SUPPORTING INFORMATION

Synthesis of Photoactivatable Analogues of Lysophosphatidic Acid and Covalent Labeling of Plasma Proteins

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General Information. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise noted) at 400 and 100 MHz, respectively. The reference chemical shifts for $CDCl_3$ were δ 7.27 (^{1}H) and 77.0 ppm (^{13}C). TLC was carried out on 0.25-mm thick silica gel 60 F254 aluminum sheets. Visualization was with 10% sulfuric acid solution in EtOH. Flash chromatography was carried out with 230-400 mesh silica gel. The solvents were dried with the following reagents and distilled before use: CH_2Cl_2 (CaH_2); HMPA (CaH_2); THF (sodium/benzophenone).

Enzymatic Incorporation of [^{32}P]-Phosphate into Benzophenone-Containing Analogues with DGK. This protocol is a modification of a previously reported method.[S1] Twenty-five nmol of analogue **1**, **2**, **4**, **20**, or **27** was added to pH 6.6 buffer containing 20 mM imidazole, 20 mM NaCl, 40 mM, $MgCl_2$, 55 μM EDTA, 55 μM EGTA, 5.5 mM DTT, and 100 μg of DGK (recombinant protein expressed in *E. coli*). The reaction was started on addition of γ-[^{32}P]-ATP (8.33 nmol, 30 Ci/mmol), and the

reaction mixture was shaken at 37 ºC for 2 h. After the mixture was dried under vacuum, the desired products were purified by TLC ($CHCl_3$/Me_2CO/HOAc/MeOH/H_2O 50:20:15:10:5). Radioactive spots were visualized by autoradiography using X-ray film, scraped from the plate, and extracted with MeOH. Final concentrations were determined by liquid-scintillation counting using 30 Ci/mmol as the specific activity.

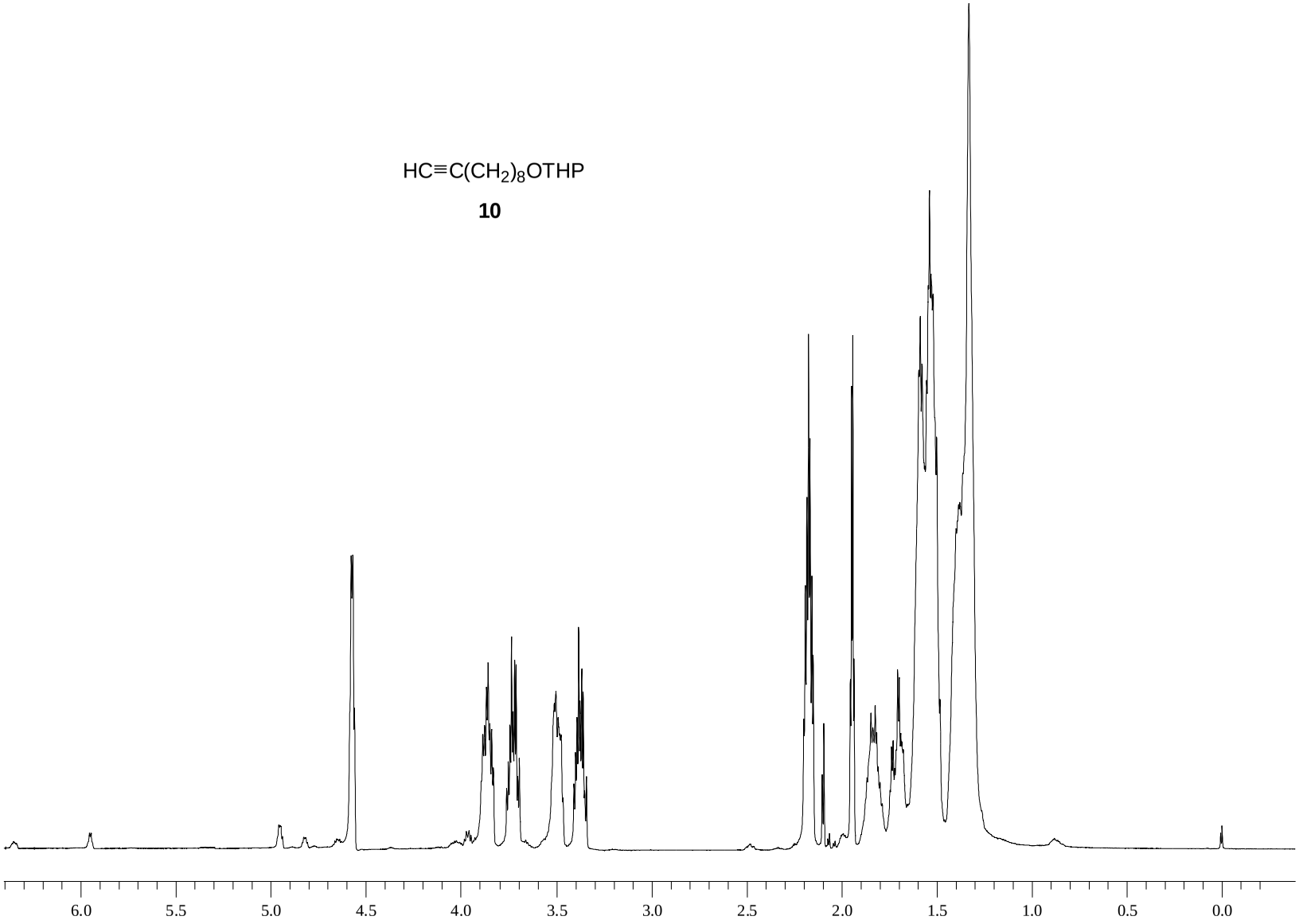
Covalent Modification of Plasma Proteins. EDTA-anticoagulated plasma from Sprague Dawley (19.4 mg albumin/mL) or Nagase rats (0.4 mg albumin/mL) was diluted to 5% in phosphate-buffered saline containing 10% DMSO and 50 nM [^{32}P]-benzophenone-containing analogue. Samples were preincubated in the dark for 20 min and then exposed to UV (365 nm) for up to 10 min on ice using a Spectrolinker XL-1500 crosslinker. Samples (20 μL) were diluted with equal volumes of 2 x loading buffer, incubated at 37 ºC for 3 h, and separated by 12% SDS-PAGE. Gels were equilibrated in 10% aqueous glycerol and dried under vacuum at 50 ºC for 2 h. Radioactive bands were visualized by autoradiography using X-ray film and an intensifying screen at -80 ºC.

Dec-9-yn-1-ol (9). Compound **9** was prepared by a reported procedure[S2] in 90% yield. ^{1}H NMR δ 1.22-1.62 (m, 12H), 1.89 (t, 1H, *J* = 2.8 Hz), 2.11 (m, 2H), 2.97 (br s, 1H), 3.53 (t, 2H, *J* = 6.4 Hz); ^{13}C NMR δ 18.1, 25.5, 28.2, 28.5, 28.9, 29.1, 32.4, 62.4, 68.0, 84.5.

2-(Dec-9-ynyloxy)-tetrahydro-2*H*-pyran (10). To a solution of **9** (2.50 g, 16.2 mmol) and dihydropyran (2.04 g, 24.3 mmol) in 15 mL of dry CH_2Cl_2, 100 mg (0.40 mmol) of PPTS was added and the mixture was stirred overnight at room temperature. After the addition of saturated aqueous $NaHCO_3$ (15 mL), the organic layer was separated and dried (Na_2SO_4). The solvent was removed to give 3.84 g (99%) of **10** as a colorless oil. ^{1}H NMR δ 1.19-1.84 (m, 18H), 1.87 (q, 1H, *J* = 2.4 Hz), 2.05-2.15 (m, 2H), 3.25-3.35 (m, 1H), 3.38-3.48 (m, 1H), 3.61-3.69 (m, 1H), 3.75-3.83 (m, 1H), 4.46-4.53 (m, 1H); ^{13}C NMR δ 18.1, 19.4, 25.3, 26.0, 28.2, 28.5, 28.8, 29.1, 29.5, 30.6, 62.0, 67.3, 68.0, 84.3, 98.5; HR-MS [MNa^+] *m/z* calcd for $C_{15}H_{26}O_2Na$ 261.1825, found 261.1827.

(S1) Waggoner, D. W.; Gómez-Muñoz, A.; Dewald, J.; Brindley, D. N. *J. Biol. Chem.* **1996**, *271*, 16506-16509.

(S2) Abrams, S. R.; Shaw, A. C. *Org. Synth*. Coll. Vol. 8, 146-148.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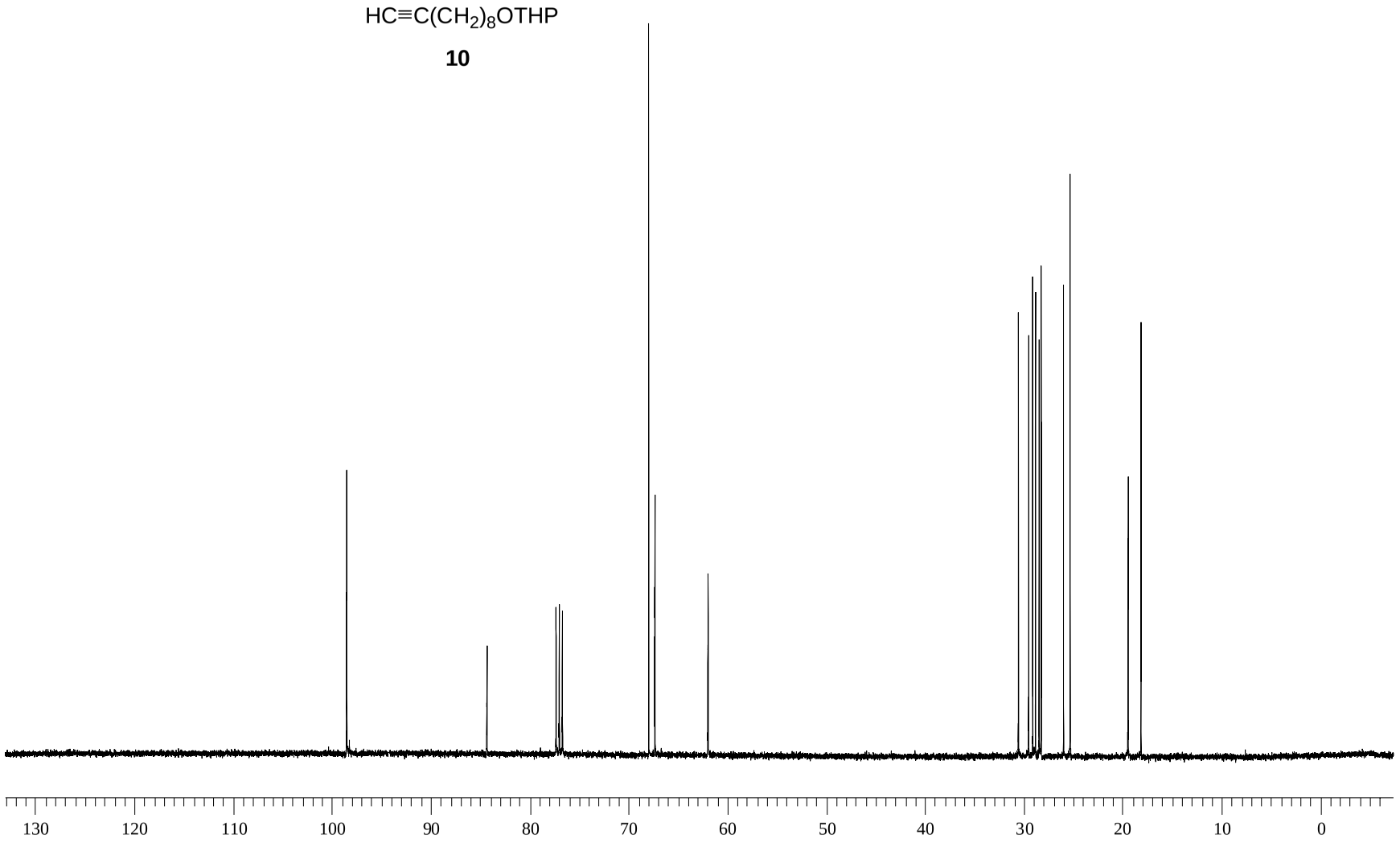
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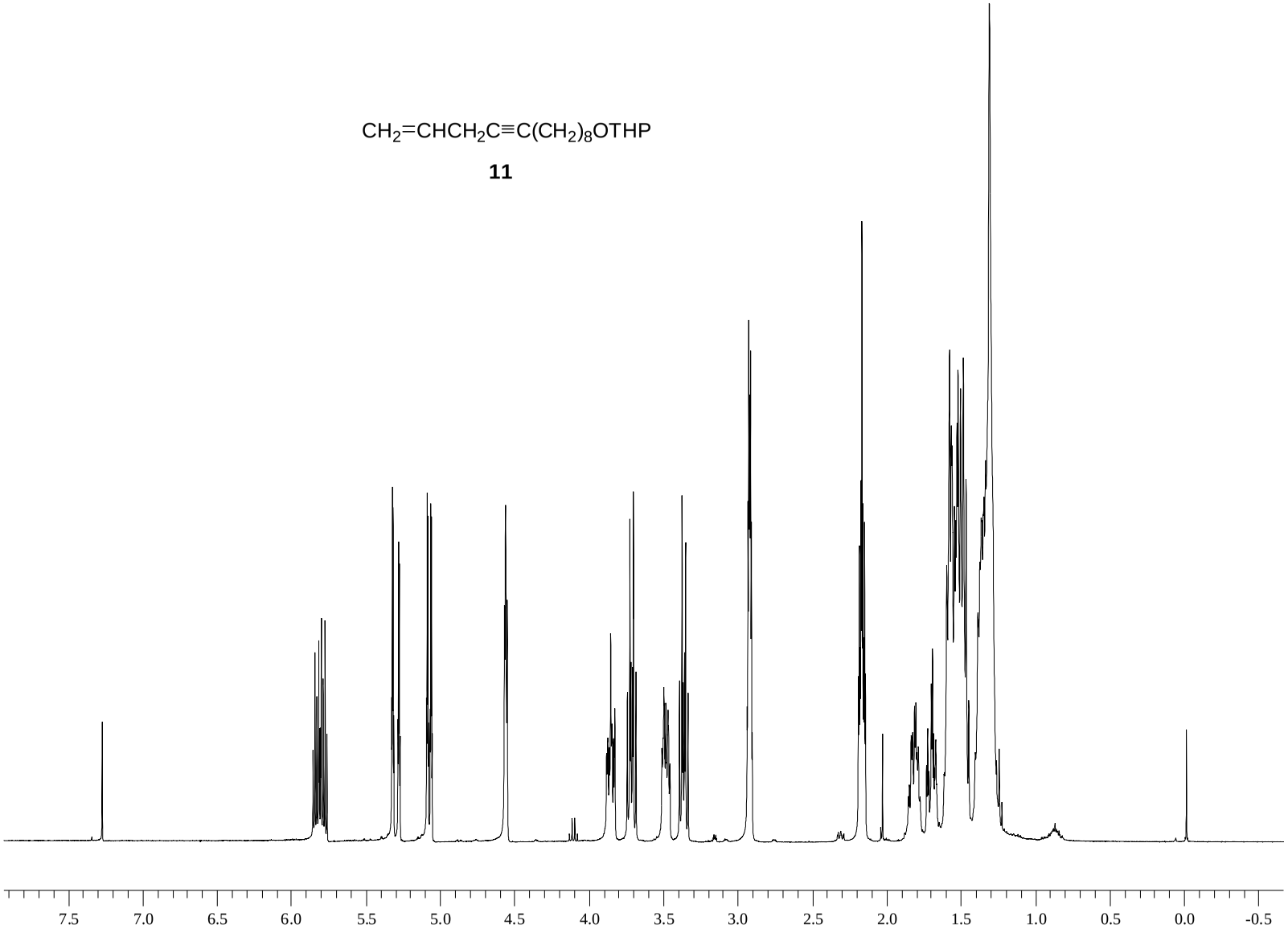
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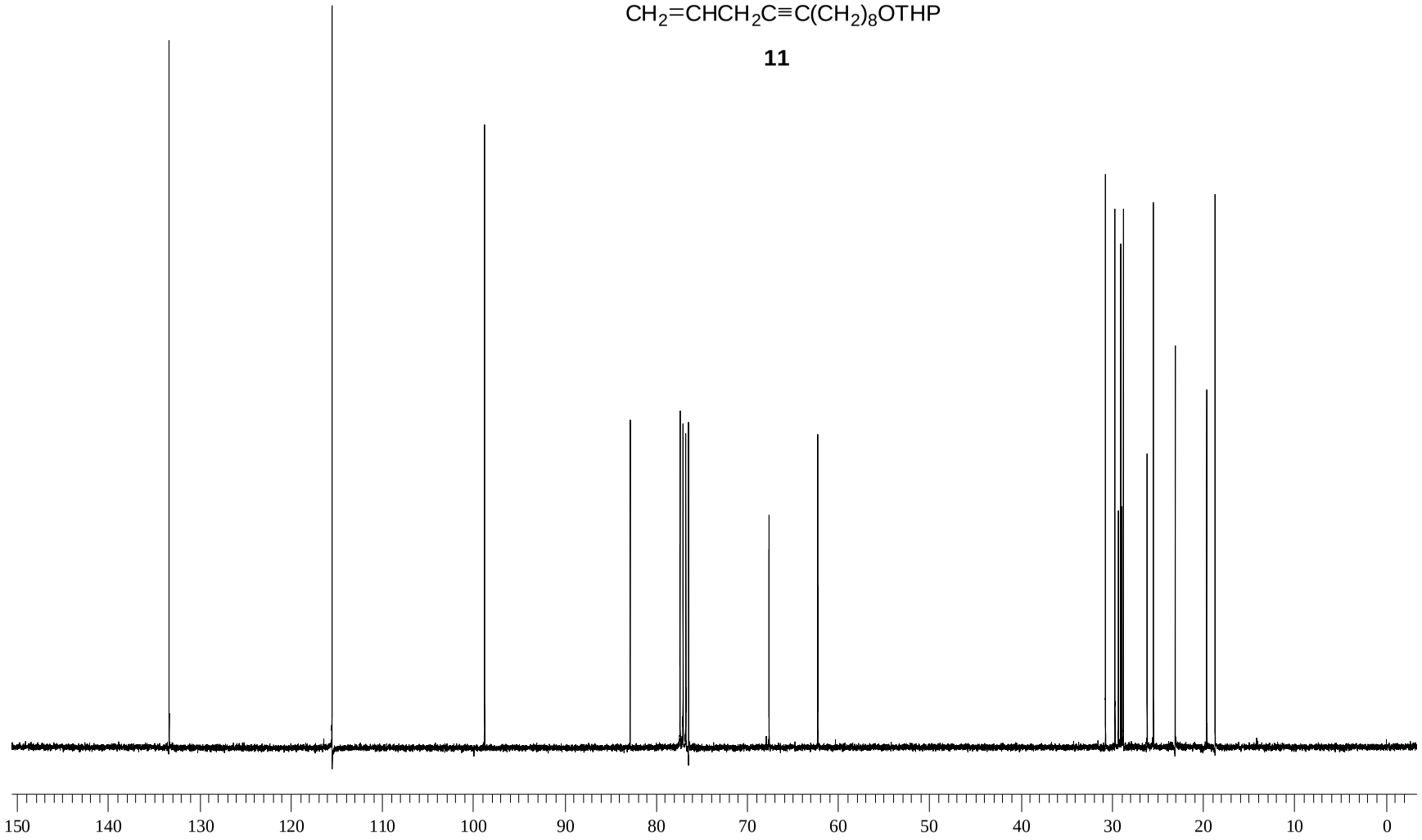

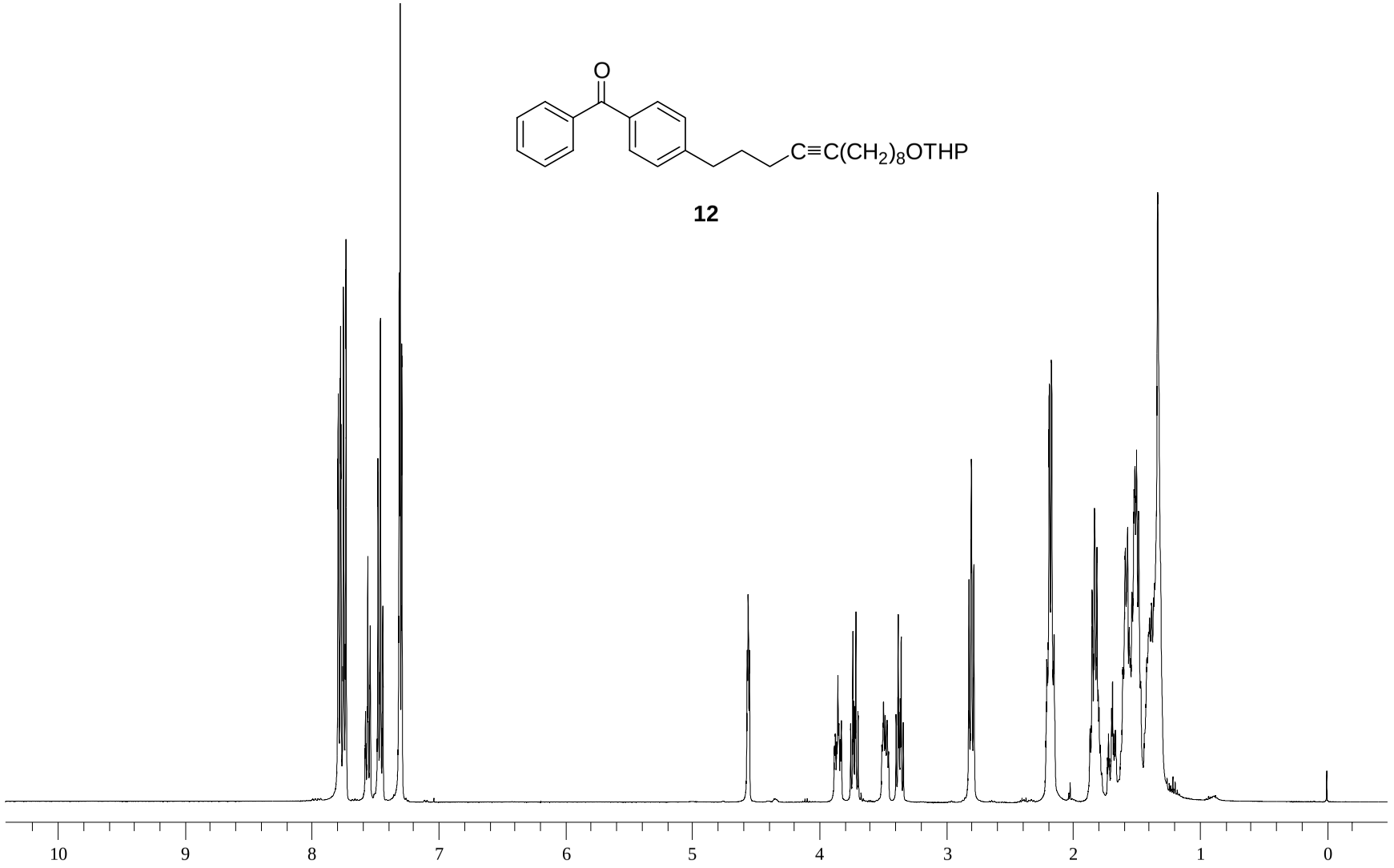
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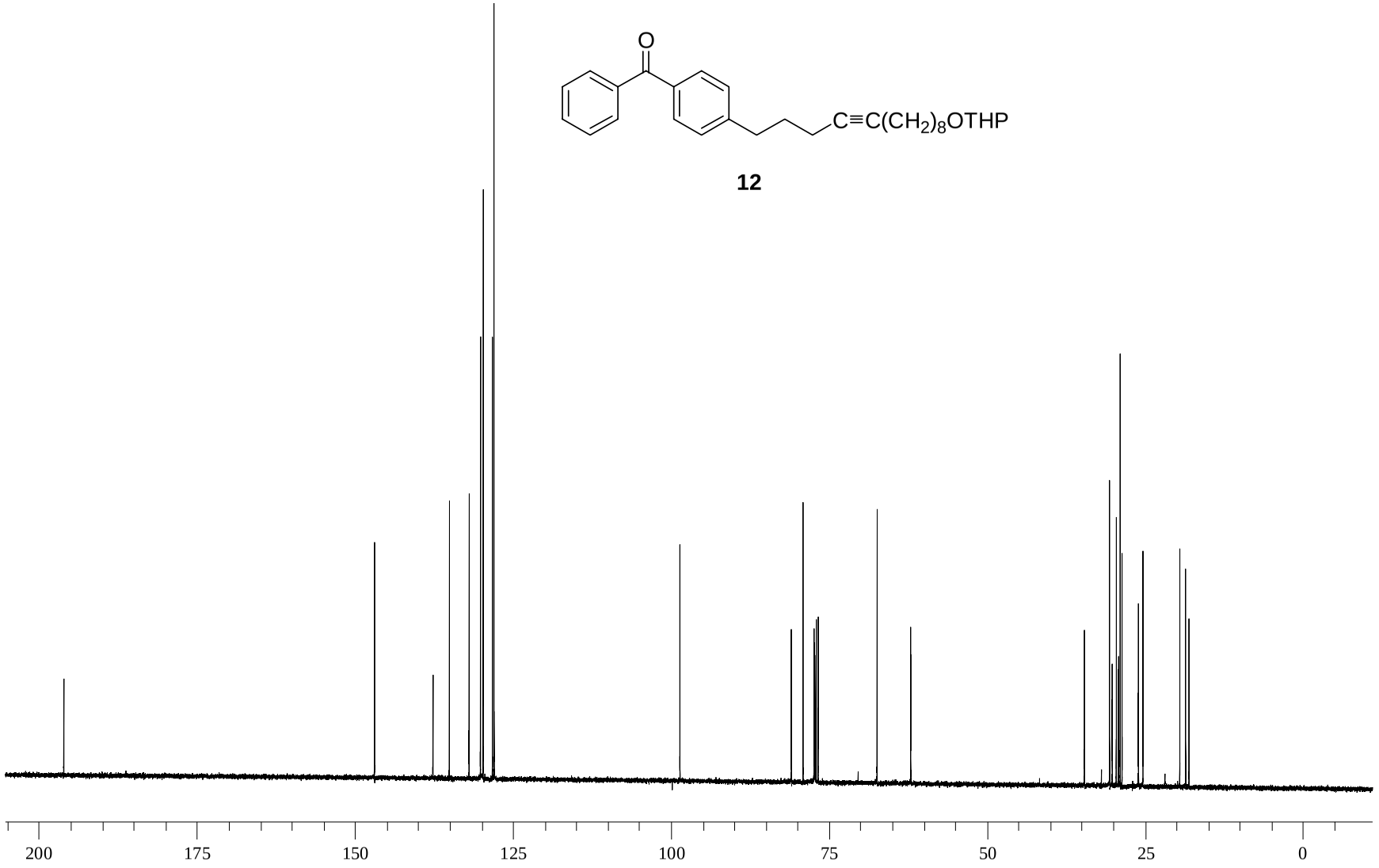

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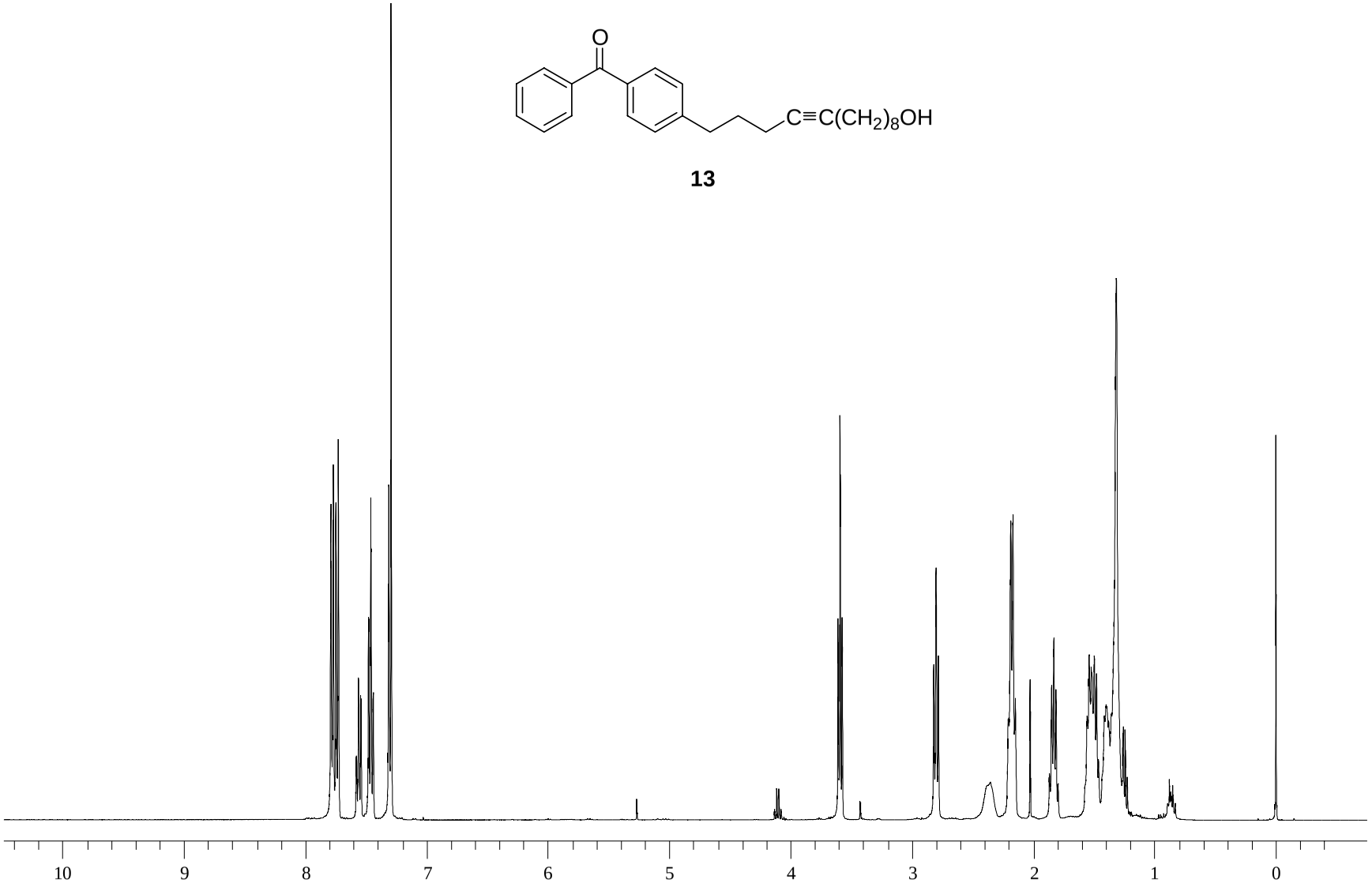

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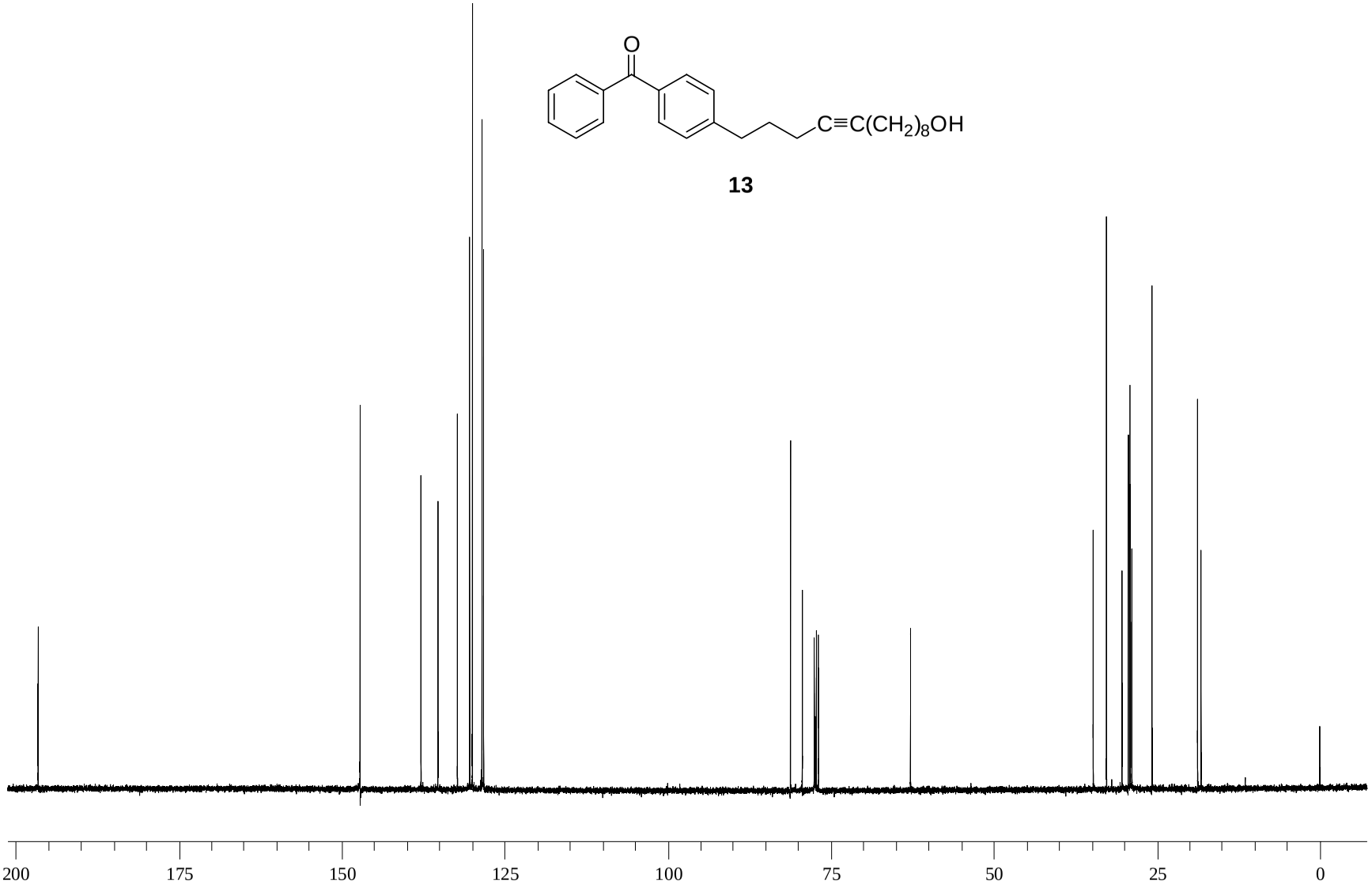

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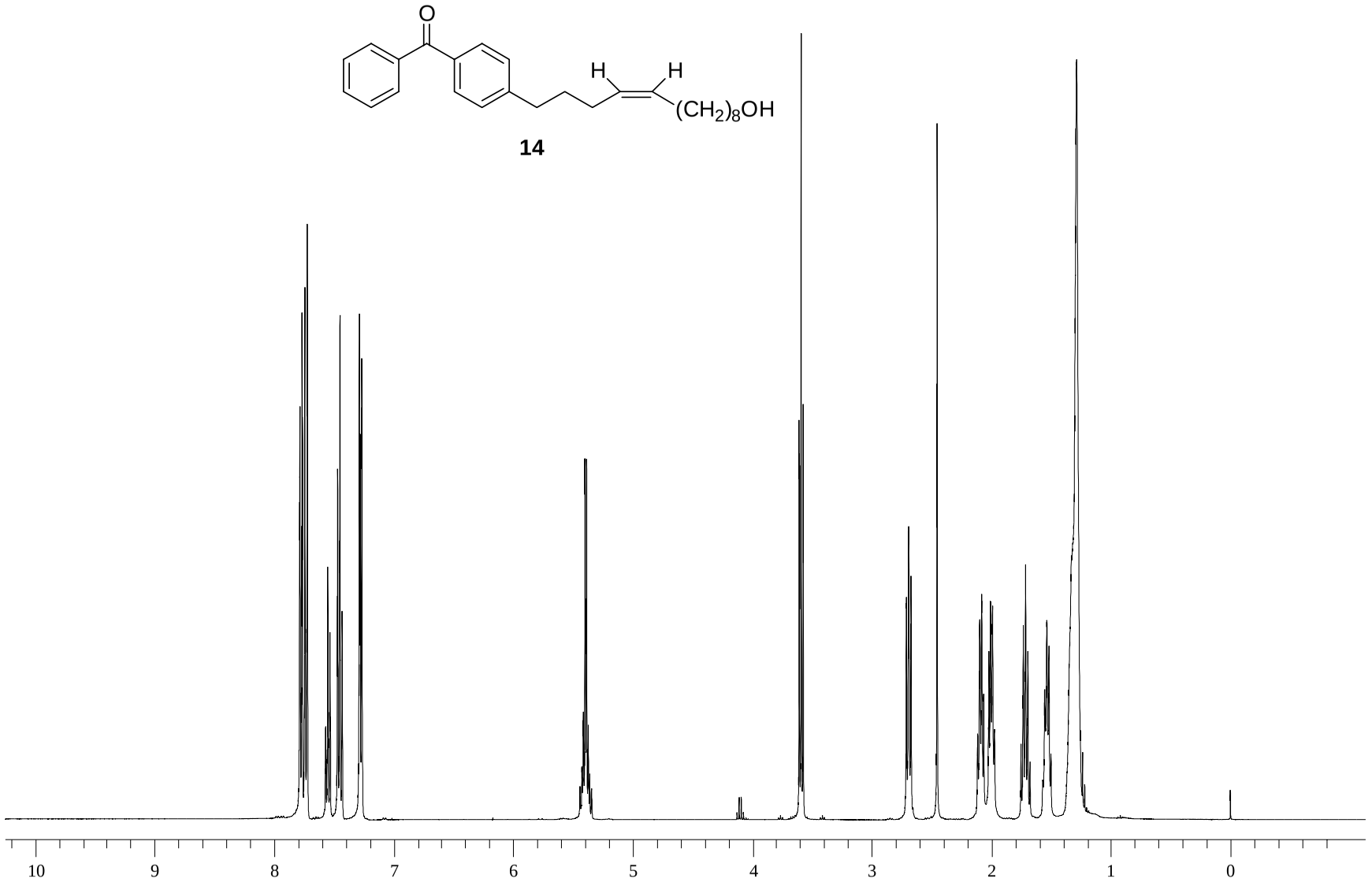
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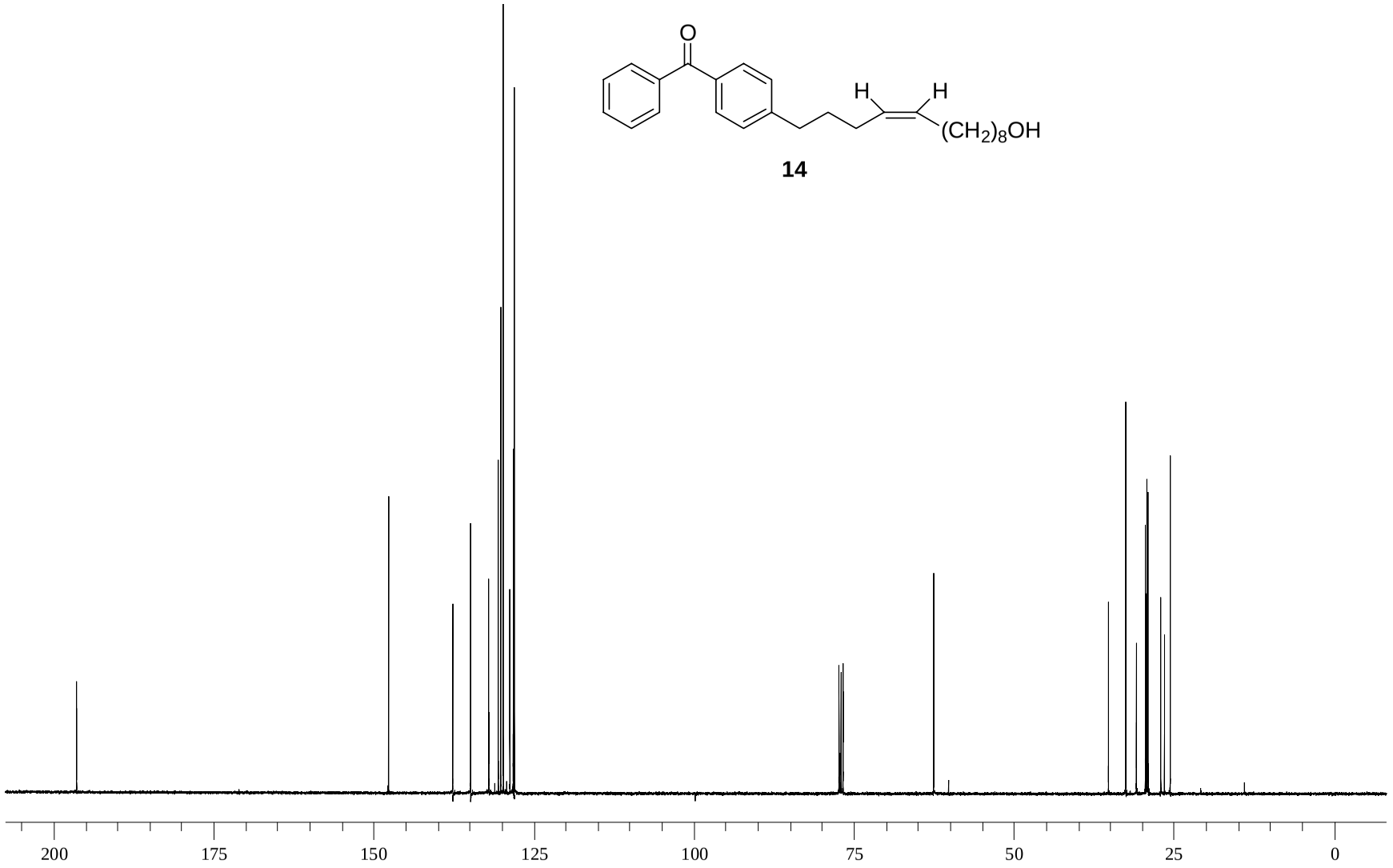

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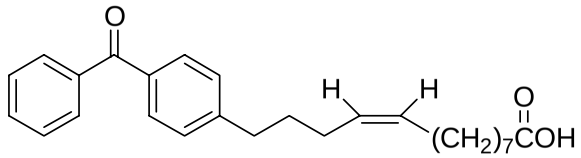

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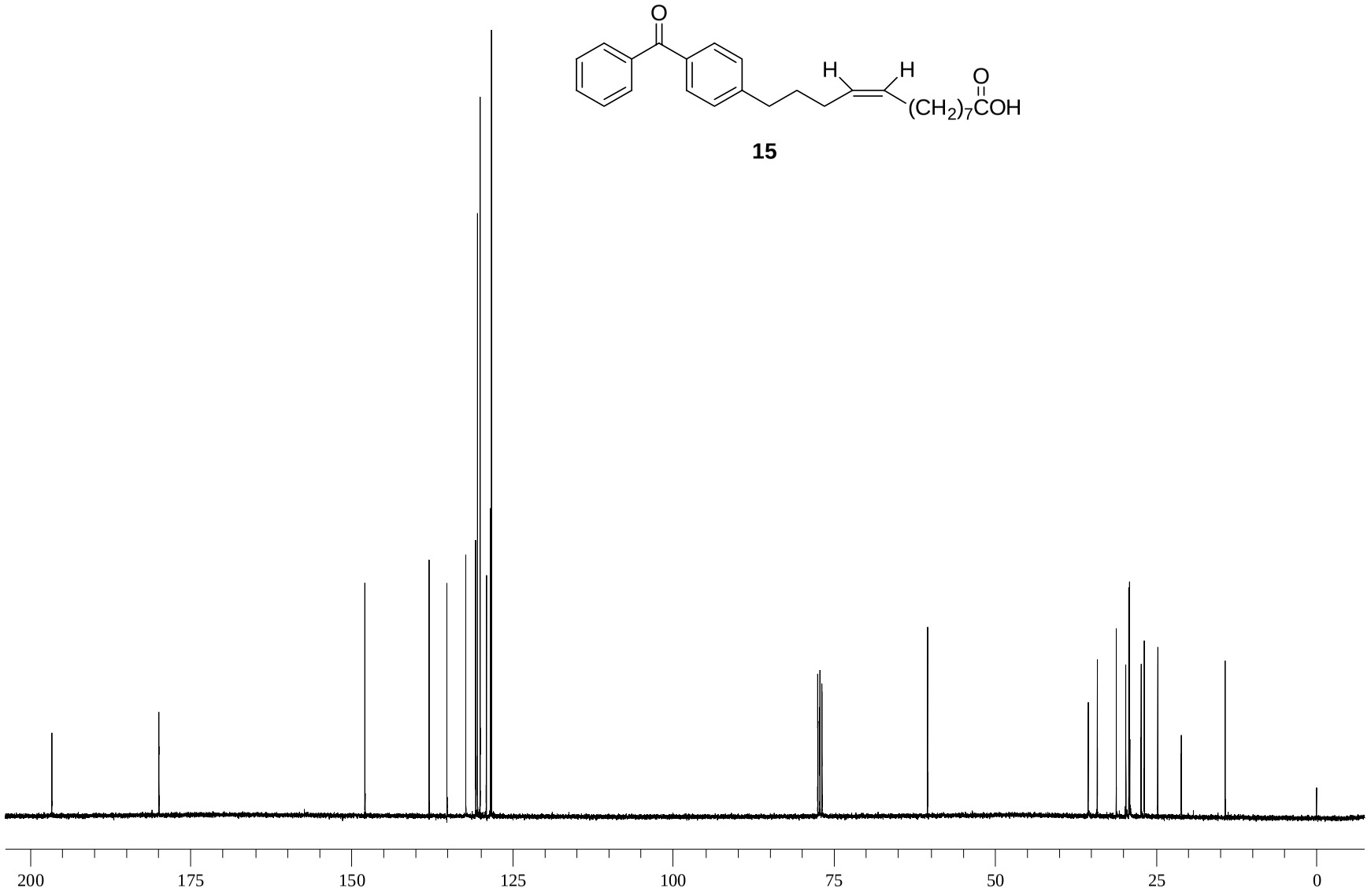

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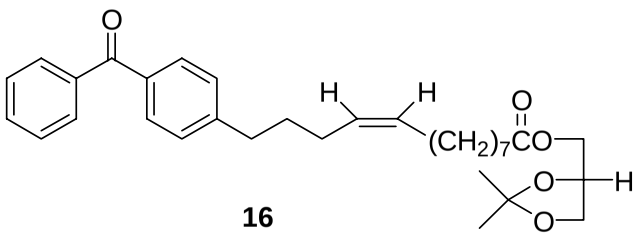
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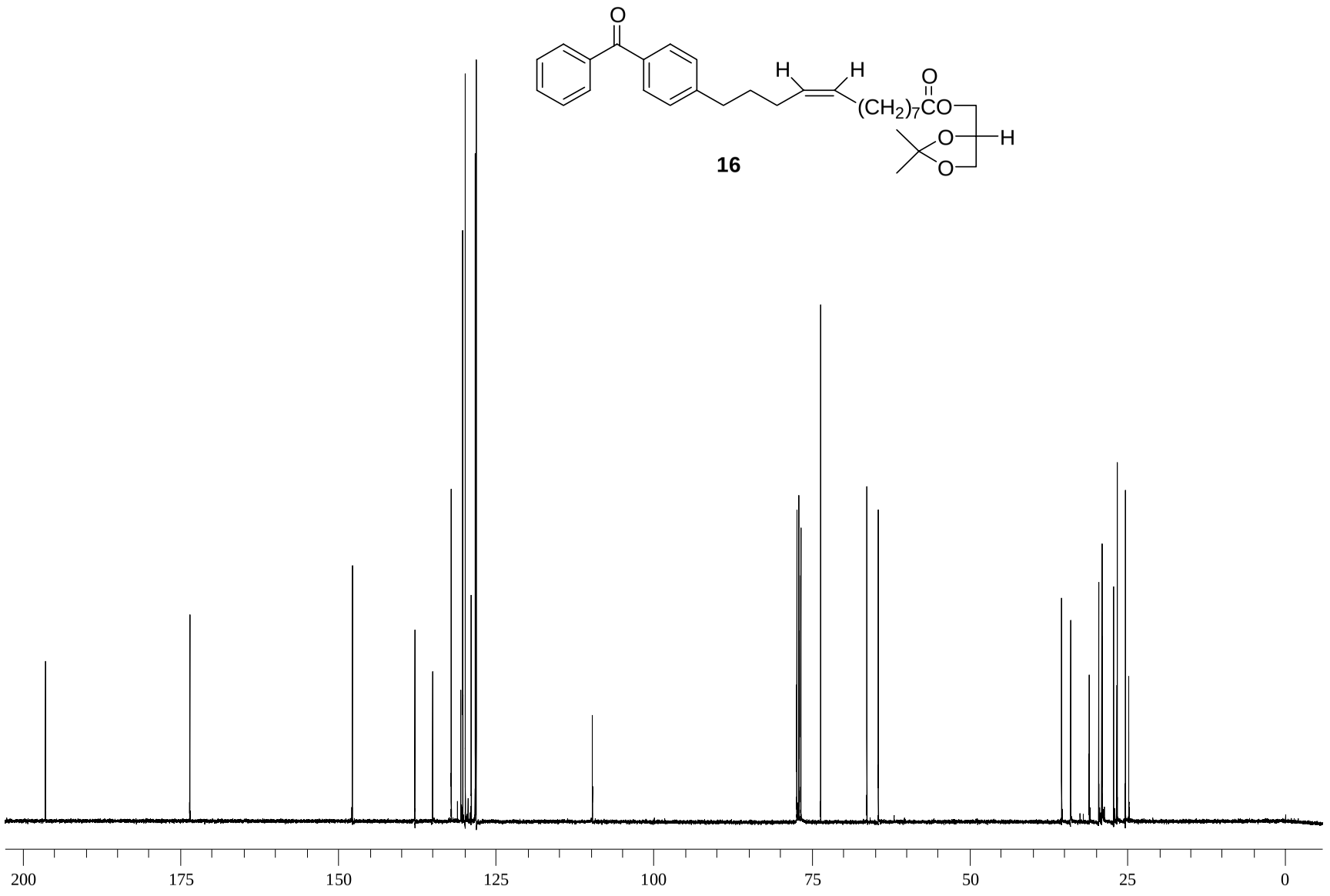
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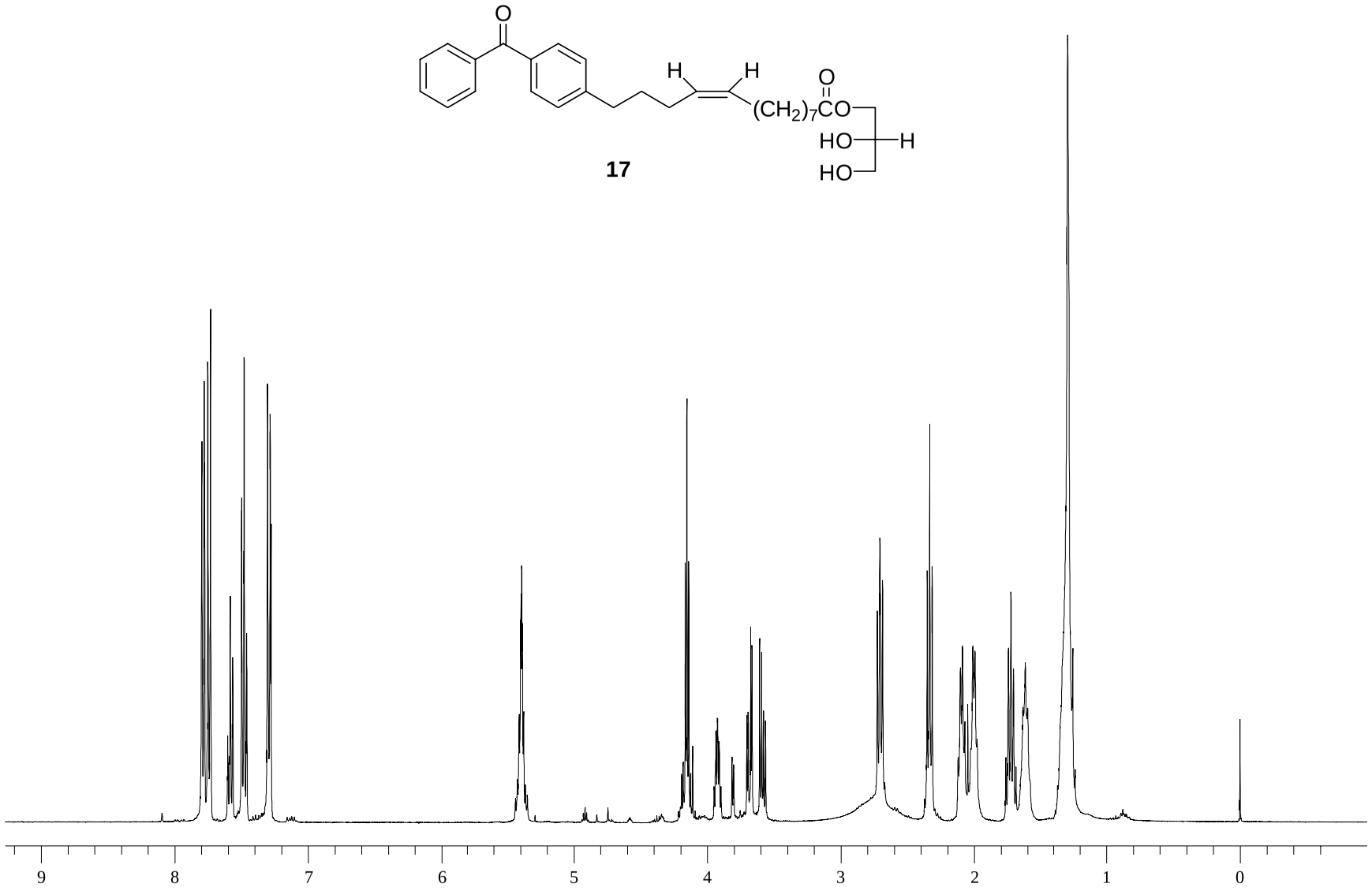

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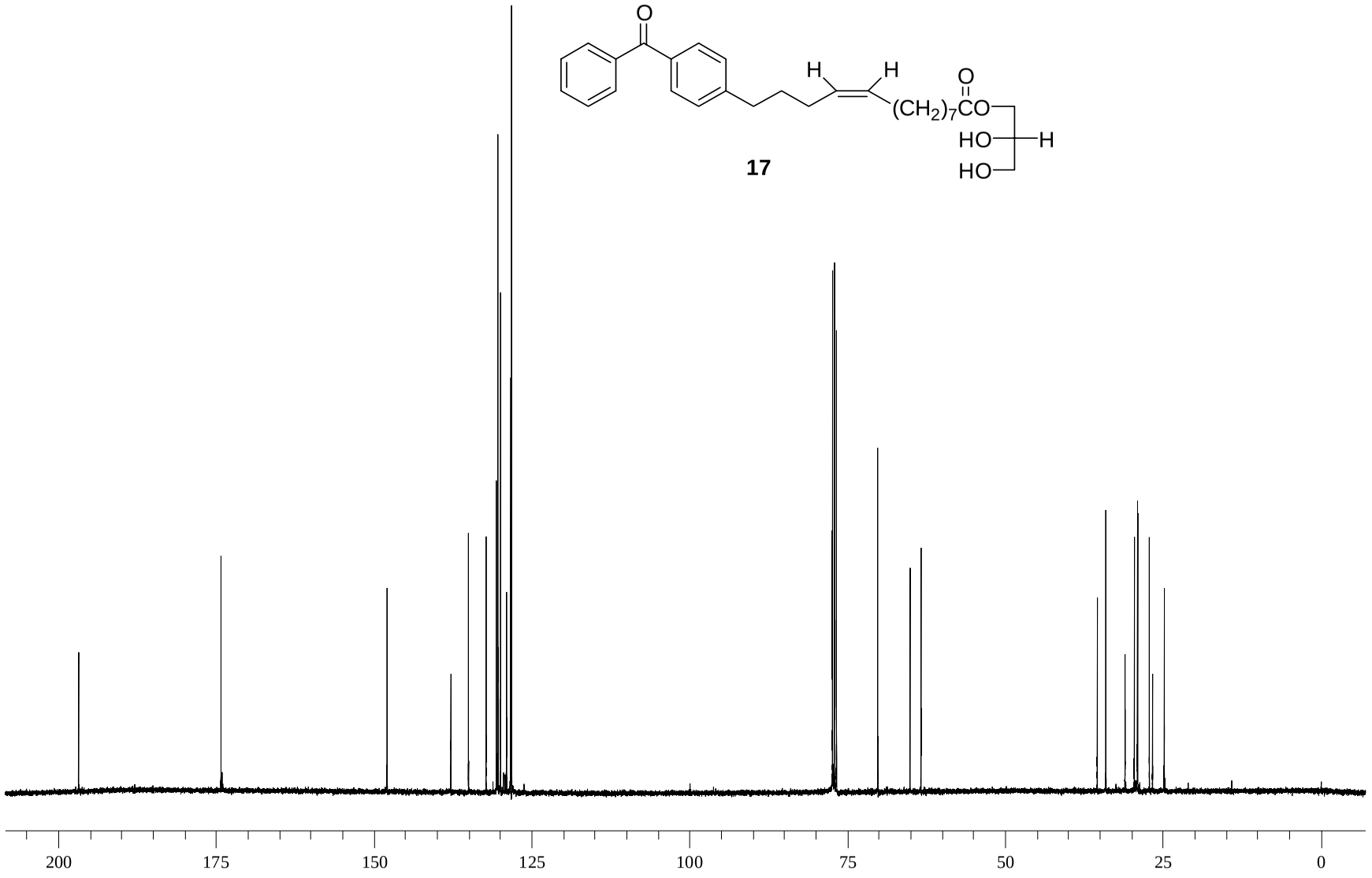
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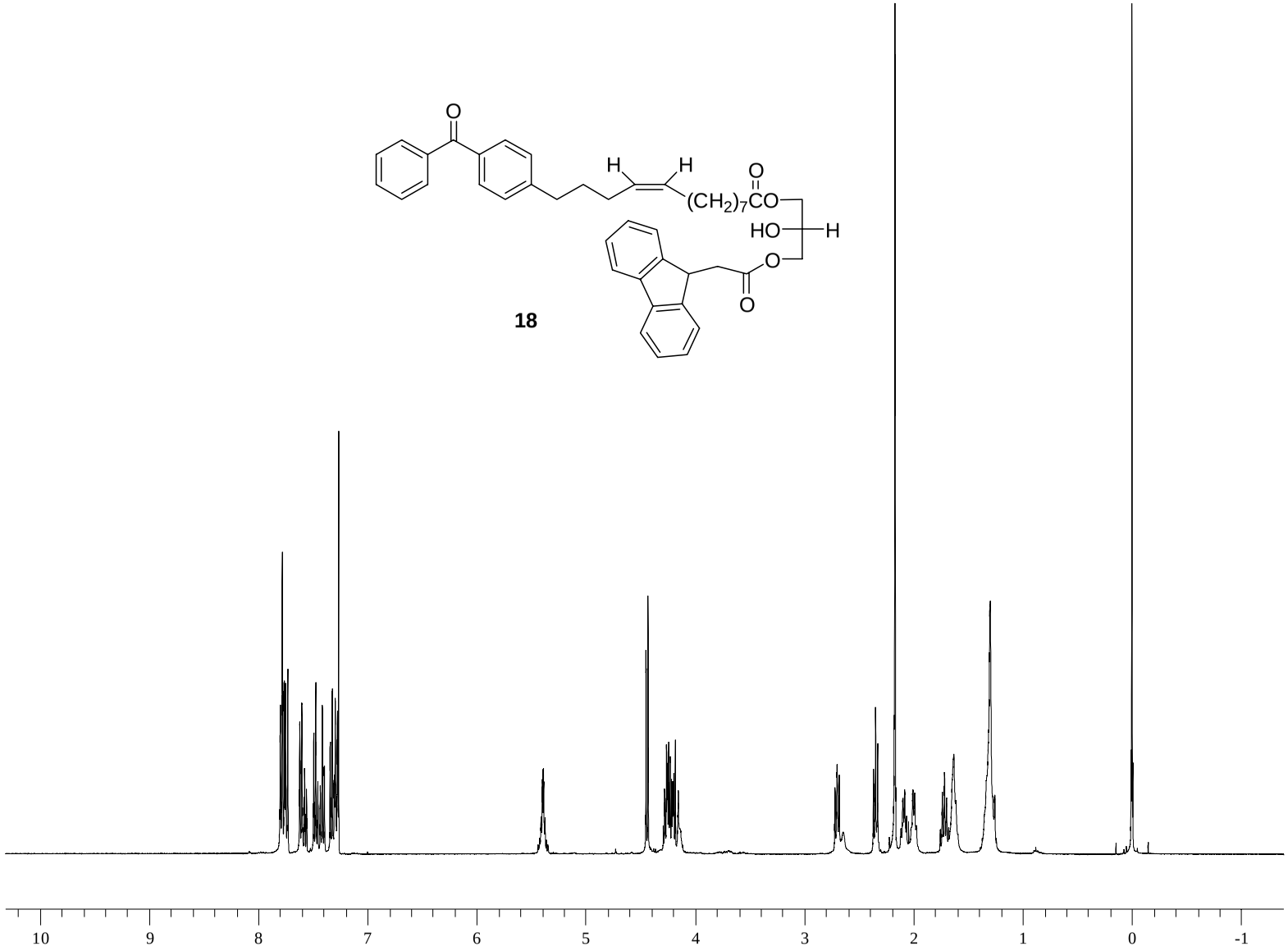
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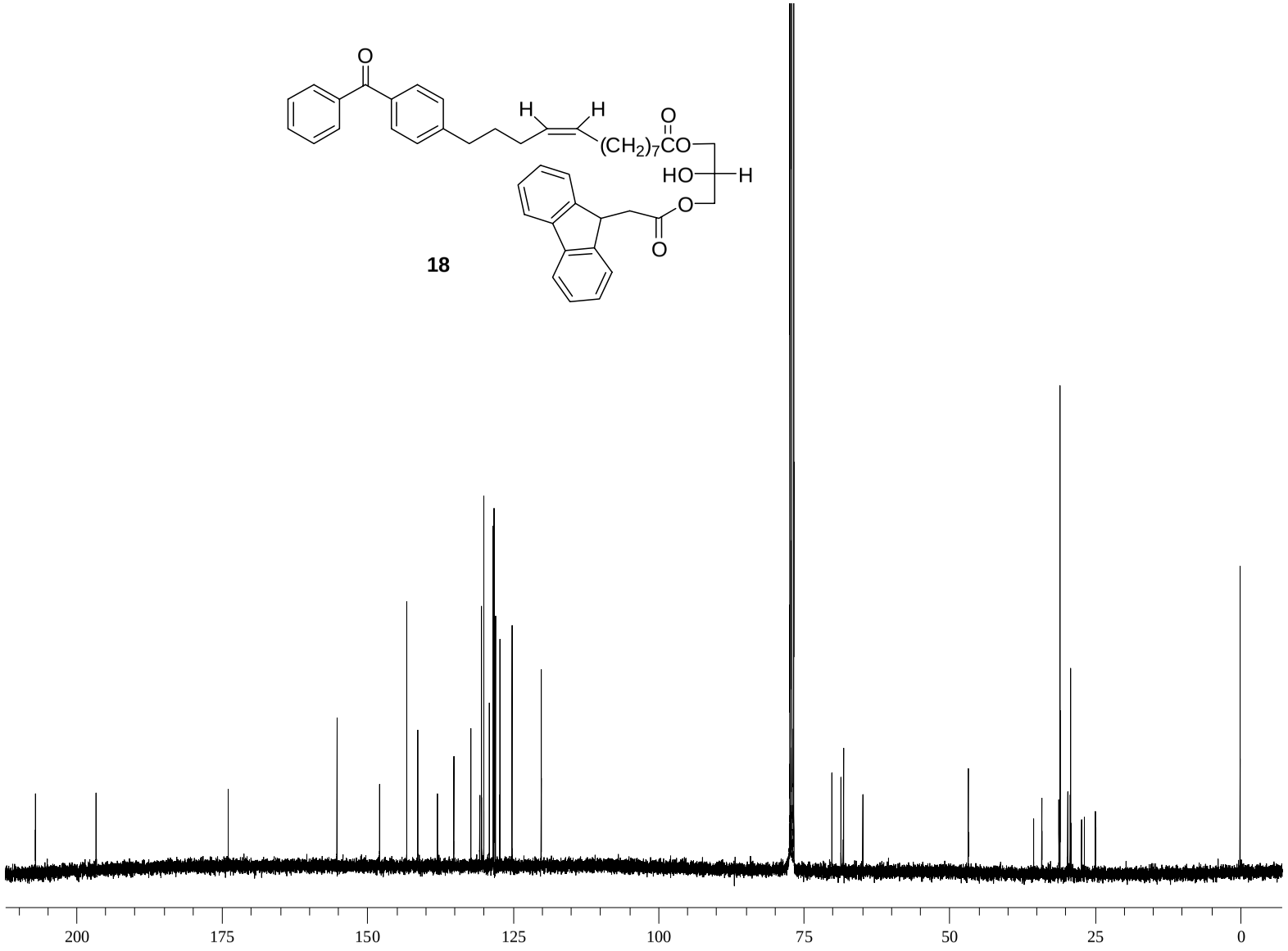
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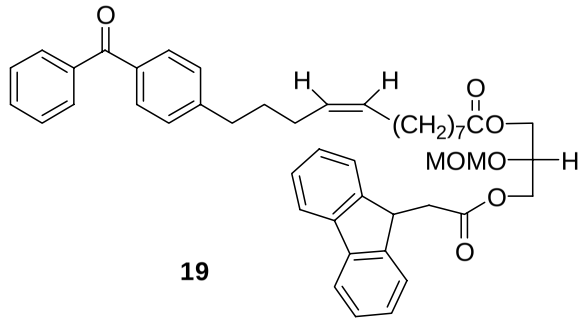

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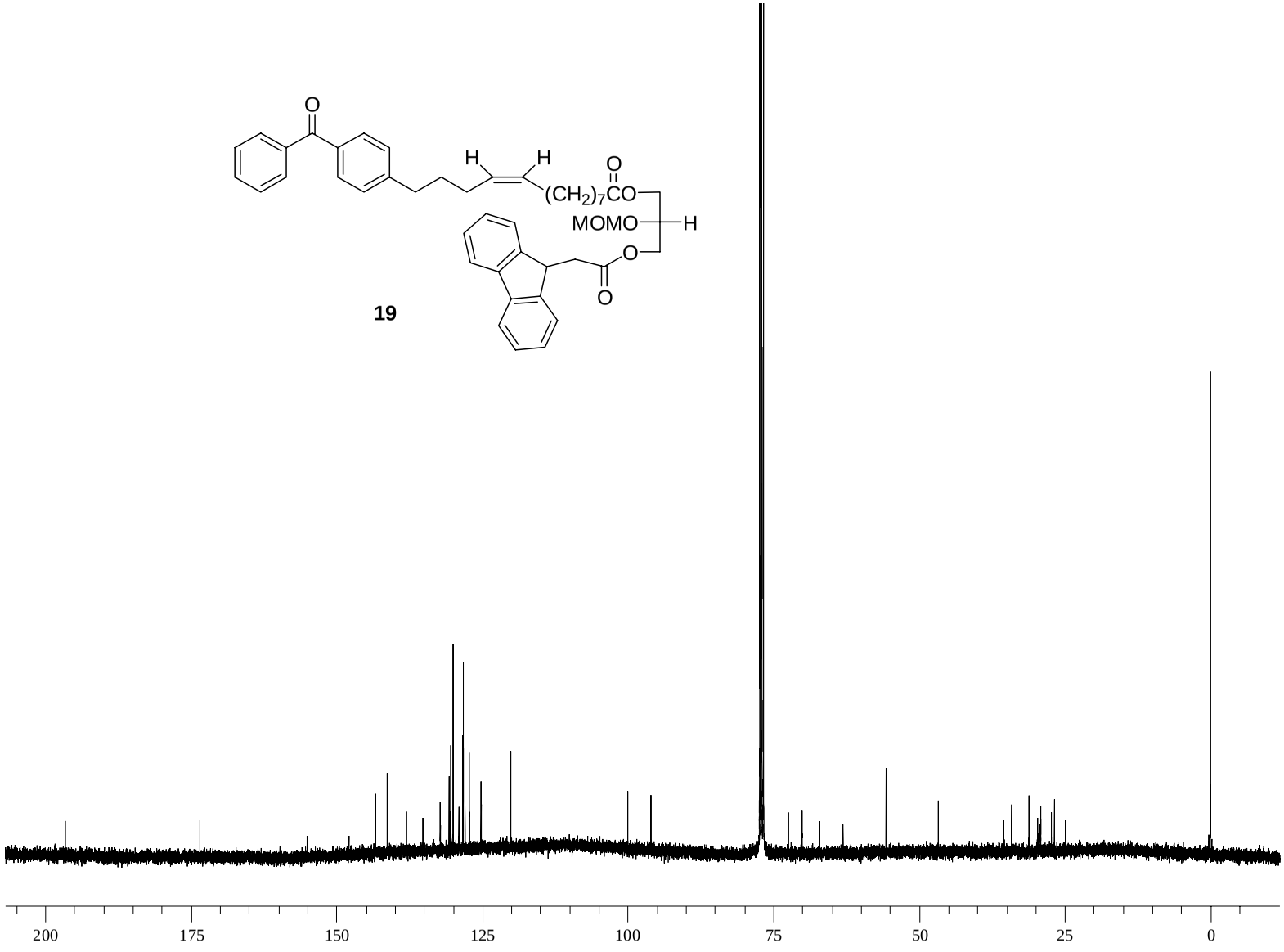
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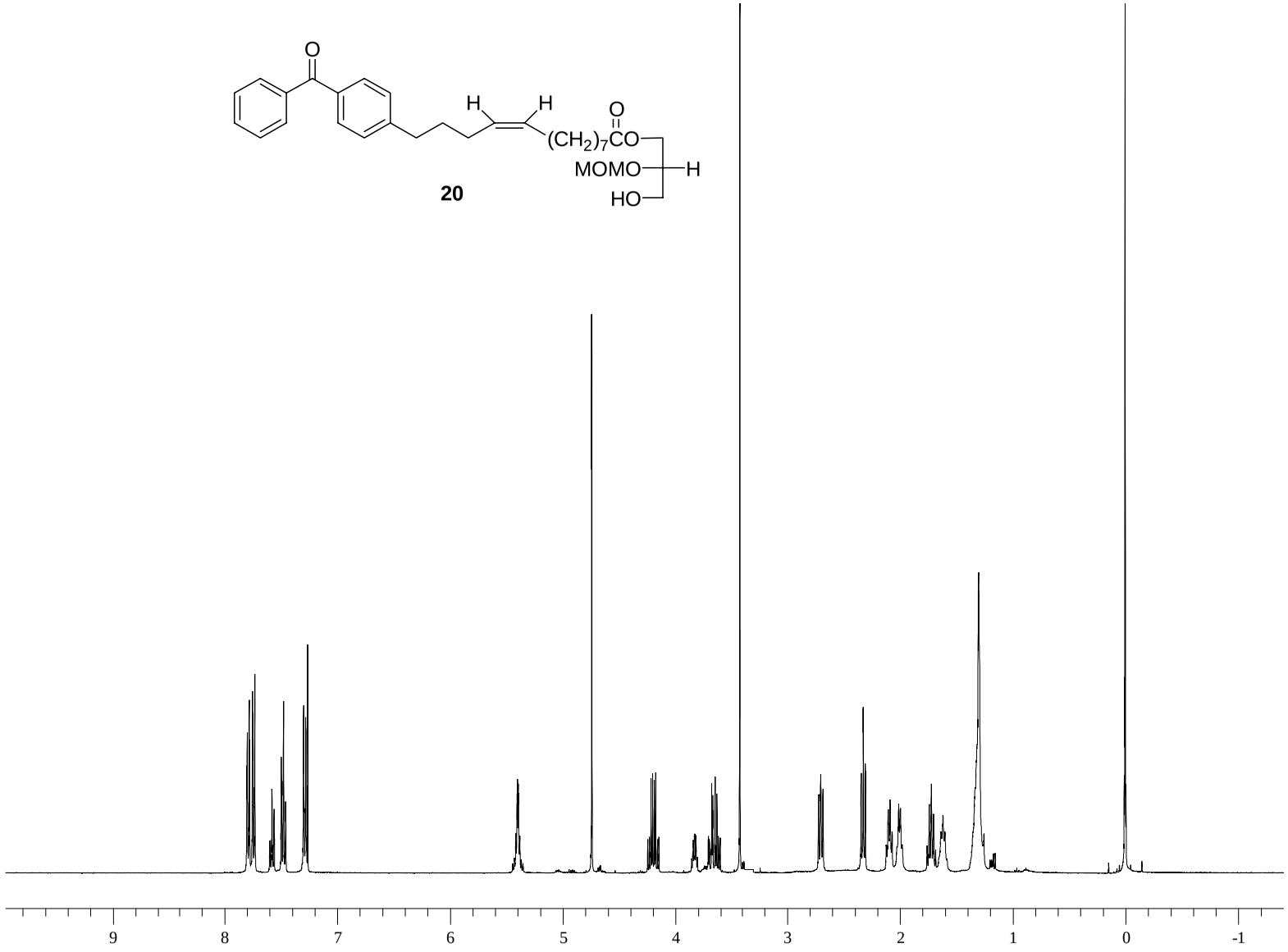
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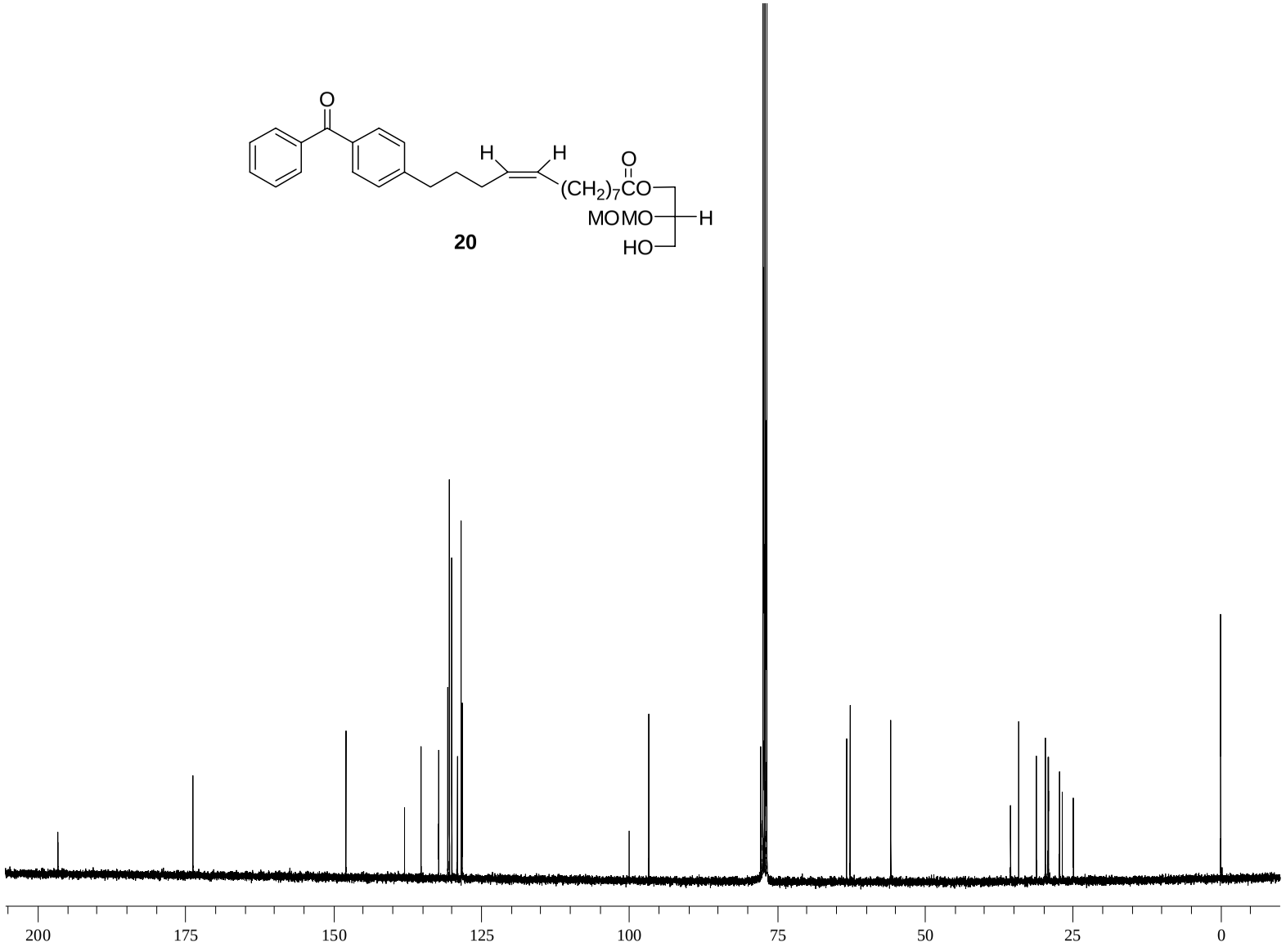
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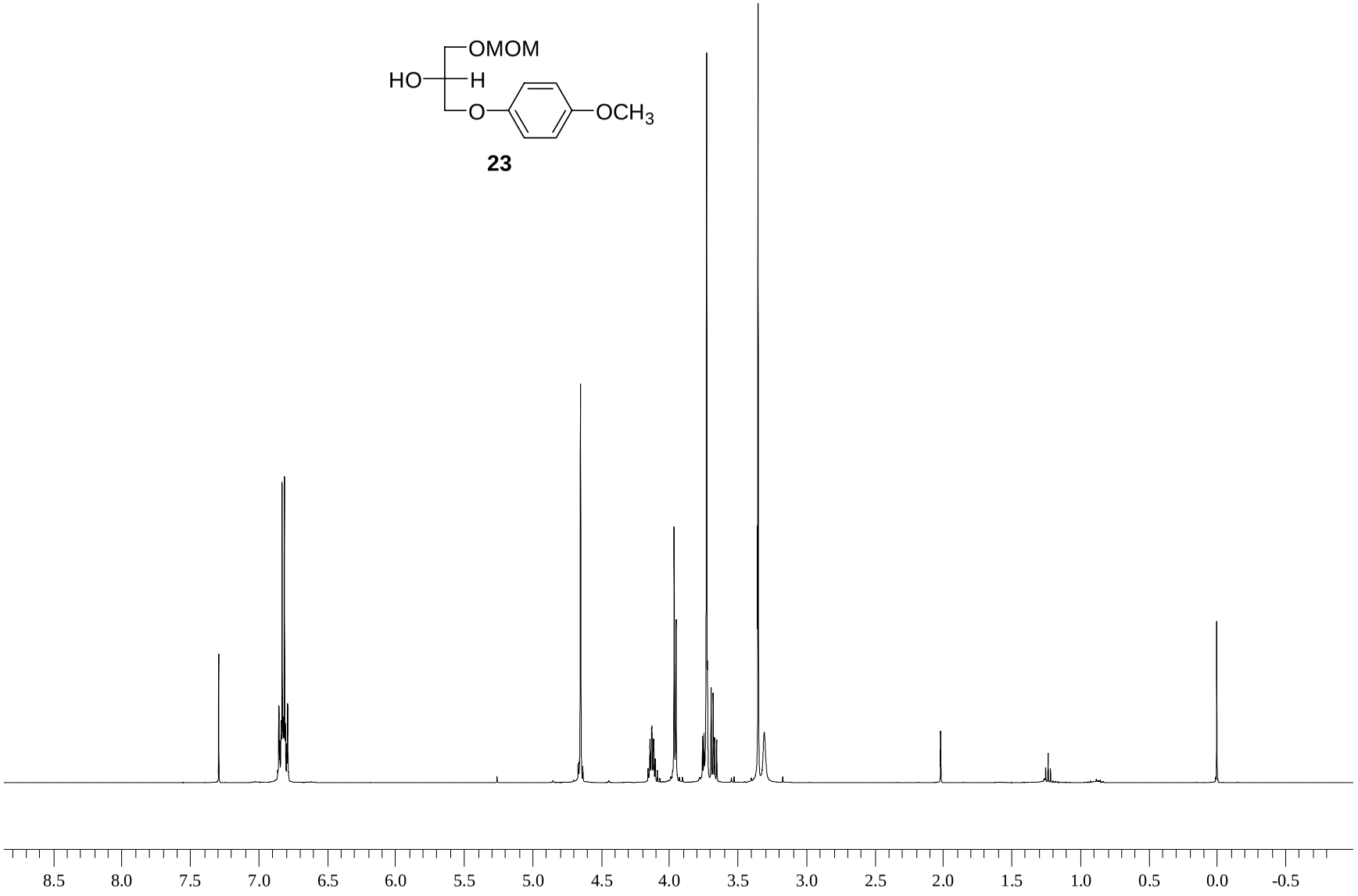
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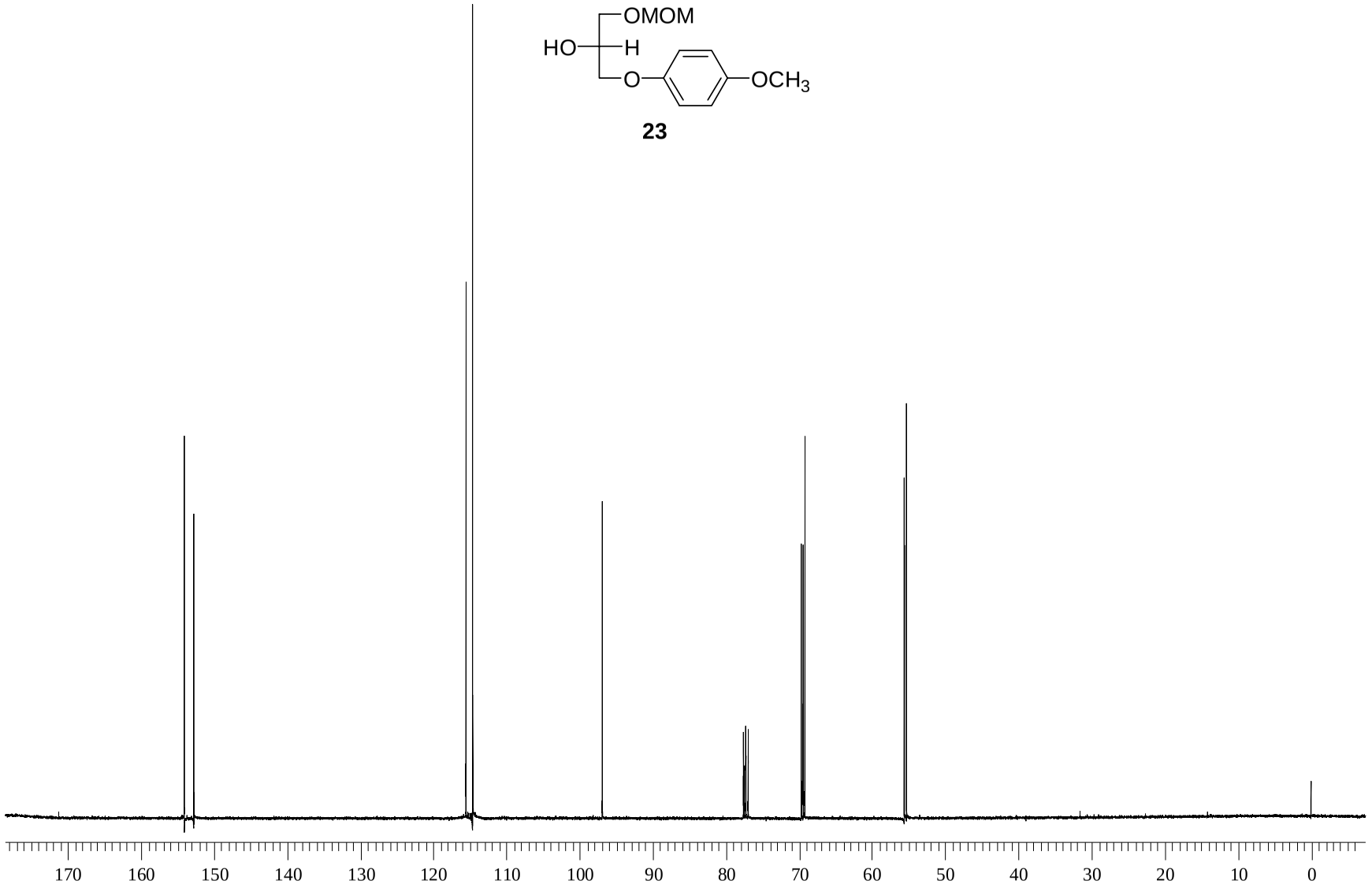
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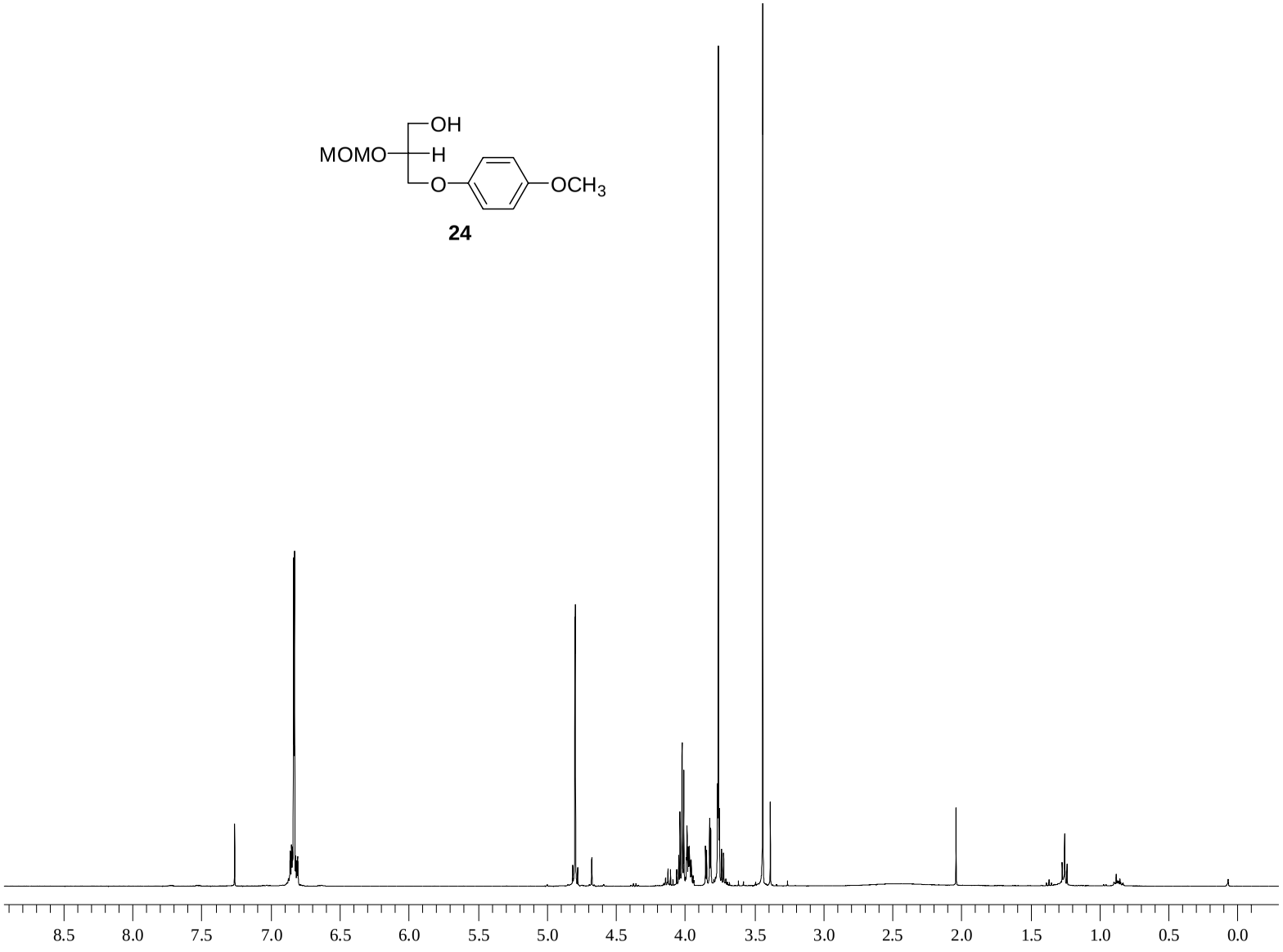
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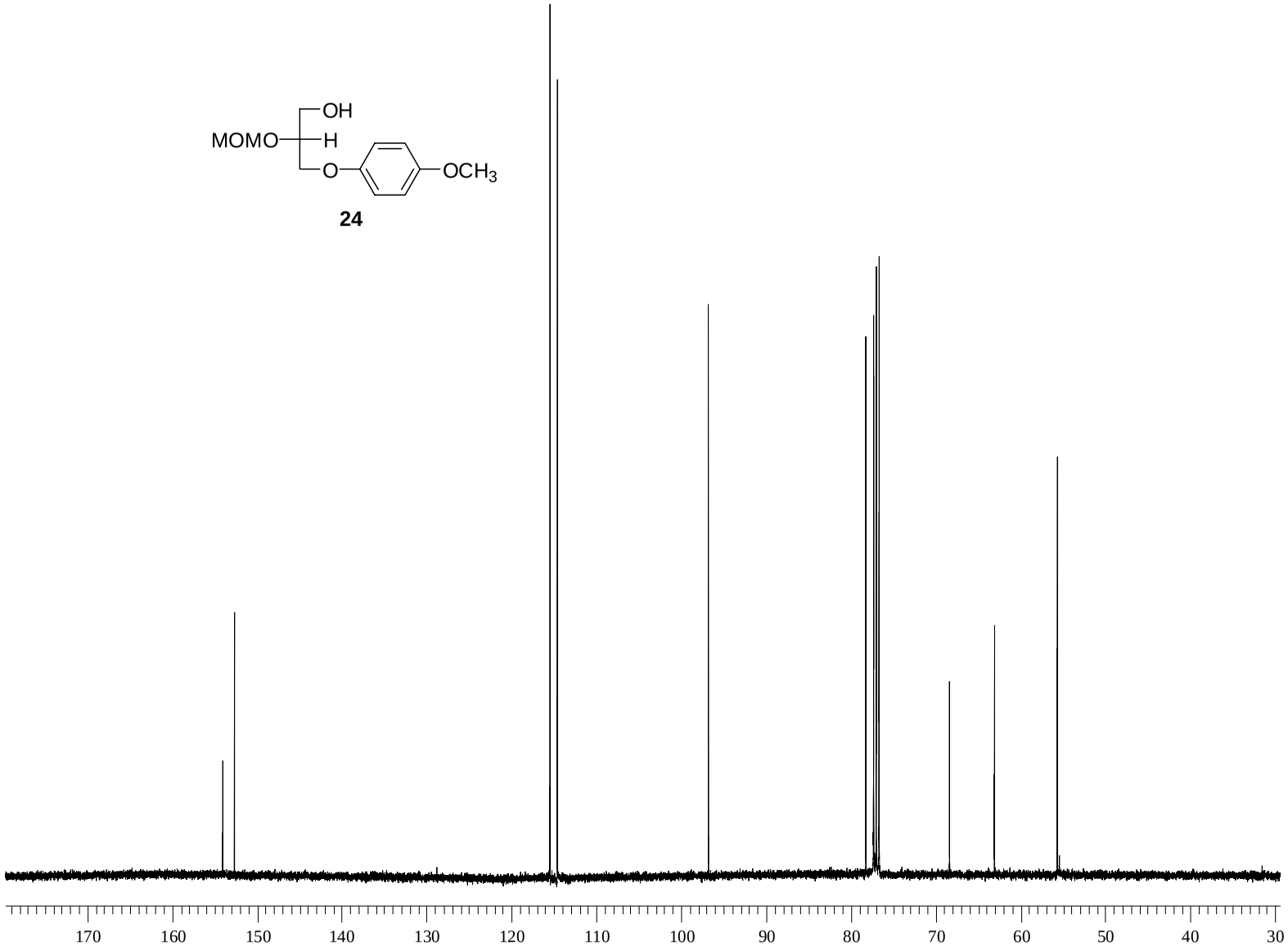
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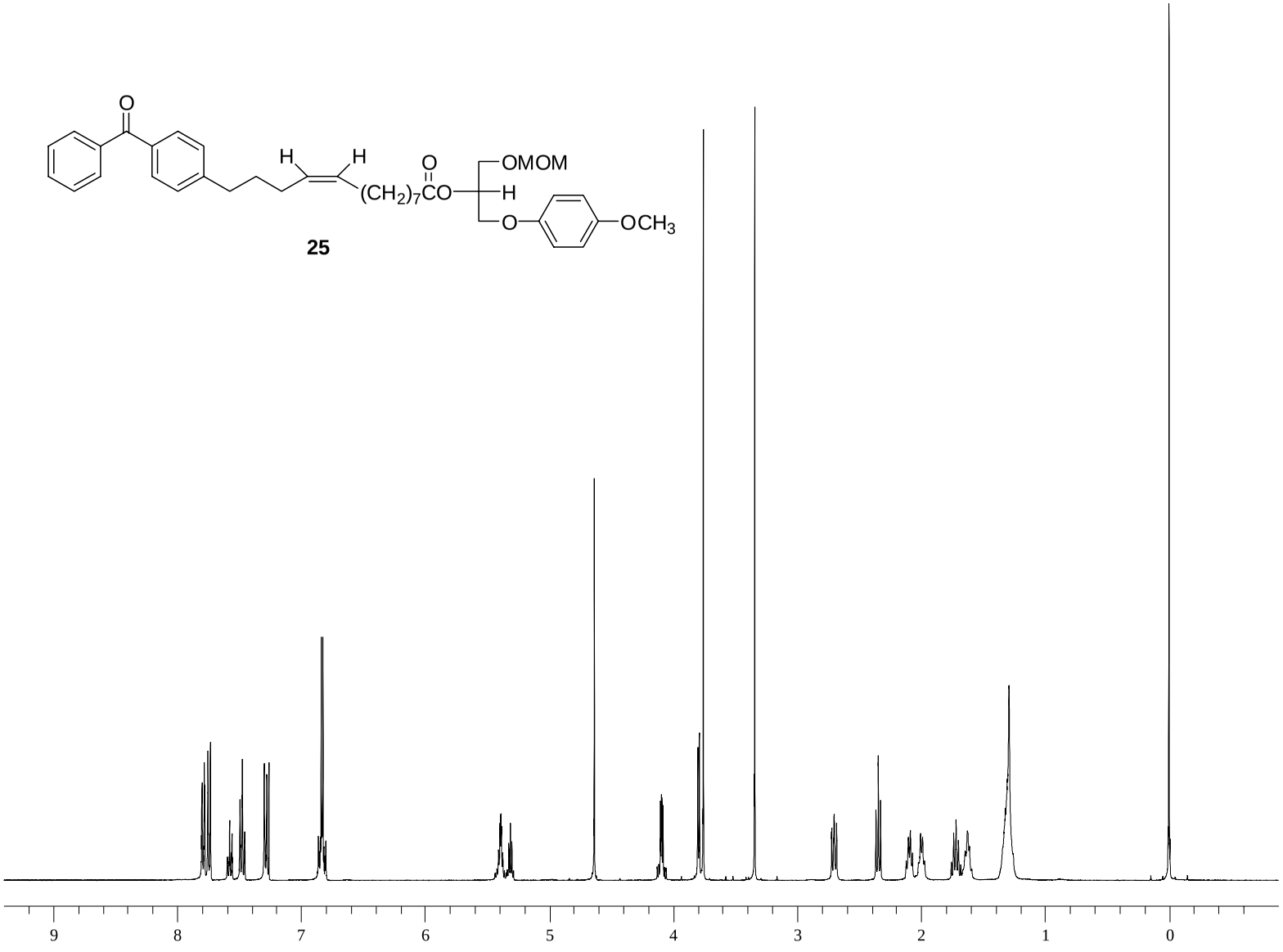
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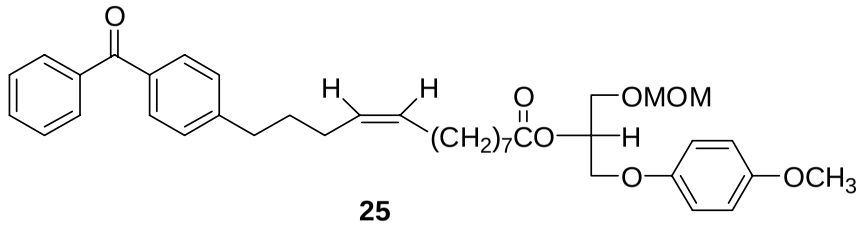

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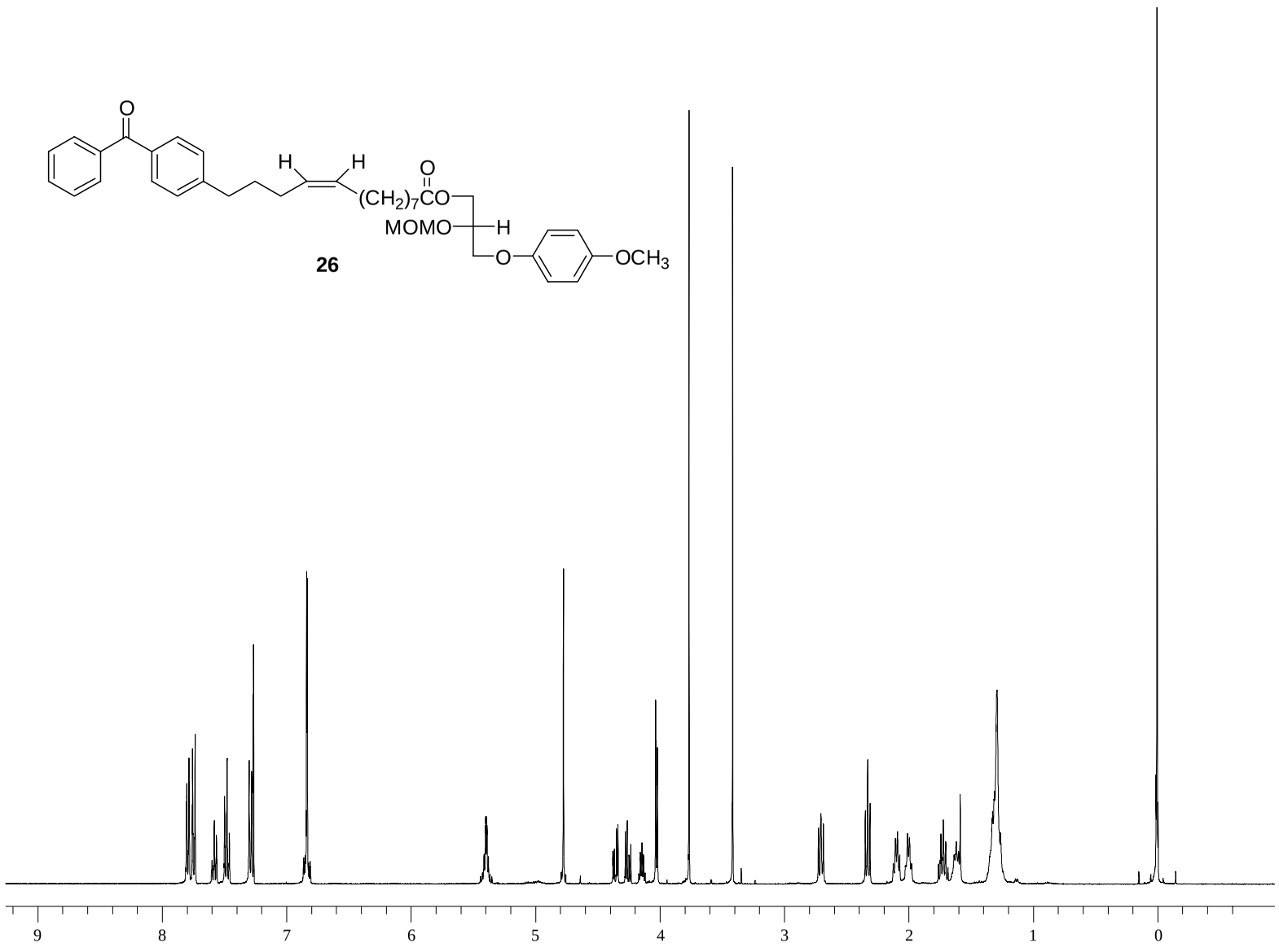
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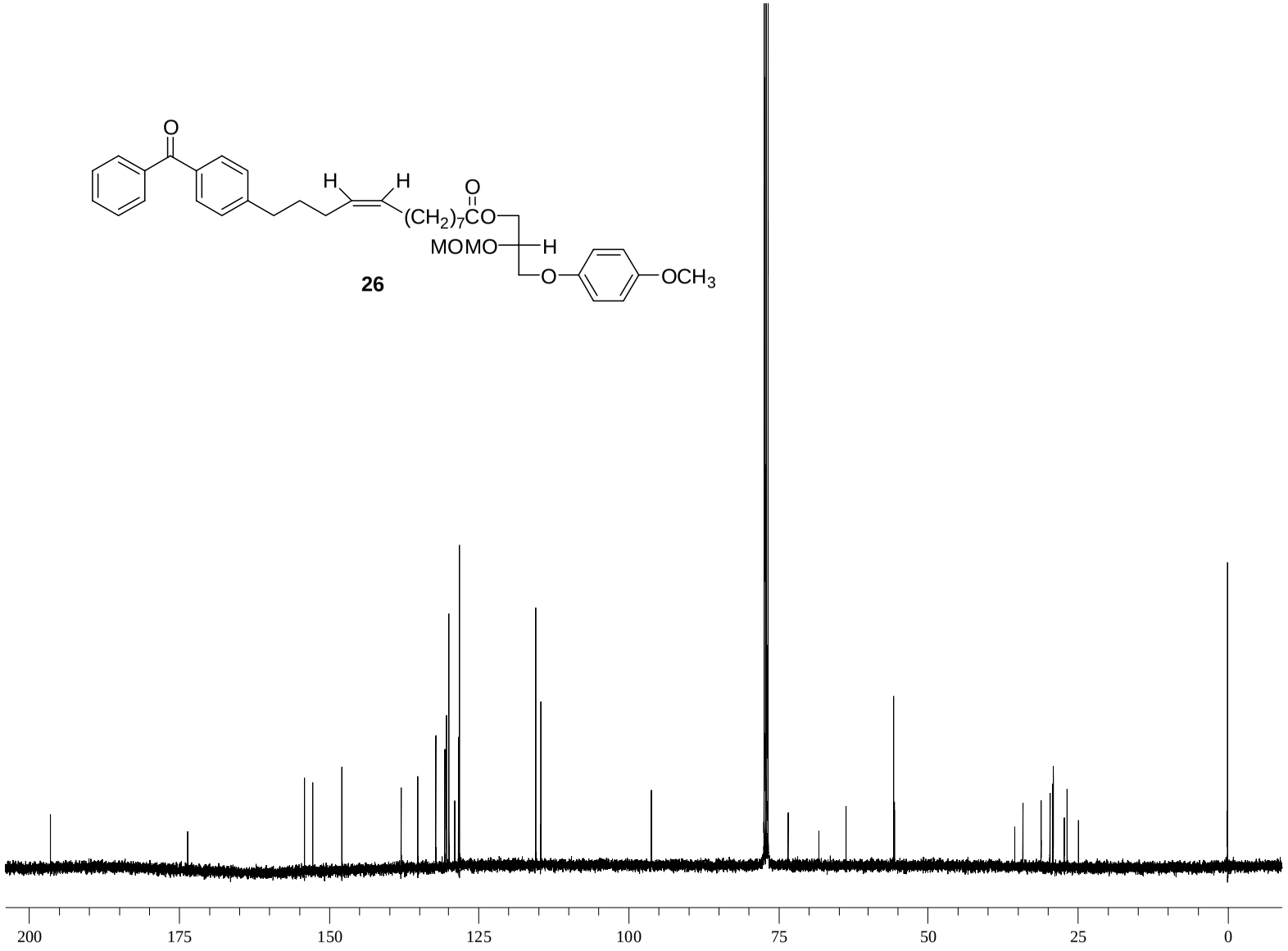
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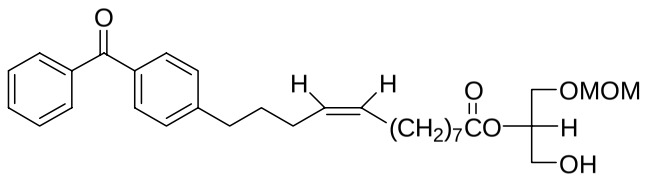

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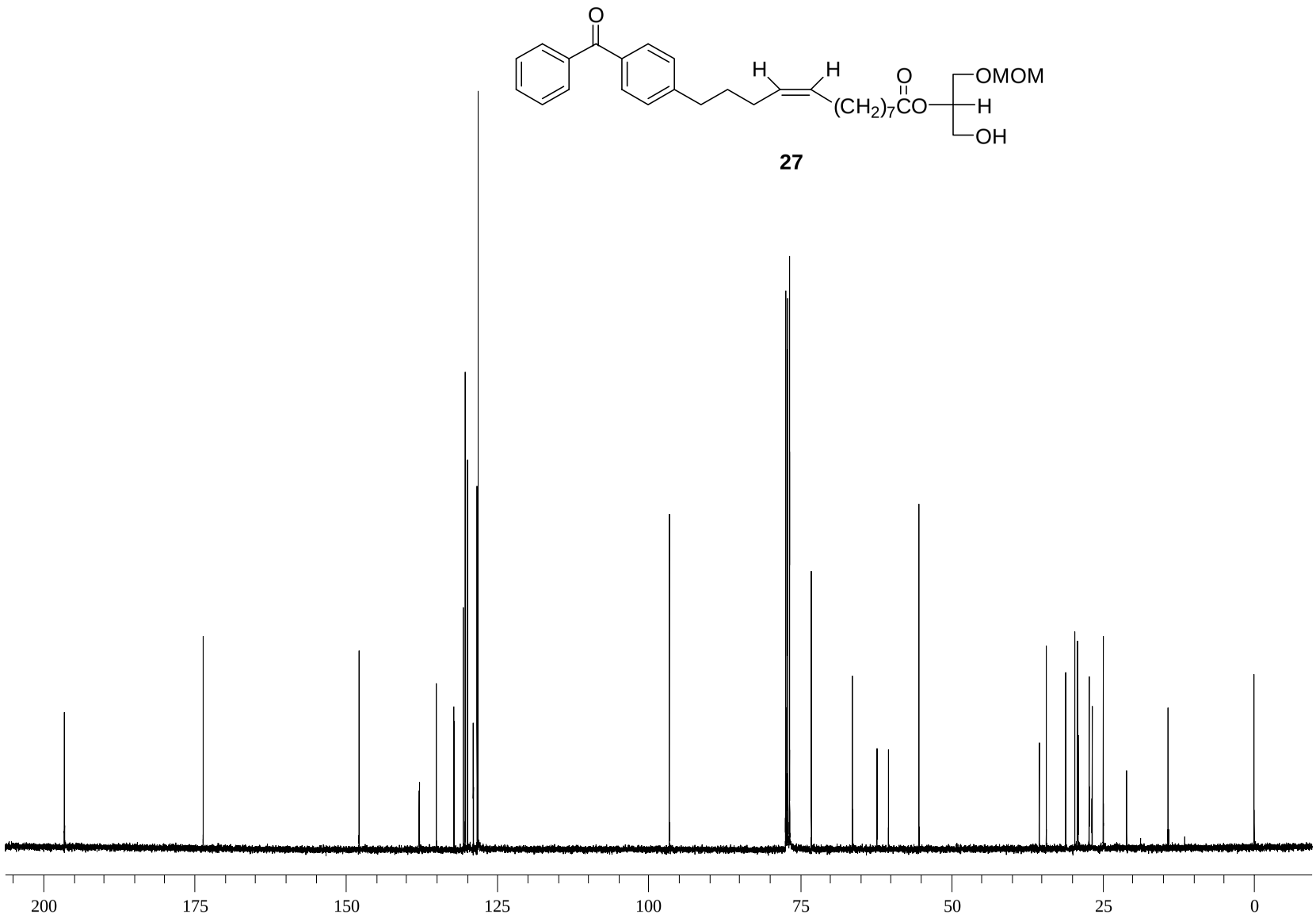

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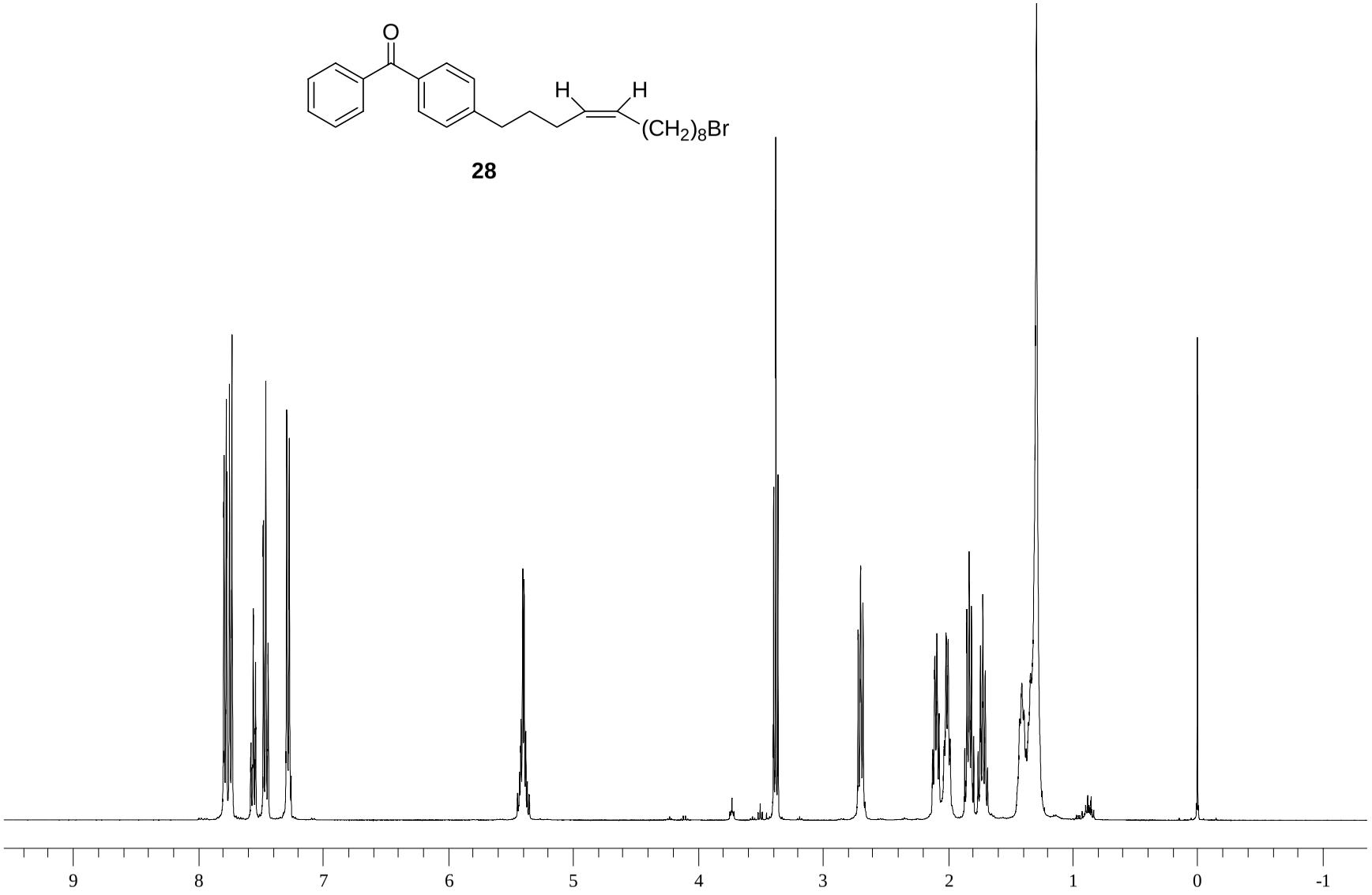

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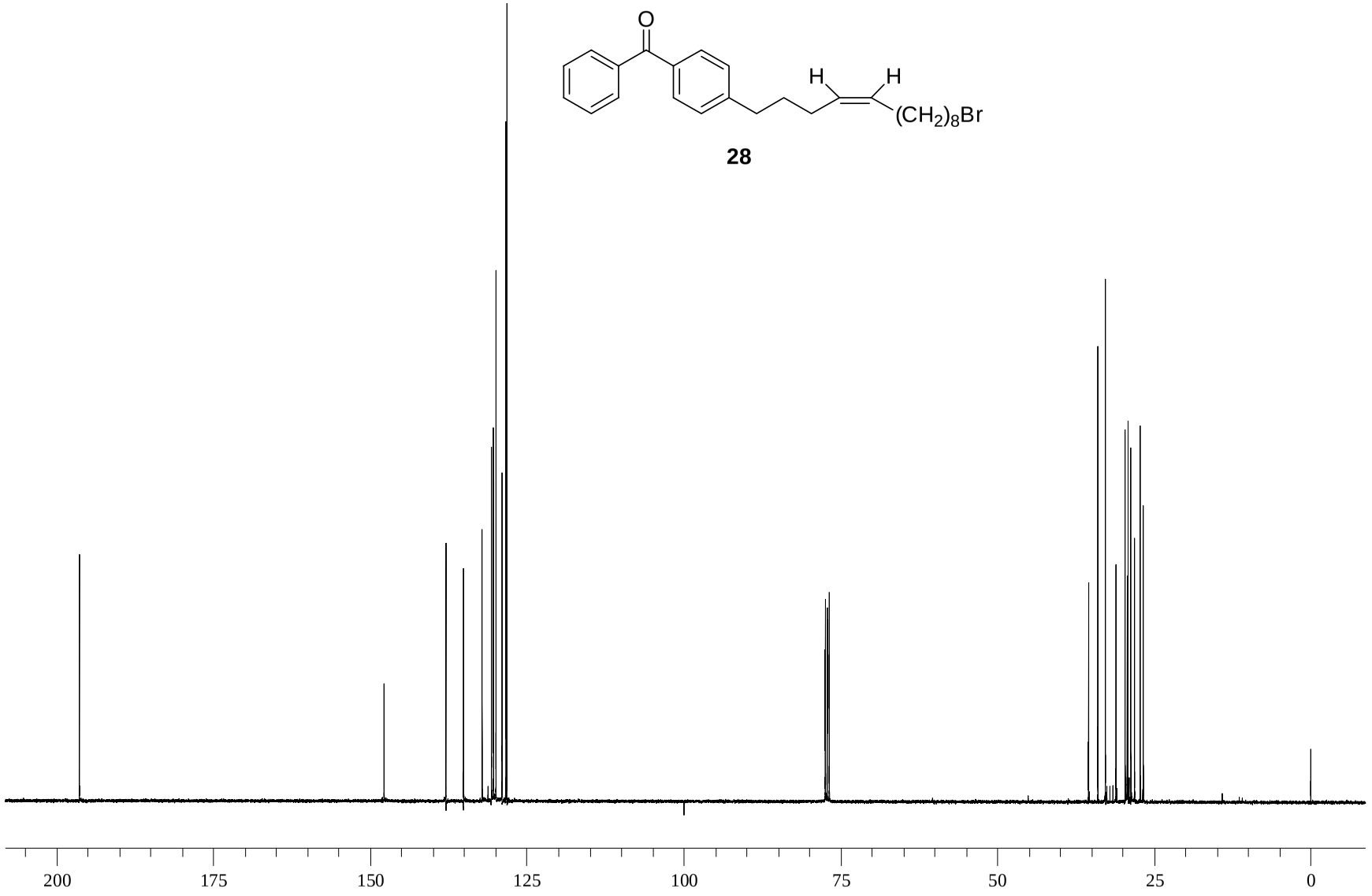
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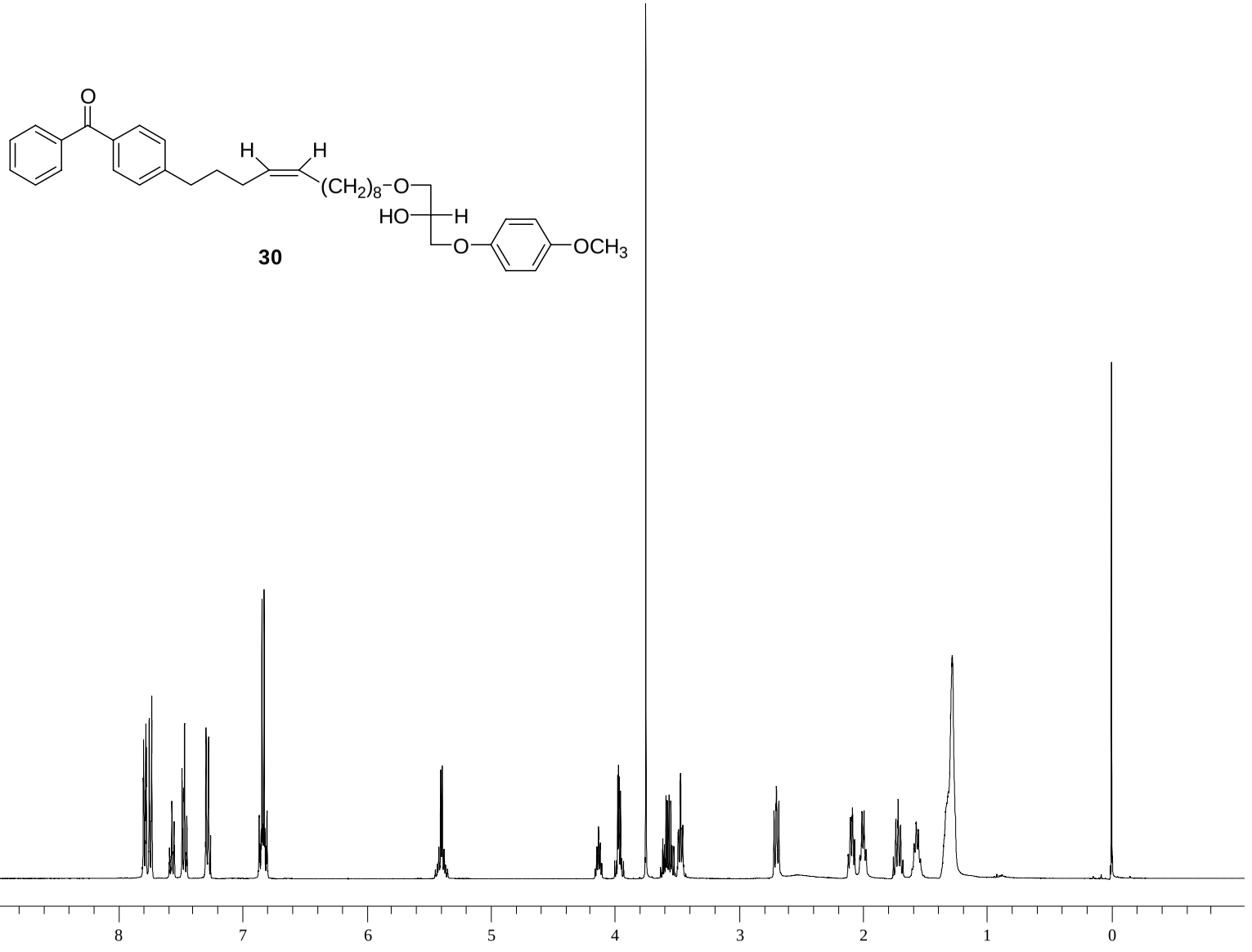
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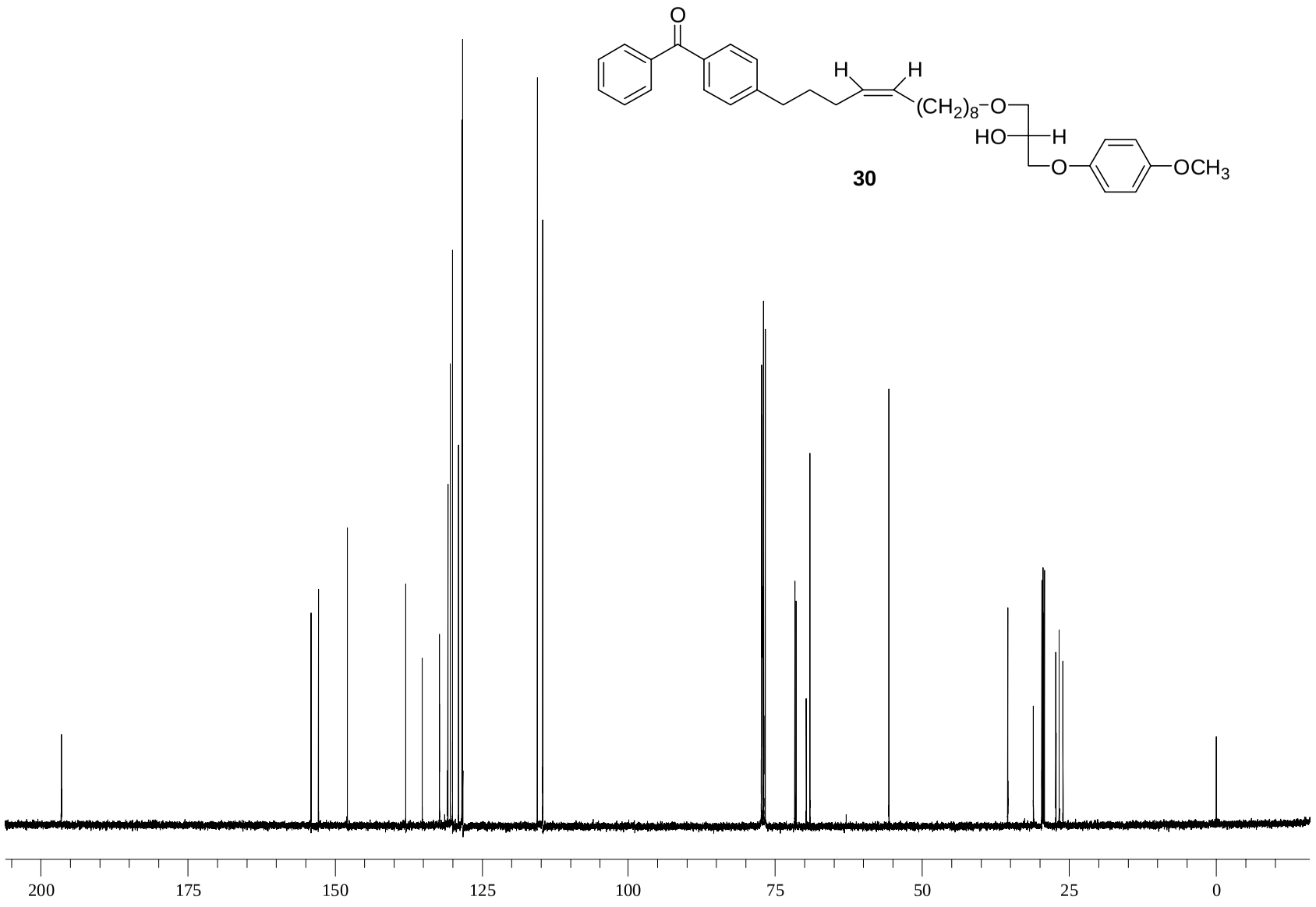
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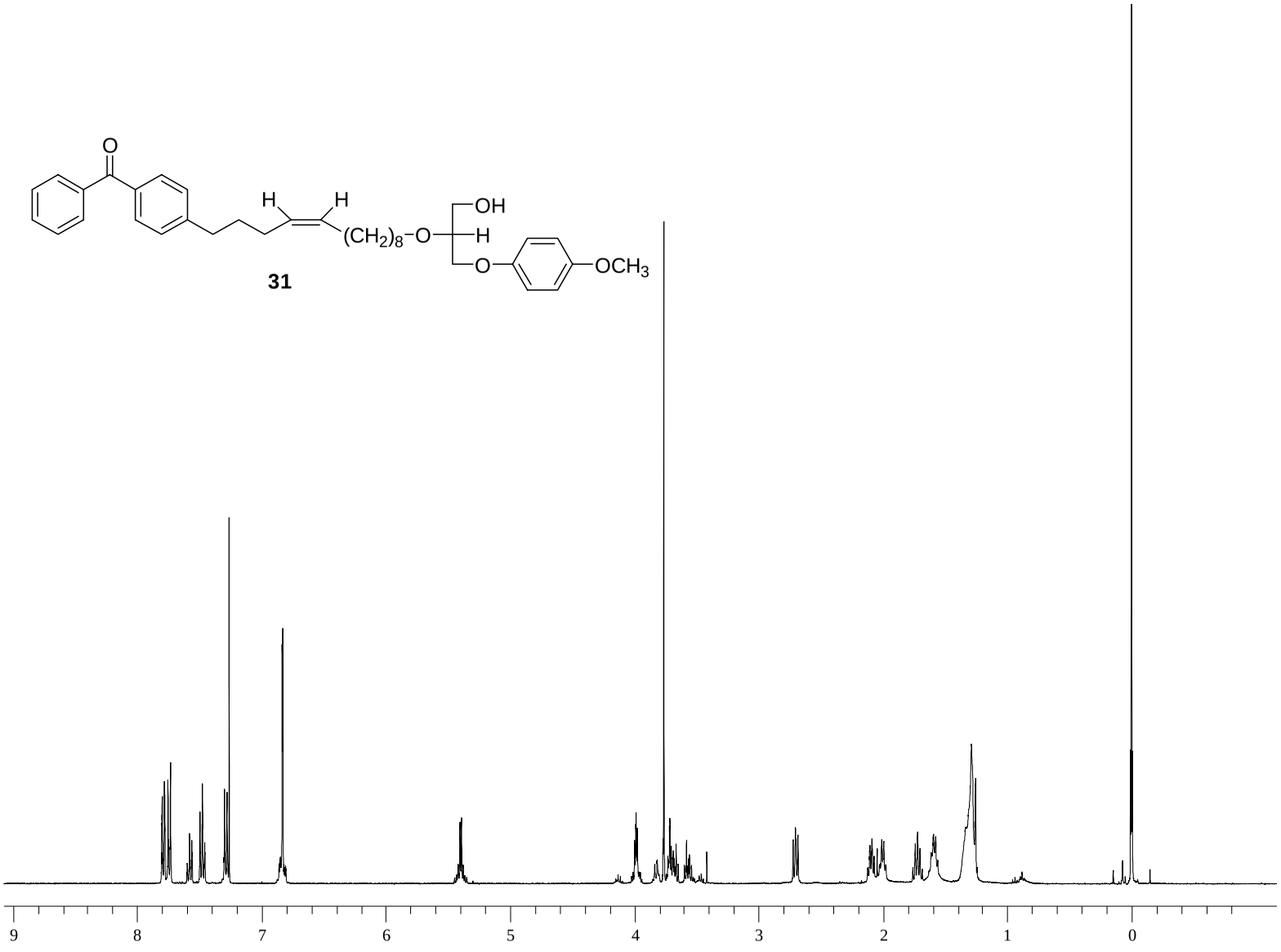
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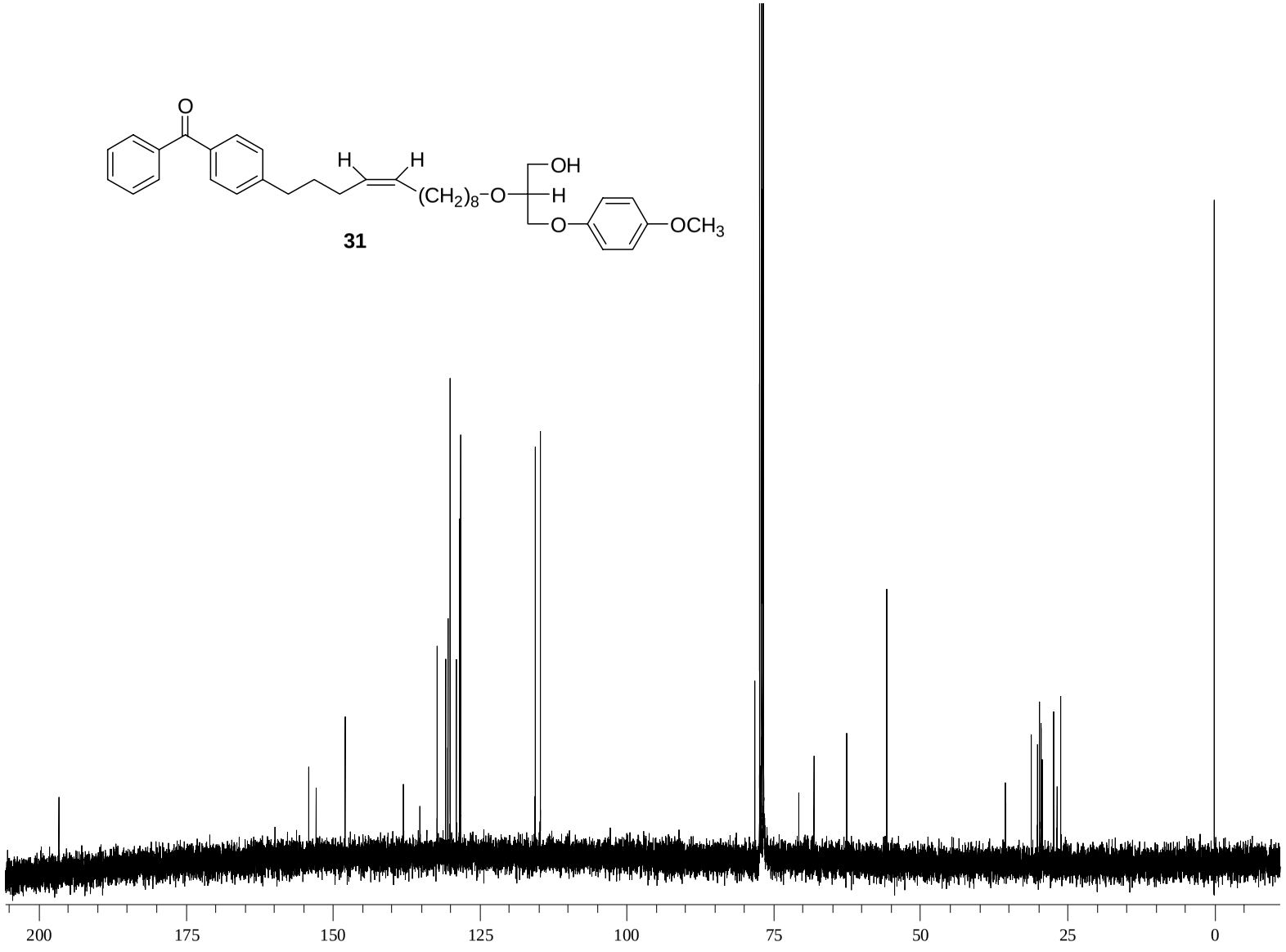
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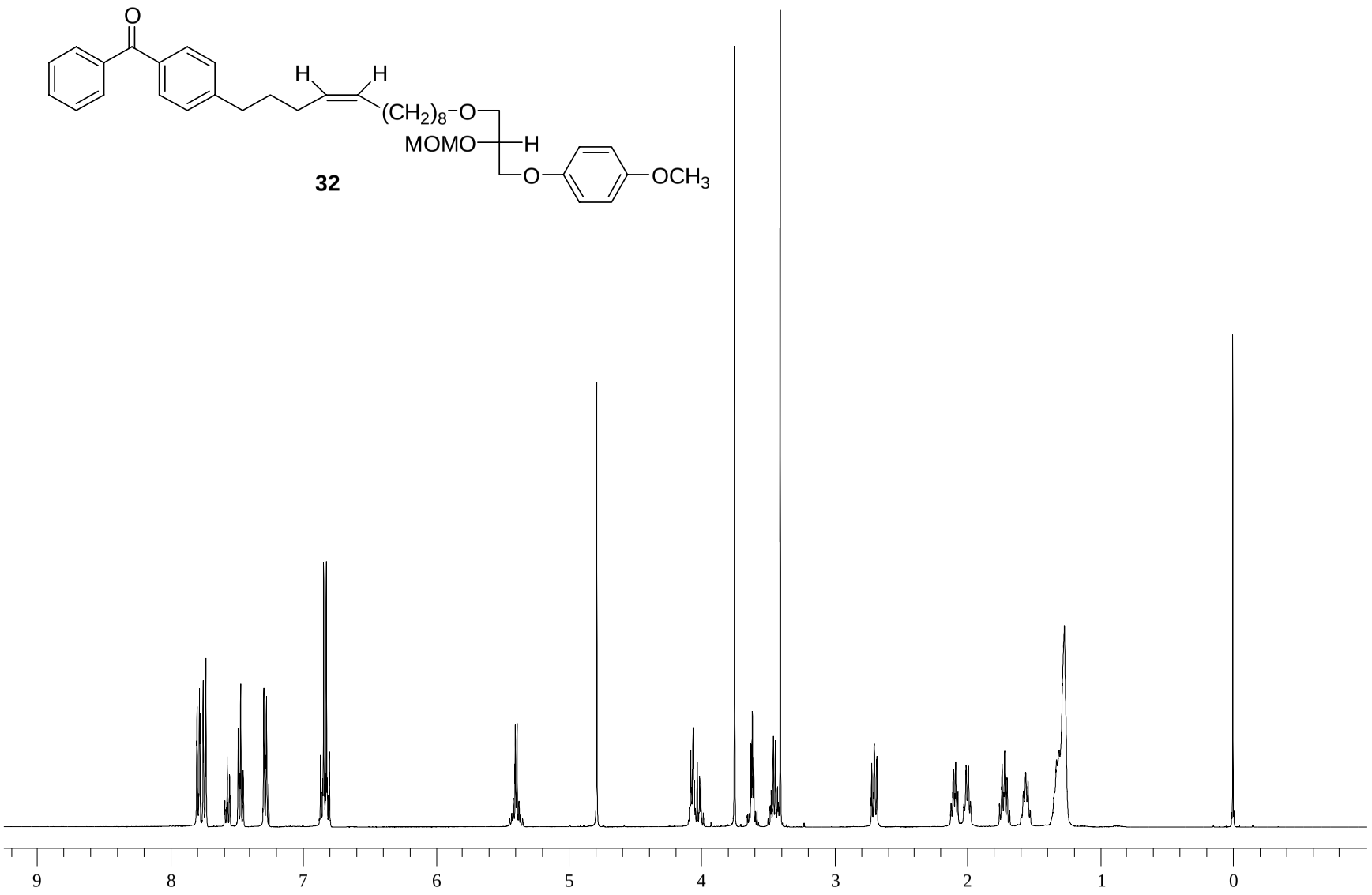
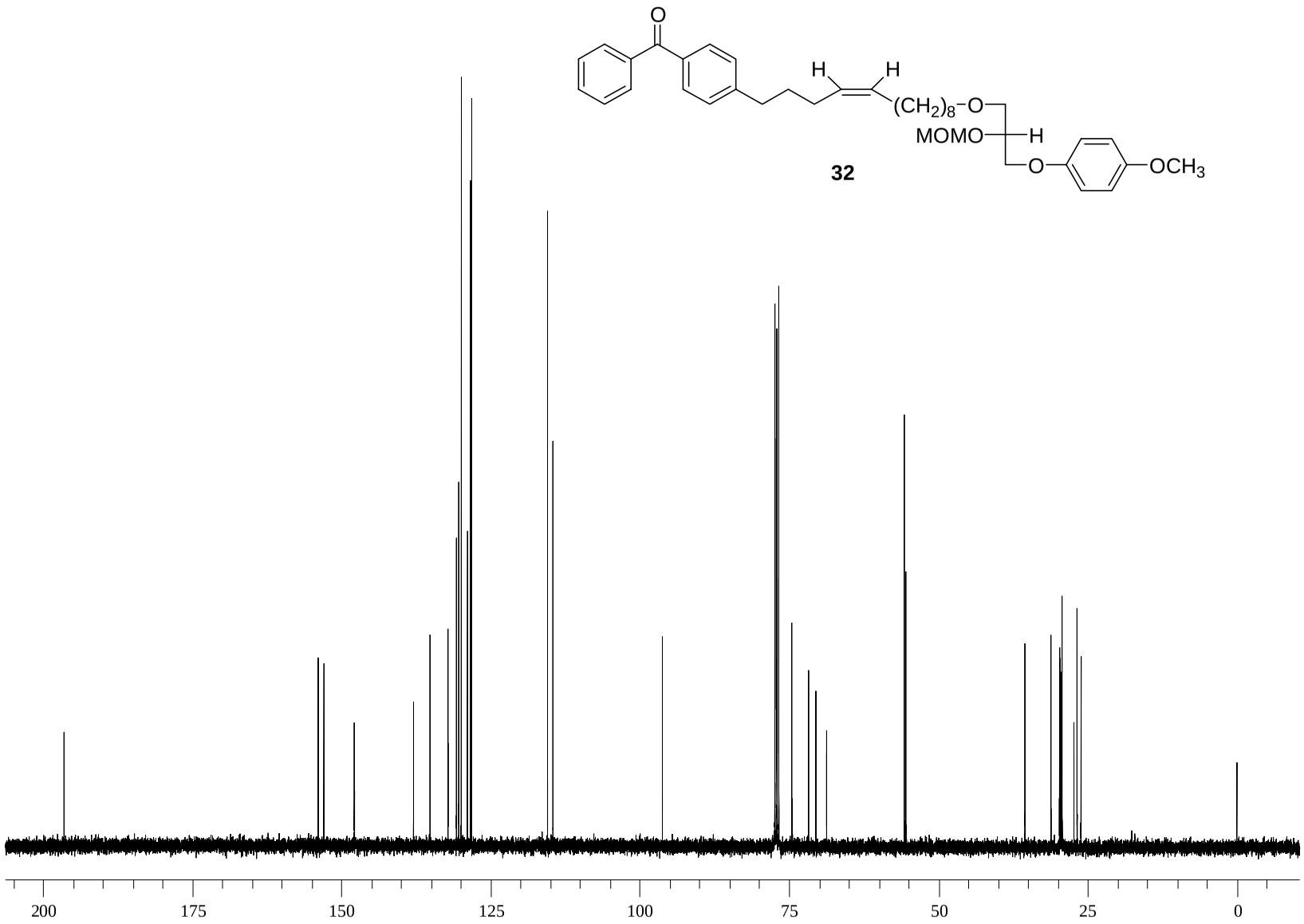
H
H
OH
(CH2)8–O
H
O
OCH3
31
200
175
150
125
100
75
50
25
0


O
H
H
(CH2)8–O
MOMO
H
O
OCH3
32
9
8
7
6
5
4
3
2
1
0


O
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(CH2)8–O
MOMO
H
O
OCH3
32
200
175
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125
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75
50
25
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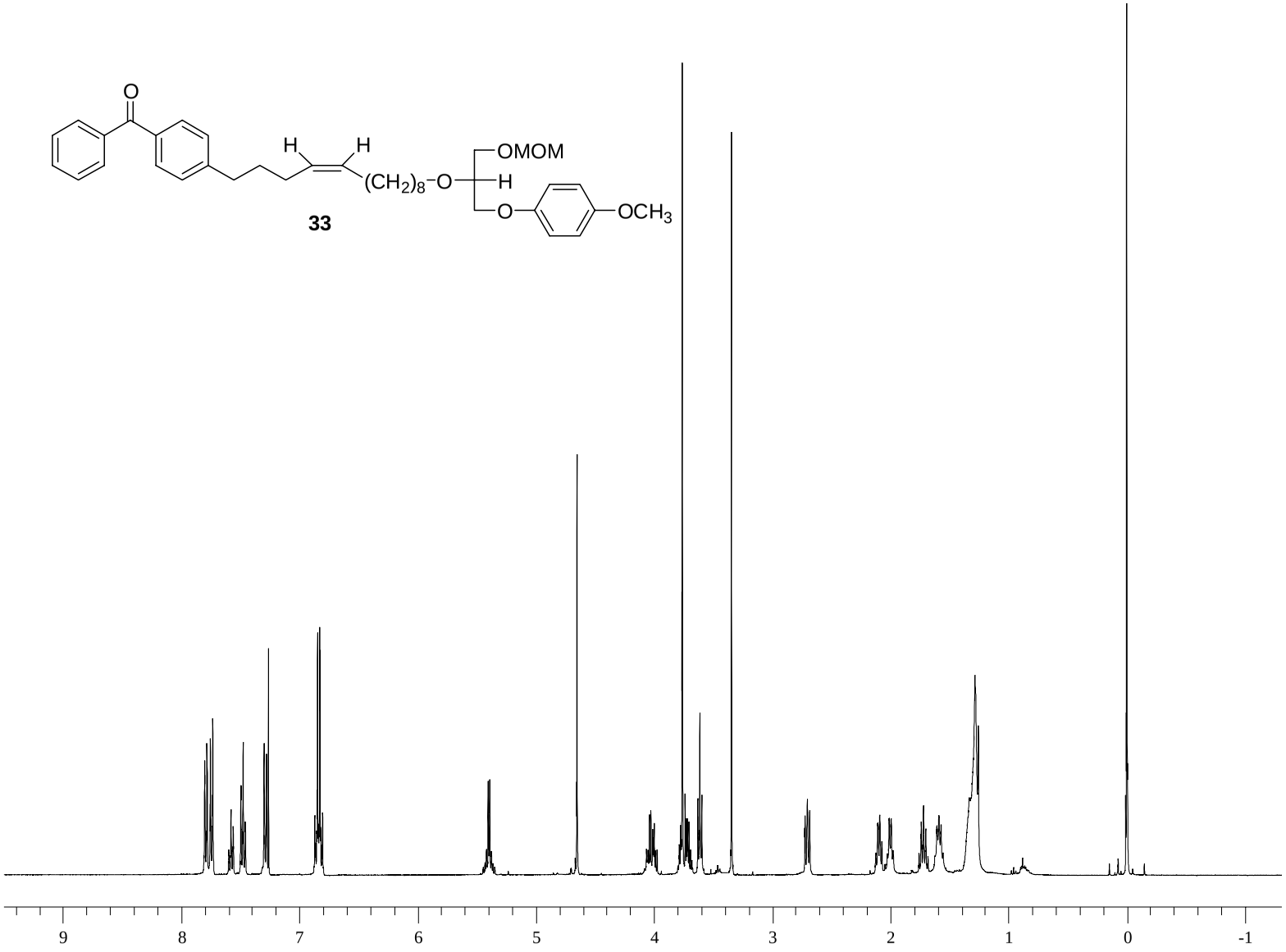
O
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H
(CH2)8
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OMOM
H
O
OCH3
33
9
8
7
6
5
4
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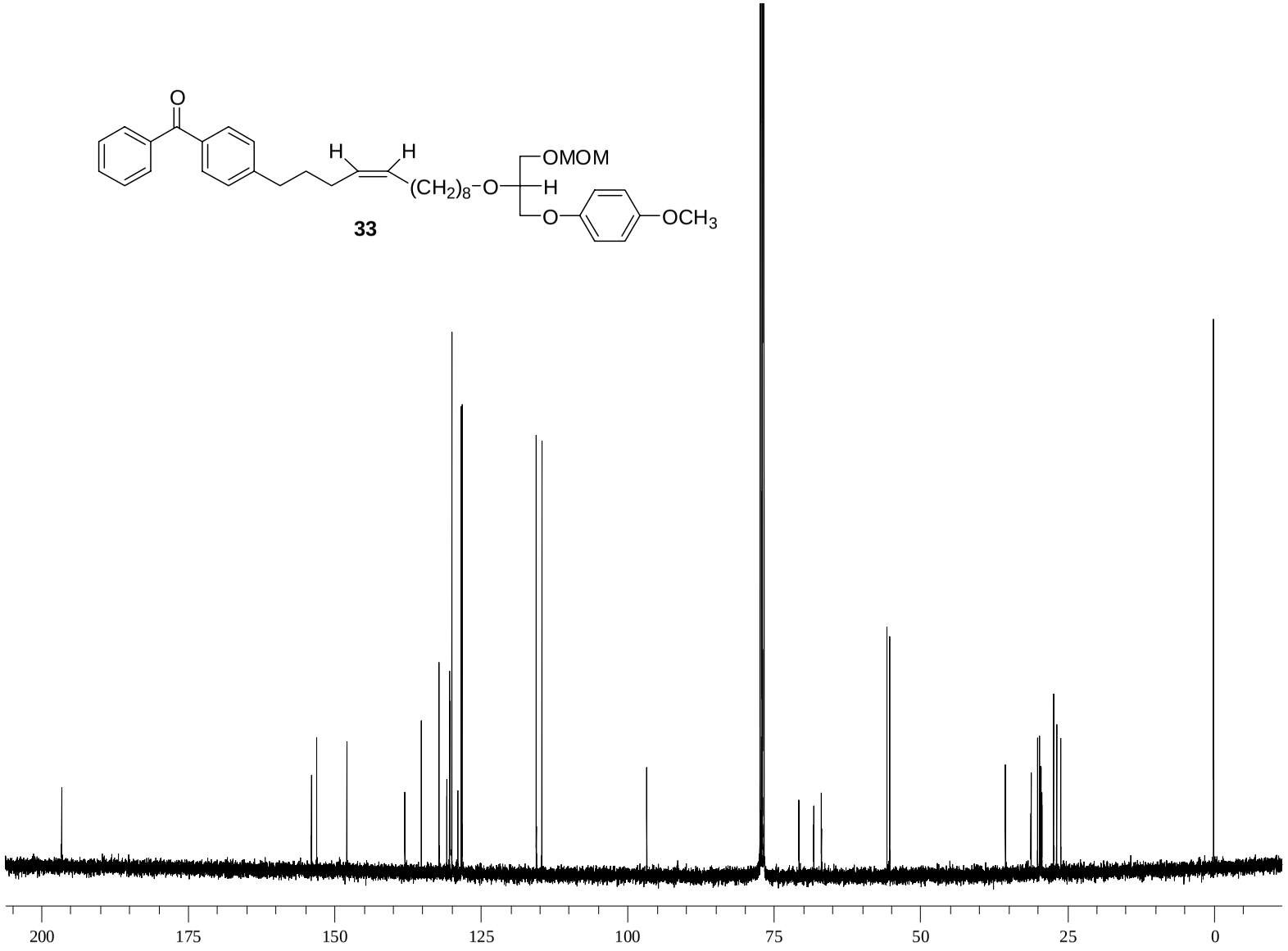
2
1
0
-1


O
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(CH2)8
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OMOM
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OCH3
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175
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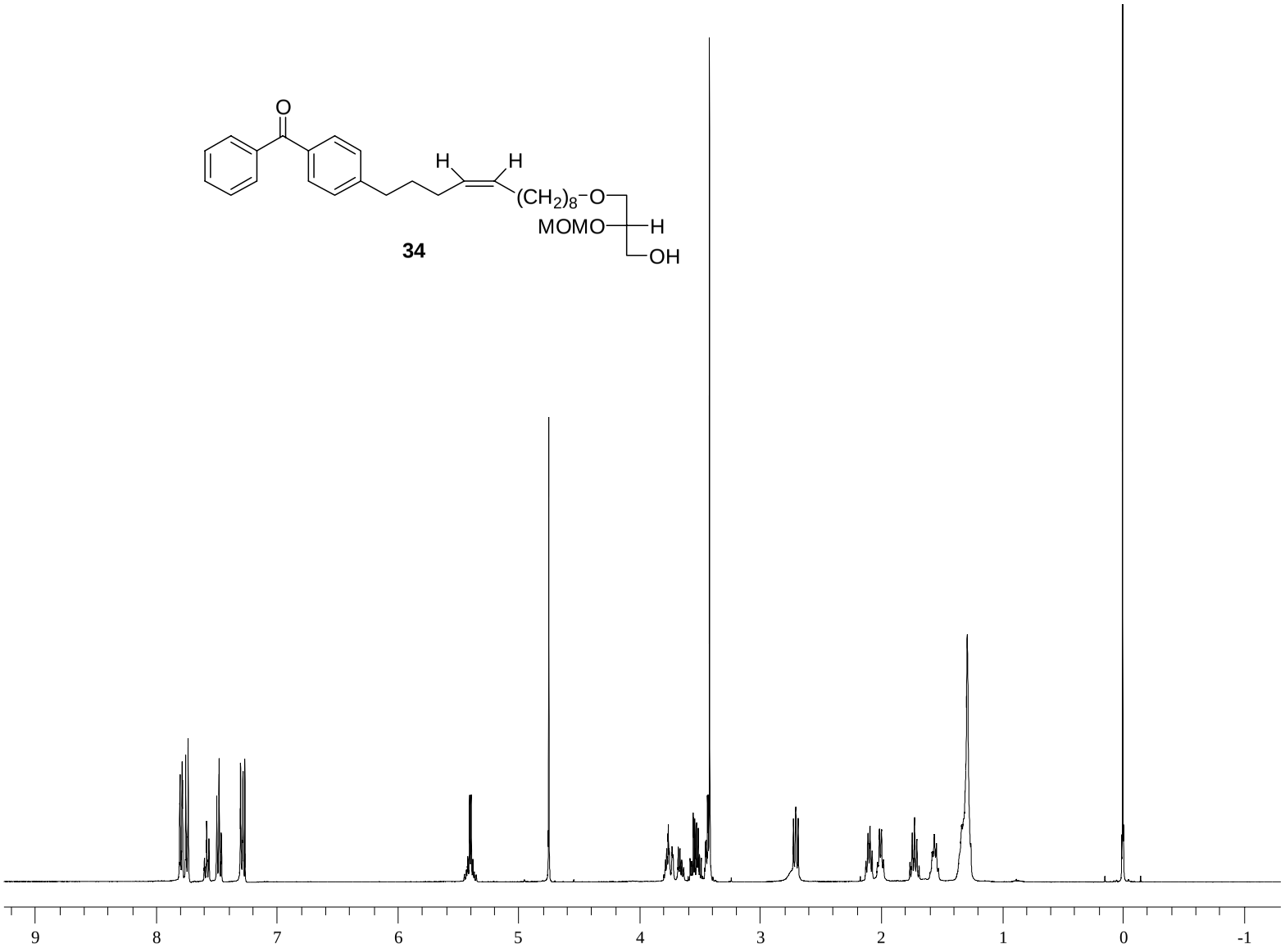
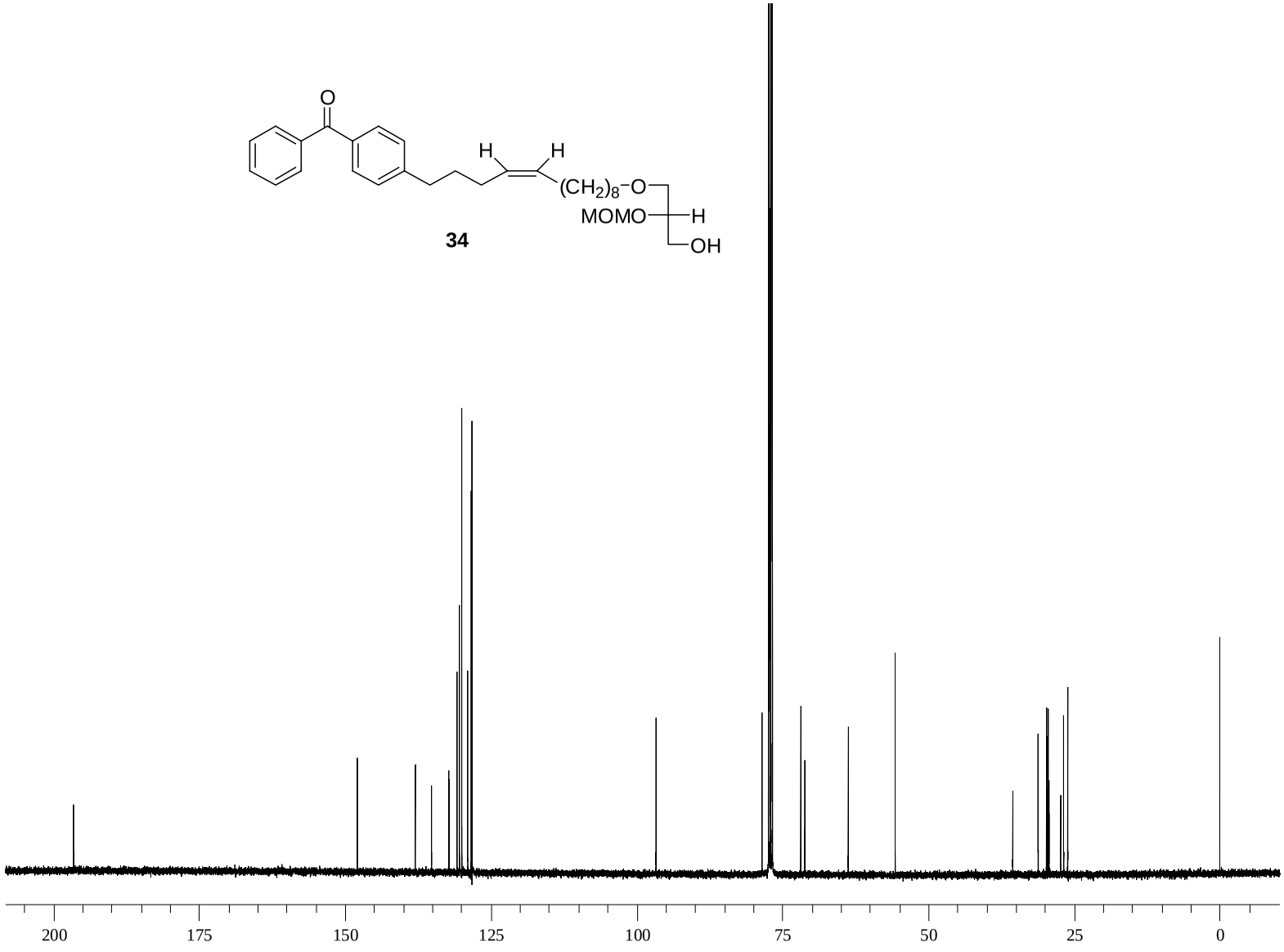

O
H
H
(CH2)8
O
MOMO
H
OH
34
9
8
7
6
5
4
3
2
1
0
-1


O
H
H
(CH2)8–O
MOMO
H
OH
34
200
175
150
125
100
75
50
25
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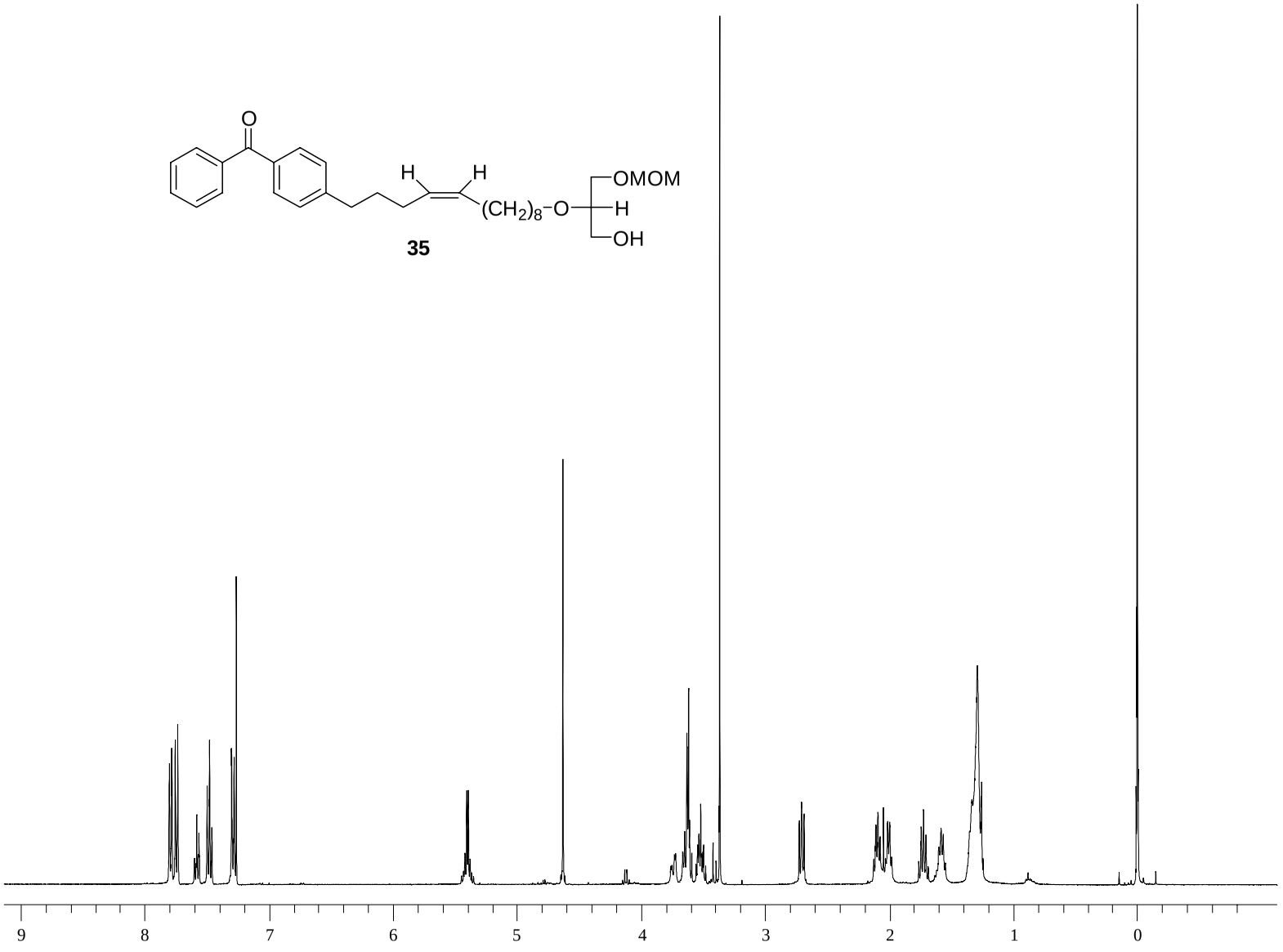
O
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H
OMOM
(CH2)8
O
H
OH
35
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8
7
6
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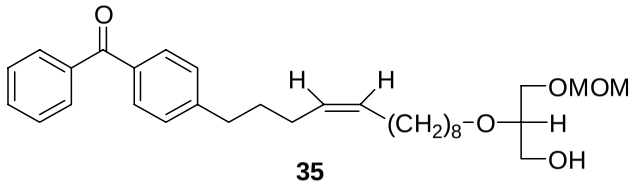
4
3
2
1
0



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