Supporting Information

Bis(oxazoline)-Copper Catalyzed Enantioselective Hydrophosphonylation of Aldehydes

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General

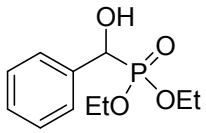
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. NMR spectra were recorded at 500 MHz and tetramethylsilane (TMS) was used as a reference. Optical rotations were measured on a commerical polarimeter and reported as follows: $[\alpha]_D^T$ (c = g/100 mL, solvent). All products were known compounds and were identified by comparison of their physical and spectra data with those of authentic samples. The enantiomeric excess of the products was determined by HPLC on Ultron ES-OVM column.

General experimental details

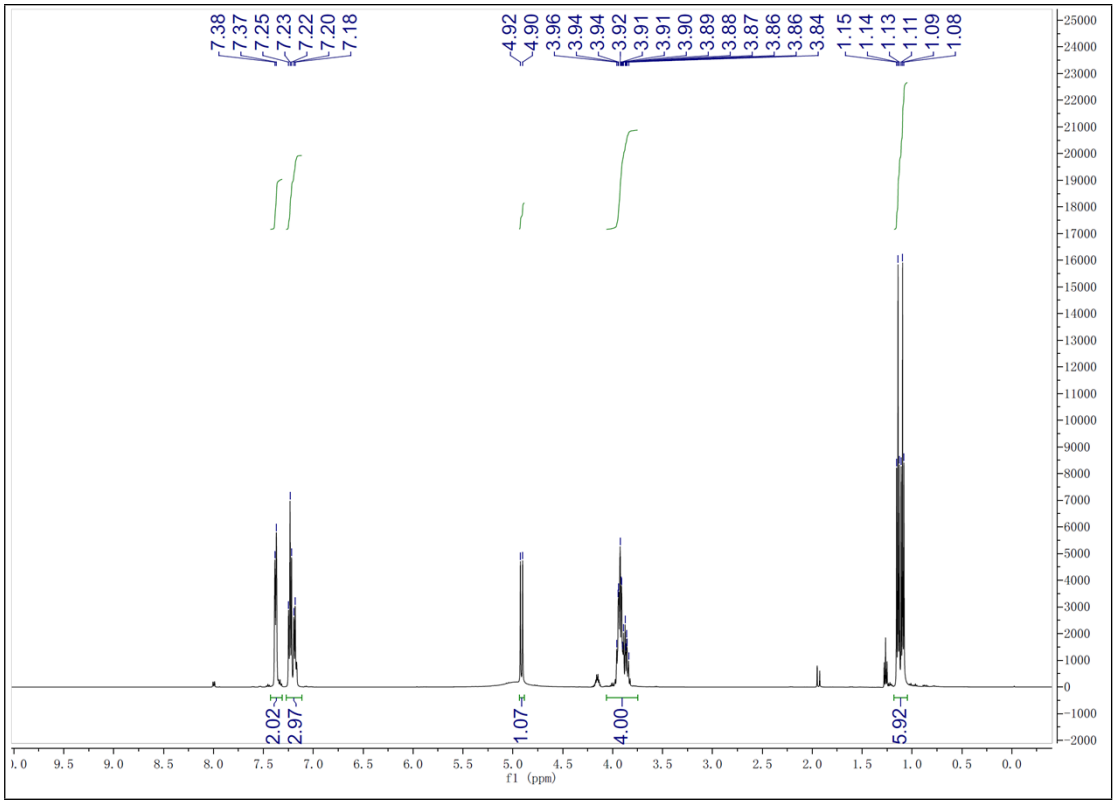
A mixture of $Cu(OAc)_2$ (0.1 mmol) and L3 (0.1 mmol) in THF (1 mL) was stirred for 1 h at room temperature. Subsequently, aldehyde (1.0 mmol), diethyl phosphite (1.2 mmol), K_3PO_4 (0.2 mmol) were added to this mixture, and stirred for 24 h at the same temperature. Upon completion, the THF was evaporated to obtain a residue that was purified using column chromatography.

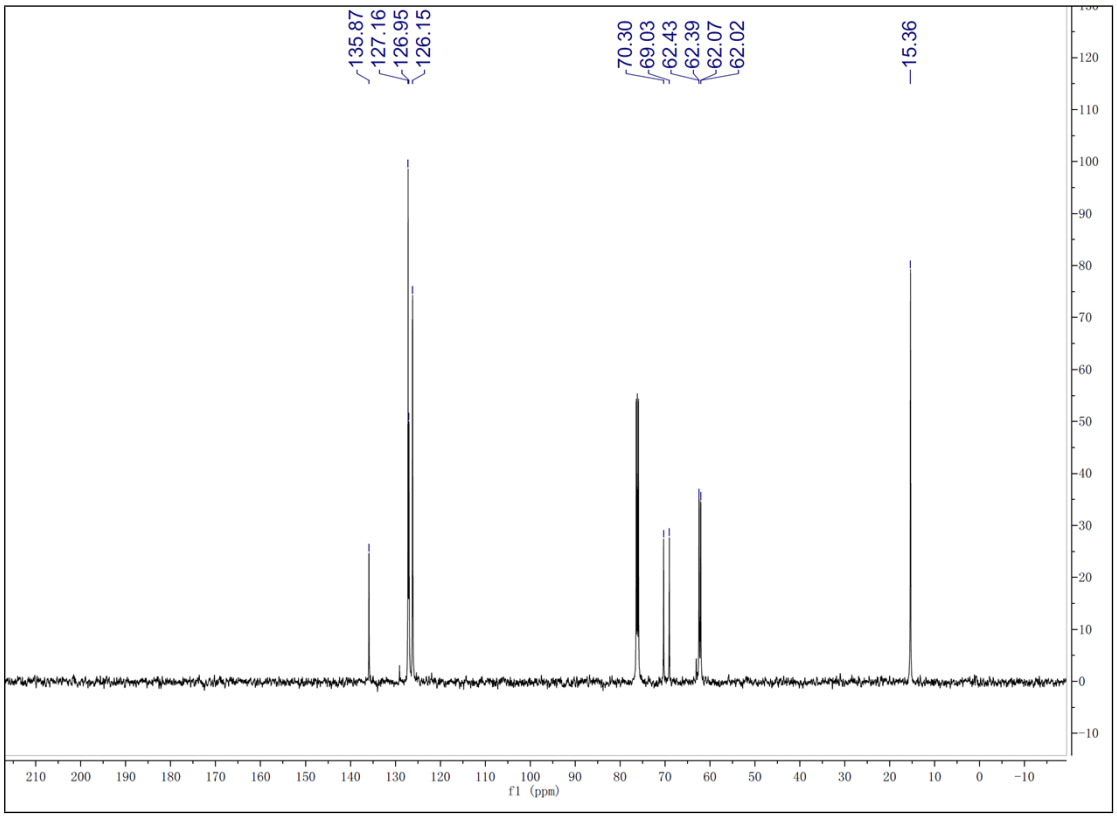
Characterization data of compounds

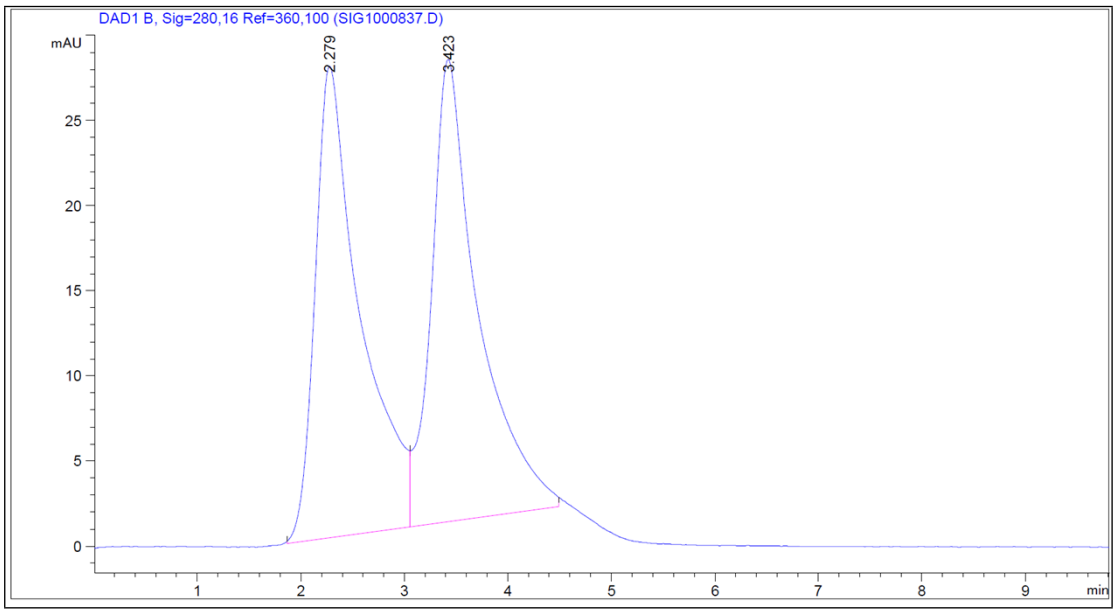
Diethyl hydroxy(phenyl)methylphosphonate(1a)

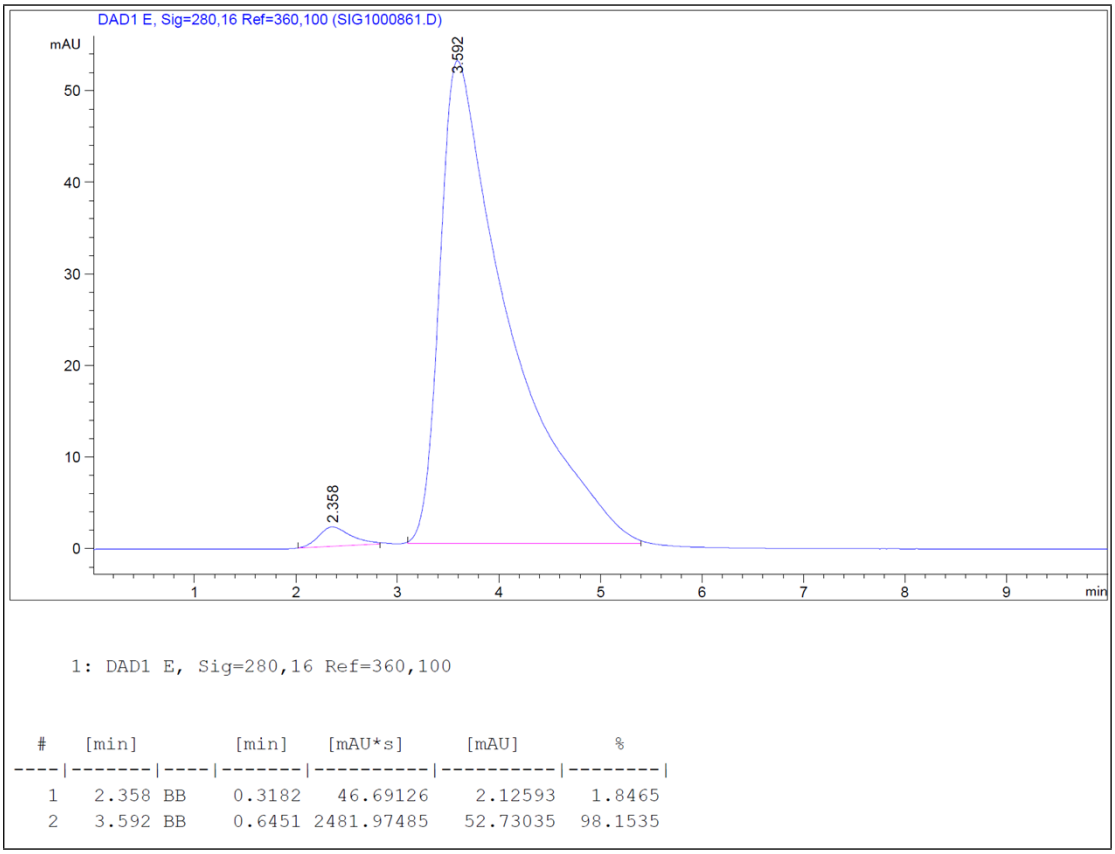


This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (81% yield); $[\alpha]_D^{18}$ -34.9 (c 1.01, $CHCl_3$) for 96% ee (S). [lit.[1] $[\alpha]_D^{20}$ +19.1 (c 1.0, $CHCl_3$) for 53% ee (R)]; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38 (d, J = 7.4 Hz, 2H), 7.25-7.22 (m, 2H), 7.20-7.17 (m, 1H), 4.91 (d, J = 11.2 Hz, 1H), 3.94-3.86 (m, 4H), 1.15-1.08 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ:135.9, 127.2, 127.0, 126.2, 69.7 (d, J = 159.6 Hz), 62.4 (d, J = 5.0 Hz), 62.0 (d, J = 6.3 Hz), 15.4. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.5 ml/min, UV = 280 nm, minor enantiomer t_1 = 2.35 min, major enantiomer t_2 = 3.59 min; 96% ee.




135.87
127.16
126.95
126.15
70.30
69.03
62.43
62.39
62.07
62.02
15.36
f1 (ppm)

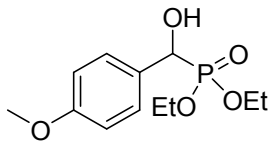

DAD1 B, Sig=280,16 Ref=360,100 (SIG1000837.D)
mAU
2.279
3.423
min



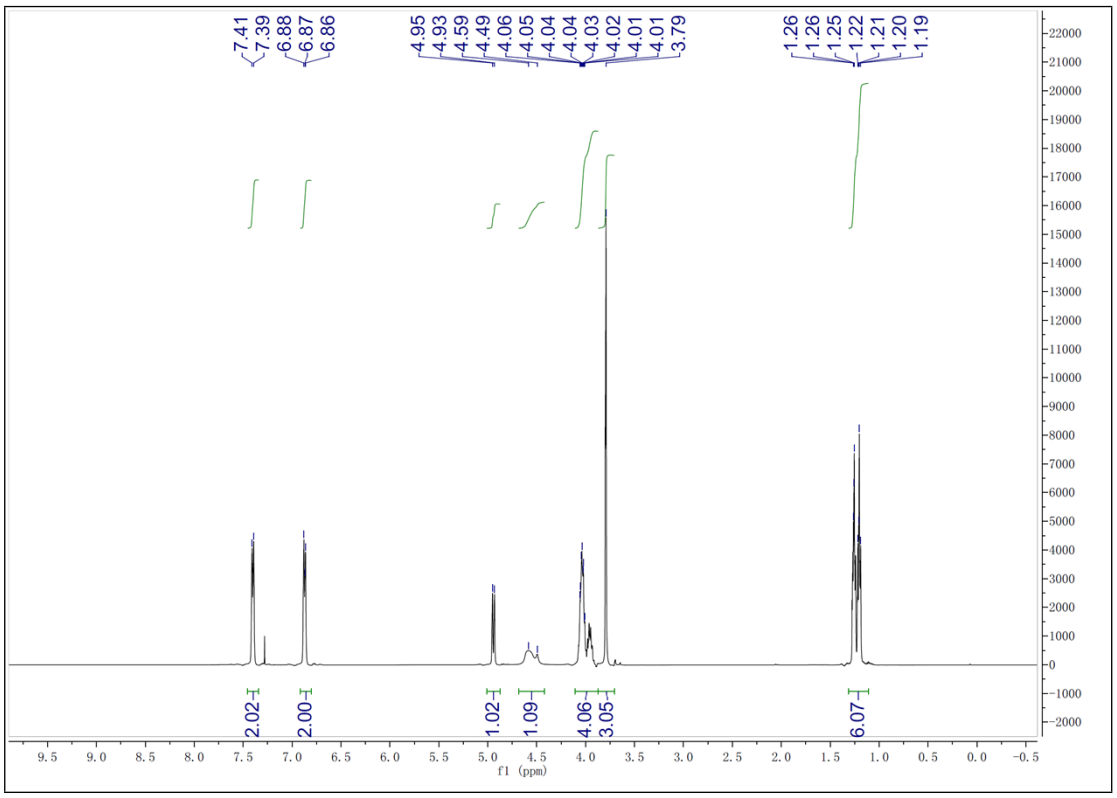
1: DAD1 E, Sig=280,16 Ref=360,100

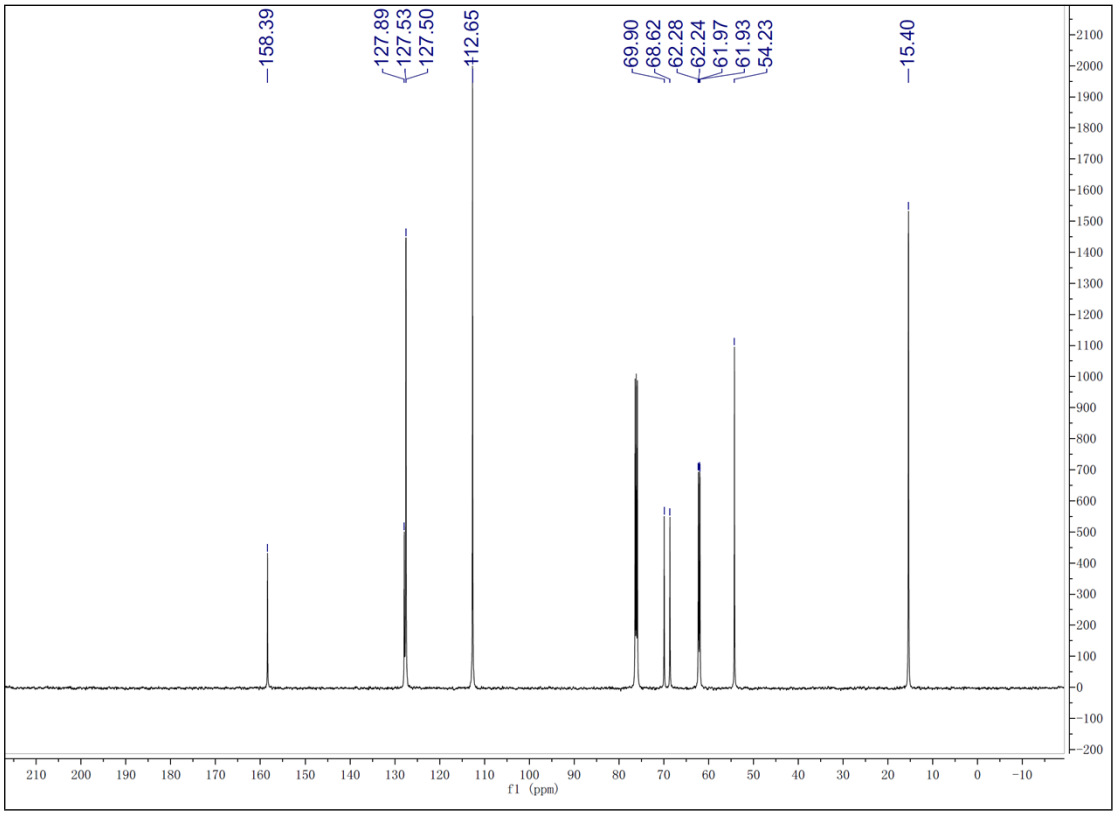
#	[min]		[min]	[mAU*s]	[mAU]	%
1	2.358	BB	0.3182	46.69126	2.12593	1.8465
2	3.592	BB	0.6451	2481.97485	52.73035	98.1535

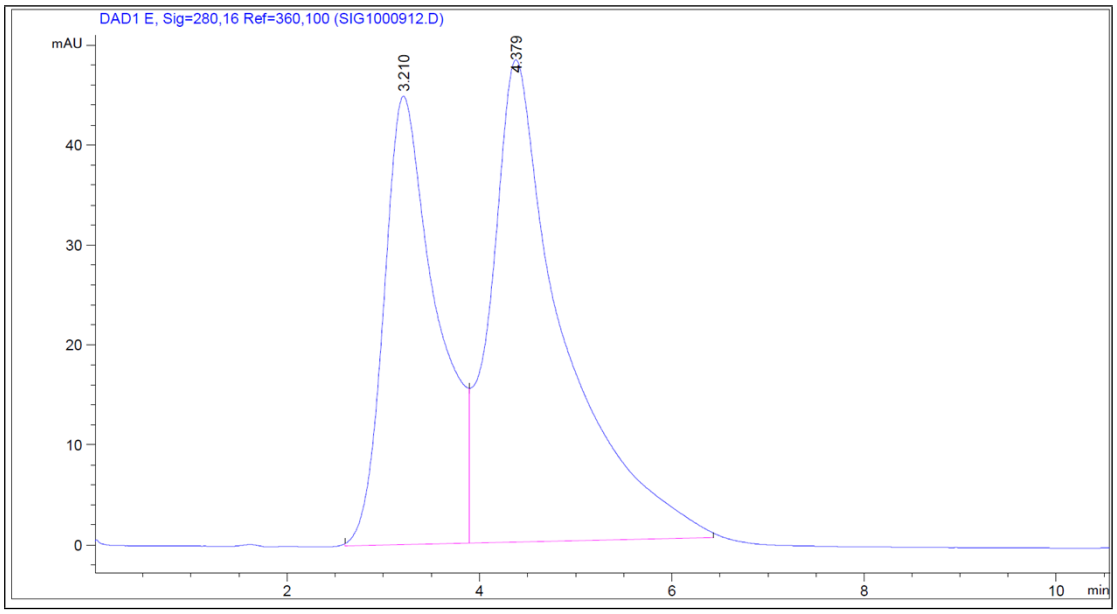
Diethyl hydroxy(4-methoxyphenyl)methylphosphonate (2a)

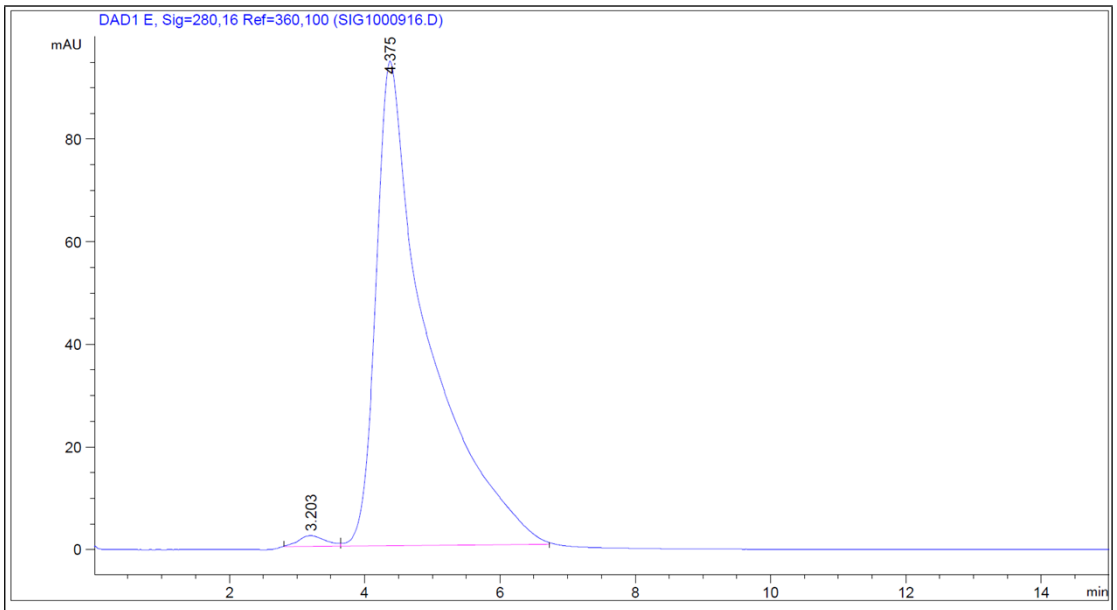


This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (75% yield); $[\alpha]_D^{20}$ -48.7 (c 0.80, $CHCl_3$) for 98% ee (S). [lit.[2] $[\alpha]_D^{20}$ -45 (c 0.80, $CHCl_3$) for 90% ee (S)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 6.88-6.86 (m, 2H), 4.94 (d, J = 10.2 Hz, 1H), 4.54 (d, J = 45.5 Hz, 1H), 4.06-4.01 (m, 4H), 3.79 (s, 3H), 1.31 – 1.11 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.4, 127.9, 127.5 (d, J = 3.8 Hz), 112.7, 68.8 (d, J = 35.0 Hz), 62.3 (d, J = 5.0 Hz), 62.0 (d, J = 5.0 Hz), 54.2, 15.4. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.2 ml/min, UV = 280 nm, minor enantiomer t_1 = 3.20 min, major enantiomer t_2 = 4.37 min; 98% ee.


7.41
7.39
6.88
6.87
6.86
4.95
4.93
4.59
4.49
4.06
4.05
4.04
4.04
4.03
4.02
4.01
4.01
3.79
1.26
1.26
1.25
1.22
1.21
1.20
1.19
2.02
2.00
1.02
1.09
4.06
3.05
6.07
f1 (ppm)


158.39
127.89
127.53
127.50
112.65
69.90
68.62
62.28
62.24
61.97
61.93
54.23
15.40
f1 (ppm)

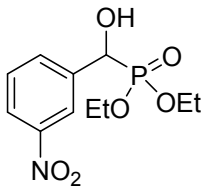




1: DAD1 E, Sig=280,16 Ref=360,100

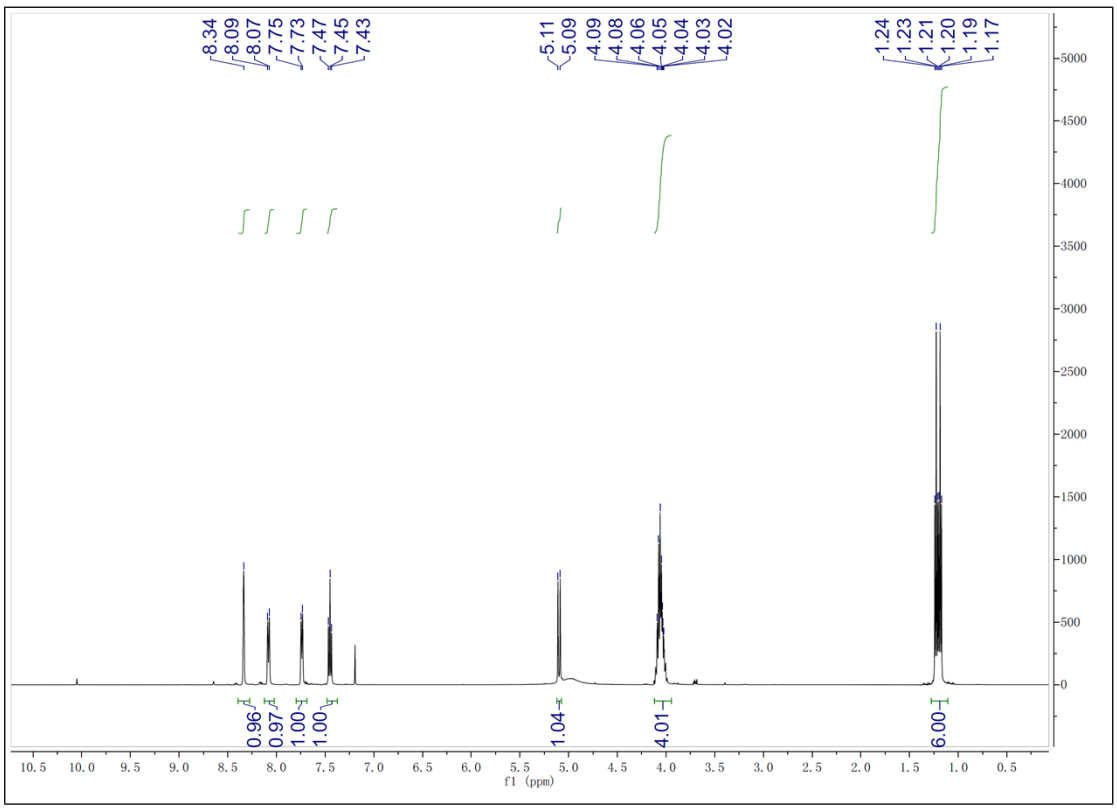
#	[min]		[min]	[mAU*s]	[mAU]	%
1	3.203	BV	0.3886	59.85679	2.13844	1.1701
2	4.375	VB	0.7240	5055.56543	94.52269	98.8299

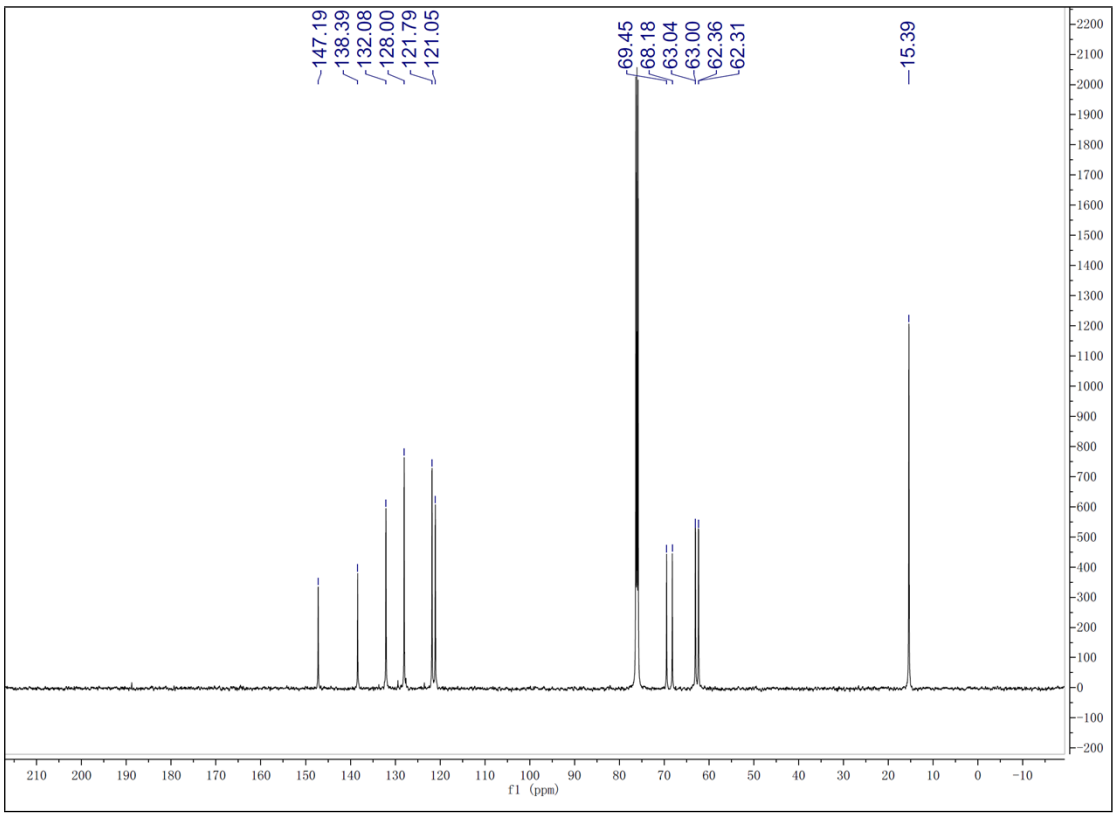
Diethyl hydroxy(3-nitrophenyl)methylphosphonate(3a)

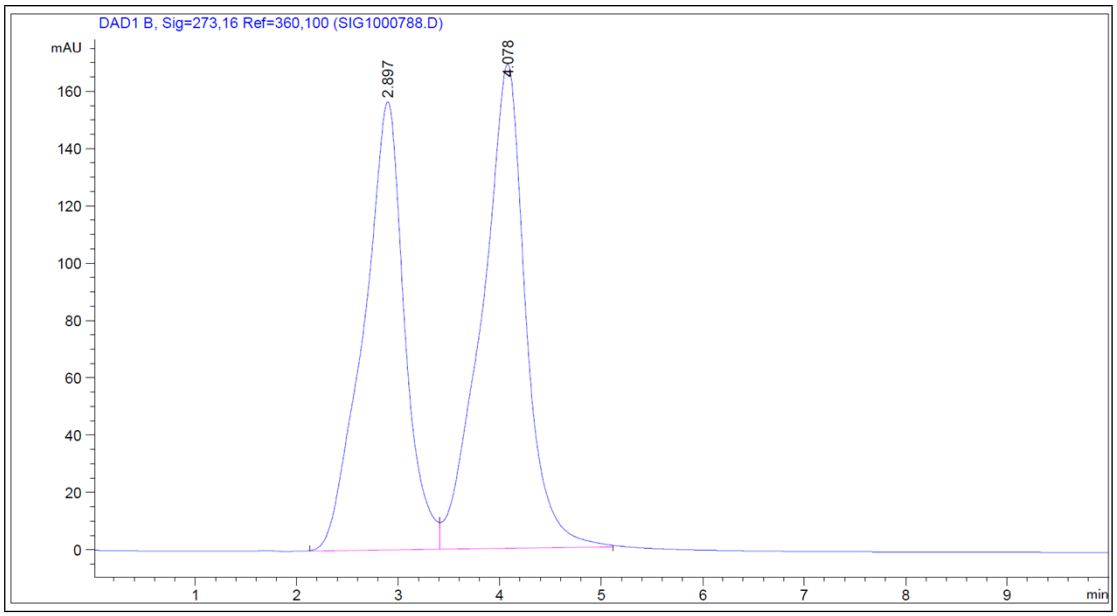


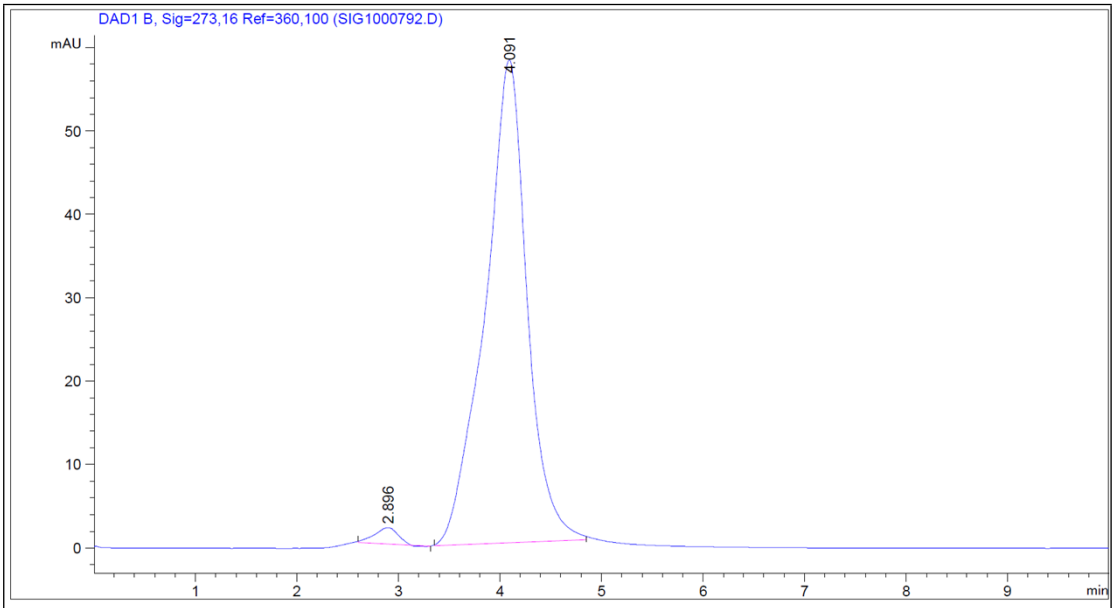
This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (67% yield); $[\alpha]_D^{19}$ -31.5 (c 1.0, $CHCl_3$) for 96% ee (S). [lit.[3]

$[\alpha]_D^{20}$ -31.1 (c 0.94, $CHCl_3$) for 94% ee (S)]; ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.47-7.43 (m, 1H), 5.10 (d, *J* = 11.5 Hz, 1H), 4.09 -4.02 (m, 4H), 1.24-1.17 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.2, 138.4, 132.1, 128.0, 121.8, 121.1, 68.8 (d, *J* = 33.8 Hz), 63.0 (d, *J*= 5.0 Hz), 62.3 (d, *J*= 6.3 Hz), 15.4. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.5 ml/min, UV = 273 nm, minor enantiomer t_1 = 2.89 min, major enantiomer t_2 = 4.09 min; 96% ee.




147.19
138.39
132.08
128.00
121.79
121.05
69.45
68.18
63.04
63.00
62.36
62.31
15.39
f1 (ppm)


DAD1 B, Sig=273,16 Ref=360,100 (SIG1000788.D)
mAU
2.897
4.078
min



1: DAD1 B, Sig=273,16 Ref=360,100

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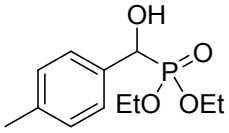
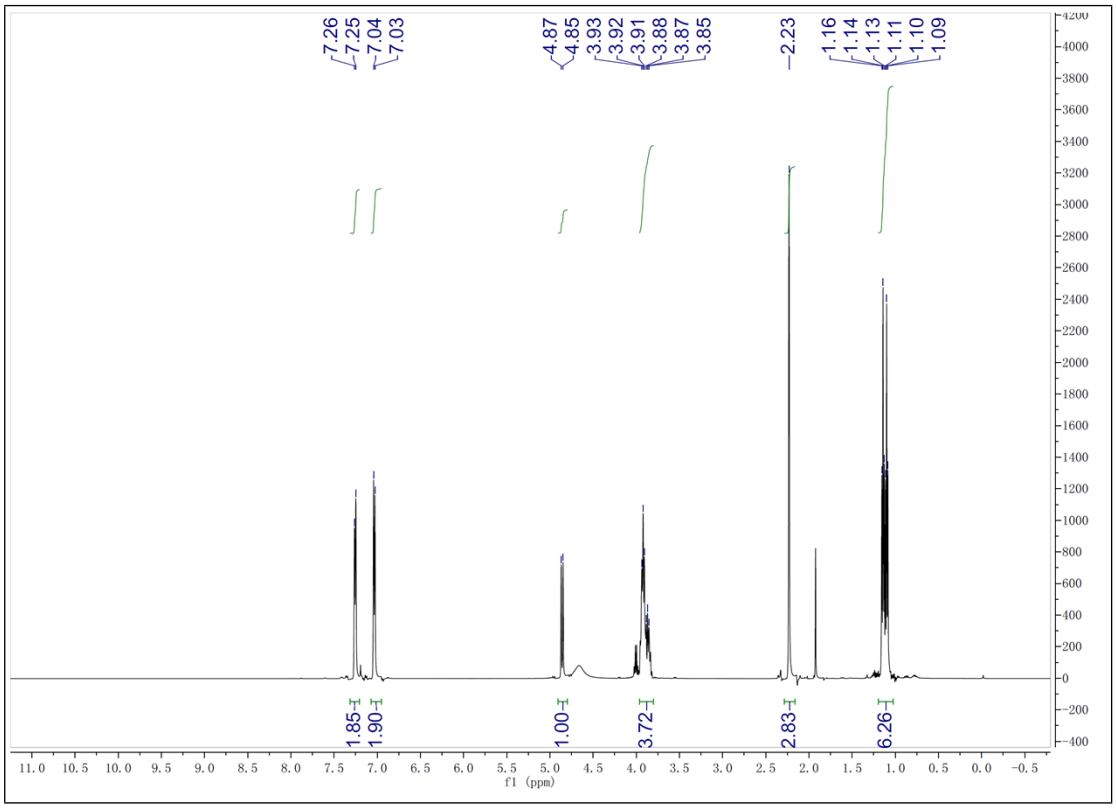
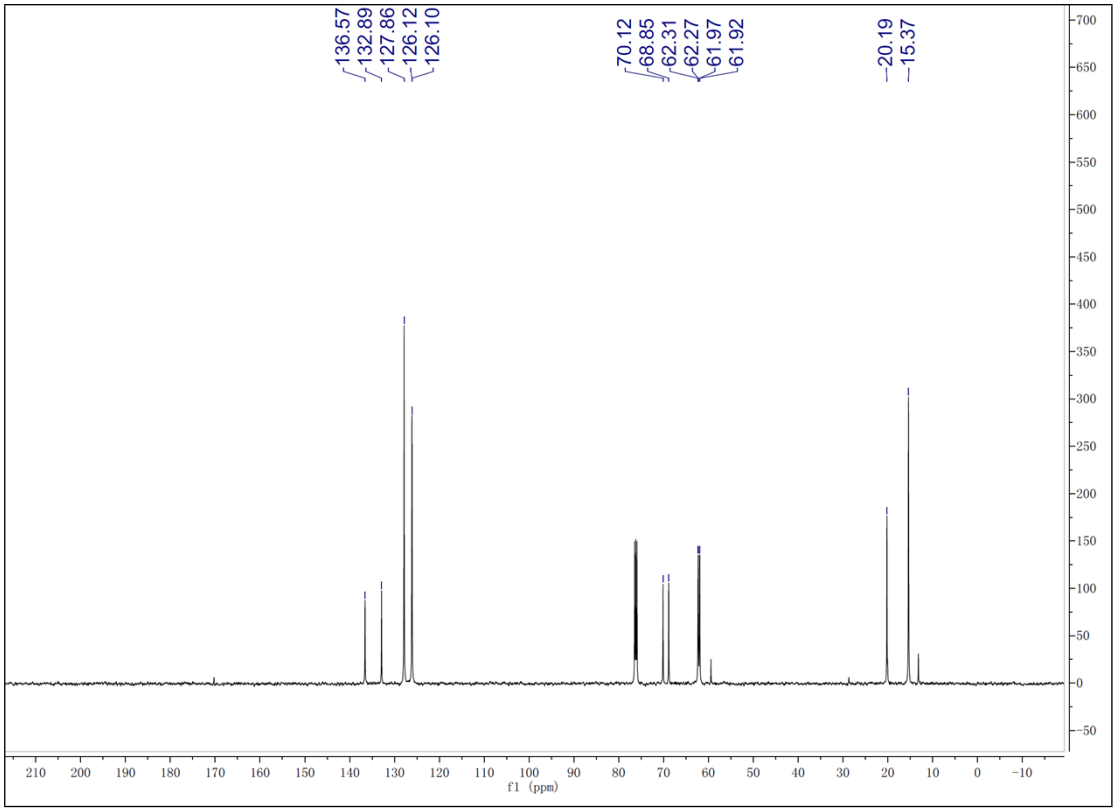
1	2.896	BB	0.2317	30.61638	1.96574	1.8079
2	4.091	BB	0.4110	1662.86963	57.90622	98.1921

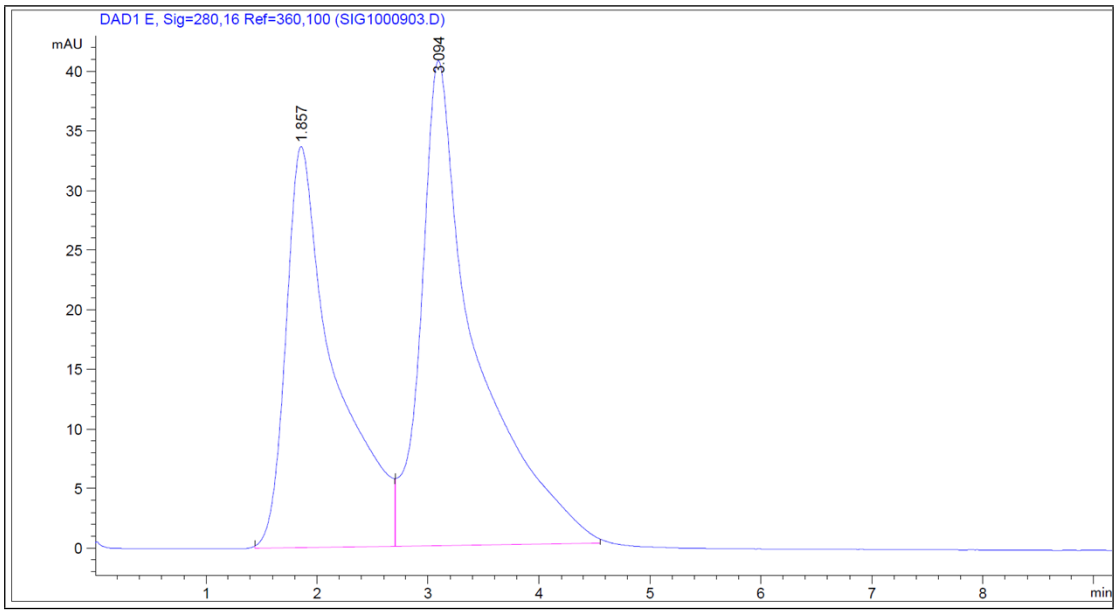
Diethyl hydroxy(4-methylphenyl)methylphosphonate(4a)

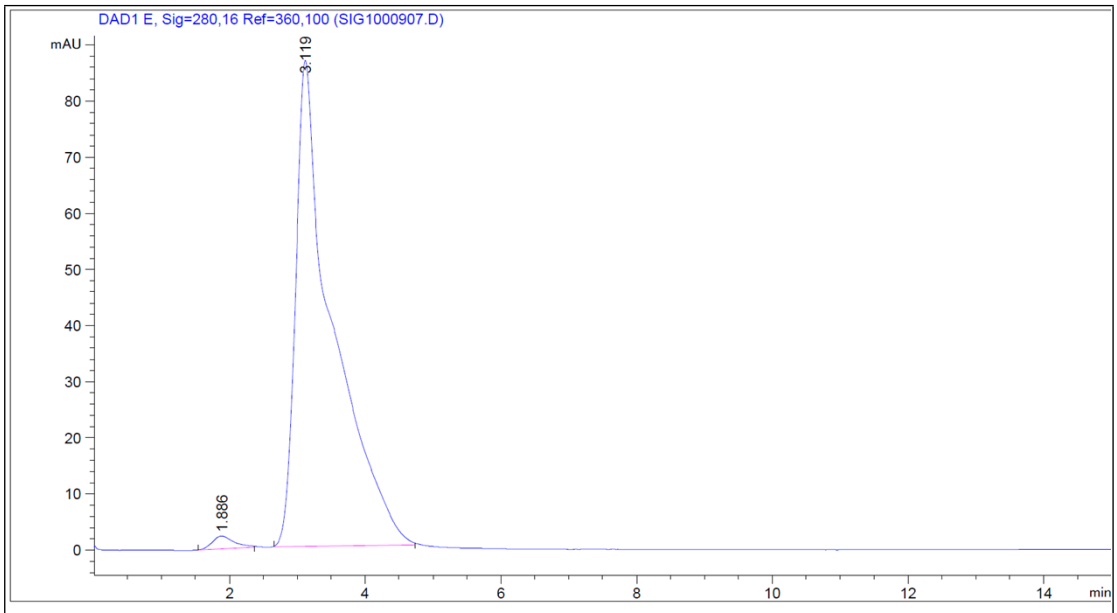


This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (76% yield); $[\alpha]_D^{25}$ -33.9 (c 0.30, $CHCl_3$) for 97% ee (S). [lit.[4] $[\alpha]_D^{20}$ +27.7 (c 0.22, $CHCl_3$) for 80% ee (R)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.66 (s, 1H), 3.95-3.83 (m, 4H), 2.23 (s, 3H), 1.09-1.06 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.6, 132.9, 127.9, 126.1 (d, *J* = 2.5 Hz), 69.5 (d, *J* = 158.8 Hz), 62.3 (d, *J*= 5.0 Hz), 61.9 (d, *J*= 6.3 Hz), 20.2, 15.4. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.5 ml/min, UV = 280 nm, minor enantiomer t_1 = 1.88 min, major enantiomer t_2 = 3.11 min; 97% ee.


7.26
7.25
7.04
7.03
4.87
4.85
3.93
3.92
3.91
3.88
3.87
3.85
2.23
1.16
1.14
1.13
1.11
1.10
1.09
1.85
1.90
1.00
3.72
2.83
6.26
f1 (ppm)


136.57
132.89
127.86
126.12
126.10
70.12
68.85
62.31
62.27
61.97
61.92
20.19
15.37
f1 (ppm)





1: DAD1 E, Sig=280,16 Ref=360,100

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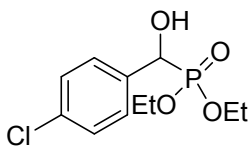
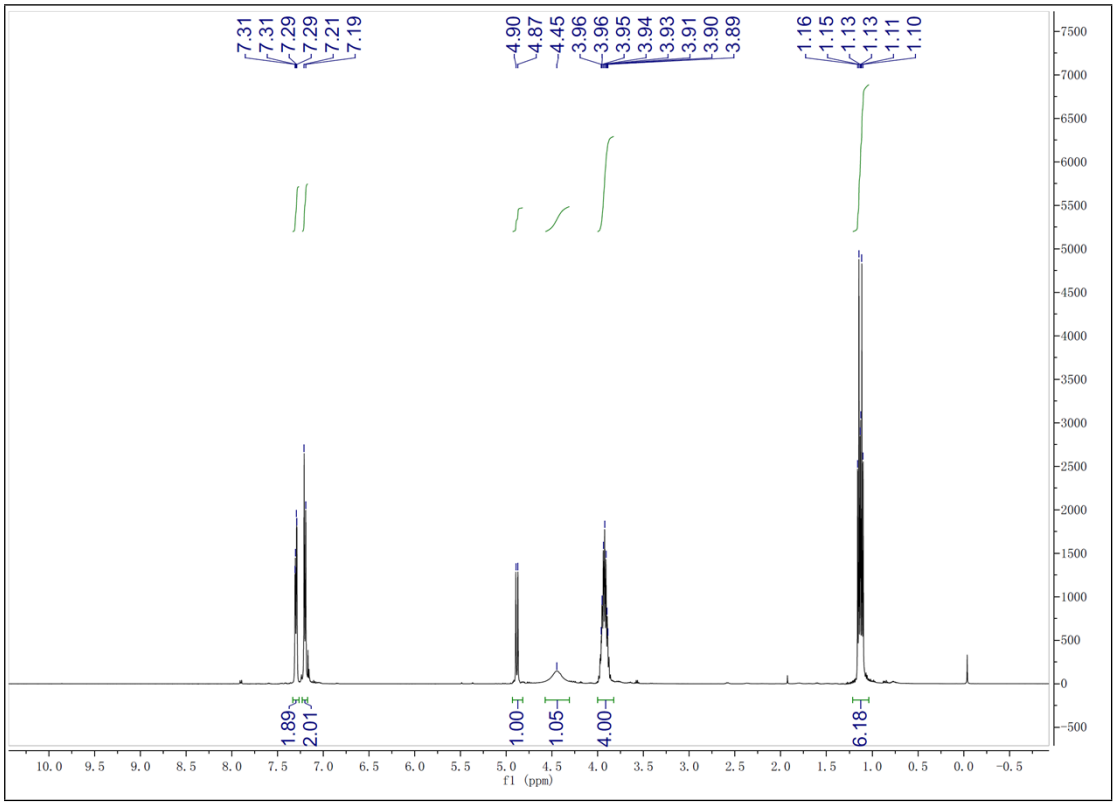
1	1.886	BB	0.3119	50.11817	2.28472	1.4988
2	3.119	BB	0.5056	3293.84302	86.61917	98.5012

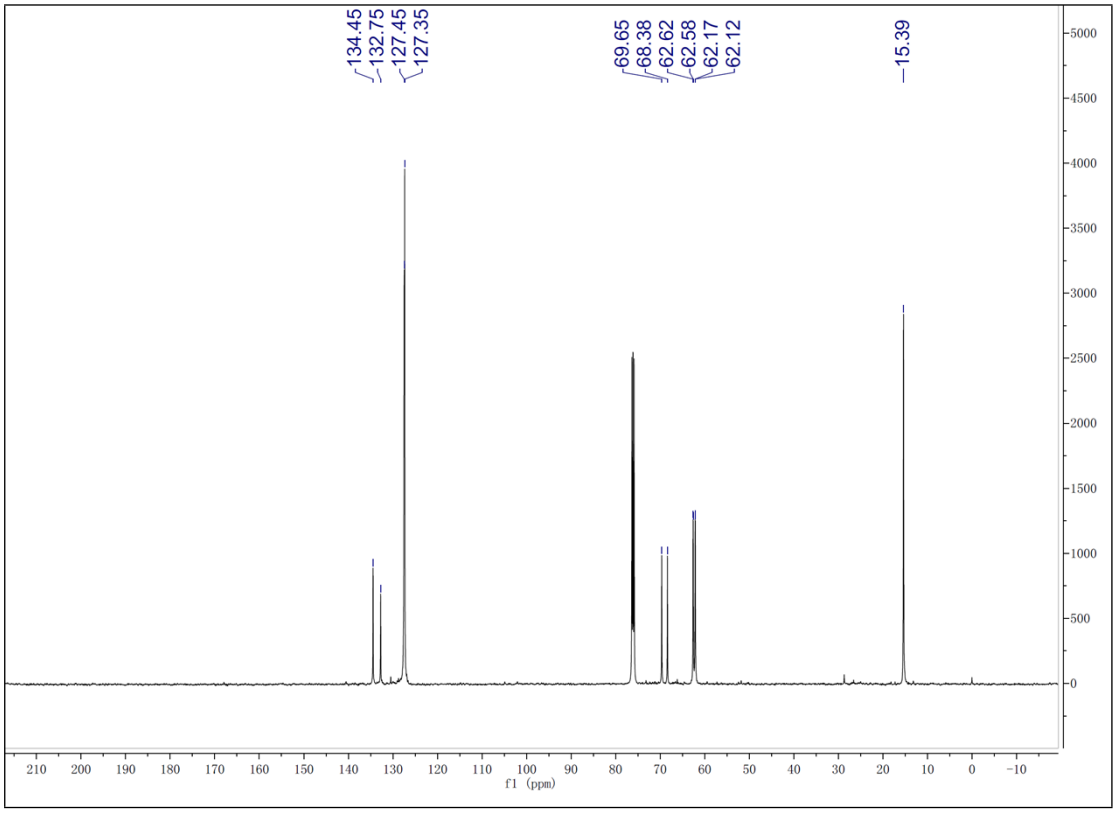
Diethyl hydroxy(4-chlorophenyl)methylphosphonate(5a)

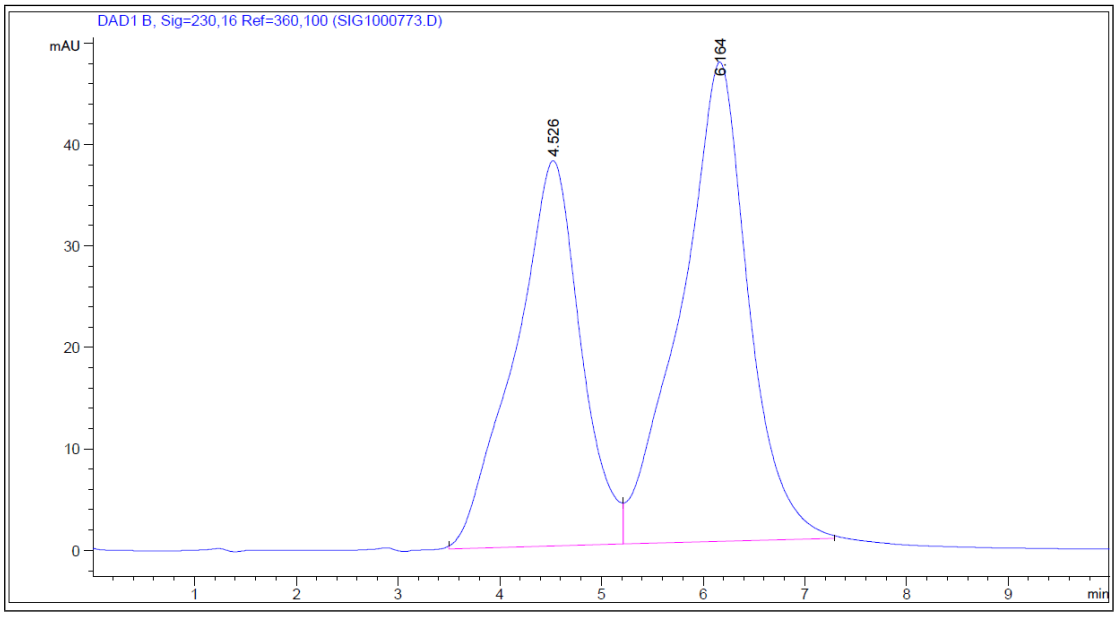


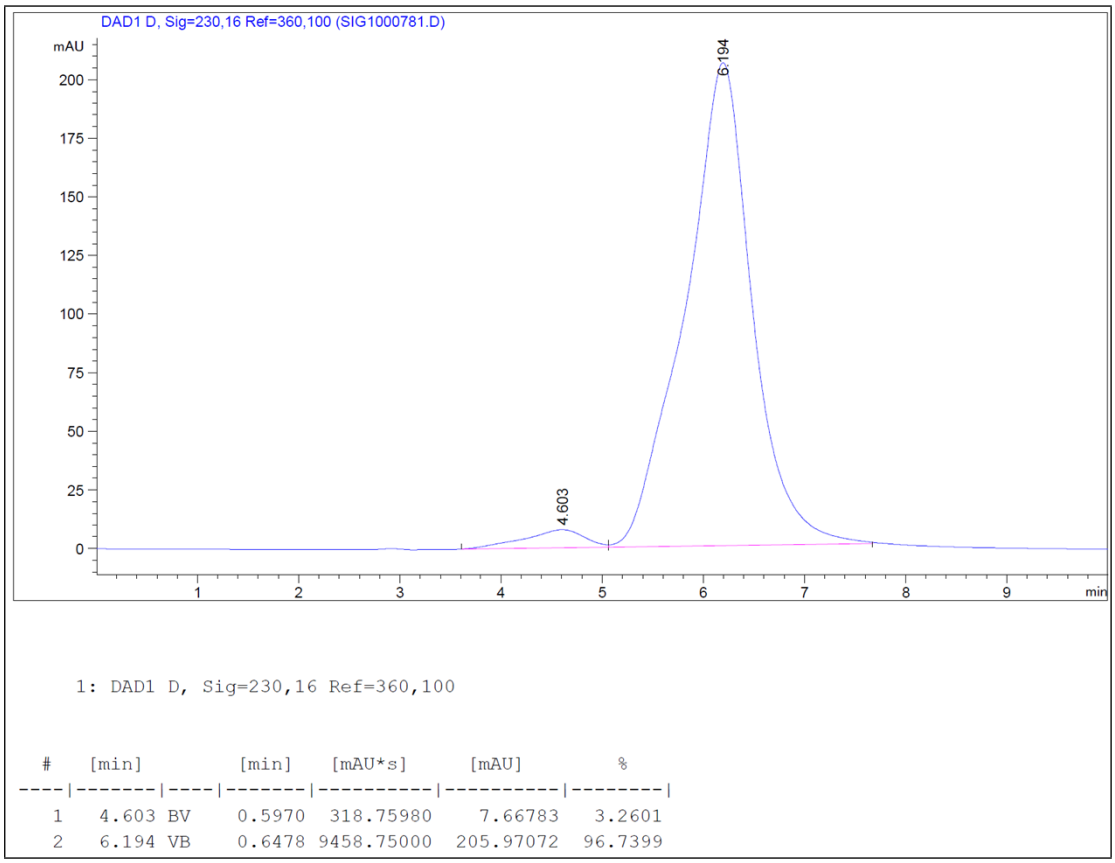
This compound was prepared according to the Experimental Section and purified by column

chromatography to give a colorless oil (73% yield); $[\alpha]_D^{19}$ -42.8 (c 0.40, $CHCl_3$) for 94% ee (S). [lit.[3] $[\alpha]_D^{20}$ -43.1 (c 0.39, $CHCl_3$) for 95% ee (S)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.29 (m, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 4.88 (d, *J* = 11.1 Hz, 1H), 4.45 (s, 1H), 3.96-3.90 (m, 4H), 1.16-1.10 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.5, 132.8, 127.5, 127.4, 69.0(d, *J* = 158.8 Hz), 62.6 (d, *J*= 5.0 Hz), 62.1(d, *J*= 6.3 Hz), 15.4. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (30:70 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.0 ml/min, UV = 230 nm, minor enantiomer t_1 = 4.60 min, major enantiomer t_2 = 6.19 min; 94% ee.




134.45
132.75
127.45
127.35
69.65
68.38
62.62
62.58
62.17
62.12
15.39
f1 (ppm)

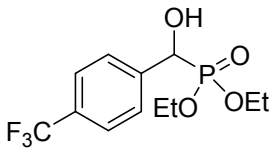

DAD1 B, Sig=230,16 Ref=360,100 (SIG1000773.D)
mAU
4.526
6.164
min



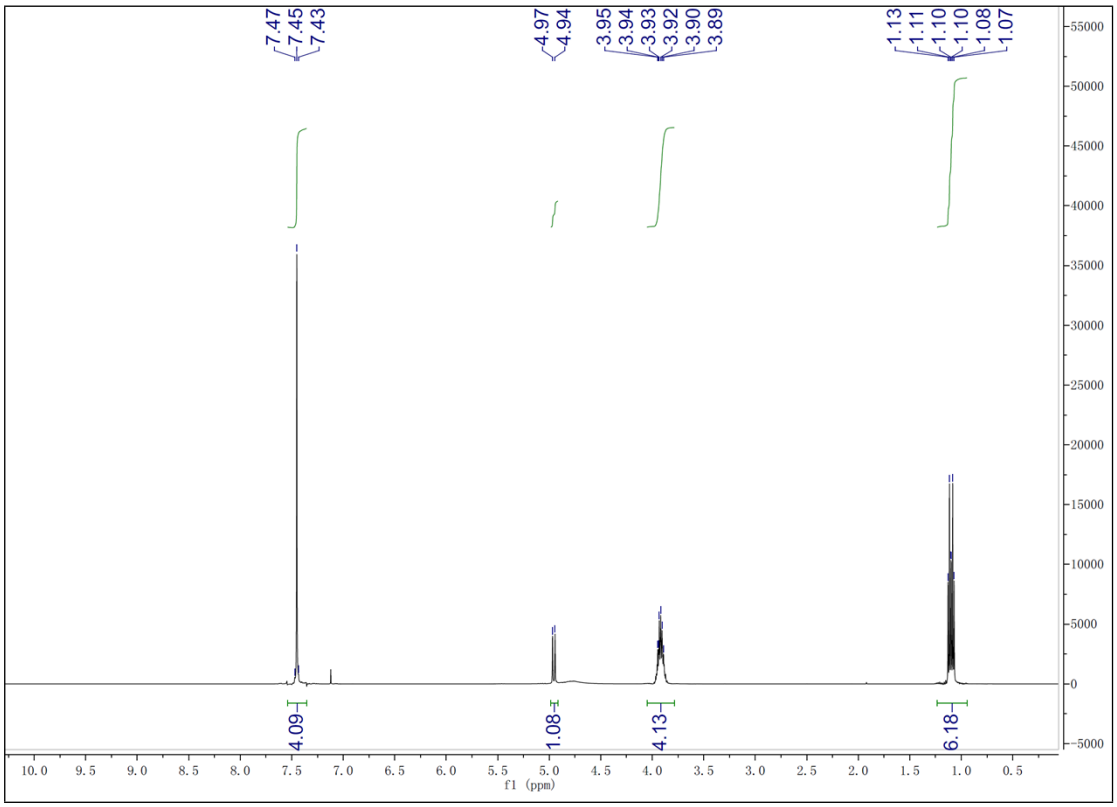
1: DAD1 D, Sig=230,16 Ref=360,100

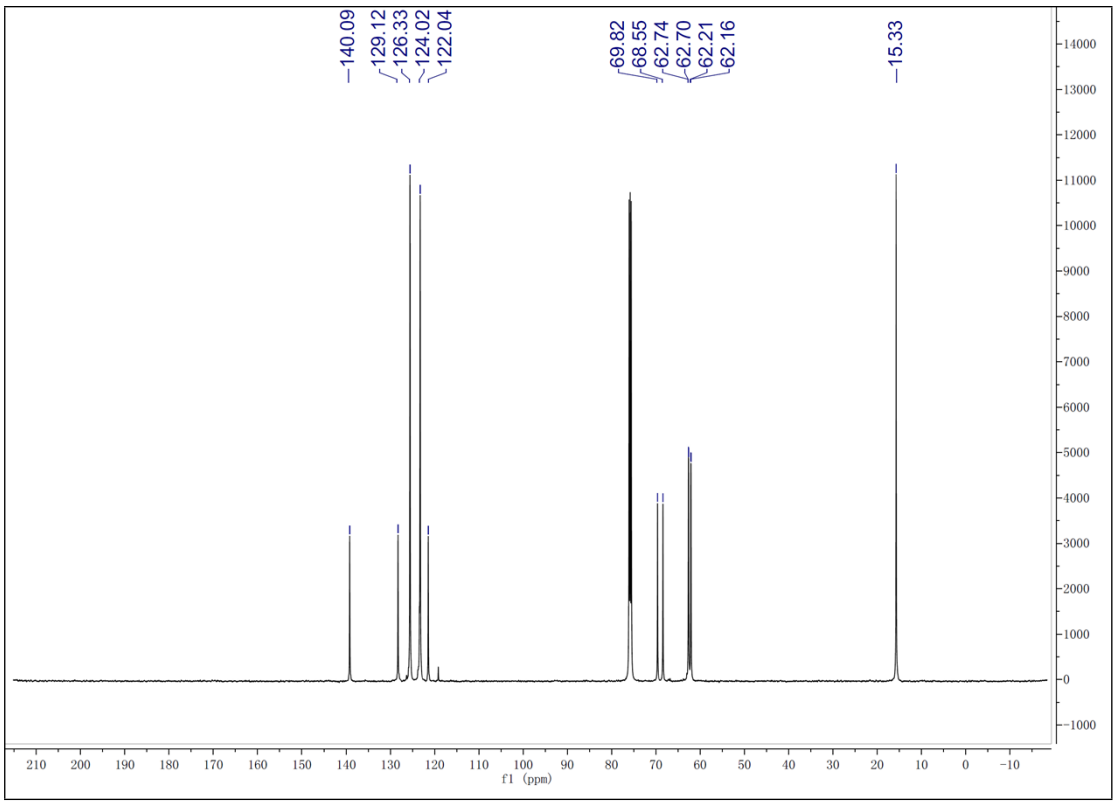
#	[min]		[min]	[mAU*s]	[mAU]	%
1	4.603	BV	0.5970	318.75980	7.66783	3.2601
2	6.194	VB	0.6478	9458.75000	205.97072	96.7399

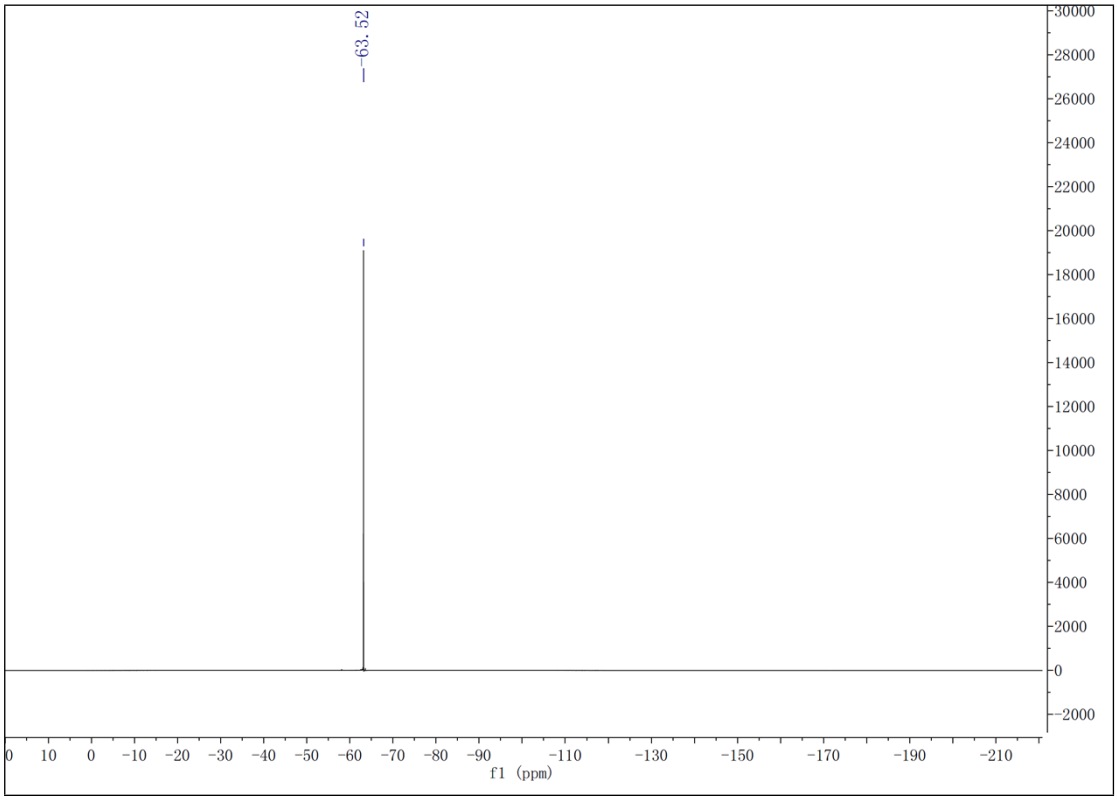
Diethyl hydroxy(4-trifluromethylphenyl)methylphosphonate(6a)

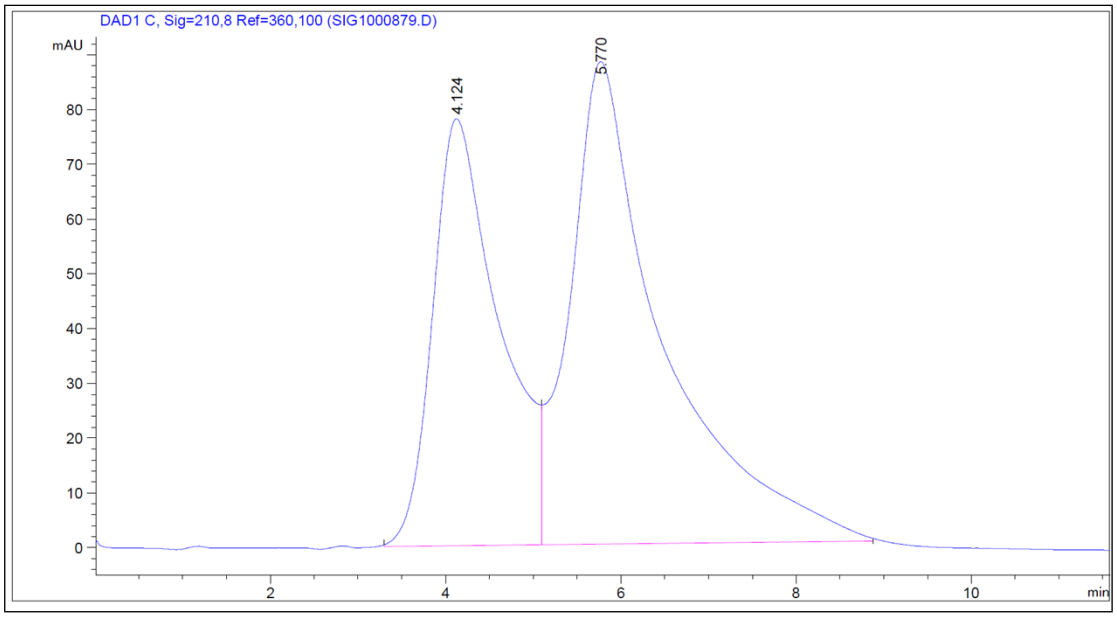


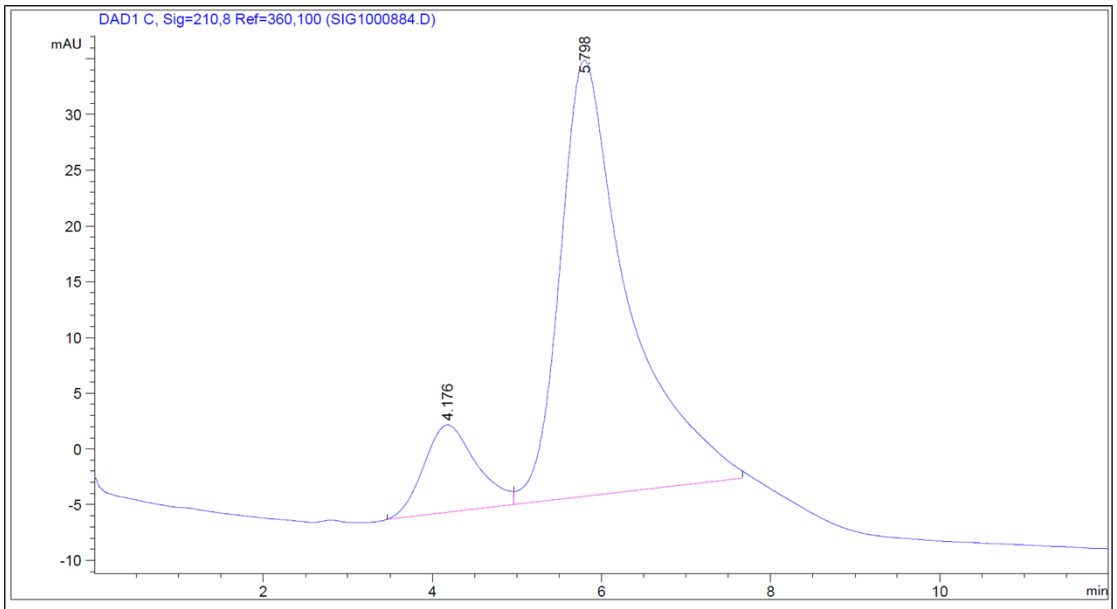
This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (91% yield); $[\alpha]_D^{20}$ -19.3 (c 2.5, $CHCl_3$) for 74% ee; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 4H), 5.01 (d, J = 11.6 Hz, 1H), 3.94-3.90 (m, 4H), 1.13-1.07 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.01, 129.1, 126.3, 124.0, 122.0, 69.2(d, J = 158.8 Hz), 62.7(d, J = 5.0 Hz), 62.2(d, J = 6.3 Hz), 15.3. ^{19}F NMR (500 MHz, $CDCl_3$) δ: -63.52. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (30:70 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.0 ml/min, UV = 210 nm, minor enantiomer t_1 = 4.17 min, major enantiomer t_2 = 5.79 min; 74% ee.


7.47
7.45
7.43
4.97
4.94
3.95
3.94
3.93
3.92
3.90
3.89
1.13
1.11
1.10
1.10
1.08
1.07
4.09
1.08
4.13
6.18
f1 (ppm)


140.09
129.12
126.33
124.02
122.04
69.82
68.55
62.74
62.70
62.21
62.16
15.33
f1 (ppm)


-63.52
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

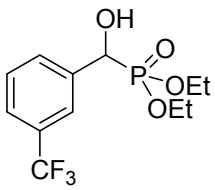

DAD1 C, Sig=210,8 Ref=360,100 (SIG1000879.D)
mAU
4.124
5.770
80
70
60
50
40
30
20
10
0
2
4
6
8
10
min



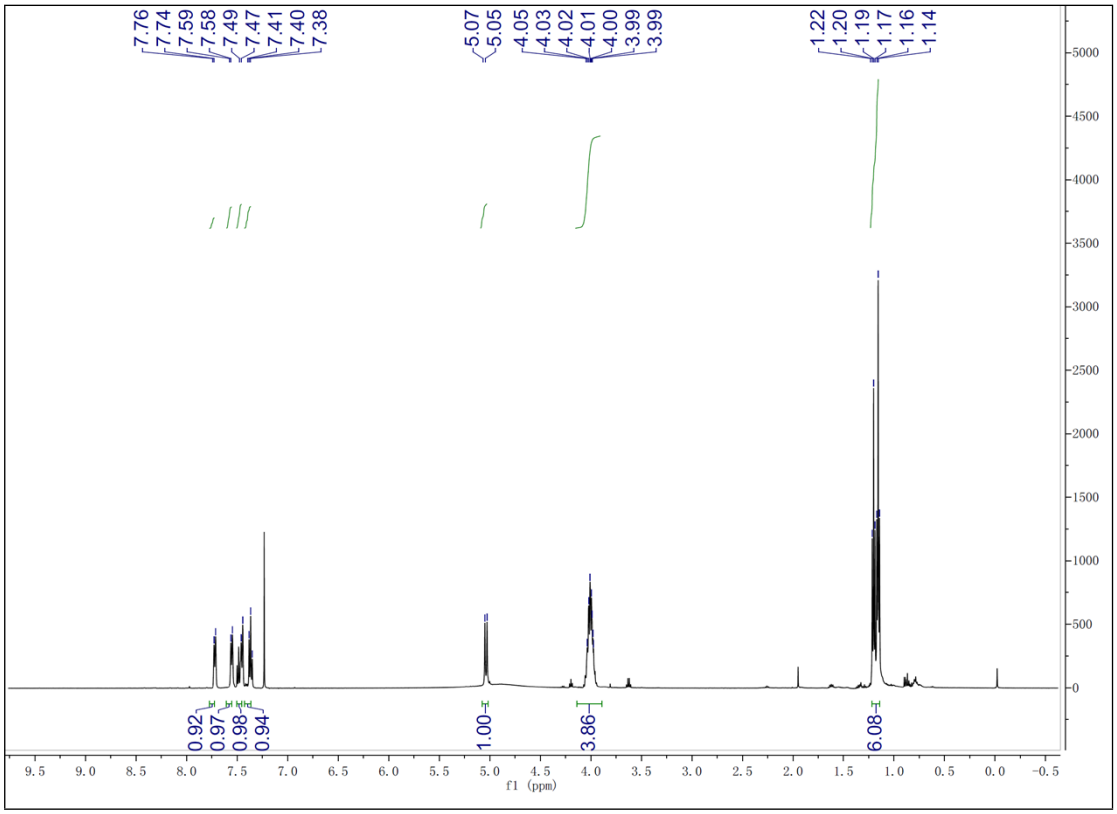
1: DAD1 C, Sig=210,8 Ref=360,100

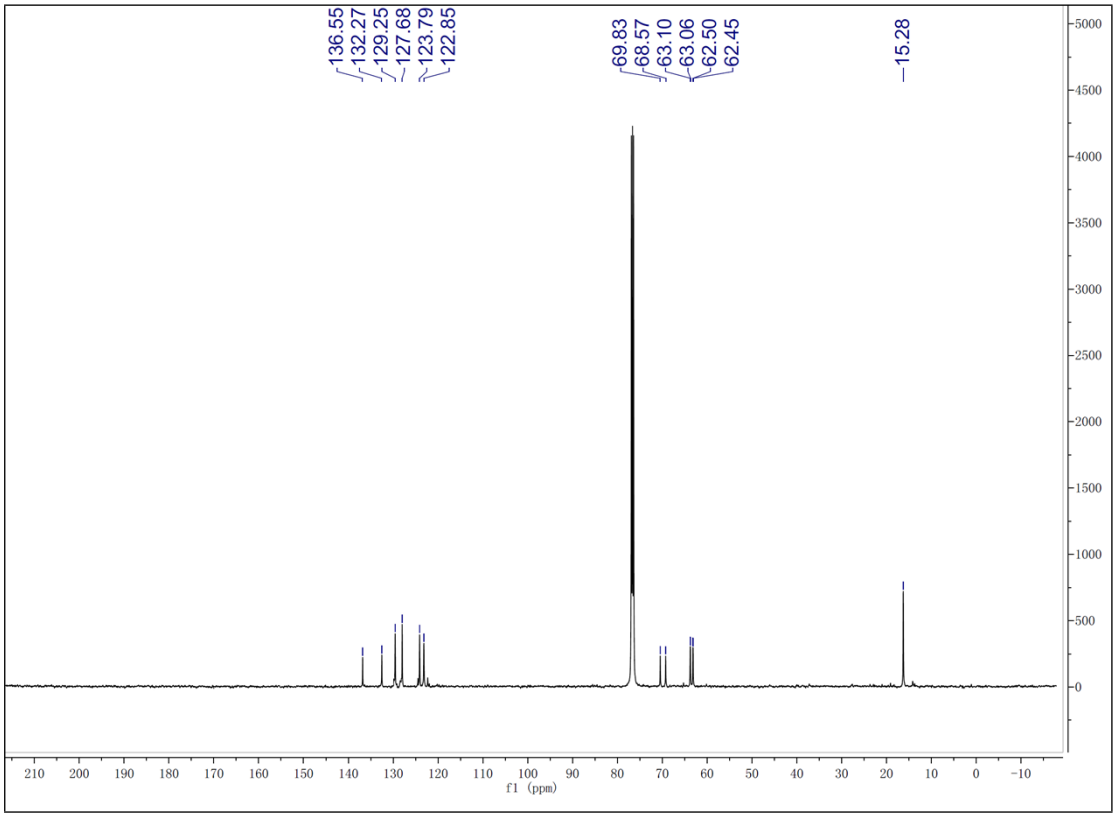
#	[min]		[min]	[mAU*s]	[mAU]	%
1	4.176	BV	0.5778	338.51340	7.83967	13.3634
2	5.798	VB	0.7845	2194.62598	39.11881	86.6366

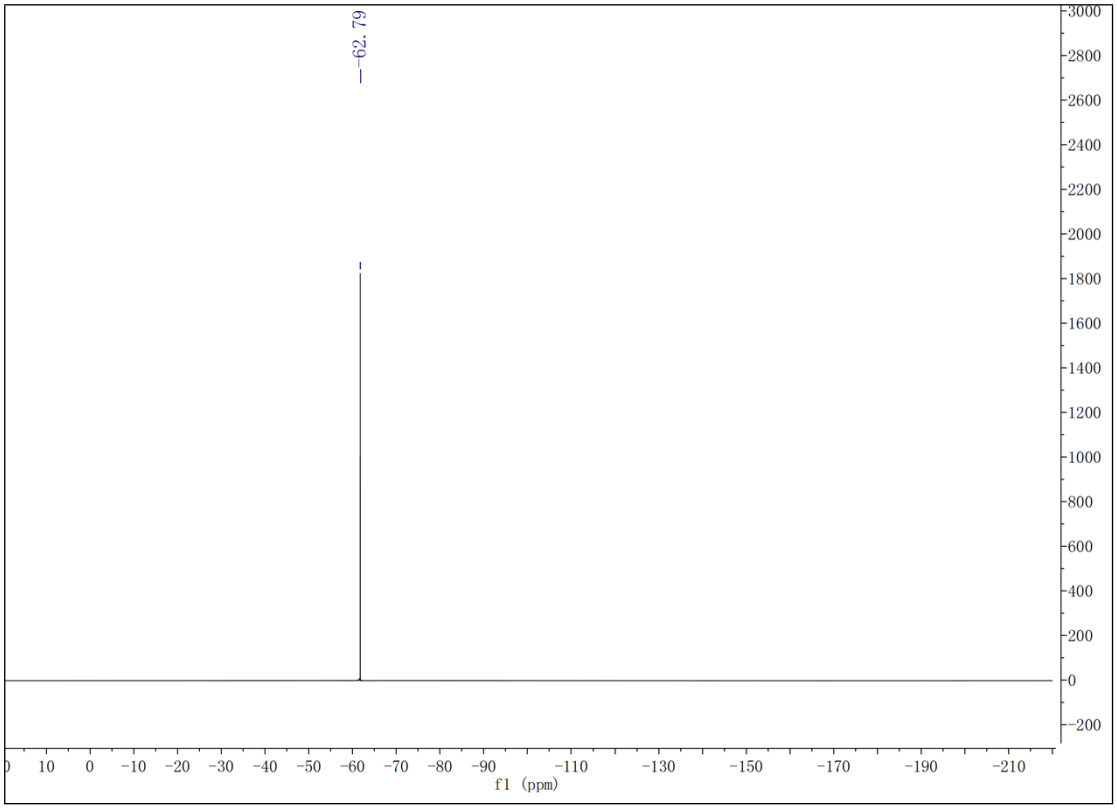
Diethyl hydroxy(3-trifluromethylphenyl)methylphosphonate(7a)

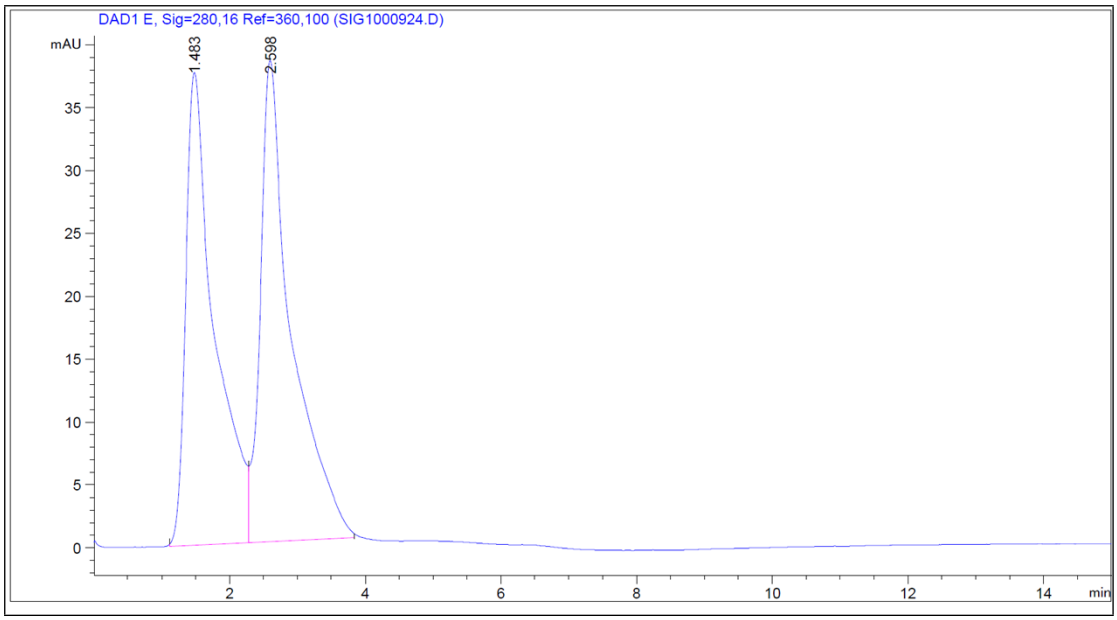


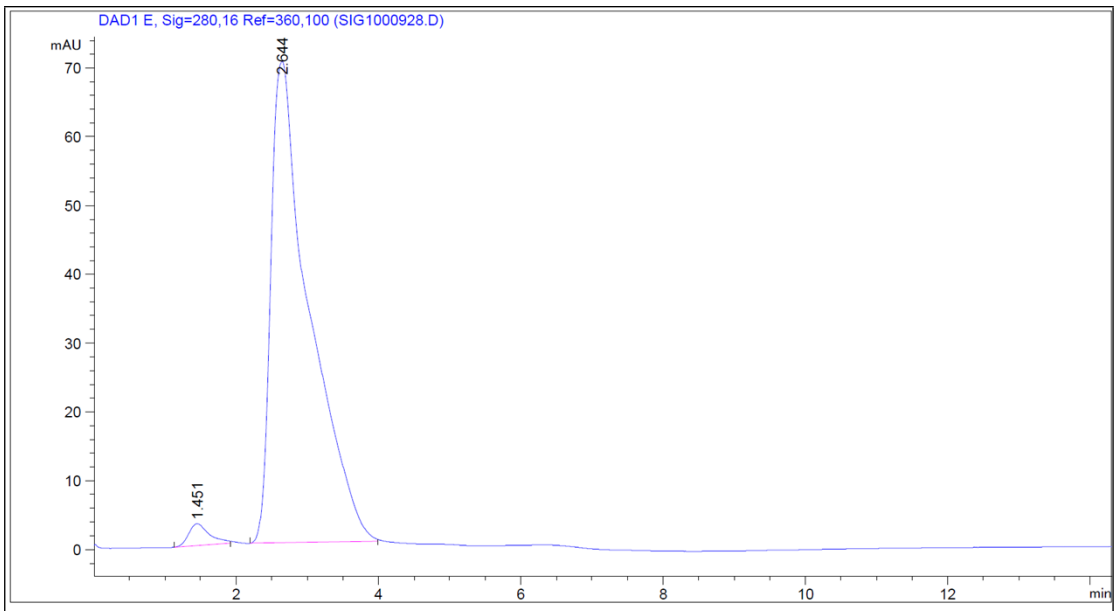
This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (86% yield); $[\alpha]_D^{18}$ -25.9 (c 2.52, $CHCl_3$) for 95% ee (S). [lit.[5] $[\alpha]_D^{20}$ -27 (c 2.4 $CHCl_3$) for 98 % ee (S)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75(d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.41-7.38 (m, 1H), 5.06 (d, *J* = 10.5 Hz, 1H), 4.03-4.00 (m, 4H), 1.22-1.14 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.6, 132.3, 129.3, 127.7, 123.8, 122.9, 68.7 (d, *J* = 157.5 Hz), 63.1 (d, *J* = 5.0 Hz), 62.5 (d, *J* = 6.3 Hz), 15.3. ^{19}F NMR (500 MHz, $CDCl_3$) δ: -62.79. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.5 ml/min, UV = 280 nm, minor enantiomer t_1 = 1.45 min, major enantiomer t_2 = 2.64 min; 95% ee.


7.76
7.74
7.59
7.58
7.49
7.47
7.41
7.40
7.38
5.07
5.05
4.05
4.03
4.02
4.01
4.00
3.99
3.99
1.22
1.20
1.19
1.17
1.16
1.14
0.92
0.97
0.98
0.94
1.00
3.86
6.08
f1 (ppm)


136.55
132.27
129.25
127.68
123.79
122.85
69.83
68.57
63.10
63.06
62.50
62.45
15.28
f1 (ppm)


-62.79
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

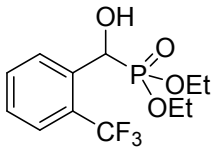

DAD1 E, Sig=280,16 Ref=360,100 (SIG1000924.D)
mAU
1.483
2.598
35
30
25
20
15
10
5
0
2
4
6
8
10
12
14
min



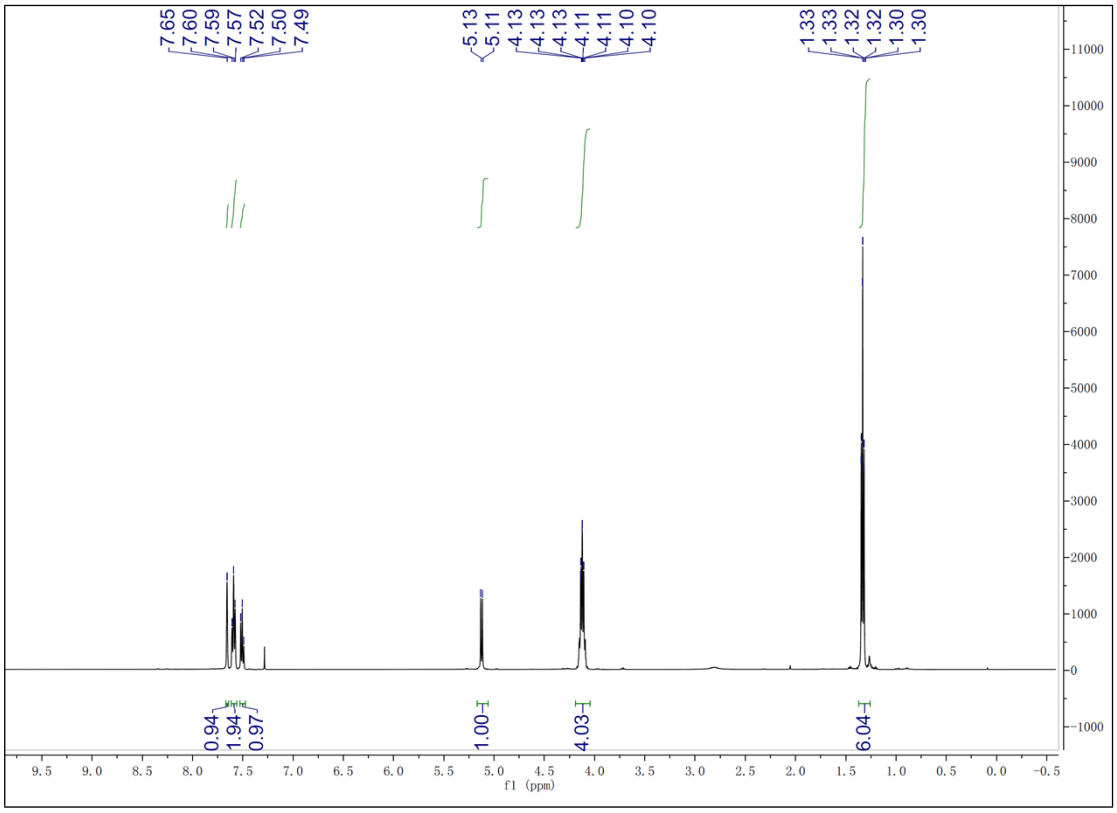
1: DAD1 E, Sig=280,16 Ref=360,100

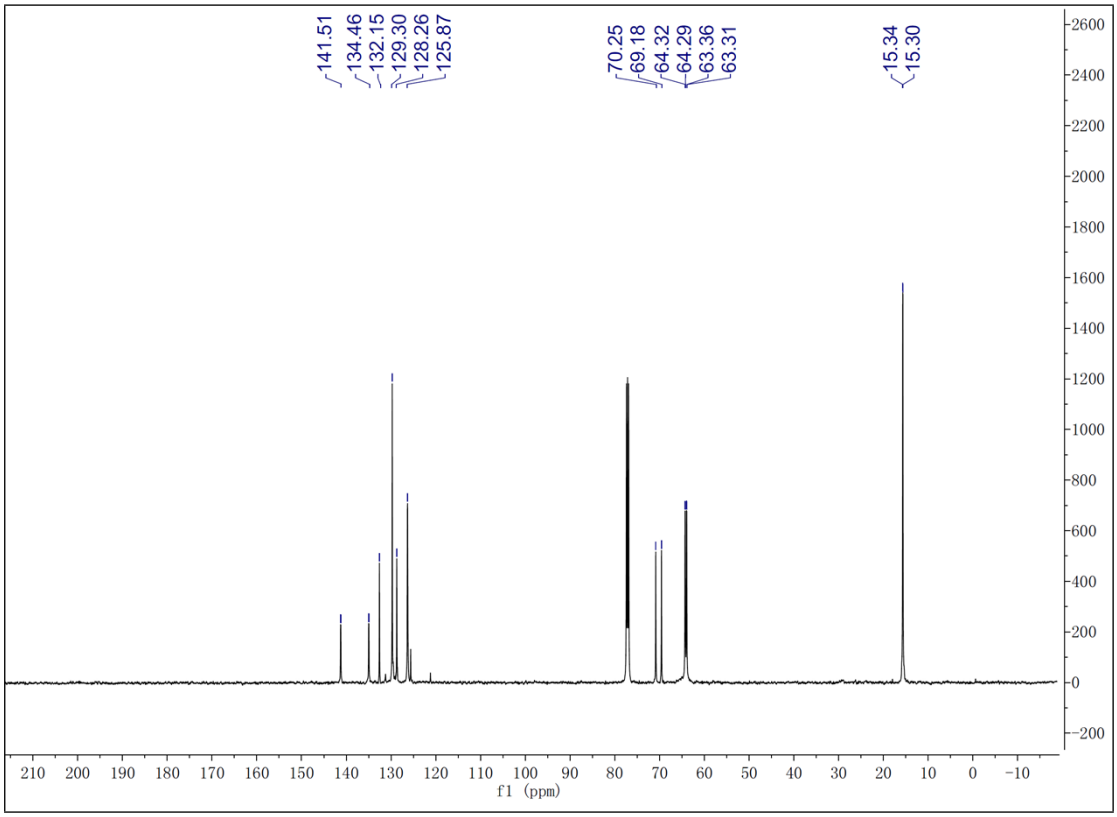
#	[min]		[min]	[mAU*s]	[mAU]	%
1	1.451	BB	0.2976	63.89064	3.16378	2.3772
2	2.644	BB	0.5216	2623.75977	69.94803	97.6228

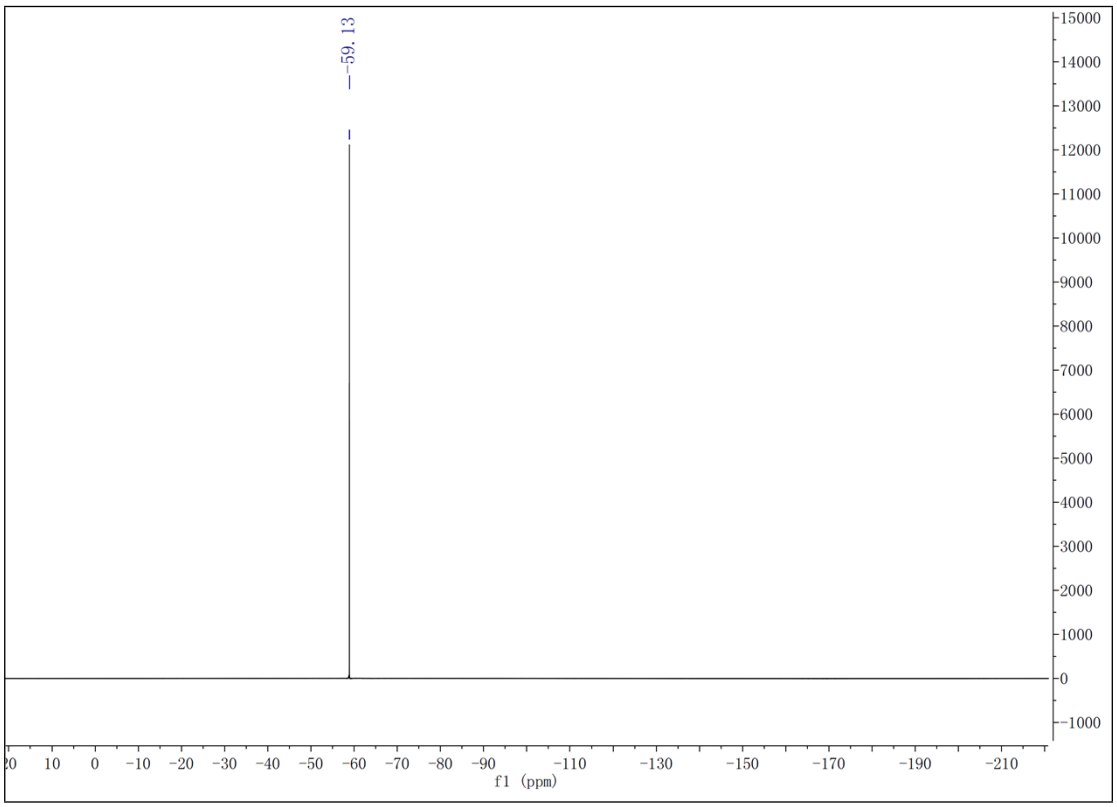
Diethyl hydroxy(2-trifluromethylphenyl)methylphosphonate(8a)

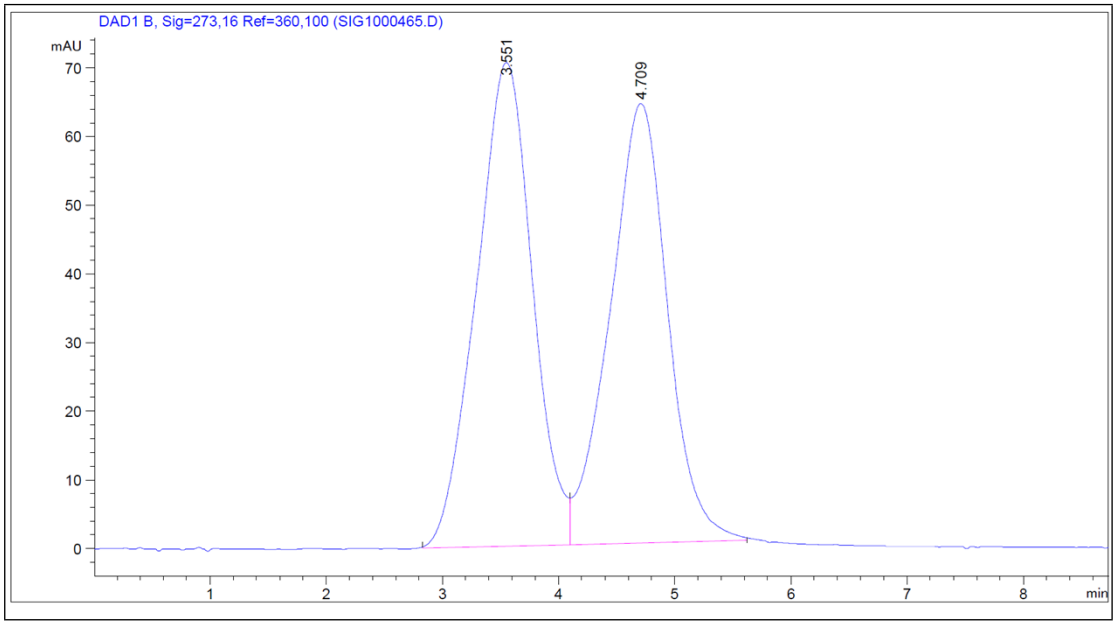


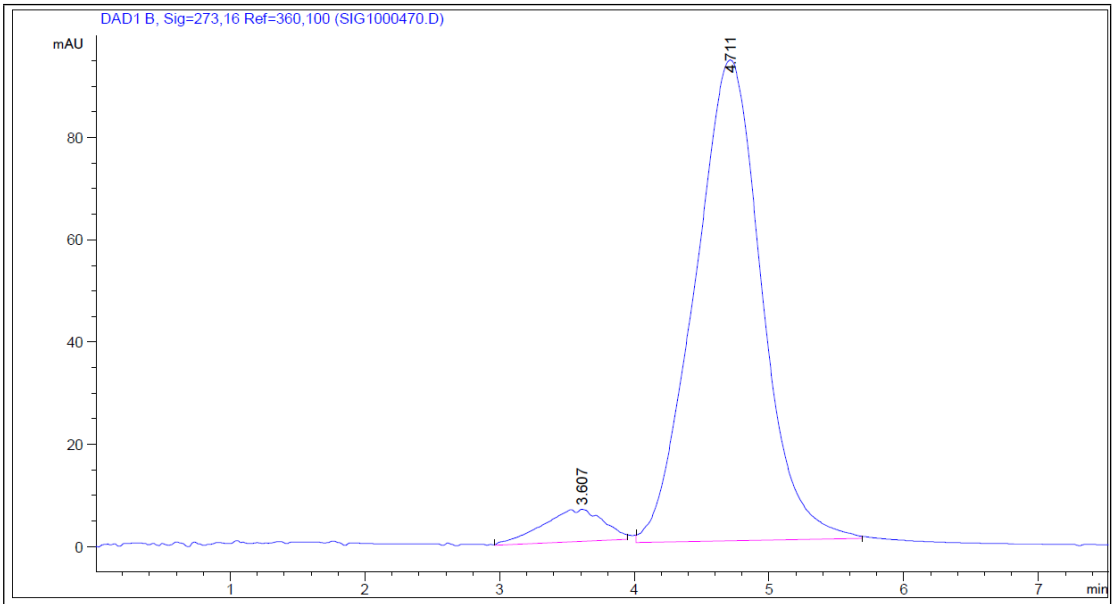
This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (83% yield); $[\alpha]_D^{18}$ -25.9 (c 1.51, $CHCl_3$) for 88% ee; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.60-7.57 (m, 2H), 7.52-7.49 (m, 1H), 5.12 (d, J = 8.2 Hz, 1H), 4.13-4.10 (m, 4H), 1.33-1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 141.5, 134.5, 132.2, 129.3, 128.3, 125.9, 69.7 (d, J = 133.8 Hz), 64.3 (d, J = 3.8 Hz), 63.3 (d, J = 6.3 Hz), 15.3 (d, J = 5.0 Hz). ^{19}F NMR (500 MHz, $CDCl_3$) δ: -59.13. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.2 ml/min, UV = 273 nm, minor enantiomer t_1 = 3.50 min, major enantiomer t_2 = 4.71 min; 88% ee.


7.65
7.60
7.59
7.57
7.52
7.50
7.49
5.13
5.11
4.13
4.13
4.13
4.11
4.11
4.10
4.10
1.33
1.33
1.32
1.32
1.30
1.30
0.94
1.94
0.97
1.00
4.03
6.04
f1 (ppm)


141.51
134.46
132.15
129.30
128.26
125.87
70.25
69.18
64.32
64.29
63.36
63.31
15.34
15.30
f1 (ppm)


-59.13
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

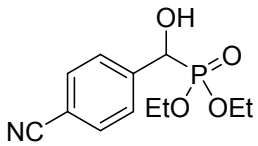

DAD1 B, Sig=273,16 Ref=360,100 (SIG1000465.D)
mAU
70
60
50
40
30
20
10
0
3.551
4.709
1 2 3 4 5 6 7 8
min



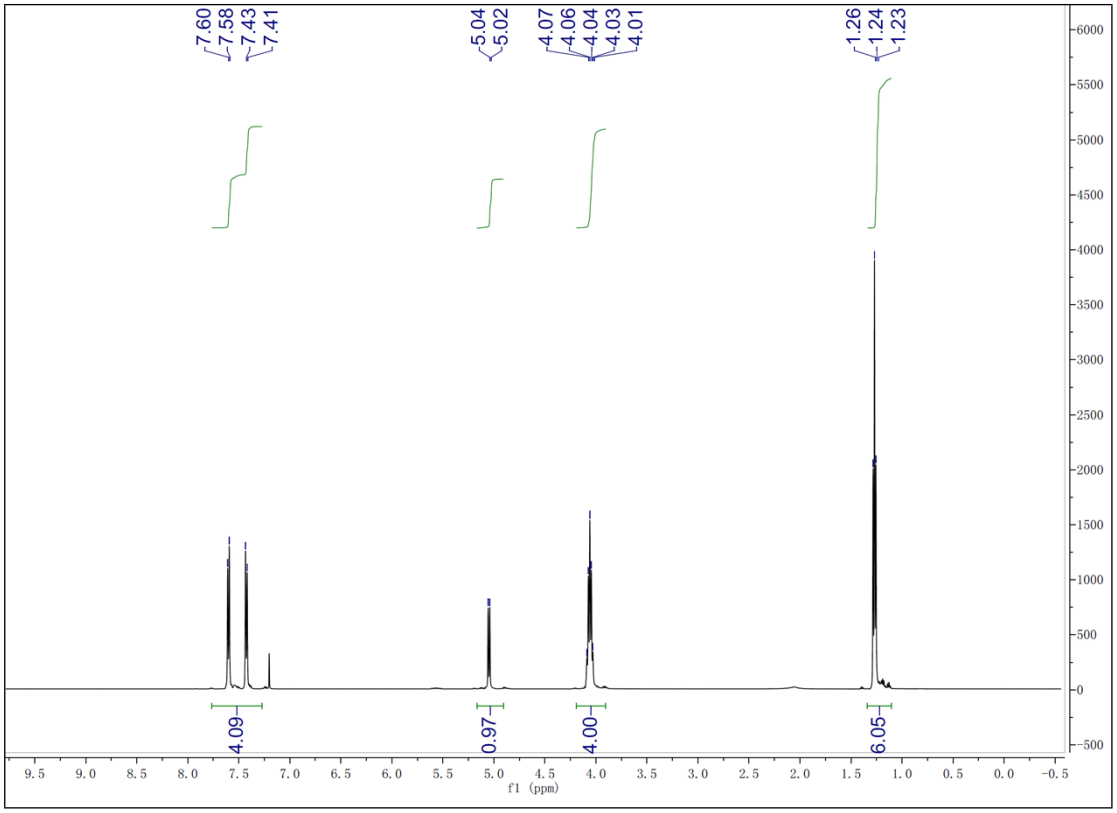
1: DAD1 B, Sig=273,16 Ref=360,100

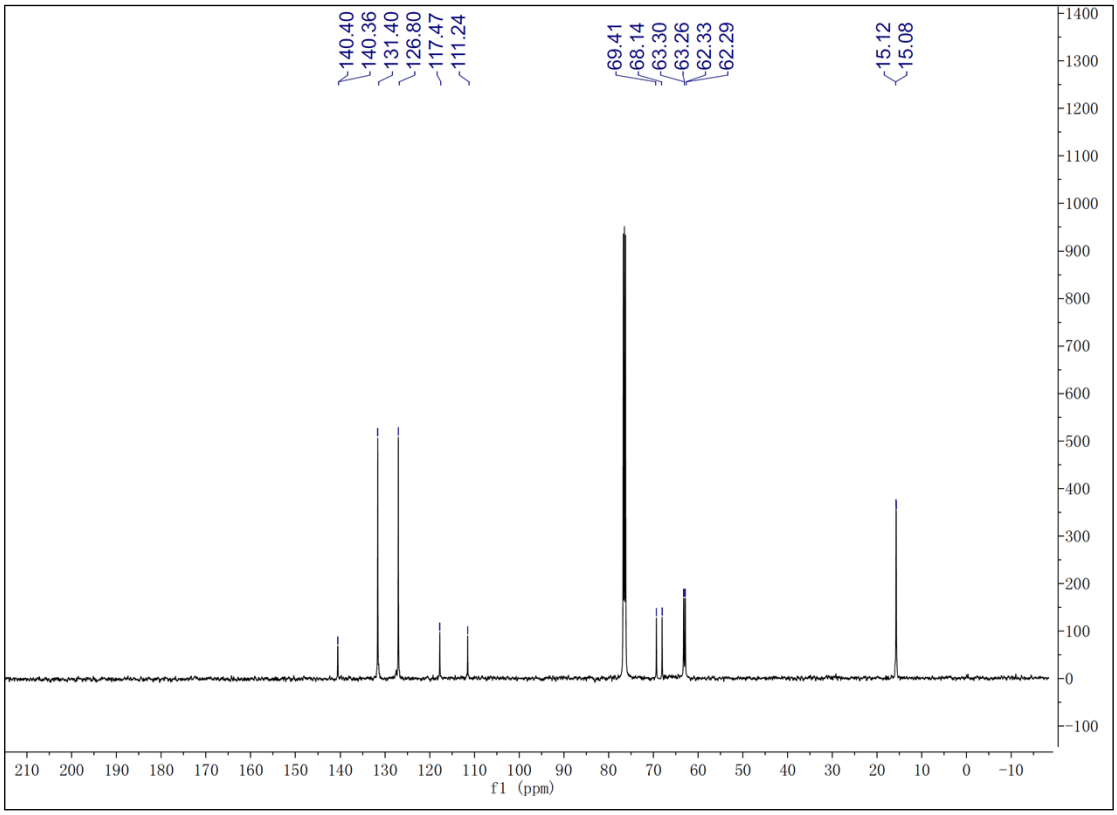
#	[min]		[min]	[mAU*s]	[mAU]	%
1	3.607	MM	0.5282	200.30765	6.32100	5.8268
2	4.711	BB	0.5117	3237.40161	94.03396	94.1732

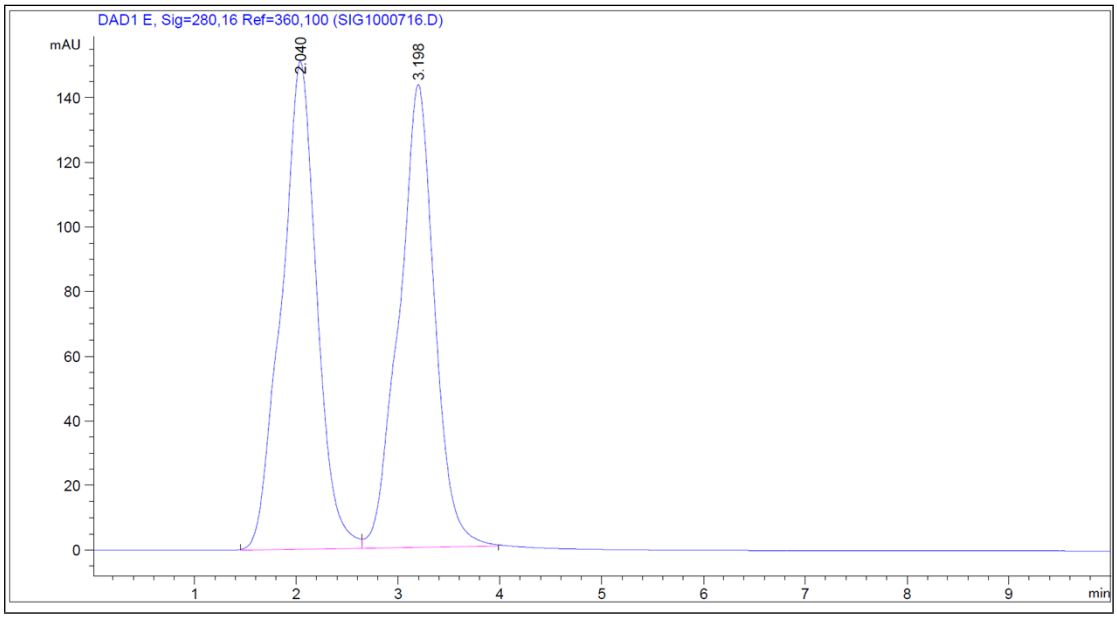
Diethyl hydroxy(4-cyanophenyl)methylphosphonate(9a)

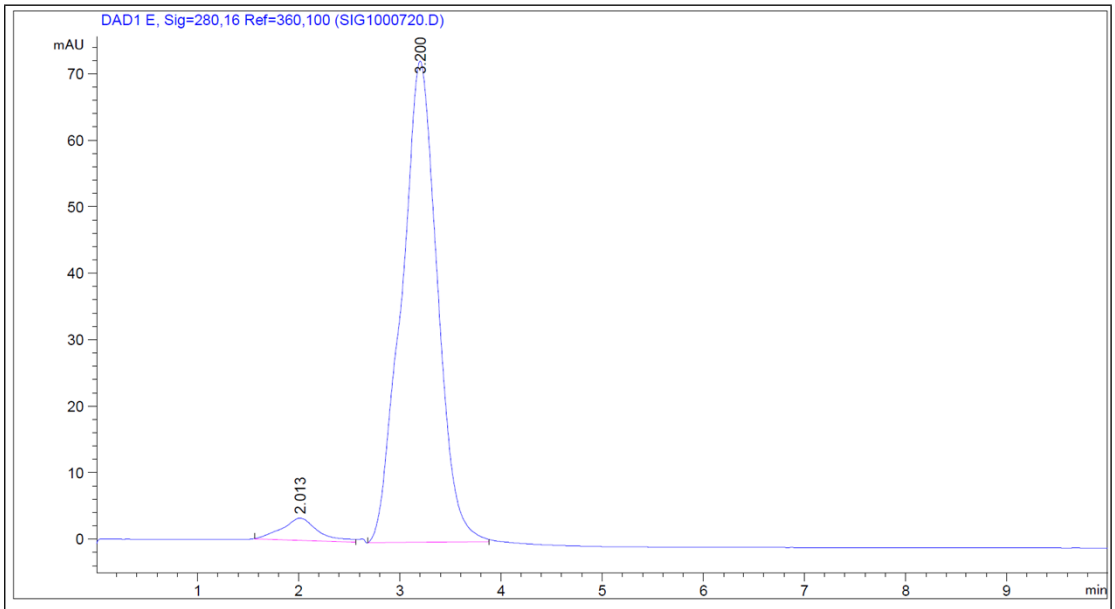


This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (69% yield); $[\alpha]_D^{18}$ -47.9 (c 0.90, $CHCl_3$) for 91% ee (S). [lit.[3] $[\alpha]_D^{20}$ -46.2 (c 0.92, $CHCl_3$) for 89% ee (S)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 5.03 (d, *J* = 8.0 Hz, 1H), 4.07-4.01 (m, 4H), 1.26-1.23 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.4 (d, *J* = 5.0 Hz), 131.4, 126.8, 117.5, 111.2, 68.8 (d, *J* = 158.8 Hz), 63.3 (d, *J* = 5.0 Hz), 62.3 (d, *J* = 5.0 Hz), 15.1 (d, *J* = 5.0 Hz). Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.5 ml/min, UV = 280 nm, minor enantiomer t_1 = 2.01 min, major enantiomer t_2 = 4.20 min; 91% ee.


7.60
7.58
7.43
7.41
5.04
5.02
4.07
4.06
4.04
4.03
4.01
1.26
1.24
1.23
4.09
0.97
4.00
6.05
f1 (ppm)


140.40
140.36
131.40
126.80
117.47
111.24
69.41
68.14
63.30
63.26
62.33
62.29
15.12
15.08
f1 (ppm)

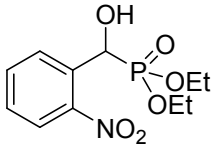




1: DAD1 E, Sig=280,16 Ref=360,100

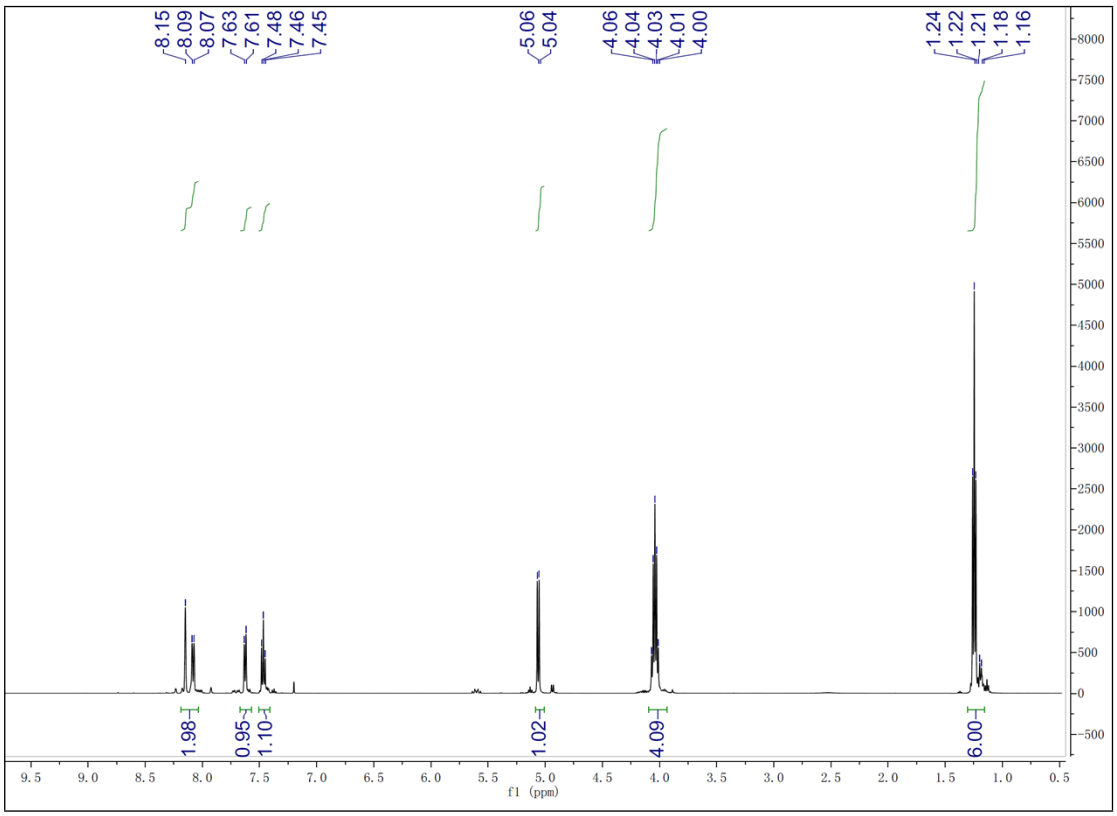
#	[min]		[min]	[mAU*s]	[mAU]	%
1	2.013	BB	0.3499	84.03442	3.35874	4.5188
2	3.200	BB	0.3623	1775.63342	72.36314	95.4812

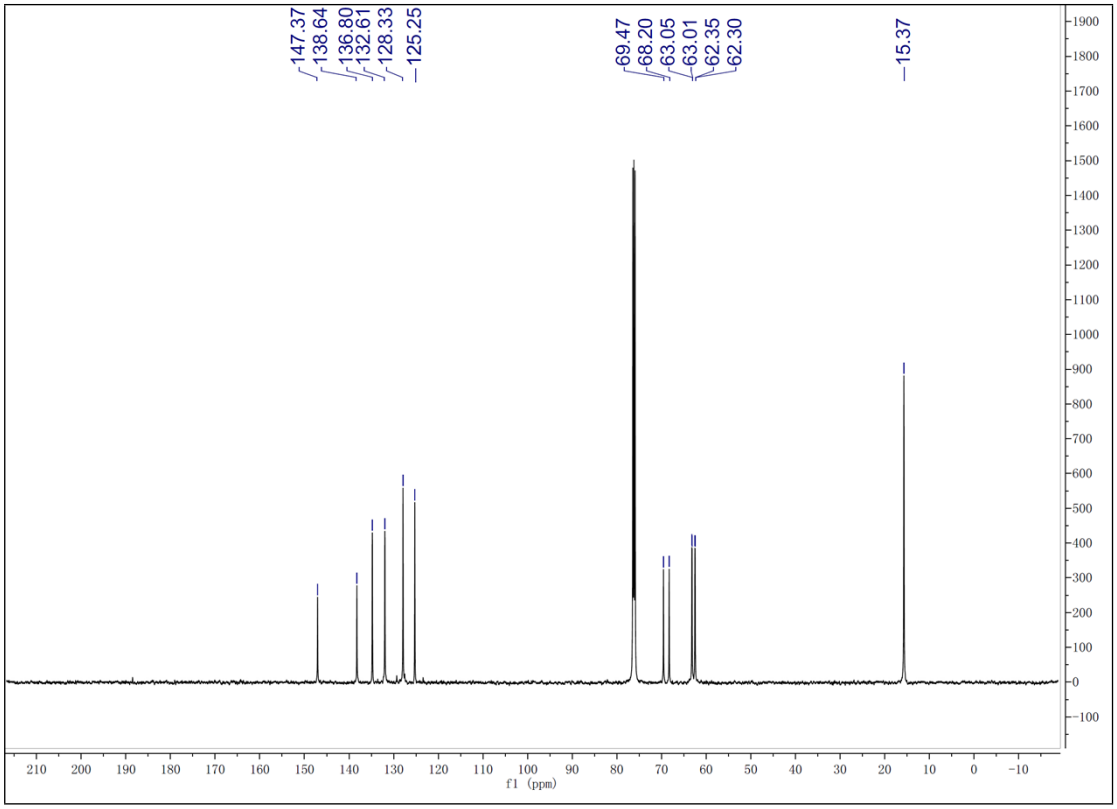
Diethyl hydroxy(2-nitrophenyl)methylphosphonate(10a)

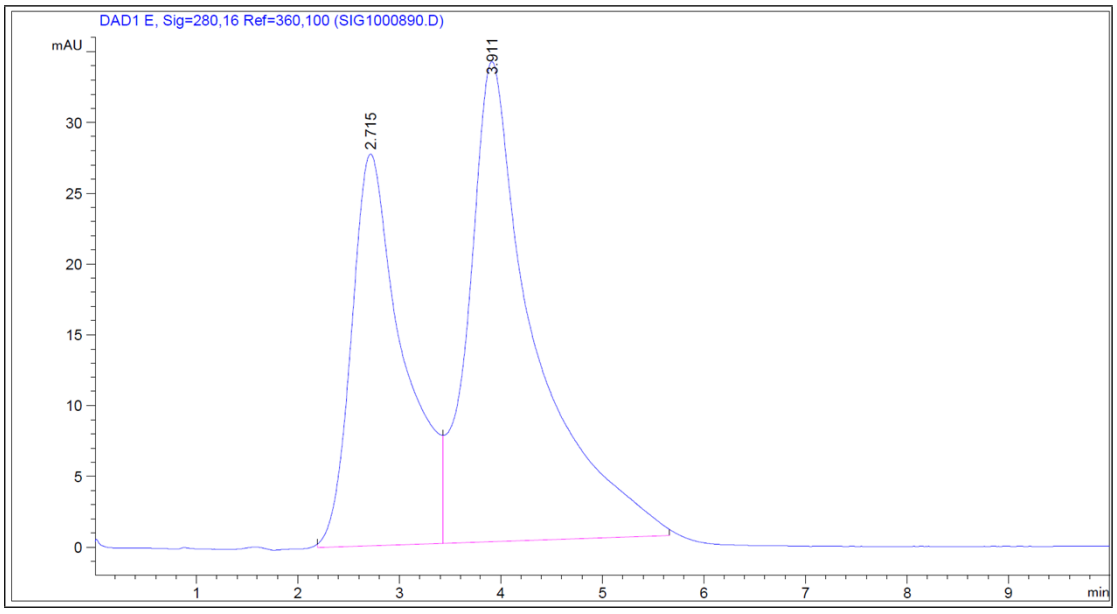


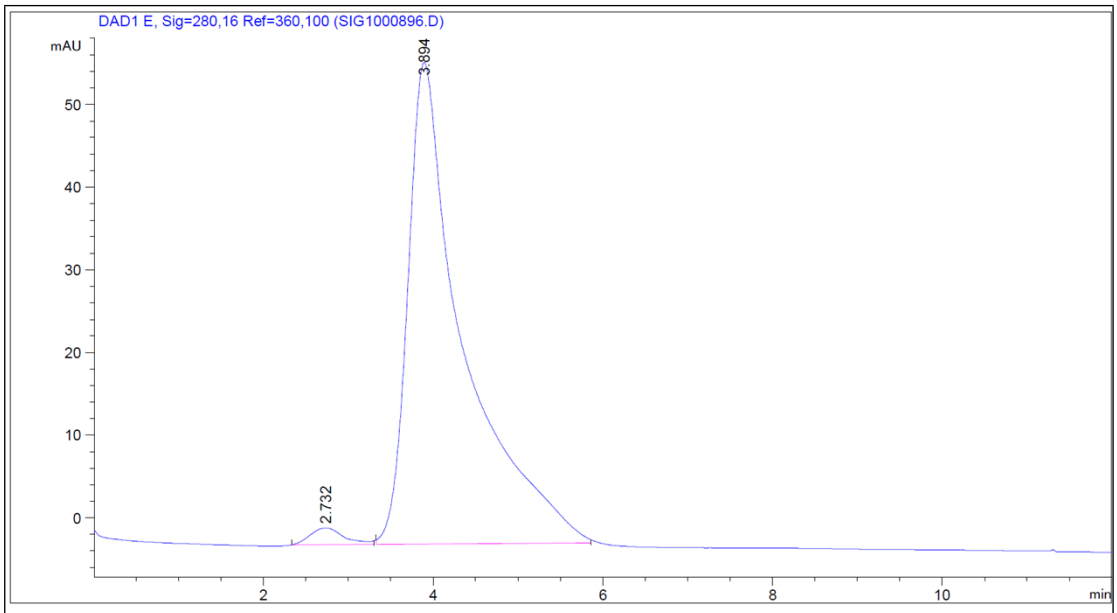
This compound was prepared according to the Experimental Section and purified by column chromatography to give a white solid (42% yield); $[\alpha]_D^{18}$ -32.3 (c 0.96, $CHCl_3$) for 96% ee; ^1H

NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.48-7.45 (m, 1H), 5.05 (d, *J* = 8.1 Hz, 1H), 4.06-4.00 (m, 4H), 1.24-1.16 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.8, 138.6, 136.8, 132.6, 128.3, 125.3, 68.8(d, *J* = 158.8 Hz), 63.0(d, *J* = 5.0 Hz), 62.3(d, *J* = 6.3 Hz), 15.4. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.5 ml/min, UV = 280 nm, minor enantiomer t_1 = 2.73 min, major enantiomer t_2 = 3.89 min; 96% ee.




147.37
138.64
136.80
132.61
128.33
125.25
69.47
68.20
63.05
63.01
62.35
62.30
15.37
f1 (ppm)

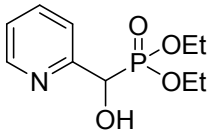

DAD1 E, Sig=280,16 Ref=360,100 (SIG1000890.D)
mAU
2.715
3.911
min



1: DAD1 E, Sig=280,16 Ref=360,100

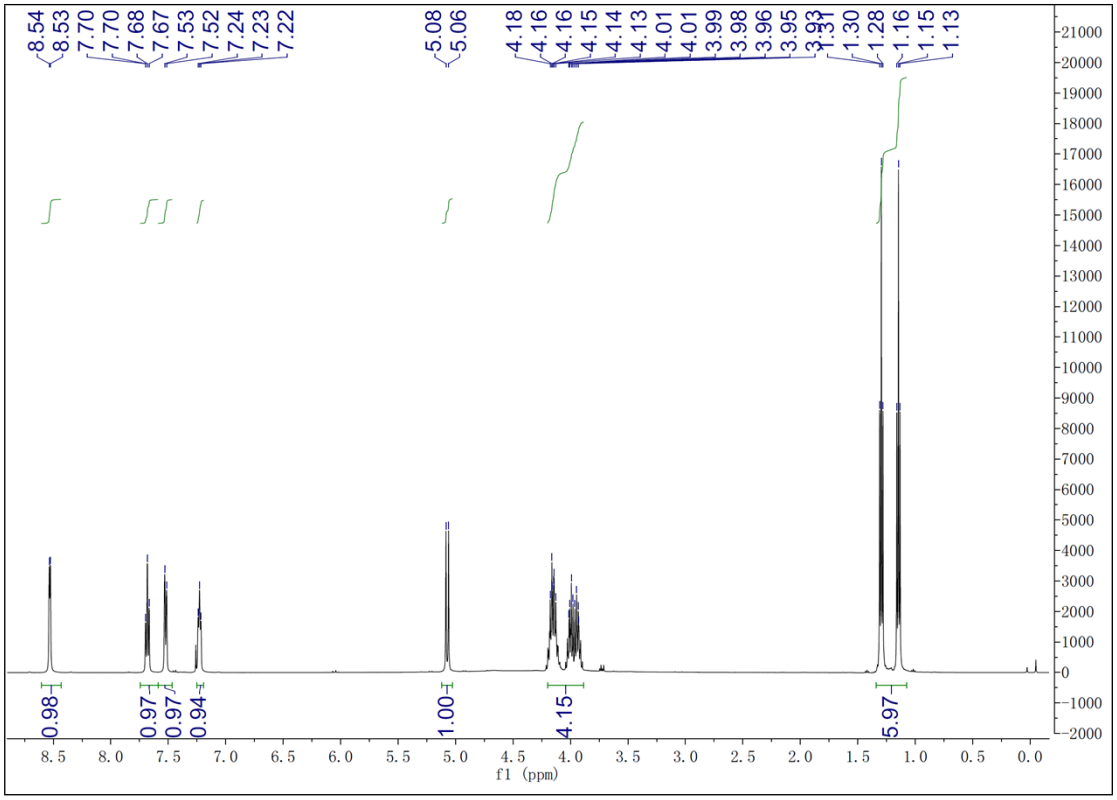
#	[min]		[min]	[mAU*s]	[mAU]	%
1	2.732	BB	0.3961	56.62169	2.03806	2.0918
2	3.894	BB	0.6227	2650.23486	58.25663	97.9082

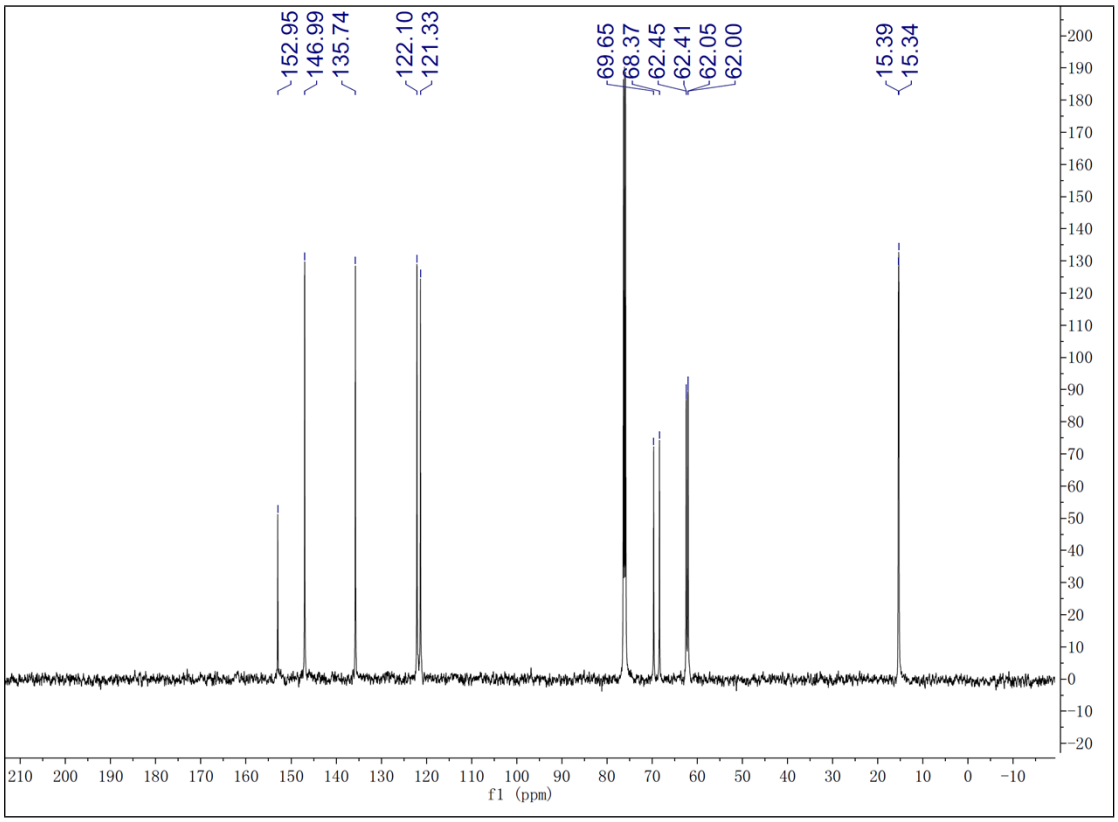
diethyl (hydroxy(pyridin-2-yl)methyl)phosphonate(11a)

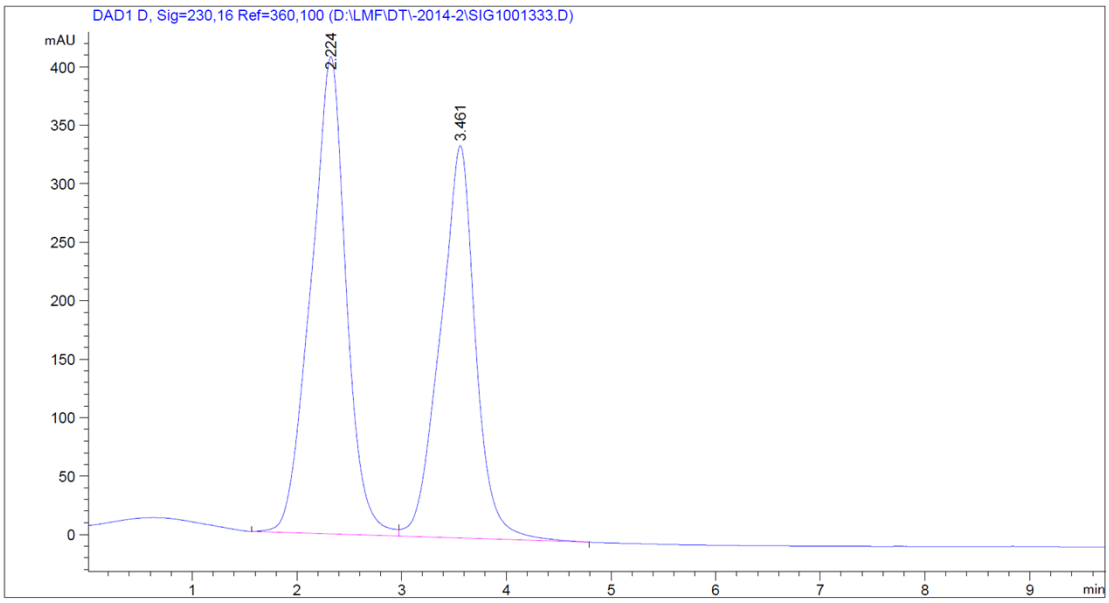


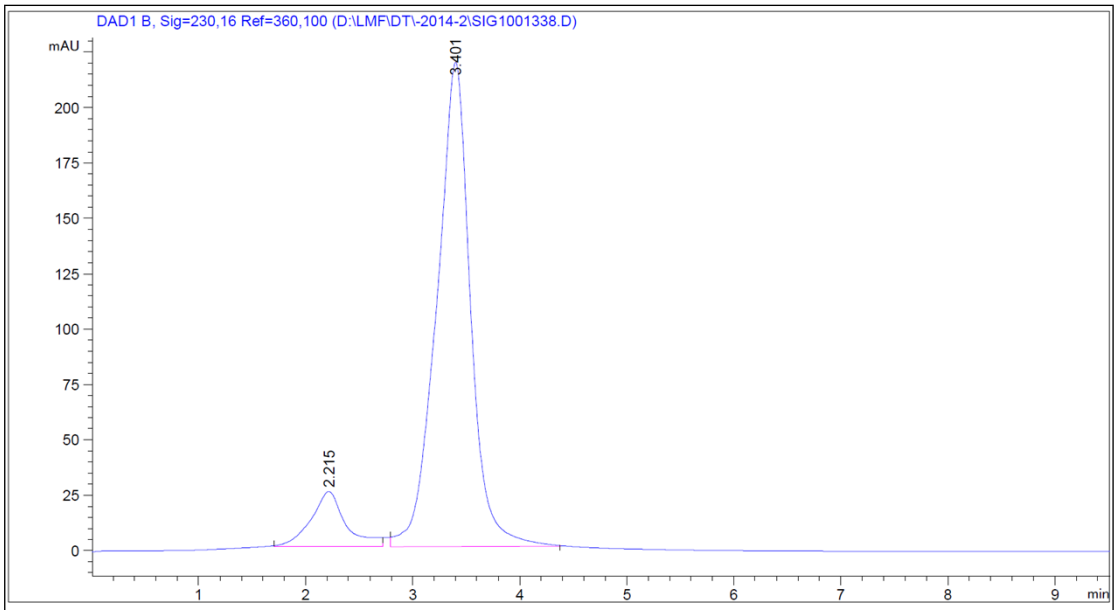
This compound was prepared according to the Experimental Section and purified by column chromatography to give a yellow oil (71% yield); $[\alpha]_D^{18}$ -33.8 (c 1.05, $CHCl_3$) for 79% ee; ^1H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.7 Hz, 1H), 7.70-7.67 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.24-7.22 (m, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 4.18- 3.93 (m, 4H), 1.31- 1.13 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 147.0, 135.7, 122.1, 121.3, 69.0 (d, *J* = 160 Hz), 62.4 (d, *J* = 5.0 Hz), 62.0 (d, *J* = 6.3 Hz), 15.3 (d, *J* = 6.7 Hz). Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (30:70 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.2 ml/min, UV = 230 nm,

minor enantiomer t_1 = 2.22 min, major enantiomer t_2 = 3.40 min; 79% ee.



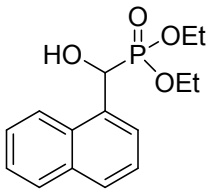






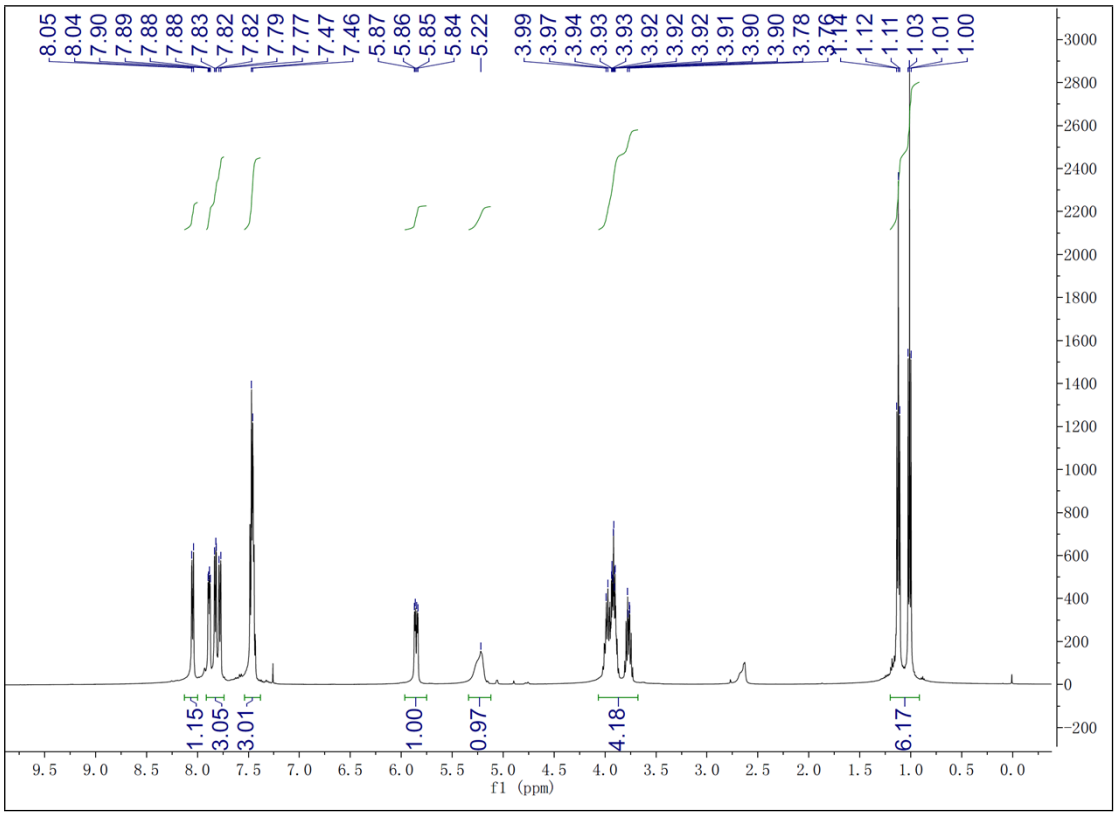
#	[min]		[min]	[mAU*s]	[mAU]	%
1	2.215	BB	0.3170	566.41663	24.93429	10.5721
2	3.401	BB	0.3136	4791.24023	218.67499	89.4279

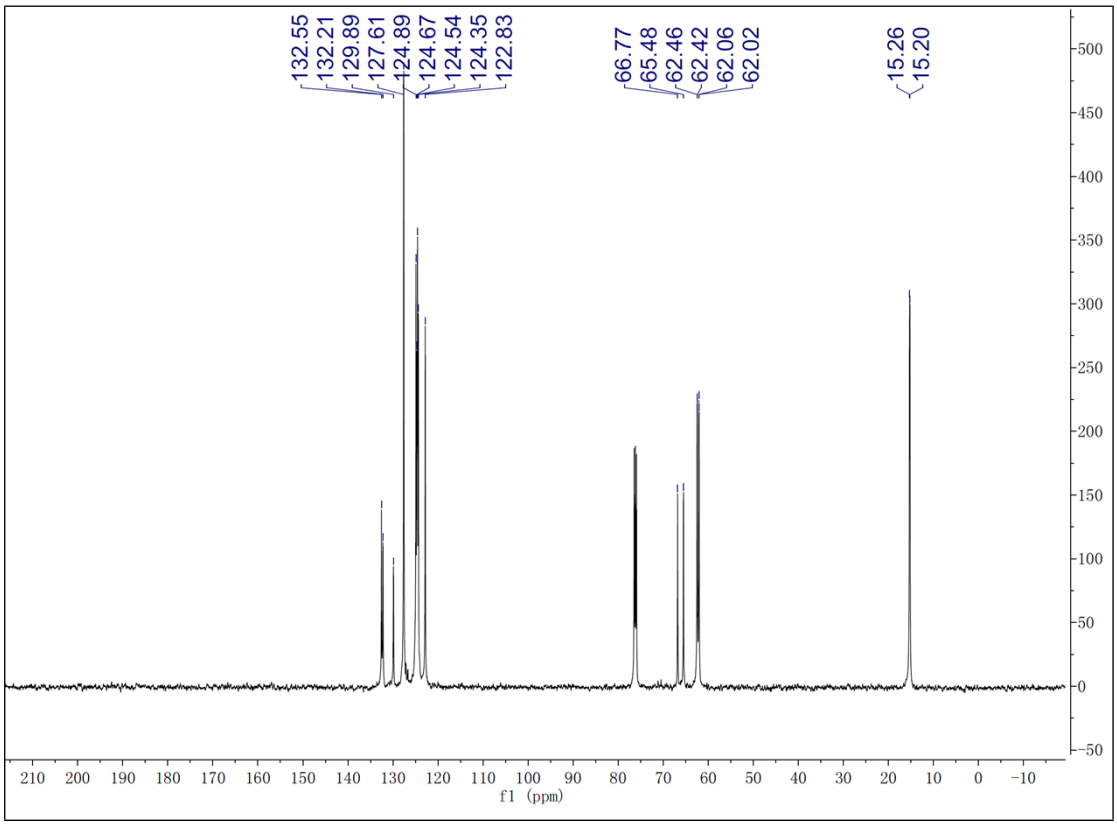
diethyl (hydroxy(naphthalen-1-yl)methyl)phosphonate(12a)

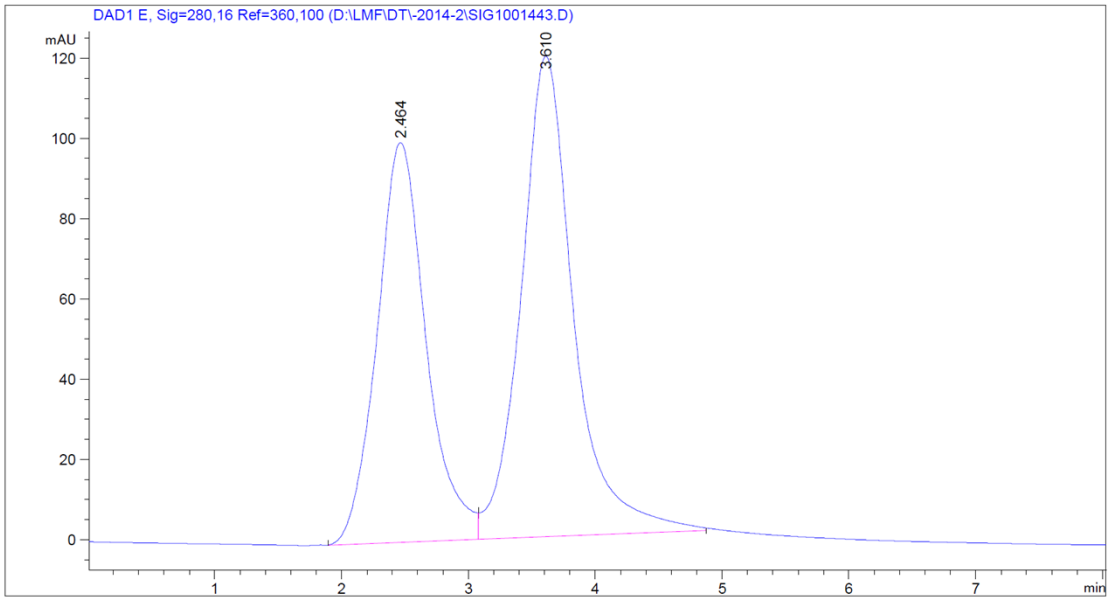


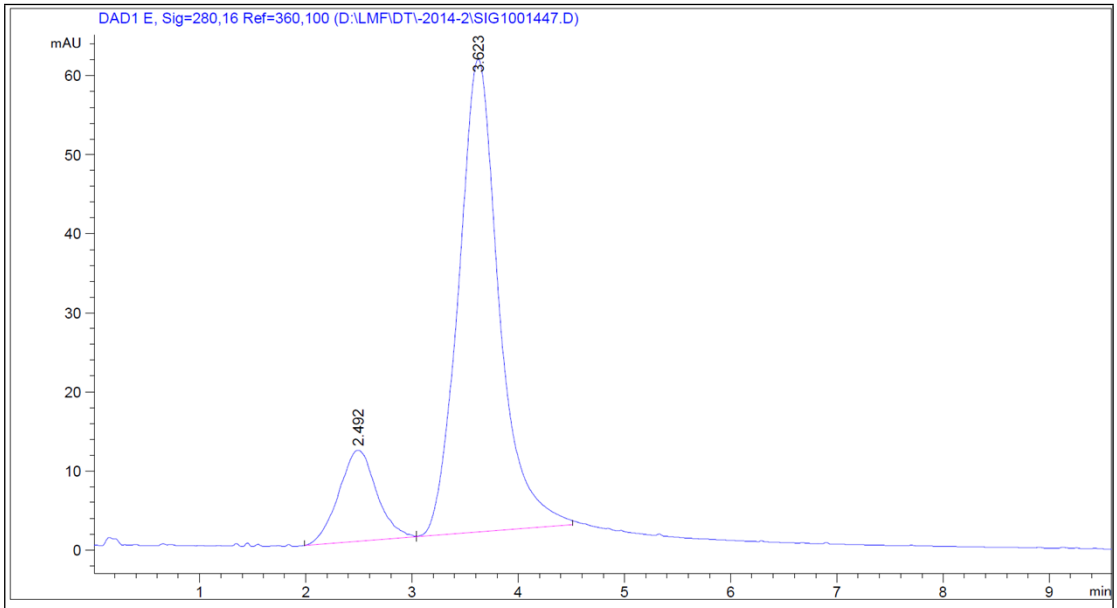
This compound was prepared according to the Experimental Section and purified by column chromatography to give a yellow oil (84% yield); $[\alpha]_D^{20}$ -78.7 (c 1.0, $CHCl_3$) for 69% ee (S). [lit.[3]

$[\alpha]_D^{20}$ -108.4 (c 0.80 $CHCl_3$) for 96% ee (S)]; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.90-7.77(m, 3H), 7.46 (d, *J* = 5.9 Hz, 3H), 5.87-5.84 (m, 1H), 5.22 (s, 1H), 3.99-3.76 (m, 4H), 1.14-1.00 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.6, 132.2, 129.9, 127.6, 124.9, 124.7, 124.5, 124.4, 122.8, 66.1(d, *J* = 161 Hz), 62.4 (d, *J* = 5.0 Hz), 62.0 (d, *J* = 5.0 Hz),15.2 (d, *J* = 7.1 Hz). Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.2 ml/min, UV = 280 nm, minor enantiomer t_1 = 2.49 min, major enantiomer t_2 = 3.62 min; 69% ee.



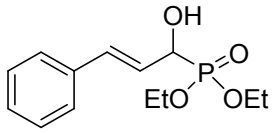

132.55
132.21
129.89
127.61
124.89
124.67
124.54
124.35
122.83
66.77
65.48
62.46
62.42
62.06
62.02
15.26
15.20
f1 (ppm)


DAD1 E, Sig=280,16 Ref=360,100 (D:\LMF\DT\-2014-2\SIG1001443.D)
mAU
2.464
3.610
min

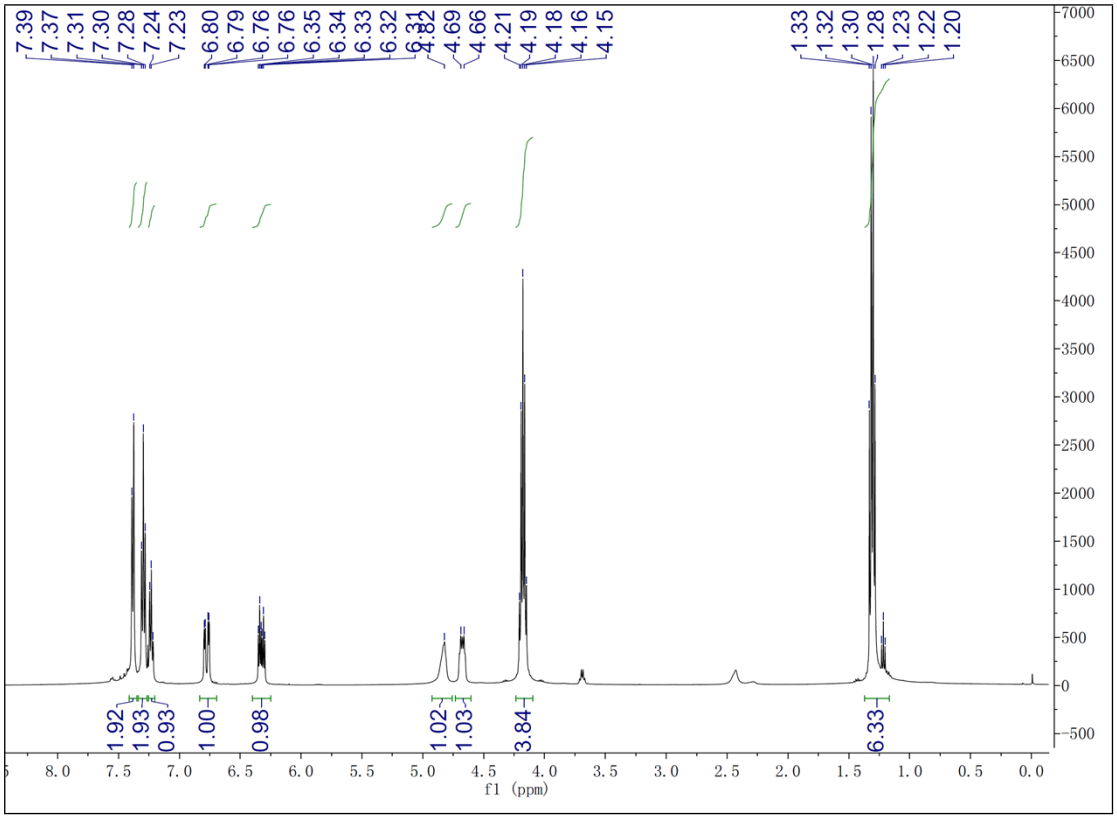


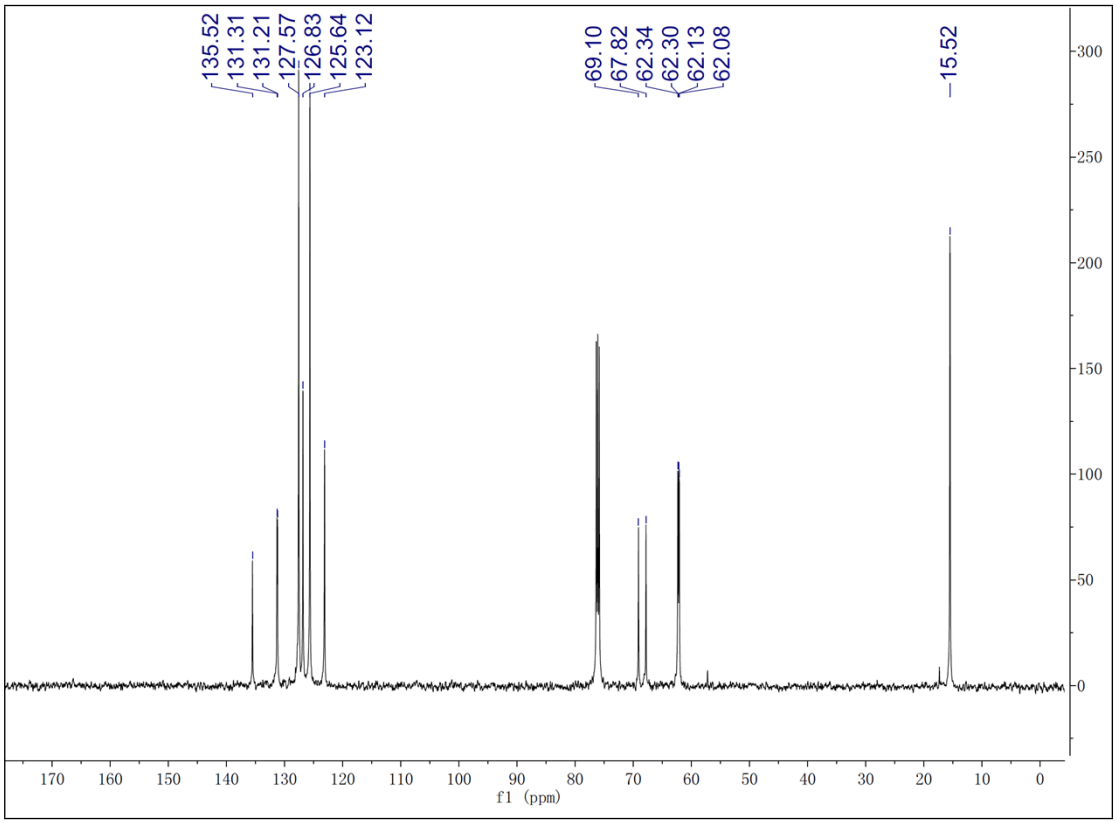
#	[min]		[min]	[mAU*s]	[mAU]	%
1	2.492	BV	0.3360	286.53372	11.52525	15.3211
2	3.623	VB	0.3871	1583.65479	59.77518	84.6789

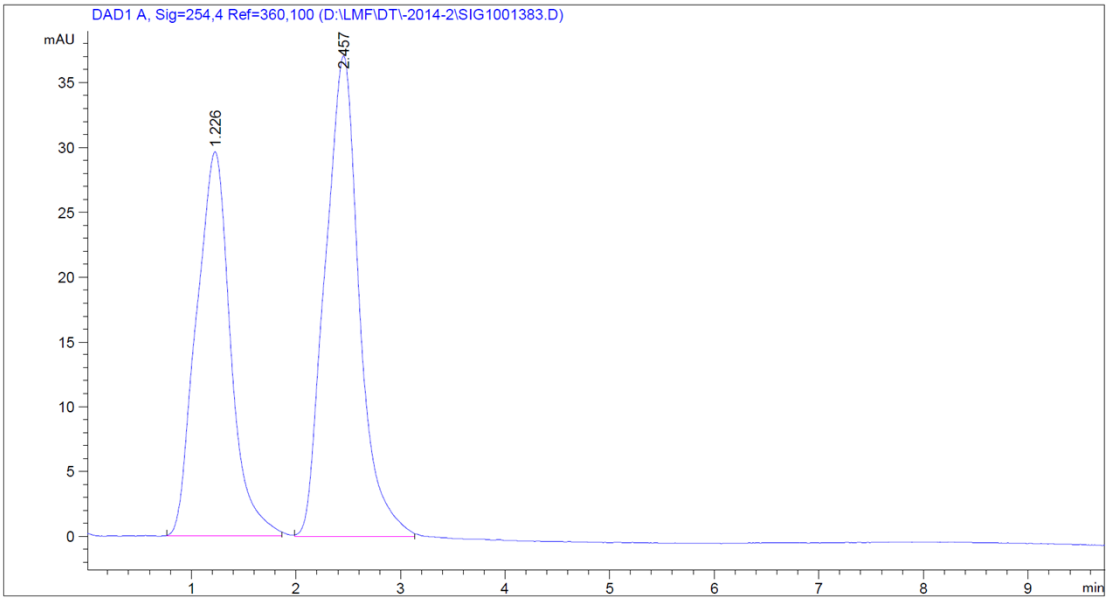
diethyl (E)-(1-hydroxy-3-phenylallyl)phosphonate(13a)

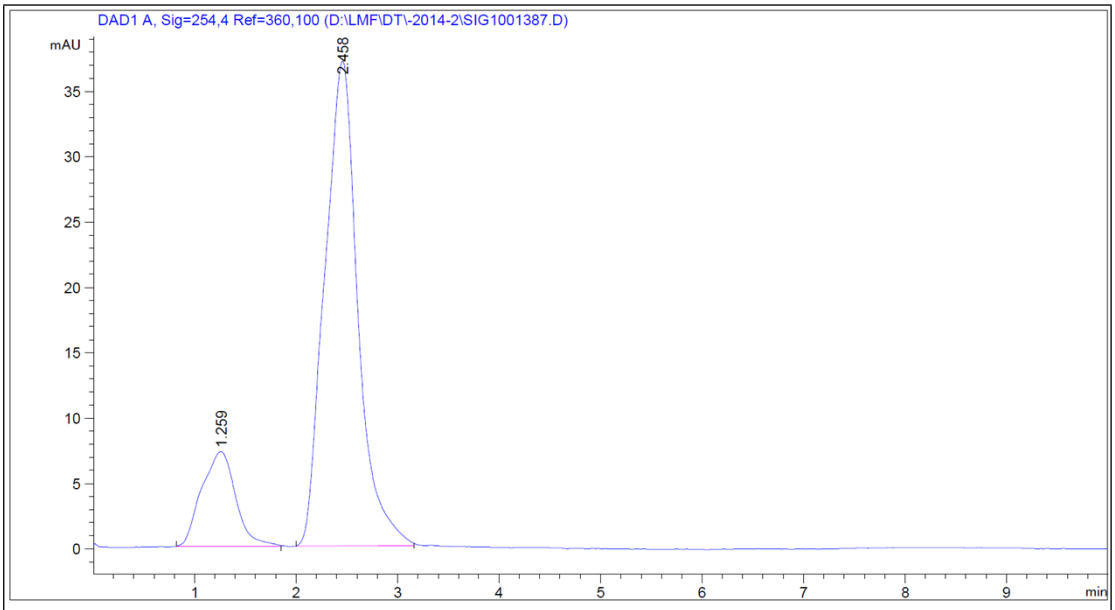


This compound was prepared according to the Experimental Section and purified by column chromatography to give a yellow oil (53% yield); $[\alpha]_D^{20}$ -8.7 (c 0.6, $CHCl_3$) for 67% ee (S). [lit.[3] $[\alpha]_D^{20}$ -11.3 (c 0.54 $CHCl_3$) for 85% ee (S)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.31-7.28 (m, 2H), 7.24-7.22 (m, 2H), 6.80-6.76 (m, 1H), 6.35-6.31(m, 1H), 4.82 (s, 1H), 4.68 (d, *J* = 13.0 Hz, 1H), 4.21-4.15 (m, 4H), 1.33-1.20 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 131.26 (d, *J* = 12.8 Hz), 127.6, 126.8, 125.6, 123.1, 68.5 (d, *J* = 160 Hz), 62.3 (d, *J* = 6.3 Hz), 62.1(d, *J* = 5.0 Hz), 15.5. Enantiomeric excess was determined by chiral HPLC with a Ultron ES-OVM column (35:65 alcohol/KH_2PO_4(0.02 mol/L), flow rate = 1.5 ml/min, UV = 254 nm, minor enantiomer t_1 = 1.26 min, major enantiomer t_2 = 2.46 min; 67% ee.


7.39
7.37
7.31
7.30
7.28
7.24
7.23
6.80
6.79
6.76
6.76
6.35
6.34
6.33
6.32
4.82
4.69
4.66
4.21
4.19
4.18
4.16
4.15
1.33
1.32
1.30
1.28
1.23
1.22
1.20
1.92
1.93
0.93
1.00
0.98
1.02
1.03
3.84
6.33
f1 (ppm)


135.52
131.31
131.21
127.57
126.83
125.64
123.12
69.10
67.82
62.34
62.30
62.13
62.08
15.52
f1 (ppm)





#	[min]		[min]	[mAU*s]	[mAU]	%
1	1.259	BB	0.3322	169.43143	7.26208	16.7776
2	2.458	BB	0.3243	840.43506	37.10258	83.2224

Reference

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