

***Supporting Information***  
***for***  
**Cross-Coupling of Aldehydes and**  
 **$\alpha$ -Bromophosphonates to Modularly Access**  
 **$\alpha$ -Substituted- $\beta$ -Ketophosphonates under Dual**  
**Nickel/Photoredox Catalysis**

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## 1. General Considerations

$^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a Bruker Avance 400, 600 spectrometers, and  $\text{CDCl}_3$  was purchased from J&K. Chemical shifts are given in ppm with the internal standards as TMS (0 ppm for  $^1\text{H}$ ) and  $\text{CDCl}_3$  (77.0 ppm for  $^{13}\text{C}$ ). Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. GC spectra were recorded on Agilent Technologies 7890A spectrometer; GC-MS spectra were conducted on Shimadzu GC-MS-QP2010 SE W spectrometer; High-resolution mass spectra HRMS-ESI were obtained from a Bruker microTOF-II instrument;

The 390nm LEDs were purchased from [www.taobao.com](http://www.taobao.com). The reaction tubes were positioned 4-6 cm from the LEDs (**Figure S1**), and the temperature was controlled between 20 °C and 30 °C using fans and an air conditioner.



**Figure S1.** Photochemical Setup

$\alpha$ -bromophosphonates,  $\alpha$ -bromosulfonamides and  $\alpha$ -bromosulfones were conveniently synthesized in gram scale according to the literature<sup>[S1-3]</sup>. The aldehydes were purified before using, and other reagents and starting materials were purchased from commercial sources and used without further purification. TBADT and TBPDT were prepared according to the literature<sup>[S4,5]</sup>. All reactions were performed under a  $\text{N}_2$  atmosphere using dried solvents which were dried and purified according to the procedure from ‘Purification of Laboratory Chemicals book’. For the NMR spectra, data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet; coupling constants in Hz; integration.

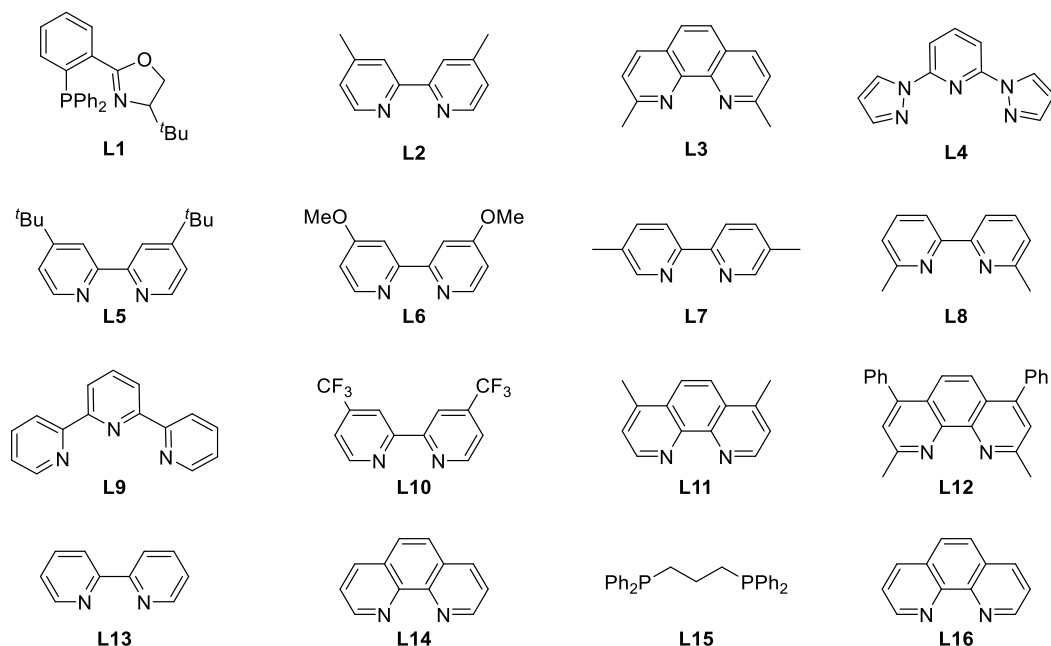
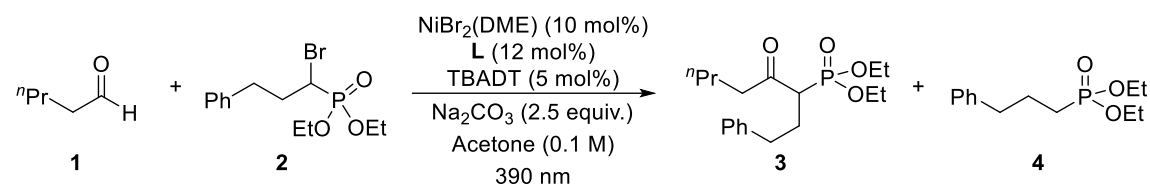
## 2. Reaction Optimization

### General procedure for Reaction Optimization

All optimization reactions were set up in a glove box under a N<sub>2</sub> atmosphere.

An oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with TBADT (0.005 mmol, 5 mol%), Ni-catalyst (0.01 mmol, 10 mol%), ligand (0.012 mmol, 12 mol%), base (0.25 mmol, 2.5 equiv.), and solvent (1 mL). Then aldehyde **1** (0.15 mmol, 1.5 equiv.) and **2** (0.1 mmol, 1.0 equiv.) were added via micro-syringes. Once added, the tube was sealed, and the reaction mixture was stirred and irradiated under LED lamps ( $\lambda = 390\text{-}395\text{ nm}$ ) for 12 hours, while the temperature was controlled at approximately 18 °C-25 °C by cooling with fans and an air-conditioner. Upon completion, the reaction mixture was quenched with water and diluted with EtOAc before the internal standard (*n*-dodecane) was added. The yield was determined by GC analysis.

### Supplementary Table 1. Screening results on ligand

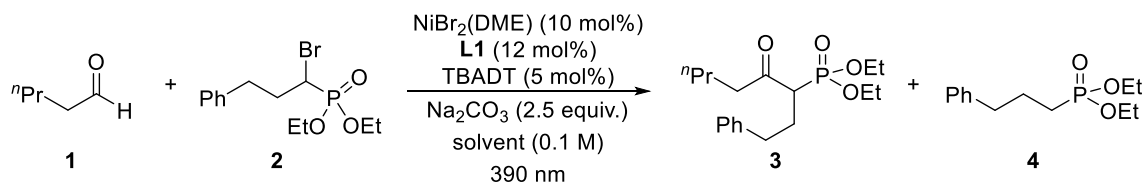


Entry	Ni-cat	Ligand	solvent	base	PC	3 Yield (%)	4 Yield (%)
1	NiBr <sub>2</sub> (DME)	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	96(91) <sup>a</sup>	2
2	NiBr <sub>2</sub> (DME)	L2	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	42	36
3	NiBr <sub>2</sub> (DME)	L3	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	50	29

4	NiBr <sub>2</sub> (DME)	L4	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	17	60
5	NiBr <sub>2</sub> (DME)	L5	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	77	22
6	NiBr <sub>2</sub> (DME)	L6	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	39	25
7	NiBr <sub>2</sub> (DME)	L7	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	40	26
8	NiBr <sub>2</sub> (DME)	L8	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	38	38
9	NiBr <sub>2</sub> (DME)	L9	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	30	67
10	NiBr <sub>2</sub> (DME)	L10	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	52	25
11	NiBr <sub>2</sub> (DME)	L11	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	35	27
12	NiBr <sub>2</sub> (DME)	L12	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	11	84
13	NiBr <sub>2</sub> (DME)	L13	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	n.d.	23
14	NiBr <sub>2</sub> (DME)	L14	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	n.d.	24
15	NiBr <sub>2</sub> (DME)	L15	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	17	60
16	NiBr <sub>2</sub> (DME)	L16	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	77	22

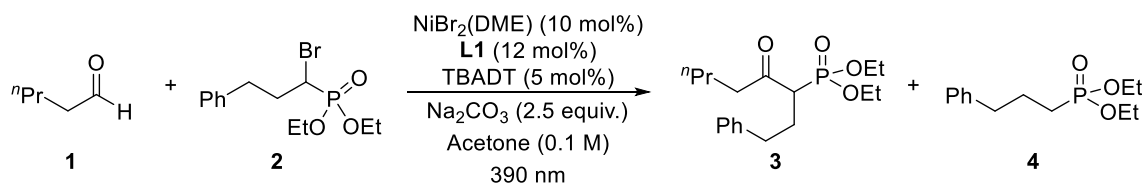
<sup>a</sup> Isolated yield on 0.2 mmol scale

**Supplementary Table 2.** Screening results on solvent



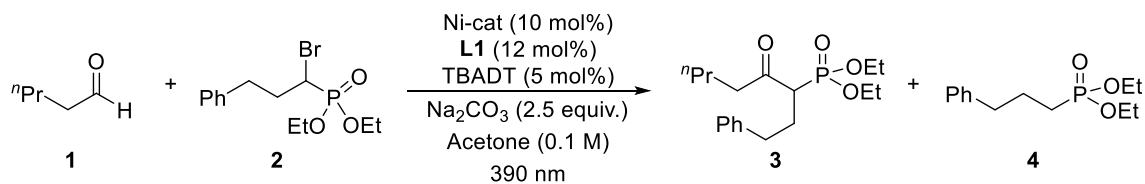
Entry	Ni-cat	Ligand	solvent	base	PC	3 Yield (%)	4 Yield (%)
1	NiBr <sub>2</sub> (DME)	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	96(91)	2
2	NiBr <sub>2</sub> (DME)	L1	MeCN	Na <sub>2</sub> CO <sub>3</sub>	TBADT	89	9
3	NiBr <sub>2</sub> (DME)	L1	DMA	Na <sub>2</sub> CO <sub>3</sub>	TBADT	n.d.	57
4	NiBr <sub>2</sub> (DME)	L1	THF	Na <sub>2</sub> CO <sub>3</sub>	TBADT	n.d.	17
5	NiBr <sub>2</sub> (DME)	L1	Dioxane	Na <sub>2</sub> CO <sub>3</sub>	TBADT	n.d.	5
6	NiBr <sub>2</sub> (DME)	L1	DME	Na <sub>2</sub> CO <sub>3</sub>	TBADT	n.d.	17

**Supplementary Table 3.** Screening results on base



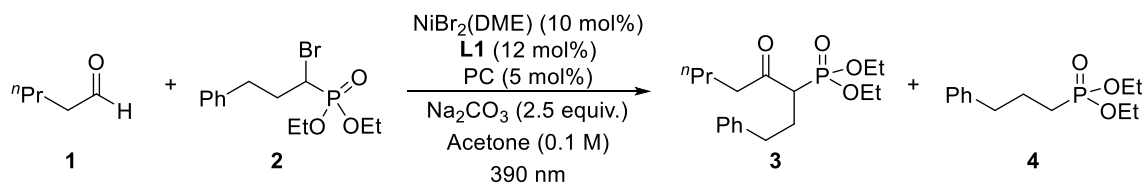
Entry	Ni-cat	Ligand	solvent	base	PC	3 Yield (%)	4 Yield (%)
1	NiBr <sub>2</sub> (DME)	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	96(91)	2
2	NiBr <sub>2</sub> (DME)	L1	Acetone	NaHCO <sub>3</sub>	TBADT	66	5
3	NiBr <sub>2</sub> (DME)	L1	Acetone	Li <sub>3</sub> PO <sub>4</sub>	TBADT	n.d.	22
4	NiBr <sub>2</sub> (DME)	L1	Acetone	K <sub>2</sub> HPO <sub>4</sub>	TBADT	65	8
5	NiBr <sub>2</sub> (DME)	L1	Acetone	Cs <sub>2</sub> CO <sub>3</sub>	TBADT	48	15
6	NiBr <sub>2</sub> (DME)	L1	Acetone	KH <sub>2</sub> PO <sub>4</sub>	TBADT	n.d.	14

**Supplementary Table 4.** Screening results on Ni-cat



Entry	Ni-cat	Ligand	solvent	base	PC	3 Yield (%)	4 Yield (%)
1	NiBr <sub>2</sub> (DME)	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	96(91)	2
2	NiCl <sub>2</sub> (DME)	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	85	9
3	NiI <sub>2</sub>	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	79	6
4	Ni(COD) <sub>2</sub>	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	84	10
5	NiBr <sub>2</sub>	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	83	12

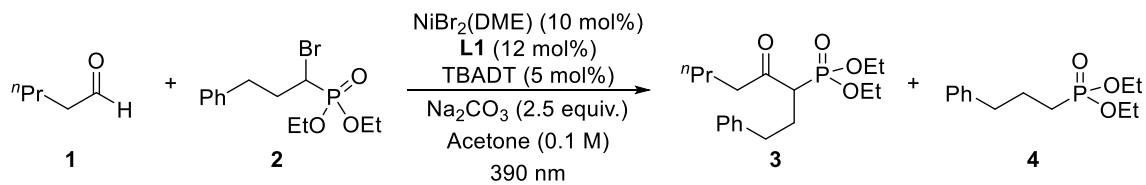
**Supplementary Table 5.** Screening results on PC



Entry	Ni-cat	Ligand	solvent	base	PC	3 Yield (%)	4 Yield (%)
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1	NiBr <sub>2</sub> (DME)	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBADT	96(91)	2
2	NiBr <sub>2</sub> (DME)	L1	Acetone	Na <sub>2</sub> CO <sub>3</sub>	TBPDT	74	11

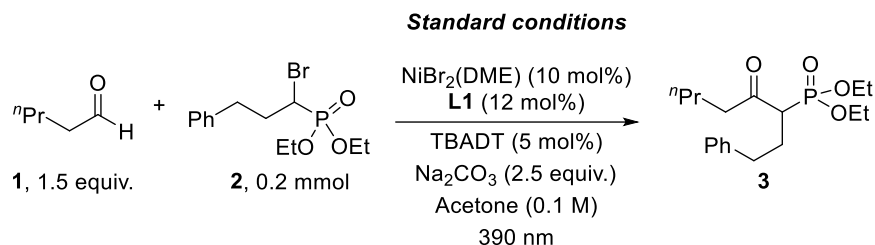
**Supplementary Table 6.** Control reactions



Entry	Change	3 Yield (%)	4 Yield (%)
1	No changes	96(91)	2
2	Without Ni-cat	n.d.	n.d.
3	Without ligand	85	n.d.
4	Without base	n.d.	8
5	Without TBADT	n.d.	n.d.
6	Without light	n.d.	n.d.

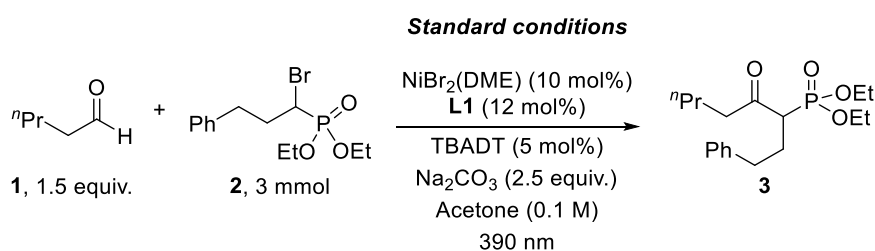
### 3. Supplementary Methods

#### 3.1 General procedure for $\beta$ -ketophosphonates:



In a glove box, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with TBADT (0.01 mmol, 5 mol%),  $\text{NiBr}_2(\text{DME})$  (0.02 mmol, 10 mol%), ligand **L1** (0.024 mmol, 12 mol%),  $\text{Na}_2\text{CO}_3$  (0.5 mmol, 2.5 equiv.), and Acetone (2 ml). Then aldehyde **1** (0.3 mmol, 1.5 equiv.) and alkyl bromide (0.2 mmol, 1.0 equiv.) were added via micro-syringes. Once added, the tube was sealed, and the reaction mixture was stirred and irradiated under LED lamps ( $\lambda = 390\text{-}395$  nm) for 12 hours, while the temperature was controlled at approximately  $18^\circ\text{C}$ - $25^\circ\text{C}$  by cooling with fans and an air-conditioner. Upon completion, the reaction mixture was quenched with water and diluted with EtOAc. The aqueous solution was extracted with EtOAc three times. The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered through Celite, and concentrated *in vacuo*. The residues were purified by silica gel column chromatography with a gradient eluent of petroleum ether/ethyl acetate or petroleum ether/dichloromethane affording product **3** (61.8 mg, 91% yield).

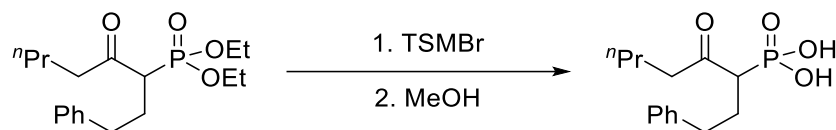
#### 3.2 General procedure for the scale-up reaction:



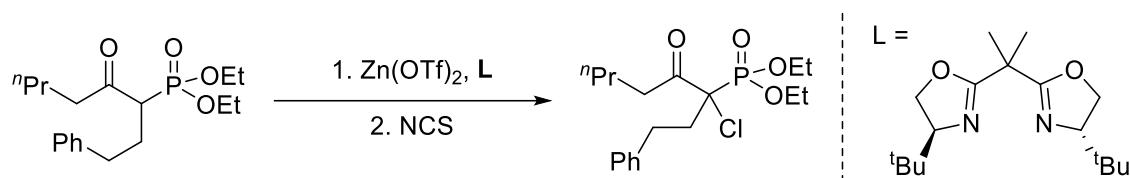
In a glove box, an oven-dried 50-mL Schlenk tube containing a Teflon stir bar was charged with TBADT (0.15 mmol, 5 mol%),  $\text{NiBr}_2(\text{DME})$  (0.3 mmol, 10 mol%), **L1** (0.36 mmol, 12 mol%),  $\text{Na}_2\text{CO}_3$  (7.5 mmol, 2.5 equiv.), and Acetone (15 ml). Then aldehyde **1** (4.5 mmol, 1.5 equiv.) and **2** (3 mmol, 1.0 equiv.) were added via micro-syringes. Once added, the tube was sealed, and the reaction mixture was stirred and irradiated under LED lamps ( $\lambda = 390\text{-}395$  nm) for 24 hours, while the temperature was controlled at approximately  $18^\circ\text{C}$ - $25^\circ\text{C}$  by cooling with fans and an air-conditioner. Upon completion, the reaction mixture was quenched with water and diluted with EtOAc. The aqueous solution was extracted with EtOAc three times. The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered through Celite, and concentrated *in vacuo*. The residues were purified by silica gel column

chromatography with a gradient eluent of petroleum ether/ethyl acetate or petroleum ether/dichloromethane affording product **3** (0.903 g, 88% yield).

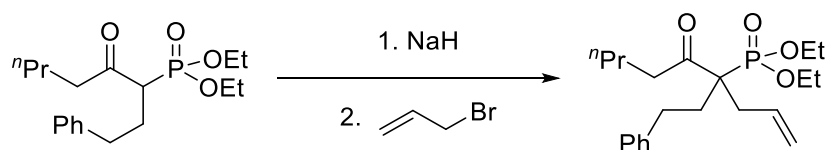
### 3.3 General procedure for applications of the products:



According to the literature<sup>[S6]</sup>,  $\beta$ -ketophosphonate **3** (0.1 mmol) was mixed with bromotrimethylsilane (0.13 mL, 1 mmol, 10 equiv.) and stirred at room temperature for 36 hours. The excess of bromotrimethylsilane was then evaporated, and the mixture was hydrolyzed with MeOH (5 ml) for 5 hours. MeOH was then evaporated and the crude dried under high vacuum conditions, affording the desired product **50** (27.0 mg 96% yield) as an orange solid.

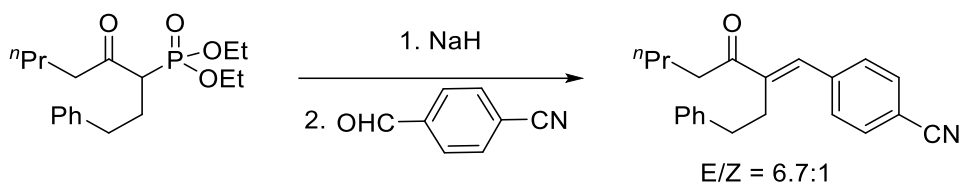


According to the literature<sup>[S7]</sup>, In a flame-dried Schlenk tube equipped with a magnetic stirring bar,  $\text{Zn}(\text{OTf})_2$  (0.01 mmol, 0.1 equiv.) and (*S,S*)-(-)-2,2'-isopropylidenebis(4-tert-butyl-2-oxazoline) (0.011 mmol, 0.12 equiv.) were added, followed by dry  $\text{CH}_2\text{Cl}_2$  (1 mL) and the suspension was stirred in the dark for 6 h.  $\beta$ -ketophosphonates **3** (0.1 mmol, 1 equiv.) was then added, followed by *N*-chlorosuccinimide (0.11 mmol, 1.1 equiv.). After 20 h stirring in the dark at room temperature, the solution was concentrated *in vacuo*. The residues were purified by silica gel column chromatography (petroleum ether / ethyl acetate = 7:1) to give compound **51** (35.8 mg 96% yield) as a colorless oil.



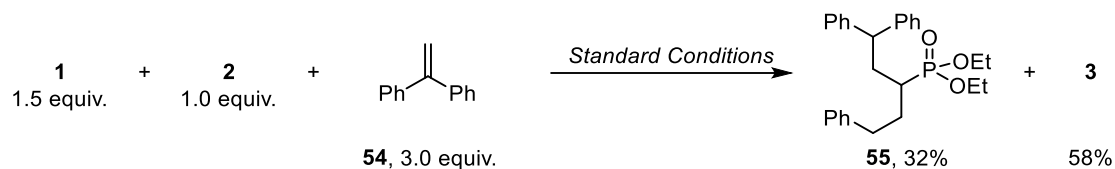
According to the literature<sup>[S8]</sup>, to a suspension of 60% NaH (0.2 mmol, 1 equiv.) in dry THF (1 mL),  $\beta$ -ketophosphonate **3** (0.2 mmol, 1 equiv.) in dry THF (1 mL) was added slowly under  $\text{N}_2$  at rt. The mixture was stirred for 1 hour. Allyl bromide (0.4 mmol, 2 equiv.) was added followed by stirring of the mixture for 4 h.  $\text{NH}_4\text{Cl}$  (2 mL, aq) was added, and the resulting solution was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 3$  mL). The combined organic extracts were washed with  $\text{H}_2\text{O}$  ( $2 \times 5$  mL) and dried ( $\text{MgSO}_4$ ). After removal of the solvent, the residue was chromatographed (silica gel, petroleum ether / ethyl acetate) to give compound **52** (18.4 mg, 48 % yield) as a colorless oil.



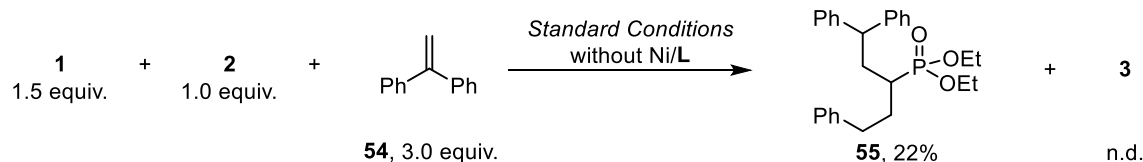


According to the literature<sup>[S9]</sup>, to a suspension of 60% NaH (0.22 mmol, 1.1 equiv.) in dry THF (1 mL),  $\beta$ -ketophosphonate **3** (0.2 mmol, 1 equiv.) in dry THF (1 mL) was added under N<sub>2</sub> at rt. The mixture was stirred for 1 hour. 4-Cyanobenzaldehyde (0.4 mmol, 2 equiv.) was added followed by stirring of the mixture overnight. NH<sub>4</sub>Cl (2 mL, aq) was added, and the resulting solution was extracted with Et<sub>2</sub>O (3 × 3 mL). The combined organic extracts were washed with H<sub>2</sub>O (2 × 5 mL) and dried (MgSO<sub>4</sub>). After removal of the solvent, the residue was chromatographed (silica gel, petroleum ether / ethyl acetate) to give compound **53** (54.9 mg, 86% yield, E/Z = 6.7:1, determined by HNMR) as a colorless oil.

### 3.4 General procedure for mechanism studies:



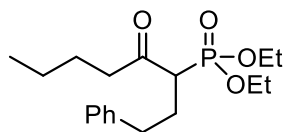
An oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with TBADT (0.01 mmol, 5 mol%), Ni-catalyst (0.02 mmol, 10 mol%), ligand (0.024 mmol, 12 mol%), base (0.5 mmol, 2.5 equiv.), and solvent (2 mL). Then aldehyde **1** (0.3 mmol, 1.5 equiv.), **2** (0.2 mmol, 1.0 equiv.), and compound **54** (0.6 mmol, 3.0 equiv.) were added via micro-syringes. Once added, the tube was sealed, and the reaction mixture was stirred and irradiated under LED lamps ( $\lambda = 390\text{-}395$  nm) for 12 hours, while the temperature was controlled at approximately 18 °C-25 °C by cooling with fans and an air-conditioner. Upon completion, the reaction mixture was quenched with water and diluted with EtOAc. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered through Celite, and concentrated *in vacuo*. Flash chromatography on silica gel eluting with petroleum ether/ethyl acetate afforded the pure product **55** (27.9 mg, 32% yield, light yellow oil).



An oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with TBADT (0.01 mmol, 5 mol%), 20base (0.5 mmol, 2.5 equiv.), and solvent (2 mL). Then aldehyde **1** (0.3 mmol, 1.5 equiv.), **2** (0.2 mmol, 1.0 equiv.), and compound **54**

(0.6 mmol, 3.0 equiv.) were added via micro-syringes. Once added, the tube was sealed, and the reaction mixture was stirred and irradiated under LED lamps ( $\lambda = 390\text{-}395\text{ nm}$ ) for 12 hours, while the temperature was controlled at approximately 18 °C-25 °C by cooling with fans and an air-conditioner. Upon completion, the reaction mixture was quenched with water and diluted with EtOAc. The yields were determined by FNMR analysis.

## 4. The characterization of the compounds



3

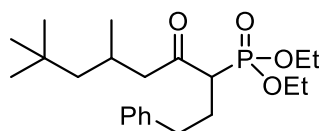
The title compound **3** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 91% yield, 61.8 mg, colorless oil).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.35-7.26 (m, 2H), 7.22-7.18 (m, 1H), 7.18-7.12 (m, 2H), 4.14-4.03 (m, 4H), 3.16 (ddd, *J* = 24.7, 10.6, 3.3 Hz, 1H), 2.79-2.71 (m, 1H), 2.69-2.61 (m, 1H), 2.54-2.46 (m, 1H), 2.44-2.33 (m, 2H), 2.13-2.03 (m, 1H), 1.58-1.50 (m, 2H), 1.35-1.27 (m, 8H), 0.90 (t, *J* = 7.3 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 205.8 (d, *J* = 4.4 Hz), 140.5, 128.49, 128.48, 126.2, 62.6 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.7 Hz), 51.8 (d, *J* = 124.5 Hz), 44.1, 34.2 (d, *J* = 15.1 Hz), 27.8 (d, *J* = 4.6 Hz), 25.5, 22.1, 16.3 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz), 13.9.

<sup>31</sup>P NMR (243 MHz, CDCl<sub>3</sub>) δ 22.43.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>30</sub>O<sub>4</sub>P: 341.1786, found: 341.1786.



5

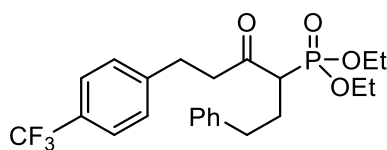
The title compound **5** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 65% yield, 51.3 mg, yellow oil, 1:1 *dr* determined by H NMR).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.30-7.26 (m, 4H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 4H), 4.14-4.03 (m, 8H), 3.17-3.07 (m, 2H), 2.79 (dd, *J* = 18.1, 5.4 Hz, 1H), 2.70-2.64 (m, 2H), 2.62 (dd, *J* = 17.5, 8.8 Hz, 1H), 2.53-2.46 (m, 2H), 2.44 (dd, *J* = 17.6, 4.3 Hz, 1H), 2.41-2.32 (m, 2H), 2.28 (dd, *J* = 18.1, 7.6 Hz, 1H), 2.19-2.13 (m, 1H), 2.13-2.04 (m, 3H), 1.30 (td, *J* = 7.1, 3.2 Hz, 12H), 1.23-1.13 (m, 2H), 1.12-1.05 (m, 2H), 0.93 (dd, *J* = 10.5, 6.7 Hz, 6H), 0.91 (s, 18H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 205.10, 205.07, 204.98, 204.95, 140.6, 140.50, 128.49, 128.47, 126.25, 126.24, 62.6 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 3.3 Hz), 62.4 (d, *J* = 3.4 Hz), 54.01, 54.00, 52.2 (d, *J* = 124.9 Hz), 51.8 (d, *J* = 124.4 Hz), 50.9, 50.5, 34.2 (d, *J* = 11.6 Hz), 34.1 (d, *J* = 11.6 Hz), 31.1, 31.1, 30.03, 29.98, 27.9 (d, *J* = 4.7 Hz), 27.6 (d, *J* = 4.6 Hz), 25.0, 24.9, 22.8, 22.4, 16.34 (d, *J* = 6.1 Hz), 16.33 (d, *J* = 6.1 Hz).

**<sup>31</sup>P NMR** (243 MHz, CDCl<sub>3</sub>) δ 22.53, 22.44.

**HRMS** (ESI) m/z: [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>38</sub>O<sub>4</sub>P: 397.2502, found: 397.2502.



**6**

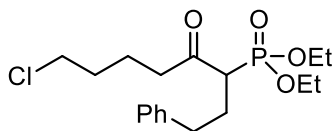
The title compound **6** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3.5:1, 69% yield, 63.4 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.35-7.17 (m, 5H), 7.07 (d, *J* = 7.4 Hz, 2H), 4.10-3.93 (m, 4H), 3.24-3.05 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.70-2.54 (m, 2H), 2.52-2.29 (m, 2H), 2.20-1.93 (m, 1H), 1.33-1.20 (m, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 204.0 (d, *J* = 4.4 Hz), 145.1, 140.3, 128.9, 128.5, 128.44, 128.42 (q, *J* = 32.4 Hz), 126.3, 125.2 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.7 Hz), 62.7 (d, *J* = 6.8 Hz), 62.5 (d, *J* = 6.7 Hz), 52.0 (d, *J* = 124.5 Hz), 45.1, 34.0 (d, *J* = 14.6 Hz), 29.1, 27.5 (d, *J* = 4.7 Hz), 16.25 (d, *J* = 5.9 Hz), 16.22 (d, *J* = 6.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 21.93.

**HRMS** (ESI) m/z: [M+H]<sup>+</sup> calcd. for C<sub>23</sub>H<sub>29</sub>FO<sub>4</sub>P: 457.1750, found: 457.1750.



**7**

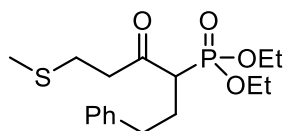
The title compound **7** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 81% yield, 60.6 mg, colorless oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.39-7.18 (m, 5H), 4.22-4.01 (m, 4H), 3.60 (t, *J* = 6.2 Hz, 2H), 3.22 (ddd, *J* = 24.7, 10.4, 3.3 Hz, 1H), 2.89 (dt, *J* = 18.1, 6.8 Hz, 1H), 2.72 (ddd, *J* = 14.1, 8.9, 5.5 Hz, 1H), 2.59 (dt, *J* = 13.6, 7.8 Hz, 1H), 2.51-2.40 (m, 2H), 2.24-2.09 (m, 1H), 1.90-1.72 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 204.9 (d, *J* = 4.6 Hz), 140.4, 128.5, 128.4, 126.2, 62.7 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.9 Hz), 51.9 (d, *J* = 124.6 Hz), 44.5, 43.2, 34.1 (d, *J* = 14.7 Hz), 31.6, 27.6 (d, *J* = 4.8 Hz), 20.6, 16.3 (d, *J* = 6.0 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 22.19.

**HRMS** (ESI) m/z: [M+H]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>29</sub>ClO<sub>4</sub>P: 375.1487, found: 375.1487.



8

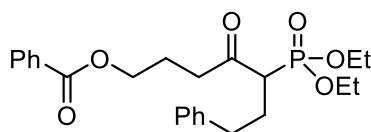
The title compound **8** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 46% yield, 33.3 mg, colorless oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.25-7.17 (m, 2H), 7.17-7.10 (m, 1H), 7.10-7.05 (m, 2H), 4.09-3.94 (m, 4H), 3.08 (ddd, *J* = 24.9, 10.6, 3.3 Hz, 1H), 3.04-2.93 (m, 1H), 2.70-2.53 (m, 4H), 2.51-2.41 (m, 1H), 2.39-2.26 (m, 1H), 2.04 (s, 3H), 2.03-1.94 (m, 1H), 1.23 (td, *J* = 7.1, 2.1 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 203.9 (d, *J* = 4.4 Hz), 140.4, 128.49, 128.48, 126.3, 62.7 (d, *J* = 7.0 Hz), 62.5 (d, *J* = 6.6 Hz), 52.0 (d, *J* = 124.7 Hz), 43.9, 34.1 (d, *J* = 14.7 Hz), 27.7, 27.6 (d, *J* = 4.4 Hz), 16.3 (d, *J* = 5.9 Hz), 15.7.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 21.91.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>28</sub>O<sub>4</sub>PS: 359.1440, found: 359.1440.



9

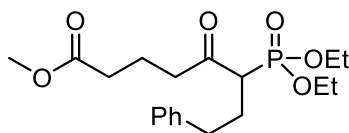
The title compound **9** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 2:1, 54% yield, 48.2 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.07-8.00 (m, 2H), 7.60-7.51 (m, 1H), 7.47-7.39 (m, 2H), 7.28-7.22 (m, 2H), 7.21-7.15 (m, 1H), 7.14-7.10 (m, 2H), 4.32 (td, *J* = 6.5, 2.1 Hz, 2H), 4.15-4.02 (m, 4H), 3.16 (ddd, *J* = 24.7, 10.4, 3.4 Hz, 1H), 2.97 (dt, 1H), 2.72-2.61 (m, 1H), 2.59-2.46 (m, 2H), 2.45-2.33 (m, 1H), 2.17-2.09 (m, 1H), 2.09-2.00 (m, 2H), 1.28 (td, *J* = 7.1, 3.5 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 204.4 (d, *J* = 4.8 Hz), 166.4, 140.3, 132.9, 130.2, 129.49, 128.47, 128.46, 128.3, 126.3, 63.9, 62.7 (d, *J* = 6.7 Hz), 62.4 (d, *J* = 6.7 Hz), 51.9 (d, *J* = 124.8 Hz), 40.5, 34.1 (d, *J* = 14.7 Hz), 27.6 (d, *J* = 4.7 Hz), 22.7, 16.27 (d, *J* = 6.2 Hz), 16.25 (d, *J* = 5.9 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 22.17.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>32</sub>O<sub>6</sub>P: 447.1931, found: 447.1923.



**10**

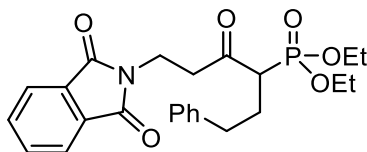
The title compound **10** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 63% yield, 48.4 mg, yellow oil).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.32-7.26 (m, 2H), 7.22-7.18 (m, 1H), 7.16-7.11 (m, 2H), 4.13-4.03 (m, 4H), 3.67 (s, 3H), 3.13 (ddd, *J* = 24.7, 10.6, 3.4 Hz, 1H), 2.85 (dt, *J* = 18.3, 7.1 Hz, 1H), 2.64 (ddd, *J* = 14.1, 9.0, 5.4 Hz, 1H), 2.51 (dt, *J* = 13.7, 7.9 Hz, 1H), 2.47-2.36 (m, 2H), 2.36-2.29 (m, 2H), 2.13-2.04 (m, 1H), 1.93-1.83 (m, 2H), 1.30 (td, *J* = 7.1, 2.8 Hz, 6H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 204.8 (d, *J* = 4.6 Hz), 173.5, 140.4, 128.48, 128.46, 126.3, 62.7 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.9 Hz), 51.8 (d, *J* = 124.8 Hz), 51.5, 43.1, 34.1 (d, *J* = 14.8 Hz), 32.8, 27.7 (d, *J* = 4.8 Hz), 18.5, 16.3 (d, *J* = 6.0 Hz).

**<sup>31</sup>P NMR** (243 MHz, CDCl<sub>3</sub>) δ 22.16.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>30</sub>O<sub>6</sub>P: 385.1775, found: 385.1764.



**11**

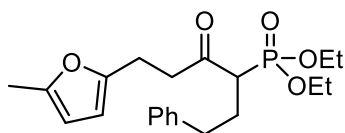
The title compound **11** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 1:1, 59% yield, 53.6 mg, white powder).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.87-7.68 (m, 4H), 7.30-7.10 (m, 5H), 4.11-4.03 (m, 4H), 4.01-3.90 (m, 2H), 3.22 (dt, *J* = 17.4, 7.5 Hz, 1H), 3.13 (ddd, *J* = 25.0, 10.5, 3.3 Hz, 1H), 2.81 (dt, *J* = 17.3, 7.1 Hz, 1H), 2.69-2.62 (m, 1H), 2.57-2.48 (m, 1H), 2.43-2.33 (m, 1H), 2.15-2.06 (m, 1H), 1.33-1.24 (m, 6H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 202.8 (d, *J* = 4.6 Hz), 167.9, 140.2, 133.9, 132.0, 128.5, 128.4, 126.2, 123.1, 62.7 (d, *J* = 6.7 Hz), 52.0 (d, *J* = 124.5 Hz), 41.7, 34.0 (d, *J* = 14.6 Hz), 32.7, 27.4 (d, *J* = 4.4 Hz), 16.23 (d, *J* = 5.5 Hz), 16.21 (d, *J* = 6.1 Hz).

**<sup>31</sup>P NMR** (243 MHz, CDCl<sub>3</sub>) δ 22.43.

**HRMS** (ESI) *m/z*: [M+CH<sub>3</sub>OH+H]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>33</sub>NO<sub>7</sub>P: 490.1989, found: 490.1990.



**12**

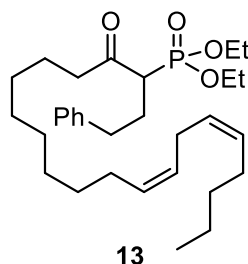
The title compound **12** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 60% yield, 47.1 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.24 (m, 1H), 7.11-7.16 (m, 1H), 7.14-7.05 (m, 2H), 5.85 (dd, *J* = 21.0, 3.4 Hz, 2H), 4.16–3.98 (m, 4H), 3.23–3.04 (m, 2H), 2.93-2.78 (m, 2H), 2.75-2.65 (m, 1H), 2.62 (td, *J* = 8.8, 4.7 Hz, 1H), 2.51–2.43 (m, 1H), 2.42-2.30 (m, 1H), 2.23 (s, 3H), 2.13–2.02 (m, 1H), 1.29 (td, *J* = 7.1, 2.4 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 204.2 (d, *J* = 4.6 Hz), 152.5, 150.4, 140.5, 128.47, 128.46, 126.2, 105.90, 105.89, 62.7 (d, *J* = 6.6 Hz), 62.5 (d, *J* = 7.0 Hz), 51.9 (d, *J* = 124.7 Hz), 42.6, 34.1 (d, *J* = 14.8 Hz), 27.8 (d, *J* = 4.7 Hz), 22.0, 16.28 (d, *J* = 5.9 Hz), 16.26 (d, *J* = 6.1 Hz), 13.4.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 22.09.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>30</sub>O<sub>5</sub>P: 393.1825, found: 393.1816.



**13**

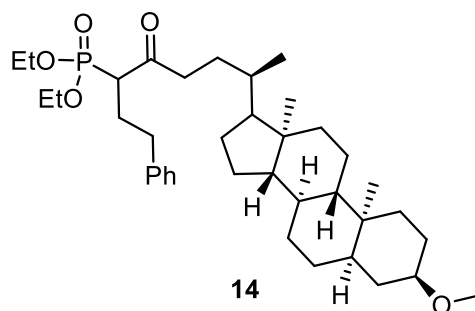
The title compound **13** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 6:1, 49% yield, 50.4 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.05 (m, 5H), 5.45-5.27 (m, 4H), 4.15-3.99 (m, 4H), 3.15 (ddd, *J* = 24.6, 10.4, 3.4 Hz, 1H), 2.82-2.74 (m, 2H), 2.72 (t, *J* = 7.3 Hz, 1H), 2.69-2.60 (m, 1H), 2.56-2.44 (m, 1H), 2.44-2.32 (m, 2H), 2.05 (q, *J* = 7.0 Hz, 4H), 2.00-1.92 (m, 1H), 1.59-1.47 (m, 2H), 1.37-1.26 (m, 20H), 0.89 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 205.6 (d, *J* = 4.5 Hz), 140.5, 130.2, 130.0, 128.47, 128.46, 128.0, 127.9, 126.2, 62.6 (d, *J* = 7.0 Hz), 62.4 (d, *J* = 7.0 Hz), 51.8 (d, *J* = 124.7 Hz), 44.3, 34.2 (d, *J* = 14.8 Hz), 31.5, 29.6, 29.3, 29.1, 29.0, 27.8 (d, *J* = 4.8 Hz), 27.18, 27.17, 25.6, 23.4, 22.5, 16.3 (d, *J* = 6.1 Hz), 14.0.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 22.43.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>31</sub>H<sub>52</sub>O<sub>4</sub>P: 519.3598, found: 519.3595.



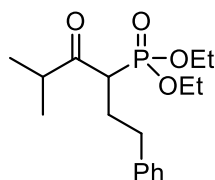
The title compound **14** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 6:1, 53% yield, 66.9 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.46-7.02 (m, 5H), 4.17-4.02 (m, 4H), 3.35 (s, 3H), 3.24-3.10 (m, 2H), 2.82-2.67 (m, 1H), 2.67-2.59 (m, 1H), 2.57-2.45 (m, 1H), 2.44-2.37 (m, 1H), 2.36-2.24 (m, 1H), 2.15-2.06 (m, 1H), 1.94 (d, *J* = 11.7 Hz, 1H), 1.90-1.63 (m, 8H), 1.59 (d, *J* = 14.0 Hz, 2H), 1.44-1.35 (m, 5H), 1.30 (t, *J* = 7.4 Hz, 6H), 1.27-1.19 (m, 5H), 1.17-0.99 (m, 5H), 0.92 (s, 3H), 0.89 (d, *J* = 6.2 Hz, 3H), 0.63 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 206.0, 140.6, 128.51, 128.48, 126.2, 80.4, 62.6 (d, *J* = 6.6 Hz), 62.5 (d, *J* = 6.3 Hz), 56.5, 56.4, 56.01, 55.99, 55.5, 52.6, 52.5, 51.4, 51.2, 42.7, 42.1, 41.3, 41.2, 40.4, 40.2, 35.9, 35.3, 35.2, 35.0, 34.9, 34.2 (d, *J* = 14.9 Hz), 32.8, 29.4, 28.2 (d, *J* = 2.6 Hz), 27.8, 27.3, 26.8, 26.4, 24.2, 23.4, 20.8, 18.5, 18.4, 16.4 (d, *J* = 6.0 Hz), 12.05, 12.03.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 22.53.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>38</sub>H<sub>62</sub>O<sub>5</sub>P: 629.4329, found: 629.4304.



**15**

The title compound **15** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 4:1, 70% yield, 45.3 mg, yellow oil).

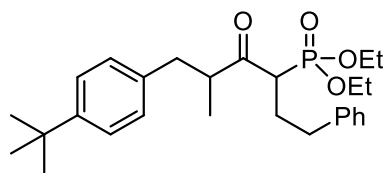
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.34-7.25 (m, 3H), 7.23-7.15 (m, 1H), 4.16-4.03 (m, 4H), 3.38 (ddd, *J* = 25.0, 10.3, 3.5 Hz, 1H), 2.95 (hept, *J* = 6.9 Hz, 1H), 2.62 (ddd, *J* = 13.5, 9.9, 5.2 Hz, 1H), 2.47 (ddd, *J* = 13.5, 9.5, 6.6 Hz, 1H), 2.42-2.32 (m, 1H), 2.09 (m, 1H), 1.30 (td, *J* = 7.1, 1.4 Hz, 6H), 1.11 (d, *J* = 6.6 Hz, 3H), 1.05 (d, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 209.6 (d, *J* = 4.5 Hz), 140.7, 128.5, 128.4, 126.2, 62.7 (d, *J* = 6.7 Hz), 62.6 (d, *J* = 6.7 Hz), 50.4 (d, *J* = 124.7 Hz), 41.8, 34.4 (d, *J* = 14.9 Hz), 27.8 (d, *J* = 4.5 Hz), 18.6, 17.4, 16.4 (d, *J* = 5.5 Hz).

**<sup>31</sup>P NMR** (243 MHz, CDCl<sub>3</sub>) δ 22.40.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>28</sub>O<sub>4</sub>P: 327.1720, found: 327.1720.





**16**(1:1 *dr*)

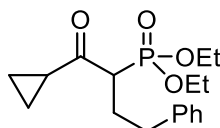
The title compound **16** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 40% yield, 36.7 mg, yellow oil, 1:1 *dr* determined by H NMR).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.37-7.23 (m, 8H), 7.21-7.04 (m, 10H), 4.15-3.97 (m, 6H), 3.94-3.87 (m, 2H), 3.36 (ddd, *J* = 25.7, 10.2, 3.3 Hz, 1H), 3.26-3.16 (m, 2H), 3.10 (ddd, *J* = 25.3, 8.9, 4.1 Hz, 1H), 3.04 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.84 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.66-2.59 (m, 1H), 2.57-2.47 (m, 2H), 2.47-2.41 (m, 1H), 2.41-2.32 (m, 1H), 2.32-2.25 (m, 1H), 2.23-2.13 (m, 2H), 2.13-2.05 (m, 1H), 2.01-1.91 (m, 1H), 1.31 (t, *J* = 6.3 Hz, 3H), 1.30-1.25 (m, 24H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 209.4 (d, *J* = 4.8 Hz), 208.5 (d, *J* = 4.3 Hz), 149.4, 148.8, 141.0, 140.7, 136.7, 136.1, 129.0, 128.7, 128.45, 128.44, 128.37, 128.3, 126.2, 126.1, 125.4, 125.0, 62.6 (d, *J* = 10.5 Hz), 62.53 (d, *J* = 6.6 Hz), 62.52 (d, *J* = 16.6 Hz), 52.7 (d, *J* = 124.0 Hz), 50.7 (d, *J* = 124.2 Hz), 49.2, 48.7, 39.4, 37.2, 34.4, 34.31, 34.28 (d, *J* = 6.7 Hz), 34.2 (d, *J* = 5.3 Hz), 31.4, 31.3, 27.8 (d, *J* = 4.5 Hz), 27.5 (d, *J* = 4.7 Hz), 16.37 (d, *J* = 6.1 Hz), 16.35 (d, *J* = 6.6 Hz), 16.2.

**<sup>31</sup>P NMR** (243 MHz, CDCl<sub>3</sub>) δ 22.54, 22.07.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>40</sub>O<sub>4</sub>P: 459.2659, found: 459.2659.



**17**

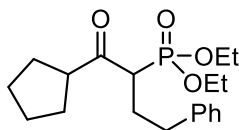
The title compound **17** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 71% yield, 46.3 mg, yellow oil).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.31-7.26 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 4.16-4.03 (m, 4H), 3.30 (ddd, *J* = 24.3, 10.8, 3.4 Hz, 1H), 2.72-2.65 (m, 1H), 2.56-2.48 (m, 1H), 2.47-2.37 (m, 1H), 2.24-2.17 (m, 1H), 2.16-2.07 (m, 1H), 1.30 (td, *J* = 7.1, 2.7 Hz, 6H), 1.18-1.13 (m, 1H), 1.10-1.05 (m, 1H), 1.01-0.92 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 205.5 (d, *J* = 4.0 Hz), 140.6, 128.5, 128.4, 126.2, 62.53 (d, *J* = 6.6 Hz), 62.48 (d, *J* = 7.2 Hz), 53.0 (d, *J* = 125.5 Hz), 34.2 (d, *J* = 15.4 Hz), 27.9 (d, *J* = 4.4 Hz), 21.7, 16.34 (d, *J* = 6.1 Hz), 16.32 (d, *J* = 6.1 Hz), 12.2, 12.0.

**<sup>31</sup>P NMR** (243 MHz, CDCl<sub>3</sub>) δ 22.68.

**HRMS** (ESI)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{17}H_{26}O_4P$ : 325.1563, found: 325.1563.



**18**

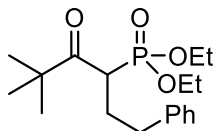
The title compound **18** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 64% yield, 45.3 mg, yellow oil).

**$^1H$  NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.31-7.26 (m, 2H), 7.22-7.14 (m, 3H), 4.14-4.02 (m, 4H), 3.32 (ddd,  $J = 24.8, 10.4, 3.4$  Hz, 1H), 3.26-3.19 (m, 1H), 2.67-2.59 (m, 1H), 2.52-2.43 (m, 1H), 2.43-2.32 (m, 1H), 2.14-2.04 (m, 1H), 1.99-1.92 (m, 1H), 1.92-1.85 (m, 1H), 1.77-1.68 (m, 2H), 1.68-1.62 (m, 1H), 1.62-1.54 (m, 2H), 1.53-1.46 (m, 1H), 1.30 (t,  $J = 7.1$  Hz, 6H).

**$^{13}C$  NMR** (151 MHz,  $CDCl_3$ )  $\delta$  208.4 (d,  $J = 4.3$  Hz), 140.6, 128.39, 128.37, 126.1, 62.6 (d,  $J = 6.7$  Hz), 62.4 (d,  $J = 6.9$  Hz), 52.4, 51.7 (d,  $J = 124.4$  Hz), 34.3 (d,  $J = 14.8$  Hz), 30.3, 28.0, 27.8 (d,  $J = 4.8$  Hz), 26.0, 25.9, 16.31 (d,  $J = 6.1$  Hz), 16.29 (d,  $J = 6.1$  Hz).

**$^{31}P$  NMR** (243 MHz,  $CDCl_3$ )  $\delta$  22.52.

**HRMS** (ESI)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{19}H_{30}O_4P$ : 353.1876, found: 353.1876.



**19**

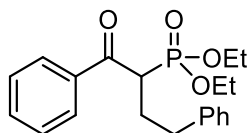
The title compound **19** was synthesized according to General Procedure (SI 3.1, without **L1**), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 25% yield, 17.3 mg, colorless oil).

**$^1H$  NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.23-7.18 (m, 2H), 7.16-7.08 (m, 3H), 4.16-3.96 (m, 4H), 3.61 (ddd,  $J = 20.7, 8.0, 5.9$  Hz, 1H), 2.54 (t,  $J = 8.0$  Hz, 2H), 2.20-2.06 (m, 2H), 1.25 (t,  $J = 7.0$  Hz, 6H), 1.08 (s, 9H).

**$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  212.0 (d,  $J = 5.5$  Hz), 140.8, 128.45, 128.41, 126.2, 62.6 (d,  $J = 6.6$  Hz), 62.4 (d,  $J = 7.0$  Hz), 45.8 (d,  $J = 129.5$  Hz), 45.4 (d,  $J = 1.8$  Hz), 34.5 (d,  $J = 11.7$  Hz), 30.8 (d,  $J = 5.5$  Hz), 26.6, 16.4 (d,  $J = 6.2$  Hz).

**$^{31}P$  NMR** (243 MHz,  $CDCl_3$ )  $\delta$  23.38.

**HRMS** (ESI)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{18}H_{30}O_4P$ : 341.1876, found: 341.1875.



**20**

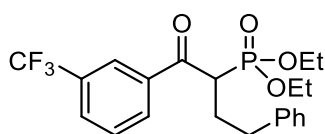
The title compound **20** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 2:1, 42% yield, 30.3 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.98-7.85 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.31-7.19 (m, 3H), 7.15-7.08 (m, 2H), 4.18-3.98 (m, 5H), 2.80-2.69 (m, 1H), 2.67-2.49 (m, 2H), 2.36-2.24 (m, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 196.0 (d, *J* = 5.3 Hz), 140.4, 137.5, 133.3, 128.7, 128.6, 128.42, 128.39, 126.2, 62.8 (d, *J* = 7.0 Hz), 62.5 (d, *J* = 6.7 Hz), 46.2 (d, *J* = 127.7 Hz), 34.0 (d, *J* = 15.1 Hz), 28.9 (d, *J* = 4.4 Hz), 16.3 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 6.2 Hz).

**<sup>31</sup>P NMR** (243 MHz, CDCl<sub>3</sub>) δ 22.21.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>P: 361.1563, found: 361.1563.



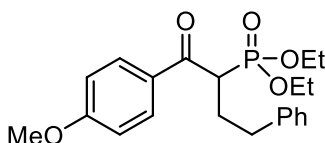
**21**

The title compound **21** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 48% yield, 40.9 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.35-7.17 (m, 5H), 7.07 (d, *J* = 7.4 Hz, 2H), 4.10-3.93 (m, 4H), 3.24-3.05 (m, 1H), 2.94 (t, *J* = 7.4 Hz, 1H), 2.70-2.54 (m, 1H), 2.52-2.29 (m, 1H), 2.20-1.93 (m, 1H), 1.33-1.20 (m, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 204.0 (d, *J* = 4.4 Hz), 140.1, 138.1, 131.8, 131.1 (q, *J* = 33.2 Hz), 129.6 (q, *J* = 3.3 Hz), 129.1, 128.6, 128.5, 126.4, 125.5 (q, *J* = 3.9 Hz), 123.6 (q, *J* = 273.3 Hz), 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.9 Hz), 46.6 (d, *J* = 127.2 Hz), 34.0 (d, *J* = 14.8 Hz), 28.7 (d, *J* = 4.3 Hz), 16.3 (d, *J* = 5.9 Hz), 16.0 (d, *J* = 6.3 Hz).

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>25</sub>F<sub>3</sub>O<sub>4</sub>P: 429.1437, found: 429.1435.



**22**

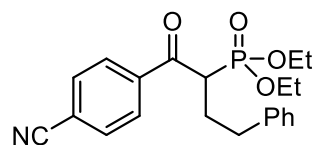
The title compound **22** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 1:1, 73% yield, 57.0 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.94-7.86 (m, 2H), 7.28-7.13 (m, 3H), 7.13-7.05 (m, 2H), 6.96-6.88 (m, 2H), 4.17-3.92 (m, 5H), 3.88 (s, 3H), 2.71 (ddd, *J* = 13.4, 9.0, 4.6 Hz, 1H), 2.63-2.54 (m, 1H), 2.54-2.45 (m, 1H), 2.32-2.20 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.2 (d, *J* = 5.2 Hz), 163.8, 140.7, 131.2, 130.7, 128.6, 128.4, 126.2, 113.6, 62.7 (d, *J* = 6.9 Hz), 62.5 (d, *J* = 6.9 Hz), 55.5, 45.9 (d, *J* = 128.0 Hz), 34.1 (d, *J* = 15.0 Hz), 29.1 (d, *J* = 4.6 Hz), 16.3 (d, *J* = 5.9 Hz), 16.2 (d, *J* = 6.3 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 22.67.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>28</sub>O<sub>5</sub>P: 391.1669, found: 391.1654.



**23**

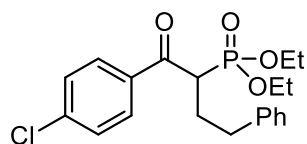
The title compound **23** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 4:1, 36% yield, 28.0 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99-7.68 (m, 4H), 7.25-7.14 (m, 3H), 7.09-7.02 (m, 2H), 4.19-3.92 (m, 5H), 2.78-2.67 (m, 1H), 2.65-2.47 (m, 2H), 2.37-2.23 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.9 (d, *J* = 5.6 Hz), 140.5, 140.0, 132.2, 129.0, 128.61, 128.55, 126.4, 117.8, 116.4, 63.0 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.9 Hz), 46.9 (d, *J* = 127.0 Hz), 34.0 (d, *J* = 14.4 Hz), 28.6 (d, *J* = 4.4 Hz), 16.3 (d, *J* = 5.9 Hz), 16.2 (d, *J* = 6.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 21.08.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>25</sub>NO<sub>4</sub>P: 386.1516, found: 386.1486.



**24**

The title compound **24** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 4:1, 57% yield, 45.3 mg, yellow oil).

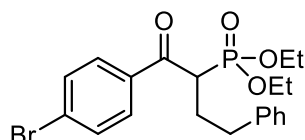
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.86-7.78 (m, 2H), 7.47-7.37 (m, 2H), 7.29-7.13 (m, 3H), 7.10-7.04 (m, 2H), 4.18-3.92 (m, 5H), 2.76-2.67 (m, 1H), 2.65-2.56 (m, 1H),

2.55-2.46 (m, 1H), 2.34-2.22 (m, 1H), 1.26 (t,  $J = 7.0$  Hz, 3H), 1.17 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.7 (d,  $J = 5.3$  Hz), 140.3, 139.8, 135.9, 130.1, 128.69, 128.6, 128.4, 126.3, 62.8 (d,  $J = 6.9$  Hz), 62.6 (d,  $J = 6.9$  Hz), 46.3 (d,  $J = 127.7$  Hz), 34.0 (d,  $J = 14.7$  Hz), 28.8 (d,  $J = 4.5$  Hz), 16.2 (d,  $J = 5.9$  Hz), 16.1 (d,  $J = 6.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.84.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{20}\text{H}_{25}\text{ClO}_4\text{P}$ : 395.1173, found: 395.1173.



**25**

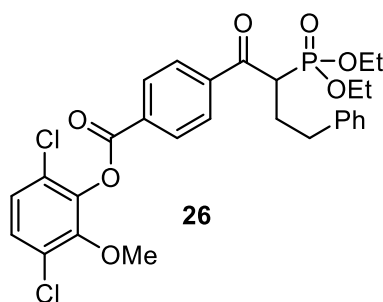
The title compound **25** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 4:1, 52% yield, 45.5 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.70 (m, 2H), 7.62-7.54 (m, 2H), 7.27-7.15 (m, 3H), 7.10-7.04 (m, 2H), 4.17-3.92 (m, 5H), 2.76-2.66 (m, 1H), 2.65-2.55 (m, 1H), 2.55-2.46 (m, 1H), 2.35-2.21 (m, 1H), 1.26 (t,  $J = 7.1$  Hz, 3H), 1.17 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.9 (d,  $J = 5.4$  Hz), 140.3, 136.3, 131.7, 130.2, 128.58, 128.57, 128.5, 126.3, 62.8 (d,  $J = 6.9$  Hz), 62.7 (d,  $J = 7.0$  Hz), 46.3 (d,  $J = 127.7$  Hz), 34.0 (d,  $J = 14.8$  Hz), 28.8 (d,  $J = 4.4$  Hz), 16.3 (d,  $J = 5.9$  Hz), 16.1 (d,  $J = 6.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.79.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{20}\text{H}_{25}\text{BrO}_4\text{P}$ : 439.0668, found: 439.0673.



**26**

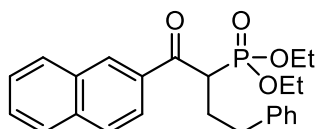
The title compound **26** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 4:1, 58% yield, 67.4 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03-7.97 (m, 2H), 7.44 (d,  $J = 8.7$  Hz, 1H), 7.40-7.32 (m, 2H), 7.28-7.18 (m, 4H), 7.14-7.06 (m, 2H), 4.16-4.02 (m, 5H), 4.01 (s, 3H), 2.78-2.68 (m, 1H), 2.67-2.48 (m, 2H), 2.36-2.25 (m, 1H), 1.27 (t,  $J = 7.1$  Hz, 3H), 1.18 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.7 (d,  $J = 5.5$  Hz), 162.4, 154.20, 154.16, 140.4, 135.7, 132.6, 130.6, 129.8, 129.4, 128.6, 128.5, 126.9, 126.3, 126.0, 121.5, 62.8 (d,  $J = 6.9$  Hz), 62.7 (d,  $J = 6.9$  Hz), 62.4, 46.5 (d,  $J = 127.6$  Hz), 34.1 (d,  $J = 14.8$  Hz), 28.9 (d,  $J = 4.4$  Hz), 16.3 (d,  $J = 6.0$  Hz), 16.2 (d,  $J = 6.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.90.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{NH}_4]^+$  calcd. for  $\text{C}_{28}\text{H}_{33}\text{Cl}_2\text{NO}_7\text{P}$ : 596.1366, found: 596.1343.



27

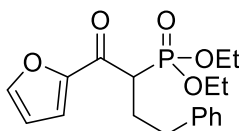
The title compound **27** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 67% yield, 55.1 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (s, 1H), 8.00 (dd,  $J = 8.7, 2.0$  Hz, 1H), 7.94-7.84 (m, 3H), 7.65-7.50 (m, 2H), 7.28-7.15 (m, 3H), 7.11 (dd,  $J = 8.0, 1.7$  Hz, 2H), 4.27 (ddd,  $J = 23.4, 10.1, 3.5$  Hz, 1H), 4.17-3.95 (m, 4H), 2.82-2.72 (m, 1H), 2.71-2.62 (m, 1H), 2.61-2.51 (m, 1H), 2.43-2.28 (m, 1H), 1.26 (t,  $J = 7.1$  Hz, 3H), 1.12 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8 (d,  $J = 5.5$  Hz), 140.5, 135.6, 134.91, 134.89, 132.3, 130.7, 129.7, 128.6, 128.4, 128.3, 127.6, 126.7, 126.2, 124.2, 62.8 (d,  $J = 6.9$  Hz), 62.5 (d,  $J = 6.9$  Hz), 46.2 (d,  $J = 128.3$  Hz), 34.0 (d,  $J = 14.8$  Hz), 29.0 (d,  $J = 4.4$  Hz), 16.3 (d,  $J = 6.0$  Hz), 16.1 (d,  $J = 6.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  22.45.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{24}\text{H}_{28}\text{O}_4\text{P}$ : 411.1720, found: 411.1713.



28

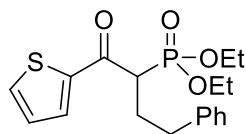
The title compound **28** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 38% yield, 26.4 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 2.1$  Hz, 1H), 7.20-7.07 (m, 4H), 7.06-7.01 (m, 2H), 6.48 (dd,  $J = 3.7, 1.7$  Hz, 1H), 4.10-3.93 (m, 4H), 3.85 (ddd,  $J = 23.7, 10.5, 3.7$  Hz, 1H), 2.70-2.57 (m, 1H), 2.56-2.40 (m, 2H), 2.26-2.07 (m, 1H), 1.20 (t,  $J = 7.1$  Hz, 3H), 1.12 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  184.0 (d,  $J = 5.5$  Hz), 153.0, 146.8, 140.5, 128.6, 128.4, 126.2, 112.6, 62.73 (d,  $J = 2.9$  Hz), 62.66 (d,  $J = 2.9$  Hz), 46.9 (d,  $J = 128.4$  Hz), 34.2 (d,  $J = 15.0$  Hz), 28.4 (d,  $J = 4.8$  Hz), 16.3 (d,  $J = 5.9$  Hz), 16.2 (d,  $J = 6.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.99.

MS (EI): [M]<sup>+</sup>:350.15.



29

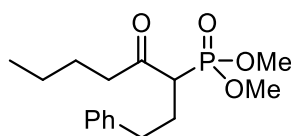
The title compound **29** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 57% yield, 42.0 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 (ddd, *J* = 13.4, 4.4, 1.2 Hz, 2H), 7.20-7.14 (m, 2H), 7.14-7.08 (m, 1H), 7.07-7.00 (m, 3H), 4.14-3.87 (m, 4H), 3.79 (ddd, *J* = 23.0, 10.3, 3.5 Hz, 1H), 2.72-2.61 (m, 1H), 2.56-2.40 (m, 2H), 2.26-2.11 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 188.1 (d, *J* = 5.0 Hz), 144.9, 140.4, 134.7, 133.2, 128.6, 128.4, 128.2, 126.2, 62.9 (d, *J* = 6.6 Hz), 62.7 (d, *J* = 6.6 Hz), 48.1 (d, *J* = 128.8 Hz), 34.1 (d, *J* = 14.9 Hz), 28.9 (d, *J* = 4.4 Hz), 16.3 (d, *J* = 6.1 Hz), 16.2 (d, *J* = 6.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 21.83.

MS (EI): [M]<sup>+</sup>:366.15.



30

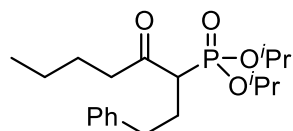
The title compound **30** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 64% yield, 39.7 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.00 (m, 5H), 3.74 (dd, *J* = 11.0, 3.6 Hz, 6H), 3.20 (ddd, *J* = 24.6, 10.4, 3.5 Hz, 1H), 2.83-2.71 (m, 1H), 2.70-2.61 (m, 1H), 2.57-2.47 (m, 1H), 2.46-2.33 (m, 2H), 2.17-2.02 (m, 1H), 1.63-1.48 (m, 2H), 1.39-1.25 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 205.5 (d, *J* = 4.4 Hz), 140.4, 128.5, 128.4, 126.3, 53.2 (d, *J* = 6.7 Hz), 53.0 (d, *J* = 6.8 Hz), 51.2 (d, *J* = 125.1 Hz), 44.1, 34.1 (d, *J* = 14.9 Hz), 27.8 (d, *J* = 4.8 Hz), 25.4, 22.0, 13.8.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 24.99.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>26</sub>O<sub>4</sub>P: 313.1563, found: 313.1554.



**31**

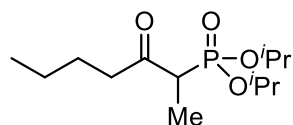
The title compound **31** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 86% yield, 63.0 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.24 (m, 2H), 7.22-7.17 (m, 1H), 7.17-7.11 (m, 2H), 4.74-4.56 (m, 2H), 3.17 - 3.02 (ddd, *J* = 25.0, 10.6, 3.2 Hz, 1H), 2.78 (dt, *J* = 17.7, 7.5 Hz, 1H), 2.64 (ddd, *J* = 13.9, 9.2, 5.2 Hz, 1H), 2.54-2.28 (m, 3H), 2.13-1.99 (m, 1H), 1.54 (p, *J* = 7.5 Hz, 2H), 1.40-1.23 (m, 14H), 0.90 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 205.7 (d, *J* = 4.4 Hz), 140.7, 128.5, 128.4, 126.1, 71.3 (d, *J* = 7.0 Hz), 71.0 (d, *J* = 7.0 Hz), 52.6 (d, *J* = 125.7 Hz), 43.9, 34.2 (d, *J* = 15.0 Hz), 27.8 (d, *J* = 4.8 Hz), 25.5, 24.0 (t, *J* = 3.8 Hz), 23.8 (d, *J* = 5.1 Hz), 23.7 (d, *J* = 5.1 Hz), 22.1, 13.8.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 20.42.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>34</sub>O<sub>4</sub>P: 369.2189, found: 369.2189.



**32**

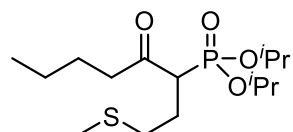
The title compound **32** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 64% yield, 35.4 mg, yellow oil).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 4.77-4.62 (m, 2H), 3.17 (dq, *J* = 25.3, 7.1 Hz, 1H), 2.81 (dt, *J* = 17.6, 7.4 Hz, 1H), 2.54 (dt, *J* = 17.5, 7.2 Hz, 1H), 1.59-1.52 (m, 2H), 1.35-1.30 (m, 17H), 0.91 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 206.2 (d, *J* = 3.9 Hz), 71.2 (d, *J* = 7.0 Hz), 71.0 (d, *J* = 7.0 Hz), 47.3 (d, *J* = 128.1 Hz), 42.8, 25.7, 24.0 (t, *J* = 3.9 Hz), 23.8 (t, *J* = 4.8 Hz), 22.1, 13.8, 11.0 (d, *J* = 6.5 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 21.73.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>28</sub>O<sub>4</sub>P: 279.1720, found: 279.1720.



**33**



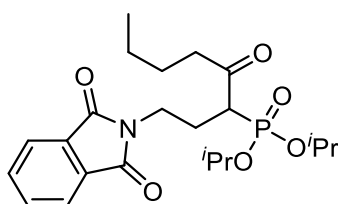
The title compound **33** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 41% yield, 27.6 mg, yellow oil).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.72-4.50 (m, 2H), 3.33 (ddd,  $J = 25.4, 10.1, 3.3$  Hz, 1H), 2.84-2.71 (m, 1H), 2.56-2.38 (m, 2H), 2.38-2.20 (m, 2H), 1.97 (s, 3H), 1.94-1.85 (m, 1H), 1.56-1.43 (m, 2H), 1.34-1.16 (m, 14H), 0.84 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.4 (d,  $J = 4.4$  Hz), 71.4 (d,  $J = 7.0$  Hz), 71.2 (d,  $J = 7.0$  Hz), 51.7 (d,  $J = 125.8$  Hz), 44.2, 32.7 (d,  $J = 15.8$  Hz), 25.6, 25.1 (d,  $J = 4.4$  Hz), 24.05 (d,  $J = 3.3$  Hz), 24.0 (d,  $J = 3.7$  Hz), 23.84 (d,  $J = 4.8$  Hz), 23.77 (d,  $J = 5.5$  Hz), 22.1, 14.8, 13.8.

$^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.23.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{15}\text{H}_{32}\text{O}_4\text{PS}$ : 339.1753, found: 339.1753.



**34**

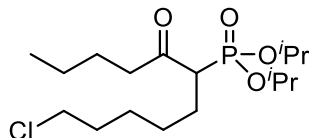
The title compound **34** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 86% yield, 75.2 mg, white solid).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (ddd,  $J = 46.8, 5.5, 3.1$  Hz, 4H), 4.75-4.55 (m, 2H), 3.77-3.57 (m, 2H), 3.19 (ddd,  $J = 26.0, 10.9, 2.9$  Hz, 1H), 2.93 (dt,  $J = 18.1, 7.4$  Hz, 1H), 2.58 (dt,  $J = 18.3, 7.2$  Hz, 1H), 2.52-2.37 (m, 1H), 2.18-2.02 (m, 1H), 1.59-1.48 (m, 2H), 1.38-1.32 (m, 2H), 1.32-1.24 (m, 12H), 0.91 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.0, 168.3, 134.0, 132.0, 123.2, 71.6 (d,  $J = 7.1$  Hz), 71.3 (d,  $J = 7.0$  Hz), 51.2 (d,  $J = 126.0$  Hz), 43.7, 36.6 (d,  $J = 16.3$  Hz), 25.42, 25.37, 24.0 (d,  $J = 3.7$  Hz), 23.9 (d,  $J = 4.0$  Hz), 23.7 (d,  $J = 5.2$  Hz), 22.1, 13.9.

$^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  19.62.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{NH}_4]^+$  calcd. for  $\text{C}_{22}\text{H}_{36}\text{N}_2\text{O}_6\text{P}$ : 455.2305, found: 455.2305.



**35**

The title compound **35** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 86% yield, 63.1 mg, yellow oil).

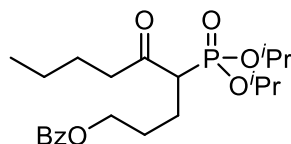
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.76-4.60 (m, 2H), 3.51 (t,  $J = 6.6$  Hz, 2H), 3.09 (ddd,  $J = 24.6, 10.8, 3.4$  Hz, 1H), 2.77 (dt,  $J = 17.5, 7.2$  Hz, 1H), 2.48 (ddd,  $J = 17.5, 8.1, 6.5$  Hz, 1H), 2.11-1.96 (m, 1H), 1.88-1.80 (m, 1H), 1.79-1.70 (m, 2H), 1.62-1.51 (m,

2H), 1.50-1.38 (m, 2H), 1.36-1.30 (m, 12H), 1.30-1.24 (m, 4H), 0.91 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.9 (d,  $J = 4.5$  Hz), 71.3 (d,  $J = 7.0$  Hz), 71.1 (d,  $J = 7.1$  Hz), 53.6 (d,  $J = 126.1$  Hz), 44.8, 43.9, 32.1, 27.8 (d,  $J = 15.0$  Hz), 26.6, 26.2 (d,  $J = 5.1$  Hz), 25.6, 24.05 (d,  $J = 3.5$  Hz), 23.99 (d,  $J = 3.9$  Hz), 23.8 (t,  $J = 5.4$  Hz), 22.2, 13.8.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.51.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{17}\text{H}_{35}\text{ClO}_4\text{P}$ : 369.1956, found: 369.1953.



36

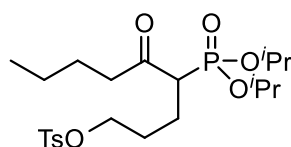
The title compound **36** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 4:1, 75% yield, 63.9 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07-8.01 (m, 2H), 7.58-7.52 (m, 1H), 7.47-7.38 (m, 2H), 4.76-4.60 (m, 2H), 4.30 (t,  $J = 6.3$  Hz, 2H), 3.17 (ddd,  $J = 24.8, 10.6, 3.7$  Hz, 1H), 2.82 (dt,  $J = 17.5, 7.3$  Hz, 1H), 2.56-2.44 (m, 1H), 2.25-2.08 (m, 1H), 2.02-1.85 (m, 1H), 1.83-1.64 (m, 2H), 1.61-1.50 (m, 2H), 1.34-1.26 (m, 14H), 0.90 (t,  $J = 7.4$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.6 (d,  $J = 4.5$  Hz), 166.4, 132.8, 130.2, 129.5, 128.3, 71.4 (d,  $J = 7.0$  Hz), 71.1 (d,  $J = 7.1$  Hz), 64.2, 53.1 (d,  $J = 126.2$  Hz), 43.9, 27.5 (d,  $J = 14.7$  Hz), 25.5, 24.0 (d,  $J = 3.6$  Hz), 23.9 (d,  $J = 3.9$  Hz), 23.8 (d,  $J = 5.1$  Hz), 23.7 (d,  $J = 5.4$  Hz), 23.1 (d,  $J = 5.0$  Hz), 22.1, 13.8.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.05.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{22}\text{H}_{36}\text{O}_6\text{P}$ : 427.2244, found: 427.2244.



37

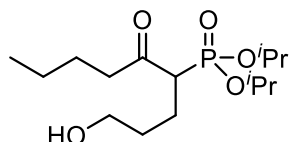
The title compound **37** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 2:1, 49% yield, 46.7 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.3$  Hz, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 4.73-4.59 (m, 2H), 3.99 (t,  $J = 6.3$  Hz, 2H), 3.06 (ddd,  $J = 25.0, 10.3, 3.9$  Hz, 1H), 2.78 (dt,  $J = 17.5, 7.5$  Hz, 1H), 2.50-2.40 (m, 4H), 2.06-1.92 (m, 1H), 1.81-1.73 (m, 1H), 1.67-1.58 (m, 2H), 1.56-1.47 (m, 2H), 1.37-1.34 (m, 2H), 1.33-1.29 (m, 12H), 0.90 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.4, 144.7, 133.1, 129.8, 127.8, 71.5 (d,  $J = 6.9$  Hz), 71.2 (d,  $J = 7.1$  Hz), 69.8, 52.8 (d,  $J = 127.2$  Hz), 43.8, 27.6 (d,  $J = 14.4$  Hz), 25.5, 24.0 (d,  $J = 3.3$  Hz), 23.9 (d,  $J = 3.7$  Hz), 23.8 (d,  $J = 4.8$  Hz), 23.7 (d,  $J = 5.1$  Hz), 22.6 (d,  $J = 4.7$  Hz), 22.1, 21.5, 13.8.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  19.69.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{22}\text{H}_{38}\text{O}_7\text{P}$ : 477.2070, found: 477.2070.



**38**

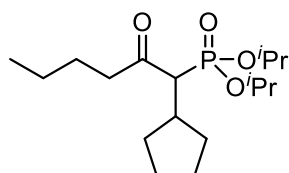
The title compound **38** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 1:3, 73% yield, 47.1 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.77-4.61 (m, 2H), 3.37 (t,  $J = 6.5$  Hz, 2H), 3.10 (ddd,  $J = 24.9, 10.3, 3.6$  Hz, 1H), 2.81 (dt,  $J = 17.6, 7.2$  Hz, 1H), 2.55-2.43 (m, 1H), 2.18-2.05 (m, 1H), 1.99-1.89 (m, 1H), 1.87-1.73 (m, 2H), 1.67-1.50 (m, 2H), 1.40-1.28 (m, 14H), 0.91 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.5 (d,  $J = 4.4$  Hz), 71.5 (d,  $J = 7.0$  Hz), 71.2 (d,  $J = 7.1$  Hz), 52.8 (d,  $J = 126.4$  Hz), 43.8, 32.6, 31.3 (d,  $J = 14.6$  Hz), 25.5, 25.1 (d,  $J = 5.1$  Hz), 24.03 (d,  $J = 3.6$  Hz), 23.97 (d,  $J = 4.0$  Hz), 23.8 (d,  $J = 5.1$  Hz), 23.7 (d,  $J = 5.3$  Hz), 22.1, 13.8.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  19.82.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{15}\text{H}_{31}\text{NaO}_5\text{P}$ : 345.1801, found: 345.1801.



**39**

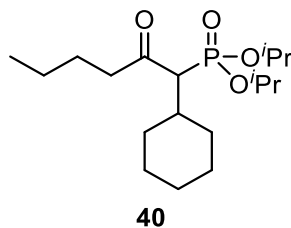
The title compound **39** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 5:1, 67% yield, 44.3 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.80-4.60 (m, 2H), 2.92 (dd,  $J = 21.2, 10.9$  Hz, 1H), 2.75-2.62 (m, 1H), 2.54-2.33 (m, 2H), 2.07-1.94 (m, 1H), 1.80-1.70 (m, 1H), 1.69-1.60 (m, 2H), 1.59-1.48 (m, 4H), 1.37-1.25 (m, 16H), 0.91 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.6 (d,  $J = 4.2$  Hz), 71.0 (d,  $J = 6.8$  Hz), 70.7 (d,  $J = 7.2$  Hz), 59.3 (d,  $J = 127.7$  Hz), 43.9, 39.0 (d,  $J = 5.3$  Hz), 32.2 (d,  $J = 17.0$  Hz), 31.6 (d,  $J = 1.8$  Hz), 25.4, 24.71, 24.15, 24.14 (d,  $J = 2.9$  Hz), 24.06 (d,  $J = 3.8$  Hz), 23.88 (d,  $J = 5.1$  Hz), 23.78 (d,  $J = 5.5$  Hz), 22.16, 13.84.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.46.

**HRMS** (ESI)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{17}H_{34}O_4P$ : 333.2189, found: 333.2198.



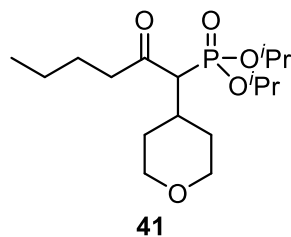
The title compound **40** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 9:1, 46% yield, 32.0 mg, yellow oil).

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  4.80-4.63 (m,  $J = 5.9$  Hz, 2H), 2.93 (dd,  $J = 21.3, 9.9$  Hz, 1H), 2.65 (ddd,  $J = 18.1, 8.7, 6.4$  Hz, 1H), 2.44 (ddd,  $J = 18.0, 8.6, 6.2$  Hz, 1H), 2.11-2.07 (m, 1H), 1.79-1.68 (m, 2H), 1.66-1.43 (m, 6H), 1.34-1.25 (m, 16H), 1.17-1.05 (m, 2H), 0.90 (t,  $J = 7.3$  Hz, 3H).

**$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  206.8 (d,  $J = 4.8$  Hz), 71.0 (d,  $J = 7.0$  Hz), 70.8 (d,  $J = 7.3$  Hz), 60.0 (d,  $J = 128.0$  Hz), 44.6, 37.6 (d,  $J = 4.8$  Hz), 32.2 (d,  $J = 15.8$  Hz), 31.7 (d,  $J = 3.7$  Hz), 26.10, 26.06, 26.04, 26.00, 25.3, 24.14 (d,  $J = 3.3$  Hz), 24.07 (d,  $J = 3.7$  Hz), 23.85 (d,  $J = 4.8$  Hz), 23.78 (d,  $J = 5.5$  Hz), 13.9.

**$^{31}P$  NMR** (162 MHz,  $CDCl_3$ )  $\delta$  20.74.

**HRMS** (ESI)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{18}H_{36}O_4P$ : 347.2346, found: 347.2346.



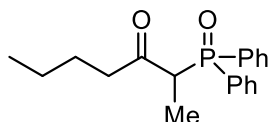
The title compound **41** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 3:1, 77% yield, 53.8 mg, yellow oil).

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  4.83-4.62 (m, 2H), 3.93 (ddd,  $J = 26.0, 11.6, 4.3$  Hz, 2H), 3.44-3.32 (m, 2H), 2.97 (dd,  $J = 21.5, 10.2$  Hz, 1H), 2.78-2.65 (m, 1H), 2.50-2.37 (m, 1H), 2.37-2.25 (m, 1H), 1.64-1.51 (m, 2H), 1.50-1.41 (m, 2H), 1.38-1.27 (m, 16H), 0.91 (t,  $J = 7.3$  Hz, 3H).

**$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  206.2 (d,  $J = 4.9$  Hz), 71.3 (d,  $J = 6.9$  Hz), 71.0 (d,  $J = 7.3$  Hz), 67.7, 67.6 (d,  $J = 2.0$  Hz), 59.3 (d,  $J = 127.5$  Hz), 45.2, 34.8 (d,  $J = 4.8$  Hz), 32.0 (d,  $J = 16.3$  Hz), 31.7 (d,  $J = 3.4$  Hz), 25.2, 24.1 (d,  $J = 3.3$  Hz), 24.0 (d,  $J = 3.9$  Hz), 23.9 (d,  $J = 5.0$  Hz), 23.8 (d,  $J = 5.5$  Hz), 22.1, 13.8.

**$^{31}P$  NMR** (162 MHz,  $CDCl_3$ )  $\delta$  19.46.

**HRMS** (ESI)  $m/z$ :  $[M+H]^+$  calcd. for  $C_{17}H_{34}O_5P$ : 349.2138, found: 349.2138.



**42**

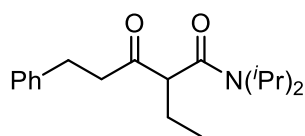
The title compound **42** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 2:1, 88% yield, 55.4 mg, yellow solid).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.86-7.74 (m, 4H), 7.57-7.44 (m, 6H), 3.68 (dq, *J* = 14.2, 7.2 Hz, 1H), 2.53 (t, *J* = 7.3 Hz, 2H), 1.43-1.35 (m, 5H), 1.14 (h, *J* = 7.4 Hz, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 207.5 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 8.8 Hz), 131.2 (d, *J* = 8.7 Hz), 131.0 (d, *J* = 99.8 Hz), 130.9 (d, *J* = 108.9 Hz), 128.6 (d, *J* = 5.3 Hz), 128.5 (d, *J* = 5.2 Hz), 50.3 (d, *J* = 57.6 Hz), 42.6, 25.3, 21.9, 13.7, 11.4 (d, *J* = 3.6 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 30.37.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>P: 315.1508, found: 315.1489.



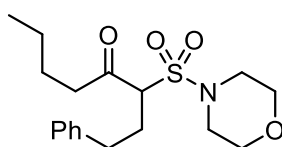
**45**

The title compound **45** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 30:1, 64% yield, 39.0 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.20 (m, 2H), 7.20-7.11 (m, 3H), 4.12-3.96 (m, 1H), 3.39 (t, *J* = 7.1 Hz, 2H), 2.93-2.84 (m, 2H), 2.84-2.71 (m, 2H), 2.02-1.87 (m, 1H), 1.86-1.75 (m, 1H), 1.37 (t, *J* = 7.0 Hz, 6H), 1.15 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 206.5, 167.6, 141.0, 128.38, 128.36, 126.0, 61.1, 48.7, 46.2, 40.6, 29.5, 22.5, 20.9, 20.59, 20.55, 20.3, 12.1.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>30</sub>NO<sub>2</sub>: 304.2271, found: 304.2264.



**47**

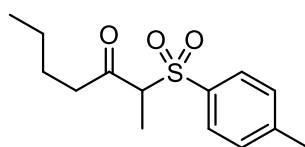
The title compound **47** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 15:1, 57% yield, 40.5 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.34-7.28 (m, 2H), 7.27-7.20 (m, 1H), 7.18-7.11 (m,

2H), 4.03 (dd,  $J = 10.4, 3.4$  Hz, 1H), 3.73-3.60 (m, 4H), 3.36-3.21 (m, 4H), 2.82 (dt,  $J = 18.4, 7.4$  Hz, 1H), 2.72-2.59 (m, 1H), 2.58-2.38 (m, 3H), 2.31-2.18 (m, 1H), 1.58-1.48 (m, 2H), 1.36-1.29 (m, 2H), 0.91 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  203.35, 139.44, 128.75, 128.42, 126.70, 72.03, 66.87, 46.84, 44.04, 32.88, 28.56, 25.23, 22.02, 13.80.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{CH}_3\text{CN}+\text{Na}]^+$  calcd. for  $\text{C}_{20}\text{H}_{30}\text{N}_2\text{NaO}_4\text{S}$ : 417.1818, found: 417.1818.



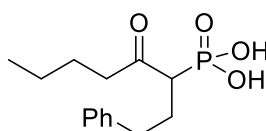
49

The title compound **49** was synthesized according to General Procedure (SI 3.1), and it was purified by column chromatography on silica gel (PE:EA = 30:1, 41% yield, 22.1 mg, yellow oil).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 8.1$  Hz, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 4.16 (q,  $J = 7.1$  Hz, 1H), 2.89 (dt,  $J = 18.1, 7.3$  Hz, 1H), 2.64 (dt,  $J = 18.1, 7.1$  Hz, 1H), 2.45 (s, 3H), 1.55 (q,  $J = 7.5$  Hz, 2H), 1.38 (d,  $J = 7.1$  Hz, 3H), 1.36-1.22 (m, 2H), 0.91 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 145.4, 133.3, 129.7, 129.4, 70.0, 43.5, 25.4, 22.0, 21.6, 13.7, 12.0.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{K}]^+$  calcd. for  $\text{C}_{14}\text{H}_{20}\text{KO}_3\text{S}$ : 307.0765, found: 307.0735.



50

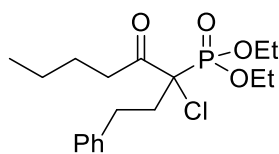
The title compound **50** was synthesized according to General Procedure (SI 3.3) without purified (95% yield, 27.0 mg, yellow solid).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD\_SPE}$ )  $\delta$  7.31-7.24 (m, 2H), 7.22-7.15 (m, 3H), 3.20 (ddd,  $J = 24.5, 10.5, 3.4$  Hz, 1H), 2.77 (dt,  $J = 17.9, 7.4$  Hz, 1H), 2.67-2.51 (m, 2H), 2.50-2.30 (m, 2H), 2.17-2.01 (m, 1H), 1.58-1.47 (m, 2H), 1.37-1.31 (m, 2H), 0.92 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{OD\_SPE}$ )  $\delta$  207.6 (d,  $J = 4.4$  Hz), 140.9, 128.2, 128.1, 125.8, 52.8 (d,  $J = 122.1$  Hz), 43.6, 33.9 (d,  $J = 14.7$  Hz), 28.1 (d,  $J = 4.4$  Hz), 25.2 (d,  $J = 2.2$  Hz), 21.8, 12.8.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{OD\_SPE}$ )  $\delta$  19.59.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{14}\text{H}_{22}\text{O}_4\text{P}$ : 285.1250, found: 285.1250.



**51**

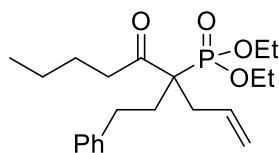
The title compound **51** was synthesized according to General Procedure (SI 3.3), and it was purified by column chromatography on silica gel (PE:EA = 8:1, 96% yield, 35.8 mg, colorless oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.24 (m, 2H), 7.24-7.15 (m, 3H), 4.30-4.15 (m, 4H), 2.96-2.69 (m, 4H), 2.49 (td, *J* = 12.0, 4.0 Hz, 1H), 2.35-2.20 (m, 1H), 1.63-1.52 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 8H), 0.92 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 203.7, 140.60, 128.6, 128.5, 126.2, 74.9 (d, *J* = 142.0 Hz), 64.7 (d, *J* = 7.3 Hz), 64.6 (d, *J* = 7.3 Hz), 40.1, 37.7, 37.6, 30.6 (d, *J* = 10.6 Hz), 26.0, 22.0, 16.39 (d, *J* = 5.5 Hz), 16.35 (d, *J* = 5.9 Hz), 13.8.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 15.31.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>29</sub>ClO<sub>4</sub>P: 375.1487, found: 375.1487.



**52**

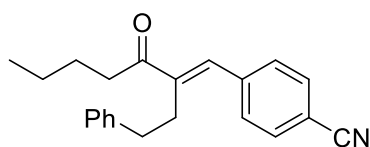
The title compound **52** was synthesized according to General Procedure (SI 3.3), and it was purified by column chromatography on silica gel (PE:EA = 6:1, 48% yield, 18.4 mg, yellow oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.25 (m, 2H), 7.23-7.15 (m, 3H), 5.92-5.75 (m, 1H), 5.27-5.11 (m, 2H), 4.15 (p, *J* = 7.2 Hz, 4H), 2.90-2.56 (m, 5H), 2.52 (td, *J* = 12.8, 4.6 Hz, 1H), 2.30-2.09 (m, 2H), 1.62-1.53 (m, 2H), 1.37-1.29 (m, 8H), 0.91 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 207.2, 142.1, 133.3 (d, *J* = 9.2 Hz), 128.42, 128.36, 126.0, 118.6, 62.6 (d, *J* = 7.3 Hz), 62.5 (d, *J* = 7.4 Hz), 58.1 (d, *J* = 127.3 Hz), 39.6, 35.1 (d, *J* = 3.3 Hz), 33.2, 30.7 (d, *J* = 8.1 Hz), 25.9, 22.2, 16.4 (d, *J* = 5.9 Hz), 13.9.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 25.77.

**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>34</sub>O<sub>4</sub>P: 381.2189, found: 381.2156.



**53**

The title compound **53** was synthesized according to General Procedure (SI 3.3), and it was purified by column chromatography on silica gel (PE:EA = 50:1, 86% yield, 54.9 mg, E/Z = 6.7:1, determined by HNMR, colorless oil).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.44 (s, 1H), 7.29–7.19 (ovrlp, 5H), 7.11–7.05 (m, 2H), 2.81–2.69 (ovrlp, 6H), 1.68 (p, *J* = 7.6 Hz, 2H), 1.43–1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 202.0, 143.8, 141.0, 140.4, 136.5, 132.1, 129.3, 128.39, 128.38, 126.1, 118.4, 111.7, 37.6, 34.8, 28.6, 26.8, 22.4, 13.9.

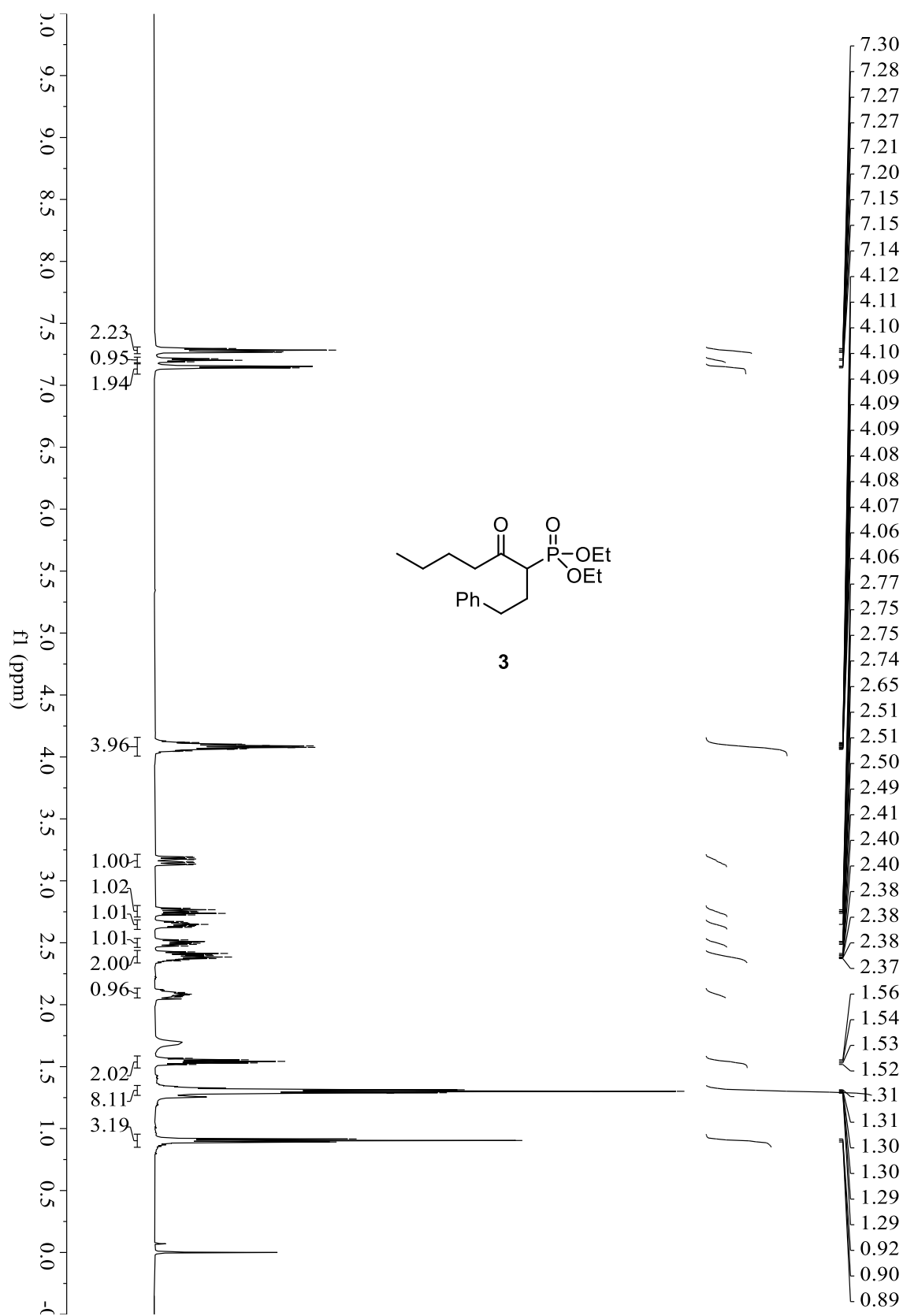
**HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>24</sub>NO<sub>4</sub>: 318.1852, found: 318.1852.

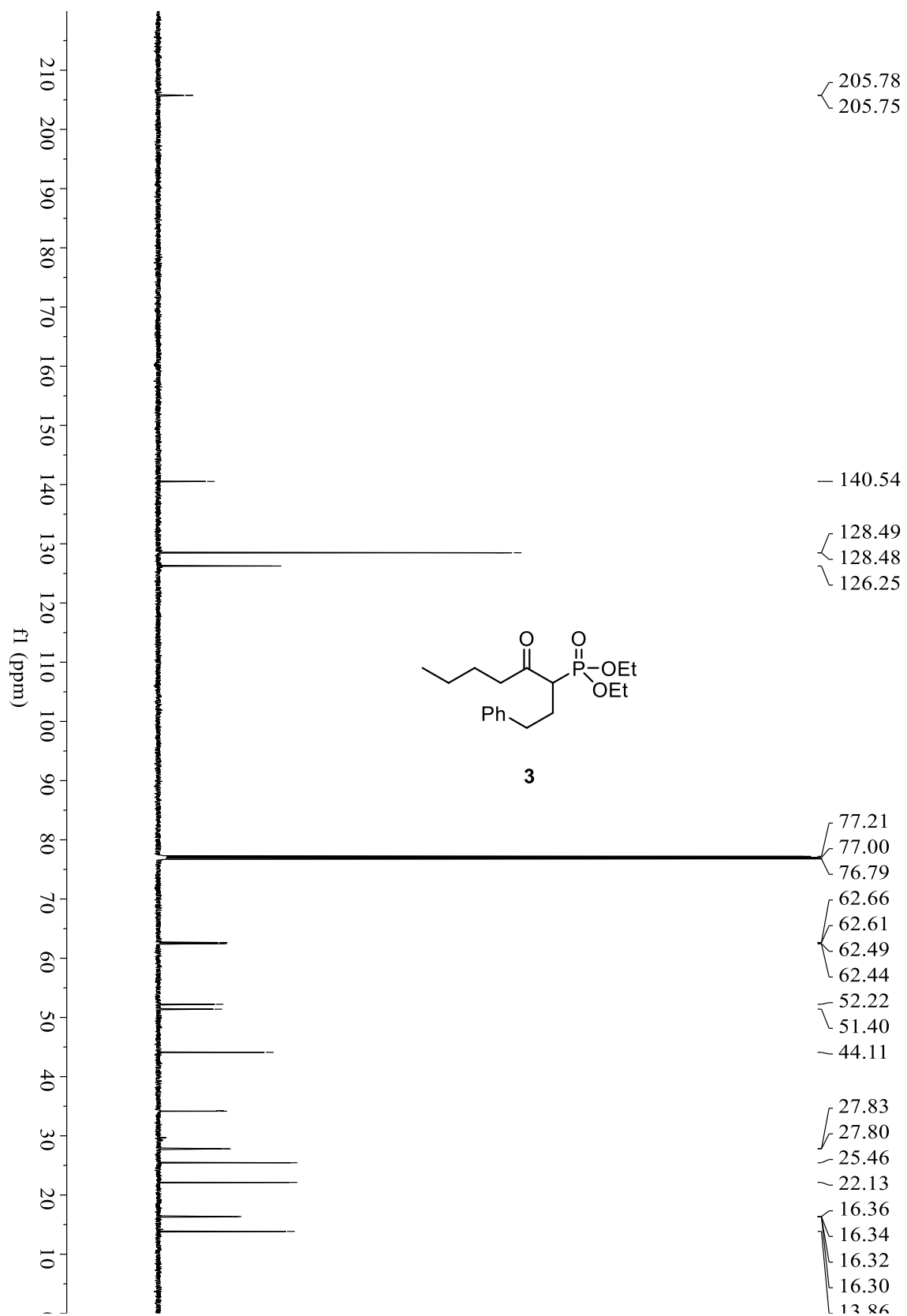


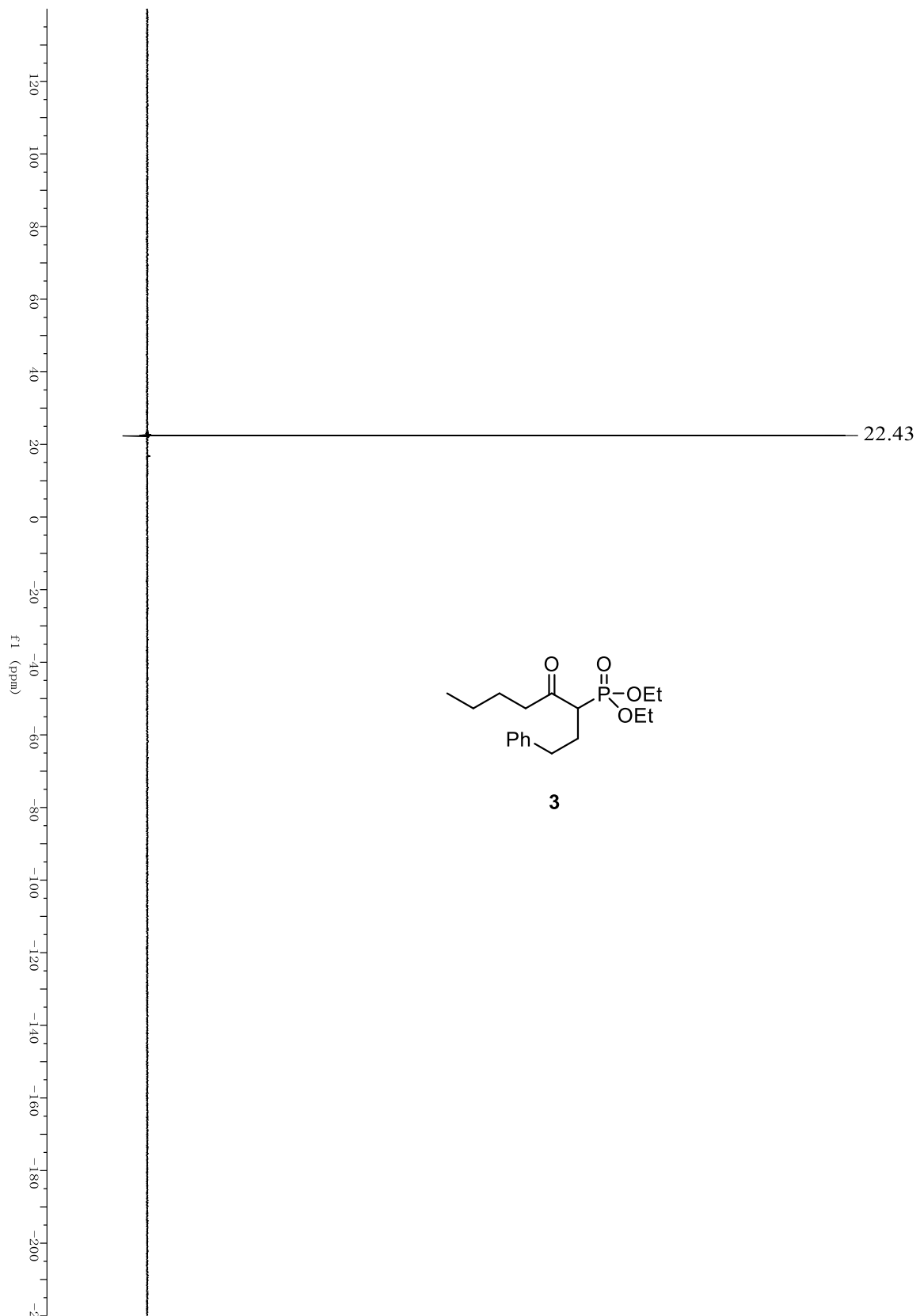
## 5. Supplementary References

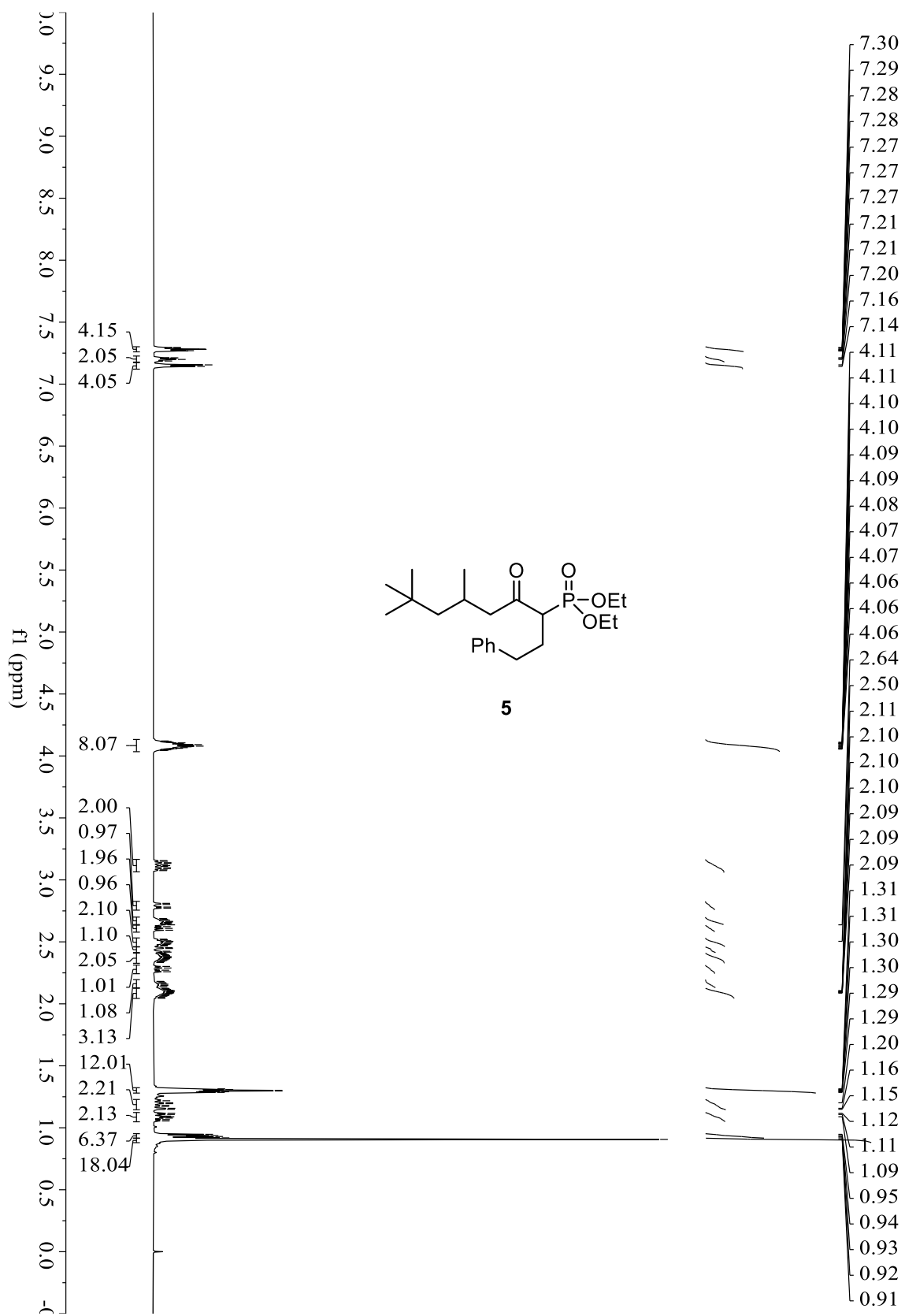
- [S1] Matsuzawa, A.; Shiraiwa, J.; Kasamatsu, A.; Sugita, K. Enantioselective, Protecting-Group-Free Total Synthesis of Boscartin F. *Organic Letters* **2018**, *20*, 1031-1033.
- [S2] Lee, S. Y.; Lee, C.-W.; Oh, D. Y. Regiocontrolled Synthetic Approach to  $\alpha,\alpha'$ -Disubstituted Unsymmetrical Ketones. *The Journal of Organic Chemistry* **2000**, *65*, 245-248.
- [S3] Bernardi, L.; Jørgensen, K. A. Enantioselective chlorination and fluorination of  $\beta$ -keto phosphonates catalyzed by chiral Lewis acids. *Chemical Communications* **2005**, 1324-1326.
- [S4] Li, X.; Yuan, M.; Chen, F.; Huang, Z.; Qing, F.-L.; Gutierrez, O.; Chu, L. Three-component enantioselective alkenylation of organophosphonates via nickel metallaphotoredox catalysis. *Chem* **2023**, *9*, 154-169.
- [S5] Oswood, C. J.; MacMillan, D. W. C., Selective Isomerization via Transient Thermodynamic Control: Dynamic Epimerization of trans to cis Diols. *Journal of the American Chemical Society* **2022**, *144* (1), 93-98.
- [S6] Perry, I. B.; Brewer, T. F.; Sarver, P. J.; Schultz, D. M.; DiRocco, D. A.; MacMillan, D. W. C. Direct arylation of strong aliphatic C–H bonds. *Nature* **2018**, *560*, 70-75.
- [S7] He, S.-J.; Wang, J.-W.; Li, Y.; Xu, Z.-Y.; Wang, X.-X.; Lu, X.; Fu, Y., Nickel-Catalyzed Enantioconvergent Reductive Hydroalkylation of Olefins with  $\alpha$ -Heteroatom Phosphorus or Sulfur Alkyl Electrophiles. *Journal of the American Chemical Society* **2020**, *142*, 214-221.
- [S8] Choi, J.; Martín-Gago, P.; Fu, G. C. Stereoconvergent Arylations and Alkenylations of Unactivated Alkyl Electrophiles: Catalytic Enantioselective Synthesis of Secondary Sulfonamides and Sulfones. *Journal of the American Chemical Society* **2014**, *136*, 12161-12165.
- [S9] Wang, H.; Zheng, P.; Wu, X.; Li, Y.; XU, T. Modular and Facile Access to Chiral  $\alpha$ -Aryl Phosphates via Dual Nickel- and Photoredox-Catalyzed Reductive Cross-Coupling. *Journal of the American Chemical Society* **2022**, *144*, 3989-3997.

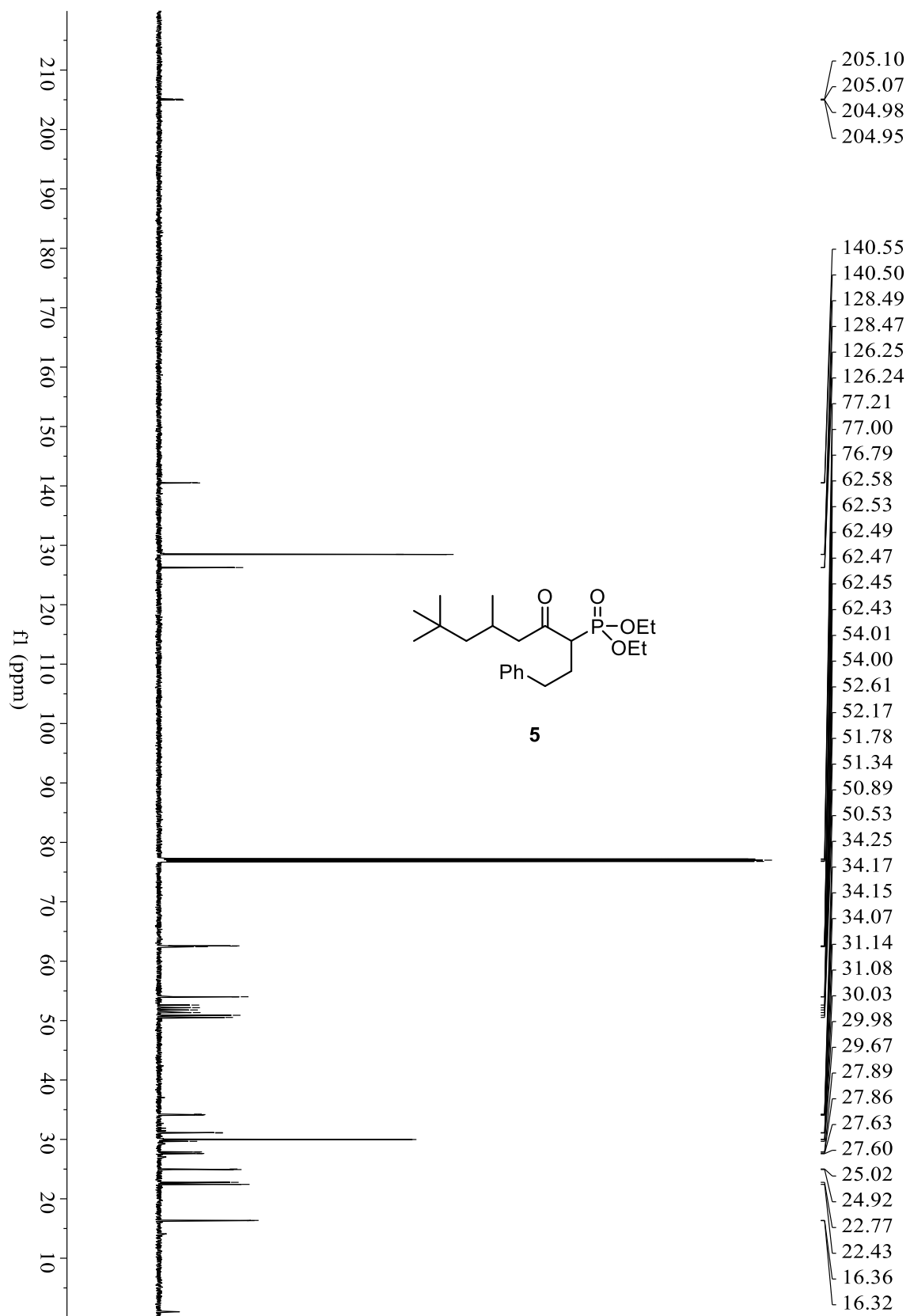
## 6. Spectra data for the compounds

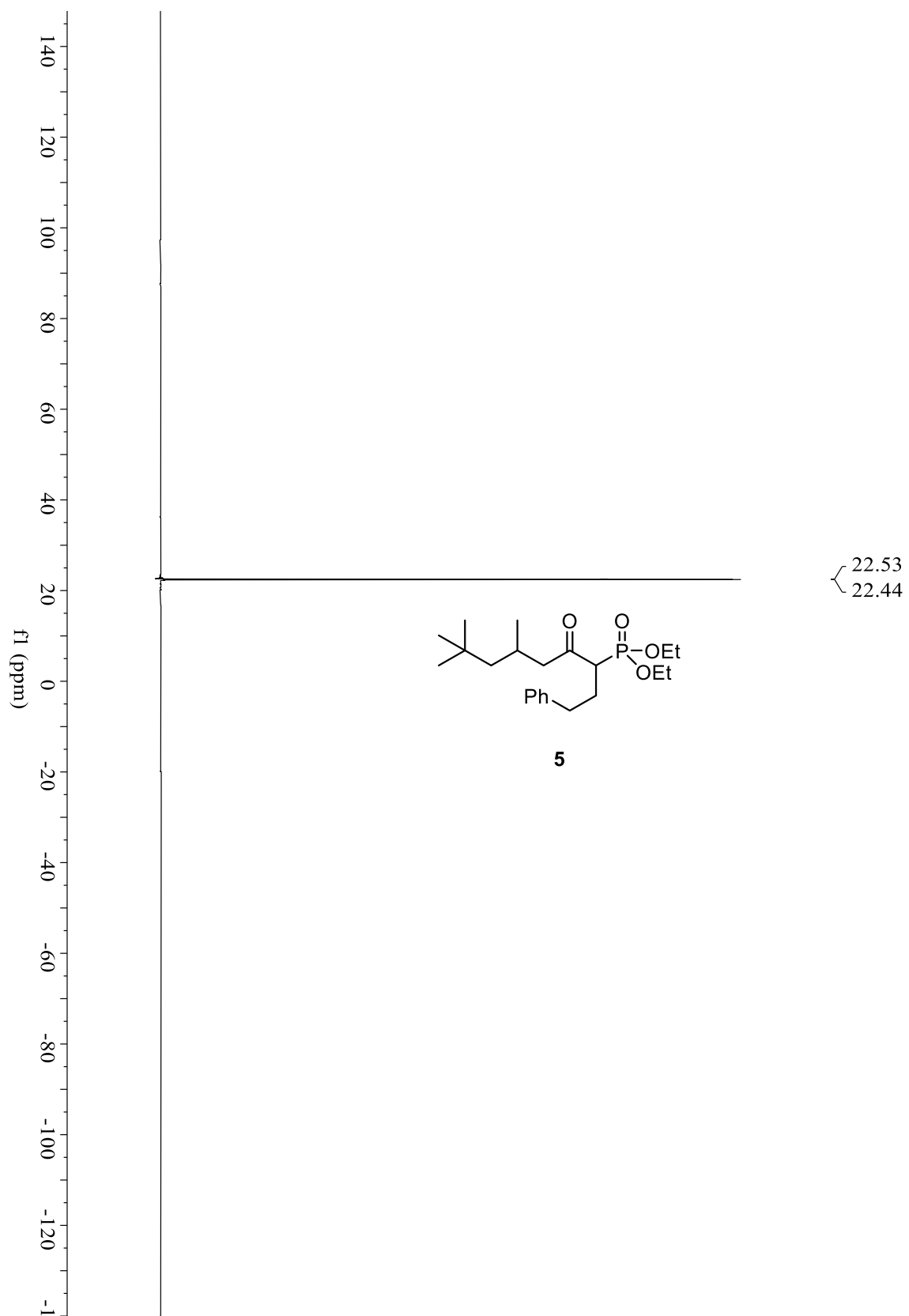


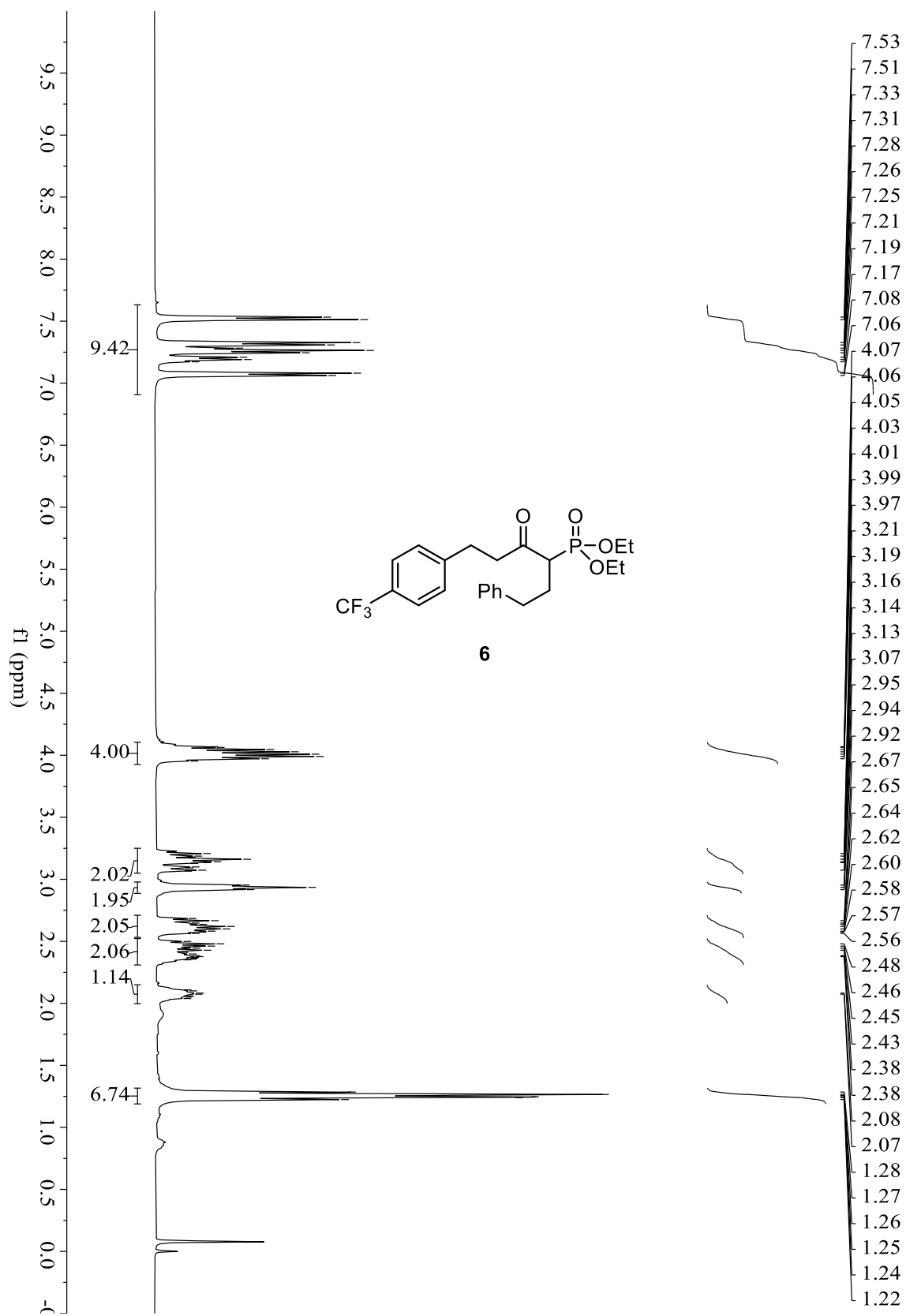




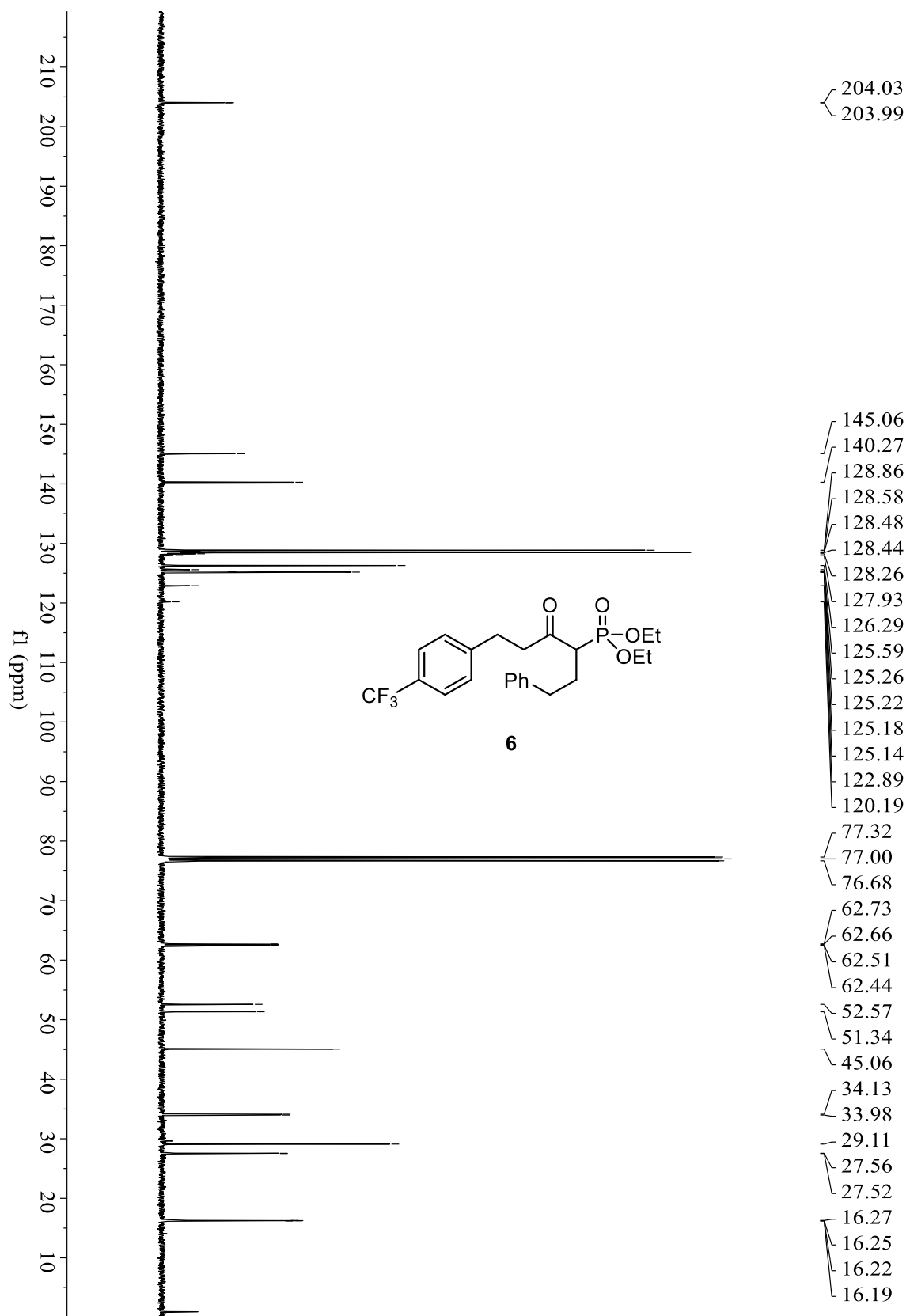


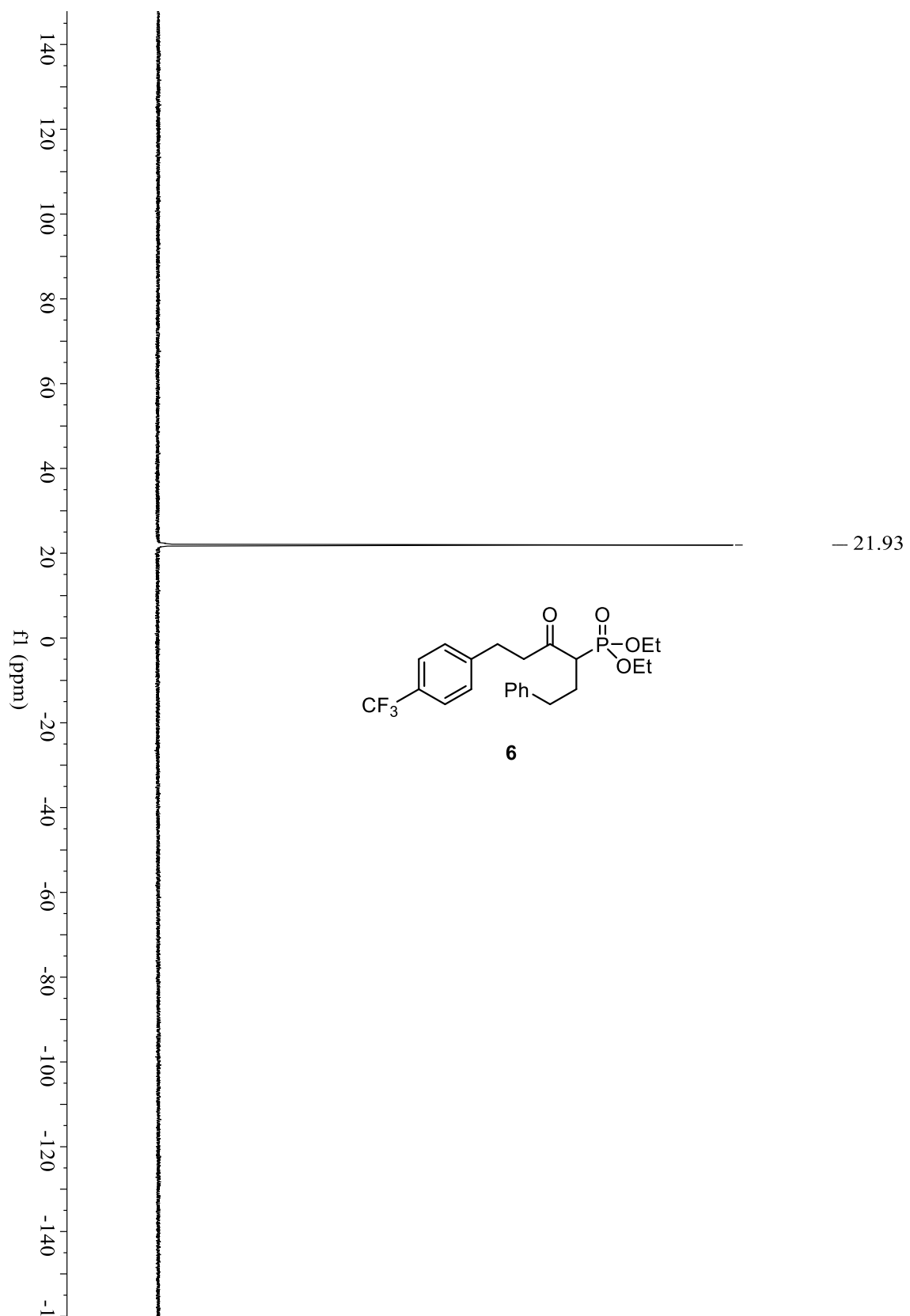


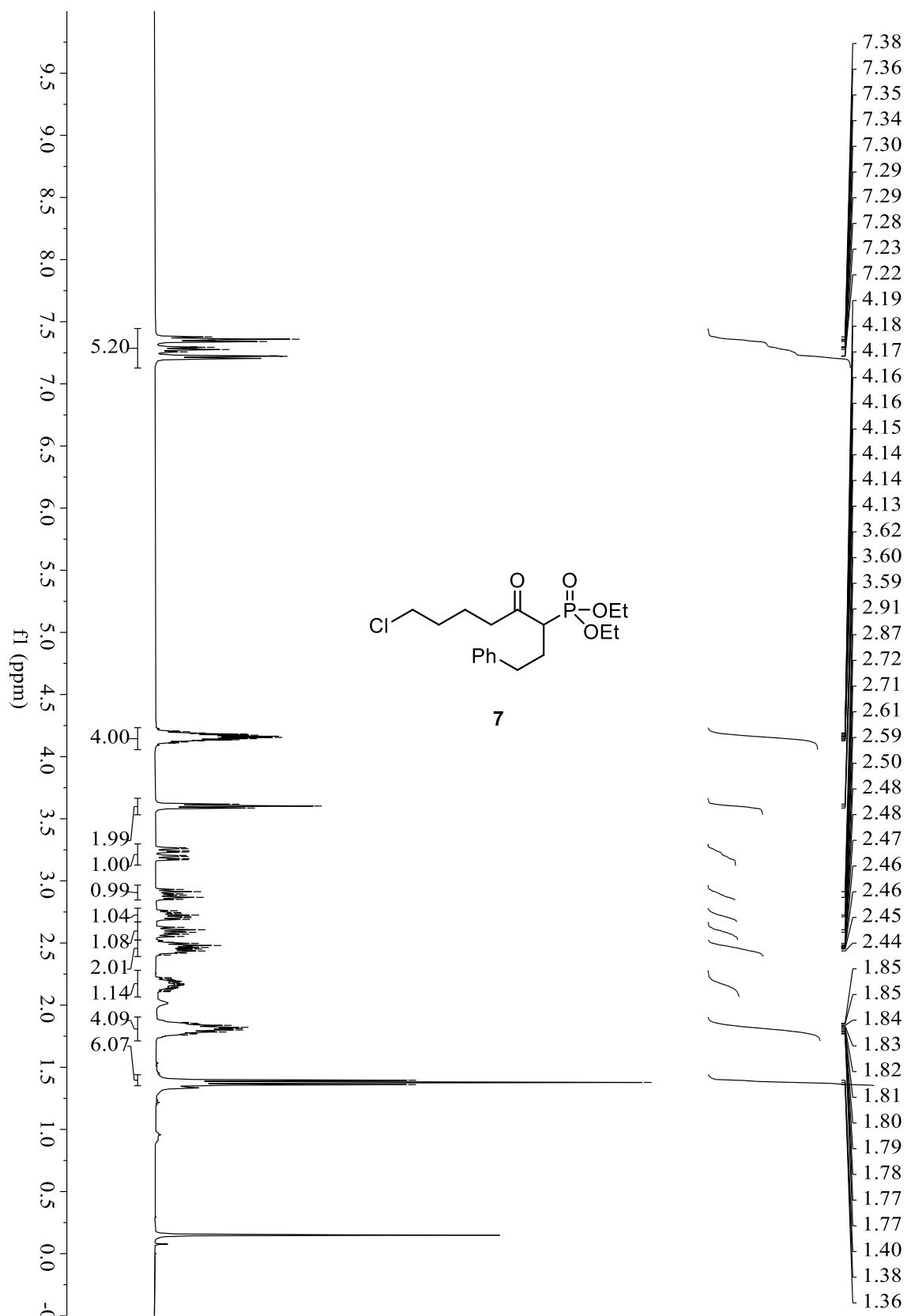


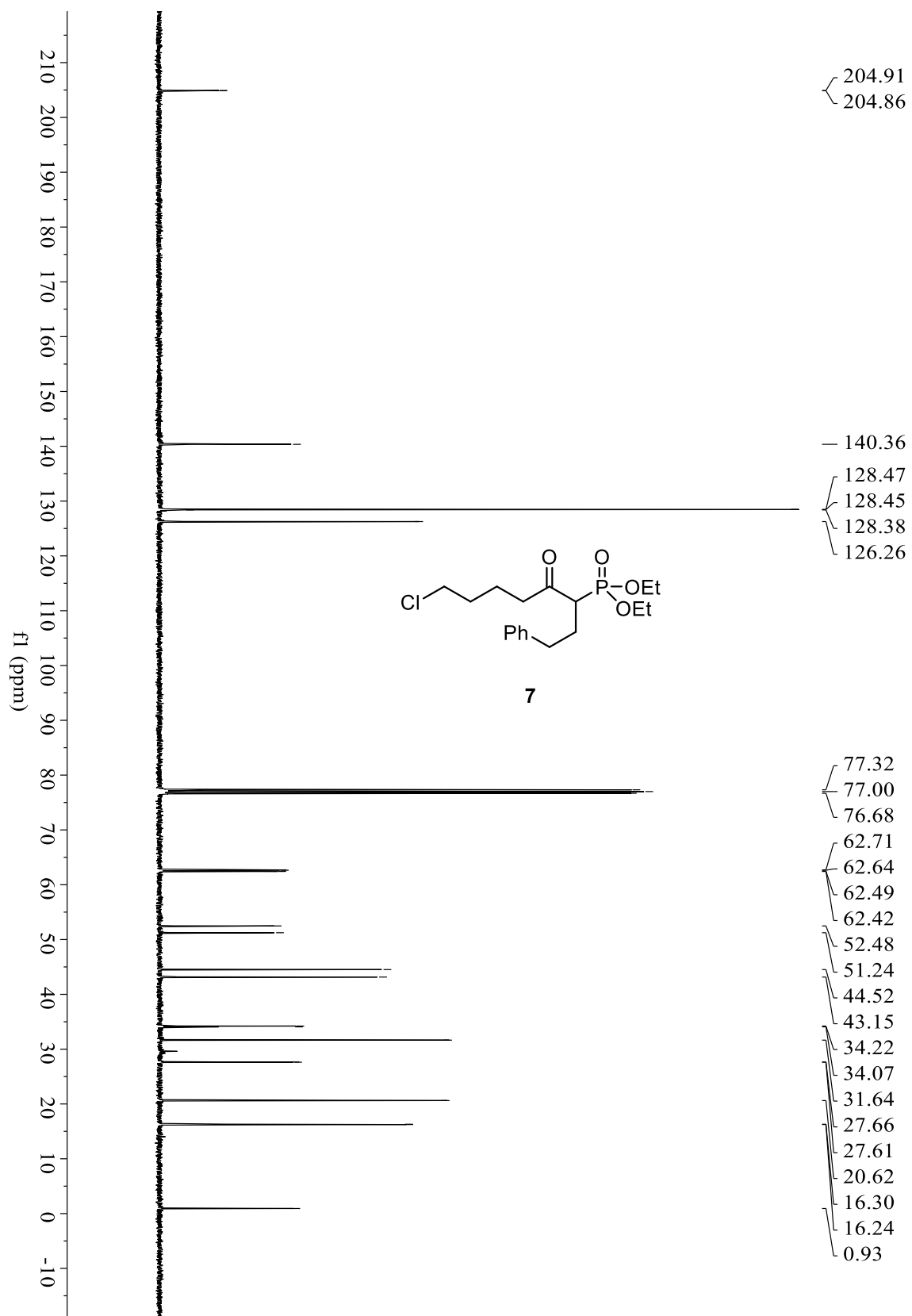






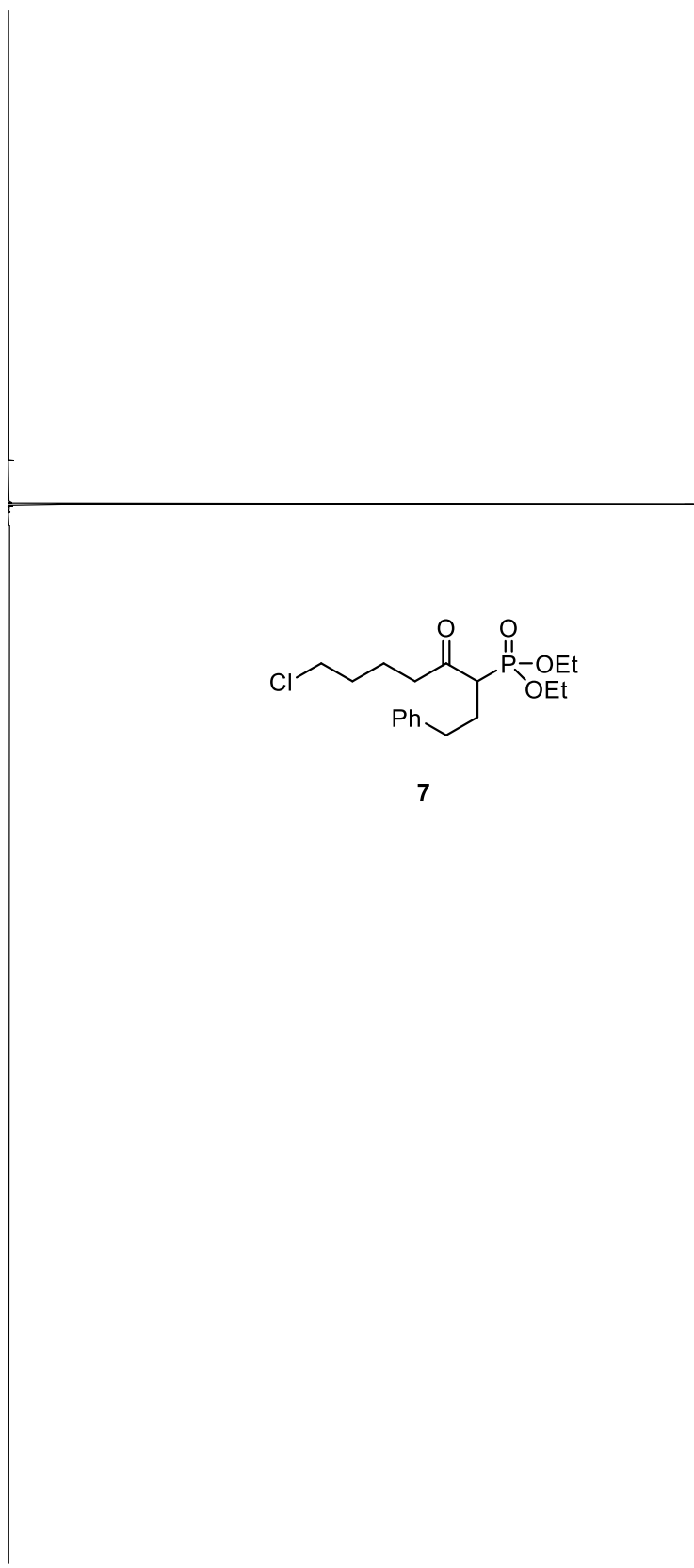




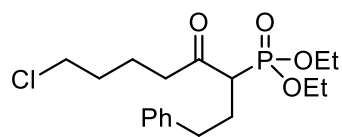


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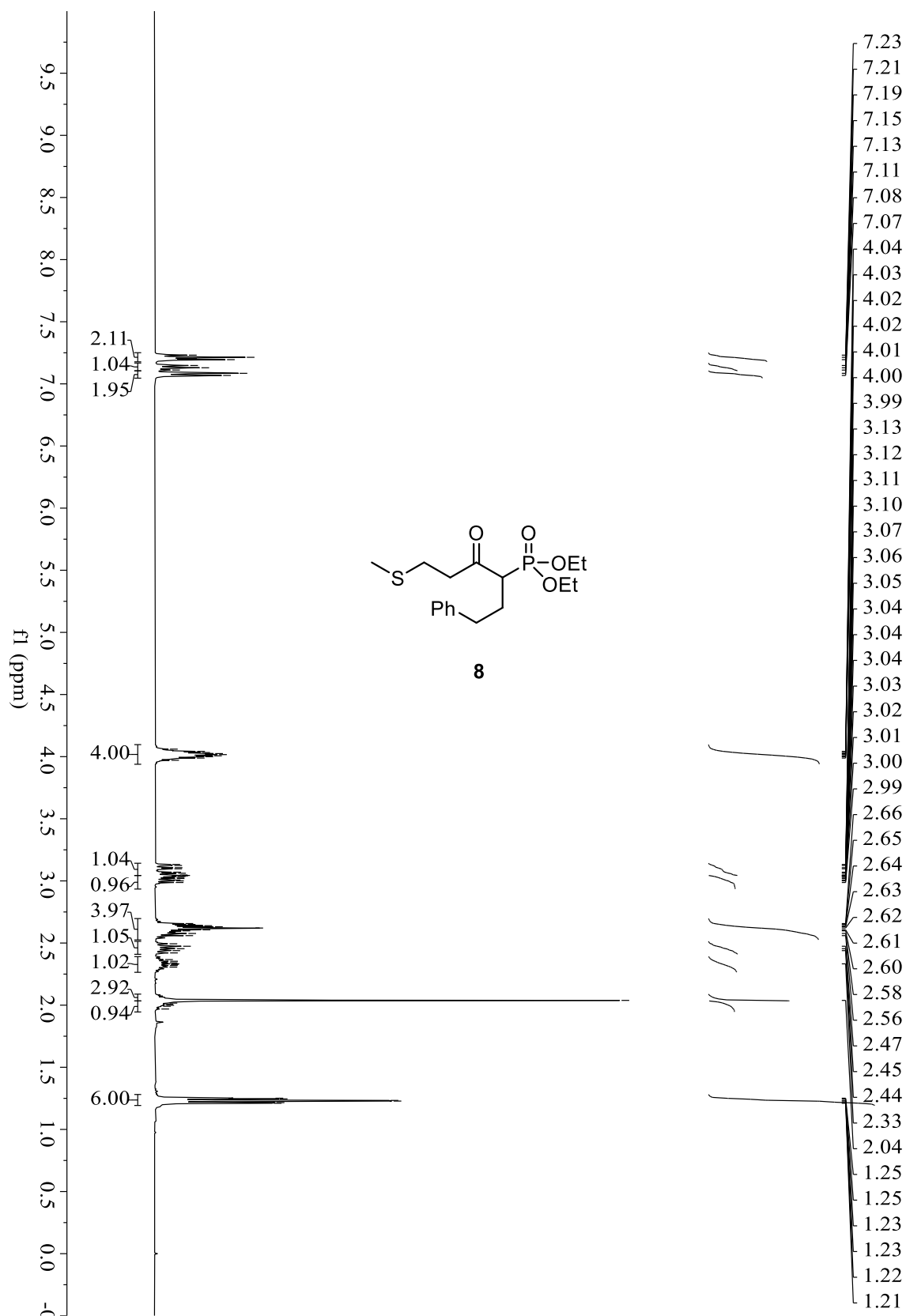
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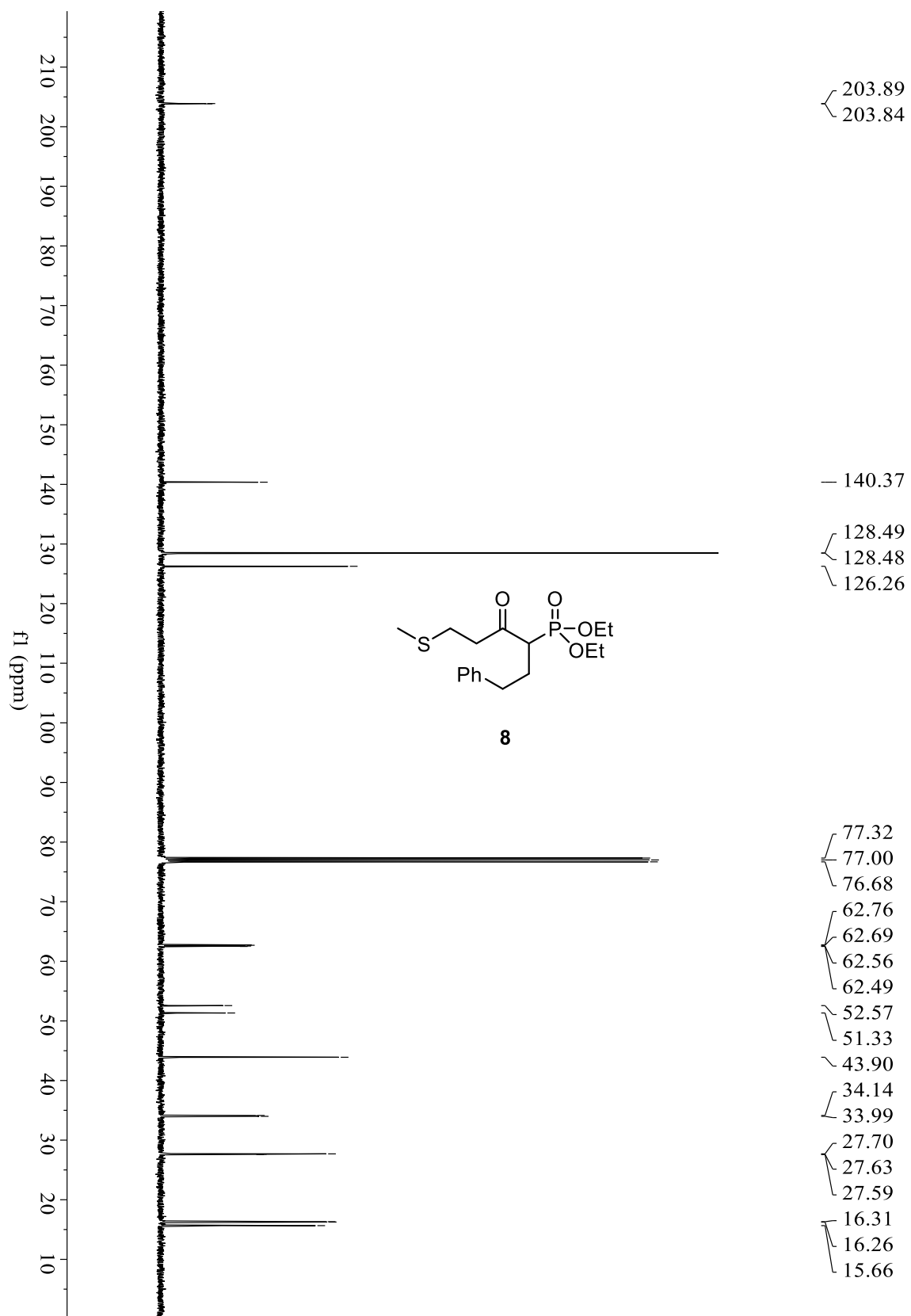


— 22.19

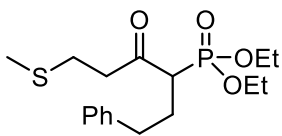
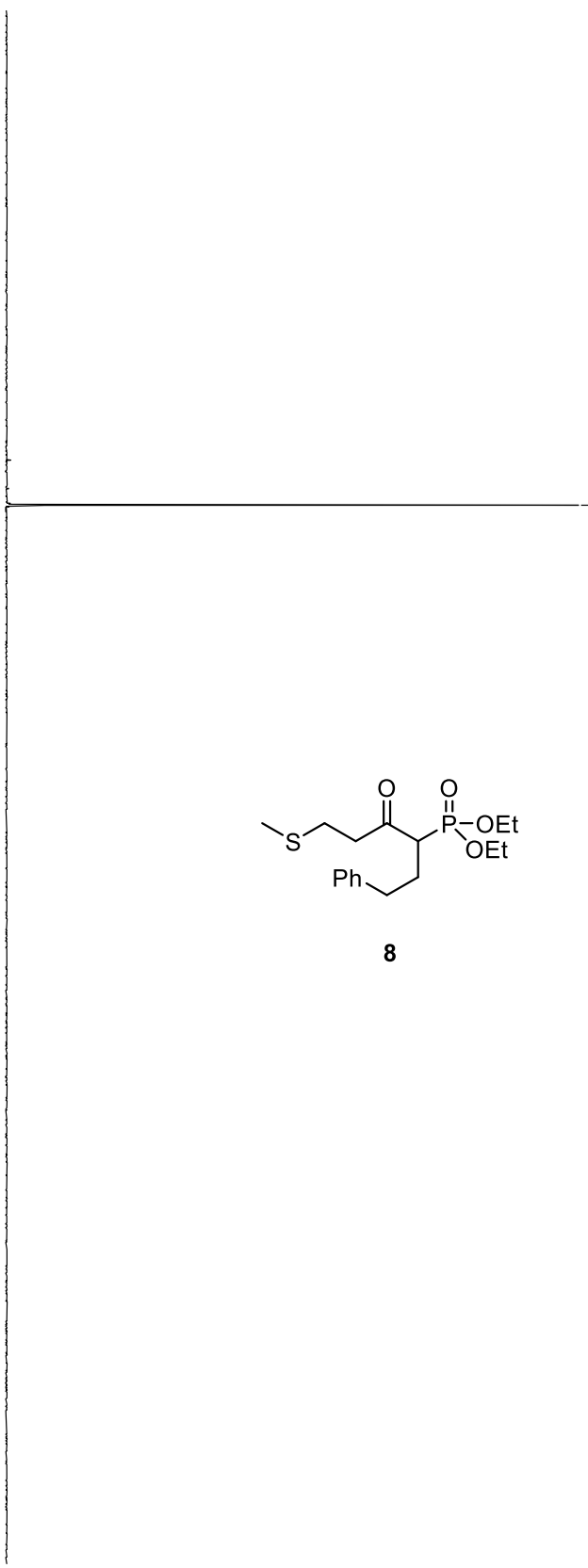


7



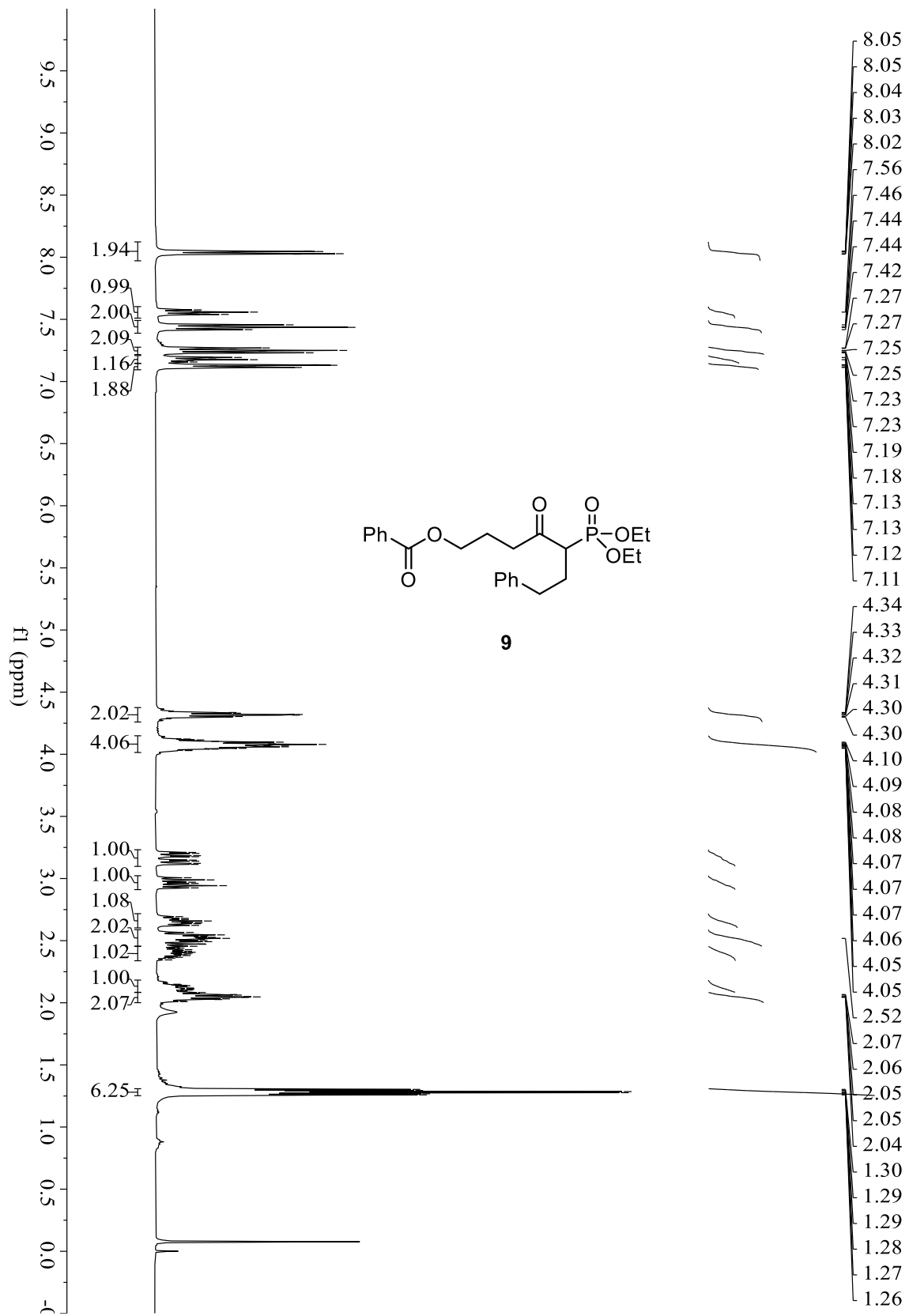


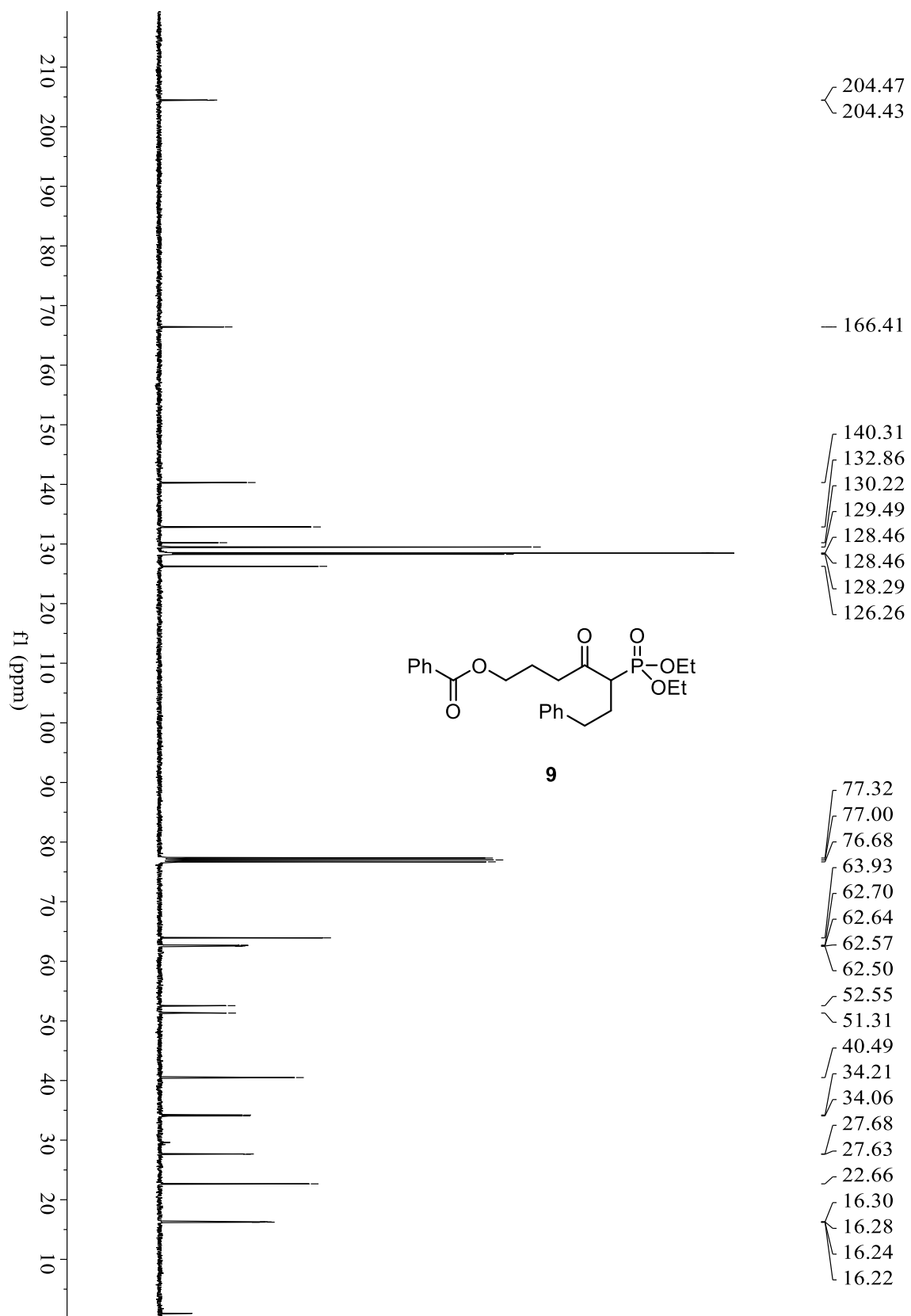
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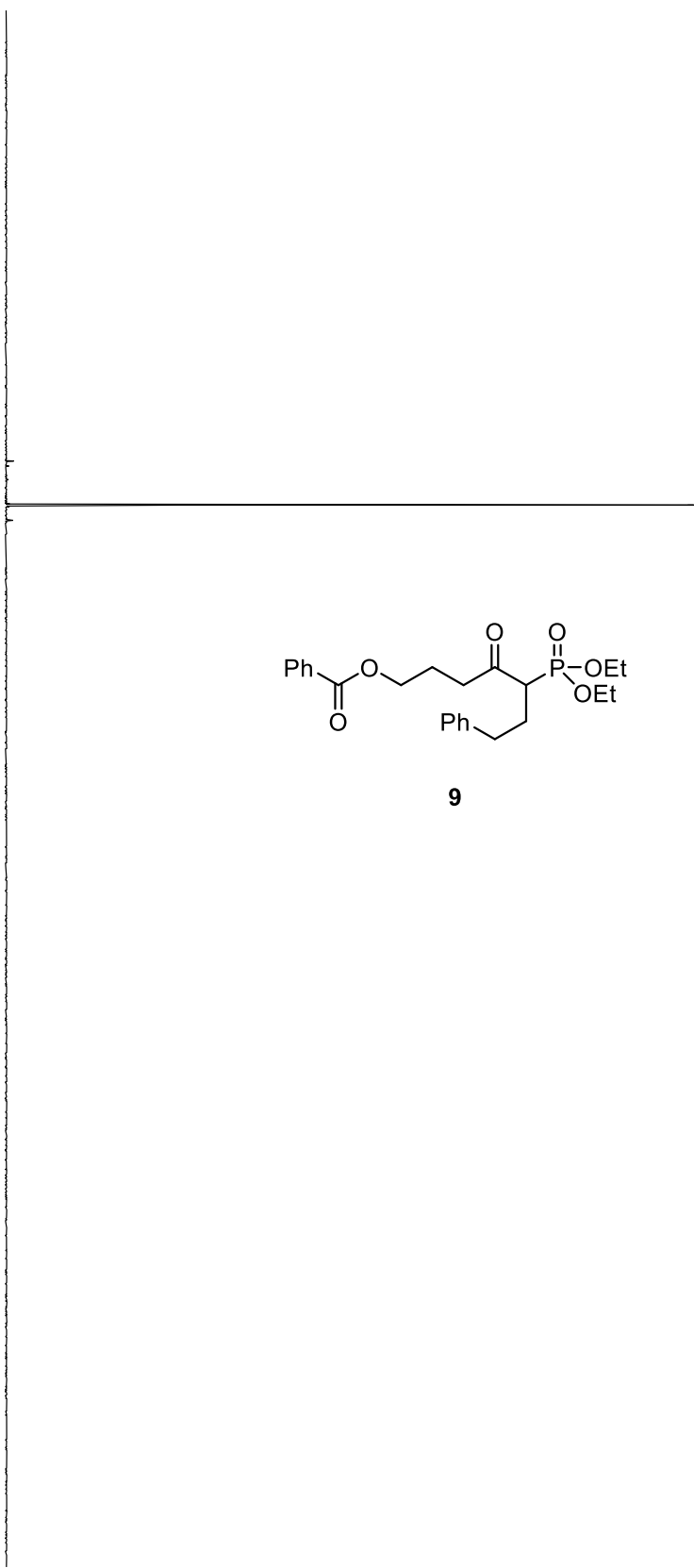




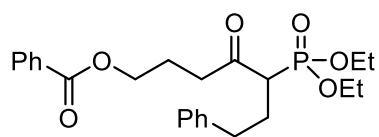


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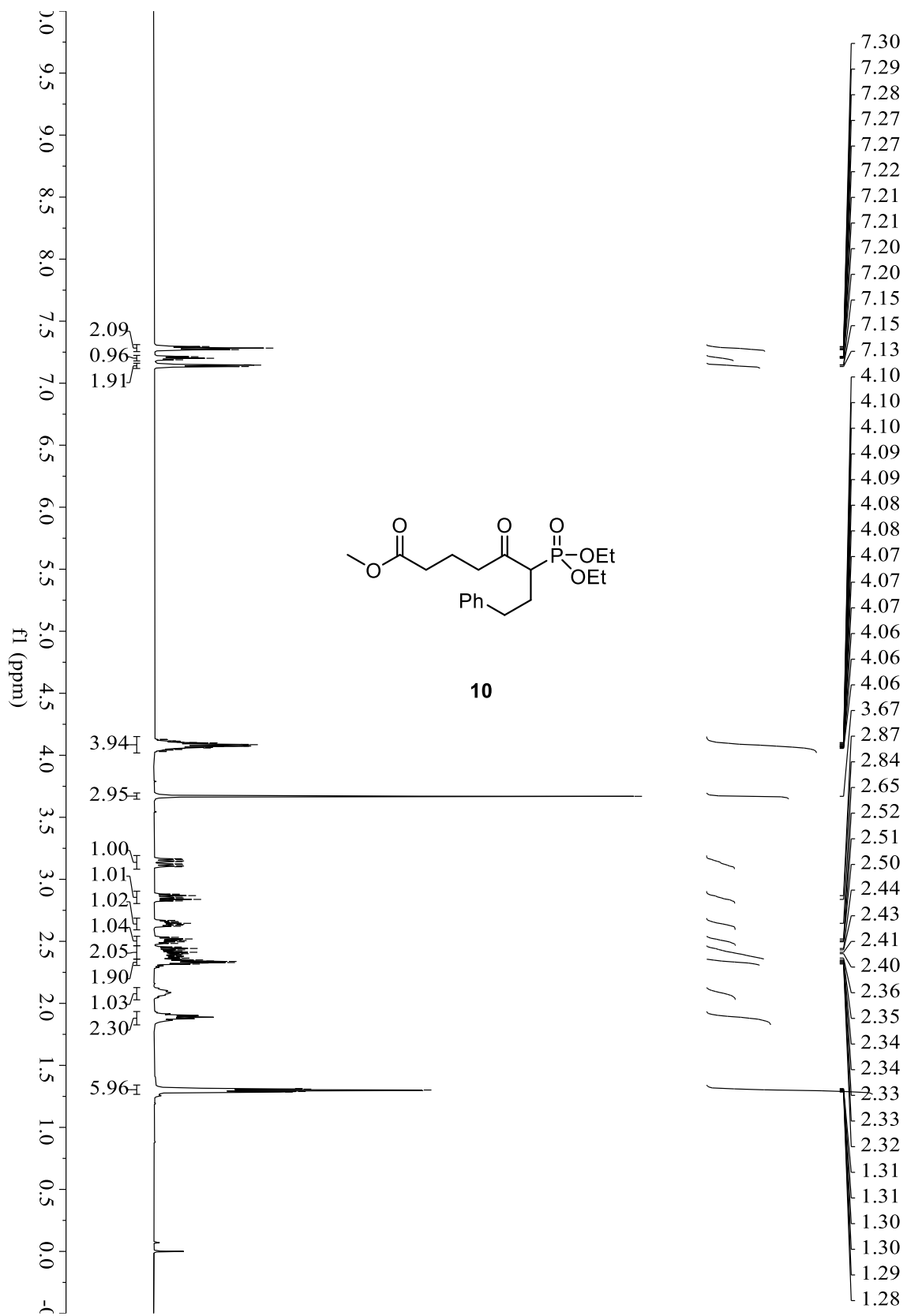
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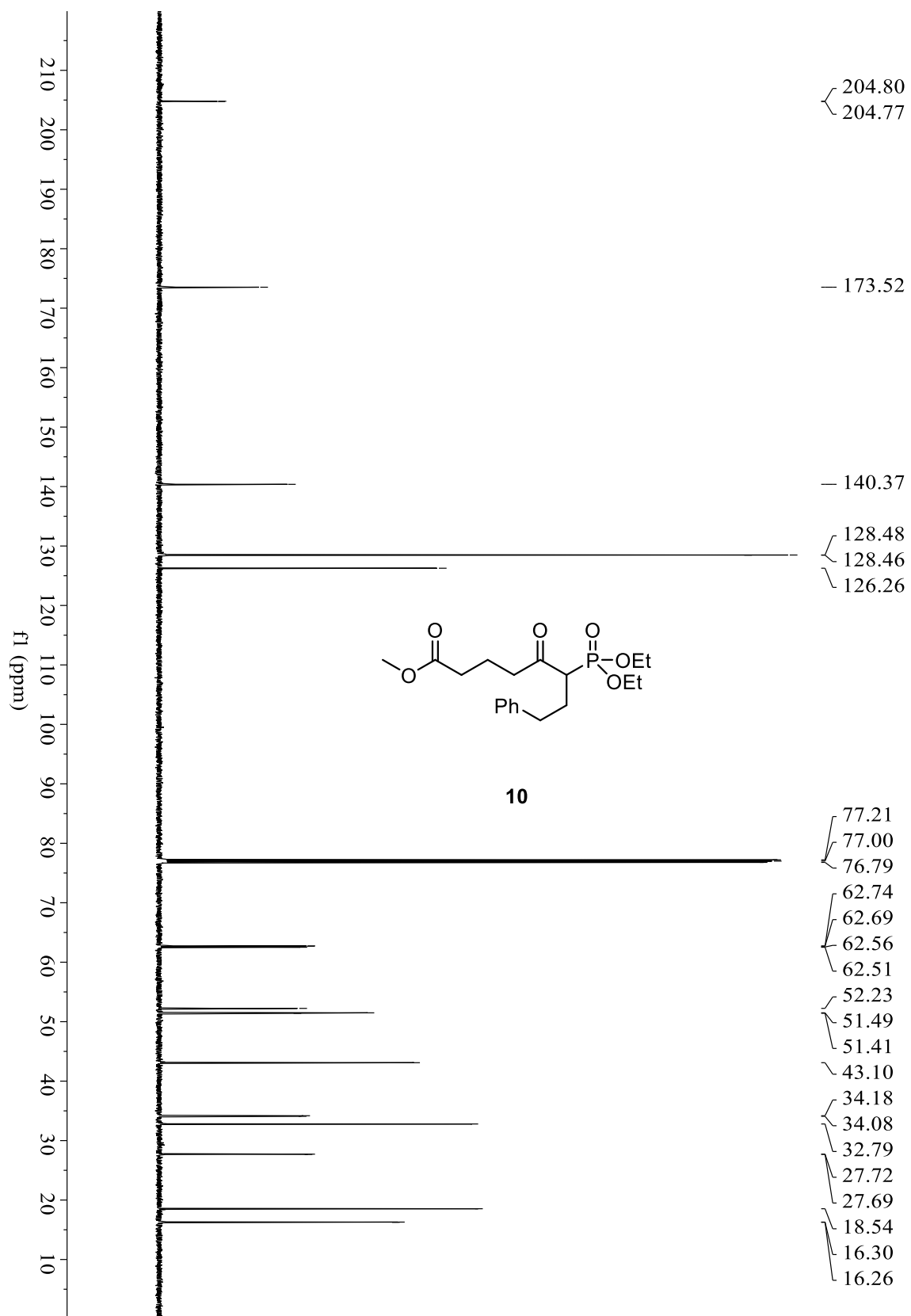


— 22.17



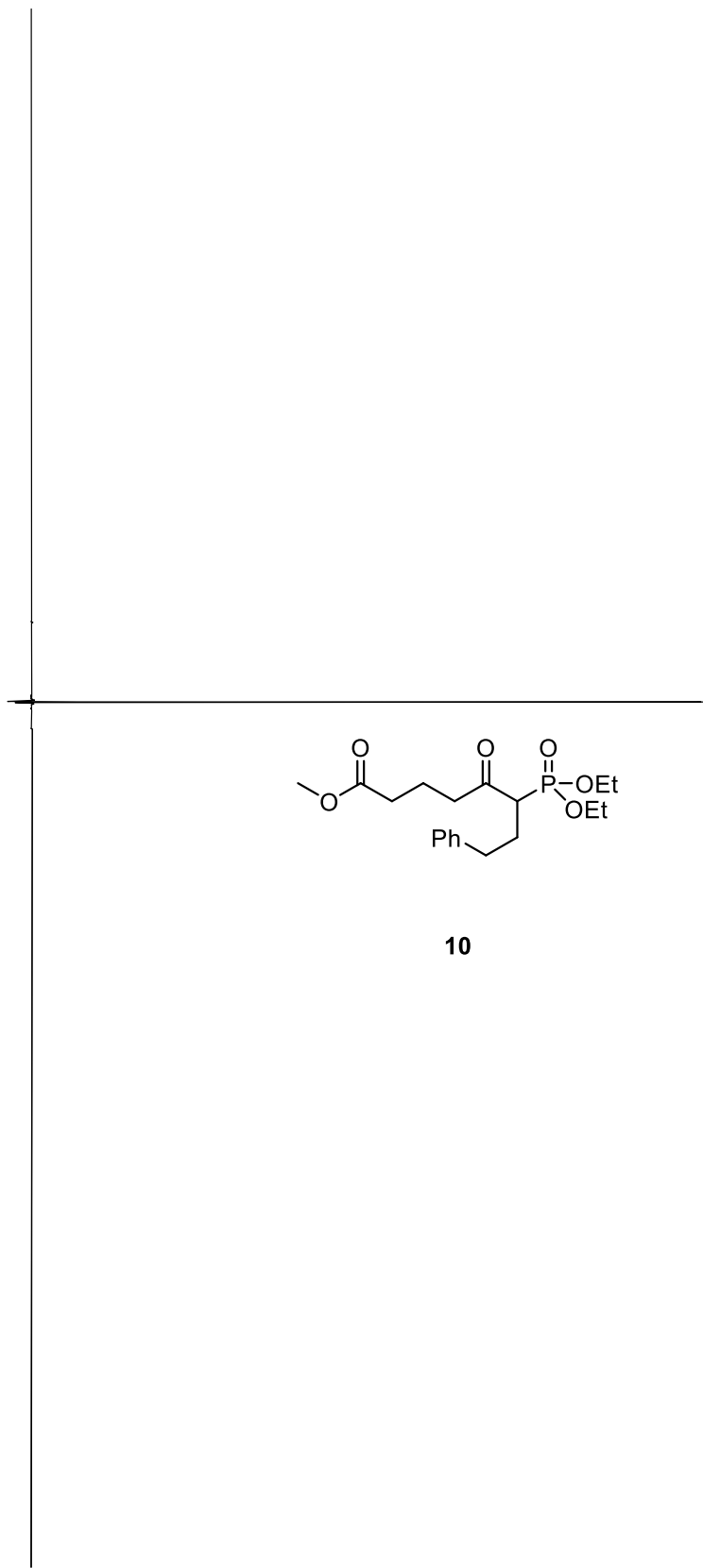
**9**



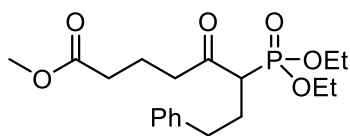


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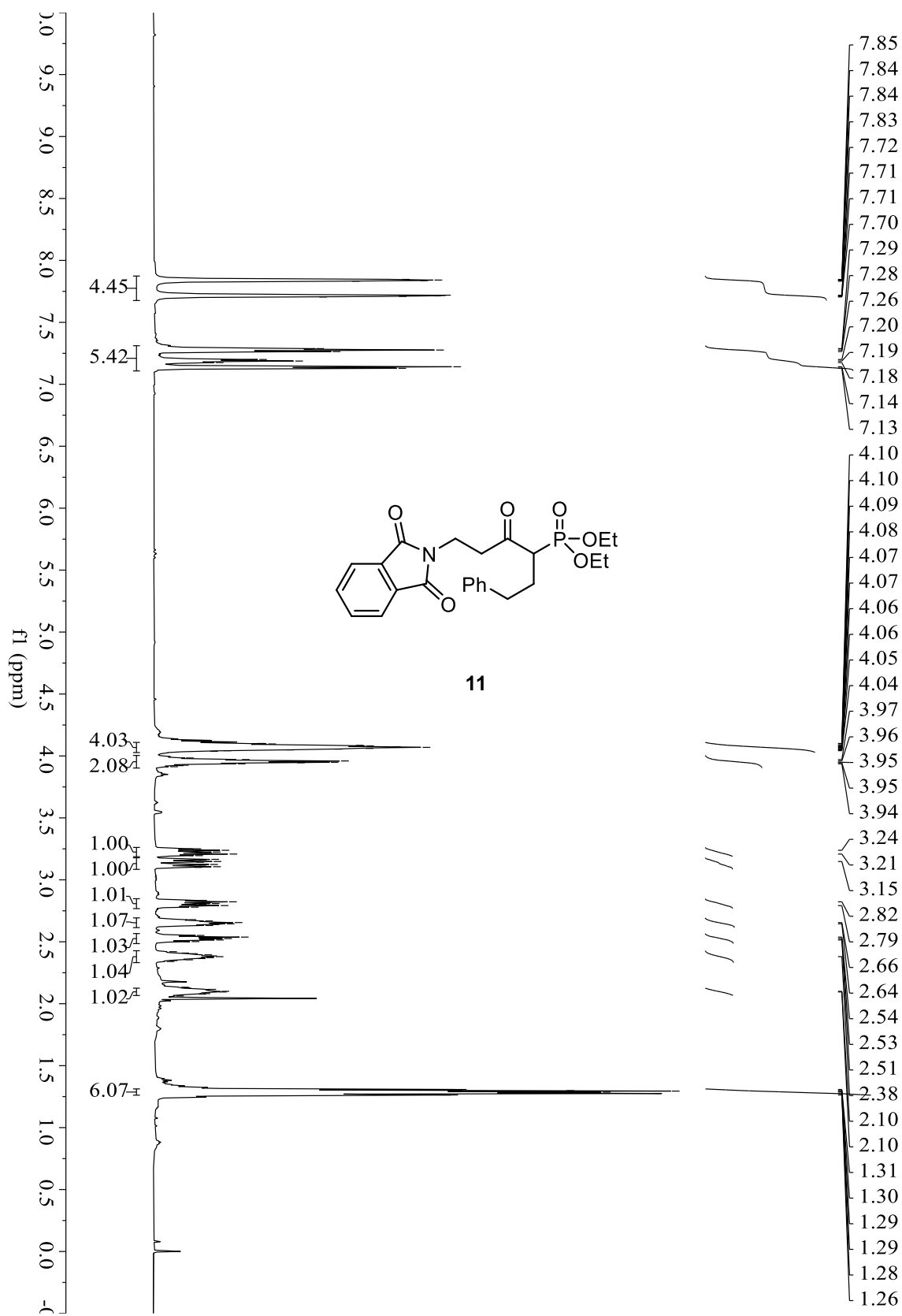
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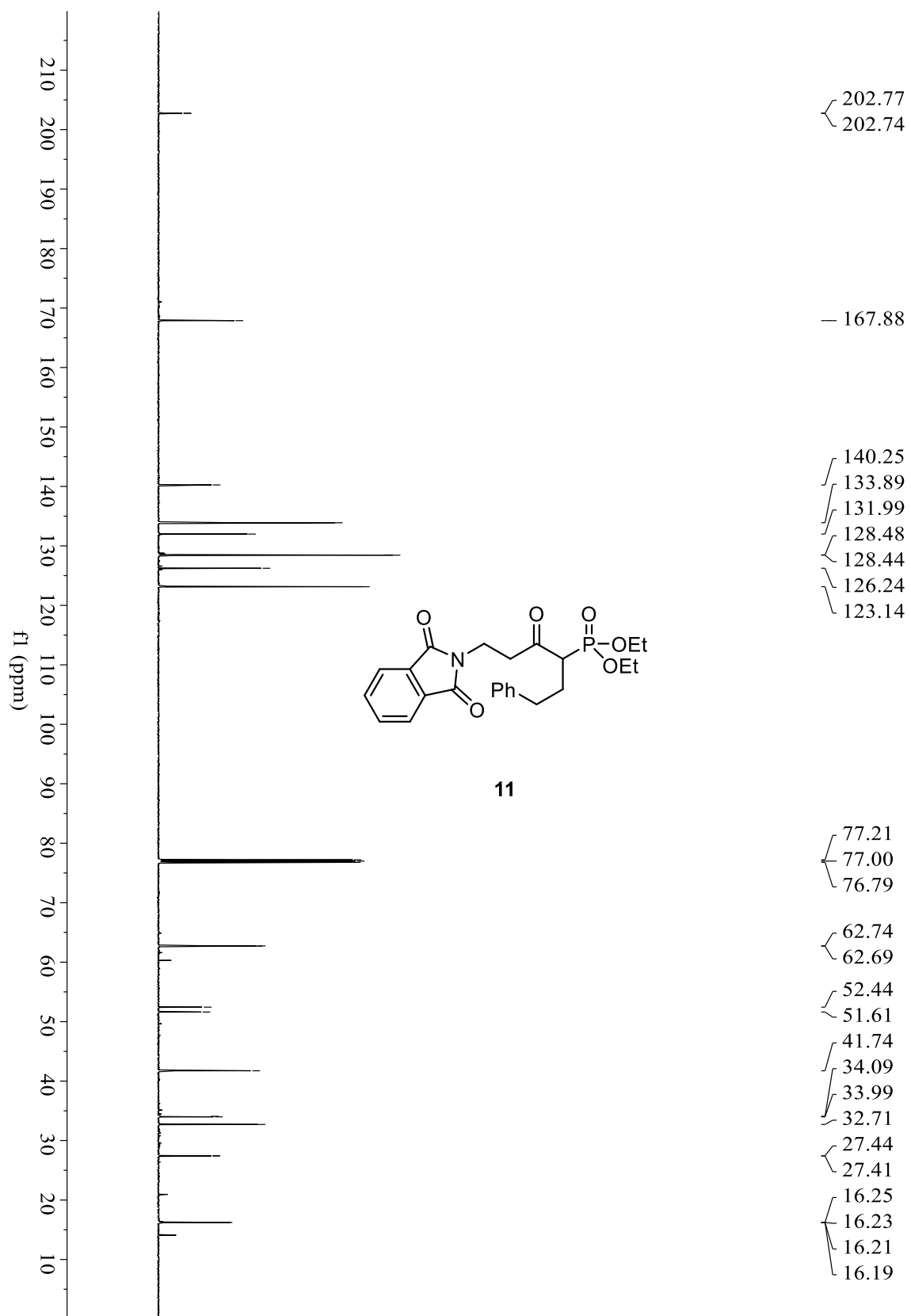


— 22.16



**10**

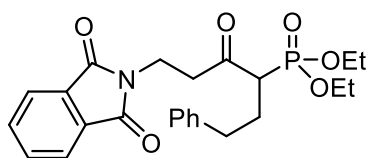
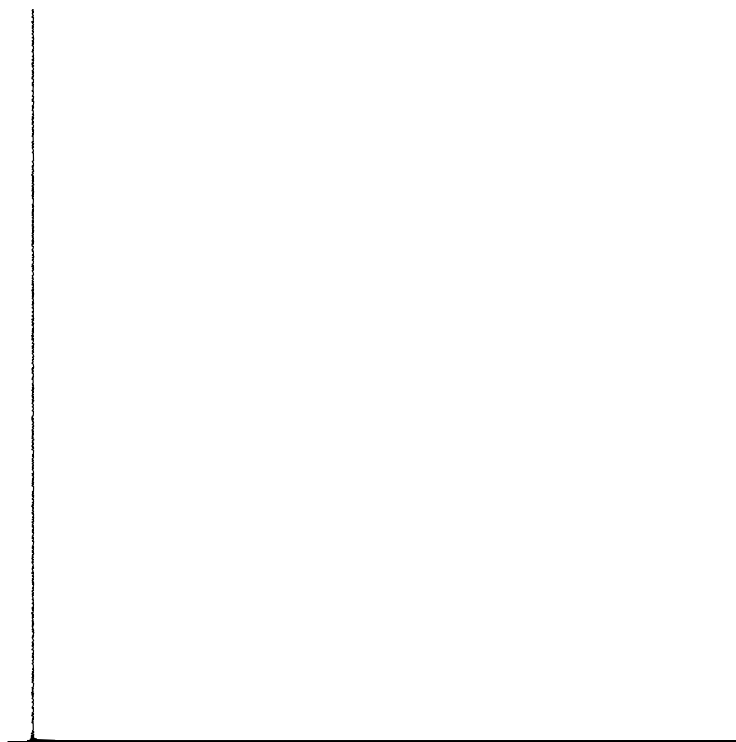




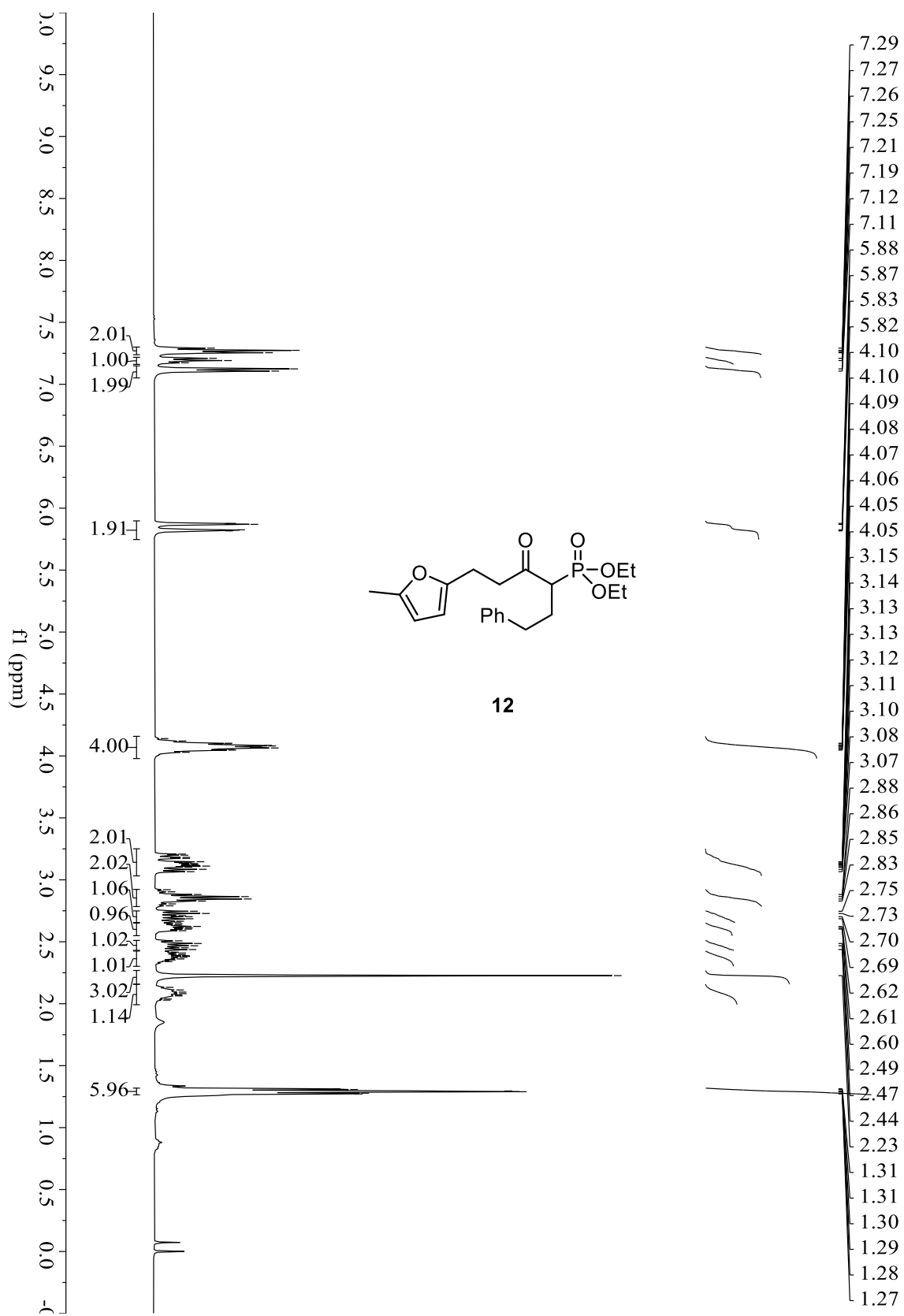


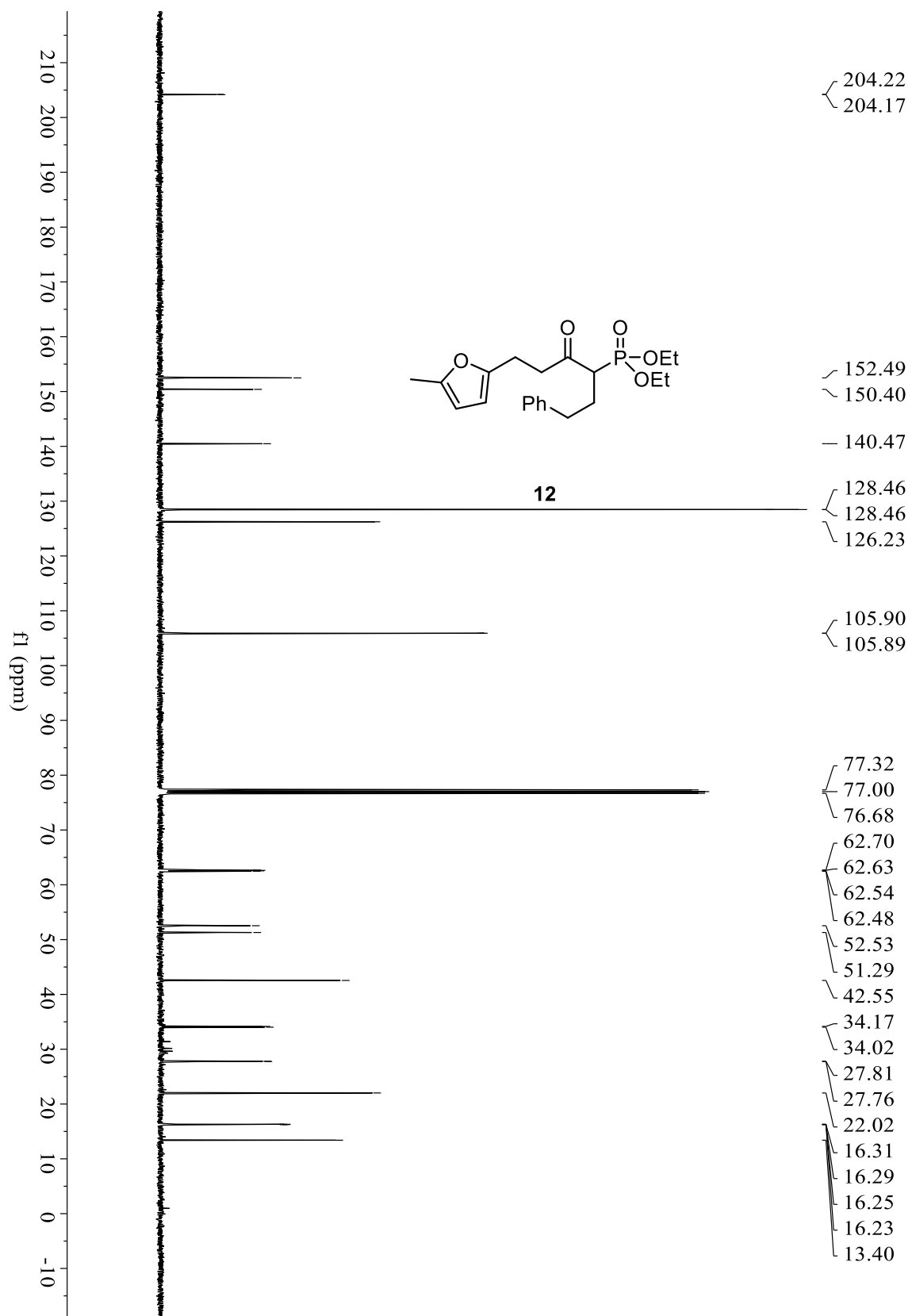
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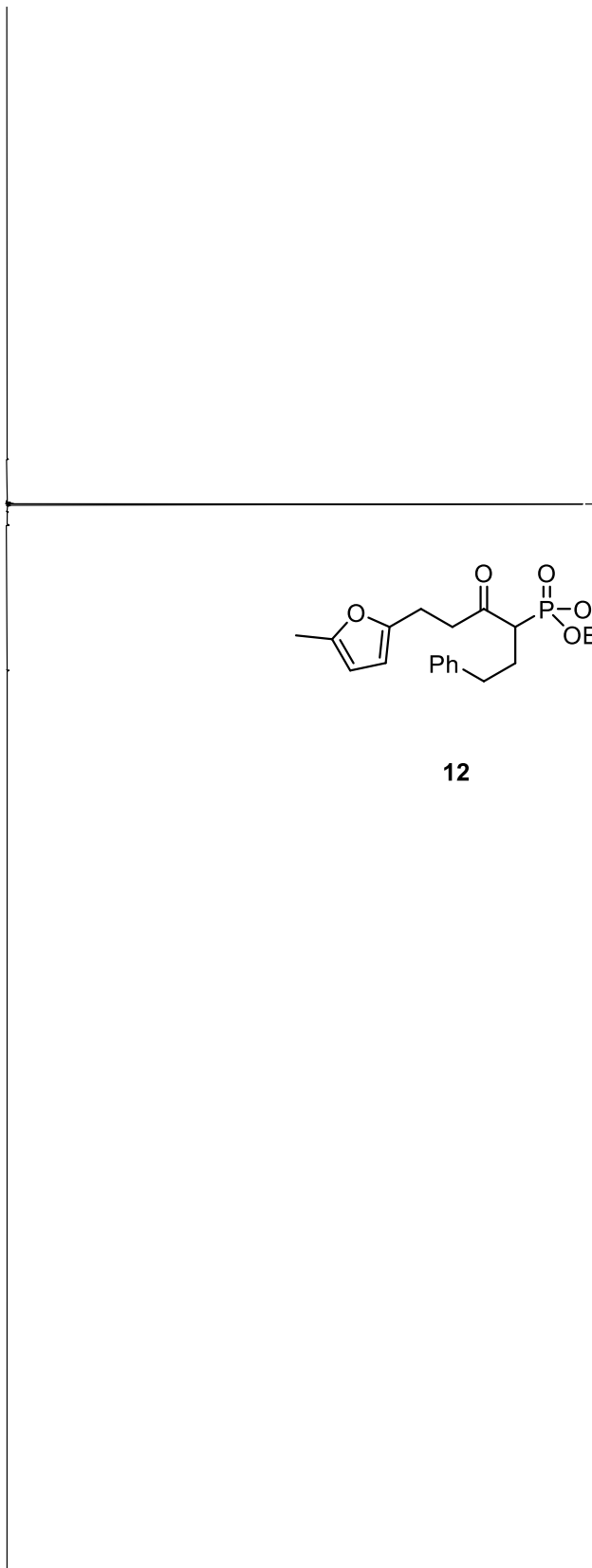
11



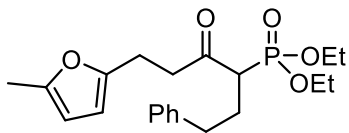


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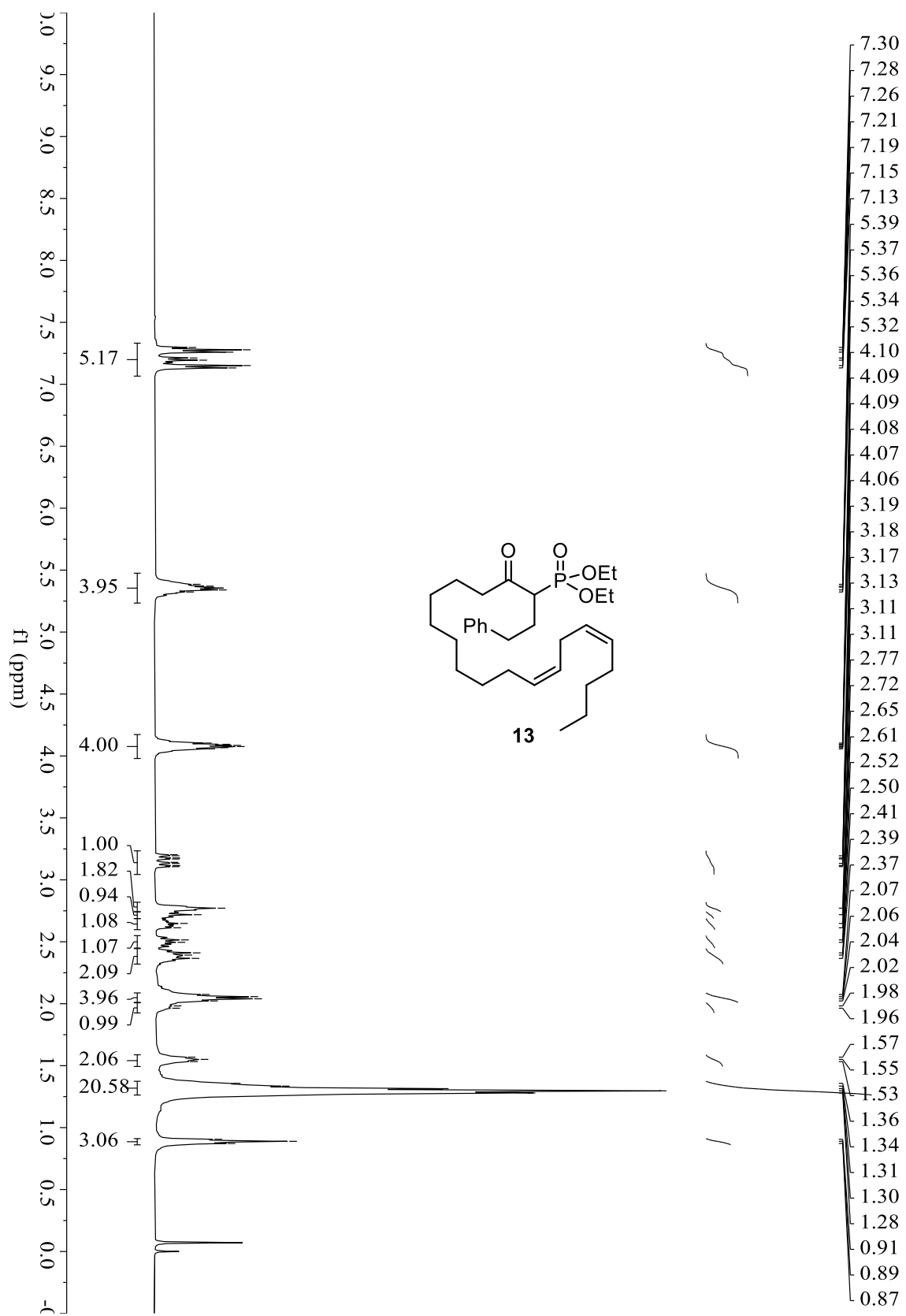
f1 (ppm)

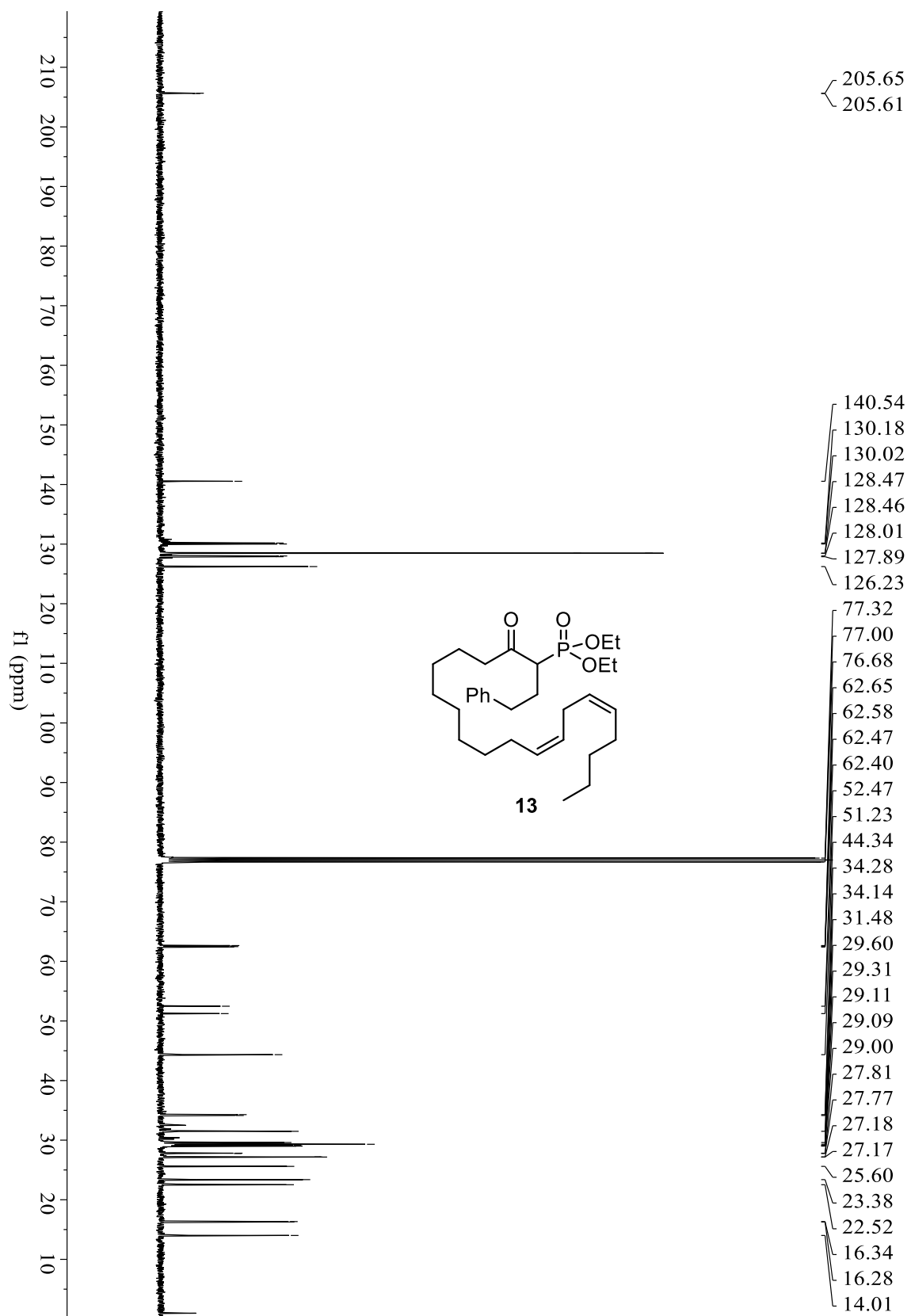


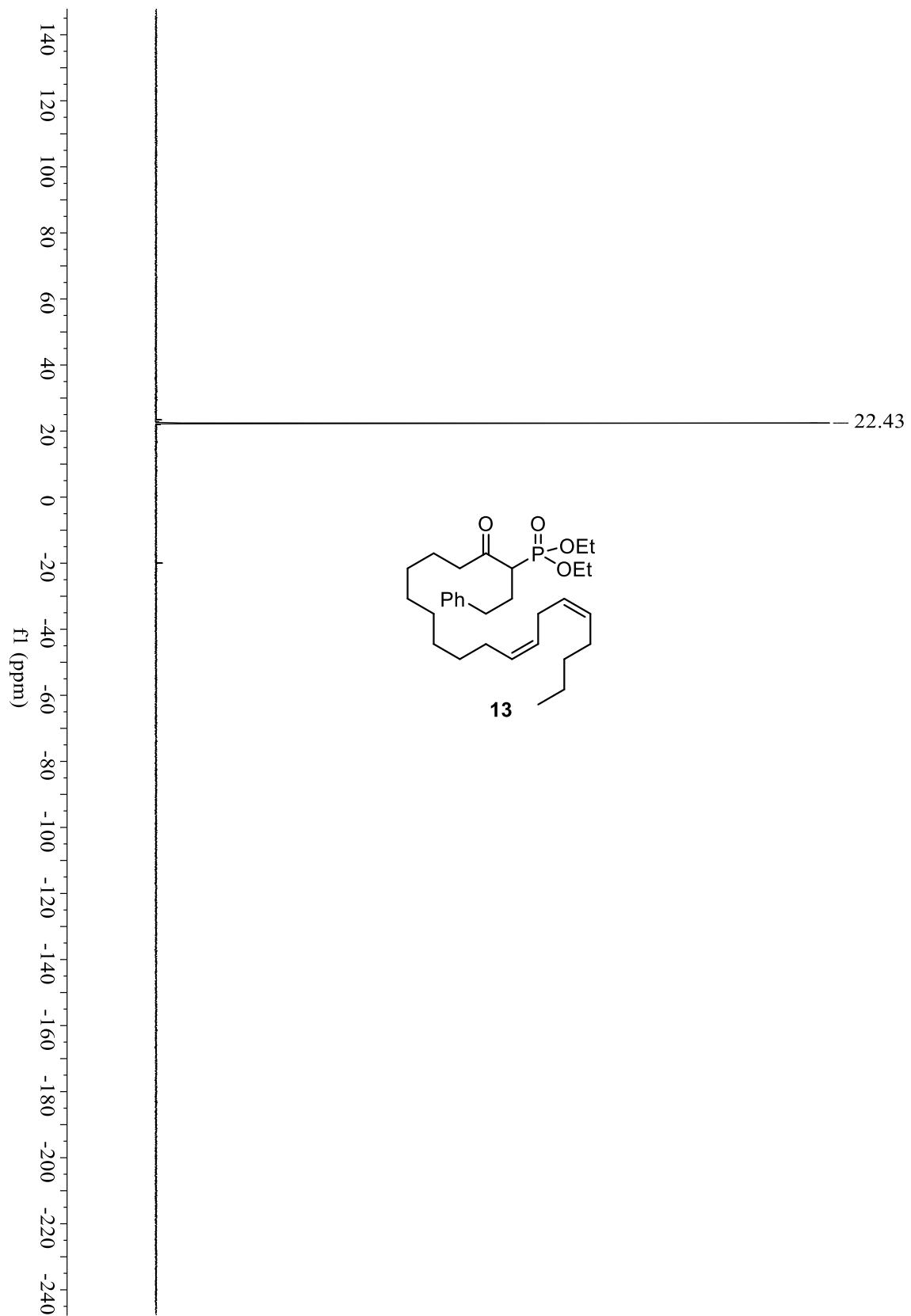
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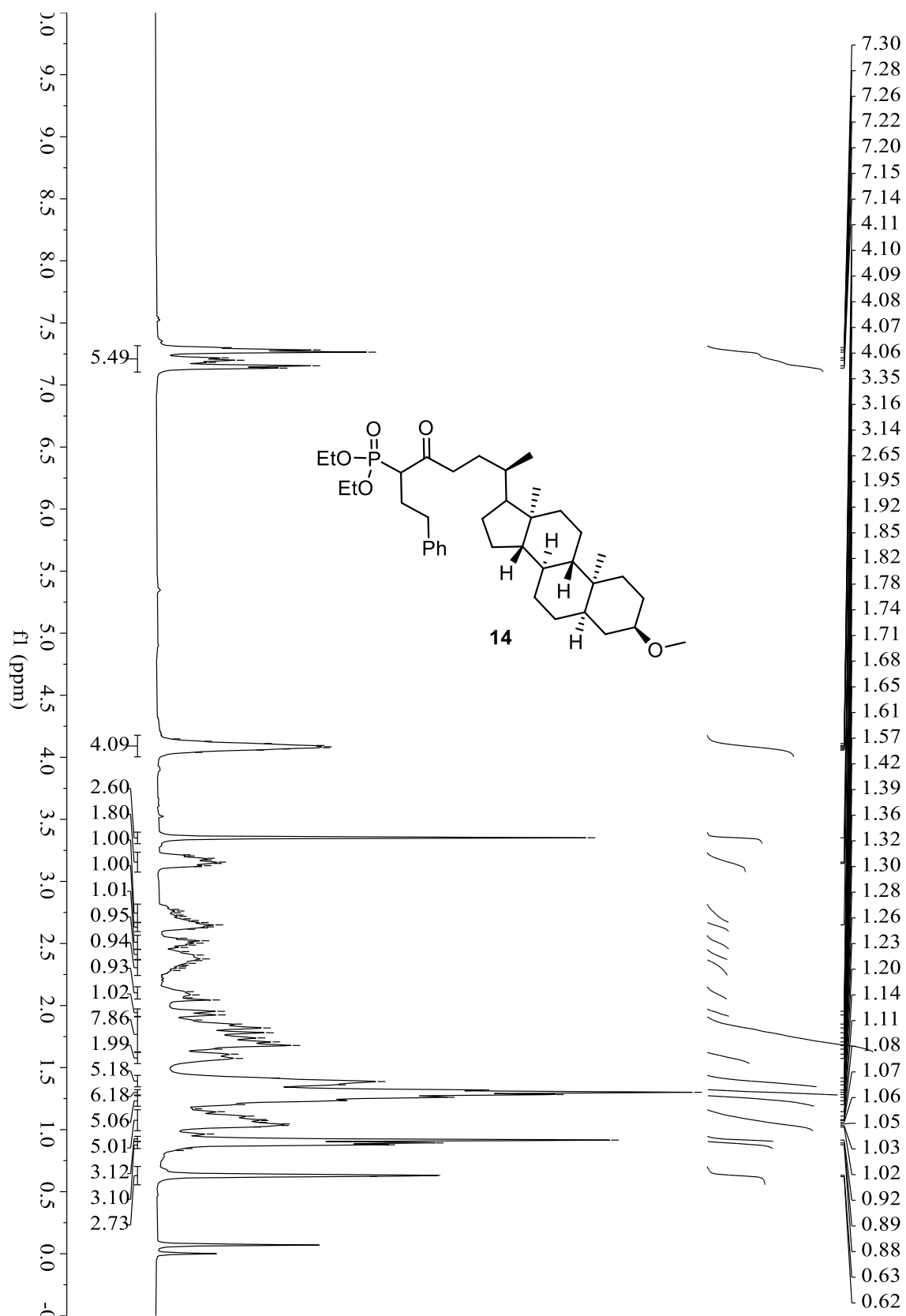


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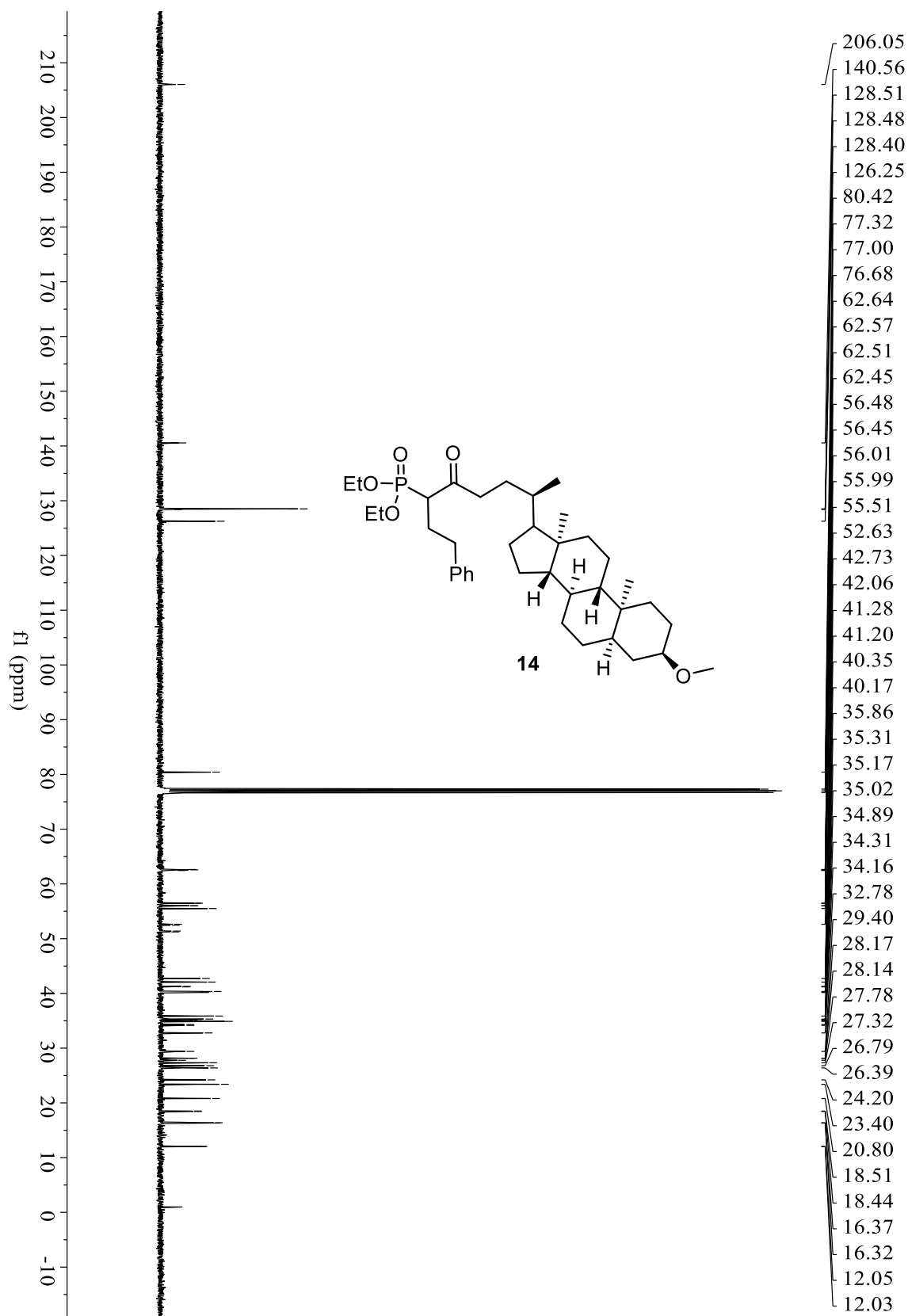


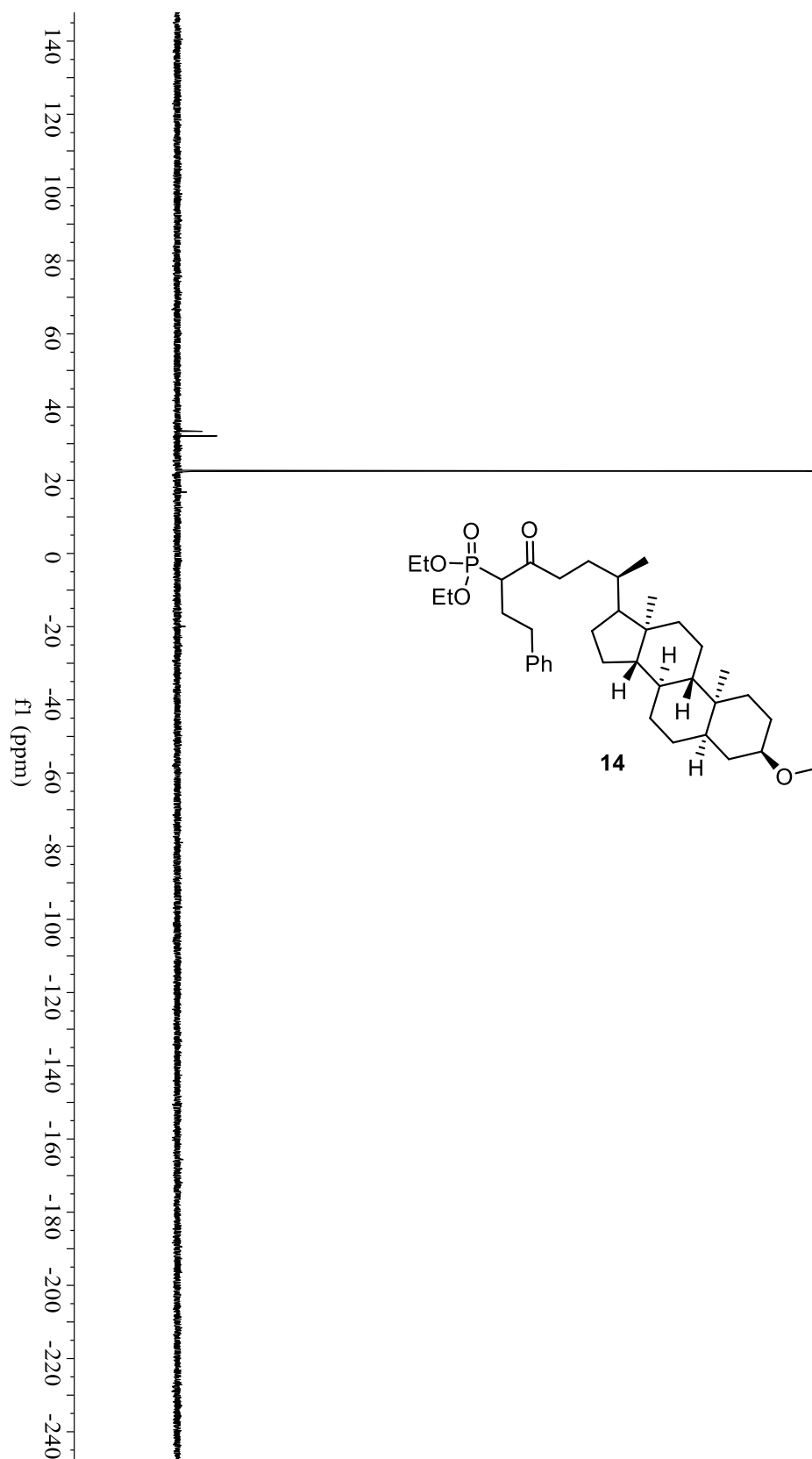




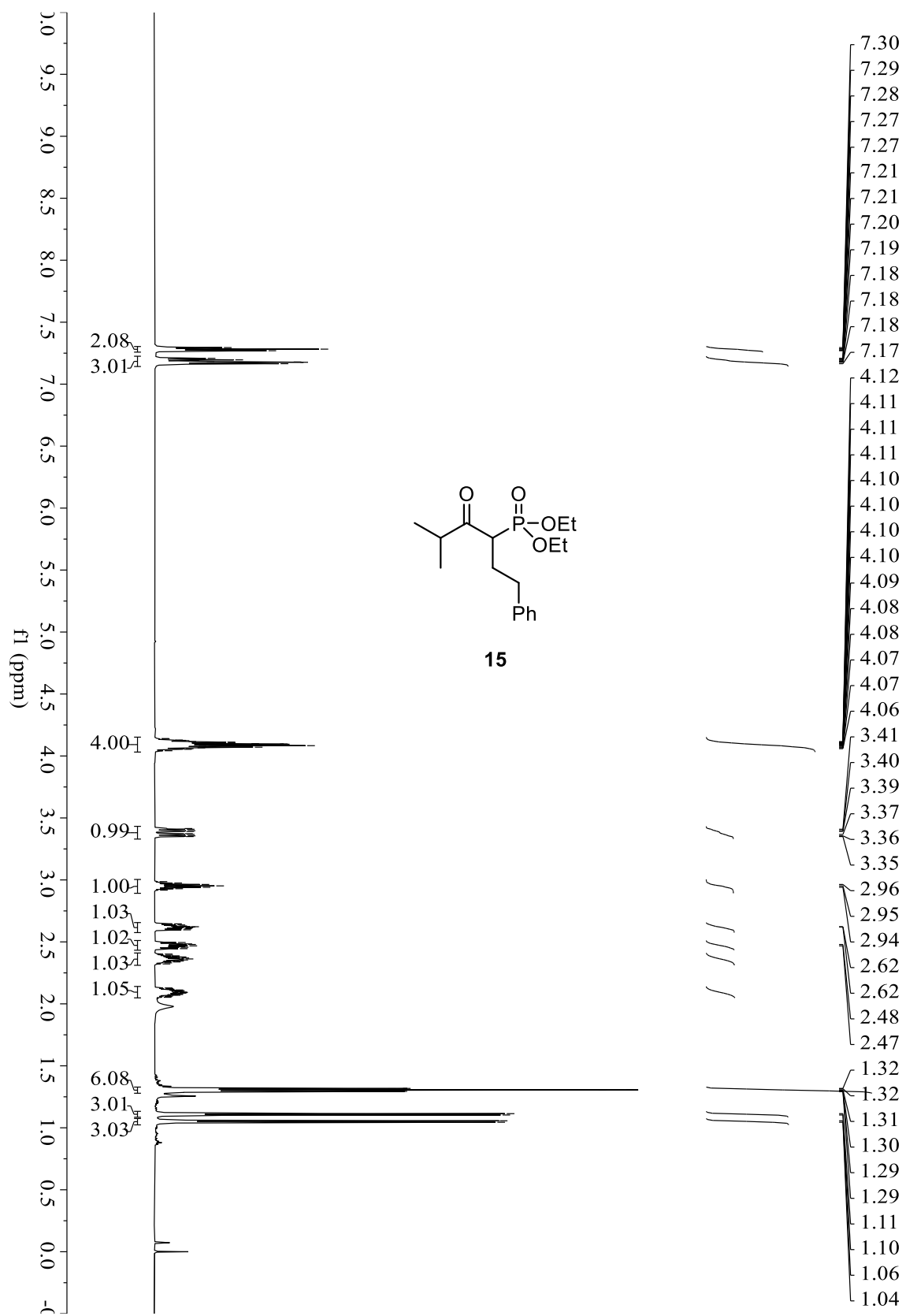


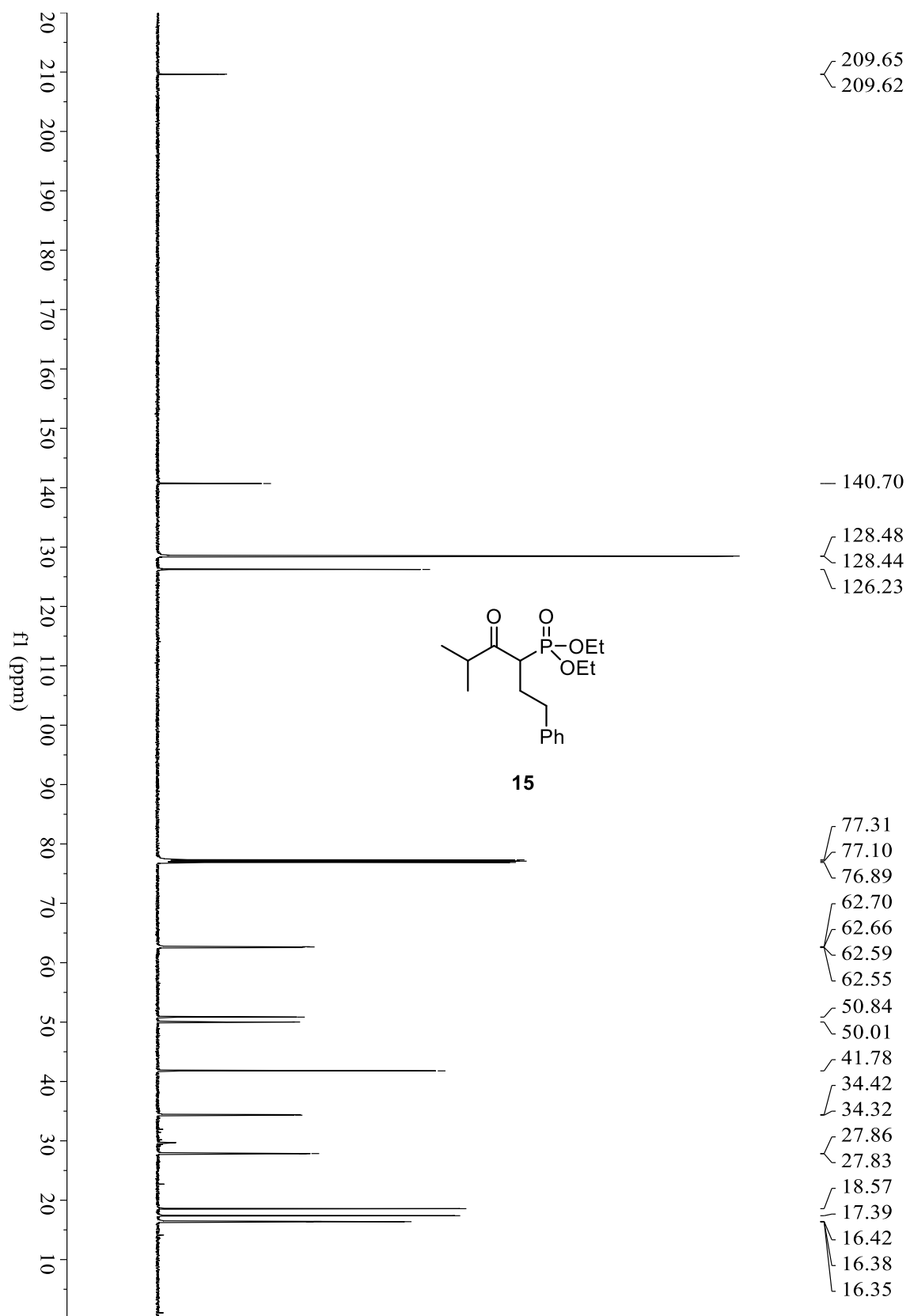




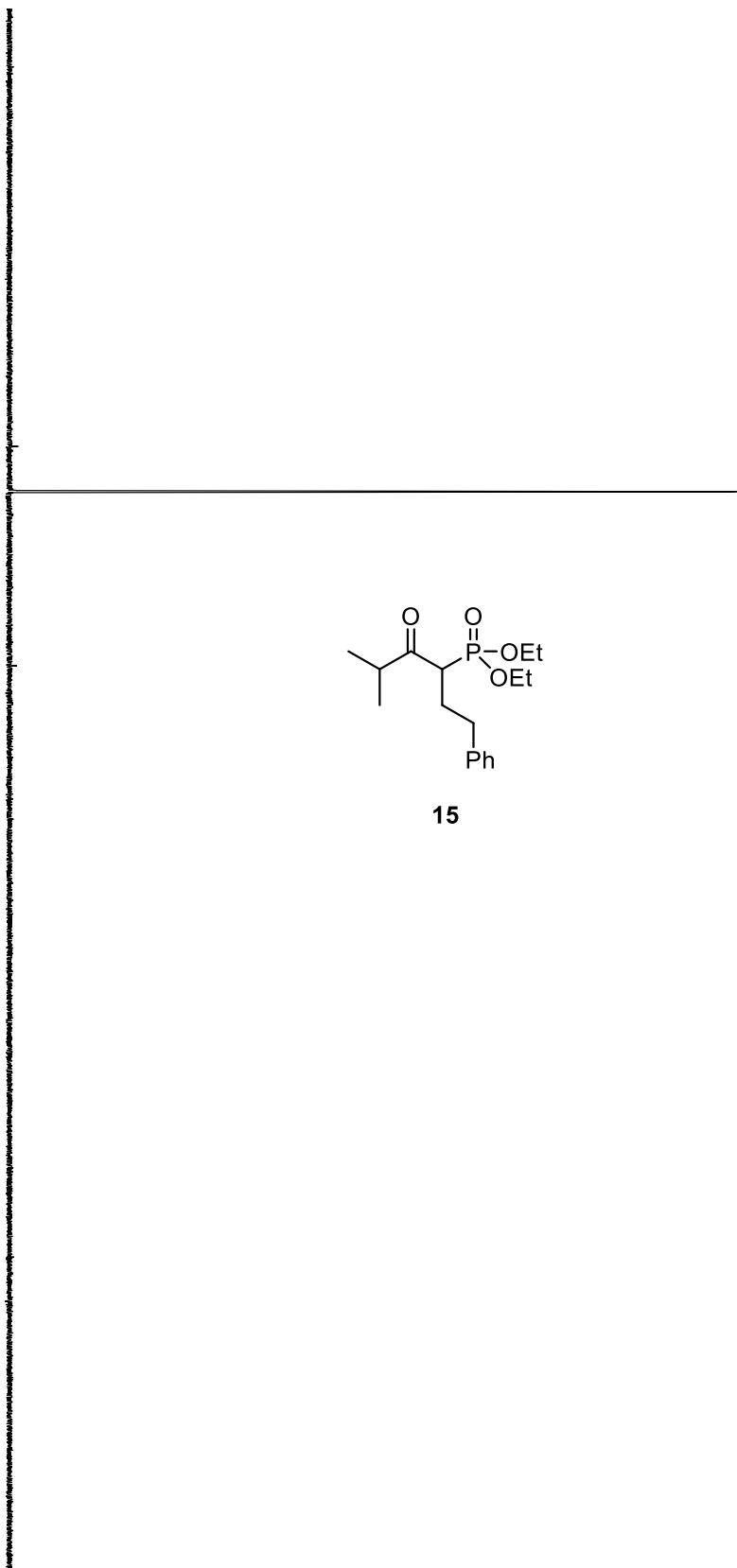


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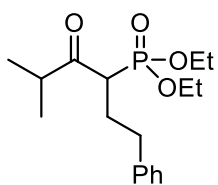




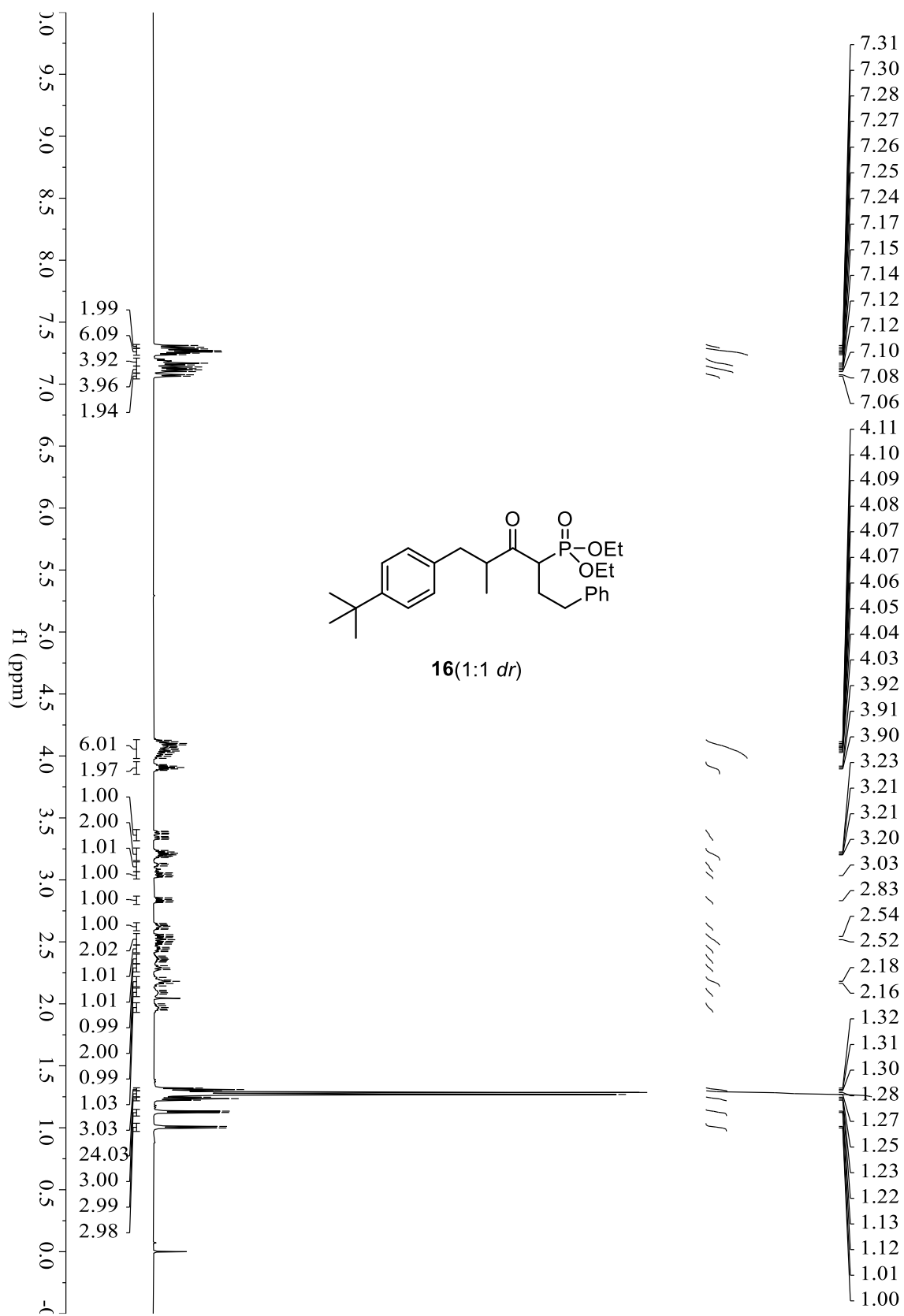
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f1 (ppm)

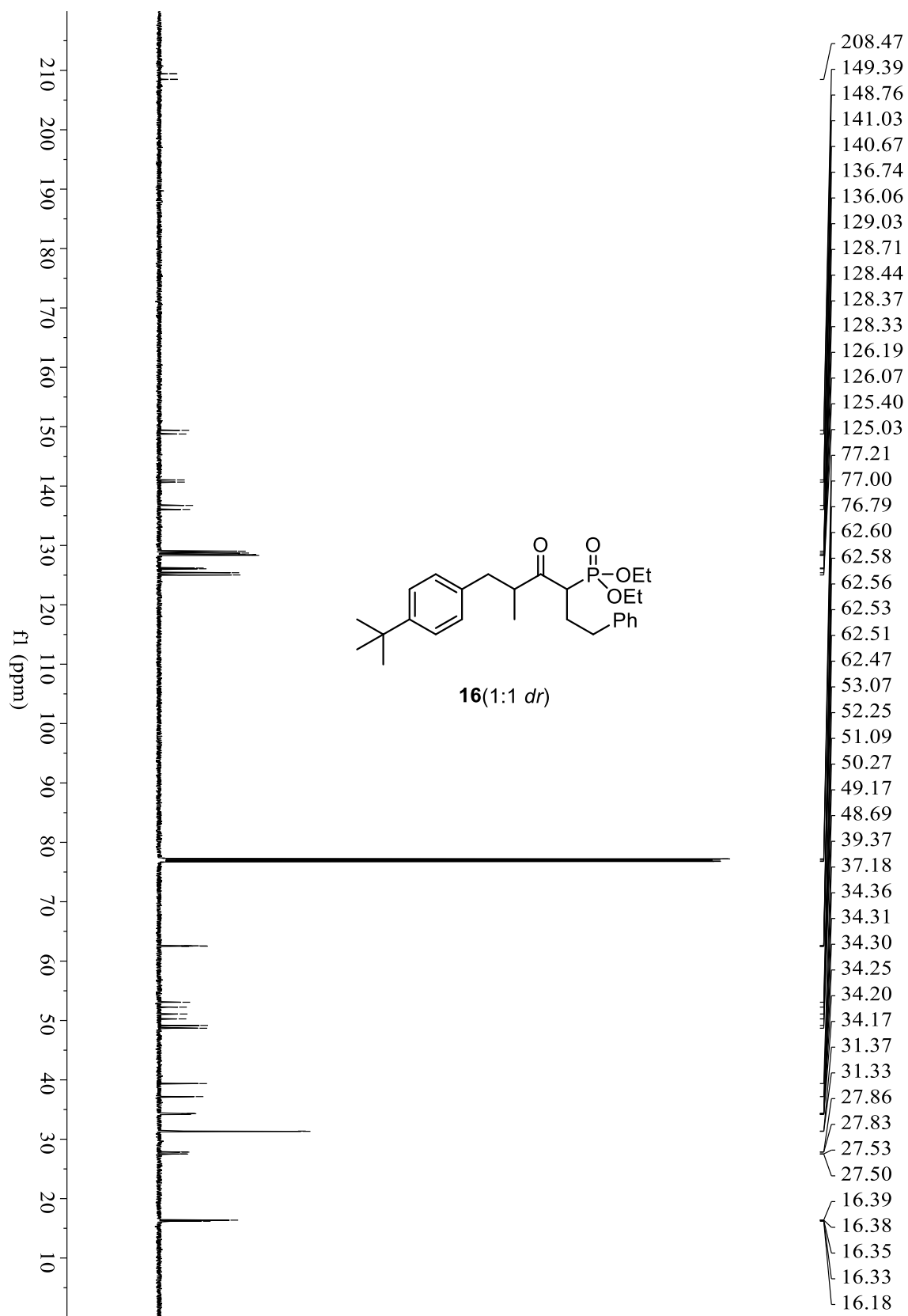


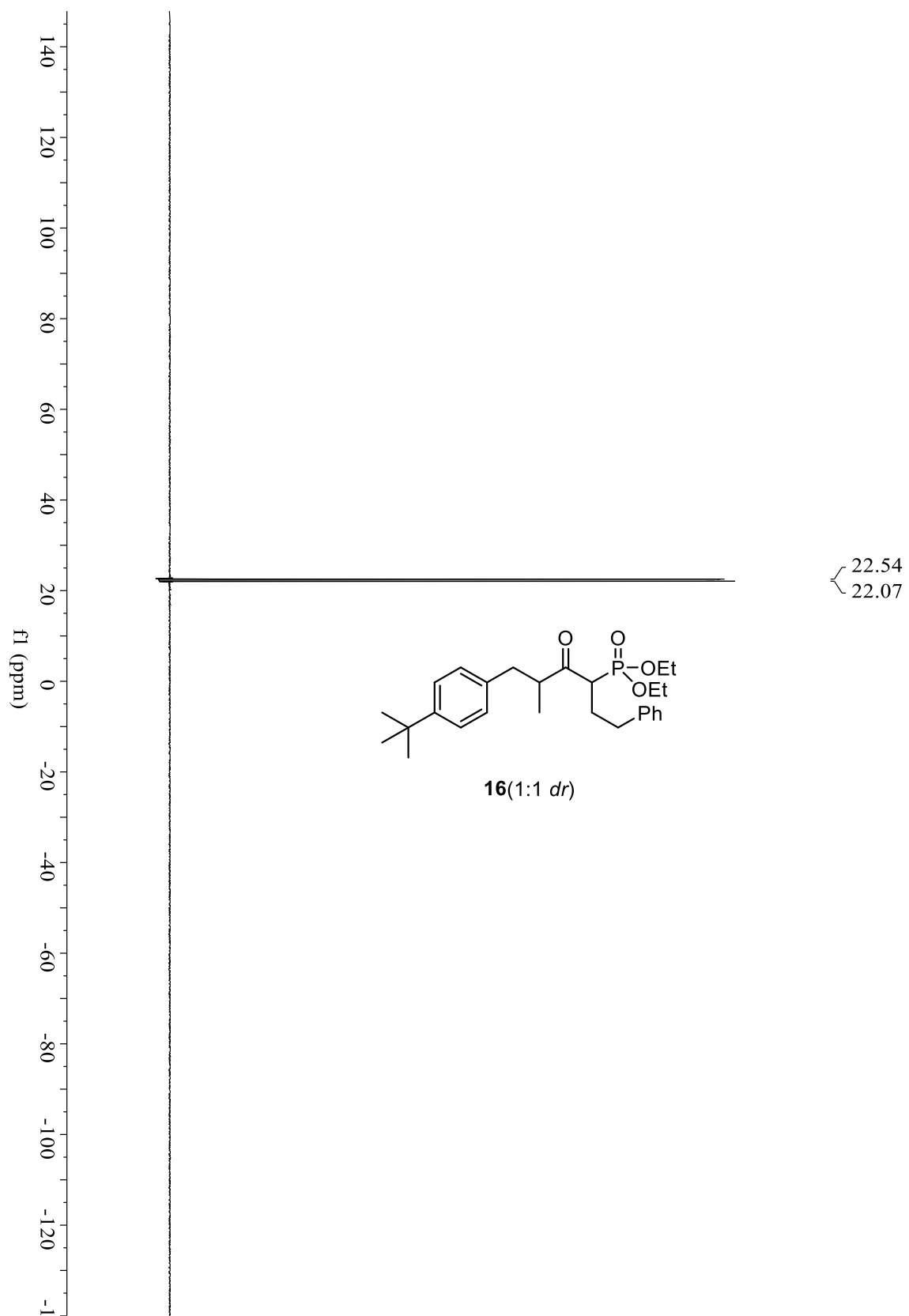
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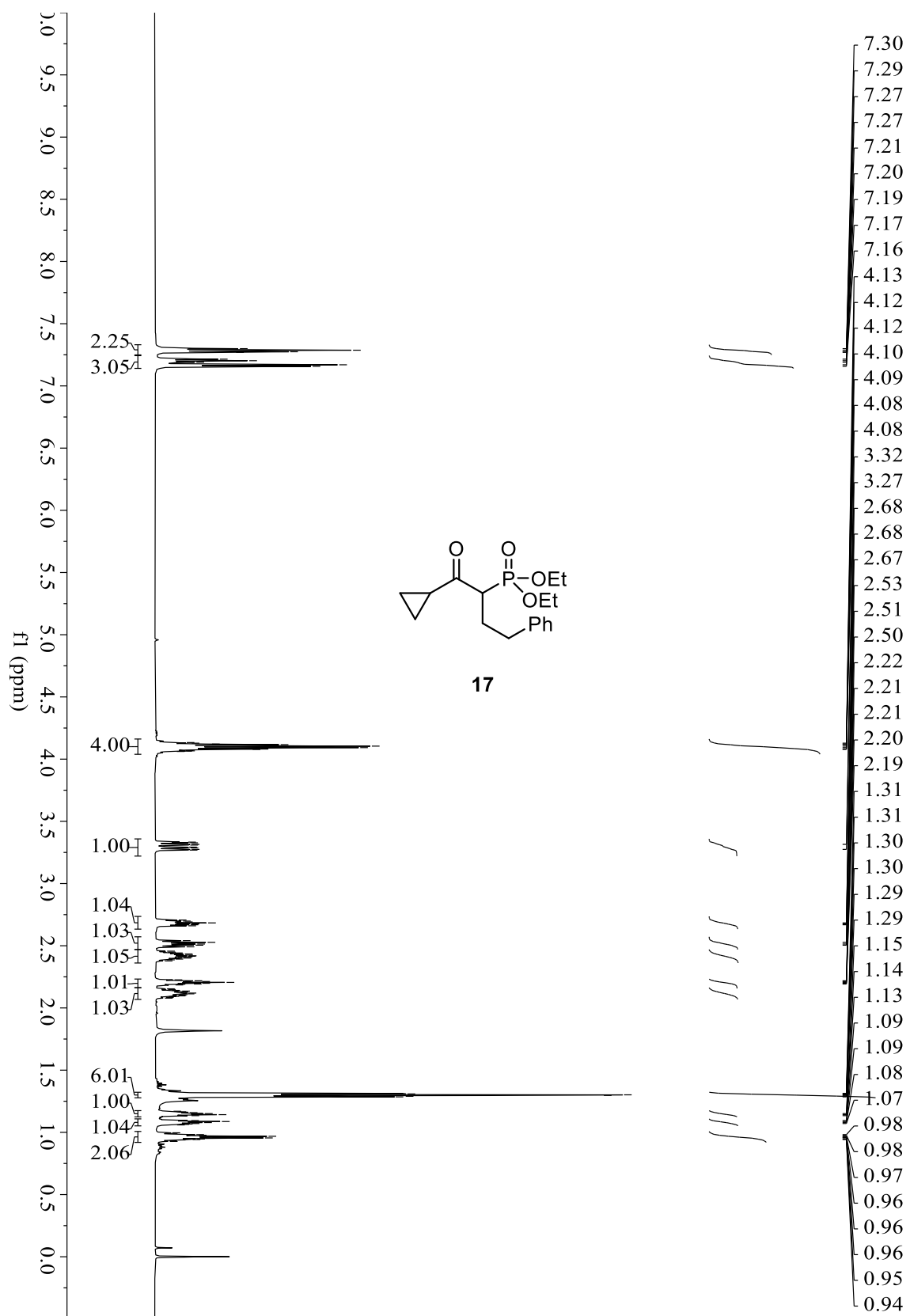
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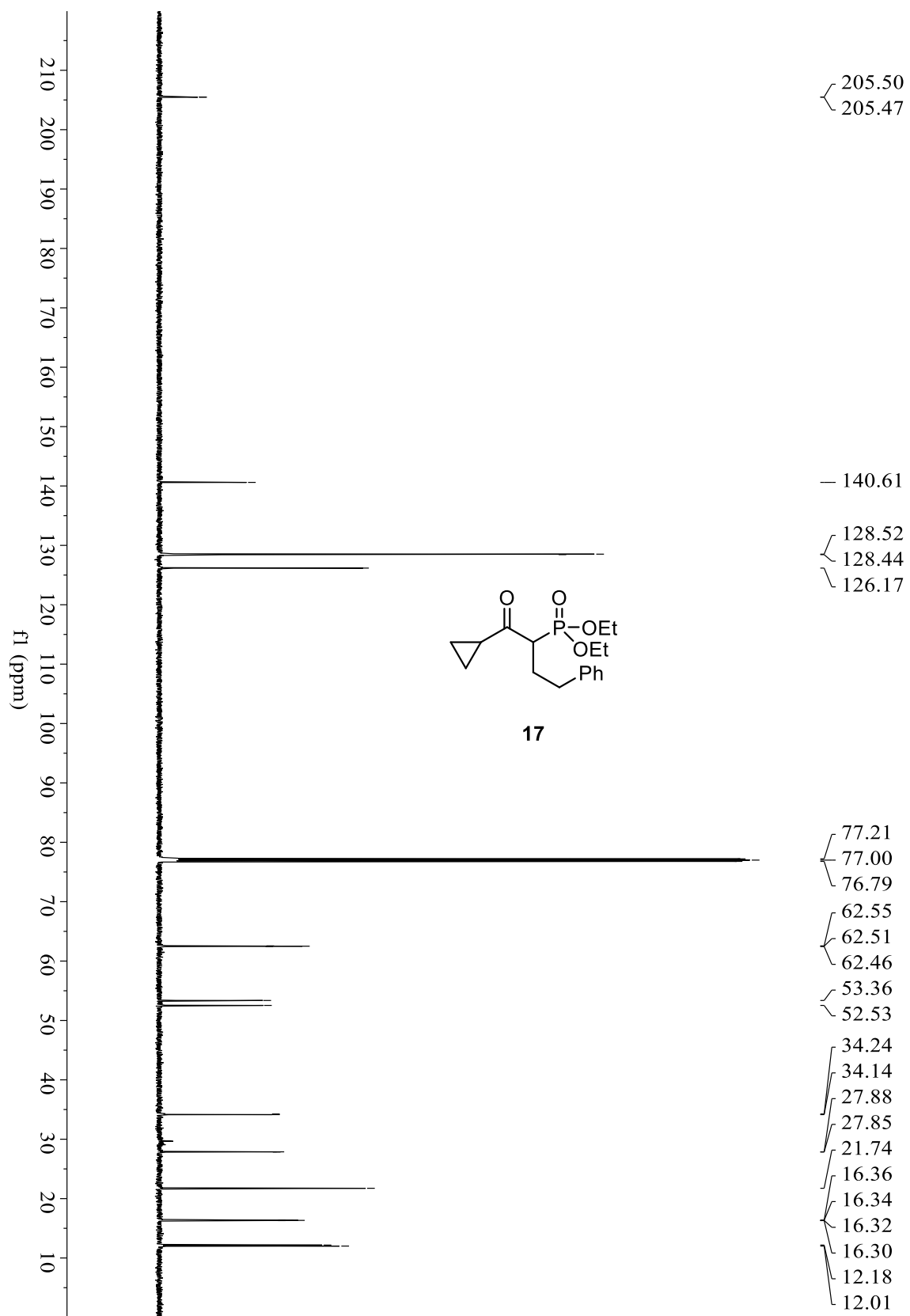


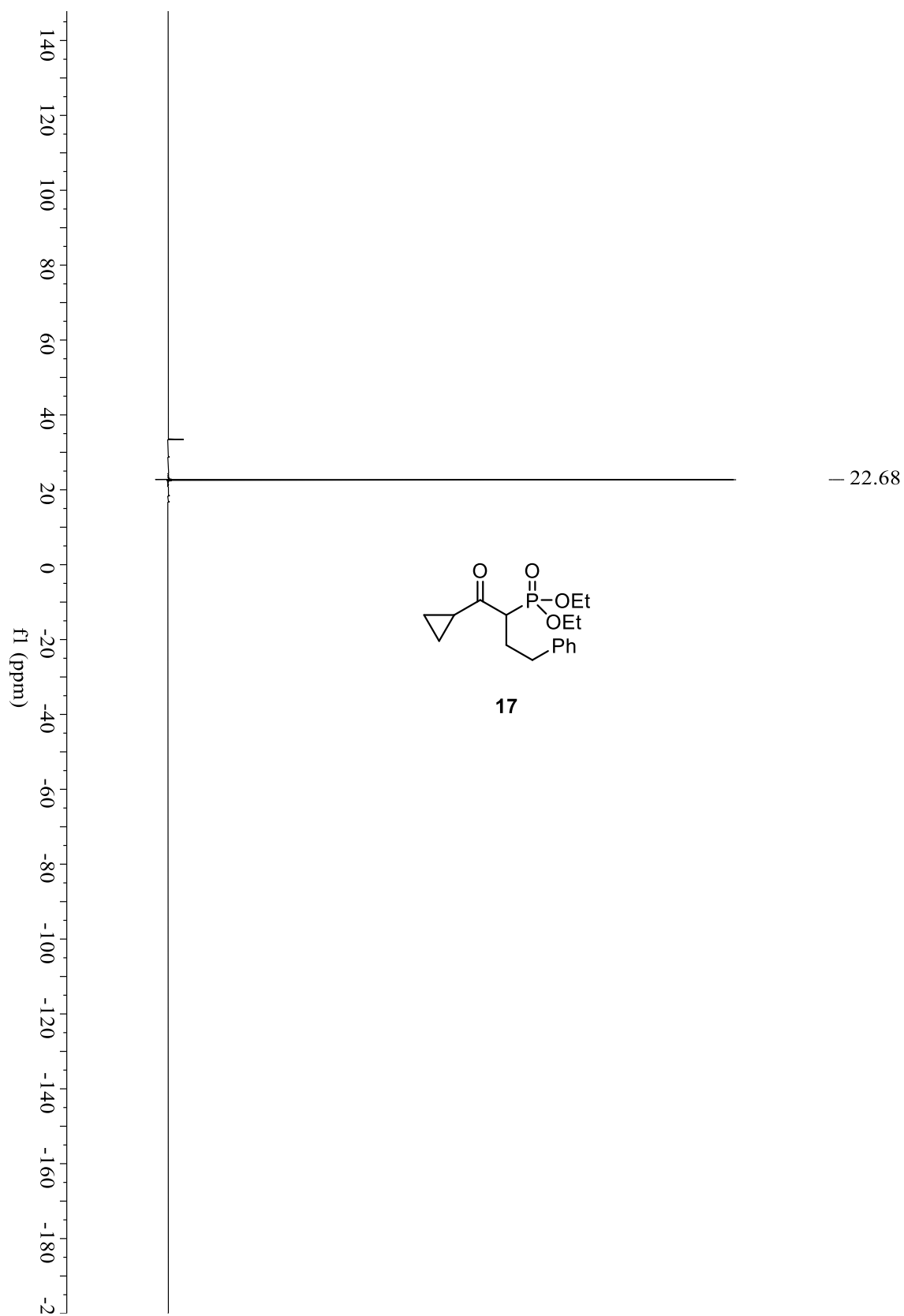


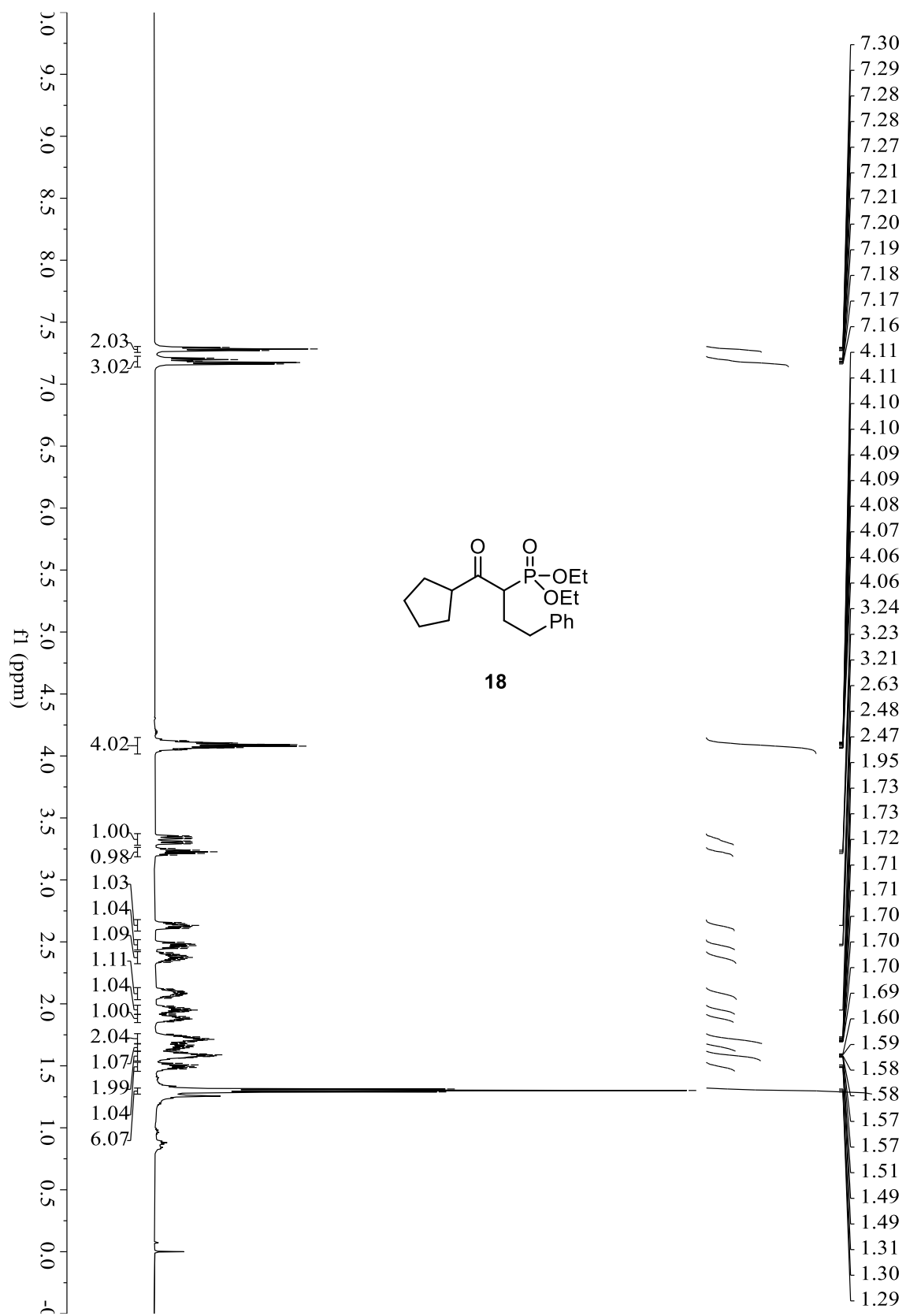


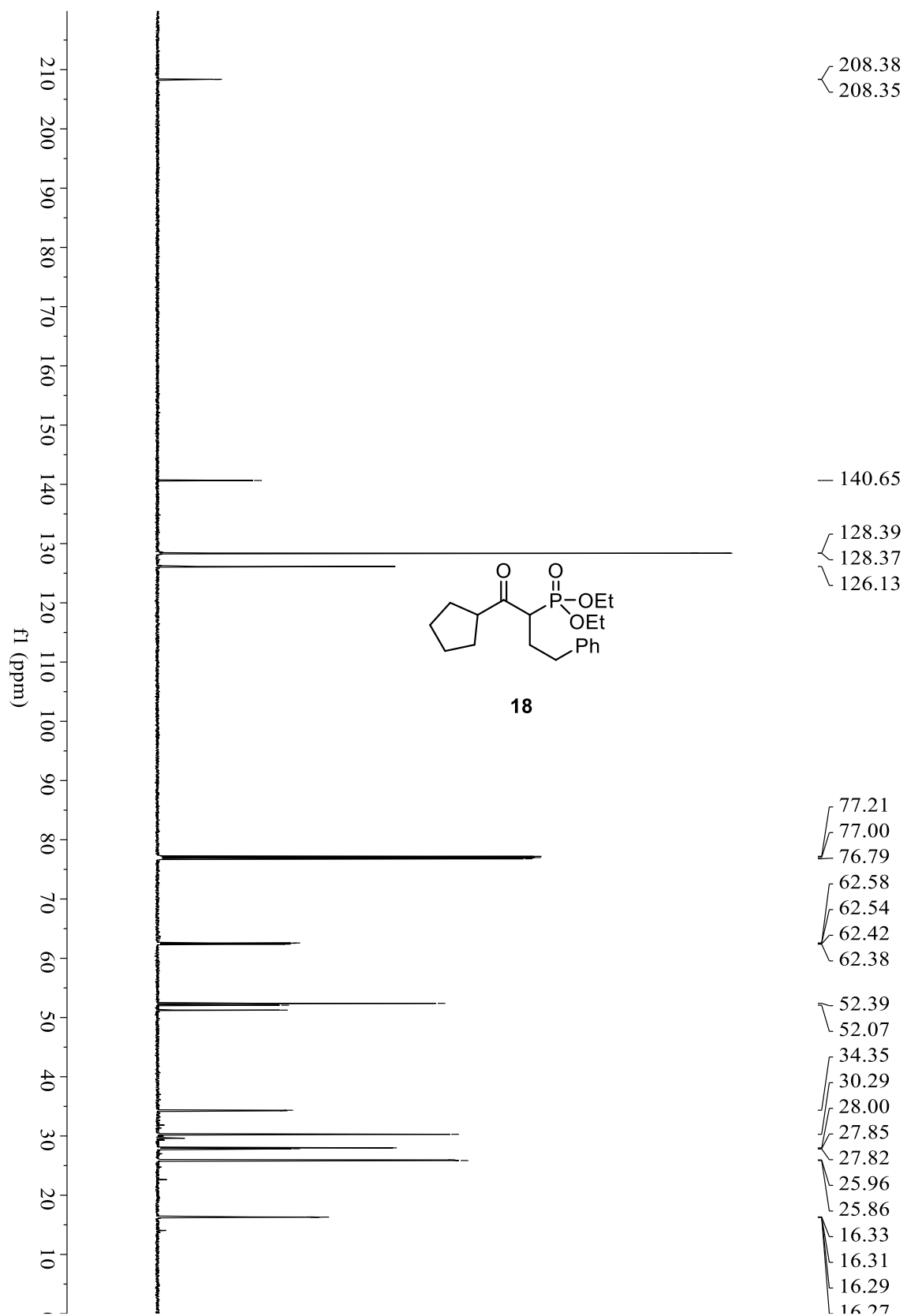




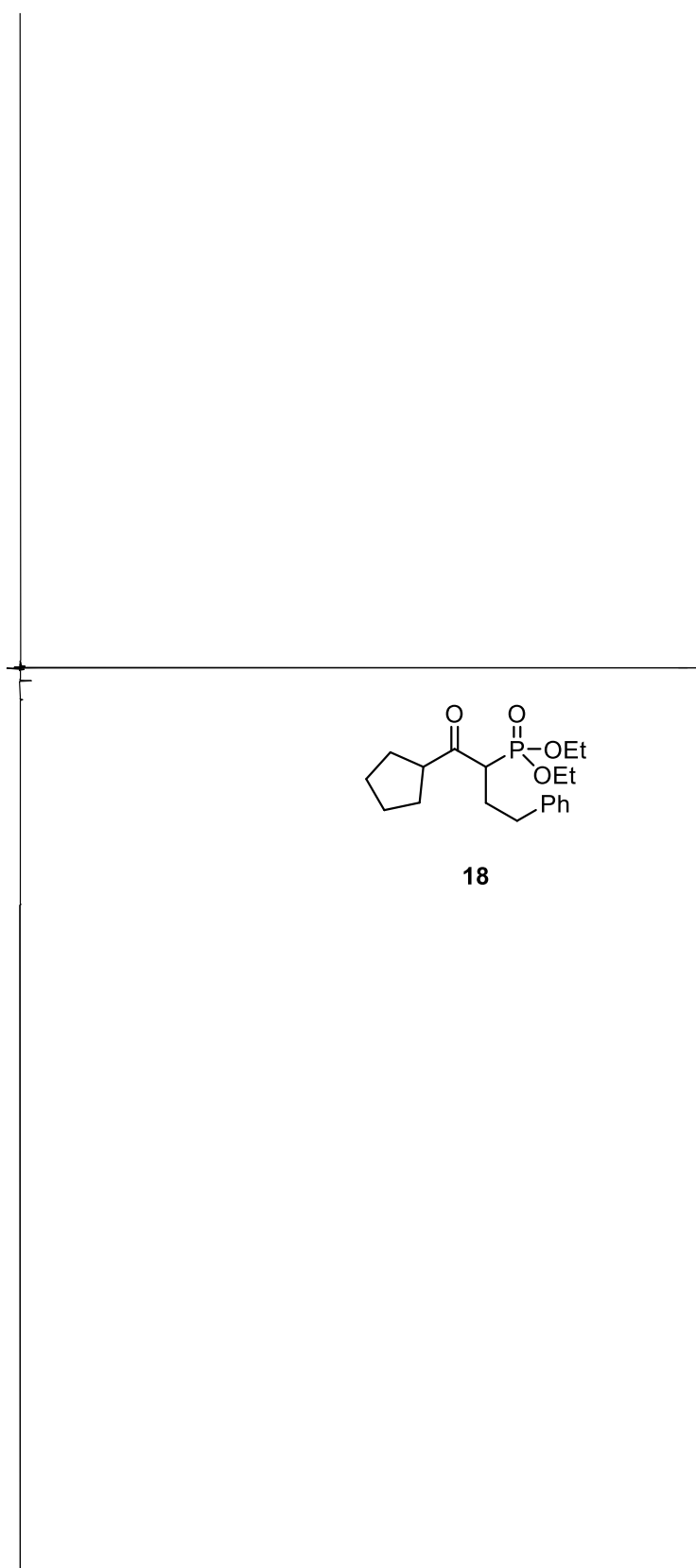


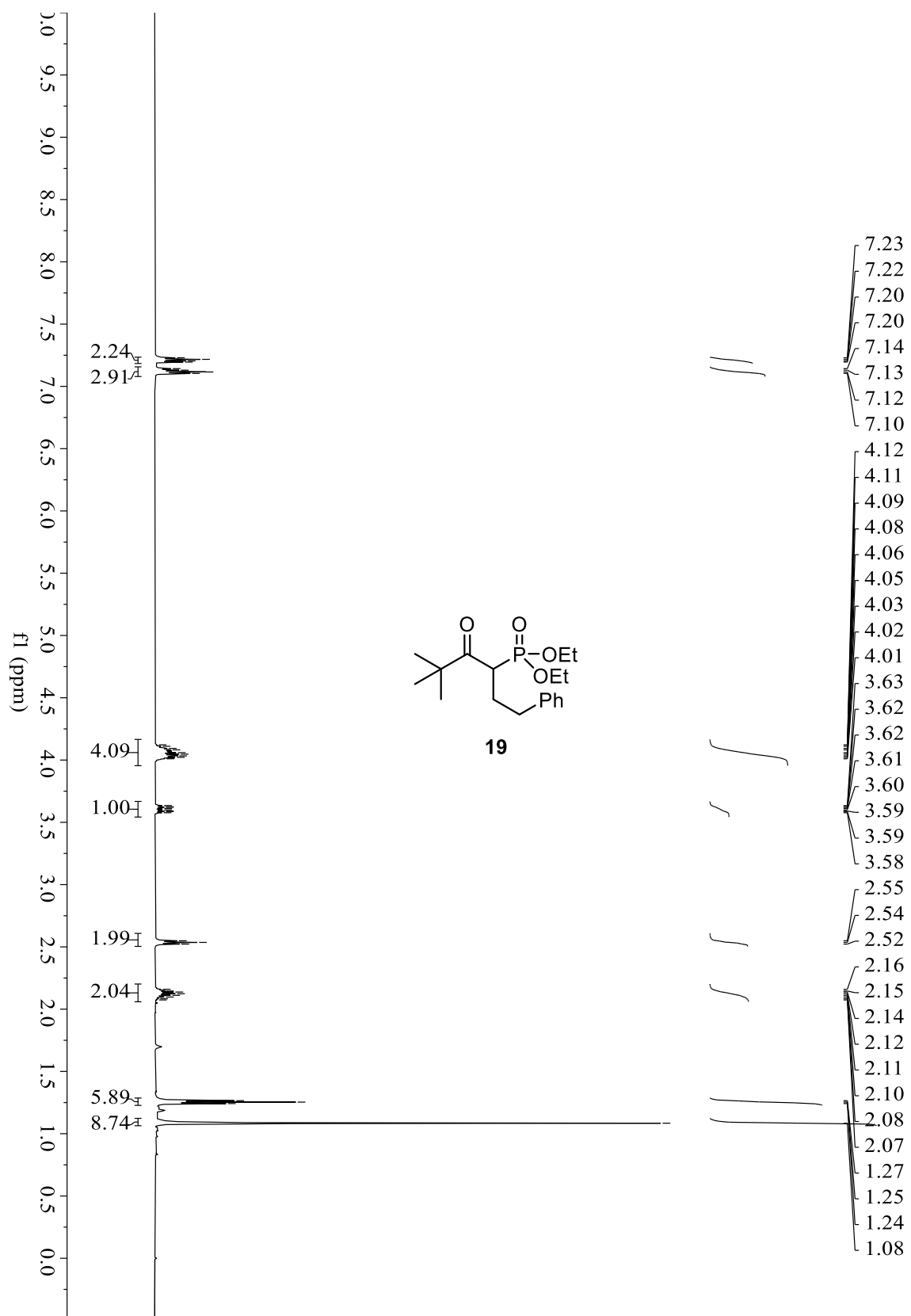


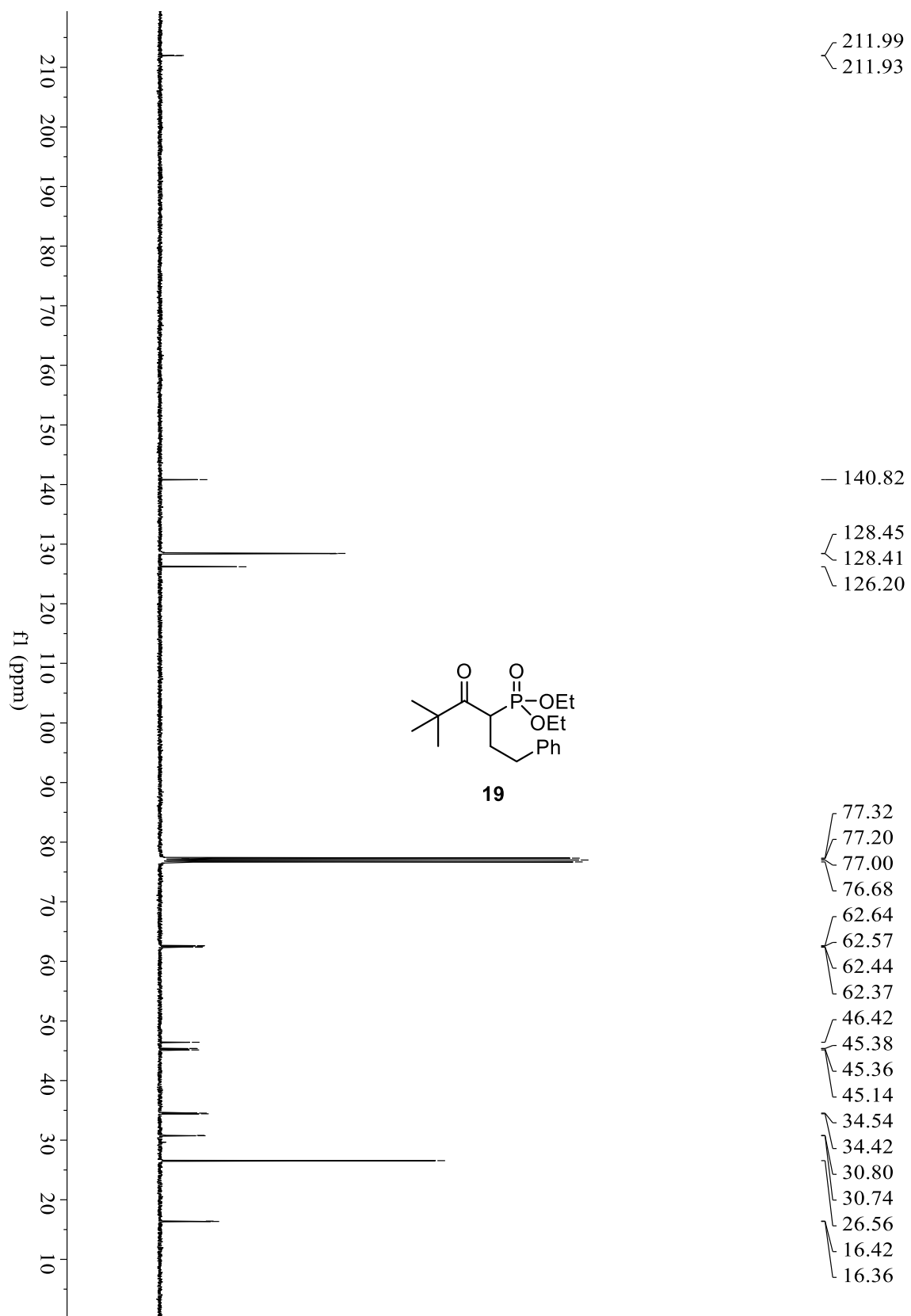




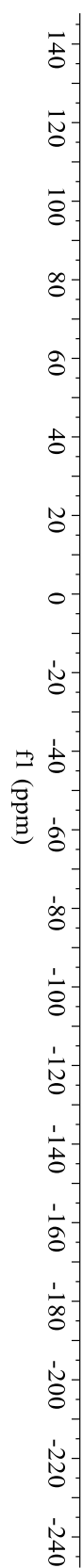
f1 (ppm)



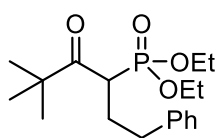




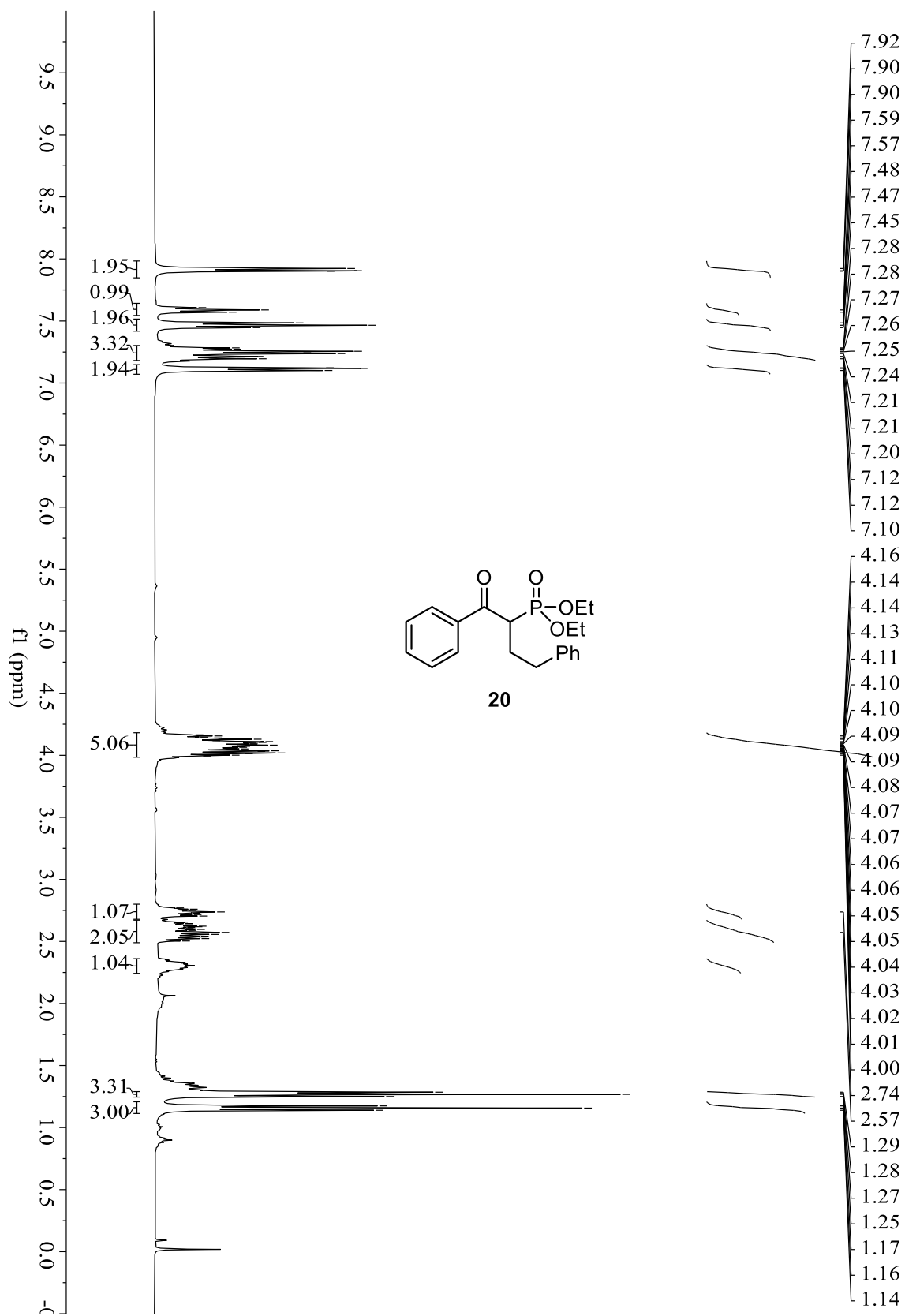


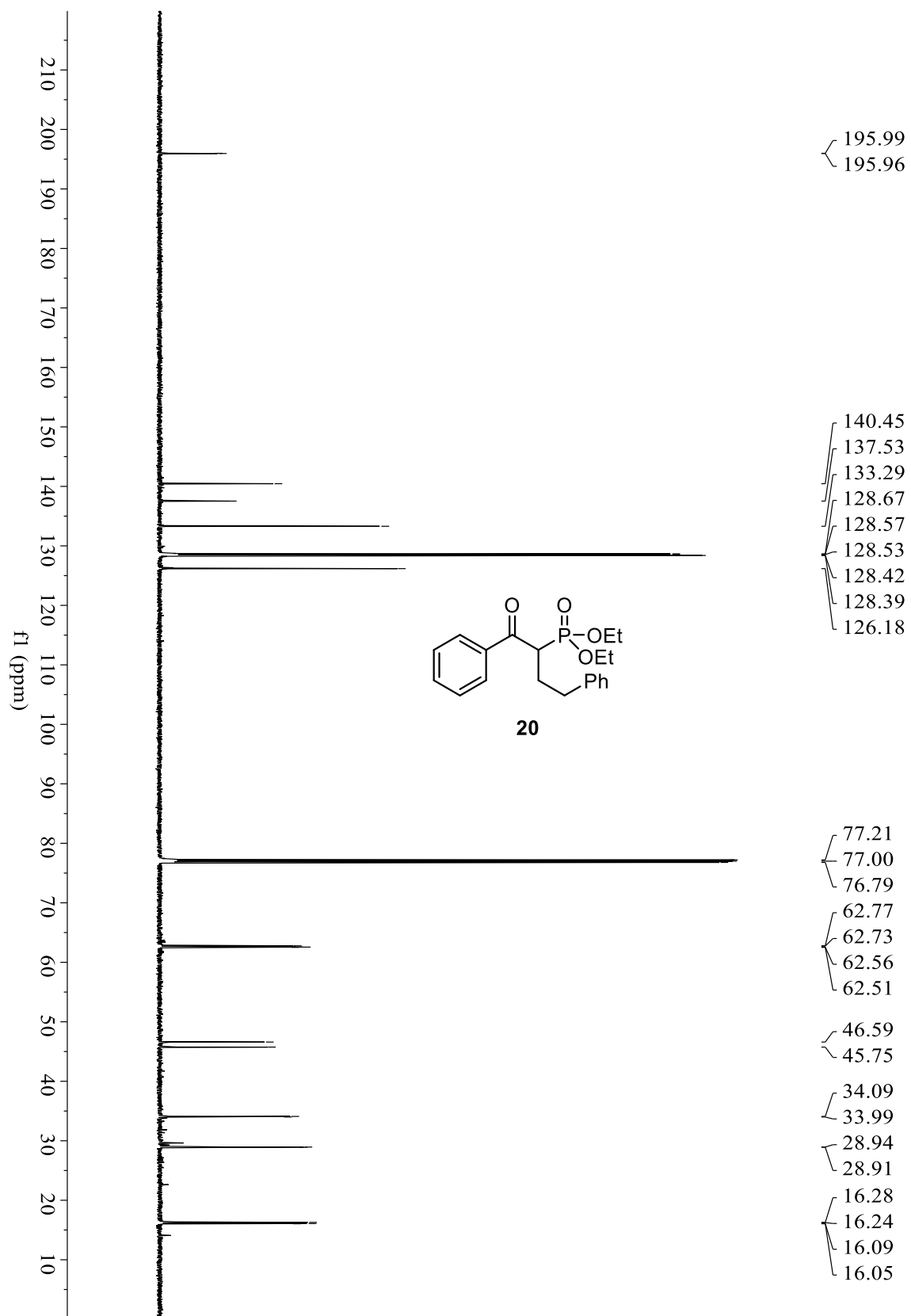


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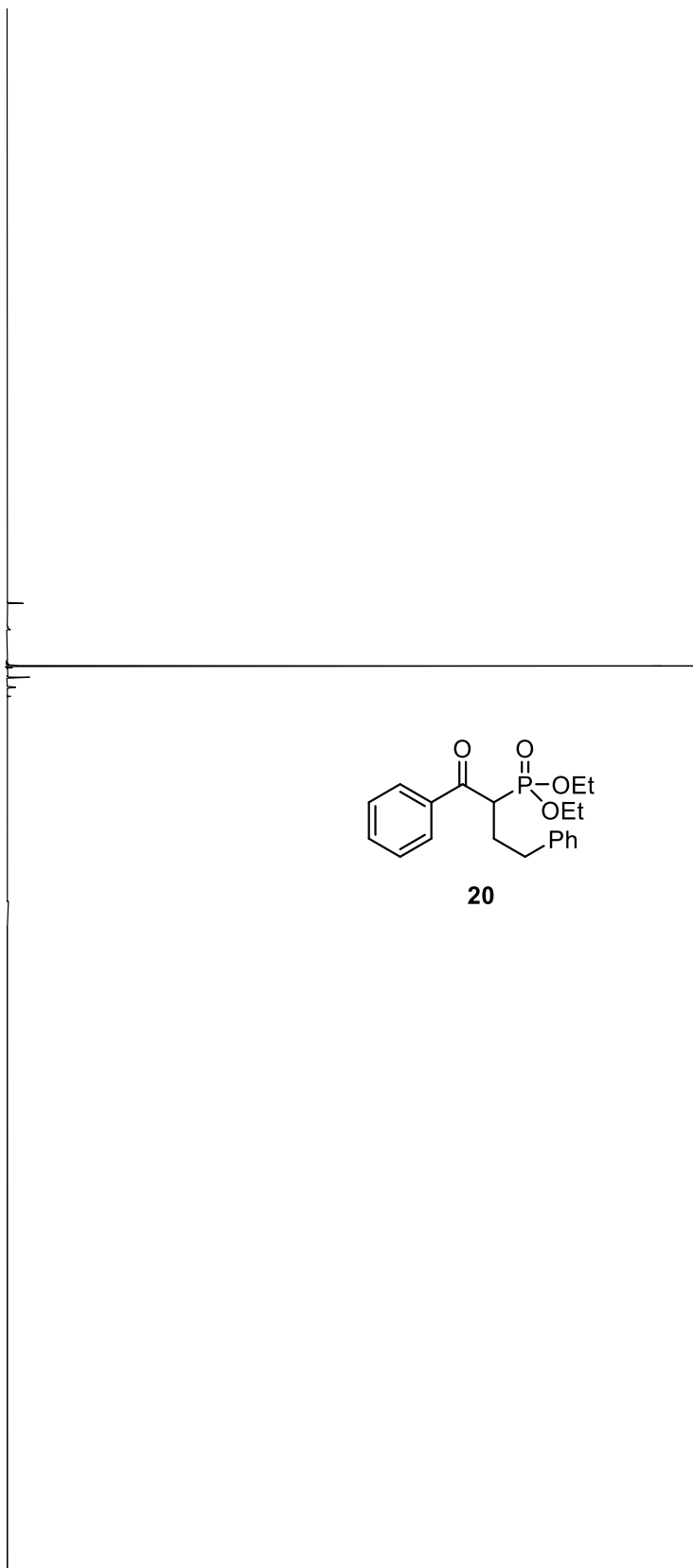


**19**

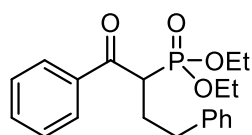




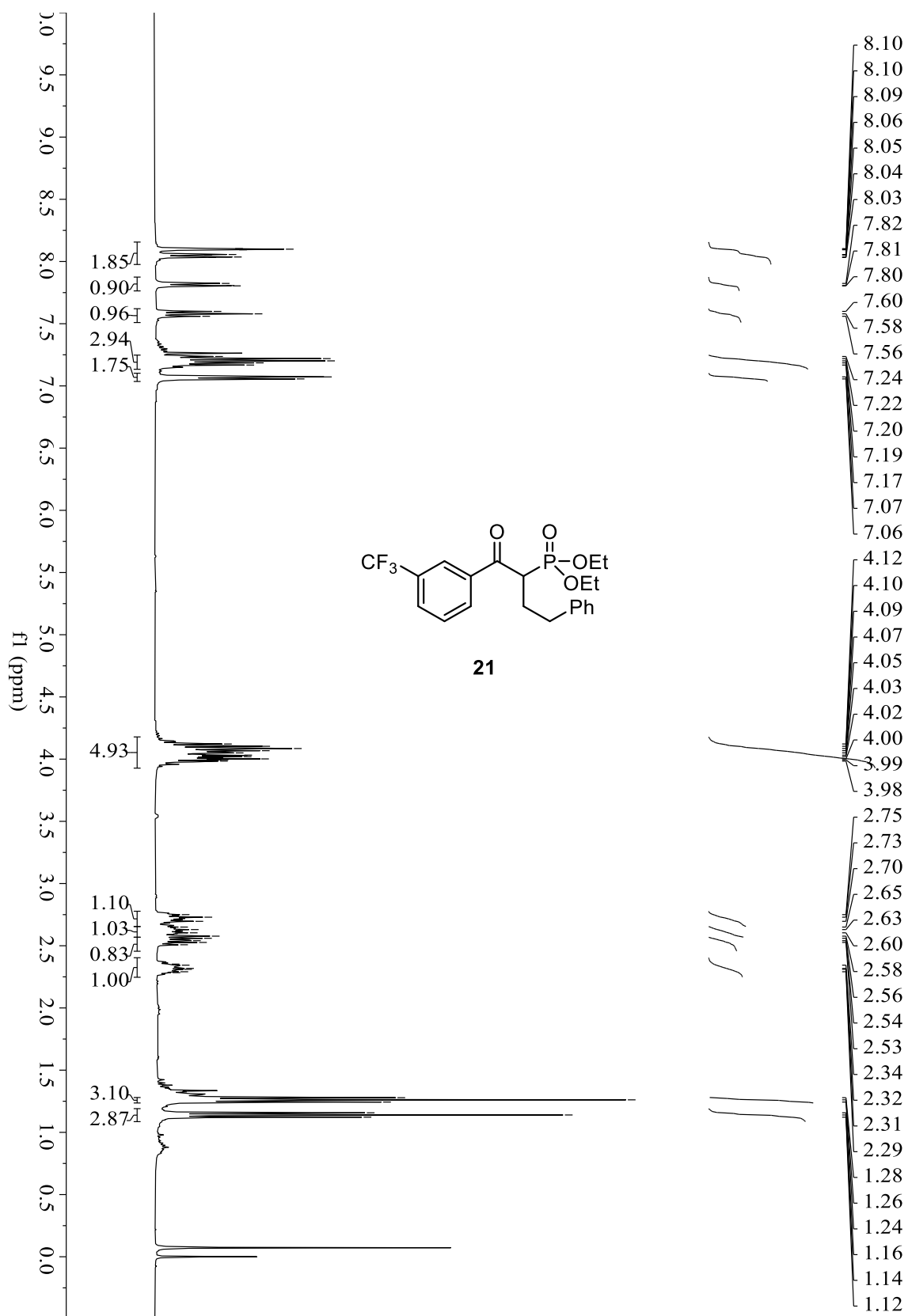
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f1 (ppm)

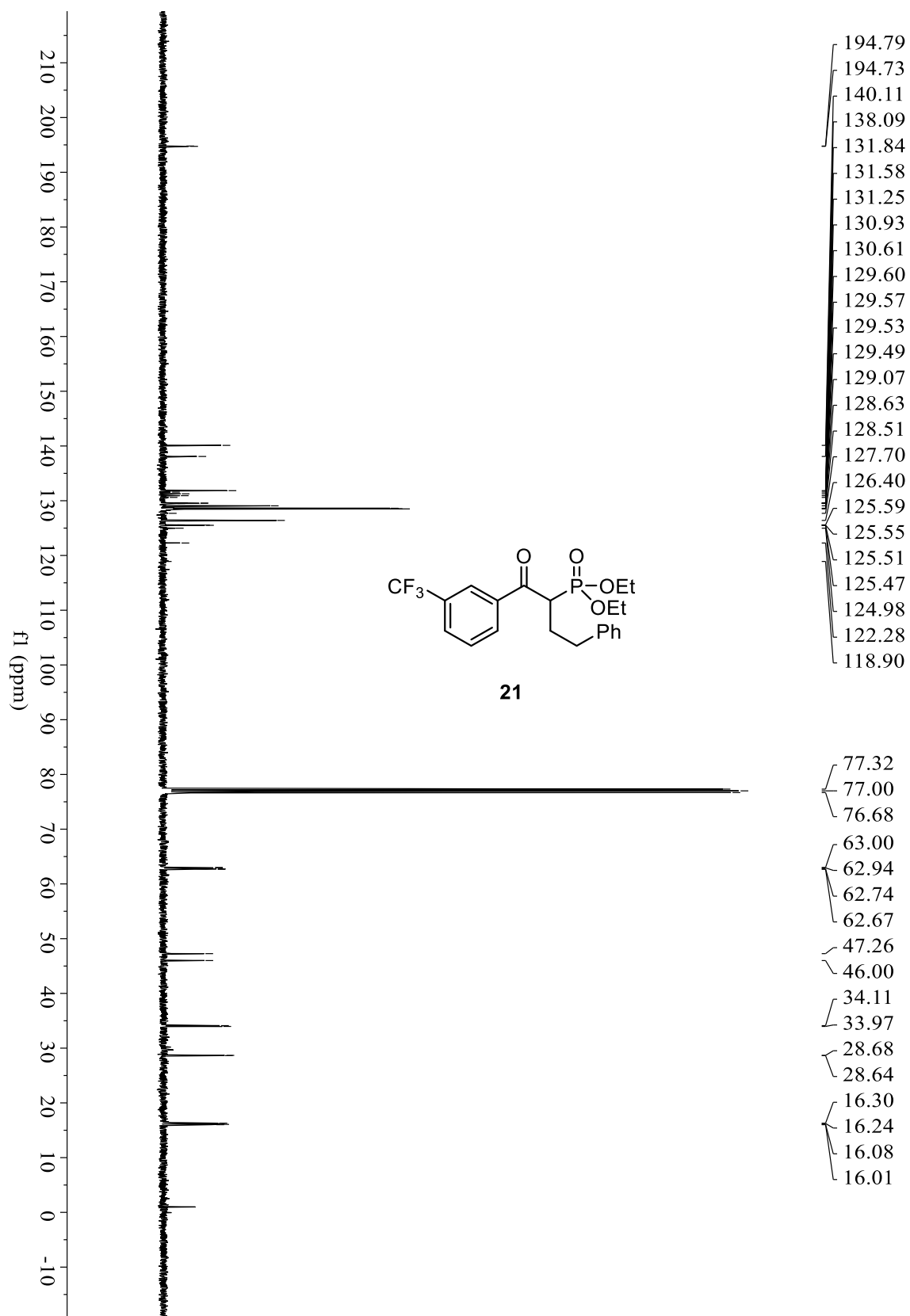


— 22.21

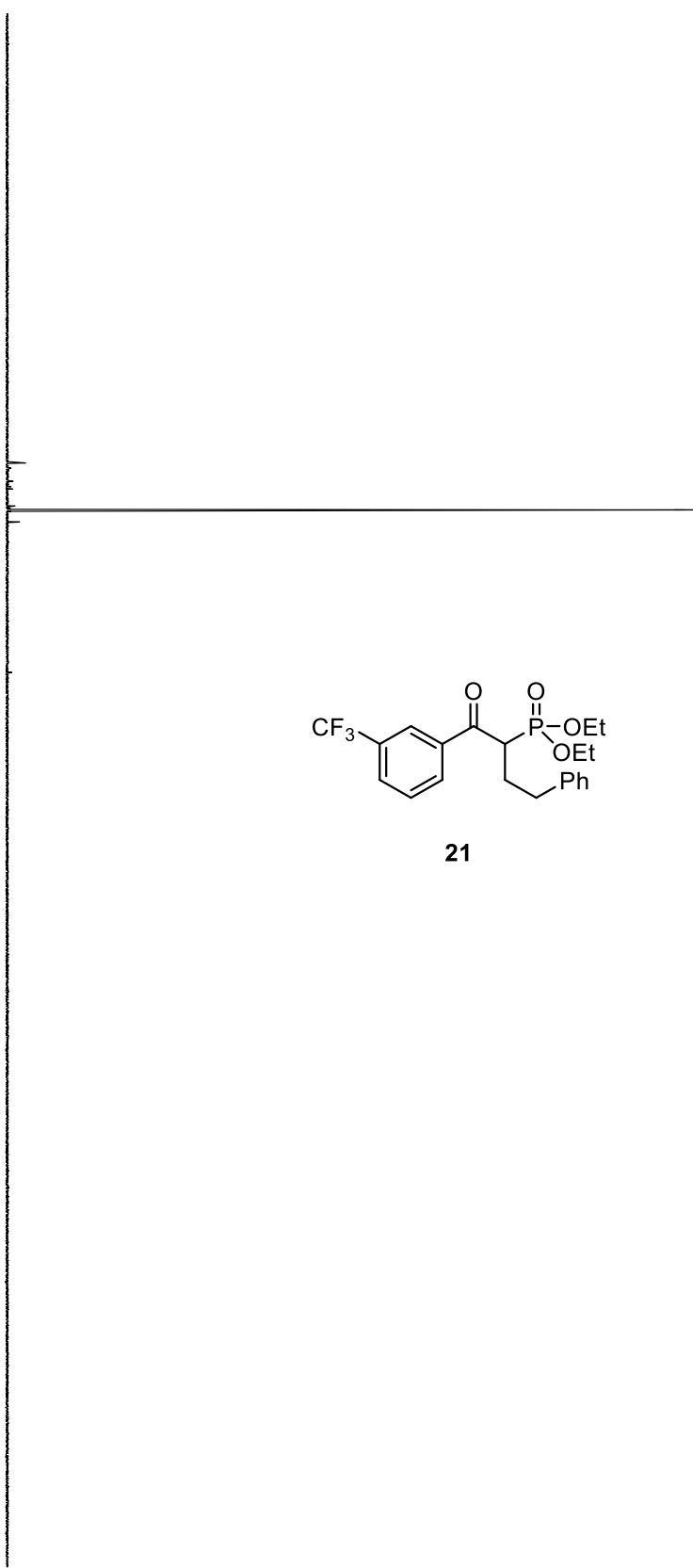


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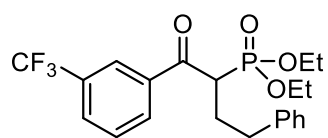




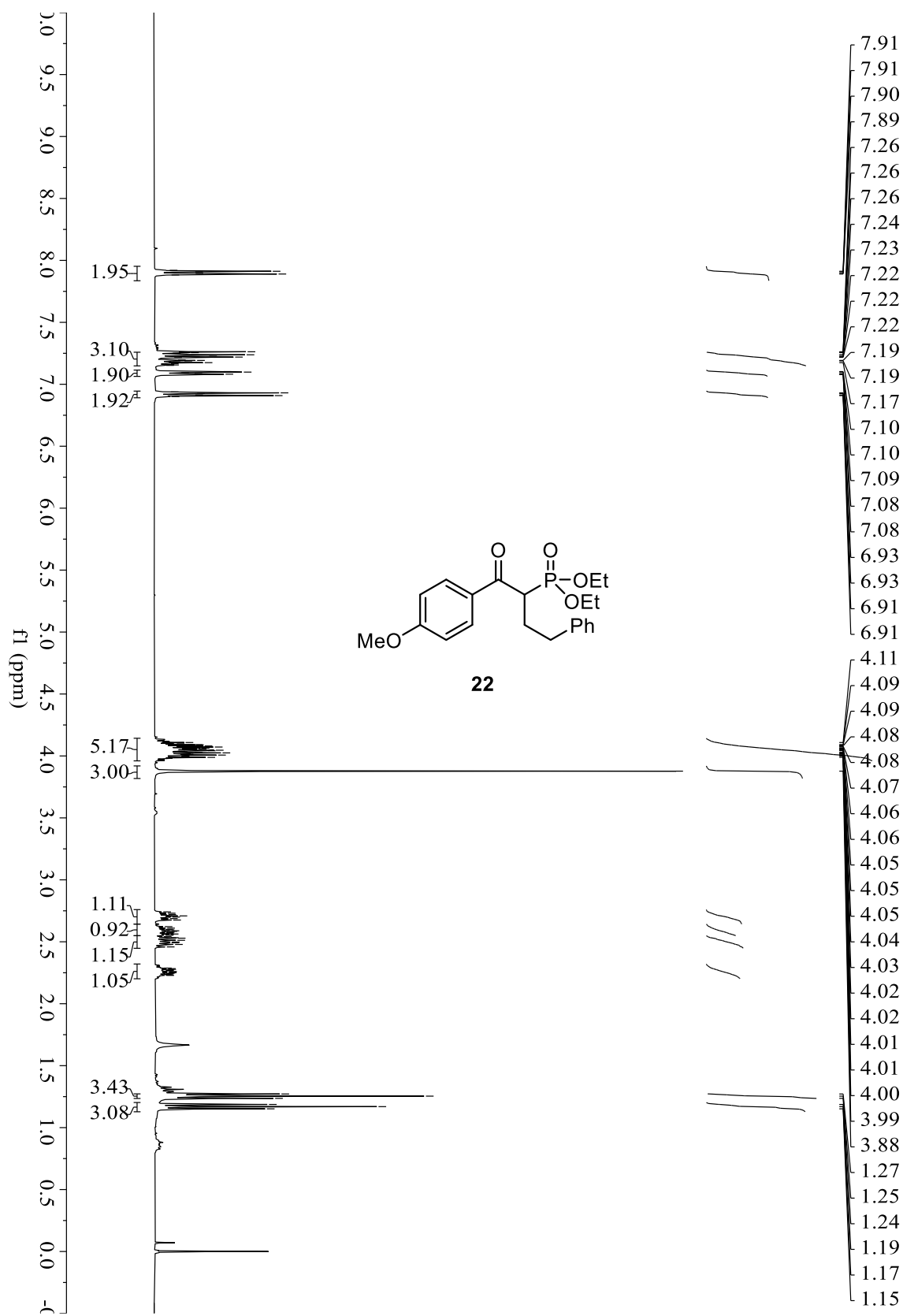
f1 (ppm)



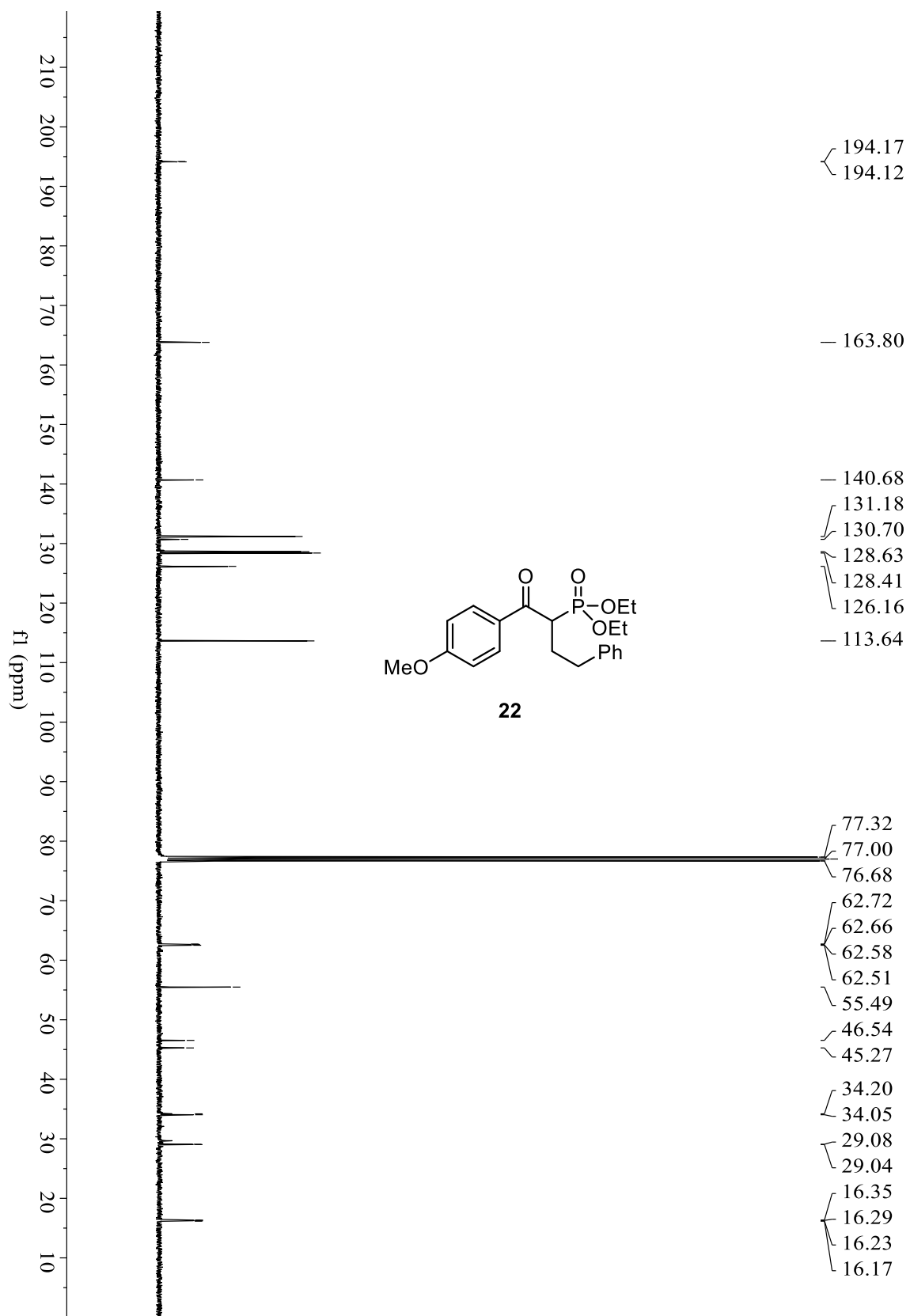
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**21**

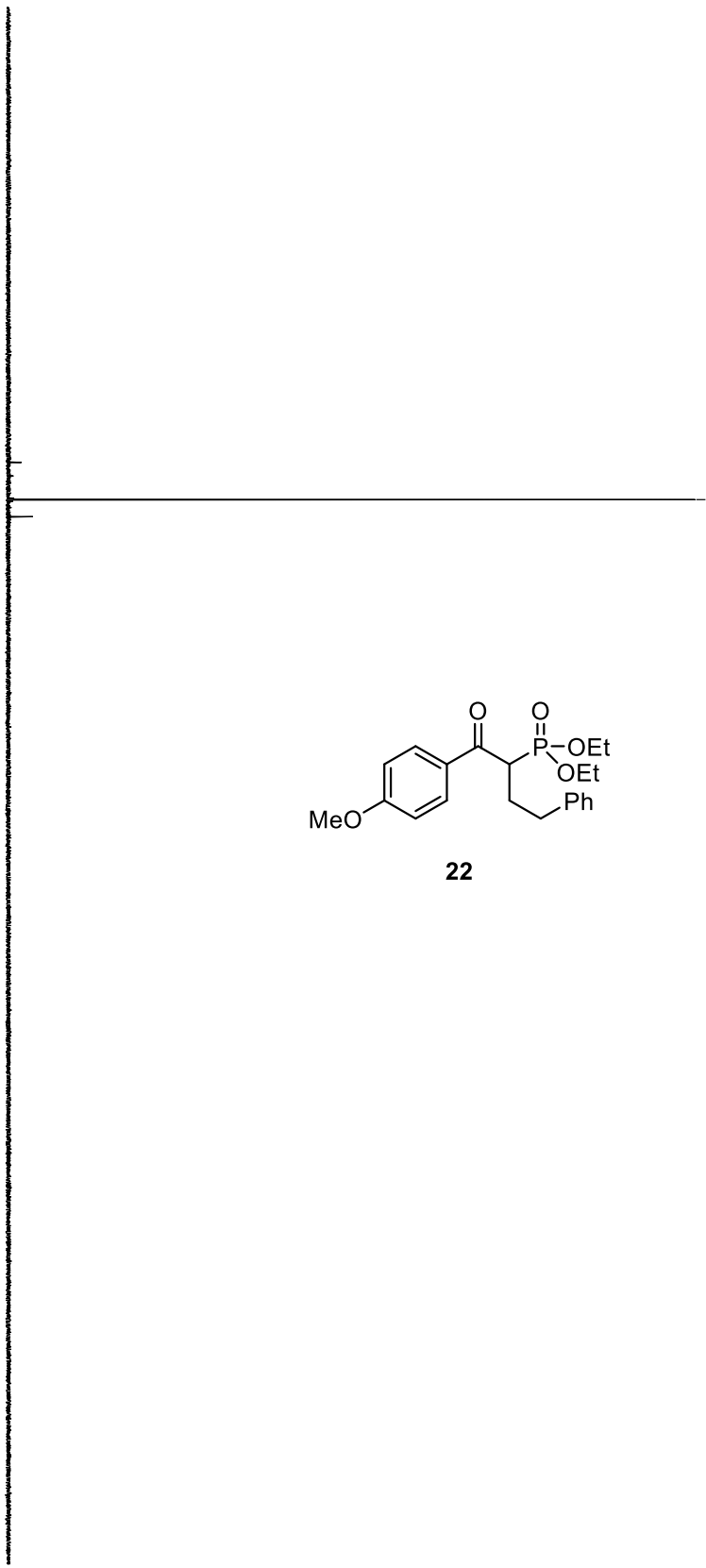




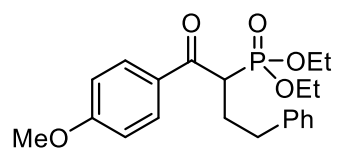


f1 (ppm)

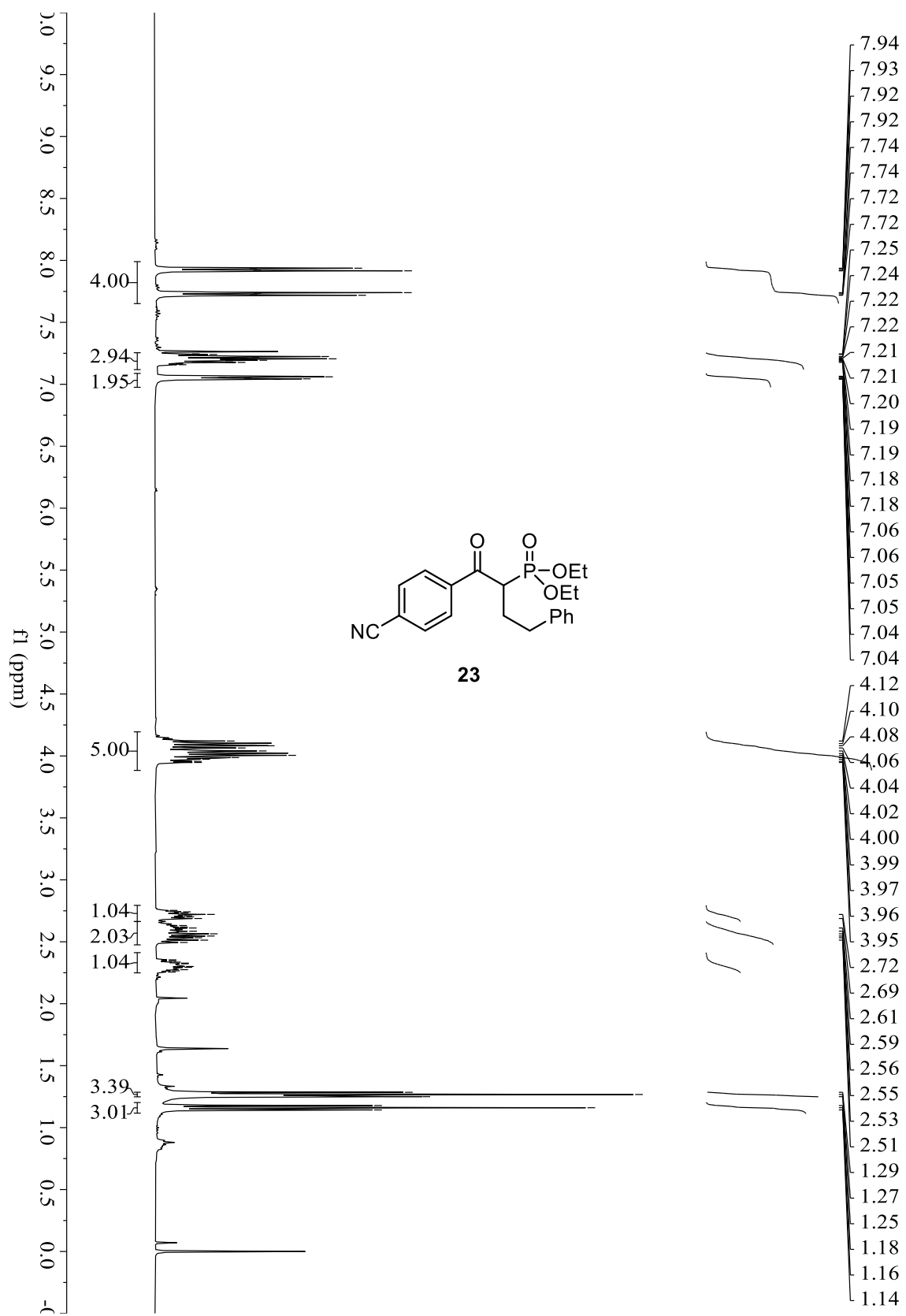
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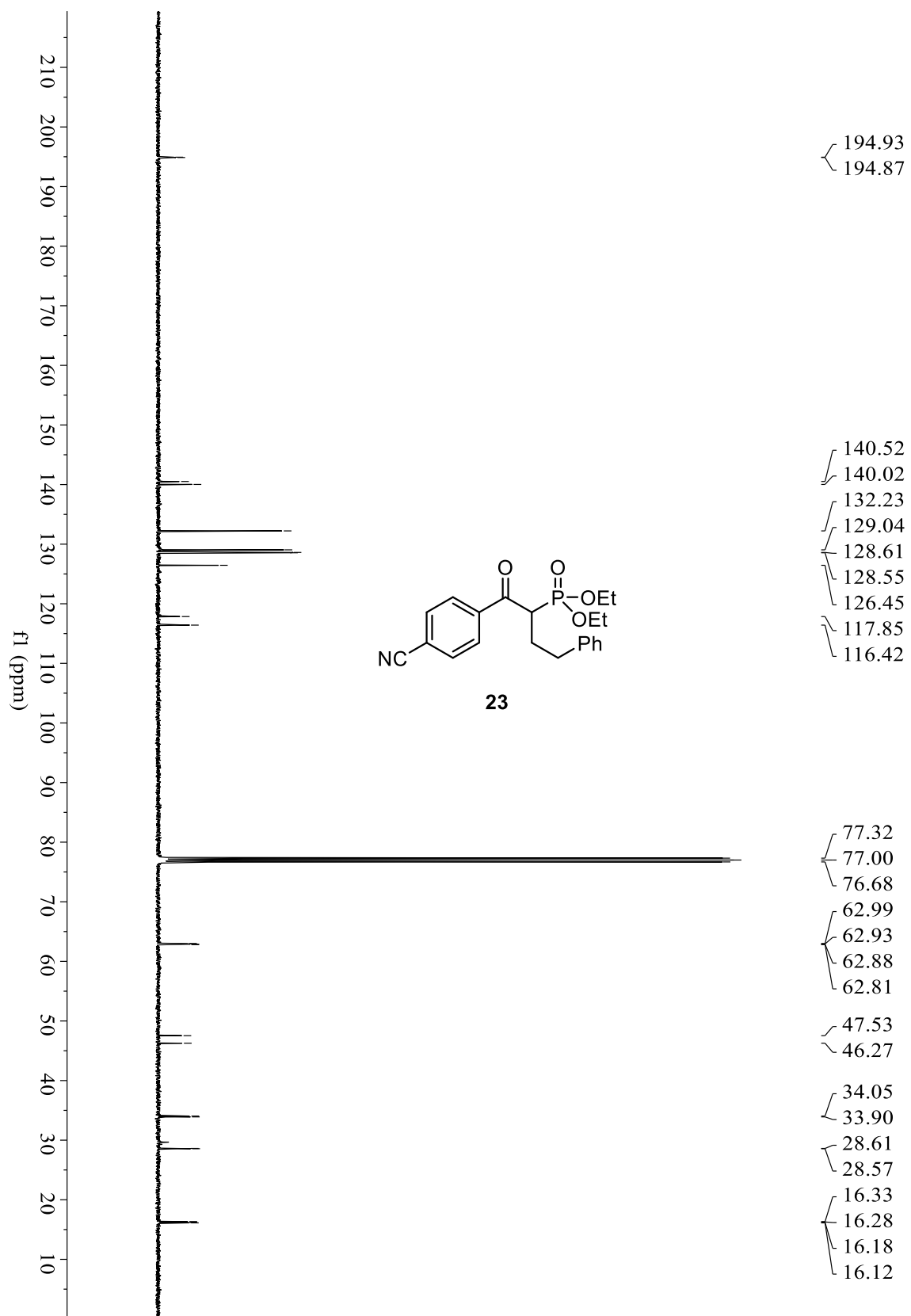


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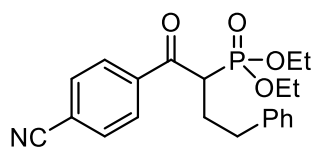
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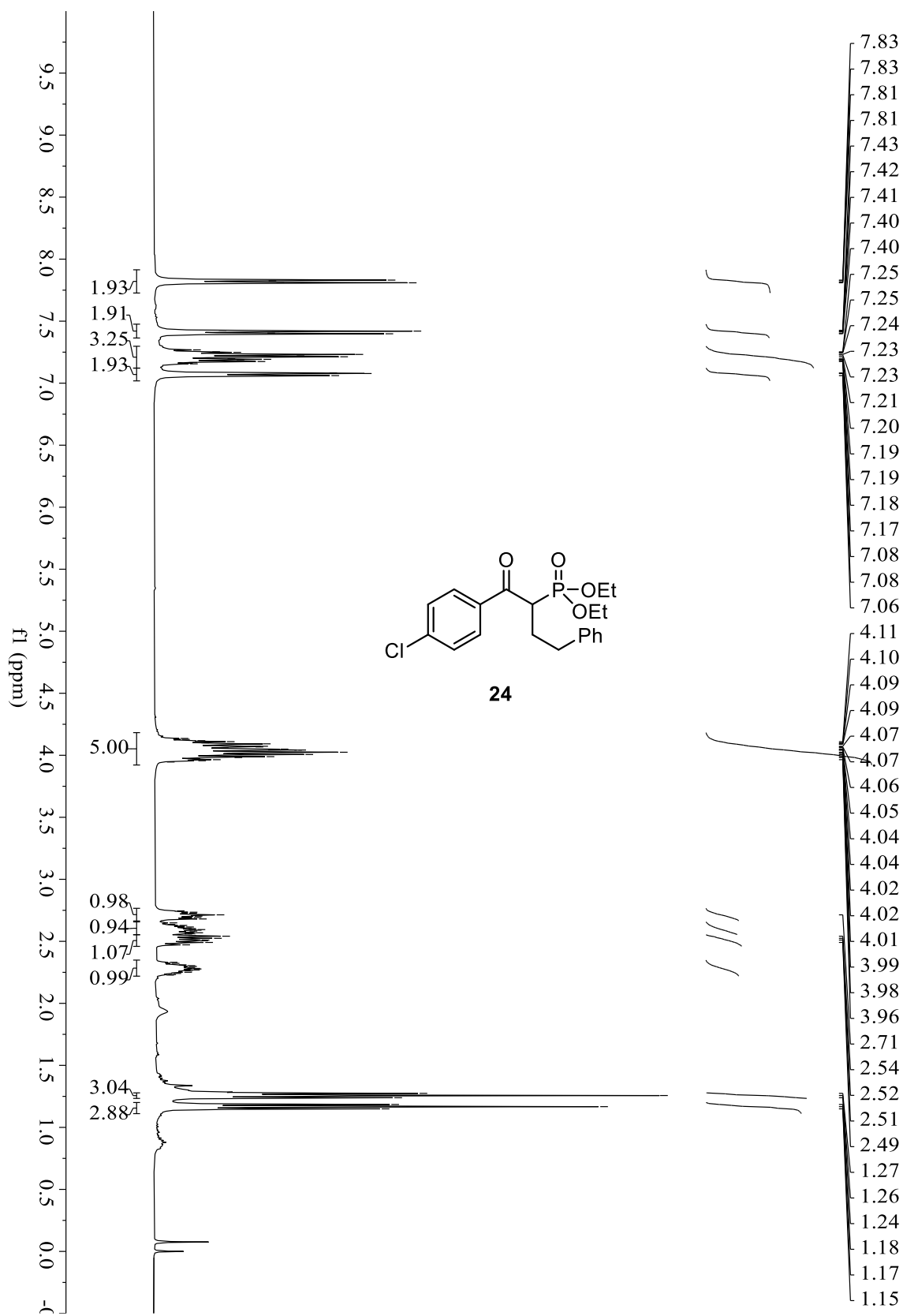


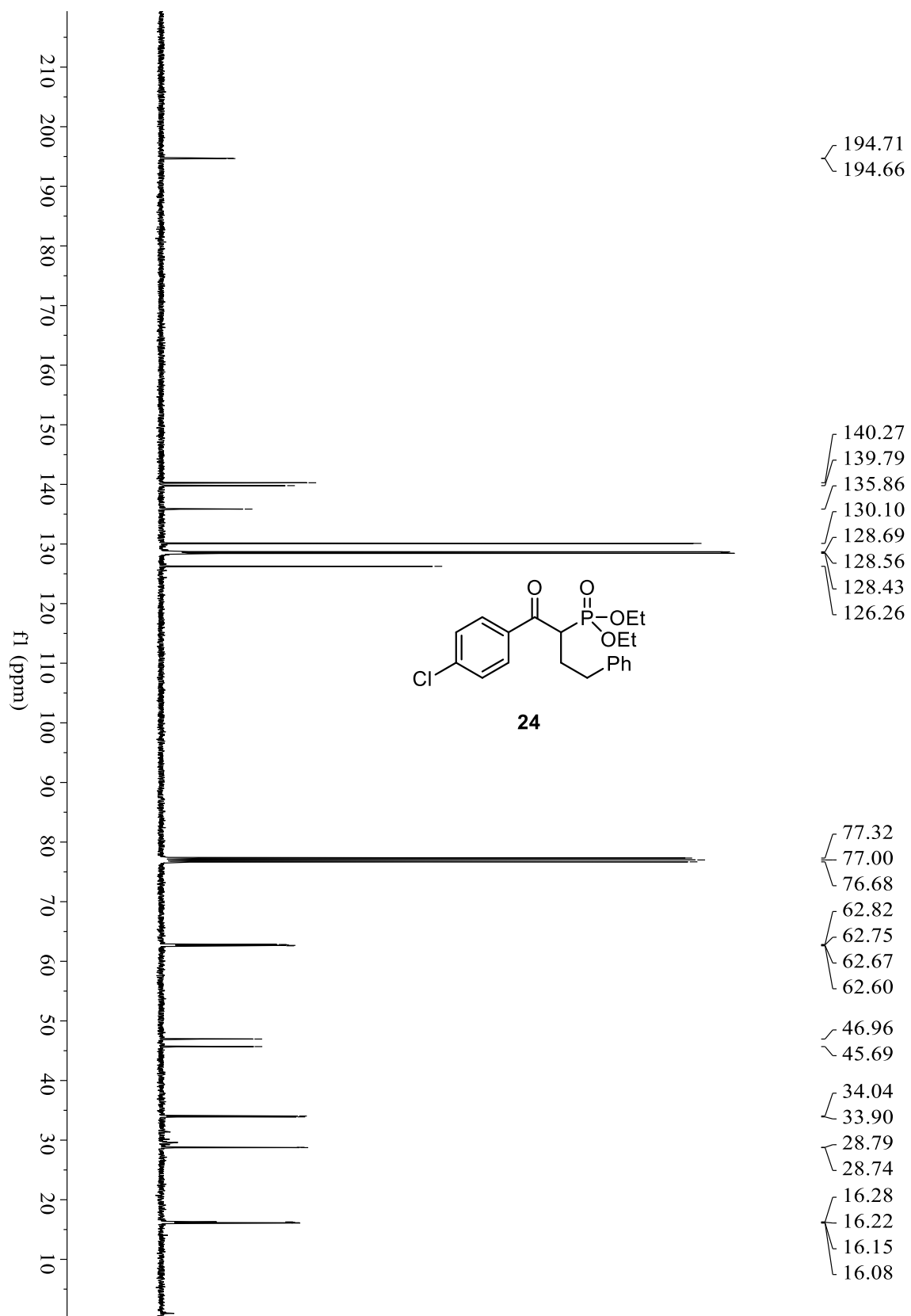
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f1 (ppm)

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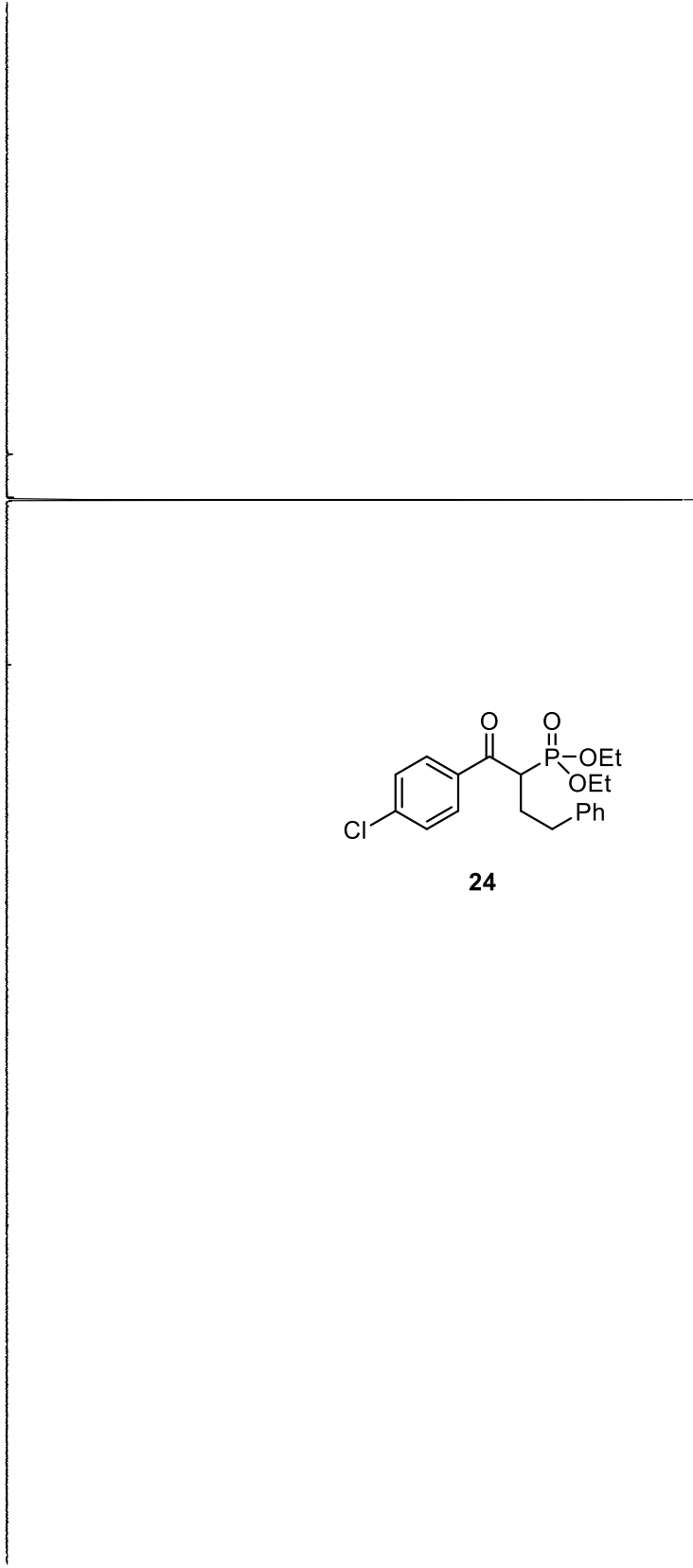
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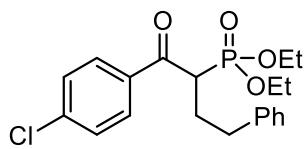


f1 (ppm)

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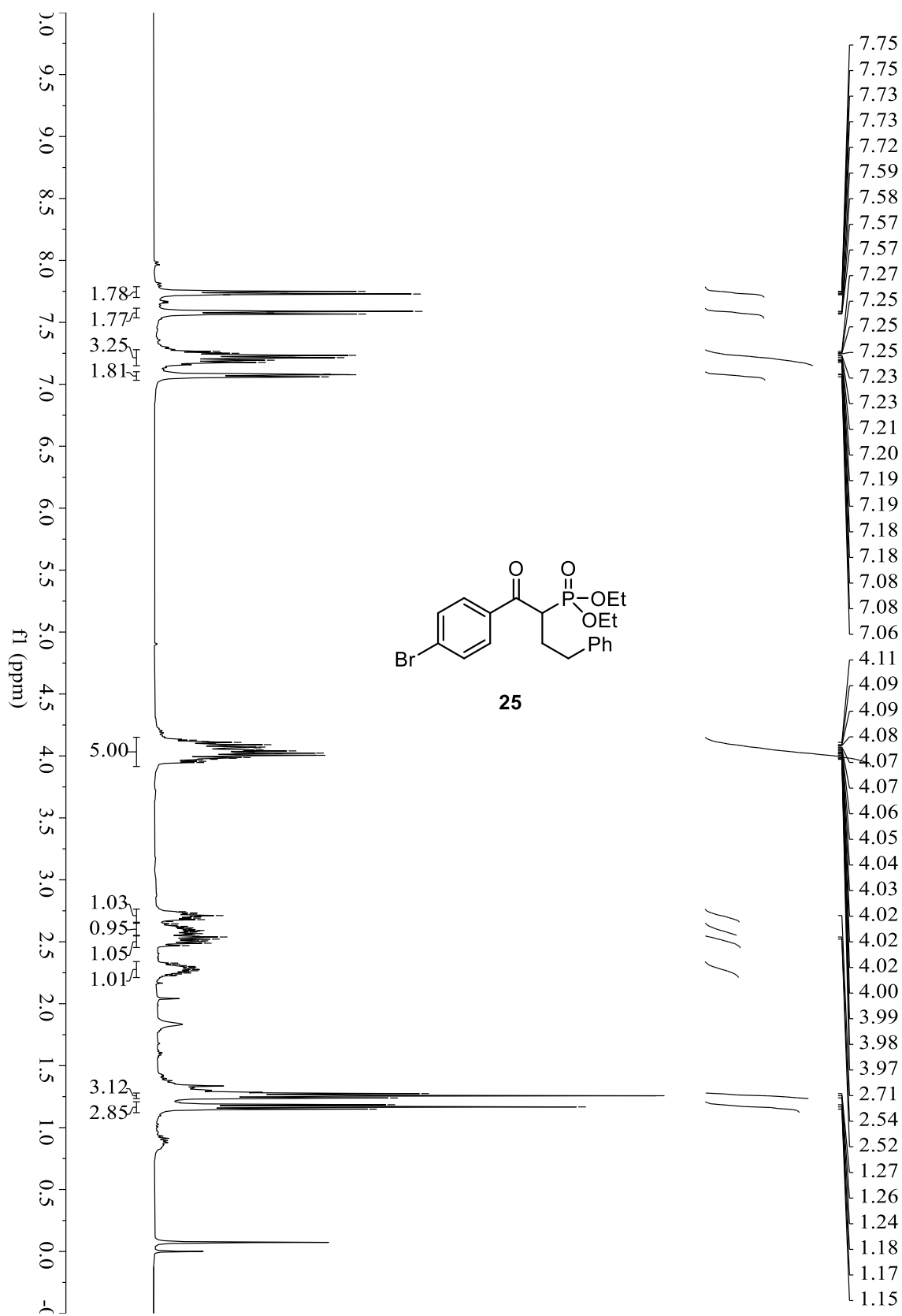


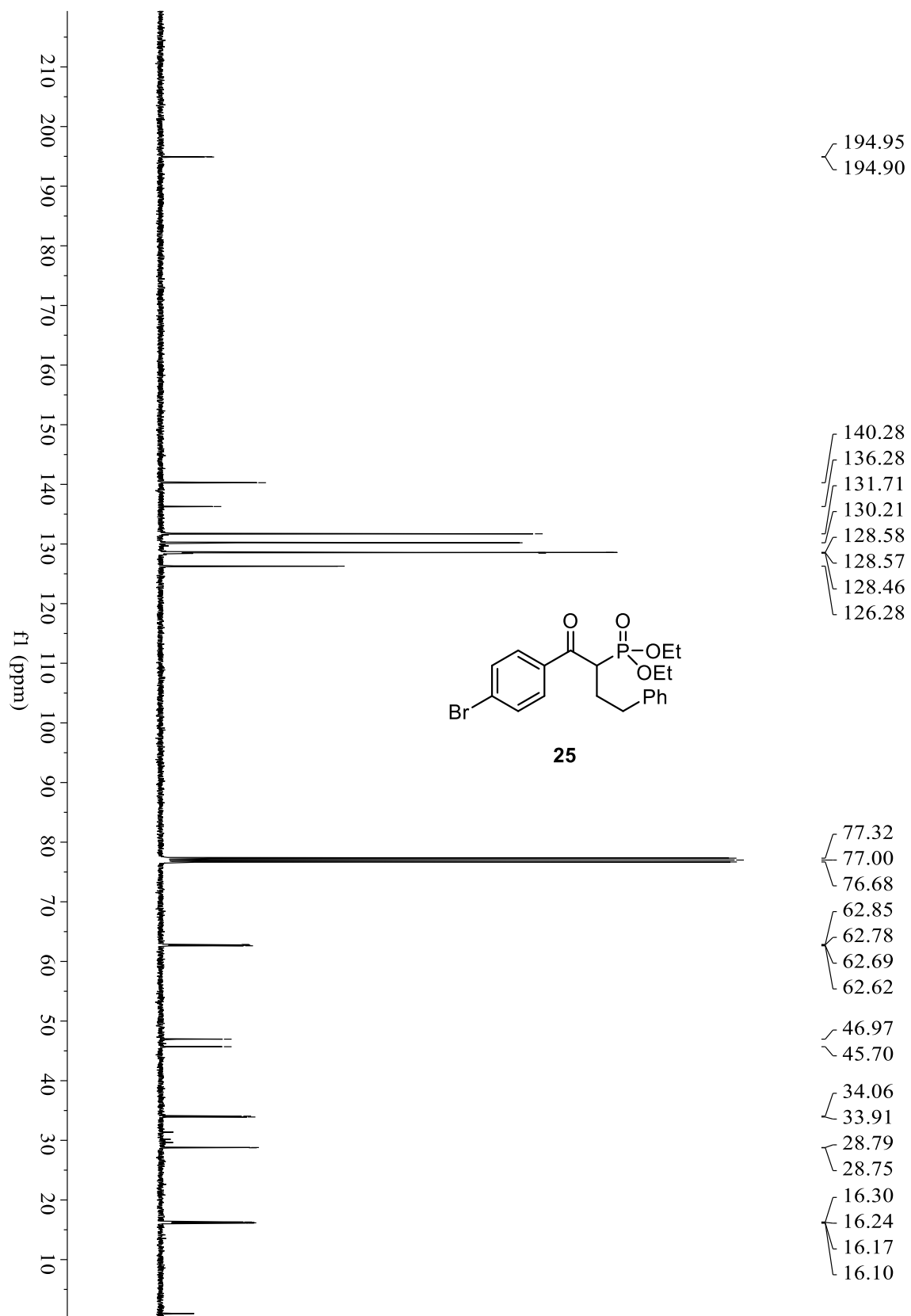
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**24**

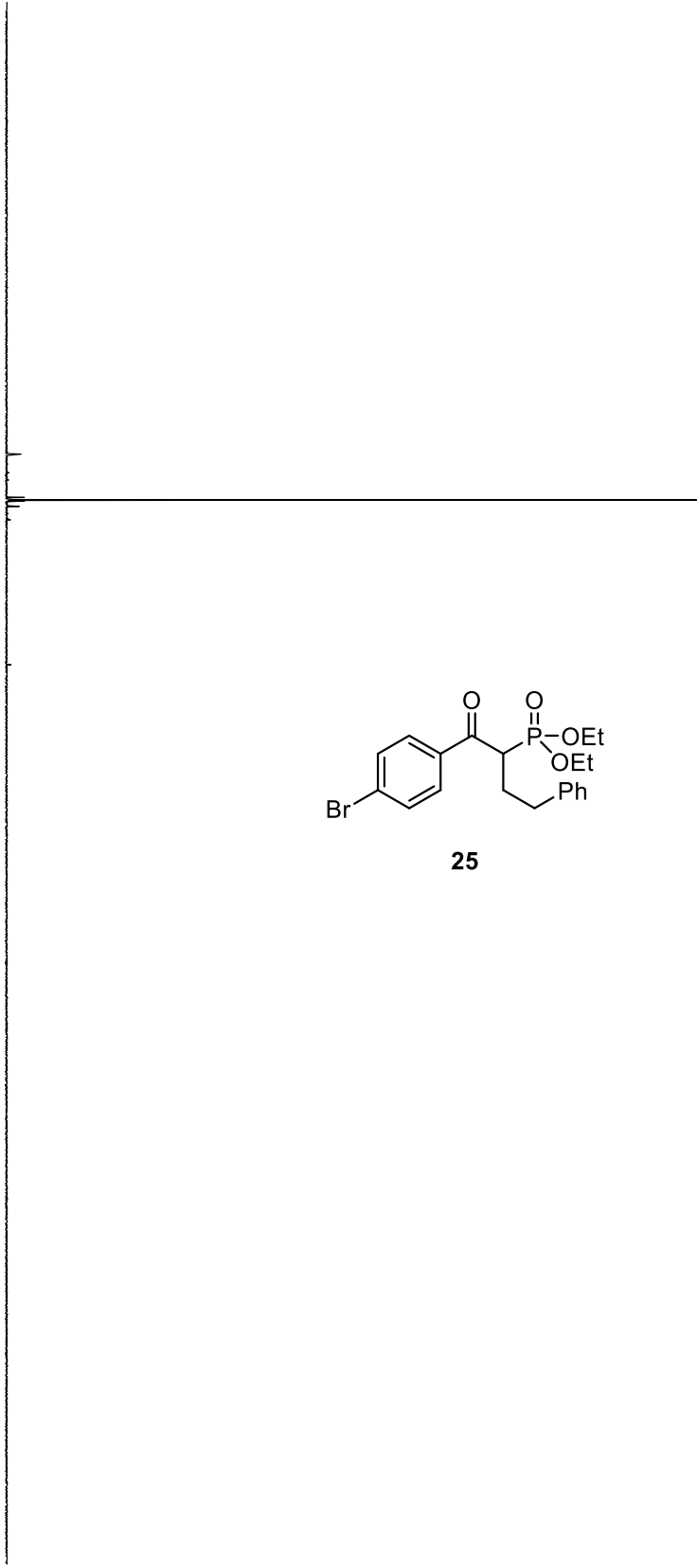




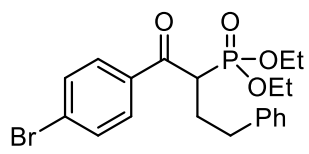


f1 (ppm)

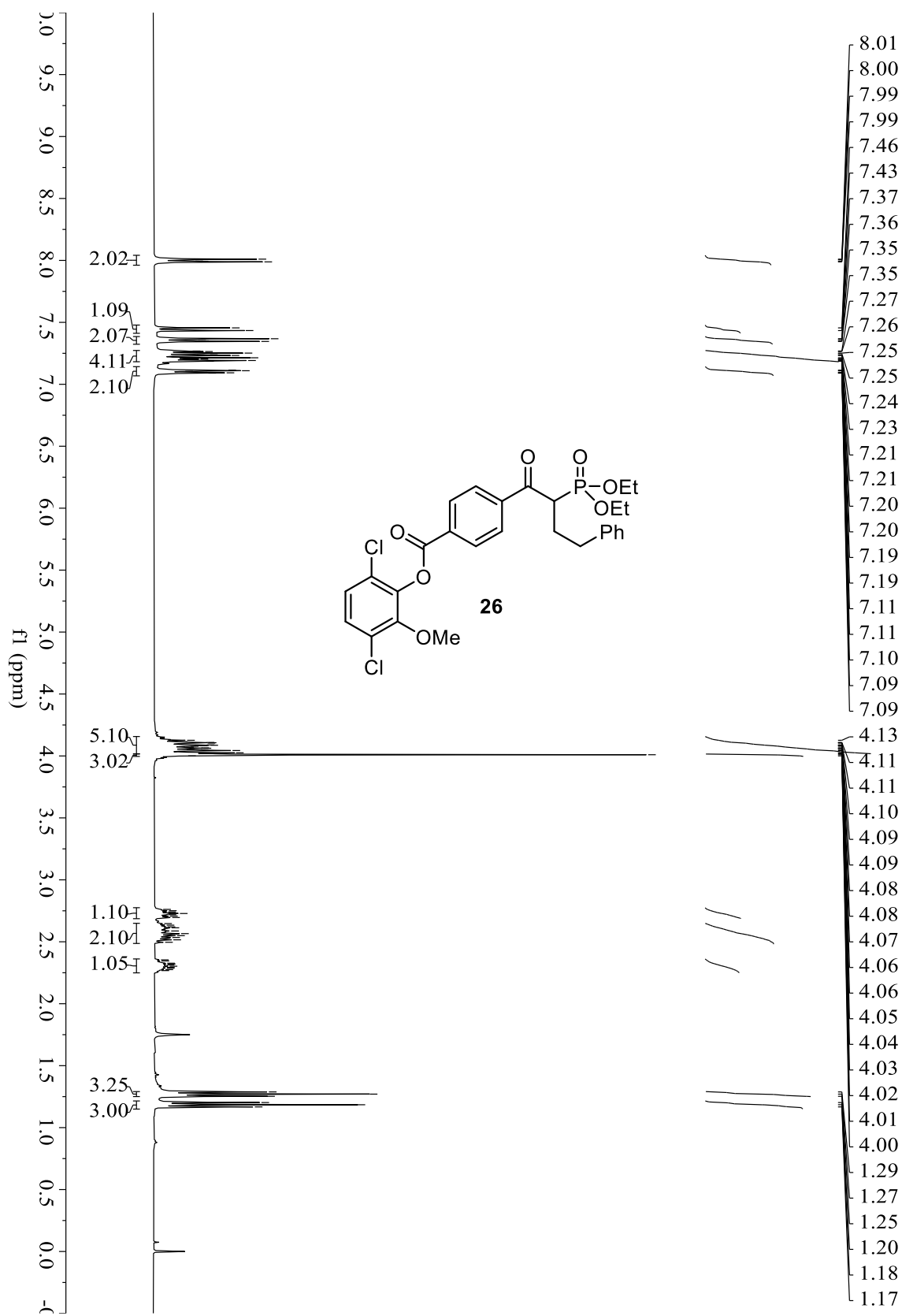
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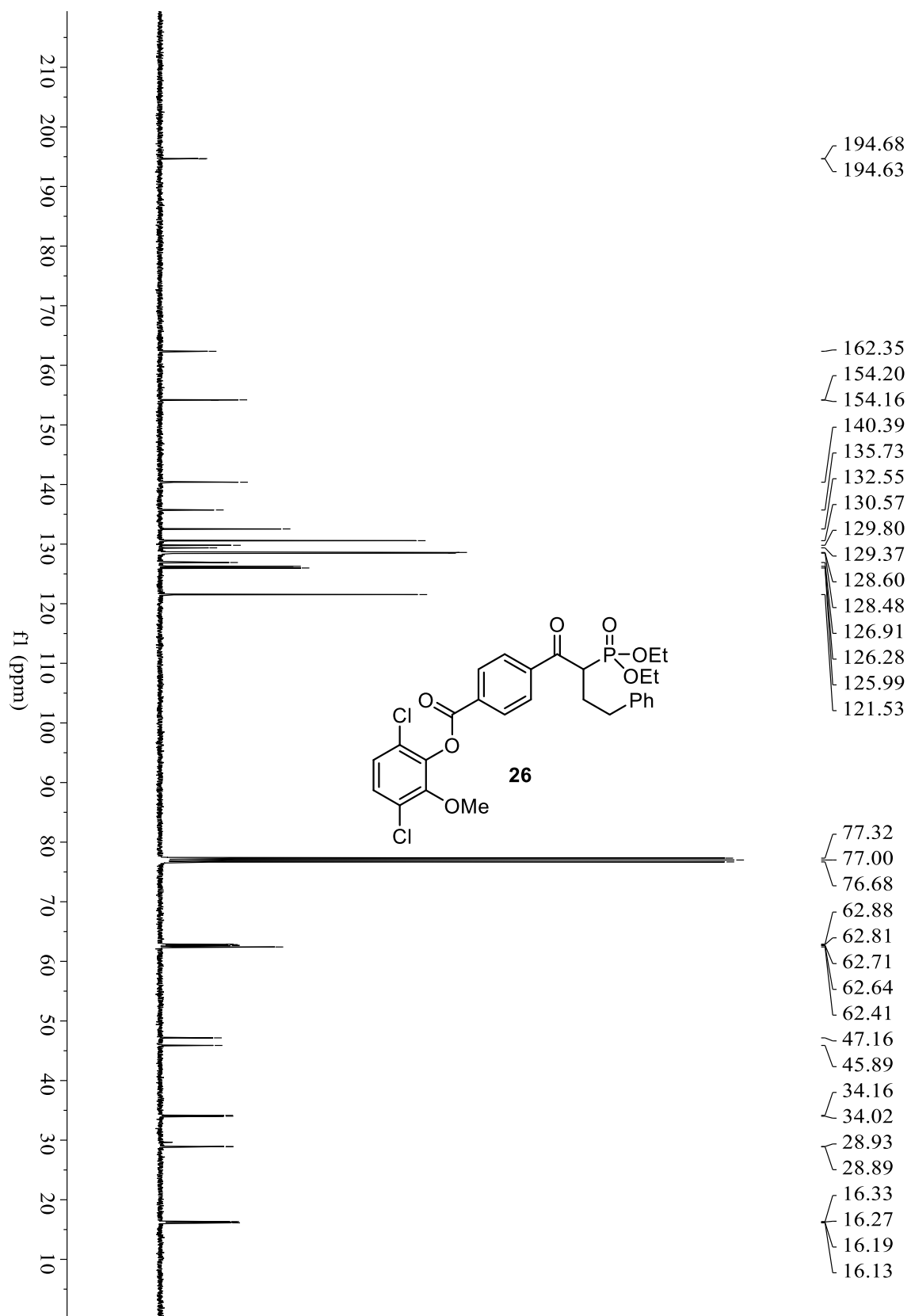


- 21.79

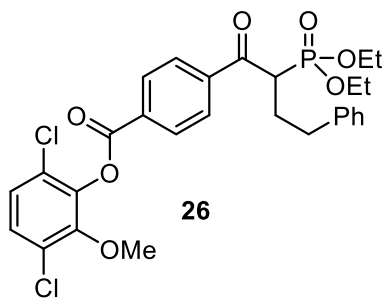


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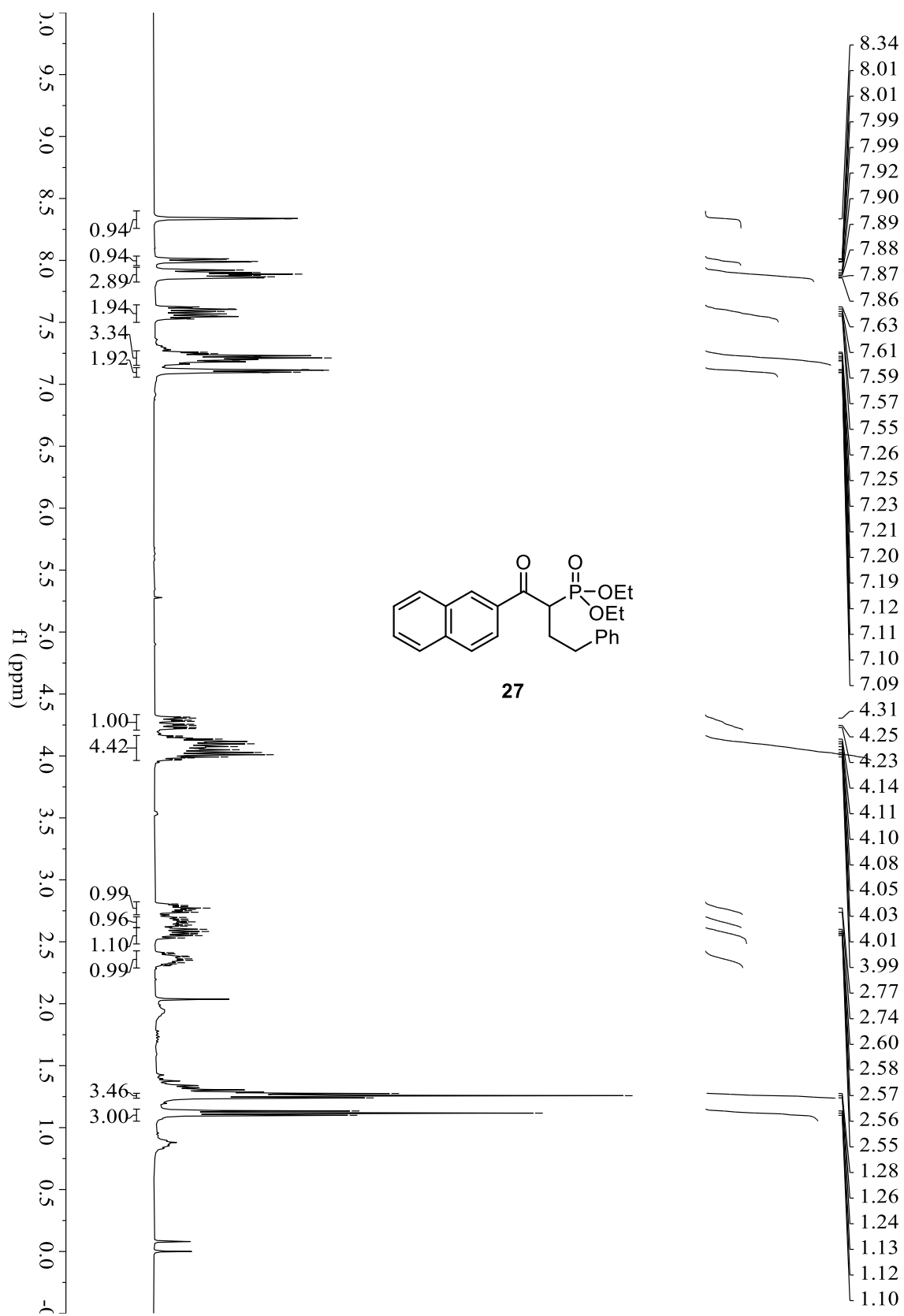


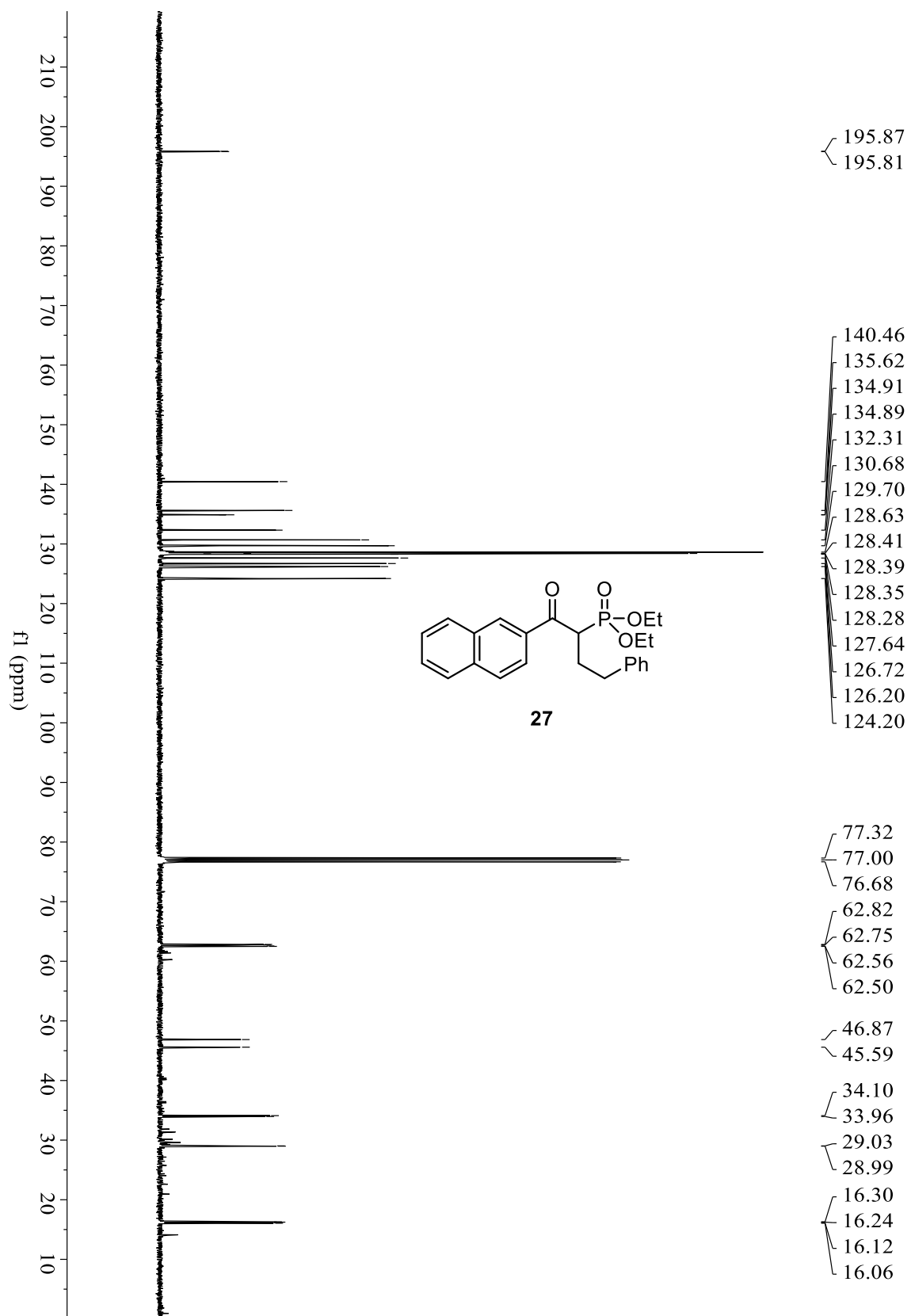


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f1 (ppm)

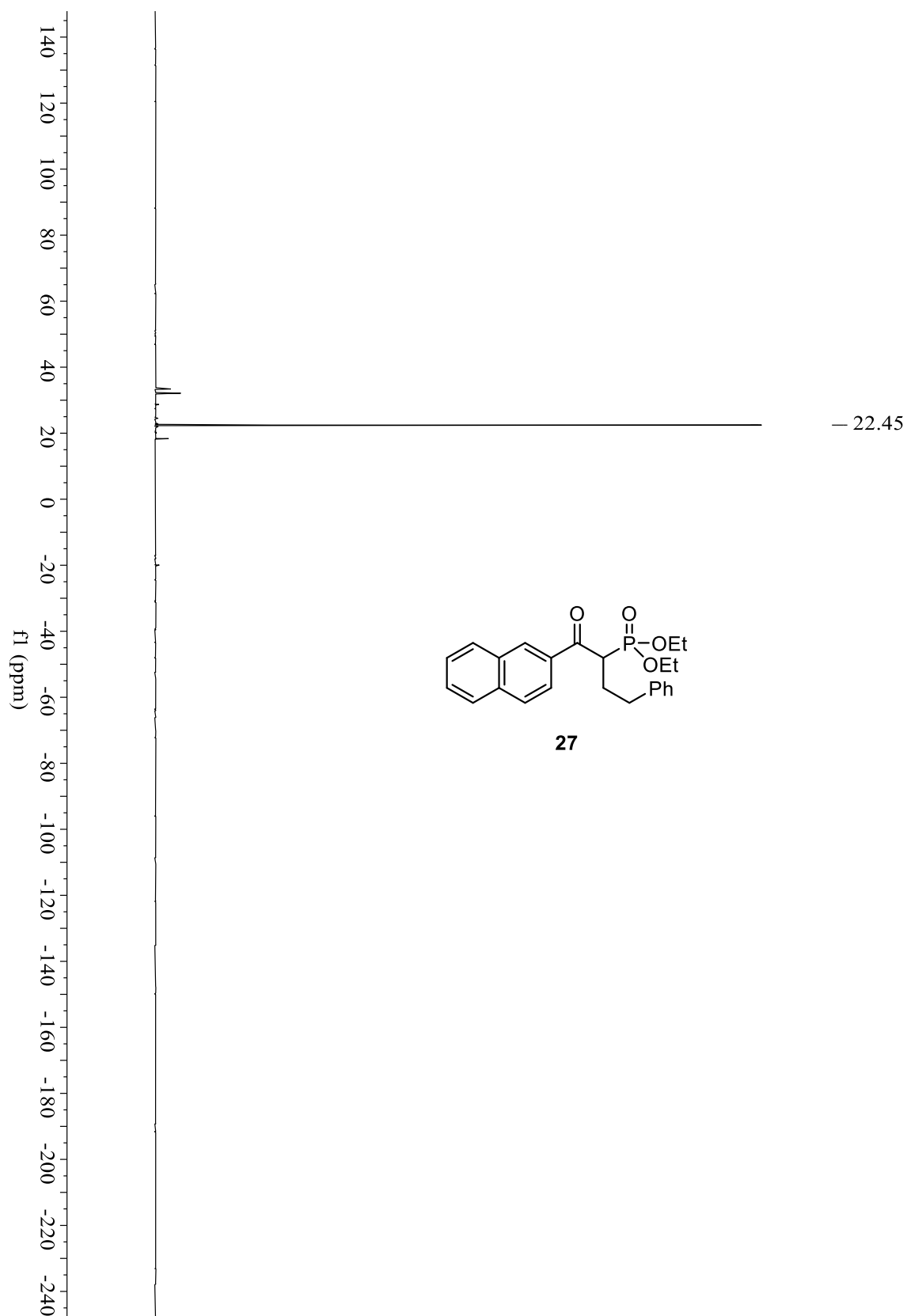


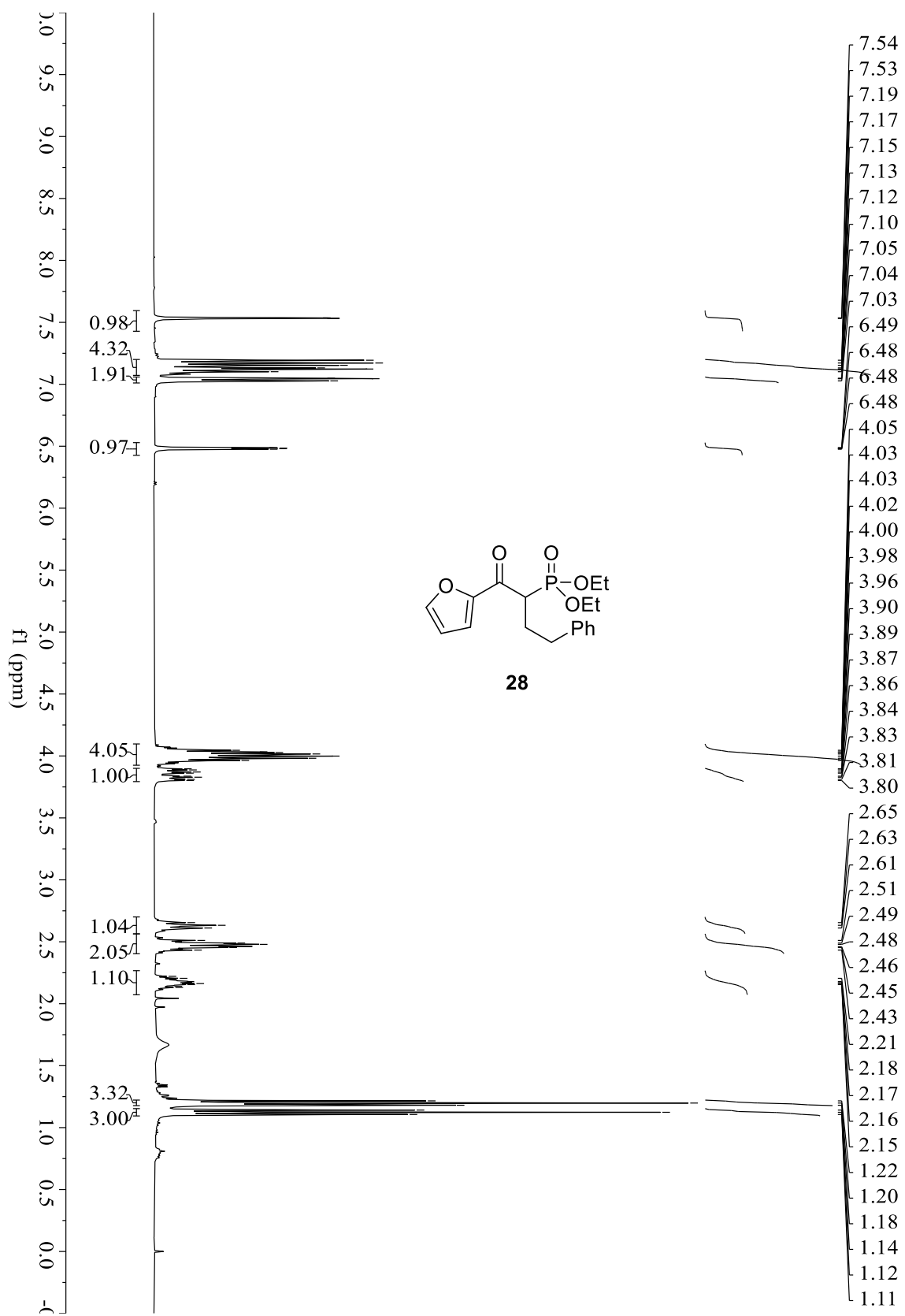
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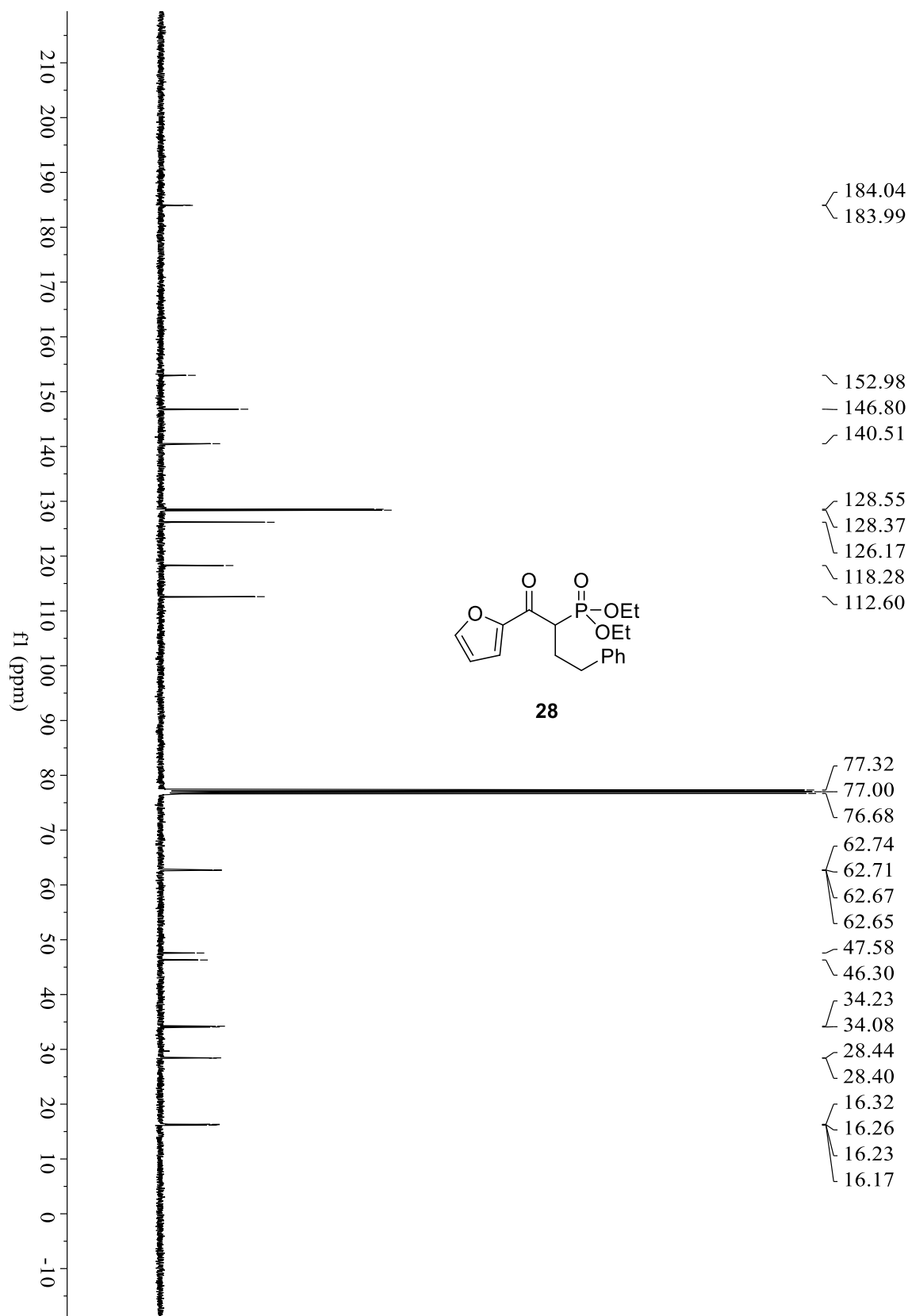






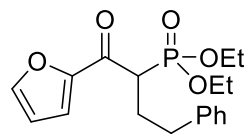
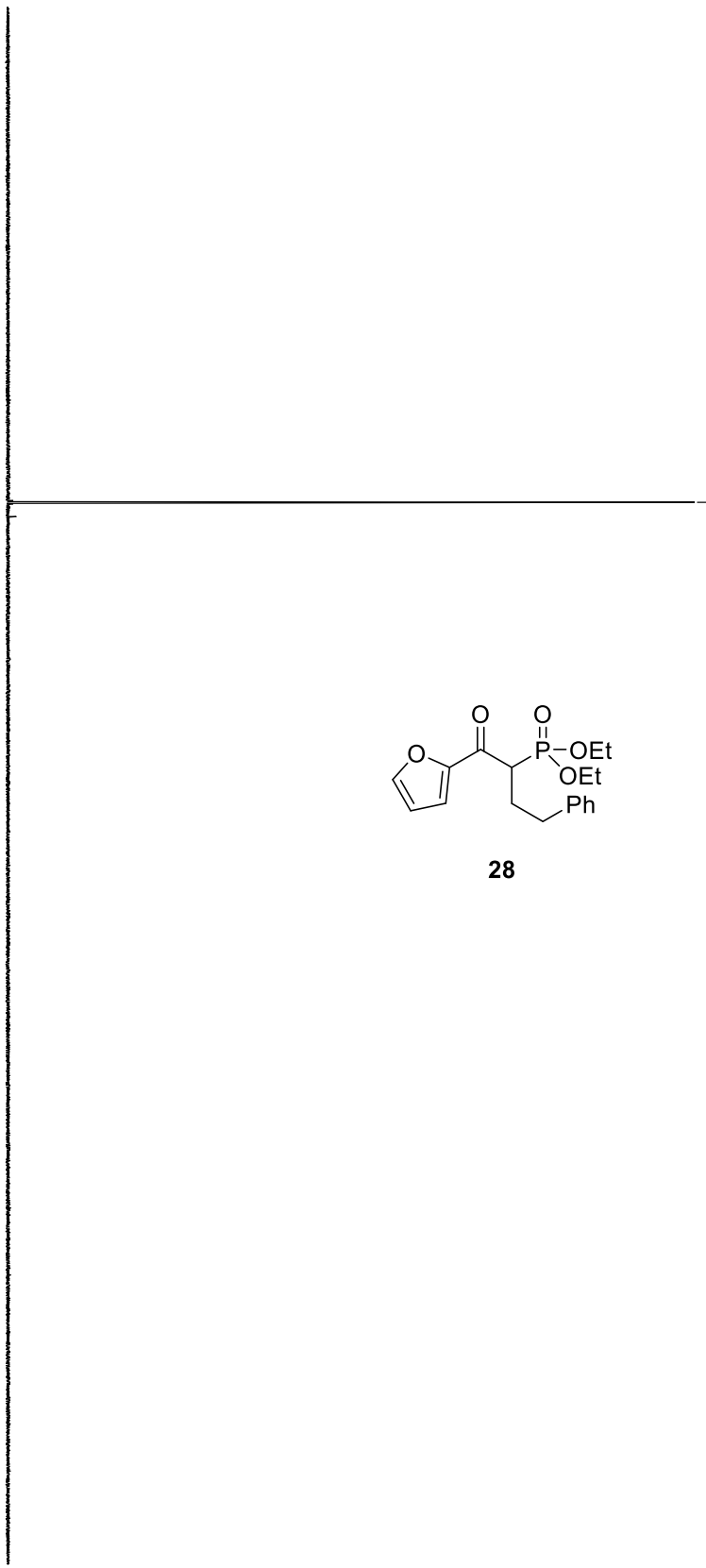




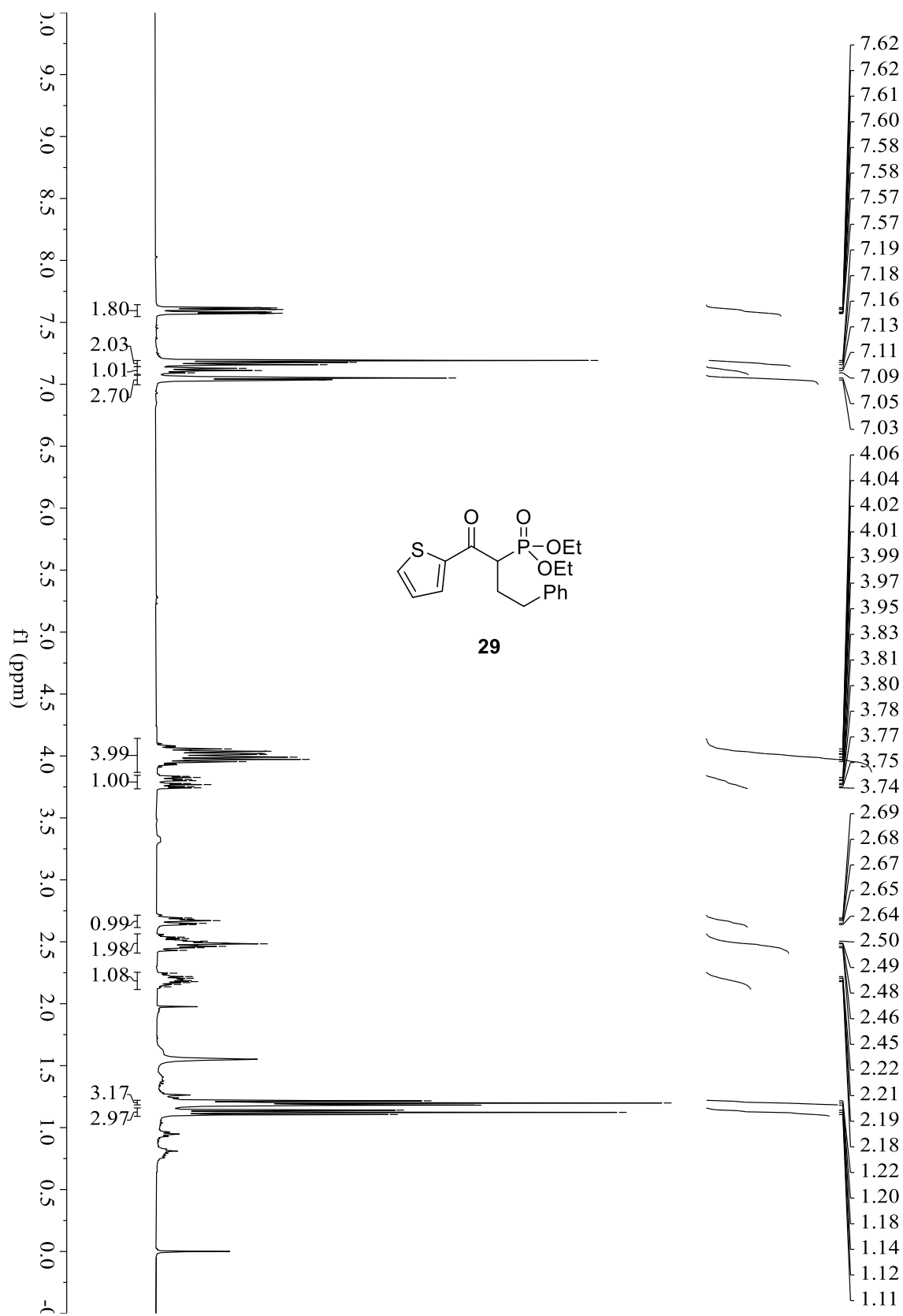


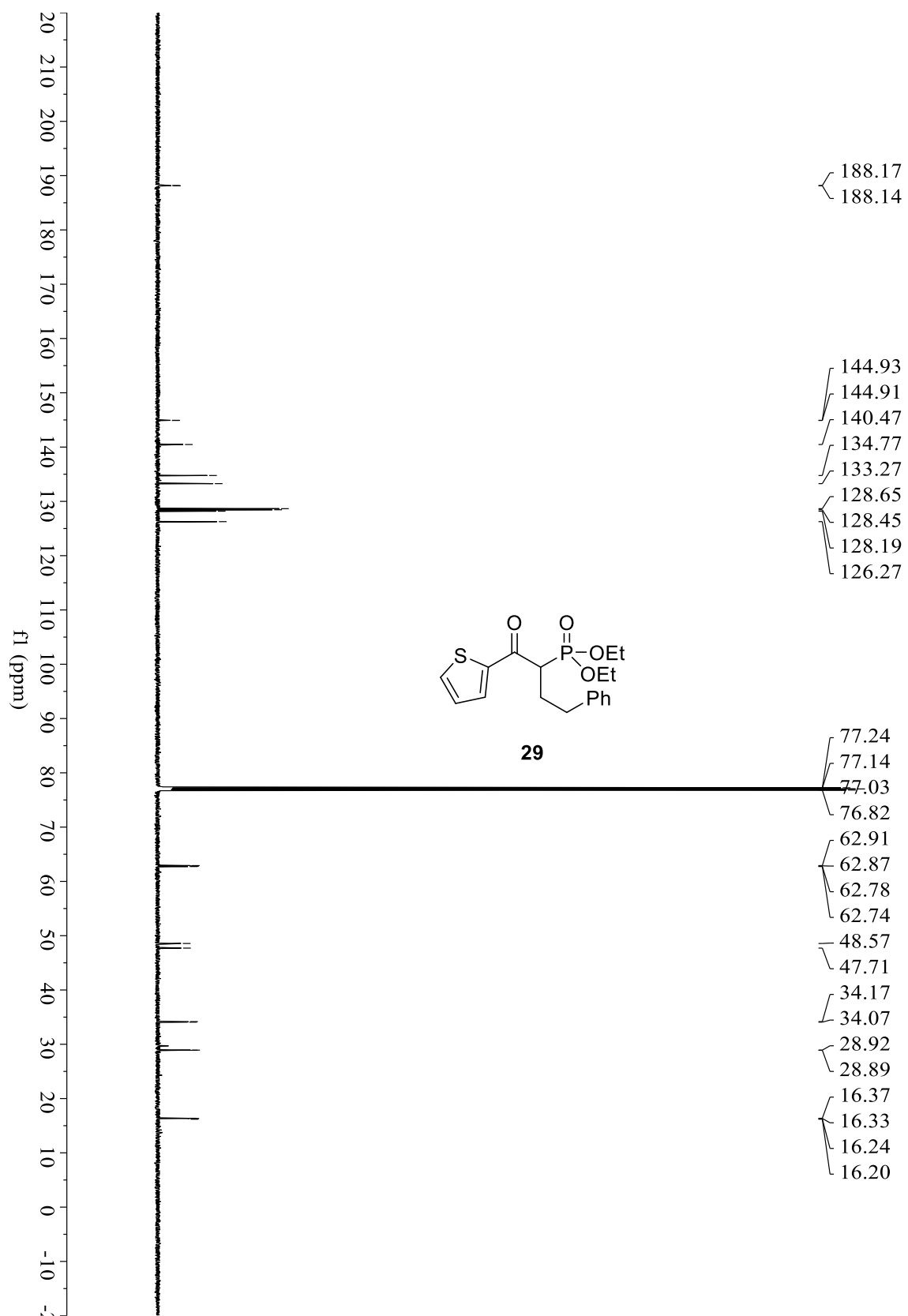
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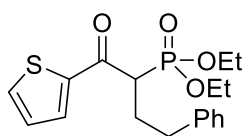
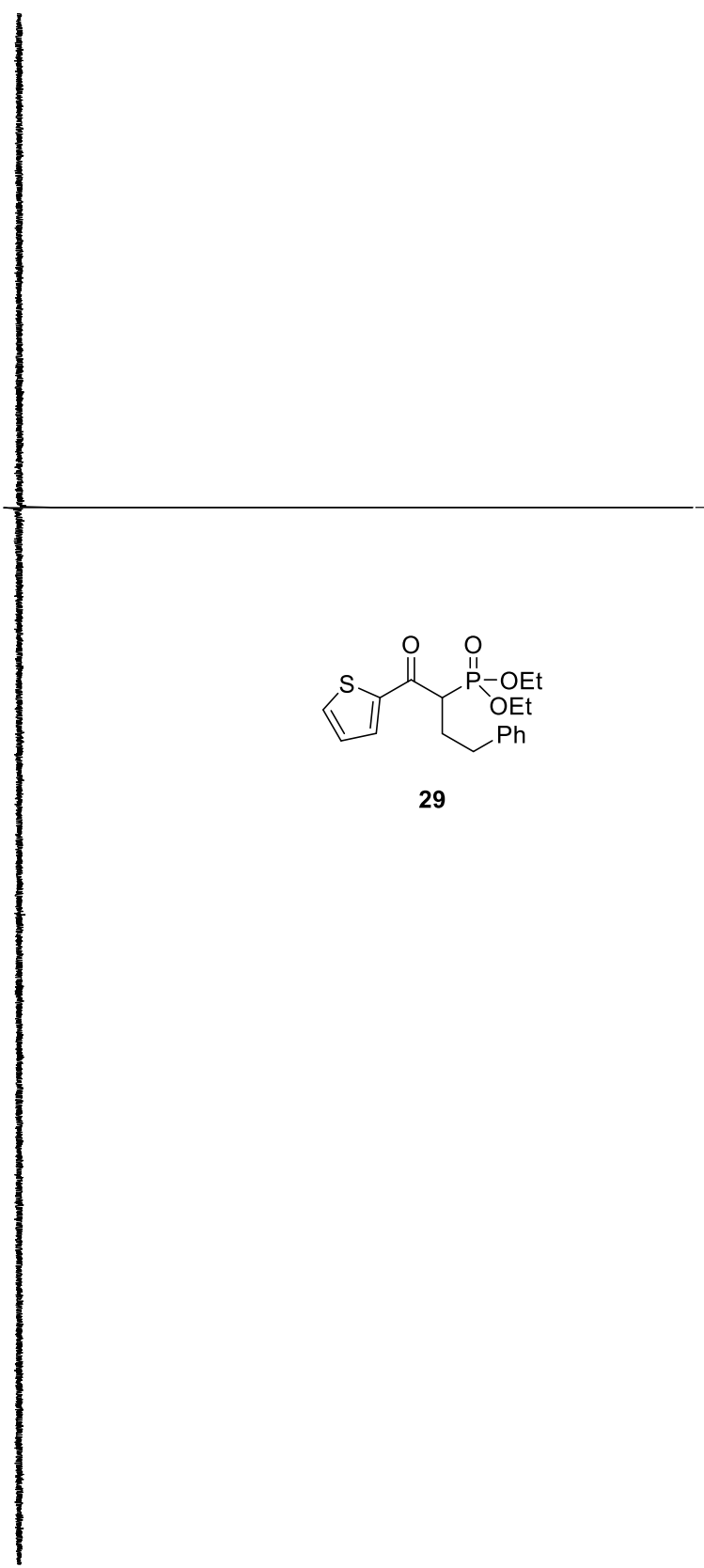


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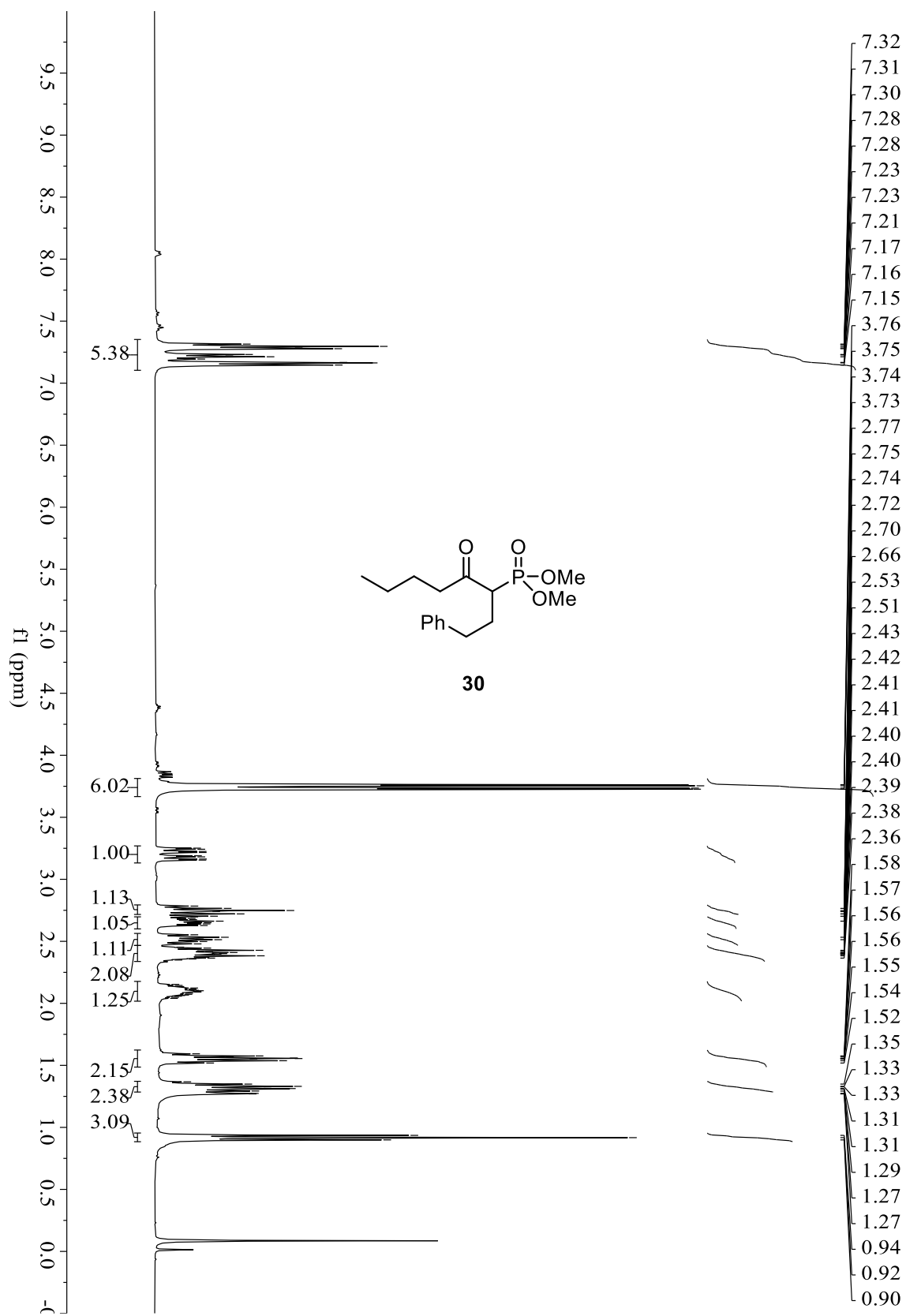




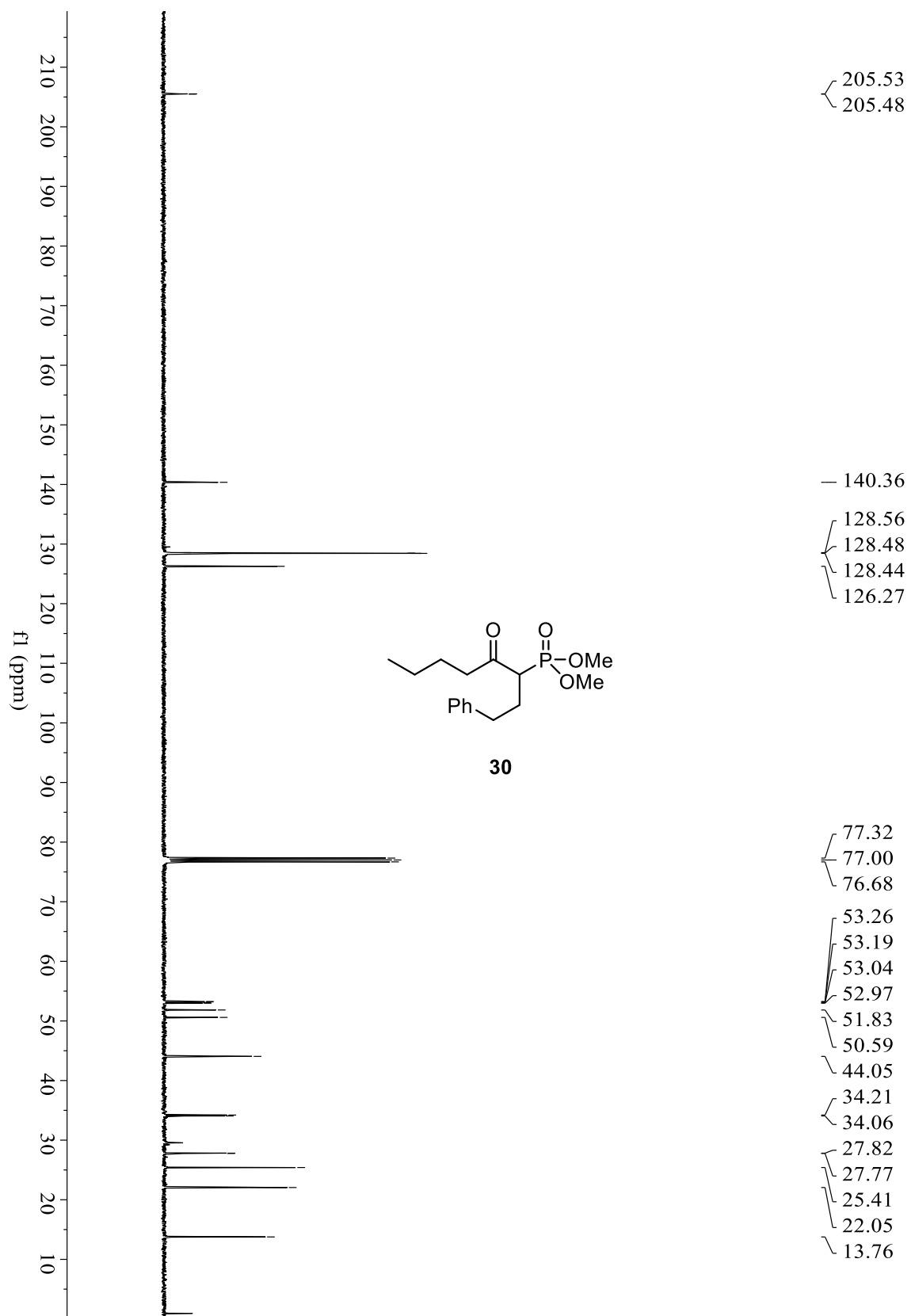
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f1 (ppm)



29

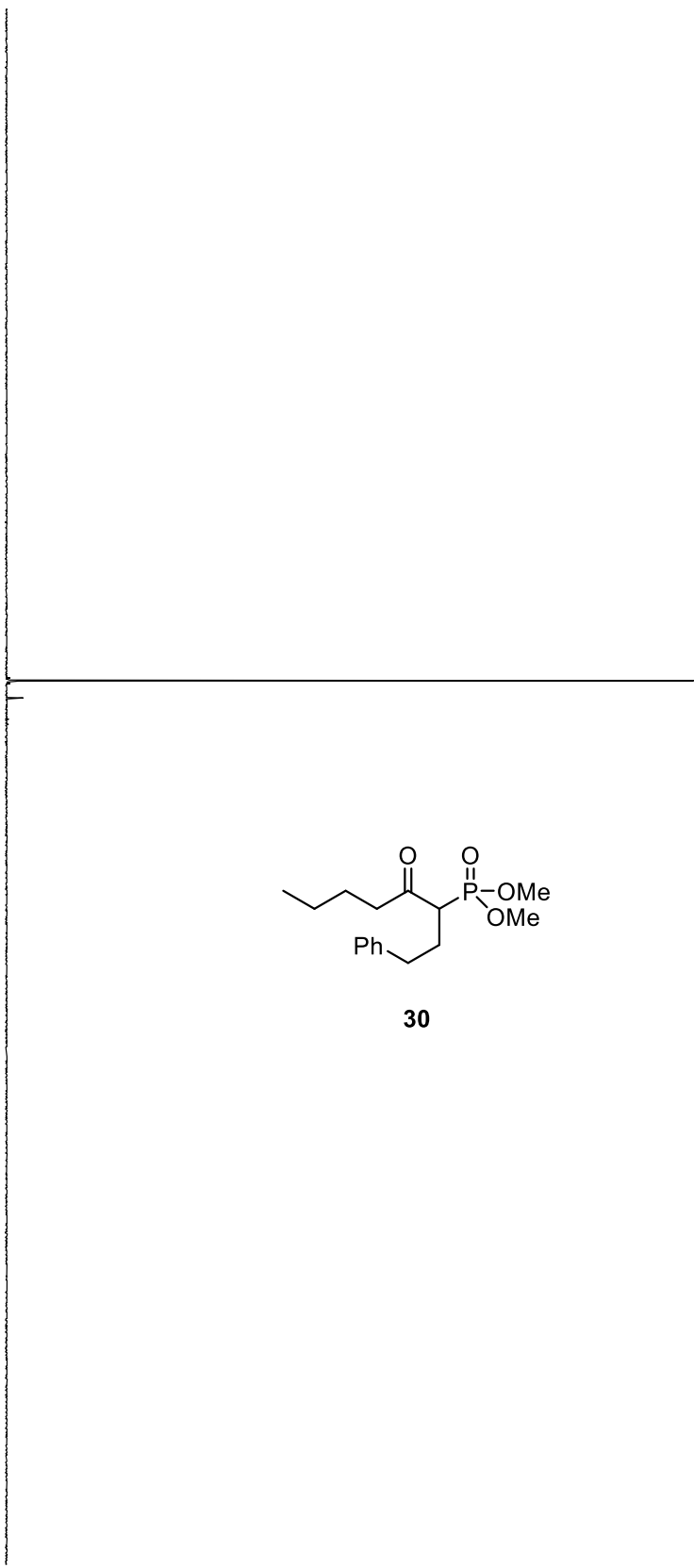




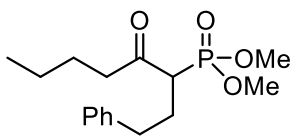


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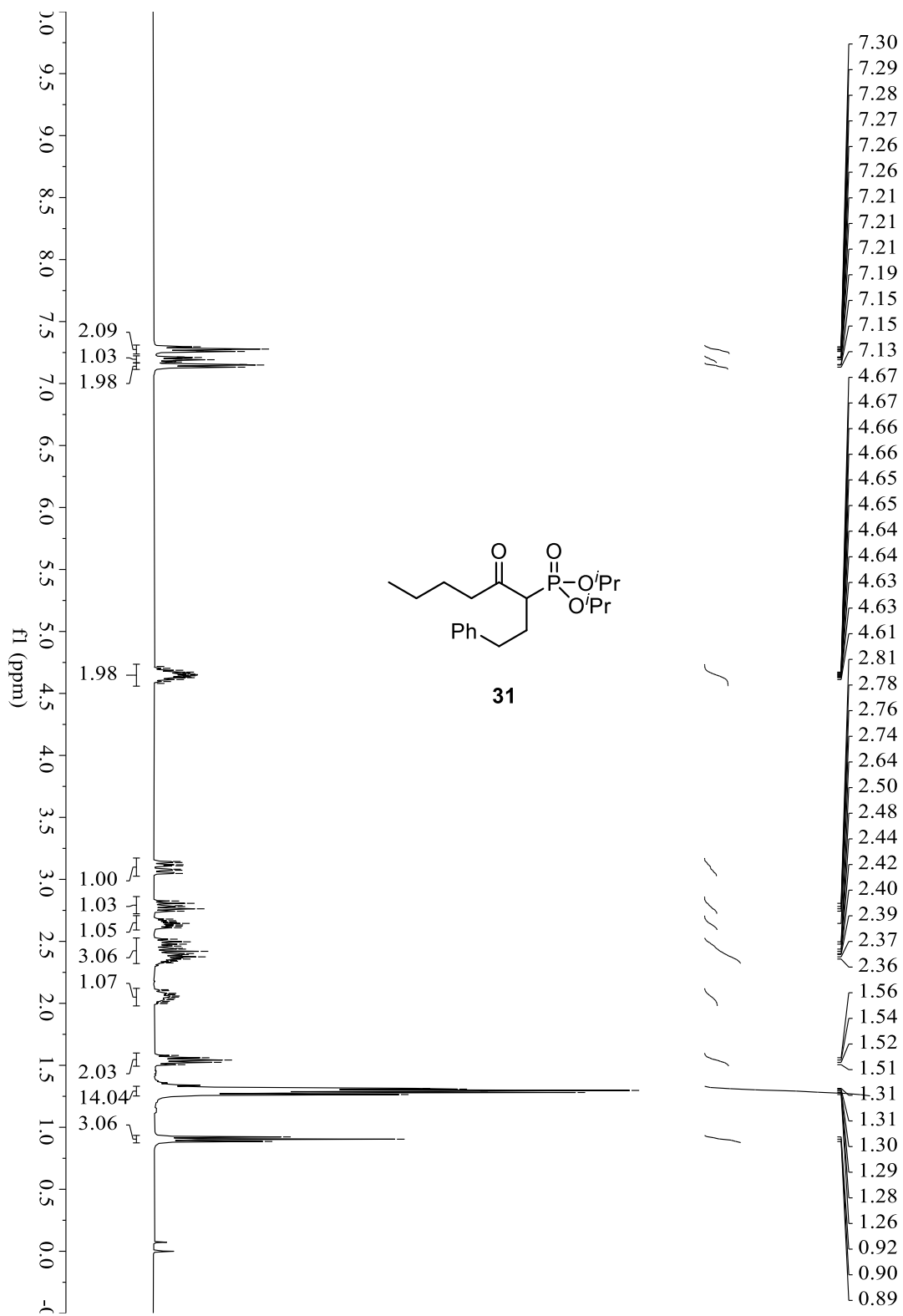
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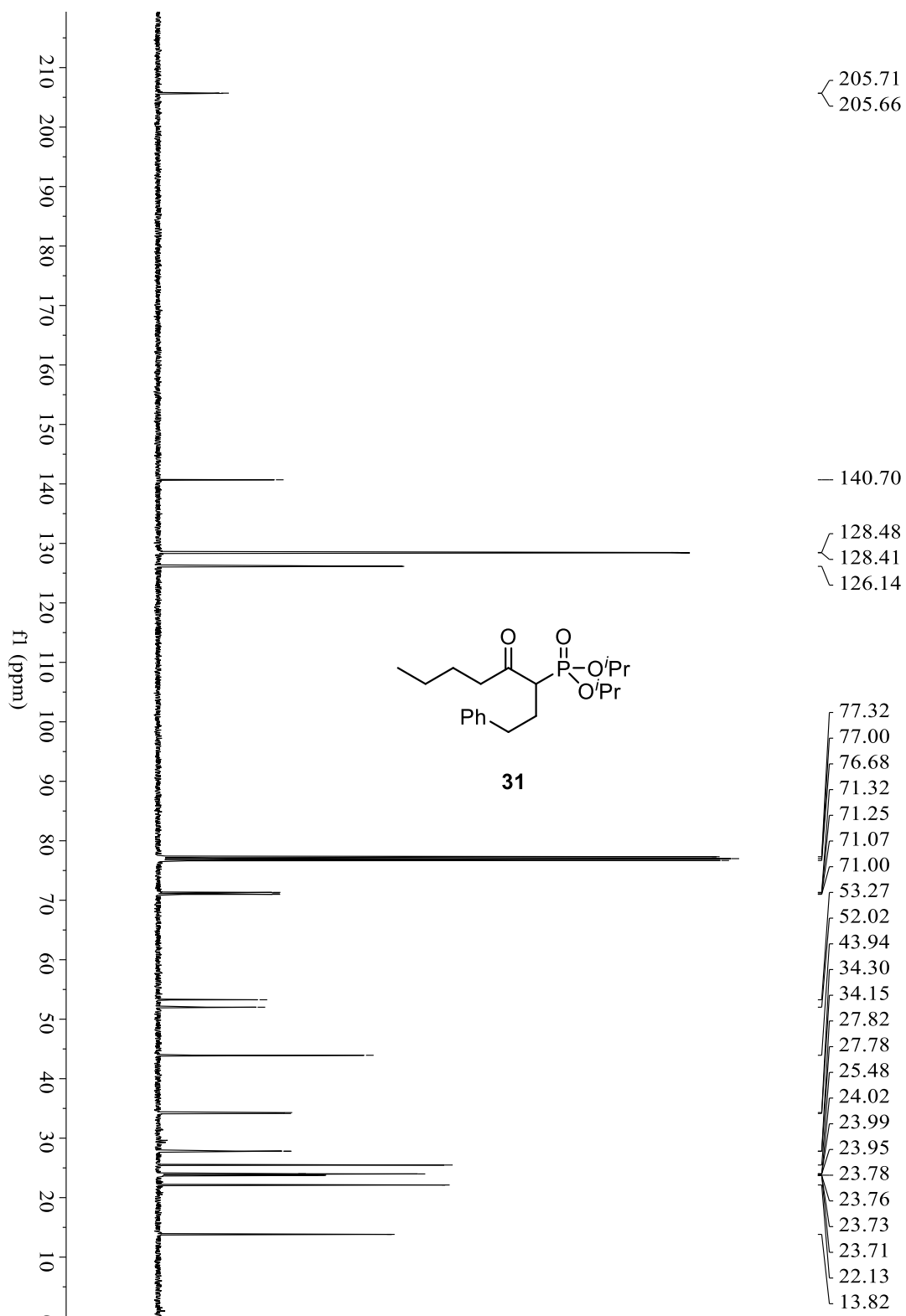


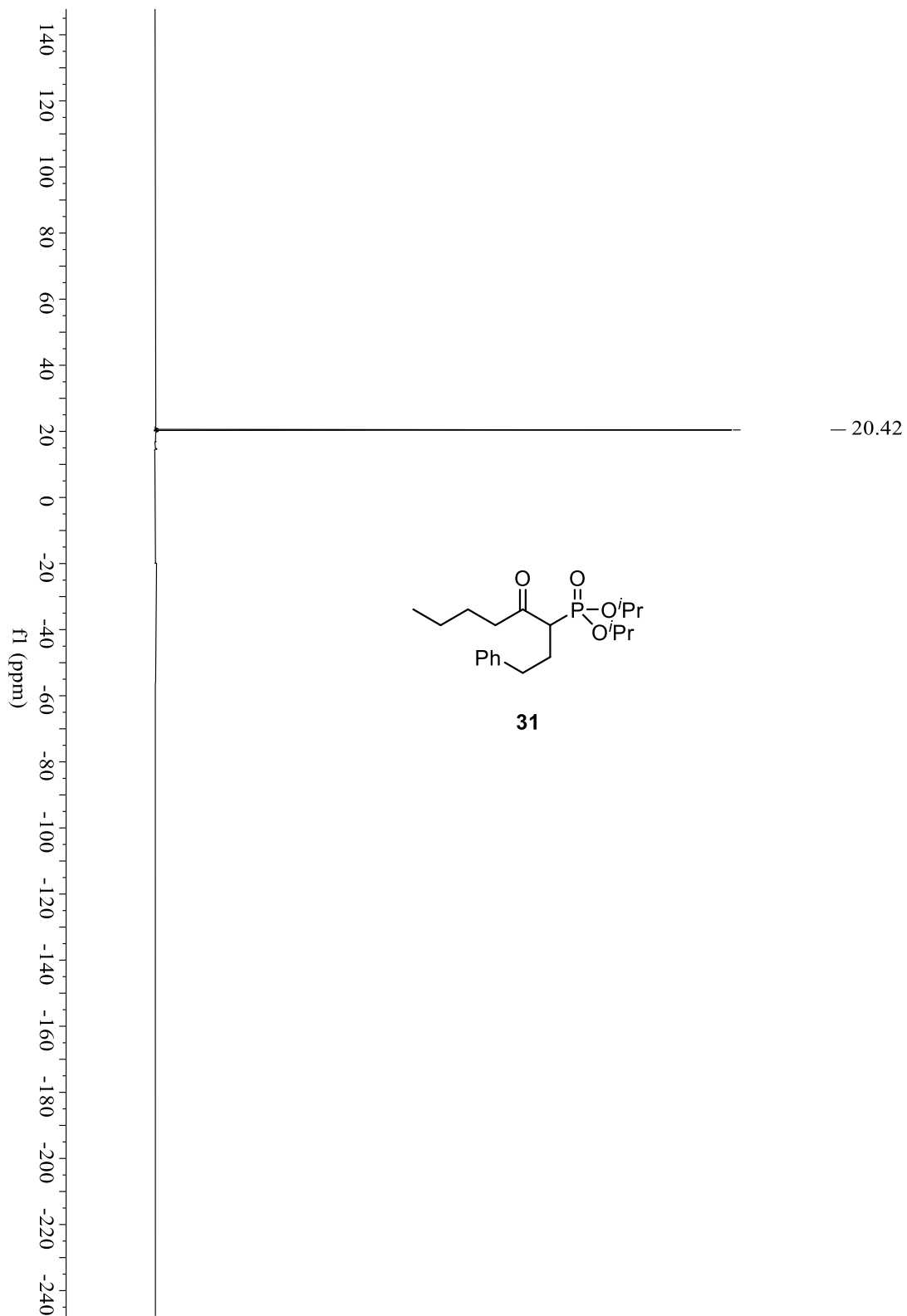
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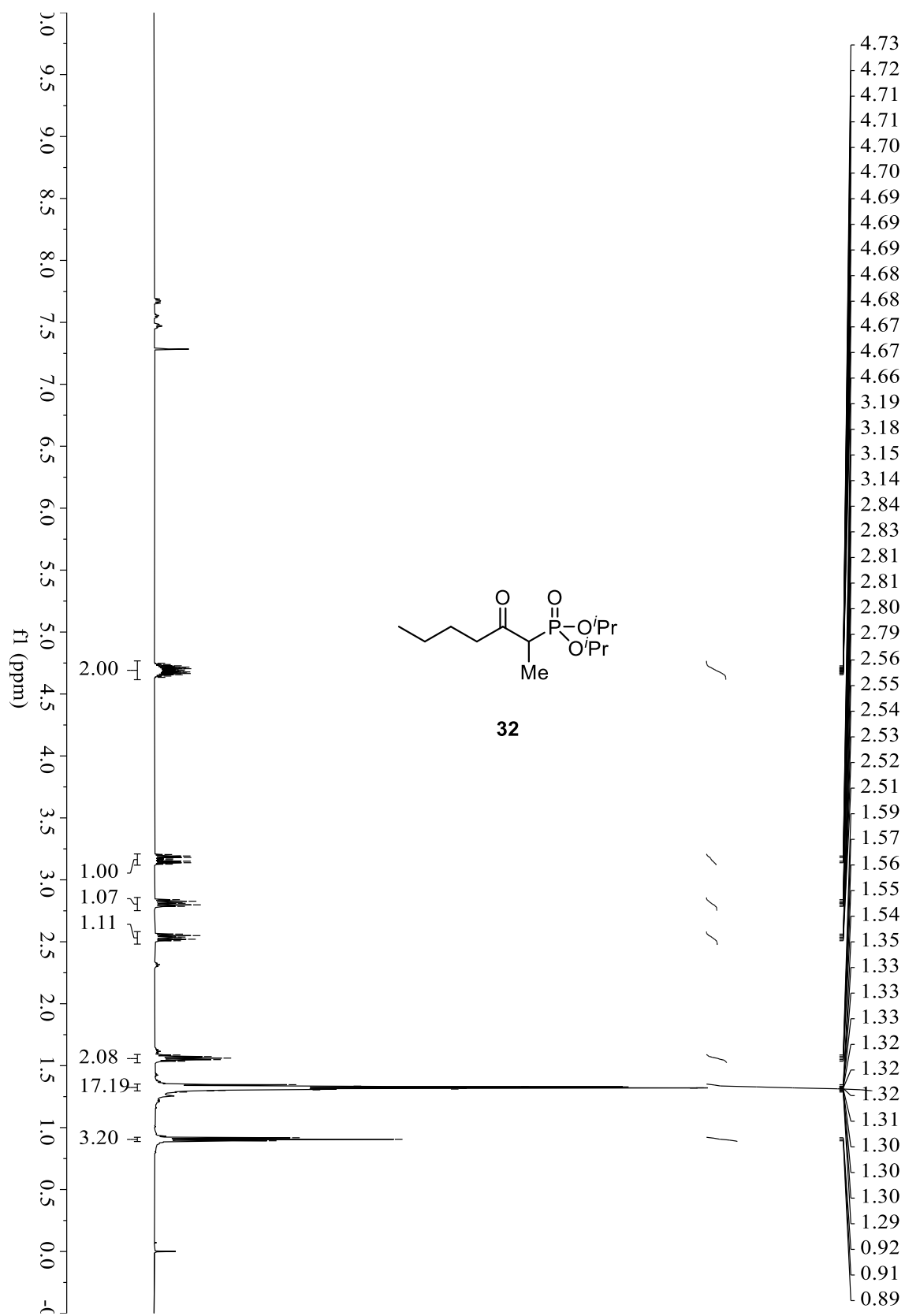


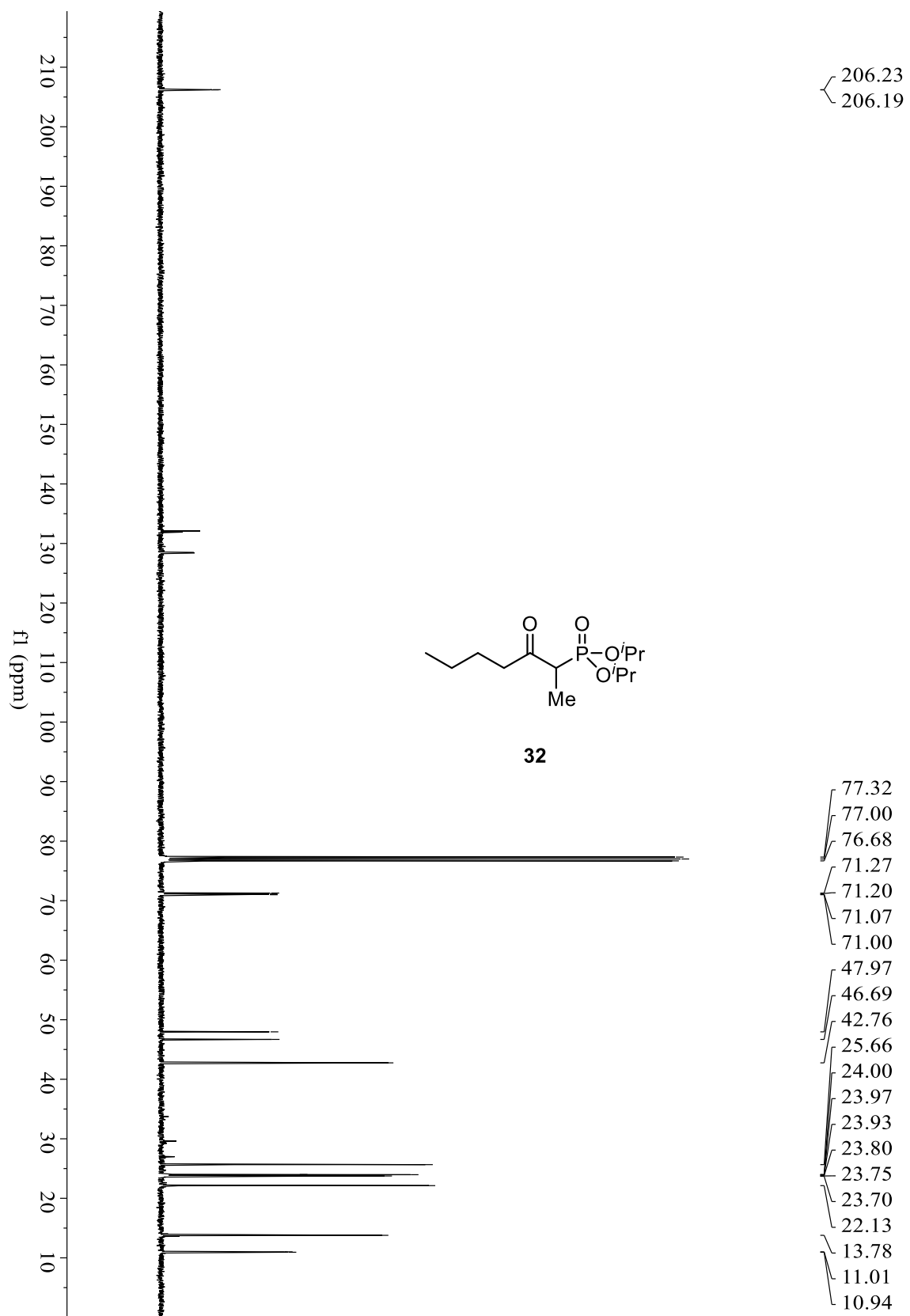
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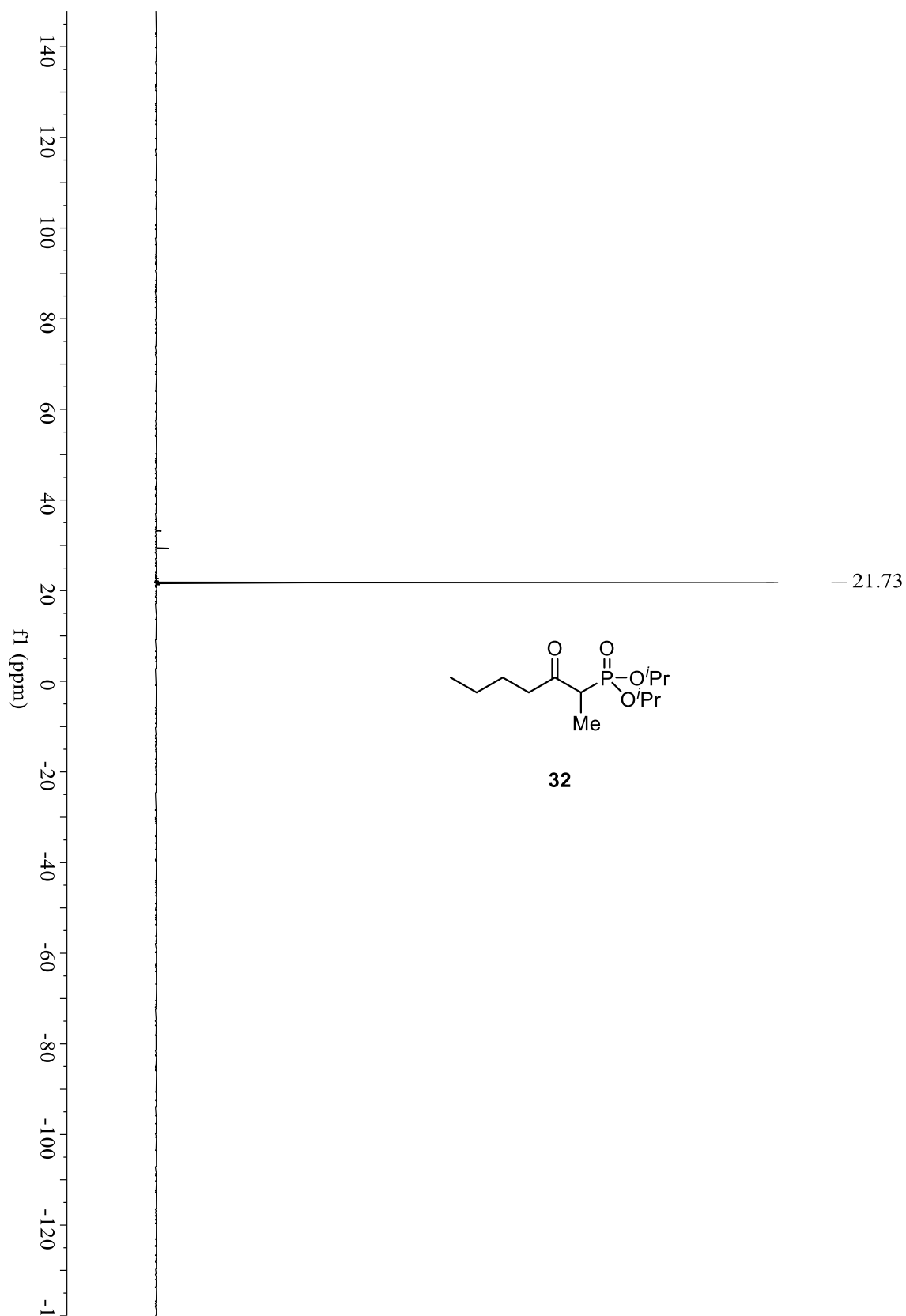




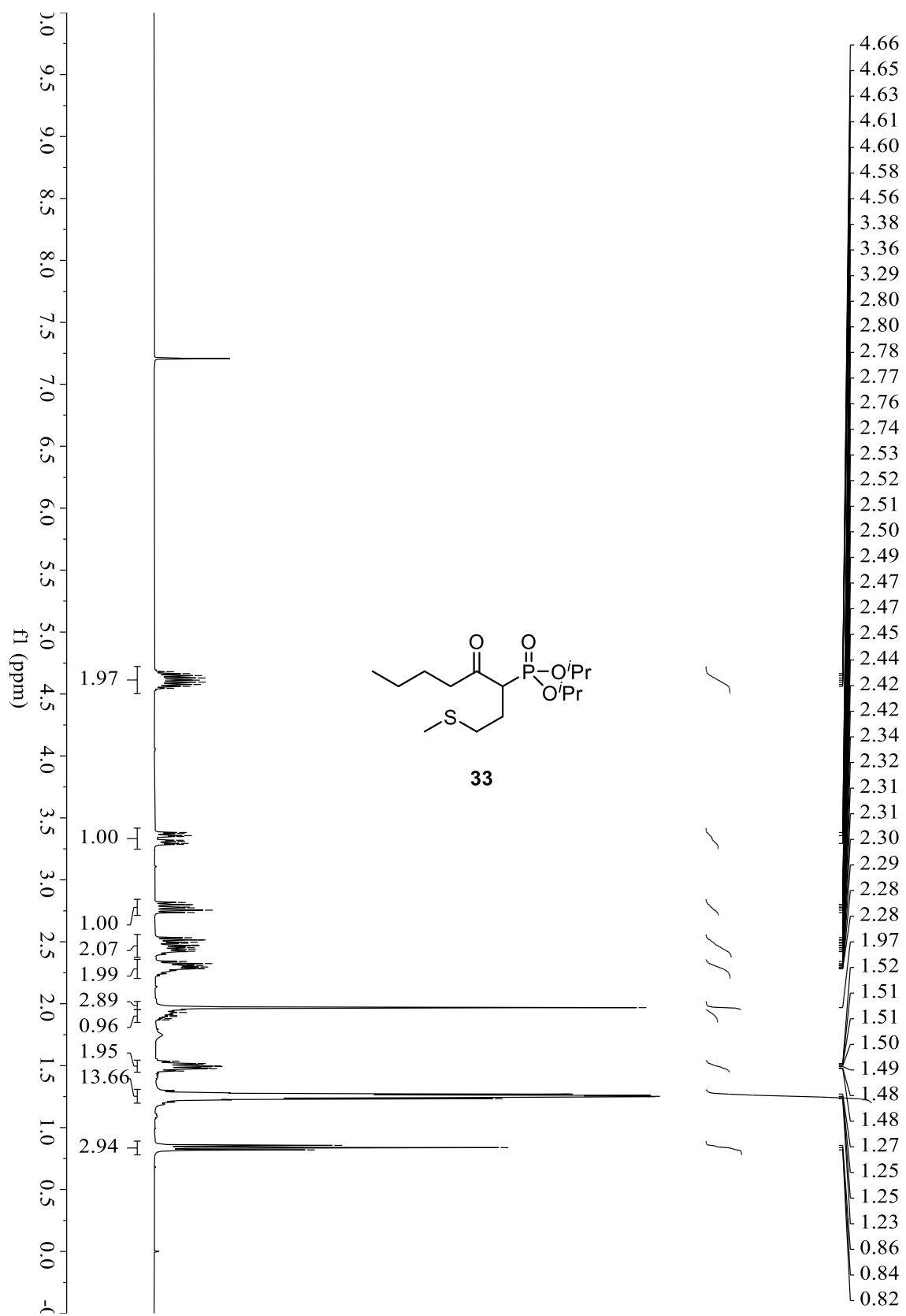


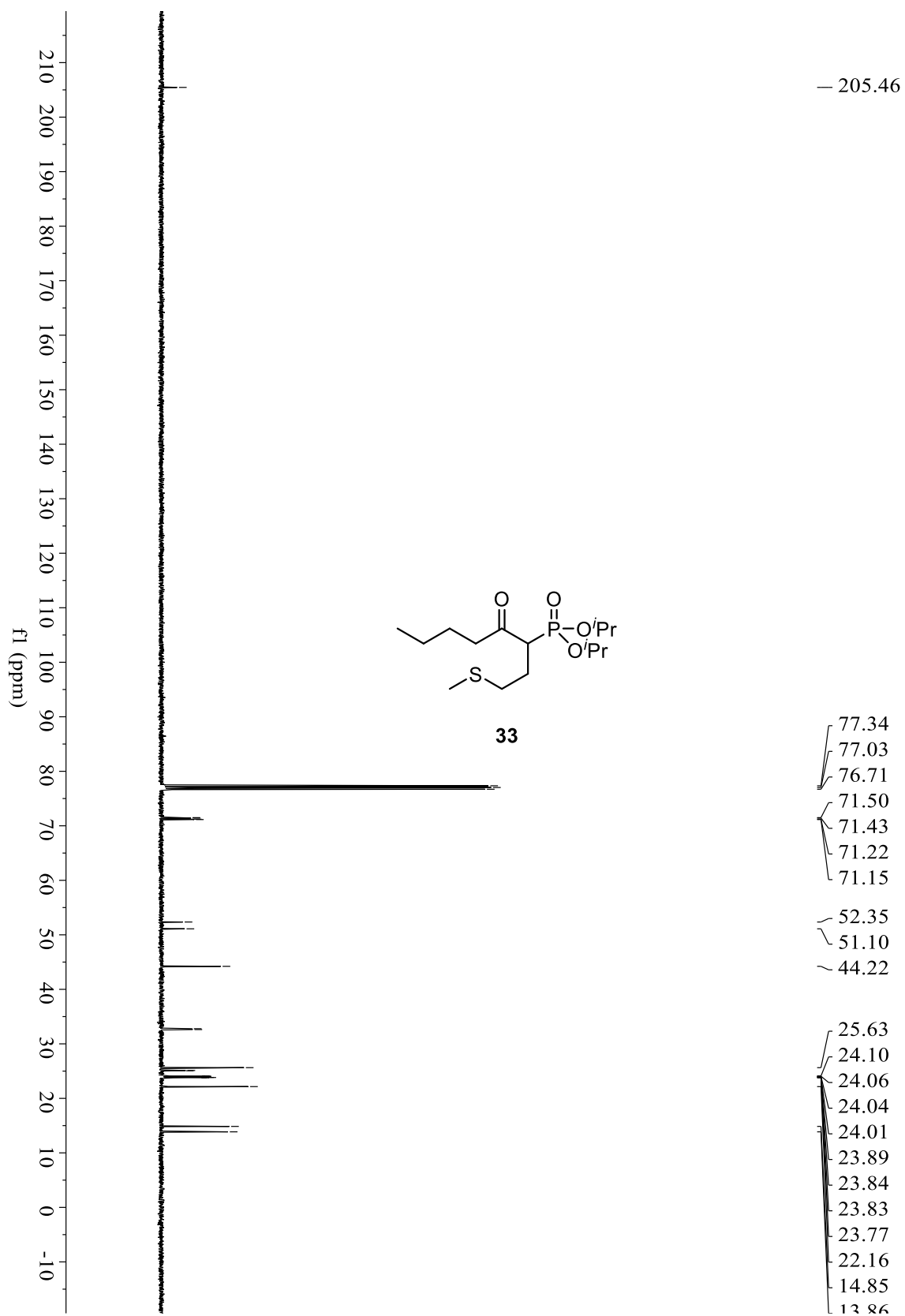




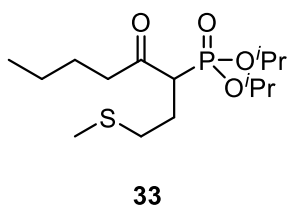
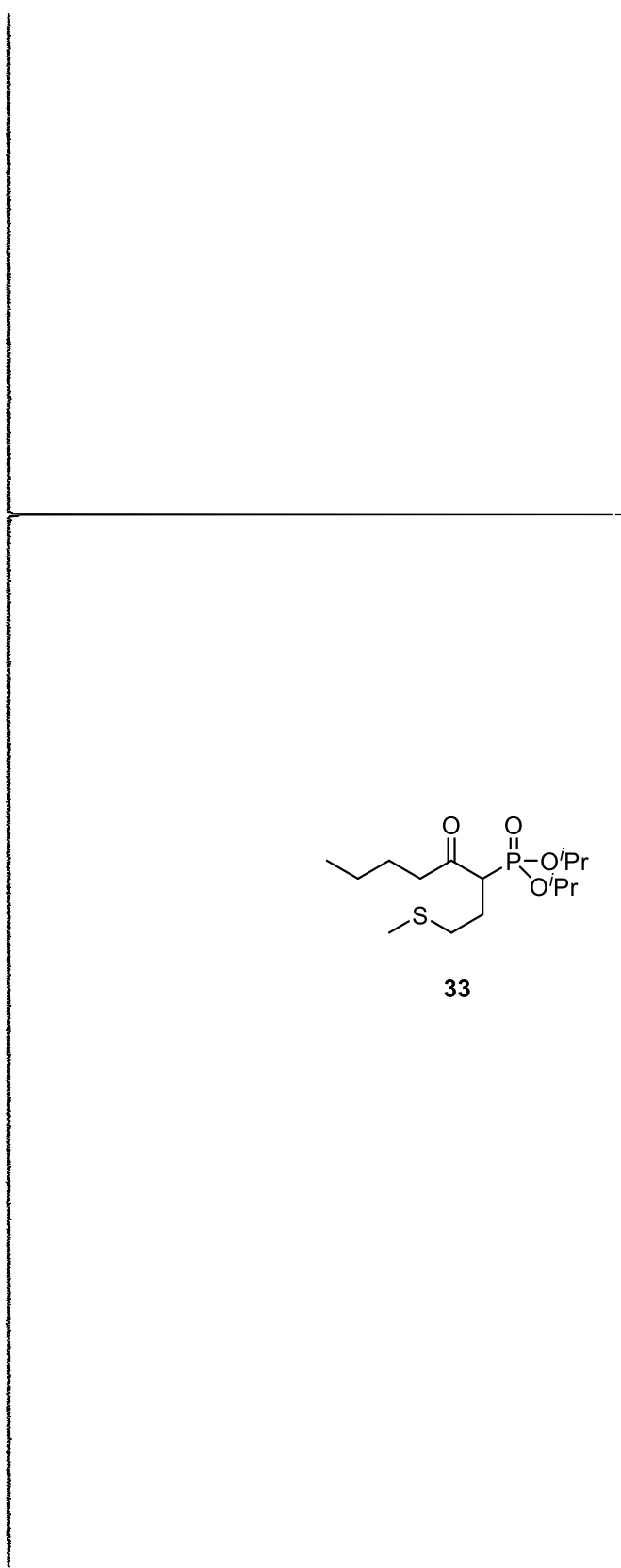


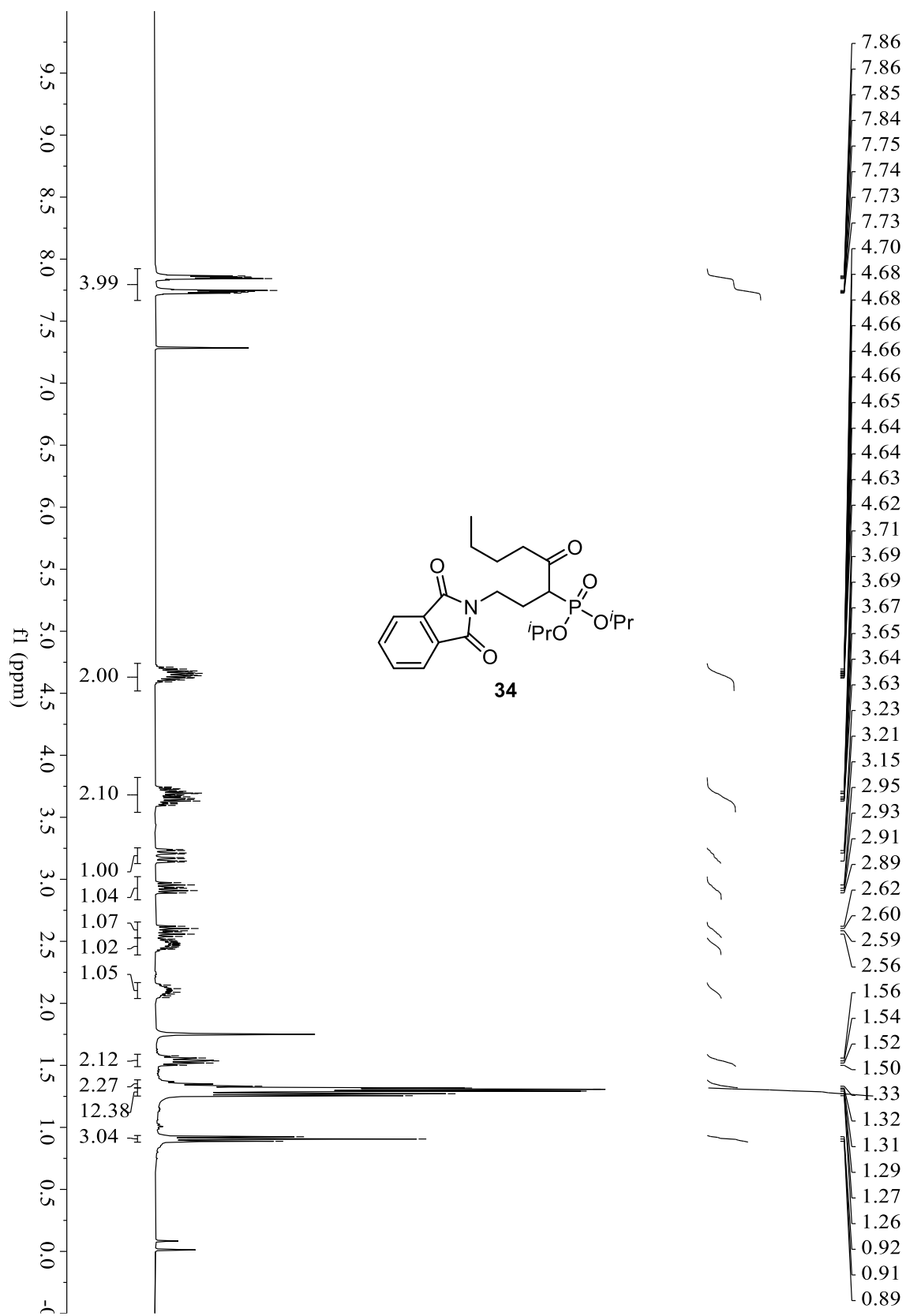


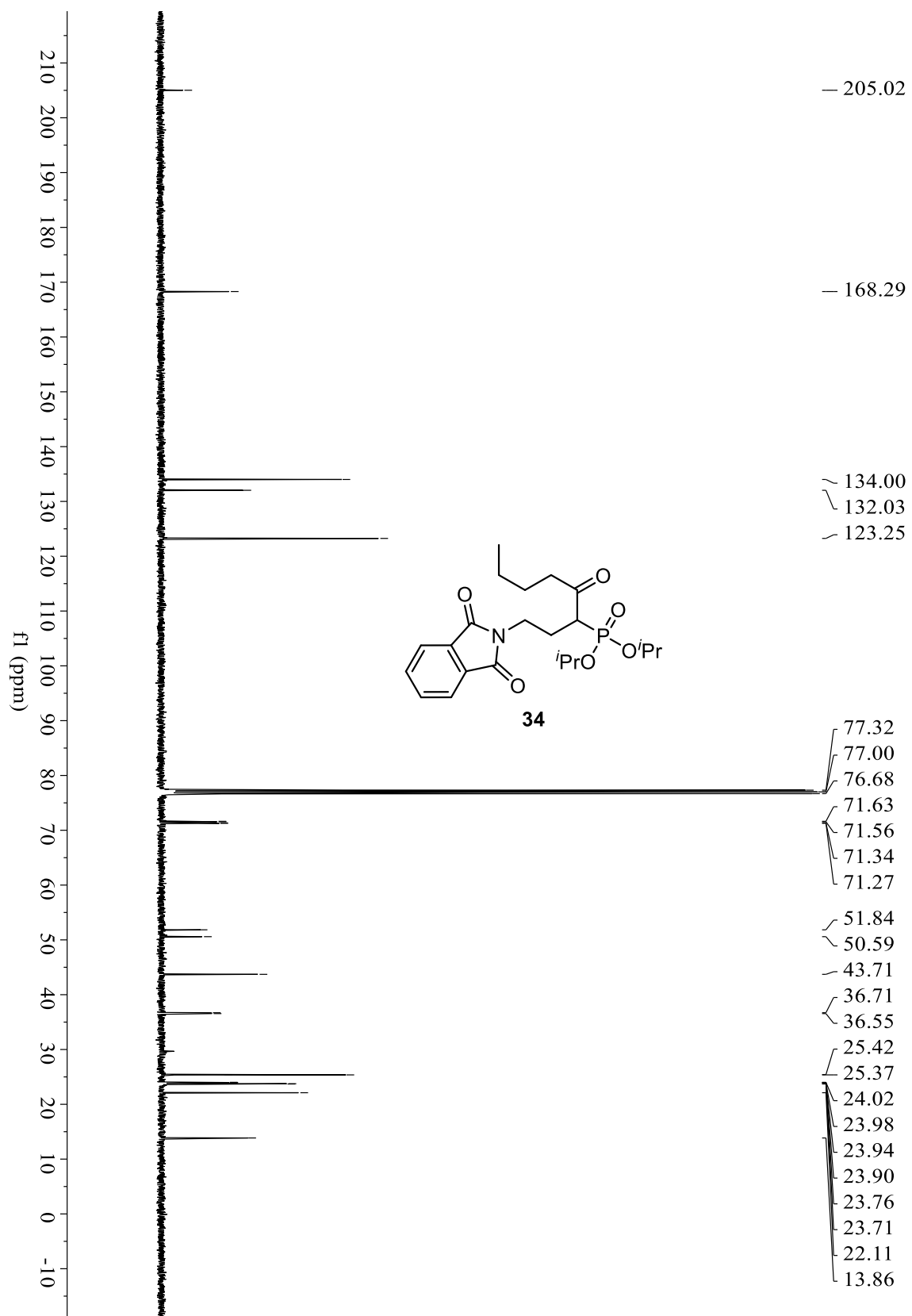




f1 (ppm)



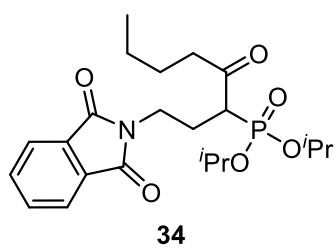


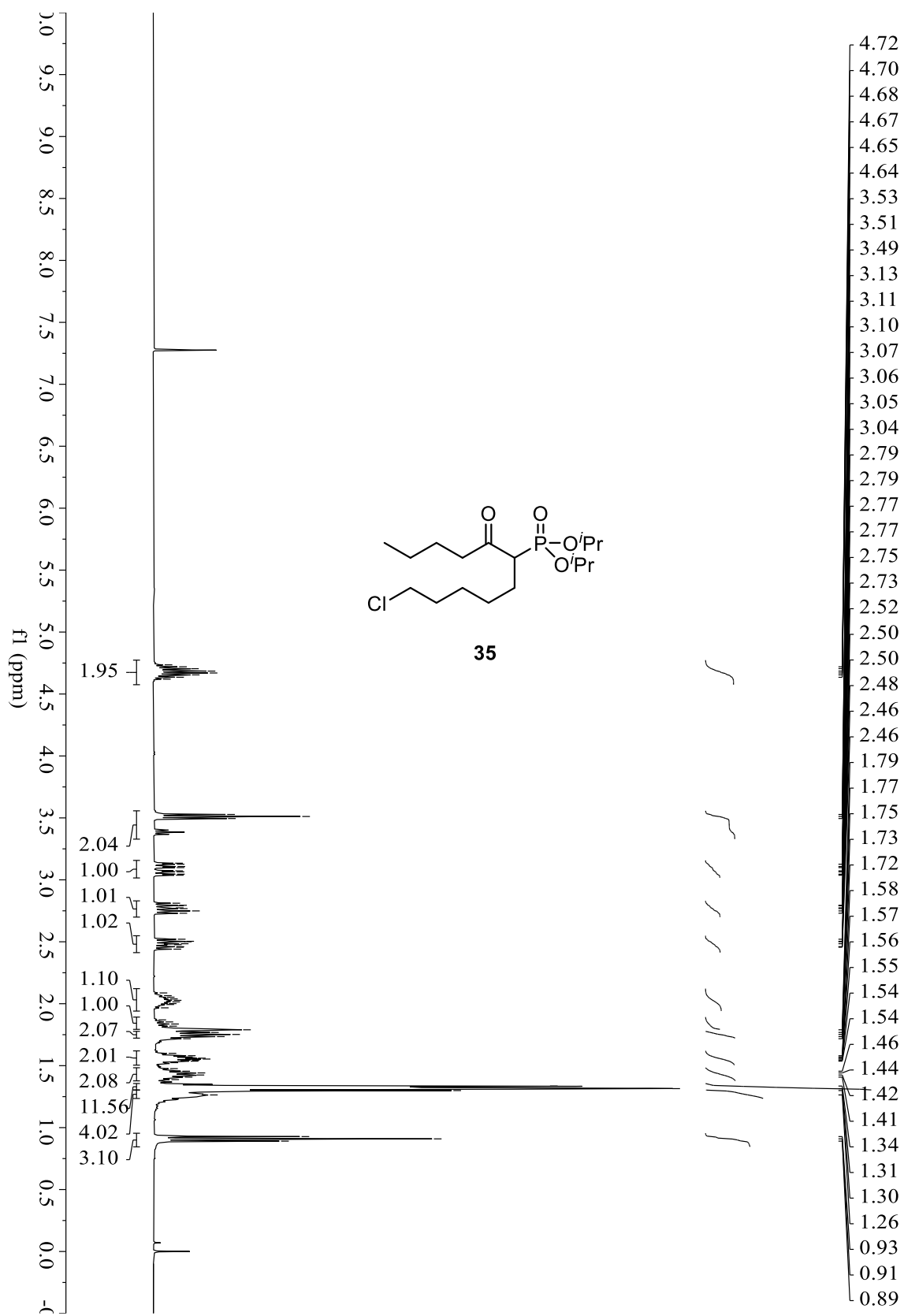


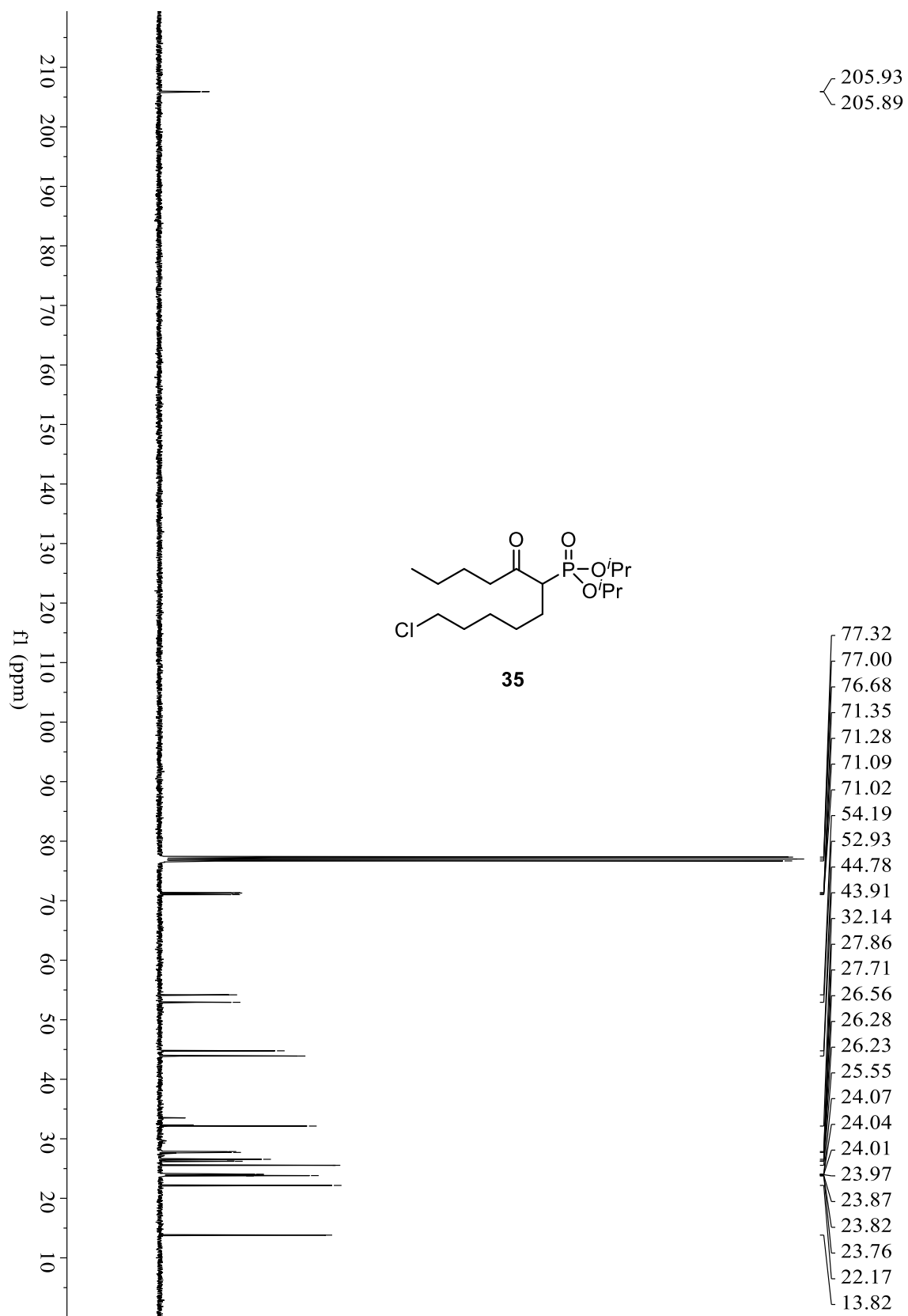
f1 (ppm)

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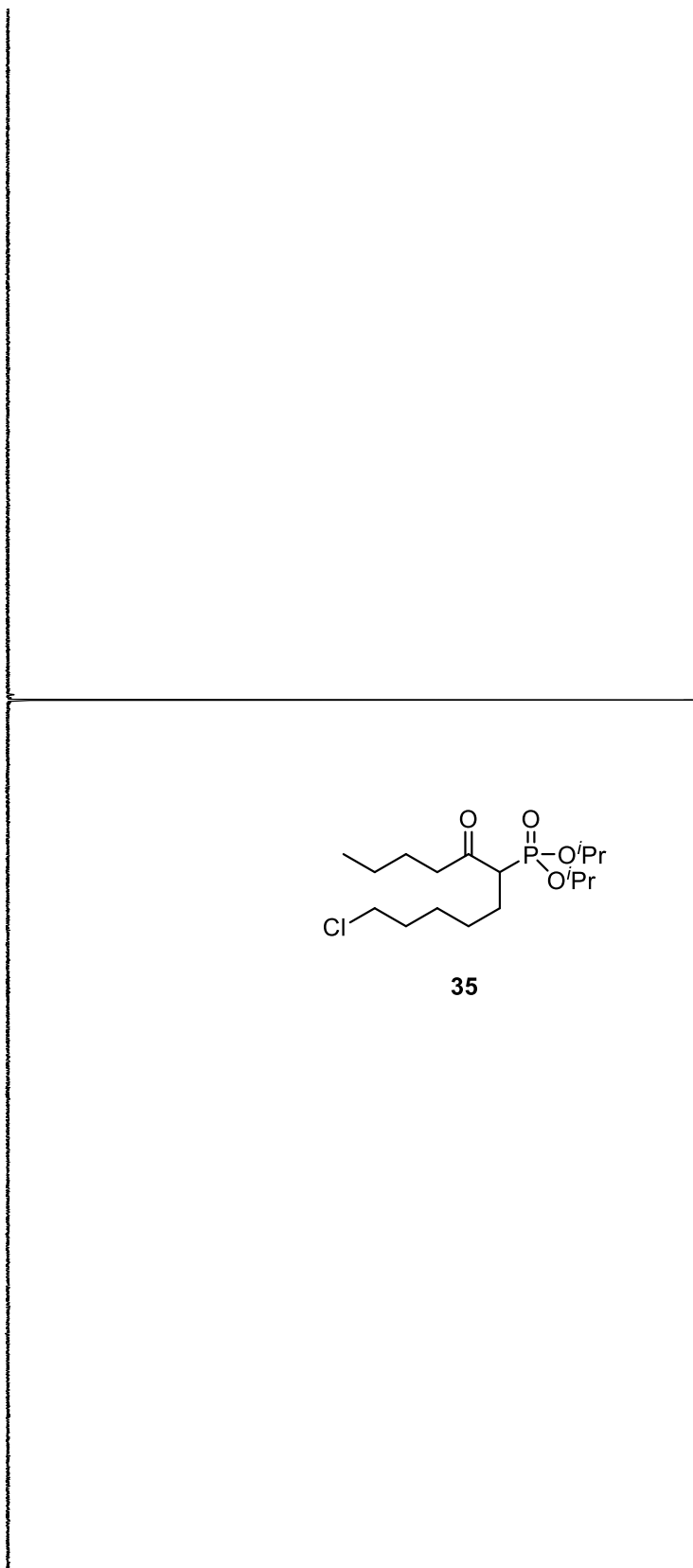




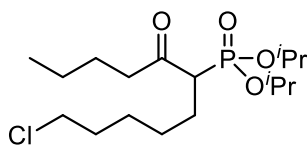


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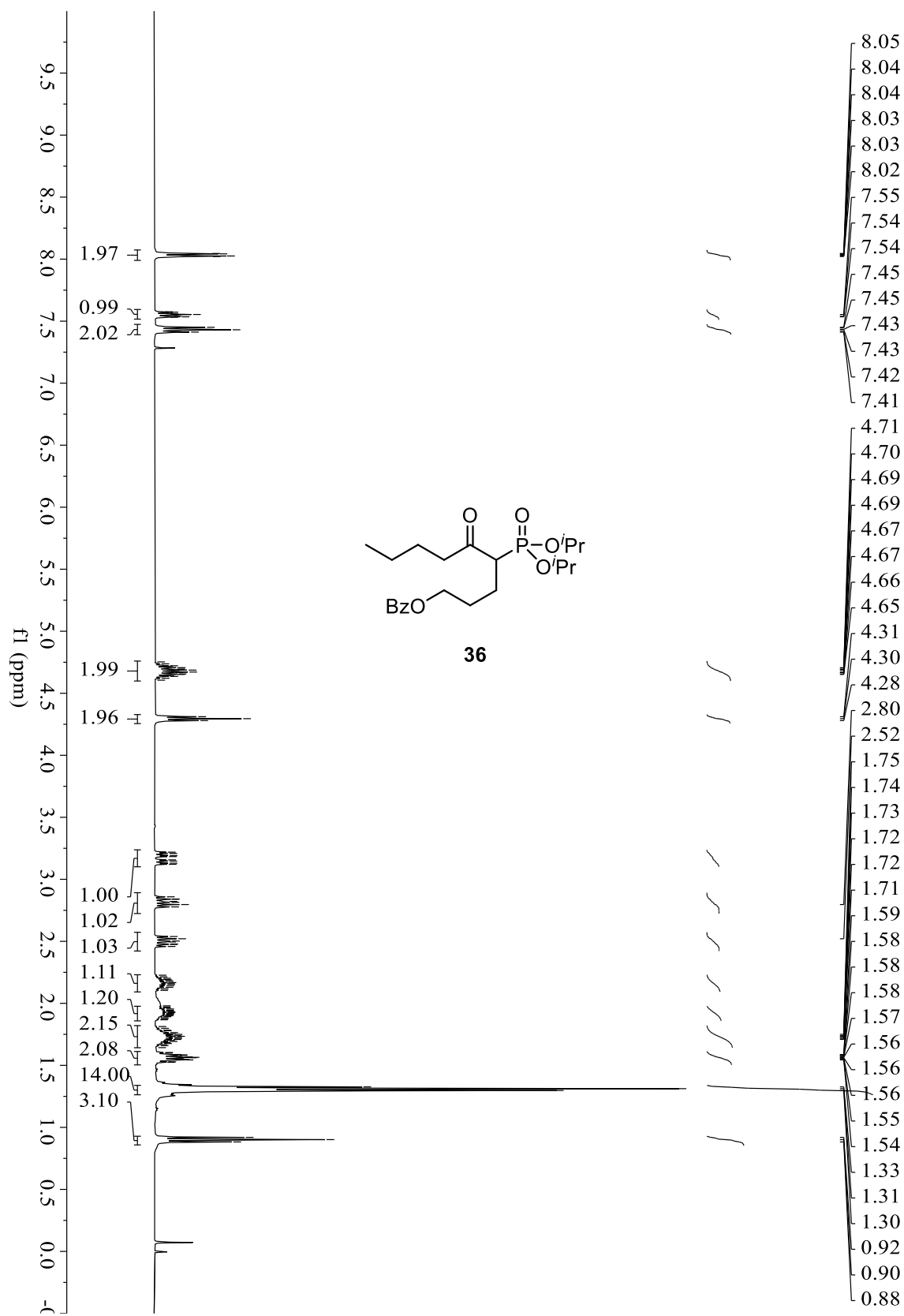
f1 (ppm)

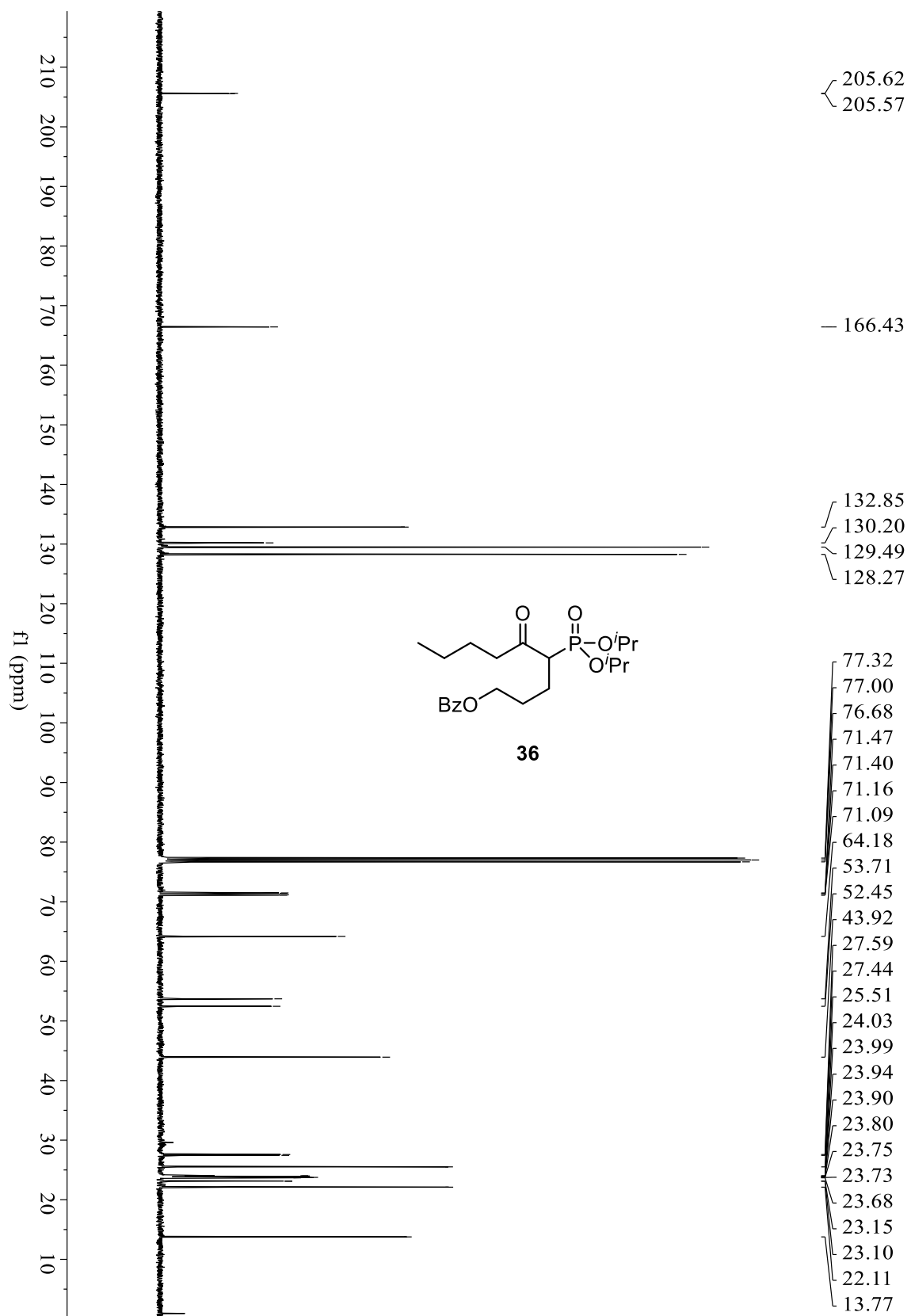


— 20.51



**35**

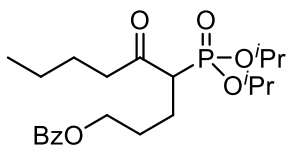




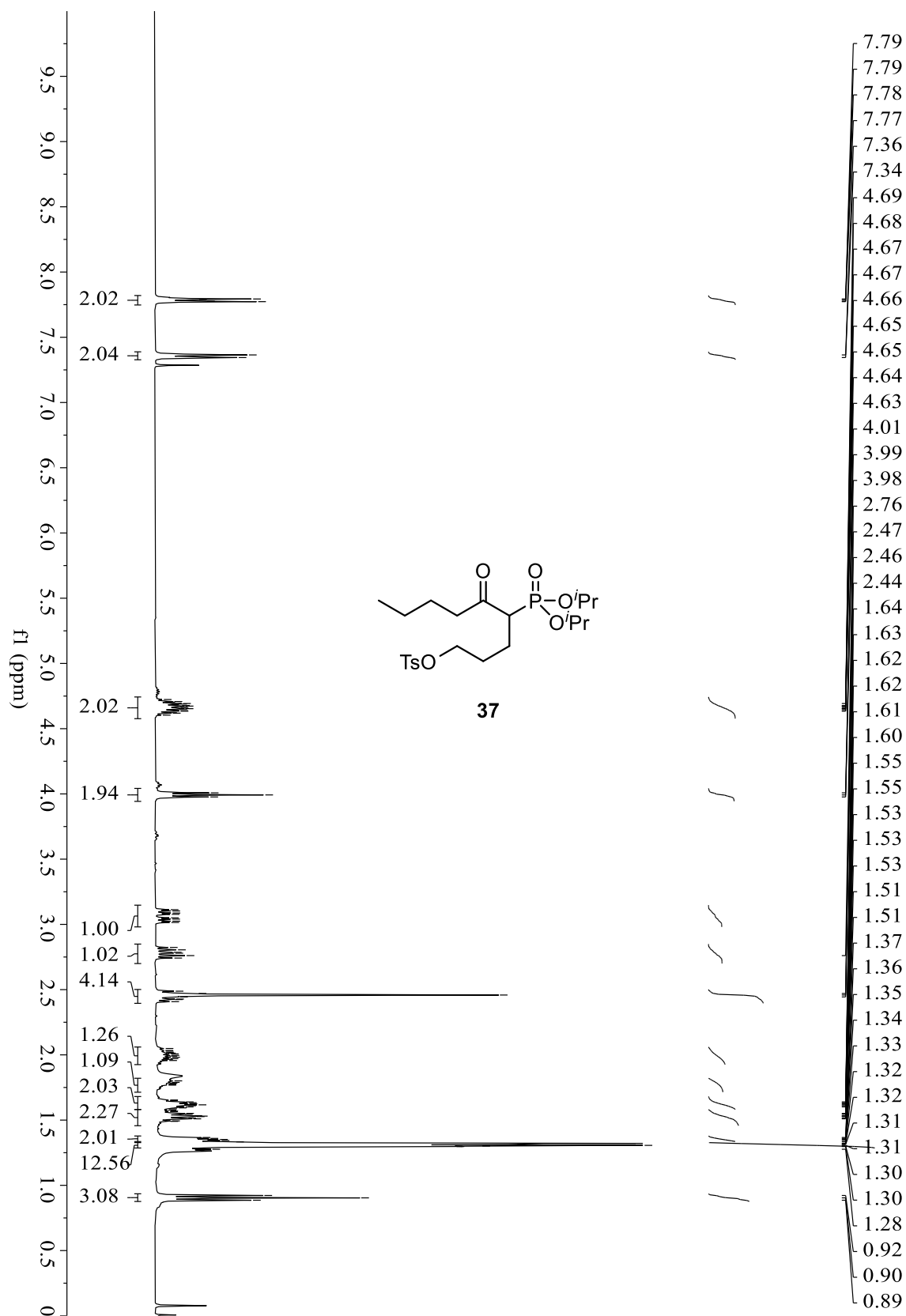
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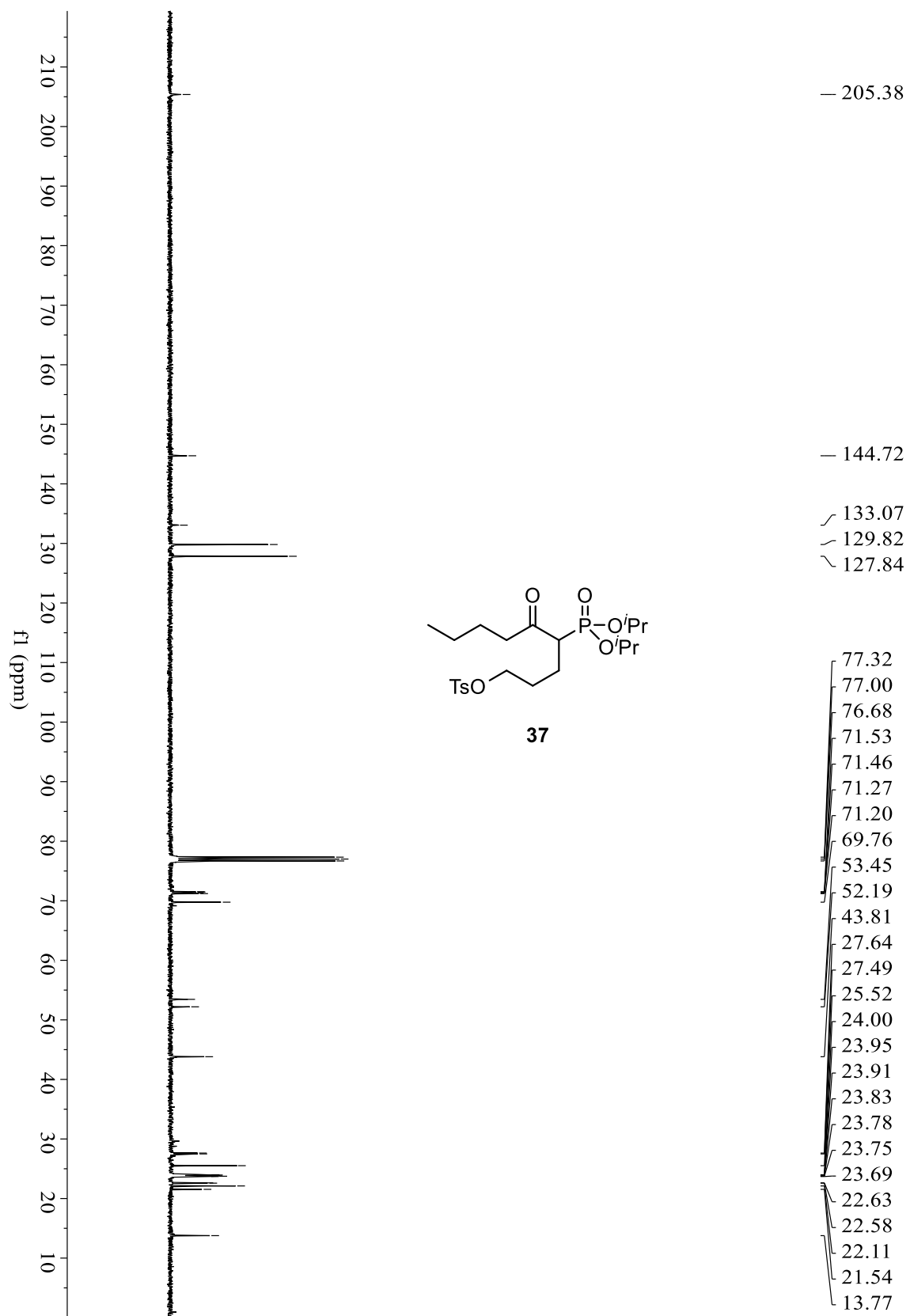
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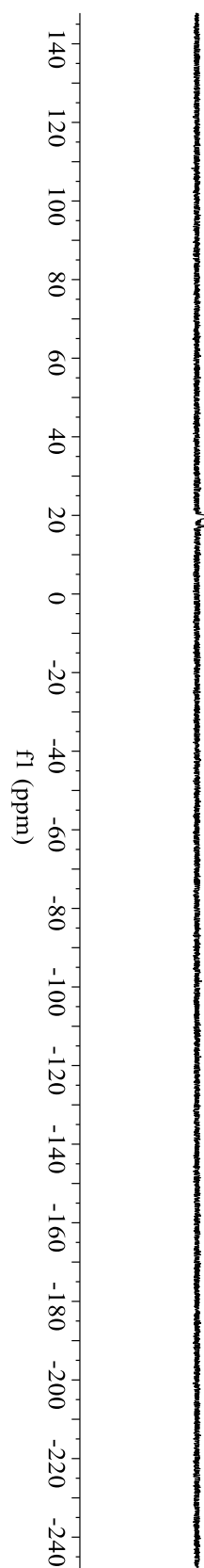
— 20.05



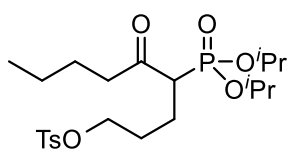
**36**



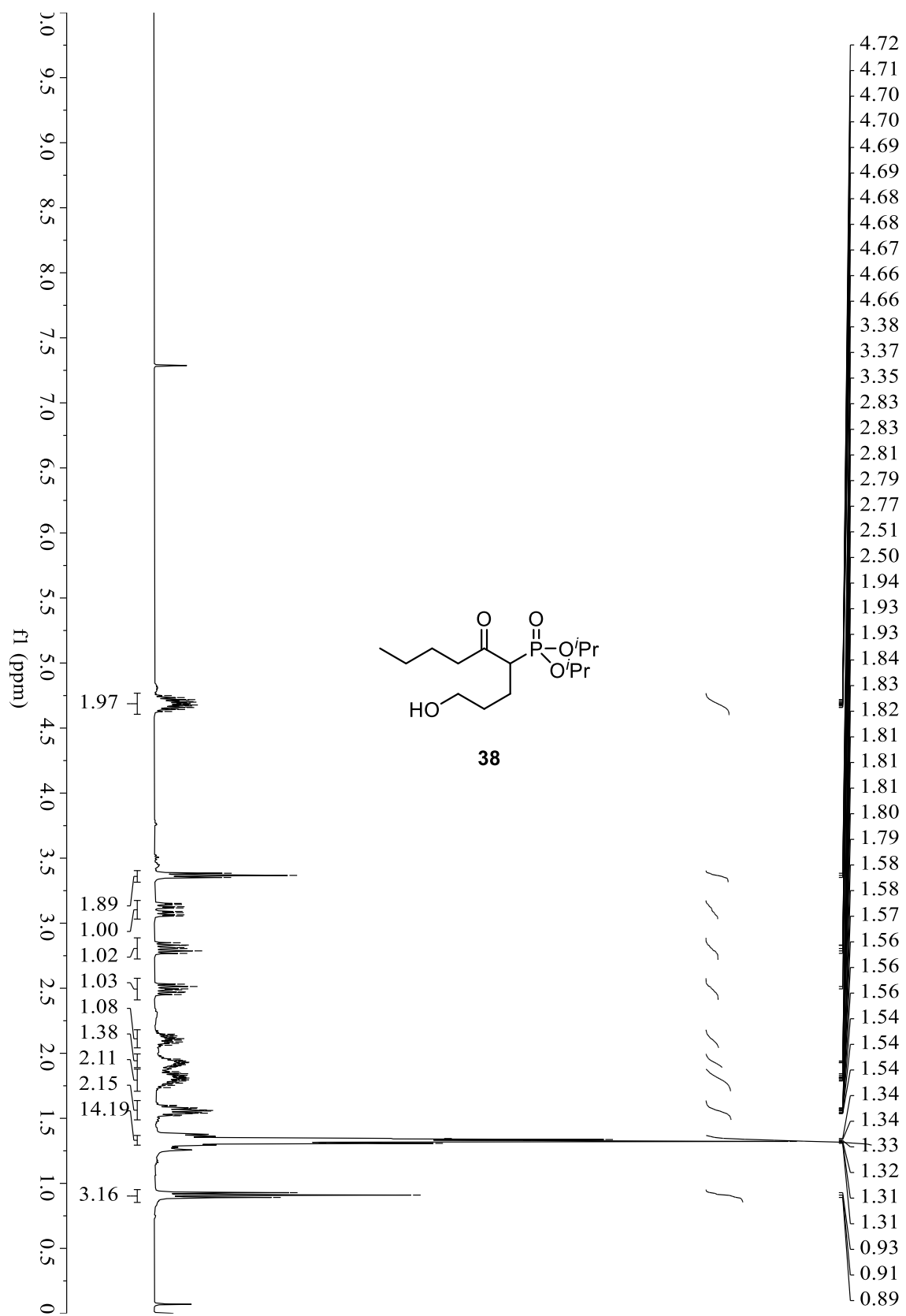




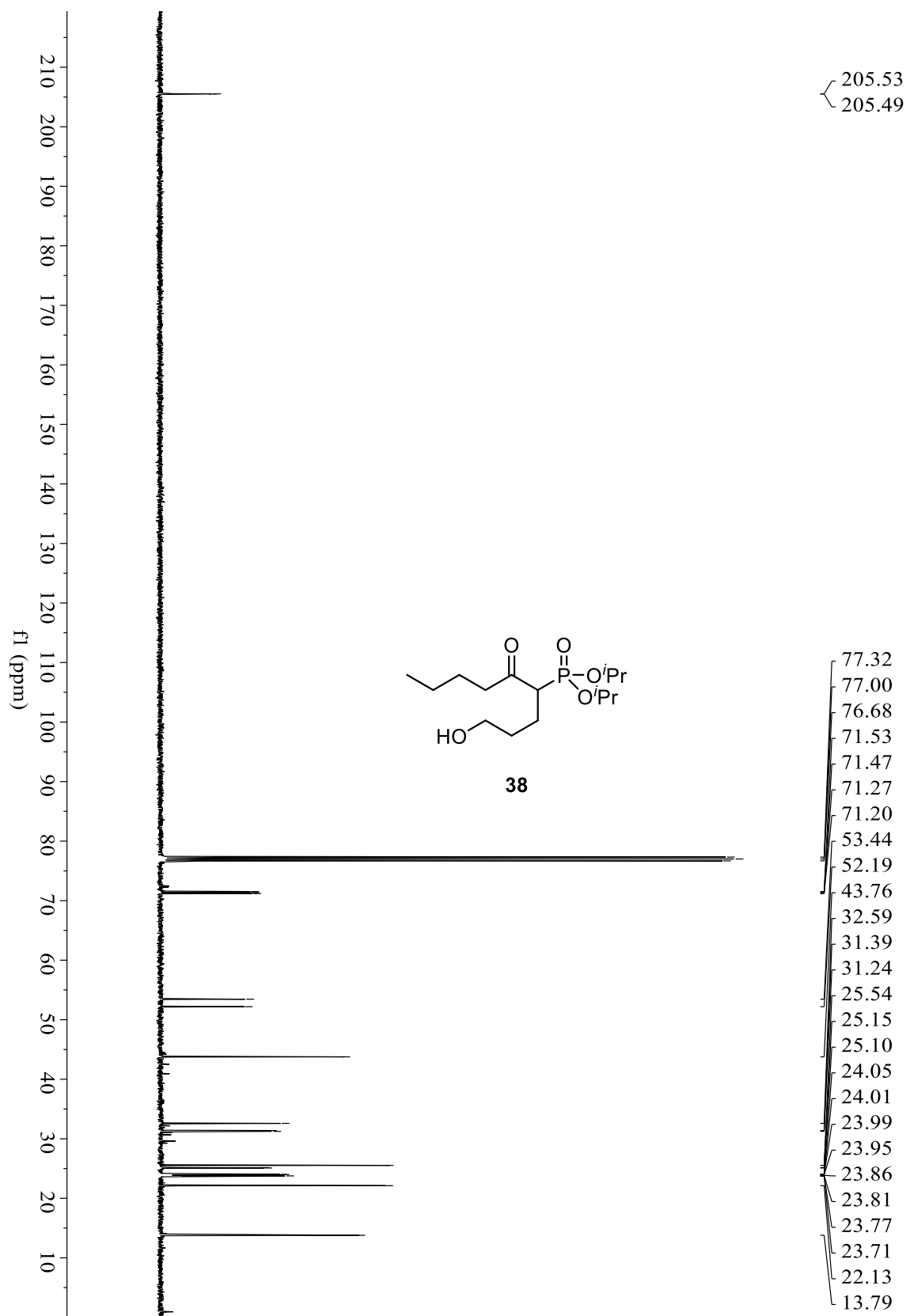
— 19.69

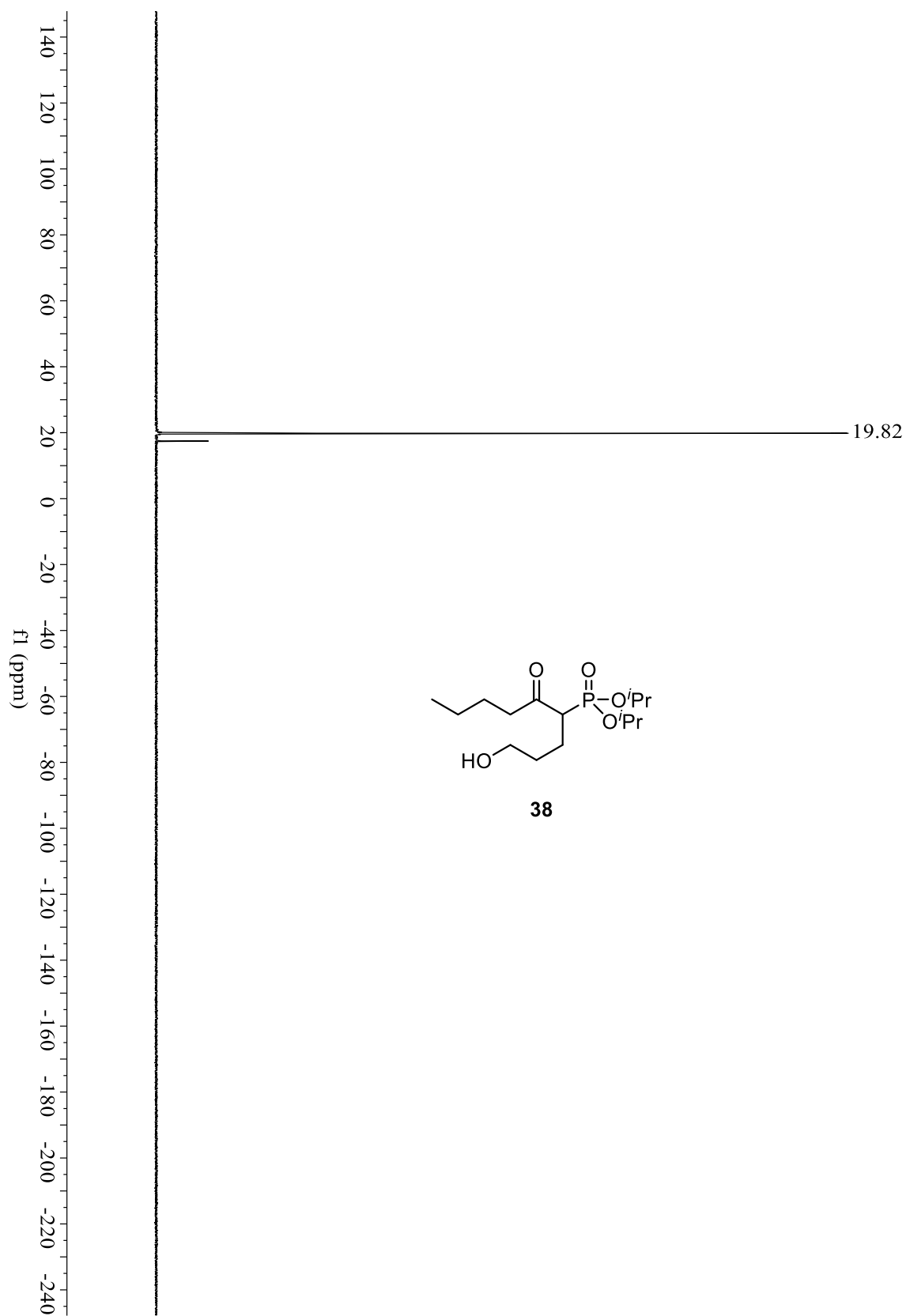


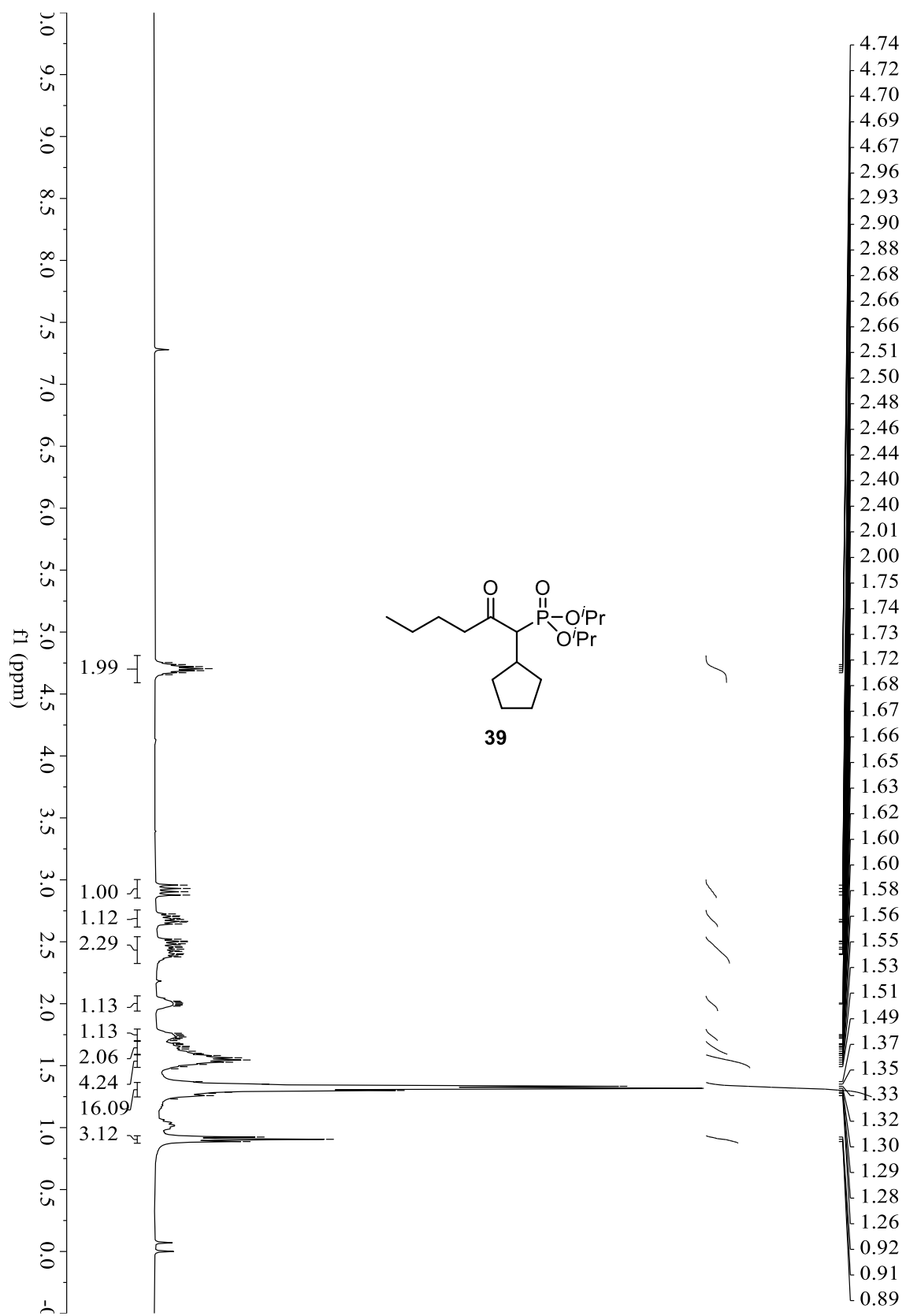
**37**

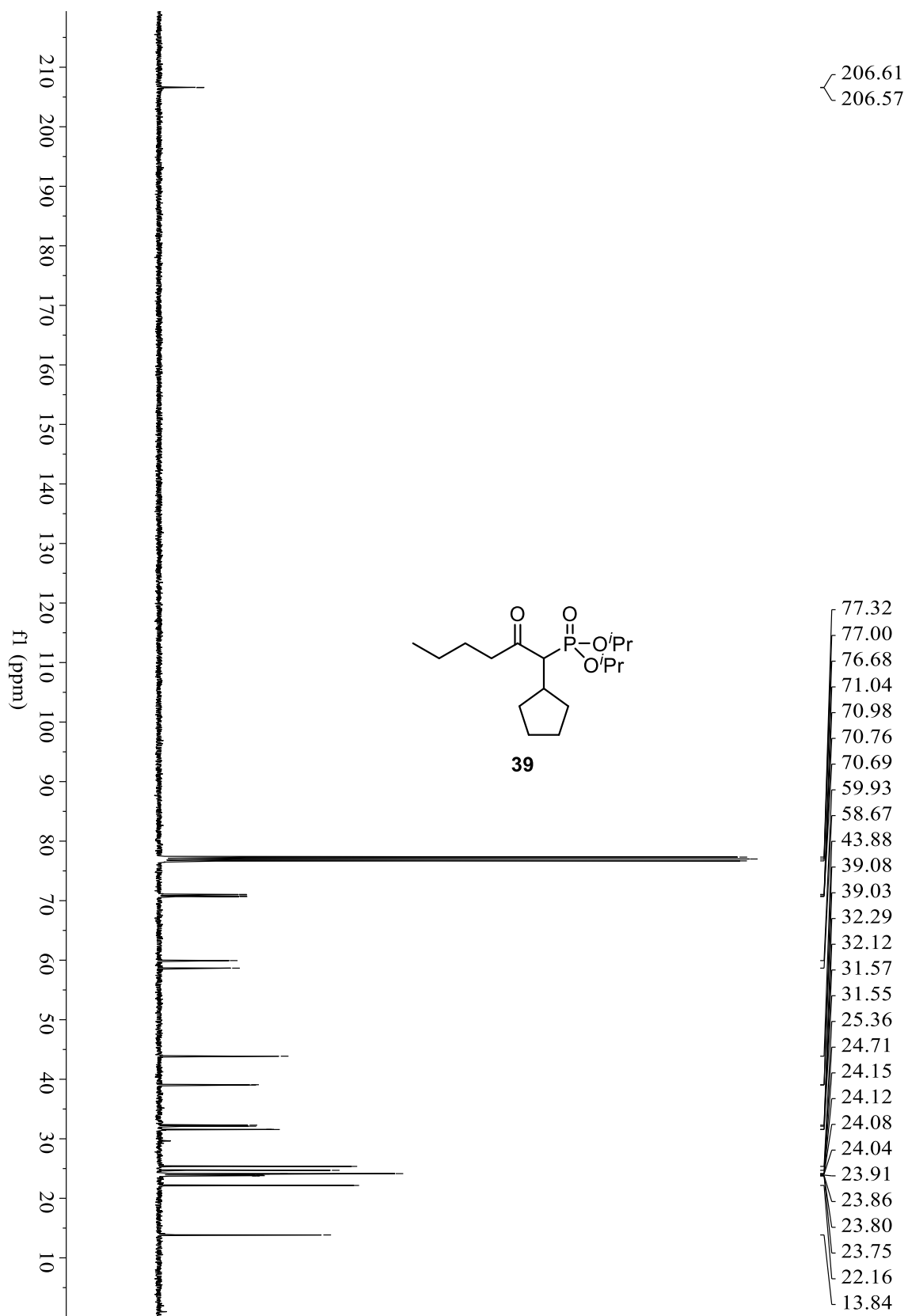






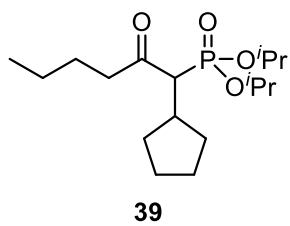


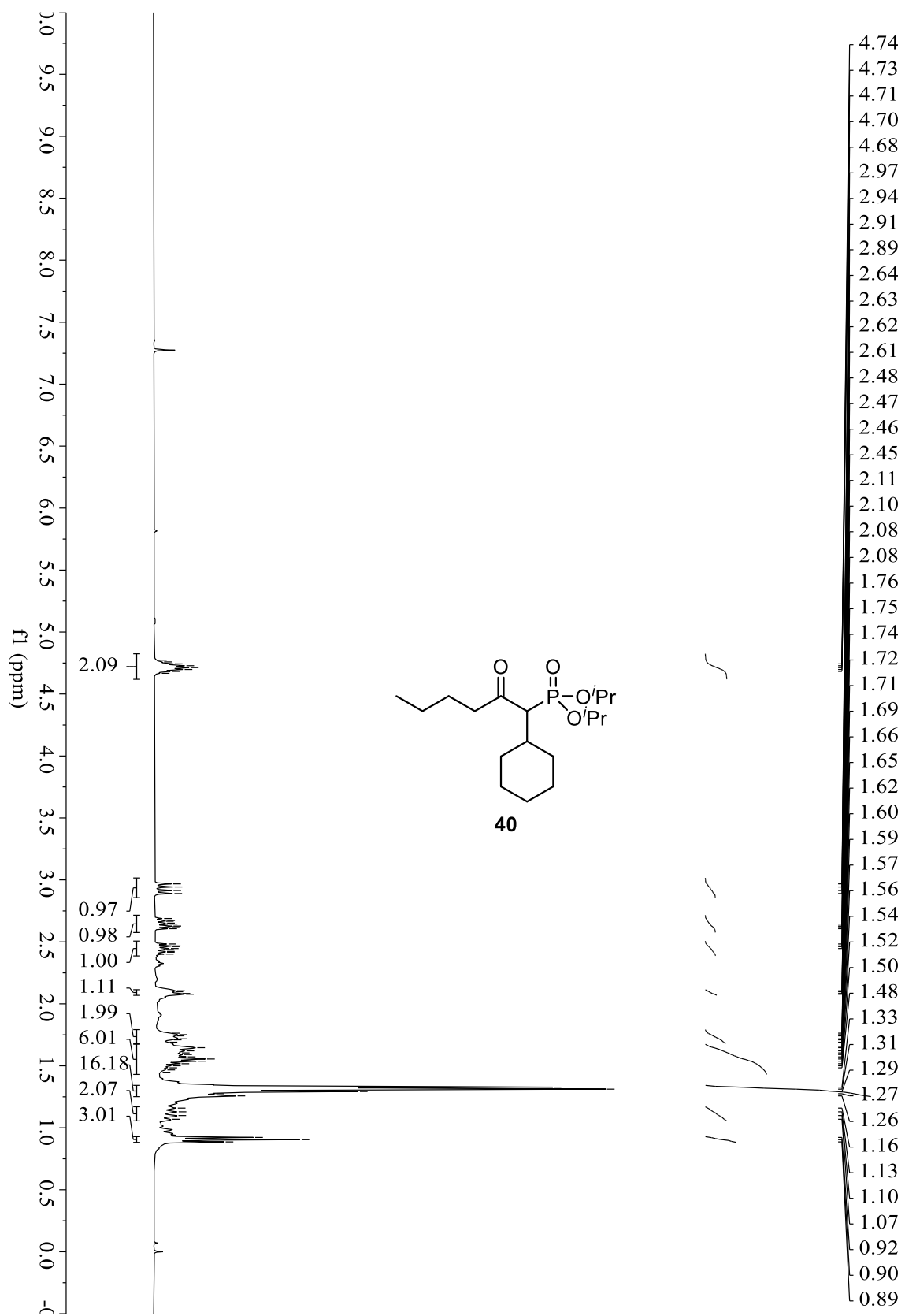


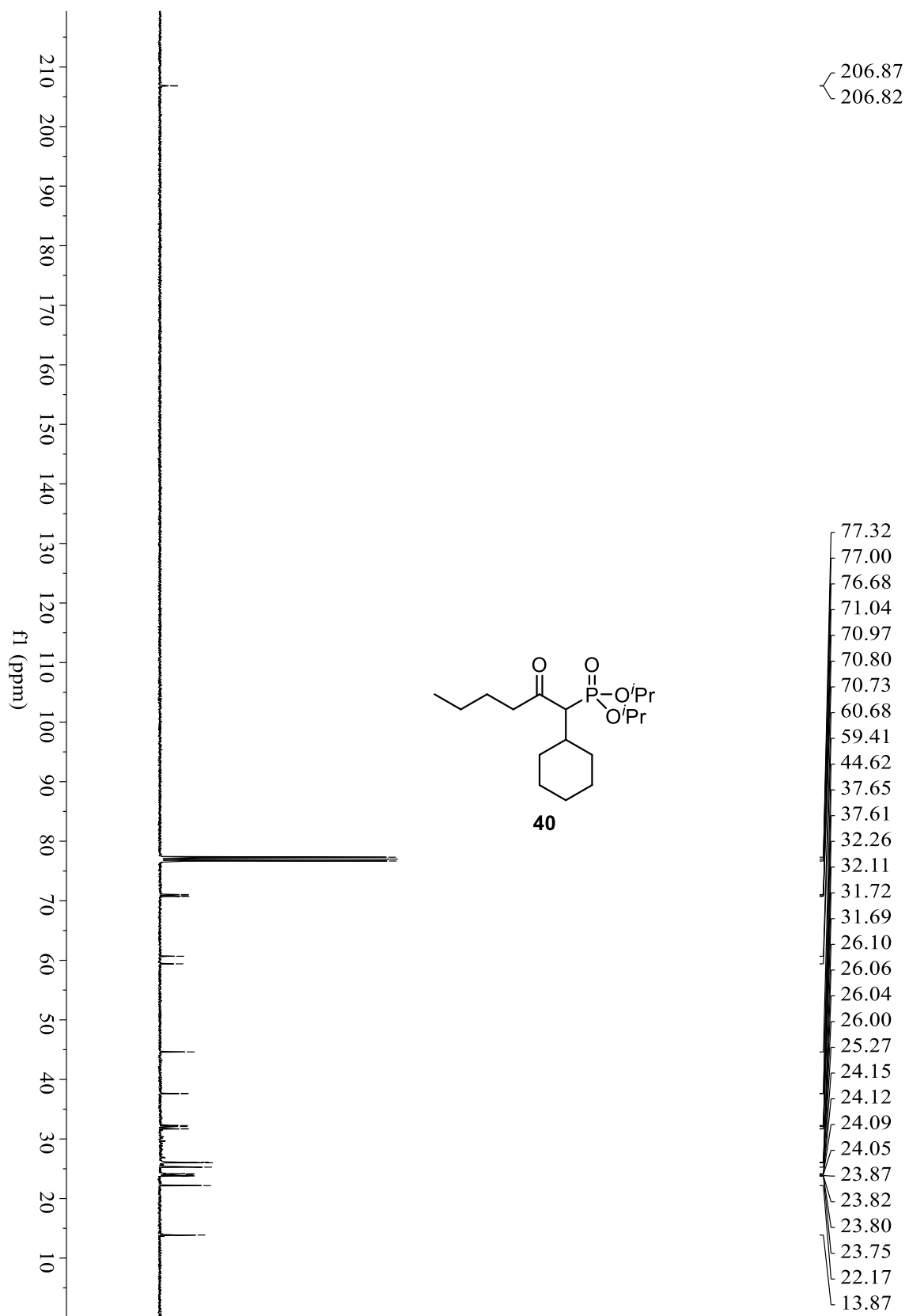


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f1 (ppm)

— 20.46

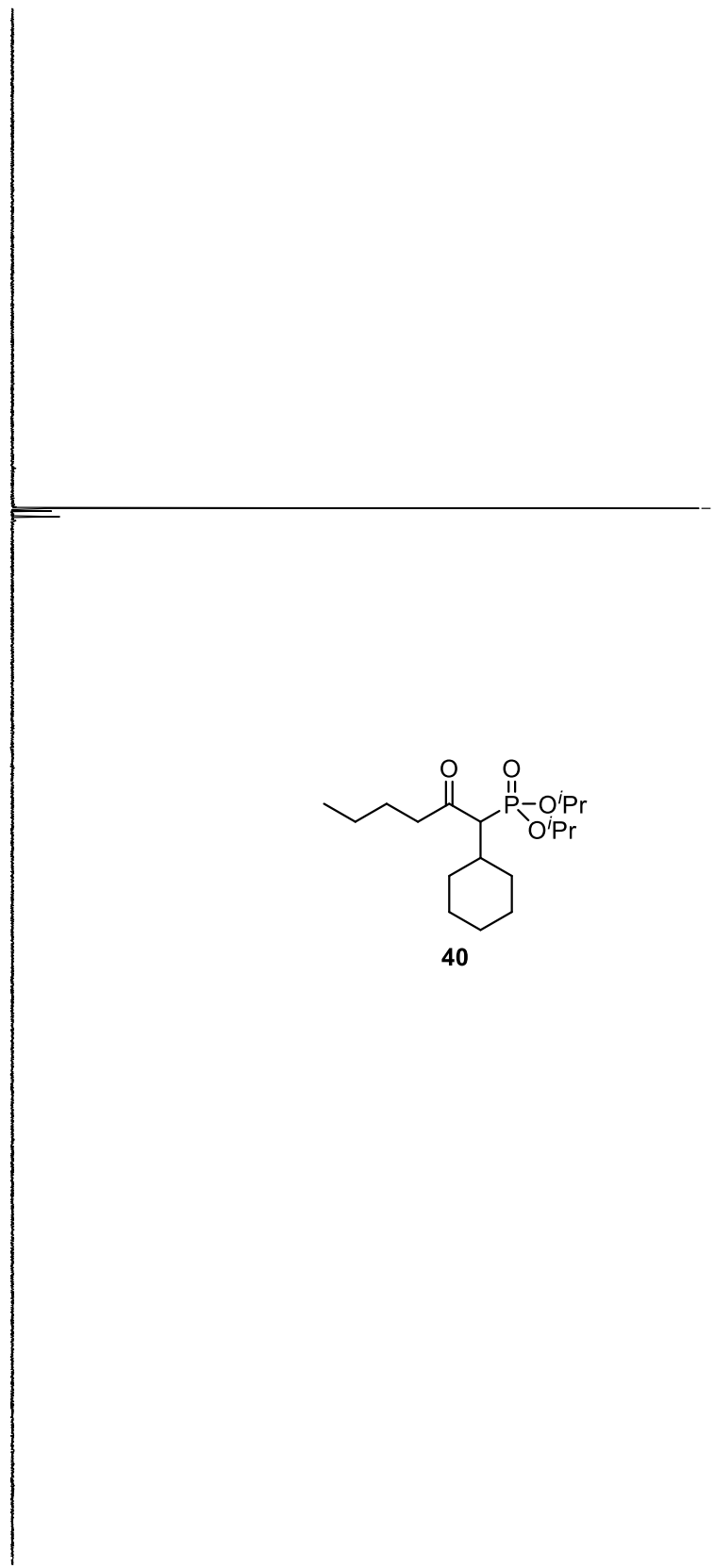




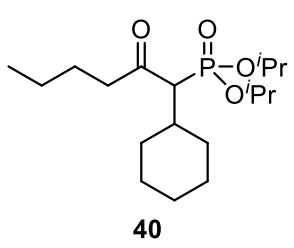


f1 (ppm)

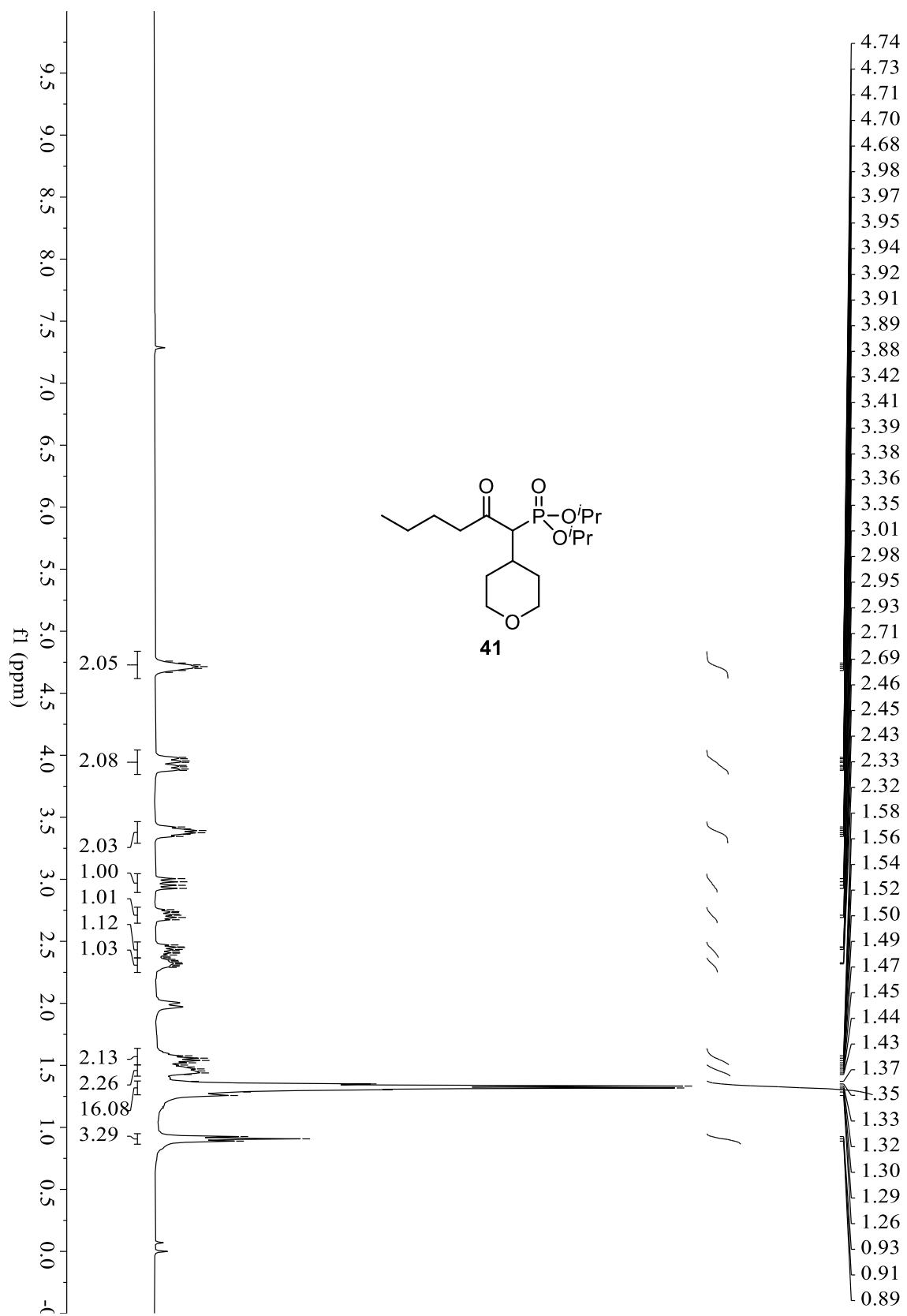
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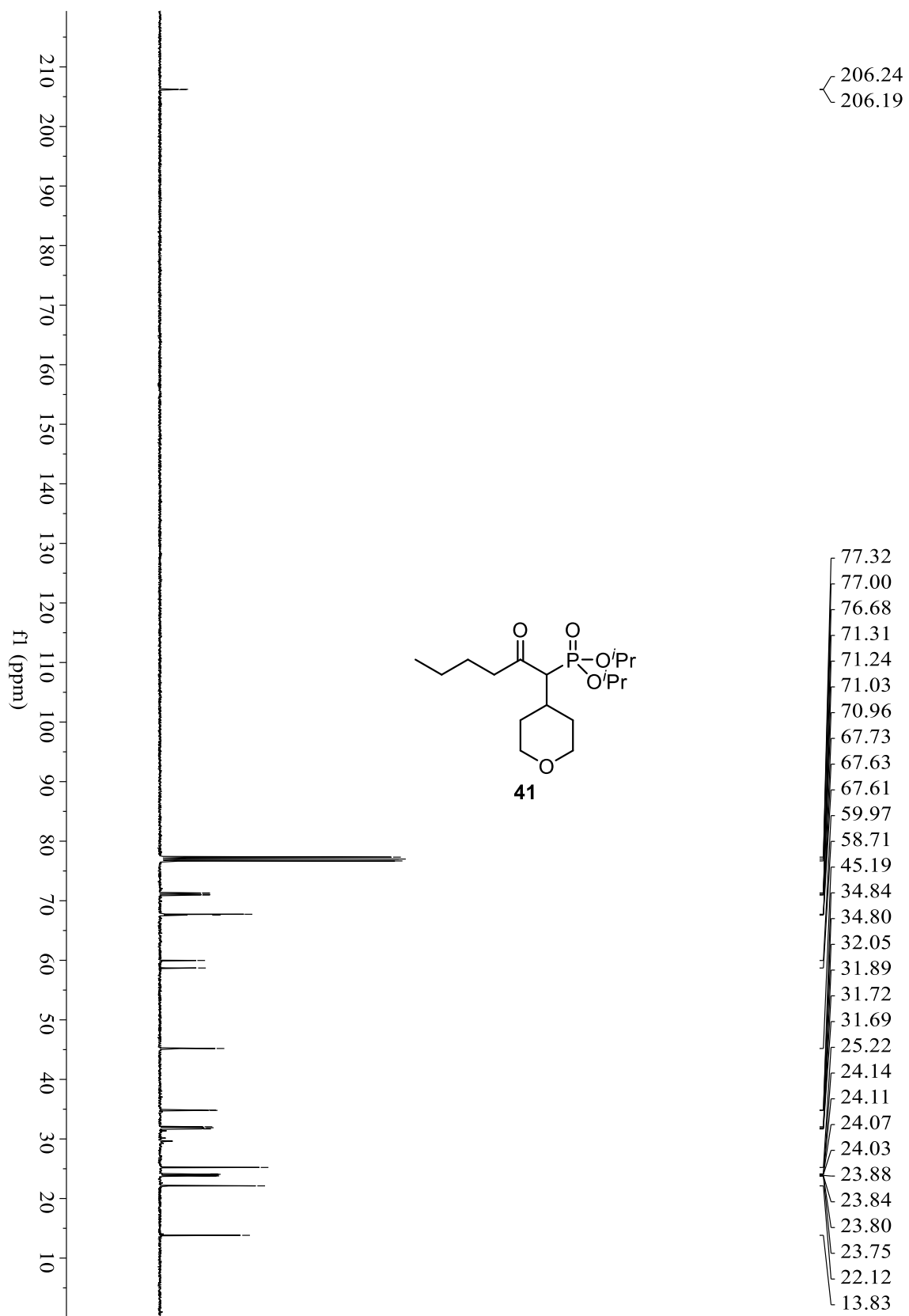


— 20.74

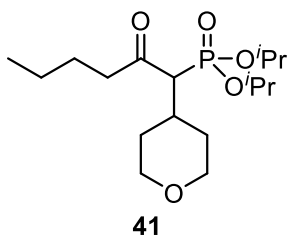
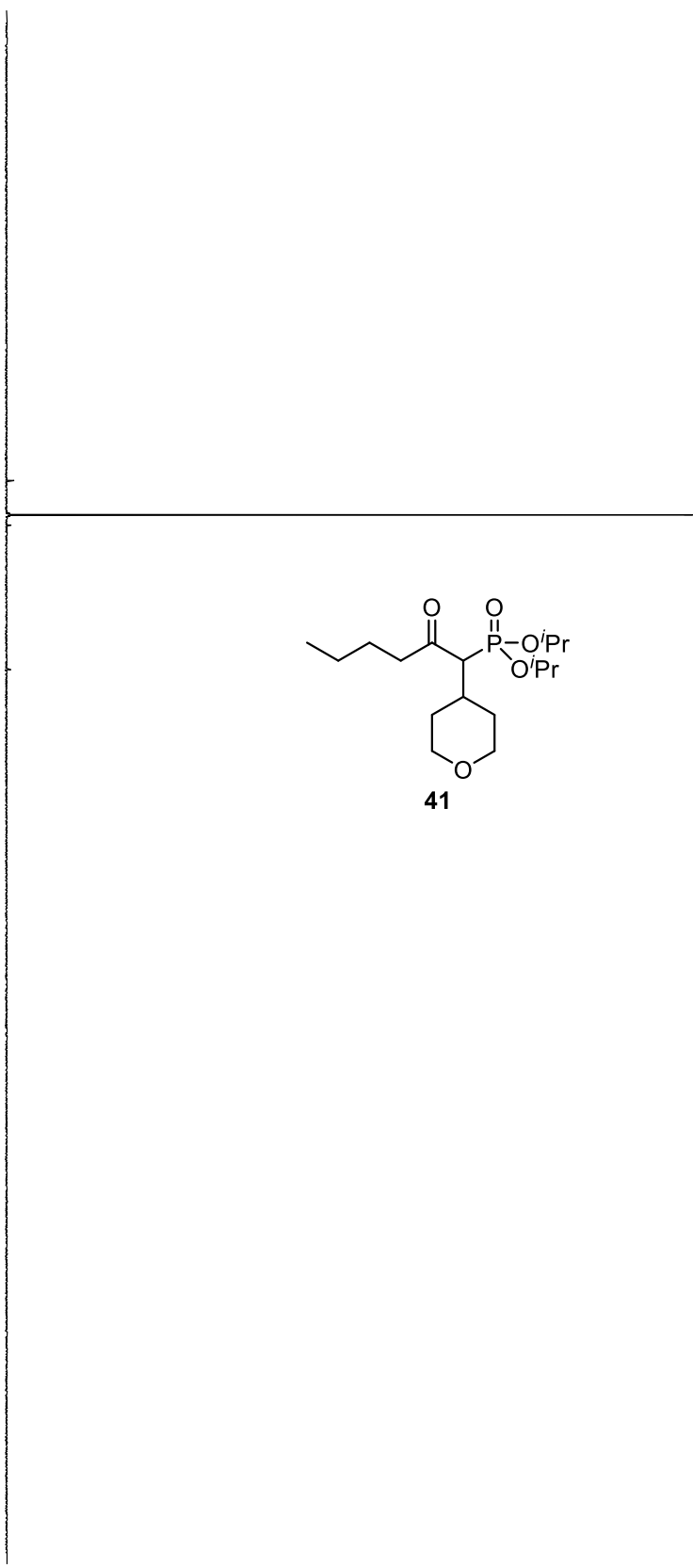


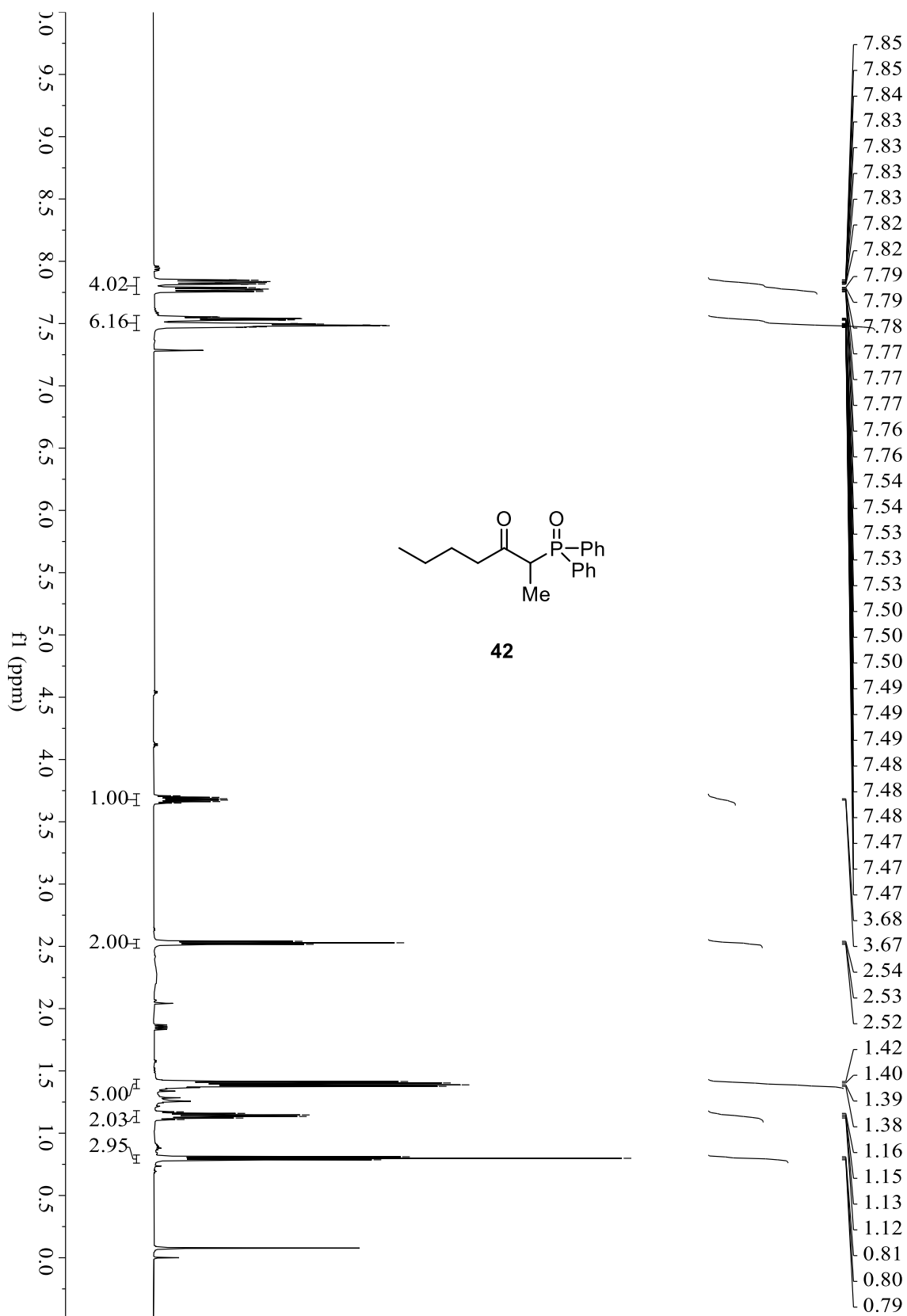


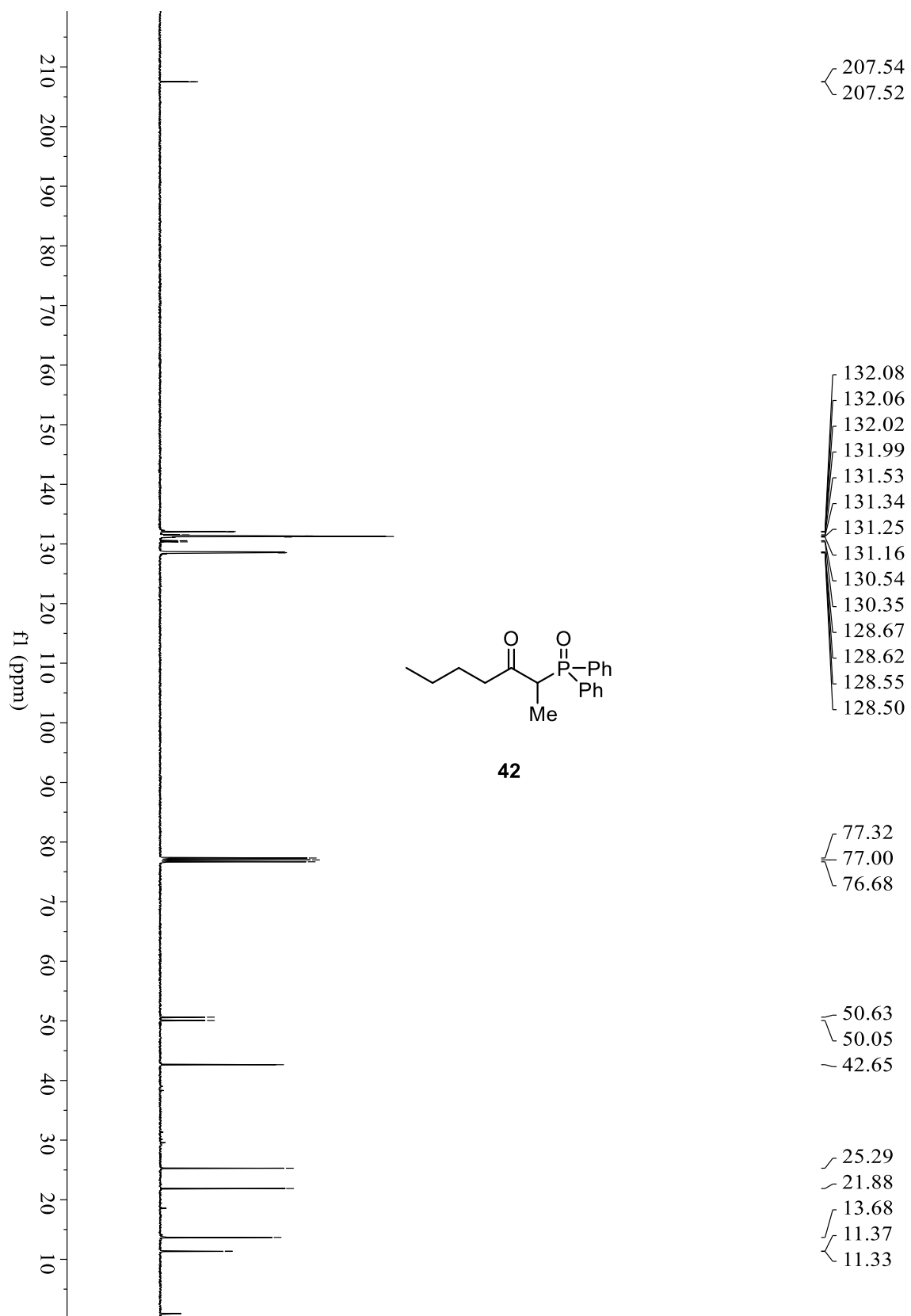




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f1 (ppm)

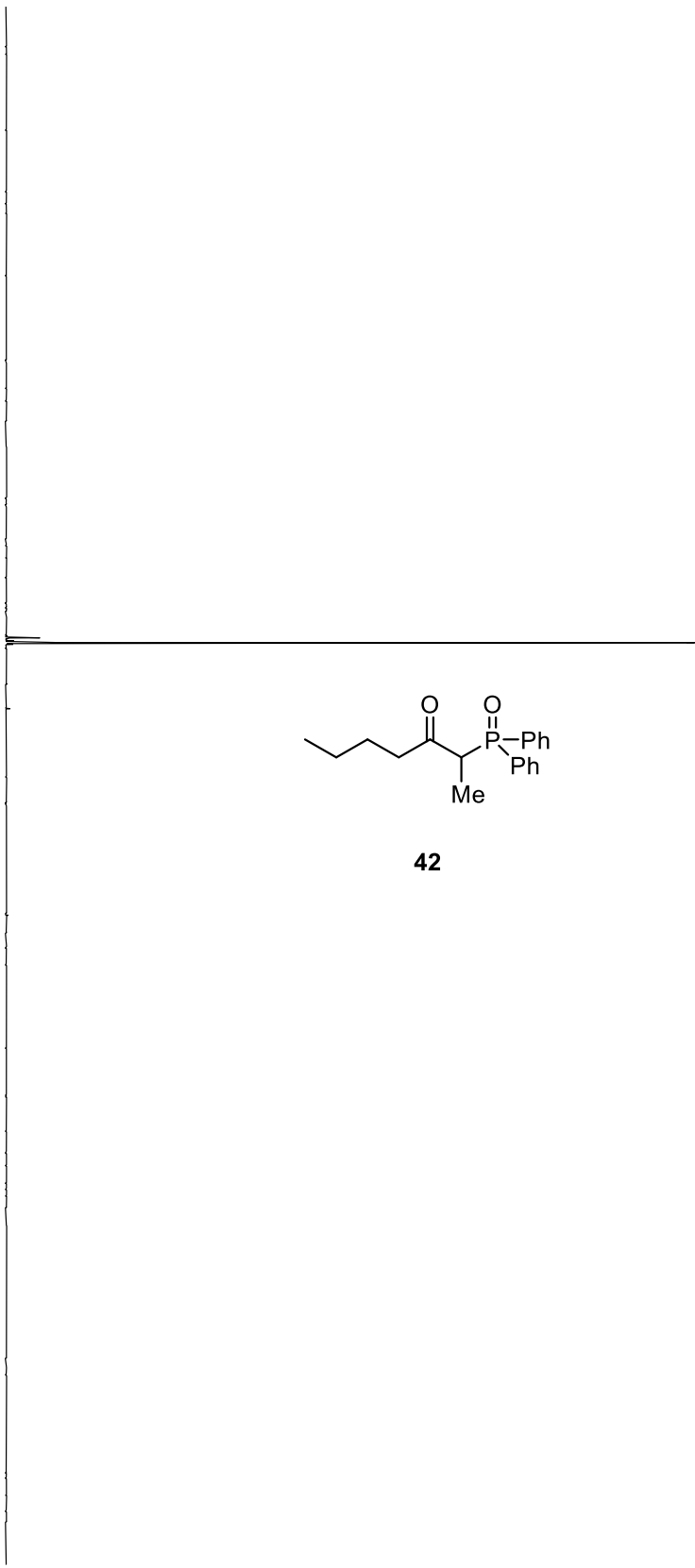




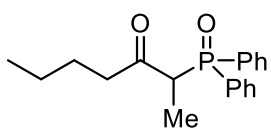


f1 (ppm)

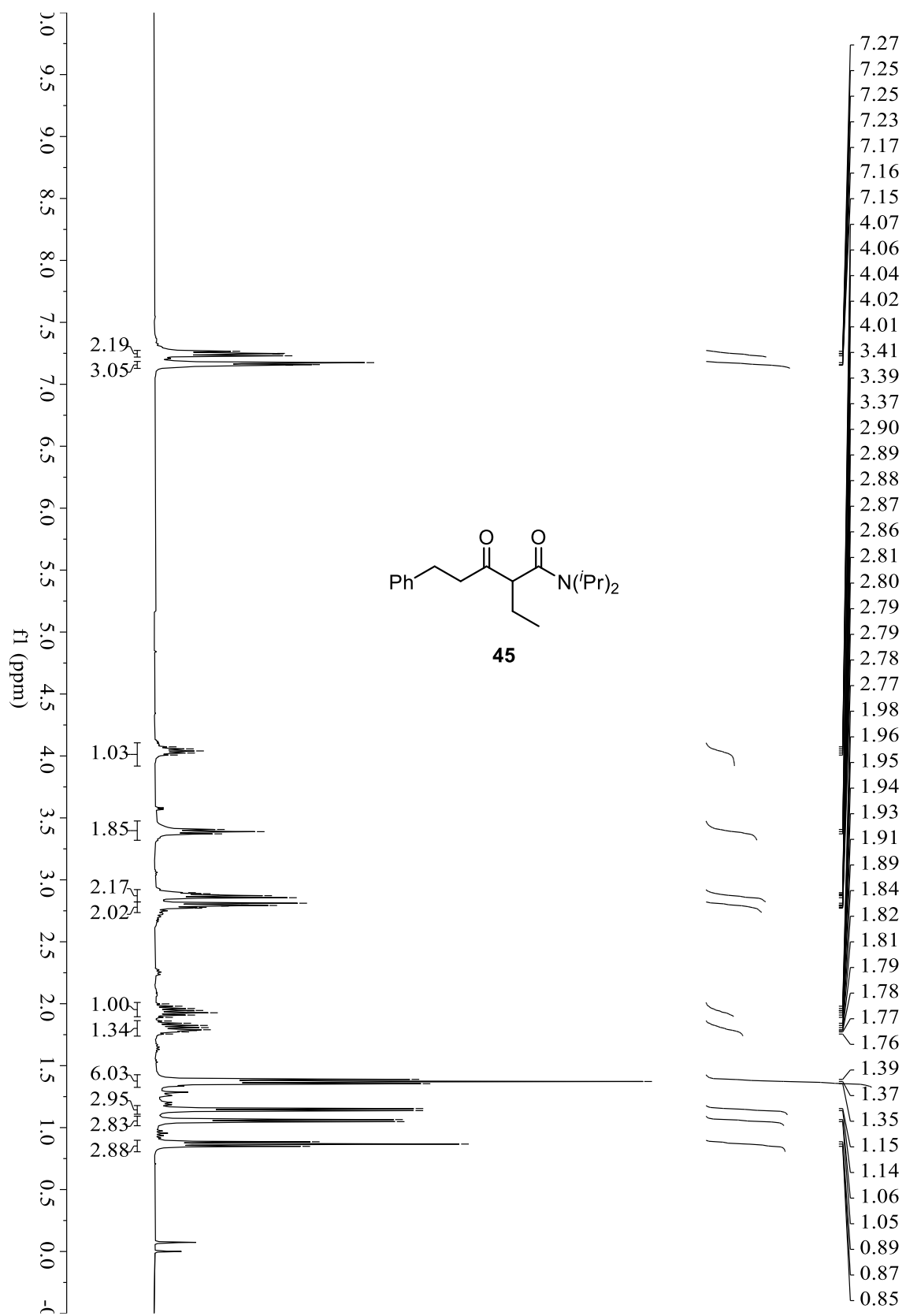
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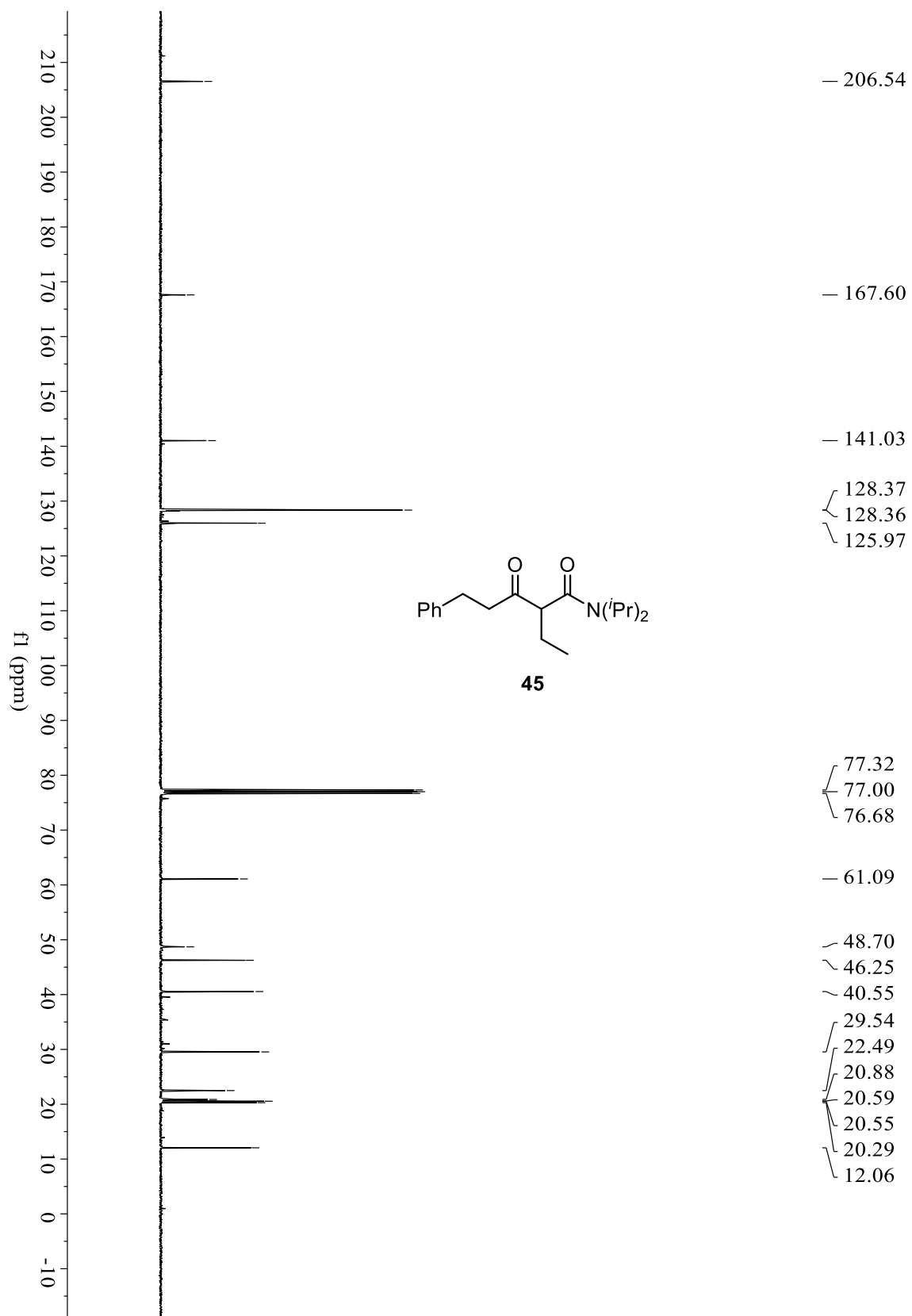


— 30.37

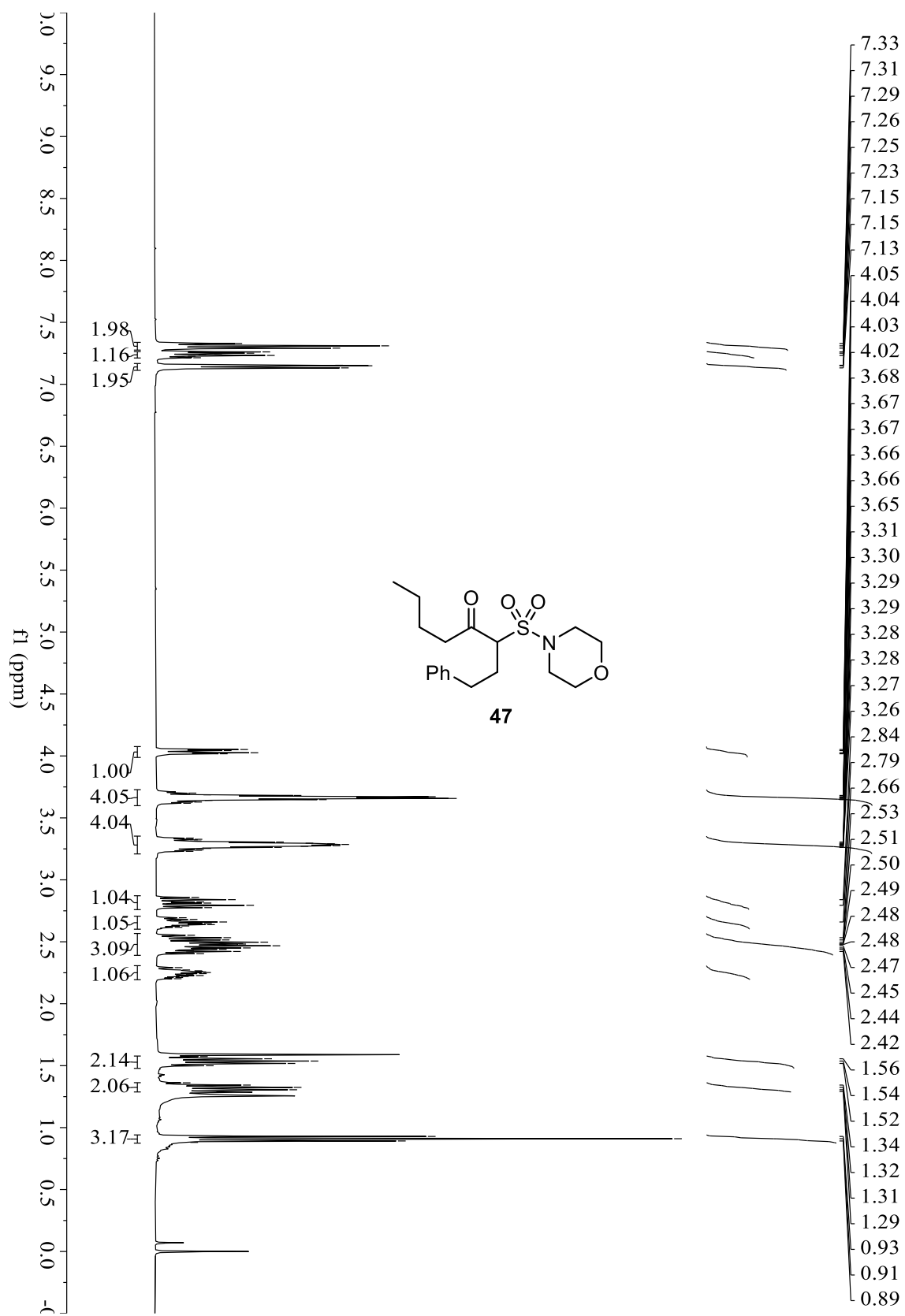


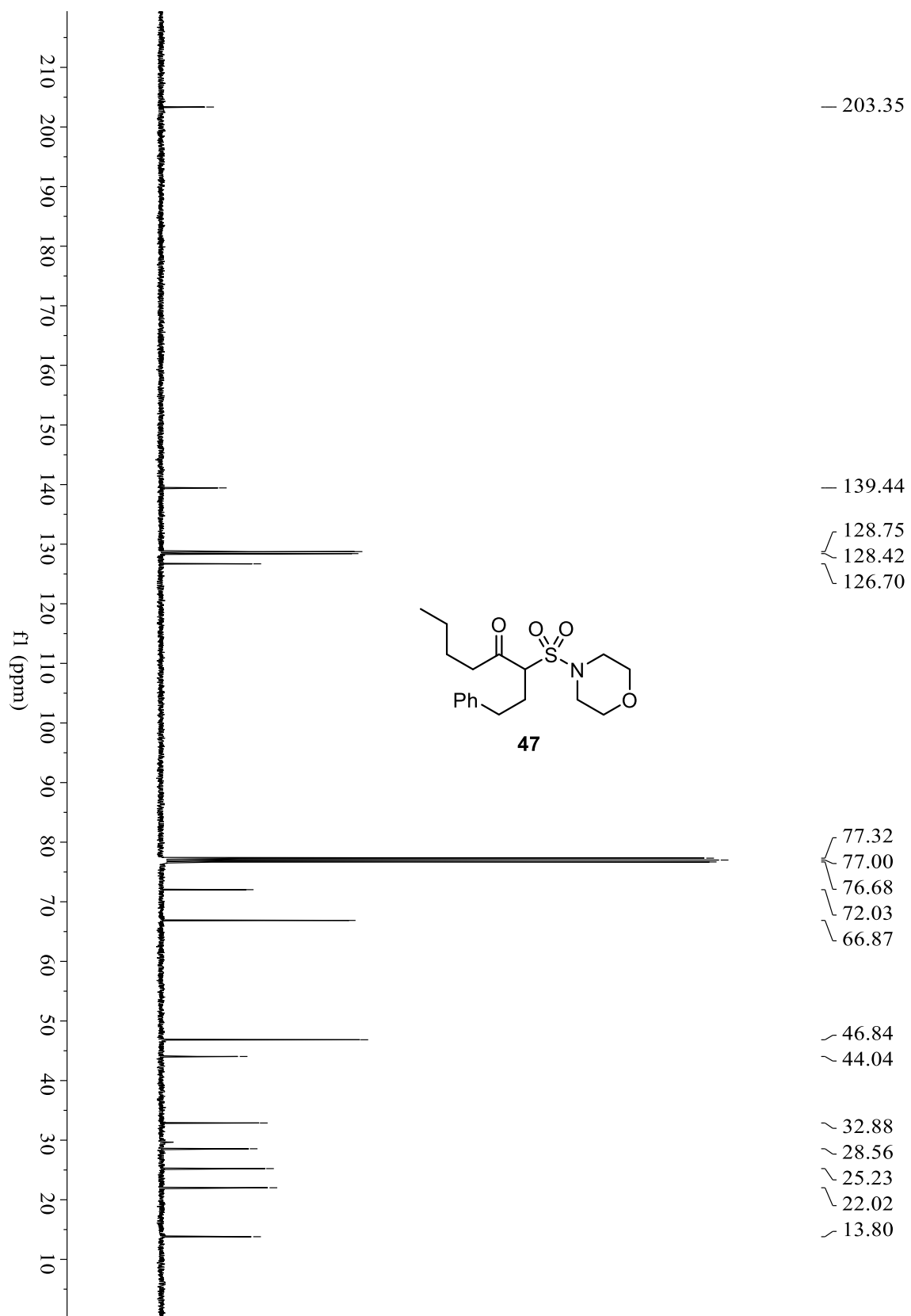
42

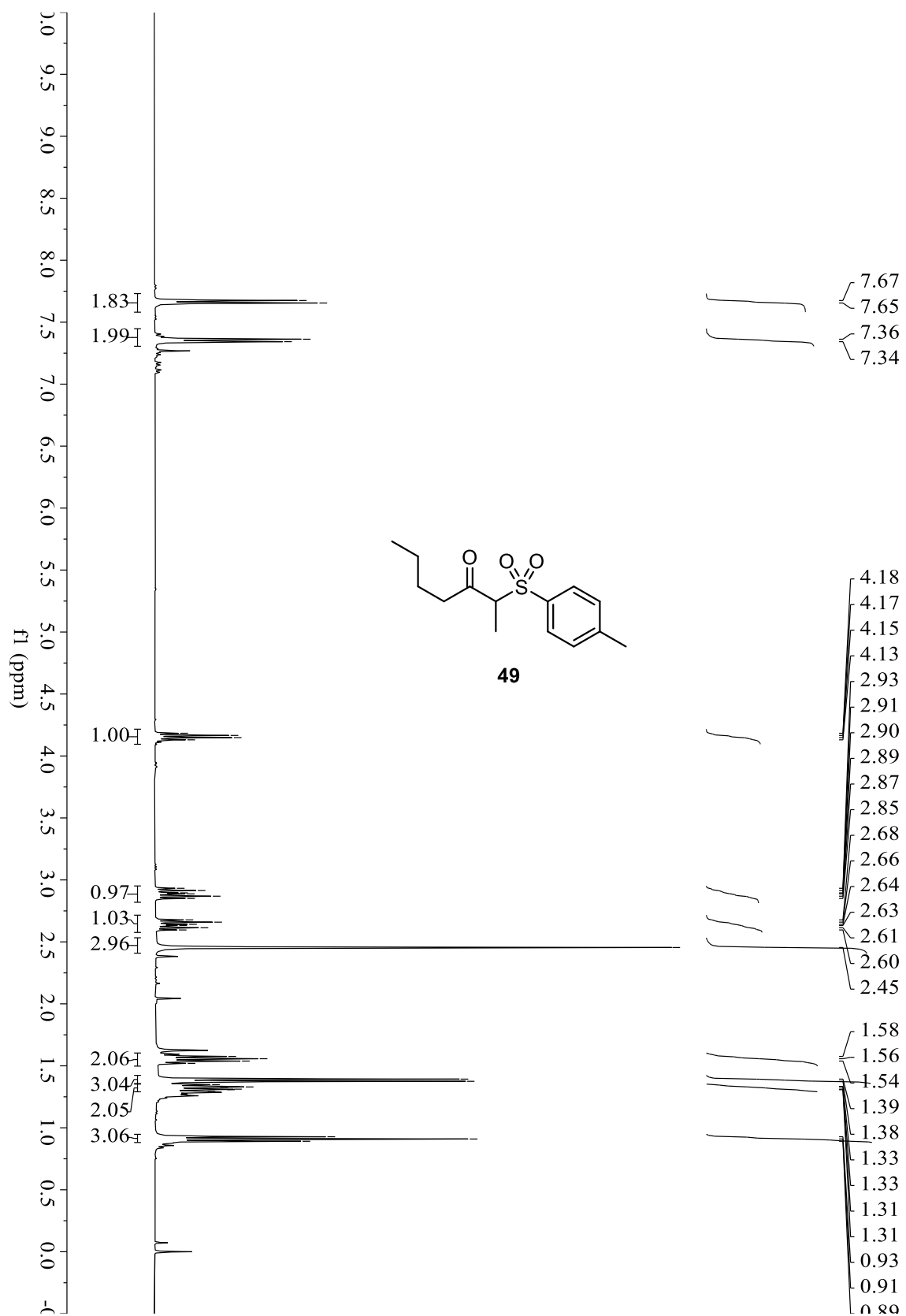


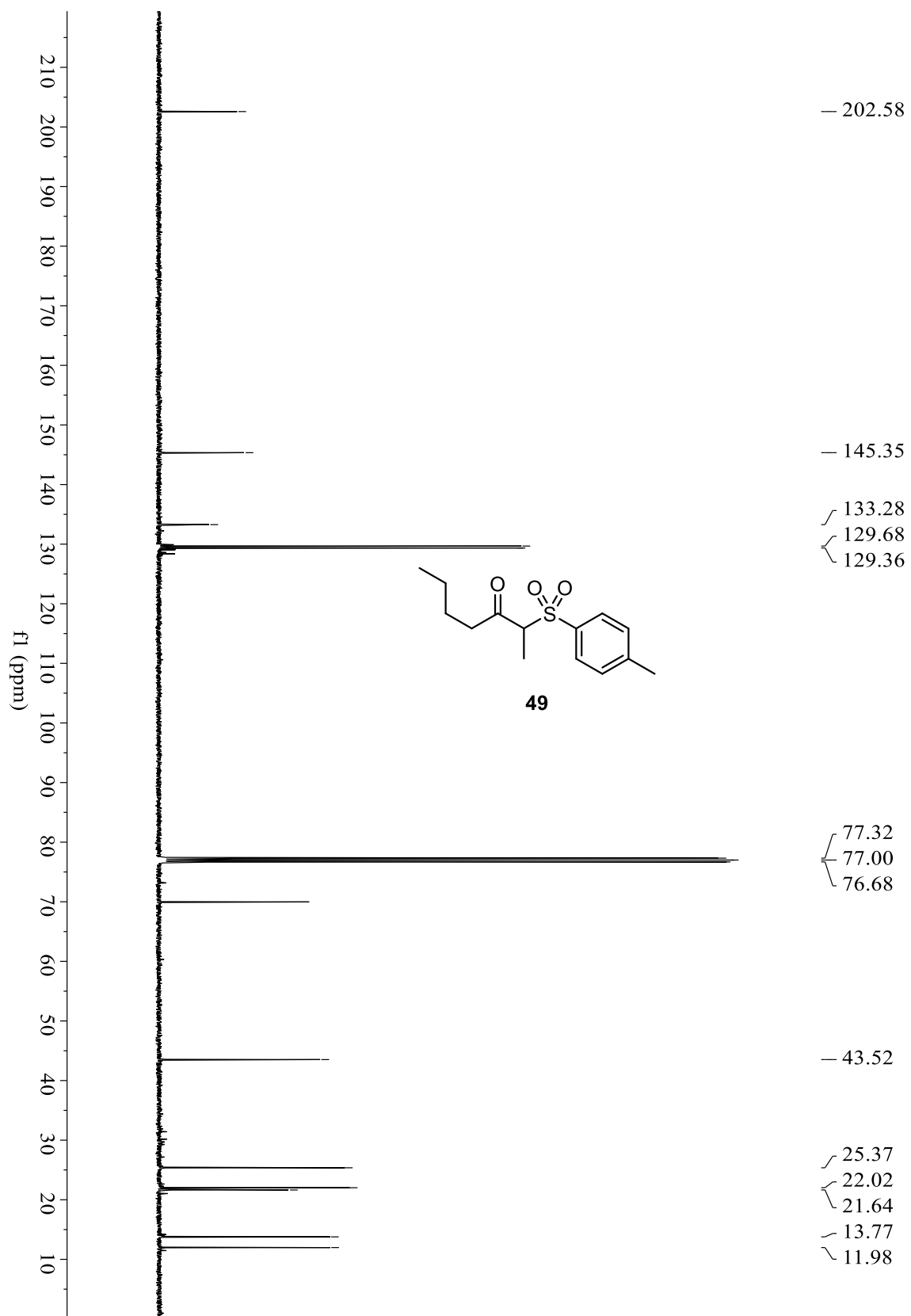


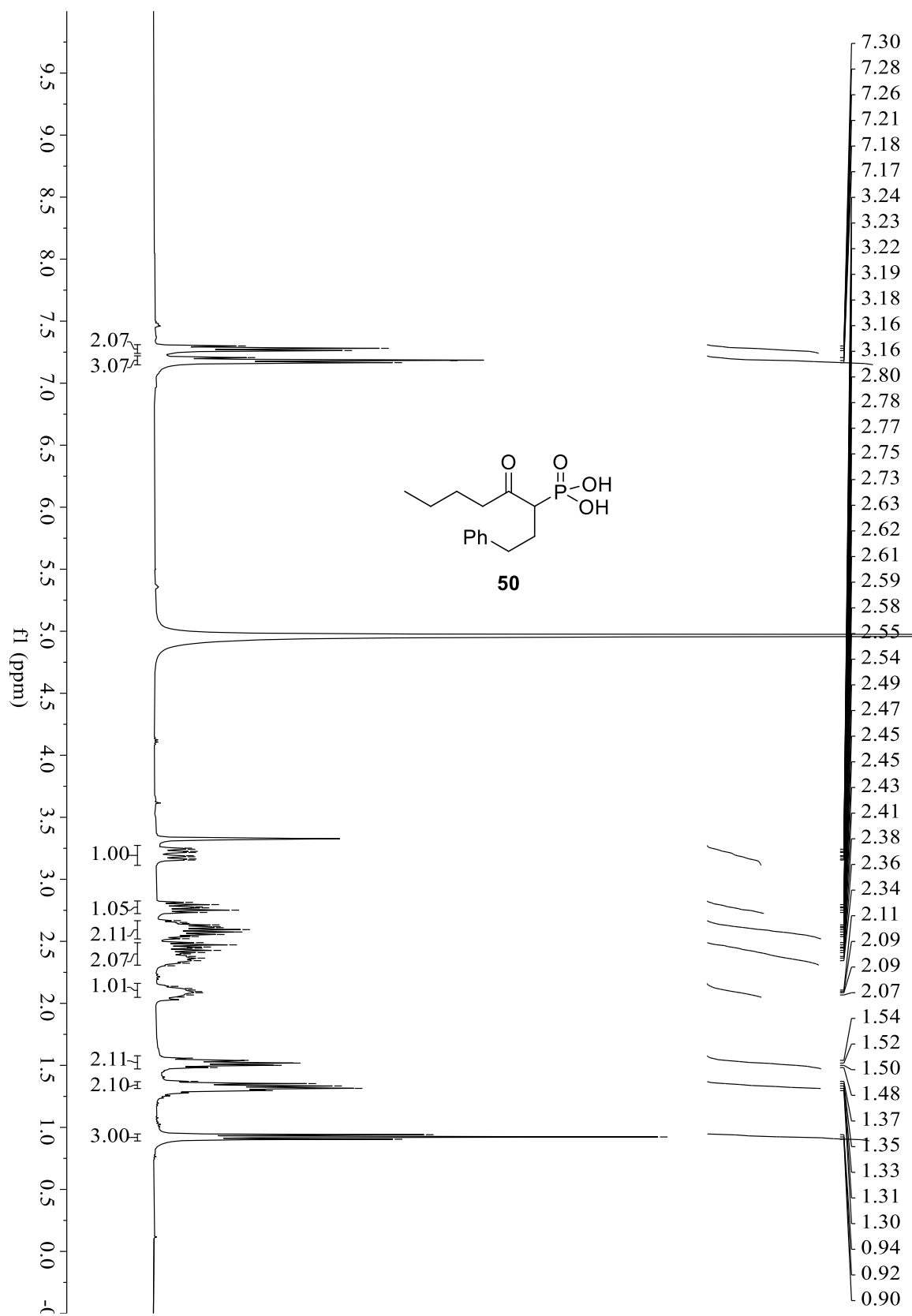


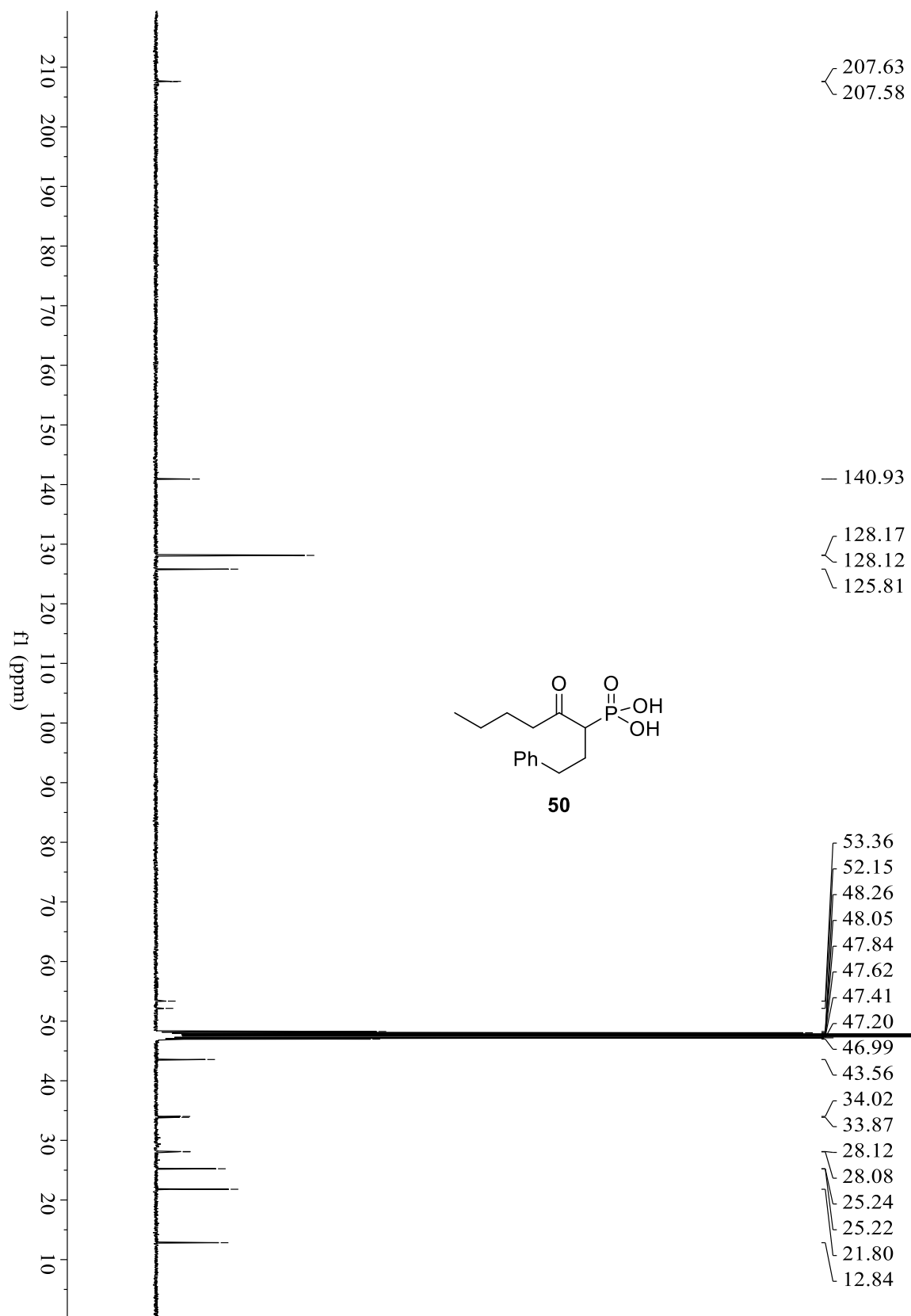


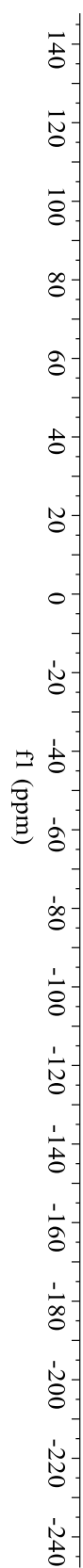




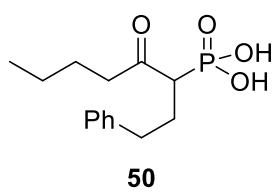


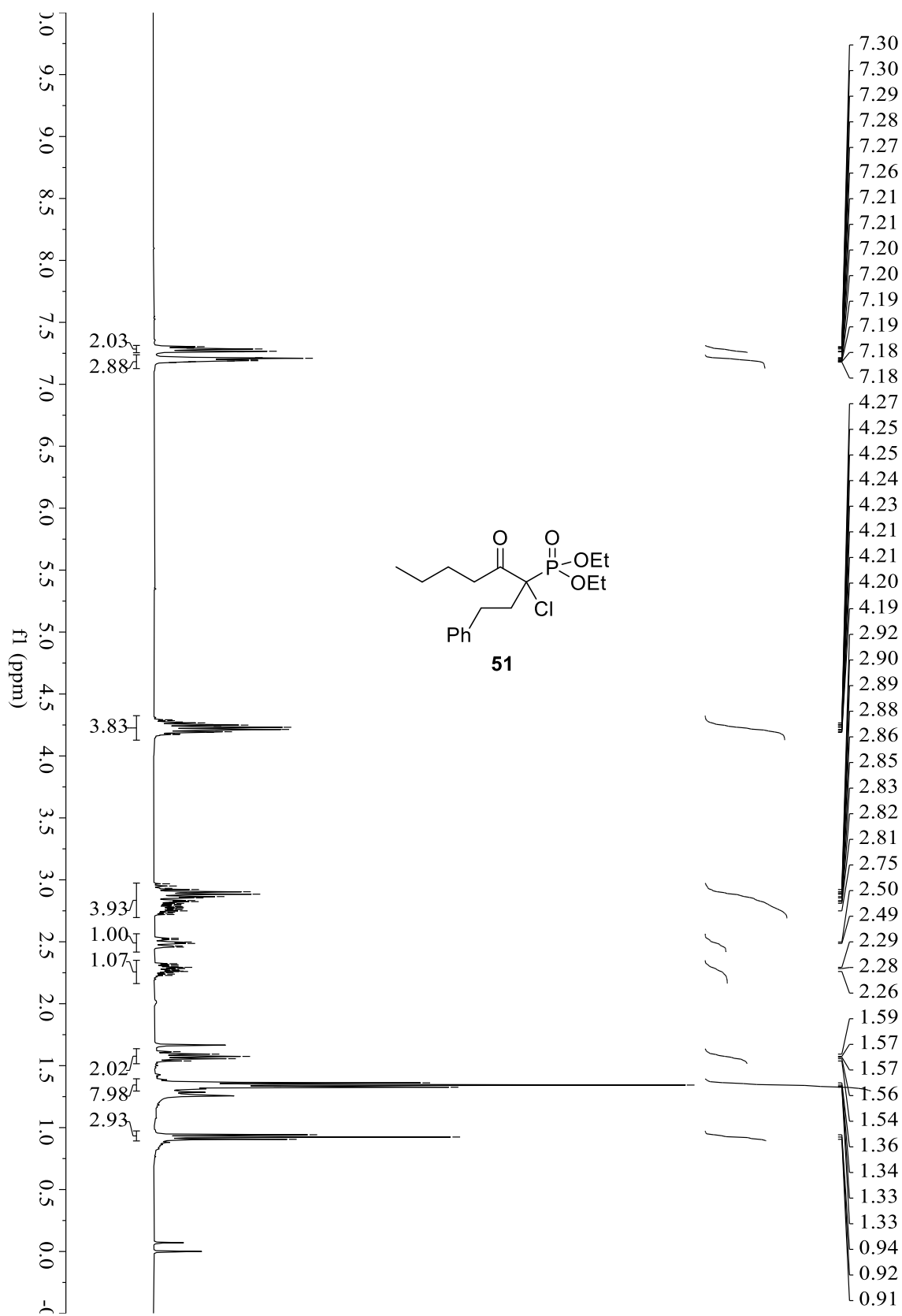




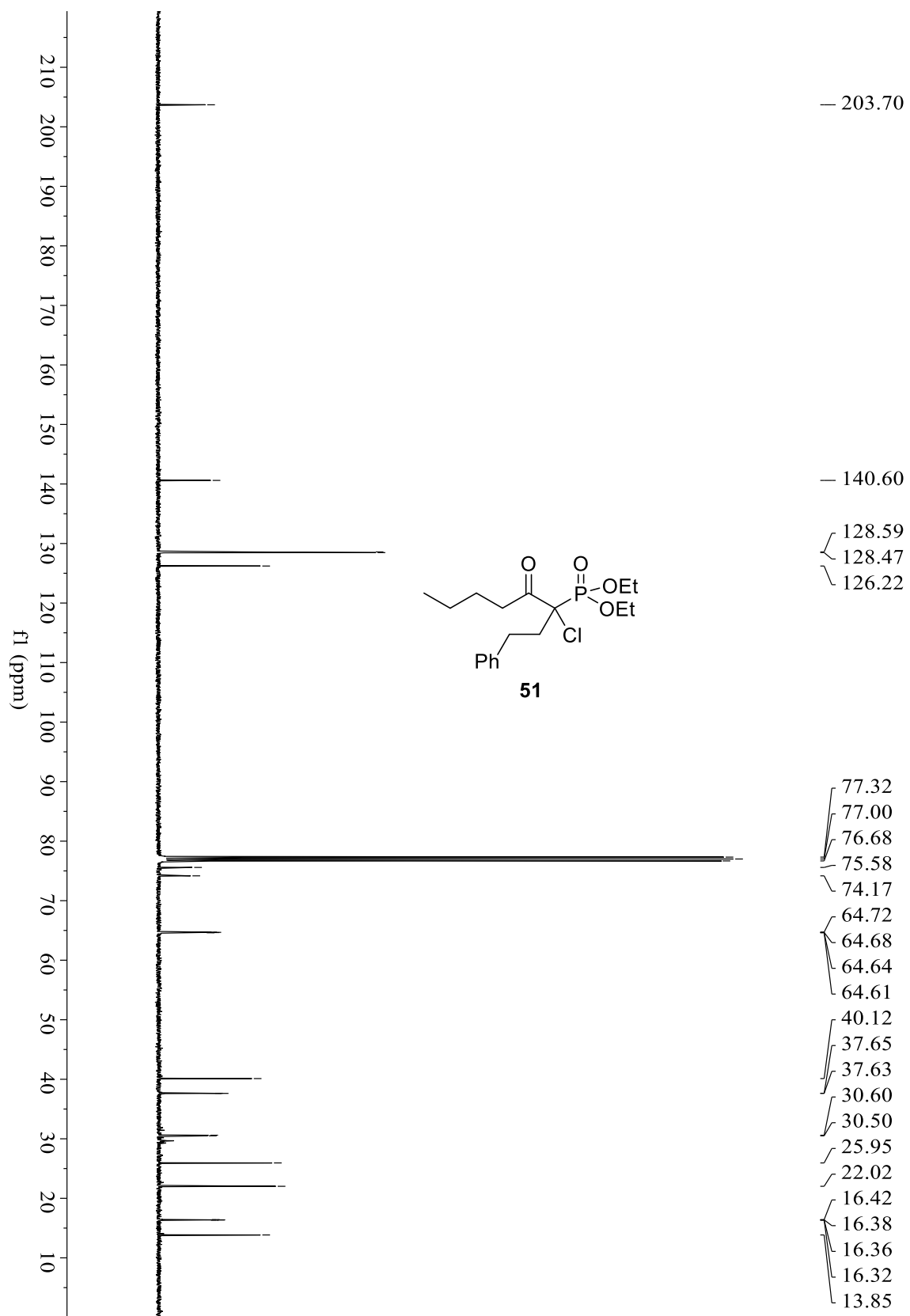


— 19.59





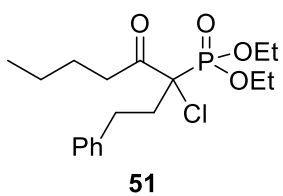


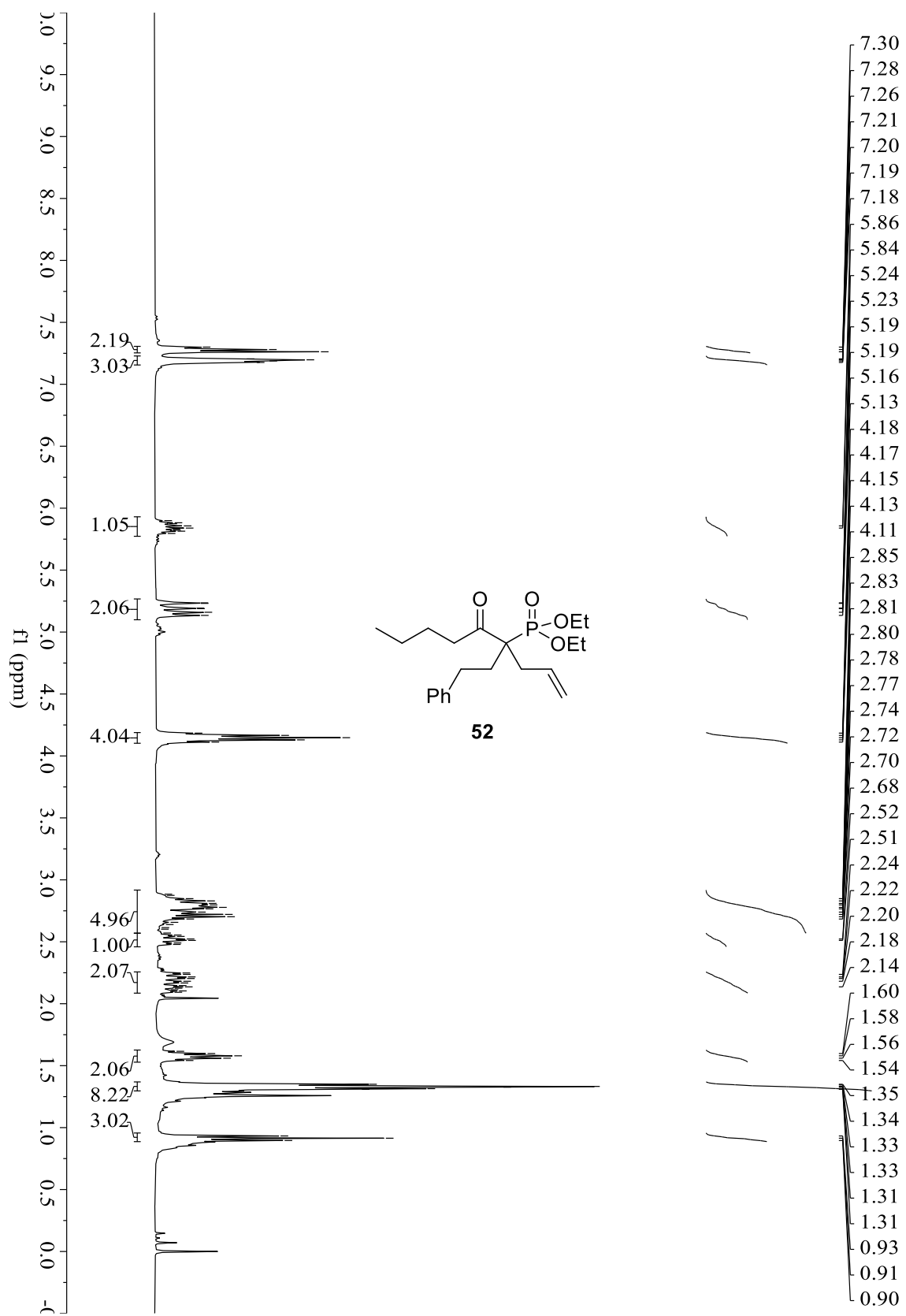


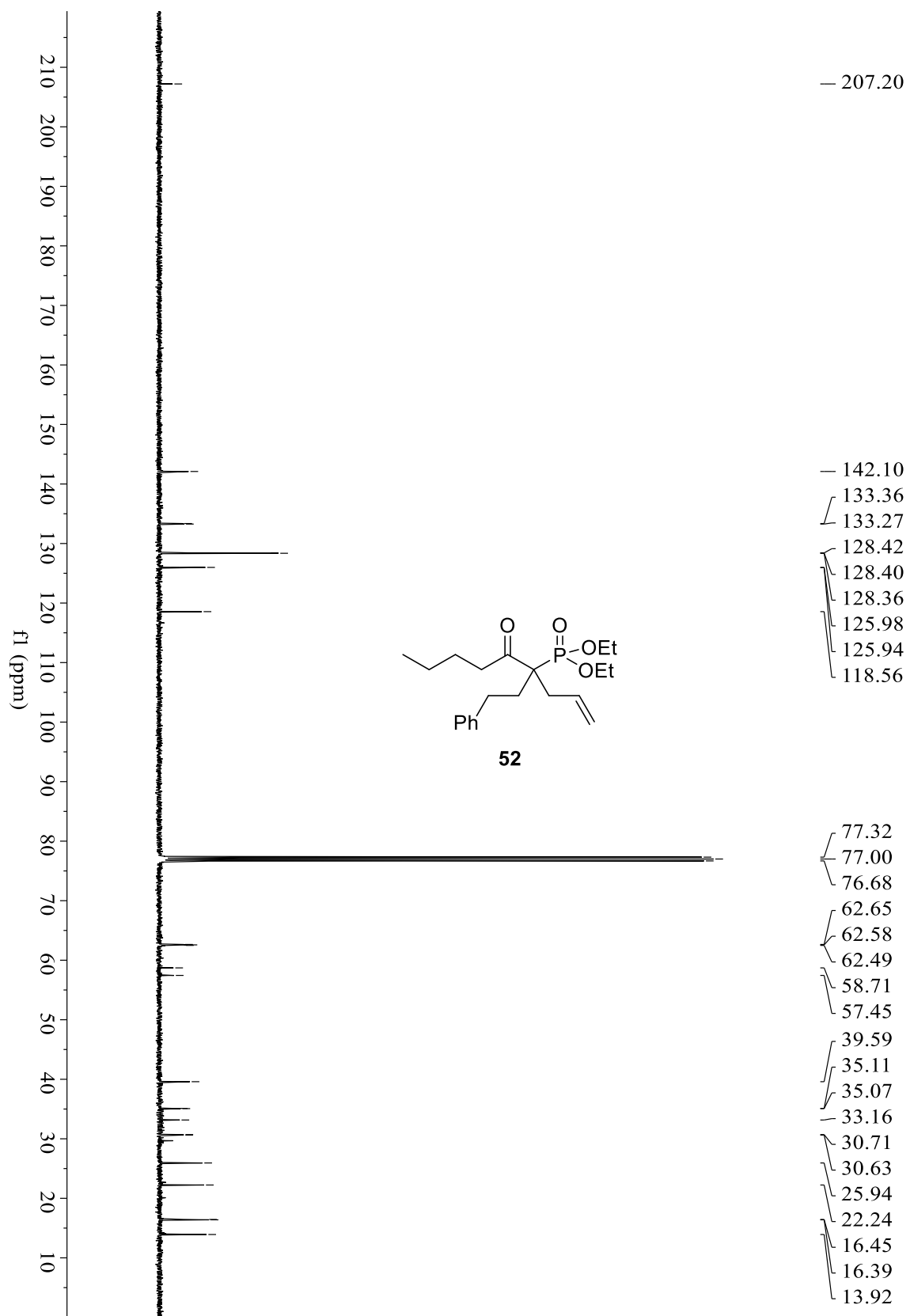
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f1 (ppm)

— 15.31







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f1 (ppm)

-25.77

