

Supporting Information for

Rhodium–Catalyzed Asymmetric Hydrogenation of Unprotected β -Enamine Phosphonates

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I. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^1H , ^{13}C and ^{31}P NMR spectra were recorded with a Bruker ADVANCE III (400 MHz) spectrometer with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl_3 at 7.26 ppm (for ^1H NMR) or 77.0 ppm (for ^{13}C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR and ^{31}P NMR analyses were run with decoupling. Optical rotations $[\alpha]_{\text{D}}$ were determined using a PERKIN ELMER polarimeter 343 instrument. HPLC analysis was conducted on an Agilent 1260 Series instrument. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh).

II. Typical procedure for the synthesis of compound 1

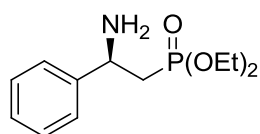
A 250 mL flask was charged with diethylmethylphosphonate (33 mmol, 5.02 g) in dry THF (90 mL). At $-78\text{ }^\circ\text{C}$, a 1.6 M n-BuLi/hexane-solution (36.3 mmol, 22.7 mL) was slowly added and the solution was stirred for 1 h. After addition of 1.0 equiv of benzonitrile (33 mmol, 3.41 g), stirring was continued for 15 min at this temperature and further 2 h at $0\text{ }^\circ\text{C}$. After quenching the reaction with water (25 mL), the mixture was evaporated on a rotavapor to remove the THF. The aqueous residue was extracted with dichloromethane (3×30 mL), the combined extracts were dried (Na_2SO_4), and concentrated to yield **1a** as a pale yellow oil (88%). The physical data were identical in all respect to those previously reported.^[1]

III. General procedure for asymmetric hydrogenation of compound 1

A stock solution was made by mixing $[\text{Rh}(\text{cod})_2]\text{BF}_4$ with ligand in a 1:1.1 molar ratio in TFE at room temperature for 30 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (0.1 mL, 0.001 mmol) was transferred by syringe into the vials charged with different substrates (0.1 mmol for each) in anhydrous TFE (0.9 mL). The vials were subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was then stirred under H_2 (40 atm) at $40\text{ }^\circ\text{C}$ for 20 h. The hydrogen gas was released carefully. The solution was

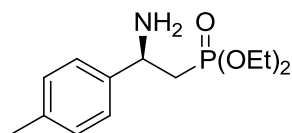
concentrated and passed through a short column of silica gel (eluant: EA) to remove the metal complex. The ee values of all compounds were determined by HPLC analysis of the corresponding benzamide.

Diethyl 2-amino-2-phenylethylphosphonate **1a**



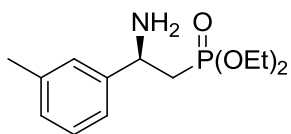
Colorless oil; 86% ee; $[\alpha]_{\text{D}}^{20} = -2.9$ ($c = 1$, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; $t_{\text{R}} = 11.1$ min (minor), 17.1 min (major). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.39\text{--}7.28$ (m, 5H), 4.44–4.38 (m, 1H), 4.12–4.04 (m, 4H), 2.18–2.11 (m, 4H), 1.32–1.28 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 145.3$ (d, $J = 26.3$ Hz), 128.7, 127.5, 126.2, 61.8 (t, $J = 6.1$ Hz), 51.2 (d, $J = 4.0$ Hz), 35.9 (d, $J = 137.4$ Hz), 16.4 (d, $J = 6.1$ Hz); ^{31}P NMR (161.7 MHz, CDCl_3) $\delta = 29.2$. ESI-HRMS Calculated for $\text{C}_{12}\text{H}_{21}\text{NO}_3\text{P}^+$ ($[\text{M}+\text{H}]^+$): 258.1259, found 258.1254.

Diethyl 2-amino-2-p-tolyethylphosphonate **1b**



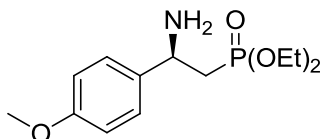
Colorless oil; 86% ee; $[\alpha]_{\text{D}}^{20} = -0.4$ ($c = 1$, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 210 nm; $t_{\text{R}} = 5.4$ min (minor), 9.8 min (major). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.28\text{--}7.26$ (m, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 4.41–4.35 (m, 1H), 4.12–4.05 (m, 4H), 2.33 (s, 3H), 2.17–2.05 (m, 4H), 1.33–1.29 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 142.5$ (d, $J = 16.2$ Hz), 137.1, 129.3, 126.0, 61.7 (t, $J = 7.1$ Hz), 50.9 (d, $J = 3.0$ Hz), 36.0 (d, $J = 136.4$ Hz), 21.1, 16.5 (d, $J = 6.1$ Hz); ^{31}P NMR (161.7 MHz, CDCl_3) $\delta = 29.4$. ESI-HRMS Calculated for $\text{C}_{13}\text{H}_{23}\text{NO}_3\text{P}^+$ ($[\text{M}+\text{H}]^+$): 272.1416, found 272.1412.

Diethyl 2-amino-2-m-tolyethylphosphonate **1c**



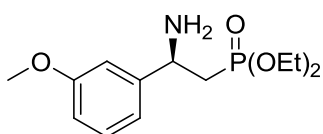
Colorless oil; 86% ee; $[\alpha]_D^{20} = -2.4$ ($c = 1$, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; $t_R = 9.5$ min (minor), 16.8 min (major). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.27$ -7.18 (m, 3H), 7.09-7.07 (m, 1H), 4.41-4.35 (m, 1H), 4.13-4.05 (m, 4H), 2.35 (s, 3H), 2.18-2.09 (m, 4H), 1.31 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 145.3$ (d, $J = 16.2$ Hz), 138.3, 128.6, 128.2, 126.8, 123.2, 61.7 (t, $J = 7.1$ Hz), 51.1 (d, $J = 2.0$ Hz), 35.9 (d, $J = 136.4$ Hz), 21.5, 16.5 (d, $J = 6.1$ Hz); ^{31}P NMR (161.7 MHz, CDCl_3) $\delta = 29.4$. ESI-HRMS Calculated for $\text{C}_{13}\text{H}_{23}\text{NO}_3\text{P}^+$ ($[\text{M}+\text{H}]^+$): 272.1416, found 272.1411.

Diethyl 2-amino-2-(4-methoxyphenyl)ethylphosphonate **1d**



Colorless oil; 86% ee; $[\alpha]_D^{20} = 6.0$ ($c = 1$, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 210 nm; $t_R = 8.0$ min (minor), 13.4 min (major). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.31$ (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.09-5.04 (m, 1H), 4.16-4.07 (m, 4H), 3.8 (s, 1H), 2.25-2.14 (m, 3H), 1.36-1.29 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 129.4$, 127.5, 127.2, 113.9, 74.0, 72.1, 61.1 (d, $J = 5.1$ Hz), 55.4, 16.5 (d, $J = 7.1$ Hz); ^{31}P NMR (161.7 MHz, CDCl_3) $\delta = 26.3$. ESI-HRMS Calculated for $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{P}^+$ ($[\text{M}+\text{H}]^+$): 288.1365, found 288.1360.

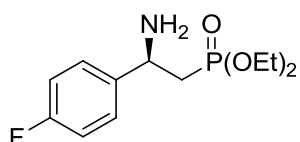
Diethyl 2-amino-2-(3-methoxyphenyl)ethylphosphonate **1e**



Colorless oil; 85% ee; $[\alpha]_D^{20} = -3.7$ ($c = 1$, CH_2Cl_2); The enantiomeric excess was determined

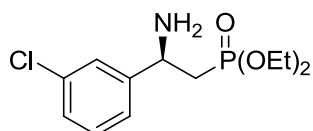
by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 85:15; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 10.1 min (minor), 21.0 min (major). ^1H NMR (400 MHz, CDCl_3) δ = 7.27-7.23 (m, 1H), 6.96-6.95 (m, 2H), 6.82-6.79 (m, 1H), 4.42-4.36 (m, 1H), 4.14-4.06 (m, 4H), 3.82 (s, 3H), 2.17-1.98 (m, 4H), 1.34-1.30 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ = 159.8, 147.2 (d, J = 16.2 Hz), 129.7, 118.4, 113.0, 111.6, 61.8 (t, J = 6.1 Hz), 55.3, 51.2 (d, J = 4.0 Hz), 36.0 (d, J = 137.4 Hz), 16.5 (d, J = 6.1 Hz); ^{31}P NMR (161.7 MHz, CDCl_3) δ = 29.3. ESI-HRMS Calculated for $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{P}^+$ ($[\text{M}+\text{H}]^+$): 288.1365, found 288.1359.

Diethyl 2-amino-2-(4-fluorophenyl)ethylphosphonate **1f**



Colorless oil; 80% ee; $[\alpha]_{\text{D}}^{20}$ = -3.1 (c = 1, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 10.6 min (minor), 16.8 min (major). ^1H NMR (400 MHz, CDCl_3) δ = 7.38-7.35 (m, 2H), 7.04-7.00 (m, 2H), 4.44-4.38 (m, 1H), 4.16-4.04 (m, 4H), 2.19-2.04 (m, 4H), 1.33-1.29 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ = 162.0 (d, J = 246.4 Hz), 127.8 (d, J = 8.1 Hz), 127.2 (d, J = 8.1 Hz), 115.4 (d, J = 21.2 Hz), 61.8 (t, J = 6.1 Hz), 50.6 (d, J = 4.0 Hz), 36.0 (d, J = 138.4 Hz), 16.4 (d, J = 4.0 Hz); ^{31}P NMR (161.7 MHz, CDCl_3) δ = 28.9. ESI-HRMS Calculated for $\text{C}_{12}\text{H}_{20}\text{FNO}_3\text{P}^+$ ($[\text{M}+\text{H}]^+$): 276.1165, found 276.1162.

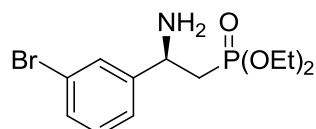
Diethyl 2-amino-2-(3-chlorophenyl)ethylphosphonate **1g**



Yellow oil; 85% ee; $[\alpha]_{\text{D}}^{20}$ = -3.6 (c = 1, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 10.3 min (minor), 16.2 min (major). ^1H NMR (400 MHz, CDCl_3) δ = 7.41 (s, 1H), 7.28-7.24 (m, 3H), 4.43-4.37 (m, 1H),

4.13-4.04 (m, 4H), 2.15-2.08 (m, 4H), 1.33-1.29 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ = 147.3 (d, J = 16.2 Hz), 134.4, 130.0, 127.6, 126.5, 124.5, 61.9 (t, J = 6.1 Hz), 50.9 (d, J = 4.0 Hz), 35.8 (d, J = 138.4 Hz), 16.4 (q, J = 4.0 Hz); ^{31}P NMR (161.7 MHz, CDCl_3) δ = 28.6. ESI-HRMS Calculated for $\text{C}_{12}\text{H}_{20}\text{ClNO}_3\text{P}^+$ ($[\text{M}+\text{H}]^+$): 292.0869, found 292.0868.

Diethyl 2-amino-2-(3-bromophenyl)ethylphosphonate **1h**



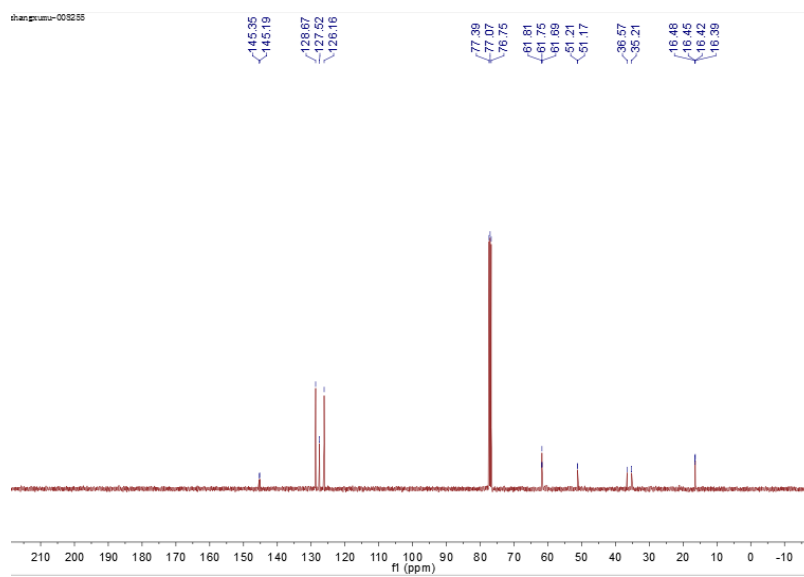
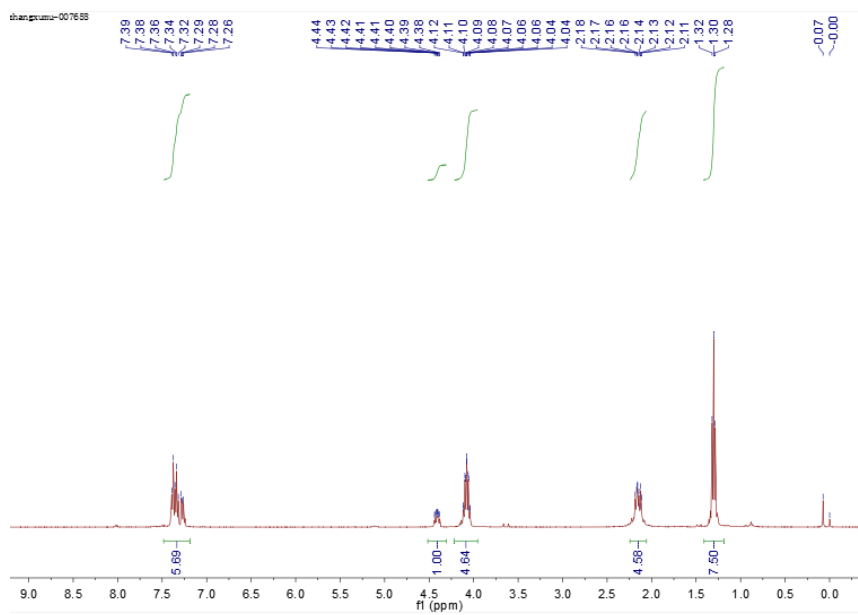
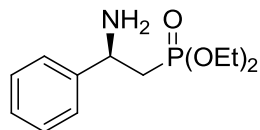
Yellow oil; 84% ee; $[\alpha]_{\text{D}}^{20}$ = -3.6 (c = 1, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis of the corresponding benzamide, Chiralpak OD-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 210 nm; t_{R} = 5.9 min (minor), 7.9 min (major). ^1H NMR (400 MHz, CDCl_3) δ = 7.56 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 8.0 Hz, 8.0 Hz, 1H), 4.41-4.35 (m, 1H), 4.13-4.05 (m, 4H), 2.14-2.00 (m, 4H), 1.33-1.29 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ = 147.7 (d, J = 16.2 Hz), 130.6, 130.3, 129.4, 124.9, 122.7, 61.8 (t, J = 6.1 Hz), 50.8 (d, J = 4.0 Hz), 35.9 (d, J = 138.4 Hz), 16.4 (q, J = 4.0 Hz); ^{31}P NMR (161.7 MHz, CDCl_3) δ = 28.6. ESI-HRMS Calculated for $\text{C}_{12}\text{H}_{20}\text{BrNO}_3\text{P}^+$ ($[\text{M}+\text{H}]^+$): 336.0364, found 336.0354.

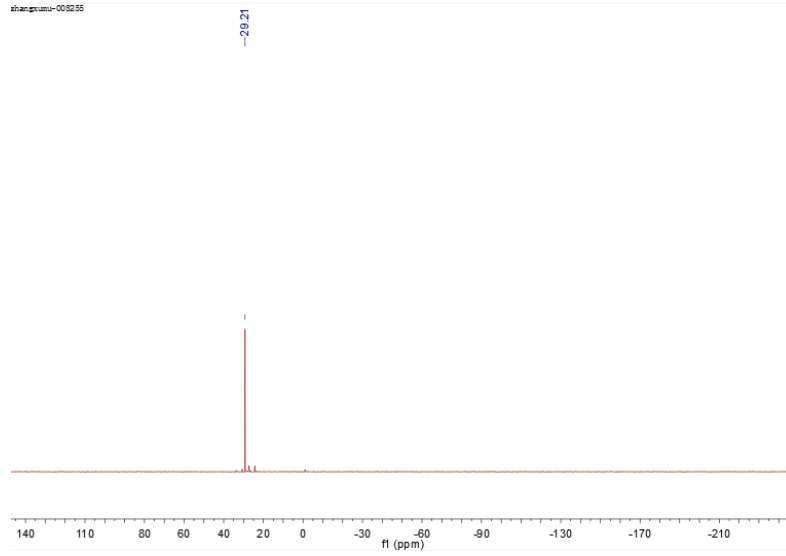
Reference

[1] R. Kadyrov, J. Holz, B. Schöffner, O. Zayas, J. Almena, A. Börner, *Tetrahedron: Asymmetry* 2008, 19, 1189-1192.

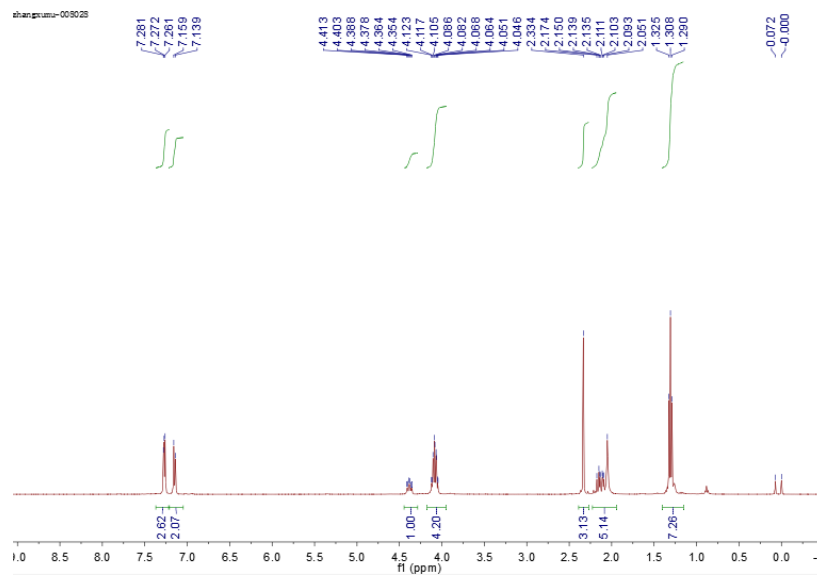
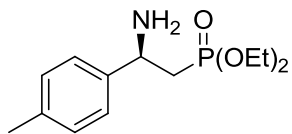
IV. NMR spectra

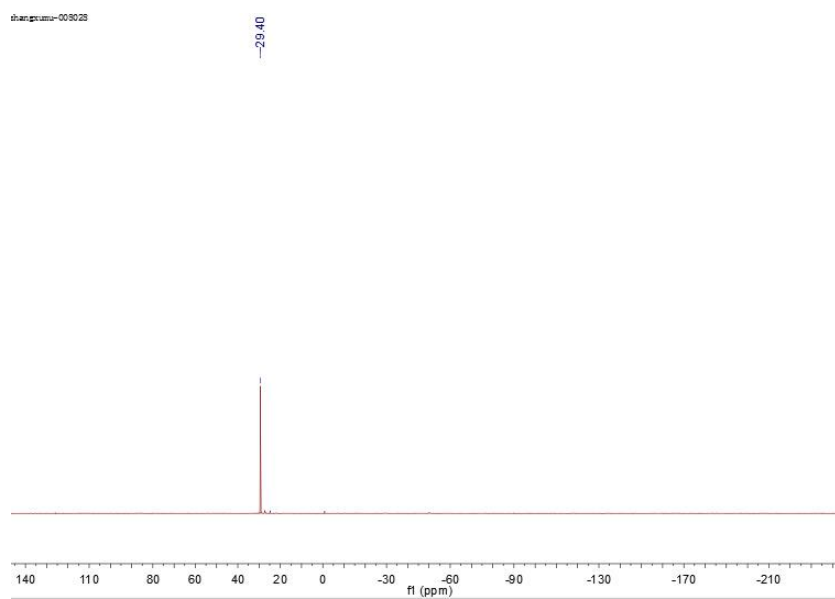
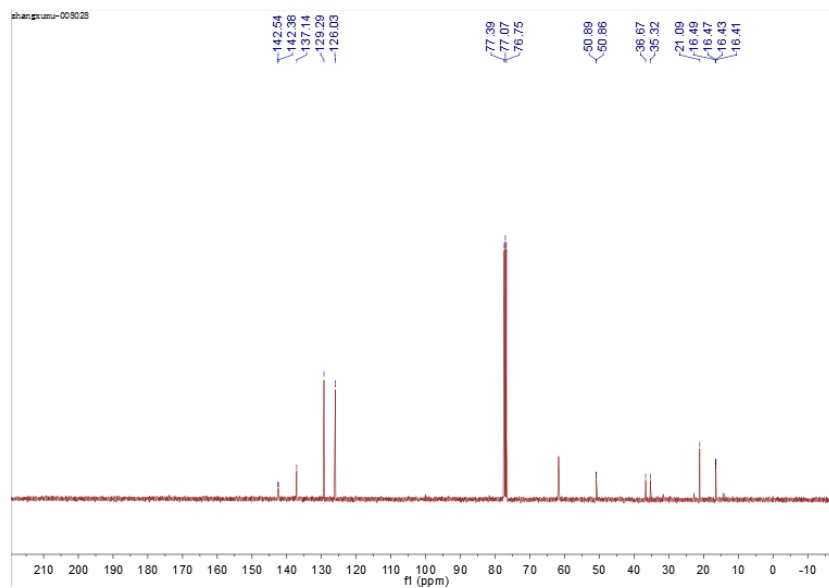
Diethyl 2-amino-2-phenylethylphosphonate **1a**



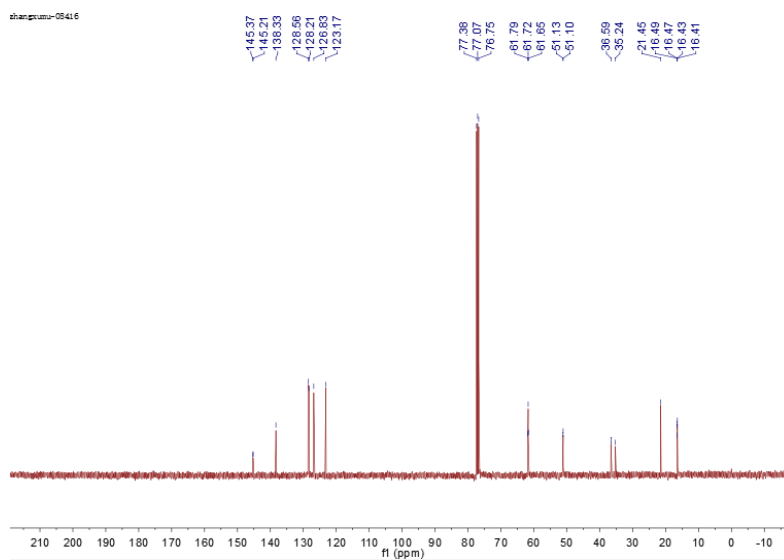
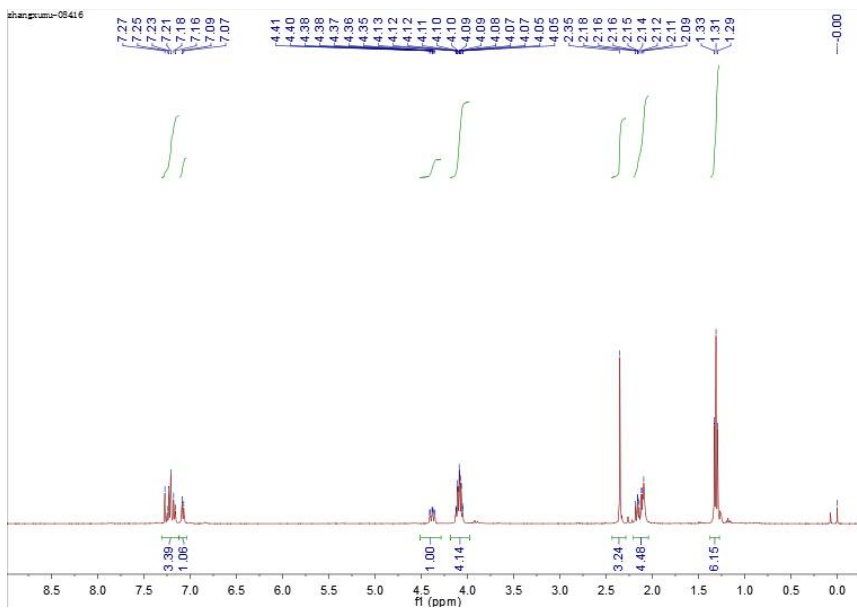
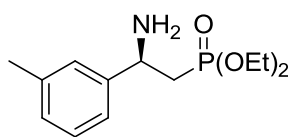


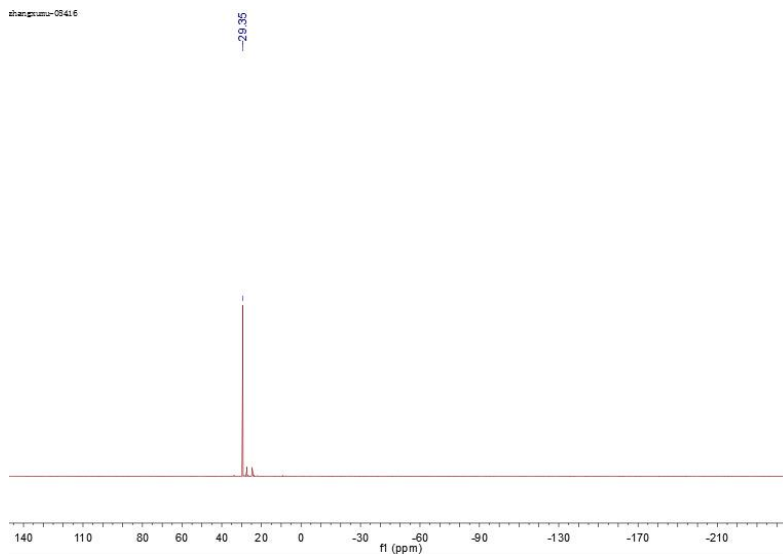
Diethyl 2-amino-2-p-tolyethylphosphonate **1b**



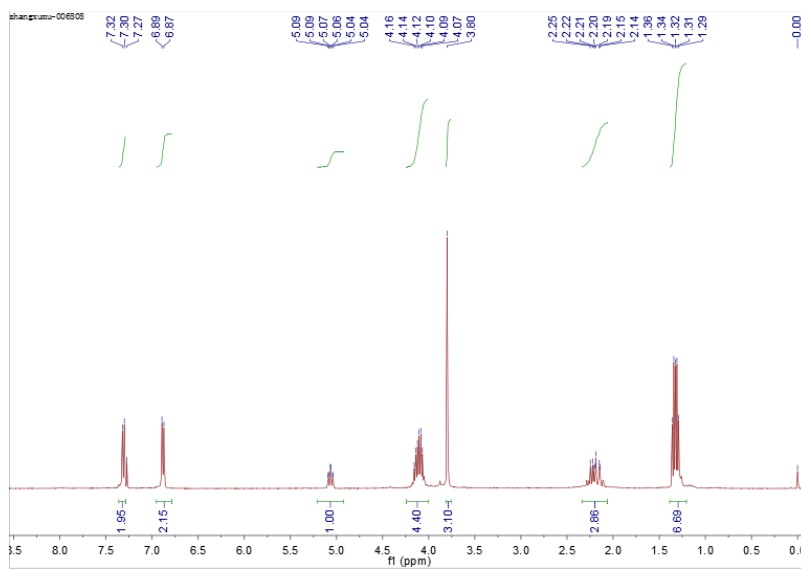
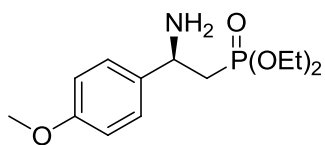


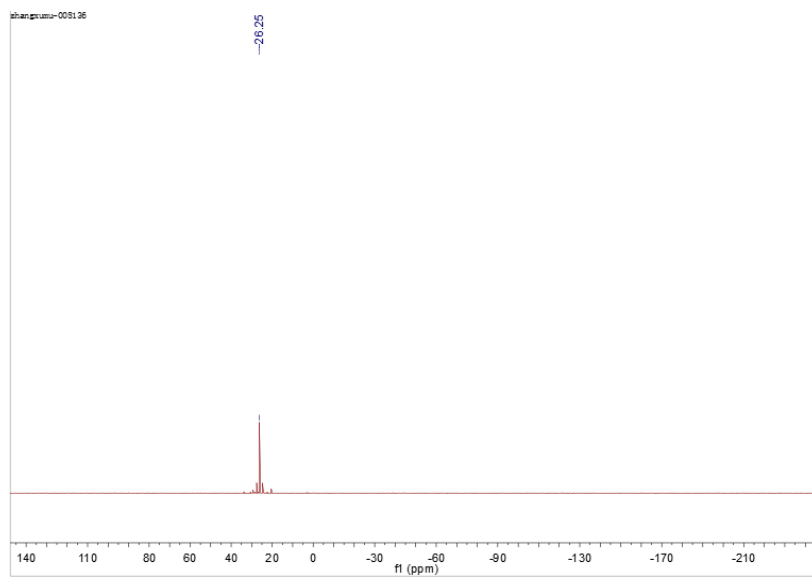
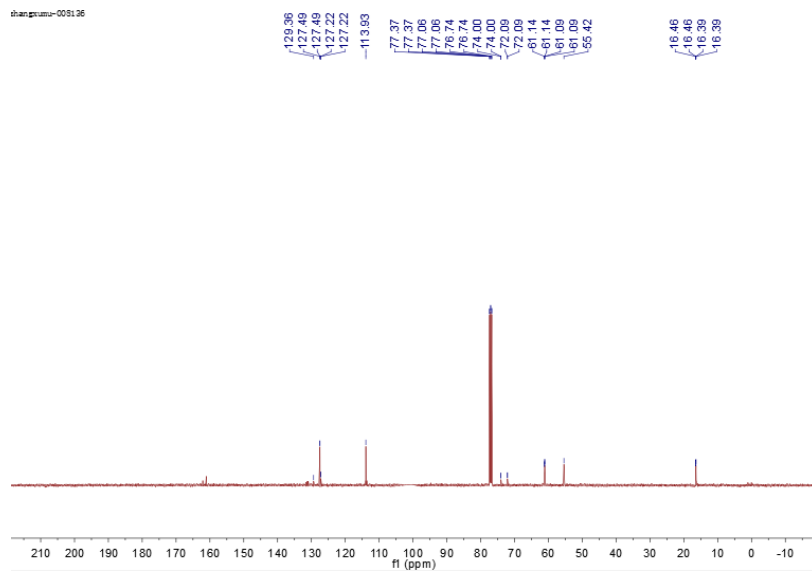
Diethyl 2-amino-2-m-tolyethylphosphonate **1c**



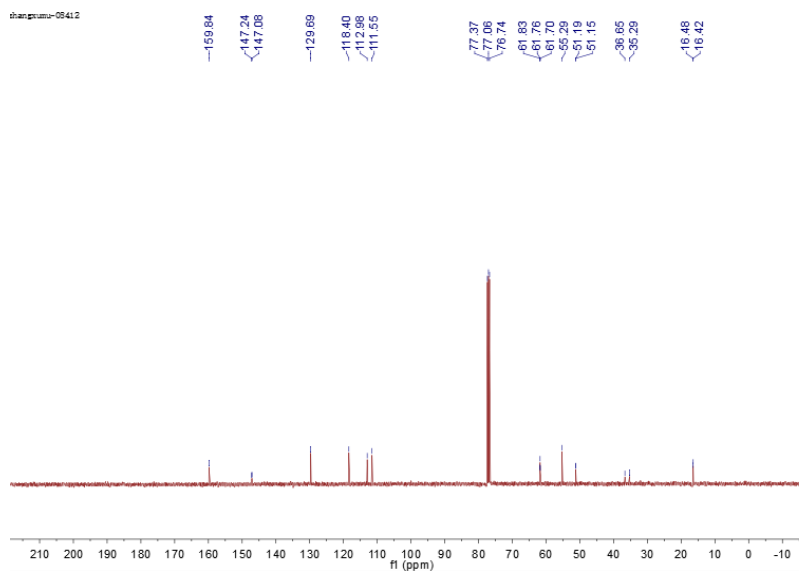
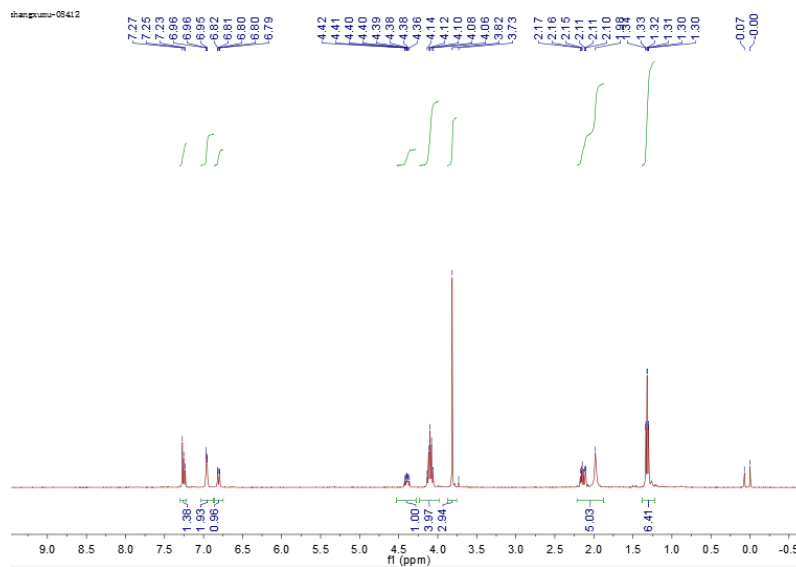
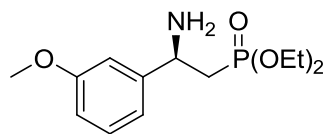


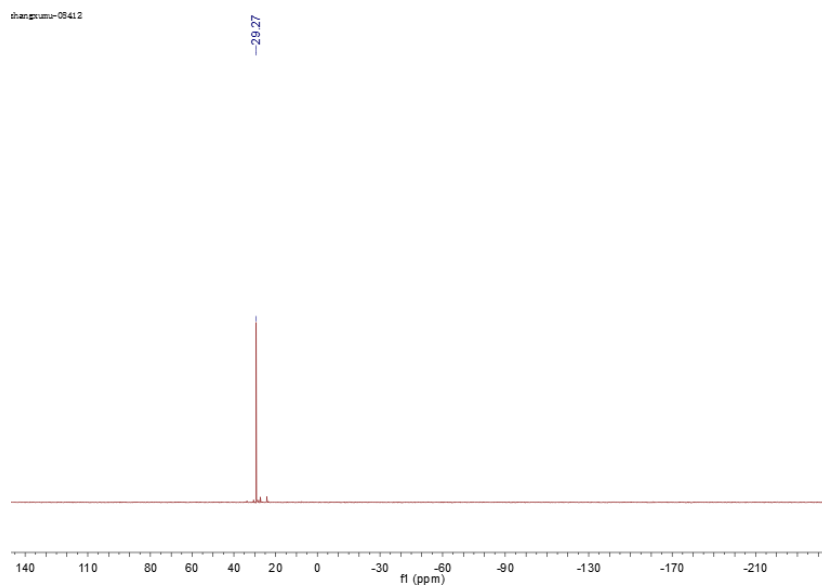
Diethyl 2-amino-2-(4-methoxyphenyl)ethylphosphonate **1d**



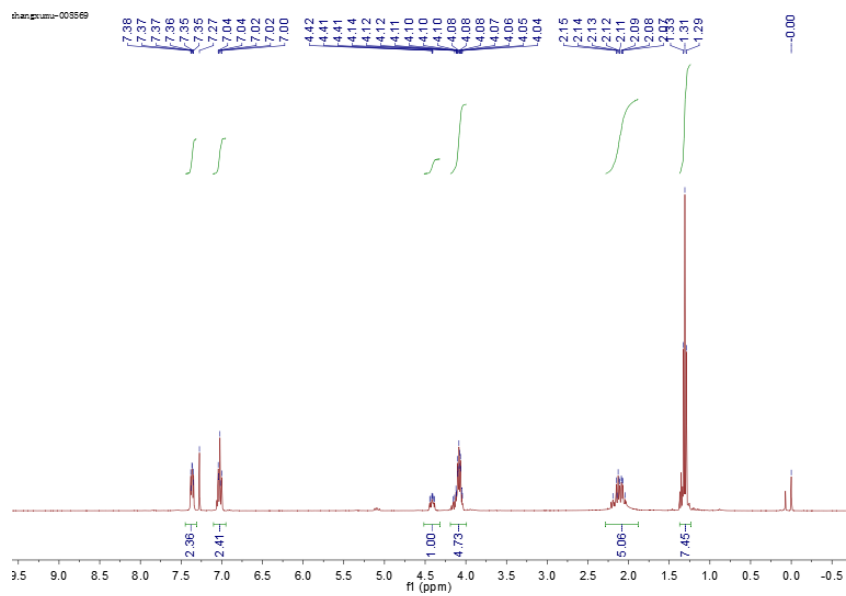
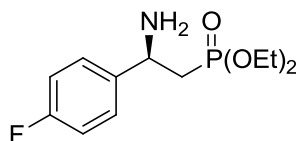


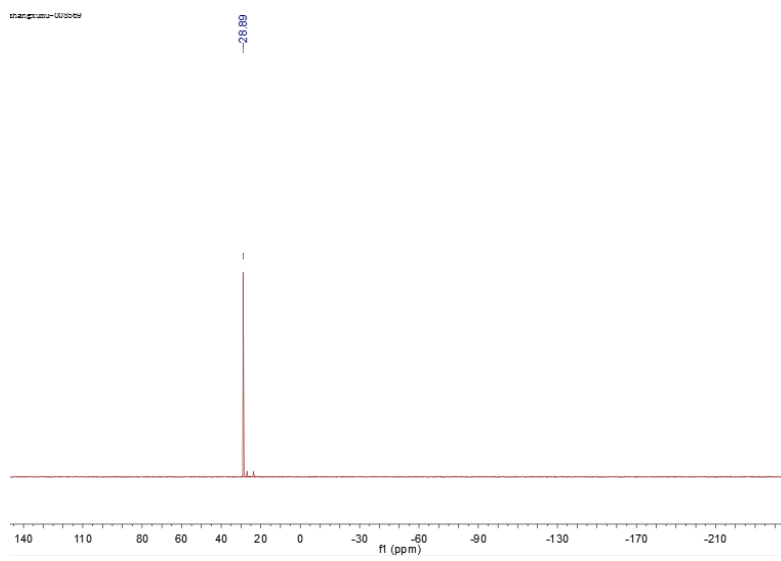
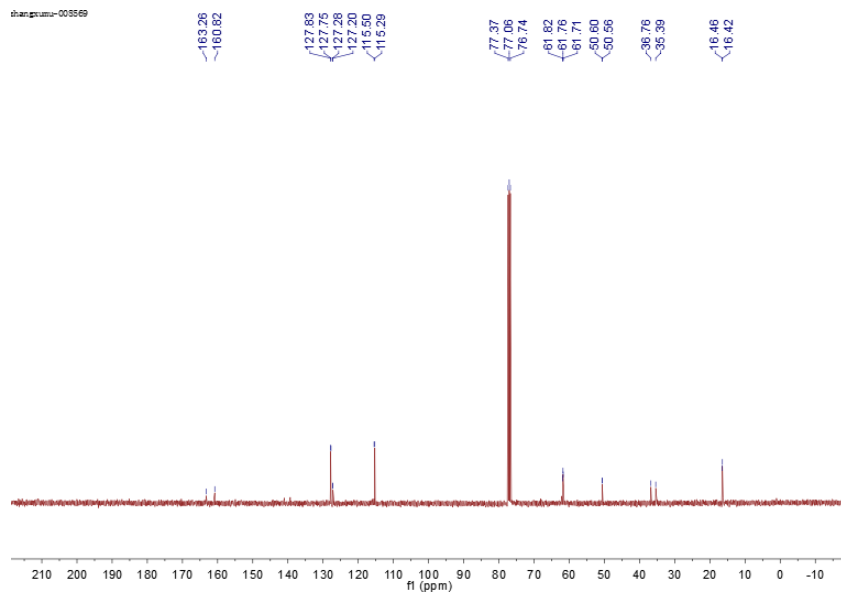
Diethyl 2-amino-2-(3-methoxyphenyl)ethylphosphonate **1e**



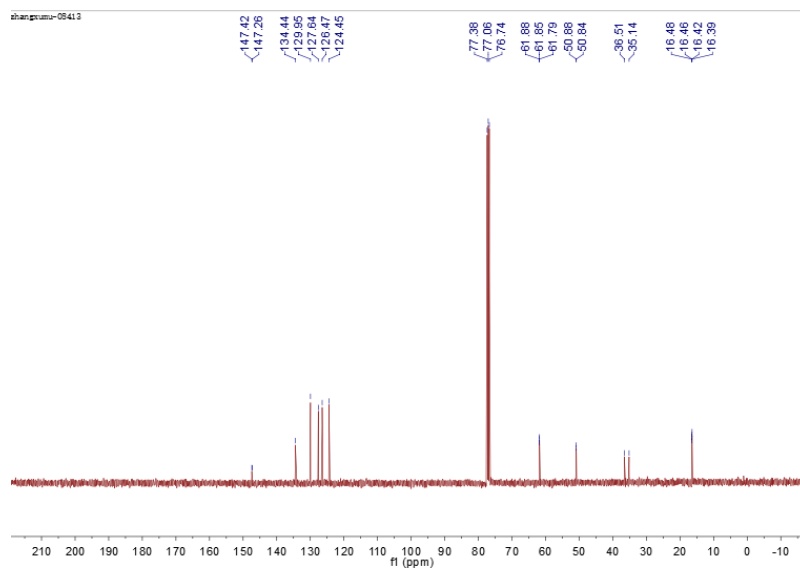
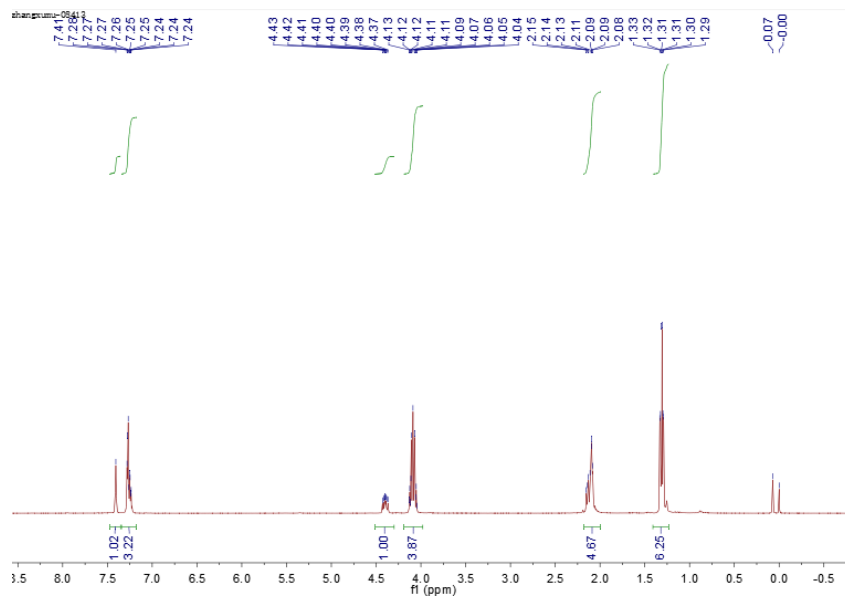
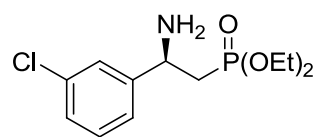


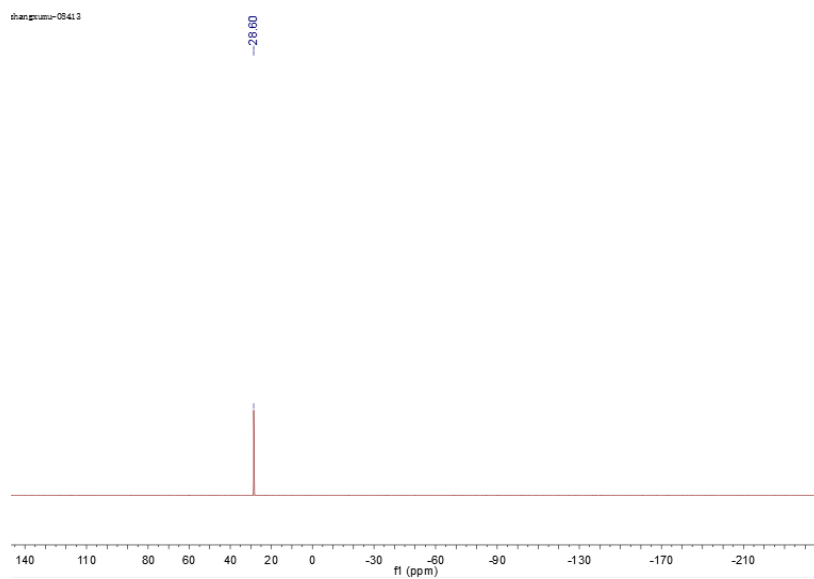
Diethyl 2-amino-2-(4-fluorophenyl)ethylphosphonate **1f**



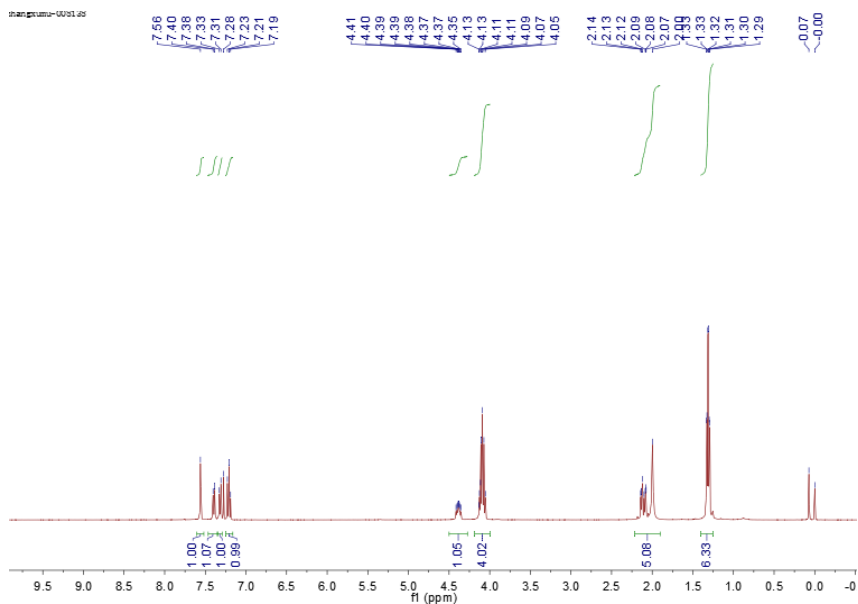
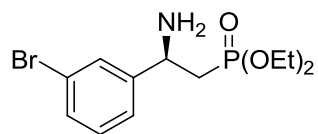


Diethyl 2-amino-2-(3-chlorophenyl)ethylphosphonate **1g**

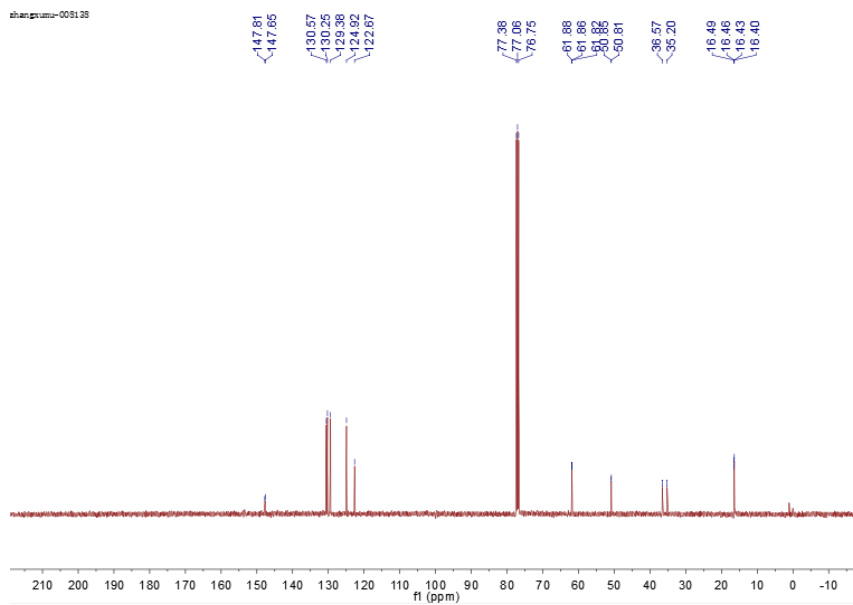




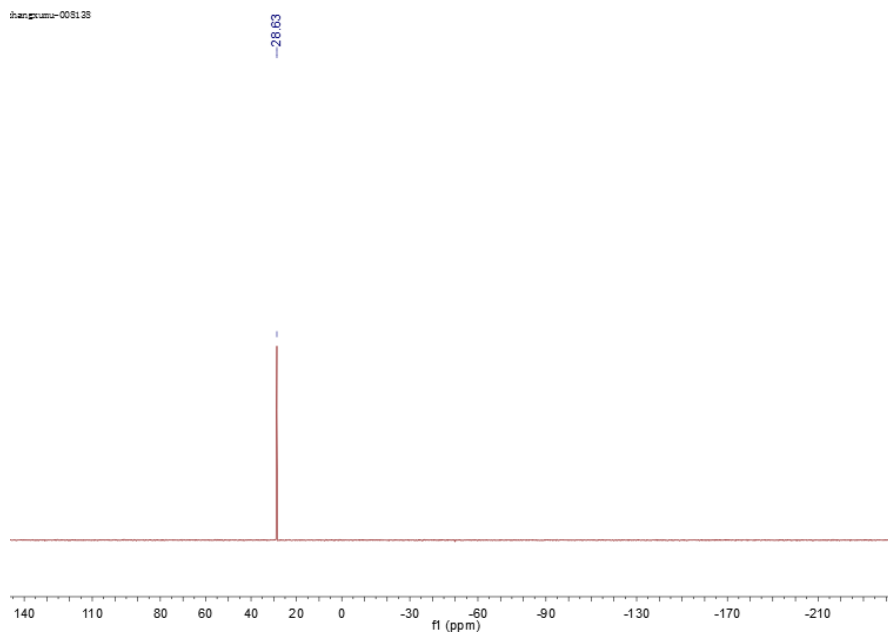
Diethyl 2-amino-2-(3-bromophenyl)ethylphosphonate **1h**



shangpin-008138



shangpin-008138

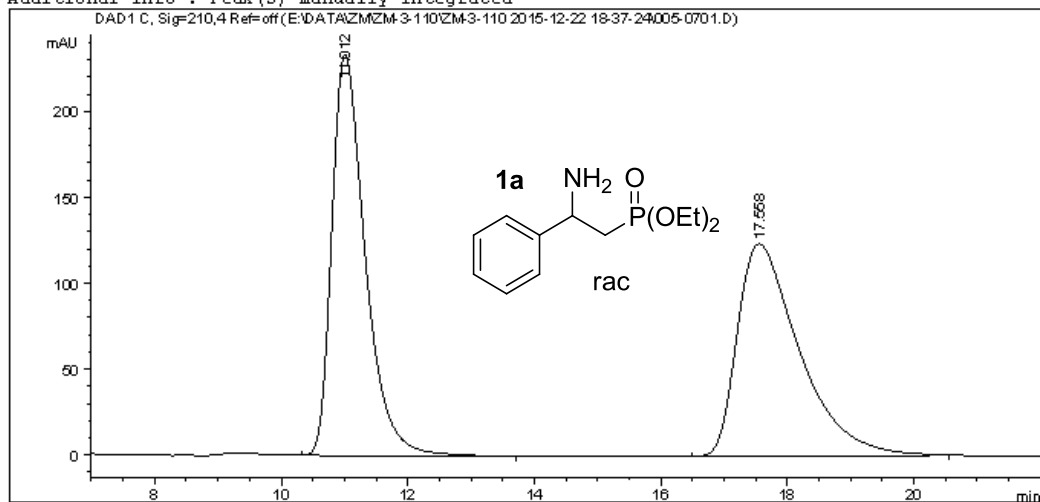


V. HPLC spectra

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                254NM-25MIN.M
Last changed    : 12/22/2015 6:52:41 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-OD(1-2)-90-10-1ML-
                254NM-25MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:02:09 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



Area Percent Report

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 C, Sig=210,4 Ref=off

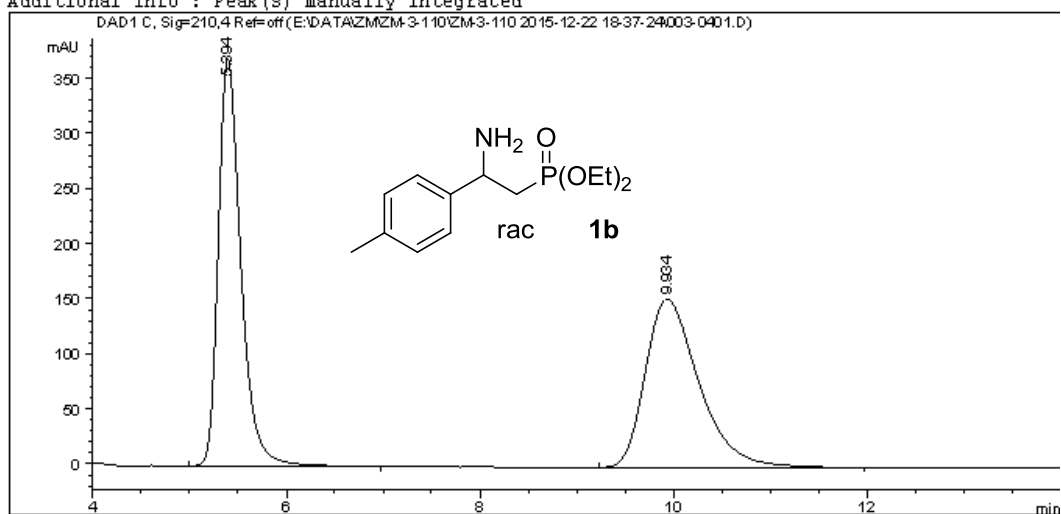
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.012	BB	0.5593	8559.85449	233.71532	50.3907
2	17.558	BB	0.9671	8427.10449	123.65019	49.6093

Totals : 1.69870e4 357.36551

*** End of Report ***

Data File E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\003-0401.D
Sample Name: zm-3-87-2

```
=====
Acq. Operator   : SYSTEM                               Seq. Line :    4
Acq. Instrument : 1260HPLC-DAD                       Location  : Vial 3
Injection Date  : 12/22/2015 7:31:02 PM              Inj       :    1
                                                    Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-ODH(1-2)-80-20-1ML-
                254NM-20MIN.M
Last changed    : 12/22/2015 6:37:25 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-ODH(1-2)-80-20-1ML-
                254NM-20MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:06:09 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.394	BB	0.2466	5981.14404	369.98022	50.4152
2	9.934	BB	0.5810	5882.63086	152.86333	49.5848

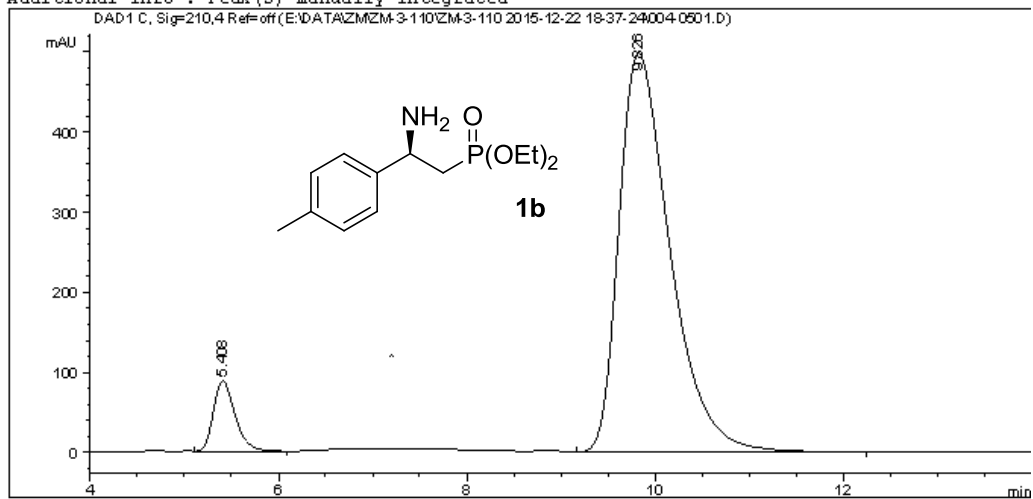
Totals : 1.18638e4 522.84355

=====
*** End of Report ***

Data File E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\004-0501.D
 Sample Name: zm-3-110-4

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    5
Acq. Instrument : 1260HPLC-DAD                Location  : Vial 4
Injection Date  : 12/22/2015 7:51:57 PM      Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-ODH(1-2)-80-20-1ML-
254NM-20MIN.M
Last changed    : 12/22/2015 6:37:25 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-ODH(1-2)-80-20-1ML-
254NM-20MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:06:09 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.408	VB	0.2459	1418.32788	88.04224	7.0314
2	9.826	BB	0.5740	1.87531e4	497.26898	92.9686

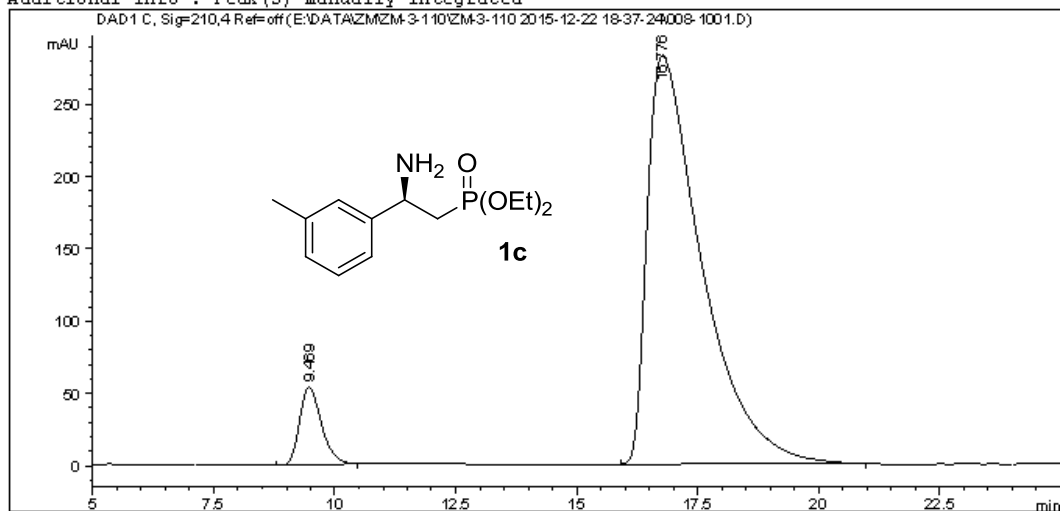
Totals : 2.01714e4 585.31123

=====
 *** End of Report ***

Data File E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\008-1001.D
 Sample Name: zm-3-110-6

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :   10
Acq. Instrument : 1260HPLC-DAD                Location  : Vial 8
Injection Date  : 12/22/2015 9:41:41 PM      Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-OD(1-2)-90-10-1ML-
                254NM-25MIN.M
Last changed    : 12/22/2015 6:52:41 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-OD(1-2)-90-10-1ML-
                254NM-25MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:20:57 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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

```

Sorted By       :      Signal
Multiplier      :      1.0000
Dilution       :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.469	BB	0.4840	1700.77222	53.91608	7.1188
2	16.776	BB	1.0736	2.21905e4	282.75879	92.8812

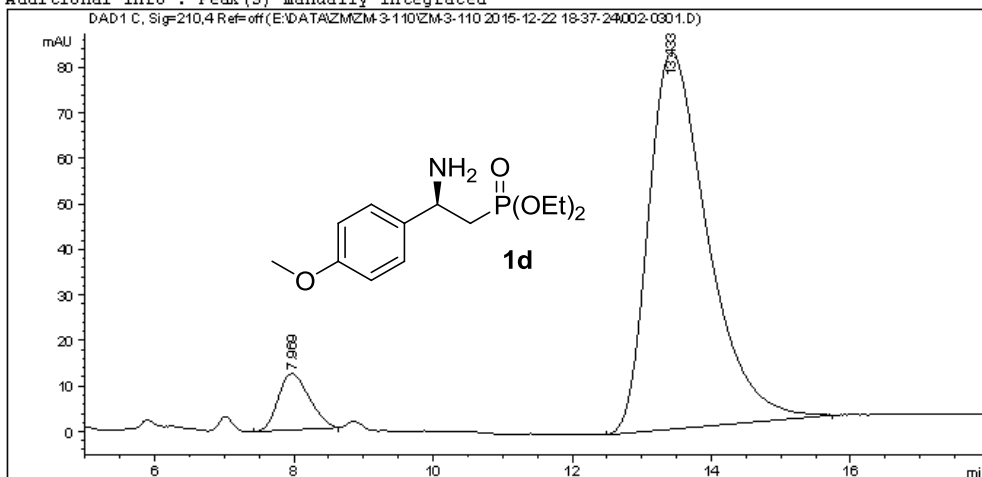
Totals : 2.38913e4 336.67487

=====
 *** End of Report ***

Data File E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\002-0301.D
 Sample Name: zm-3-110-8

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    3
Acq. Instrument : 1260HPLC-DAD                Location  : Vial 2
Injection Date  : 12/22/2015 7:10:09 PM      Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-ODH(1-2)-80-20-1ML-
254NM-20MIN.M
Last changed    : 12/22/2015 6:37:25 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-110\ZM-3-110 2015-12-22 18-37-24\DAD-ODH(1-2)-80-20-1ML-
254NM-20MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:28:11 PM by SYSTEM
                 (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 C, Sig=210,4 Ref=off

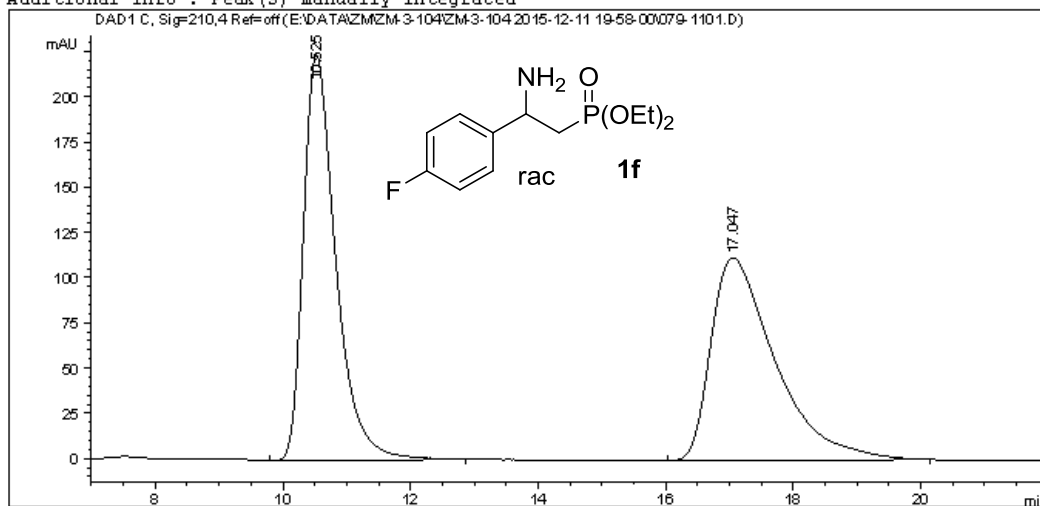
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.969	BB	0.4018	382.85391	12.34669	7.2622
2	13.433	BB	0.8388	4889.02344	82.81379	92.7378

Totals : 5271.87735 95.16048

=====
 *** End of Report ***

Data File E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\079-1101.D
Sample Name: ZM-3-103-2

```
=====
Acq. Operator   : SYSTEM                               Seq. Line : 11
Acq. Instrument : 1260HPLC-DAD                       Location  : Vial 79
Injection Date  : 12/11/2015 11:08:24 PM             Inj       : 1
                                                    Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\DAD-OD(1-2)-90-10-1ML-
                254NM-25MIN.M
Last changed    : 12/11/2015 8:19:08 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\DAD-OD(1-2)-90-10-1ML-
                254NM-25MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:34:22 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 C, Sig=210,4 Ref=off

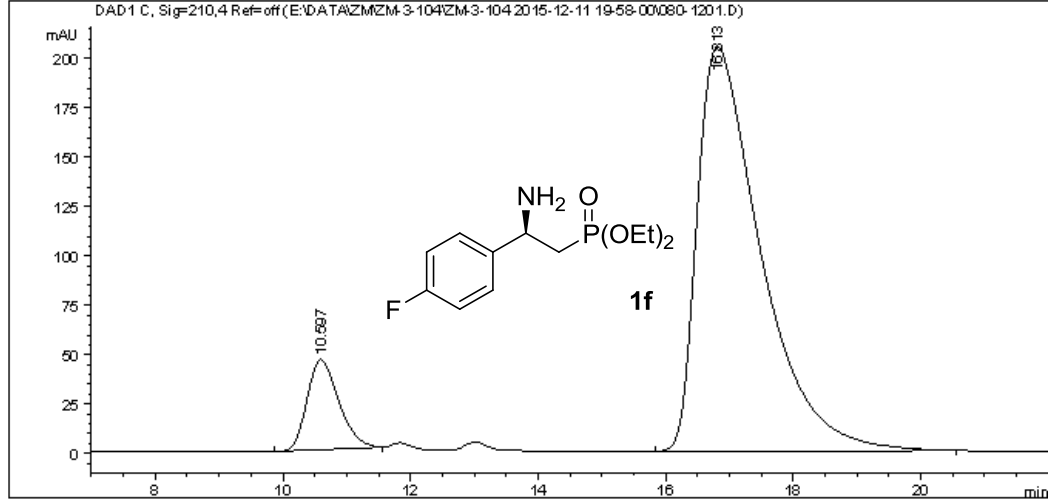
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.525	BB	0.5357	7905.39795	224.02859	50.3227
2	17.047	BB	1.0191	7804.01709	111.98026	49.6773

```
Totals :                1.57094e4  336.00886
```

```
=====
*** End of Report ***
=====
```

Data File E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\080-1201.D
Sample Name: ZM-3-104-2

```
=====
Acq. Operator   : SYSTEM                               Seq. Line : 12
Acq. Instrument : 1260HPLC-DAD                       Location  : Vial 80
Injection Date  : 12/11/2015 11:34:20 PM             Inj       : 1
                                                    Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\DAD-OD(1-2)-90-10-1ML-
                254NM-25MIN.M
Last changed    : 12/11/2015 8:19:08 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\DAD-OD(1-2)-90-10-1ML-
                254NM-25MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:34:22 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.597	BB	0.5266	1572.52502	45.57267	10.0066
2	16.813	BB	1.0202	1.41423e4	205.16388	89.9934

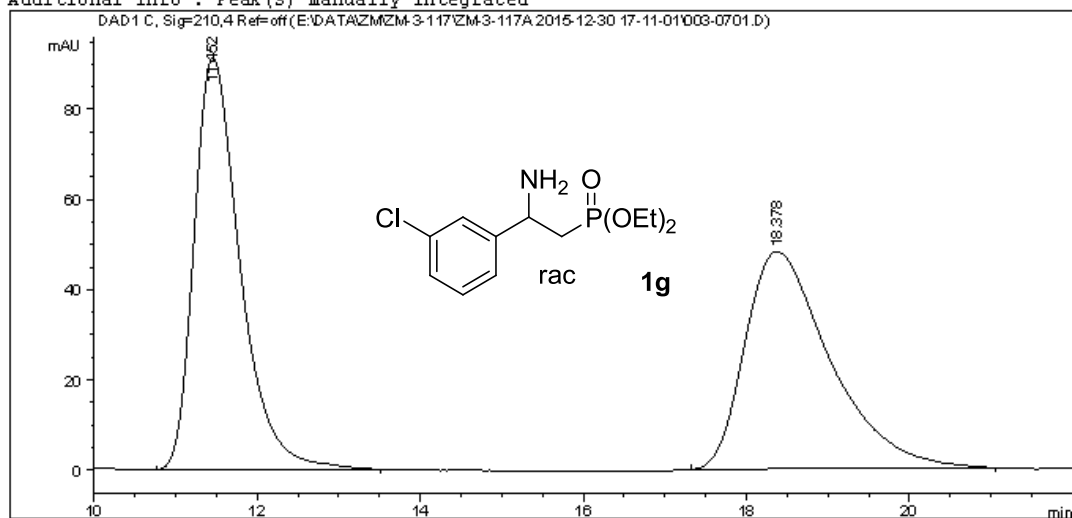
Totals : 1.57148e4 250.73655

=====
*** End of Report ***

Data File E:\DATA\ZM\ZM-3-117\ZM-3-117A 2015-12-30 17-11-01\003-0701.D
 Sample Name: zm-3-115-2

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    7
Acq. Instrument : 1260HPLC-DAD                Location  : Vial 3
Injection Date  : 12/30/2015 7:27:35 PM      Inj       :    1
                                                Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-117\ZM-3-117A 2015-12-30 17-11-01\DAD-0D(1-2)-90-10-1ML-
                254NM-25MIN.M
Last changed    : 12/30/2015 5:11:02 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-117\ZM-3-117A 2015-12-30 17-11-01\DAD-0DH(1-2)-85-15-1ML-
                254NM-30MIN.M (Sequence Method)
Last changed    : 3/9/2016 9:46:37 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.452	BB	0.5909	3581.08447	91.43313	50.6391
2	18.378	BB	0.8841	3490.68994	48.13045	49.3609

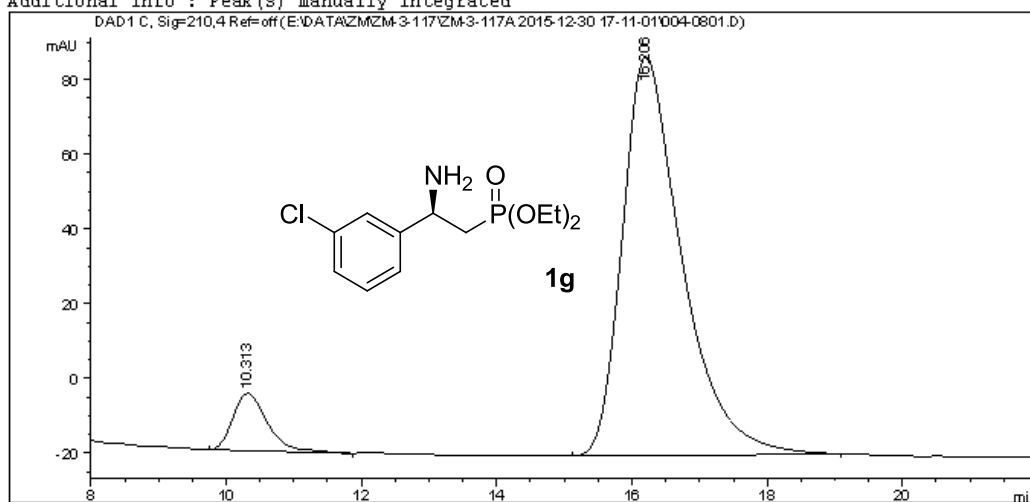
Totals : 7071.77441 139.56358

=====
 *** End of Report ***

Data File E:\DATA\ZM\ZM-3-117\ZM-3-117A 2015-12-30 17-11-01\004-0801.D
 Sample Name: zm-3-117-4

```

=====
Acq. Operator   : SYSTEM                      Seq. Line :    8
Acq. Instrument : 1260HPLC-DAD                Location  : Vial 4
Injection Date  : 12/30/2015 7:53:30 PM      Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-117\ZM-3-117A 2015-12-30 17-11-01\DAD-0D(1-2)-90-10-IML-
                254NM-25MIN.M
Last changed    : 12/30/2015 5:11:02 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-117\ZM-3-117A 2015-12-30 17-11-01\DAD-0D(1-2)-90-10-IML-
                254NM-25MIN.M (Sequence Method)
Last changed    : 3/9/2016 9:55:50 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
  
```



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

```

Sorted By       :      Signal
Multiplier      :      1.0000
Dilution       :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: DAD1 C, Sig=210,4 Ref=off

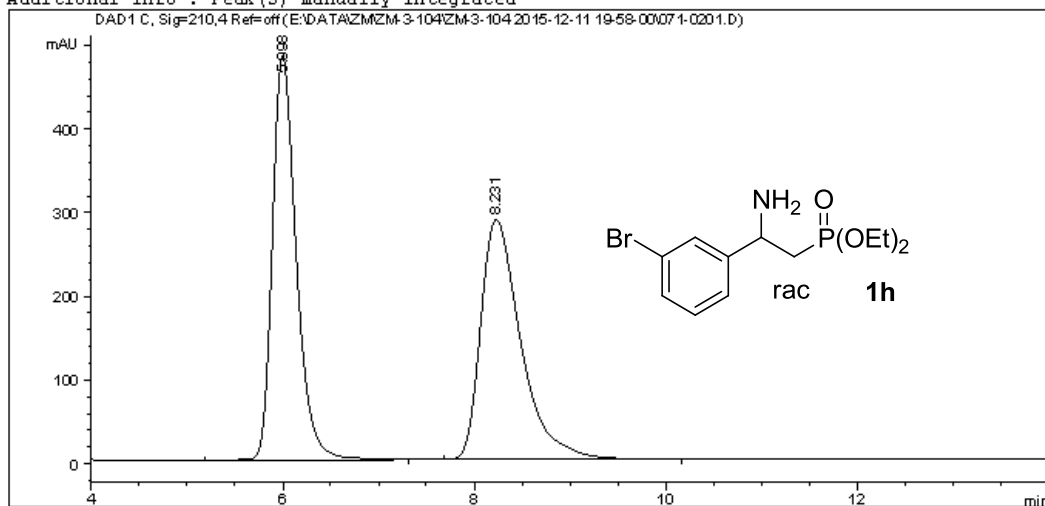
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.313	BB	0.4668	540.83594	15.28706	7.6511
2	16.206	BB	0.8555	6527.89990	106.74691	92.3489

Totals : 7068.73584 122.03397

=====
 *** End of Report ***

Data File E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\071-0201.D
Sample Name: ZM-3-107-1

```
=====
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1260HPLC-DAD                Location  : Vial 71
Injection Date  : 12/11/2015 8:09:51 PM      Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\DAD-ODH(1-2)-80-20-1ML-
                254NM-20MIN.M
Last changed    : 12/11/2015 7:58:01 PM by SYSTEM
Analysis Method : E:\DATA\ZM\ZM-3-104\ZM-3-104 2015-12-11 19-58-00\DAD-ODH(1-2)-80-20-1ML-
                254NM-20MIN.M (Sequence Method)
Last changed    : 3/9/2016 10:30:23 PM by SYSTEM
                (modified after loading)
Additional Info : Peak(s) manually integrated
=====
```



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

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.998	BB	0.2645	8412.79590	484.59744	50.0953
2	8.231	BB	0.4423	8380.79590	287.33026	49.9047

Totals : 1.67936e4 771.92770

=====
*** End of Report ***

