Supporting Information

Asymmetric Construction of Phosphono Dihydropyranones from α-Ketophosphonates Enabled by Pd/Chiral Isothiourea Relay Catalysis

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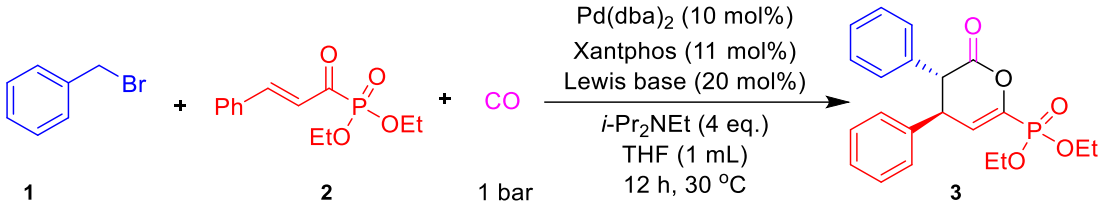
General Information

All reagents were obtained from commercial sources and were used without further purification. Room temperature (rt) refers to 20−25 °C. Analytical thin layer chromatography was performed on pre-coated silica gel plates (Kieselgel 60 F254 silica). TLC visualization was carried out with ultraviolet light (254 nm), followed by staining with a 1% aqueous $KMnO_4$ solution followed by heating. Flash column chromatography was performed on Kieselgel 60 silica in the solvent system stated. 1H, 13C, 19F and 31P nuclear magnetic resonance (NMR) spectra were acquired on a Brucker-400 MHz and 500 MHz at ambient temperature in the deuterated solvent stated spectrometer. Chemical shifts(δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). The high-resolution mass spectra (HRMS) were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Brucker Daltonics Inc (EI+). All coupling constants, J, are quoted in Hz and determined by analysis using MestReNova software. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dddd (doublet of doublet of doublet of doublets), dt (doublet of triplets) and td (triplet of doublets). The abbreviation Ar is used to denote aromatic, br. to denote broad and app. to denote apparent. HPLC analyses were obtained on a Shimadzu HPLC. All chiral HPLC traces were compared with an authentic racemic trace prepared using racemic HBTM-2.1. Mass spectrometry (m/z) data were acquired by electrospray ionization (ESI). All phosphate esters were synthesized according to the literature[1] with some modifications.

1. Additional data for optimization of the reaction condition

Table S1. Evaluation of Lewis Base Organocatalysts[a]



Entry	Lewis Base	Yield (%)[b]	d.r[c]	*ee* (%)[d]
1	**4a**	45	13:1	63
2	**4b**	80	13:1	35
3	**4c**	35	>20:1	26
4	**4d**	85	13:1	4
5	**4e**	20	14:1	44
6	**4f**	40	11:1	58
7	**4h**	60	12:1	55
8	**4i**	80	13:1	10
9	**4g**	60	9:1	20
10	**4j**	60	7:1	4
11	**4k**	**70**	**>20:1**	**90**

[a]Unless noted otherwise, the reaction of **1** (0.225 mmol) and **2** (0.1 mmol, was carried out in THF (1.0 mL) at 30 °C in the presence of $Pd(dba)_2$ (10 mol %), XantPhos (11 mol %) and isothiourea catalyst (BTM) **4** (20 mol %), *i*-Pr_2NEt (4 equiv). [b]NMR yield. [c]The d.r. value was determined by 1H NMR analysis of the crude reaction mixture. [d]The *ee* was determined by HPLC of the pure product.

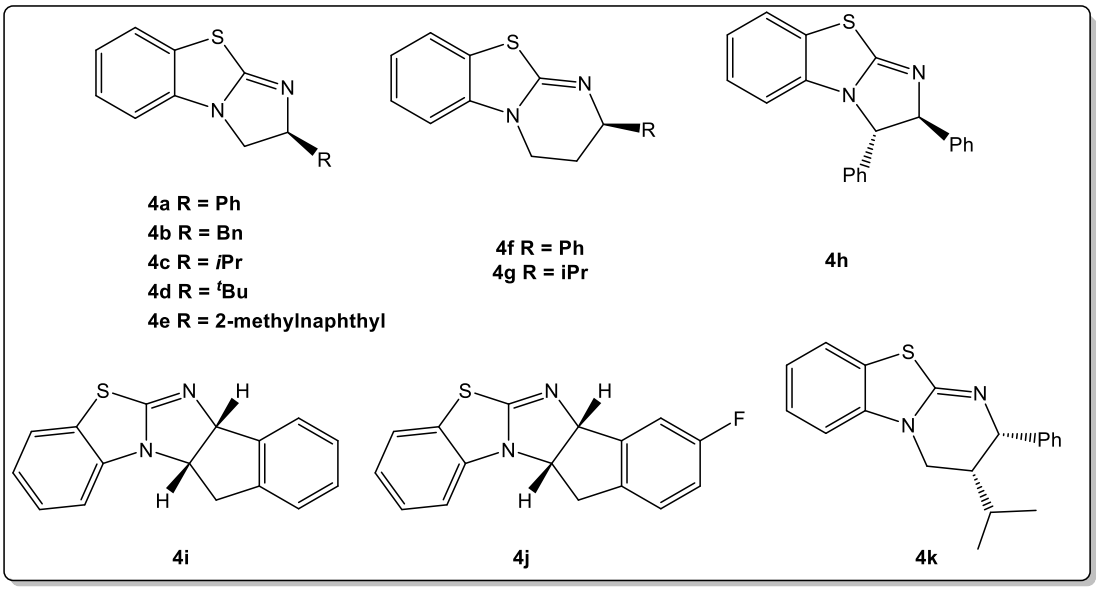
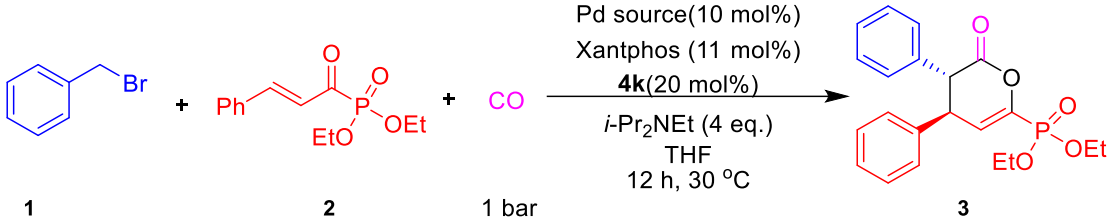


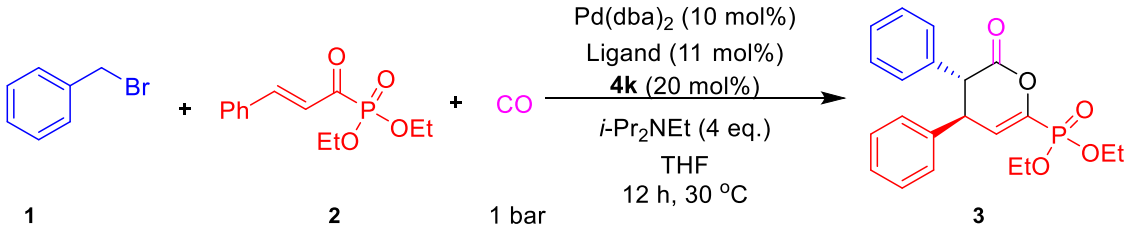
Table S2. Evaluation of Pd catalysts[a]



Entry	Pd Source	Yield (%)[b]	d.r[c]	*ee* (%)[d]
1	$Pd(OAc)_2$	30	9:1	83
2	$PdCl_2$	32	10:1	91
3	$[Pd(allyl)Cl]_2$	60	11:1	90
4	$Pd(TFA)_2$	30	11:1	84

[a]Unless noted otherwise, the reaction of **1** (0.225 mmol) and **2** (0.1 mmol, was carried out in THF (1.0 mL) at 30 °C in the presence of Pd catalyst (10 mol %), XantPhos (11 mol %) and isothiourea catalyst (BTM) **4k** (20 mol %), *i*-Pr_2NEt (4 equiv). [b]NMR yield. [c]The d.r. value was determined by 1H NMR analysis of the crude reaction mixture. [d]The *ee* was determined by HPLC of the pure product.

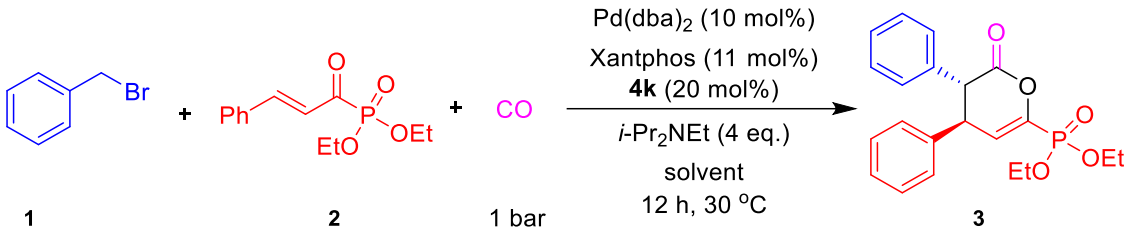
Table S3. Evaluation of Phosphine Ligands[a]



Entry	Ligand	Yield (%)[b]	d.r[c]	*ee* (%)[d]
1	Ph_3P	traces	-	-
2	$(2\text{-furyl})_3P$	22	8:1	80
3	DEPhos	45	9:1	86
4	DPPP	traces	-	-
5	DPPB	traces	-	-
6	DPPF	traces	-	-

[a]Unless noted otherwise, the reaction of **1** (0.225 mmol) and **2** (0.1 mmol, was carried out in THF (1.0 mL) at 30 °C in the presence of $Pd(dba)_2$ (10 mol %), ligand (11 mol %) and isothiourea (BTM) catalyst **4k** (20 mol %), *i*-Pr_2NEt (4 equiv). [b]NMR yield. [c]The d.r. value was determined by 1H NMR analysis of the crude reaction mixture. [d]The *ee* was determined by HPLC of the pure product.

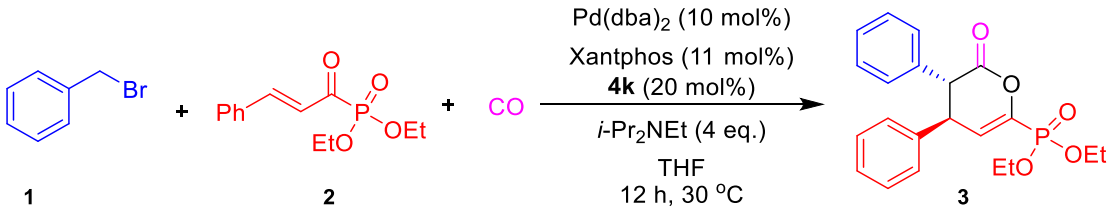
Table S4. Evaluation of Solvent[a]



Entry	Solvent	Yield (%)[b]	d.r[c]	*ee* (%)[d]
1	iPr_2O	20	12:1	50
2	2-Me-THF	40	12:1	90
3	MTBE	36	9:1	79
4	Toluene	45	9:1	73

[a]Unless noted otherwise, the reaction of **1** (0.225 mmol) and **2** (0.1 mmol, was carried out in THF (1.0 mL) at 30 °C in the presence of $Pd(dba)_2$ (10 mol %), XantPhos (11 mol %) and isothiourea (BTM) catalyst **4k** (20 mol %), *i*-Pr_2NEt (4 equiv). [b]NMR yield. [c]The d.r. value was determined by 1H NMR analysis of the crude reaction mixture. [d]The *ee* was determined by HPLC of the pure product.

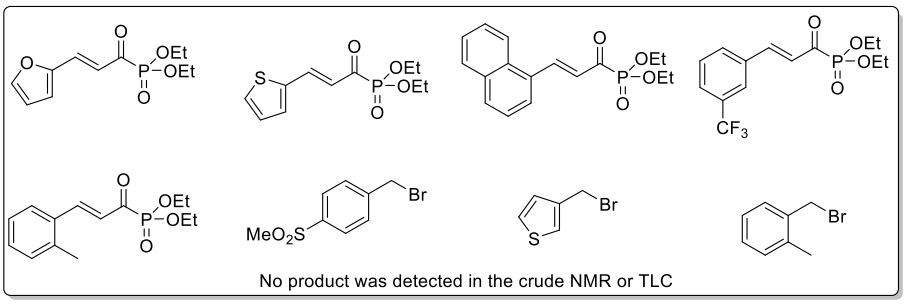
Table S5. Evaluation of CO Pressure[a]



Entry	**CO Pressure**	**Yield (%)[b]**	**d.r[c]**	***ee* (%)[d]**
1	2	traces	-	-
2	3	N.D	-	-
3	4	N.D	-	-

[a]Unless noted otherwise, the reaction of **1** (0.225 mmol) and **2** (0.1 mmol, was carried out in THF (1.0 mL) at 30 °C in the presence of $Pd(dba)_2$ (10 mol %), Xantphos (11 mol %) and benzotetramisole (BTM) catalyst **4k** (20 mol %), *i*-Pr_2NEt (4 equiv). [b]NMR yield. [c]The d.r. value was determined by 1H NMR analysis of the crude reaction mixture. [d]The *ee* was determined by HPLC of the pure product.

Scheme S1. Unsuccessful examples of benzyl bromides and α-ketophosphonates



2. Determining the absolute configuration of the products:

In previous work[2], the absolute configuration of **3h** was determined to be 3R, 4S. Through comparison of the HPLC data, **3h** in our case could also be determined as 3R, 4S. Reference HPLC data (CHIRALPAK AD-H, hexane/isopropanol = 90/10, 1 mL/min, 220 nm) tR (3R,4S): 30.4 min, tR (3S,4R) 33.6 min. Our HPLC data of **3j** (CHIRALPAK AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 220 nm, tR= 28.4 min (minor), tR= 31.7 min (major).

3. 1.0 Mmol scale reaction:

To a flame-dried and Ar-purged Schlenk tube (100 mL) were added $Pd(dba)_2$ (0.1 mmol, 58 mg), Xanthphos (0.11 mmol, 64 mg), **4k** (0.2 mmol, 62 mg) and a stirring bar. The Schlenk tube was then evacuated and filled back with argon. This cycle was repeated three times and followed by addition of 2-(bromomethyl) naphthalene (2.25 mmol, 495 mg), solution of diethyl (E)-(3-(*p*-tolyl)acryloyl)phosphonate (1 mmol, 282 mg) in THF (10 mL), and *i*-Pr_2NEt (4 mmol, 517 mg). The solution was frozen under liquid nitrogen, the nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was filled with 1 bar CO, then was stirred under CO atmosphere at 30 °C for 12 h. The reaction was directly purified by flash column chromatography on silica gel to give **3n.** The d.r. was determined by ^1H NMR analysis of the crude product. Then the reaction was directly purified through flash column chromatography on silica gel (PE: EA = 2:1) to give **3n** as a yellow oil, 360 mg, Yield: 80%. Enantiomeric excess: 94%, > 20:1 d.r.

4. Synthesis of substrates

4.1. General Procedure for the Synthesis of Allyl Alcohols[3].

To a stirred solution of requisite aldehyde (10 mmol) in dichloromethane, diethylphosphite (10 mmol) was added, then triethyl amine (10 mmol) was added dropwise. The resulting solution was stirred at r.t. for 72 h before dilution with HCl (1 M) and the reaction was washed with H_2O, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the crude product.

4.2. General Procedure for Synthesis of Phosphonate Ester.

A solution of the requisite allylic alcohol (1.0 equiv.) in CH_2Cl_2 at −10 °C was added a saturated solution of SO_3.pyridine (3.0 equiv.) in DMSO and *i*-Pr_2NEt (3.0 equiv.) and the reaction stirred at −10 °C until complete by TLC (warming to rt if necessary). Upon completion the reaction was diluted with Et2O and washed consecutively with H_2O, saturated aqueous $NaHCO_3$, saturated aqueous Na_2SO_4

and brine. The ethereal solution was dried over $MgSO_4$ and concentrated in vacuo to give the crude product.

5. General procedure for the synthesis of the products 3a-3n

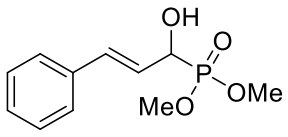
To a flame-dried and Ar-purged Schlenk tube (25 mL) were added $Pd(dba)_2$ (0.01 mmol, 5.8 mg), Xantphos (0.011 mmol, 6.4 mg), **4k** (0.02 mmol, 6.2 mg) and a stirring bar. The Schlenk tube was then evacuated and filled back with argon. This cycle was repeated three times and followed by addition of benzyl bromide derivative **1** (0.225 mmol), solution of α-Ketophosphonates **2** (0.1 mmol) in THF (1 mL), and *i*-Pr_2NEt (0.4 mmol, 51.7 mg). The solution was frozen under liquid nitrogen, the nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was filled with 1 bar CO, then was stirred under CO atmosphere at 30 ºC for 12 h. The reaction was directly purified by flash column chromatography on silica gel to give the pure product **3**.

6. General procedure for the synthesis of the products 4a-4h

To a flame-dried and Ar-purged Schlenk tube (25 mL) were added $Pd(dba)_2$ (0.01 mmol, 5.8 mg), Xantphos (0.011 mmol, 6.4 mg), **4k** (0.02 mmol, 6.2 mg) and a stirring bar. The Schlenk tube was then evacuated and filled back with argon. This cycle was repeated three times and followed by addition of benzyl bromide derivative **1** (0.225 mmol), solution of α-Ketophosphonates **2** (0.1 mmol) in THF (1 mL), and *i*-Pr2NEt (0.4 mmol, 51.7 mg). The solution was frozen under liquid nitrogen, the nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was filled with 1 bar CO. The solution then was stirred under CO atmosphere at 30 ºC for 12 h. After that, the tube was opened to release CO and 1 mL MeOH was added to the reaction mixture, then the reaction was allowed to stir at the same temperature for additional 24 h. After the reaction was completed, the solvent was removed, and the residue was purified by column chromatography to give the pure product **4**.

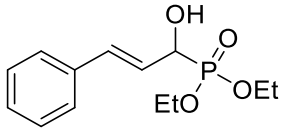
7. Characterization of allyl alcohols

Dimethyl (E)-(1-hydroxy-3-phenylallyl)phosphonate



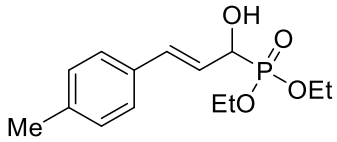
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.32 (m, 2H), 7.28 – 7.24 (m, 1H), 6.80 (ddd, *J* = 15.9, 4.9, 1.6 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.89 (s, 1H), 4.73 (ddd, *J* = 12.9, 6.2, 1.7 Hz, 1H), 3.83 (d, *J* = 10.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.30, 136.28, 132.63, 132.52, 128.60, 127.97, 126.70, 126.68, 123.58, 123.54, 69.86, 68.57, 54.08, 54.02, 53.80, 53.74. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{11}H_{15}O_4PNa$: 265.0606, found: 265.0602.

Diethyl (E)-(1-hydroxy-3-phenylallyl)phosphonate



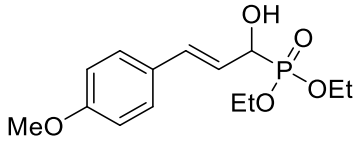
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.31 (m, 2H), 7.26 (m, 1H), 6.79 (dd, *J* = 16.0, 4.9 Hz, 1H), 6.46 – 6.22 (m, 1H), 4.69 (ddd, *J* = 13.0, 6.2, 1.6 Hz, 1H), 4.52 (s, 1H), 4.19 (p, *J* = 7.4 Hz, 4H), 1.33 (qd, *J* = 7.1, 1.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.47, 136.45, 132.32, 132.22, 128.57, 127.85, 126.65, 126.63, 123.96, 123.93, 70.10, 68.81, 63.40, 63.35, 63.16, 63.10, 16.55, 16.51. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_{19}O_4PNa$: 293.0919, found: 293.0915.

Diethyl (E)-(1-hydroxy-3-(p-tolyl)allyl)phosphonate



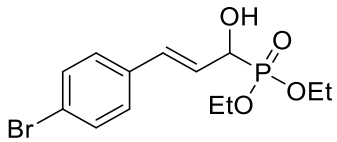
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.74 (ddd, *J* = 15.9, 4.9, 1.6 Hz, 1H), 6.27 (ddd, *J* = 15.9, 6.4, 5.3 Hz, 1H), 4.66 (ddd, *J* = 12.5, 6.4, 1.7 Hz, 1H), 4.26 – 4.12 (m, 4H), 2.34 (s, 3H), 1.33 (q, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.85, 133.57, 133.55, 132.54, 132.44, 129.29, 126.59, 126.58, 122.58, 122.54, 70.23, 68.95, 63.39, 63.33, 63.25, 63.19, 21.26, 16.56, 16.52. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{21}O_4PNa$: 307.1070, found:307.1076

Diethyl (E)-(1-hydroxy-3-(4-methoxyphenyl)allyl)phosphonate



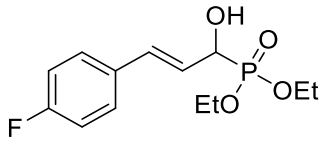
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 6.87 – 6.80 (m, 2H), 6.71 (ddd, *J* = 15.9, 4.8, 1.5 Hz, 1H), 6.18 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.64 (ddd, *J* = 12.2, 6.5, 1.6 Hz, 1H), 4.22 – 4.12 (m, 3H), 3.80 (s, 3H), 1.32 (q, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.42, 132.17, 132.06, 129.21, 129.19, 127.89, 127.88, 121.55, 121.52, 113.96, 70.23, 68.95, 63.33, 63.28, 63.16, 63.11, 55.29, 16.55, 16.51. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{14}H_{22}O_5P$: 301.1205, found: 301.1206

Diethyl (E)-(3-(4-bromophenyl)-1-hydroxyallyl)phosphonate



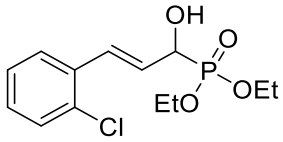
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.73 (ddd, *J* = 16.0, 5.0, 1.6 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.67 (ddd, *J* = 13.5, 5.9, 1.7 Hz, 1H), 4.55 (s, 1H), 4.19 (p, *J* = 7.2 Hz, 4H), 1.33 (q, *J* = 7.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.39, 135.36, 131.69, 130.96, 130.83, 128.13, 128.11, 124.76, 124.72, 121.67, 121.65, 70.10, 68.50, 63.43, 63.36, 63.20, 63.13, 16.55, 16.50. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_{18}BrO_4PNa$: 371.0024, found: 371.0021.

Diethyl (E)-(3-(4-fluorophenyl)-1-hydroxyallyl)phosphonate



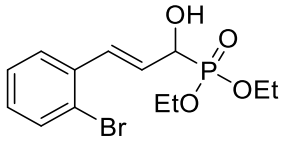
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.75 (dd, *J* = 16.0, 5.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 5.5 Hz, 1H), 5.53 (broad s, 1H), 4.69 (ddd, *J* = 13.9, 5.9, 1.8 Hz, 1H), 4.23 – 4.15 (m, 4H), 1.32 (q, *J* = 7.4 Hz, 6H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.80. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{19}FO_4P$: 289.1005, found: 289.1002.

Diethyl (E)-(3-(2-chlorophenyl)-1-hydroxyallyl)phosphonate



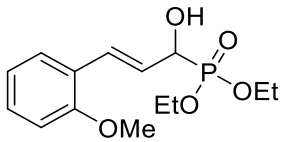
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.32 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.19 (dd, *J* = 6.9, 2.1 Hz, 2H), 7.17 – 7.12 (m, 1H), 6.30 (ddd, *J* = 15.9, 6.1, 5.0 Hz, 1H), 5.68 (s, 1H), 4.72 (ddd, *J* = 13.3, 6.1, 1.8 Hz, 1H), 4.27 – 4.07 (m, 4H), 1.32 (td, *J* = 7.1, 5.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.73, 134.70, 133.20, 133.18, 129.66, 128.81, 128.50, 128.37, 127.10, 127.08, 127.06, 126.84, 77.40, 77.08, 76.77, 70.23, 68.63, 63.64, 63.57, 63.27, 63.20, 16.51, 16.46. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_{18}ClO_4PNa$: 327.0523, found:327.0532

Diethyl (E)-(3-(2-bromophenyl)-1-hydroxyallyl)phosphonate



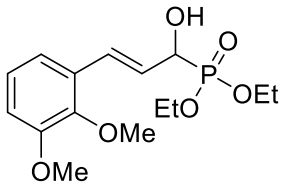
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.27 – 7.20 (m, 3H), 6.75 (ddd, *J* = 16.0, 5.0, 1.7 Hz, 1H), 6.34 (dt, *J* = 15.9, 5.3 Hz, 1H), 5.95 (d, *J* = 5.5 Hz, 1H), 4.71 (ddd, *J* = 14.0, 5.8, 1.8 Hz, 1H), 4.20 (p, *J* = 7.0 Hz, 4H), 1.33 (dt, *J* = 9.0, 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.40, 138.37, 134.46, 130.61, 130.48, 129.78, 127.69, 127.68, 126.43, 126.41, 125.66, 125.62, 124.84, 124.82, 69.90, 68.30, 63.58, 63.50, 63.27, 63.20, 16.52, 16.47. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{19}BrO_4P$: 349,0204, found: 349.0204.

Diethyl (E)-(1-hydroxy-3-(2-methoxyphenyl)allyl)phosphonate



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 (ddd, *J* = 7.4, 1.7, 0.8 Hz, 1H), 7.08 (ddd, *J* = 16.1, 4.8, 1.6 Hz, 1H), 6.92 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.35 (ddd, *J* = 16.1, 6.6, 5.3 Hz, 1H), 4.67 (ddd, *J* = 12.4, 6.6, 1.6 Hz, 1H), 4.20 (dq, *J* = 8.0, 7.1 Hz, 4H), 3.84 (s, 3H), 1.34 (td, *J* = 7.1, 2.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.91, 129.08, 127.95, 127.81, 127.24, 127.22, 125.35, 125.32, 124.21, 124.16, 120.63, 110.88, 70.91, 69.31, 63.24, 63.17, 55.42, 16.54, 16.48. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{21}O_4PNa$: 323.1024, found:323.1034.

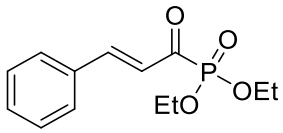
Diethyl (E)-(3-(2,3-dimethoxyphenyl)-1-hydroxyallyl)phosphonate



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 1.9 Hz, 1H), 7.01 (dt, *J* = 8.4, 2.2 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 4.11 – 4.01 (m, 5H), 3.89 (s, 3H), 3.88 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.87, 148.85, 148.81, 148.79, 128.92, 128.90, 119.71, 119.66, 110.73, 110.71, 110.24, 110.20, 71.19, 69.91, 63.31, 63.25, 63.09, 63.03, 55.86, 16.50, 16.45, 16.41. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{15}H_{23}O_6PNa$: 353.1130, found: 353.1130.

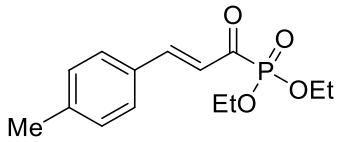
8. Characterization of Phosphate ester

Diethyl cinnamoylphosphonate



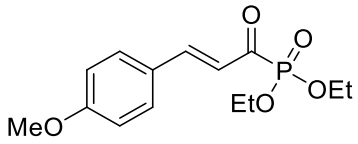
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.3 Hz, 1H), 7.63 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.10 (dd, *J* = 16.3, 12.0 Hz, 1H), 4.27 (dq, *J* = 8.1, 7.1 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.45, 197.70, 148.67, 148.65, 133.99, 133.97, 131.73, 129.10, 129.08, 128.89, 128.18, 125.29, 124.64, 63.96, 63.88, 16.45, 16.39. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{18}O_4P$: 269.0943, found: 269.0943.

Diethyl (E)-(3-(p-tolyl)acryloyl)phosphonate



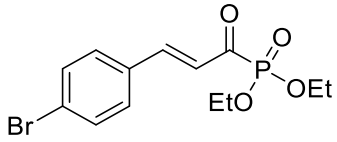
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 16.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.07 (dd, *J* = 16.2, 12.1 Hz, 1H), 4.26 (dq, *J* = 8.0, 7.1 Hz, 4H), 2.40 (s, 3H), 1.44 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.32, 197.58, 148.79, 148.77, 142.61, 131.32, 129.88, 129.17, 128.23, 124.42, 123.77, 63.87, 63.80, 21.69, 16.46, 16.40. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{14}H_{20}O_4P$: 283.1104, found: 283.1101.

Diethyl (E)-(3-(4-methoxyphenyl)acryloyl)phosphonate



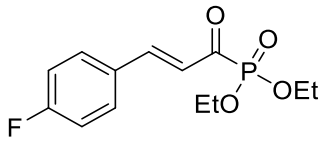
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 16.1 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.00 (dd, *J* = 16.1, 12.2 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.25 (dq, *J* = 8.0, 7.0 Hz, 4H), 3.87 (s, 3H), 1.39 (td, *J* = 7.1, 0.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.86, 197.13, 162.69, 148.57, 148.54, 131.14, 126.74, 126.72, 123.15, 122.49, 114.61, 63.81, 63.74, 55.50, 16.45, 16.40. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{19}O_5PNa$: 321.0873, found: 321.0882.

Diethyl (E)-(3-(4-bromophenyl)acryloyl)phosphonate



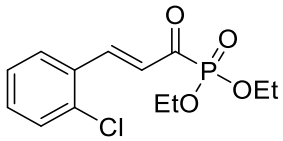
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 16.3 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.07 (dd, *J* = 16.3, 11.8 Hz, 1H), 4.29 – 4.22 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.31, 197.91, 147.10, 147.08, 132.91, 132.90, 132.42, 130.33, 126.25, 125.67, 125.15, 64.01, 63.95, 16.46, 16.41. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{17}BrO_4P$: 347.0048, found: 347.0041.

Diethyl (E)-(3-(4-fluorophenyl)acryloyl)phosphonate



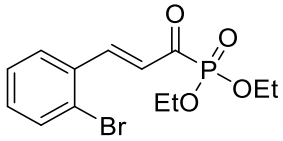
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 16.2 Hz, 1H), 7.64 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 7.02 (dd, *J* = 16.2, 11.9 Hz, 1H), 4.30 – 4.21 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.16, 197.76, 165.75, 163.73, 147.26, 131.18, 131.11, 130.30, 130.28, 130.26, 125.02, 125.00, 124.49, 124.47, 116.49, 116.31, 63.96, 63.91, 16.45, 16.41. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{17}FO_4P$: 287.0843, found: 287.0849. **^{19}F NMR** (471 MHz, CDCl3) δ -106.81.

Diethyl (E)-(3-(2-chlorophenyl)acryloyl)phosphonate



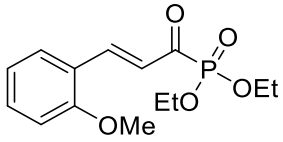
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 16.3 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.38 (td, *J* = 7.7, 1.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.06 (dd, *J* = 16.3, 11.8 Hz, 1H), 4.29 (p, *J* = 7.3 Hz, 4H), 1.41 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.45, 198.04, 144.13, 144.12, 136.27, 132.33, 132.25, 132.24, 130.42, 127.79, 127.25, 127.15, 126.63, 64.02, 63.96, 16.48, 16.43. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_{16}ClO_4PNa$: 325.0377, found: 325.0378.

Diethyl (E)-(3-(2-bromophenyl)acryloyl)phosphonate



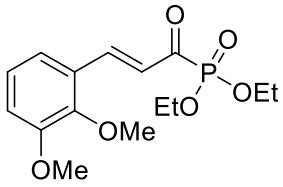
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 16.3 Hz, 1H), 7.67 (ddd, *J* = 22.9, 7.9, 1.5 Hz, 2H), 7.44 – 7.33 (m, 1H), 7.30 (td, *J* = 7.7, 1.7 Hz, 1H), 7.01 (dd, *J* = 16.2, 12.3 Hz, 1H), 4.29 (dq, *J* = 8.2, 7.1 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.41, 198.00, 146.83, 146.81, 133.99, 133.98, 133.71, 132.45, 127.94, 127.87, 127.41, 126.89, 126.75, 64.01, 63.96, 16.49, 16.44. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{17}BrO_4P$: 347.0048, found: 347.0048.

Diethyl (E)-(3-(2-methoxyphenyl)acryloyl)phosphonate



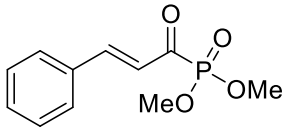
The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (500 MHz $CDCl_3$) δ 8.48 (d, *J* = 16.1 Hz, 1H), 7.71 – 7.57 (m, 1H), 7.34 (td, *J* = 7.4, 1.3 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.02 (dd, *J* = 16.1, 12.7 Hz, 1H), 4.27 (p, *J* = 7.2 Hz, 4H), 2.50 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 7H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.31, 197.92, 146.42, 146.41, 139.33, 132.85, 132.84, 131.50, 131.10, 126.56, 126.53, 126.06, 125.54, 63.89, 63.84, 19.76, 16.48, 16.44. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{19}O_4PNa$: 305.0923, found: 305.0931.

Diethyl (E)-(3-(2,3-dimethoxyphenyl)acryloyl)phosphonate



The product was obtained as yellow oil after chromatographic purification (PE:EA= 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 16.5 Hz, 1H), 7.24 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.17 – 7.07 (m, 2H), 7.01 (dd, *J* = 8.1, 1.4 Hz, 1H), 4.28 (p, *J* = 7.2 Hz, 4H), 3.91 (s, 3H), 3.89 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.53, 198.13, 153.15, 149.49, 143.37, 143.35, 128.16, 128.15, 126.09, 125.57, 124.33, 119.29, 115.29, 63.83, 63.77, 61.62, 55.92, 16.47, 16.42. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{15}H_{22}O_6P$: 329.1154, found: 329.1150.

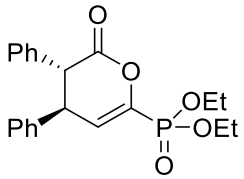
Dimethyl cinnamoylphosphonate



The product was obtained as yellow oil without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.3 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.53 – 7.35 (m, 3H), 7.08 (dd, *J* = 16.3, 13.0 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.55, 197.16, 149.16, 149.15, 133.88, 133.86, 131.87, 129.13, 125.35, 124.82, 54.14, 54.08. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{11}H_{14}O_4P$: 241.0630, found: 241.0628.

9. Characterization of products 3a-3n

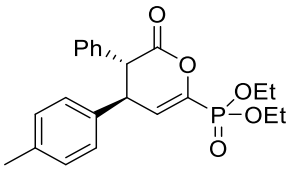
Diethyl ((3R,4S)-2-oxo-3,4-diphenyl-3,4-dihydro-2H-pyran-6-yl)phosphonate (3a)



The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3a** (yield: 70%, 27 mg, d.r. >20:1, 90% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 6H), 7.12 (m, 2H), 7.07 – 7.01 (m, 2H), 6.51 (dd, *J* = 10.1, 4.0 Hz, 1H), 4.31 – 4.09 (m, 4H), 4.06 (ddd,

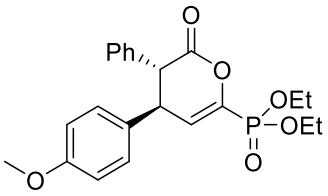
J = 8.3, 3.9, 2.6 Hz, 1H), 3.96 (d, *J* = 8.3 Hz,1H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.22 (d, *J* = 8.4 Hz), 145.40, 143.10, 138.92, 135.39, 129.05, 128.80, 128.24, 127.99, 127.87, 127.44, 122.40, 122.21, 63.50 (dd, *J* = 11.3, 5.8 Hz), 52.61, 45.51 (d, *J* = 12.7 Hz), 29.73, 16.36 (dd, *J* = 9.5, 6.3 Hz)**. ^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.31. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{21}H_{23}O_5PNa$: 409.1181, found: 409.1178. Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 13.0 min (minor), tR = 16.1 min (major).

Diethyl((3R,4S)-2-oxo-3-phenyl-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-yl)phosphonate (3b)



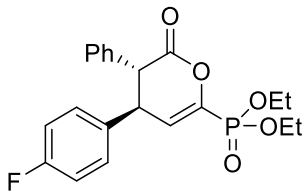
The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3b** (yield: 80%, 32 mg, d.r. >20:1, 90% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 3H), 7.13 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.50 (dd, *J* = 10.1, 4.0 Hz, 1H), 4.30 – 4.06 (m, 4H), 4.05 – 3.99 (m, 1H), 3.94 (d, *J* = 8.2 Hz, 1H), 2.29 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.32 (d, *J* = 8.7 Hz), 145.10, 142.78, 137.57, 129.71, 129.38, 128.78, 128.60, 128.23, 127.94, 127.27, 122.65 (d, *J* = 19.4 Hz), 63.53 (dd, *J* = 11.4, 5.9 Hz), 52.65, 45.06 (d, *J* = 12.6 Hz), 41.01, 21.07, 16.34 (dd, *J* = 9.8, 6.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.42. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{22}H_{25}O_5PNa$: 423.1332, found: 423.1339. Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 11.8 min (minor), tR = 13.5 min (major)

Diethyl ((3R,4S)-4-(4-methoxyphenyl)-2-oxo-3-phenyl-3,4-dihydro-2H-pyran-6-yl)phosphonate (3c)



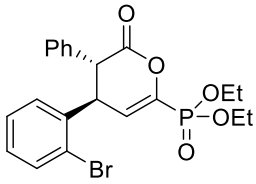
The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3c** (yield: 70%, 29.2 mg, d.r. >20:1, 88% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 3H), 7.12 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.50 (dd, *J* = 10.1, 3.9 Hz, 1H), 4.33 – 4.07 (m, 4H), 4.01 (ddd, *J* = 8.4, 4.0, 2.7 Hz, 1H), 3.92 (d, *J* = 8.3 Hz, 1H), 3.76 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.34 (d, *J* = 8.5 Hz), 159.04, 145.13, 142.82, 135.49, 130.86, 129.75, 129.68, 128.78, 128.50, 128.25, 128.00, 127.93, 122.82, 122.63, 114.35, 114.00, 63.48 (dd, *J* = 11.7, 5.8 Hz), 55.27, 52.88, 44.71 (d, *J* = 12.6 Hz), 16.35 (dd, *J* = 10.4, 6.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.41. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{22}H_{26}O_6P$: 417.1462, found: 417.1471. Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 10.8 min (minor), tR = 11.7 min (major).

Diethyl ((3R,4S)-4-(4-fluorophenyl)-2-oxo-3-phenyl-3,4-dihydro-2H-pyran-6-yl)phosphonate (3d)



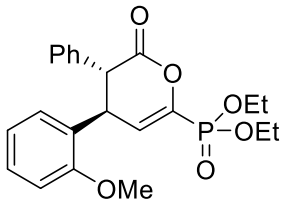
The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3d** (yield: 78%, 31.5 mg, d.r. >20:1, 94% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 3H), 7.09 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.03 – 6.88 (m, 4H), 6.48 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.32 – 4.10 (m, 4H), 4.05 (dt, *J* = 9.0, 3.3 Hz, 1H), 3.88 (d, *J* = 9.0 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.01 (d, *J* = 8.7 Hz), 163.36, 160.91, 145.69, 143.38, 135.10, 134.72, 134.69, 129.13, 129.05, 128.83, 128.53, 128.30, 128.05, 122.16, 121.97, 116.05, 115.84, 63.52 (dd, *J* = 12.2, 6.0 Hz), 52.83, 44.82 (d, *J* = 12.6 Hz), 16.36 (dd, *J* = 10.3, 6.2 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 4.11. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.05. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{21}H_{23}FO_5P$: 405.1267, found: 405.1276. Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak AD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 228 nm): tR = 21.7 min (major), tR = 31.8 min (minor).

Diethyl ((3R,4S)-4-(2-bromophenyl)-2-oxo-3-phenyl-3,4-dihydro-2H-pyran-6-yl)phosphonate (3e)



The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3e** (yield: 65%, 30.2 mg, d.r. >20:1, 88% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.33 (m, 6H), 7.22 – 7.16 (m, 2H), 6.49 – 6.38 (m, 1H), 4.63 (td, *J* = 5.3, 1.2 Hz, 1H), 4.34 – 4.24 (m, 2H), 4.22 – 4.15 (m, 2H), 4.12 – 4.02 (m, 1H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.76 (d, *J* = 8.1 Hz), 146.40, 144.09, 137.01, 135.05, 133.78, 129.66, 129.37, 129.08, 128.89, 128.62, 128.50, 128.32, 128.19, 127.75, 127.20, 124.16, 120.53, 120.34, 63.56 (dd, *J* = 15.8, 5.8 Hz), 50.71, 44.24 (d, *J* = 12.6 Hz), 16.35 (dd, *J* = 12.6, 6.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.06. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{21}H_{22}BrO_5P$: 465.0461, found: 465.0455. Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 10.5 min (major), tR = 11.5 min (minor).

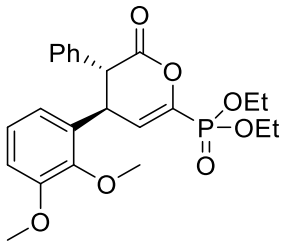
Diethyl ((3R,4S)-4-(2-methoxyphenyl)-2-oxo-3-phenyl-3,4-dihydro-2H-pyran-6-yl)phosphonate (3f)



The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3f** (yield: 75%, 31.2 mg, d.r. >20:1, 90% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 6H), 7.04 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.98 – 6.77 (m, 2H), 6.38 (ddd, *J* = 10.1, 5.2, 0.9 Hz, 1H), 4.29 – 4.08 (m, 6H), 3.80 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.25 (d, *J* = 8.2 Hz), 156.84, 144.87, 142.56, 137.09, 129.25, 128.82, 128.41, 127.84, 127.51, 126.91, 120.94, 120.84, 120.65, 110.90, 63.28 (d, *J* = 5.9 Hz), 54.93, 50.36, 41.75 (d, *J* = 12.9 Hz), 16.33

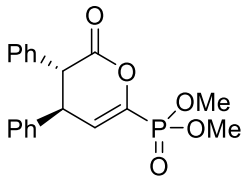
(dd, *J* = 6.3, 4.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.85. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{22}H_{26}O_6P$: 417.1467, found: 417.1461. Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 11.1 min (minor), tR = 12.0 min (major).

diethyl ((3R,4S)-4-(2,3-dimethoxyphenyl)-2-oxo-3-phenyl-3,4-dihydro-2H-pyran-6-yl)phosphonate (3g)



The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3g** (yield: 72%, 32.2 mg, d.r. >20:1, 84% ee) as yellow oil). **^{1}H NMR** (400 MHz $CDCl_3$) δ 7.34 – 7.19 (m, 5H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.66 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.37 (dd, *J* = 10.1, 4.7 Hz, 1H), 4.35 (ddd, *J* = 6.4, 4.7, 2.0 Hz, 1H), 4.30 – 4.06 (m, 5H), 3.84 (s, 3H), 3.77 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.21 (d, *J* = 8.5 Hz), 152.79, 146.72, 136.63, 132.29, 130.99, 130.50, 128.94, 128.86, 128.82, 128.61, 128.40, 127.86, 127.80, 126.88, 124.15, 121.87, 121.68, 119.89, 112.36, 63.37 (dd, *J* = 9.6, 5.9 Hz), 60.60, 55.79, 51.00, 16.35 (t, *J* = 6.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.61. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{28}O_7P$: 447.1573, found: 447.1566. Enantiomeric excess: 84%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 14.5 min (minor), tR = 23.3 min (major).

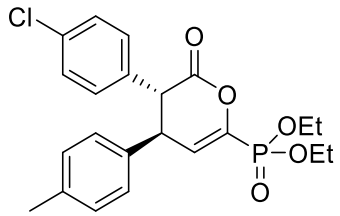
Dimethyl ((3R,4S)-2-oxo-3,4-diphenyl-3,4-dihydro-2H-pyran-6-yl)phosphonate (3h)



The reaction was directly purified by flash column chromatography (PE:EA= 1:1) on silica gel to give **3h** (yield: 80%, 28.6 mg, d.r. >20:1, 95% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (m, 4H), 7.26 – 7.18 (m, 2H), 7.12 (m, 2H), 7.04 (m, 2H), 6.53 (dd, *J* = 10.2, 3.9 Hz, 1H), 4.07 (ddd, *J* = 8.6, 3.9, 2.8 Hz, 1H), 3.97 (d, *J* = 8.5 Hz, 1H), 3.90 (d, *J* = 11.2 Hz, 3H), 3.81 (d, *J* = 11.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.96 (d, *J* = 8.6 Hz), 144.45, 142.13, 138.78, 135.33, 130.07, 130.06, 129.06, 128.81, 128.70, 128.54, 128.21, 127.41, 123.08 (d, *J* = 19.4 Hz), 53.70 (dd, *J* = 7.5, 5.8 Hz), 45.62 (d, *J* = 12.7 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 7.11. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{19}H_{20}O_5P$: 359.1048, found: 359.1054. Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak AD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 28.4 min (major), tR =

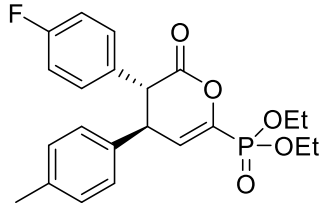
31.7 min (minor). (Daicel Chirapak ID, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 22.7 min (minor), tR = 24.4 min (major).

Diethyl ((3R,4S)-3-(4-chlorophenyl)-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-yl)phosphonate (3i)



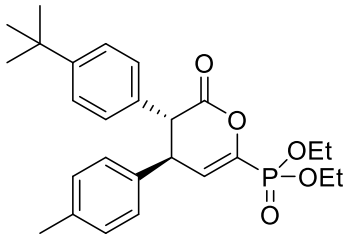
The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3i** (yield: 65%, 28.3 mg, d.r. >20:1, 87% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.09 – 6.98 (m, 4H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.46 (dd, *J* = 10.1, 3.3 Hz, 1H), 4.31 – 4.08 (m, 4H), 3.97 (dt, *J* = 9.8, 3.3 Hz, 1H), 3.87 (d, *J* = 9.8 Hz, 1H), 2.29 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.08 (d, *J* = 8.8 Hz), 145.09, 143.24, 137.70, 135.53, 133.90, 133.83, 129.86, 129.74, 128.91, 127.31, 122.73 (d, *J* = 19.3 Hz), 63.52 (dd, *J* = 11.4, 5.8 Hz), 52.19, 45.12 (d, *J* = 12.5 Hz), 16.38 (dd, *J* = 9.4, 6.2 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 4.20. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{22}H_{25}ClO_5P$: 435.1128, found: 435.1122. Enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 14 min (minor), tR = 16.1 min (major).

Diethyl ((3R,4S)-3-(4-fluorophenyl)-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-yl)phosphonate (3j)



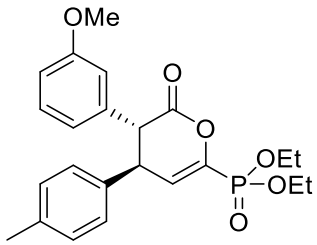
The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3j** (yield: 55%, 23 mg, d.r. >20:1, 92% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 – 7.01 (m, 4H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.45 (dd, *J* = 10.1, 3.4 Hz, 1H), 4.31 – 4.06 (m, 4H), 3.94 (dt, *J* = 9.6, 3.3 Hz, 1H), 3.85 (d, *J* = 9.5 Hz, 1H), 2.27 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.27 (d, *J* = 8.8 Hz), 163.18, 161.22, 145.08, 143.24, 137.64, 135.67, 131.21, 131.18, 130.16, 130.10, 129.70, 129.49, 129.47, 128.43, 127.90, 127.31, 126.64, 122.73 (d, *J* = 19.2 Hz), 115.70 (d, *J* = 21.6 Hz), 63.50 (dd, *J* = 12.0, 5.9 Hz), 52.06, 45.26 (d, *J* = 12.4 Hz), 16.37 (dd, *J* = 9.8, 6.2 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 4.24. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.07. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{22}H_{25}FO_5P$: 419.1424, found: 419.1423. Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 13.2 min (minor), tR = 14.3 min (major).

Diethyl ((3R,4S)-3-(4-(tert-butyl)phenyl)-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-yl)phosphonate (3k)



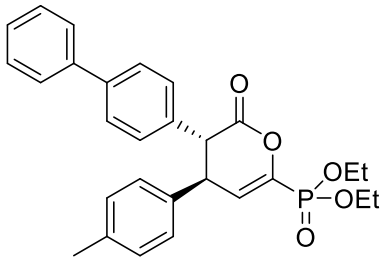
The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3k** (yield: 80%, 36.5 mg, d.r. >20:1, 86% ee) as yellow oil). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.10 (dd, *J* = 13.6, 8.1 Hz, 4H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.49 (dd, *J* = 10.1, 4.7 Hz, 1H), 4.29 – 4.00 (m, 5H), 3.97 (d, *J* = 6.2 Hz, 1H), 2.30 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 6.9 Hz, 3H), 1.28 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.28 (d, *J* = 8.4 Hz), 150.93, 144.92, 143.08, 137.56, 135.98, 132.51, 129.76, 127.53, 127.16, 125.75, 122.07 (d, *J* = 19.3 Hz), 63.39 (dd, *J* = 16.6, 5.7 Hz), 52.06, 44.85 (d, *J* = 12.5 Hz), 34.51, 31.27, 21.08, 16.33 (dd, *J* = 14.1, 6.3 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 4.50. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{34}O_5P$: 457.2144, found: 457.2143. Enantiomeric excess: 86%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 7.6 min (minor), tR = 9.6 min (major).

Diethyl ((3R,4S)-3-(3-methoxyphenyl)-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-yl)phosphonate (3l)



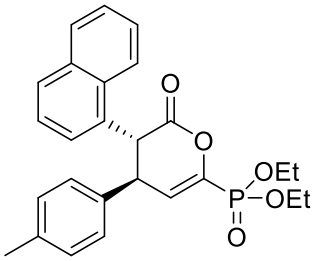
The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3l** (yield: 58%, 27.9 mg, d.r. >20:1, 88% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.80 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.74 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.68 (t, *J* = 2.2 Hz, 1H), 6.48 (dd, *J* = 10.1, 4.1 Hz, 1H), 4.32 – 4.06 (m, 4H), 4.02 (ddd, *J* = 6.8, 4.2, 2.4 Hz, 1H), 3.92 (d, *J* = 7.8 Hz, 1H), 3.75 (s, 3H), 2.29 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.11 (d, *J* = 8.6 Hz), 159.77, 145.18, 142.87, 137.59, 137.02, 135.90, 129.76 (d, *J* = 4.9 Hz), 127.22, 122.40 (d, *J* = 19.3 Hz), 120.40, 114.19, 113.15, 63.46 (dd, *J* = 8.8, 5.9 Hz), 55.24, 52.59, 45.03 (d, *J* = 12.5 Hz), 29.72, 21.05, 16.34 (dd, *J* = 10.0, 6.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.39. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{28}O_6P$: 431.1624, found: 431.1617. Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 14.3 min (minor), tR = 16.8 min (major).

Diethyl ((3R,4S)-3-([1,1'-biphenyl]-4-yl)-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-yl)phosphonate (3m)



The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3m** (yield: 60%, 28.6 mg, d.r. >20:1, 88% ee) as yellow oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 3H), 7.44 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.14 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.52 (dd, *J* = 10.1, 3.9 Hz, 1H), 4.31 – 4.08 (m, 4H), 4.09 – 4.04 (m, 1H), 4.01 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.32 (d, *J* = 8.5 Hz), 145.03, 143.18, 140.78, 140.33, 137.60, 135.85, 134.49, 130.14, 129.75, 128.82, 128.66, 128.38, 128.01, 127.45, 127.30, 127.04, 125.99, 123.12, 122.61, 122.46, 122.03, 63.48 (dd, *J* = 12.9, 5.9 Hz), 52.36, 45.05 (d, *J* = 12.5 Hz), 16.38 (dd, *J* = 10.8, 6.2 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 4.40. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{28}H_{30}O_5P$: 477.1831, found: 477.1827. Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 15.0 min (minor), tR = 23.7 min (major).

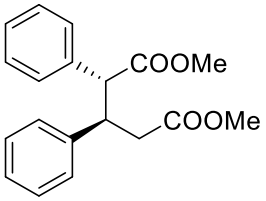
Diethyl((3R,4S)-3-(naphthalen-1-yl)-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-pyran-6yl)phosphonate (3n)



The reaction was directly purified by flash column chromatography (PE:EA= 2:1) on silica gel to give **3n** (yield: 85%, 38.3 mg, d.r. >20:1, 94% ee) as yellow oil).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.8, 3.6 Hz, 2H), 7.75 – 7.69 (m,1H), 7.54-7.45 (m, 4H), 7.31 (dd, *J* = 8.6, 2.0 Hz,1H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.52 (dd, *J* = 10.1, 3.9 Hz, 1H), 4.27 (ddq, *J* = 8.2, 7.0, 3.3 Hz, 2H), 4.21 – 4.13 (m, 2H), 4.15 – 4.08 (m, 2H), 2.27 (s, 3H), 1.42 (t, *J* = 7.1 Hz,3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.32 (d, *J* = 8.5 Hz), 144.98, 143.13, 137.59, 135.83, 133.17, 132.78 (d, *J* = 10.5 Hz), 129.76, 128.72, 127.84, 127.66, 127.48, 127.26, 126.37 (d, *J* = 7.7 Hz), 125.66, 122.58 (d, *J* = 19.3 Hz), 63.48 (dd, *J* = 17.0, 5.9 Hz), 52.77, 44.91 (d, *J* = 12.5 Hz), 21.05, 16.36 (dd, *J* = 15.6, 6.2 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$) δ 4.44. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{28}O_5P$: 451.1674, found: 451.1676. Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 31.1 min (minor), tR = 33.9 min (major).

10. Characterization of products 4a-4h

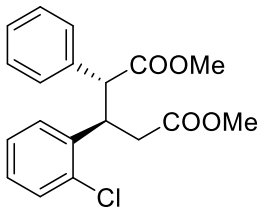
***Dimethyl (2R,3R)-2,3-diphenylpentanedioate* (4a)**



The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4a** (yield: 70%, 21.8 mg, d.r. >20:1, 92% ee) as white solid). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 7H), 7.08 – 7.03 (m, 1H), 7.02 – 6.97 (m, 2H), 3.90 – 3.80 (m, 2H), 3.69 (s, 3H), 3.51 (s, 3H),

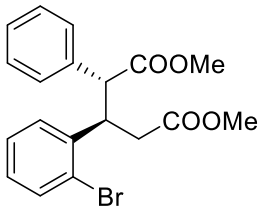
2.88 – 2.72 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.38, 171.90, 140.18, 136.59, 128.60, 128.25, 128.12, 127.26, 126.70, 57.18, 52.18, 51.57, 45.49, 39.22, 29.72. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{19}H_{20}O_4Na$: 335.1259, found: 335.1269: Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 8.6 min (minor), tR = 9.9 min (major).

Dimethyl (2R,3R)-3-(2-chlorophenyl)-2-phenylpentanedioate **(4b)**



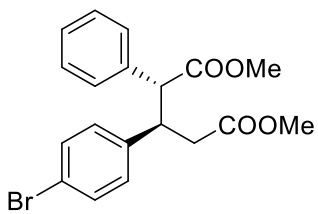
The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4b** (yield: 75%, 26 mg, d.r. >20:1, 76% ee) as colorless oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.20 – 7.05 (m, 6H), 7.04 – 6.98 (m, 1H), 4.42 (s, 1H), 4.12 (d, *J* = 10.3 Hz, 1H), 3.67 (s, 3H), 3.52 (s, 3H), 3.05 – 2.91 (m, 1H), 2.83 (dd, *J* = 15.6, 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.06, 171.81, 137.78, 136.28, 134.25, 129.81, 128.90, 128.39, 128.32, 128.07, 127.94, 127.45, 126.65, 55.26, 52.18, 51.60, 41.53, 37.48. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{19}H_{19}ClO_4Na$: 369.0870, found: 369.0885: Enantiomeric excess: 76%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 6.6 min (minor), tR = 8.8 min (major)

Dimethyl (2R,3R)-3-(2-bromophenyl)-2-phenylpentanedioate **(4c)**



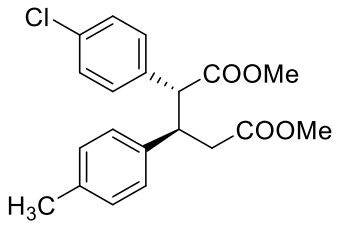
The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4c** (yield: 65%, 25.3 mg, d.r. >20:1, 84% ee) as colorless oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.30 – 7.22 (m, 2H), 7.22 – 7.12 (m, 5H), 6.95 (m, 1H), 4.42 (s, 1H), 4.12 (s, 1H), 3.66 (s, 3H), 3.52 (s, 3H), 2.97 (s, 1H), 2.82 (dd, *J* = 15.5, 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.95, 171.81, 136.20, 133.17, 128.63, 128.48, 128.35, 128.26, 127.48, 127.32, 55.58, 52.17, 51.62, 43.52, 37.48. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{19}H_{19}BrO_4Na$: 413.0364, found: 413.0357: Enantiomeric excess: 84%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 6.8 min (minor), tR = 10.3 min (major).

Dimethyl (2R,3R)-3-(4-bromophenyl)-2-phenylpentanedioate **(4d)**



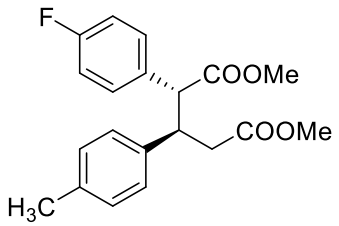
The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4d** (yield: 76%, 29.6 mg, d.r. >20:1, 91% ee) as colorless oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.19 – 7.06 (m, 5H), 6.92 – 6.81 (m, 2H), 3.89 – 3.76 (m, 2H), 3.69 (s, 3H), 3.53 (s, 3H), 2.86 – 2.65 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.13, 171.63, 139.29, 136.21, 131.27, 129.86, 128.51, 128.45, 127.50, 120.59, 56.90, 52.28, 51.68, 44.89, 38.99. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{19}H_{19}BrO_4Na$: 413.0364, found: 413.0375 Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 9 min (major), tR = 10.5 min (minor).

Dimethyl (2R,3R)-2-(4-chlorophenyl)-3-(p-tolyl)pentanedioate **(4e)**



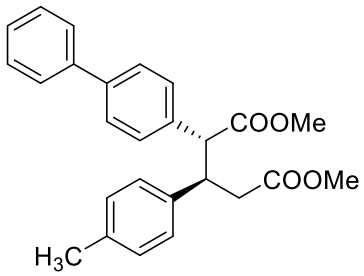
The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4e** (yield: 71%, 25.6 mg, d.r. >20:1, 90% ee) as colorless oil). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 3.85 – 3.74 (m, 1H), 3.69 (s, 2H), 3.52 (s, 2H), 2.82 – 2.67 (m, 1H), 2.20 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.18, 171.84, 136.66, 136.37, 135.20, 133.11, 129.99, 129.02, 128.43, 127.85, 56.47, 52.31, 51.63, 44.94, 39.38, 21.02. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{20}H_{21}ClO_4Na$: 383.1026, found: 383.1040: Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 5.4 min (minor), tR = 5.9 min (major)

Dimethyl (2R,3R)-2-(4-fluorophenyl)-3-(p-tolyl)pentanedioate **(4f)**



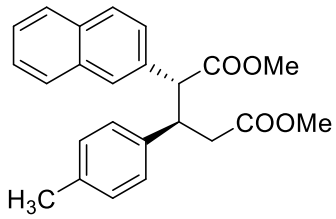
The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4f** (yield: 69%, 23.7 mg, d.r. >20:1, 88% ee) as colorless oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 6.96 (m, 1H), 7.00 – 6.68 (m, 3H), 3.88 – 3.75 (m, 1H), 3.69 (s, 1H), 3.52 (s, 1H), 2.91 – 2.54 (m, 1H), 2.20 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.39, 171.87, 163.13, 160.69, 136.79, 136.28, 132.47, 132.43, 130.22, 130.14, 128.95, 127.86, 115.23, 115.02, 56.35, 52.23, 51.60, 45.14, 39.32, 21.00. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.20. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{20}H_{21}FO_4Na$: 367.1322, found: 367.1334: Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 220 nm): tR = 5.3 min (minor), tR = 5.6 min (major).

Dimethyl (2R,3R)-2-([1,1'-biphenyl]-4-yl)-3-(p-tolyl)pentanedioate **(4g)**



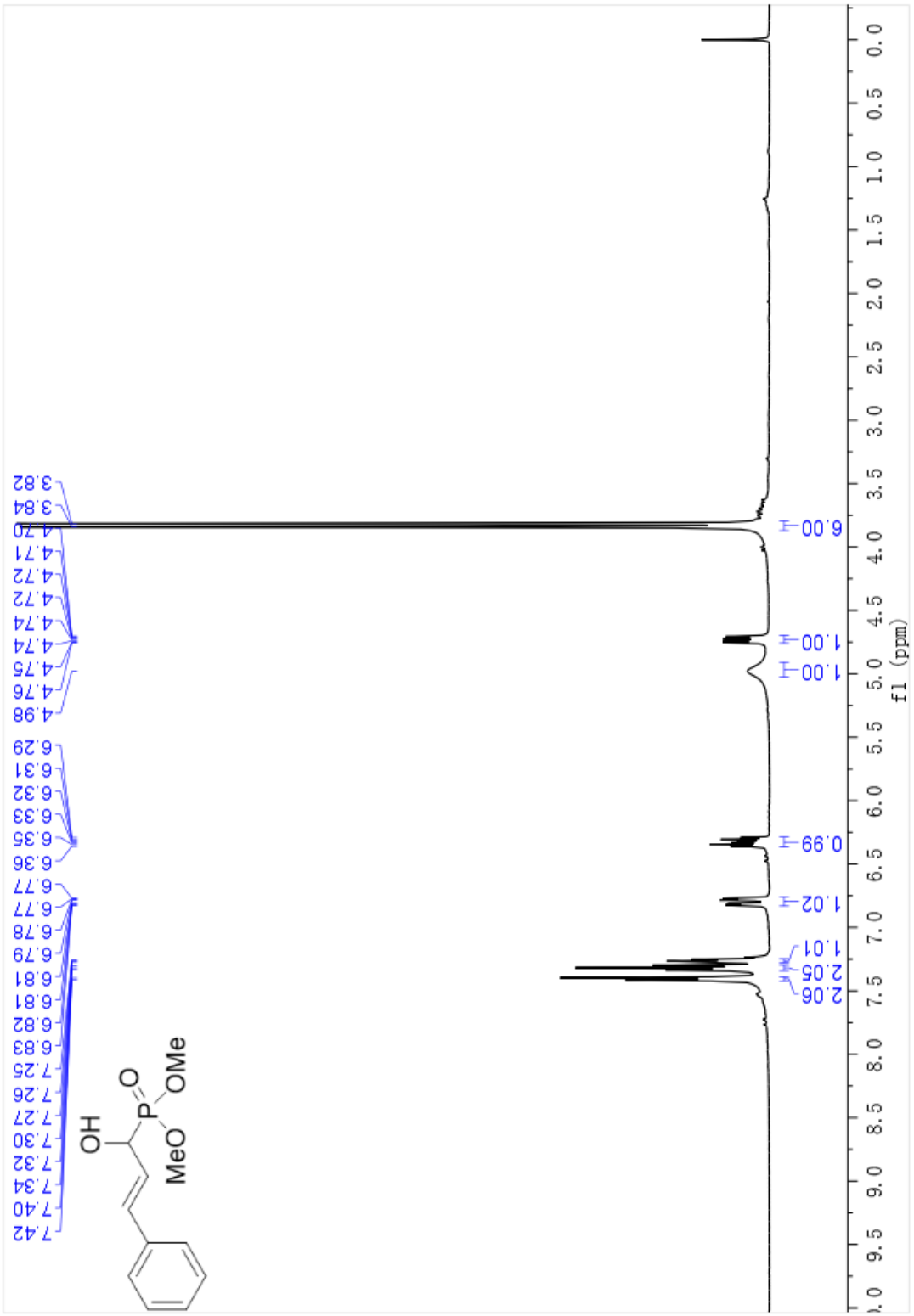
The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4g** (yield: 65%, 23.7 mg, d.r. >20:1, 84% ee) as colorless oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.43 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 4H), 3.95 – 3.81 (m, 2H), 3.70 (s, 3H), 3.52 (s, 3H), 2.87 – 2.49 (m, 2H), 2.19 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.46, 172.01, 140.53, 139.90, 137.02, 136.19, 135.72, 129.96, 129.06, 128.93, 128.80, 128.71, 127.94, 127.48, 127.34, 127.26, 127.07, 126.93, 126.89, 56.81, 52.22, 51.59, 44.97, 39.30, 21.02. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{27}O_4$: 403.1909, found: 403.1916: Enantiomeric excess: 84%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 90/10, flow rate 0.3 mL/min, T = 30 °C, 220 nm): tR = 16.3 min (minor), tR = 17.1 min (major).

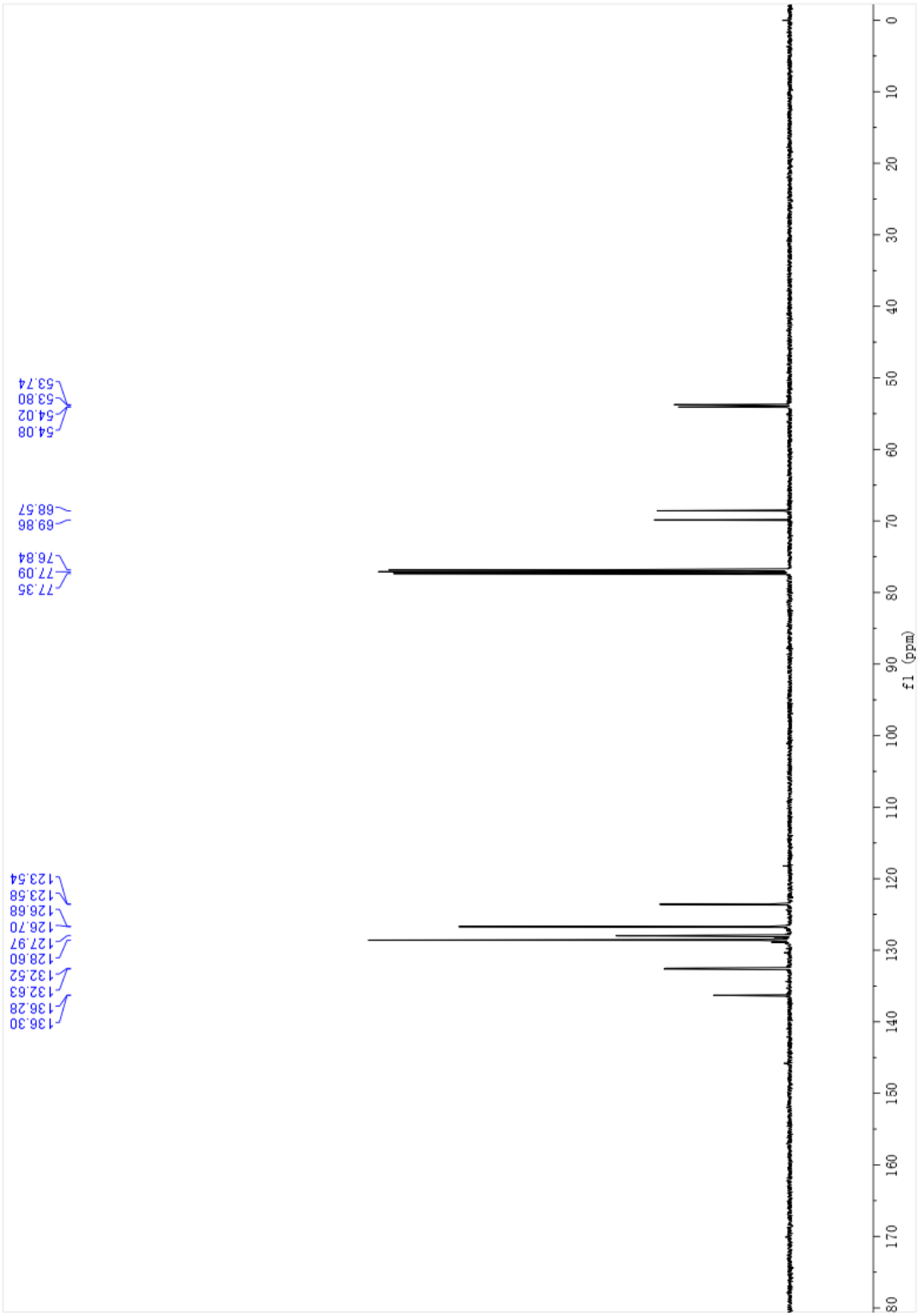
Dimethyl (2R,3R)-2-(naphthalen-2-yl)-3-(p-tolyl)pentanedioate **(4h)**



The reaction was directly purified by flash column chromatography (PE:EA= 10:1) on silica gel to give product **4h** (yield: 84%, 31.5 mg, d.r. >20:1, 86% ee) as colorless oil). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.50 (m, 1H), 7.45 – 7.28 (m, 1H), 7.06 – 6.79 (m, 1H), 4.19 – 3.84 (m, 1H), 3.69 (s, 1H), 3.53 (s, 1H), 2.99 – 2.65 (m, 0H), 2.14 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.47, 172.02, 136.98, 136.16, 134.20, 133.14, 132.53, 128.93, 127.92, 127.89, 127.86, 127.82, 127.52, 126.46, 125.91, 125.80, 57.17, 52.21, 51.59, 44.81, 39.48, 20.96. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{24}H_{25}O_4$: 377.1753, found: 377.1767: Enantiomeric excess: 86%, determined by HPLC (Daicel Chirapak OJ, hexane/ isopropanol = 90/10, flow rate 0.3 mL/min, T = 30 °C, 220 nm): tR = 35.6 min (major), tR = 41.9 min (minor).

NMR Spectra of Allyl Alchols

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127.97
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132.63
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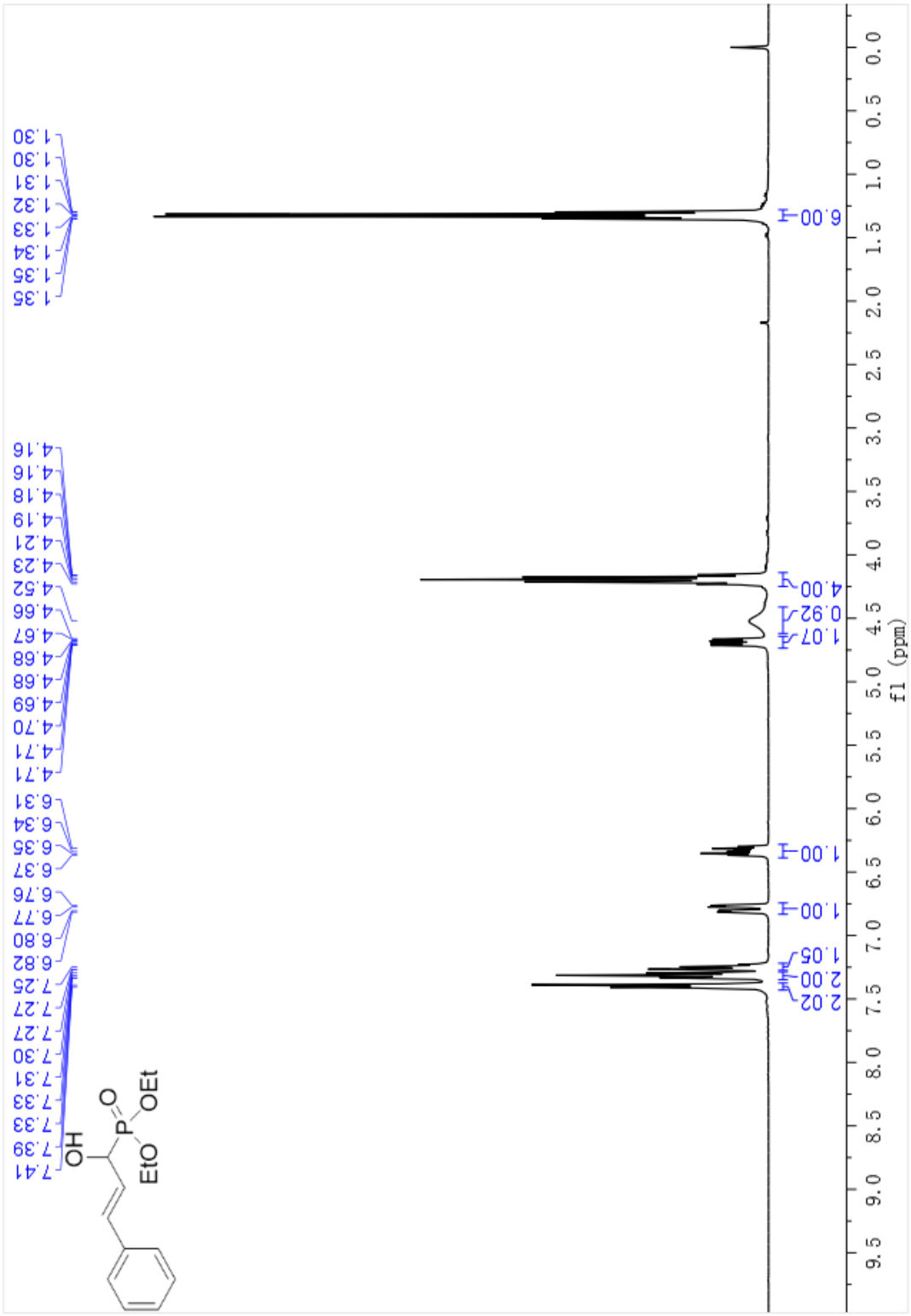
136.30
f1 (ppm)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2.02
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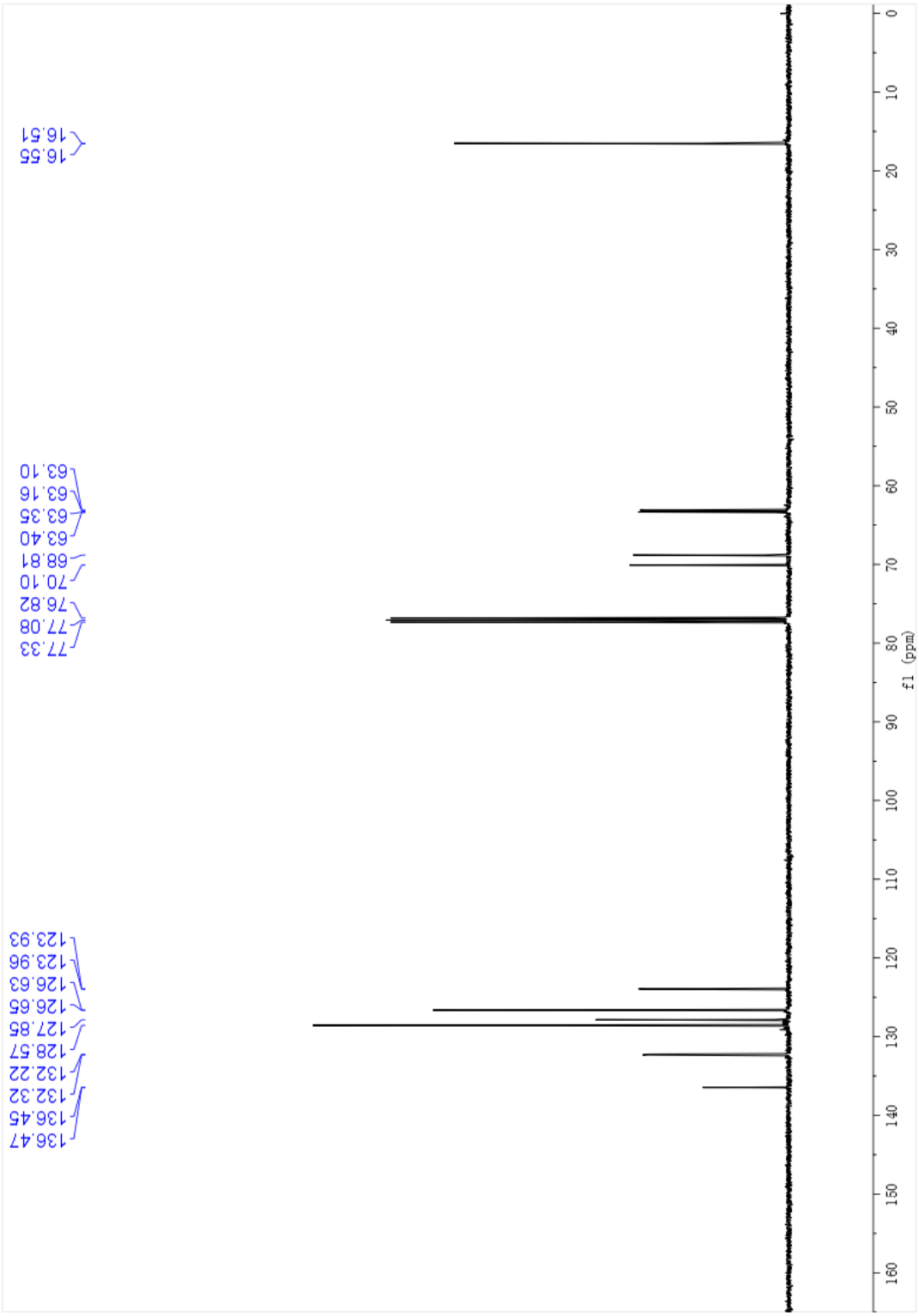
OEt
P
O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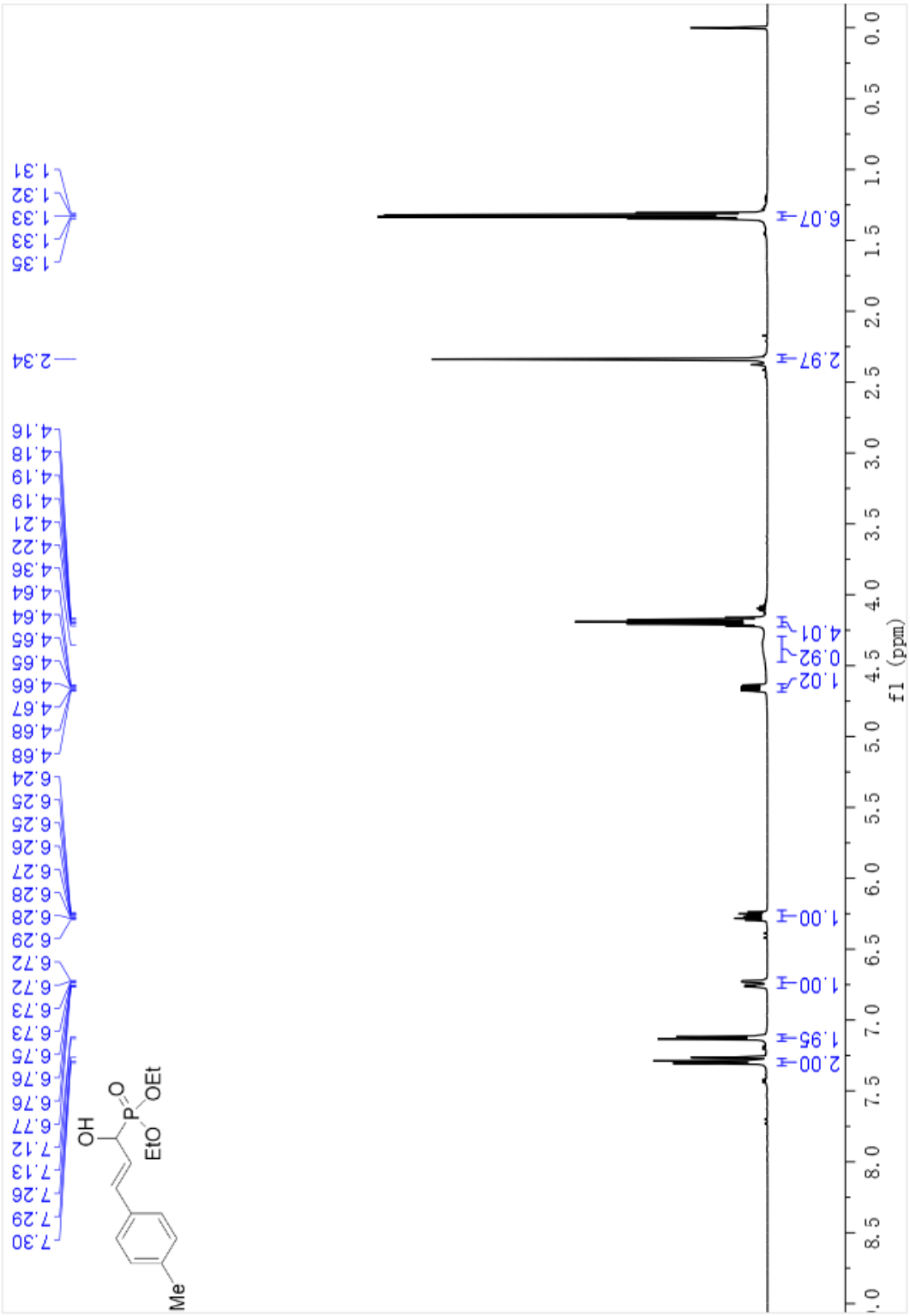
f1 (ppm)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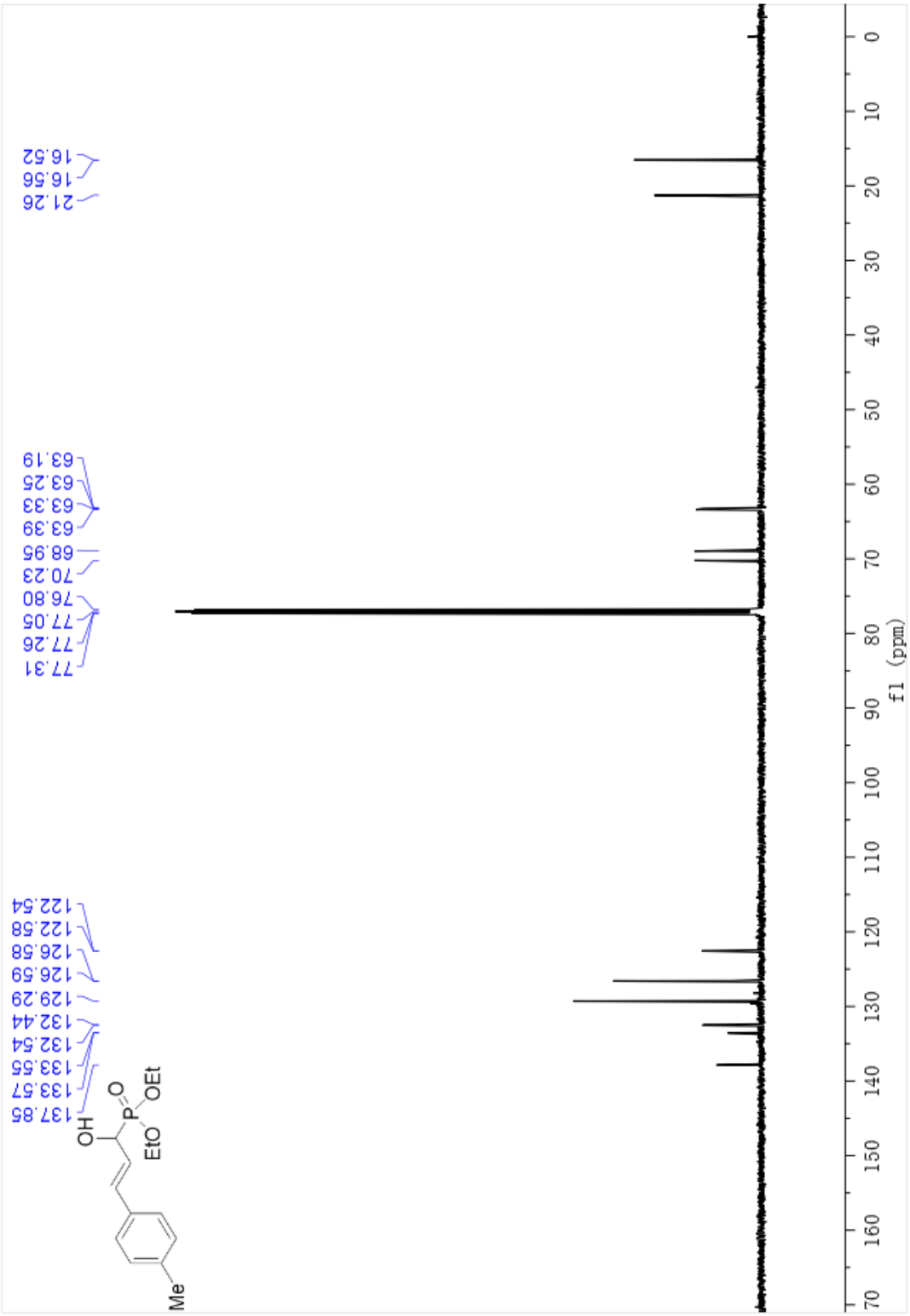
f1 (ppm)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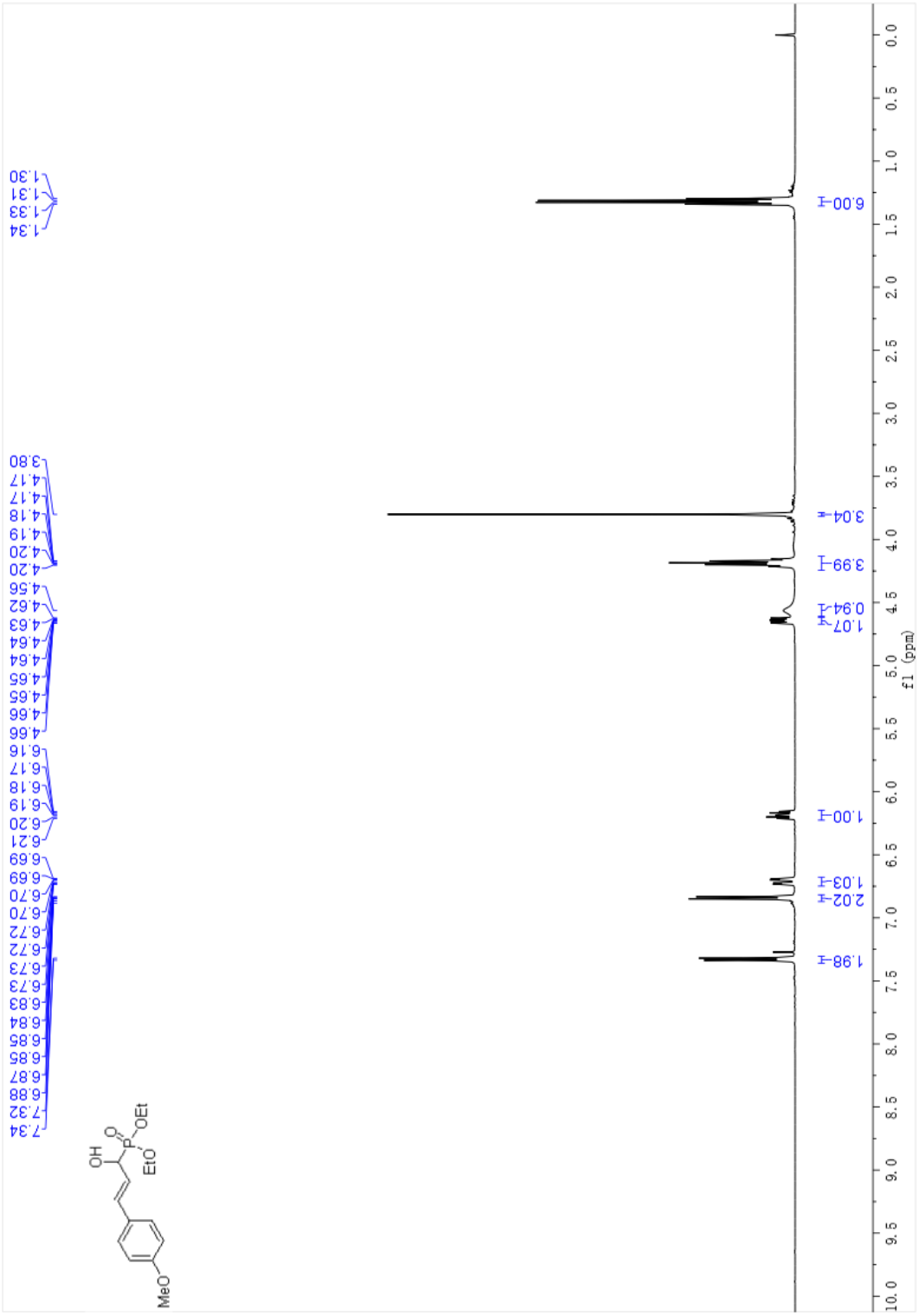
Me
f1 (ppm)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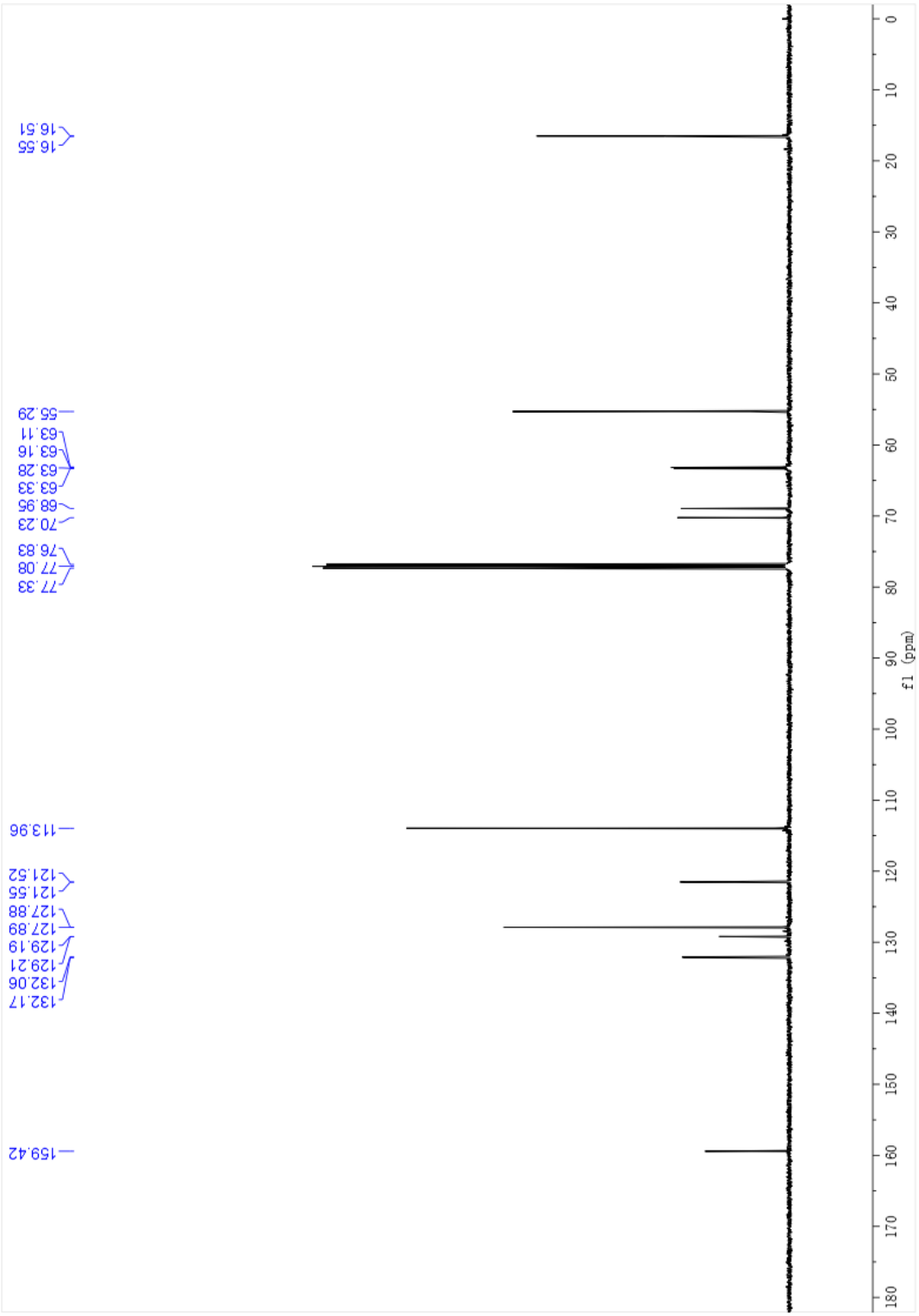
f1 (ppm)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132.06
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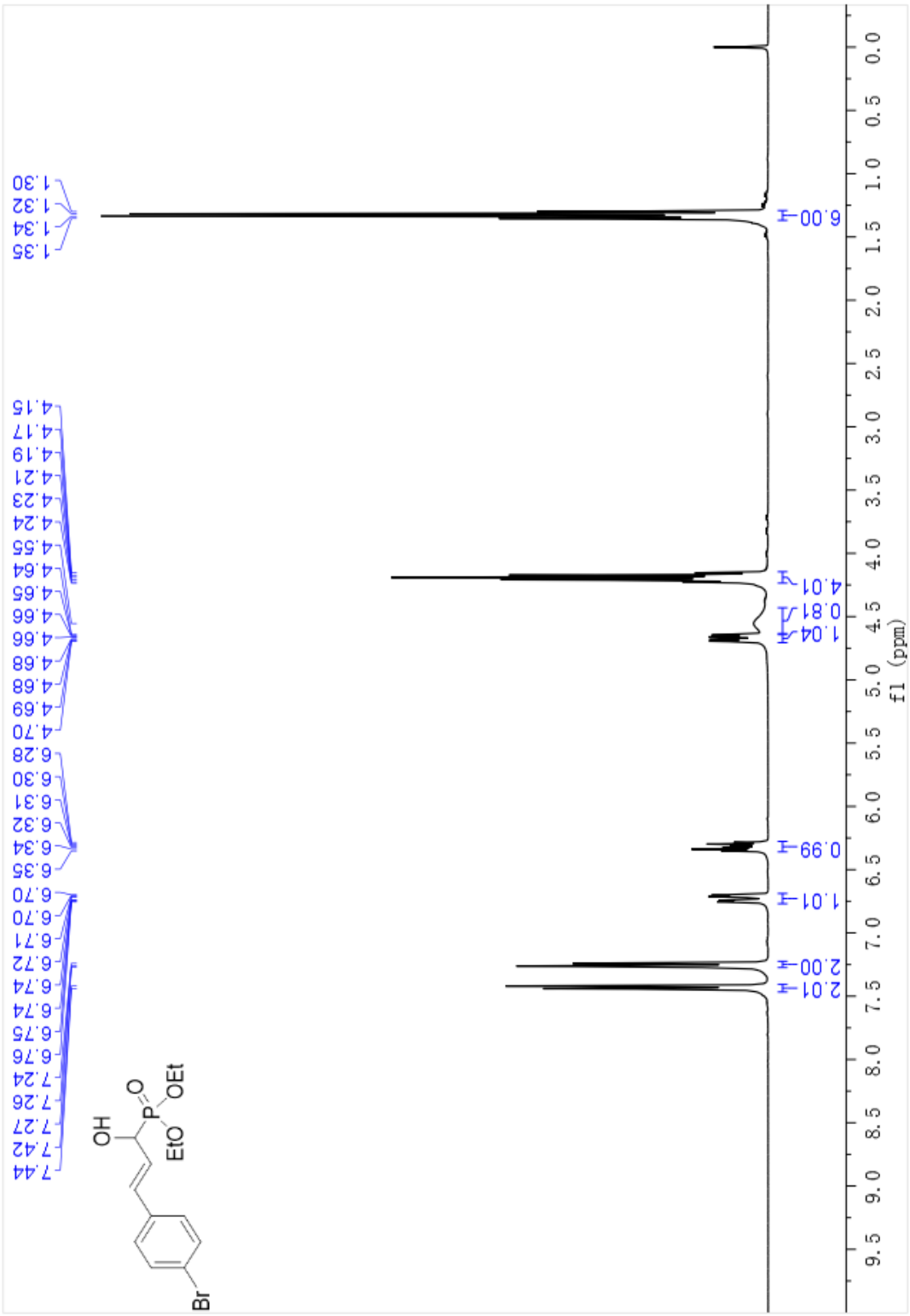
159.42
f1 (ppm)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7.44
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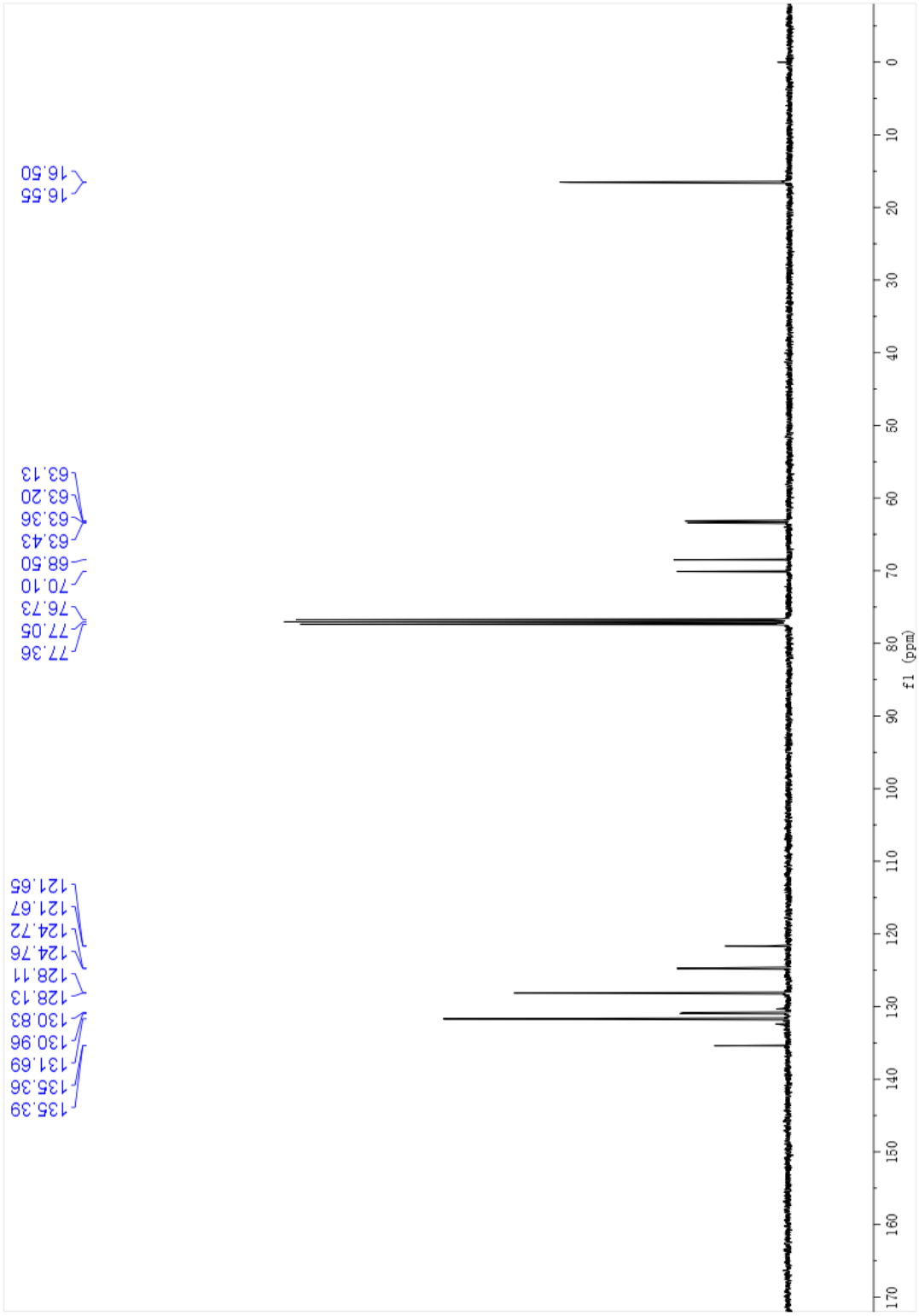
2.01
f1 (ppm)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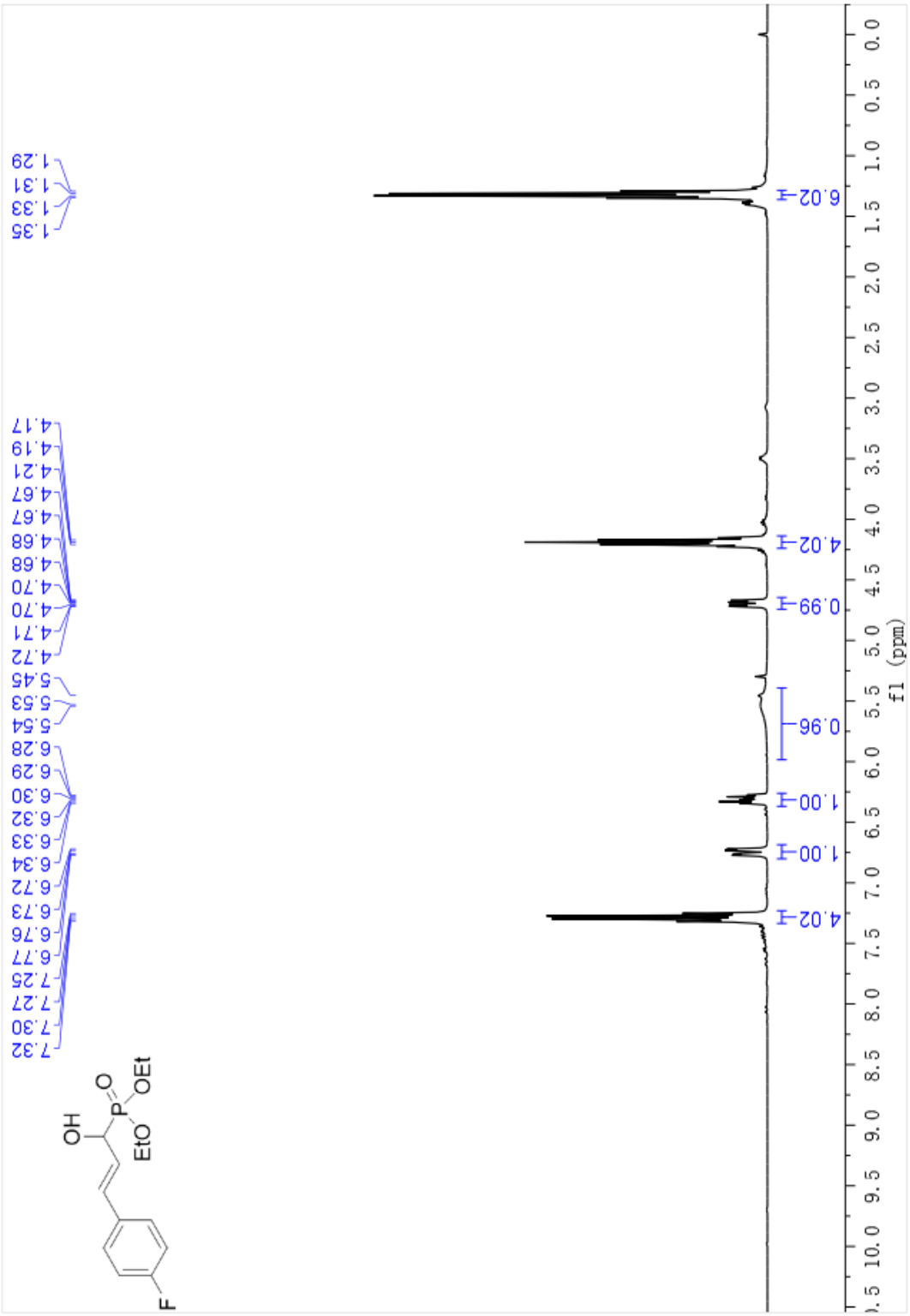
135.36
135.39
f1 (ppm)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4.19
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4.67
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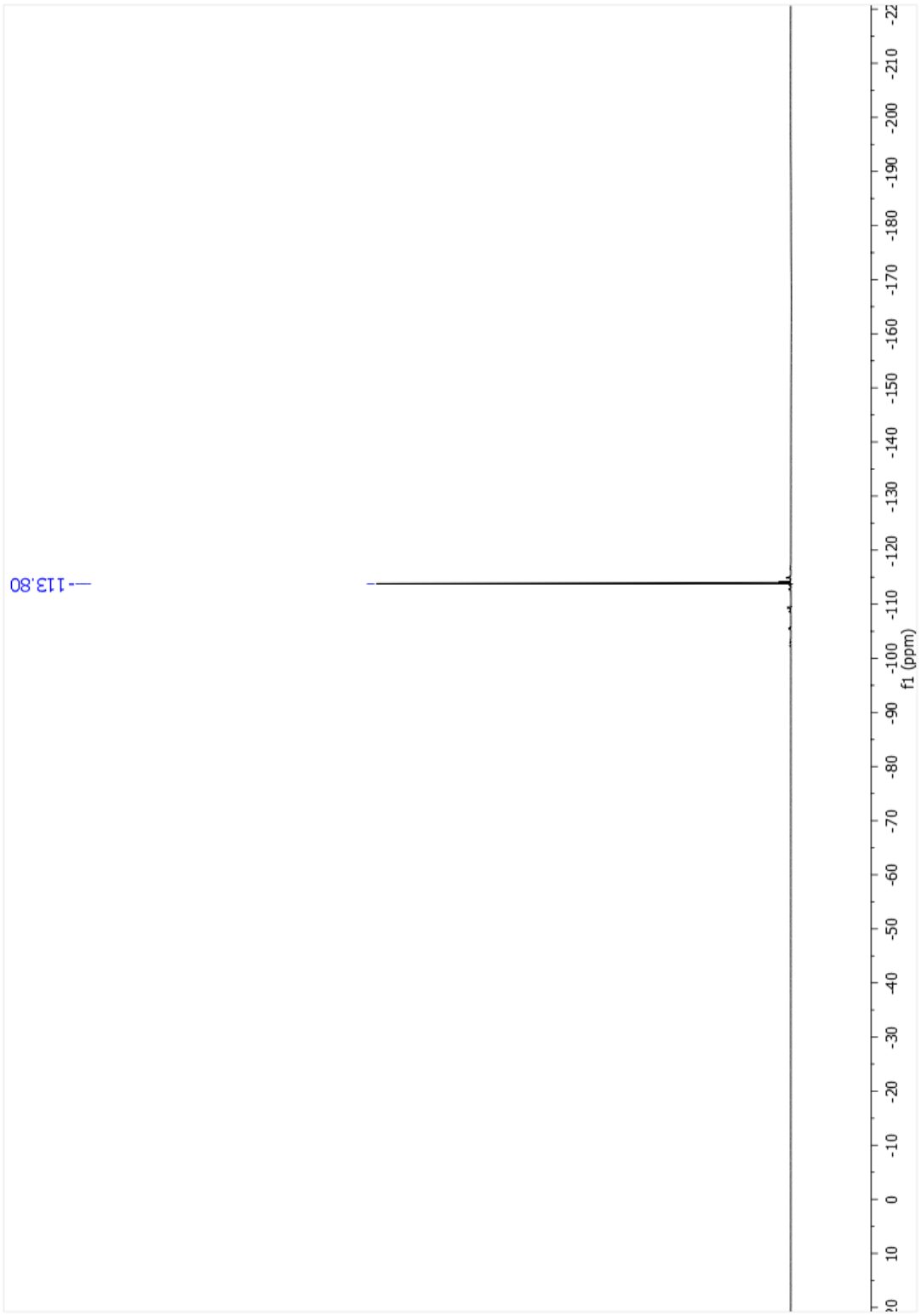
4.68
4.68
4.70
4.70
4.71
4.72
5.45
5.53
5.54
6.28
6.29
6.30
6.32
6.33
6.34
6.72
6.73
6.76
6.77
7.25
7.27
7.30
7.32
OH
EtO
OEt
F
6.02
4.02
0.99
0.96
1.00
1.00
4.02
f1 (ppm)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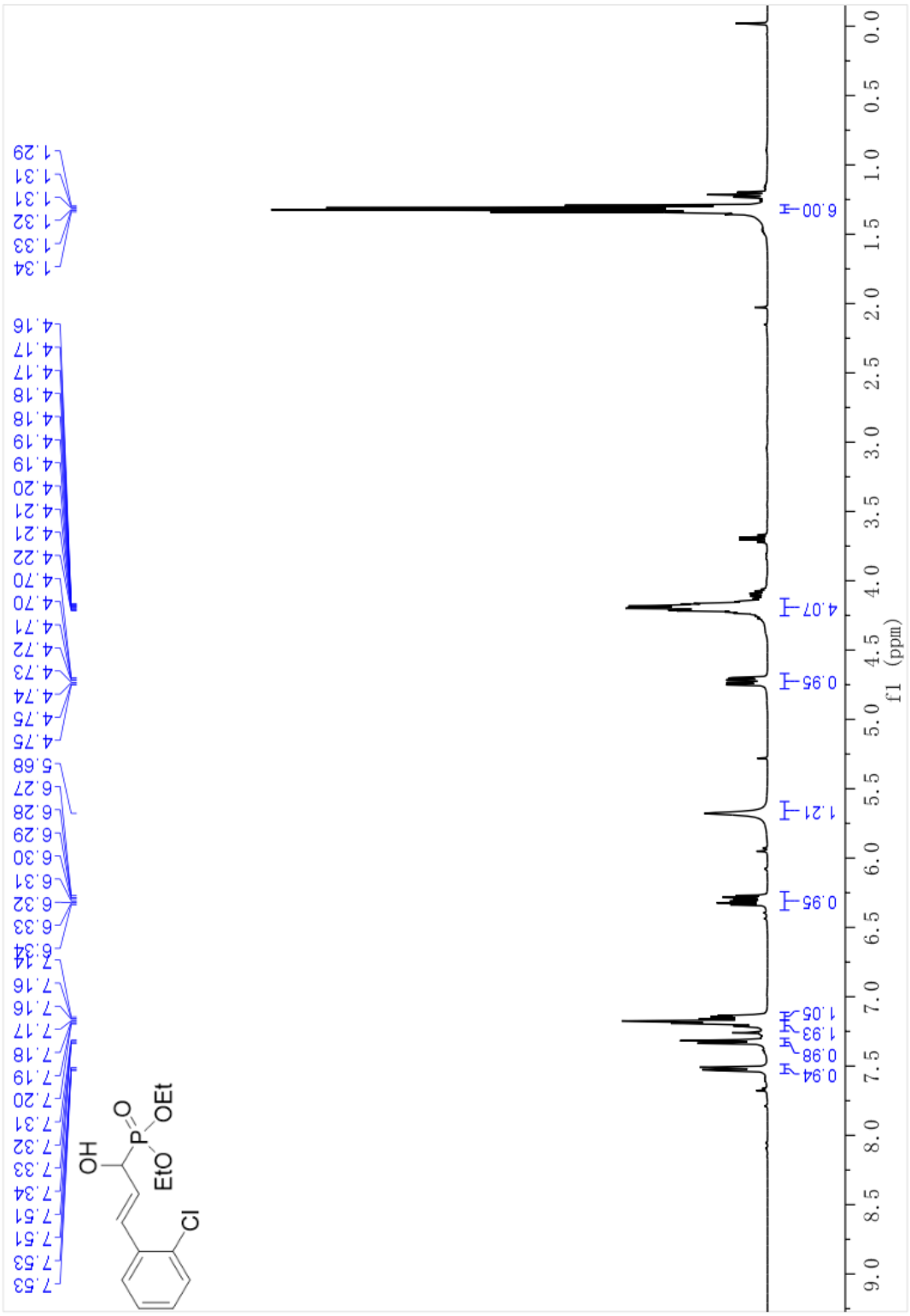
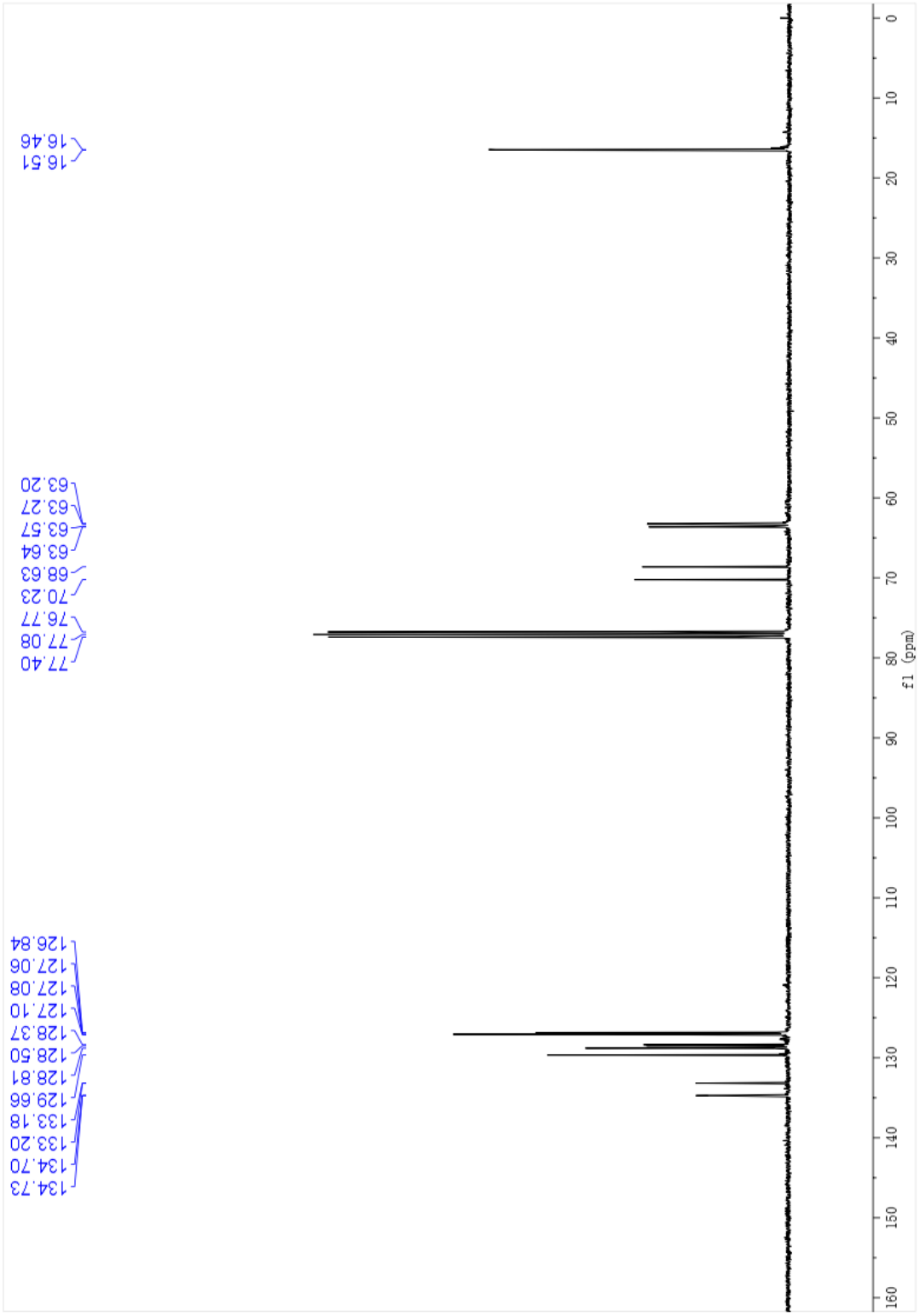

OH
EtO
P
O
OEt
Cl
f1 (ppm)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77.08
77.40
126.84
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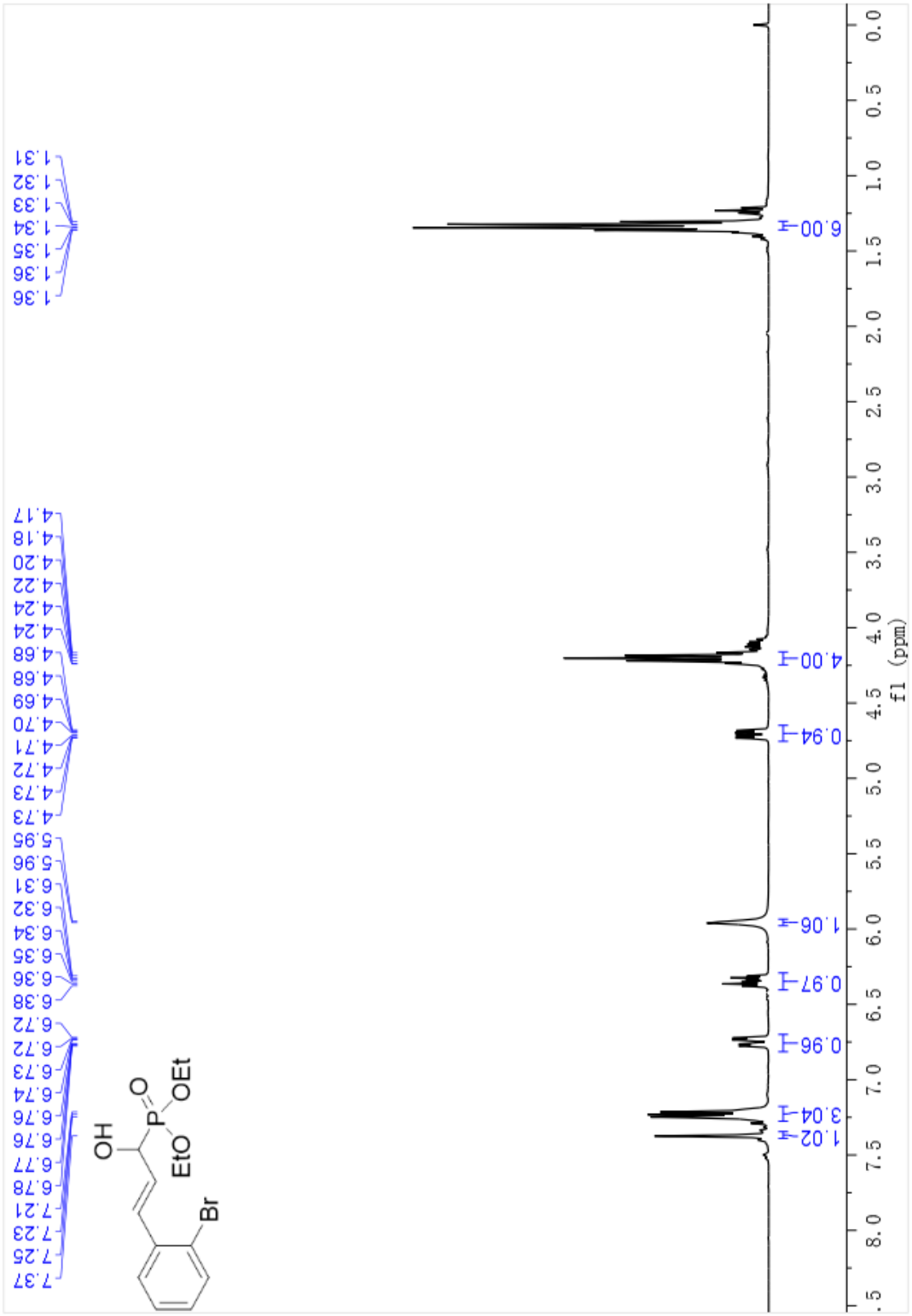
127.08
127.10
128.37
128.50
128.81
129.66
133.18
133.20
134.70
134.73
f1 (ppm)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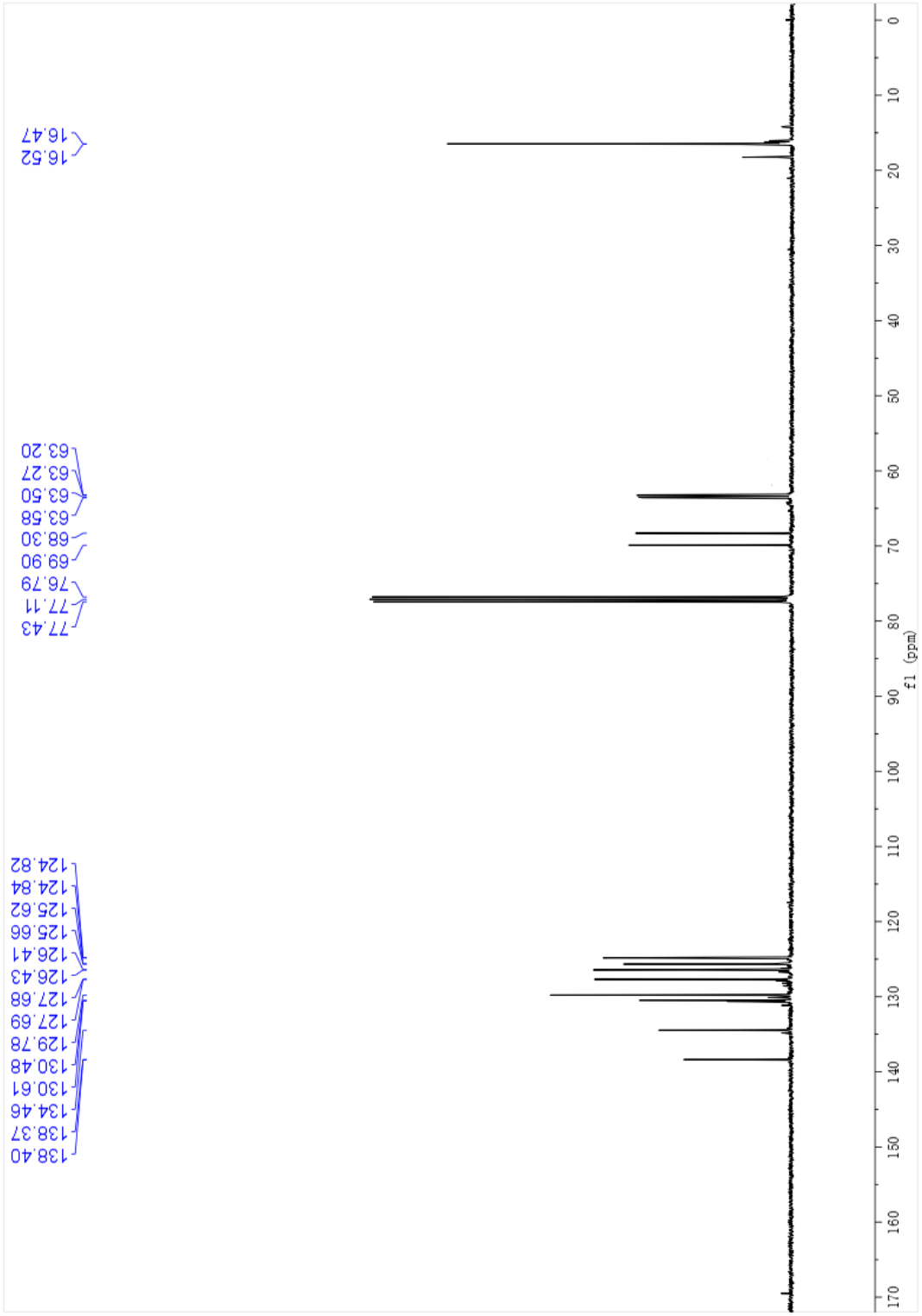
4.68
4.69
4.70
4.71
4.72
4.73
4.73
5.95
5.96
6.31
6.32
6.34
6.35
6.36
6.38
6.72
6.72
6.73
6.74
6.76
6.76
6.77
6.78
7.21
7.23
7.25
7.37
OH
P
O
EtO
OEt
Br
6.00
4.00
0.94
1.06
0.97
0.96
3.04
1.02
f1 (ppm)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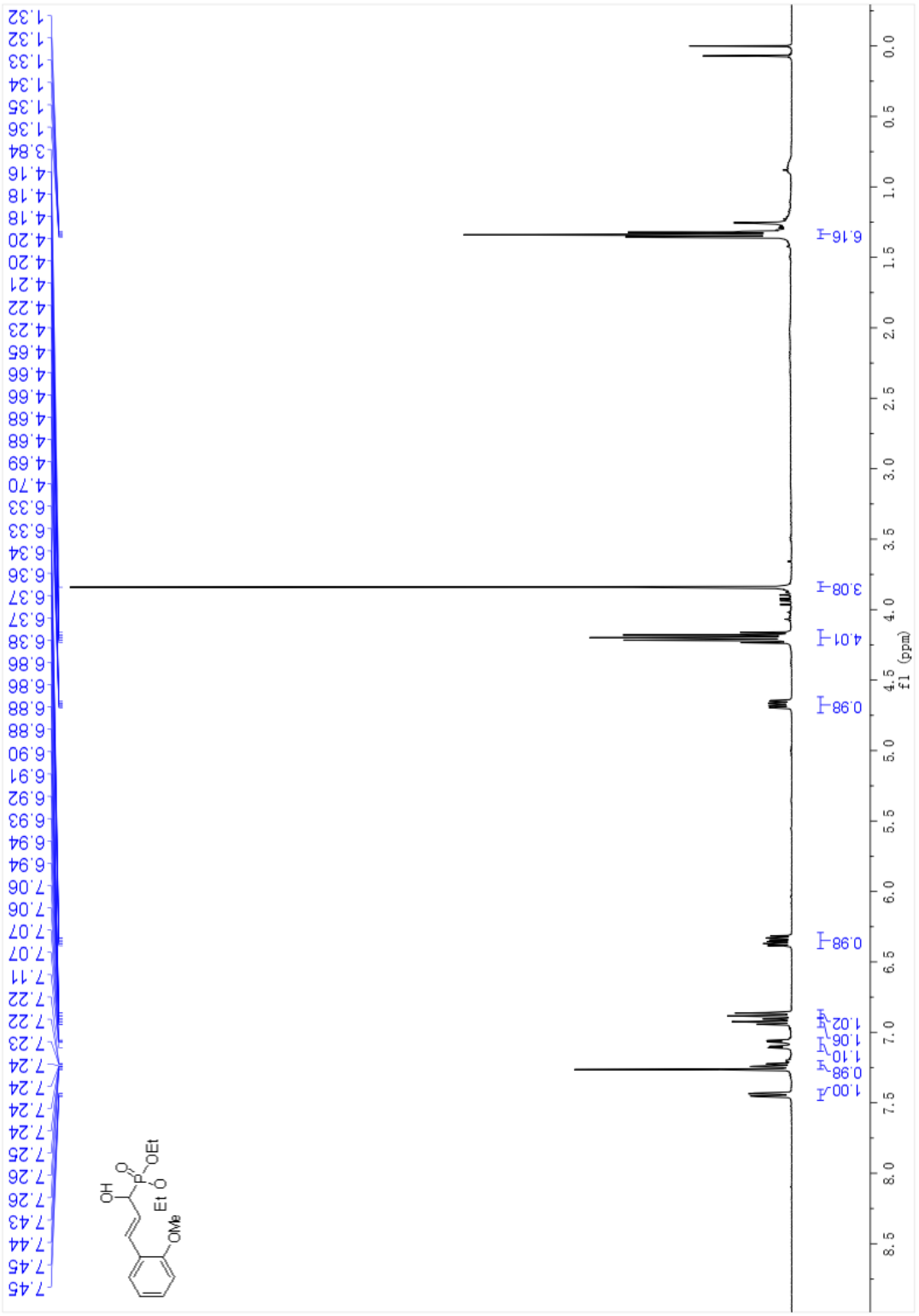
69.90
76.79
77.11
77.43
124.82
124.84
125.62
125.66
126.41
126.43
127.68
127.69
129.78
130.48
130.61
134.46
138.37
138.40
f1 (ppm)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1.33
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1.36
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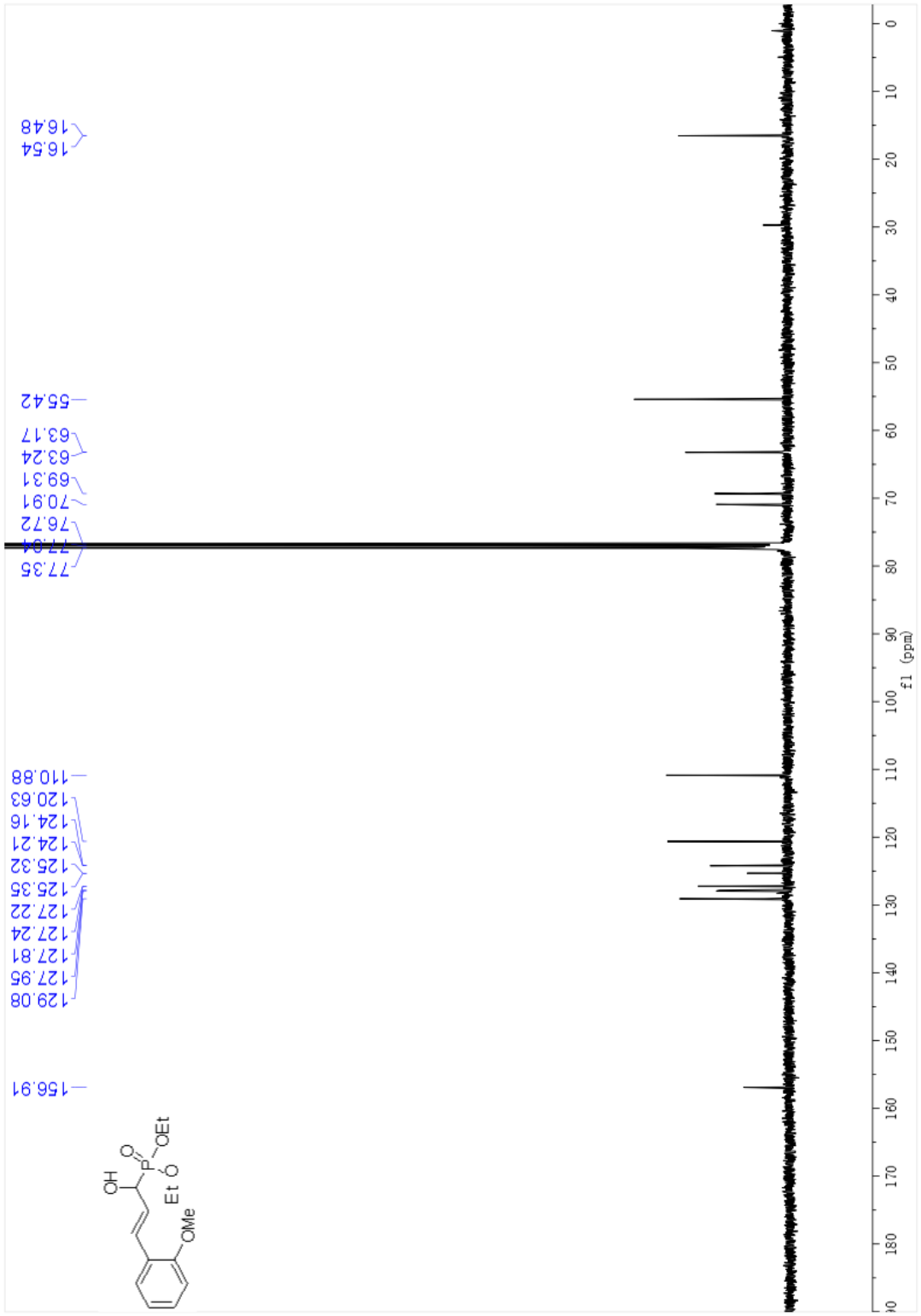
4.18
4.20
4.20
4.21
4.22
4.23
4.65
4.66
4.66
4.68
4.68
4.69
4.70
6.33
6.33
6.34
6.36
6.37
6.37
6.38
6.86
6.86
6.88
6.88
6.90
6.91
6.92
6.93
6.94
6.94
7.06
7.06
7.07
7.07
7.11
7.22
7.22
7.23
7.24
7.24
7.24
7.24
7.25
7.26
7.26
7.43
7.44
7.45
7.45
6.16
3.08
4.01
0.98
0.98
1.02
1.06
1.10
0.98
1.00
OH
O
P
OEt
Et O
OMe
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)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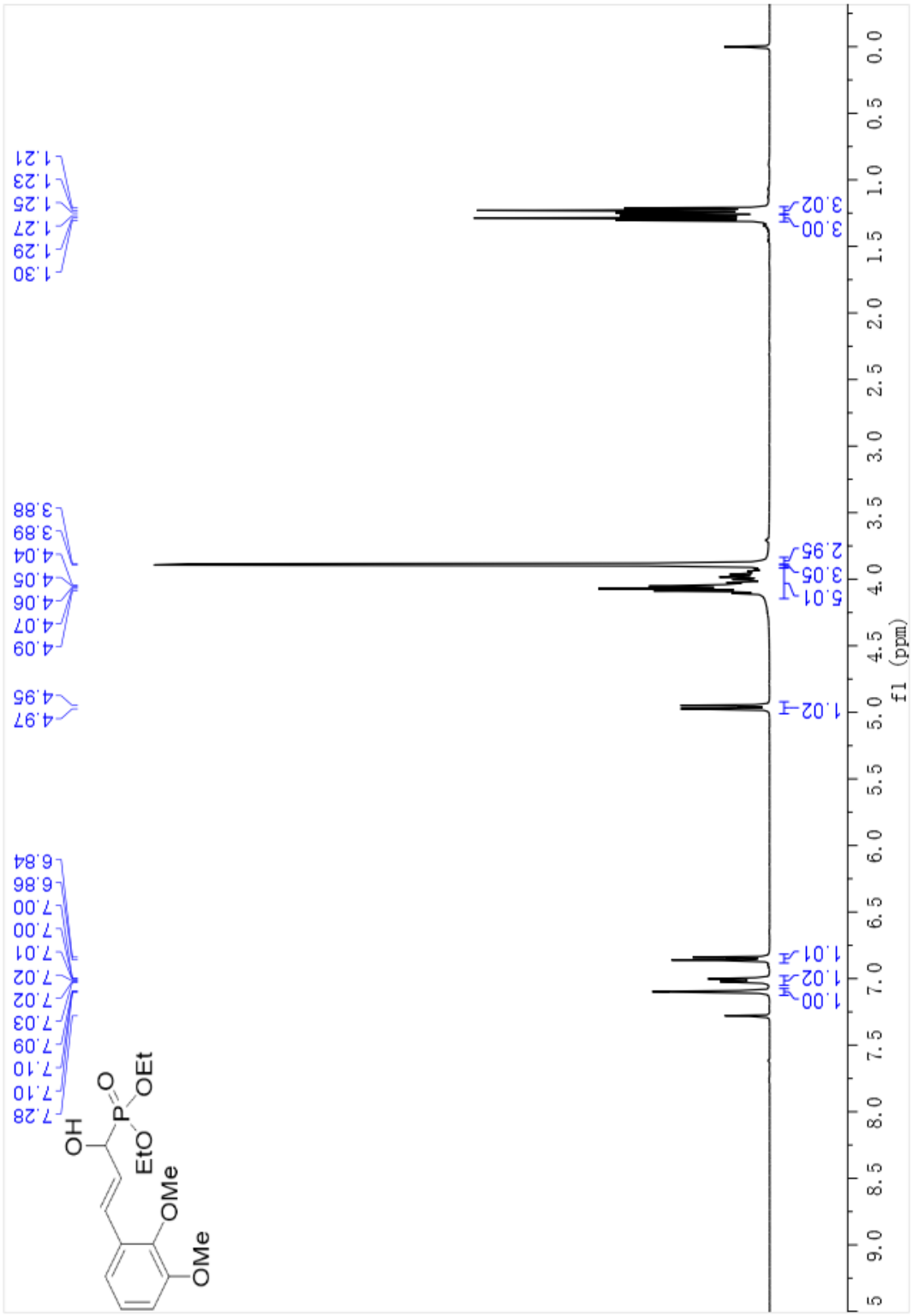
63.24
69.31
70.91
76.72
77.04
77.35
110.88
120.63
124.16
124.21
125.32
125.35
127.22
127.24
127.81
127.95
129.08
156.91
OH
O
P
OEt
Et
O
OMe
f1 (ppm)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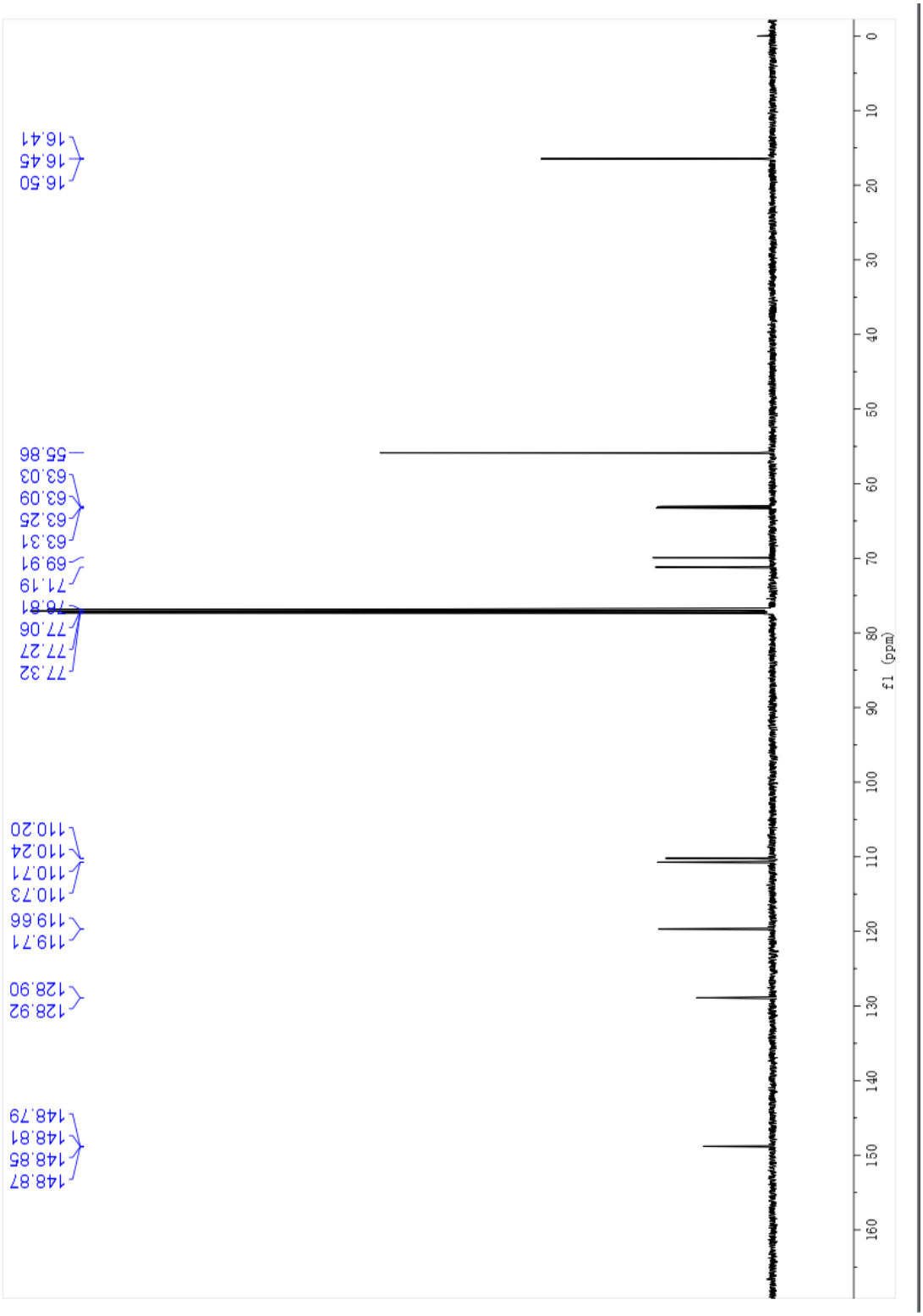
1.23
1.25
1.27
1.29
1.30
3.88
3.89
4.04
4.05
4.06
4.07
4.09
4.95
4.97
6.84
6.86
7.00
7.00
7.01
7.02
7.02
7.03
7.09
7.10
7.10
7.28
OH
EtO
P
O
OEt
OMe
OMe
3.02
3.00
2.95
3.05
5.01
1.02
1.01
1.02
1.00
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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16.50
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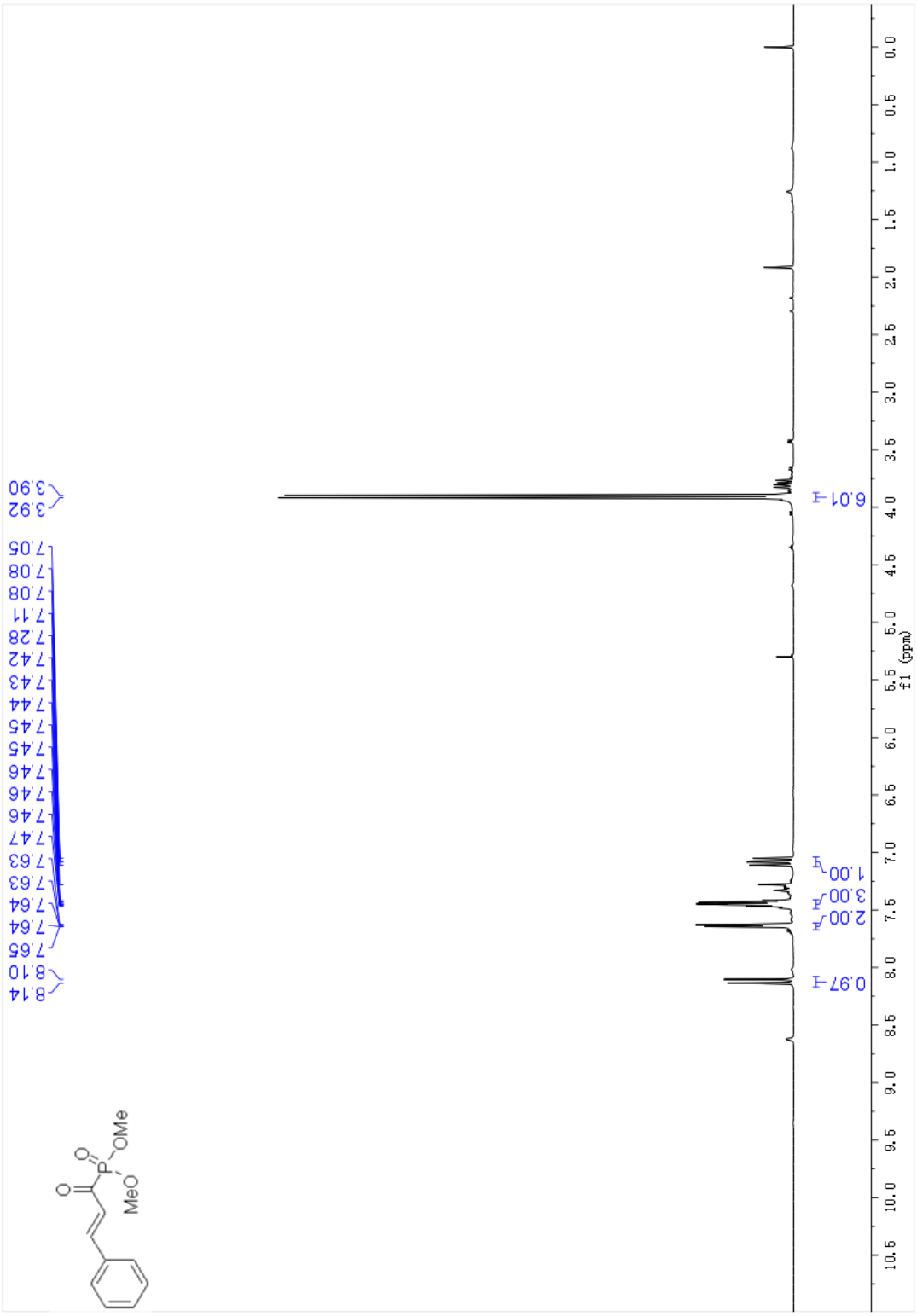
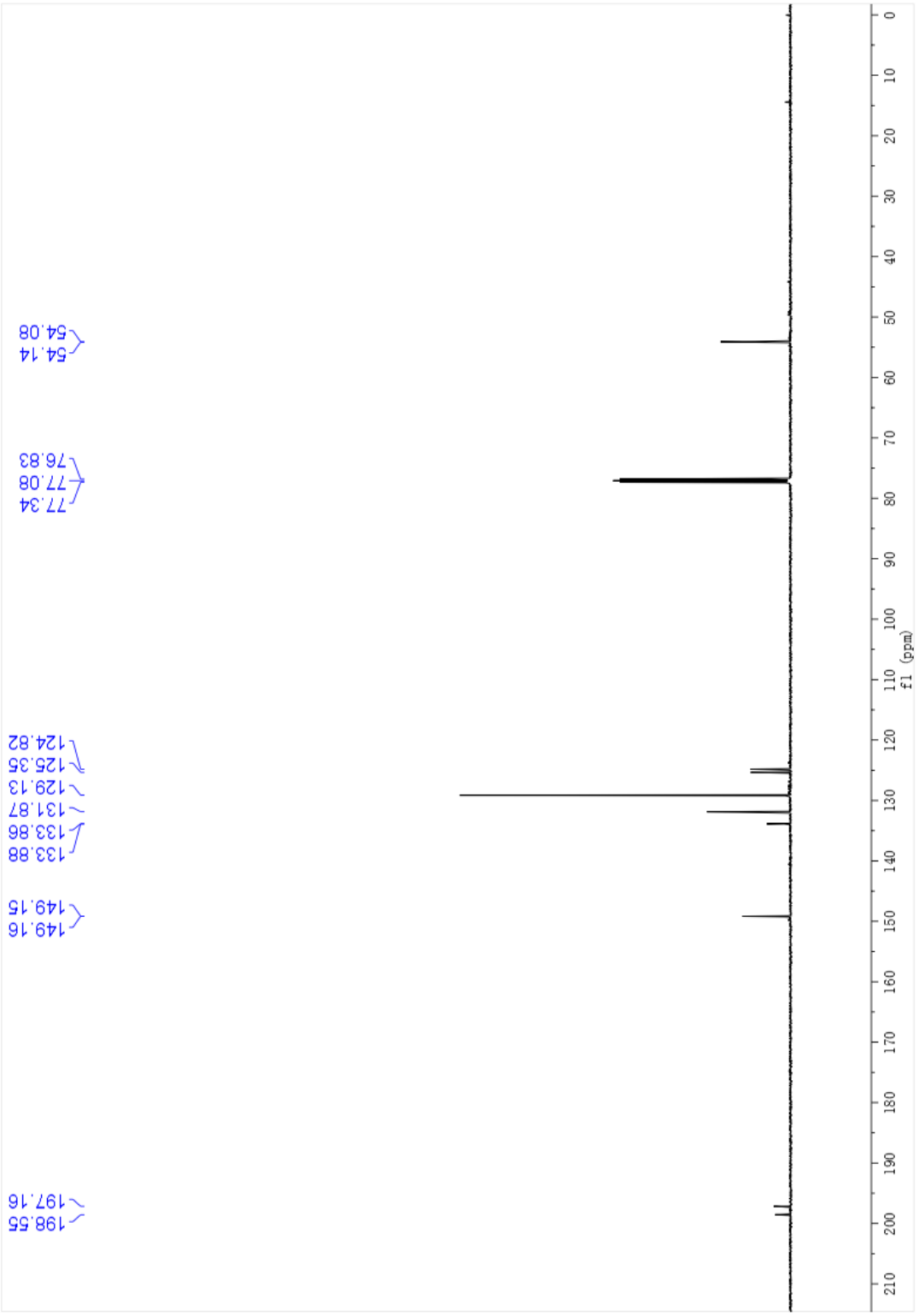
63.09
63.25
63.31
69.91
71.19
76.81
77.06
77.27
77.32
110.20
110.24
110.71
110.73
119.66
119.71
128.90
128.92
148.79
148.81
148.85
148.87
f1 (ppm)

NMR Spectra of Phosphate Ester Substrates

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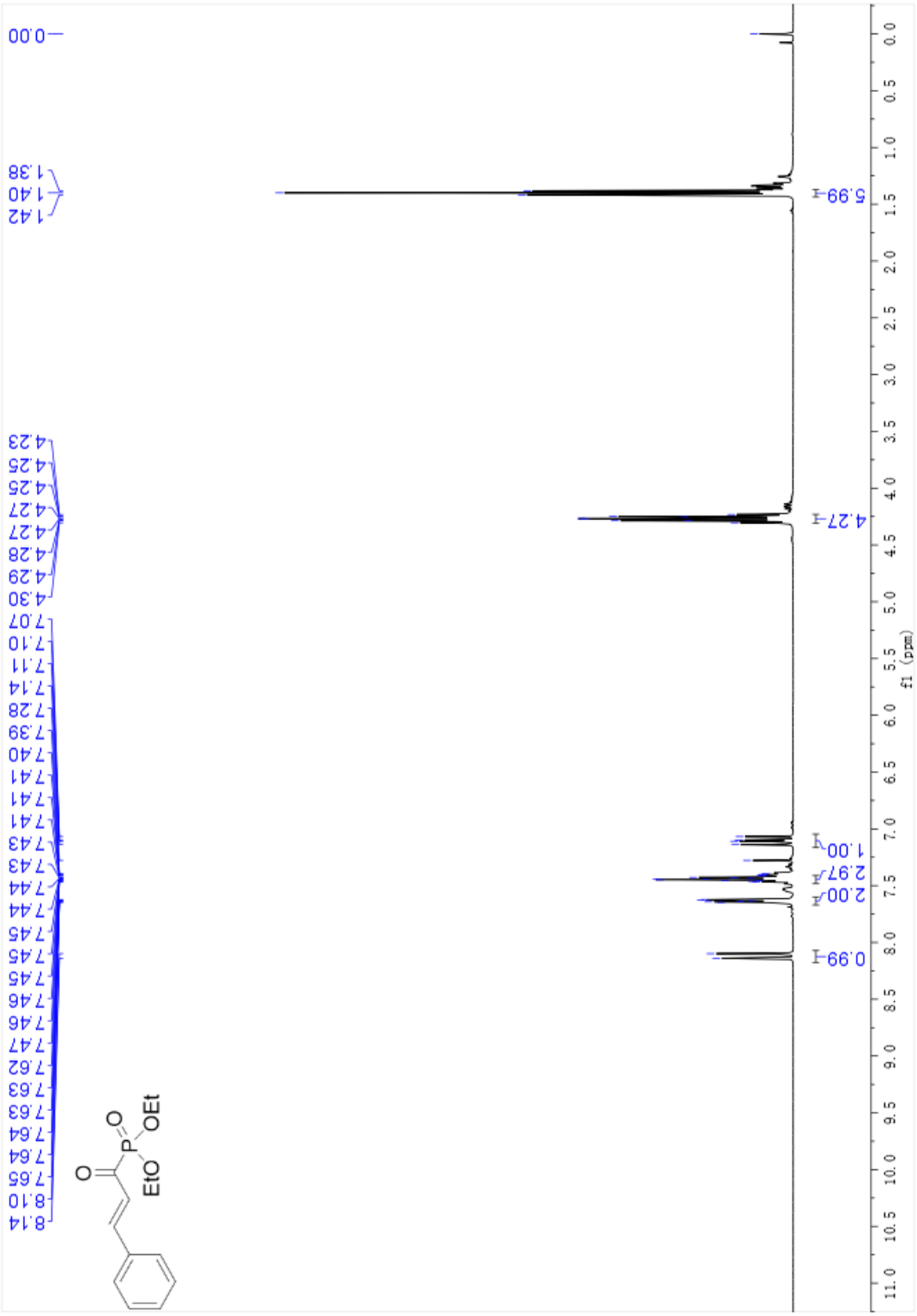
76.83
77.08
77.34
124.82
125.35
129.13
131.87
133.86
133.88
149.15
149.16
197.16
198.55
f1 (ppm)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4.28
4.29
4.30
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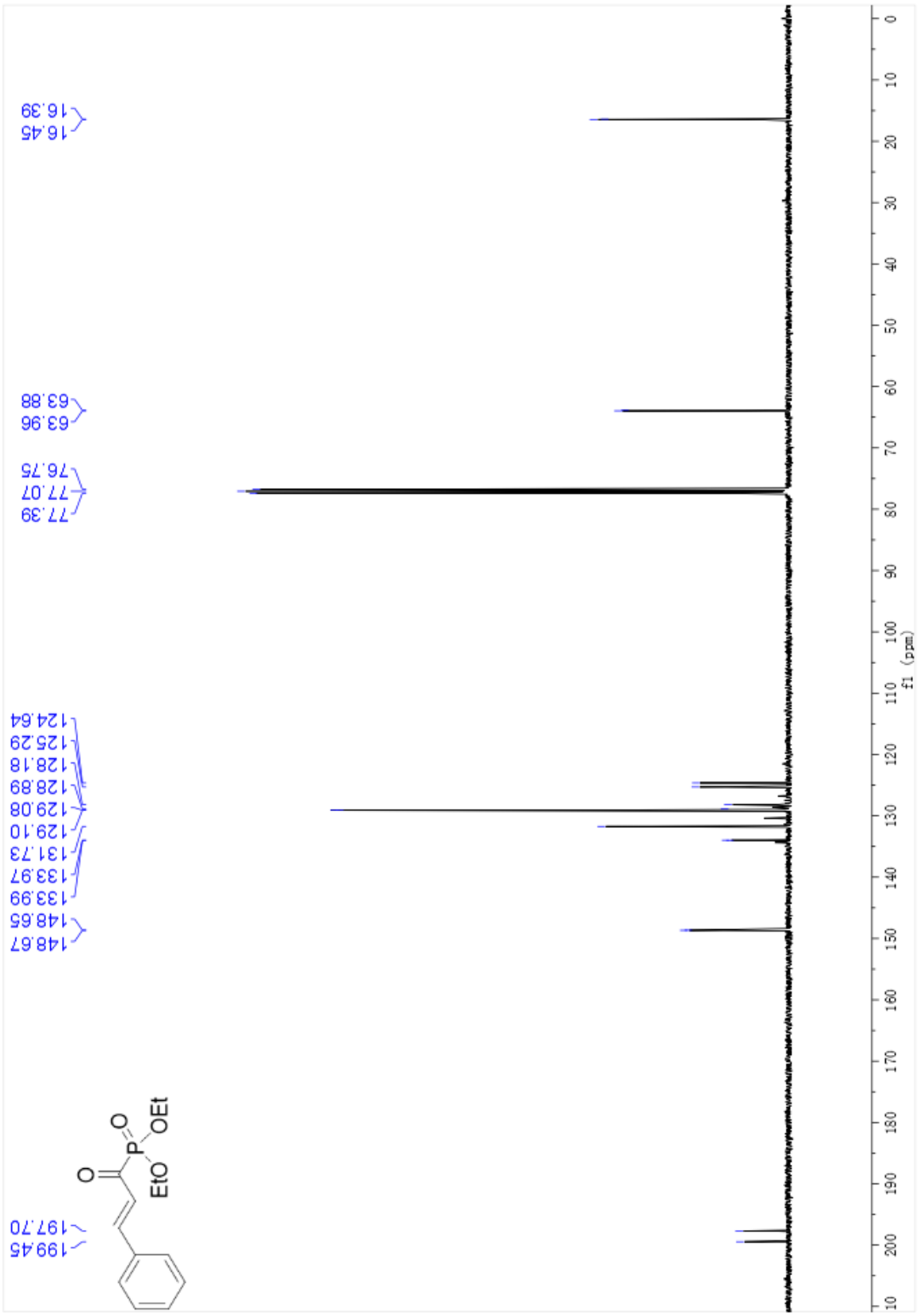
7.11
7.14
7.28
7.39
7.40
7.41
7.41
7.41
7.43
7.43
7.44
7.44
7.45
7.45
7.45
7.46
7.46
7.47
7.62
7.63
7.63
7.64
7.64
7.65
8.10
8.14
5.99
4.27
1.00
2.97
2.00
0.99
f1 (ppm)
O
P
O
EtO
OEt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77.07
77.39
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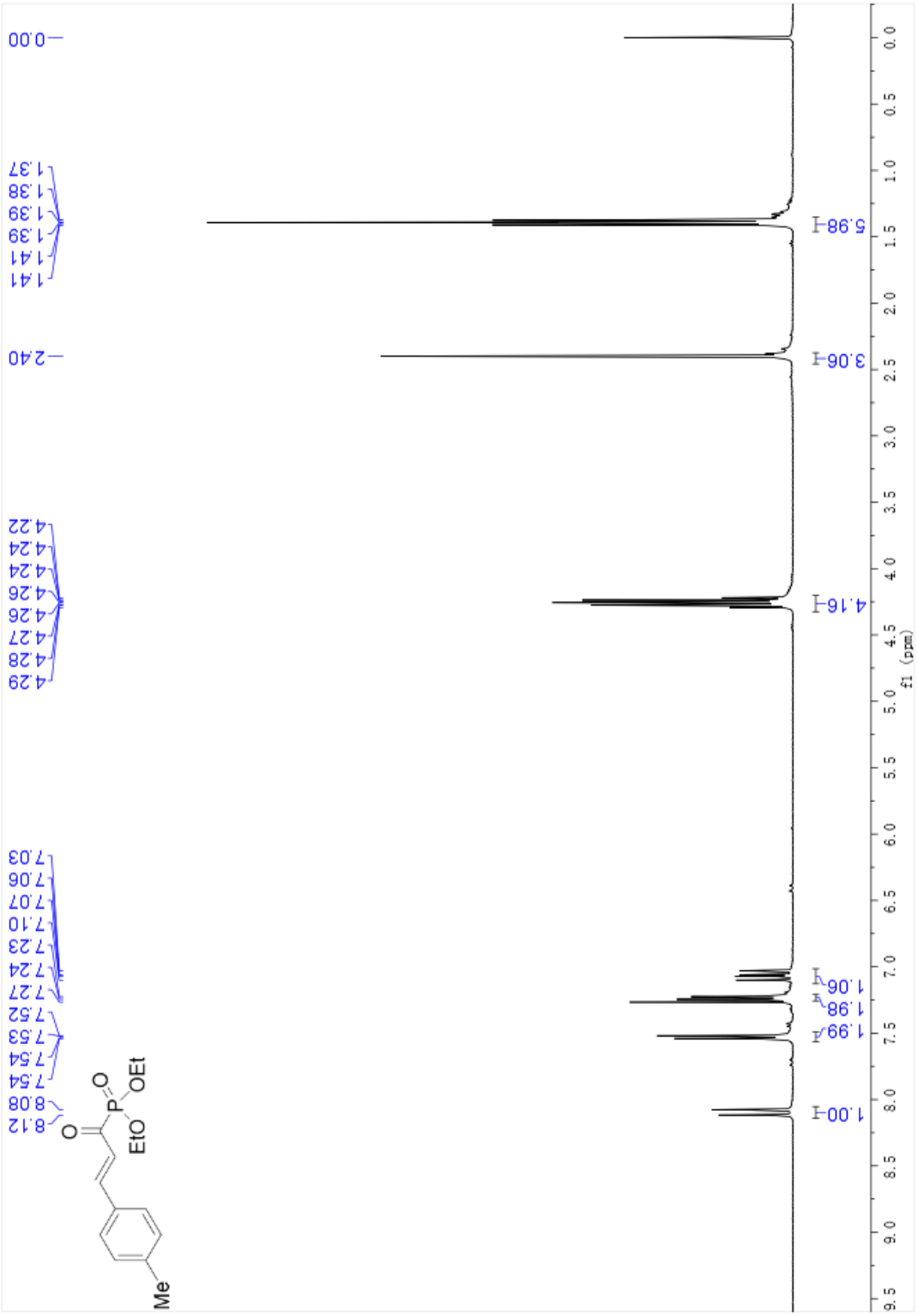
125.29
128.18
128.89
129.08
129.10
131.73
133.97
133.99
148.65
148.67
197.70
199.45
EtO
OEt
P
O
f1 (ppm)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2.40
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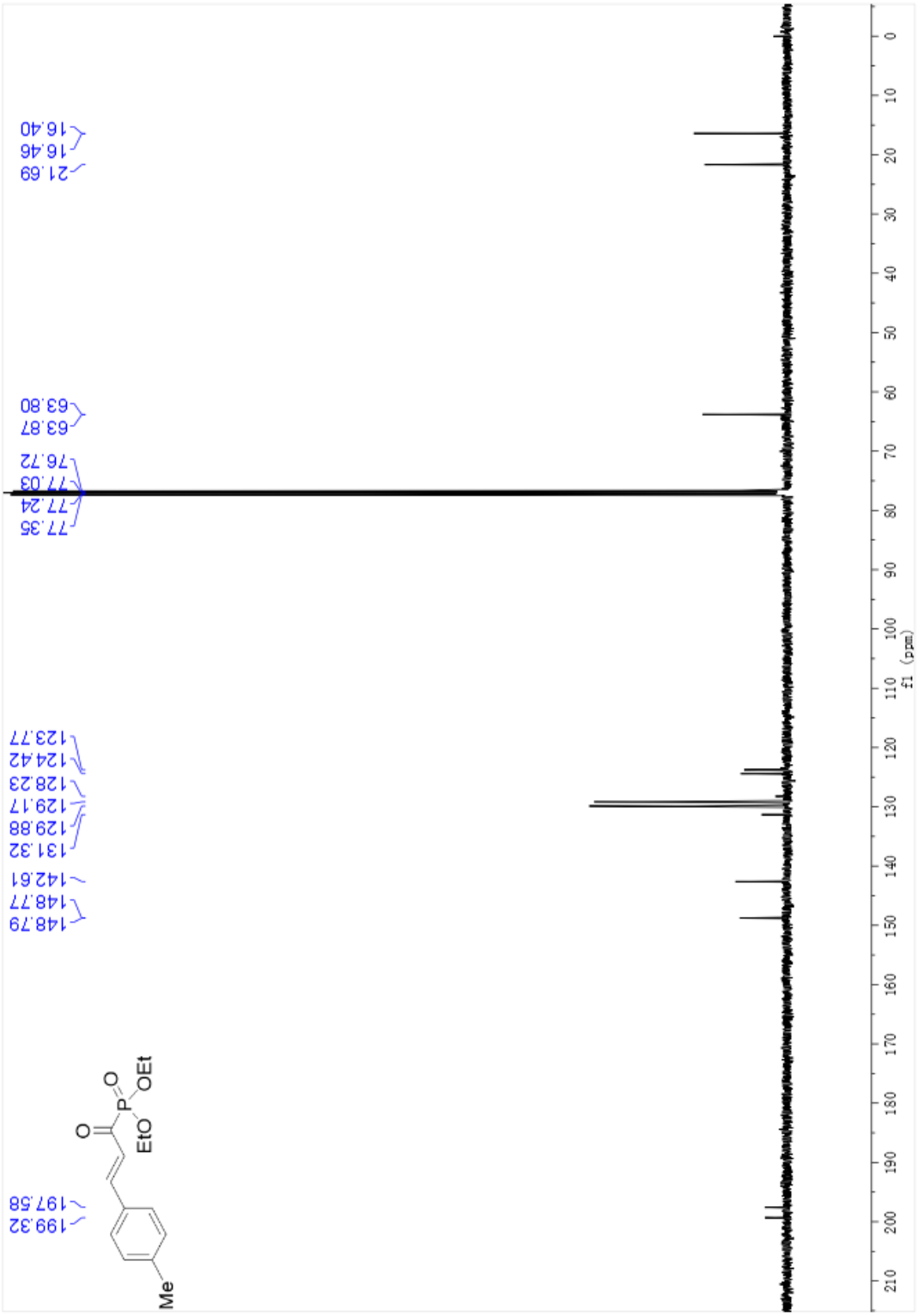
4.24
4.24
4.26
4.26
4.27
4.28
4.29
7.03
7.06
7.07
7.10
7.23
7.24
7.27
7.52
7.53
7.54
7.54
8.08
8.12
5.98
3.06
4.16
1.06
1.98
1.99
1.00
f1 (ppm)
EtO
OEt
Me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123.77
124.42
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131.32
142.61
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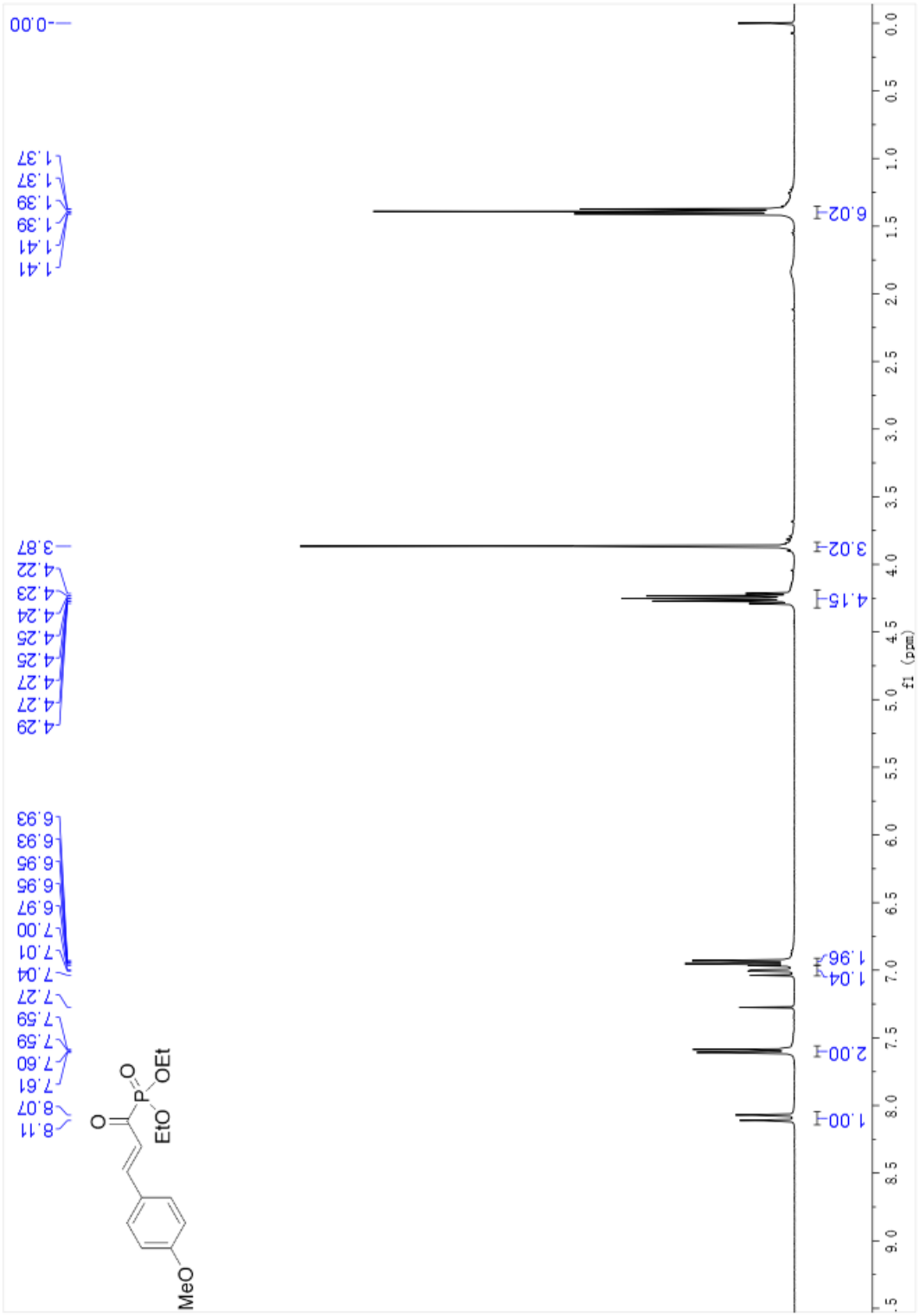
148.79
197.58
199.32
EtO
OEt
Me
f1 (ppm)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1.39
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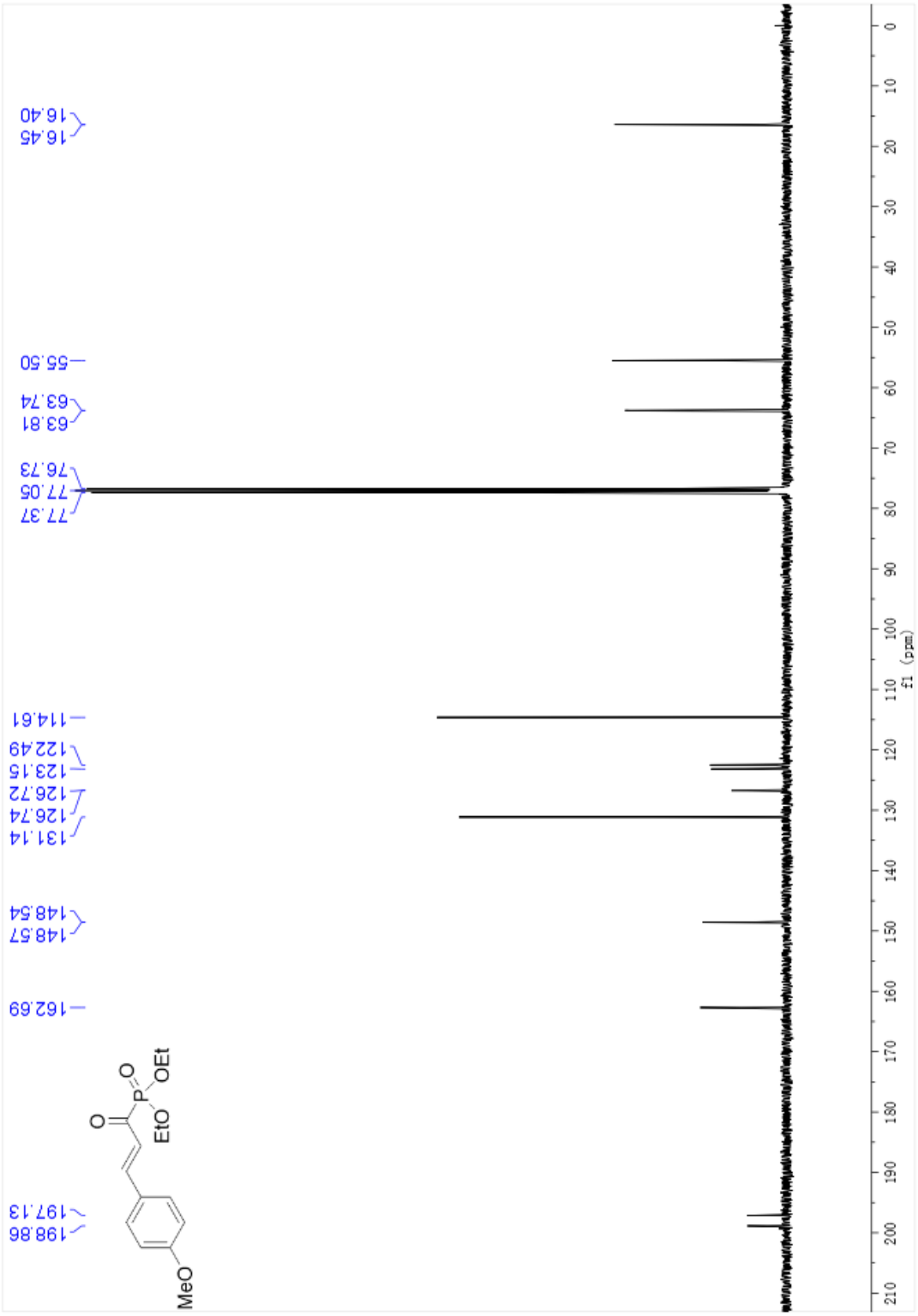
1.41
3.87
4.22
4.23
4.24
4.25
4.25
4.27
4.27
4.29
6.93
6.93
6.95
6.95
6.97
7.00
7.01
7.04
7.27
7.59
7.59
7.60
7.61
8.07
8.11
6.02
3.02
4.15
1.96
1.04
2.00
1.00
f1 (ppm)
O
P
O
EtO
OEt
MeO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77.37
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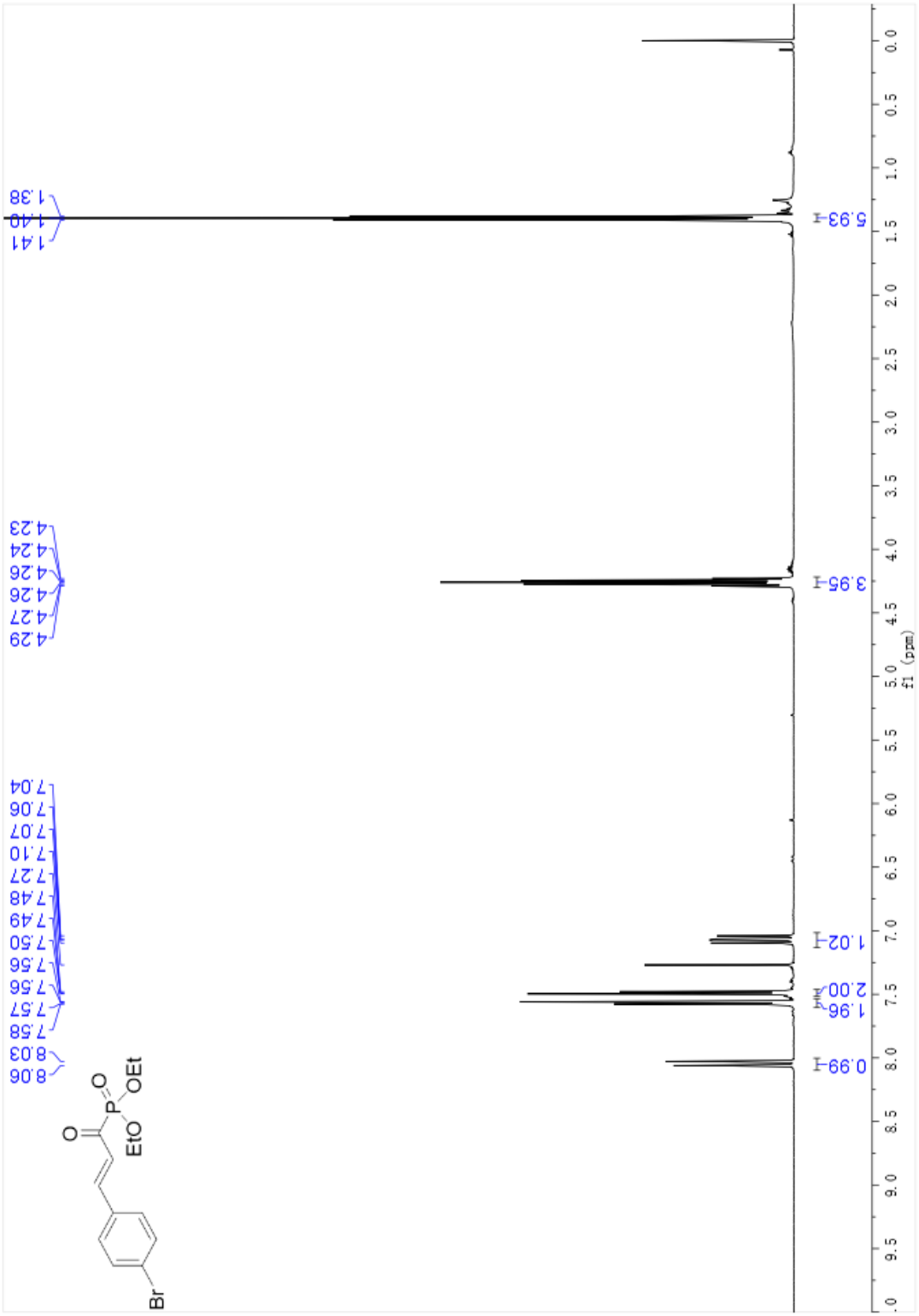
122.49
123.15
126.72
126.74
131.14
148.54
148.57
162.69
197.13
198.86
MeO
EtO
OEt
P
O
f1 (ppm)


1.38
1.40
1.41
4.23
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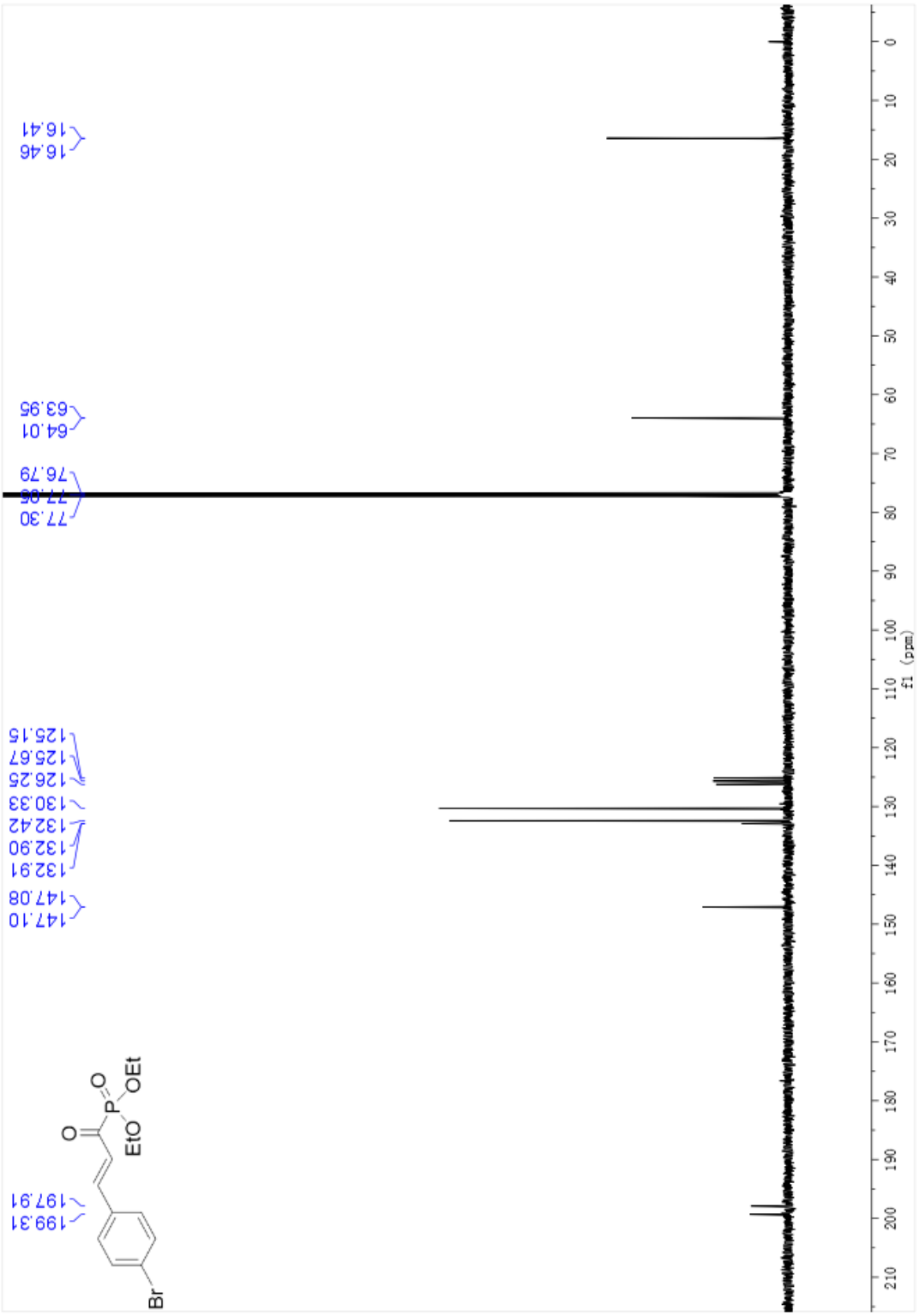
4.26
4.26
4.27
4.29
7.04
7.06
7.07
7.10
7.27
7.48
7.49
7.50
7.56
7.56
7.57
7.58
8.03
8.06
5.93
3.95
1.02
2.00
1.96
0.99
f1 (ppm)
O
P
O
EtO
OEt
Br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77.06
77.30
125.15
125.67
126.25
130.33
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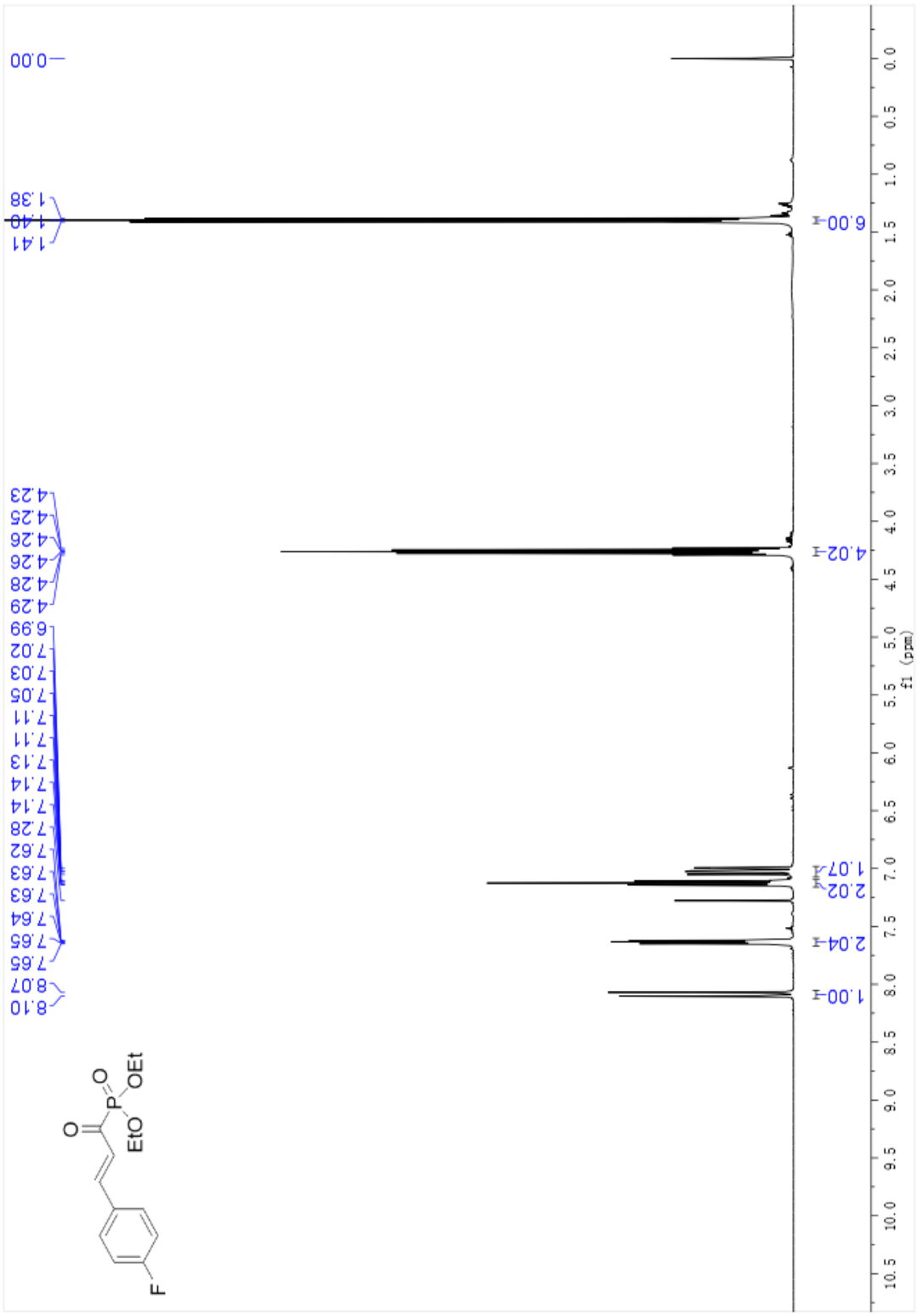
132.91
147.08
147.10
197.91
199.31
O
P
O
EtO
OEt
Br
f1 (ppm)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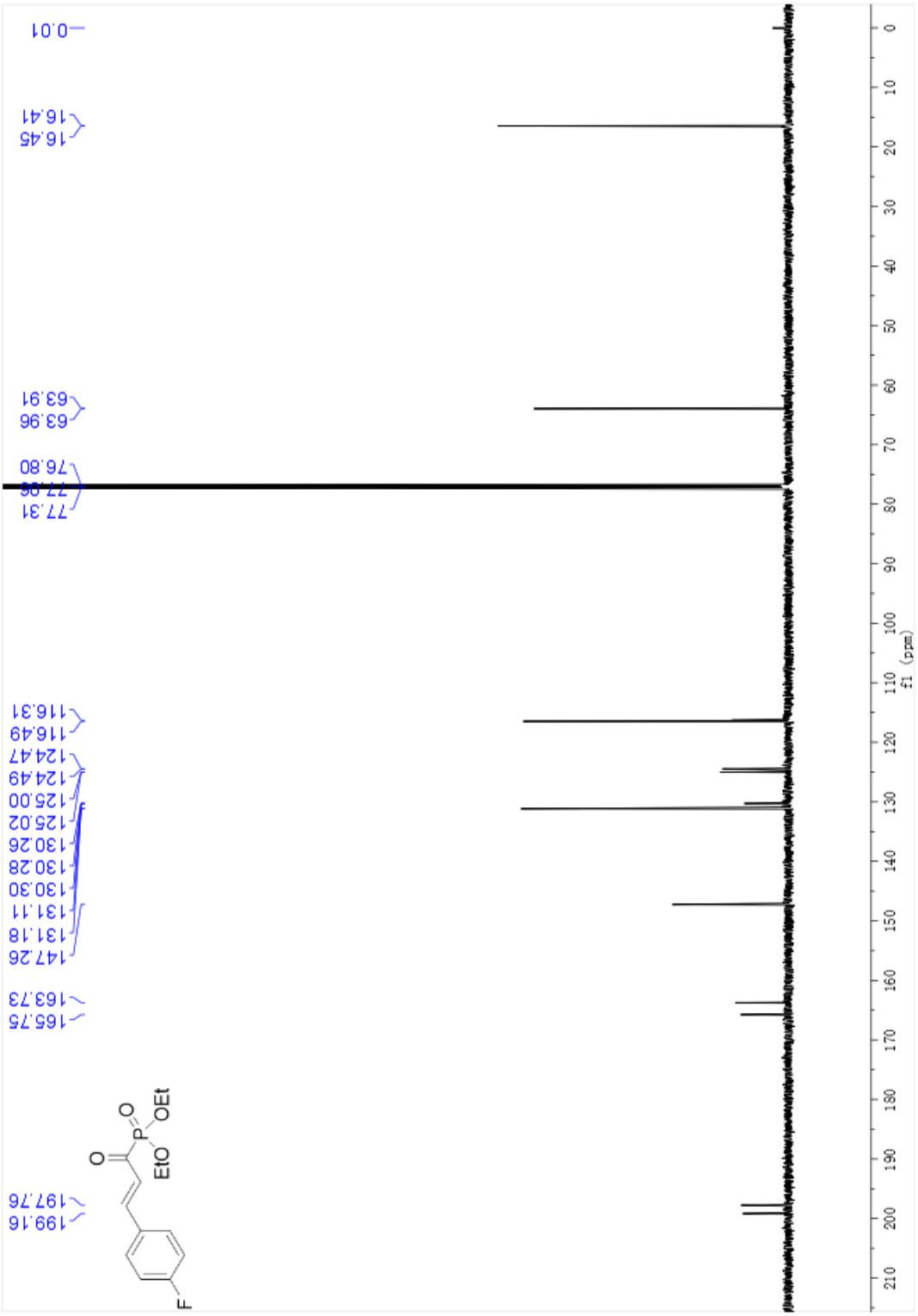
1.38
1.40
1.41
4.23
4.25
4.26
4.26
4.28
4.29
6.99
7.02
7.03
7.05
7.11
7.11
7.13
7.14
7.14
7.28
7.62
7.63
7.63
7.64
7.65
7.65
8.07
8.10
6.00
4.02
1.07
2.02
2.04
1.00
f1 (ppm)
O
P
O
OEt
EtO
F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76.80
77.00
77.31
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116.49
124.47
124.49
125.00
125.02
130.26
130.28
130.30
131.11
131.18
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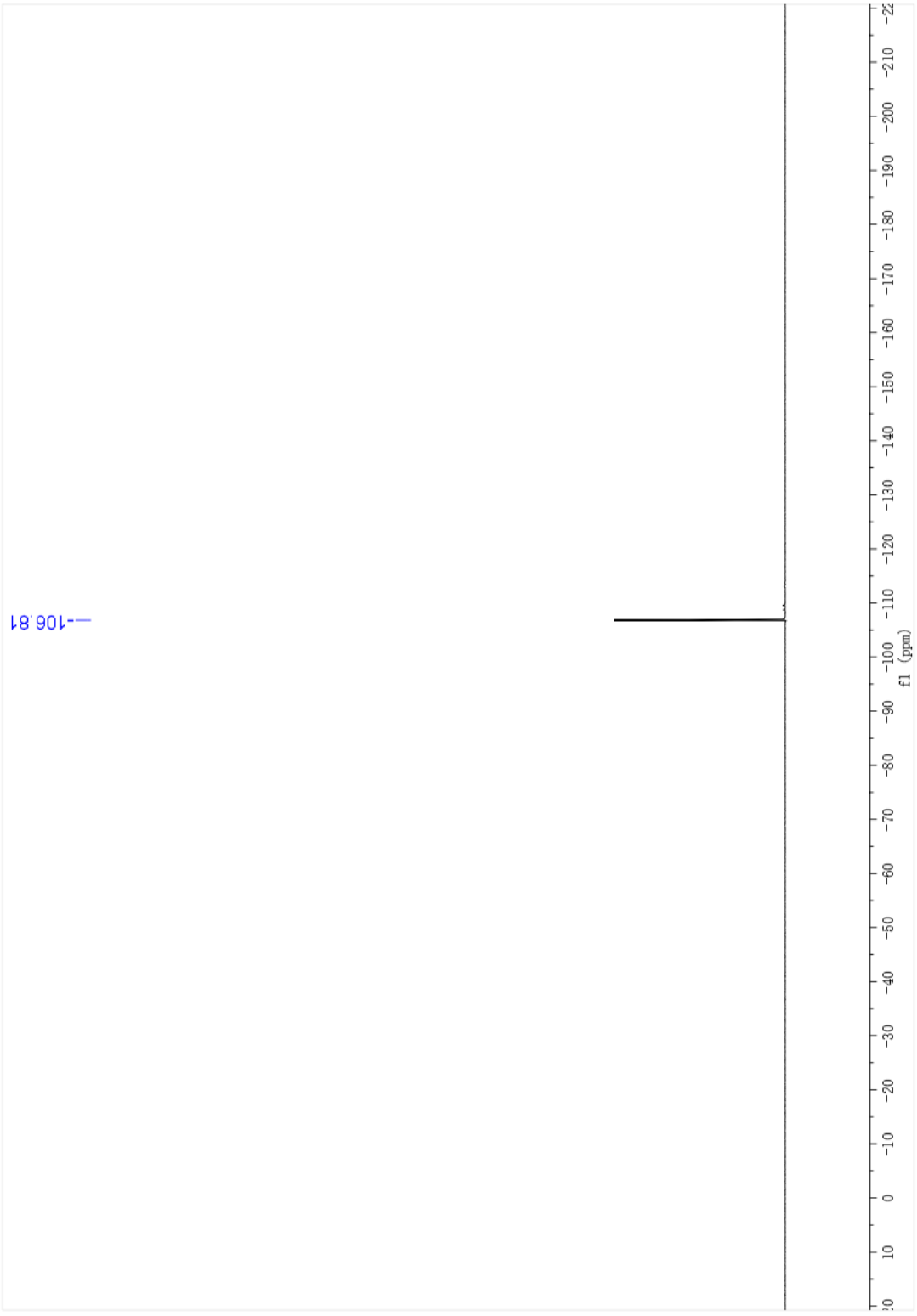
163.73
165.75
197.76
199.16
O
P
O
EtO
OEt
F
f1 (ppm)


-106.81
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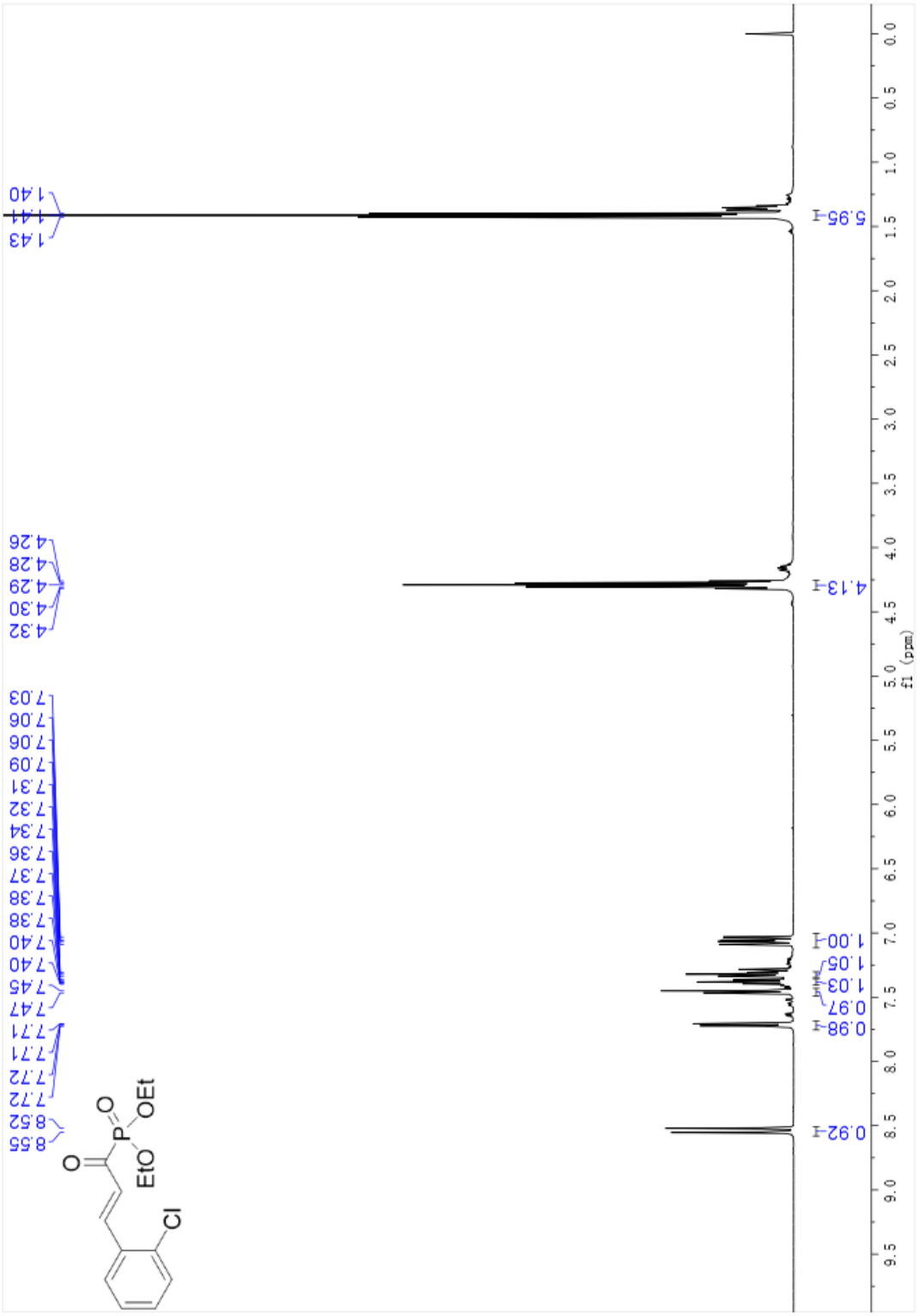
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4.28
4.29
4.30
4.32
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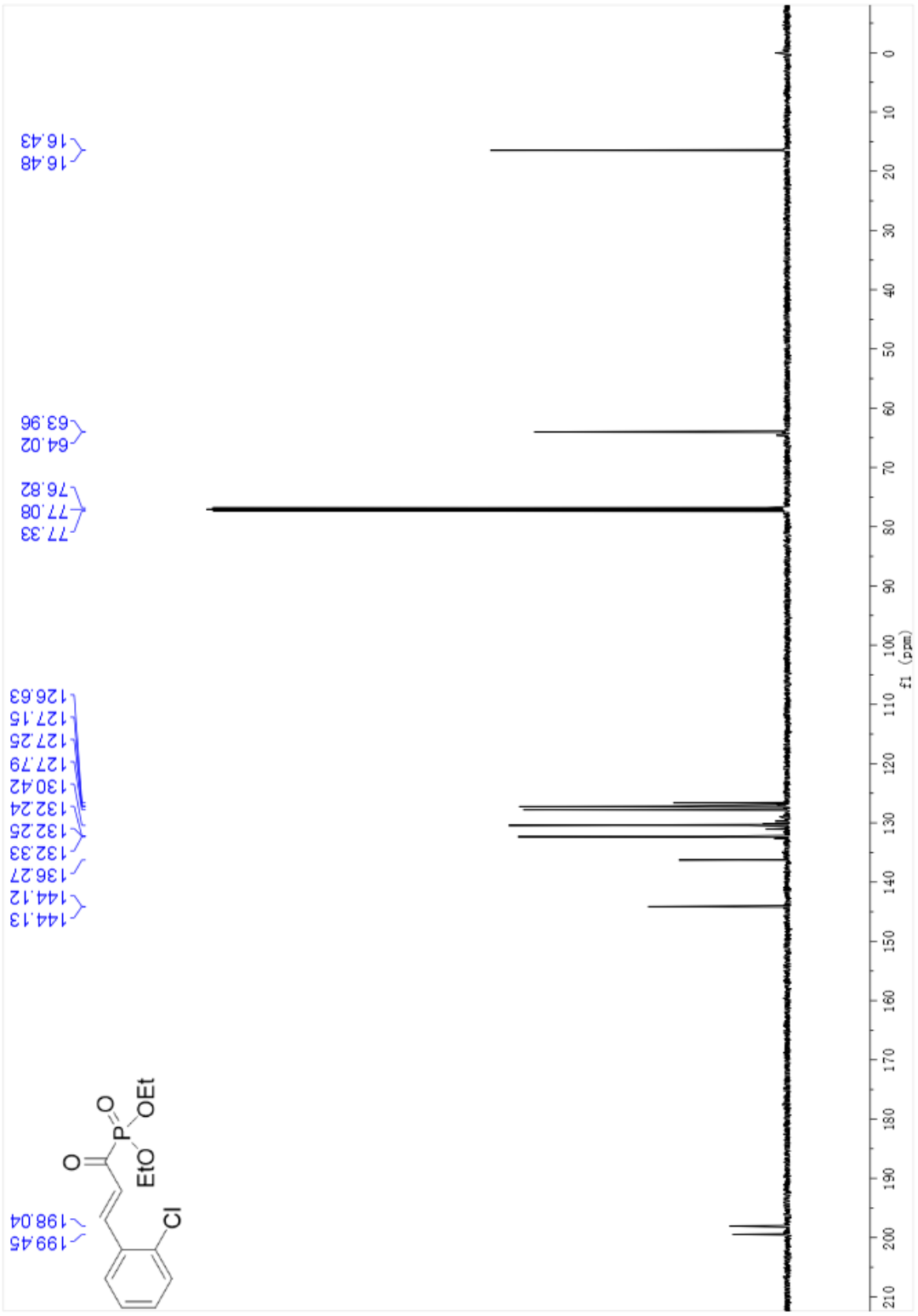
7.06
7.06
7.09
7.31
7.32
7.34
7.36
7.37
7.38
7.38
7.40
7.40
7.45
7.47
7.71
7.71
7.72
7.72
8.52
8.55
O
P
O
OEt
EtO
Cl
5.95
4.13
1.00
1.05
1.03
0.97
0.98
0.92
f1 (ppm)


16.43
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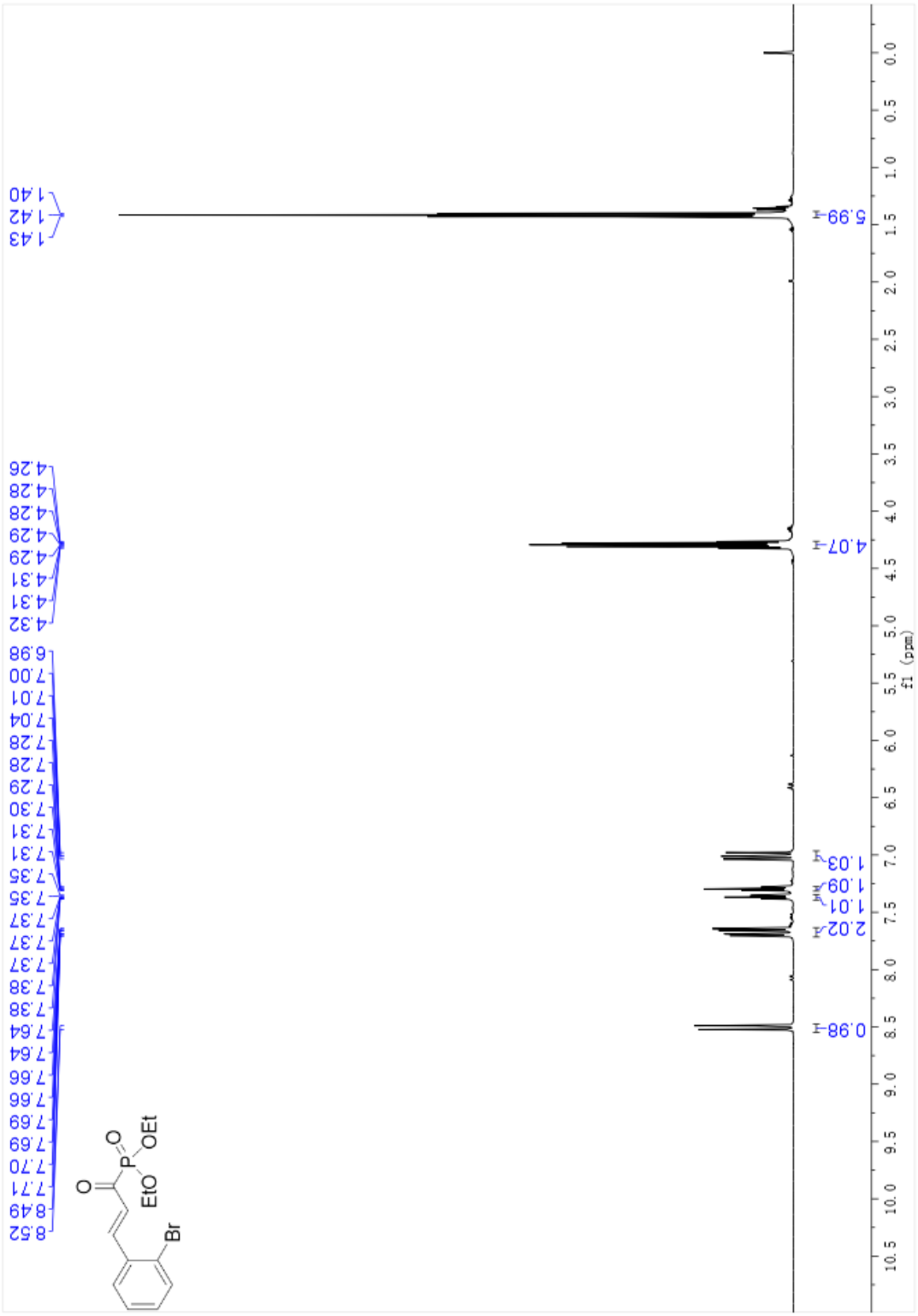
77.08
77.33
126.63
127.15
127.25
127.79
130.42
132.24
132.25
132.33
136.27
144.12
144.13
198.04
199.45
O
P
OEt
EtO
Cl
f1 (ppm)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1.42
1.43
4.26
4.28
4.28
4.29
4.29
4.31
4.31
4.32
6.98
7.00
7.01
7.04
7.28
7.28
7.29
7.30
7.31
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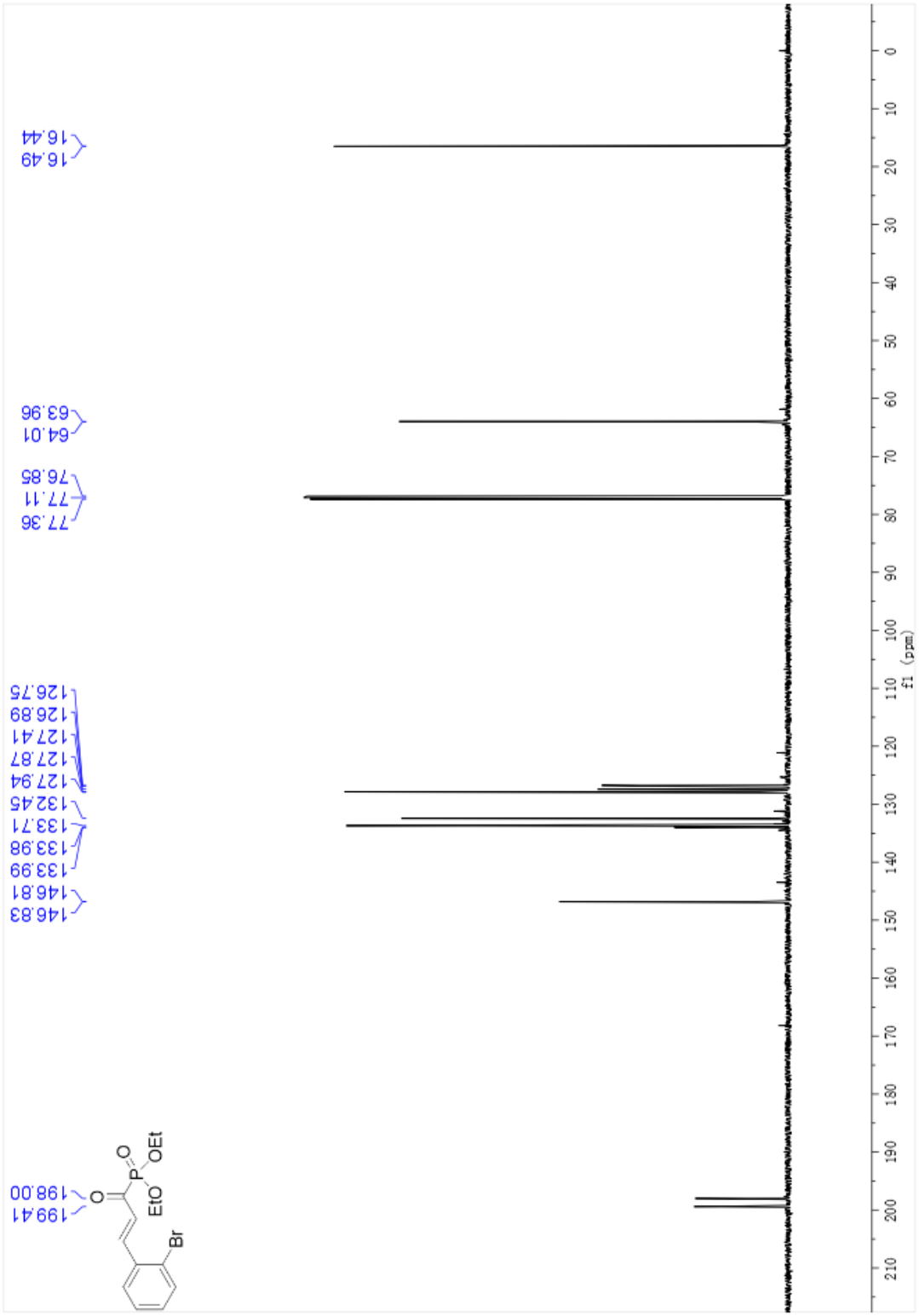
7.35
7.35
7.37
7.37
7.37
7.38
7.38
7.64
7.64
7.66
7.66
7.69
7.69
7.70
7.71
8.49
8.52
O
P
O
OEt
EtO
Br
5.99
4.07
1.03
1.09
1.01
2.02
0.98
f1 (ppm)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76.85
77.11
77.36
126.75
126.89
127.41
127.87
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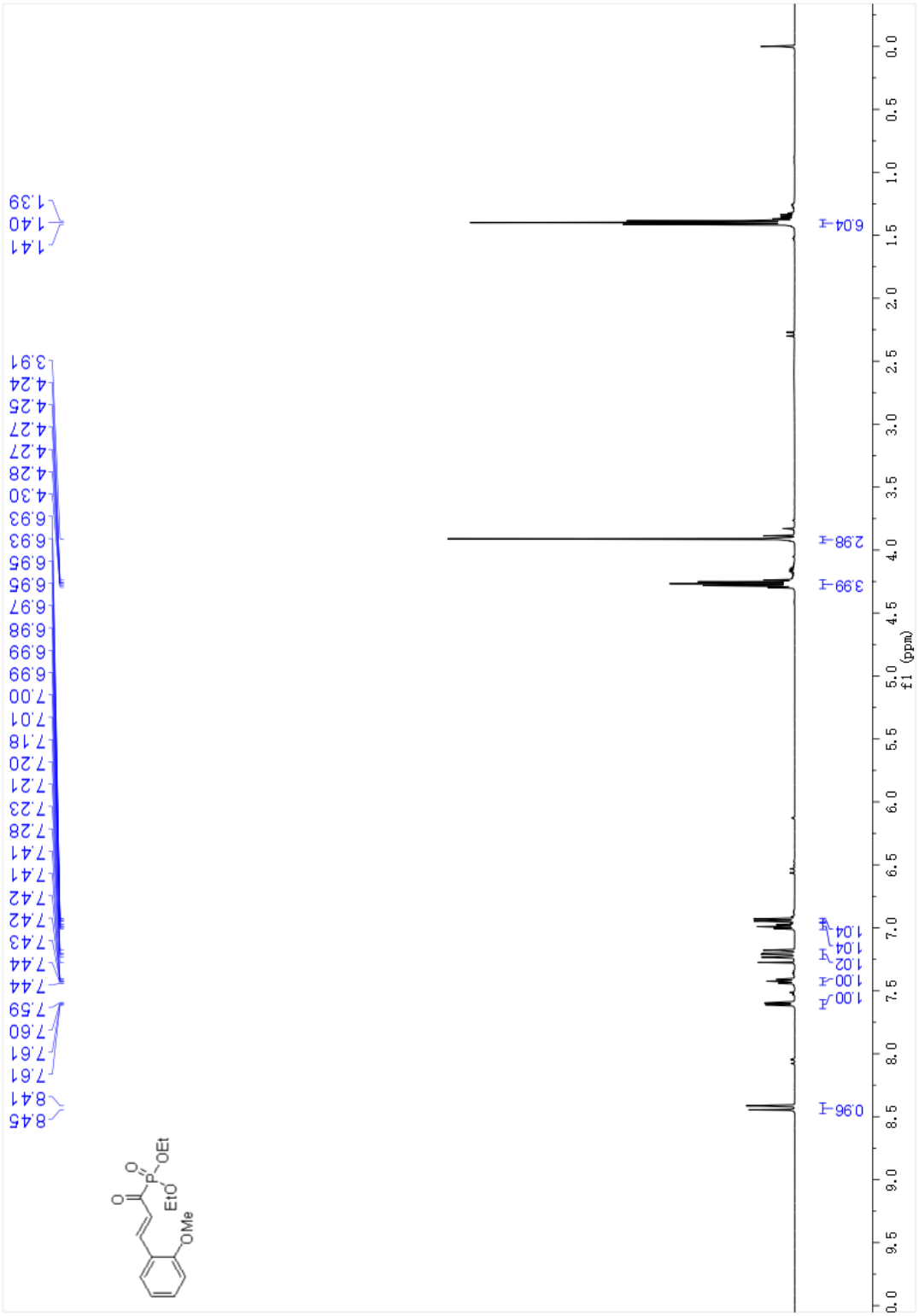
132.45
133.71
133.98
133.99
146.81
146.83
198.00
199.41
EtO
OEt
Br
f1 (ppm)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6.99
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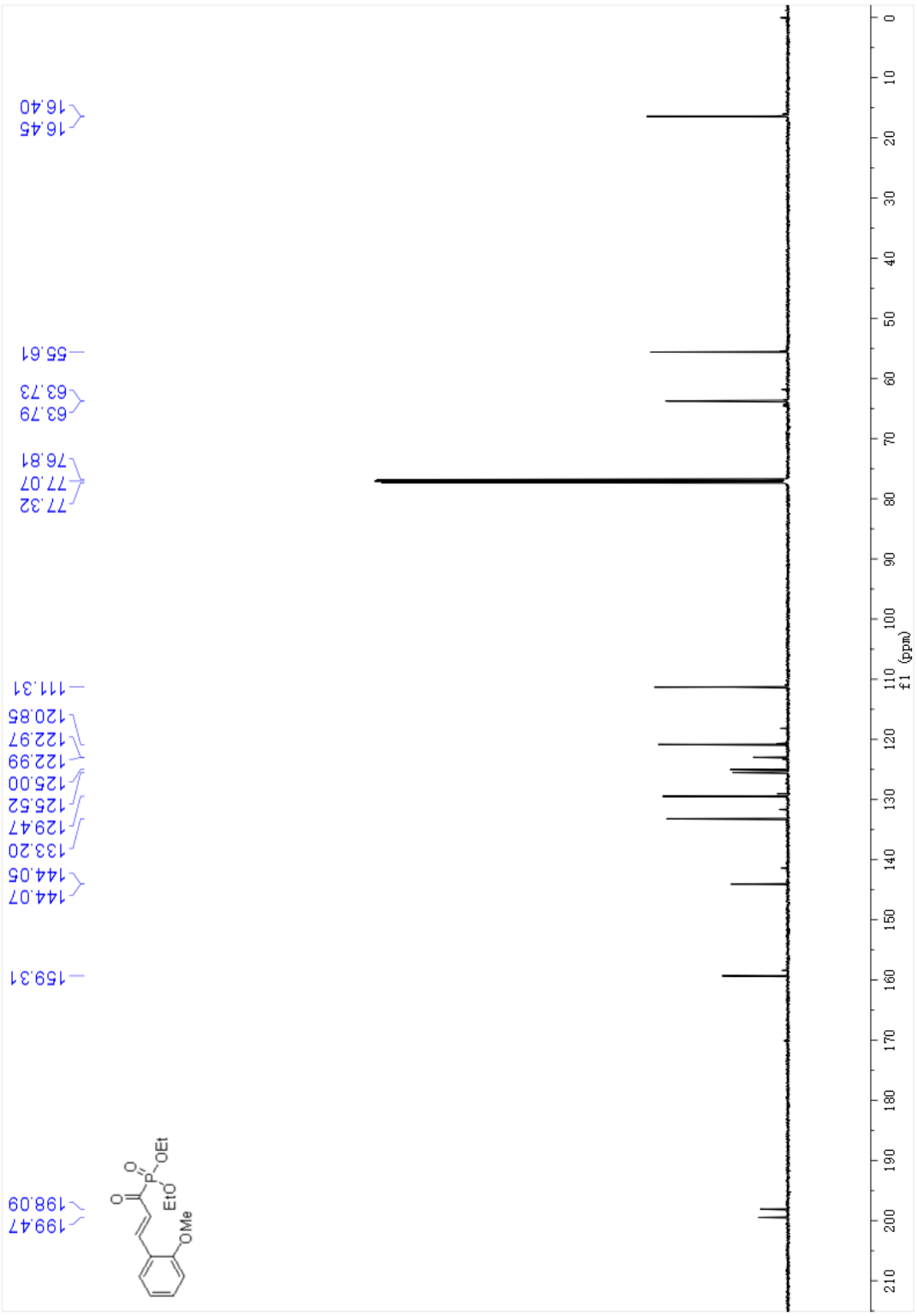
7.61
8.41
8.45
6.04
2.98
3.99
1.04
1.04
1.02
1.00
1.00
0.96
OEt
EtO
OMe
f1 (ppm)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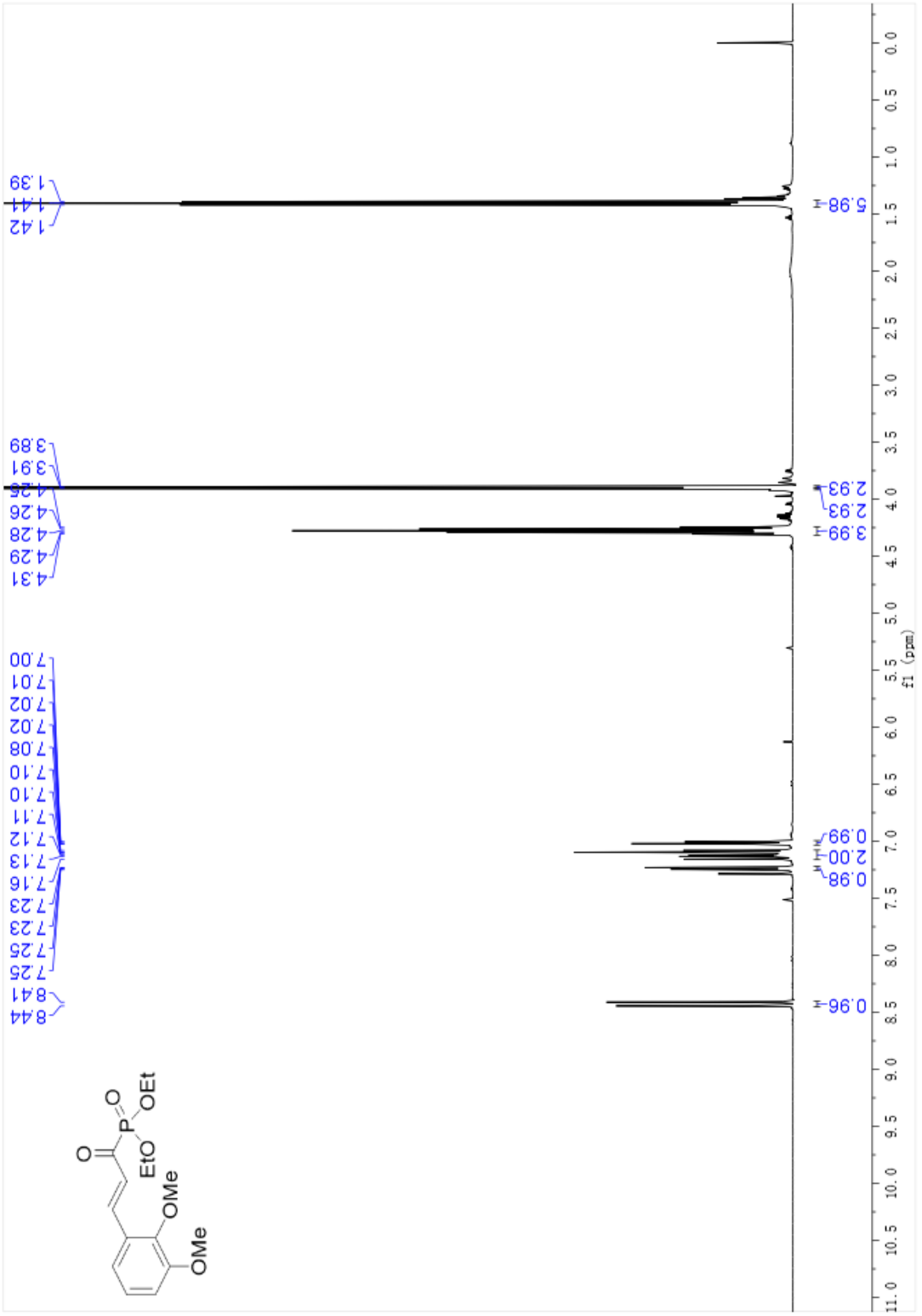
16.45
55.61
63.73
63.79
76.81
77.07
77.32
111.31
120.85
122.97
122.99
125.00
125.52
129.47
133.20
144.05
144.07
159.31
198.09
199.47
f1 (ppm)
OEt
EtO
OMe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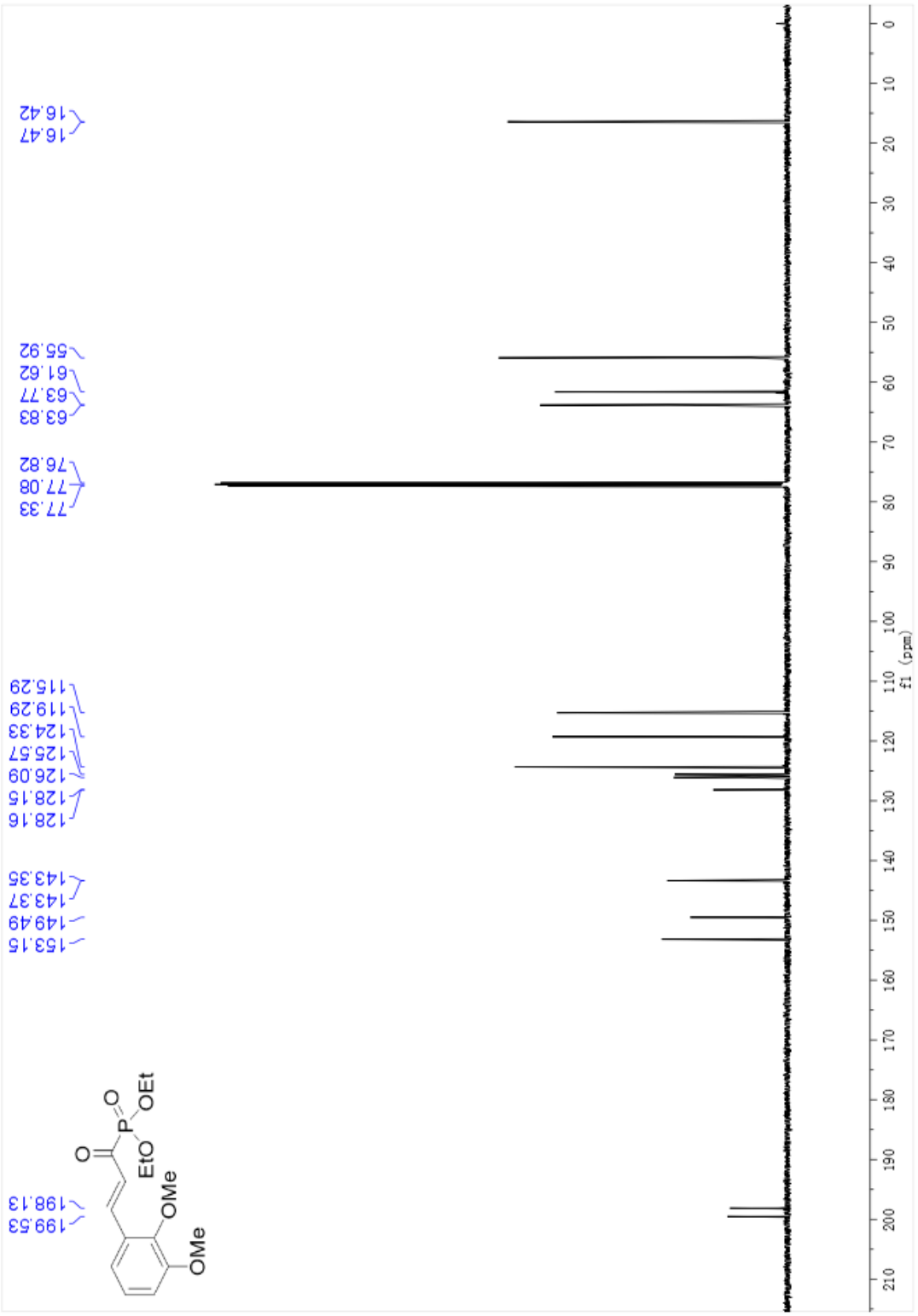
7.08
7.10
7.10
7.11
7.12
7.13
7.16
7.23
7.23
7.25
7.25
8.41
8.44
5.98
2.93
2.93
3.99
0.99
2.00
0.98
0.96
f1 (ppm)
O
P
OEt
EtO
OMe
OMe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76.82
77.08
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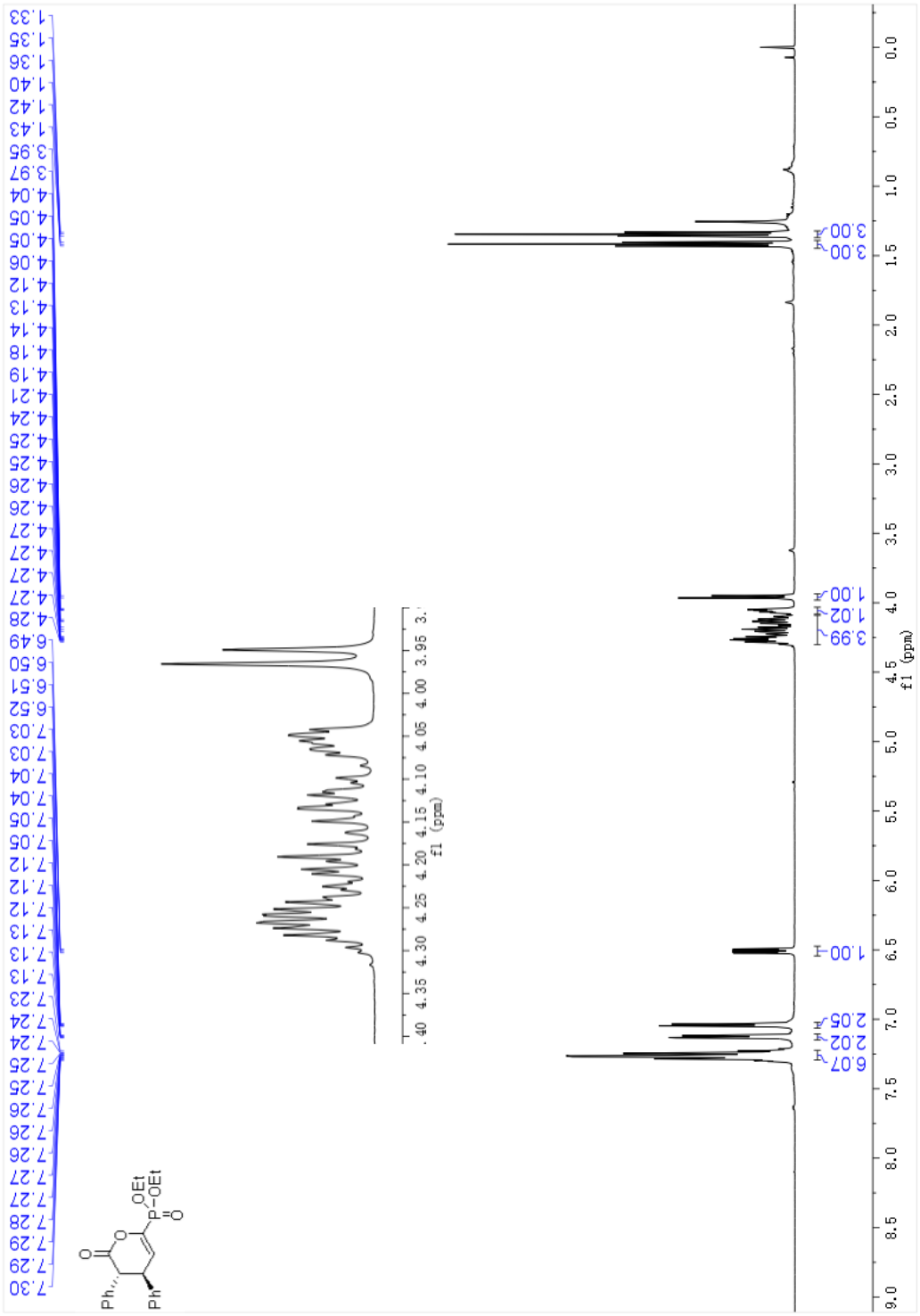
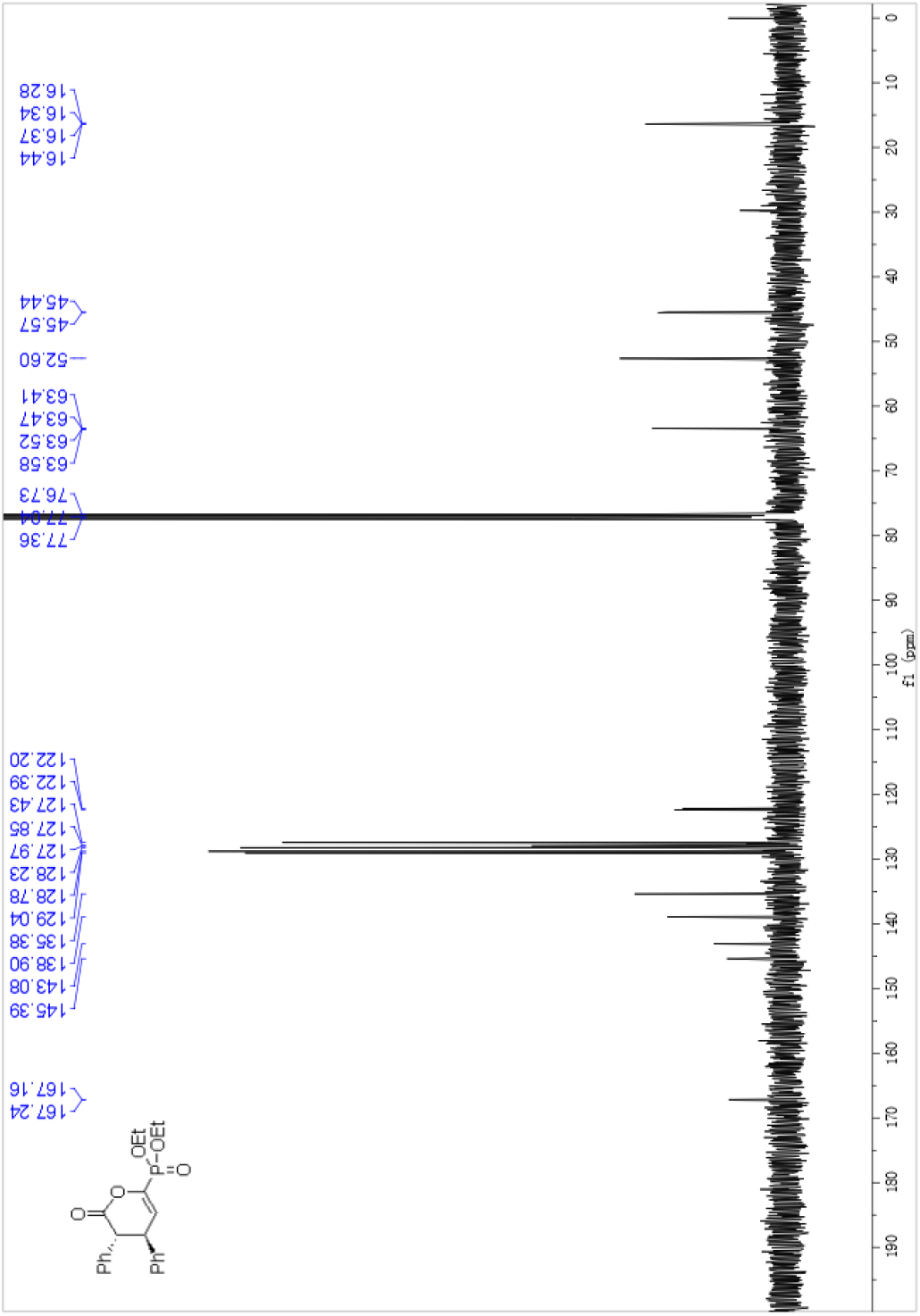
115.29
119.29
124.33
125.57
126.09
128.15
128.16
143.35
143.37
149.49
153.15
198.13
199.53
O
P
O
OEt
EtO
OMe
OMe
f1 (ppm)

NMR Spectra of Products 3a-3n

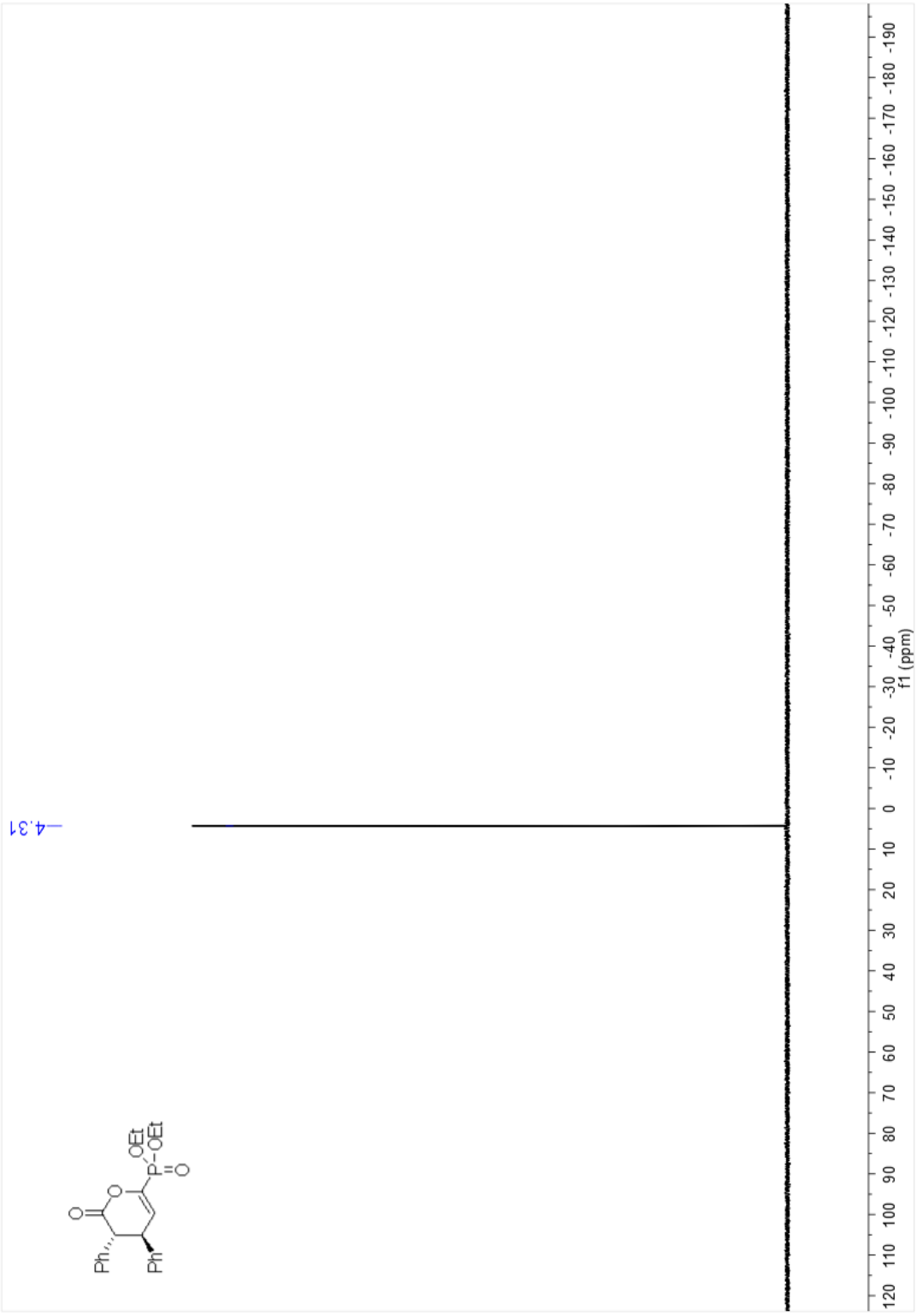
^{1}H NMR spectrum of product **3a**



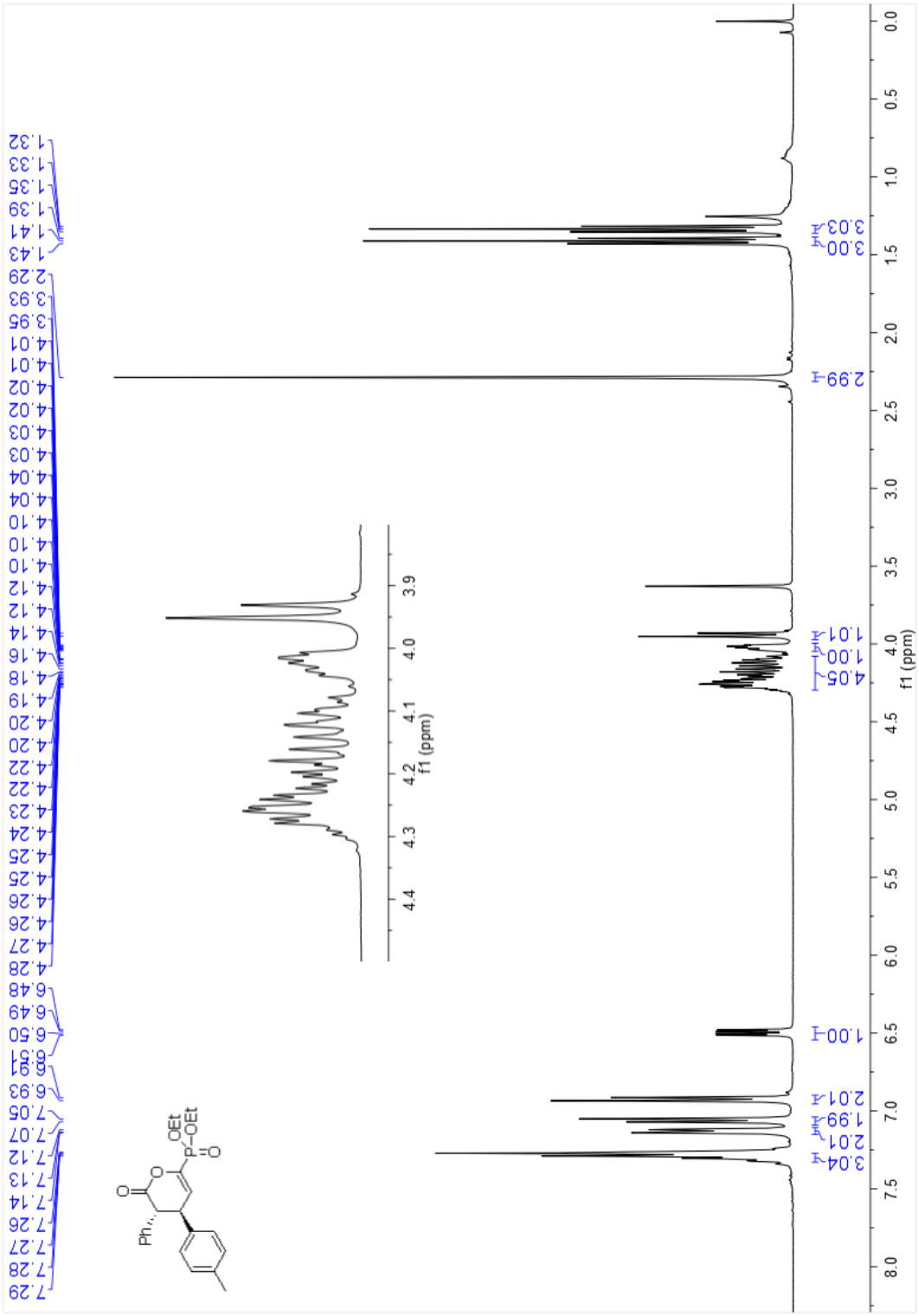
^{13}C NMR spectrum of product **3a**



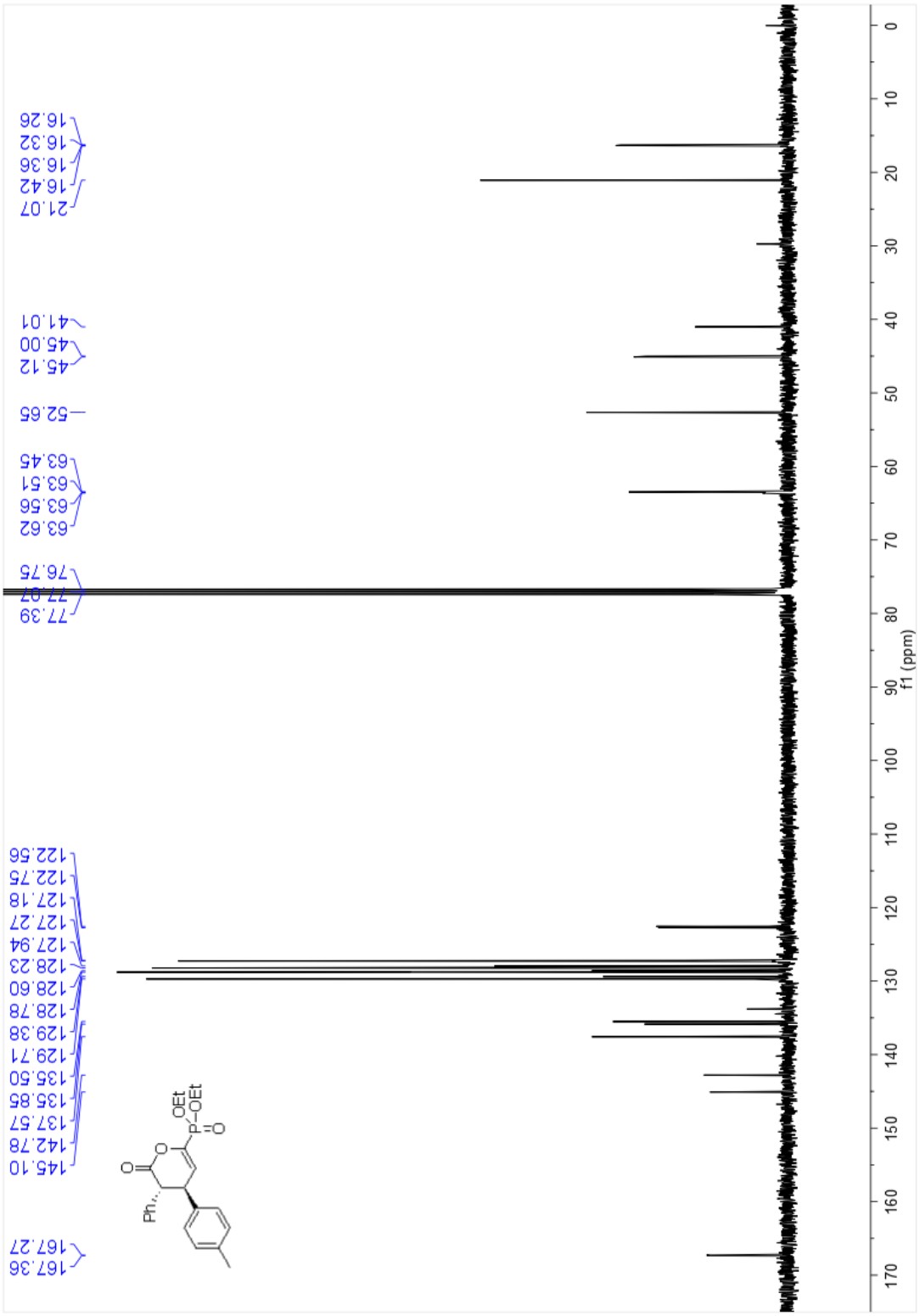
^{31}P NMR spectrum of product **3a**



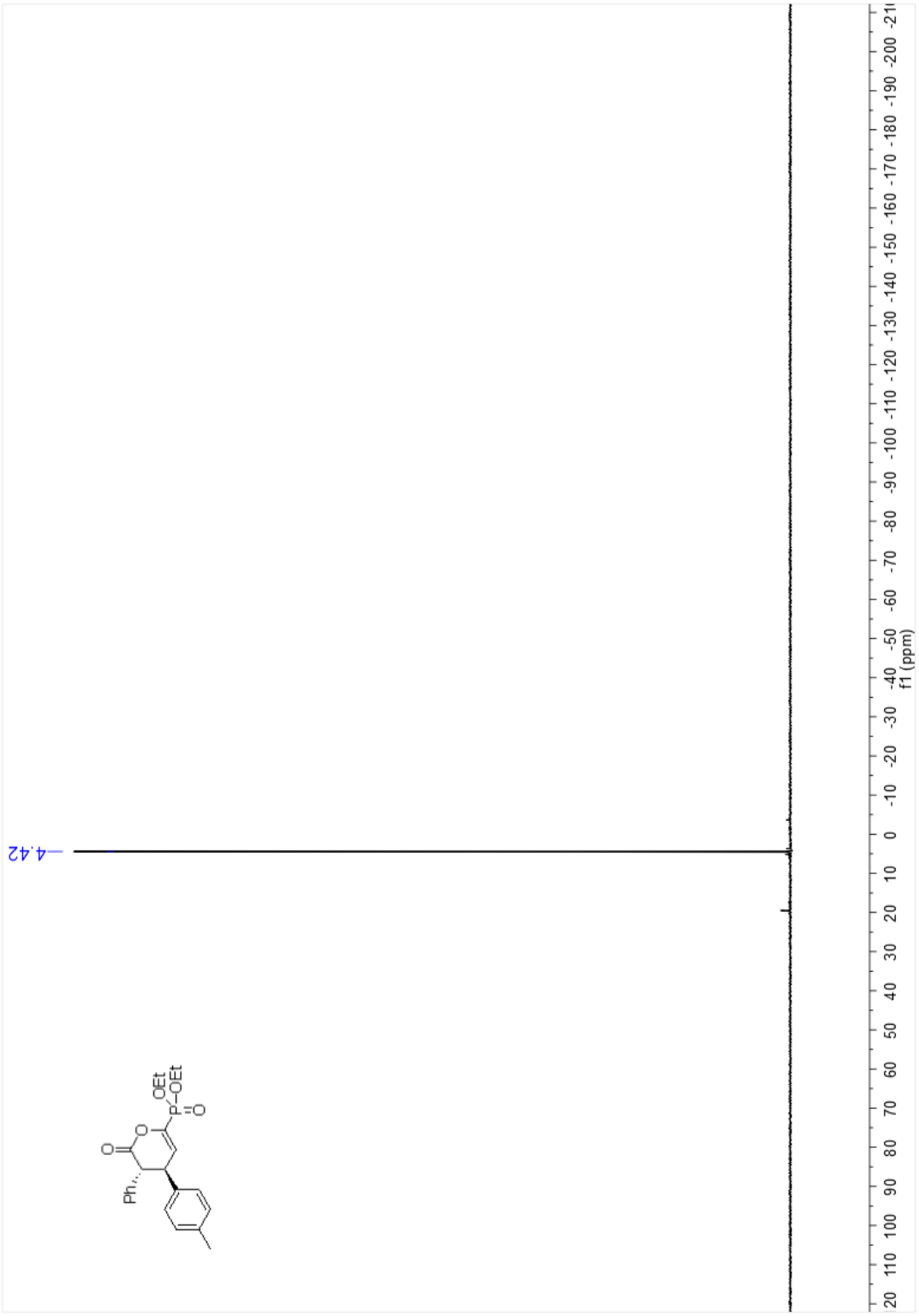
^{1}H NMR spectrum of product **3b**



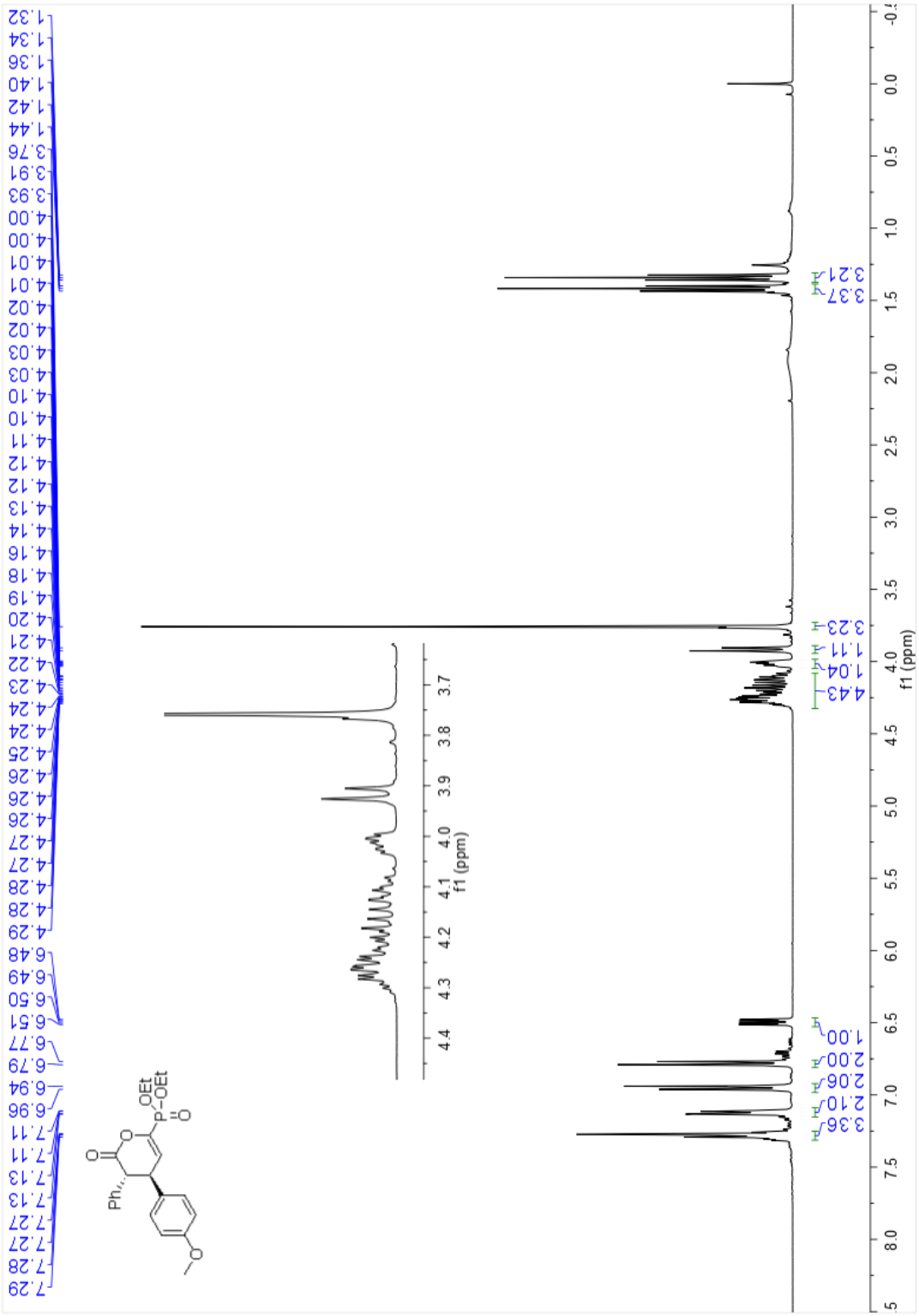
^{13}C NMR spectrum of product **3b**



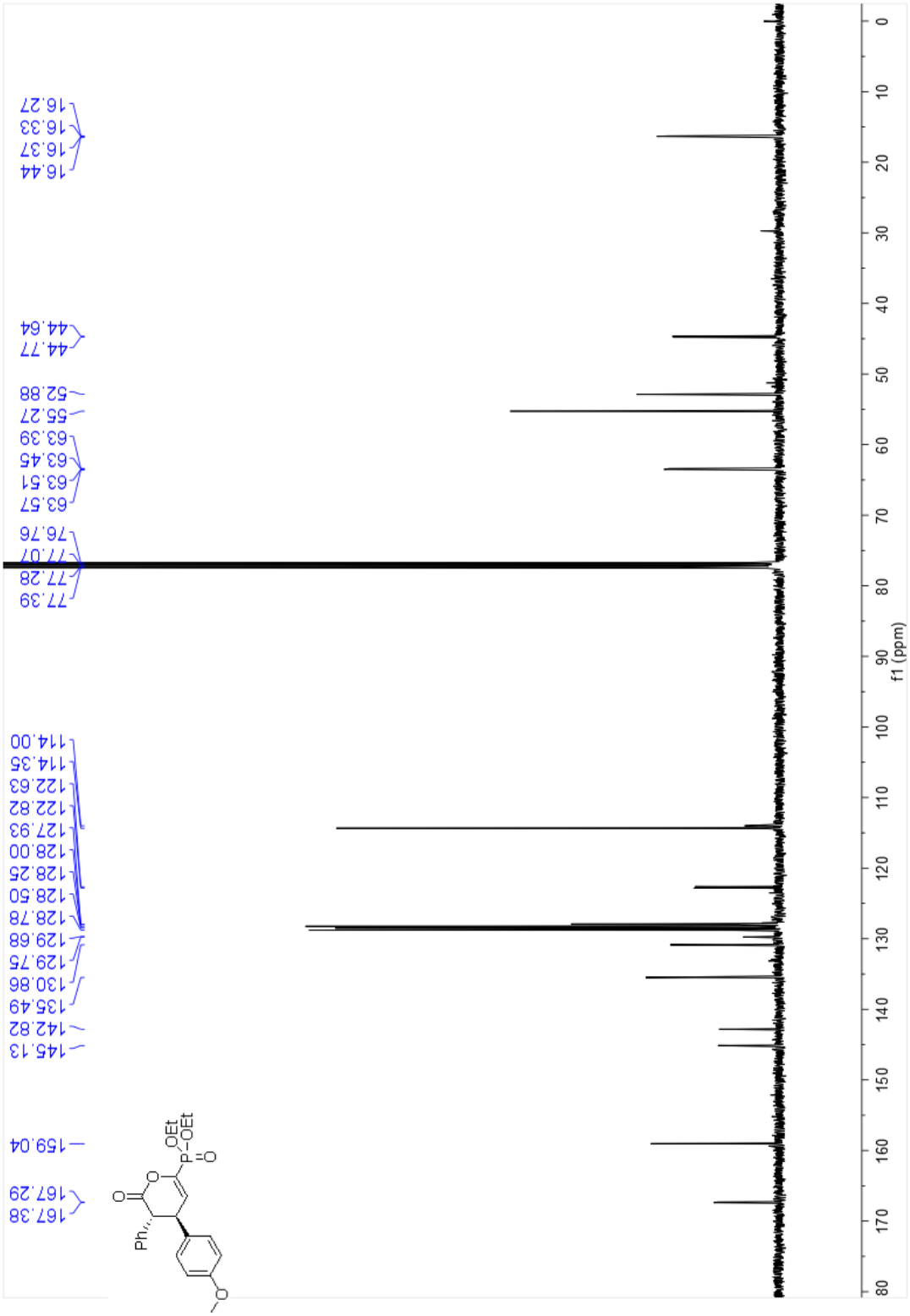
^{31}P NMR spectrum of product **3b**



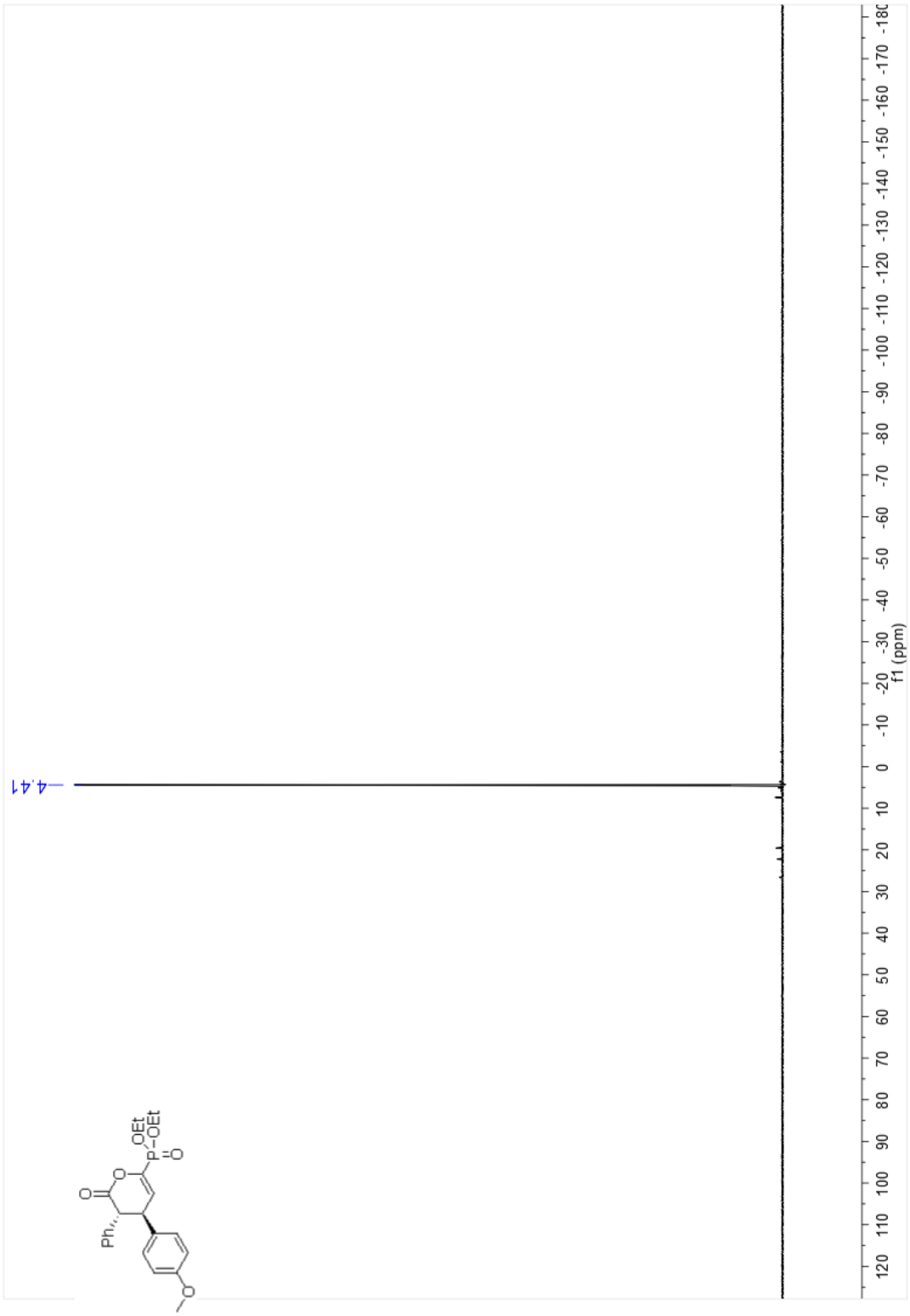
^{1}H NMR spectrum of product **3c**



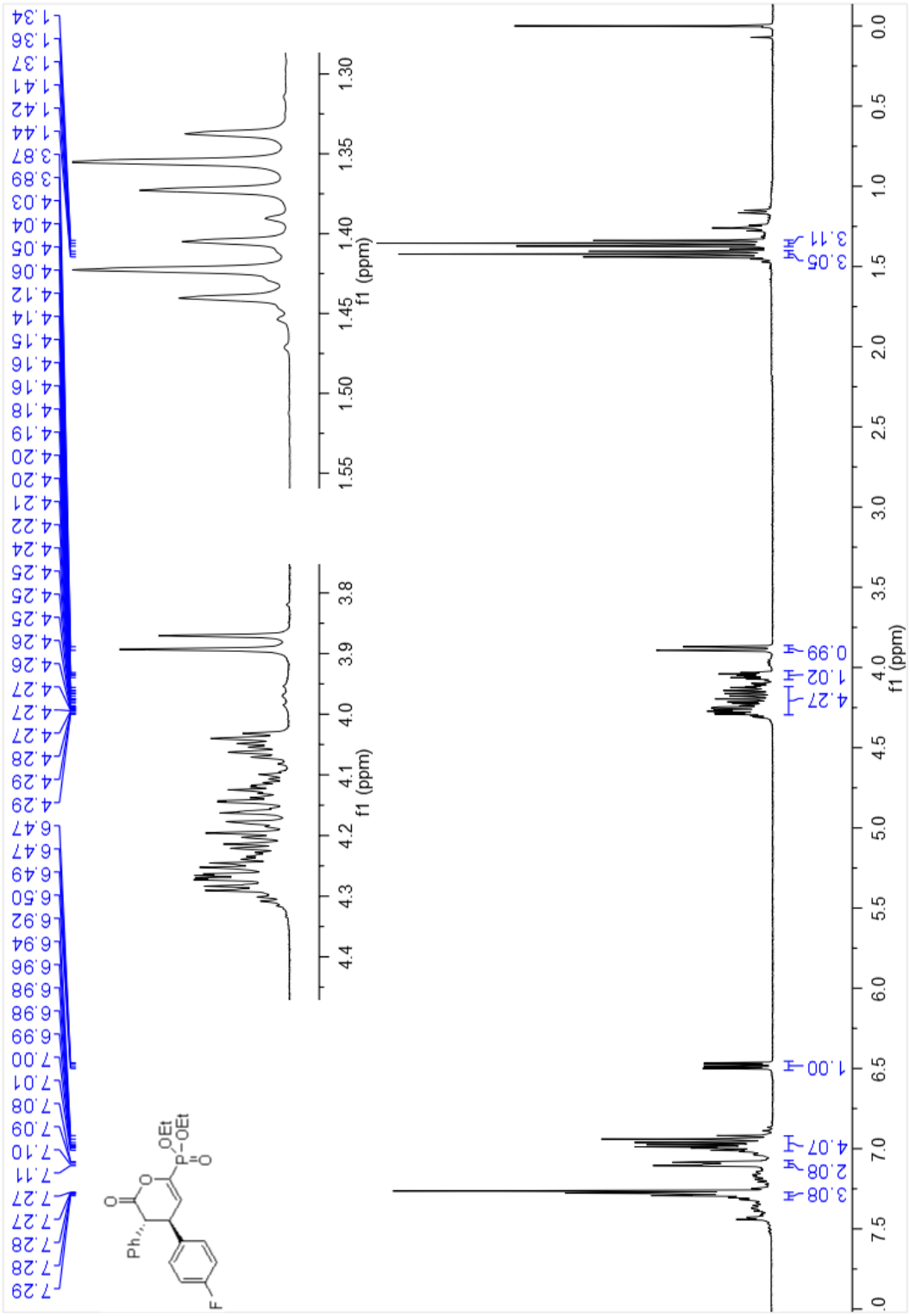
^{13}C NMR spectrum of product **3c**



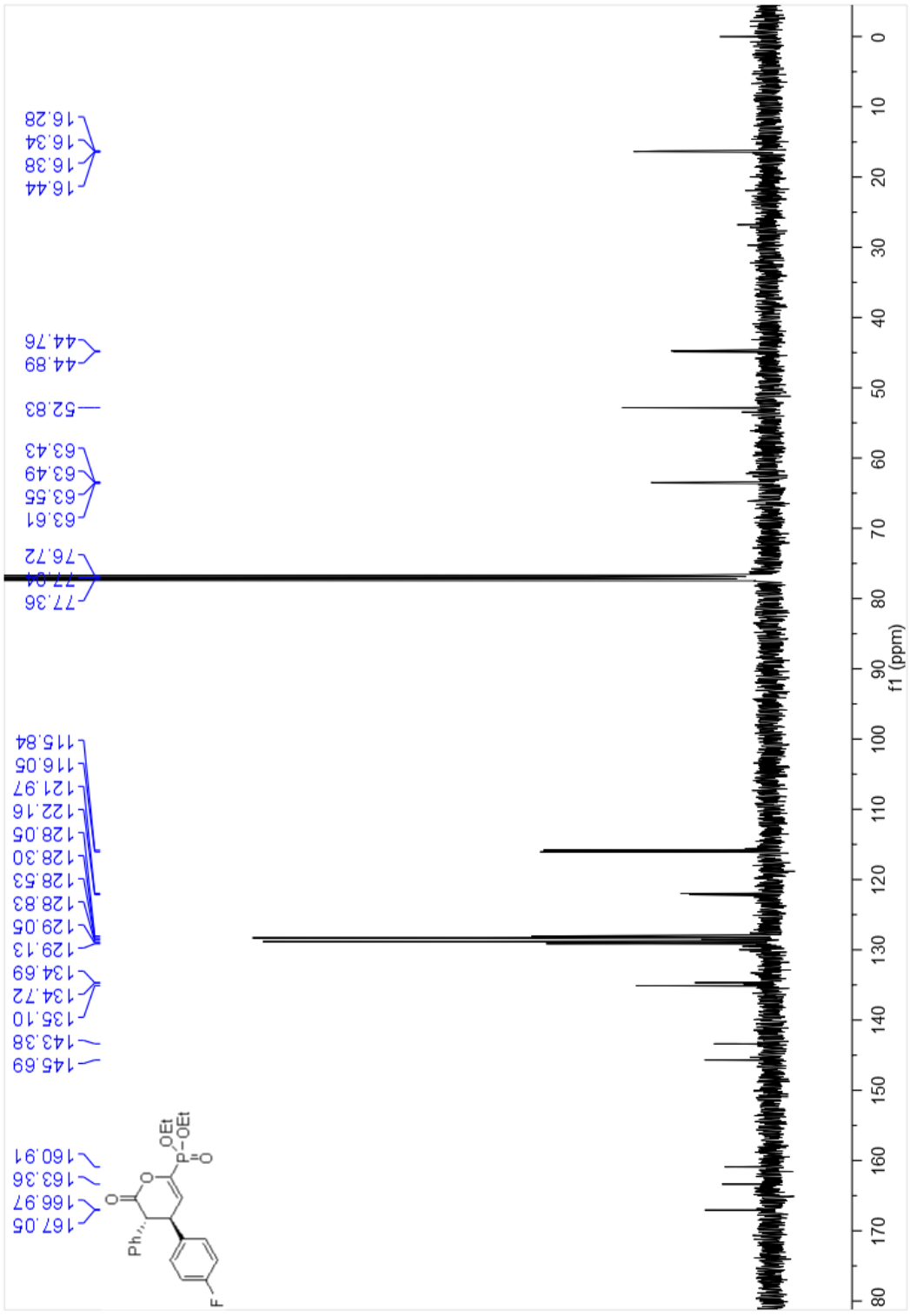
^{31}P NMR spectrum of product **3c**



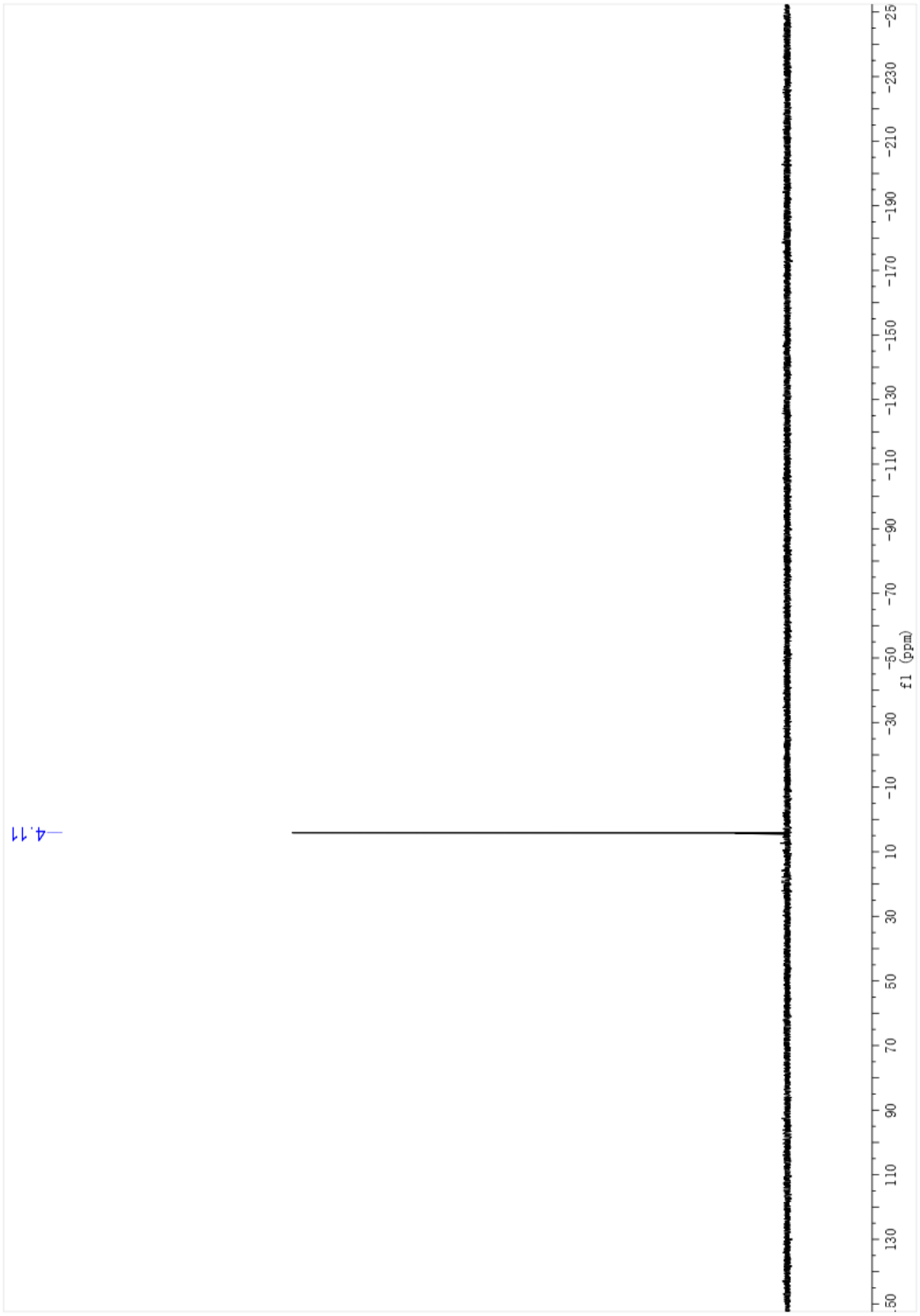
^{1}H NMR spectrum of product **3d**



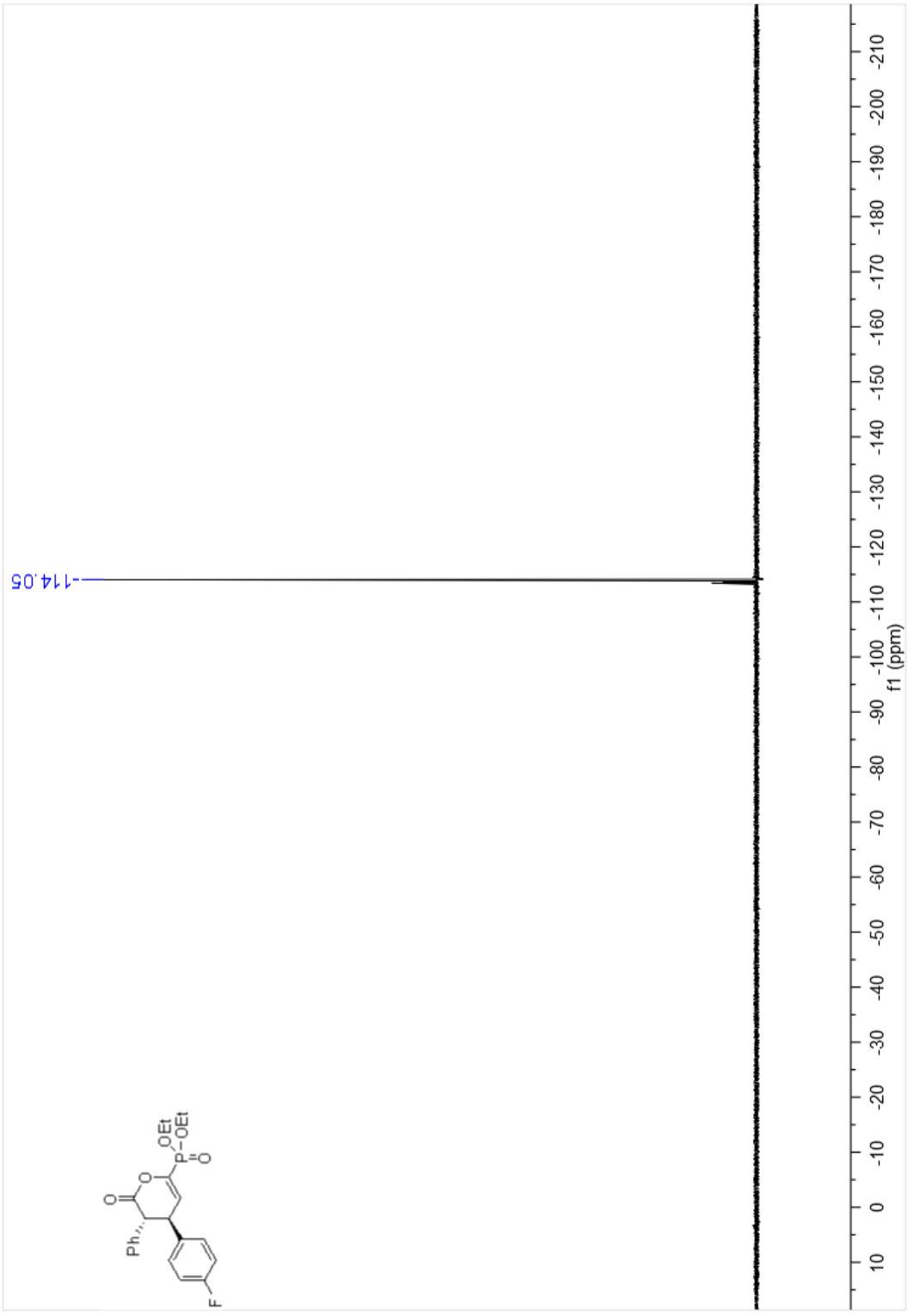
^{13}C NMR spectrum of product **3d**



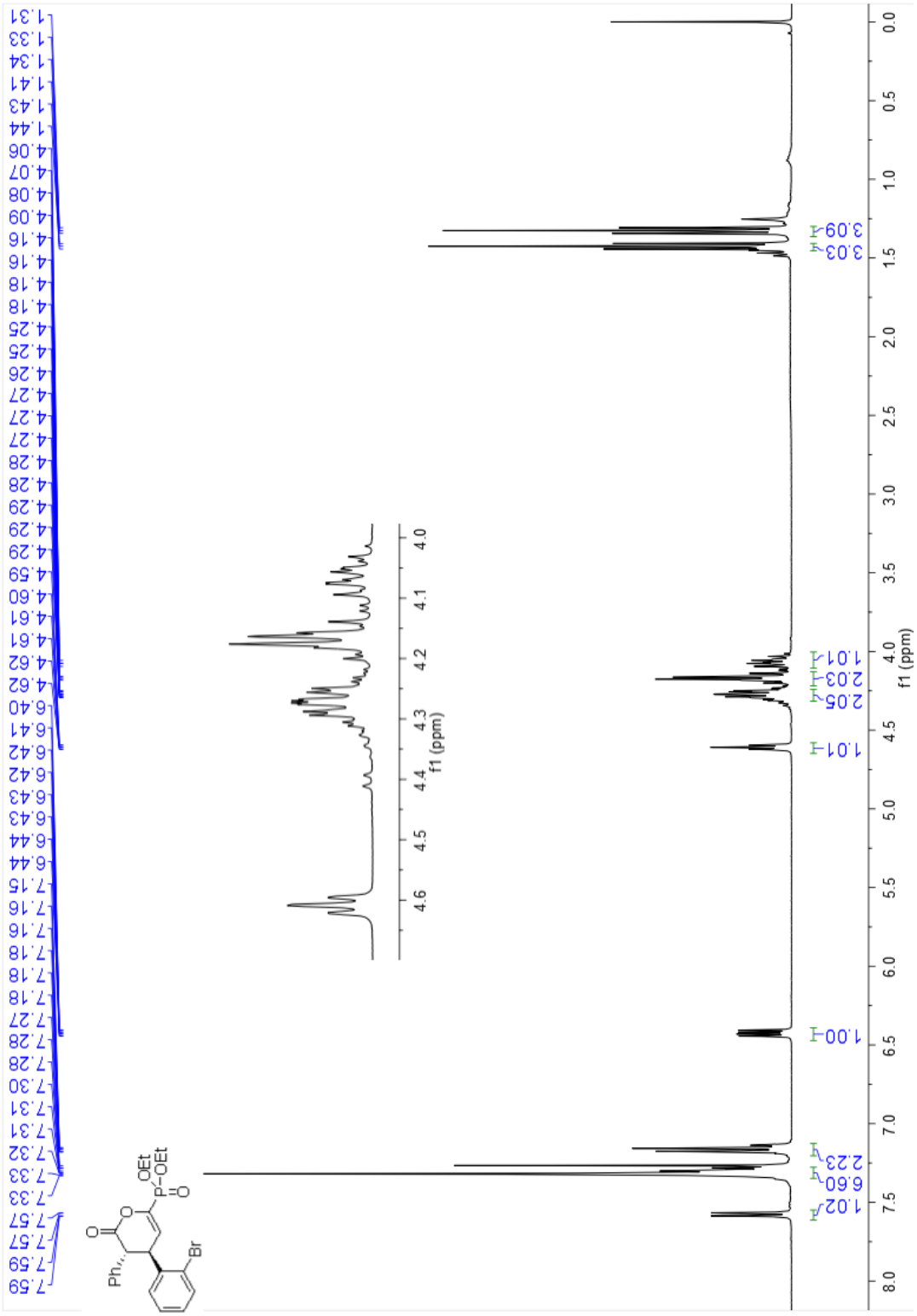
^{31}P NMR spectrum of product **3d**



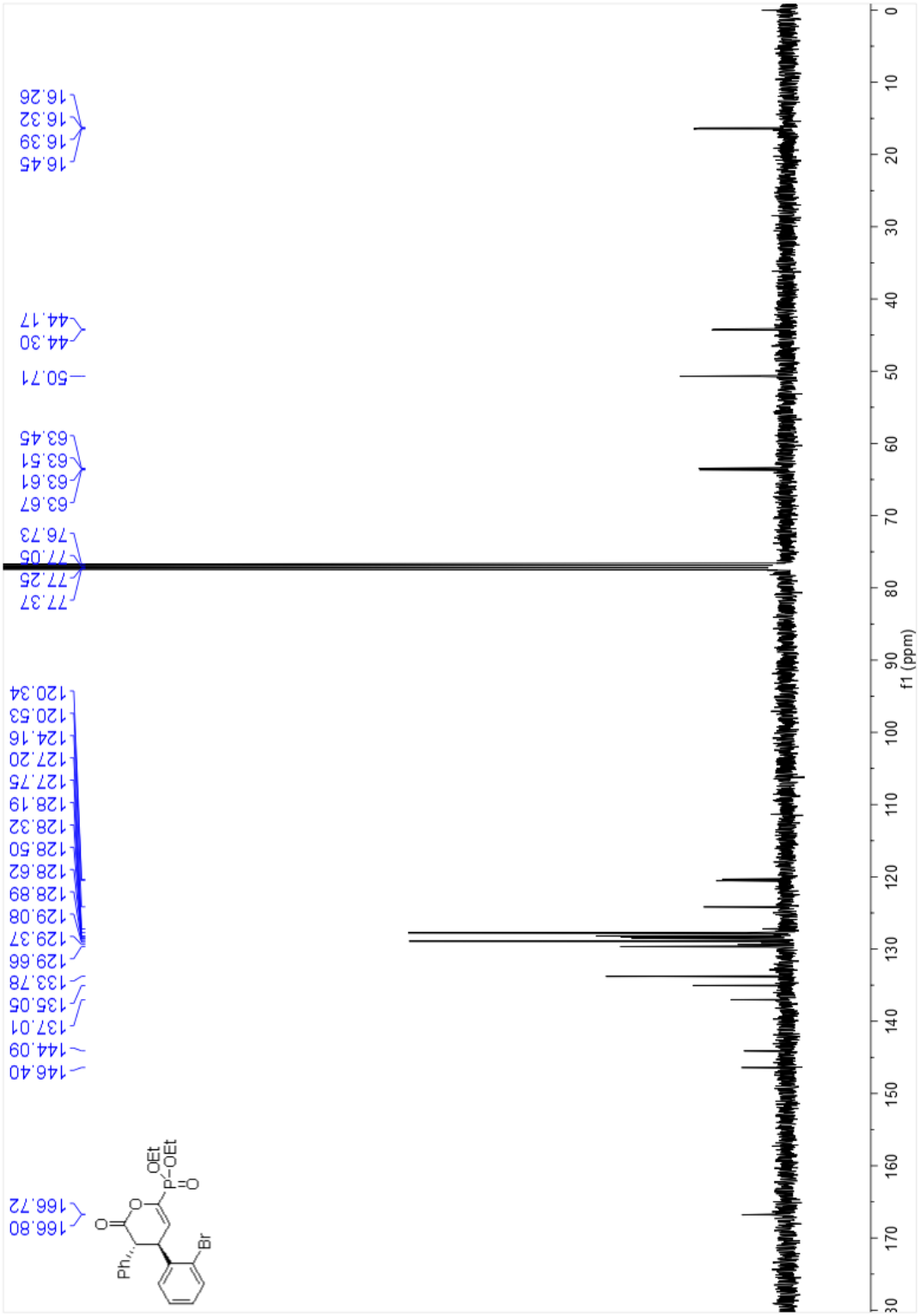
^{19}F NMR spectrum of product **3d**



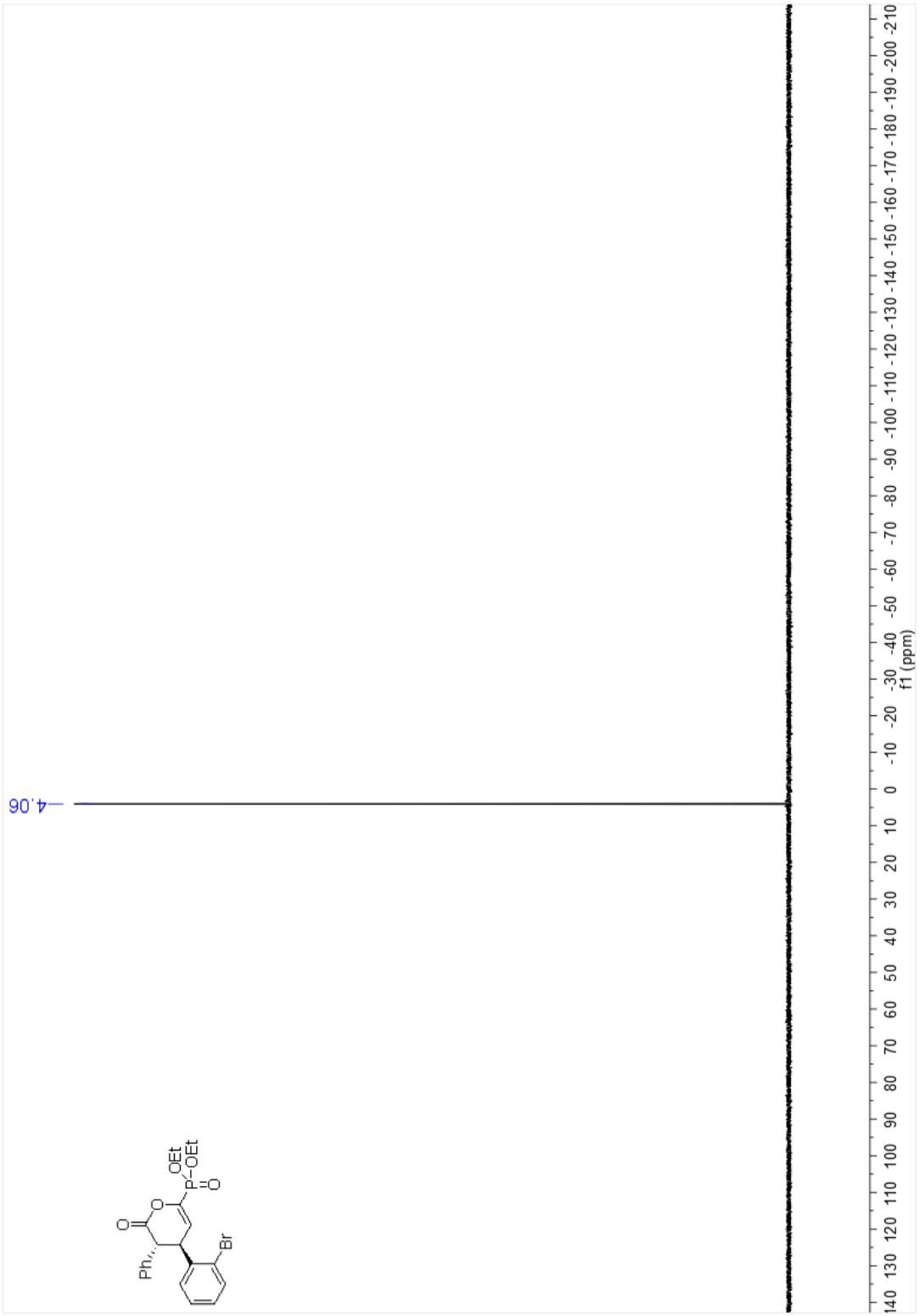
^{1}H NMR spectrum of product **3e**



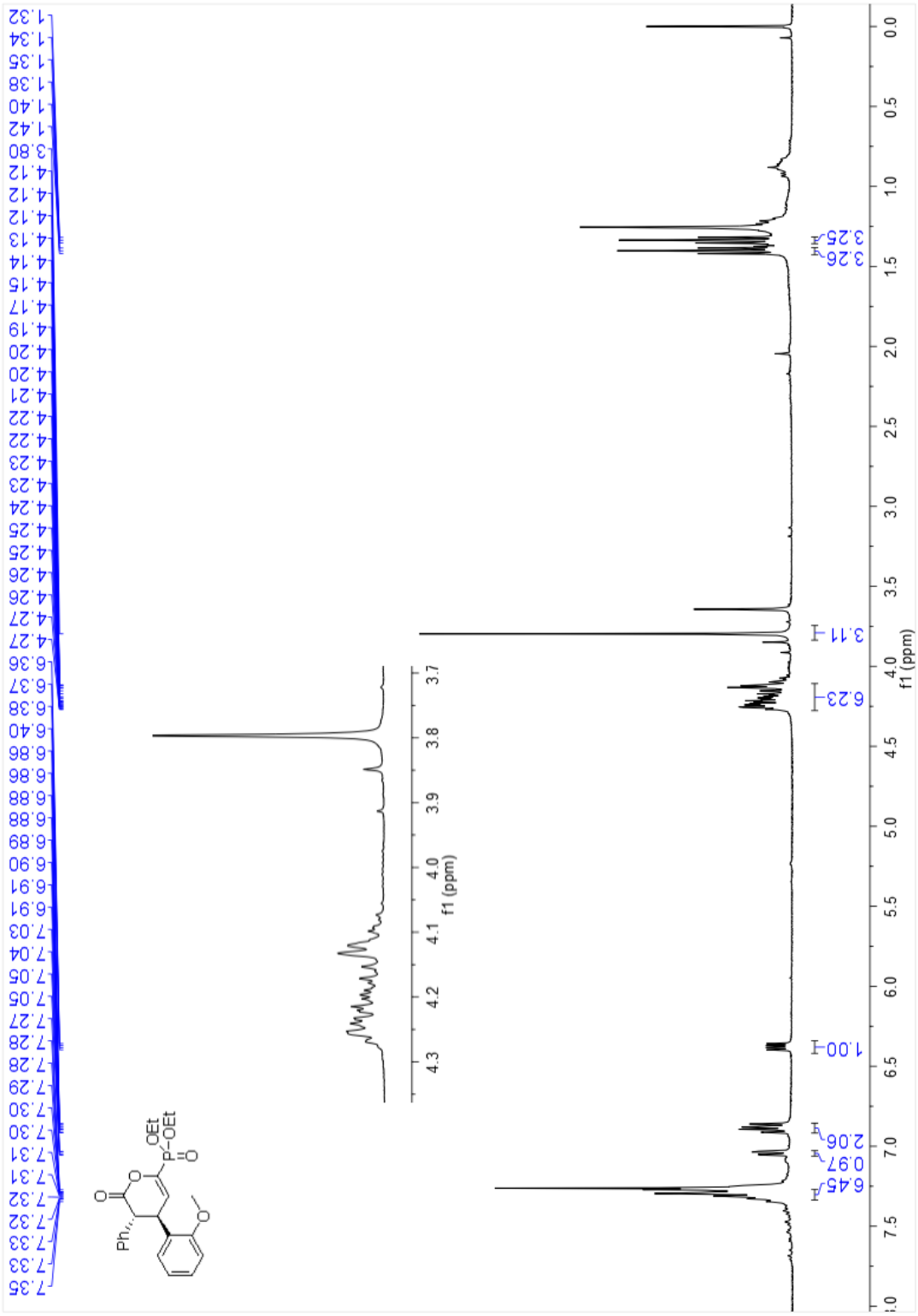
^{13}C NMR spectrum of product **3e**



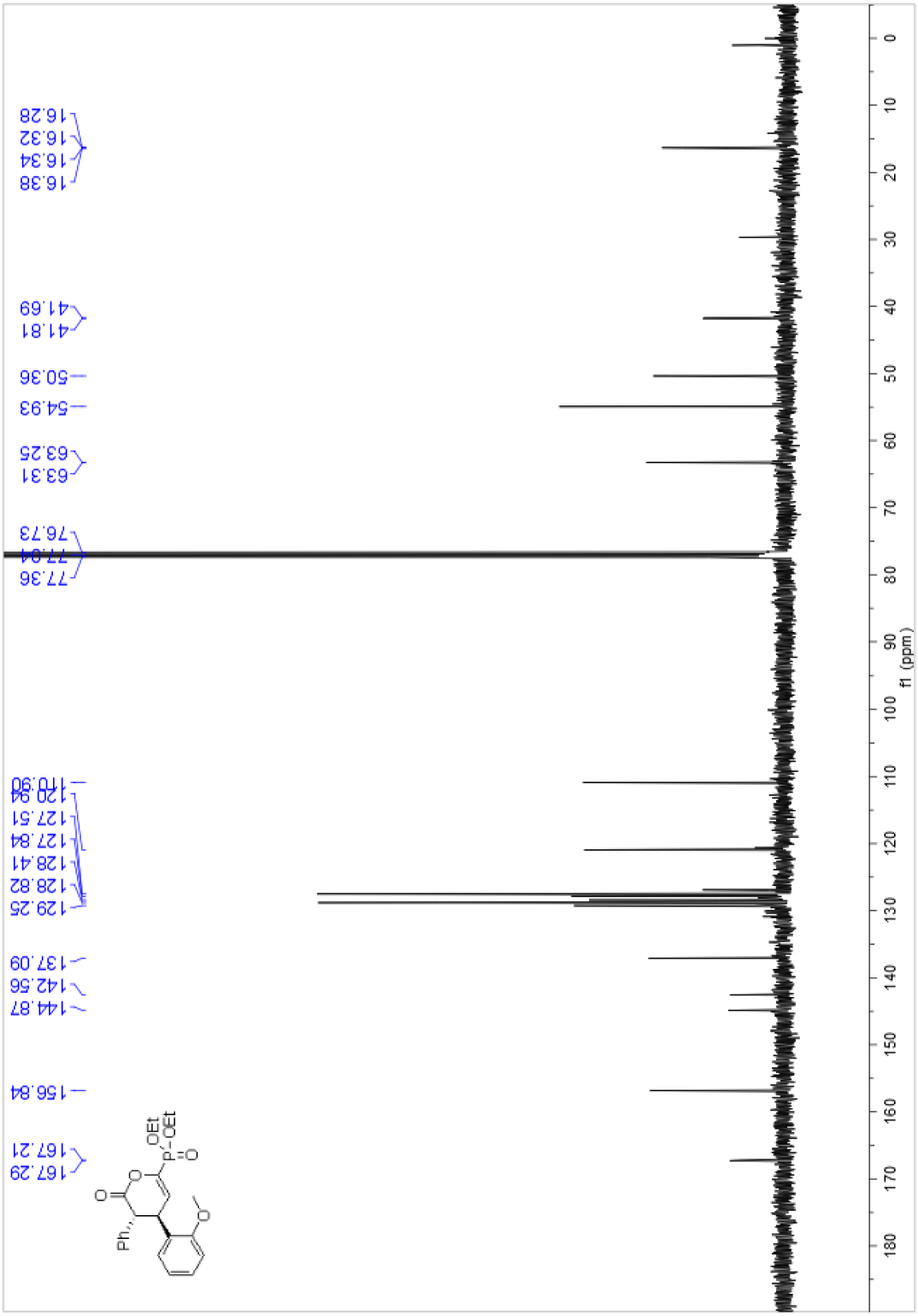
^{31}P NMR spectrum of product **3e**



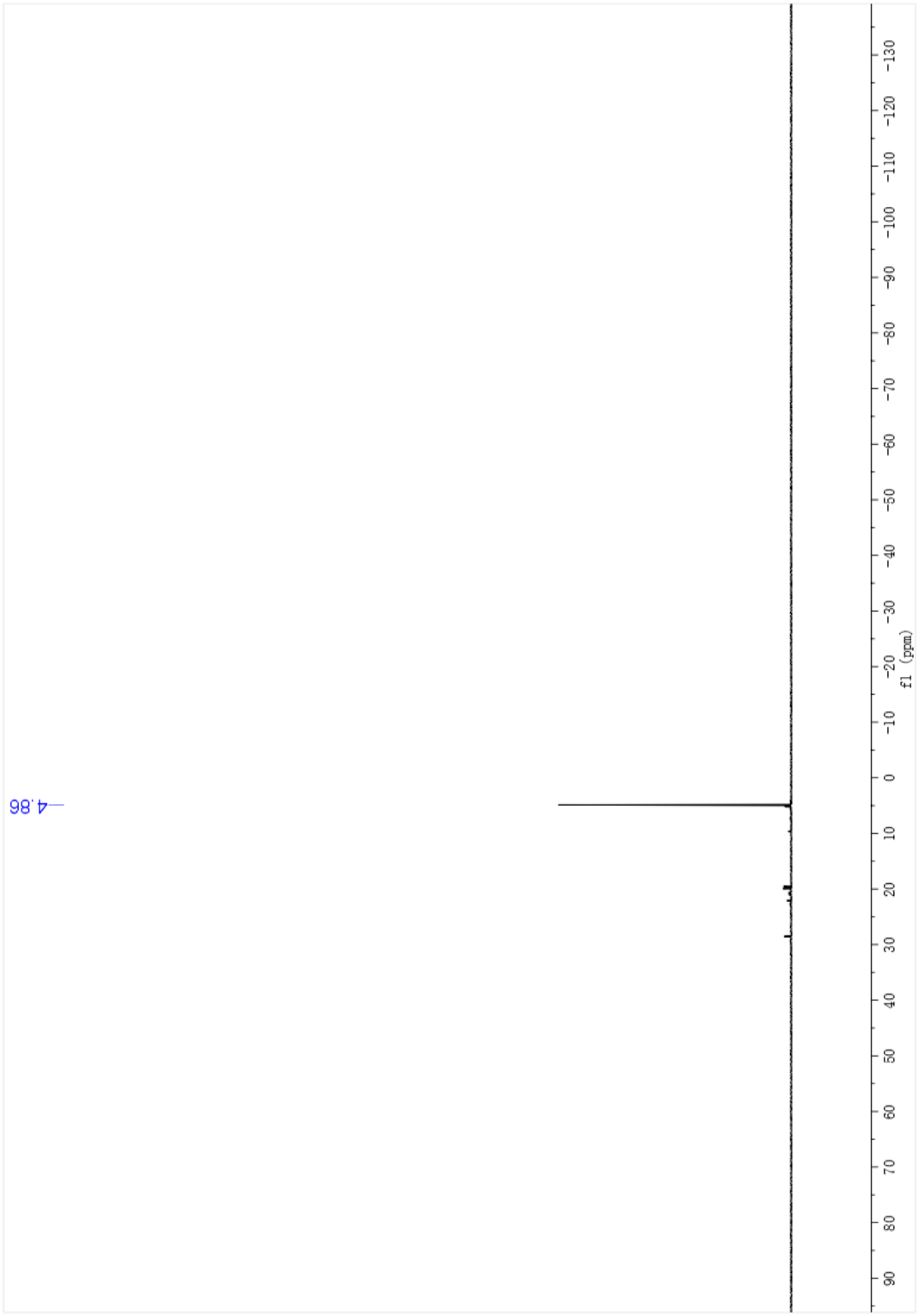
^{1}H NMR spectrum of product **3f**



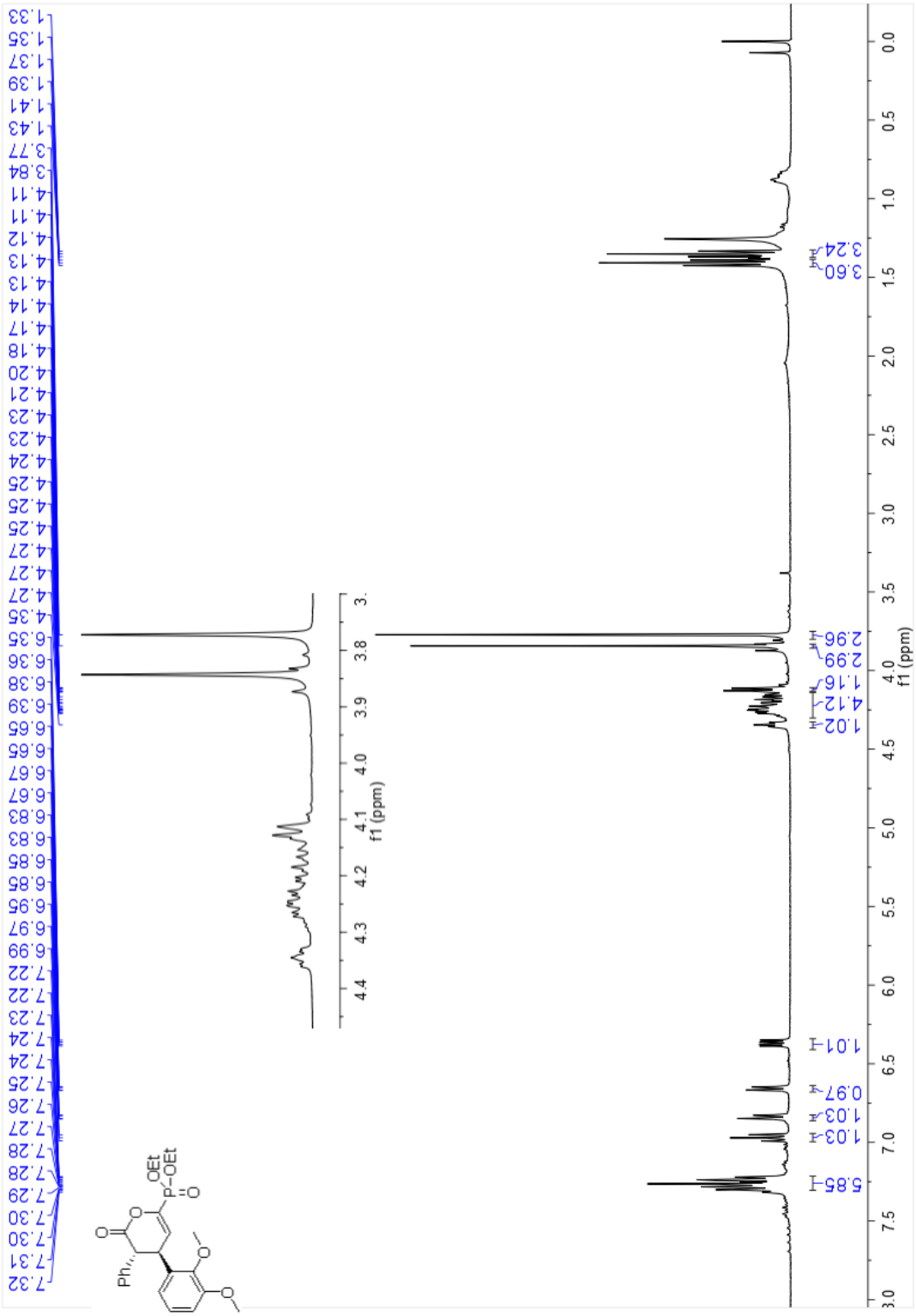
^{13}C NMR spectrum of product **3f**



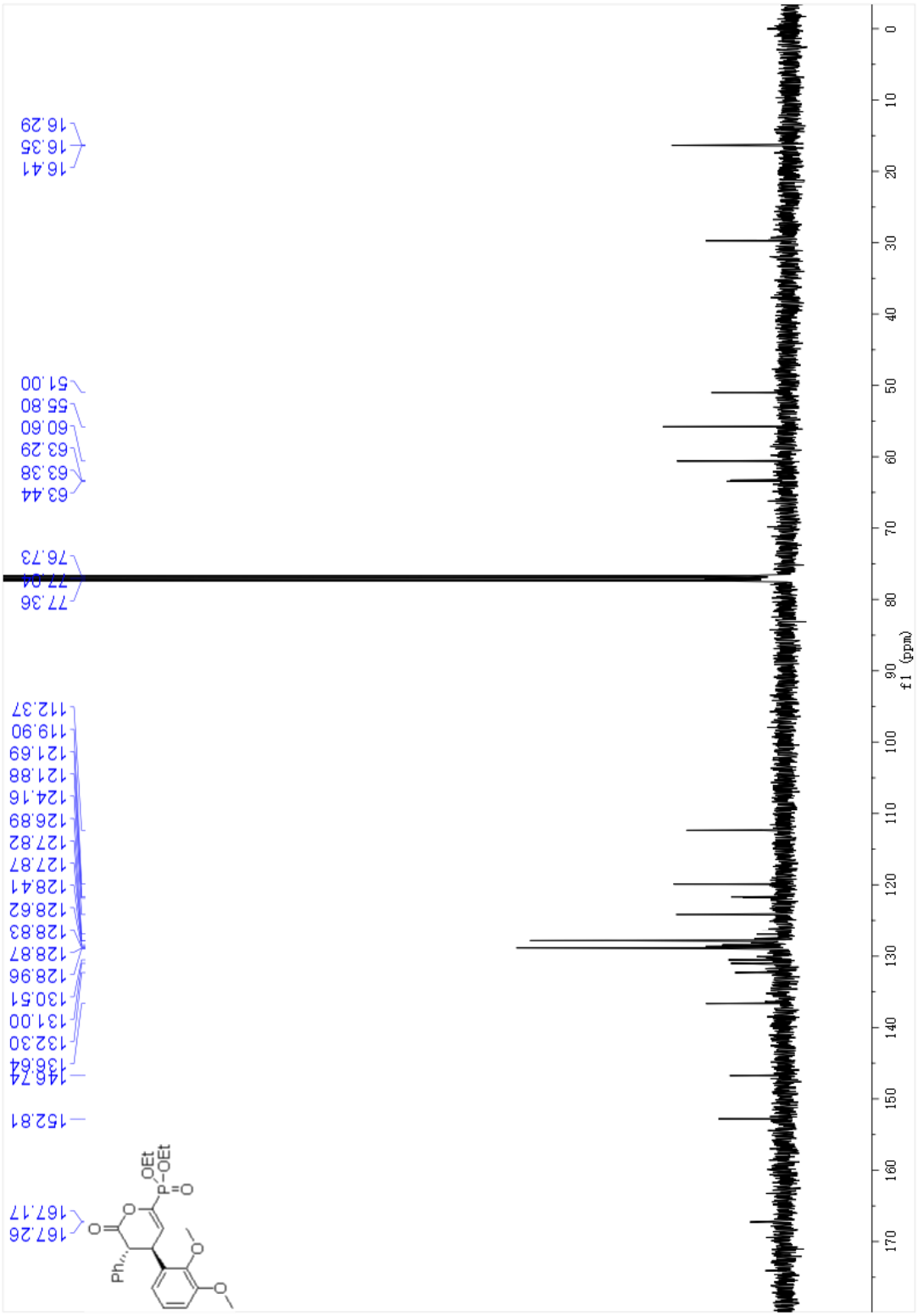
^{31}P NMR spectrum of product **3f**



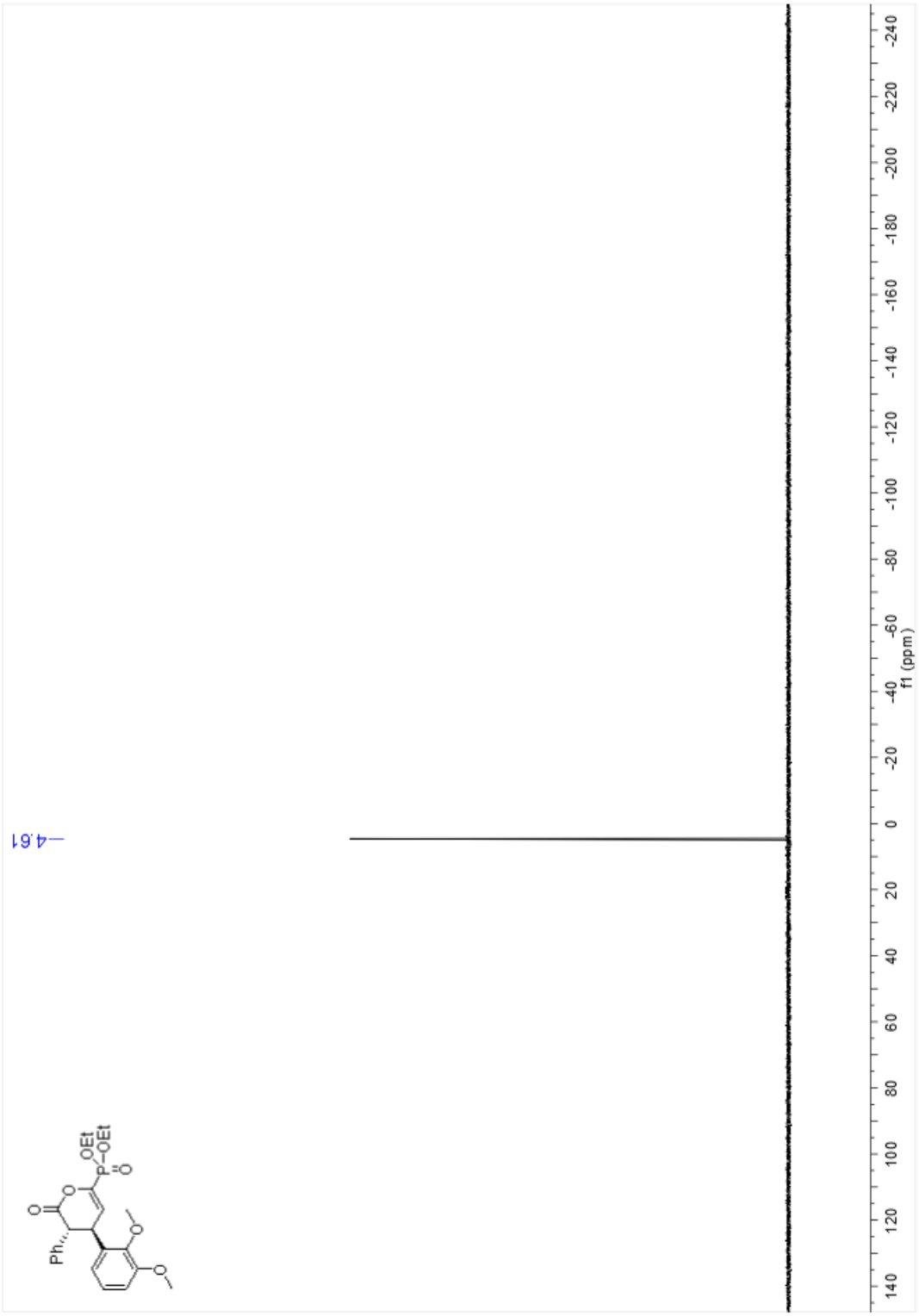
^{1}H NMR spectrum of product **3g**



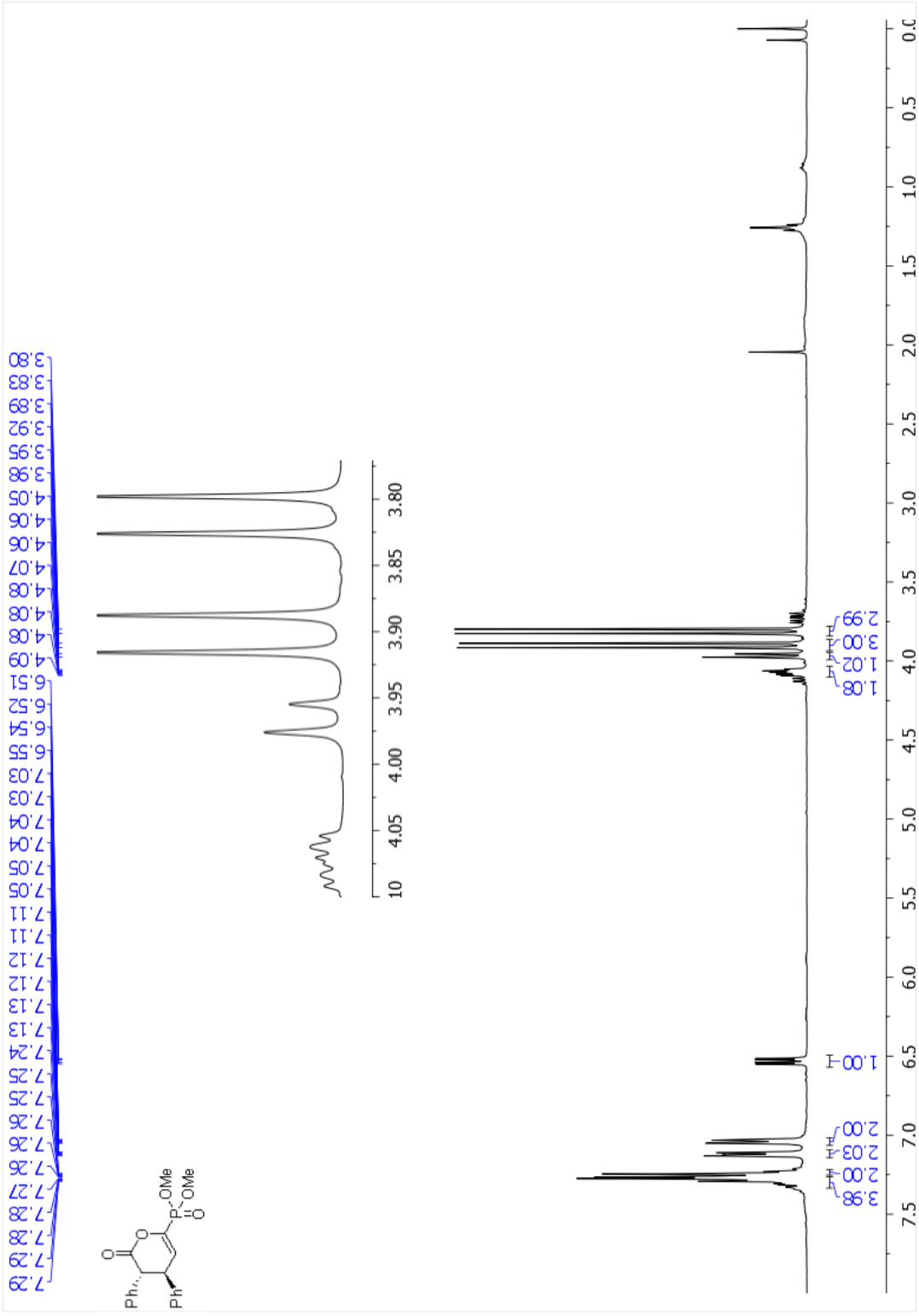
^{13}C NMR spectrum of product **3g**



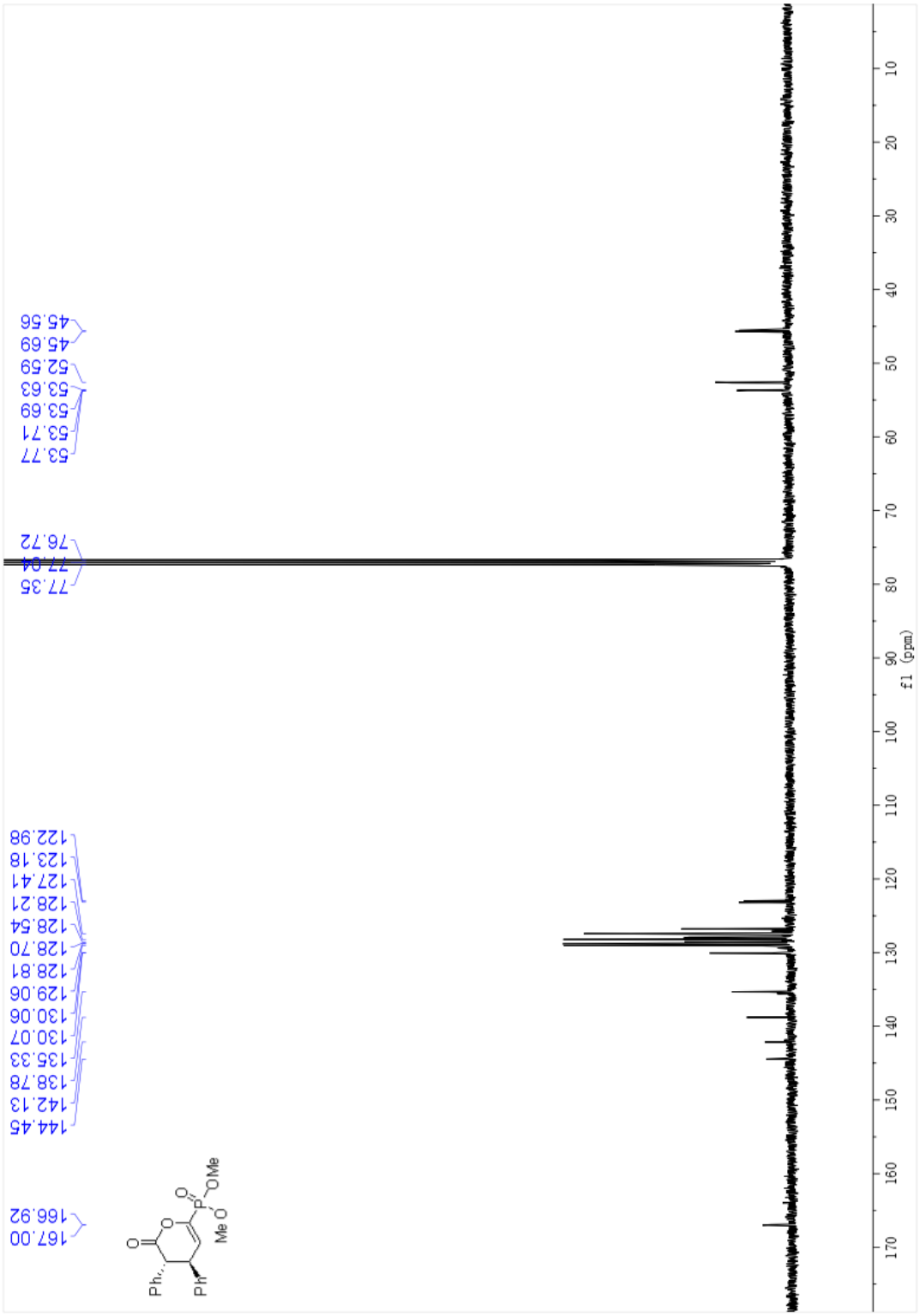
^{31}P NMR spectrum of product **3g**



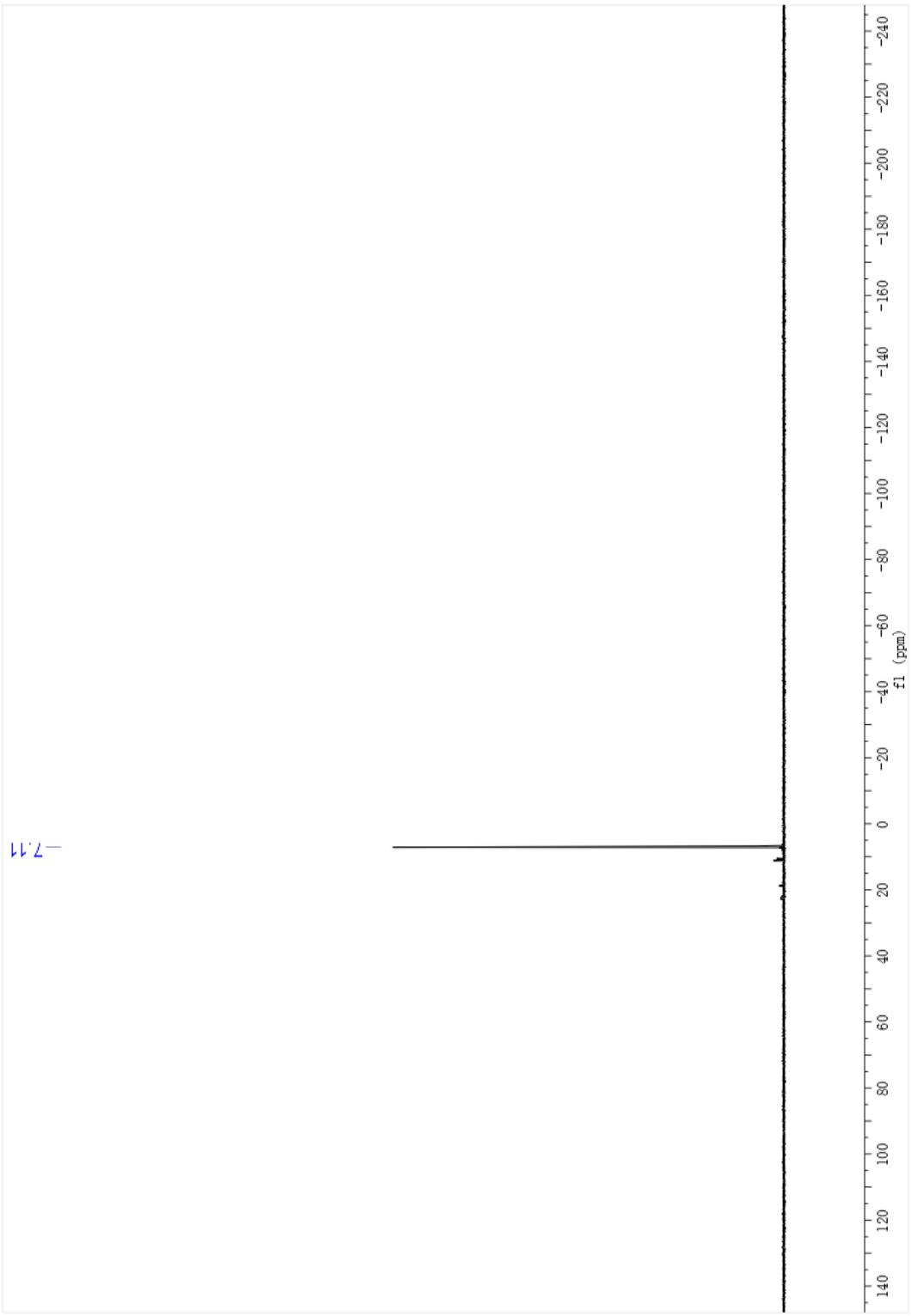
^{1}H NMR spectrum of product **3h**



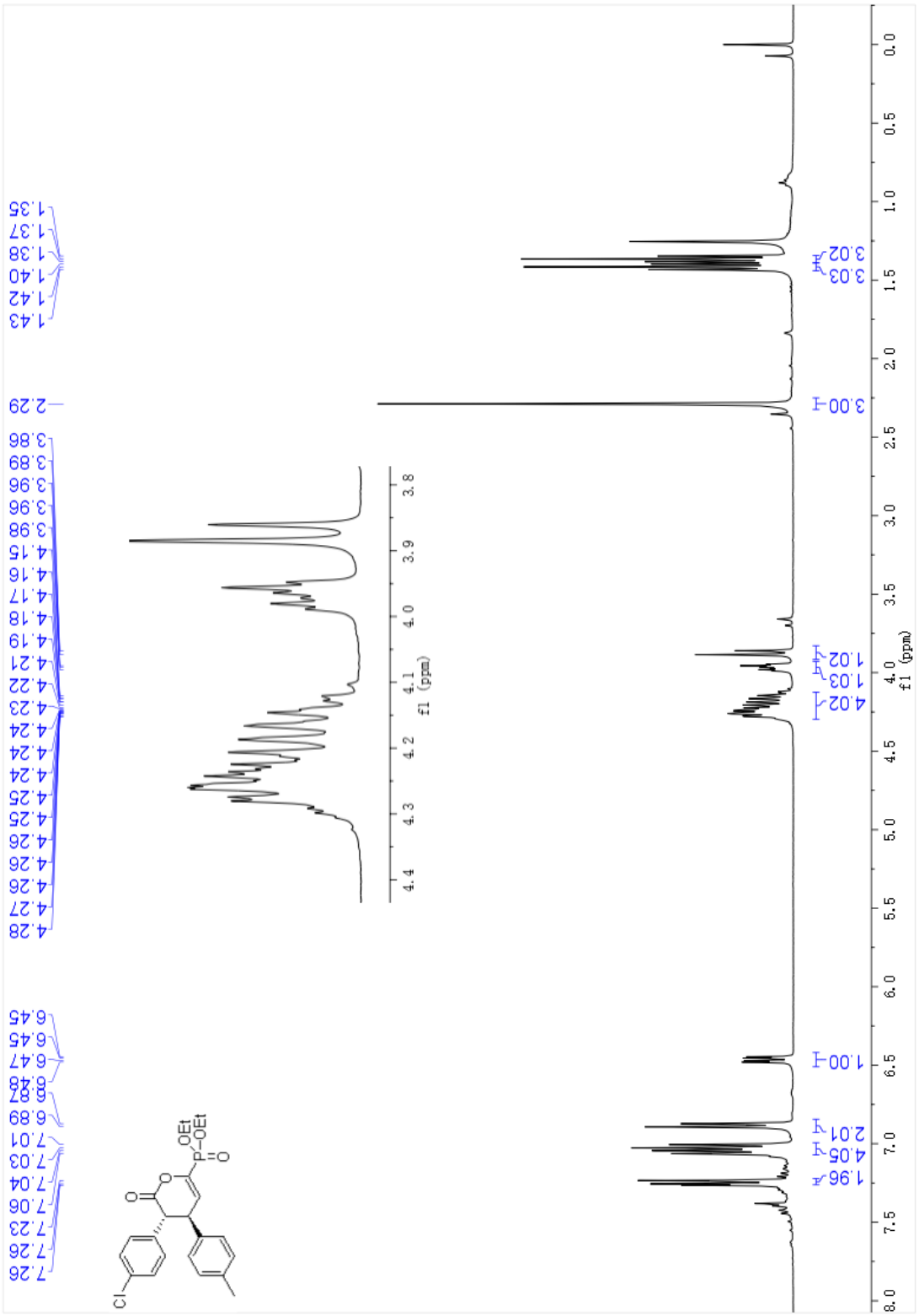
^{13}C NMR spectrum of product **3h**



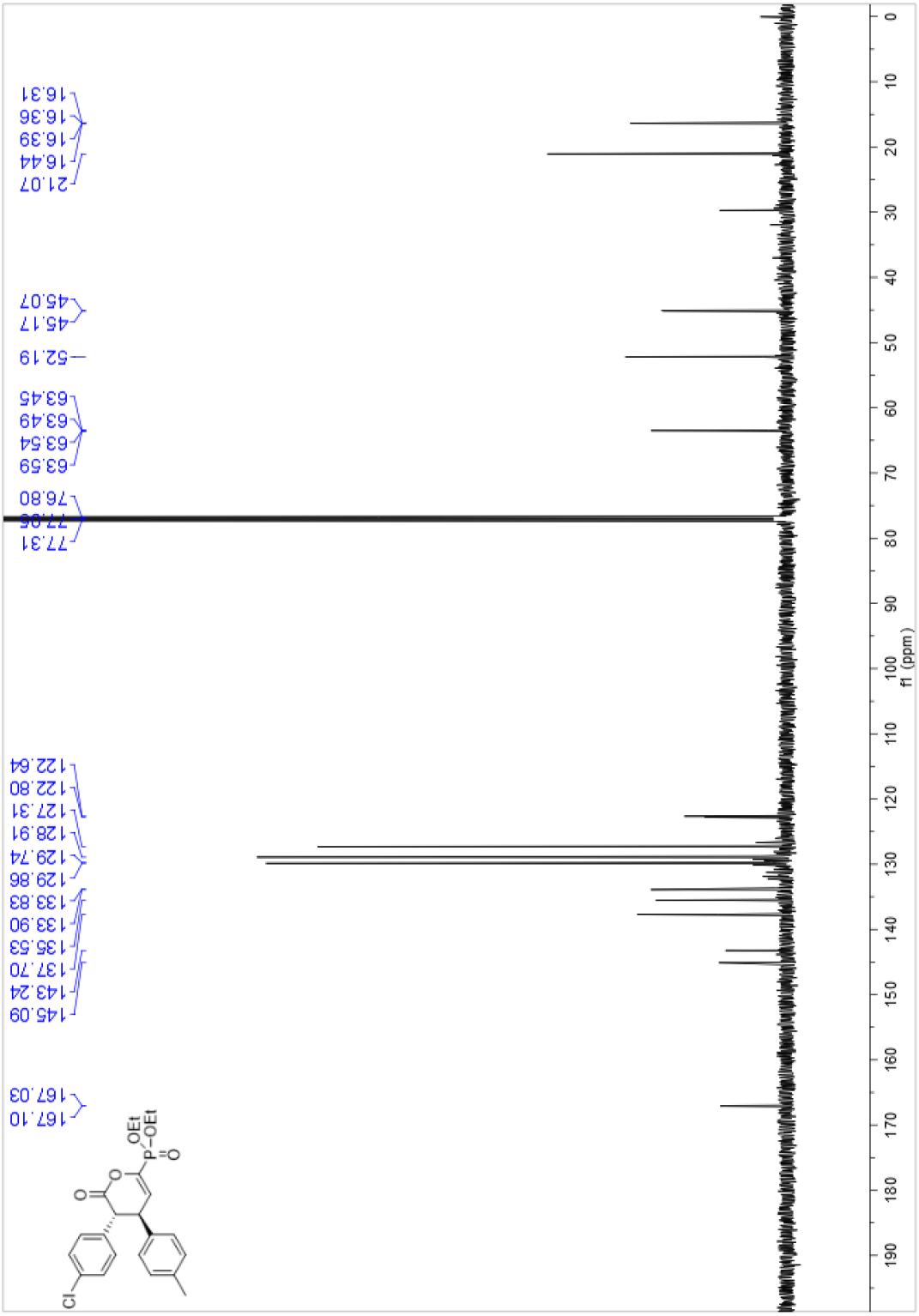
^{31}P NMR spectrum of product **3h**



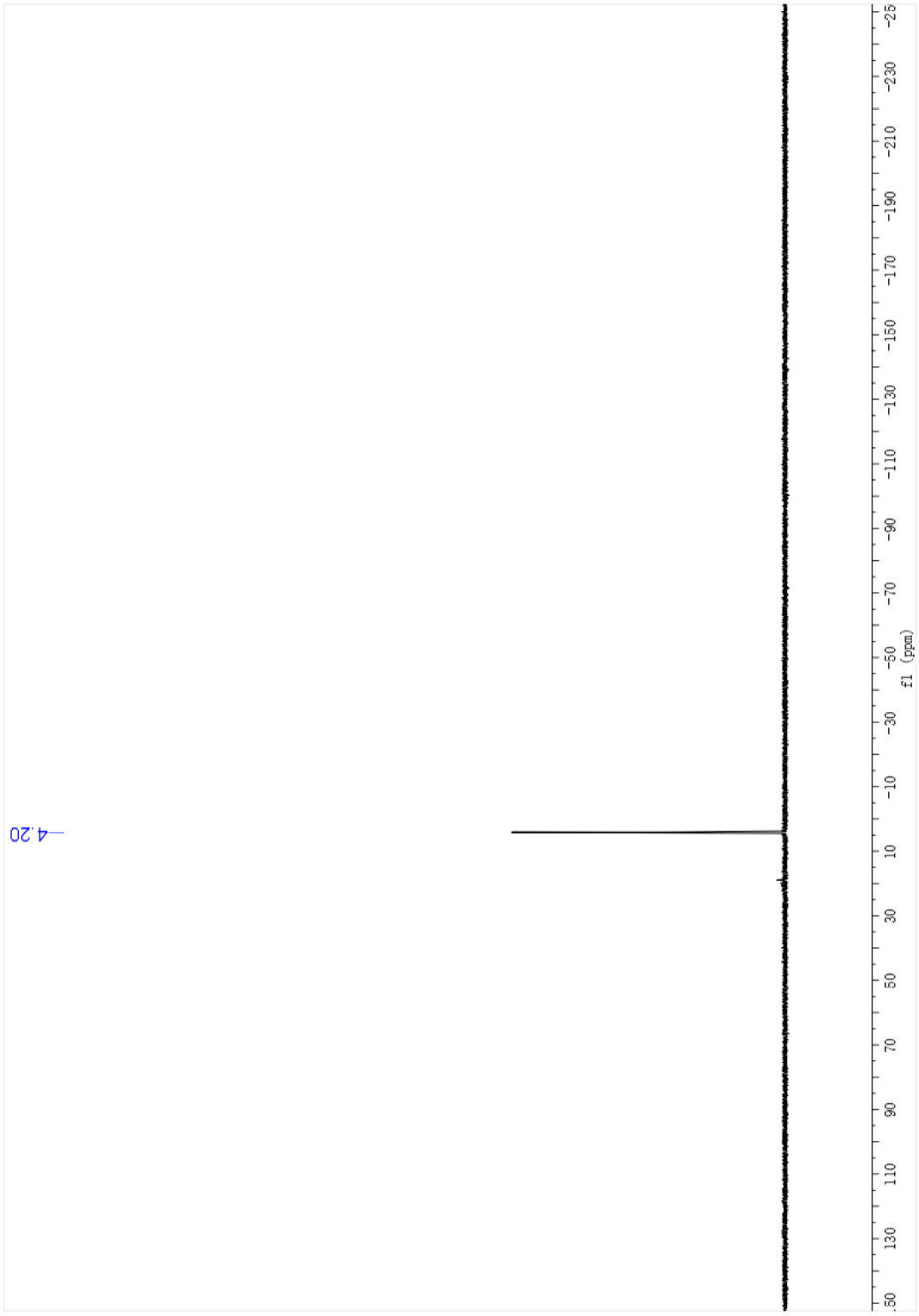
^{1}H NMR spectrum of product **3i**



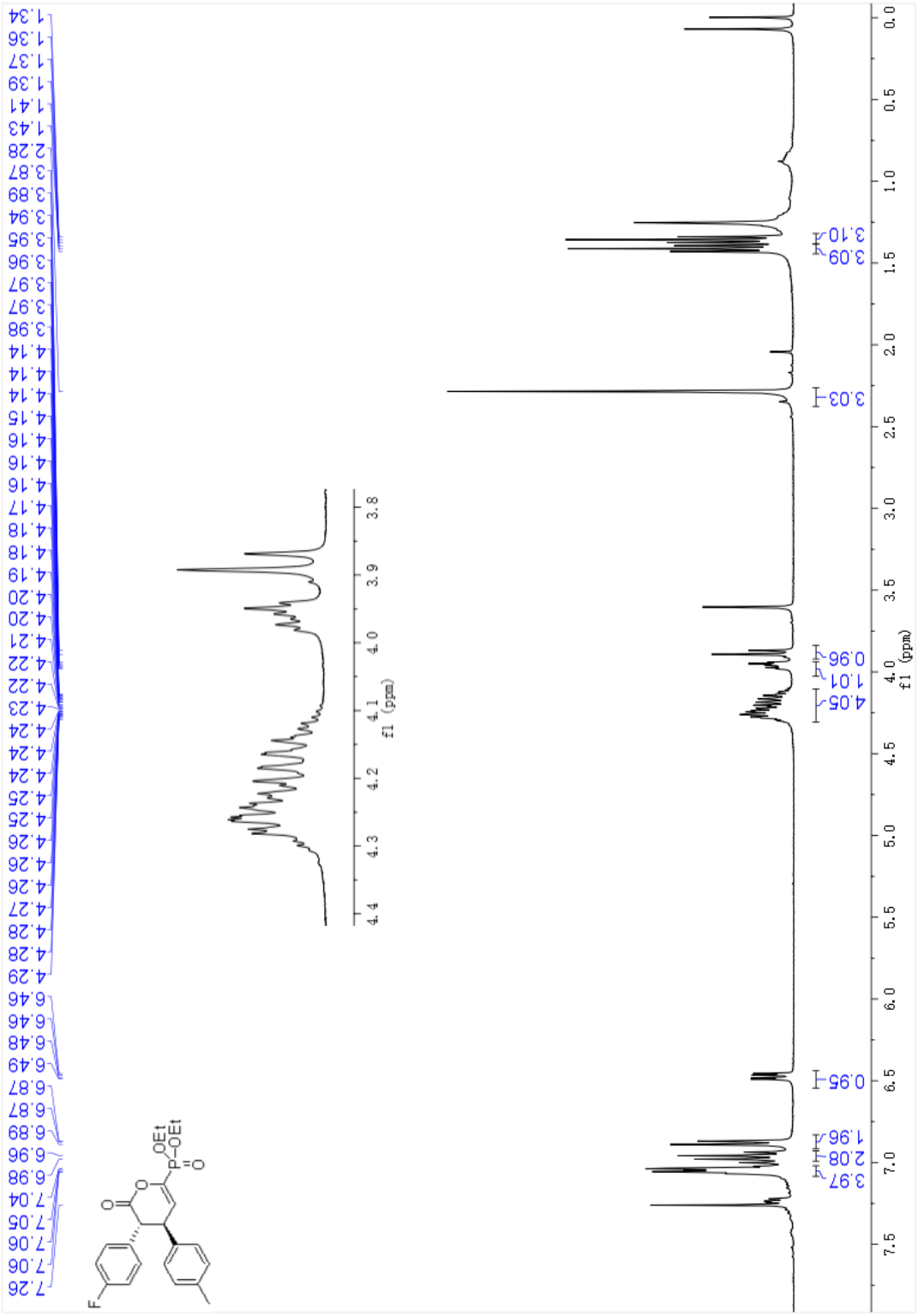
^{13}C NMR spectrum of product **3i**



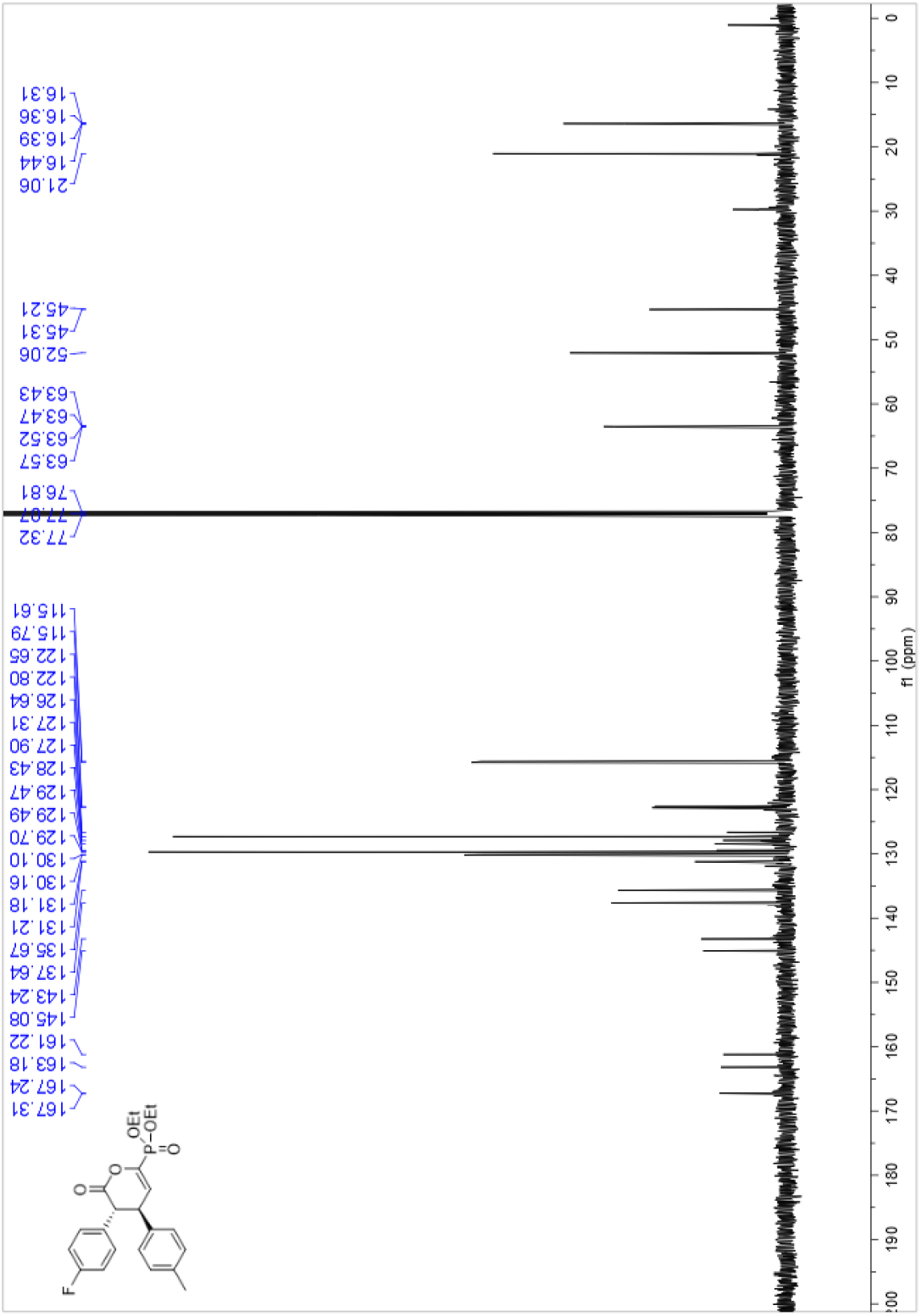
^{31}P NMR spectrum of product **3i**



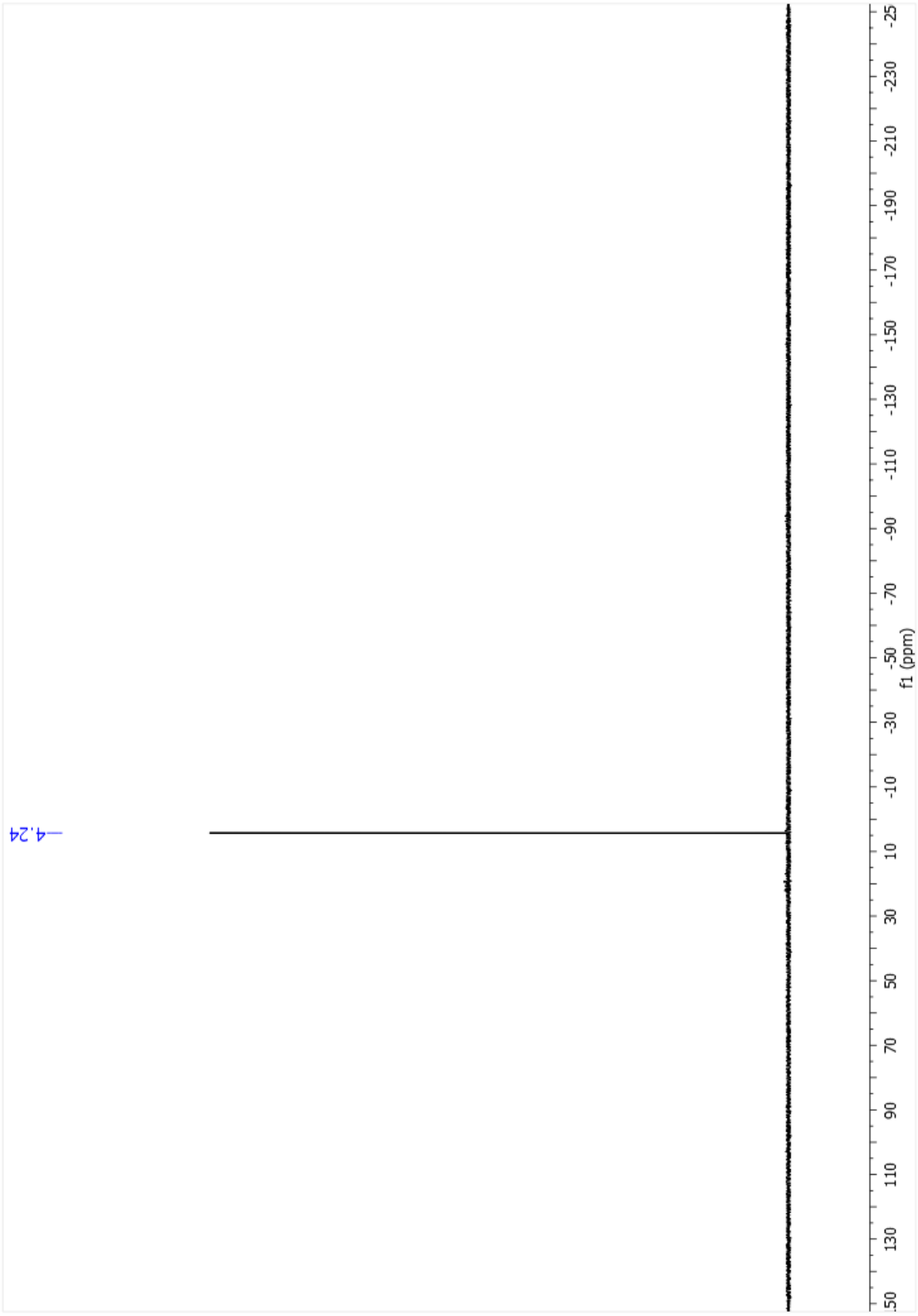
^{1}H NMR spectrum of product **3j**



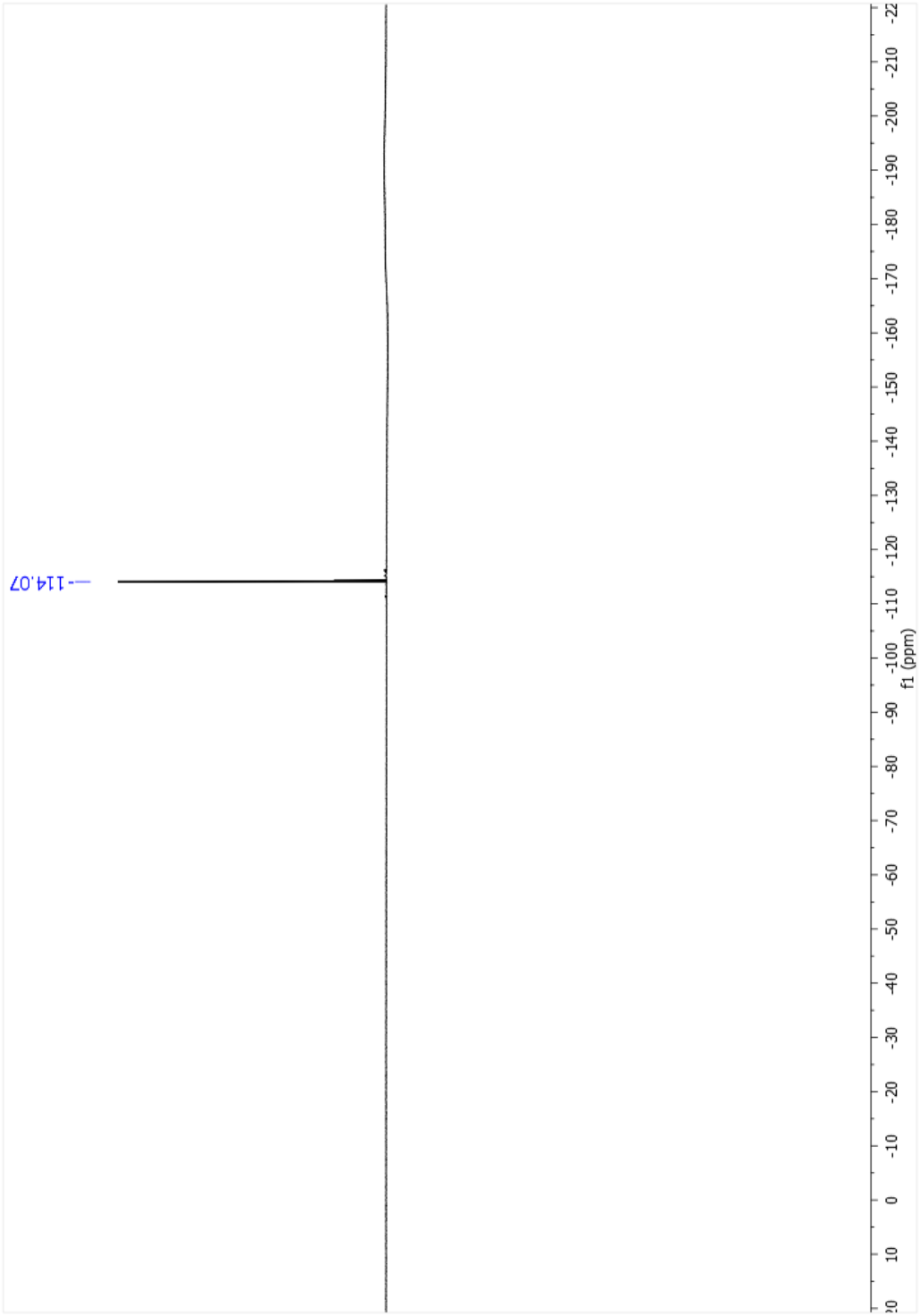
^{13}C NMR spectrum of product **3j**



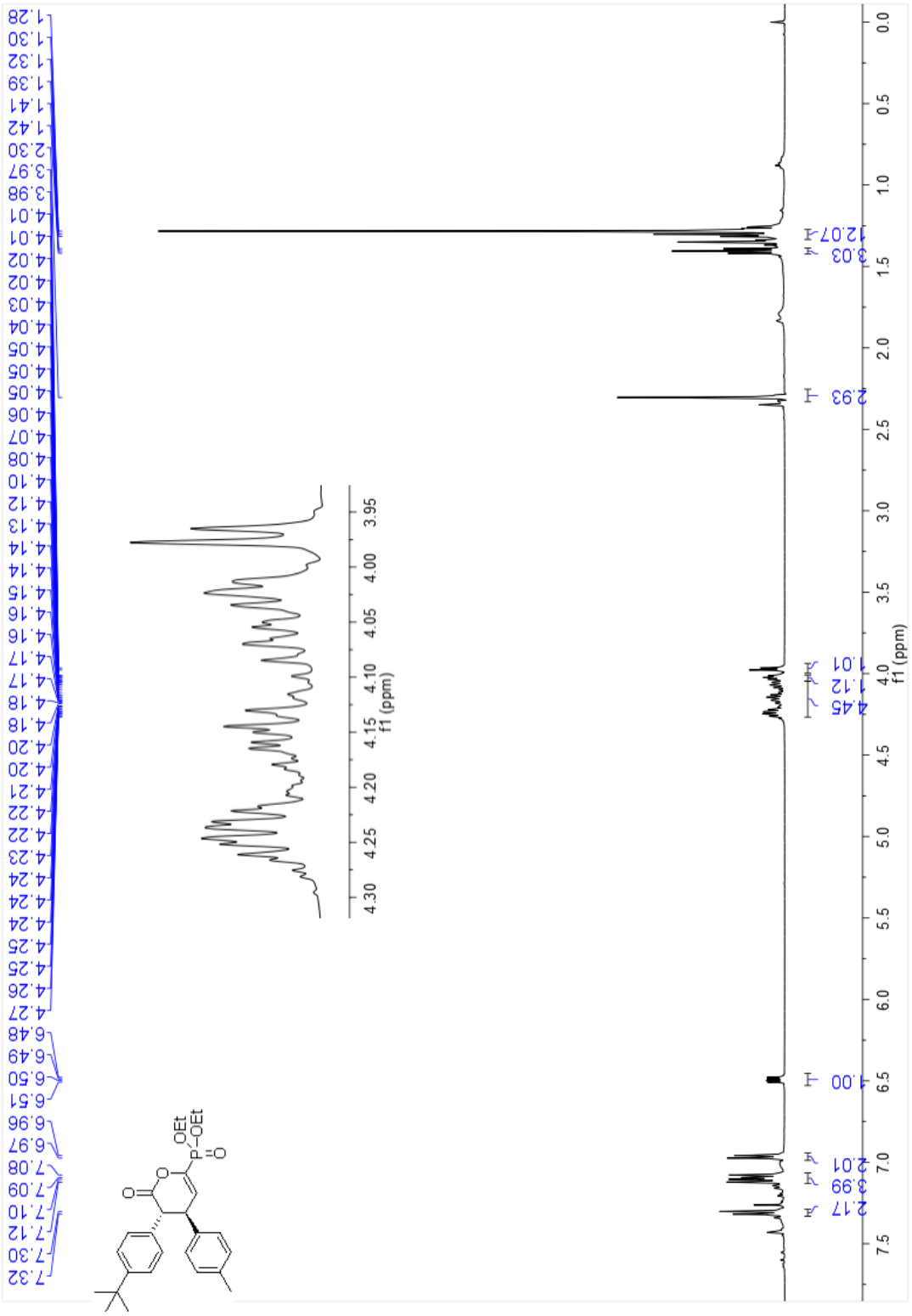
^{31}P NMR spectrum of product **3j**



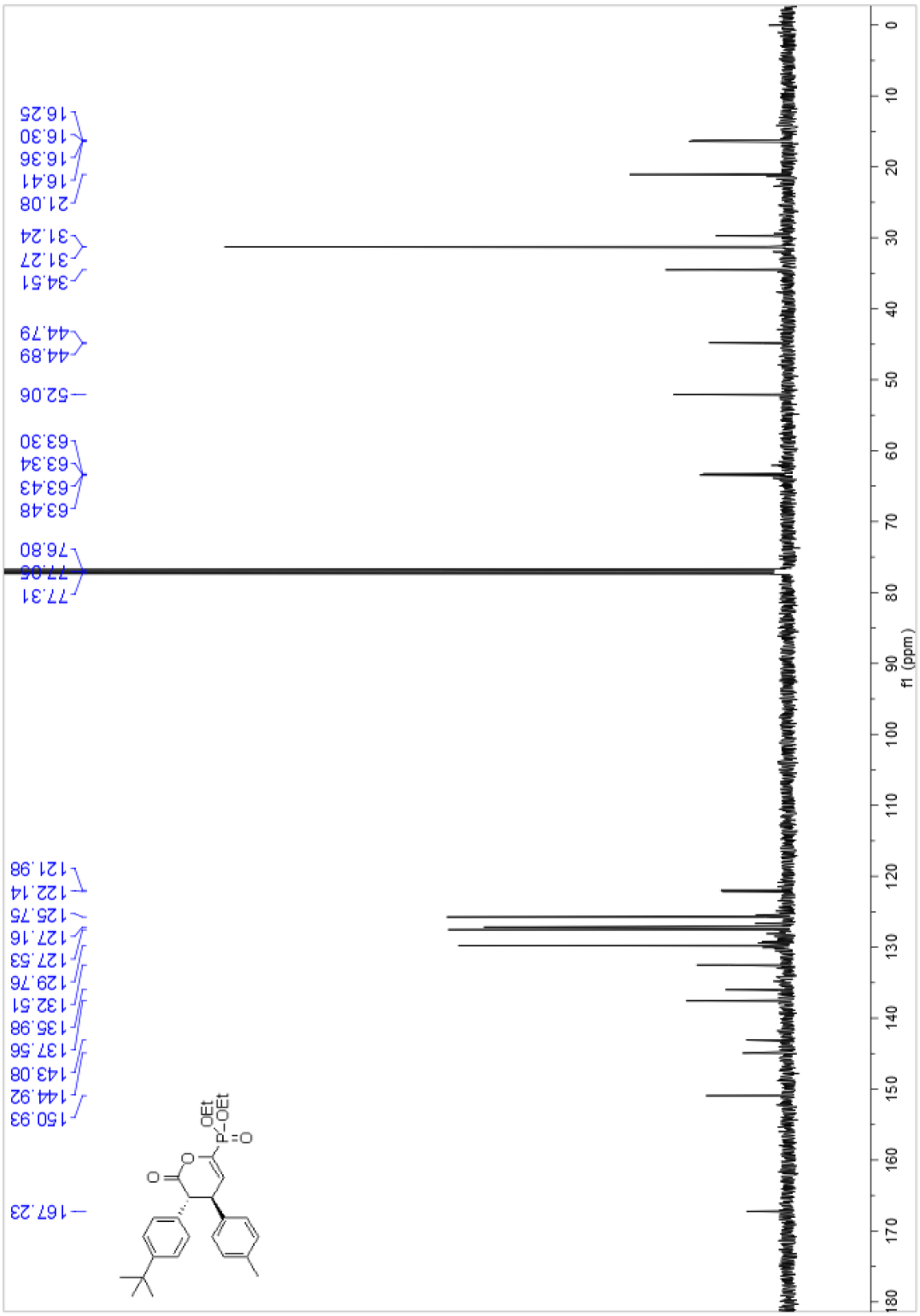
^{19}F NMR spectrum of product **3j**



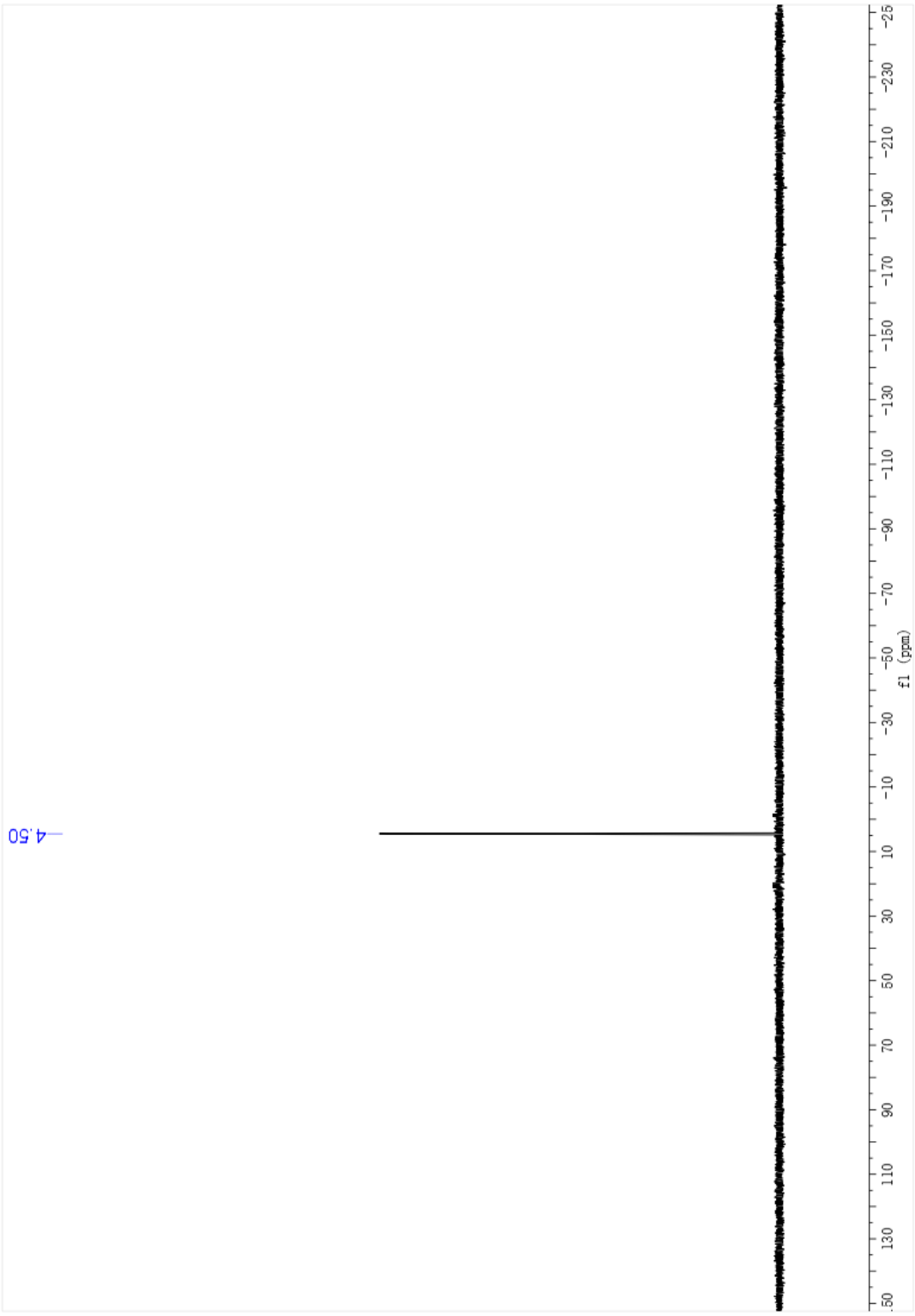
^{1}H NMR spectrum of product **3k**



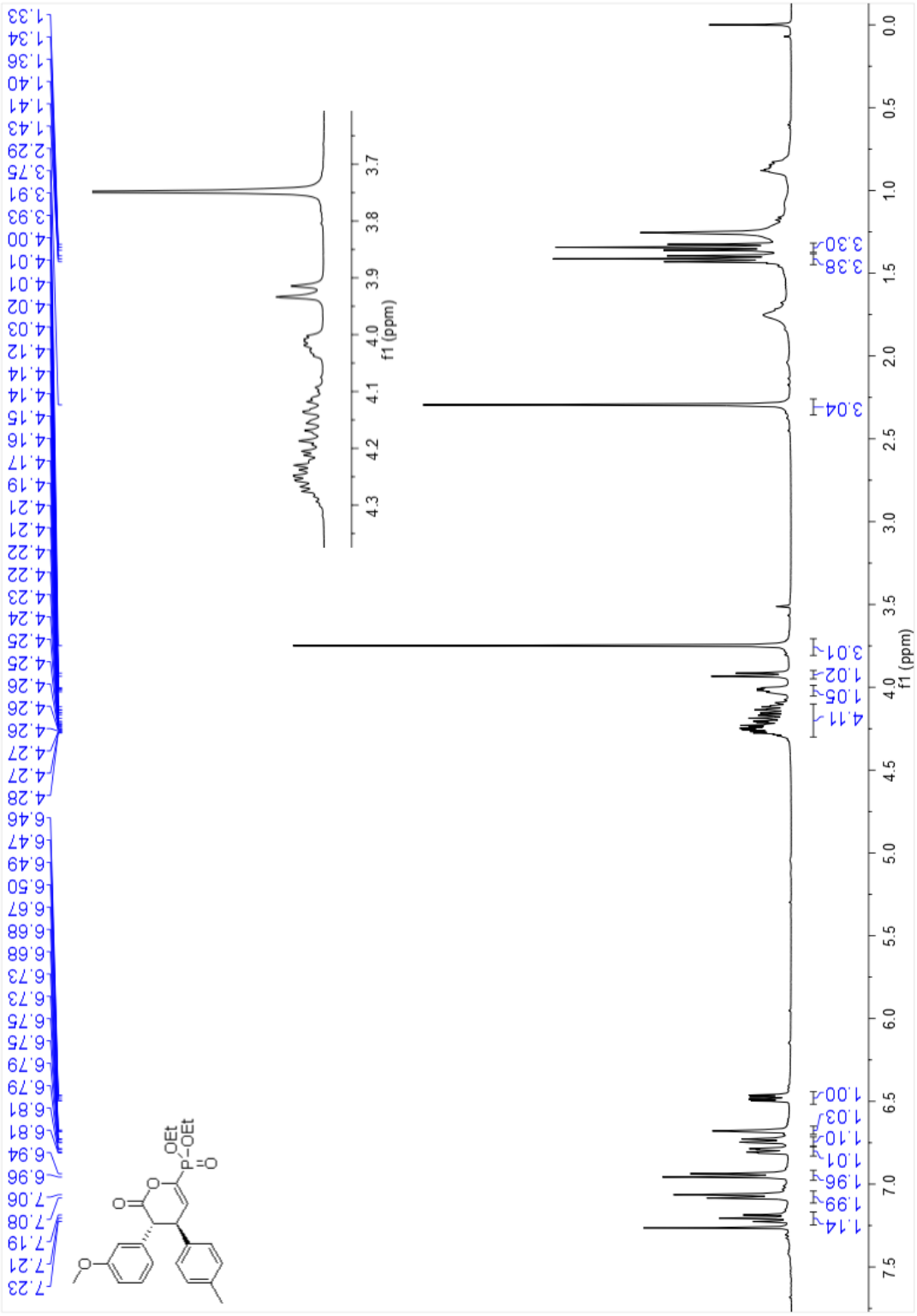
^{13}C NMR spectrum of product **3k**



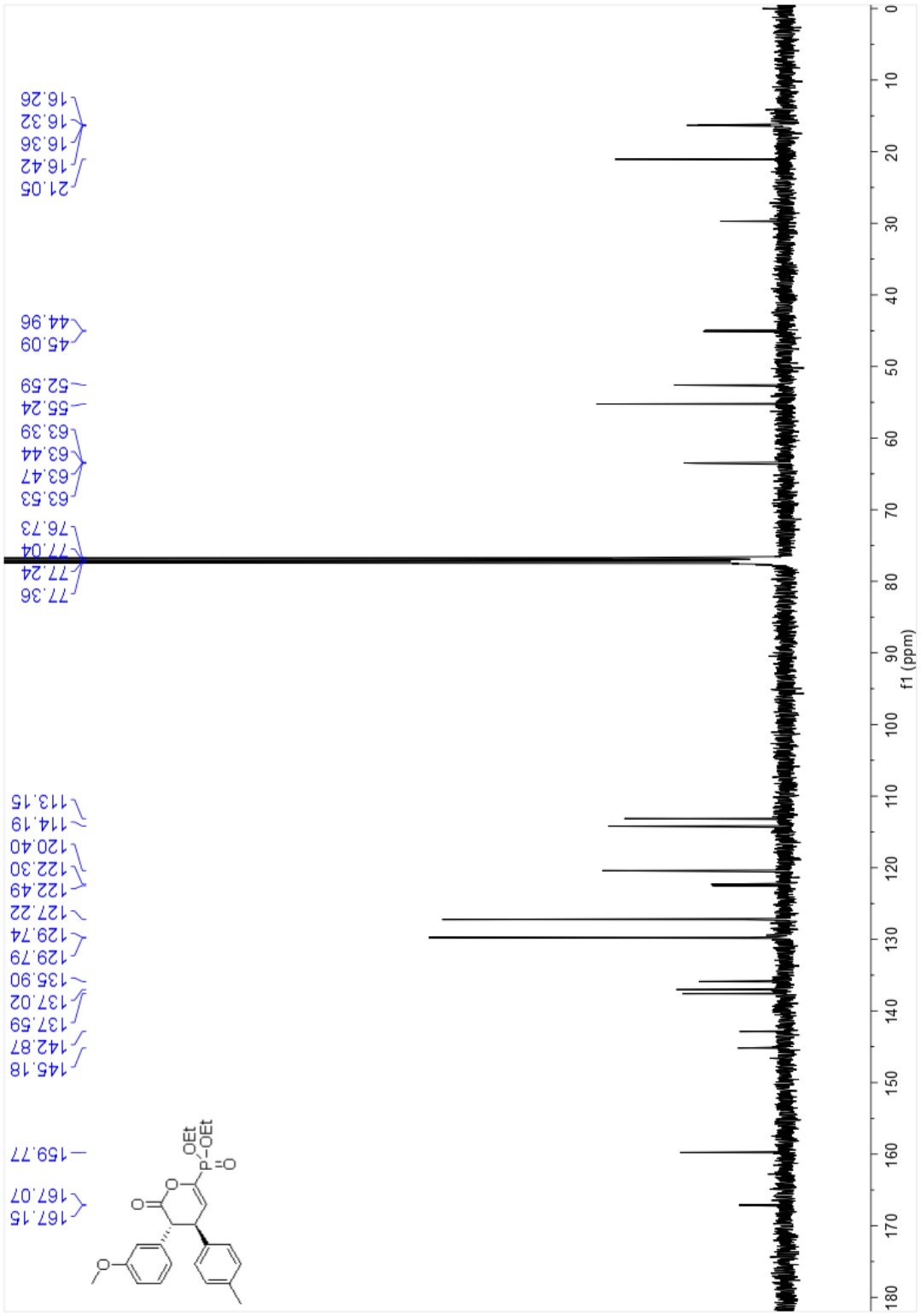
^{31}P NMR spectrum of product **3k**



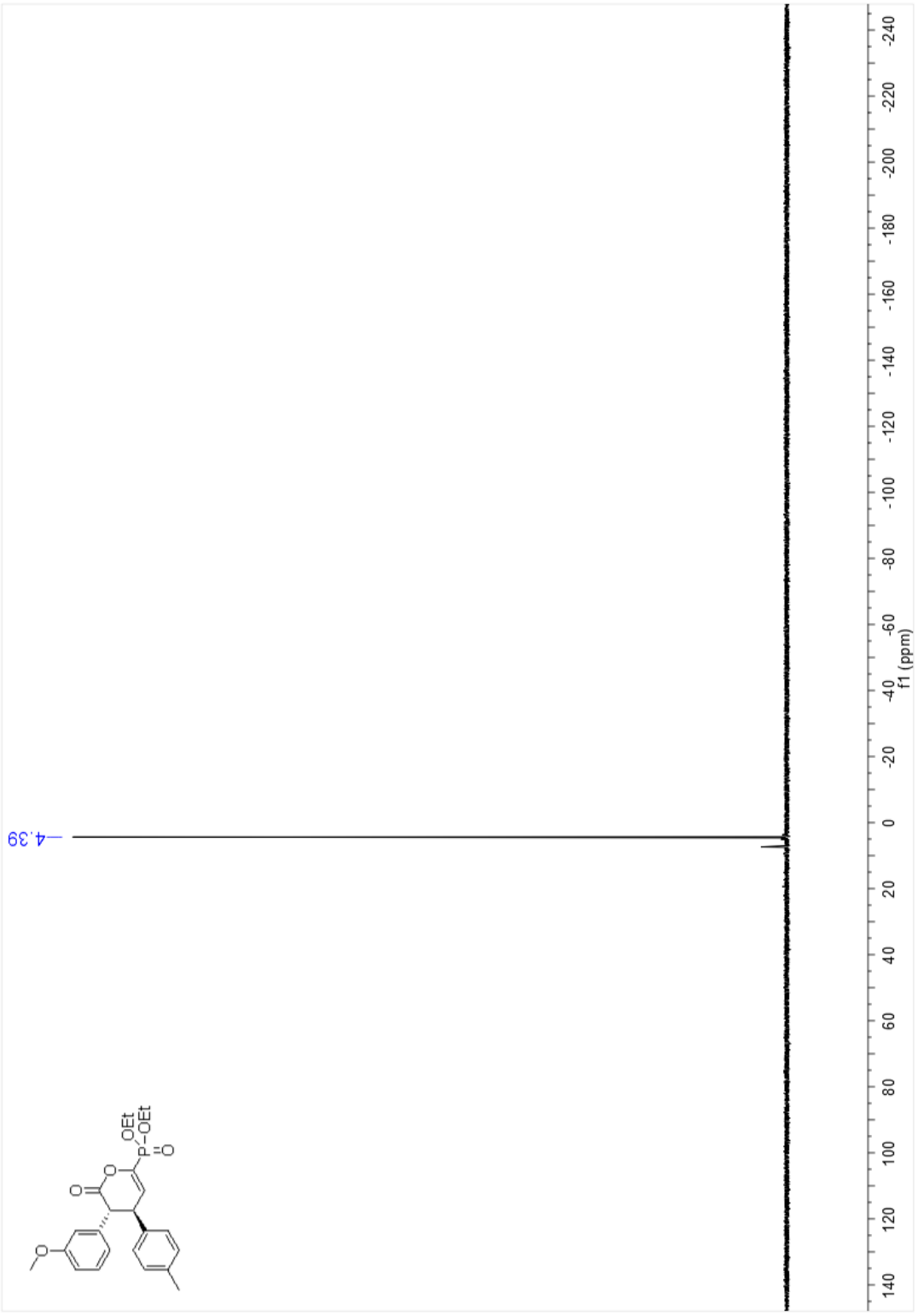
^{1}H NMR spectrum of product **3l**



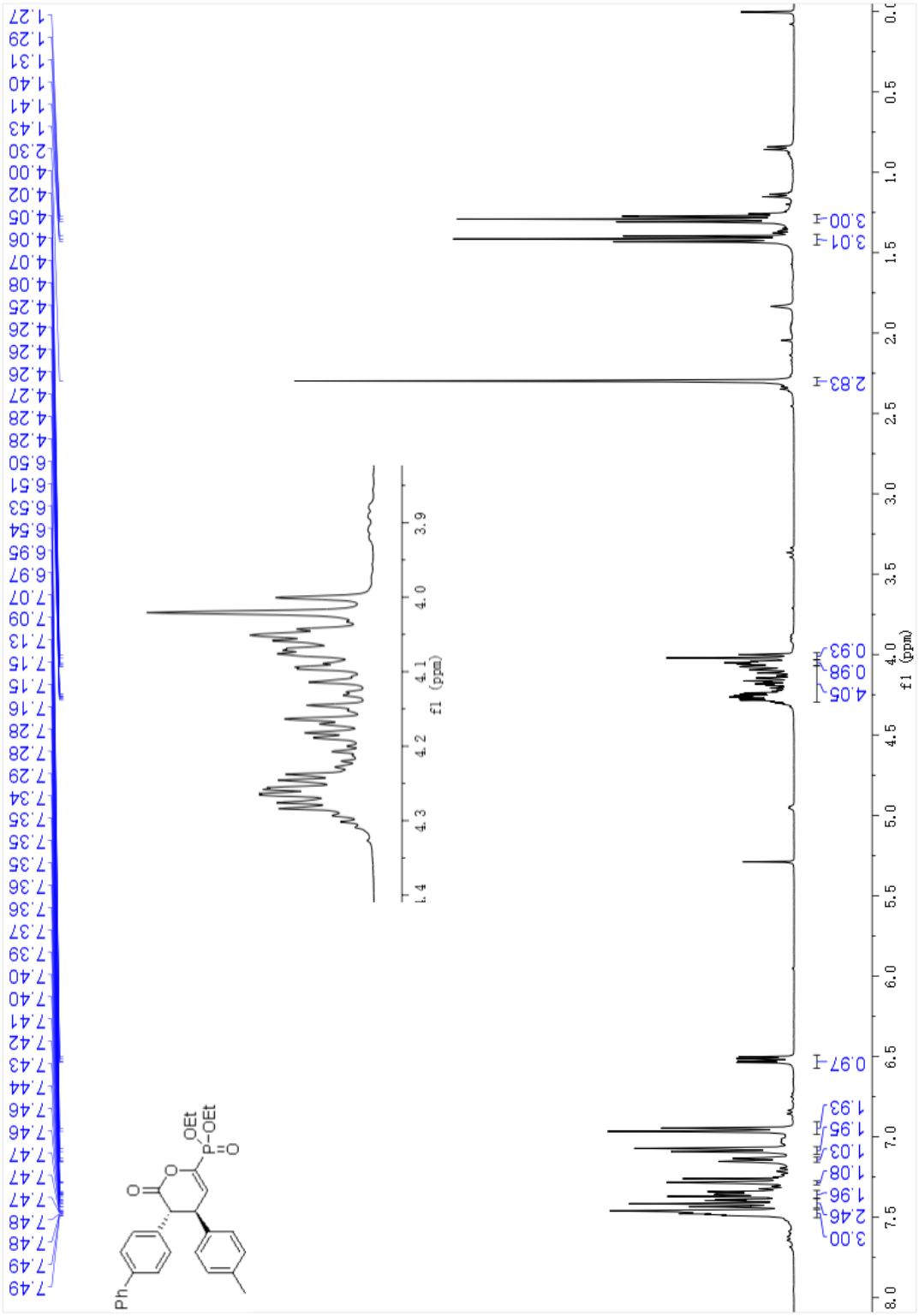
^{13}C NMR spectrum of product **3l**



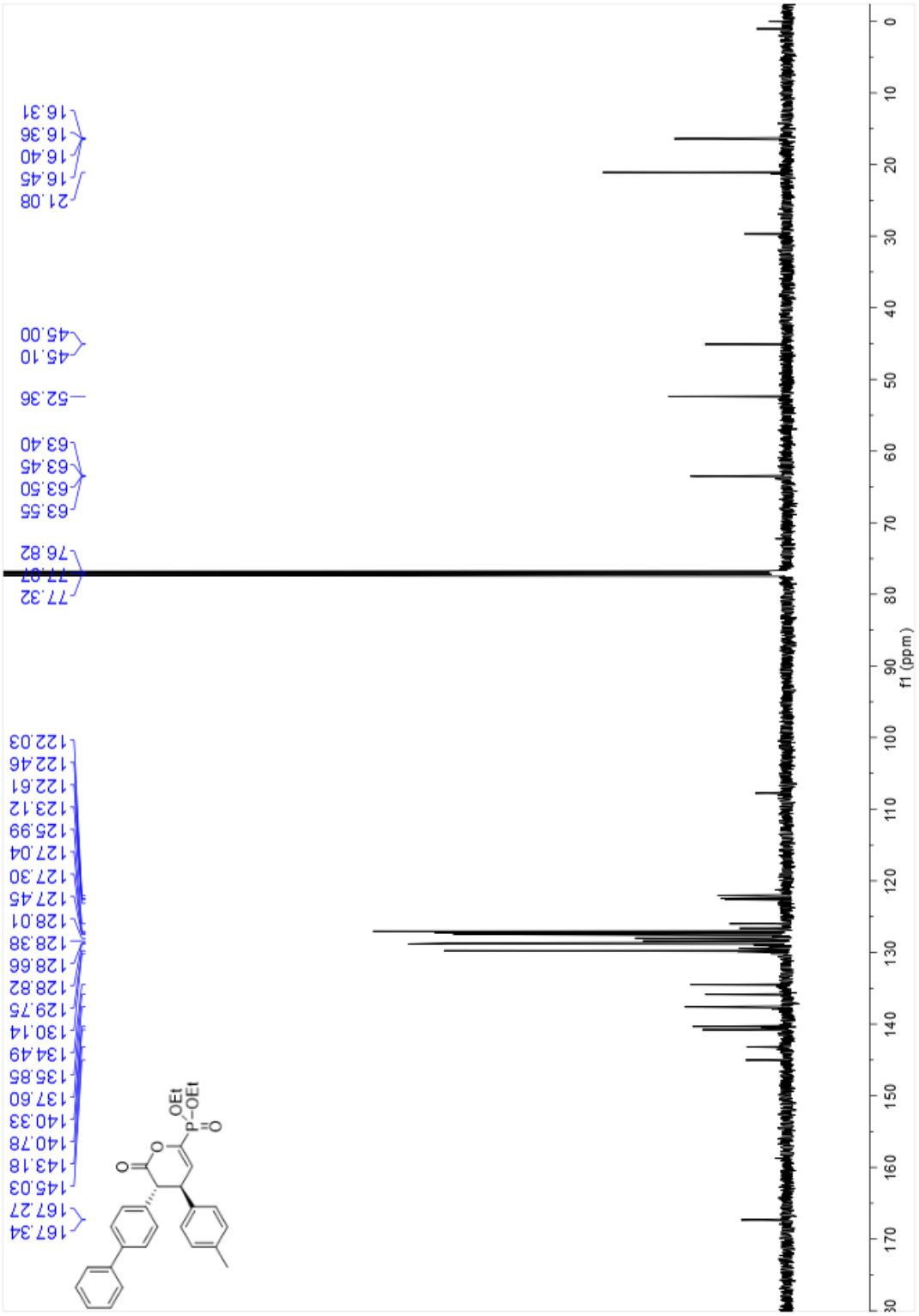
^{31}P NMR spectrum of product **3l**



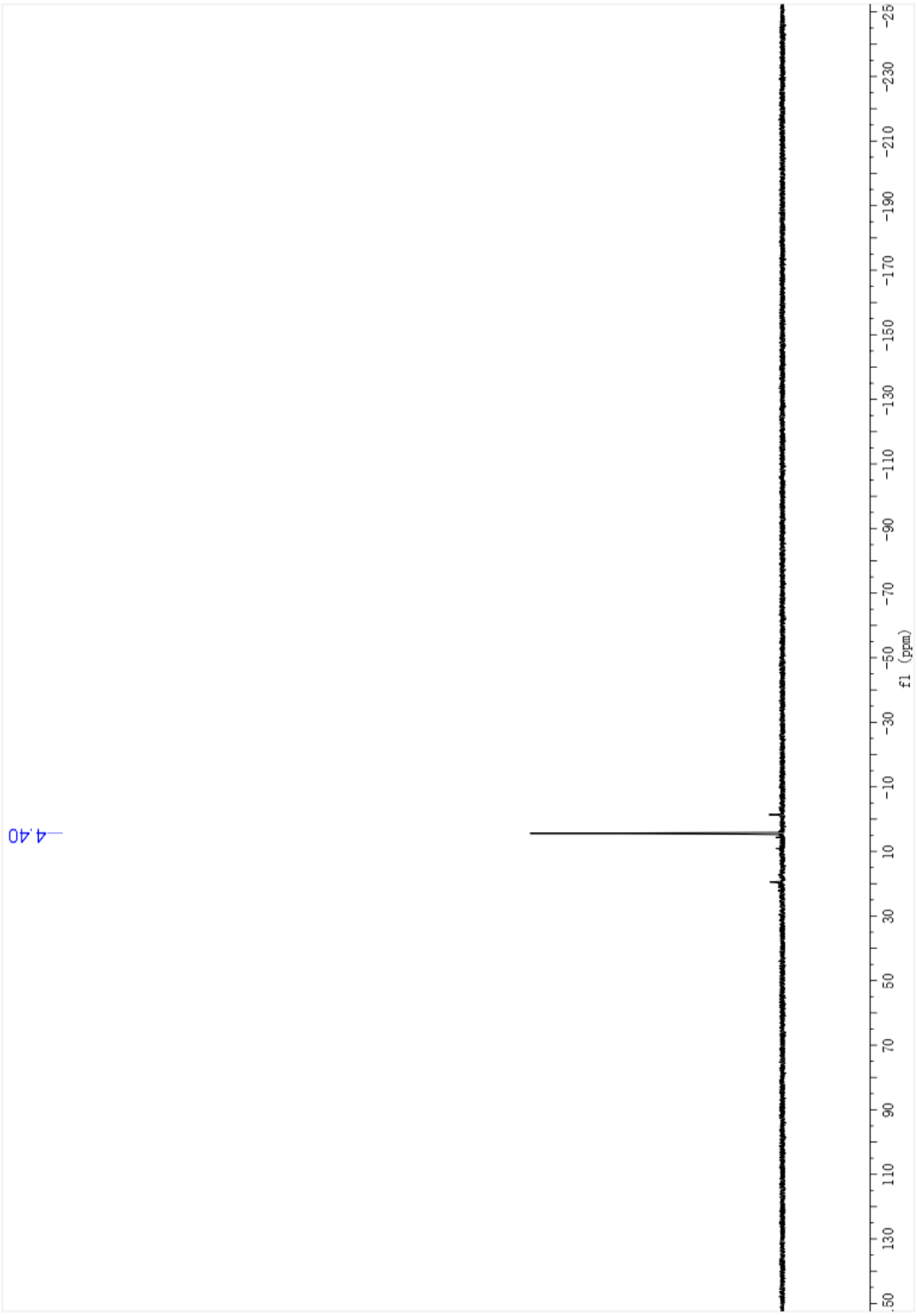
^{1}H NMR spectrum of product **3m**



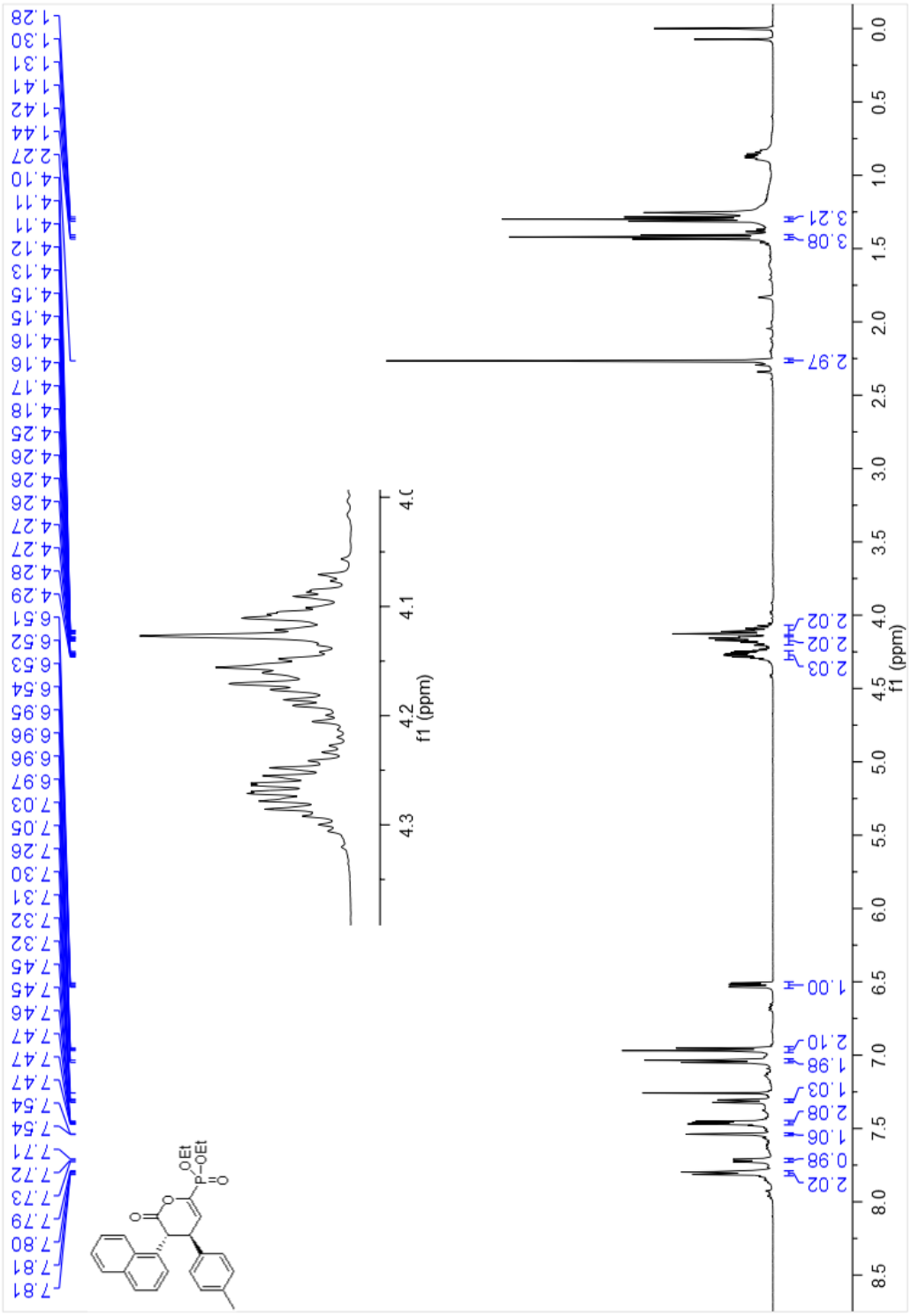
^{13}C NMR spectrum of product **3m**



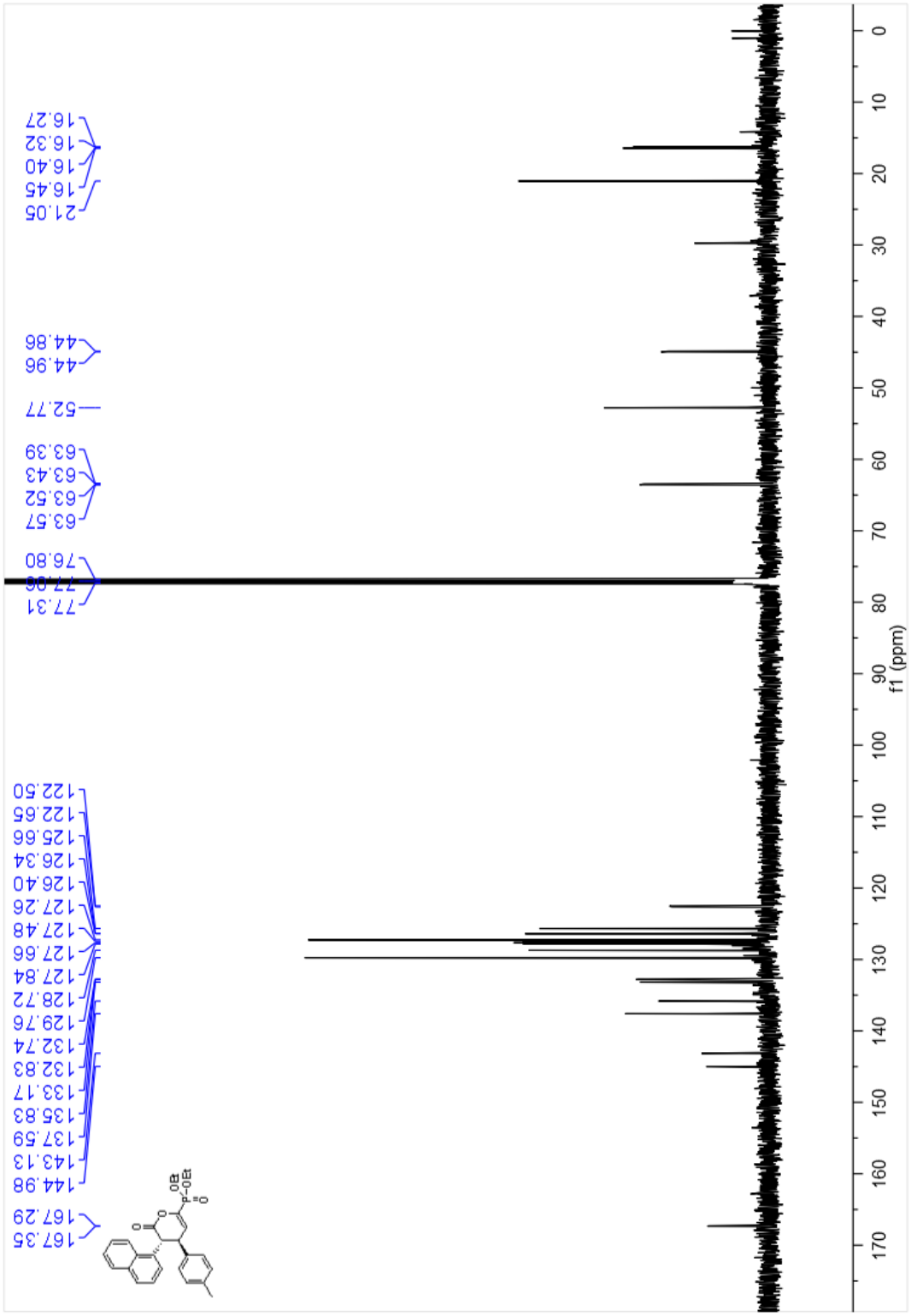
^{31}P NMR spectrum of product **3m**



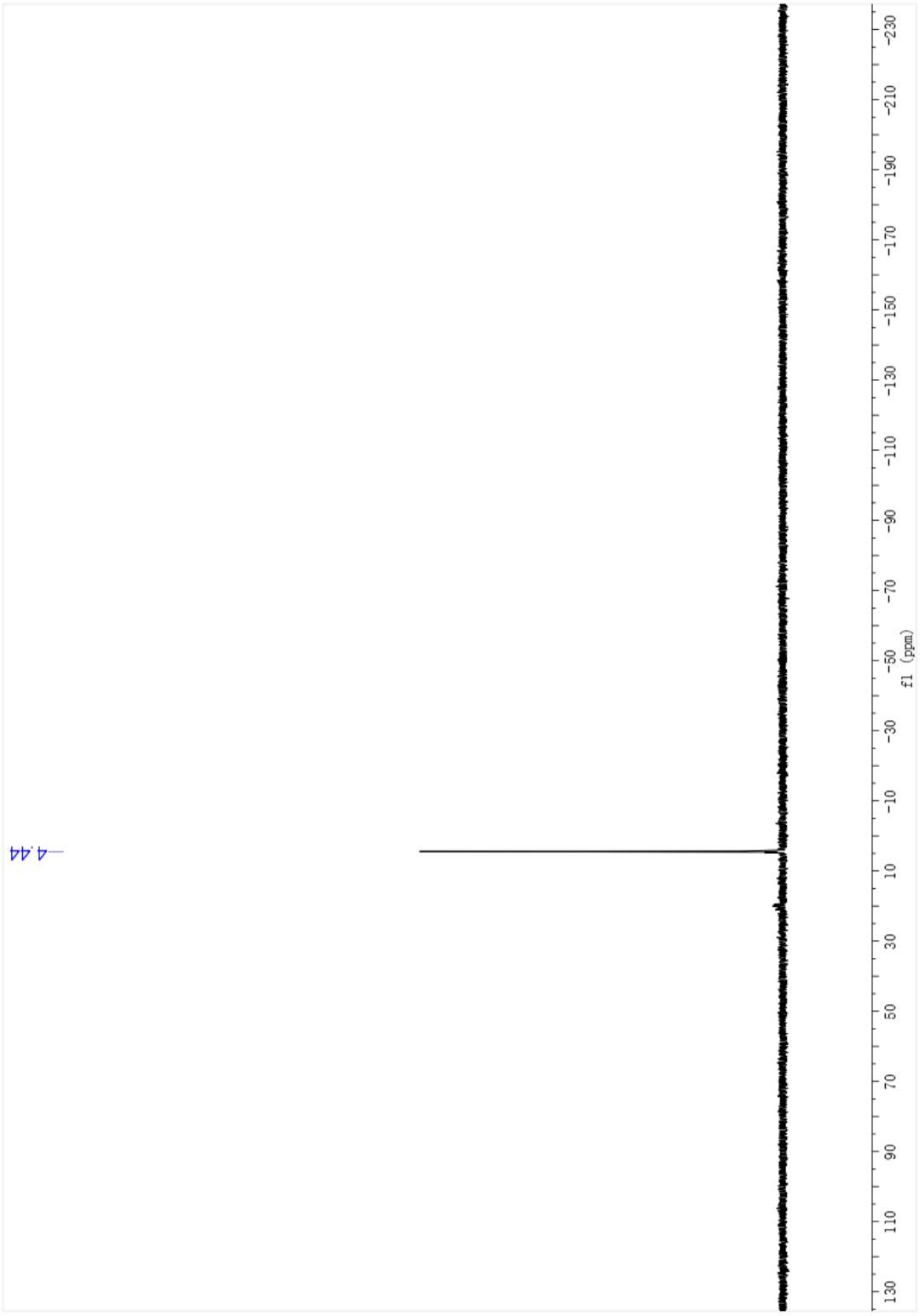
^{1}H NMR spectrum of product **3n**



^{13}C NMR spectrum of product **3n**

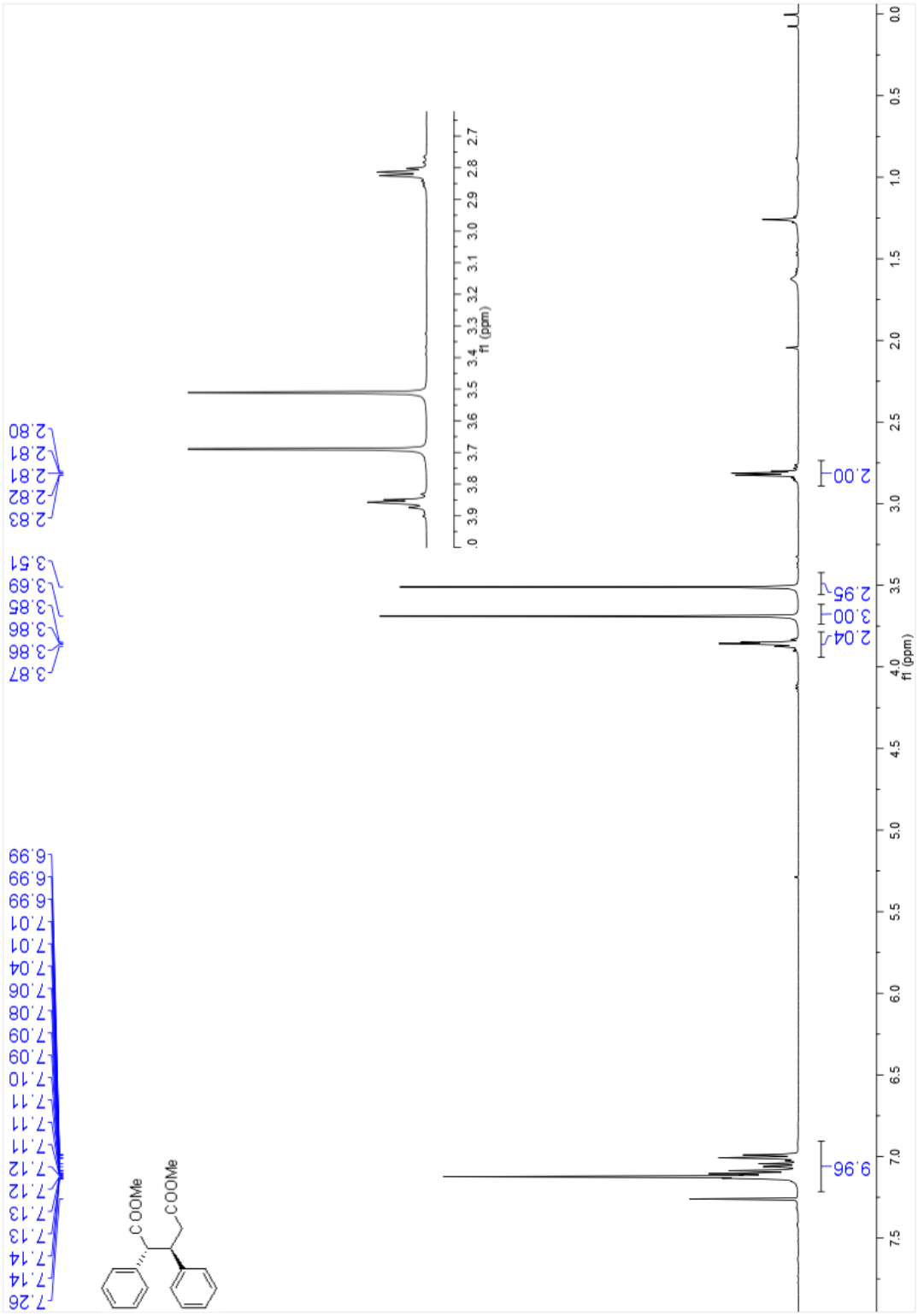


^{31}P NMR spectrum of product **3n**

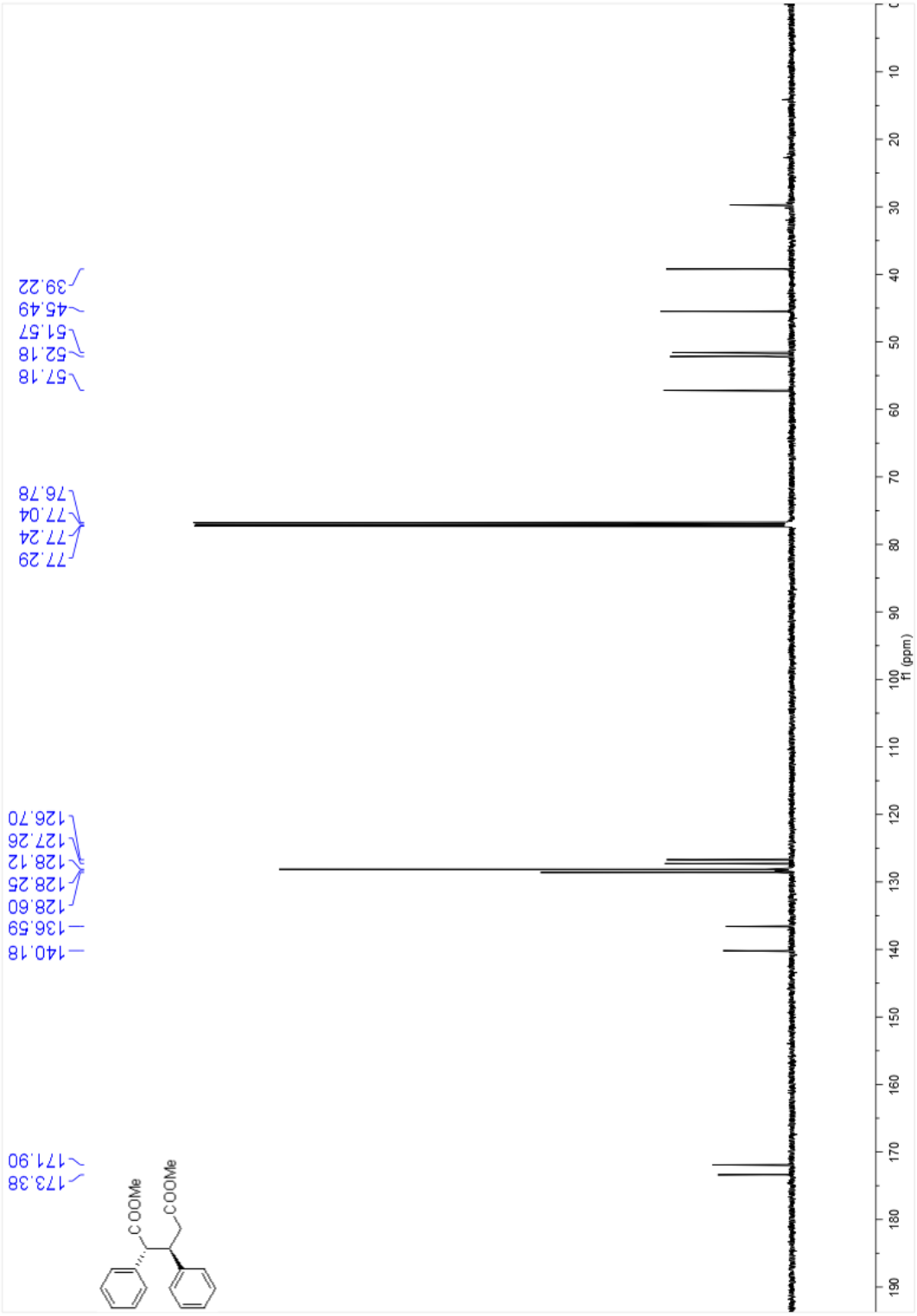


NMR Spectra of products 5a-5h

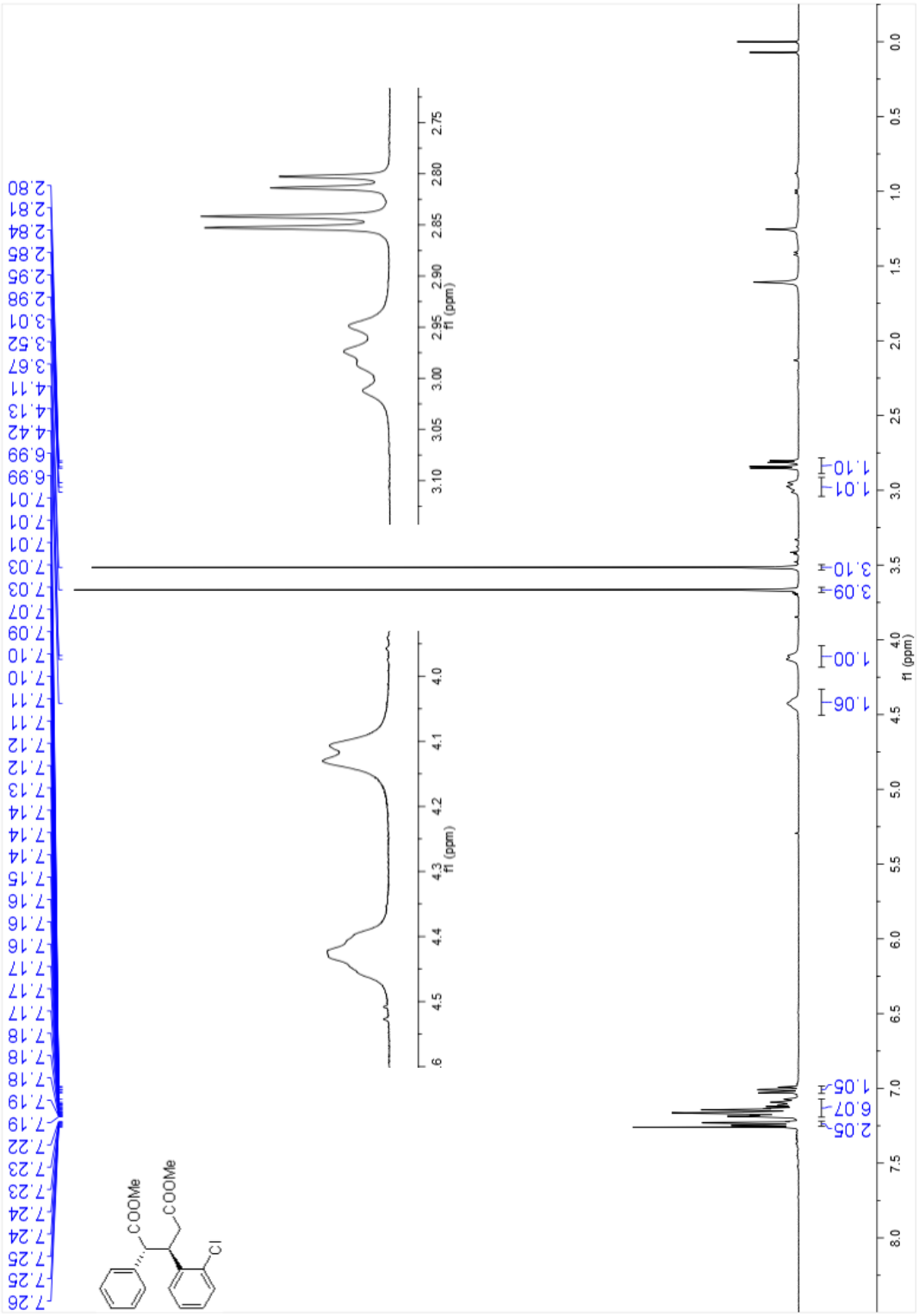
^{1}H NMR spectrum of product **4a**



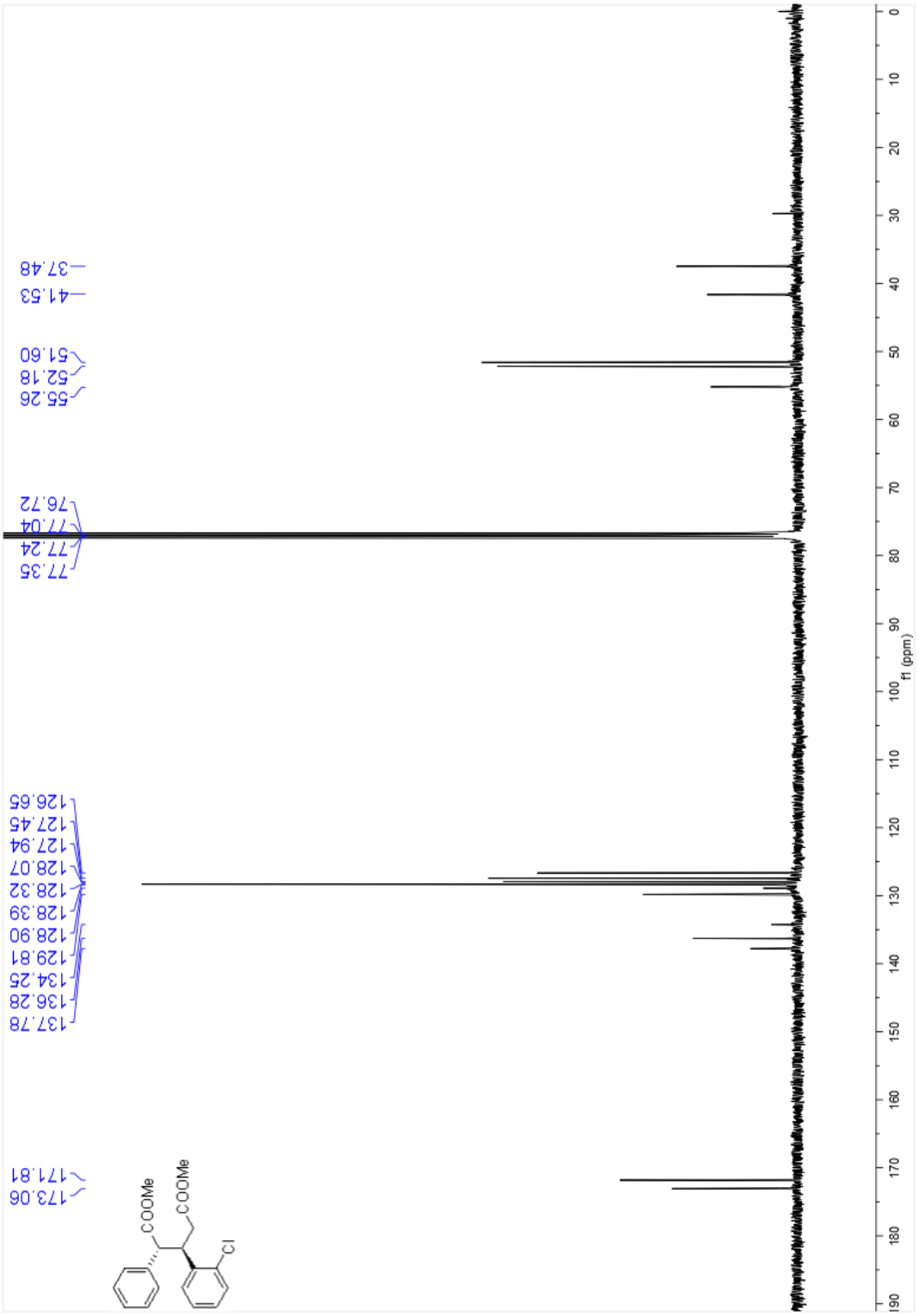
^{13}C NMR spectrum of product **4a**



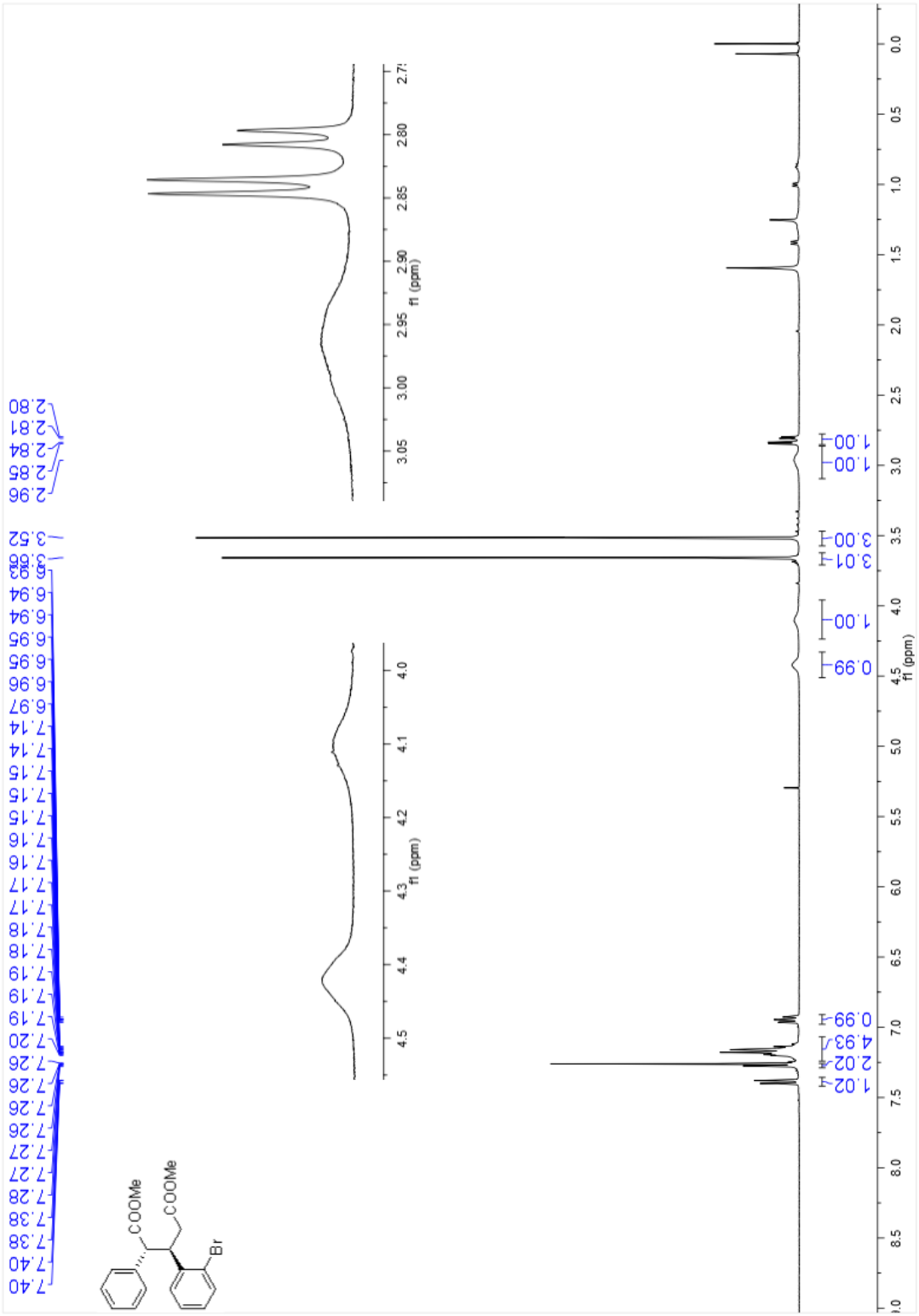
^{1}H NMR spectrum of product **4b**



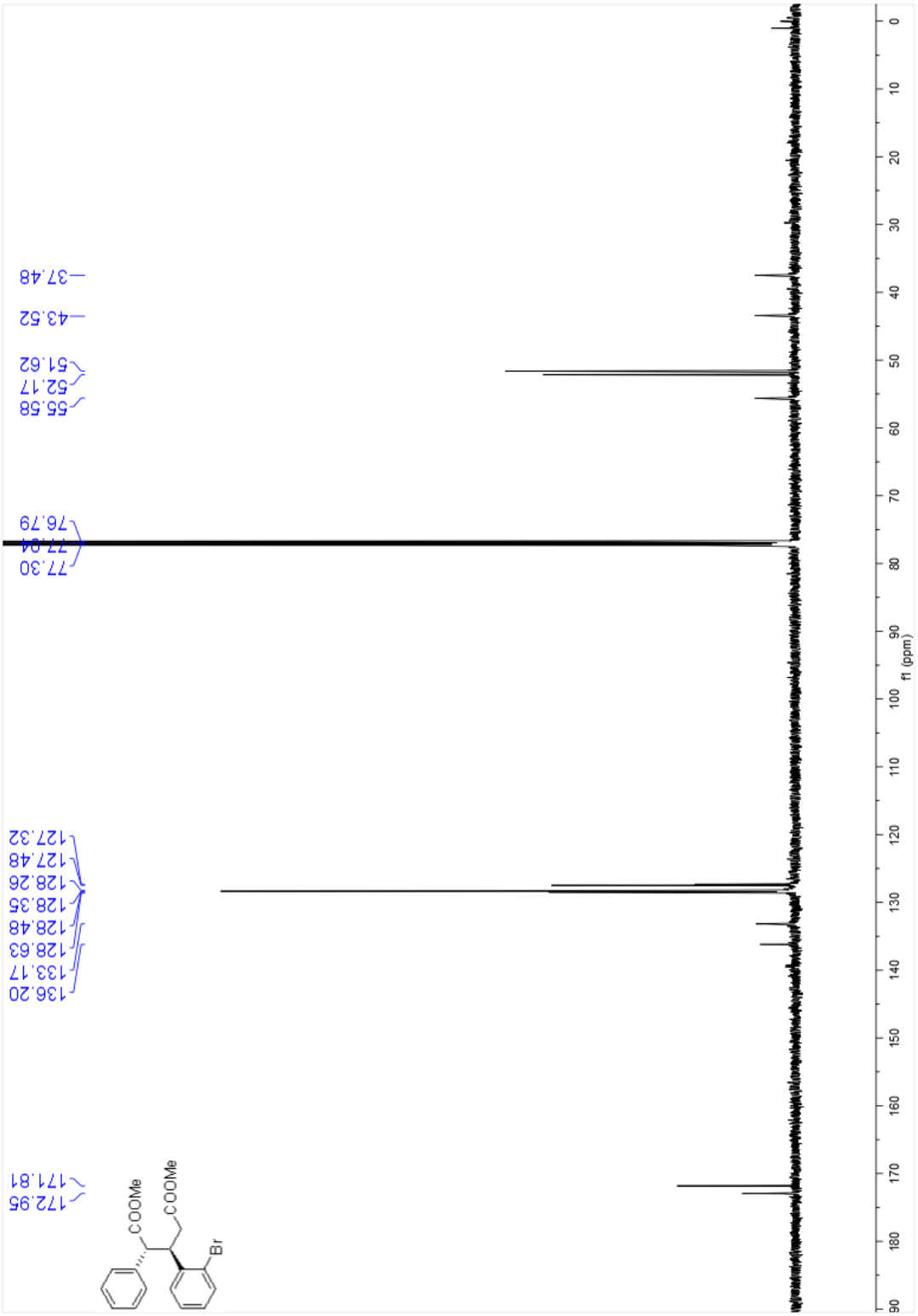
^{13}C NMR spectrum of product **4b**



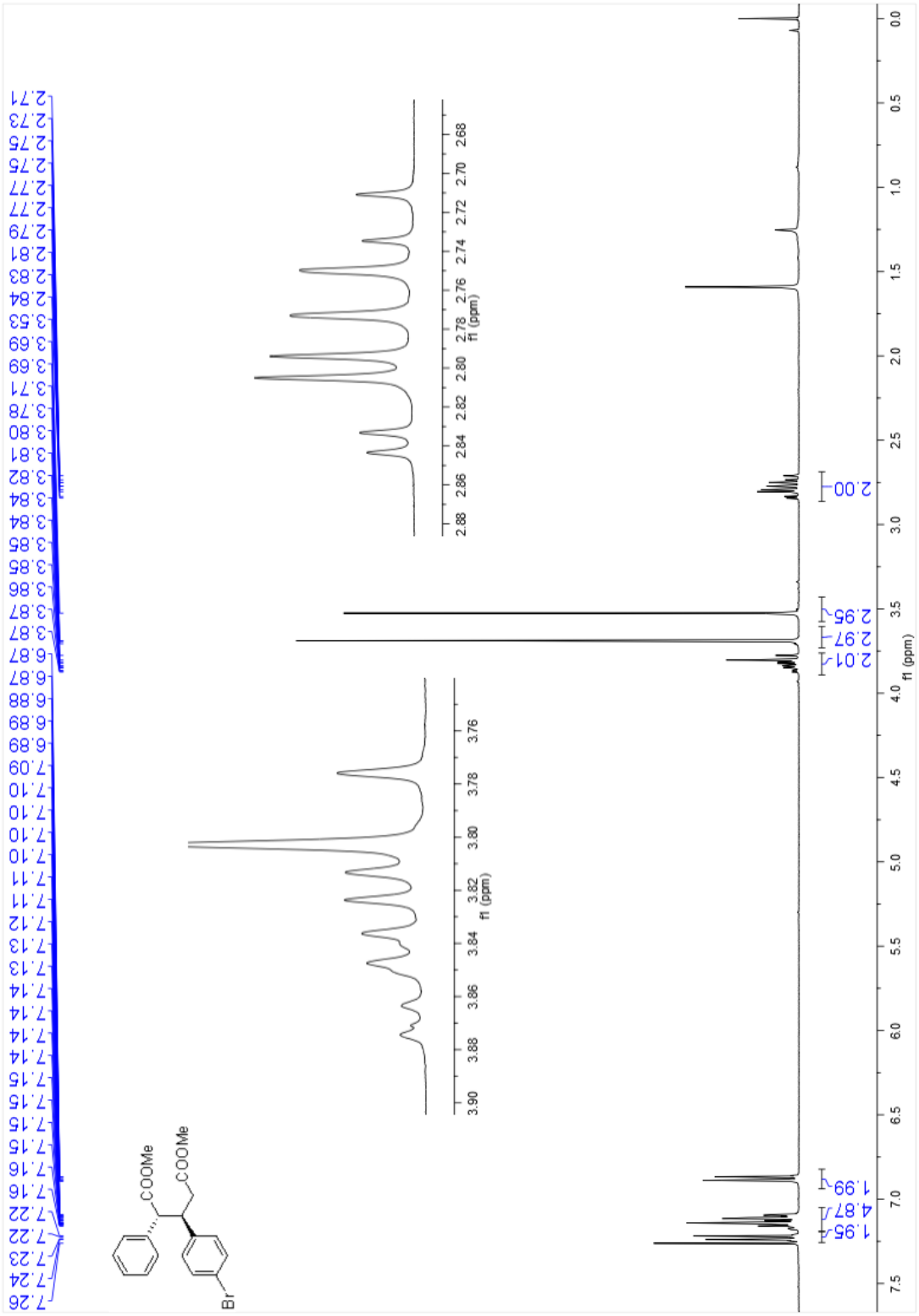
^{1}H NMR spectrum of product **4c**



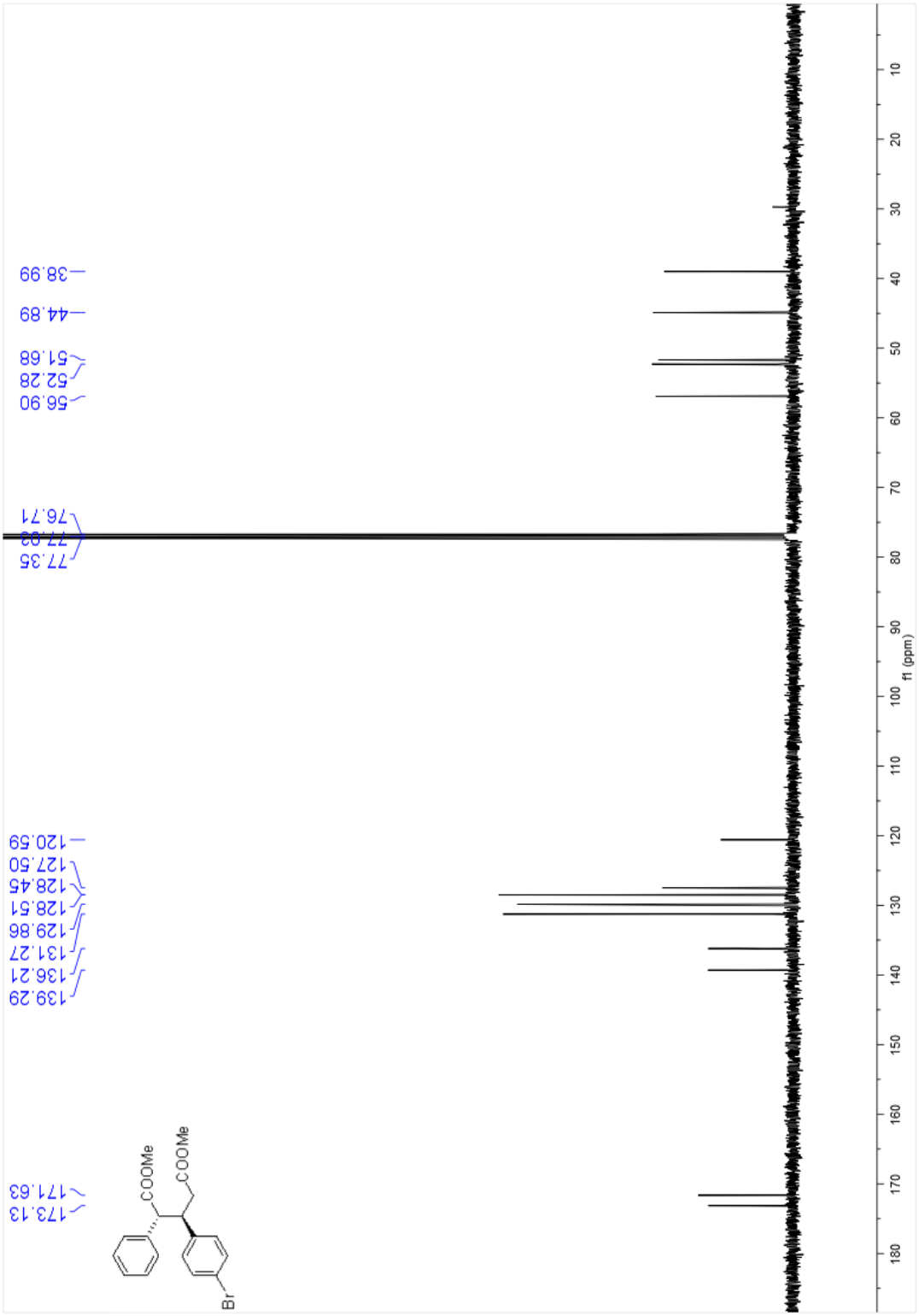
^{13}C NMR spectrum of product **4c**



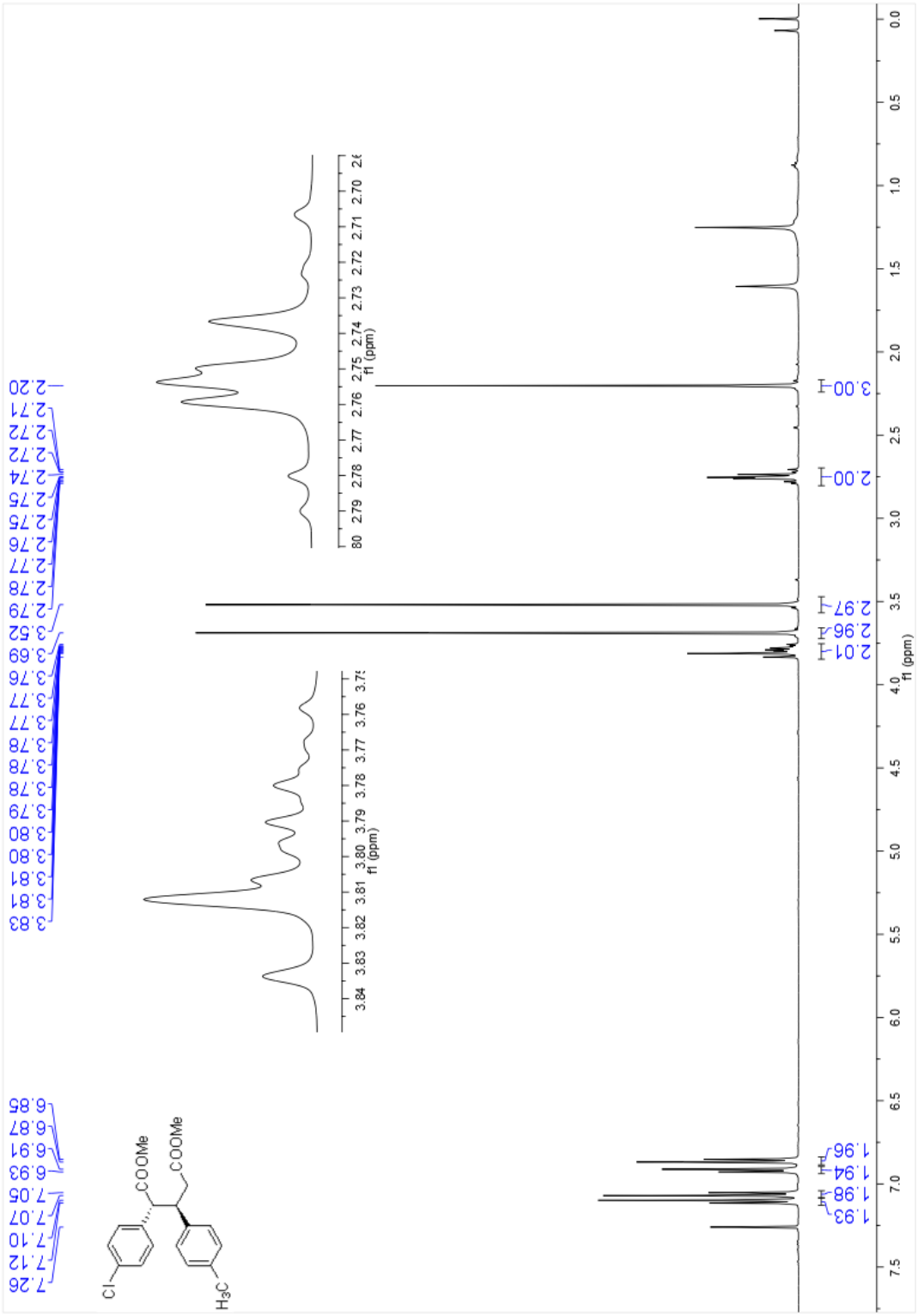
^{1}H NMR spectrum of product **4d**



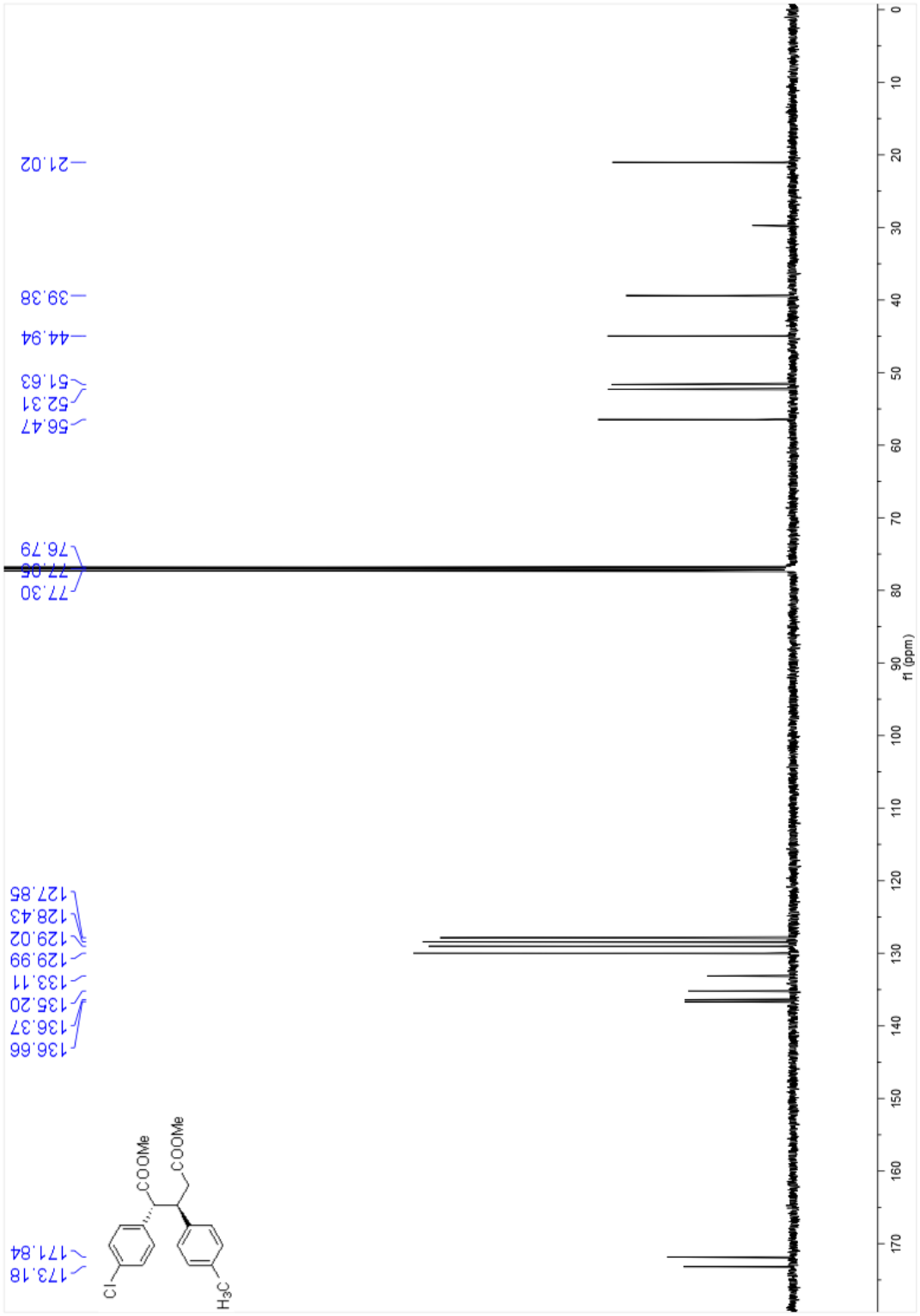
^{13}C NMR spectrum of product **4d**



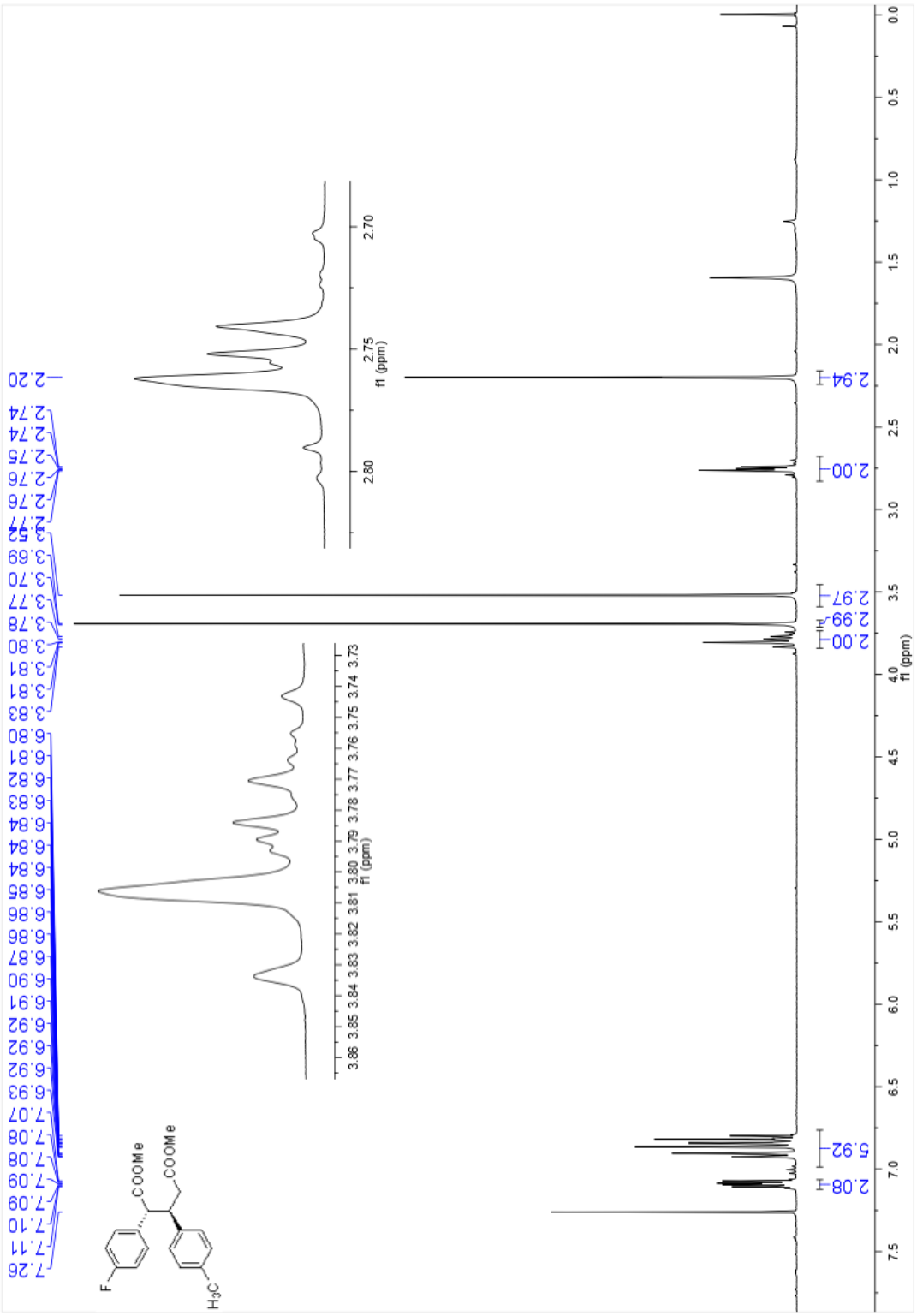
^{1}H NMR spectrum of product **4e**



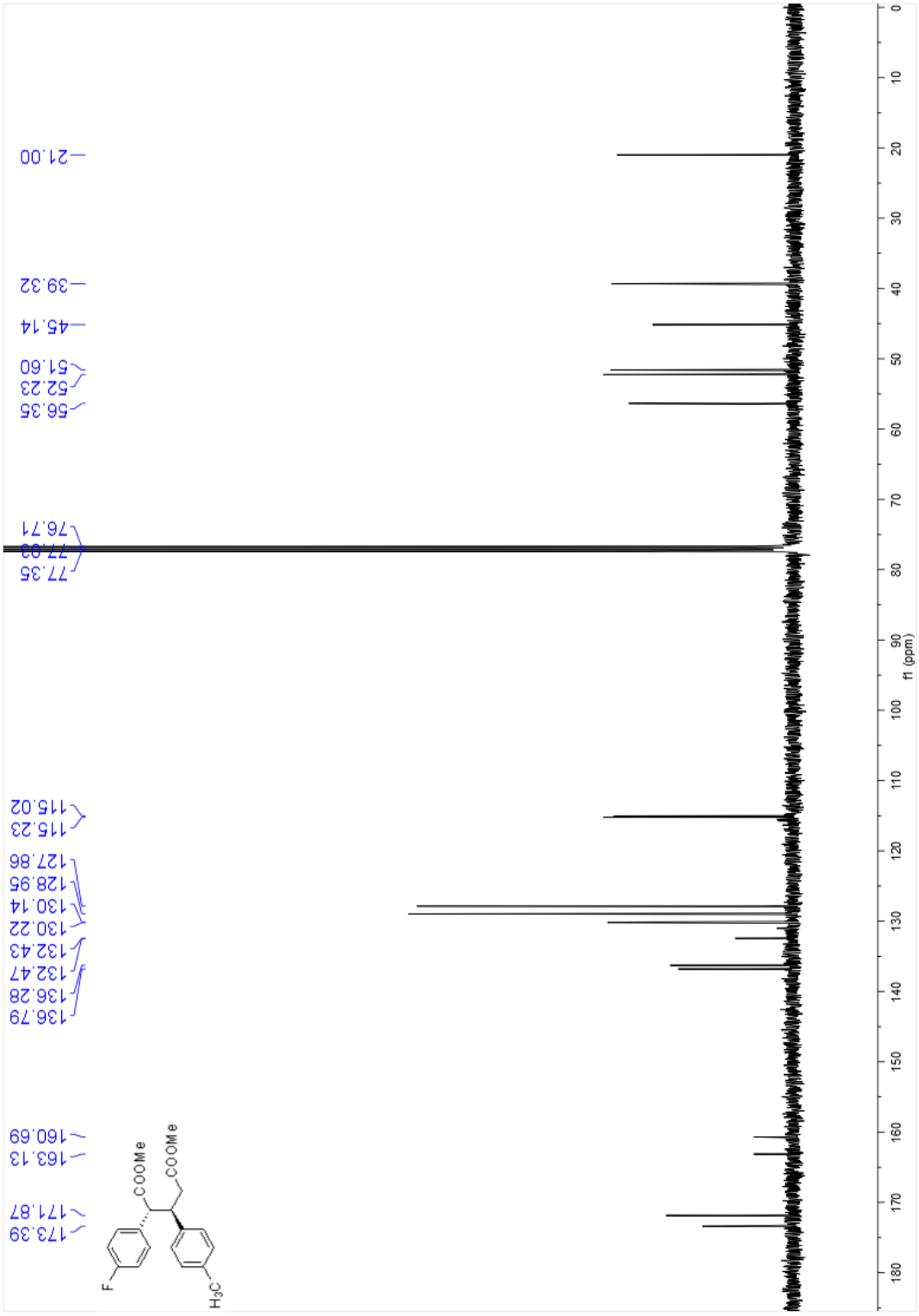
^{13}C NMR spectrum of product **4e**



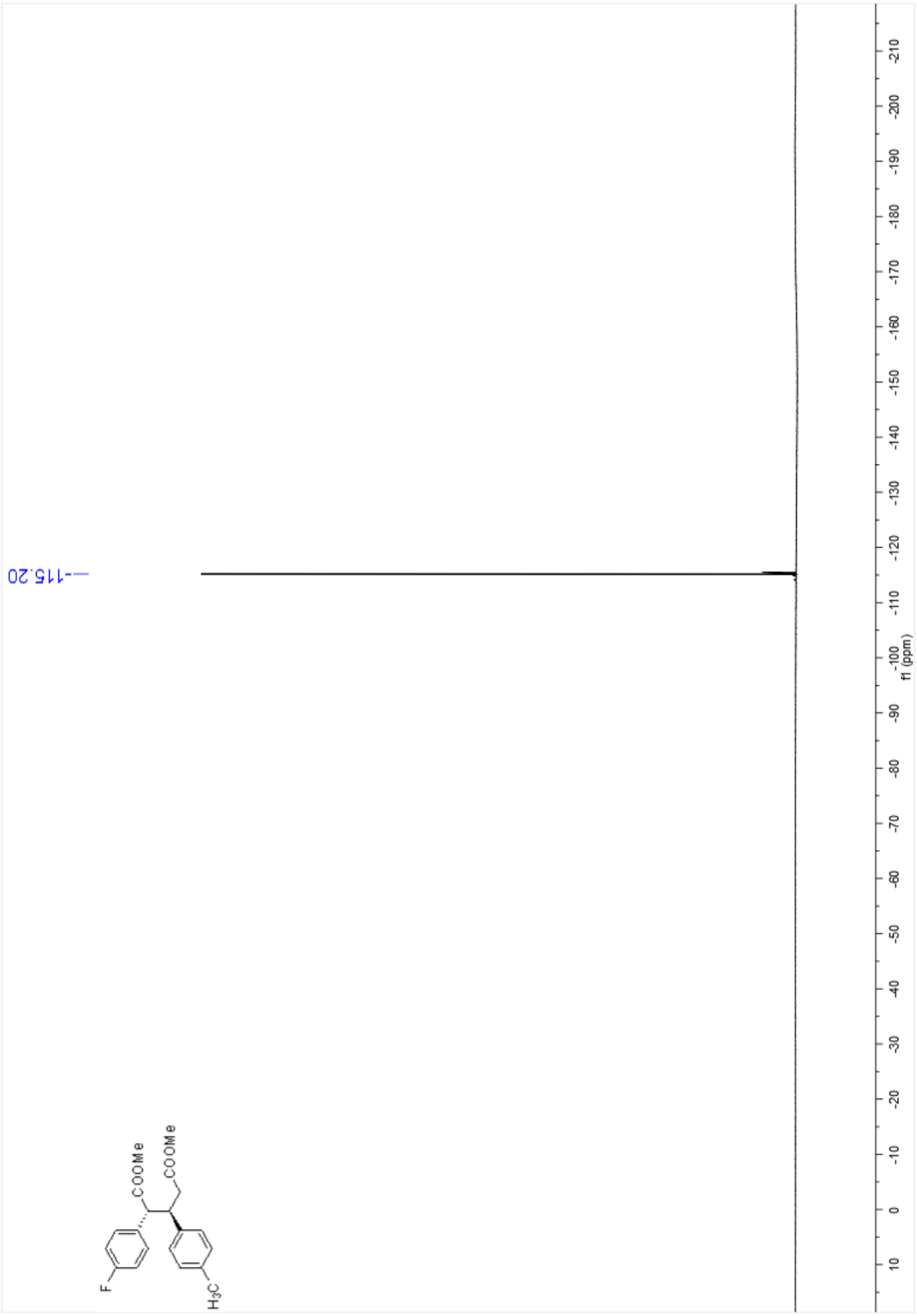
^{1}H NMR spectrum of product **4f**



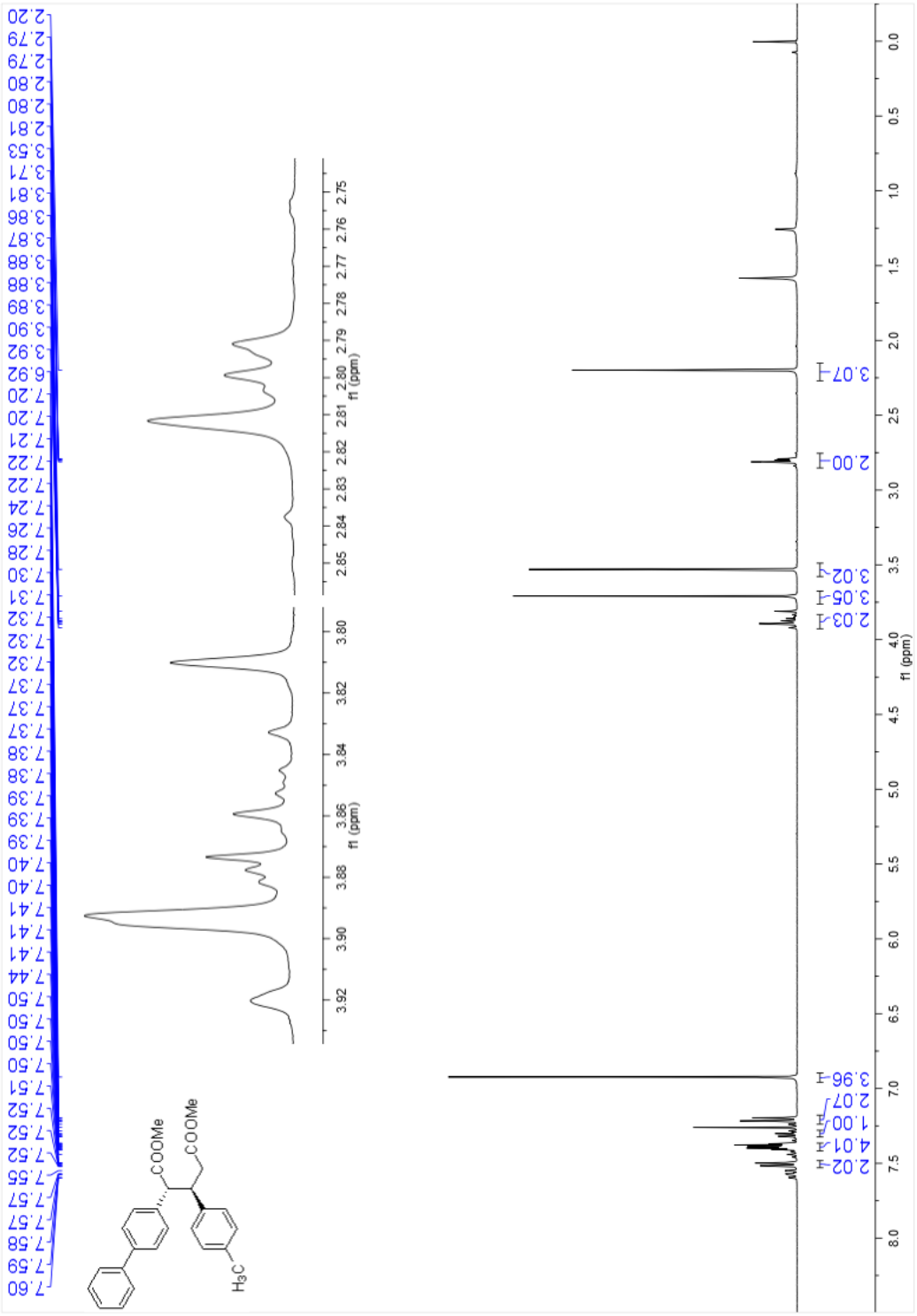
^{13}C NMR spectrum of product **4f**



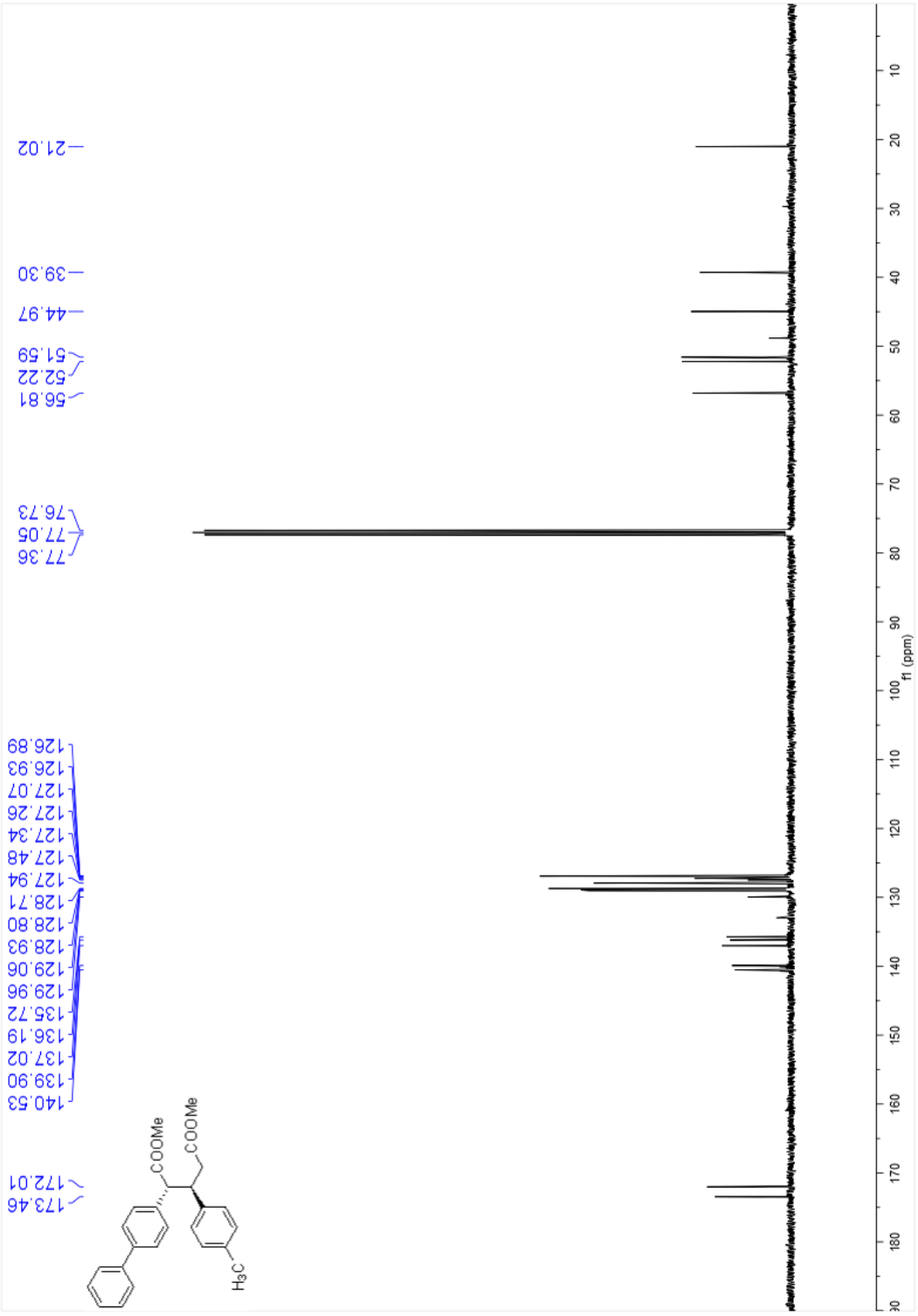
^{19}F NMR spectrum of product **4f**



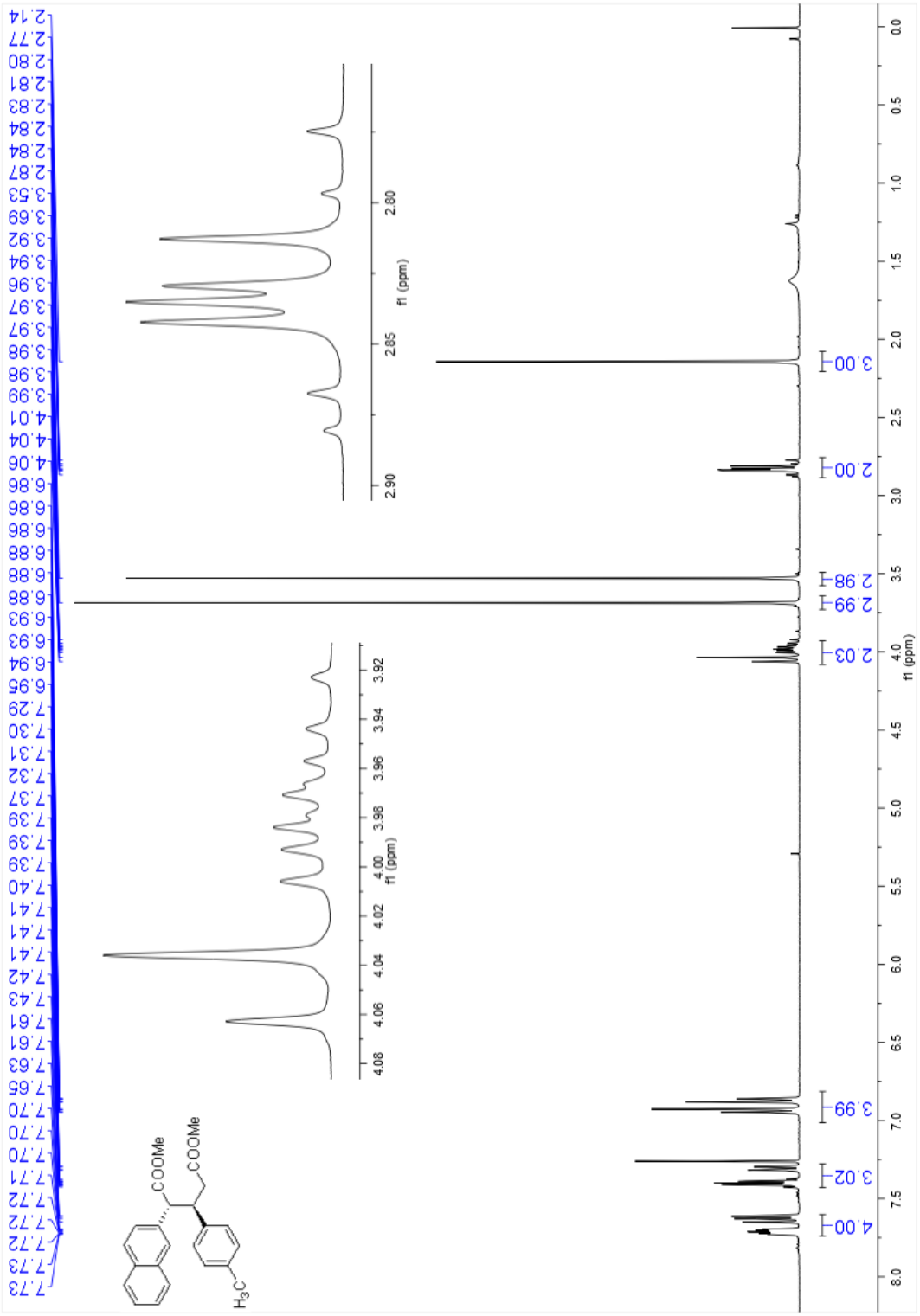
^{1}H NMR spectrum of product **4g**



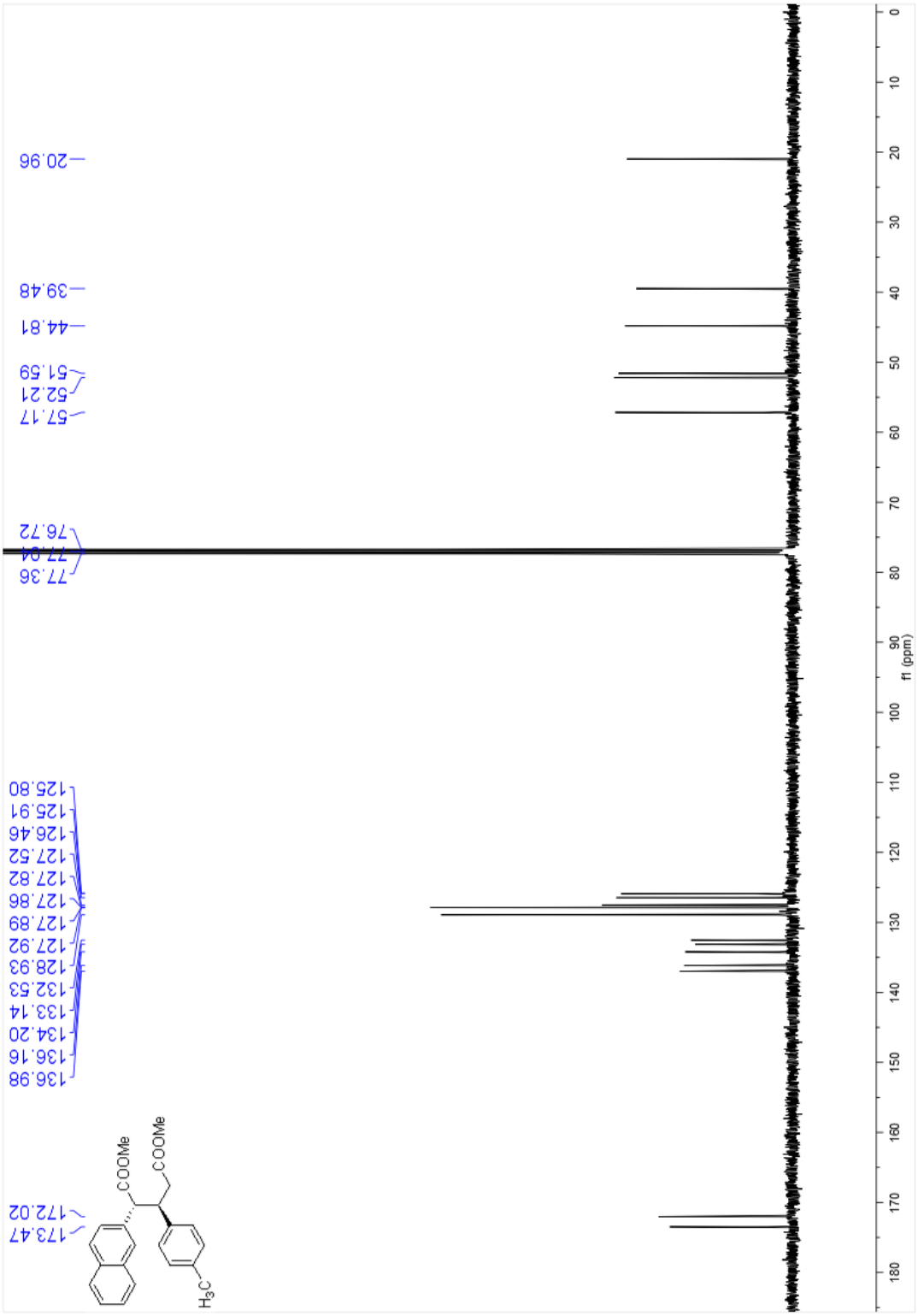
^{13}C NMR spectrum of product **4g**



^{1}H NMR spectrum of product **4h**

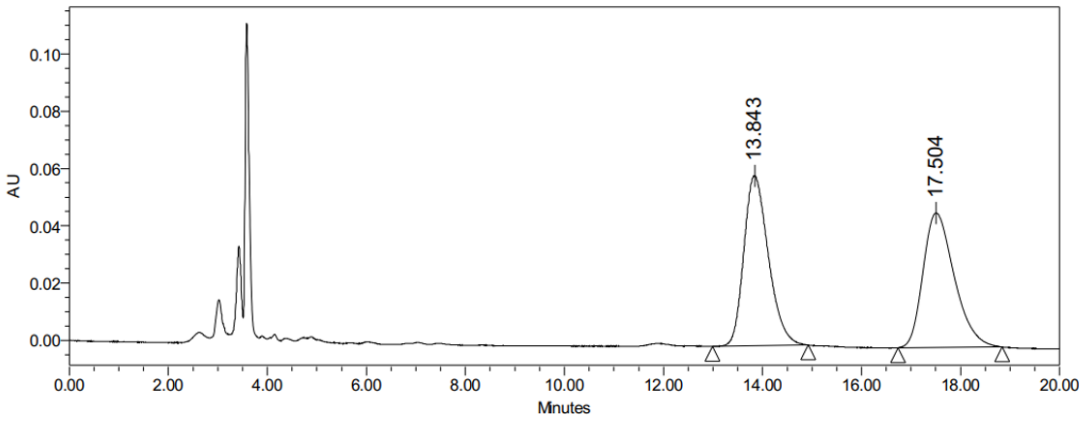


^{13}C NMR spectrum of product **4h**



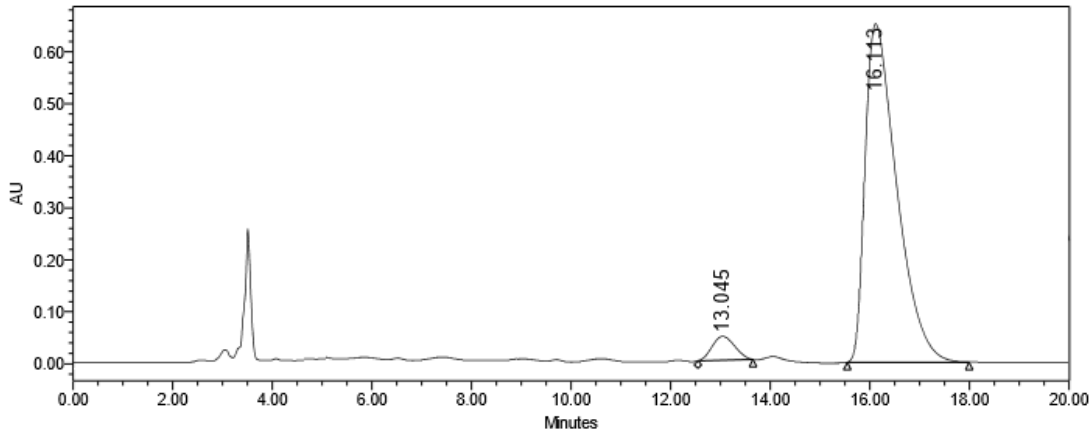
HPLC Spectra of Compounds 3a-3n

HPLC spectra of product **3a**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	13.843	2036832	49.64	59408
2	2998 PDA 220.0 nm (2998 (210-400)nm)	17.504	2066009	50.36	46964

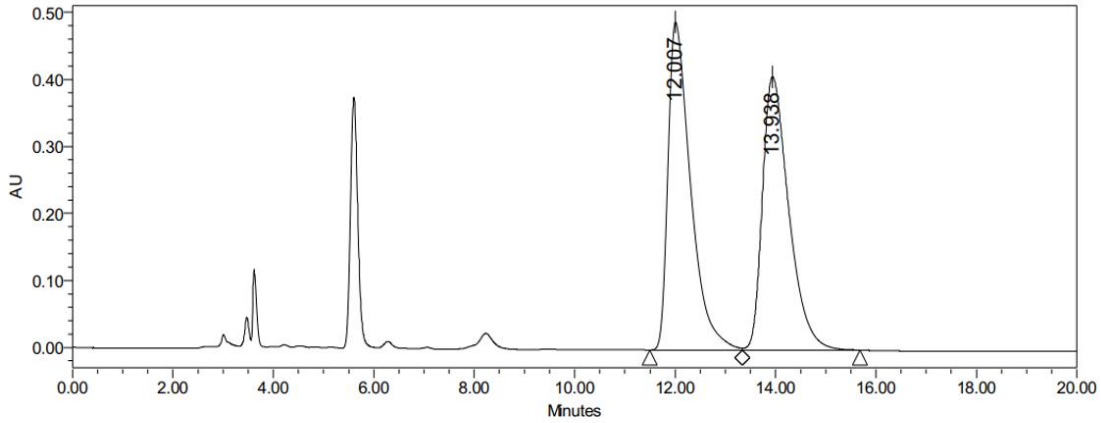


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2424; Processing Method: AsyEt

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

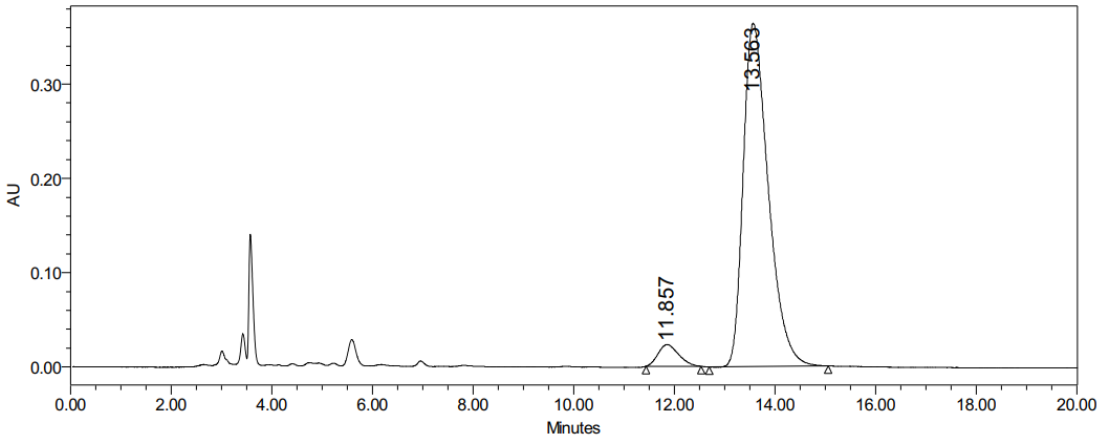
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	13.045	1458401	4.82	46003
2	2998 PDA 220.0 nm (2998 (210-400)nm)	16.113	28795520	95.18	651343

HPLC spectra of product **3b**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	12.007	15330820	50.80	489515
2	2998 PDA 220.0 nm (2998 (210-400)nm)	13.938	14846732	49.20	407896

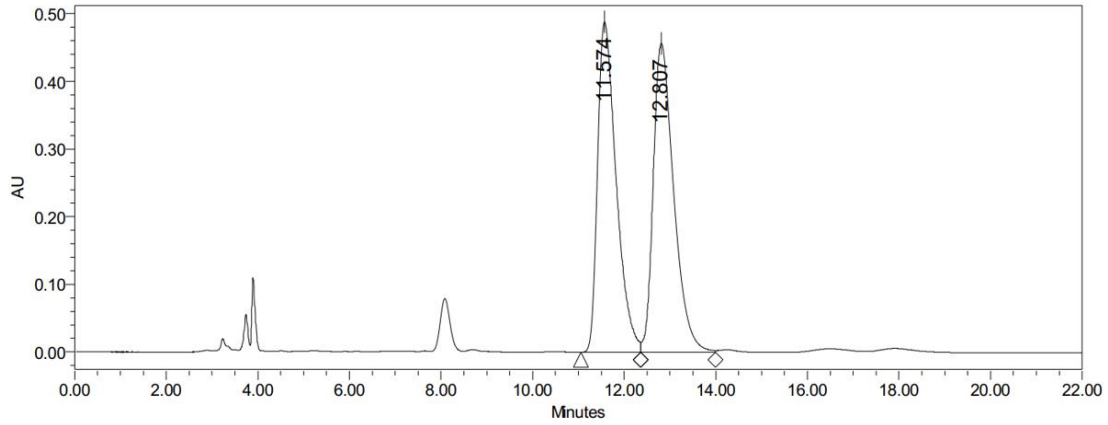


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2415; Processing Method: 4Me

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

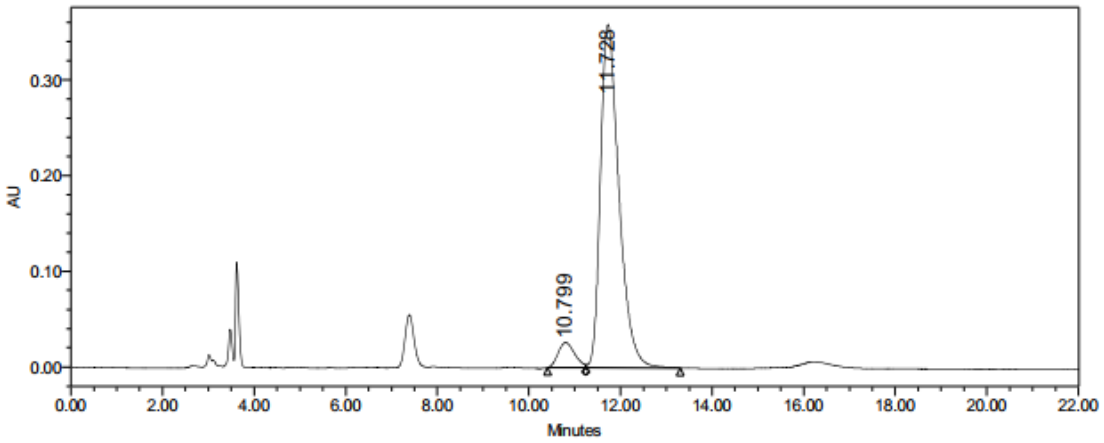
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	11.857	661783	4.98	23237
2	2998 PDA 220.0 nm (2998 (210-400)nm)	13.563	12621166	95.02	364154

HPLC spectra of product **3c**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	11.574	13779050	49.30	488371
2	2998 PDA 220.0 nm (2998 (210-400)nm)	12.807	14173161	50.70	456706

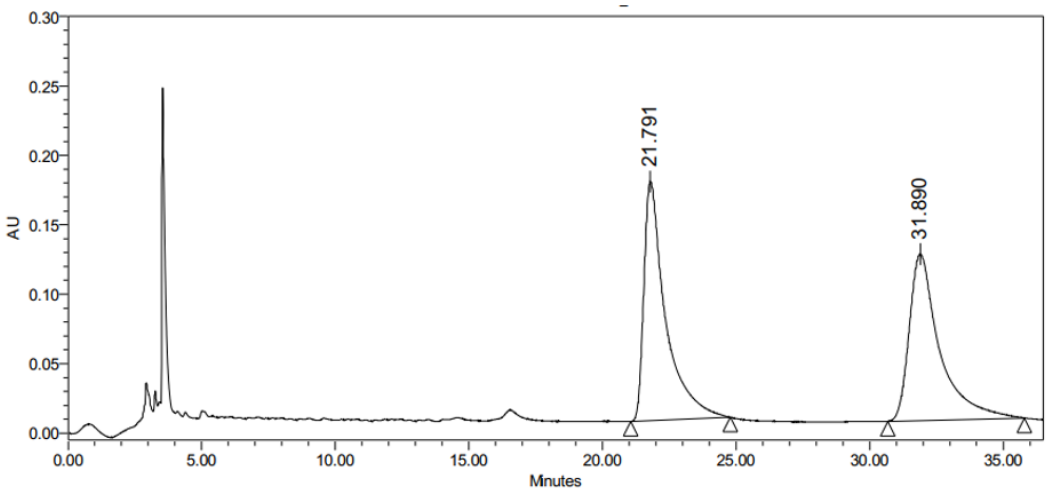


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2406; Processing Method: Asy4OMe

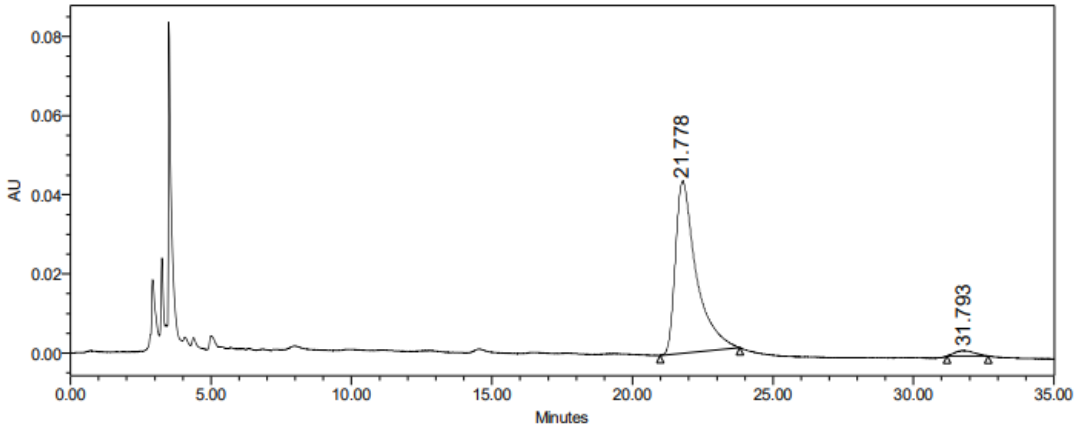
Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	10.799	657178	6.14	26159
2	2998 PDA 220.0 nm (2998 (210-400)nm)	11.728	10045121	93.86	358461

HPLC spectra of product **3d**



	Name	RT	Area	Height	% Area
1		21.791	9667183	172319	50.65
2		31.890	9418327	119865	49.35

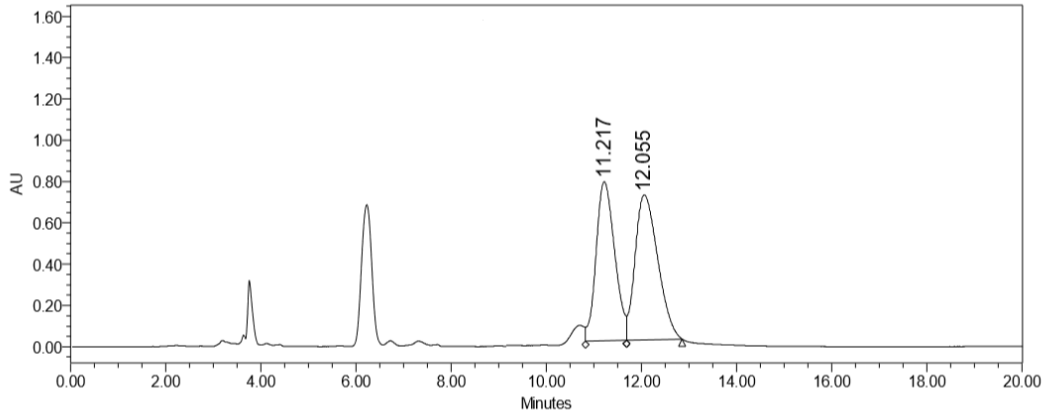


Channel: 2998; Processed Channel: 2998 PDA 228.0 nm (2998 (210-400)nm); Result Id: 1960; Processing Method: 11012023

Processed Channel Descr.: 2998 PDA 228.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 228.0 nm (2998 (210-400)nm)	21.778	2244692	97.09	43505
2	2998 PDA 228.0 nm (2998 (210-400)nm)	31.793	67343	2.91	1418

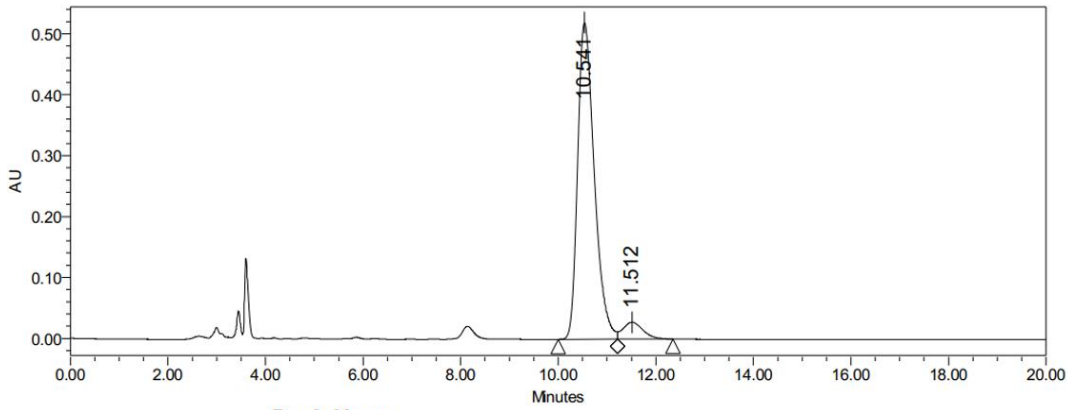
HPLC spectra of product **3e**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2765; Processing Method: 11012023

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

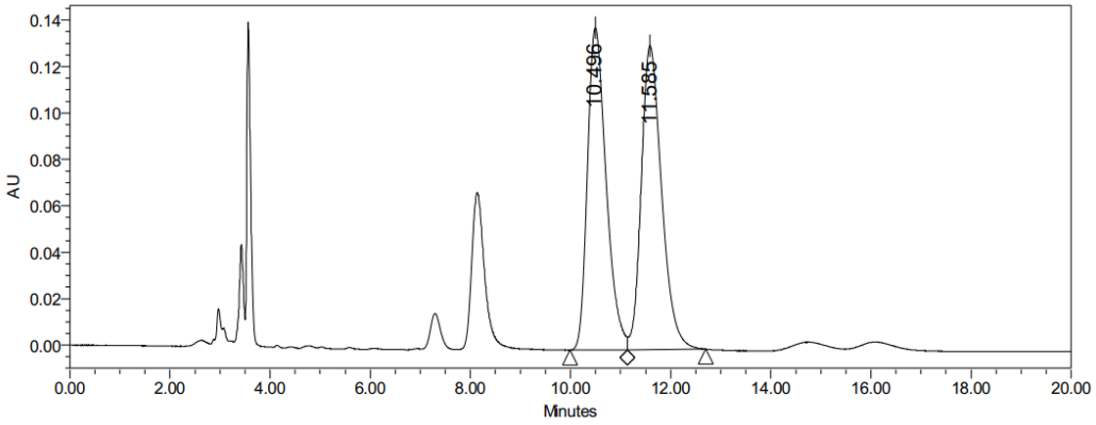
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	11.217	20888558	47.41	769999
2	2998 PDA 220.0 nm (2998 (210-400)nm)	12.055	23174874	52.59	701706



Peak Name:

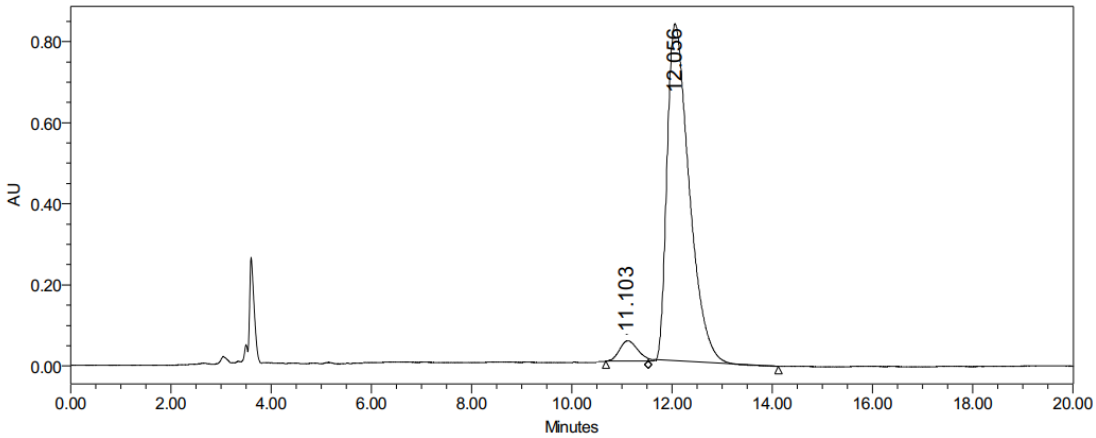
	Injection	RT	Area	% Area	Height
1	1	11.512	789520	6.03	27634
2	1	10.541	12307442	93.97	519712

HPLC spectra of product **3f**



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	11.585	3700639	50.62	131009
2	1	10.496	3610680	49.38	138849

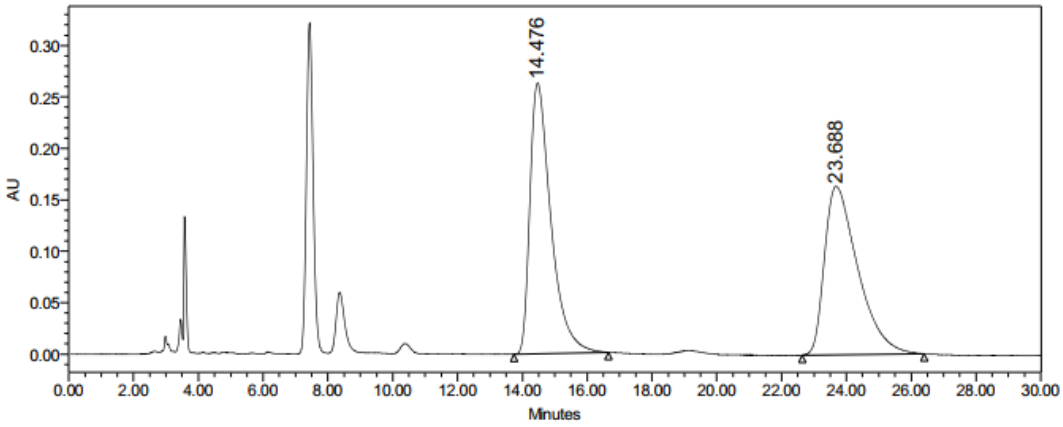


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4192; Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	11.103	1247742	4.67	56656
2	2998 PDA 220.0 nm (2998 (210-400)nm)	12.056	25448029	95.33	830920

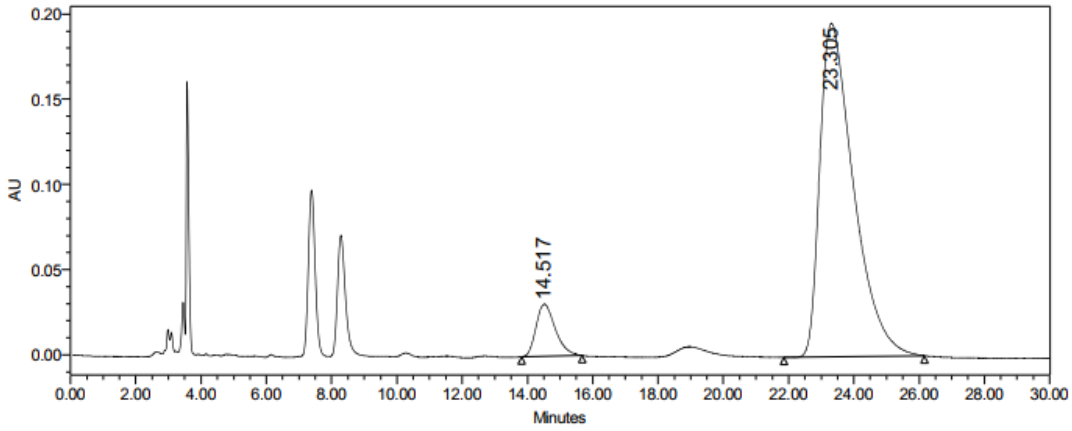
HPLC spectra of product **3g**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2442;
Processing Method: Asy4OMe

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	14.476	11833702	50.24	263277
2	2998 PDA 220.0 nm (2998 (210-400)nm)	23.688	11720884	49.76	163645

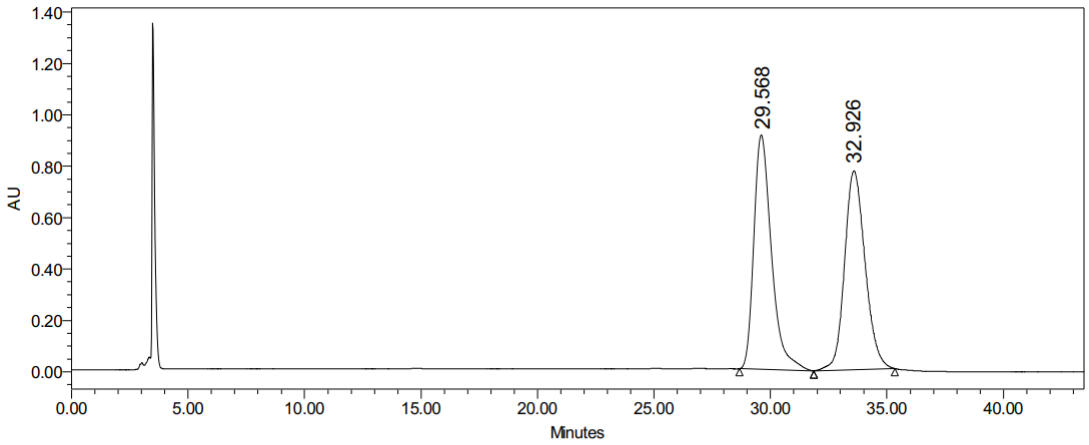


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2445;
Processing Method: hh

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	14.517	1251604	8.18	30680
2	2998 PDA 220.0 nm (2998 (210-400)nm)	23.305	14053631	91.82	195774

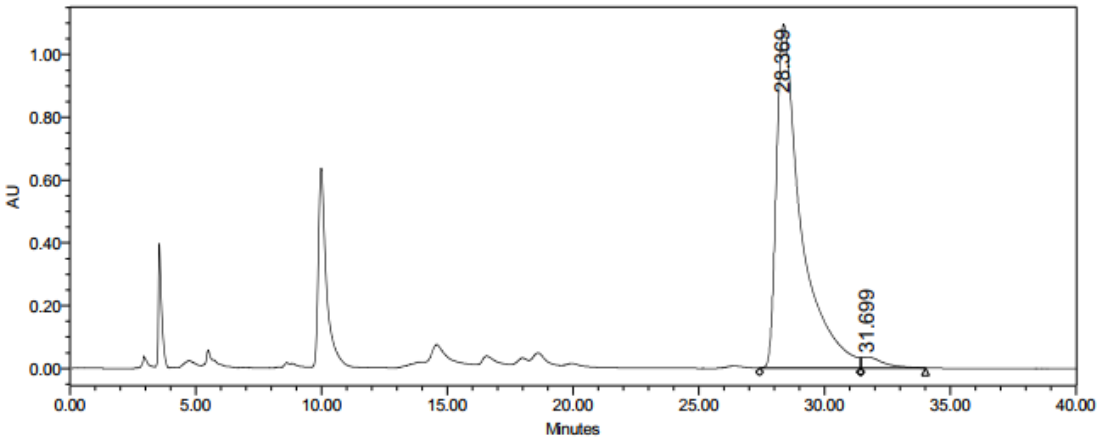
HPLC spectra of product **3h** using AD-H column



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 1644
Processing Method: mas

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	29.568	3583208	50.29	80750
2	2998 PDA 220.0 nm (2998 (210-400)nm)	32.926	3542156	49.71	68507

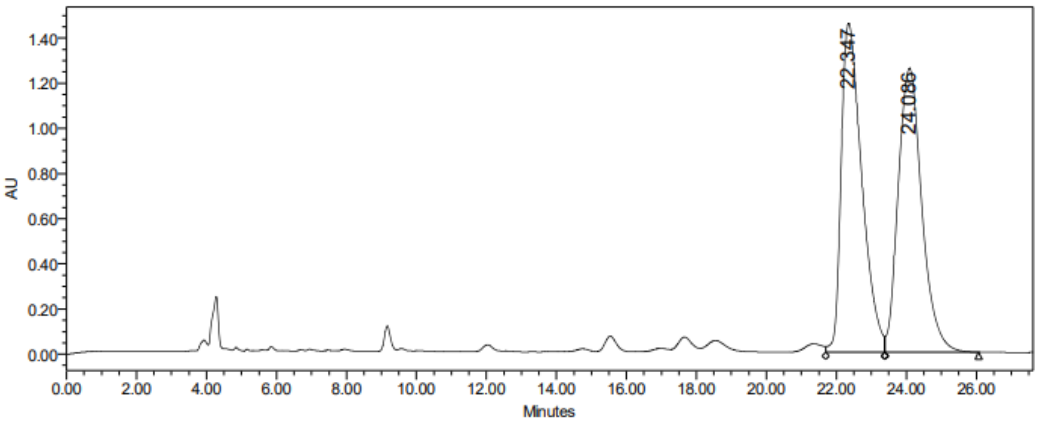


Channel: 2998; Processed Channel: 2998 PDA 219.0 nm (2998 (210-400)nm); Result Id: 2127;
Processing Method: AsyMe

Processed Channel Descr.: 2998 PDA 219.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 219.0 nm (2998 (210-400)nm)	28.369	74359735	97.23	1095390
2	2998 PDA 219.0 nm (2998 (210-400)nm)	31.699	2119327	2.77	34672

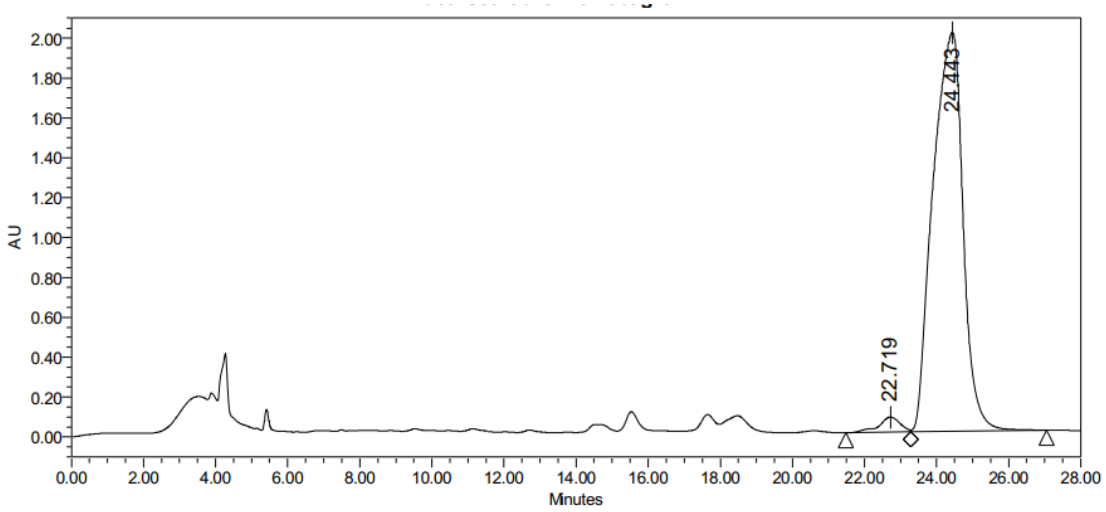
HPLC spectra of compound **3h** using ID column



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 1600;
Processing Method: masphosphate rac

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

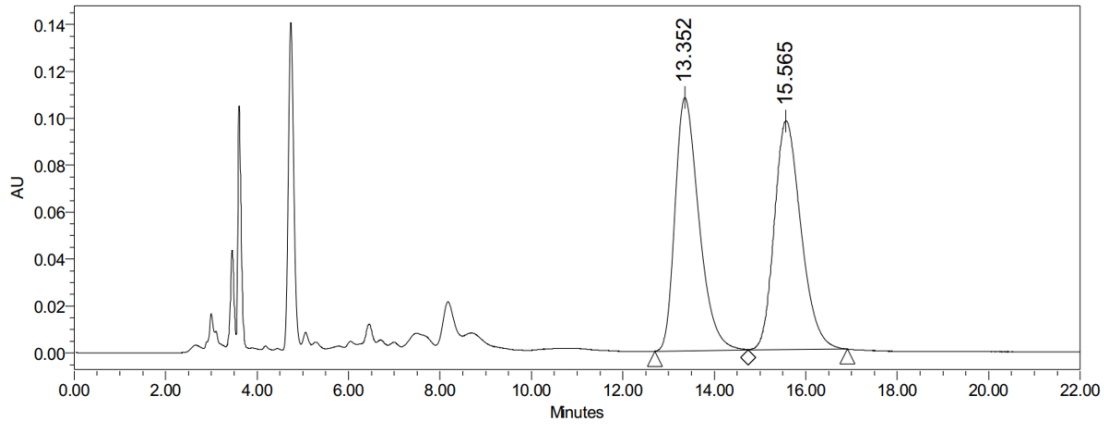
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	22.347	59683920	50.23	1454927
2	2998 PDA 220.0 nm (2998 (210-400)nm)	24.086	59143984	49.77	1256584



Peak Results

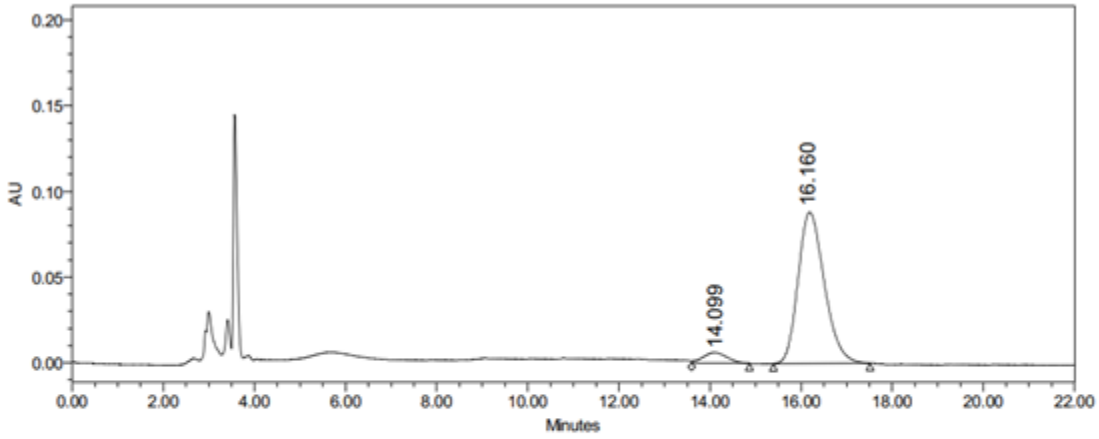
	Name	RT	Area	Height	% Area
1		22.719	3202468	76248	2.70
2		24.443	115193292	1999539	97.30

HPLC spectra of product **3i**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	13.352	3939079	49.89	107991
2	2998 PDA 220.0 nm (2998 (210-400)nm)	15.565	3955715	50.11	97592

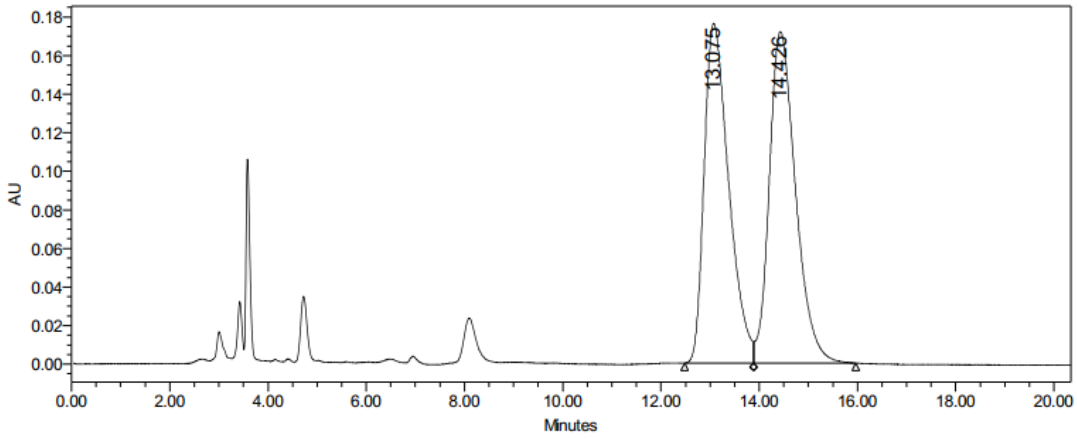


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2415; Processing Method: Ch

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	14.099	970623	5.86	47120
2	2998 PDA 220.0 nm (2998 (210-400)nm)	16.160	15601853	94.14	348202

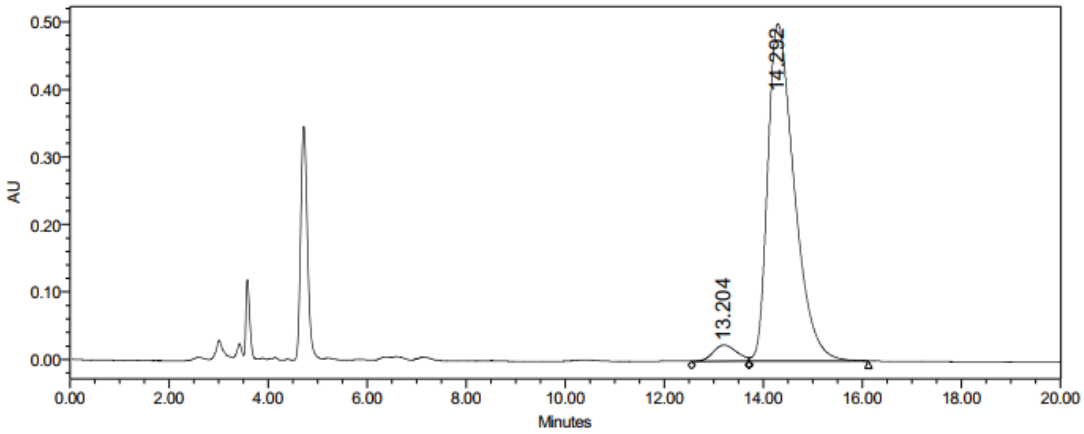
HPLC spectra of product **3j**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2421; Processing Method: 22

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	13.075	6103548	48.80	176163
2	2998 PDA 220.0 nm (2998 (210-400)nm)	14.426	6402468	51.20	171964

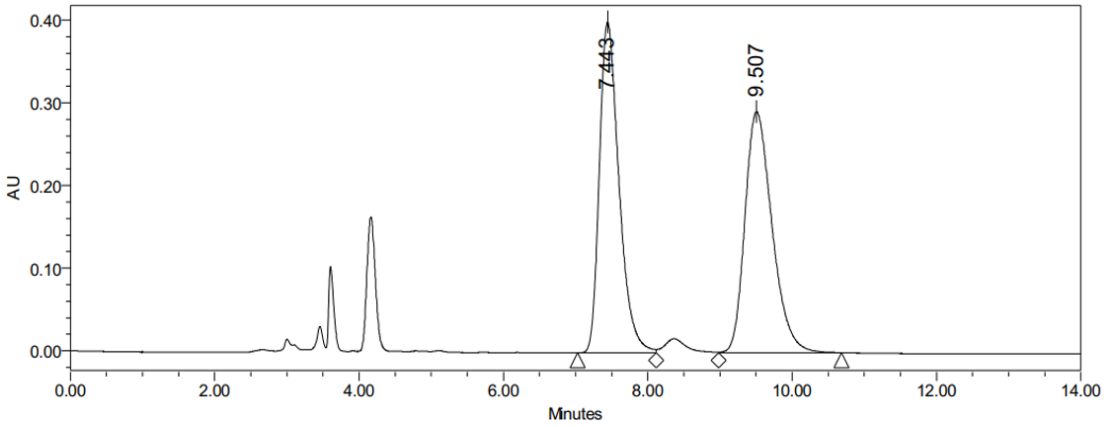


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2424; Processing Method: 22

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

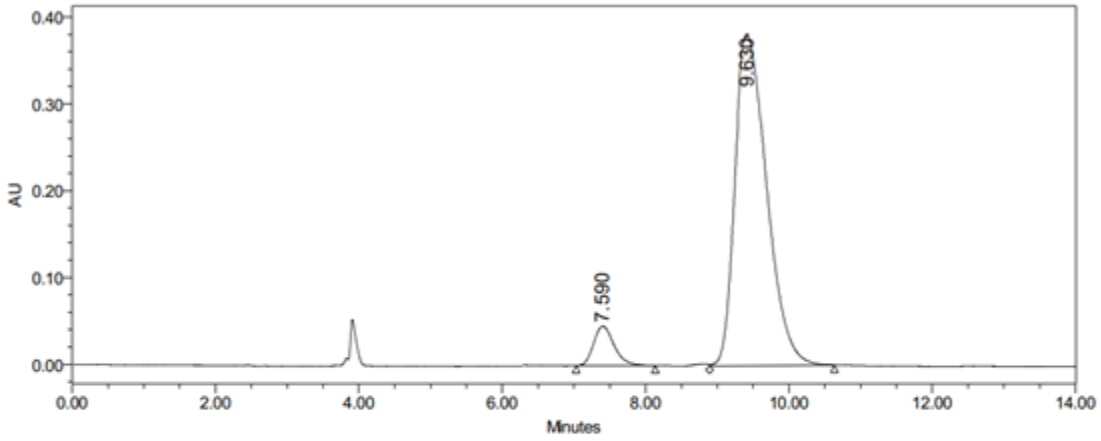
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	13.204	790793	4.09	23889
2	2998 PDA 220.0 nm (2998 (210-400)nm)	14.292	18543935	95.91	500030

HPLC spectra of product **3k**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	7.443	7547935	49.80	400171
2	2998 PDA 220.0 nm (2998 (210-400)nm)	9.507	7607255	50.20	291748

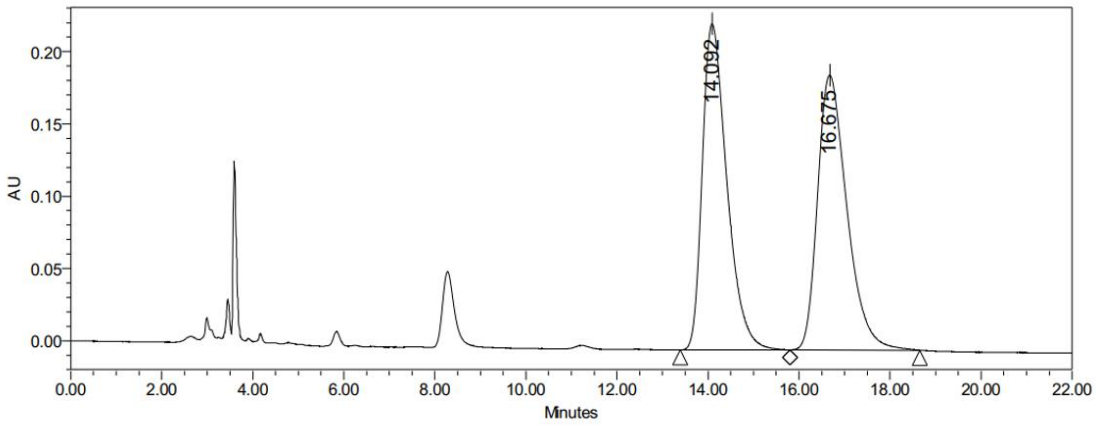


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2486; Processing Method: a

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

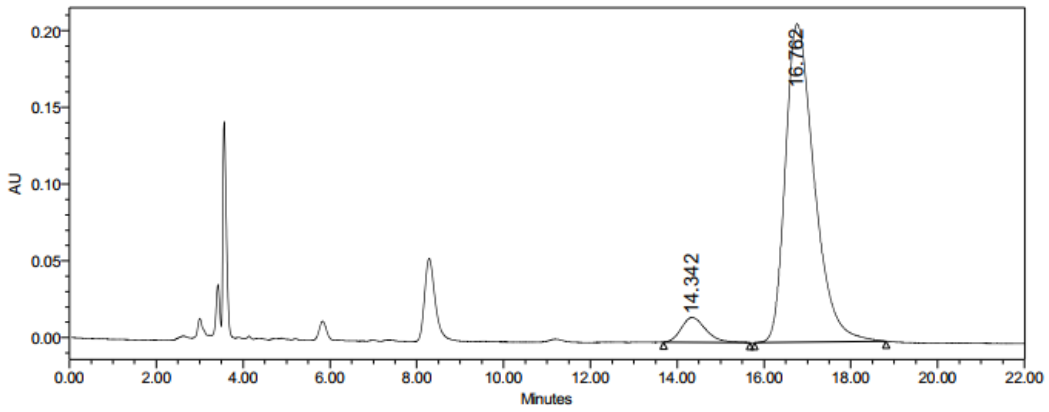
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	7.590	5929891	6.82	318695
2	2998 PDA 220.0 nm (2998 (210-400)nm)	9.630	81013355	93.18	1998778

HPLC spectra of product **3l**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	14.092	8480662	49.79	225656
2	2998 PDA 220.0 nm (2998 (210-400)nm)	16.675	8553659	50.21	190247

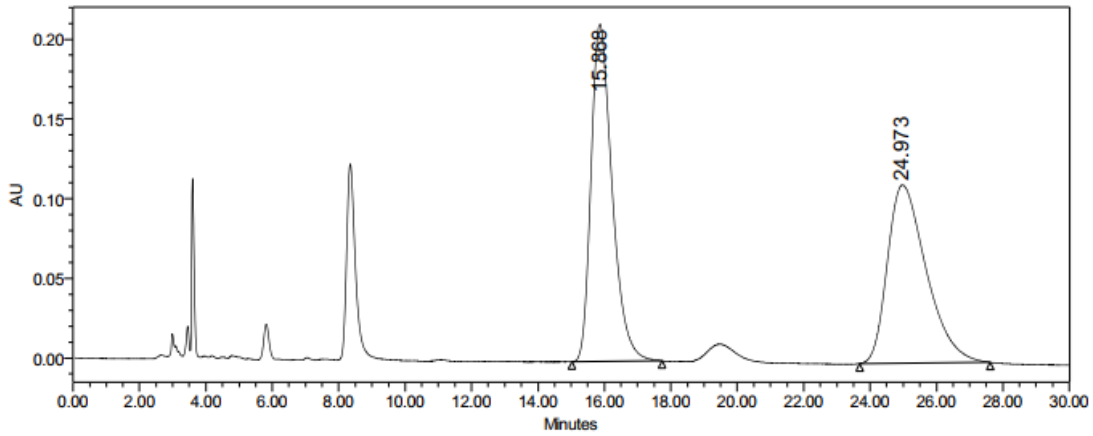


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2466; Processing Method: aa

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	14.342	635782	6.21	16209
2	2998 PDA 220.0 nm (2998 (210-400)nm)	16.762	9594148	93.79	207449

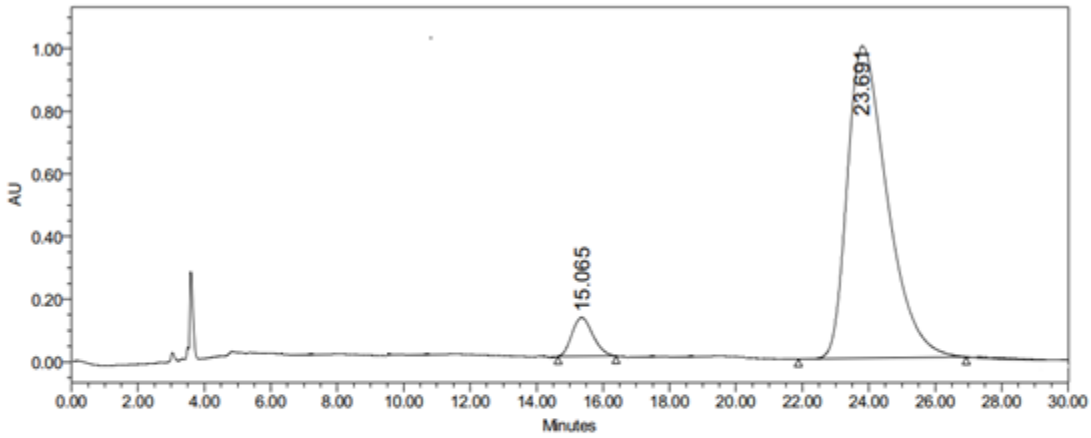
HPLC spectra of product **3m**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 2454;
Processing Method: kk

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	15.868	9324781	50.61	211628
2	2998 PDA 220.0 nm (2998 (210-400)nm)	24.973	9099145	49.39	111898

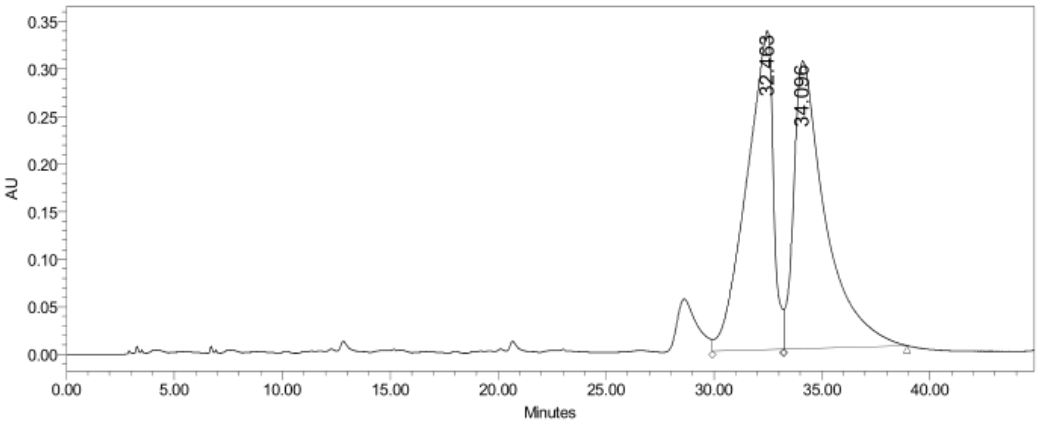


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4220;
Processing Method: 000

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	15.065	2287091	6.14	41283
2	2998 PDA 220.0 nm (2998 (210-400)nm)	23.691	34987844	93.86	436128

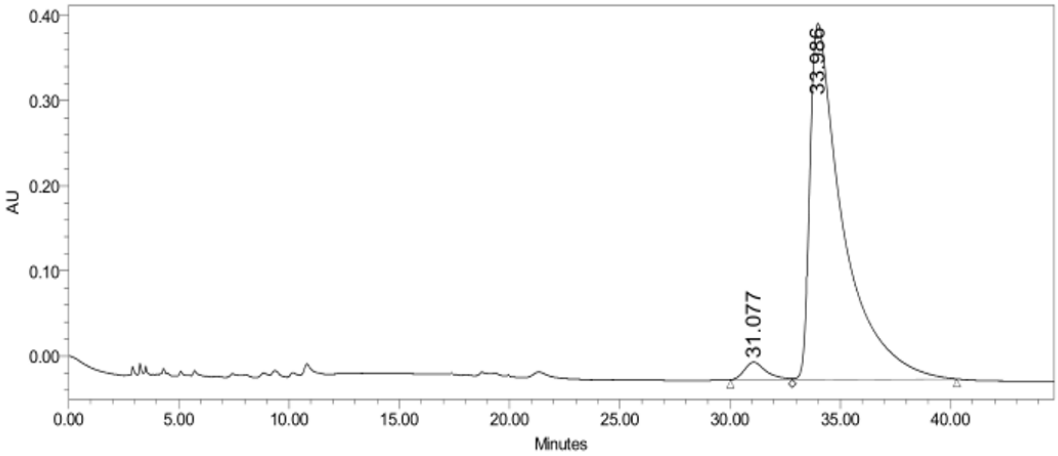
HPLC spectra of product **3n**



Channel: 2998 Ch1 254nm@4.8nm; Processed Channel: 2998 Ch1 254nm@4.8nm; Result Id: 2321; Processing Method: Ali

Processed Channel Descr.: 2998 Ch1 254nm@4.8nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 Ch1 254nm@4.8nm	32.463	28549353	48.01	335230
2	2998 Ch1 254nm@4.8nm	34.096	30913235	51.99	302338



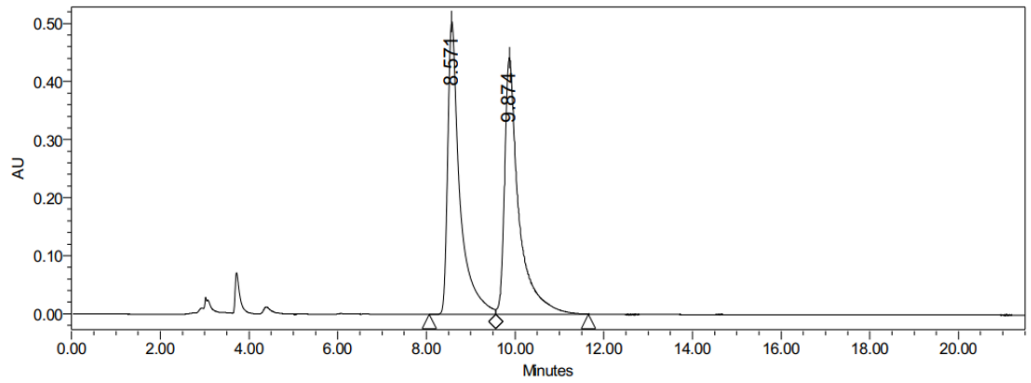
Channel: 2998 Ch1 254nm@4.8nm; Processed Channel: 2998 Ch1 254nm@4.8nm; Result Id: 2323; Processing Method: Ali

Processed Channel Descr.: 2998 Ch1 254nm@4.8nm

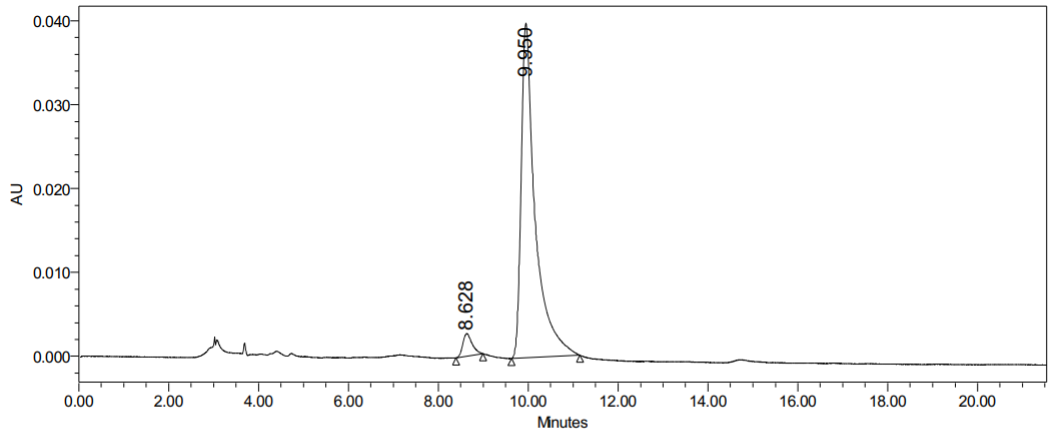
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 Ch1 254nm@4.8nm	31.077	1433574	3.18	20775
2	2998 Ch1 254nm@4.8nm	33.986	43597691	96.82	418391

HPLC Spectra of Products 4a-4h

HPLC spectra of product **4a**



	RT	Area	% Area	Height
1	8.571	9551848	49.53	504031
2	9.874	9734368	50.47	441594

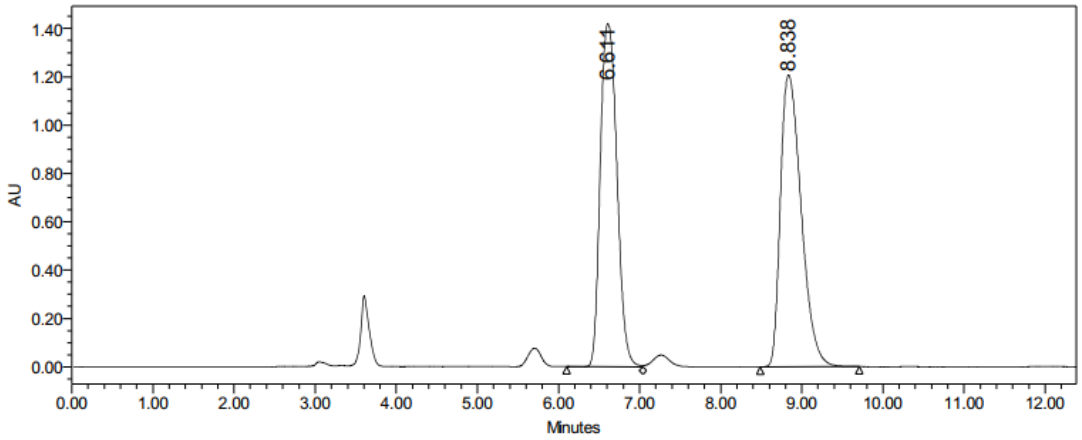


Channel: 2998; Processed Channel: 2998 PDA 254.0 nm (2998 (210-400)nm); Injection: 1; Date Acquired: 7/4/2022 9:37:37 PM CST; Result Id: 3135; Processing Method: 33

Peak Name:

	Injection	RT	Area	% Area	Height
1	1	9.950	868688	95.63	39906
2	1	8.628	39706	4.37	2727

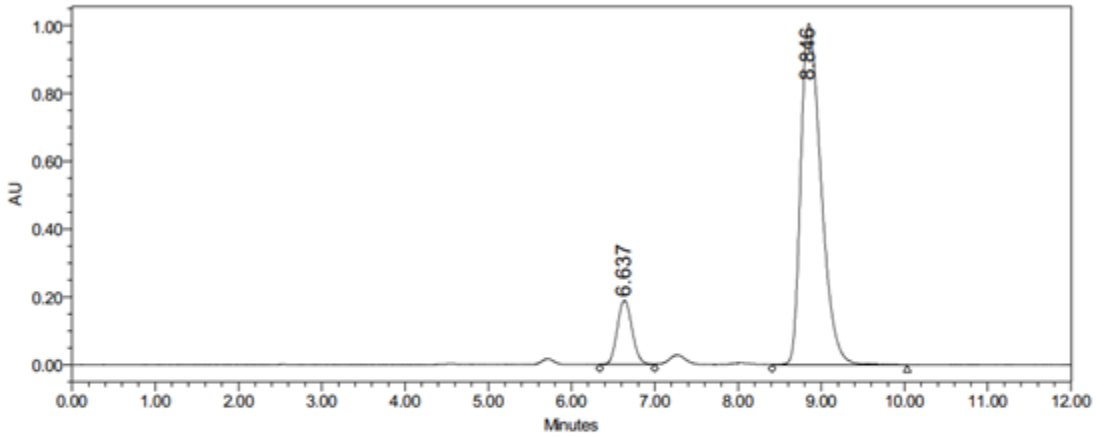
HPLC spectra of product **4b**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 3987;
Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	6.611	20229838	48.55	1420219
2	2998 PDA 220.0 nm (2998 (210-400)nm)	8.838	21436106	51.45	1207327

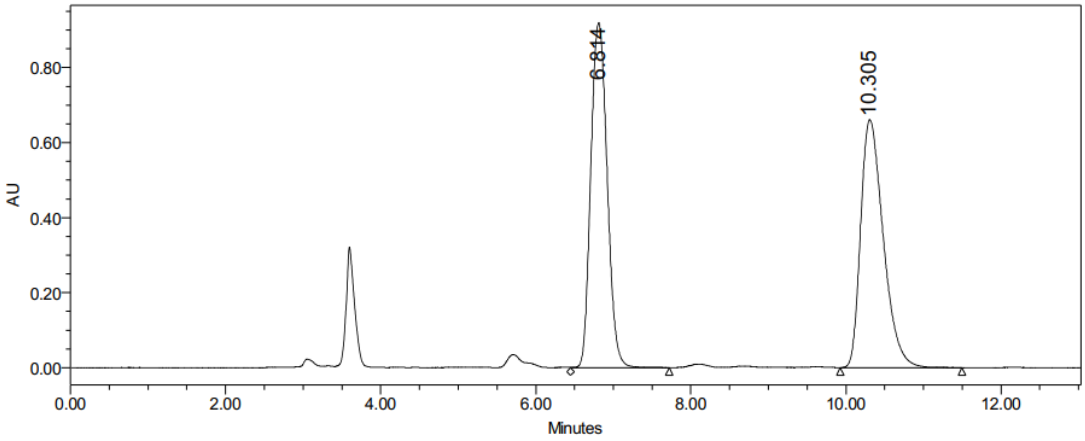


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4001;
Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	6.637	2353526	12.07	189457
2	2998 PDA 220.0 nm (2998 (210-400)nm)	8.846	17151678	87.93	1005553

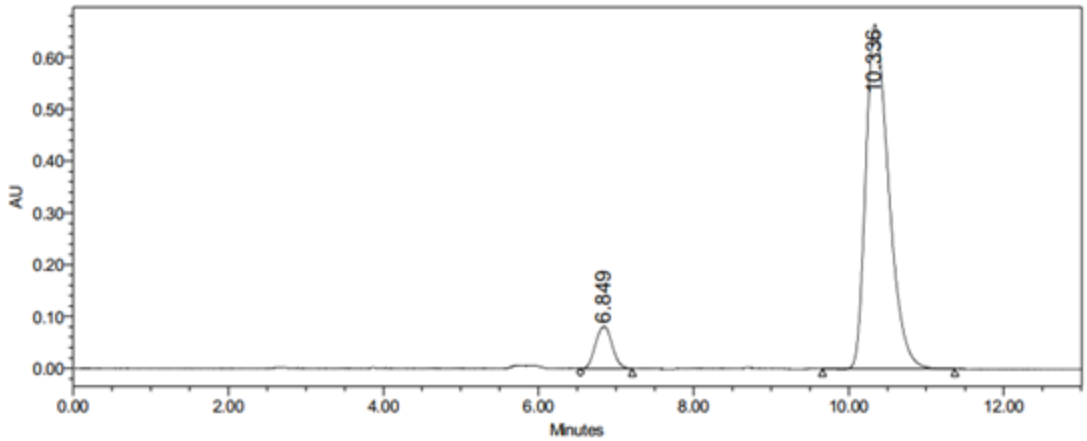
HPLC spectra of product **4c**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 3998; Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	6.814	13473081	50.08	919554
2	2998 PDA 220.0 nm (2998 (210-400)nm)	10.305	13432436	49.92	661322

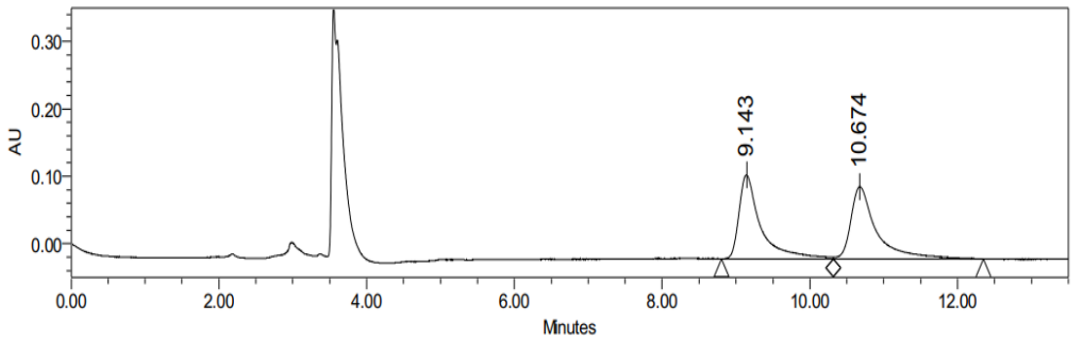


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4004; Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

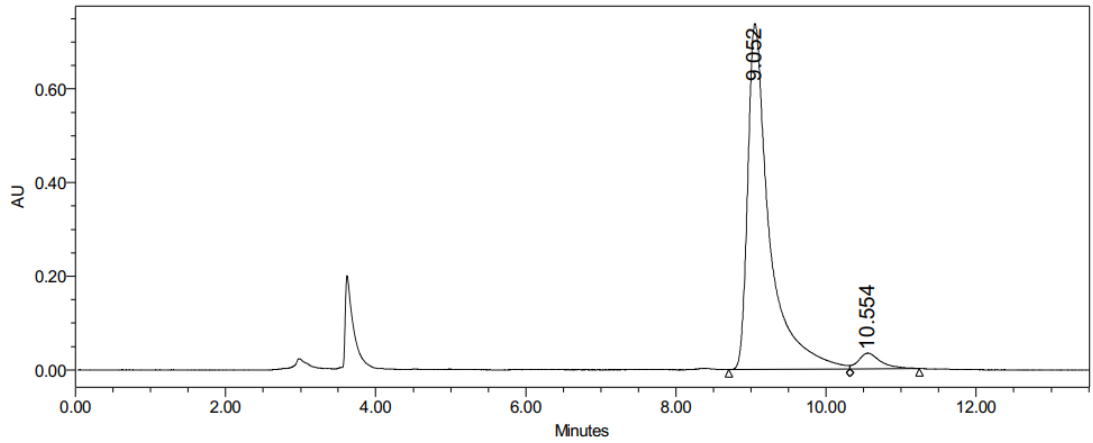
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	6.849	1215998	8.16	81277
2	2998 PDA 220.0 nm (2998 (210-400)nm)	10.336	13694813	91.84	664318

HPLC spectra of product **4d**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	9.143	2551100	49.62	124583
2	2998 PDA 220.0 nm (2998 (210-400)nm)	10.674	2590564	50.38	107349

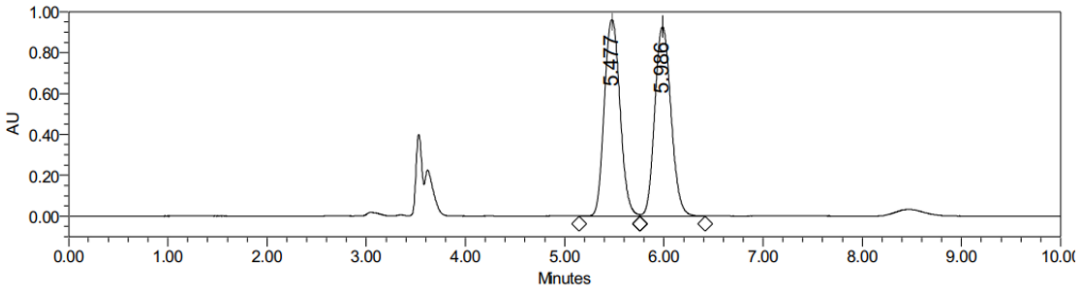


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4115; Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

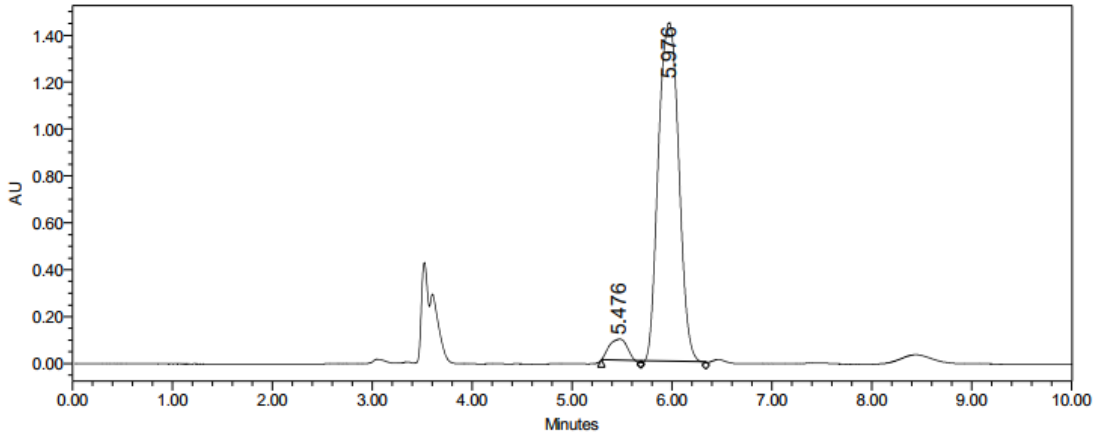
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	9.052	14799866	95.50	738716
2	2998 PDA 220.0 nm (2998 (210-400)nm)	10.554	696940	4.50	33875

HPLC spectra of product **4e**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	5.477	10579456	50.06	962785
2	2998 PDA 220.0 nm (2998 (210-400)nm)	5.986	10554106	49.94	927889

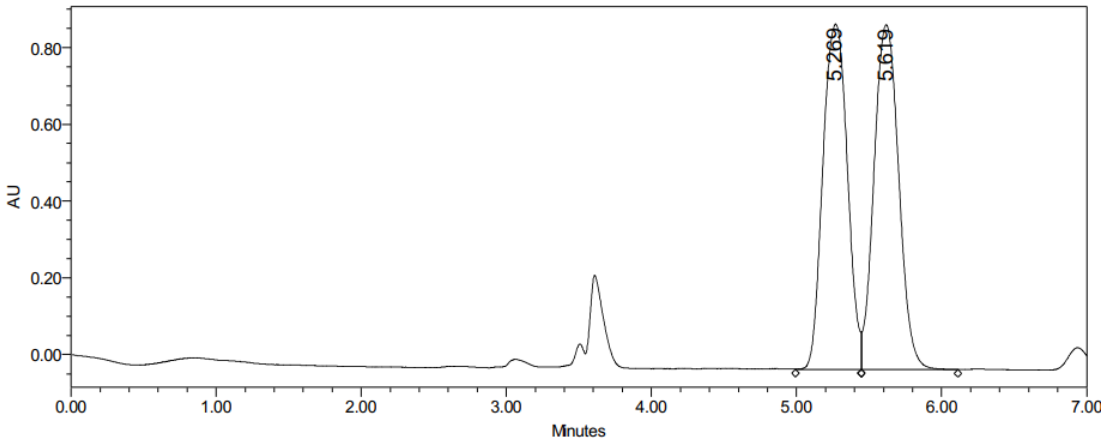


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 3969; Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	5.476	1127343	5.22	89204
2	2998 PDA 220.0 nm (2998 (210-400)nm)	5.976	20487599	94.78	1441935

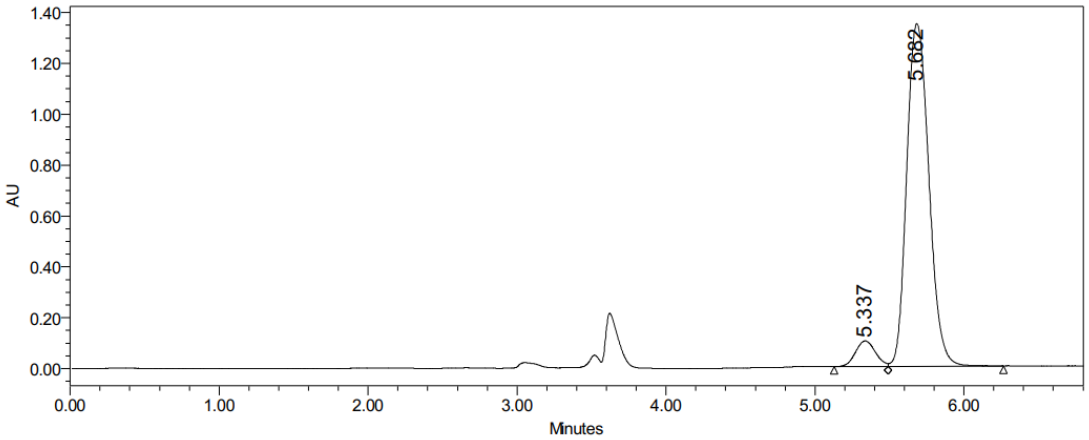
HPLC spectra of product **4f**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4051; Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	5.269	10519086	49.59	900048
2	2998 PDA 220.0 nm (2998 (210-400)nm)	5.619	10691172	50.41	898349

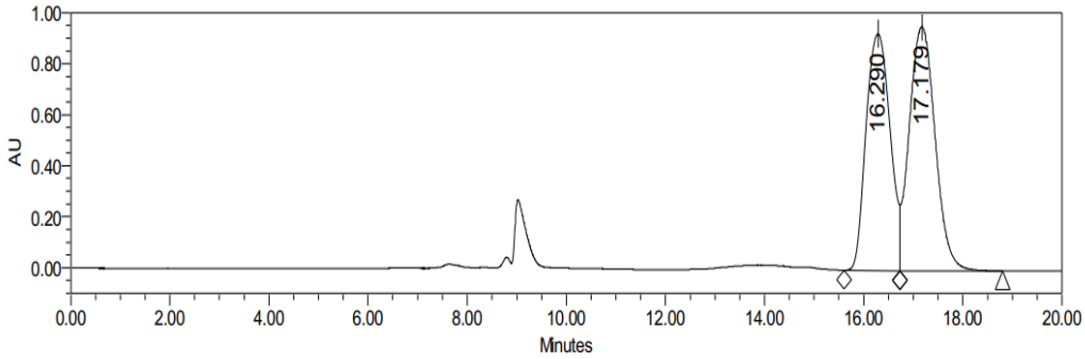


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4085; Processing Method: 00

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

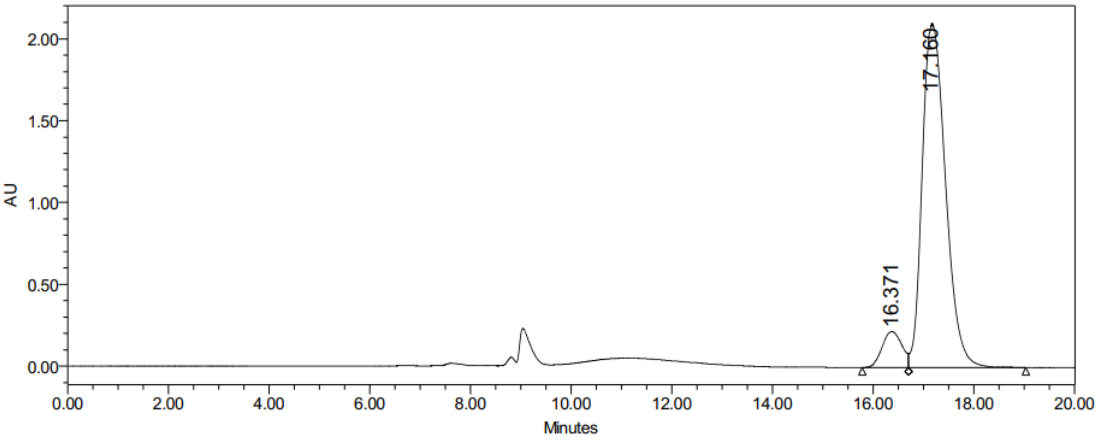
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	5.337	932542	6.29	100366
2	2998 PDA 220.0 nm (2998 (210-400)nm)	5.682	13902446	93.71	1346261

HPLC spectra of product **4g**



Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	16.290	31314417	47.49	928590
2	2998 PDA 220.0 nm (2998 (210-400)nm)	17.179	34629161	52.51	957340

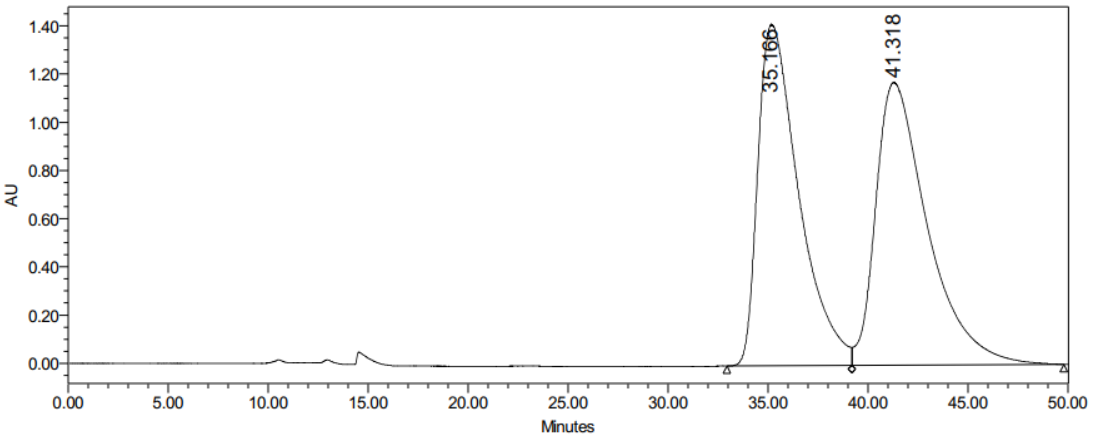


Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4078; Processing Method: 000

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	16.371	6031296	8.18	220154
2	2998 PDA 220.0 nm (2998 (210-400)nm)	17.160	67728828	91.82	2104048

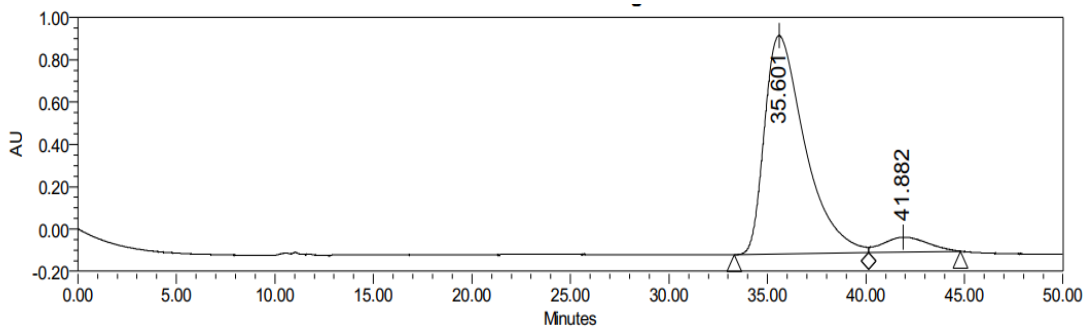
HPLC spectra of product **4h**



Channel: 2998; Processed Channel: 2998 PDA 220.0 nm (2998 (210-400)nm); Result Id: 4167; Processing Method: 000

Processed Channel Descr.: 2998 PDA 220.0 nm (2998 (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220.0 nm (2998 (210-400)nm)	35.166	201358830	48.79	1417620
2	2998 PDA 220.0 nm (2998 (210-400)nm)	41.318	211358477	51.21	1173738



Peak Results

	Name	RT	Area	Height	% Area
1		35.601	147431523	1033980	92.91
2		41.882	11245692	71091	7.09

References

1 D. A. Evans, J. S. Johnson and E. J. Olhava, *J. Am. Chem. Soc.*, 2000, **122**, 1635–1649.
2 S. R. Smith, S. M. Leckie, R. Holmes, J. Douglas, C. Fallan, P. Shapland, D. Pryde, A. M. Z. Slawin and A. D. Smith, *Org. Lett.*, 2014, **16**, 2506–2509.
3 J. K. Kozlowski, N. P. Rath and C. D. Spilling, *Tetrahedron*, 1995, **51**, 6385–6396.