Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Supporting Information

Fluorous Chiral Bisoxazolines. Application in Copper-Catalyzed Asymmetric α-Hydrophosphonylation

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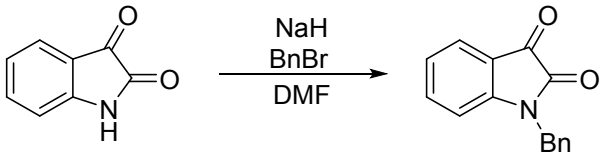
1. Experimental Section

1.1 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. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX500 (500 MHz) spectrometer and tetramethylsilane (TMS) was used as a reference. Elemental analysis was performed on a Vario EL III recorder. Mass spectra were obtained with an automated Fininigan TSQ Advantage mass spectrometer. Most of the products were known compounds and were identified by comparison of their physical and spectra data with those of authentic samples. Enantiomeric excesses (**ee**) were determined by chiral HPLC using a Venusil CA column.

1.2 Procedure for the synthesis of 1-Benzylindoline-2,3-dione



A solution of isatin (5.0 g, 34 mmol) in DMF (60 mL) was cooled to 0°C (ice bath). NaH (60% dispersion in mineral oil, 1.4 g, 36 mmol) was added portion wise to the orange solution. The color of solution changed to deep purple. When the gas evolution stopped, benzyl bromide (6.7 g, 39 mmol) was added slowly, whereupon the mixture turned red-brown. After the reaction mixture was stirred for 15 min at room temperature, H_2O (300 mL) was introduced to precipitate the product. After filtration, the product was washed with hexane to afford 1-benzylindoline-2,3-dione after drying.

1.3 General procedure for the synthesis of 3-hydroxy-3-substituted oxindole

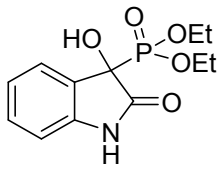
A mixture of $Cu(OAc)_2$ (0.1 mmol) and L6 (0.1 mmol) in methanol (1mL) was stirred at room temperature for 3h. To the mixture were then added isatin (1 mmol), KF (0.1 mmol) and dialkylphosphite (1.2 mmol). After the starting material was consumed as indicated by TLC, the reaction mixture was poured into water and then extracted with EtOAc (3 × 10mL). The combined organic phase was washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography.

1.4 General procedure for recovery of fluorous bis(oxazolines)

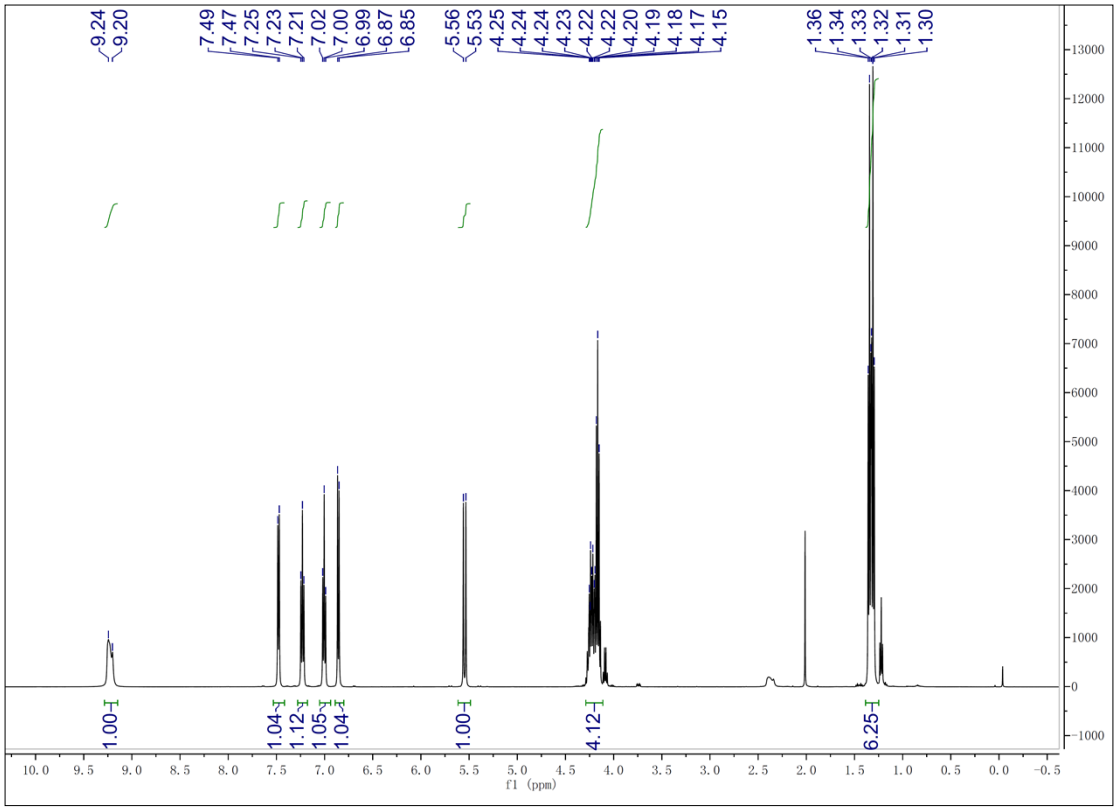
After the reaction was finished, the mixture was concentrated and then loaded onto a FluoroFlash® silica gel for F-SPE. The residue was eluted by methanol : water (v/v = 80:20) at first for the seperation of non-fluorous component, pure methanol was then added onto the fluorous gel column continuously for obtaining the elutant of fluorous bis(oxazolines). When the bulk of solvent was removed and the residue was dried in vacuo at 50°C for 8 h to give the fluorous bis(oxazolines). The recovered ligand could be used directly for the next run.

2. Characterization of compounds

*2.1 Diethyl (3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3a**)*



Purified by column chromatography eluting with hexane/EtOAc 3:1(91% yield). The *ee* (83%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=1.0 mL/min, UV= 254 nm, minor enantiomer t_1 = 15.0 min, major enantiomer t_2= 17.3 min. Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (d, *J* = 20.9 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.25-7.21 (m, 1H), 7.02-6.99 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.55 (d, *J* = 13.0 Hz, 1H), 4.25-4.15(m, 4H), 1.36-1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0 (d, *J* = 4.6 Hz), 141.0, 129.6, 125.1, 123.6, 121.84 (s), 109.7, 71.9, 63.69 (d, *J* = 4.8 Hz), 63.45 (d, *J* = 4.8 Hz), 15.03 (d, *J* = 4.8 Hz). ESI-MS *(m/z)*: 308 ($[M+Na]^+$)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7.47
7.25
7.23
7.21
7.02
7.00
6.99
6.87
6.85
5.56
5.53
4.25
4.24
4.24
4.23
4.22
4.22
4.20
4.19
4.18
4.17
4.15
1.36
1.34
1.33
1.32
1.31
1.30
1.00
1.04
1.12
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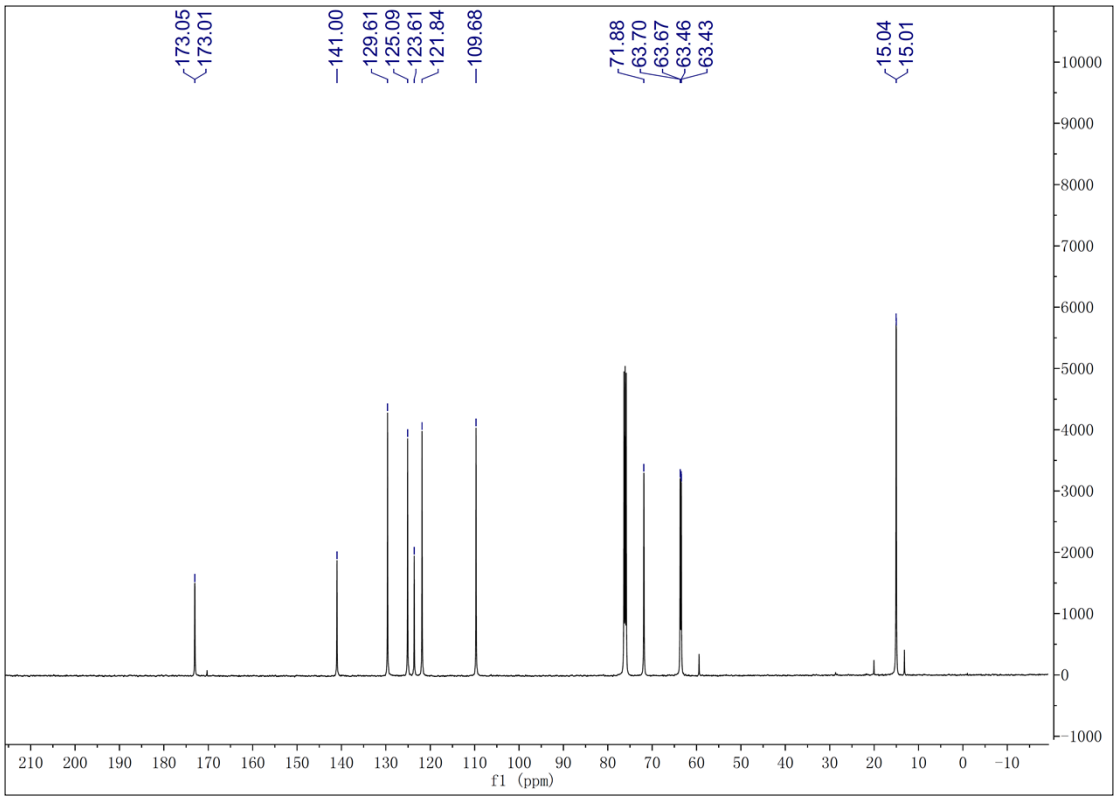
6.25
f1 (ppm)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173.01
141.00
129.61
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109.68
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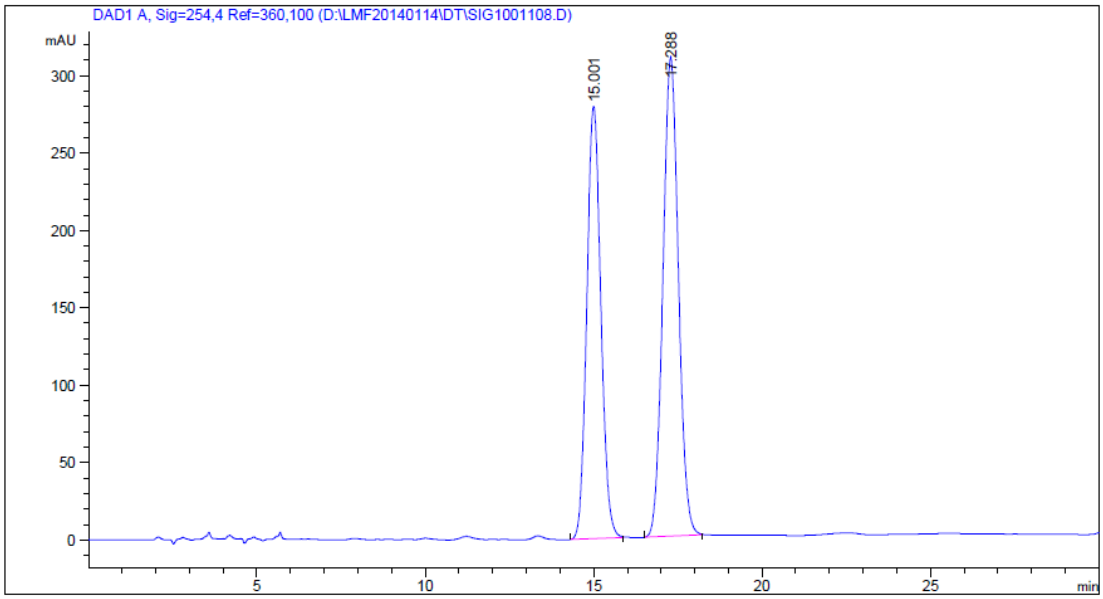
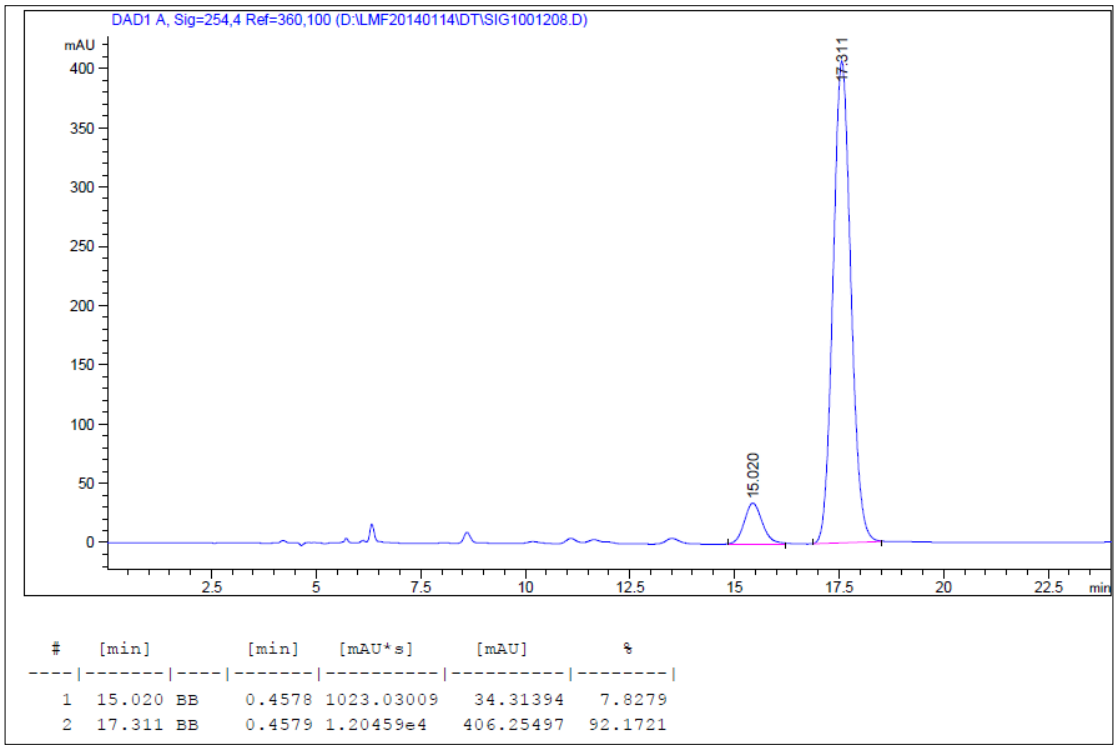
63.43
15.04
15.01
f1 (ppm)





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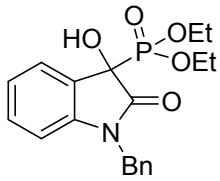
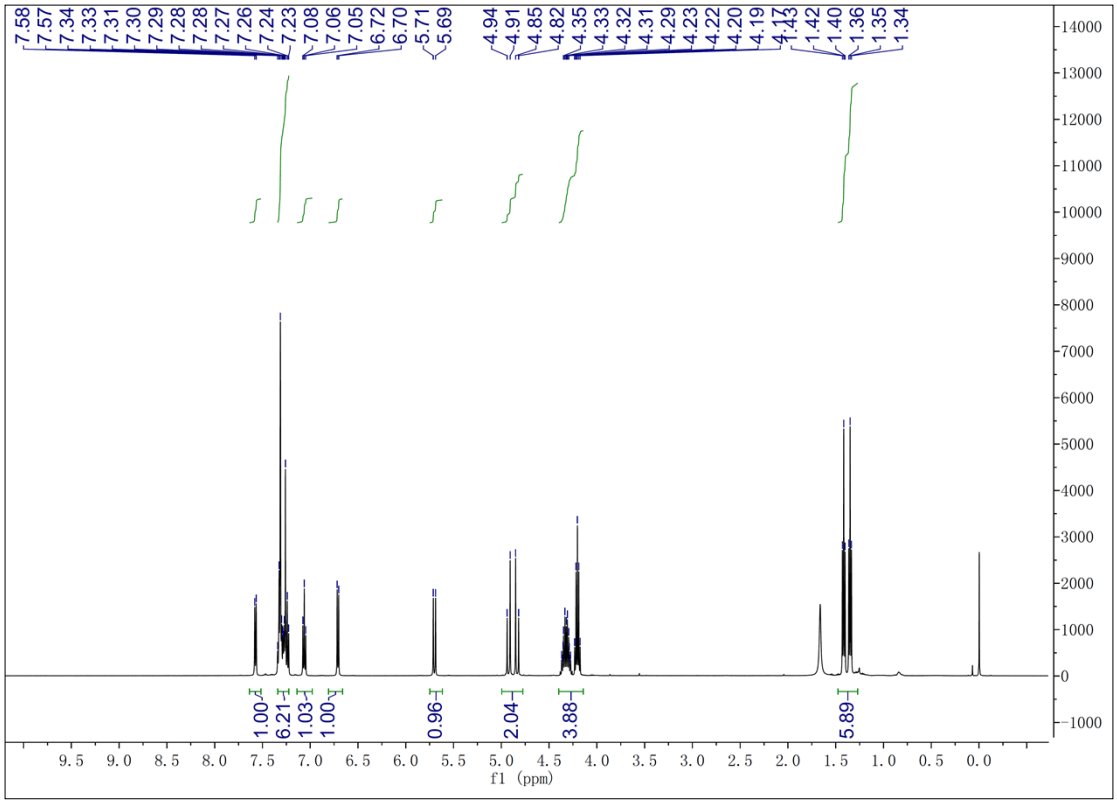
1	15.020	BB	0.4578	1023.03009	34.31394	7.8279
2	17.311	BB	0.4579	1.20459e4	406.25497	92.1721

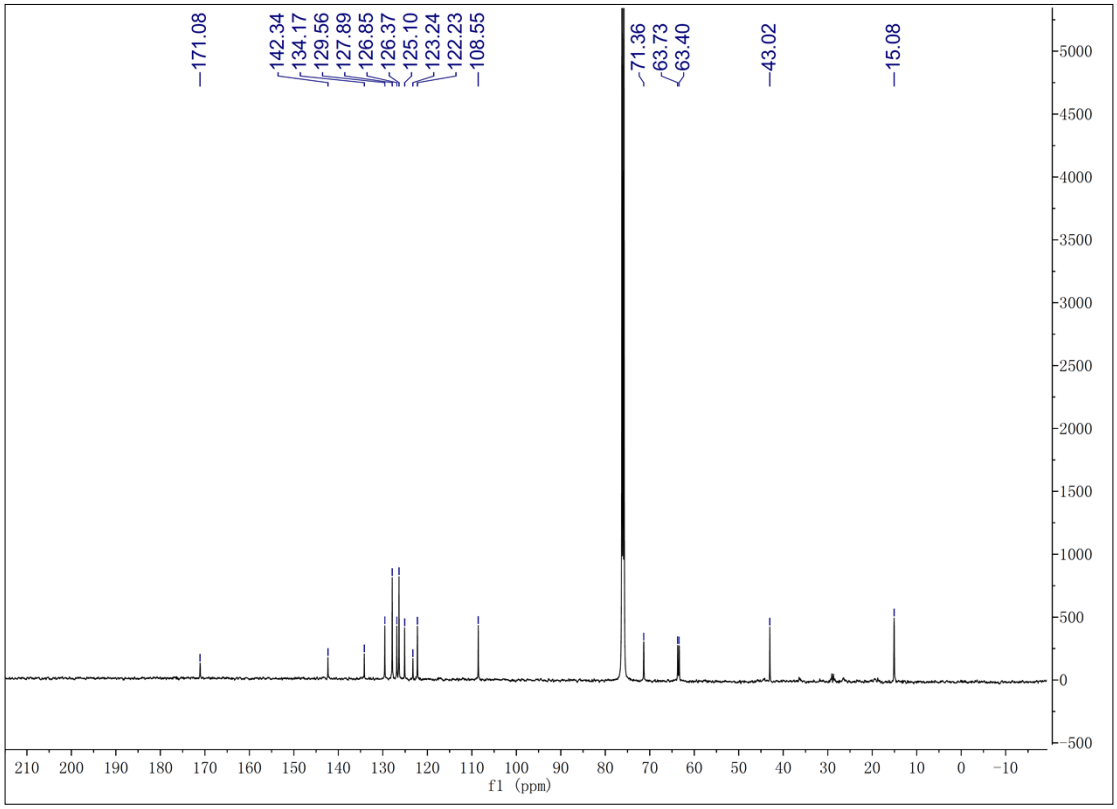
*2.2 Diethyl (1-benzyl-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3b**)*

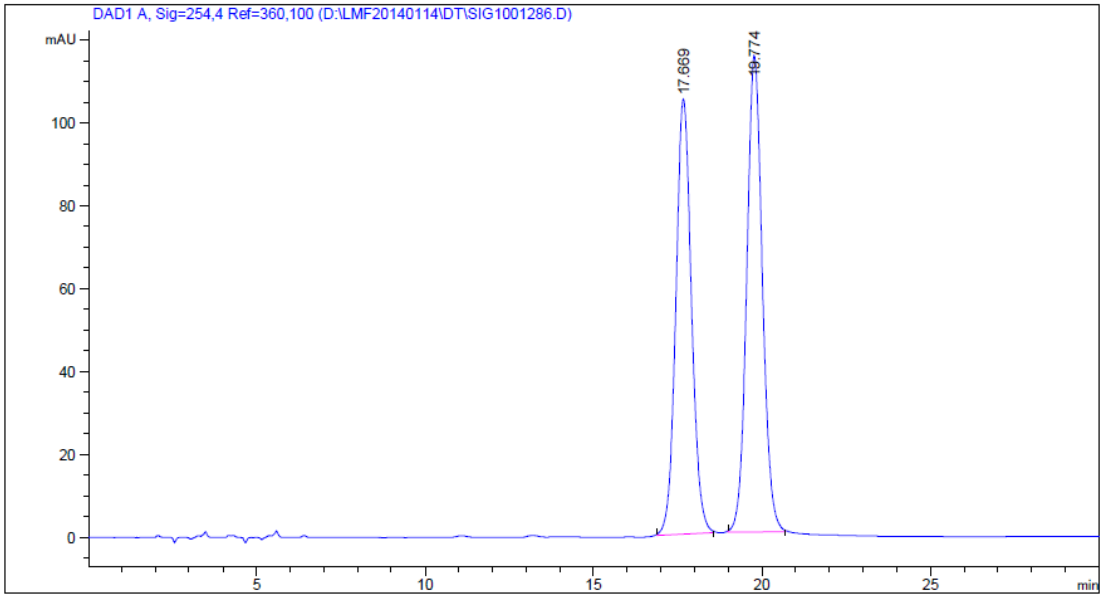


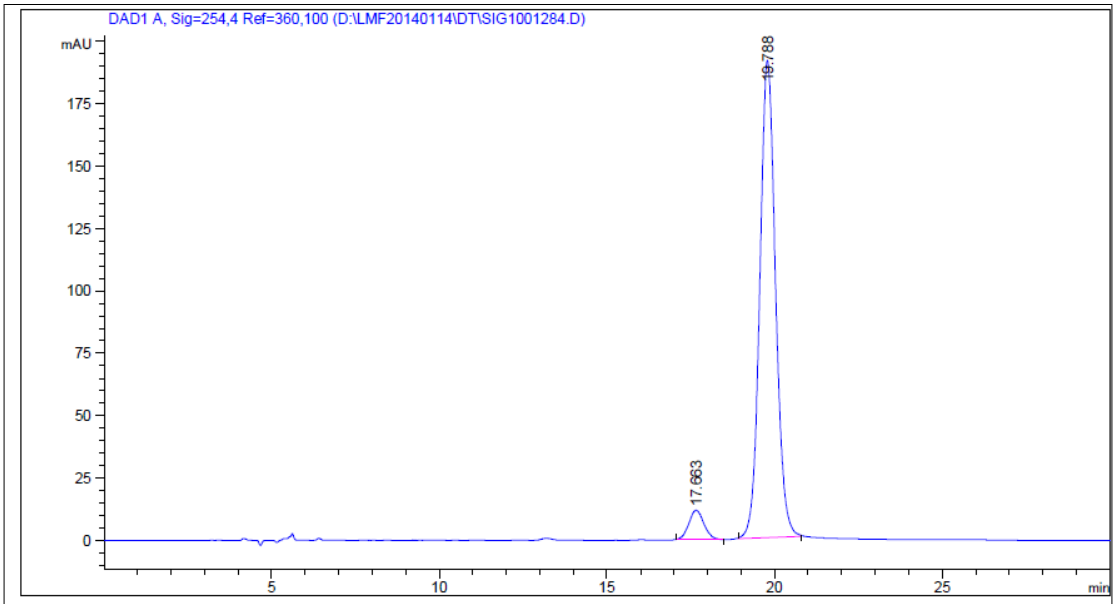
Purified by column chromatography eluting with hexane/EtOAc 5:1 (69% yield). The *ee* (89%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=1.0 mL/min, UV= 254 nm, minor enantiomer t_1 = 17.7 min, major enantiomer t_2= 19.8 min.

Yellow solid; m.p. 147-149ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.33-7.23 (m, 6H), 7.08-7.05 (m, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.70 (d, *J* = 11.9 Hz, 1H), 4.89-4.82 (m, 2H), 4.37-4.17 (m, 4H), 143-1.34 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 142.3, 134.2, 129.6, 127.9, 126.9, 126.4, 125.1, 123.2, 122.2, 108.6, 71.4, 63.6 (d, *J* = 41.1 Hz), 43.0, 15.1. ESI-MS *(m/z)*: 376 ([M+H]$^{+}$)









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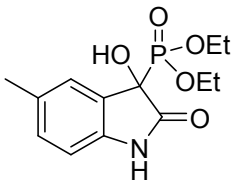
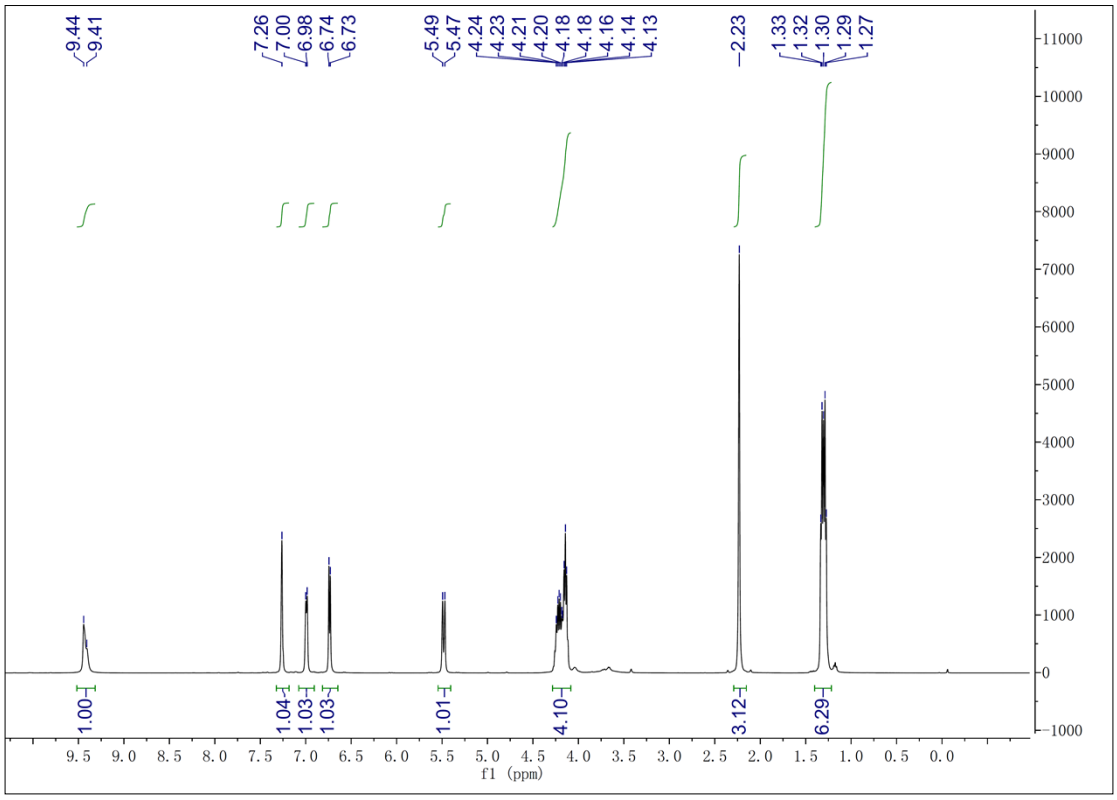
1	17.663	BB	0.4780	369.66043	11.78485	5.5973
2	19.788	BB	0.5000	6234.58447	191.40726	94.4027

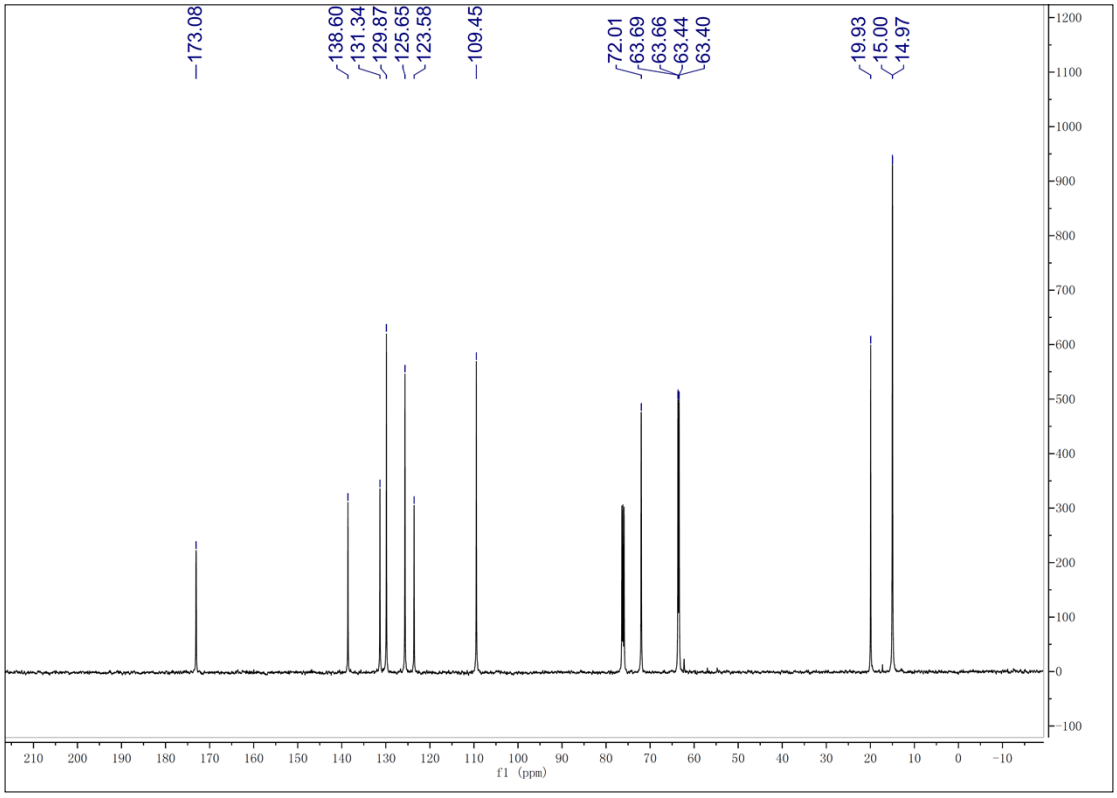
*2.3 Diethyl (3-hydroxy-5-methyl-2-oxoindolin-3-yl)phosphonate(**3c**)*

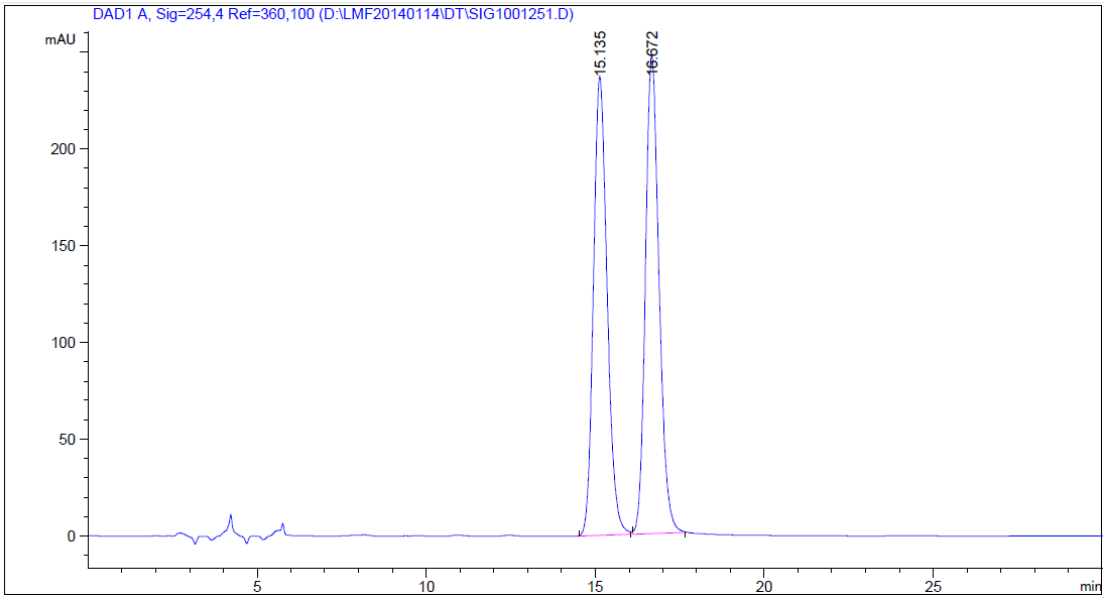


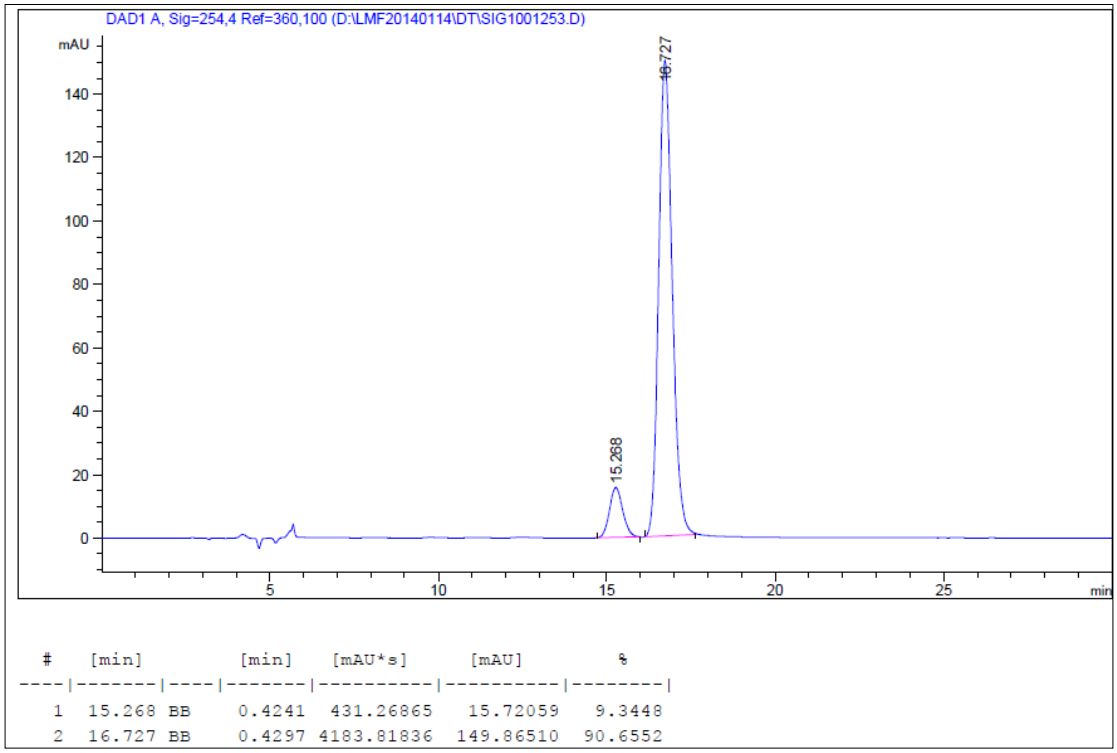
Purified by column chromatography eluting with hexane/EtOAc 3:1 (63% yield). The *ee* (82%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=1.0 mL/min, UV= 254 nm, minor enantiomer t_1 = 15.3 min, major enantiomer t_2= 16.7 min.

Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (d, *J* = 17.1 Hz, 1H), 7.26 (s, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.48 (d, *J* = 12.4 Hz, 1H), 4.24-4.13 (m, 4H), 2.23 (s, 3H), 1.33-1.27 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 138.6, 131.3, 129.9, 125.7, 123.6, 109.5, 72.0, 63.7 (d, *J* = 4.6 Hz), 63.4 (d, *J* = 4.8 Hz), 19.9, 15.0 (d, *J* = 4.8 Hz). ESI-MS *(m/z)*: 322([M+Na]$^{+}$)









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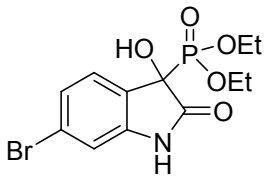
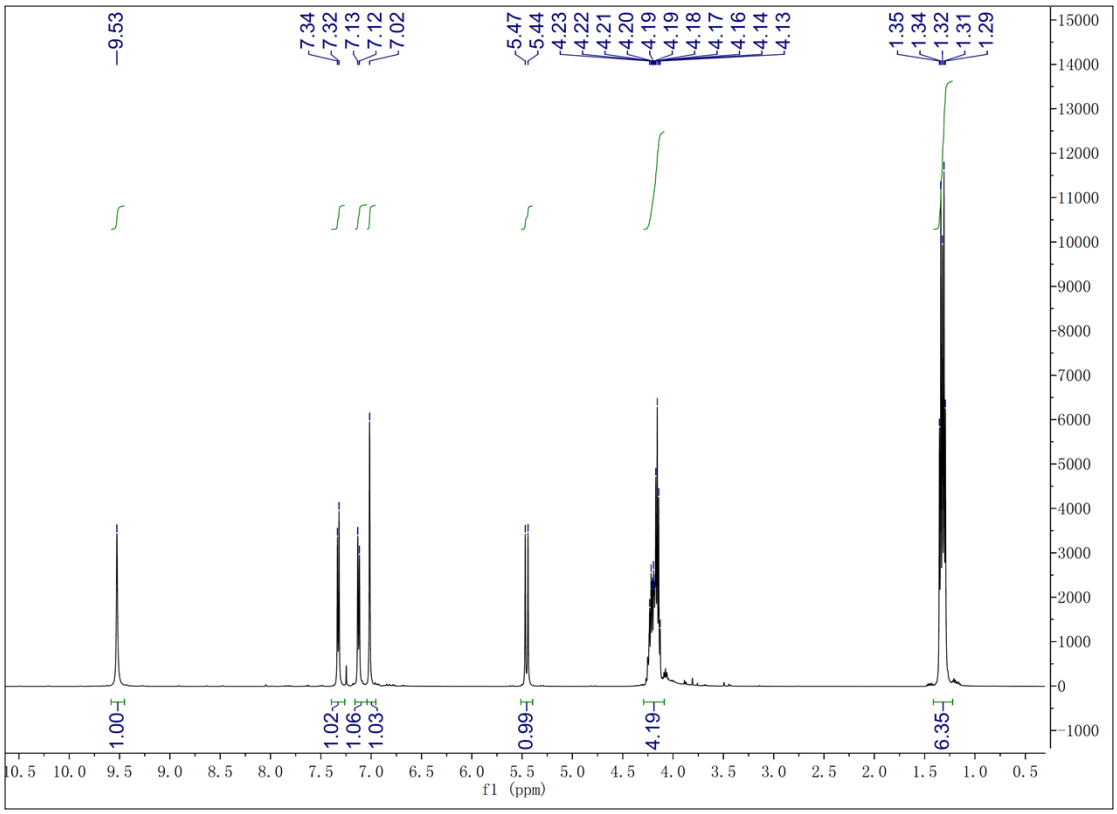
1	15.268	BB	0.4241	431.26865	15.72059	9.3448
2	16.727	BB	0.4297	4183.81836	149.86510	90.6552

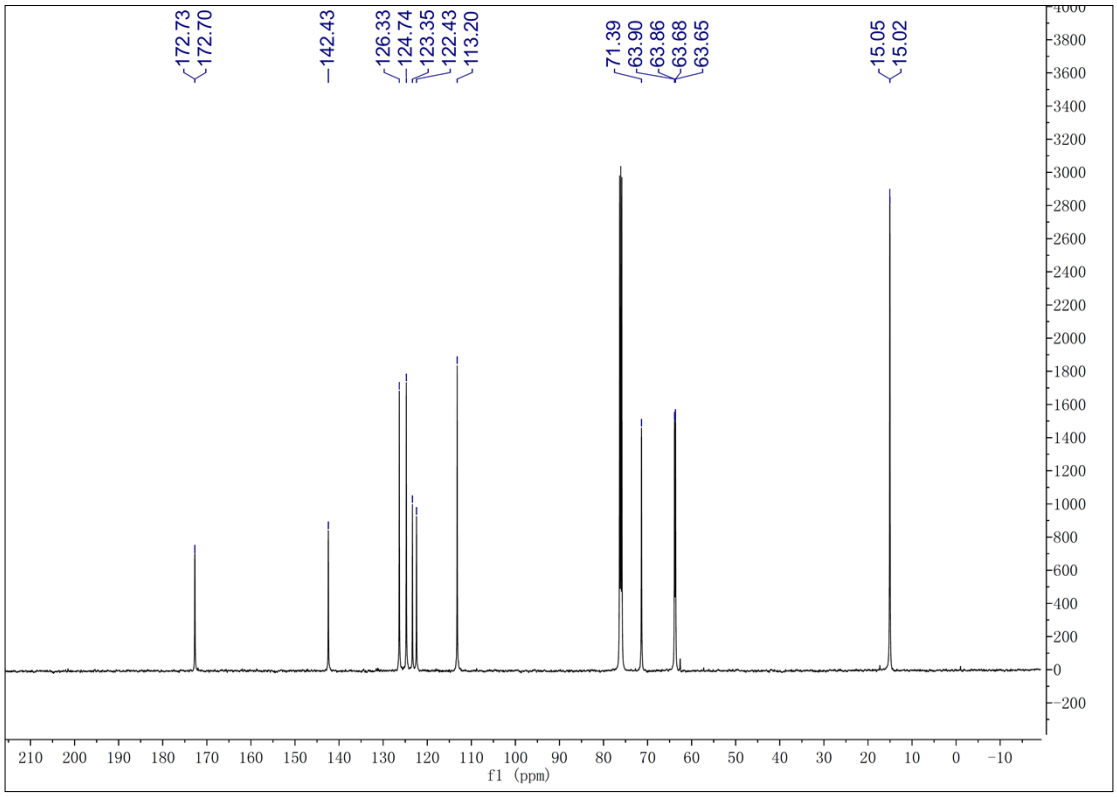
*2.4 Diethyl (6-bromo-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3d**)*

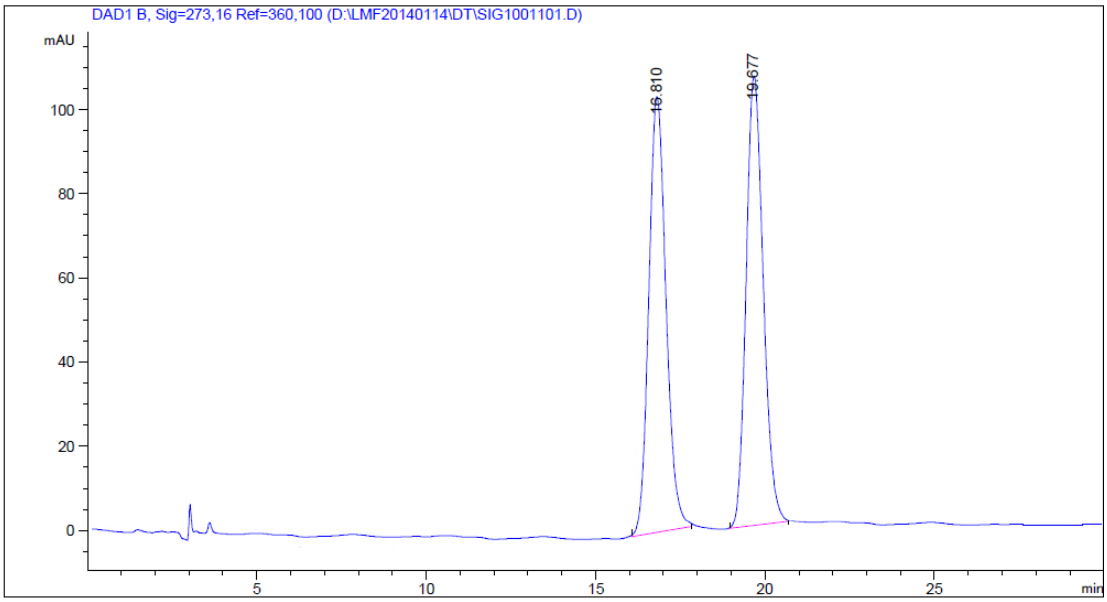


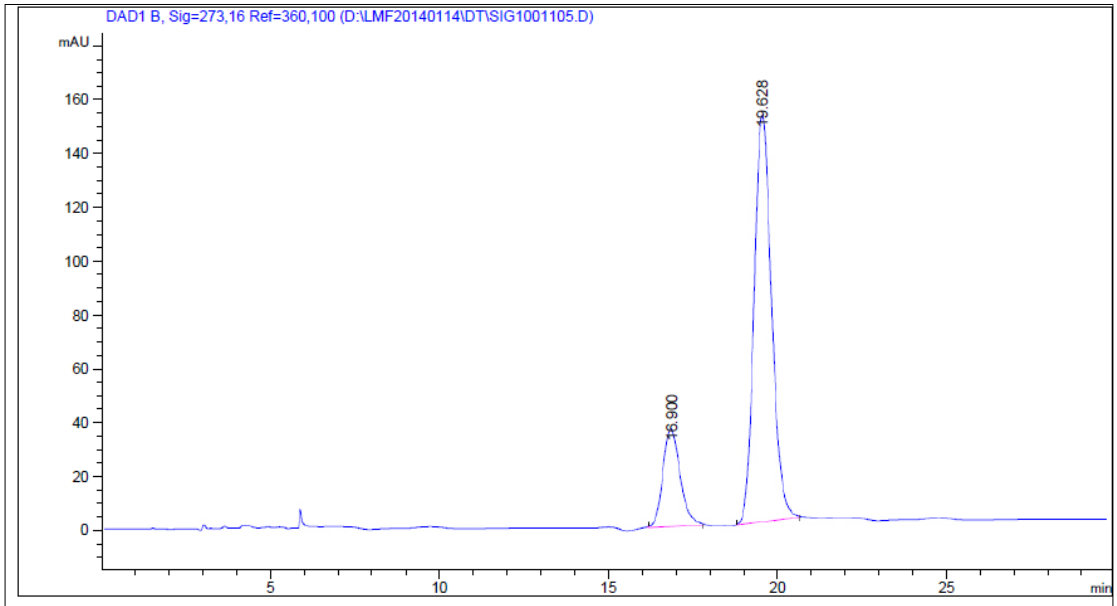
Purified by column chromatography eluting with hexane/EtOAc 3:1 (73% yield). The *ee* (61%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=0.7 mL/min, UV= 273 nm, minor enantiomer t_1 = 16.9 min, major enantiomer t_2= 19.6 min.

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.02 (s, 1H), 5.46 (d, *J* = 13.6 Hz, 1H), 4.23-4.13 (m, 4H), 1.35-1.29 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7 (d, *J* = 4.3 Hz), 142.4, 126.3, 124.7, 123.4, 122.4, 113.2, 71.4, 63.9 (d, *J* = 5.0 Hz), 63.7 (d, *J* = 4.0 Hz), 15.0 (d, *J* = 4.2 Hz). ESI-MS *(m/z)*: 363 ([M]$^{+}$). Anal. calcd. for $C_{12}H_{15}BrNO_5P$: C, 39.58; H, 4.15; N, 3.85. Found: C, 39.46; H, 4.22; N, 3.91.









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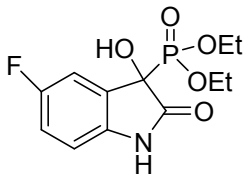
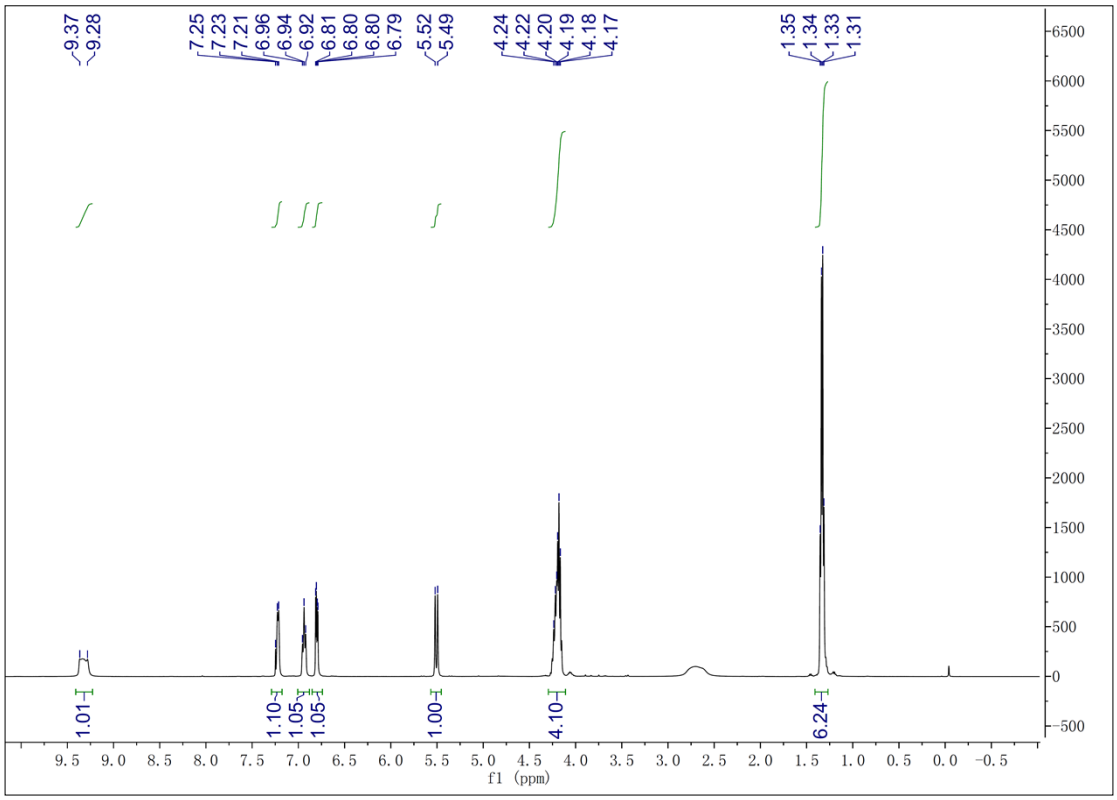
1	16.900	BB	0.5520	1498.31824	41.81682	19.3943
2	19.628	BB	0.5596	6227.24658	172.30461	80.6057

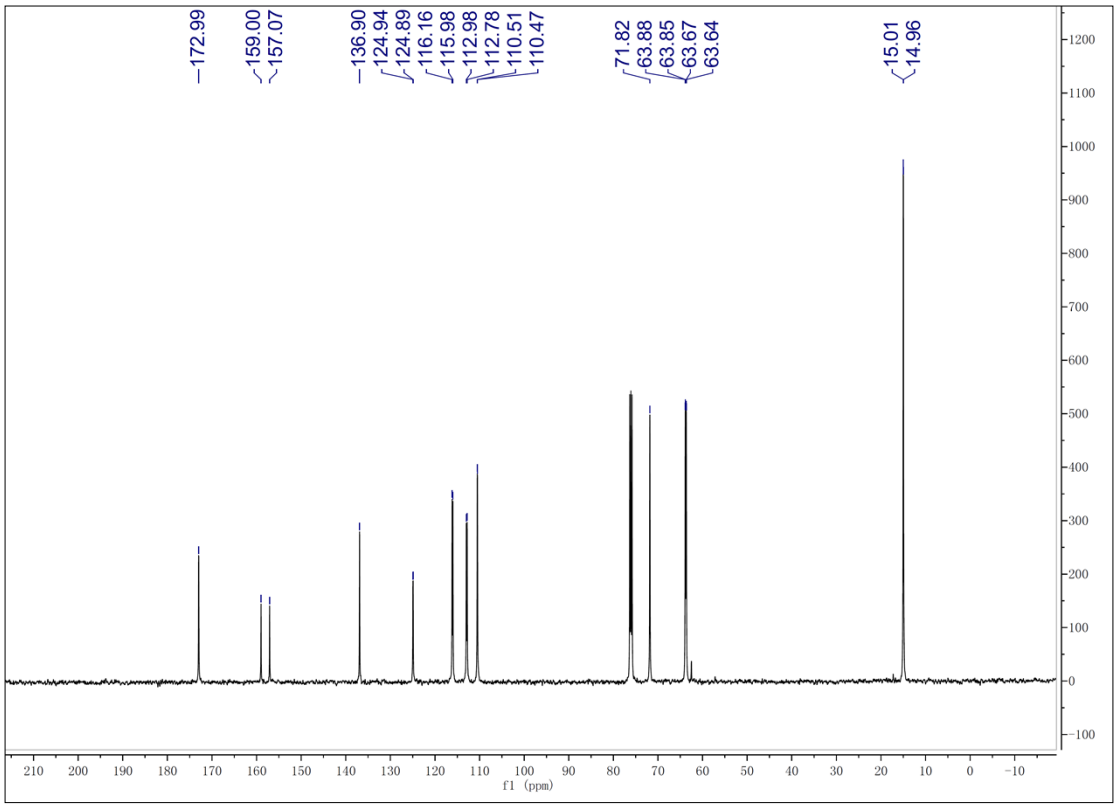
*2.5 Diethyl (5-fluoro-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3e**)*



Purified by column chromatography eluting with hexane/EtOAc 3:1 (31% yield). The *ee* (78%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=1.2 mL/min, UV= 254 nm, minor enantiomer t_1 = 11.7 min, major enantiomer t_2= 13.6 min.

Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 10.0 Hz, 1H), 7.25-7.21 (m, 1H), 6.96-6.92 (m, 1H), 6.81-6.79 (m, 1H), 5.51 (d, *J* = 13.6 Hz, 1H), 4.24-4.17 (m, 4H), 1.35-1.31 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.99, 159.0, 157.1, 136.9, 124.9 (d, *J* = 6.1 Hz), 116.1 (d, *J* = 23.4 Hz), 112.9 (d, *J* = 25.1 Hz), 110.5 (d, *J* = 5.1 Hz), 71.8, 63.9 (d, *J* = 4.0 Hz), 63.7 (d, *J* = 4.0 Hz), 15.0 (d, *J* = 5.3 Hz). ^{19}F NMR (500 MHz, $CDCl_3$) δ -119.8. ESI-MS *(m/z)*: 304 ([M+H]$^{+}$)

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159.00
157.07
136.90
124.94
124.89
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115.98
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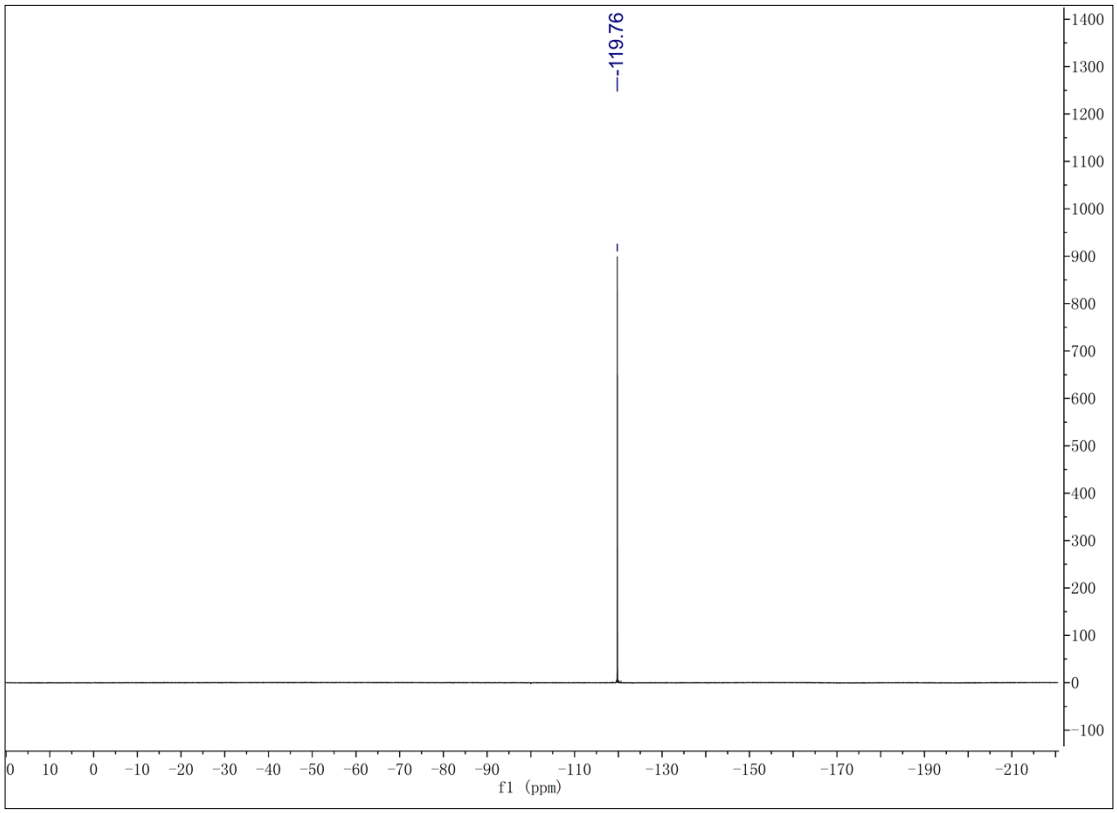
14.96
f1 (ppm)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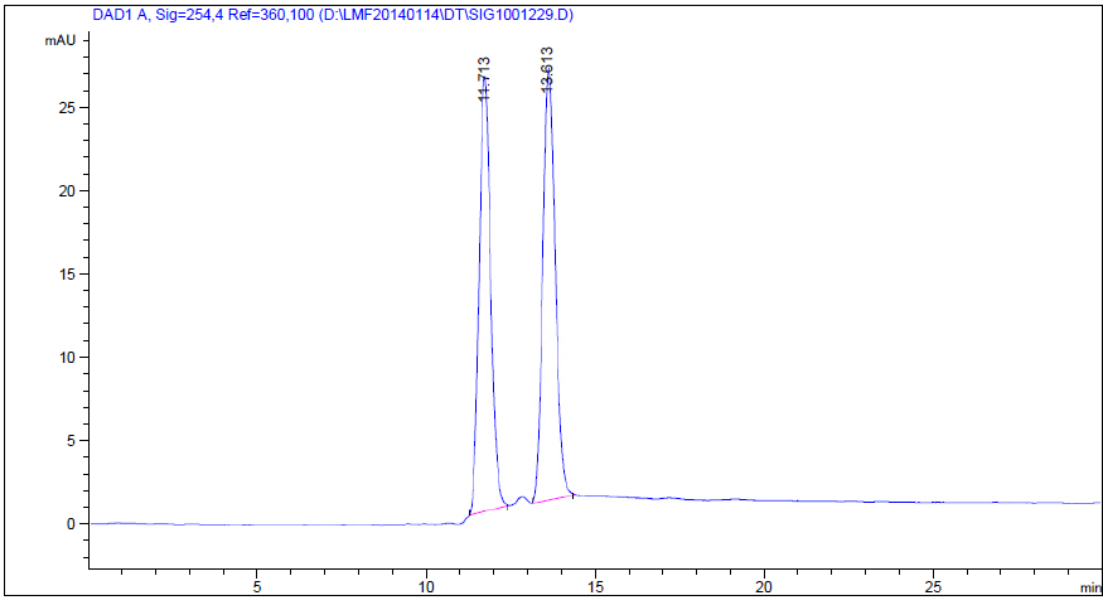

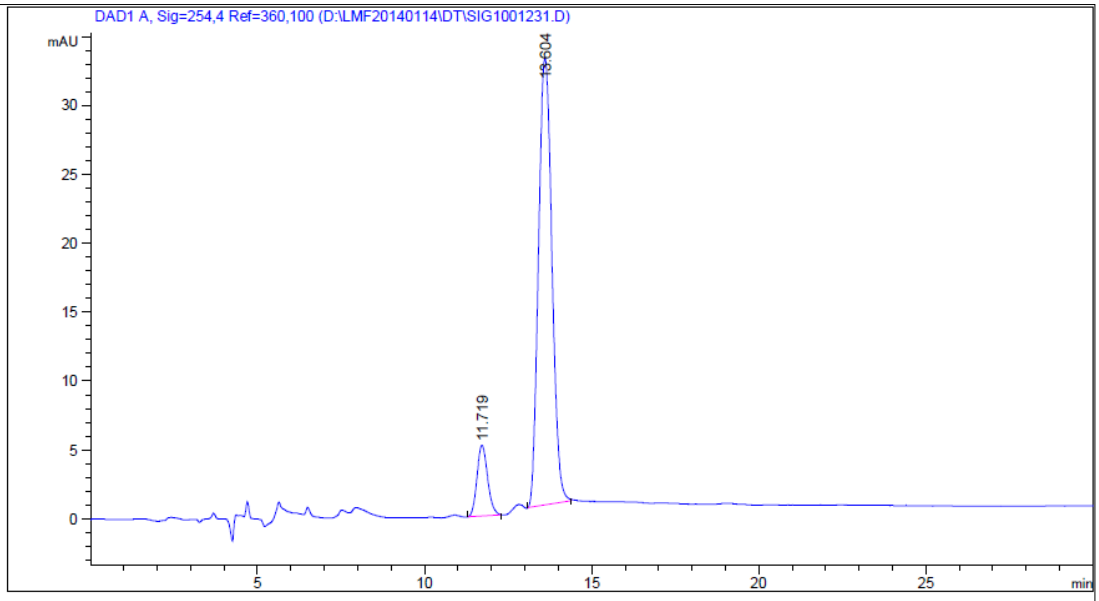

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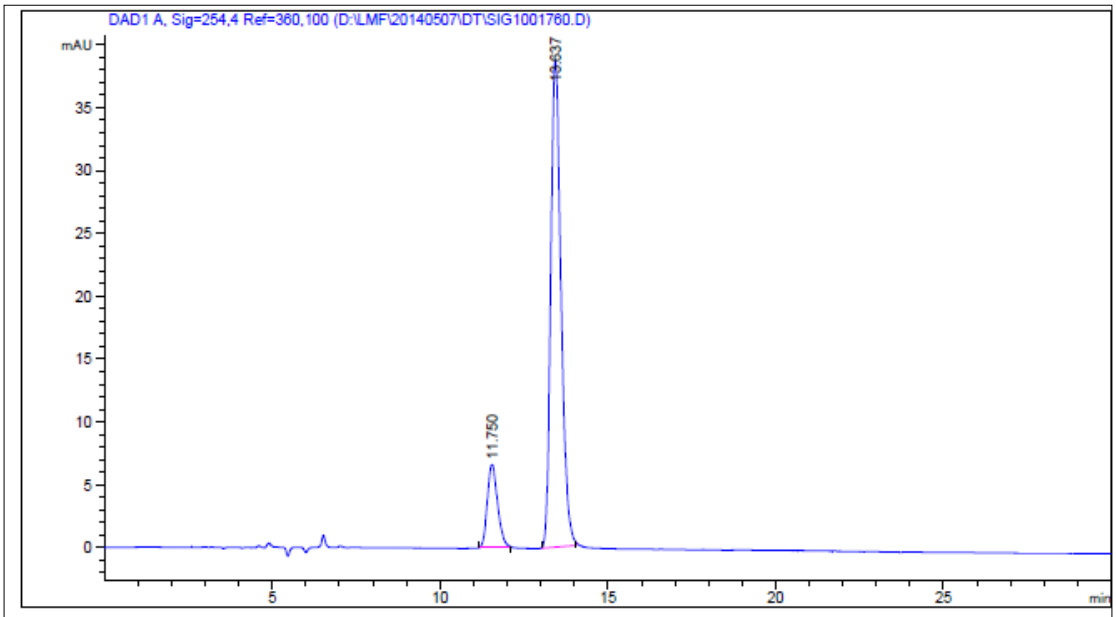

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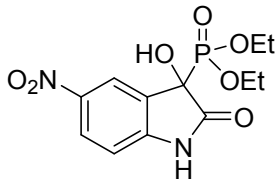
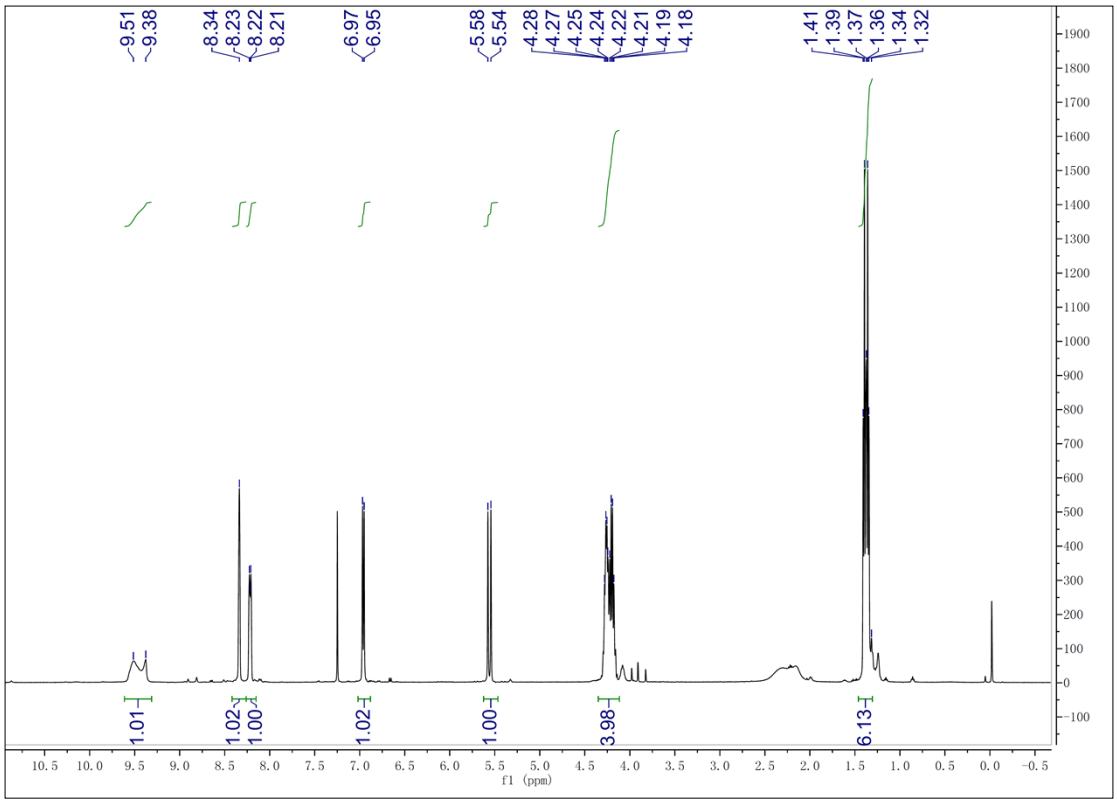
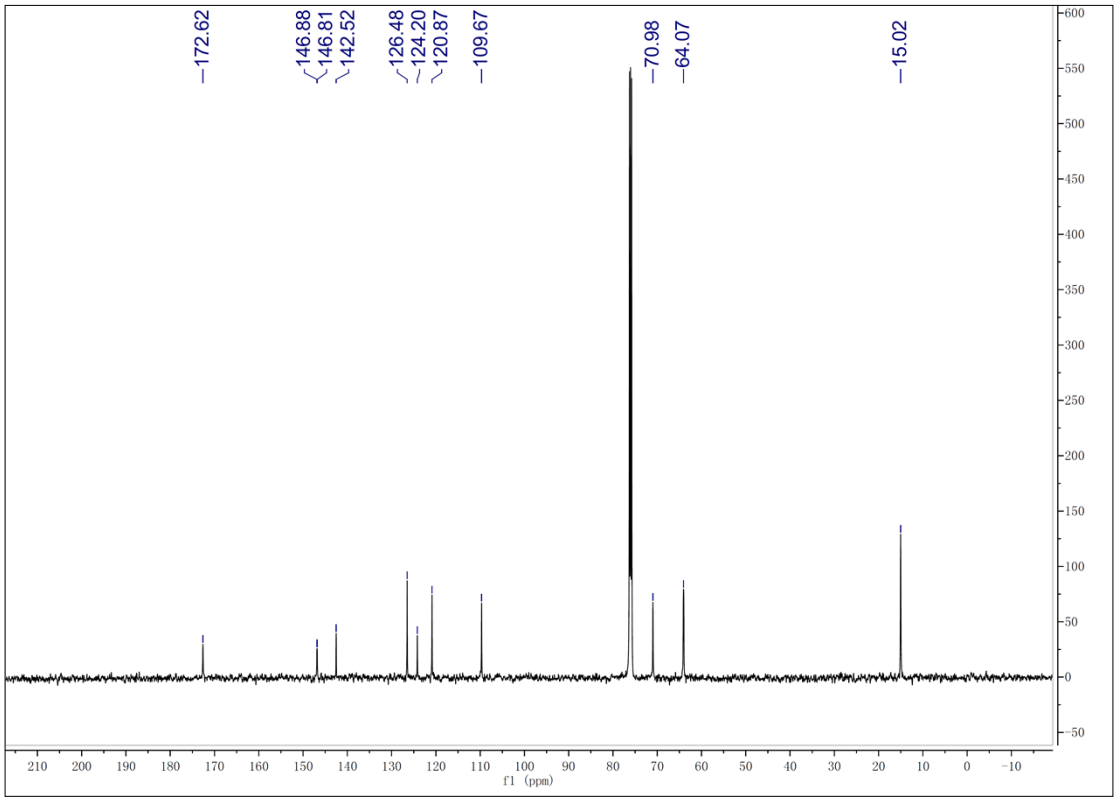
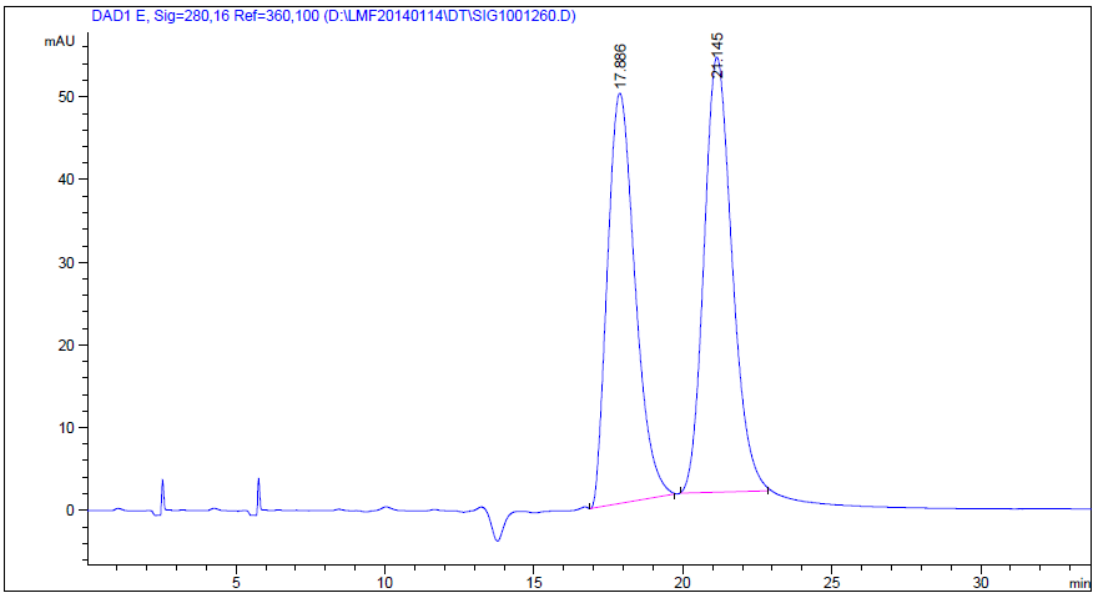
*2.6 Diethyl (3-hydroxy-5-nitro-2-oxoindolin-3-yl)phosphonate(**3f**)*

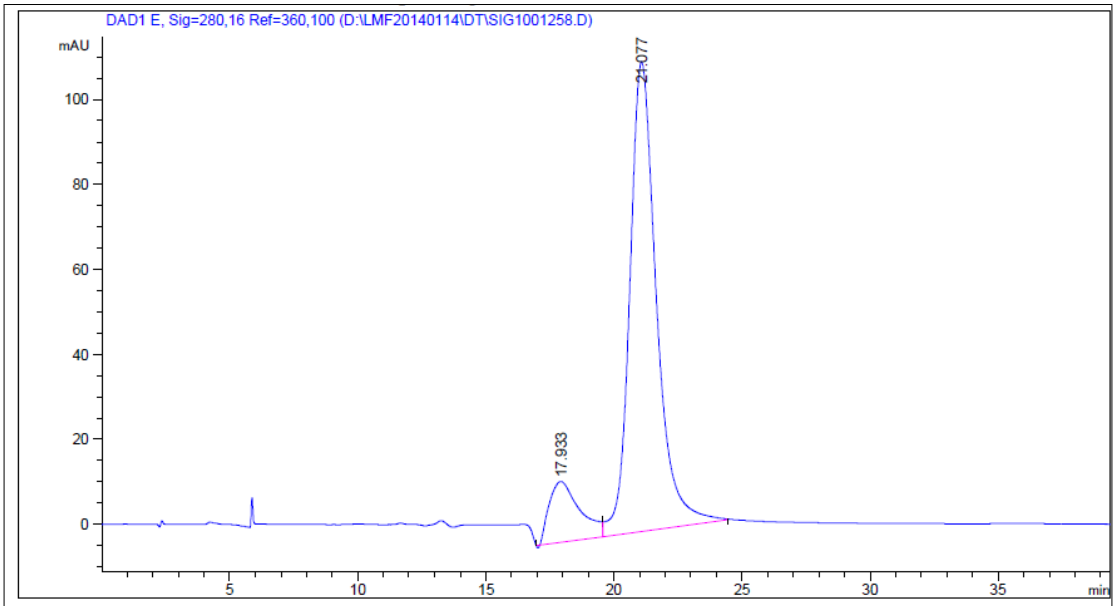


Purified by column chromatography eluting with hexane/EtOAc 3:1 (30% yield). The *ee* (74%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=1.0 mL/min, UV= 280 nm, minor enantiomer t_1 = 17.9min, major enantiomer t_2= 21.1 min. White solid; m.p. 146-148ºC;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (d, *J* = 69.0 Hz, 1H), 8.34 (s, 1H), 8.23-8.21(m, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 5.56 (d, *J* = 16.9 Hz, 1H), 4.28-4.18 (m, 4H), 1.41-1.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 146.8 (d, *J* = 9.0 Hz), 142.5, 126.5, 124.2, 120.9, 109.7, 71.0, 64.1, 15.0. ESI-MS *(m/z)*: 331 ([M+H]$^+$)

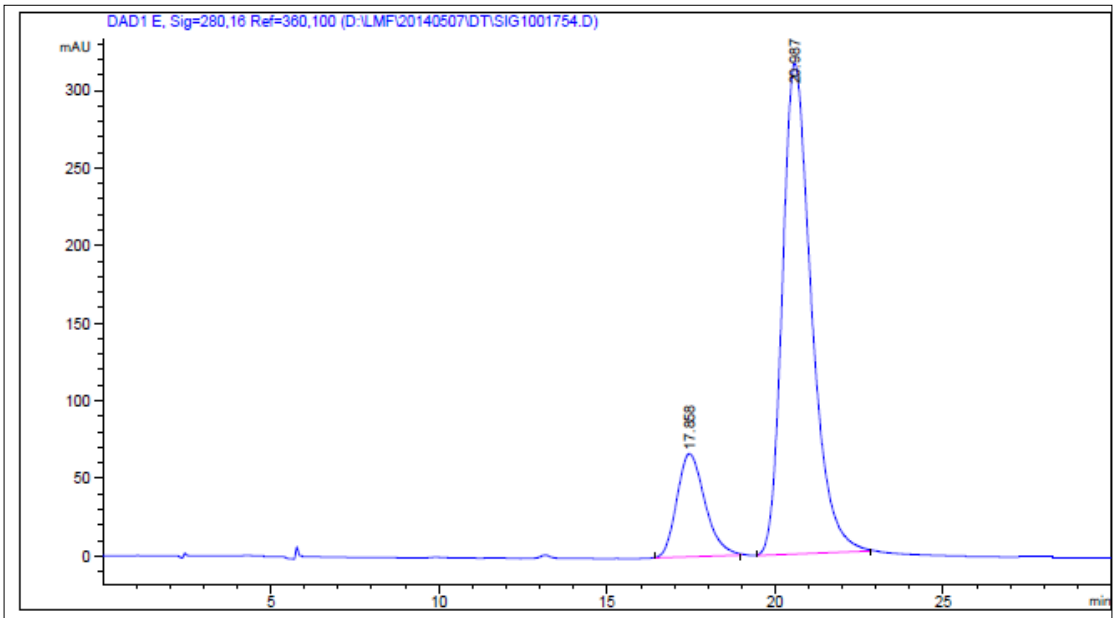

9.51
9.38
8.34
8.23
8.22
8.21
6.97
6.95
5.58
5.54
4.28
4.27
4.25
4.24
4.22
4.21
4.19
4.18
1.41
1.39
1.37
1.36
1.34
1.32
1.01
1.02
1.00
1.02
1.00
3.98
6.13
f1 (ppm)


172.62
146.88
146.81
142.52
126.48
124.20
120.87
109.67
70.98
64.07
15.02
f1 (ppm)



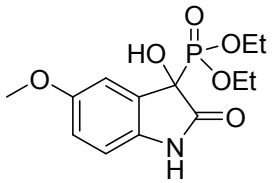


#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.933	BV	1.2407	1188.38831	14.34214	12.9128
2	21.077	VB	1.0856	8014.76611	110.57544	87.0872

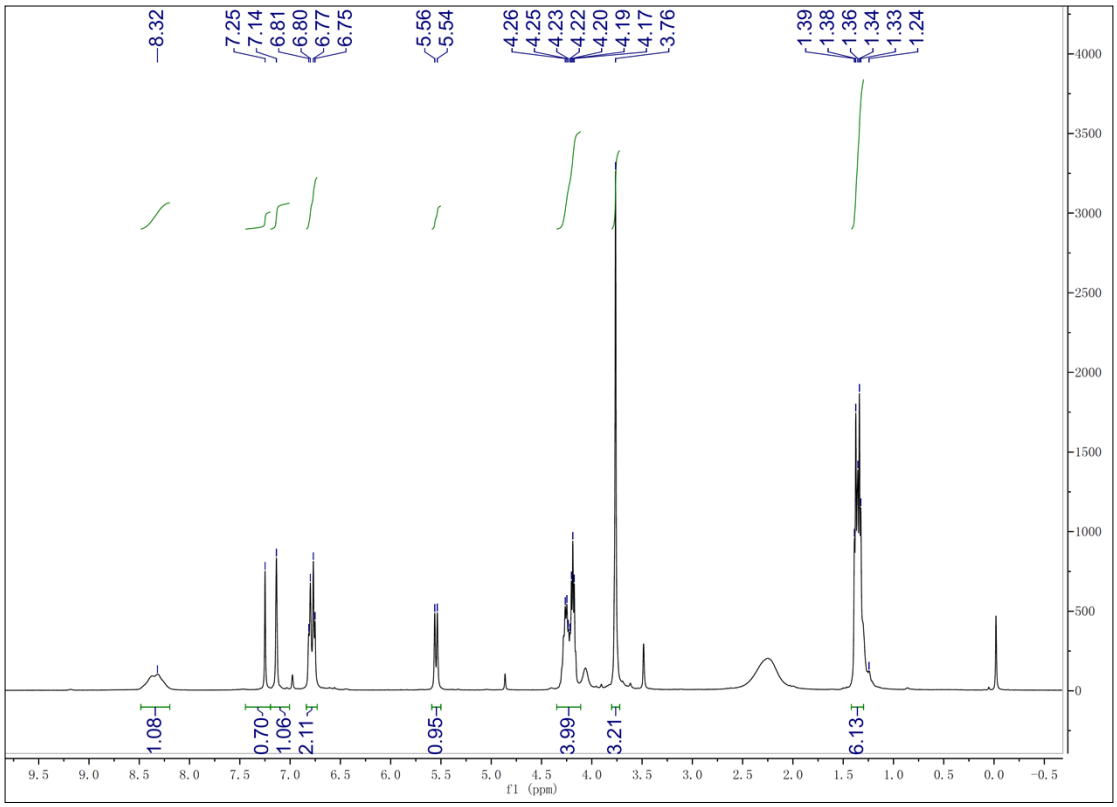


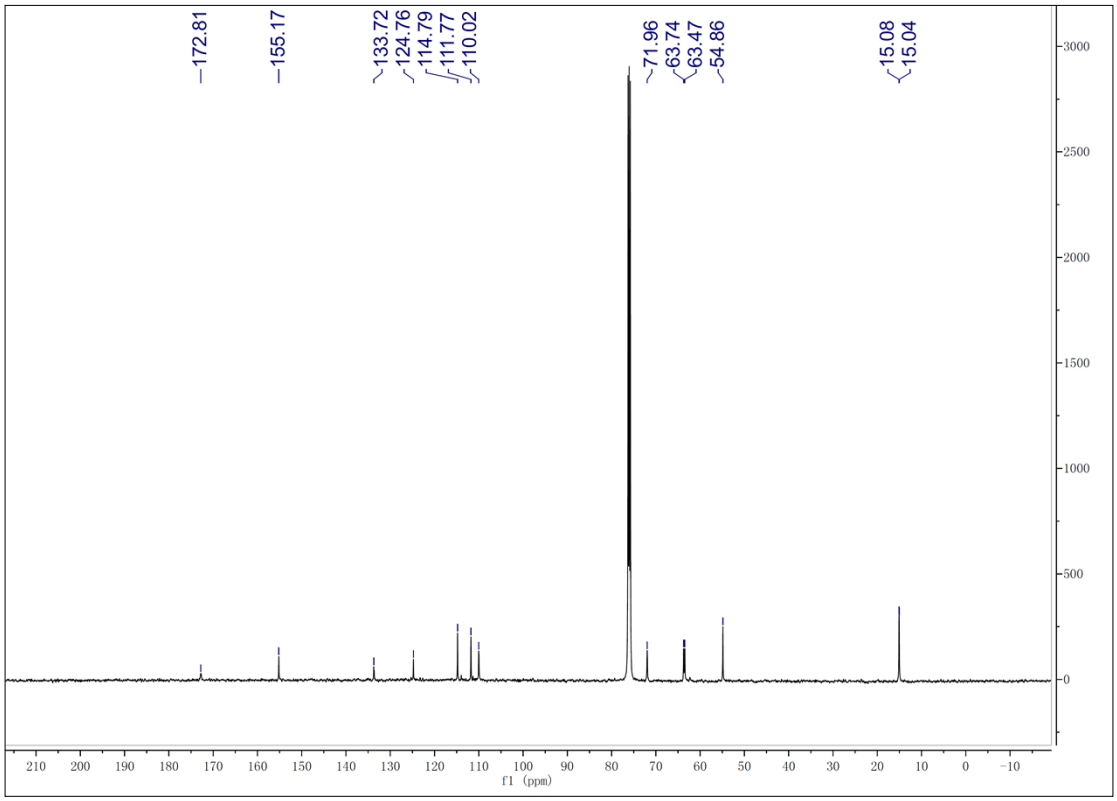
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.858	BB	0.8913	3861.04517	66.31091	16.9246
2	20.987	BB	0.9074	1.89521e4	316.14075	83.0754

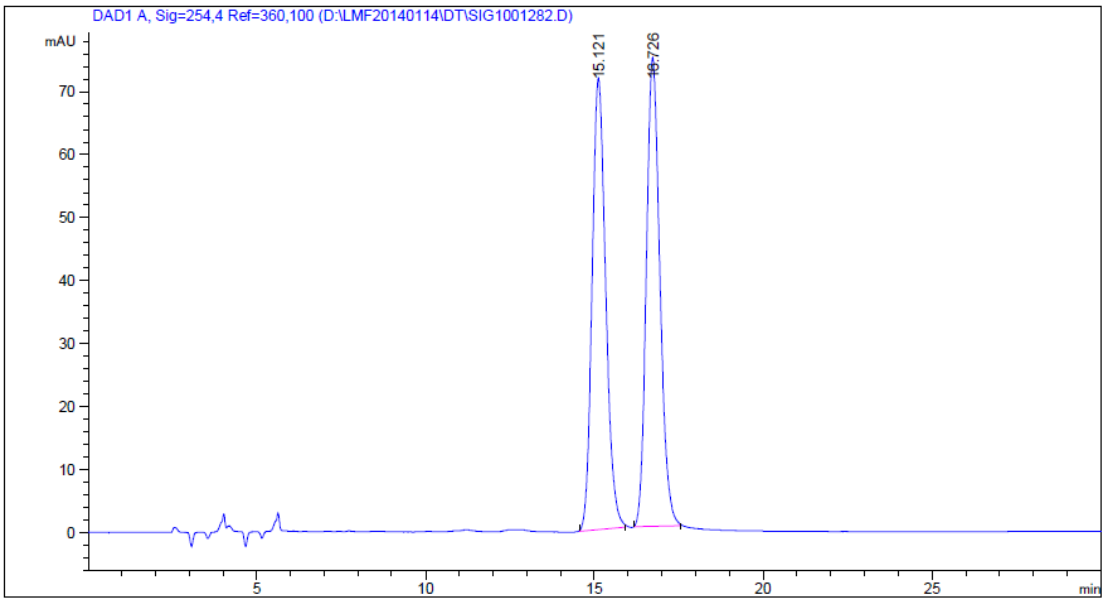
*2.7 Diethyl (3-hydroxy-5-methoxy-2-oxoindolin-3-yl)phosphonate(**3g**)*

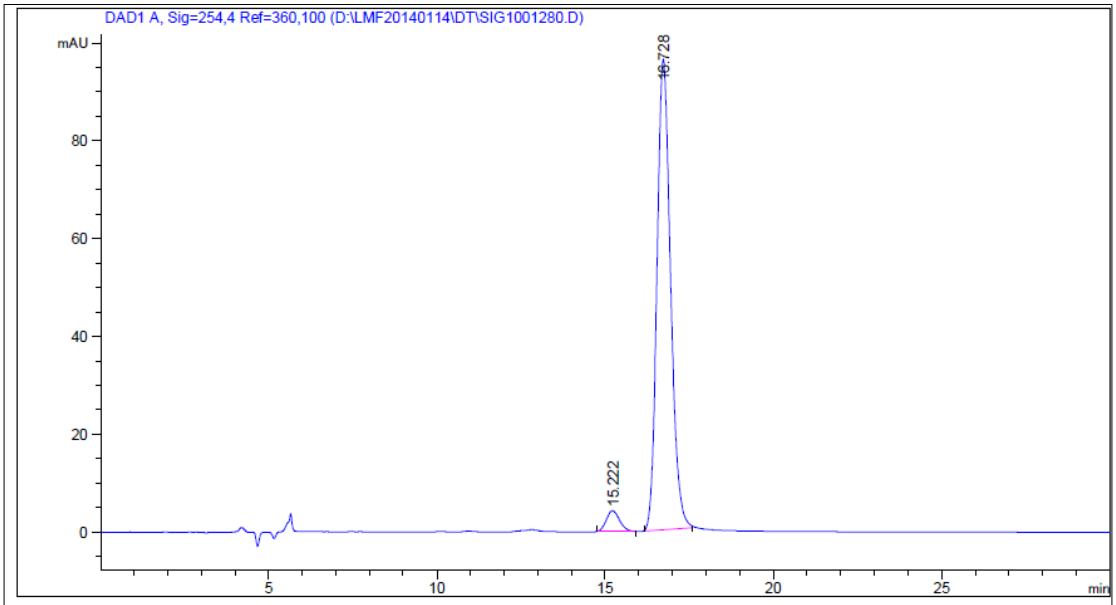


Purified by column chromatography eluting with hexane/EtOAc 3:1 (37% yield). The *ee* (92%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=1.2 mL/min, UV= 254 nm, minor enantiomer t_1 = 15.2 min, major enantiomer t_2= 16.7 min. Yellow solid; m.p. 137-139ºC;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.25 (s, 1H), 7.14 (s, 1H), 6.81-6.75 (m, 1H), 5.55 (d, *J* = 12.6 Hz, 1H), 4.26-4.17 (m, 4H), 3.76 (s, 3H), 1.39-1.24 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 155.2, 133.7, 124.8, 114.8, 111.8, 110.0, 72.0, 63.6 (d, *J* = 34.0 Hz), 54.9, 15.1 (d, *J* = 5.4 Hz). ESI-MS *(m/z)*: 316 ($[M+H]^+$)

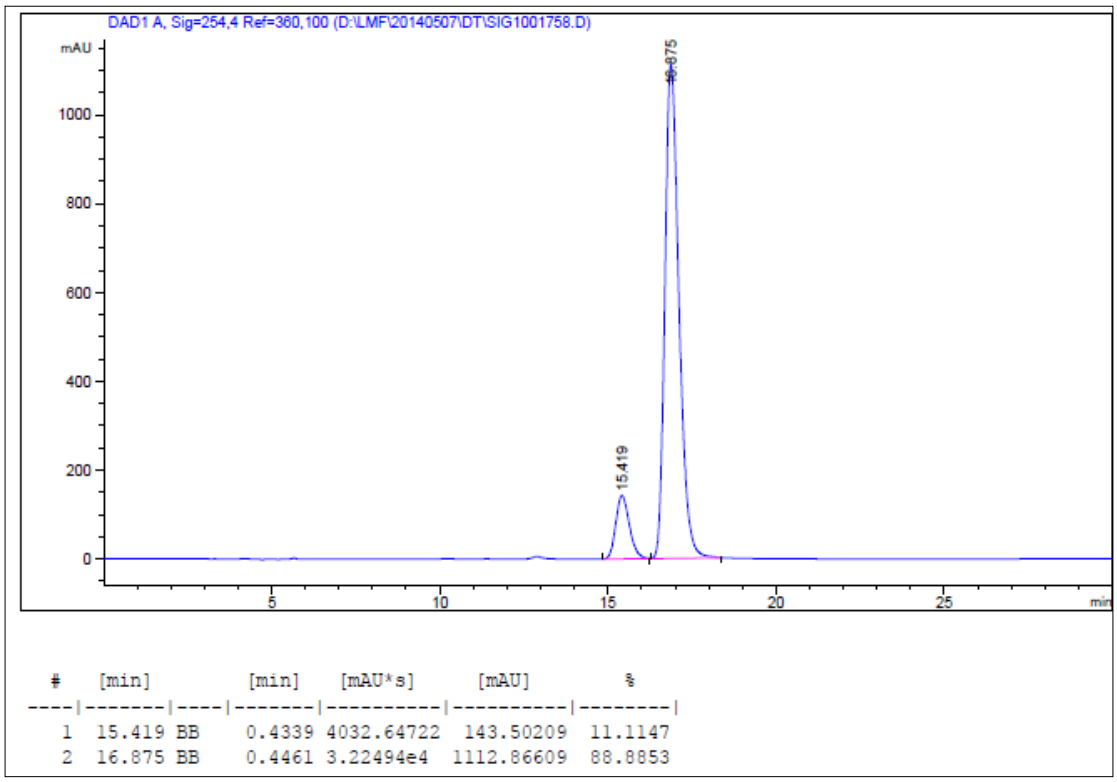

8.32
7.25
7.14
6.81
6.80
6.77
6.75
5.56
5.54
4.26
4.25
4.23
4.22
4.20
4.19
4.17
3.76
1.39
1.38
1.36
1.34
1.33
1.24
1.08
0.70
1.06
2.11
0.95
3.99
3.21
6.13
f1 (ppm)


172.81
155.17
133.72
124.76
114.79
111.77
110.02
71.96
63.74
63.47
54.86
15.08
15.04
f1 (ppm)

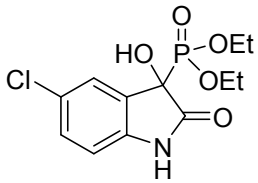




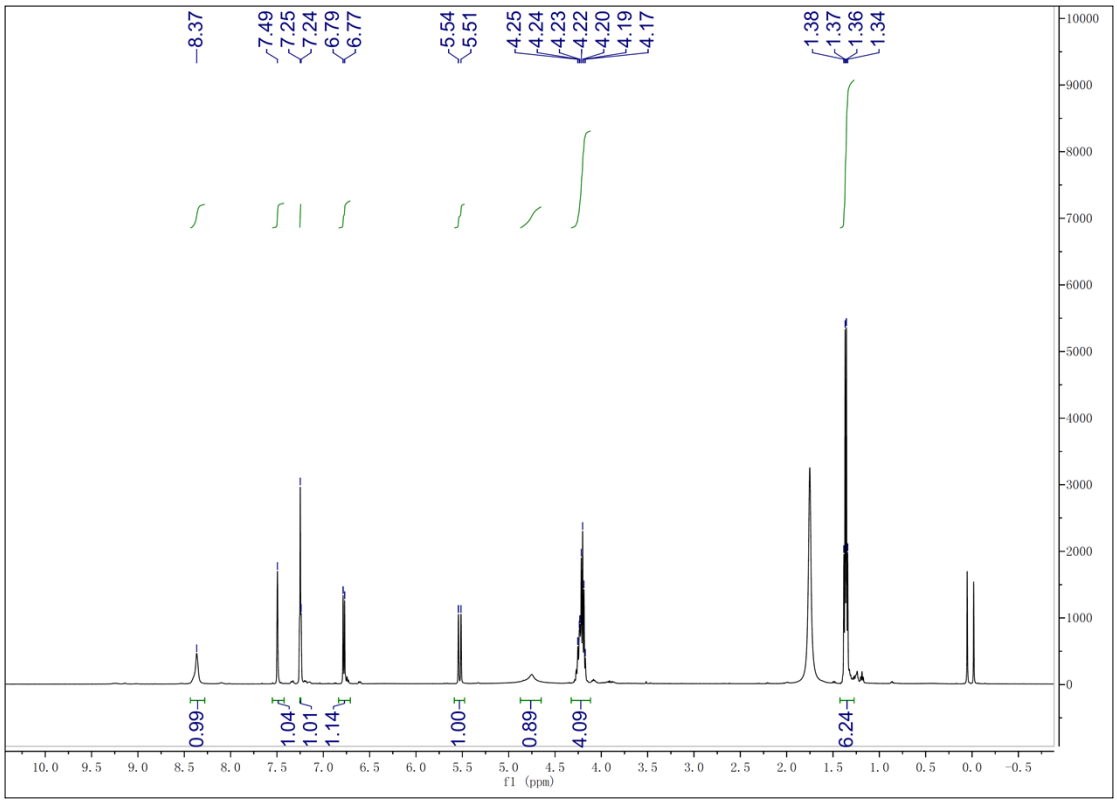
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.222	BB	0.4101	116.74391	4.25549	4.1538
2	16.728	BB	0.4307	2693.76489	96.18679	95.8462

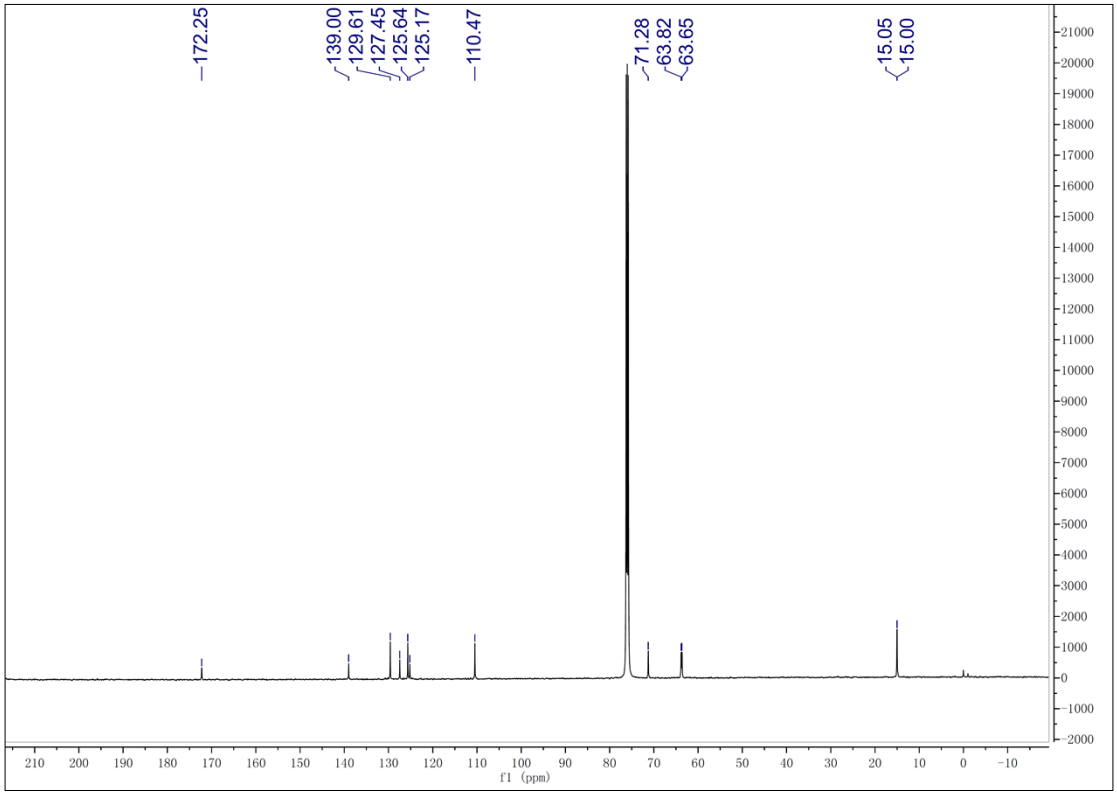


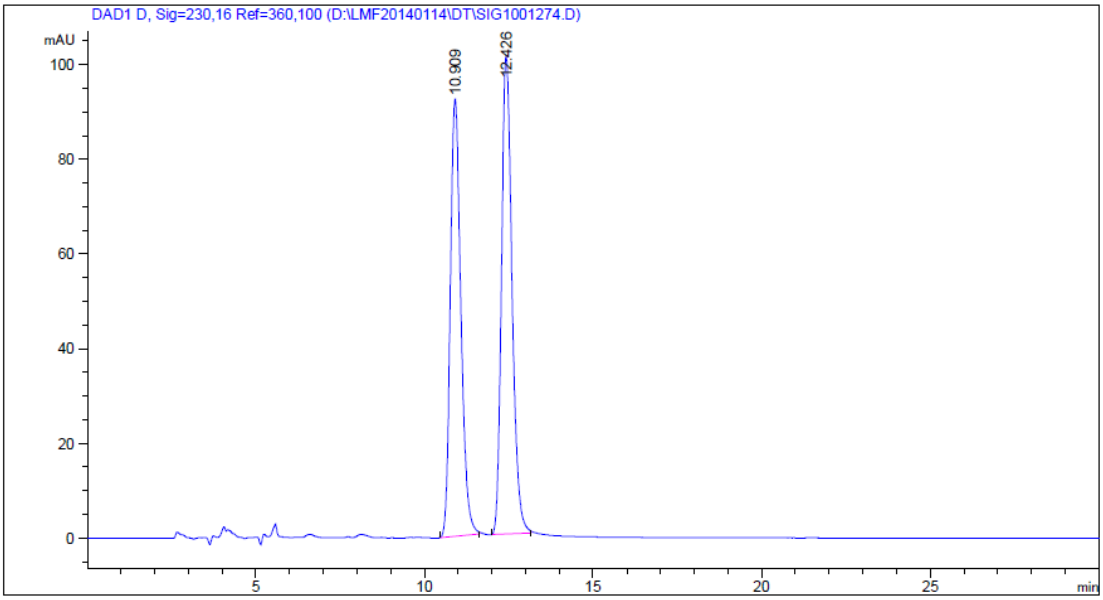
*2.8 Diethyl (5-chloro-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3h**)*

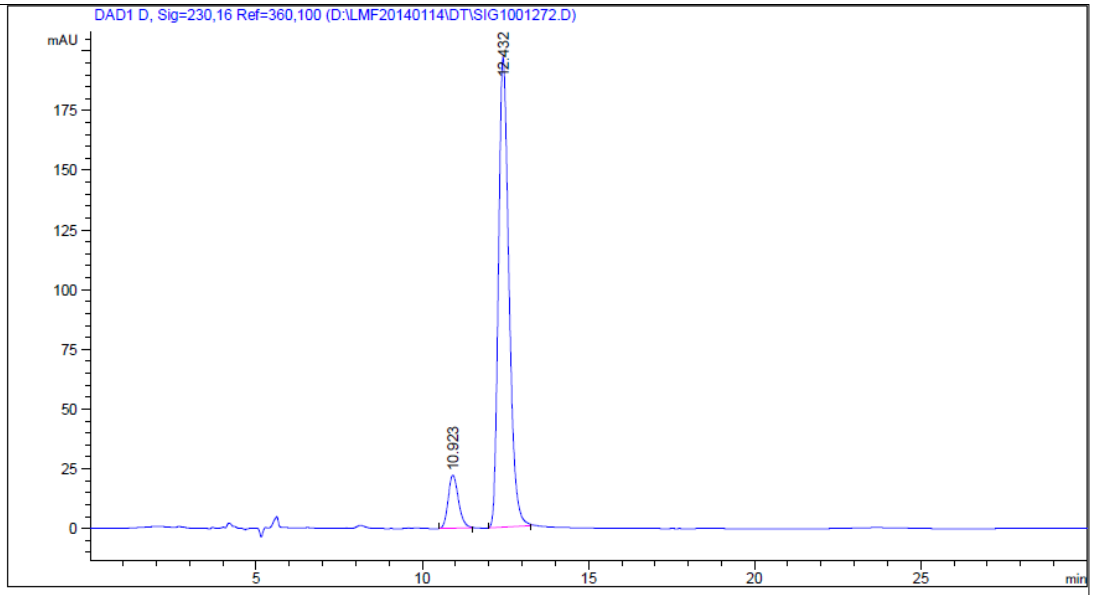


Purified by column chromatography eluting with hexane/EtOAc 3:1 (68% yield). The *ee* (80%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=0.7 mL/min, UV= 230 nm, minor enantiomer t_1 = 10.9 min, major enantiomer t_2= 12.4 min. Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.49 (s, 1H), 7.24 (d, *J* = 4.6 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 5.53 (d, *J* = 13.9 Hz, 1H), 4.25-4.17 (m, 4H), 1.38-1.34 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 139.0, 129.6, 127.5, 125.6, 125.2, 110.5, 71.3, 63.73 (d, *J* = 21.5 Hz), 15.03 (d, *J* = 5.6 Hz). ESI-MS *(m/z)*: 320 ($[M+H]^+$)


8.37
7.49
7.25
7.24
6.79
6.77
5.54
5.51
4.25
4.24
4.23
4.22
4.20
4.19
4.17
1.38
1.37
1.36
1.34
0.99
1.04
1.01
1.14
1.00
0.89
4.09
6.24
f1 (ppm)

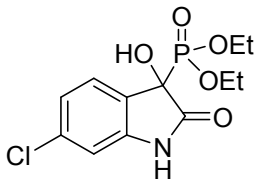

172.25
139.00
129.61
127.45
125.64
125.17
110.47
71.28
63.82
63.65
15.05
15.00
f1 (ppm)





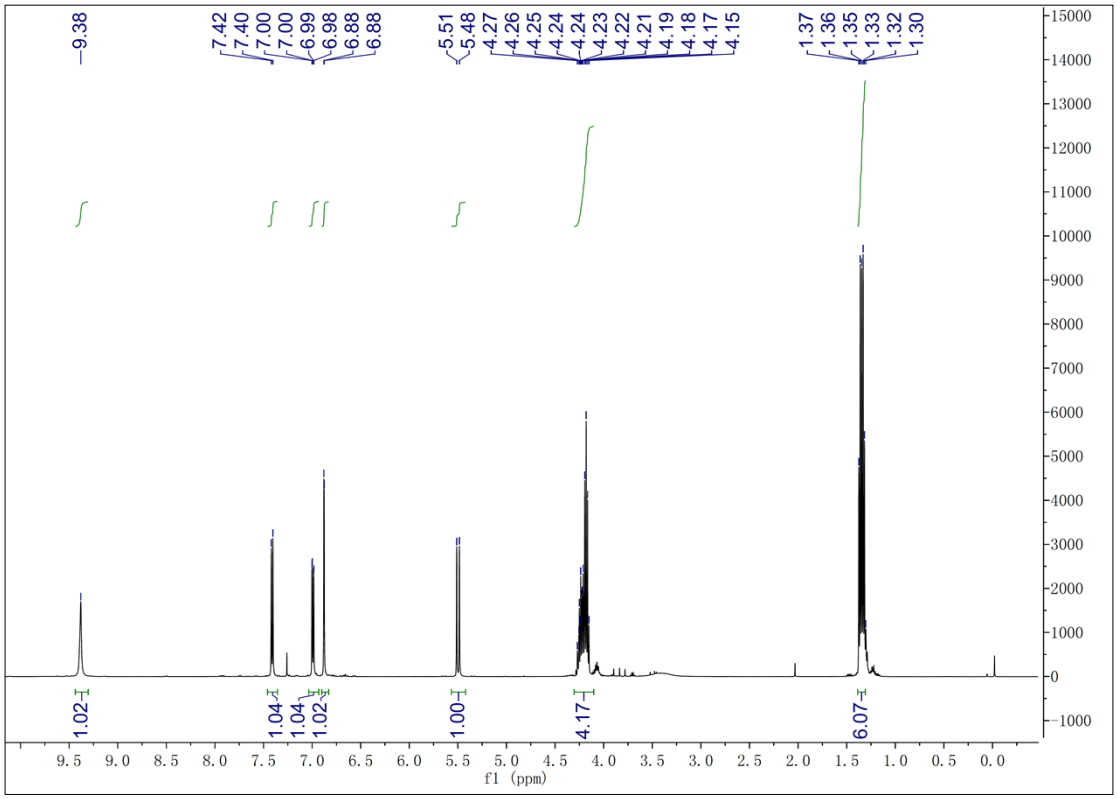
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.923	BB	0.3318	480.90121	22.28563	10.0065
2	12.432	BB	0.3357	4324.98047	197.29570	89.9935

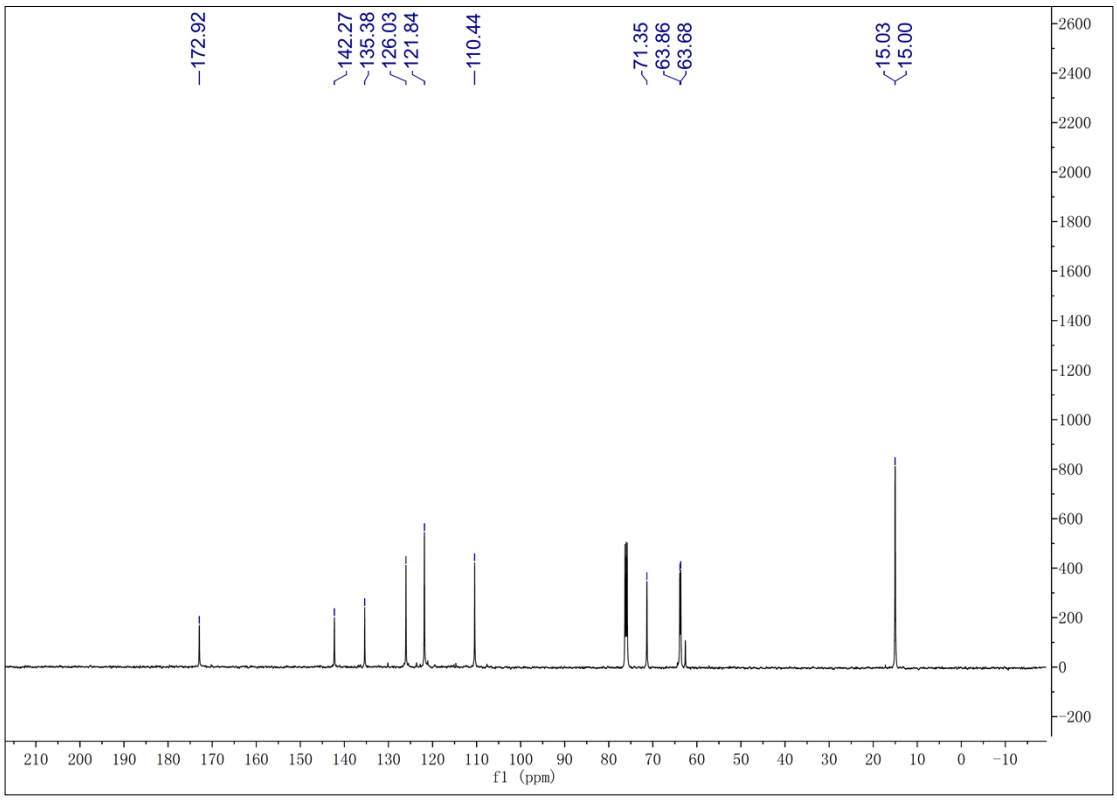
*2.9 Diethyl (6-chloro-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3i**)*

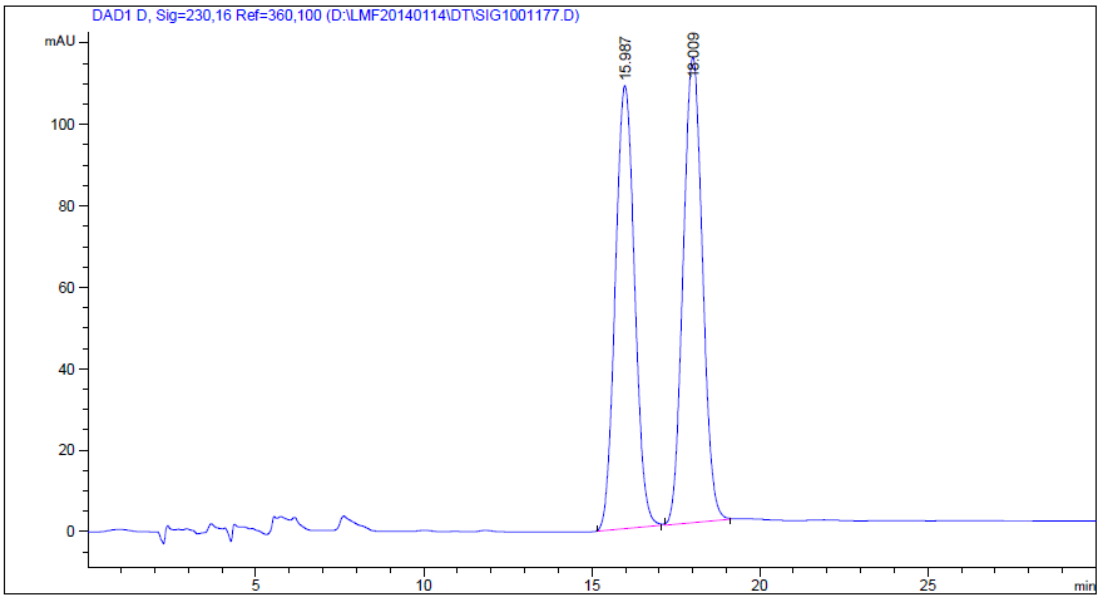


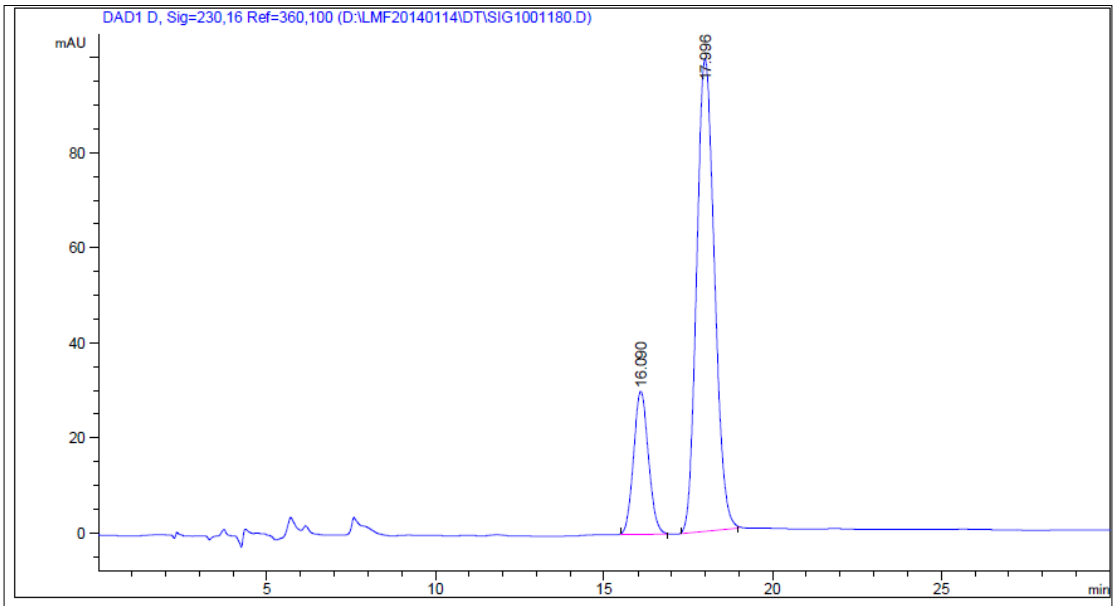
Purified by column chromatography eluting with hexane/EtOAc 3:1 (62% yield). The *ee* (60%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=1.2 mL/min, UV= 230 nm, minor enantiomer t_1 = 16.1 min, major enantiomer t_2= 18.0 min.

Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.00-6.98 (m, 1H), 6.88 (d, J = 1.6 Hz, 1H), 5.50 (d, J = 13.8 Hz, 1H), 4.26-4.15 (m, 4H), 1.37-1.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 142.3, 135.4, 126.0, 121.8, 110.4, 71.4, 63.8 (d, J = 23.5 Hz), 15.0 (d, J = 4.5 Hz). ESI-MS *(m/z)*: 320 ($[M+H]^+$). Anal. calcd. for $C_{12}H_{15}ClNO_5P$: C, 45.09; H, 4.73; N, 4.38. Found: C, 45.22; H, 4.65; N, 4.46.



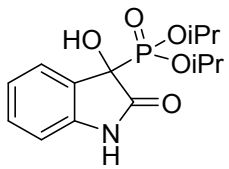






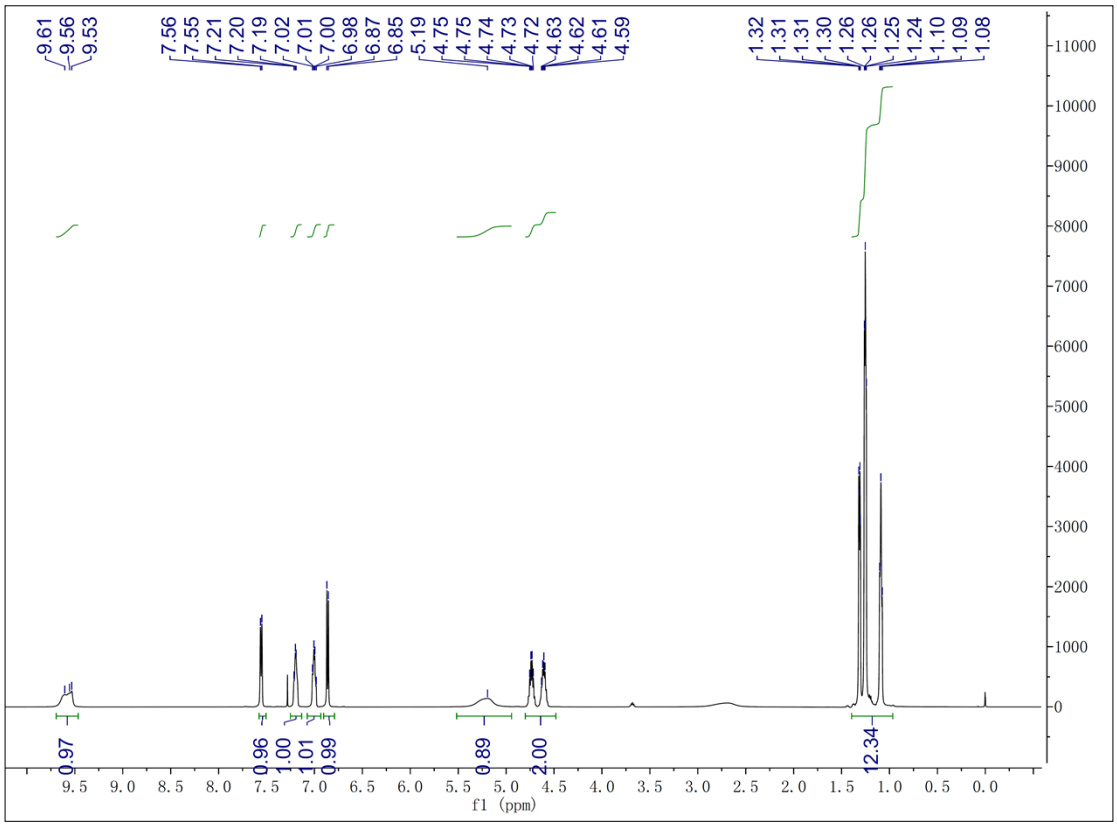
#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.090	BB	0.4734	922.44507	30.11001	20.1903
2	17.996	BB	0.5764	3646.31665	99.29790	79.8097

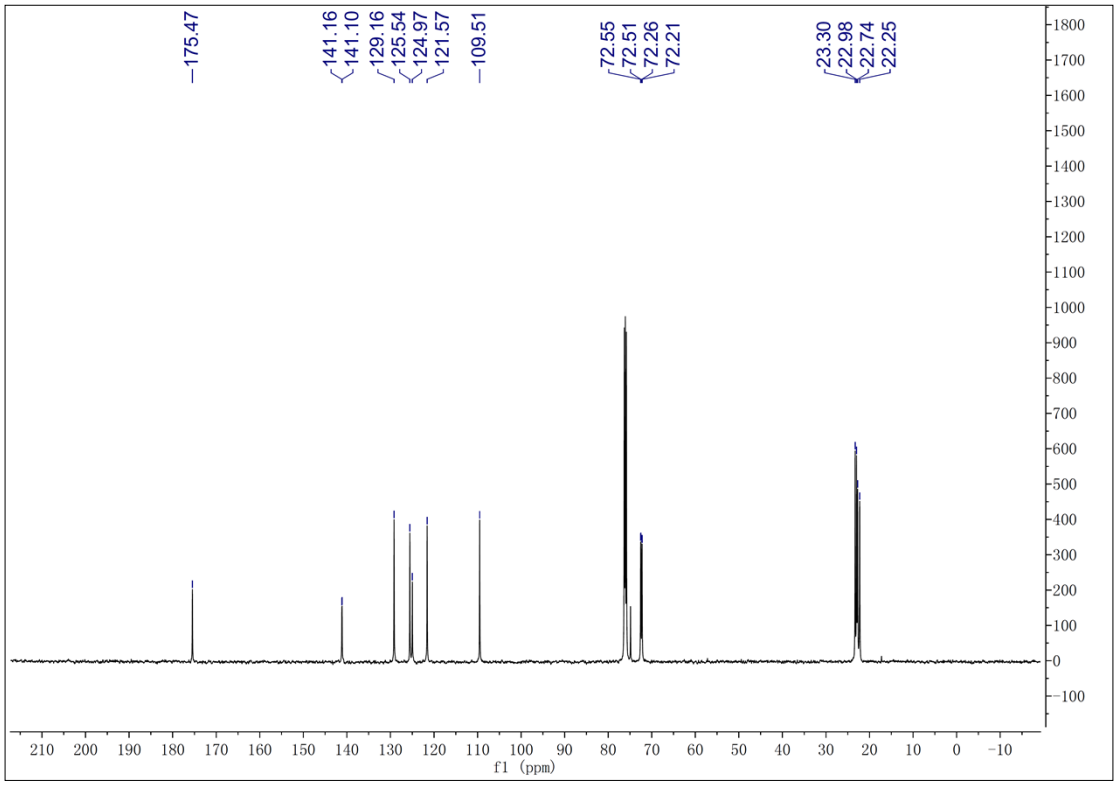
*2.10 Diisopropyl (3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3j**)*

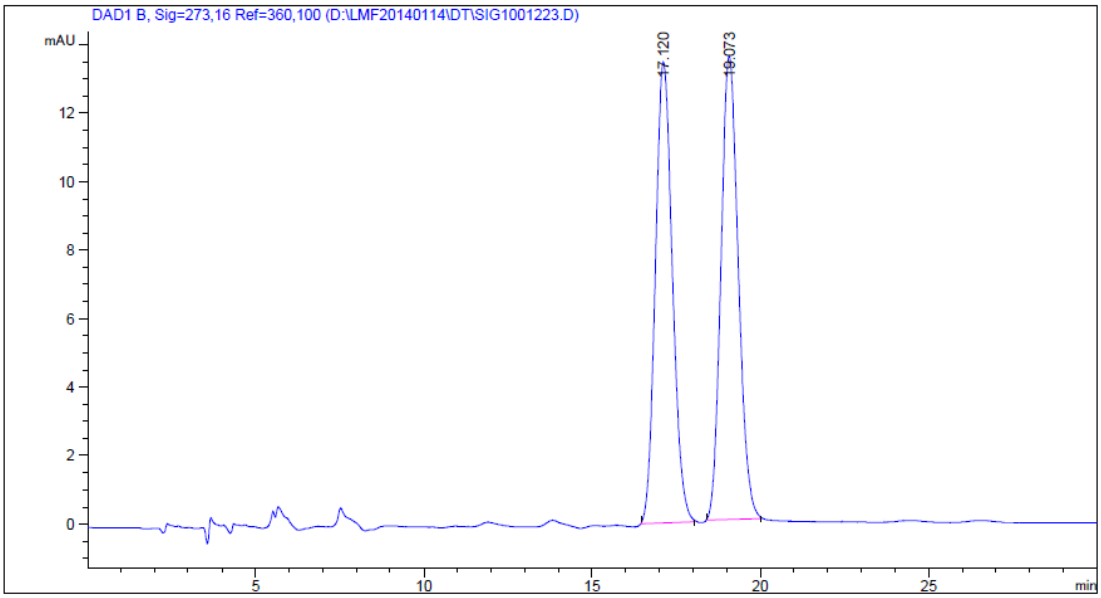


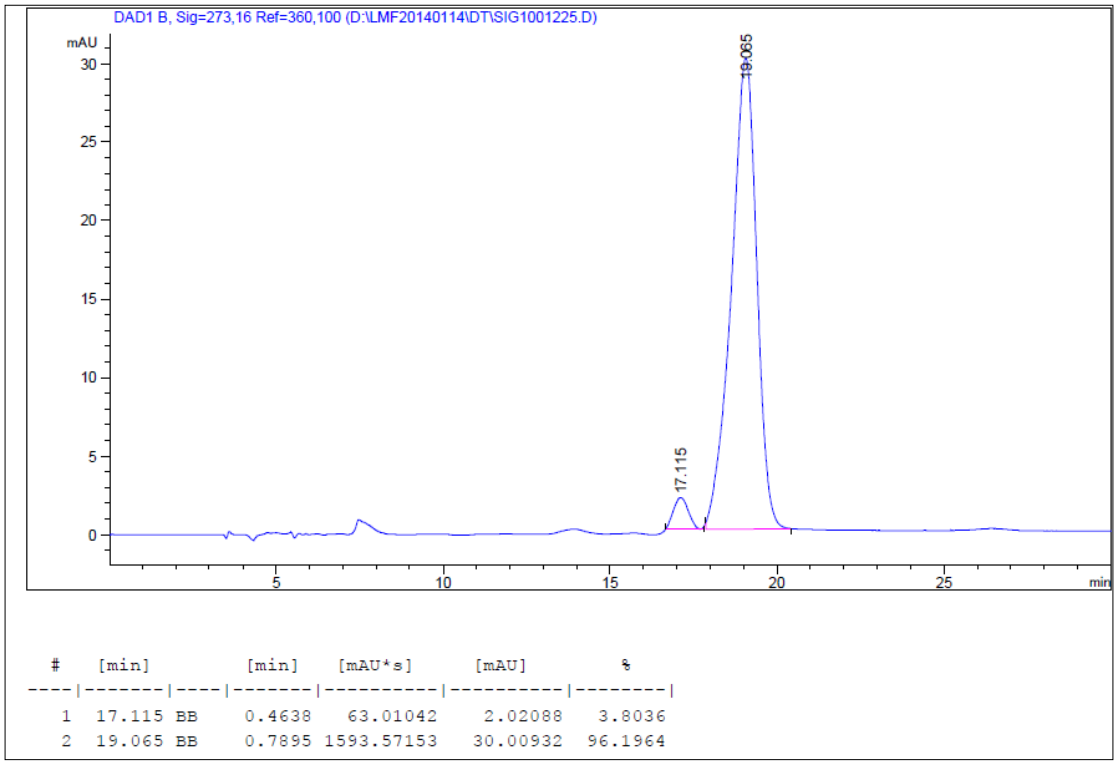
Purified by column chromatography eluting with hexane/EtOAc 3:1 (76% yield). The *ee* (92%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=0.7 mL/min, UV= 273 nm, minor enantiomer t_1 = 17.1 min, major enantiomer t_2= 19.1 min.

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61-9.53 (m, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.21-7.19 (m, 1H), 7.02-6.98 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.19 (s, 1H), 4.75-4.59 (m, 2H), 1.32-1.08 (m, 12H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 141.1, 129.2 125.5, 125.0, 121.6, 109.5, 72.5 (d, *J* = 5.0 Hz)，72.2 (d, *J* = 6.3 Hz),,23.1(d, *J* = 8.0 Hz)，22.4 (d, *J* = 61.3 Hz). ESI-MS *(m/z)*: 336 ([M+Na]$^{+}$)

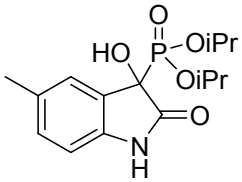



175.47
141.16
141.10
129.16
125.54
124.97
121.57
109.51
72.55
72.51
72.26
72.21
23.30
22.98
22.74
22.25
f1 (ppm)

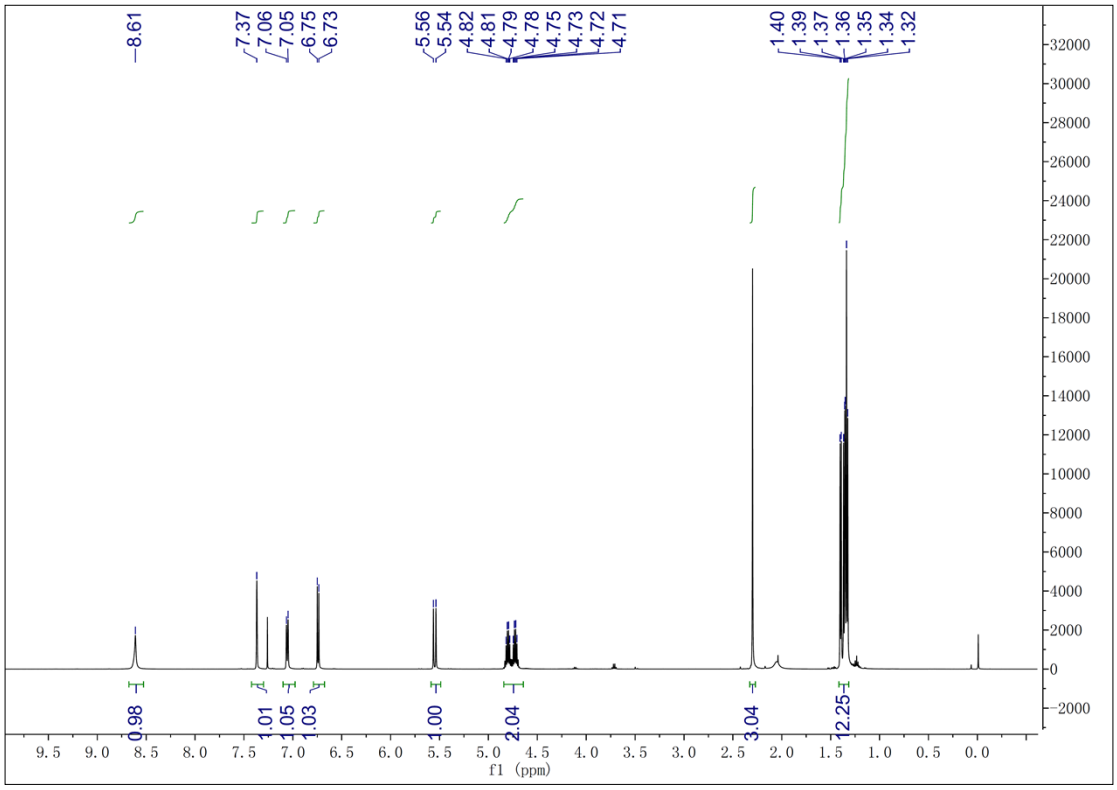

DAD1 B, Sig=273,16 Ref=360,100 (D:\LMF20140114\DT\SIG1001223.D)
mAU
17.120
19.073
min

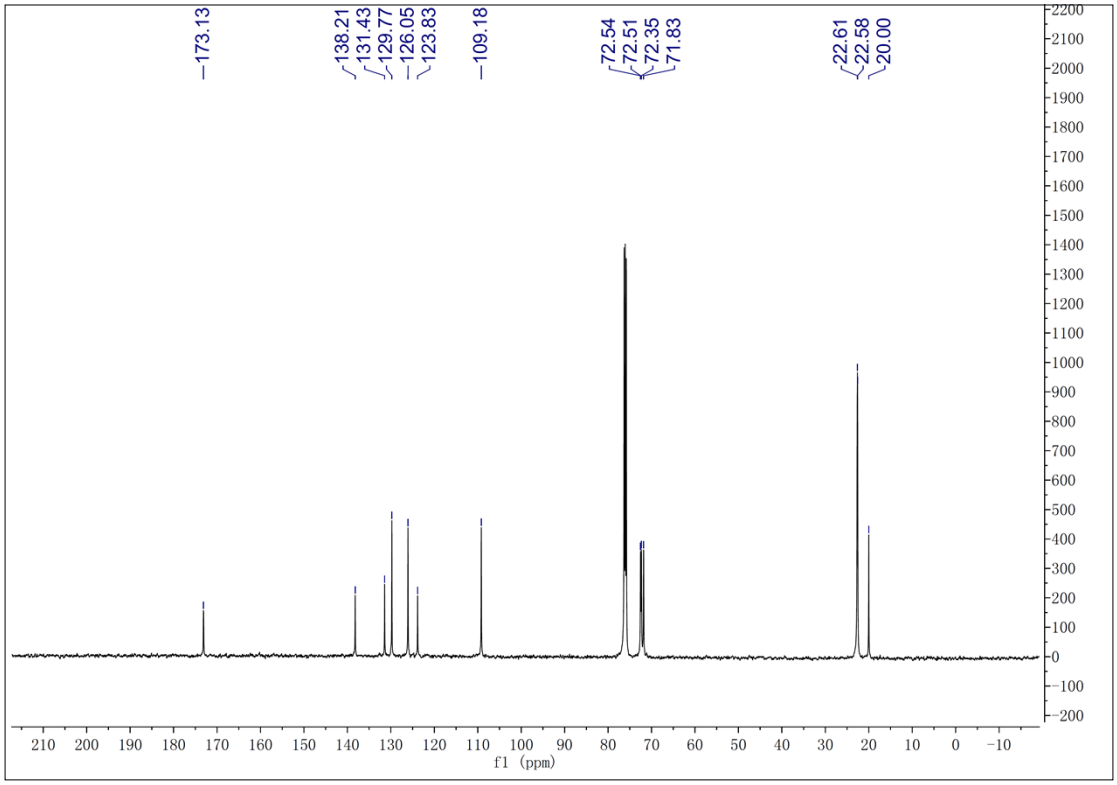


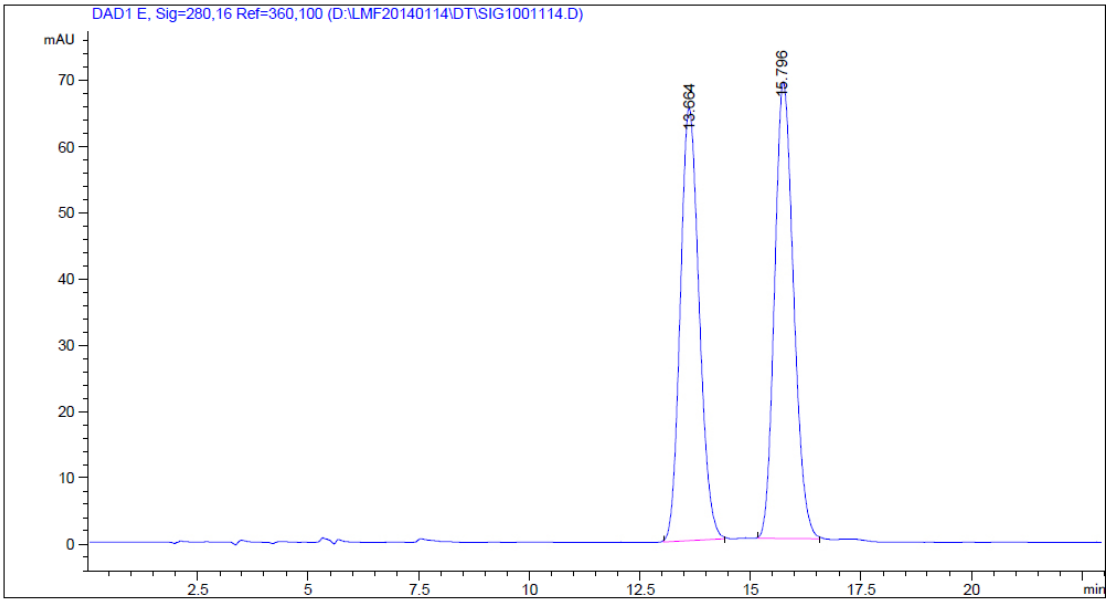
2. 11 Diisopropyl (3-hydroxy-5-methyl-2-oxoindolin-3-yl)phosphonate（***3k***）

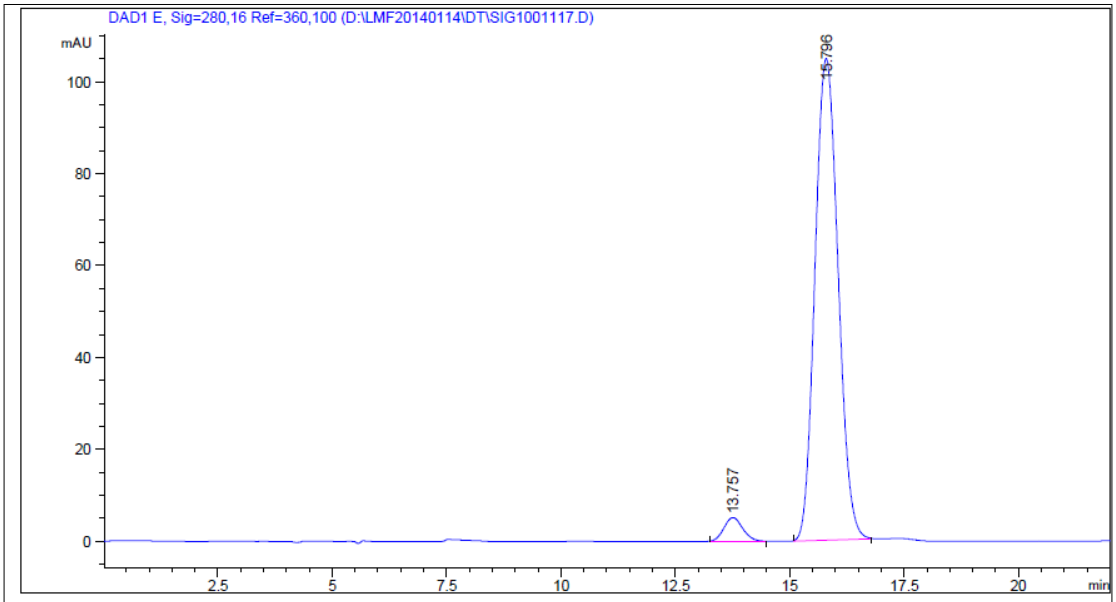


Purified by column chromatography eluting with hexane/EtOAc 3:1 (82% yield). The *ee* (92%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 85:15, flow rate=0.7 mL/min, UV= 280 nm, minor enantiomer t_1 = 13.8 min, major enantiomer t_2= 15.8 min.Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.37 (s, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.55 (d, *J* = 12.9 Hz, 1H), 4.82-4.71 (m, 2H), 2.30 (s, 3H), 1.40-1.32 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 138.2, 131.4, 129.8, 126.1, 123.8, 109.2, 72.5 (d, *J* = 3.8 Hz), 72.1 (d, *J* = 65.0 Hz), 22.6 (d, *J* = 3.8 Hz), 20.0. ESI-MS *(m/z)*: 350 ([M+Na]$^+$)


8.61
7.37
7.06
7.05
6.75
6.73
5.56
5.54
4.82
4.81
4.79
4.78
4.75
4.73
4.72
4.71
1.40
1.39
1.37
1.36
1.35
1.34
1.32
0.98
1.01
1.05
1.03
1.00
2.04
3.04
12.25
f1 (ppm)

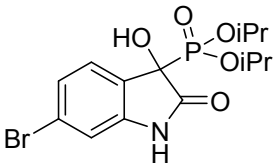

173.13
138.21
131.43
129.77
126.05
123.83
109.18
72.54
72.51
72.35
71.83
22.61
22.58
20.00
f1 (ppm)





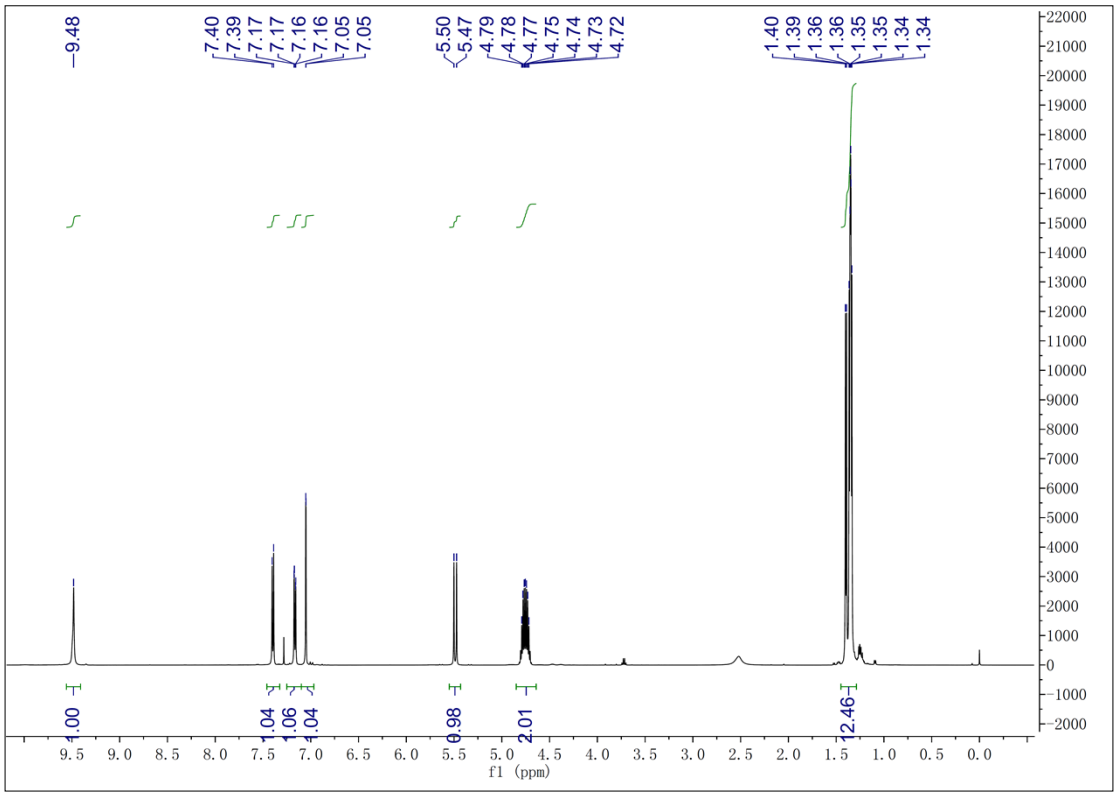
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.757	BB	0.4431	146.94566	5.14713	3.8545
2	15.796	BB	0.5559	3665.32446	104.83343	96.1455

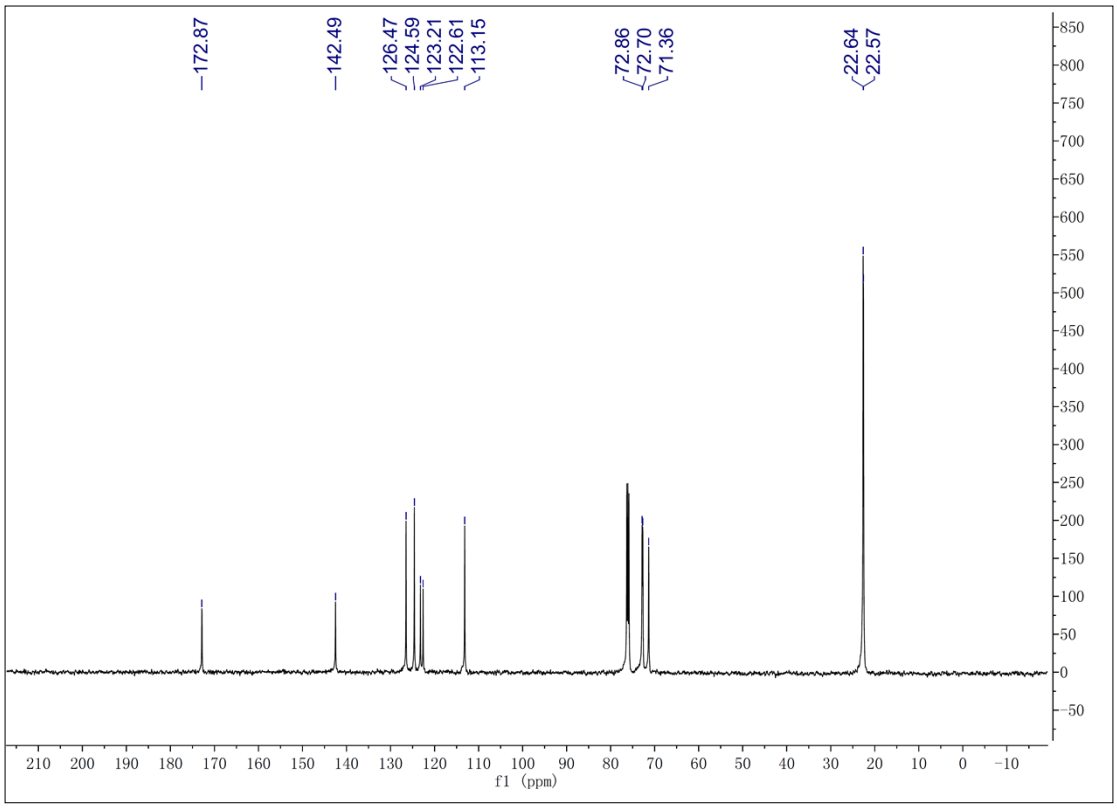
*2.12 Diisopropyl (6-bromo-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3l**)*

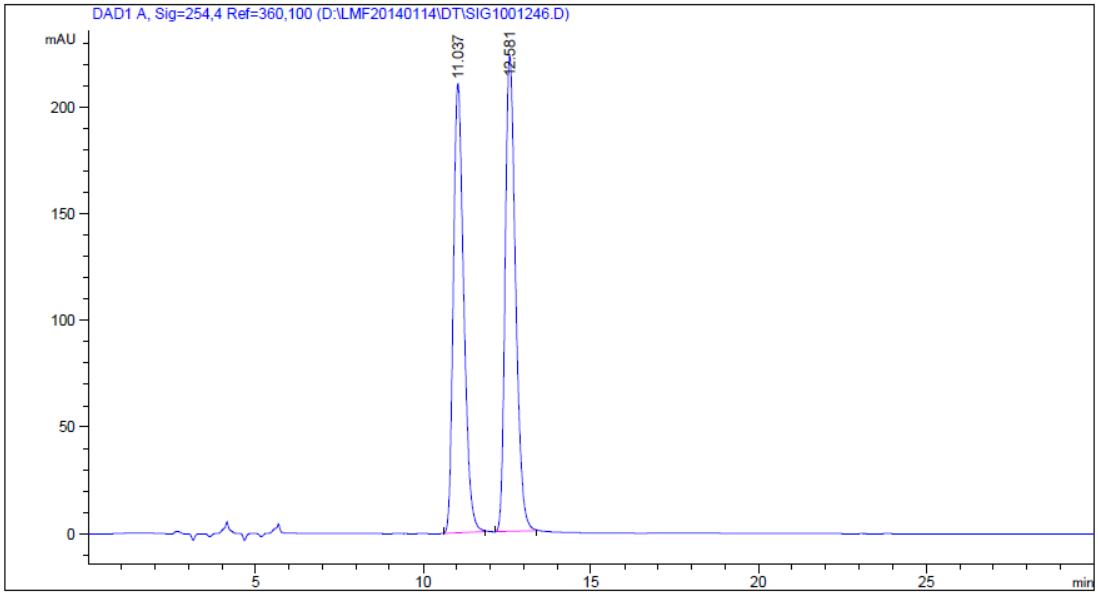


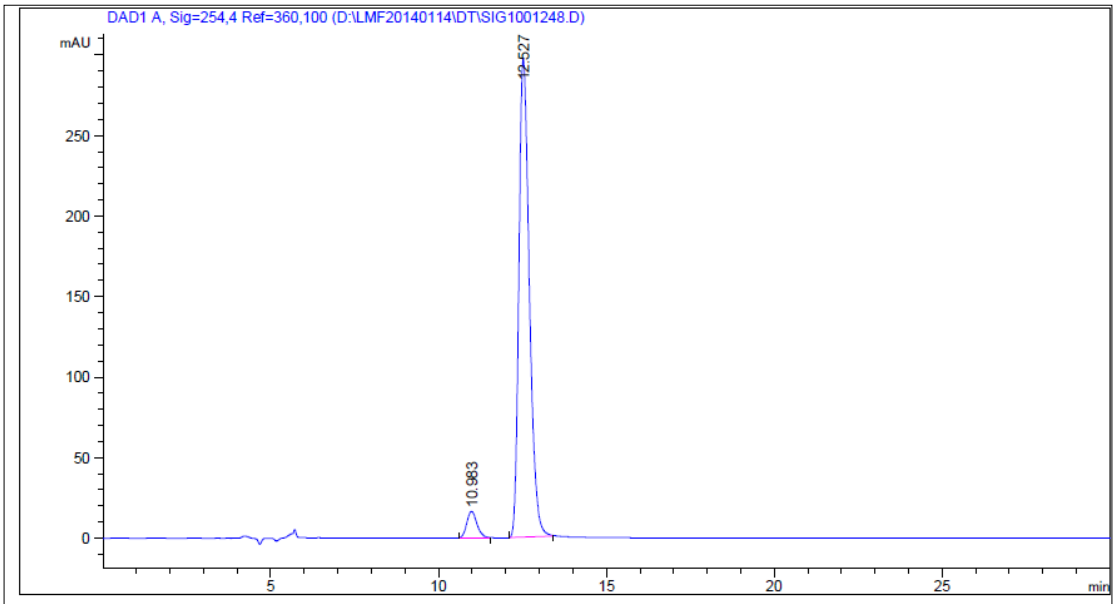
Purified by column chromatography eluting with hexane/EtOAc 3:1 (40% yield). The *ee* (90%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=1.2 mL/min, UV= 254 nm, minor enantiomer t_1 = 11.0 min, major enantiomer t_2= 12.5 min.

Brown Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.17 (m, 1H), 7.05 (d, *J* = 1.3 Hz, 1H), 5.49 (d, *J* = 14.0 Hz, 1H), 4.79-4.72 (m, 2H), 1.40-1.34 (m, 12H).^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 142.5, 126.5, 124.6, 123.2, 122.6, 113.2, 72.8 (d, *J* = 20.3 Hz), 71.4, 22.6 (d, *J* = 8.5 Hz). ESI-MS *(m/z)*: 391 ([M]$^{+}$). Anal. calcd. for $C_{14}H_{19}BrNO_5P$: C, 42.88; H, 4.88; N, 3.57. Found: C, 43.01; H, 4.81; N, 3.62.



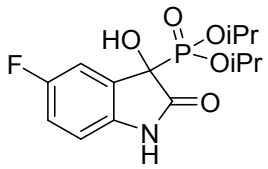

172.87
142.49
126.47
124.59
123.21
122.61
113.15
72.86
72.70
71.36
22.64
22.57
f1 (ppm)


DAD1 A, Sig=254,4 Ref=360,100 (D:\LMF20140114\DT\SIG1001246.D)
mAU
11.037
12.581
min

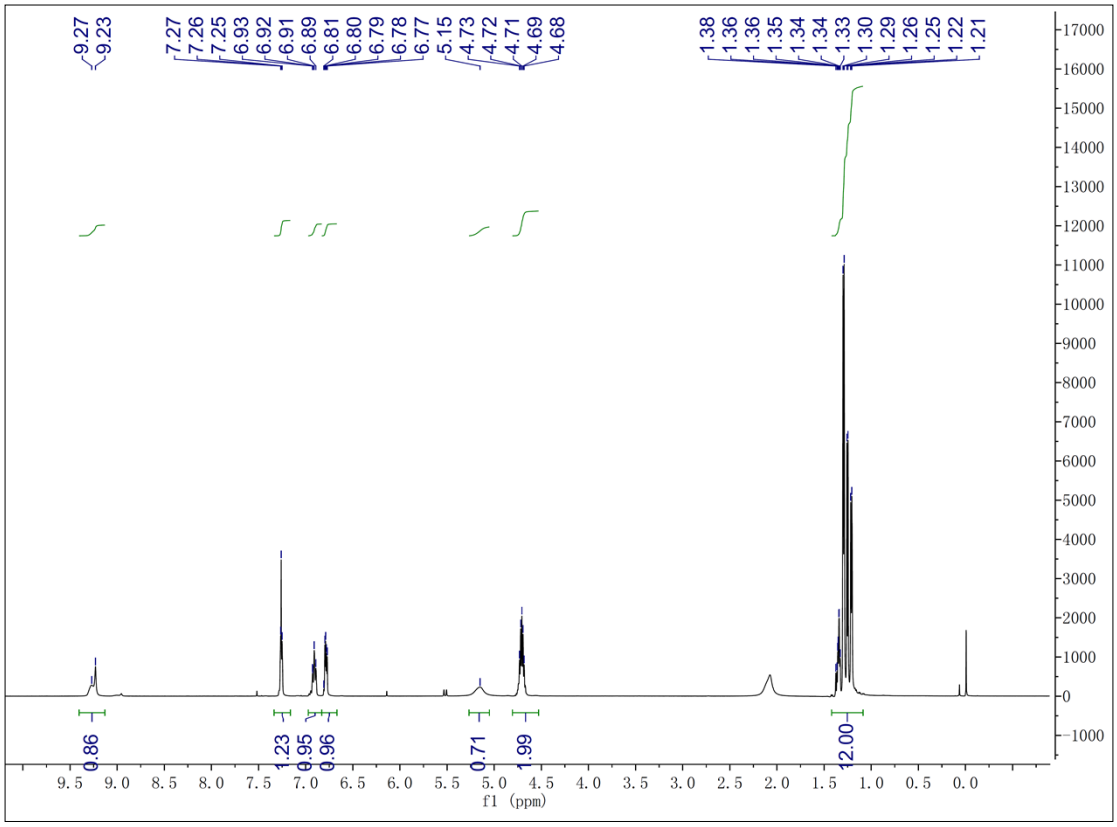


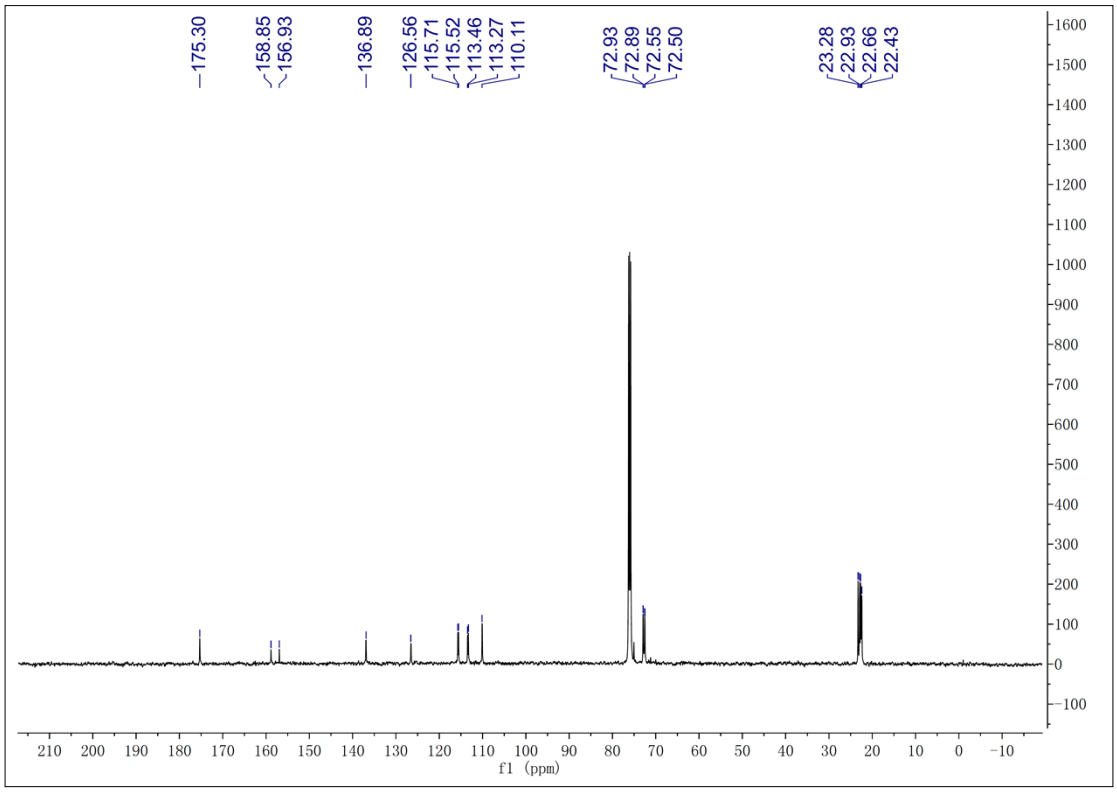
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.983	BB	0.3206	344.91461	16.45457	5.0862
2	12.527	BB	0.3330	6436.40576	296.83643	94.9138

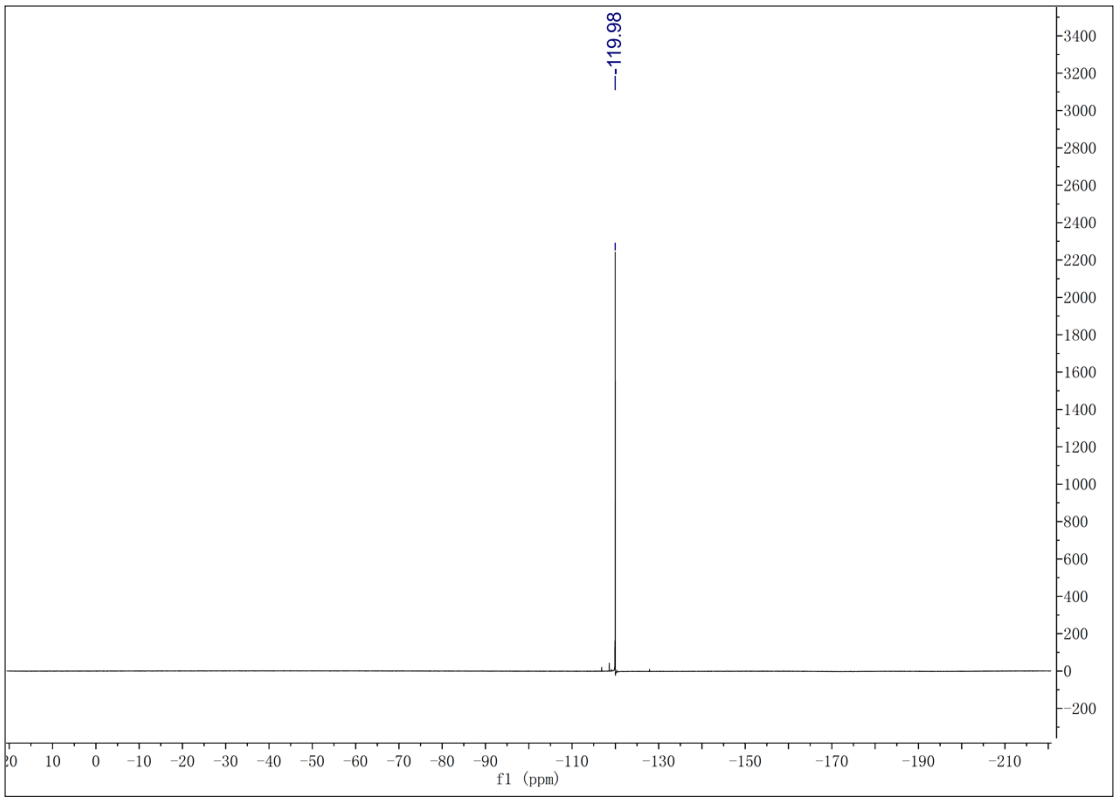
*2.13 Diisopropyl (5-fluoro-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3m**)*

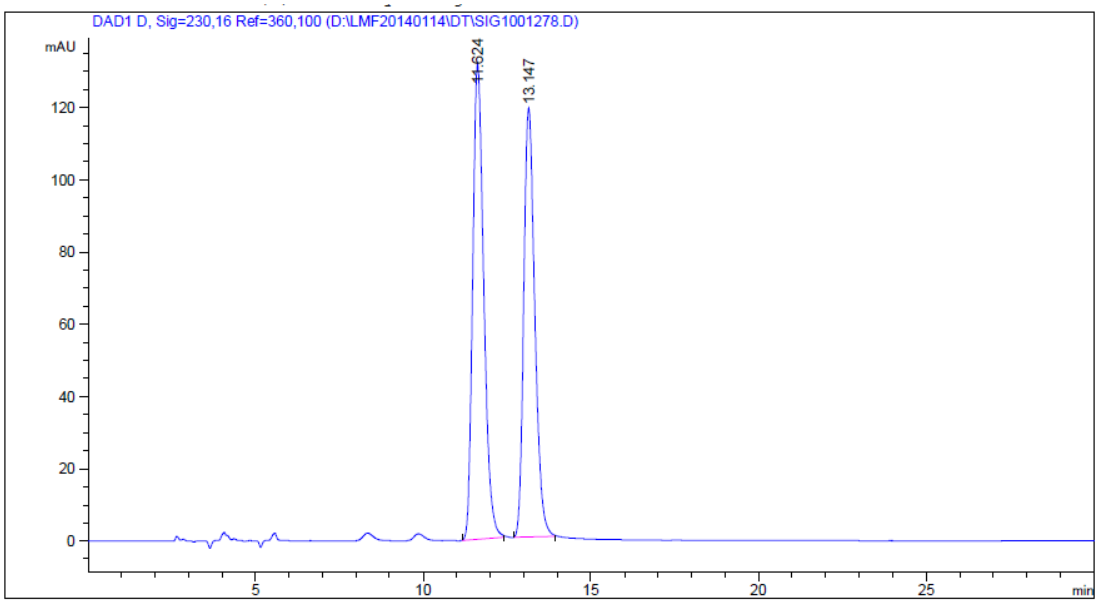


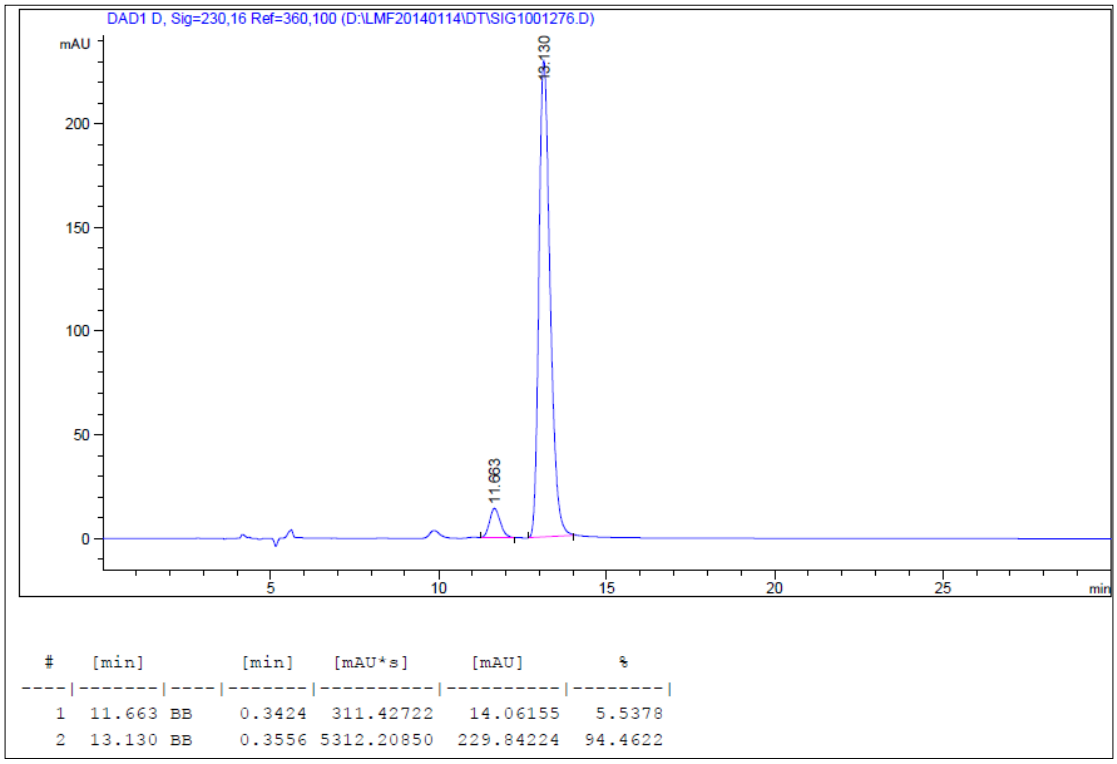
Purified by column chromatography eluting with hexane/EtOAc 5:1 (61% yield). The *ee* (88%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=1.0 mL/min, UV= 230 nm, minor enantiomer t_1 = 11.7 min, major enantiomer t_2= 13.1 min. Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, *J* = 19.9 Hz, 1H), 7.27-7.25 (m, 1H), 6.93-6.89 (m, 1H), 6.81-6.77(m, 1H), 5.15 (s, 1H), 4.73-4.68 (m, 2H), 1.38-1.21 (m, 12H). ^{19}F NMR (500 MHz, $CDCl_3$) δ -120.0. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 158.9, 156.9, 136.9, 126.6, 115.6 (d, *J* = 23.8 Hz), 113.4 (d, *J* = 23.8 Hz), 110.1, 72.9 (d, *J* = 5.0 Hz), 72.5 (d, *J* = 6.2 Hz), 22.6 (d, *J* = 43.8 Hz), 22.5 (d, *J* = 28.8 Hz). ESI-MS *(m/z)*: 332 ([M+H]$^+$). Anal. calcd. for $C_{14}H_{19}FNO_5P$: C, 50.76; H, 5.78; N, 4.23. Found: C, 50.90; H, 5.69; N, 4.29.


9.27
9.23
7.27
7.26
7.25
6.93
6.92
6.91
6.89
6.81
6.80
6.79
6.78
6.77
5.15
4.73
4.72
4.71
4.69
4.68
1.38
1.36
1.36
1.35
1.34
1.34
1.33
1.30
1.29
1.26
1.25
1.22
1.21
0.86
1.23
0.95
0.96
0.71
1.99
12.00
f1 (ppm)

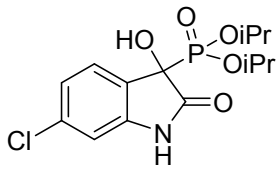

175.30
158.85
156.93
136.89
126.56
115.71
115.52
113.46
113.27
110.11
72.93
72.89
72.55
72.50
23.28
22.93
22.66
22.43
f1 (ppm)


-119.98
f1 (ppm)

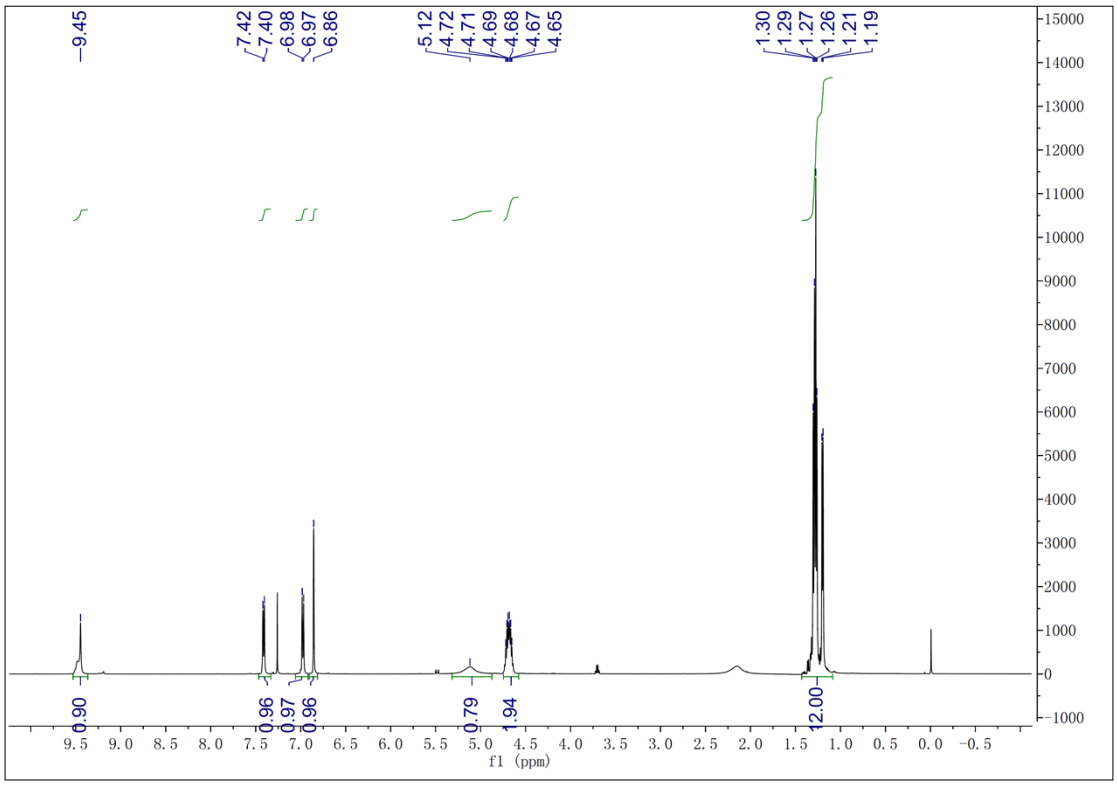

DAD1 D, Sig=230,16 Ref=360,100 (D:\LMF20140114\DT\SIG1001278.D)
mAU
11.624
13.147
min

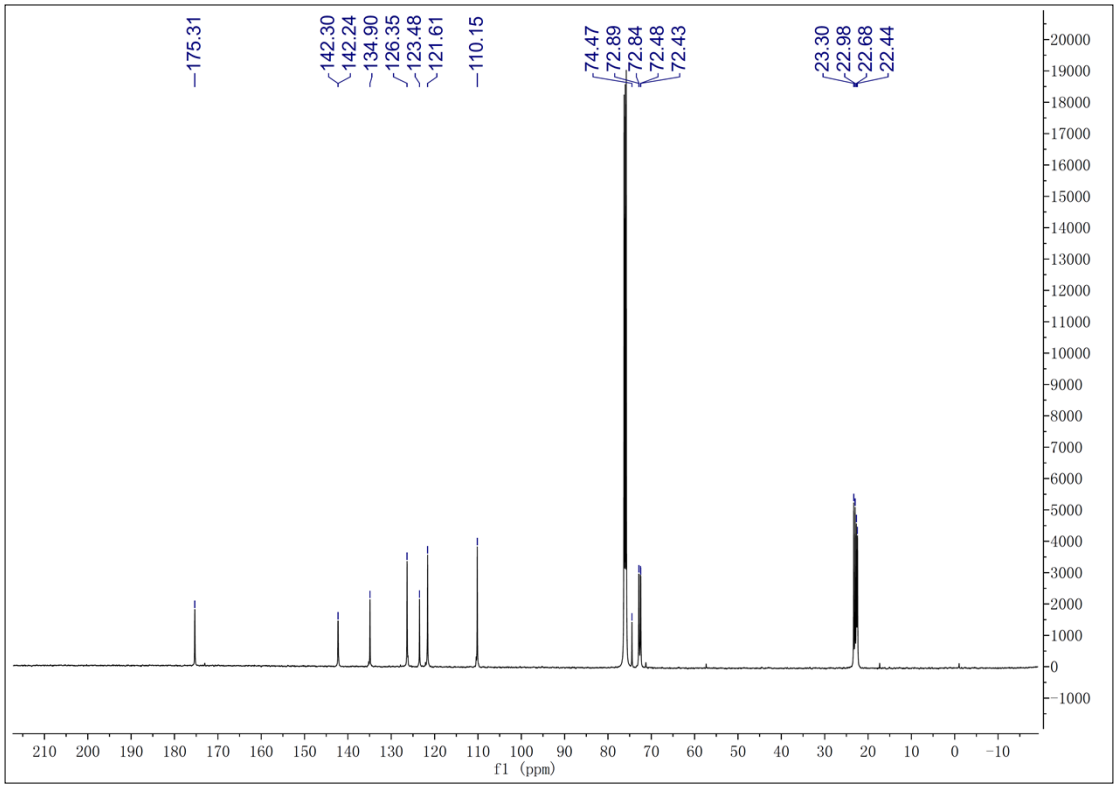


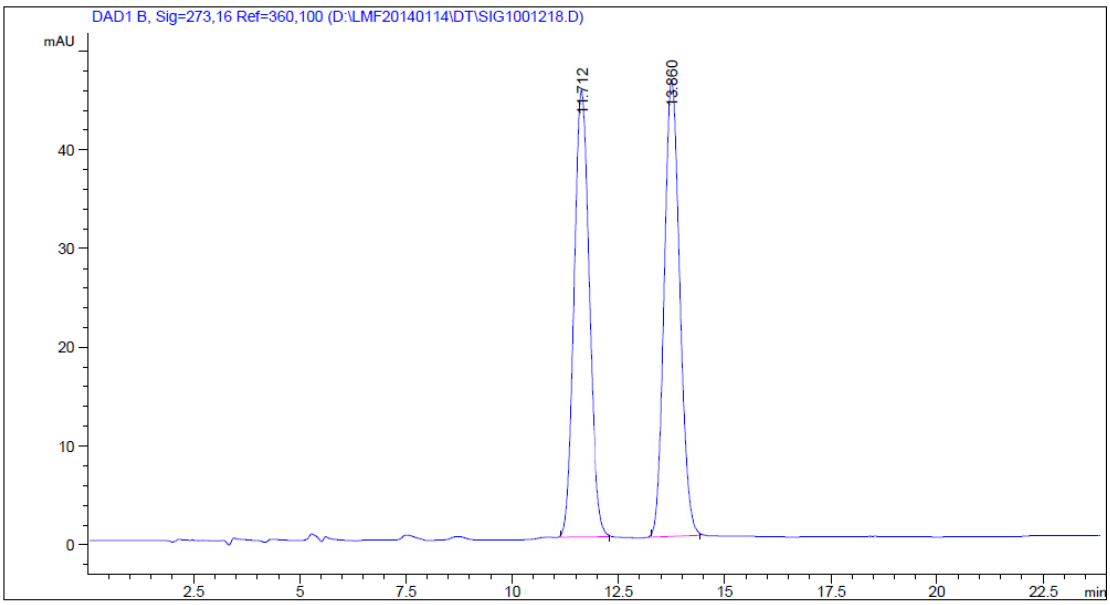
*2.14 Diisopropyl (6-chloro-3-hydroxy-2-oxoindolin-3-yl)phosphonate(**3n**)*

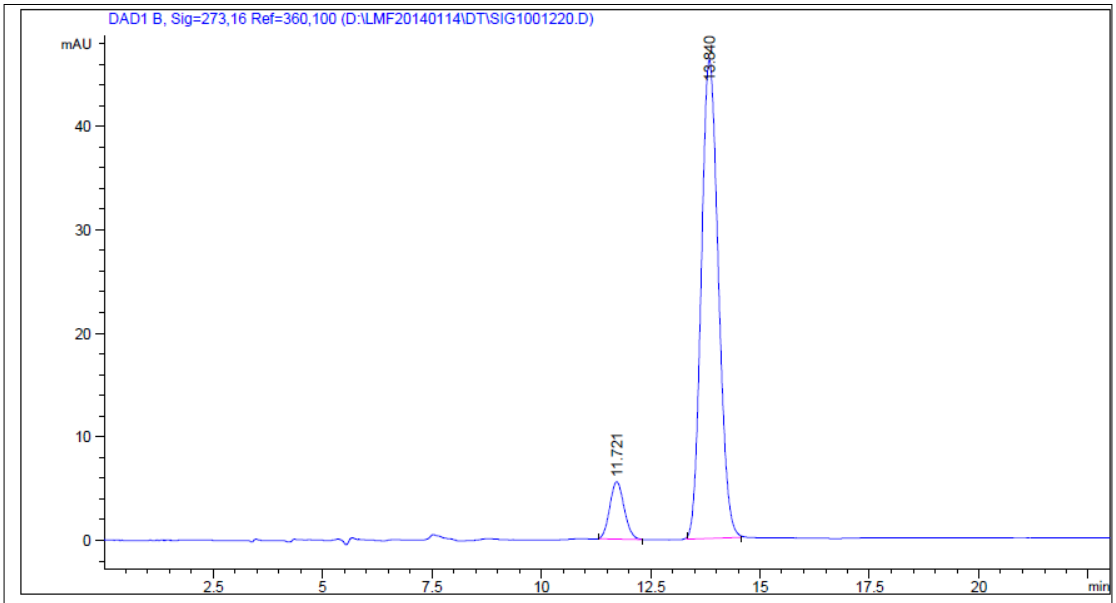


Purified by column chromatography eluting with hexane/EtOAc 3:1 (59% yield). The *ee* (82%) was determined by HPLC analysis, Venusil CA column, Hexane/*i*-PrOH 80:20, flow rate=0.7 mL/min, UV= 273 nm, minor enantiomer t_1 = 11.7 min, major enantiomer t_2= 13.8 min. Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.86 (s, 1H), 5.12 (s, 1H), 4.72-4.65 (m, 2H), 1.30-1.19 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3 142.3 (d, *J* = 7.3 Hz), 134.9, 126.4, 123.5, 121.6, 110.2, 74.5, 72.9 (d, *J* = 6.0 Hz), 72.5 (d, *J* = 6.0 Hz), 22.1 (d, *J* = 40.0 Hz), 22.6 (d, *J* = 30.0 Hz). ESI-MS *(m/z)*: 348 ($[M+H]^+$). Anal. calcd. for $C_{14}H_{19}ClNO_5P$: C, 48.36; H, 5.51; N, 4.03. Found: C, 48.50; H, 5.61; N, 4.11.


9.45
7.42
7.40
6.98
6.97
6.86
5.12
4.72
4.71
4.69
4.68
4.67
4.65
1.30
1.29
1.27
1.26
1.21
1.19
0.90
0.96
0.97
0.96
0.79
1.94
12.00
f1 (ppm)


175.31
142.30
142.24
134.90
126.35
123.48
121.61
110.15
74.47
72.89
72.84
72.48
72.43
23.30
22.98
22.68
22.44
f1 (ppm)





#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.721	BB	0.3530	127.12949	5.55501	9.1994
2	13.840	BB	0.4245	1254.80225	46.25351	90.8006