

Supporting Information for:

Phosphoramidate prodrugs of a butyrophilin ligand display extended serum stability and potent V γ 9V δ 2 T cell stimulation

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¹*Department of Chemistry, University of Iowa, Iowa City, Iowa 52242-1294, United States*

²*Department of Pharmaceutical Sciences, University of Connecticut, Storrs, CT 06269-3092, United States*

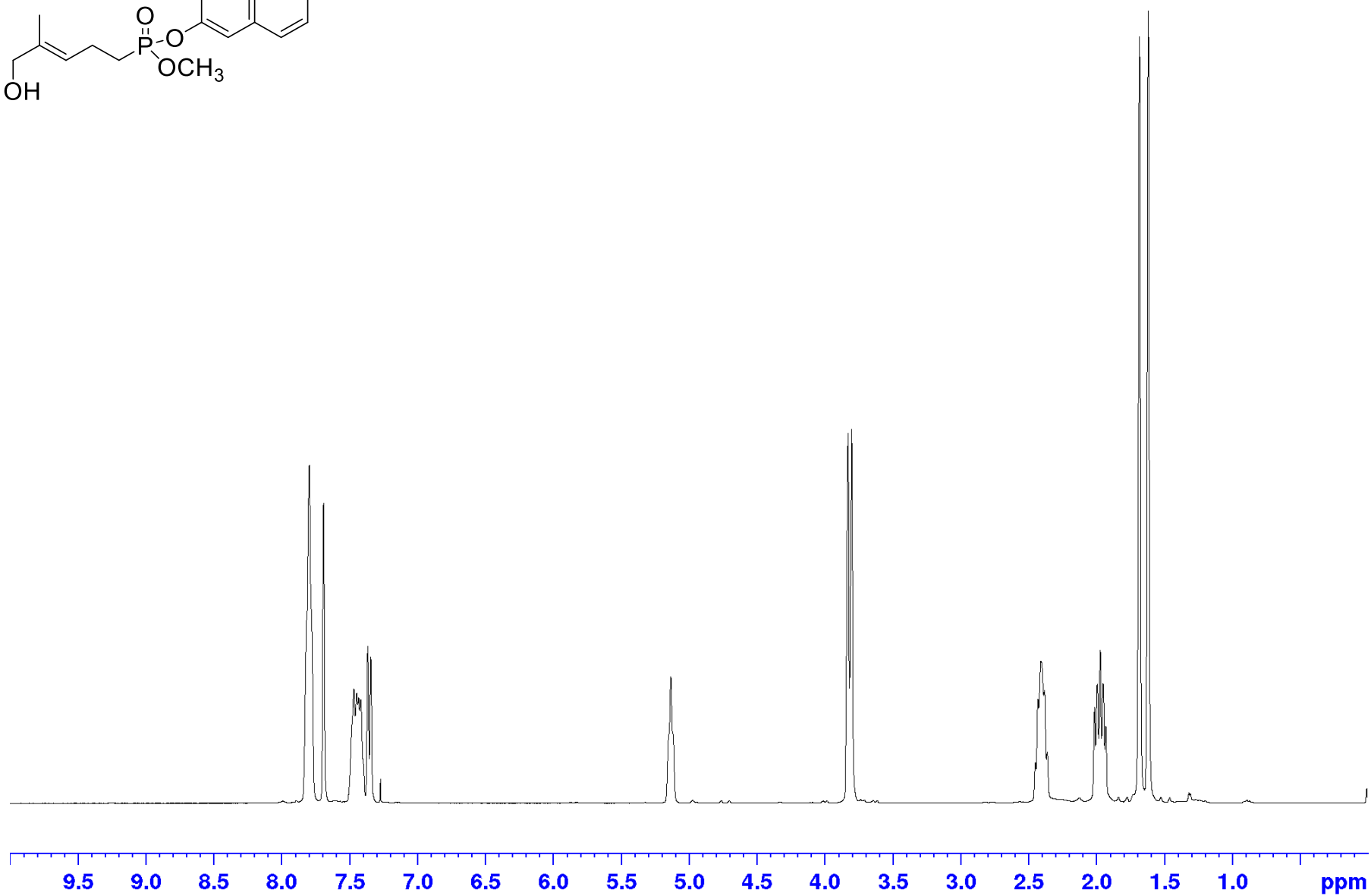
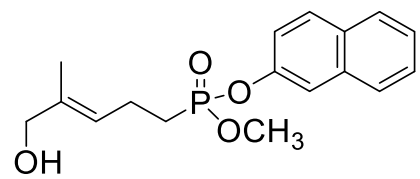
³*Institute for Systems Genomics, University of Connecticut, Storrs, CT 06269-3092, United States*

⁴*Department of Pharmacology, University of Iowa, Iowa City, Iowa 52242-1109, United States*

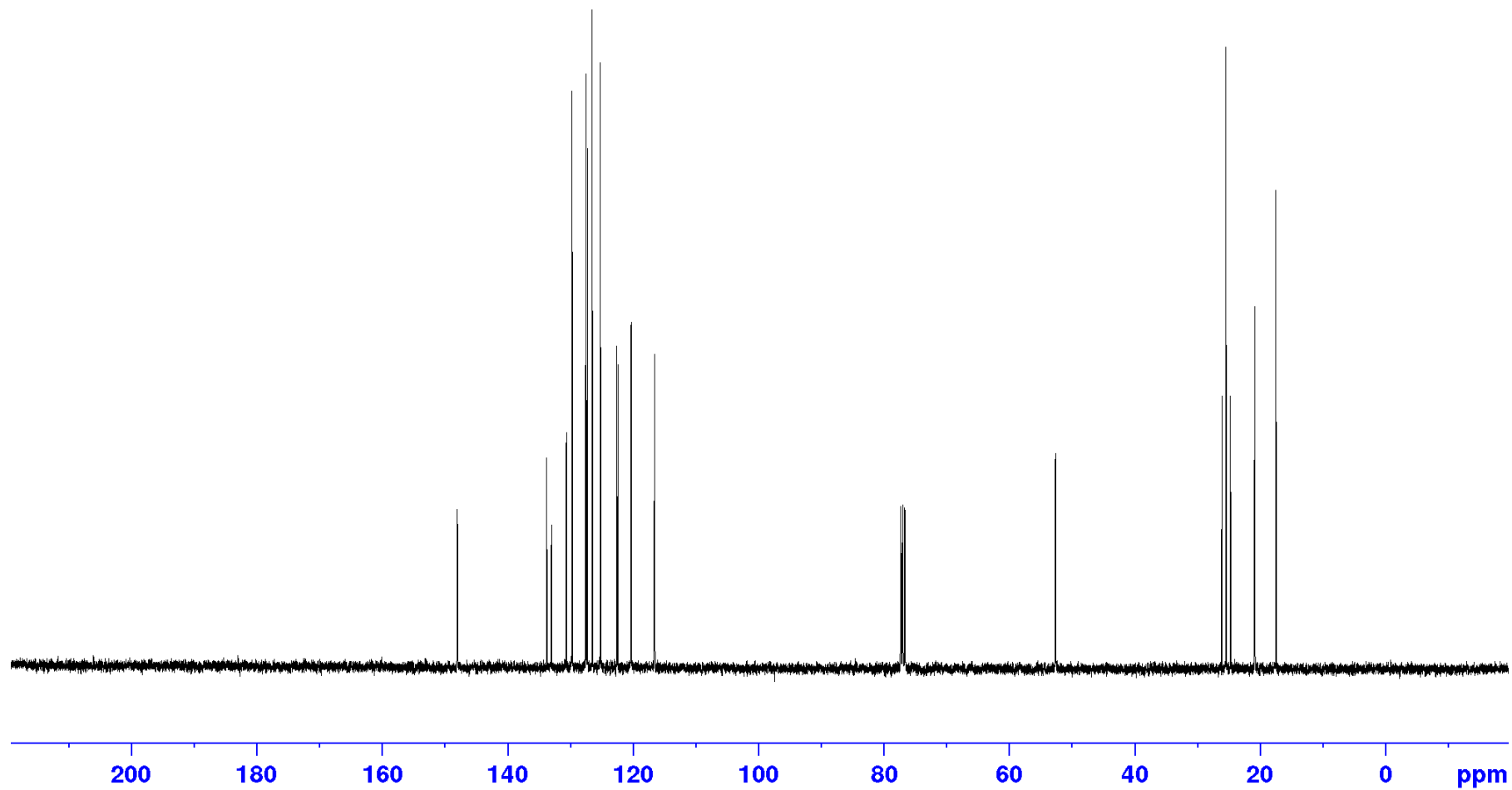
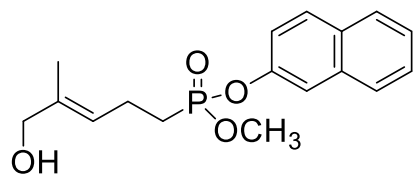
Supplemental Table of Contents

¹ H NMR spectrum of compound 6c (300 MHz)	S3
¹³ C NMR spectrum of compound 6c (75 MHz)	S4
³¹ P NMR spectrum of compound 6c (121 MHz)	S5
¹ H NMR spectrum of compound 9b (500 MHz)	S6
¹³ C NMR spectrum of compound 9b (125 MHz)	S7
³¹ P NMR spectrum of compound 9b (202MHz)	S8
¹ H NMR spectrum of compound 9a (500 MHz)	S9
¹³ C NMR spectrum of compound 9a (125 MHz)	S10

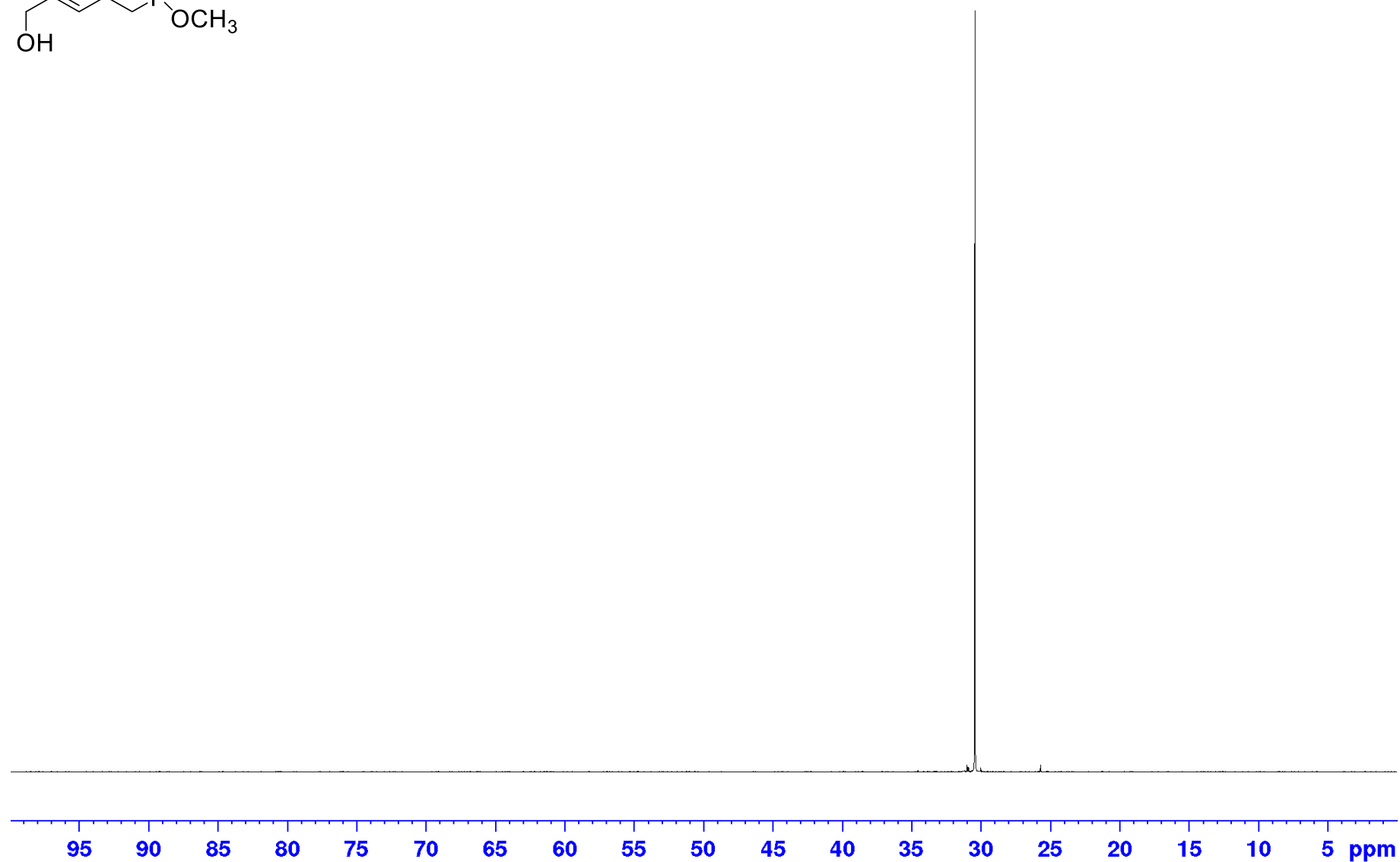
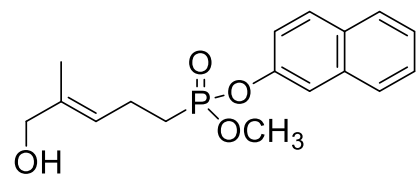
³¹ P NMR spectrum of compound 9a (161 MHz)	S11
¹ H NMR spectrum of compound 9c (400 MHz)	S12
¹³ C NMR spectrum of compound 9c (100 MHz)	S13
³¹ P NMR spectrum of compound 9c (202 MHz)	S14
¹ H NMR spectrum of compound 9d (400 MHz)	S15
¹³ C NMR spectrum of compound 9d (100 MHz)	S16
³¹ P NMR spectrum of compound 9d (161 MHz)	S17
¹ H NMR spectrum of compound 9e (400 MHz)	S18
¹³ C NMR spectrum of compound 9e (100 MHz)	S19
³¹ P NMR spectrum of compound 9e (161 MHz)	S20
¹ H NMR spectrum of compound 9f (400 MHz)	S21
¹³ C NMR spectrum of compound 9f (100 MHz)	S22
³¹ P NMR spectrum of compound 9f (161 MHz)	S23
¹ H NMR spectrum of compound 9g (400 MHz)	S24
¹³ C NMR spectrum of compound 9g (100 MHz)	S25
³¹ P NMR spectrum of compound 9g (161 MHz)	S26
¹ H NMR spectrum of compound 9h (500 MHz)	S27
¹³ C NMR spectrum of compound 9h (125 MHz)	S28
³¹ P NMR spectrum of compound 9h (202 MHz)	S29
¹ H NMR spectrum of compound 9i (500 MHz)	S30
¹³ C NMR spectrum of compound 9i (125 MHz)	S31
³¹ P NMR spectrum of compound 9i (161 MHz)	S32
HPLC traces for assayed compounds 9a - 9i .	S33



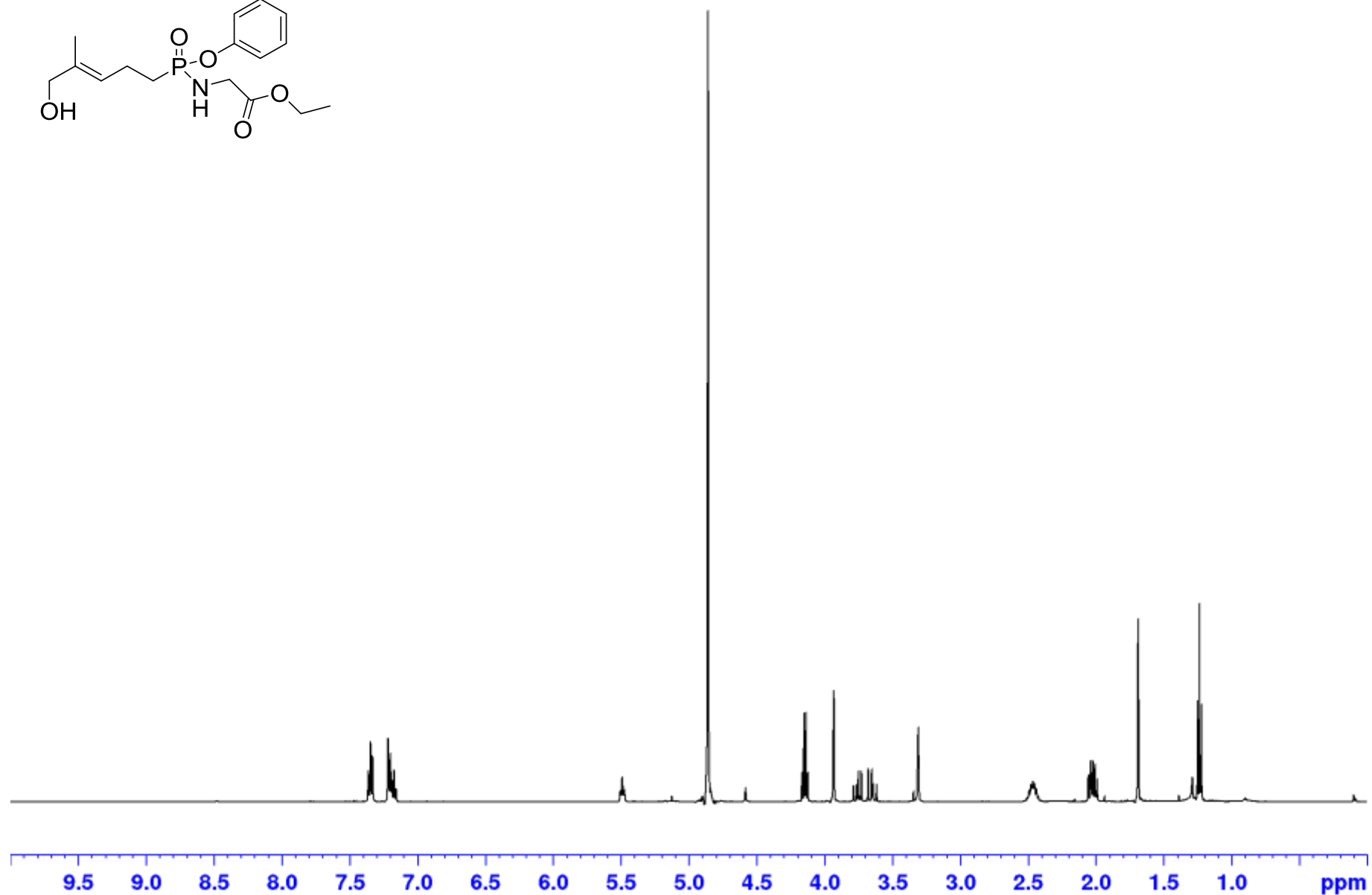
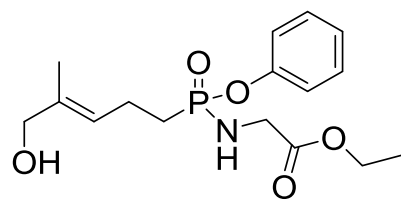
300 MHz ¹H NMR spectrum of compound 6c.



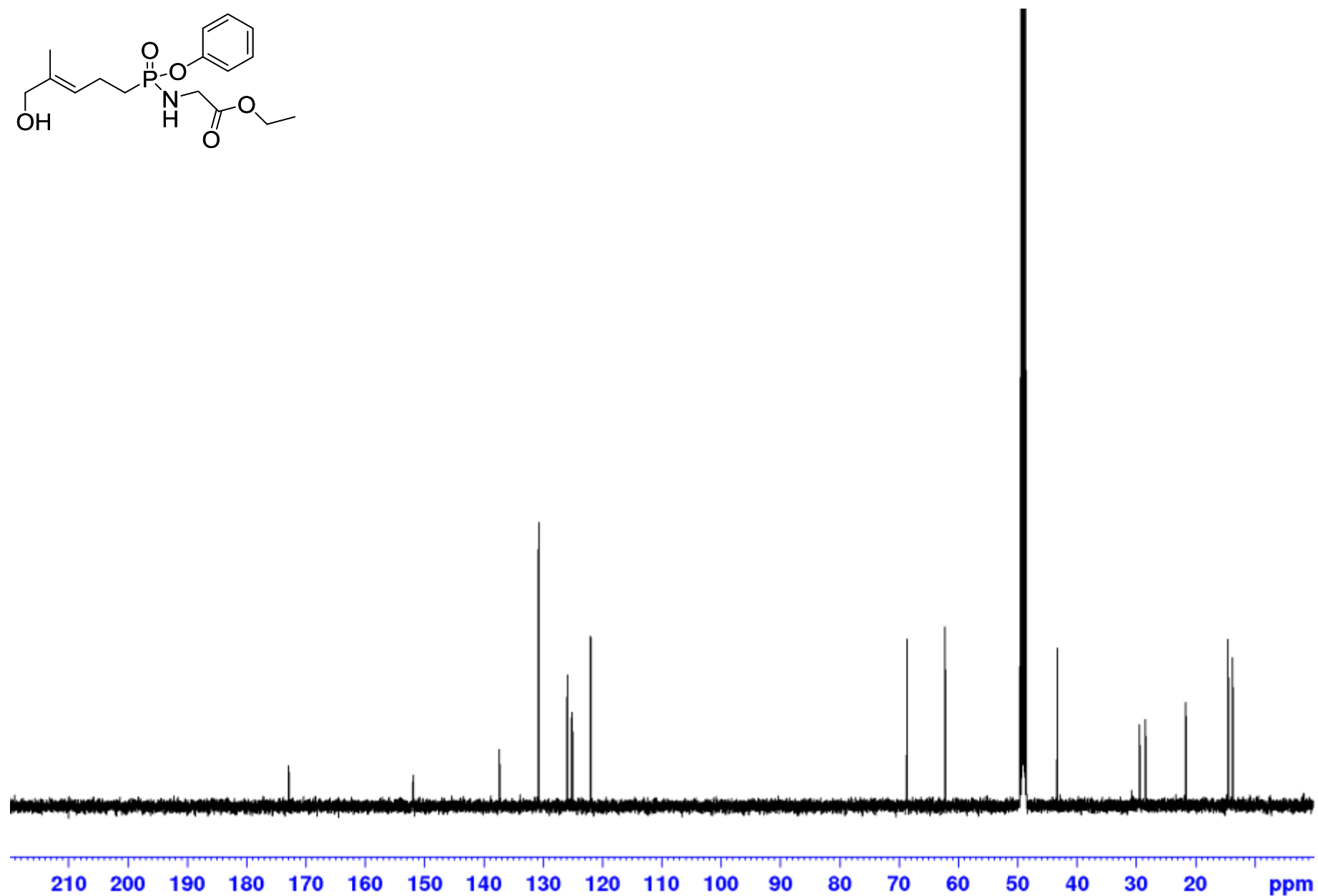
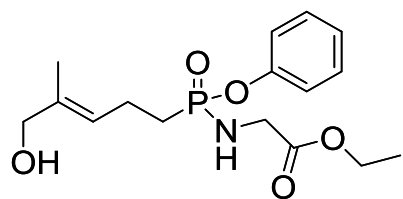
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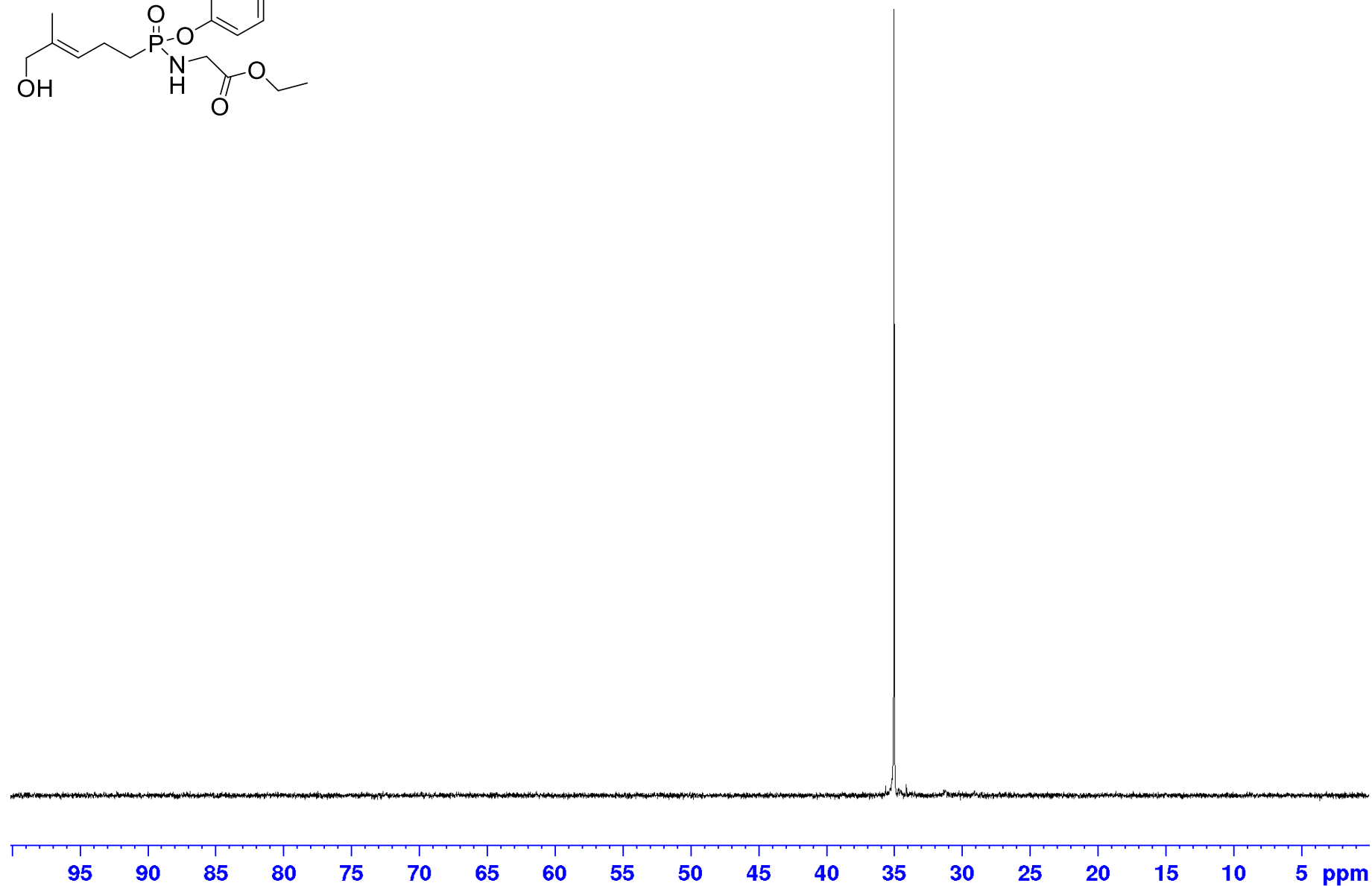
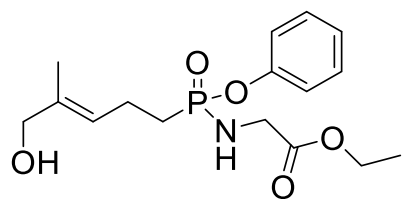
121 MHz ^{31}P NMR spectrum of compound **6c**.



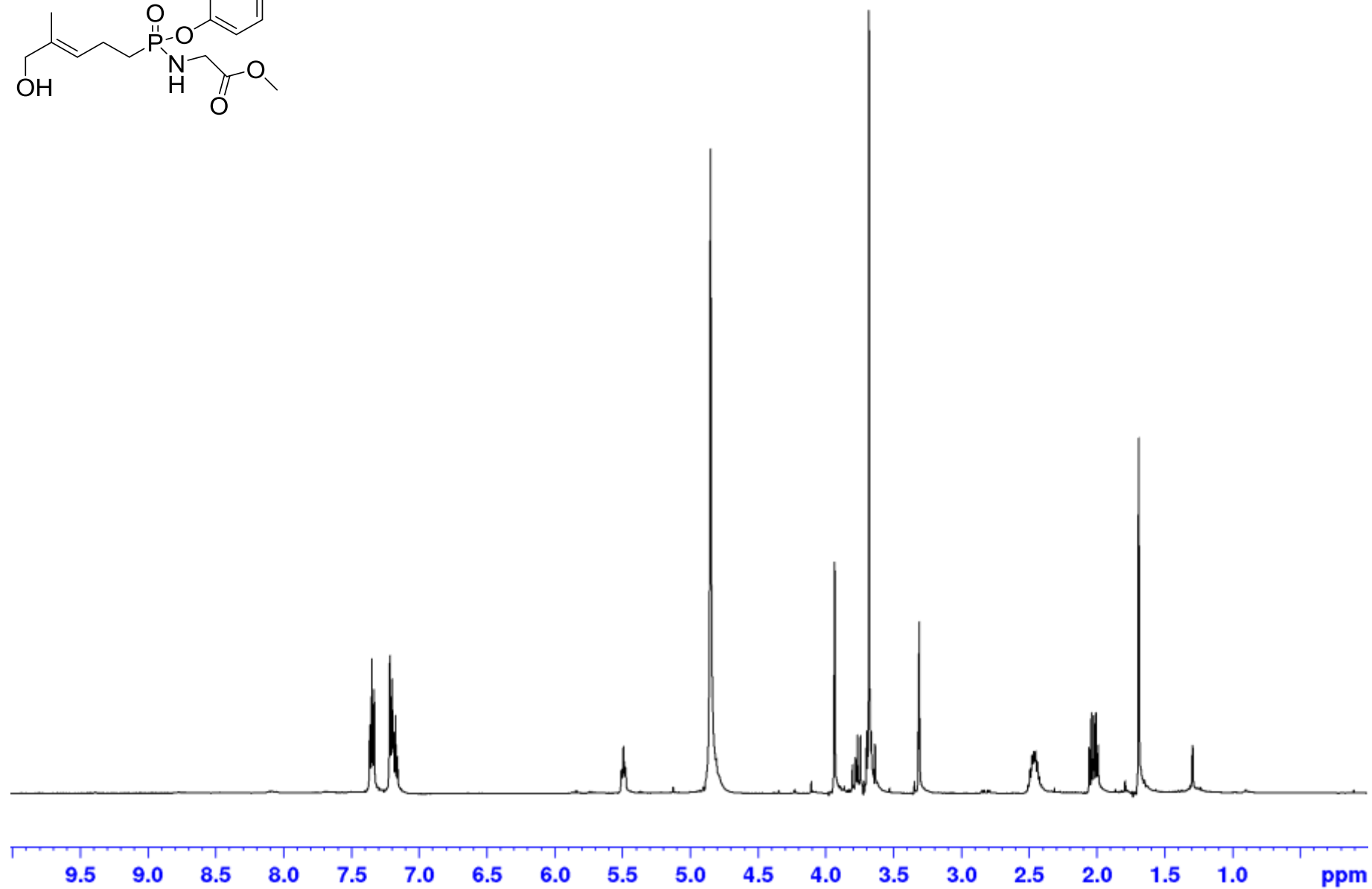
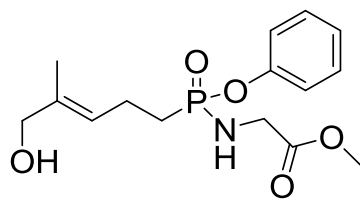
500 MHz ^1H NMR spectrum of compound **9b**.



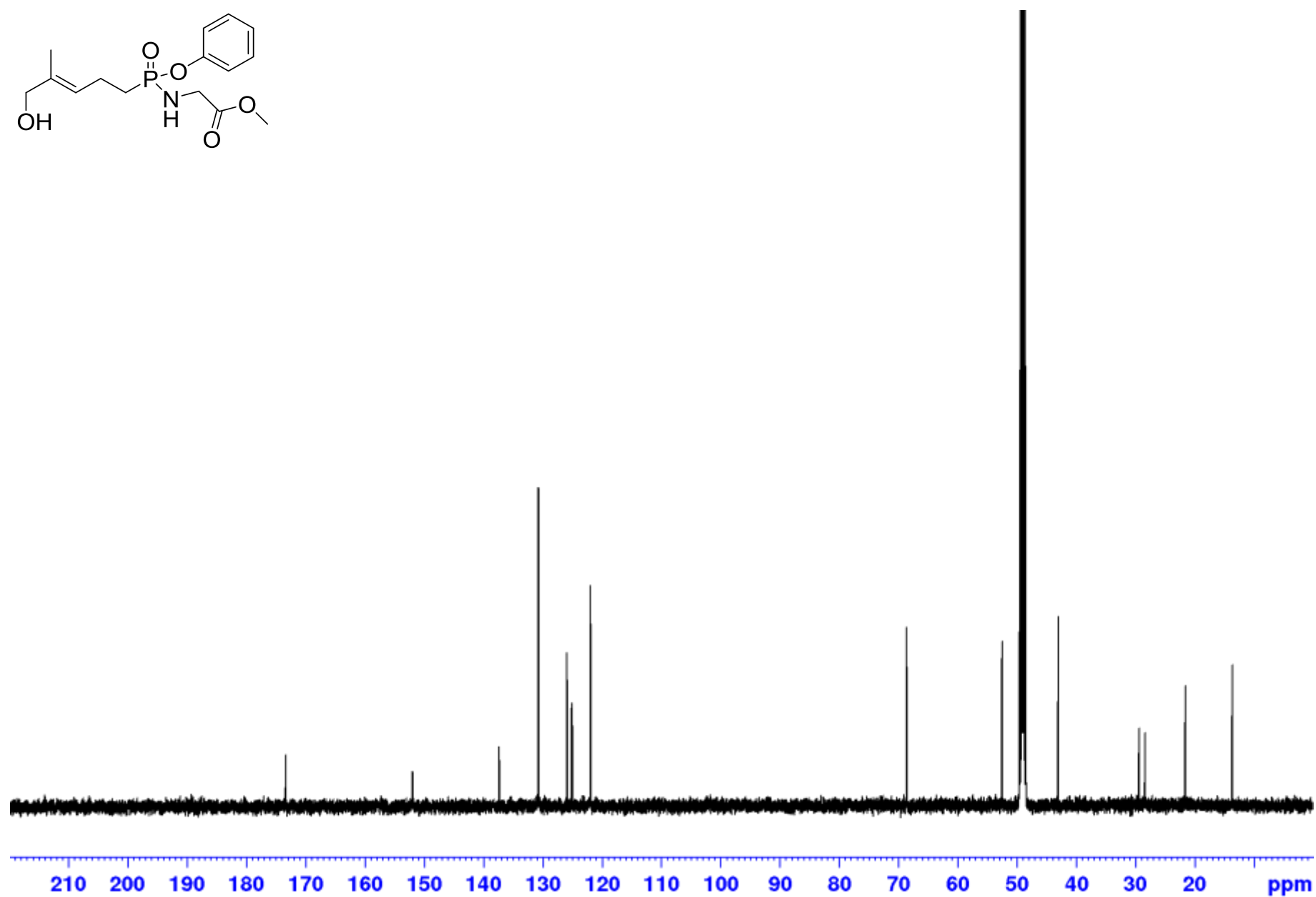
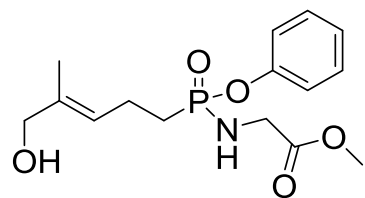
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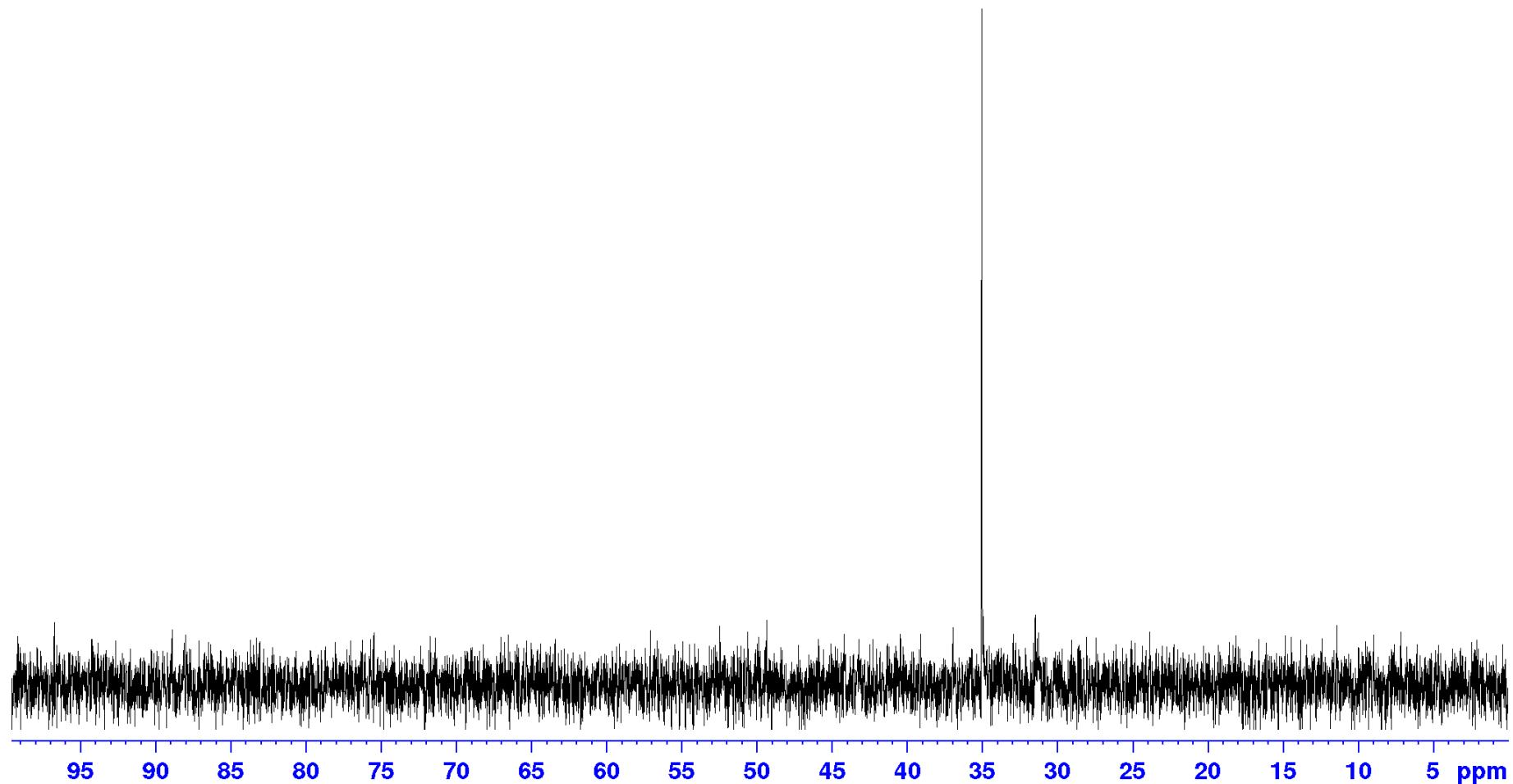
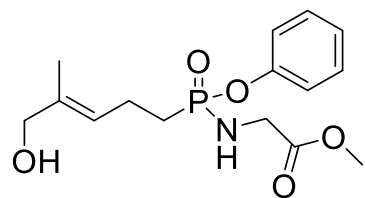
202 MHz ^{31}P NMR spectrum of compound **9b**.



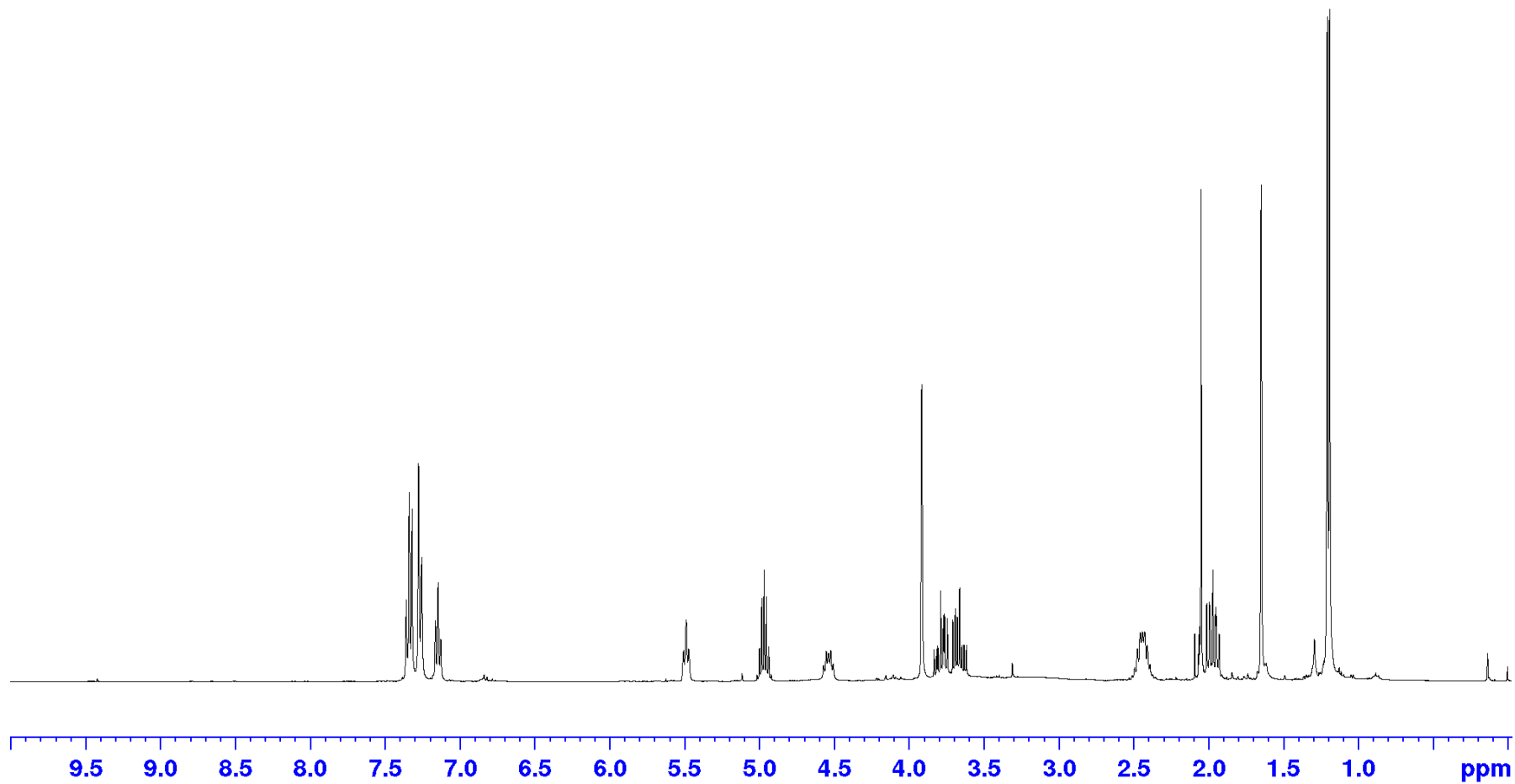
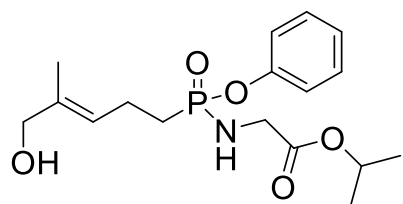
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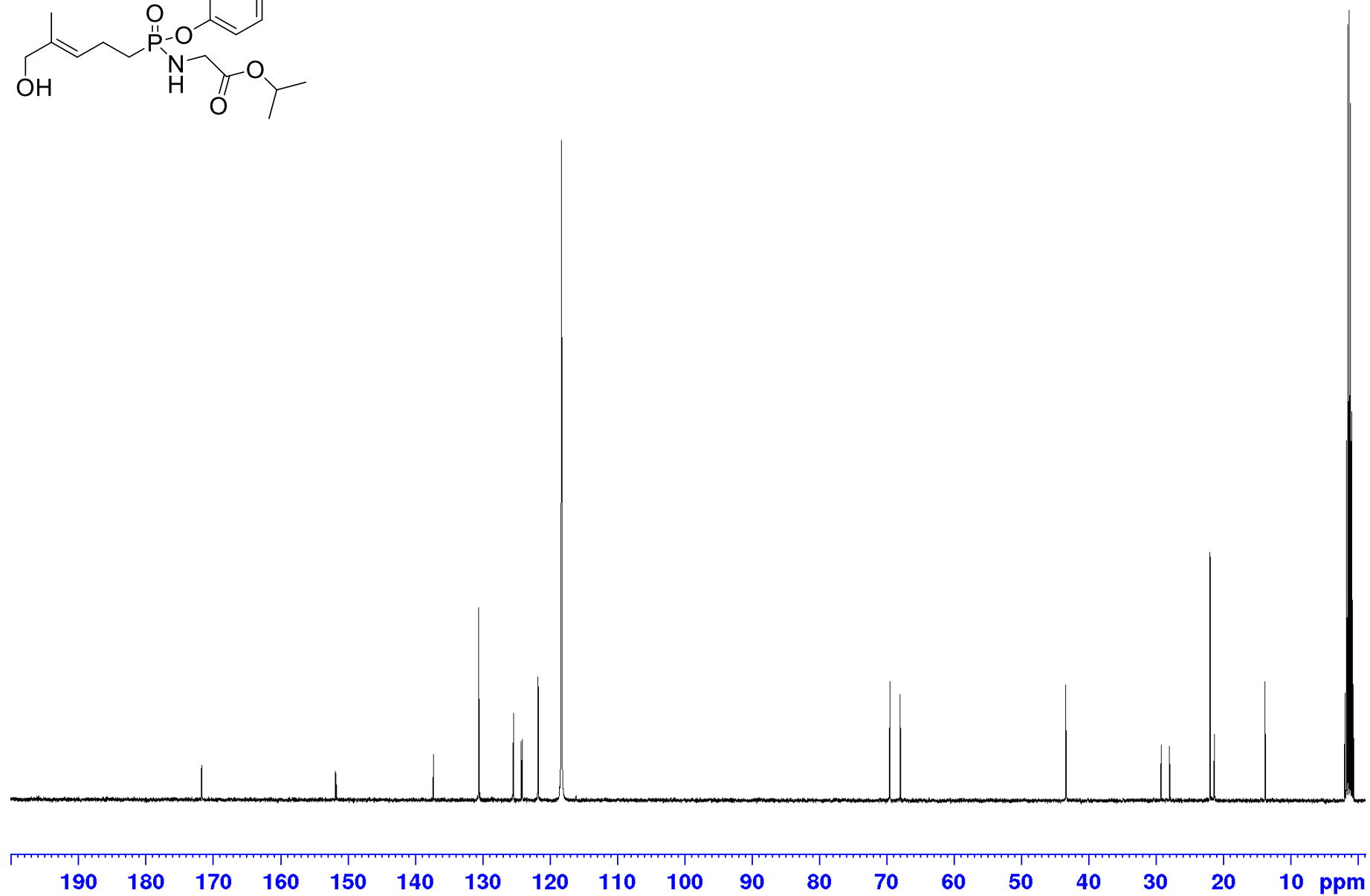
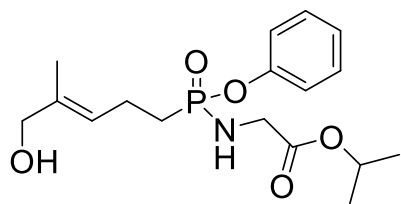


125 MHz ¹³C NMR spectrum of compound 9a.

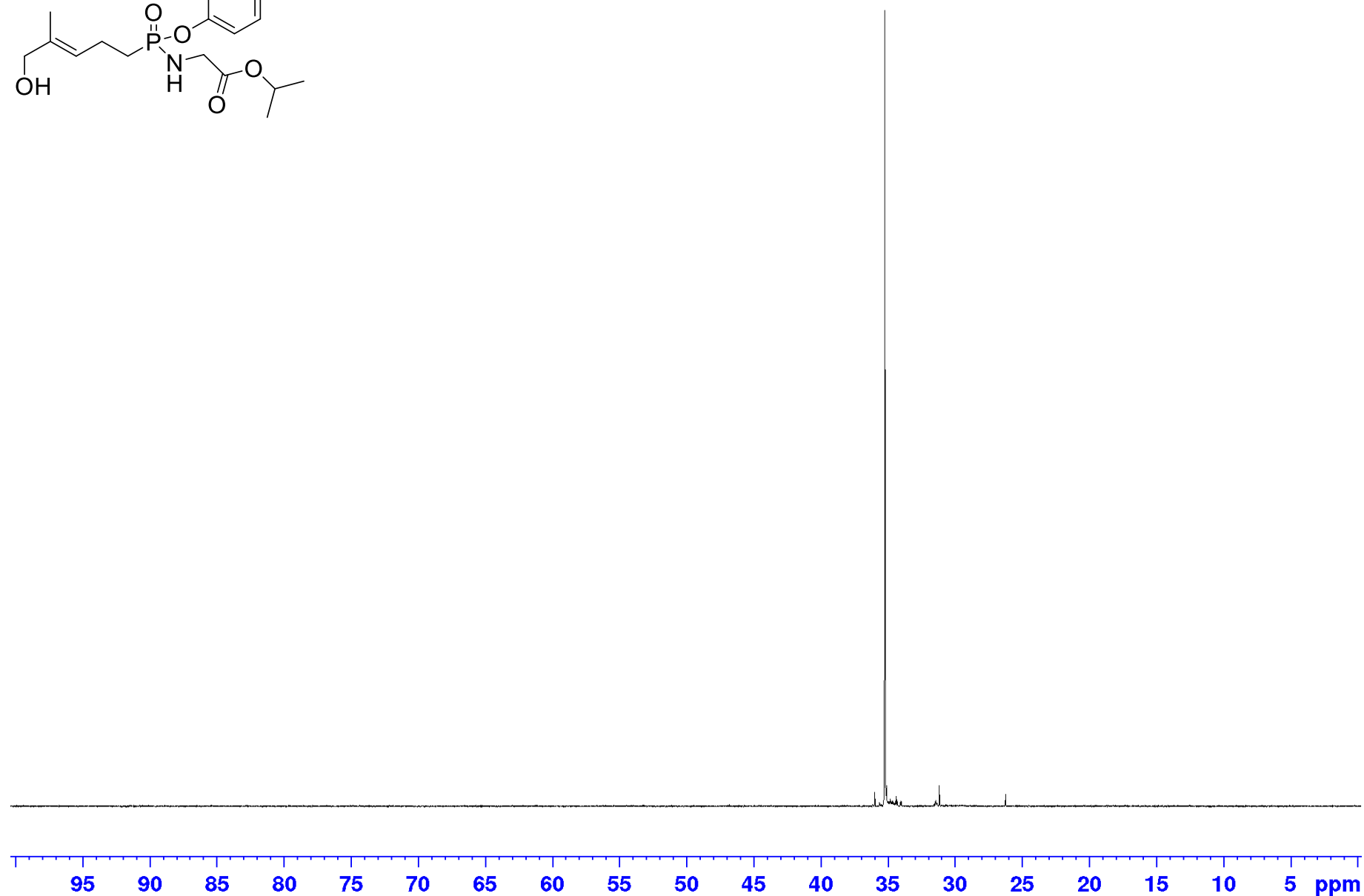
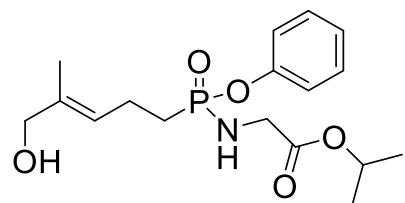


161 MHz ^{31}P NMR spectrum of compound 9a.

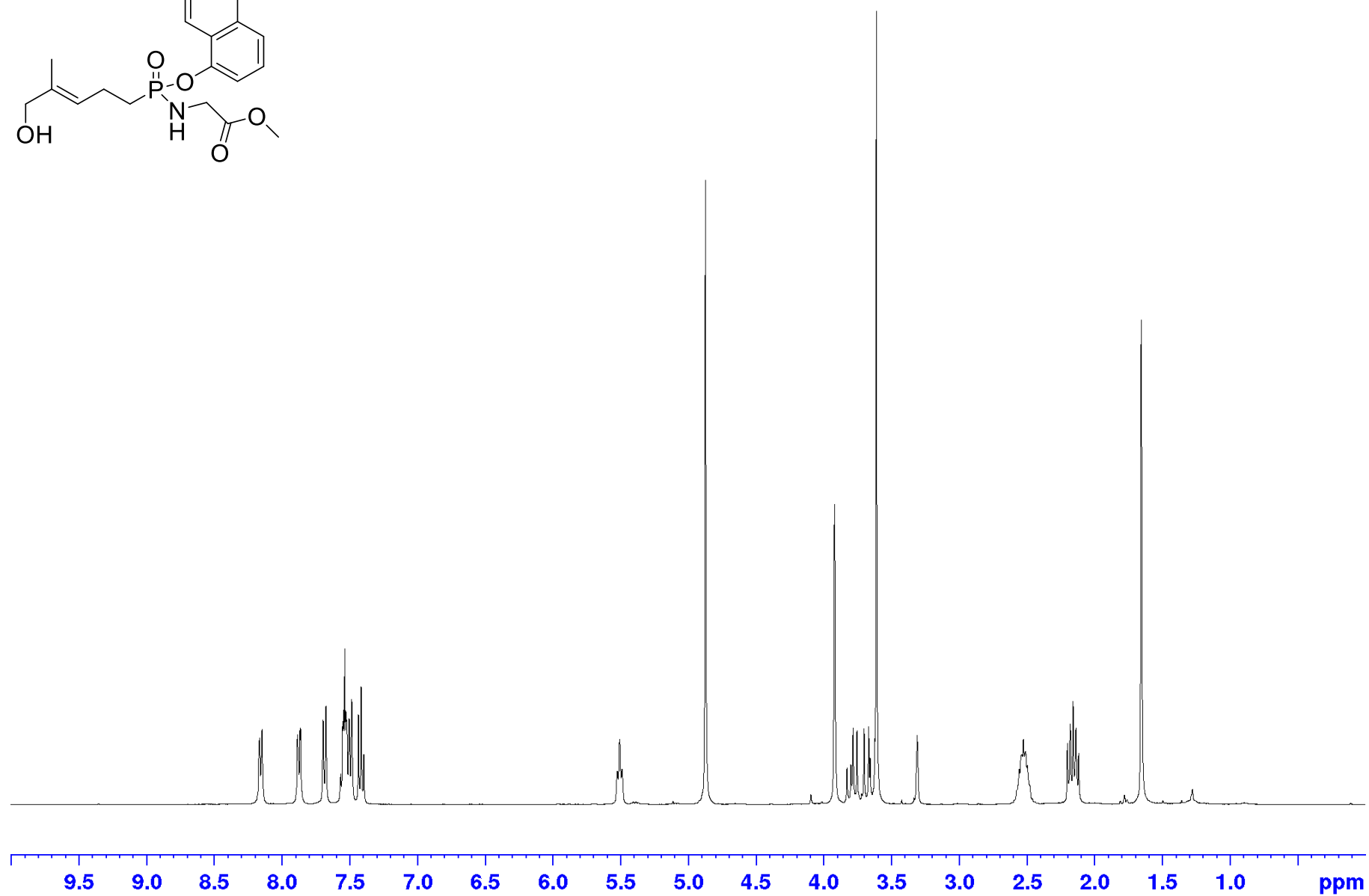
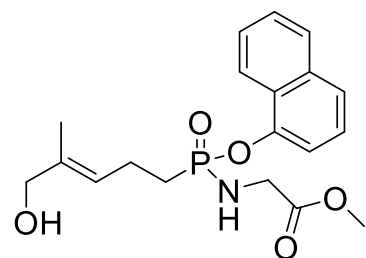




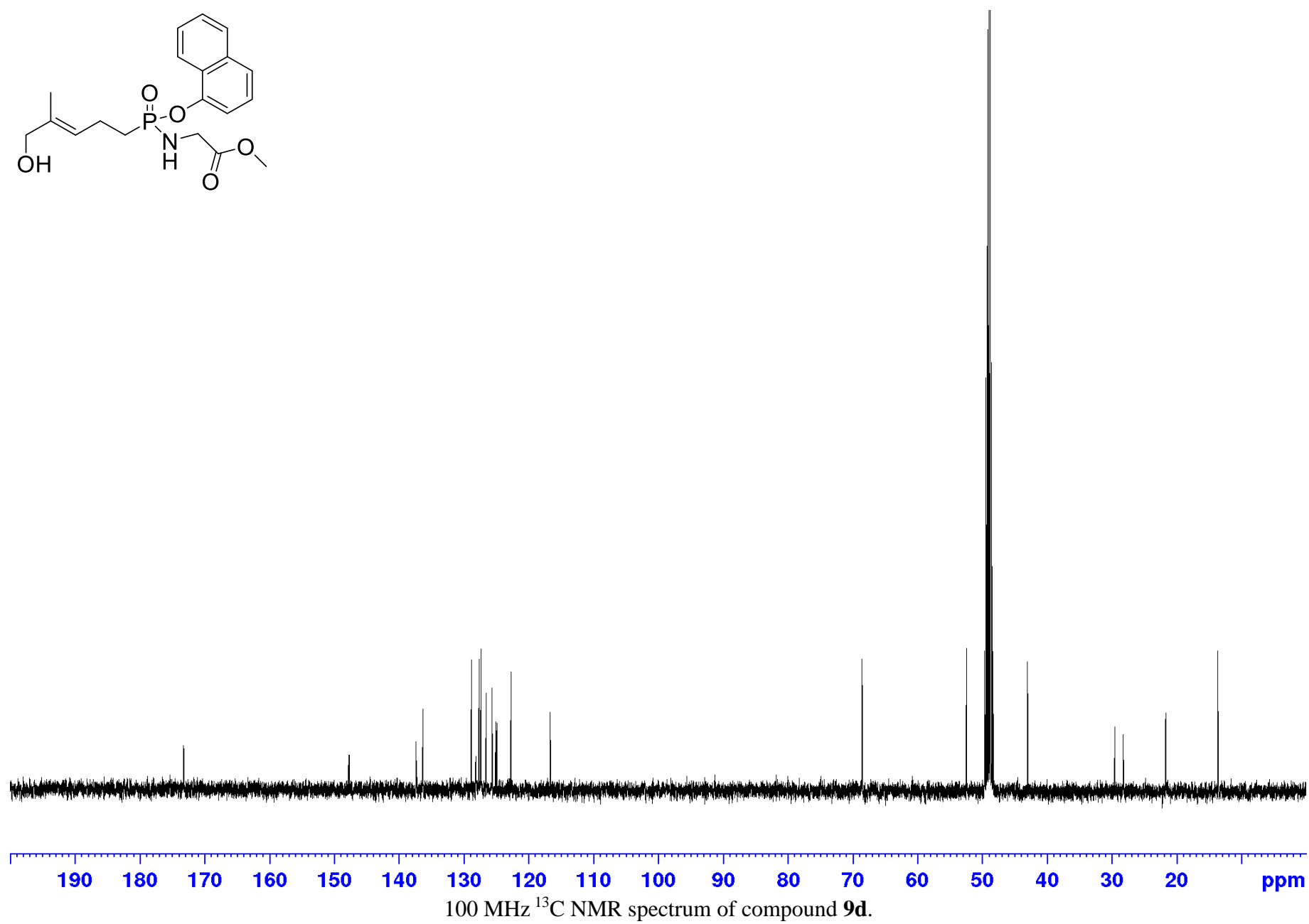
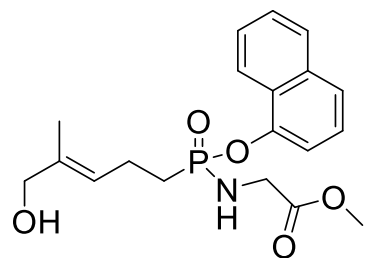
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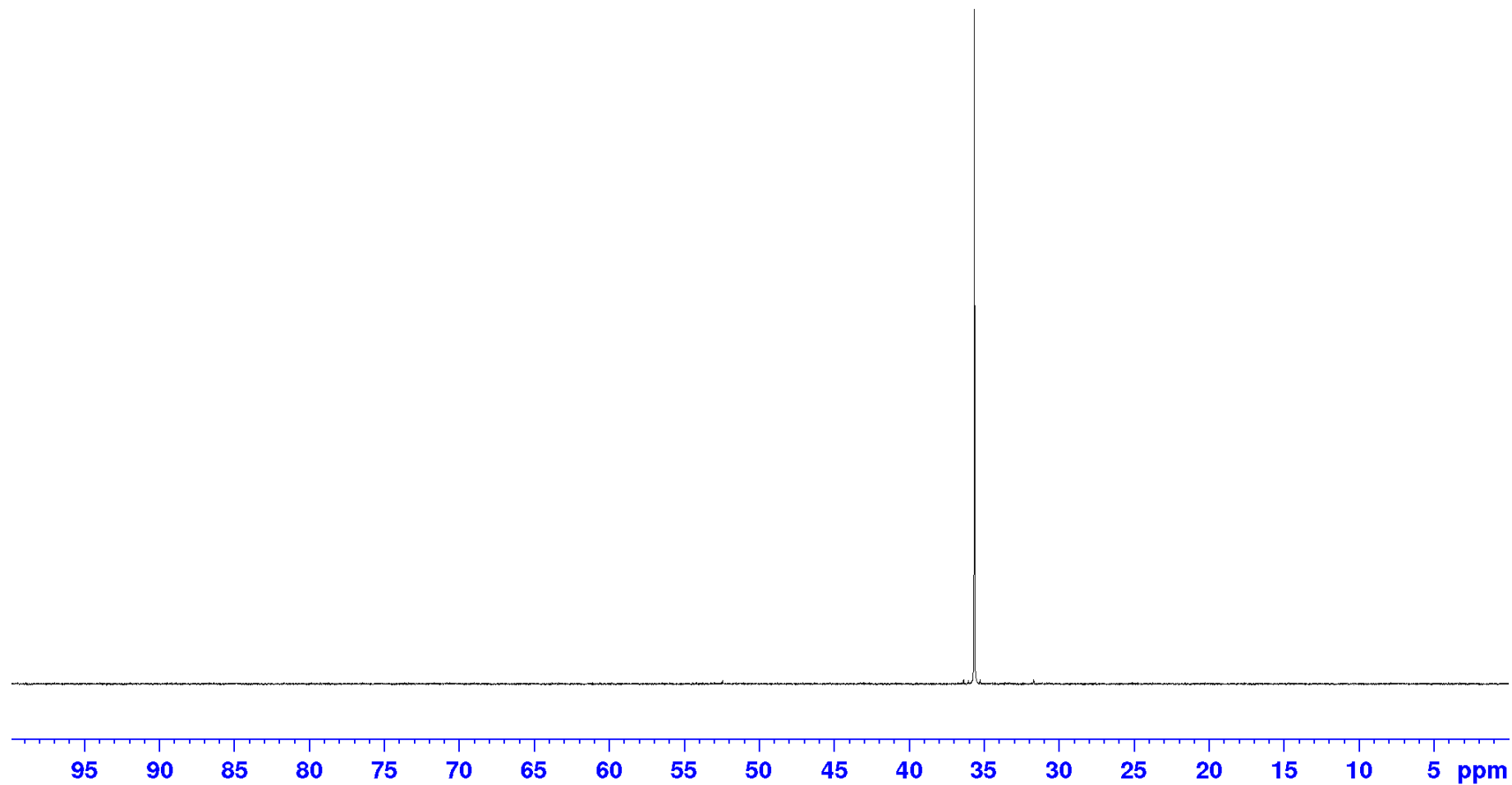
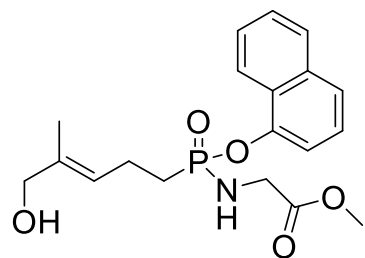


202 MHz ^{31}P NMR spectrum of compound 9c.

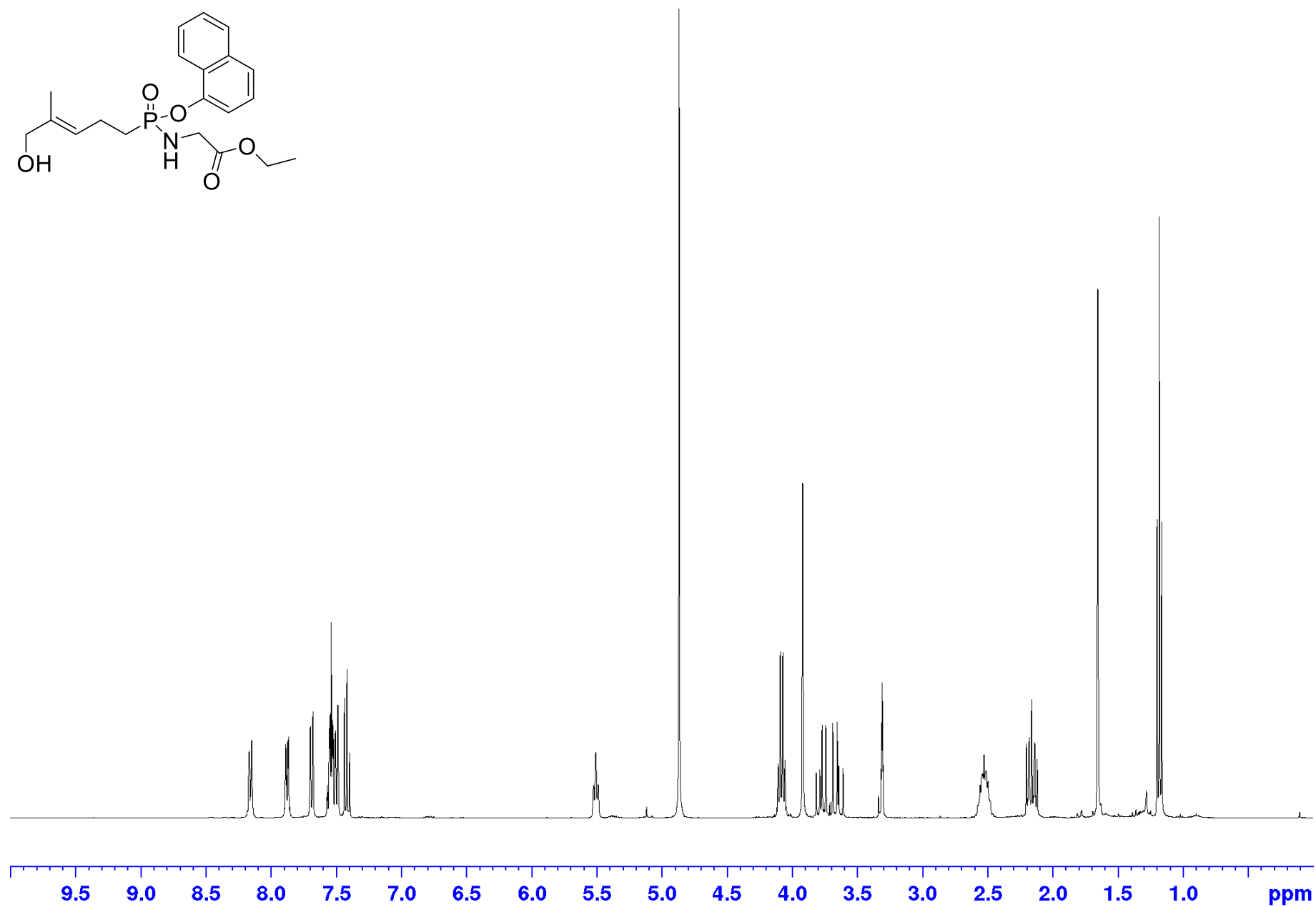
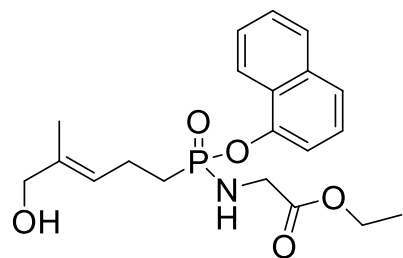


400 MHz ^1H NMR spectrum of compound **9d**.
S15

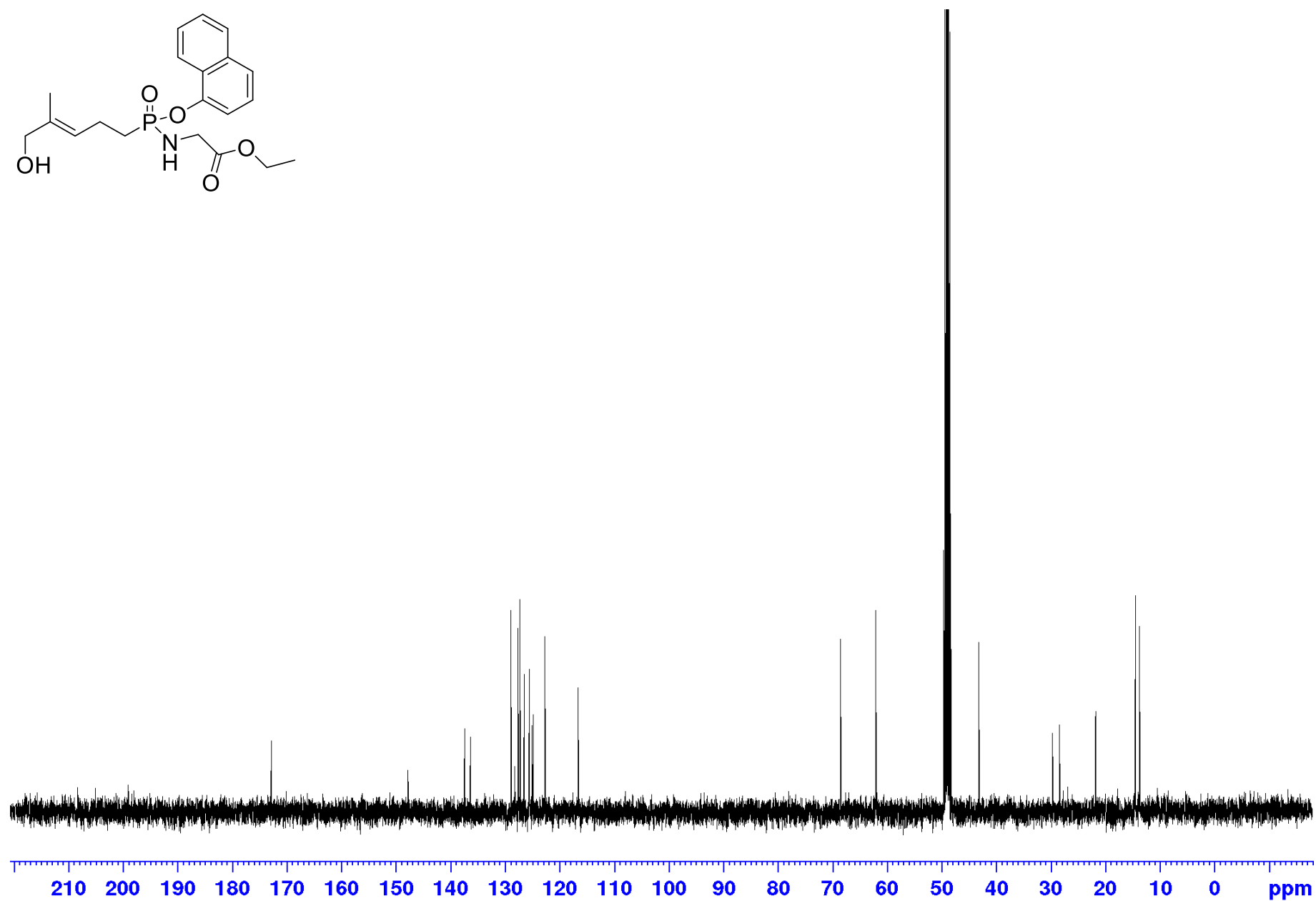
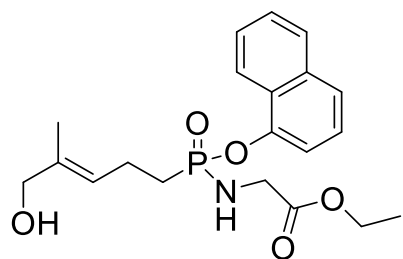




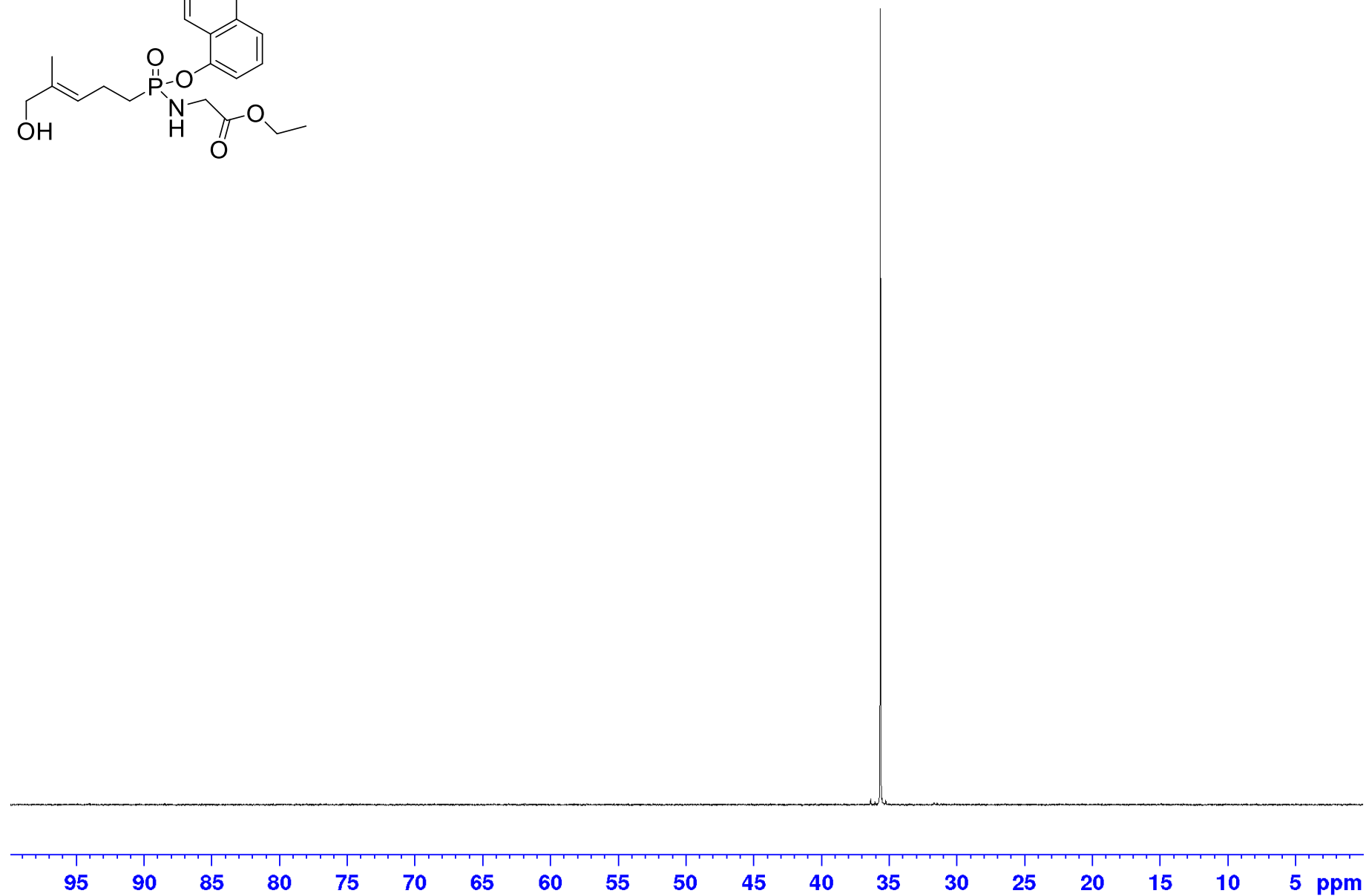
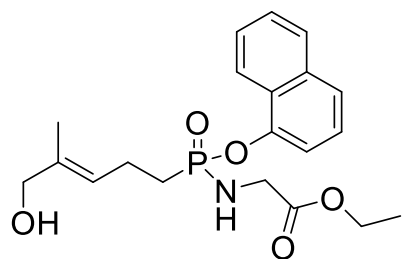
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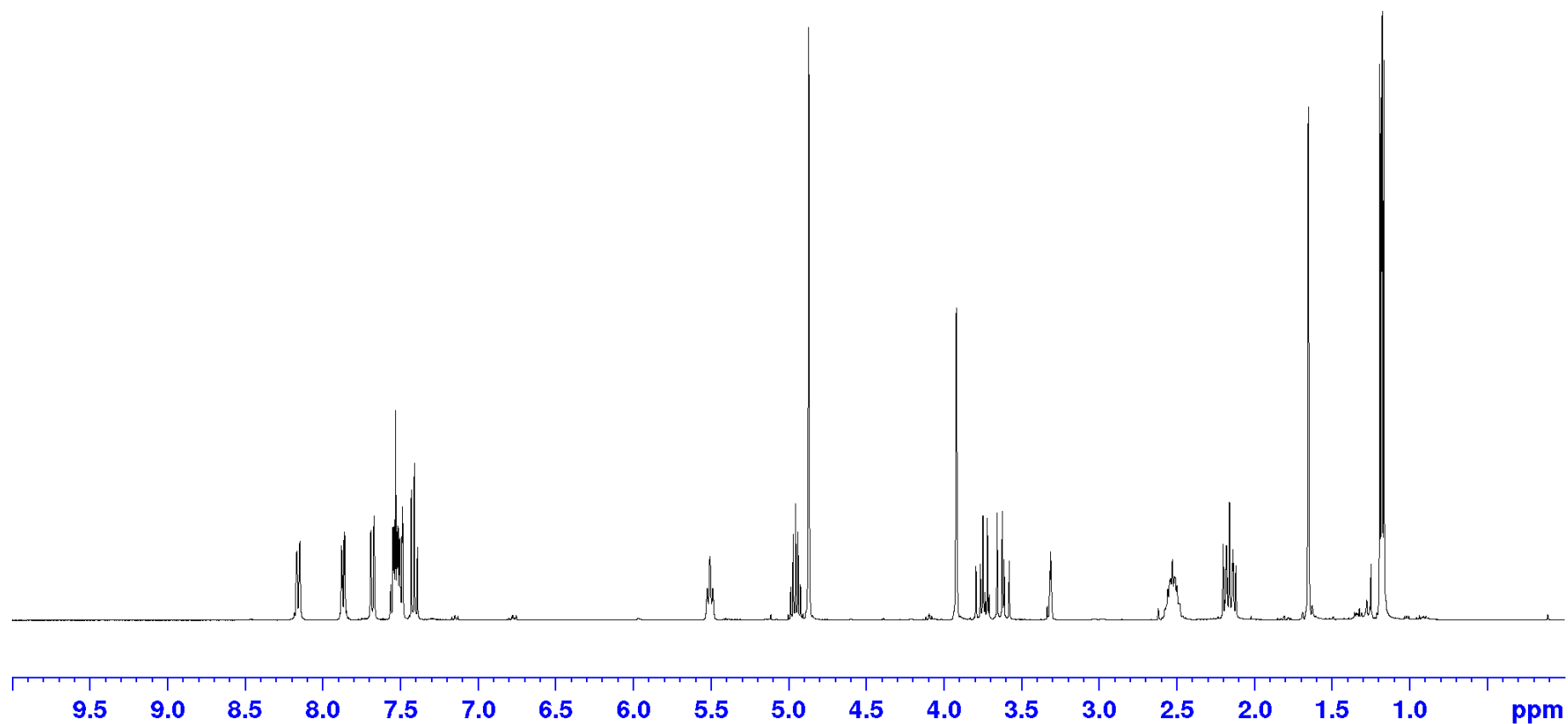
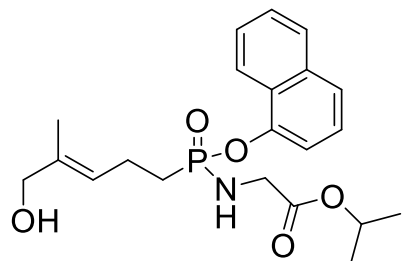
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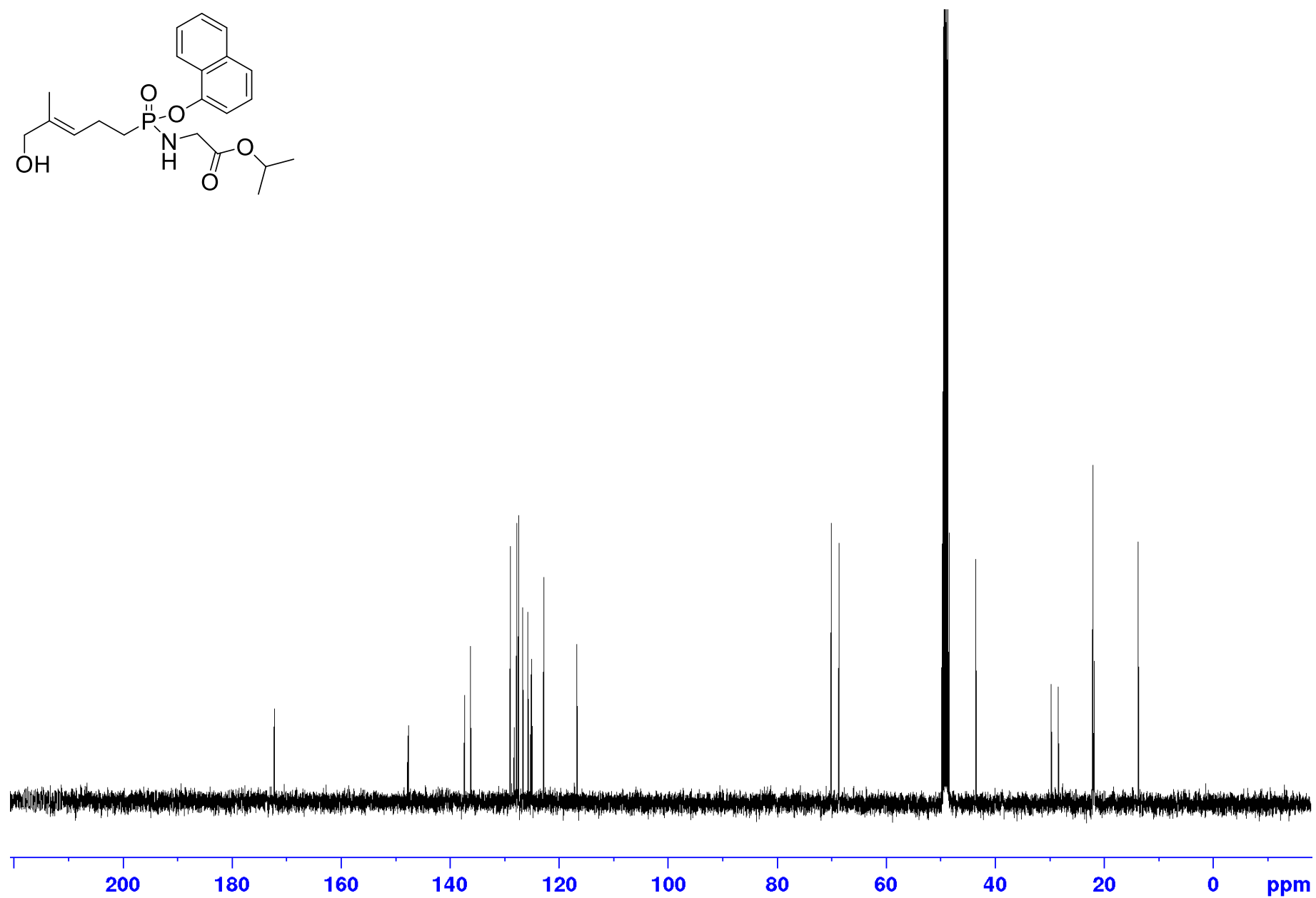
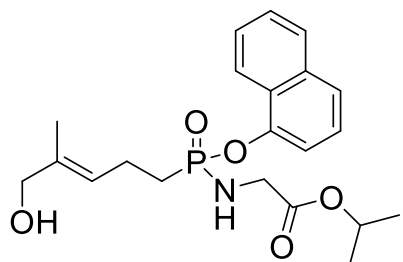
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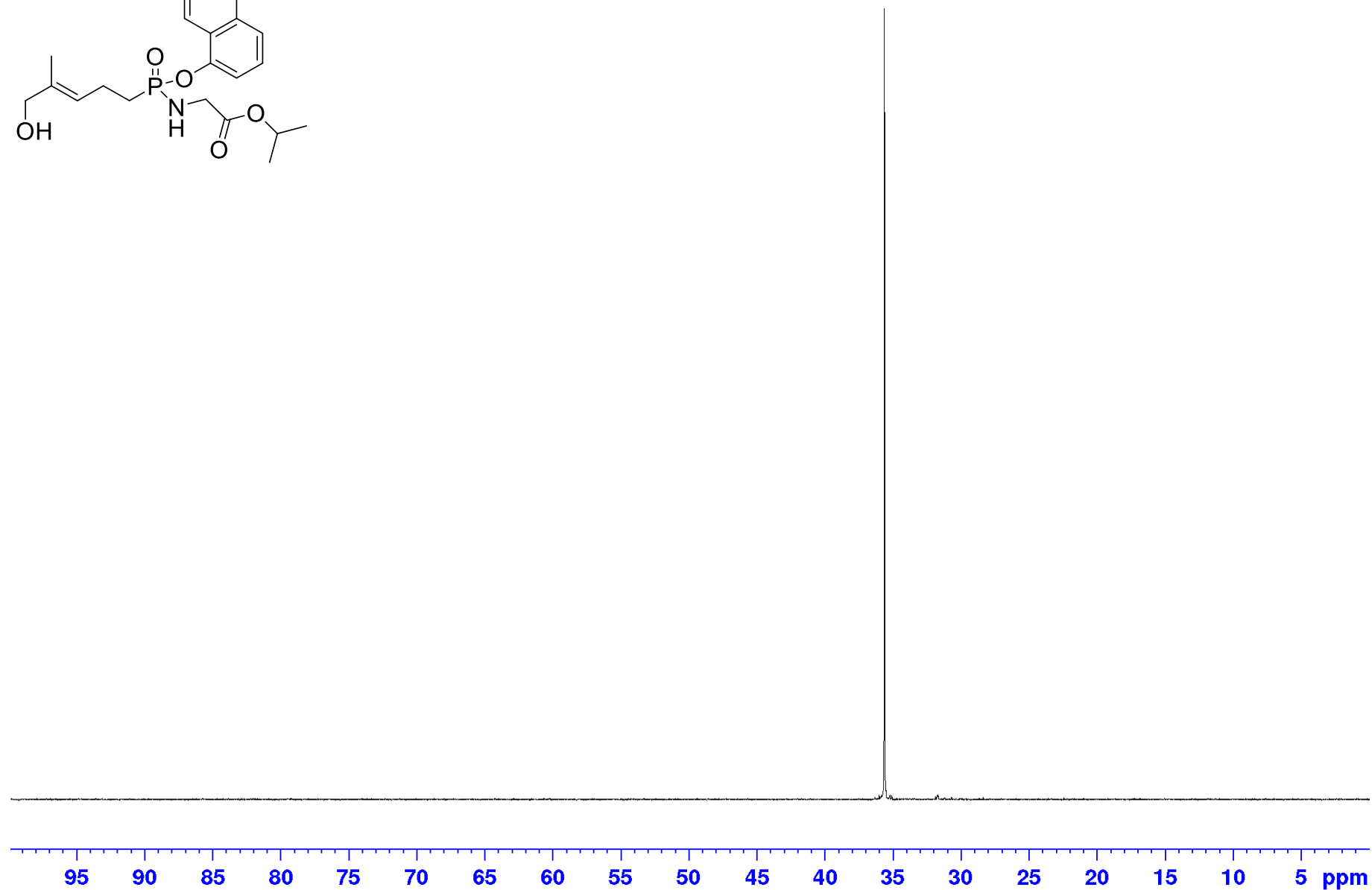
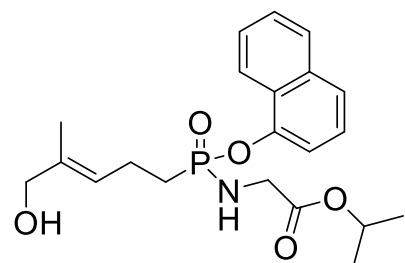
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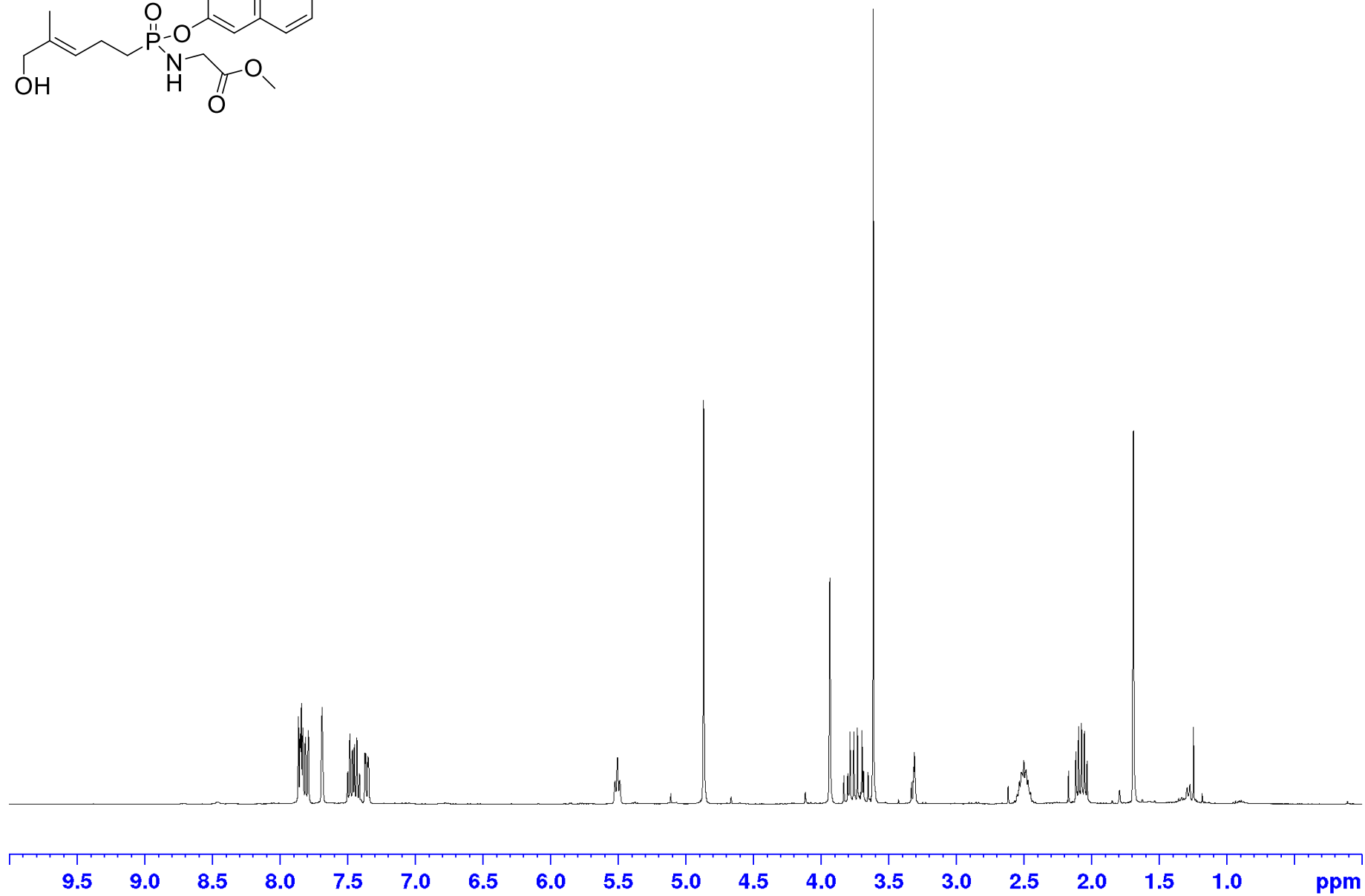
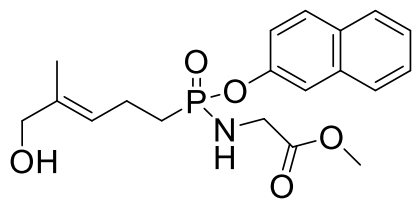
400 MHz ^1H NMR spectrum of compound **9f**.



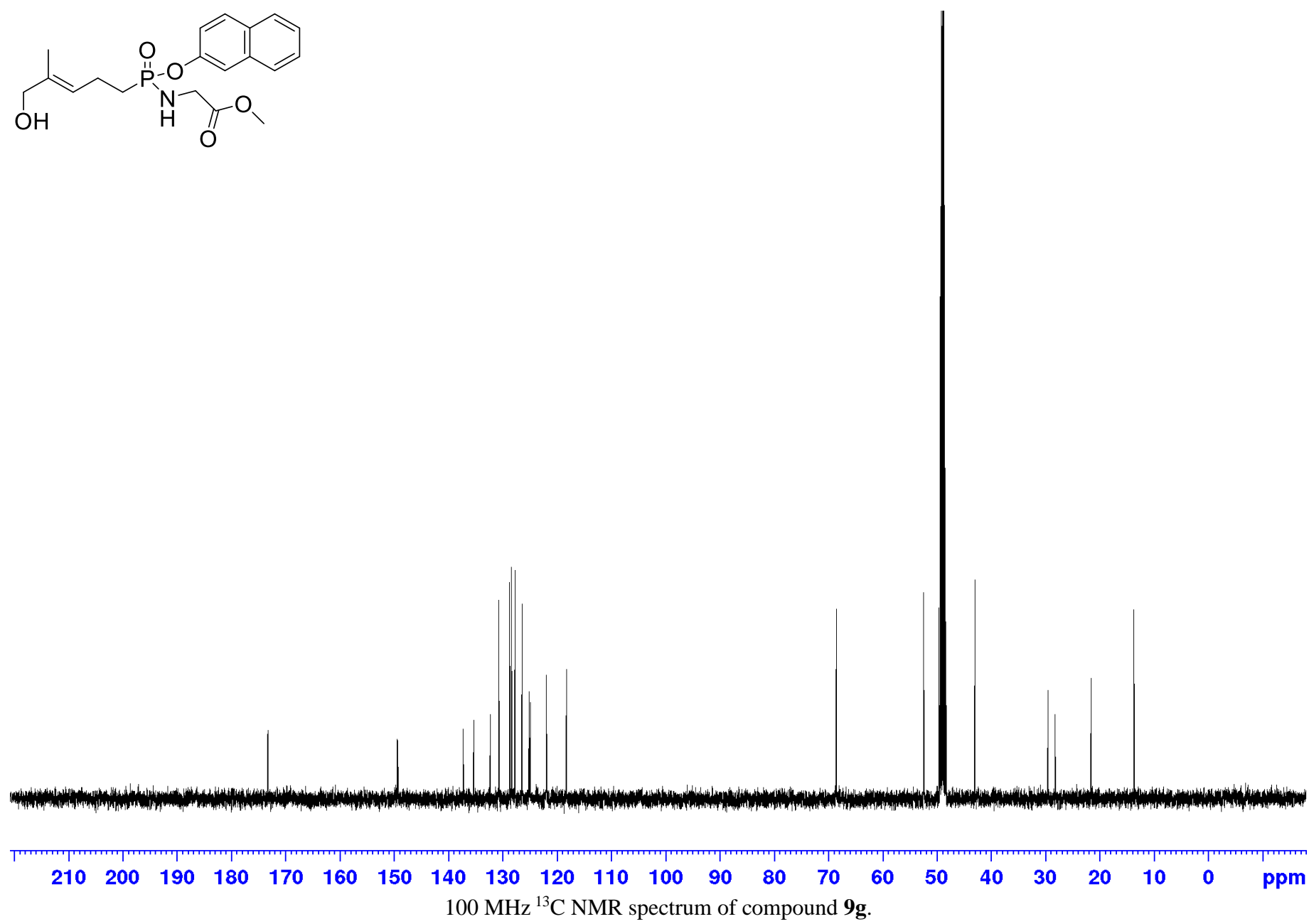
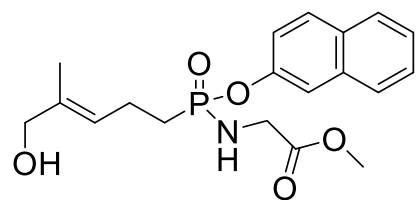
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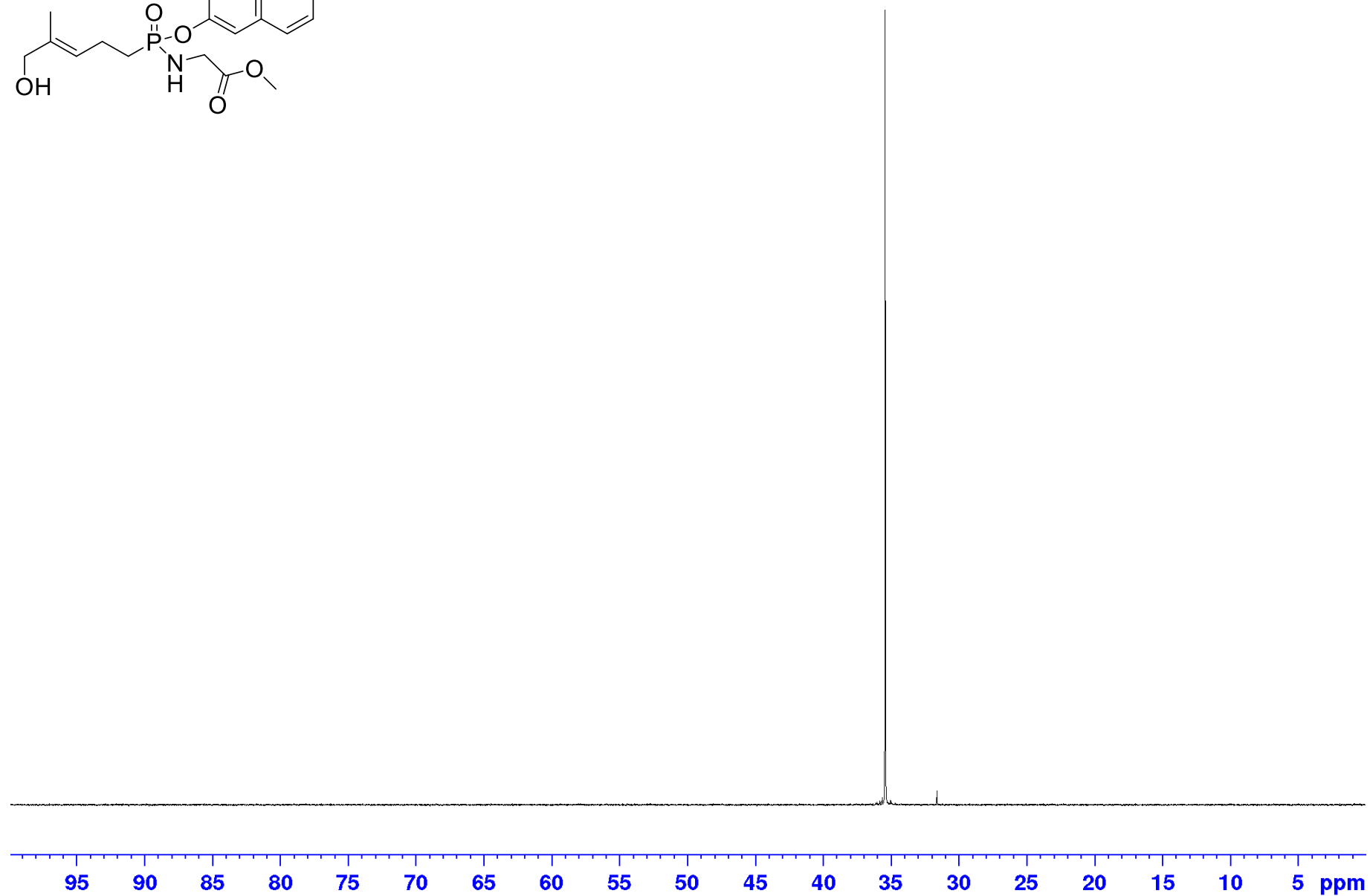
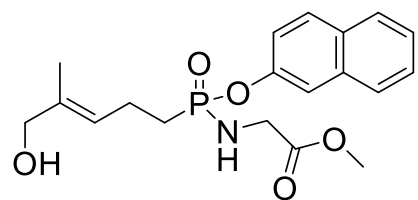


161 MHz ^{31}P NMR spectrum of compound 9f.

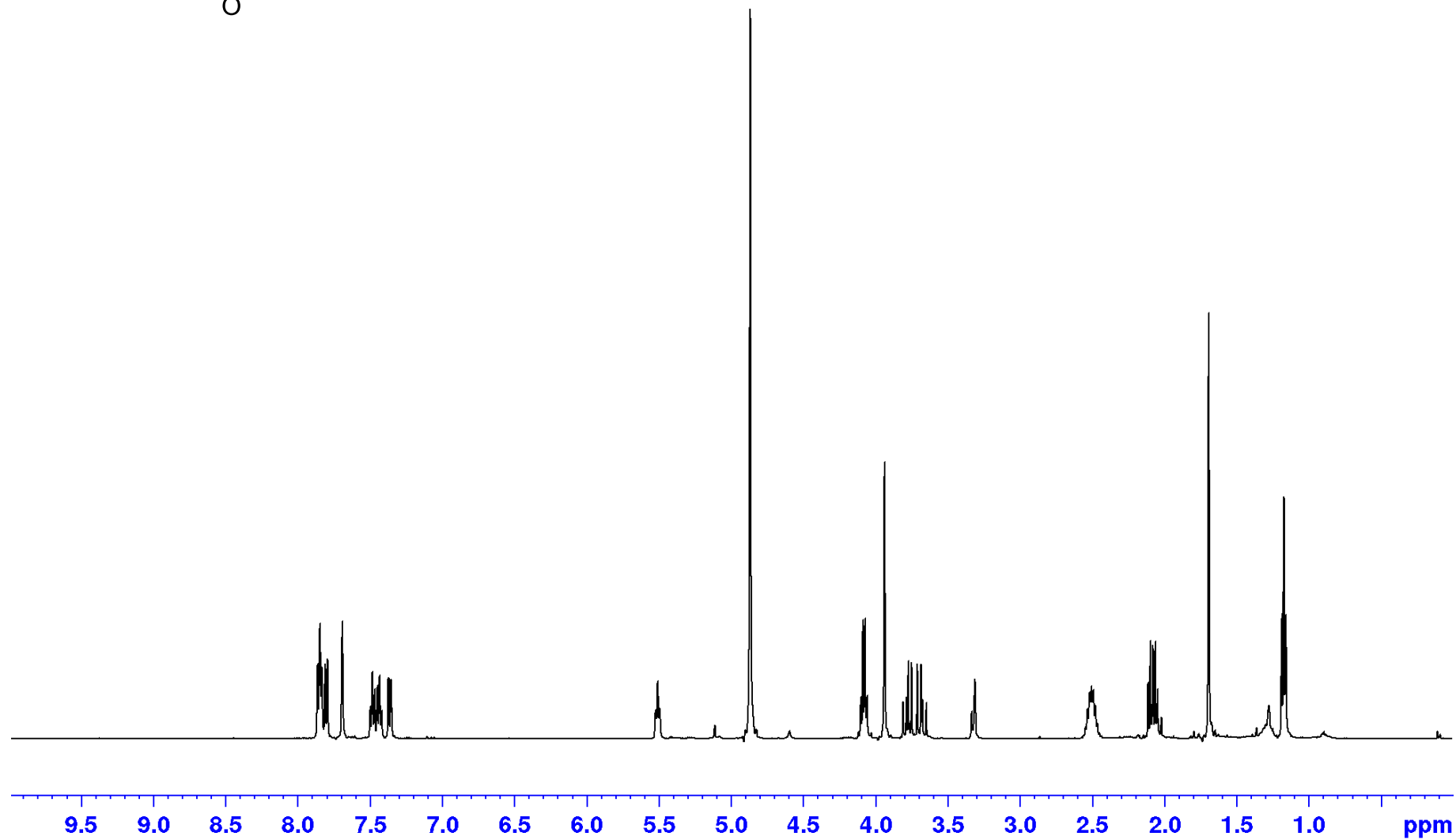
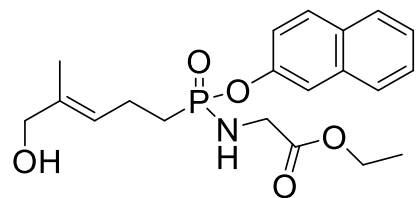


400 MHz ^1H NMR spectrum of compound **9g**.

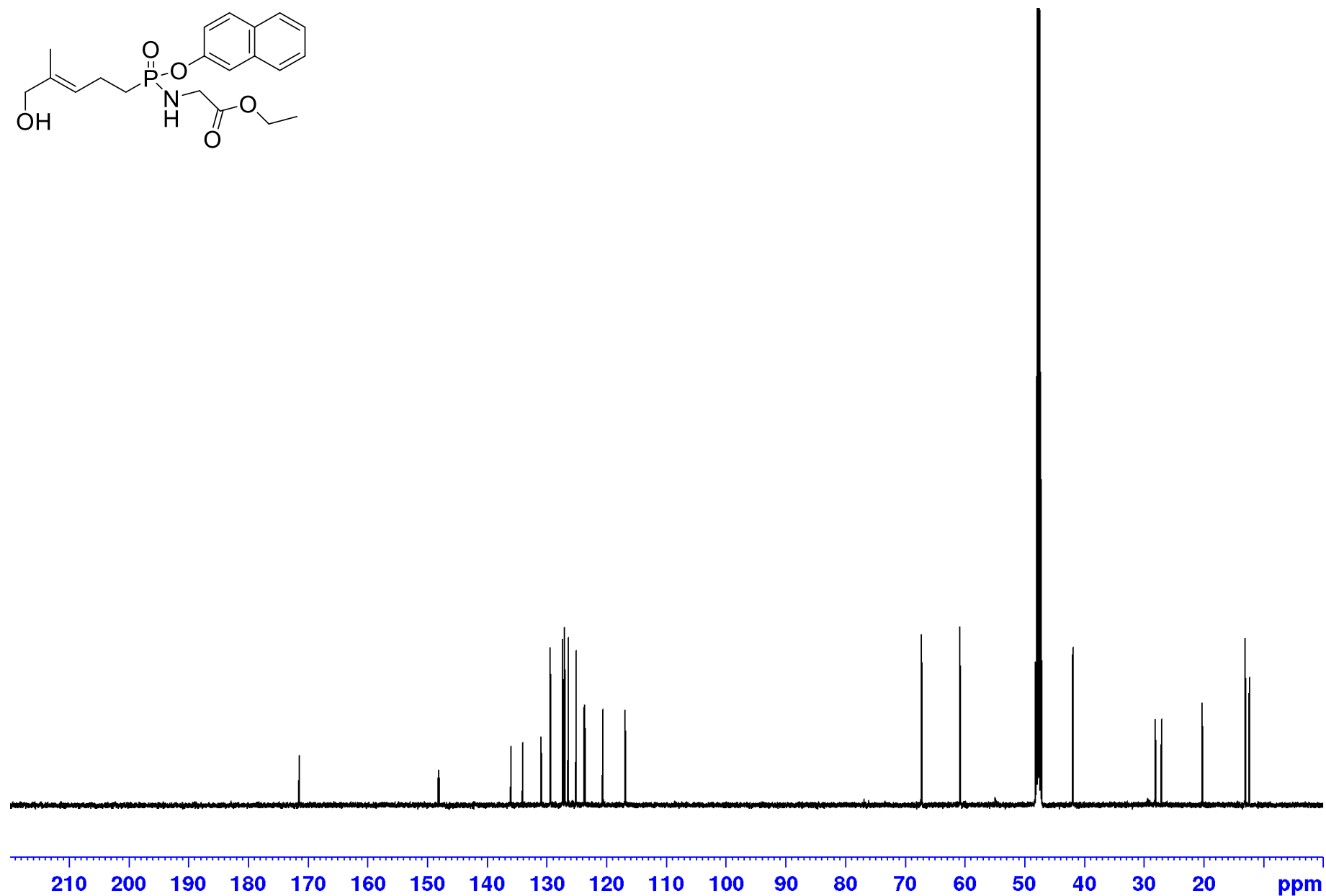
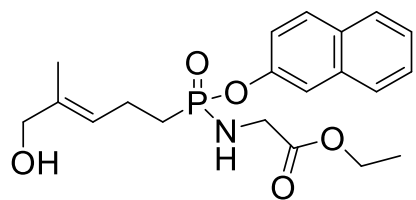


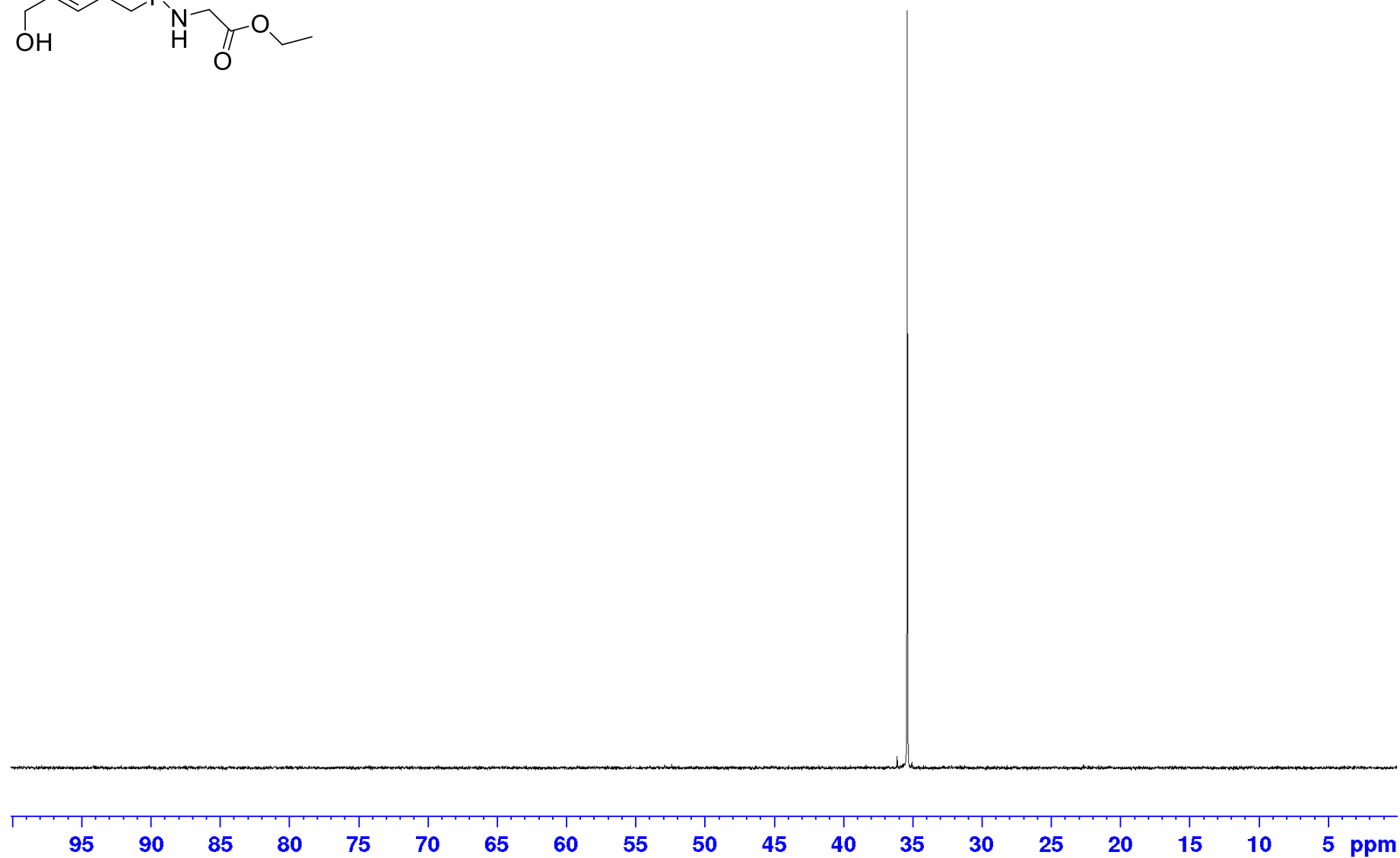
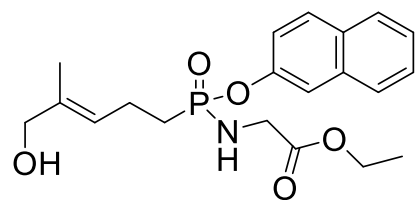


161 MHz ^{31}P NMR spectrum of compound 9g.

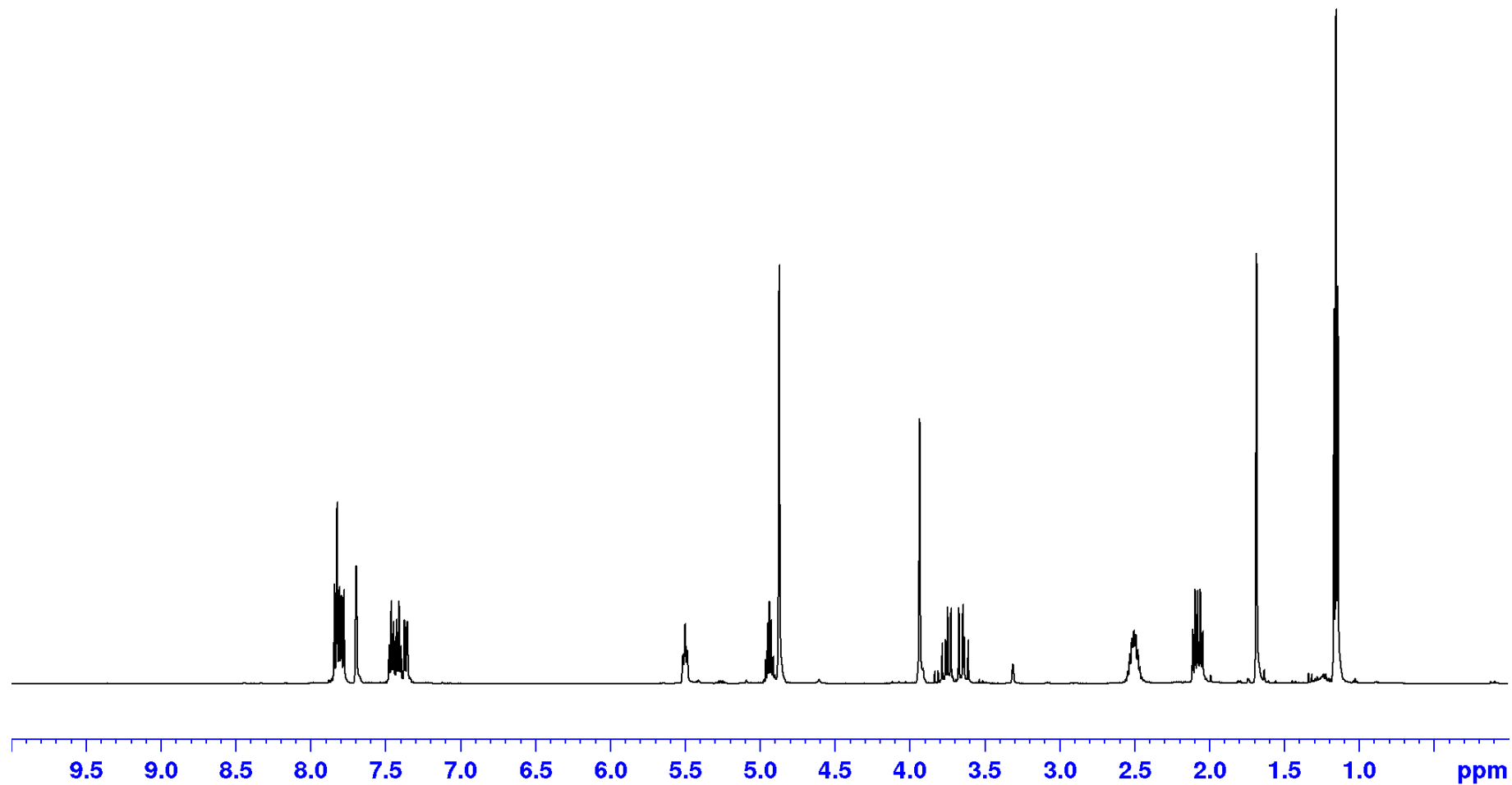
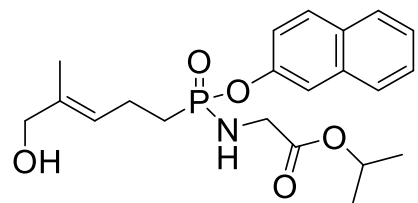


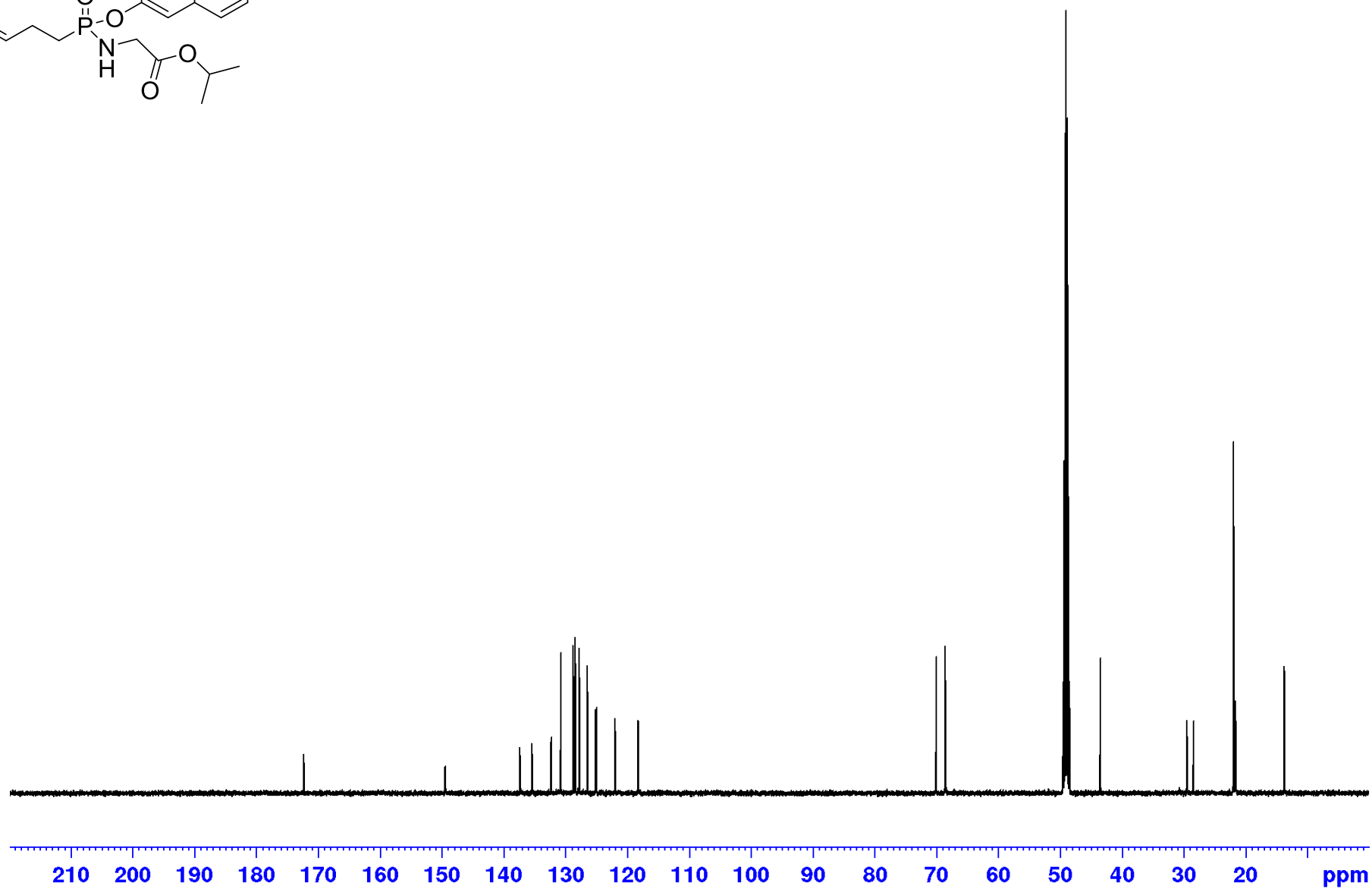
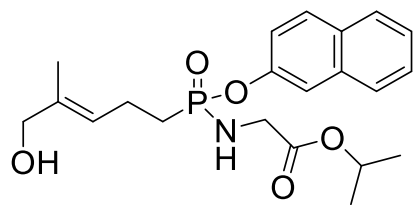
500 MHz ^1H NMR spectrum of compound **9h**.





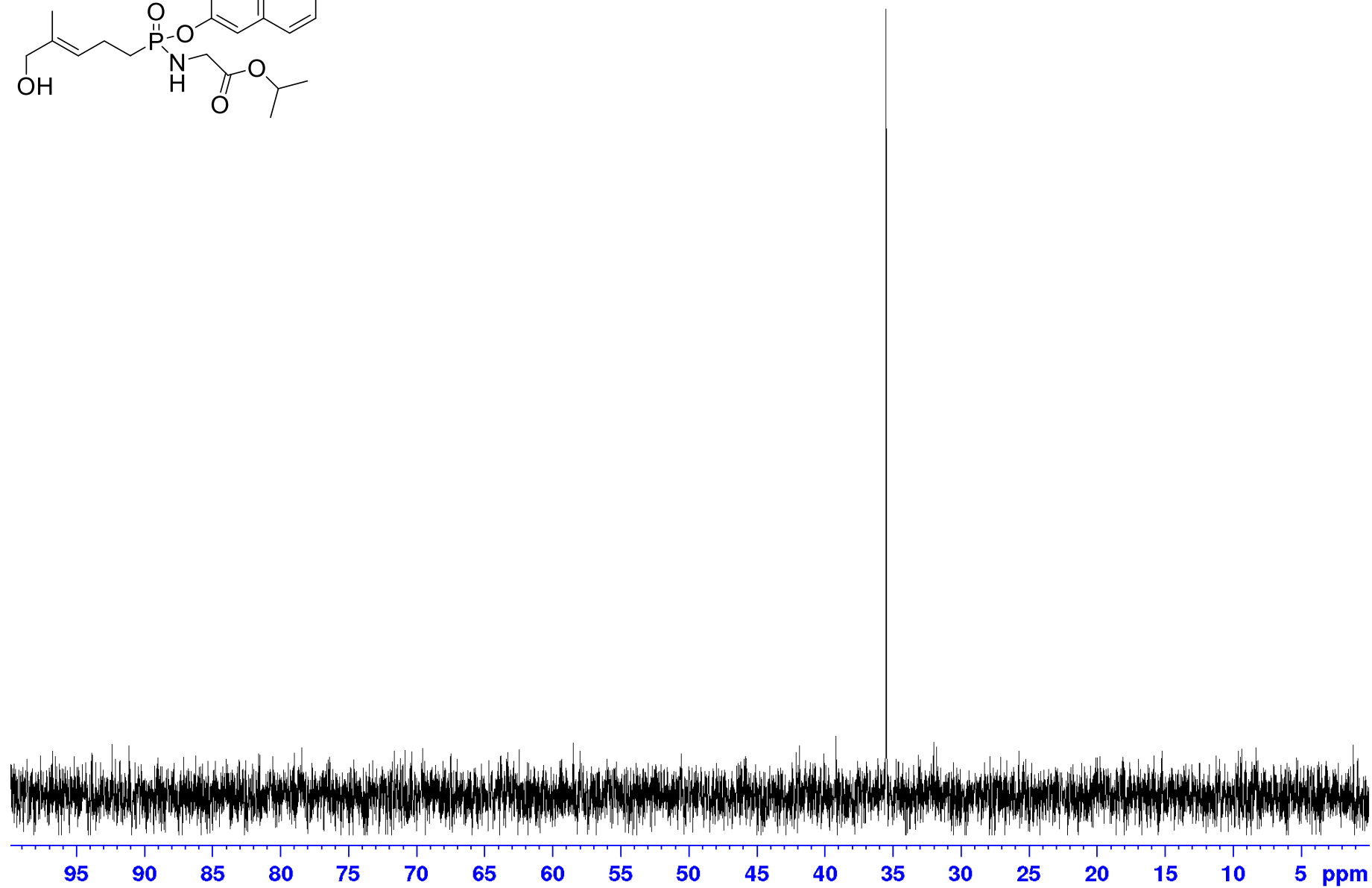
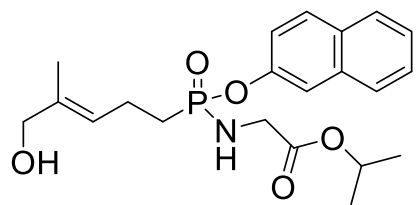
202 MHz ^{31}P NMR spectrum of compound 9h.





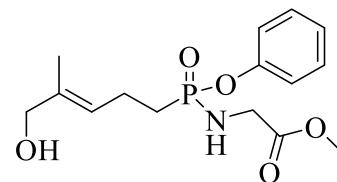
125 MHz ^{13}C NMR spectrum of compound **9i**.

S31



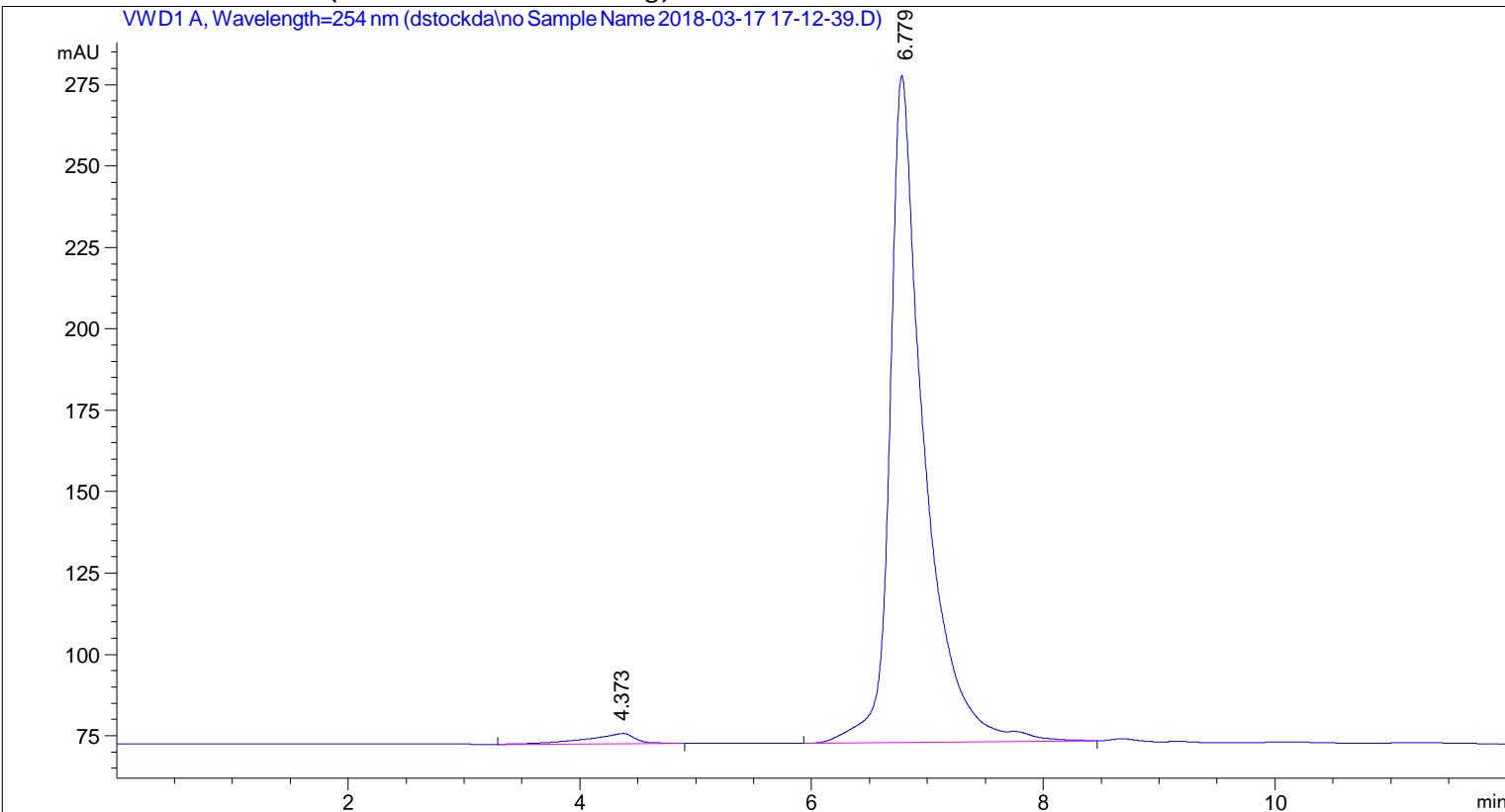
161 MHz ^{31}P NMR spectrum of compound **9i**.

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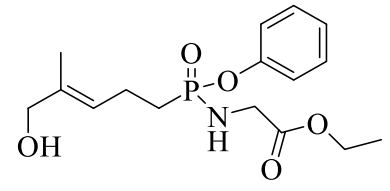
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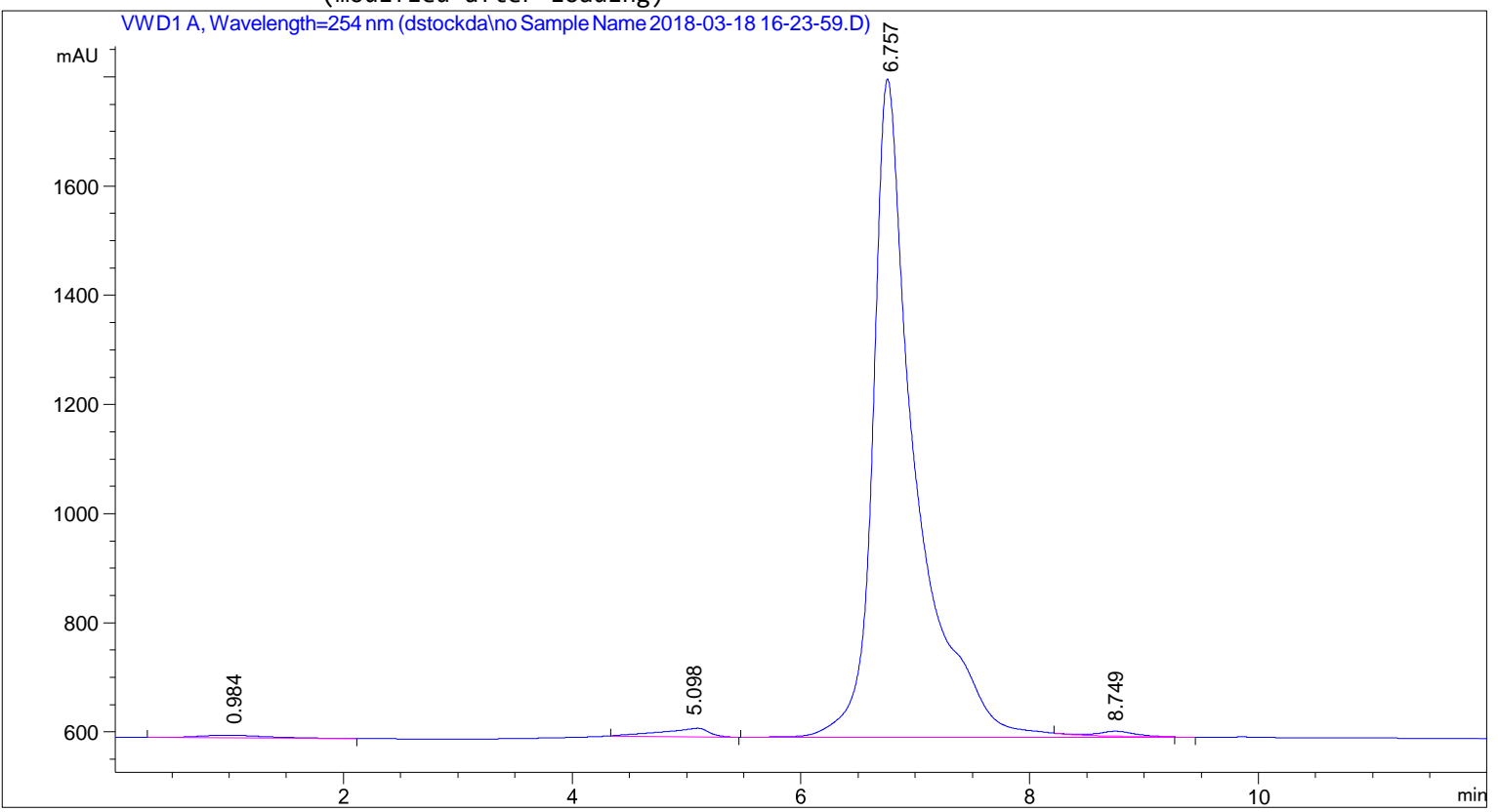
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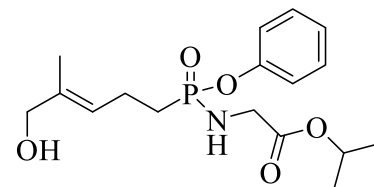
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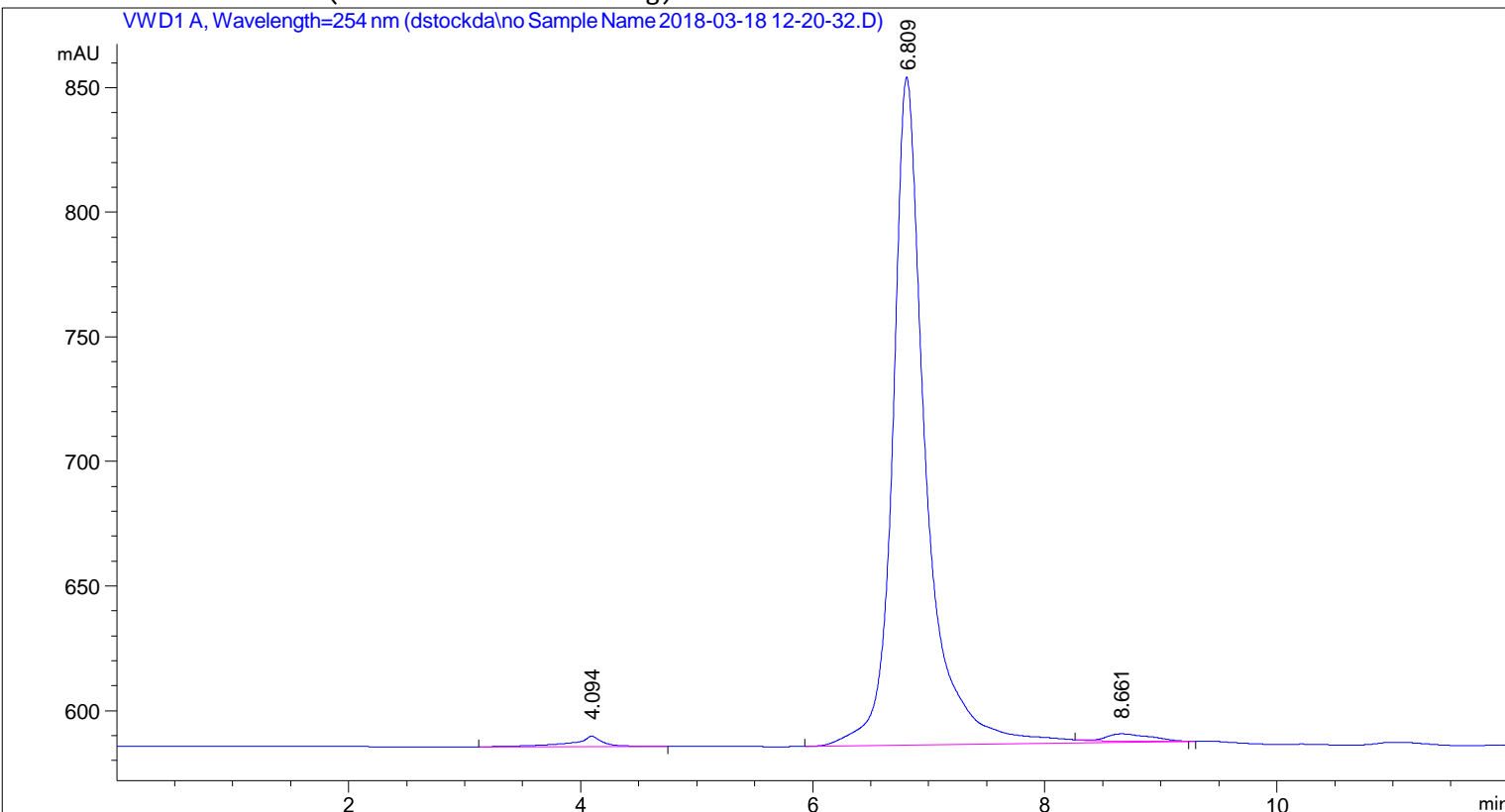
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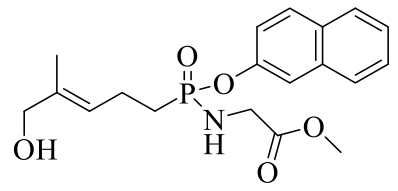
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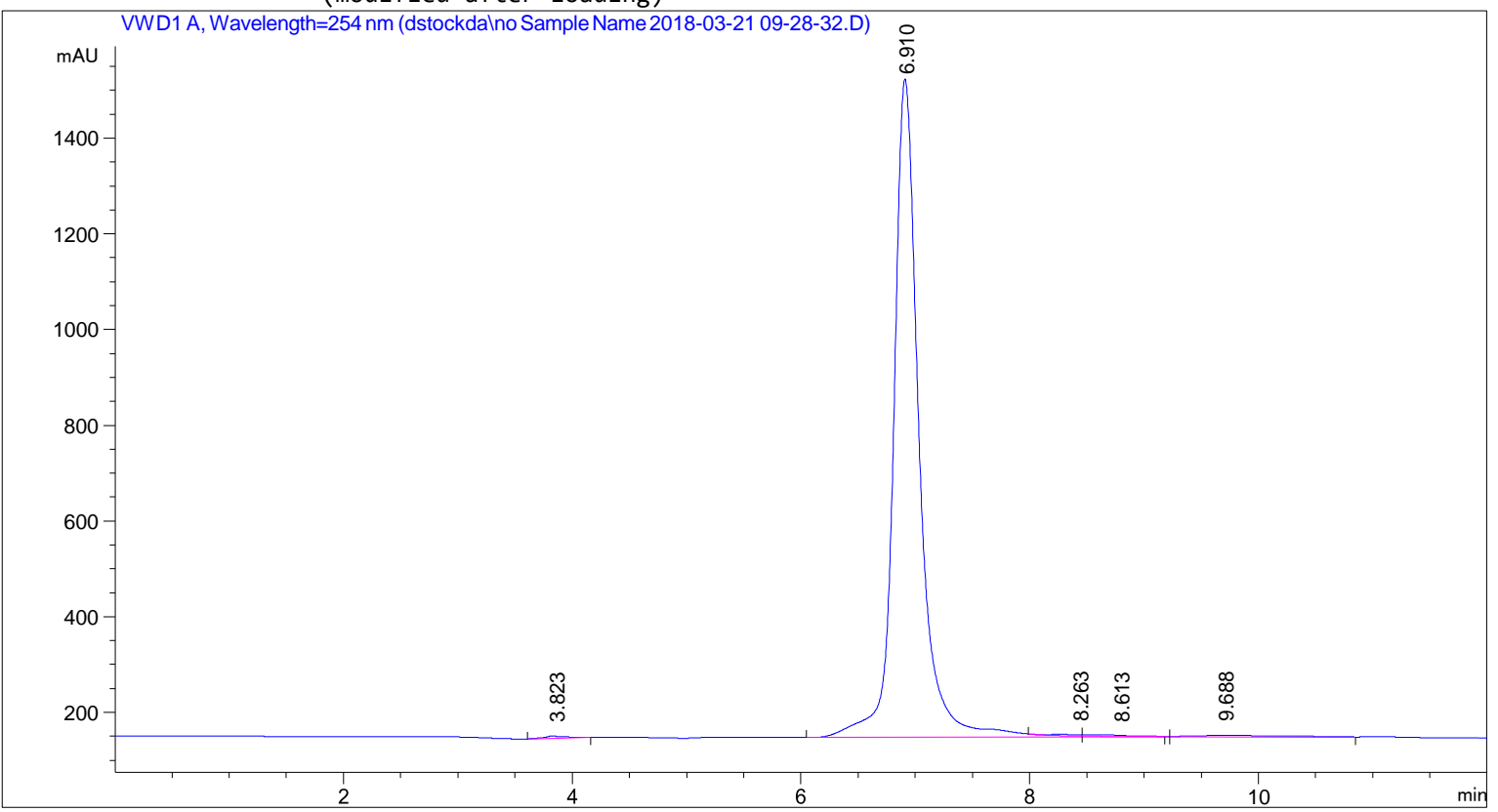
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2	6.910	BV R	0.2305	2.12870e4	1375.75159	98.5680
3	8.263	VV E	0.2542	52.19046	2.98114	0.2417
4	8.613	VB E	0.3034	79.28291	3.86300	0.3671
5	9.688	BB	0.7372	124.24326	2.19897	0.5753

Totals : 2.15963e4 1389.18820

Data File C:\Chem32\1\Data\dstockda\no Sample Name 2018-03-21 09-28-32.D Sample Name:

=====

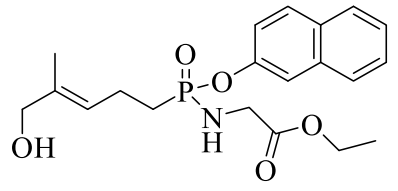
*** End of Report ***

LC 3/21/2018 9:40:44 AM SYSTEM Page 2 of 2

Sample Name:

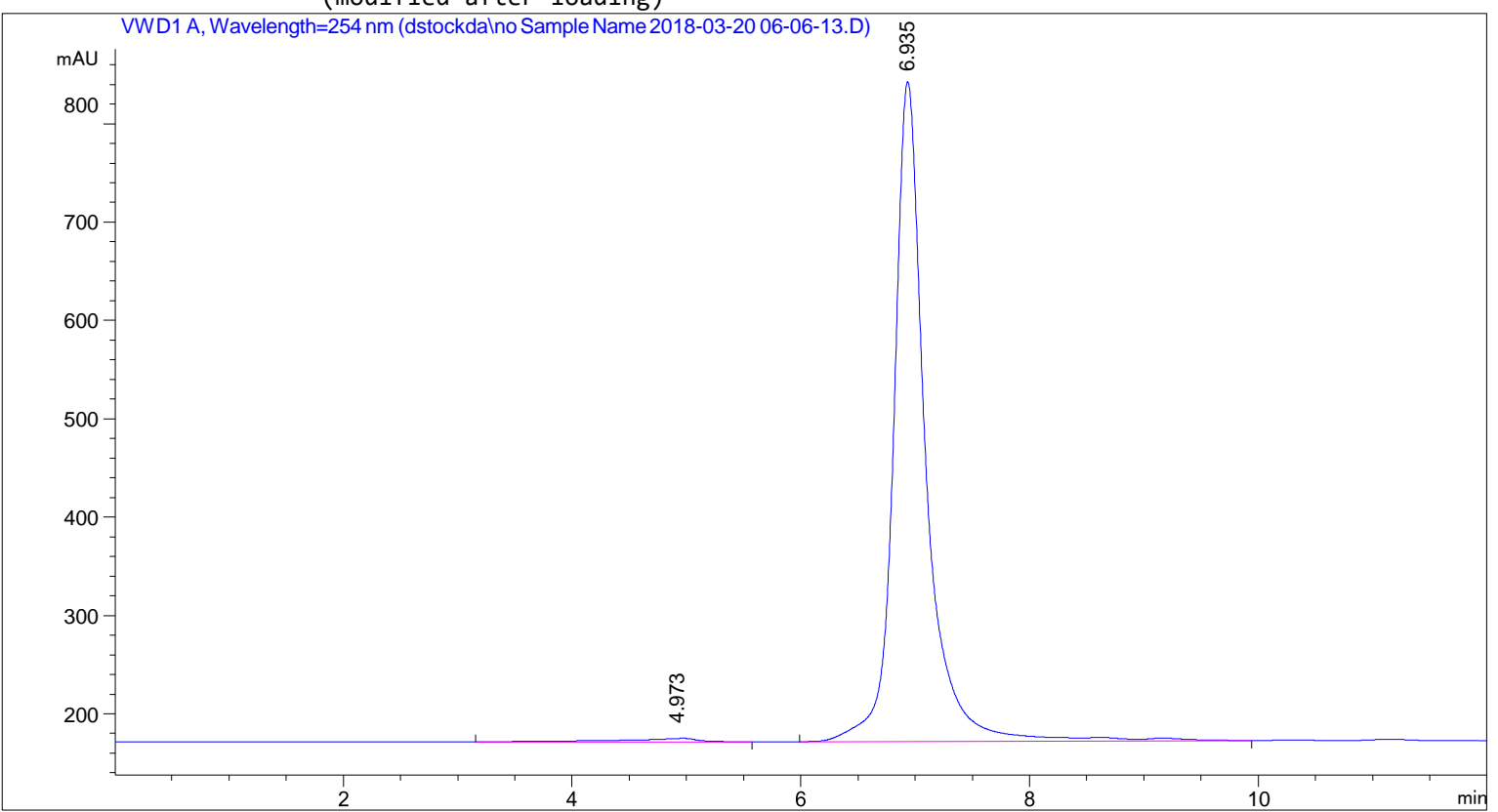
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Acq. Operator : SYSTEM
 Sample Operator : SYSTEM
 Acq. Instrument : LC Location : 1 Injection Date : 3/20/2018
 6:06:13 AM



Inj Volume : Manually

Method : C:\Chem32\1\Methods\DBG.M
 Last changed : 3/20/2018 5:35:34 AM by SYSTEM
 (modified after loading)



Sample Info : setup

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.973	BB	0.5287	139.48842	3.35755	1.0547
2	6.935	BV R	0.2856	1.30855e4	670.82220	98.9453

Totals : 1.32250e4 674.17975

Data File C:\Chem32\1\Data\dstockda\no Sample Name 2018-03-20 06-06-13.D Sample Name:

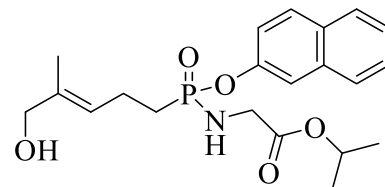
*** End of Report ***

LC 3/20/2018 6:18:26 AM SYSTEM Page 2 of 2

Sample Name:

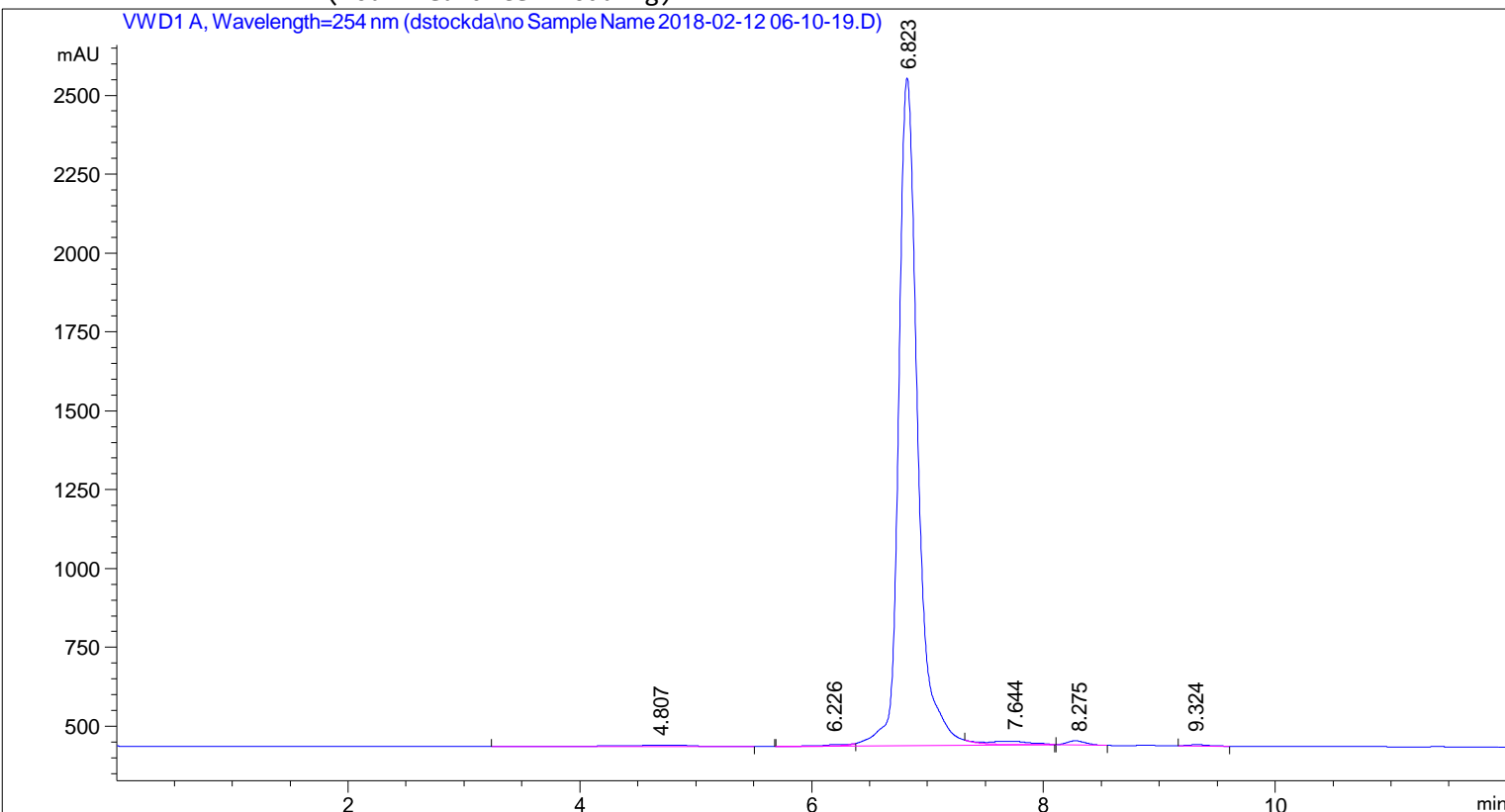
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Acq. Operator : SYSTEM
 Sample Operator : SYSTEM
 Acq. Instrument : LC Location : 1 Injection Date : 2/12/2018
 6:10:20 AM



Inj Volume : Manually

Method : C:\CHEM32\1\METHODS\DBG.M
 Last changed : 2/12/2018 6:18:22 AM by SYSTEM
 (modified after loading)



Sample Info : setup

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Area Percent Report

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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.807	BB	0.5131	203.22459	5.08716	0.8122
2	6.226	BV E	0.2134	69.04517	4.49135	0.2759
3	6.823	VV R	0.1750	2.43073e4	2117.06567	97.1428
4	7.644	VB E	0.3208	255.67728	10.22311	1.0218
5	8.275	BB	0.1725	144.00377	13.07846	0.5755
6	9.324	BB	0.1733	42.98248	3.84805	0.1718

Data File C:\Chem32\1\Data\dstockda\no Sample Name 2018-02-12 06-10-19.D Sample Name:

Totals : 2.50222e4 2153.79380

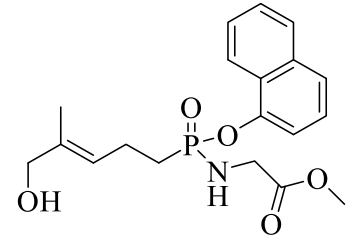
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*** End of Report ***

LC 2/12/2018 6:22:27 AM SYSTEM Page 2 of 2

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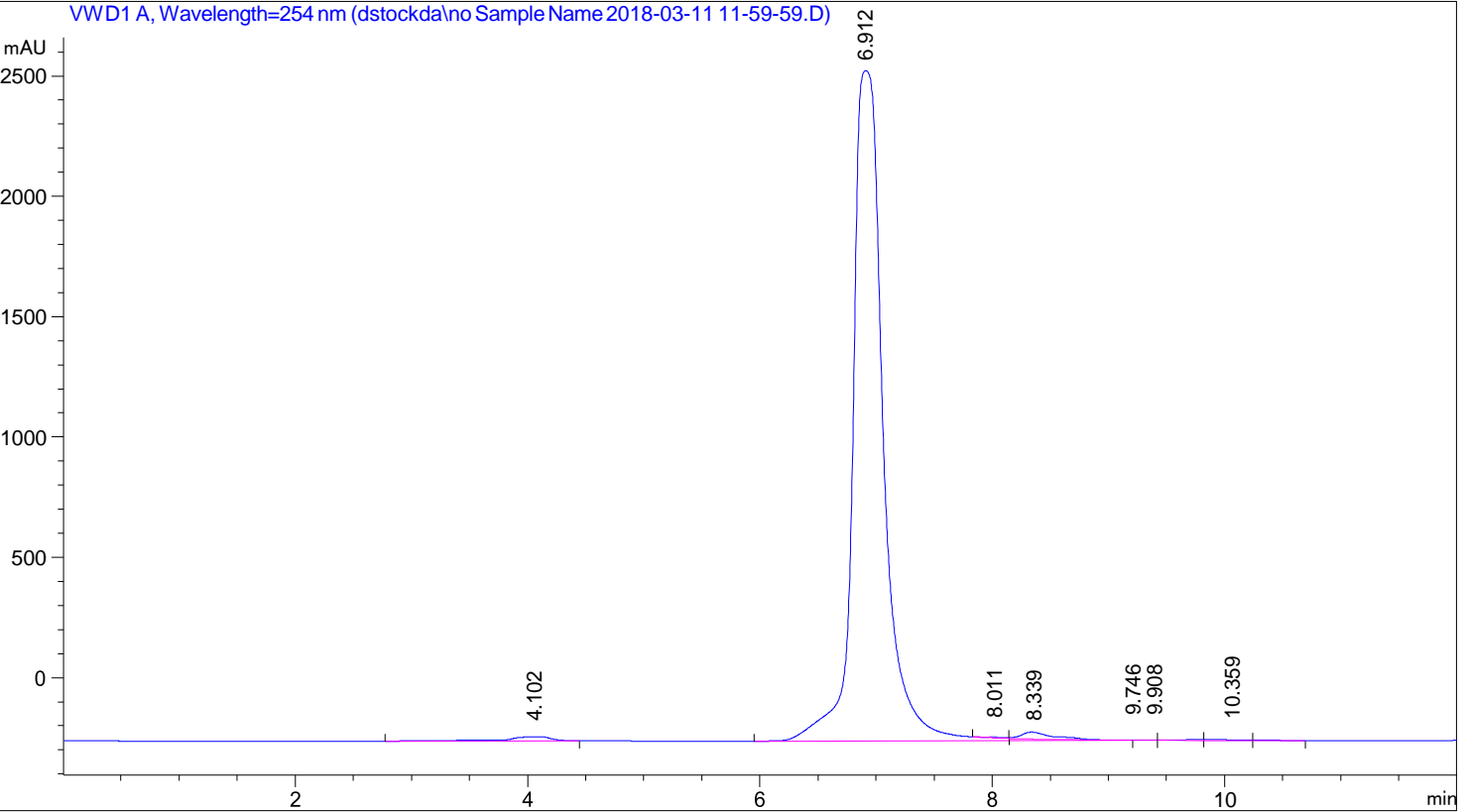
Acq. Operator : SYSTEM
 Sample Operator : SYSTEM
 Acq. Instrument : LC Location : 1 Injection Date : 3/11/2018
 12:00:00 PM



Inj Volume : Manually

Method : C:\Chem32\1\Methods\DBG.M

Last changed : 3/11/2018 12:11:49 PM by SYSTEM
 (modified after loading)



Sample Info : setup

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.102	BB	0.4176	474.37180	17.15651	0.9104
2	6.912	BV R	0.2762	5.08821e4	2784.37109	97.6500
3	8.011	VV E	0.1821	40.49734	3.16870	0.0777
4	8.339	VB E	0.2748	566.17120	29.25097	1.0866
5	9.746	BV	0.1804	40.49200	3.38813	0.0777
6	9.908	VV	0.2832	70.92496	3.69145	0.1361
7	10.359	VB	0.2362	32.02246	2.08428	0.0615

Data File C:\Chem32\1\Data\dstockda\no Sample Name 2018-03-11 11-59-59.D Sample Name:

Peak #	RetTime [min]	Type	Width	Area [mAU*s]	Height [mAU]	Area %
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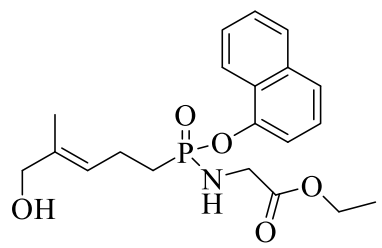
Totals : 5.21066e4 2843.11112

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*** End of Report ***

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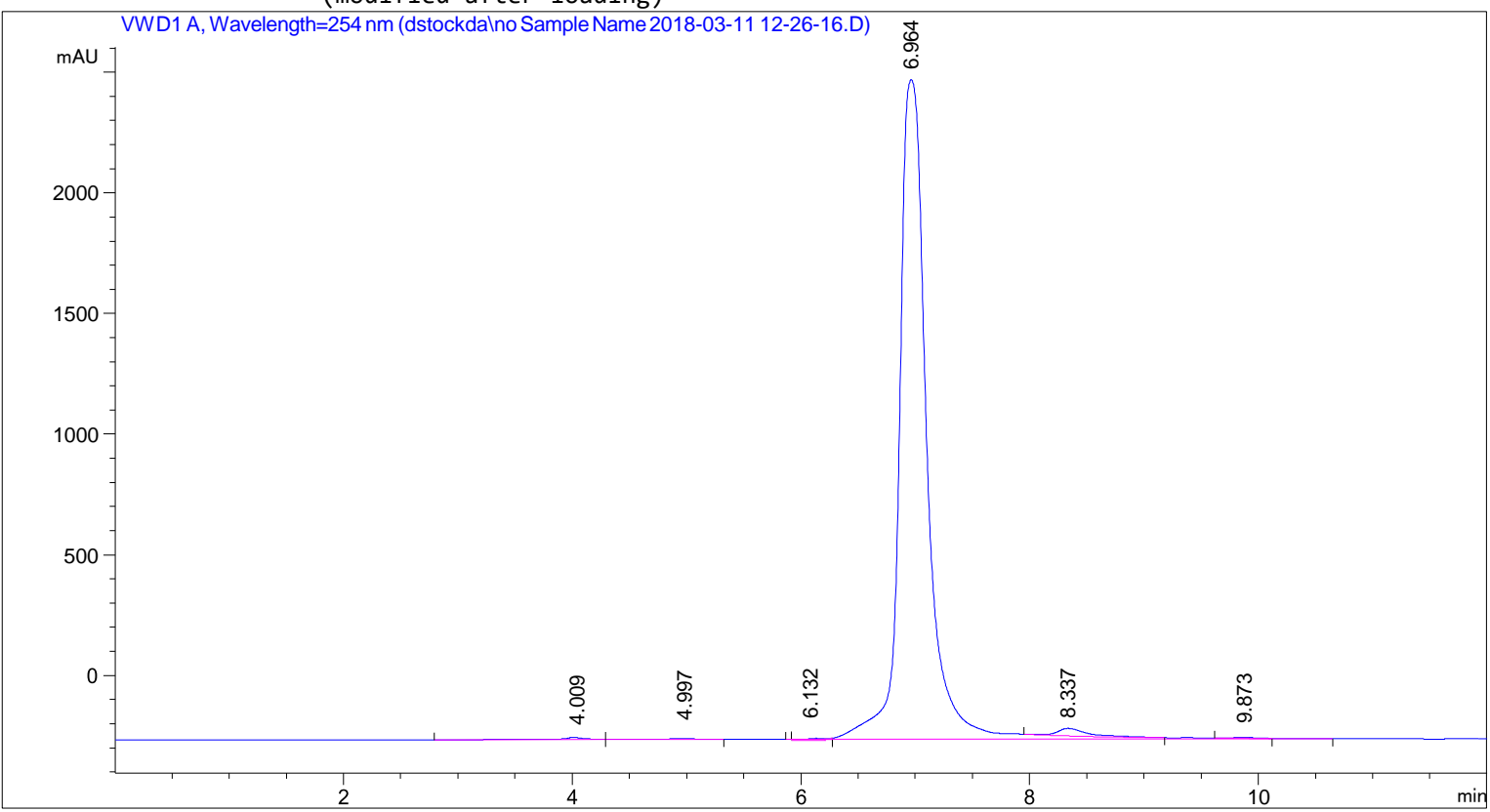
Acq. Operator : SYSTEM
 Sample Operator : SYSTEM
 Acq. Instrument : LC Location : 1 Injection Date : 3/11/2018
 12:26:16 PM



Inj Volume : Manually

Method : C:\Chem32\1\Methods\DBG.M

Last changed : 3/11/2018 12:11:49 PM by SYSTEM
 (modified after loading)



Sample Info : setup

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.009	BV	0.1962	133.35913	9.14146	0.2822
2	4.997	VB	0.4065	81.78371	2.57545	0.1731
3	6.132	BV E	0.1158	31.91494	4.14776	0.0675
4	6.964	VV R	0.2539	4.63662e4	2733.83179	98.1299
5	8.337	VV E	0.2723	581.95880	30.96692	1.2317
6	9.873	VB E	0.2682	54.58805	3.18075	0.1155

Data File C:\Chem32\1\Data\dstockda\no Sample Name 2018-03-11 12-26-16.D Sample Name:

Totals : 4.72498e4 2783.84412

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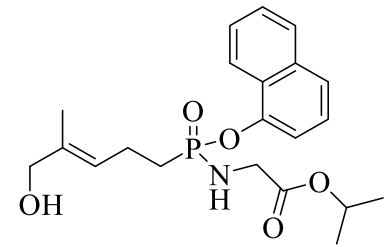
*** End of Report ***

LC 3/11/2018 12:38:24 PM SYSTEM Page 2 of 2

Sample Name:

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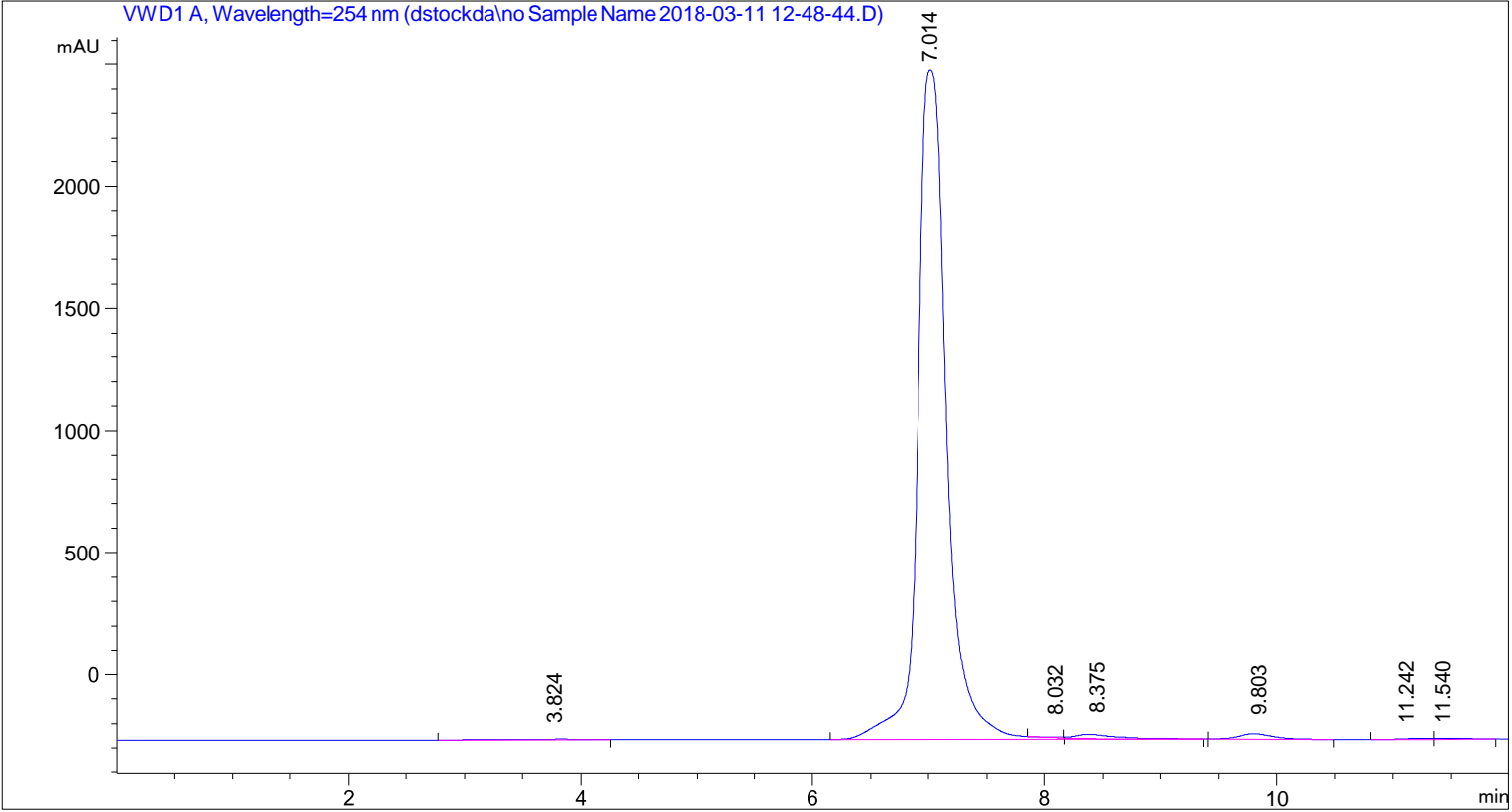
Acq. Operator : SYSTEM
 Sample Operator : SYSTEM
 Acq. Instrument : LC Location : 1 Injection Date : 3/11/2018
 12:48:45 PM



Inj Volume : Manually

Method : C:\Chem32\1\Methods\DBG.M

Last changed : 3/11/2018 12:11:49 PM by SYSTEM
 (modified after loading)



Sample Info : setup

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.824	BB	0.2435	75.83086	3.99407	0.1567
2	7.014	BV R	0.2611	4.72505e4	2741.20605	97.6667
3	8.032	VV E	0.1996	39.39473	2.82656	0.0814
4	8.375	VB E	0.3370	425.68585	17.73633	0.8799
5	9.803	BB	0.3004	429.37436	21.65242	0.8875
6	11.242	BV	0.2394	66.09976	4.20517	0.1366
7	11.540	VB	0.2978	92.42479	4.67272	0.1910

Data File C:\Chem32\1\Data\dstockda\no Sample Name 2018-03-11 12-48-44.D
Sample Name:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
----- ----- ----- ----- ----- ----- -----						
Totals :				4.83793e4	2796.29333	

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*** End of Report ***