Electronic Supplementary Material (ESI) for ChemComm.

Catalytic Allylic Cation-induced Intermolecular Allylation-Semipinacol Rearrangement

Ming-Hui Xu,[a] Kun-Long Dai,[a] Yong-Qiang Tu,*[ab] Xiao-Ming Zhang,*[a] Fu-Min Zhang,[a] Shao-Hua Wang[a]

[a.] *State Key Laboratory of Applied Organic Chemistry & School of Chemistry, Lanzhou University, Lanzhou 730000, P. R. China. E-mail: tuyq@lzu.edu.cn*

[b.] *School of Chemistry & Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China. Email: tuyq@sjtu.edu.cn*

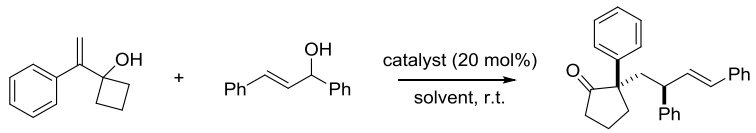
Contents:

1. General Information

All reactions were carried out under argon atmosphere. All solvents were purified and dried by standard techniques, and distilled prior to use. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. Silica gel (200~300 mesh), petroleum ether (b.p. 60~90 ^{o}C) and ethyl acetate are used for product purification by flash column chromatography. **^{1}H NMR**, **^{13}C NMR** and **^{19}F NMR** spectra, which were recorded in $CDCl_3$ solution, were acquired on a Bruker AM-400 MHz spectrometer. The spectral data were reported in ppm and calibrated by using residual undeuterated solvent $CHCl_3$ (7.27 ppm) or tetramethylsilane (0.00 ppm) as internal reference for **^{1}H NMR** and the deuterated solvent $CDCl_3$ (77.0 ppm) as internal standard for **^{13}C NMR**. The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectral analysis (HRMS) data were determined on an APEXII 47e FT-ICR spectrometer by means of the ESI technique. The X-ray single-crystal determination was performed on an Agilent SuperNova Eos diffractometer. IR spectra were recorded on a fourier transform infrared spectrometer. The diastereomers of the products were inseparable. The d.r. of the products was determined by NMR. The substrates **1a**-**1e**, **1i**-**1l**, **1p**-**1q**, **2b**-**2h** are known compounds, and **2a** is commercial available.

2. Optimation of Reaction Condition

Table 1 Optimization of the allylic cation-induced semipinacol rearrangement reaction[a]



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

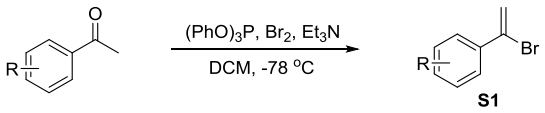
Entry	Catalyst	Solvent	Yield[b](%)	d.r.[c]
1	$ZnBr_2$	Et_2O	2%	—
2	$ZnBr_2$	THF	NR	—
3	$ZnBr_2$	MeOH	NR	—
4	$ZnBr_2$	EA	NR	—
5	$ZnBr_2$	MeCN	trace	—
6	$ZnBr_2$	toluene	29	3.7:1
7	**$ZnBr_2$**	**DCM**	**98**	**5.5:1**
8	$ZnBr_2$	$CHCl_3$	57	3.9:1
9	$ZnBr_2$	CCl_4	9	2.7:1
10	$ZnBr_2$	DCE	96	5.1:1
11	$AlCl_3$	DCM	67	5.3:1
12	$AlBr_3$	DCM	80	2.0:1
13	$Sc(OTf)_3$	DCM	95	5.0:1
14	$Cu(OTf)_2$	DCM	76	5.0:1
15	$Zn(OTf)_2$	DCM	71	5.0:1
16	$ZnCl_2$	DCM	87	5.5:1

[a]Unless otherwise noted, the reaction was conducted at room temperature with allylic alcohols **1a** (0.15 mmol, 1.0 equiv), **2a** (1.0 equiv), and catalyst (20 mol%) in solvent (1.0 mL); [b]Yield of isolated product. The diastereomers of the product were inseparable. [c]d.r. determined by ^{1}H NMR. THF = tetrahydrofuran, EA = ethyl acetate, DCM = dichloromethane, DCE = 1,2-dichloroethane.

3. Preparation of Starting Materials

3.1 Syntheses of the Tertiary Allylic Alcohols 1a-1k, 1p-1q

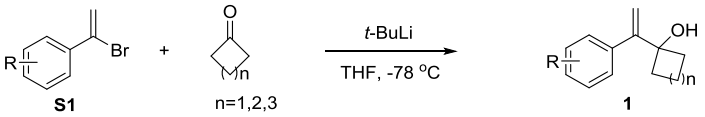
General Procedure A: Synthesis of Alkenyl Bromide S1[1]



S1

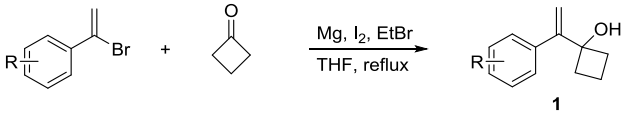
To a stirred solution of triphenyl phosphite (1.1 equiv) in anhydrous dichloromethane (0.5 M) cooled to -78 ℃ under Ar atmosphere. Bromine (1.2 equiv) dissolved in DCM (0.5 M) was dropped in. Anhydrous triethylamine (1.3 equiv) and ketone (1.0 equiv) were added sequence to the faint orange solution. The reaction mixture was warming to r.t. and kept stirring for 18 h. After the mixture was refluxed for a further 2 h, the reaction was quenched with saturated aqueous Na_2SO_3. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified via column chromatography on silica gel (petroleum ether) to give alkenyl bromide **S1**.

General Procedure B: Synthesis of Tertiary Allylic Alcohols 1a-1h, 1p-1q[2]



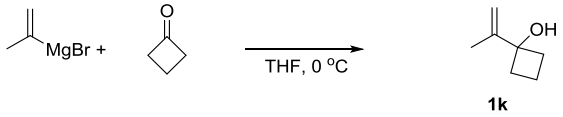
To a stirred solution of alkenyl bromide **S1** (1.0 equiv) in anhydrous THF cooled to -78 ℃ was added *t*-BuLi (1.3 M solution in hexane, 2.2 equiv) dropwise under argon atmosphere. The mixture was kept stirring at the same temperature for 30 min. Then ketone (1.05 equiv) was added dropwise. After stirring at -78 °C for 30 min, the mixture was allowed to warm to r.t. After stirring another 1 h, the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/20, v/v) to give tertiary allylic alcohol **1**.

General Procedure C: Synthesis of Tertiary Allylic Alcohols 1i-1j[3]



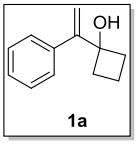
A dried two-neck round-bottomed flask equipped with a condenser and a magnetic stir bar was charged with Mg turnings (3.0 equiv) under argon atmosphere. Anhydrous THF (5 mL/mmol) and bromoethane (0.4 equiv) were added gradually. Then iodine (0.05 equiv) was added under Ar. After stirring at r.t. for 10 min, α-bromostyrene (1.0 equiv) in anhydrous THF was then added dropwise. The reaction was then placed in an oil bath and heated at reflux for 3 h. After cooling to room temperature, cyclobutanone (1.5 equiv) was added. After stirring for 9 h, the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/20, v/v) to give corresponding allylic alcohol **1**.

General Procedure D: Synthesis of Tertiary Allylic Alcohols 1k[4]



To a solution of cyclobutanone (770 mg, 11mmol) in THF (10 mL) at 0 ℃ was added isopropenyl magnesium bromide (0.5 M solution in THF, 1.5 equiv) over 10 min. The mixture was stirred at R.T. for 6 h. The reaction was quenched by the addition of a saturated solution of NH_4Cl. The organic layer was extracted with diethyl ether. The combined organics were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/60, v/v) to afford **1k** (717 mg, 58% yield) as colorless oil.

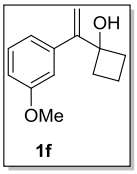
1-(1-phenylvinyl)cyclobutan-1-ol (1a):



Compound 1a was obtained in 61% yield as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ

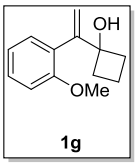
7.47-7.50 (m, 2H), 7.26-7.36 (m, 3H), 5.38 (d, *J* = 7.6 Hz, 2H), 2.45-2.53 (m, 2H), 2.22-2.29 (m, 2H), 1.94-2.03 (m, 1H), 1.95 (s, 1H), 1.60-1.68 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.40, 139.08, 128.16, 127.57, 127.51, 112.80, 78.08, 35.69, 13.33.

1-(1-(3-methoxyphenyl)vinyl)cyclobutan-1-ol (1f):



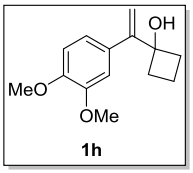
Compound 1f was obtained in 54% yield as colorless oil. **IR** (neat) cm^{-1} 3412, 2930, 2853, 1598, 1576, 1487, 1463, 1251, 1153, 1045, 909, 788; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.27 (m, 1H), 7.03-7.08 (m, 2H), 6.83-6.87 (m, 1H), 5.37 (d, *J* =5.6 Hz, 2H), 3.83 (s, 3H), 2.45-2.52 (m, 2H), 2.21-2.28 (m, 2H), 1.96- 2.03 (m, 2H), 1.56- 1.68 (m, 1H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.39, 152.39, 140.63, 129.14, 120.05, 113.48, 112.92, 112.90, 78.07, 55.20, 35.69, 13.35; **HRMS** (ESI) Calcd for $C_{13}H_{16}O_2Na_1$ $[M+Na]^+$: 227.1043, Found: 227.1042, Error: 0.4 ppm.

1-(1-(2-methoxyphenyl)vinyl)cyclobutan-1-ol (1g):



Compound 1g was obtained in 49% yield as colorless oil. **IR** (neat) cm^{-1} 3419, 2940, 1576, 1486, 1251, 1046, 910, 787; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.31 (m, 1H), 7.15-7.17 (dd, *J* =1.6 Hz, 7.2Hz, 1H), 6.97 (td, *J* =7.6 Hz, 0.8 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 5.19 (d, *J* =1.2 Hz, 1H), 3.94 (s, 1H), 3.84 (s, 3H), 2.24-2.31 (m, 2H), 2.09-2.17 (m, 2H), 1.81-1.84 (m, 1H), 1.48-1.53 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.59, 152.08, 131.13, 129.99, 128.68, 121.12, 116.19, 110.42, 77.03, 55.48, 35.30, 12.77; **HRMS** (ESI) Calcd for $C_{13}H_{16}O_2Na_1$ $[M+Na]^+$: 227.1043, Found: 227.1037, Error: 2.6 ppm.

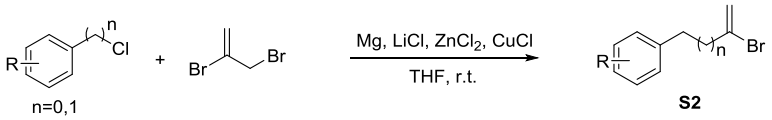
1-(1-(3,4-dimethoxyphenyl)vinyl)cyclobutan-1-ol (1h):



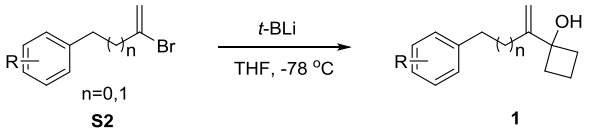
Compound 1h was obtained in 29% yield as colorless oil. **IR** (neat) cm^{-1} 3457, 2933, 1514, 1463, 1256, 1142, 1027, 901, 768; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03-7.06 (m, 2H), 6.83 (d, *J* =8.8 Hz, 1H), 5.31 (d, *J* =5.6 Hz, 2H), 3.88 (s, 6H), 2.43-2.51 (m, 2H), 2.20-2.28 (m, 2H), 2.04 (s, 1H), 1.94-2.03 (m, 1H), 1.58-1.69 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.86, 148.55, 148.43, 131.66, 119.85, 111.67, 110.92, 110.71, 78.19, 55.80, 33.61, 13.38; **HRMS** (ESI) Calcd for $C_{14}H_{18}O_3Na_1$ $[M+Na]^+$: 257.1148, Found: 257.1143, Error: 1.9 ppm.

3.2 Syntheses of the Allylic Alcohols 1l-1n

General Procedure E: Synthesis of Tertiary Allylic Alcohols 1l-1n[4]

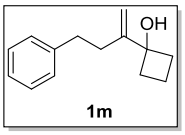


To a stirred solution of magnesium turnings (2.5 equiv) in anhydrous THF were added lithium chloride (1.2 equiv), zinc chloride (1.1 equiv) and benzyl chloride (1.0 equiv) in one portion. The reaction mixture was allowed to stir for 1 h before transferring to a mixture of 2,3-dibromopropene (1.2 equiv) and copper chloride (6 mol%) in THF. After a 5 h stir, the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified via column chromatography on silica gel (petroleum ether) to give product compound S**2**.



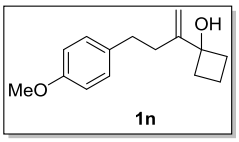
Preparation according to the general procedure of **B** to get the allylic alcohols **1l-1n**.

1-(4-phenylbut-1-en-2-yl)cyclobutan-1-ol (1m):



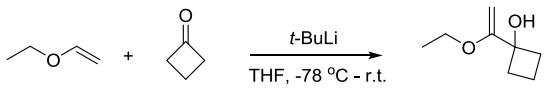
Compound 1m was obtained in 57% yield as colorless oil. **IR** (neat) cm^{-1} 3355, 2938, 1642, 1453, 1247, 1143, 900, 698; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.30 (m, 2H), 7.16-7.23 (m, 3H), 5.13 (s, 1H), 4.97 (d, *J* =0.4 Hz, 1H), 2.80-2.84 (m, 2H), 2.41-2.45 (m, 2H), 2.01-2.08 (m, 2H), 1.89-1.94 (m, 1H), 1.64 (s, 1H), 1.55-1.63 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.52, 142.19, 128.34, 128.30, 125.82, 108.65, 78.42, 34.76, 34.64, 32.00, 13.10; **HRMS** (ESI) Calcd for $C_{14}H_{18}O_1Na_1$ $[M+Na]^+$: 225.1250, Found: 225.1246, Error: 1.8 ppm.

1-(4-(4-methoxyphenyl)but-1-en-2-yl)cyclobutan-1-ol (1n):



Compound 1n was obtained in 66% yield as white solid. **IR** (neat) cm^{-1} 3378, 2930, 1611, 1512, 1246, 1038, 823; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* =8.4 Hz, 2H), 6.85 (d, *J* =8.8 Hz, 2H), 5.14 (s, 1H), 4.98 (s, 1H), 3.80 (s, 3H), 2.76-2.80 (m, 2H), 2.39-2.43 (m, 2H), 2.31-2.38 (m, 2H), 2.03-2.10 (m, 2H), 1.88-1.97 (m, 1H), 1.77 (s, 1H), 1.54-1.62 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.71, 151.57, 134.25, 129.19, 113.70, 108.58, 78.38, 55.18, 34.62, 33.85, 32.22, 13.08 ; **HRMS** (ESI) Calcd for $C_{15}H_{20}O_2Na_1$ $[M+Na]^+$: 255.1356, Found: 255.1351, Error: 1.9 ppm.

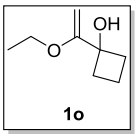
3.3 Syntheses of the Substrates 1o



1o

To a stirred solution of ethyl vinyl ether (2.0 g, 5.0 equiv) in anhydrous THF cooled to -78 ℃ was added *t*-BuLi (6.9 ml, 1.6 M solution in hexane, 2.0 equiv) dropwise under argon flow. After stirring at the same temperature for 15 min, the mixture was allowed to warm to r.t. to stir 2 h. Then cyclobutanone (0.4 ml, 1.0 equiv) was added dropwise after the mixture was cooled to -78 ℃ again. The mixture was allowed to slowly warm to r.t. to stir another 2 h. The reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/30, v/v) to give product compound **1o** (522 mg, 49%) as a colorless oil.

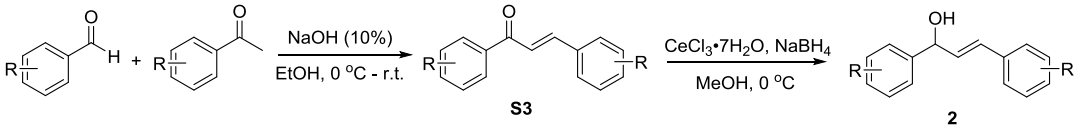
1-(1-ethoxyvinyl)cyclobutan-1-ol (1o):



Compound 1o was obtained in 49% yield as colorless oil. **IR** (neat) cm^{-1} 3430, 2979, 2943, 1617, 1250, 1153, 1063, 808; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.26 (d, *J* =2.4 Hz, 1H), 4.10 (d, *J* =2.8 Hz, 1H), 3.78 (q, *J* =7.0 Hz, 2H), 2.82 (s, 1H), 2.30-2.37 (m, 2H), 2.09-2.17 (m, 2H), 1.79-1.87 (m, 2H), 1.58-1.66 (m, 2H), 1.33 (t, *J* =7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.19, 79.29, 75.43, 63.01, 34.21, 14.30, 12.83; **HRMS** (ESI) Calcd for $C_8H_{14}O_2Na_1$ $[M+Na]^+$: 165.0886, Found: 165.0884, Error: 1.2 ppm.

3.2 Syntheses of the Allylic Alcohols 2a-2h[5]

General Procedure: Synthesis of Allylic Alcohols 2a-2d

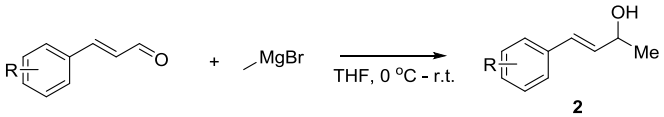


To a stirred solution of corresponding substituted acetophenone (2.5 mmol, 1.0 equiv) in ethanol (10 mL) was addd aqueous NaOH (10%) dropwise at 0 °C. After the reaction mixture was stirred at room temprature for 1 h the corresponding substituted benzaldehyde (2.5 mmol, 1.0 equiv) was added slowly. The reaction mixture was stirred at room temperature until the complete consumption of the starting materials (monitored by TLC). The solvent was removed under vacuum and the residue was treated with water and extracted with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered, concentrated and purified via silica-gel column chromatography (ethyl acetate/petroleum ether = 1/40, v/v) to obtain the corresponding α,β-unsaturated ketones **S3**.

To a stirred solution of $CeCl_3 \cdot 7H_2O$ (3.0 mmol, 1.2 equiv) and α,β-unsaturated ketones **S3** (2.5 mmol, 1.0 equiv) in MeOH (10 mL) at 0 ℃ was added sodium borohydride (3.0 mmol, 1.2 equiv). The reaction was stirred at room temperature until the consumption of **S3** (monitored by TLC). Then, the reaction mixture was adjusted to pH 7 using a 10% HCl solution and extracted three

times with EtOAc. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Then the solvent was removed under vacuum and the crude residue was purified via silica-gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to obtain the corresponding allylic alcohols **2**.

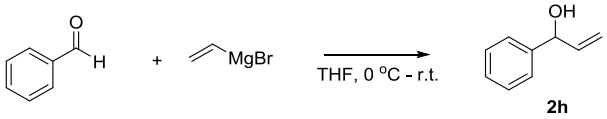
General Procedure: Synthesis of Allylic Alcohols 2e-2g



2

To a stirred solution of aldehyde (1.0 equiv) in dry THF (0.5 M) was added methylmagnesium bromide (1.5 equiv., 3.0 M in THF) at 0 °C under an argon atmosphere. After 15 min, the reaction was allowed to warm to r.t. and stirred for additional 1 h. Then the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified on silica gel chromatography (EtOAc/petroleum ether = 1:20, v/v) to afford the product **2**.

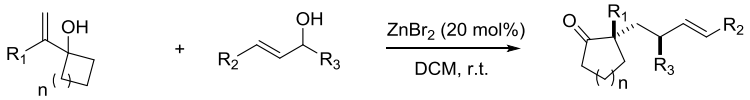
General Procedure: Synthesis of Allylic Alcohol 2h



2h

To a stirred solution of benzaldehyde (9.4 mmol, 1.0 equiv) in dry THF (20 mL) was added vinyl magnesium bromide (1.5 equiv., 2.0 M in THF) at 0 °C under an argon atmosphere. After 15 min, the reaction was allowed to warm to r.t. and stirred for additional 1 h. Then the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified on silica gel chromatography (EtOAc/petroleum ether = 1:20, v/v) to afford the product **2h** (1.02 g, 81% yield) as colorless oil .

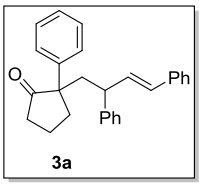
4. General Procedure of the Semipinacol Rearrangement



1 **2** **3**

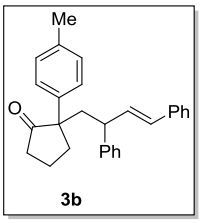
General procedure: In an oven-dried reaction tube was added tertiary allylic alcohol **1**(0.15 mmol, 1.0 equiv), allylic alcohol **2** (0.15 mmol, 1.0 equiv) and freshly distilled dichloromethane (1 mL) at room temperature. Then, to the resulting mixture was added a catalytic amount of $ZnBr_2$ (20 mol%). The reaction was stirred at room temperature until the consumption of **1** (monitored by TLC) and then quenched by addition of saturated $NaHCO_3$ aqueous solution (5 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 × 10 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified on silica gel chromatography (ethyl acetate/petroleum ether = 1/100, v/v) to afford the corresponding product **3**.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-phenylcyclopentan-1-one (3a):



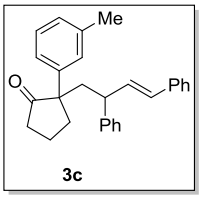
Compound 3a was obtained as colorless oil (98% yield, d.r. 5.5:1). **IR** (neat) cm^{-1} 3397, 2924, 2854, 1734, 1684, 1598, 1452, 1265, 1152, 969, 740, 702; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.39 (m, 2H), 7.25-7.34 (m, 6H), 7.16-7.23 (m, 4H), 7.07-7.13 (m, 3H), 6.07-6.25 (m, 2H), 3.14-3.27 (m, 1H), 2.69-2.79 (m, 1H), 2.50-2.55 (m, 1H), 2.12-2.24 (m, 2H), 1.98-2.11 (m, 2H), 1.83-1.91 (m, 1H), 1.63-1.76 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.11, 144.77, 138.32, 137.31, 134.02, 129.76, 128.54, 128.48, 128.41, 127.14, 127.08, 127.02, 126.86, 126.09, 126.06, 56.88, 46.14, 45.26, 36.62, 33.63, 18.63; **HRMS** (ESI) Calcd for $C_{27}H_{27}O_1$ $[M+H]^+$: 367.2056, Found: 367.2058, Error: 0.5 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(p-tolyl)cyclopentan-1-one (3b):



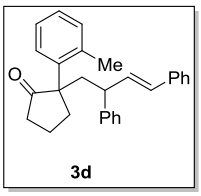
Compound 3b was obtained as white solid (97% yield, d.r. 12.5:1). **Mp** 82.0-84.5 ^oC; **IR** (neat) cm^{-1} 3392, 2925, 2854, 1733, 1682, 1452, 1265, 1152, 969, 739, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.32 (m, 6H), 7.17-7.21 (m, 3H), 7.08-7.13 (m, 5H), 6.05-6.20 (m, 2H), 3.14-3.29 (m, 1H), 2.68-2.78 (m, 1H), 2.46-2.53 (m, 1H), 2.31 (s, 3H), 2.12-2.25 (m, 2H), 1.95-2.10 (m, 2H), 1.83-1.90 (m, 1H), 1.65-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.29, 144.92, 137.39, 136.53, 135.19, 134.10, 129.74, 129.30, 128.48, 128.40, 127.11, 126.94, 126.06, 56.59, 46.09, 45.28, 36.58, 33.81, 20.87, 18.64; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_1Na_1$ $[M+Na]^+$: 403.2032, Found: 403.2029, Error: 0.7 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(m-tolyl)cyclopentan-1-one (3c):



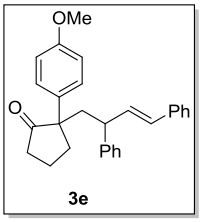
Compound 3c was obtained as colorless oil (95% yield, d.r. 7.1:1). **IR** (neat) cm^{-1} 3362, 2923, 2853, 1733, 1601, 1492, 1466, 1265, 1149, 969, 741, 702; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.30 (m, 4H), 7.17-7.23 (m, 6H), 7.08-7.14 (m, 3H), 7.02-7.04 (m, 1H), 6.07-6.25 (m, 2H), 3.16-3.30 (m, 1H), 2.66-2.79 (m, 1H), 2.51 (dd, *J* = 4 Hz, 14 Hz, 1H), 2.31 (s, 3H), 2.15-2.27 (m, 2H), 1.97-2.13 (m, 2H), 1.84-1.92 (m, 1H), 1.67-1.76 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.28, 144.84, 138.12, 137.40, 134.16, 129.75, 128.52, 128.41, 127.83, 127.66, 127.17, 126.10, 124.02, 56.90, 46.20, 45.22, 36.69, 33.73, 21.58, 18.66; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_1Na_1$ $[M+Na]^+$: 403.2032, Found: 403.2026, Error: 1.5 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(o-tolyl)cyclopentan-1-one (3d):



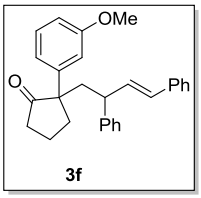
Compound 3d was obtained as colorless oil (50% yield, d.r. 5.4:1). **IR** (neat) cm^{-1} 3058, 3024, 2957, 2924, 1733, 1598, 1492, 1451, 1157, 969, 746, 698; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.26 (m, 9H), 7.06-7.15 (m, 5H), 6.10-6.30 (m, 2H), 3.27-3.50 (m, 1H), 2.61-2.77 (m, 1H), 2.54-2.59 (m, 1H), 2.43-2.46 (m, 1H), 2.39 (s, 3H), 2.23-2.31 (m, 1H), 2.02-2.12 (m, 1H), 1.61-1.82 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.01, 144.90, 137.98, 137.23, 136.80, 134.28, 133.12, 129.47, 128.52, 128.41, 127.50, 127.23, 127.05, 126.99, 126.18, 126.03, 125.67, 57.90, 46.40, 41.02, 36.90, 34.50, 21.85, 18.14; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_1Na_1$ $[M+Na]^+$: 403.2032, Found: 403.2025, Error: 1.7 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(4-methoxyphenyl)cyclopentan-1-one (3e):



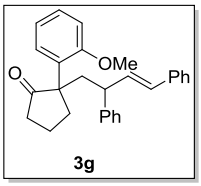
Compound 3e was obtained as colorless oil (98% yield, d.r. > 20:1). **IR** (neat) cm^{-1} 3442, 3026, 2958, 2251, 1731, 1606, 1510, 1265, 1185, 1034, 909, 736, 700; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.32 (m, 6H), 7.17-7.21 (m, 3H), 7.08-7.13 (m, 3H), 6.83-6.86 (m, 2H), 6.06-6.25 (m, 2H), 3.76 (s, 3H), 3.15-3.28 (m, 1H), 2.66-2.76 (m, 1H), 2.50 (dd, *J* = 4 Hz, 14 Hz, 1H), 2.12-2.25 (m, 2H), 1.95-2.10 (m, 2H), 1.83-1.90 (m, 1H), 1.66-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.21, 158.44, 144.88, 137.35, 134.09, 129.94, 129.69, 128.47, 128.39, 128.21, 127.10, 126.05, 113.92, 56.13, 55.14, 46.09, 45.22, 36.49, 33.93, 18.60; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_2K_1$ $[M+K]^+$: 435.1721, Found: 435.1714, Error: 1.6 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(3-methoxyphenyl)cyclopentan-1-one (3f):



Compound 3f was obtained as colorless oil (88% yield, d.r. 6.4:1). **IR** (neat) cm^{-1} 3362, 2923, 2852, 1733, 1598, 1466, 1264, 1052, 968, 739, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.32 (m, 4H), 7.17-7.25 (m, 4H), 7.09-7.15 (m, 3H), 6.93-6.99 (m, 2H), 6.76 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 6.08-6.22 (m, 2H), 3.76 (s, 3H), 3.27-3.31 (m, 1H), 2.72-2.77 (m, 1H), 2.51 (dd, *J* = 4.0 Hz, 14.4 Hz, 1H), 2.14-2.25 (m, 2H), 1.98-2.12 (m, 2H), 1.87-1.90 (m, 1H), 1.56-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.05, 159.85, 144.85, 140.09, 137.37, 134.12, 129.80, 129.45, 128.51, 128.43, 127.15, 126.12, 126.10, 119.39, 113.15, 112.20, 56.97, 55.17, 46.14, 45.24, 36.69, 33.86, 18.70; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_2Na_1$ $[M+Na]^+$: 419.1982, Found: 419.1978, Error: 1.0 ppm.

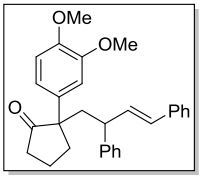
(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(2-methoxyphenyl)cyclopentan-1-one (3g):



3g

Compound 3g was obtained as colorless oil (90% yield, d.r. 6.9:1). **IR** (neat) cm^{-1} 3024, 2957, 2930, 1733, 1598, 1491, 1451, 1242, 1156, 1028, 968, 746, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.30 (m, 8H), 7.13-7.20 (m, 4H), 6.76-6.89 (m, 2H), 6.15-6.25 (m, 2H), 3.67-3.73 (m, 4H), 2.46-2.56 (m, 3H), 2.32-2.41 (m, 1H), 2.03-2.13 (m, 2H), 1.69-1.95 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.03, 157.11, 145.41, 137.35, 134.95, 130.82, 128.92, 128.47, 128.32, 128.09, 128.02, 127.47, 126.92, 126.05, 126.03, 120.43, 111.87, 55.57, 54.91, 45.82, 39.79, 37.66, 35.12, 18.99; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_2Na_1$ $[M+Na]^+$: 419.1982, Found: 419.1973, Error: 2.1 ppm.

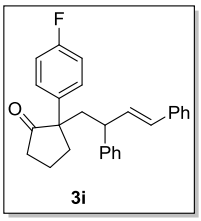
(E)-2-(3,4-dimethoxyphenyl)-2-(2,4-diphenylbut-3-en-1-yl)cyclopentan-1-one (3h):



3h

Compound 3h was obtained as colorless oil (96% yield, d.r. > 20:1). **IR** (neat) cm^{-1} 3372, 2925, 2854, 1732, 1599, 1516, 1264, 1148, 1027, 739, 702; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.32 (m, 4H), 7.18-7.23 (m, 3H), 7.07-7.15 (m, 3H), 6.91-6.93 (m, 2H), 6.80 (d, *J* = 9.2 Hz, 1H), 6.09-6.23 (m, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.23-3.28 (m, 1H), 2.73-2.78 (m, 1H), 2.53 (dd, *J* = 4.0 Hz, 14.0 Hz, 1H), 2.21-2.28 (m, 1H), 2.07-2.17 (m, 2H), 1.97-2.05 (m, 1H), 1.86-1.93 (m, 1H), 1.71-1.79 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.11, 148.95, 147.96, 144.84, 137.27, 134.07, 130.34, 129.65, 128.48, 128.37, 127.13, 127.07, 126.05, 125.99, 119.26, 110.93, 110.53, 56.33, 55.81, 55.76, 46.11, 45.26, 36.51, 33.95, 18.66; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_2Na_1$ $[M+Na]^+$: 419.1982, Found: 419.1979, Error: 0.7 ppm.

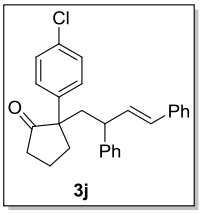
(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(4-fluorophenyl)cyclopentan-1-one (3i):



3i

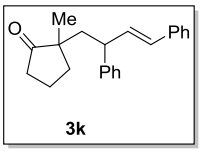
Compound 3i was obtained as colorless oil (93% yield, d.r. 5.2:1). **IR** (neat) cm^{-1} 3360, 2923, 1734, 1676, 1600, 1508, 1458, 1265, 1154, 969, 741, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.36 (m, 6H), 7.18-7.23 (m, 3H), 7.07-7.15 (m, 3H), 6.97-7.01 (m, 2H), 6.07-6.21 (m, 2H), 3.19-3.25 (m, 1H), 2.72-2.77 (m, 1H), 2.48-2.53 (dd, *J* = 4 Hz, 14.4 Hz, 1H), 2.01-2.27 (m, 4H), 1.90-1.95 (m, 1H), 1.67-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.08, 161.80 (d, *J* = 244 Hz), 144.48, 137.15, 133.81, 133.76 (d, *J* = 4 Hz) 129.75, 128.76 (d, *J* = 8 Hz), 128.53, 128.45, 127.24, 127.07, 126.18, 126.05, 115.33 (d, *J* = 21 Hz), 56.22, 46.17, 45.19, 36.58, 33.79, 18.63; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.84; **HRMS** (ESI) Calcd for $C_{27}H_{26}F_1O_1$ $[M+H]^+$: 385.1962, Found: 385.1962, Error: 0 ppm.

(E)-2-(4-chlorophenyl)-2-(2,4-diphenylbut-3-en-1-yl)cyclopentan-1-one (3j):



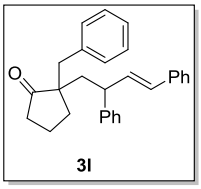
Compound 3j was obtained as colorless oil (95% yield, d.r. 5.6:1). **IR** (neat) cm^{-1} 3360, 2955, 2924, 2869, 1734, 1492, 1454, 1094, 1012, 745, 697; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.32 (m, 8H), 7.18-7.23 (m, 3H), 7.06-7.14 (m, 3H), 6.04-6.20 (m, 2H), 3.20-3.26 (m, 1H), 2.71-2.77 (m, 1H), 2.50 (dd, *J* = 4.4 Hz, 14.4 Hz, 1H), 2.12-2.26 (m, 3H), 2.01-2.10 (m, 1H), 1.88-1.96 (m, 1H), 1.66-1.74 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 218.85, 144.39, 137.13, 136.72, 133.72, 132.86, 129.81, 128.64, 128.54, 128.47, 128.31, 127.26, 127.07, 126.21, 126.06, 125.98, 56.38, 46.16, 45.13, 36.62, 33.68, 18.66; **HRMS** (ESI) Calcd for $C_{27}H_{26}Cl_1O_1$ $[M+H]^+$: 401.1667, Found: 401.1664, Error: 0.7 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-methylcyclopentan-1-one (3k):



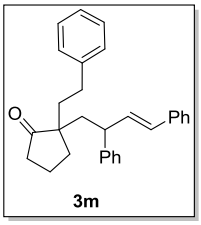
Compound 3k was obtained as colorless oil (78% yield, d.r. 2.2:1). **IR** (neat) cm^{-1} 3363, 3058, 2960, 2926, 1732, 1453, 1265, 1065, 739, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.31 (m, 8H), 7.15-7.21 (m, 2H), 6.14-6.39 (m, 2H), 3.57-3.63 (m, 1H), 2.16-2.25 (m, 1H), 2.07-2.14 (m, 1H), 1.93-2.03 (m, 2H), 1.70-1.80 (m, 3H), 1.47-1.50 (m, 1H), 1.03 (s, 2H), 0.97 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 223.20, 222.88, 144.91, 144.31, 137.37, 137.21, 135.02, 134.43, 129.55, 129.03, 128.60, 128.52, 128.50, 128.44, 127.94, 127.30, 127.18, 127.09, 126.43, 126.32, 126.09, 48.38, 48.34, 46.33, 45.63, 42.86, 42.22, 37.47, 37.01, 35.80, 34.60, 23.51, 22.20, 18.66, 18.63; **HRMS** (ESI) Calcd for $C_{22}H_{24}O_1Na_1$ $[M+Na]^+$: 327.1719, Found: 327.1712, Error: 2.1 ppm.

(E)-2-benzyl-2-(2,4-diphenylbut-3-en-1-yl)cyclopentan-1-one (3l):



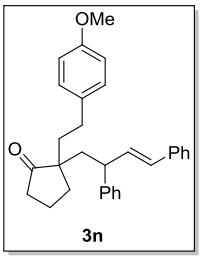
Compound 3l was obtained as colorless oil (59% yield, d.r. 1.0:1). **IR** (neat) cm^{-1} 3360, 3026, 2923, 1731, 1493, 1452, 1265, 1152, 969, 740, 702; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.30 (m, 13H), 7.06 (t, *J* = 6.2 Hz, 2H), 6.12-6.37 (m, 2H), 3.56-3.64 (m, 1H), 2.81-2.93 (m, 1H), 2.49-2.65 (m, 1H), 2.03-2.33 (m, 2H), 1.80-2.01 (m, 4H), 1.62-1.77 (m, 1H), 1.27-1.44 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 223.48, 222.92, 144.79, 144.28, 137.63, 137.32, 137.26, 137.12, 134.80, 134.53, 130.38, 130.33, 129.55, 129.24, 128.58, 128.52, 128.46, 128.15, 127.97, 127.31, 127.24, 127.16, 126.53, 126.50, 126.45, 126.37, 126.10, 53.40, 53.13, 46.27, 45.54, 43.27, 42.38, 42.19, 41.88, 38.58, 38.31, 31.30, 30.13, 18.49; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_1Na_1$ $[M+Na]^+$: 403.2032, Found: 403.2021, Error: 2.7 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-phenethylcyclopentan-1-one (3m):



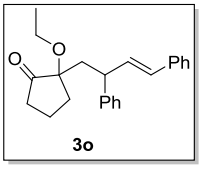
Compound 3m was obtained as colorless oil (54% yield, d.r. 1.0:1). **IR** (neat) cm^{-1} 3361, 2926, 2855, 1729, 1494, 1452, 1153, 969, 745, 698; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.32 (m, 8H), 7.12-7.27 (m, 5H), 7.05-7.07 (m, 2H), 6.16-6.40 (m, 2H), 3.59-3.65 (m, 1H), 2.46-2.60 (m, 2H), 2.18-2.27 (m, 2H), 1.86-2.10 (m, 4H), 1.64-1.84 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 222.40, 222.02, 144.95, 144.29, 141.97, 141.93, 137.23, 137.12, 134.78, 134.42, 129.64, 129.10, 128.67, 128.58, 128.49, 128.43, 128.34, 128.33, 128.23, 127.94, 127.27, 127.21, 127.13, 126.48, 126.39, 126.10, 125.82, 51.71, 51.63, 46.23, 45.47, 40.64, 39.97, 38.21, 37.80, 37.51, 37.04, 34.16, 32.72, 30.31, 30.20, 18.53, 18.50; **HRMS** (ESI) Calcd for $C_{29}H_{30}O_1Na_1$ $[M+Na]^+$: 417.2189, Found: 417.2176, Error: 3.1 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-(4-methoxyphenethyl)cyclopentan-1-one (3n):



Compound 3n was obtained as colorless oil (67% yield, d.r. 1.0:1). **IR** (neat) cm^{-1} 3440, 2928, 1729, 1511, 1246, 1177, 1035, 969, 821, 745, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.32 (m, 8H), 7.17-7.23 (m, 2H), 6.96-6.99 (m, 2H), 6.75-6.78 (m, 2H), 6.16-6.40 (m, 2H), 3.75 (s, 3H), 3.61-3.63 (m, 1H), 2.44-2.49 (m, 2H), 2.17-2.26 (m, 2H), 1.86-2.10 (m, 4H), 1.73-1.84 (m, 2H), 1.62-1.71 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 222.48, 222.10, 157.78, 145.00, 144.35, 137.27, 137.16, 134.84, 134.47, 134.04, 133.98, 129.65, 129.12, 128.68, 128.58, 128.51, 128.45, 127.96, 127.30, 127.22, 127.14, 126.48, 126.39, 126.11, 113.80, 113.78, 55.20, 51.75, 51.67, 46.24, 45.49, 40.69, 40.02, 38.47, 37.83, 37.54, 37.31, 34.17, 32.74, 29.40, 29.29, 18.56, 18.52; **HRMS** (ESI) Calcd for $C_{30}H_{32}O_2Na_1$ $[M+Na]^+$: 447.2295, Found: 447.2282, Error: 2.9 ppm.

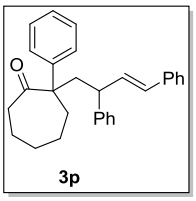
(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-ethoxycyclopentan-1-one (3o):



Compound 3o was obtained as colorless oil (39% yield, d.r. 1.5:1). **IR** (neat) cm^{-1} 3456, 3026, 2972, 2926, 1738, 1599, 1493, 1451, 1160, 1065, 966, 746, 698, 530; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.32 (m, 8H), 7.15-7.21 (m, 2H), 6.22-6.43 (m, 2H), 3.64-3.68 (m, 1H), 3.23-3.49 (m, 2H), 2.26-2.54 (m, 2H), 1.95-2.04 (m, 3H), 1.77-1.83 (m, 1H), 1.37-1.70 (m, 2H), 1.13 (t, J = 7.0 Hz, 2H), 1.03 (t, J = 7.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.21, 215.81, 144.86, 144.29, 137.27, 137.16, 134.62, 134.30, 129.59, 128.63, 128.60, 128.54, 128.46, 128.41, 128.07, 127.27,

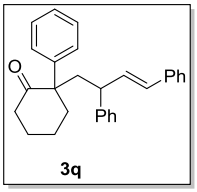
127.16, 127.04, 126.43, 126.30, 126.06, 81.32, 81.29, 58.79, 58.56, 44.59, 43.92, 36.25, 35.89, 35.61, 35.30, 35.23, 17.99, 17.84, 15.56, 15.47; **HRMS** (ESI) Calcd for $C_{23}H_{26}O_2Na_1$ $[M+Na]^+$: 357.1825, Found: 357.1815, Error: 2.8 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-phenylcycloheptan-1-one (3p):



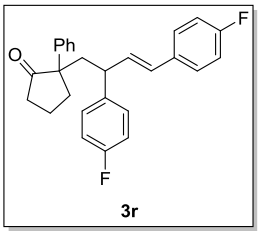
Compound 3p was obtained as colorless oil (55% yield, d.r. 2.8:1). **IR** (neat) cm^{-1} 3356, 2926, 2854, 1676, 1460, 1264, 741, 703; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10-7.29 (m, 12H), 6.92-7.07 (m, 3H), 5.82-6.19 (m, 2H), 3.08-3.19 (m, 1H), 2.59-2.65 (m, 2H), 2.43-2.50 (m, 1H), 2.09-2.30 (m, 3H), 1.76-1.86 (m, 3H), 1.30-1.59 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.06, 145.80, 141.45, 137.48, 135.04, 129.08, 128.49, 128.39, 128.29, 127.75, 127.20, 127.19, 126.02, 125.74, 59.20, 45.18, 42.58, 40.61, 32.07, 30.42, 26.87, 23.90; **HRMS** (ESI) Calcd for $C_{29}H_{31}O_1$ $[M+H]^+$: 395.2369, Found: 395.2367, Error: 0.5 ppm.

(E)-2-(2,4-diphenylbut-3-en-1-yl)-2-phenylcyclohexan-1-one (3q):



Compound 3q was obtained as colorless solid (69% yield, d.r. 4.2:1). **Mp** 119.5-121.5 ^oC; **IR** (neat) cm^{-1} 3362, 2929, 2860, 1704, 1598, 1493, 1449, 1265, 1119, 968, 744, 700; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.32 (m, 6H), 7.12-7.21 (m, 6H), 6.97-7.10 (m, 3H), 5.88-6.27 (m, 2H), 3.15-3.26 (m, 1H), 2.84-2.87 (m, 1H), 2.23-2.56 (m, 4H), 1.87-1.89 (m, 1H), 1.50-1.80 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.06, 145.61, 140.43, 137.55, 135.32, 128.87, 128.79, 128.38, 128.32, 127.27, 127.03, 126.92, 126.74, 126.05, 125.80, 57.82, 46.04, 45.21, 40.05, 35.31, 28.00, 21.65; **HRMS** (ESI) Calcd for $C_{28}H_{28}O_1Na_1$ $[M+Na]^+$: 403.2032, Found: 403.2029, Error: 0.7 ppm.

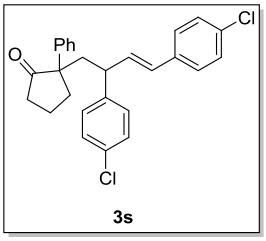
(E)-2-(2,4-bis(4-fluorophenyl)but-3-en-1-yl)-2-phenylcyclopentan-1-one (3r):



Compound 3r was obtained as colorless oil (94% yield, d.r. 5.0:1). **IR** (neat) cm^{-1} 3054, 2925, 2854, 1733, 1601, 1507, 1265, 1225, 1157, 970, 834, 739, 701, 521; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.37 (m, 7H), 6.96-7.10 (m, 4H), 6.85-6.92 (m, 2H), 6.00-6.16 (m, 2H), 3.22-3.28 (m, 1H), 2.74-2.79 (m, 1H), 2.49 (dd, *J* = 4.4 Hz, 14.4 Hz, 1H), 2.07-2.26 (m, 3H), 1.98-2.06 (m, 1H), 1.90-1.93 (m, 1H), 1.73-1.75 (m, 1H); **^{3}C NMR** (100 MHz, $CDCl_3$) δ 219.20, 162.10 (d, *J* = 245 Hz), 161.20 (d, *J* = 242 Hz), 140.25 (d, *J* = 3 Hz), 138.07, 133.56, 133.27 (d, *J* = 3 Hz), 129.47 (d, *J* = 8.0 Hz), 128.61, 128.53, 128.45, 127.57, 127.49, 126.97, 115.44 (d, *J* = 22 Hz), 115.16 (d, *J* =

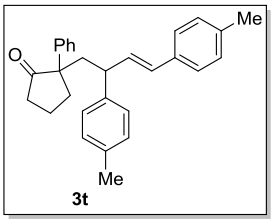
21 Hz), 56.80, 45.36, 45.28, 36.65, 33.54, 18.62; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.82, -116.94; **HRMS** (ESI) Calcd for $C_{27}H_{24}F_2O_1Na_1$ $[M+ Na]^+$: 425.1687, Found: 425.1689, Error: 0.5 ppm.

(E)-2-(2,4-bis(4-chlorophenyl)but-3-en-1-yl)-2-phenylcyclopentan-1-one (3s):



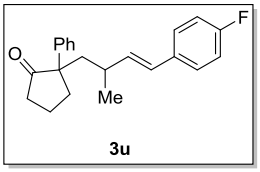
Compound 3s was obtained as white solid (90% yield, d.r. 5.8:1). **Mp** 110.8-114.6 ^oC; **IR** (neat) cm^{-1} 3362, 2924, 2853, 1734, 1490, 1405, 1265, 1091, 1024, 738, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.40 (m, 4H), 7.23-7.32 (m, 5H), 7.18-7.22 (m, 2H), 7.02-7.09 (m, 2H), 6.03-6.17 (m, 2H), 3.27-3.32 (m, 1H), 2.76-2.81 (m, 1H), 2.50-2.55 (dd, *J* = 4.4 Hz, 14.4 Hz, 1H), 2.11-2.32 (m, 3H), 1.91-2.09 (m, 2H), 1.73-1.82 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 218.94, 142.86, 138.04, 135.57, 134.21, 132.92, 131.86, 128.81, 128.68, 128.53, 128.50, 127.28, 126.98, 126.95, 56.73, 45.50, 45.03, 36.62, 33.64, 18.58; **HRMS** (ESI) Calcd for $C_{27}H_{25}Cl_2O_1$ $[M+H]^+$: 435.1277, Found: 435.1281, Error: 0.9 ppm.

(E)-2-(2,4-di-p-tolylbut-3-en-1-yl)-2-phenylcyclopentan-1-one (3t):



Compound 3t was obtained as colorless oil (52% yield, d.r. 2.4:1). **IR** (neat) cm^{-1} 3446, 3049, 2923, 2858, 1734, 1681, 1597, 1511, 1445, 1187, 1153, 967, 801, 737, 701, 510; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.38 (m, 4H), 7.20-7.26 (m, 3H), 7.08-7.11 (m, 2H), 6.94-7.05 (m, 4H), 6.03-6.15 (m, 1H), 3.16-3.20 (m, 1H), 2.68-2.81 (m, 1H), 2.48-2.53 (m, 1H), 2.32 (s, 3H), 2.25 (s, 3H), 1.98-2.20 (m, 4H), 1.86-1.90 (m, 1H), 1.67-1.75 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.43, 141.88, 138.25, 136.86, 135.56, 134.55, 133.10, 129.44, 129.17, 129.07, 128.52, 127.04, 126.91, 125.95, 56.90, 45.70, 45.33, 36.64, 33.58, 21.13, 21.07, 20.90, 18.67; **HRMS** (ESI) Calcd for $C_{29}H_{30}O_1Na_1$ $[M+ Na]^+$: 417.2189, Found: 417.2188, Error: 0.2 ppm.

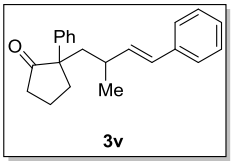
(E)-2-(4-(4-fluorophenyl)-2-methylbut-3-en-1-yl)-2-phenylcyclopentan-1-one (3u):



Compound 3u was obtained as colorless solid (88% yield, d.r. 11.4:1). **Mp** 64.5-66.3 ^oC; **IR** (neat) cm^{-1} 3361, 2924, 2868, 1734, 1508, 1228, 1156, 970, 739, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.31-7.35 (m, 2H), 7.23-7.28 (m, 3H), 6.97-7.01 (m, 2H), 6.09 (d, *J* = 15.6 Hz, 1H), 5.82 (dd, *J* = 8.8 Hz, 15.6 Hz, 1H), 2.69-2.74 (m, 1H), 2.04-2.25 (m, 4H), 1.94-2.02 (m, 1H), 1.85-1.92 (m, 1H), 1.70-1.77 (m, 2H), 0.93 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.52, 161.99 (d, *J* = 244 Hz), 138.90, 136.77 (d, *J* = 2 Hz), 133.84 (d, *J* = 4 Hz), 128.54, 127.37,

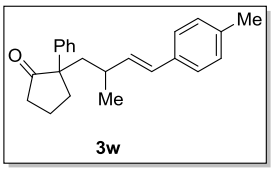
127.29, 127.09, 127.00, 126.81, 115.38 (d, *J* = 21 Hz), 56.88, 46.22, 36.80, 34.97, 33.67, 22.75, 18.65; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.43; **HRMS** (ESI) Calcd for $C_{22}H_{23}F_1O_1Na_1$ $[M+Na]^+$: 345.1625, Found: 345.1614, Error: 3.2 ppm.

(E)-2-(2-methyl-4-phenylbut-3-en-1-yl)-2-phenylcyclopentan-1-one (3v):



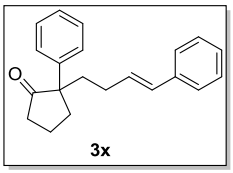
Compound 3v was obtained as colorless oil (54% yield, d.r. 10.2:1). **IR** (neat) cm^{-1} 3361, 3057, 2957, 2924, 1734, 1493, 1447, 1151, 969, 749, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.41 (m, 2H), 7.30-7.37 (m, 6H), 7.01-7.29 (m, 2H), 6.13 (d, *J* = 16 Hz, 1H), 5.92 (dd, *J* = 9.2 Hz, 16 Hz, 1H), 2.72-2.77 (m, 1H), 2.05-2.24 (m, 4H), 1.86-2.03 (m, 1H), 1.61-1.75 (m, 2H), 0.94 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.61, 138.79, 137.71, 137.00, 128.55, 128.53, 128.33, 127.05, 126.95, 126.79, 125.94, 56.92, 46.24, 45.27, 36.74, 35.02, 33.72, 22.82, 18.66; **HRMS** (ESI) Calcd for $C_{22}H_{24}O_1Na_1$ $[M+Na]^+$: 327.1719, Found: 327.1710, Error: 2.7 ppm.

(E)-2-(2-methyl-4-(p-tolyl)but-3-en-1-yl)-2-phenylcyclopentan-1-one (3w):



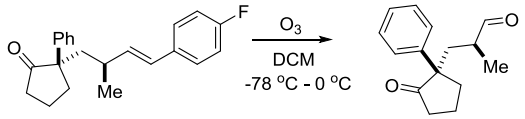
Compound 3w was obtained as colorless oil (71% yield, d.r. 12:1). **IR** (neat) cm^{-1} 3448, 2958, 2923, 1734, 1454, 1151, 970, 801, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.41 (m, 2H), 7.31-7.35 (m, 2H), 7.21-7.26 (m, 3H), 7.11-7.13 (m, 2H), 6.93 (d, *J* = 15.6 Hz, 1H), 5.86 (dd, *J* = 9.6 Hz, 16 Hz, 1H), 2.75 (dd, *J* = 6.0 Hz, 13.6 Hz, 1H), 2.33 (s, 3H), 2.02-2.25 (m, 4H), 1.84-1.99 (m, 2H), 1.62-1.73 (m, 2H), 0.93 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.83, 138.57, 136.66, 135.88, 134.79, 129.22, 128.47, 128.08, 127.00, 126.73, 125.77, 56.88, 46.20, 36.68, 35.04, 33.56, 22.86, 21.13, 18.63; **HRMS** (ESI) Calcd for $C_{23}H_{16}O_1Na_1$ $[M+Na]^+$: 341.1876, Found: 341.1864, Error: 3.5 ppm.

(E)-2-phenyl-2-(4-phenylbut-3-en-1-yl)cyclopentan-1-one (3x):



Compound 3x was obtained as colorless oil (26.9% yield). **IR** (neat) cm^{-1} 3361, 2925, 2853, 1734, 1494, 1446, 1265, 1154, 965, 739, 701; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.43 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 4.4 Hz, 1H), 6.28 (d, *J* = 16 Hz, 1H), 6.03-6.11 (m, 1H), 2.65-2.70 (m, 1H), 2.20-2.36 (m, 2H), 1.91-2.13 (m, 5H), 1.76-1.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.39, 139.12, 137.64, 130.20, 129.89, 128.57, 128.41, 126.86, 126.83, 125.85, 56.58, 38.37, 37.43, 33.97, 28.31, 18.66; **HRMS** (ESI) Calcd for $C_{21}H_{22}O_1Na_1$ $[M+Na]^+$: 313.1563, Found: 313.1554, Error: 2.9 ppm.

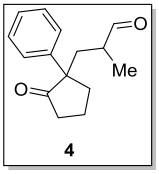
5. Transformations of Cyclopentanone 3u



3u **4**

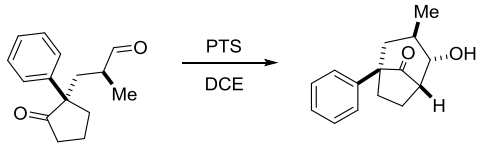
To a stirred solution of **3u** (679 mg, 2.2 mmol) in freshly distilled dichloromethane (10 mL) was cooled to -78 ℃. Then ozone was blown into the resulting mixture slowly. The reaction was stirred at -78 ℃ until the consumption of **3u** (monitored by TLC) and then quenched by addition two drops of dimethyl sulfide (10 equiv). After stirring at 0 °C for 1 h, the reaction was extracted with DCM (2 × 10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by preparative TLC (ethyl acetate/petroleum ether = 1/40, v/v) to afford the product **4** (403 mg, 78% yield, d.r. 8.1:1) as colorless oil.

(S)-2-methyl-3-((S)-2-oxo-1-phenylcyclopentyl)propanal (4):



4

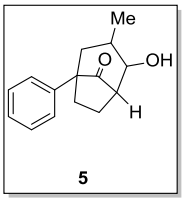
Compound 4 was obtained as colorless oil (78% yield, d.r. 8.1:1). **IR** (neat) cm^{-1} 3329, 2968, 1735, 1457, 1242, 1155, 702; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 2.8 Hz, 1H), 7.32-7.40 (m, 4H), 7.23-7.27 (m, 1H), 2.57-2.70 (m, 1H), 2.12-2.34 (m, 4H), 1.88-2.00 (m, 3H), 1.73-1.83 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 218.76, 204.35, 138.17, 128.82, 127.26, 126.91, 56.33, 43.19, 39.75, 36.85, 34.24, 18.40, 15.70; **HRMS** (ESI) Calcd for $C_{15}H_{18}O_2Na_1$ $[M+Na]^+$: 253.1199, Found: 253.1198, Error: 0.6 ppm.



4 **5**

To a stirred solution of **4** (46 mg, 0.2 mmol) in freshly distilled DCE (0.5 ml/mg) was added PTS (34.4mg, 0.2 mmol) at room temperature. Then the reaction was stirred at 70 ℃ until the consumption of **1a** (monitored by TLC). The mixture was concentrated under vacuum after cooled to room temperature. The residue was purified via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2, v/v) to afford the product **5** (28 mg, 60% yield, d.r. 2.9:1) as colorless oil.

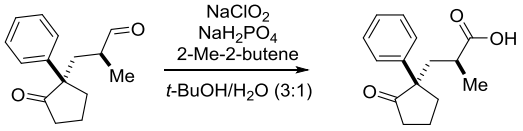
(1R,3R,4S,5S)-4-hydroxy-3-methyl-1-phenylbicyclo[3.2.1]octan-8-one (5):



5

Compound 5 was obtained as colorless oil (60% yield, d.r. 2.9:1). **IR** (neat) cm^{-1} 3428, 2957, 1737, 1456, 1048, 700; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.37 (m, 4H), 7.21-7.27 (m, 1H), 3.64 (dd, *J* = 2.8 Hz, 9.6 Hz, 1H), 2.63-2.66 (m, 1H), 2.30-2.40 (m, 1H), 2.18-2.25 (m, 1H), 2.09-2.16

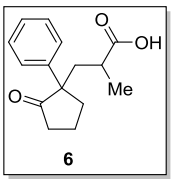
(m, 2H), 1.95-2.06 (m, 2H), 1.88-1.94 (m, 1H), 1.57-1.63 (m, 1H), 1.11 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 215.41, 140.64, 128.96, 128.15, 127.25, 126.65, 79.36, 54.12, 53.56, 45.44, 32.88, 31.88, 17.18, 16.93; **HRMS** (ESI) Calcd for $C_{15}H_{18}O_2Na_1$ $[M+Na]^+$: 253.1199, Found: 253.1190, Error: 3.7 ppm.



4 **6**

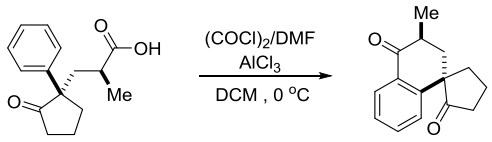
The aldehyde **4** (42 mg, 0.18 mmol) was dissolved in *t*-butanol (6 mL) followed by adding 2-methyl-2-butene (0.15 mL, 10 equive) at room temperature. Then, to the resulting mixture was added dropwise followed by a solution of $NaClO_2$ (49 mg, 3 equive) and NaH_2PO_4 (108 mg, 5.0 equive) in H_2O (2 mL). After stirring for 5 h, the reaction was concentrated in vacuo. The residue was dissolved in EtOAc (10 mL), diluted with 10% HCl (untill the PH < 3). The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified via column chromatography on silica gel (ethyl acetate/petroleum ether = 2/1, v/v) to give product compound **6** (33.4 mg, 75% yield, d.r. 7.0:1) as a colorless oil.

(S)-2-methyl-3-((S)-2-oxo-1-phenylcyclopentyl)propanoic acid (6):



6

Compound 6 was obtained as colorless solid (75% yield, d.r. 7.0:1). **Mp** 71.7-75.0 ^oC; **IR** (neat) cm^{-1} 2970, 1736, 1459, 1157, 702; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.40-7.42 (m, 2H), 7.31-7.36 (m, 2H), 7.22-7.26 (m, 1H), 2.68-2.73 (m, 1H), 2.21-2.28 (m, 3H), 1.93-2.14 (m, 4H), 1.67-1.84 (m, 1H), 1.02 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 218.74, 183.19, 137.46, 128.70, 127.17, 127.10, 56.40, 42.33, 36.52, 35.89, 33.01, 19.40, 18.43; **HRMS** (ESI) Calcd for $C_{15}H_{18}O_3Na_1$ $[M+Na]^+$: 269.1148, Found: 269.1140, Error: 3.1 ppm.

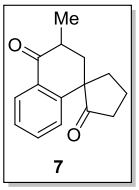


6 **7**

To a stirred solution of **6** (62 mg, 0.25 mmol) in freshly distilled DCM was added one drop DMF at 0 ^oC under an argon atmosphere. To the vigorously stirred mixture was added oxalyl chloride (32 μL, 1.5 equive) dropwise. After stirring for 1.5 h, the reaction was concentrated in vacuo. The residue was put into the next step directly without purification. The residue was then redissolved in freshly distilled dichloromethane was added $AlCl_3$ at 0 ^oC under an argon atmosphere. The reaction was quenched by addition of saturated $NaHCO_3$ (aq) until the consumption of **6** (monitored by TLC). The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified via column chromatography on silica gel (ethyl

acetate/petroleum ether = 1/20, v/v) to give product compound **7** (35 mg, 60% yield, d.r. 1.5:1) as a colorless solid.

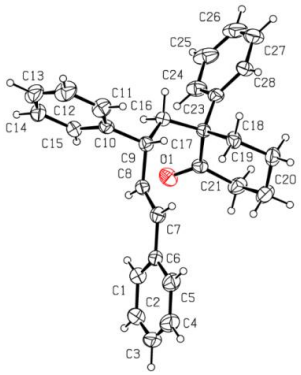
(1S,3'S)-3'-methyl-2',3'-dihydro-4'H-spiro[cyclopentane-1,1'-naphthalene]-2,4'-dione (7):

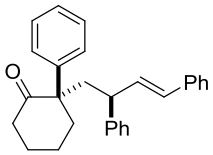


7

Compound 7 was obtained as white solid (60% yield, d.r. 1.5:1). **IR** (neat) cm^{-1} 2965, 1735, 1686, 1599, 1453, 1229, 1200, 947, 759, 557; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06-8.12 (m, 1H) 7.48-7.56 (m, 1H), 7.33-7.38 (m, 1H), 7.24-7.27 (m, 1H), 2.94-3.04 (m, 1H), 2.69-2.78 (m, 1H), 2.56-2.64 (m, 1H), 2.39-2.51 (m, 1H), 2.29-2.34 (m, 1H), 2.08-2.22 (m, 3H), 1.86-1.93 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 217.53, 199.85, 143.57, 133.37, 133.30, 127.82, 127.28, 125.84, 52.34, 39.38, 38.31, 37.26, 36.91, 18.89, 15.13; **HRMS** (ESI) Calcd for $C_{15}H_{16}O_2Na_1$ $[M+Na]^+$: 251.1043, Found: 251.1034, Error: 3.2 ppm.

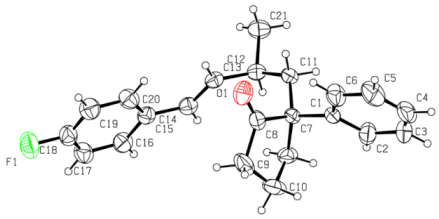
6. X-Ray Ellipsoid Plots of 3q and 3u

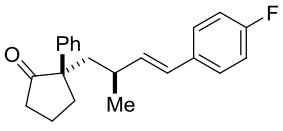




3q

The CCDC Number of compound **3q** is 1836270;





3u

The CCDC Number of compound **3u** is 1836259.

7. References

1. A. Spaggiari, D. Vaccari, P. Davoli, G. Torre and F. Prati, *J. Org. Chem.*, 2007, **72**, 2216-2219.
2. W. Z. Weng, J. G. Sun, P. Li and B. Zhang, *Chem. Eur. J.*, 2017, **23**, 9752-9755.
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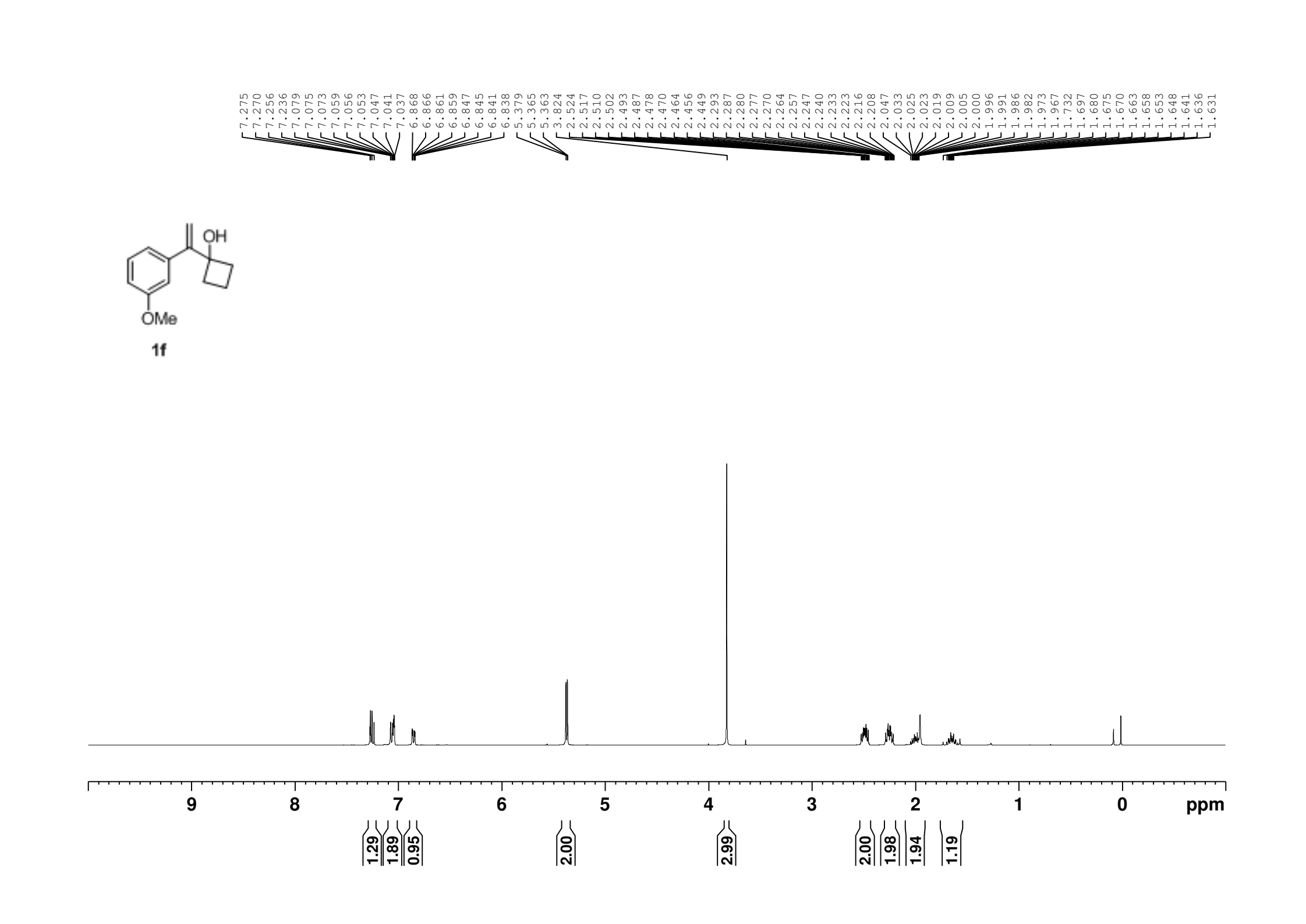
4. (a) A. Bigot, D. Breuninger and B. Breit, *Org. Lett.*, 2008, **10**, 5321-5324. (b) S. M. Smith, G. L. Hoang, R. Pal, M. O. B. Khaled, L. S. W. Pelter, X. C. Zeng and J. M. Takacs, *Chem. Commun.*, 2012, **48**,

12180-12182.

5. H.-X. Zheng, Z.-F. Xiao, C.-Z. Yao, Q.-Q. Li, X.-S. Ning, Y.-B. Kang and Y. Tang, *Org. Lett.*, 2015, **17**, 6102-6105.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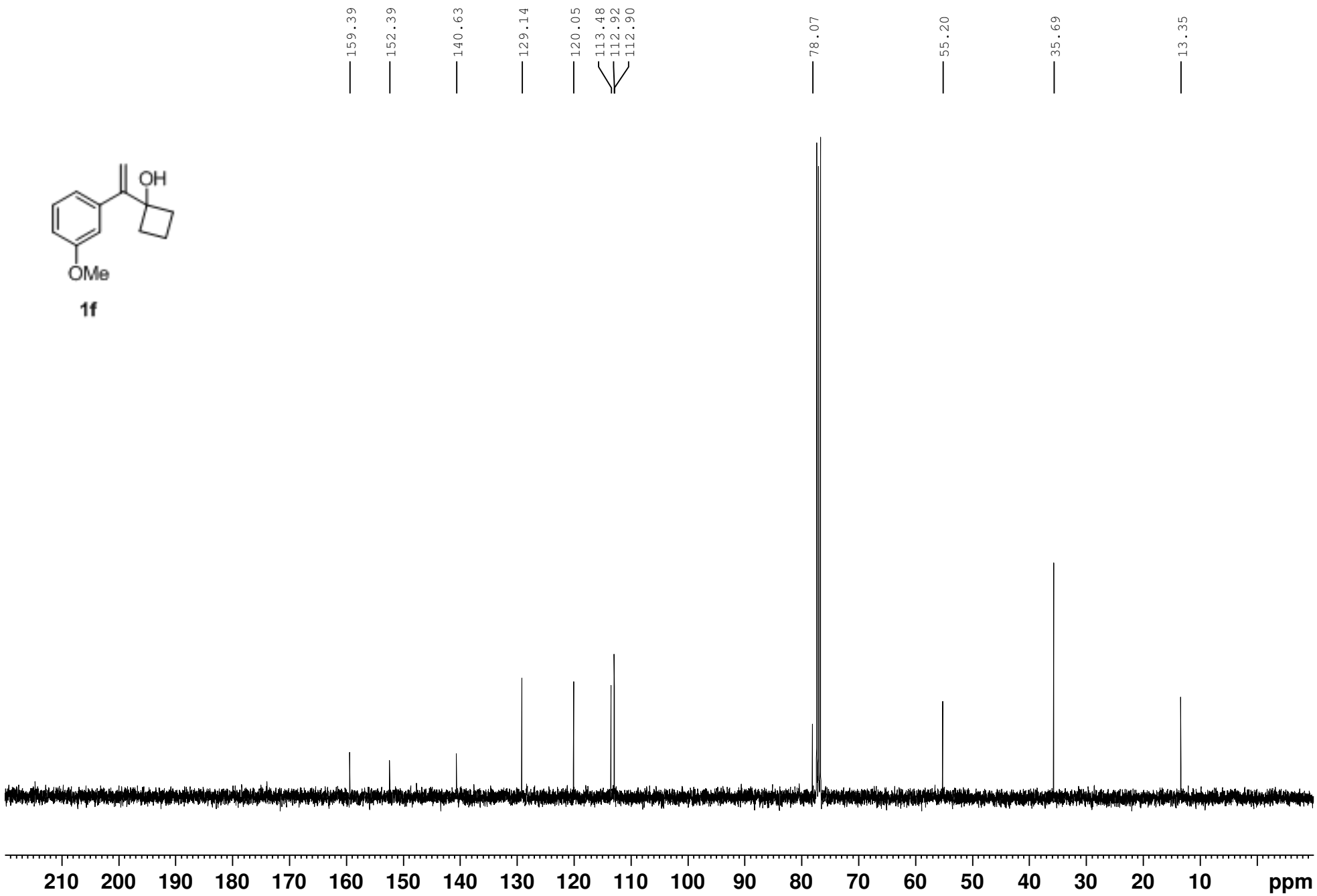
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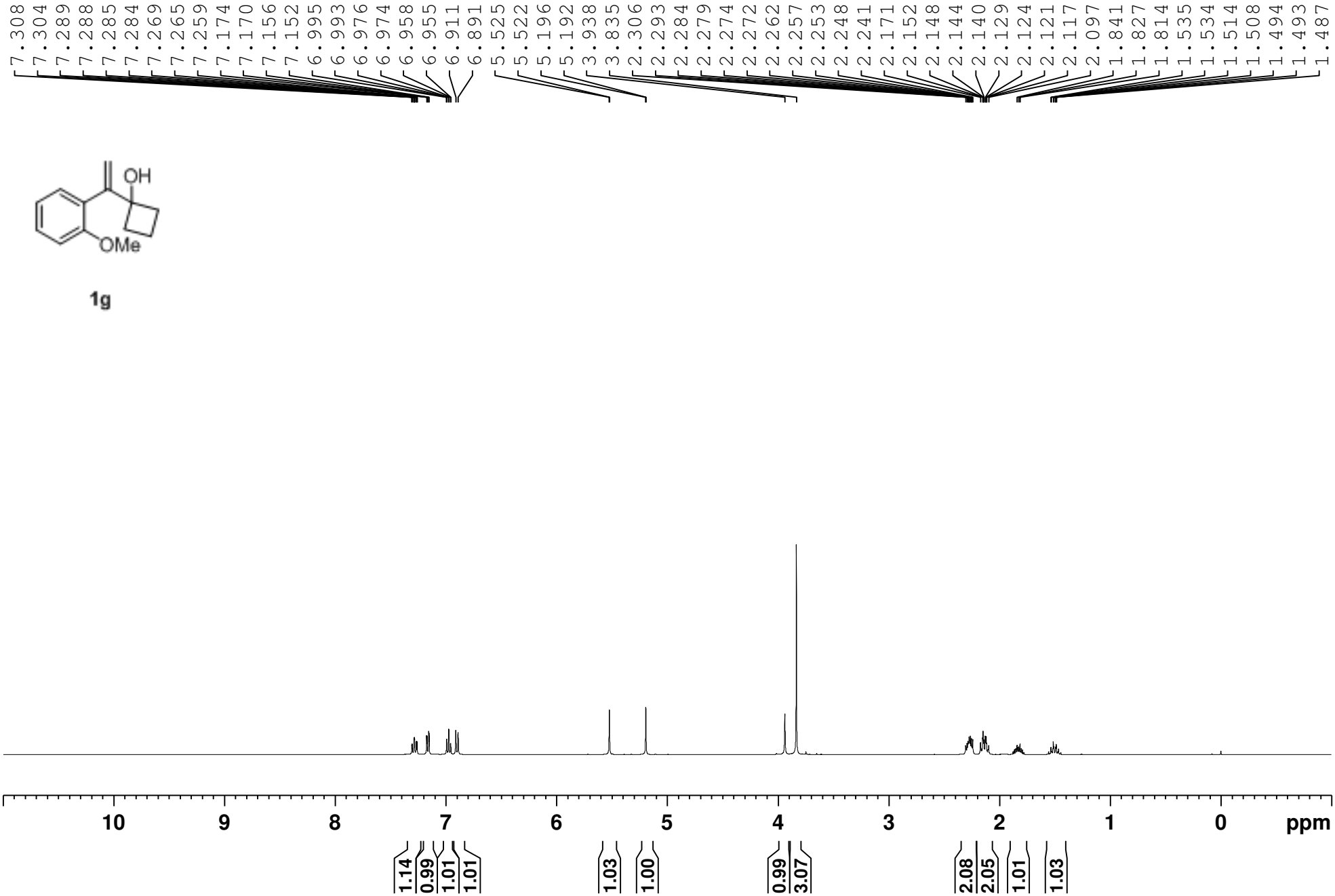
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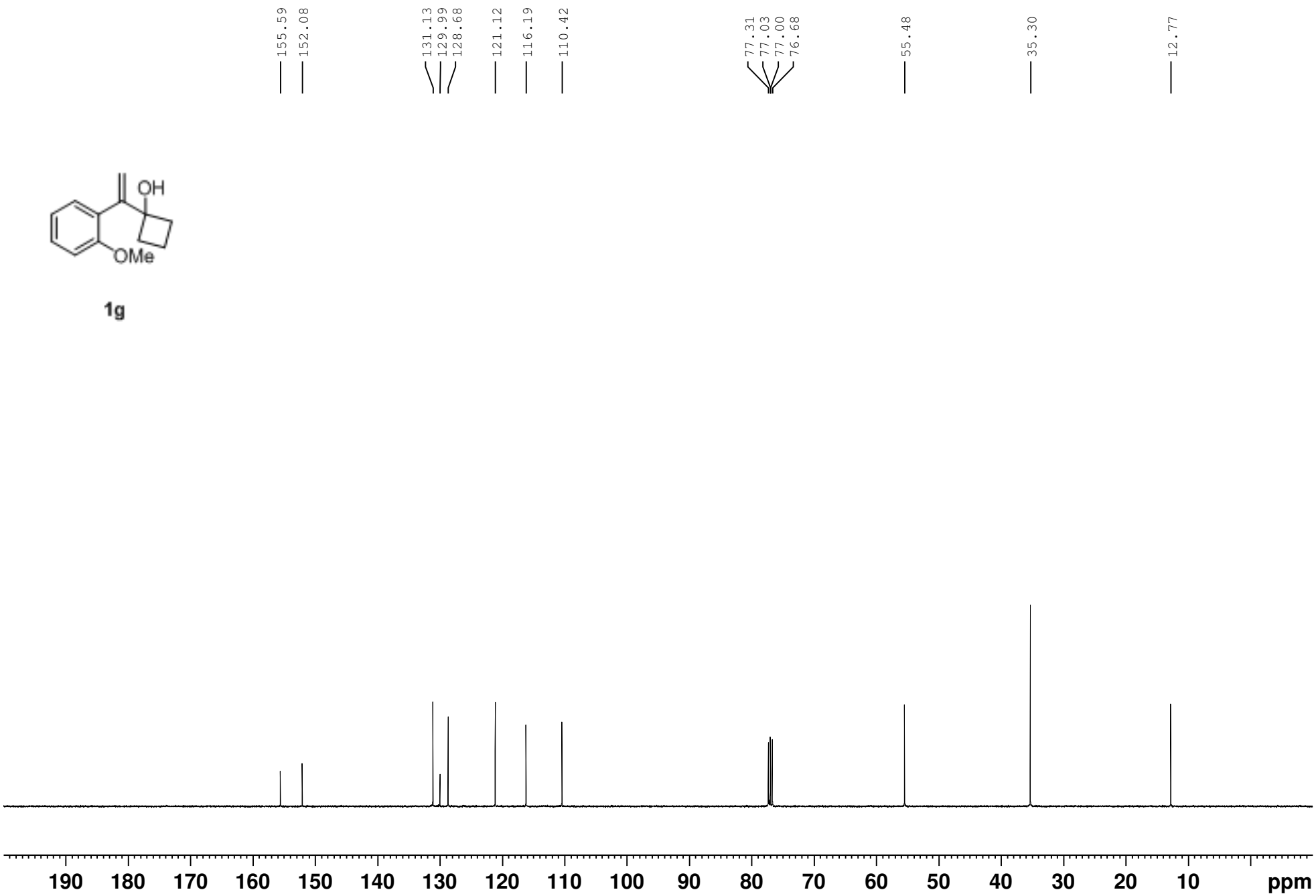
1g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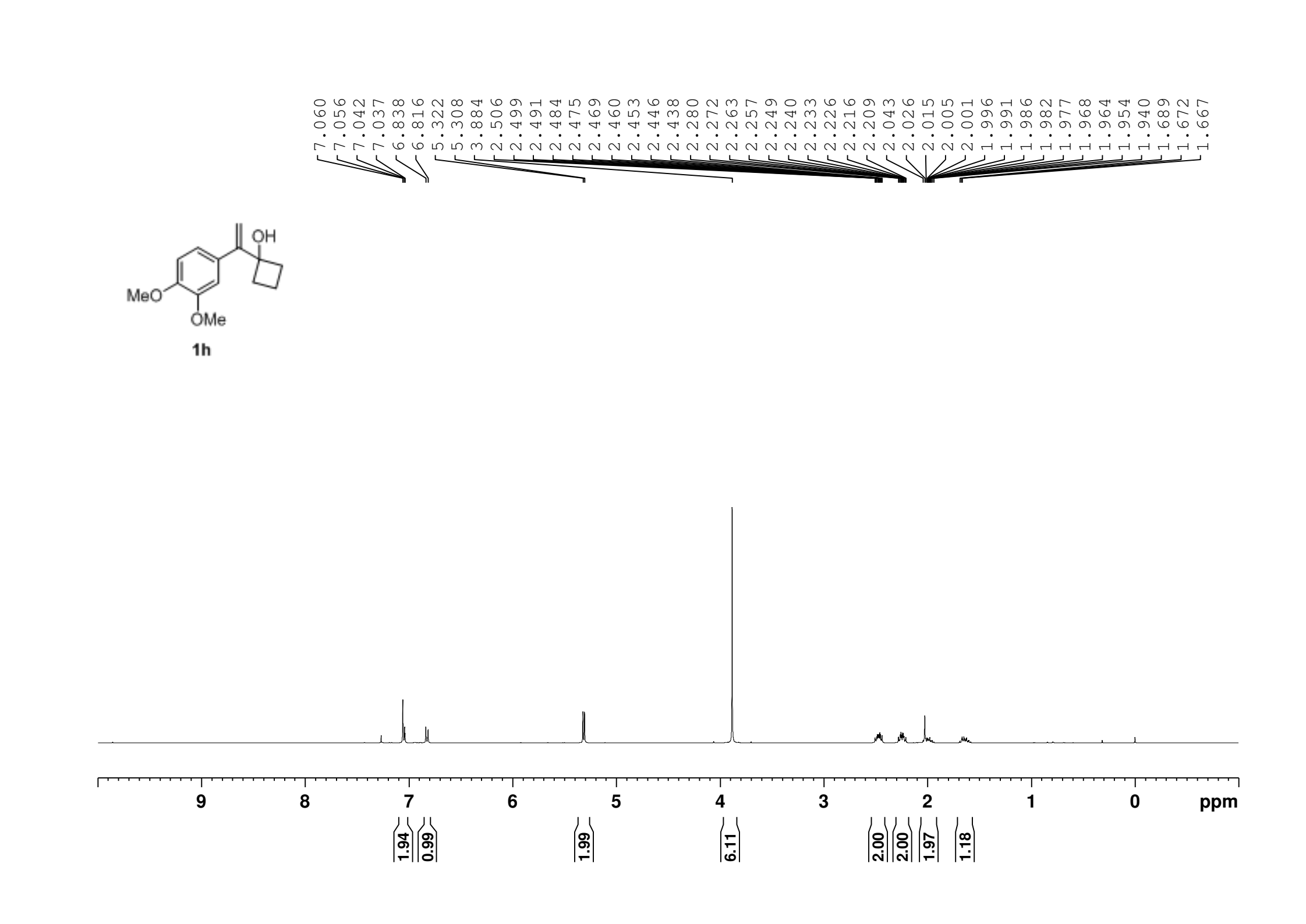
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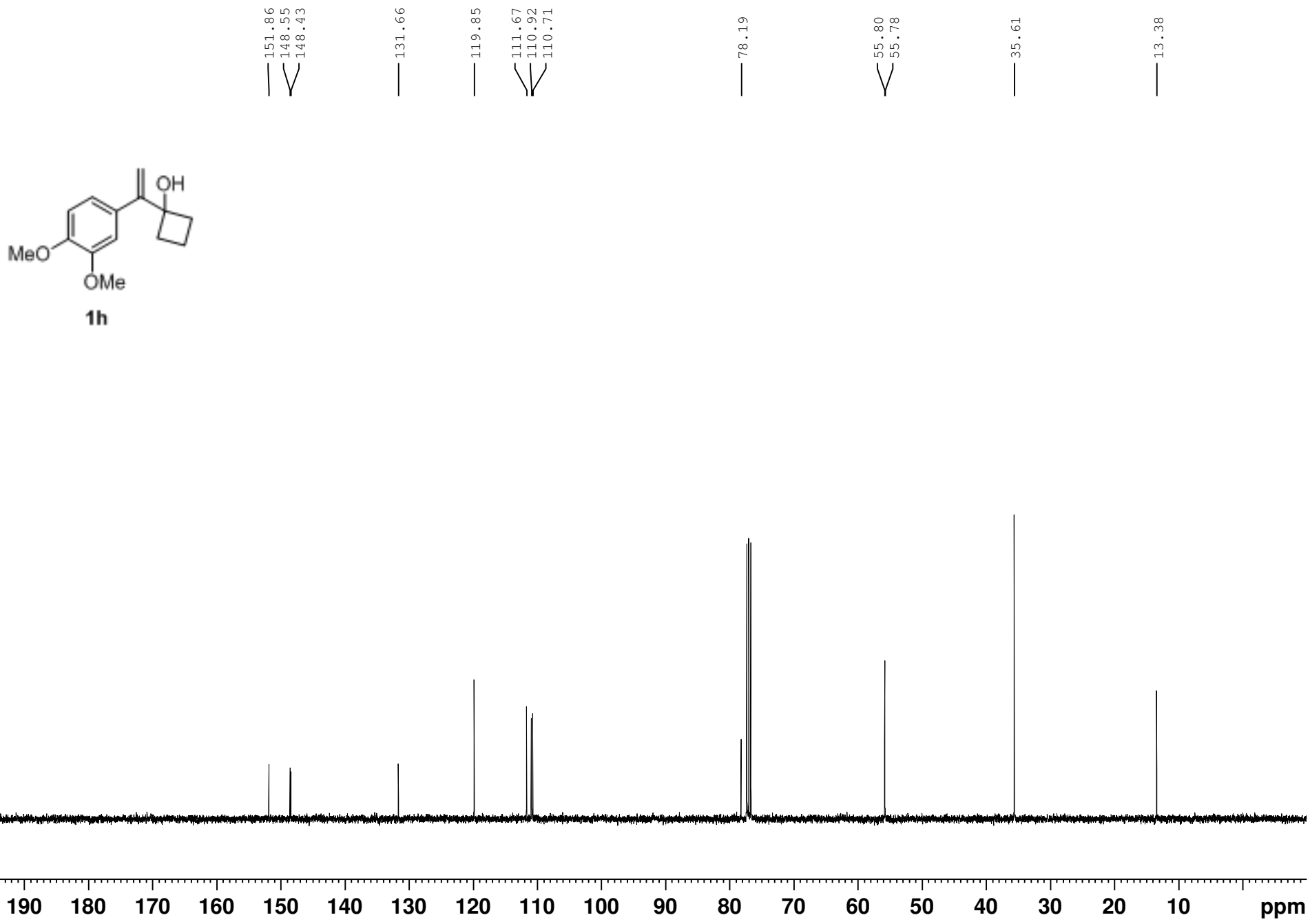
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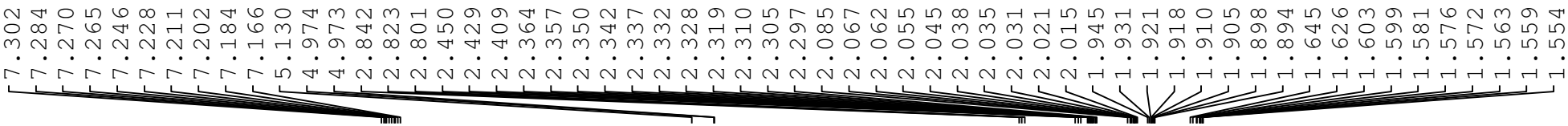
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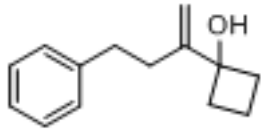
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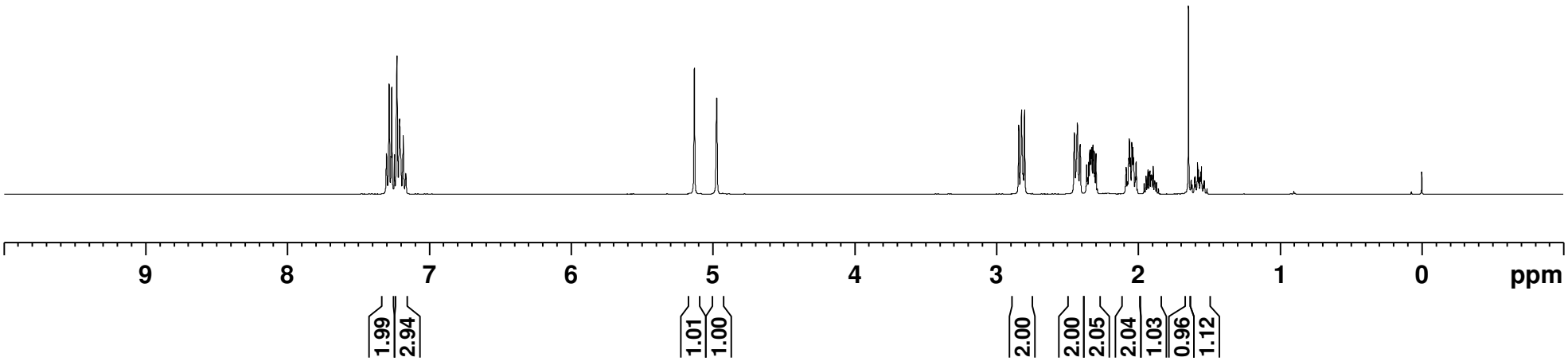
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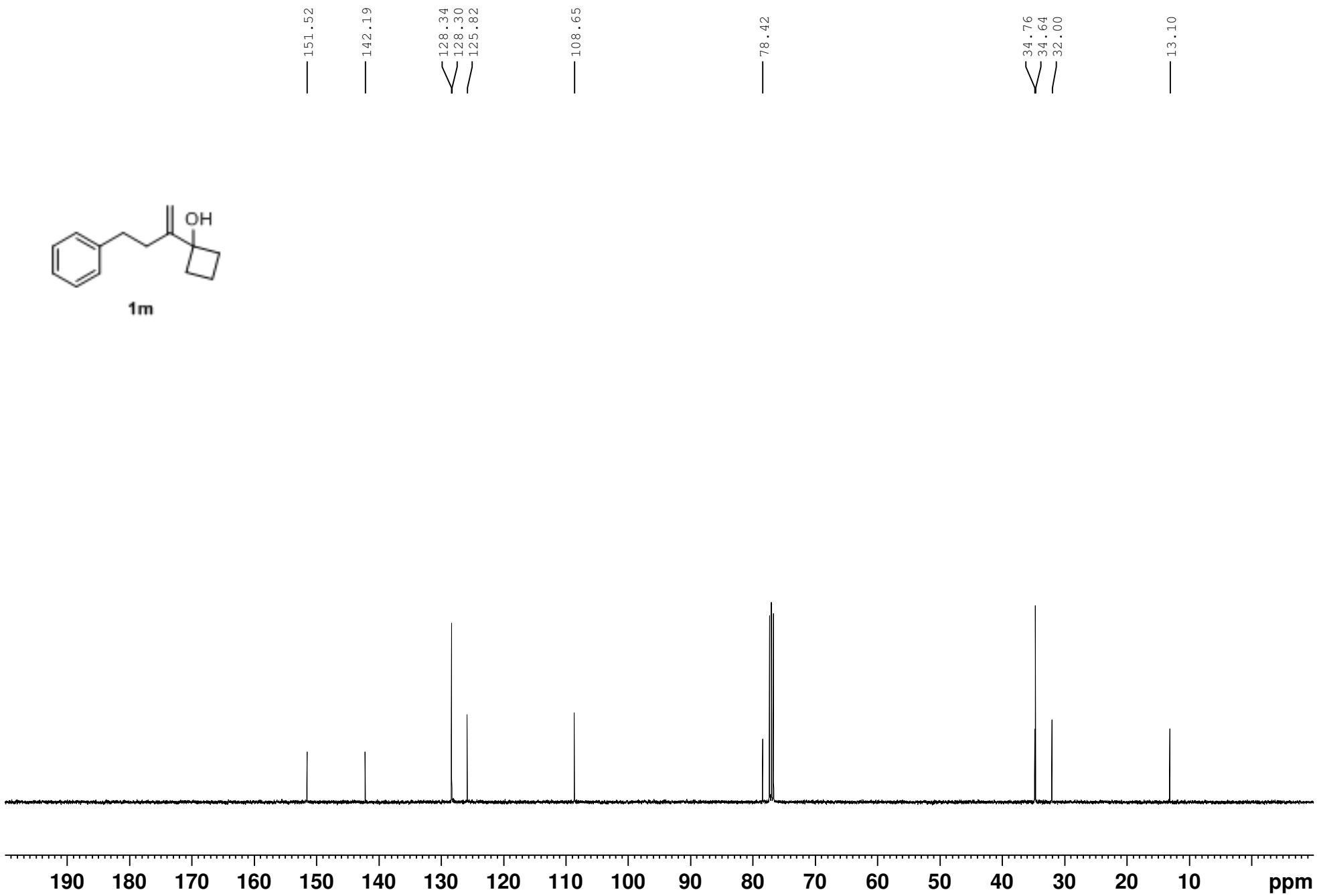
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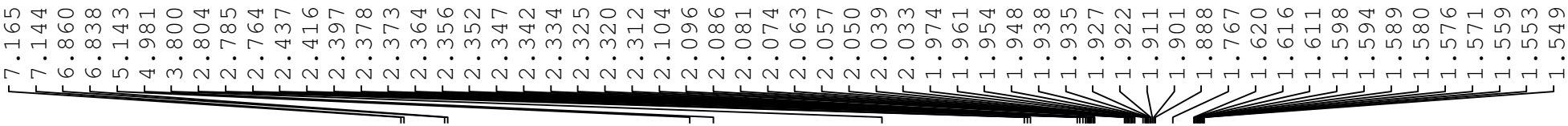
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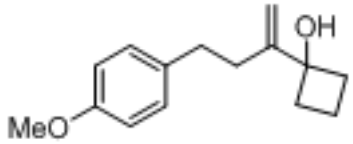
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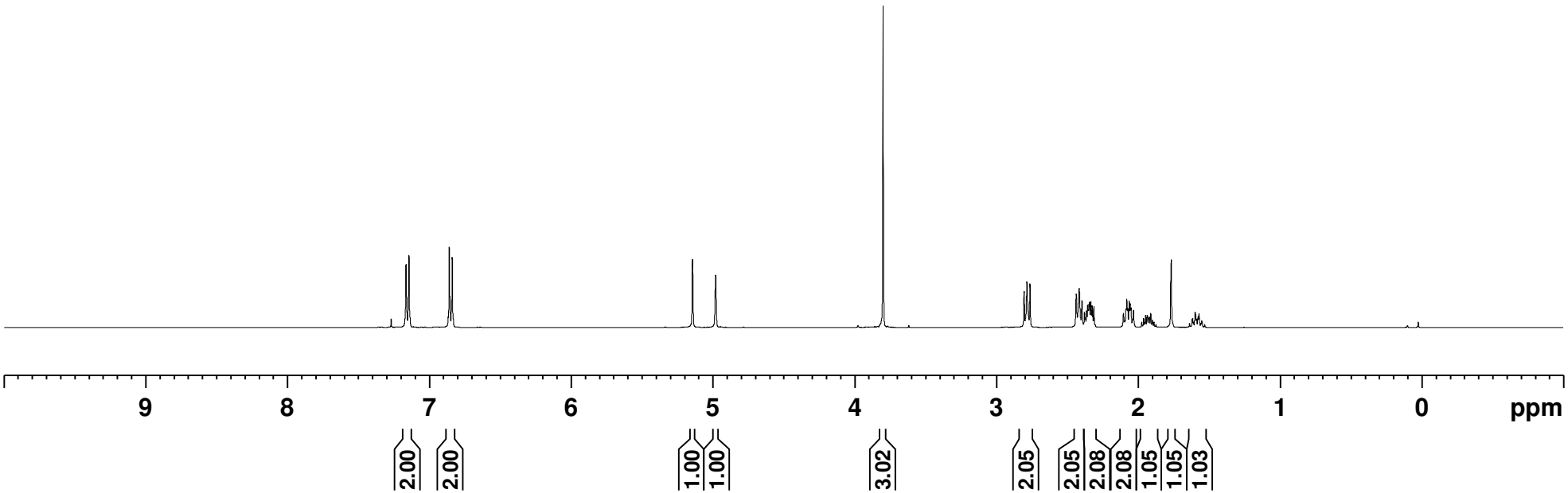
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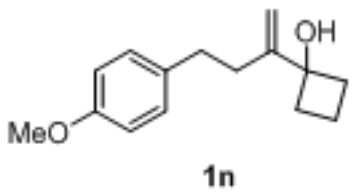

1n

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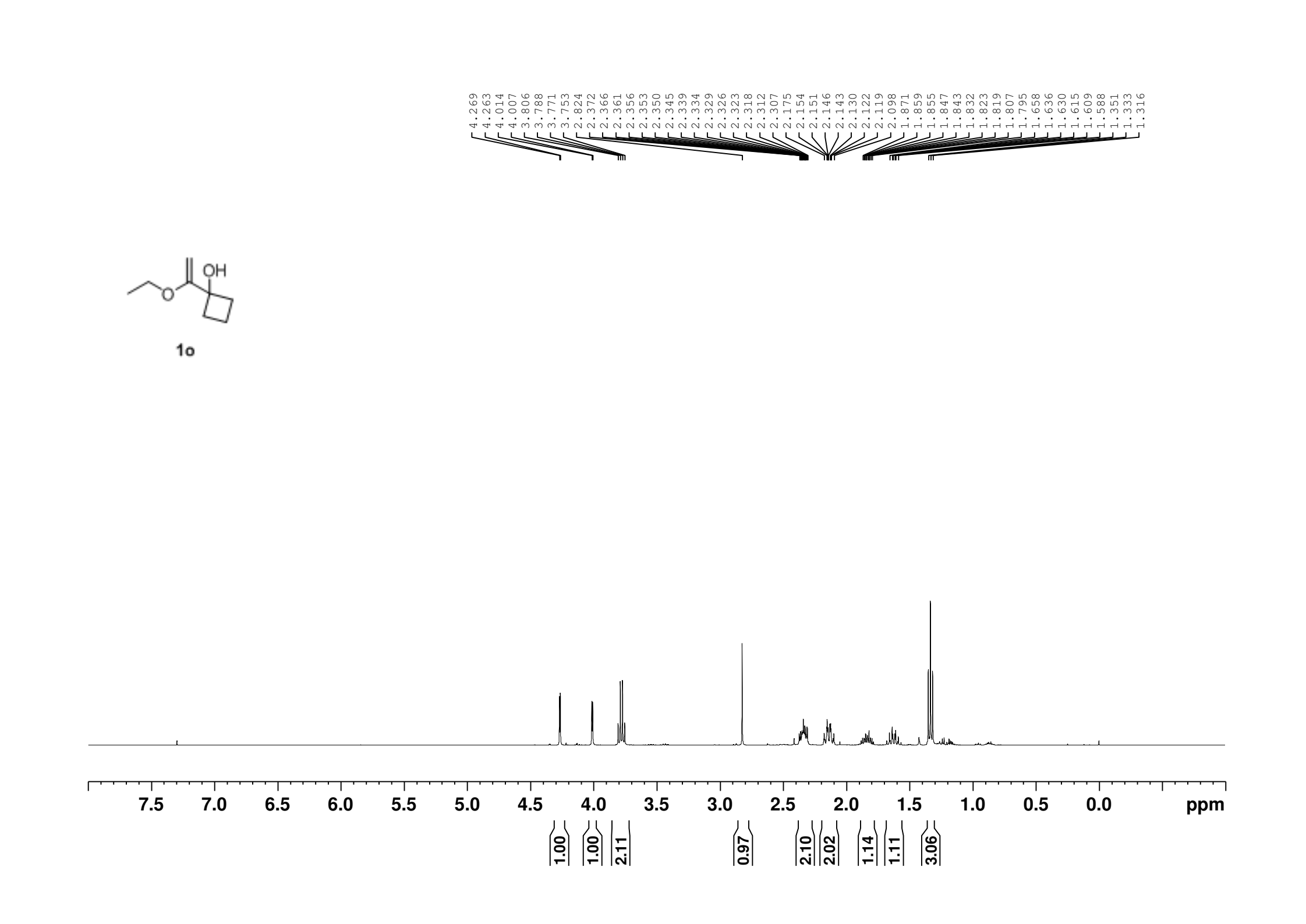
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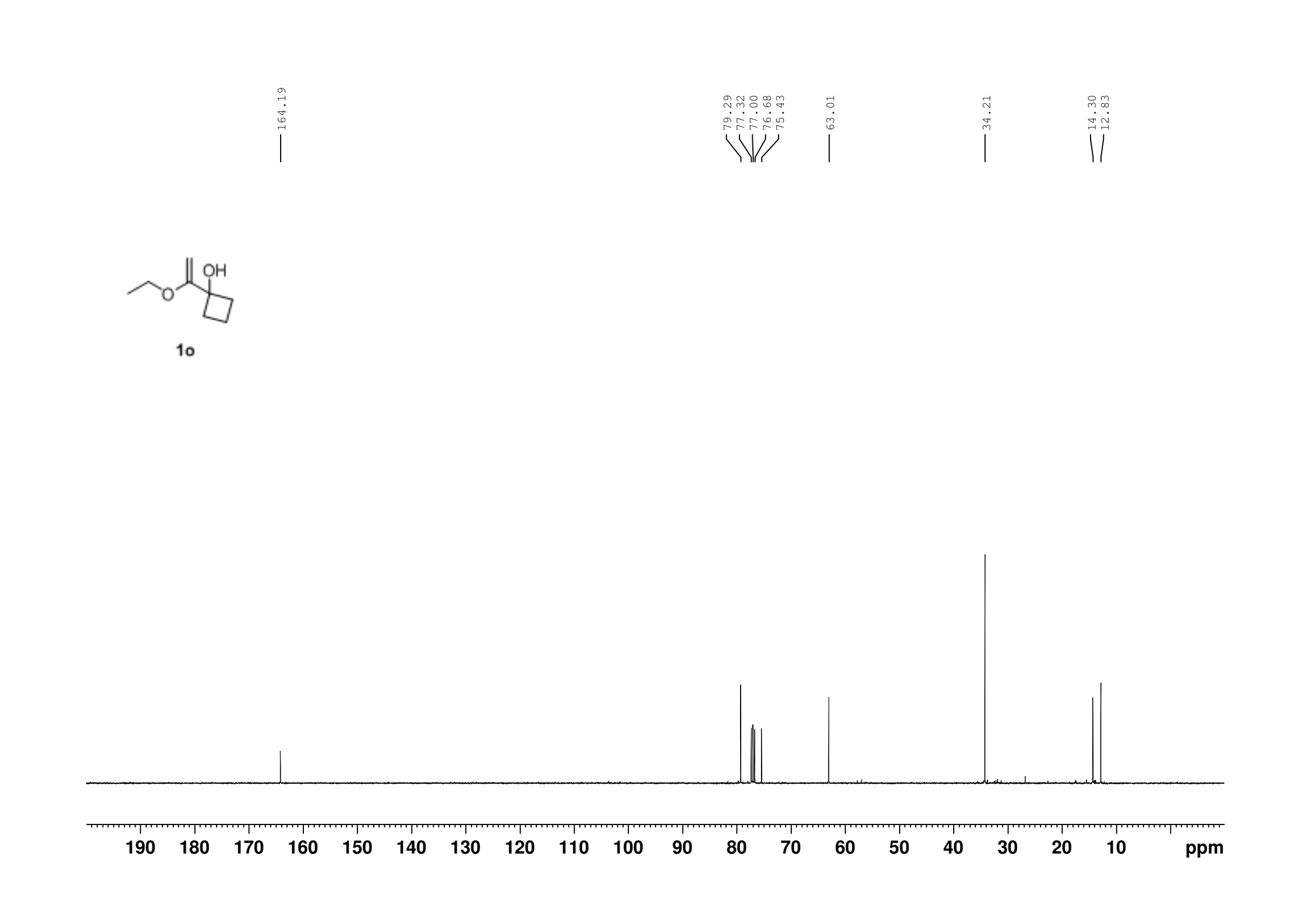
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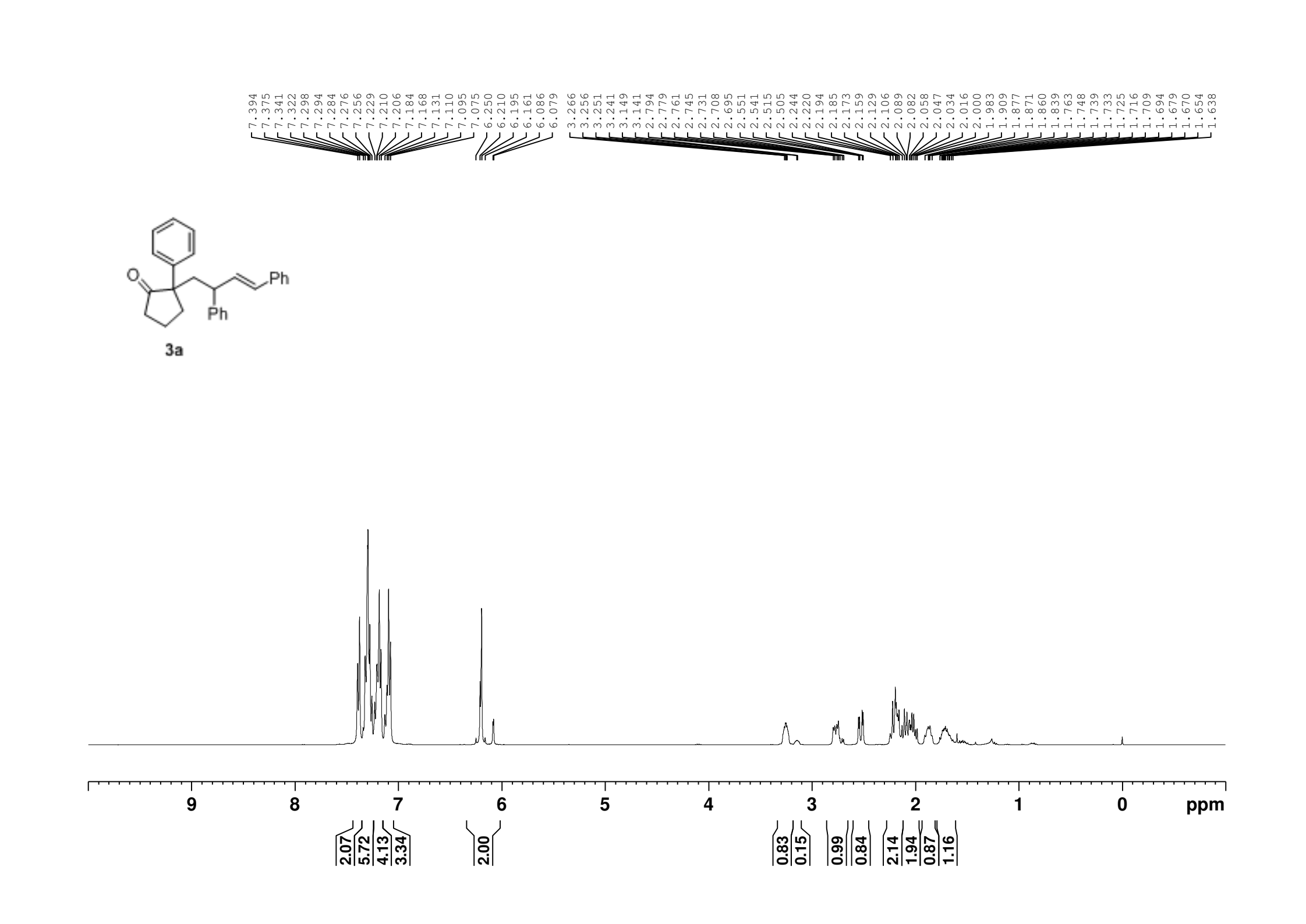
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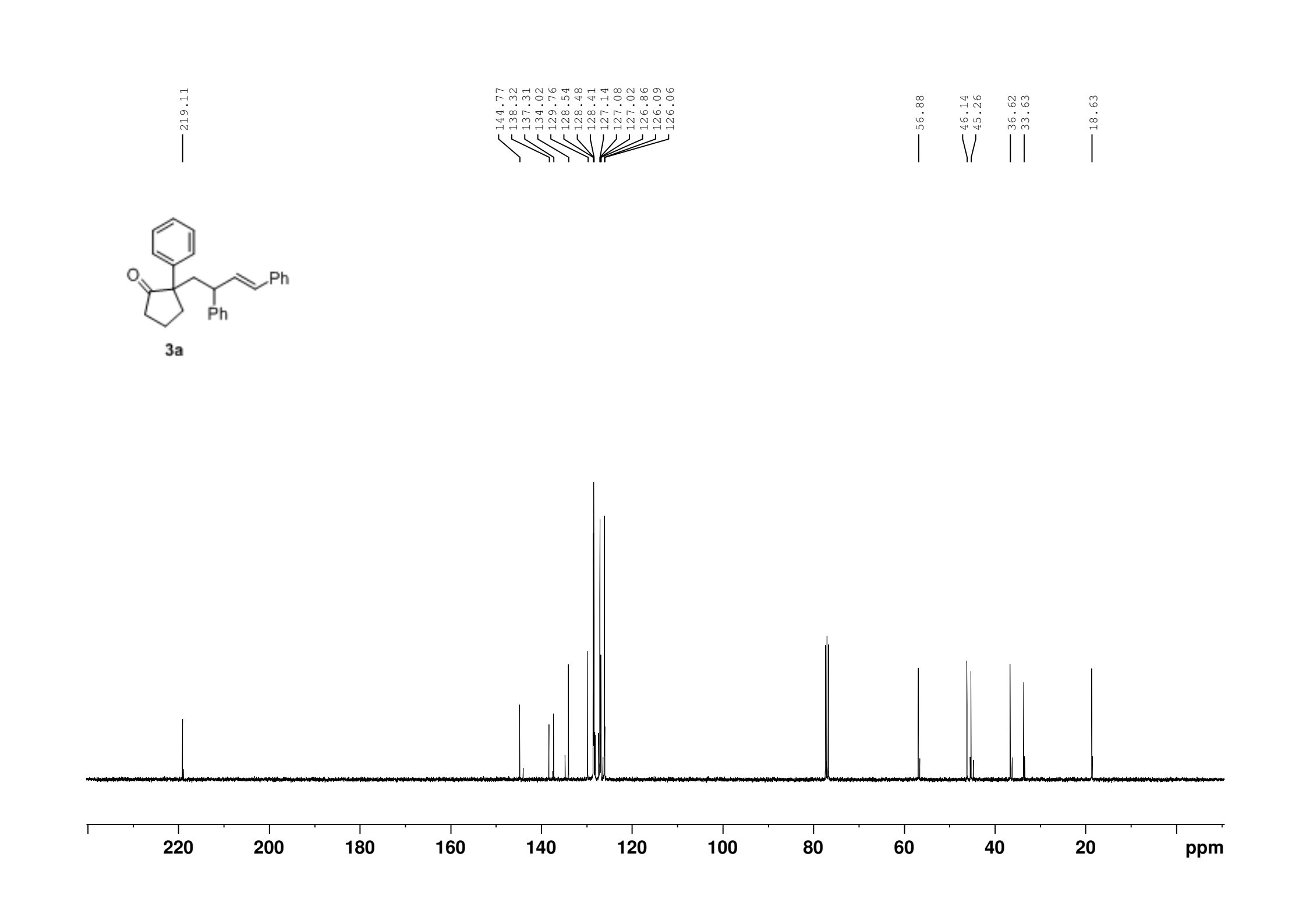
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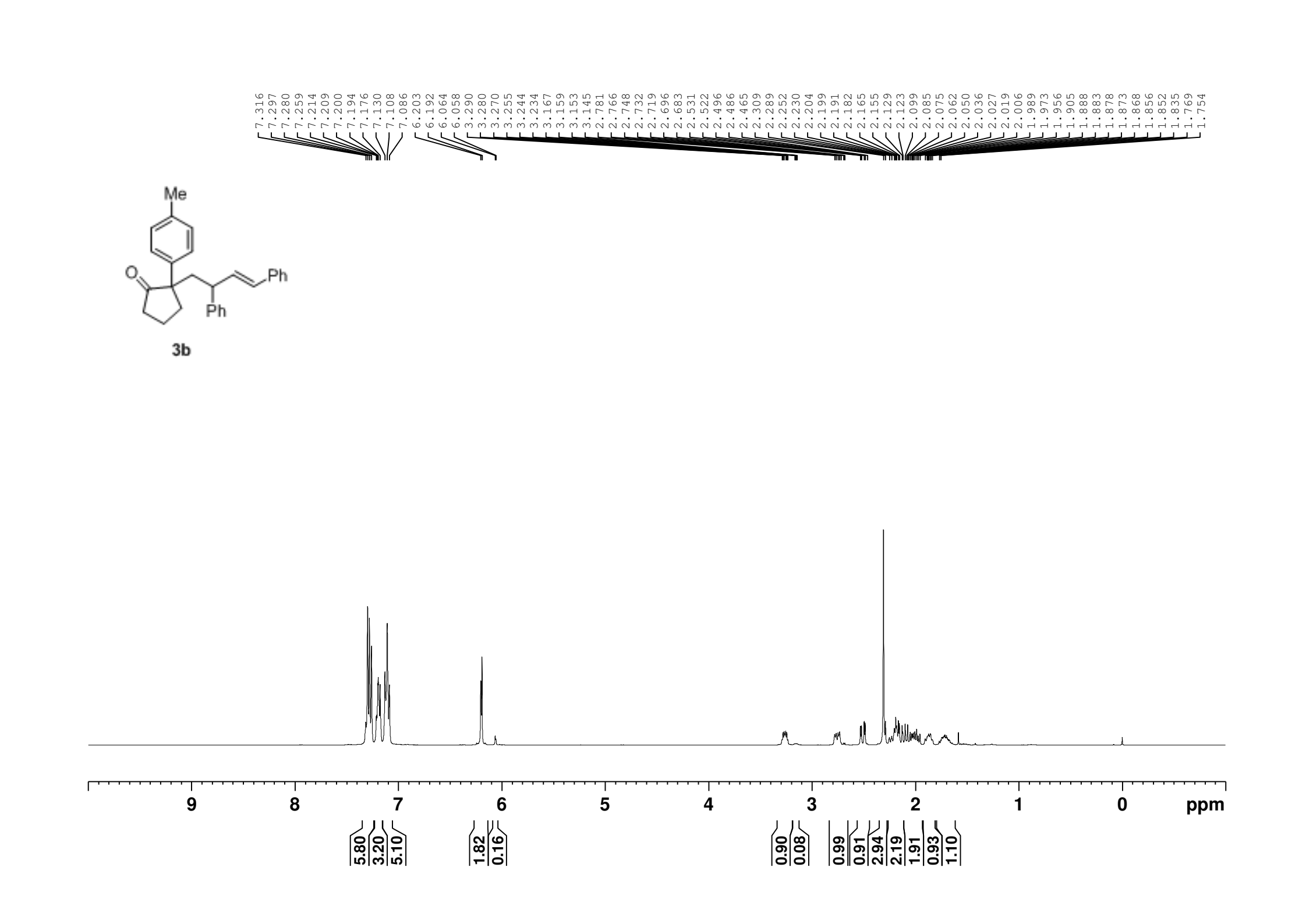
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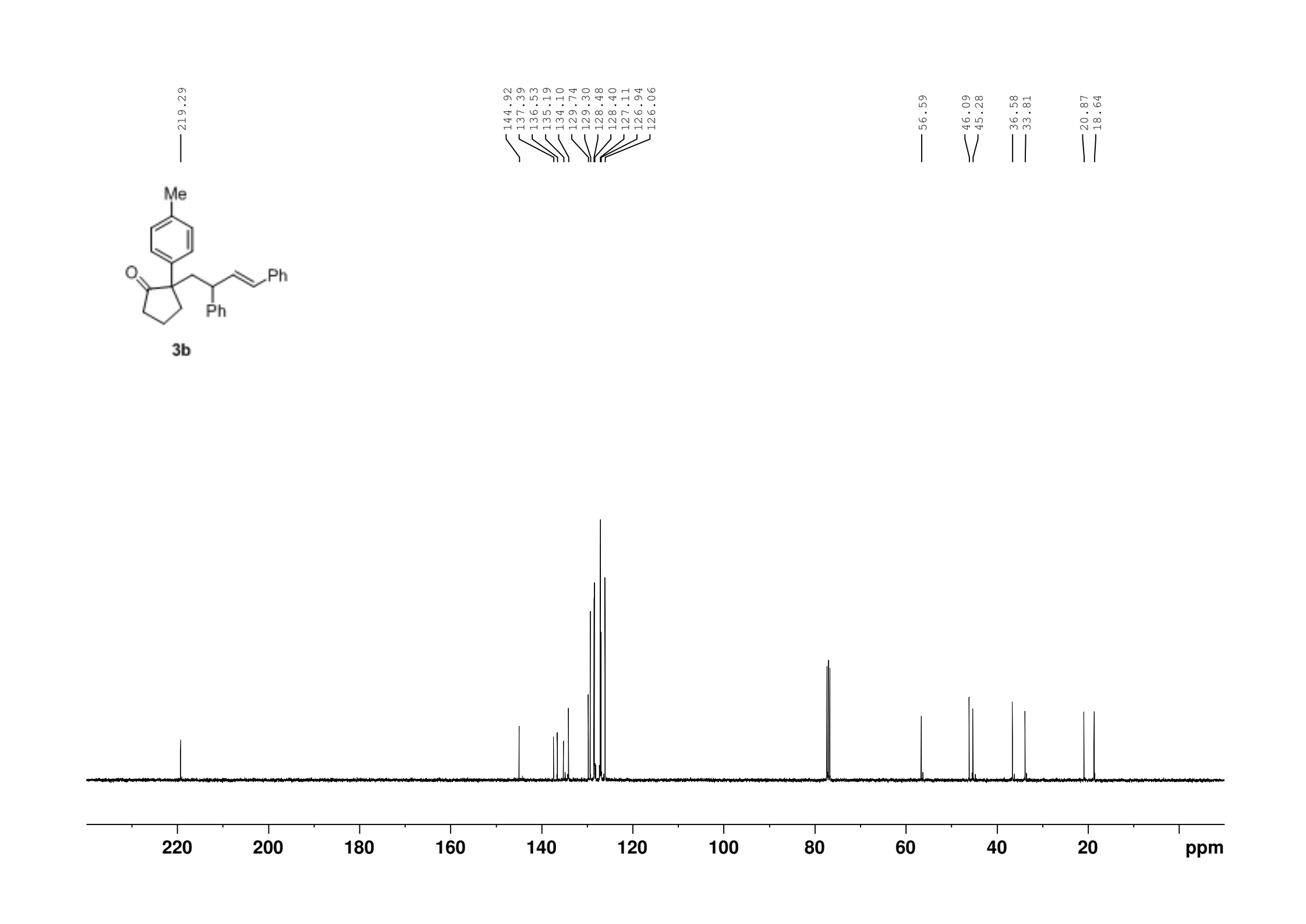
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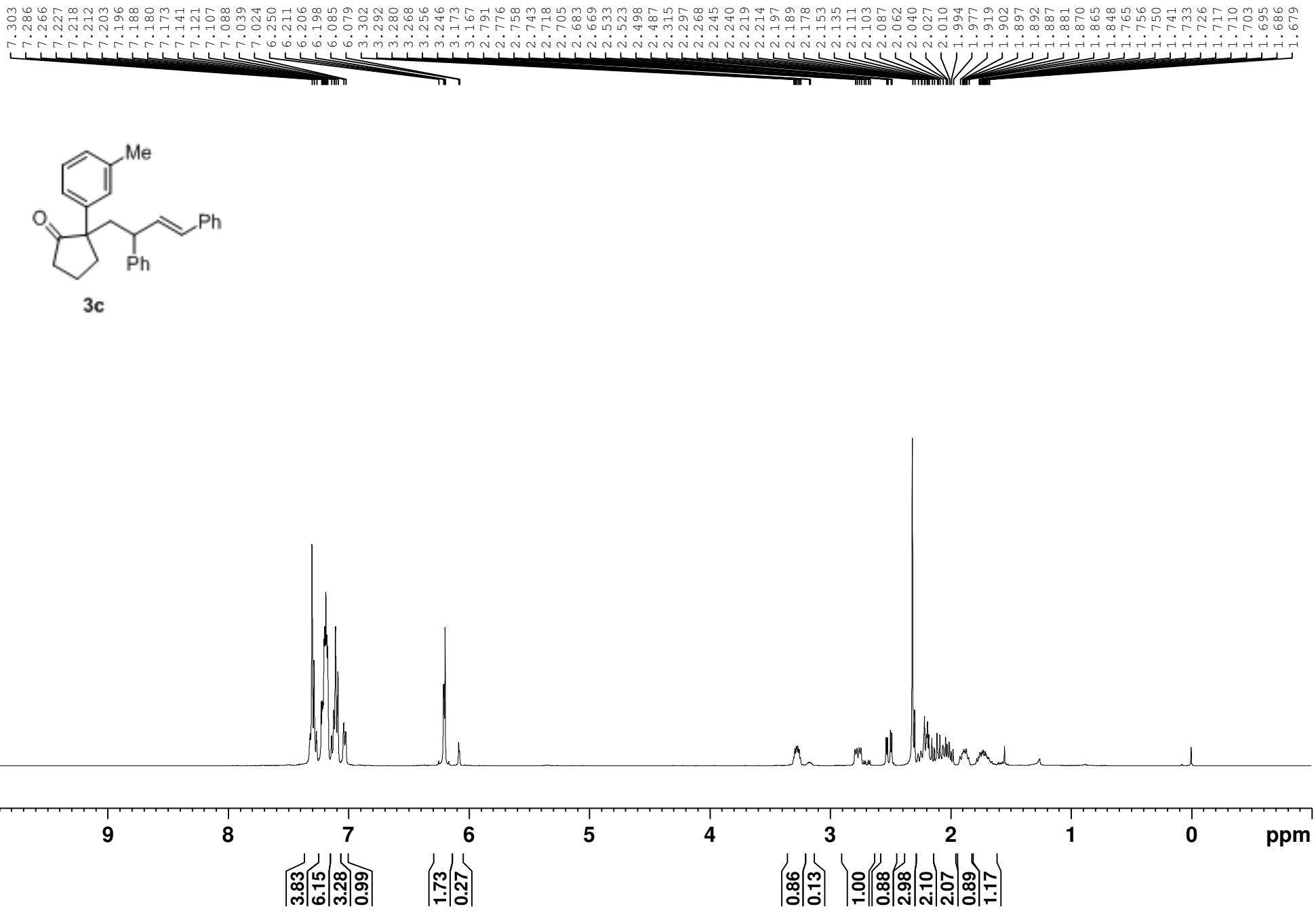
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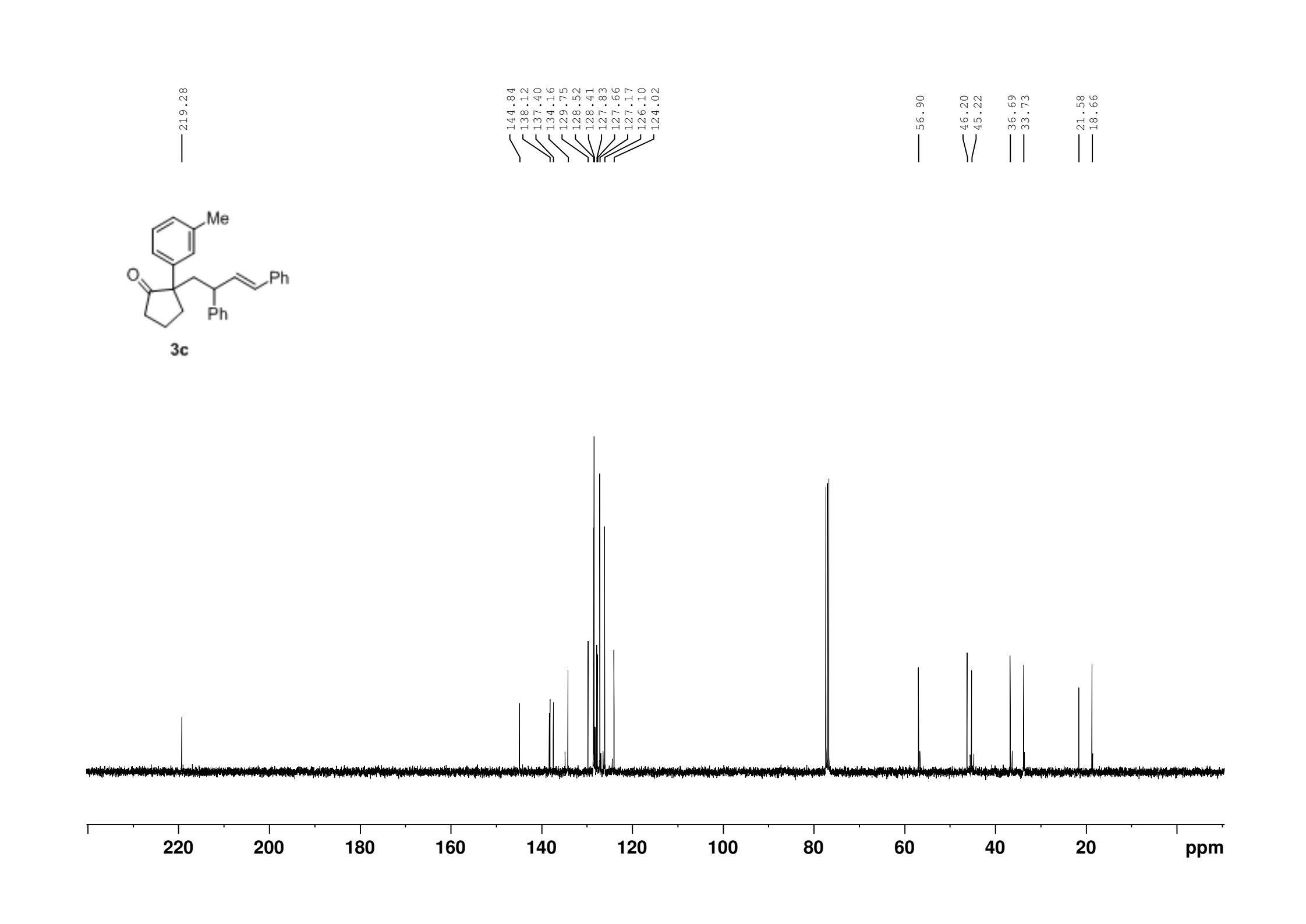
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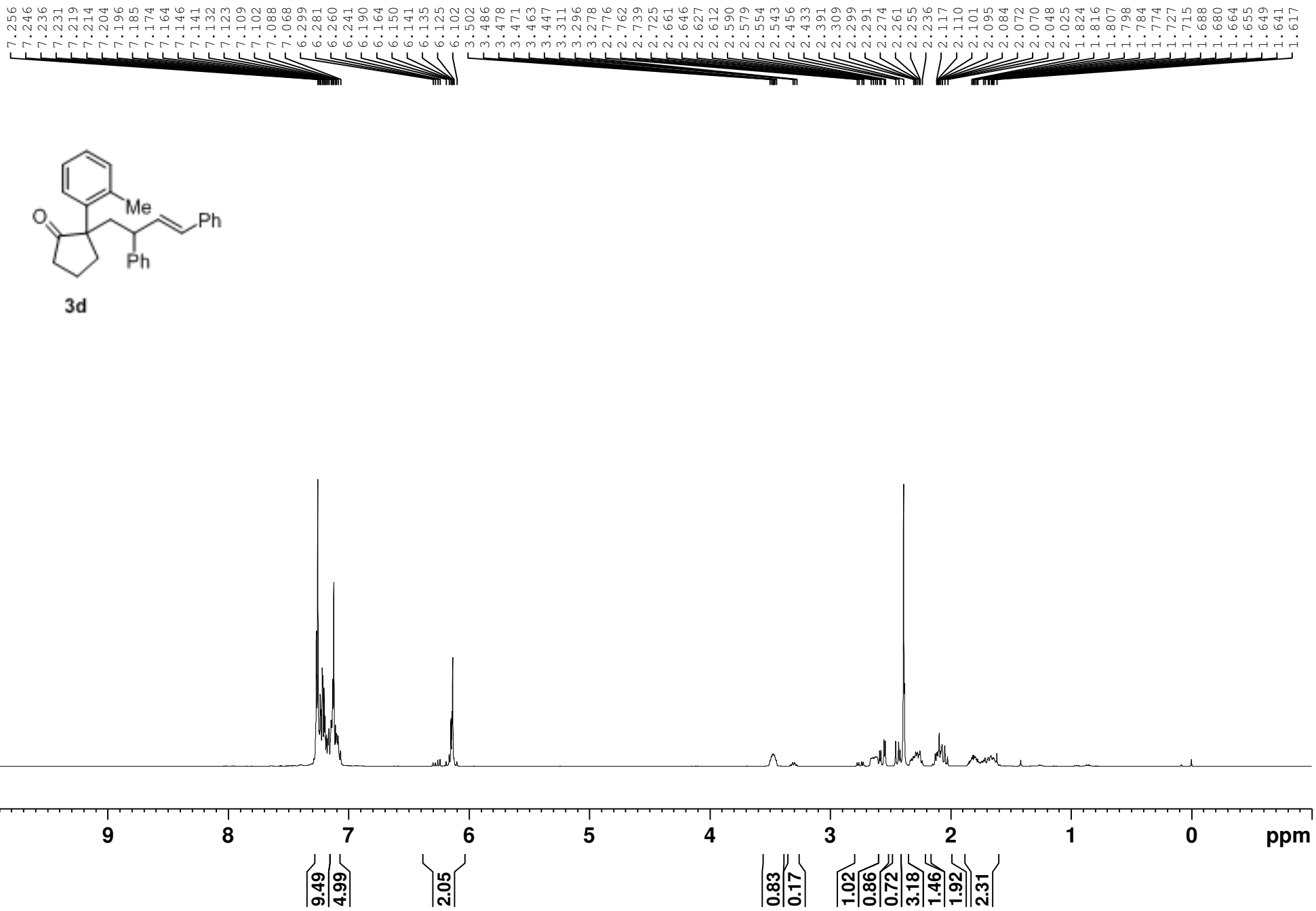
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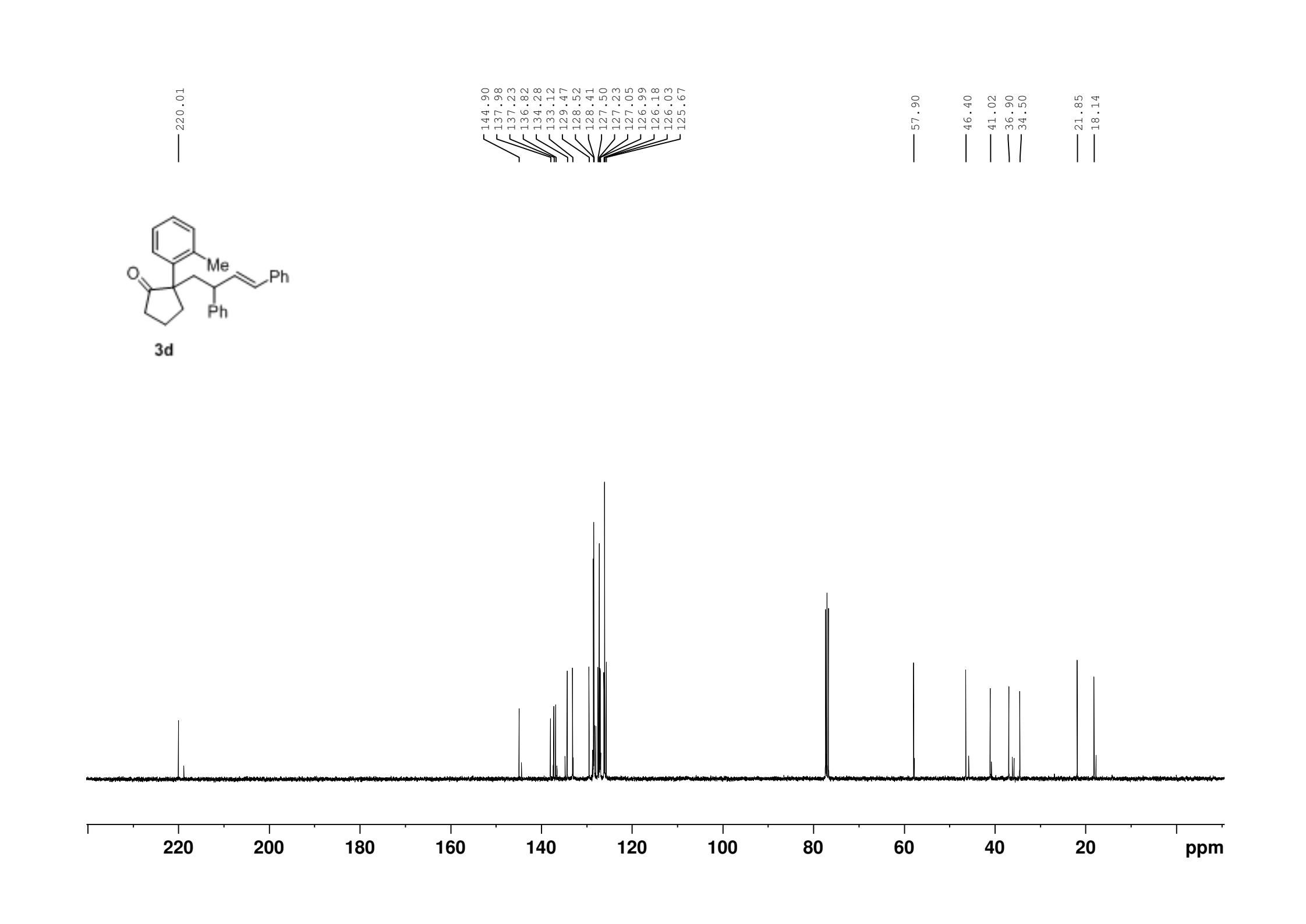
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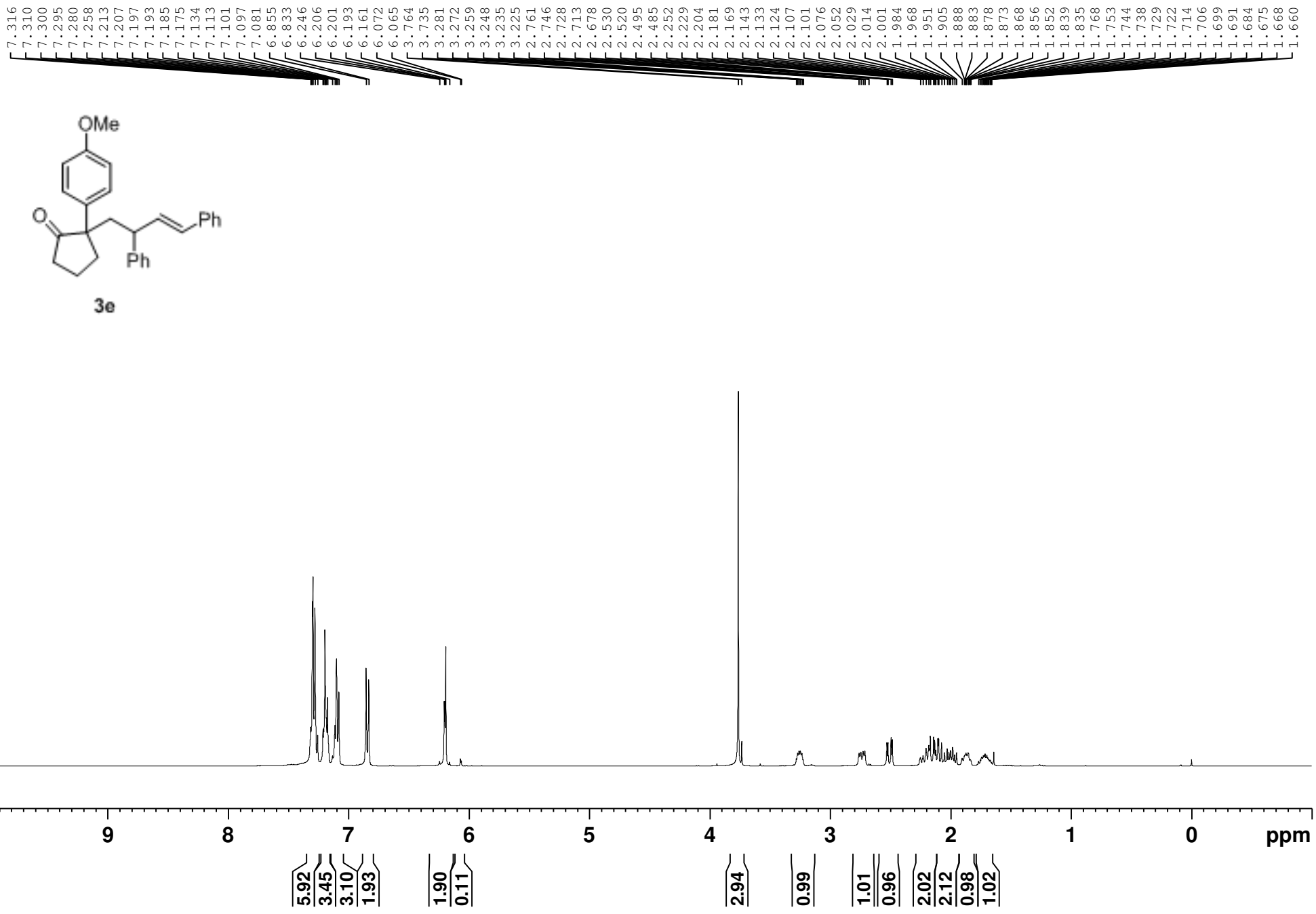
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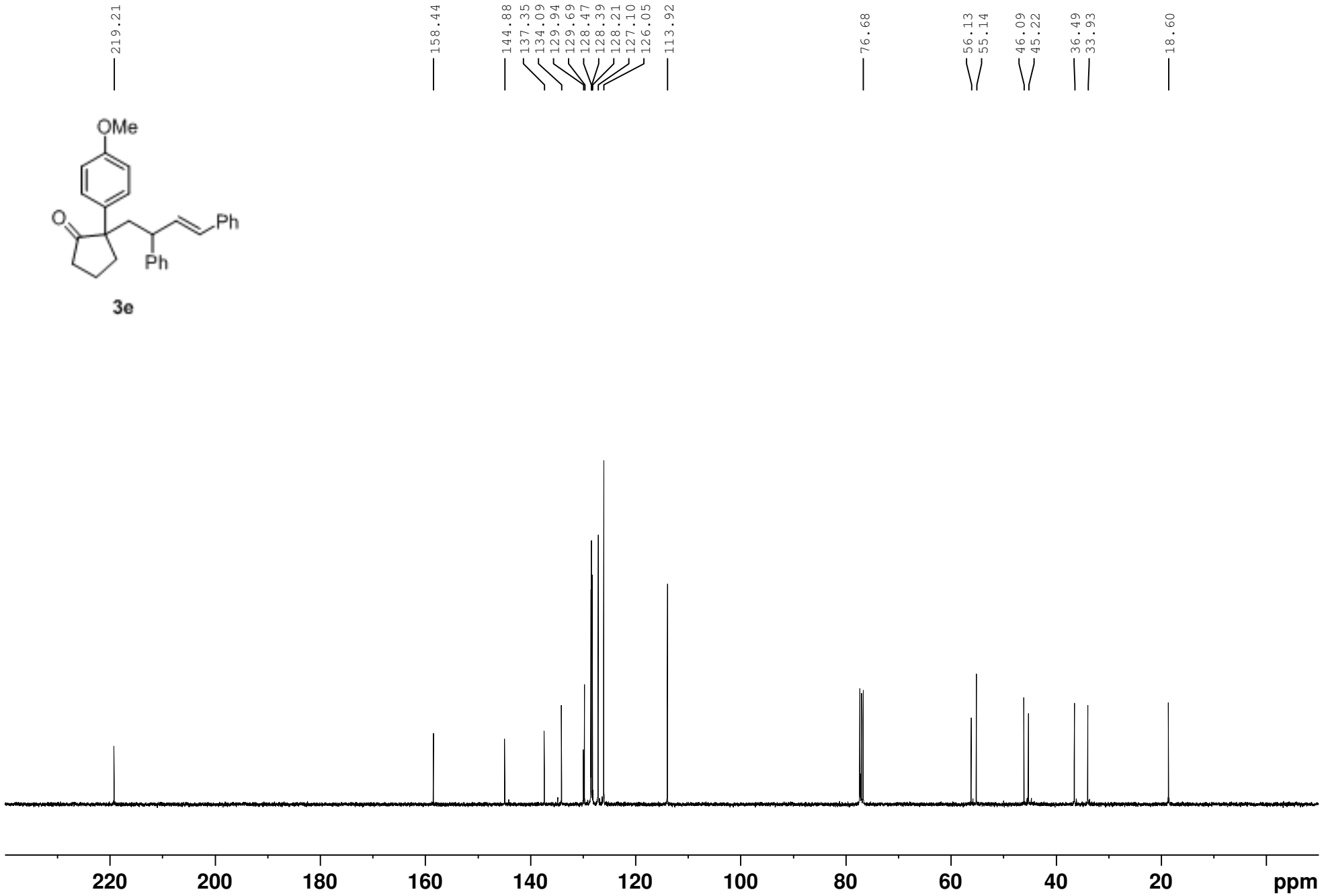
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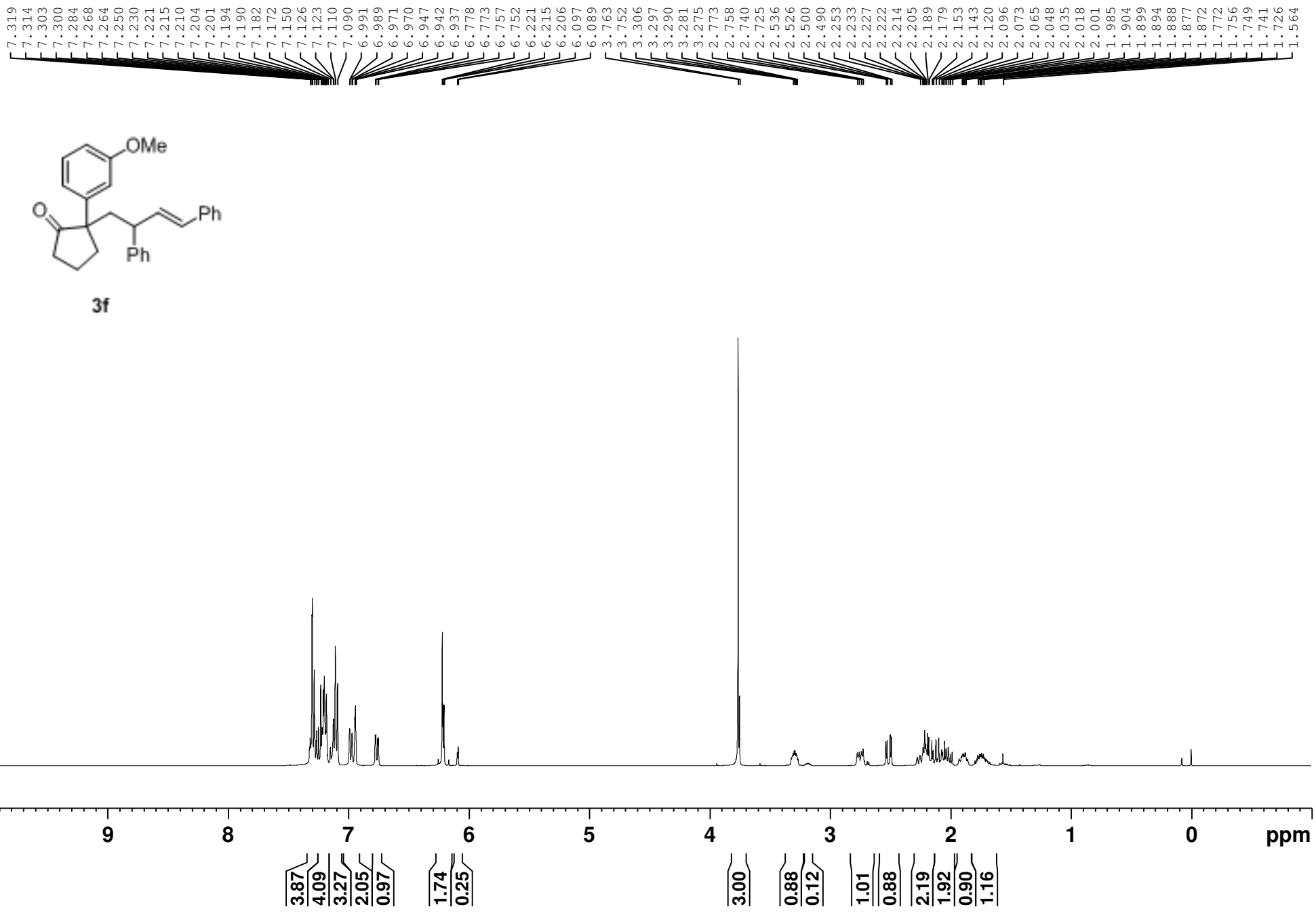
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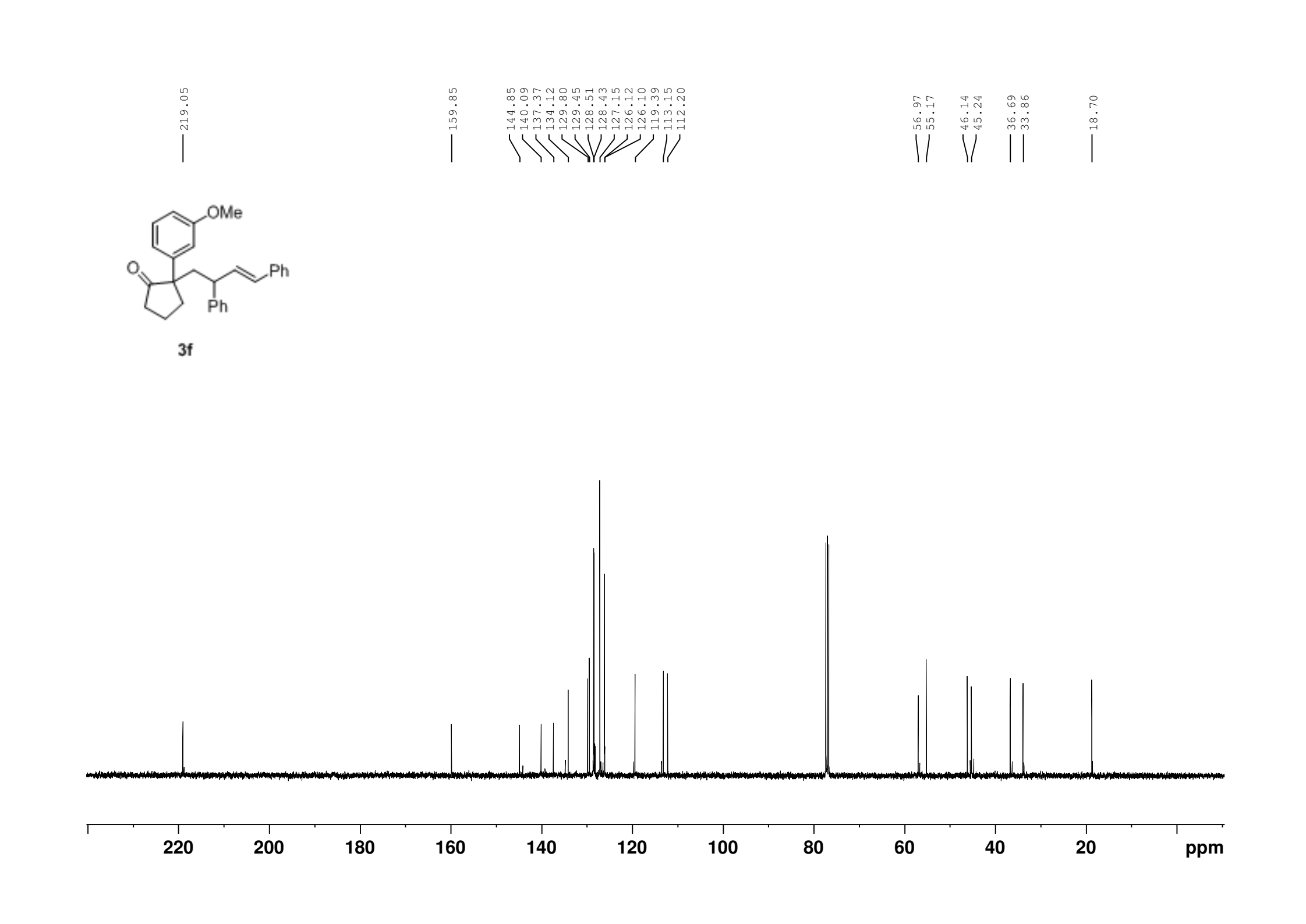
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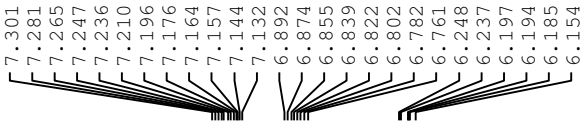
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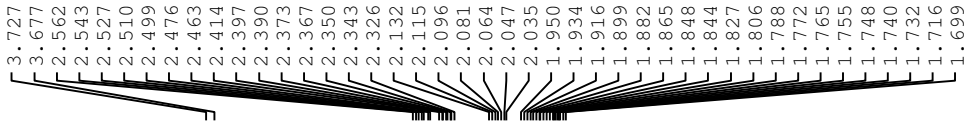
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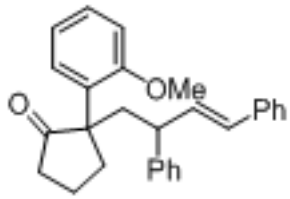
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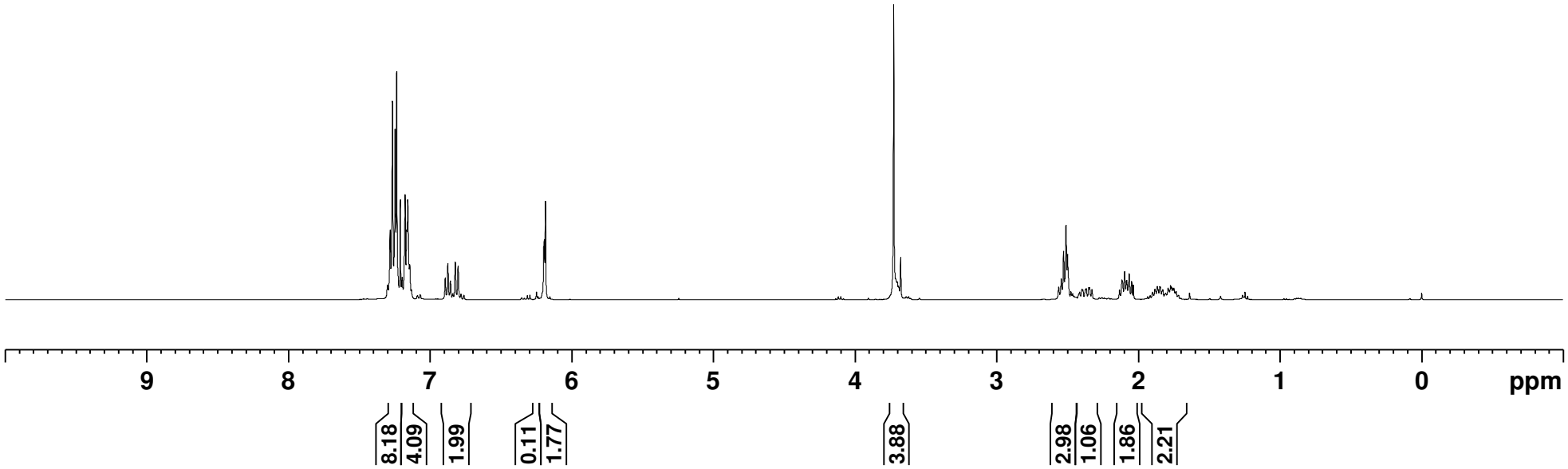
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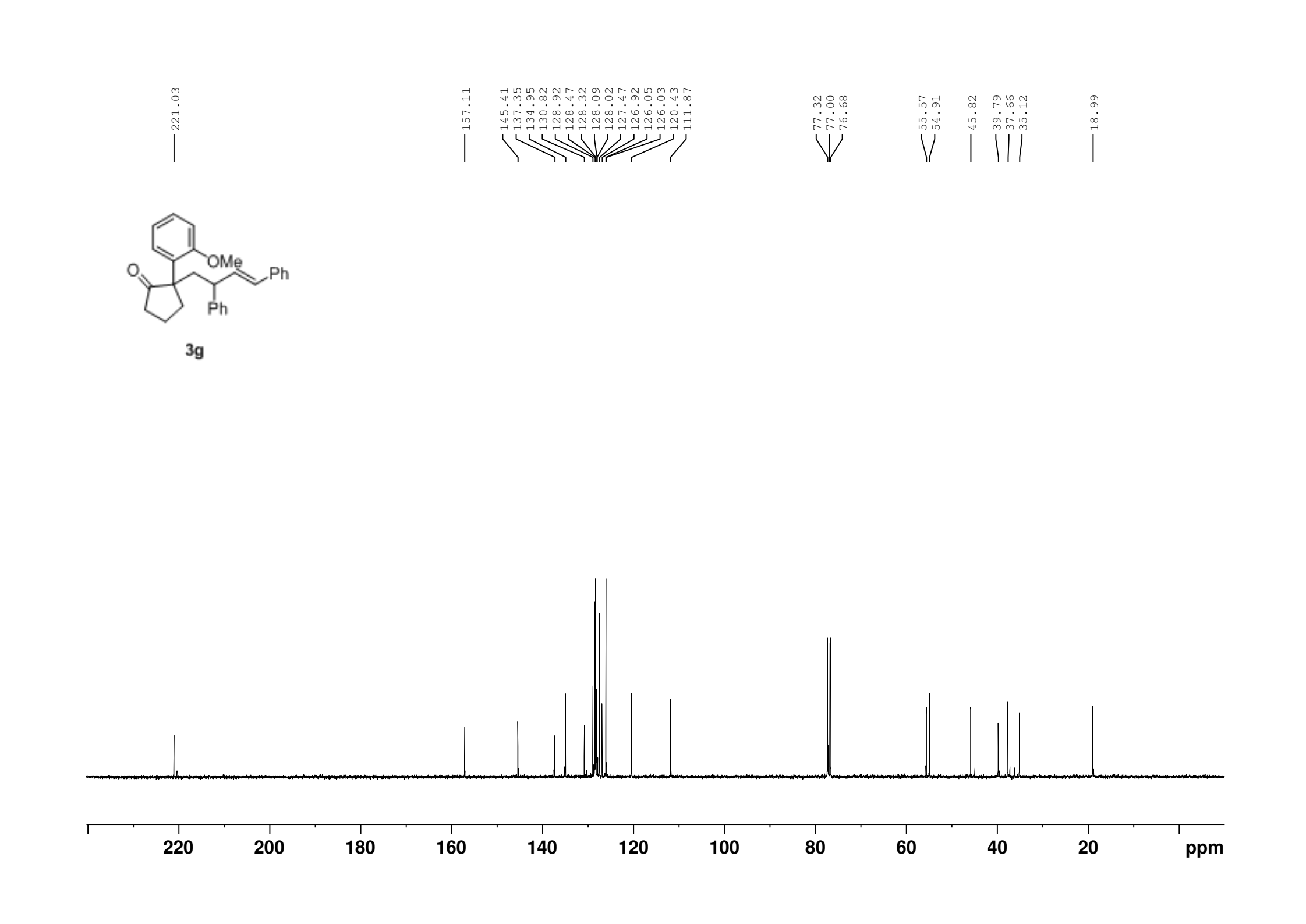
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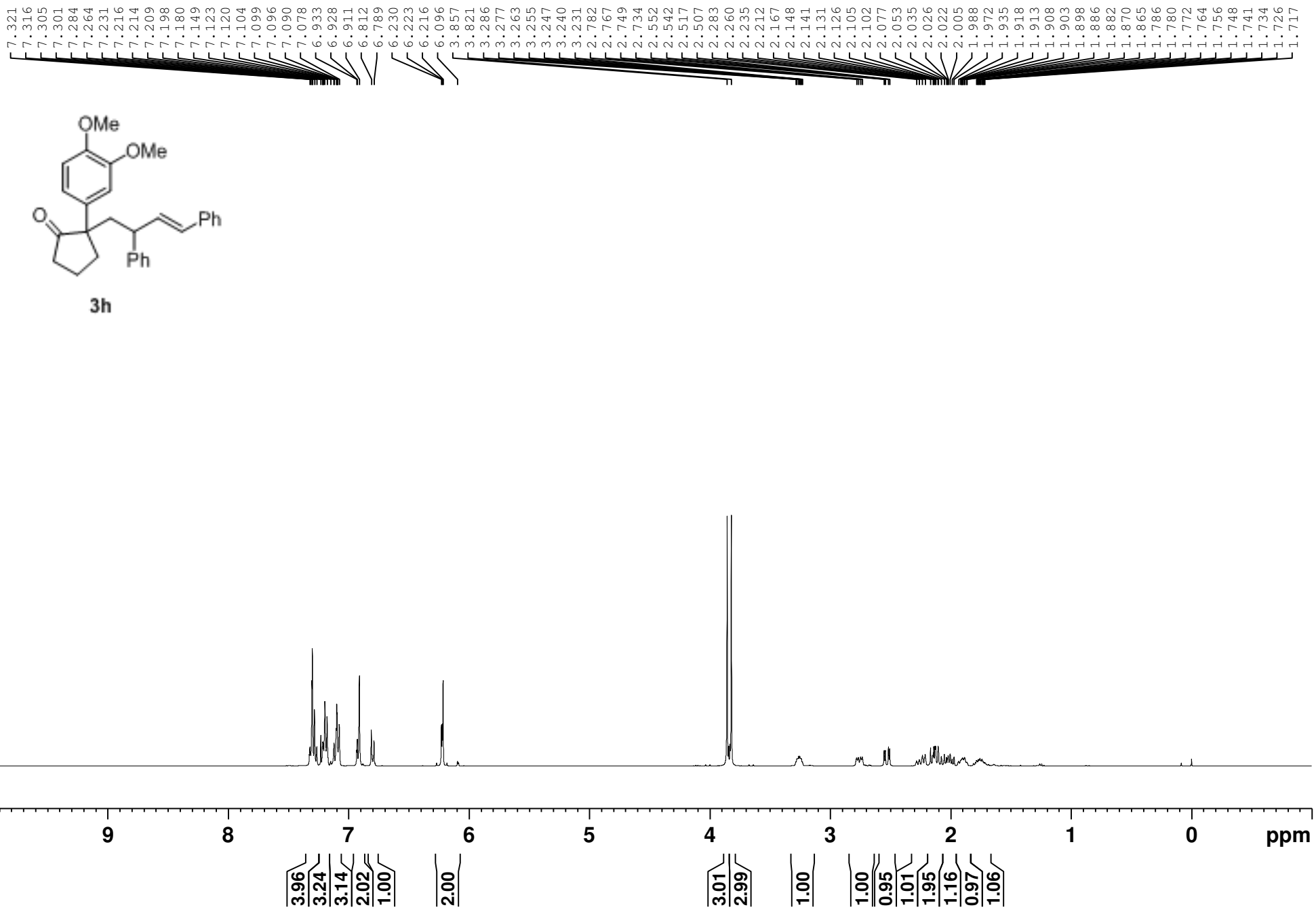
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OMe
OMe
O
Ph
Ph
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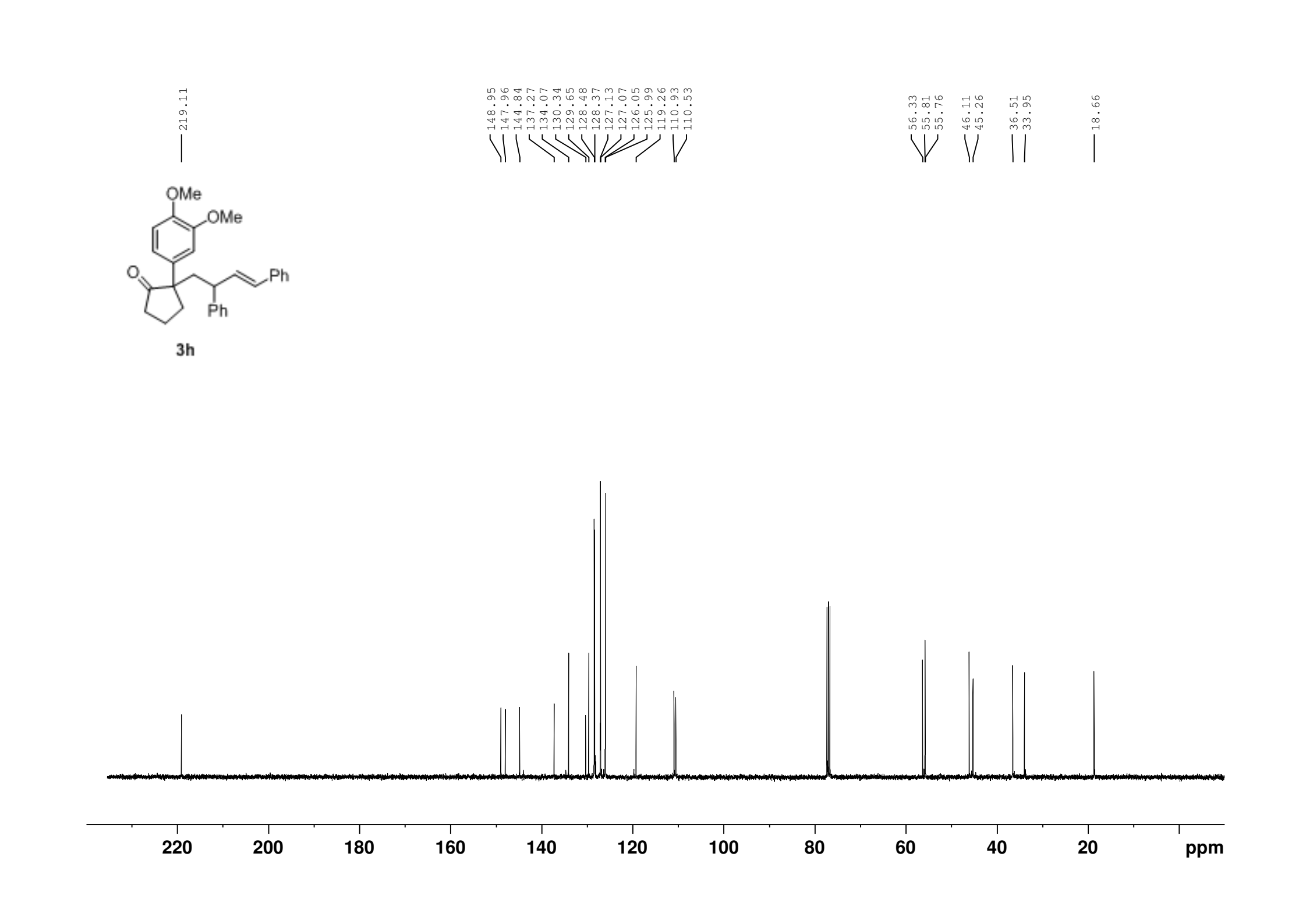
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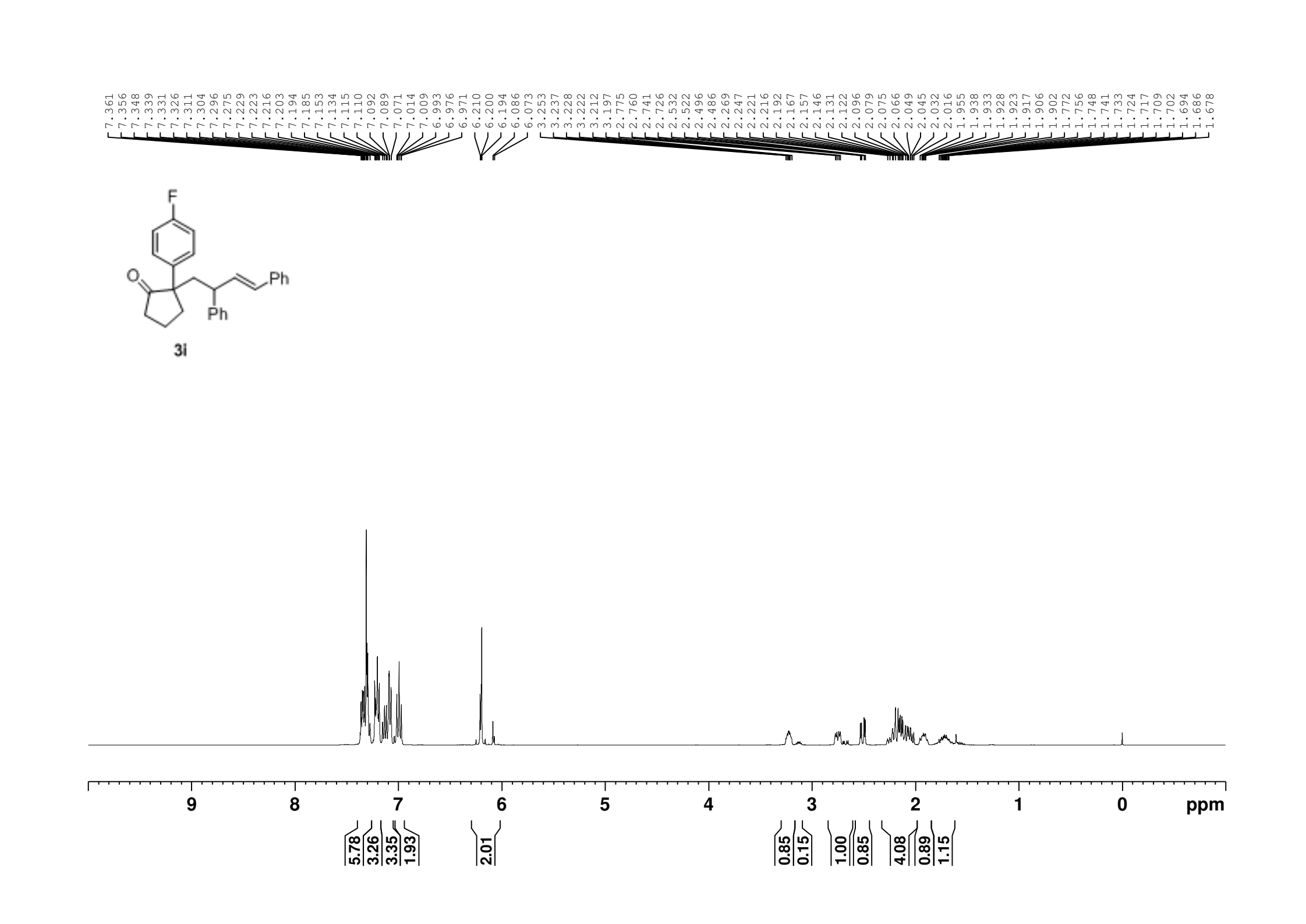
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O
Ph
Ph
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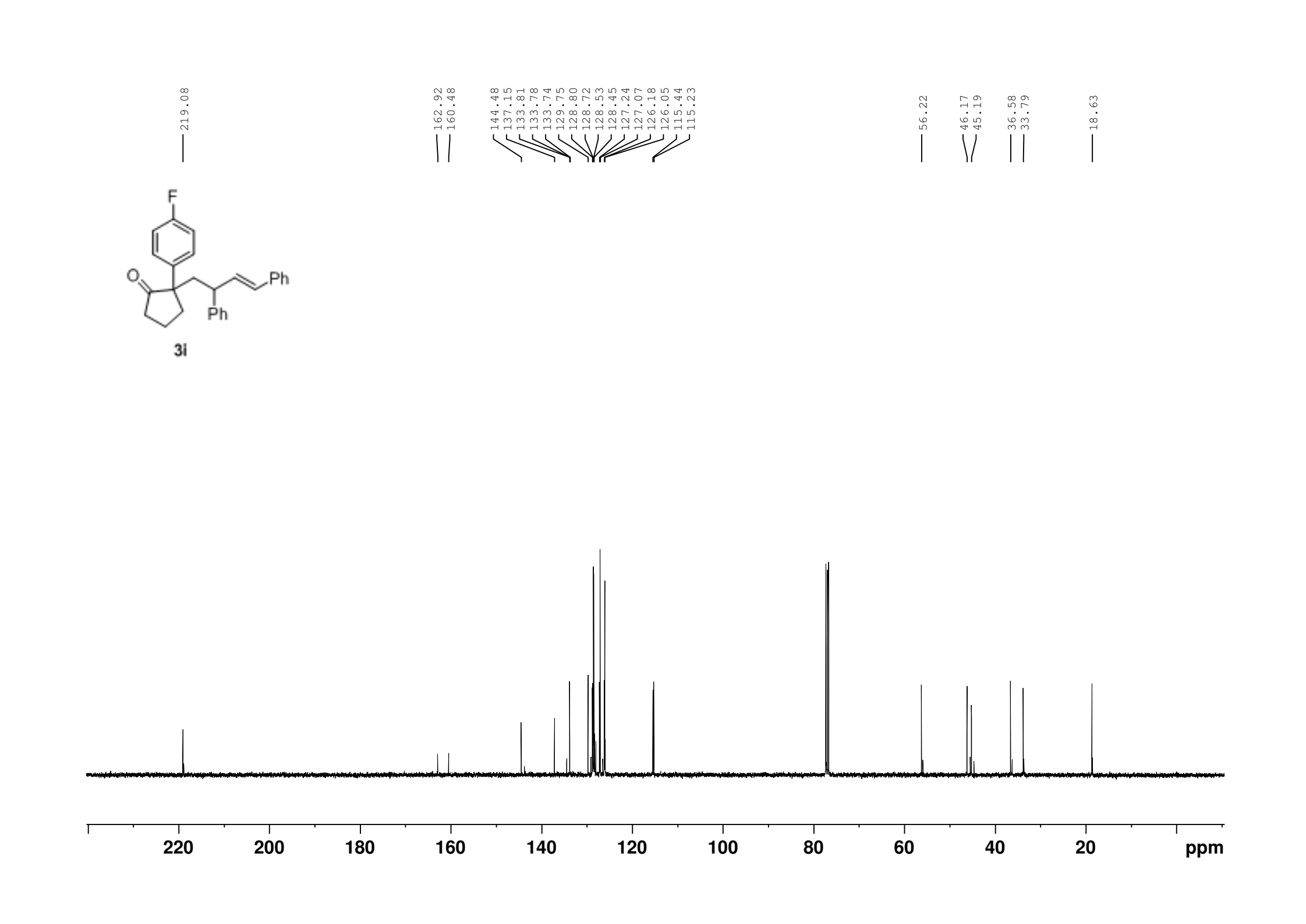
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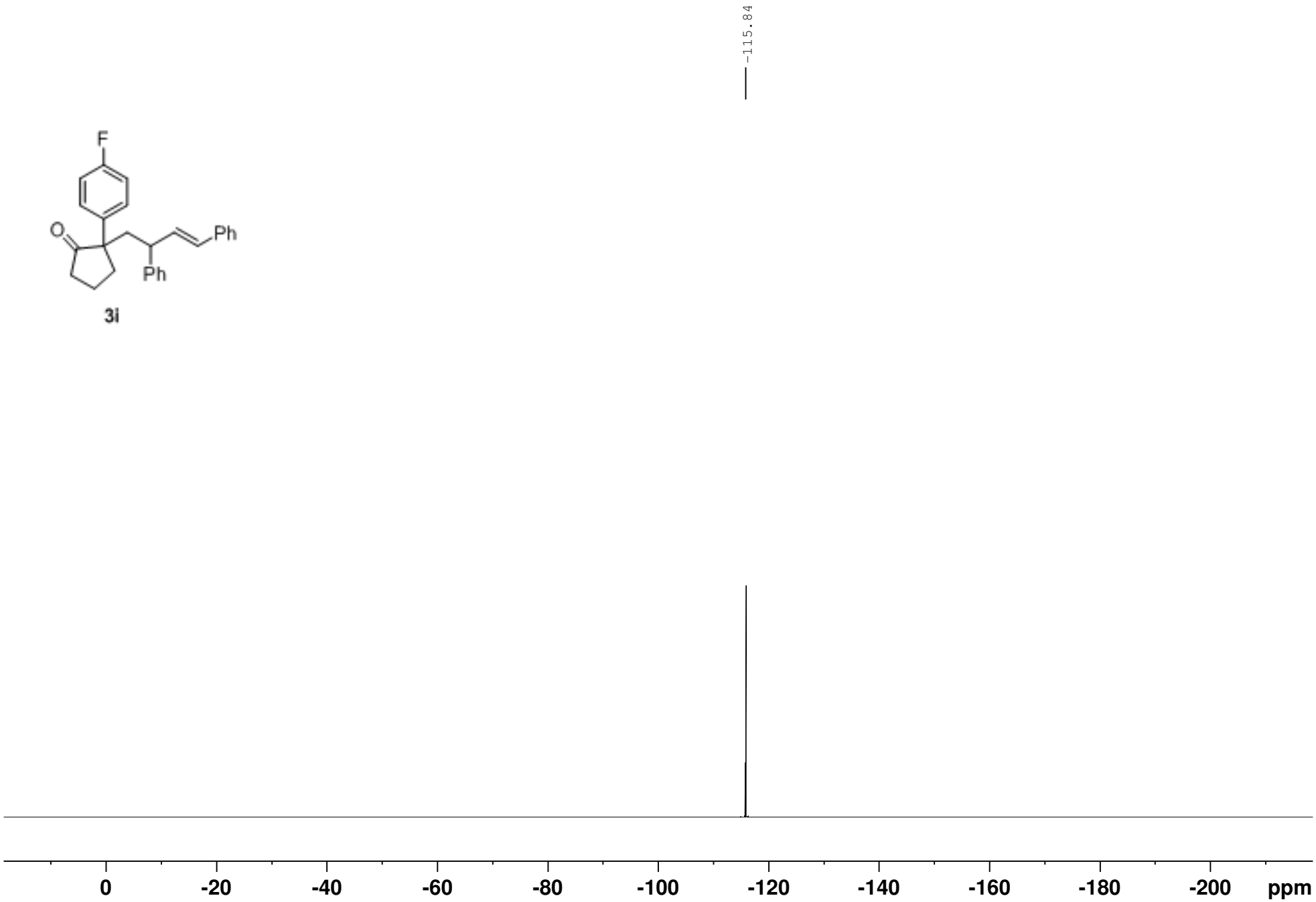
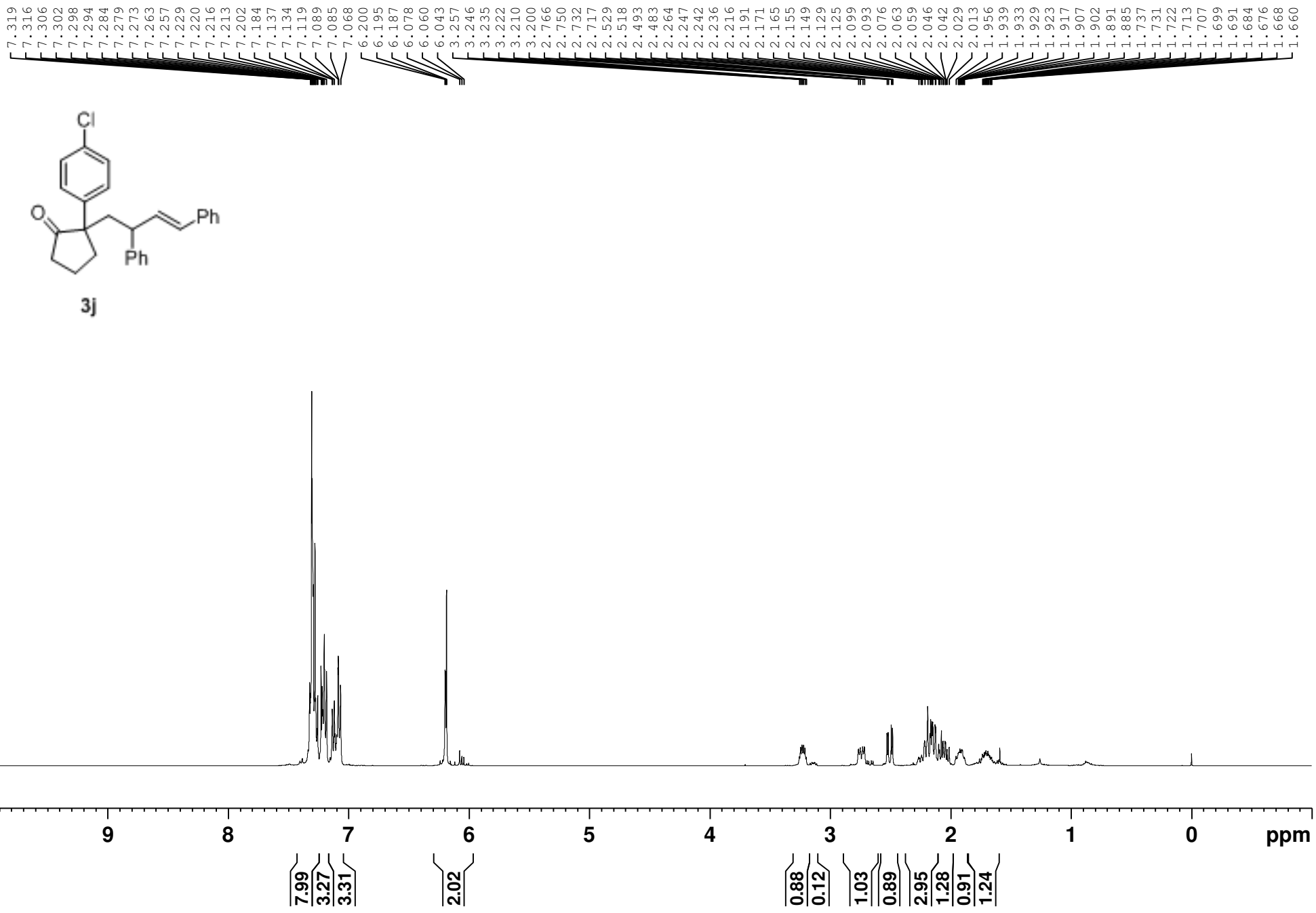
3i

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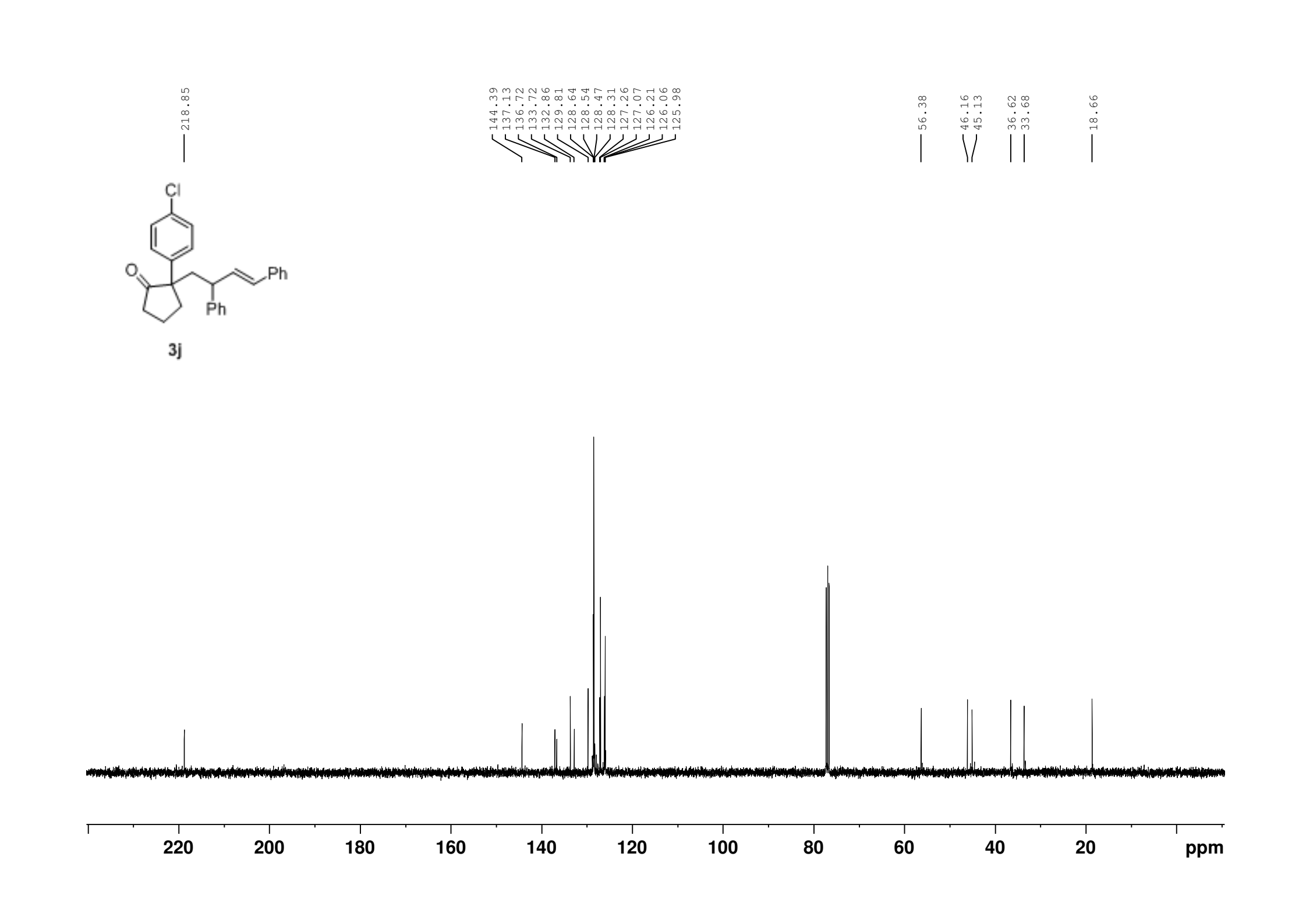
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Ph
Ph
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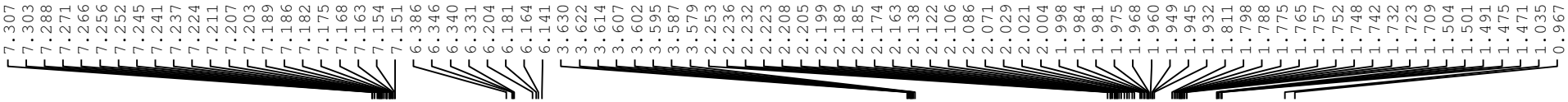
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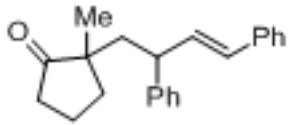
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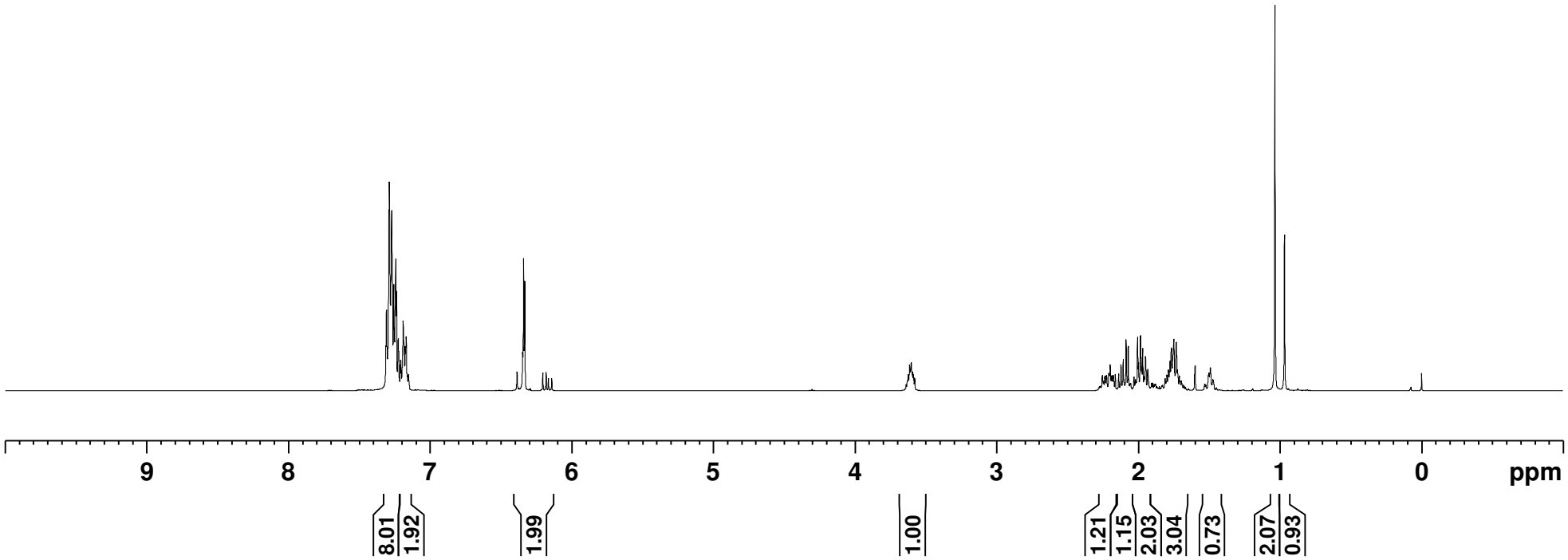
Ph
Ph

3k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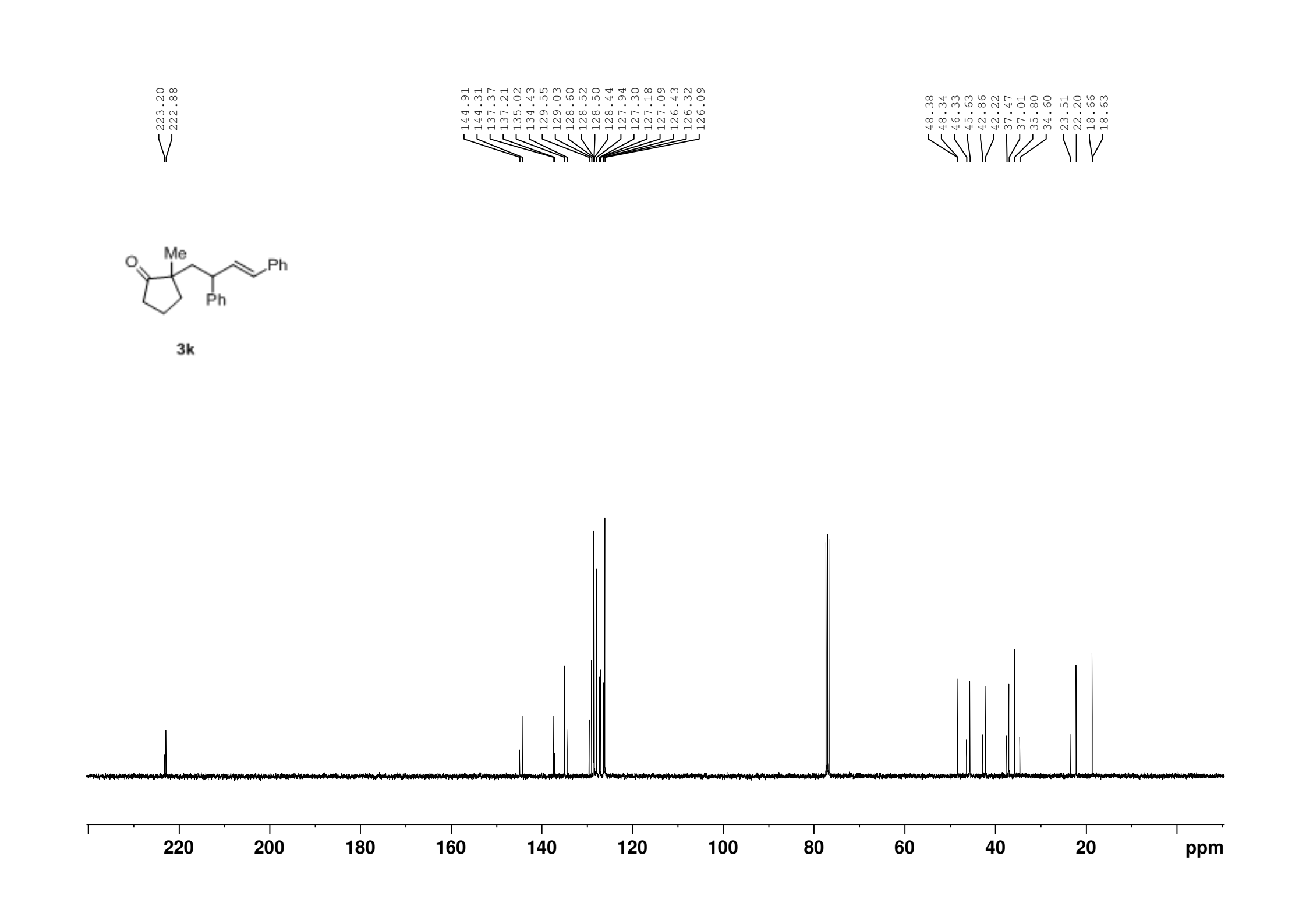
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Ph
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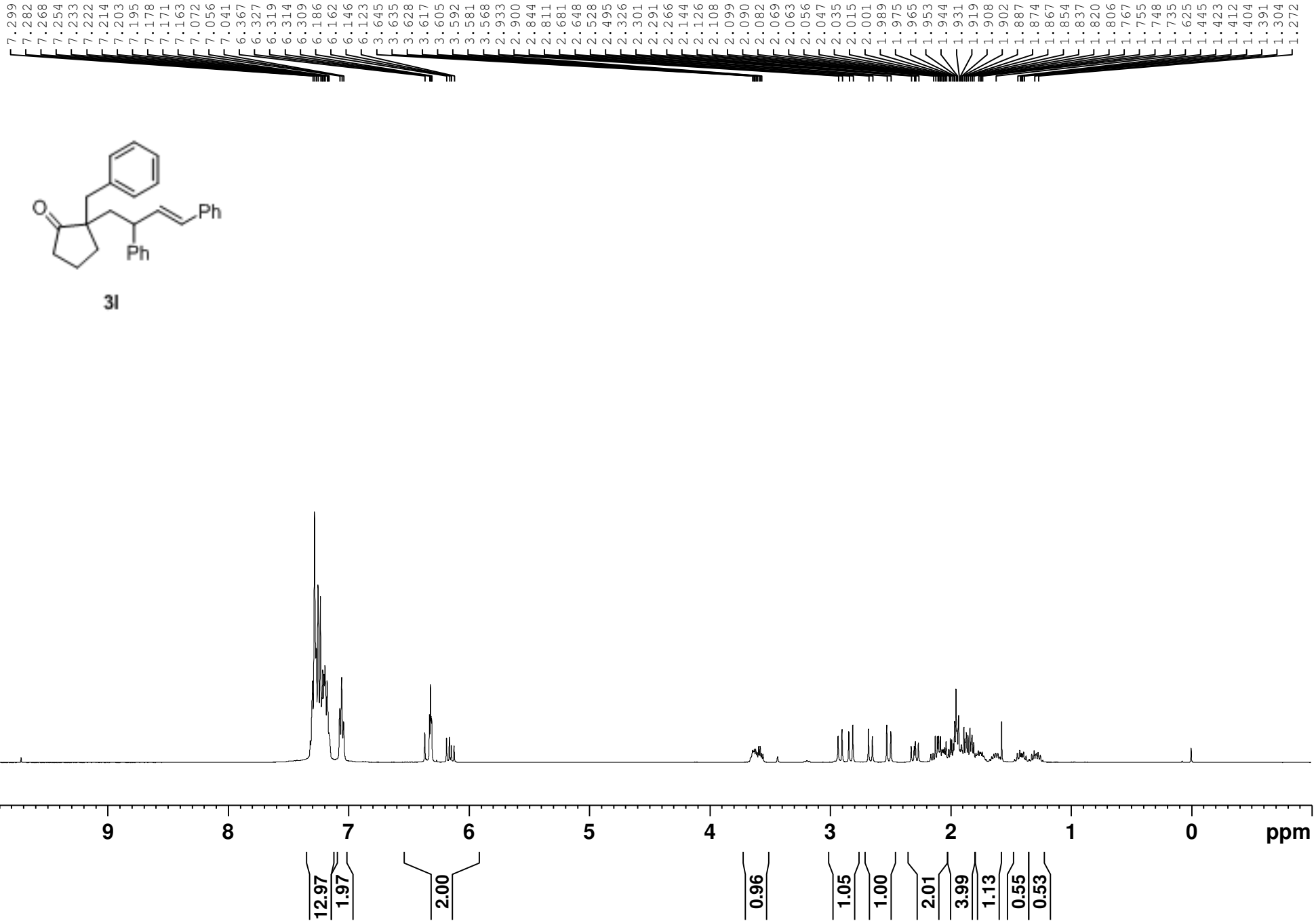
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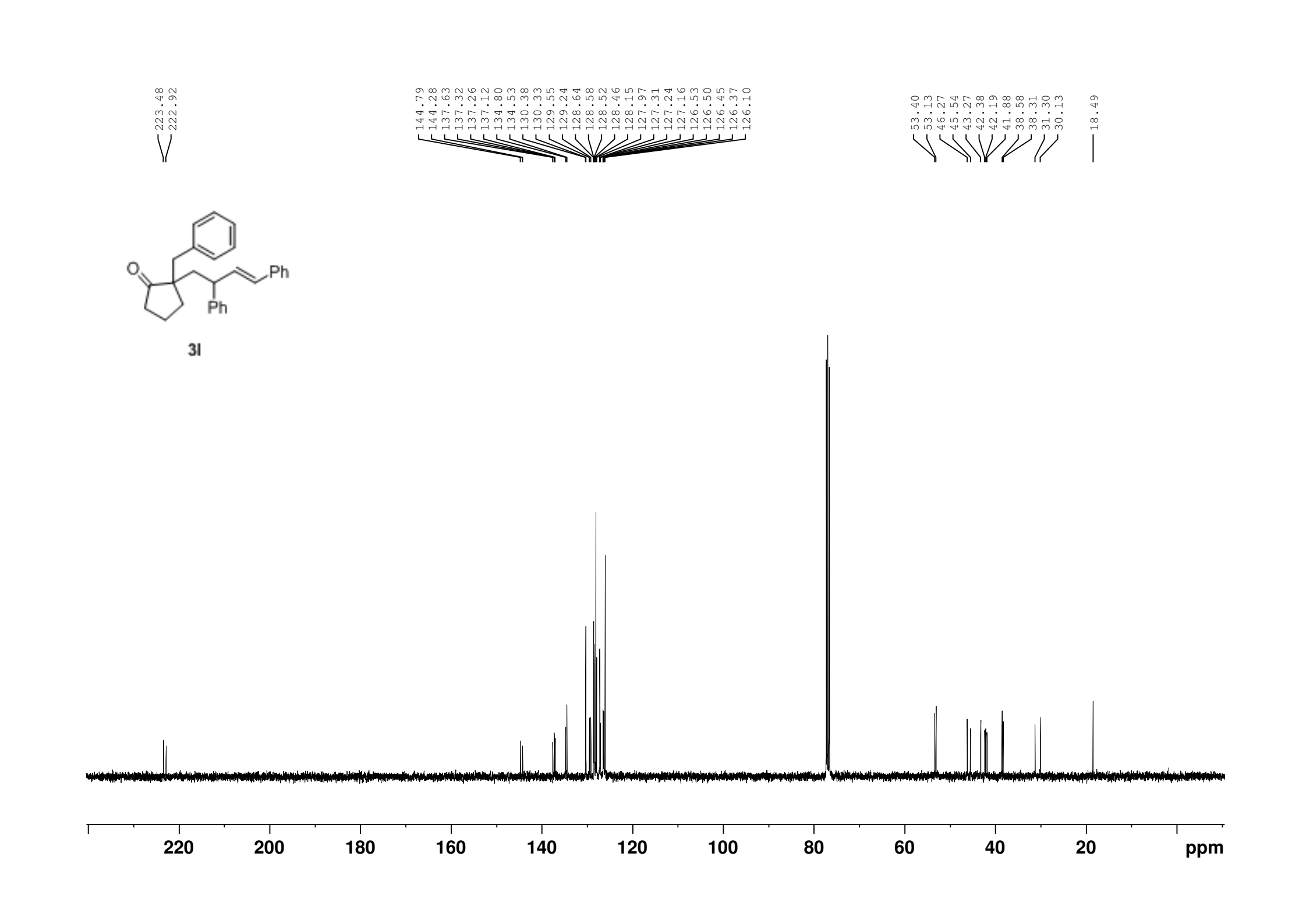
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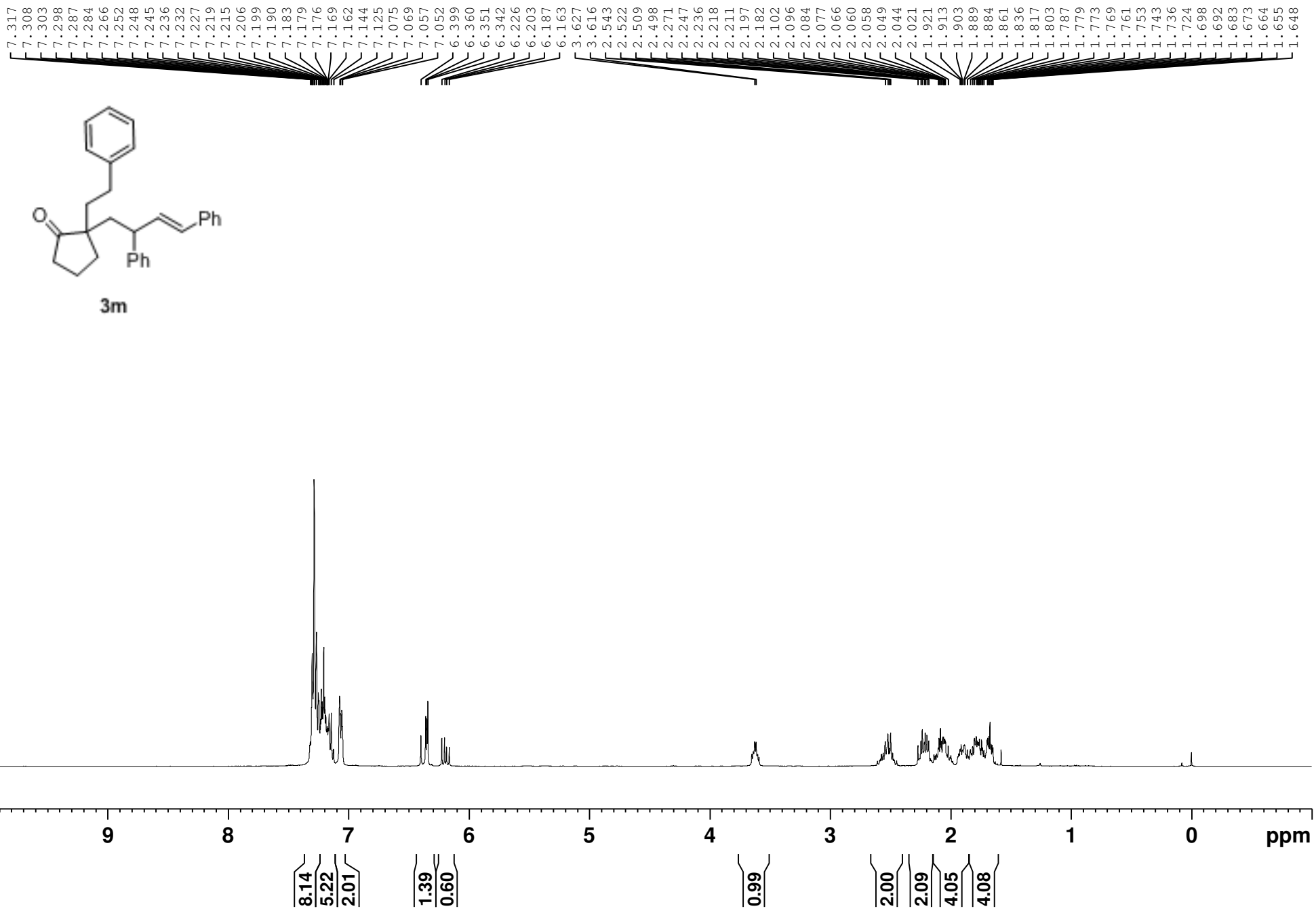
3l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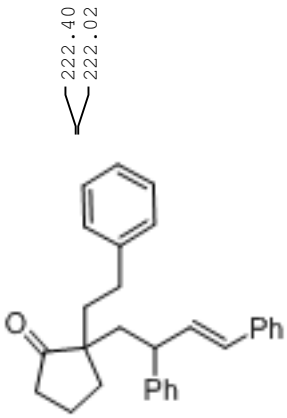

3m

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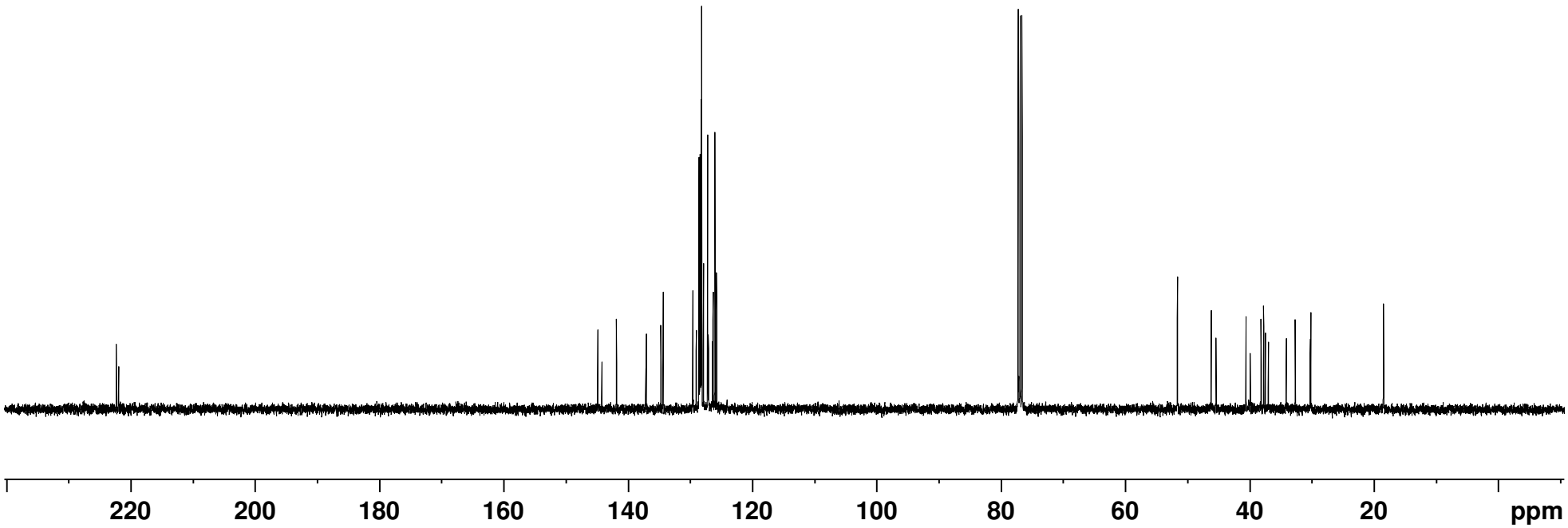

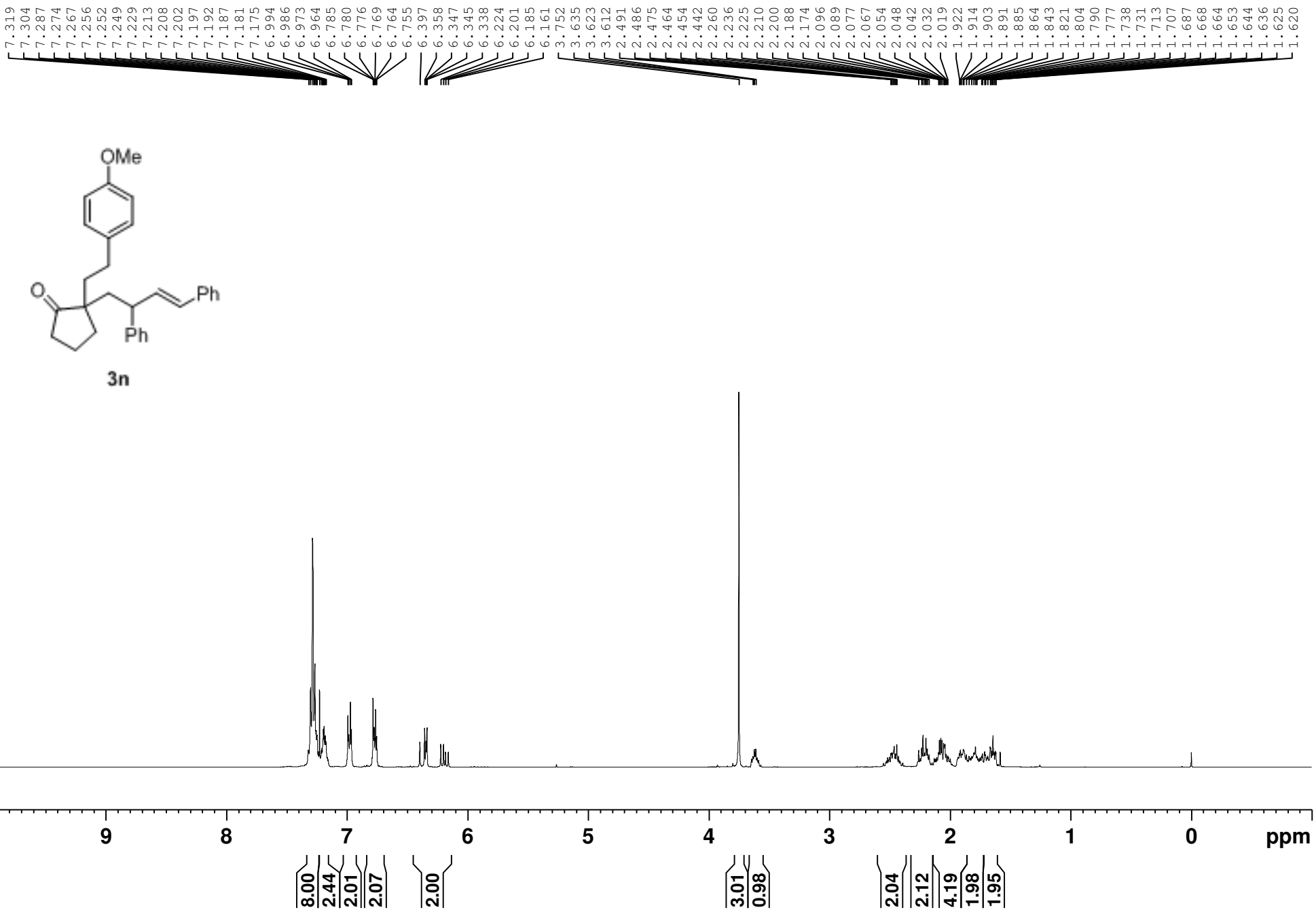
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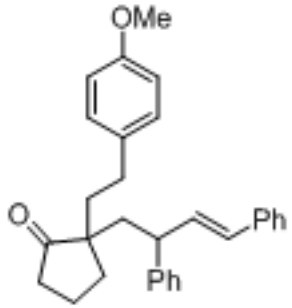

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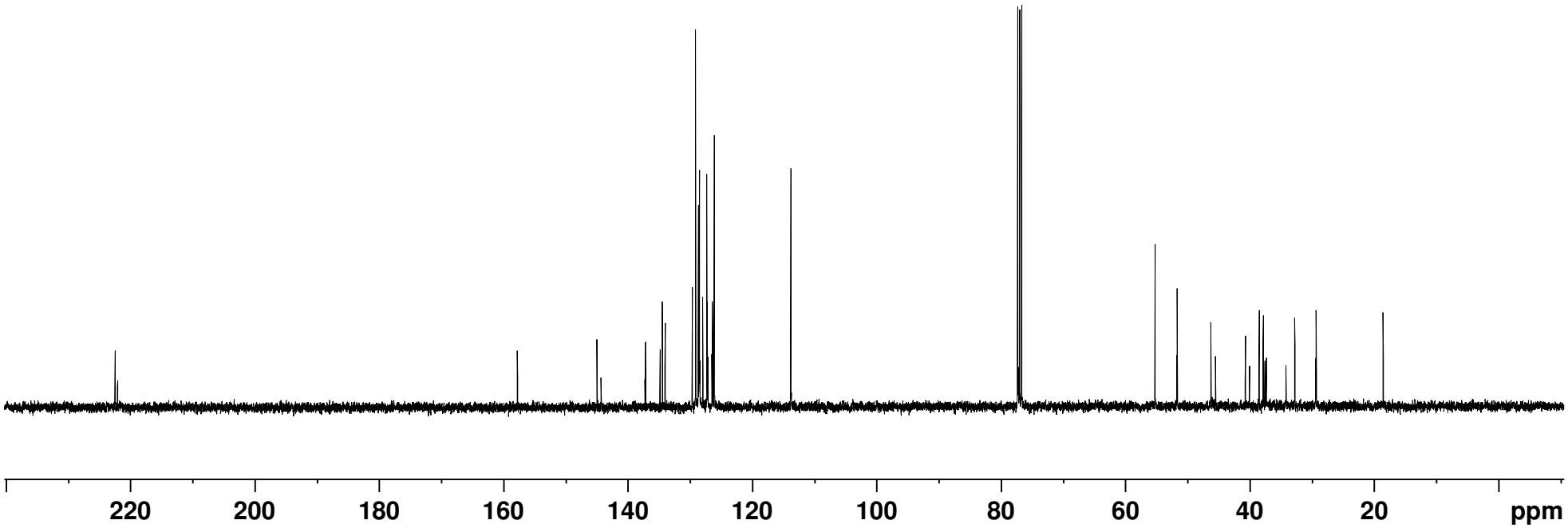

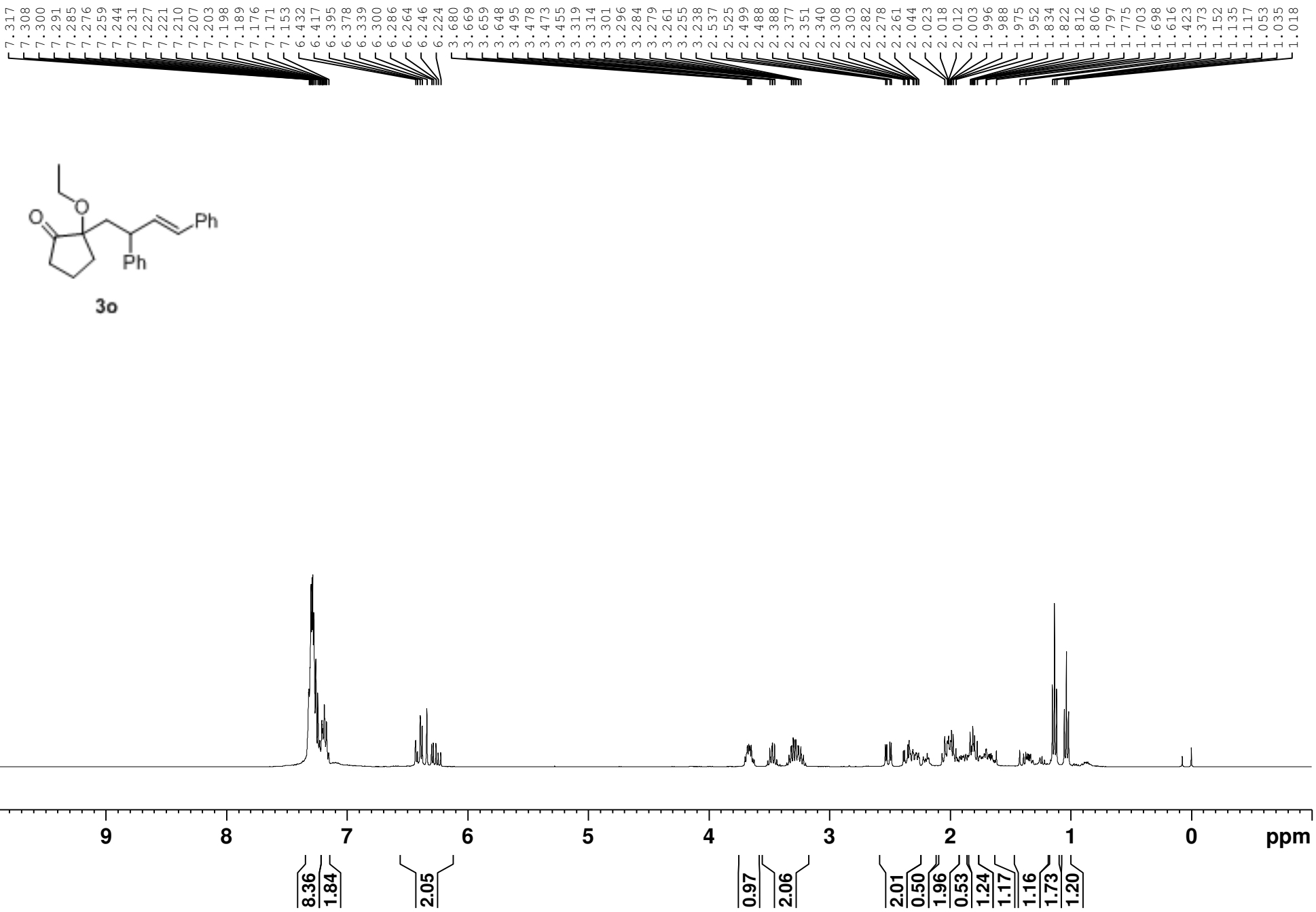
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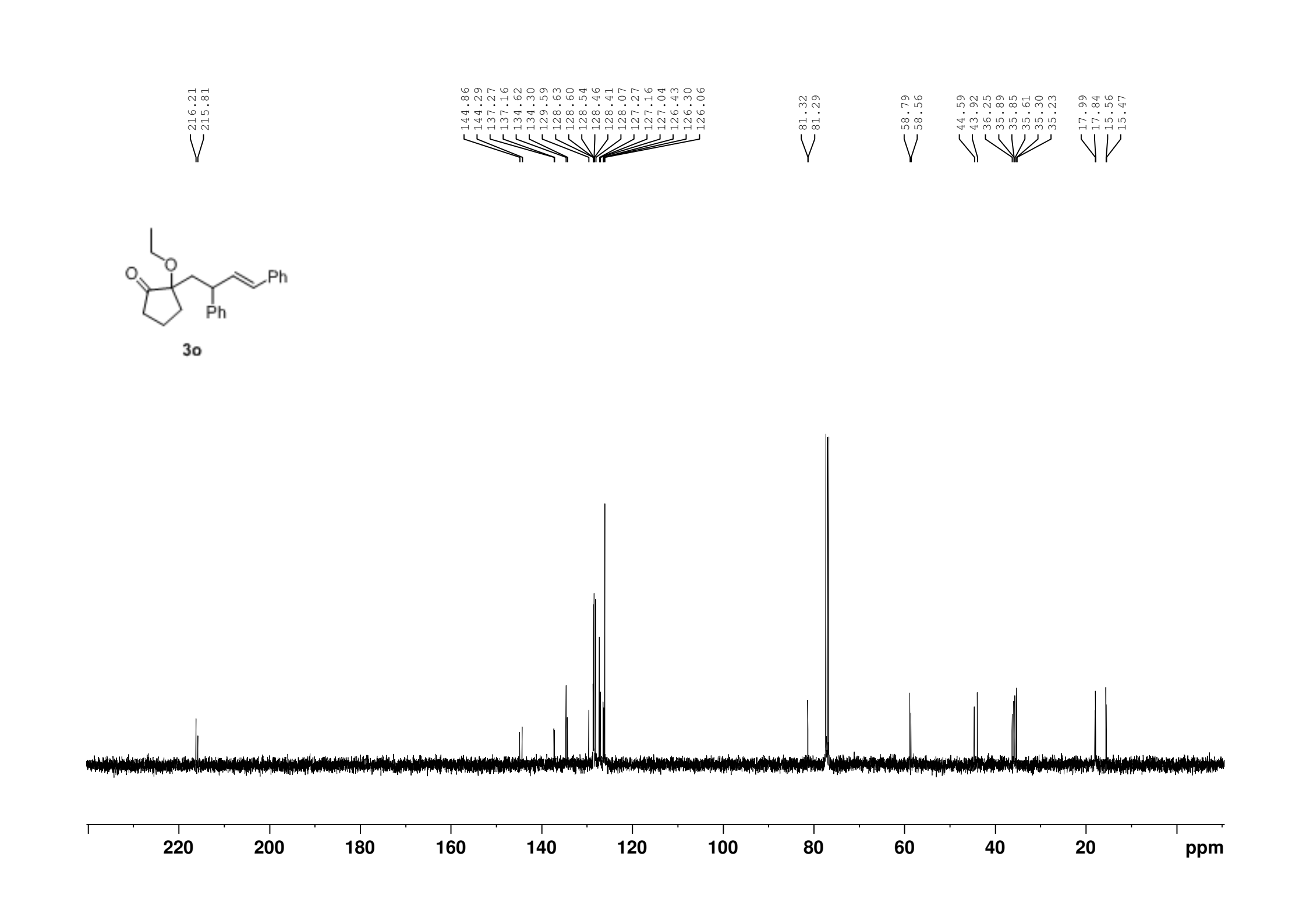
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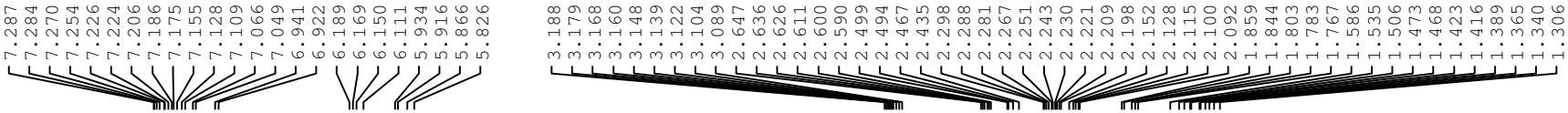
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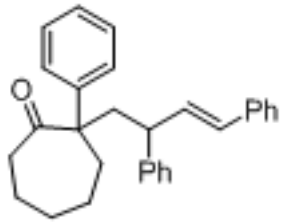
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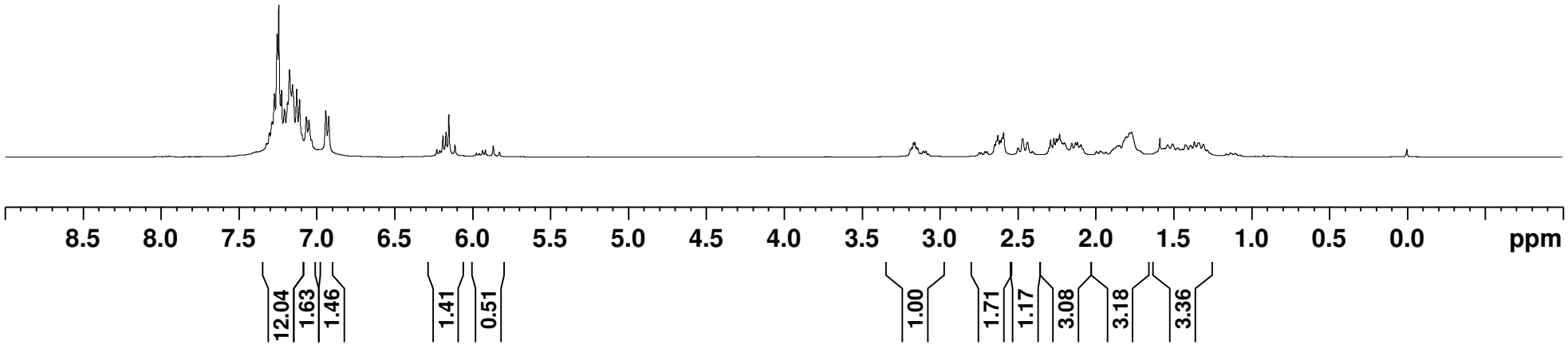
Ph
Ph

3p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2.5
2.0
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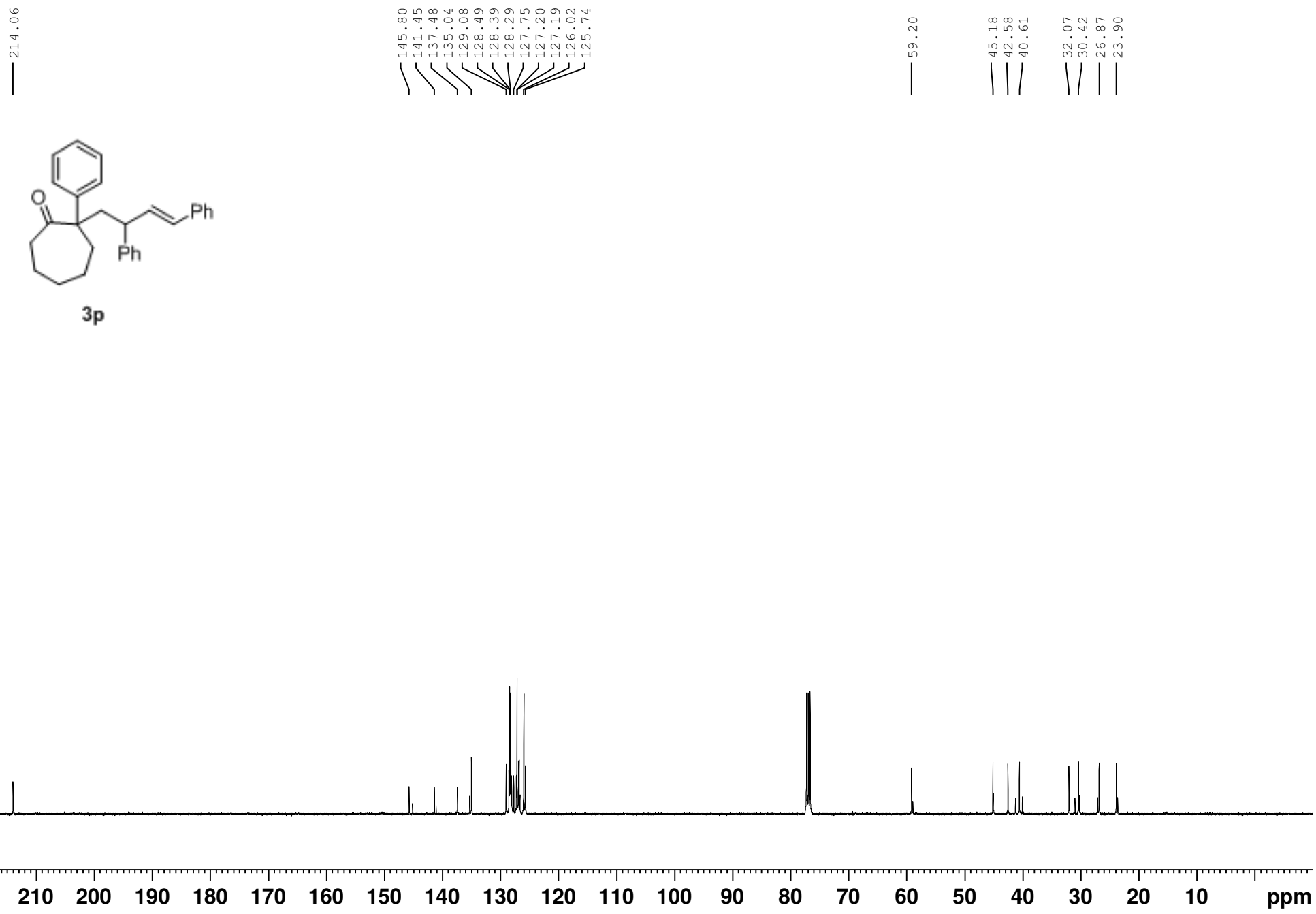
3.18
3.36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127.19
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42.58
40.61
32.07
30.42
26.87
23.90
O
Ph
Ph
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200
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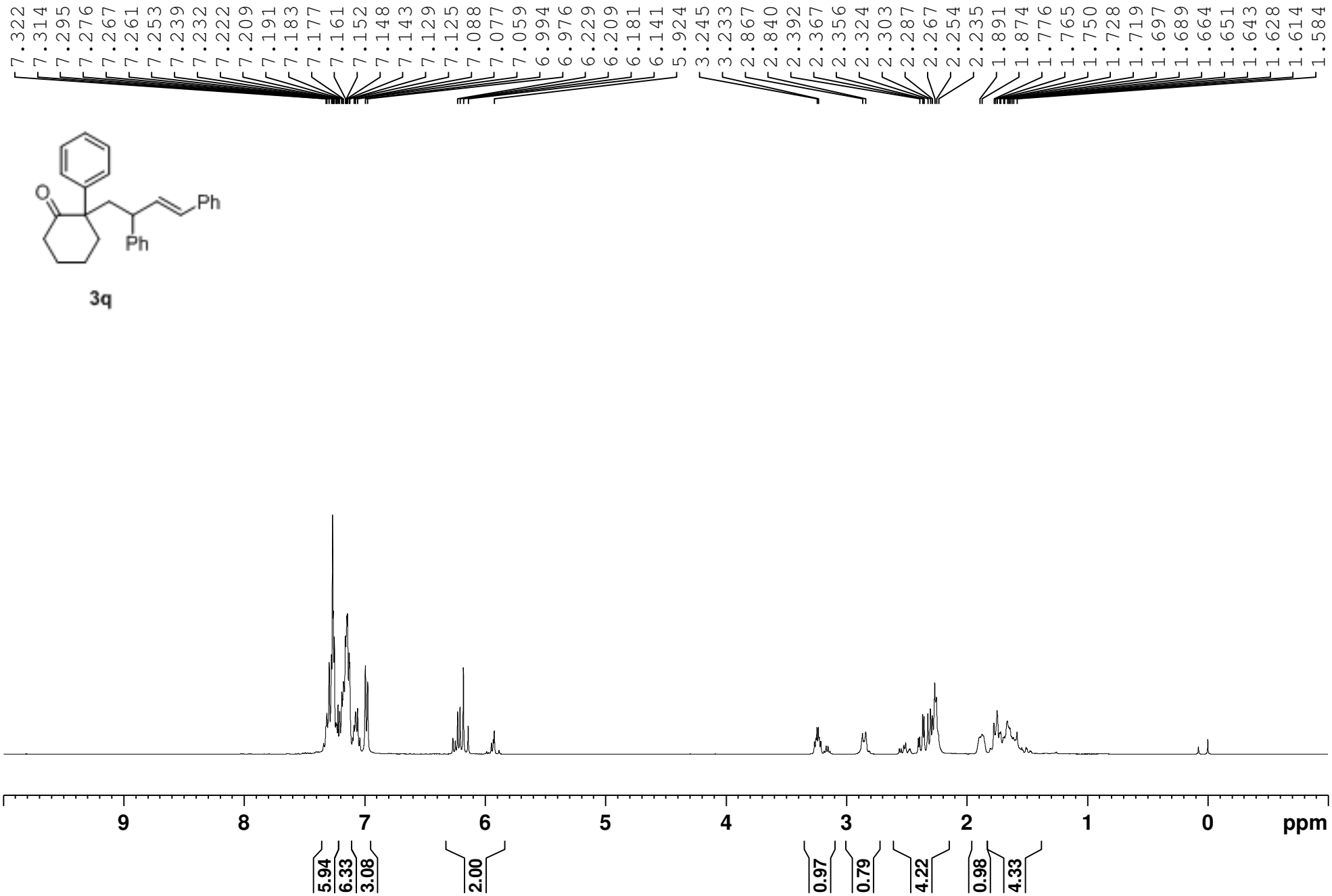
ppm

3p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7.239
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7.191
7.183
7.177
7.161
7.152
7.148
7.143
7.129
7.125
7.088
7.077
7.059
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6.976
6.229
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6.181
6.141
5.924
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3.233
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1.643
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1.614
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O
Ph
Ph
3q
9
8
7
6
5
4
3
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0
ppm
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3.08
2.00
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0.79
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0.98
4.33

213.06

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137.55
135.32
128.87
128.79
128.38
128.32
127.27
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57.82

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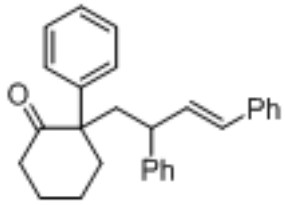

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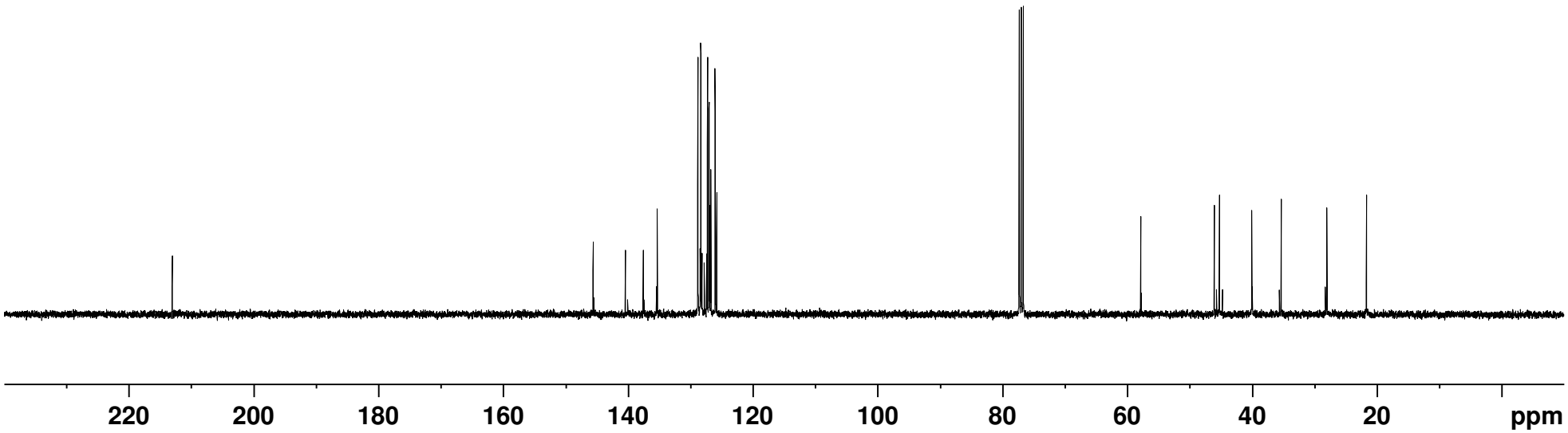

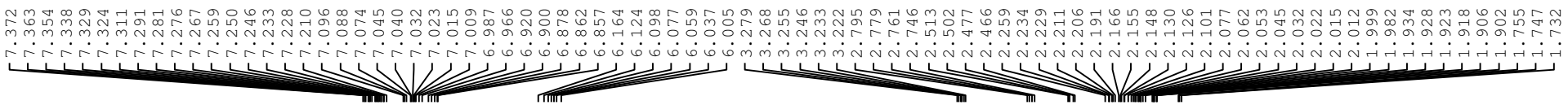
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7.259
7.250
7.246
7.233
7.228
7.210
7.096
7.088
7.074
7.045
7.040
7.032
7.023
7.015
7.009
6.987
6.966
6.920
6.900
6.878
6.862
6.857
6.164
6.124
6.098
6.077
6.059
6.037
6.005
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3.268
3.255
3.246
3.233
3.222
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2.761
2.746
2.513
2.502
2.477
2.466
2.259
2.234
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2.191
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2.062
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2.012
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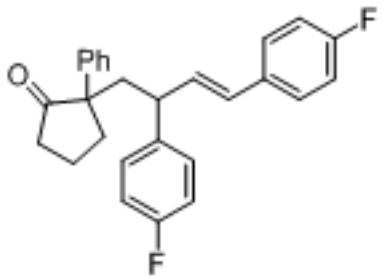
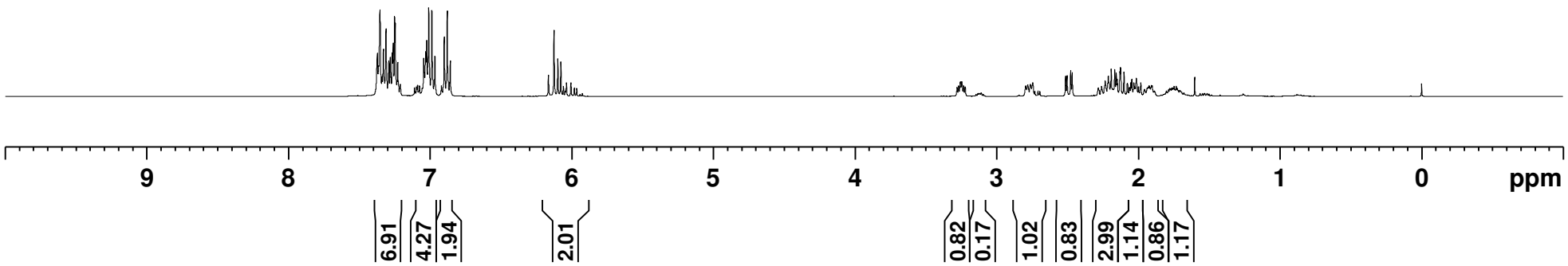
1.747
1.732


O
Ph
F
F

3r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8
7
6
5
4
3
2
1
0
ppm
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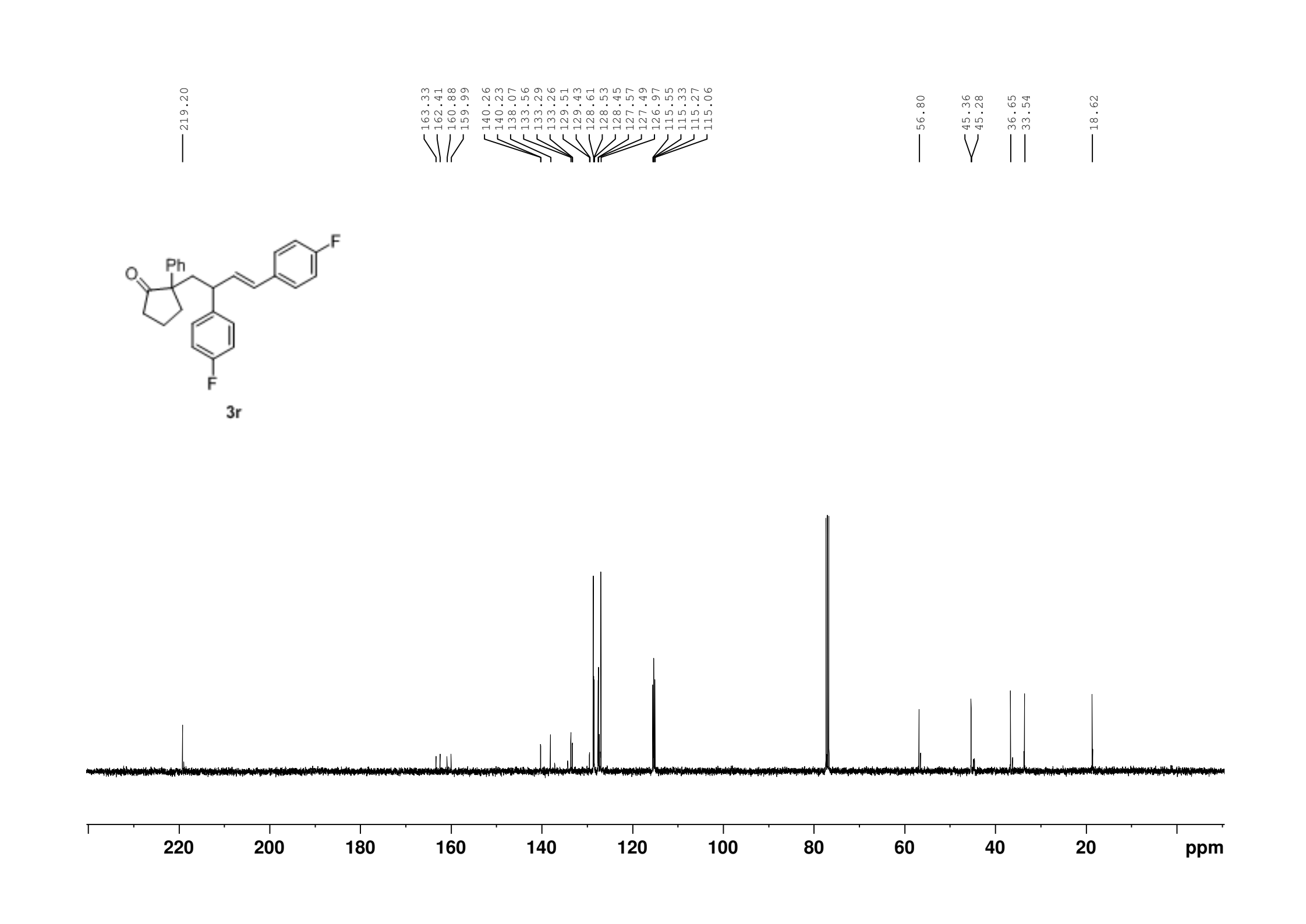
4.27
1.94
2.01
0.82
0.17
1.02
0.83
2.99
1.14
0.86
1.17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138.07
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133.29
133.26
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129.43
128.61
128.53
128.45
127.57
127.49
126.97
115.55
115.33
115.27
115.06
56.80
45.36
45.28
36.65
33.54
18.62
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Ph
F
F
3r
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140
120
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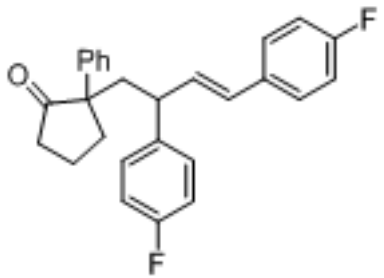
80
60
40
20
ppm



3r

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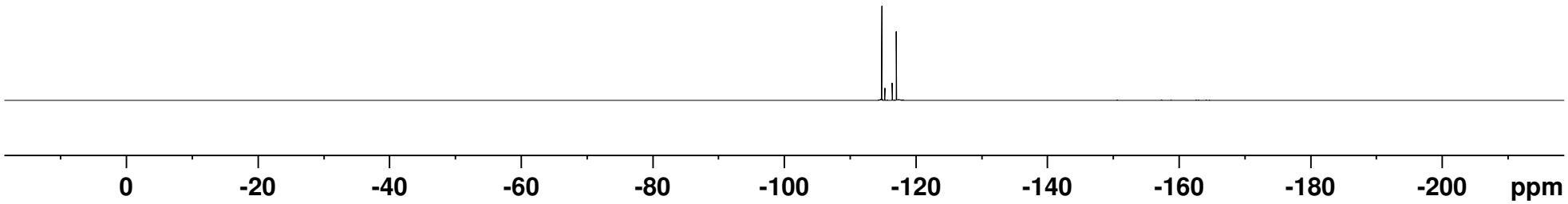
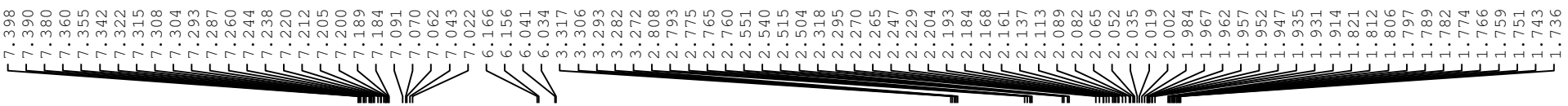
-116.94

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7.260
7.244
7.238
7.220
7.212
7.205
7.200
7.189
7.184
7.091
7.070
7.062
7.043
7.022
6.166
6.156
6.041
6.034
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3.306
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3.282
3.272
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2.515
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2.265
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2.229
2.204
2.193
2.184
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2.161
2.137
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2.089
2.082
2.065
2.052
2.035
2.019
2.002
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1.967
1.962
1.957
1.952
1.947
1.935
1.931
1.914
1.821
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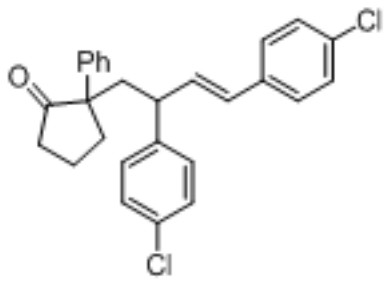
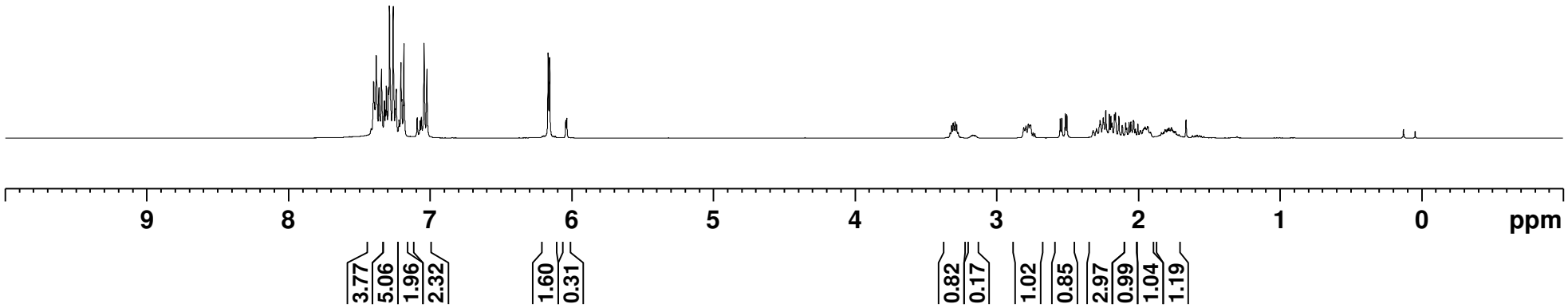
1.736


O
Ph
Cl
Cl

3s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5
4
3
2
1
0
ppm
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0.85
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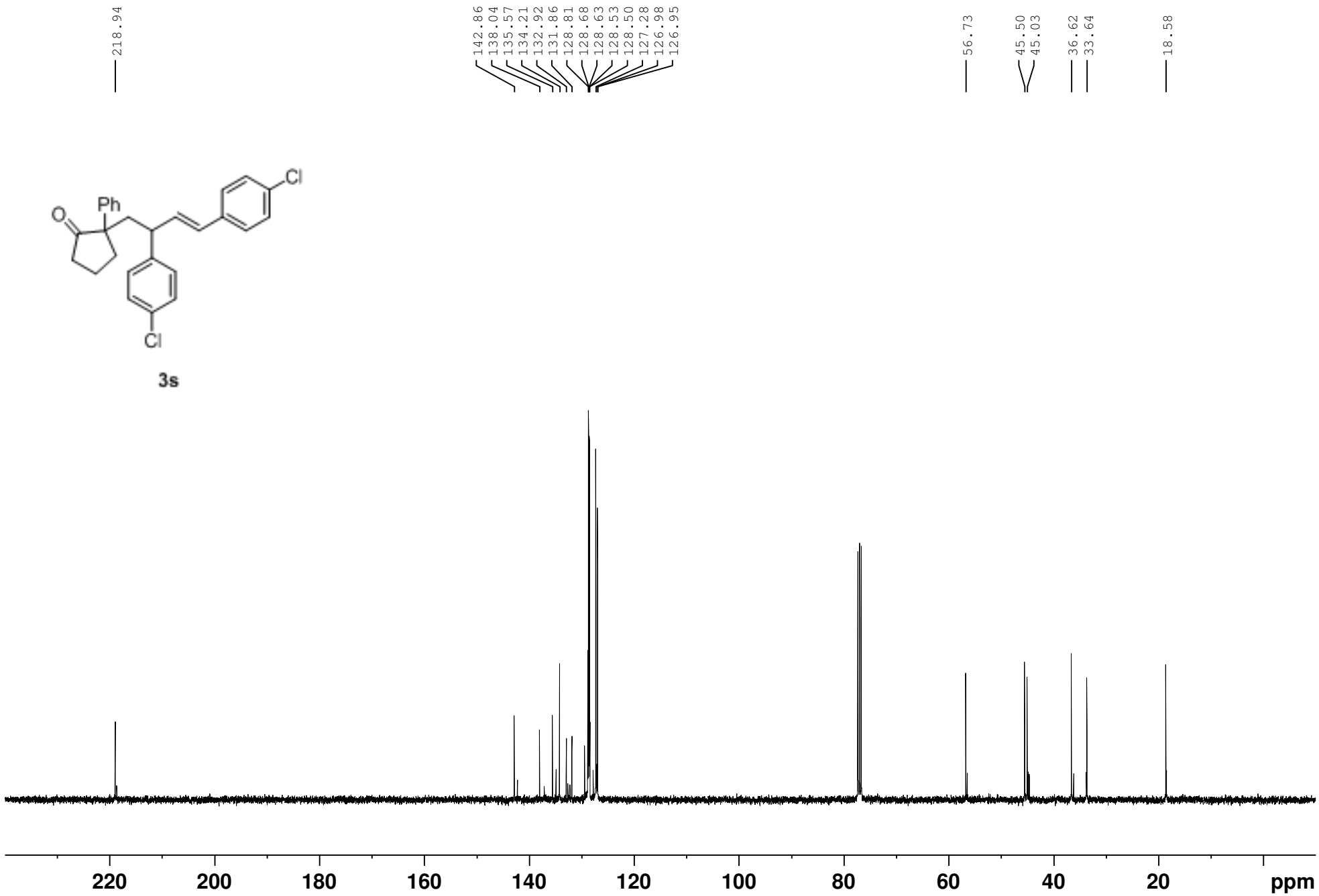
1.19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128.63
128.53
128.50
127.28
126.98
126.95
56.73
45.50
45.03
36.62
33.64
18.58
O
Ph
Cl
Cl
3s
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140
120
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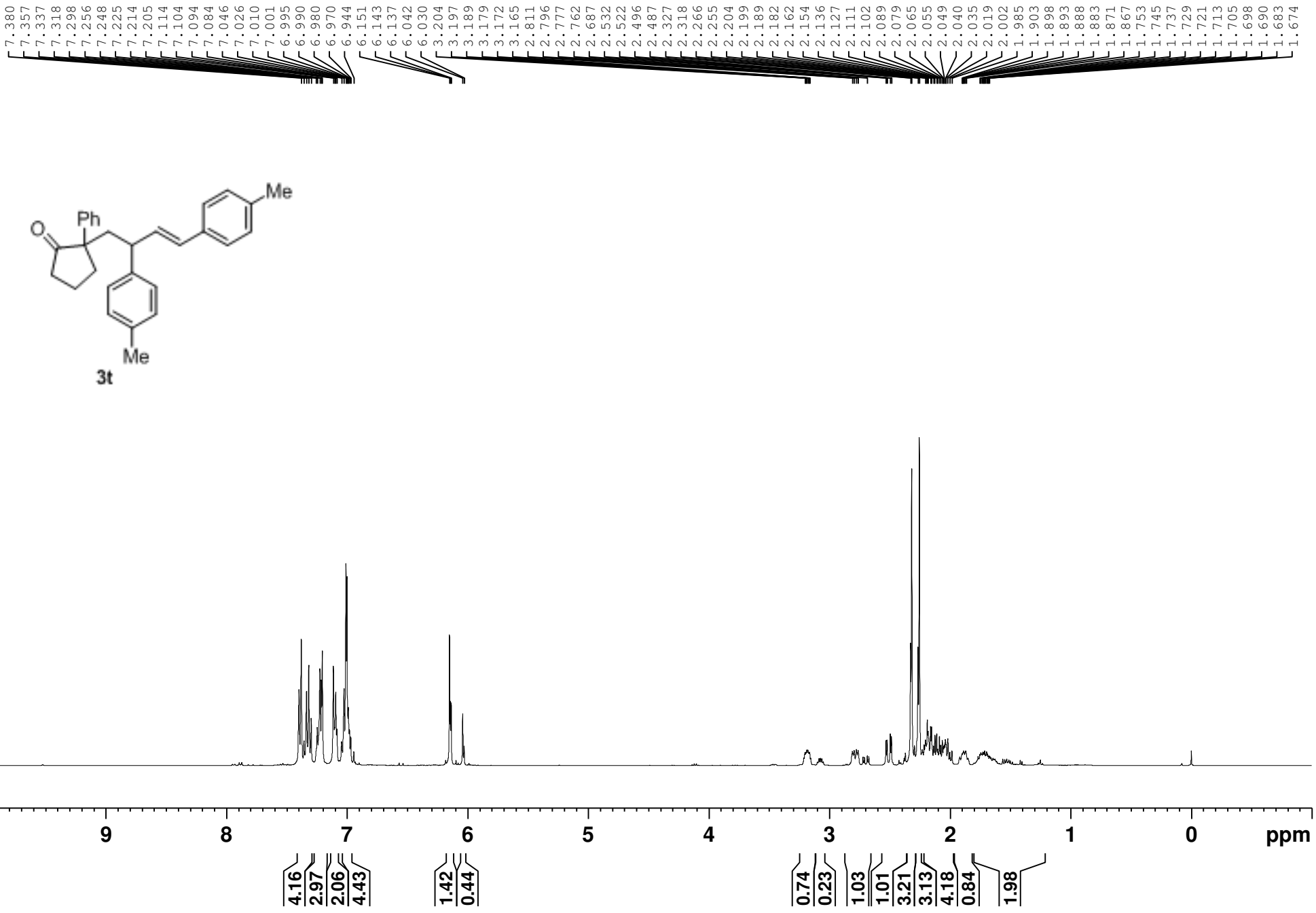
80
60
40
20
ppm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7.026
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6.970
6.944
6.151
6.143
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1.737
1.729
1.721
1.713
1.705
1.698
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1.683
1.674
O
Ph
Me
Me
3t
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8
7
6
5
4
3
2
1
0
ppm
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2.06
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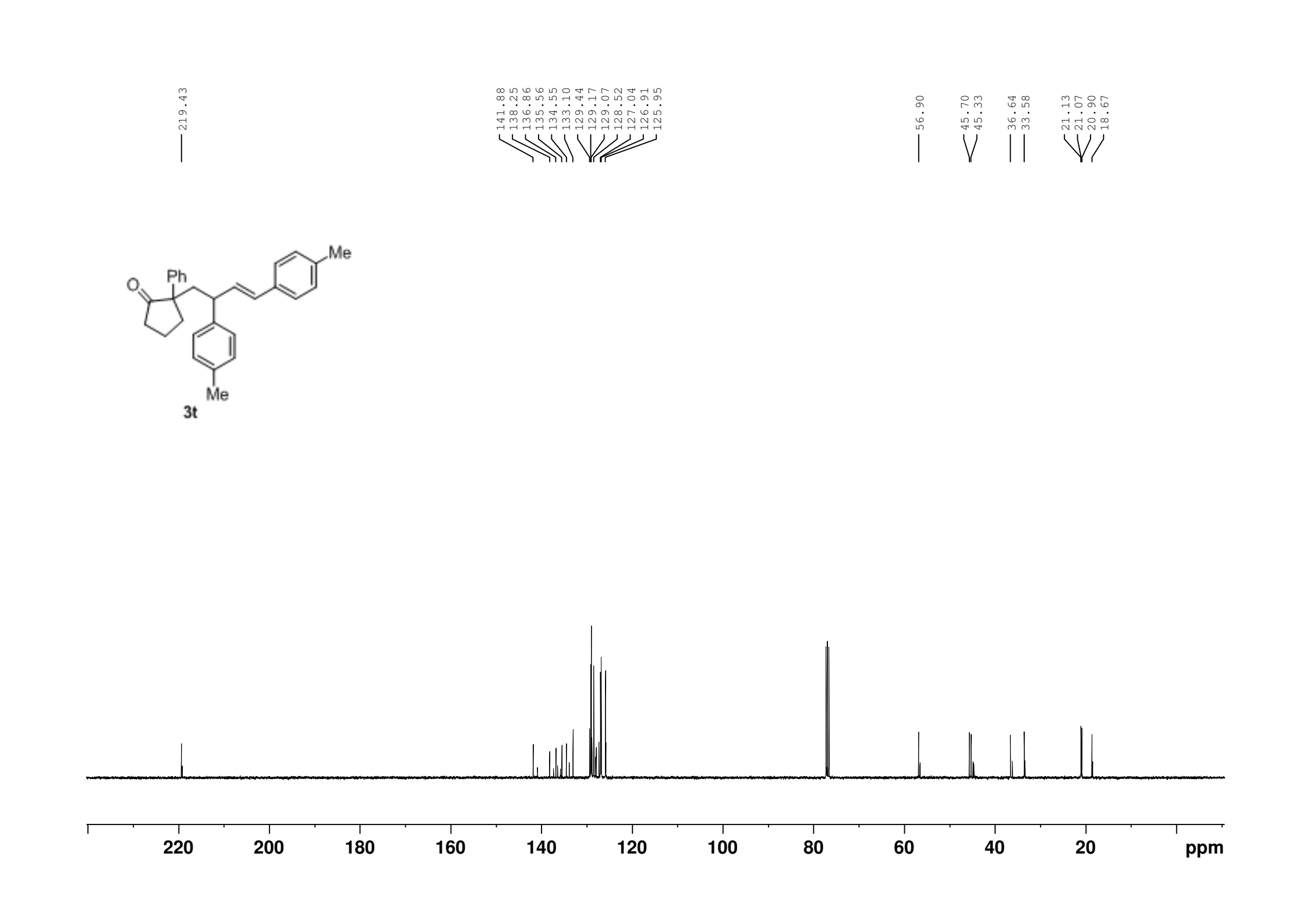
1.98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129.07
128.52
127.04
126.91
125.95
56.90
45.70
45.33
36.64
33.58
21.13
21.07
20.90
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Ph
Me
Me
3t
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200
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140
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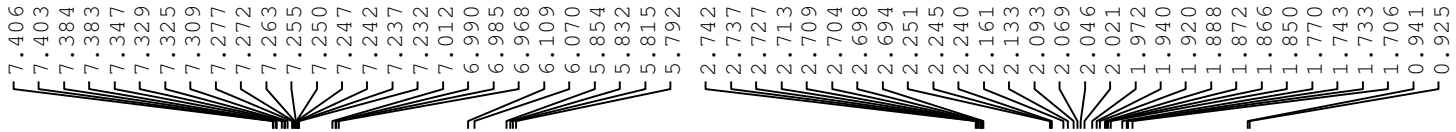
20
ppm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7.250
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7.242
7.237
7.232
7.012
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6.985
6.968
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5.832
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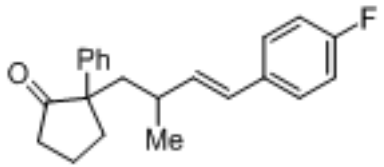
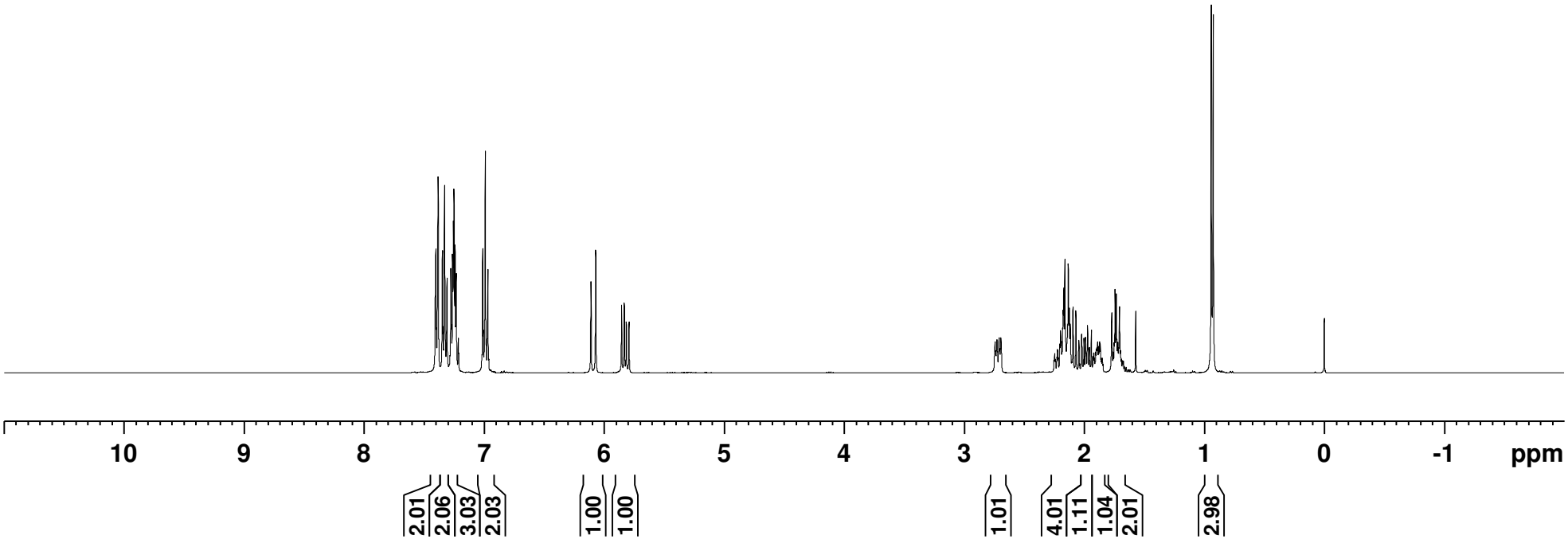
0.925


O
Ph
Me
F

3u


10
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8
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6
5
4
3
2
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-1
ppm
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3.03
2.03
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1.01
4.01
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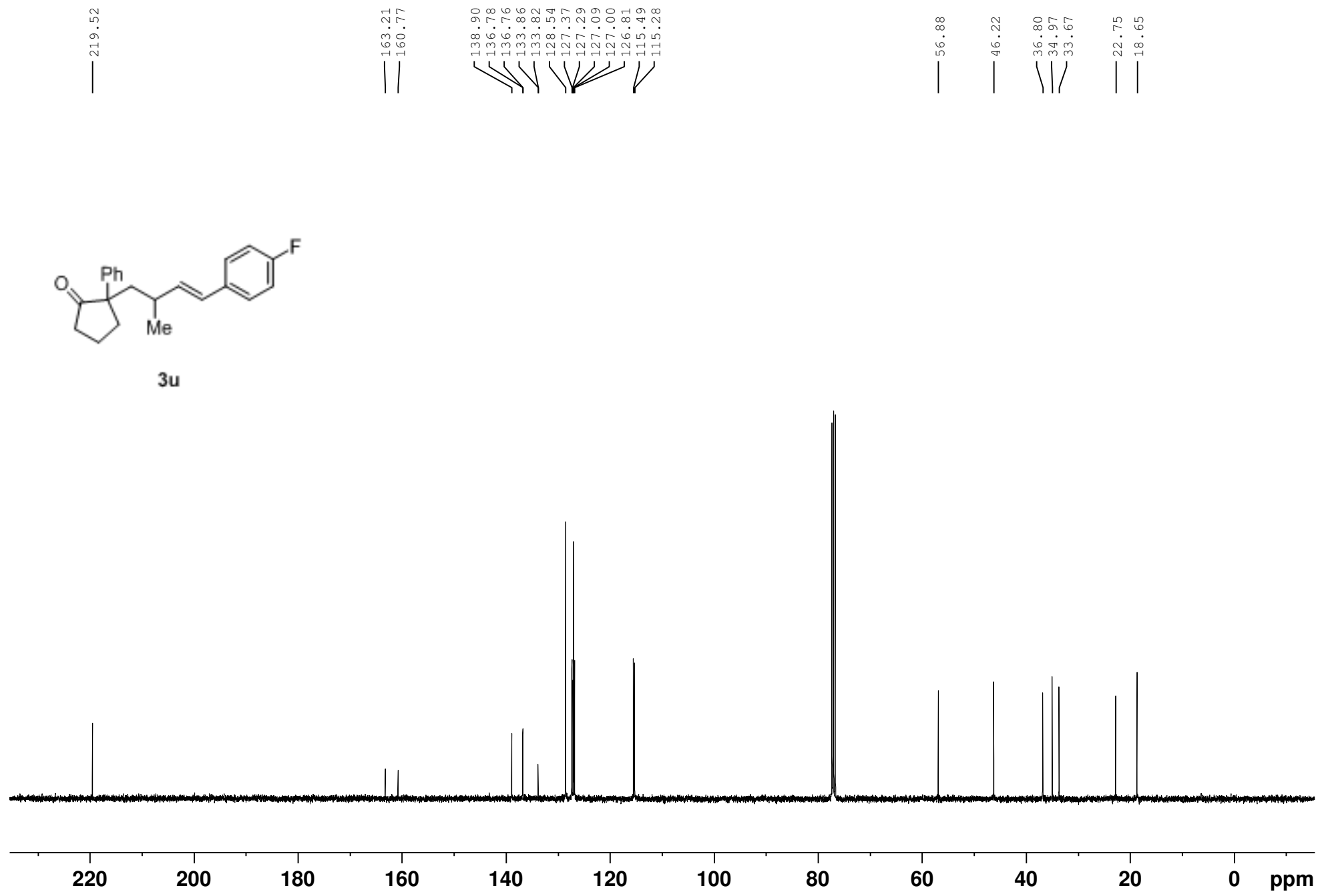
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127.29
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127.00
126.81
115.49
115.28
56.88
46.22
36.80
34.97
33.67
22.75
18.65
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Ph
Me
F
3u
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100
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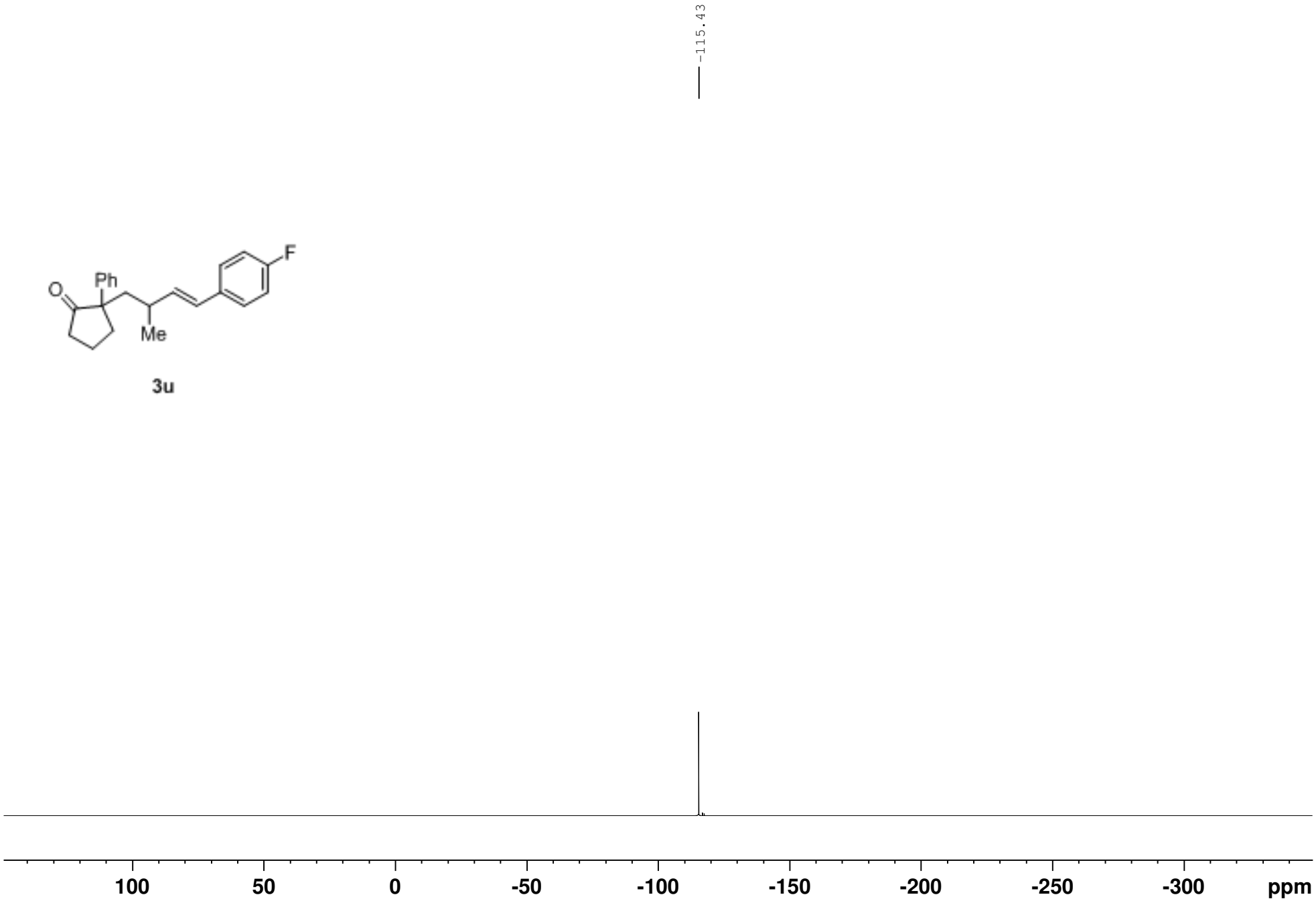
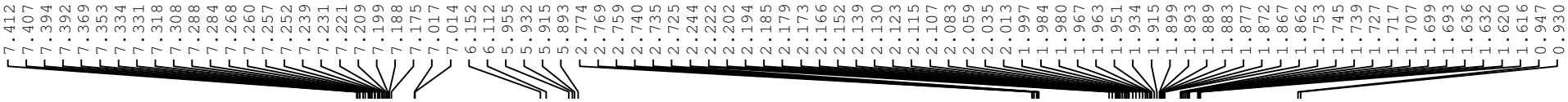
20
0
ppm

3u

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7.308
7.288
7.284
7.268
7.260
7.257
7.252
7.239
7.231
7.221
7.209
7.199
7.188
7.175
7.017
7.014
6.152
6.112
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5.932
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5.893
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2.173
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2.152
2.139
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2.123
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1.951
1.934
1.915
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1.867
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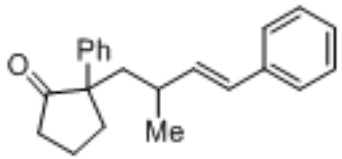
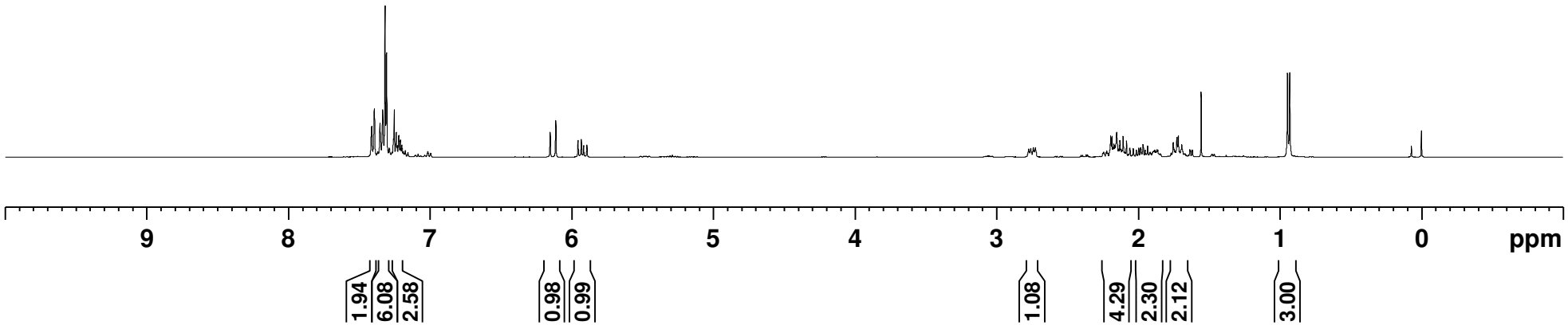

O
Ph
Me

3v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5
4
3
2
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ppm
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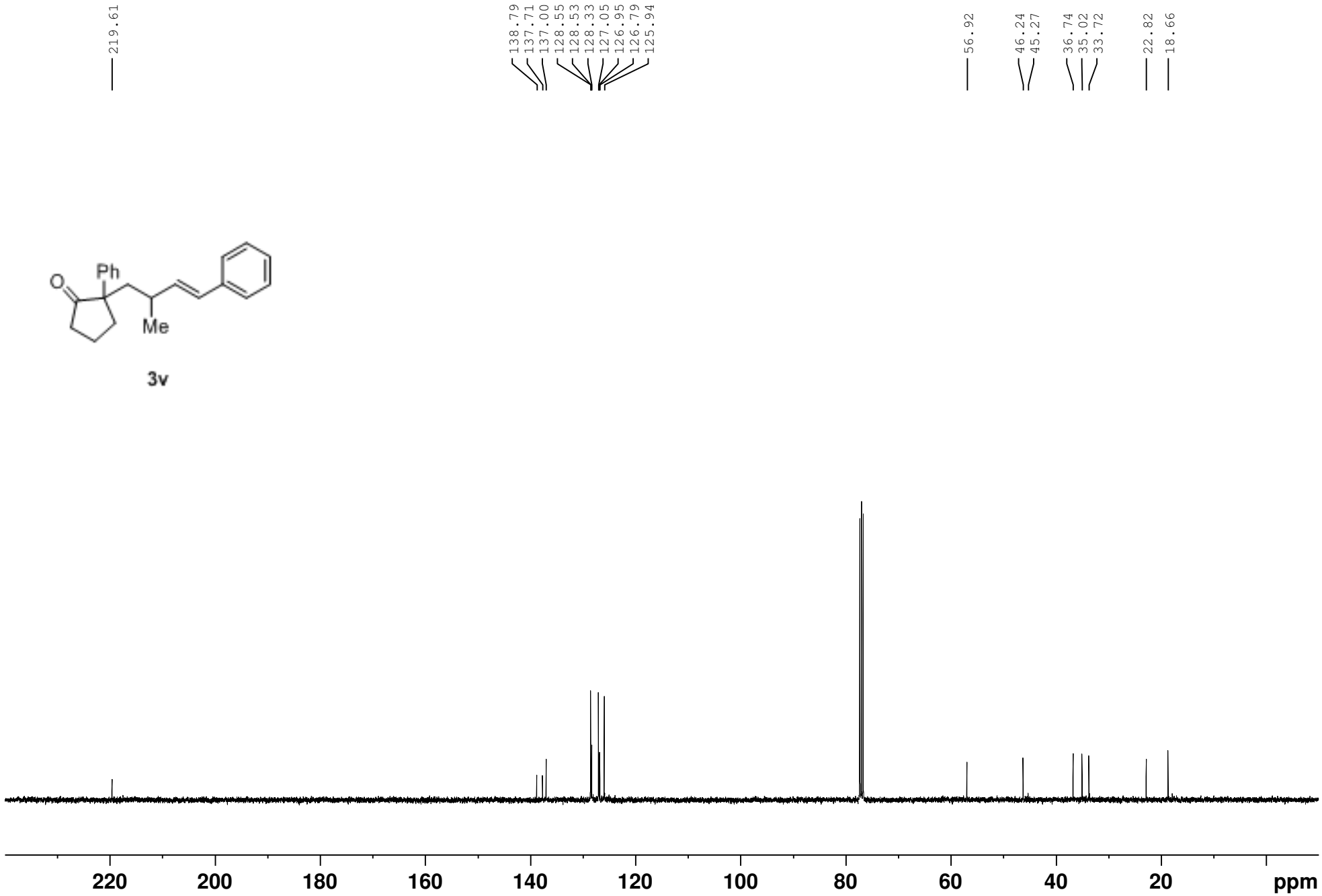
6.08
2.58
0.98
0.99
1.08
4.29
2.30
2.12
3.00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127.05
126.95
126.79
125.94
56.92
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45.27
36.74
35.02
33.72
22.82
18.66
O
Ph
Me
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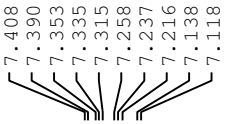
120
100
80
60
40
20
ppm

3v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7.216
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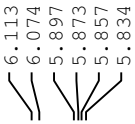
7.118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6.074
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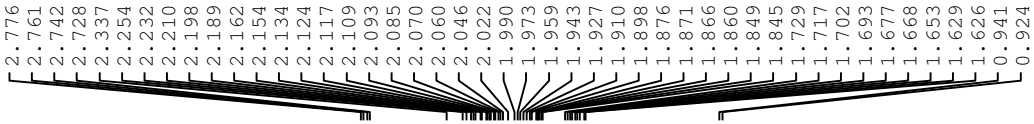
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2.189
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2.154
2.134
2.124
2.117
2.109
2.093
2.085
2.070
2.060
2.046
2.022
1.990
1.973
1.959
1.943
1.927
1.910
1.898
1.876
1.871
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1.860
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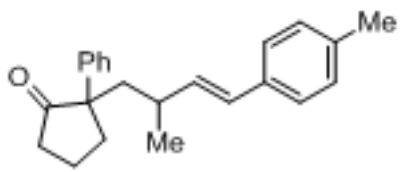
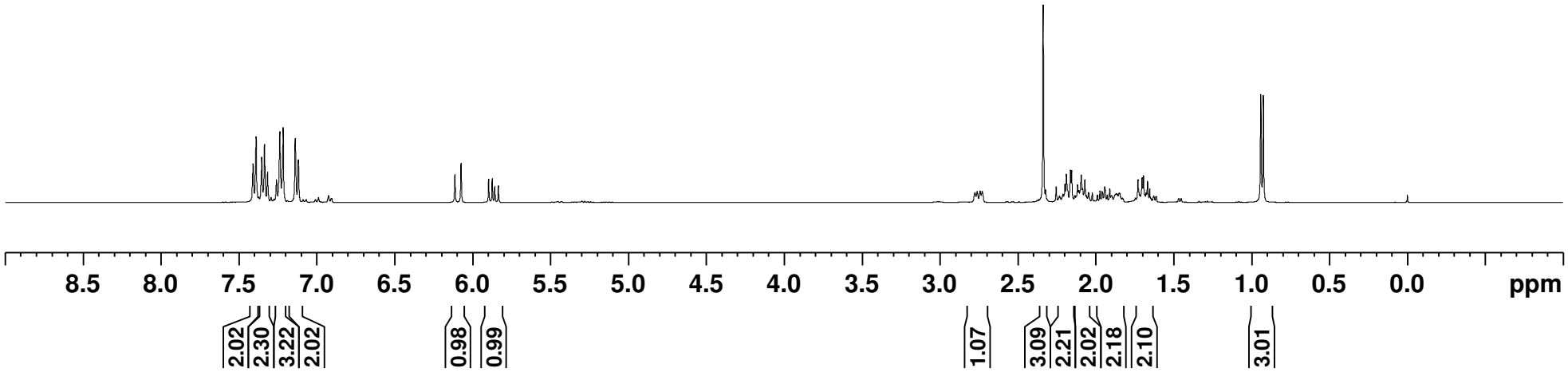

Me
Ph
O
Me

3w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3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
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2.21
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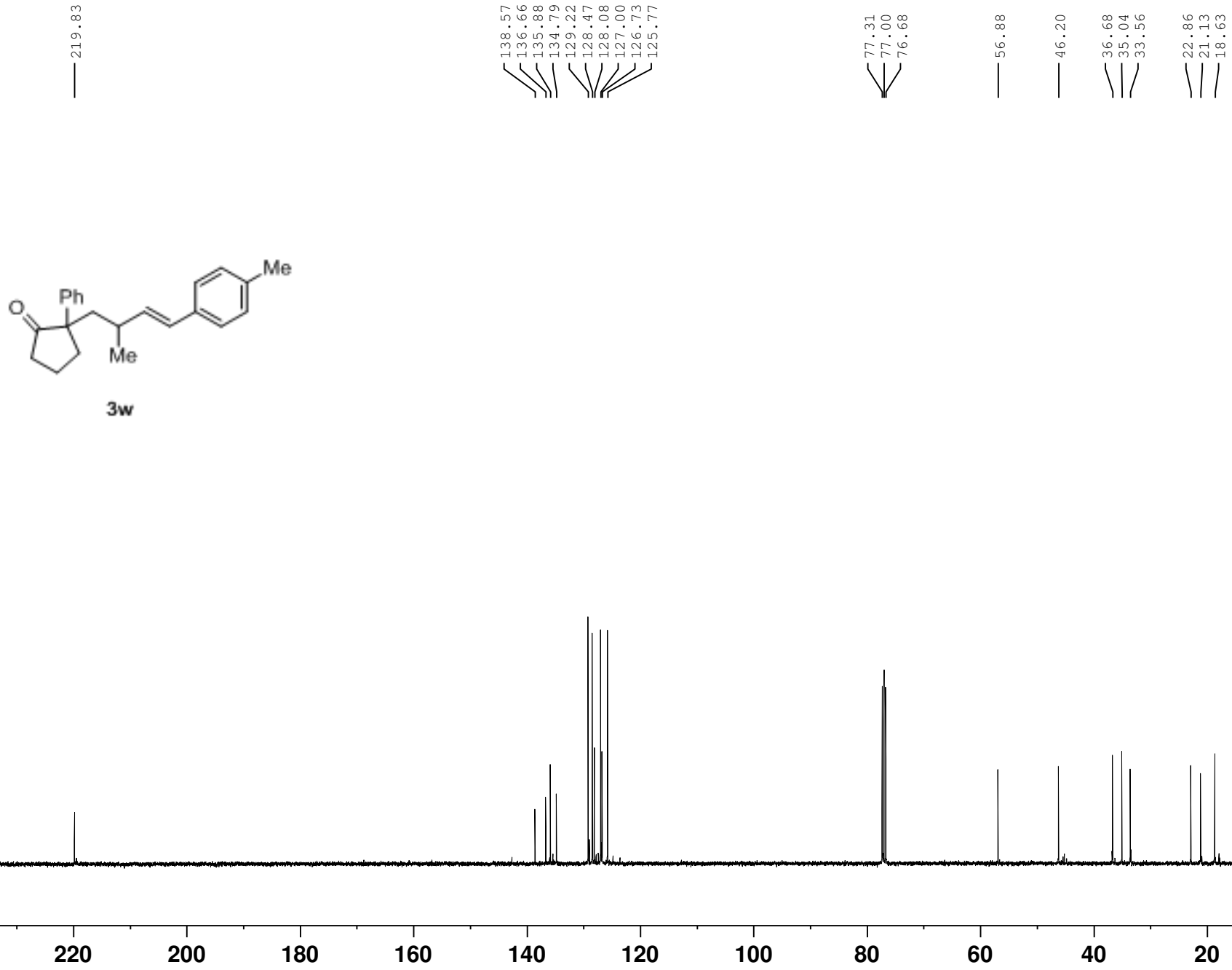
2.18
2.10
3.01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129.22
128.47
128.08
127.00
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125.77
77.31
77.00
76.68
56.88
46.20
36.68
35.04
33.56
22.86
21.13
18.63
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Ph
O
Me
3w
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200
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140
120
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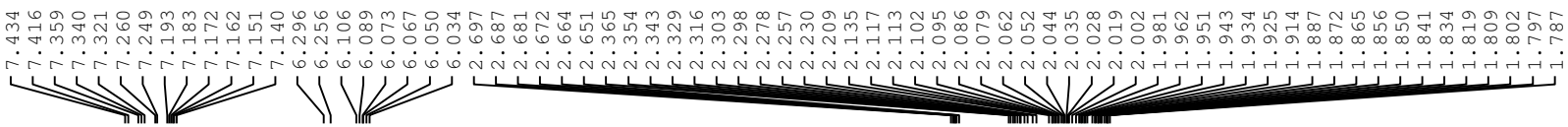
60
40
20
ppm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7.193
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7.151
7.140
6.296
6.256
6.106
6.089
6.073
6.067
6.050
6.034
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2.672
2.664
2.651
2.365
2.354
2.343
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2.316
2.303
2.298
2.278
2.257
2.230
2.209
2.135
2.117
2.113
2.102
2.095
2.086
2.079
2.062
2.052
2.044
2.035
2.028
2.019
2.002
1.981
1.962
1.951
1.943
1.934
1.925
1.914
1.887
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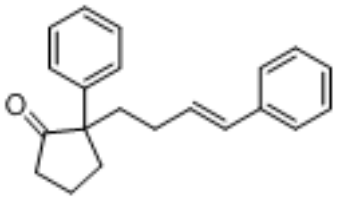
1.797
1.787



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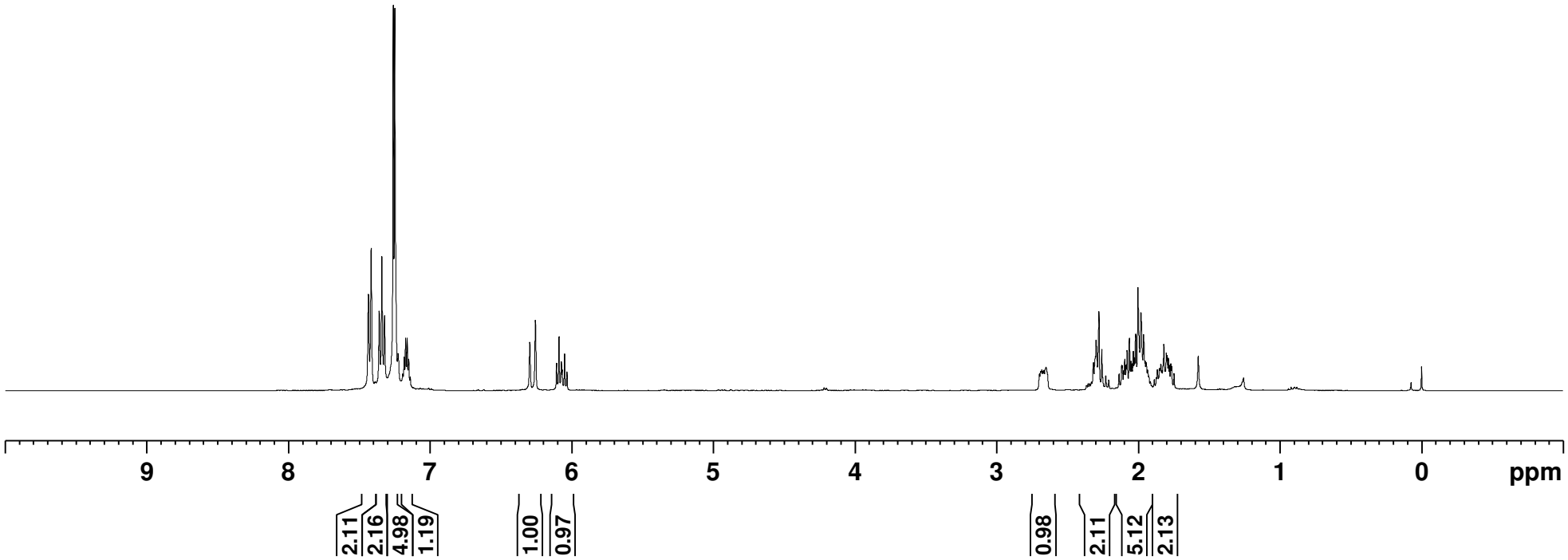
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8
7
6
5
4
3
2
1
0
ppm
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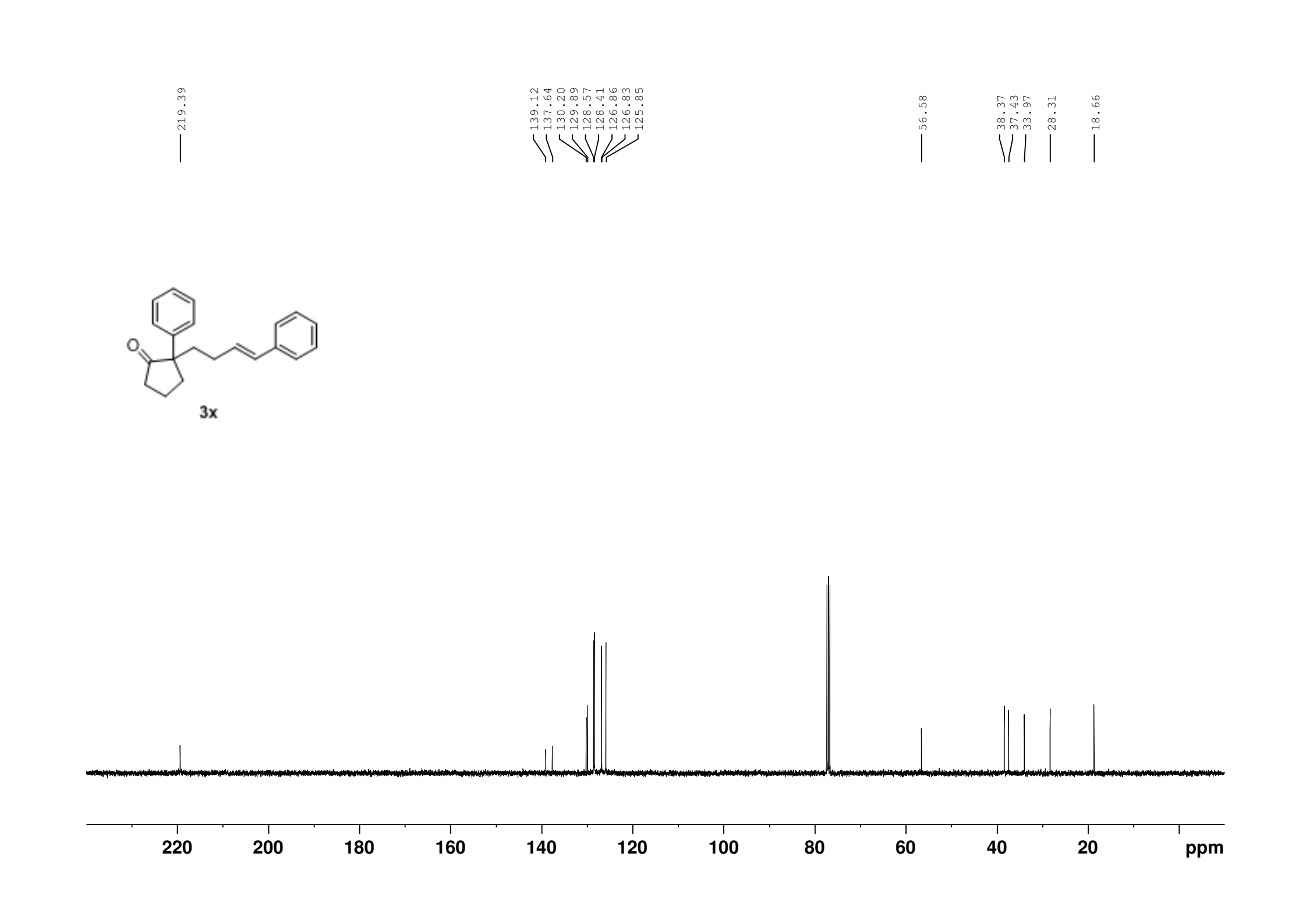
2.16
4.98
1.19
1.00
0.97
0.98
2.11
5.12
2.13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126.86
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125.85
56.58
38.37
37.43
33.97
28.31
18.66
3x
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200
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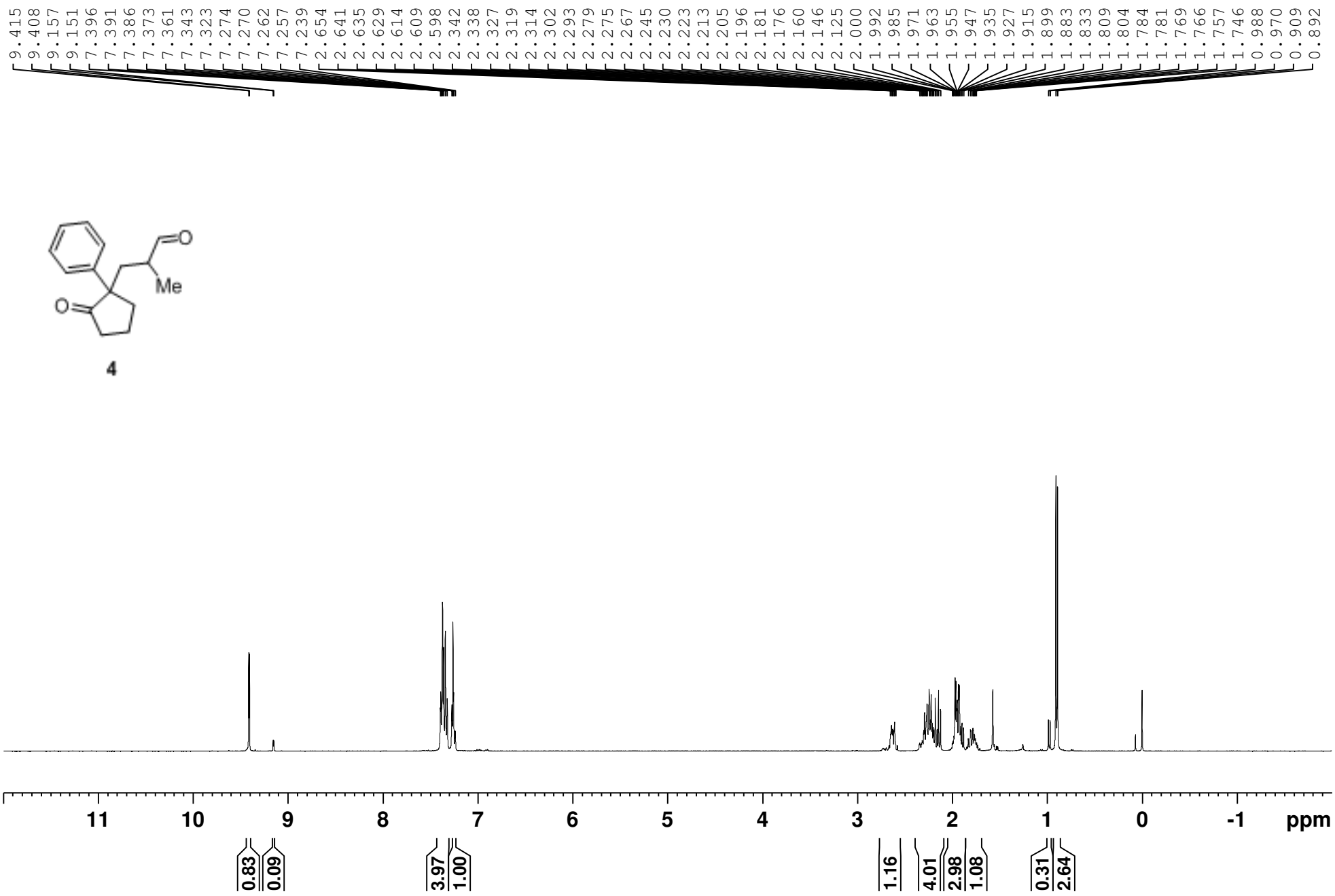
160
140
120
100
80
60
40
20
ppm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7.323
7.274
7.270
7.262
7.257
7.239
2.654
2.641
2.635
2.629
2.614
2.609
2.598
2.342
2.338
2.327
2.319
2.314
2.302
2.293
2.279
2.275
2.267
2.245
2.230
2.223
2.213
2.205
2.196
2.181
2.176
2.160
2.146
2.125
2.000
1.992
1.985
1.971
1.963
1.955
1.947
1.935
1.927
1.915
1.899
1.883
1.833
1.809
1.804
1.784
1.781
1.769
1.766
1.757
1.746
0.988
0.970
0.909
0.892
O
Me
O
4
11
10
9
8
7
6
5
4
3
2
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-1
ppm
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0.09
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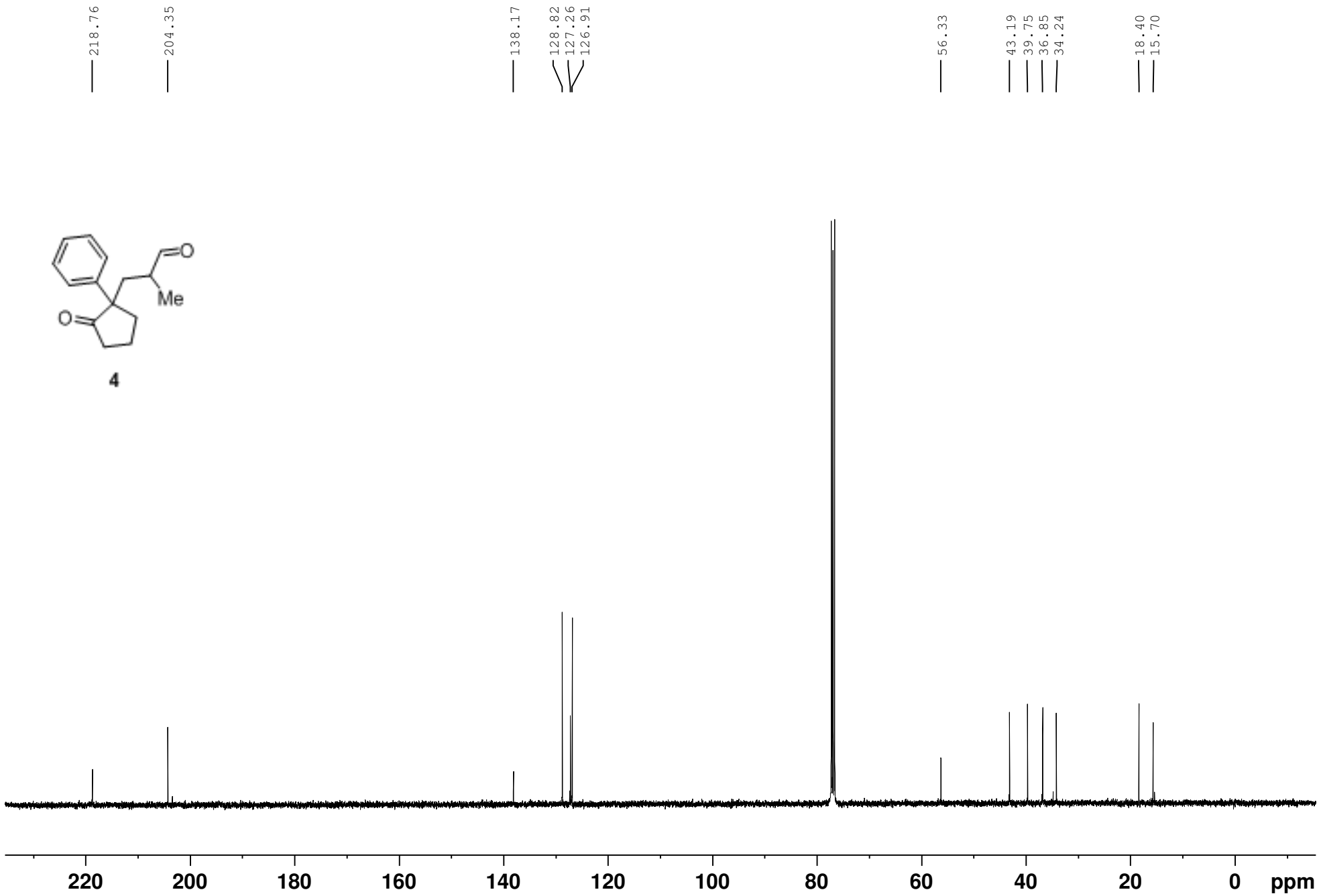
1.00
1.16
4.01
2.98
1.08
0.31
2.64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43.19
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36.85
34.24
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15.70
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Me
O
4
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200
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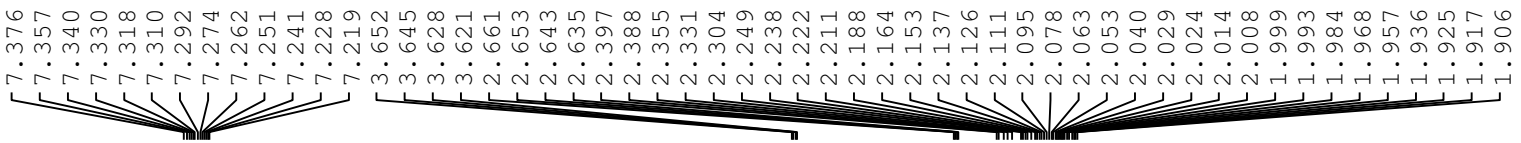
140
120
100
80
60
40
20
0
ppm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7.310
7.292
7.274
7.262
7.251
7.241
7.228
7.219
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3.645
3.628
3.621
2.661
2.653
2.643
2.635
2.397
2.388
2.355
2.331
2.304
2.249
2.238
2.222
2.211
2.188
2.164
2.153
2.137
2.126
2.111
2.095
2.078
2.063
2.053
2.040
2.029
2.024
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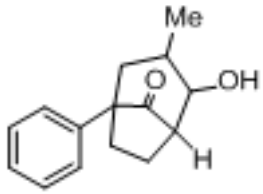
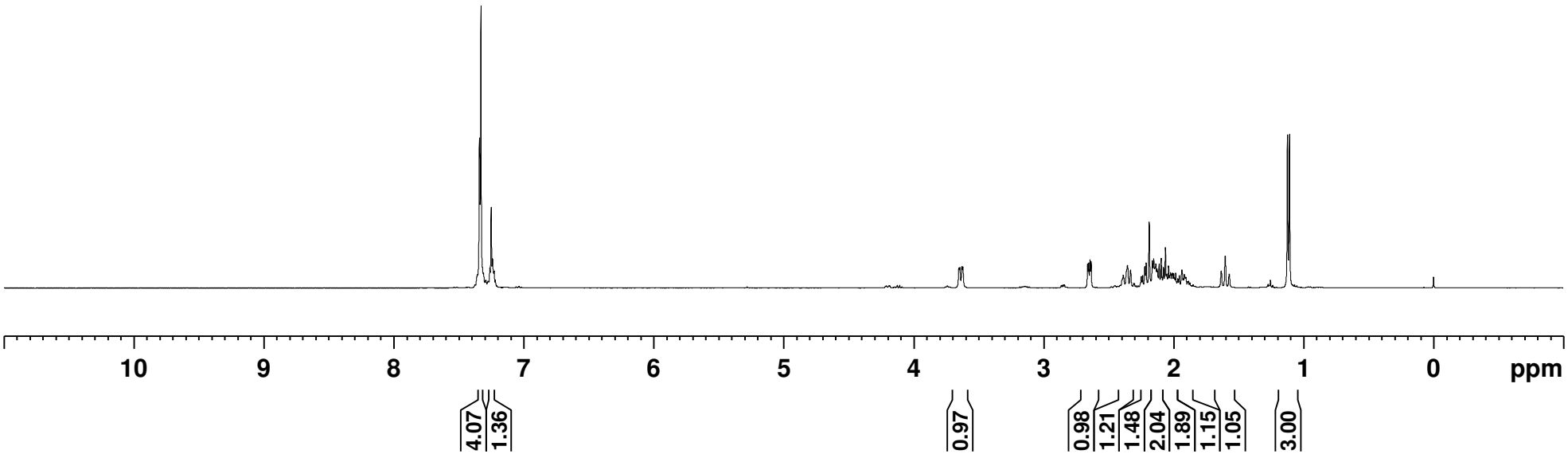
1.925
1.917
1.906


Me
O
OH
H

5


10
9
8
7
6
5
4
3
2
1
0
ppm
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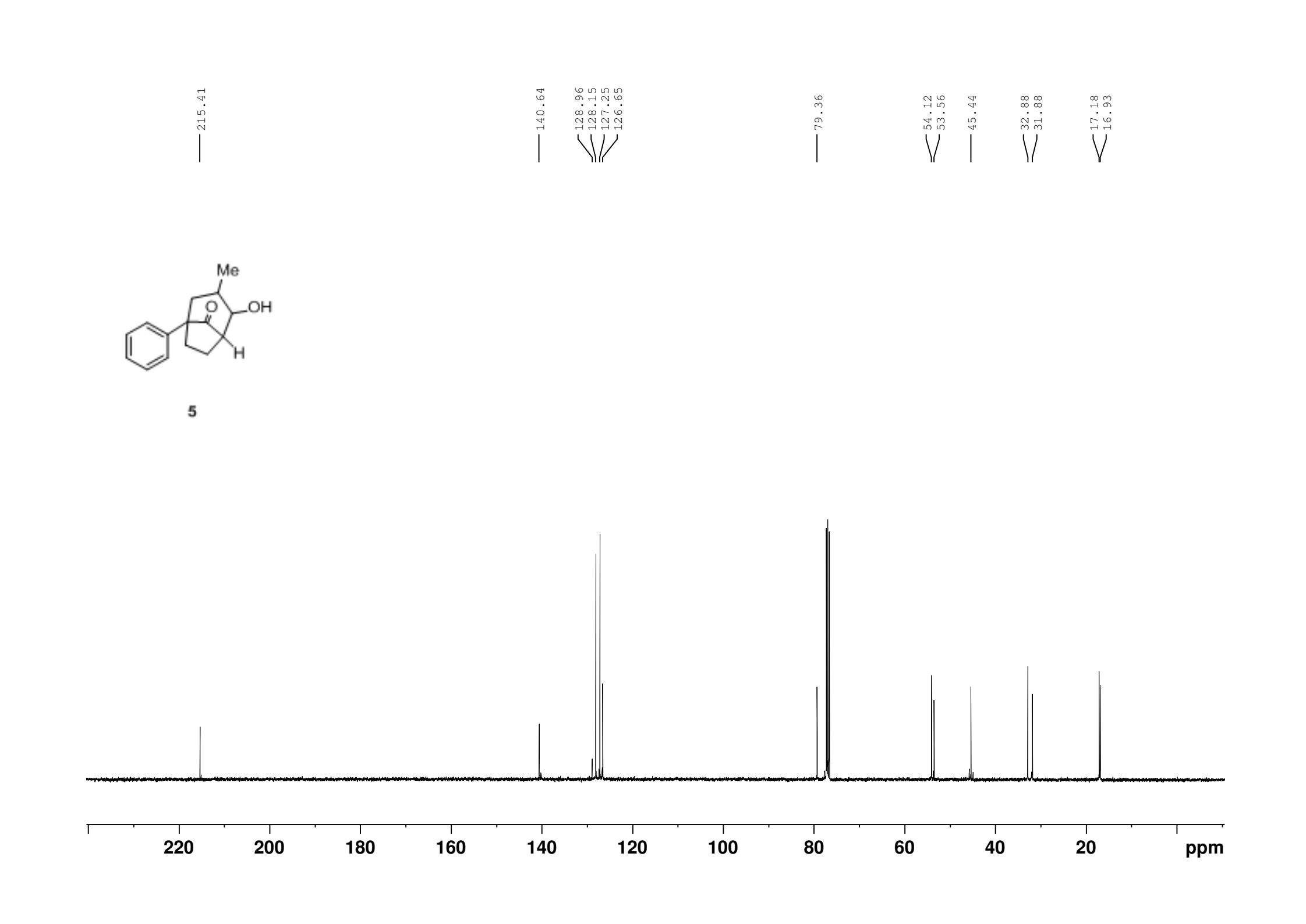
0.97
0.98
1.21
1.48
2.04
1.89
1.15
1.05
3.00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127.25
126.65
79.36
54.12
53.56
45.44
32.88
31.88
17.18
16.93
Me
OH
O
H
5
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180
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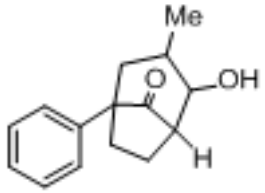
140
120
100
80
60
40
20
ppm

NOE 600M



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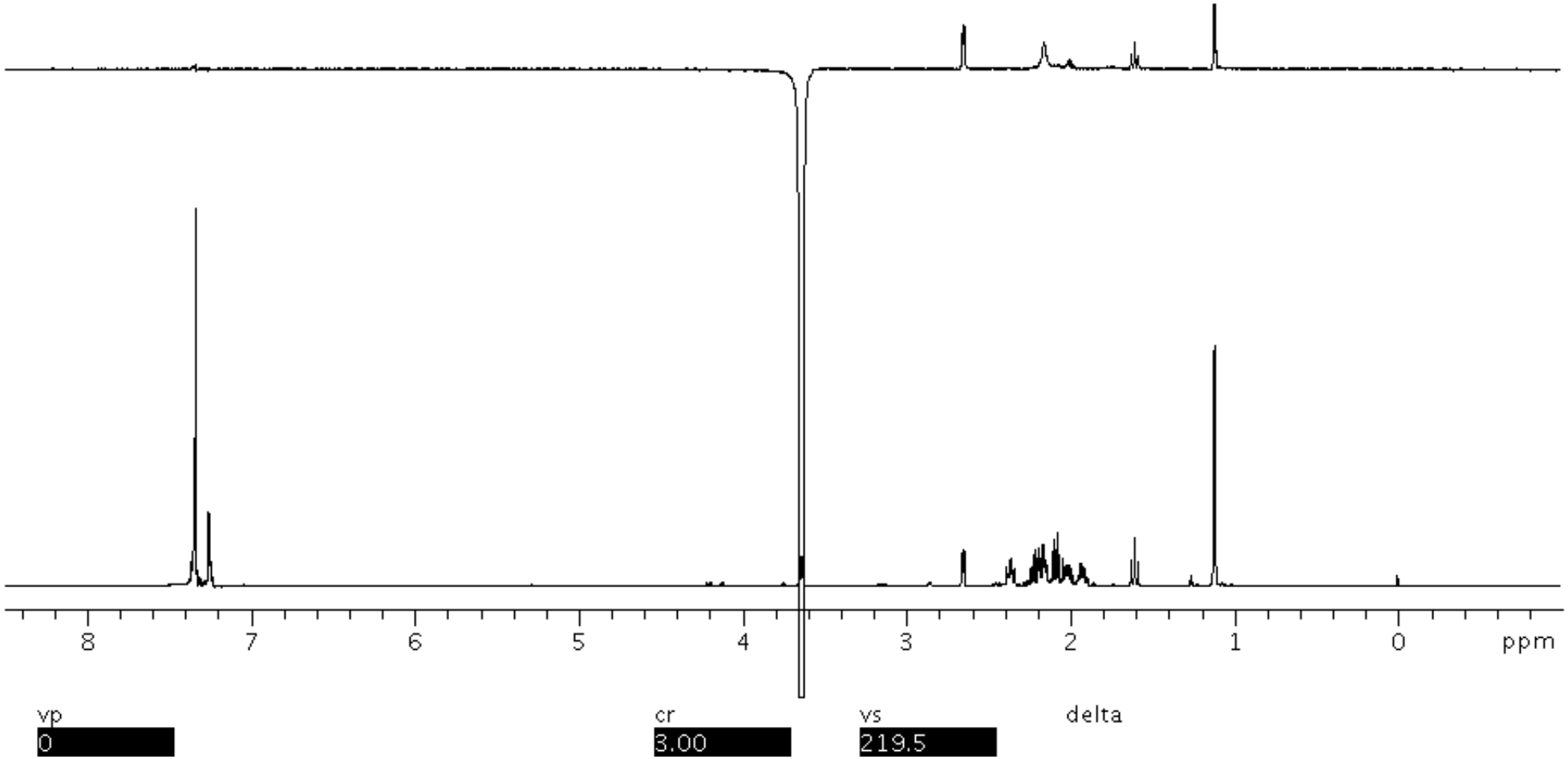

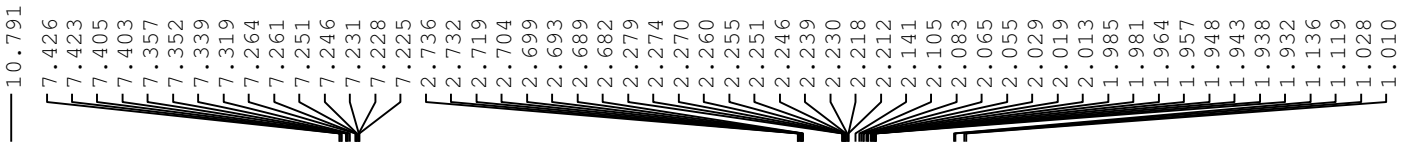
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7.246
7.231
7.228
7.225
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2.732
2.719
2.704
2.699
2.693
2.689
2.682
2.279
2.274
2.270
2.260
2.255
2.251
2.246
2.239
2.230
2.218
2.212
2.141
2.105
2.083
2.065
2.055
2.029
2.019
2.013
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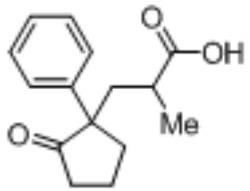
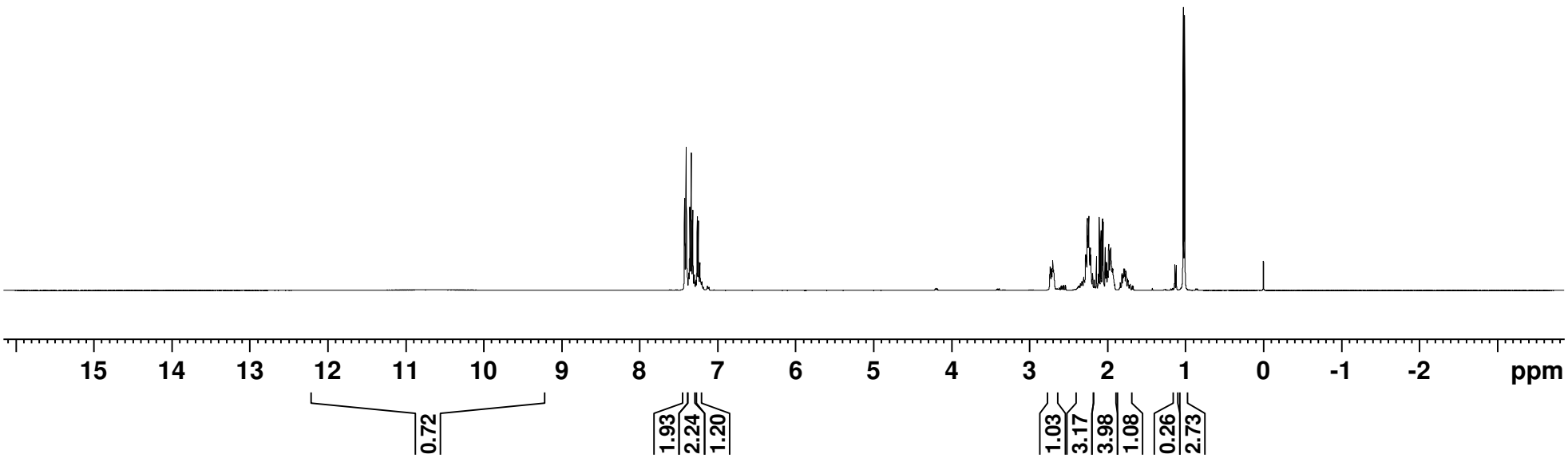
1.028
1.010


O
OH
Me
O

6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13
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11
10
9
8
7
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5
4
3
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0
-1
-2
ppm
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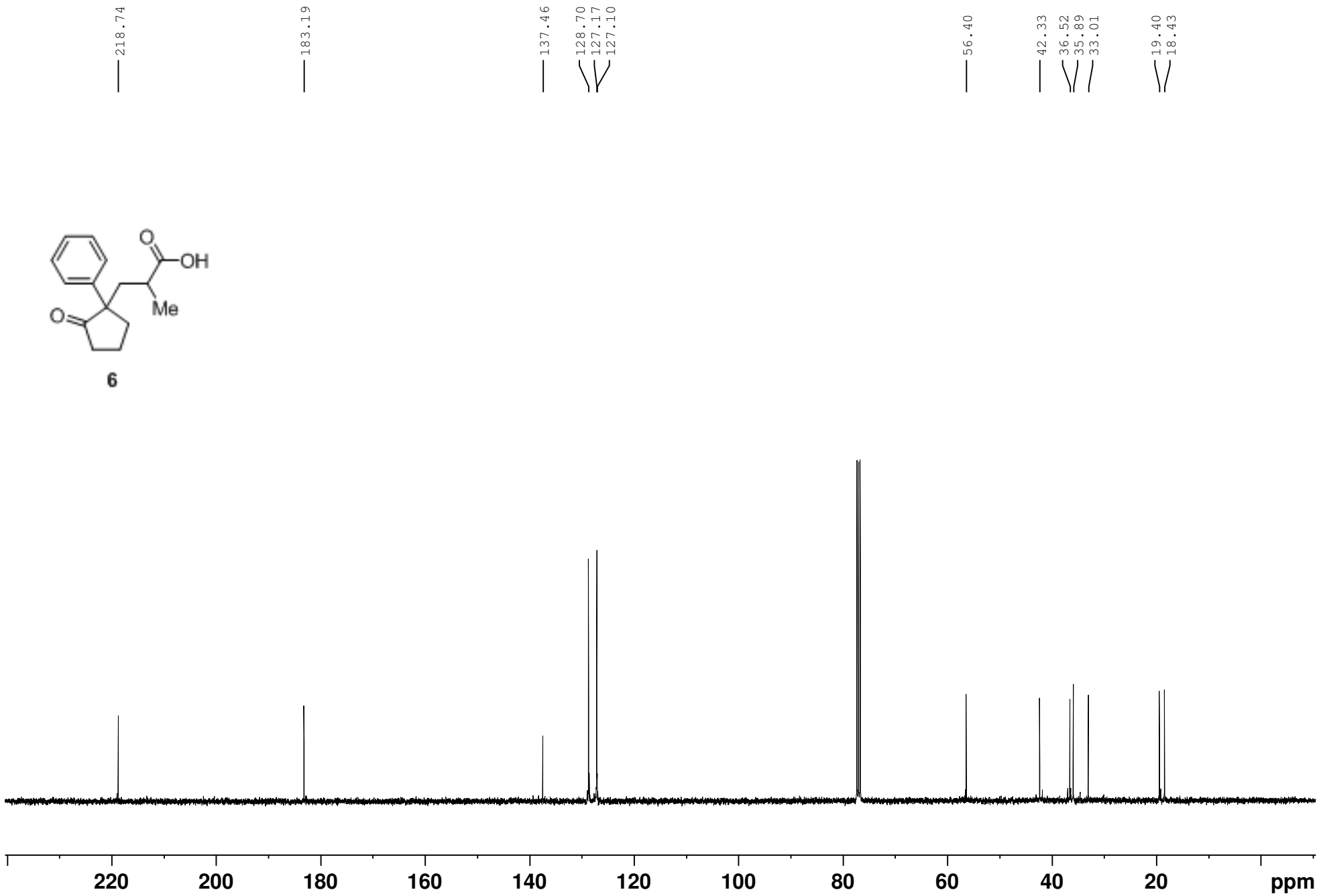
3.17
3.98
1.08
0.26
2.73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42.33
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35.89
33.01
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OH
Me
O
6
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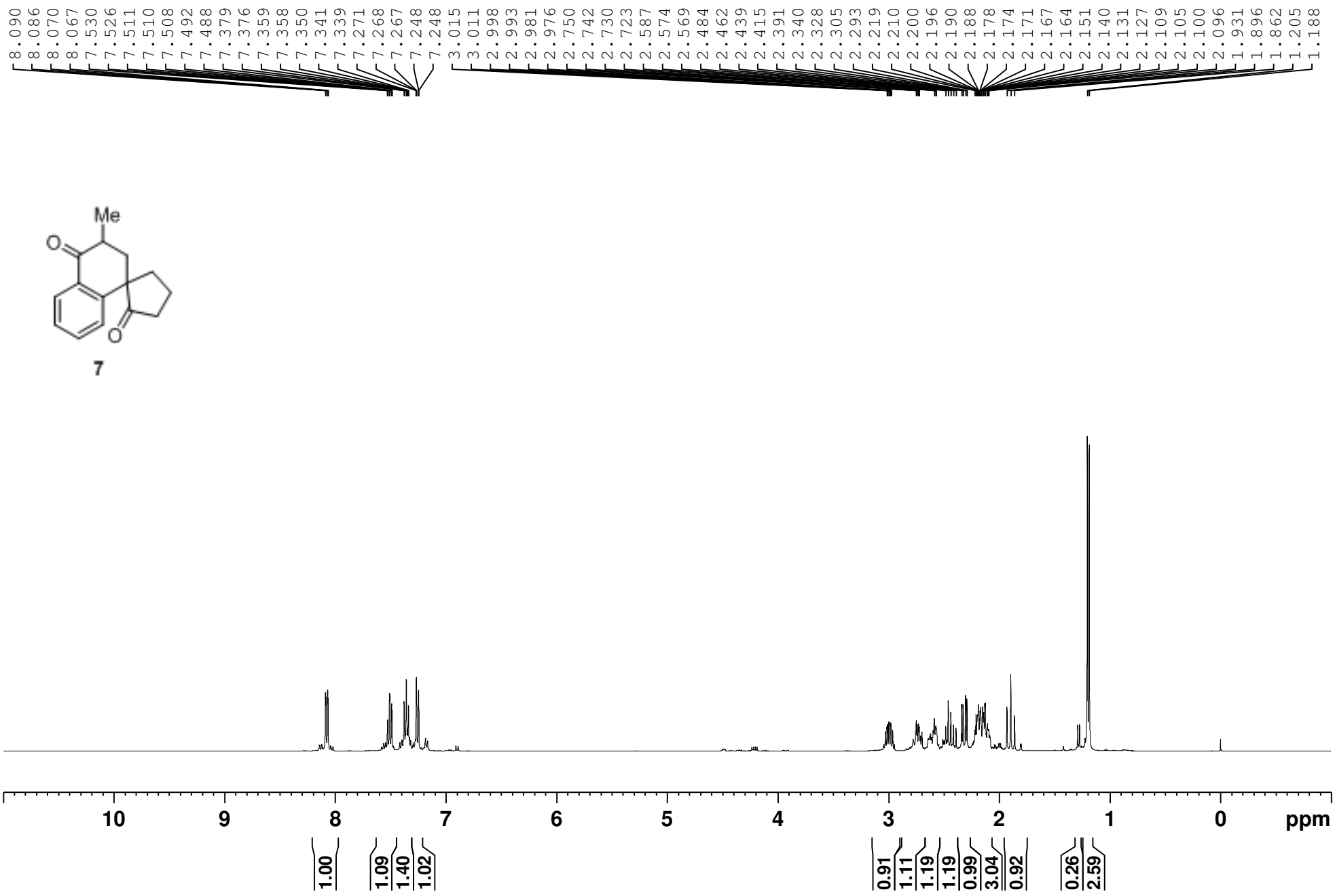
140
120
100
80
60
40
20
ppm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7.359
7.358
7.350
7.341
7.339
7.271
7.268
7.267
7.248
7.248
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3.011
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2.993
2.981
2.976
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2.742
2.730
2.723
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2.200
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2.190
2.188
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2.174
2.171
2.167
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2.100
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1.931
1.896
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1.205
1.188
Me
O
O
7
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.19
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0.99
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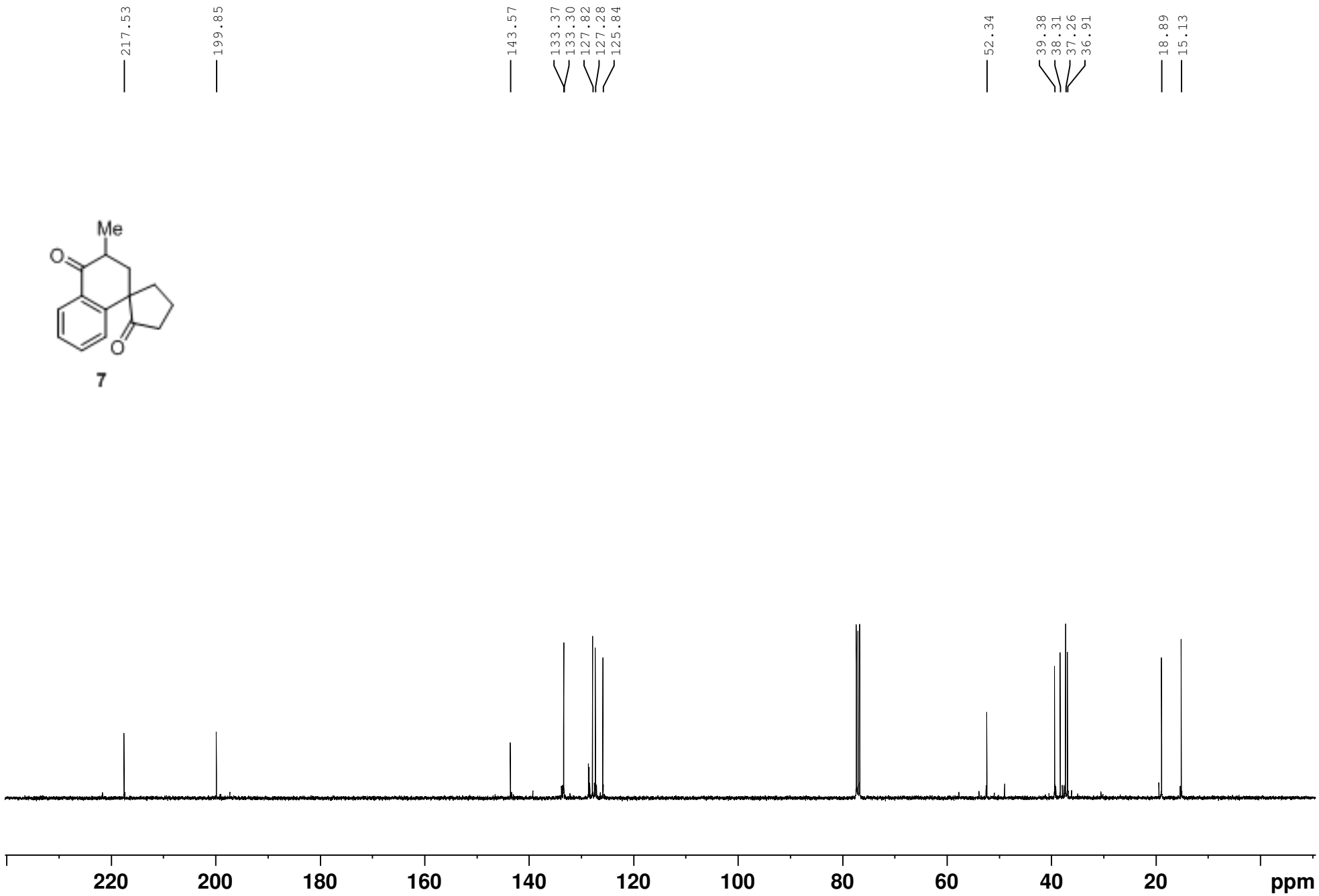
0.92
0.26
2.59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37.26
36.91
18.89
15.13
Me
O
O
7
220
200
180
160
140
120
100
80
60
40
20
ppm