8.7 Hz, 1H), 1.28 (s, 3H), 2.05 (dt, *J* = 1.4, 5.5 Hz, 1H), 2.10–2.14 (m, 1H), 2.22–2.36 (m, 2H), 2.40 (td, *J* = 4.4, 8.7 Hz, 1H), 3.06 (q, *J* = 1.2 Hz, 2H), 5.47 (quin, *J* = 1.4 Hz, 1H), 9.59 (t, *J* = 2.8 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 21.1, 26.1, 31.5, 31.6, 38.2, 40.3, 46.0, 51.9, 122.5, 139.3, 200.1.



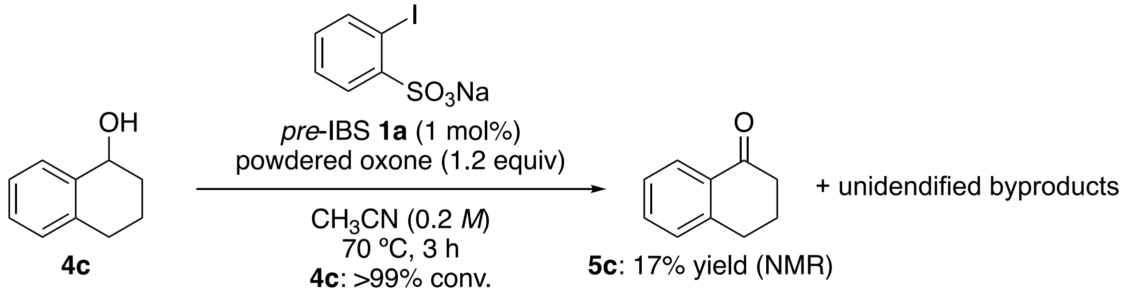
cf. Method A, 8 h: **4k**, >99% conv.; **5k**, 11% NMR yield (multiple unidentified byproducts were observed).

8-(Oxiran-2-yl)octanal (5k):[5] Method C, 72% yield (0.123 g, 0.722 mmol). This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O =

10:1). Pale yellow oil; **TLC,** R_f = 0.38 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.33–1.67 (m, 12H), 2.43 (dt, *J* = 1.8, 7.3 Hz, 2H), 2.47 (dd, *J* = 2.8, 5.0 Hz, 1H), 2.75 (dd, *J* = 4.1, 5.0 Hz, 1H), 2.88–2.93 (m, 1H), 9.77 (t, *J* = 1.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.8, 25.7, 28.8, 28.97, 29.03, 32.2, 43.6, 46.8, 52.1, 202.6.

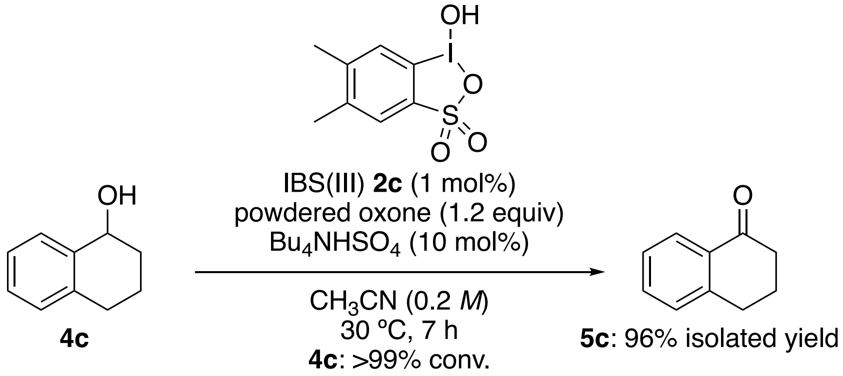
Representative Procedures for Oxidation of Secondary Alcohols to Ketones

Previous Method (Method A):



To a rigorously stirring mixture of powdered oxone (0.369 g, 1.20 mmol, 1.2 equiv), **1a** (as a monohydrate, 0.00320 g, 0.0100 mmol, 1 mol%), and biphenyl (0.0771 g, 0.500 mmol, as an internal standard) in CH_3CN (5.00 mL, 0.200 *M*) was added **4c** (0.148 g,1.00 mmol) at room temperature under a nitrogen atmosphere. The reaction mixture was then heated to 70 °C and monitored by TLC and ^{1}H NMR analysis. Upon completion, the mixture was cooled to room temperature, filtered through a tightly packed celite plug, and washed thoroughly with diethyl ether. The combined filtrates were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The yield of the **5c** was determined to be 17% by ^{1}H NMR analysis of the crude using biphenyl as a calibrated internal standard. Multiple unidentified byproducts were observed, indicating competing side reactions under the reaction conditions.

Current Method (Method B):

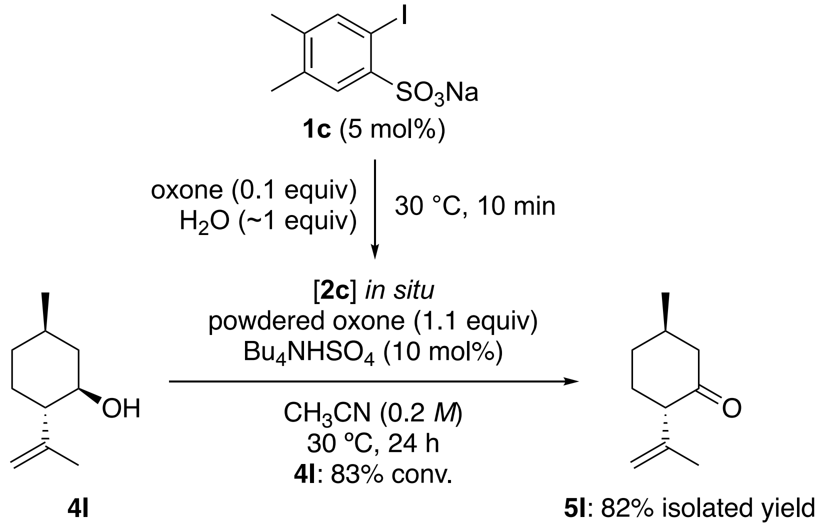


To a rigorously stirring mixture of powdered oxone (0.369 g,1.20 mmol), **2c** (0.00330 g, 0.0100 mmol, 1 mol%), Bu_4NHSO_4 (0.0340 g, 0.100 mmol, 10 mol%) and anhydrous Na_2SO_4 (1.00 g, pre-dried under vacuum with a heat gun) in CH_3NO_2 (5.00 mL, 0.200 *M*) was added **4c** (0.148 g, 1.00

mmol) at 30 °C using a thermostated bath under a nitrogen atmosphere. The reaction progress was monitored by TLC analysis. Upon completion, the mixture was filtered through a tightly packed celite plug and washed thoroughly with diethyl ether. The combined filtrates were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 10:1) to afford product **5c** (0.140 g, 0.958 mmol, 96% yield) in analytically pure form.

3,4-Dihydronaphthalen-1(2*H*)-one (5c): This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. Light yellow oil; **TLC,** R_f = 0.27 (hexane–EtOAc = 4:1); **^{1}H NMR** (CD_3CN, 400 MHz) δ 2.10 (quin, *J* = 6.3 Hz, 2H), 2.60 (t, *J* = 6.6 Hz, 2H), 2.97 (t, *J* = 6.2 Hz, 2H), 7.30–7.34 (m, 2H), 7.51 (dt, *J* = 1.4, 7.3 Hz, 1H), 7.91–7.94 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 23.1, 29.5, 38.9, 126.4, 126.9, 128.6, 132.4, 133.2, 144.3, 198.1.

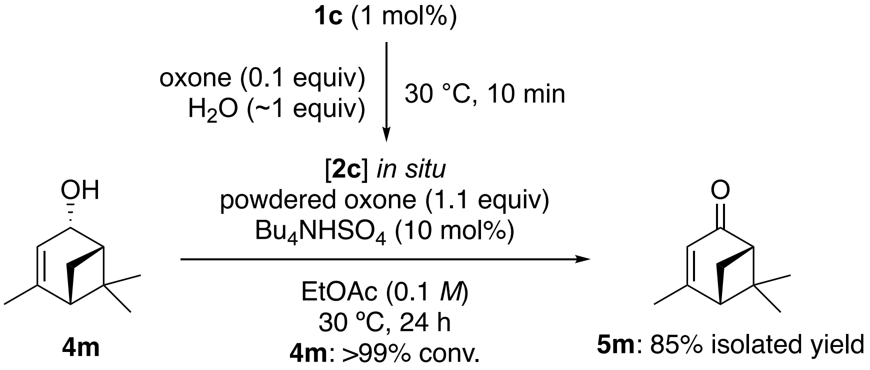
Current Method (Method C):



A mixture of **1c** (as 1.5 hydrate, 0.0173 g, 0.0500 mmol, 5 mol%), oxone (0.0307 g, 0.100 mmol), and H_2O (ca. 20 μL) was stirred at 30 °C for 10 min. To this stirring mixture were added powdered oxone (0.338 g, 0.110 mmol), Bu_4NHSO_4 (0.0340 g, 0.100 mmol, 10 mol%), CH_3CN (10.0 mL, 0.100 M), and **4l** (0.154 g, 1.00 mmol) at 30 °C using a thermostated bath under a nitrogen atmosphere. The reaction progress was monitored by TLC analysis. Upon completion, the mixture was filtered through a tightly packed celite plug and washed with diethyl ether. The combined organic layers were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 20:1) to afford **5l** (0.125 g, 0.818 mmol, 82% yield) in analytically pure form.

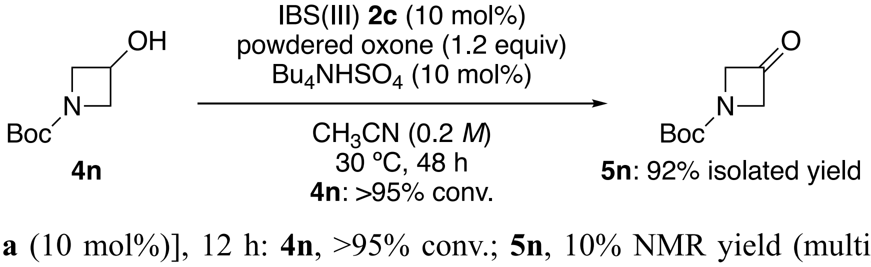
cf. Method A [**1a** (5 mol%)], 12 h: **4l**, 92% conv.; **5l**, 6% NMR yield (multiple unidentified byproducts were observed).

(2*S*,5*R*)-5-Methyl-2-(prop-1-en-2-yl)cyclohexan-1-one (5l): This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. Colorless oil; **TLC**, R_f = 0.40 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.04 (d, *J* = 6.4 Hz, 3H), 1.38–1.48 (m, 1H), 1.74–1.85 (m, 1H), 1.75 (s, 3H), 1.86–1.96 (m, 2H), 2.02–2.09 (m, 2H), 2.41 (ddd, *J* = 2.0, 3.7, 13.3 Hz, 1H), 2.96 (dd, *J* = 5.5, 12.8 Hz, 1H), 4.72 (t, *J* = 0.92 Hz, 1H), 4.94 (t, *J* = 1.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.2, 22.2, 31.0, 33.7, 35.2, 50.4, 57.5, 112.6, 143.3, 210.0.



cf. Method A [**1a** (1 mol%), EtOAc], 6 h: **4m**, >99% conv.; **5m**, 10% NMR yield (multiple unidentified byproducts were observed).

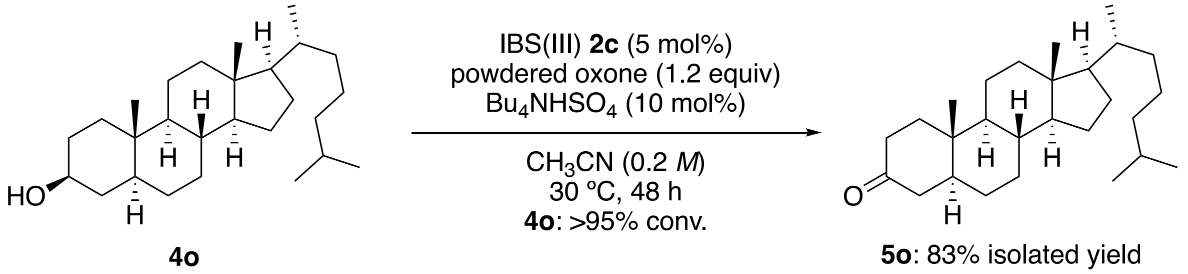
(1*S*,5*S*)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-one (5m): Method C, 85% yield (0.127 g, 0.847 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 20:1). Pale yellow oil; **TLC,** R_f = 0.40 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.01 (s, 3H), 1.50 (s, 3H), 2.02 (d, *J* = 1.4 Hz, 3H), 2.08 (d, *J* = 9.2 Hz, 1H), 2.40–2.43 (m, 1H), 2.63–2.67 (m, 1H), 2.81 (td, *J* = 4.6, 11.0 Hz, 1H), 5.73 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.8, 23.3, 26.3, 40.6, 49.4, 53.7, 57.3, 120.9, 170.0, 203.6.



cf. Method A [**1a** (10 mol%)], 12 h: **4n**, >95% conv.; **5n**, 10% NMR yield (multiple unidentified byproducts were observed).

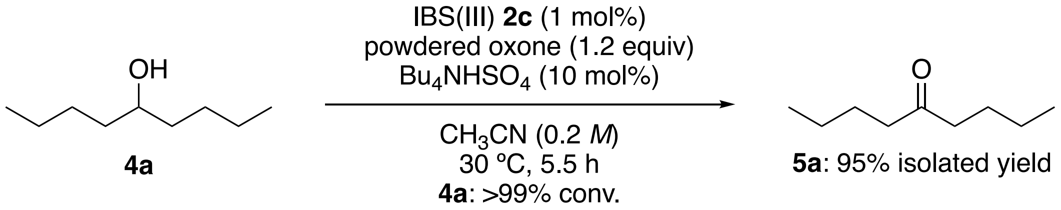
***tert*-Butyl 3-oxoazetidine-1-carboxylate (5n):** Method B, 92% yield (0.158 g, 0.920 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 10:1). Yellow solid; **TLC,** R_f = 0.57 (hexane–EtOAc = 2:1);

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.49 (s, 9H), 4.69 (s, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 28.2, 70.9, 80.9, 155.9, 196.6.



cf. Method A [**1a** (5 mol%)], 60 h: **4o**, 11% conv.; **5o**, <10% NMR yield (unreacted **4o** was recovered).

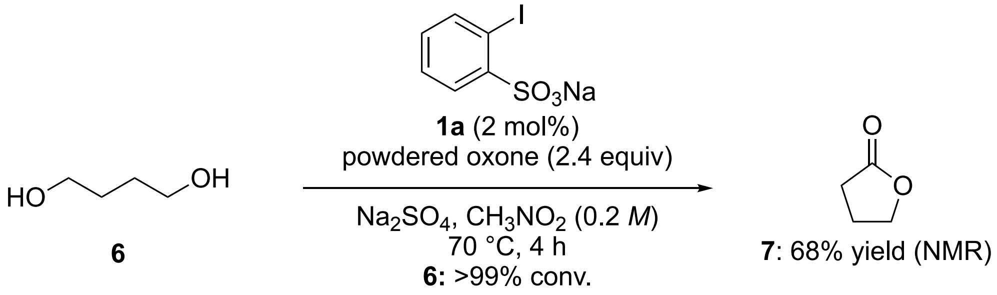
(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-3*H*-cyclopenta[a]phenanthren-3-one (5o): Method B, 83% yield (0.320 g, 0.827 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 20:1). Yellow solid; **TLC,** R_f = 0.23 (hexane–EtOAc = 10:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.68 (s, 3H), 0.85 (d, *J* = 1.8 Hz, 3H), 0.87 (d, *J* = 1.8 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.95–1.41 (m, 22H), 1.49–1.60 (m, 4H), 1.67–1.71 (m, 1H), 1.77–1.85 (m, 1H), 1.97–2.10 (m, 3H), 2.23–2.43 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 11.4, 12.0, 18.6, 21.4, 22.5, 22.8, 23.8, 24.2, 28.0, 28.2, 28.9, 31.7, 35.3, 35.6, 35.7, 36.1, 38.2, 38.5, 39.5, 39.8, 42.5, 44.7, 46.7, 53.7, 56.20, 56.22, 212.2.



Nonan-5-one (5a): Method B, 95% yield (0.137 g, 0.952 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 20:1). Colorless oil; **TLC,** R_f = 0.55 (hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.90 (t, *J* = 7.3 Hz, 6H), 1.31 (sext, *J* = 7.4 Hz, 4H), 1.55 (quin, *J* = 7.5 Hz, 4H), 2.40 (t, *J* = 7.6 Hz, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 13.8, 22.3, 25.9, 42.4, 211.7.

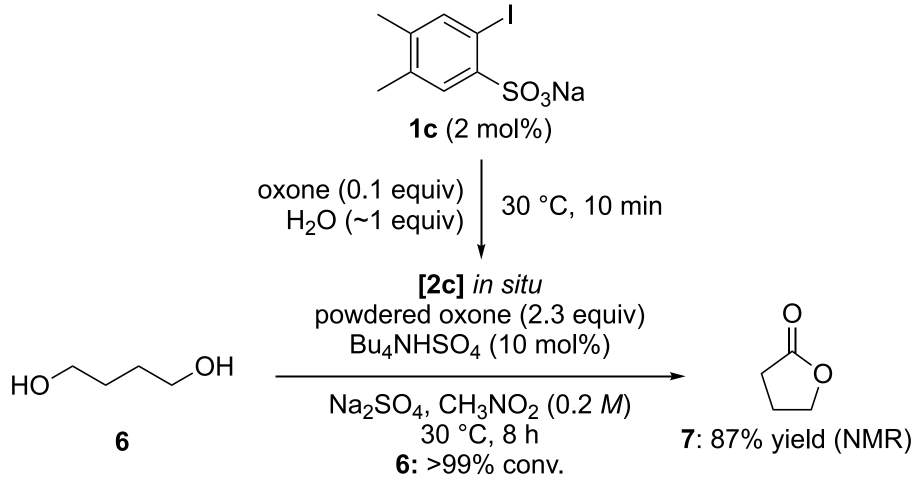
Procedures for Oxidative Lactonization

Previous Method (Method A):



To a rigorously stirring mixture of powdered oxone (0.738 g, 2.40 mmol, 2.4 equiv), **1a** (as a monohydrate, 0.00650 g, 0.0200 mmol, 2 mol%), biphenyl (0.0771 g, 0.500 mmol, as an internal standard) and anhydrous Na_2SO_4 (1.00 g, pre-dried under vacuum with a heat gun) in CH_3NO_2 (5.00 mL, 0.200 *M*) was added **6** (0.0901 g, 1.00 mmol) at room temperature under a nitrogen atmosphere. The reaction mixture was then heated to 70 °C and monitored by TLC and ^{1}H NMR analysis. Upon completion, the mixture was cooled to room temperature, filtered through a tightly packed celite plug, and washed thoroughly with diethyl ether. The combined filtrates were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The yield of lactone **7** was determined to be 68% by ^{1}H NMR analysis of the crude using biphenyl as a calibrated internal standard.

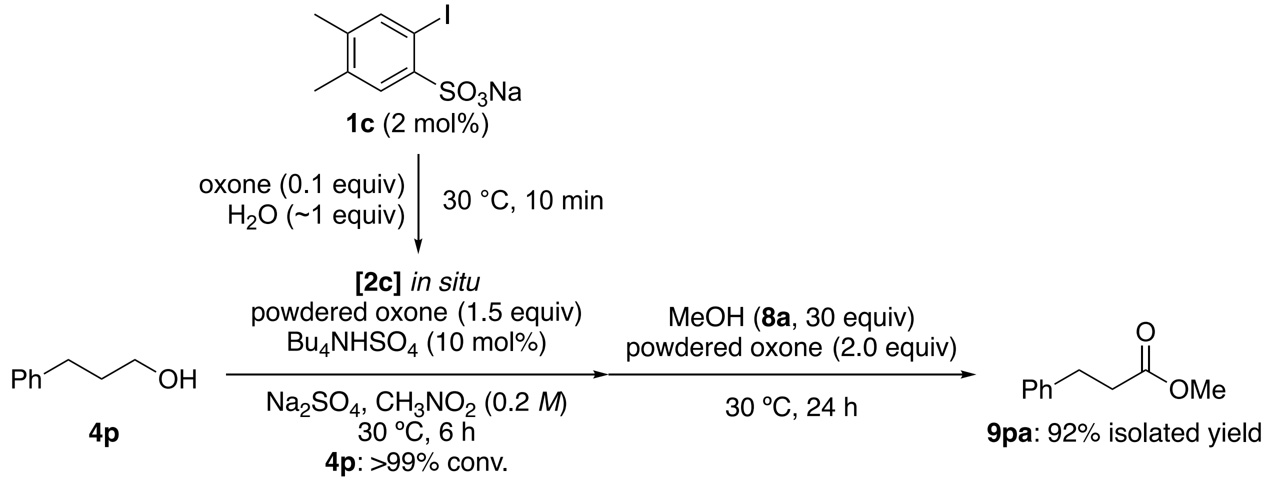
Current Method (Method C):



A mixture of **1c** (as 1.5 hydrate, 0.00720 g, 0.0200 mmol, 2 mol%), oxone (0.0307 g, 0.100 mmol), and H_2O (ca. 20 μL) was stirred at 30 °C for 10 min. To this stirring mixture were added powdered oxone (0.707 g, 2.30 mmol), Bu_4NHSO_4 (0.0340 g, 0.100 mmol, 10 mol%), anhydrous Na_2SO_4 (1.00 g, pre-dried under vacuum with a heat gun), CH_3NO_2 (5.00 mL, 0.200 M), and **6** (0.0901 g, 1.00 mmol) at 30 °C using a thermostated bath under a nitrogen atmosphere. The reaction progress was monitored by TLC analysis. Upon completion, the mixture was filtered through a tightly packed celite plug and washed with diethyl ether. The combined organic layers were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous MgSO$_4$, and concentrated under reduced pressure. The yield of the **7** was determined to be 87% by ^{1}H NMR analysis of the crude using biphenyl as a calibrated internal standard.

Dihydrofuran-2(3*H*)-one (7): This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. Colorless oil; **TLC,** $R_f = 0.63$ (hexane–EtOAc = 4:1); ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 2.27 (quin, J = 7.7 Hz, 2H), 2.50 (t, J = 8.0 Hz, 2H), 4.36 (t, J = 7.1 Hz, 2H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 21.8, 27.4, 68.2, 177.6.

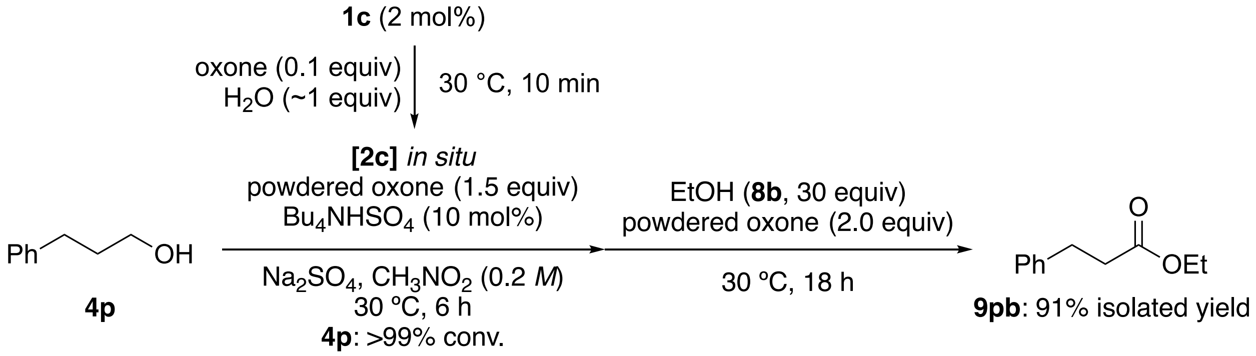
Representative Procedure for Oxidative Esterification (Method C)



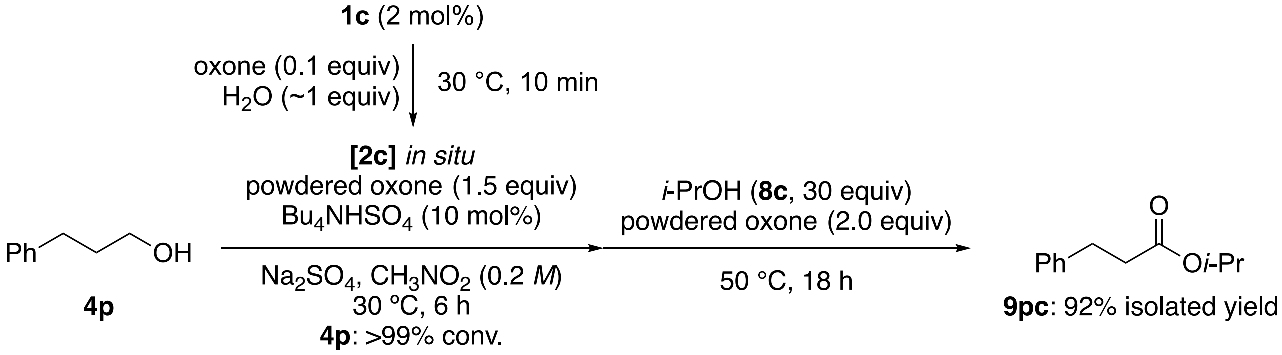
A mixture of **1c** (as 1.5 hydrate, 0.00722 g, 0.0200 mmol, 2 mol%), oxone (0.0307 g, 0.100 mmol, 0.1 equiv.), and H$_2$O (ca. 20 μL) was stirred at 30 °C for 10 min. To this stirred mixture were added powdered oxone (0.461 g, 1.50 mmol, 1.5 equiv.), Bu$_4$NHSO$_4$ (0.0340 g, 0.100 mmol, 10 mol%), anhydrous Na$_2$SO$_4$ (1.00 g, pre-dried under vacuum with a heat gun), CH$_3$NO$_2$ (5.00 mL, 0.200 *M*), and **4p** (1.00 mmol) were added at 30 °C under nitrogen. The reaction progress was monitored by TLC or ^{1}H NMR analysis. After complete consumption of **4p** and formation of aldehyde **5p**, to the resulting mixture were added powdered oxone (0.615 g, 2.00 mmol) and methanol (**8a**, 0.961 g, 30.0 mmol, 30.0 equiv.) at 30 °C under a nitrogen atmosphere. The reaction was again monitored by TLC or ^{1}H NMR analysis. Upon completion, the reaction mixture was filtered through a plug of tightly packed celite, which was then thoroughly washed with diethyl ether. The combined filtrates were washed successively with water (2 x 5 mL) and brine (1 x 5 mL), dried over anhydrous MgSO4, and concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O = 20:1) to yield **7pa** (0.151 g, 0.922 mmol, 92% yield) in analytically pure form.

Methyl 3-phenylpropanoate (7pa): This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. Colorless oil; **TLC,** R_f = 0.33

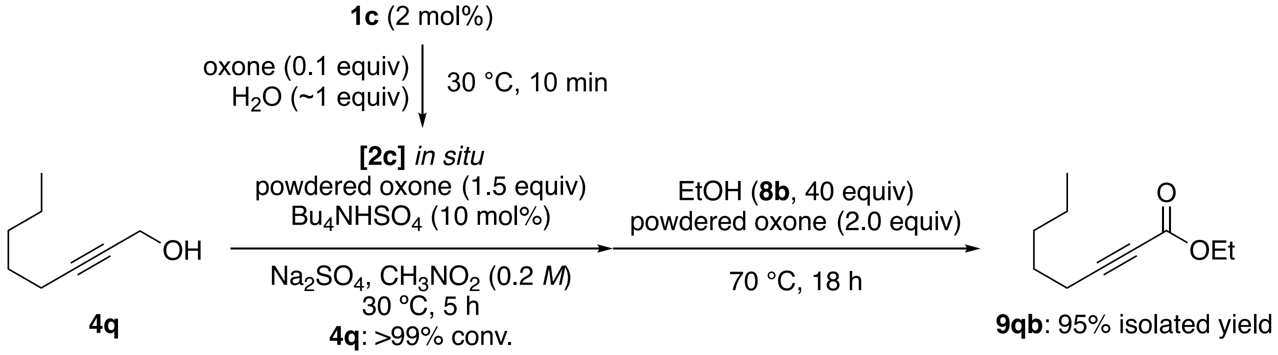
(hexane–EtOAc = 10:1); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 2.62–2.66 (m, 2H), 2.96 (t, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 7.19–7.22 (m, 3H), 7.27–7.31 (m, 2H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 30.6, 35.3, 51.2, 126.0, 128.0, 128.2, 140.2, 172.9.



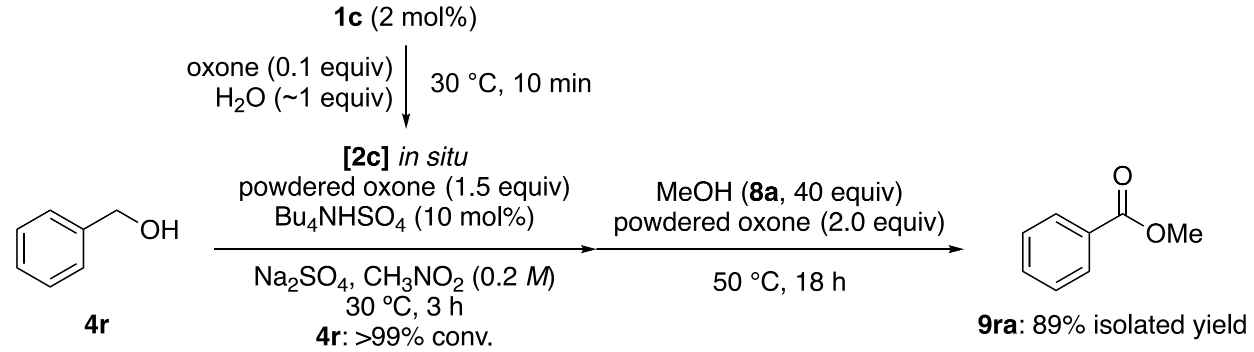
Ethyl 3-phenylpropanoate (9pb): Method C, 91% yield (0.162 g, 0.909 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O = 30:1). Colorless oil; **TLC,** *R*f = 0.40 (hexane–EtOAc = 10:1); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 1.23 (t, *J* = 7.3 Hz, 3H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 7.18–7.21 (m, 3H), 7.26–7.31 (m, 2H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 14.2, 30.9, 35.9, 60.4, 126.2, 128.3, 128.4, 140.5, 172.9.



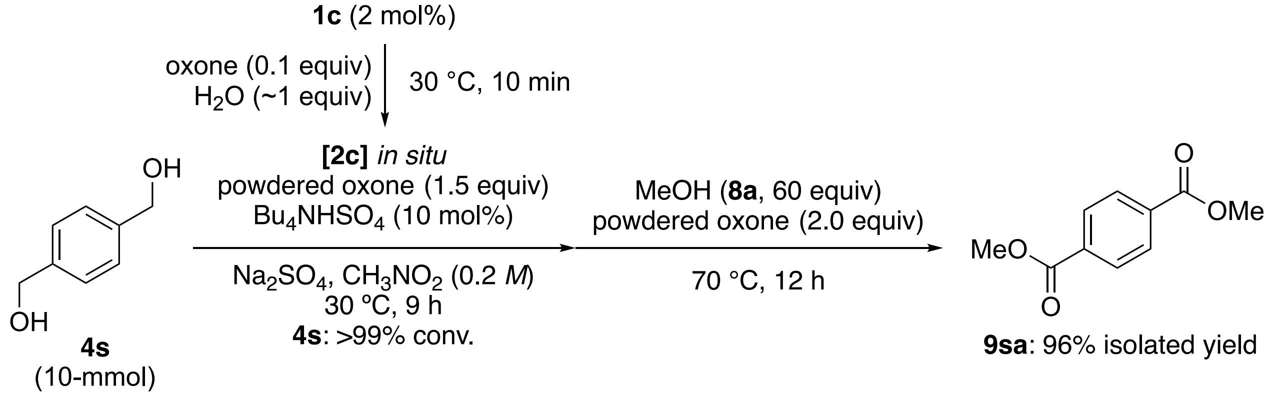
Isopropyl 3-phenylpropanoate (9pc): Method C, 92% yield (0.177 g, 0.920 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O = 30:1). Pale yellow oil; **TLC,** *R*f = 0.42 (hexane–EtOAc = 10:1); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 1.20 (d, *J* = 6.4 Hz, 6H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 5.00 (sept, *J* = 6.3 Hz, 1H), 7.18–7.22 (m, 3H), 7.27–7.30 (m, 2H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 21.7, 30.9, 36.1, 67.5, 126.0, 128.2, 128.3, 140.4, 172.2.



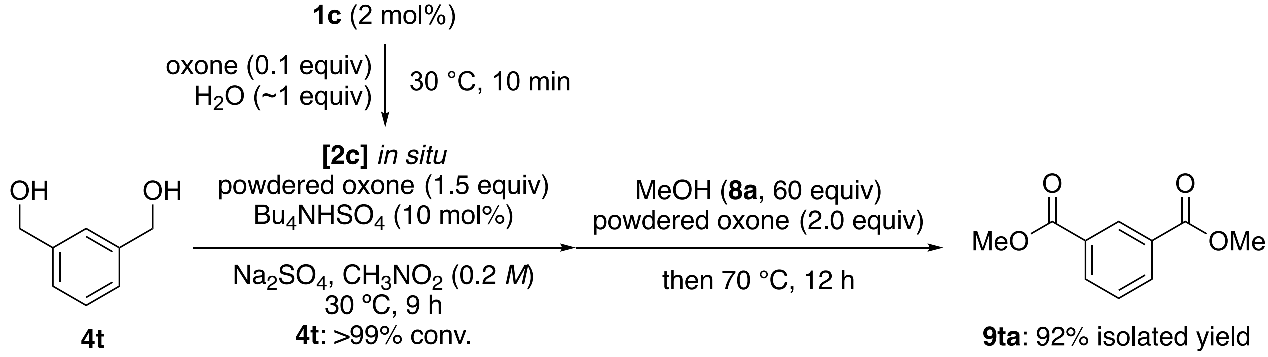
Ethyl oct-2-ynoate (9qb): Method C, 95% yield (0.160 g, 0.951 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 30:1). Pale yellow oil; **TLC,** R_f = 0.46 (hexane–EtOAc = 10:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 7.3 Hz, 3H), 1.29–1.42 (m, 7H), 1.59 (quin, J = 7.3 Hz, 2H), 2.33 (t, J = 7.1 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 13.8, 14.0, 18.6, 22.0, 27.2, 30.9, 61.7, 73.1, 89.4, 153.8.



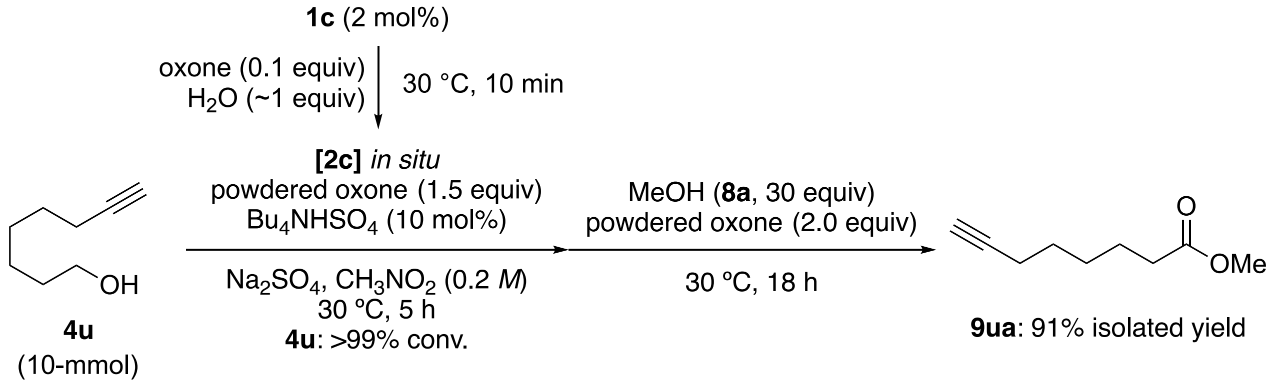
Methyl benzoate (9ra): Method C, 89% yield (0.122 g, 0.894 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 30:1). Yellow oil; **TLC,** R_f = 0.45 (hexane–EtOAc = 10:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.92 (s, 3H), 7.42–7.46 (m, 2H), 7.56 (tt, J = 1.4, 7.6 Hz, 1H), 8.03–8.06 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 51.9, 128.2, 129.4, 130.0, 132.8, 166.9.



Dimethyl terephthalate (9sa): Method C, 96% yield (1.86 g, 9.58 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O = 10:1). White solid; **TLC,** R_f = 0.71 (hexane–EtOAc = 2:1); ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 3.95 (s, 6H), 8.11 (s, 4H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 52.4, 129.5, 133.8, 166.2.



Dimethyl isophthalate (9ta): Method C, 92% yield (0.179 g, 0.920 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et$_2$O = 10:1). White solid; **TLC,** R_f = 0.66 (hexane–EtOAc = 2:1); ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 3.95 (s, 6H), 7.54 (t, J = 7.8 Hz, 1H), 8.24 (dd, J = 1.8, 7.8 Hz, 2H), 8.70 (t, J = 1.8 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 52.3, 128.6, 130.51, 130.65, 133.7, 166.2.



Methyl oct-7-ynoate (9ua): Method C, 91% yield (1.408 g, 9.13 mmol). This compound is commercially available. The spectral and physical data were consistent with those of an authentic sample. This compound was purified by flash column chromatography on silica gel (E. Merck Art. 9385, eluent: hexane–Et_2O = 20:1). Colorless oil; **TLC,** R_f = 0.29 (hexane–EtOAc = 10:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.40–1.48 (m, 2H), 1.55 (quin, J = 7.3 Hz, 2H), 1.65 (quin, J = 7.6 Hz, 2H), 1.95 (t, J = 2.8 Hz, 1H), 2.20 (dt, J = 2.8, 7.1 Hz, 2H), 2.33 (t, J = 7.6 Hz, 2H), 3.67 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 17.8, 24.0, 27.68, 27.73, 33.4, 50.9, 68.1, 83.6, 173.3.

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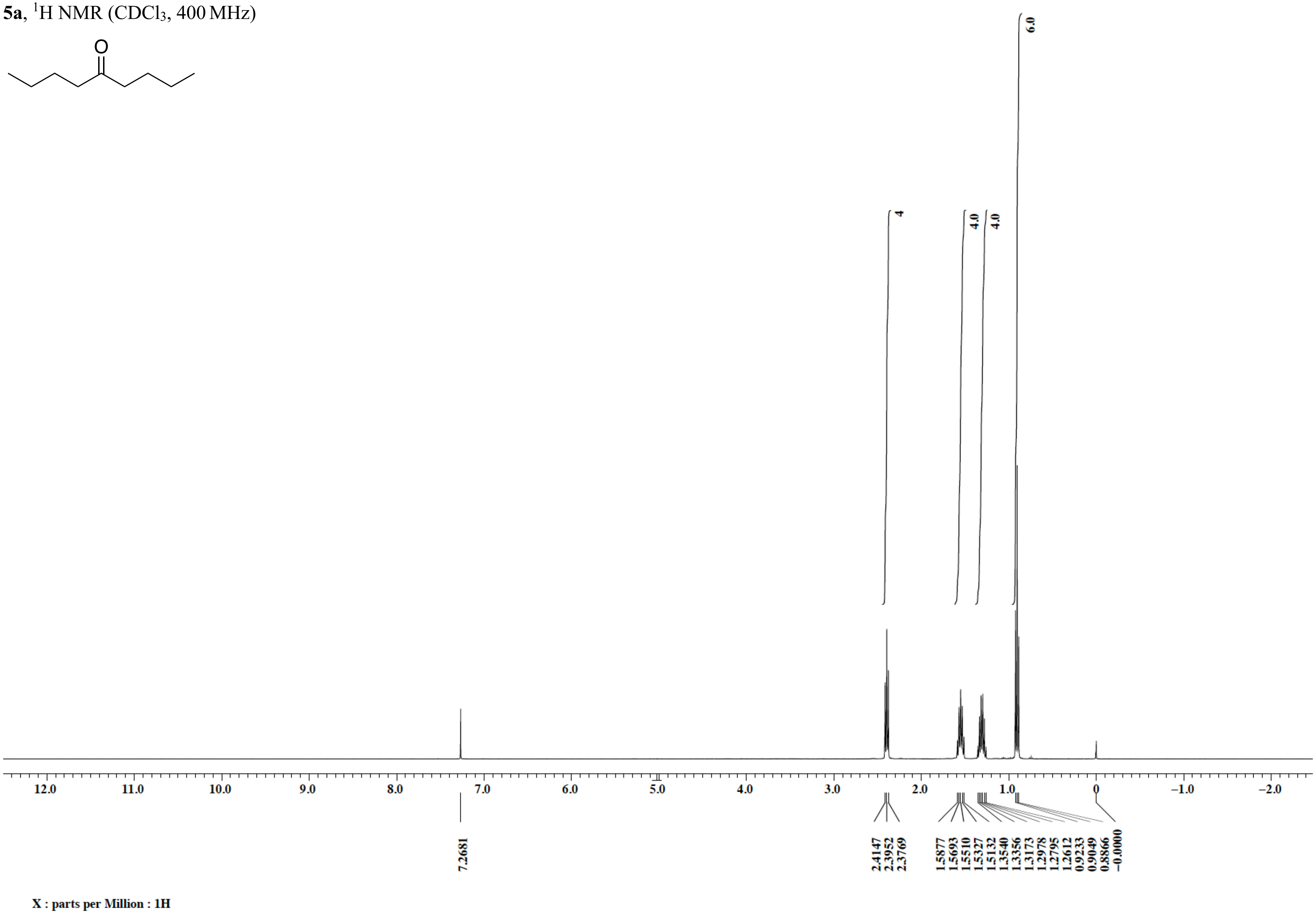
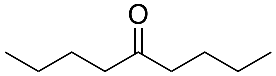
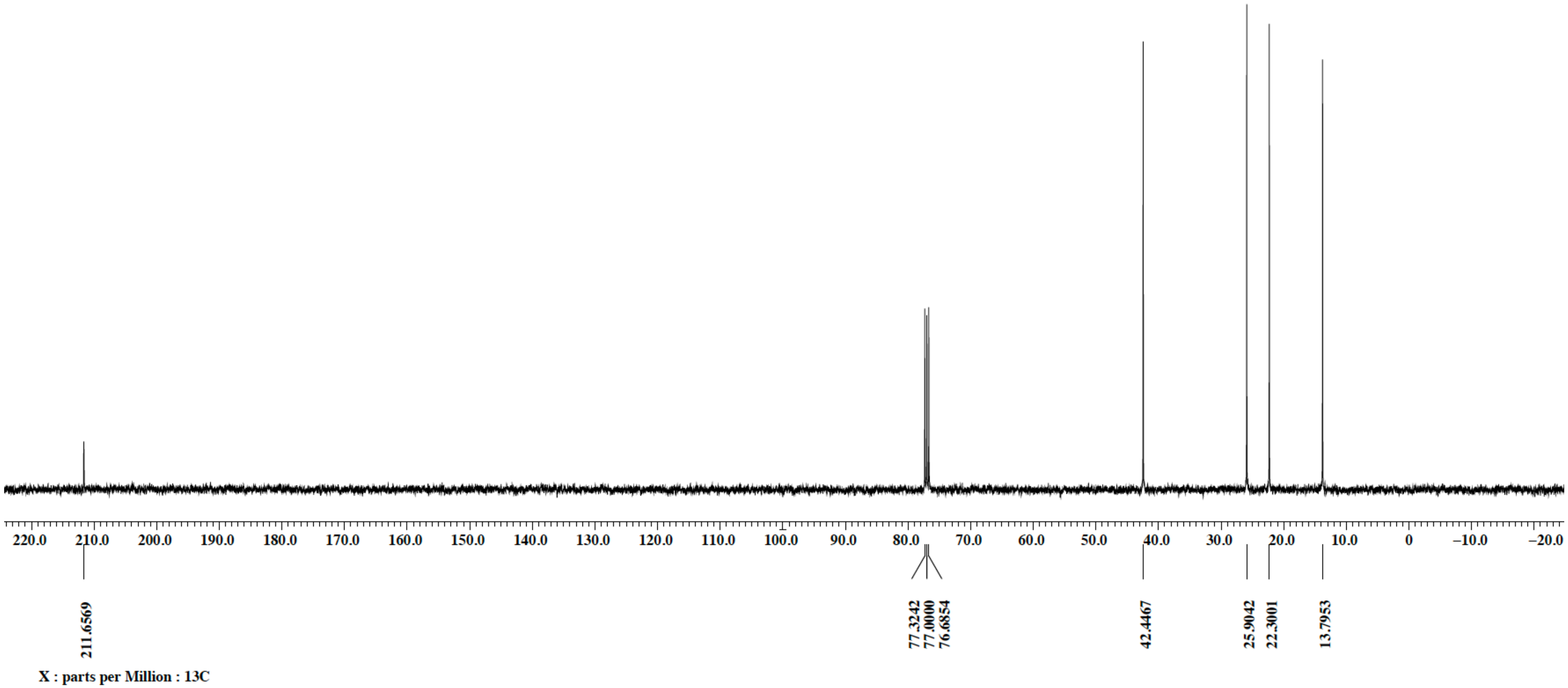
5a, ^{1}H NMR ($CDCl_3$, 400 MHz)

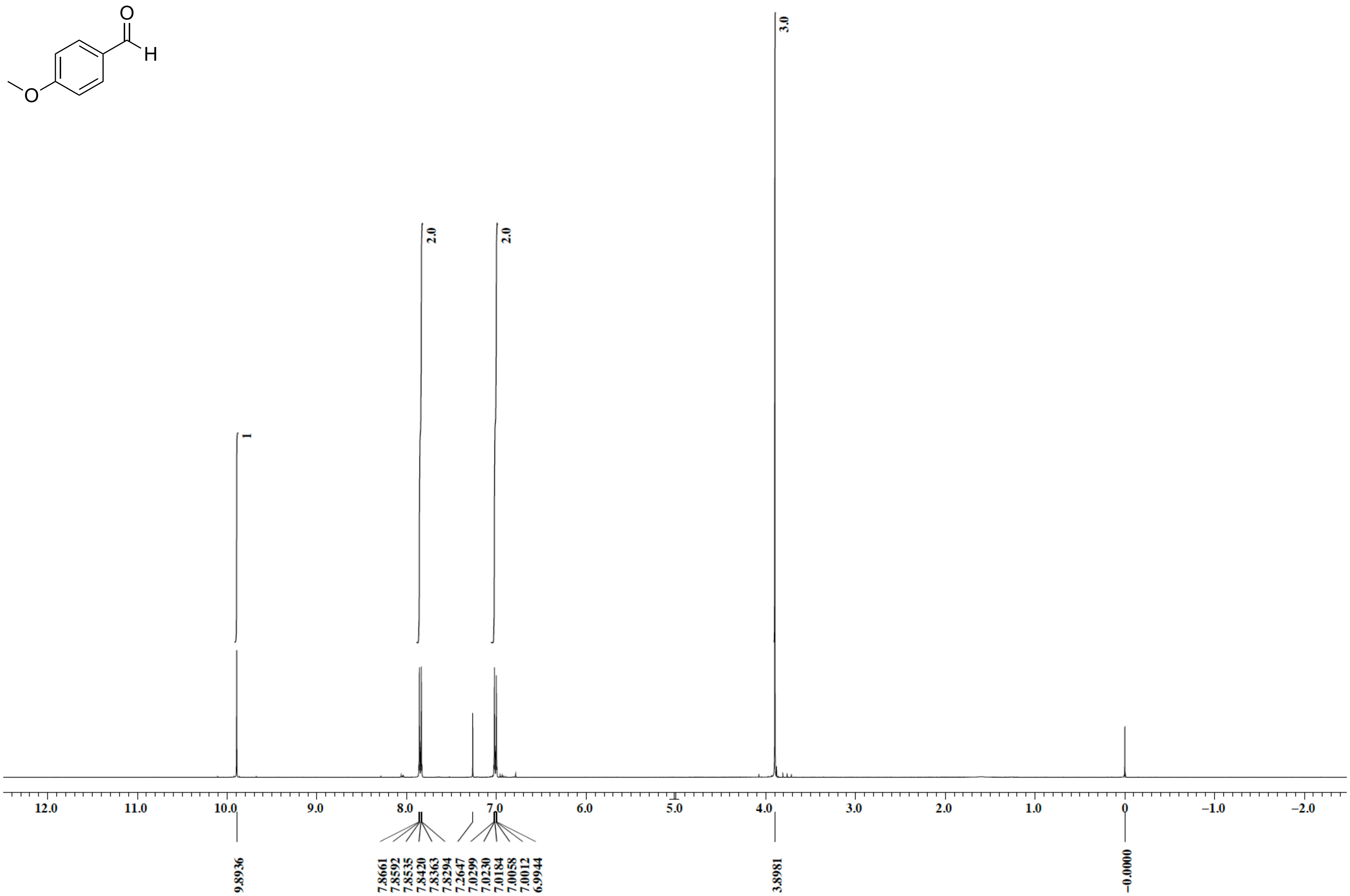


5a, ^{13}C NMR (CDCl$_3$, 100 MHz)





5b, ^{1}H NMR (CD_3CN, 400 MHz)



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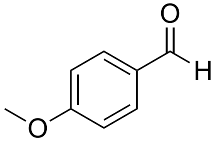

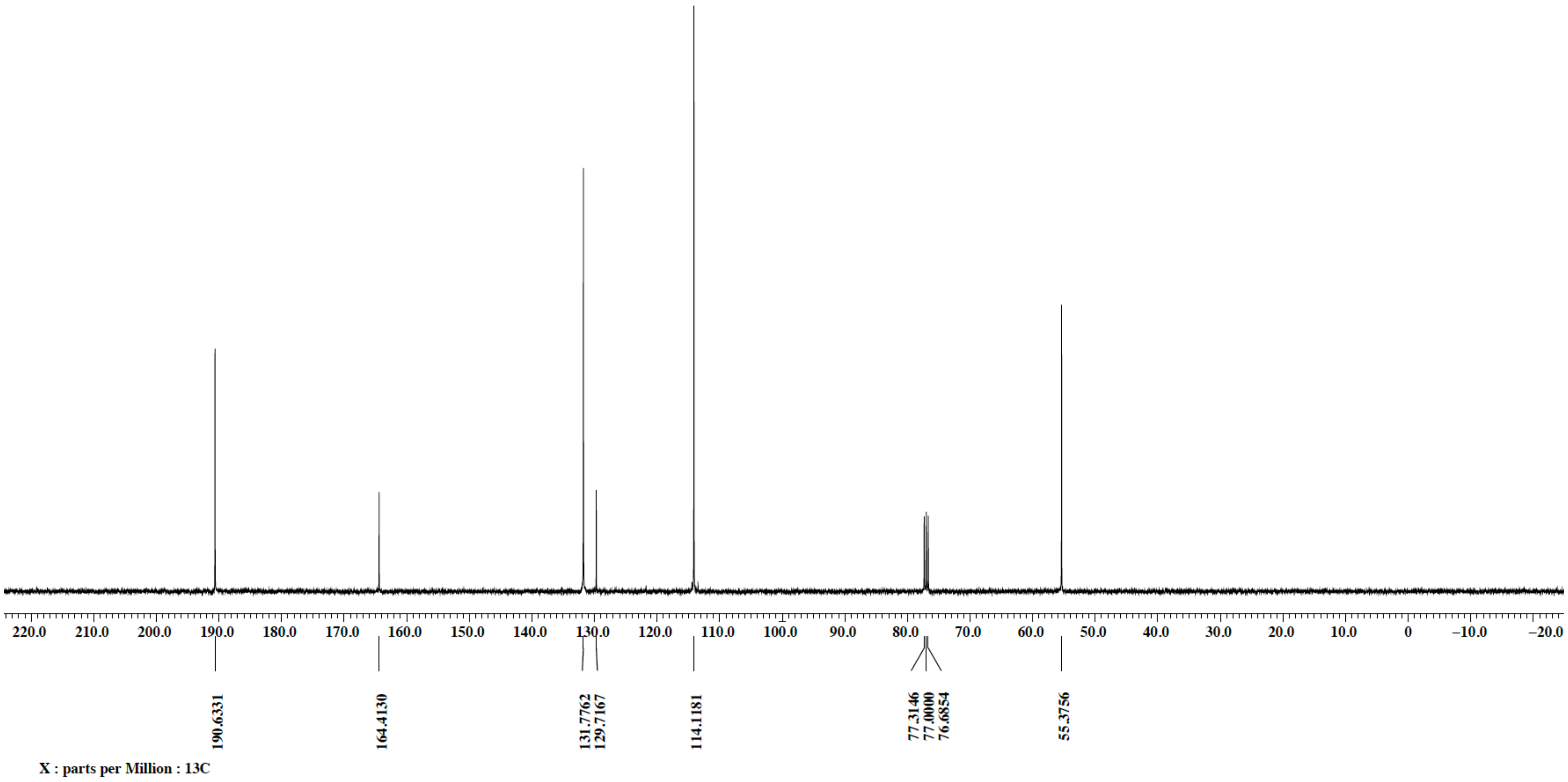

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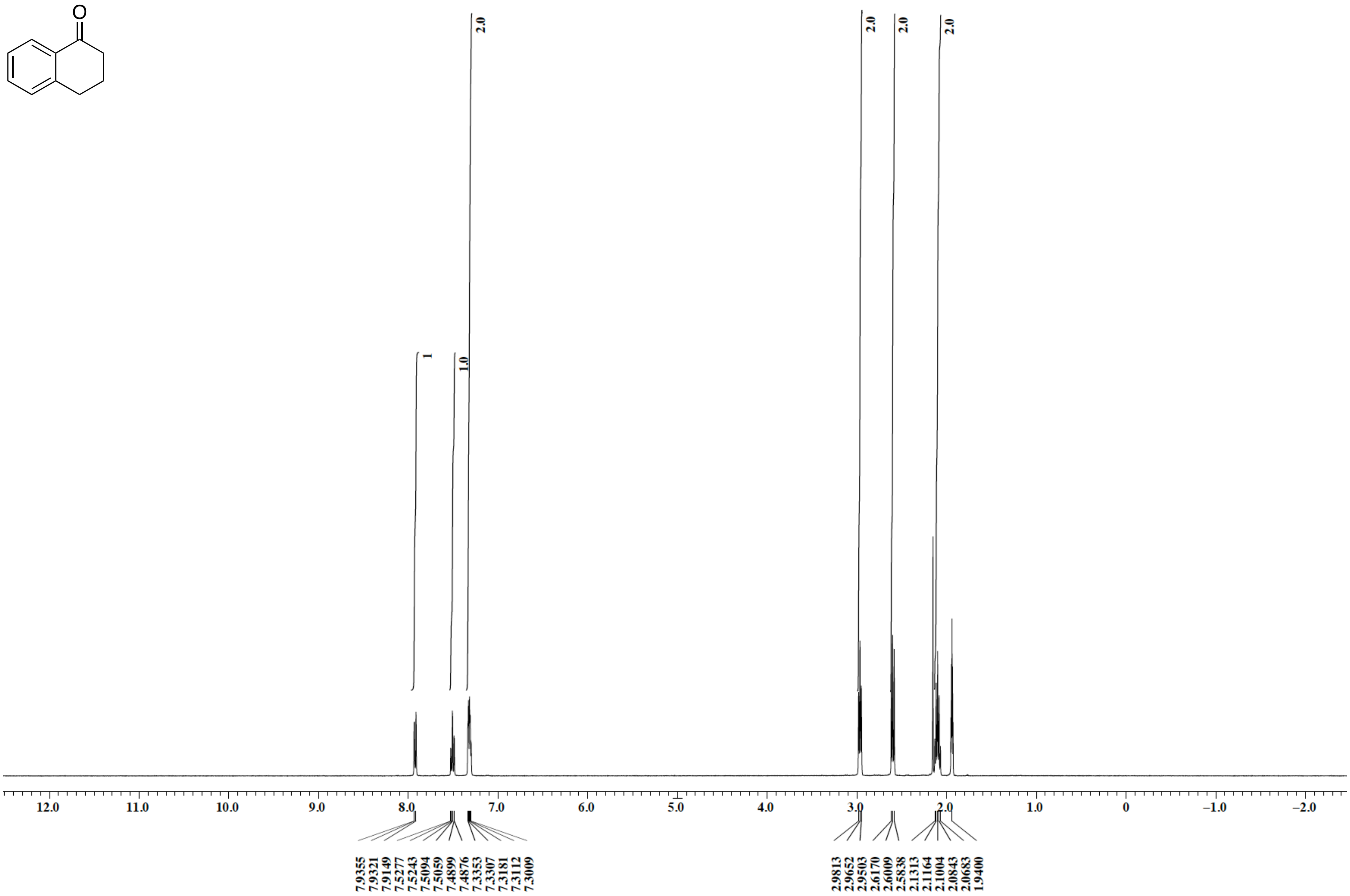

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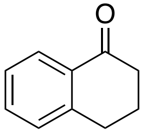

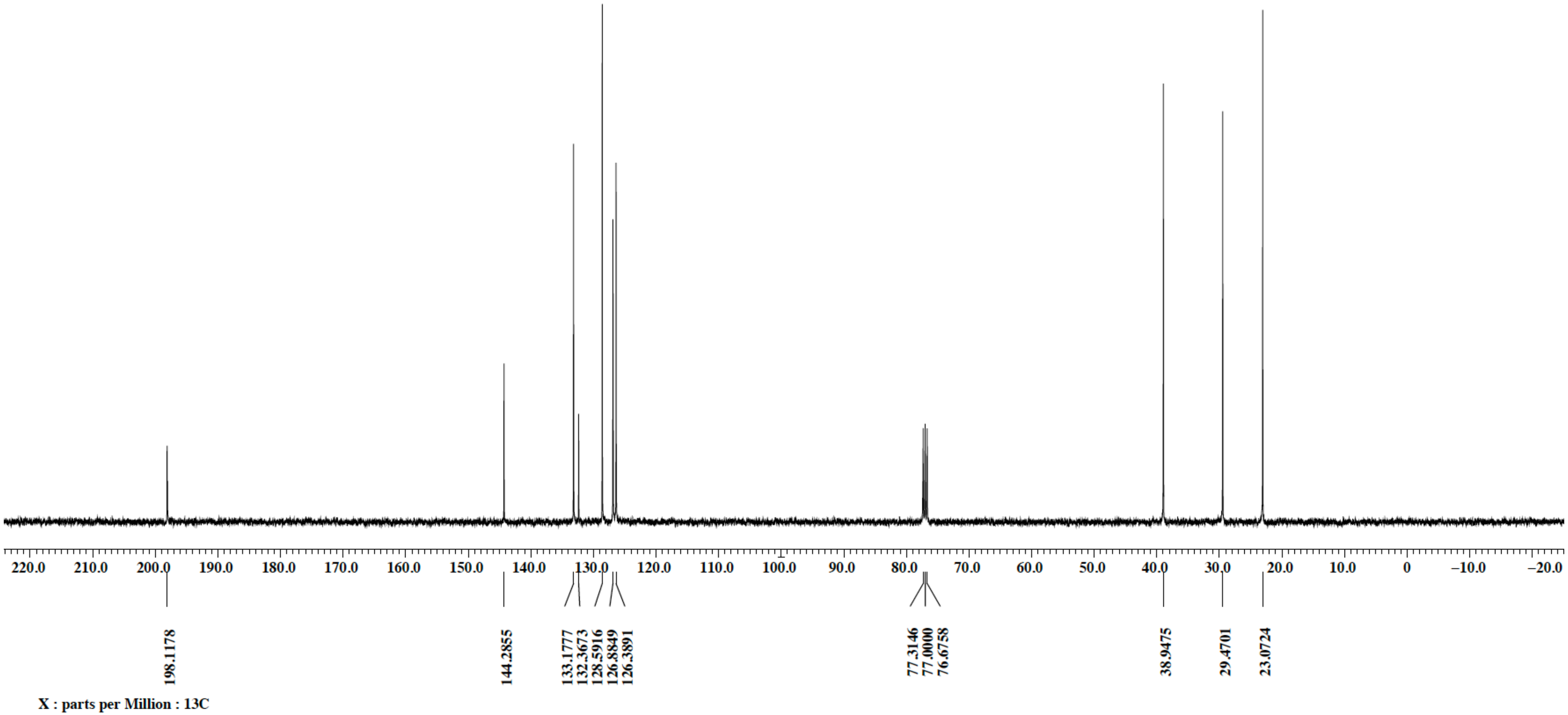

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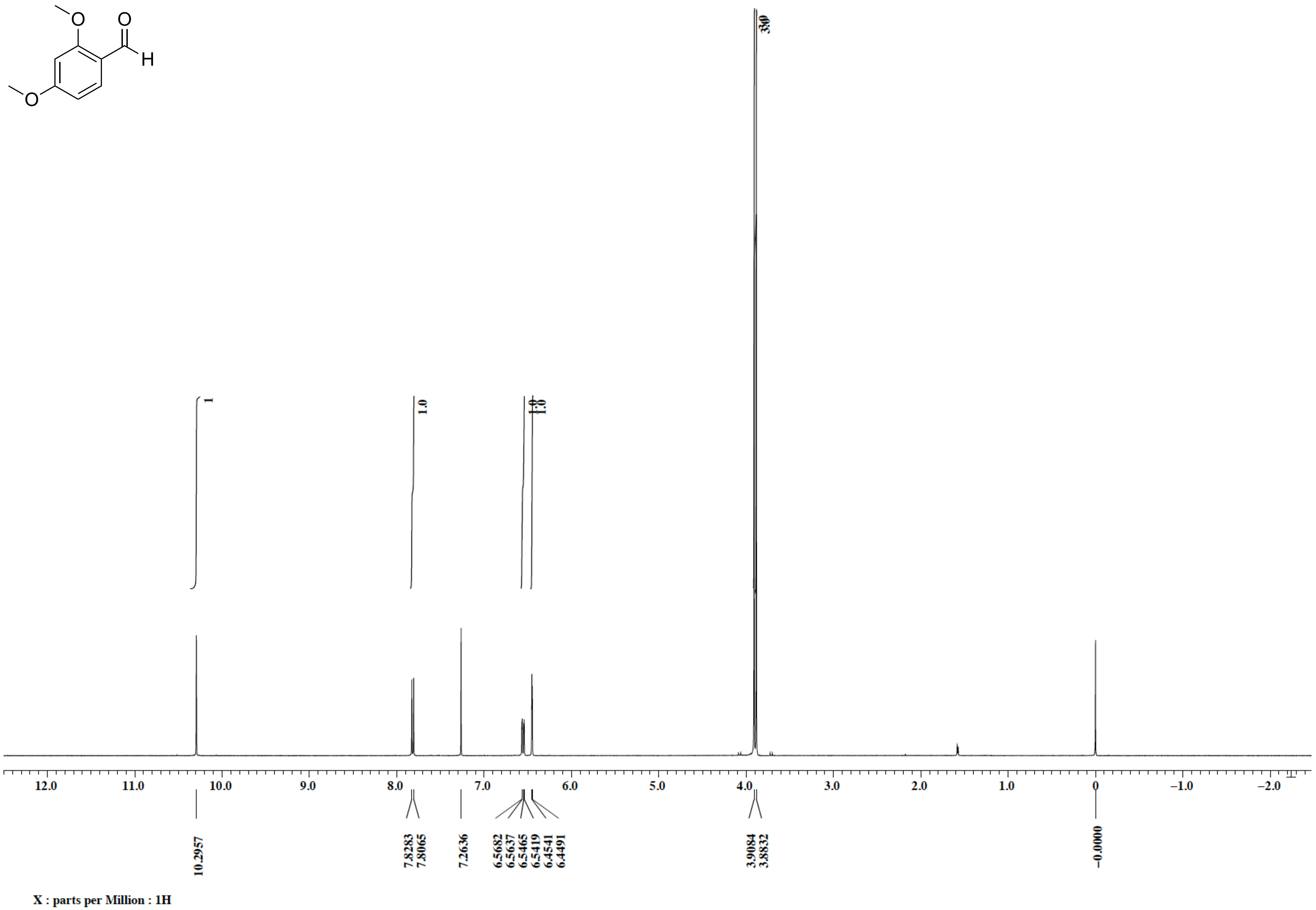

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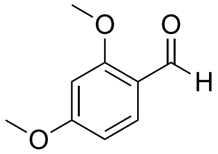

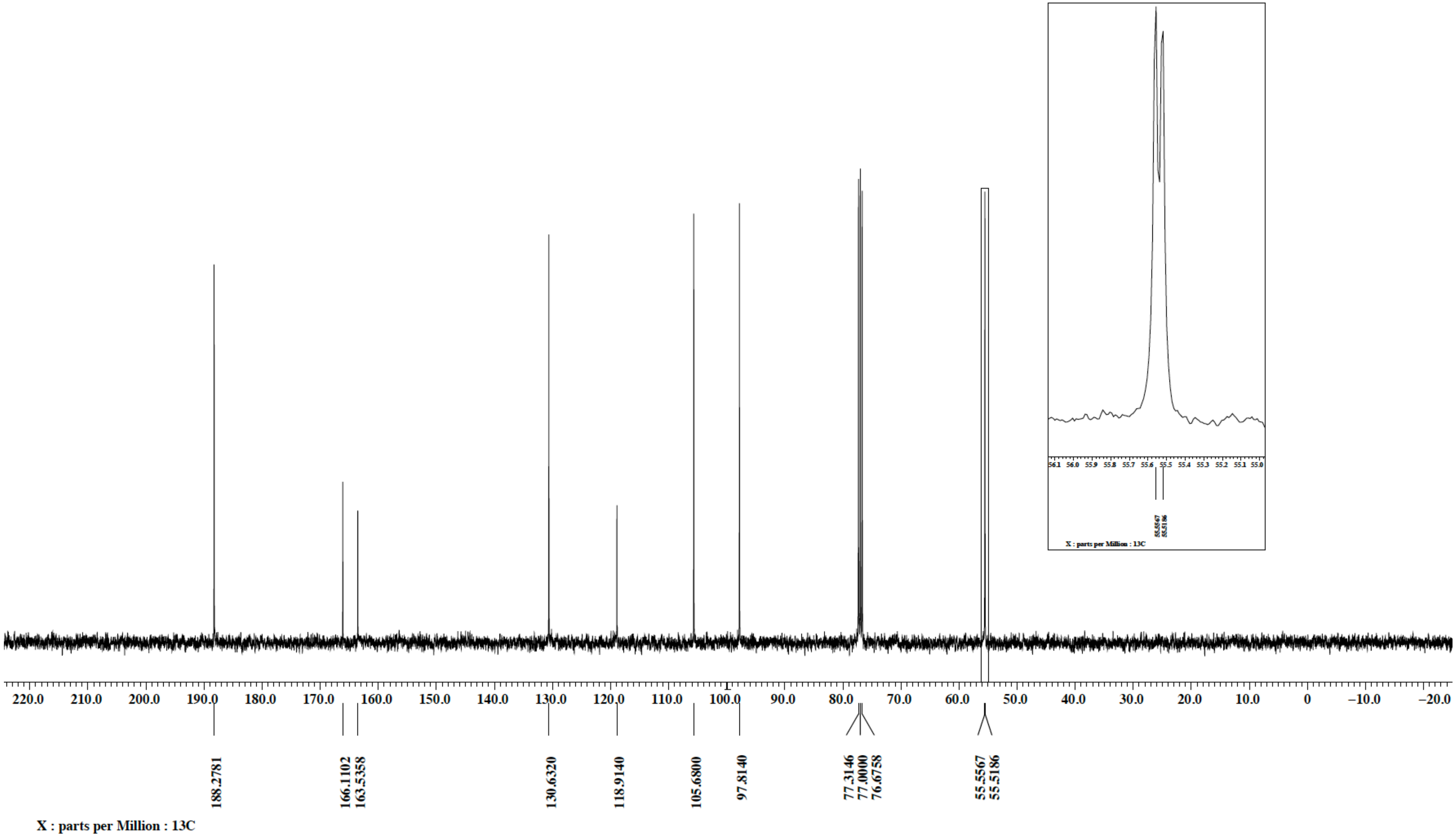

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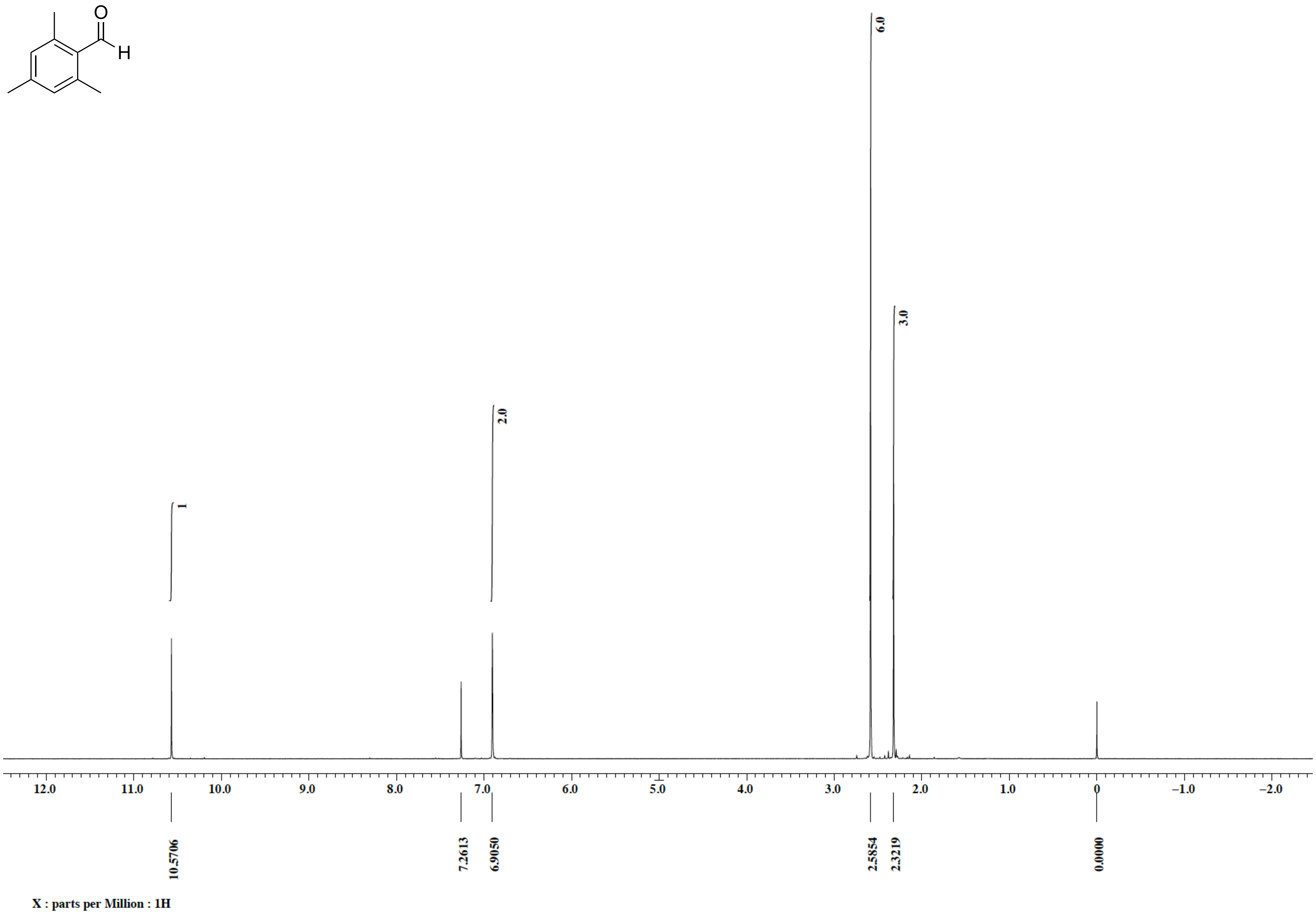

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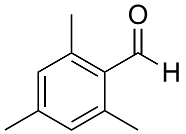

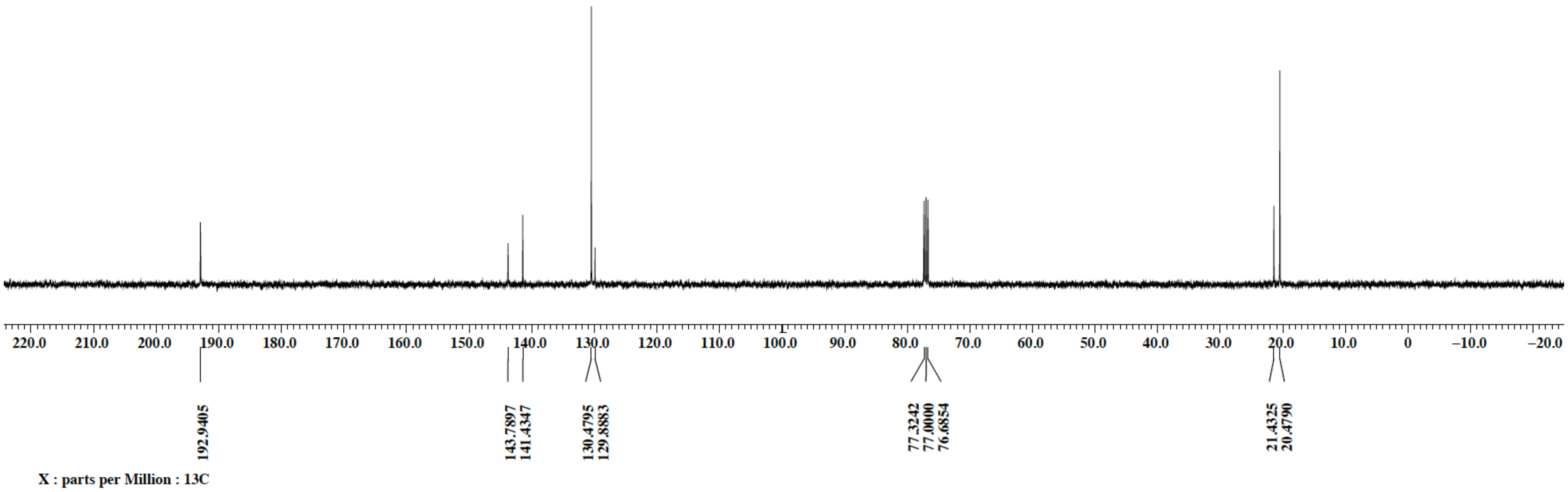

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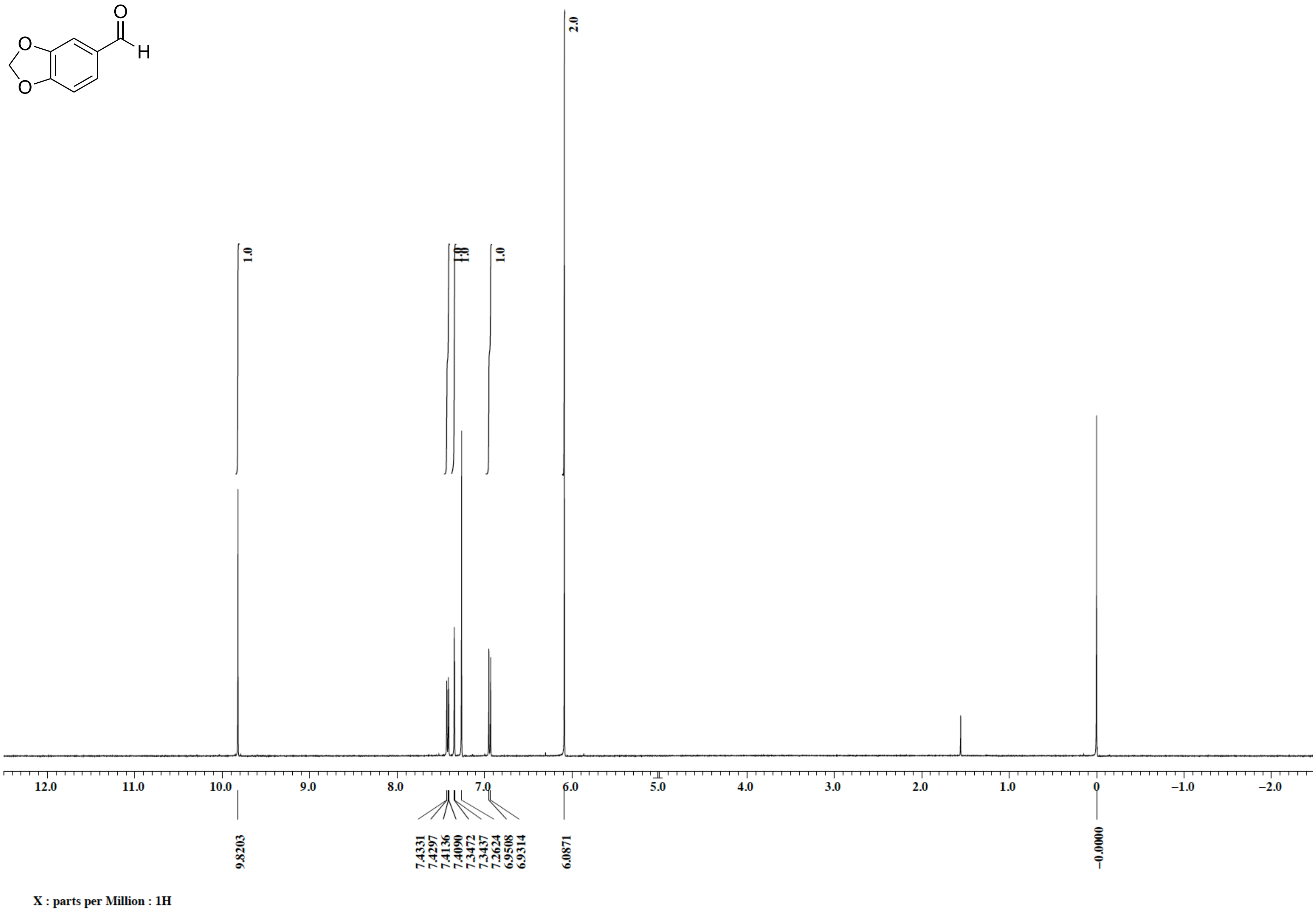
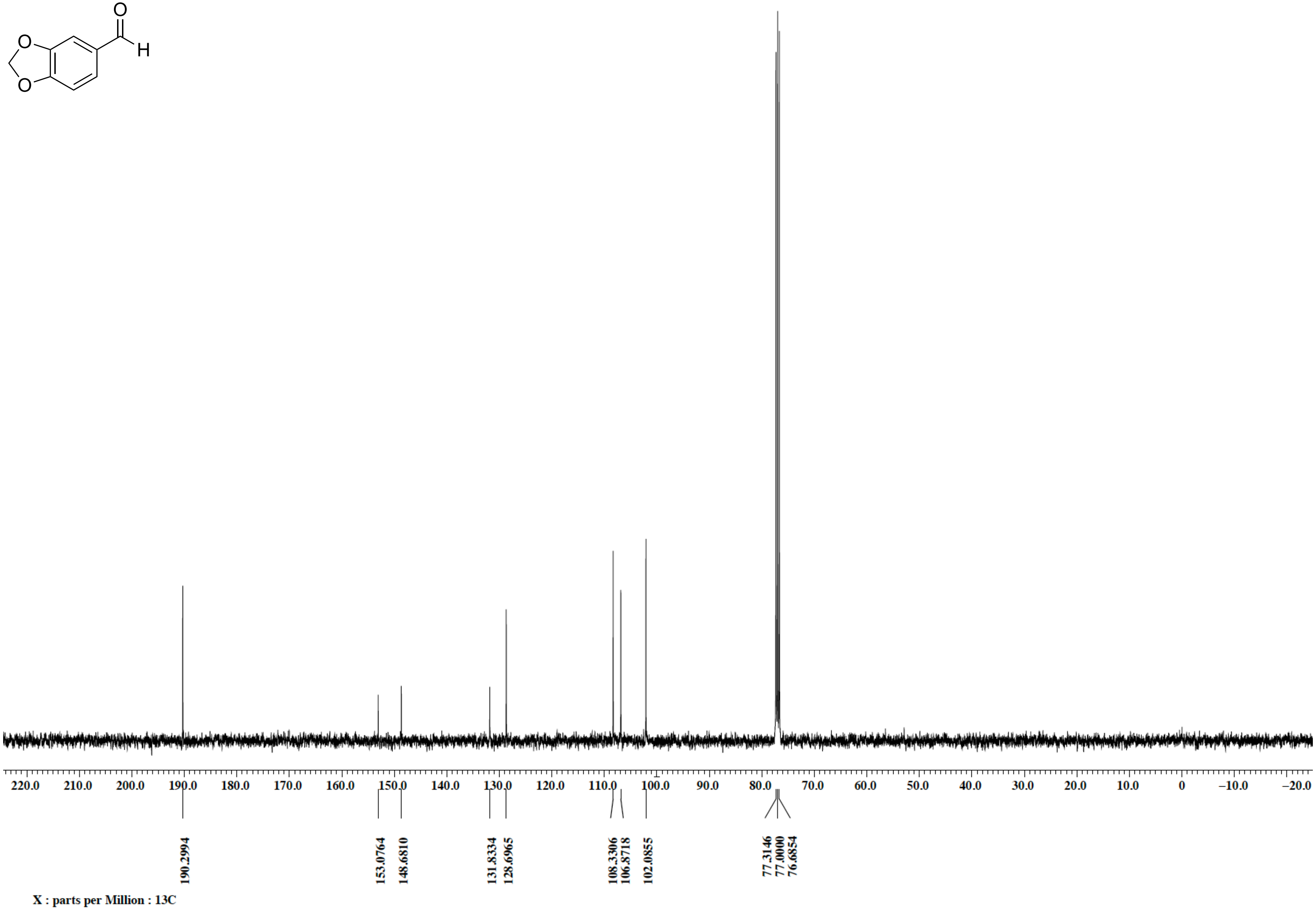
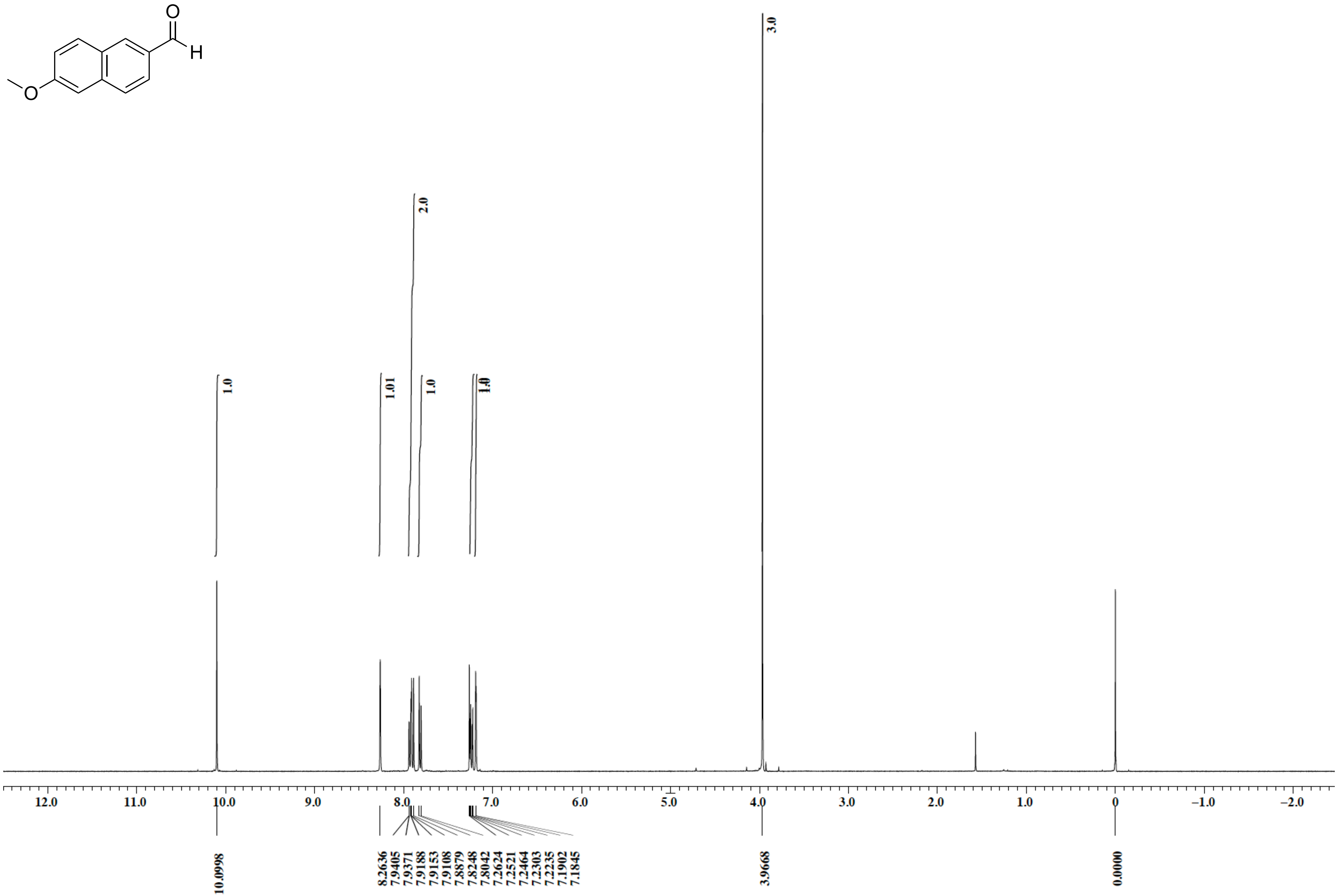


5f, ^{13}C NMR (CDCl$_3$, 100 MHz)



5g, ^{1}H NMR (CDCl$_3$, 400 MHz)



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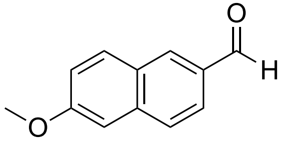

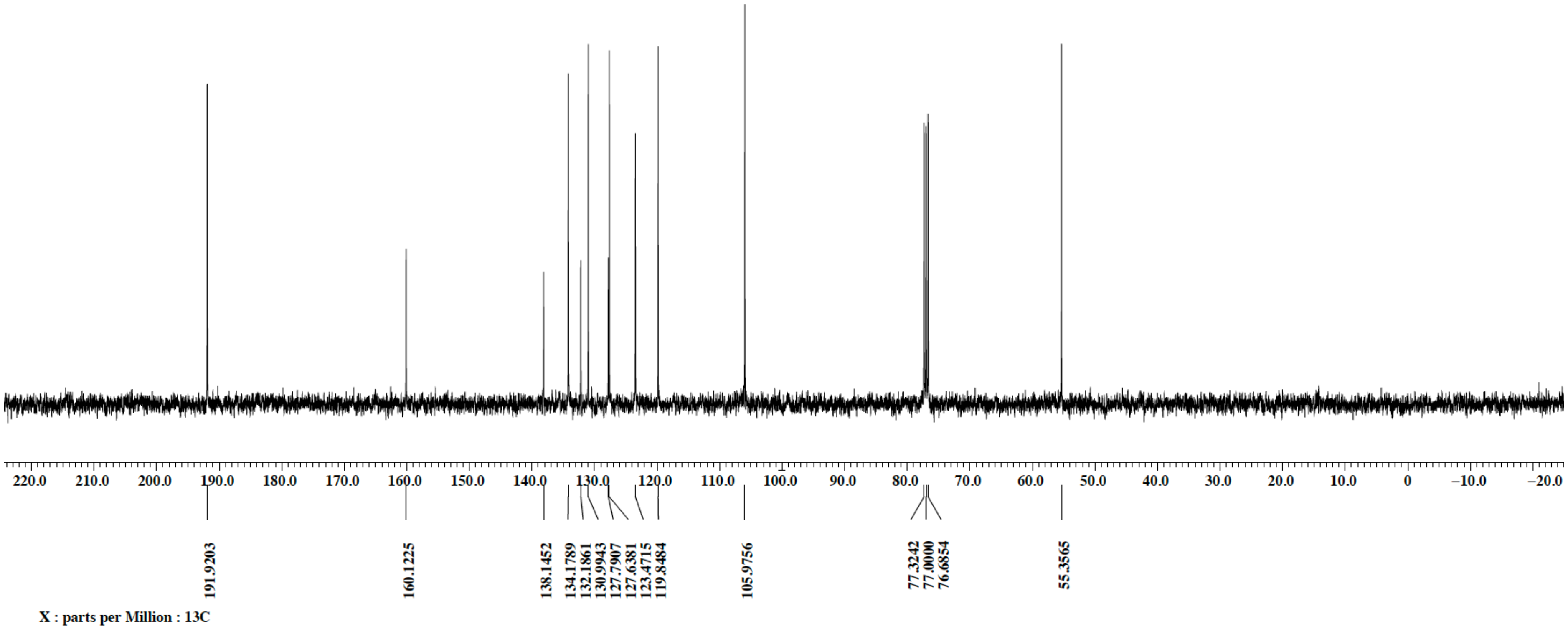

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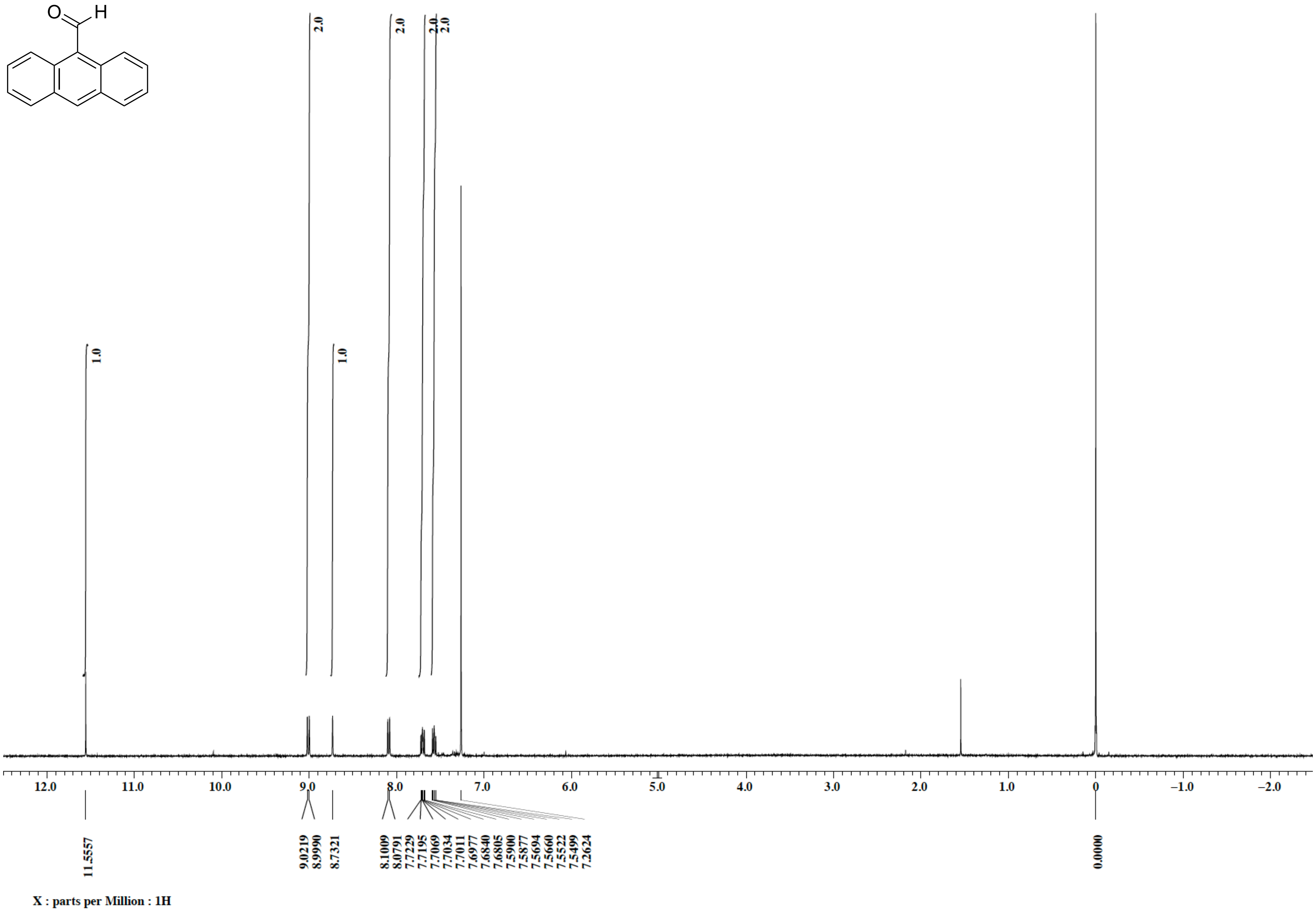
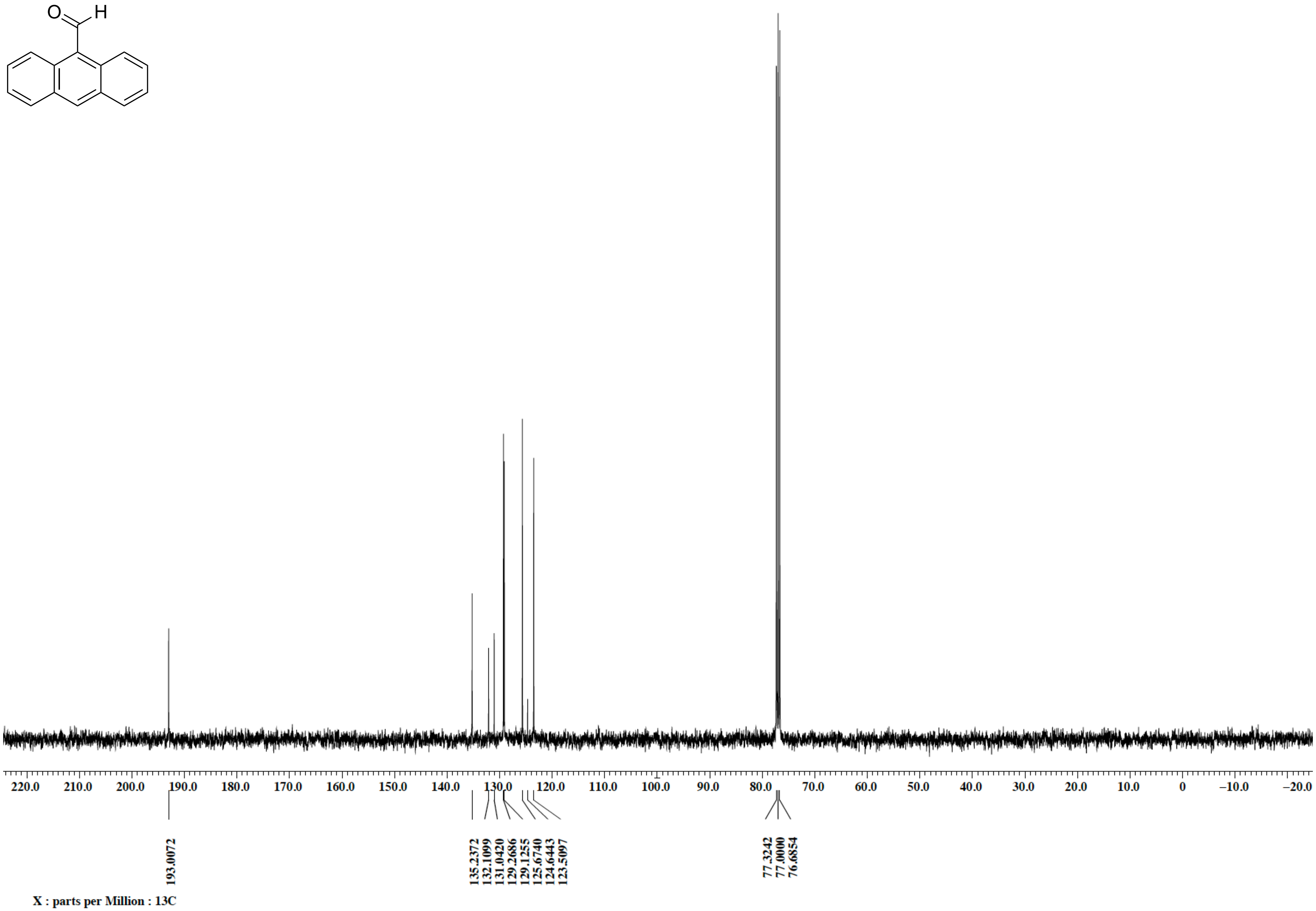


5h, ^{13}C NMR (CDCl$_3$, 100 MHz)



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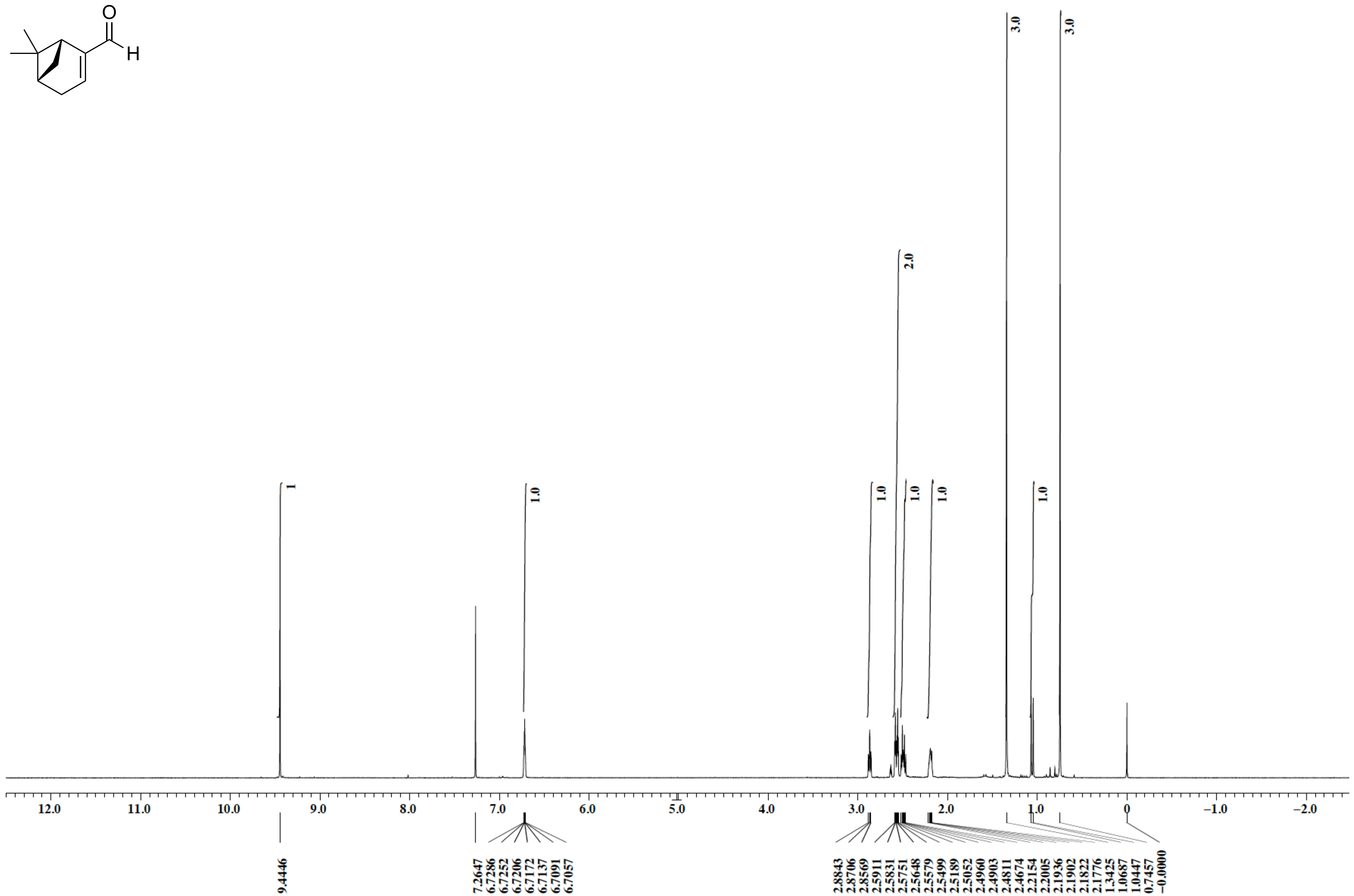

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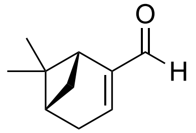

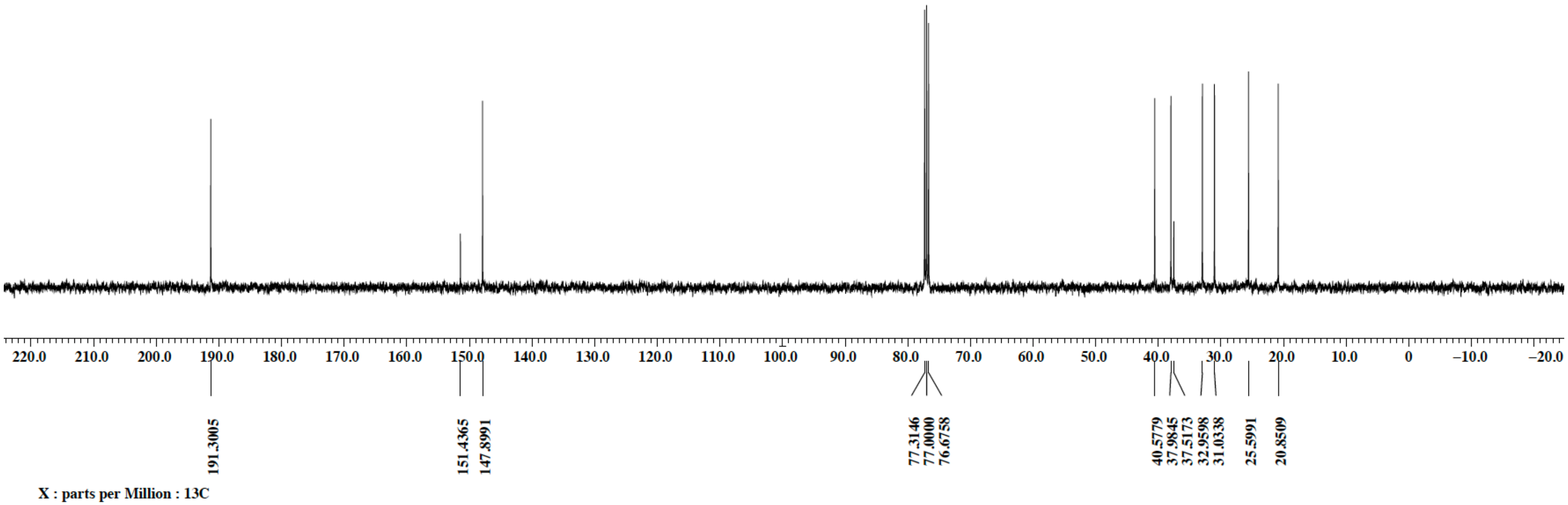

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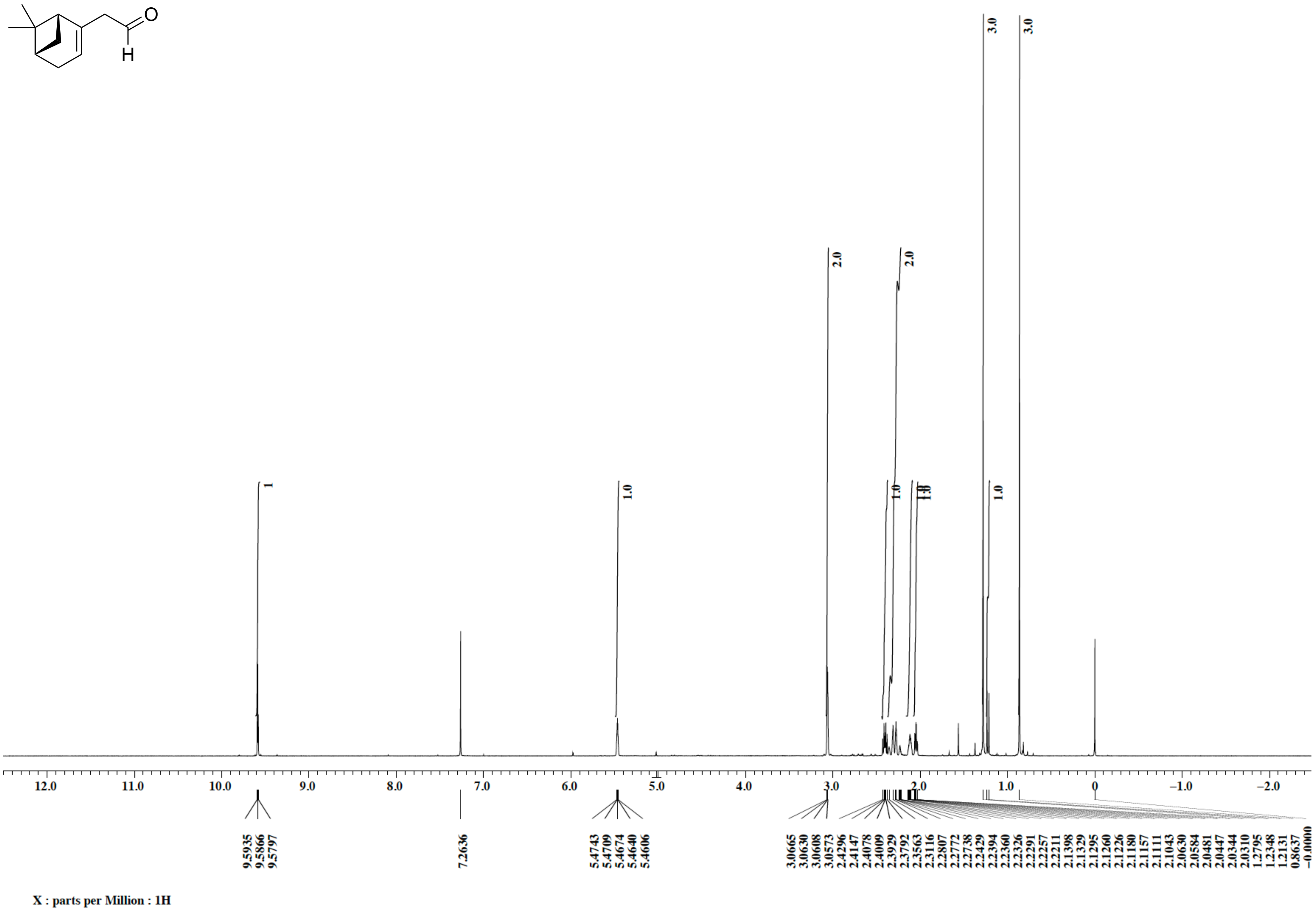

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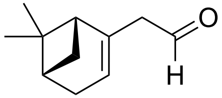

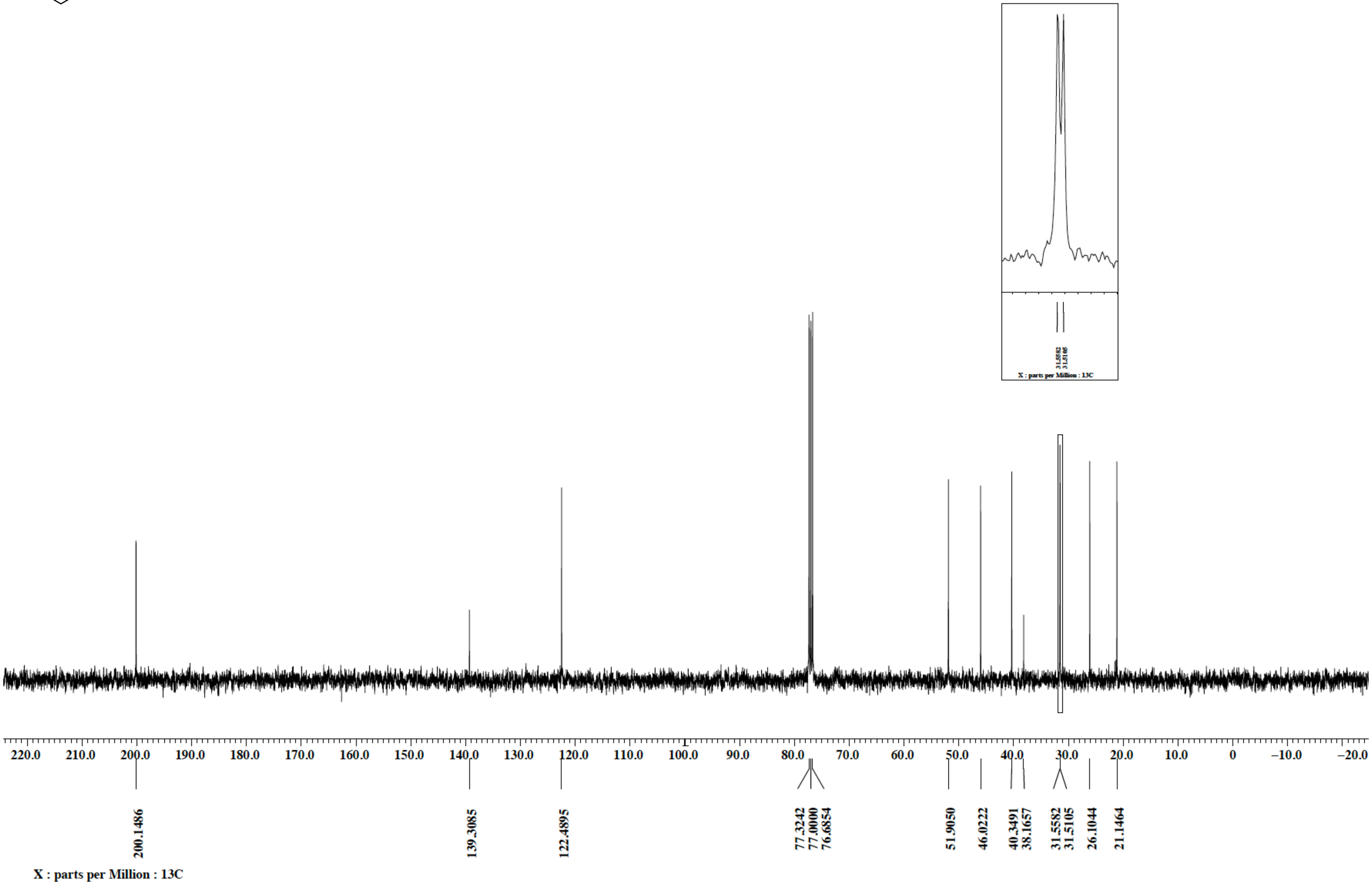

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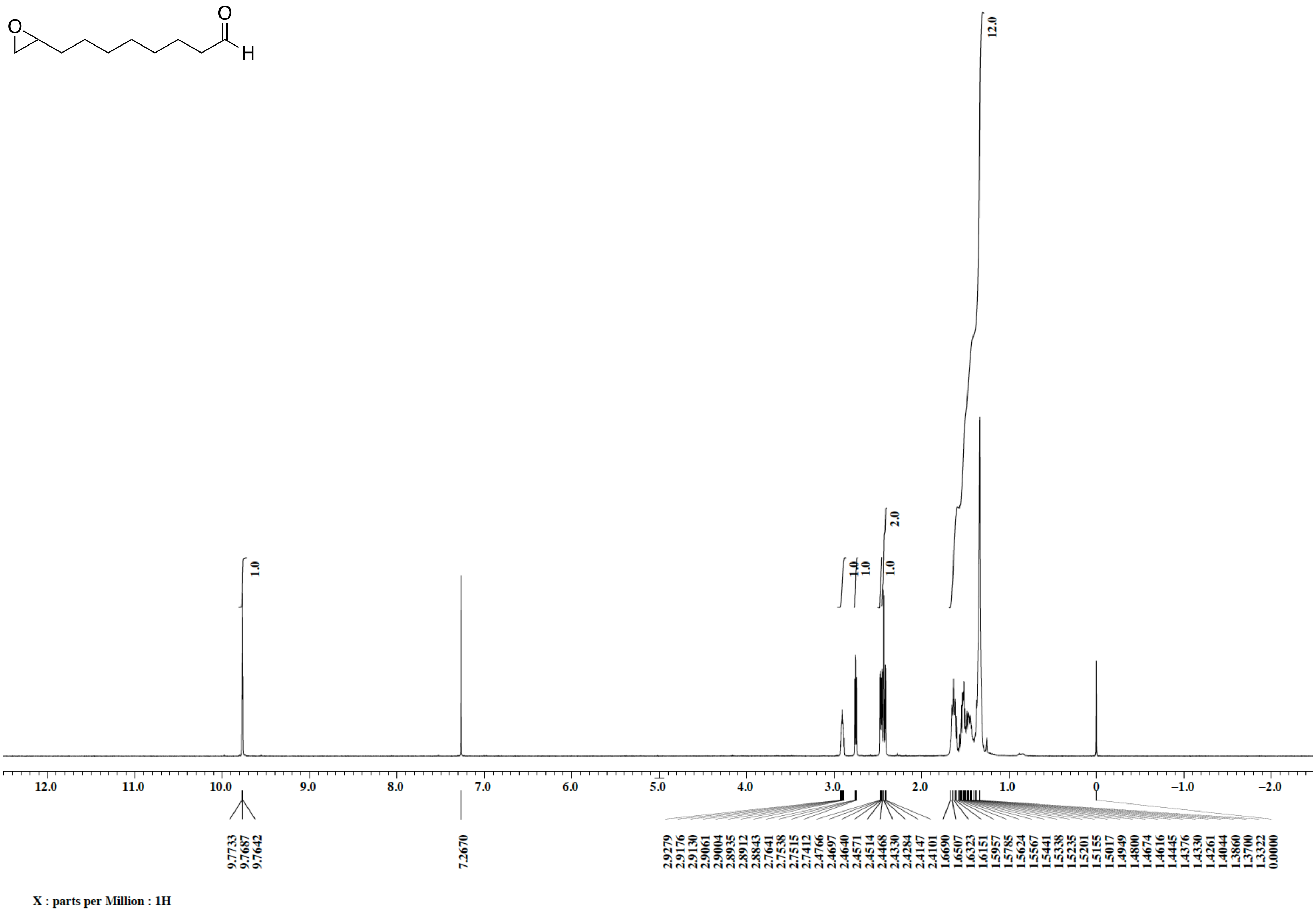

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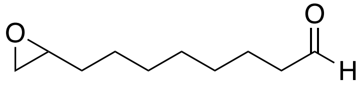

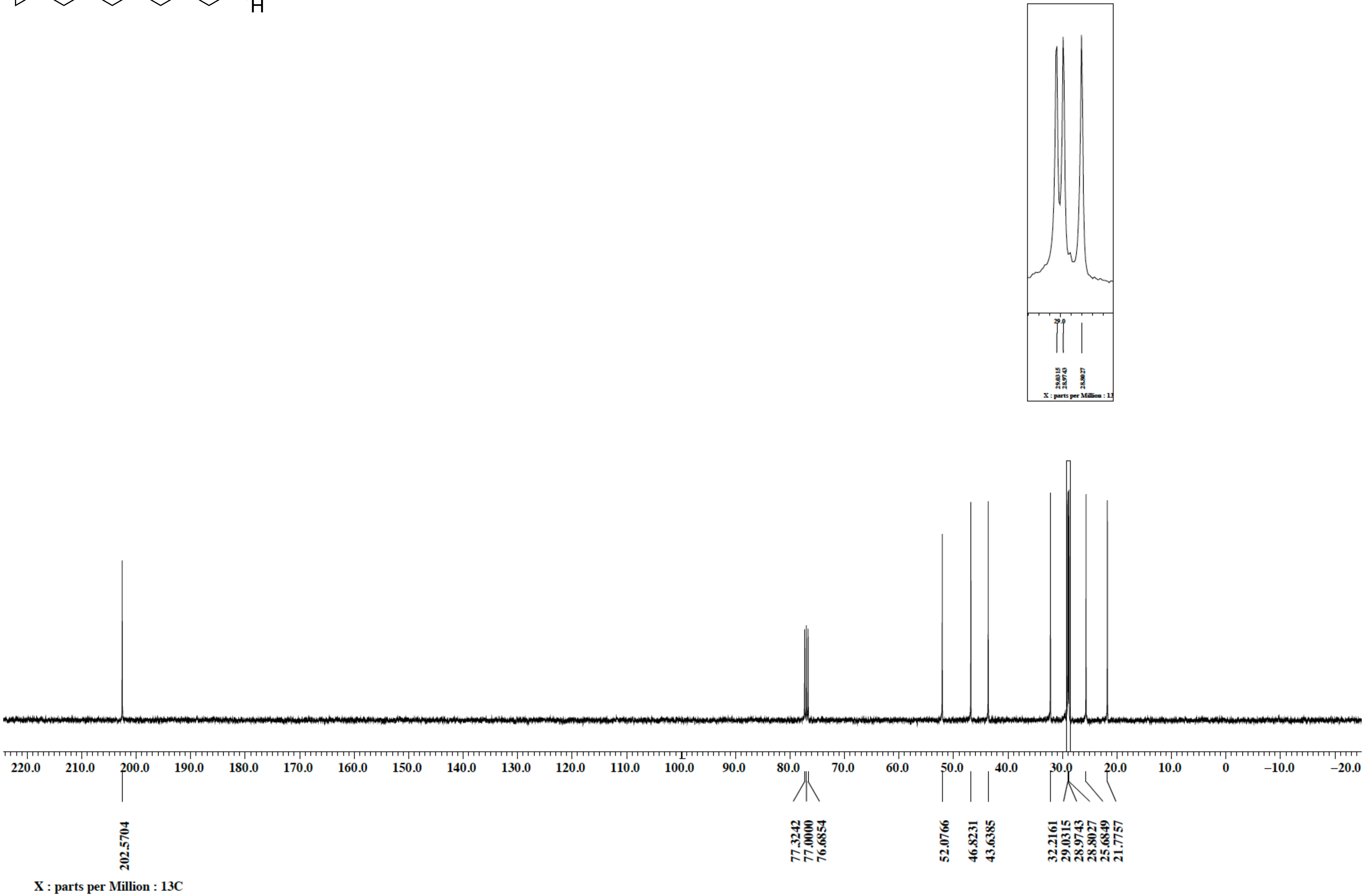

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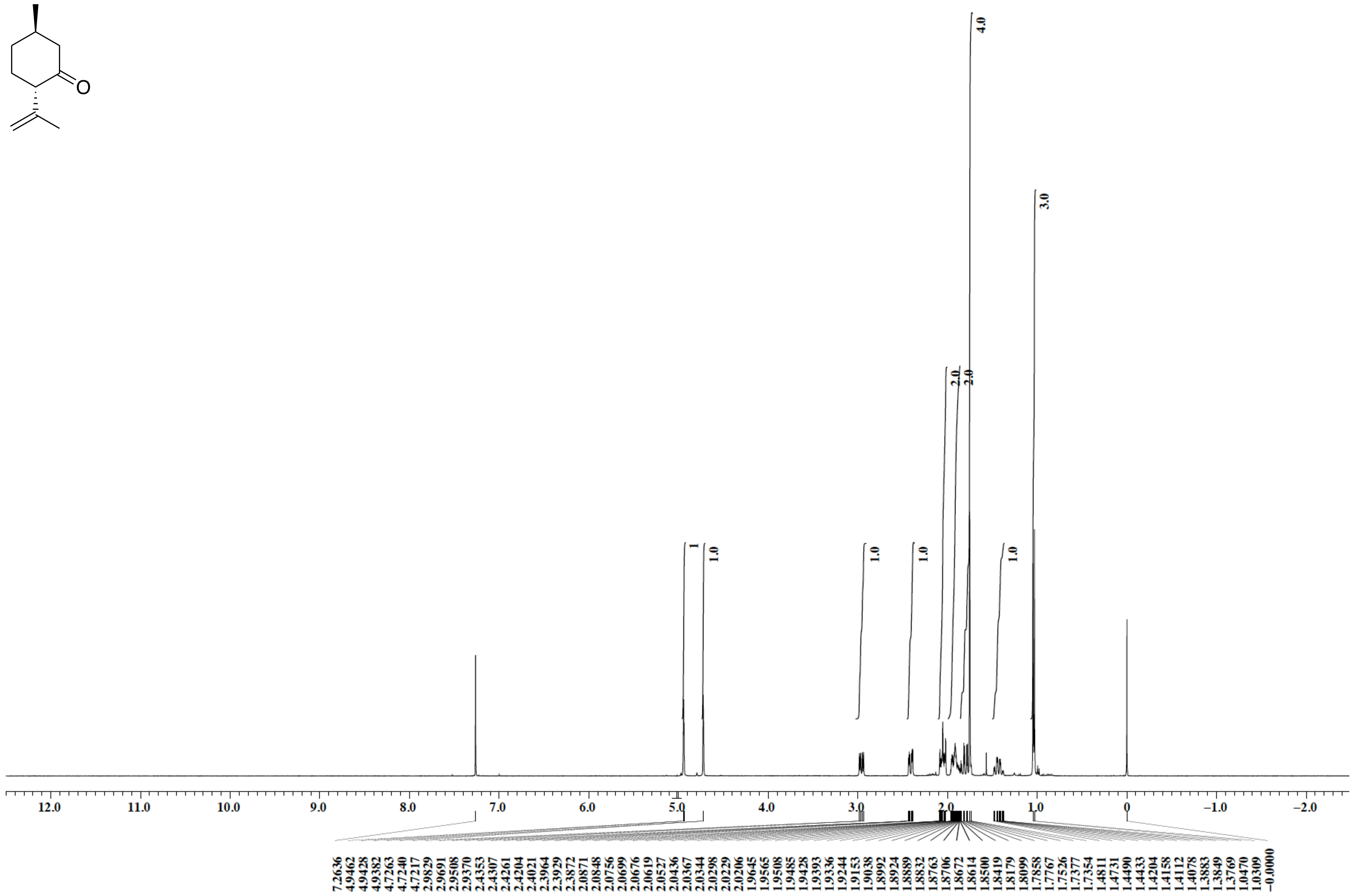

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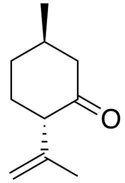

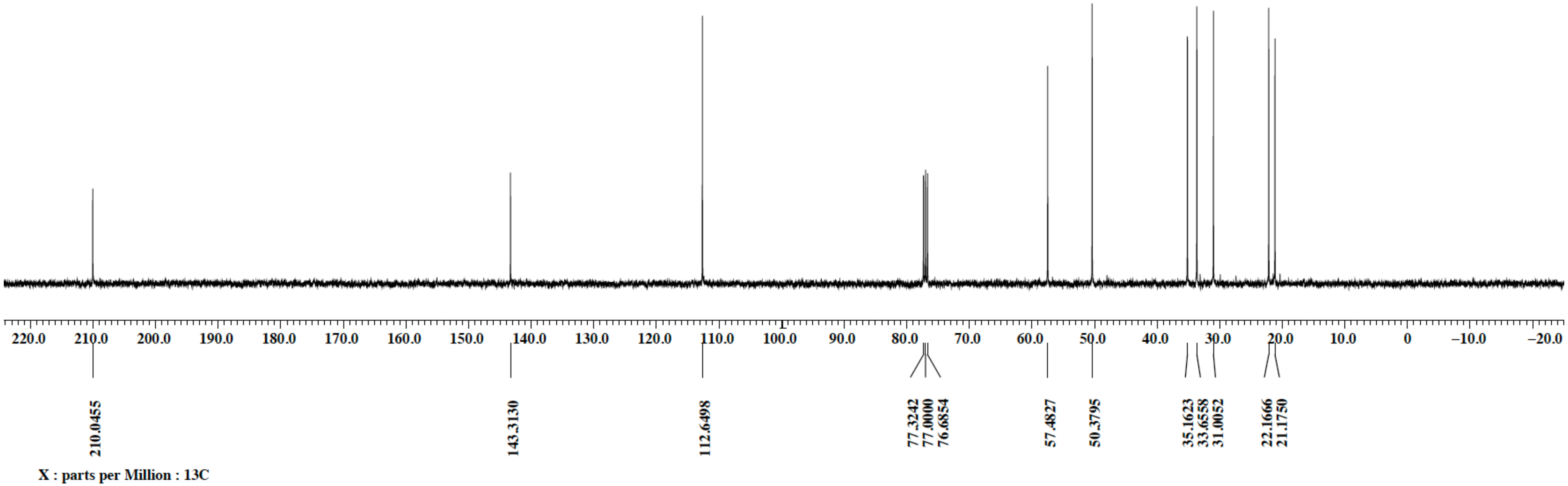

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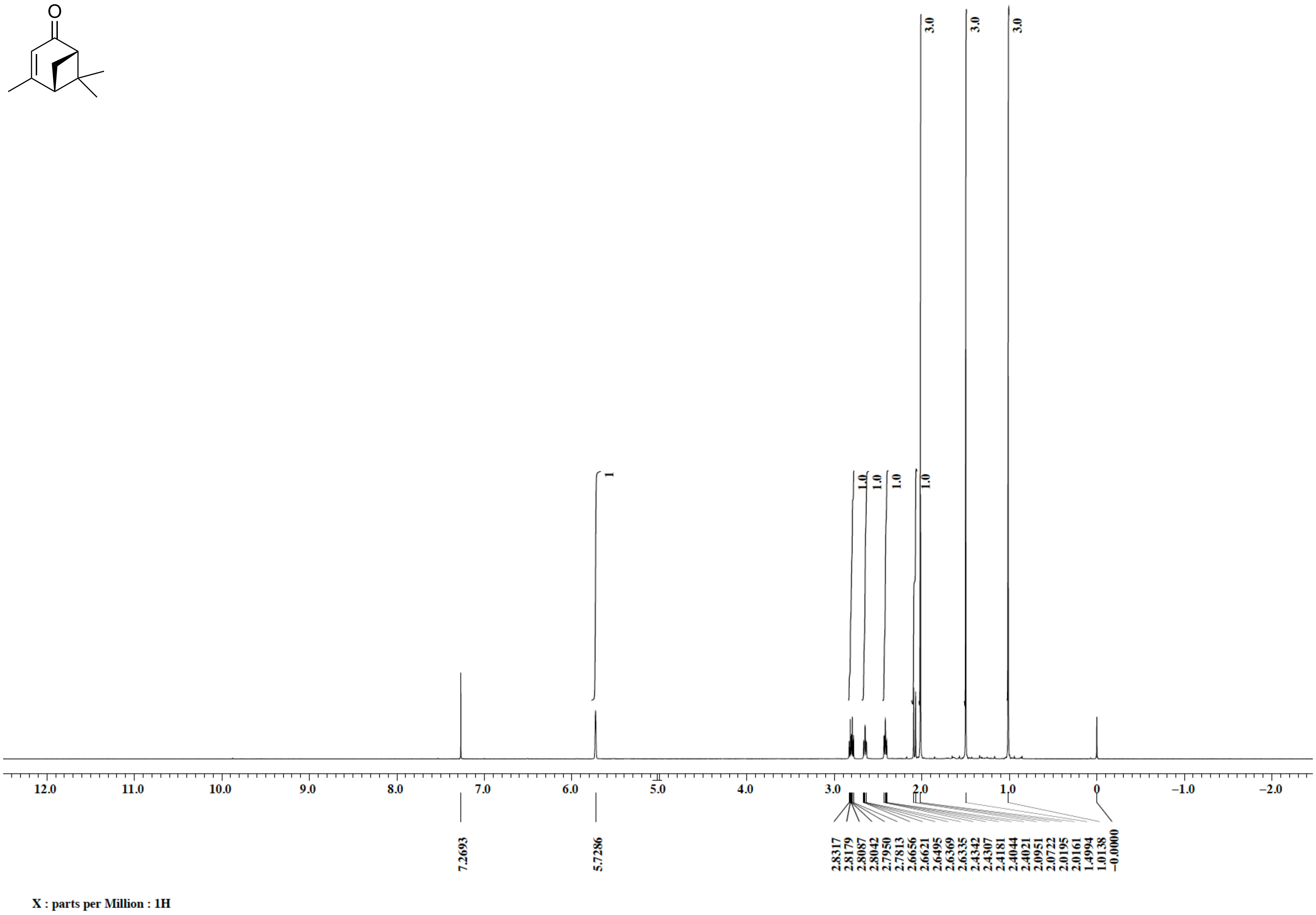

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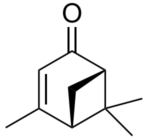

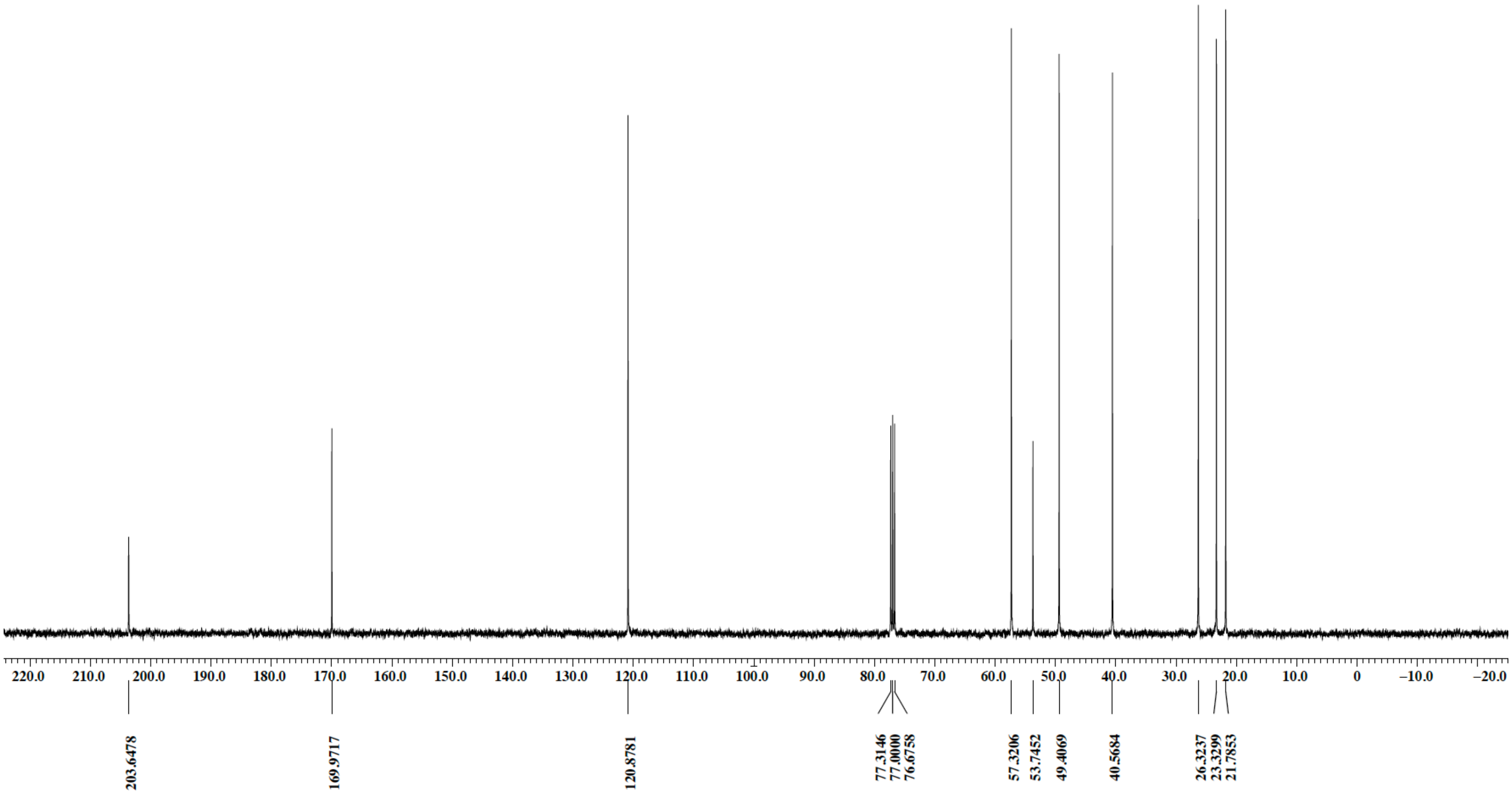

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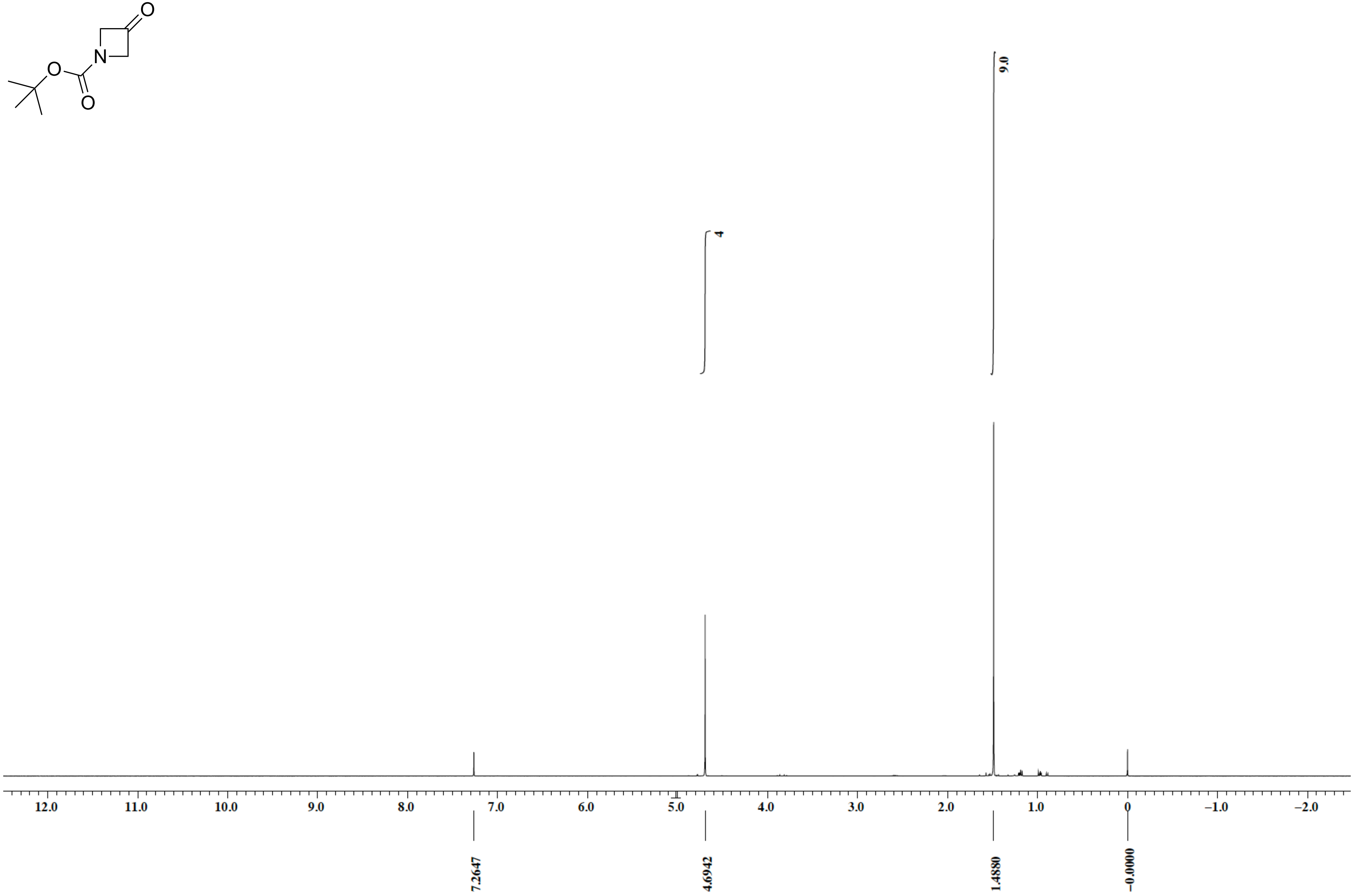

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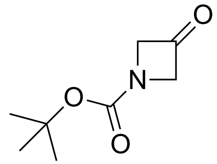

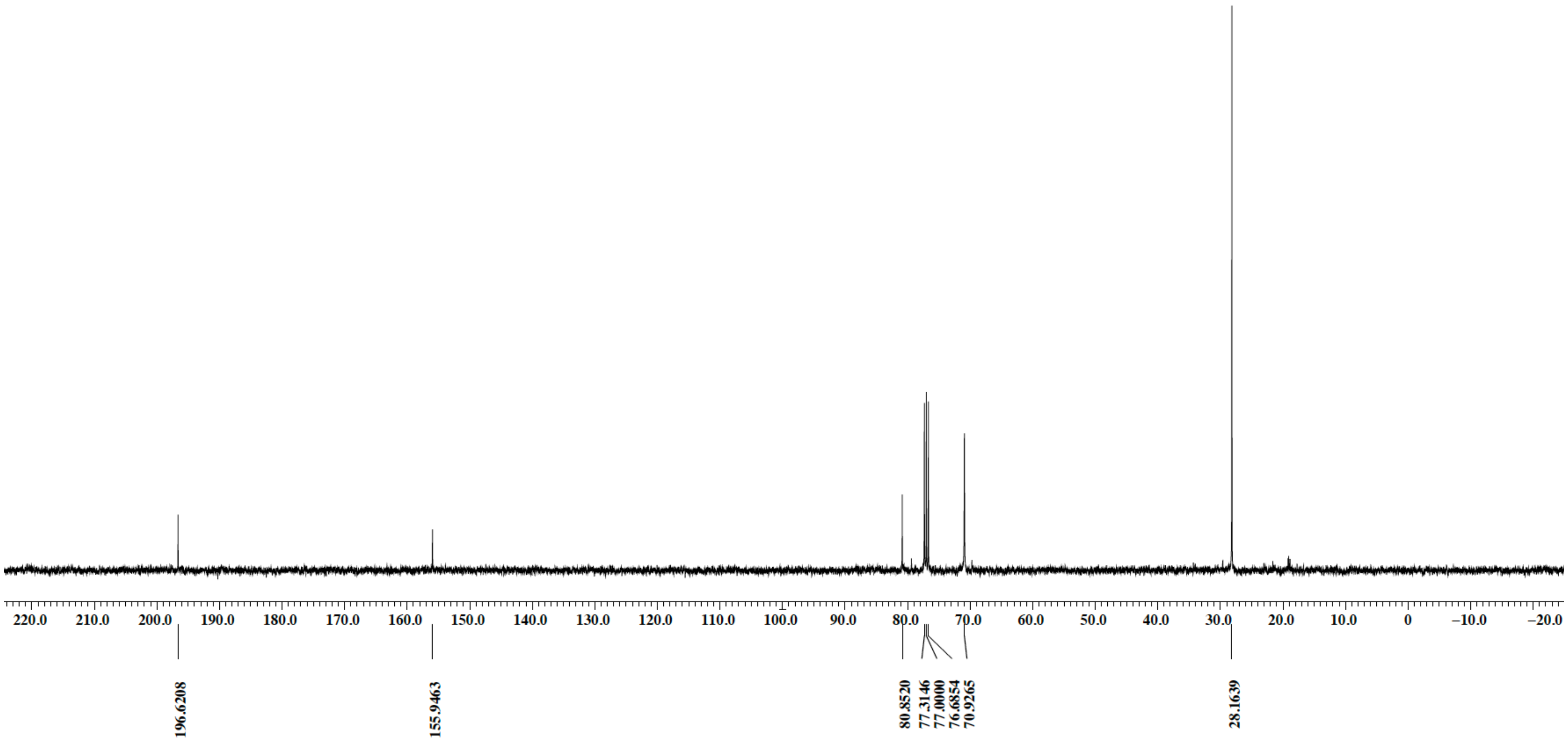

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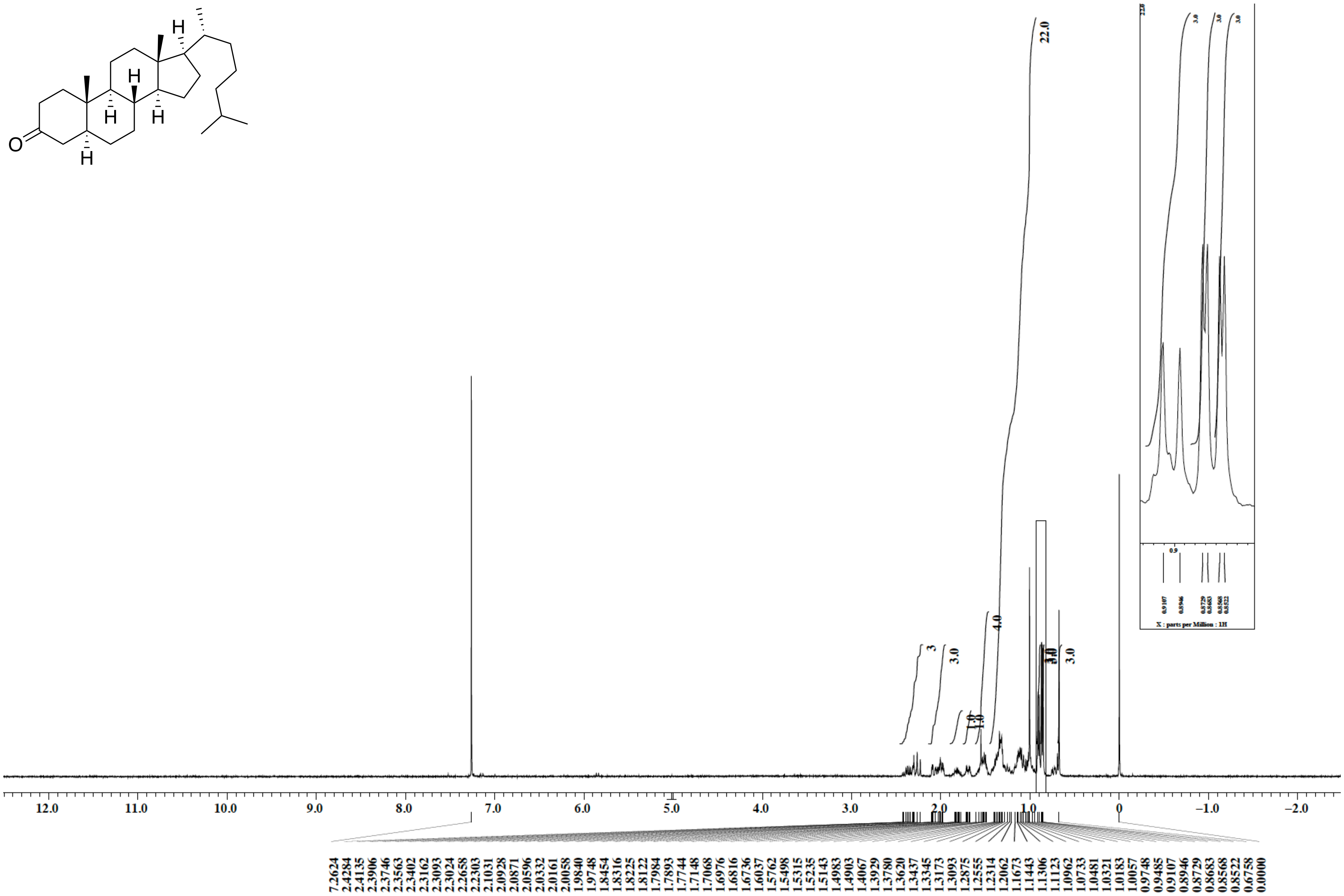

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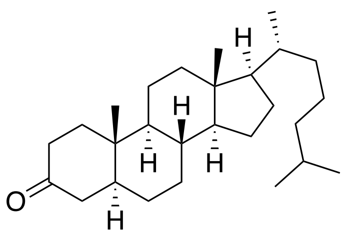

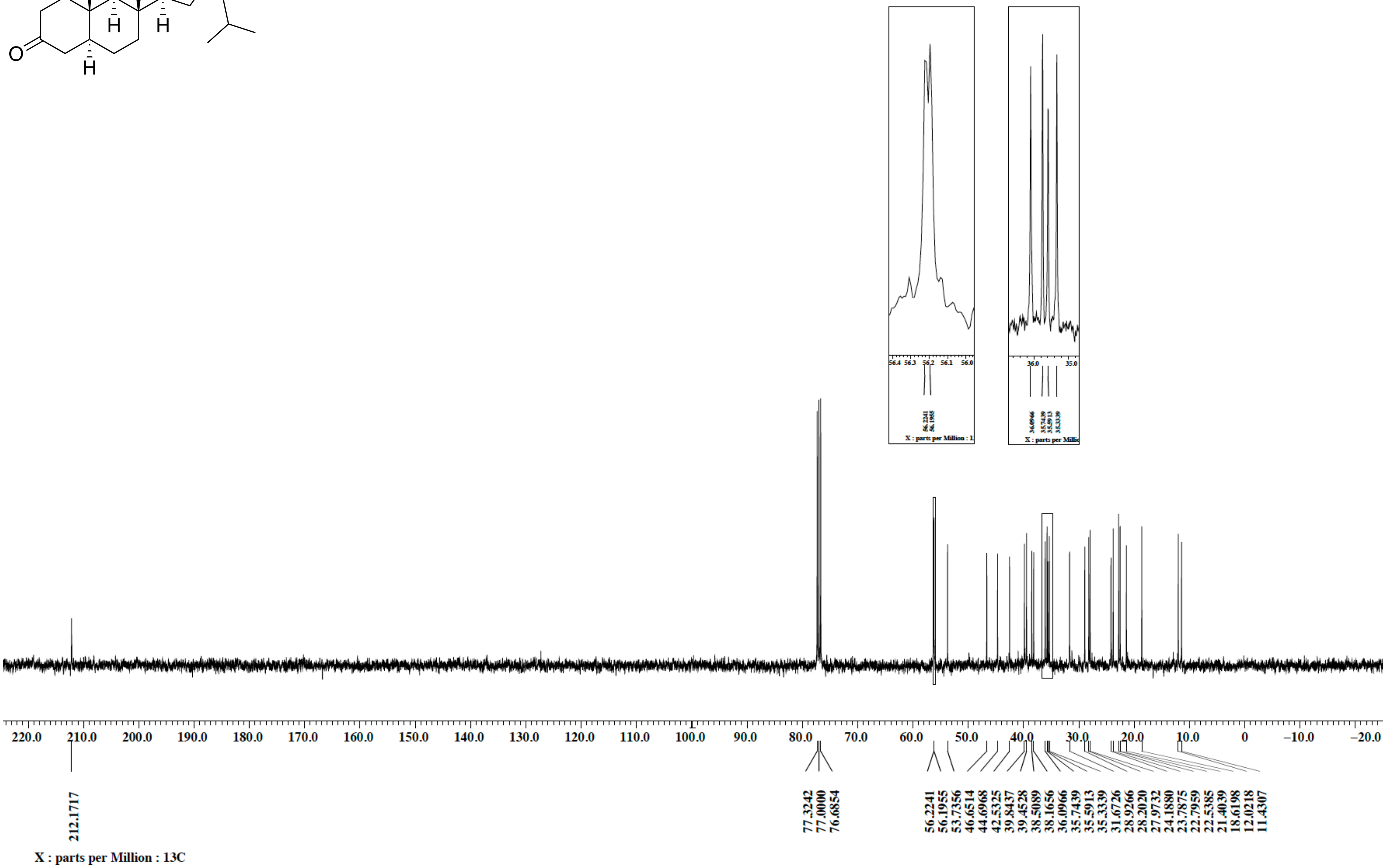

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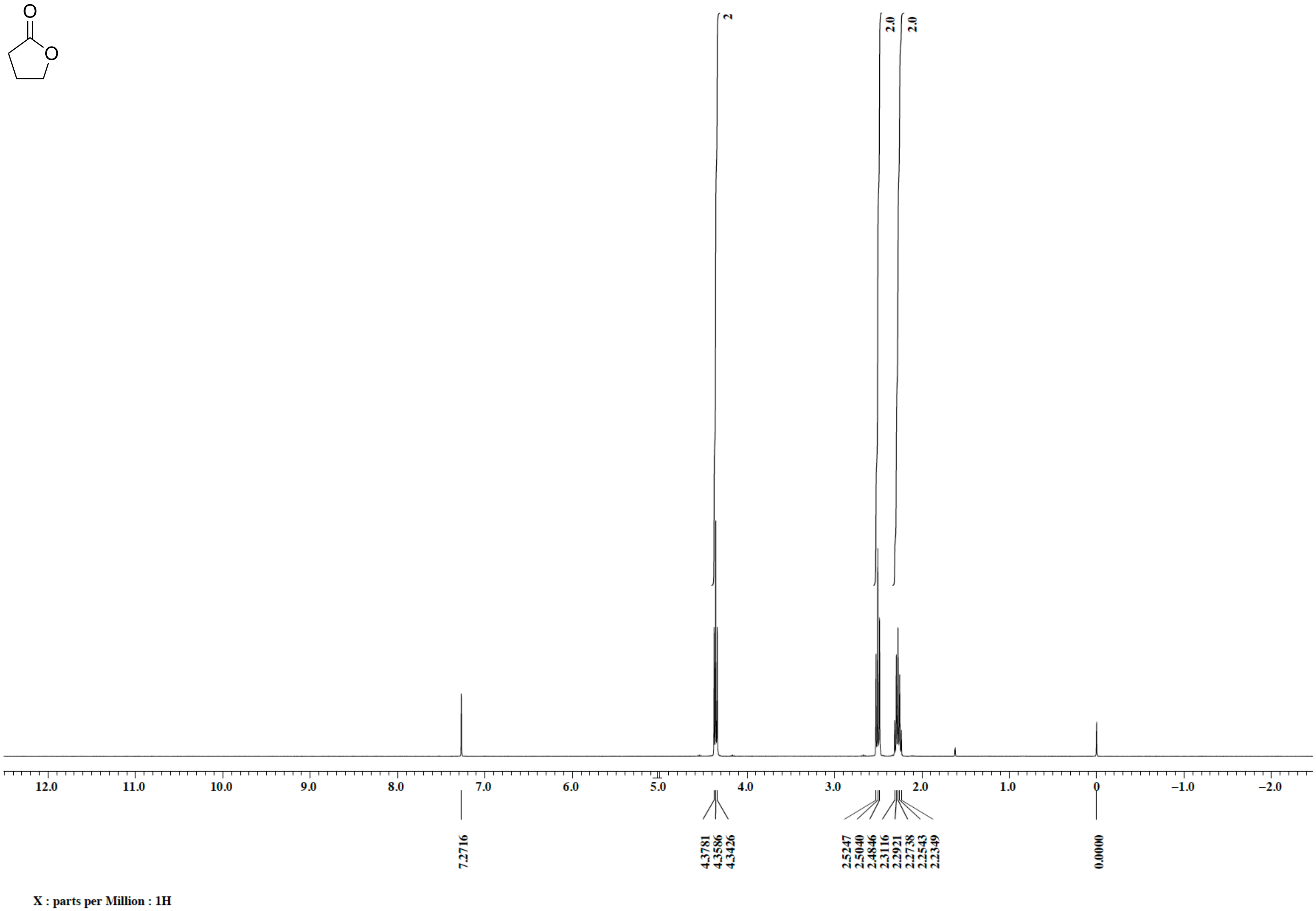
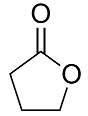
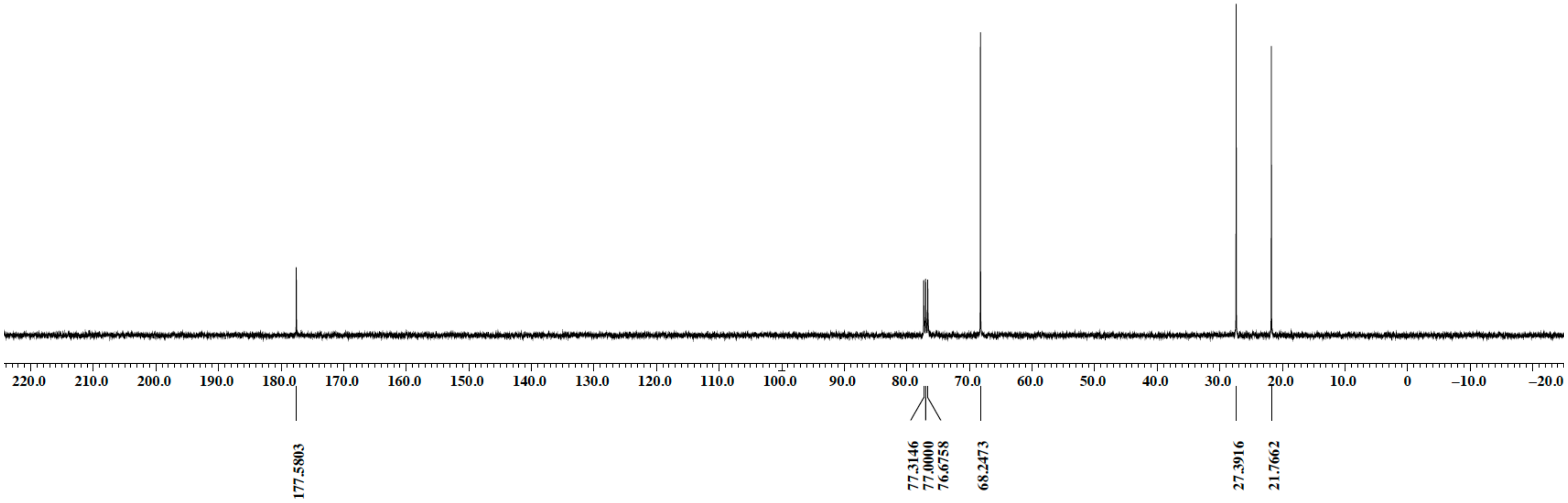
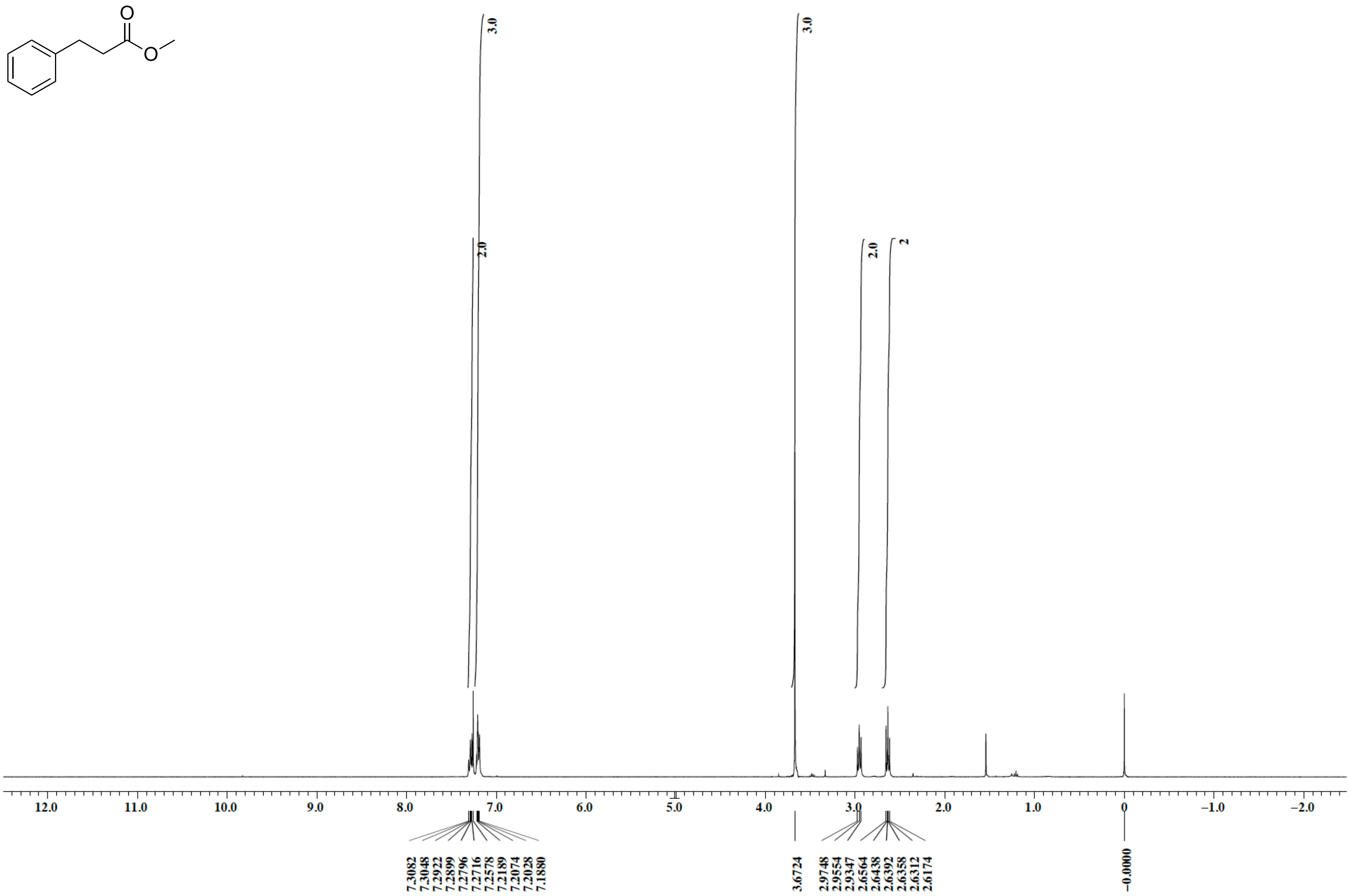


7, ^{13}C NMR ($CDCl_3$, 100 MHz)

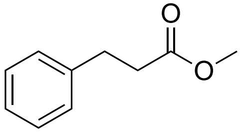


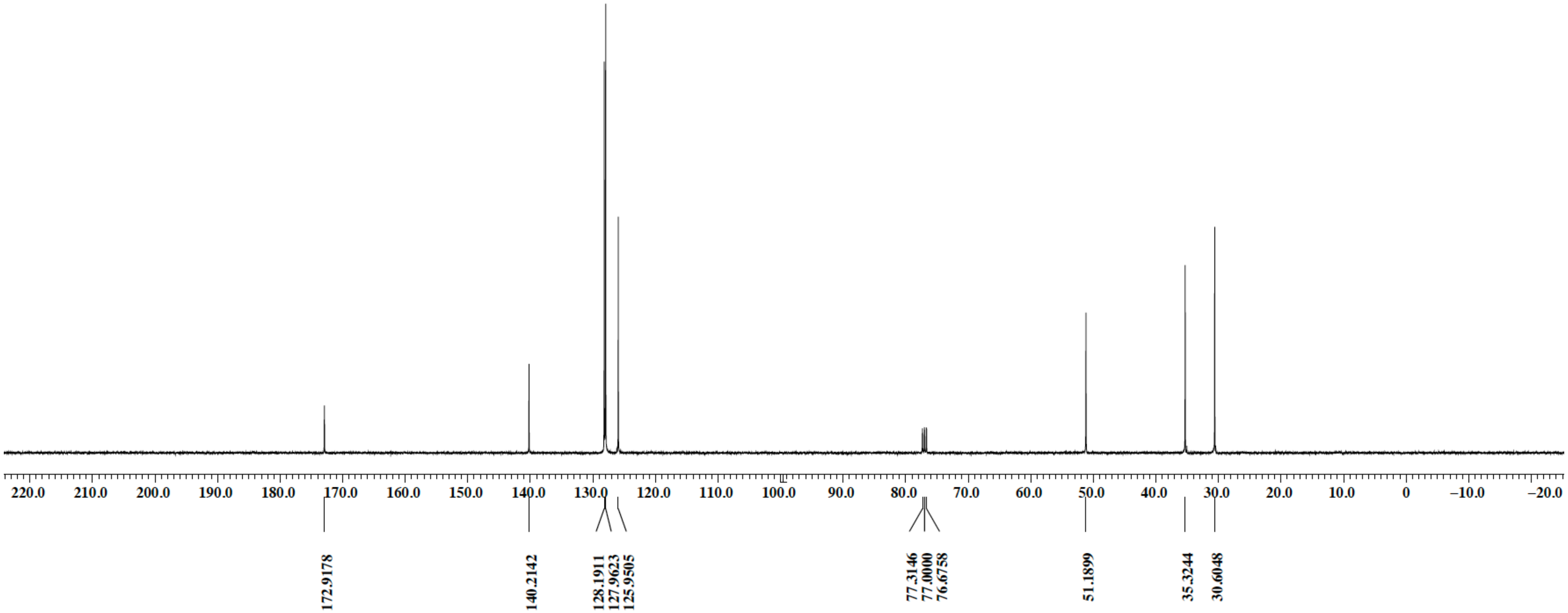


9pa, ^{1}H NMR ($CDCl_3$, 400 MHz)



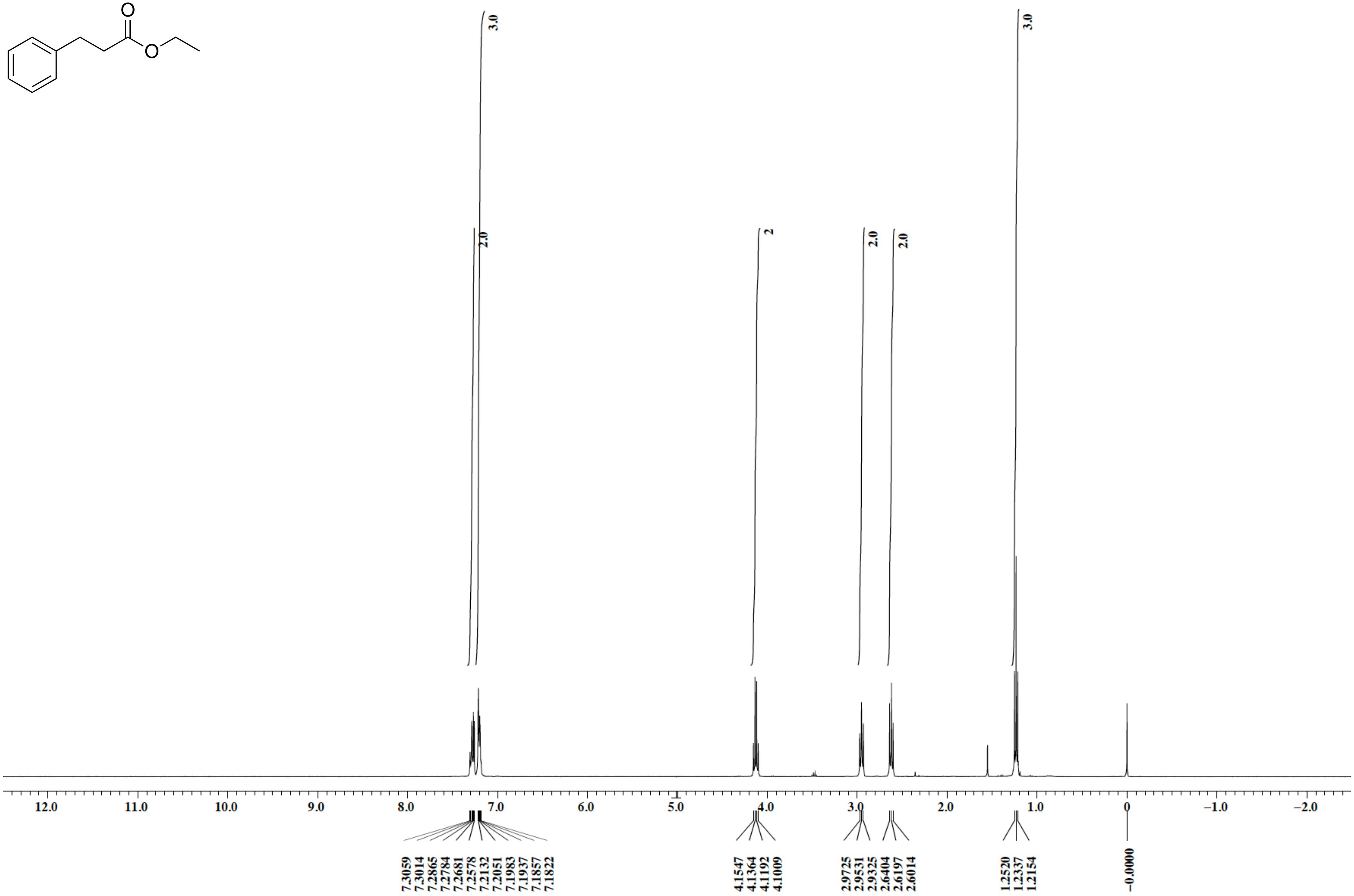
9pa, ^{13}C NMR ($CDCl_3$, 100 MHz)





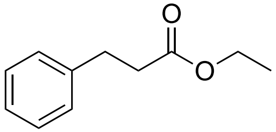
X : parts per Million : 13C

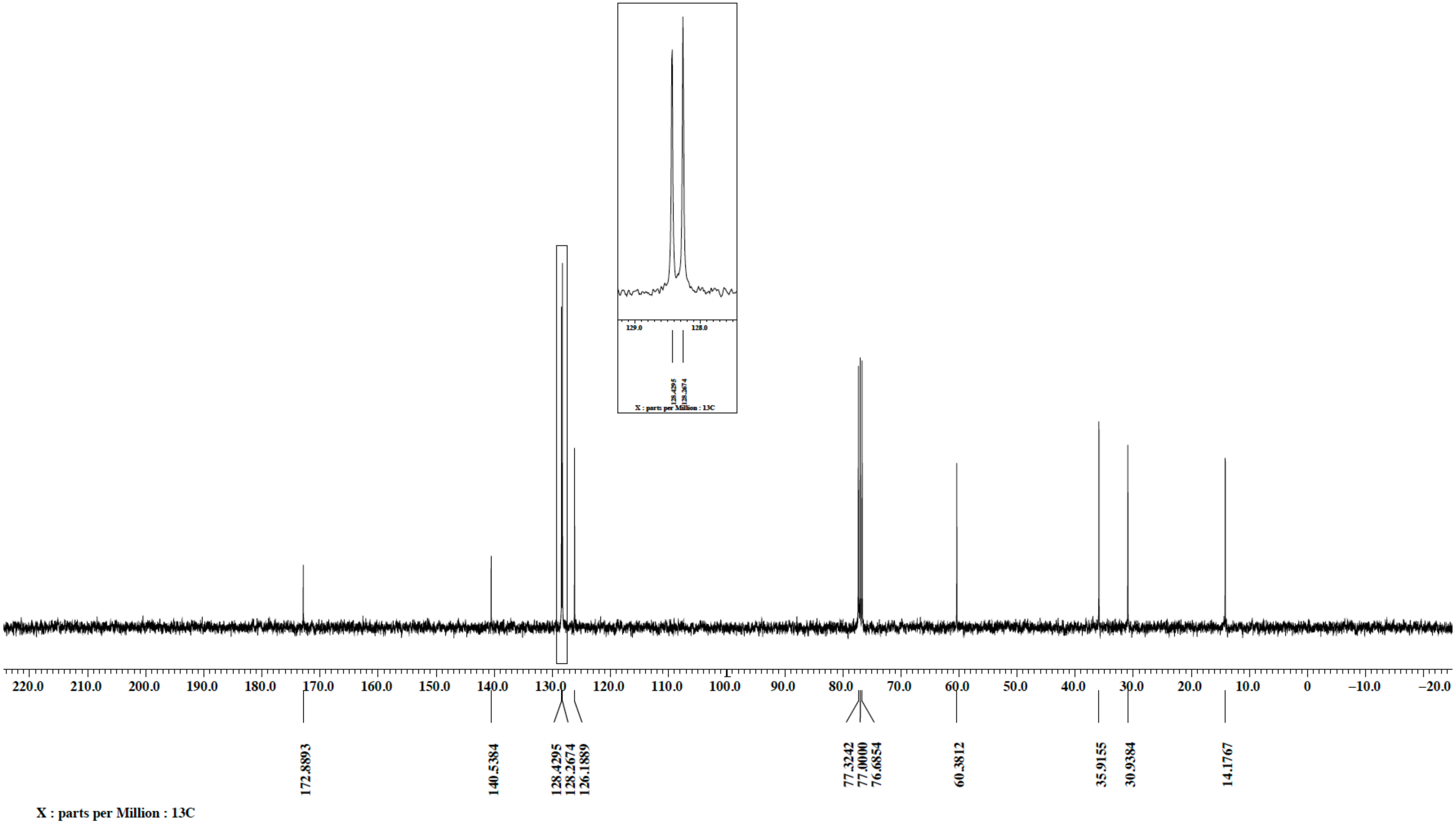
9pb, ^{1}H NMR ($CDCl_3$, 400 MHz)



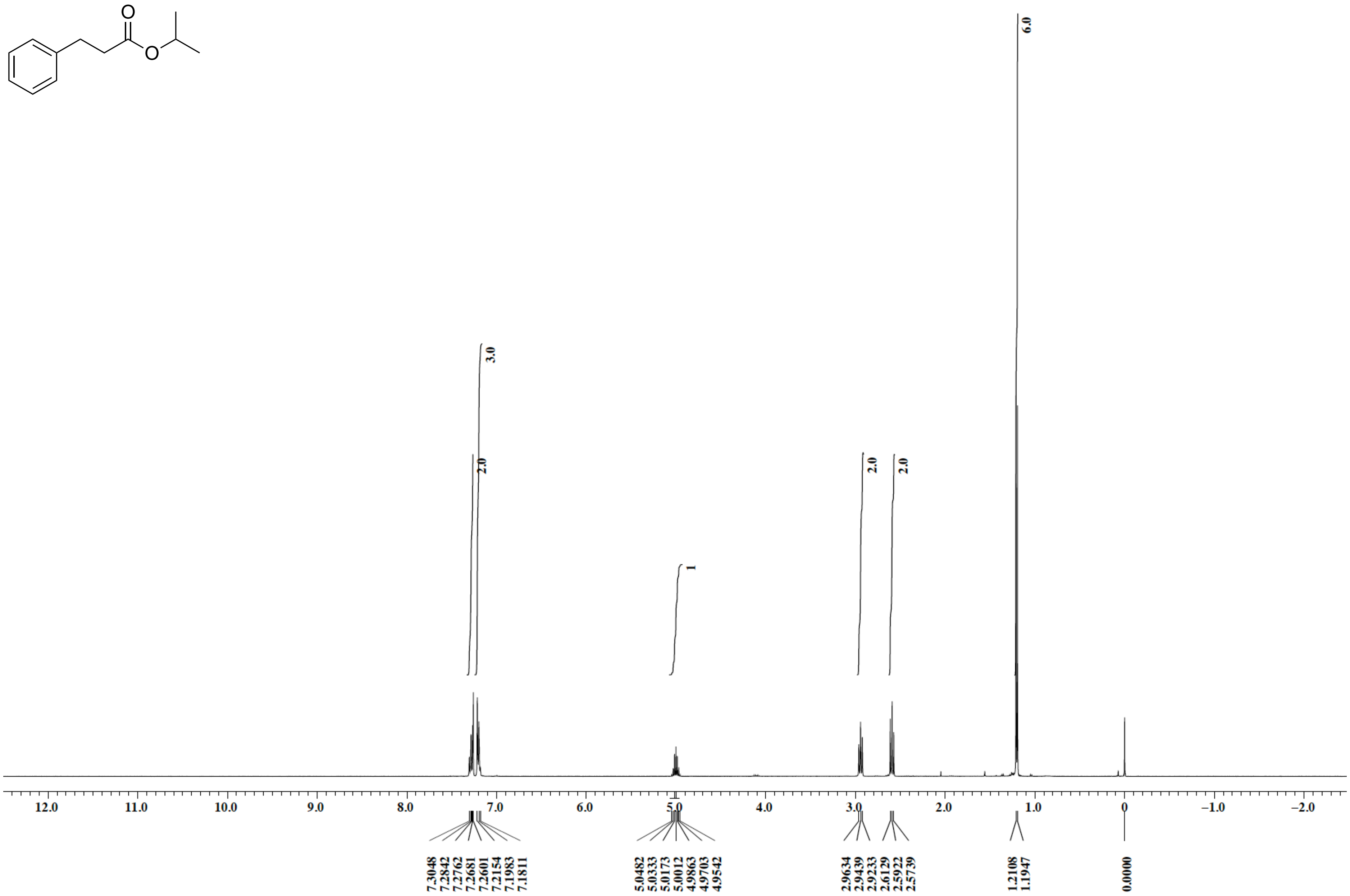
X : parts per Million : 1H

9pb, ^{13}C NMR (CDCl$_3$, 100 MHz)

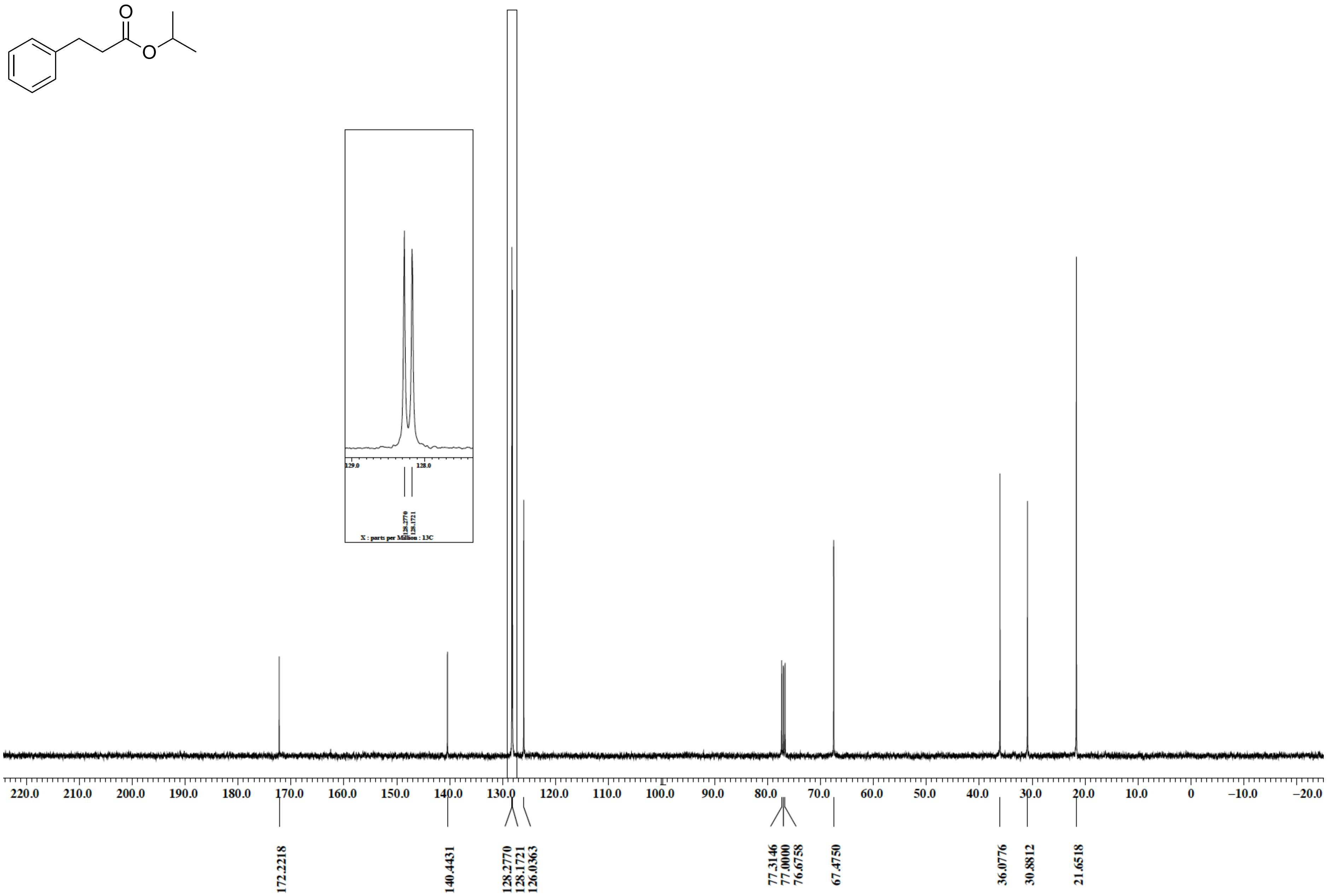




9pc, ^{1}H NMR ($CDCl_3$, 400 MHz)

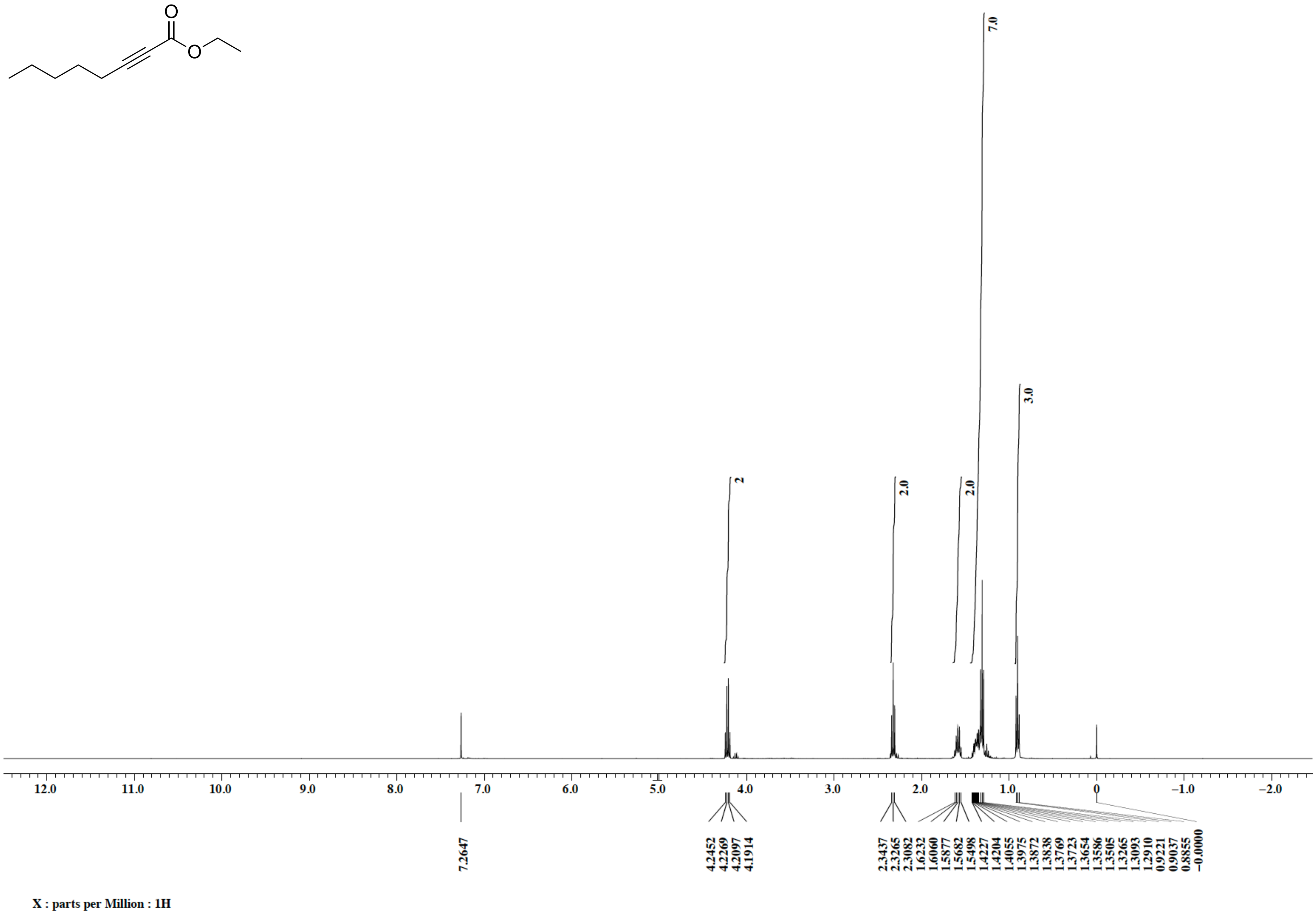


9pc, ^{13}C NMR (CDCl$_3$, 100 MHz)

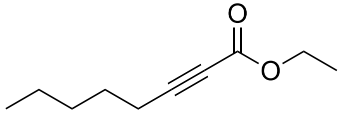


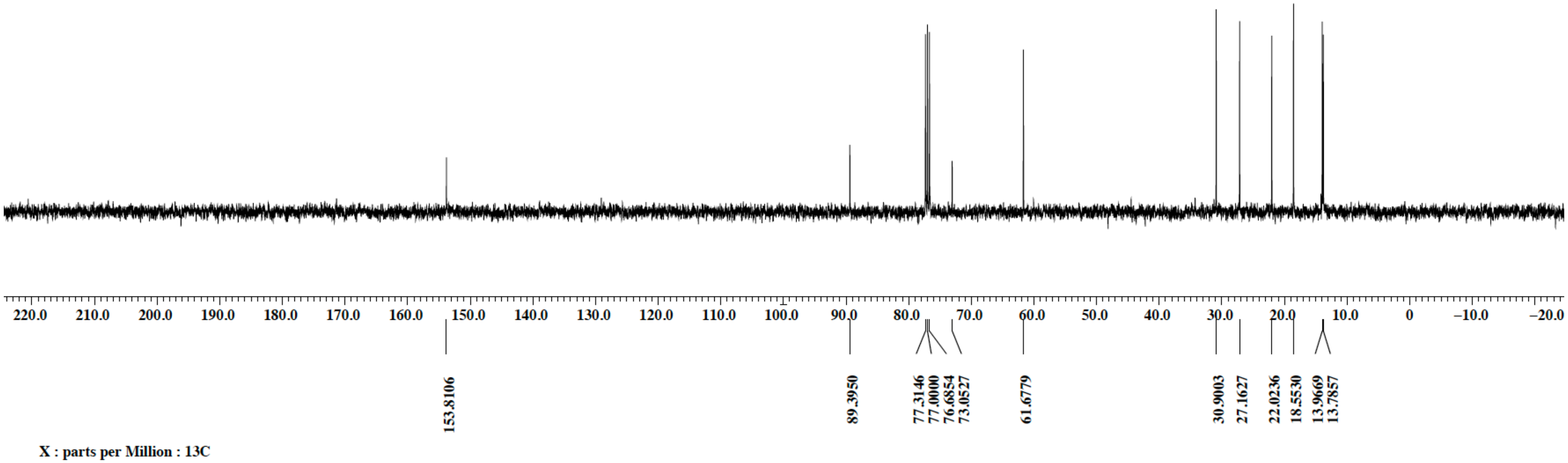
X : parts per Million : 13C

9qb, ^{1}H NMR (CDCl$_3$, 400 MHz)

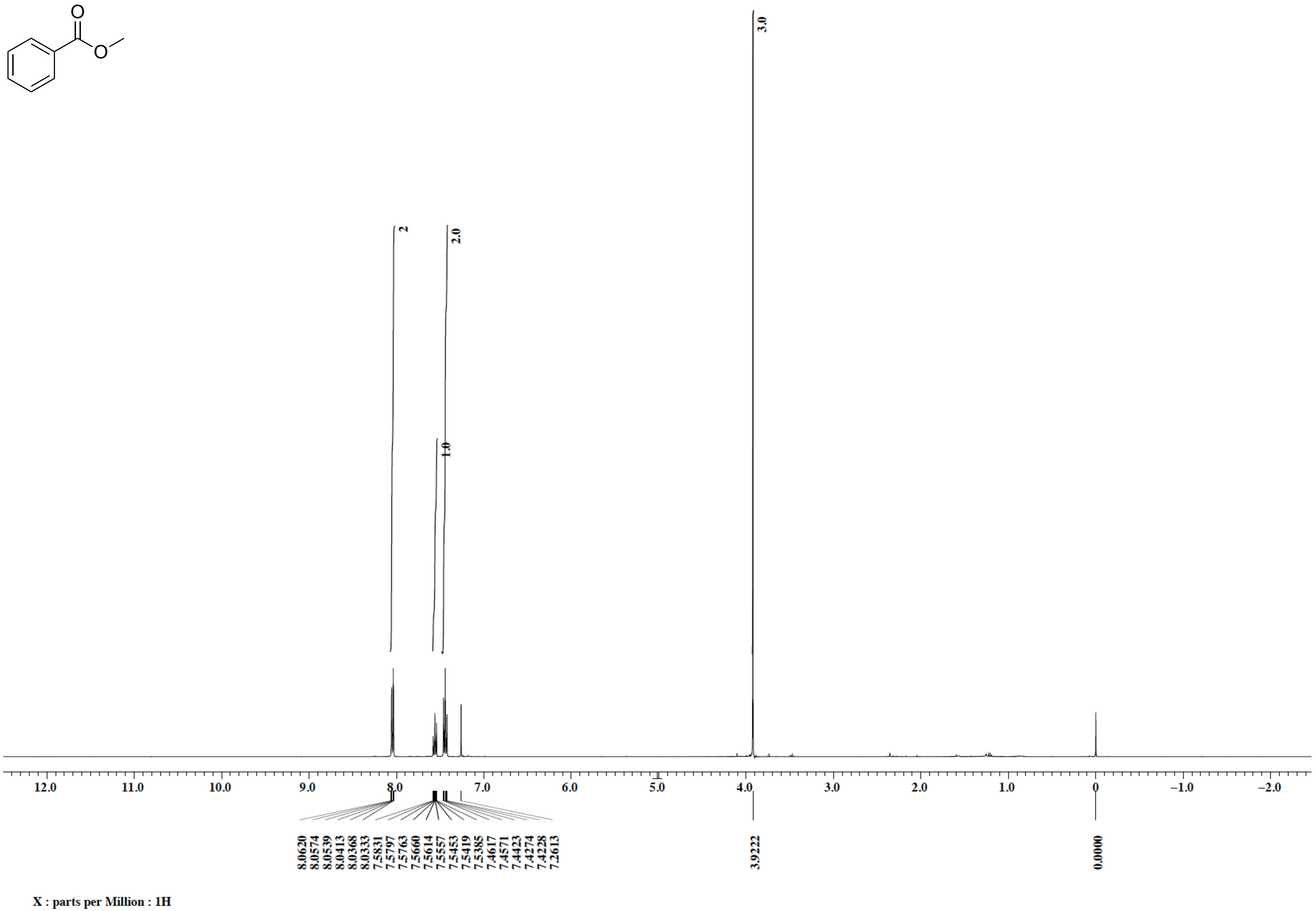


9qb, ^{13}C NMR (CDCl$_3$, 100 MHz)

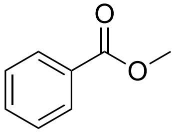


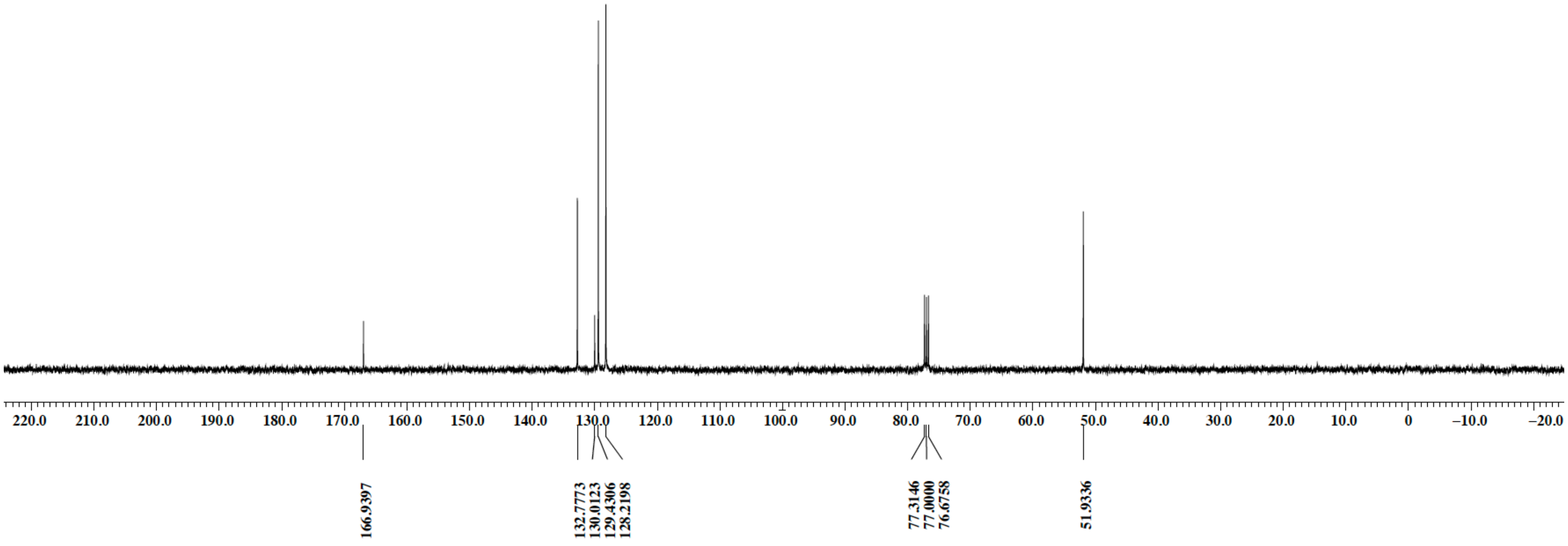


9ra, ^{1}H NMR (CDCl$_3$, 400 MHz)

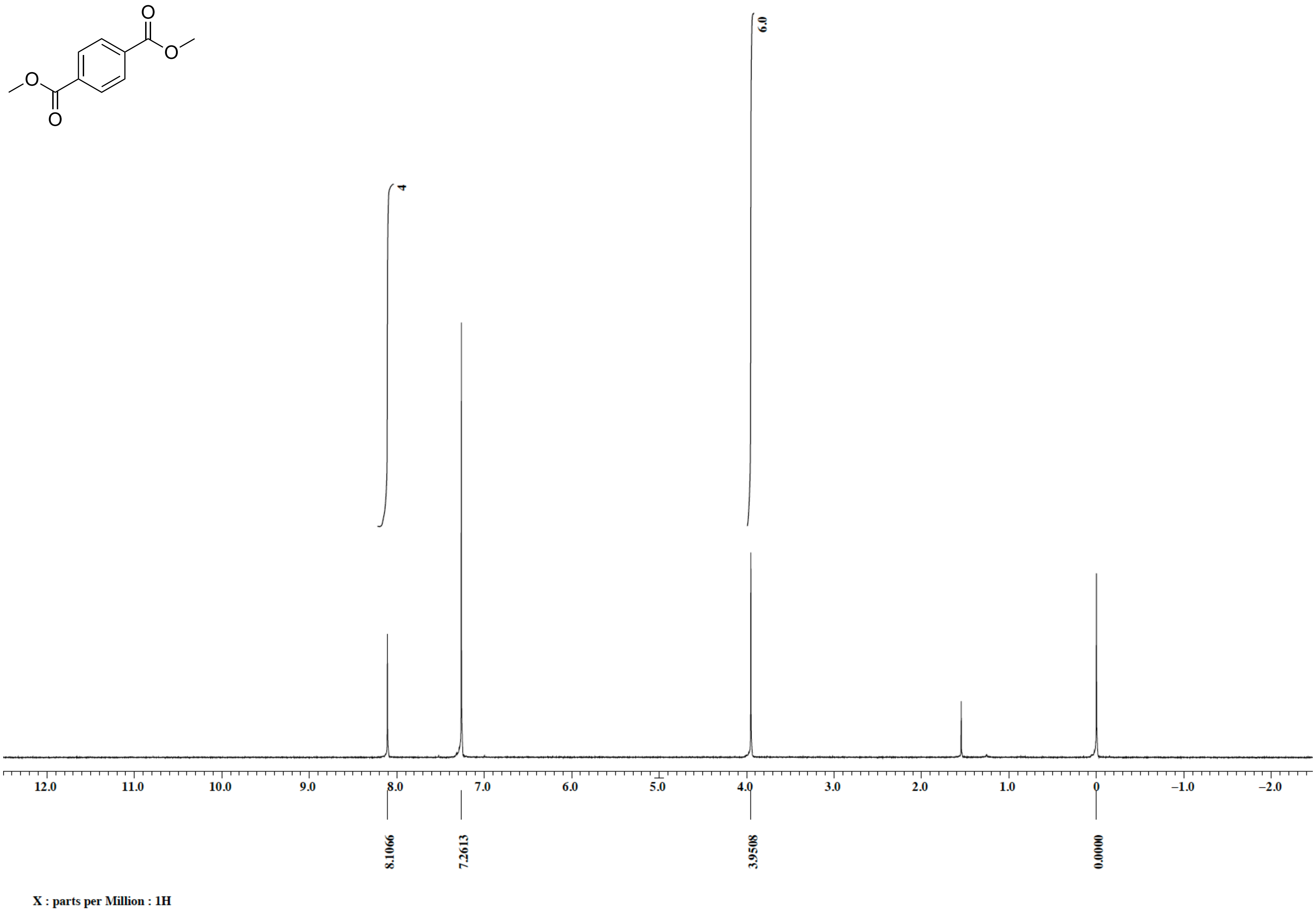


9ra, ^{13}C NMR ($CDCl_3$, 100 MHz)

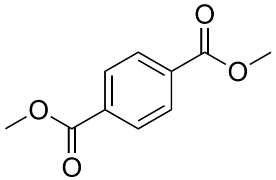


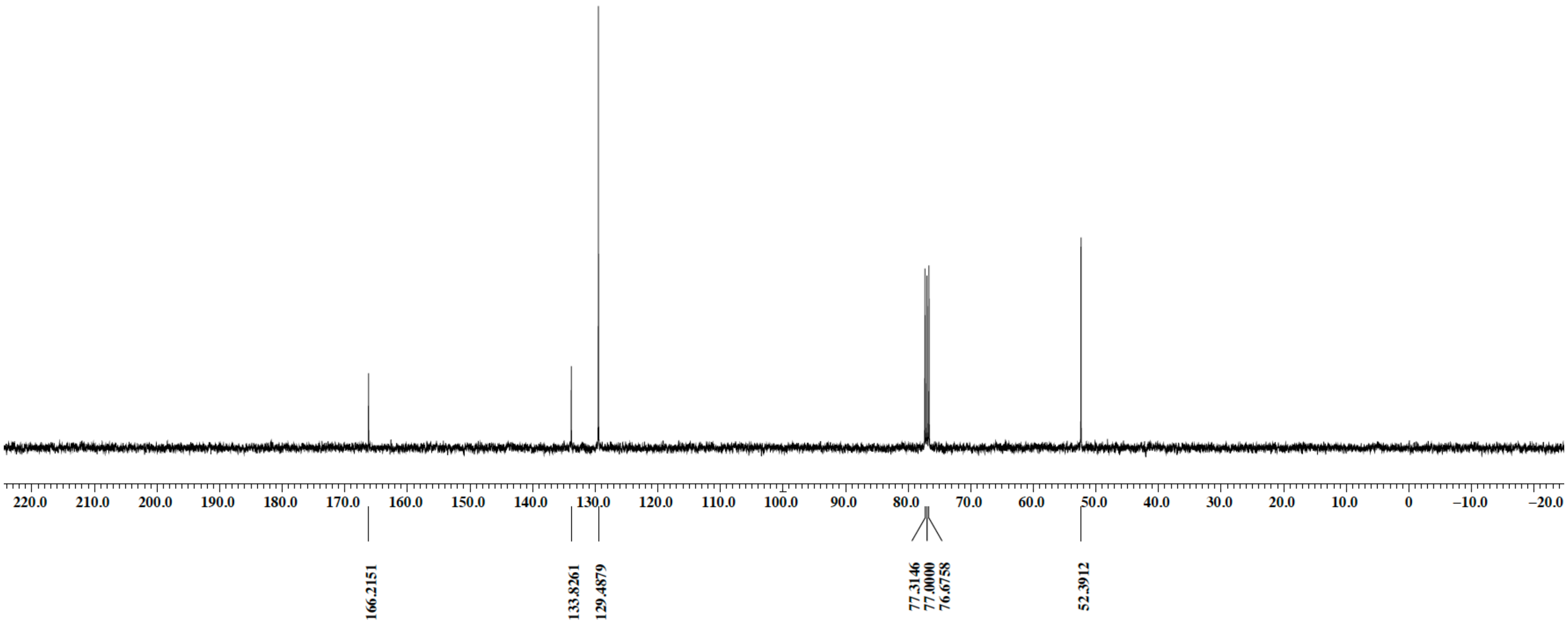


9sa, ^{1}H NMR ($CDCl_3$, 400 MHz)



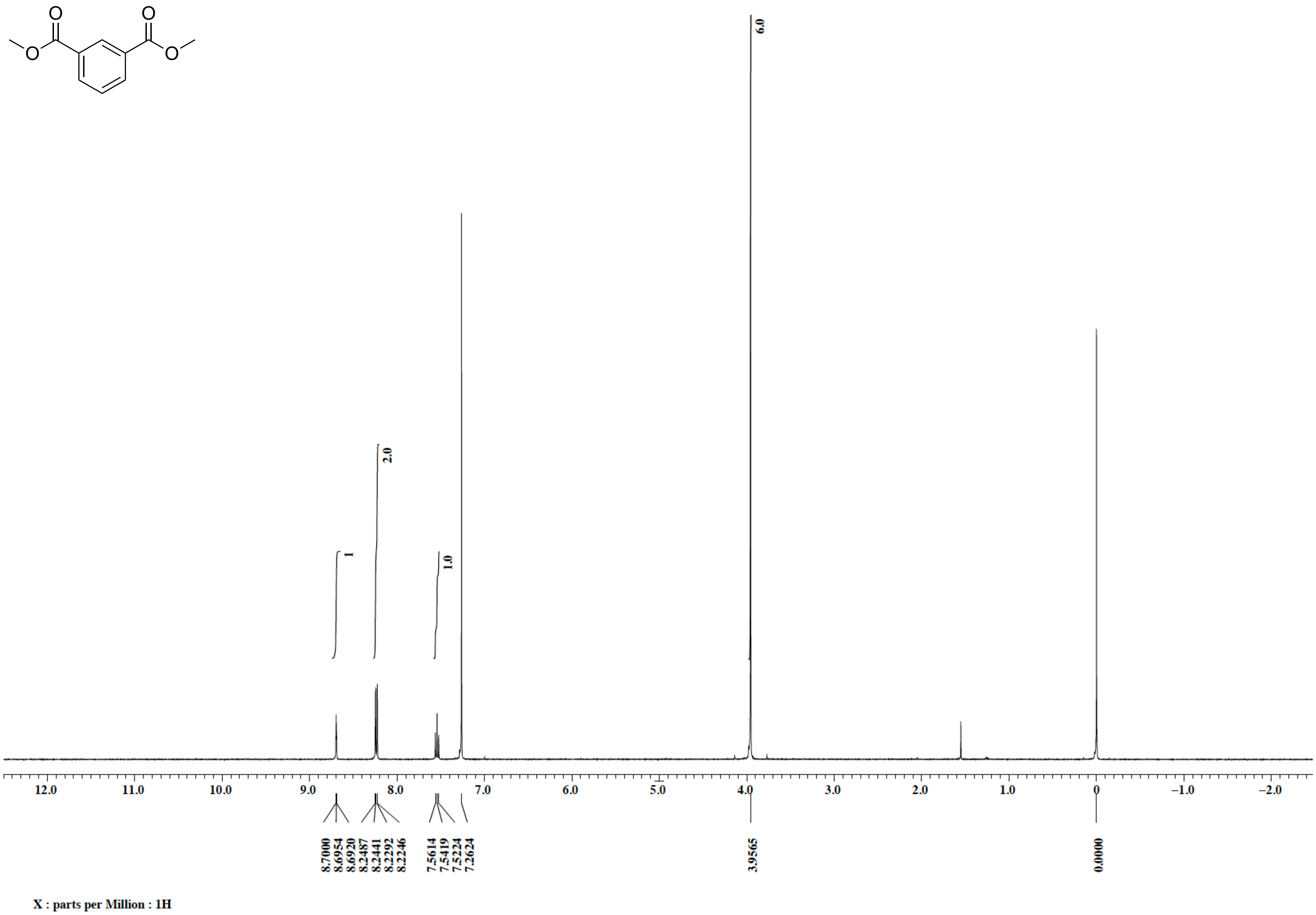
9sa, ^{13}C NMR (CDCl$_3$, 100 MHz)



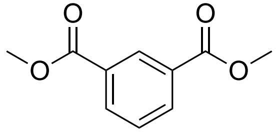


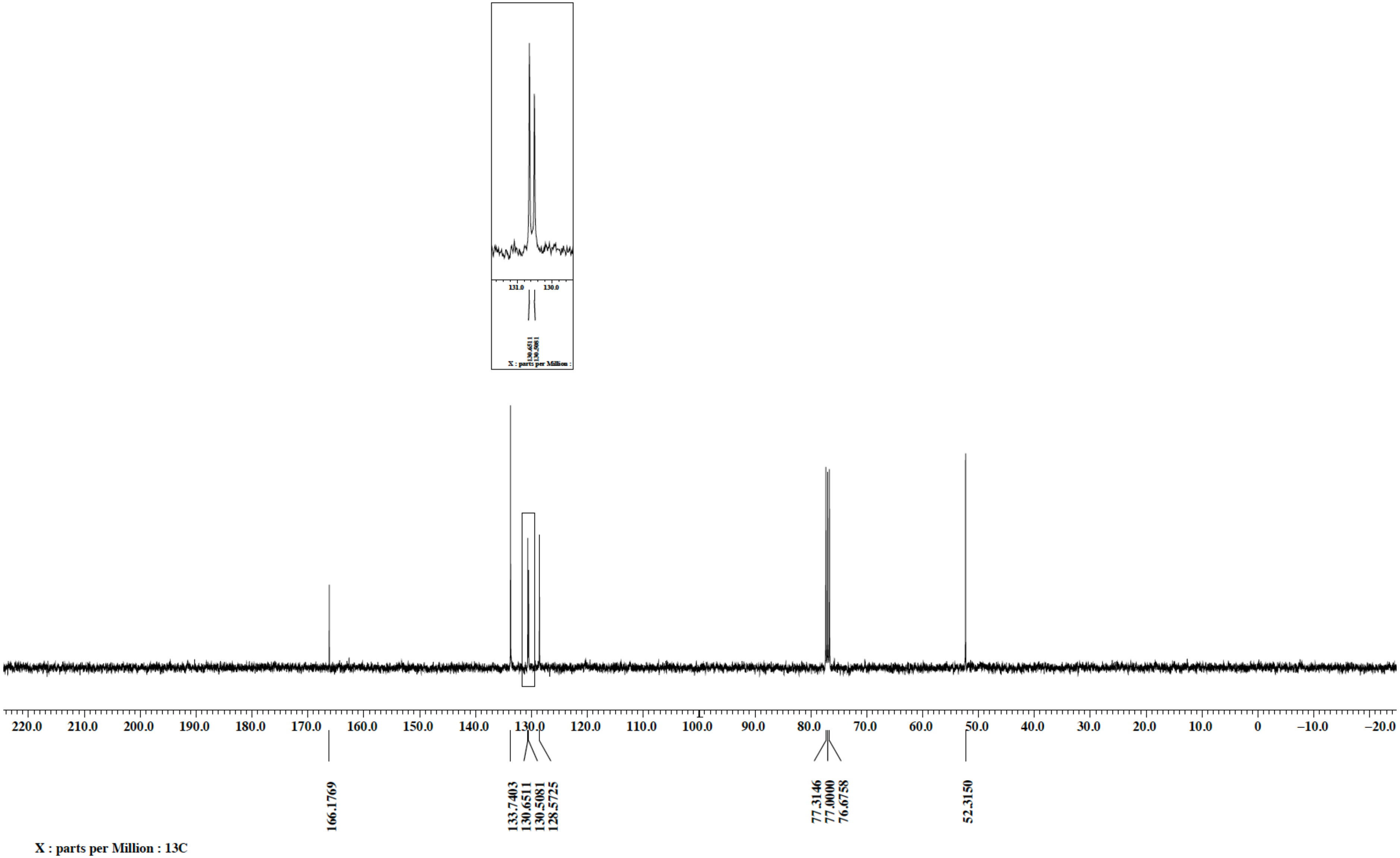
X : parts per Million : 13C

9ta, ^{1}H NMR (CDCl$_3$, 400 MHz)

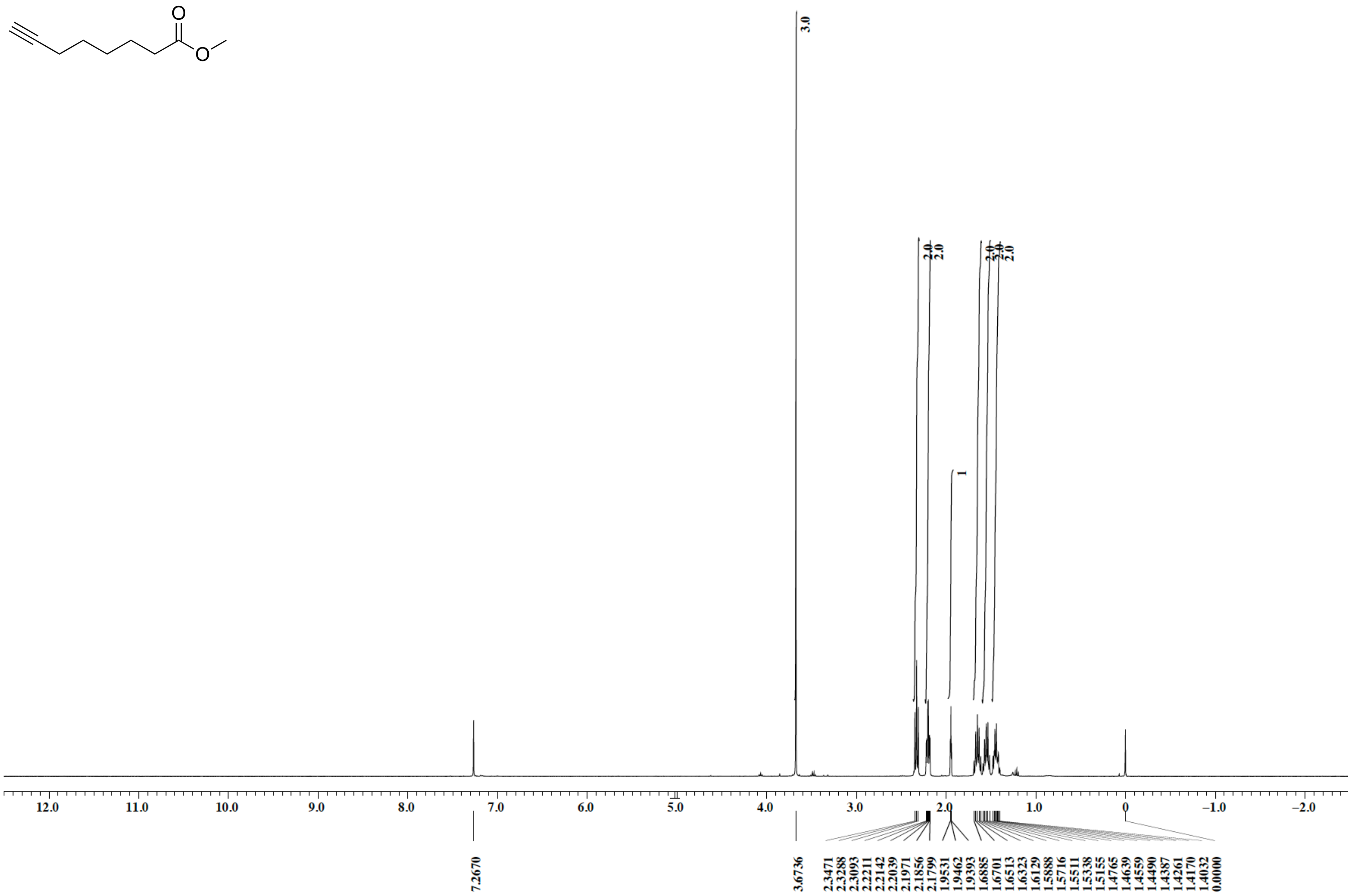


9ta, ^{13}C NMR (CDCl$_3$, 100 MHz)





9ua, ^{1}H NMR (CDCl$_3$, 400 MHz)



9ua, ^{13}C NMR (CDCl$_3$, 100 MHz)