

Supporting Information For:

Highly Enantioselective Hydrophosphonylation of Imines Catalyzed by SPINOL-Phosphoric Acid

*Yanyan Zhao, Xuejian Li, Fan Mo, Luhang Li, and Xufeng Lin**

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

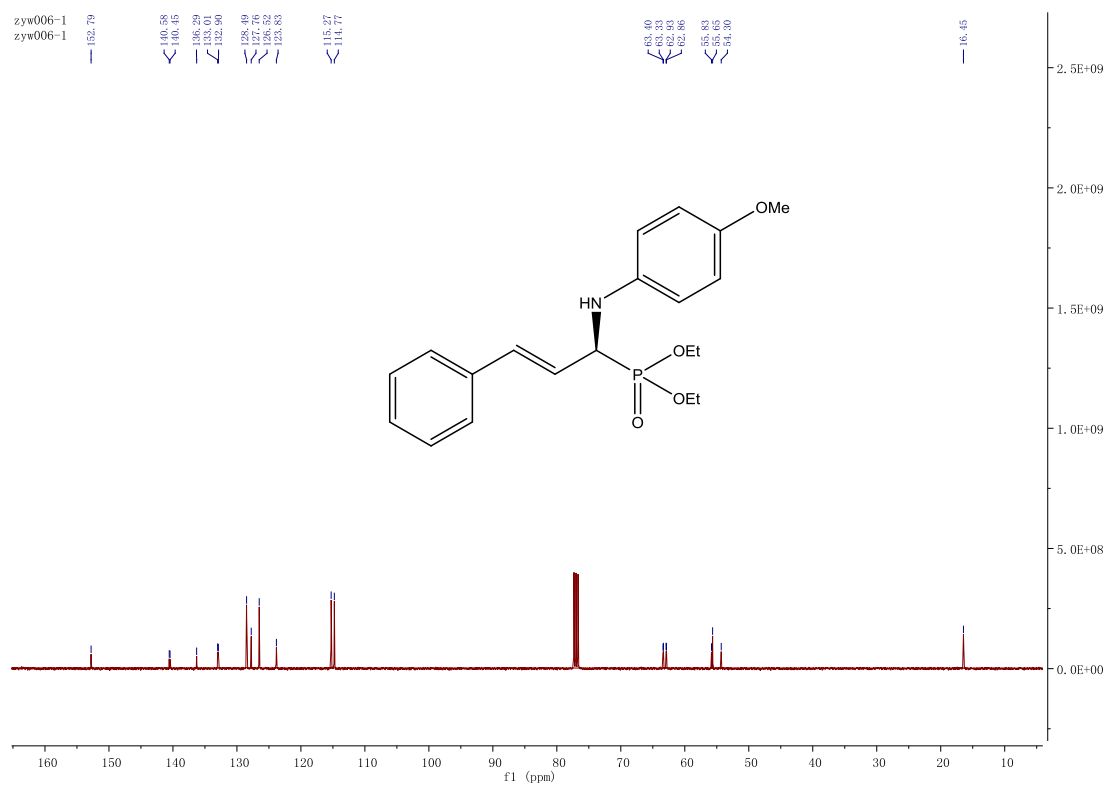
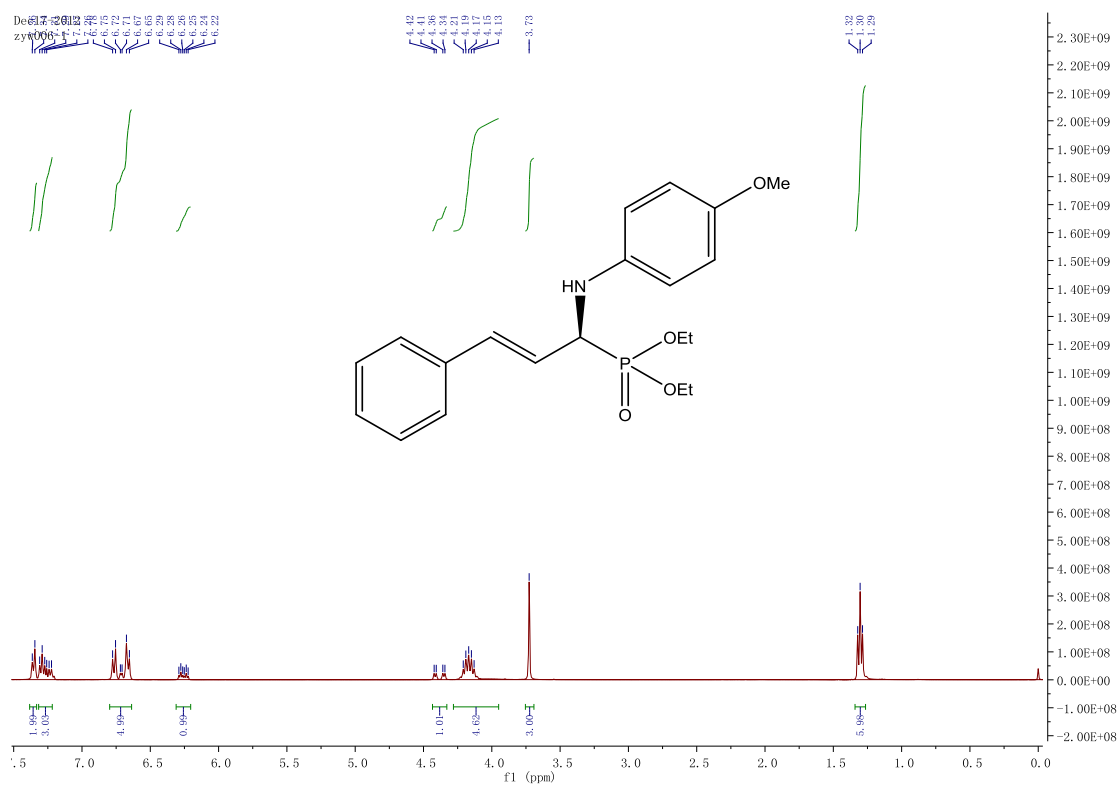
Email: lxfok@zju.edu.cn

CONTENTS

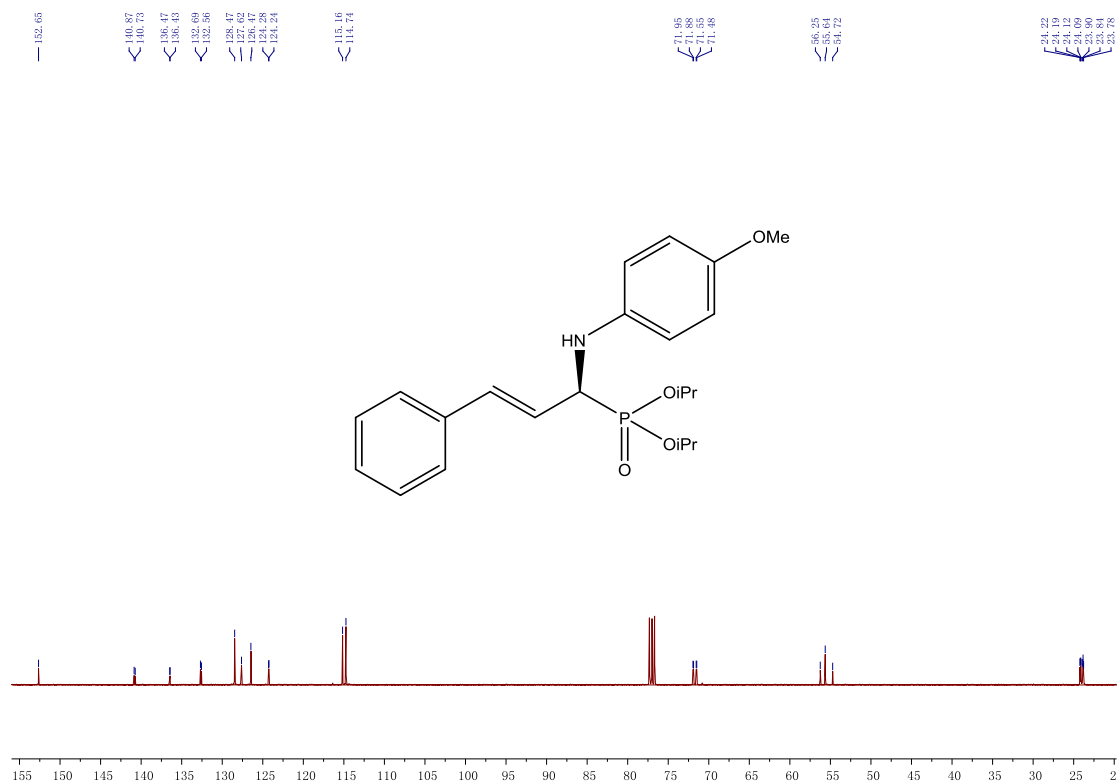
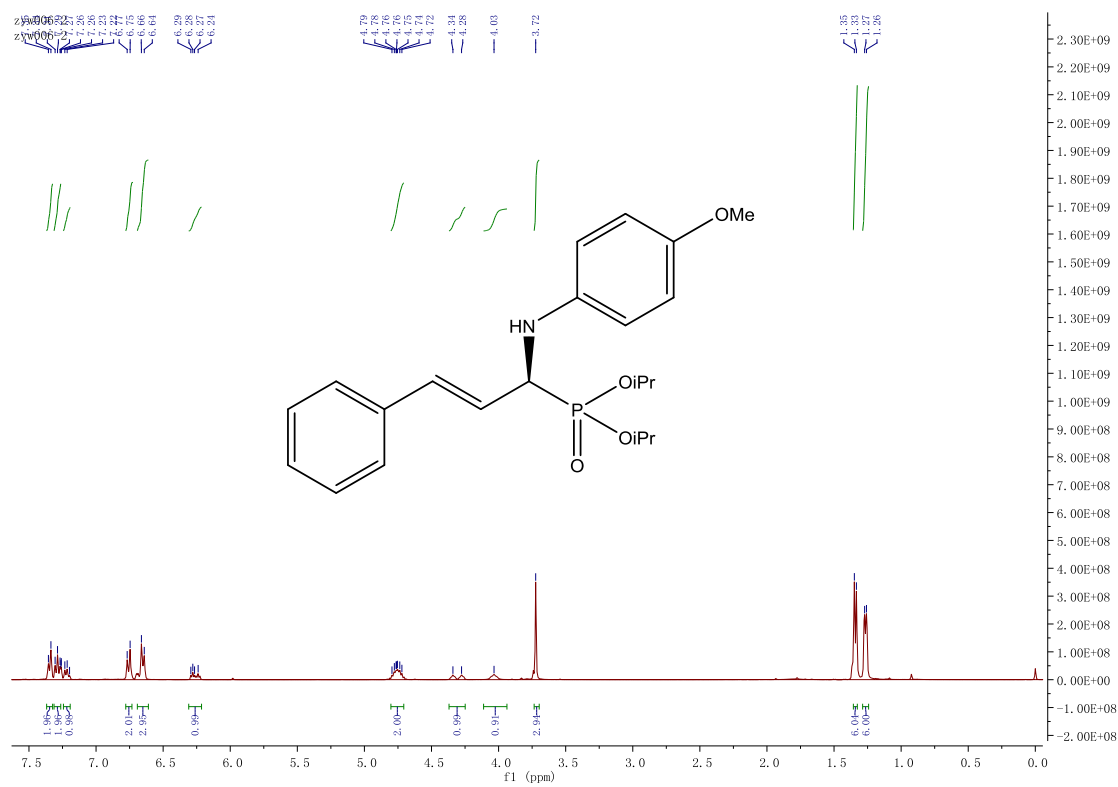
1. ^1H and ^{13}C NMR spectra	S2
2. HPLC spectra	S17

1. ^1H and ^{13}C NMR spectra

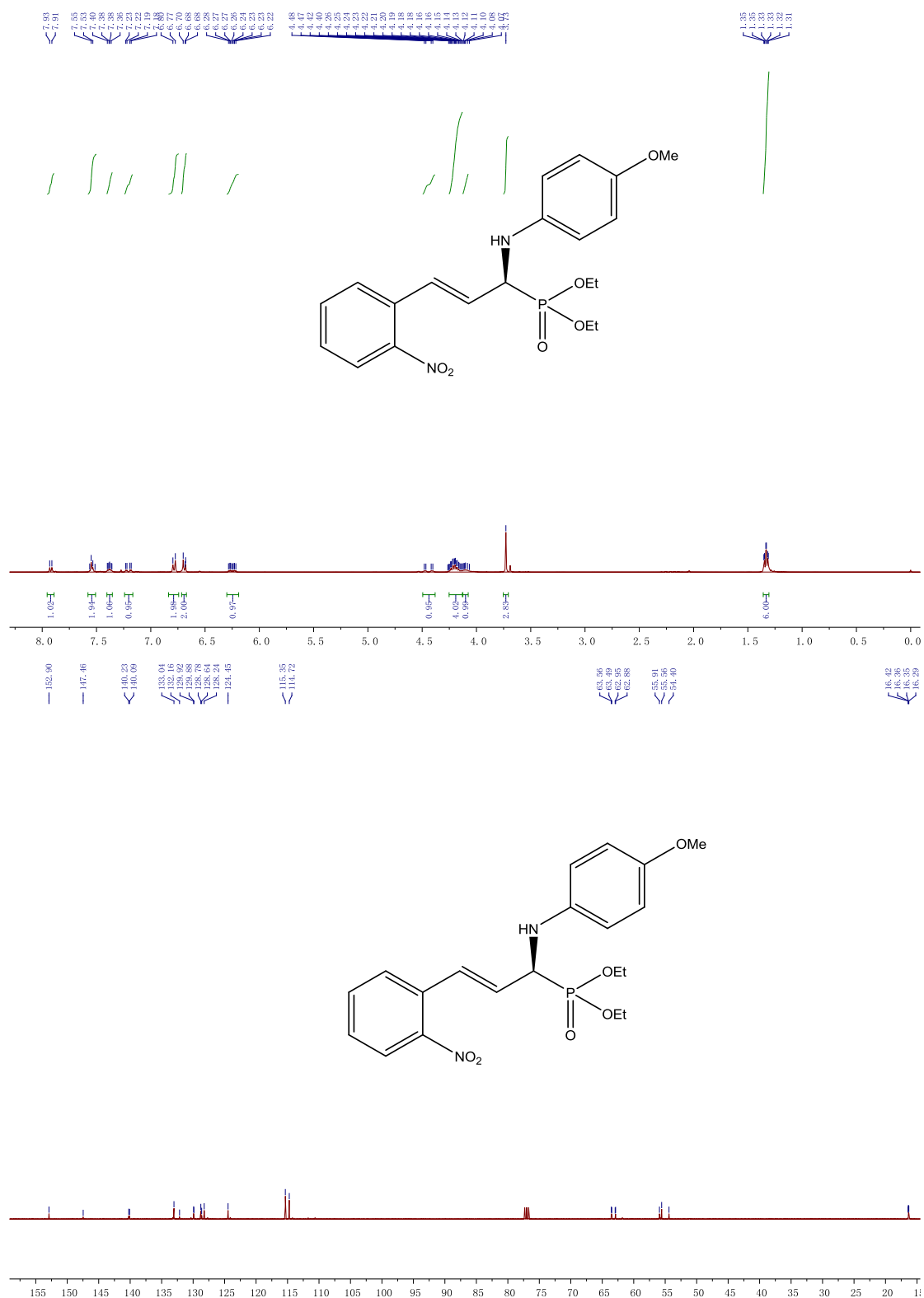
Diethyl (S)-(((4-methoxyphenyl)amino)(2-nitrophenyl)methyl)phosphonate (4a)



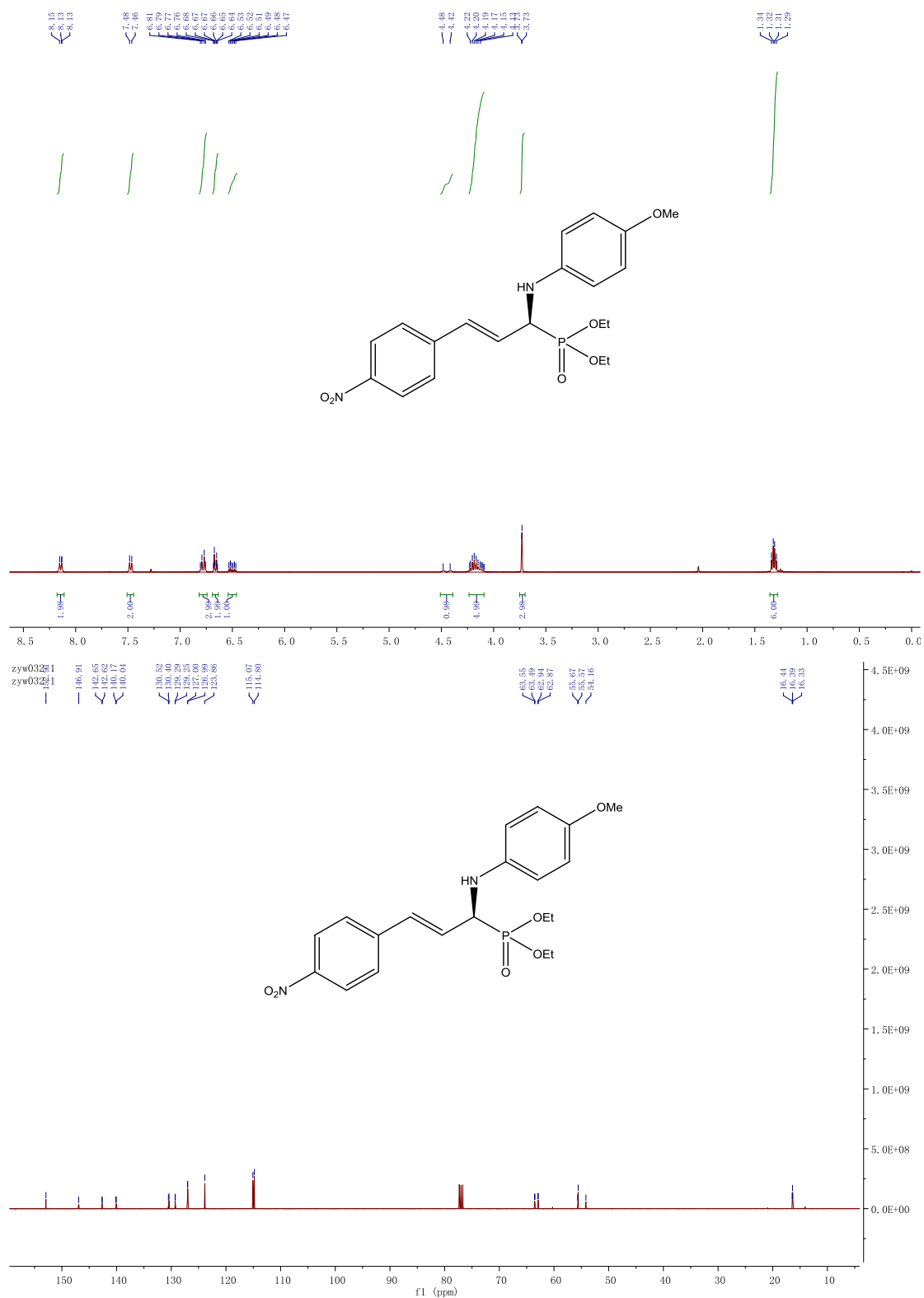
Diisopropyl (S,E)-1-((4-methoxyphenyl)amino)-3-phenylallyl)phosphonate (4ab)



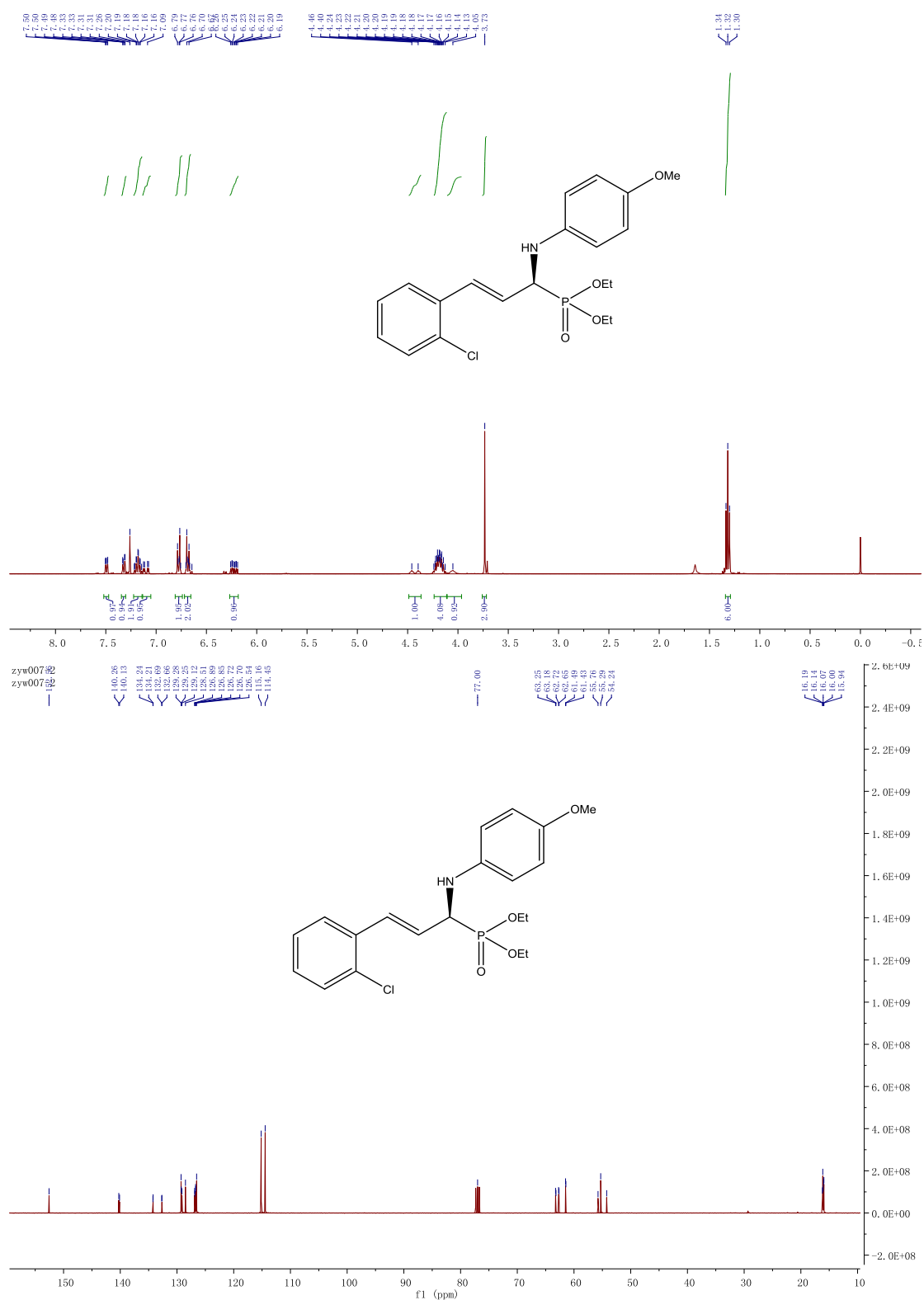
Diethyl (S,E)-1-((4-methoxyphenyl)amino)-3-(2-nitrophenyl)allyl)phosphonate (4b)



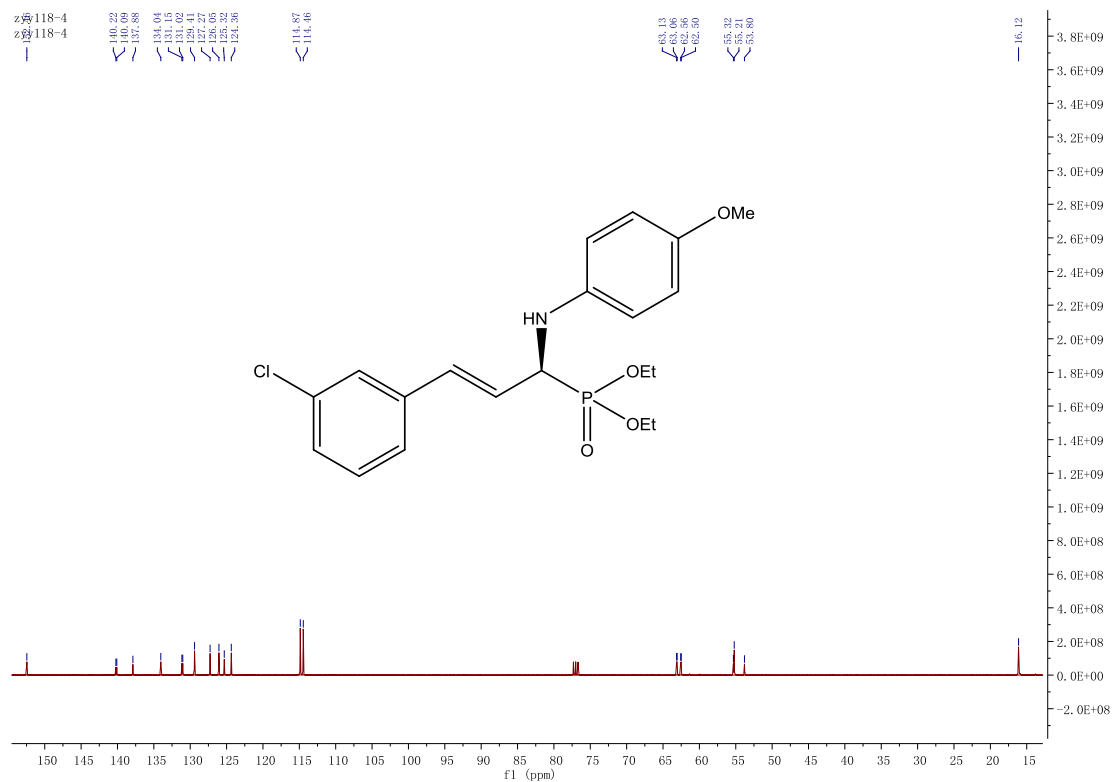
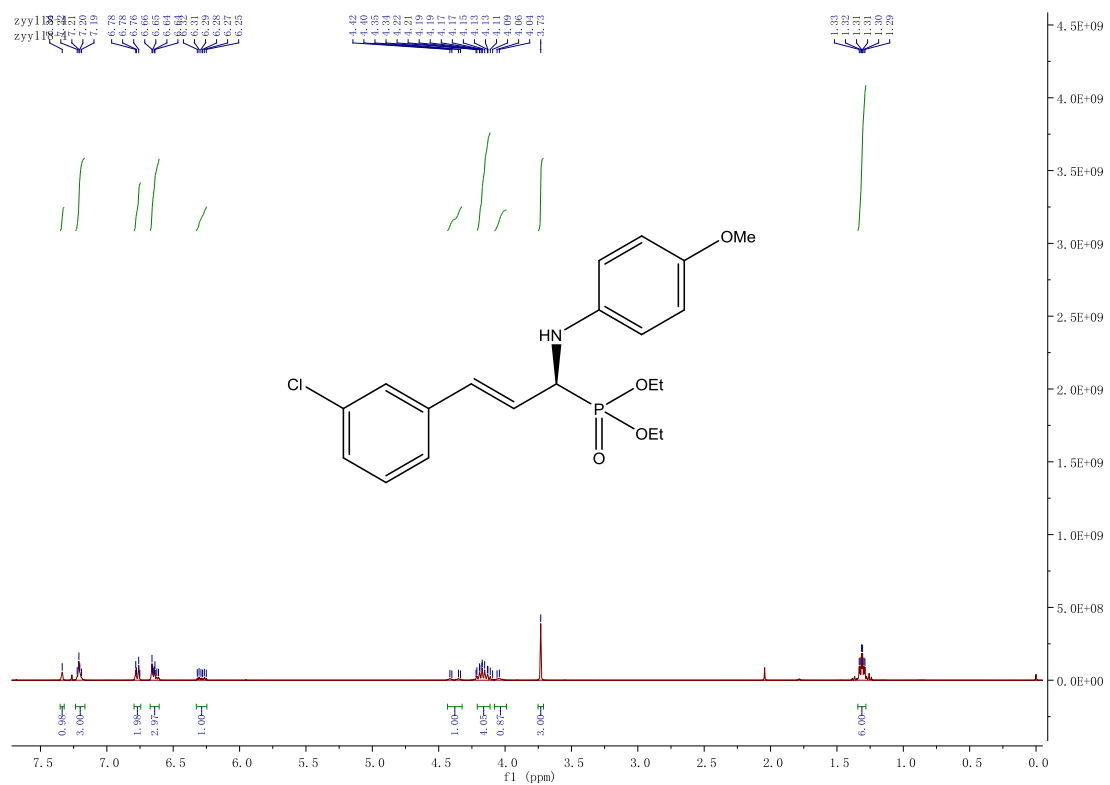
Diethyl (S,E)-1-((4-methoxyphenyl)amino)-3-(4-nitrophenyl)allyl)phosphonate (4c)



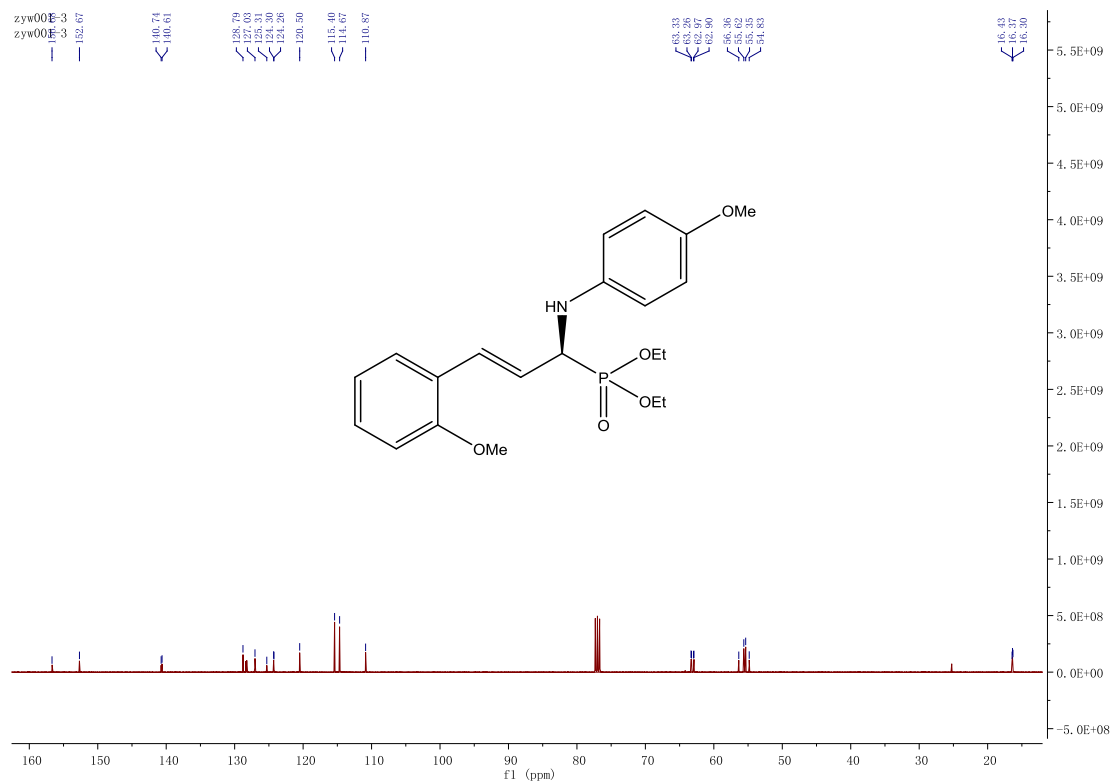
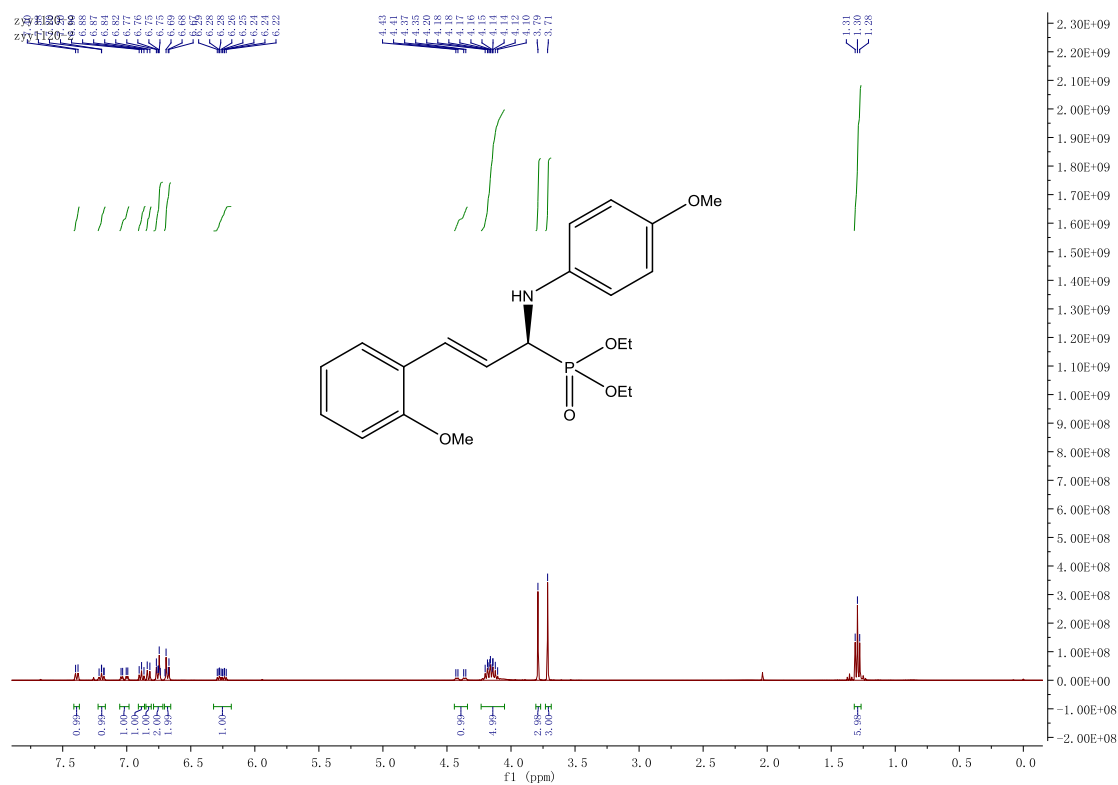
Diethyl (S,E)-(3-(2-chlorophenyl)-1-((4-methoxyphenyl)amino)allyl)phosphonate (4d)



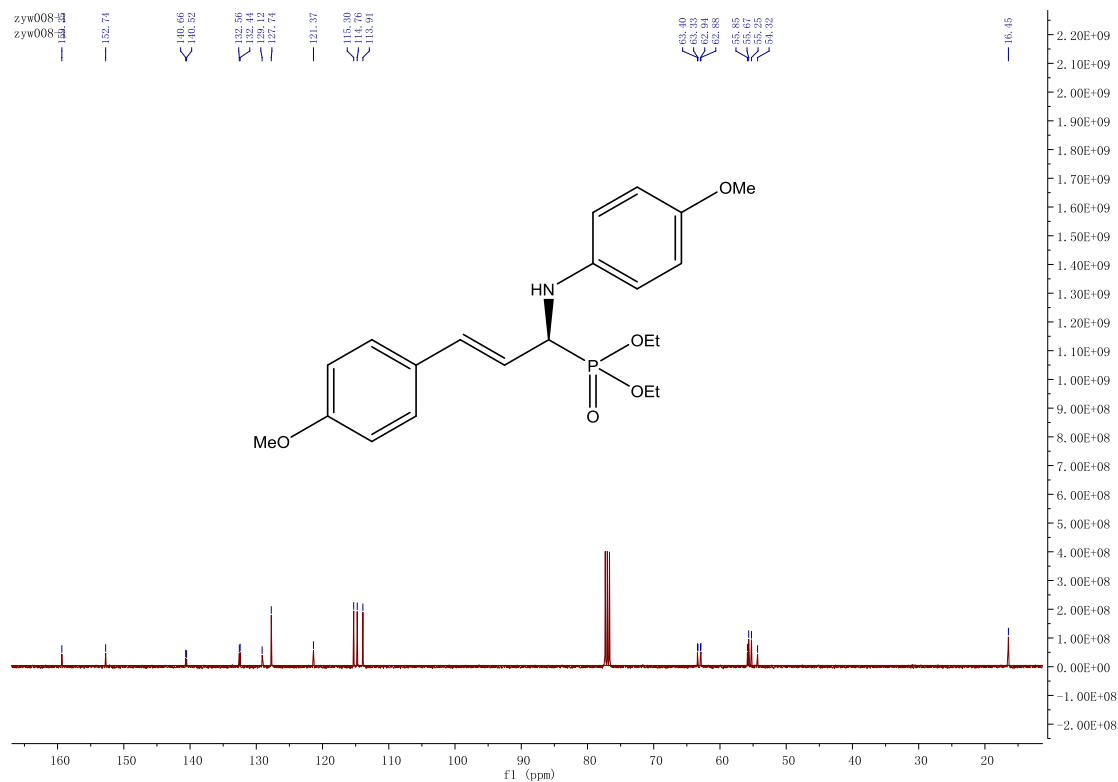
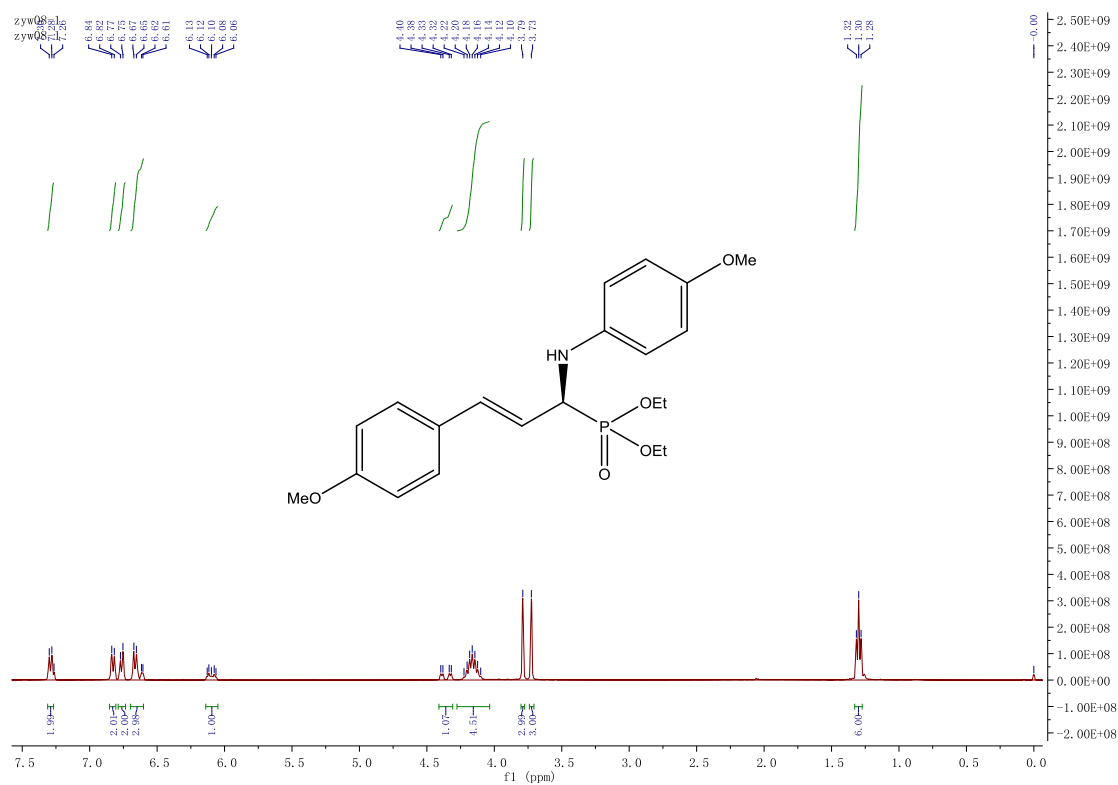
Diethyl (S,E)-(3-(3-chlorophenyl)-1-((4-methoxyphenyl)amino)allyl)phosphonate (4e)



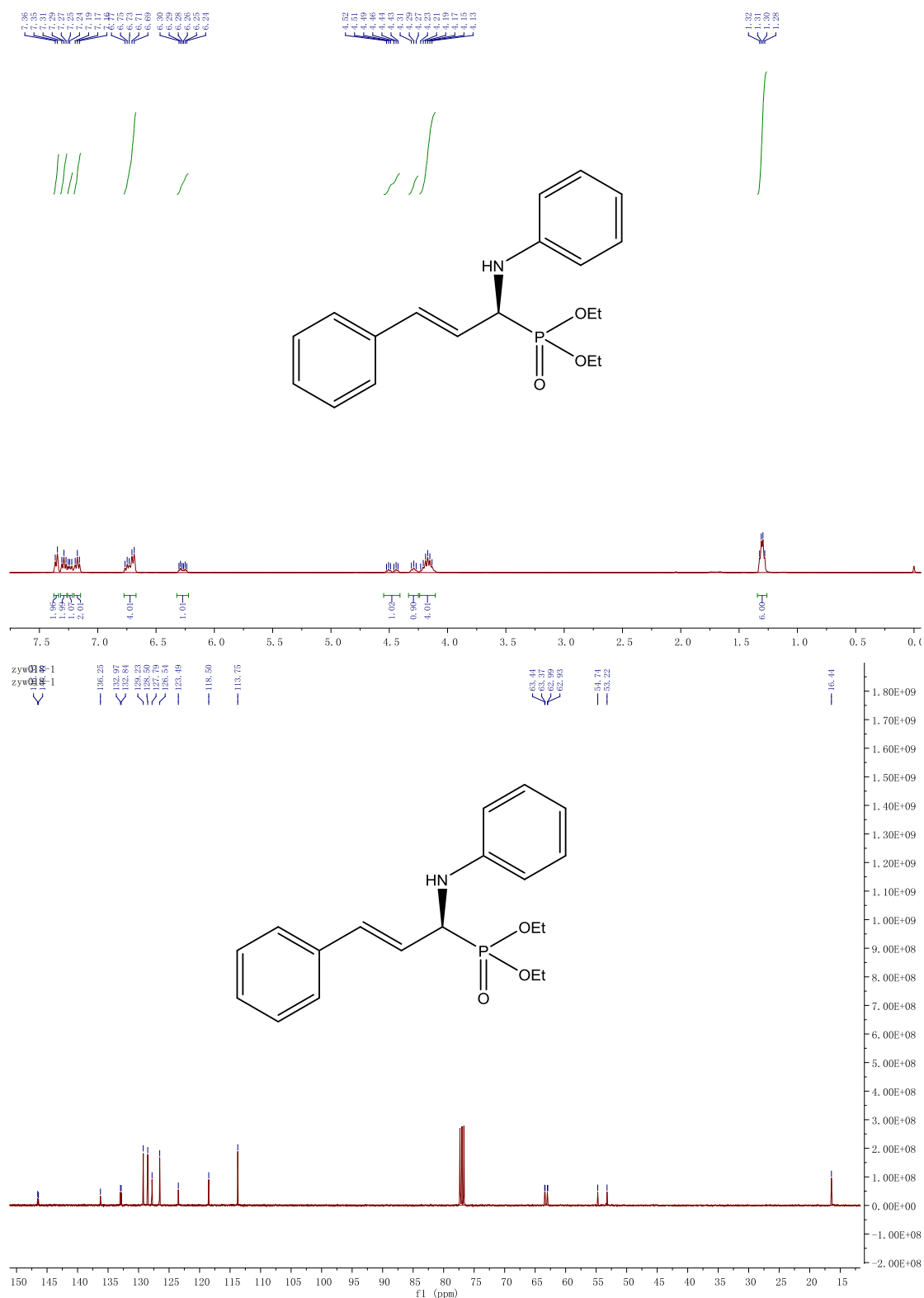
Diethyl (S,E)-3-(2-methoxyphenyl)-1-((4-methoxyphenyl)amino)allylphosphonate (4f)



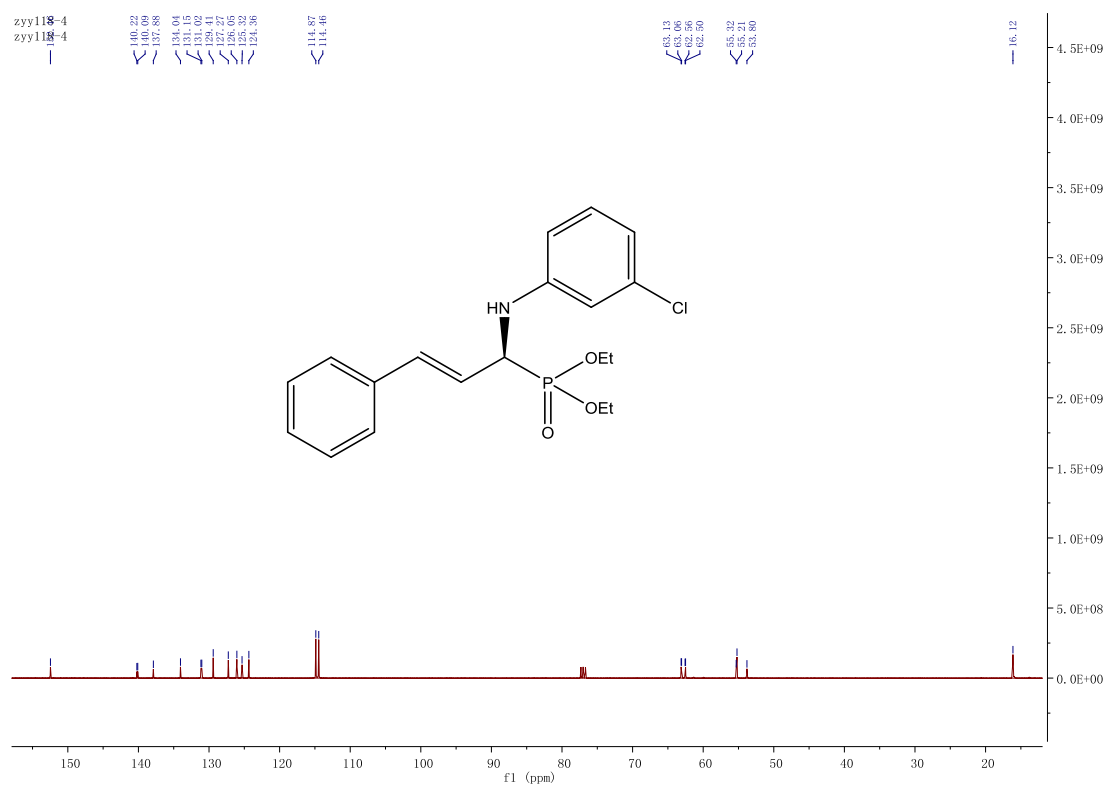
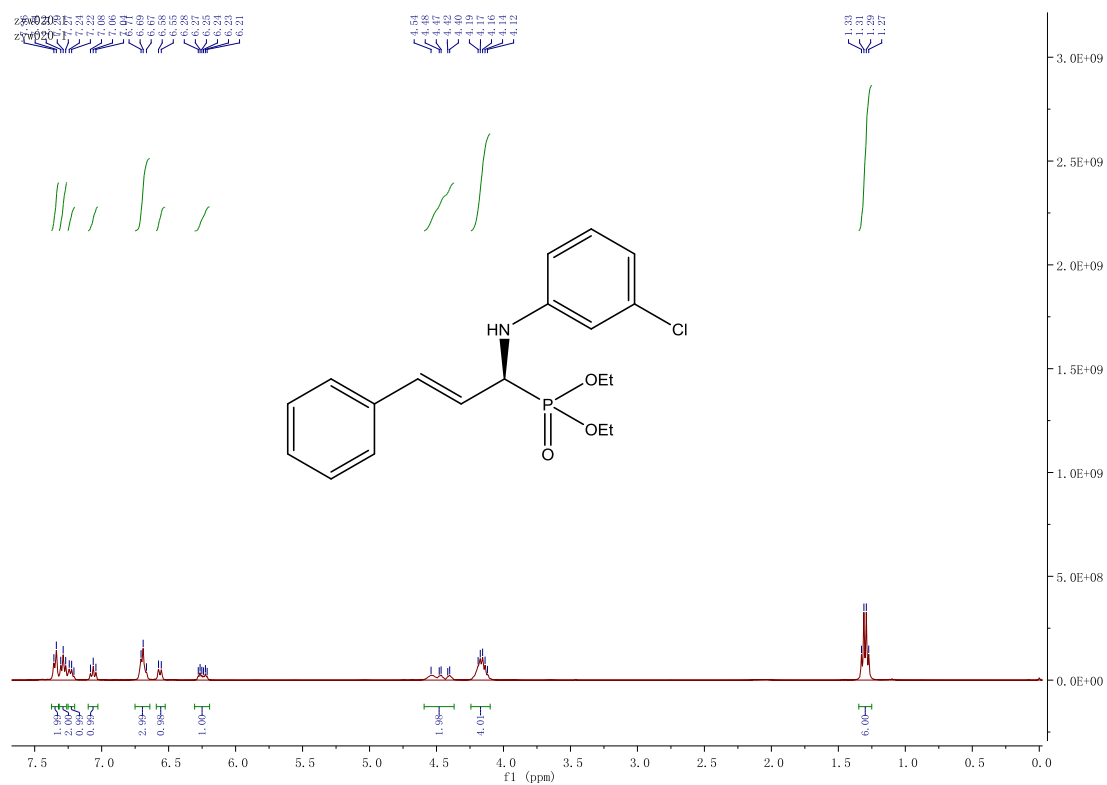
Diethyl (S,E)-3-(4-methoxyphenyl)-1-((4-methoxyphenyl)amino)allylphosphonate (4g)



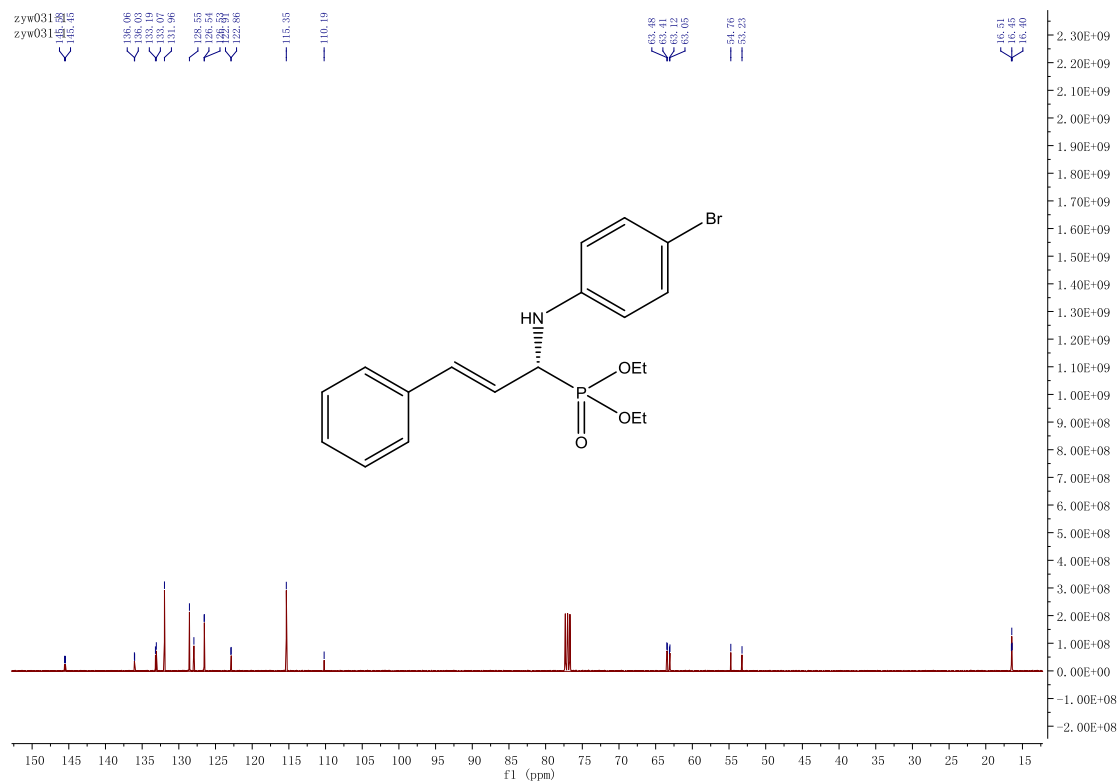
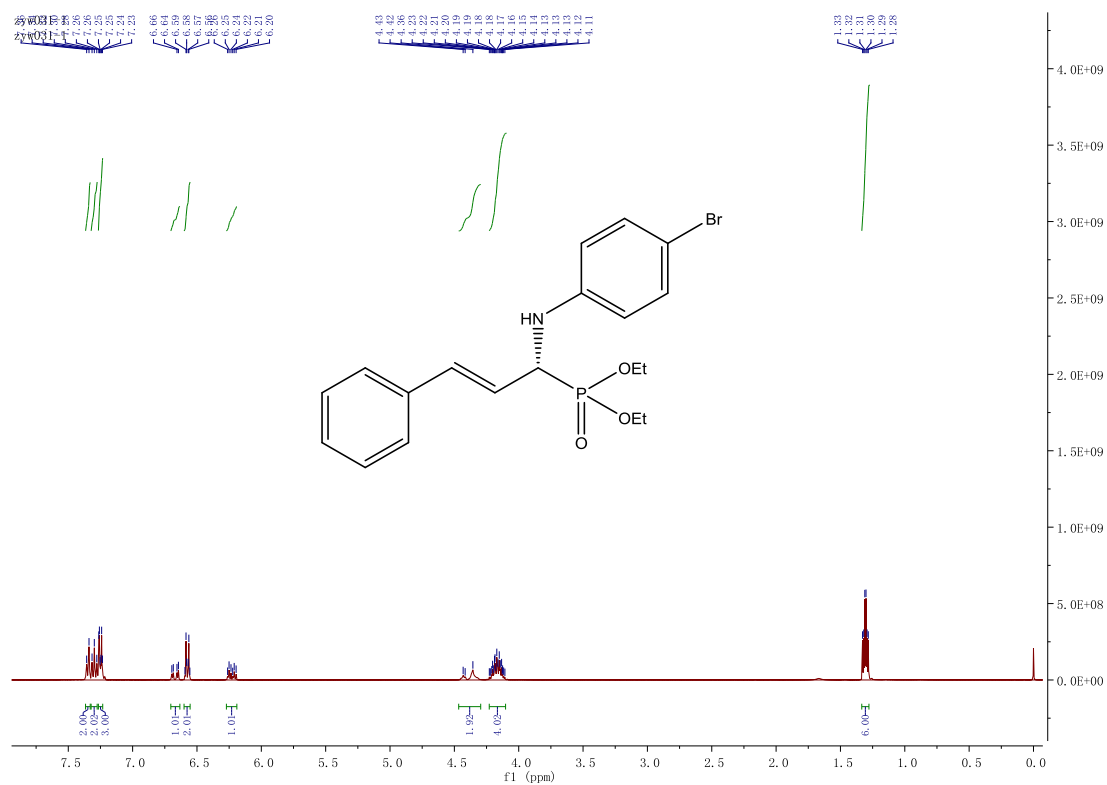
Diethyl (S,E)-(3-phenyl-1-(phenylamino)allyl)phosphonate (4h)



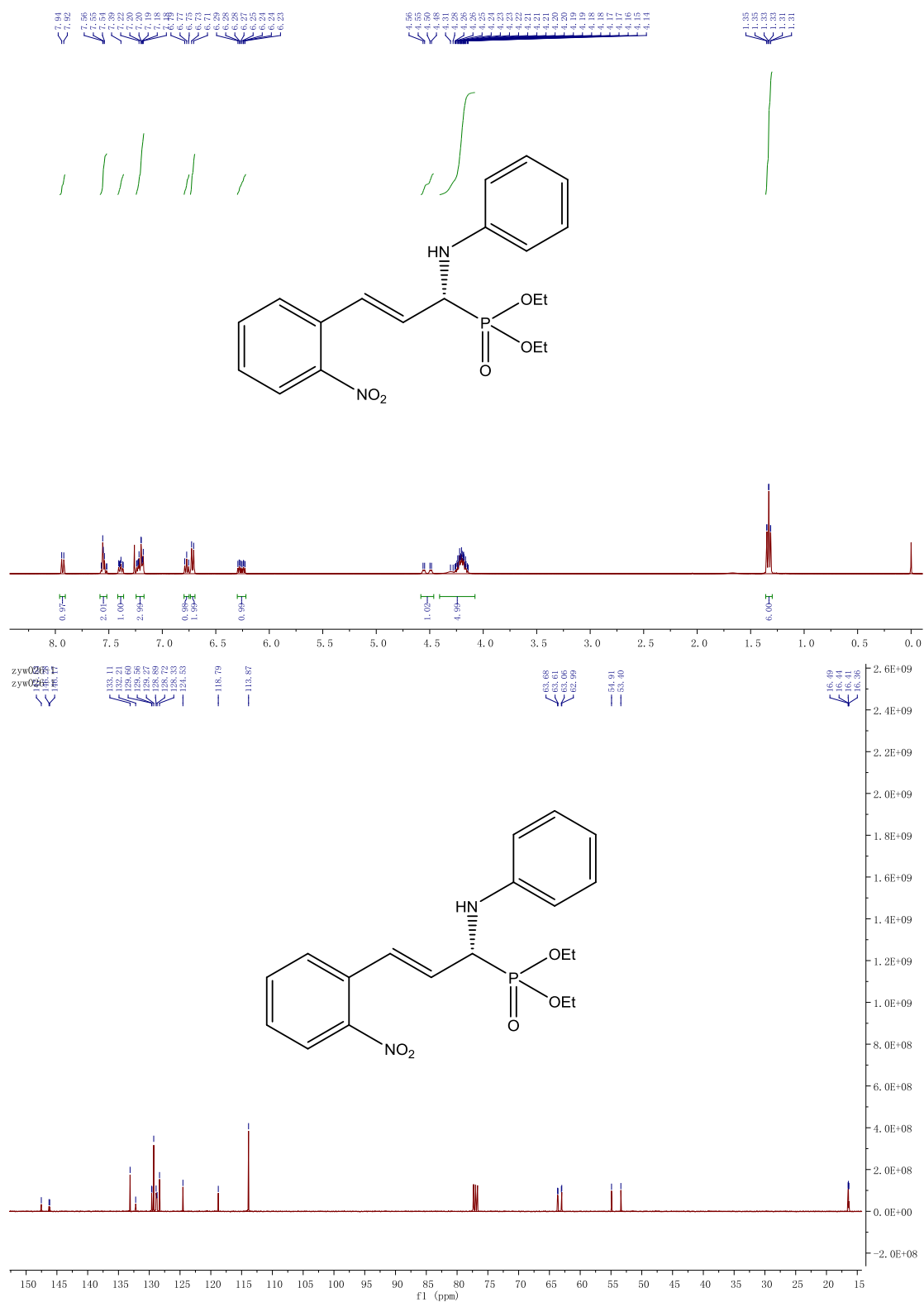
Diethyl (S,E)-1-((3-chlorophenyl)amino)-3-phenylallyl)phosphonate (4i)



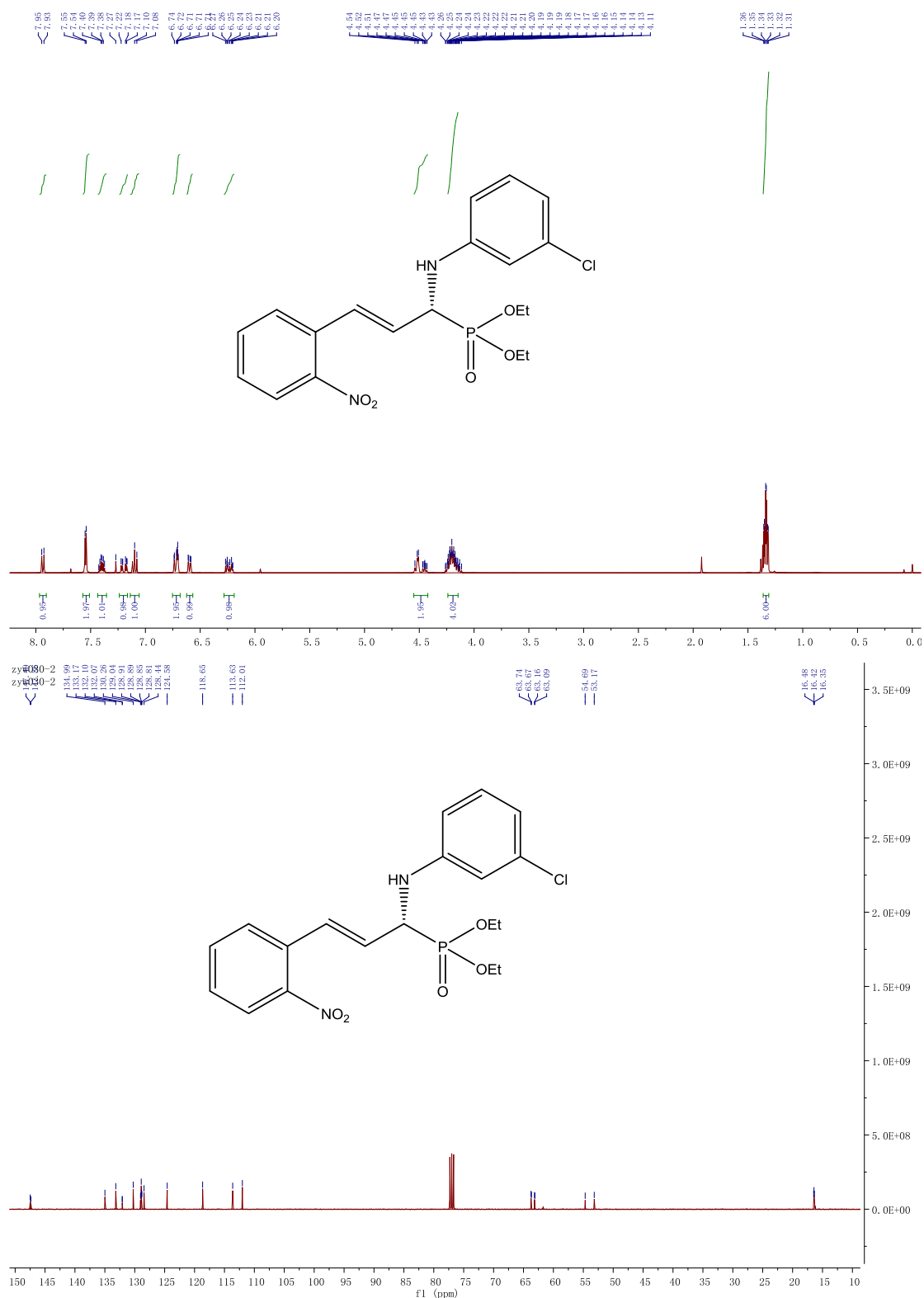
Diethyl (R,E)-1-((4-bromophenyl)amino)-3-phenylallyl)phosphonate (4j)



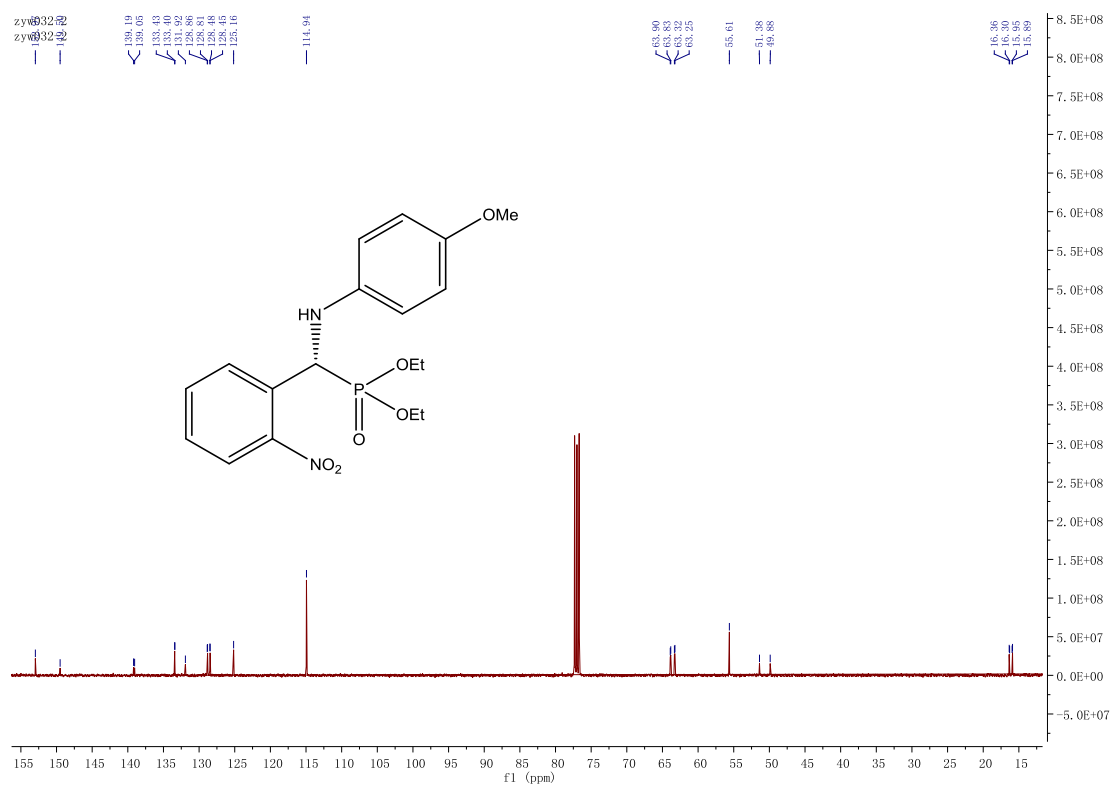
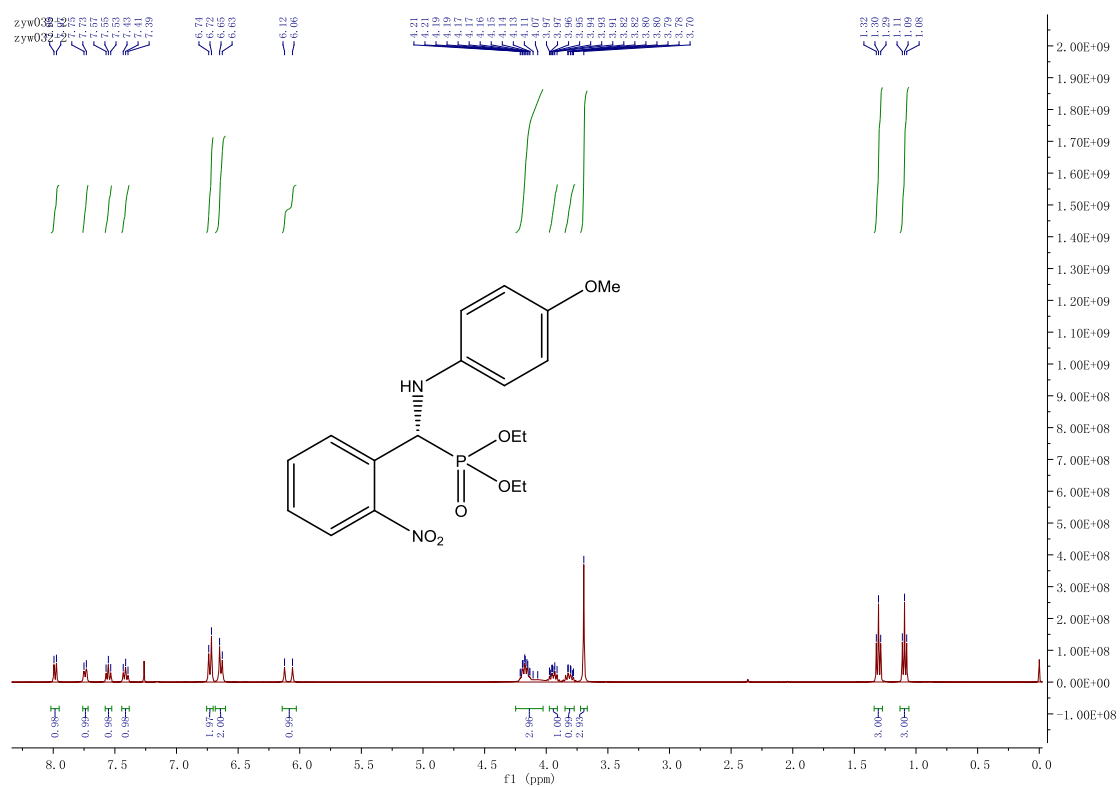
Diethyl (*R,E*)-1-(3-chlorophenyl)amino-3-(2-nitrophenyl)allylphosphonate (**4k**)



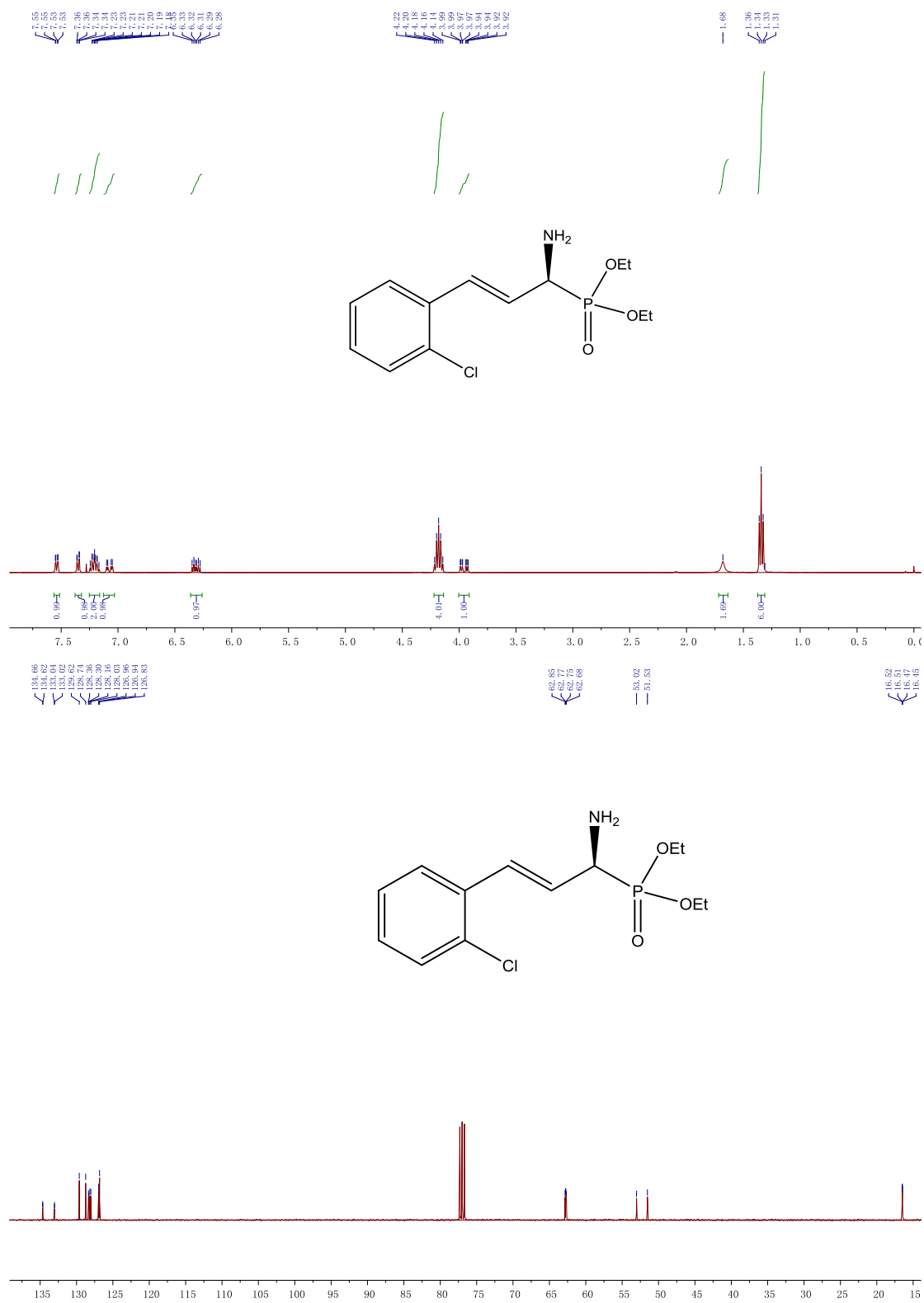
Diethyl (R,E)-1-((3-chlorophenyl)amino)-3-(2-nitrophenyl)allylphosphonate (4l)



Diethyl (R)-(((4-methoxyphenyl)amino)(2-nitrophenyl)methyl)phosphonate (4m)

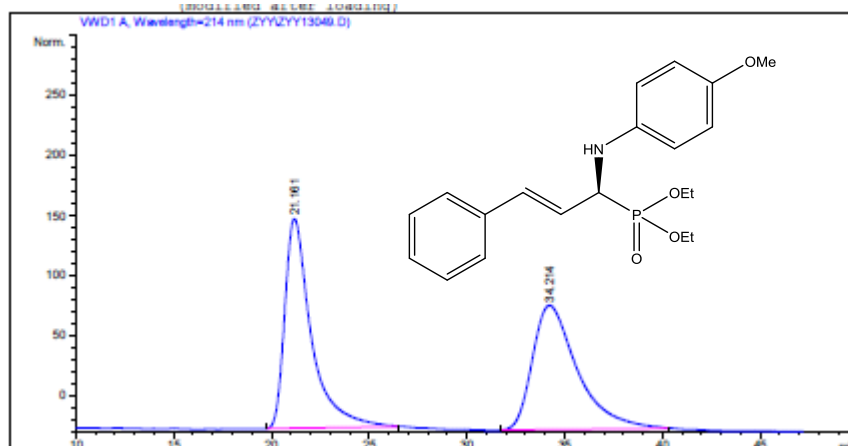


Diethyl (S,E)-(1-amino-3-(2-chlorophenyl)allyl)phosphonate (5)



2. HPLC spectra

Diethyl (S,E)-1-((4-methoxyphenyl)amino)-3-phenylallyl)phosphonate (4a)



Area Percent Report

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Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

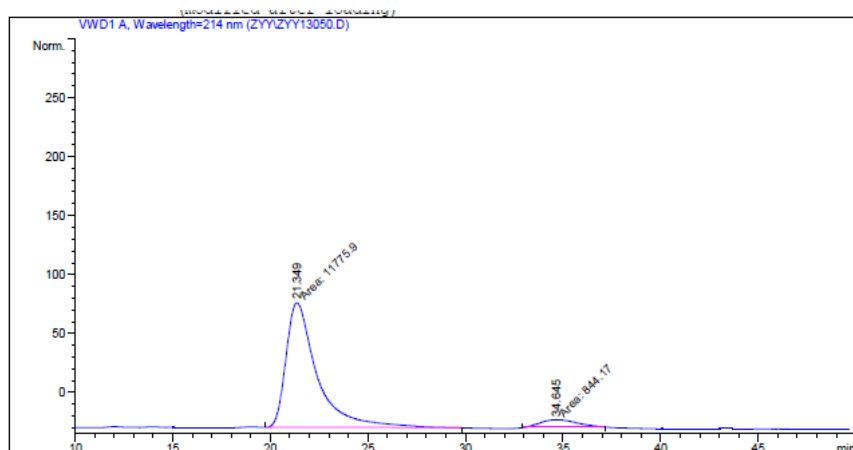
Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	21.161	BB	1.4050	1.66208e4	49.9756	174.55481	49.9756
2	34.214	BB	2.3610	1.66370e4	50.0244	103.53429	50.0244

Totals : 3.32578e4 278.08910

Results obtained with enhanced integrator!

*** End of Report ***



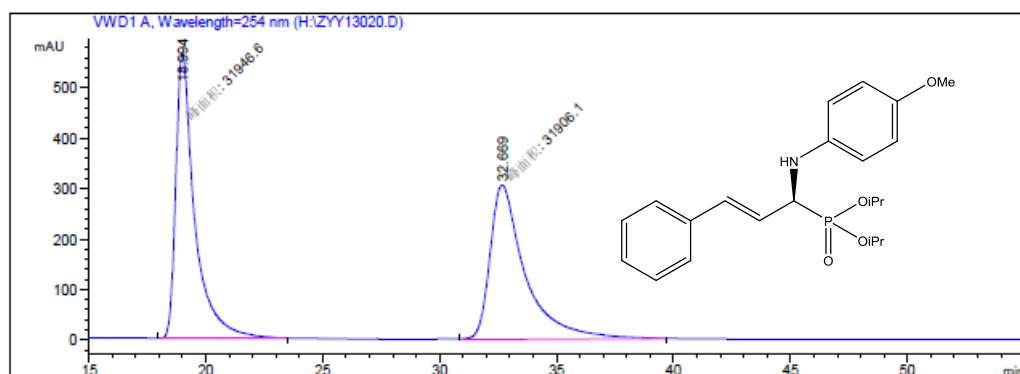
Area Percent Report

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

Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	21.349	MM	1.8564	1.17759e4	93.3109	105.72190	93.3109
2	34.645	MM	2.1668	844.17041	6.6891	6.49313	6.6891

Diisopropyl (S,E)-1-((4-methoxyphenyl)amino)-3-phenylallyl)phosphonate (4ab)

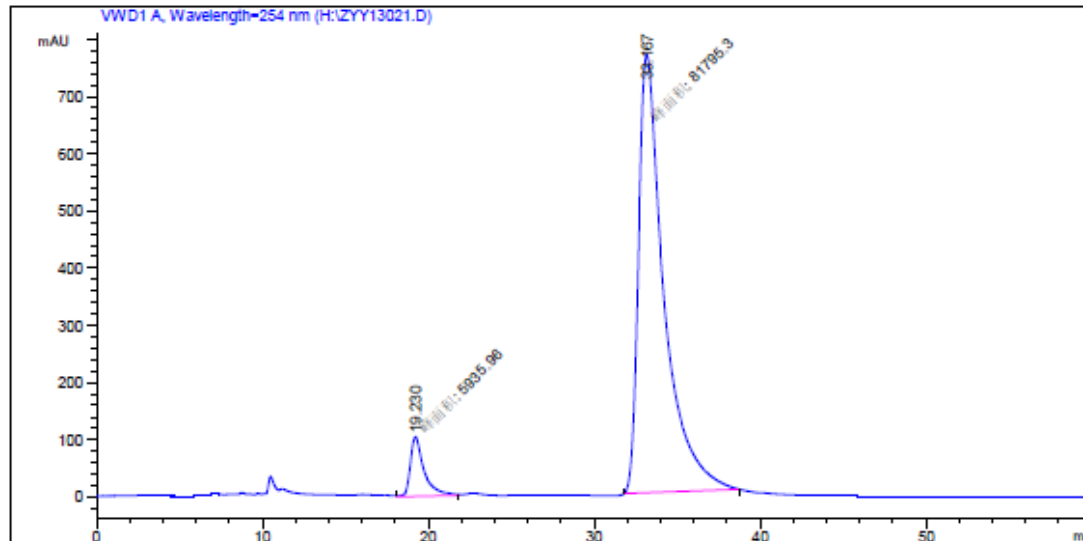


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 面积百分比报告
 =====

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	18.994	MM	0.9391	3.19466e4	566.97290	50.0317
2	32.669	MM	1.7357	3.19061e4	306.37756	49.9683

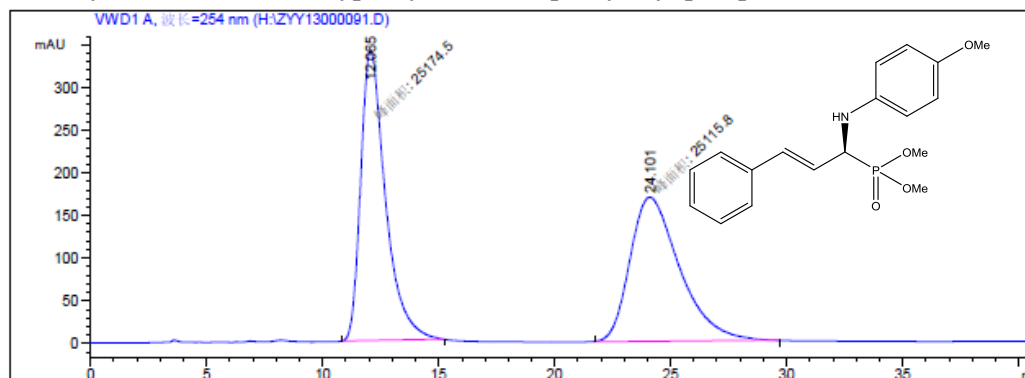


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	19.230	MM	0.9512	5935.96240	104.01104	6.7661
2	33.167	MM	1.7819	8.17953e4	765.07147	93.2339

总量 : 8.77313e4 869.08251

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 *** 报告结束 ***

Dimethyl (S,E)-1-((4-methoxyphenyl)amino)-3-phenylallyl)phosphonate (4ac)

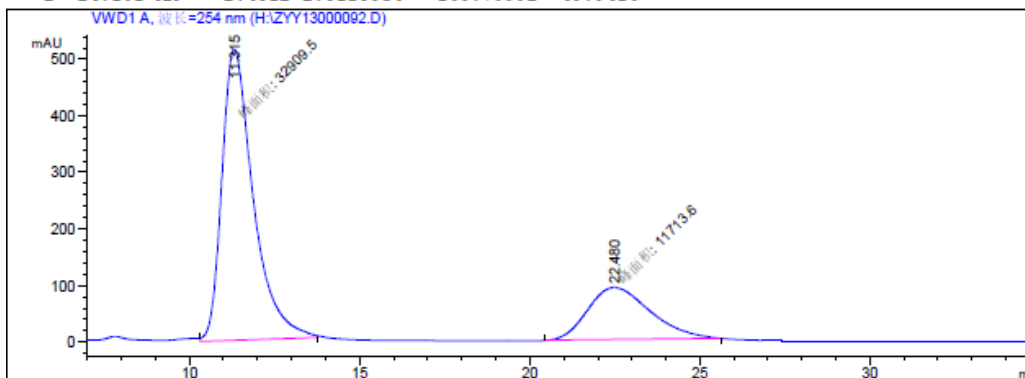


面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	12.065	MM	1.2361	2.51745e4	339.44324	50.0584
2	24.101	MM	2.4812	2.51158e4	168.70992	49.9416



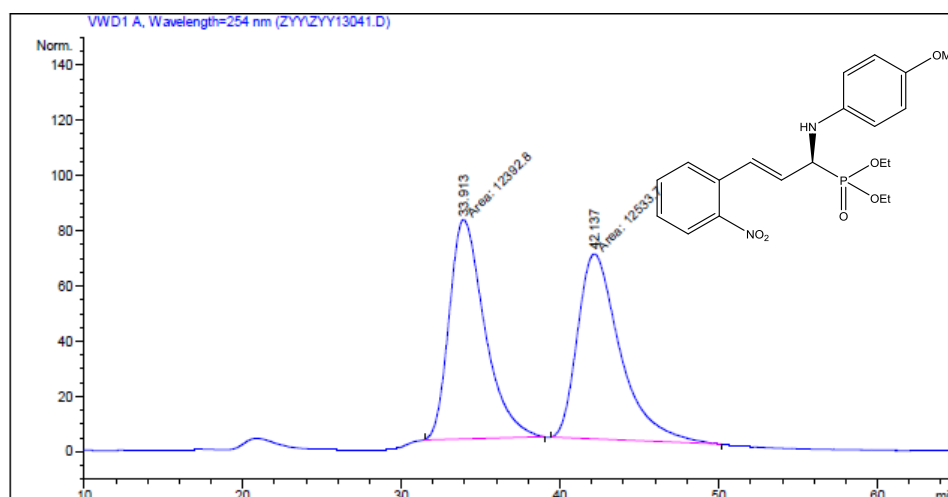
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 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	11.315	MM	1.0673	3.29095e4	513.92810	73.7499
2	22.480	MM	2.1238	1.17136e4	91.92217	26.2501

Diethyl (S,E)-1-((4-methoxyphenyl)amino)-3-(2-nitrophenyl)allyl)phosphonate (4b)

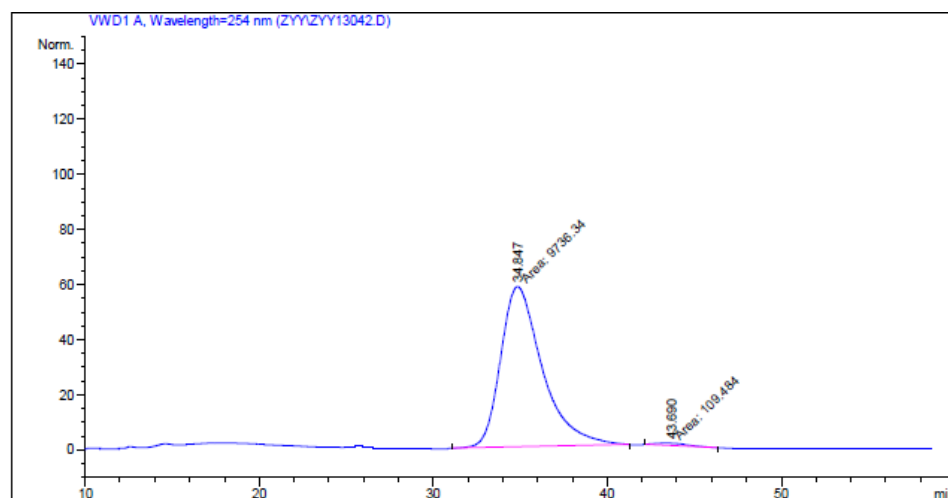


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 Area Percent Report
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 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.913	MM	2.5997	1.23928e4	79.44897	49.7173
2	42.137	MM	3.1149	1.25337e4	67.06396	50.2827



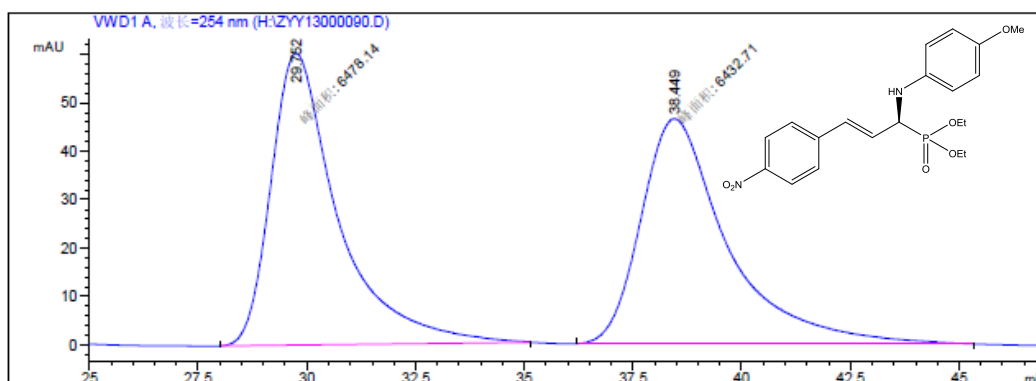
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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.847	MM	2.7882	9736.33887	58.19878	98.8880
2	43.690	MM	2.1118	109.48378	8.64047e-1	1.1120

Diethyl (S,E)-1-((4-methoxyphenyl)amino)-3-(4-nitrophenyl)allyl)phosphonate (4c)

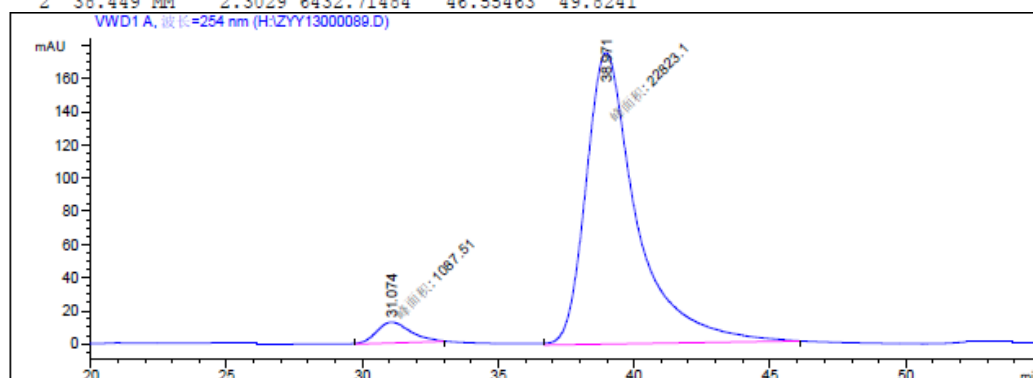


面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU * s	峰高 [mAU]	峰面积 %
1	29.752	MM	1.7867	6478.13623	60.42803	50.1759
2	38.449	MM	2.3029	6432.71484	46.55463	49.8241



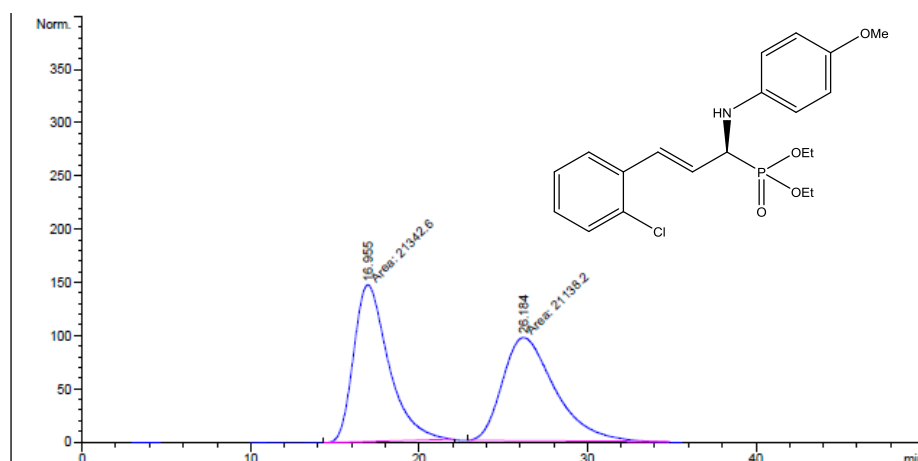
面积百分比报告

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 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU * s	峰高 [mAU]	峰面积 %
1	31.074	MM	1.4401	1087.50989	12.58645	4.5482
2	38.971	MM	2.1641	2.28231e4	175.76933	95.4518

Diethyl (S,E)-3-(2-chlorophenyl)-1-((4-methoxyphenyl)amino)allyl)phosphonate (4d)



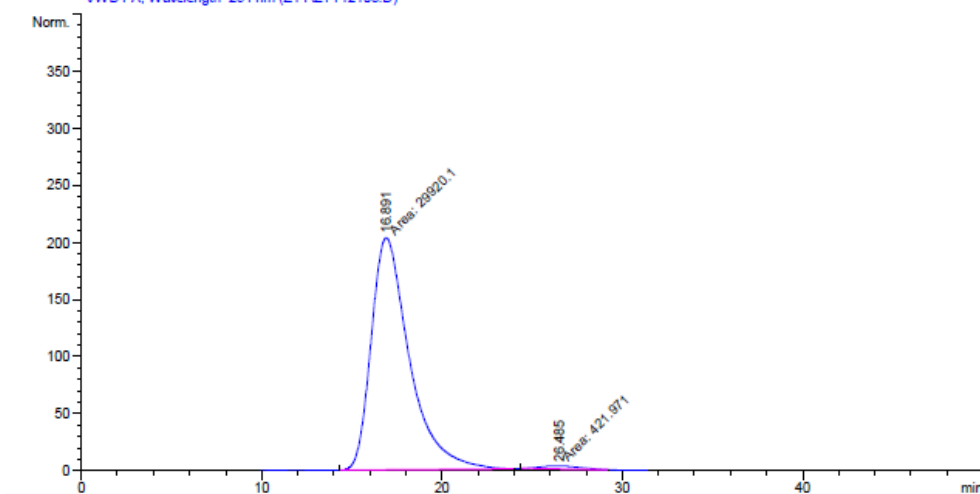
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Area Percent Report
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Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.955	MM	2.4106	2.13426e4	147.55788	50.2405
2	26.184	MM	3.6314	2.11382e4	97.01599	49.7595

VWD1 A, Wavelength=254 nm (ZYYZY12103.D)



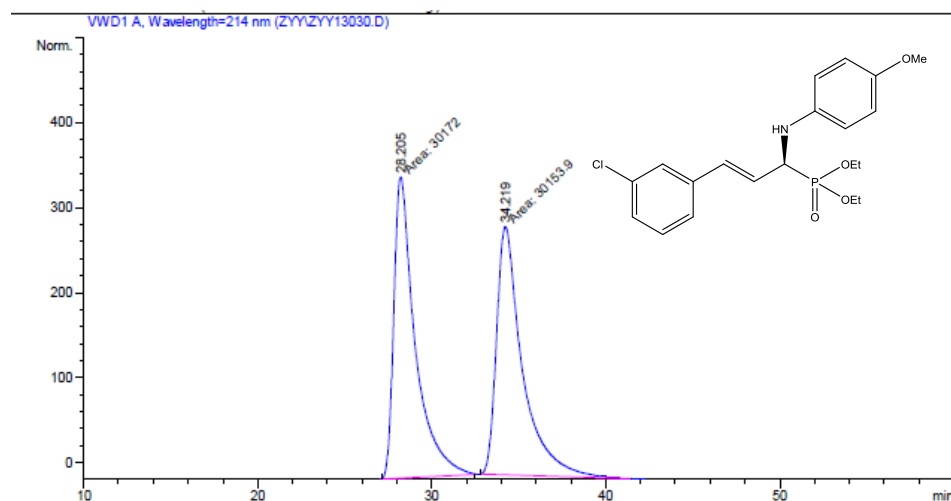
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Area Percent Report
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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.891	MM	2.4550	2.99201e4	203.12671	98.6093
2	26.485	MM	2.6037	421.97055	2.70109	1.3907

Diethyl (S,E)-3-(3-chlorophenyl)-1-((4-methoxyphenyl)amino)allylphosphonate (4c)

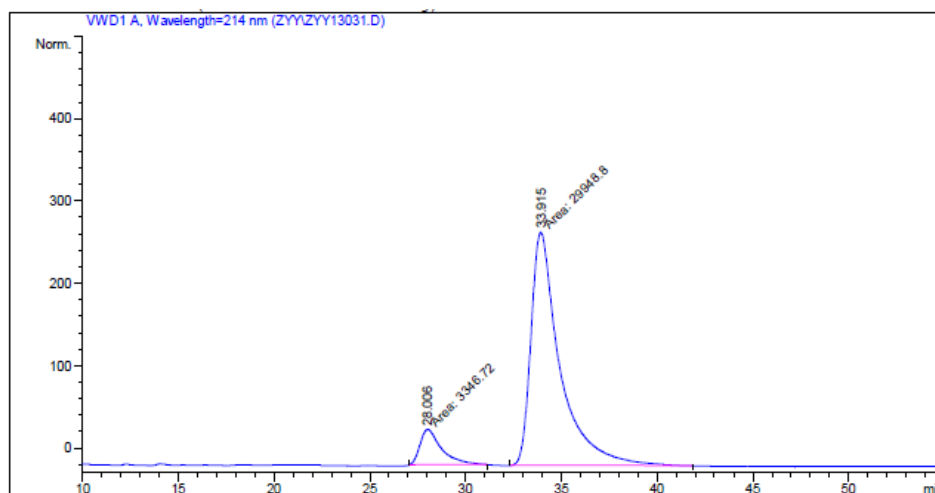


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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.205	MM	1.4196	3.01720e4	354.23856	50.0150
2	34.219	MM	1.7210	3.01539e4	292.01779	49.9850



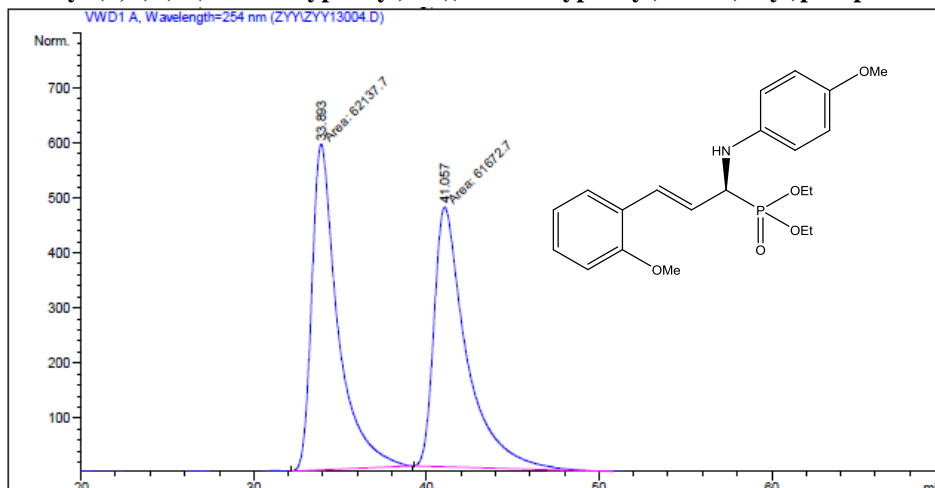
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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.006	MM	1.3031	3346.72095	42.80469	10.0516
2	33.915	MM	1.7624	2.99488e4	283.22610	89.9484

Diethyl (S,E)-3-(2-methoxyphenyl)-1-((4-methoxyphenyl)amino)allylphosphonate (4f)

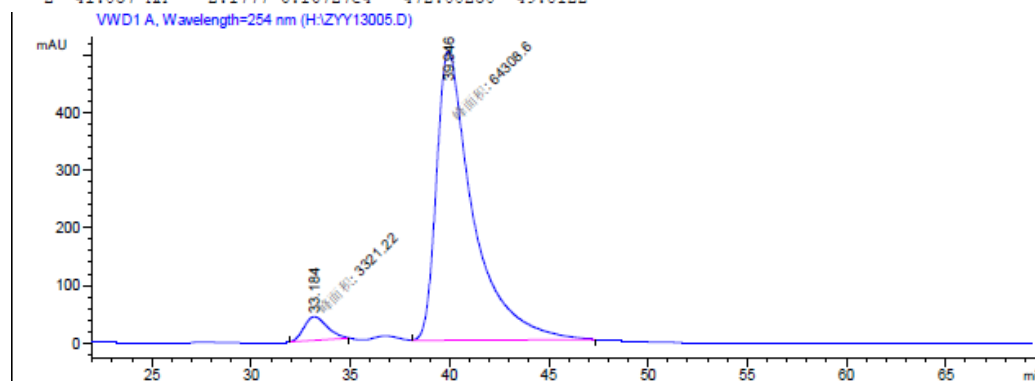


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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	33.893	MM	1.7497	6.21377e4	50.1878	591.88098	50.1878
2	41.057	MM	2.1777	6.16727e4	49.8122	472.00250	49.8122



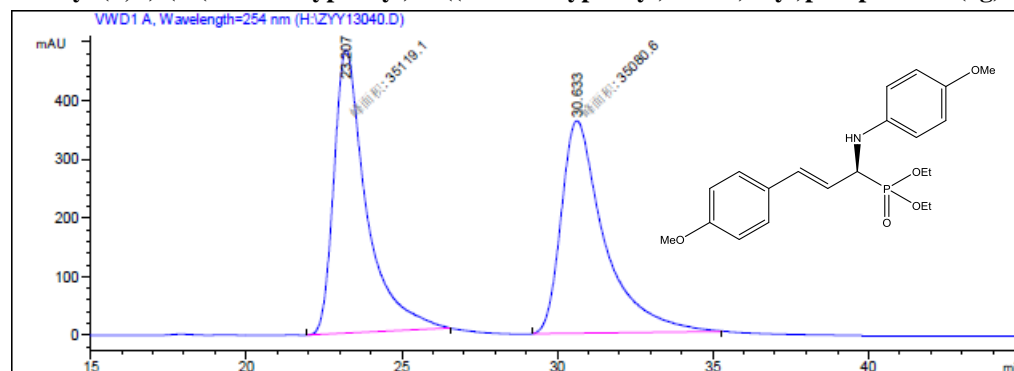
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 面积百分比报告
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排序 : 信号
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 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU	峰面积 %	峰高 [mAU]	峰面积 %
1	33.184	MM	1.3418	3321.21973	4.9109	41.25361	4.9109
2	39.946	MM	2.1351	6.43086e4	95.0891	501.99896	95.0891

Diethyl (S,E)-3-(4-methoxyphenyl)-1-((4-methoxyphenyl)amino)allylphosphonate (4g)

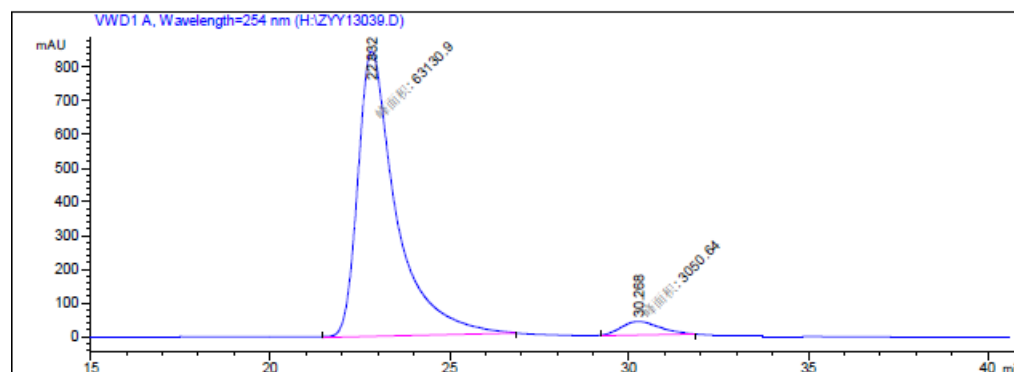


面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	23.207	MM	1.2113	3.51191e4	483.21561	50.0274
2	30.633	MM	1.6127	3.50806e4	362.54532	49.9726



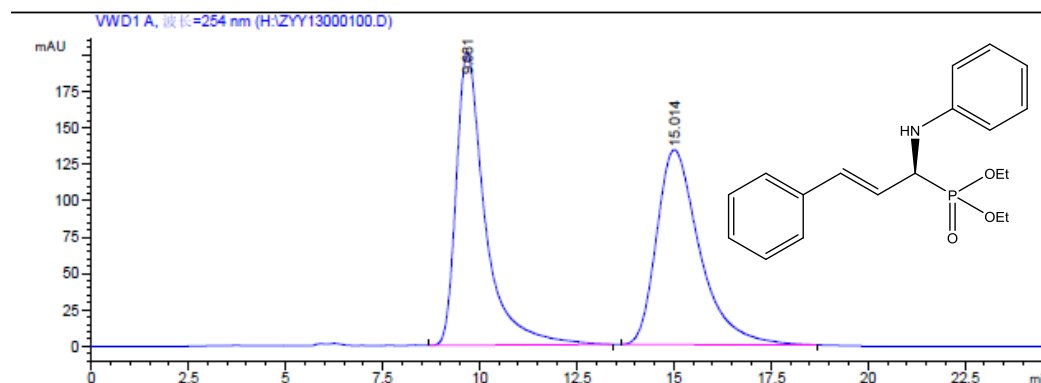
面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	22.832	MM	1.2419	6.31309e4	847.21466	95.3905
2	30.268	MM	1.2563	3050.64233	40.46988	4.6095

Diethyl (S,E)-(3-phenyl-1-(phenylamino)allyl)phosphonate (4h)

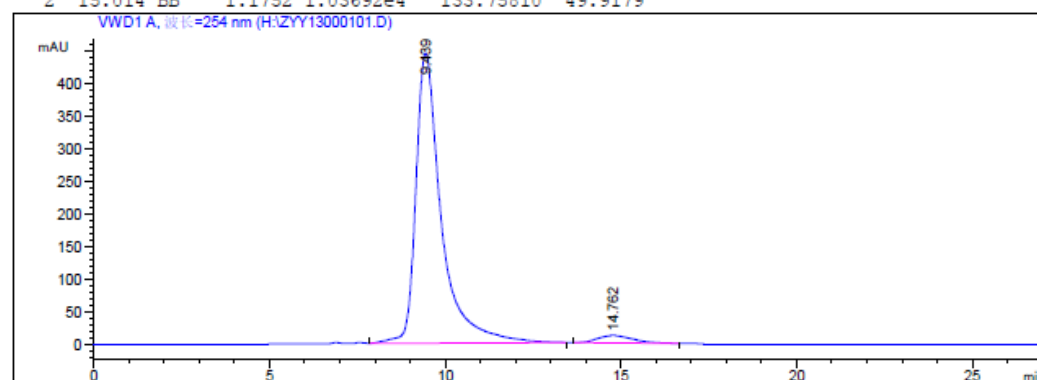


面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	9.681	VB	0.7653	1.04034e4	201.06274	50.0821
2	15.014	BB	1.1752	1.03692e4	133.75810	49.9179



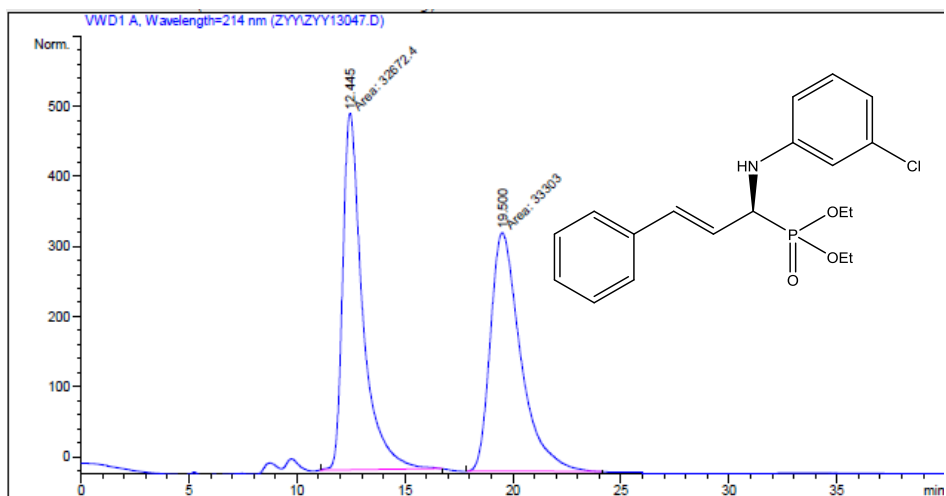
面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	9.439	VB	0.7479	2.25537e4	444.37250	96.6251
2	14.762	BB	0.9279	787.74506	11.32580	3.3749

Diethyl (S,E)-1-((3-chlorophenyl)amino)-3-phenylallyl)phosphonate (4i)

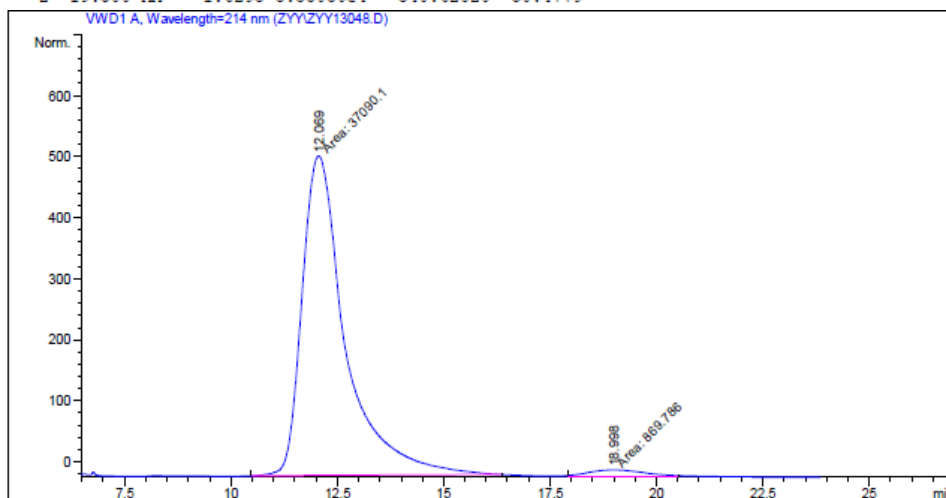


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 Area Percent Report
 =====

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

Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.445	MM	1.0699	3.26724e4	508.94403	49.5221
2	19.500	MM	1.6295	3.33030e4	340.62820	50.4779



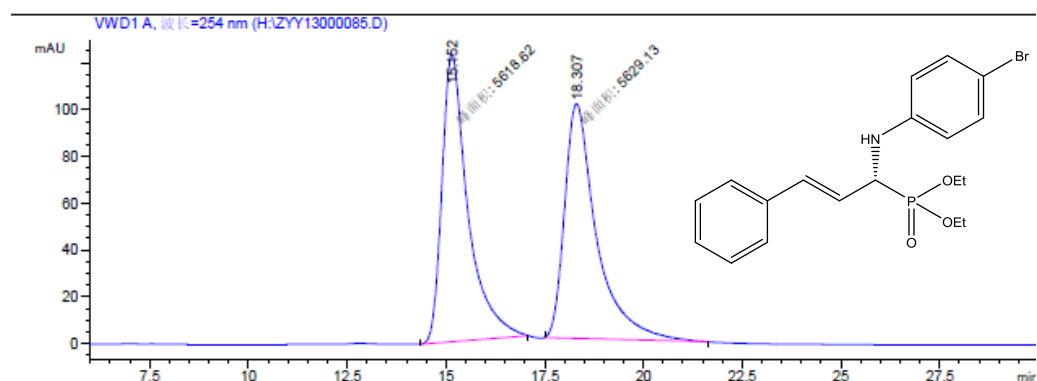
=====
 Area Percent Report
 =====

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

Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.069	MM	1.1800	3.70901e4	523.87054	97.7087
2	18.998	MM	1.4303	869.78632	10.13509	2.2913

Diethyl (R,E)-1-((4-bromophenyl)amino)-3-phenylallyl)phosphonate (4j)

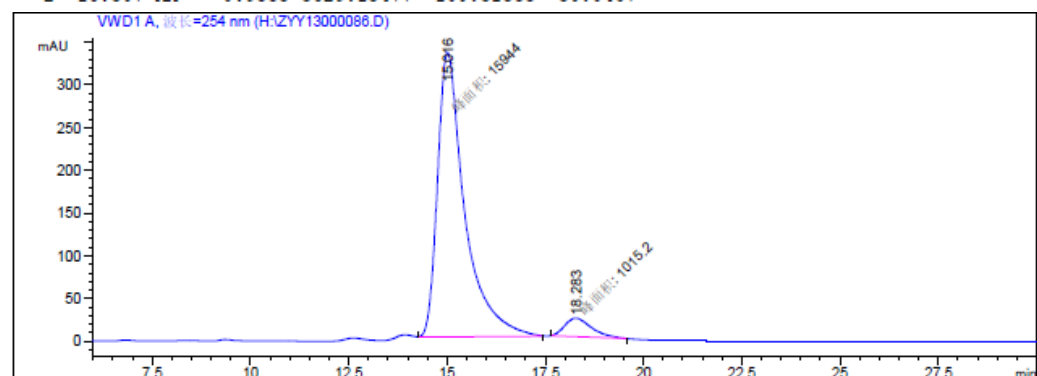


面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU * s	峰高 [mAU]	峰面积 %
1	15.152	MM	0.7617	5618.62451	122.93317	49.9533
2	18.307	MM	0.9353	5629.13477	100.31355	50.0467



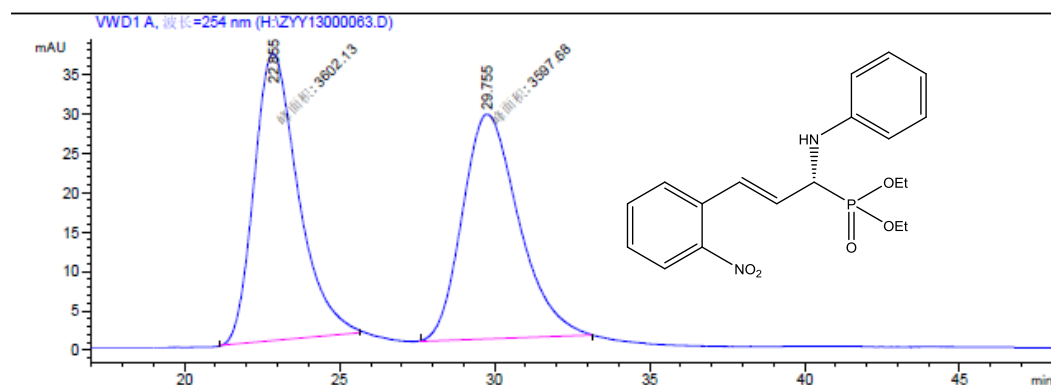
面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU * s	峰高 [mAU]	峰面积 %
1	15.016	MM	0.7988	1.59440e4	332.67679	94.0139
2	18.283	MM	0.7857	1015.20050	21.53367	5.9861

Diethyl (S,E)-(3-(2-nitrophenyl)-1-(phenylamino)allyl)phosphonate (4k)

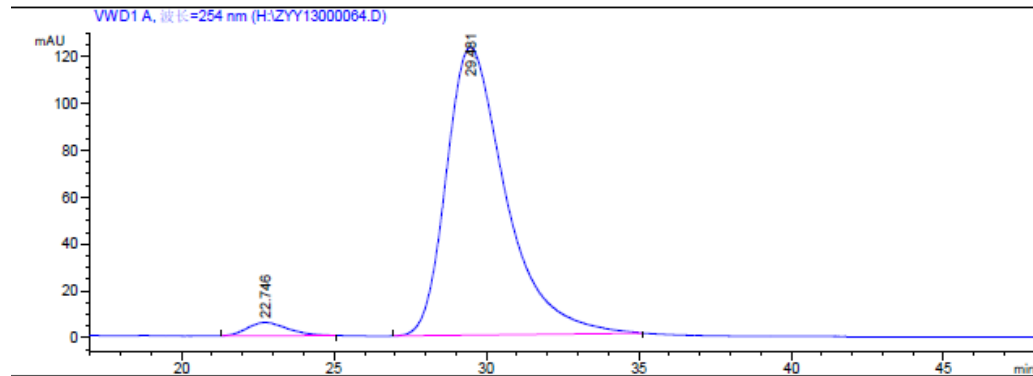


面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	22.855	MM	1.6485	3602.13232	36.41857	50.0309
2	29.755	MM	2.1041	3597.68213	28.49687	49.9691



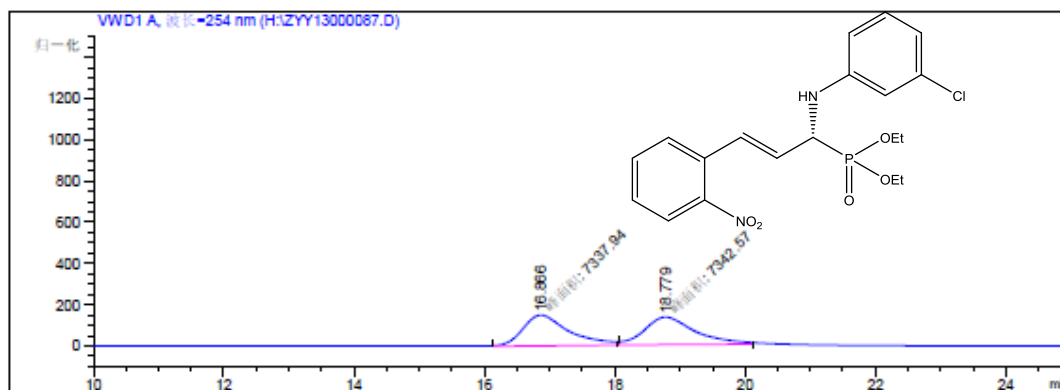
面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	22.746	BB	1.1701	527.80609	5.63404	3.0716
2	29.481	BB	1.9851	1.66555e4	122.84379	96.9284

Diethyl (S,E)-(1-((3-chlorophenyl)amino)-3-(2-nitrophenyl)allyl)phosphonate (4I)

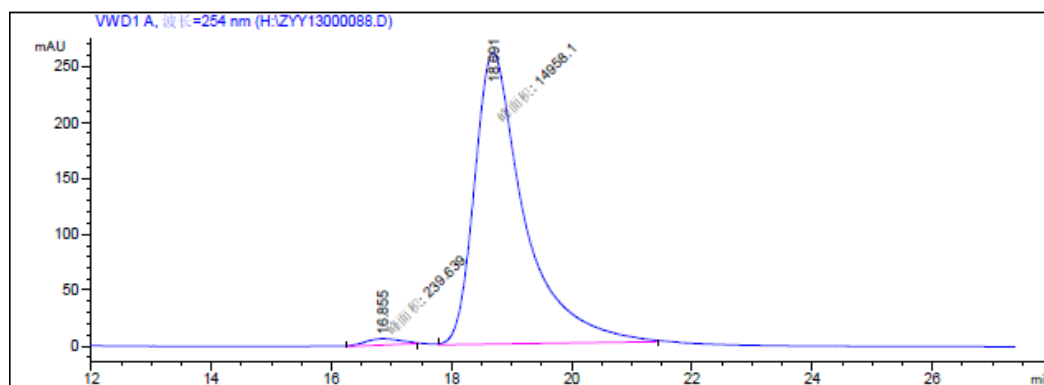


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 面积百分比报告
 =====

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	16.866	MF	0.8198	7337.93750	149.18555	49.9842
2	18.779	MM	0.9115	7342.56738	134.26286	50.0158



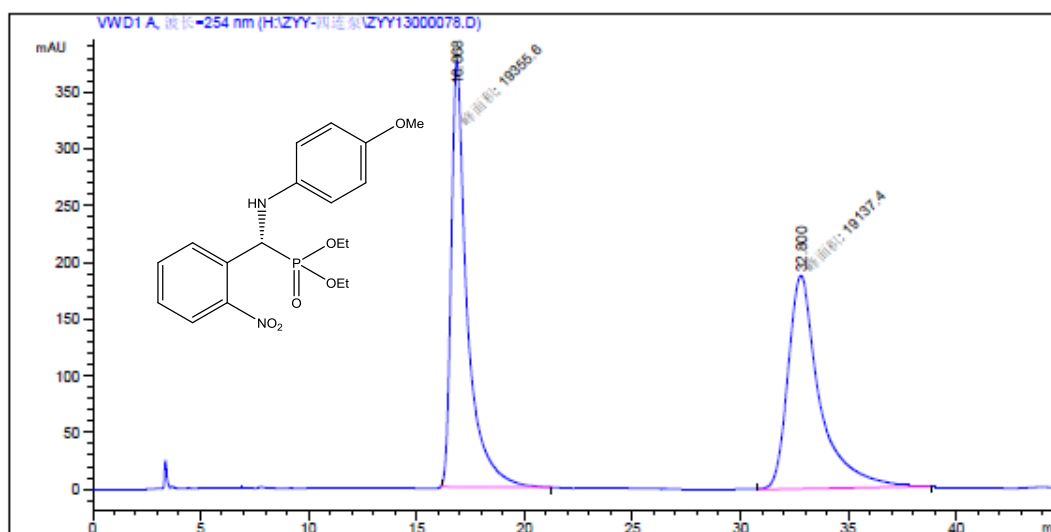
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 面积百分比报告
 =====

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	16.855	MM	0.6900	239.63919	5.78853	1.5768
2	18.691	MM	0.9588	1.49581e4	260.02487	98.4232

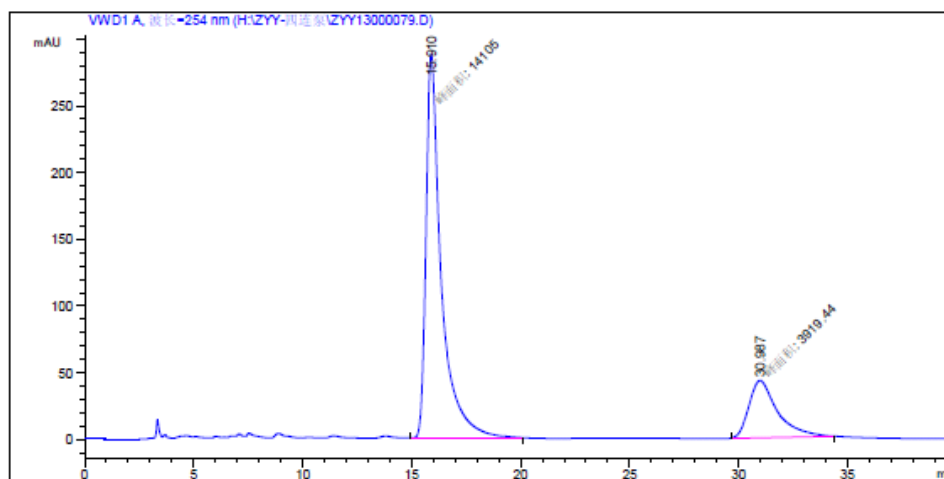
Diethyl (R)-(((4-methoxyphenyl)amino)(2-nitrophenyl)methyl)phosphonate (4m)



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 *
1	16.868	MM	0.8593	1.93556e4	375.40598	50.2824
2	32.800	MM	1.6989	1.91374e4	187.74457	49.7166

总量 : 3.84930e4 563.15054

*** 报告结束 ***

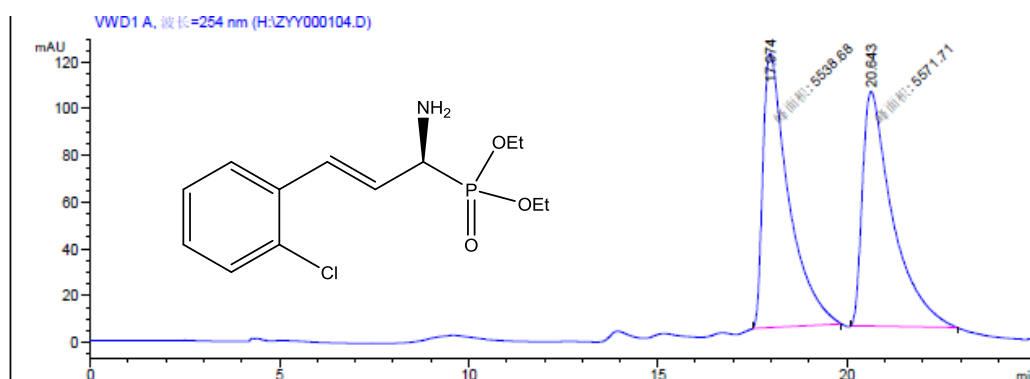


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 *
1	15.910	MM	0.8181	1.41050e4	287.34915	78.2548
2	30.987	MM	1.5280	3919.44360	42.75269	21.7452

总量 : 1.80244e4 330.10184

*** 报告结束 ***

Diethyl (S,E)-(1-amino-3-(2-chlorophenyl)allyl)phosphonate (5)

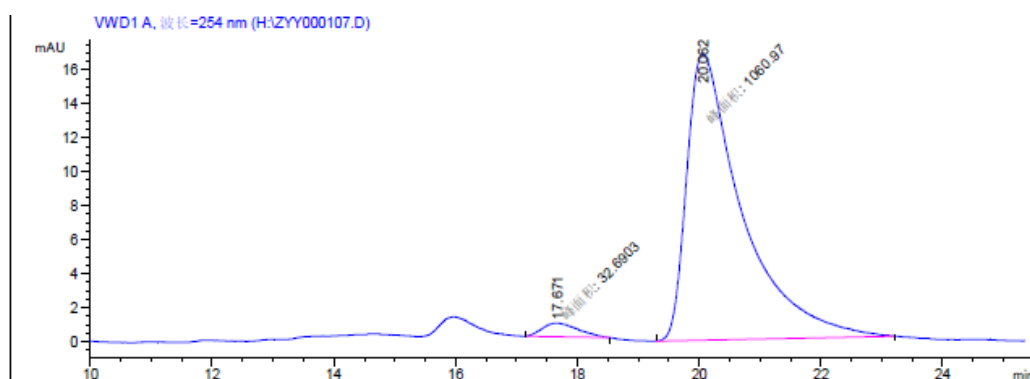


面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	17.974	MM	0.7866	5538.67529	117.35621	49.8513
2	20.643	MM	0.9251	5571.71484	100.37855	50.1487



面积百分比报告

排序 : 信号
 乘积因子 : 1.0000
 稀释因子 : 1.0000
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	17.671	MM	0.6857	32.69025	7.94548e-1	2.9891
2	20.062	MM	1.0485	1060.96594	16.86471	97.0109