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Supporting Information for

Cu-mediated one-pot Michael addition/α-arylation strategy using diaryliodonium salt: Direct and efficient approach to α-aryl-β-substituted cyclic ketone scaffolds

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1. General Information

Solvents: All anhydrous solvents were dried using standard techniques and freshly distilled prior to use. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium; dichloromethane (DCM) from calcium hydride. *N*,*N*-dimethylformamide (DMF) was purchased in anhydrous form.

Reagents: All reagents obtained from commercial sources were of analytical grade and were used as received without further purification, unless otherwise noted.

Chromatography: Thin layer chromatography (TLC) was carried out on silica gel 60 F254 precoated glass plates. Visualization was detected by irradiation with UV light (254 nm), or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Flash chromatography was carried out on 200–300 mesh silica gel, eluting with a mixture of petroleum ether (b.p. 60–90 ℃) and ethyl acetate.

Reactions: All reactions were performed in oven-dried glassware under an atmosphere of argon unless otherwise stated. All reactions under standard conditions were monitored by TLC. All yields reported were averages of at least two experimental runs.

NMR Spectroscope: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer or a Varian Mercury Plus 300BB spectrometer. Chemical shifts (δ) were given in parts per million (ppm), and referenced relative to residual solvent $CHCl_3$ (7.26 ppm) in $CDCl_3$, 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 used to indicate the multiplicity of the signals: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; brs = broad singlet.

Mass Spectrometry: Electron ionization mass spectra (EI-MS) were measured on a Shimadzu GCMS-QP2010SE 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 recorded on a Bruker Daltonics APEX II 47e FTMS or a Thermo Scientfic Orbitrap Elite Mass Spectrometer by means of the ESI (electrospray ionisation) technique.

X-Ray Crystallography: The X-ray crystal structure determination was performed on

an Agilent SuperNova Eos diffractometer.

Melting Points: Melting points (m.p.) of compounds were measured on a melting point apparatus and are uncorrected.

2. Preparation of Diaryliodonium Salts

Commercially available diphenyliodonium bromide was purchased. Other diaryliodonium salts used in this investigation were prepared according to the reported procedures: diphenyliodonium triflate,[1] diphenyliodonium tetrafluoroborate,[2] diphenyliodonium hexafluorophosphate,[3] diphenyliodonium trifluoroacetate,[4] bis(4-fluorophenyl)iodonium triflate,[5] bis(4-chlorophenyl)iodonium triflate,[5] bis(4-bromophenyl)iodonium triflate,[5] di-*p*-tolyliodonium triflate,[5] bis(4-isopropylphenyl)iodonium triflate,[5] bis(4-(*tert*-butyl)phenyl)iodonium triflate,[5] bis(4-(trifluoromethyl)phenyl)iodonium triflate,[2] bis(4-methoxyphenyl)iodonium triflate,[6] di-*o*-tolyliodonium triflate,[2] di-*m*-tolyliodonium triflate,[2] bis(3-bromophenyl)iodonium triflate,[2] bis(2,4-dimethylphenyl)iodonium triflate,[5] (4-nitrophenyl)(phenyl)iodonium triflate,[5] (4-(ethoxycarbonyl)phenyl)(2,4,6-triisopropylphenyl)iodonium triflate,[7] (6-chloropyridin-3-yl)(4-methoxyphenyl)iodonium triflate.[5]

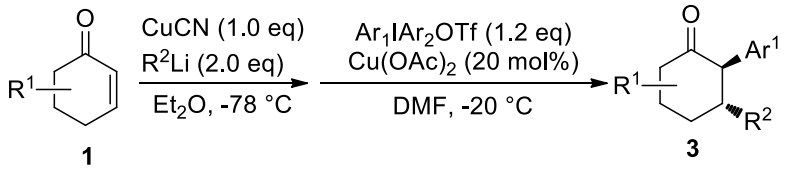
3. Preparation of Enones

Commercially available 2-cyclohexen-1-one and 4,4-dimethyl-2-cyclohexen-1-on were purified by reduced pressure distillation prior to use. Other enones used in this investigation were prepared according to the reported procedures: 6-methylcyclohex-2-en-1-one,[8] 5-methylcyclohex-2-en-1-one,[9] 5-phenylcyclohex-2-en-1-one,[9] cyclohept-2-en-1-one,[10] and 4-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-methylcyclohex-2-en-1-one.[11]

4. Experimental Details and Characterization Data

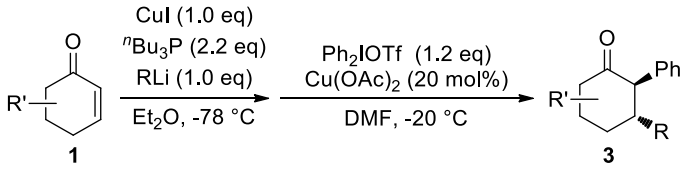
4.1 General Procedure A and General Procedure B

General Procedure A:



Under an argon atmosphere, to a stirred suspension of CuCN (18.0 mg, 0.20 mmol, 1.0 eq) in Et_2O (1.5 mL) was slowly added via syringe a solution of organolithium reagent (0.40 mmol, 2.0 eq) at –78 ℃. The mixture was stirred for approximate 30 to 60 min at –78 ℃ until a homogeneous solution was observed, and enone **1** was then added at this temperature. After the starting material disappeared, the reaction mixture was allowed to warm to –20 ℃, diluted with dry DMF (1.0 mL), and $Cu(OAc)_2$ (3.4 mg, 0.04 mmol, 20 mol%) and the appropriate diaryliodonium triflate (0.24 mmol, 1.2 eq) was sequentially added. The reaction mixture was stirred for another 30 min to 2 h at –20 ℃, and quenched with a saturated aqueous solution of NH_4Cl. The mixture was extracted with EtOAc (30 mL × 3) 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 purified by flash column chromatography to give the desired product **3**.

General Procedure B:



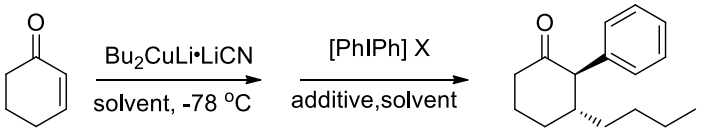
To a stirred suspension of CuI (38.1 mg, 0.2 mmol, 1.0 eq) in Et_2O (1.0 mL) was added *n*-Bu_3P (0.11 mL, 0.44 mmol, 2.2 eq) under an argon atmosphere, and stirring for approximate 5 min at room temperature resulted a colorless homogeneous solution. The resulting solution was cooled to –78 ℃, and organolithium reagent (0.2 mmol, 1.0 eq) was rapidly transferred via syringe. After 30 to 60 min, 2-cyclohexen-1-one (19.4 μL,

0.2 mmol, 1.0 eq) was added dropwise at –78 ℃. When the starting material disappeared, the reaction mixture was allowed to warm to –20 ℃, diluted with dry DMF (1.0 mL), and $Cu(OAc)_2$ (3.4 mg, 0.04 mmol, 20 mol%) and diphenyliodonium triflate (103.2 mg, 0.24 mmol, 1.2 eq) 1.2 eq) was sequentially added. The reaction mixture was stirred for another 30 min to 2 h at –20 ℃, and quenched with a saturated aqueous solution of NH_4Cl. The mixture was extracted with EtOAc (30 mL × 3) 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 purified by flash column chromatography to give the desired product **3**.

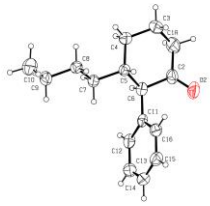
4.2 The details for the reaction conditions screen

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

Table S1 The optimization of the reaction conditions[a]



3a



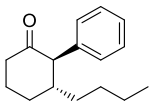
entry	reagent	equiv.	additive	solvent[b]	Temp. [c]	yield[d]
1	PhI	1.0	–	Et_2O/DMF	−78	/
2	PhOTf	1.0	–	Et_2O/DMF	−78	/
3	Ph_2IOTf	1.0	–	Et_2O/DMF	−78	21
4	Ph_2IOTf	1.0	–	Et_2O/DMF	−40	41
5	Ph_2IOTf	1.0	–	Et_2O/DMF	−30	43
6	Ph_2IOTf	1.0	–	Et_2O/DMF	−20	46
7	Ph_2IOTf	1.0	–	Et_2O/DMF	−10	35
8	Ph_2IOTf	1.0	–	Et_2O/DMF	0	33
9	Ph_2IOTf	1.0	–	Et_2O/DMF	25	28
10	Ph_2IOTf	1.0	Li_2CO_3	Et_2O/DMF	−20	19
11	Ph_2IOTf	1.0	Na_2CO_3	Et_2O/DMF	−20	18
12	Ph_2IOTf	1.0	K_2CO_3	Et_2O/DMF	−20	23
13	Ph_2IOTf	1.0	Cs_2CO_3	Et_2O/DMF	−20	23
14	Ph_2IOTf	1.0	NaH	Et_2O/DMF	−20	18
15	Ph_2IOTf	1.0	*t*-BuOK	Et_2O/DMF	−20	15
16	Ph_2IOTf	1.0	Et_3N	Et_2O/DMF	−20	18
17	Ph_2IOTf	1.0	DIPEA	Et_2O/DMF	−20	16
18	Ph_2IOTf	1.0	DBU	Et_2O/DMF	−20	16
19	Ph_2IOTf	1.0	DMAP	Et_2O/DMF	−20	17
20	Ph_2IOTf	1.0	2,6-lutidine	Et_2O/DMF	−20	16
21	Ph_2IOTf	1.0	BDMEP	Et_2O/DMF	−20	16
22	Ph_2IOTf	1.0	Imidazole	Et_2O/DMF	−20	17
23	Ph_2IOTf	1.0	DABCO	Et_2O/DMF	−20	19
24	Ph_2IOTf	1.0	LDA	Et_2O/DMF	−20	15
25	Ph_2IOTf	1.0	4Å MS	Et_2O/DMF	−20	/
26	Ph_2IOTf	0.8	–	Et_2O/DMF	−20	40
27	Ph_2IOTf	1.2	–	Et_2O/DMF	−20	48
28	Ph_2IOTf	1.5	–	Et_2O/DMF	−20	48
29	Ph_2IOTf	2.0	–	Et_2O/DMF	−20	48
30	Ph_2IOTf	1.2	CuCl	Et_2O/DMF	−20	51
31	Ph_2IOTf	1.2	CuBr	Et_2O/DMF	−20	38
32	Ph_2IOTf	1.2	CuBr • SMe_2	Et_2O/DMF	−20	50
33	Ph_2IOTf	1.2	CuI	Et_2O/DMF	−20	59
34	Ph_2IOTf	1.2	CuTc	Et_2O/DMF	−20	49
35	Ph_2IOTf	1.2	CuOAc	Et_2O/DMF	−20	61
36	Ph_2IOTf	1.2	$Cu(MeCN)_4BF_4$	Et_2O/DMF	−20	40
37	Ph_2IOTf	1.2	$Cu(MeCN)_4PF_6$	Et_2O/DMF	−20	50
38	Ph_2IOTf	1.2	CuF_2	Et_2O/DMF	−20	42
39	Ph_2IOTf	1.2	$CuCl_2$	Et_2O/DMF	−20	44
40	Ph_2IOTf	1.2	$CuBr_2$	Et_2O/DMF	−20	38
41	Ph_2IOTf	1.2	$Cu(acac)_2$	Et_2O/DMF	−20	49
42	Ph_2IOTf	1.2	$Cu(tf\text{-}acac)_2$	Et_2O/DMF	−20	48

43	Ph_2IOTf	1.2	$Cu(OTf)_2$	Et_2O/DMF	−20	54
44	Ph_2IOTf	1.2	$Cu(OAc)_2$	Et_2O/DMF	−20	68
45	Ph_2IOTf	1.2	$Pd(OAc)_2$	Et_2O/DMF	−20	31
46	Ph_2IOTf	1.2	$Cu(OAc)_2$	Et_2O/Et_2O	−20	6
47	Ph_2IOTf	1.2	$Cu(OAc)_2$	Et_2O/DCM	−20	23
48	Ph_2IOTf	1.2	$Cu(OAc)_2$	Et_2O/DME	−20	26
49	Ph_2IOTf	1.2	$Cu(OAc)_2$	Et_2O/PhMe	−20	24
50	Ph_2IOTf	1.2	$Cu(OAc)_2$	Et_2O/NMP	−20	47
51	Ph_2IOTf	1.2	$Cu(OAc)_2$	THF/DMF	−20	34
52	Ph_2IBF_4	1.2	$Cu(OAc)_2$	Et_2O/DMF	−20	66
53	Ph_2IPF_6	1.2	$Cu(OAc)_2$	Et_2O/DMF	−20	63
54	Ph_2ITFA	1.2	$Cu(OAc)_2$	Et_2O/DMF	−20	59
55	Ph_2IBr	1.2	$Cu(OAc)_2$	Et_2O/DMF	−20	21

a) Reaction was performed using enone (0.2 mmol) and Gilman reagent (0.2 mmol) in 1.5 mL solvent at -78 ℃, then electrophile was added to reaction mixture at the noted temperature; b) The Michael addition was performed in the former, and the arylation in the latter; c) The arylation reaction temperature; d) isolated yield of product **3a**.

4.3 Scope of Diaryliodonium Salts

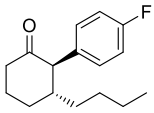
trans-3-Butyl-2-phenylcyclohexanone (**3a**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a white solid (31.3 mg, 0.136 mmol, 68%). Slow evaporation of an ether solution gave crystals of **3a** suitable for X-ray analysis.

m.p. = 49-51 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2 H), 7.27-7.23 (m, 1 H), 7.07-7.05 (m, 2 H), 3.28 (d, J = 11.6 Hz, 1 H), 2.55-2.50 (m, 1 H), 2.47-2.42 (m, 1 H), 2.18-2.11 (m, 2 H), 2.04-1.99 (m, 1 H), 1.80-1.76 (m, 1 H), 1.53-1.50 (m, 1 H), 1.30-1.27 (m, 1 H), 1.26-1.04 (m, 5 H), 0.77 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.5, 137.6, 129.5, 128.4, 126.9, 63.8, 45.0, 42.1, 34.3, 30.9, 28.6, 26.0, 22.7, 14.1; **EI-MS** *m/z* 57 (40), 69 (39), 91 (100), 97 (40), 105 (35), 117 (71), 129 (67), 173 (21), 230 (42); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{23}O$ [M+H$^+$] 231.1743, found 231.1746.

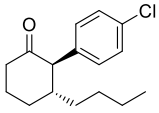
trans-3-Butyl-2-(4-fluorophenyl)cyclohexan-1-one (**3b**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(4-fluorophenyl)iodonium triflate (111.9 mg, 0.24 mmol), providing the title compound as an amorphous solid (29.3 mg, 0.118 mmol, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2 H), 7.01 (s, 2 H), 3.28 (d, J = 12 Hz, 1 H), 2.55-2.50 (m, 1 H), 2.43 (td, J = 13.2, 5.6 Hz, 1 H), 2.20-2.10 (m, 2 H), 1.98-1.91 (m, 1 H), 1.80-1.72 (m, 1 H), 1.60-1.47 (m, 1 H), 1.31-1.25 (m, 1 H), 1.20-1.05 (m, 5 H), 0.77 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.2, 161.9 (d, J = 243 Hz), 133.3 (d, J = 3.0 Hz), 130.9 (d, J = 8.0 Hz), 115.2 (d, J = 21.0 Hz), 63.1, 45.4, 42.1, 34.3, 30.9, 28.5, 26.1, 22.7, 14.0; **EI-MS** *m/z* 57 (80), 71 (61), 97 (100), 123 (59), 153 (90), 169 (8), 191 (10), 248 (11); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{22}OF$ [M+H$^+$] 249.1649, found 249.1653.

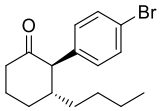
trans-3-Butyl-2-(4-chlorophenyl)cyclohexan-1-one (**3c**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(4-chlorophenyl)iodonium triflate (119.8 mg, 0.24 mmol), providing the title compound as an amorphous solid (26.0 mg, 0.098 mmol, 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2 H), 7.01-6.97 (m, 2 H), 3.27 (d, J = 11.6 Hz, 1 H), 2.54-2.50 (m, 1 H), 2.47-2.42 (m, 1 H), 2.20-2.11 (m, 2 H), 1.98-1.94 (m, 1 H), 1.79-1.74 (m, 1 H), 1.56-1.49 (m, 1 H), 1.29-1.26 (m, 2 H), 1.18-1.03 (m, 4 H), 0.78 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.0, 136.1, 132.7, 130.8, 128.6, 63.2, 45.2, 42.1, 34.3, 30.9, 28.5, 26.1, 22.8, 14.1. **EI-MS** *m/z* 57 (89), 111 (44), 125 (36), 139 (100), 155 (22), 167 (16), 207 (17), 264 (16); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{21}OClNa$ [M+Na$^+$] 287.1173, found 287.1174.

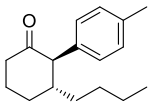
trans-2-(4-Bromophenyl)-3-butylcyclohexan-1-one (**3d**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(4-bromophenyl)iodonium triflate (141.1 mg, 0.24 mmol), providing the title compound as an amorphous solid (39.6 mg, 0.128 mmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2 H), 6.95-6.92 (m, 2 H), 3.26 (d, J = 11.6 Hz, 1 H), 2.55-2.50 (m, 1 H), 2.49-2.38 (m, 1 H), 2.19-2.10 (m, 2 H), 1.98-1.92 (m,1 H), 1.81-1.71 (m, 1 H), 1.59-1.49 (m, 1 H), 1.31-1.20 (m, 1 H), 1.18-1.02 (m, 5 H), 0.78 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.9, 136.7, 131.5, 131.2, 120.9, 63.3, 45.2, 42.1, 34.3, 30.9, 28.5, 26.1, 22.7, 14.1. **EI-MS** *m/z* 57 (15), 116 (100), 129 (47), 139 (27), 169 (39), 171 (34), 182 (59), 184 (57), 211 (28), 251 (12), 253 (12), 308 (54), 310 (52); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{22}BrO$ [M+H$^+$] 309.0849, found 309.0847.

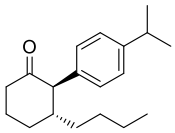
trans-3-Butyl-2-(*p*-tolyl)cyclohexan-1-one (**3e**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and di-*p*-tolyliodonium triflate (110.0 mg, 0.24 mmol), providing the title compound as an amorphous solid (29.5 mg, 0.121 mmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 8.0 Hz, 2 H), 6.94 (d, J = 8.0 Hz, 2 H), 3.25 (d, J = 11.6 Hz, 1 H), 2.54-2.49 (m, 1 H), 2.45-2.37 (m, 1 H), 2.33 (s, 3 H), 2.17-2.10 (m, 2 H), 2.02-1.98 (m, 1 H), 1.79-1.74 (m, 1 H), 1.54-1.48 (m, 1 H), 1.31-1.26 (m, 1 H), 1.24-1.04 (m, 5 H), 0.78 (t, J = 6.9 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.7, 136.3, 134.5, 129.2, 129.1, 63.4, 44.9, 42.1, 34.3, 30.8, 28.6, 26.0, 22.7, 21.3, 14.1; **EI-MS** *m/z* 57 (14), 77 (16), 91 (36), 105 (70), 118 (100), 131 (78), 143 (23), 187 (8), 244 (35); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{25}O$ [M+H$^+$] 245.1900, found 245.1890.

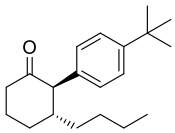
trans-3-Butyl-2-(4-isopropylphenyl)cyclohexan-1-one (**3f**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(4-isopropylphenyl)iodonium triflate (123.4 mg, 0.24 mmol), providing the title compound as an amorphous solid (29.5 mg, 0.108 mmol, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.6 Hz, 2 H), 6.97 (d, J = 7.6 Hz, 2 H), 3.25 (d, J = 11.6 Hz, 1 H), 2.94-2.84 (m, 1 H), 2.54-2.49 (m, 1 H), 2.45-2.37 (m, 1 H), 2.17-2.10 (m, 2 H), 2.04-1.96 (m, 1 H), 1.83-1.71 (m, 1 H), 1.57-1.45 (m, 2 H), 1.25 (d, J = 7.2 Hz, 6 H), 1.19-1.03 (m, 5 H), 0.77 (t, J = 6.5 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.7, 147.1, 134.8, 129.2, 126.4, 63.4, 45.0, 42.1, 34.3, 33.8, 30.8, 29.8, 28.7, 26.0, 24.10, 24.07, 22.7, 14.1; **EI-MS** *m/z* 55 (86), 57 (100), 69 (73), 97 (56), 109 (62), 137 (38), 159 (9), 191 (12), 211 (7), 272 (12); **HRMS** (ESI) *m/z* calculated for $C_{19}H_{28}ONa$ [M+Na$^+$] 295.2032, found 295.2019.

trans-3-Butyl-2-(4-(*tert*-butyl)phenyl)cyclohexan-1-one (**3g**)

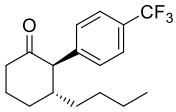


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(4-(*tert*-butyl)phenyl)iodonium triflate (130.2 mg, 0.24 mmol), providing the title compound as an amorphous solid (26.9 mg, 0.094 mmol, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2 H), 6.97 (d, J = 8.0 Hz, 2 H), 3.26 (d, J = 11.6 Hz, 1 H), 2.54-2.50 (m, 1 H), 2.46-2.38 (m, 1 H), 2.17-2.10 (m, 2 H), 2.04-1.96 (m, 1 H), 1.83-1.71 (m, 1 H), 1.55-1.45 (m, 1 H), 1.31 (s, 9 H), 1.27-1.02 (m, 6 H), 0.75 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.9, 149.4, 134.4, 128.9, 125.3, 63.3, 44.9, 42.1, 34.5, 34.3, 31.5, 30.8, 28.7, 26.0, 22.7, 14.1; **EI-MS** *m/z* 57

(100), 91 (51), 109 (42), 129 (31), 137 (32), 169(10), 185 (11), 211 (9), 243(23), 257(5), 271 (27), 286 (14); **HRMS** (ESI) *m/z* calculated for $C_{20}H_{31}O$ [M+H$^+$] 287.2369, found 287.2360.

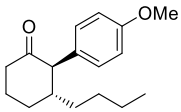
trans-3-Butyl-2-(4-(trifluoromethyl)phenyl)cyclohexan-1-one (**3h**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(4-(trifluoromethyl)phenyl)iodonium triflate (135.9 mg, 0.24 mmol), providing the title compound as an amorphous solid (24.5 mg, 0.082 mmol, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2 H), 7.18 (d, J = 8.0 Hz, 2 H), 3.37 (d, J = 11.6 Hz, 1 H), 2.57-2.52 (m, 1 H), 2.49-2.41 (m, 1 H), 2.22-2.12 (m, 2 H), 2.05-1.98 (m, 1 H), 1.82-1.74 (m, 1 H), 1.58-1.51 (m, 1 H), 1.31-1.26 (m, 1 H), 1.20-1.04 (m, 5 H), 0.77 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.6, 141.8, 129.9, 129.2 (q, J = 32.0 Hz), 125.3 (q, J = 4.0 Hz), 124.4 (q, J = 270 Hz), 63.7, 45.2, 42.1, 34.3, 30.9, 28.5, 26.1, 22.7, 14.0; **EI-MS** *m/z* 55 (100), 57 (78), 69 (61), 97 (78), 109 (73), 115 (48), 129 (38), 137 (45), 159 (49), 185 (34), 197 (54), 211 (15), 241 (17), 298 (22); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{21}F_3ONa$ [M+Na$^+$] 321.1437, found 321.1424.

trans-3-Butyl-2-(4-methoxyphenyl)cyclohexan-1-one (**3i**)

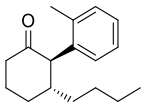


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(4-methoxyphenyl)iodonium triflate (117.7 mg, 0.24 mmol), providing the title compound as a white solid (18.3 mg, 0.070 mmol, 35%).

m.p. = 58-61 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99-6.95 (m, 2 H), 6.89-6.86 (m, 2 H), 3.80 (s, 3 H), 3.24 (d, J = 11.6 Hz, 1 H), 2.54-2.50 (m, 1 H), 2.46-2.38 (m, 1 H),

2.18-2.10 (m, 2 H), 1.99-1.94 (m, 1 H), 1.79-1.74 (m, 1 H), 1.56-1.48 (m, 1 H), 1.30-1.26 (m, 1 H), 1.22-1.03 (m, 5 H), 0.78 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.9, 158.5, 130.4, 129.7, 113.9, 63.0, 55.3, 45.2, 42.2, 34.3, 30.9, 28.6, 26.1, 22.8, 14.1; **EI-MS** *m/z* 57 (100), 91 (39), 109 (67), 121 (70), 137 (48), 147 (56), 203 (4), 260 (20); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{24}O_2Na$ [M+Na$^+$] 283.1669, found 283.1658.

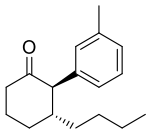
trans-3-Butyl-2-(*o*-tolyl)cyclohexan-1-one (**3j**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and di-*o*-tolyliodonium triflate (110.0 mg, 0.24 mmol), providing the title compound as an amorphous solid (25.4 mg, 0.104 mmol, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.12 (m, 3 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 3.51 (d, *J* = 11.6 Hz, 1 H), 2.58-2.53 (m, 1 H), 2.48-2.40 (m, 1 H), 2.20 (s, 3 H), 2.17-2.04(m, 3 H), 1.84-1.72 (m, 1 H), 1.56-1.45 (m, 1 H), 1.30-1.04 (m, 6 H), 0.77 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.1, 136.8, 136.3, 130.4, 128.8, 126.7, 126.0, 59.8, 44.6, 42.3, 34.3, 31.2, 28.9, 25.9, 22.7, 20.3, 14.1; **EI-MS** *m/z* 55 (42), 57 (25), 91 (46), 105 (63), 119 (100), 131 (33), 169 (12), 187 (35), 244 (23); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{25}O$ [M+H$^+$] 245.1900, found 245.1891.

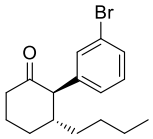
trans-3-Butyl-2-(*m*-tolyl)cyclohexan-1-one (**3k**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and di-*m*-tolyliodonium triflate (110.0 mg, 0.24 mmol), providing the title compound as an amorphous solid (29.5 mg, 0.121 mmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.19 (m, 1 H), 7.05 (d, J = 7.6 Hz, 1 H), 6.86 (s, 1 H), 6.84 (s, 1 H), 3.24 (d, J = 11.6 Hz, 1 H), 2.54-2.49 (m, 1 H), 2.45-2.37 (m, 1 H), 2.33 (s, 3 H), 2.17-2.10 (m, 2 H), 2.07-1.98 (m, 1 H), 1.82-1.72 (m, 1 H), 1.55-1.44 (m, 1 H), 1.32-1.23 (m, 1 H), 1.23-1.02 (m, 5 H), 0.77 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.5, 137.7, 137.5, 130.2, 128.2, 127.7, 126.4, 63.7, 44.7, 42.1, 34.3, 30.7, 28.5, 25.9, 22.7, 21.6, 14.0; **EI-MS** *m/z* 55 (44), 57 (30), 91 (57), 105 (100), 131 (73), 143 (57), 187 (44), 244 (57); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{25}O$ [M+H$^+$] 245.1900, found 245.1897.

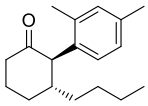
trans-2-(3-Bromophenyl)-3-butylcyclohexan-1-one (**3l**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(3-bromophenyl)iodonium triflate (141.1 mg, 0.24 mmol), providing the title compound as an amorphous solid (44.6 mg, 0.144 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 1 H), 7.21-7.18 (m, 2 H), 7.00-6.98 (m, 1 H), 3.25 (d, J = 12.0 Hz, 1 H), 2.54-2.49 (m, 1 H), 2.46-2.37 (m, 1 H), 2.19-2.10 (m, 2 H), 2.00-1.96 (m, 1 H), 1.79-1.75 (m, 1 H), 1.54-1.48 (m, 1 H), 1.29-1.26 (m, 1 H), 1.21-1.04 (m, 5 H), 0.78 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 209.6, 140.0, 132.6, 130.1, 129.9, 128.2, 122.5, 63.5, 45.1, 42.1, 34.3, 30.8, 28.5, 26.0, 22.7, 14.0; **EI-MS** *m/z* 57 (23), 91 (51), 115 (61), 129 (85), 139 (45), 169 (32), 171 (27), 211 (31), 251 (20), 253 (19), 308 (43), 310 (41); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{22}BrO$ [M+H$^+$] 309.0849, found 309.0851.

trans-3-Butyl-2-(2,4-dimethylphenyl)cyclohexan-1-one (**3m**)

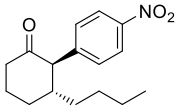


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in

hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and bis(2,4-dimethylphenyl)iodonium triflate (116.7 mg, 0.24 mmol), providing the title compound as an amorphous solid (26.5 mg, 0.103 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.89 (m, 2 H), 6.90 (d, J = 7.6 Hz, 1 H), 3.47 (d, J = 11.6 Hz, 1 H), 2.57-2.52 (m, 1 H), 2.47-2.38 (m, 1 H), 2.29 (s, 3 H), 2.19-2.12 (m, 2 H), 2.15 (s, 3 H), 2.09-2.04 (m, 1 H), 1.81-1.70 (m, 1 H), 1.54-1.44 (m, 1 H), 1.28-1.02 (m, 6 H), 0.78 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.3, 136.5, 136.0, 133.1, 131.3, 128.7, 126.8, 59.5, 44.5, 42.3, 34.3, 31.2, 28.9, 25.8, 22.7, 21.2, 20.2, 14.1; **EI-MS** *m/z* 57 (68), 91 (100), 105 (87), 119 (100), 131 (77), 145 (74), 201 (30), 258 (31); **HRMS** (ESI) *m/z* calculated for $C_{18}H_{27}O$ [M+H$^+$] 259.2056, found 259.2049.

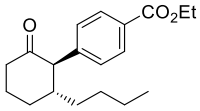
trans-3-Butyl-2-(4-nitrophenyl)cyclohexan-1-one (**3n**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and (4-nitrophenyl)(phenyl)iodonium triflate (114.0 mg, 0.24 mmol), providing the title compound as a yellow oil (26.6 mg, 0.097 mmol, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.18 (m, 2 H), 7.25-7.22 (m, 2 H), 3.44 (d, J = 12.0 Hz, 1 H), 2.57-2.53 (m, 1 H), 2.50-2.42 (m, 1 H), 2.24-2.14 (m, 2 H), 2.09-2.00 (m, 1 H), 1.82-1.77 (m, 1 H), 1.59-1.52 (m, 1 H), 1.30-1.26 (m, 1 H), 1.18-1.05 (m, 5 H), 0.77 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 209.0, 147.0, 145.6, 130.5, 123.6, 63.7, 45.4, 42.0, 34.4, 30.8, 28.4, 26.1, 22.7, 14.0; **EI-MS** *m/z* 55 (81), 69 (32), 97 (100), 115 (98), 128 (75), 174 (30), 202 (11), 214 (35), 240 (27), 257 (46), 275 (41); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{25}N_2O_3$ [M+NH$_4^+$] 293.1860, found 293.1857.

trans-Ethyl 4-(2-butyl-6-oxocyclohexyl)benzoate (**3o**)

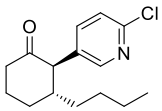


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in

hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and ethyl 4-(4-(ethoxycarbonyl)phenyl)(2,4,6-triisopropylphenyl)iodonium triflate (150.8 mg, 0.24 mmol), providing the title compound as an amorphous solid (24.4 mg, 0.081 mmol, 40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2 H), 7.15-7.12 (m, 2 H), 4.37 (q, J = 7.2 Hz, 2 H), 3.36 (d, J = 11.6 Hz, 1 H), 2.55-2.51 (m, 1 H), 2.48-2.43 (m, 1 H), 2.21-2.12 (m, 2 H), 2.06-2.02 (m, 1 H), 1.81-1.77 (m, 1 H), 1.57-1.40 (m, 1 H), 1.39 (t, J = 7.2 Hz, 3 H), 1.31-1.24 (m, 1 H), 1.18-1.02 (m, 5 H), 0.76 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.7, 166.7, 143.0, 129.63, 129.57, 129.2, 63.8, 60.9, 45.1, 42.1, 34.3, 30.8, 28.5, 26.1, 22.7, 14.5, 14.0; **EI-MS** *m/z* 57 (24), 91 (64), 115 (100), 131 (93), 185 (33), 201 (28), 211 (45), 245 (25), 257 (40), 302 (56); **HRMS** (ESI) *m/z* calculated for $C_{19}H_{26}O_3Na$ [M+Na$^+$] 325.1774, found 325.1761.

trans-3-Butyl-2-(6-chloropyridin-3-yl)cyclohexan-1-one (**3p3**)

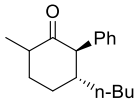


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol) and (6-chloropyridin-3-yl)(4-methoxyphenyl)iodonium triflate (119.0 mg, 0.24 mmol), providing the title compound as a colorless oil (20.3 mg, 0.076 mmol, 38%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 2.0 Hz, 1 H), 7.39 (dd, J = 8.2, 2.4 Hz, 1 H), 7.32 (d, J = 8.2 Hz, 1 H), 3.33 (d, J = 12.0 Hz, 1 H), 2.58-2.52 (m, 1 H), 2.52-2.41 (m, 1 H), 2.23-2.13 (m, 2 H), 1.97-1.89 (m, 1 H), 1.84-1.73 (m, 1 H), 1.59-1.48 (m, 1 H), 1.32-1.26 (m, 1 H), 1.21-1.05 (m, 5 H), 0.78 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.9, 150.6, 150.2, 139.7, 132.1, 124.1, 60.4, 45.5, 42.0, 34.4, 30.9, 28.4, 26.2, 22.7, 14.0; **EI-MS** *m/z* 55 (63), 69 (25), 97 (43), 117 (58), 127 (100), 139 (85), 152 (42), 164 (47), 208 (32), 222 (38), 265 (85), 267 (29); **HRMS** (ESI) *m/z* calculated for $C_{15}H_{21}ClNO$ [M+H$^+$] 266.1306, found 266.1302.

4.4 Scope of Michael acceptors

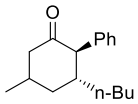
trans-3-butyl-6-methyl-2-phenylcyclohexan-1-one (**3q**, dr =78:22)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), 6-methylcyclohex-2-en-1-one (22.0 mg, 0.20 mmol) and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a colorless oil (30.8 mg, 0.126 mmol, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) (***major***) δ 7.34-7.29 (m, 2 H), 7.25-7.21 (m, 1 H), 7.06-7.03 (m, 2 H), 3.29 (d, *J* = 12.0 Hz, 1 H), 2.58-2.49 (m, 1 H), 2.20-2.15 (m, 1 H), 2.13-2.08 (m, 1 H), 2.04-1.92 (m, 1 H), 1.64-1.43 (m, 2 H), 1.34-1.12 (m, 5 H), 1.09-1.07 (m, 1 H), 1.04 (d, *J* = 6.4 Hz, 3 H), 0.76 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) (***major***) δ 211.3, 137.6, 129.7, 128.2, 126.8, 64.0, 46.1, 45.5, 35.6, 34.5, 31.3, 28.5, 22.7, 14.8, 14.0; **^{1}H NMR** (400 MHz, $CDCl_3$) (**minor**) 7.34-7.29 (m, 0.6 H), 7.25-7.21 (m, 0.6 H), 7.15-7.13 (m, 0.3 H), 3.49 (d, *J* = 8.0 Hz, 0.3 H), 2.68-2.56 (m, 0.3 H), 2.32-2.20 (m, 0.3 H), 1.78-1.65 (m, 0.6 H), 1.60-1.43 (m, 0.6 H), 1.15-1.03 (m, 1.8 H), 1.05 (d, *J* = 8.0 Hz, 1 H) , 0.82 (d, *J* = 7.2 Hz, 1 H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) (***minor***) δ 214.2, 138.2, 128.6, 128.5, 126.8, 60.0, 43.2, 42.1, 33.7, 31.5, 29.1, 25.5, 22.8, 16.1, 14.1;**EI-MS** *m/z* 55 (42), 69 (32), 91 (100), 117 (96), 129 (79), 153 (25), 167 (31), 187 (15), 217 (9), 244 (24); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{25}O$ [M+H$^+$] 245.1900, found 245.1890.

trans-3-butyl-5-methyl-2-phenylcyclohexan-1-one (**3r**, dr = 87:13)

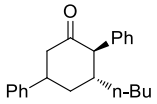


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), 5-methylcyclohex-2-en-1-one (22.0 mg, 0.20 mmol) and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a colorless oil (22.5 mg, 0.092 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) (***major***) δ 7.33 (t, *J* = 7.6 Hz, 2 H), 7.26-7.23 (m, 1 H),

7.10 (d, *J* = 7.2 Hz, 2 H), 3.30 (d, *J* = 9.6 Hz, 1 H), 2.59-2.54 (m, 1 H), 2.45-2.38 (m, 1 H), 2.34-2.23 (m, 2 H), 1.90-1.84 (m, 1 H), 1.76-1.69 (m, 1 H), 1.20-1.14 (m, 4 H), 1.09 (d, *J* = 6.4 Hz, 1 H), 1.04 (d, *J* = 7.2 Hz, 3 H), 0.90-0.40 (m, 1 H), 0.80 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) (***major***) δ 210.9, 137.9, 129.0, 128.5, 126.9, 62.6, 48.1, 39.3, 36.2, 34.2, 30.2, 28.9, 22.7, 20.2, 14.1; **EI-MS** *m/z* 55 (67), 69 (56), 91 (100), 117 (85), 129 (61), 153 (45), 159 (46), 197 (24), 215 (31), 244 (15); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{25}O$ [M+H$^+$] 245.1900, found 245.1891.

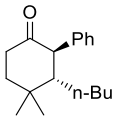
trans-3-butyl-2,5-diphenylcyclohexan-1-one (**3s**, dr = 89:11)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M*, 0.40 mmol), 5-phenylcyclohex-2-en-1-one (34.4 mg, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a colorless oil (28.2 mg, 0.092 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) (***major***) δ 7.37-7.30 (m, 4 H), 7.24-7.20 (m, 4 H), 7.11-7.09 (m, 2 H), 3.51-3.47 (m, 1 H), 3.42 (d, *J* = 8.0 Hz, 1 H), 2.87-2.82 (m, 1 H), 2.71-2.66 (m, 1 H), 2.32-2.20 (m, 2 H), 2.02-1.96 (m, 1 H), 1.29-1.22 (m, 3 H), 1.21-1.12 (m, 3 H), 0.78 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) (***major***) δ 211.3, 144.3, 137.9, 128.72, 128.67, 128.6, 127.1, 127.0, 126.6, 61.9, 45.7, 39.5, 38.2, 35.7, 33.6, 28.8, 22.7, 14.1; **EI-MS** *m/z* 55 (9), 77 (14), 91 (77), 117 (100), 131 (72), 173 (40), 249 (10), 306 (21); **HRMS** (ESI) *m/z* calculated for $C_{22}H_{26}ONa$ [M+Na$^+$] 329.1876, found 329.1861.

trans-3-butyl-4,4-dimethyl-2-phenylcyclohexan-1-one (**3t**)

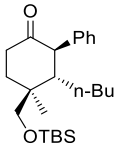


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M*, 0.40 mmol), 4,4-dimethylcyclohex-2-en-1-one (24.8 mg, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a

colorless oil (23.8 mg, 0.092 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2 H), 7.26-7.22 (m, 1 H), 7.09-7.07 (m, 2 H), 3.33 (d, J = 12.4 Hz, 1 H), 2.62-2.56 (m, 1 H), 2.45-2.40 (m, 1 H), 1.80-1.77 (m, 1 H), 1.71-1.60 (m, 1 H), 1.35-1.26 (m, 1 H), 1.15 (s, 3 H), 1.05 (s, 3 H), 1.03-0.94 (m, 2 H), 0.90-0.79 (m, 3 H), 0.58 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.7, 138.0, 130.2, 128.1, 126.9, 60.8, 53.4, 41.2, 38.4, 34.6, 32.4, 30.9, 29.7, 22.9, 19.6, 13.7; **EI-MS** *m/z* 55 (98), 57 (99), 69 (93), 91 (100), 117 (58), 145 (19), 167 (22), 201 (8), 258 (36); **HRMS** (ESI) *m/z* calculated for $C_{18}H_{26}ONa$ [M+Na$^+$] 281.1876, found 281.1865.

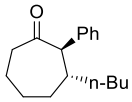
(2*R**,3*S**,4*S**)-3-butyl-4-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-methyl-2-phenylcyclohexan-1-one (**3u**)



Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), 4-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-methylcyclohex-2-en-1-one (50.9 mg, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a colorless oil (35.0 mg, 0.090 mmol, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 3 H), 7.08-7.06 (m, 2 H), 3.94 (d, J = 10.4 Hz, 1 H), 3.67 (d, J = 11.6 Hz, 1 H), 3.59 (d, J = 10.0 Hz, 1 H), 2.79-2.45 (m, 1 H), 2.45-2.43 (m, 1 H), 2.22-2.16 (m, 1 H), 1.88-1.83 (m, 1 H), 1.67-1.59 (m, 1 H), 1.51-1.42 (m, 1 H), 1.15-1.06 (m, 2 H), 0.99 (s, 3 H), 0.93 (s, 9 H), 0.90-0.88 (m, 1 H), 0.84-0.76 (m, 1 H), 0.60 (t, J = 7.2 Hz, 3 H), 0.56-0.48 (m, 1 H), 0.11 (s, 3H), 0.105 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.5, 138.9, 130.0, 128.2, 126.9, 66.6, 60.6, 52.2, 38.8, 38.4, 36.2, 32.2, 30.3, 26.0, 25.2, 23.0, 18.4, 13.8, -5.4, -5.5; **EI-MS** *m/z* 55 (23), 75 (86), 91 (65), 117(100), 157 (20), 169 (18), 183 (14), 227 (21), 239 (30), 331 (67), 388 (1); **HRMS** (ESI) *m/z* calculated for $C_{24}H_{41}O_2Si$ [M+H$^+$] 389.2870, found 389.2878.

trans-3-butyl-2-phenylcycloheptan-1-one (**3v**)

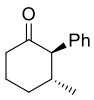


Prepared according to general procedure A using *n*-butyllithium (0.16 mL, 2.5 *M* in hexane, 0.40 mmol), cyclohept-2-en-1-one (22.0 mg, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as an amorphous solid (16.7 mg, 0.068 mmol, 34%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 3 H), 7.28-7.23 (m, 2 H), 3.38 (d, J = 10.8 Hz, 1 H), 2.81-2.74 (m, 1 H), 2.31-2.26 (m, 1 H), 2.11-2.03 (m, 1 H), 2.00-1.92 (m, 3 H), 1.63-1.50 (m, 2 H), 1.36-1.01 (m, 7 H), 0.80 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.8, 138.2, 128.9, 128.4, 127.3, 66.6, 41.3, 40.2, 33.8, 32.9, 29.7, 29.0, 27.4, 22.9, 14.1; **EI-MS** *m/z* 55 (38), 69 (39), 91 (100), 117 (72), 129 (32), 143 (18), 153 (16), 187 (13), 217 (9), 244 (34); **HRMS** (ESI) *m/z* calculated for $C_{17}H_{24}ONa$ [M+Na$^+$] 267.1719, found 267.1707.

4.5 Scope of Michael donors

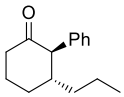
trans-3-Methyl-2-phenylcyclohexan-1-one (**3w**)[12]



Prepared according to general procedure A using methyllithium (0.31 mL, 1.3 *M* in Et_2O, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as an amorphous solid (18.1 mg, 0.096 mmol, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2 H), 7.25-7.23 (m, 1 H), 7.08-7.05 (m, 2 H), 3.18 (d, J = 11.6 Hz, 1 H), 2.55-2.50 (m, 1 H), 2.48-2.39 (m, 1 H), 2.15-2.07 (m, 2 H), 2.06-1.99 (m, 1 H), 1.88-1.76 (m, 1 H), 1.64-1.53 (m, 1 H), 0.82 (d, J = 6.4 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.1, 137.6, 129.4, 128.3, 126.9, 65.3, 41.9, 40.8, 34.4, 26.1, 21.3; **EI-MS** *m/z* 55 (77), 57 (100), 69 (62), 71 (69), 91 (62), 97 (51), 117 (58), 129 (40), 169 (12), 175 (10), 188(36); **HRMS** (ESI) *m/z* calculated for $C_{13}H_{17}O$ [M+H$^+$] 189.1274, found 189.1276.

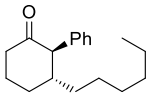
trans-2-Phenyl-3-propylcyclohexan-1-one (**3x**)



Prepared according to general procedure A using *n*-propyllithium (0.40 mL, 1.0 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a white solid (22.5 mg, 0.104 mmol, 52%).

m.p. = 57-59 ºC.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2 H), 7.26-7.23 (m, 1 H), 7.07-7.05 (m, 2 H), 3.28 (d, *J* = 11.6 Hz, 1 H), 2.55-2.50 (m, 1 H), 2.47-2.39 (m, 1 H), 2.18-2.11 (m, 2 H), 2.07-2.00 (m, 1 H), 1.83-1.73 (m, 1 H), 1.56-1.46 (m, 1 H), 1.39-1.32 (m, 1 H), 1.18-1.03 (m, 3 H), 0.74 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.4, 137.6, 129.5, 128.4, 126.9, 63.9, 44.8, 42.1, 36.9, 30.8, 26.0, 19.5, 14.2; **EI-MS** *m/z* 55 (42), 91 (100), 117 (68), 129 (64), 145 (23), 173 (10), 216 (37); **HRMS** (ESI) *m/z* calculated for $C_{15}H_{21}O$ [M+H$^+$] 217.1587, found 217.1578.

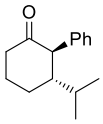
trans-3-Hexyl-2-phenylcyclohexan-1-one (**3y**)



Prepared according to general procedure A using *n*-hexyllithium (0.20 mL, 2.0 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as an amorphous solid (26.4 mg, 0.102 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2 H), 7.26-7.22 (m, 1 H), 7.07-7.05 (m, 2 H), 3.28 (d, *J* = 11.2 Hz, 1 H), 2.54-2.50 (m, 1 H), 2.46-2.38 (m, 1 H), 2.18-2.10 (m, 2 H), 2.04-2.00 (m, 1 H), 1.80-1.75 (m, 1 H), 1.55-1.49 (m, 1 H), 1.30-1.25 (m, 1 H), 1.24-1.04 (m, 9 H), 0.82 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.4, 137.6, 129.5, 128.4, 126.9, 63.8, 45.0, 42.1, 34.6, 31.8, 30.9, 29.3, 26.3, 26.0, 22.7, 14.1; **EI-MS** *m/z* 55 (27), 91 (100), 117 (71), 129 (71), 149 (16), 173 (32), 258 (34); **HRMS** (ESI) *m/z* calculated for $C_{18}H_{27}O$ [M+H$^+$] 259.2056, found 259.2046.

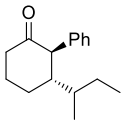
trans-3-Isopropyl-2-phenylcyclohexan-1-one (**3z**)



Prepared according to general procedure A using isopropyllithium (0.40 mL, 1.0 *M* in hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a white solid (19.5 mg, 0.091 mmol, 45%).

m.p. = 62-64 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2 H), 7.27-7.23 (m, 1 H), 7.07-7.05 (m, 2 H), 3.44 (d, *J* = 12.4 Hz, 1 H), 2.56-2.51 (m, 1 H), 2.46-2.38 (m, 1 H), 2.22-2.16 (m, 1 H), 2.02-1.92 (m, 2 H), 1.78-1.72 (m, 1 H), 1.61-1.53 (m, 1 H), 1.39-1.35 (m, 1 H), 0.85 (d, *J* = 6.8 Hz, 3 H), 0.77 (d, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.7, 137.4, 129.5, 128.4, 126.9, 62.0, 50.5, 42.3, 28.2, 26.0, 24.2, 21.6, 14.9; **EI-MS** *m/z* 55 (36), 91 (100), 117 (75), 129 (37), 145 (28), 173 (25), 216 (19); **HRMS** (ESI) *m/z* calculated for $C_{15}H_{21}O$ [M+H$^+$] 217.1587, found 217.1579.

trans-3-(*sec*-Butyl)-2-phenylcyclohexan-1-one (**3aa**, 50:50)

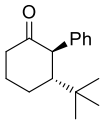


Prepared according to general procedure A using *sec*-butyllithium (0.31 mL, 1.3 *M* in cyclohexane/hexane (92/8), 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a colorless oil (21.7 mg, 0.094 mmol, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2 H), 7.26-7.23 (m, 1 H), 7.06-7.04 (m, 2 H), 3.52 (d *J* = 12.0 Hz, 0.5 H), 3.48 (d, *J* = 12.0 Hz, 0.5 H), 2.55-2.51 (m, 1 H), 2.45-2.41(m, 1 H), 2.21-2.15 (m, 1 H), 1.98-1.94 (m, 1 H), 1.86-1.72 (m, 1 H), 1.58-1.48 (m, 2 H), 1.23-1.18 (m, 1 H), 1.06-1.02 (m, 1 H), 0.95-0.82 (m, 1 H), 0.77-0.69 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.83, 210.80, 137.6, 137.3, 129.50, 129.49, 128.4, 126.9, 61.7, 61.6, 51.4, 48.0, 42.4, 42.3, 35.5, 35.1, 28.2, 26.21, 26.19, 25.2, 24.4, 22.5, 18.1, 12.9, 12.6, 12.2; **EI-MS** *m/z* 55 (32), 69 (22), 91 (100), 117 (53), 129 (40), 139 (23), 159 (14), 183 (13), 230 (45); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{23}O$ [M+H$^+$]

231.1743, found 231.1735.

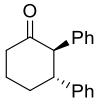
trans-3-(*tert*-Butyl)-2-phenylcyclohexan-1-one (**3ab**)



Prepared according to general procedure A using *tert*-butyllithium (0.25 mL, 1.6 *M* in pentane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a colorless oil (19.8 mg, 0.086 mmol, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5 H), 3.54 (d, J = 7.6 Hz, 1 H), 2.60-2.53 (m, 1 H), 2.31-2.21 (m, 2 H), 2.10-2.02 (m, 2 H), 1.95-1.84 (m, 1 H), 1.50-1.39 (m, 1 H), 0.80 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.5, 140.5, 128.9, 128.6, 126.8, 59.7, 51.7, 38.4, 34.7, 28.4, 25.3, 22.9; **EI-MS** *m/z* 57 (74), 91 (100), 117 (39), 129 (22), 145 (22), 173 (32), 230 (35); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{22}ONa$ [M+Na$^+$] 253.1563, found 253.1551.

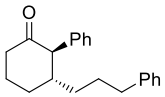
trans-2,3-Diphenylcyclohexan-1-one (**3ac**)[13]



Prepared according to general procedure A using phenyllithium (0.21 mL, 1.9 *M* in di-*n*-butyl ether, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a white solid (16.0 mg, 0.064 mmol, 32%).

m.p. = 68-71 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15-7.12 (m, 4 H), 7.09-7.02 (m, 4 H), 6.92-6.91 (m, 2 H), 3.80 (d, J = 12.0 Hz, 1 H), 3.26-3.19 (m, 1 H), 2.68-2.57 (m, 2 H), 2.28-2.21(m, 1 H), 2.20-2.05 (m, 2 H), 2.01-1.90 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.4, 143.2, 136.8, 129.6, 128.4, 128.0, 127.4, 126.7, 126.5, 63.7, 52.5, 42.2, 34.7, 26.3; **EI-MS** *m/z* 55 (12), 91 (33), 117 (100), 133 (53), 159 (19), 250 (63); **HRMS** (ESI) *m/z* calculated for $C_{18}H_{19}O$ [M+H$^+$] 251.1430, found 251.1422.

trans-2-Phenyl-3-(3-phenylpropyl)cyclohexan-1-one (**3ad**)

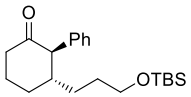


Prepared according to general procedure B using (3-phenylpropyl)lithium (0.5 mL, 0.4 *M* in Et_2O/pentane, 0.20 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a white solid (33.4 mg, 0.114 mmol, 57%).

(3-phenylpropyl)lithium was prepared in the following manner: to a precooled (–78 ℃) solution of 3-phenyl-1-iodopropane[13] (492.2 mg, 2.0 mmol, 1.0 eq) in Et_2O (2.3 mL) was added *t*-BuLi (2.63 mL, 1.6 *M* in pentane, 4.2 mmol, 2.1 eq) via syringe. The resulting solution was stirred at –78 ℃ for 30 min, and then used immediately.

m.p. = 58-62 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2 H), 7.26-7.20 (m, 3 H), 7.15-7.12 (m, 1 H), 7.05-7.03 (m, 4 H), 3.27 (d, *J* = 11.2 Hz, 1 H), 2.53-2.33 (m, 4 H), 2.17-2.00 (m, 3 H), 1.79-1.75 (m, 1 H), 1.66-1.61 (m, 1 H), 1.56-1.44 (m, 2 H), 1.27-1.23 (m, 1 H), 1.15-1.11 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.2, 142.4, 137.5, 129.5, 128.4, 128.35, 127.0, 125.8, 63.7, 44.9, 42.0, 35.9, 34.4, 30.8, 28.2, 26.0; **EI-MS** *m/z* 55 (12), 91 (100), 117 (36), 129 (16), 173 (96), 292 (24); **HRMS** (ESI) *m/z* calculated for $C_{21}H_{25}O$ [M+H$^+$] 293.1900, found 293.1902.

trans-3-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)-2-phenylcyclohexan-1-one (**3ae**)



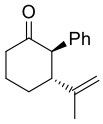
Prepared according to general procedure A using (3-((*tert*-butyldimethylsilyl)oxy)propyl)lithium (1.0 mL, 0.4 M in Et_2O/pentane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a colorless oil (25.8 mg, 0.074 mmol, 37%).

(3-((tert-butyldimethylsilyl)oxy)propyl)lithium was prepared in the following manner: To a precooled (–78 ℃) solution of *tert*-butyl(3-iodopropoxy)dimethylsilane [14] (360.3 mg, 1.2 mmol, 1.0 eq) in Et_2O (1.4 mL) was added *t*-BuLi (1.58 mL, 1.6 *M* in pentane,

2.52 mmol, 2.1 eq) via syringe. The resulting solution was stirred at –78 ℃ for 30 min, and then used immediately.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2 H), 7.26-7.22 (m, 1 H), 7.06-7.04 (m, 2 H), 3.42 (t, J = 6.4 Hz, 2 H), 3.28 (d, J = 11.6 Hz, 1 H), 2.55-2.50 (m, 1 H), 2.47-2.42 (m, 1 H), 2.19-2.11 (m, 2 H), 2.06-2.02 (m, 1 H), 1.80-1.77 (m, 1 H), 1.60-1.51 (m, 2 H), 1.36-1.24 (m, 2 H), 1.08-1.04 (m, 1 H), 0.81 (s, 9 H), -0.05 (s, 3 H), -0.06 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.2, 137.5, 129.5, 128.4, 127.0, 63.9, 63.3, 45.1, 42.1, 31.0, 30.9, 29.8, 26.0, 26.0, 18.4, -5.2; **EI-MS** *m/z* 75 (100), 91 (80), 117 (51), 145 (98), 173 (31), 183 (35), 197 (31), 289 (88); **HRMS** (ESI) *m/z* calculated for $C_{21}H_{35}O_2Si$ [M+H$^+$] 347.2401, found 347.2404.

trans-2-Phenyl-3-(prop-1-en-2-yl)cyclohexan-1-one (**3af**)[15]

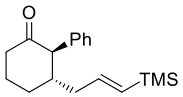


Prepared according to general procedure B using isopropenyllithium (0.5 mL, 0.4 M in Et_2O/pentane, 0.20 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as a white solid (16.4 mg, 0.077 mmol, 38%).

Isopropenyllithium[16] was prepared in the following manner: to a precooled (–78 ℃) solution of 2-bromopropene (139.3 μL, 1.6 mmol) in Et_2O (1.9 mL) was added *tert*-butyllithium (2.0 mL, 1.6 *M* in pentane, 3.2 mmol). The resulting solution was stirred at –78 ℃ for 30 min, and then used immediately.

m.p. = 123-125 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2 H), 7.25-7.20 (m, 1 H), 7.05-7.02 (m, 2 H), 4.59-4.57 (m, 2 H), 3.59 (d, J = 12.0 Hz, 1 H), 2.82-2.75 (m, 1 H), 2.58-2.53 (m, 1 H), 2.51-2.45 (m, 1 H), 2.21-2.15 (m, 1 H), 1.99-1.94 (m, 1 H), 1.94-1.90 (m, 1 H), 1.89-1.82 (m, 1 H), 1.57 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.8, 145.7, 137.0, 129.5, 128.1, 126.9, 112.9, 61.4, 53.4, 42.1, 31.9, 26.2, 19.0; **EI-MS** *m/z* 55 (87), 57 (92), 91 (50), 105 (65), 129 (35), 149 (100), 167 (37), 187 (11), 214 (18); **HRMS** (ESI) *m/z* calculated for $C_{15}H_{19}O$ [M+H$^+$] 215.1436, found 215.1431.

trans-2-Phenyl-3-((*E*)-3-(trimethylsilyl)allyl)cyclohexan-1-one (**3ag**)



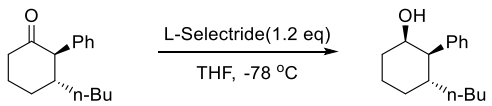
Prepared according to general procedure B using (3-(trimethylsilyl)allyl)lithium (1.0 mL, 0.4 M in THF/hexane, 0.40 mmol), cyclohex-2-en-1-one (19.4 μL, 0.20 mmol), and diphenyliodonium triflate (103.2 mg, 0.24 mmol), providing the title compound as an amorphous solid (24.1 mg, 0.084 mmol, 42%).

(3-(trimethylsilyl)allyl)lithium[17] was prepared in the following manner: to a precooled (–40 ℃) solution of allytrimethylsilane (190.2 μL, 1.2 mmol) in THF (1.6 mL) was added *sec*-butyllithium (1.2 mL, 1.0 *M* in hexane, 1.2 mmol). The resulting yellow colored solution was stirred at –40 ℃ for 30 min, and then was used immediately.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2 H), 7.28-7.24 (m, 1 H), 7.07-7.05 (m, 2 H), 5.88-5.80 (m, 1 H), 5.53 (d, *J* = 18.4 Hz, 1 H), 3.29 (d, *J* = 11.6 Hz, 1 H), 2.56-2.51 (m, 1 H), 2.48-2.34 (m, 1 H), 2.19-2.11 (m, 2 H), 2.09-2.03 (m, 2 H), 1.87-1.76 (m, 2 H), 1.59-1.49 (m, 1 H), 0.02 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.2, 143.6, 137.3, 133.5, 129.6, 128.5, 127.1, 63.4, 44.9, 42.2, 42.1, 30.9, 25.9, -1.1; **EI-MS** *m/z* 59 (39), 73 (100), 75 (63), 91 (74), 75 (33), 129 (26), 145 (14), 173 (18), 195 (12), 245 (83), 271 (9), 286 (6); **HRMS** (ESI) *m/z* calculated for $C_{18}H_{26}OSiNa$ [M+Na$^+$] 309.1645, found 309.1651.

4.6. Further Transformations of 3a

(1*R**,2*R**,3*R**)-3-Butyl-2-phenylcyclohexan-1-ol (**4a**)[18, 19]

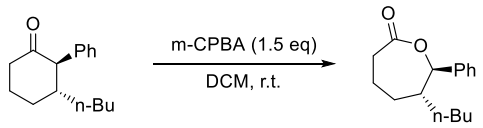


To a precooled solution of **3a** (46.1 mg, 0.20 mmol, 1.0 eq) in THF (2.0 mL) was added lithium tri-*sec*-butylborohydride (0.24 mL, 1.0 *M* in THF, 0.24 mmol, 1.2 eq) via syringe at –78 ℃. After stirring for 15 min at –78 ℃, the reaction was quenched with a saturated aqueous solution of NH_4Cl. The mixture was extracted with ethyl acetate (30 mL ×3) 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 purified by flash column chromatography to give **4a** as an amorphous solid (40.7 mg, 0.175 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2 H), 7.26-7.20 (m, 3 H), 3.83 (s, 1 H), 2.43 (dd, J = 11.6, 2.0 Hz, 1 H), 2.10-2.07 (m, 1 H), 2.03-1.94 (m, 2 H), 1.80-1.72 (m, 1 H), 1.62-1.55 (m, 2 H), 1.43 (s, 1 H), 1.29-1.00 (m, 6 H), 0.89-0.85 (m, 1 H), 0.78 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.1, 128.8, 126.5, 71.2, 55.0, 34.0, 33.3, 33.1, 31.8, 28.7, 22.9, 20.0, 14.2; **EI-MS** *m/z* 55 (46), 57 (51), 67 (39), 81 (69), 91 (100), 123 (43), 129 (31), 141 (15), 157 (6), 232 (31); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{28}NO$ [M+NH_4^+] 250.2165, found 250.2167.

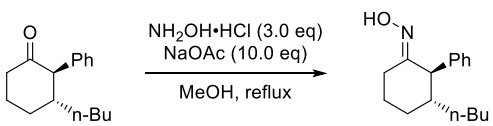
trans-6-butyl-7-phenyloxepan-2-one (**4b**)[19]



To a solution of **3a** (46.1 mg, 0.20 mmol, 1.0 eq) in CH_2Cl_2 (2.0 mL) was added *m*-CPBA (60.9 mg, 0.30 mmol, 80%, 1.5 eq). After stirring for 24 h, the mixture was concentrated under vacuum. The resulting residues were purified by flash column chromatography to give **4b** as a white solid (43.4 mg, 0.176 mmol, 88%).

m.p. = 67-69 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 5 H), 4.99 (d, J = 8.8 Hz, 1 H), 2.84-2.76 (m, 1 H), 2.70-2.64 (m, 1 H), 2.10-2.03 (m, 2 H), 1.98-1.93 (m, 1 H), 1.79-1.75 (m, 1 H), 1.64-1.58 (m, 1 H), 1.22-1.19 (m, 1 H), 1.17-1.11 (m, 1 H), 1.10-1.00 (m, 4 H), 0.74 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 139.0, 128.6, 128.4, 127.5, 86.5, 43.0, 34.0, 31.3, 31.2, 28.9, 22.6, 20.1, 13.9; **EI-MS** *m/z* 55 (11), 84 (100), 97 (9), 190 (16); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{23}O_2$ [M+H^+] 247.1698, found 247.1695.

(±)-*trans*-3-Butyl-2-phenylcyclohexan-1-one oxime (**4c**)[15, 19]

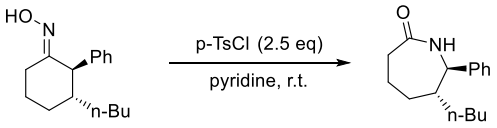


To a solution of **3a** (230.4 mg, 1.0 mmol, 1.0 eq) in MeOH (5.0 mL) was added hydroxylamine hydrochloride (208.5 mg, 3.0 mmol, 3.0 eq) and anhydrous sodium

acetate (820.3 mg, 10.0 mmol, 10.0 eq). The reaction was refluxed for 1 hour, and cooled to room temperature. The mixture was concentrated under vacuum, and purified by flash column chromatography to give **4c** as a white solid (240.2 mg, 0.979 mmol, 98%).

m.p. = 151-154 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (brs, 1 H), 7.31-7.25 (m, 2 H), 7.22-7.19 (m, 1 H), 7.12-7.10 (m, 2 H), 3.17-3.11 (m, 1 H), 3.05 (d, J = 10.4 Hz, 1 H), 2.01-1.96 (m, 1 H), 1.93-1.83 (m, 3 H), 1.54-1.42 (m, 1 H), 1.34-1.25 (m, 2 H), 1.22-1.06 (m, 4 H), 1.04-0.95 (m, 1 H), 0.76 (t, J = 6.9 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 139.6, 129.1, 128.3, 126.6, 54.5, 42.2, 33.6, 30.4, 28.7, 24.3, 24.1, 22.8, 14.1; **EI-MS** *m/z* 55 (100), 57 (75), 91 (98), 105 (85), 129 (71), 143 (53), 149 (31), 188 (62), 244 (35), 245 (41); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{24}NO$ [M+H$^+$] 246.1852, found 246.1854.

(±)-*trans*-6-butyl-7-phenylazepan-2-one (**4d**)[15, 19]

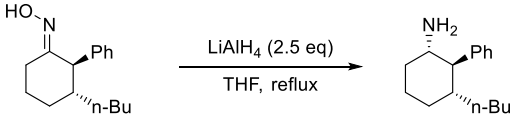


To a solution of **4c** (49.1 mg, 0.20 mmol, 1.0 eq) in pyridine (0.5 mL) was added *p*-tosyl chloride (95.4 mg, 0.50 mmol, 2.5 eq) at room temperature. After 6 hours, the reaction was quenched with a solution of 10% HCl (3 mL) at 0 ℃. The mixture was extracted with CH_2Cl_2 (20 mL × 3), and the combined organic layers were washed successively with water and brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography to give **4d** as a white solid (32.8 mg, 0.134 mmol, 67%).

m.p. = 79-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2 H), 7.32-7.25 (m, 3 H), 5.79 (d, J = 4.8 Hz, 1 H), 4.22-4.18 (m, 1 H), 2.56-2.50 (m, 1 H), 2.48-2.46 (m, 1 H), 2.11-2.05 (m, 1 H), 2.00-1.96 (m, 1 H), 1.90-1.85 (m, 1 H), 1.69-1.65 (m, 1 H), 1.55-1.49 (m, 1 H), 1.26-1.02 (m, 6 H), 0.76 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.4, 141.2, 129.1, 128.0, 127.1, 62.7, 42.7, 36.5, 33.3, 32.4, 28.8, 22.7, 21.1, 14.0; **EI-MS** *m/z* 106 (100), 149 (22), 160 (84), 245 (14); **HRMS** (ESI) *m/z* calculated

for $C_{16}H_{24}NO$ [M+H$^+$] 246.1852, found 246.1854.

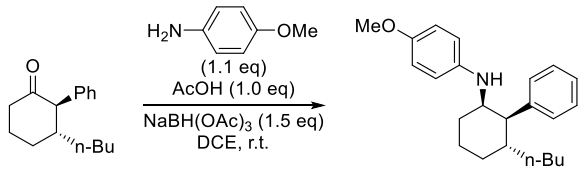
(1*S**, 2*R**, 3*R**)-3-Butyl-2-phenylcyclohexan-1-amine (**4e**)[15]



To a suspension of $LiAlH_4$ (19.0 mg, 0.50 mmol, 2.5 eq) in THF (3.0 mL) was added **4c** (49.1 mg, 0.20 mmol, 1.0 eq). The reaction was refluxed for 6 hours, and cooled to room temperature. The mixture was diluted with EtOAc (3 mL) and quenched with a solution of NaOH (3 mL, 1.0 M) at 0 ℃. The mixture was extracted with ethyl acetate (15 mL ×3) 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 purified by flash column chromatography to give **4e** as a white solid (27.8 mg, 0.12 mmol, 60%).

m.p. = 57-60 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2 H), 7.27-7.18 (m, 3 H), 2.56 (d, *J* = 13.6 Hz, 1 H), 2.38 (brs, 1 H), 2.18-2.12 (m, 2 H), 1.87-1.76 (m, 1 H), 1.56-1.50 (m, 1 H), 1.32-0.85 (m, 9 H), 0.74 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 128.53, 128.48, 126.2, 49.2, 41.1, 36.0, 33.5, 31.1, 28.6, 25.5, 22.89, 22.88, 14.1; **EI-MS** *m/z* 55 (33), 91 (100), 115 (49), 129 (49), 146 (86), 158 (44), 172 (47), 230 (48); **HRMS** (ESI) *m/z* calculated for $C_{16}H_{24}N$ [M+H$^+$] 230.1909, found 230.1905.

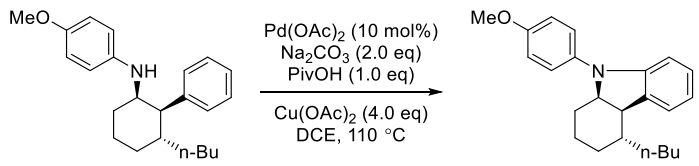
N-((1*R**, 2*R**, 3*R**)-3-butyl-2-phenylcyclohexyl)-4-methoxyaniline (**4f**)[20]



To a solution of **3a** (230.4 mg, 1.00 mmol, 1.0 eq) in 1,2-dichloroethane (5.0 mL) was added *p*-anisidine (135.5 mg, 1.10 mmol, 1.1 eq) and acetic acid (57.2 μL, 1.00 mmol, 1.0 eq) and the mixture was stirred for 1 hour at room temperature. Then sodium triacetoxyborohydride (317.9 mg, 1.50 mmol, 1.5 eq) was added to the solution and the

suspension was allowed to stir for 20 hours at room temperature. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), extracted with EtOAc (40 mL × 3). The combined organic layers were washed successively with water and brine, dried with Na_2SO_4, concentrated under vacuum. The crude product was purified by flash column chromatography to give **4f** as a brown oil (185.8 mg, 0.55 mmol, 55%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26-7.19 (m, 4 H), 7.17-7.10 (m, 1 H), 6.59 (d, J = 8.7 Hz, 2 H), 6.24 (d, J = 9.0 Hz, 2 H), 3.65 (s, 3 H), 3.52-3.50 (m, 2 H), 2.61 (dd, J = 11.4, 3.0 Hz, 1 H), 2.07-1.91 (m, 3 H), 1.67-1.49 (m, 3 H), 1.32-1.26 (m, 3 H), 1.23-1.00 (m, 3 H), 0.94-0.86 (m, 1 H), 0.80 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.7, 143.0, 142.6, 128.9, 128.2, 126.1, 115.0, 114.7, 56.2, 55.8, 53.7, 34.2, 34.1, 31.7, 30.8, 28.7, 22.9, 20.4, 14.2; **EI-MS** *m/z* 91 (24), 123 (22), 136 (29), 149 (47), 162 (74), 280 (5), 337 (100); **HRMS** (ESI) *m/z* calculated for $C_{23}H_{32}NO$ [M+H$^+$] 338.2478, found 338.2473.

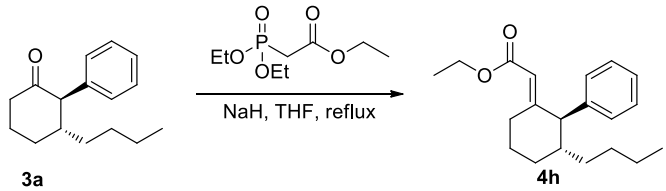
(4*R**,4a*R**,9a*R**)-4-butyl-9-(4-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**4g**)[20]



To a solution of **4f** (67.5 mg, 0.20 mmol, 1.0 eq) in 1,2-dichloroethane (5.0 mL) were added palladium acetate (4.5 mg, 0.02 mmol, 10 mol%), sodium bicarbonate (42.4 mg, 0.40 mmol, 2.0 eq), pivalic acid (20.4 mg, 0.20 mmol, 1.0 eq) and copper acetate (145.3 mg, 0.8 mmol, 4.0 eq). The solution was bubbled for 5 min with argon, and then the tube was sealed and heated at 110 ℃ for 24 h. The reaction was cooled to room temperature, and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography to give **4g** as a brown oil (41.7 mg, 0.124 mmol, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, J =7.2 Hz, 1 H), 7.15-7.13 (m, 2 H), 7.01-6.97 (m, 1 H), 6.95-6.93 (m, 2 H), 6.72-6.68 (m, 1 H), 6.41 (d, J = 8.0 Hz, 1 H), 3.91-3.87

(m, 1 H), 3.82 (s, 3 H), 2.61 (dd, *J* = 10.0, 6.4 Hz, 1 H), 1.88-1.87 (m, 1 H), 1.84-1.79 (m, 1 H), 1.74-1.66 (m, 1 H), 1.55-1.48 (m, 3 H), 1.45-1.32 (m, 3 H), 1.30-1.21 (m, 2 H), 1.19-1.07 (m, 1 H), 1.00-0.92 (m, 1 H), 0.87 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.2, 152.2, 137.0, 134.6, 127.4, 127.2, 124.7, 118.1, 114.7, 108.9, 66.5, 55.6, 46.4, 38.6, 33.5, 29.4, 28.8, 25.8, 23.2, 20.8, 14.3; **EI-MS** *m/z* 208 (10), 234 (15), 236 (48), 237 (32), 250 (14), 277 (38), 278 (40), 292 (33), 334 (8), 335 (100); **HRMS** (ESI) *m/z* calculated for $C_{23}H_{30}NO$ [M+H$^+$] 336.2322, found 336.2318.

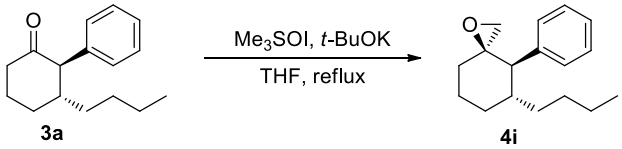
(*E*)-ethyl- 2-((2*S**,3*R**)-3-butyl-2-phenylcyclohexylidene)acetate (**4h**)



To a suspension solution of NaH (9.3 mg, 60%) in dry THF (2.0 mL) was added triethyl phosphonoacetate (47.5 mg), and the mixture was stirred for 1 h, and compound **3a** was then added (46.1 mg). The reaction was refluxed until the starting material **3a** disappeared completely, and quenched by addition a solution of NH_4Cl at 0 ℃. The reaction mixture was extracted with ethyl acetate (3×20 mL) and then washed with H_2O and brine, dried over Na_2SO_4 and concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel yielding the pure ester **4h** (48.2 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2 H), 7.26-7.22 (m, 1 H), 7.12-7.10 (m, 2 H), 5.05 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 2 H), 3.82-3.79 (m, 1 H), 3.07 (d, *J* = 10.4 Hz, 1 H), 2.10-2.03 (m, 2 H), 2.01-1.87 (m, 2 H), 1.56-1.45 (m, 1 H), 1.36-1.23 (m, 2 H), 1.21-1.07 (m, 7 H), 1.03-0.95 (m, 1 H), 0.77 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 165.0, 140.5, 129.4, 128.6, 126.7, 115.2, 59.7, 57.8, 43.1, 34.5, 31.4, 30.3, 28.6, 26.7, 22.8, 14.4, 14.1. **EI-MS** *m/z* 55 (26), 77 (34), 91 (62), 105 (100), 115 (28), 129 (52), 169 (38), 243 (10), 300 (51); **HRMS** (ESI) *m/z* calculated for $C_{20}H_{29}O_2$ [M+H$^+$] 301.2168, found 301.2165.

(3*R**, 4*R**, 5*R**)-5-butyl-4-phenyl-1-oxaspiro[2.5]octane **(4i)**



To a suspension solution of *t*-BuOK（33.7 mg. 0.30 mmol) in THF (2.0 mL) was added Me_3SOI (66 mg, 0.30 mmol) at room temperature under an argon atmosphere, and the reaction mixture was warmed to 90 ℃ for 2 h. The mixture was cooled to room temperature, and then added compound **3a**. The reaction was refluxed for 3h and then quenched with a solution of $NaHCO_3$ (10 mL). The aqueous layer was extracted with $EtOA_C$ (3×30 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel yielding compound **4i** (41.7 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 3 H), 7.16-7.13 (m, 2 H), 2.70 (d, J = 11.6 Hz, 1 H), 2.25 (d, J = 5.2 Hz, 1 H), 2.09-2.03 (m, 1 H), 2.01-1.92 (m, 2 H), 1.85-1.76 (m, 3 H), 1.41-1.36 (m, 1 H), 1.27-1.19 (m, 1 H), 1.18-1.02 (m, 5 H), 0.92-0.83 (m, 1 H), 0.74 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 129.6, 127.8, 126.5, 59.7, 52.7, 51.4, 39.7, 34.8, 34.1, 31.6, 28.6, 23.6, 22.8, 14.1. EI-MS m/z 55 (10), 69 (8), 91 (100), 115 (14), 129 (18), 157 (8), 187 (15), 244 (12); HRMS (ESI) calculated for $C_{17}H_{28}NO$ $[M+NH_4]^+$ 262.2165, found 262.2166.

5. X-Ray Crystallography of 3a

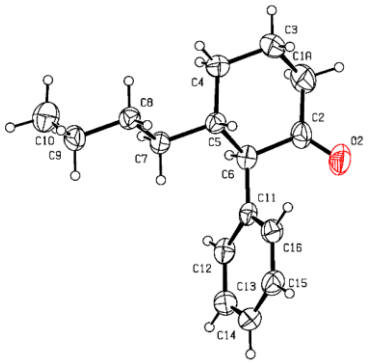


Figure S1. X-Ray Crystal Structure of **3a** (CCDC number 1429348)

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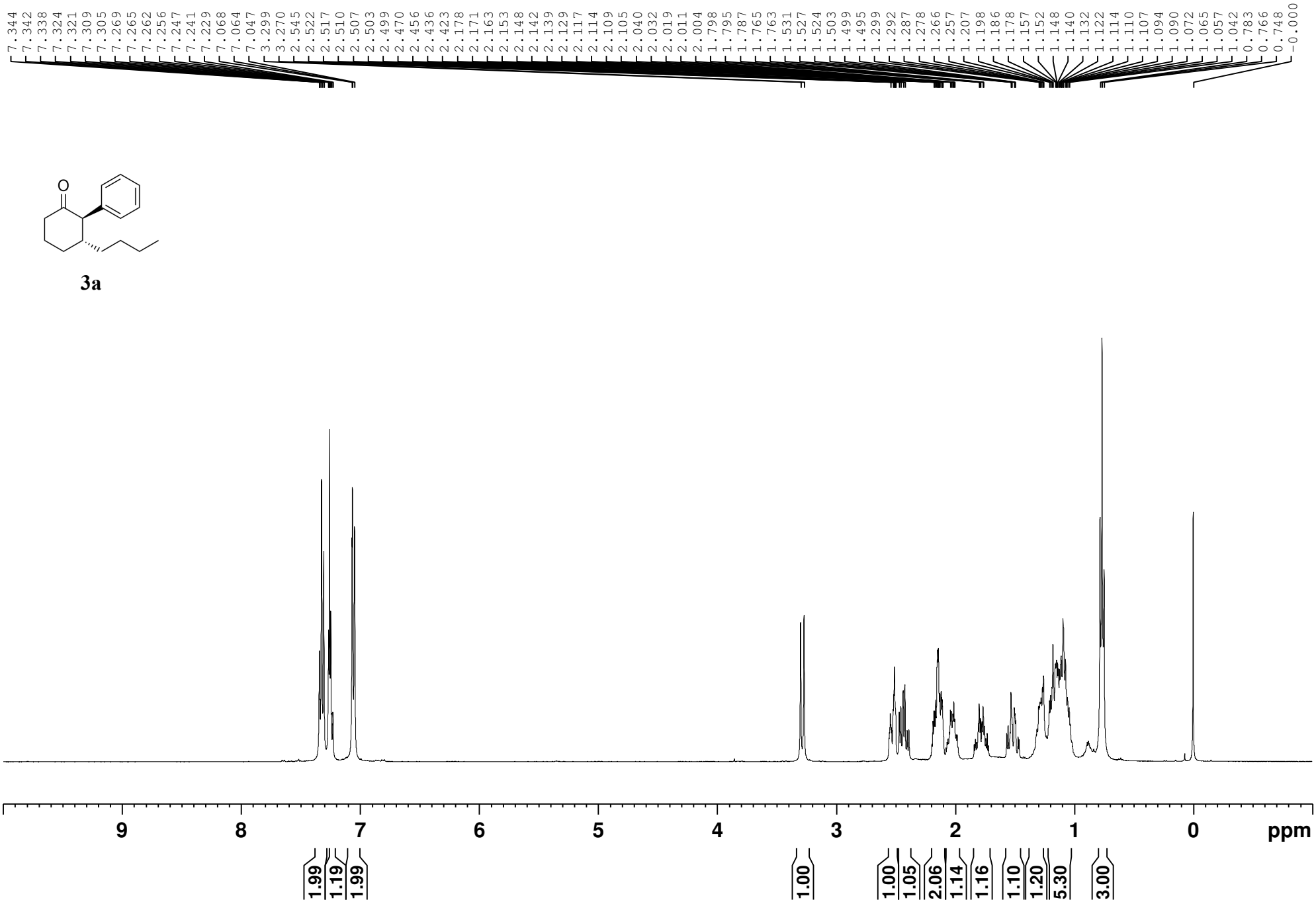
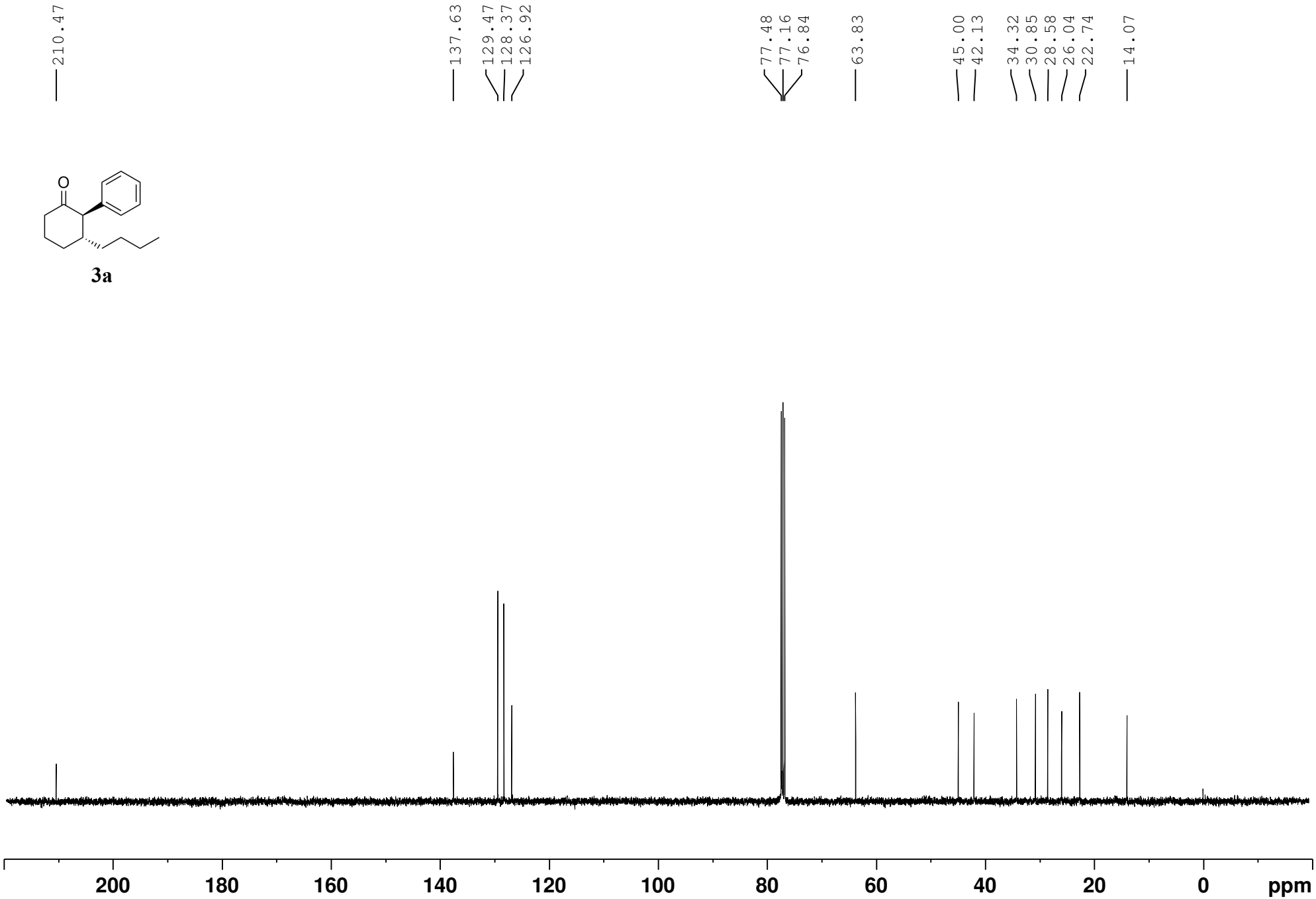
7. Copies of ^{1}H and ^{13}C NMR Spectra



3a

3a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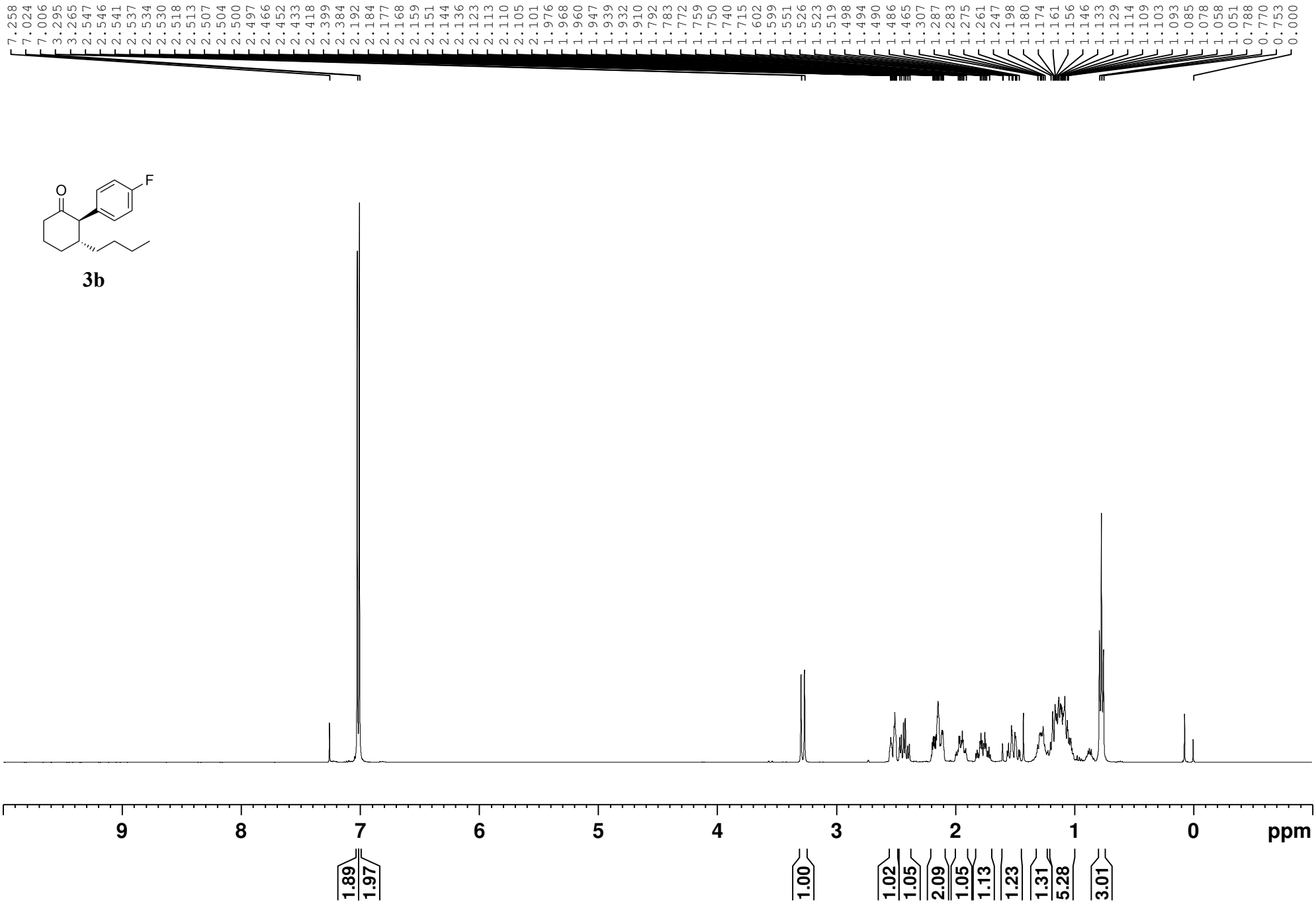
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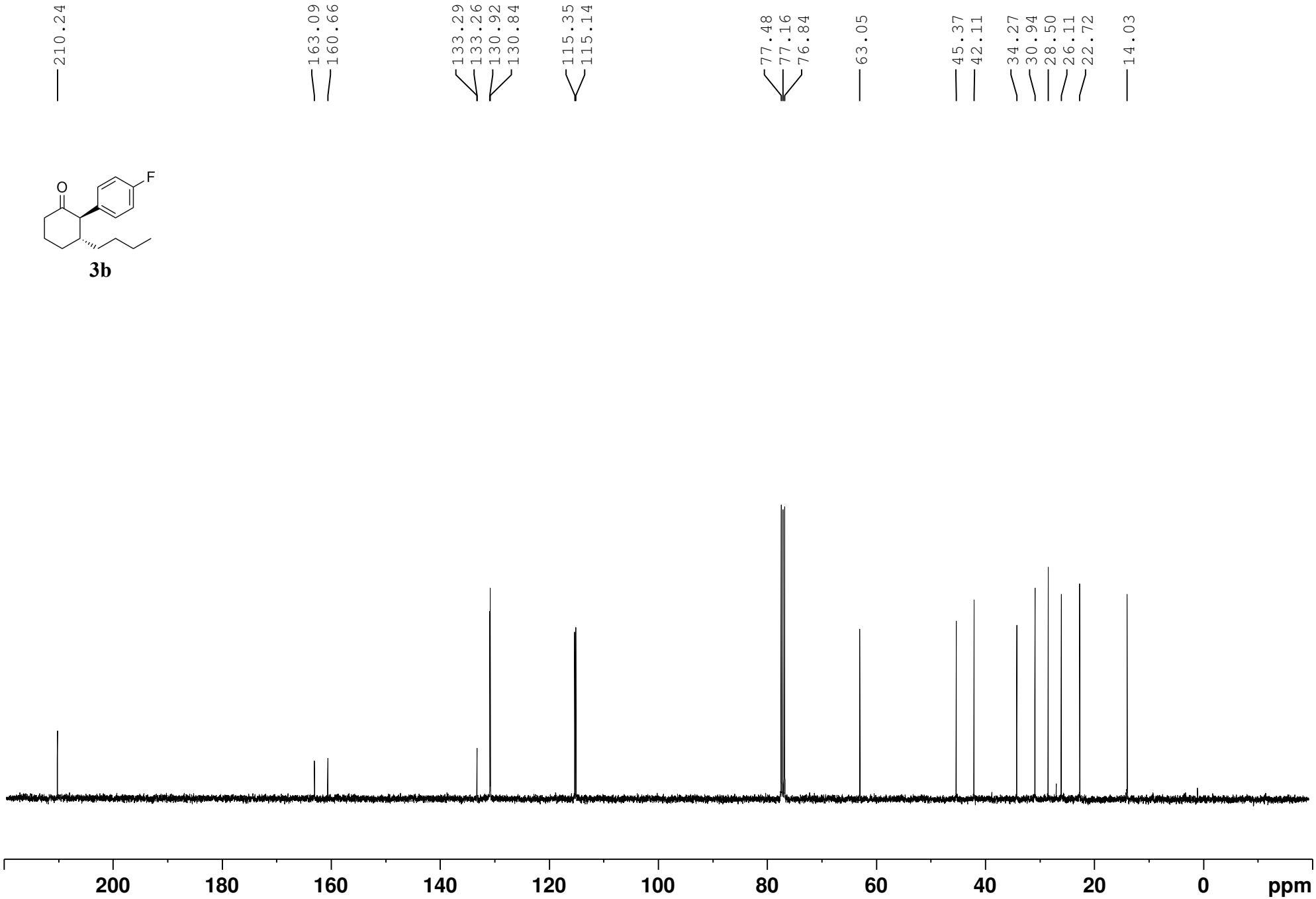
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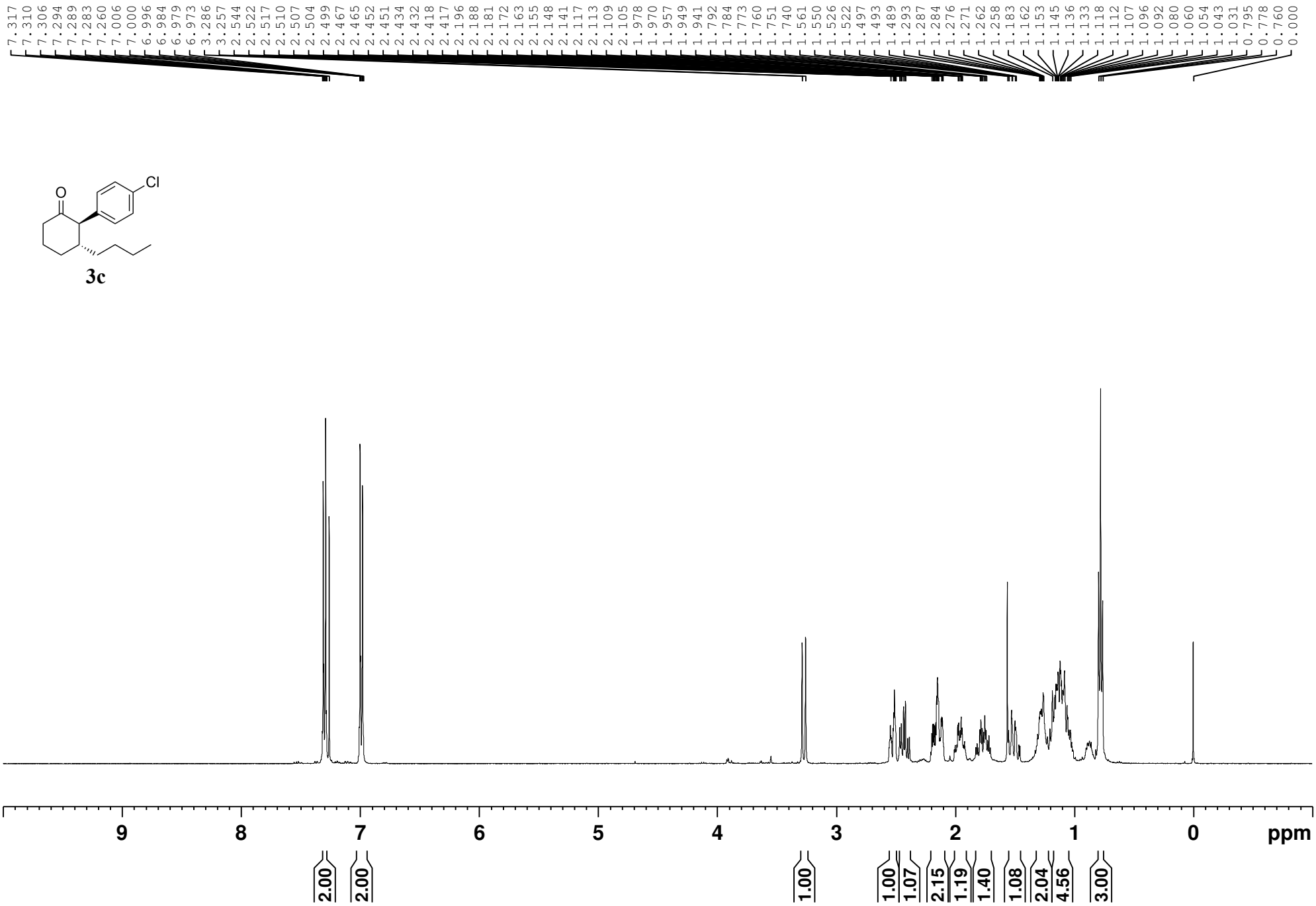
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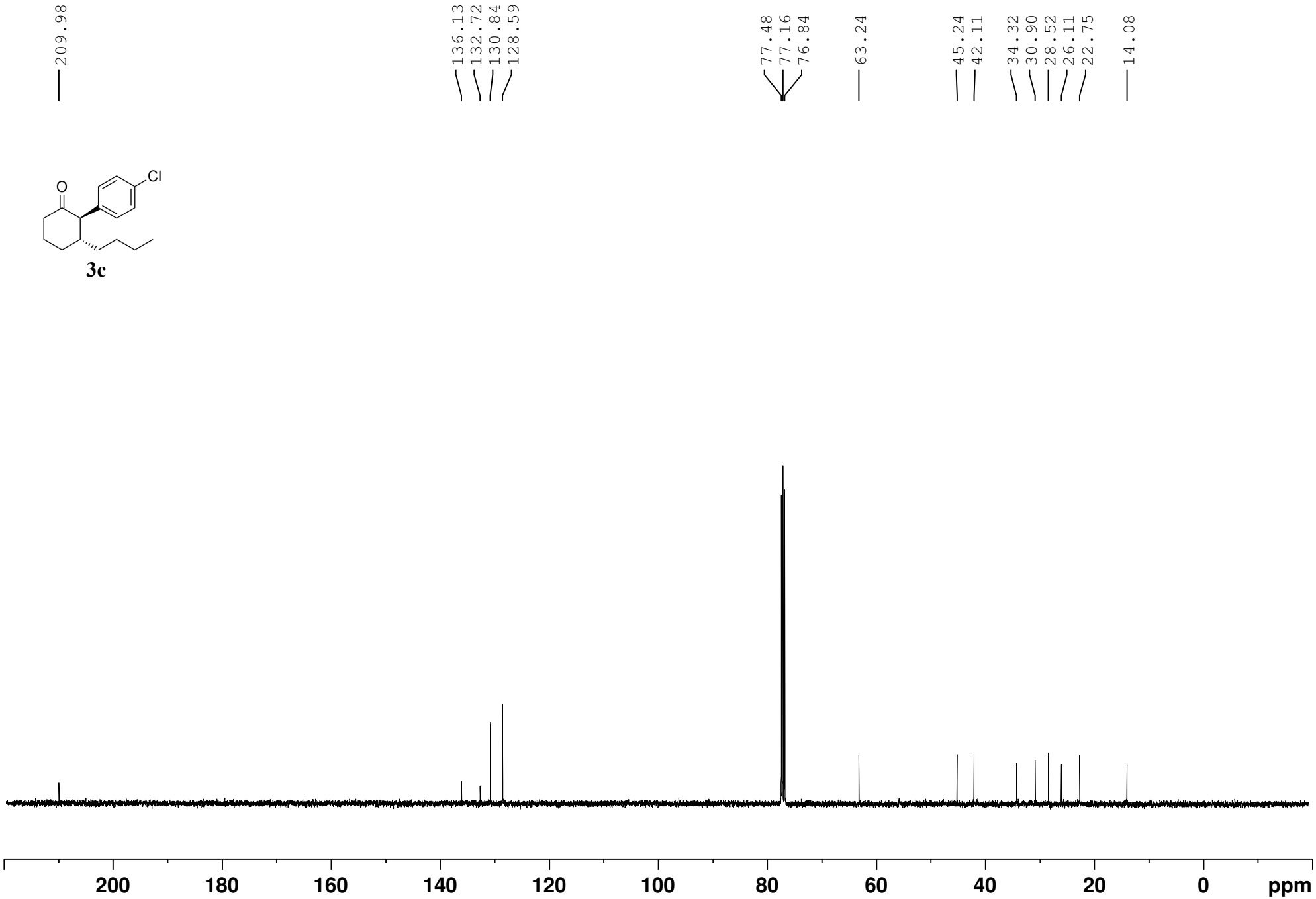
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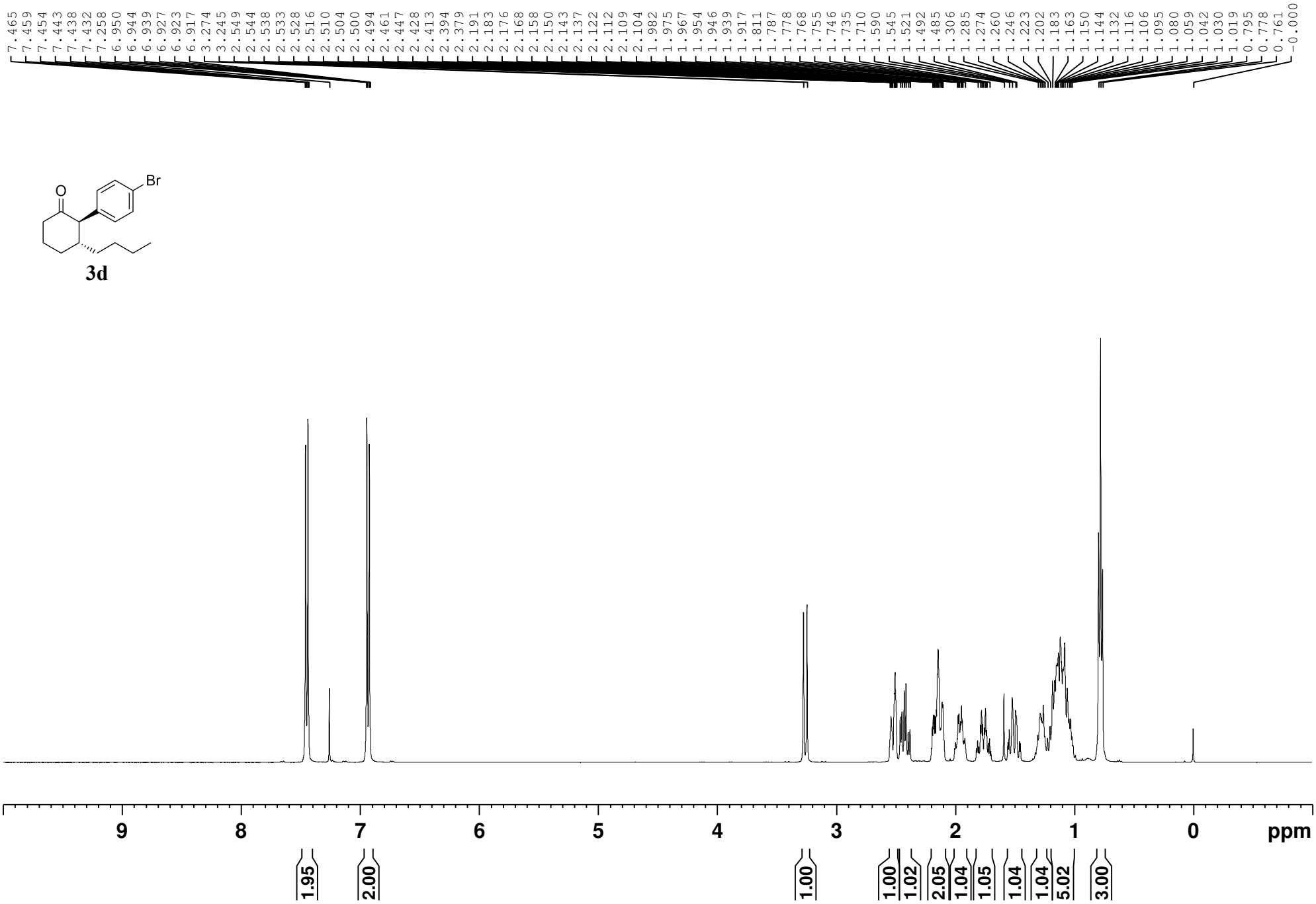
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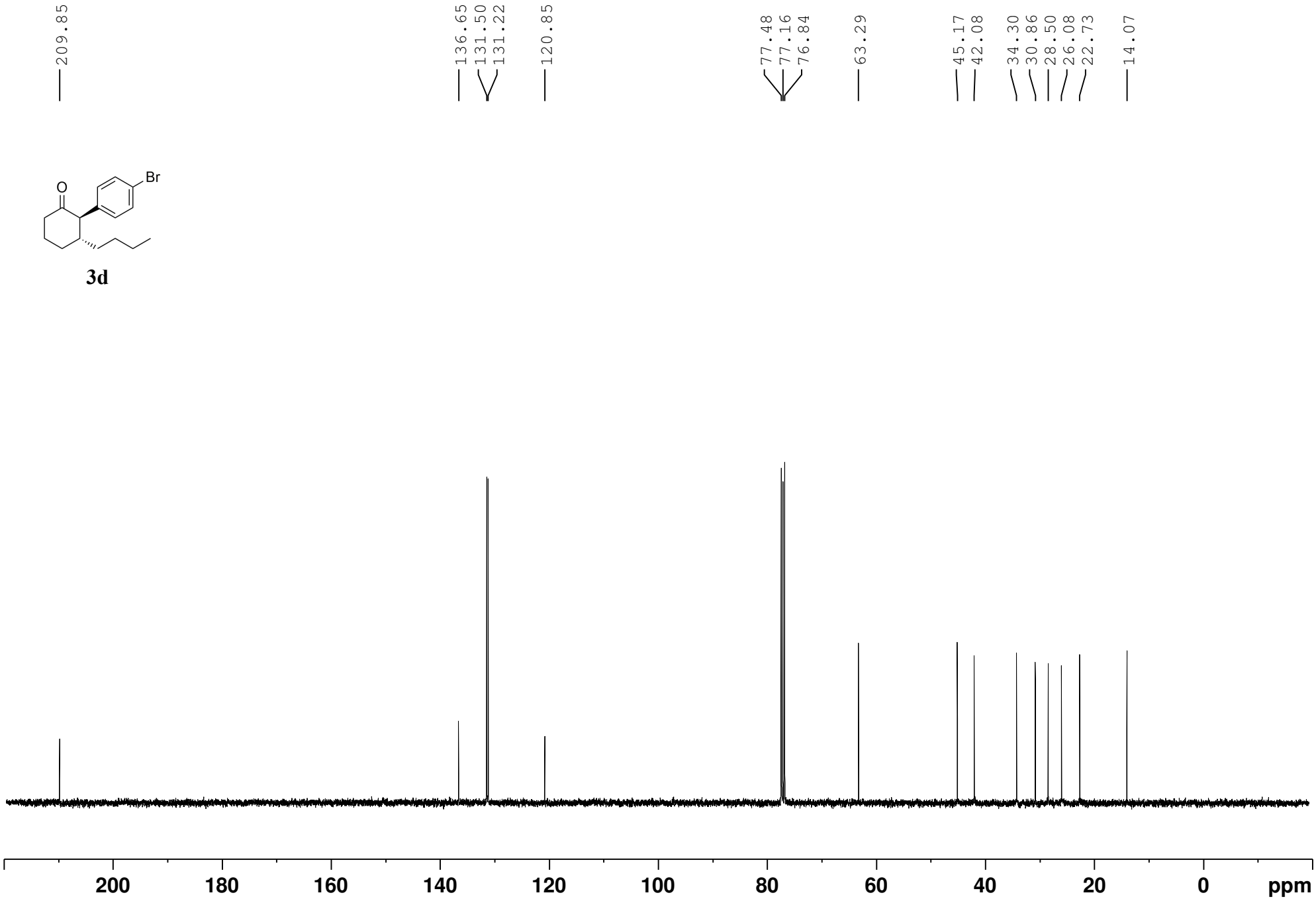
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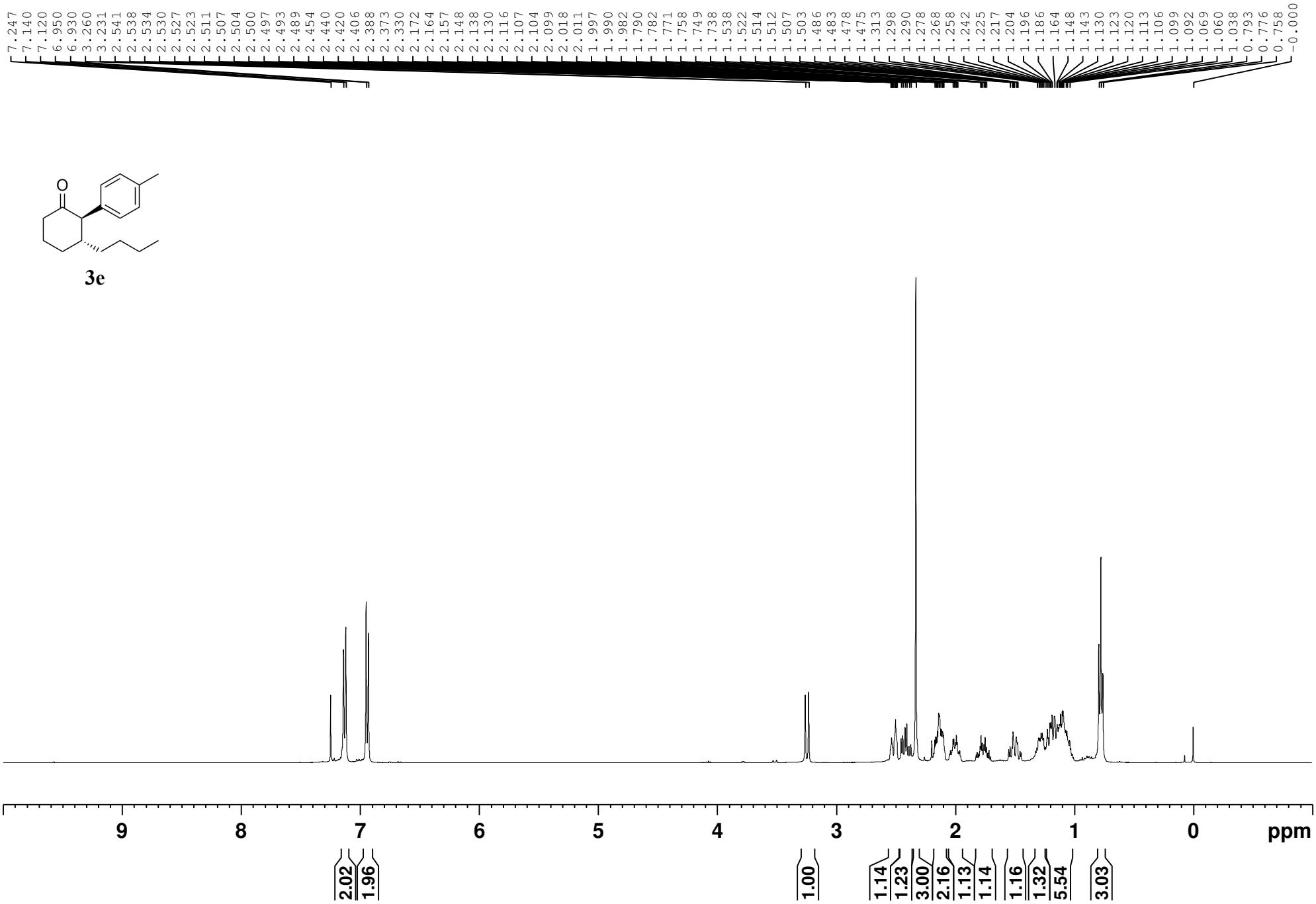
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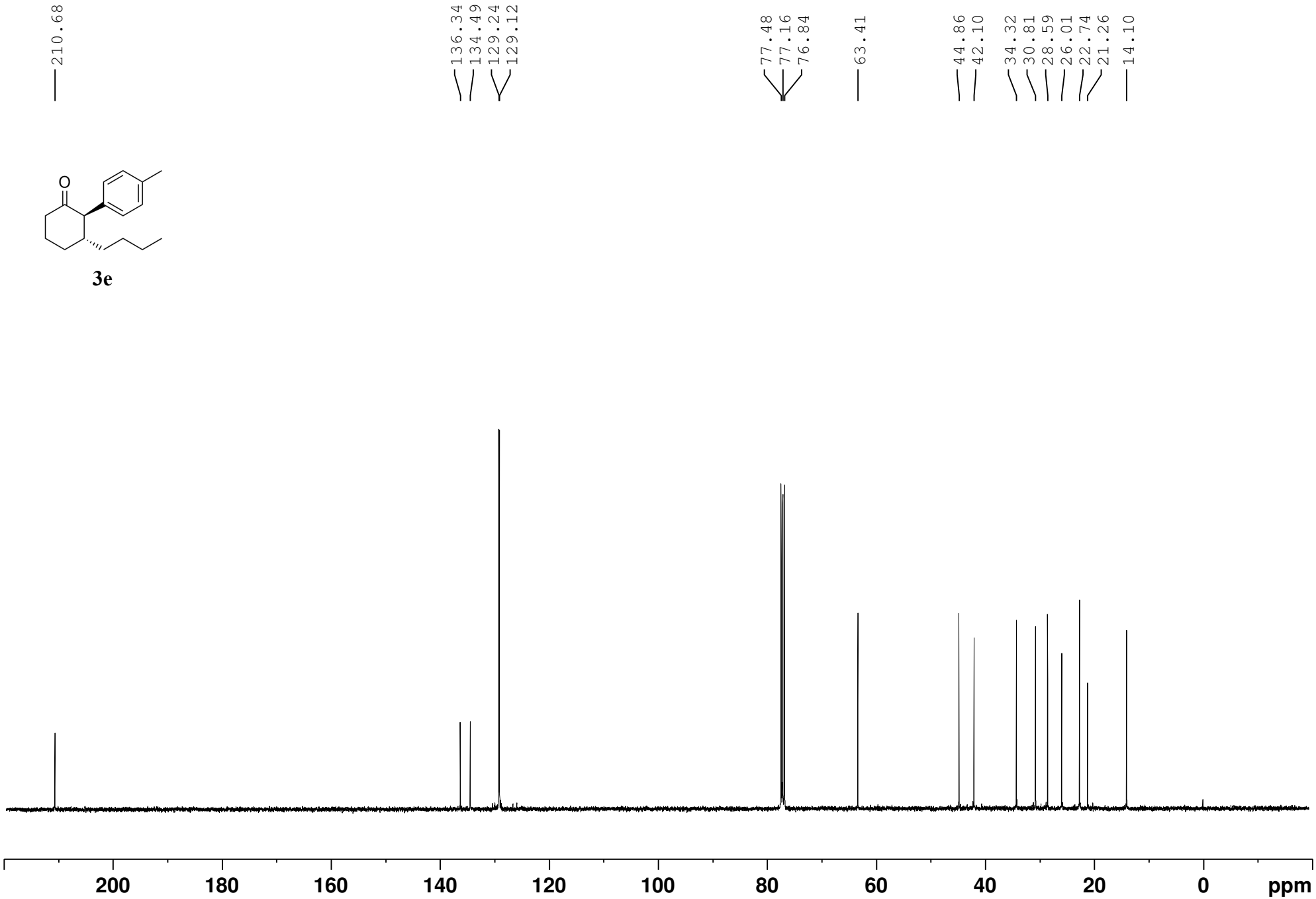
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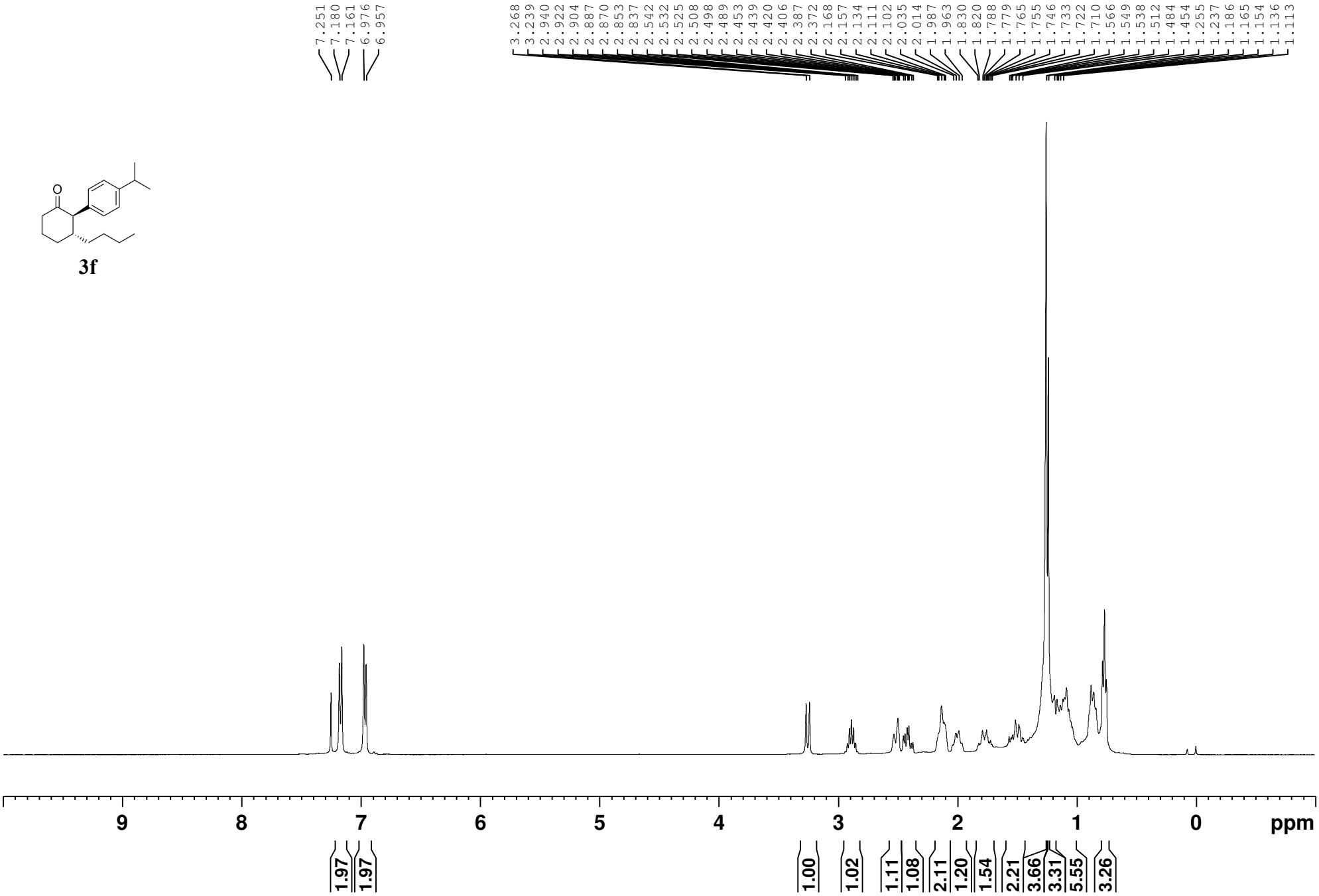
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1.746
1.733
1.722
1.710
1.566
1.549
1.538
1.512
1.484
1.454
1.255
1.237
1.186
1.165
1.154
1.136
1.113
O
3f
9
8
7
6
5
4
3
2
1
0
ppm
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1.97
1.00
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3.66
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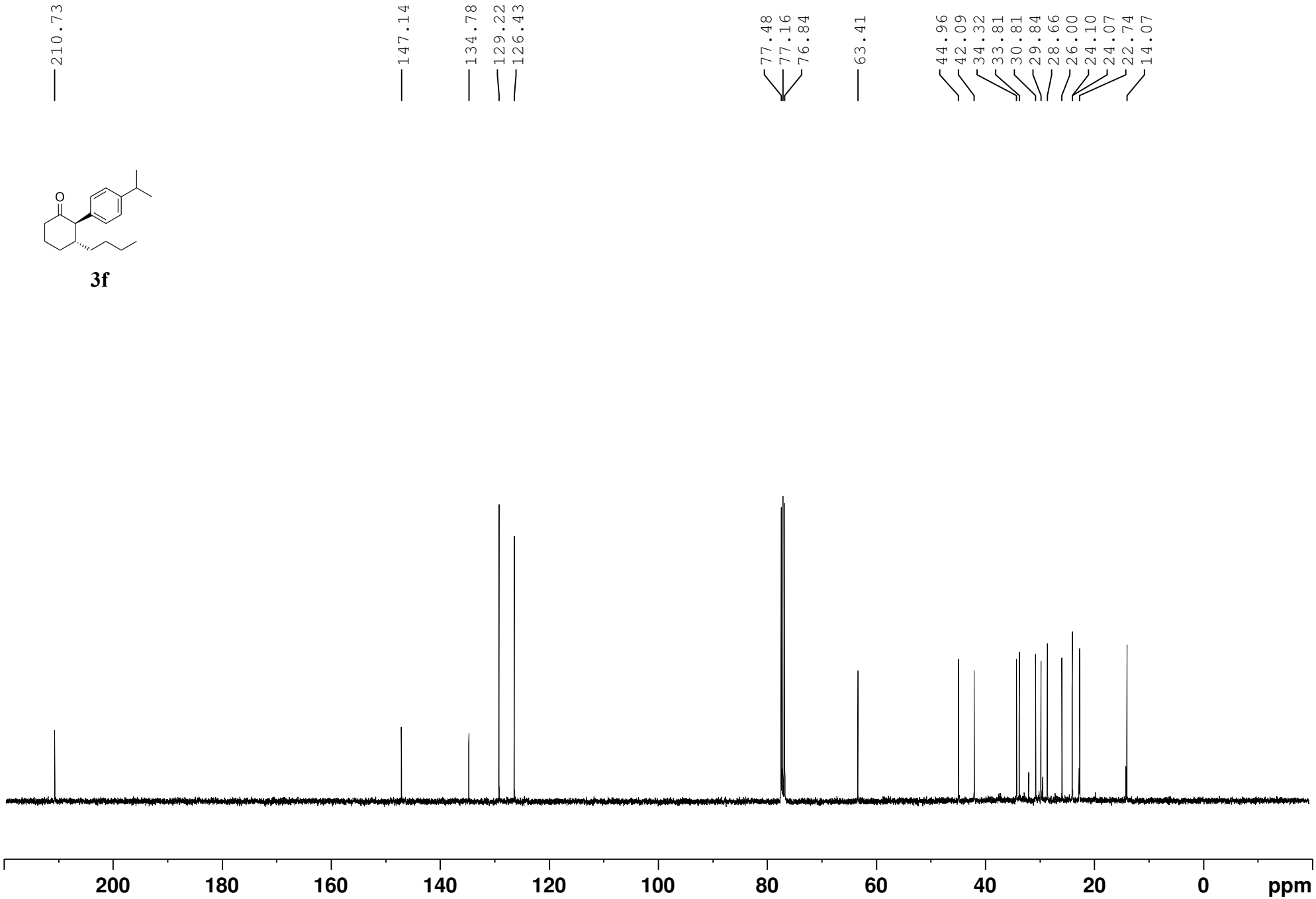
3.26

3f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42.09
34.32
33.81
30.81
29.84
28.66
26.00
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22.74
14.07
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80
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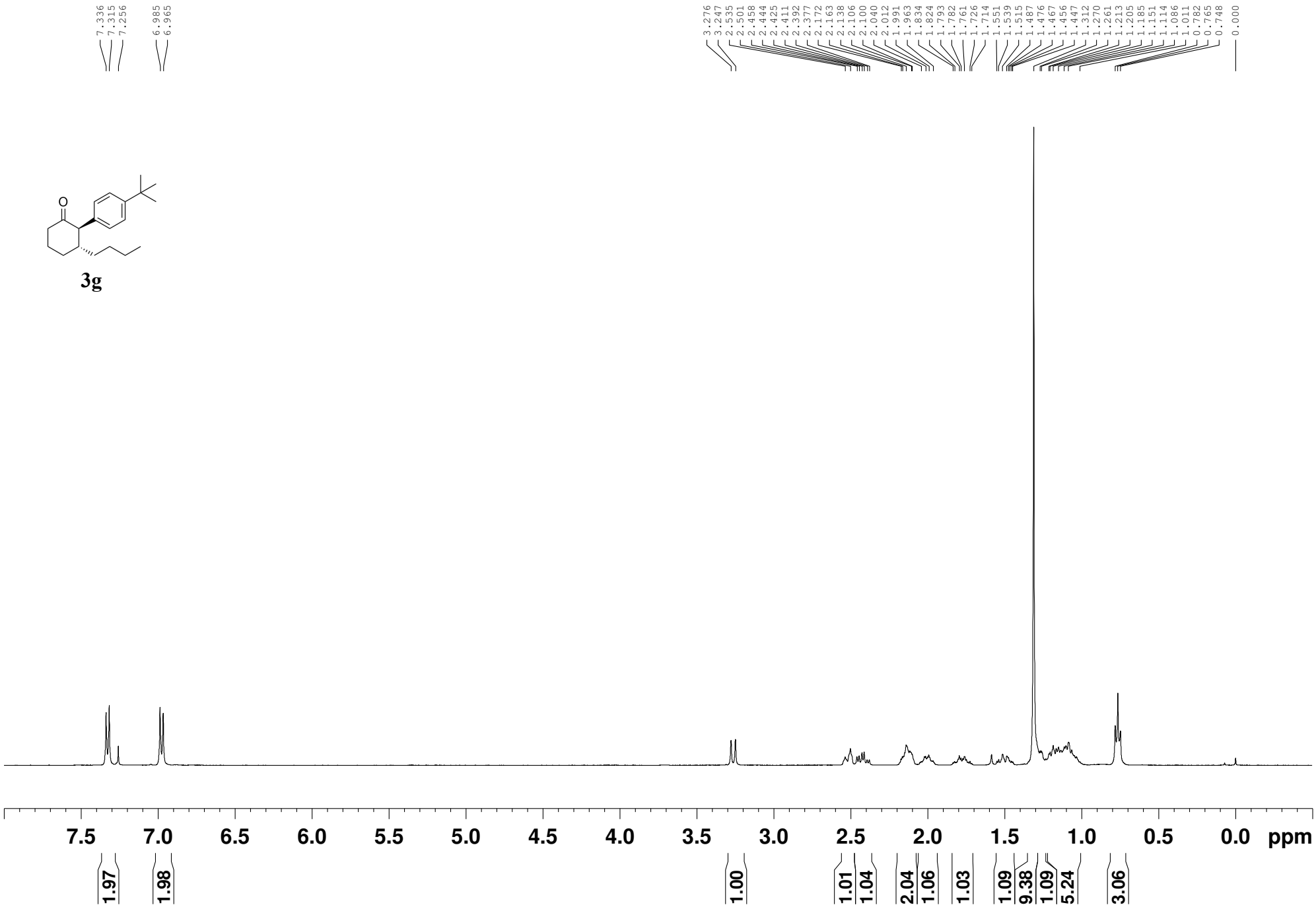
20
0
ppm

3g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2.411
2.392
2.377
2.172
2.163
2.138
2.106
2.100
2.040
2.012
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1.963
1.834
1.824
1.793
1.782
1.761
1.726
1.714
1.551
1.539
1.515
1.487
1.476
1.467
1.456
1.447
1.312
1.270
1.261
1.213
1.205
1.185
1.151
1.114
1.086
1.011
0.782
0.765
0.748
0.000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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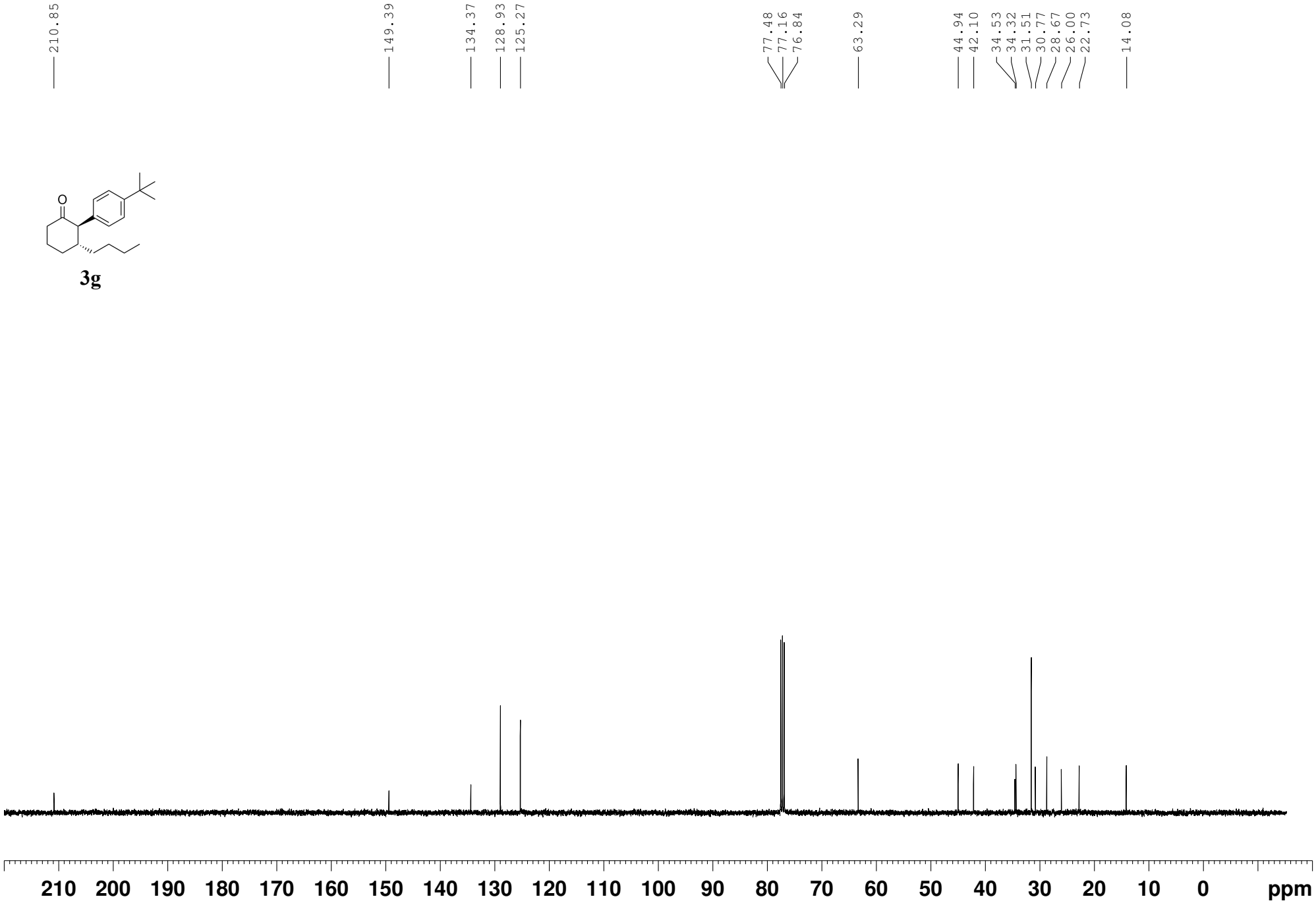
3g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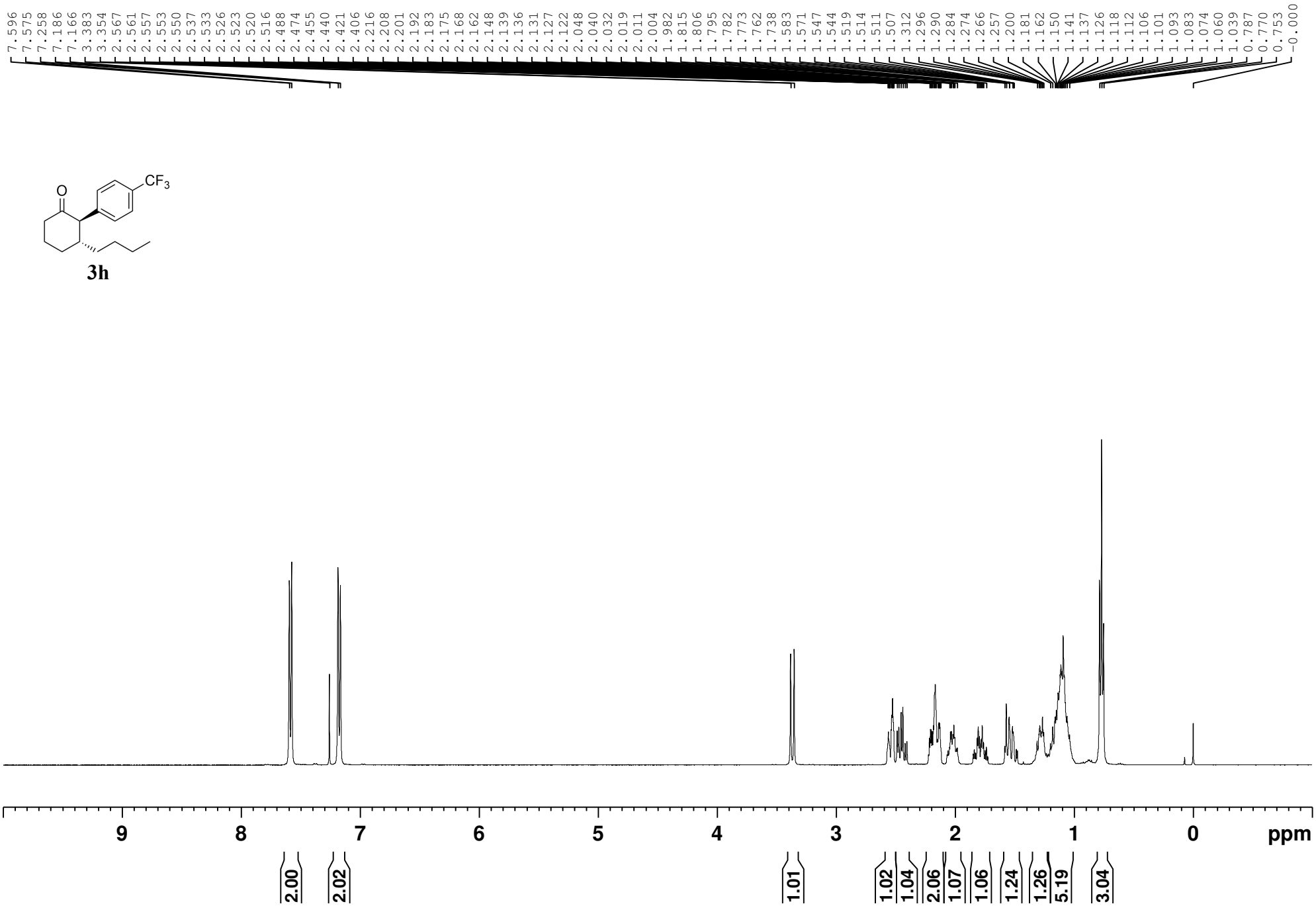
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2.537
2.533
2.526
2.523
2.520
2.516
2.488
2.474
2.455
2.440
2.421
2.406
2.216
2.208
2.201
2.192
2.183
2.175
2.168
2.162
2.148
2.139
2.136
2.131
2.127
2.122
2.048
2.040
2.032
2.019
2.011
2.004
1.982
1.815
1.806
1.795
1.782
1.773
1.762
1.738
1.583
1.571
1.547
1.544
1.519
1.514
1.511
1.507
1.312
1.296
1.290
1.284
1.274
1.266
1.257
1.200
1.181
1.162
1.150
1.141
1.137
1.126
1.118
1.112
1.106
1.101
1.093
1.083
1.074
1.060
1.039
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0.770
0.753
-0.000
O
CF3
3h
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
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1.07
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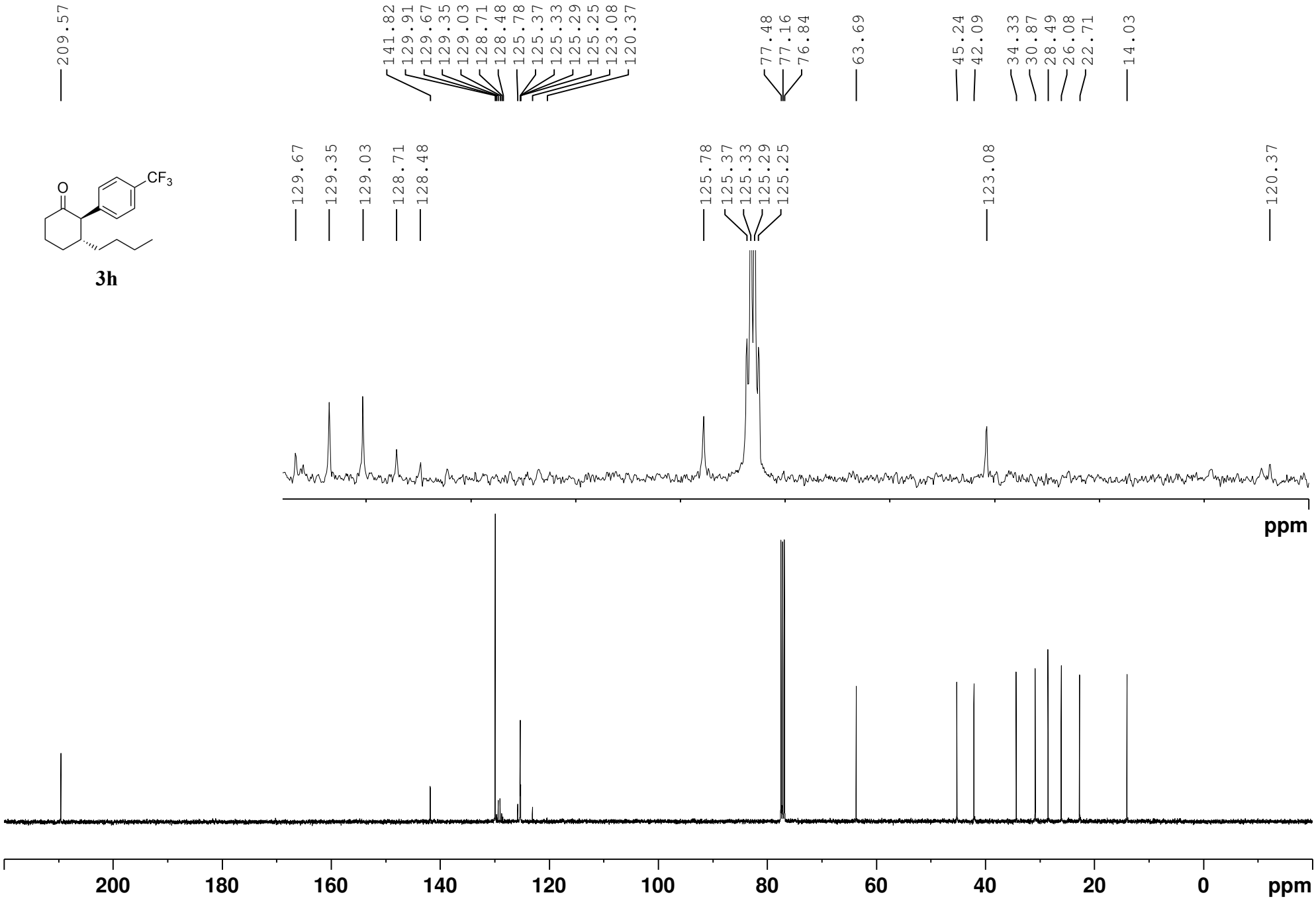
O
CF3

3h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128.48
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125.33
125.29
125.25
123.08
120.37
77.48
77.16
76.84
63.69
45.24
42.09
34.33
30.87
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22.71
14.03
ppm
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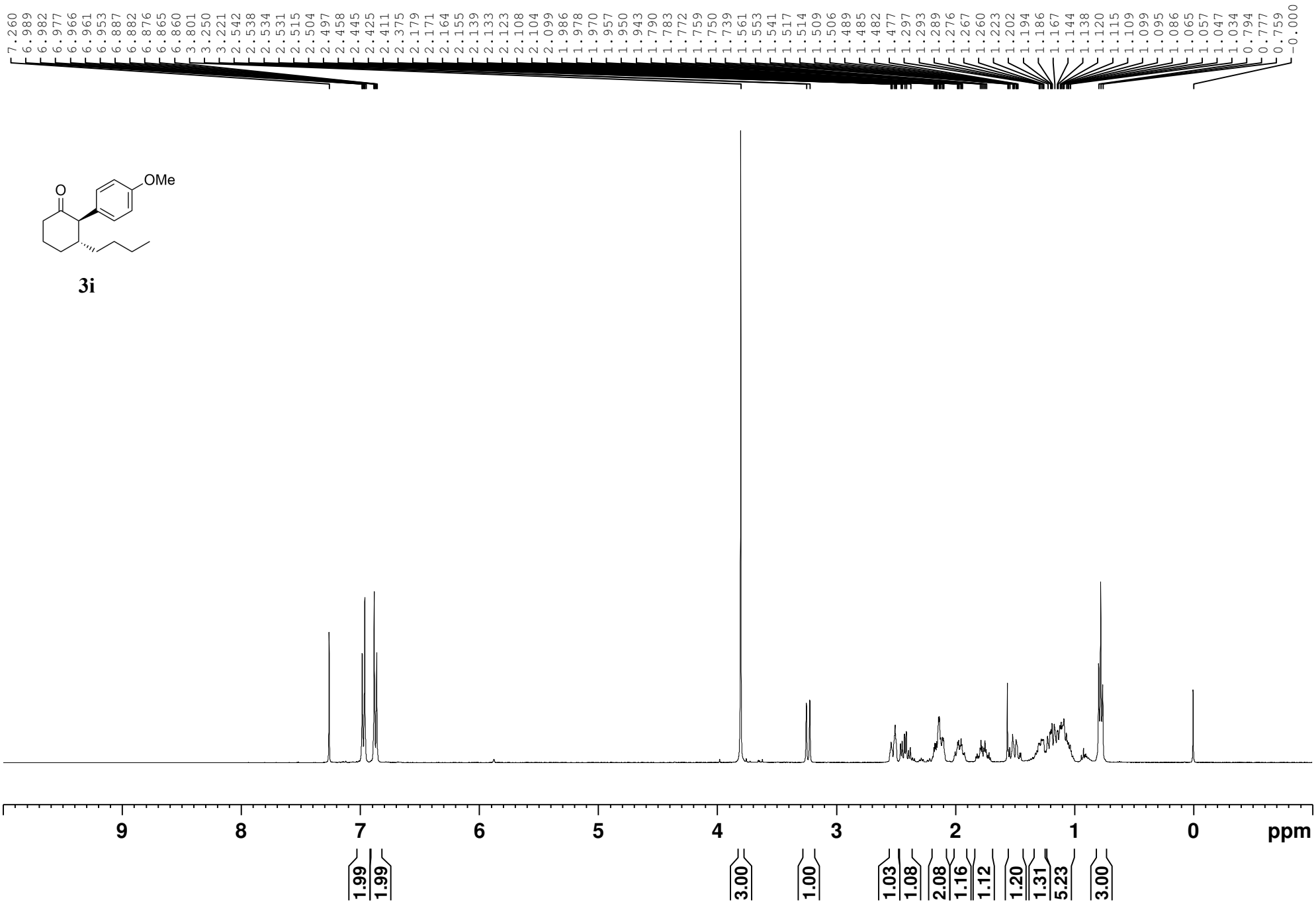
140
120
100
80
60
40
20
0
ppm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O
OMe
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.99
3.00
1.00
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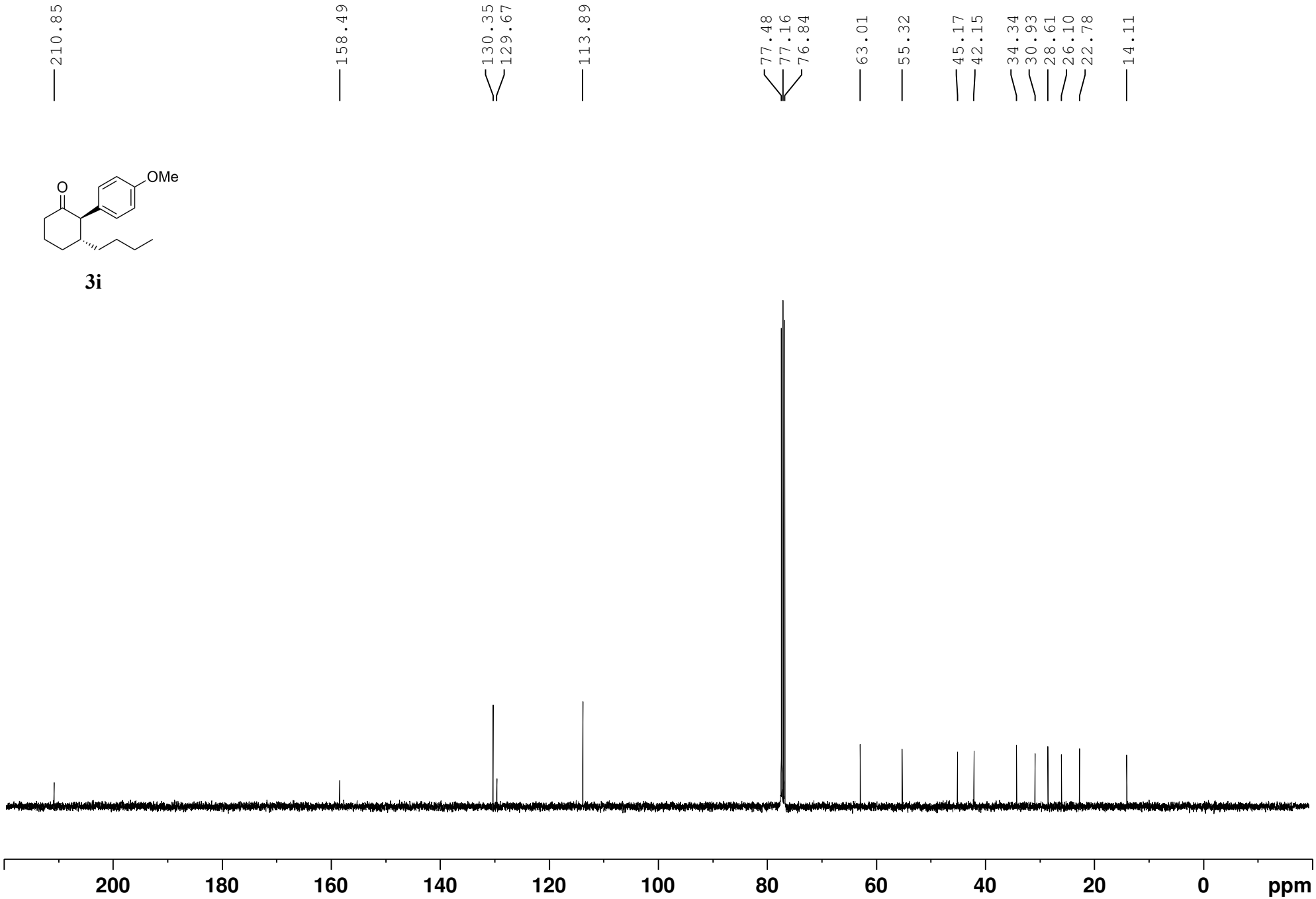
5.23
3.00

3i

O
OMe

3i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63.01
55.32
45.17
42.15
34.34
30.93
28.61
26.10
22.78
14.11
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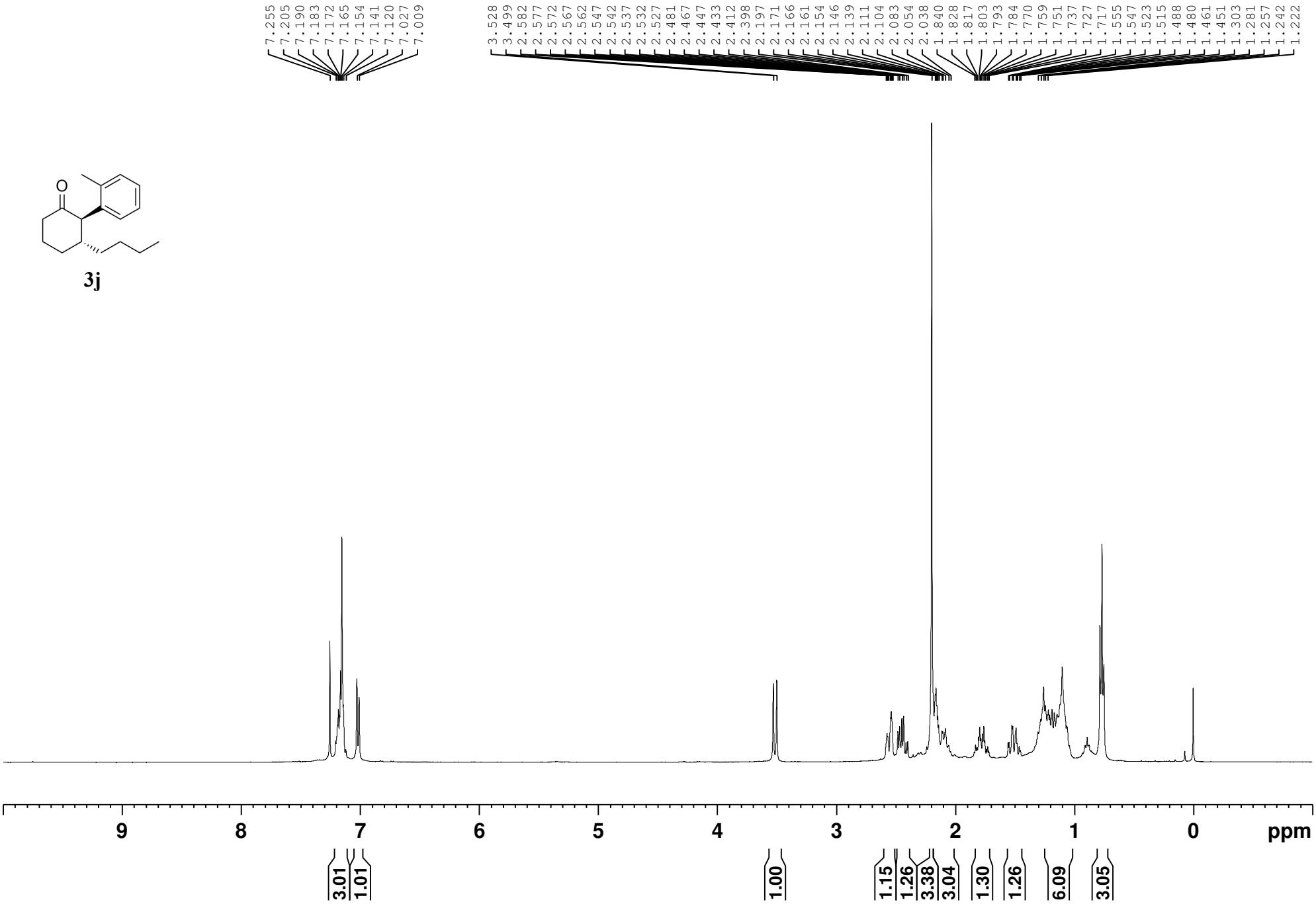
180
160
140
120
100
80
60
40
20
0
ppm

3j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7.154
7.141
7.120
7.027
7.009
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3.499
2.582
2.577
2.572
2.567
2.562
2.547
2.542
2.537
2.532
2.527
2.481
2.467
2.447
2.433
2.412
2.398
2.197
2.171
2.166
2.161
2.154
2.146
2.139
2.111
2.104
2.083
2.054
2.038
1.840
1.828
1.817
1.803
1.793
1.784
1.770
1.759
1.751
1.737
1.727
1.717
1.555
1.547
1.523
1.515
1.488
1.480
1.461
1.451
1.303
1.281
1.257
1.242
1.222
9
8
7
6
5
4
3
2
1
0
ppm
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1.00
1.15
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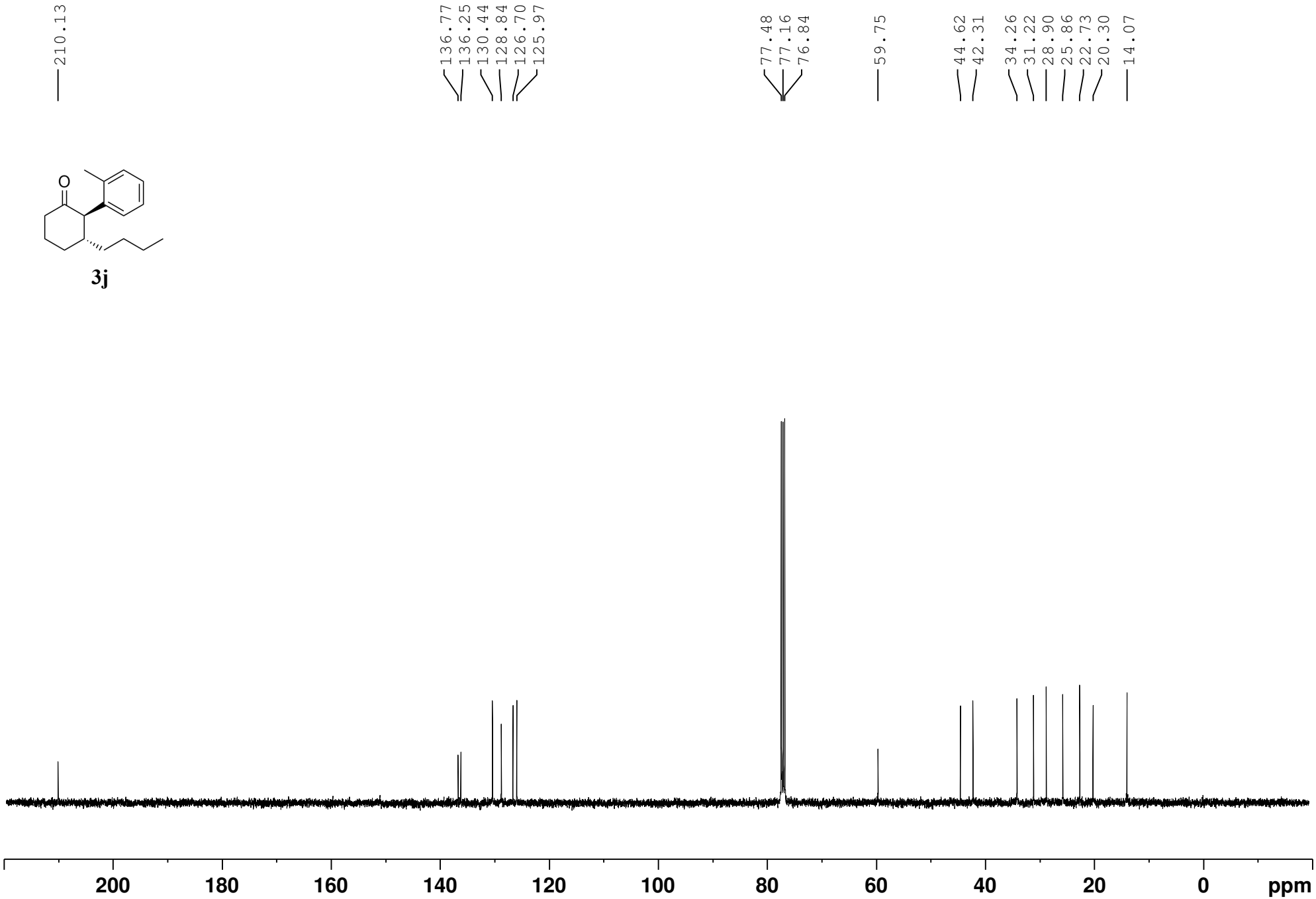
3.38
3.04
1.30
1.26
6.09
3.05

3j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76.84
59.75
44.62
42.31
34.26
31.22
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14.07
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160
140
120
100
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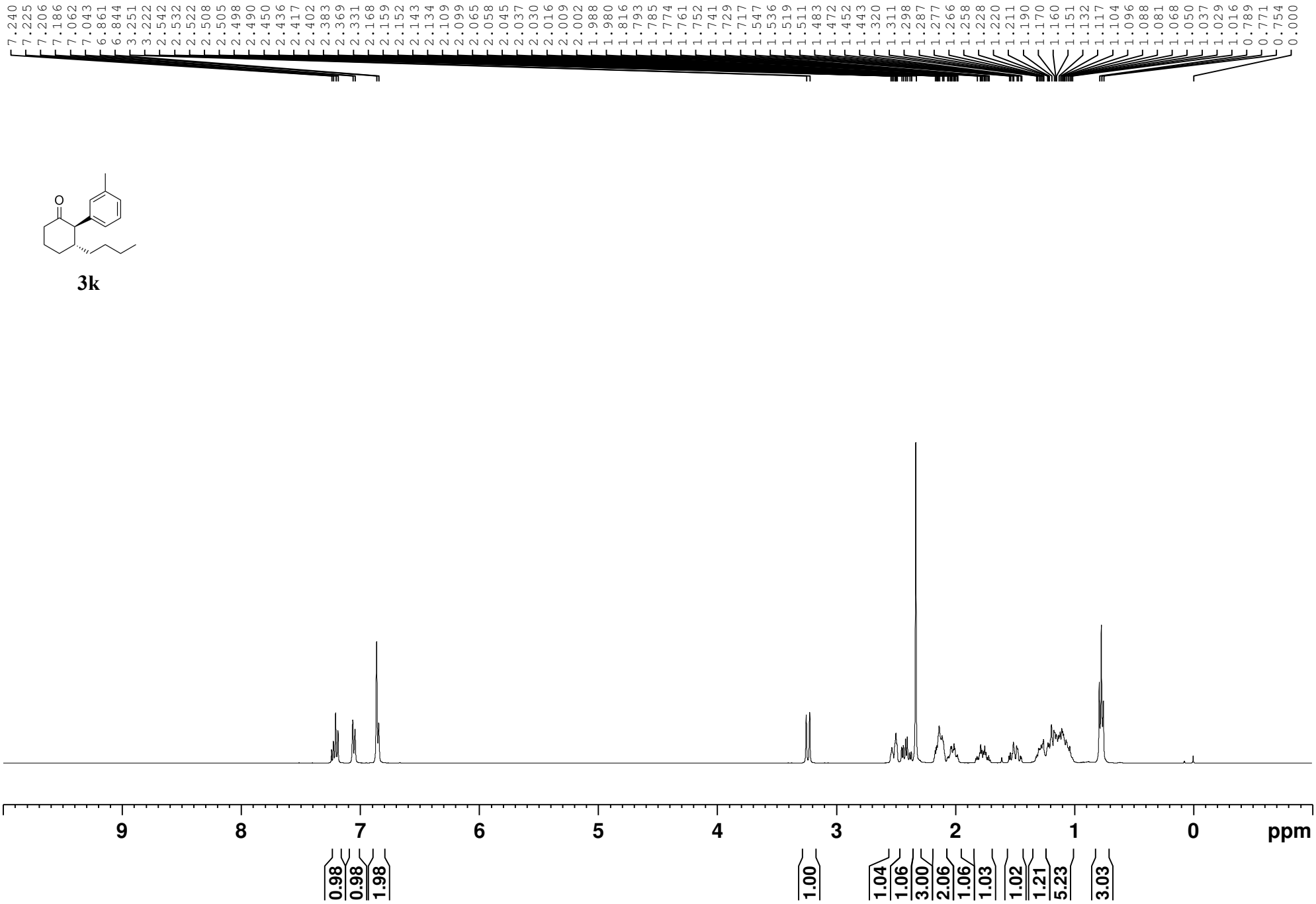
60
40
20
0
ppm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O
3k
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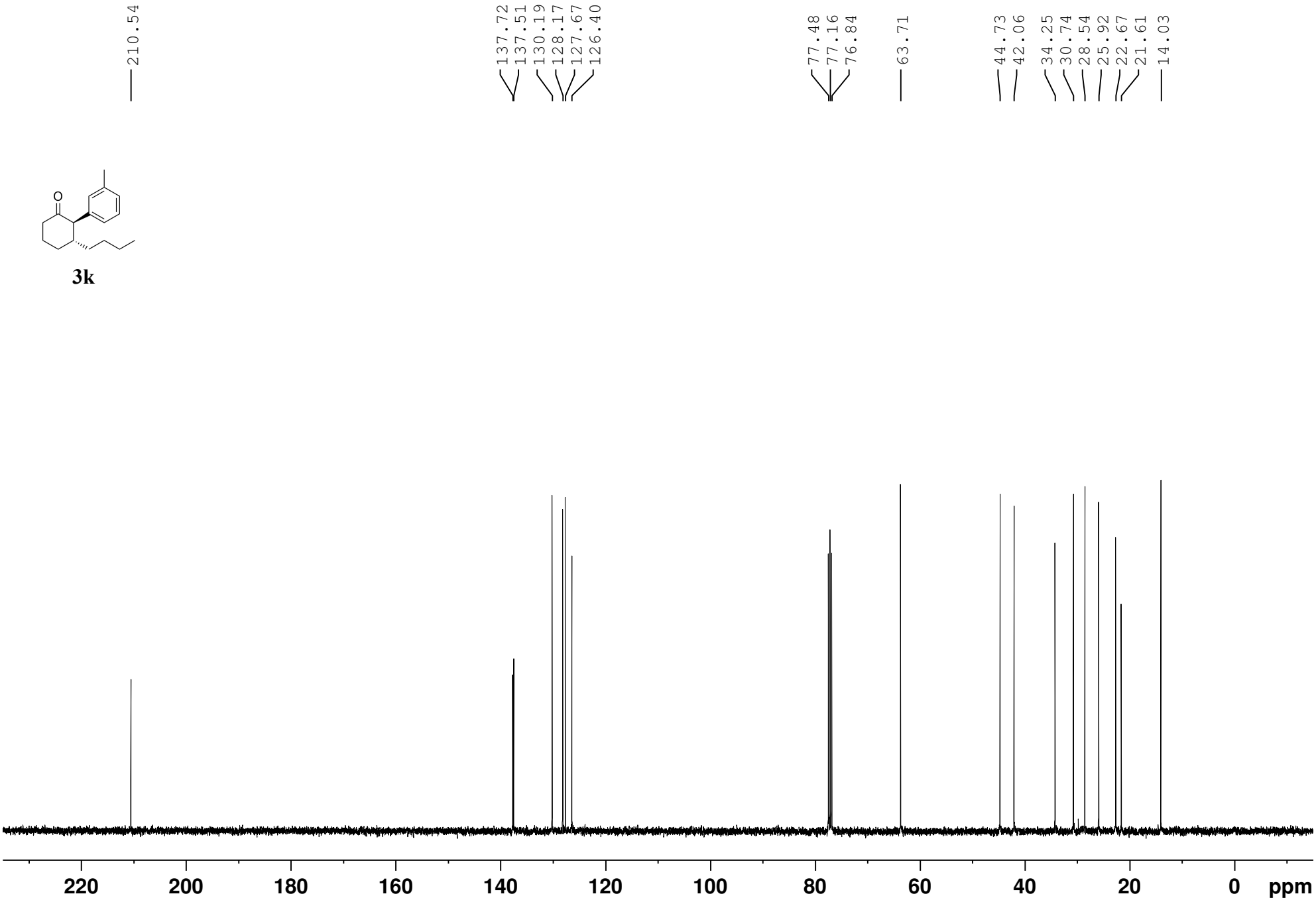
0.98 0.98 1.98 1.00 1.04 1.06 3.00 2.06 1.06 1.03 1.02 1.21 5.23 3.03

3k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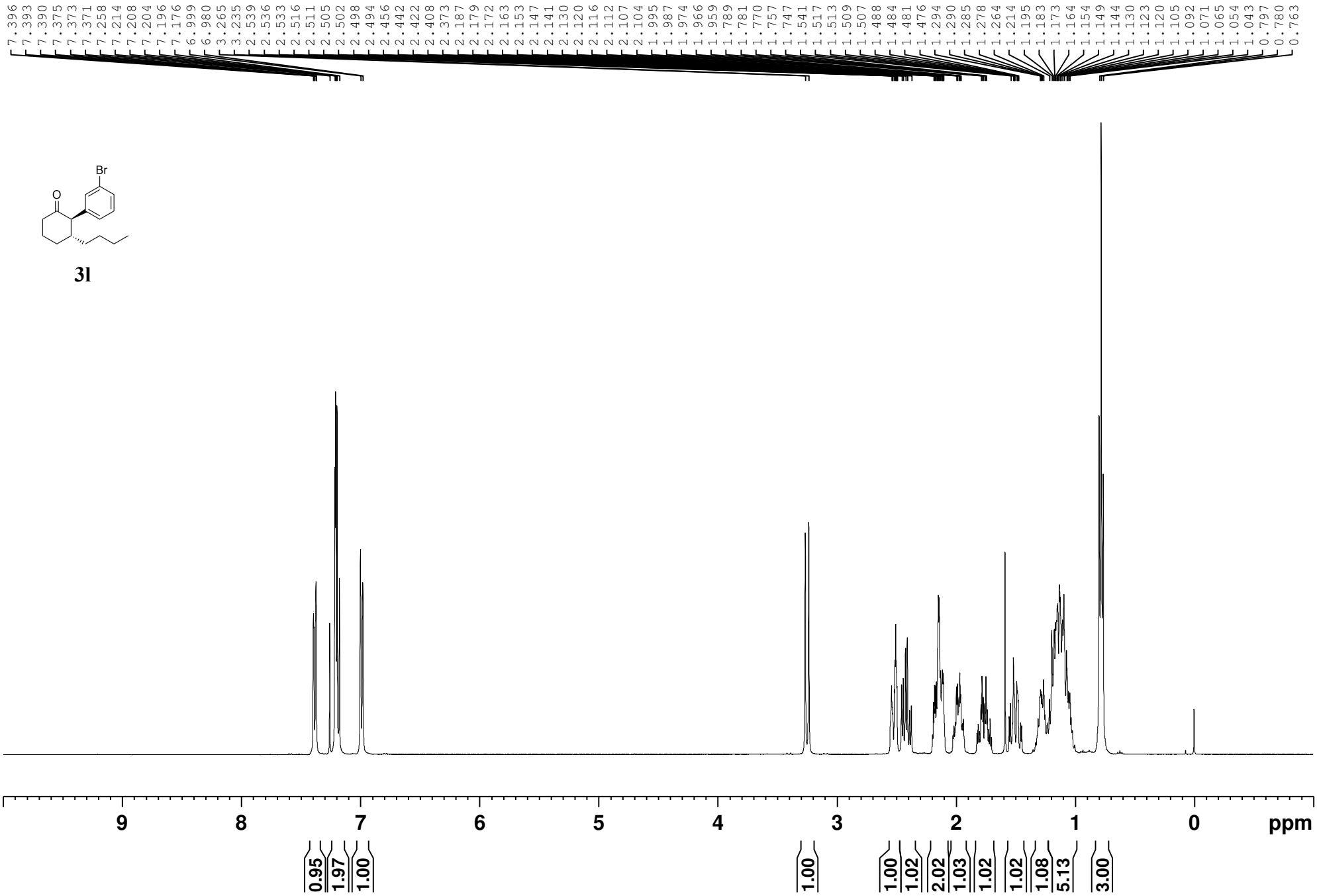
77.16
76.84
63.71
44.73
42.06
34.25
30.74
28.54
25.92
22.67
21.61
14.03
220
200
180
160
140
120
100
80
60
40
20
0
ppm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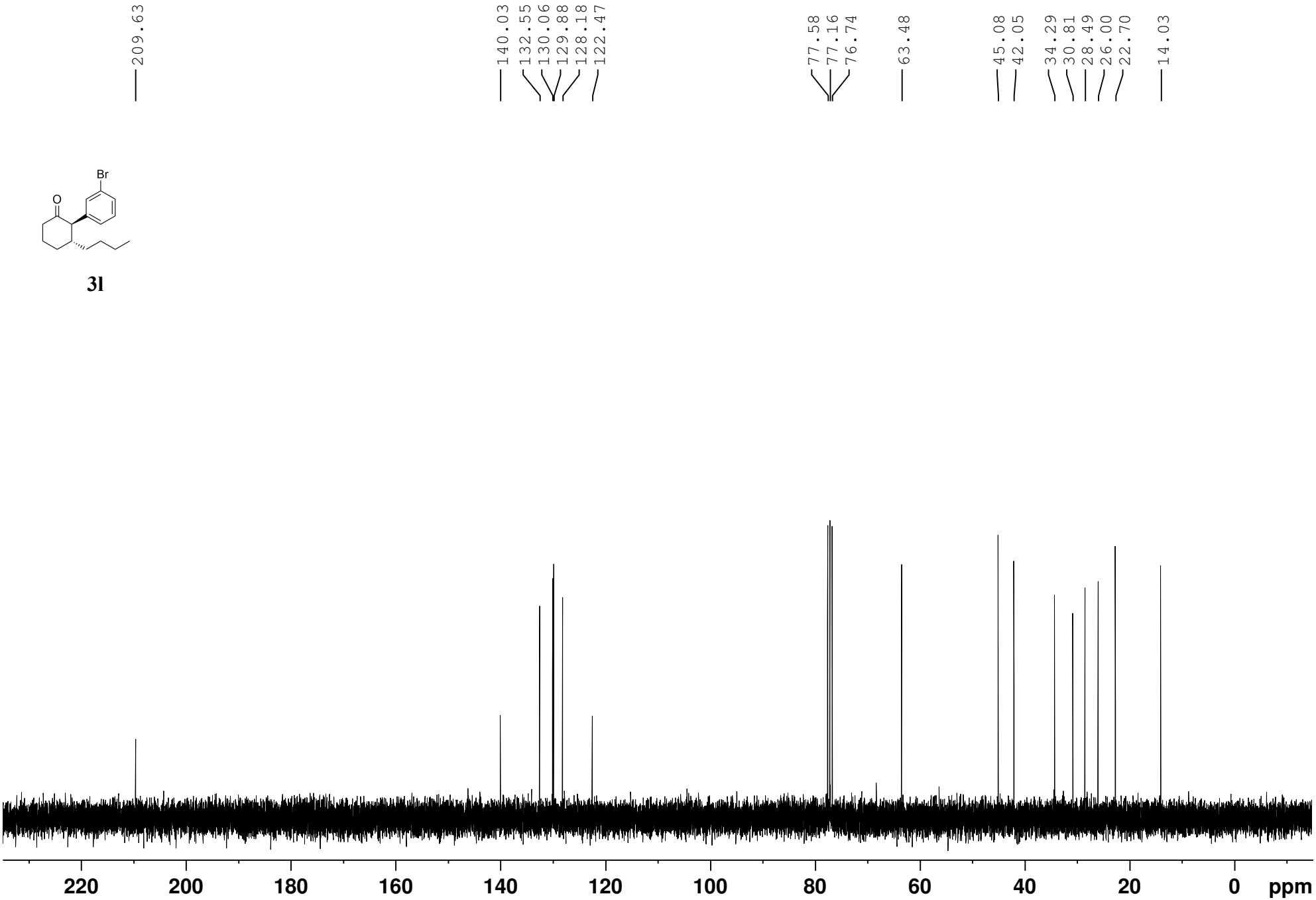
Br
O
9
8
7
6
5
4
3
2
1
0
ppm
0.95
1.97
1.00
1.00
1.00
1.02
2.02
1.03
1.02
1.02
1.08
5.13
3.00

3l

Br
O

3l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77.16
76.74
63.48
45.08
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30.81
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22.70
14.03
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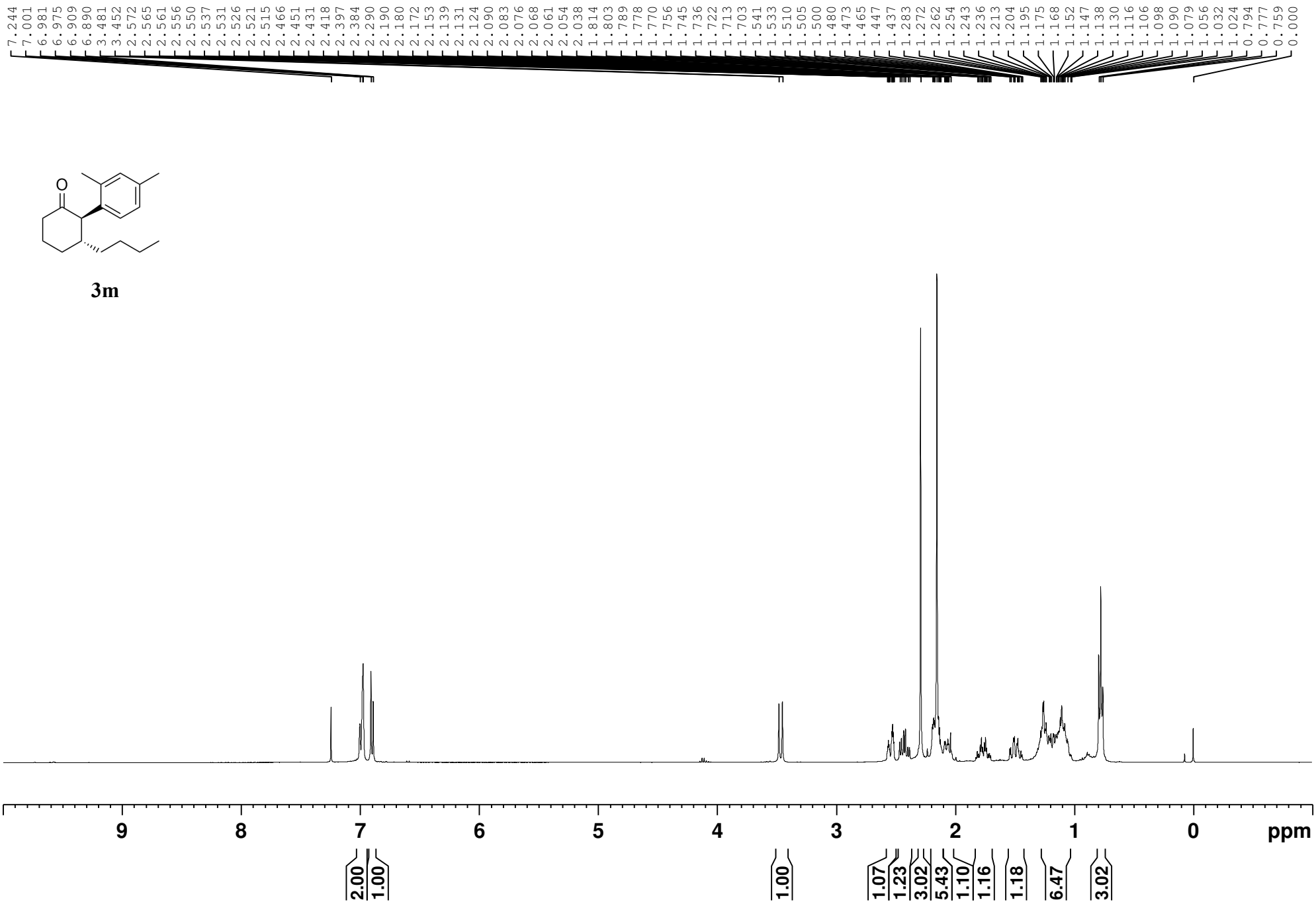
200
180
160
140
120
100
80
60
40
20
0
ppm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O
3m
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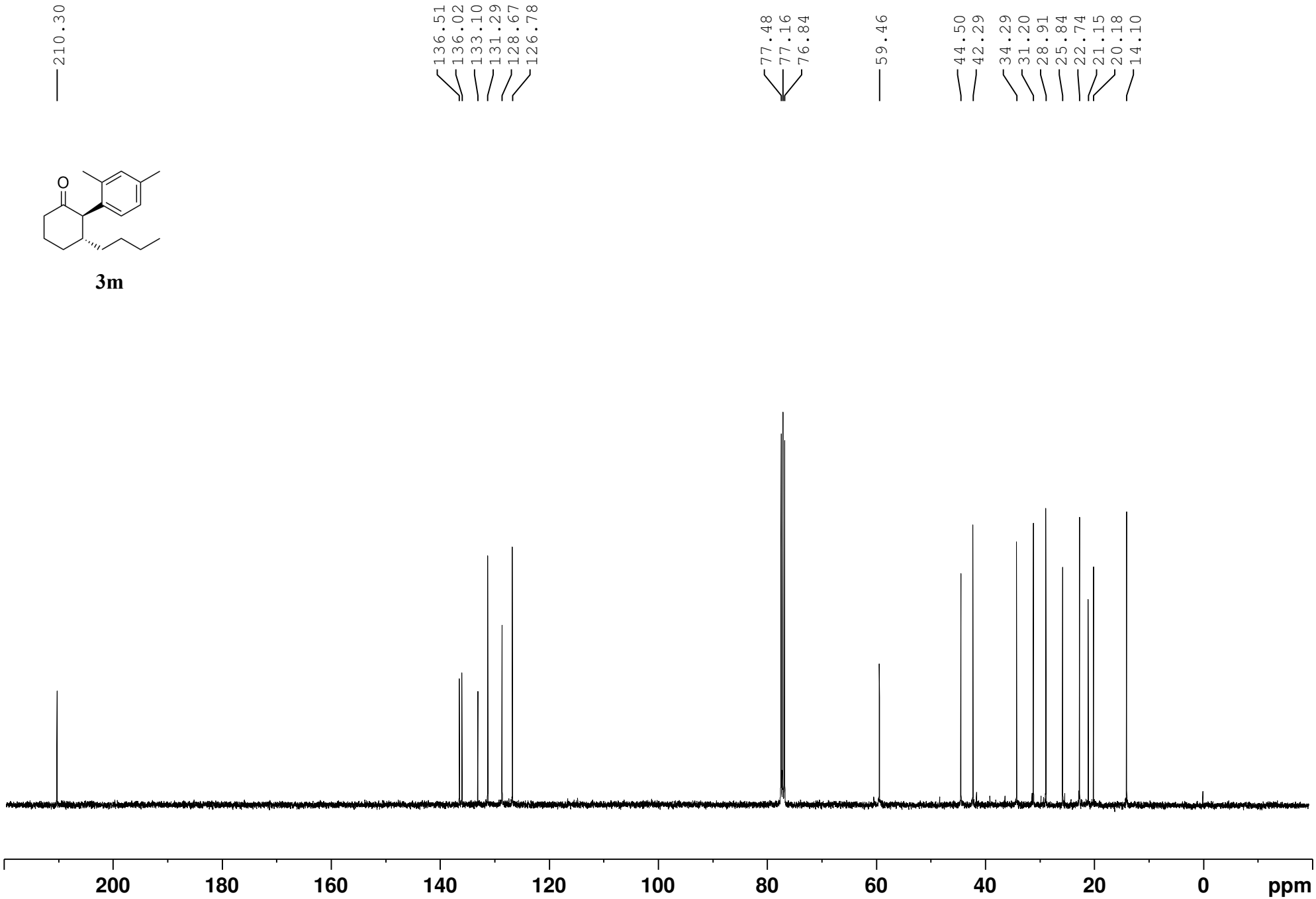
2.00 1.00 1.00 1.07 1.23 3.02 5.43 1.10 1.16 1.18 6.47 3.02

3m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77.16
76.84
59.46
44.50
42.29
34.29
31.20
28.91
25.84
22.74
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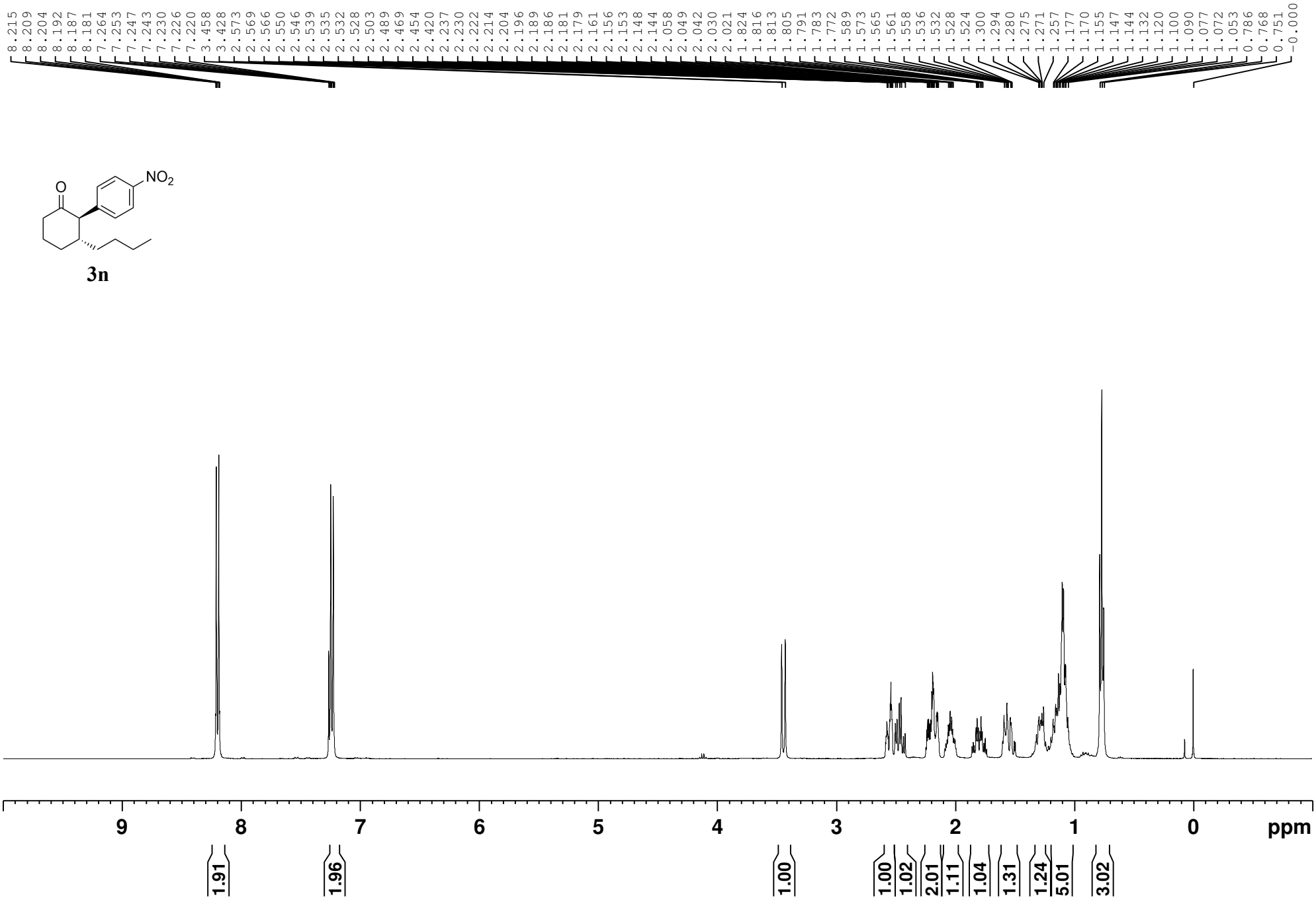
20.18
14.10
200
180
160
140
120
100
80
60
40
20
0
ppm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7.247
7.243
7.230
7.226
7.220
3.458
3.428
2.573
2.569
2.566
2.550
2.546
2.539
2.535
2.532
2.528
2.503
2.489
2.469
2.454
2.420
2.237
2.230
2.222
2.214
2.204
2.196
2.189
2.186
2.181
2.179
2.161
2.156
2.153
2.148
2.144
2.058
2.049
2.042
2.030
2.021
1.824
1.816
1.813
1.805
1.791
1.783
1.772
1.589
1.573
1.565
1.561
1.558
1.536
1.532
1.528
1.524
1.300
1.294
1.280
1.275
1.271
1.257
1.177
1.170
1.155
1.147
1.144
1.132
1.120
1.100
1.090
1.077
1.072
1.053
0.786
0.768
0.751
-0.000
O
NO2
9
8
7
6
5
4
3
2
1
0
ppm
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1.96
1.00
1.00
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1.11
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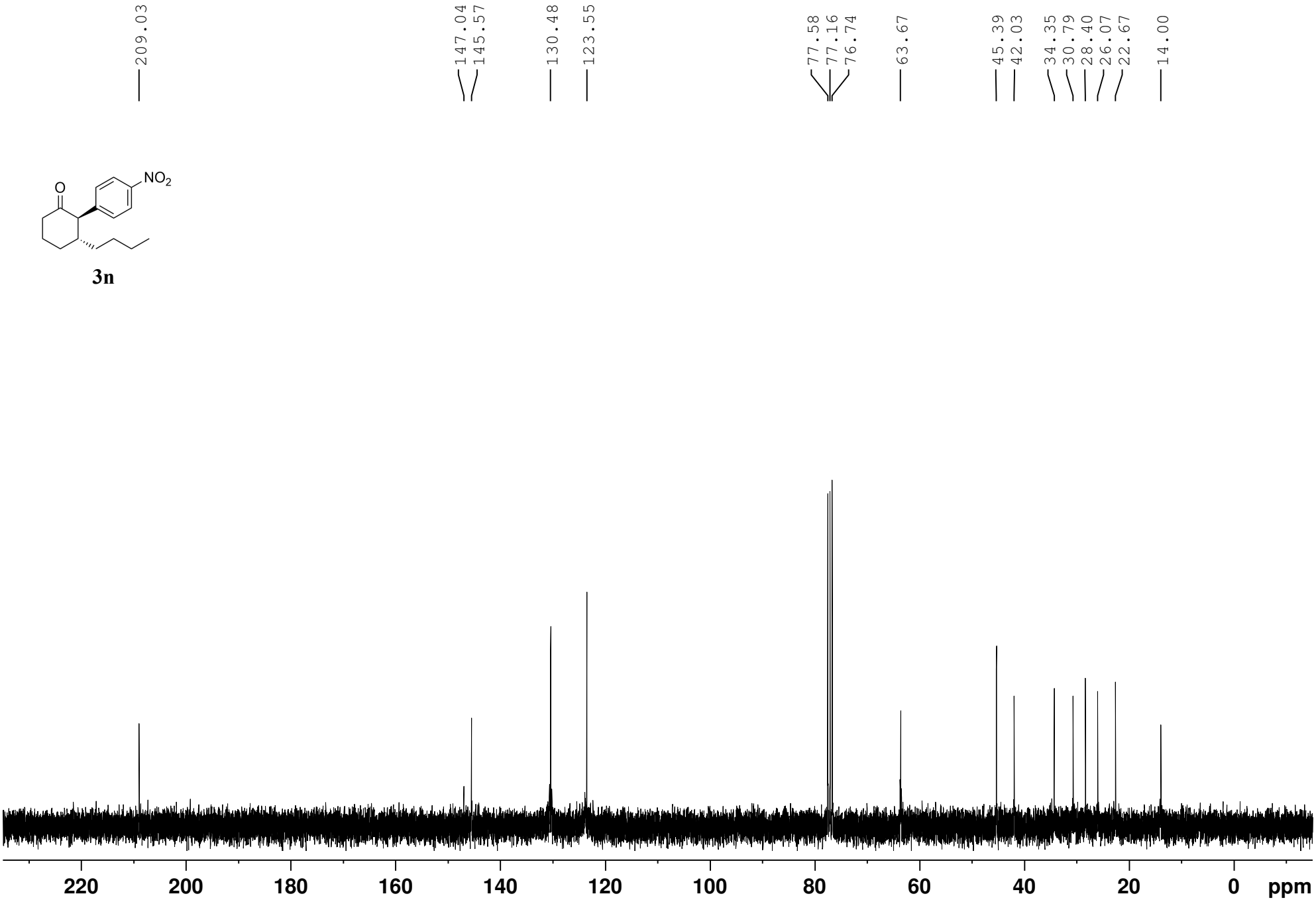
1.24
5.01
3.02

3n

O
NO2

3n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77.16
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45.39
42.03
34.35
30.79
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14.00
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200
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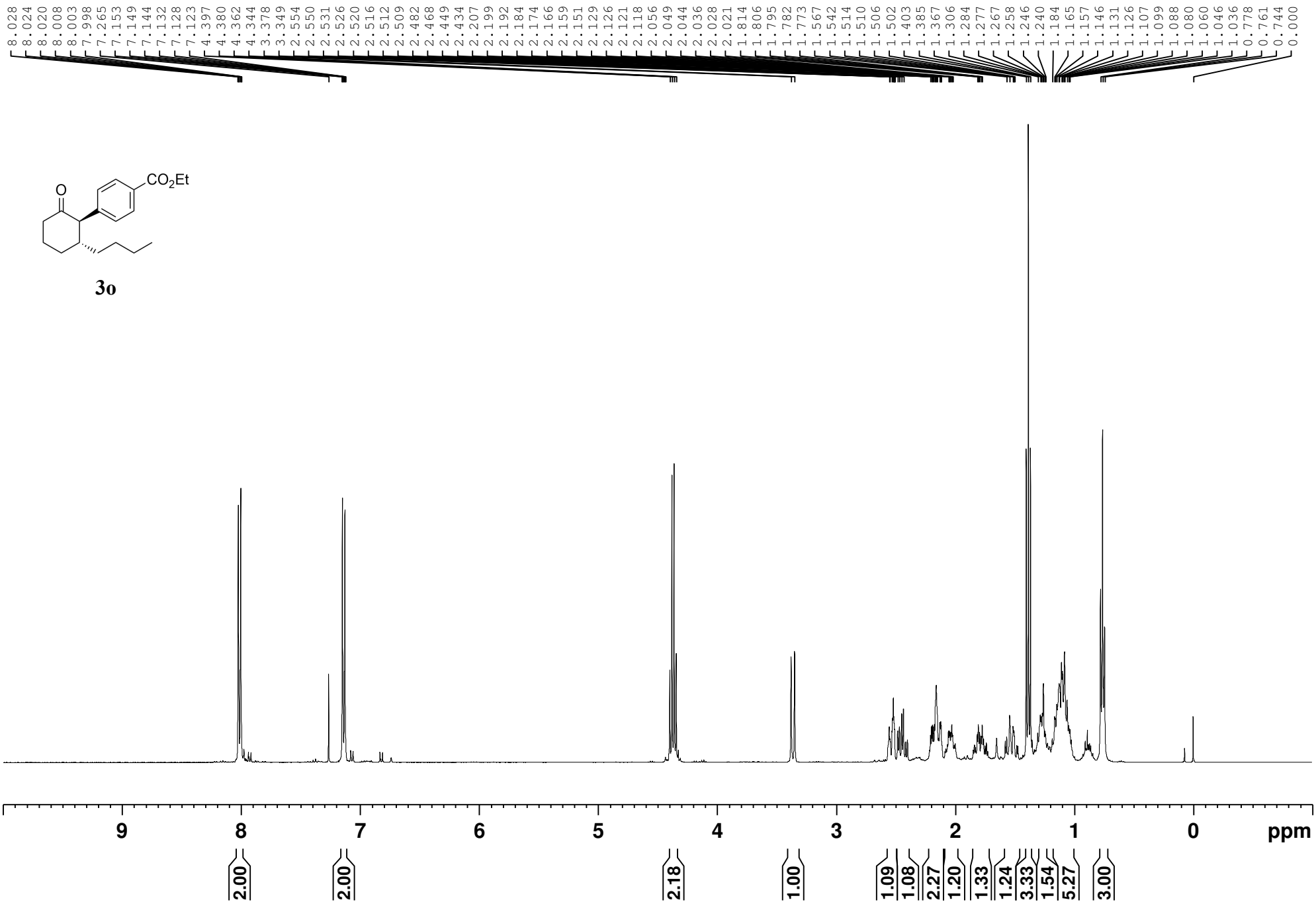
160
140
120
100
80
60
40
20
0
ppm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O
CO2Et
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
2.18
1.00
1.09
1.08
2.27
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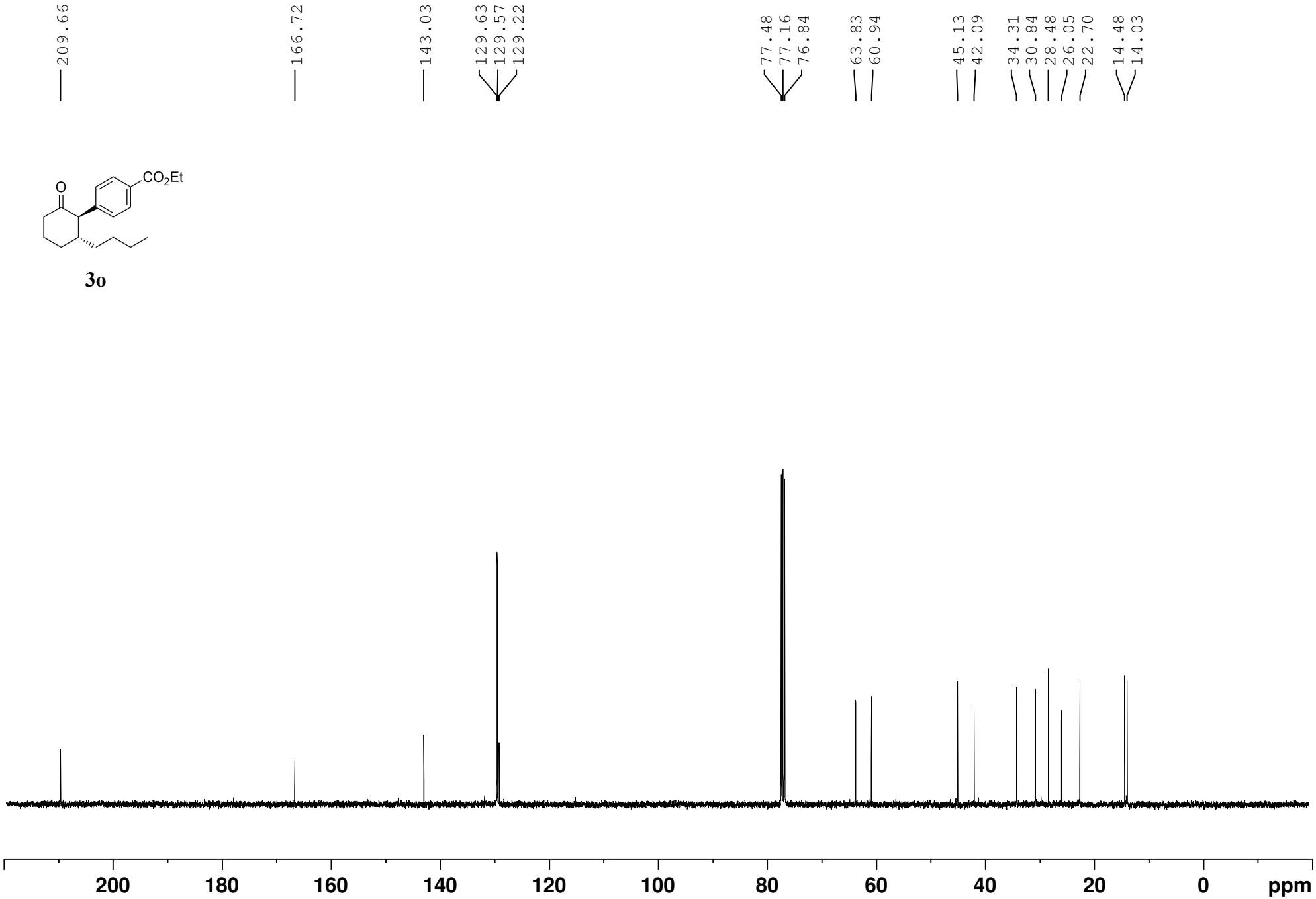
1.33
1.24
3.33
1.54
5.27
3.00

3o

O
CO2Et

3o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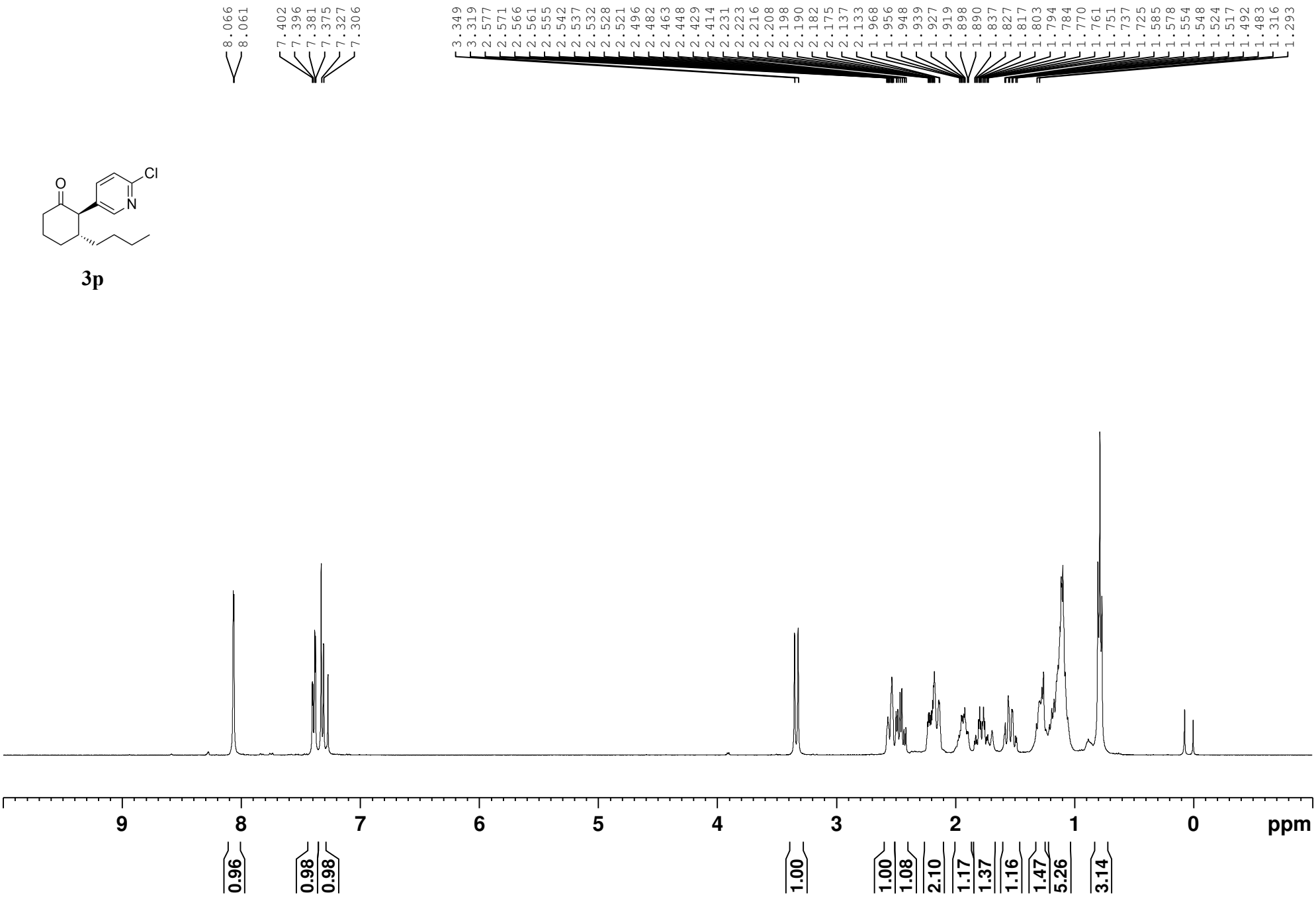
34.31
30.84
28.48
26.05
22.70
14.48
14.03
200
180
160
140
120
100
80
60
40
20
0
ppm

O
Cl
N

3p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2.566
2.561
2.555
2.542
2.537
2.532
2.528
2.521
2.496
2.482
2.463
2.448
2.429
2.414
2.231
2.223
2.216
2.208
2.198
2.190
2.182
2.175
2.137
2.133
1.968
1.956
1.948
1.939
1.927
1.919
1.898
1.890
1.837
1.827
1.817
1.803
1.794
1.784
1.770
1.761
1.751
1.737
1.725
1.585
1.578
1.554
1.548
1.524
1.517
1.492
1.483
1.316
1.293
9
8
7
6
5
4
3
2
1
0
ppm
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0.98
0.98
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2.10
1.17
1.37
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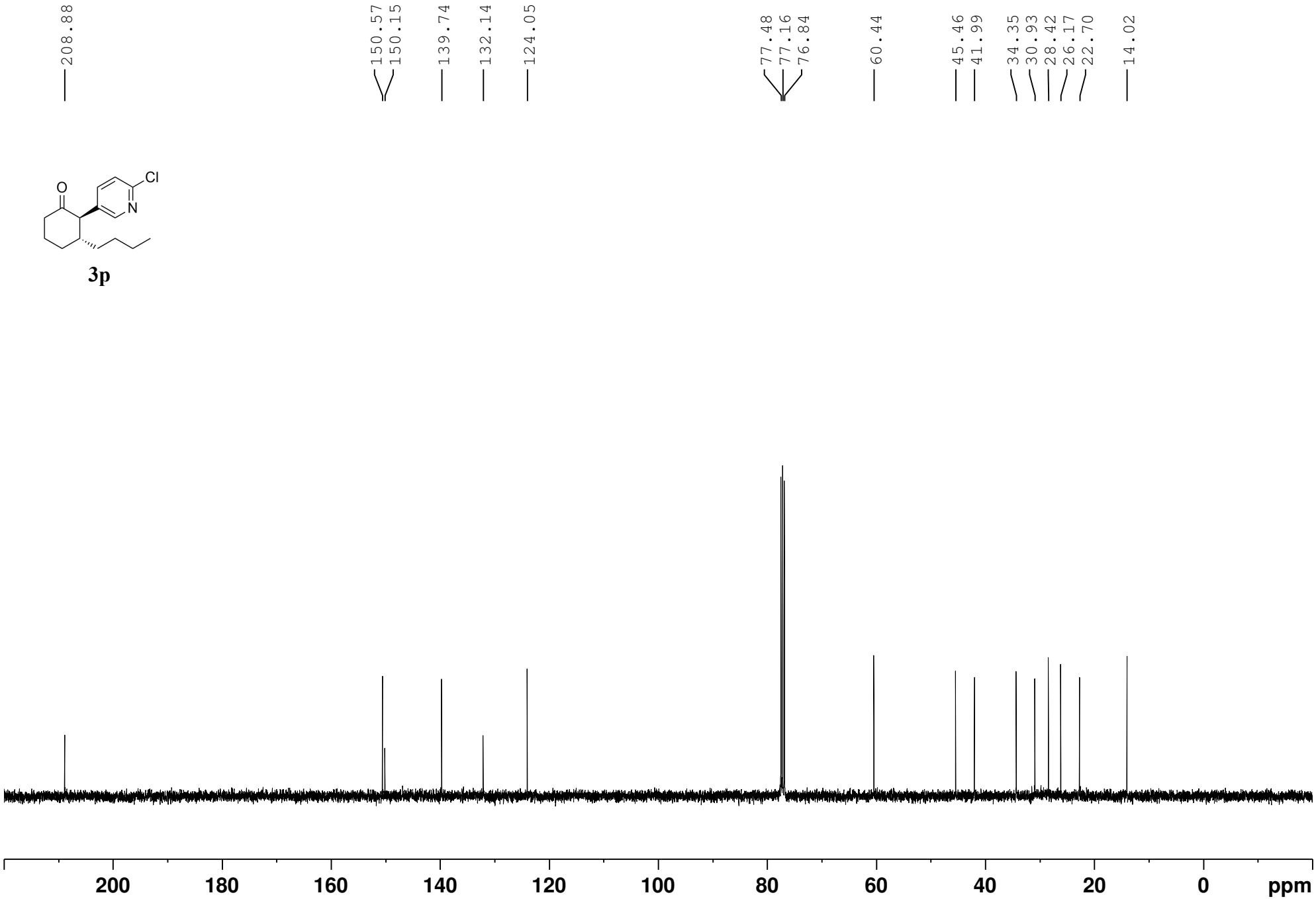
5.26
3.14

O
Cl
N

3p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60.44
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41.99
34.35
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120
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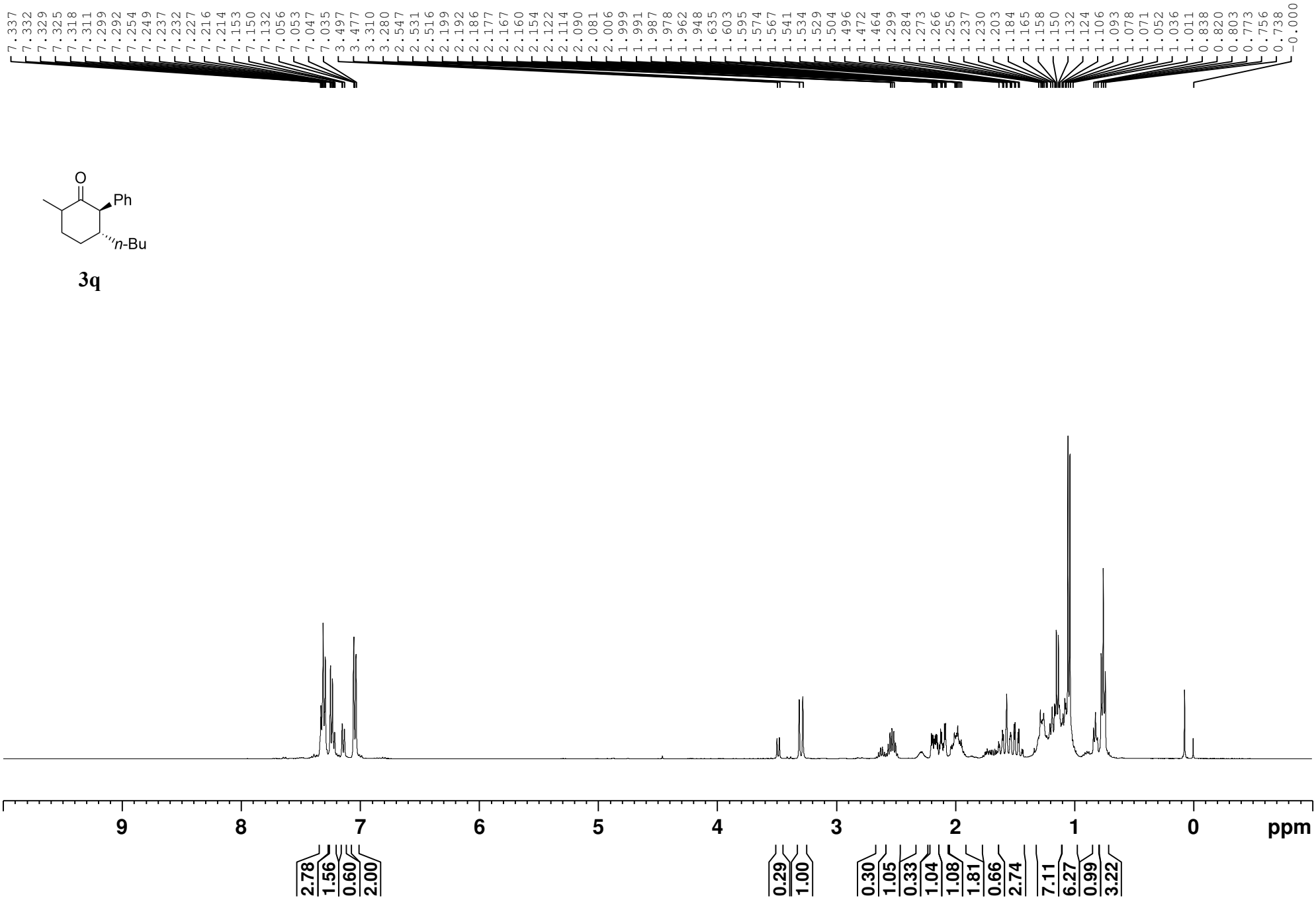
20
0
ppm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O
Ph
n-Bu
3q
9 8 7 6 5 4 3 2 1 0 ppm
2.78 1.56 0.60 2.00
0.29 1.00
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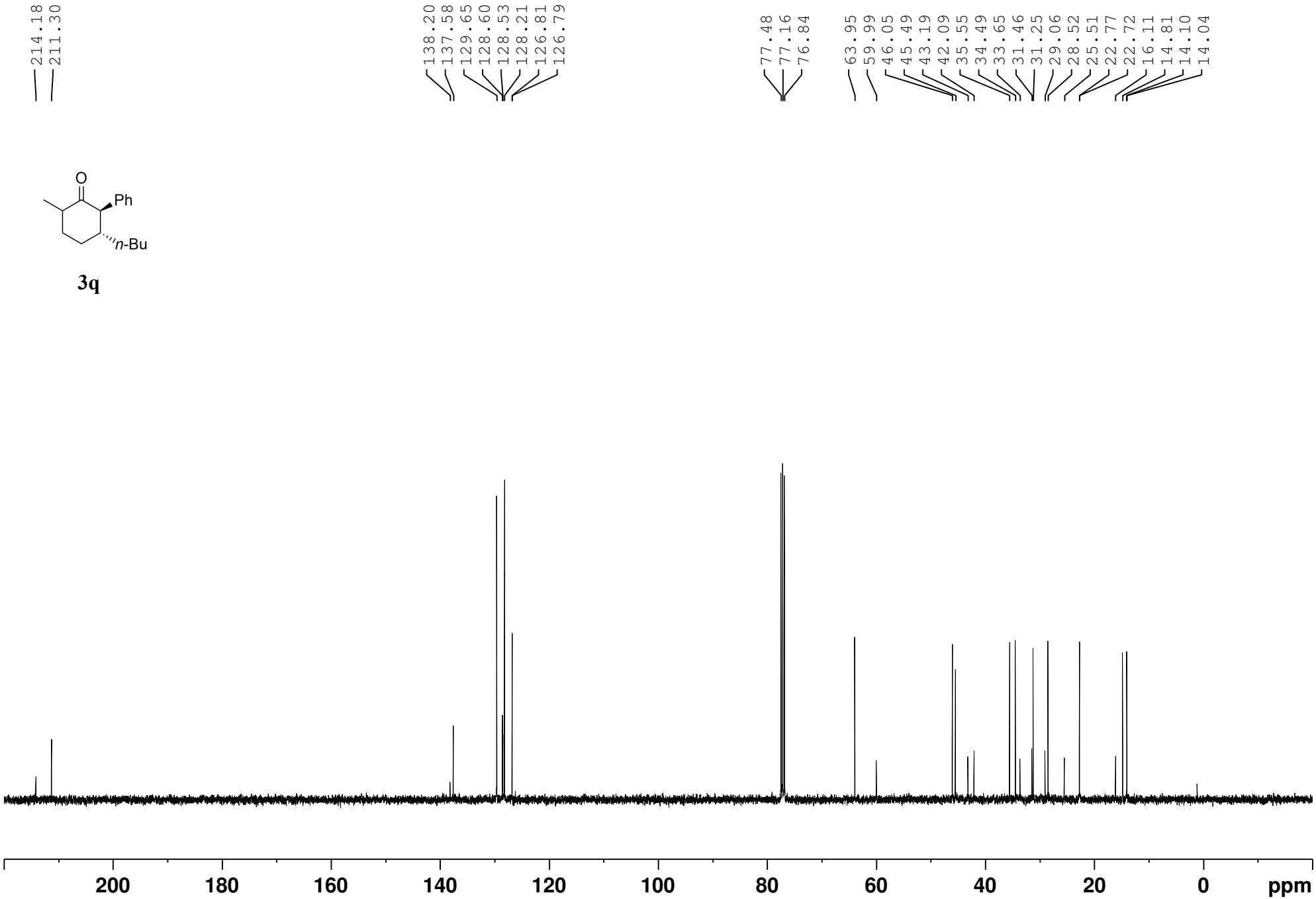
O
Ph
n-Bu

3q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63.95
59.99
46.05
45.49
43.19
42.09
35.55
34.49
33.65
31.46
31.25
29.06
28.52
25.51
22.77
22.72
16.11
14.81
14.10
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180
160
140
120
100
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60
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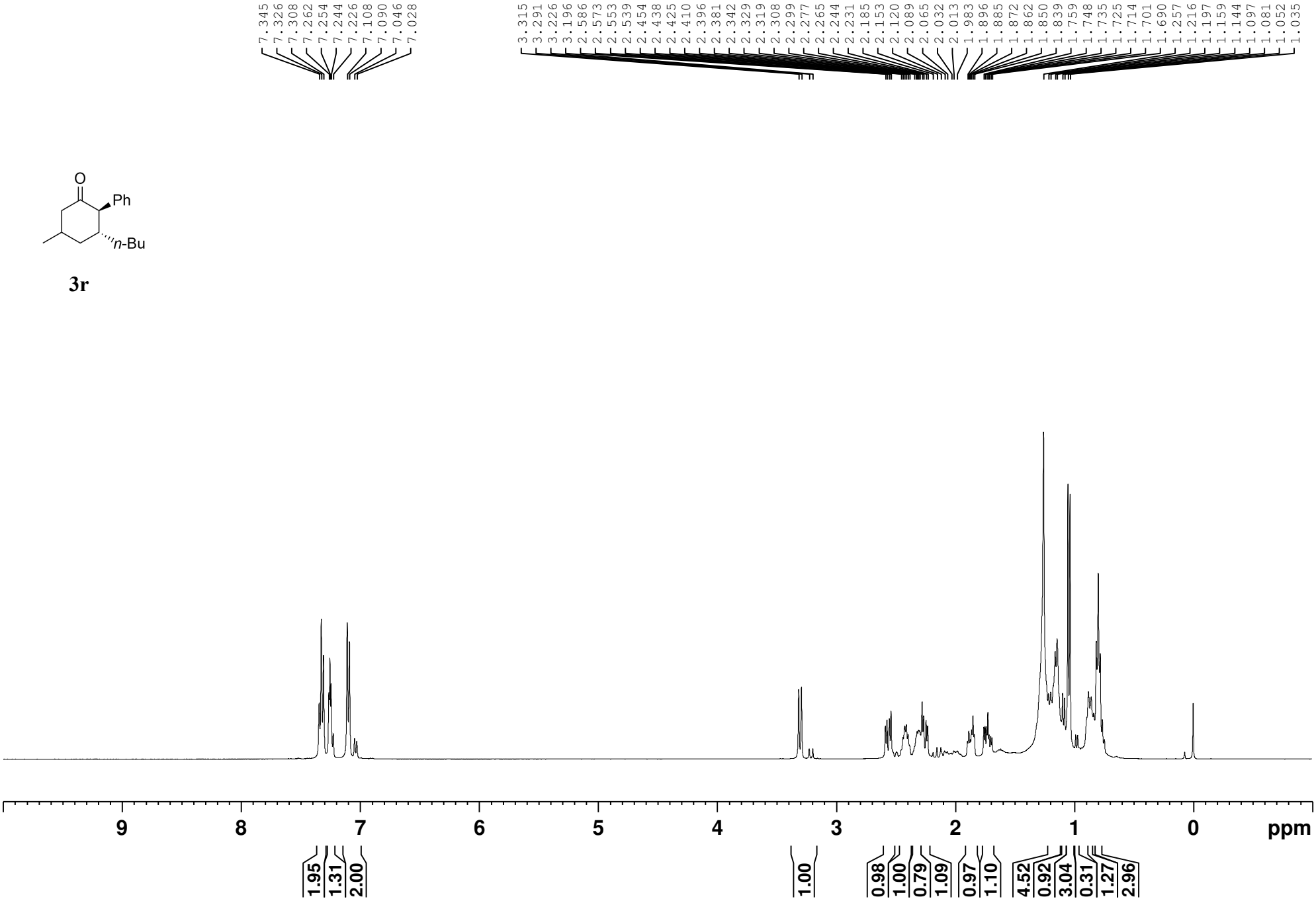
20
0
ppm

O
Ph
n-Bu

3r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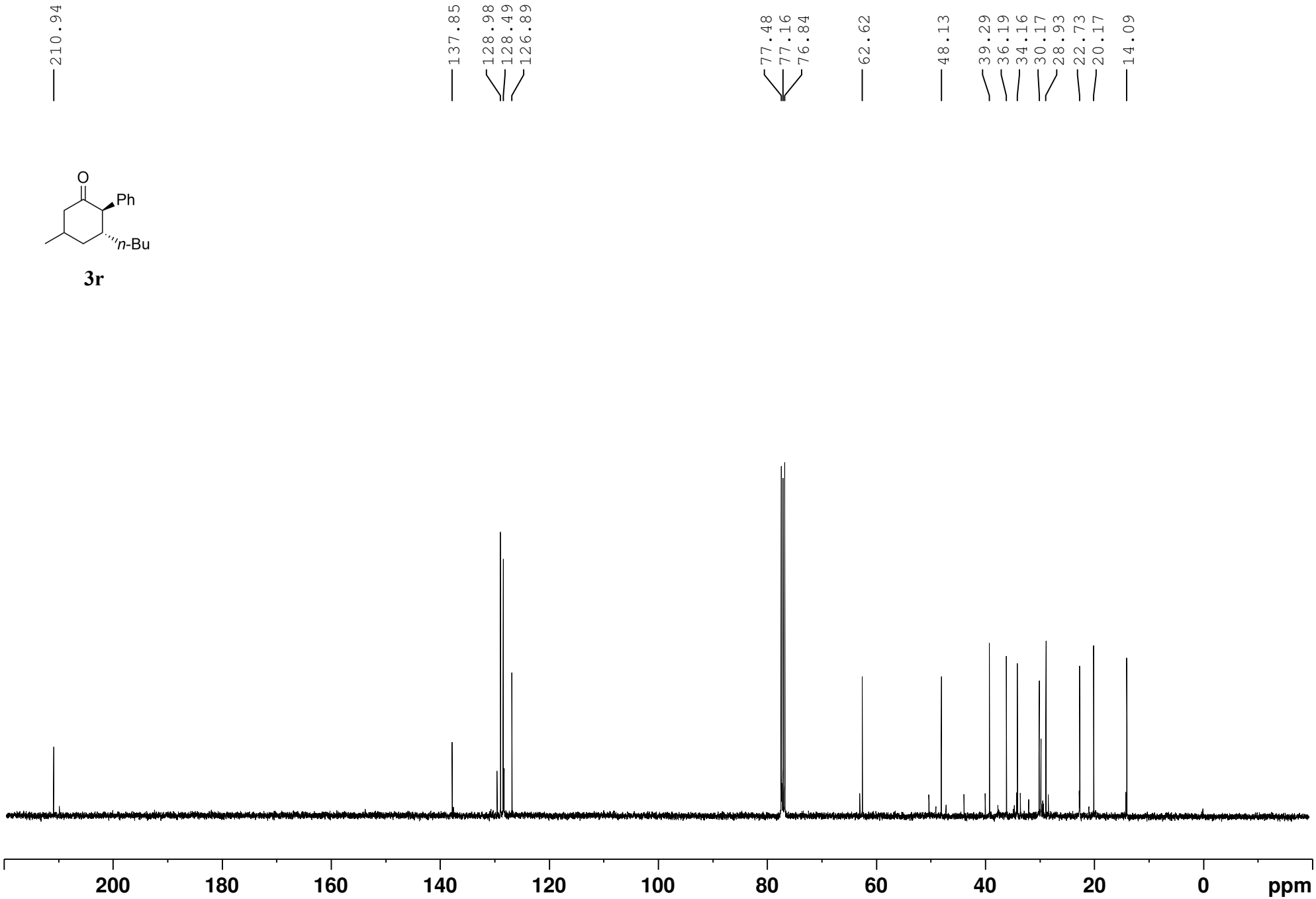
3.315 3.291 3.226 3.196 2.586 2.573 2.553 2.539 2.454 2.438 2.425 2.410 2.396 2.381 2.342 2.329 2.319 2.308 2.299 2.277 2.265 2.244 2.231 2.185 2.153 2.120 2.089 2.065 2.032 2.013 1.983 1.896 1.885 1.872 1.862 1.850 1.839 1.759 1.748 1.735 1.725 1.714 1.701 1.690 1.257 1.216 1.197 1.159 1.144 1.097 1.081 1.052 1.035
9 8 7 6 5 4 3 2 1 0 ppm
1.95 1.31 2.00
1.00
0.98 1.00 0.79 1.09
0.97 1.10
4.52 0.92 3.04 0.31 1.27 2.96

O
Ph
n-Bu

3r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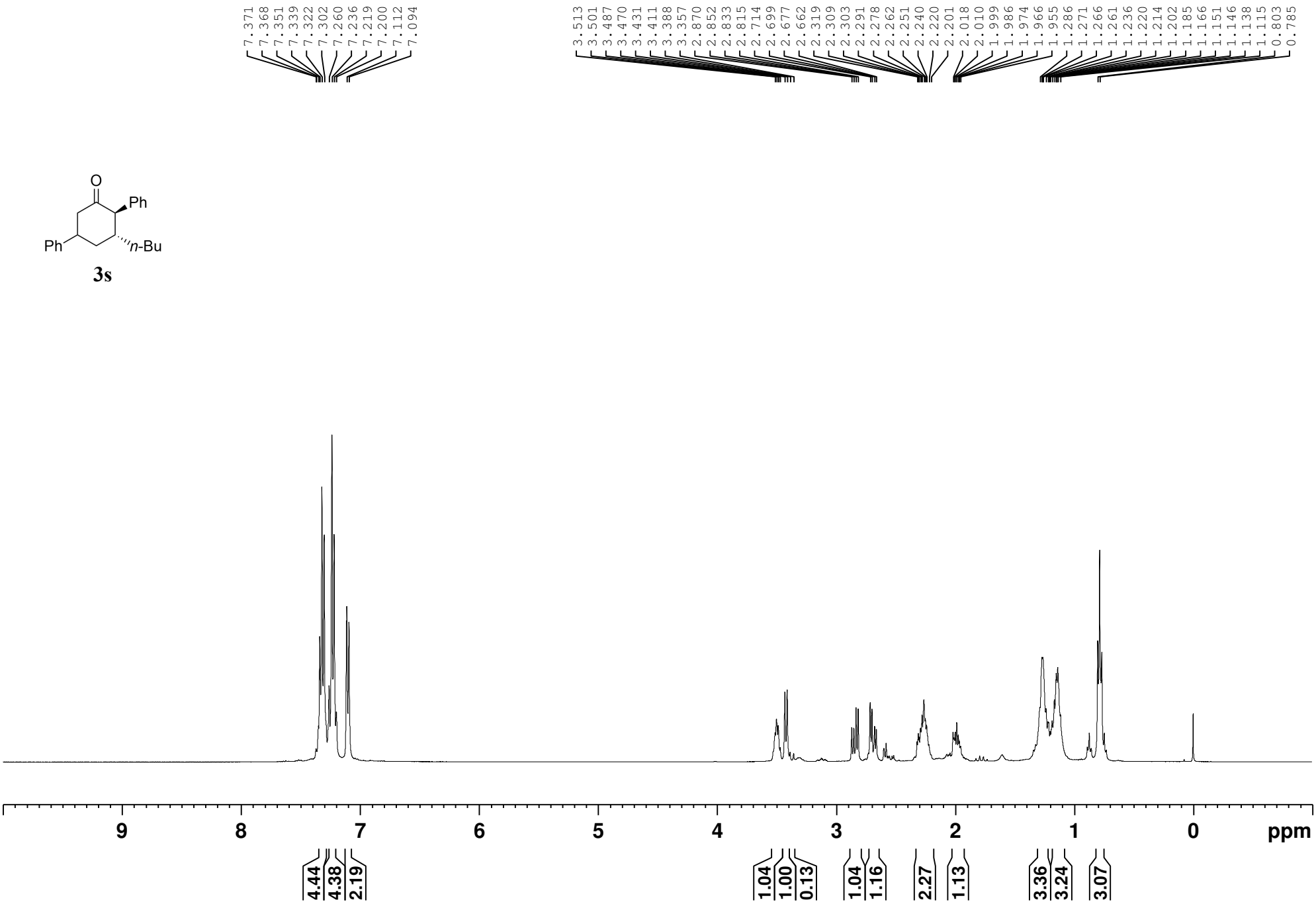
77.16
76.84
62.62
48.13
39.29
36.19
34.16
30.17
28.93
22.73
20.17
14.09
200
180
160
140
120
100
80
60
40
20
0
ppm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7.260
7.236
7.219
7.200
7.112
7.094
3.513
3.501
3.487
3.470
3.431
3.411
3.388
3.357
2.870
2.852
2.833
2.815
2.714
2.699
2.677
2.662
2.319
2.309
2.303
2.291
2.278
2.262
2.251
2.240
2.220
2.201
2.018
2.010
1.999
1.986
1.974
1.966
1.955
1.286
1.271
1.266
1.261
1.236
1.220
1.214
1.202
1.185
1.166
1.151
1.146
1.138
1.115
0.803
0.785
O
Ph
Ph
n-Bu
3s
9
8
7
6
5
4
3
2
1
0
ppm
4.44
4.38
2.19
1.04
1.00
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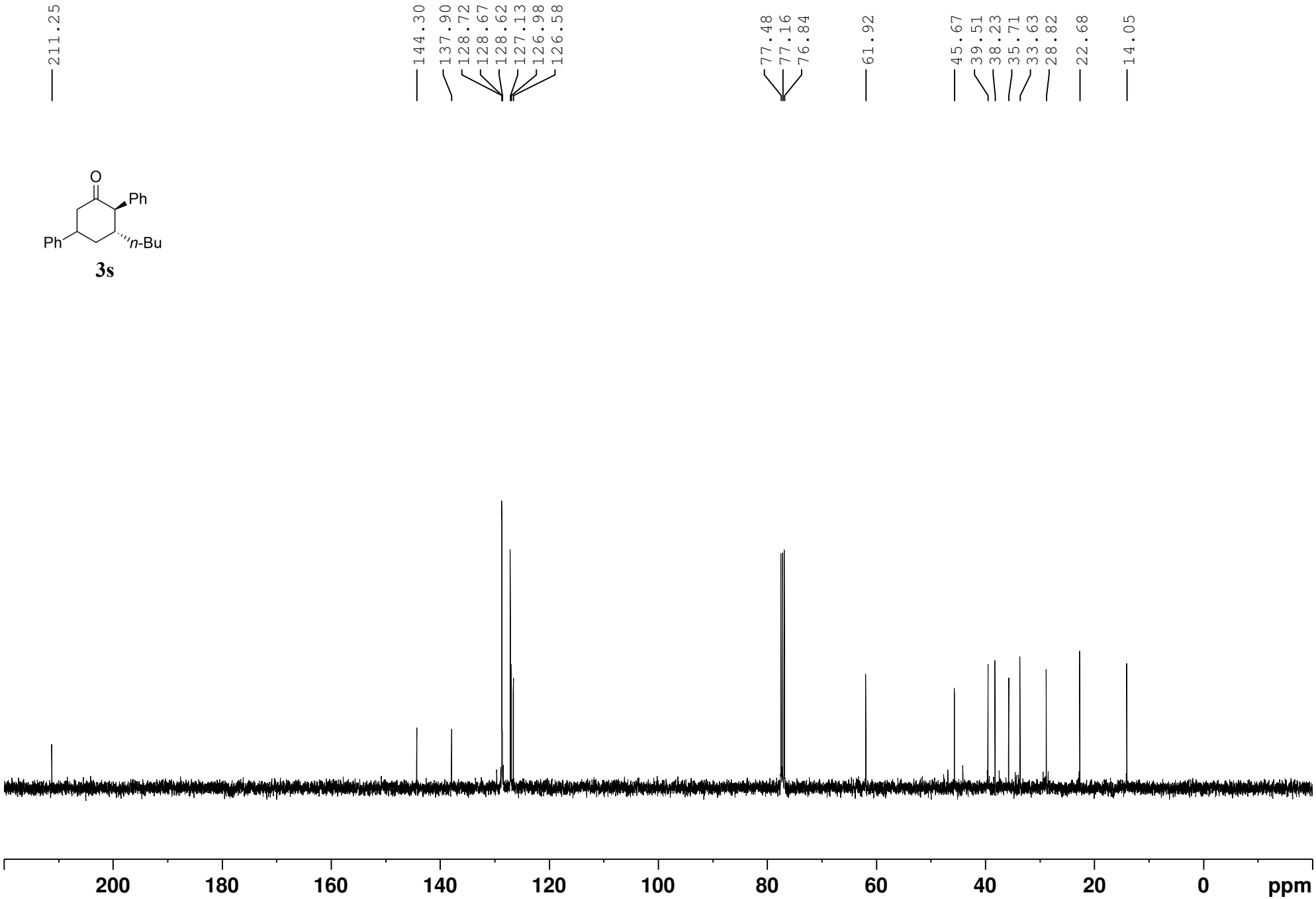
1.04
1.16
2.27
1.13
3.36
3.24
3.07

O
Ph
Ph
n-Bu

3s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128.62
127.13
126.98
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77.48
77.16
76.84
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45.67
39.51
38.23
35.71
33.63
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22.68
14.05
200
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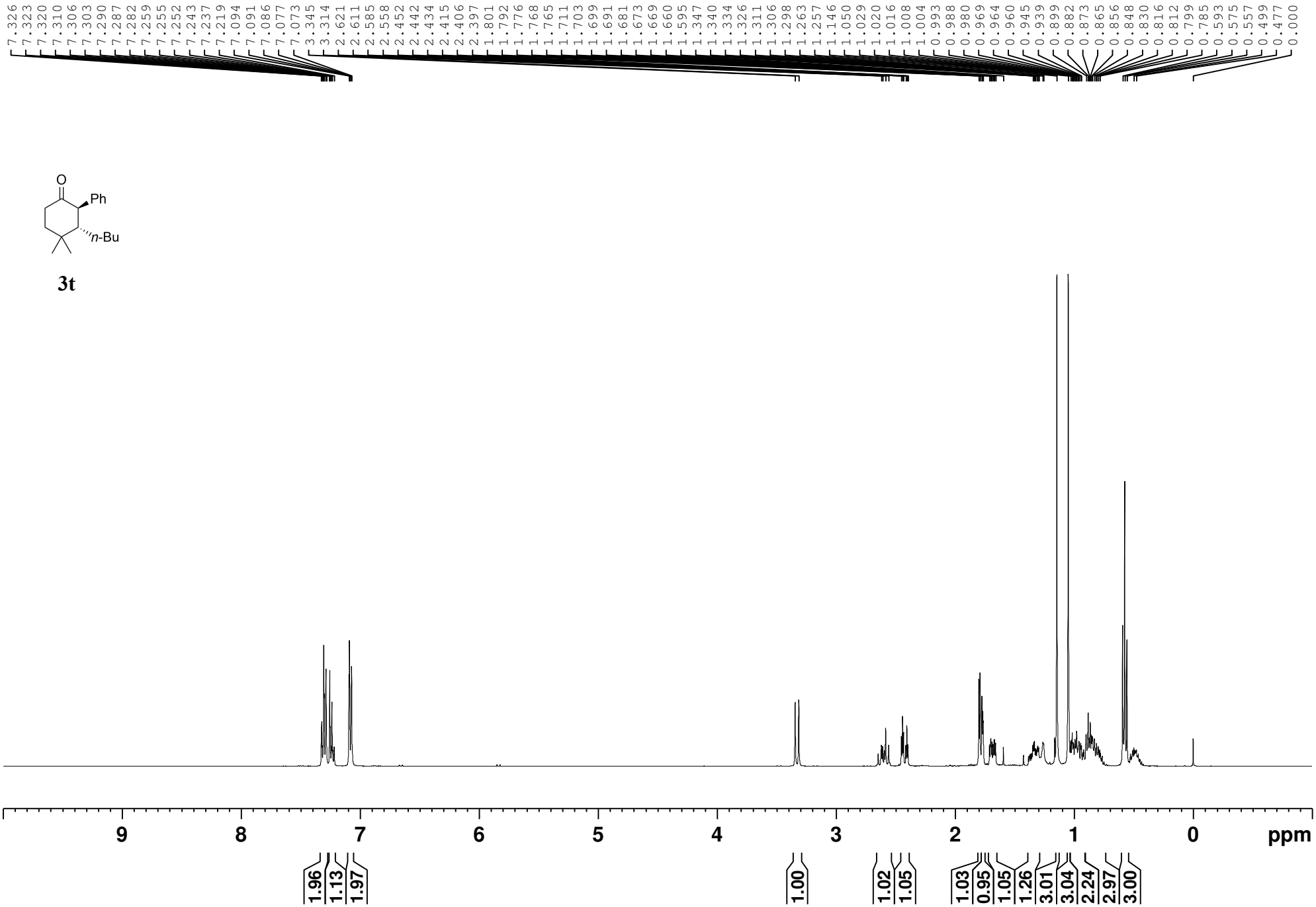
160
140
120
100
80
60
40
20
0
ppm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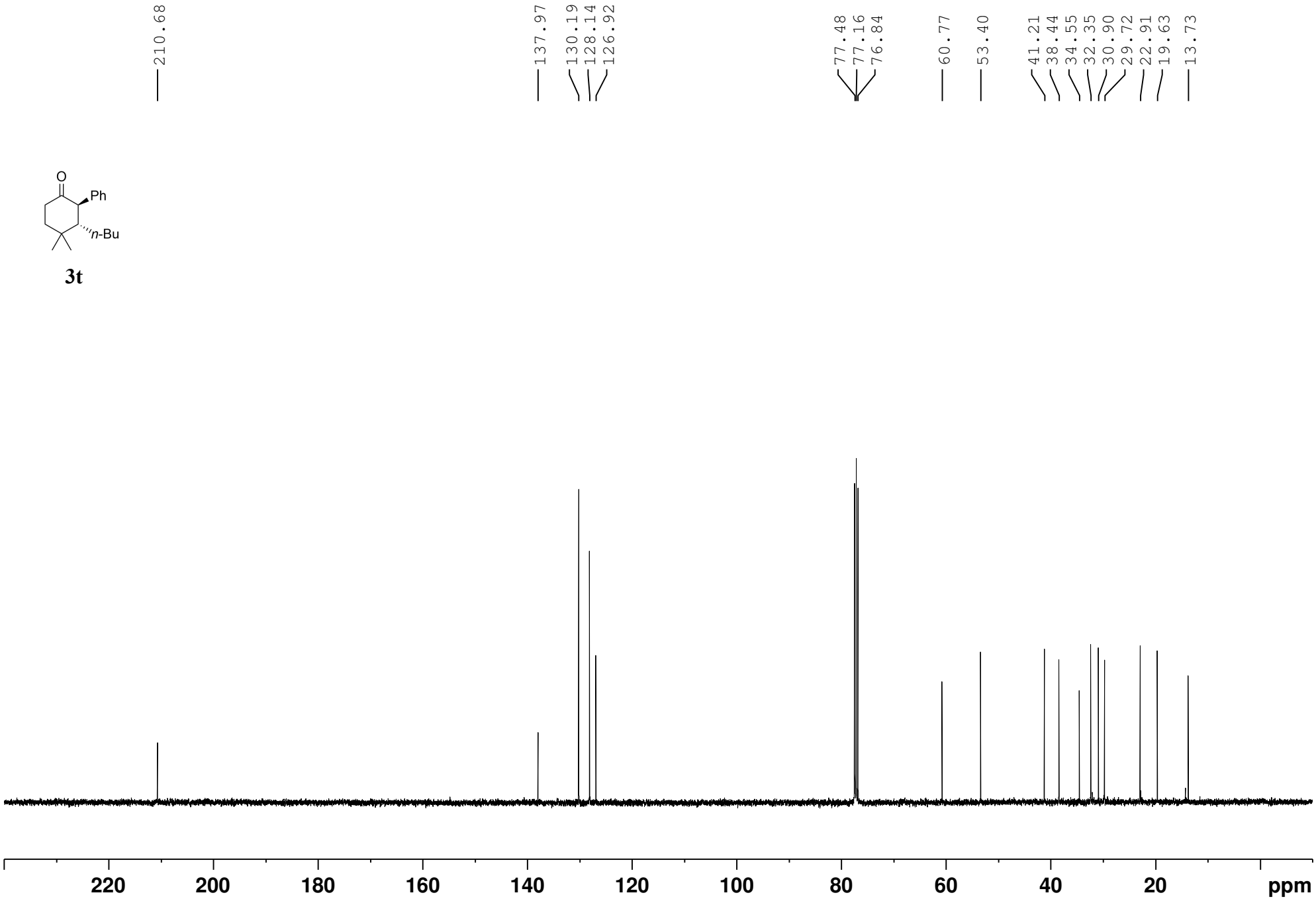
O
Ph
n-Bu
3t
9
8
7
6
5
4
3
2
1
0
ppm
1.96
1.13
1.97
1.00
1.02
1.05
1.03
0.95
1.05
1.26
3.01
3.04
2.24
2.97
3.00

O
Ph
n-Bu

3t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76.84
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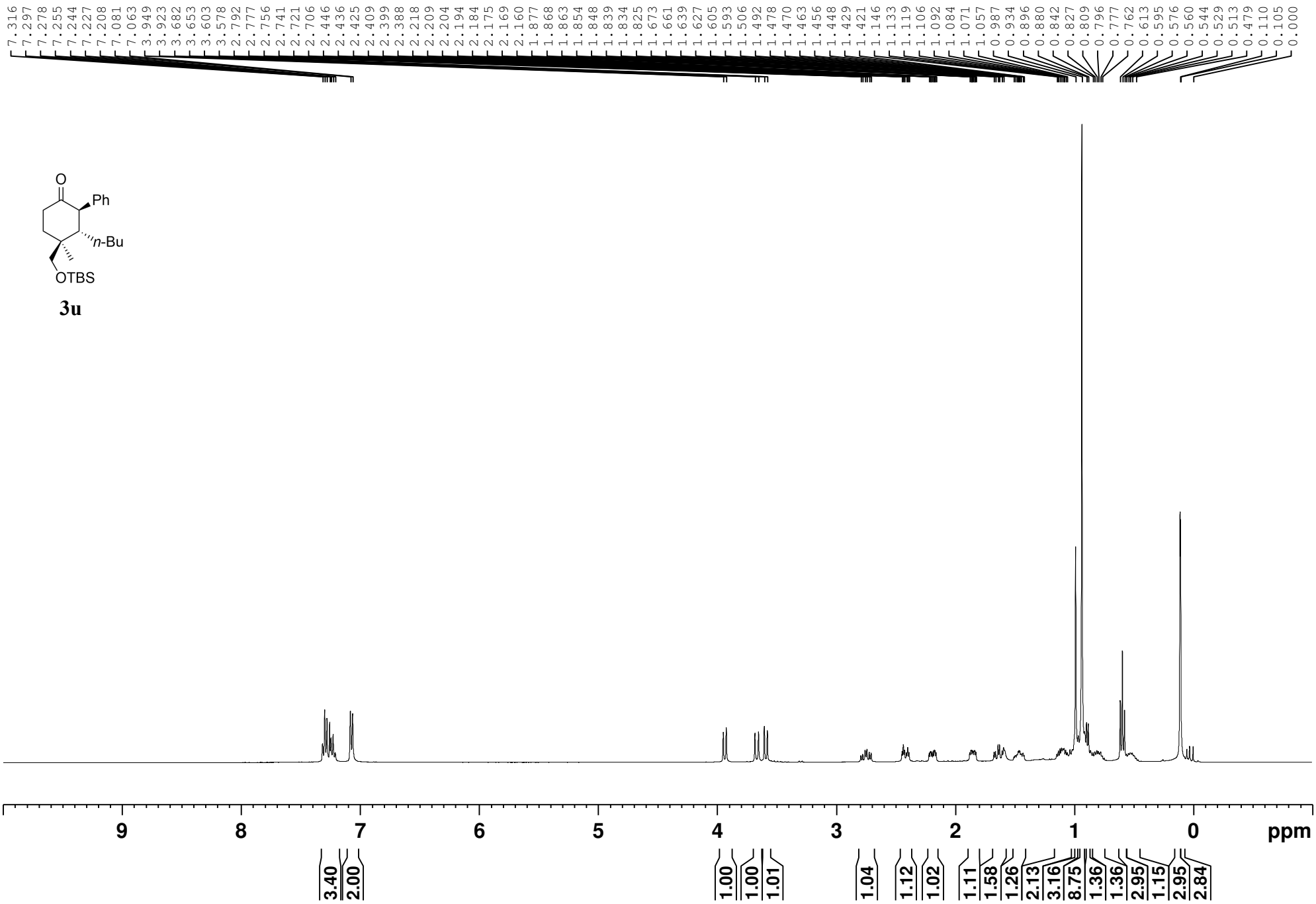
53.40
41.21
38.44
34.55
32.35
30.90
29.72
22.91
19.63
13.73
220
200
180
160
140
120
100
80
60
40
20
ppm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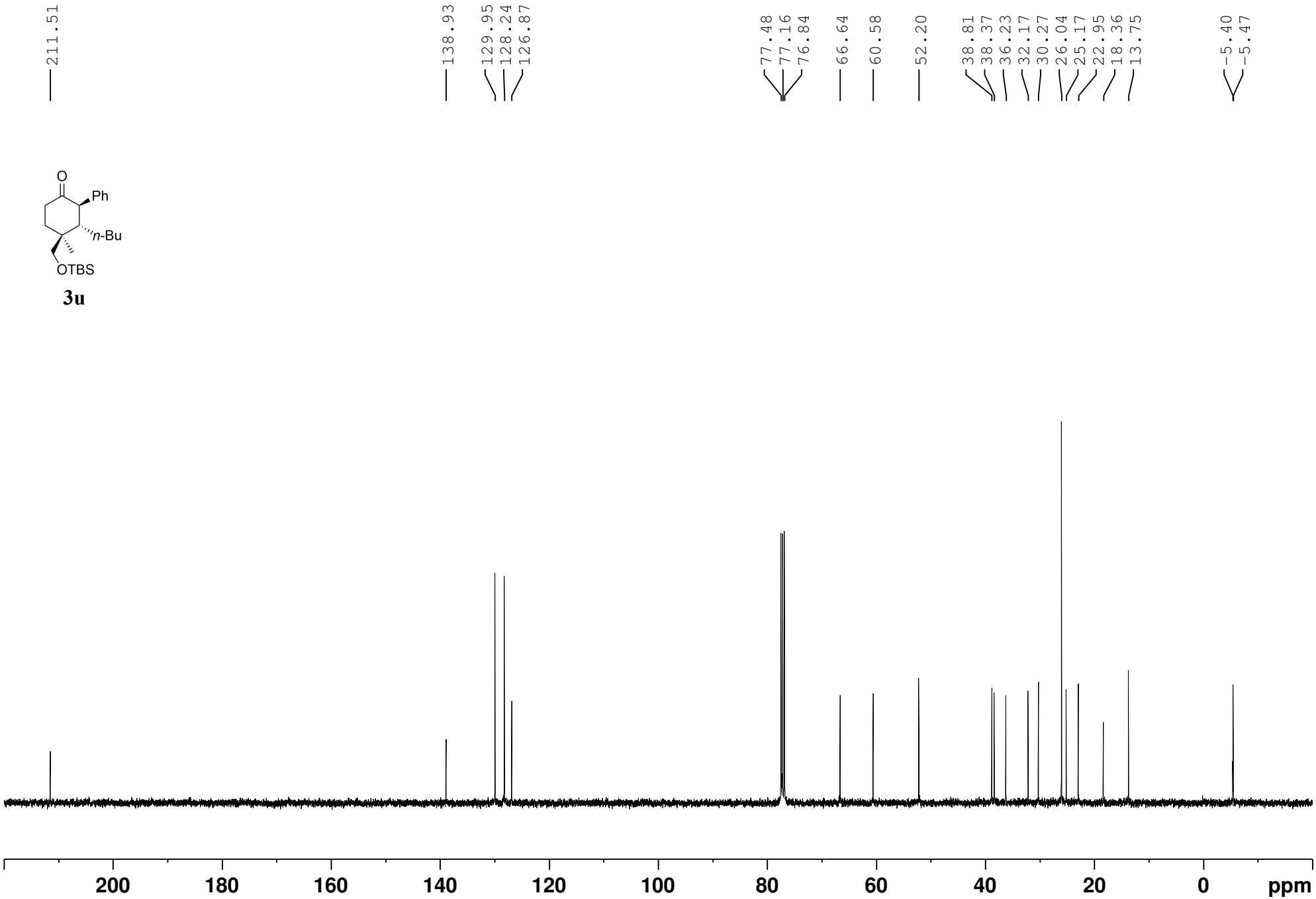
O
Ph
n-Bu
OTBS
3u
9
8
7
6
5
4
3
2
1
0
ppm
3.40
2.00
1.00
1.00
1.01
1.04
1.12
1.02
1.11
1.58
1.26
2.13
3.16
8.75
1.36
1.36
2.95
1.15
2.95
2.84

O
Ph
n-Bu
OTBS

3u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52.20
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38.37
36.23
32.17
30.27
26.04
25.17
22.95
18.36
13.75
-5.40
-5.47
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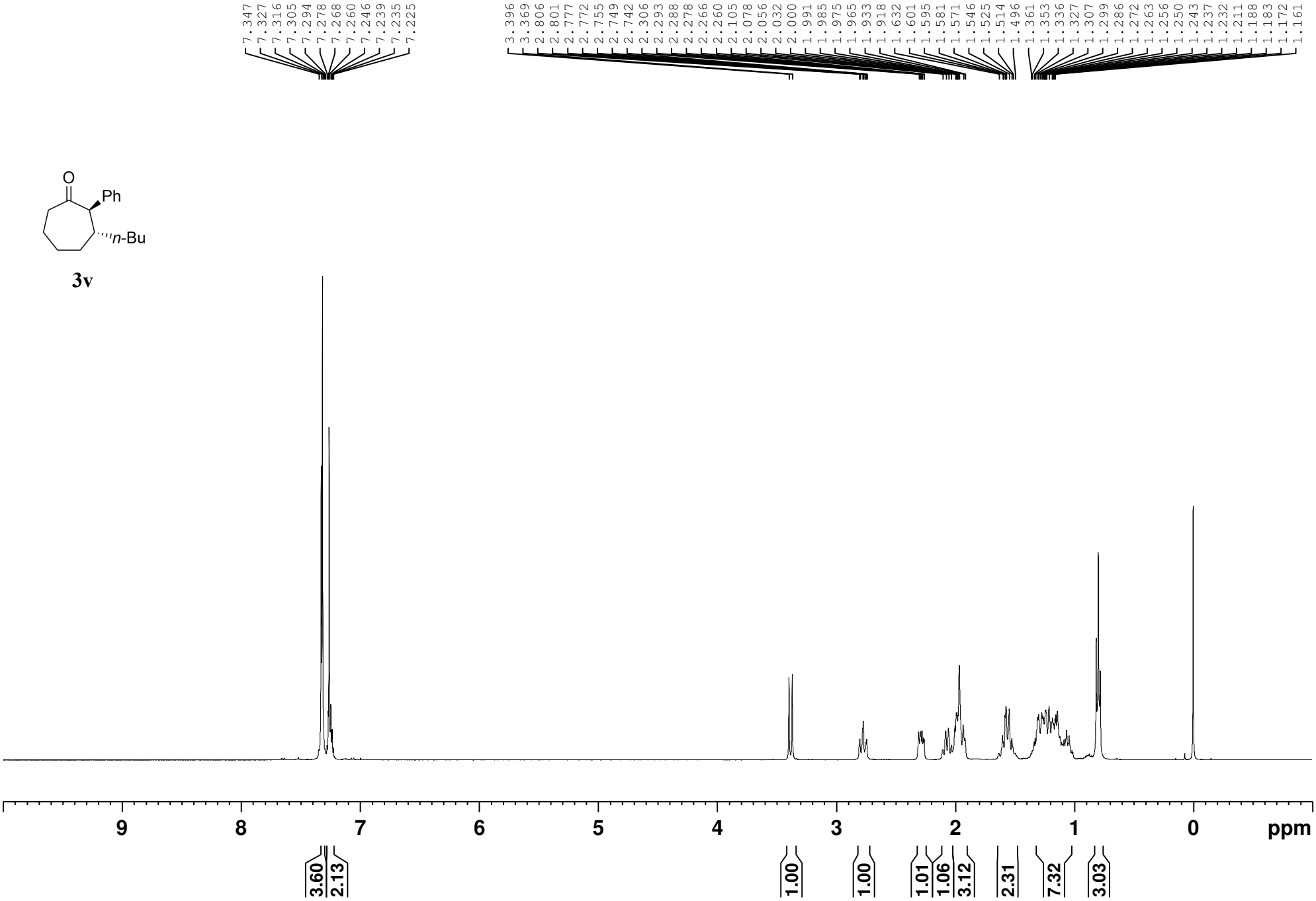
180
160
140
120
100
80
60
40
20
0
ppm

O
Ph
n-Bu

3v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3.369
2.806
2.801
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2.772
2.755
2.749
2.742
2.306
2.293
2.288
2.278
2.266
2.260
2.105
2.078
2.056
2.032
2.000
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1.965
1.933
1.918
1.632
1.601
1.595
1.581
1.571
1.546
1.525
1.514
1.496
1.361
1.353
1.336
1.327
1.307
1.299
1.286
1.272
1.263
1.256
1.250
1.243
1.237
1.232
1.211
1.188
1.183
1.172
1.161
9
8
7
6
5
4
3
2
1
0
ppm
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1.01
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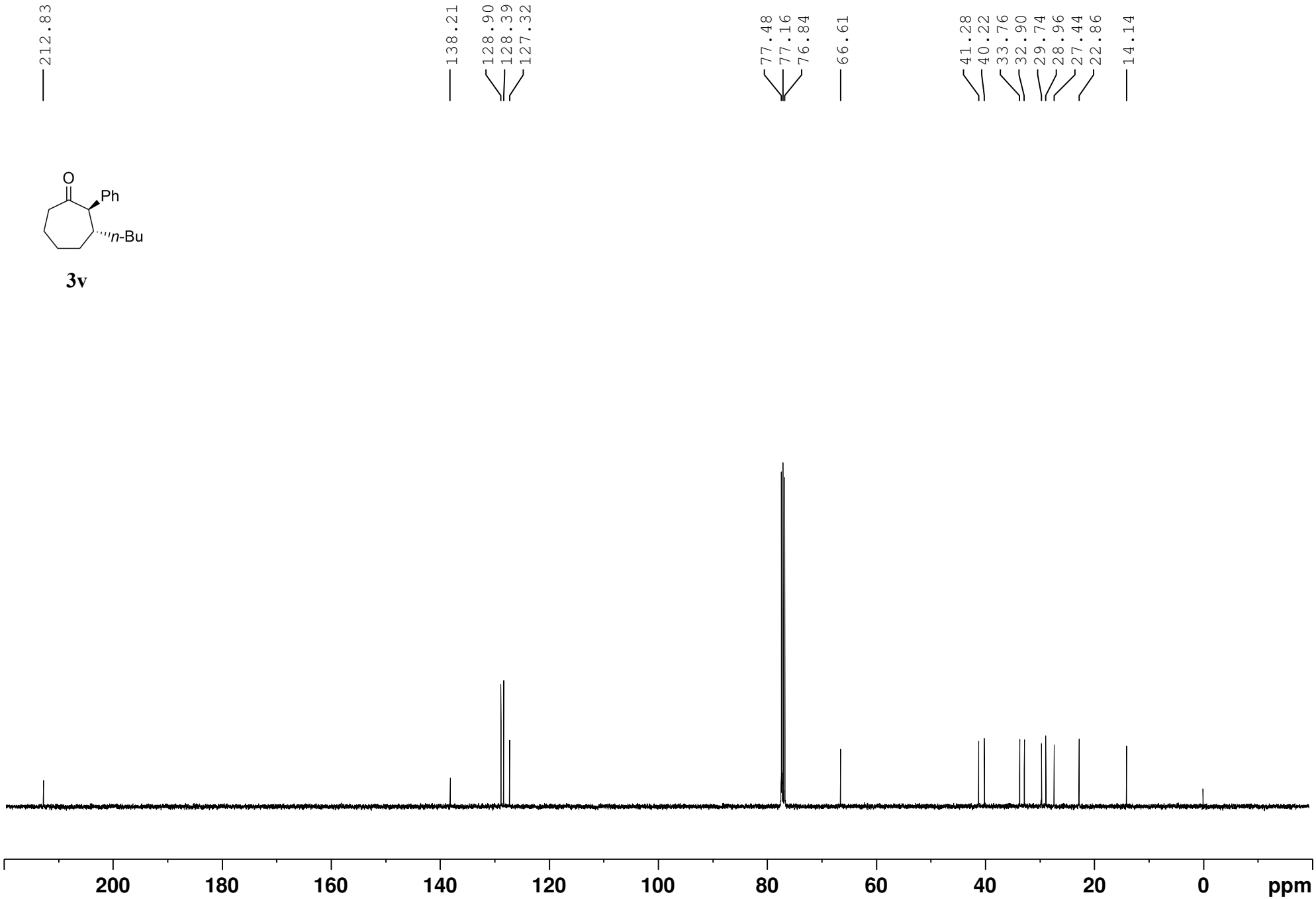
2.31
7.32
3.03

O
Ph
n-Bu

3v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41.28
40.22
33.76
32.90
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22.86
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120
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60
40
20
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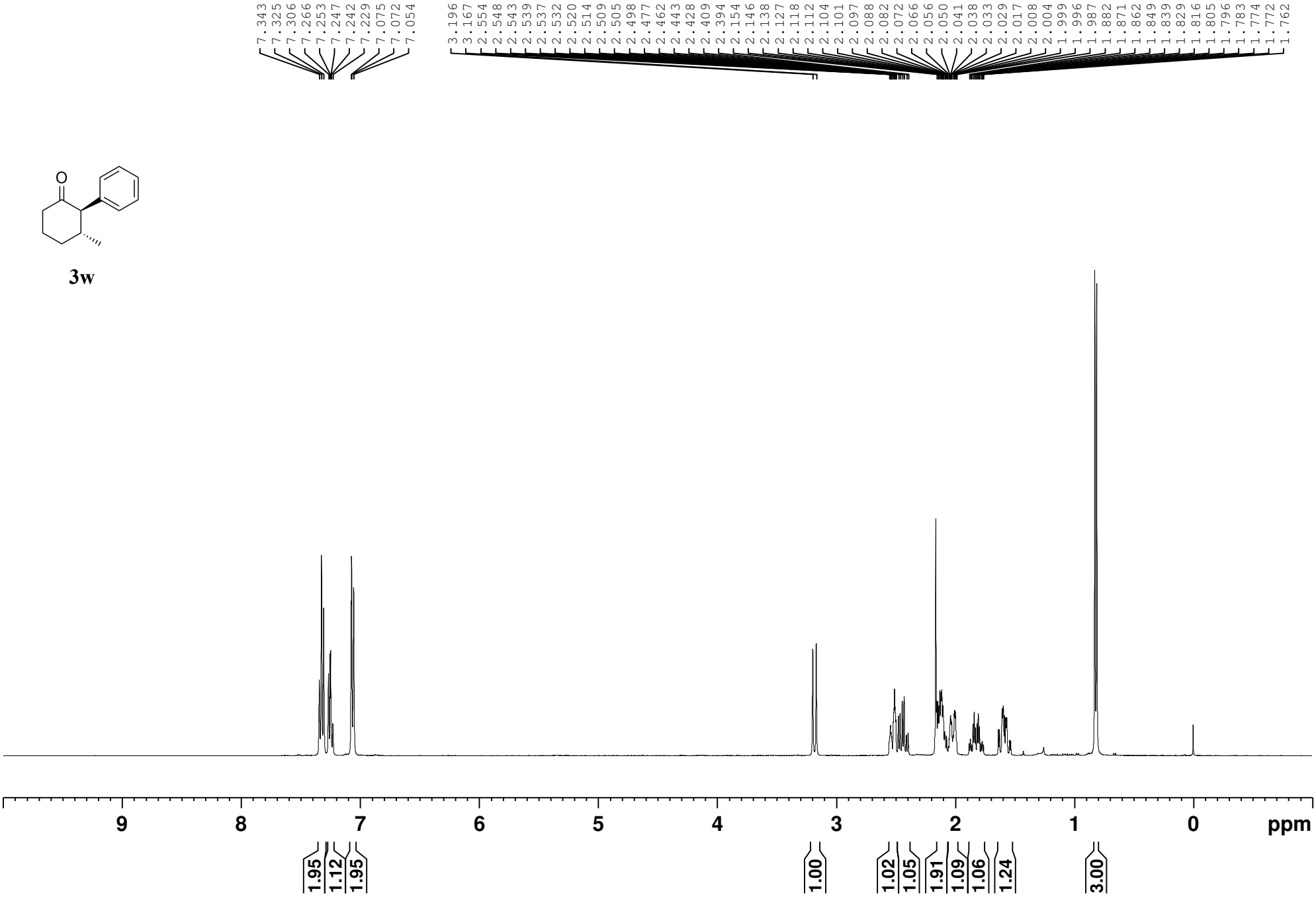
ppm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2.509
2.505
2.498
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2.154
2.146
2.138
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2.112
2.104
2.101
2.097
2.088
2.082
2.072
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1.805
1.796
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1.774
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1.762
O
3w
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8
7
6
5
4
3
2
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1.09
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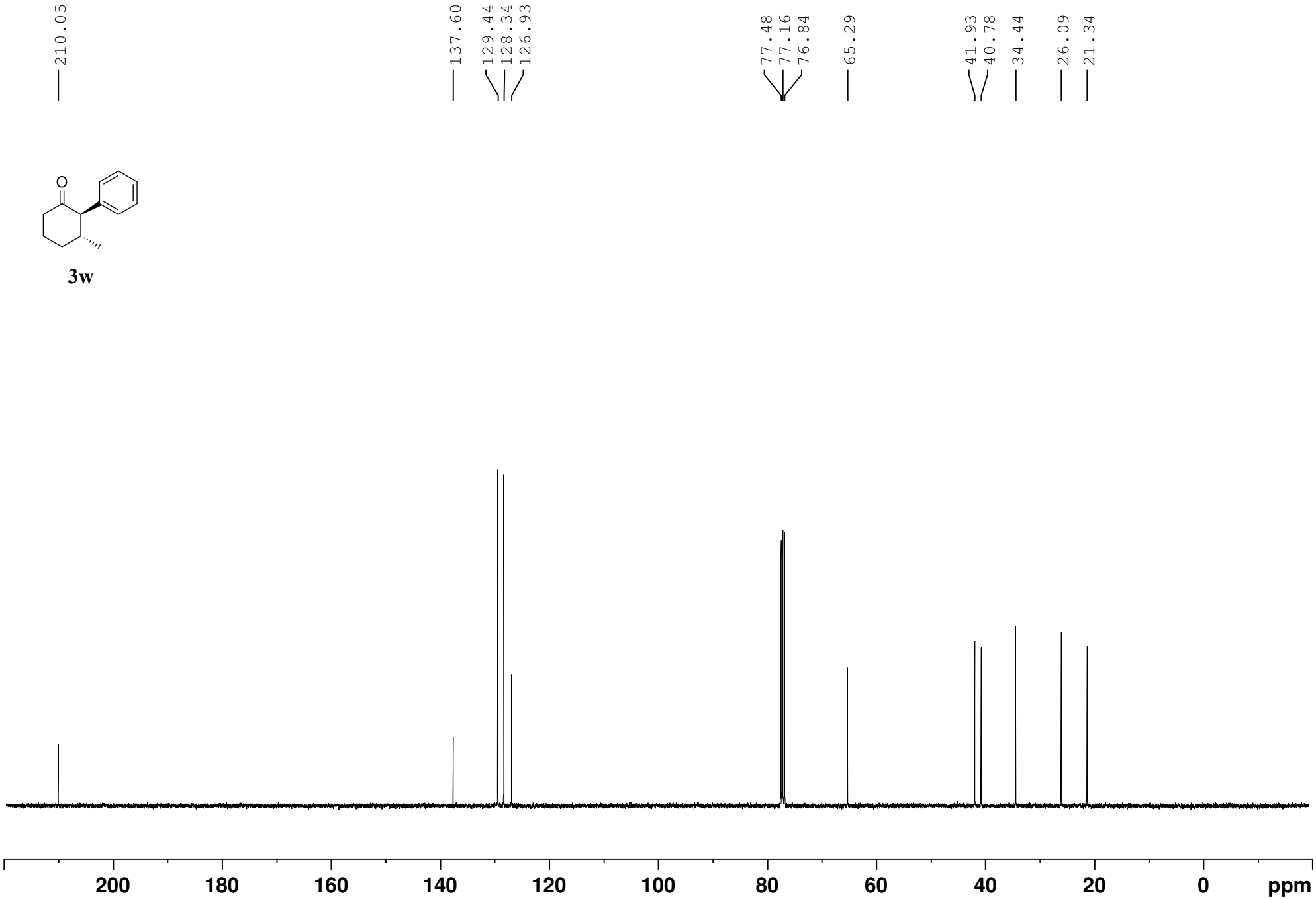
1.24
3.00

3w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77.16
76.84
65.29
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40.78
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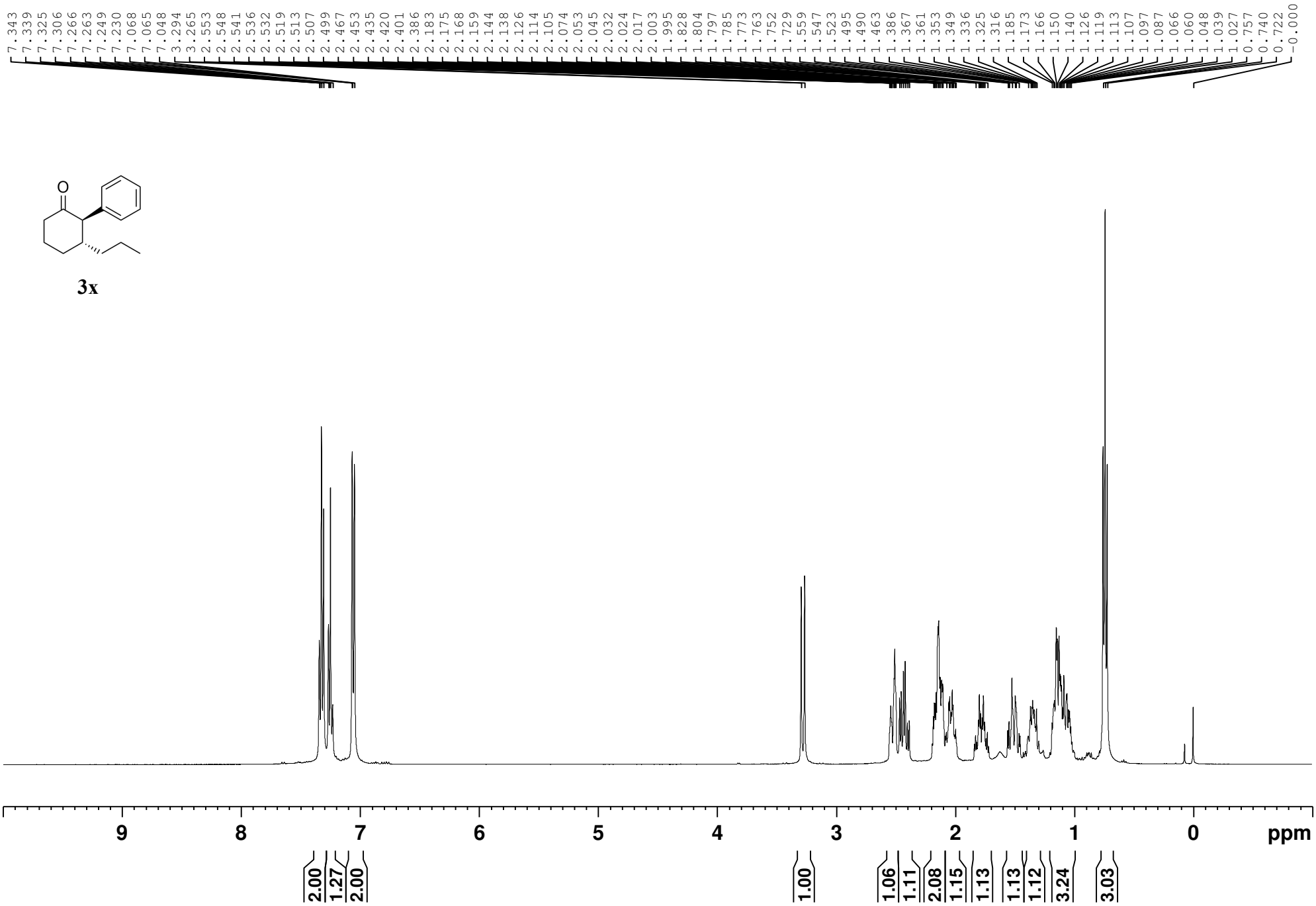
26.09
21.34
200
180
160
140
120
100
80
60
40
20
0
ppm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O
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.27
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1.11
2.08
1.15
1.13
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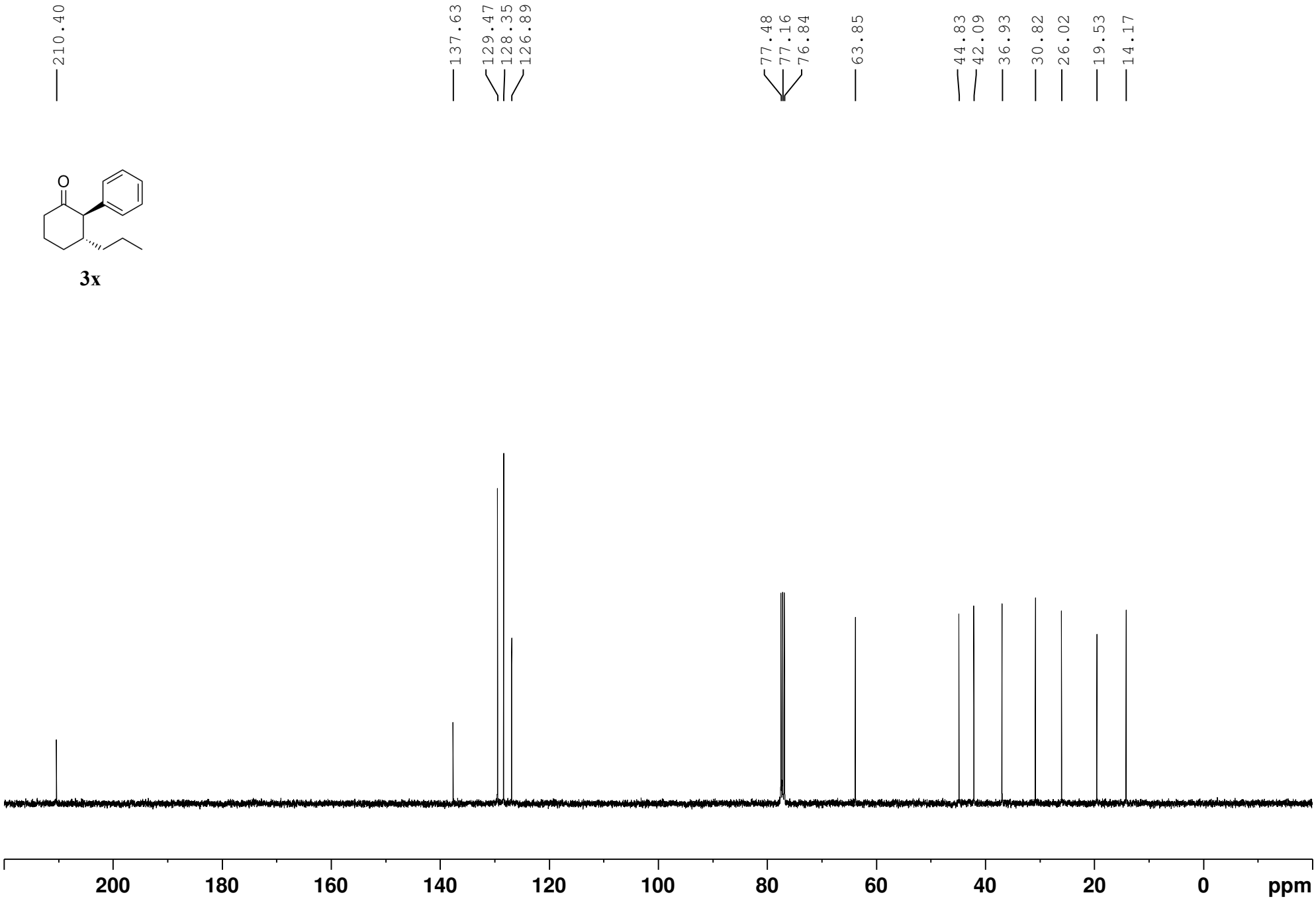
1.12
3.24
3.03

3x

3x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44.83
42.09
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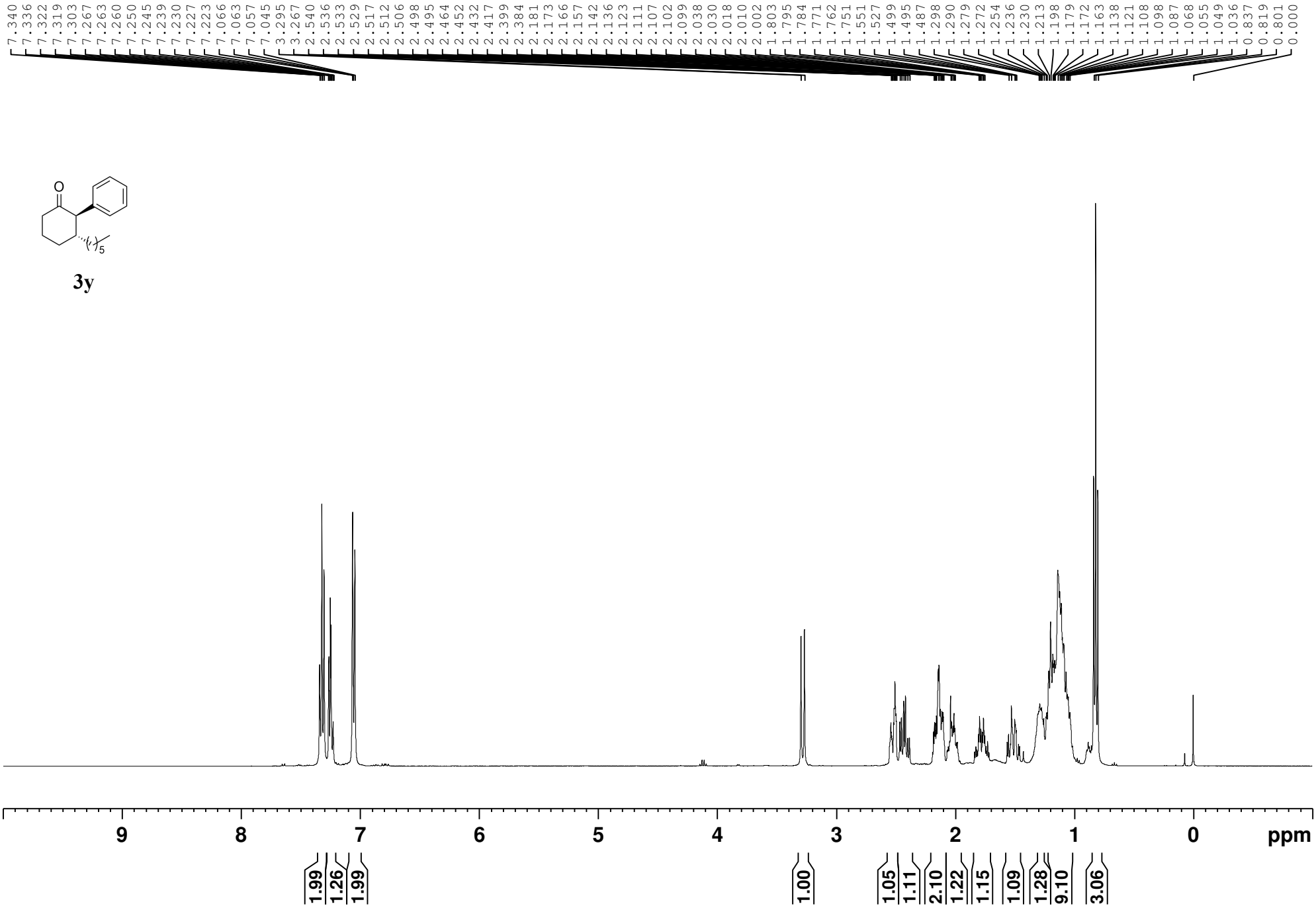
19.53
14.17
200
180
160
140
120
100
80
60
40
20
0
ppm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O
5
3y
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.26
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1.05
1.11
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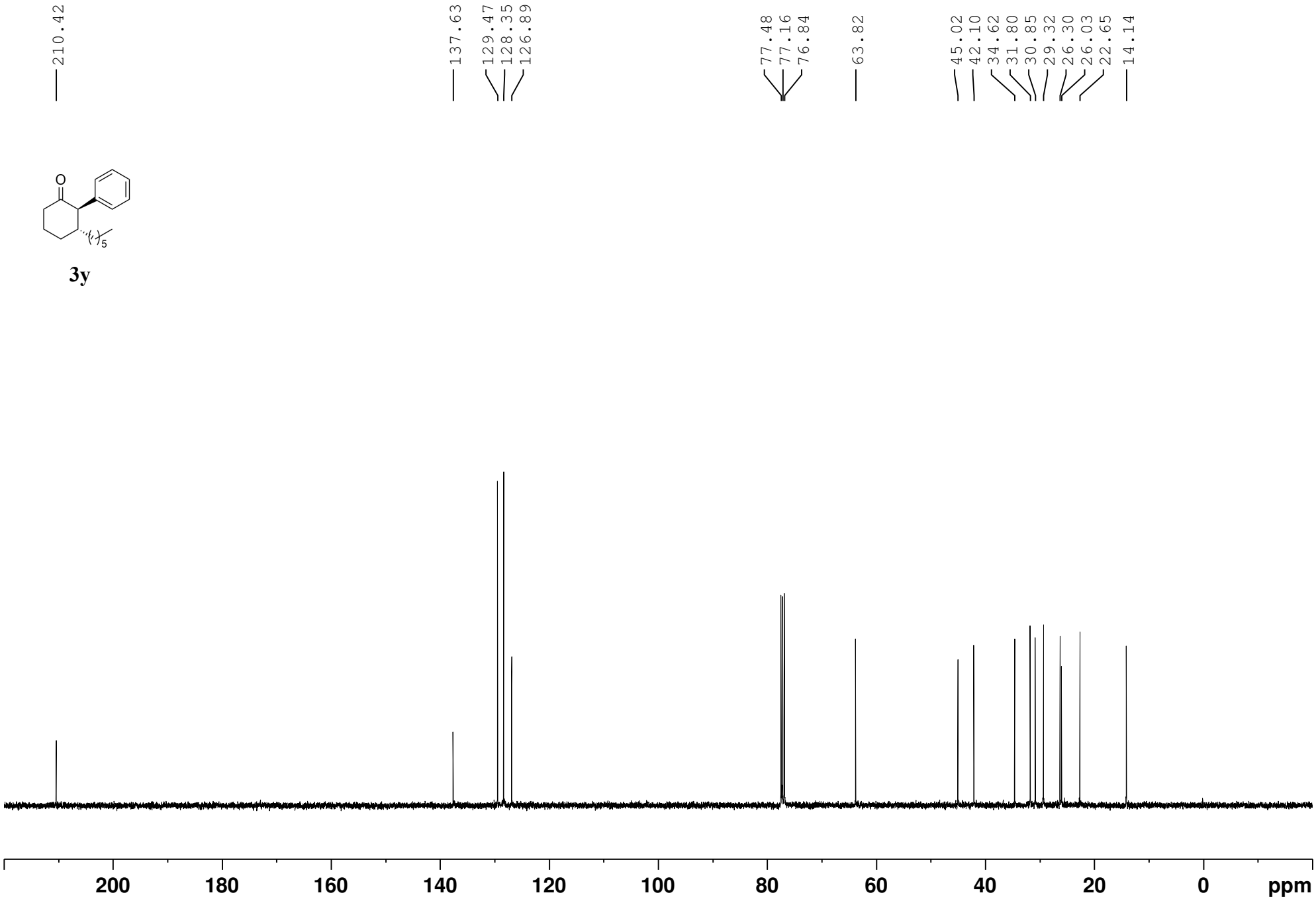
1.15
1.09
1.28
9.10
3.06

3y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30.85
29.32
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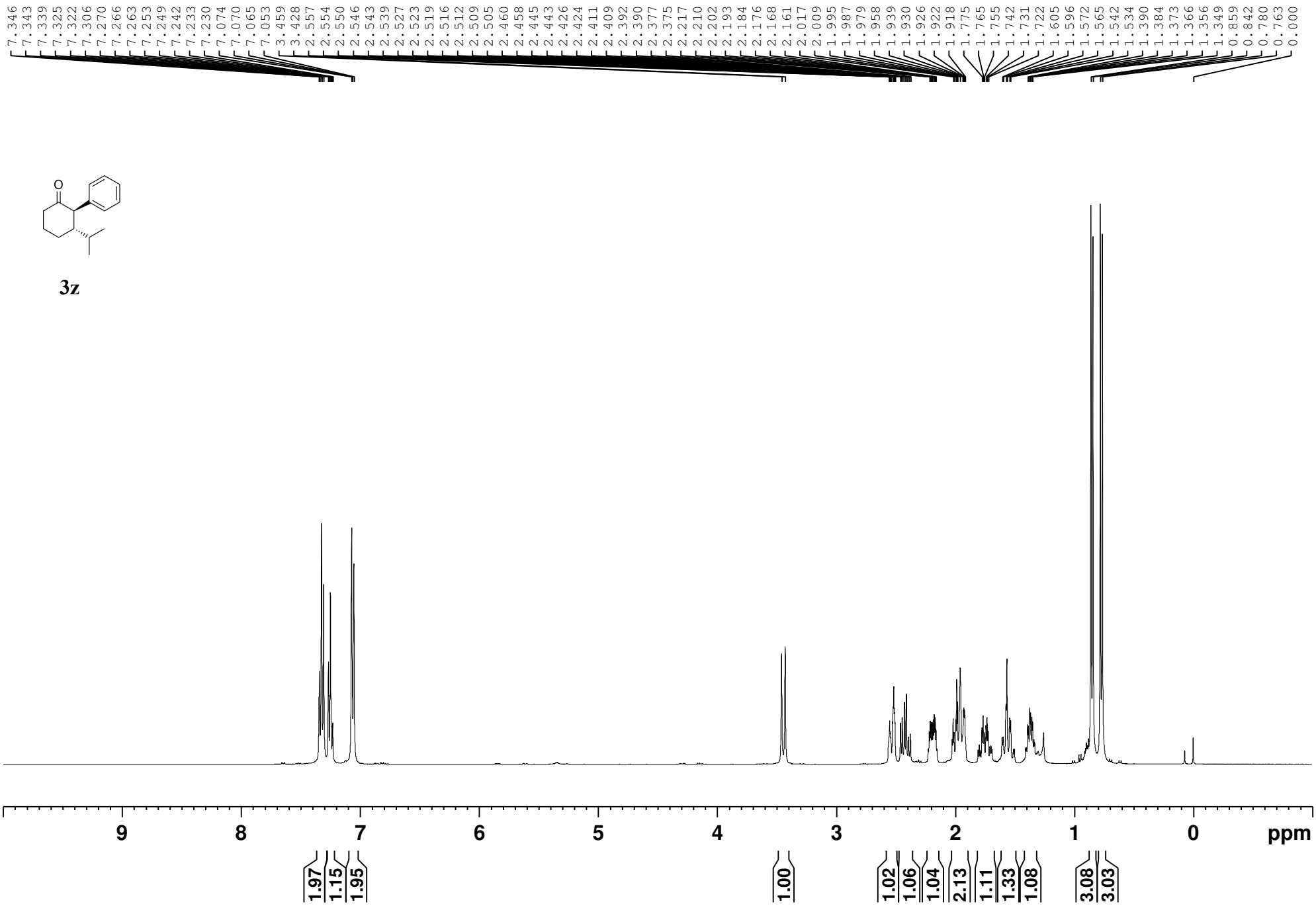
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O
3z
9
8
7
6
5
4
3
2
1
0
ppm
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1.15
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2.13
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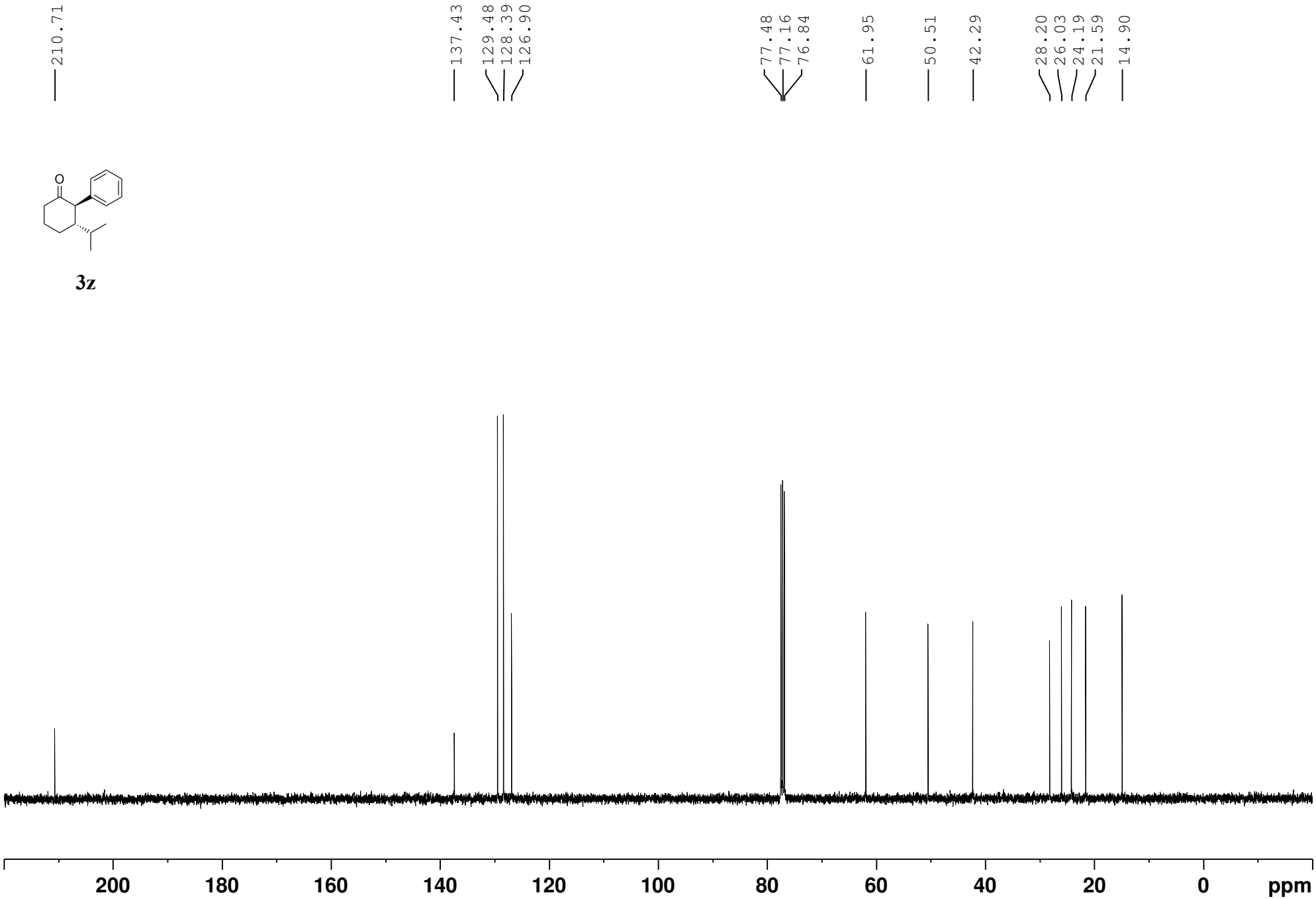
1.33
1.08
3.08
3.03

3z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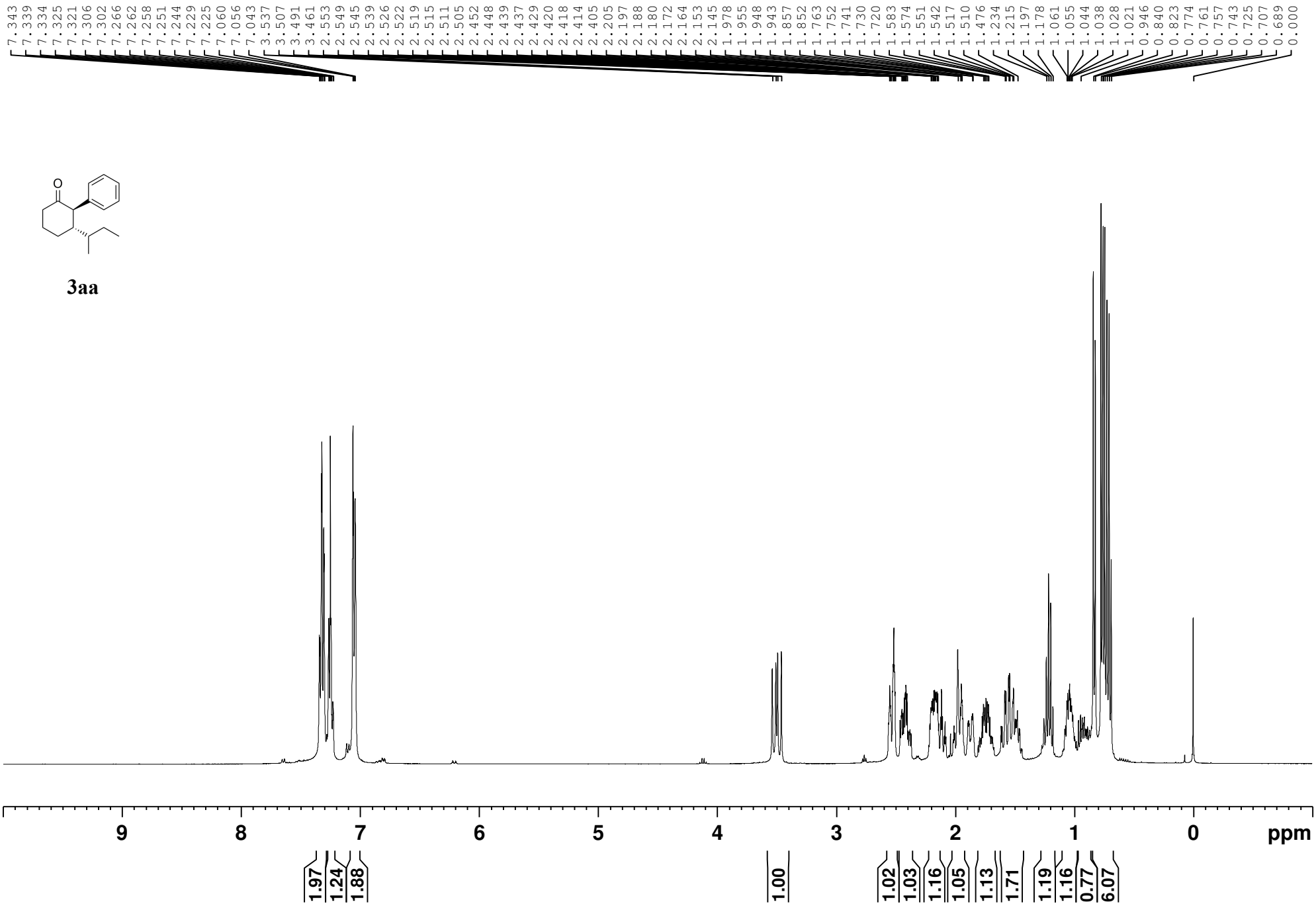
ppm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O
3aa
9
8
7
6
5
4
3
2
1
0
ppm
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1.24
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1.03
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1.05
1.13
1.71
1.19
1.16
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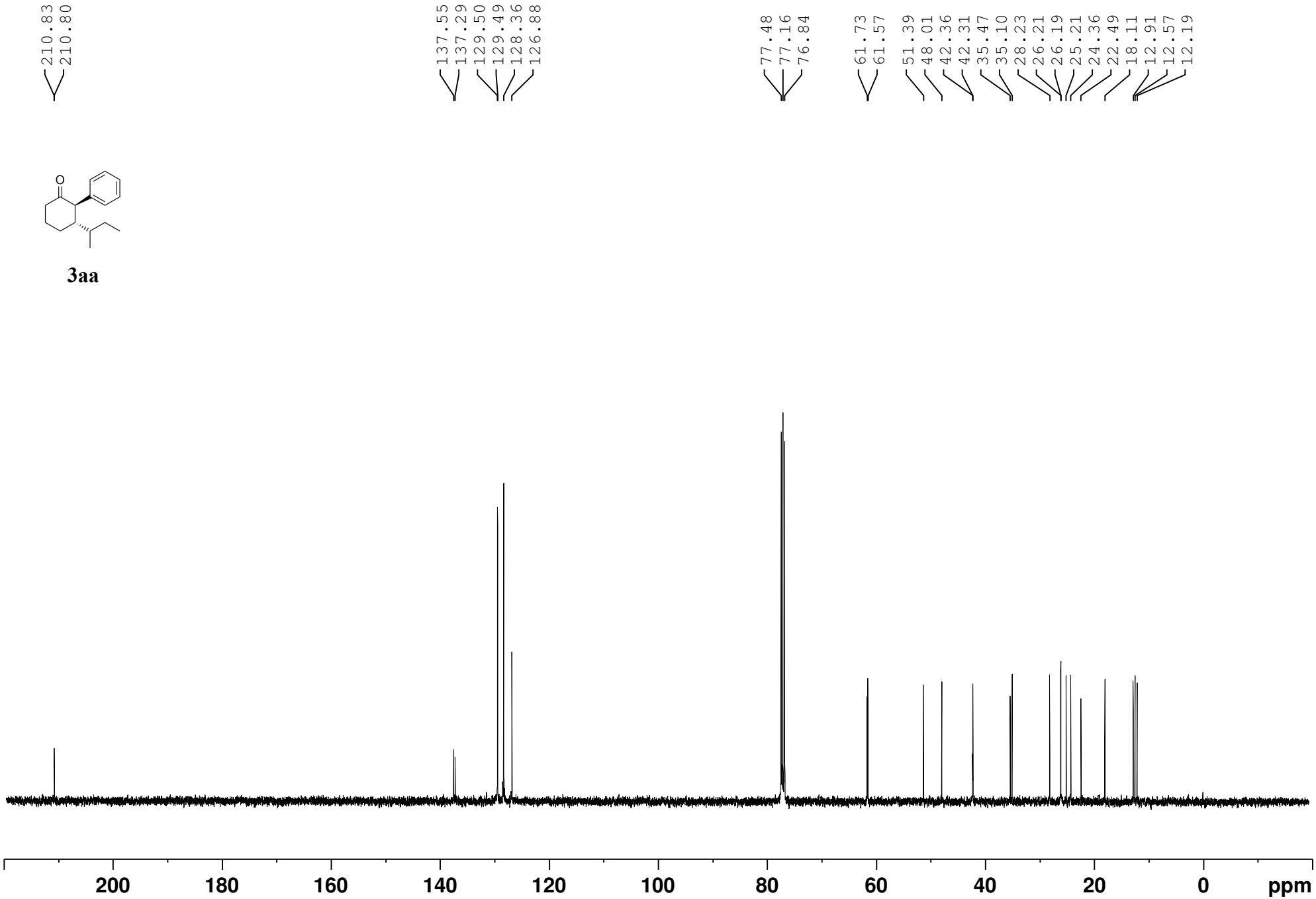
6.07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61.57
51.39
48.01
42.36
42.31
35.47
35.10
28.23
26.21
26.19
25.21
24.36
22.49
18.11
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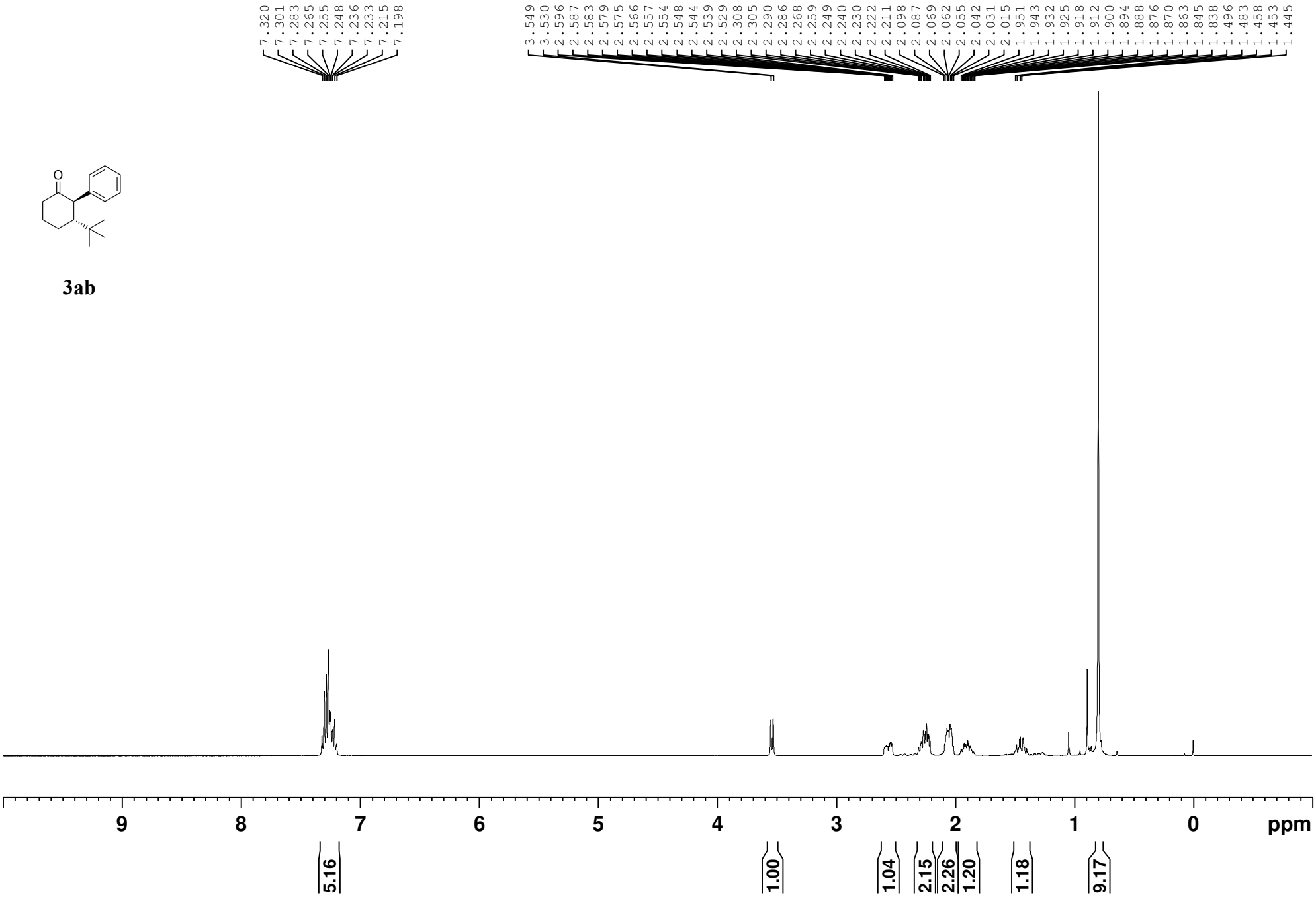
ppm

3aa

3ab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2.596
2.587
2.583
2.579
2.575
2.566
2.557
2.554
2.548
2.544
2.539
2.529
2.308
2.305
2.290
2.286
2.268
2.259
2.249
2.240
2.230
2.222
2.211
2.098
2.087
2.069
2.062
2.055
2.042
2.031
2.015
1.951
1.943
1.932
1.925
1.918
1.912
1.900
1.894
1.888
1.876
1.870
1.863
1.845
1.838
1.496
1.483
1.458
1.453
1.445
9
8
7
6
5
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2.15
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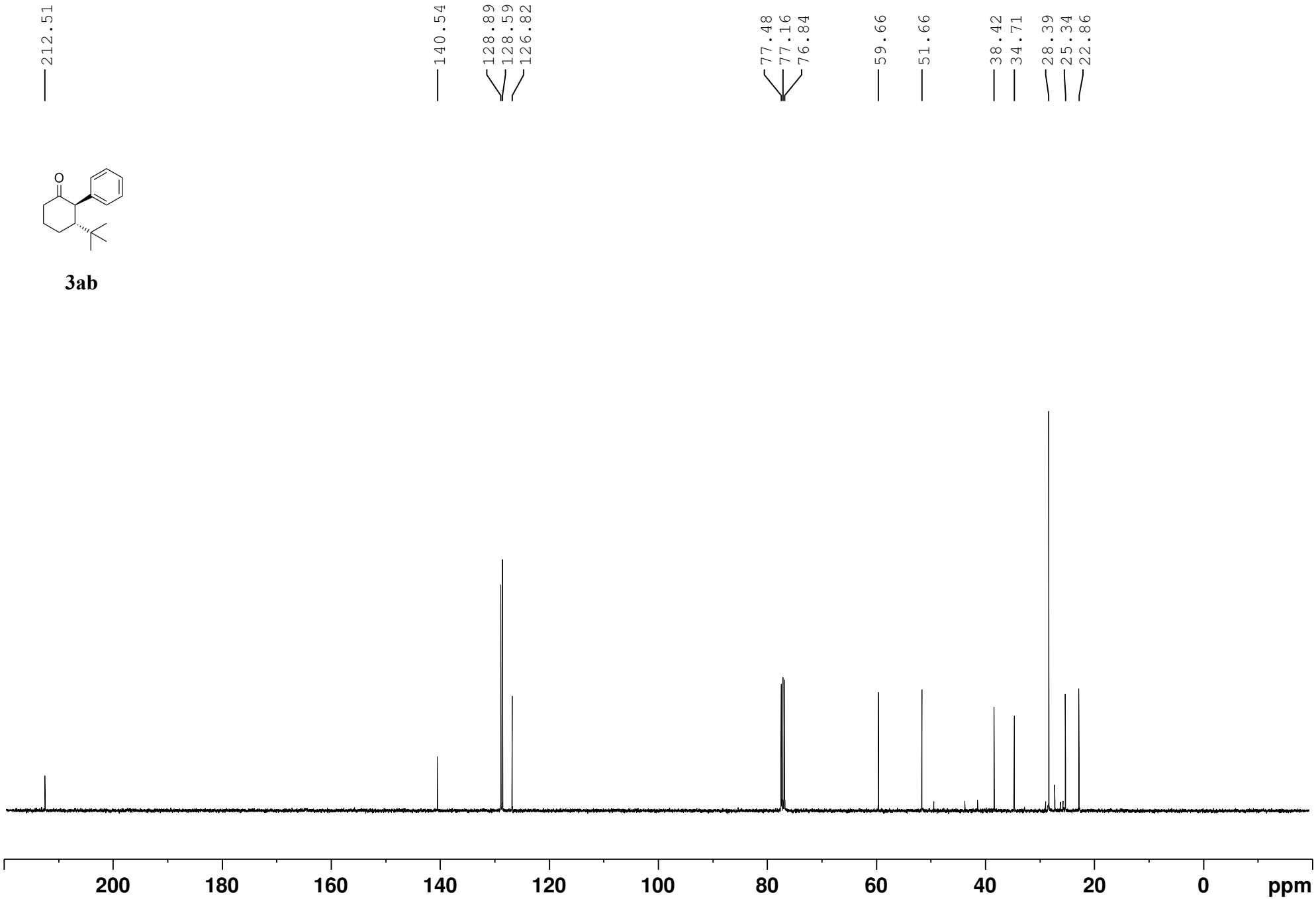
1.20
1.18
9.17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51.66
38.42
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22.86
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140
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100
80
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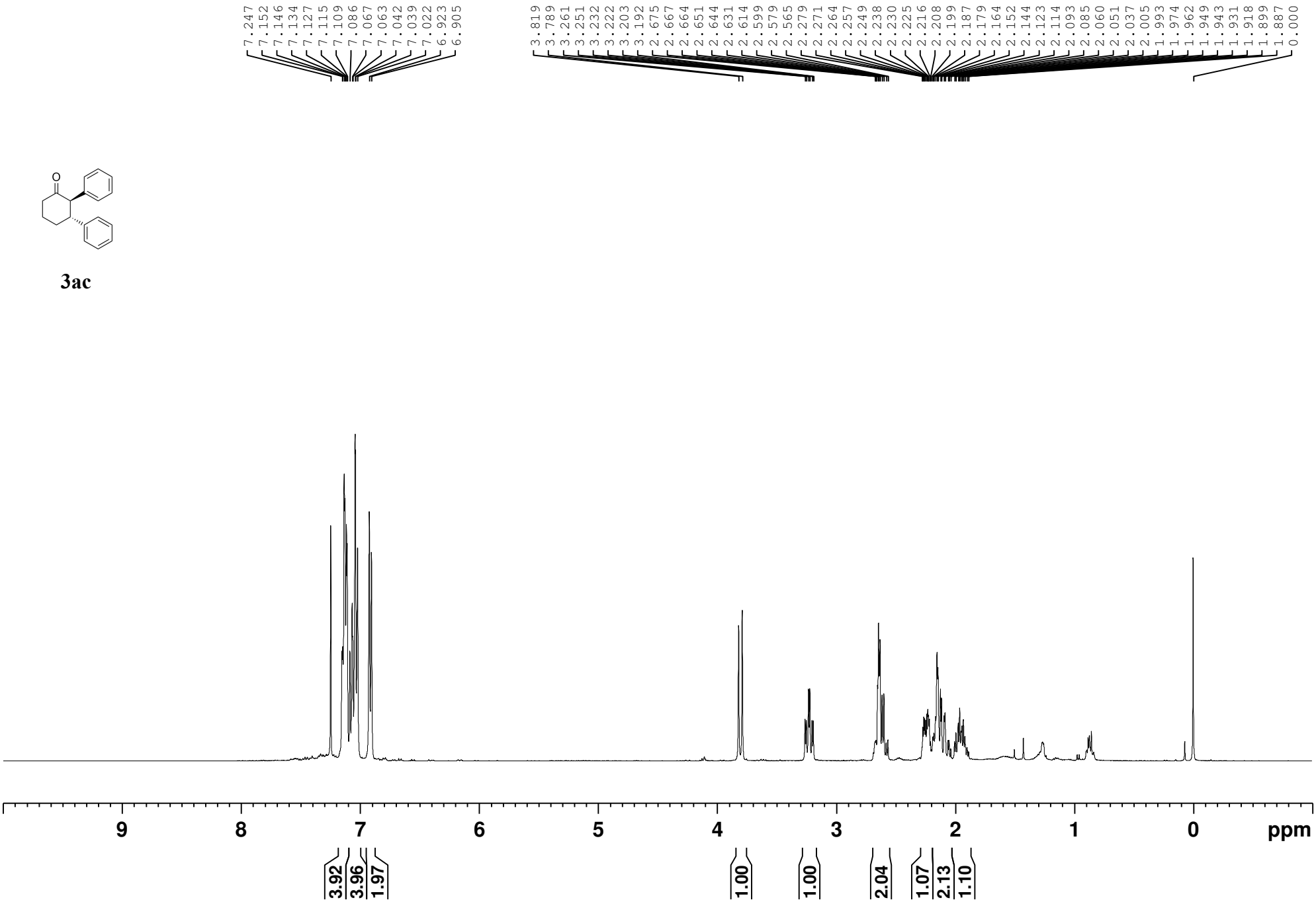
40
20
0
ppm

3ab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7.109
7.086
7.067
7.063
7.042
7.039
7.022
6.923
6.905
3.819
3.789
3.261
3.251
3.232
3.222
3.203
3.192
2.675
2.667
2.664
2.651
2.644
2.631
2.614
2.599
2.579
2.565
2.279
2.271
2.264
2.257
2.249
2.238
2.230
2.225
2.216
2.208
2.199
2.187
2.179
2.164
2.152
2.144
2.123
2.114
2.093
2.085
2.060
2.051
2.037
2.005
1.993
1.974
1.962
1.949
1.943
1.931
1.918
1.899
1.887
0.000
O
3ac
9
8
7
6
5
4
3
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1.00
2.04
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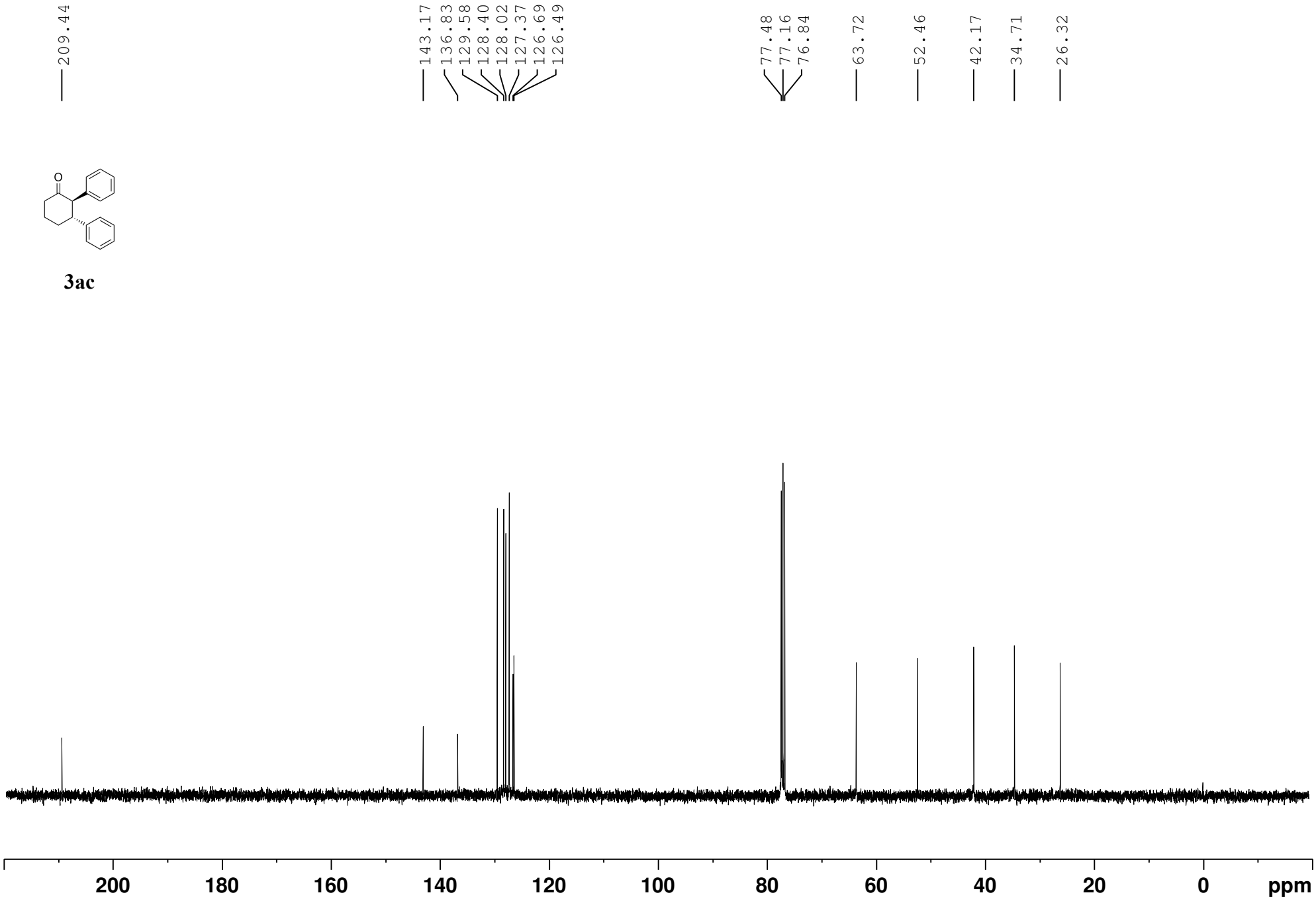
2.13
1.10

3ac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77.16
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34.71
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120
100
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60
40
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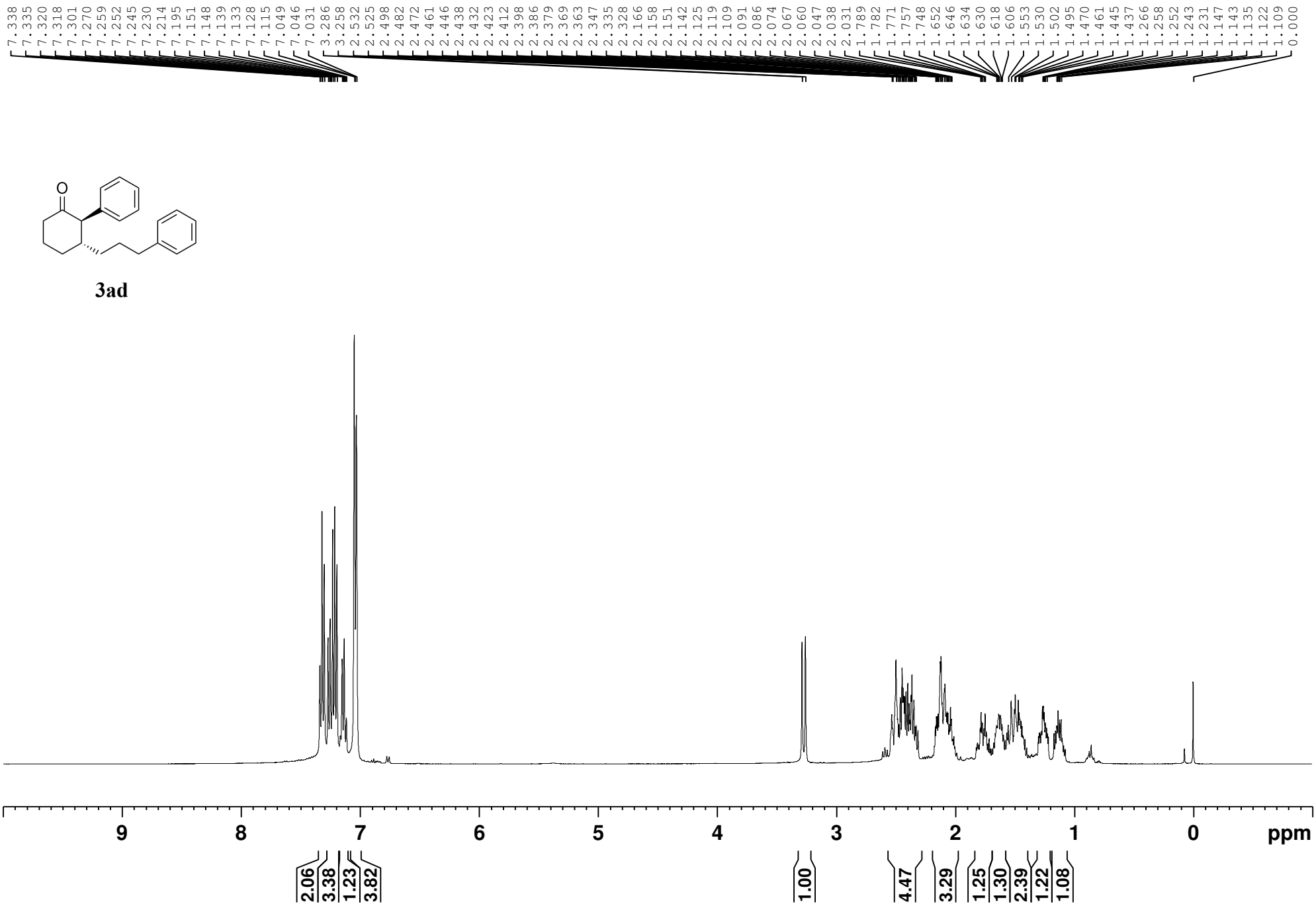
ppm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7.214
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7.151
7.148
7.139
7.133
7.128
7.115
7.049
7.046
7.031
3.286
3.258
2.532
2.525
2.498
2.482
2.472
2.461
2.446
2.438
2.432
2.423
2.412
2.398
2.386
2.379
2.369
2.363
2.347
2.335
2.328
2.166
2.158
2.151
2.142
2.125
2.119
2.109
2.091
2.086
2.074
2.067
2.060
2.047
2.038
2.031
1.789
1.782
1.771
1.757
1.748
1.652
1.646
1.634
1.630
1.618
1.606
1.553
1.530
1.502
1.495
1.470
1.461
1.445
1.437
1.266
1.258
1.252
1.243
1.231
1.147
1.143
1.135
1.122
1.109
0.000
O
3ad
9
8
7
6
5
4
3
2
1
0
ppm
2.06
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1.00
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1.30
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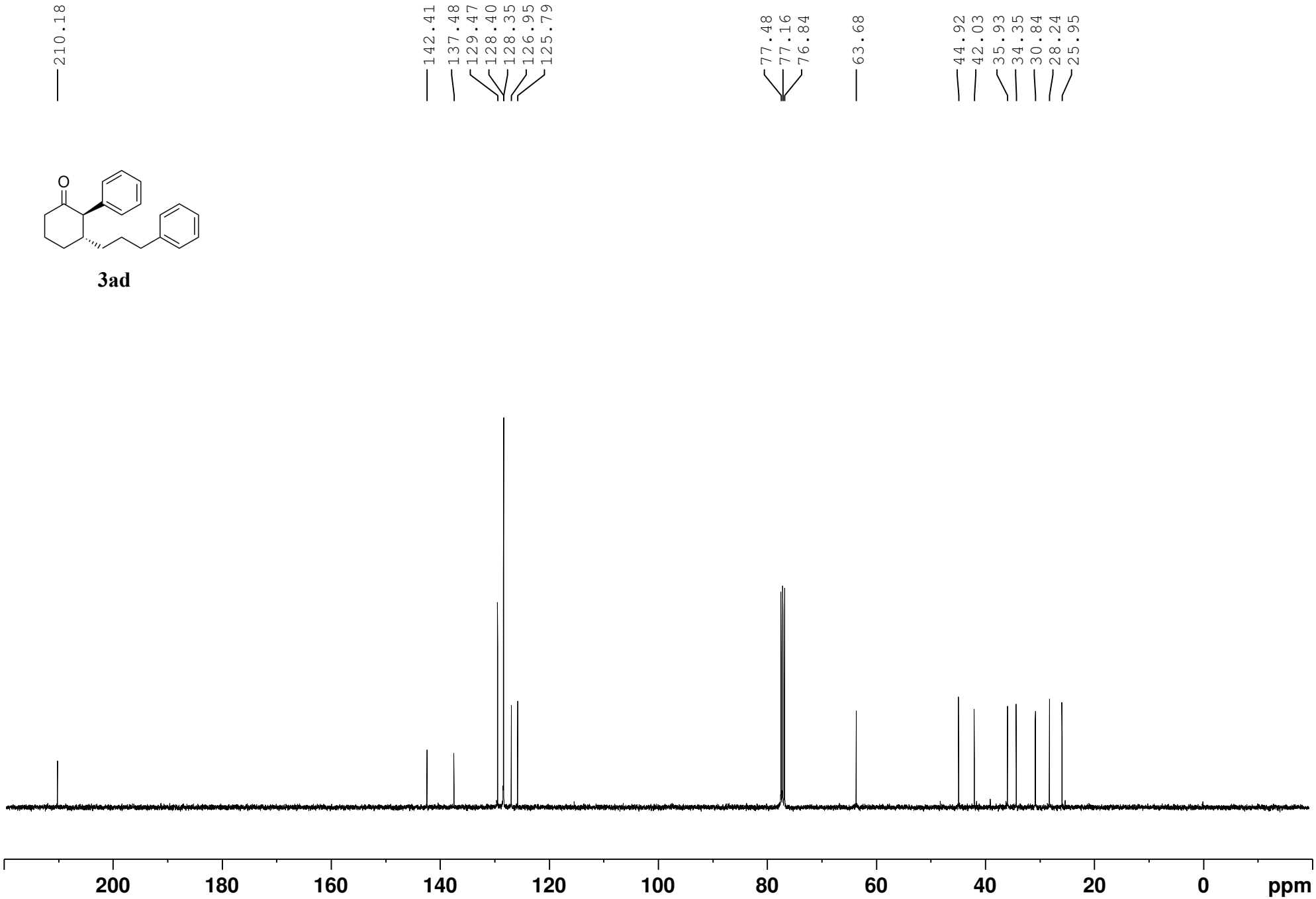
1.08

3ad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77.16
76.84
63.68
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42.03
35.93
34.35
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28.24
25.95
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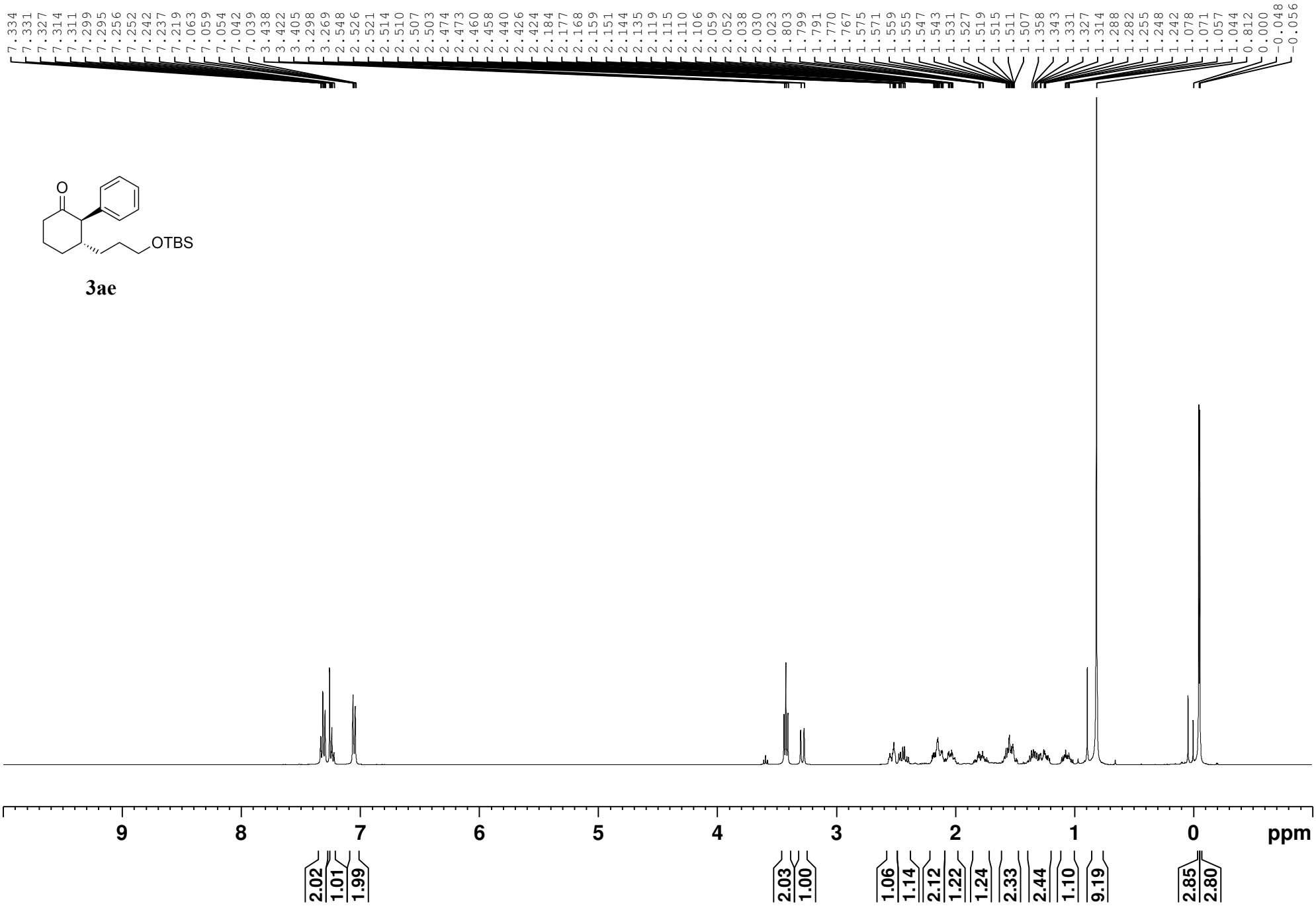
140
120
100
80
60
40
20
0
ppm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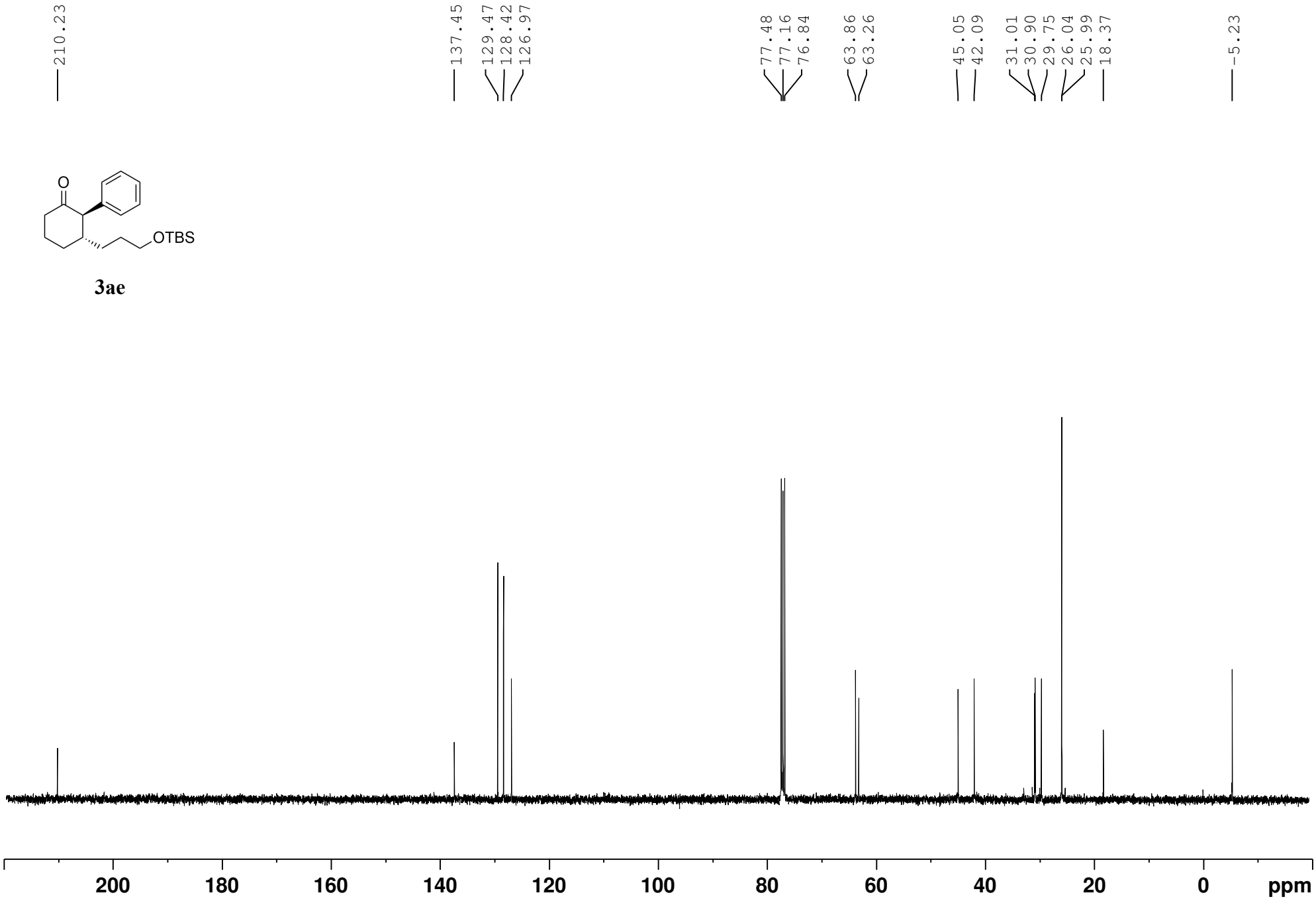
O
OTBS
9 8 7 6 5 4 3 2 1 0 ppm
2.02 1.01 1.99
2.03 1.00
1.06 1.14 2.12 1.22 1.24 2.33 2.44 1.10 9.19
2.85 2.80

3ae

O
OTBS

3ae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76.84
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45.05
42.09
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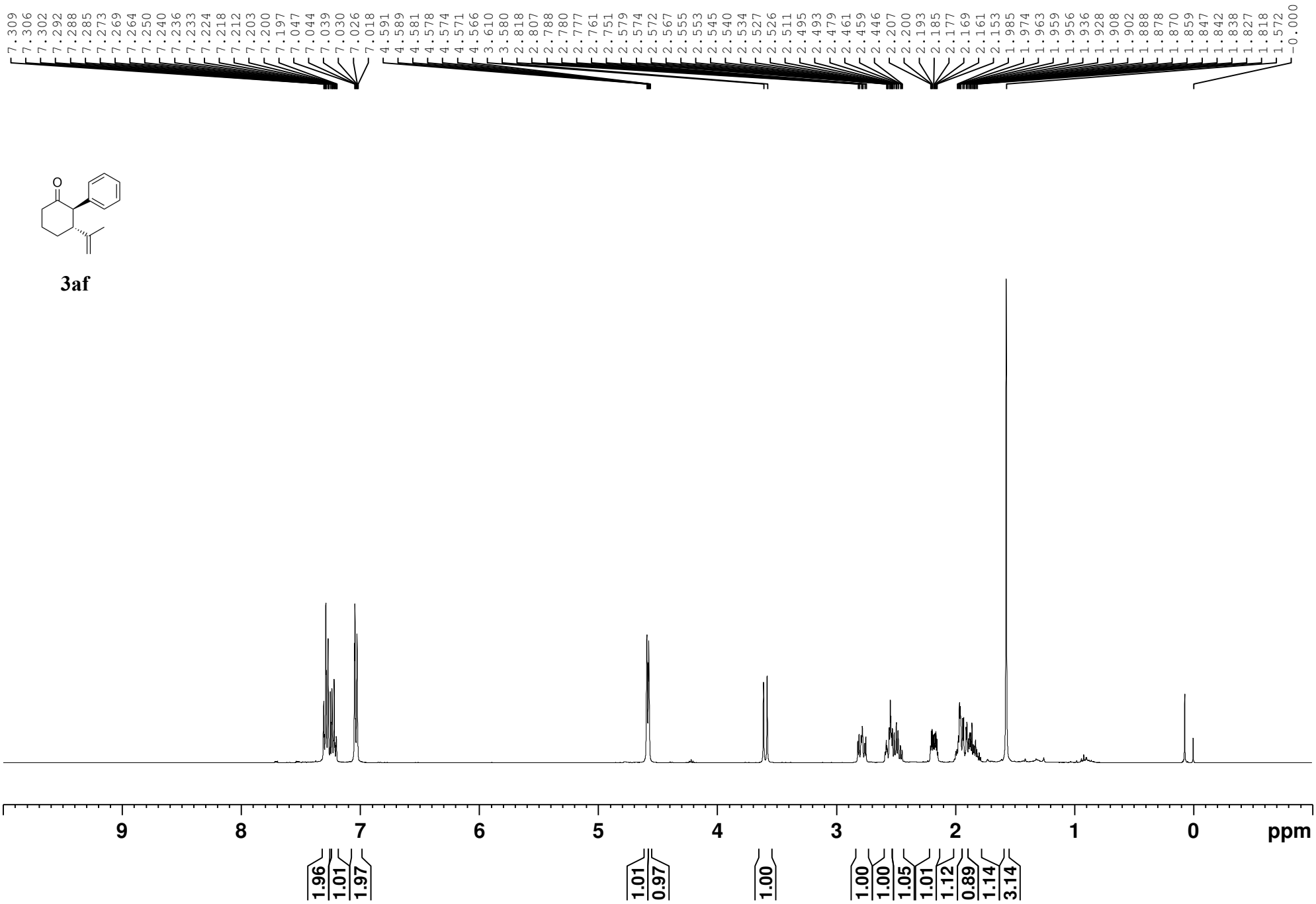
30.90
29.75
26.04
25.99
18.37
-5.23
200
180
160
140
120
100
80
60
40
20
0
ppm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4.591 4.589 4.581 4.578 4.574 4.571 4.566 3.610 3.580 2.818 2.807 2.788 2.780 2.777 2.761 2.751 2.579 2.574 2.572 2.567 2.555 2.553 2.545 2.540 2.534 2.527 2.526 2.511 2.495 2.493 2.479 2.461 2.459 2.446 2.207 2.200 2.193 2.185 2.177 2.169 2.161 2.153 1.985 1.974 1.963 1.959 1.956 1.936 1.928 1.908 1.902 1.888 1.878 1.870 1.859 1.847 1.842 1.838 1.827 1.818 1.572 -0.000
O
9 8 7 6 5 4 3 2 1 0 ppm
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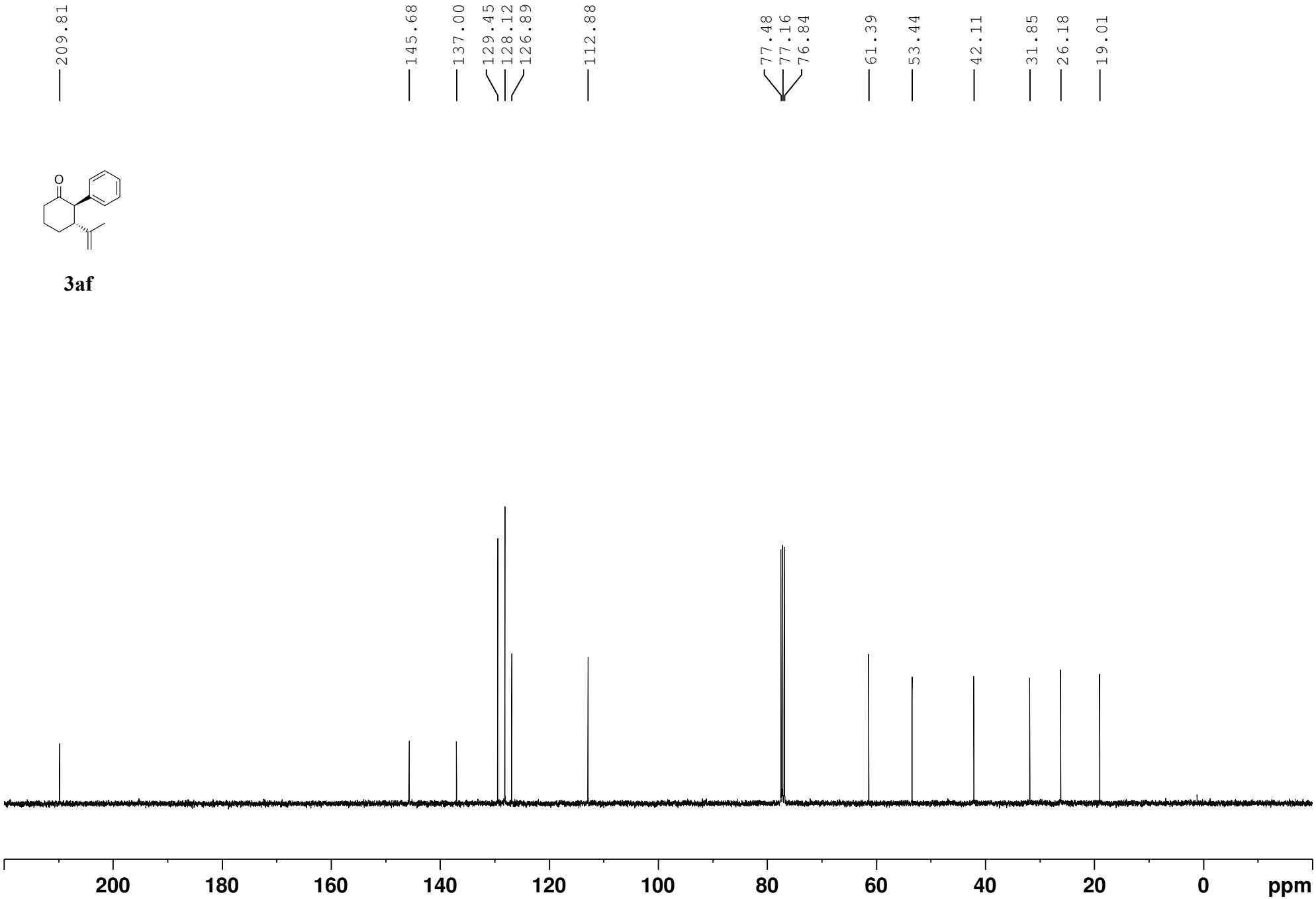
1.01 0.97
1.00
1.00 1.00 1.05 1.01 1.12 0.89 1.14 3.14

3af

3af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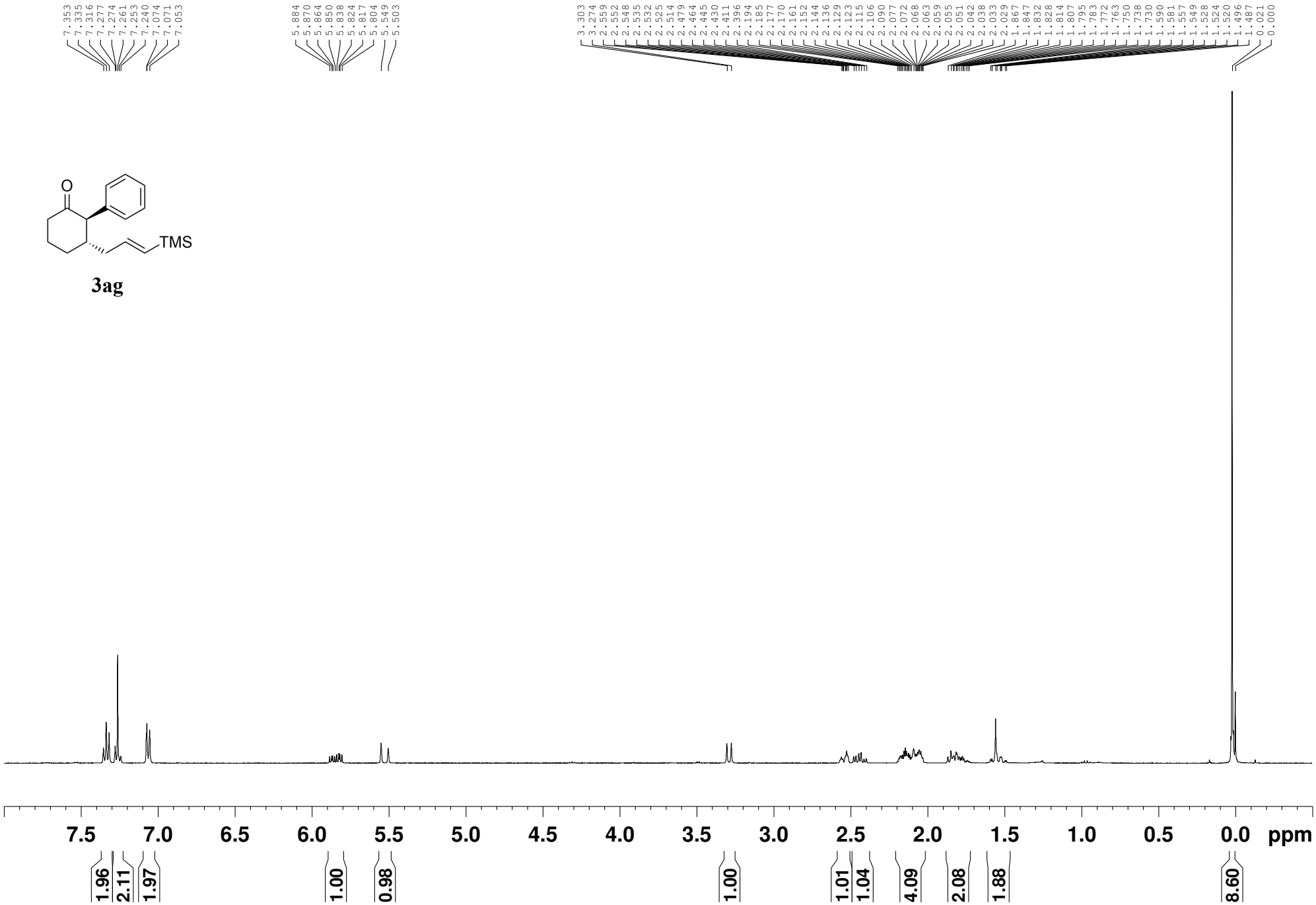
128.12
126.89
112.88
77.48
77.16
76.84
61.39
53.44
42.11
31.85
26.18
19.01
200
180
160
140
120
100
80
60
40
20
0
ppm

O
TMS

3ag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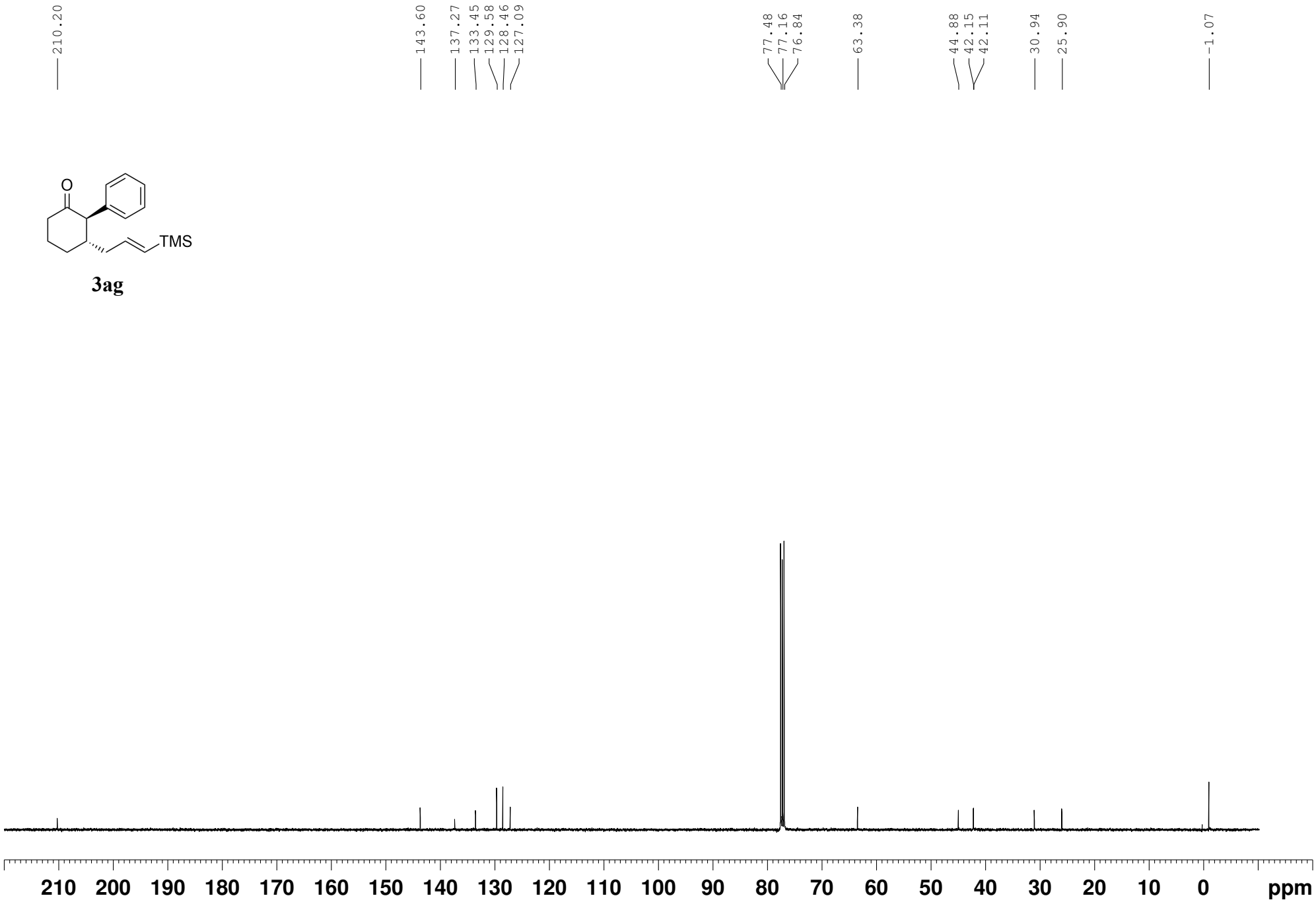
5.884 5.870 5.864 5.850 5.838 5.824 5.817 5.804 5.549 5.503
3.303 3.274 2.559 2.552 2.548 2.535 2.532 2.525 2.514 2.479 2.464 2.445 2.430 2.411 2.396 2.194 2.185 2.177 2.170 2.161 2.152 2.144 2.136 2.129 2.123 2.115 2.106 2.090 2.077 2.072 2.068 2.063 2.059 2.055 2.051 2.042 2.038 2.033 2.029 1.867 1.847 1.832 1.828 1.814 1.807 1.795 1.783 1.772 1.763 1.750 1.738 1.730 1.590 1.581 1.557 1.549 1.528 1.524 1.520 1.496 1.487 0.021 0.000
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.96 2.11 1.97 1.00 0.98 1.00 1.01 1.04 4.09 2.08 1.88 8.60

O
TMS

3ag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129.58
128.46
127.09
77.48
77.16
76.84
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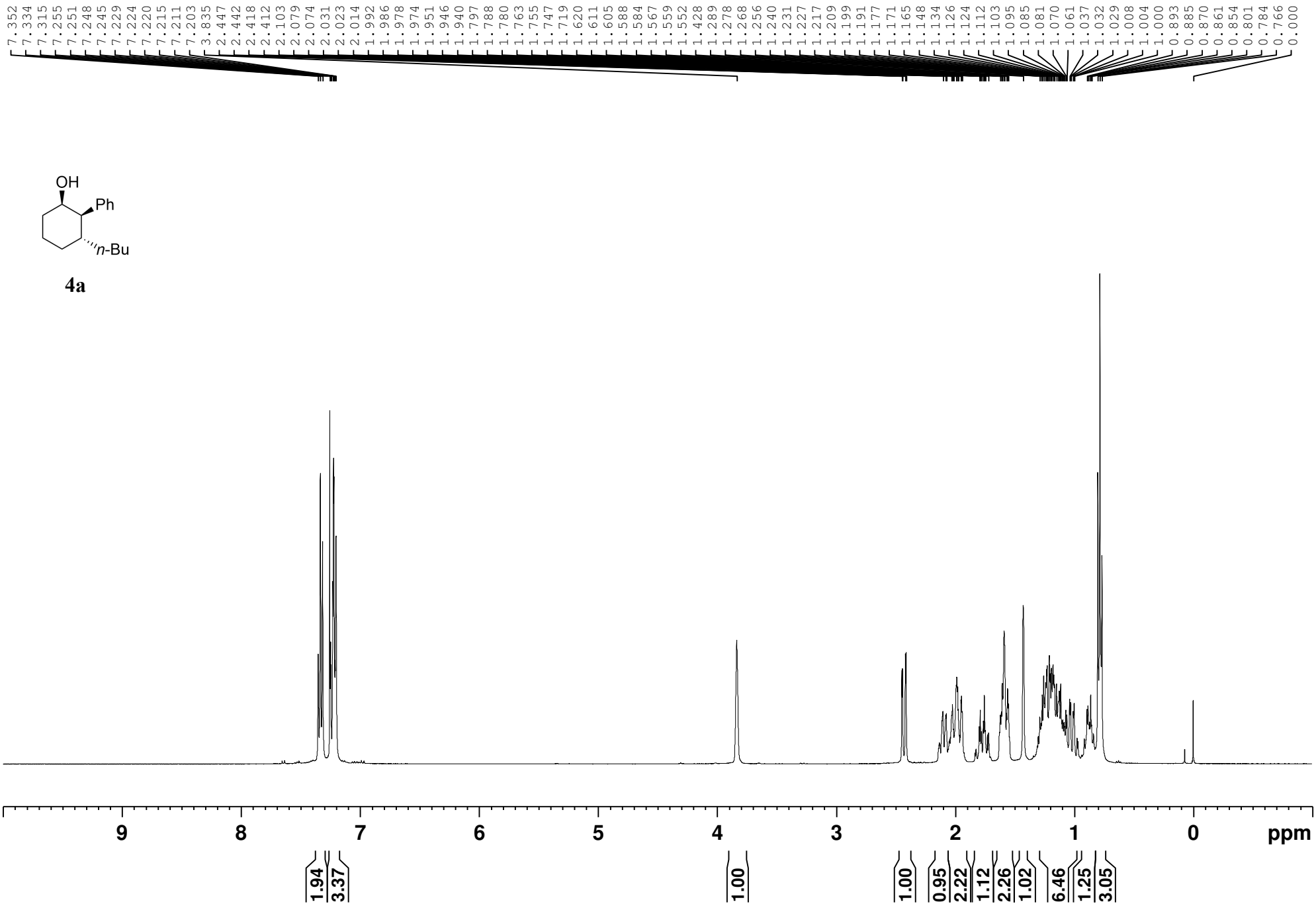
44.88
42.15
42.11
30.94
25.90
-1.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.215
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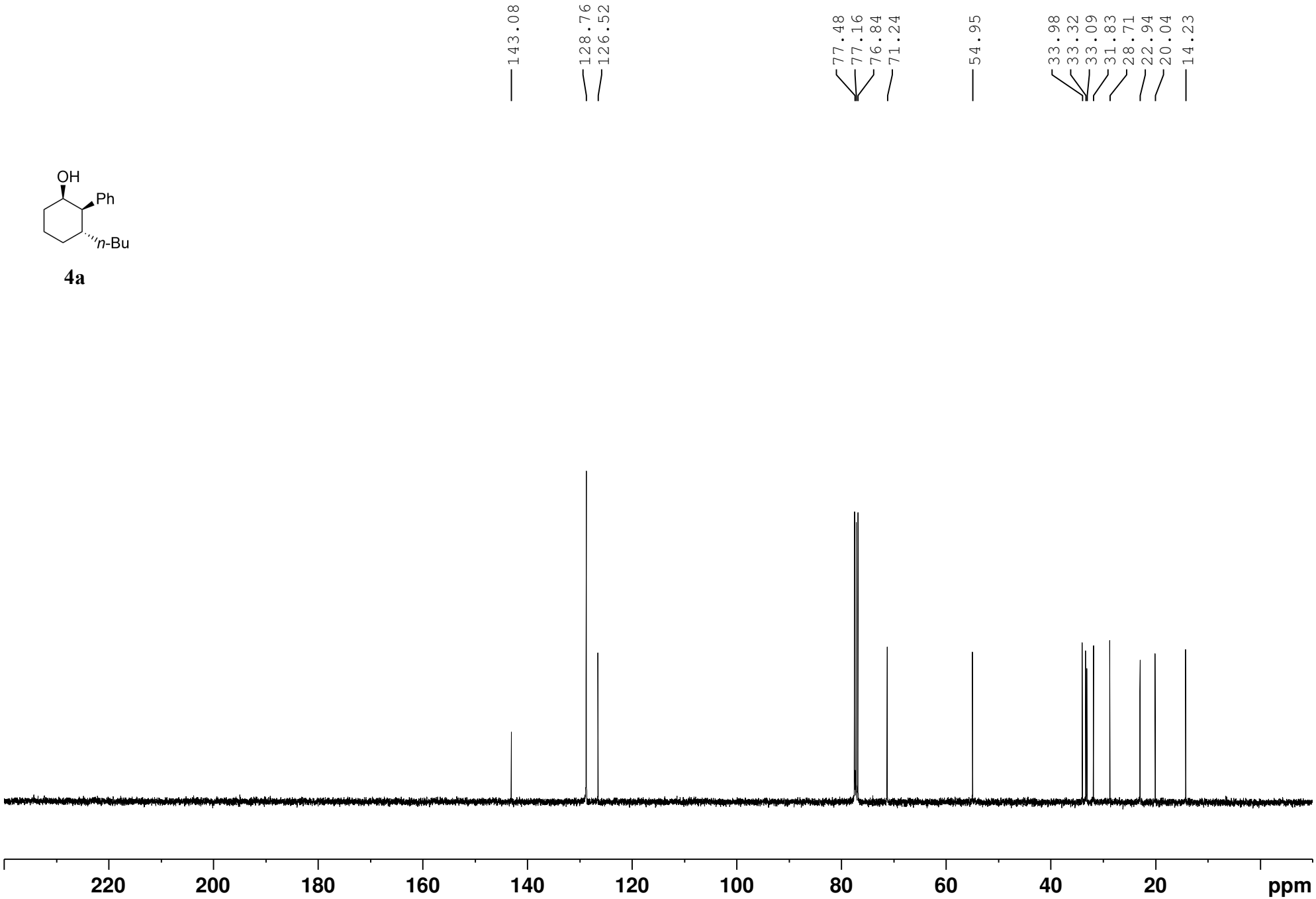
7.203
3.835
2.447
2.442
2.418
2.412
2.103
2.079
2.074
2.031
2.023
2.014
1.992
1.986
1.978
1.974
1.951
1.946
1.940
1.797
1.788
1.780
1.763
1.755
1.747
1.719
1.620
1.611
1.605
1.588
1.584
1.567
1.559
1.552
1.428
1.289
1.278
1.268
1.256
1.240
1.231
1.227
1.217
1.209
1.199
1.191
1.177
1.171
1.165
1.148
1.134
1.126
1.124
1.112
1.103
1.095
1.085
1.081
1.070
1.061
1.037
1.032
1.029
1.008
1.004
1.000
0.893
0.885
0.870
0.861
0.854
0.801
0.784
0.766
0.000
OH
Ph
n-Bu
4a
9
8
7
6
5
4
3
2
1
0
ppm
1.94
3.37
1.00
1.00
0.95
2.22
1.12
2.26
1.02
6.46
1.25
3.05

OH
Ph
n-Bu

4a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54.95
33.98
33.32
33.09
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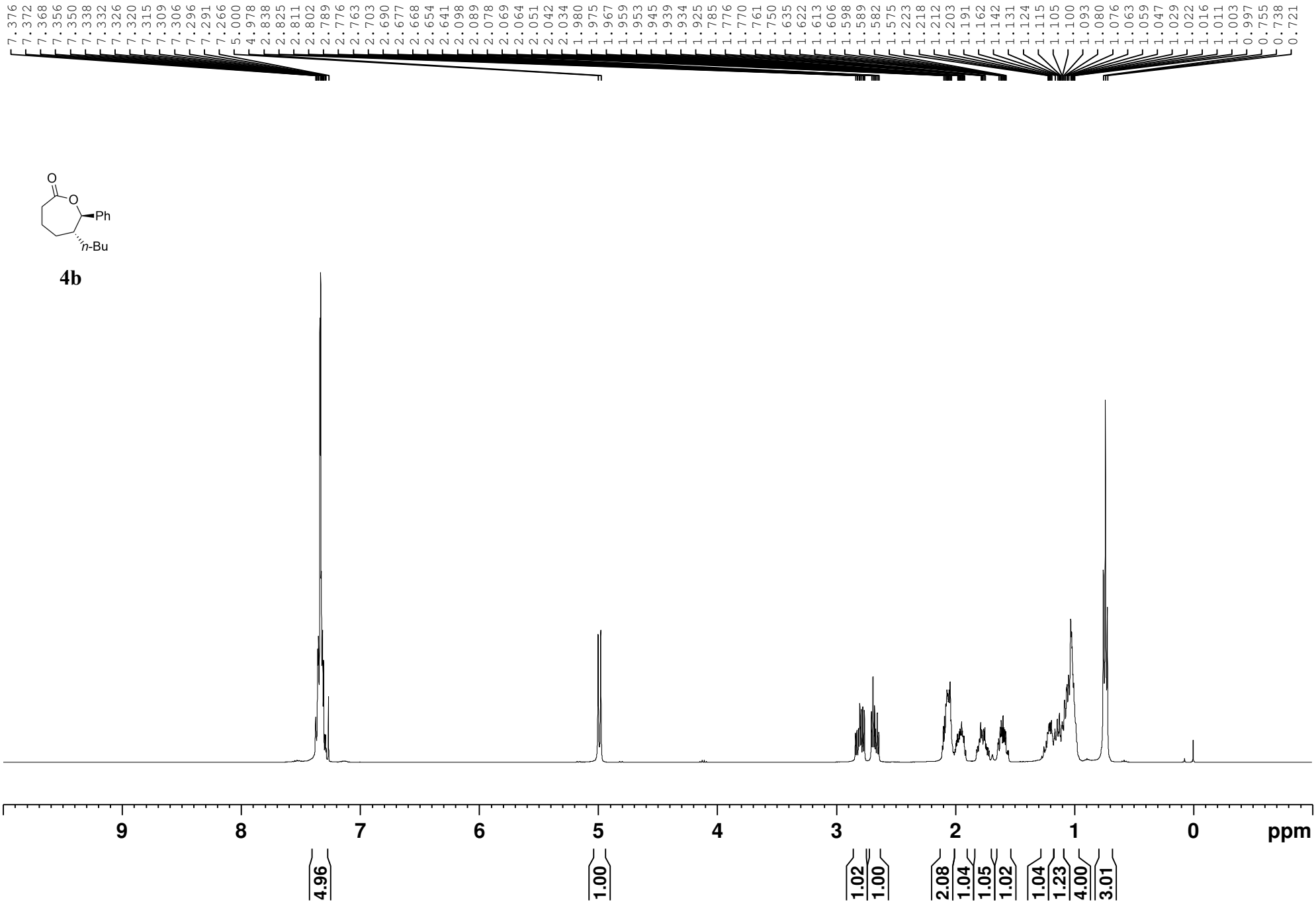
28.71
22.94
20.04
14.23
220
200
180
160
140
120
100
80
60
40
20
ppm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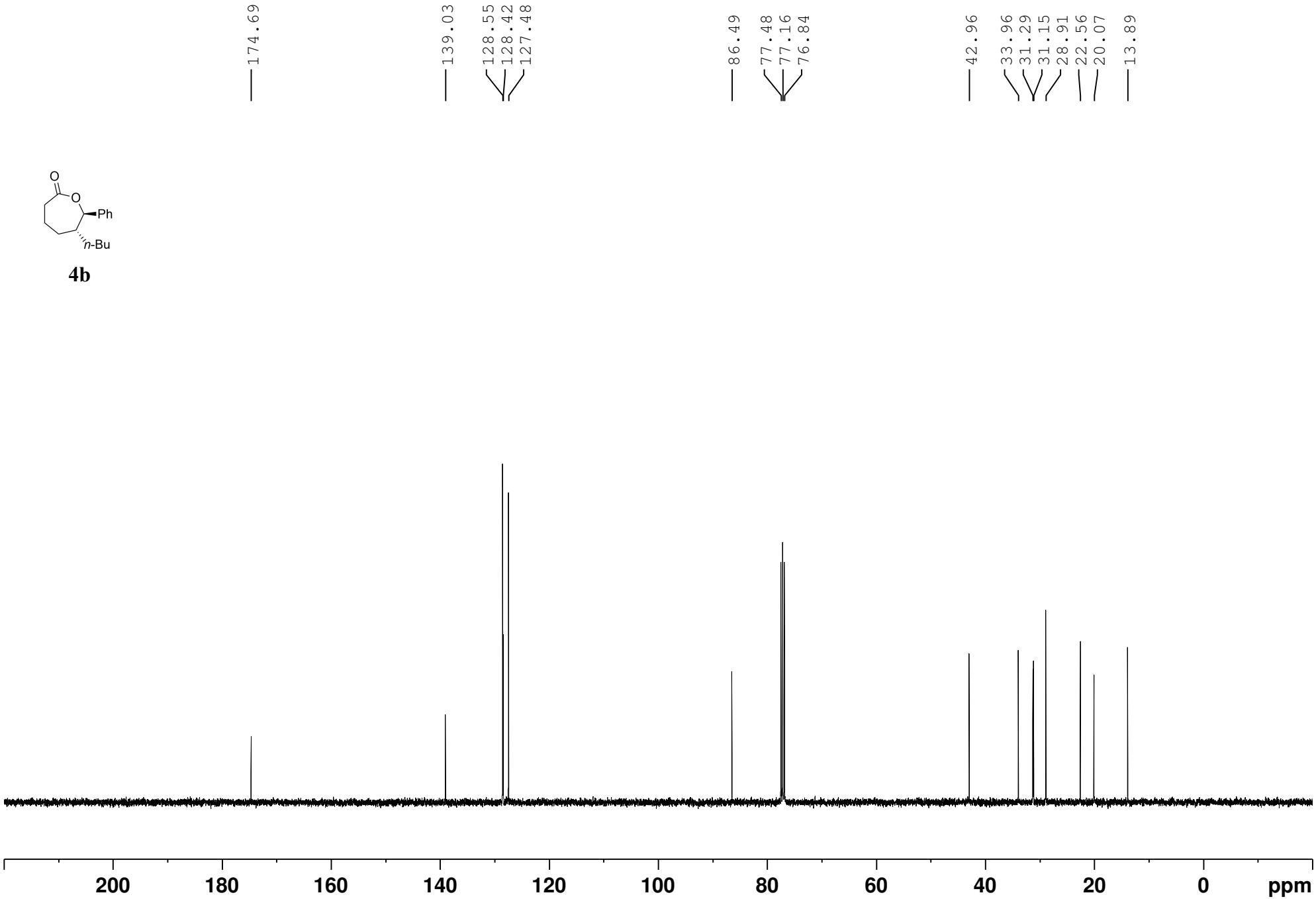
O
O
Ph
n-Bu
4b
9
8
7
6
5
4
3
2
1
0
ppm
4.96
1.00
1.02
1.00
2.08
1.04
1.05
1.02
1.04
1.23
4.00
3.01

O
O
Ph
n-Bu

4b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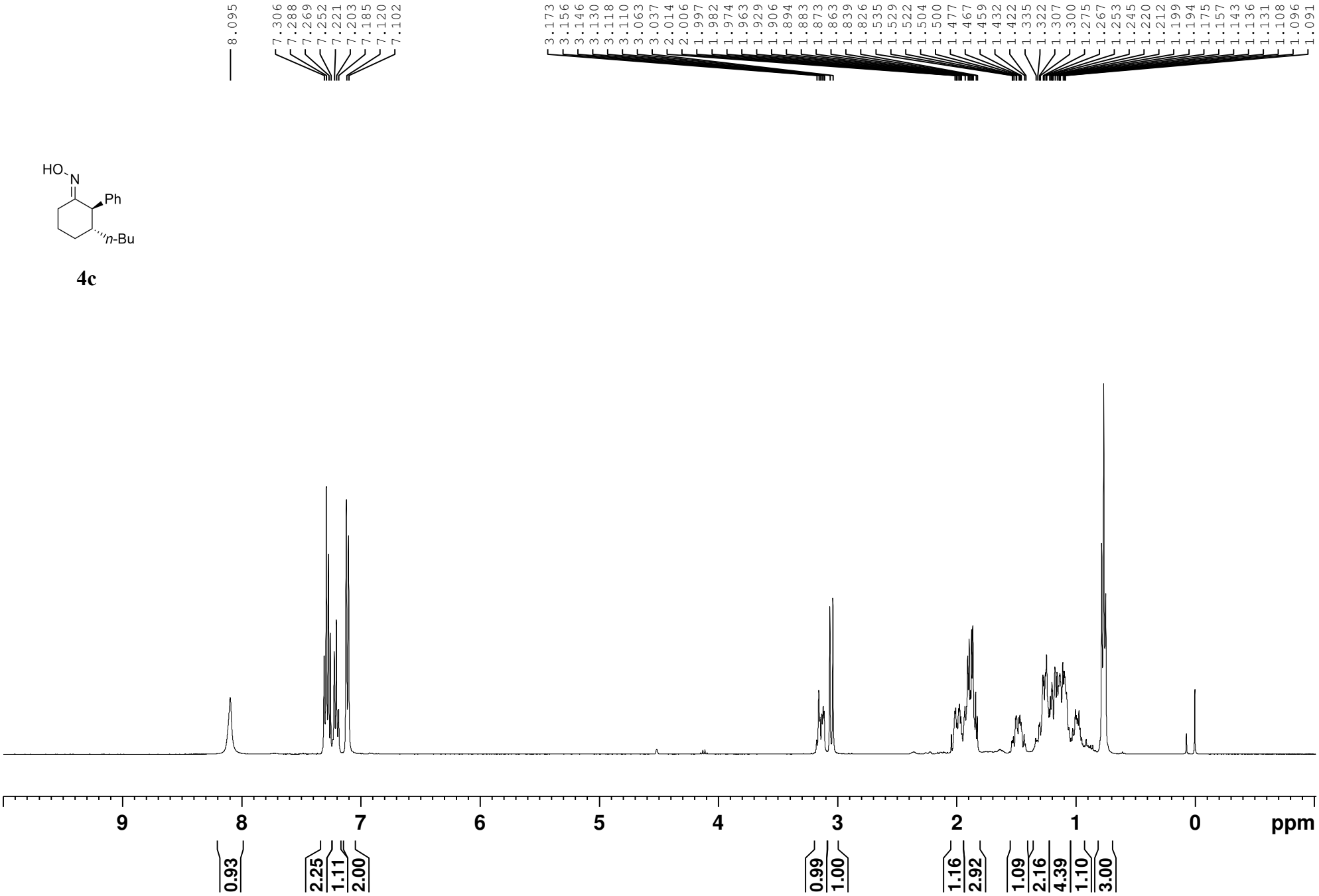
128.42
127.48
86.49
77.48
77.16
76.84
42.96
33.96
31.29
31.15
28.91
22.56
20.07
13.89
200
180
160
140
120
100
80
60
40
20
0
ppm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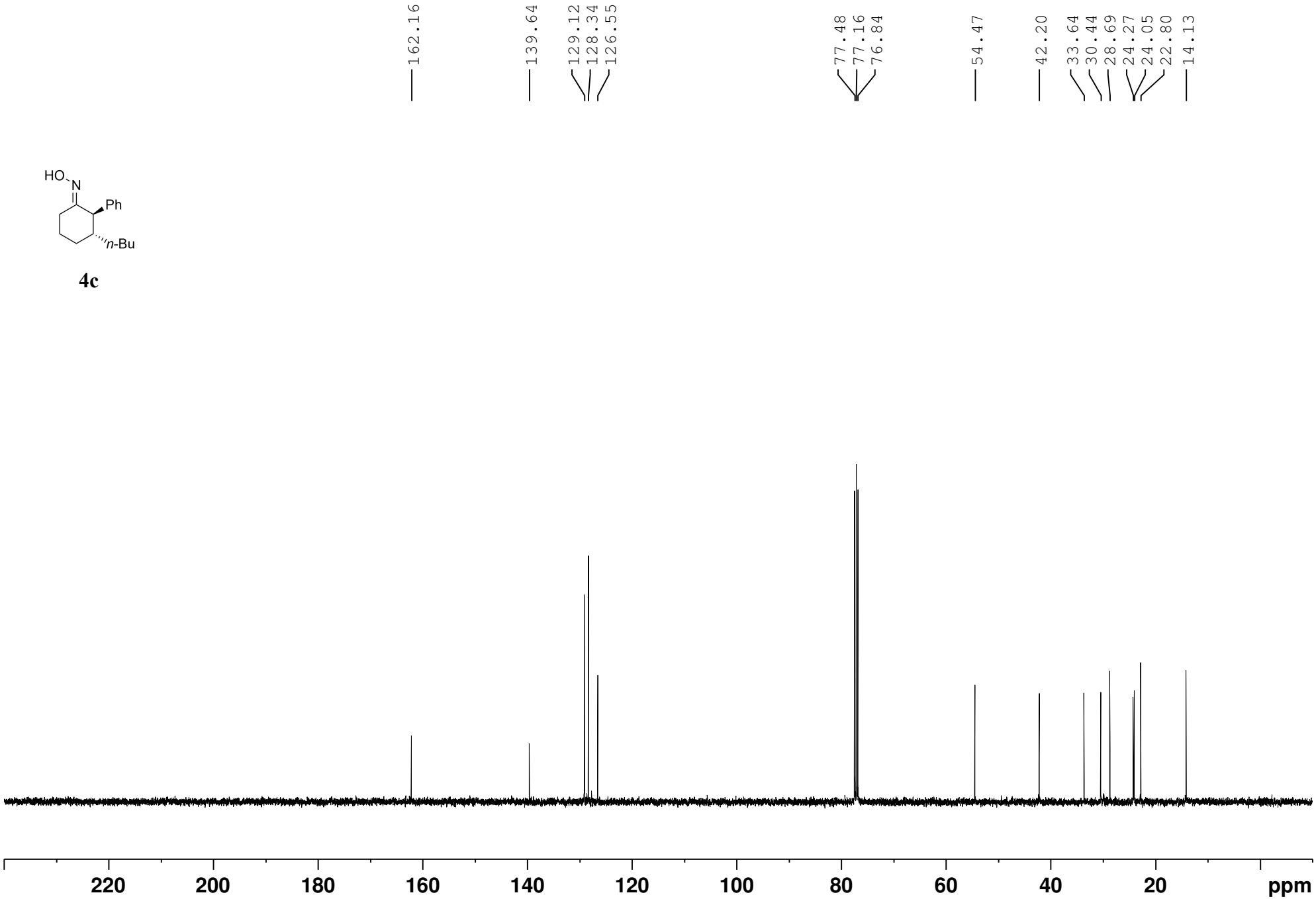
7.269
7.252
7.221
7.203
7.185
7.120
7.102
3.173
3.156
3.146
3.130
3.118
3.110
3.063
3.037
2.014
2.006
1.997
1.982
1.974
1.963
1.929
1.906
1.894
1.883
1.873
1.863
1.839
1.826
1.535
1.529
1.522
1.504
1.500
1.477
1.467
1.459
1.432
1.422
1.335
1.322
1.307
1.300
1.275
1.267
1.253
1.245
1.220
1.212
1.199
1.194
1.175
1.157
1.143
1.136
1.131
1.108
1.096
1.091
HO
N
Ph
n-Bu
4c
9
8
7
6
5
4
3
2
1
0
ppm
0.93
2.25
1.11
2.00
0.99
1.00
1.16
2.92
1.09
2.16
4.39
1.10
3.00

HO
N
Ph
n-Bu

4c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126.55
77.48
77.16
76.84
54.47
42.20
33.64
30.44
28.69
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24.05
22.80
14.13
220
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180
160
140
120
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80
60
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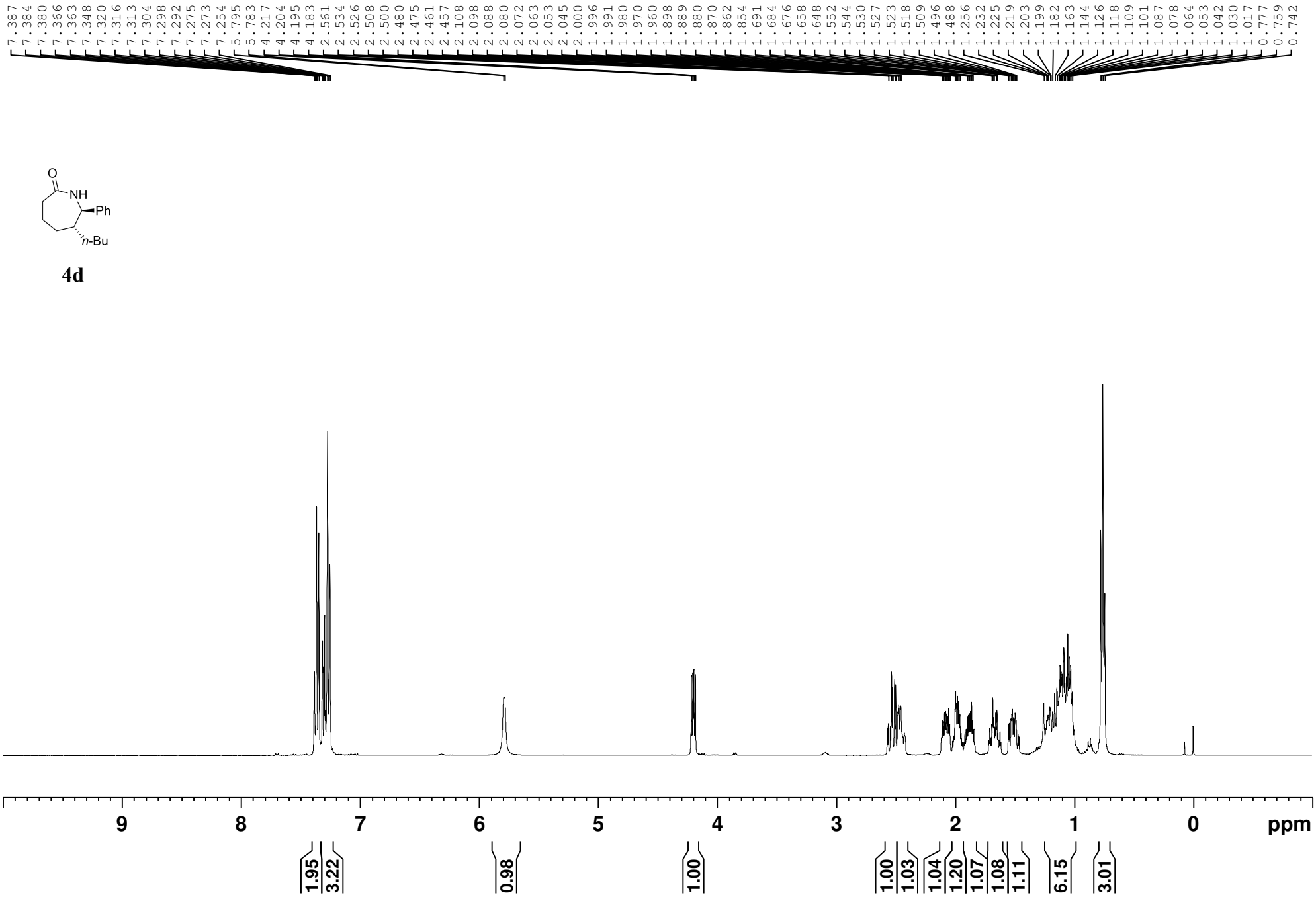
20
ppm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7.366
7.363
7.348
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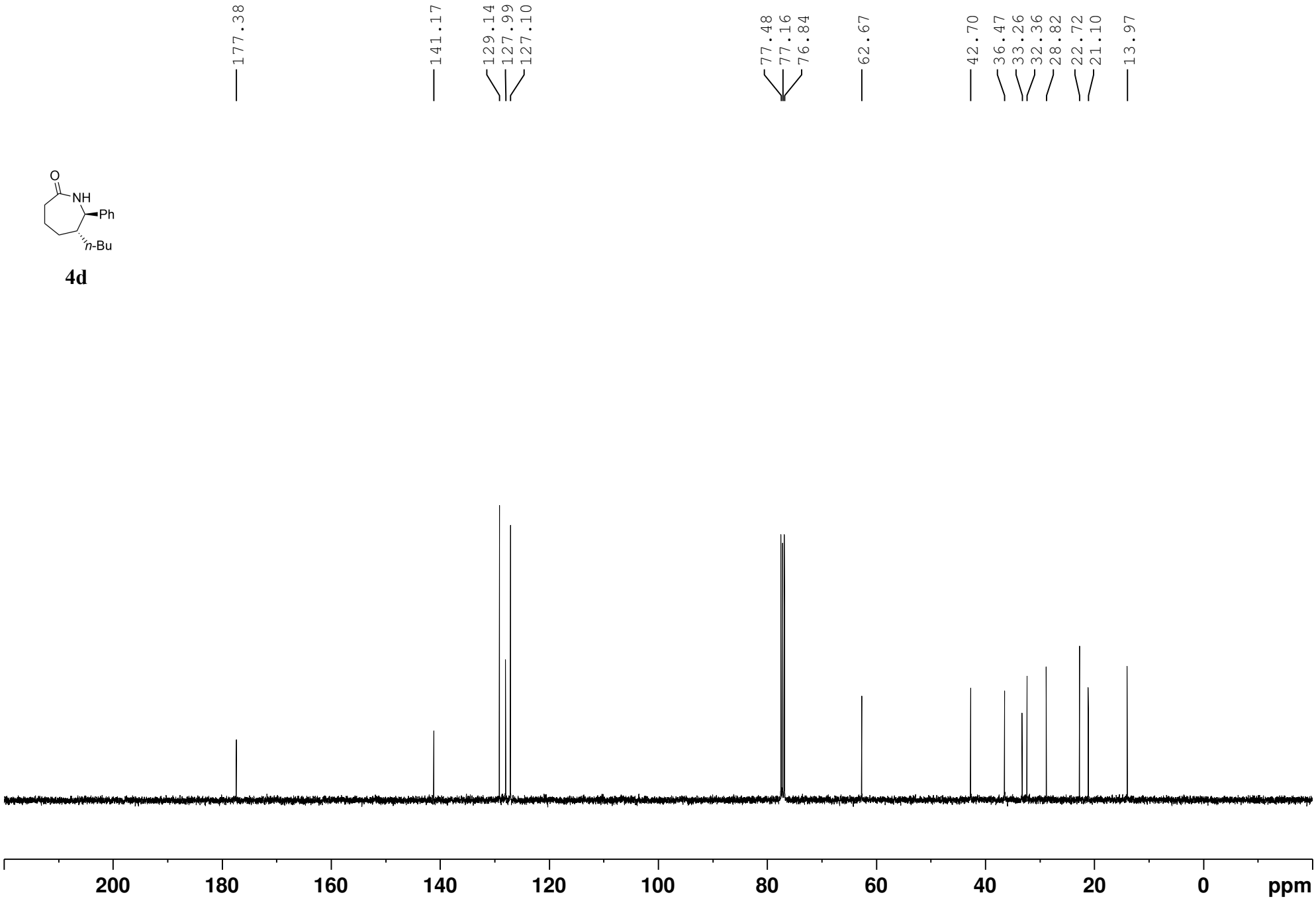
7.316
7.313
7.304
7.298
7.292
7.275
7.273
7.254
5.795
5.783
4.217
4.204
4.195
4.183
2.561
2.534
2.526
2.508
2.500
2.480
2.475
2.461
2.457
2.108
2.098
2.088
2.080
2.072
2.063
2.053
2.045
2.000
1.996
1.991
1.980
1.970
1.960
1.898
1.889
1.880
1.870
1.862
1.854
1.691
1.684
1.676
1.658
1.648
1.552
1.544
1.530
1.527
1.523
1.518
1.509
1.496
1.488
1.256
1.232
1.225
1.219
1.203
1.199
1.182
1.163
1.144
1.126
1.118
1.109
1.101
1.087
1.078
1.064
1.053
1.042
1.030
1.017
0.777
0.759
0.742
O
NH
Ph
n-Bu
4d
9
8
7
6
5
4
3
2
1
0
ppm
1.95
3.22
0.98
1.00
1.00
1.03
1.04
1.20
1.07
1.08
1.11
6.15
3.01

O
NH
Ph
n-Bu

4d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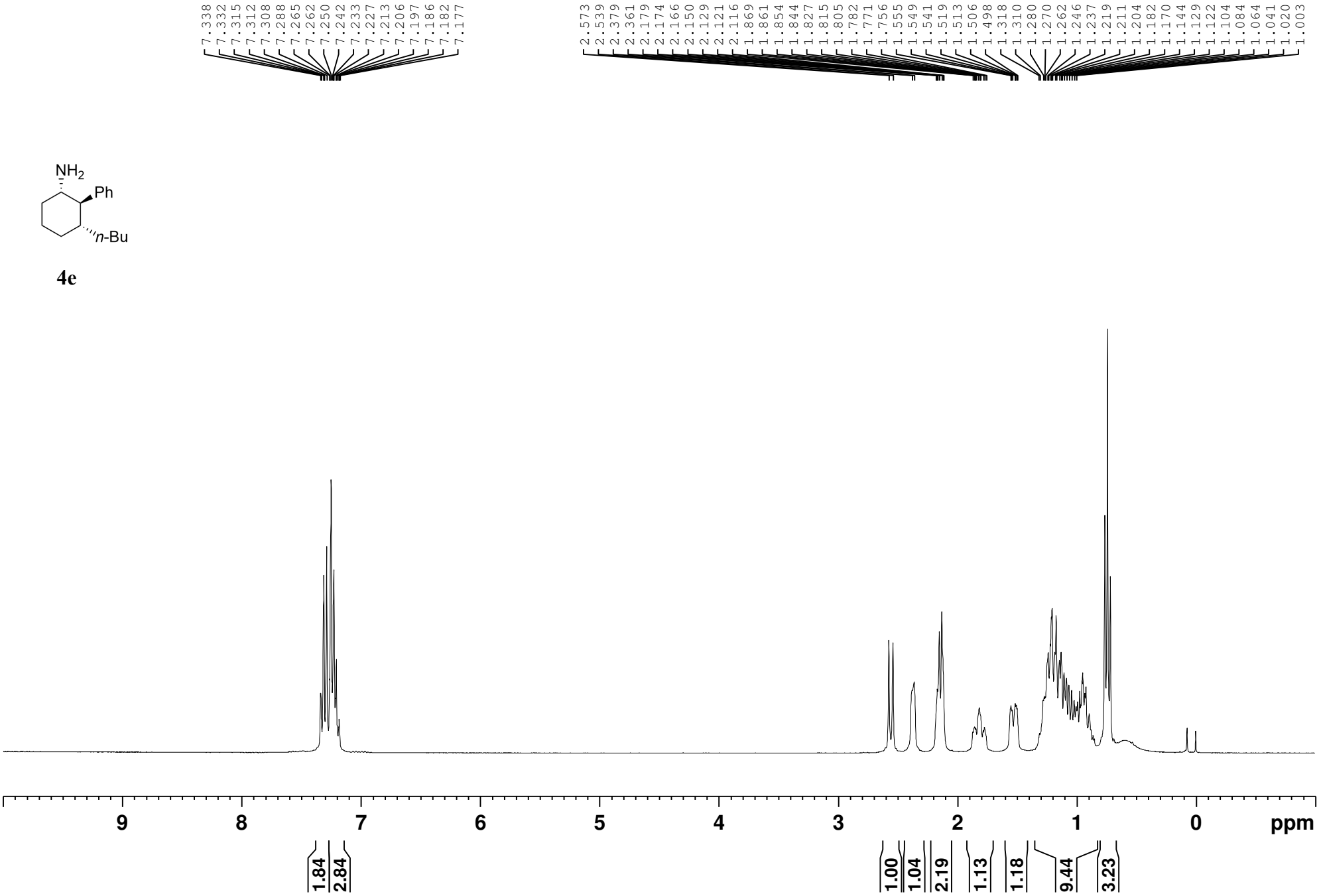
141.17
129.14
127.99
127.10
77.48
77.16
76.84
62.67
42.70
36.47
33.26
32.36
28.82
22.72
21.10
13.97
200
180
160
140
120
100
80
60
40
20
0
ppm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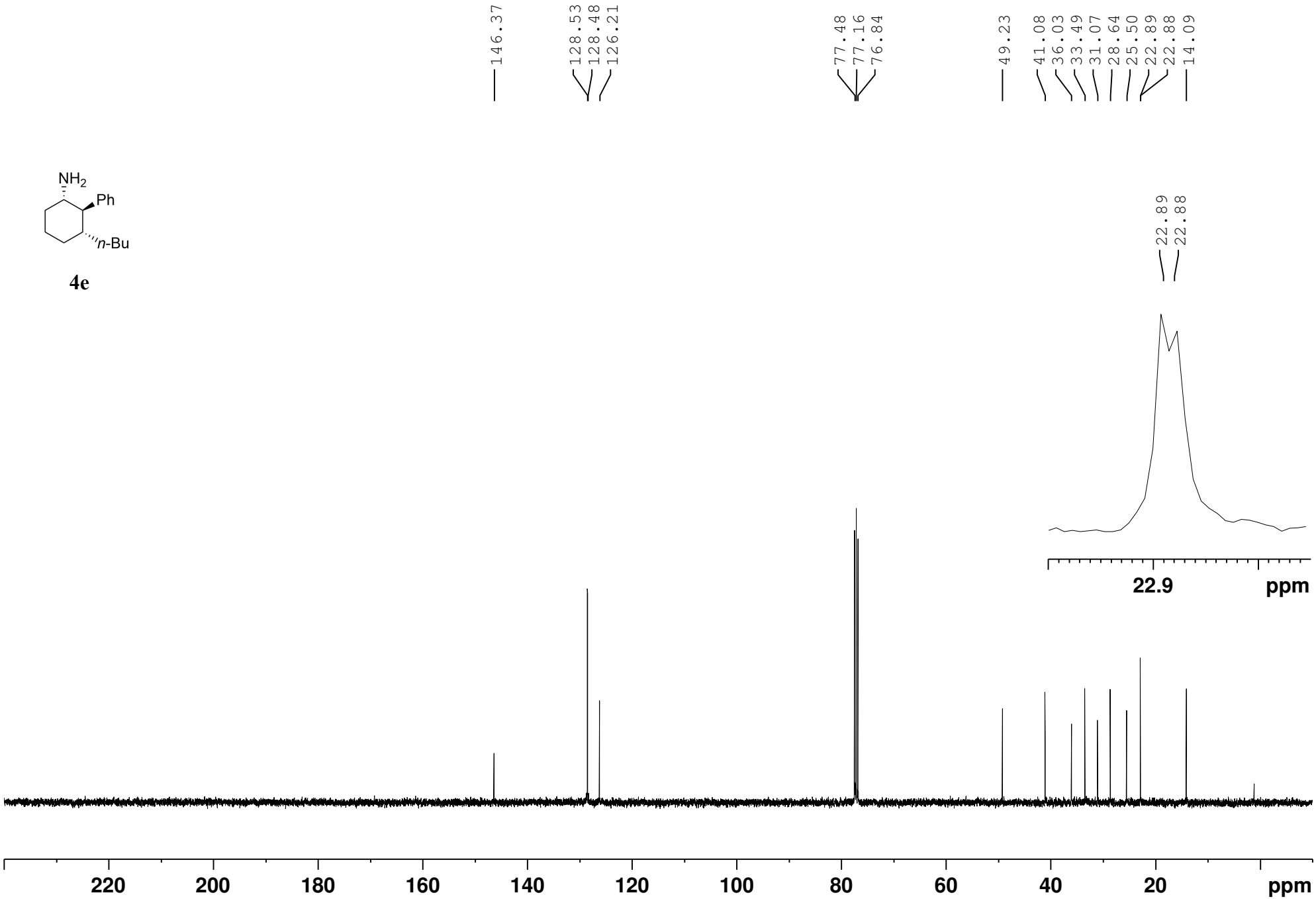
7.315
7.312
7.308
7.288
7.265
7.262
7.250
7.242
7.233
7.227
7.213
7.206
7.197
7.186
7.182
7.177
2.573
2.539
2.379
2.361
2.179
2.174
2.166
2.150
2.129
2.121
2.116
1.869
1.861
1.854
1.844
1.827
1.815
1.805
1.782
1.771
1.756
1.555
1.549
1.541
1.519
1.513
1.506
1.498
1.318
1.310
1.280
1.270
1.262
1.246
1.237
1.219
1.211
1.204
1.182
1.170
1.144
1.129
1.122
1.104
1.084
1.064
1.041
1.020
1.003
NH2
Ph
n-Bu
4e
9
8
7
6
5
4
3
2
1
0
ppm
1.84
2.84
1.00
1.04
2.19
1.13
1.18
9.44
3.23

NH2
Ph
n-Bu

4e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128.48
126.21
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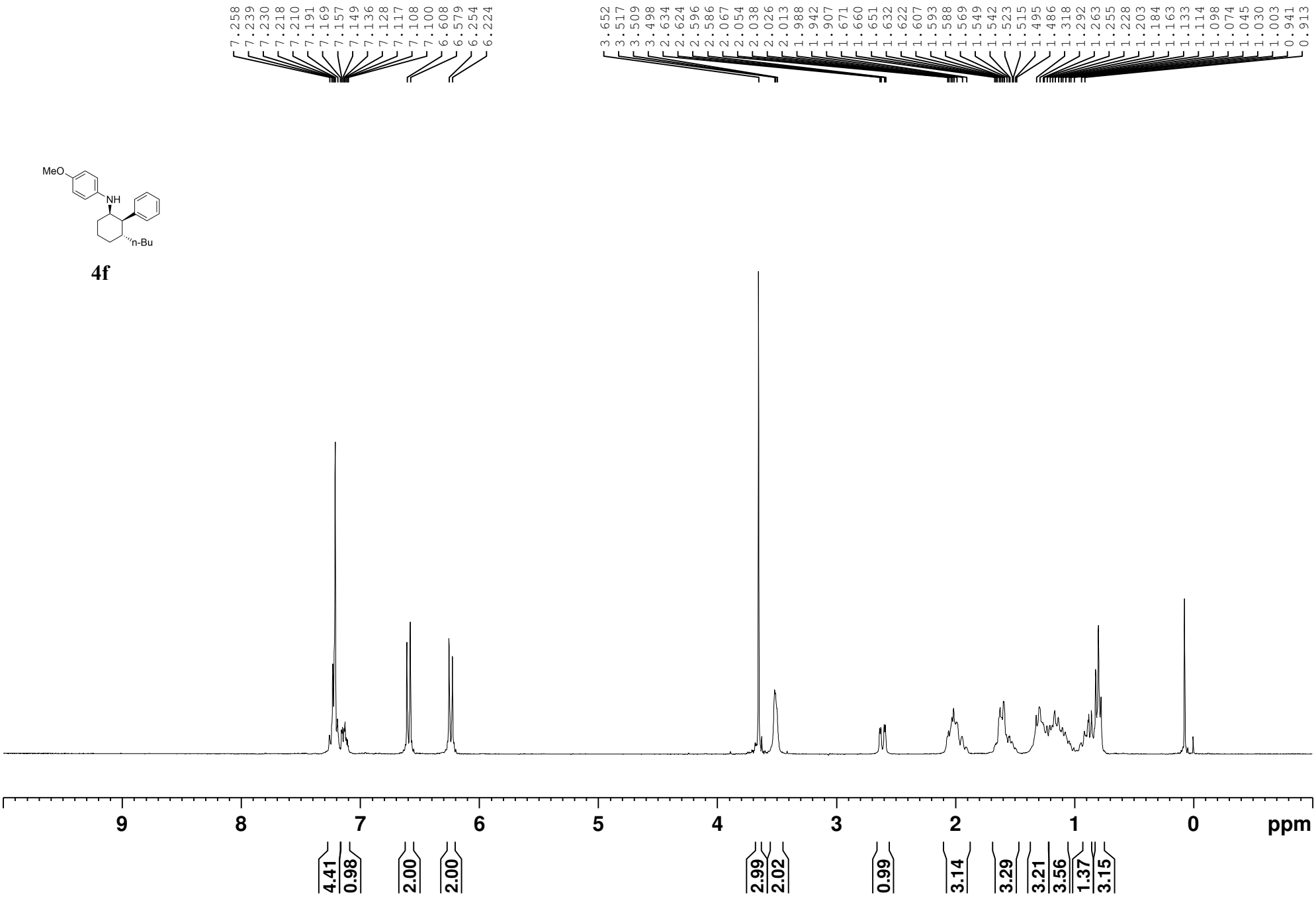
77.16
76.84
49.23
41.08
36.03
33.49
31.07
28.64
25.50
22.89
22.88
14.09
22.89
22.88
22.9
ppm
220
200
180
160
140
120
100
80
60
40
20
ppm

MeO
NH
n-Bu

4f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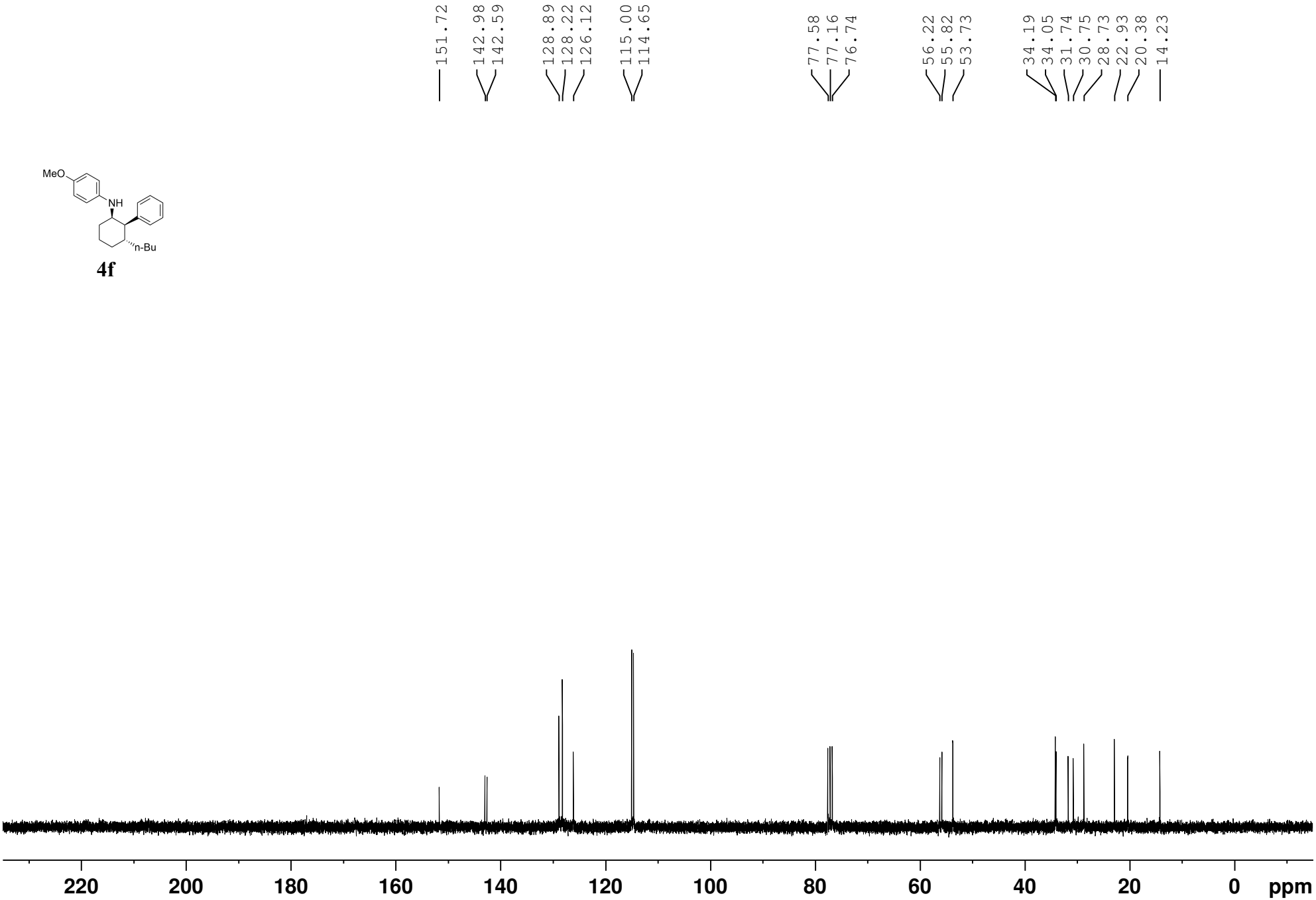
7.239
7.230
7.218
7.210
7.191
7.169
7.157
7.149
7.136
7.128
7.117
7.108
7.100
6.608
6.579
6.254
6.224
3.652
3.517
3.509
3.498
2.634
2.624
2.596
2.586
2.067
2.054
2.038
2.026
2.013
1.988
1.942
1.907
1.671
1.660
1.651
1.632
1.622
1.607
1.593
1.588
1.569
1.549
1.542
1.523
1.515
1.495
1.486
1.318
1.292
1.263
1.255
1.228
1.203
1.184
1.163
1.133
1.114
1.098
1.074
1.045
1.030
1.003
0.941
0.913
9
8
7
6
5
4
3
2
1
0
ppm
4.41
0.98
2.00
2.00
2.99
2.02
0.99
3.14
3.29
3.21
3.56
1.37
3.15

MeO
NH
n-Bu

4f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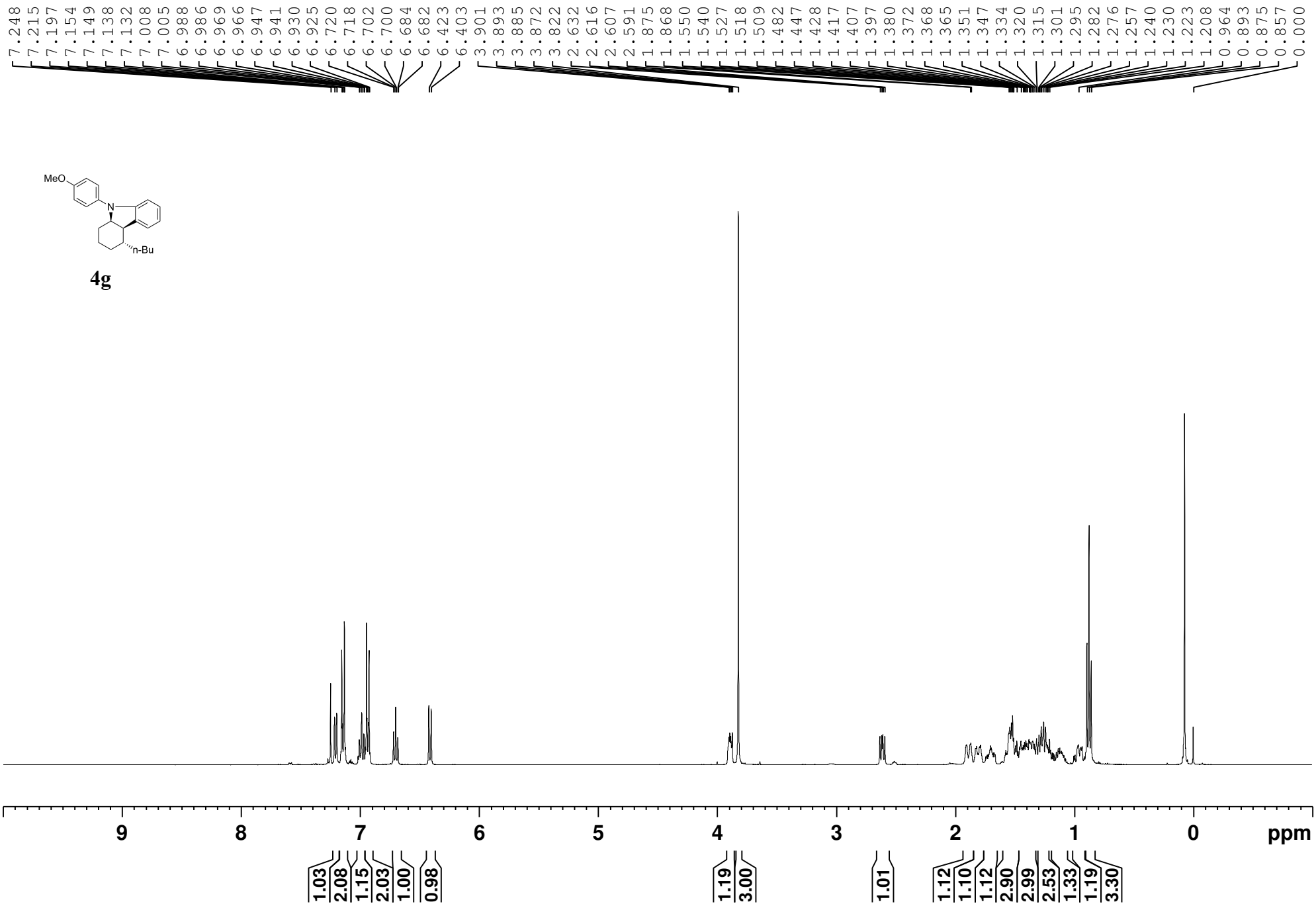
142.98
142.59
128.89
128.22
126.12
115.00
114.65
77.58
77.16
76.74
56.22
55.82
53.73
34.19
34.05
31.74
30.75
28.73
22.93
20.38
14.23
220
200
180
160
140
120
100
80
60
40
20
0
ppm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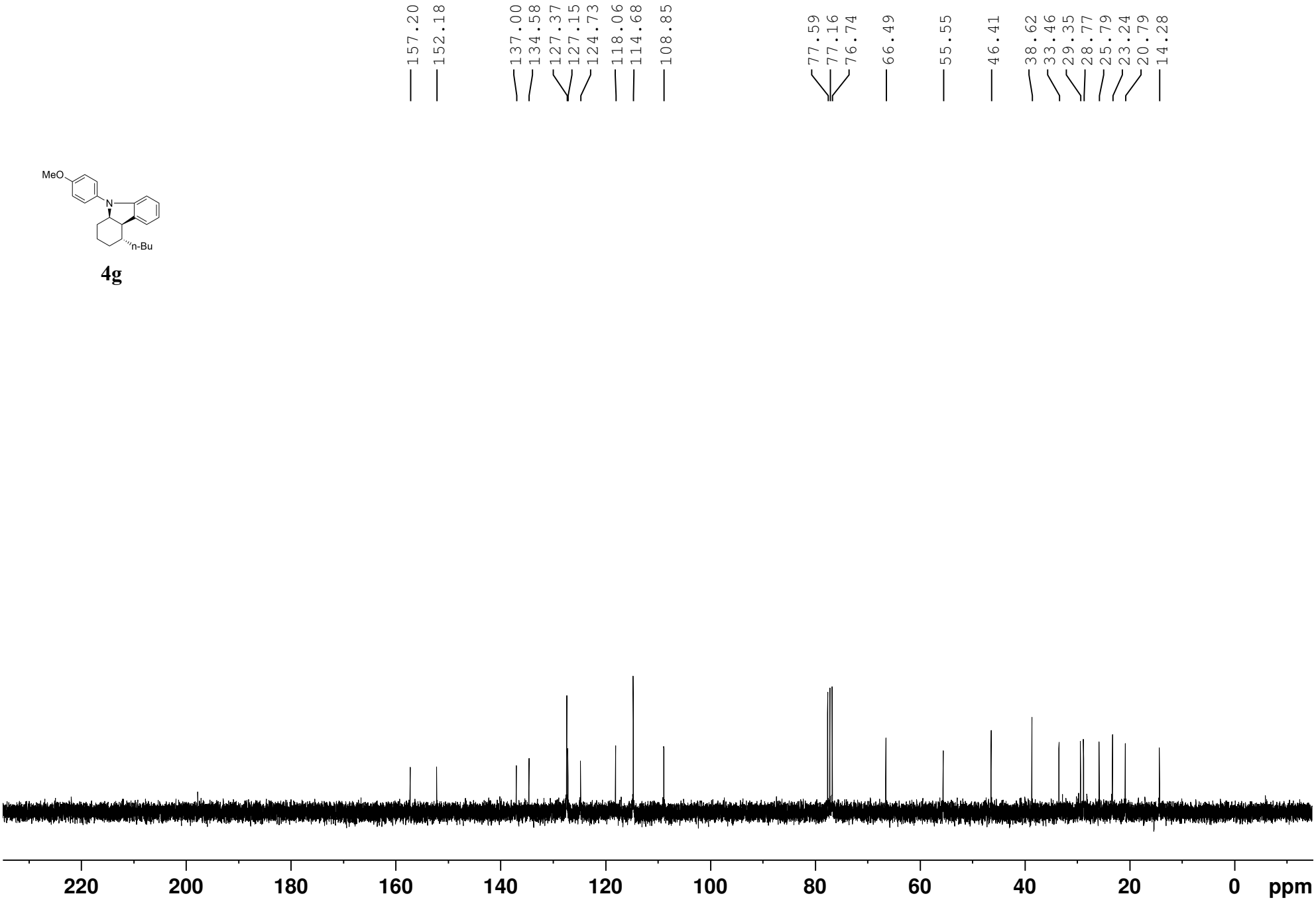
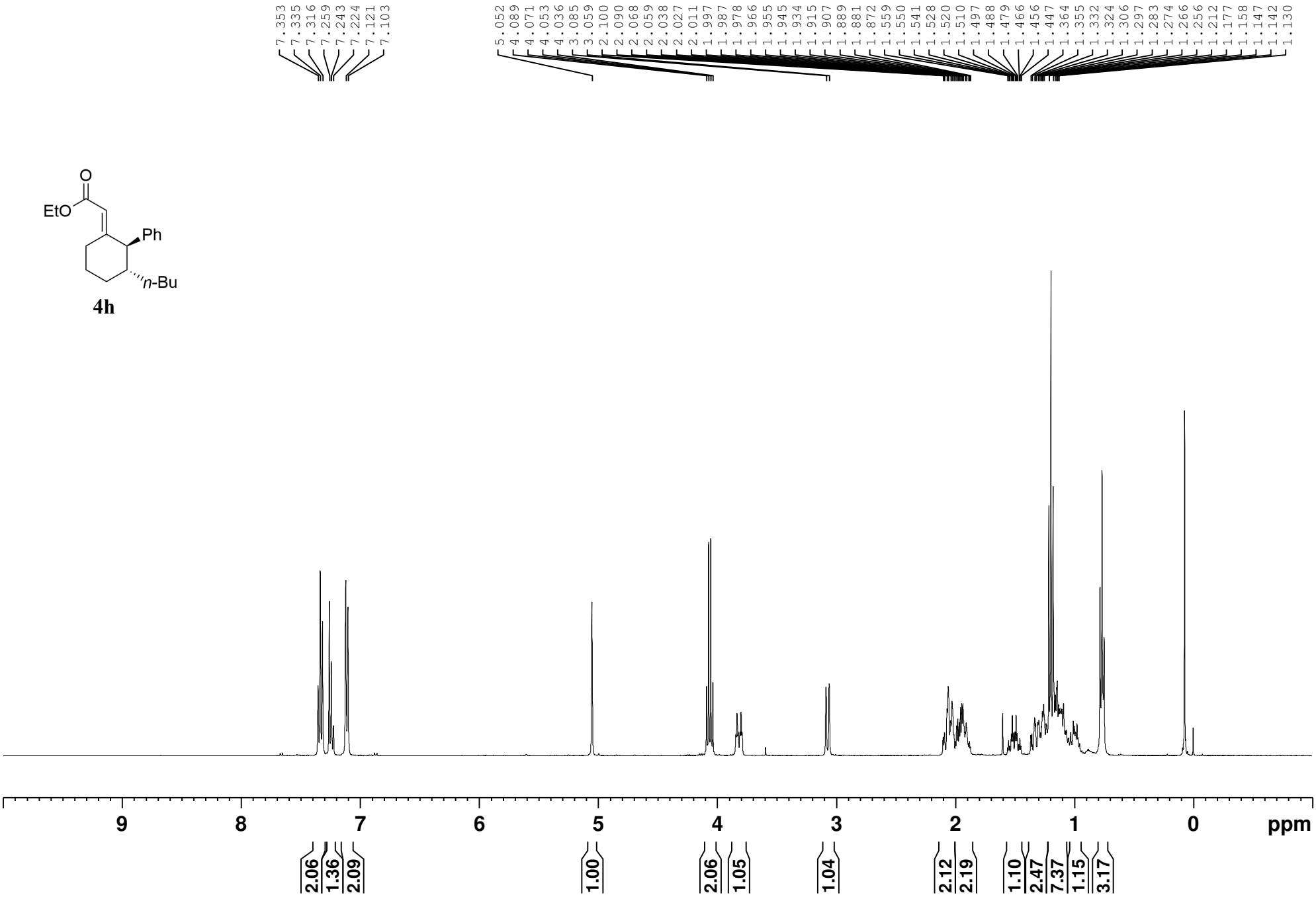
7.197
7.154
7.149
7.138
7.132
7.008
7.005
6.988
6.986
6.969
6.966
6.947
6.941
6.930
6.925
6.720
6.718
6.702
6.700
6.684
6.682
6.423
6.403
3.901
3.893
3.885
3.872
3.822
2.632
2.616
2.607
2.591
1.875
1.868
1.550
1.540
1.527
1.518
1.509
1.482
1.447
1.428
1.417
1.407
1.397
1.380
1.372
1.368
1.365
1.351
1.347
1.334
1.320
1.315
1.301
1.295
1.282
1.276
1.257
1.240
1.230
1.223
1.208
0.964
0.893
0.875
0.857
0.000
MeO
N
n-Bu
4g
9
8
7
6
5
4
3
2
1
0
ppm
1.03
2.08
1.15
2.03
1.00
0.98
1.19
3.00
1.01
1.12
1.10
1.12
2.90
2.99
2.53
1.33
1.19
3.30

MeO
N
n-Bu

4g


157.20
152.18
137.00
134.58
127.37
127.15
124.73
118.06
114.68
108.85
77.59
77.16
76.74
66.49
55.55
46.41
38.62
33.46
29.35
28.77
25.79
23.24
20.79
14.28
220
200
180
160
140
120
100
80
60
40
20
0
ppm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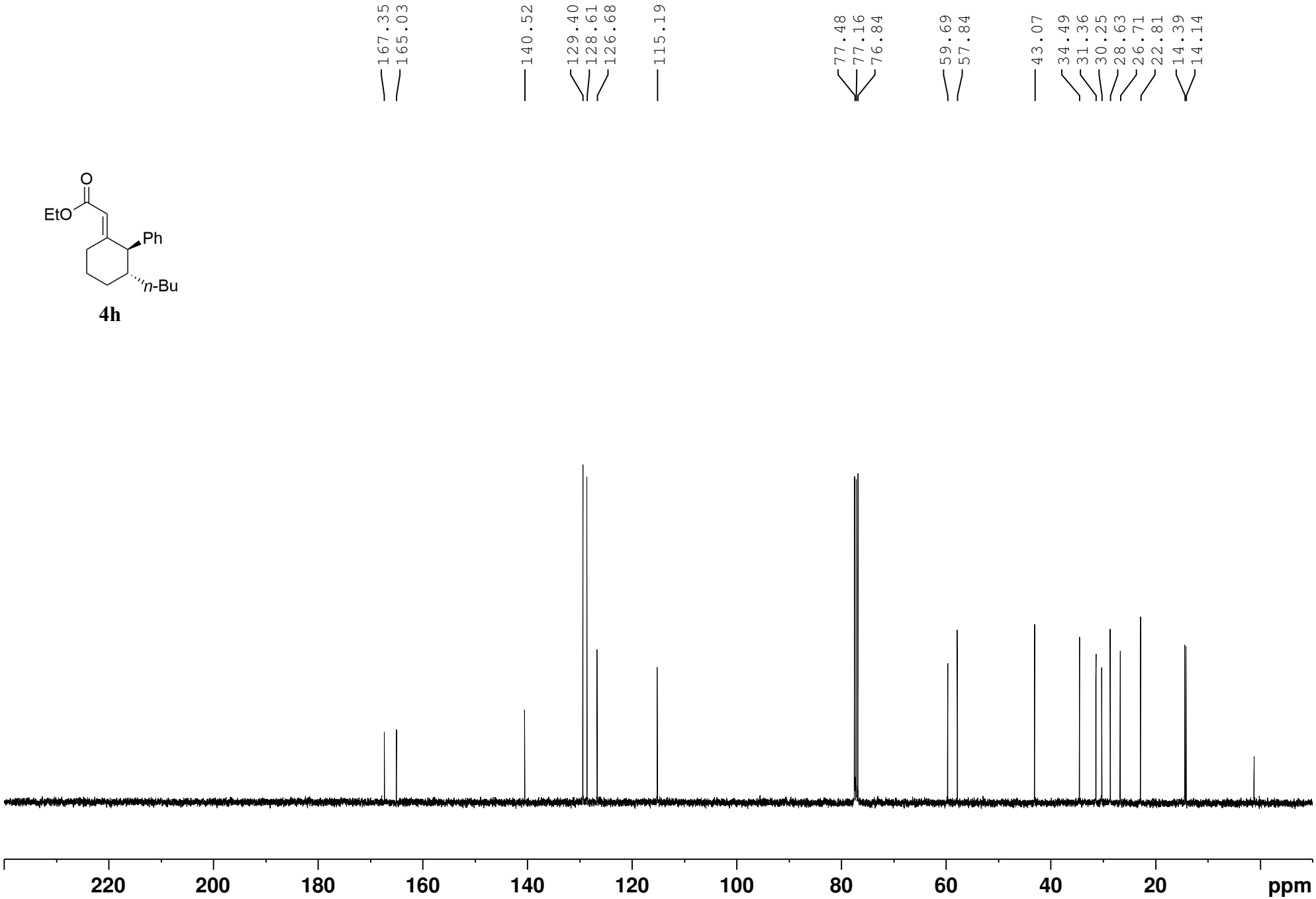
7.316
7.259
7.243
7.224
7.121
7.103
5.052
4.089
4.071
4.053
4.036
3.085
3.059
2.100
2.090
2.068
2.059
2.038
2.027
2.011
1.997
1.987
1.978
1.966
1.955
1.945
1.934
1.915
1.907
1.889
1.881
1.872
1.559
1.550
1.541
1.528
1.520
1.510
1.497
1.488
1.479
1.466
1.456
1.447
1.364
1.355
1.332
1.324
1.306
1.297
1.283
1.274
1.266
1.256
1.212
1.177
1.158
1.147
1.142
1.130
O
EtO
Ph
n-Bu
4h
9
8
7
6
5
4
3
2
1
0
ppm
2.06
1.36
2.09
1.00
2.06
1.05
1.04
2.12
2.19
1.10
2.47
7.37
1.15
3.17

O
EtO
Ph
n-Bu

4h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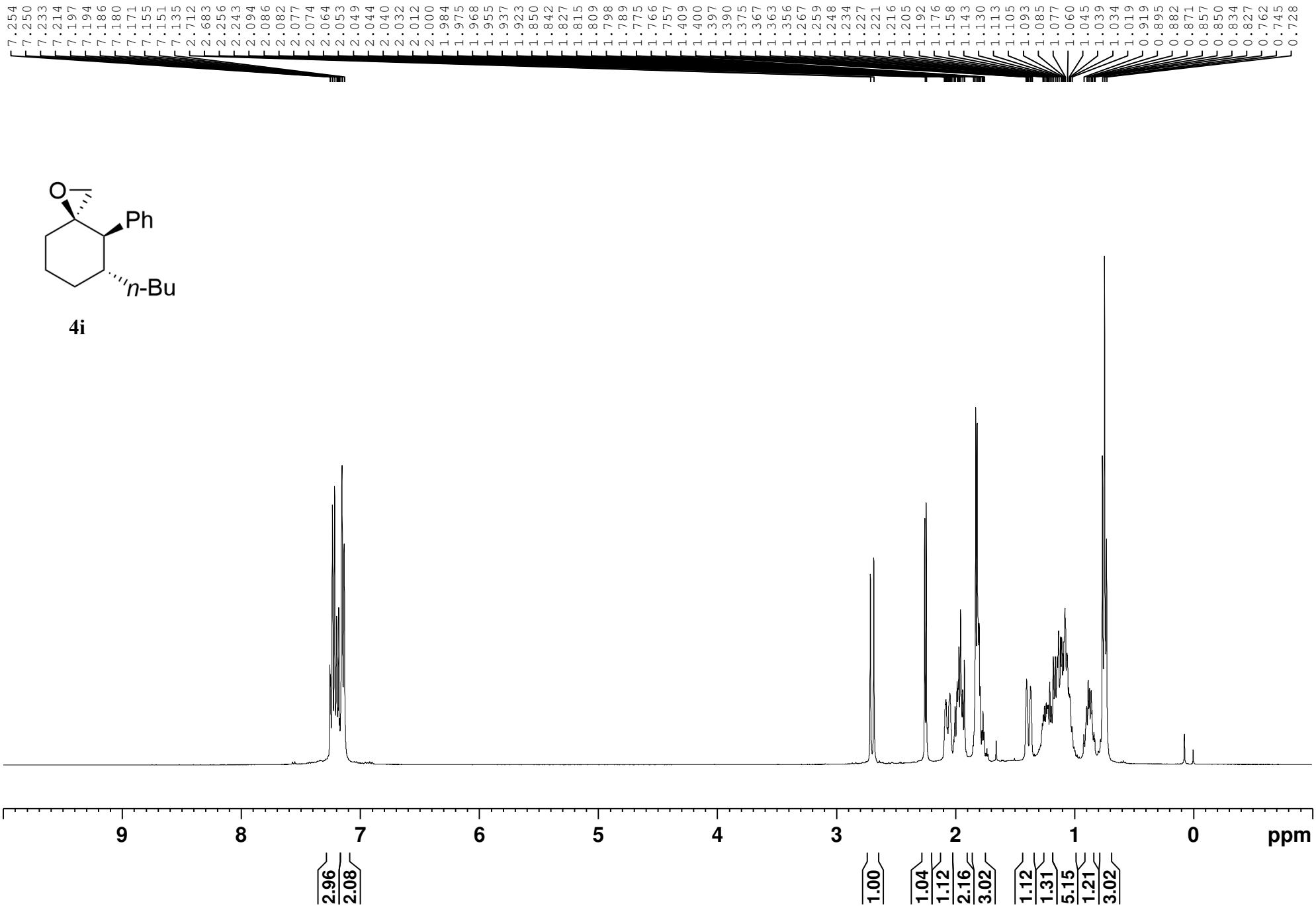
140.52
129.40
128.61
126.68
115.19
77.48
77.16
76.84
59.69
57.84
43.07
34.49
31.36
30.25
28.63
26.71
22.81
14.39
14.14
220
200
180
160
140
120
100
80
60
40
20
ppm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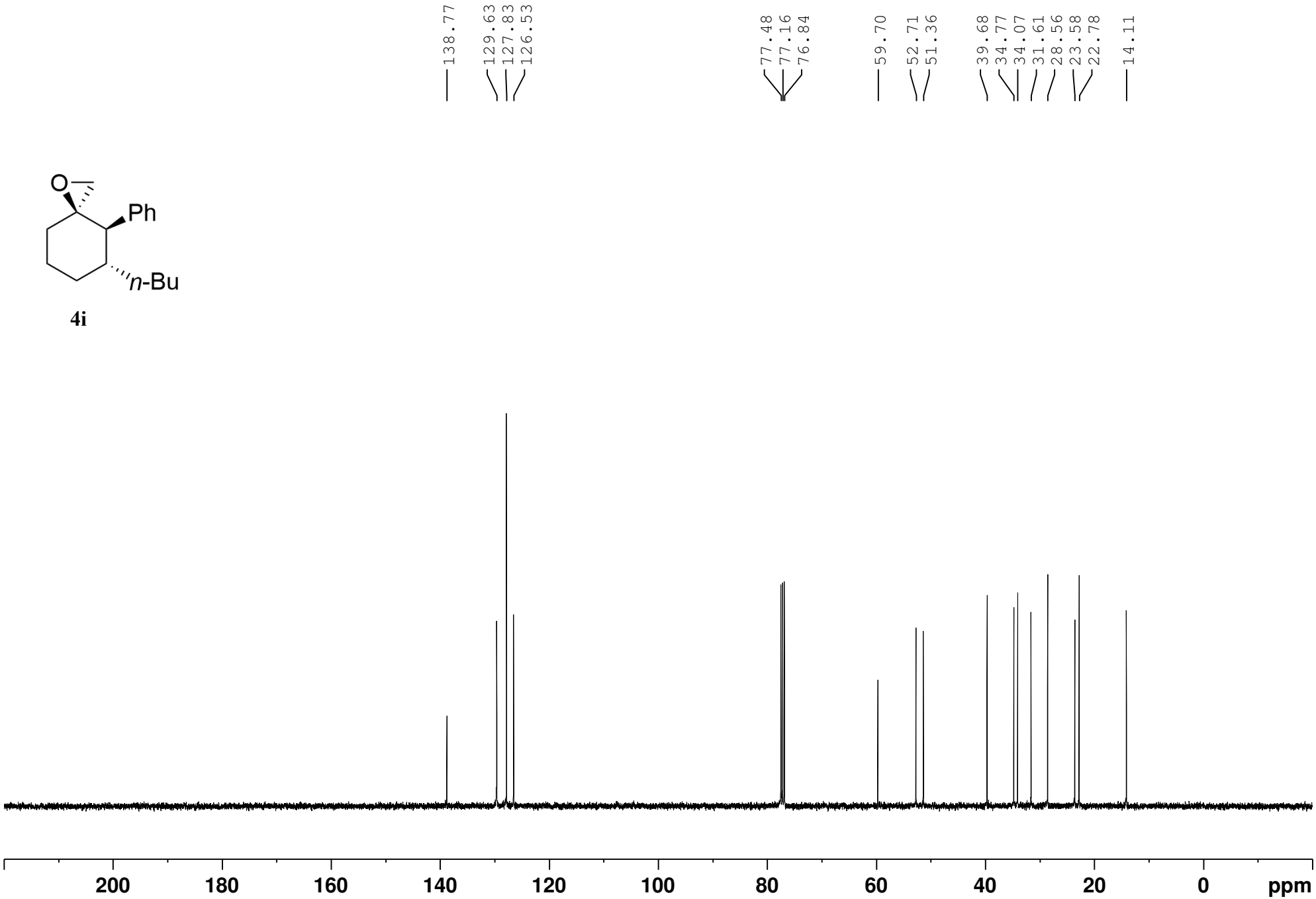
O
Ph
n-Bu
9
8
7
6
5
4
3
2
1
0
ppm
2.96
2.08
1.00
1.04
1.12
2.16
3.02
1.12
1.31
5.15
1.21
3.02

4i

O
Ph
n-Bu

4i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126.53
77.48
77.16
76.84
59.70
52.71
51.36
39.68
34.77
34.07
31.61
28.56
23.58
22.78
14.11
200
180
160
140
120
100
80
60
40
20
0
ppm