– Electronic Supplementary Information (ESI) –

Asymmetric hydrogenation of α- or β-acyloxy α,β-unsaturated phosphonates catalyzed by Rh(I) complex of monodentate phosphoramidite

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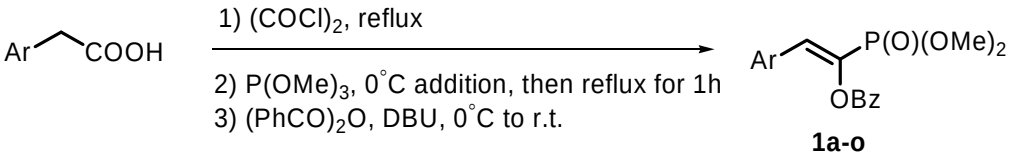
Table of Contents

1. General

All reactions and manipulations were performed using standard Schlenk techniques. Anhydrous THF, Et_2O and toluene were distilled from sodium benzophenone ketyl. Anhydrous CH_2Cl_2, $ClCH_2CH_2Cl$, and *i*PrOH were distilled from CaH_2 under an atmosphere of argon. Anhydrous MeOH were distilled from magnesium under argon atmosphere. Melting points were measured on a RY-I apparatus and uncorrected. ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on Varian Mercury 300 MHz or 400 MHz spectrometers. Chemical shifts (δ values) were reported in ppm downfield from internal TMS (^1H NMR) or $CDCl_3$ (^{13}C NMR), external 85% H_3PO_4 (^{31}P NMR) and external CF_3CO_2H (^{19}F NMR), respectively. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. EI (70 eV) and ESI-MS mass spectra were obtained on Shimadzu GCMS-QP 2010, Agilent 5973N, Agilent LC/MSD SL, or Shimadzu LCMS-2010EV, respectively. HRMS (EI) and HRMS (ESI) were determined on Waters Micromass GCT Premier and APEX III 7.0 TESLA FTMS spectrometers. Elemental analyses were performed on an Elementar VARIO EL III instrument. The IR spectra were measured on a Bruker Tensor 27 spectrometer. Chiral HPLC analyses were performed on a JASCO 2089, JASCO 1580, Techcomp N2000 liquid chromatography, or the HPLC system consisted of a Waters 515 HPLC pump plus a Waters 2487 Dual λ absorbance detector. The chiral monodentate phosphoramidite ligands (*R*,*R*)-**L1**,[1] (*R*)-**L2** and **MonoPhos**,[2] (*S*,*S*)-**L3**-**L5**[3] were prepared by published procedures.

2 Synthesis of α-acyloxy α,β-unsaturated phosphonic acid dimethyl esters 1a-v

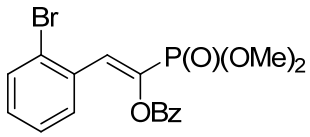
2.1 General procedure for the preparation of β-aryl α-benzoloxy α,β-unsaturated phosphonic acid dimethyl esters.



1a-o

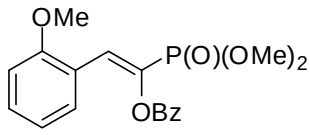
The β-aryl-α-enol ester phosphonates **1a-g** and **1n-o** were synthesized by following the procedure reported by Zheng et al,[4] while **1h-m** were prepared by using a similar protocol.

(*E*)-2-(2-bromophenyl)-1-(dimethoxyphosphoryl)vinyl benzoate, 1h



White solid, 19% yield; m.p. 89-91°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 7.63-7.53 (m, 4H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.16-7.12 (m, 2H), 3.88 (d, *J* = 11.6 Hz, 3H), 3.87 (d, *J* = 11.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (d, *J* = 1.6 Hz),138.5 (d, *J* = 224.8 Hz), 133.9, 133.4 (d, *J* = 28.2 Hz), 133.0 (d, *J* = 0.8 Hz), 132.1 (d, *J* = 15.9 Hz), 130.5, 130.1, 129.6 (d, *J* = 1.9 Hz), 128.6, 128.3, 127.3, 124.2 (d, *J* = 0.8 Hz) 53.4 (d, *J* = 5.1 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 11.6 ppm; FTIR ν 3011, 2852, 1743, 1641, 1600, 1561, 1463, 1240, 1178, 1122, 1094, 1018, 826, 797, 751, 705, 664 cm^{-1}; ESI-MS(m/z): 411.1 $[M+H^+]$, 433.1 $[M+Na^+]$; HRMS (ESI) m/z: calc. for $[C_{17}H_{16}BrNaO_5P]^+$: 432.9811, Found: 432.9821 $[M+Na^+]$.

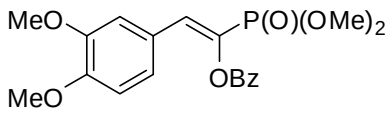
(*E*)-1-(dimethoxyphosphoryl)-2-(2-methoxyphenyl)vinyl benzoate, 1i



White solid, 54% yield; m.p. 73-74°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 12.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.50-7.46 (m, 2H), 7.27-7.23 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.79-6.75 (m, 1H), 3.85 (d, *J* = 11.2 Hz, 6H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 1.9 Hz), 157.3, 136.2 (d, *J* = 228.4 Hz), 133.7, 131.1, 130.1, 129.2 (d, *J* = 1.5 Hz), 129.1 (d, *J* = 28.7 Hz), 128.7, 128.5 (d, *J* = 2.3 Hz), 120.8 (d, *J* = 16.2 Hz), 120.4, 110.7 (d, *J* = 0.8 Hz), 55.4, 53.1 (d, *J* = 5.1 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 13.0 ppm. FTIR ν 3007, 2851, 1741, 1637,

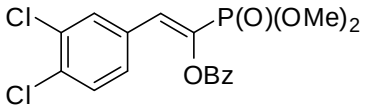
1598, 1485, 1237, 1176, 1093, 1018, 827, 781, 752, 707 cm^{-1}.

(*E*)-1-(dimethoxyphosphoryl)-2-(3, 4-dimethoxyphenyl)vinyl benzoate, 1j[5]



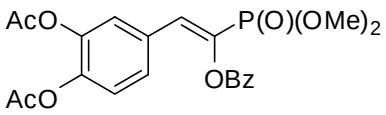
White solid, 61% yield; m.p. 113-114°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 12.0 Hz, 1H), 7.10 (d, *J* = 10.8 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.86 (d, *J* = 7.5 Hz, 6H), 3.83 (s, 3H), 3.46 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4 (d, *J* = 1.6 Hz), 150.3, 148.6, 134.8 (d, *J* = 229.2 Hz), 134.6 (d, *J* = 27.8 Hz), 134.0, 130.1, 128.7, 128.6, 124.7 (d, *J* = 16.3 Hz), 124.1, 111.3, 110.8 (d, *J* = 1.0 Hz), 55.7, 55.1, 53.1 (d, *J* = 4.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.3 ppm. EI-MS(m/z): 392 [M^+]; HRMS (EI) m/z: calc. for [$C_{19}H_{21}O_7P$]$^+$: 392.1019, Found: 392.1030 [M^+].

(*E*)-1-(dimethoxyphosphoryl)-2-(3,4-dichlorophenyl)vinyl benzoate, 1k



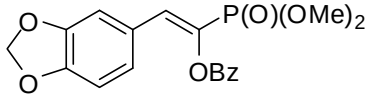
White solid, 58% yield; m.p. 100°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.5 Hz, 2H), 7.67-7.60 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.33 (s, 2H), 7.20 (d, *J* = 11.4 Hz, 1H), 3.82 (d, *J* = 11.4 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 138.7 (d, *J* = 225.3 Hz), 134.2, 133.7, 132.9 (d, *J* = 1.6 Hz), 132.3, 131.9 (d, *J* = 9.0 Hz), 131.7, 130.9 (d, *J* = 32.7 Hz), 130.2, 128.8, 128.3, 128.1, 53.3 (d, *J* = 4.9 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 12.7 ppm; FTIR ν 2980, 2906, 1719, 1504, 1453, 1392, 1228, 1134, 1015, 962, 857, 814, 797, 770, 696, 644 cm^{-1}; EI-MS (m/z): 400 (M^+, 2.5), 186 (10.1), 123 (5.8), 105 (100.0), 93 (6.2), 77 (27.8), 51 (5.3); HRMS(EI) calcd. for [$C_{17}H_{15}O_5PCl_2$]$^+$ [M^+]: 400.0029, Found: 400.0035.

(*E*)-1-(dimethoxyphosphoryl)-2-(3,4-diacetoxylphenyl)vinyl benzoate, 1l



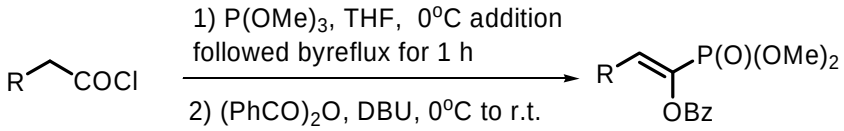
Yellow liquid, 32% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 2H), 7.42-7.26 (m, 2H), 7.21 (d, *J* = 11.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.82 (d, *J* = 11.4 Hz, 3H), 3.80 (d, *J* = 10.8 Hz, 3H), 2.20 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6 (d, *J* = 3.0 Hz), 163.2, 142.8, 141.9, 138.0 (d, *J* = 225.9 Hz), 133.9, 133.7, 132.4, 130.5, 130.3, 130.1, 128.6, 128.1, 127.6, 124.0 (d, *J* = 65.5 Hz), 53.2 (d, *J* = 4.8 Hz), 20.4, 20.2 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 13.2 ppm; FTIR: ν 3011, 2852, 1742, 1600, 1508, 1451, 1316, 1236, 1177, 1102, 1017, 909, 869, 829, 779, 704, 686 cm^{-1}; EI-MS (m/z): 448 (M^+, 5.8), 296 (5.4), 234 (30.3), 192 (80.6), 150 (44.0), 122 (7.4), 105 (100.0), 93 (6.0), 77 (25.2), 43 (17.9); HRMS(EI) calcd. for $C_{21}H_{21}O_9P^+$ [M^+]: 448.0918, Found: 448.0921.

(*E*)- 1-(dimethoxyphosphoryl)-2-(benzo[d][1,3]dioxol-5-yl)vinyl benzoate, 1m



White solid, 47% yield; m.p. 80-81°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 12.0 Hz, 1H), 7.05-7.02 (m, 2H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.91 (s, 2H), 3.83 (d, *J* = 11.1 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5 (d, *J* = 1.6 Hz), 148.8, 147.9 (d, *J* = 1.1 Hz), 134.8 (d, *J* = 228.1 Hz), 134.4 (d, *J* = 27.8 Hz), 133.9, 130.2, 128.7, 128.5, 125.9 (d, *J* = 12.2 Hz), 125.3, 108.7 (d, *J* = 0.6 Hz), 108.4 (d, *J* = 0.8 Hz), 101.3, 53.1 (d, *J* = 4.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.2 ppm; FTIR ν 2955, 2852, 1741, 1637, 1601, 1503, 1489, 1448, 1237, 1178, 1092, 1017, 925, 820, 754, 730, 706, 687 cm^{-1}; EI-MS (m/z): 376 (M^+, 7.1), 162 (100.0), 134 (23.2), 105 (100.0), 93 (8.7), 77 (23.3), 51 (7.5); HRMS(EI) calcd. for $C_{18}H_{17}O_7P^+$ [M^+]: 376.0706, Found: 376.0722.

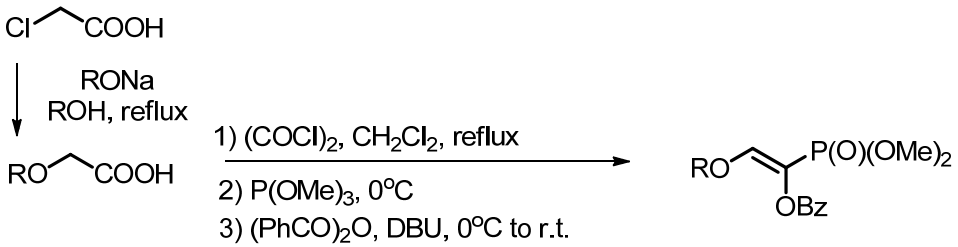
2.2 Preparation of β-H or alkyl α-enol ester phosphonates 1p and 1q.



1p-q

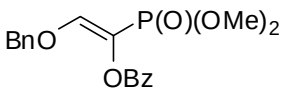
The procedure for synthesis of **1p**[4,6] and **1q**[4,6] is similar to that described above except using the corresponding (commercially available) acid chlorides as the starting material.

2.3 General procedure for the preparation of β-alkoxy substituted α-benzoloxy α,β-unsaturated phosphonic acid dimethyl esters 1r-u.



The general procedure for the preparation of **1r-u** is similar to that described above for synthesis of **1a-o** except using the corresponding alkoxyacetic acids as the starting material, which were synthesized by following a reported procedure[7]

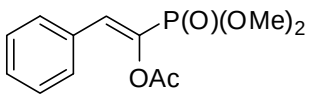
(*E*)-2-(benzyloxy)-1-(dimethoxyphosphoryl)vinyl benzoate, 1u



Yellow oil, 21% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 6.9 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.32-7.25 (m, 5H), 7.15 (d, *J* = 3.9 Hz, 1H), 4.99 (s, 2H), 3.73 (d, *J* = 11.4 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 151.9 (d, *J* = 43.2 Hz), 135.1, 133.2, 129.9, 128.5, 128.4, 128.3, 128.2, 127.1, 117.3 (d, *J* = 238.5 Hz), 75.8, 52.6 (d, *J* = 4.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 15.7 ppm; FTIR ν 3011, 2853, 1743, 1644, 1601, 1508, 1239, 1178, 1161, 1093, 1018, 833, 785, 706, 687 cm^{-1}; EI-MS (m/z): 362 (M^+, 0.6), 271 (10.1), 105 (100.0), 91 (35.0), 77

(16.5), 65 (3.3), 51 (3.9); HRMS(EI) calcd. for $[C_{18}H_{19}O_6P]^+$ [M^+]: 362.0914, Found: 362.0905.

Synthesis of (*E*)-1-(dimethoxyphosphoryl)-2-phenylvinyl acetate, 1v[8]

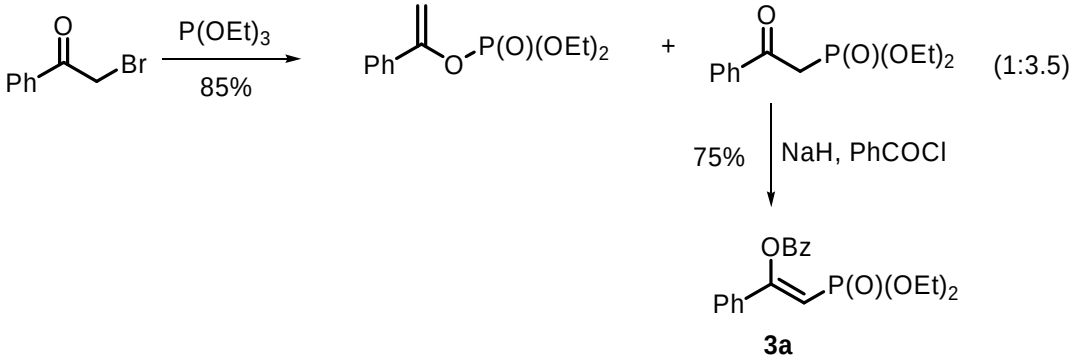


Compound **1v** was prepared by following a literature procedure reported by Afarinkia et al.[8]

Yellow oil, 84% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.38-7.36 (m, 3H), 7.19 (d, *J* = 11.7 Hz, 1H), 3.81 (d, *J* = 11.1 Hz, 6H), 2.27 (s, 3H) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 13.9 ppm. EI-MS (m/z): 270 (M^+); HRMS(EI) calcd. for $[C_{12}H_{15}O_5P]^+$ [M^+]: 270.0652, Found: 270.0653.

3 Preparation of β-substituted β-benzoloxy α,β-unsaturated phosphonic acid diethyl esters 3a-c

3.1 Synthesis of β-phenyl-β-benzoloxy α,β-unsaturated phosphonic acid diethyl ester 3a.[9]



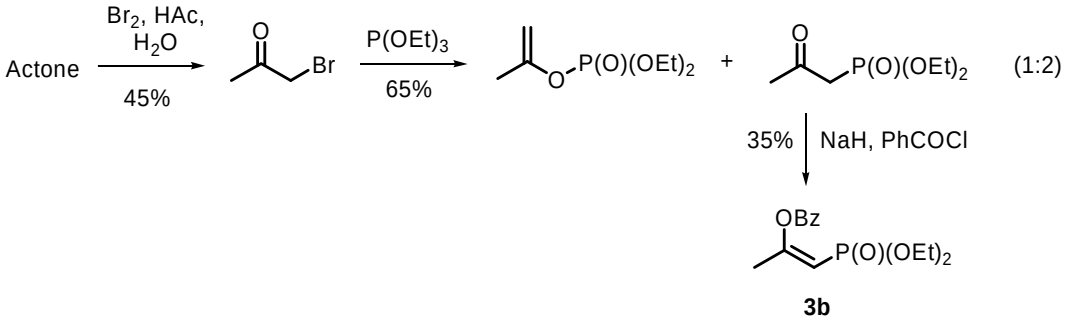
3a

2-Bromoacetophenone (2.0 g, 10.05 mmol) was added to triethyl phosphite (1.8 g, 10.83 mmol) at 90°C within 2 min and the mixture was stirred for a further 15 min at 90°C with a simultaneous release of ethyl bromide. The unreacted triethyl phosphite and resultant ethyl bromide were removed under vacuum. The resulting viscous, oily

mixture of phosphonate and enol phosphate was shaken in an aqueous solution of potassium hydroxide (2.0 g KOH in 150 mL H_2O) and extracted twice with a mixture of petroleum ether (30–60°C) and dichloromethane 19:1 (2 × 100 mL). The combined organic phase was dried over anhydrous $MgSO_4$. After evaporation of the solvents, 1-[(diethoxyphosphinyl)oxo]styrene was isolated as a colorless oil. The aqueous phase was acidified with concentrated hydrochloric acid to *p*H=4, followed by extraction with dichloromethane (2 × 50 mL). The combined organic phase was dried over anhydrous $MgSO_4$. Removal of the solvent under vacuum afforded 2-(diethoxyphosphinyl)acetophenone as a colorless oil.

To a solution of 2-(diethoxyphosphinyl)acetophenone (4.60 g, 17.9 mmol) in THF (30 mL) was added NaH (1.11 g, 60 % w/w dispersion in mineral oil) in small portions. The mixture was stirred for 30 min, benzoyl chloride (3.2 mL, 27.8 mmol) was then added slowly. The resulting mixture was stirred for 16 h and then CH_2Cl_2 (50 mL) and HCl (3 mL, 1M solution) were added sequentially to the above obtained suspension. The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phase were dried over $MgSO_4$ and the solvent was evaporated under vacuum. The resultant residue was purified by column chromatography on silica gel (AcOEt/MeOH, 9:1) to give (*Z*)-2-(diethoxyphosphoryl)-1-phenylvinyl benzoate **3a** as a pale yellow oil in 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.6 Hz, 2H), 7.64 (m, 1H), 7.58-7.50 (m, 4H), 7.42-7.38 (m, 3H), 6.10 (d, *J* = 8.8 Hz, 1H), 4.13-4.06 (m, 4H), 1.27-1.23 (m, 6H) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 13.9 ppm; FTIR ν 3062, 3036, 2981, 2928, 1740, 1626, 1478, 1233, 1083, 1065, 1020, 833, 754, 705 cm^{-1}; EI-MS (m/z): 360 (M^+, 2.9), 255 (2.6), 105 (100.0), 77 (28.0); HRMS(EI) calcd. for $[C_{19}H_{21}O_5P]^+$, 360.1121 [M^+]:, Found: 360.1129.

3.2 Procedure for the preparation of β-methyl-β-benzoloxy α,β-unsaturated phosphonic acid diethyl ester 3b.

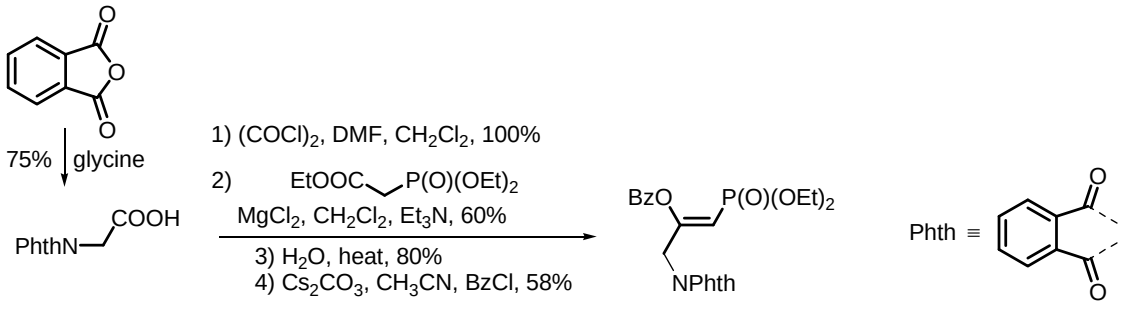


3b

β-Methyl-β-benzoloxy□-α,β-unsaturated phosphonic acid diethyl ester **3b** was prepared by following a procedure analogous to that reported by Pizzano et al.[9]

3b: Yellow liquid, 75% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.1, 0.9 Hz, 2H), 7.63-7.58 (m, 1H), 7.50-7.45 (m, 2H), 5.45 (dt, J = 11.1, 0.9 Hz, 1H), 4.08-3.98 (m, 4H), 2.22 (s, 3H), 1.24-1.19 (m, 6H) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.4 ppm; FTIR ν 3063, 2983, 2928, 1736, 1671, 1644, 1450, 1243, 1198, 1017, 785, 705 cm^{-1}; EI-MS (m/z): 298 (M^+, 1.7), 105 (100.0), 77 (22.3); HRMS(EI) calcd. for $[C_{14}H_{19}O_5P]^+$, 298.0965 [M^+], Found: 298.0966.

3.3 Preparation of β-PhtNHmethyl-β-benzoloxy α,β-unsaturated phosphonic acid diethyl ester 3c.



3c

Glycine (6.1 g, 80 mmol) and phthalic anhydride (16.7 g, 120 mmol) were added to a 25-mL round flask and heated to melt, and then cooled to room temperature. White needles of 2-(1,3-dioxoisoindolin-2-yl)acetic acid was obtained by recrystallization from 95% EtOH.

2-(1,3-dioxoisoindolin-2-yl)acetic acid (4.1 g, 20 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL), oxalyl chloride (100 mmol) and catalytic amount DMF were added to the above solution. The mixture was heated to reflux for 2 hours, the

solvent and excessive oxalyl chloride were removed under vacuum and the solids were washed with CH_2Cl_2 (2 × 10 mL). A light yellow powder was obtained which can be used without further purification.

Under argon, ethyl 2-(diethoxyphosphoryl)acetate (3.58 g, 16 mmol), magnesium chloride (1.71 g, 18 mmol), anhydrous CH_2Cl_2 (30 mL), freshly distilled Et_3N (5.6 mL) were added to a 100-mL round flask and the mixture was cooled to 0°C. The above prepared acid chloride in CH_2Cl_2 (10 mL) was added dropwise to the mixture. Once the substrate was consumed up as the TLC indicates, 1-M HCl (30 mL) was added to the solution. The mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent in vacuo, the residue was obtained as viscous oil, which was used without further purification.

Water (3 mL) was added to the above residue, and heated to 130°C for 2 hours. The mixture was cooled down to room temperature and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent in vacuo, the resultant residue was treated with cesium carbonate (35 mmol) and acetonitrile (30 mL), stirred at room temperature for 3 hours, and then benzoyl chloride (20 mmol) in acetonitrile (10 mL) was added dropwise at 0°C. Once the substrates were comsumed up, CH_2Cl_2 (20 mL) was added, and the reaction mixture was washed with 2-M HCl (3 × 10 mL), water (2 × 5 mL). The organic phase was dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the resulting residue was purified by column chromatography on silica with EA/PE as the eluent to afford **3c** as a yellow solid in 58% yield. M.p. 134-135°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 6.3, 0.9 Hz, 2H), 7.86-7.83 (m, 2H), 7.77-7.74 (m, 2H), 7.62-7.57 (m, 1H), 7.45 (t, *J* = 6.0 Hz, 2H), 5.69 (dd, *J* = 6.9, 0.3 Hz, 1H), 4.65 (s, 2H), 4.06-3.98 (m, 4H), 1.20 (t, *J* = 5.4 Hz, 6H) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 11.8 ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 163.8 (d, *J* = 1.7 Hz), 158.5 (d, *J* = 3.3 Hz), 134.1, 133.6, 131.6, 130.1, 128.4, 123.4, 107.2 (d, *J* = 139.4 Hz), 61.8 (d, *J* = 3.9 Hz), 40.2 (d, *J* = 11.7 Hz), 15.9 (d, *J* = 5.0 Hz) ppm; FTIR ν 3062, 2981, 1774, 1716, 1663, 1468, 1452, 1418, 1315, 1256, 1110, 1080, 1020, 953, 797, 732, 707 cm^{-1}; ESI-MS (m/z): 444.3 ($M+H^+$), 466.3 ($M+Na^+$); HRMS(EI) calcd. for $[C_{22}H_{22}NNaO_7P]^+$, 466.1026 [$M+Na^+$],

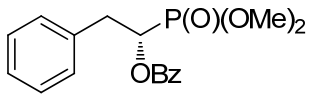
Found: 466.1034.

4 Asymmetric hydrogenation procedures

See the text for general procedures for hydrogenation of substrates **1a-v** and **3a-c**.

5. Characterization of the chiral products 2a-v and 4a-c

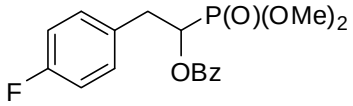
(*S*)-1-(dimethoxyphosphoryl)-2-phenylethyl benzoate, (*S*)-2a[10]



Oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +110.6 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.26-7.14 (m, 5H), 5.80-5.73 (m, 1H), 3.78 (d, *J* = 10.8 Hz, 3H), 3.76 (d, *J* = 10.2 Hz, 3H), 3,39-3.17 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 (d, *J* = 4.5 Hz), 136.0 (d, *J* = 13.7 Hz), 133.3, 129.7, 129.1, 129.0, 128.4, 128.3, 126.8, 68.4 (d, *J* = 164.8 Hz), 53.4 (d, *J* = 6.9 Hz), 53.2 (d, *J* = 6.3 Hz), 35.6 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.5 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel OD column, hexane: isopropanol = 97:3; flow rate = 1.0 mL/min; UV detection at 230 nm; t_R = 37.7 min (major), 57.0 min (minor).

(+)-1-(dimethoxyphosphoryl)-2-(4-fluorophenyl)ethyl benzoate, 2b[10]

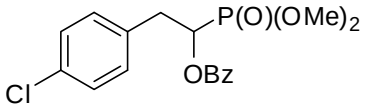


Oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +112.9 (*c* = 0.52, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.57(t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 2H), 7.24-7.19 (m, 2H), 6.91 (t, *J* = 8.4 Hz, 2H), 5.76-5.68 (m, 1H), 3.79 (d, *J* = 10.5 Hz, 3H), 3.77 (d, *J* = 10.5 Hz, 3H), 3.36-3.14 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ

164.9 (d, *J* = 5.2 Hz), 161.7 (d, *J* = 243.9 Hz), 133.4, 130.7 (d, *J* = 7.2 Hz), 129.7, 128.9, 128.4, 115.3 (d, *J* = 20.8 Hz), 68.5 (d, *J* = 164.3 Hz), 53.4 (d, *J* = 8,8 Hz), 53.3 (d, *J* = 8.8 Hz), 34.9 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.3 ppm, ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.2 (h) ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 14.9 min (minor), 18.4 min (major).

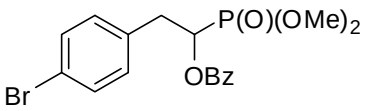
(+)-1-(dimethoxyphosphoryl)-2-(4-chlorophenyl)ethyl benzoate, 2c[10]



Pale oil, >99% conv. 99% ee, $[\alpha]_D^{20}$ = +118.7 (*c* = 0.91, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.19 (s, 4H), 5.76-5.68 (m, 1H), 3.78 (d, *J* = 10.5 Hz, 6H), 3,33-3.18 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 (d, *J* = 4.5 Hz), 134.5 (d, *J* = 13.6 Hz), 133.5, 132.7, 130.5, 129.7, 128.8, 128.6, 128.5, 68.1 (d, *J* = 164.8 Hz), 53.4 (d, *J* = 7.4 Hz), 53.2 (d, *J* = 7.4 Hz), 35.0 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.2 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 27.1 min (minor), 35.1 min (major).

(+)-1-(dimethoxyphosphoryl)-2-(4-bromophenyl)ethyl benzoate, 2d[10]

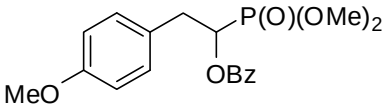


Pale yellow oil, >99% conv. 98% ee, $[\alpha]_D^{20}$ = +128.5 (*c* = 1.30, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.76-5.68 (m, 1H), 3.79 (d, *J* =

10.5 Hz, 3H), 3.78 (d, *J* = 10.5 Hz, 3H), 3.34-3.13 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 135.1 (d, *J* = 13.9 Hz), 133.4, 131.5, 130.8, 129.7, 128.8, 128.4, 120.8, 68.1 (d, *J* = 165.6 Hz), 53.5 (d, *J* = 6.6 Hz), 53.2 (d, *J* = 6.0 Hz), 35.1 (d, *J* = 1.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.2 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 16.1 min (minor), 20.7 min (major).

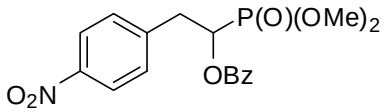
(*S*)-1-(dimethoxyphosphoryl)-2-(4-methoxyphenyl)ethyl benzoate, (*S*)-2e[10]



Pale oil, >99% conv. 98% ee, $[\alpha]_D^{20}$ = +117.7 (*c* = 1.36, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.75-5.68 (m, 1H), 3.78 (d, *J* = 10.5 Hz, 3H), 3.77 (d, *J* = 10.8 Hz, 3H), 3.68 (s, 3H), 3.34-3.11 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 (d, *J* = 4.5 Hz), 158.3, 133.2, 130.1, 129.6, 128.9, 128.3, 127.9 (d, *J* = 13.7 Hz), 113.7, 68.5 (d, *J* = 164.2 Hz), 55.0, 53.4 (d, *J* = 6.8 Hz), 53.1 (d, *J* = 6.8 Hz), 34.7 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.6 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 33.4 min (minor), 39.0 min (major).

(+)-1-(dimethoxyphosphoryl)-2-(4-nitrophenyl)ethyl benzoate, 2f[10]

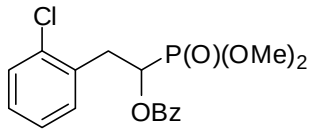


Oil, >99% conv. 98% ee, $[\alpha]_D^{20}$ = +126.0 (*c* = 1.05, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H),

7.47-7.42 (m, 4H), 5.81-5.74 (m, 1H), 3.81 (d, J = 10.5 Hz, 3H), 3.81 (d, J = 10.5 Hz, 3H), 3.79 (d, J = 11.1 Hz, 3H), 3.49-3.28 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 (d, J = 4.5 Hz), 147.0, 143.8 (d, J = 13.7 Hz), 133.7, 130.1, 129.7, 128.6, 128.5, 123.6, 67.6 (d, J = 167.1 Hz), 53.6 (d, J = 7.4 Hz), 53.4 (d, J = 7.4 Hz), 35.5 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.6 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 30.7 min (minor), 45.2 min (major).

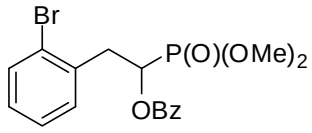
(+)-1-(dimethoxyphosphoryl)-2-(2-chlorophenyl)ethyl benzoate, 2g[10]



Yellow oil, >99% conv. 97% ee, $[\alpha]_D^{20}$ = +128.4 (*c* = 1.05, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.33-7.24 (m, 2H), 7.14-7.04 (m, 2H), 5.93-5.86 (m, 1H), 3.82 (d, J = 10.8 Hz, 6H), 3.56-3.49 (m, 1H), 3.40-3.28 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 134.2, 133.5, 133.3, 131.4, 129.7, 129.5, 128.8, 128.5, 128.3, 126.6, 66.9 (d, J = 166.2 Hz), 53.6 (d, J = 6.6 Hz), 53.3 (d, J = 6.6 Hz), 33.5 (d, J = 3.0 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.2 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 14.9 min (minor), 16.6 min (major).

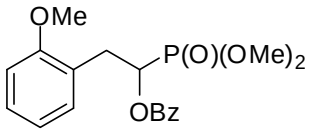
(+)-1-(dimethoxyphosphoryl)-2-(2-bromophenyl)ethyl benzoate, 2h



Oil, >99% conv. 98% ee, $[\alpha]_D^{20}$ = +128.7 (*c* = 0.92, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.58-7.49 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.28-7.23 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05-6.99 (m, 1H), 5.95-5.88 (m, 1H), 3.83 (d, *J* = 10.8 Hz, 6H), 3.57-3.49 (m, 1H), 3.42-3.30 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8 (d, *J* = 4.4 Hz), 135.3 (d, *J* = 14.9 Hz), 133.3, 132.9, 131.5, 129.7, 128.8, 128.7, 128.4, 127.2, 124.6, 66.9 (d, *J* = 165.8 Hz), 53.6 (d, *J* = 6.7 Hz), 53.3 (d, *J* = 6.7 Hz), 36.0 (d, *J* = 2.3 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.1 ppm; FTIR υ 3062, 3030, 2925, 1743, 1494, 1240, 1019, 800, 706 cm^{-1}; ESI-MS m/z: 414.9 $[M+H^+]$; HRMS (ESI) m/z: calc. for $[C_{17}H_{19}O_5PBr]^+$ $[M+H^+]$: 413.0148, Found: 413.0139.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 17.1 min (minor), 18.8 min (major).

(+)-1-(dimethoxyphosphoryl)-2-(2-methoxyphenyl)ethyl benzoate, 2i[10]

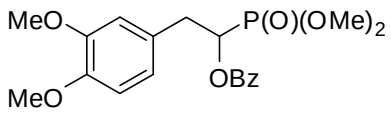


Pale yellow oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +140.1 (*c* = 1.36, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.16-7.12 (m, 2H), 6.80-6.73 (m, 2H), 5.94-5.87 (m, 1H), 3.81 (s, 3H), 3.80 (d, *J* = 10.2 Hz, 3H), 3.78 (d, *J* = 11.4 Hz, 3H), 3.49-3.41 (m, 1H), 3.20-3.08 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 157.4, 133.0, 131.0, 129.5, 129.1, 128.2 (d, *J* = 3.0 Hz), 124.1, 123.9, 120.0, 110.0, 67.0 (d, *J* = 164.4 Hz), 55.1, 53.3 (d, *J* = 6.6 Hz), 53.1 (d, *J* = 6.6 Hz), 30.7 (d, *J* = 1.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.1 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R =

18.7 min (major), 21.1 min (minor).

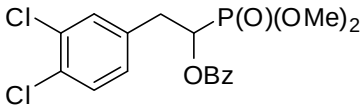
(+)-1-(dimethoxyphosphoryl)-2-(3,4-dimethoxyphenyl)ethyl benzoate, 2j[5]



Pale oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +130.3 (*c* = 1.03, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 6.78-6.68 (m, 3H), 5.74-5.67 (m, 1H), 3.77 (d, *J* = 9.9 Hz, 3H), 3.76 (d, *J* = 10.8 Hz, 3H), 3.76 (s, 3H), 3.65 (s, 3H), 3.29-3.09 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 148.4, 147.6, 133.3, 129.6, 128.9, 128.5, 128.3 (d, *J* = 4.2 Hz), 121.0 (d, *J* = 7.8 Hz), 112.0, 110.9, 68.6 (d, *J* = 163.8 Hz), 55.6, 55.4, 53.3 (d, *J* = 6.6 Hz), 53.1 (d, *J* = 6.6 Hz), 35.1 (d, *J* = 1.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.6 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 19.7 min (minor), 26.4 min (major).

(+)-1-(dimethoxyphosphoryl)-2-(3,4-dichlorophenyl)ethyl benzoate, 2k

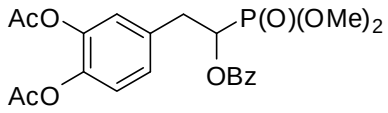


Pale yellow oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +113.0 (*c* = 1.28, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36-7.31 (m, 2H), 7.11-7.08 (m, 1H), 5.74-5.67 (m, 1H), 3.80 (d, *J* = 10.5 Hz, 6H), 3.33-3.13 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 136.0 (d, *J* = 13.4 Hz), 133.4, 129.8, 129.7, 129.1, 129.0, 128.5, 128.4, 128.2, 126.9, 68.7 (d, *J* = 165.1 Hz), 53.5 (d, *J* = 7.4 Hz), 53.2 (d, *J* = 6.0 Hz), 35.7 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.6 ppm; FTIR υ 3030, 2956, 2853, 1724, 1452, 1256, 1022, 799, 709 cm^{-1}; ESI (MS) m/z: 403.0 [$M+H^+$], 425.1 [$M+Na^+$]; HRMS (ESI) m/z: calc. for $[C_{17}H_{18}Cl_2O_5P]^+$:

403.0263, Found: 403.0266 [M+H$^+$].

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 14.4 min (minor), 15.9 min (major).

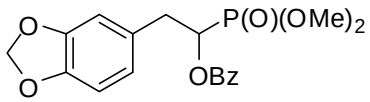
(+)-1-(dimethoxyphosphoryl)-2-(3,4-diacetoxylphenyl)ethyl benzoate, 2l



Yellow oil, >99% conv. 98% ee, $[\alpha]_D^{20}$ = +65.2 (*c* = 1.07, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.24-7.06 (m, 3H), 5.75-5.73 (m, 1H), 3.74 (d, *J* = 10.5 Hz, 6H), 3.33-3.18 (m, 2H), 2.23 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 167.9, 164.9, 141.7, 140.9, 134.7 (d, *J* = 11.4 Hz), 133.4, 129.7, 128.8, 128.4, 127.3, 124.2, 123.2, 68.1 (d, *J* = 165.6 Hz), 53.4 (d, *J* = 7.2 Hz), 53.2 (d, *J* = 7.2 Hz), 35.0, 20.5, 20.4 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.0 ppm. FTIR υ 2957, 2927, 1769, 1724, 1505, 1370, 1256, 1109, 1023, 899, 710 cm^{-1}; HRMS (EI) m/z: calc. for $[C_{21}H_{23}O_9P]^+$: 450.1074, Found: 450.1068 [M$^+$].

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 230 nm; t_R = 43.0 min (minor), 53.3 min (major).

(+)-1-(dimethoxyphosphoryl)-2-(benzo[d][1,3]dioxol-5-yl)ethyl benzoate, 2m

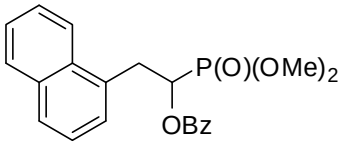


Yellow oil, >99% conv. 98% ee, $[\alpha]_D^{20}$ = +121.9 (*c* = 0.99, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.9 Hz, 2H), 7.59-7.54 (m, 1H), 7.46-7.41 (m, 2H), 6.74-6.63 (m, 3H), 5.86 (d, *J* = 3.9 Hz, 1H), 5.85 (d, *J* = 3.9 Hz, 1H), 5.73-5.66 (m,

1H), 3.79 (d, *J* = 10.8 Hz, 3H), 3.78 (d, *J* = 10.5 Hz, 3H), 3.30-3.08 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 (d, *J* = 4.2 Hz), 147.5, 146.3, 133.3, 129.7, 129.5 (d, *J* = 9.7 Hz), 128.9, 122.2, 109.3, 108.1, 100.7, 68.0 (d, *J* = 163.8 Hz), 53.4 (d, *J* = 6.6 Hz), 53.2 (d, *J* = 6.6 Hz), 35.3 (d, *J* = 1.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 27.9 ppm; FTIR υ 2956, 2853, 1743, 1644, 1508, 1239, 1093, 1018, 833, 706 cm^{-1}; EI-MS (m/z): 378 (M^+, 6.9), 256 (100), 161 (16.9), 146 (20.6), 135 (30.8), 105 (51.2), 77 (50.1), 51 (12.2); HRMS(EI) calcd. for $C_{18}H_{19}O_7P^+$ [M^+]: 378.0863, Found: 378.0871.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 230 nm; t_R = 23.6 min (minor), 28.1 min (major).

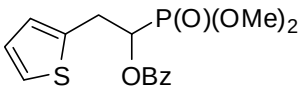
(+)-1-(dimethoxyphosphoryl)-2-(naphthalen-1-yl)ethyl benzoate, 2n[10]



White solid, >99% conv. 98% ee, m.p. 112-113°C; $[\alpha]_D^{20}$ = +177.6 (*c* = 1.13, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.57-7.31 (m, 6H), 7.29-7.25 (m, 1H), 5.93-5.85 (m, 1H), 3.91-3.58 (m, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 (d, *J* = 5.1 Hz), 133.7, 133.2, 131.8, 131.7, 129.6, 128.8, 128.7, 128.3, 127.8, 127.6, 126.3, 125.6, 125.1, 123.3, 67.9 (d, *J* = 165.1 Hz), 53.5 (d, *J* = 6.6 Hz), 53.2 (d, *J* = 6.6 Hz), 32.7 (d, *J* = 1.2 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.7 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column, hexane: isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 56.3 min (minor), 65.2 min (major).

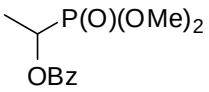
(+)-1-(dimethoxyphosphoryl)-2-(thiophen-2-yl)ethyl benzoate, 2o[10]



White solid, >99% conv. 90% ee, m.p. 82-83°C; $[\alpha]_D^{20}$ = +86.8 (*c* = 1.40, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 4.8 Hz, 1H), 6.89-6.84 (m, 2H), 5.76-5.69 (m, 1H), 3.80 (d, *J* = 10.5 Hz, 3H), 3.78 (d, *J* = 10.8 Hz, 3H), 3.60-3.42 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 137.8 (d, *J* = 15.7 Hz), 133.4, 129.8, 128.9, 128.4, 126.7, 126.4, 124.7, 68.2 (d, *J* = 163.8 Hz), 53.4 (d, *J* = 7.2 Hz), 53.2 (d, *J* = 7.2 Hz), 29.9 (d, *J* = 2.4 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.8 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 15.9 min (minor), 17.8 min (major).

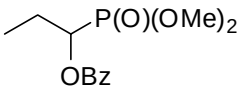
(*S*)-1-(dimethoxyphosphoryl)ethyl benzoate, (*S*)-2p[10]



Oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = –15.9 (*c* = 0.98, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 5.59-5.54 (m, 1H), 3.84 (d, *J* = 10.5 Hz, 3H), 3.82 (d, *J* = 10.5 Hz, 3H), 1.61 (dd, *J* = 7.2, 16.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2 (d, *J* = 7.3 Hz), 133.3, 129.7, 129.2, 128.4, 64.5 (d, *J* = 169.9 Hz), 53.4 (d, *J* = 6.8 Hz), 53.2 (d, *J* = 6.8 Hz), 15.1 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.9 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 96: 4; flow rate = 0.8 mL/min; UV detection at 254 nm; t_R = 28.6 min (major), 31.2 min (minor).

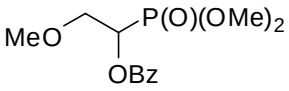
(*S*)-1-(dimethoxyphosphoryl)propyl benzoate, (*S*)-2q[10]



Oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +15.9 (*c* = 1.25, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.95 (m, 2H), 7.49-7.44 (m, 1H), 7.36-7.31 (m, 2H), 5.40-5.33 (m, 1H), 3.70-3.62 (m, 6H), 1.93-1.87 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2 (d, *J* = 4.8 Hz), 133.1, 129.5, 128.9, 128.2, 68.8 (d, *J* = 165.6 Hz), 53.1 (d, *J* = 7.2 Hz), 52.8 (d, *J* = 6.6 Hz), 22.6, 9.9 (d, *J* = 12.7 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.2 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column, hexane: isopropanol = 98: 2; flow rate = 0.9 mL/min; UV detection at 254 nm; t_R = 33.4 min (minor), 35.9 min (major).

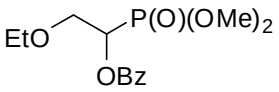
(*S*)-1-(dimethoxyphosphoryl)-2-methoxyethyl benzoate, (*S*)-2r[10]



Oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +7.3 (*c* = 1.24, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.06 (m, 2H), 7.61-7.57 (m, 1H), 7.48-7.44 (m, 2H), 5.80-5.74 (m, 1H), 3.96-3.80 (m, 8H), 3.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 5.5 Hz), 133.3, 129.8, 129.3 (d, *J* = 67.2 Hz), 128.3, 70.2 (d, *J* = 5.5 Hz), 67.3 (d, *J* = 164.0 Hz), 58.8, 53.4 (d, *J* = 6.7 Hz), 53.1 (d, *J* = 6.7 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 20.8 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel OD column, hexane: isopropanol = 98: 2; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 41.6 min (minor), 47.5 min (major).

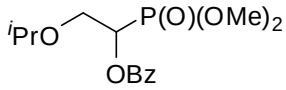
(+)-1-(dimethoxyphosphoryl)-2-ethoxyethyl benzoate, 2s[10]



Pale oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +13.0 (*c* = 1.26, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 5.80-5.73 (m, 1H), 3.98-3.86 (m, 2H), 3.82 (d, *J* = 10.8 Hz, 3H), 3.81 (d, *J* = 10.8 Hz, 3H), 3.63-3.49 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2 (d, *J* = 5.1 Hz), 133.3, 129.8, 129.4 (d, *J* = 47.2 Hz), 128.4, 68.2 (d, *J* = 5.1 Hz), 67.5 (d, *J* = 163.6 Hz), 66.7, 53.5 (d, *J* = 6.8 Hz), 53.1 (d, *J* = 6.8 Hz), 14.9 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.1 ppm.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 18.1 min (minor), 20.4 min (major).

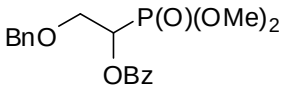
(+)-1-(dimethoxyphosphoryl)-2-isopropoxyethyl benzoate, 2t



Pale oil, >99% conv. >99% ee, $[\alpha]_D^{20}$ = +15.2 (*c* = 1.06, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.60-7.56 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.75-5.69 (m, 1H), 3.94-3.89 (m, 2H), 3.85-3.75 (m, 6H), 3.66-3.63 (m, 1H), 1.14 (d, *J* = 6.4 Hz, 3H), 1.12 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 5.1 Hz), 133.2, 129.7, 129.4 (d, *J* = 47.4 Hz), 128.3, 72.1, 67.8 (d, *J* = 163.2 Hz), 65.8 (d, *J* = 5.5 Hz), 53.4 (d, *J* = 6.4 Hz), 53.0 (d, *J* = 6.4 Hz), 21.8, 21.6 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 21.1 ppm; HRMS (EI) m/z: calc. for $[C_{14}H_{21}O_6P]^+$: 316.1070, Found: 316.1078.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 96:4; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 21.1 min (minor), 22.3 min (major).

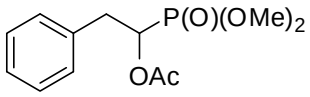
(+)-1-(dimethoxyphosphoryl)-2-(benzyloxy)ethyl benzoate, 2u



Oil, >99% conv. 98% ee, $[\alpha]_D^{20}$ = +19.8 (*c* = 1.10, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.34-7.22 (m, 5H), 5.85-5.78 (m, 1H), 4.65-4.52 (m, 2H), 4.01-3.92 (m, 2H), 3.79 (d, *J* = 10.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 137.4, 133.4, 129.9, 129.1, 128.4, 128.3, 127.7, 127.6, 73.1, 67.9 (d, *J* = 5.7 Hz), 67.5 (d, *J* = 163.6 Hz), 53.6 (d, *J* = 6.8 Hz), 53.2 (d, *J* = 6.8 Hz) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.9 ppm; FTIR υ 2956, 2856, 1726, 1493, 1251, 1107, 1026, 831, 711 cm^{-1}; GCMS (EI) (m/z): 365 ($M+H^+$, 0.4), 258 (3.5), 242 (2.6), 214 (2.0), 153 (30.0), 137 (100.0), 105 (84.5), 91 (58.7), 77 (38.3), 57 (13.1); HRMS(EI) calcd. for $C_{18}H_{21}O_6P^+$ [M^+]: 364.1070, Found: 364.1073.

The enantiomeric excess was determined by HPLC on a Chiralcel OJ column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 230 nm; t_R = 16.3 min (major), 27.8 min (minor).

(+)-1-(dimethoxyphosphoryl)-2-phenylethyl acetate, 2v

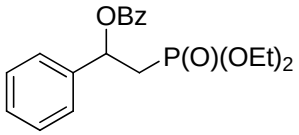


Pale oil, >99% conv. 96% ee, $[\alpha]_D^{20}$ = +40.0 (*c* = 1.06, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.08 (m, 5H), 5.54-5.46 (m, 1H), 3.78 (d, *J* = 9.9 Hz, 3H), 3.75 (d, *J* = 10.2 Hz, 3H), 3.25-3.14 (m, 1H), 3.10-2.93 (m, 1H), 1.96 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1 (d, *J* = 5.1 Hz), 135.9 (d, *J* = 13.6 Hz), 128.9, 128.2 (d, *J* = 5.5 Hz), 126.7, 67.6 (d, *J* = 165.3 Hz), 53.1 (d, *J* = 5.1 Hz), 53.0 (d, *J* = 3.9 Hz), 35.2, 20.2 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.7 ppm. FTIR υ 3030, 2960, 2854, 1749, 1496, 1259, 1017, 874, 796 cm^{-1}; GCMS (EI) (m/z): 272 (M^+); HRMS(EI) calcd. for

$C_{18}H_{21}O_6P^+$ [M^+]: 272.0808, Found: 272.0816.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column, hexane: isopropanol = 95: 5; flow rate = 0.75 mL/min; UV detection at 217 nm; t_R = 19.5 min (major), 21.0 min (minor).

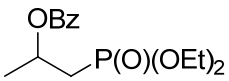
(+)-1-phenyl-2-(diethoxyphosphoryl)ethyl benzoate, 4a



Pale oil, >99% conv. 95% ee, $[\alpha]_D^{20}$ = +12.5 (*c* = 1.13, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.57-7.53 (m, 1H), 7.48-7.27 (m, 7H), 6.35-6.28 (m, 1H), 4.07-3.94 (m, 4H), 2.76-2.63 (m, 1H), 2.49-2.35 (m, 1H), 1.25-1.16 (m, 6H) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 26.5 ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 139.8 (d, *J* = 10.7 Hz), 133.0, 129.9, 129.6, 128.5, 128.3, 128.2, 126.4, 71.5 (d, *J* = 2.2 Hz), 61.8 (d, *J* = 6.7 Hz), 61.6 (d, *J* = 6.2 Hz), 33.5 (d, *J* = 139.9 Hz), 16.2 (d, *J* = 6.1 Hz) ppm; FTIR υ 2961, 2926, 1716, 1452, 1259, 1097, 1017, 796, 711 cm^{-1}; EI-MS (m/z): 362 (M^+, 4.4), 257 (100.0), 201 (24.9), 105 (60.5), 77 (30.1); HRMS(EI) calcd. for $C_{19}H_{23}O_5P^+$ [M^+]: 362.1278, Found: 362.1279.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 214 nm; t_R = 10.2 min (minor), 14.3 min (major).

(+)-1-(diethoxyphosphoryl)isopropyl benzoate, 4b

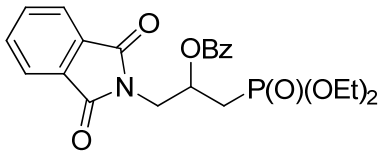


Pale oil, >99% conv. 96% ee, $[\alpha]_D^{20}$ = -3.9 (*c* = 1.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.57-7.53 (m, 1H), 7.45-7.41 (m, 2H), 5.46-5.42 (m, 1H), 4.14-4.06 (m, 4H), 2.41-2.31 (m, 1H), 2.19-2.09 (m, 1H), 1.51 (dd, *J* = 6.4, 0.8 Hz, 3H)

1.32-1.24 (m, 6H) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 27.6 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 132.8, 130.2, 129.5, 128.2, 66.8, 61.73 (d, *J* = 6.4 Hz), 61.72 (d, *J* = 7.5 Hz), 32.7 (d, *J* = 139.3 Hz), 21.1 (d, *J* = 8.1 Hz), 16.3 (d, *J* = 5.1 Hz), 16.2 (d, *J* = 5.1 Hz) ppm; EI-MS (m/z): 300 (M^+, 3.0), 195 (100.0), 179 (36.2), 105 (87.3), 77 (28.8); HRMS(EI) calcd. for $C_{14}H_{21}O_5P^+$ [M^+]: 300.1121, Found: 300.1129.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 214 nm; t_R = 11.1 min (major), 12.2 min (minor).

(+)-1-(diethoxyphosphoryl)-3-(1,3-dioxoisoindolin-2-yl)propan-2-yl benzoate, 4c



Pale oil, 86% conv. 93% ee, $[\alpha]_D^{20}$ = +29.0 (*c* = 1.24, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.6 Hz, 2H), 7.85-7.79 (m, 2H), 7.74-7.68 (m, 2H), 7.53 (t, *J* = 10.0 Hz, 1H), 7.40 (t, *J* = 10.0 Hz, 2H), 5.68-5.60 (m, 1H), 4.20-4.05 (m, 6H), 2.46-2.24 (m, 2H), 1.34-1.21 (m, 6H) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 25.3 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 165.6, 134.0, 133.0, 131.7, 129.6, 129.5, 128.2, 123.3, 67.8 (d, *J* = 2.3 Hz), 62.11 (d, *J* = 6.6 Hz), 62.04 (d, *J* = 7.4 Hz), 41.2 (d, *J* = 9.7 Hz), 29.3 (d, *J* = 140.9 Hz), 16.2 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 6.2 Hz) ppm; FTIR υ 3063, 2962, 1774, 1714, 1468, 1452, 1425, 1393, 1317, 1176, 1098, 1045, 958, 887, 797, 709 cm^{-1}; ESI-MS (m/z): 446.2 ($M+H^+$), 468.1 ($M+Na^+$); HRMS(ESI) calcd. for $[C_{22}H_{25}NO_7P]^+$ [$M+H^+$]: 446.1363, Found: 446.1364.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 214 nm; t_R = 72.8 min (major), 85.1 min (minor).

6. References

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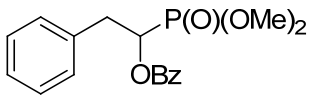
7. HPLC spectra of chiral products



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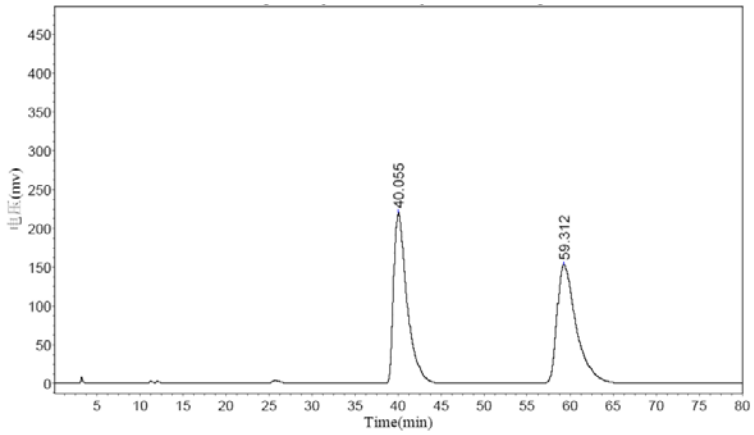
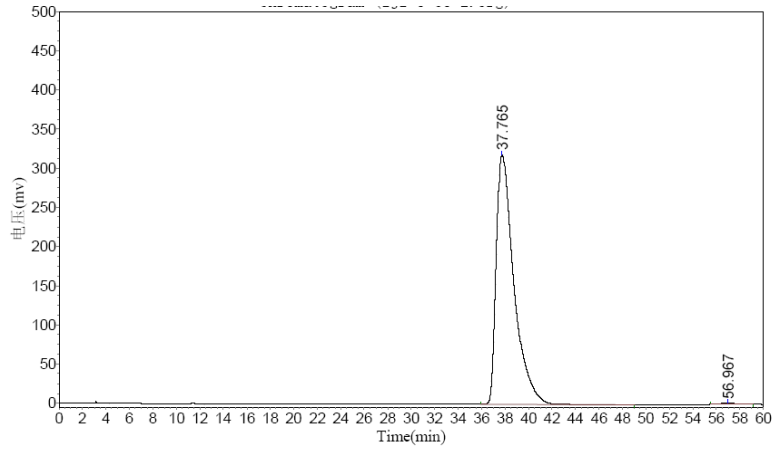


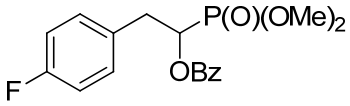
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		40.055	220038.484	23685210.000	49.9996
2		59.312	153045.469	23685618.000	50.0004
Total			373083.953	47370828.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		37.765	318808.563	33443142.000	99.5353
2		56.967	1436.455	156140.313	0.4647
Total			320245.018	33599282.313	100.0000



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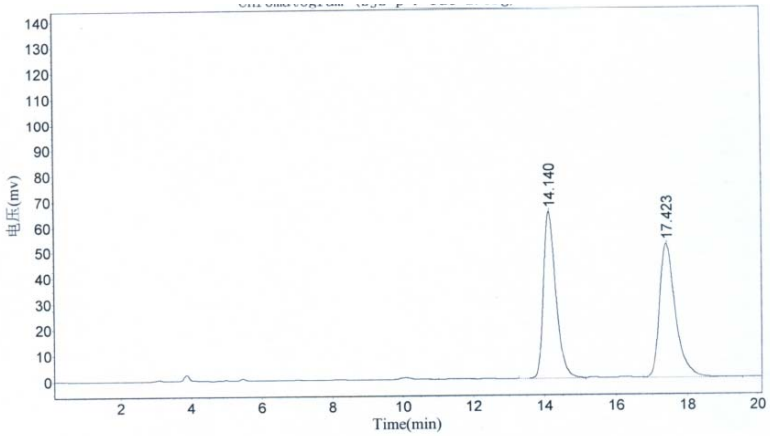
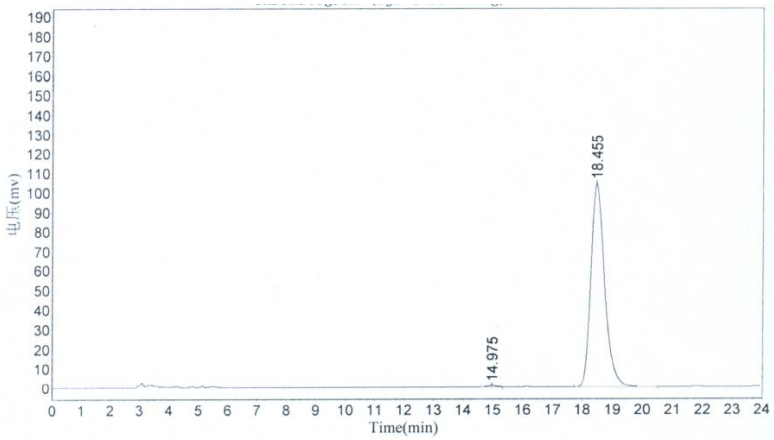


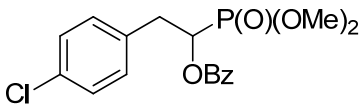
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.140	64558.586	1546047.250	49.3196
2		17.423	51704.863	1588706.250	50.6804
Total			116263.449	3134753.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.975	618.134	13030.300	0.3901
2		18.455	104232.195	3327167.250	99.6099
Total			104850.329	3340197.550	100.0000



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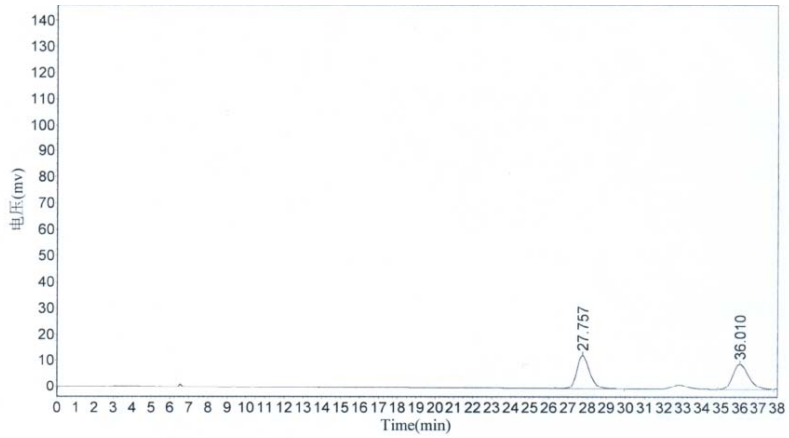
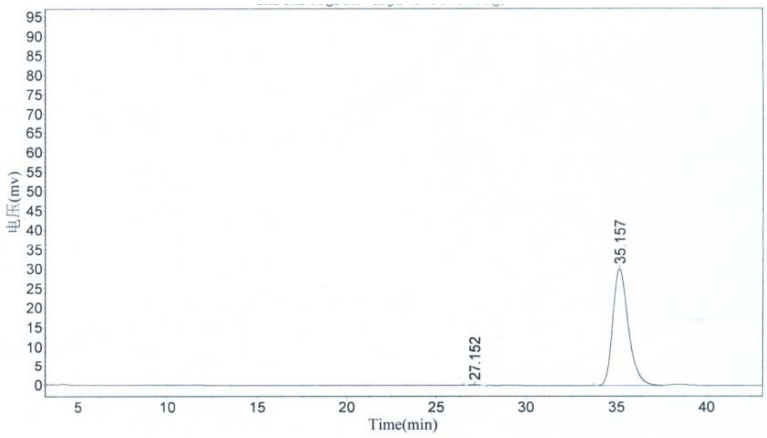


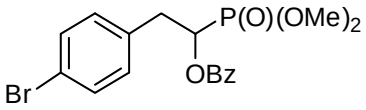
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.757	12870.440	603530.938	50.2448
2		36.010	9939.397	597649.875	49.7552
Total			22809.838	1201180.813	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.152	162.135	6077.400	0.3350
2		35.157	30203.377	1808229.375	99.6650
Total			30365.512	1814306.775	100.0000



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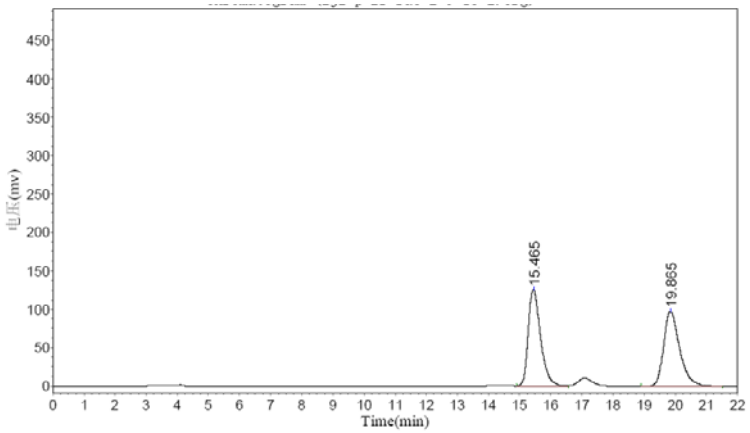
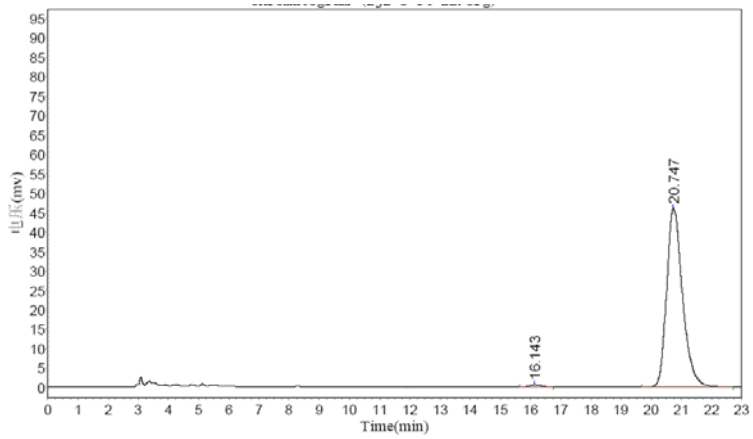


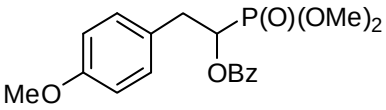
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.465	125339.563	3428878.250	50.0082
2		19.865	96402.172	3427753.000	49.9918
Total			221741.734	6856631.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.143	575.610	15096.900	0.8891
2		20.747	46048.645	1682806.125	99.1109
Total			46624.255	1697903.025	100.0000



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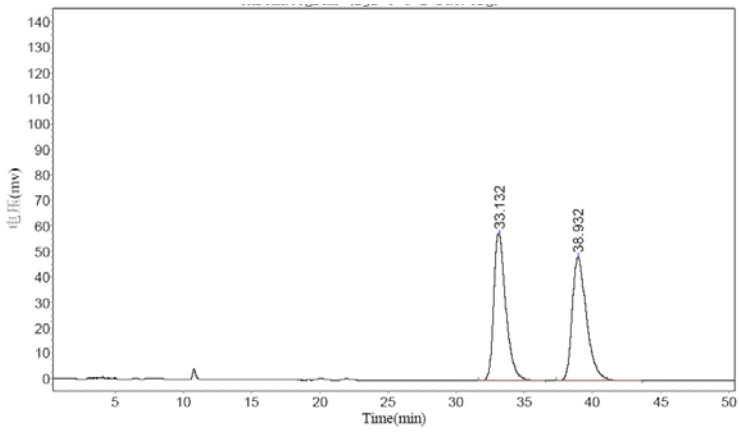
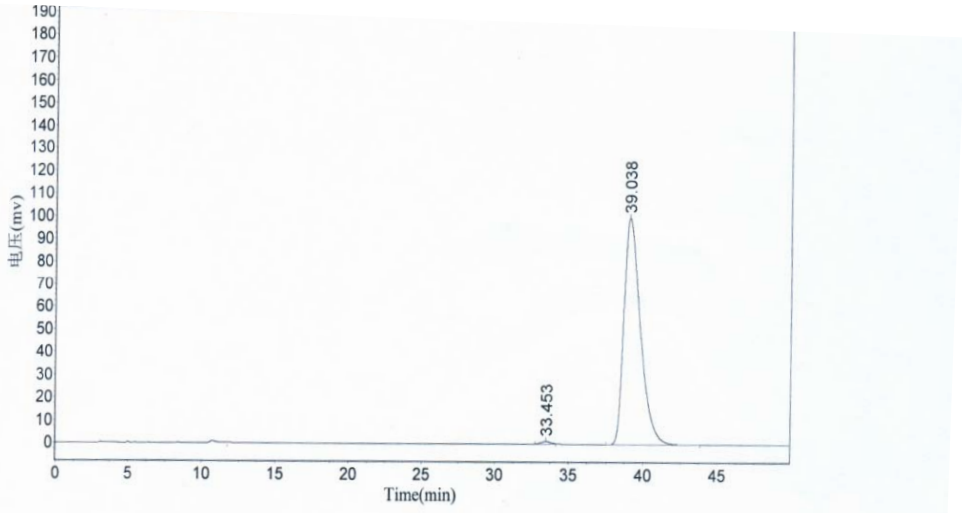


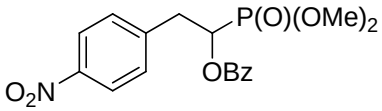
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		33.132	57405.199	3495765.000	49.9406
2		38.932	48236.684	3504079.500	50.0594
Total			105641.883	6999844.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		33.453	949.408	42598.797	0.5526
2		39.038	99546.406	7665752.500	99.4474
Total			100495.814	7708351.297	100.0000



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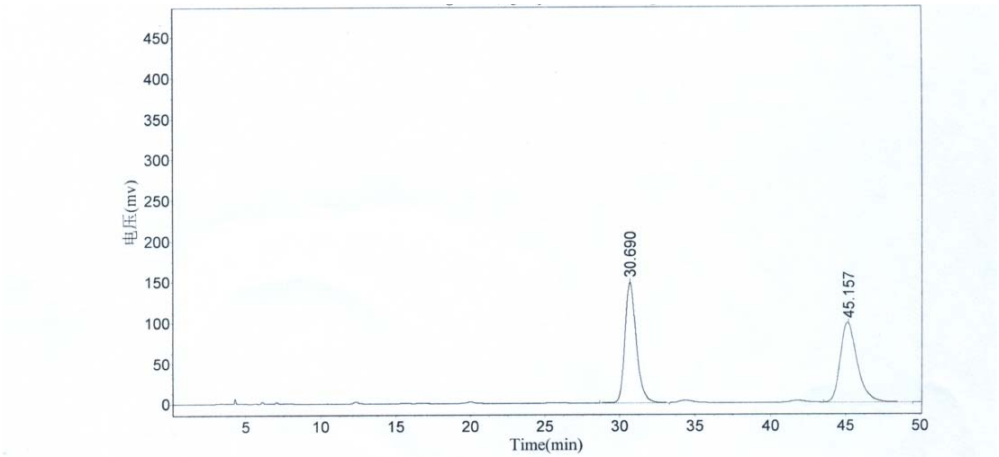
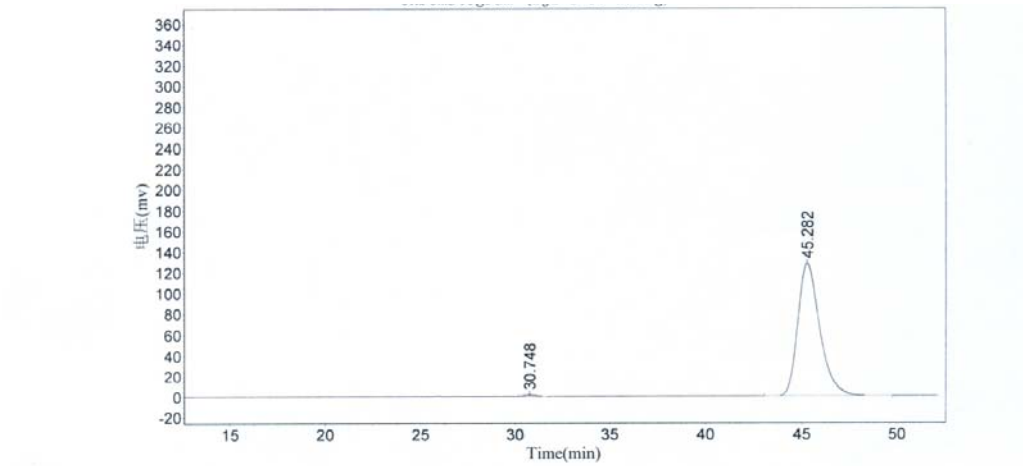


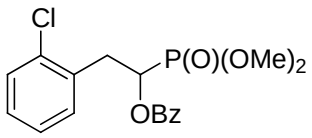
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.690	146932.297	7770098.000	50.0592
2		45.157	98010.961	7751709.500	49.9408
Total			244943.258	15521807.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.748	1306.846	58244.297	0.5676
2		45.282	128006.984	10202868.000	99.4324
Total			129313.831	10261112.297	100.0000



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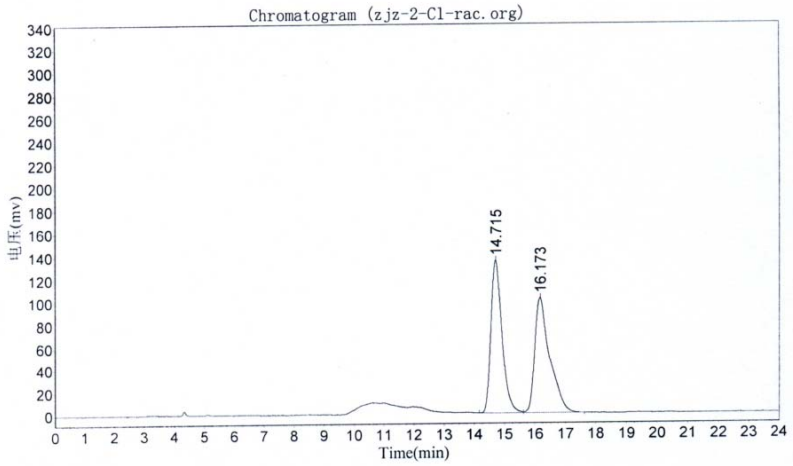
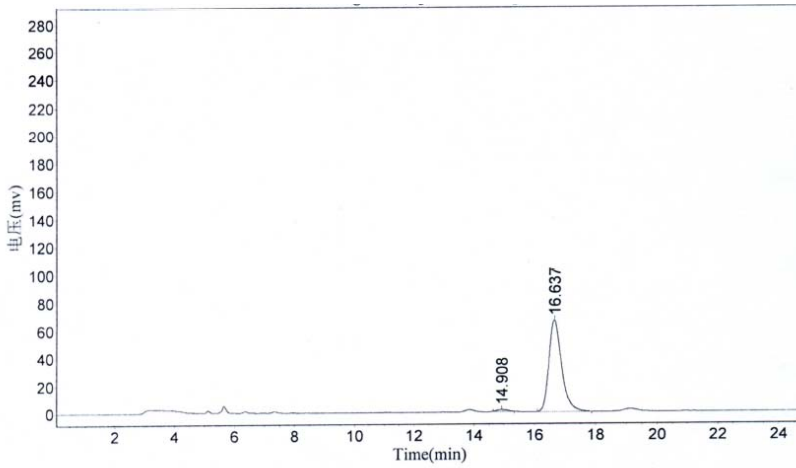


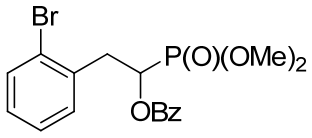
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.715	135001.828	3456545.000	49.8858
2		16.173	101928.891	3472374.250	50.1142
Total			236930.719	6928919.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.908	1196.457	28771.199	1.4806
2		16.637	66061.508	1914408.375	98.5194
Total			67257.964	1943179.574	100.0000



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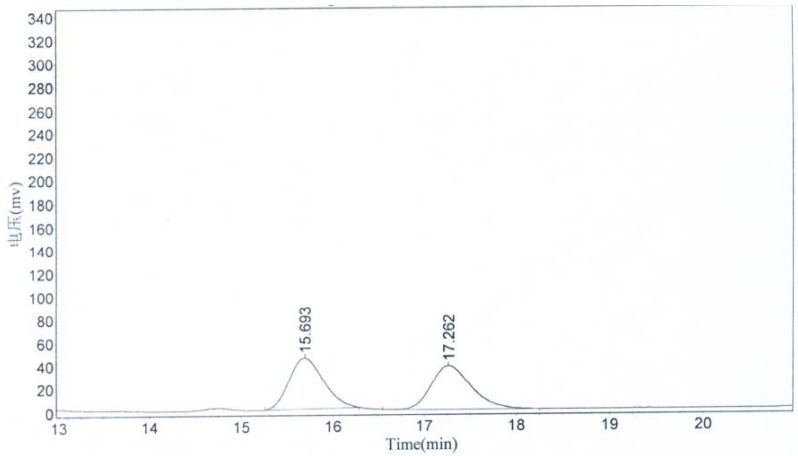
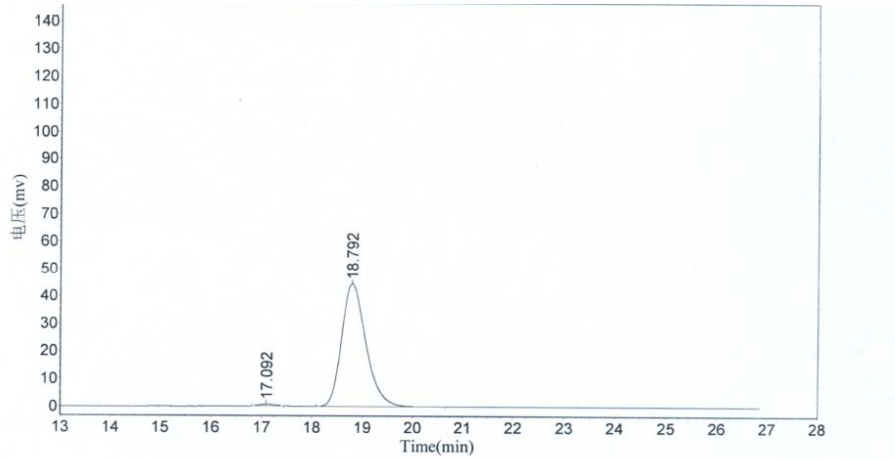


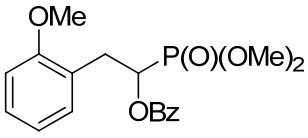
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.693	44048.031	1138550.750	50.4809
2		17.262	37463.922	1116857.125	49.5191
Total			81511.953	2255407.875	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.092	575.103	12170.450	0.8065
2		18.792	44512.398	1496787.250	99.1935
Total			45087.501	1508957.700	100.0000



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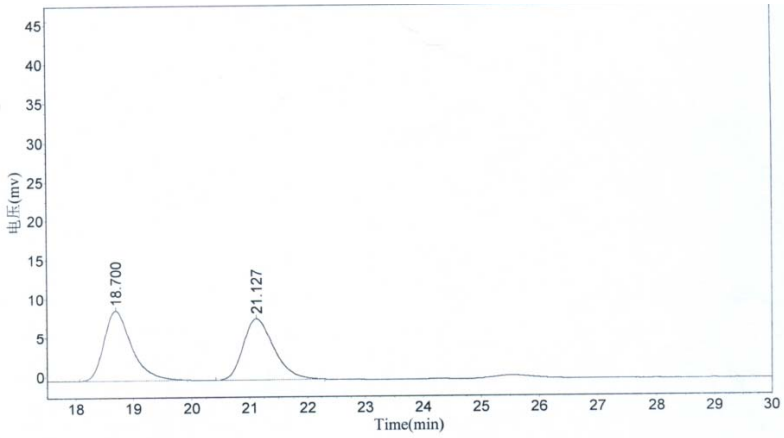
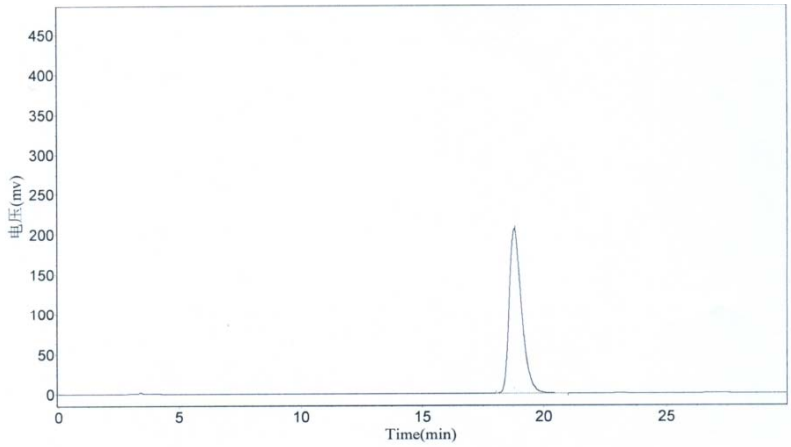


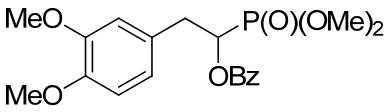
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.700	8955.226	295477.906	50.8956
2		21.127	7843.194	285078.813	49.1044
Total			16798.420	580556.719	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.815	205872.000	7212824.000	100.0000
Total			205872.000	7212824.000	100.0000



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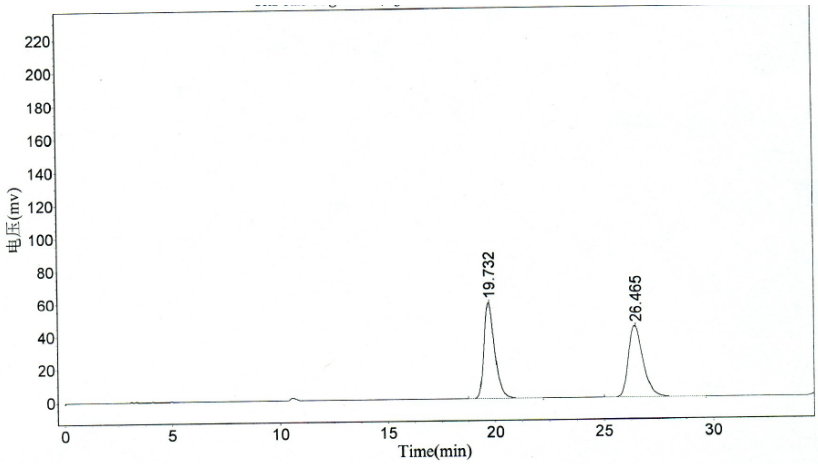
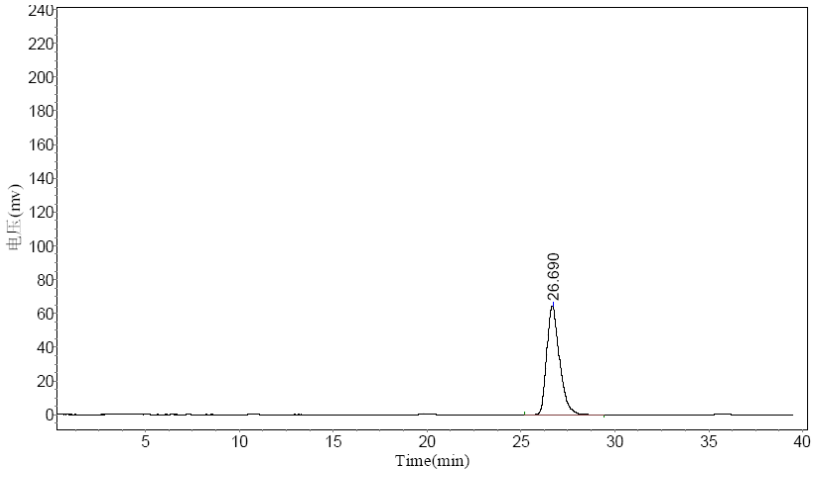


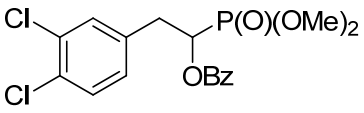
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.732	58278.152	2006443.375	50.0281
2		26.465	42889.887	2004189.000	49.9719
Total			101168.039	4010632.375	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.690	64312.758	3036840.000	100.0000
Total			64312.758	3036840.000	100.0000



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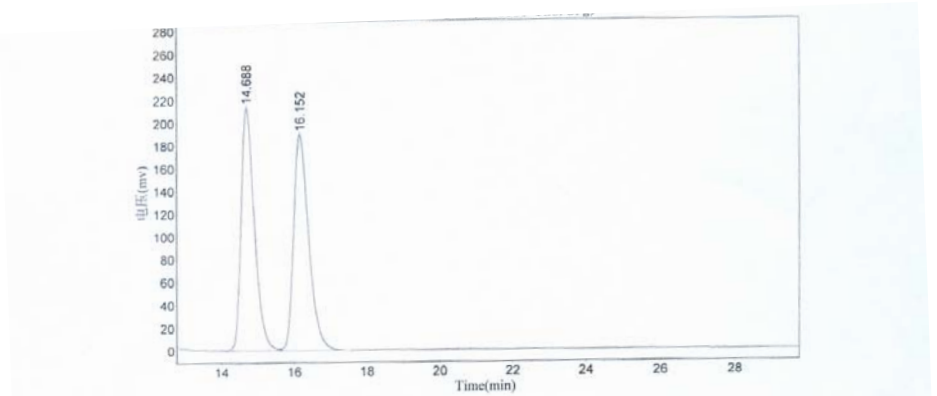
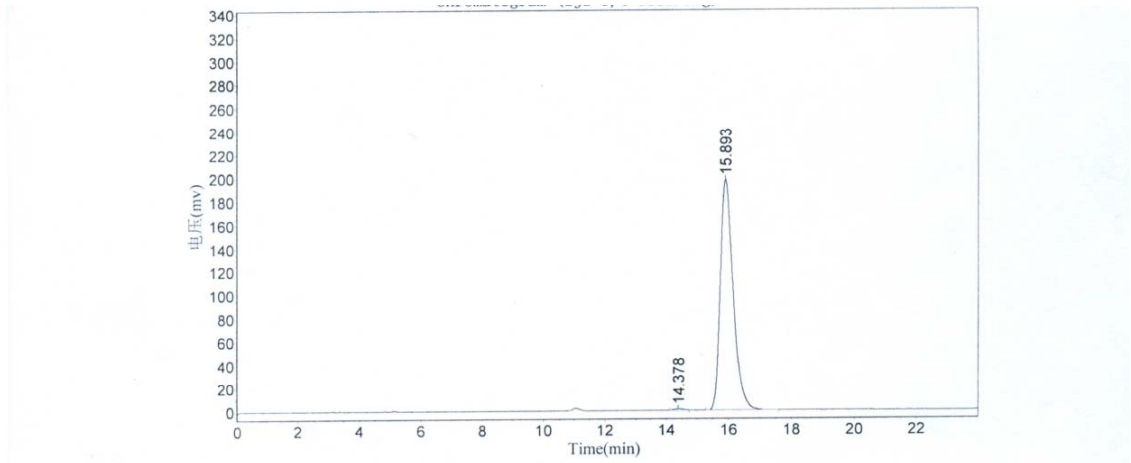


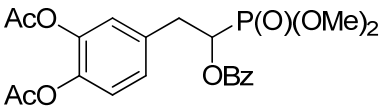
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.688	213336.125	5443739.000	49.8612
2		16.152	190007.641	5474049.500	50.1388
Total			403343.766	10917788.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.378	1063.372	20776.900	0.3656
2		15.893	197785.953	5662615.500	99.6344
Total			198849.325	5683392.400	100.0000



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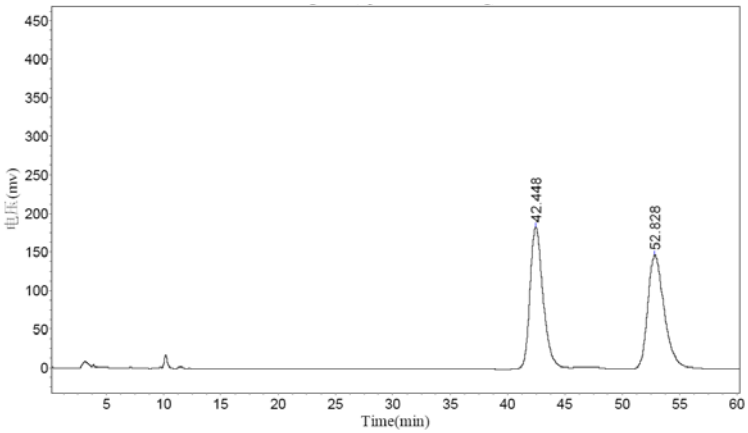
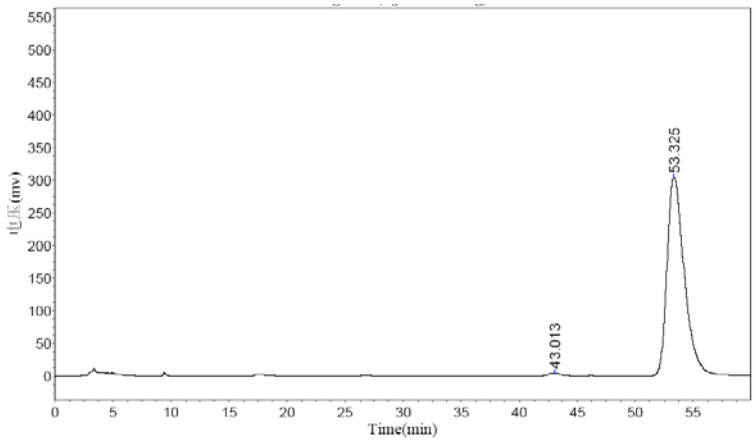


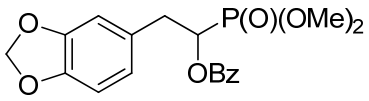
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		42.448	183592.766	14413630.000	49.8561
2		52.828	147096.828	14496808.000	50.1439
Total			330689.594	28910438.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		43.013	3171.642	180940.359	0.5718
2		53.325	303294.500	31461396.000	99.4282
Total			306466.142	31642336.359	100.0000



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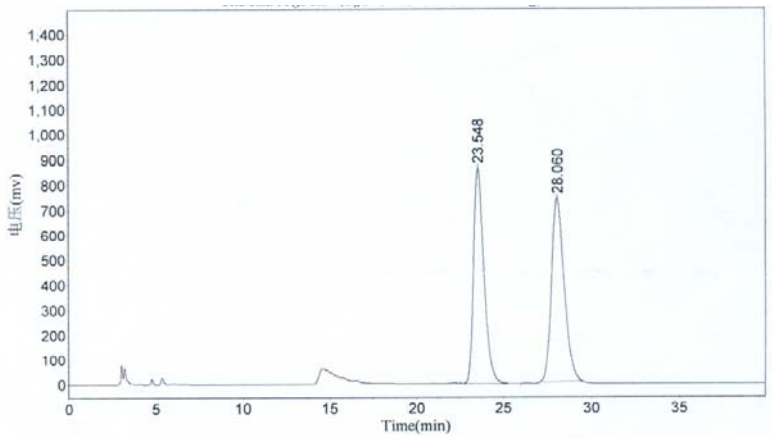
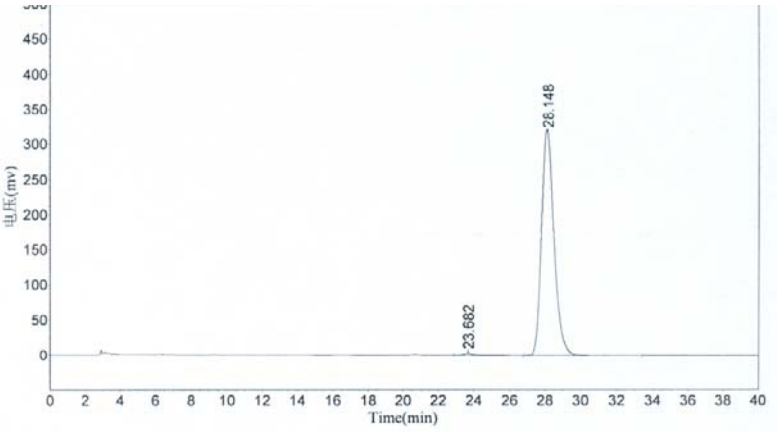


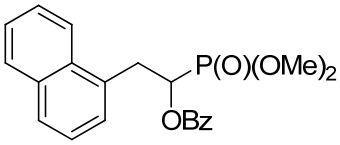
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.548	862295.250	35590900.000	49.1631
2		28.060	736040.938	36802652.000	50.8369
Total			1598336.188	72393552.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.682	3176.207	129854.500	0.8216
2		28.148	321080.219	15676152.000	99.1785
Total			324256.426	15806006.500	100.0000



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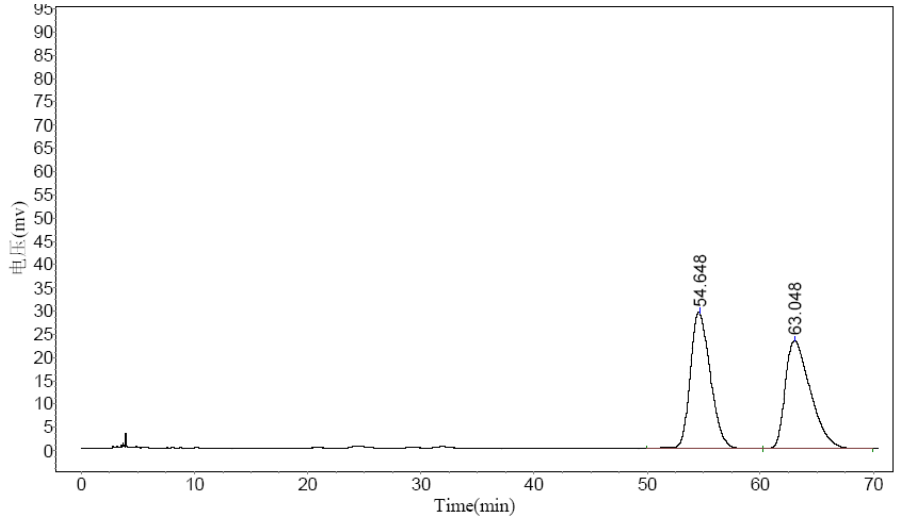
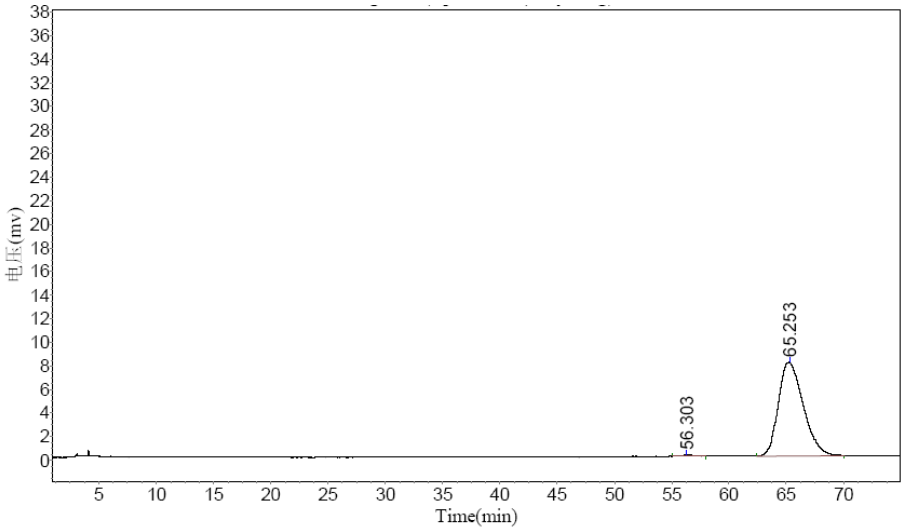


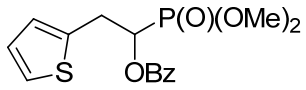
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		54.648	29408.721	3633888.000	50.1886
2		63.048	23214.143	3606583.500	49.8114
Total			52622.863	7240471.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		56.303	101.257	8572.146	0.7121
2		65.253	7944.277	1195142.625	99.2879
Total			8045.535	1203714.771	100.0000



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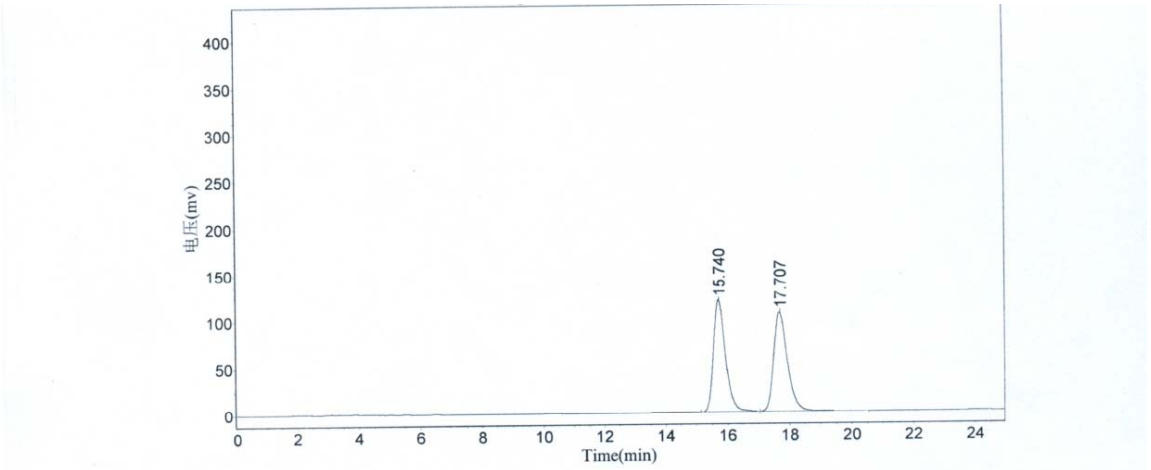
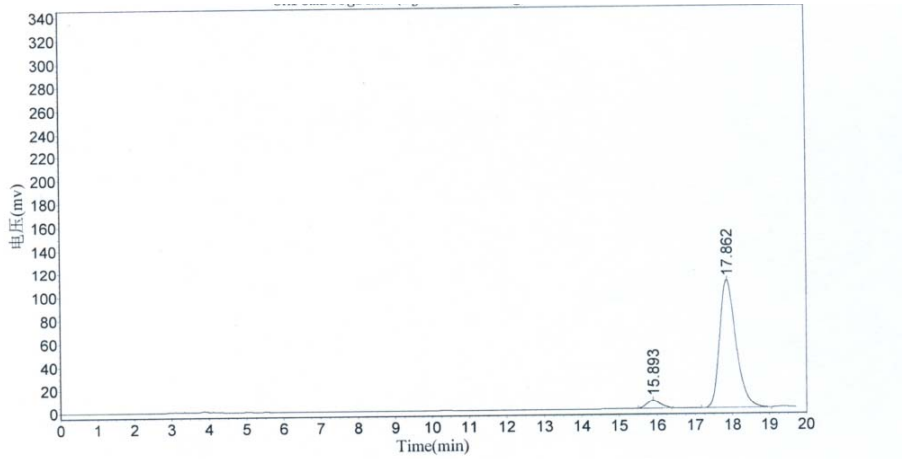


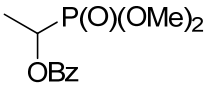
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.740	119328.922	3248367.000	49.8150
2		17.707	105969.094	3272489.250	50.1850
Total			225298.016	6520856.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.893	6813.240	164188.203	4.6615
2		17.862	109624.711	3358045.750	95.3385
Total			116437.951	3522233.953	100.0000



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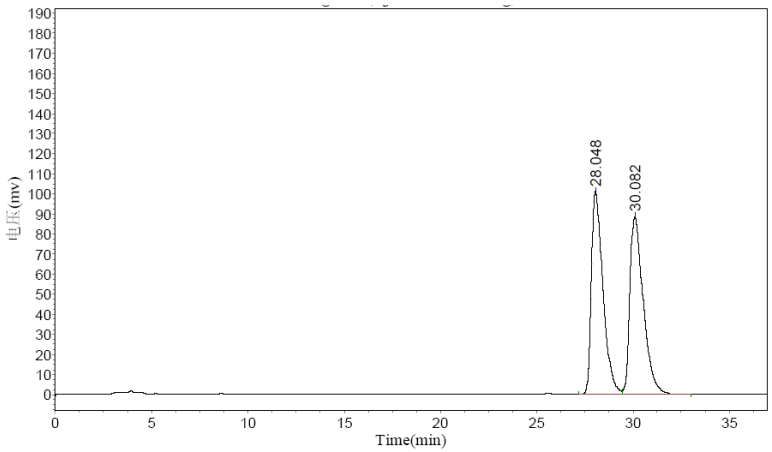
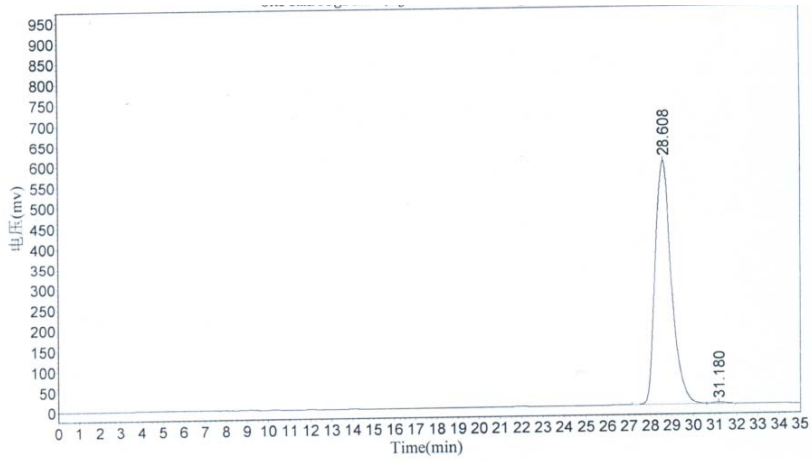


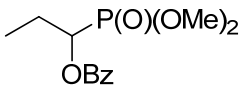
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.048	100934.102	4238598.000	49.8094
2		30.082	88523.922	4271034.000	50.1906
Total			189458.023	8509632.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.608	596967.500	31250366.000	99.5933
2		31.180	3277.941	127617.609	0.4067
Total			600245.441	31377983.609	100.0000



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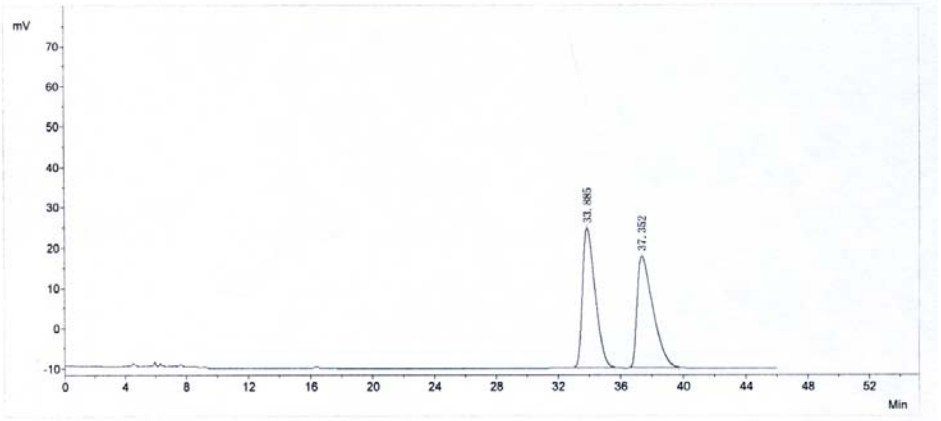
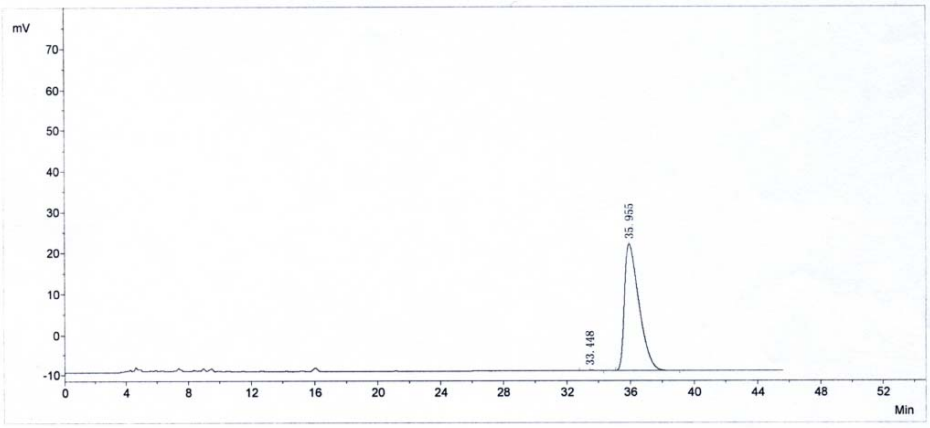
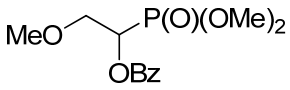


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	33.885	34438.4	1931556.7	50.0339
2	2	37.352	27638.9	1928936.4	49.9661
Total			62077.3	3860493.1	100.0000



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	33.448	80.9	3516.8	0.1788
2	2	35.955	31057.0	1963363.5	99.8212
Total			31137.9	1966880.3	100.0000



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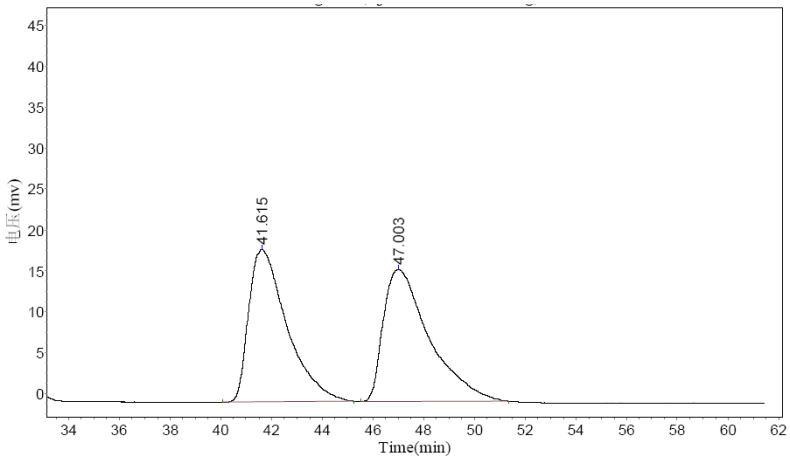
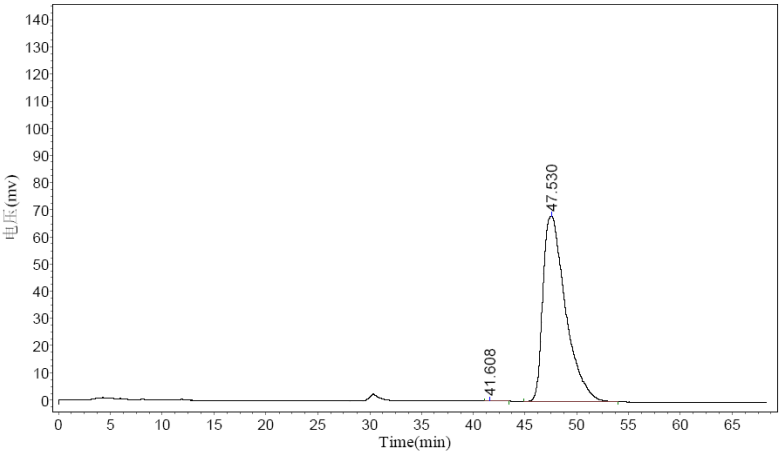


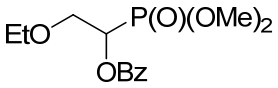
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		41.615	18630.910	1945516.875	49.1301
2		47.003	16095.930	2014410.000	50.8699
Total			34726.840	3959926.875	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		41.608	137.478	8783.104	0.0847
2		47.530	68326.258	10355696.000	99.9153
Total			68463.736	10364479.104	100.0000



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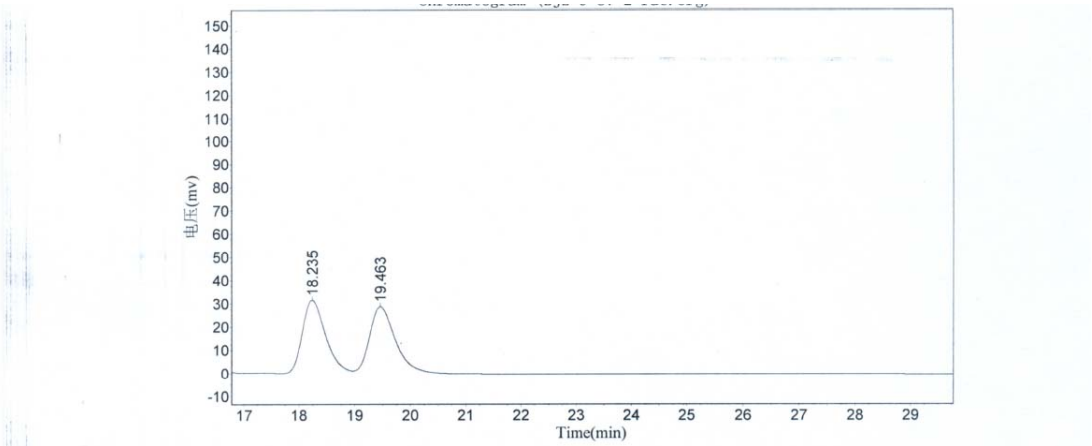
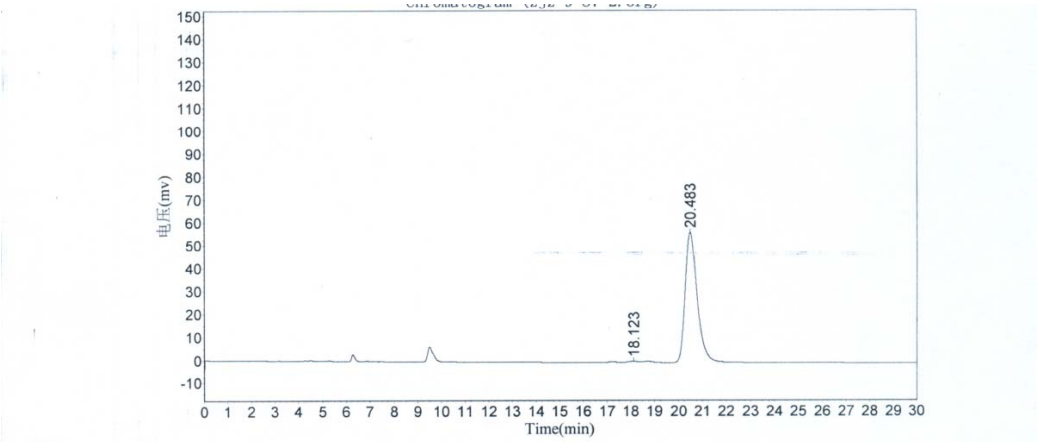


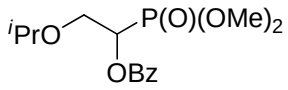
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.235	32025.313	954161.125	49.5068
2		19.463	29110.891	973170.688	50.4932
Total			61136.203	1927331.813	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.123	145.353	4412.502	0.2235
2		20.483	56793.594	1969855.000	99.7765
Total			56938.947	1974267.502	100.0000



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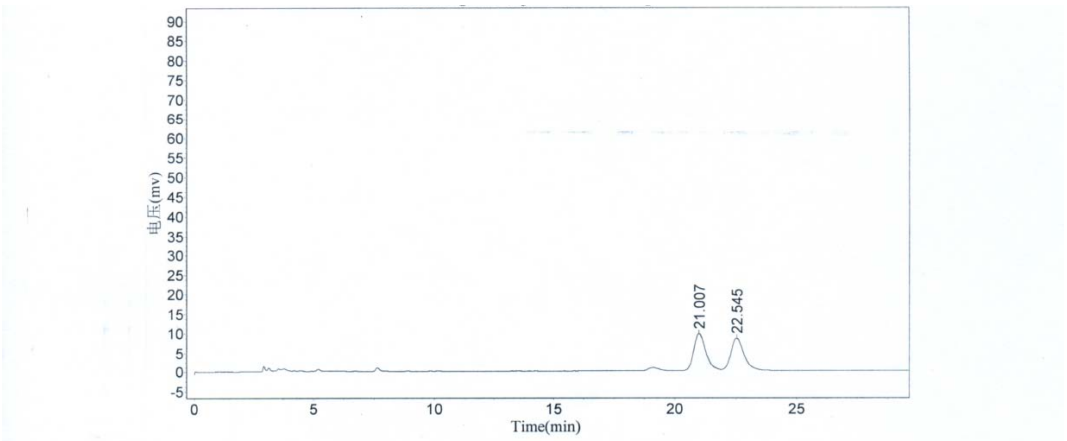
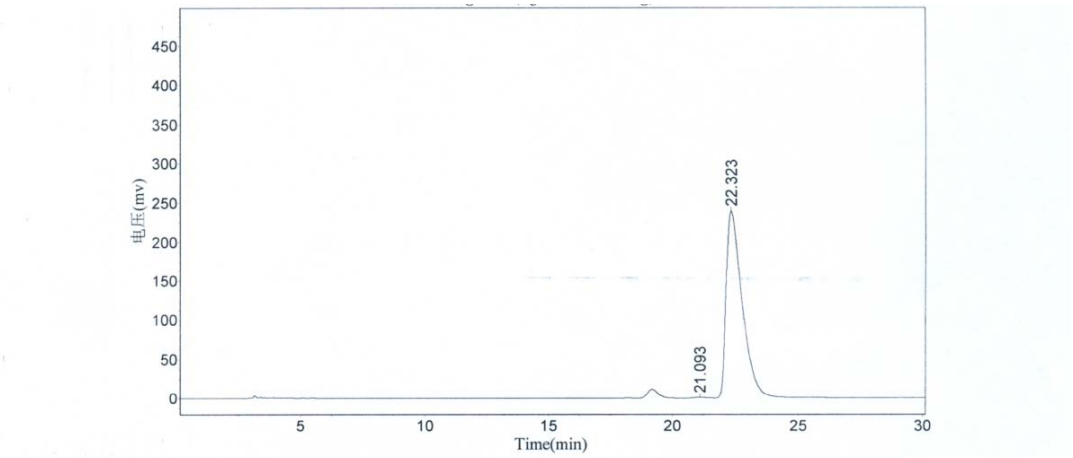


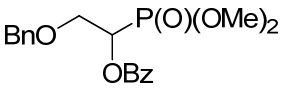
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.007	9349.437	304014.344	50.5365
2		22.545	8259.232	297559.500	49.4635
Total			17608.669	601573.844	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.093	1108.297	34378.023	0.3249
2		22.323	238780.063	10545837.000	99.6751
Total			239888.360	10580215.023	100.0000



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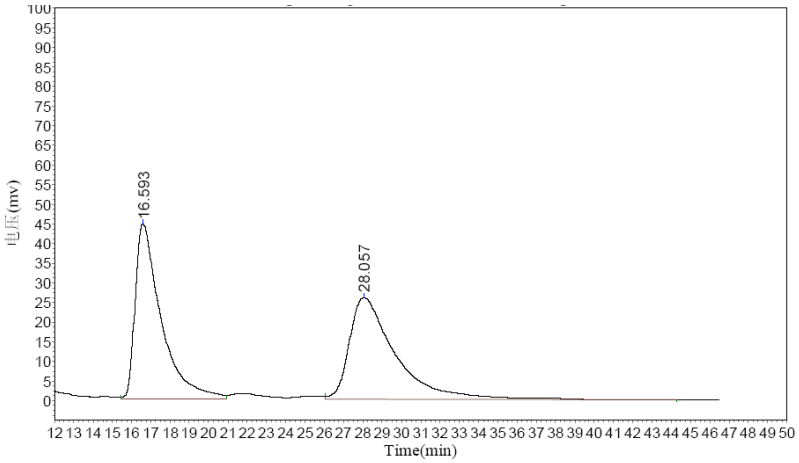
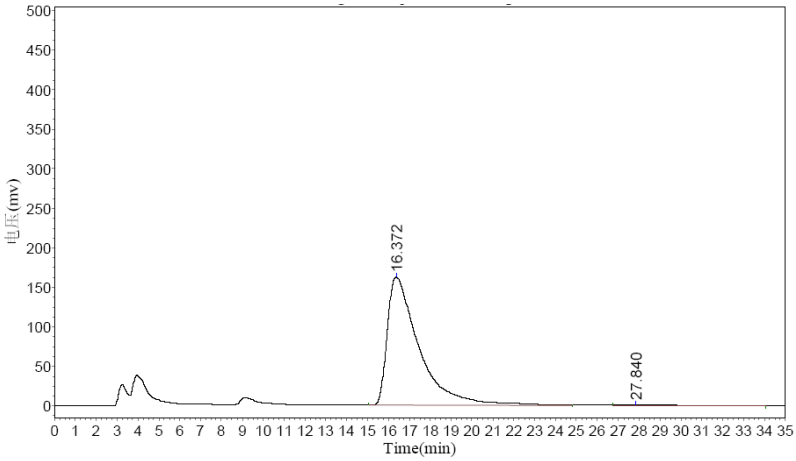


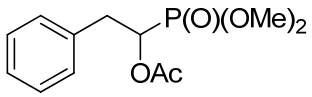
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.593	44528.926	4167733.250	49.3476
2		28.057	25919.570	4277930.000	50.6524
Total			70448.496	8445663.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.372	162423.531	17316186.000	99.1778
2		27.840	924.936	143546.094	0.8222
Total			163348.467	17459732.094	100.0000



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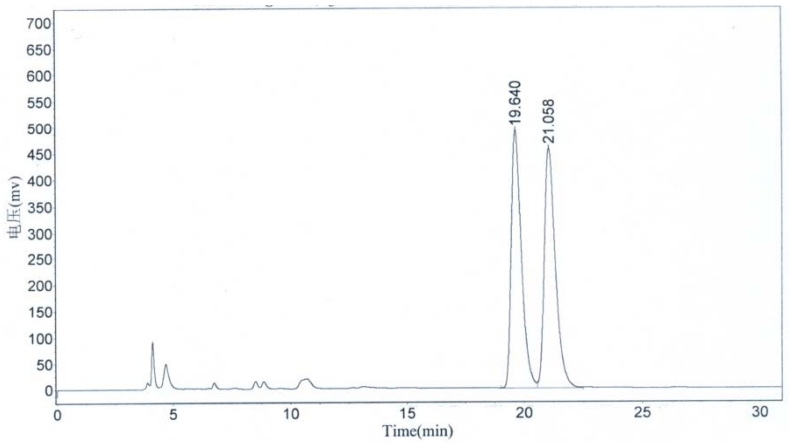
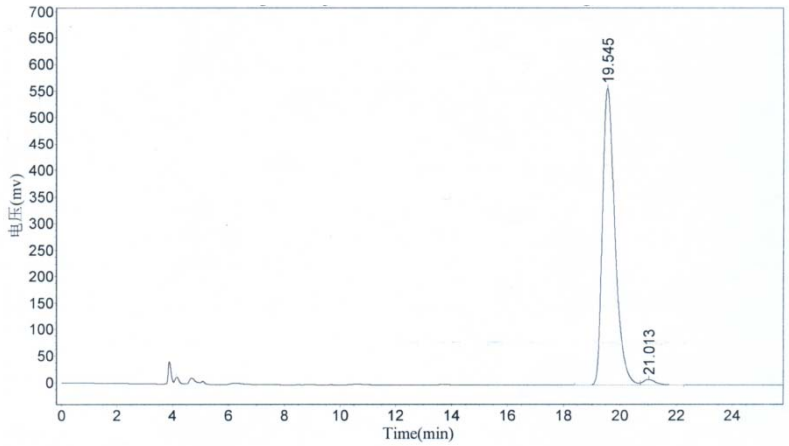


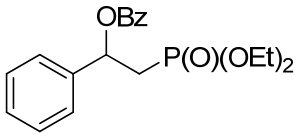
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.640	491593.344	14782284.000	49.6551
2		21.058	455793.594	14987659.000	50.3449
Total			947386.938	29769943.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.545	559208.500	17164188.000	98.2766
2		21.013	9885.608	300985.813	1.7233
Total			569094.108	17465173.813	100.0000



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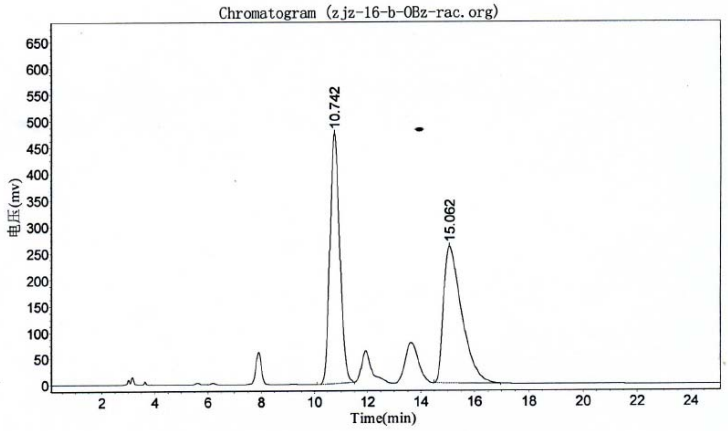
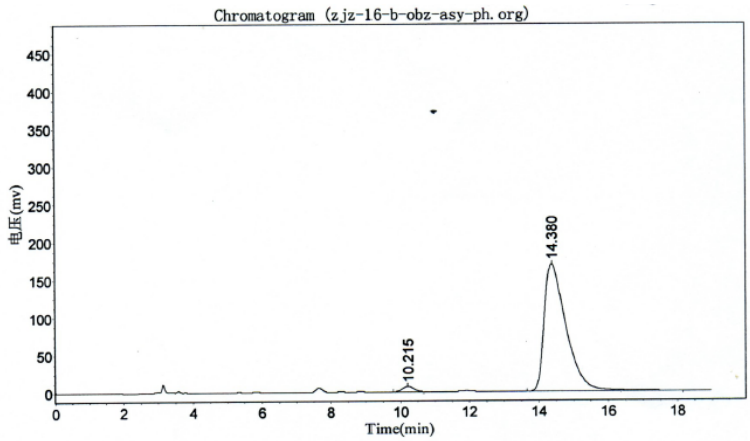


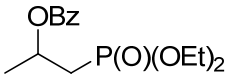
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.742	473321.938	12214255.000	50.0520
2		15.062	258556.563	12188884.000	49.9480
Total			731878.500	24403139.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.215	7206.964	164844.844	2.2008
2		14.380	168375.141	7325481.000	97.7992
Total			175582.105	7490325.844	100.0000



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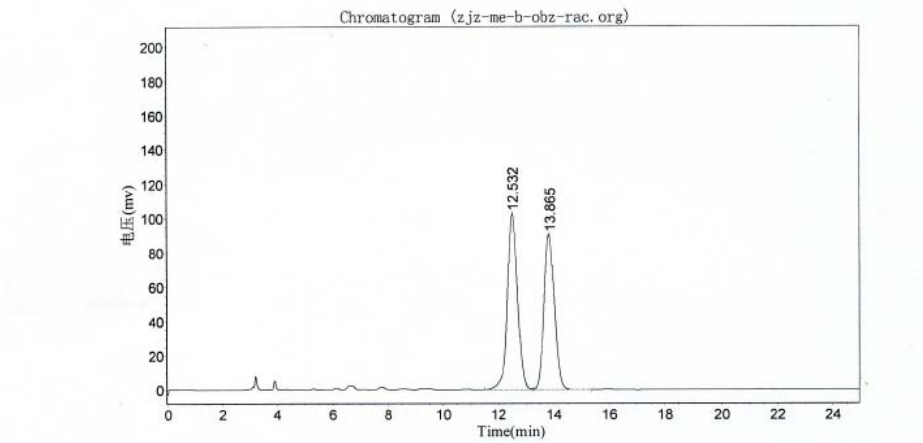
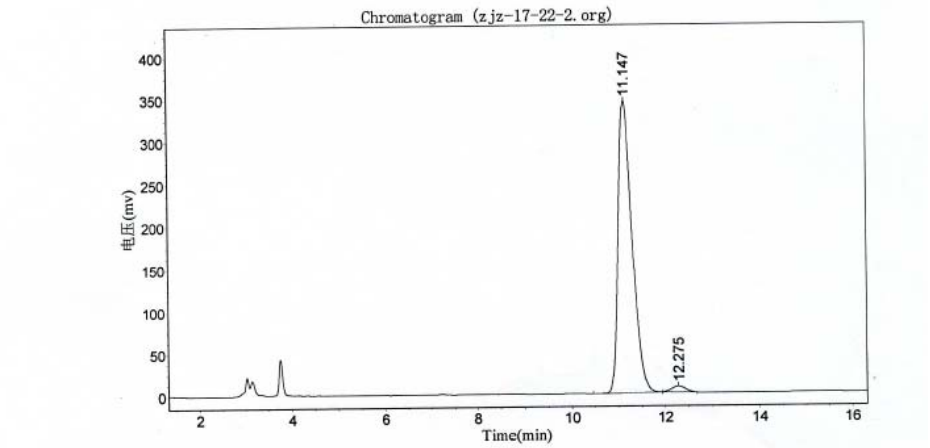


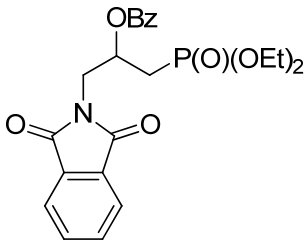
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.532	102257.570	2625177.500	52.2638
2		13.865	90301.695	2397759.750	47.7362
Total			192559.266	5022937.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.147	343977.031	7208207.000	98.0448
2		12.275	7033.746	143742.391	1.9552
Total			351010.777	7351949.391	100.0000



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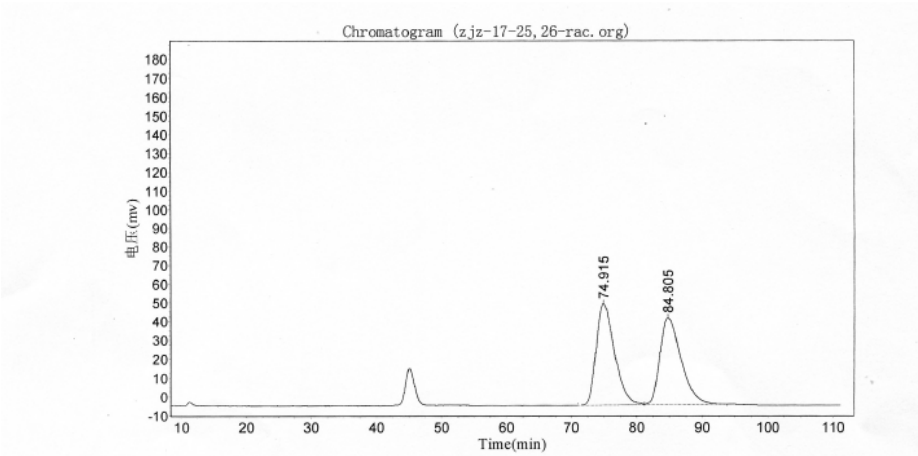
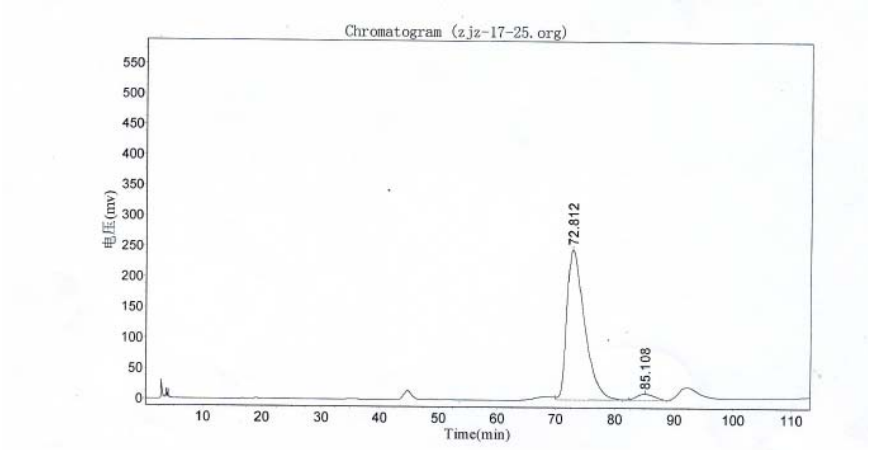


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		74.915	54124.969	10535911.000	50.4393
2		84.805	46108.559	10352397.000	49.5607
Total			100233.527	20888308.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		72.812	244604.031	50746420.000	96.5555
2		85.108	9642.323	1810311.500	3.4445
Total			254246.354	52556731.500	100.0000