Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Iron(III) chloride hexahydrate-promoted selective hydroxylation and chlorination of benzyl ketone derivatives for construction hetero-quaternary scaffolds

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Contents

1. General Information

1,2-dichloroethane (DCE) and ethyl acetate (EA) were purified and dried using standard techniques and distilled prior to use.

All reagents were obtained from commercial sources and were directly used without further purification, unless otherwise noted.

All reactions were monitored by thin-layer chromatography (TLC), which was carried out on silica gel 60 F254 precoated glass plates, detected by irradiation with UV light (254 nm), and treated with a solution of phosphomolybdic acid in ethanol. Flash chromatography was carried out on 200–300 mesh silica gel, eluting with a mixture of petroleum ether (b.p. 60–90°C) and ethyl acetate or petroleum ether (b.p. 60–90°C) and dichloromethane, unless otherwise noted.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on 400 spectrometer or a 300BB spectrometer. Chemical shifts (δ) were given in parts per million (ppm), and calibrated by using the residual un-deuterated solvent $CHCl_3$ (7.27 ppm) or tetramethylsilane (0.00 ppm) as internal standard for ^{1}H NMR spectra and deuterated solvent $CDCl_3$ (77.16 ppm) for ^{13}C NMR spectra. Coupling constants (J) were reported in hertz (Hz). The following abbreviations are applied to indicate the multiplicity of the signals: s = singlet; d = doublet; t = triplet; m = multiplet. Electron ionization mass spectra (EI-MS) were measured on a spectrometer by direct inlet at 70 eV and signals were given in *m/z* with relative intensity (%) in brackets. High-resolution mass spectra (HRMS) were measured on a Mass Spectrometer by means of the ESI technique. High Performance Liquid Chromatography (HPLC) equipped with a UV-detector.

2. Preparation of substrates

Besides commercially available 2-phenylcyclohexan-1-one, 2-(3-methoxyphenyl)-cyclohexan-1-one, 2,6-diphenylcyclohexan-1-one, 1-methyl-3,4-dihydronaphthalen-2(1*H*)-one and 2-benzoylcyclohexan-1-one, other substrates were prepared according to the reported procedures [1-8].

3. Experimental details

3.1 General Procedure

3.1.1 Hydroxylation

Under an argon atmosphere, to a stirred suspension of 2-phenylcyclohexan-1-one (34.9 mg, 0.20 mmol), DDQ (45.4 mg, 0.20 mmol, 1.0 equiv) and $FeCl_3 \cdot 6H_2O$ (27.0 mg, 0.10 mmol, 0.5 equiv) in DCE (2.0 mL) was added acetic acid (11.4 μL, 0.20 mmol, 1.0 equiv) at room temperature, then the mixture was stirred at 55 °C. After the starting material disappeared, the reaction mixture was allowed to cool to room temperature, and diluted with 1.0 mL petroleum ether. The crude product was directly purified by flash column chromatography with petroleum ether/ethyl acetate as eluent to afford the desired product **2a** (27.8 mg, 73% yield, a colorless oil).

3.1.2 Chlorination

Under an argon atmosphere, to a stirred suspension of 2-phenylcyclohexan-1-one (34.9 mg, 0.20 mmol) and DMP (101.8 mg, 0.24 mmol, 1.2 equiv) in the mixed solvent (EtOAc /AcOH = 1:1, 2.0 mL) was added $FeCl_3 \cdot 6H_2O$ (108.1 mg, 0.40 mmol, 2.0 equiv) at room temperature. The mixture was then stirred at this temperature. After the starting material disappeared, the reaction mixture was quenched with a saturated aqueous solution of Na_2CO_3. The mixture was extracted with EtOAc (40 mL × 2) and the combined organic layers were washed successively with water and brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The mixture was preliminarily purified by flash column chromatography with petroleum ether/ethyl acetate as eluent to afford crude product **3a**, and continuously isolated by HPLC with acetonitrile/water as eluent to afford the product **3a** (27.1 mg, 65% yield, an amorphous solid). The pure products **3b-3d** were obtained through the same procedure for preparation of **3a**, while the pure products **3f-3i** could be isolated by flash column chromatography with petroleum ether/ethyl acetate as eluent.

3.2 The details of the reaction conditions

3.2.1 Hydroxylation

Unless otherwise noted, the reaction was performed according to the general procedure, and the details were listed in Table S1.

Table S1 Optimization of hydroxylation reaction conditions[a]

entries	cat. (equiv)	solvent	oxidant (equiv)	additives (equiv)	temp. (℃)	yield (%)[b]
1	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ[c] (1.0)	—	RT	48
2	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	—	45	55
3	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	—	55	56
4	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	—	65	61
5	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	—	75	57
6	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	—	85	36
7	$FeCl_3\cdot 6H_2O$ (0.5)	DMF	DDQ (1.0)	—	65	0
8	$FeCl_3\cdot 6H_2O$ (0.5)	DMSO	DDQ (1.0)	—	65	0
9	$FeCl_3\cdot 6H_2O$ (0.5)	THF	DDQ (1.0)	—	65	0
10	$FeCl_3\cdot 6H_2O$ (0.5)	CH_3NO_2	DDQ (1.0)	—	65	trace
11	$FeCl_3\cdot 6H_2O$ (0.5)	toluene	DDQ (1.0)	—	65	trace
12	$FeCl_3\cdot 6H_2O$ (0.5)	hexane	DDQ (1.0)	—	65	trace
13	$FeCl_3\cdot 6H_2O$ (0.5)	CH_3CN	DDQ (1.0)	—	65	19
14	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DMP[d] (1.0)	—	65	0
15	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	PIDA[e] (1.0)	—	65	trace
16	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	PIFA[f] (1.0)	—	65	trace
17	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	$NaIO_4$ (1.0)	—	65	33%
18	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	$K_2S_2O_8$ (1.0)	—	65	trace
19	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	BQ[g] (1.0)	—	65	trace
20	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	$Na_2SO_4\cdot 10H_2O$ (1.0)	65	41
21	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	$Na_3PO_4\cdot 12H_2O$ (1.0)	65	0
22	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	65	60
23	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	73
24	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	45	59
25	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	35	45
26	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	PhCOOH (1.0)	55	70
27	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	picolinic acid (1.0)	55	18
28	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	$(CH_3)_3CCOOH$ (1.0)	55	64
29	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	HCOOH (1.0)	55	71
30	$FeCl_3\cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	CF_3COOH (1.0)	55	70

31	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (0.5)	55	56
32	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (2.0)	55	48
33	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (4.0)	55	40
34	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.2)	AcOH (1.0)	55	40
35	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.2)	AcOH (1.0)	55	39
36	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.2)	AcOH (1.0)	55	70
37	$FeCl_3 \cdot 6H_2O$ (0.8)	DCE	DDQ (1.2)	AcOH (1.0)	55	70
38	$FeCl_3 \cdot 6H_2O$ (1.0)	DCE	DDQ (1.2)	AcOH (1.0)	55	68
39	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	—	AcOH (1.0)	55	trace
40	—	DCE	DDQ (1.0)	AcOH (1.0)	55	0
41	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (0.6)	AcOH (1.0)	55	36
42	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.5)	AcOH (1.0)	55	48
43	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (2.0)	AcOH (1.0)	55	49
44	$Fe(OTs)_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	35
45	$Fe(NO_3)_3 \cdot 9H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	trace
46	$NH_4Fe(SO_4)_2 \cdot 12H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	0
47	$CoCl_2 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	0
48	$NiCl_2 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	0
49	$CuCl_2 \cdot 2H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	trace
50	$RuCl_3 \cdot 3H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	0
51	$Mn(OAc)_2 \cdot 4H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	trace
52	$Mn(OAc)_3 \cdot 2H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	7
53	$FeCl_3$ (0.5)[h]	DCE	DDQ (1.0)	AcOH (1.0)	55	trace
54	$FeCl_3$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0) + H_2O (3.0)	55	62
55	$FeCl_3 \cdot 6H_2O$ (0.2)	DCE	DDQ (1.2)	AcOH (1.0)+18.0 µl H_2O	55	43
56	$FeCl_3 \cdot 6H_2O$ (0.4)	DCE	DDQ (1.2)	AcOH (1.0)+18.0 µl H_2O	55	57
57	$FeCl_3 \cdot 6H_2O$ (0.5)	DCE	DDQ (1.0)	AcOH (1.0)	55	29[i]

a) Reaction was performed using 2-phenylcyclohexan-1-one (0.2 mmol) in 2.0 mL solvent at the noted temperature under argon atmosphere; b) isolated yield; c) DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; d) DMP = Dess-Martin periodinane; e) PIDA = (diacetoxyiodo)benzene; f) PIFA = [bis(trifluoroacetoxy)iodo]benzene; g) BQ = *p*-benzoquinone; h) the anhydrous $FeCl_3$ was prepared according the reported method[9]; i) Reaction was performed under air atmosphere.

3.2.2 Chlorination

Unless otherwise noted, the reaction was performed according to the general procedure, and the details were listed in Table S2.

Table S2 Optimization of chlorination reaction conditions[a]

entries	cat. (equiv)	oxidant (equiv)	solvent	yield (%)[b]
1	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	DCE	52
2	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	hexane	45
3	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	toluene	31
4	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	DMSO	trace
5	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	THF	trace
6	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	ethyl acetate	63
7	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	AcOH	71
8	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	CF_3COOH	trace
9	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (1.2)	EA+AcOH (v/v 1:1)	72
10	$FeCl_3 \cdot 6H_2O$ (2.0)	IBX[c] (1.2)	EA+AcOH (v/v 1:1)	70
11	$FeCl_3 \cdot 6H_2O$ (2.0)	30% H_2O_2 (1.2)	EA+AcOH (v/v 1:1)	trace
14	$FeCl_3 \cdot 6H_2O$ (2.0)	Na_2IO_4 (1.2)	EA+AcOH (v/v 1:1)	57
15	$FeCl_3 \cdot 6H_2O$ (2.0)	$K_2S_2O_8$ (1.2)	EA+AcOH (v/v 1:1)	13
12	$FeCl_3 \cdot 6H_2O$ (2.0)	O_2	EA+AcOH (v/v 1:1)	trace
13	$FeCl_3 \cdot 6H_2O$ (2.0)	air	EA+AcOH (v/v 1:1)	trace
16	$FeCl_3 \cdot 6H_2O$ (1.0)	DMP (1.2)	EA+AcOH (v/v 1:1)	58
17	$FeCl_3 \cdot 6H_2O$ (1.5)	DMP (1.2)	EA+AcOH (v/v 1:1)	60
18	$FeCl_3 \cdot 6H_2O$ (2.5)	DMP (1.2)	EA+AcOH (v/v 1:1)	66
19	$FeCl_3 \cdot 6H_2O$ (3.0)	DMP (1.2)	EA+AcOH (v/v 1:1)	57
20	$CoCl_2 \cdot 6H_2O$ (2.0)	DMP (1.2)	EA+AcOH (v/v 1:1)	0
21	$NiCl_2 \cdot 6H_2O$ (2.0)	DMP (1.2)	EA+AcOH (v/v 1:1)	trace
22	$CuCl_2 \cdot 2H_2O$ (2.0)	DMP (1.2)	EA+AcOH (v/v 1:1)	trace
23	$FeCl_2 \cdot 4H_2O$ (2.0)	DMP (1.2)	EA+AcOH (v/v 1:1)	13
24	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (0.8)	EA+AcOH (v/v 1:1)	66
25	$FeCl_3 \cdot 6H_2O$ (200)	DMP (1.5)	EA+AcOH (v/v 1:1)	72
26	$FeCl_3 \cdot 6H_2O$ (2.0)	DMP (2.0)	EA+AcOH (v/v 1:1)	62
27	$FeCl_3 \cdot 6H_2O$ (2.0)	—	EA+AcOH (v/v 1:1)	trace

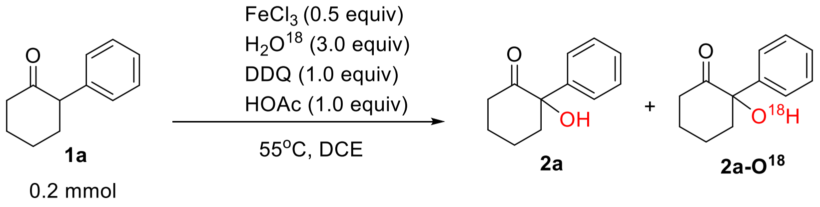
a) Reaction was performed using 2-phenylcyclohexan-1-one (0.2 mmol) in 2.0 mL solvent at RT under an argon atmosphere; b) yield by ^{1}HNMR; c) IBX = 2-iodoxybenzoic acid.

3.3 Some control experiments

3.3.1 Isotope experiment

Under an argon atmosphere, to a stirred suspension of 2-phenylcyclohexan-1-one (34.9 mg, 0.20 mmol), DDQ (45.4 mg, 0.20 mmol, 1.0 equiv), $FeCl_3$ (16.2 mg, 0.10 mmol, 0.5 equiv) and acetic acid (11.4 μL, 0.20 mmol, 1.0 equiv) in DCE (2.0 mL) was added H_2O^{18} (5.4 μL, 0.3 mmol, 3.0 equiv) at room temperature. The mixture was stirred at 55 °C. After the starting material disappeared, the reaction mixture was allowed to cool to room temperature. The reaction mixture was diluted with 1.0 mL petroleum ether, and the crude product was purified by flash column chromatography with petroleum ether/ethyl acetate as eluent to afford the desired product **2a** and **2a-O^{18}** (Scheme 3.3.1).

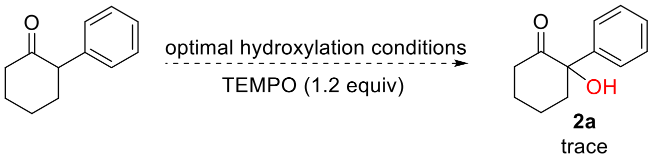
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 4.49 (s, 1 H), 3.02-2.98 (m, 1 H), 2.55-2.51 (m, 1 H), 2.47-2.40 (m, 1 H), 2.07-2.03 (m, 1 H), 1.89-1.71 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 212.8, 140.1, 129.3, 128.4, 126.5, 80.18, 80.16, 39.02, 38.99, 28.5, 23.2. HRMS (**2a-O^{18}**, ESI) m/z calculated for $C_{12}H_{14}OO^{18}Na$ [M+Na$^+$] 215.0929, found 215.0925; HRMS (**2a**, ESI) m/z calculated for $C_{12}H_{14}O_2Na$ [M+Na$^+$] 213.0886, found 213.0883. The contents of **2a-O^{18}** and **2a** were 60% and 40% based on the MS spectra analysis, respectively.



Scheme 3.3.1 H_2O^{18} isotope experiment

3.3.2 Hydroxylation

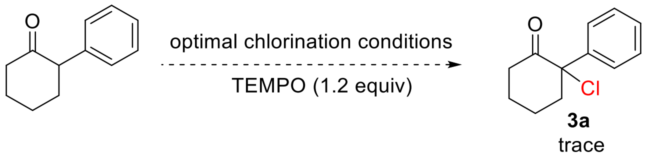
Under an argon atmosphere, to a stirred suspension of 2-phenylcyclohexan-1-one (34.9 mg, 0.20 mmol), DDQ (45.4 mg, 0.20 mmol, 1.0 equiv), $FeCl_3 \cdot 6H_2O$ (27.0 mg, 0.10 mmol, 0.5 equiv) and acetic acid (11.4 μL, 0.20 mmol, 1.0 equiv) in DCE (2.0 mL) was added TEMPO (37.5 mg, 1.2 equiv) at room temperature. The mixture was stirred at 55 °C for 24 h (Scheme 3.3.2).



Scheme 3.3.2 The radical test experiment

3.3.3 Chlorination

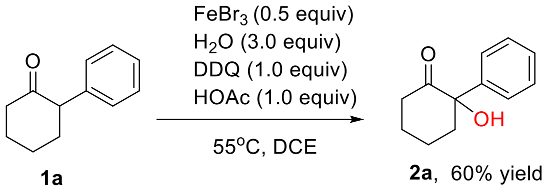
Under an argon atmosphere, to a stirred suspension of 2-phenylcyclohexan-1-one (34.9 mg, 0.20 mmol), DMP (101.8 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3 \cdot 6H_2O$ (108.1 mg, 0.40 mmol, 2.0 equiv) in the mixture solvent of EA (1.0 mL) and AcOH (1.0 mL) was added TEMPO (37.5 mg, 1.2 equiv) at room temperature. The mixture was stirred at RT for 24 h (Scheme 3.3.3).



Scheme 3.3.3 The radical test experiment

3.3.4 $FeBr_3$-promoted hydroxylation transformation

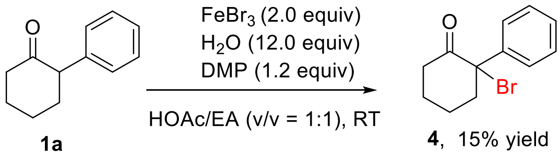
Under an argon atmosphere, to a stirred suspension of 2-phenylcyclohexan-1-one (34.9 mg, 0.20 mmol), DDQ (45.4 mg, 0.20 mmol, 1.0 equiv), $FeBr_3$ (29.6 mg, 0.10 mmol, 0.5 equiv) and acetic acid (11.4 μL, 0.20 mmol, 1.0 equiv) in DCE (2.0 mL) was added H_2O (5.4 μL, 0.3 mmol, 3.0 equiv) at room temperature. The mixture was stirred at 55 °C. After the starting material disappeared, the reaction mixture was allowed to cool to room temperature. The reaction mixture was diluted with 1.0 mL petroleum ether, and the crude product was purified by flash column chromatography with petroleum ether/ethyl acetate as eluent to afford the desired product **2a** (22.7 mg) (Scheme 3.3.4).



Scheme 3.3.4 $FeBr_3$-promoted hydroxylation transformation

3.3.5 $FeBr_3$-promoted bromination transformation

Under an argon atmosphere, to a stirred suspension of 2-phenylcyclohexan-1-one (34.9 mg, 0.20 mmol), DMP (101.8 mg, 0.24 mmol, 1.2 equiv) and $FeBr_3$ (118.2 mg, 0.40 mmol, 2.0 equiv) in the mixture solvent of EA (1.0 mL) and AcOH (1.0 mL) was added H_2O (21.6 μL, 1.2 mmol, 12.0 equiv) at room temperature. The mixture was stirred at RT. After the starting material disappeared, the reaction mixture was quenched with a saturated aqueous solution of Na_2CO_3. The mixture was extracted with EtOAc (40 mL × 2) and the combined organic layers were washed successively with water and brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was preliminarily purified by flash column chromatography with petroleum ether/ethyl acetate as eluent to afford crude product **4**, and continuously isolated by HPLC with acetonitrile/water as eluent to afford the pure product **4**[10] (7.7 mg, 15% yield, an amorphous solid (Scheme 3.3.5).



Scheme 3.3.5 $FeBr_3$-promoted bromination transformation

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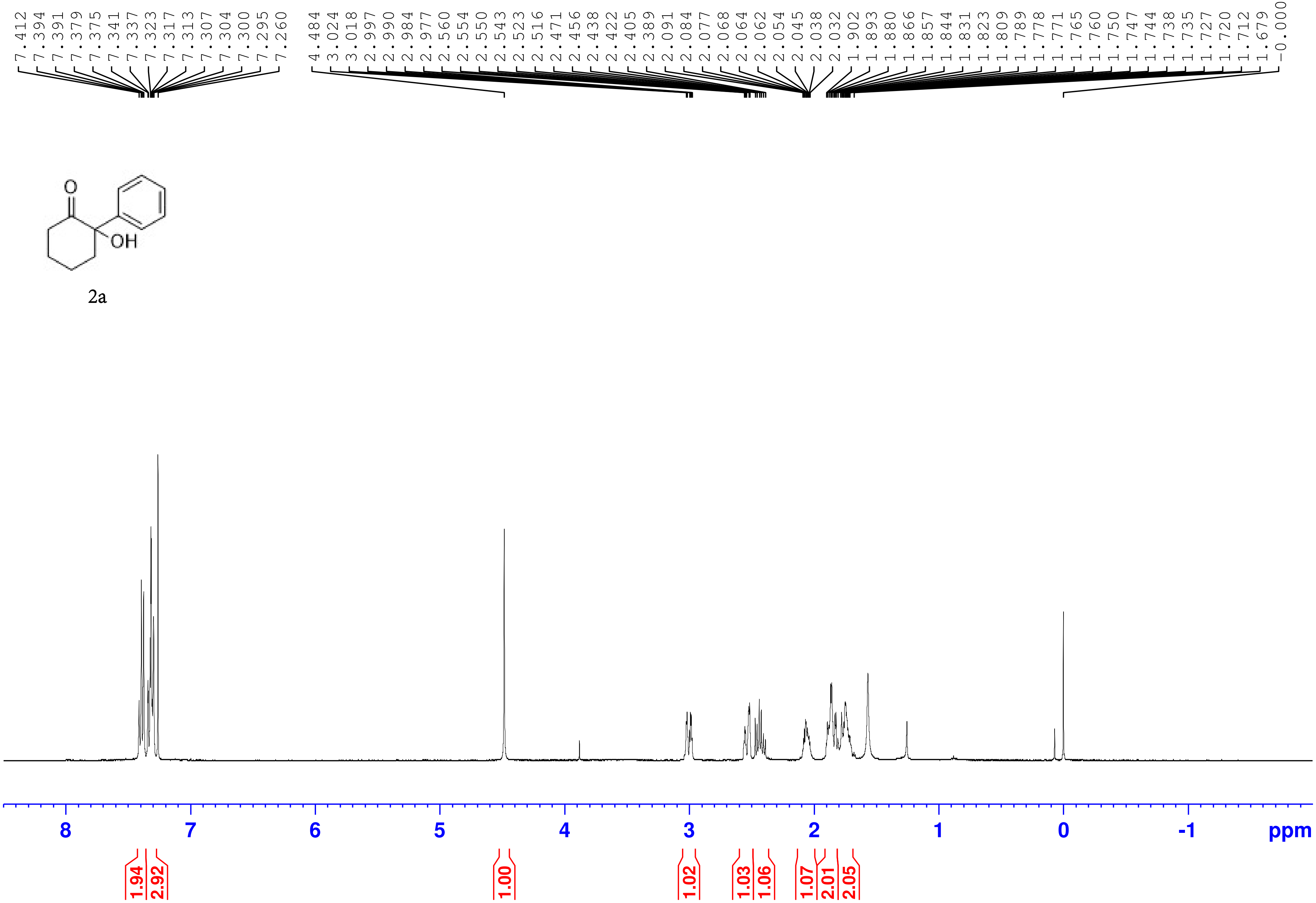
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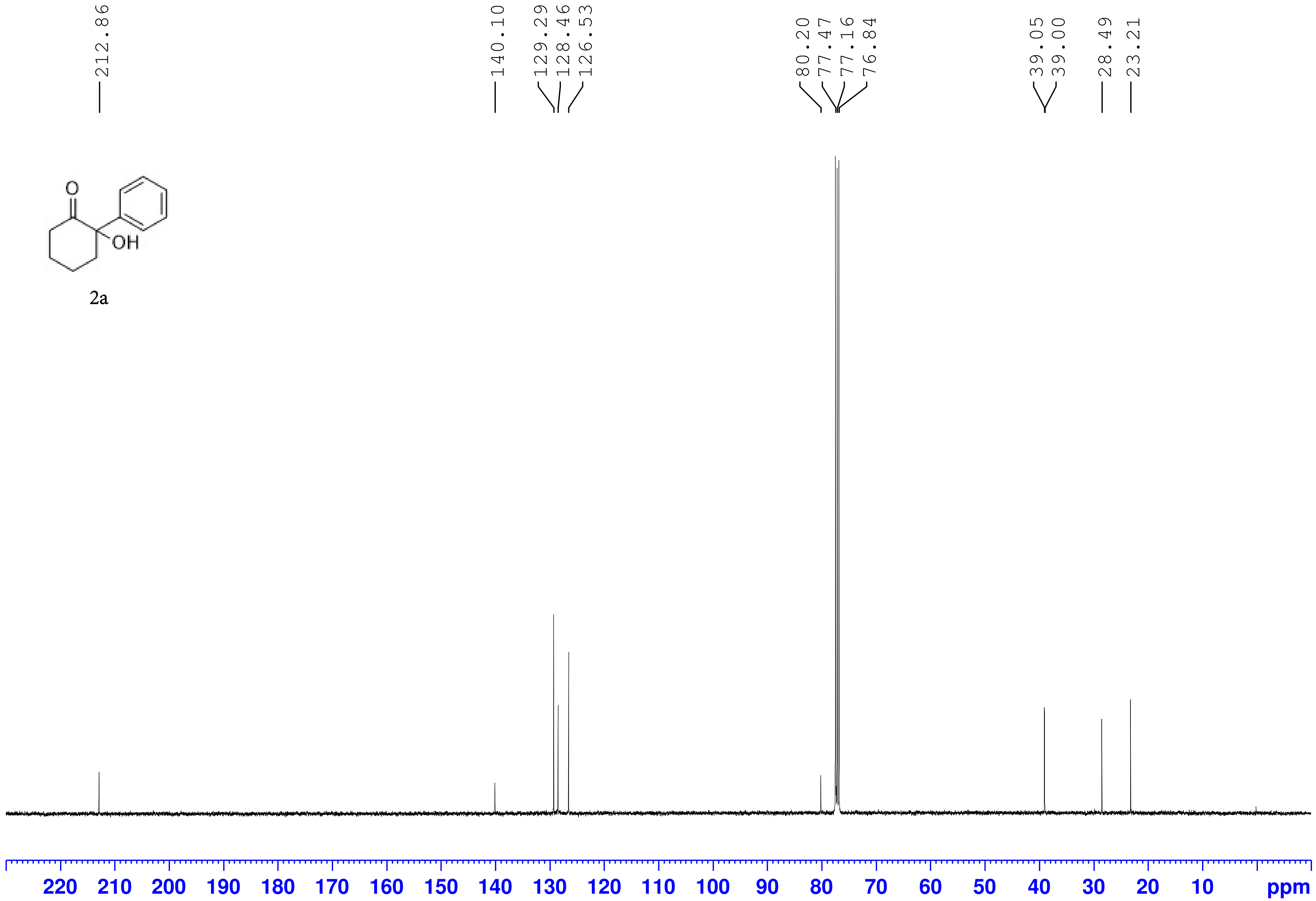
2.01
2.05

2a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O
OH
2a
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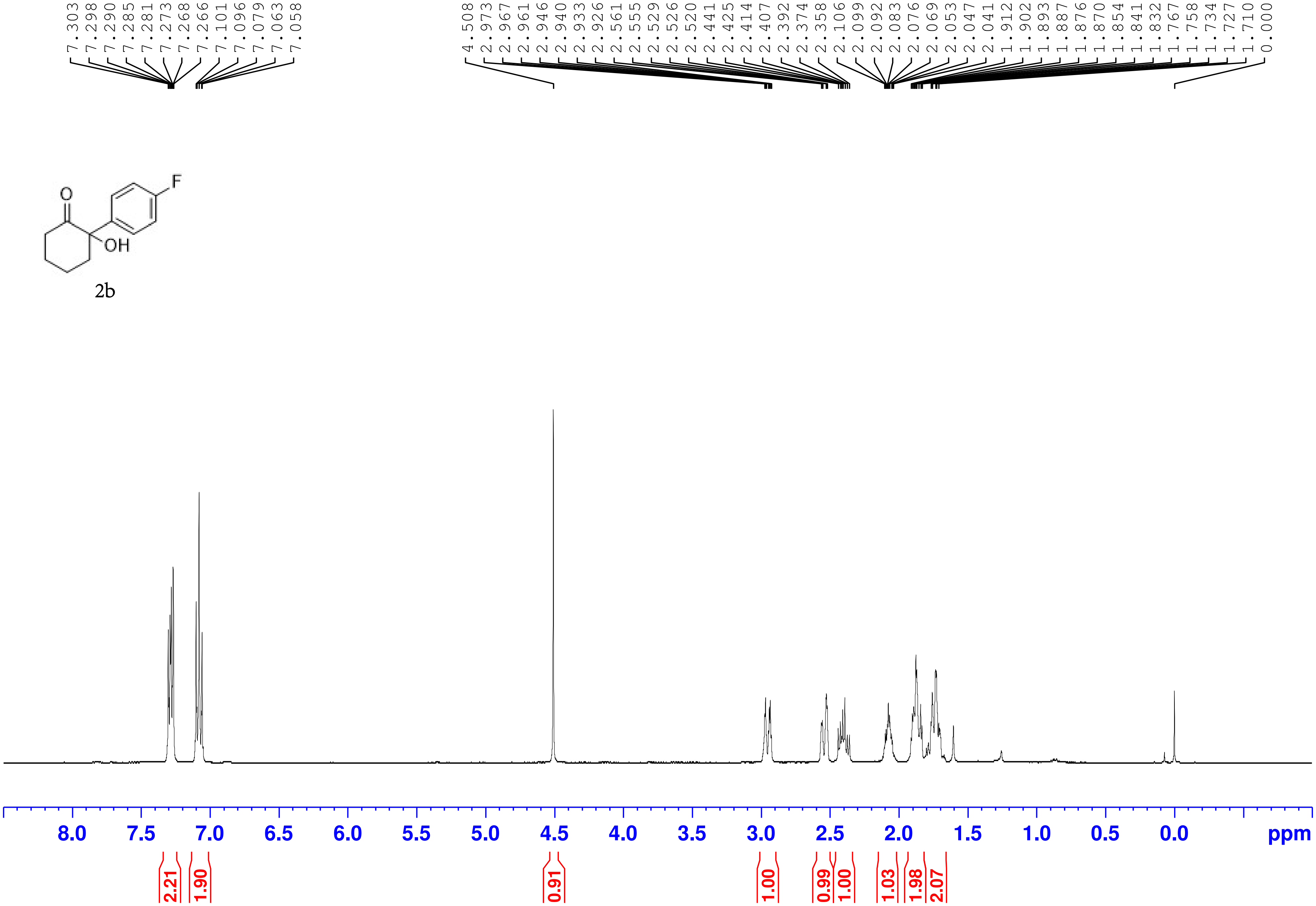
2b

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2.374
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2.069
2.053
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1.887
1.876
1.870
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1.841
1.832
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1.758
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1.727
1.710
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O
F
OH
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6.5
6.0
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5.0
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4.0
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2.5
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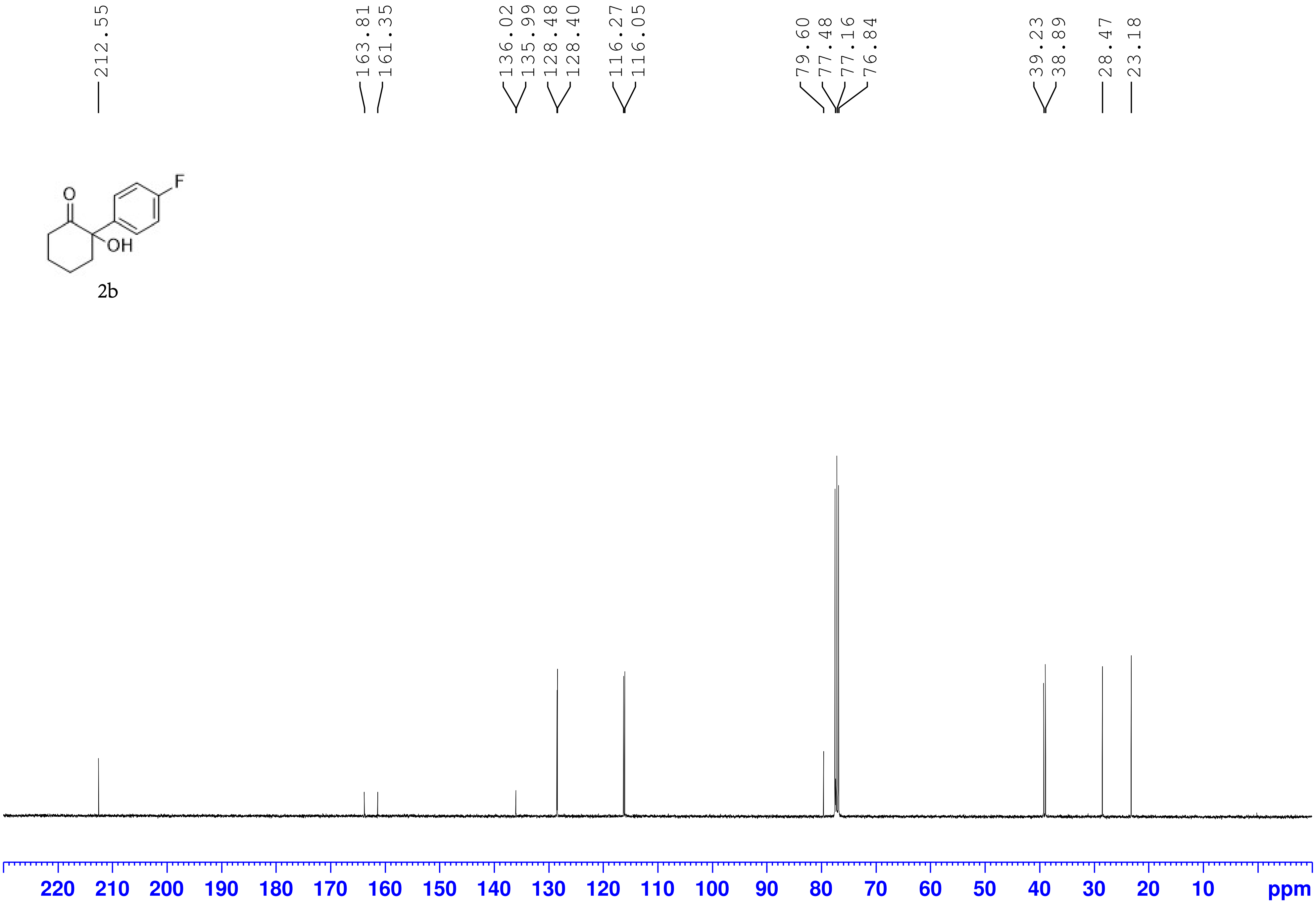
2.07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23.18
O
F
OH
2b
220
210
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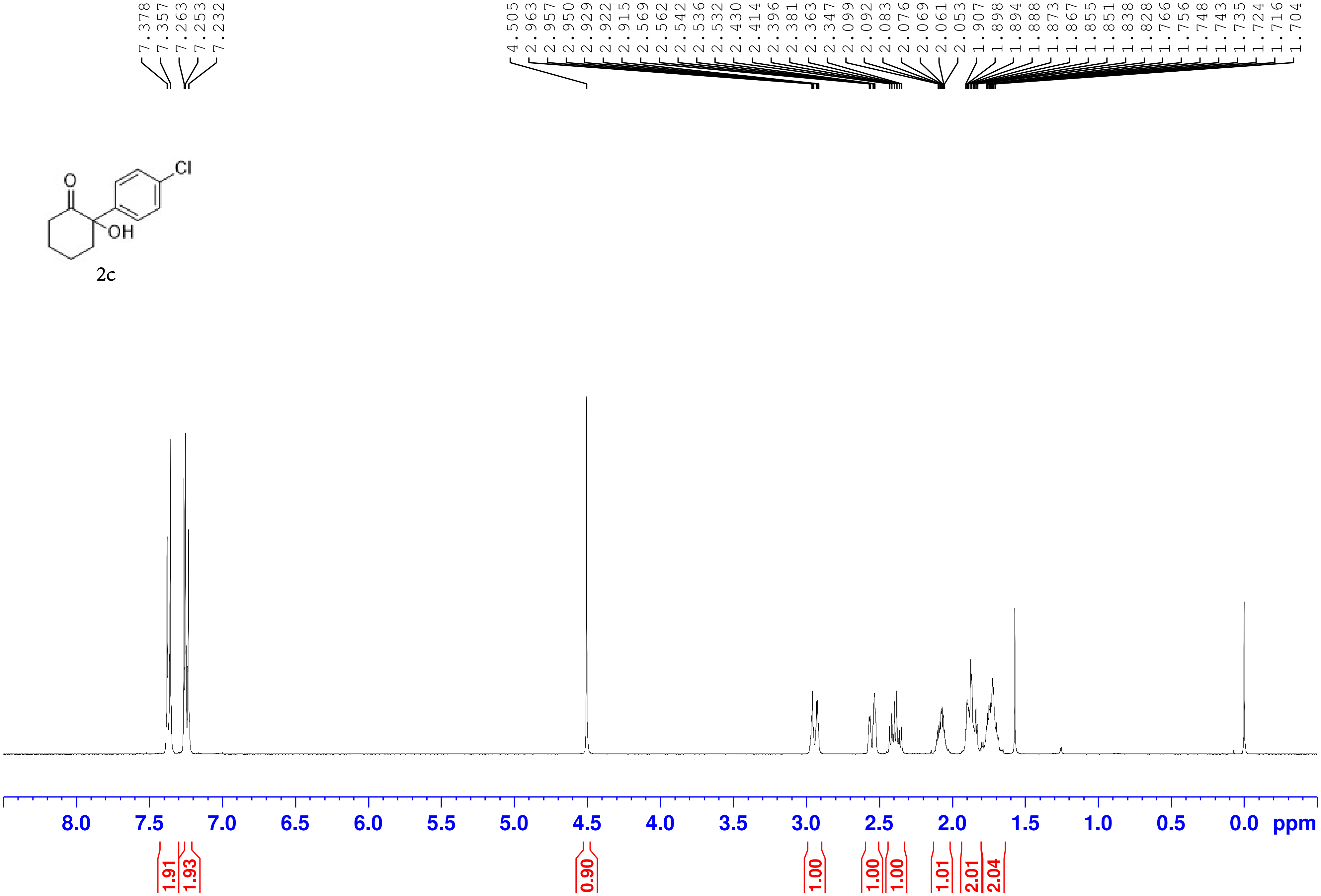
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2.536
2.532
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2.414
2.396
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2.347
2.099
2.092
2.083
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2.069
2.061
2.053
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1.873
1.867
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1.851
1.838
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1.756
1.748
1.743
1.735
1.724
1.716
1.704
O
Cl
OH
2c
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6.0
5.5
5.0
4.5
4.0
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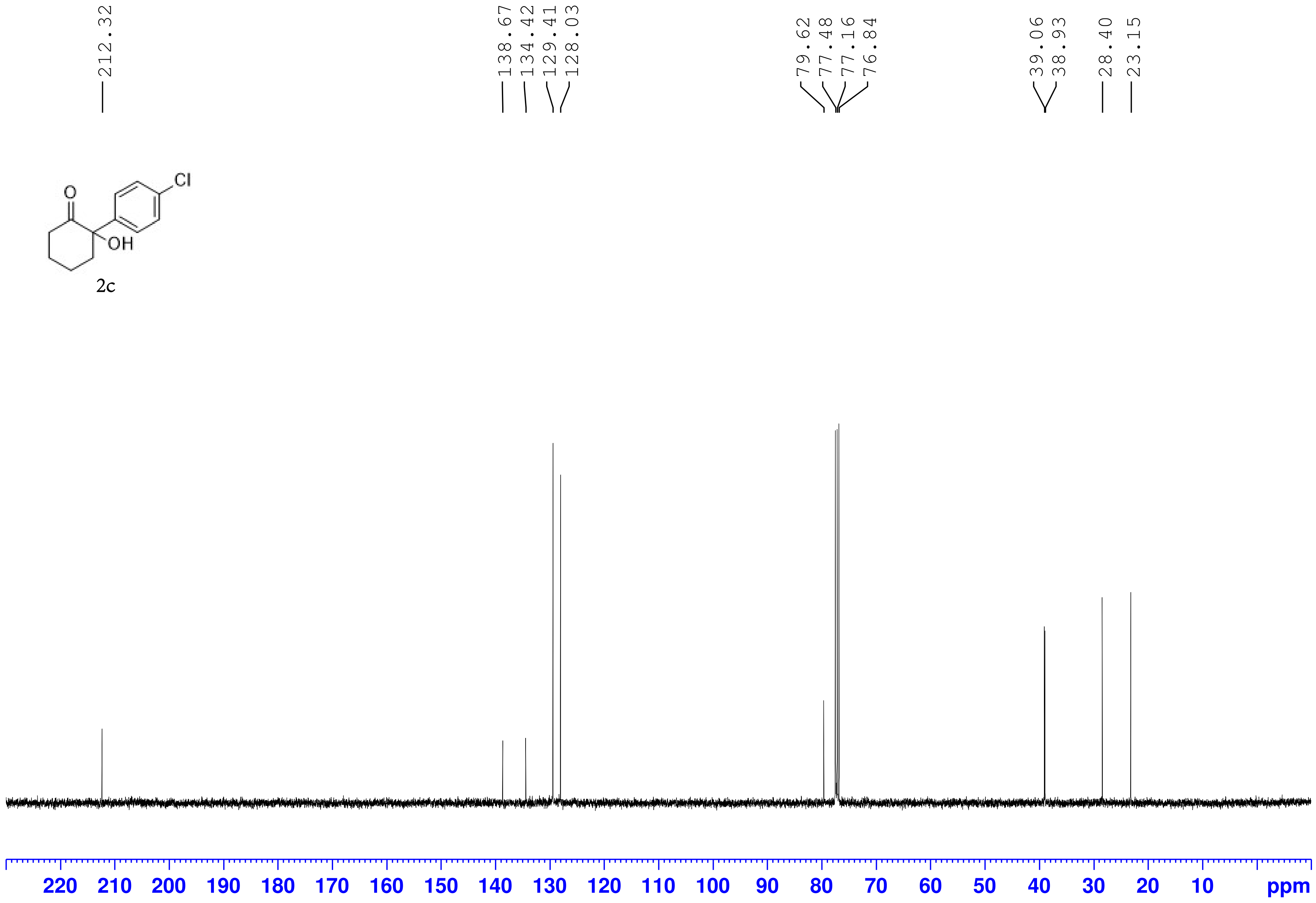
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Cl
OH
2c
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210
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190
180
170
160
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100
90
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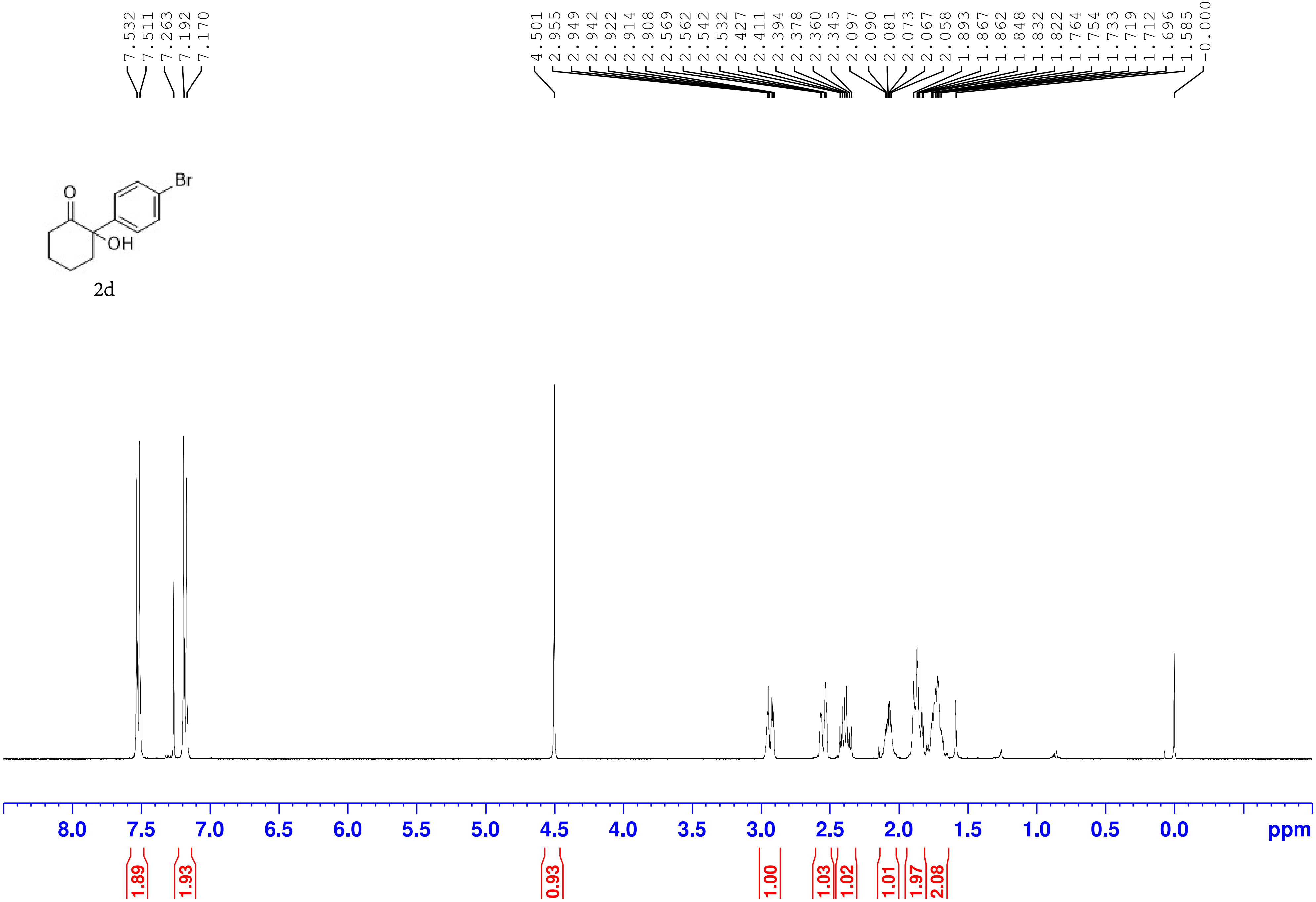
30
20
10
ppm

O
Br
OH

2d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2.073
2.067
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1.585
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5.0
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4.0
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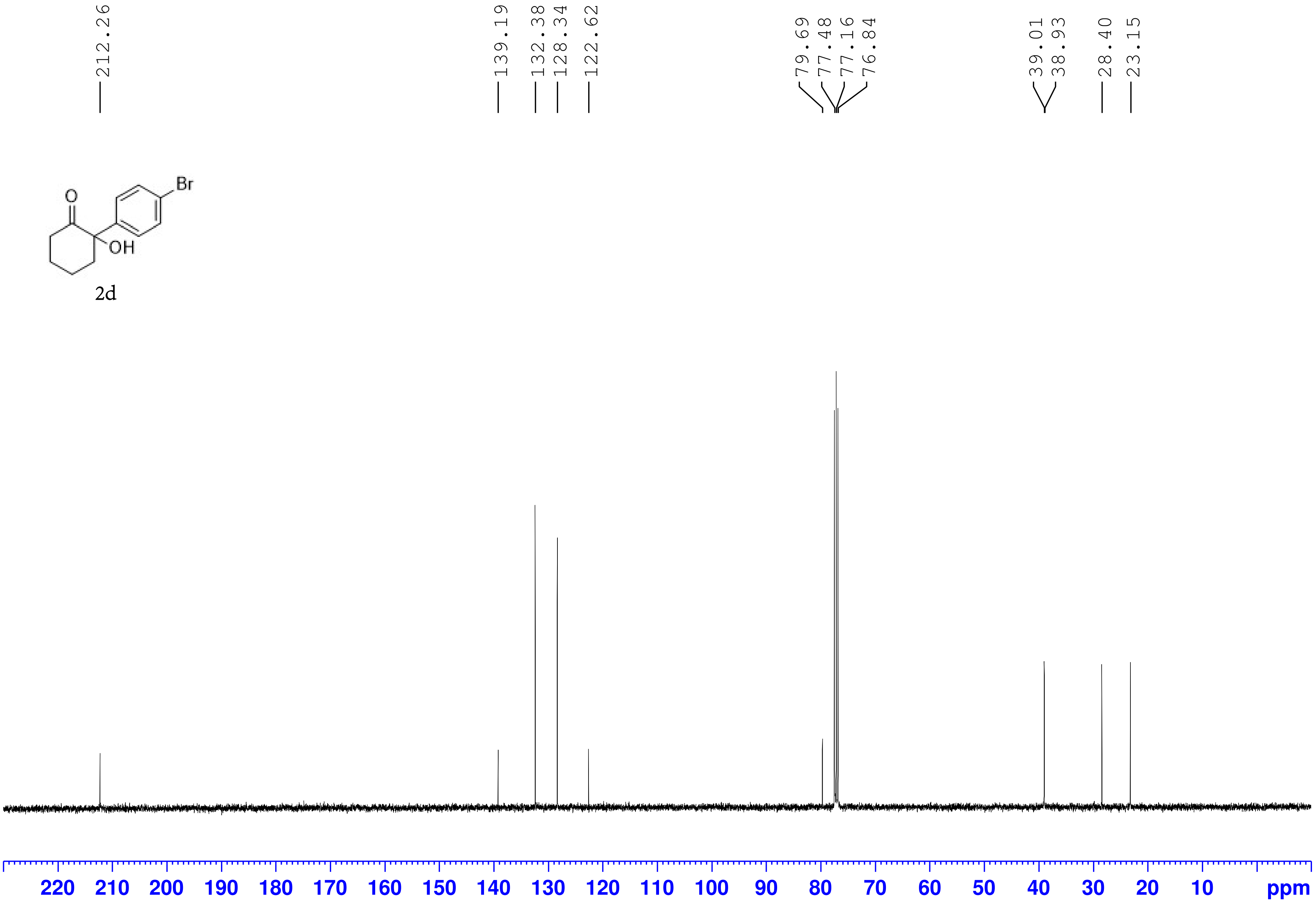
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39.01
38.93
28.40
23.15
O
Br
OH
2d
220
210
200
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150
140
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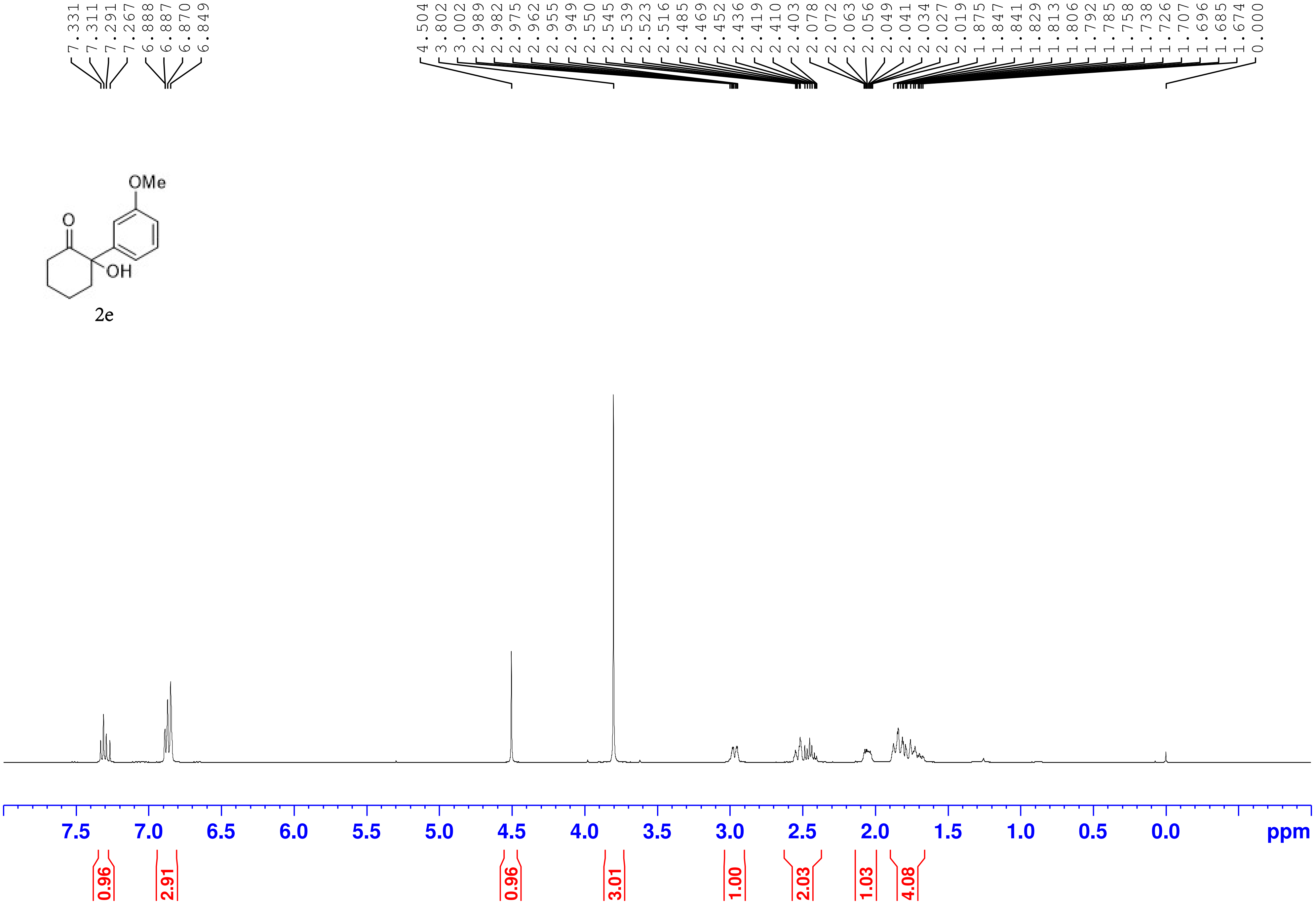
ppm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2.975
2.962
2.955
2.949
2.550
2.545
2.539
2.523
2.516
2.485
2.469
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2.049
2.041
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1.841
1.829
1.813
1.806
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1.758
1.738
1.726
1.707
1.696
1.685
1.674
0.000
OMe
O
OH
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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ppm
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0.96
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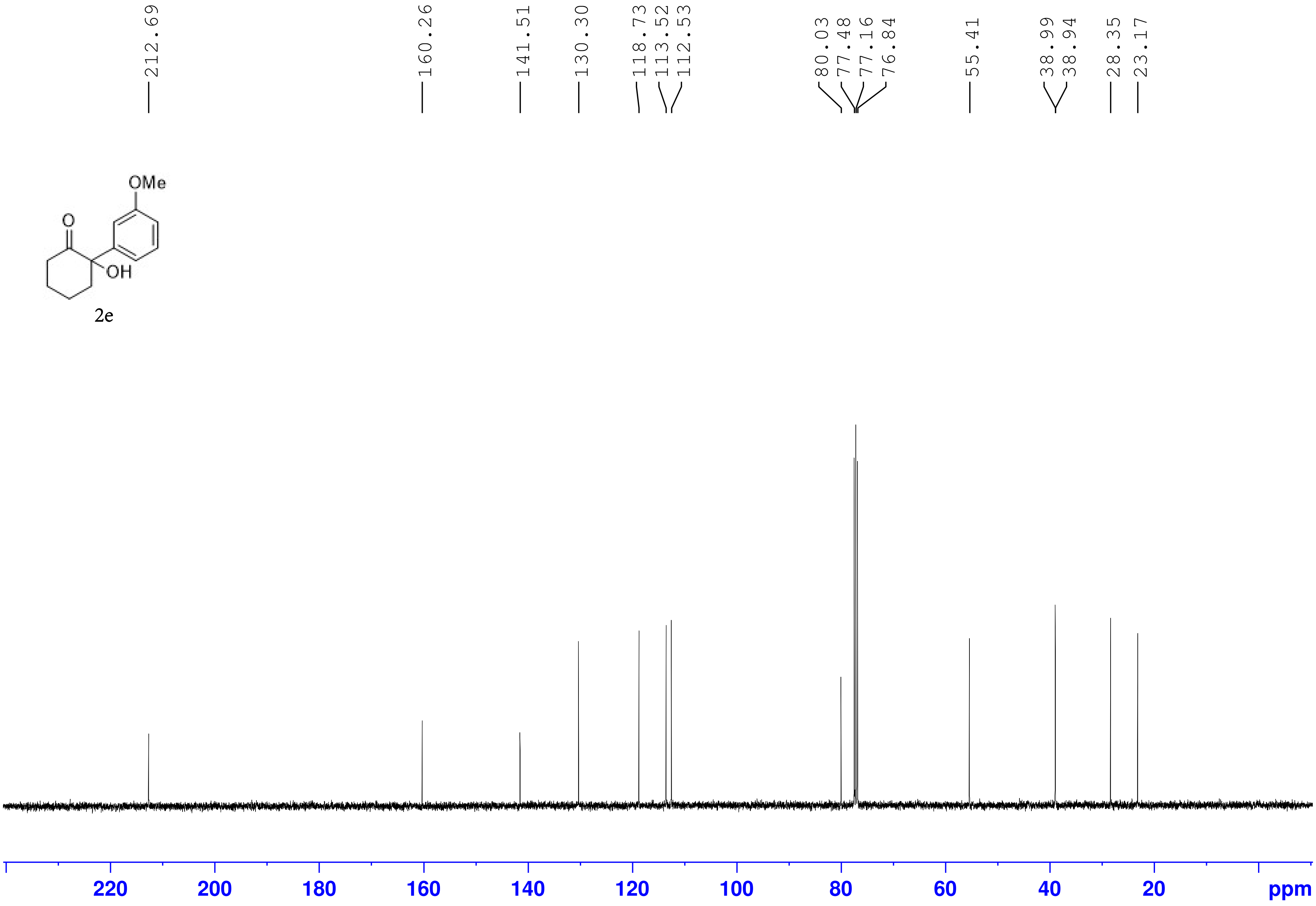
1.00
2.03
1.03
4.08

2e



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113.52
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80.03
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77.16
76.84
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200
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160
140
120
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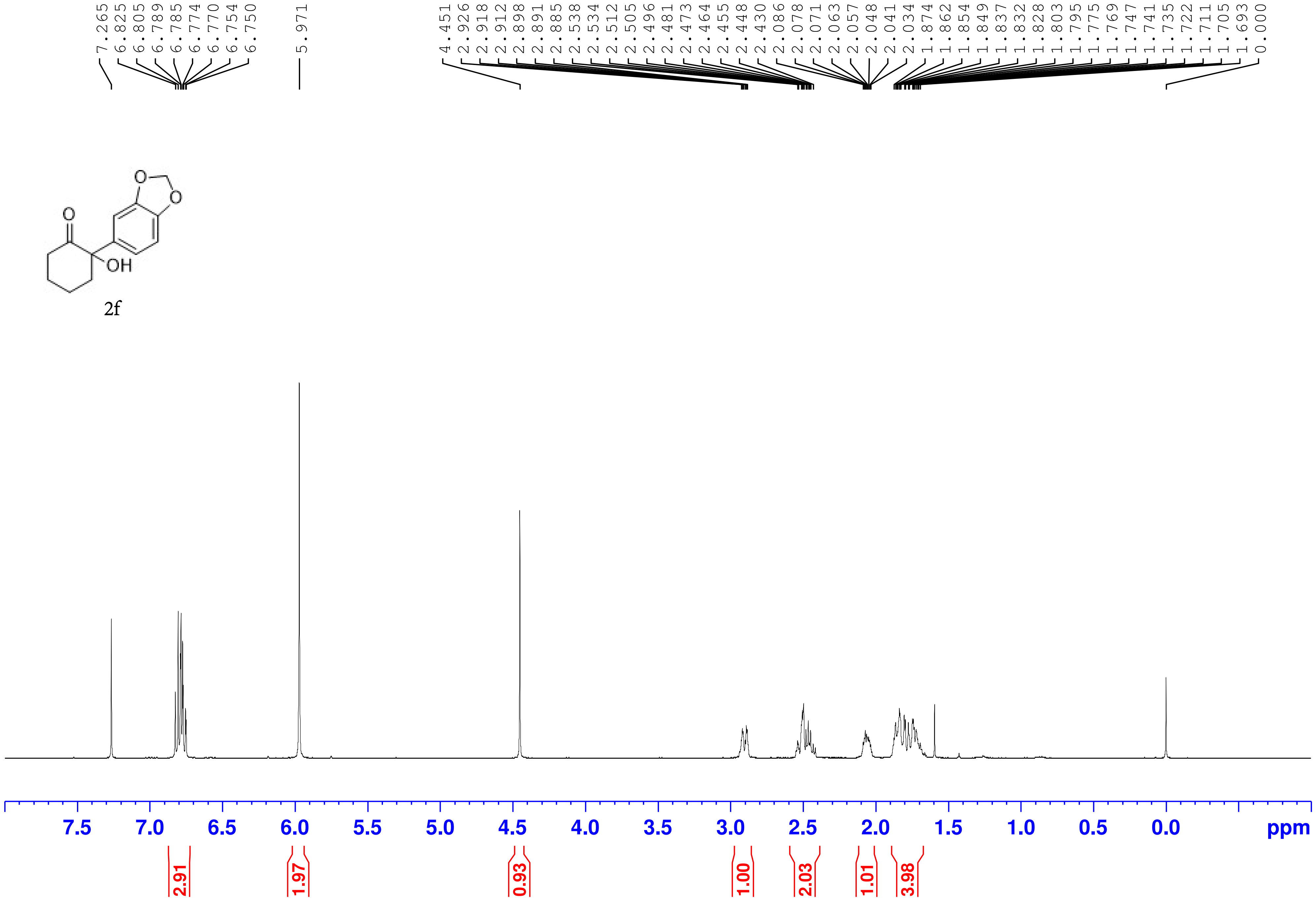
80
60
40
20
ppm



2f

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2.891
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2.534
2.512
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2.473
2.464
2.455
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2.063
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2.048
2.041
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1.837
1.832
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4.5
4.0
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3.0
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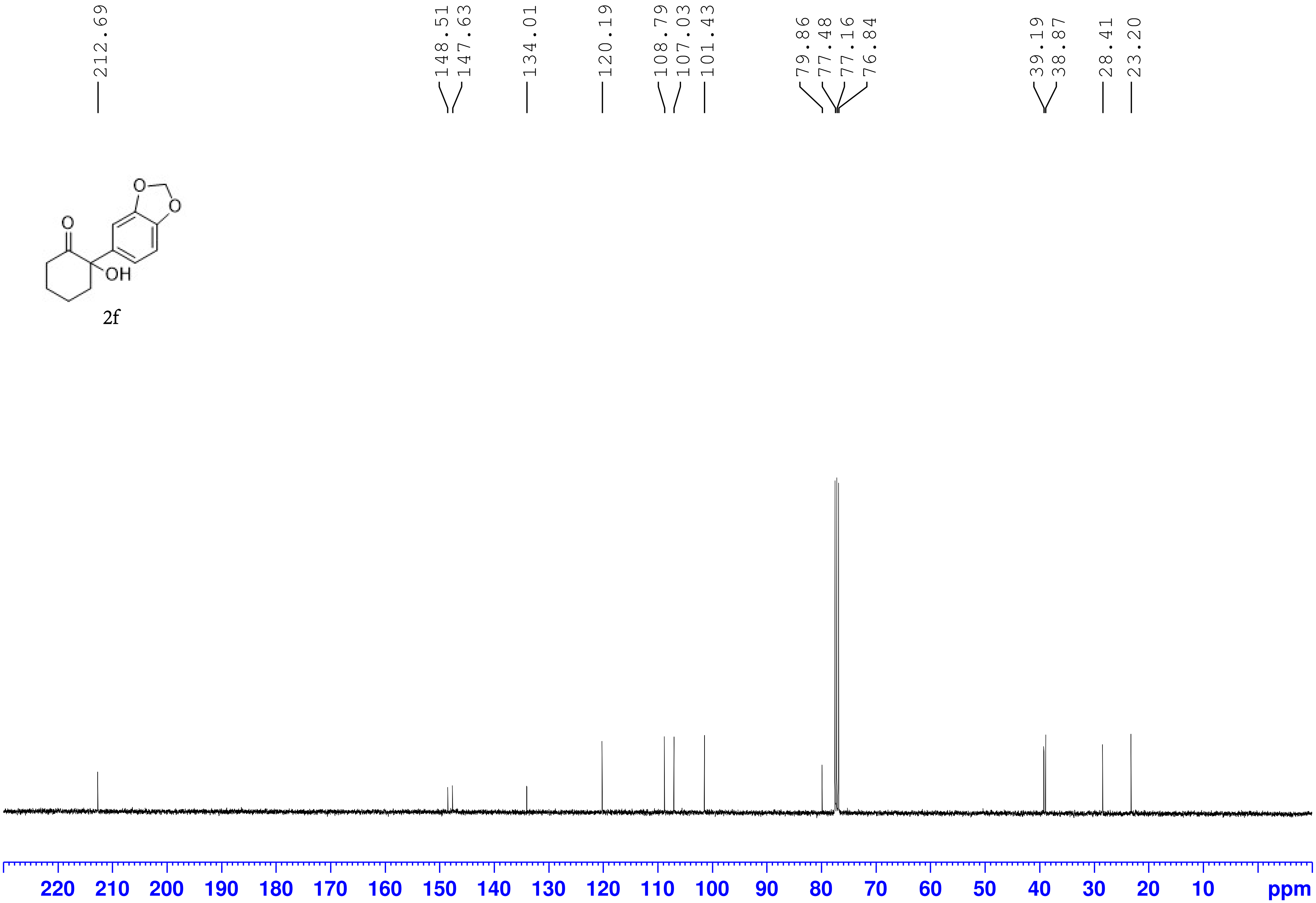
1.01
3.98



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39.19
38.87
28.41
23.20
O
O
O
OH
220
210
200
190
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120
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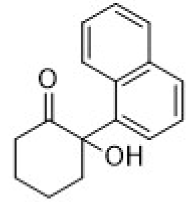
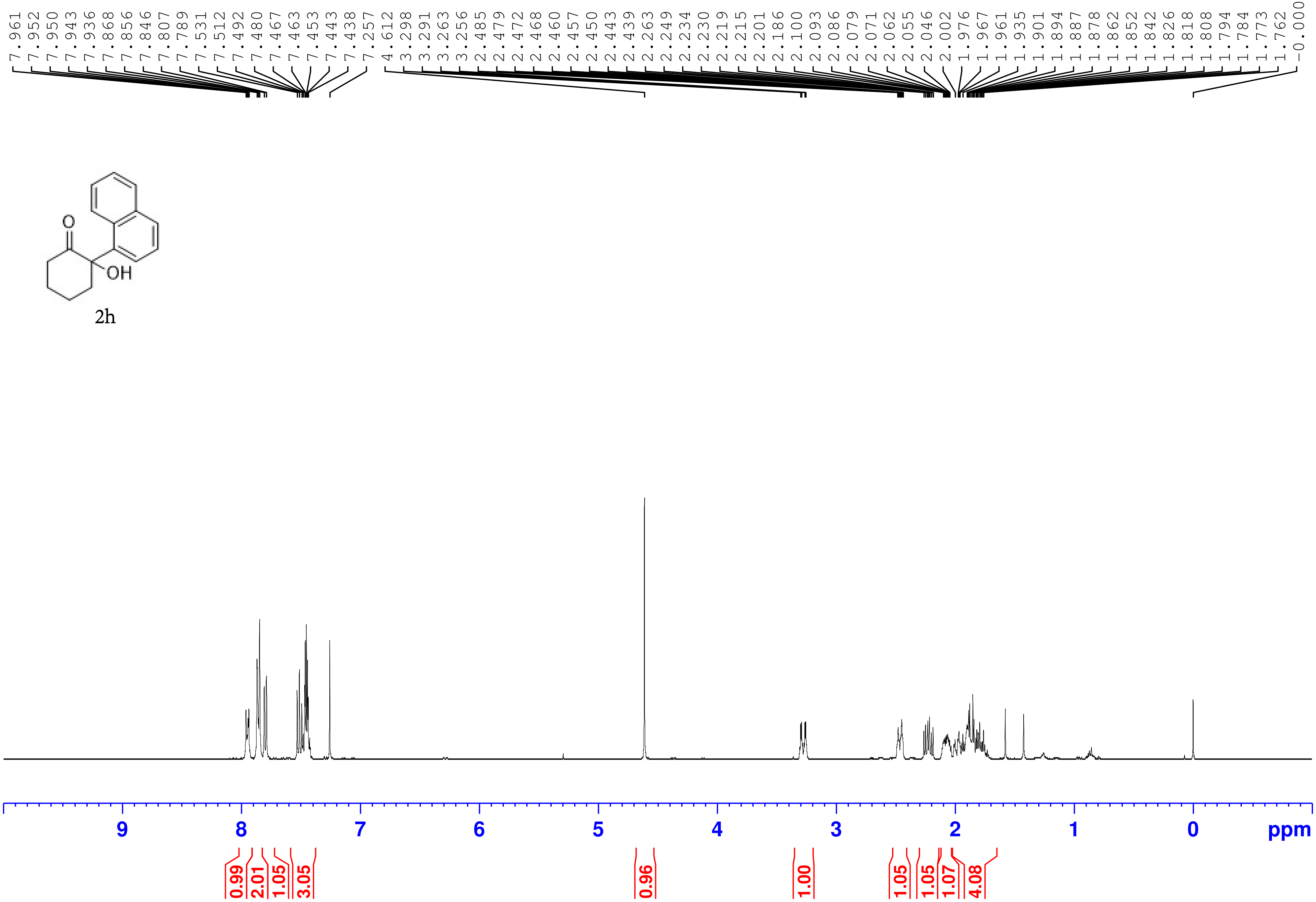
20
10
ppm

2f


O
OH

2h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2.230
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2.215
2.201
2.186
2.100
2.093
2.086
2.079
2.071
2.062
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1.961
1.935
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1.887
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6
5
4
3
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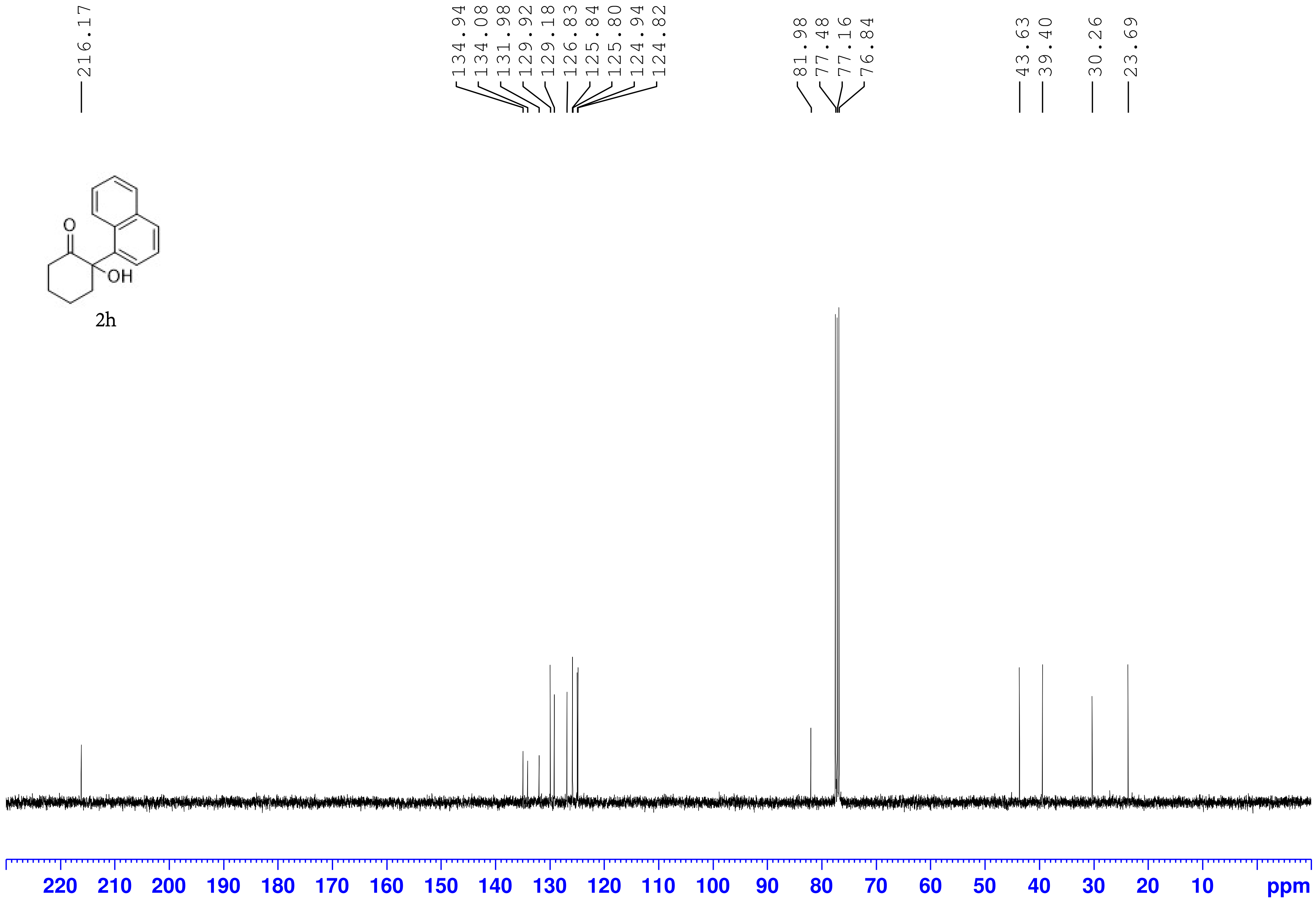
4.08



2h

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81.98
77.48
77.16
76.84
43.63
39.40
30.26
23.69
O
OH
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110
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10
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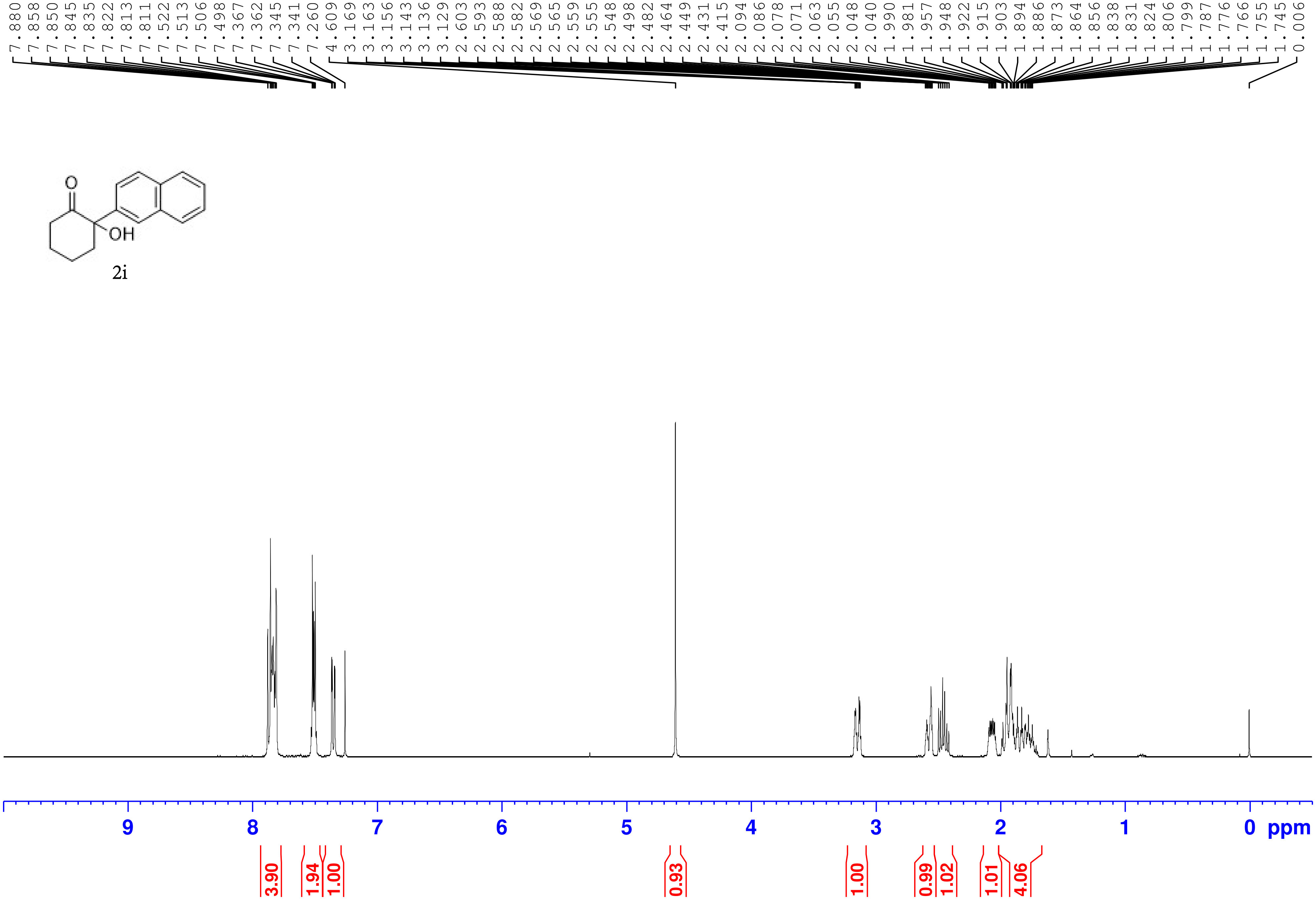
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3.136
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2.593
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2.582
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OH
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8
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6
5
4
3
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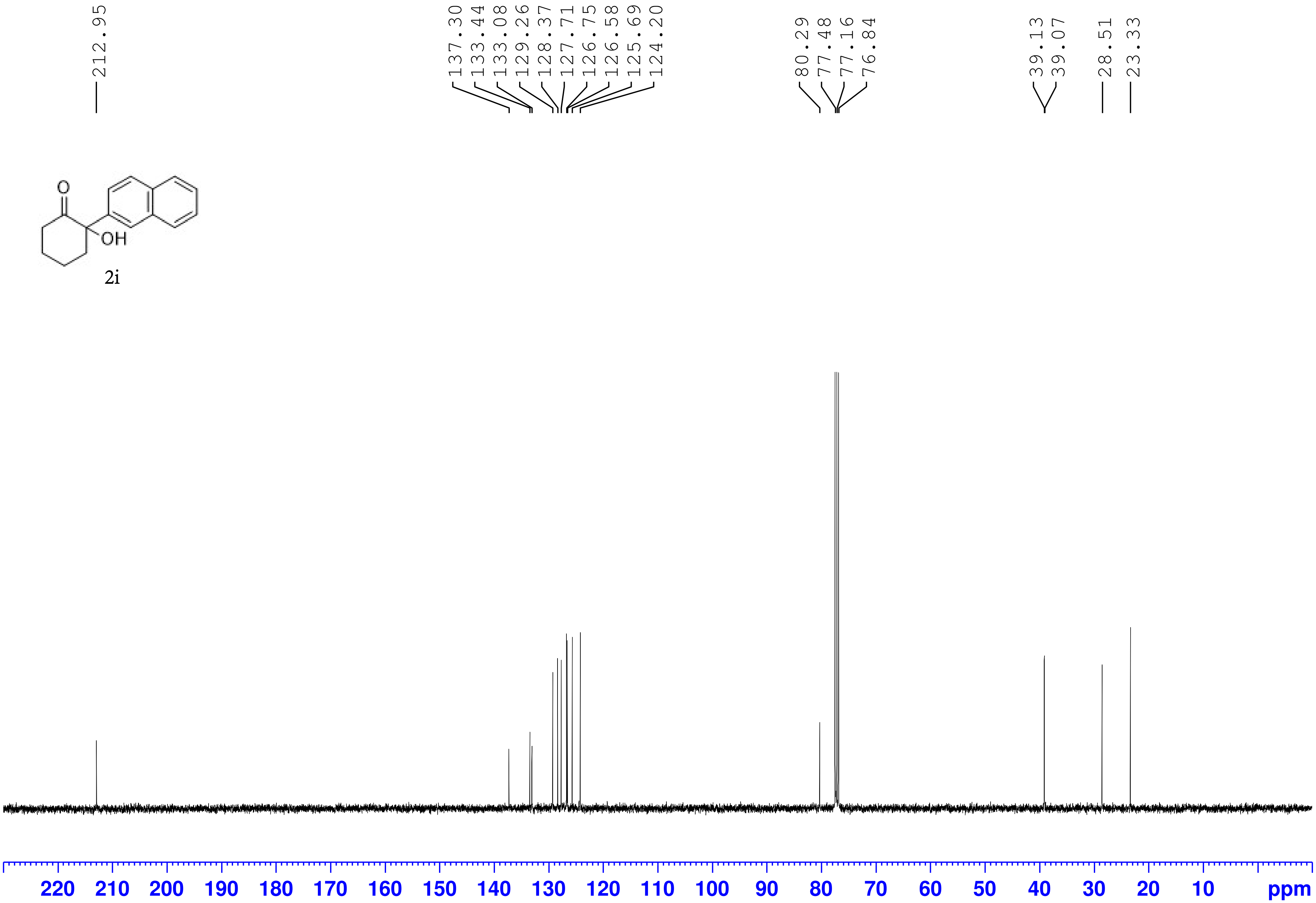
1.01
4.06

2i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77.16
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39.13
39.07
28.51
23.33
O
OH
2i
220
210
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70
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30
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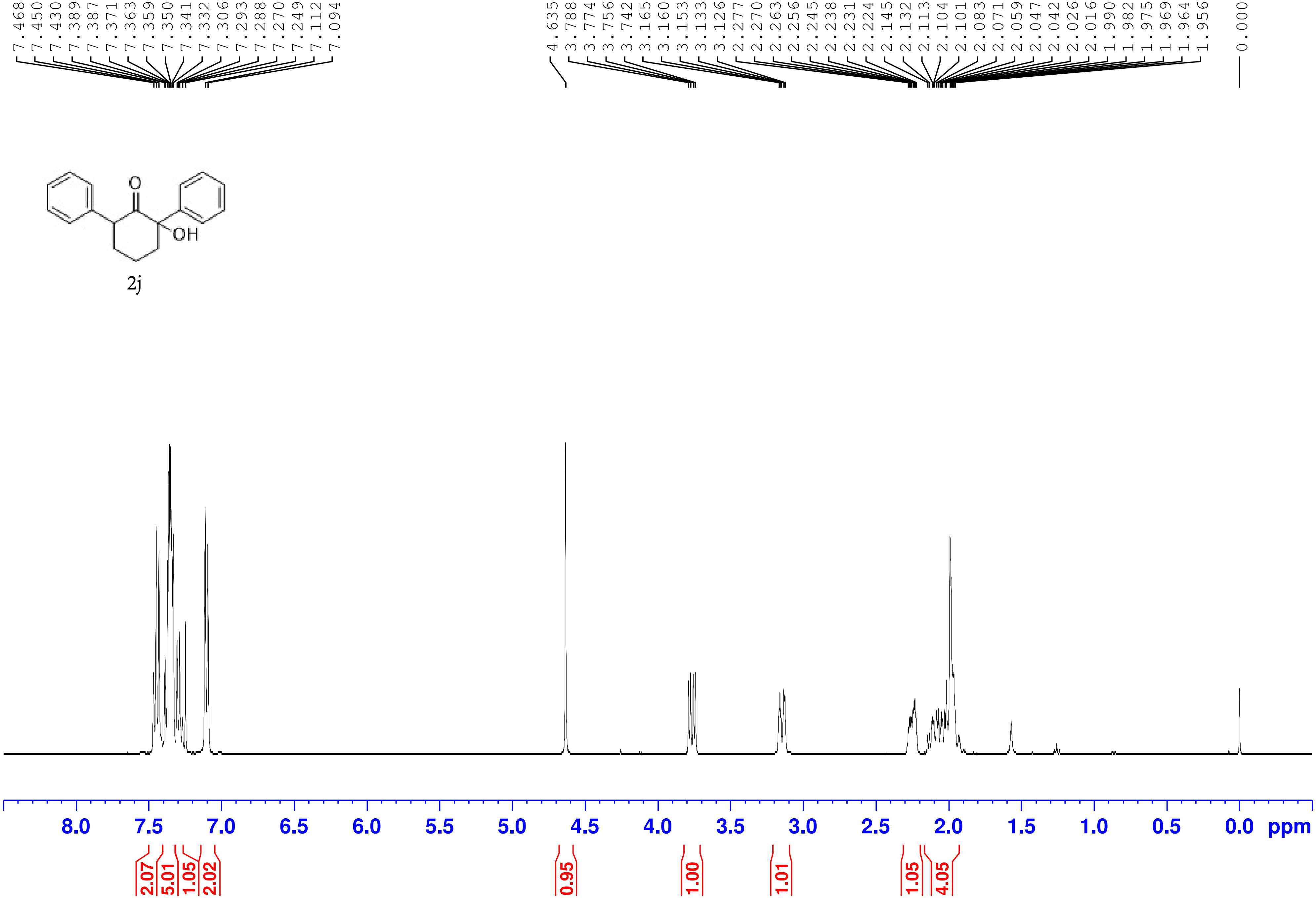
ppm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7.270
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2.238
2.231
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2.145
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2.101
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OH
2j
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6.0
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4.0
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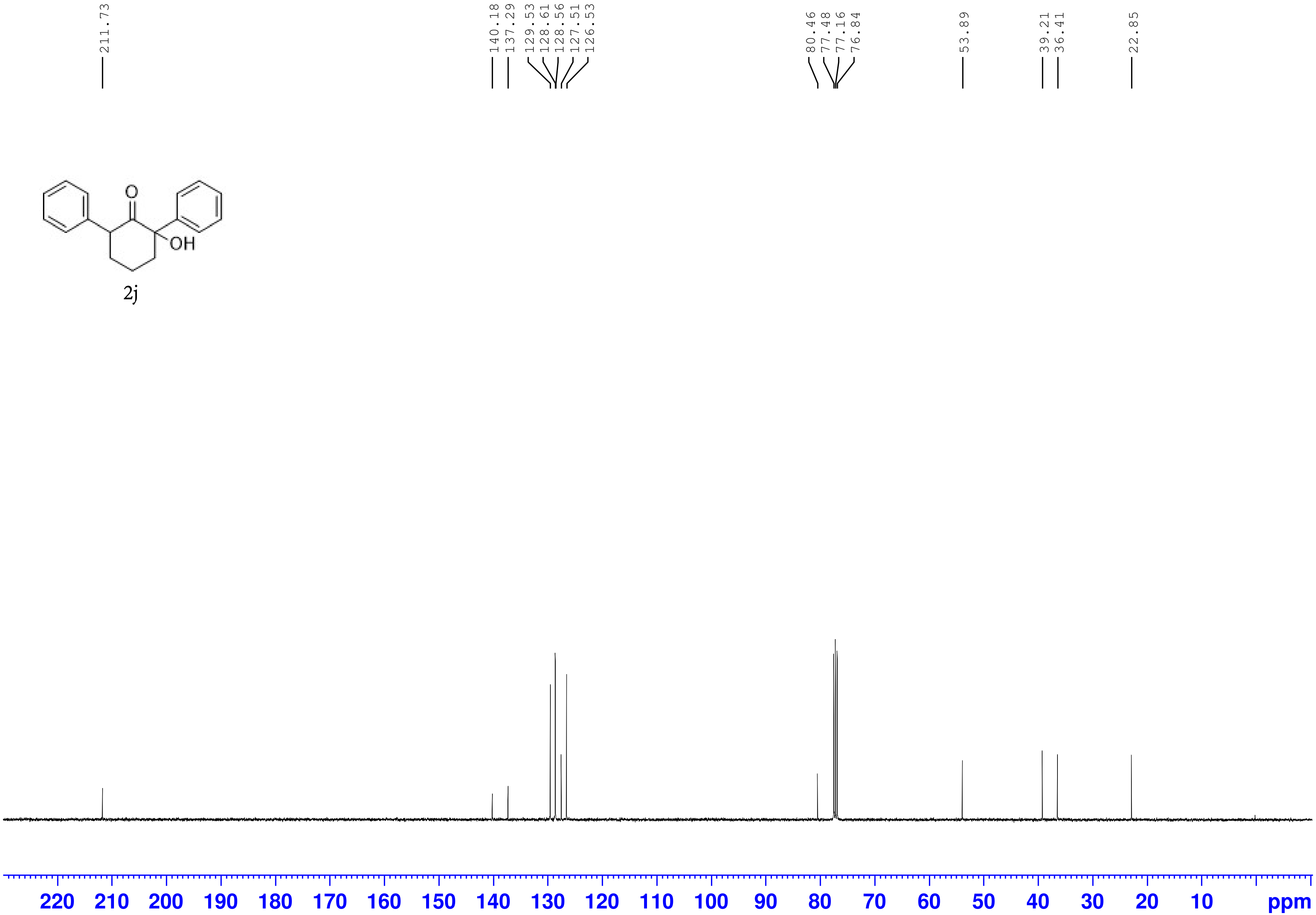
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36.41
22.85
O
OH
2j
220
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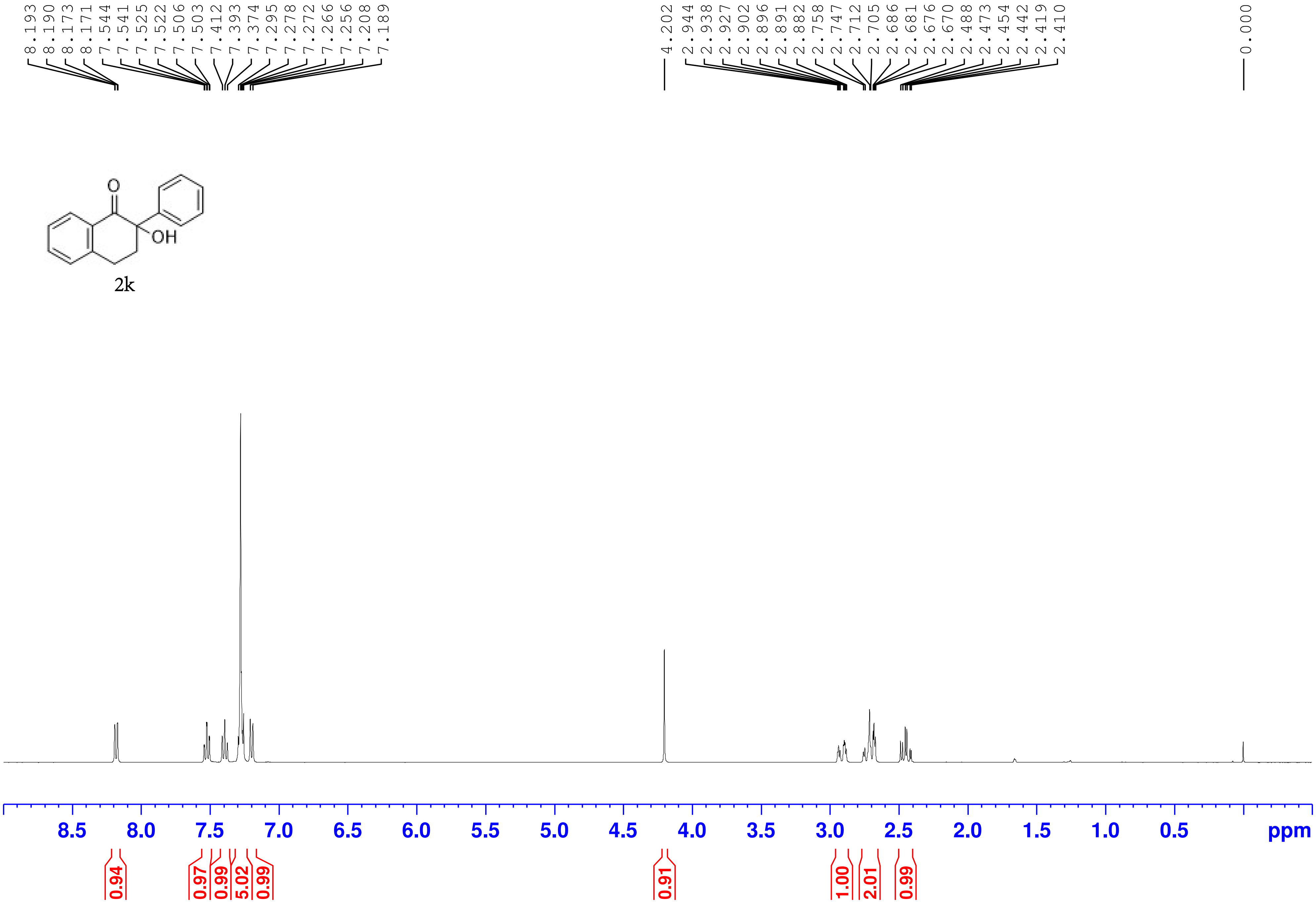
10
ppm



2k

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7.272
7.266
7.256
7.208
7.189
4.202
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2.938
2.927
2.902
2.896
2.891
2.882
2.758
2.747
2.712
2.705
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2.681
2.676
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2.473
2.454
2.442
2.419
2.410
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
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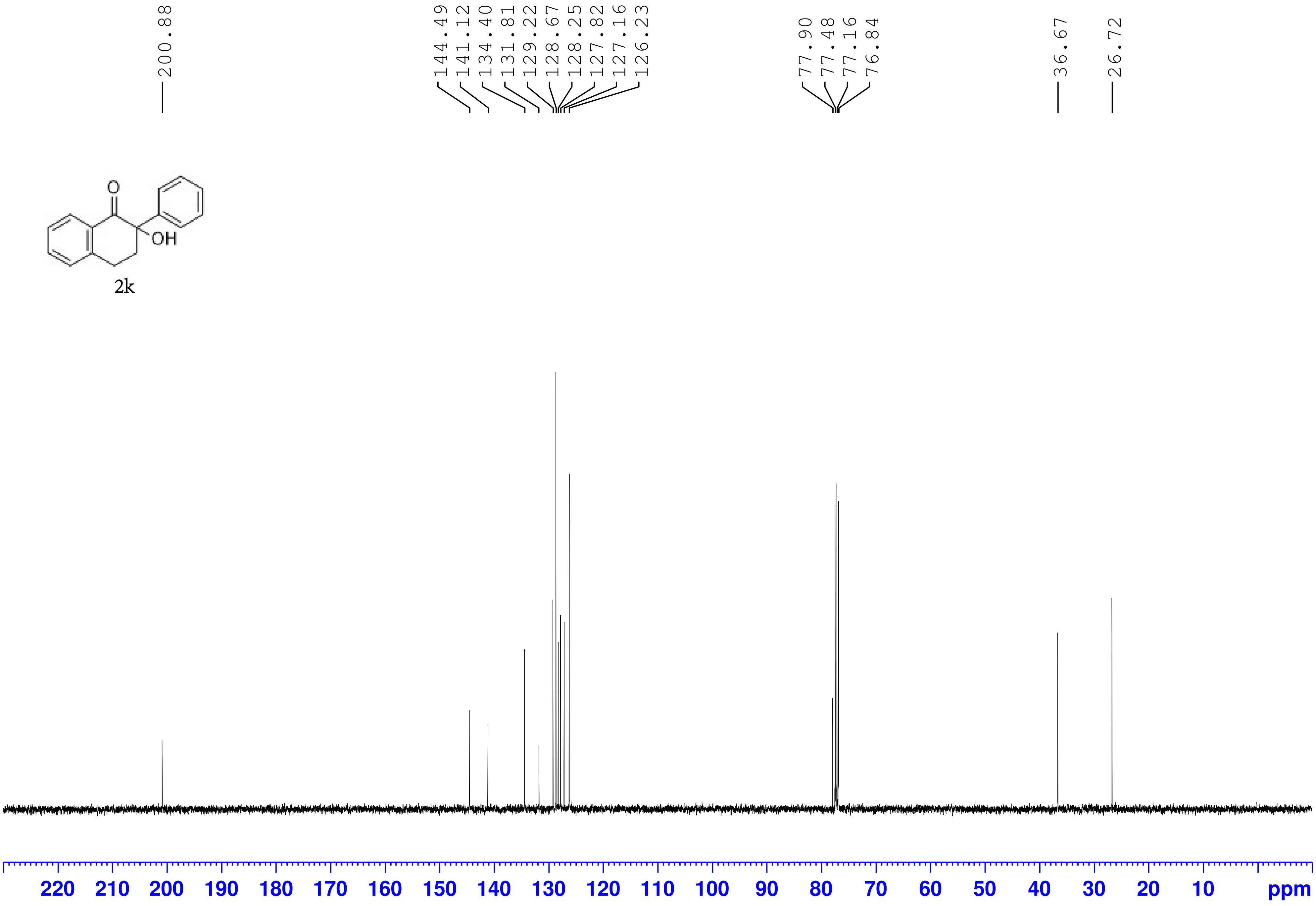
0.99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127.16
126.23
77.90
77.48
77.16
76.84
36.67
26.72
O
OH
2k
220
210
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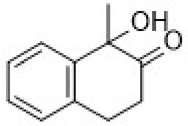
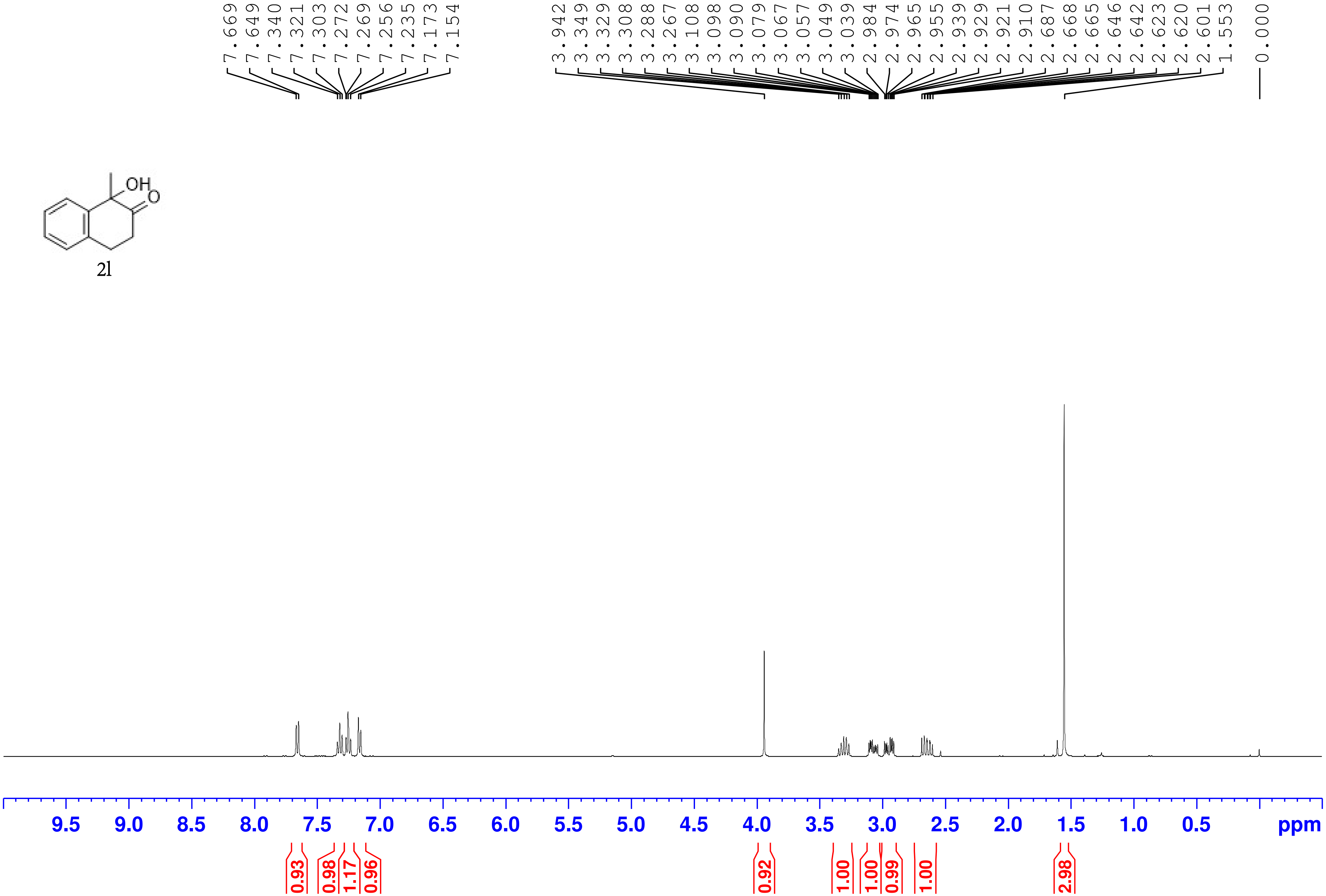
30
20
10
ppm


OH
O

2l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3.308
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3.267
3.108
3.098
3.090
3.079
3.067
3.057
3.049
3.039
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2.955
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8.0
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6.0
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3.5
3.0
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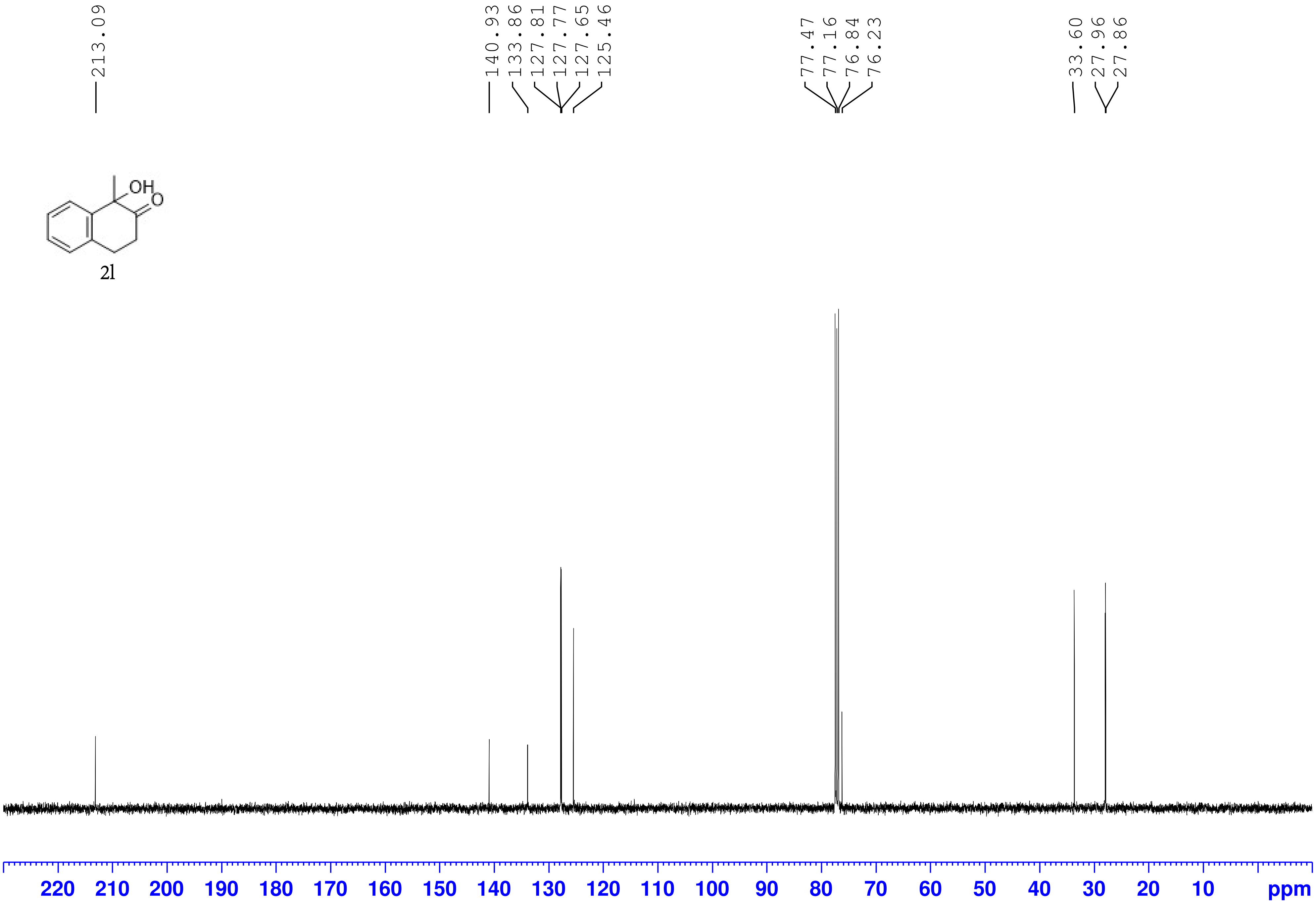
2.98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76.84
76.23
33.60
27.96
27.86
OH
O
2l
220
210
200
190
180
170
160
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140
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120
110
100
90
80
70
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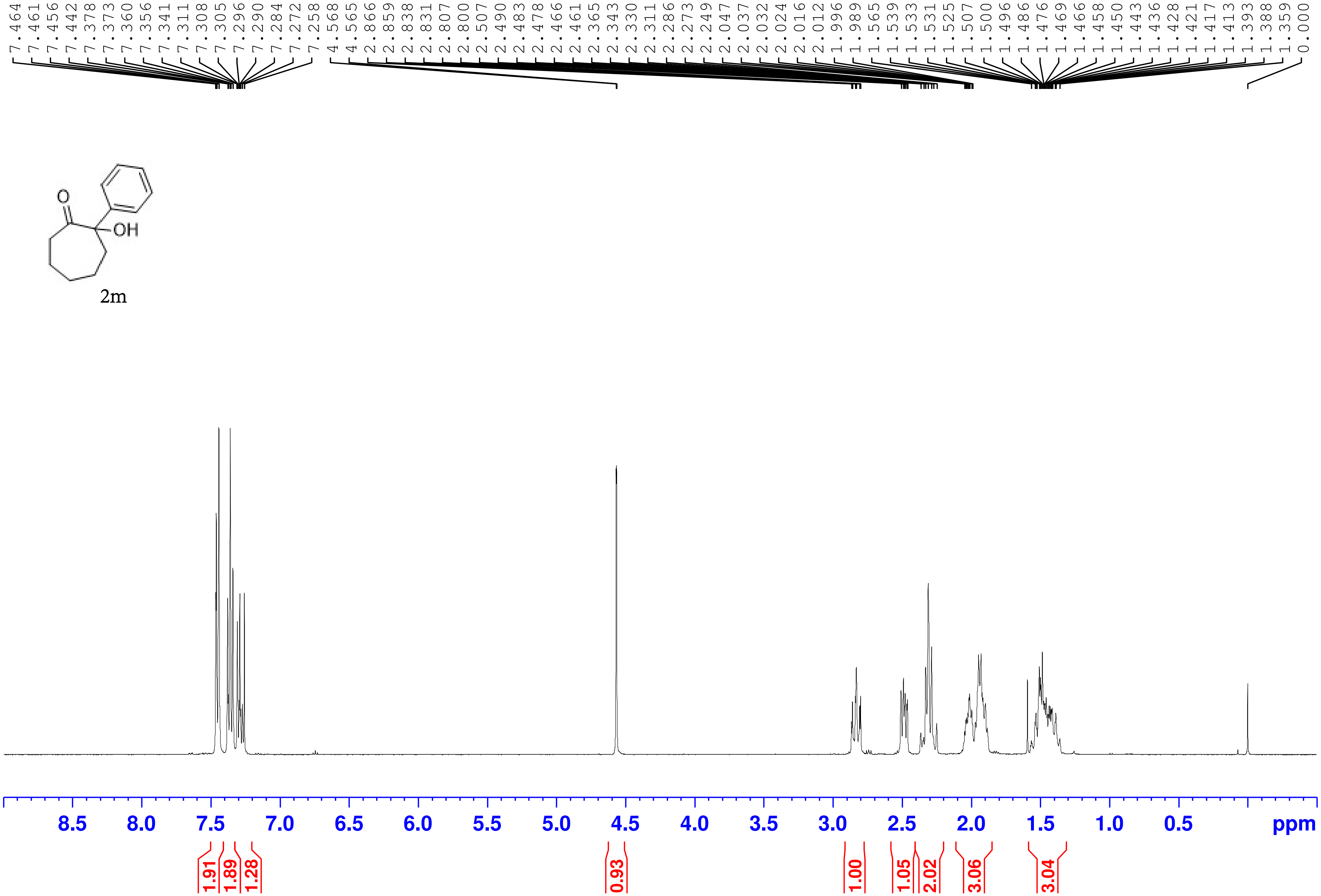
50
40
30
20
10
ppm

O
OH

2m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7.290
7.284
7.272
7.258
4.568
4.565
2.866
2.859
2.838
2.831
2.807
2.800
2.507
2.490
2.483
2.478
2.466
2.461
2.365
2.343
2.330
2.311
2.286
2.273
2.249
2.047
2.037
2.032
2.024
2.016
2.012
1.996
1.989
1.565
1.539
1.533
1.531
1.525
1.507
1.500
1.496
1.486
1.476
1.469
1.466
1.458
1.450
1.443
1.436
1.428
1.421
1.417
1.413
1.393
1.388
1.359
0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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ppm
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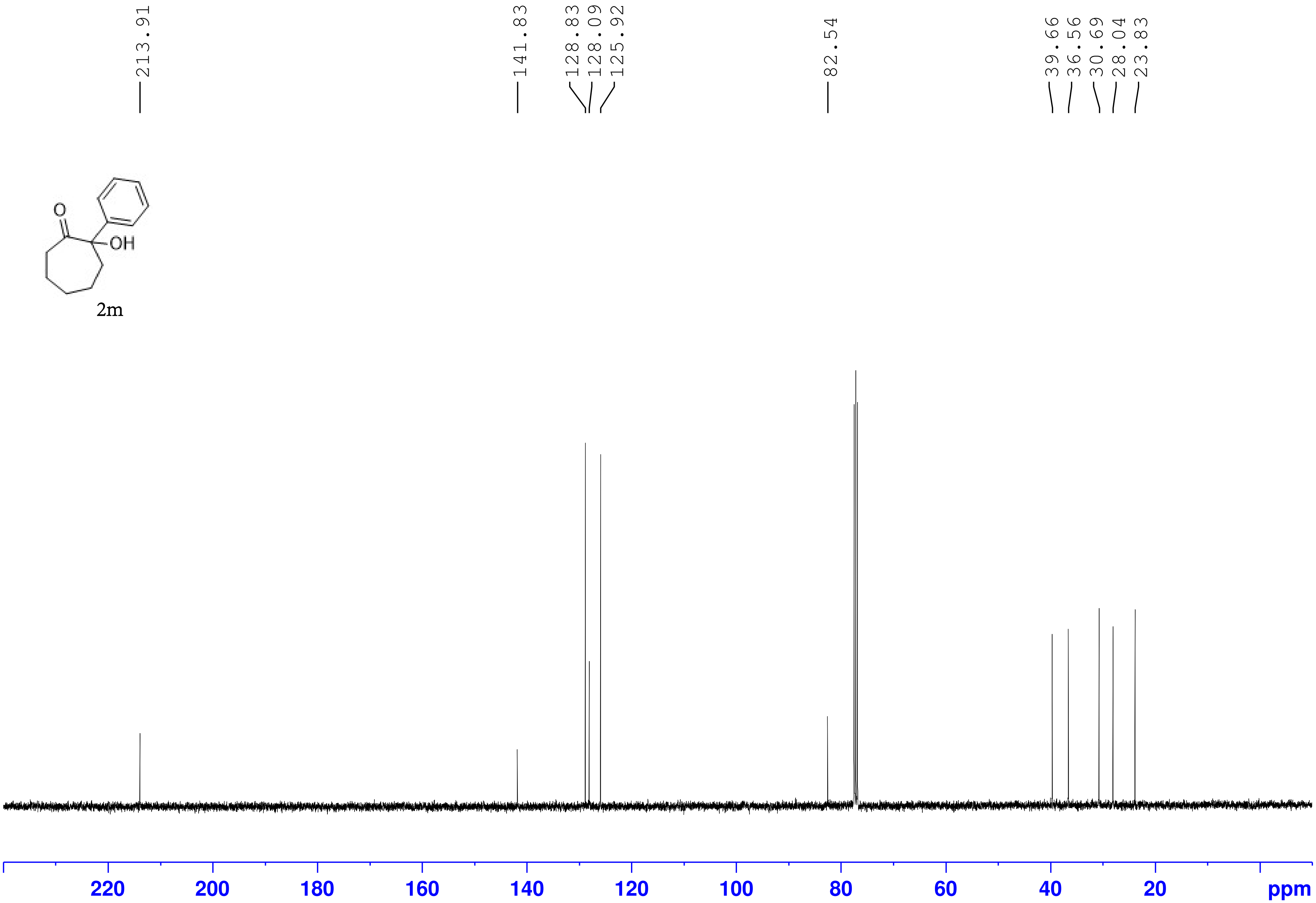
1.89
1.28
0.93
1.00
1.05
2.02
3.06
3.04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141.83
128.83
128.09
125.92
82.54
39.66
36.56
30.69
28.04
23.83
O
OH
2m
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200
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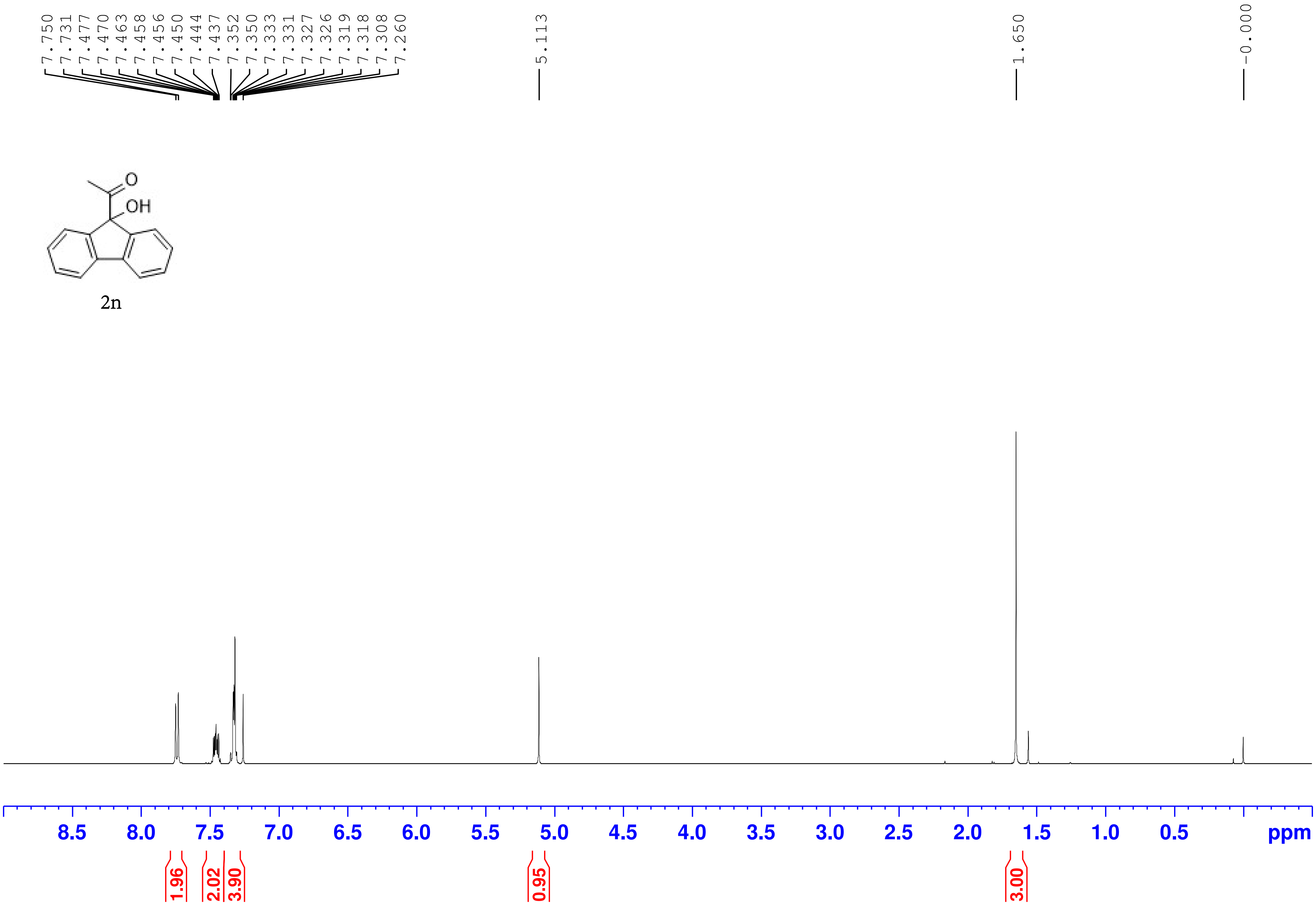
140
120
100
80
60
40
20
ppm



2n

7.750
7.731
7.477
7.470
7.463
7.458
7.456
7.450
7.444
7.437
7.352
7.350
7.333
7.331
7.327
7.326
7.319
7.318
7.308
7.260
5.113
1.650
-0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
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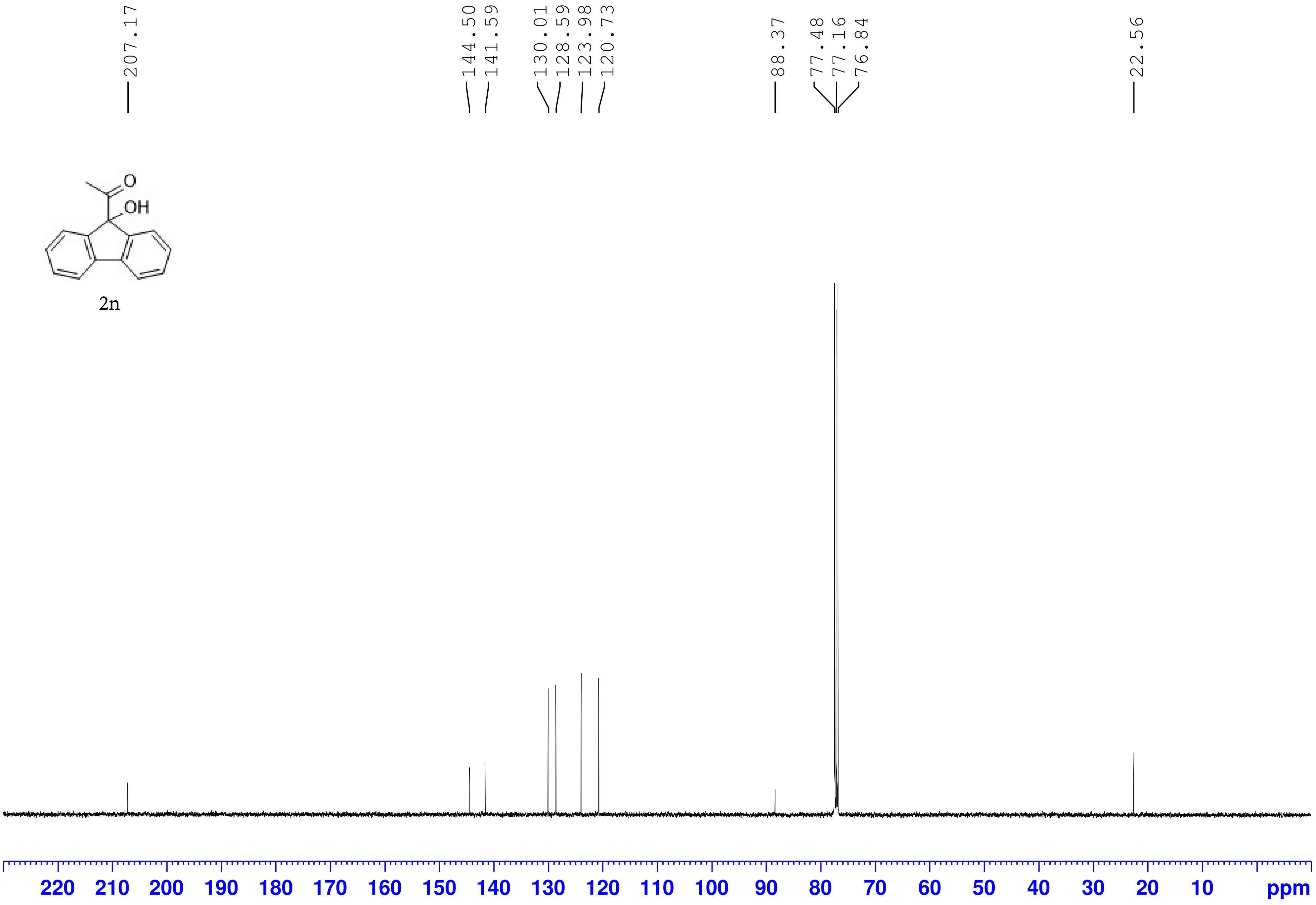
3.00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123.98
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88.37
77.48
77.16
76.84
22.56
O
OH
220
210
200
190
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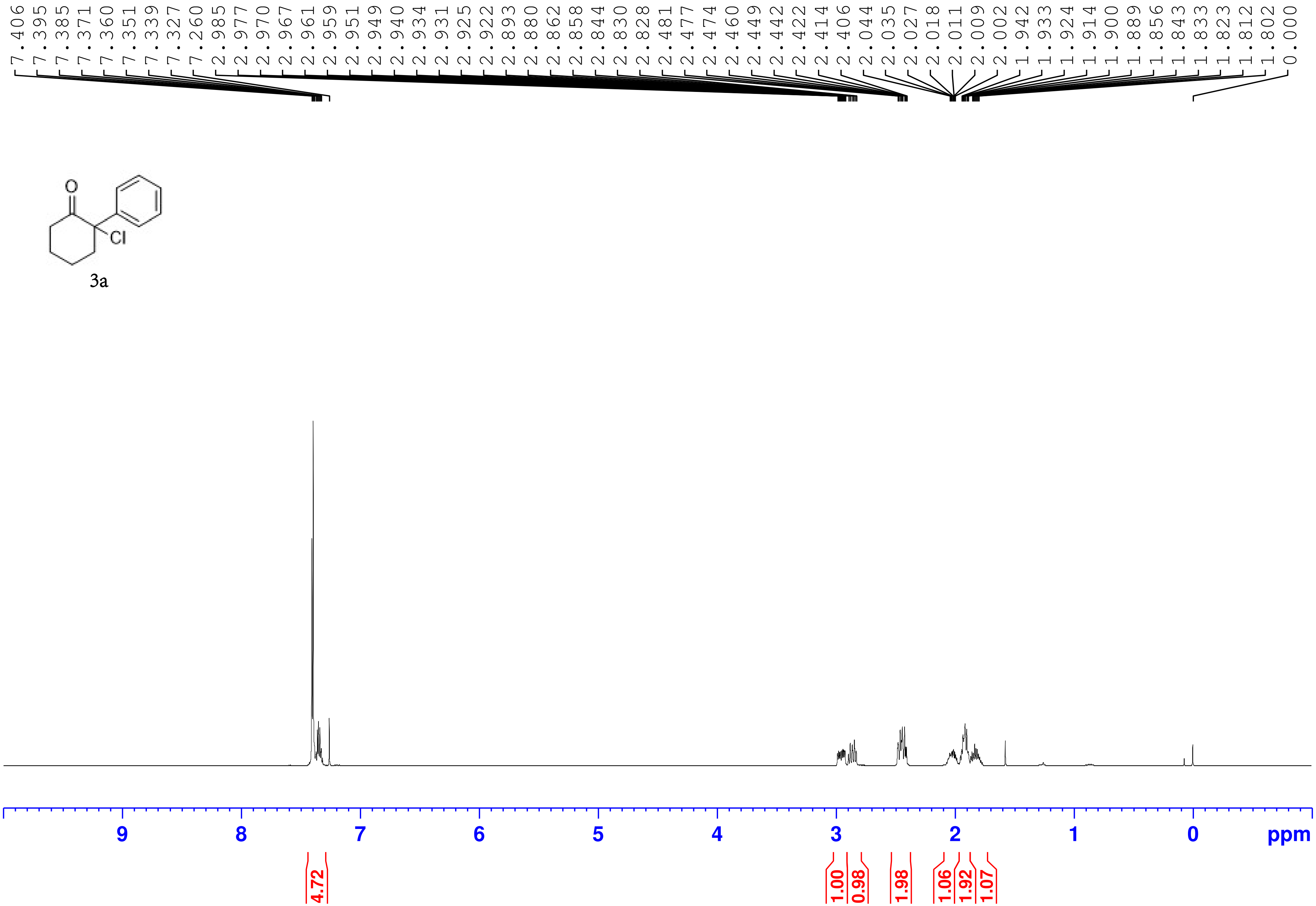
30
20
10
ppm

2n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7.395
7.385
7.371
7.360
7.351
7.339
7.327
7.260
2.985
2.977
2.970
2.967
2.961
2.959
2.951
2.949
2.940
2.934
2.931
2.925
2.922
2.893
2.880
2.862
2.858
2.844
2.830
2.828
2.481
2.477
2.474
2.460
2.449
2.442
2.422
2.414
2.406
2.044
2.035
2.027
2.018
2.011
2.009
2.002
1.942
1.933
1.924
1.914
1.900
1.889
1.856
1.843
1.833
1.823
1.812
1.802
0.000
O
Cl
9
8
7
6
5
4
3
2
1
0
ppm
4.72
1.00
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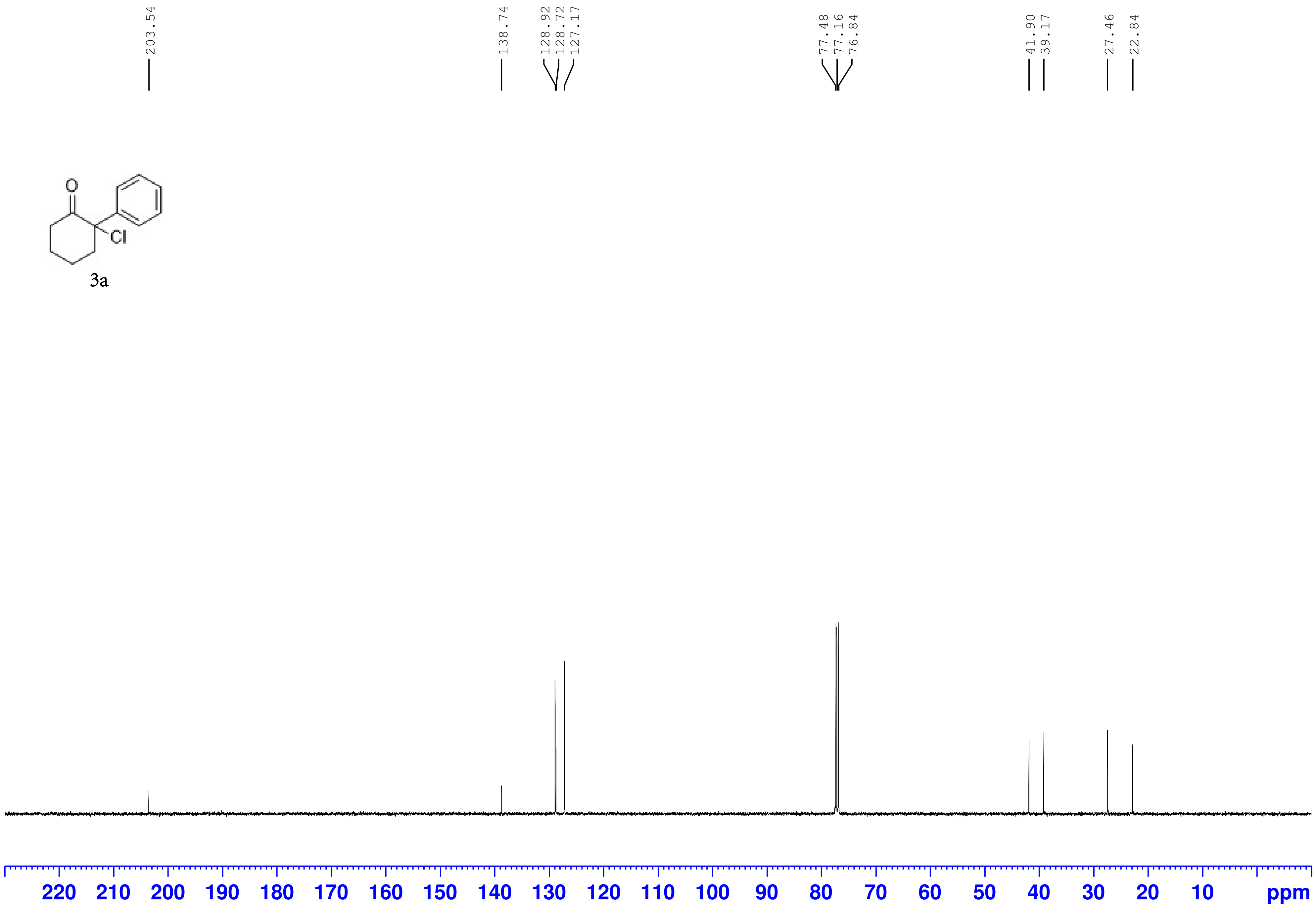
1.98
1.06
1.92
1.07

3a


3a

203.54
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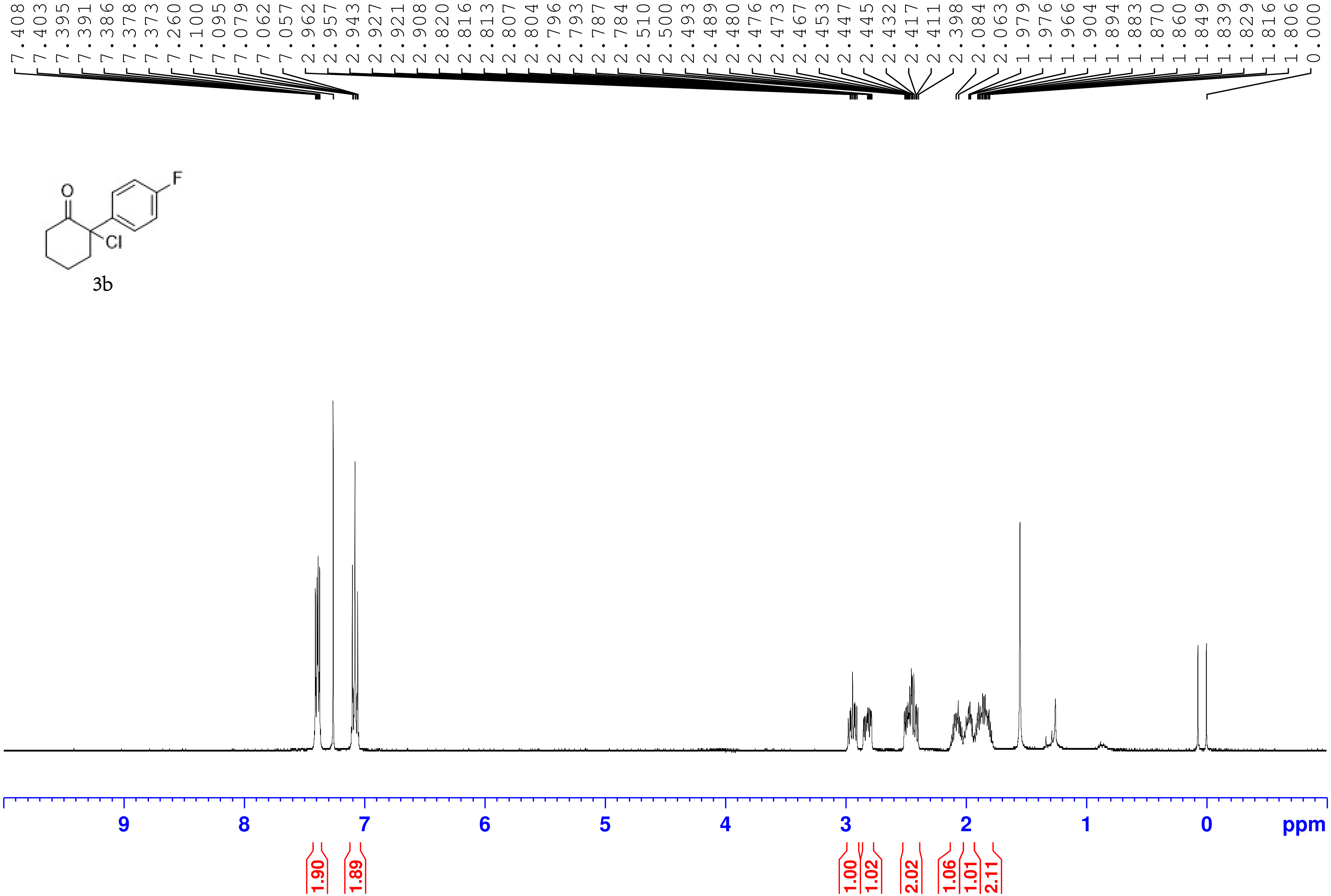
128.92
128.72
127.17
77.48
77.16
76.84
41.90
39.17
27.46
22.84
O
Cl
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3b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7.403
7.395
7.391
7.386
7.378
7.373
7.260
7.100
7.095
7.079
7.062
7.057
2.962
2.957
2.943
2.927
2.921
2.908
2.820
2.816
2.813
2.807
2.804
2.796
2.793
2.787
2.784
2.510
2.500
2.493
2.489
2.480
2.476
2.473
2.467
2.453
2.447
2.445
2.432
2.417
2.411
2.398
2.084
2.063
1.979
1.976
1.966
1.904
1.894
1.883
1.870
1.860
1.849
1.839
1.829
1.816
1.806
0.000
9
8
7
6
5
4
3
2
1
0
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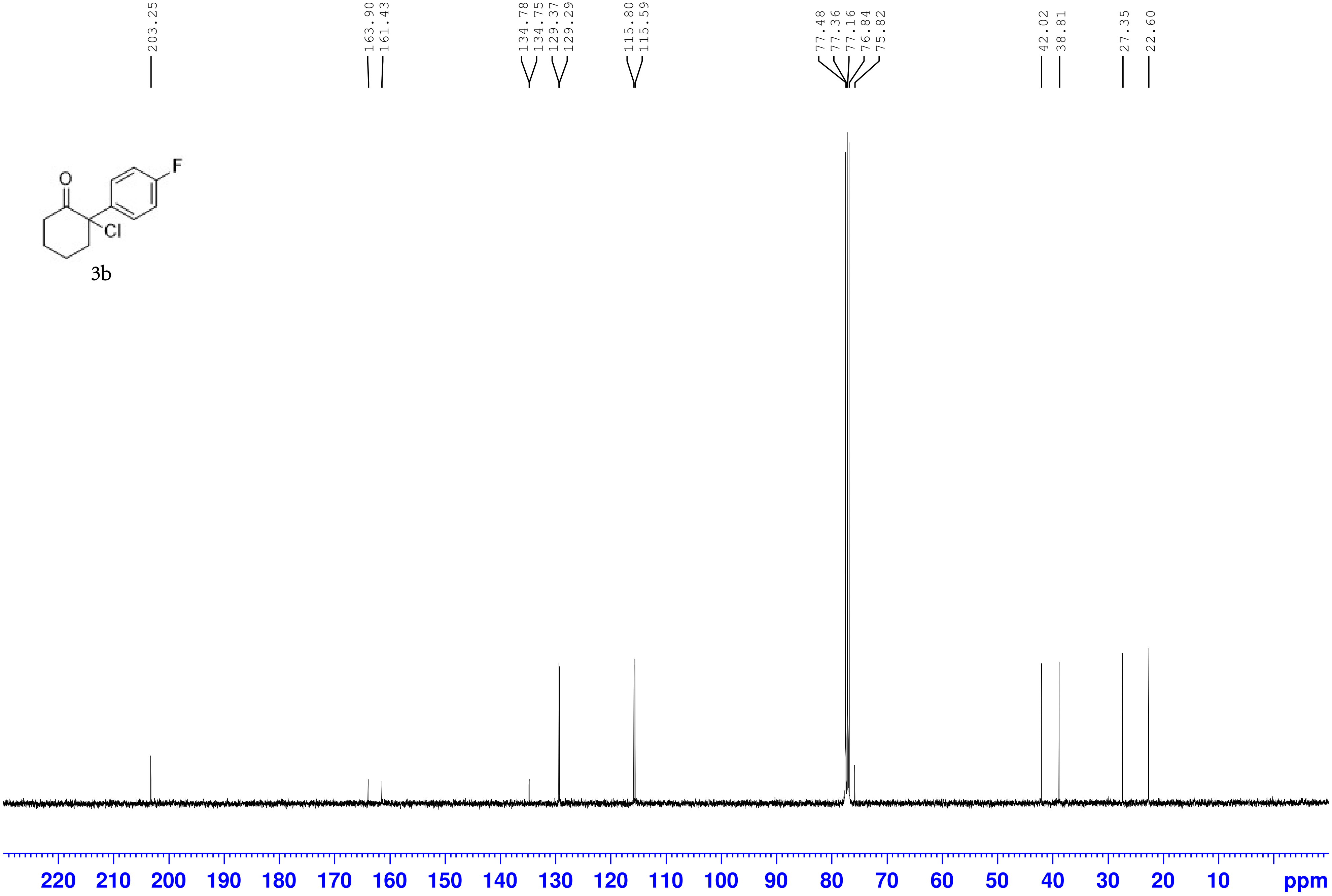
1.89
1.00
1.02
2.02
1.06
1.01
2.11

O
F
Cl

3b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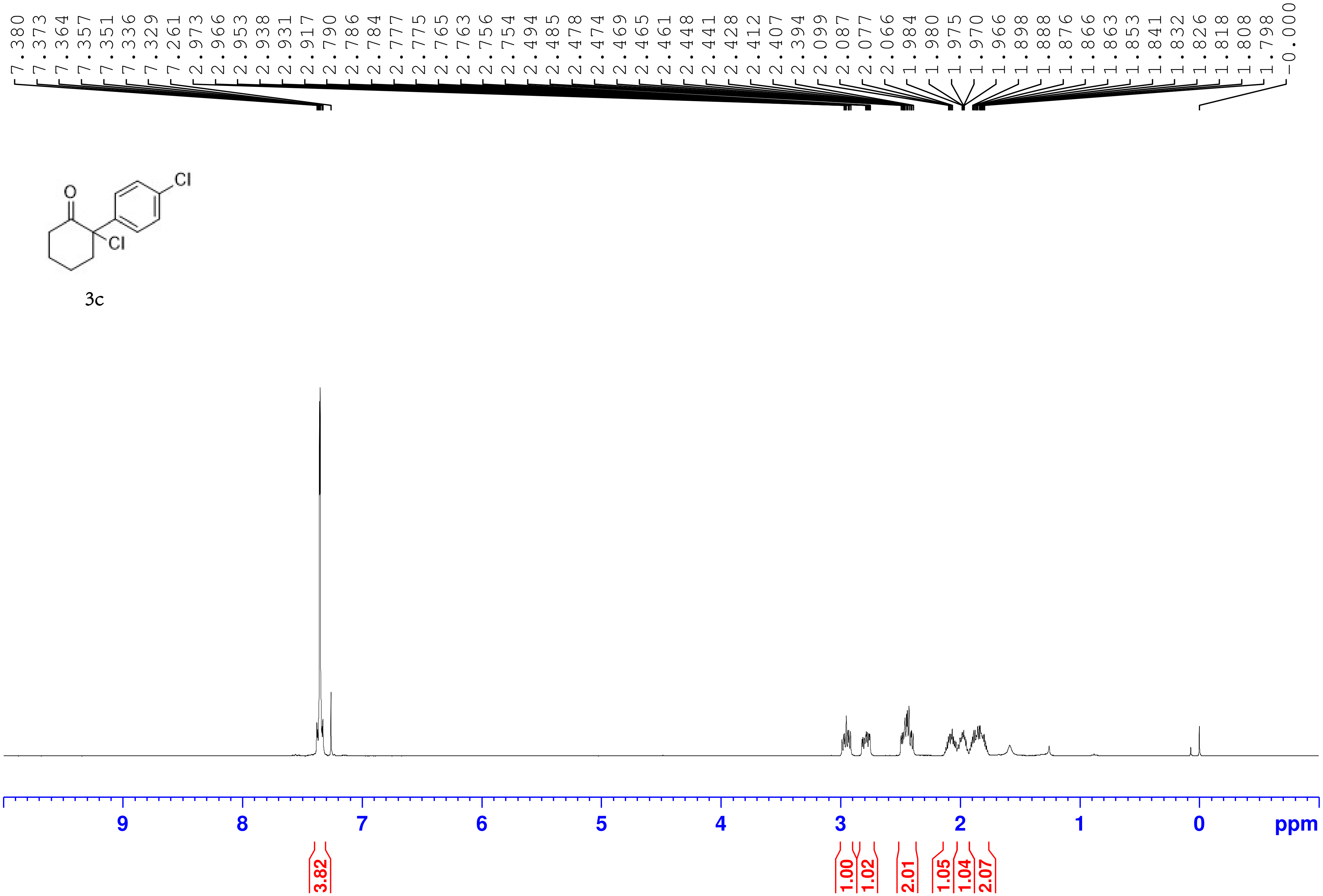
161.43
134.78
134.75
129.37
129.29
115.80
115.59
77.48
77.36
77.16
76.84
75.82
42.02
38.81
27.35
22.60
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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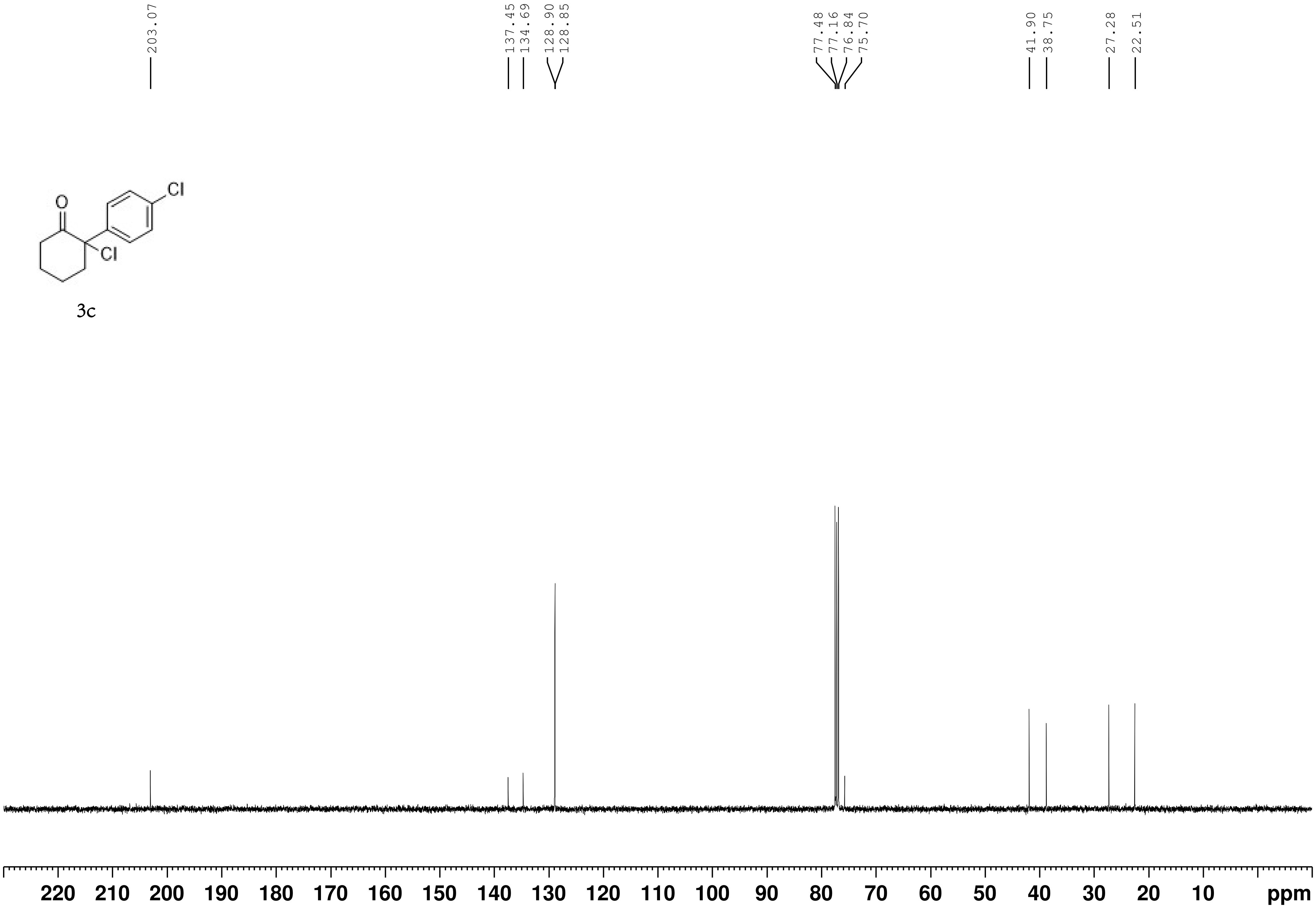
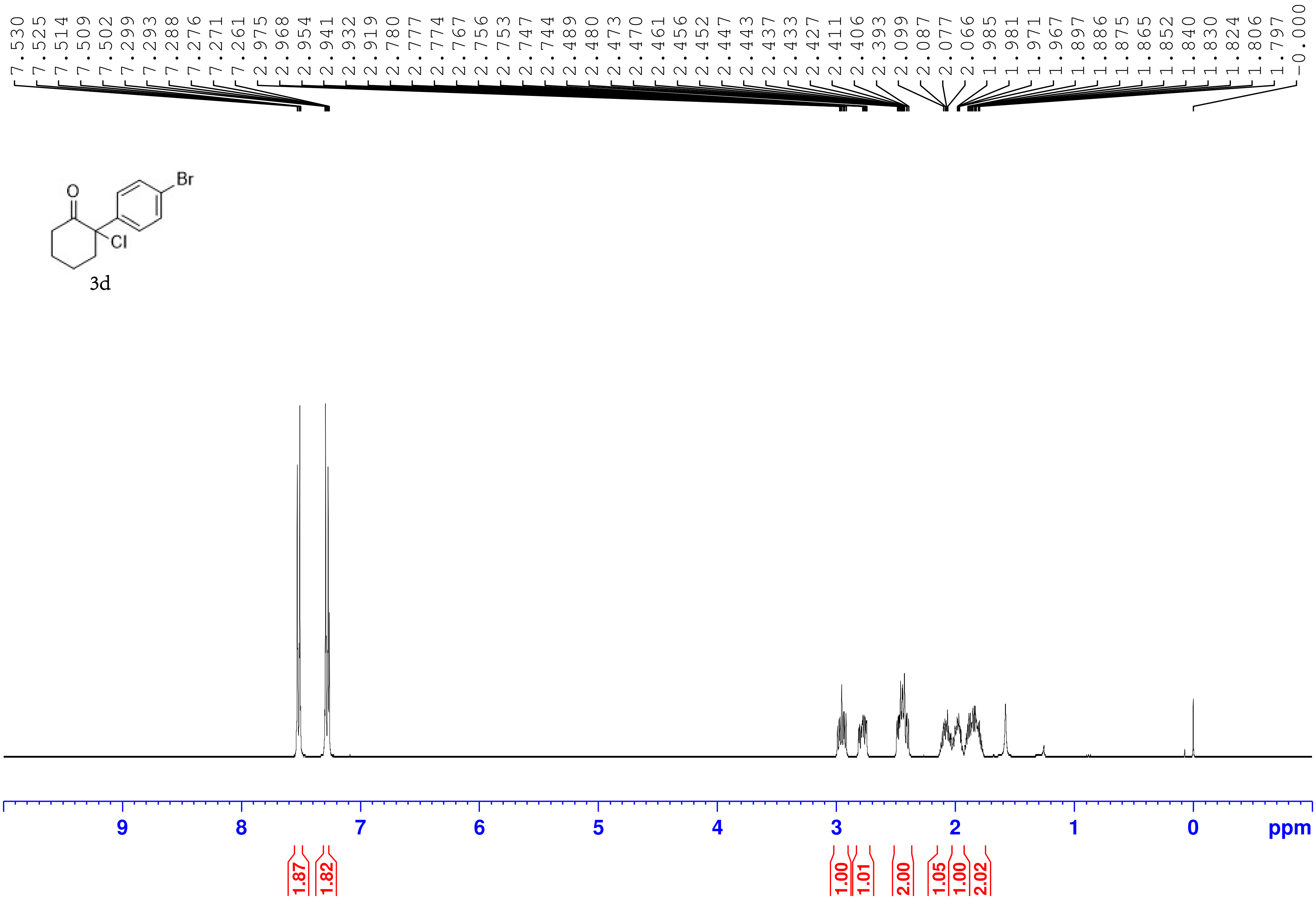
7.364
7.357
7.351
7.336
7.329
7.261
2.973
2.966
2.953
2.938
2.931
2.917
2.790
2.786
2.784
2.777
2.775
2.765
2.763
2.756
2.754
2.494
2.485
2.478
2.474
2.469
2.465
2.461
2.448
2.441
2.428
2.412
2.407
2.394
2.099
2.087
2.077
2.066
1.984
1.980
1.975
1.970
1.966
1.898
1.888
1.876
1.866
1.863
1.853
1.841
1.832
1.826
1.818
1.808
1.798
-0.000
O
Cl
Cl
9
8
7
6
5
4
3
2
1
0
ppm
3.82
1.00
1.02
2.01
1.05
1.04
2.07

3c



3c

203.07
137.45
134.69
128.90
128.85
77.48
77.16
76.84
75.70
41.90
38.75
27.28
22.51
O
Cl
Cl
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.514
7.509
7.502
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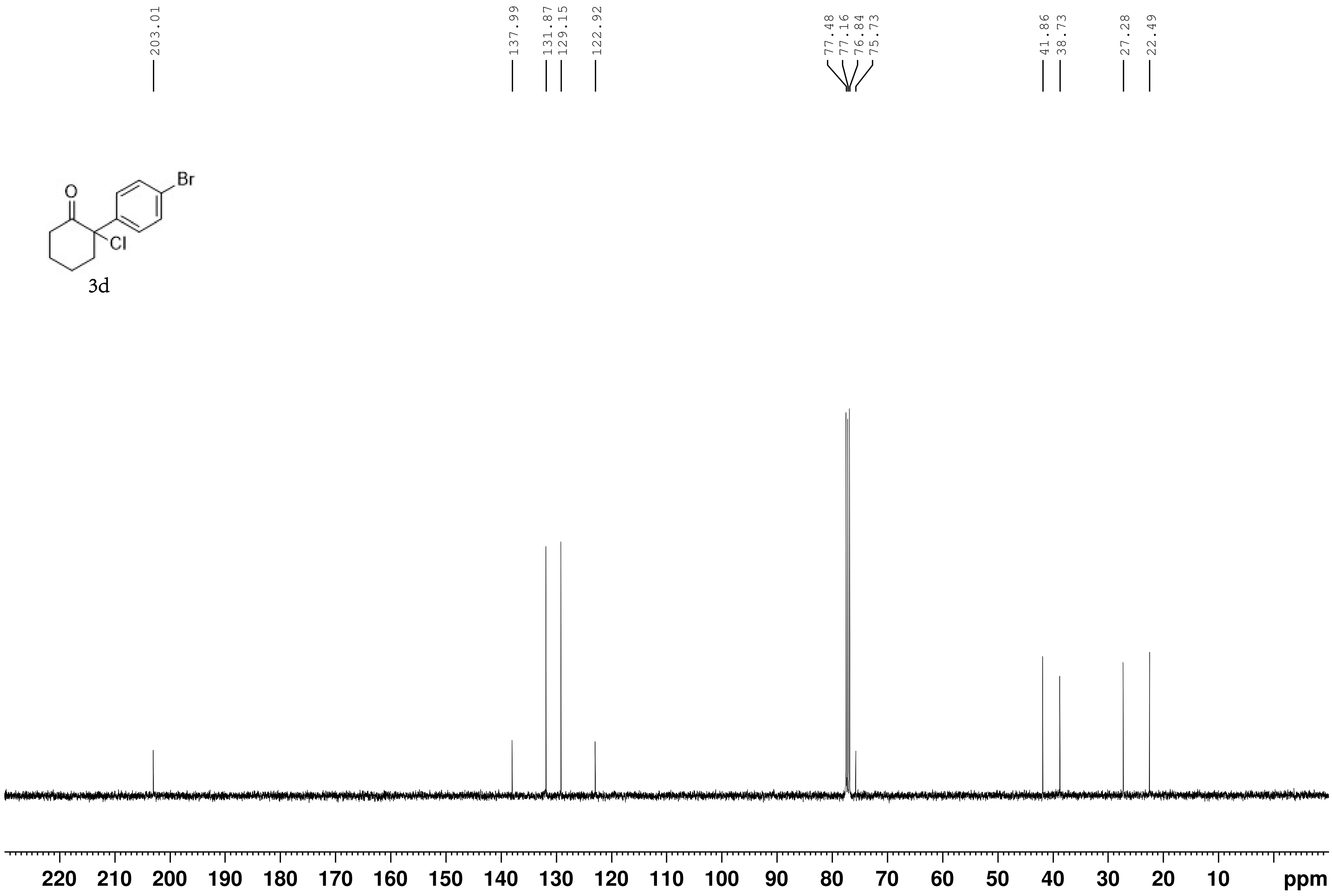
7.293
7.288
7.276
7.271
7.261
2.975
2.968
2.954
2.941
2.932
2.919
2.780
2.777
2.774
2.767
2.756
2.753
2.747
2.744
2.489
2.480
2.473
2.470
2.461
2.456
2.452
2.447
2.443
2.437
2.433
2.427
2.411
2.406
2.393
2.099
2.087
2.077
2.066
1.985
1.981
1.971
1.967
1.897
1.886
1.875
1.865
1.852
1.840
1.830
1.824
1.806
1.797
-0.000
O
Br
Cl
9
8
7
6
5
4
3
2
1
0
ppm
1.87
1.82
1.00
1.01
2.00
1.05
1.00
2.02

3d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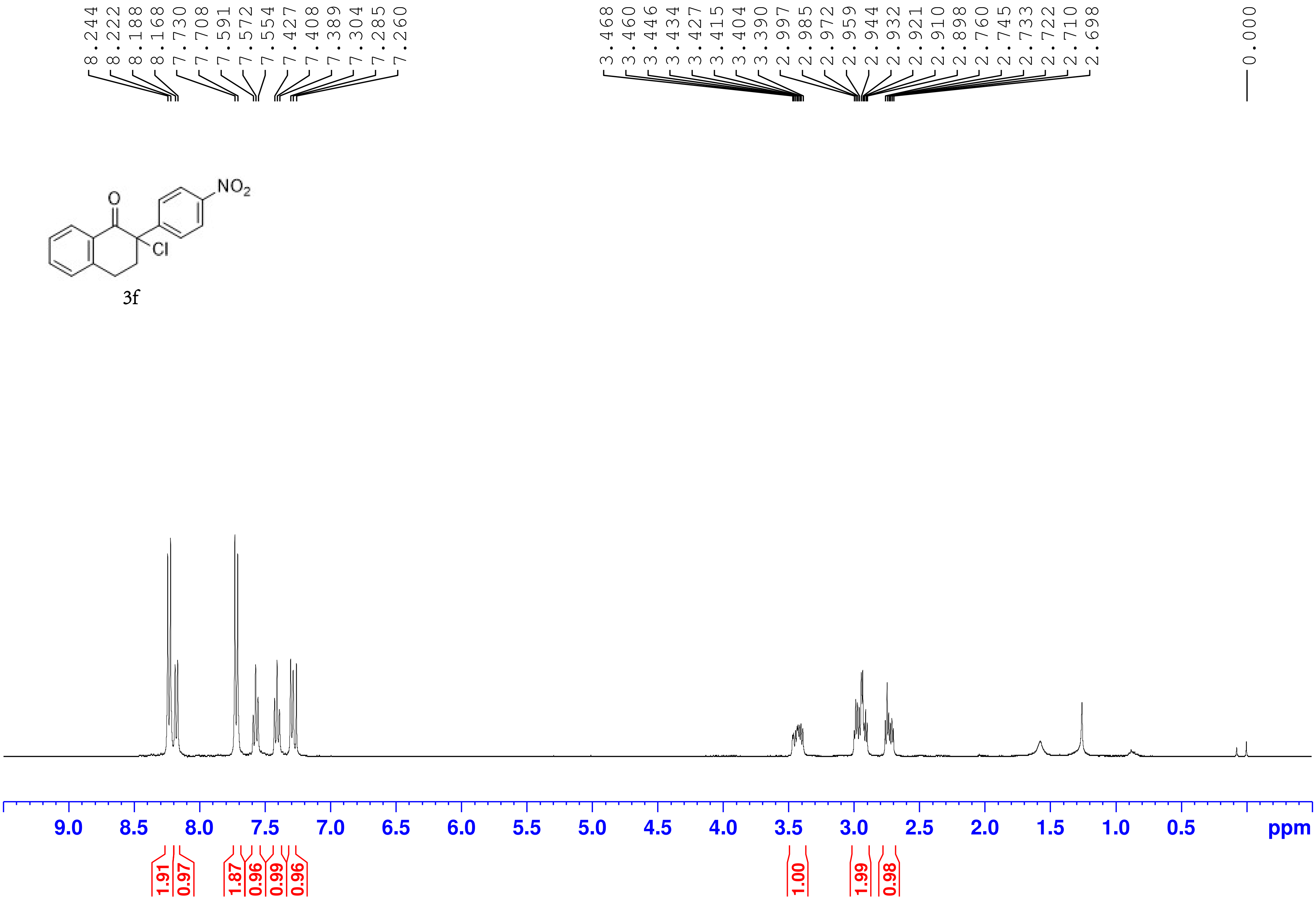
137.99
131.87
129.15
122.92
77.48
77.16
76.84
75.73
41.86
38.73
27.28
22.49
O
Br
Cl
3d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.708
7.591
7.572
7.554
7.427
7.408
7.389
7.304
7.285
7.260
3.468
3.460
3.446
3.434
3.427
3.415
3.404
3.390
2.997
2.985
2.972
2.959
2.944
2.932
2.921
2.910
2.898
2.760
2.745
2.733
2.722
2.710
2.698
0.000
O
NO2
Cl
3f
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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0.99
0.96
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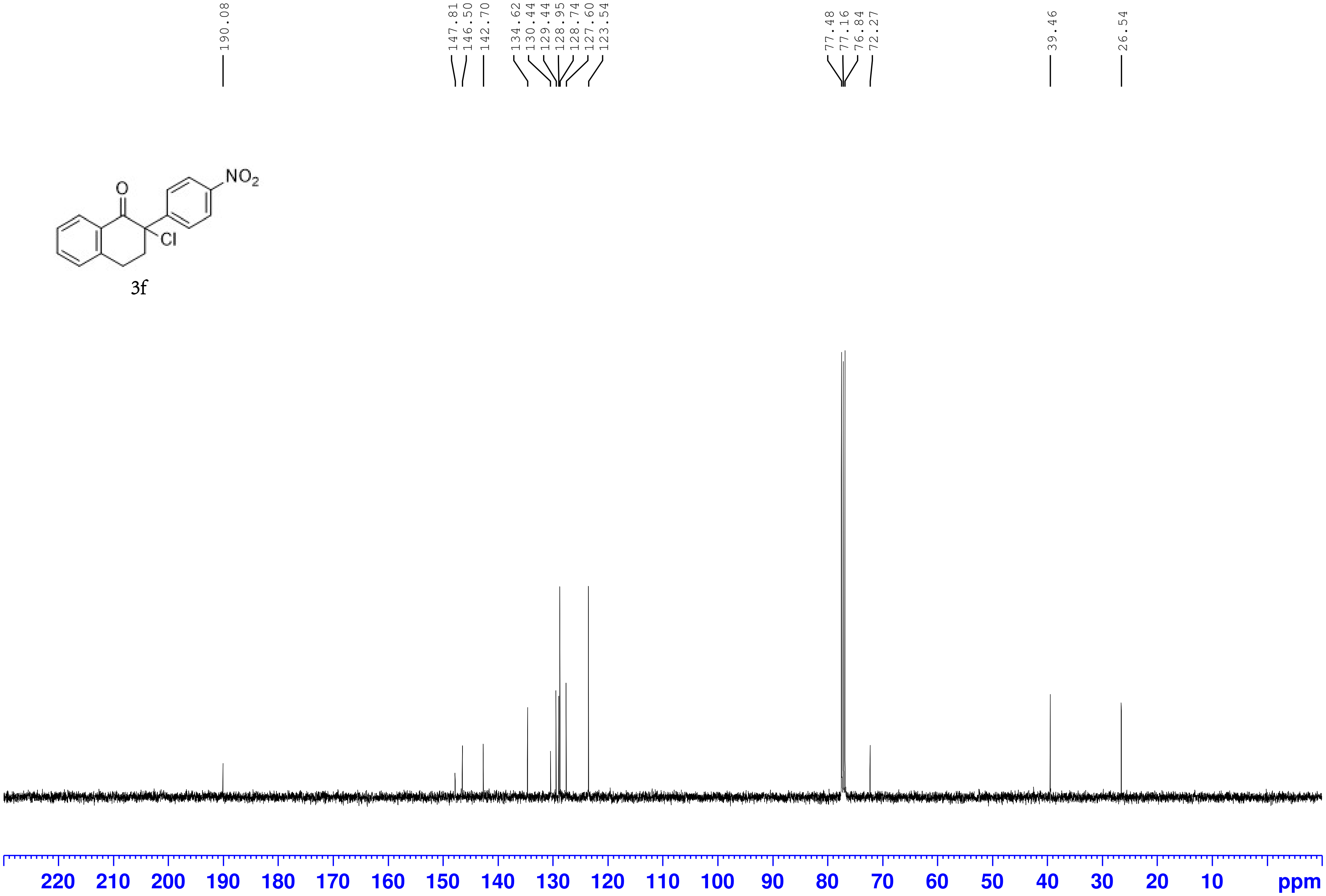
1.99
0.98


3f
190.08
147.81
146.50
142.70
134.62
130.44
129.44
128.95
128.74
127.60
123.54
77.48
77.16
76.84
72.27
39.46
26.54
O
NO2
Cl
220
210
200
190
180
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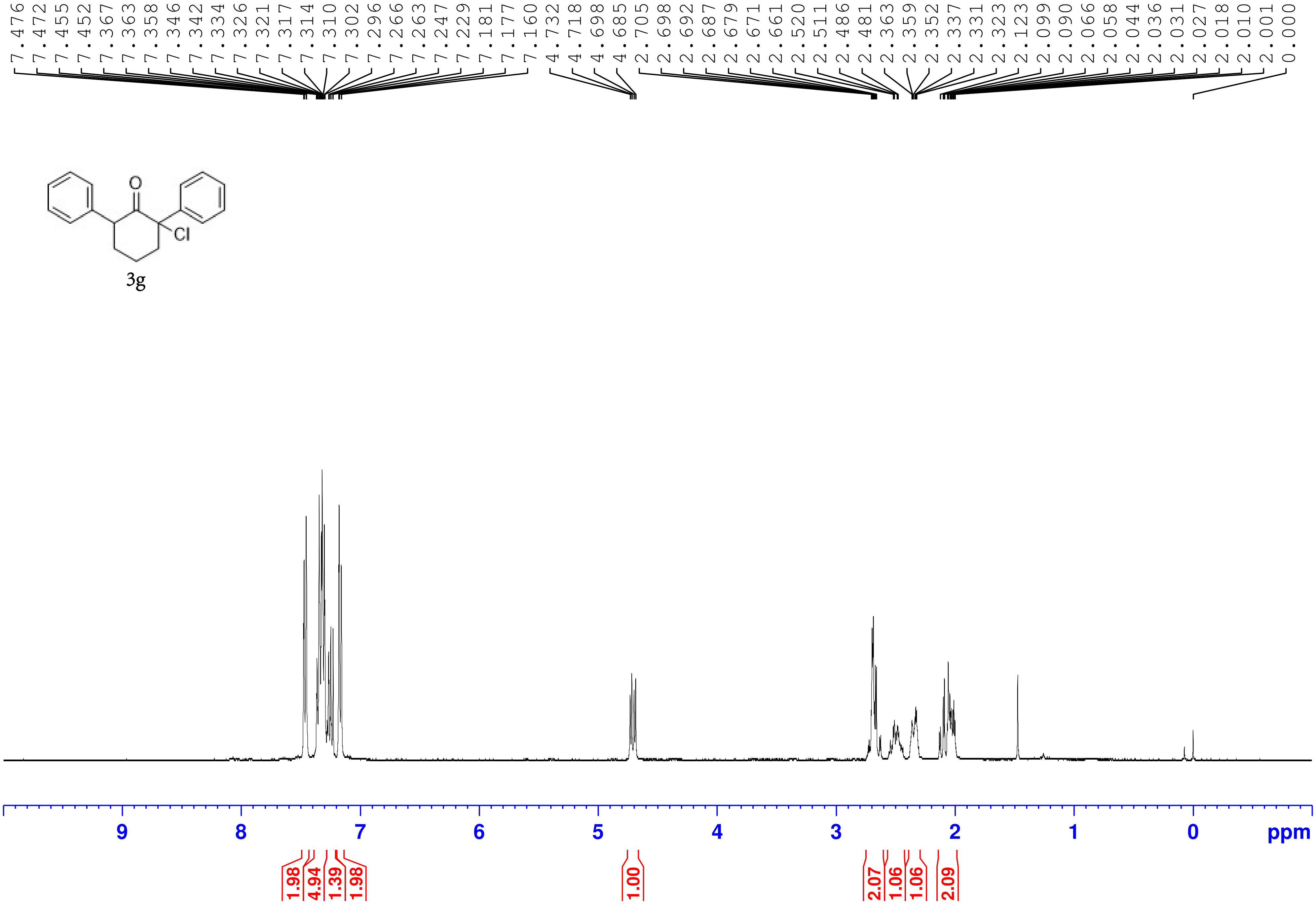
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.321
7.317
7.314
7.310
7.302
7.296
7.266
7.263
7.247
7.229
7.181
7.177
7.160
4.732
4.718
4.698
4.685
2.705
2.698
2.692
2.687
2.679
2.671
2.661
2.520
2.511
2.486
2.481
2.363
2.359
2.352
2.337
2.331
2.323
2.123
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2.090
2.066
2.058
2.044
2.036
2.031
2.027
2.018
2.010
2.001
0.000
O
Cl
3g
9
8
7
6
5
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ppm
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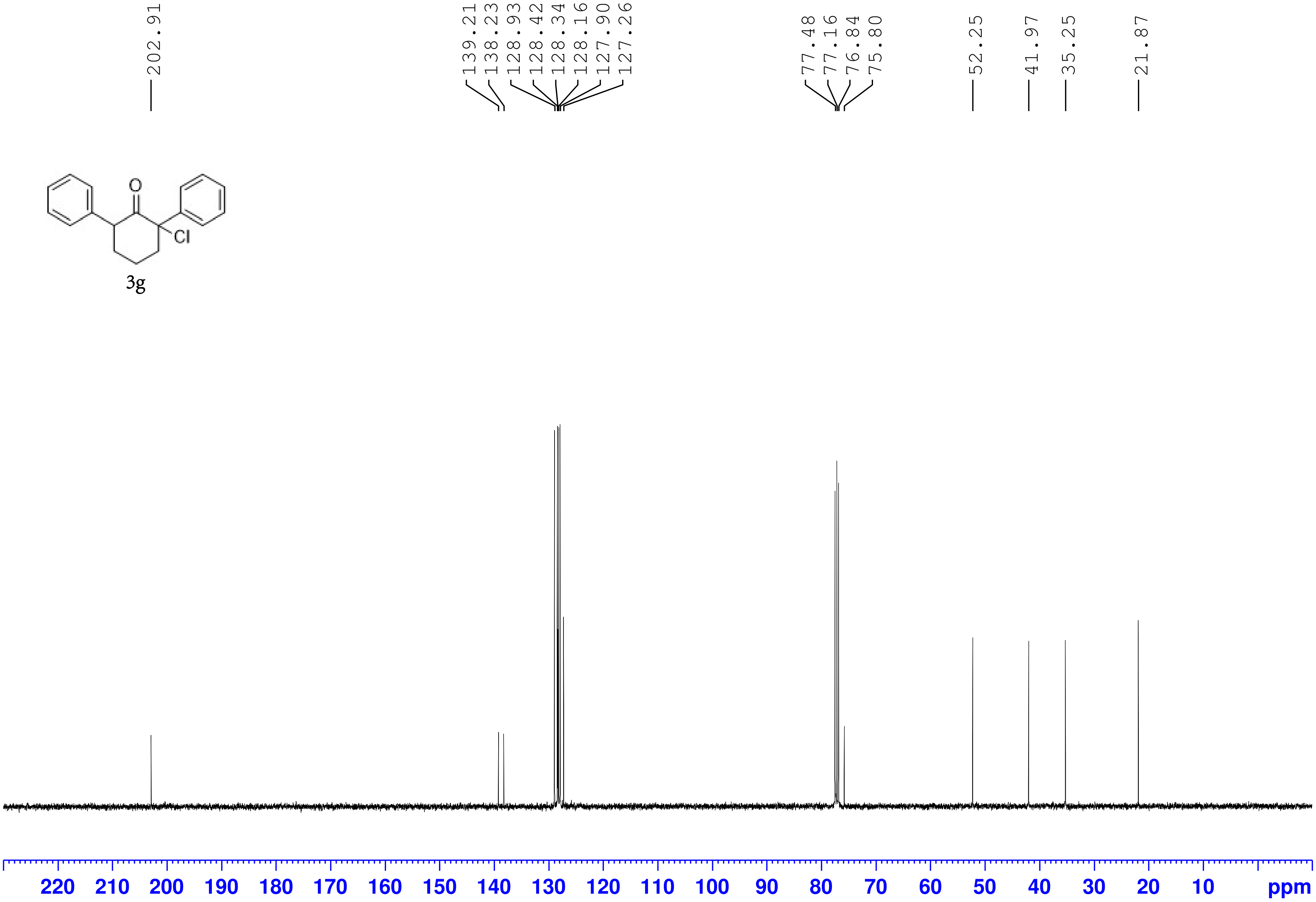
2.07
1.06
1.06
2.09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128.34
128.16
127.90
127.26
77.48
77.16
76.84
75.80
52.25
41.97
35.25
21.87
O
Cl
3g
220
210
200
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150
140
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120
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70
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40
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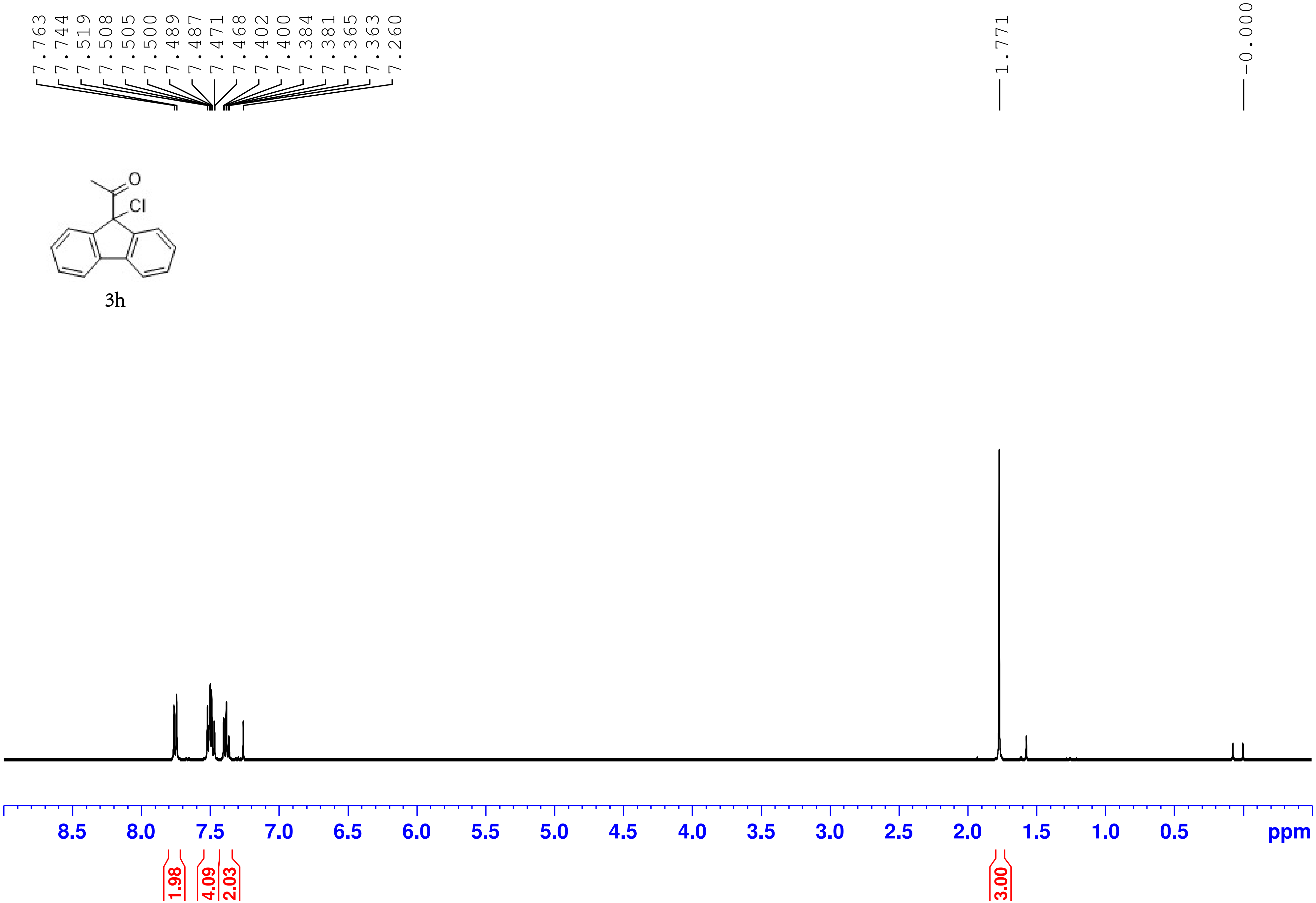
10
ppm



3h

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7.489
7.487
7.471
7.468
7.402
7.400
7.384
7.381
7.365
7.363
7.260
1.771
-0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
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ppm
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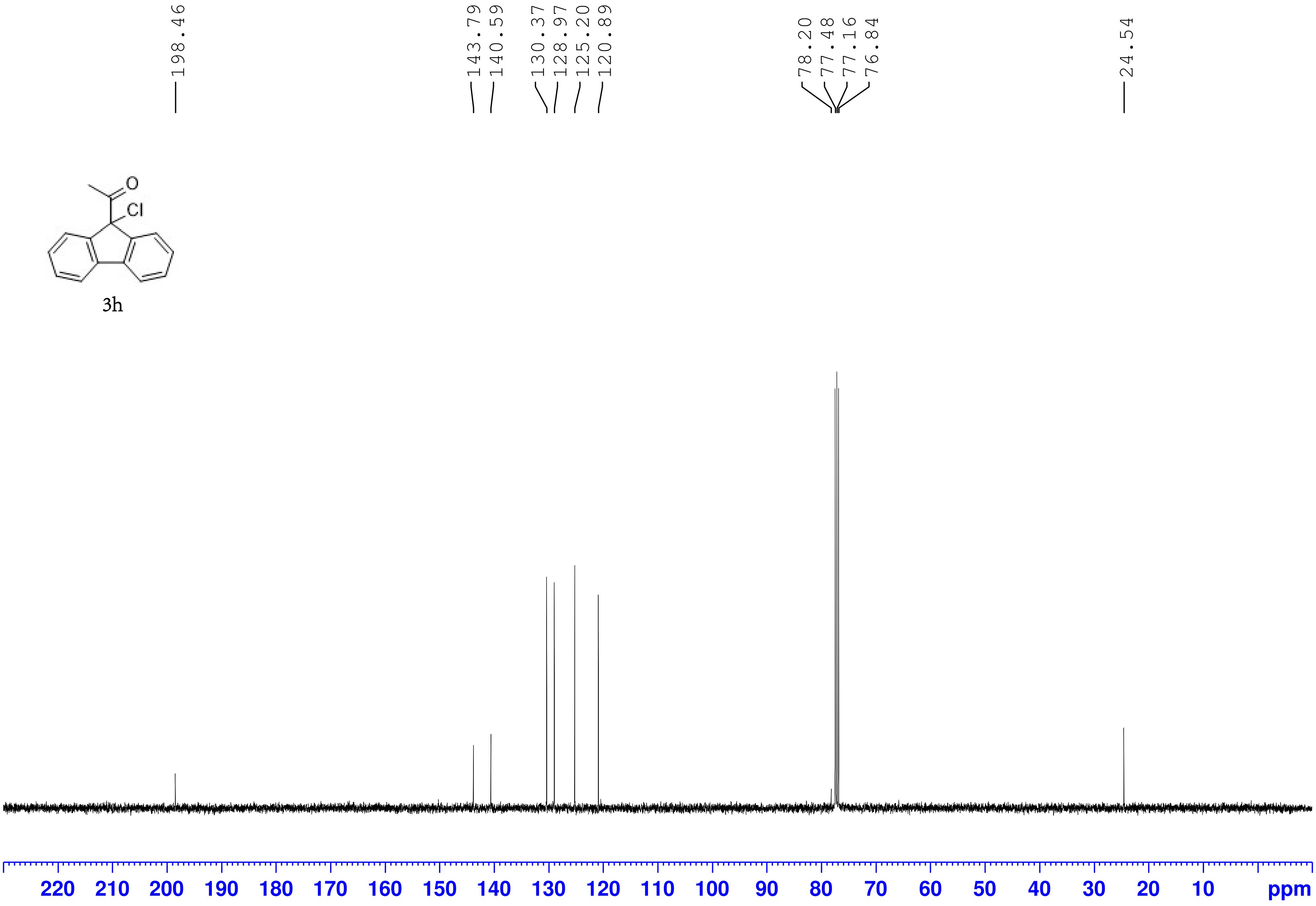
2.03
3.00



3h

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130.37
128.97
125.20
120.89
78.20
77.48
77.16
76.84
24.54
O
Cl
220
210
200
190
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170
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150
140
130
120
110
100
90
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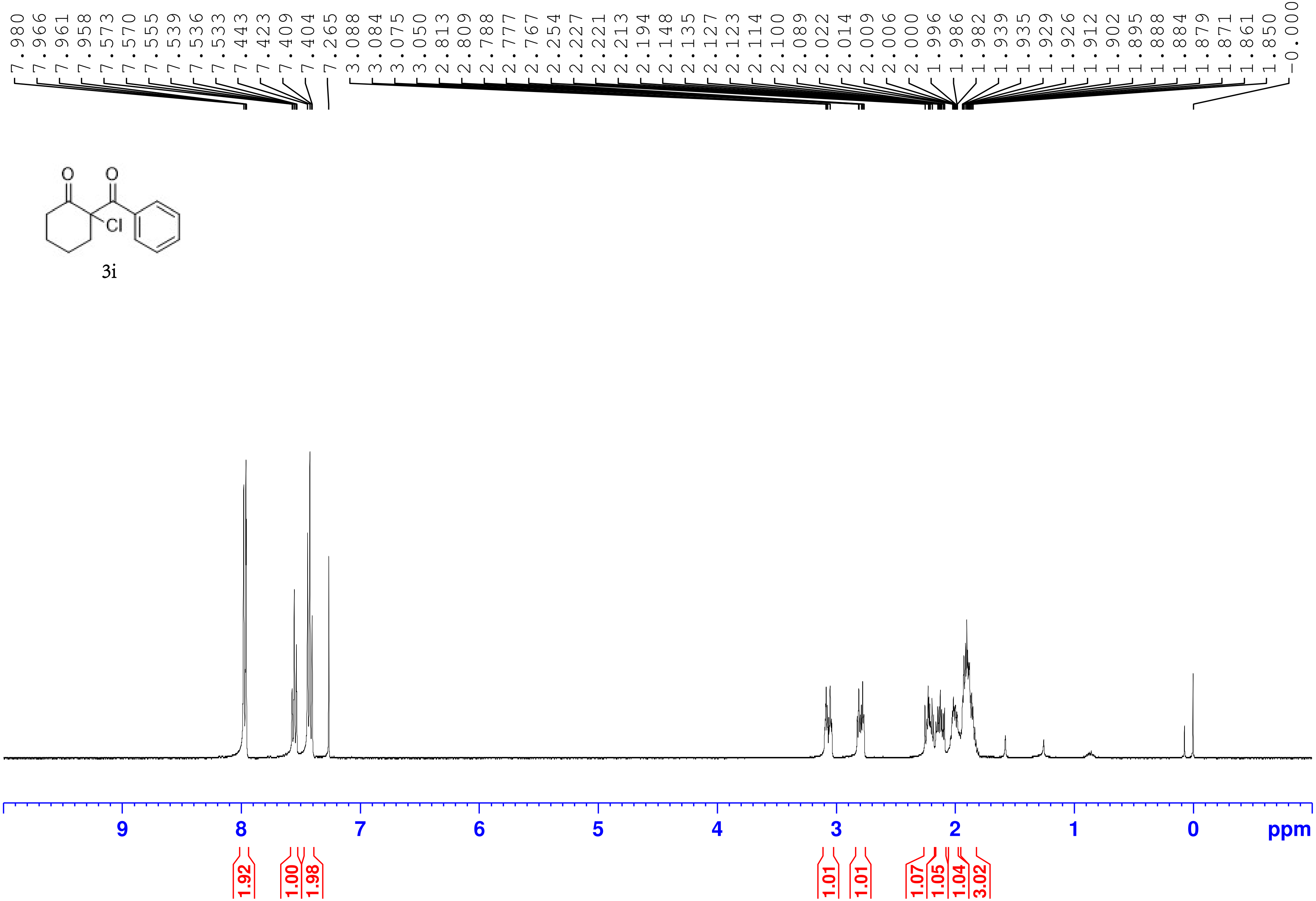
50
40
30
20
10
ppm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7.423
7.409
7.404
7.265
3.088
3.084
3.075
3.050
2.813
2.809
2.788
2.777
2.767
2.254
2.227
2.221
2.213
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2.127
2.123
2.114
2.100
2.089
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2.014
2.009
2.006
2.000
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1.986
1.982
1.939
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1.929
1.926
1.912
1.902
1.895
1.888
1.884
1.879
1.871
1.861
1.850
-0.000
O
O
Cl
9
8
7
6
5
4
3
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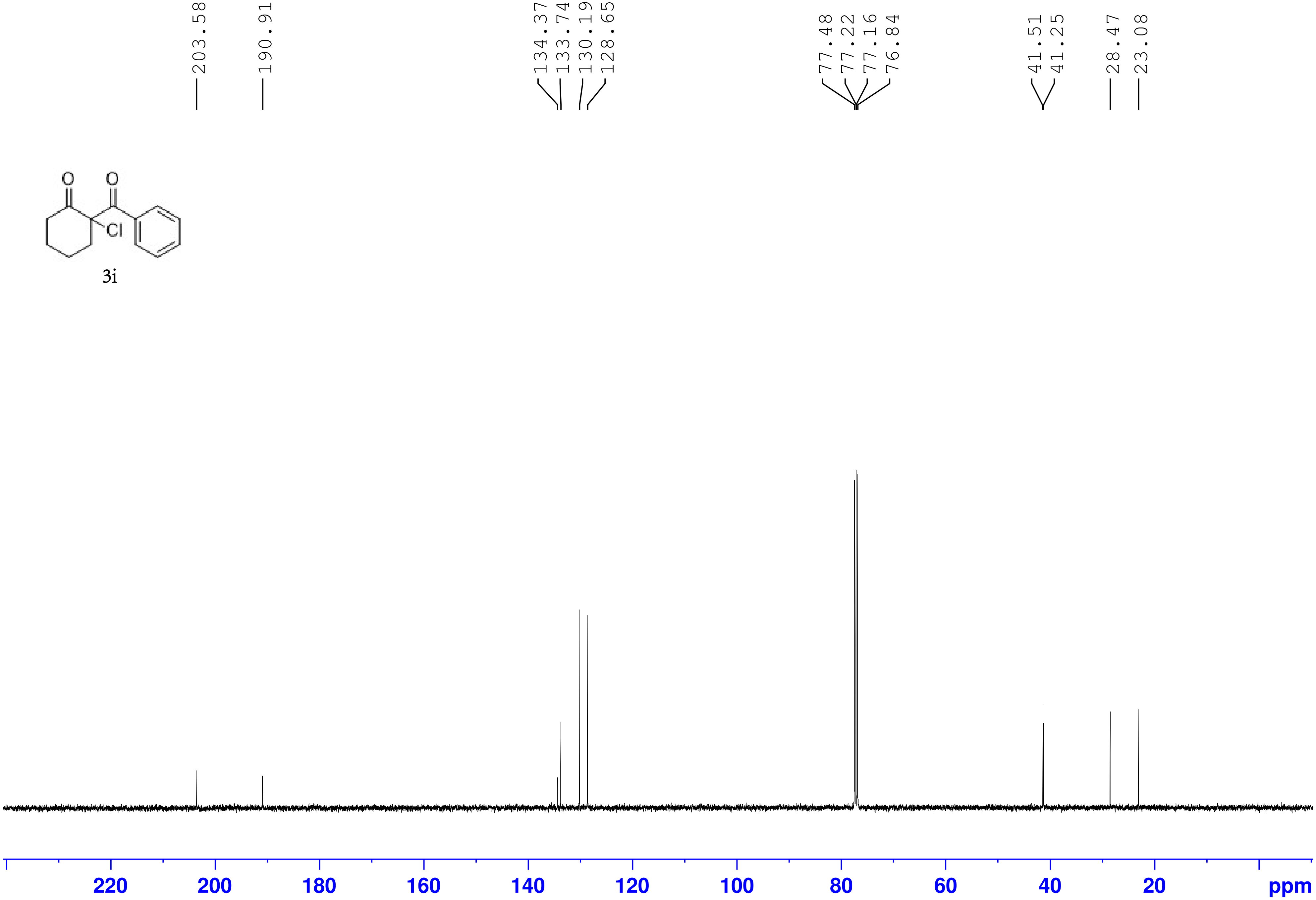
1.01
1.07
1.05
1.04
3.02

3i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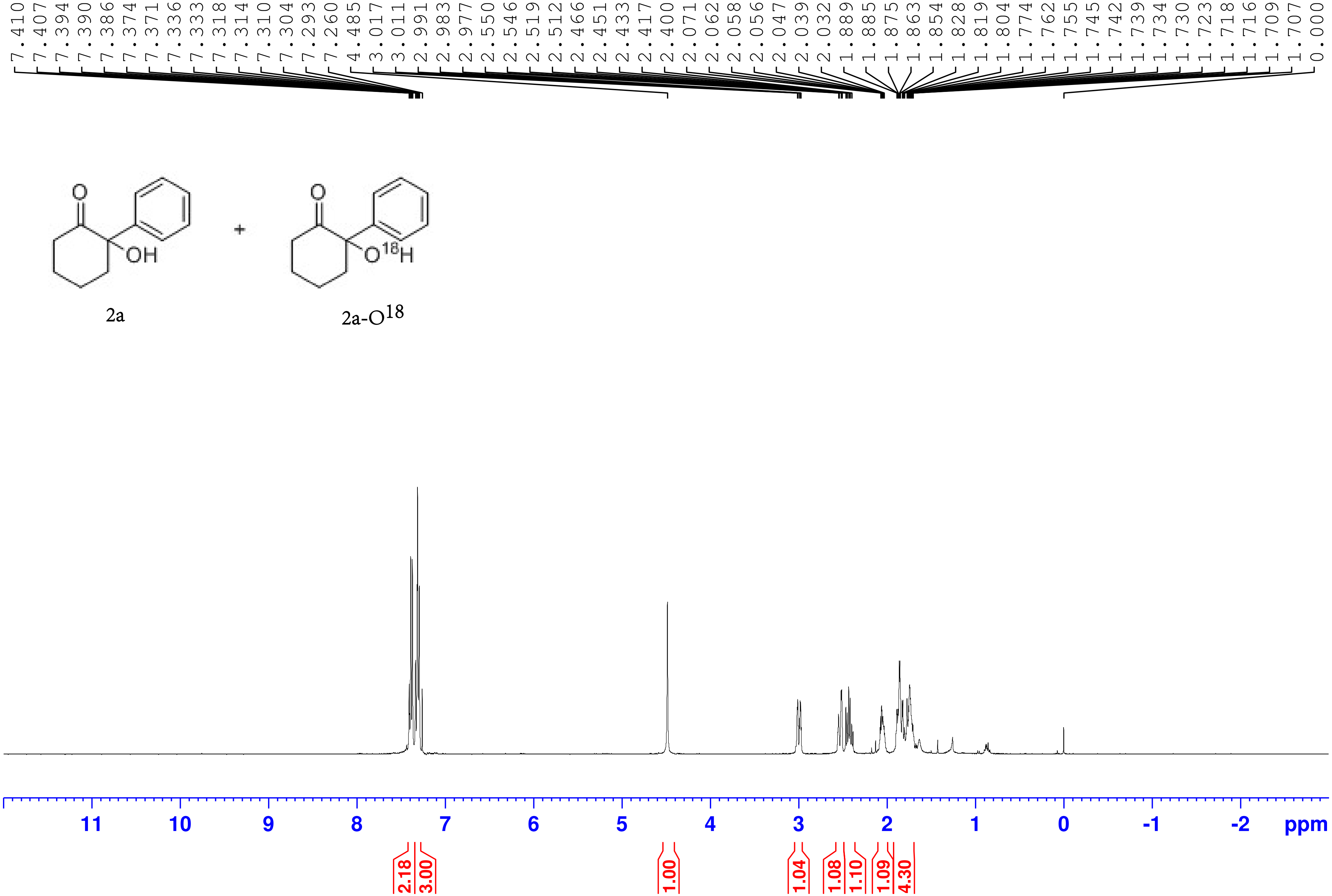
77.22
77.16
76.84
41.51
41.25
28.47
23.08
O
O
Cl
3i
220
200
180
160
140
120
100
80
60
40
20
ppm


7.410
7.407
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7.390
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7.336
7.333
7.318
7.314
7.310
7.304
7.293
7.260
4.485
3.017
3.011
2.991
2.983
2.977
2.550
2.546
2.519
2.512
2.466
2.451
2.433
2.417
2.400
2.071
2.062
2.058
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2.047
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1.804
1.774
1.762
1.755
1.745
1.742
1.739
1.734
1.730
1.723
1.718
1.716
1.709
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0.000
O
OH
2a
+
O
O18H
2a-O18
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
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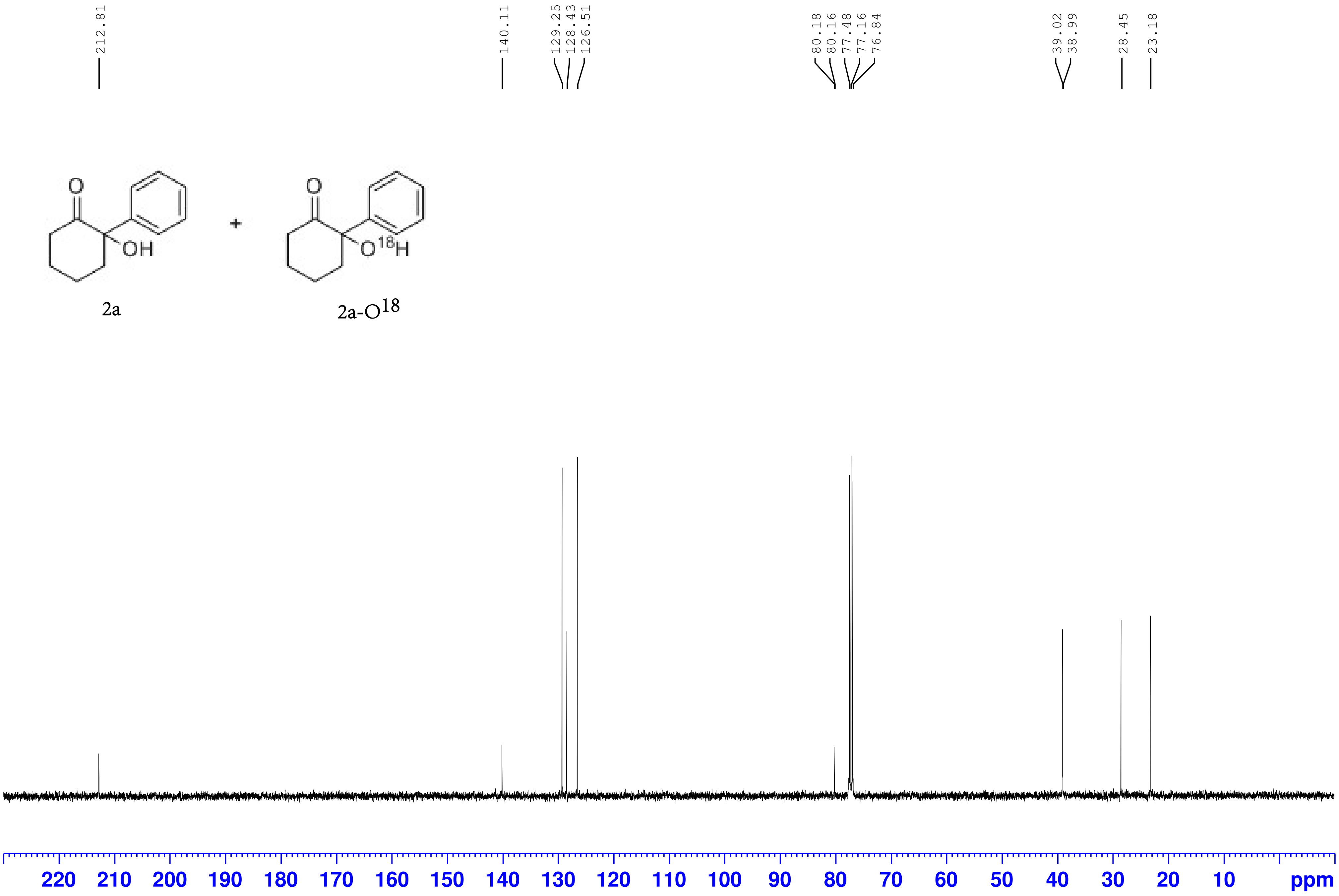
3.00
1.00
1.04
1.08
1.10
1.09
4.30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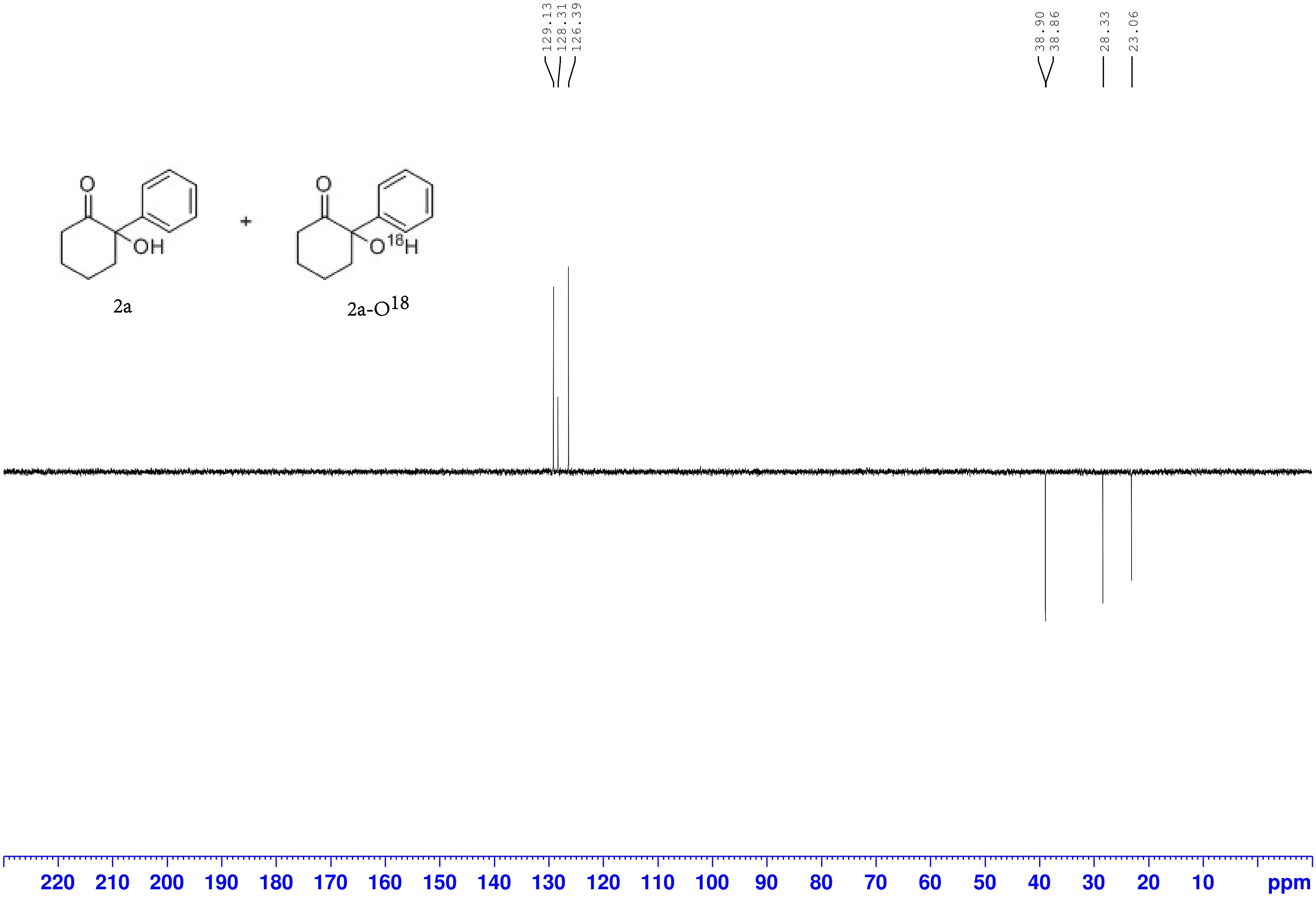
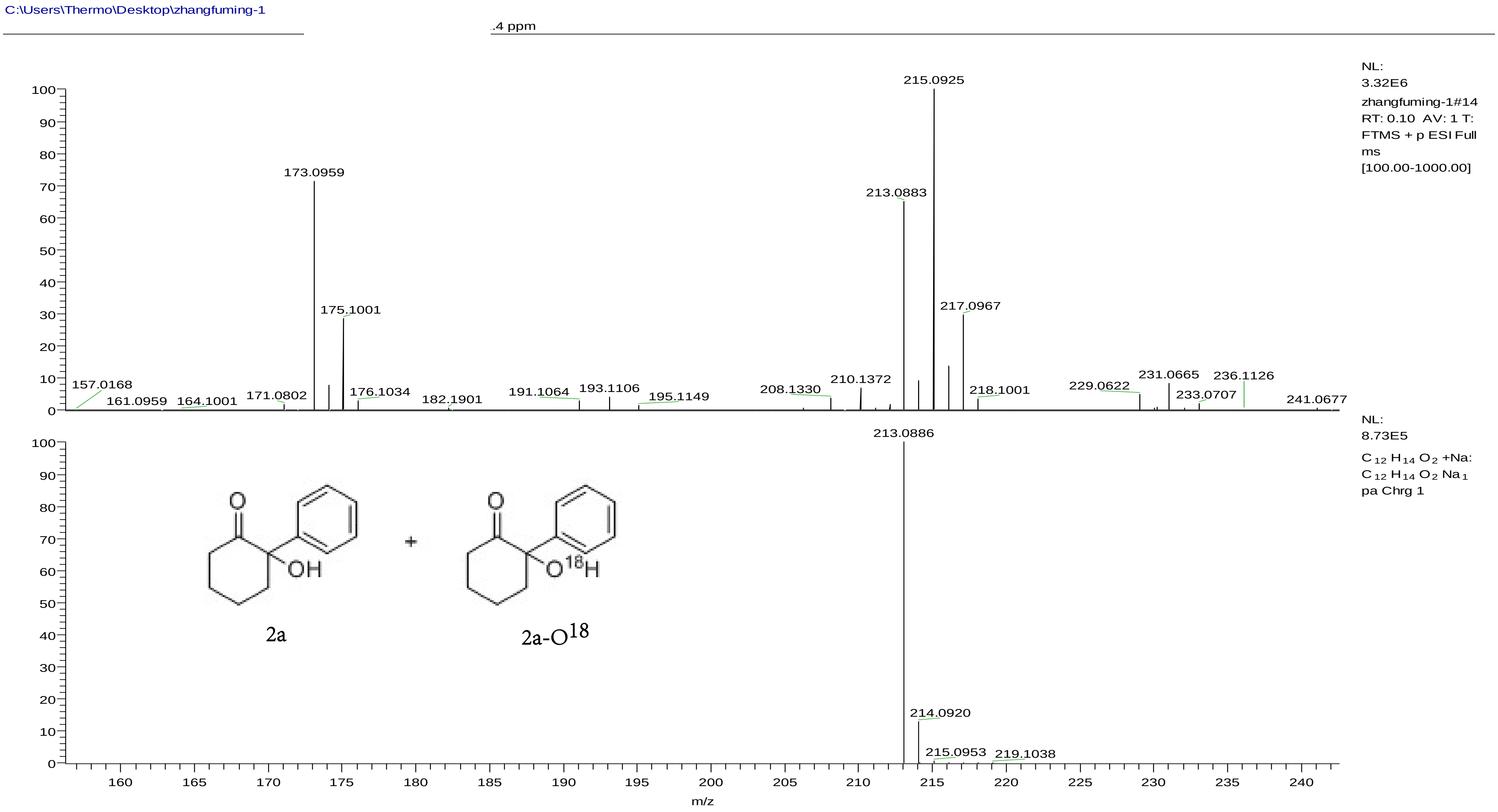
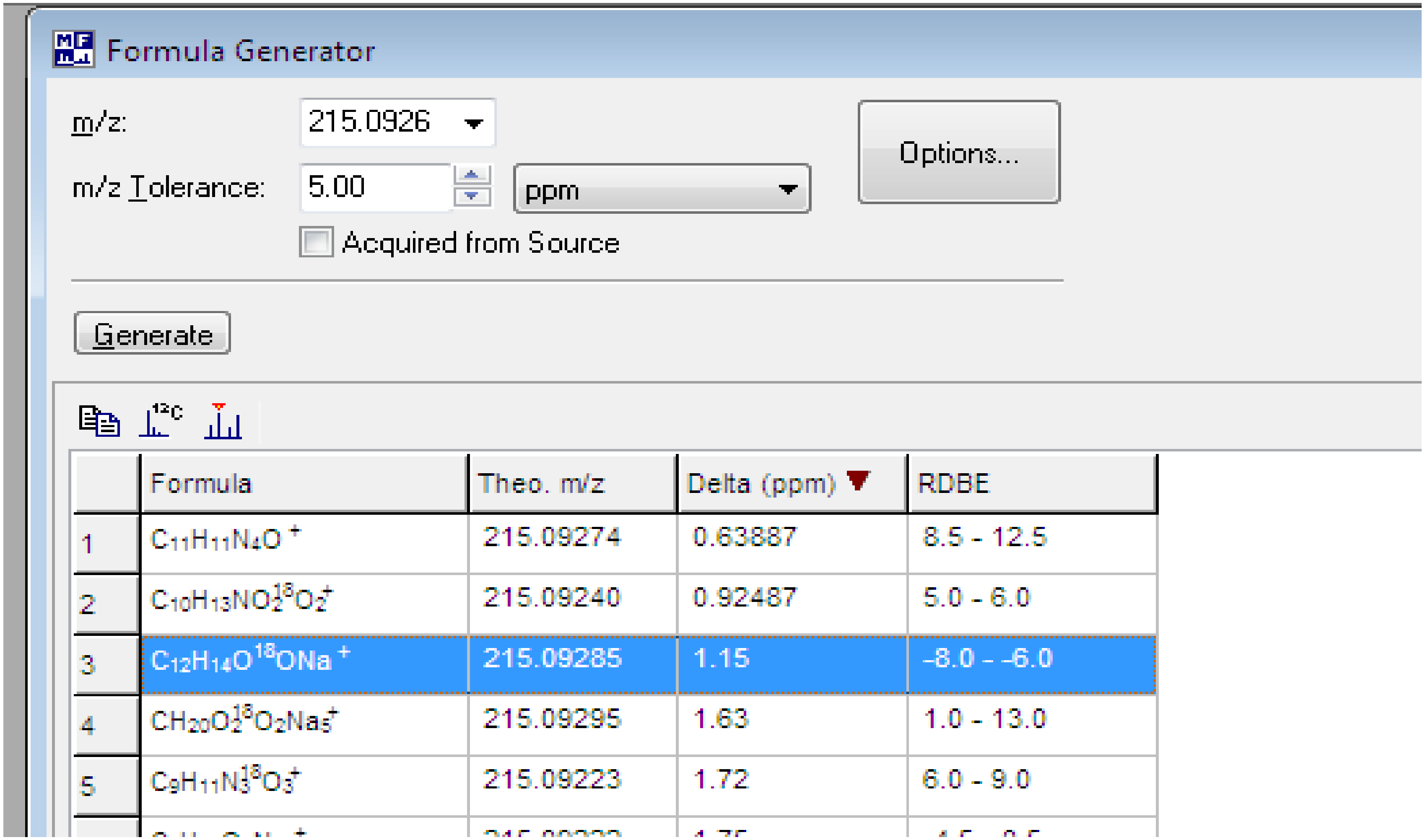
128.43
126.51
80.18
80.16
77.48
77.16
76.84
39.02
38.99
28.45
23.18
O
OH
+
O
$O^{18}H$
2a
2a-O^{18}
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


129.13
128.31
126.39
38.90
38.86
28.33
23.06
O
OH
+
O
$O^{18}H$
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

2a

2a-O^{18}


C:\Users\Thermo\Desktop\zhangfuming-1
.4 ppm
NL:
3.32E6
zhangfuming-1#14
RT: 0.10 AV: 1 T:
FTMS + p ESI Full
ms
[100.00-1000.00]
215.0925
173.0959
213.0883
175.1001
217.0967
157.0168
161.0959
164.1001
171.0802
176.1034
182.1901
191.1064
193.1106
195.1149
208.1330
210.1372
218.1001
229.0622
231.0665
233.0707
236.1126
241.0677
NL:
8.73E5
C 12 H 14 O 2 +Na:
C 12 H 14 O 2 Na 1
pa Chrg 1
213.0886
214.0920
215.0953
219.1038
0
10
20
30
40
50
60
70
80
90
100
160
165
170
175
180
185
190
195
200
205
210
215
220
225
230
235
240
m/z
O
OH
O
O18H
+
2a
2a-O18



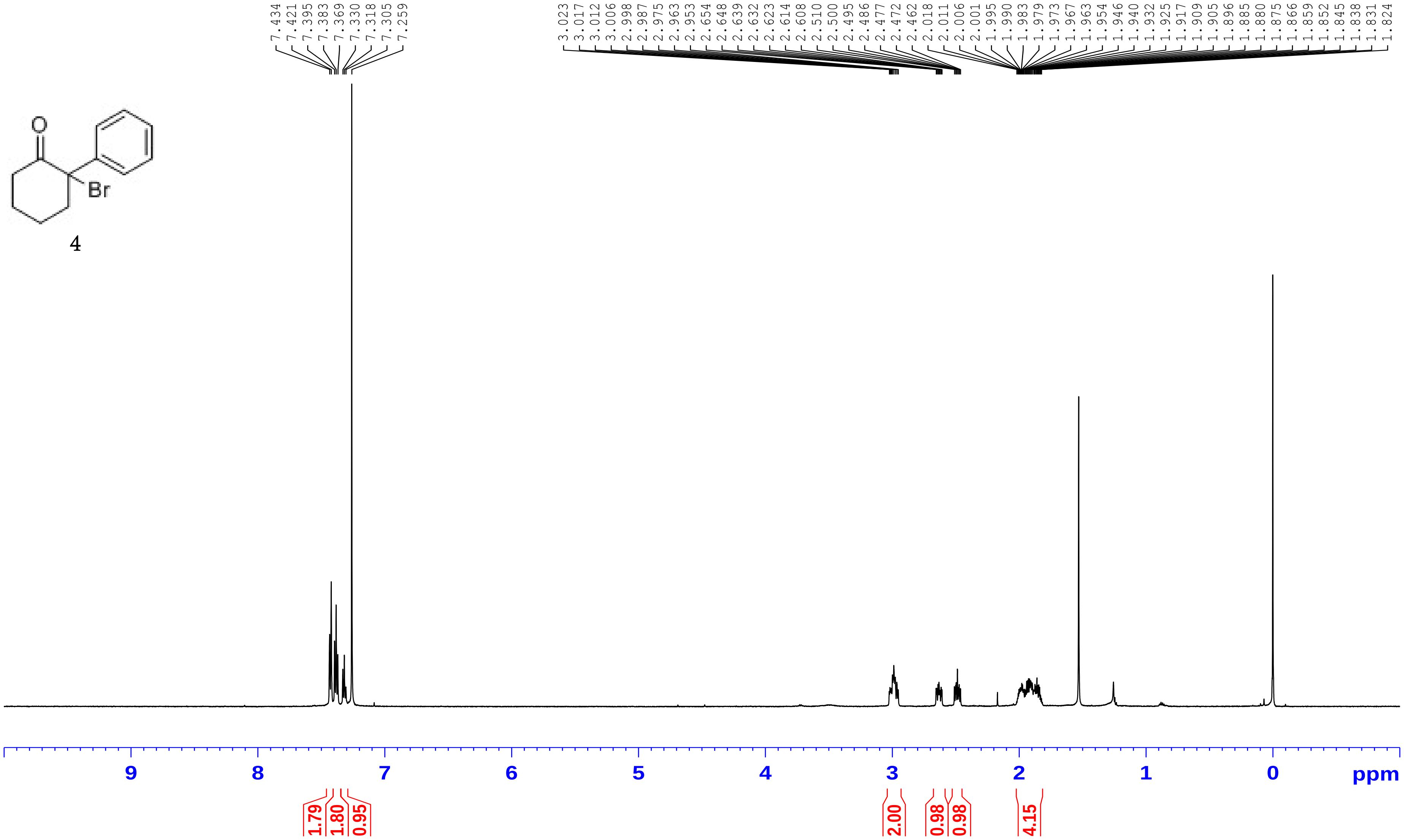
m/z: 215.0926

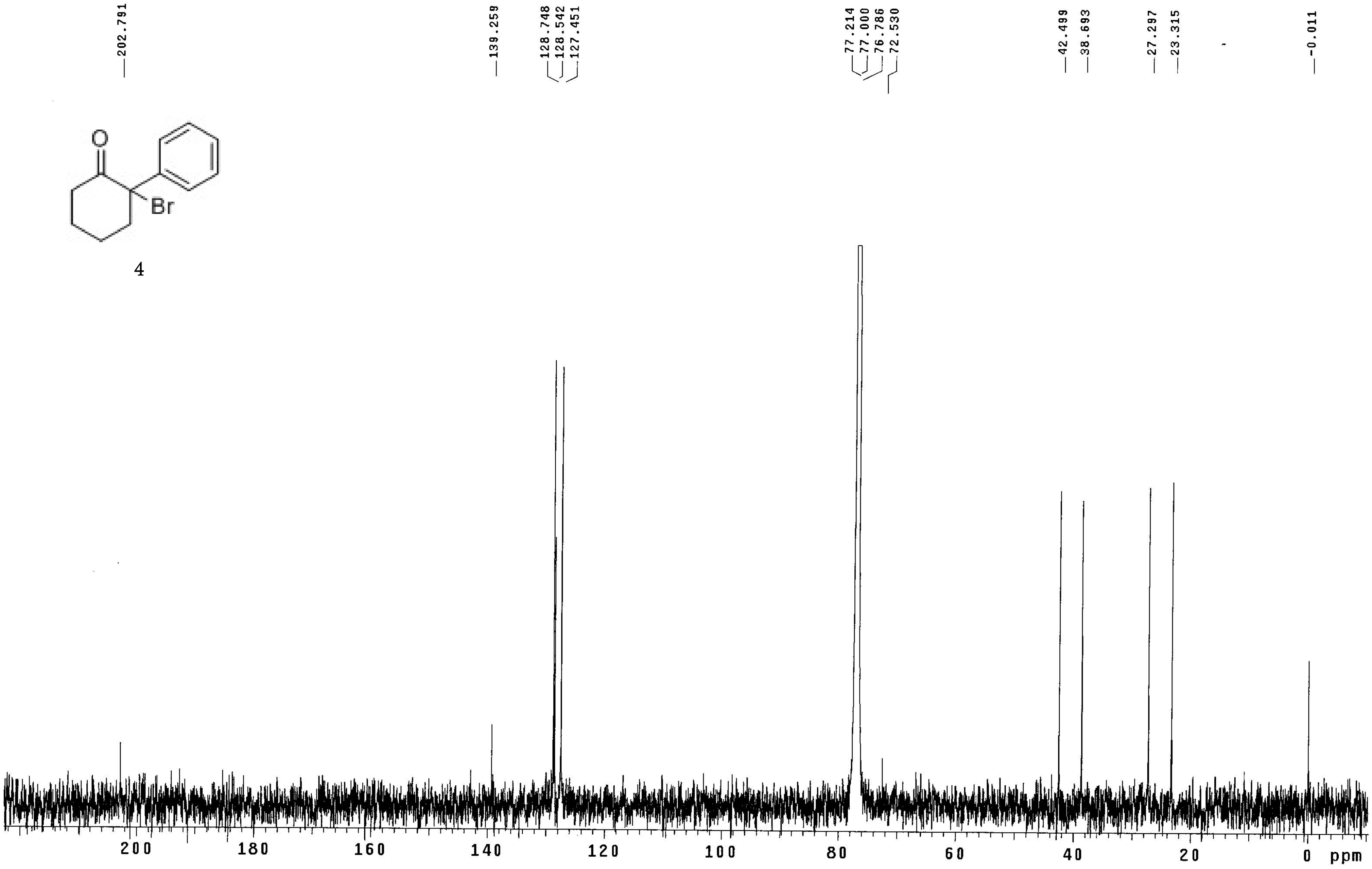
m/z Tolerance: 5.00 ppm

☐ Acquired from Source

	Formula	Theo. m/z	Delta (ppm)	RDBE
1	$C_{11}H_{11}N_4O^+$	215.09274	0.63887	8.5 - 12.5
2	$C_{10}H_{13}NO_2{}^{18}O_2^+$	215.09240	0.92487	5.0 - 6.0
3	$C_{12}H_{14}O^{18}ONa^+$	215.09285	1.15	-8.0 - -6.0
4	$CH_{20}O_2{}^{18}O_2Na_5^+$	215.09295	1.63	1.0 - 13.0
5	$C_9H_{11}N_3{}^{18}O_3^+$	215.09223	1.72	6.0 - 9.0

4


7.434
7.421
7.395
7.383
7.369
7.330
7.318
7.305
7.259
3.023
3.017
3.012
3.006
2.998
2.987
2.975
2.963
2.953
2.654
2.648
2.639
2.632
2.623
2.614
2.608
2.510
2.500
2.495
2.486
2.477
2.472
2.462
2.018
2.011
2.006
2.001
1.995
1.990
1.983
1.979
1.973
1.967
1.963
1.954
1.946
1.940
1.932
1.925
1.917
1.909
1.905
1.896
1.885
1.880
1.875
1.866
1.859
1.852
1.845
1.838
1.831
1.824
9
8
7
6
5
4
3
2
1
0
ppm
1.79
1.80
0.95
2.00
0.98
0.98
4.15


202.791
139.259
128.748
128.542
127.451
77.214
77.000
76.786
72.530
42.499
38.693
27.297
23.315
-0.011
O
Br
4
200
180
160
140
120
100
80
60
40
20
0
ppm