Pd(II)-Catalyzed Decarboxylative Cross-Coupling of Potassium Aryltrifluoroborates with α-Oxocarboxylic Acids at Room Temperature

Mingzong Li, Cong Wang, and Haibo Ge*

Department of Chemistry and Chemical Biology, Indiana University Purdue University Indianapolis, Indianapolis, IN 46202, USA

Supporting information

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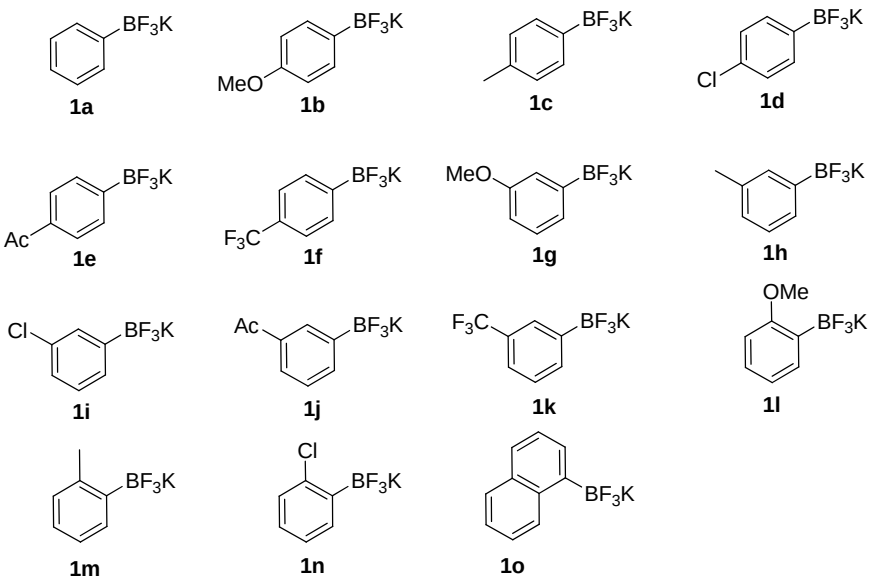
I. General Information

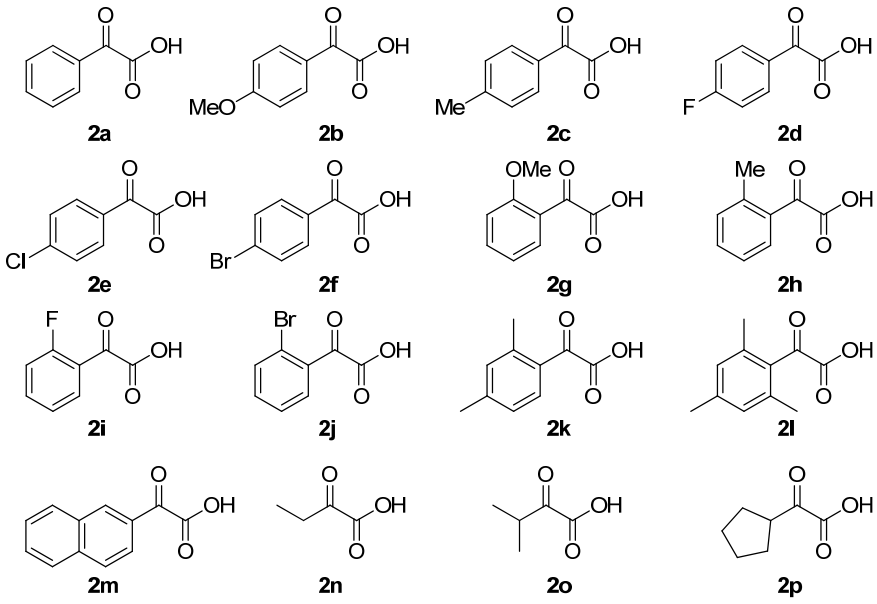
All reactions were carried out in oven-dried glassware. Pd (II) catalysts, $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ were purchased from Acros or Sigma-Aldrich. Anhydrous dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich and used directly. All other solvents and commercially available reagents (SeO_2, boronic acids and KHF_2) were purchased from Fisher, Sigma-Aldrich, Acros or TCI and used directly. For TLC analysis, precoated plates (w/h F254, Dynamic Adsorbents Inc, 0.25 mm thick) were used; for air-flashed column chromatography, Flash Silica Gel (Dynamic Adsorbents Inc, 32-63 μm) was used. The ^1H and ^{13}C NMR spectra were obtained on a Bruker 500 MHz NMR Fourier transform spectrometer. ^1H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Analytical gas chromatography (GC) was performed on an Agilent 6890-5975 GC-MS system with electron impact (EI) ionization detector, using diphenyl ether as internal standard to determine the crude yields.

II. Experimental Section

Preparation of starting materials:



Aryltrifluoroborates (**1**)

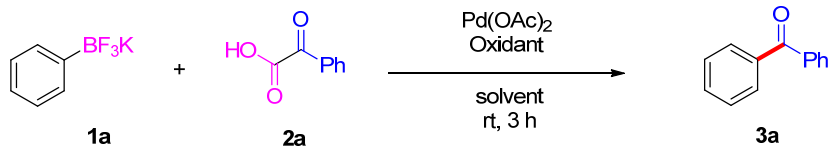


α-Oxocarboxylic acids (**2**)

Potassium aryltrifluoroborate (**1a**, **1d**, and **1g)**, and α-oxocarboxylic acids (**2a**, **2l**, and **2n**) were purchased from Sigma-Aldrich, TCI or Acros. Other potassium aryltrifluoroborates were

prepared from boronic acids with KHF_2 according to the reported procedure[1]. Other α-oxocarboxylic acids were prepared from oxidation of corresponding methyl ketones with SeO_2 according to the reported procedure.[2]

General procedure of reaction conditions screening

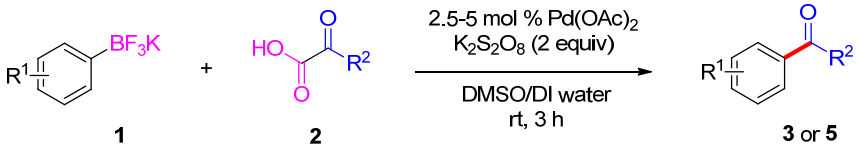


An 8 mL vial was charged with magnetic stir bar, $PhBF_3K$ (**1a**, 0.3 mmol), phenylglyoxylic acids (**2a**, 0.6 mmol), oxidant (0.6 mmol), Pd source, followed by DMSO and DI water (3 mL in total). After stirring at room temperature for 3 h, diphenyl ether (48 μL, 0.3 mmol) was added. The reaction mixture was quenched with NaOH (1 N, 3 mL), extracted with EtOAc. The combined organic phase was dried over Na_2SO_4, and analyzed on GC-MS for GC yields. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Hexanes: 0 ~ 2%, v/v) (entry 12, table 1).

GC Method

The samples were analyzed on an Agilent 6890-5973 GC-MS system. The mass detector is the 5973 mass spectrum operating with electron impact (EI) ionization. Column is an Agilent J & W GC column, 30 m long, 0.250 mm I. D., 0.25 μm film. Method details: A 1 μL injection using a 100:1 split and a 280 degree split/splitless injector. Oven temperature: starting at 50 degrees, holding for 2 min, ramping 20 degrees/min to 280, passing through a 280 degree transfer line to the MS which scanned from 50-500 m/z.

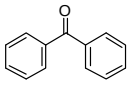
General procedure of the optimal reaction condition



An 8 mL vial was charged with magnetic stir bar, $ArBF_3K$ (**1**, 0.3mmol), α-oxocarboxylic acids (**2**, 0.6 or 0.9 mmol, 2 or 3 equiv), $K_2S_2O_8$ (0.6 mmol, 2 equiv), followed by $Pd(OAc)_2$

(DMSO solution, 0.0075 mmol/1.2 mL, 2.5 mol % or 0.015 mmol/1.2 mL, 5 mol %, 1.2 mL) and DI water (1.8 mL, DMSO: DI water = 1/1.5, v/v, 3 ml). After stirring at room temperature for 3 hours, the reaction was quenched with NaOH (1 N, 3 mL), extracted with EtOAc. Then the combined organic phase was dried over Na_2SO_4, concentrated, and purified by flash chromatography column on silica gel (gradient eluent of EtOAc in Hexanes: 0 ~ 5%, v/v) to yield the product **3** or **5**.

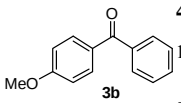
NMR Data of Products



3a

Benzophenone[3]

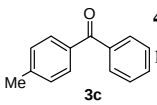
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47-7.50 (m, 4 H), 7.58-7.61 (m, 2 H), 7.80-7.82 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 128.3, 130.1, 132.4, 137.6, 196.8.



3b

4-Methoxybenzophenone[4]

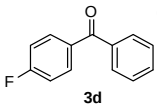
^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.89 (s, 3 H), 6.95-6.98 (m, 2 H), 7.47 (dd, J = 7.5, 7.8 Hz, 2 H), 7.55-7.58 (m, 1 H), 7.75 (dd, J = 1.4, 8.4 Hz, 2 H), 7.82-7.84 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.5, 113.8, 128.2, 129.8, 130.2, 131.9, 132.6, 138.3, 163.2, 195.6.



3c

4-Methylbenzophenone[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.44 (s, 3 H), 7.28 (t, J = 8.0 Hz, 2 H), 7.47 (dd, J = 7.6, 7.7 Hz, 2 H); 7.58 (dd, J = 7.4, 7.5 Hz, 1 H), 7.73 (d, J = 8.1 Hz, 2 H), 7.79 (d, J = 7.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.7, 128.2, 129.0, 130.0, 130.3, 132.2, 134.9, 138.0, 143.3, 196.5.

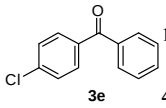


3d

4-Fluorobenzophenone[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.14-7.19 (m, 2 H), 7.49 (dd, J = 7.5, 7.8 Hz, 2 H), 7.60 (m, 1 H), 7.77 (dd, J = 1.2, 8.3 Hz, 2 H), 7.83-7.86 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 115.5 (d, $J_{C,F}$ = 21.3 Hz), 128.4, 129.9, 132.5, 132.6 (d, $J_{C,F}$ = 20.0 Hz), 133.8 (d, $J_{C,F}$ = 2.5 Hz), 137.5, 165.4 (d, $J_{C,F}$ = 252.5 Hz), 195.3.

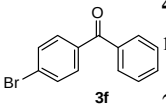
4-Chlorobenzophenone[4]



3e

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45-7.51 (m, 4 H), 7.59-7.62 (m, 1 H), 7.45-7.78 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 128.4, 128.7, 130.0, 131.5, 132.7, 135.9, 137.3, 138.9, 195.5.

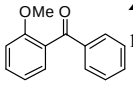
4-Bromobenzophenone[6]



3f

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48-7.51 (m, 2 H), 7.59-7.64 (m, 3 H), 7.67-7.69 (m, 2 H), 7.68 (dd, J = 1.4, 8.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 127.5, 128.4, 129.9, 131.5, 131.6, 132.6, 136.3, 137.2, 195.6.

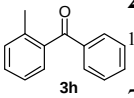
2-Methoxybenzophenone[4]



3g

^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.72 (s, 3 H), 6.99-7.05 (m, 2 H), 7.36 (dd, J = 1.7, 7.5 Hz, 1 H), 7.41-7.49 (m, 3 H), 7.55 (m, 1 H), 7.81 (dd, J = 1.25, 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.6, 111.5, 120.5, 128.2, 128.9, 129.6, 129.9, 131.9, 133.0, 127.8, 157.4, 196.5.

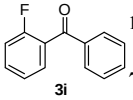
2-Methylbenzophenone[6]



3h

^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.34 (s, 3 H), 7.24-7.27 (m, 1 H), 7.29-7.34 (m, 2 H), 7.38-7.41 (m, 1 H), 7.44-7.50 (m, 2 H), 7.57-7.60 (m, 1 H), 7.80-7.81 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.0, 125.2, 128.47, 128.53, 130.2, 130.3, 131.0, 133.2, 136.8, 137.7, 138.6, 198.7.

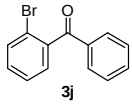
2-Fluorobenzophenone[7]



3i

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.16 (dd, J = 9.0, 9.2 Hz, 1 H), 7.24-7.29 (m, 1 H), 7.46-7.49 (m, 2 H), 7.51-7.62 (m, 3 H), 7.84 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 116.3 (d, $J_{C,F}$ = 21.3 Hz), 124.3 (d, $J_{C,F}$ = 3.8 Hz), 127.0 (d, $J_{C,F}$ = 21.3 Hz), 128.5, 129.8, 130.8 (d, $J_{C,F}$ = 2.5 Hz), 133.1 (d, $J_{C,F}$ = 8.8 Hz), 133.4, 137.4 , 160.1 (d, $J_{C,F}$ = 250.0 Hz), 193.5.

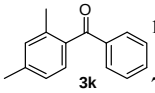
2-Bromobenzophenone[8]



3j

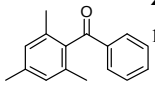
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.36 (m, 2 H), 7.41-7.48 (m, 3 H), 7.59-7.66 (m, 2 H), 7.81 (dd, J = 1.2, 8.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 119.5, 127.2, 128.7, 129.0, 130.3, 131.2, 133.2, 133.8, 136.1, 140.7, 195.9.

2,4-Dimethylbenzophenone[5]



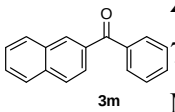
^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.33 (s, 3 H), 2.38 (s, 3 H), 7.05 (d, *J* = 7.7 Hz, 1 H), 7.11 (s, 1 H), 7.23 (d, *J* = 7.7 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 2 H), 7.55-7.58 (m, 1 H), 7.79 (dd, *J* = 0.6, 7.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.1, 21.4, 125.8, 128.4, 129.3, 130.1, 131.9, 132.9, 135.6, 137.3, 138.2, 140.7, 198.6.

2,4,6-Trimethylbenzophenone[9]



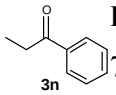
^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.08 (s, 6 H), 2.33 (s, 3 H), 6.90 (s, 2 H), 7.44 (dd, *J* = 7.6, 7.9 Hz, 2 H), 7.56-7.59 (m, 1 H), 7.81 (d, *J* = 7.9 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 19.4, 21.2, 128.3, 128.8, 129.4, 133.6, 134.2, 136.9, 137.3, 138.5, 200.8.

2-Naphthylphenone[10]



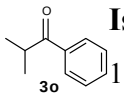
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51-7.58 (m, 3 H), 7.60-7.64 (m, 2 H), 7.86-7.87 (m, 2 H), 7.91-7.95 (m, 4 H), 8.27 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 125.8, 126.8, 127.8, 128.29, 128.33, 128.4, 129.4, 130.1, 131.9, 132.3, 132.4, 134.8, 135.3, 137.9, 196.8.

Propiophenone[11]



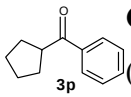
^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.23 (t, *J* = 7.2 Hz, 3 H), 3.01 (q, *J* = 7.2 Hz, 2 H), 7.45-7.48 (m, 2 H), 7.54-7.55 (m, 1 H), 7.96-7.98 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 8.3, 31.8, 128.0, 128.6, 132.9, 136.9, 200.9.

Isobutyrophenone[3]



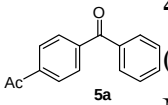
^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.22 (d, *J* = 6.9 Hz, 6 H), 3.56 (m, 1 H), 7.47 (dd, 7.5, 7.9 Hz, 2 H), 7.54-7.55 (m, 1 H), 7.95 (dd, *J* = 1.4, 7.9 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 19.2, 35.4, 128.3, 128.6, 132.8, 136.2, 204.6.

Cyclopentylphenone[11]

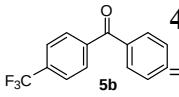


^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.62-1.75 (m, 4 H), 1.90-1.94 (m, 4 H), 3.69-3.75 (m, 1 H), 7.46 (dd, *J* = 7.2, 7.9 Hz, 2 H), 7.53-7.56 (m, 1 H), 7.98 (dd, *J* = 1.4, 8.9 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.3, 30.0, 46.4, 128.47, 128.51, 132.7, 136.9, 202.9.

4-Acetobenzophenone[3]

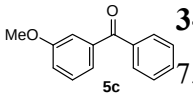


^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.67 (s, 3 H), 7.49-7.52 (m, 2 H), 7.59-7.64 (m, 1 H), 7.80-7.87 (m, 4 H), 8.06 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.9, 128.2, 128.5, 130.06, 130.12, 133.0, 136.9, 139.6, 141.4, 196.0, 197.6.



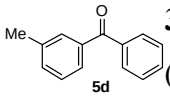
5b

4-Trifluoromethylbenzophenone[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (dd, *J* = 7.7, 7.8 Hz, 2 H), 7.61-7.64 (m, 1 H), 7.75-7.82 (m, 4 H), 7.90 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 123.7 (q, $J_{C,F}$ = 271.3 Hz), 125.4 (q, $J_{C,F}$ = 3.8 Hz), 128.5, 130.12, 130.15, 133.1, 133.7 (q, $J_{C,F}$ = 32.5 Hz), 136.7, 140.7, 195.6.



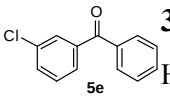
5c

3-Methoxybenzophenone[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.86 (s, 3 H), 7.12-7.15 (m, 1 H), 7.33-7.39 (m, 3 H), 7.48 (dd, *J* = 7.6, 7.8 Hz, 2 H), 7.57-7.60 (m, 1 H), 7.81 (dd, *J* = 1.3, 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.5, 114.3, 118.9, 122.9, 128.3, 129.2, 130.1, 132.4, 137.6, 138.9, 159.6, 196.5.



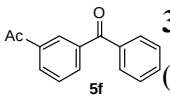
5d

3-Methylbenzophenone[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.42 (s, 3 H), 7.35-7.41 (m, 2 H), 7.48 (dd, *J* = 7.6, 7.8 Hz, 2 H), 7.57-7.63 (m, 3 H), 7.81 (dd, *J* = 1.2, 8.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.4, 127.4, 128.1, 128.3, 130.1, 130.5, 132.4, 133.2, 137.6, 137.8, 138.2, 197.0.



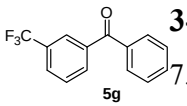
5e

3-Chlorobenzophenone[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 (dd, *J* = 7.8, 7.9 Hz, 1 H), 7.52 (dd, *J* = 7.6, 7.8 Hz, 2 H), 7.55-7.57 (m, 1 H), 7.60-7.63 (m, 1 H), 7.66-7.68 (m, 1 H), 7.78-7.80 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 128.1, 128.5, 129.7, 129.9, 130.0, 132.4, 132.9, 134.6, 137.0, 139.3, 195.3.



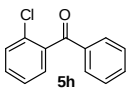
5f

3-Acetobenzophenone[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.65 (s, 3 H), 7.47-7.52 (m, 2 H), 7.59-7.62 (m, 2 H), 7.79-7.81 (m, 2 H), 7.98-8.00 (m, 1 H), 8.17-8.19 (m, 1 H), 8,36-8.37 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.8, 128.5, 128.8, 129.7, 130.1, 131.8, 132.9, 134.3, 137.0, 137.2, 138.1, 196.9, 197.4.



5g

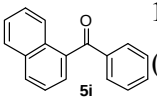
3-Trifluoromethylbenzophenone[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 (dd, *J* = 7.6, 7.8 Hz, 2 H), 7.64 (dd, , *J* = 7.3, 7.5 Hz, 2 H), 7.79-7.86 (m, 3 H), 7.98 (d, *J* = 7.7 Hz, 1 H), 8.07 (s 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 123.7 (q, $J_{C,F}$ = 271.3 Hz), 126.7 (q, $J_{C,F}$ = 3.8 Hz), 128.6, 128.8 (q, $J_{C,F}$ = 3.8 Hz), 129.0, 130.0, 131.1 (q, $J_{C,F}$ = 33.1 Hz), 133.0, 133.1, 136.8, 138.3, 195.2.



5h

2-Chlorobenzophenone[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.38 (m, 2 H), 7.44-

7.62 (m, 4 H), 7.59-7.59 (m, 1 H), 7.81-7.83 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 126.7, 128.3, 128.6, 129.1, 130.1, 131.1, 131.3, 133.7, 136.5, 138.6, 195.3.



5i

1-Naphthylphenone[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45-56 (m, 5 H), 7.59-7.62 (m, 2 H), 7.87 (d, *J* = 7.5 Hz, 2 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 8.01 (d, *J* = 8.2 Hz, 1 H), 8.09 (d, *J* = 8.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 124.3, 125.7, 126.5, 127.3, 127.8, 128.4, 128.5, 129.7, 130.4, 131.3, 133.2, 133.7, 136.4, 138.3, 195.6.

III. References and notes:

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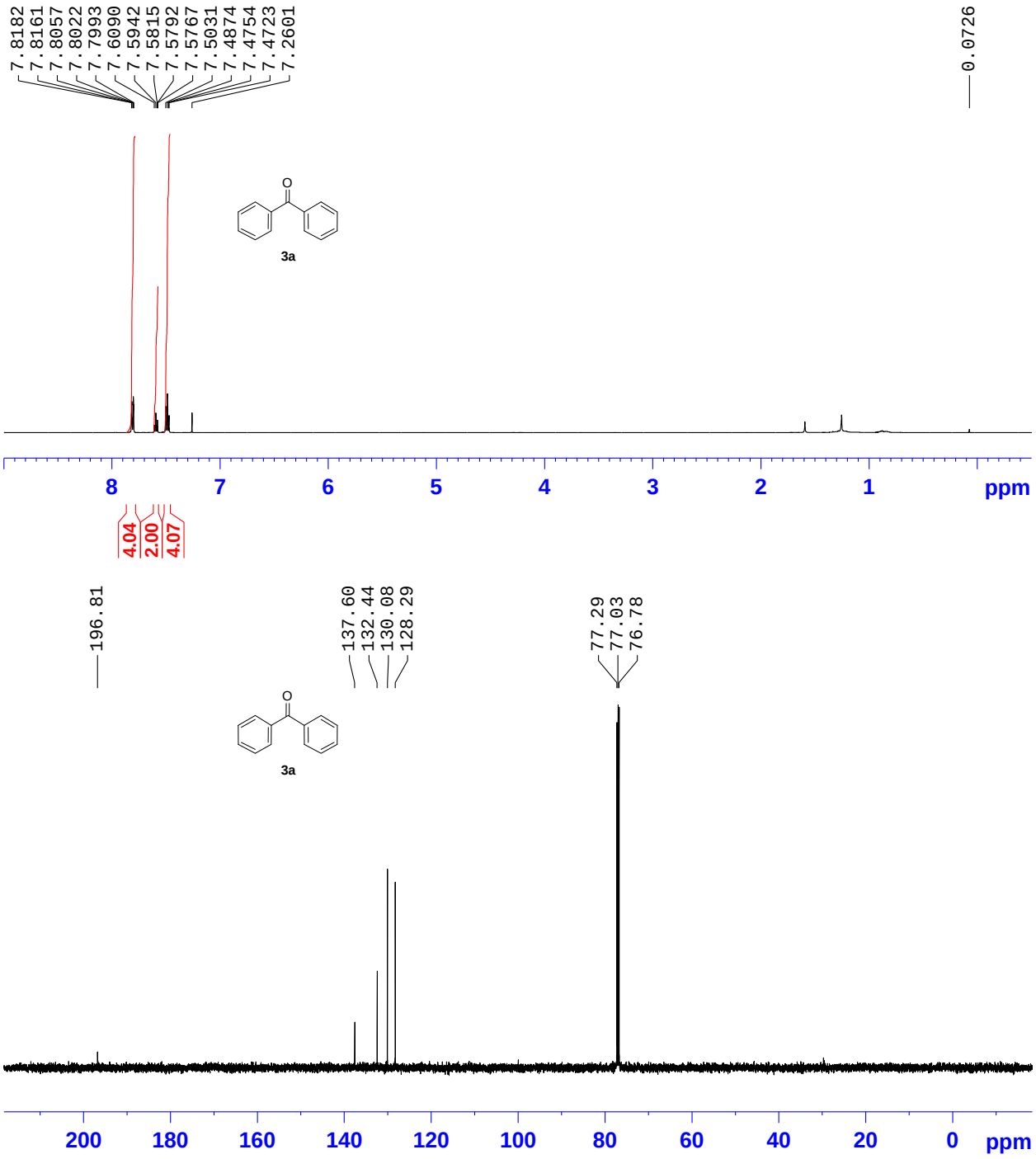
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7.4723
7.2601
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7
6
5
4
3
2
1
ppm
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2.00
4.07
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130.08
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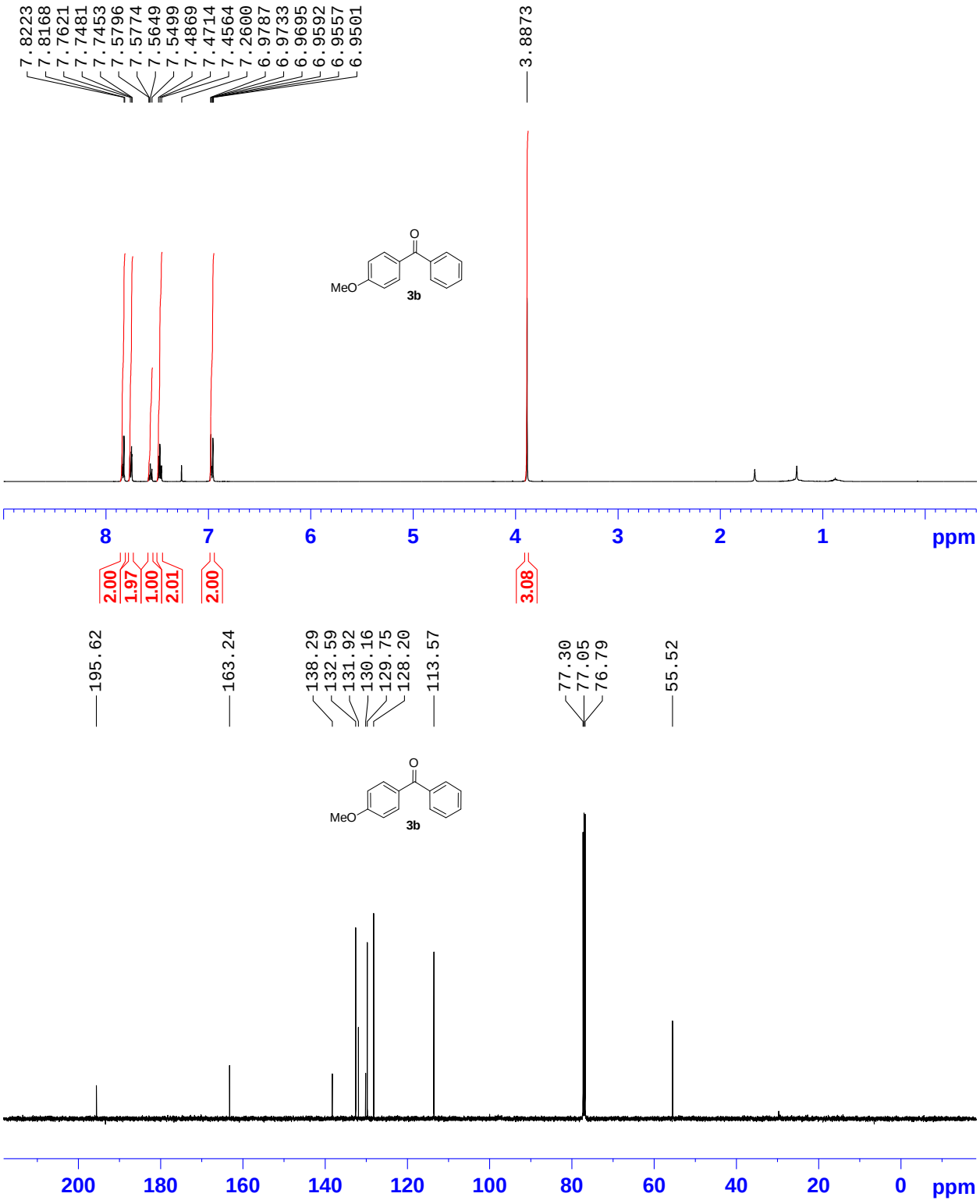
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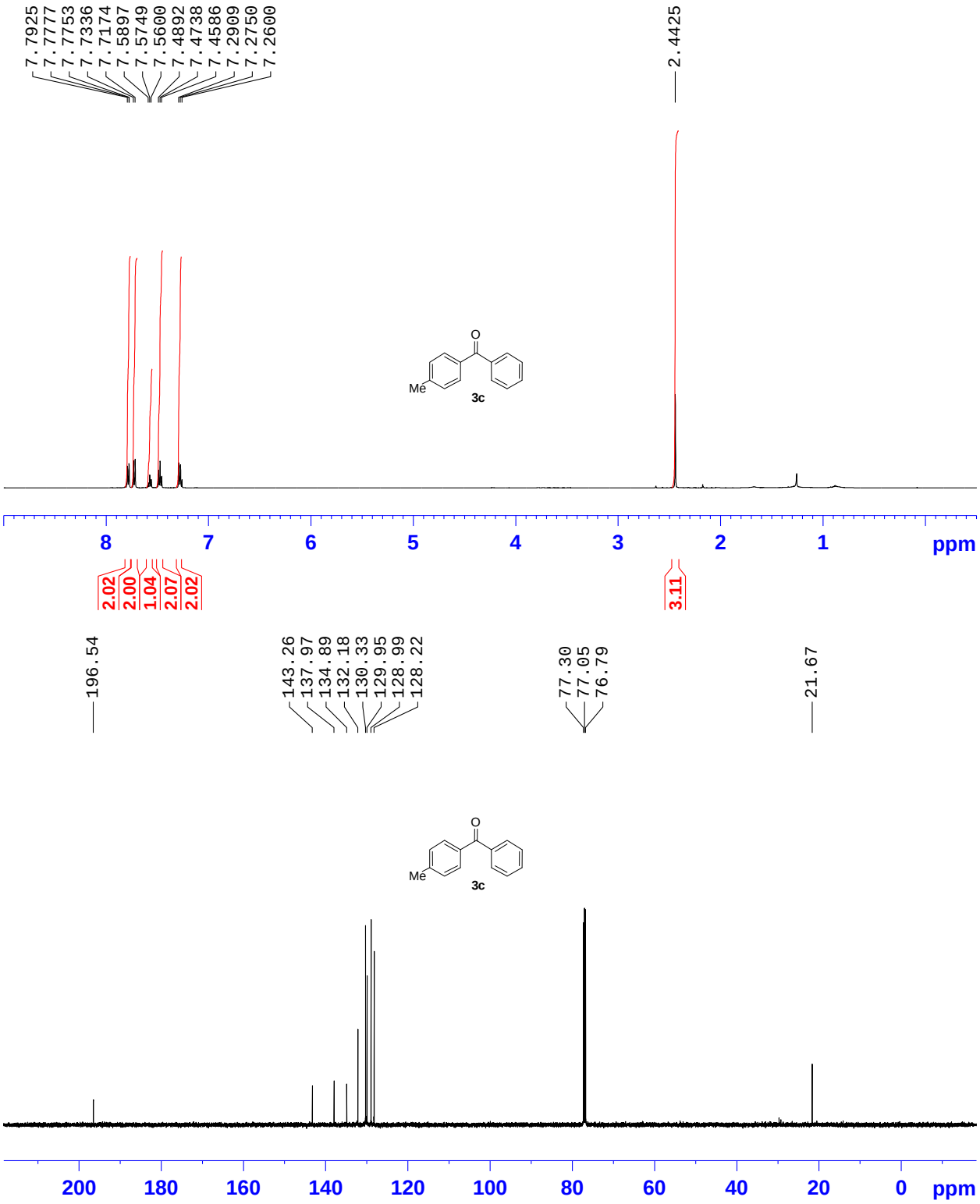
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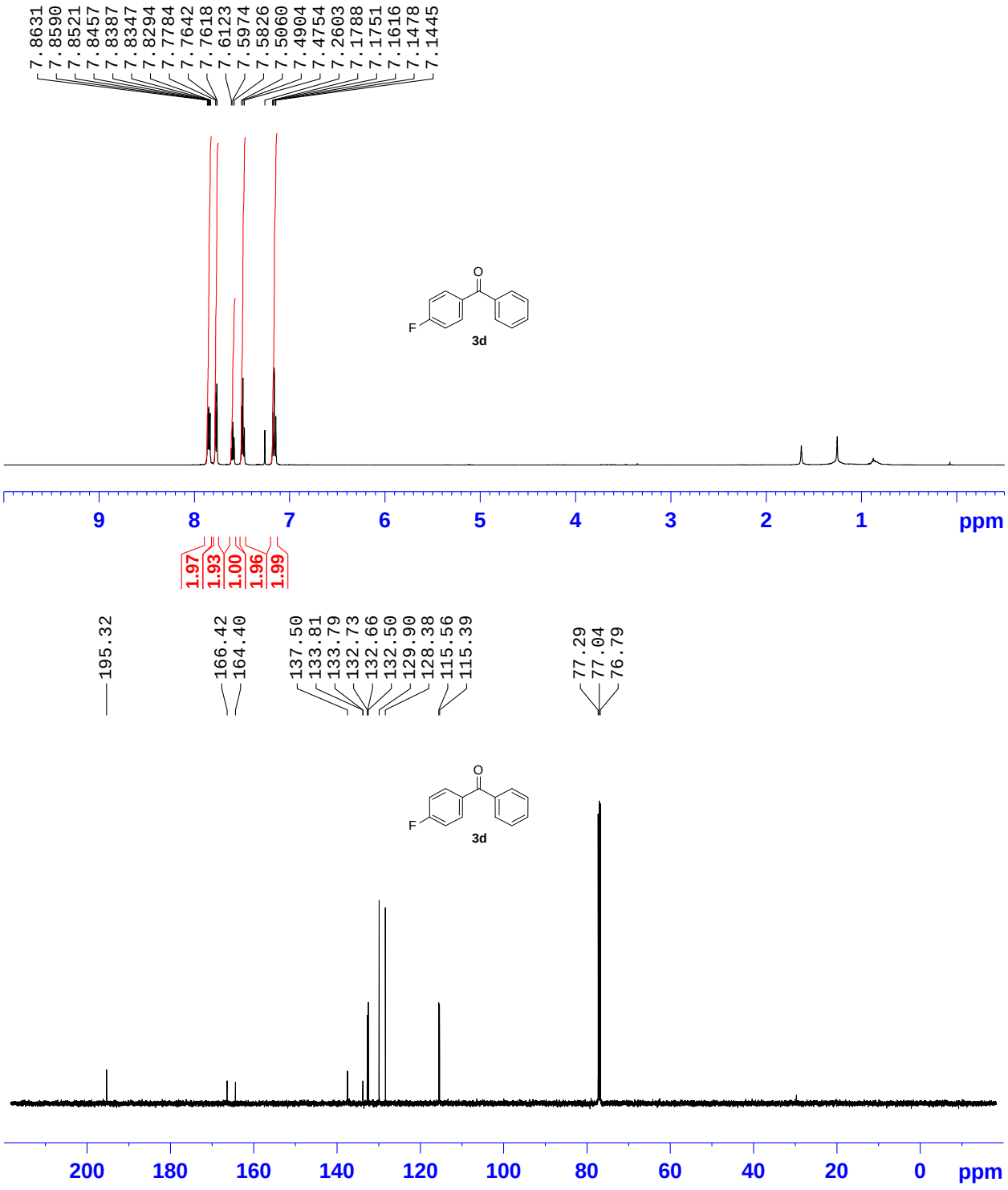
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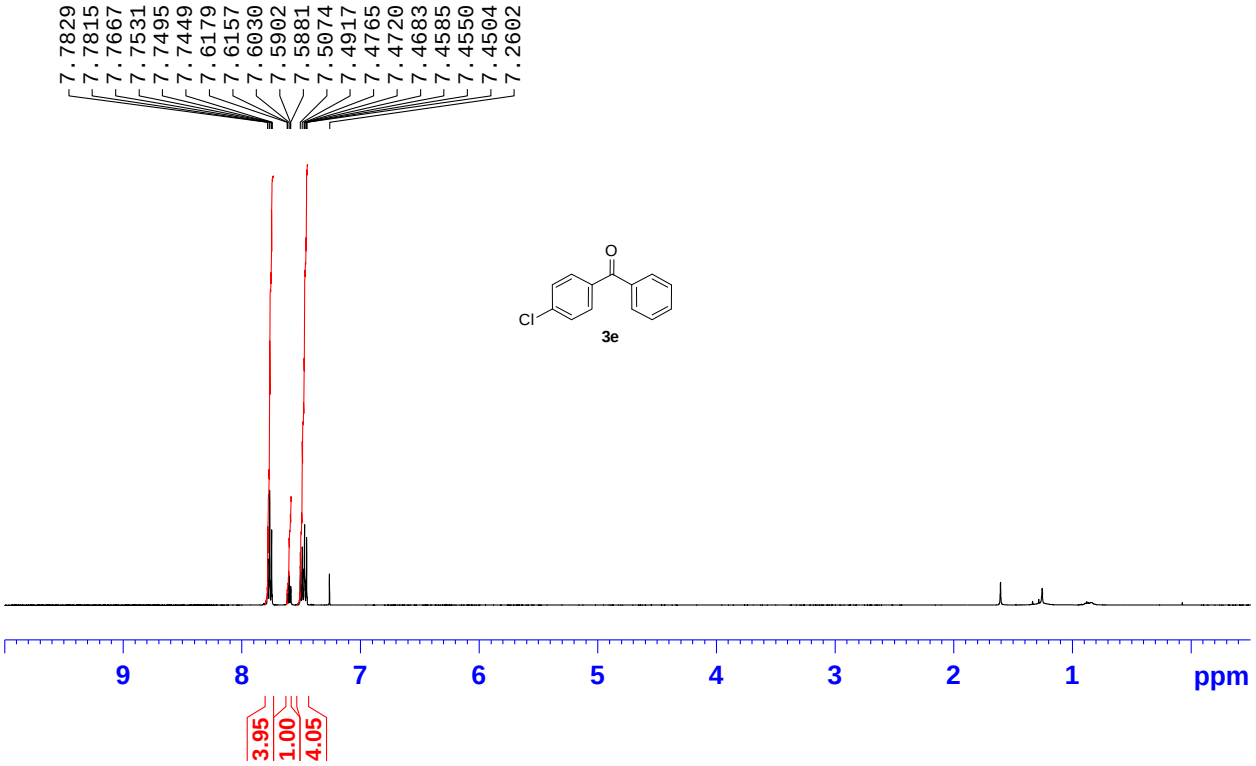
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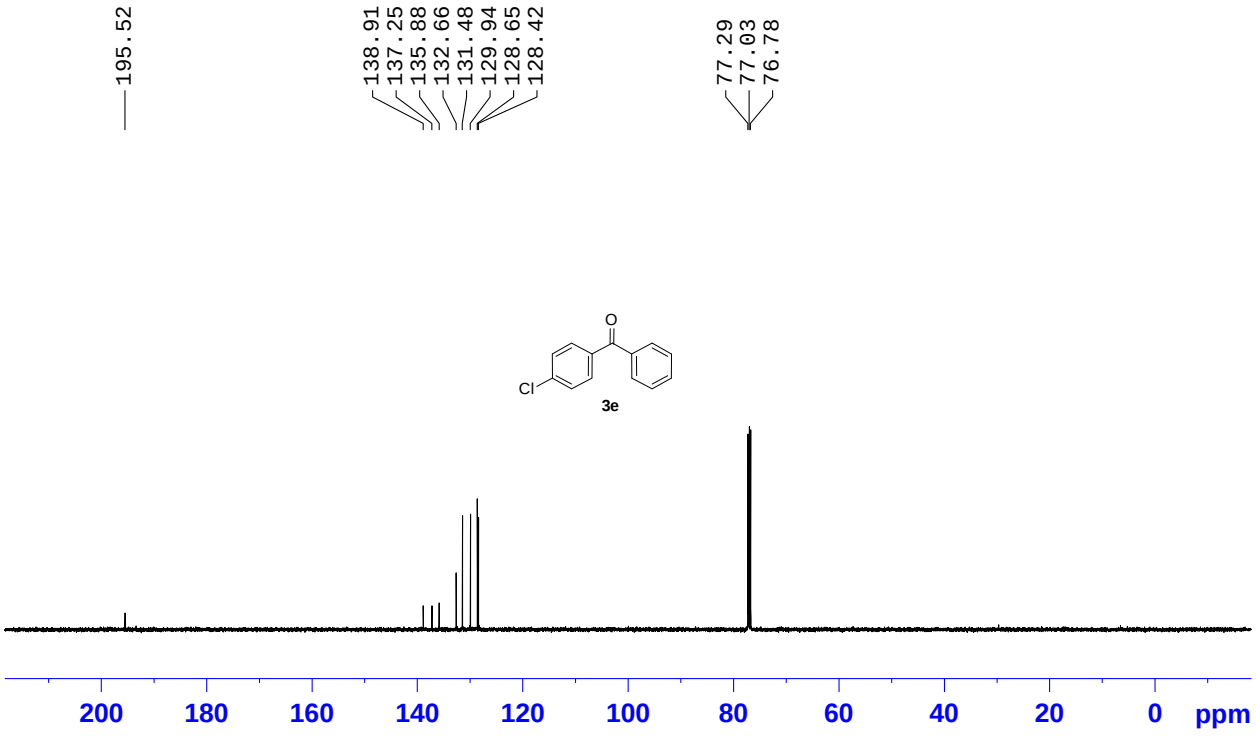
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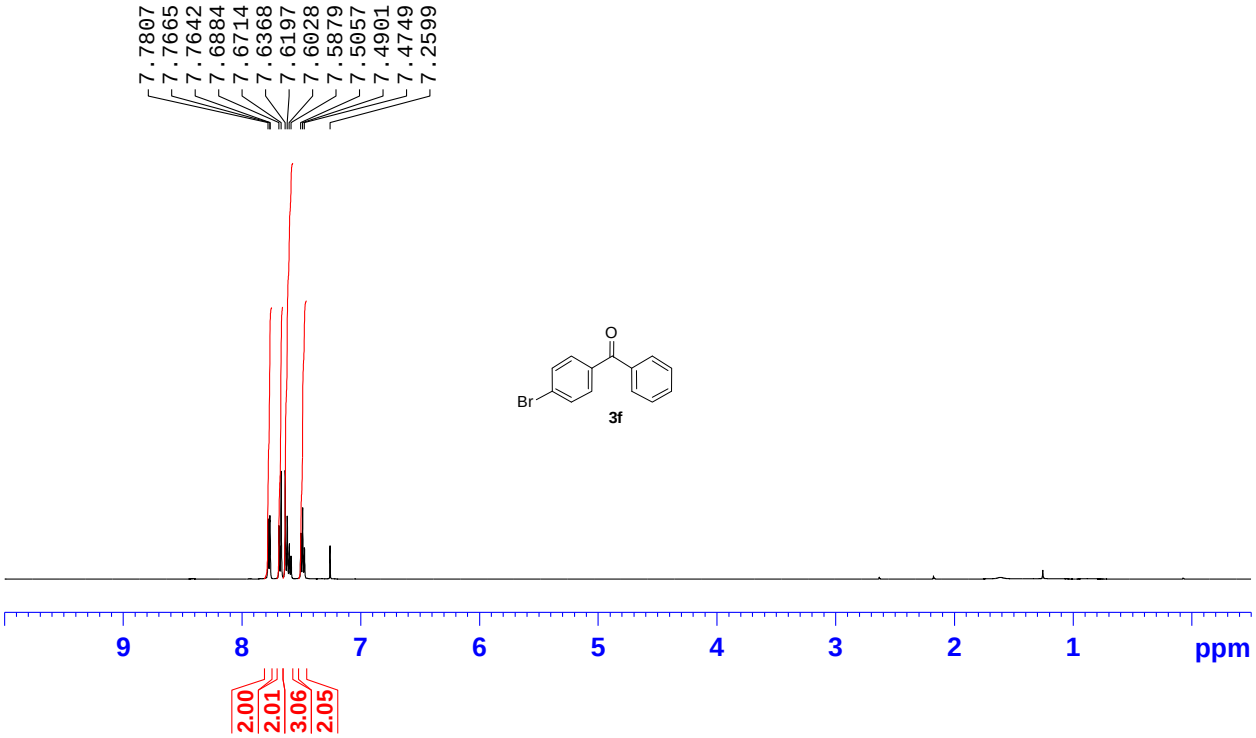
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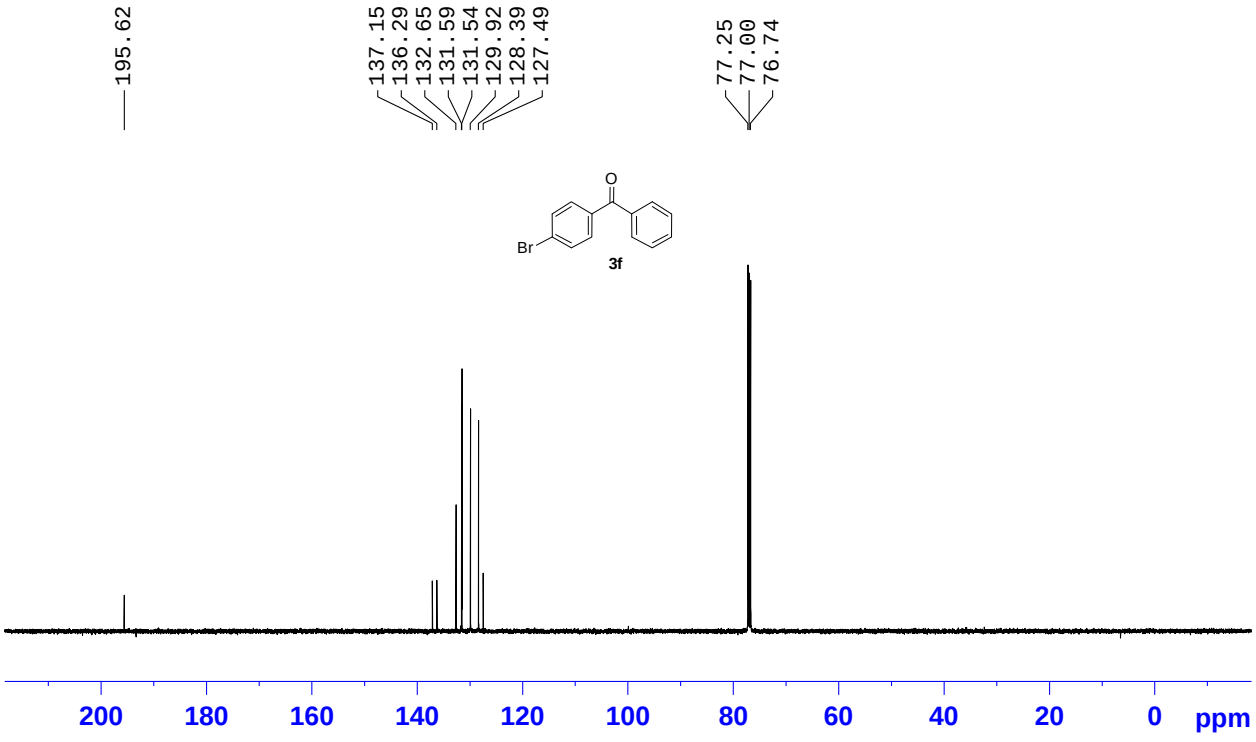
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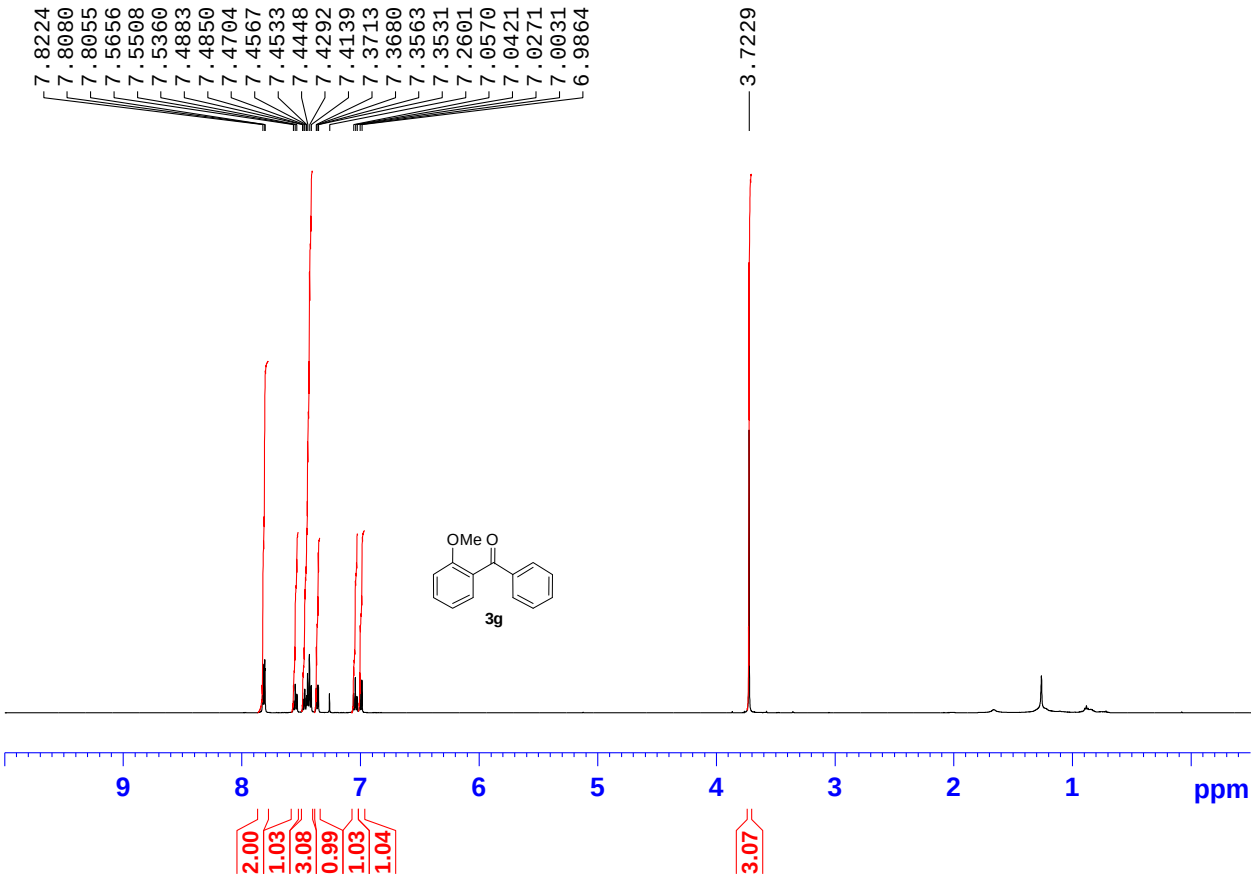
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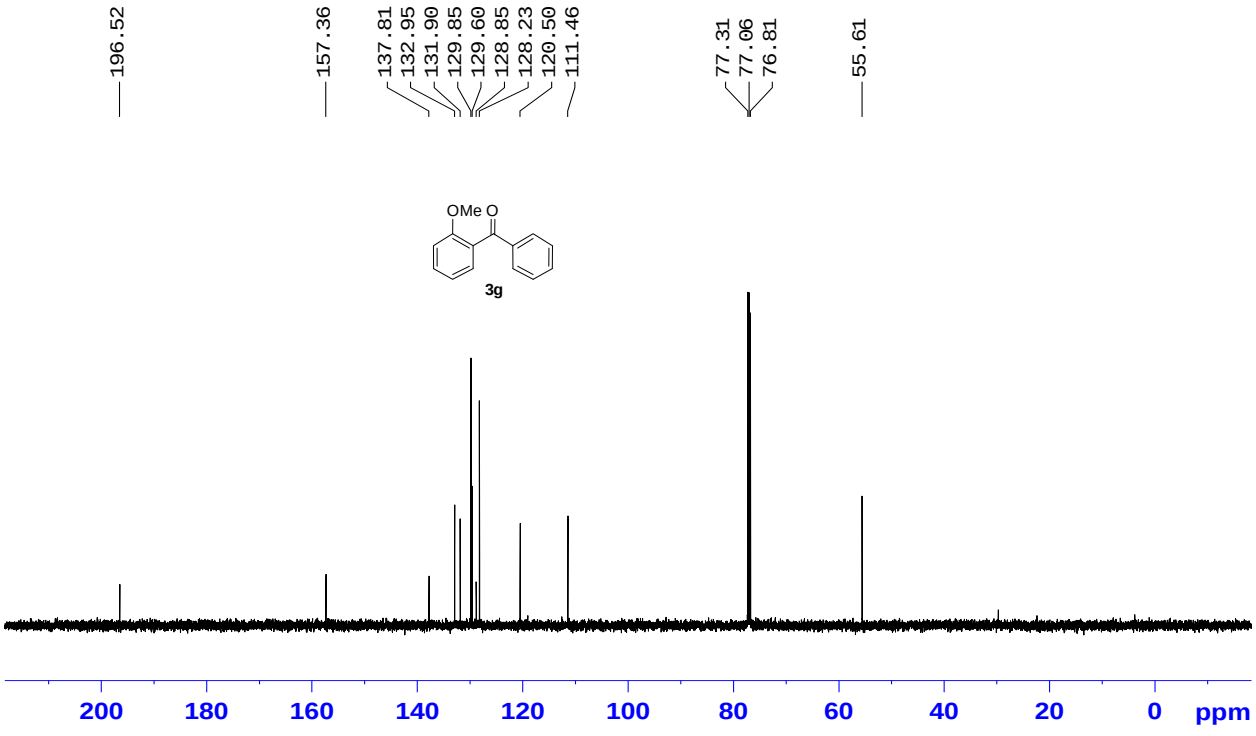
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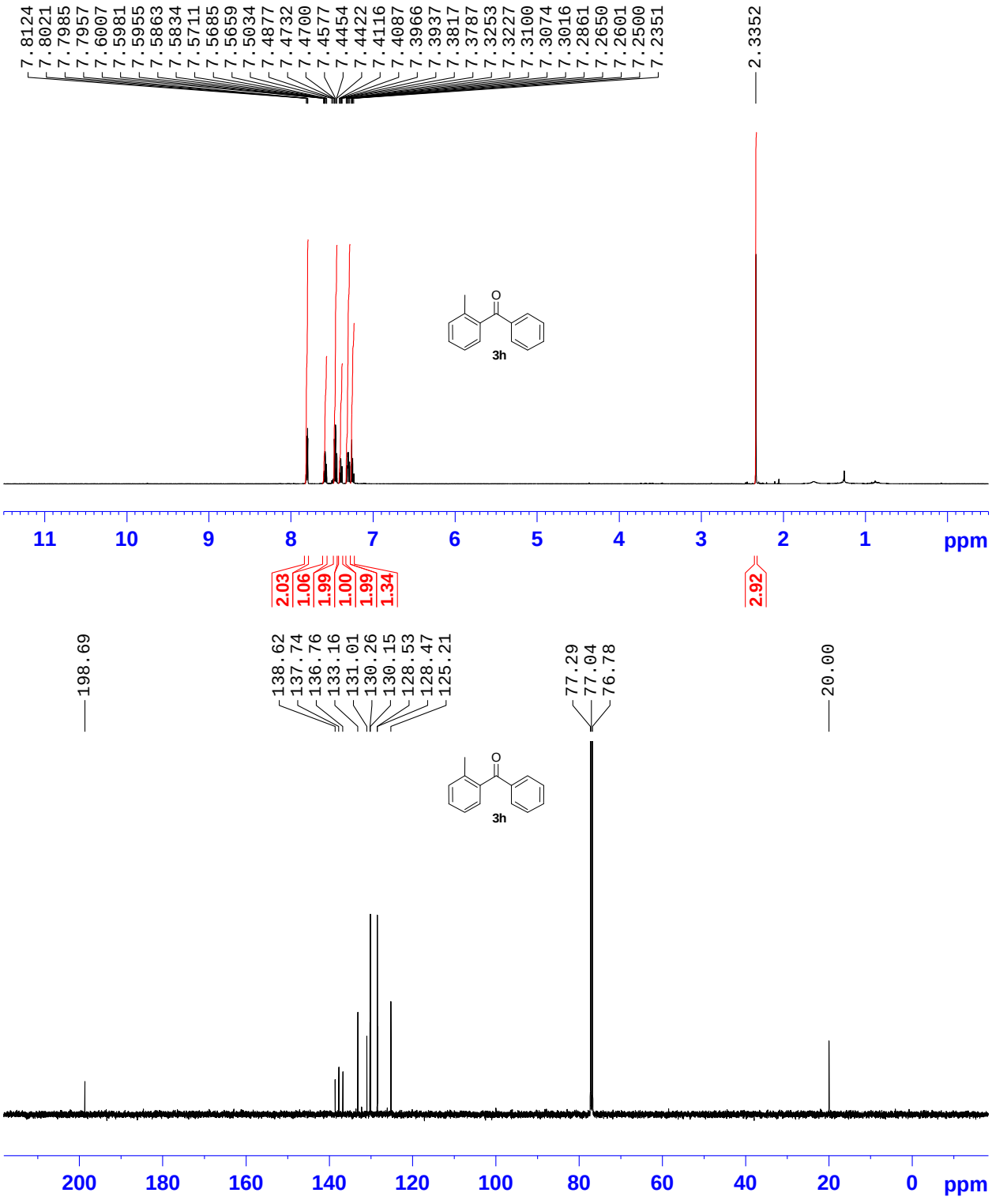
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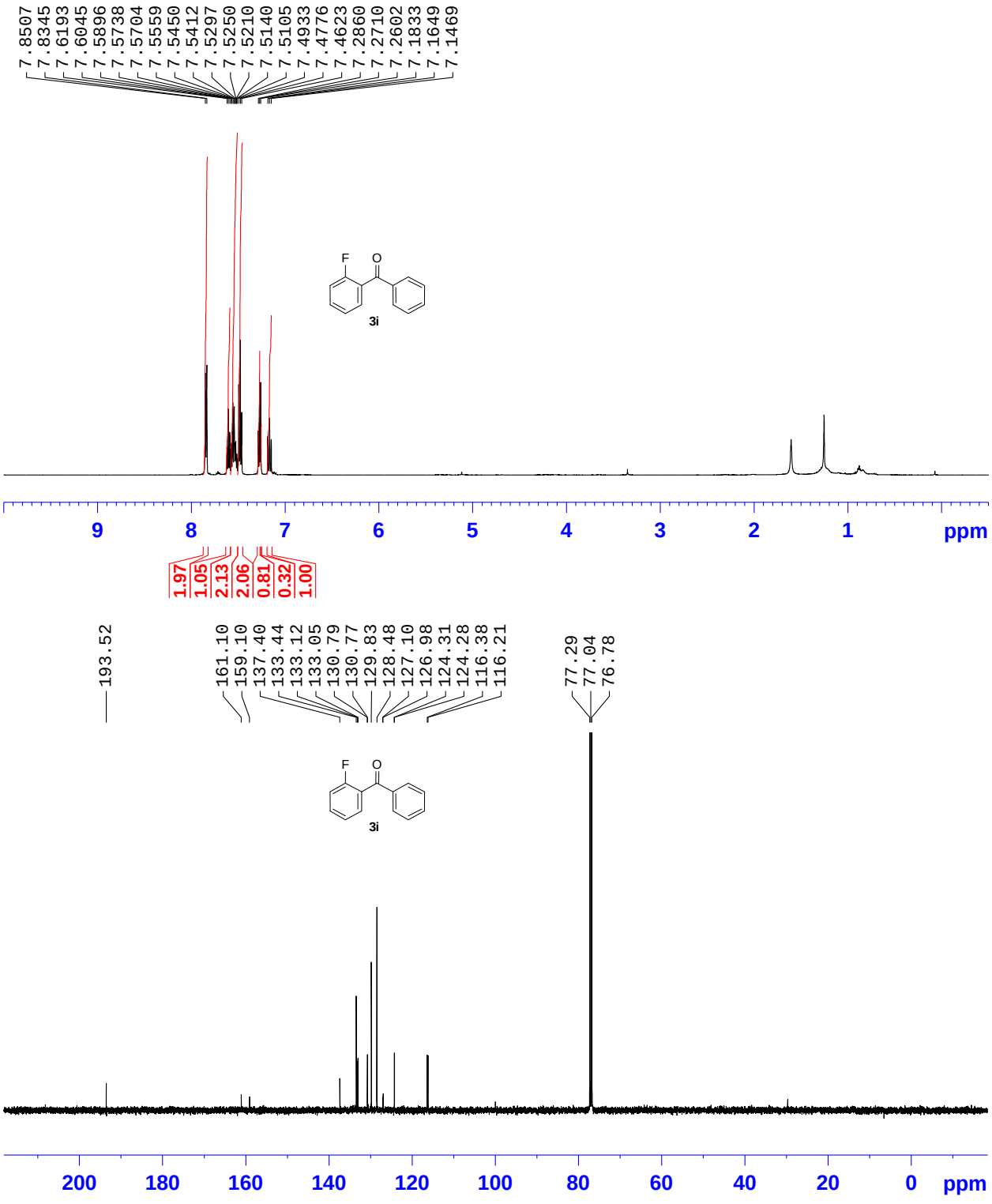
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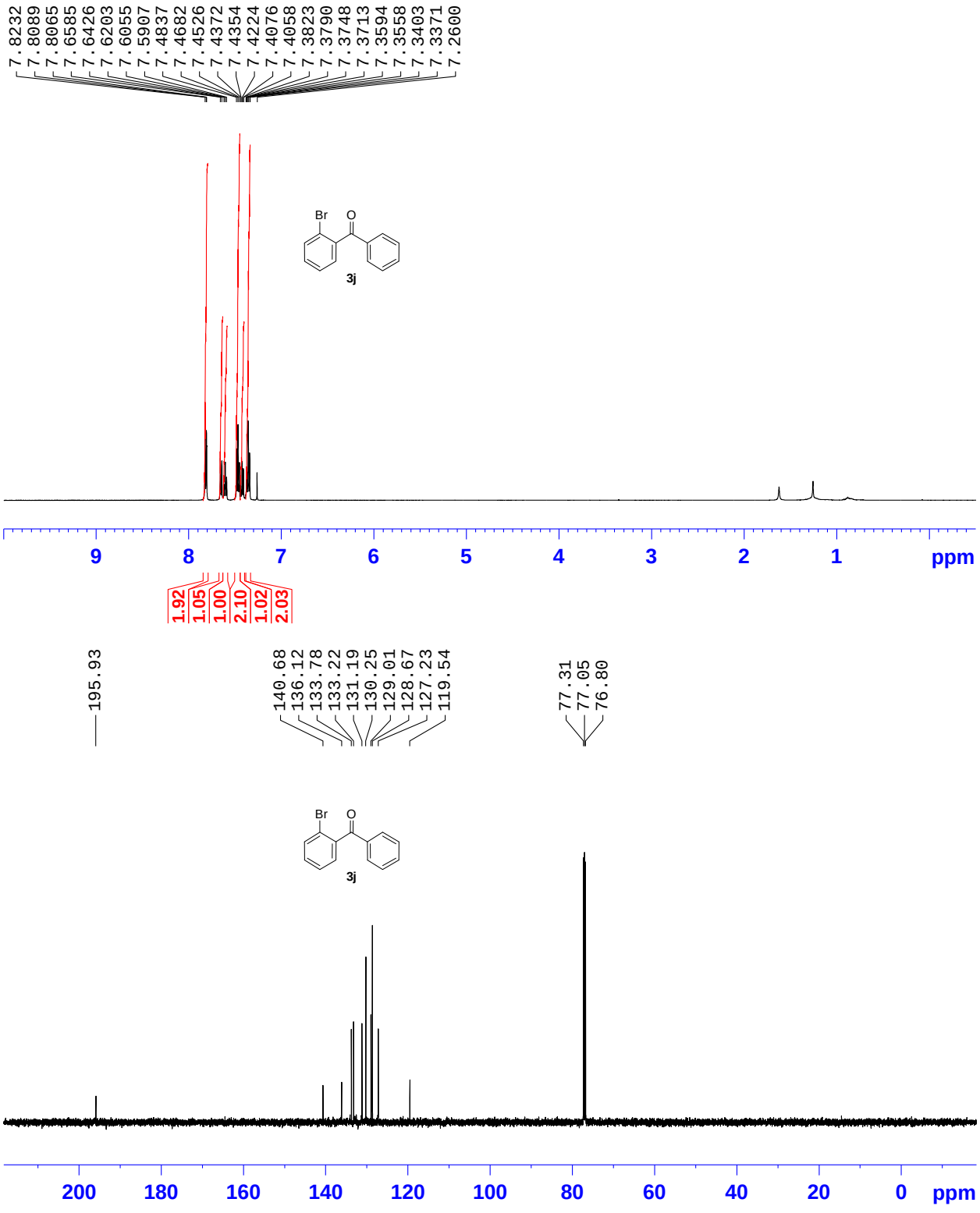
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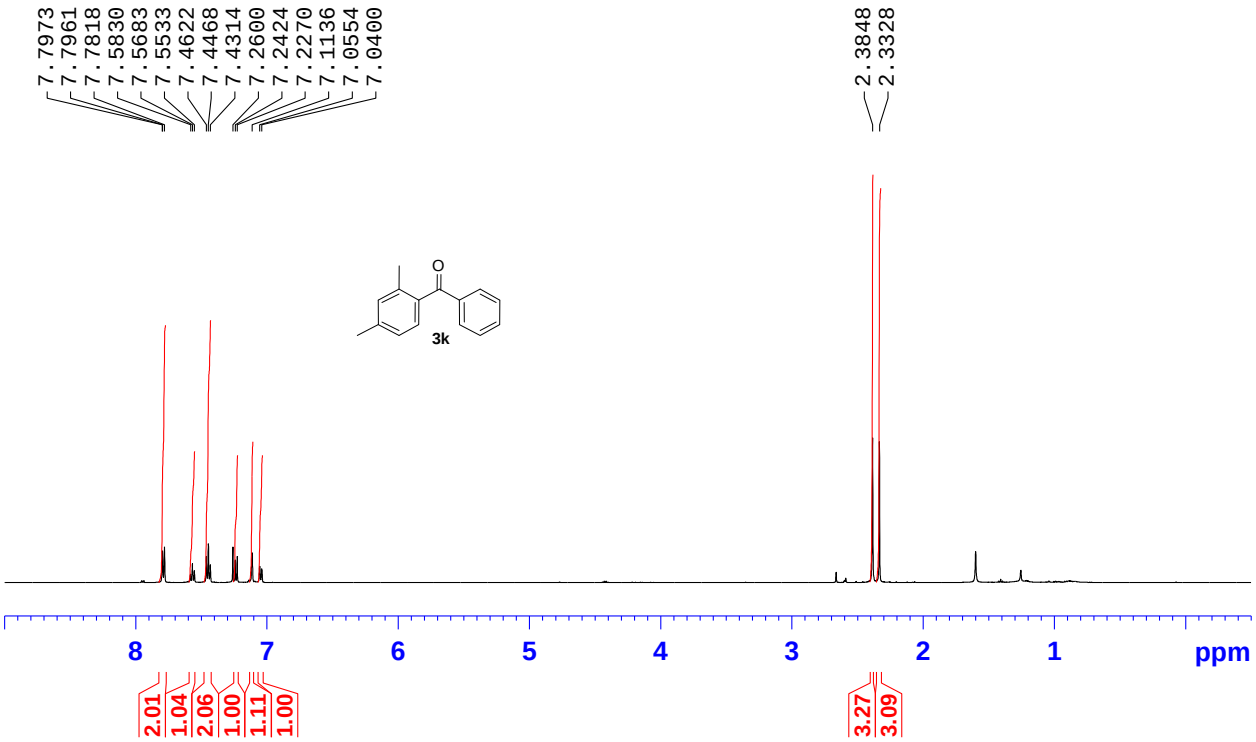
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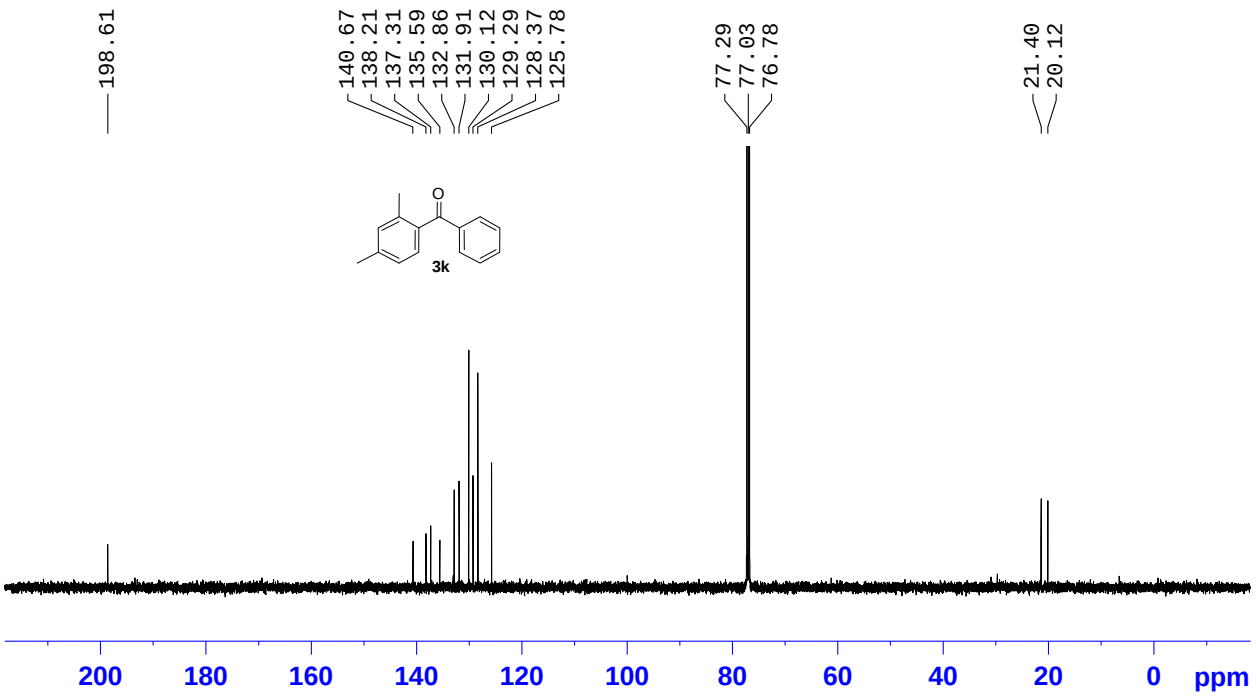
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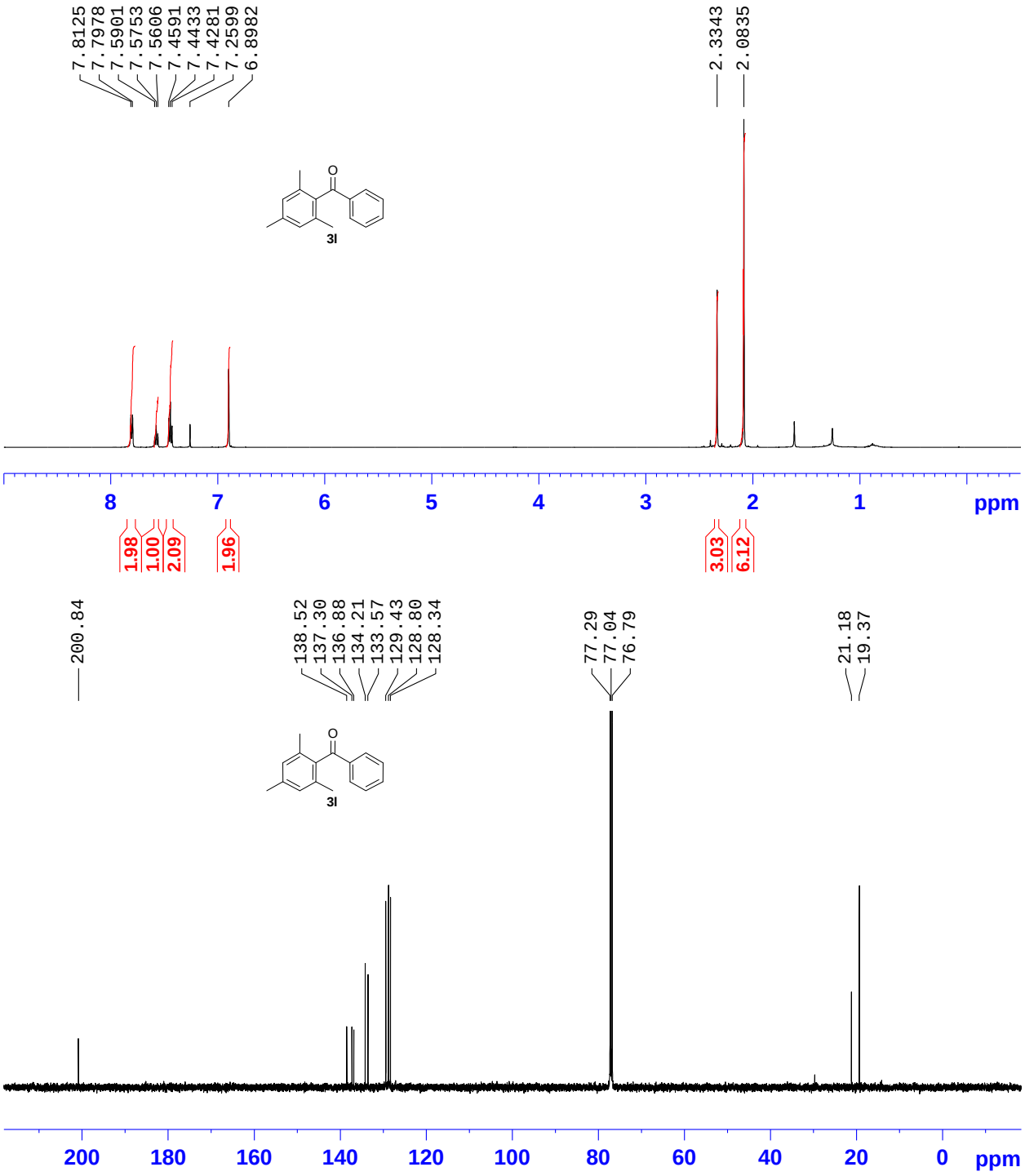
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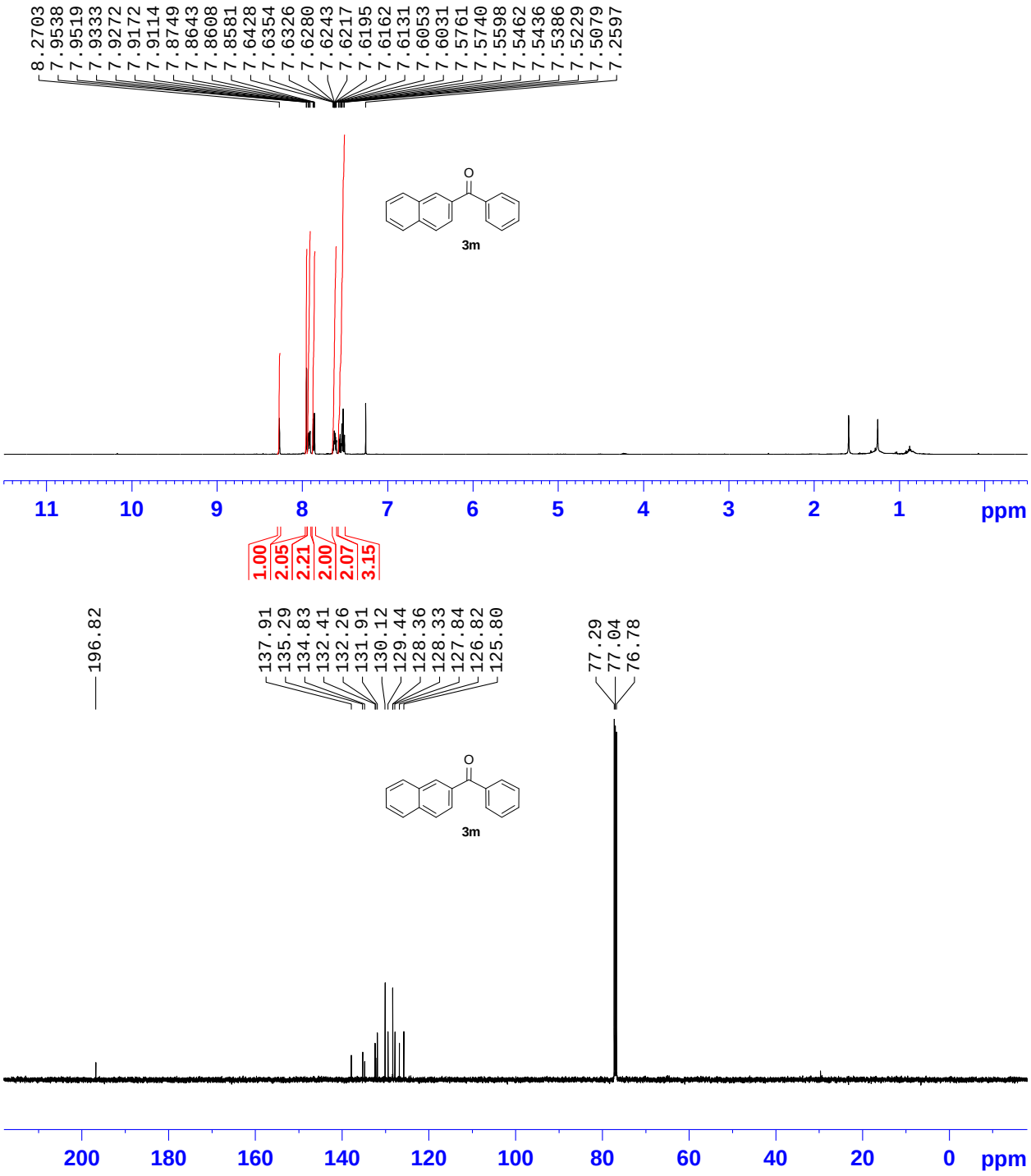
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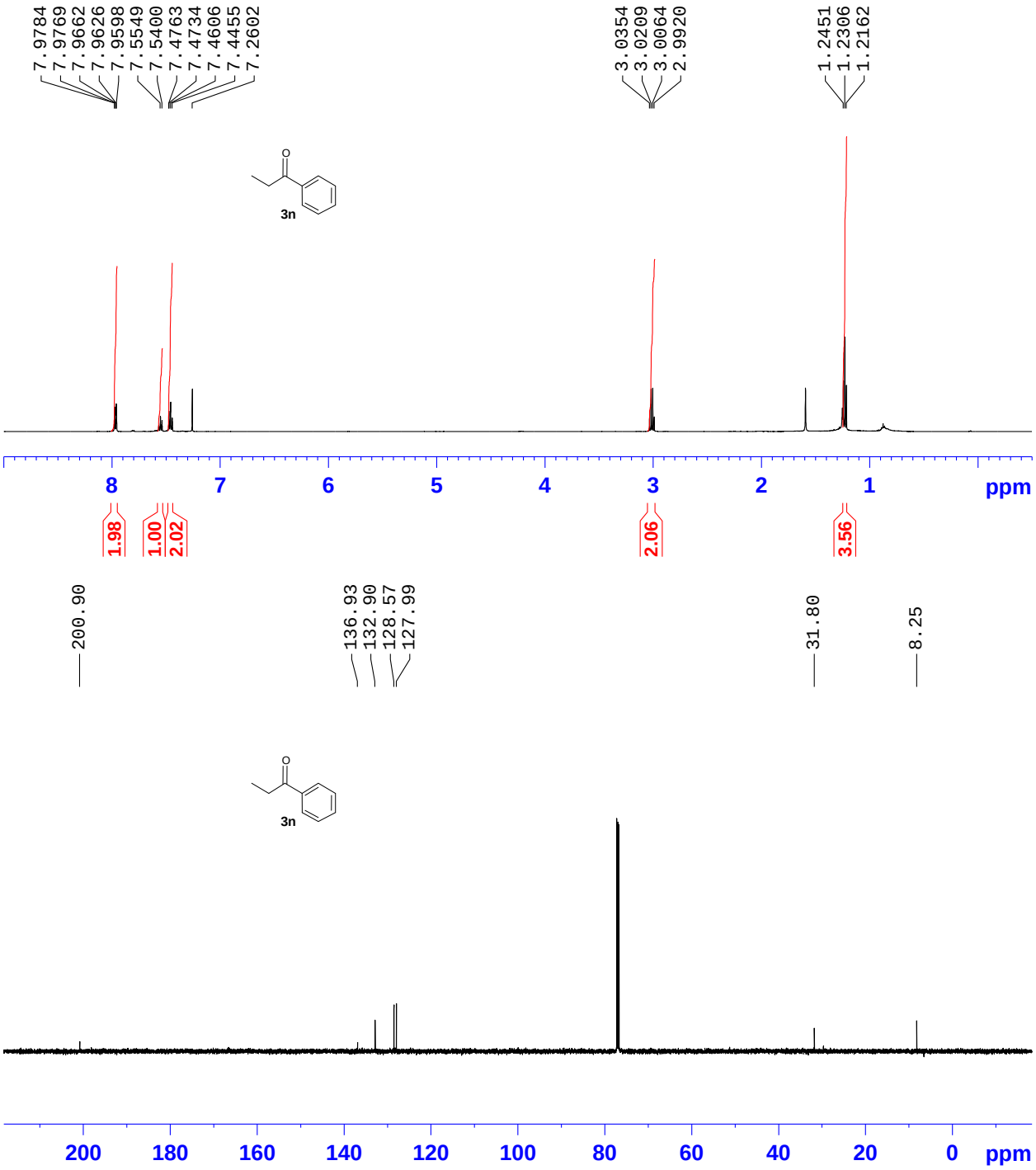
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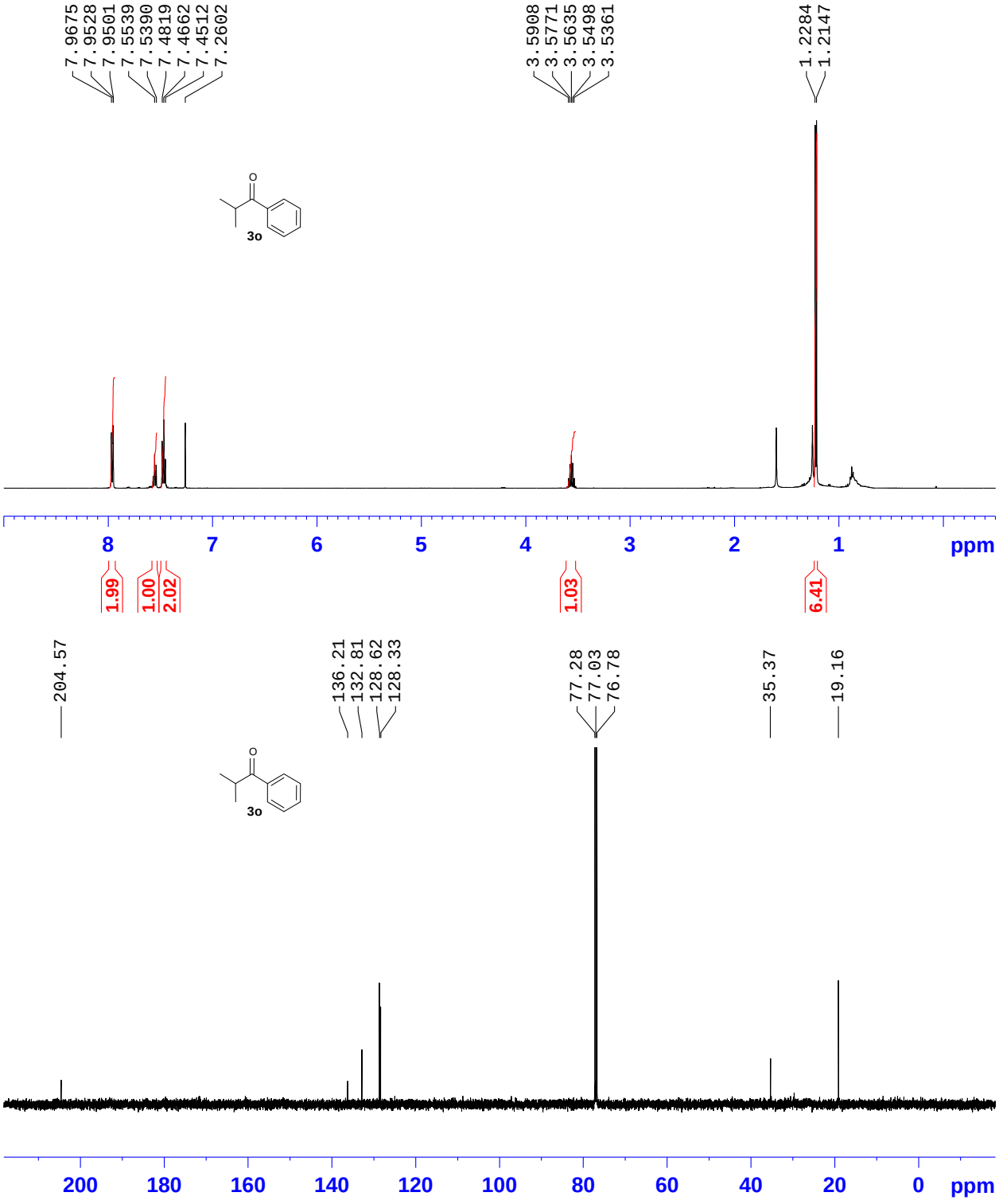
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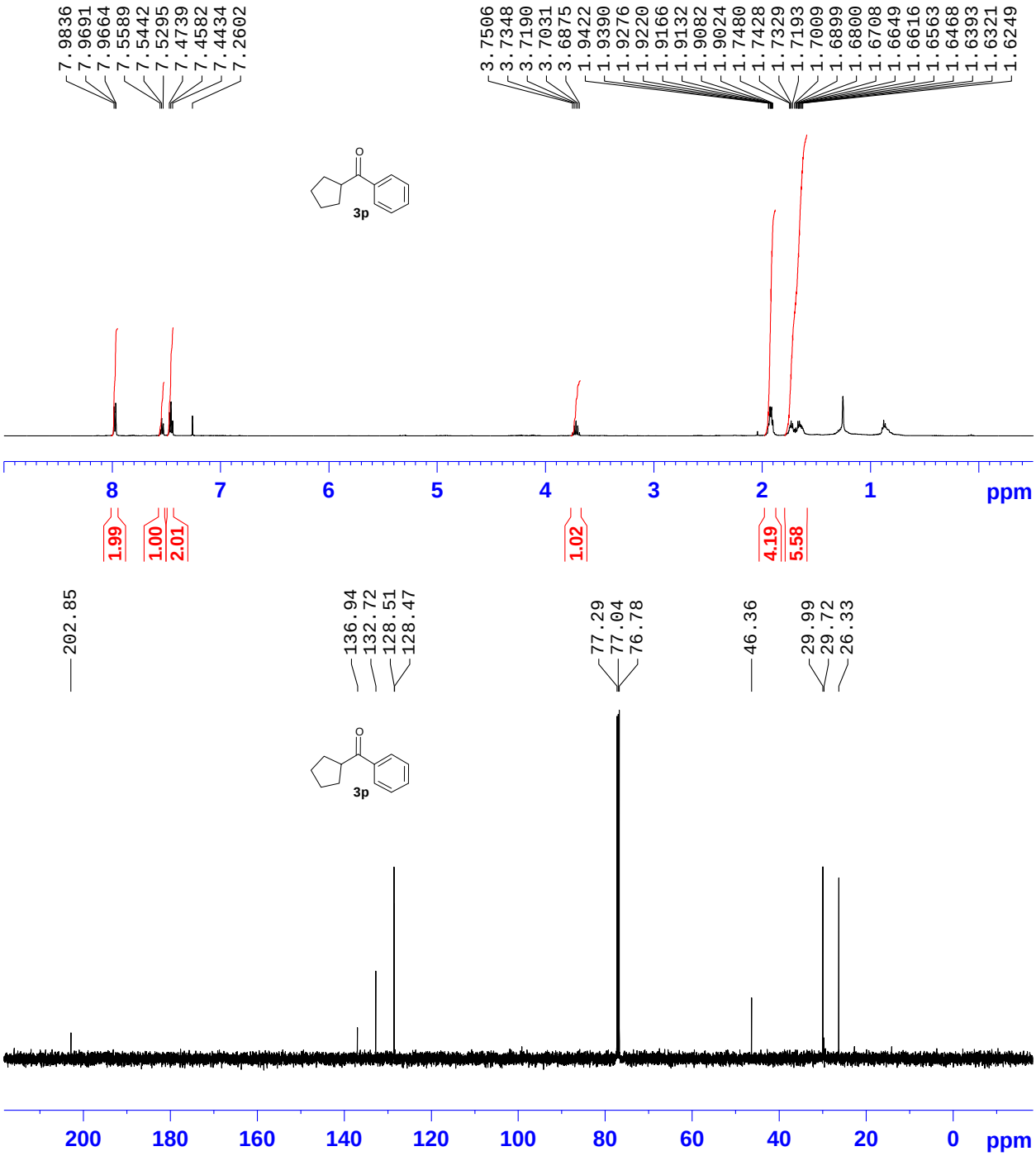
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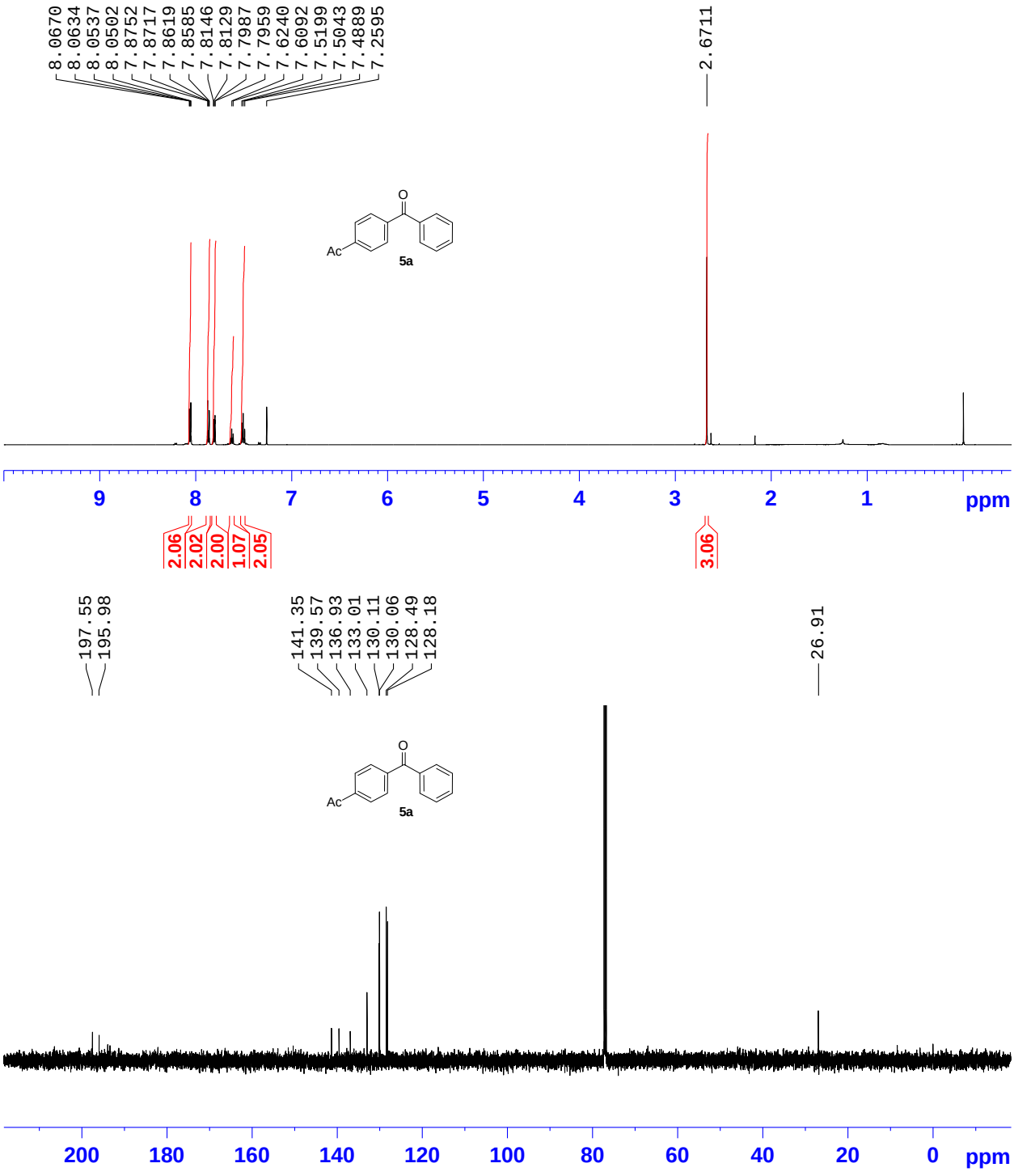
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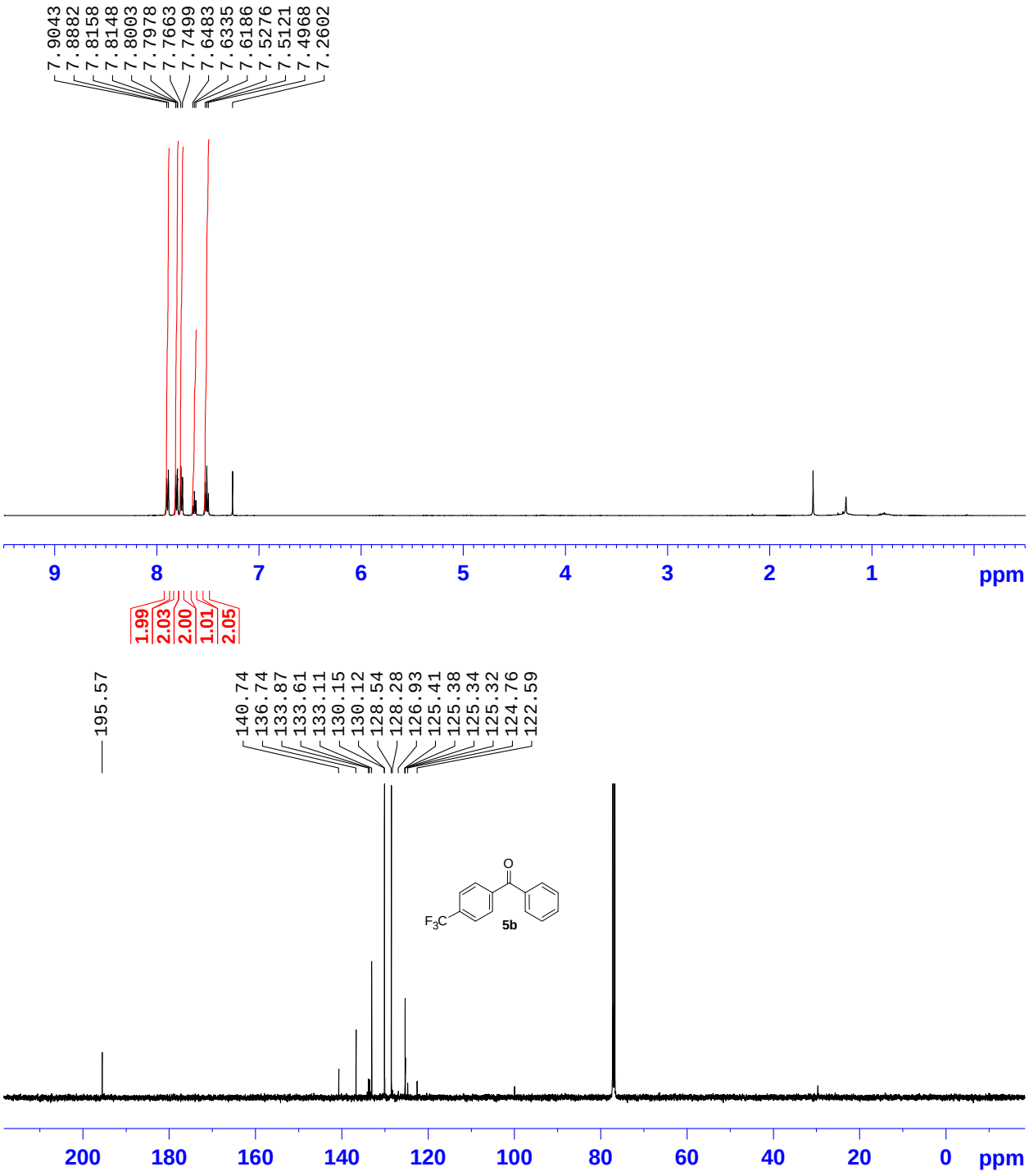
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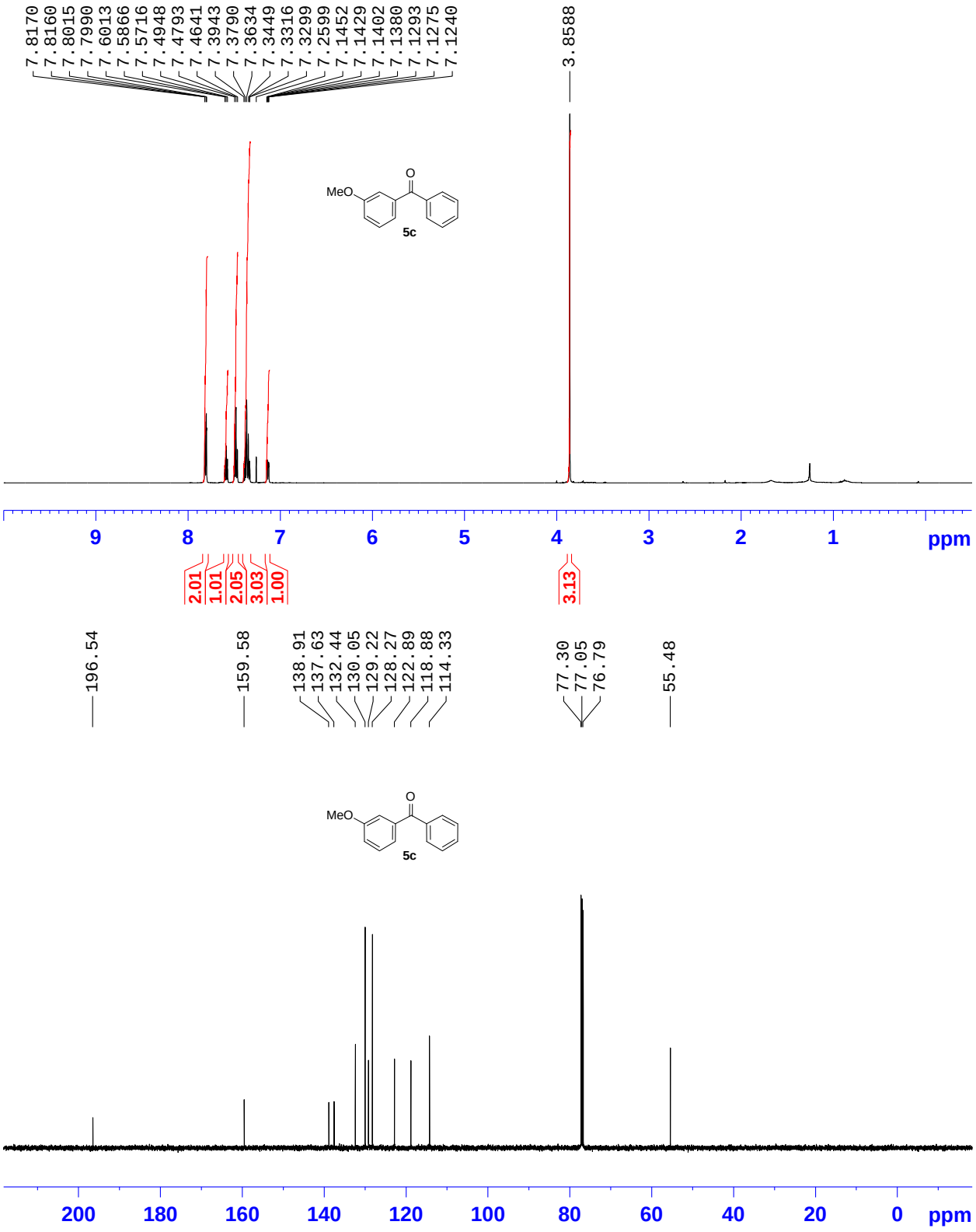
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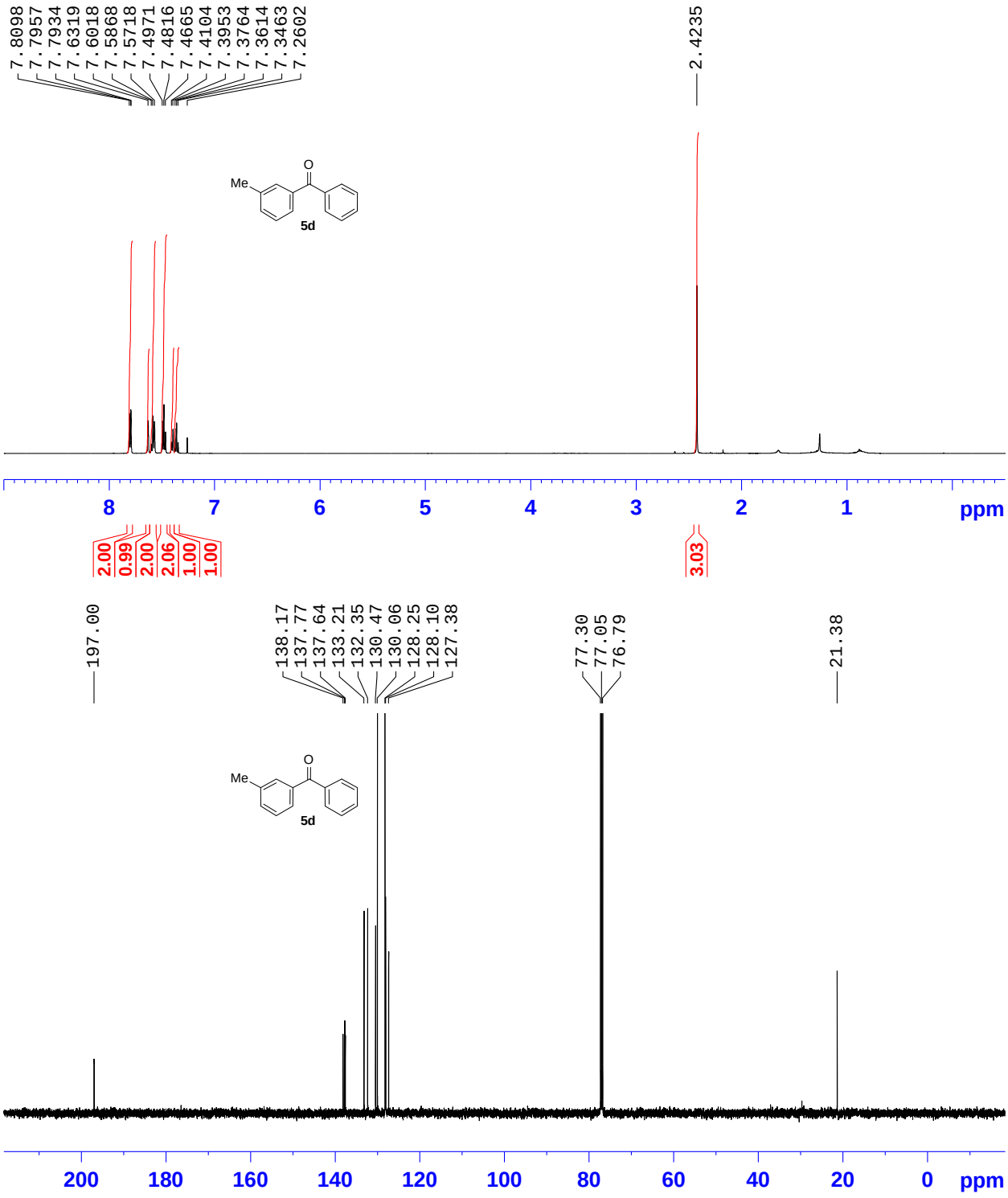
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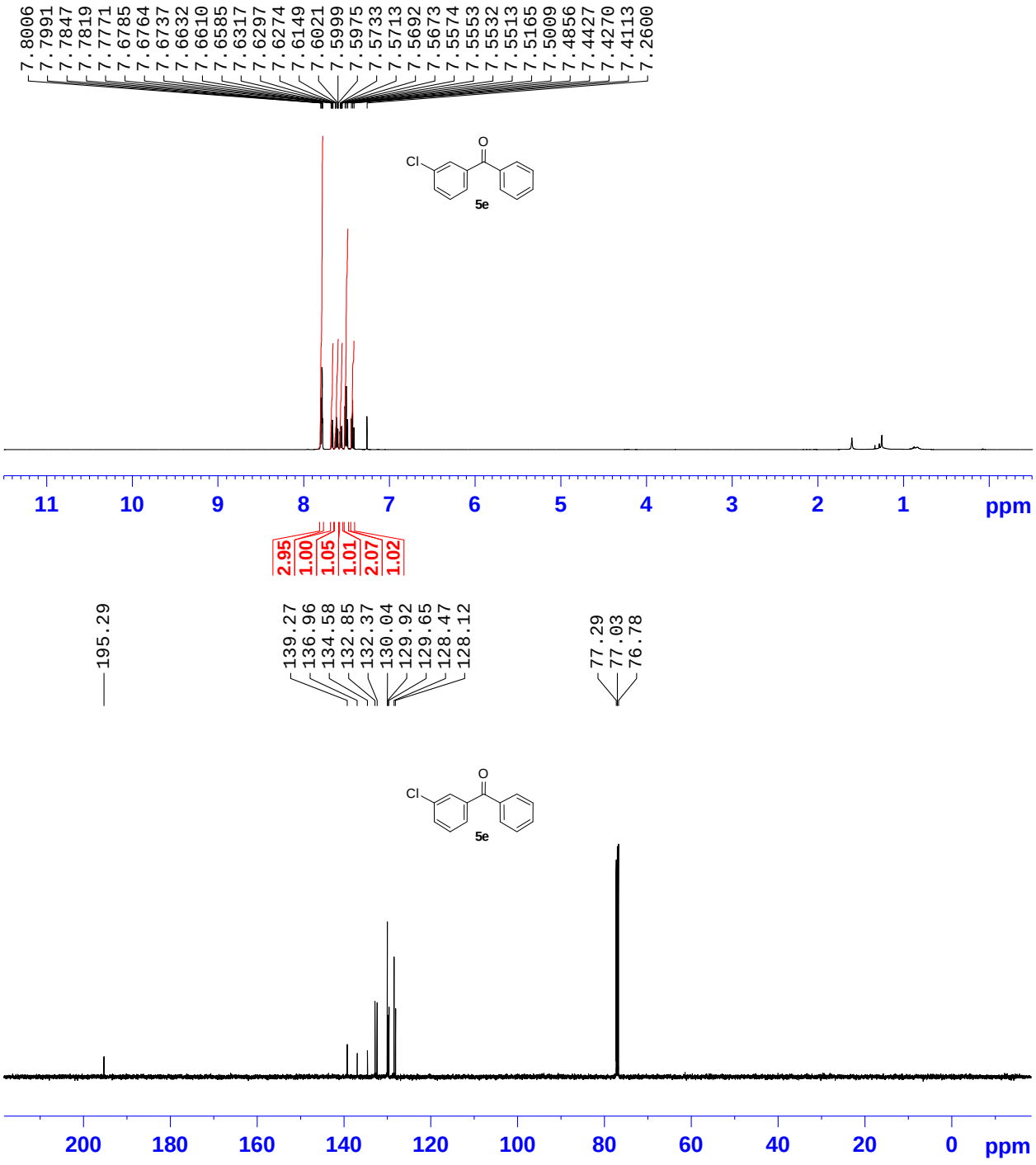
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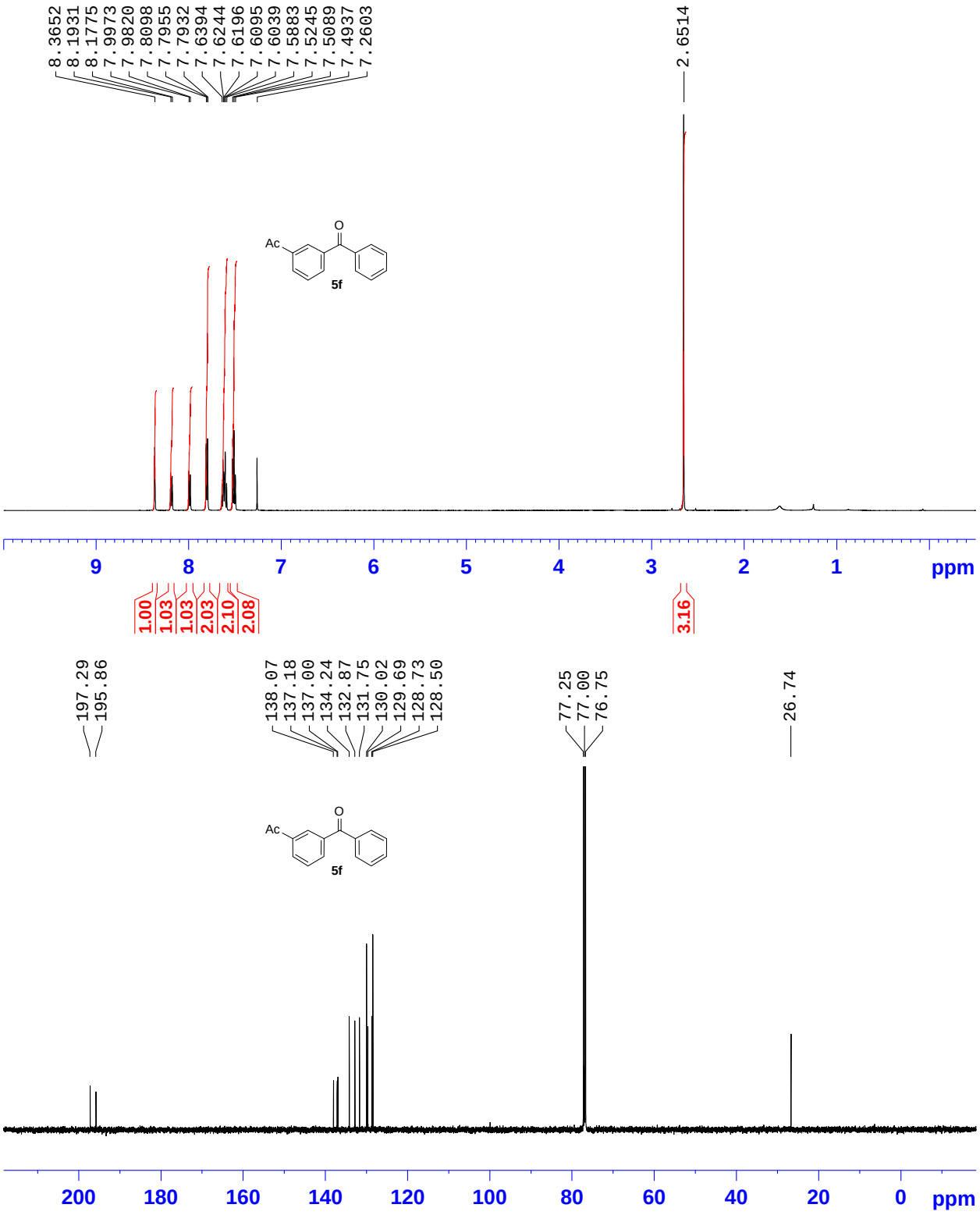
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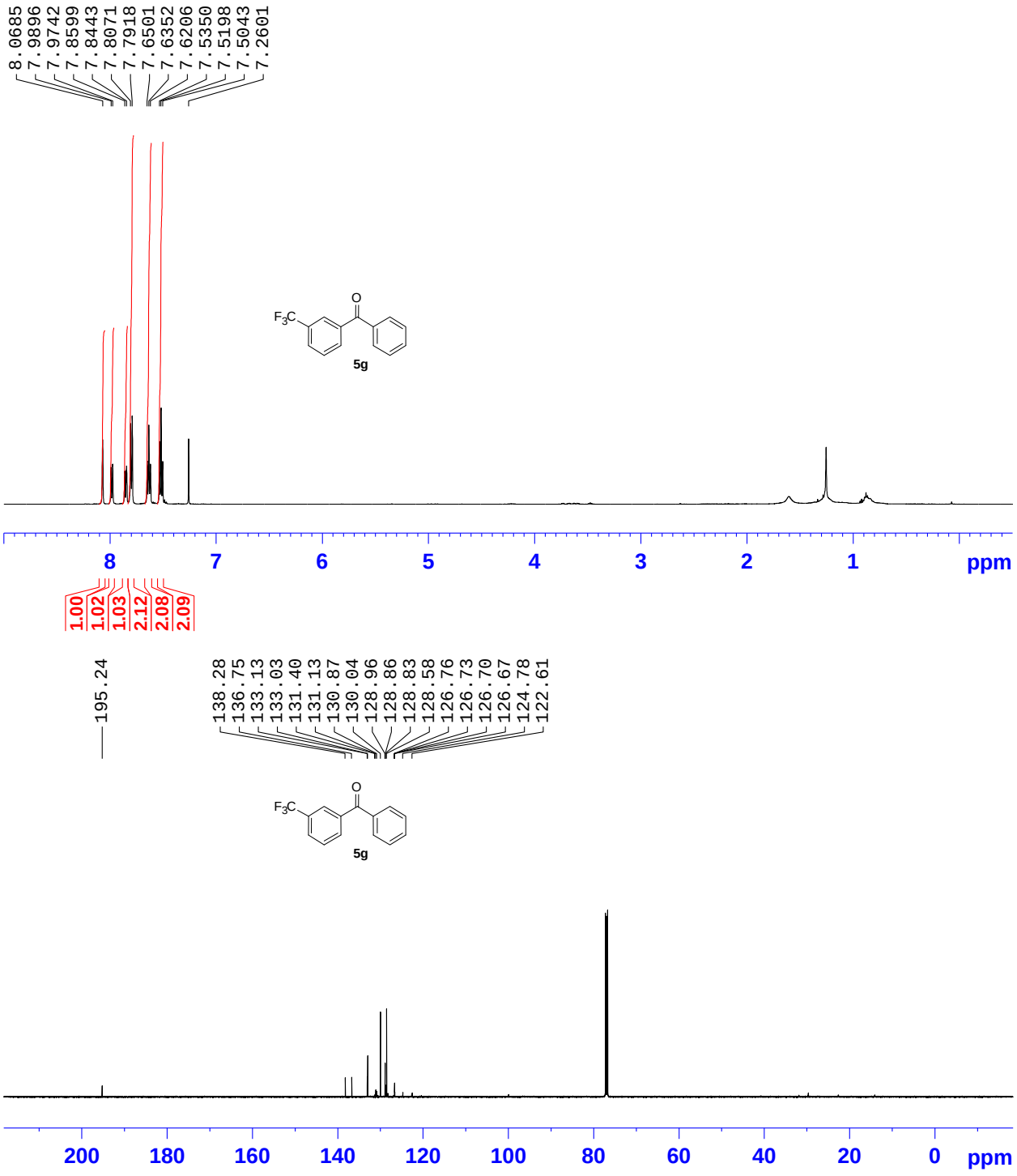
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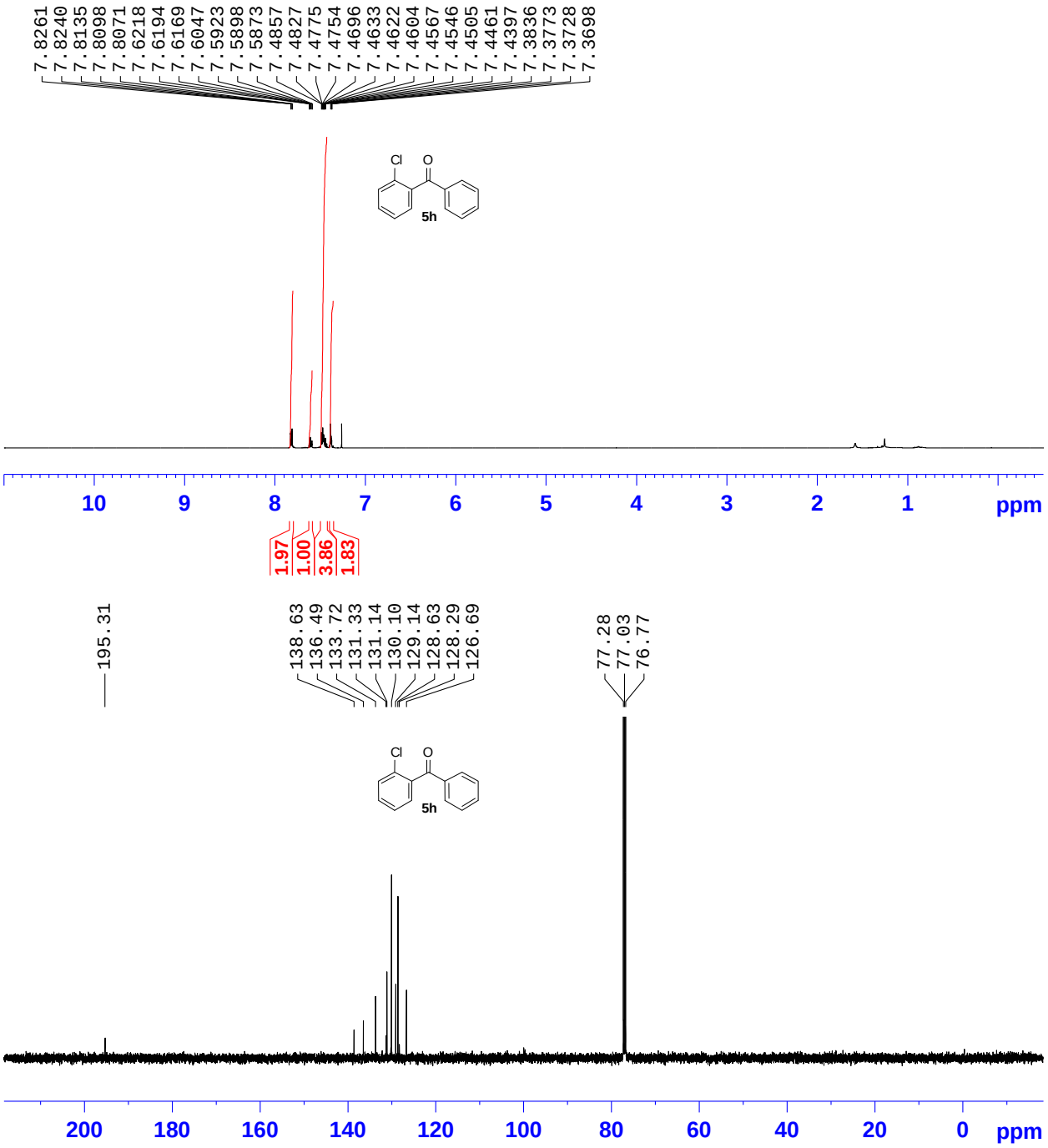
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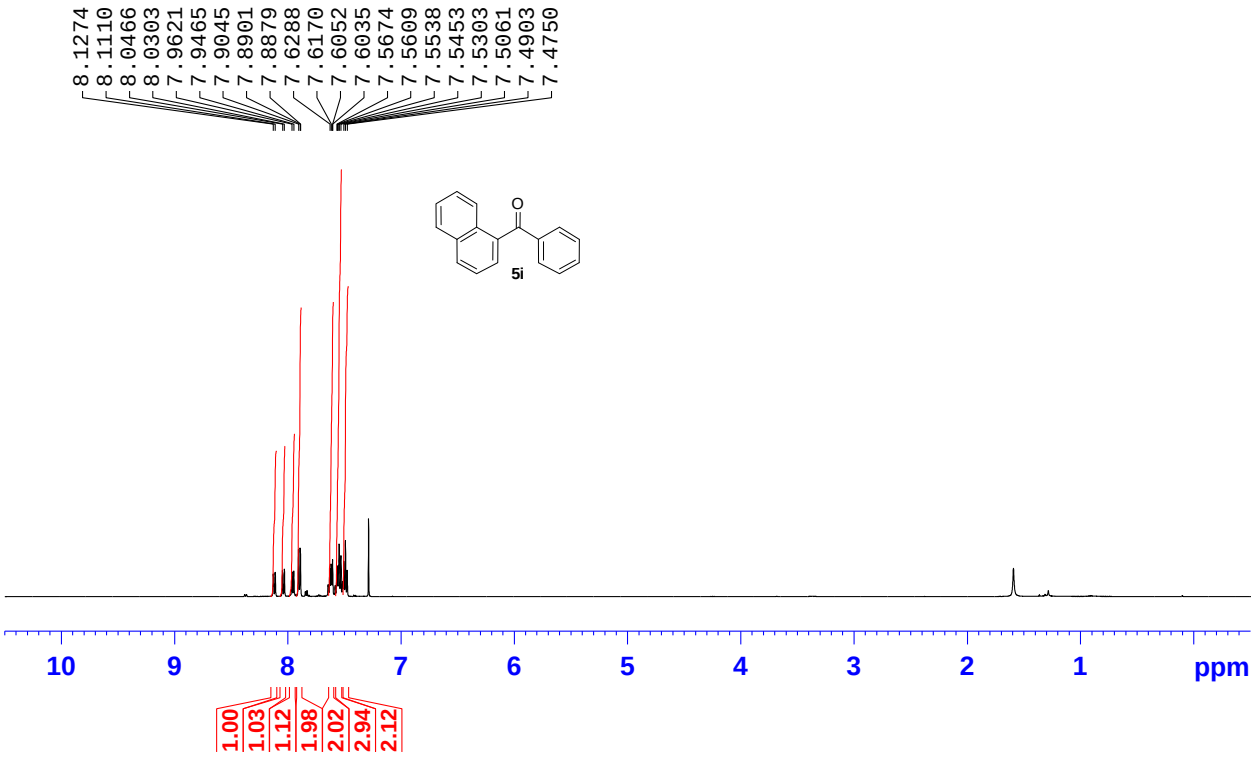
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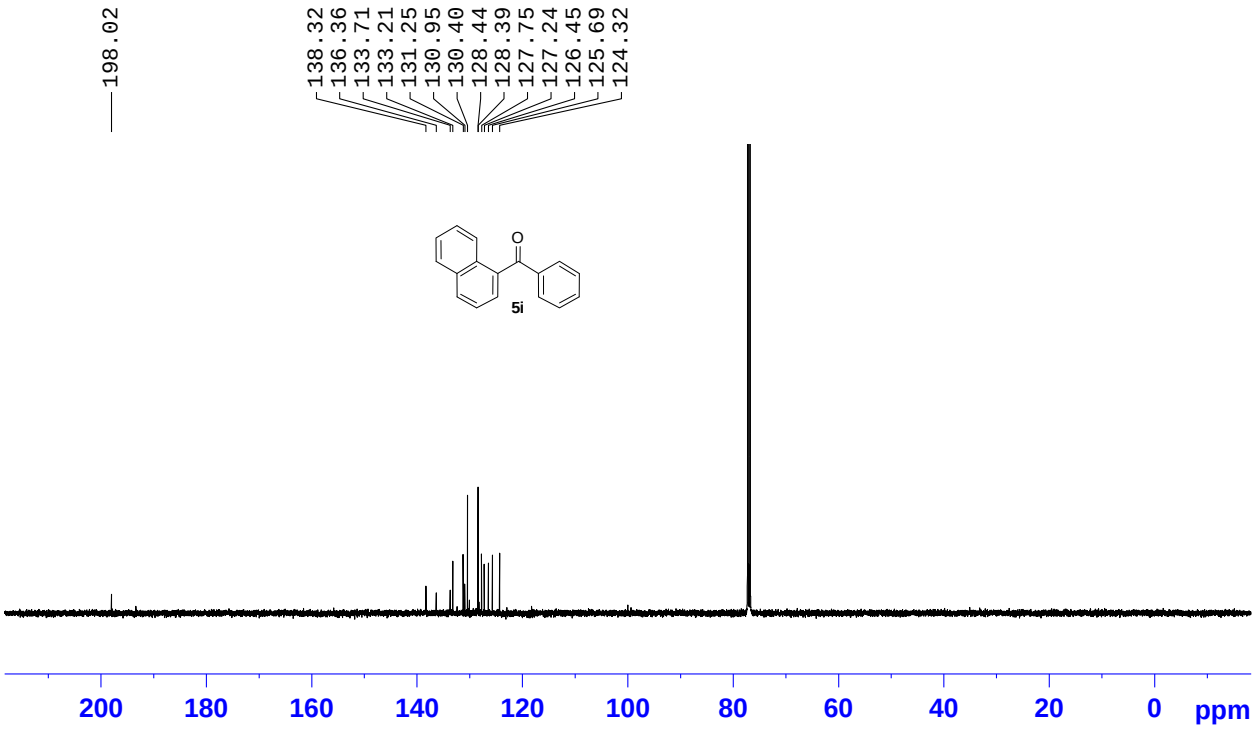
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