Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Pyridine-*N*-oxide Catalyzed Acylative Desymmetrization of Bisphenols: Access to P-Stereogenic Phosphinates with Low Catalyst Loadings

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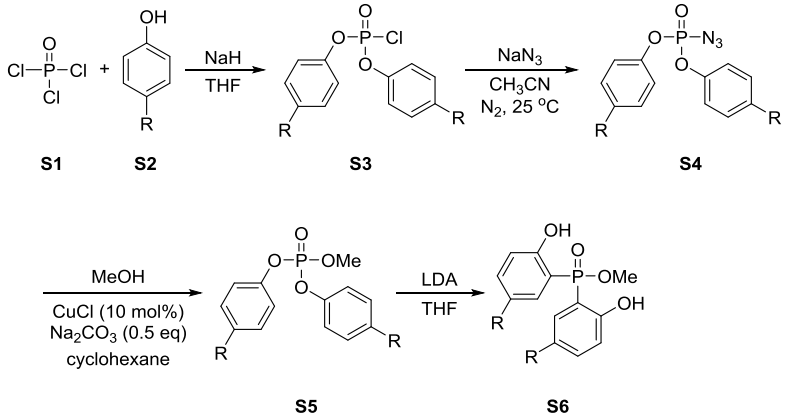
General information

^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet; t = triplet; q = quartet; dd = doublet of doublets; sept = septet; m = multiplet; br = broad and etc), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel AS/ADH/IA/IC in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). CH_2Cl_2 and THF were purchased extra dry solvents. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use. Single crystal X-ray crystallography data were obtained on Supernova Atlas S2 CCD detector. The chiral 3-substituted PPY-*N*-oxide catalysts **C1a** were prepared according to literature precedebts.[1] Chiral 4-aryl-pyridine-*N*-oxides **C2a-C2l**, **C3d** were prepared by literature precedents.[2]

Substrate synthesis.



General procedure A To a dry round bottomed flask equipped with a magnetic stir bar, added Phenols **S2** (1 equiv) in THF, then NaH (1.2 equiv) was added with nitrogen. The reaction was stirring at 0 °C for 30 minutes. When the reaction completed, phosphoryl trichloride **S1** (0.5 equiv) was added to the mixture at 0 °C for 1 h with nitrogen, and then 24 h at room temperature. Extracted with $CHCl_3$ and the organic phase was dried over $MgSO_4$. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products diphenyl phosphorochloridate **S3**.

General procedure B An appropriate diphenyl phosphorochloridate **S3** (5.0 mmol) was added dropwise to a suspension of sodium azide (7.5 mmol, 1.5 equiv) in acetonitrile (10 mL) at 0 °C under argon. After stirring at 25 °C for 12 h, the reaction mixture was filtered, the solvent was removed under reduced pressure at 25 °C and the reaction mixture was diluted with EtOAc (20 mL). The organic layer was washed with water (2 x 5 mL), 5% Na_2CO_3 (2 x 5 mL), water (5 mL) and brine (5 mL), dried over $NaSO_4$. The solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (PE/EtOAc = 10/1 to 5/1) to obtain the desired products **S4**.

General procedure C A flame-dried Schlenk tube equipped with a magnetic stir bar was successively charged with the diphenylphosphoryl azide **S4** (0.50 mmol, 1.0 equiv), aliphatic alcohol (0.2 mL), CuCl (0.05 mmol, 10 mol%) and Na_2CO_3 (0.25 mmol, 0.5 equiv) in cyclohexane (1.8 mL). The reaction mixture was stirred at the indicated temperature and time. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and diluted with EtOAc (25 mL). The crude reaction mixture was washed with 1% HCl aq (5 mL) and H_2O (5 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (PE/EtOAc = 15/1 to 5/1) to obtain the desired products **S5**.

General procedure D To a dry round bottomed flask equipped with a magnetic stir bar, added LDA (4.0 equiv) at -78 °C, **S5** (1.0 equiv) dissolved in pure and dry THF was added in 60 min at -78 °C. The resulting reaction mixture was stirred at -78 °C for another 60 min, then it was allowed to warm up to rt and it was stirred at rt for 12 h. After the reaction was completed, quenched with saturated aqueous NH_4Cl solution, then extracted with $CHCl_3$. The organic phase was separated and the combined organic phase was dried over $MgSO_4$, filtered and the solvent was removed. The crude mixture was purified by silica gel column chromatography (PE/EtOAc = 10/1 to 4/1) to obtain the desired products **S6**.

Optimization study

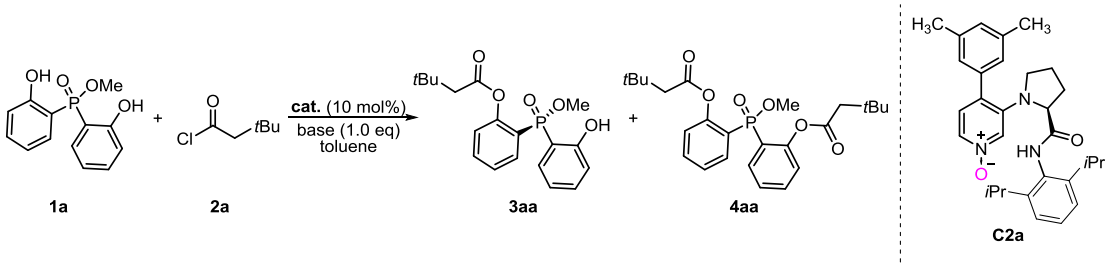
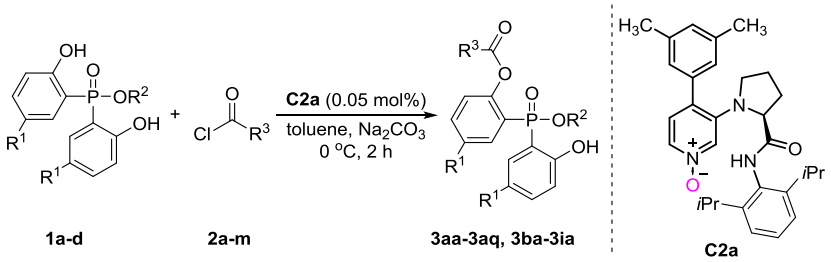


Table S1. Base screening

entry[a]	base	**3aa:4aa**	yield (%) (**3aa**)[b]	ee (%)[c]
1	Et_3N	1.4:1	54	91
2	DIPEA	1.4:1	54	90
3	DBU	1.7:1	54	87
4	Na_2CO_3	1.4:1	55	92
5	K_2CO_3	1.4:1	48	90
6	$NaHCO_3$	1.4:1	52	89

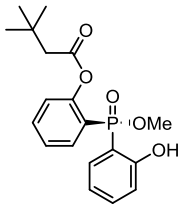
[a]Unless otherwise noted, the reaction conditions are as follows: **1a** (0.1 mmol), **2** (0.2 equiv), catalyst (10 mol%), and base (1.0 equiv) in toluene (1.0 mL) at 10 °C for 10 min. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

General procedure for the catalytic reactions



General procedure E Chiral ArPNO **C2a** (5 mg) was added in 5 mL toluene. In a dry test tube, chiral ArPNO **C2a** (24 μL, 0.0005 mmol, 0.05 mol%), substrate **1** (0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol, 1.0 eq) were added. Then, toluene (2.0 mL) and acyl chloride **2** (1.0 eq) were added and the reaction was stirred at 0 ^oC for 2 h. The test tube was sealed with a screw rubber stopper. Purification by flash column chromatography using gradient elution to give the title product **3**. The eluents were pure Pet and Pet/EtOAc, respectively.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl 3,3-dimethylbutanoate (3aa)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3aa** as a white solid (33.3 mg, 92% yield, 94% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.51 (Pet/EtOAc, 2/1, v/v). m.p: 108.2-109.4 ^oC.

HPLC analysis: 94% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 9.2 min (major), 10.9 min (minor).

$[\alpha]_D^{22}$ = -95.5 (*c* 0.47, $CHCl_3$).

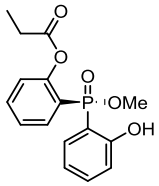
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.96 (s, 1H), 7.94 (ddd, *J* = 12.4, 7.6, 1.6 Hz, 1H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.41 (tt, *J* = 7.6, 1.6 Hz, 1H), 7.34 (tdd, *J* = 7.6, 2.8, 1.2 Hz, 1H), 7.18-7.15 (m, 1H), 7.07 (ddd, *J* = 14.8, 8.0, 2.0 Hz, 1H), 6.98-6.95 (m, 1H), 6.84-6.79 (m, 1H), 3.79 (d, *J* = 11.6 Hz, 3H), 2.46 (d, *J* = 14.4 Hz, 1H), 2.26 (d, *J* = 14.4 Hz, 1H), 1.05 (s, 9H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 170.0, 163.3 (d, J_{C-P} = 5.0 Hz), 153.1 (d, J_{C-P} = 4.0 Hz), 135.2 (d, J_{C-P} = 2.0 Hz), 134.3 (d, J_{C-P} = 2.0 Hz), 133.0 (d, J_{C-P} = 5.0 Hz), 131.6 (d, J_{C-P} = 10.0 Hz), 125.7 (d, J_{C-P} = 11.0 Hz), 124.1 (d, J_{C-P} = 8.0 Hz), 123.1 (d, J_{C-P} = 146.0 Hz), 119.7 (d, J_{C-P} = 13.0 Hz), 118.0 (d, J_{C-P} = 9.0 Hz), 110.5 (d, J_{C-P} = 133.0 Hz), 51.8 (d, J_{C-P} = 6.0 Hz), 46.9, 30.9, 29.7.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 37.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{23}NaO_5P^+$ 385.1174, found 385.1169.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl propionate (3ab)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the propionyl chloride **2b** (8.7 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ab** as a white solid (29.8 mg, 93% yield, 91% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.46 (Pet/EtOAc, 2/1, v/v). m.p: 110.0-111.4 ^oC.

HPLC analysis: 91% ee (IA, 2-propanol/*n*-hexane = 10/90, flow rate = 0.5 mL/min; λ = 256 nm) t_R = 21.9 min (major), 25.4 min (minor).

$[\alpha]_D^{22}$ = -104.3 (*c* 0.51, $CHCl_3$).

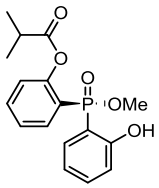
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.96 (s, 1H), 7.94 (ddd, *J* = 12.0, 7.6, 1.6 Hz, 1H), 7. 61-7.57 (m, 1H), 7.44-7.39 (m, 1H), 7.35 (ddd, *J* = 7.6, 2.8, 0.8 Hz, 1H), 7.17 (ddd, *J* = 8.4, 5.6, 1.2 Hz, 1H), 7.06 (ddd, *J* = 14.8, 8.0, 2.0 Hz, 1H), 6.96 (ddd, *J* = 8.8, 5.6, 1.2 Hz, 1H), 6.82 (tdd, *J* = 7.6, 3.2, 1.2 Hz, 1H), 3.79 (d, *J* = 11.6 Hz, 3H), 2.63-2.41 (m, 2H), 1.12 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 163.3 (d, J_{C-P} = 5.0 Hz), 153.2, 135.2 (d, J_{C-P} = 2.0 Hz), 134.4 (d, J_{C-P} = 2.0 Hz), 132.9 (d, J_{C-P} = 5.0 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 125.8 (d, J_{C-P} = 12.0 Hz), 124.2 (d, J_{C-P} = 9.0 Hz), 123.8, 119.8 (d, J_{C-P} = 13.0 Hz), 118.0 (d, J_{C-P} = 9.0 Hz), 110.5 (d, J_{C-P} = 132.0 Hz), 51.8 (d, J_{C-P} = 6.0 Hz), 27.3, 8.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ 49.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{17}NaO_5P^+$ 343.0706, found 343.0705.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl isobutyrate (3ac)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the isobutyryl chloride **2c** (10.5 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ac** as a white solid (31.7 mg, 95% yield, 94% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.45 (Pet/EtOAc, 2/1, v/v). m.p: 105.9-106.4 ^oC.

HPLC analysis: 94% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 8.9 min (major), 10.4 min (minor).

$[\alpha]_D^{22}$ = -56.3 (*c* 0.45, $CHCl_3$).

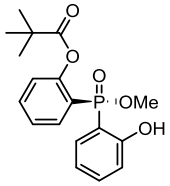
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.92 (s, 1H), 7.93 (tdd, *J* = 12.4, 7.6, 1.6 Hz, 1H), 7.61-7.57 (m, 1H), 7.43-7.39 (m, 1H), 7.34 (tdd, *J* = 7.6, 2.8, 0.8 Hz, 1H), 7.15 (tdd, *J* = 8.0, 5.6, 0.8 Hz 1H), 7.08 (ddd, *J* = 14.8, 7.6, 2.0 Hz, 1H), 6.96 (tdd, *J* = 8.4, 5.6, 1.2 Hz, 1H), 6.85-6.80 (m, 1H), 3.78 (d, *J* = 11.6 Hz, 3H), 2.82-2.72 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 3H), 1.12 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 175.0, 163.3, 153.4 (d, J_{C-P} = 4.5 Hz), 135.2, 134.4, 133.1 (d, J_{C-P} = 4.5 Hz), 131.6 (d, J_{C-P} = 10.5 Hz), 125.7 (d, J_{C-P} = 12.0 Hz), 124.0 (d, J_{C-P} = 7.5 Hz), 122.9 (d, J_{C-P} = 145.5 Hz), 119.7 (d, J_{C-P} = 13.5 Hz), 118.0 (d, J_{C-P} = 9.0 Hz), 110.5 (d, J_{C-P} = 132.0 Hz), 51.8 (d, J_{C-P} = 6.0 Hz), 33.9, 19.0, 18.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 38.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{19}NaO_5P^+$ 357.0862, found 357.0859.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl pivalate (3ad)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the pivaloyl chloride **2d** (12.3 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ad** as a white solid (32.4 mg, 93% yield, 91% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.52 (Pet/EtOAc, 2/1, v/v). m.p: 120.8-121.4 ^oC.

HPLC analysis: 91% ee (AS, 2-propanol/*n*-hexane = 20/80, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 16.1 min (major), 9.2 min (minor).

$\mathbf{[\alpha]_D^{22}}$ = -76.2 (*c* 0.41, $CHCl_3$).

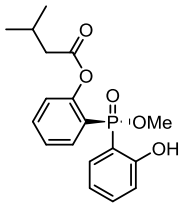
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.82 (s, 1H), 7.86 (tdd, *J* = 12.8, 7.6, 1.6 Hz, 1H), 7.60 (t, *J* = 8.0 Hz 1H), 7.44-7.39 (m, 1H), 7.33 (tdd, *J* = 7.6, 2.8, 1.2 Hz, 1H), 7.13-7.07 (m, 2H), 6.96 (tdd, *J* = 8.4, 5.6, 1.2 Hz, 1H), 6.86-6.81 (m, 1H), 3.76 (d, *J* = 11.6 Hz, 3H), 1.29 (s, 9H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 176.7, 163.3 (d, J_{C-P} = 6.0 Hz), 153.6 (d, J_{C-P} = 3.0 Hz), 135.1, 134.5, 133.7 (d, J_{C-P} = 7.5 Hz), 131.6 (d, J_{C-P} = 10.5 Hz), 125.7 (d, J_{C-P} = 12.0 Hz), 124.0 (d, J_{C-P} = 7.5 Hz), 122.6 (d, J_{C-P} = 144.0 Hz), 119.6 (d, J_{C-P} = 13.5 Hz), 118.1 (d, J_{C-P} = 9.0 Hz), 110.3 (d, J_{C-P} = 133.5 Hz), 51.8 (d, J_{C-P} = 6.0 Hz), 39.3, 27.1.

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 33.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{21}NaO_5P^+$ 371.1019, found 371.1017.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl 3-methylbutanoate (3ae)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3-methylbutanoyl chloride **2e** (12.2 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ae** as a white solid (33.1 mg, 95% yield, 94% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.54 (Pet/EtOAc, 2/1, v/v). m.p: 106.9-107.4 ^oC.

HPLC analysis: 94% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 10.4 min (major), 12.1 min (minor).

$[\alpha]_D^{22}$ = -123.3 (*c* 0.54, $CHCl_3$).

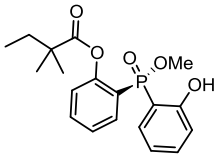
^{1}H NMR (600 MHz, $CDCl_3$): δ 10.94 (s, 1H), 7.94 (tdd, *J* = 12.6, 7.8, 1.8 Hz, 1H), 7.58 (td, *J* = 8.4, 1.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.34 (td, *J* = 7.2, 2.4 Hz, 1H), 7.16 (dd, *J* = 7.8, 5.4 Hz, 1H), 7.07 (ddd, *J* = 15.0, 7.8, 1.8 Hz, 1H), 6.96 (dd, *J* = 8.4, 5.4 Hz, 1H), 6.82 (td, *J* = 7.2, 3.0 Hz, 1H), 3.78 (d, *J* = 11.4 Hz, 3H), 2.43 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.29 (dd, *J* = 15.6, 6.6 Hz, 1H), 2.12-2.05 (m, 1H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 163.3 (d, J_{C-P} = 6.0 Hz), 153.1 (d, J_{C-P} = 4.5 Hz), 135.2, 134.3, 132.9 (d, J_{C-P} = 4.5 Hz), 131.6 (d, J_{C-P} = 10.5 Hz), 125.7 (d, J_{C-P} = 12.0 Hz), 124.1 (d, J_{C-P} = 9.0 Hz), 123.0 (d, J_{C-P} = 145.5 Hz), 119.7 (d, J_{C-P} = 13.5 Hz), 118.0 (d, J_{C-P} = 9.0 Hz), 110.5 (d, J_{C-P} = 133.5 Hz), 51.8 (d, J_{C-P} = 4.5 Hz), 42.6, 25.4, 22.5.

^{31}P NMR (243 MHz, $CDCl_3$): δ 37.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{21}NaO_5P^+$ 371.1019, found 371.1016.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl 2,2-dimethylbutanoate (3af)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 2,2-dimethylbutanoyl chloride **2f** (13.7 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3af** as a yellow solid (32.2 mg, 89% yield, 91% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.60 (Pet/EtOAc, 2/1, v/v). m.p: 118.3-120.9 ^oC.

HPLC analysis: 91% ee (IA, 2-propanol/*n*-hexane = 10/90, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 14.8 min (major), 17.1 min (minor).

$[\alpha]_D^{22}$ = -67.5 (*c* 0.35, $CHCl_3$).

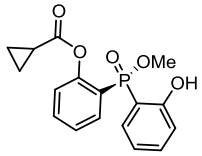
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.82 (s, 1H), 7.86 (ddd, *J* = 13.2, 8.0, 1.6 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.44-7.39 (m, 1H), 7.32 (tdd, *J* = 7.6, 2.8, 0.8 Hz, 1H), 7.15-7.07 (m, 2H), 6.97-6.94 (m, 1H), 6.86-6.81 (m, 1H), 3.76 (d, *J* = 11.6 Hz, 3H), 1.72-1.61 (m, 2H), 1.27 (s, 3H), 1.22 (s, 3H), 0.92 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 163.3 (d, J_{C-P} = 5.0 Hz), 153.7 (d, J_{C-P} = 3.0 Hz), 135.1 (d, J_{C-P} = 3.0 Hz), 134.4 (d, J_{C-P} = 3.0 Hz), 133.8 (d, J_{C-P} = 6.0 Hz), 131.6 (d, J_{C-P} = 10.0 Hz), 125.6 (d, J_{C-P} = 12.0 Hz), 124.0 (d, J_{C-P} = 8.0 Hz), 122.5 (d, J_{C-P} = 145.0 Hz), 119.7 (d, J_{C-P} = 14.0 Hz), 118.1 (d, J_{C-P} = 9.0 Hz), 110.4 (d, J_{C-P} = 132.0 Hz), 51.8 (d, J_{C-P} = 5.0 Hz), 43.1, 33.3, 24.4 (d, J_{C-P} = 17.0 Hz), 9.2.

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{23}NaO_5P^+$ 385.1175, found 385.1170.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl cyclopropanecarboxylate (3ag)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the cyclopropanecarbonyl chloride **2g** (9.1 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ag** as a white solid (29.9 mg, 90% yield, 86% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.63 (Pet/EtOAc, 2/1, v/v). m.p: 100.8-101.2 ^oC.

HPLC analysis: 86% ee (IA, 2-propanol/*n*-hexane = 10/90, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 22.0 min (major), 26.7 min (minor).

$[\alpha]_D^{22}$ = -80.7 (*c* 0.44, $CHCl_3$).

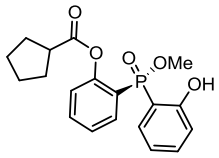
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.95 (s, 1H), 7.94 (ddd, *J* = 12.4, 7.6, 2.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.34 (td, *J* = 7.6, 2.8 Hz, 1H), 7.18 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.10 (ddd, *J* = 14.8, 8.0, 2.0 Hz, 1H), 6.97 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.82 (td, *J* = 7.2, 2.8 Hz, 1H), 3.80 (d, *J* = 11.6 Hz, 3H), 1.88-1.81 (m, 1H), 1.13-1.07 (m, 1H), 1.05-0.98 (m, 1H), 0.95-0.86 (m, 2H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.9, 163.4 (d, J_{C-P} = 5.0 Hz), 153.2 (d, J_{C-P} = 4.0 Hz), 135.1 (d, J_{C-P} = 2.0 Hz), 134.3 (d, J_{C-P} = 2.0 Hz), 133.0 (d, J_{C-P} = 6.0 Hz), 131.6 (d, J_{C-P} = 10.0 Hz), 125.8 (d, J_{C-P} = 12.0 Hz), 124.2 (d, J_{C-P} = 8.0 Hz), 123.2 (d, J_{C-P} = 146.0 Hz), 119.7 (d, J_{C-P} = 13.0 Hz), 118.1 (d, J_{C-P} = 10.0 Hz), 110.4 (d, J_{C-P} = 132.0 Hz), 51.8 (d, J_{C-P} = 5.0 Hz), 12.8, 9.9 (d, J_{C-P} = 16.0 Hz).

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 33.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{17}NaO_5P^+$ 355.0706, found 355.0705.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl cyclopentanecarboxylate (3ah)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the cyclopentanecarbonyl chloride **2h** (12.2 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ah** as a white solid (33.8 mg, 94% yield, 96% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.60 (Pet/EtOAc, 2/1, v/v). m.p: 110.5-110.9 ^oC.

HPLC analysis: 96% ee (IA, 2-propanol/*n*-hexane = 10/90, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 17.1 min (major), 29.0 min (minor).

$[\alpha]_D^{22}$ = -58.6 (*c* 0.31, $CHCl_3$).

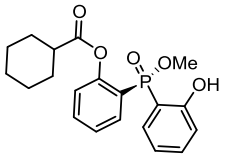
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 10.92 (s, 1H), 7.93 (ddd, *J* = 12.6, 7.8, 1.8 Hz, 1H), 7. 58 (td, *J* = 8.4, 2.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.34 (td, *J* = 7.8, 3.0 Hz, 1H), 7.15 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.09 (ddd, *J* = 15.0, 7.8, 1.8 Hz, 1H), 6.96 (dd, *J* = 8.4, 5.4 Hz, 1H), 6.82 (td, *J* = 7.8, 3.0 Hz, 1H), 3.78 (d, *J* = 12.0 Hz, 3H), 2.98-2.92 (m, 1H), 2.07-2.01 (m, 1H), 1.92-1.78 (m, 2H), 1.76-1.66 (m, 3H), 1.64-1.58 (m, 2H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 174.7, 163.3 (d, J_{C-P} = 5.4 Hz), 153.4 (d, J_{C-P} = 4.4 Hz), 135.1, 134.3, 133.1 (d, J_{C-P} = 5.4 Hz), 131.6 (d, J_{C-P} = 9.8 Hz), 125.7 (d, J_{C-P} = 11.9 Hz), 124.0 (d, J_{C-P} = 8.7 Hz), 123.0 (d, J_{C-P} = 145.5 Hz), 119.7 (d, J_{C-P} = 13.5 Hz), 118.0 (d, J_{C-P} = 9.0 Hz), 110.5 (d, J_{C-P} = 133.5 Hz), 51.8 (d, J_{C-P} = 6.0 Hz), 43.5, 30.1 (d, J_{C-P} = 8.4 Hz), 26.0.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 38.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}NaO_5P^+$ 383.1019, found 383.1018.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl cyclohexanecarboxylate (3ai)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the cyclohexanecarbonyl chloride **2i** (13.4 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ai** as a yellow solid (36.3 mg, 97% yield, 94% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.51 (Pet/EtOAc, 2/1, v/v). m.p: 108.8-109.8 ^oC.

HPLC analysis: 94% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 10.3 min (major), 19.2 min (minor).

$[\alpha]_D^{22}$ = -63.7 (*c* 0.51, $CHCl_3$).

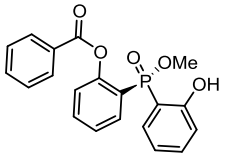
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 10.91 (s, 1H), 7.93-7.90 (m, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.33 (td, *J* = 7.8, 3.0 Hz, 1H), 7.17-7.15 (m, 1H), 7.07 (ddd, *J* = 15.0, 7.8, 1.8 Hz, 1H), 6.96 (dd, *J* = 8.4, 5.4 Hz, 1H), 6.82 (td, *J* = 7.8, 3.0 Hz, 1H), 3.78 (d, *J* = 11.4 Hz, 3H), 2.49 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.08 (dd, *J* = 12.6, 4.2 Hz, 1H), 1.80-1.72 (m, 3H), 1.66 (dt, *J* = 12.6, 4.2 Hz, 1H), 1.47 (tdd, *J* = 24.0, 12.0, 3.6 Hz, 1H), 1.41-1.20 (m, 4H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 173.9, 163.3 (d, J_{C-P} = 6.0 Hz), 153.4 (d, J_{C-P} = 4.5 Hz), 135.2, 134.4, 133.1 (d, J_{C-P} = 6.0 Hz), 131.6 (d, J_{C-P} = 9.0 Hz), 125.6 (d, J_{C-P} = 12.0 Hz), 124.0 (d, J_{C-P} = 9.0 Hz), 122.9 (d, J_{C-P} = 145.5 Hz), 119.7 (d, J_{C-P} = 13.5 Hz), 118.0 (d, J_{C-P} = 10.5 Hz), 110.5 (d, J_{C-P} = 133.5 Hz), 51.8 (d, J_{C-P} = 4.5 Hz), 42.9, 29.0, 28.7, 25.8, 25.5, 25.4.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 38.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}NaO_5P^+$ 397.1175, found 397.1181.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl benzoate (3aj)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the benzoyl chloride **2j** (11.6 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3aj** as a white solid (32.4 mg, 88% yield, 69% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.38 (Pet/EtOAc, 2/1, v/v). m.p: 120.4-121.4 ^oC.

HPLC analysis: 69% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 16.5 min (major), 22.5 min (minor).

$[\alpha]_D^{22}$ = -55.7 (*c* 0.42, $CHCl_3$).

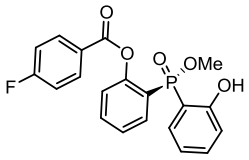
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.67(s, 1H), 8.07-8.04 (m, 2H), 7.95 (ddd, *J* = 12.8, 7.6, 1.6 Hz, 1H), 7.68-7.60 (m, 2H), 7.49-7.45 (m, 2H), 7.40 (tdd, *J* = 7.6, 2.8, 1.2 Hz, 1H), 7.30-7.26 (m, 2H), 7.10 (ddd, *J* = 14.8, 8.0, 2.0 Hz, 1H), 6.78 (tdd, *J* = 7.6, 3.2, 1.2 Hz, 1H), 6.66 (ddd, *J* = 8.4, 5.6, 0.8 Hz, 1H), 3.70 (d, *J* = 11.6 Hz, 3H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 164.5, 163.3 (d, J_{C-P} = 6.0 Hz), 153.1 (d, J_{C-P} = 4.5 Hz), 135.1, 134.5, 134.0, 133.3 (d, J_{C-P} = 6.0 Hz), 131.6 (d, J_{C-P} = 10.5 Hz), 130.5, 128.5, 128.5, 126.1 (d, J_{C-P} = 12.0 Hz), 124.4 (d, J_{C-P} = 9.0 Hz), 123.4 (d, J_{C-P} = 145.5 Hz), 119.5 (d, J_{C-P} = 12.0 Hz), 118.0 (d, J_{C-P} = 10.5 Hz), 110.0 (d, J_{C-P} = 132.0 Hz), 51.8 (d, J_{C-P} = 4.5 Hz).

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 38.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{17}NaO_5P^+$ 391.0706, found 391.0707.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl 4-fluorobenzoate (3ak)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 4-fluorobenzoyl chloride **2k** (11.8 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ak** as a white solid (35.1 mg, 91% yield, 74% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.63 (Pet/EtOAc, 2/1, v/v). m.p: 147.3-148.5 ^oC.

HPLC analysis: 74% ee (IA, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 7.7 min (major), 18.3 min (minor).

$[\alpha]_D^{22}$ = -62.7 (*c* 0.53, $CHCl_3$).

^{1}**H NMR** (600 MHz, $CDCl_3$): δ 10.68 (s, 1H), 8.05 (dd, *J* = 5.6, 3.6 Hz, 2H), 7.96 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.66 (t, *J* = 5.2 Hz, 1H), 7.41 (td, *J* = 5.2, 1.6 Hz, 1H), 7.29-7.26 (m, 2H), 7.13 (t, *J* = 5.6 Hz, 2H), 7.05 (q, *J* = 5.2 Hz, 1H), 6.78 (td, *J* = 5.2, 2.0 Hz, 1H), 6.65 (dd, *J* = 5.6, 3.6 Hz, 1H), 3.72 (d, *J* = 7.6 Hz, 3H).

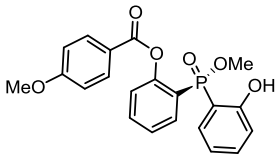
^{13}**C NMR** (150 MHz, $CDCl_3$): δ 167.3, 165.6, 163.4, 163.2 (d, J_{C-P} = 5.3 Hz), 153.0 (d, J_{C-P} = 4.1 Hz), 135.1, 134.5, 133.2 (d, J_{C-P} = 9.2 Hz), 131.5 (d, J_{C-P} = 10.1 Hz), 126.1 (d, J_{C-P} = 11.9 Hz), 124.7 (d, J_{C-P} = 3.0 Hz), 124.4 (d, J_{C-P} = 8.6 Hz), 123.3 (d, J_{C-P} = 147.6 Hz), 119.6 (d, J_{C-P} = 13.2 Hz), 117.9 (d, J_{C-P} = 9.2 Hz), 115.7 (d, J_{C-P} = 22.1 Hz), 110.0 (d, J_{C-F} = 134.0 Hz), 51.8 (d, J_{C-P} = 5.6 Hz).

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 38.0.

^{19}**F NMR** (376 MHz, $CDCl_3$): δ -104.01.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}FNaO_5P^+$ 409.0612, found 409.0620.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl 4-methoxybenzoate (3al)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 4-methoxybenzoyl chloride **2l** (13.5 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3al** as a white solid (32.6 mg, 82% yield, 60% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.63 (Pet/EtOAc, 2/1, v/v). m.p: 112.9-113.4 ^oC.

HPLC analysis: 60% ee (IA, 2-propanol/*n*-hexane = 25/75, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 11.0 min (major), 26.8 min (minor).

$[\alpha]_D^{22}$ = -107.7 (*c* 0.61, $CHCl_3$).

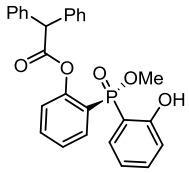
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 10.70 (s, 1H), 8.00 (d, *J* = 9.0 Hz, 2H), 7.93 (ddd, *J* = 12.6, 7.2, 1.2 Hz, 1H), 7.66-7.63 (m, 1H), 7.38 (td, *J* = 7.8, 3.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.10 (ddd, *J* = 15.0, 7.8, 1.8 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.78 (td, *J* = 7.8, 3.0 Hz, 1H), 6.69 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.90 (s, 3H), 3.70 (d, *J* = 12.0 Hz, 3H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 164.2 (d, J_{C-P} = 10.1 Hz), 163.3 (d, J_{C-P} = 5.4 Hz), 153.2 (d, J_{C-P} = 3.3 Hz), 135.1, 134.4, 133.3 (d, J_{C-P} = 6.5 Hz), 132.7, 131.6 (d, J_{C-P} = 9.8 Hz), 125.9 (d, J_{C-P} = 12.0 Hz), 124.5 (d, J_{C-P} = 7.7 Hz), 123.4 (d, J_{C-P} = 145.5 Hz), 120.9, 119.5 (d, J_{C-P} = 13.1 Hz), 117.9 (d, J_{C-P} = 9.8 Hz), 113.8, 110.6, 109.7, 55.6, 51.8 (d, J_{C-P} = 5.6 Hz).

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 38.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}NaO_6P^+$ 421.0811, found 421.0819.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl 2,2-diphenylacetate (3am)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 2,2-diphenylacetyl chloride **2m** (23.0 mg, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3am** as a white solid (41.7 mg, 91% yield, 87% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.55 (Pet/EtOAc, 2/1, v/v). m.p: 123.6-124.4 ^oC.

HPLC analysis: 87% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 13.6 min (major), 28.4 min (minor).

$[\alpha]_D^{22}$ = -116.9 (*c* 0.58, $CHCl_3$).

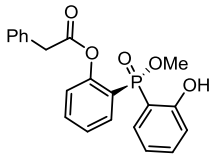
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.98 (s, 1H), 7.91 (ddd, *J* = 12.4, 7.6, 2.0 Hz, 1H), 7.54 (td, *J* = 8.0, 1.6 Hz, 1H), 7.44-7.42 (m, 2H), 7.36-7.23 (m, 10H), 7.12-7.06 (m, 2H), 6.89 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.77 (td, *J* = 7.6, 2.8 Hz, 1H), 5.31 (s, 1H), 3.65 (d, *J* = 11.6 Hz, 3H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 170.6, 163.2 (d, J_{C-P} = 5.6 Hz), 152.9 (d, J_{C-P} = 4.1 Hz), 138.0 (d, J_{C-P} = 39.8 Hz), 135.2, 134.3, 133.1 (d, J_{C-P} = 5.6 Hz), 131.5 (d, J_{C-P} = 9.2 Hz), 128.8 (d, J_{C-P} = 8.9 Hz), 128.8, 127.6 (d, J_{C-P} = 4.2 Hz), 126.0 (d, J_{C-P} = 12.2 Hz), 123.6 (t, J_{C-P} = 8.0 Hz), 122.7, 119.7 (d, J_{C-P} = 13.4 Hz), 118.1 (d, J_{C-P} = 9.8 Hz), 110.5 (d, J_{C-P} = 132.3 Hz), 56.4, 51.8 (d, J_{C-P} = 5.6 Hz).

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 37.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{23}NaO_5P^+$ 481.1175, found 481.1172.

(*S*)-2-((2-hydroxyphenyl)(methoxy)phosphoryl)phenyl 2-phenylacetate (3an)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the phenylacetyl choride **2n** (13.2 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3an** as a white solid (35.1 mg, 92% yield, 86% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.52 (Pet/EtOAc, 2/1, v/v). m.p: 113.8-114.2^oC.

HPLC analysis: 86% ee (IC, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 19.5 min (minor), 22.6 min (major).

$[\alpha]_D^{22}$ = -123.5 (*c* 0.52, $CHCl_3$).

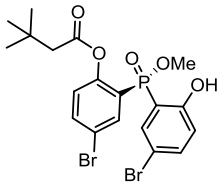
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 11.05 (s, 1H), 7.95 (ddd, *J* = 12.6, 7.8, 1.8 Hz, 1H), 7.57-7.54 (m, 1H), 7.45-7.42 (m, 1H), 7.36-7.30 (m, 3H), 7.29-7.27 (m, 3H), 7.12-7.06 (m, 2H), 7.00 (ddd, *J* = 8.4, 5.4, 1.2 Hz, 1H), 6.84 (tdd, *J* = 7.8, 3.0, 1.2 Hz, 1H), 3.87 (d, *J* = 16.2 Hz, 1H), 3.78 (d, *J* = 11.4 Hz, 3H), 3.72 (d, *J* = 11.4 Hz, 1H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 169.4, 163.2 (d, J_{C-P} = 4.5 Hz), 153.1 (d, J_{C-P} = 4.5 Hz), 135.3, 134.4, 133.1, 132.9 (d, J_{C-P} = 6.0 Hz), 131.7 (d, J_{C-P} = 9.0 Hz), 129.2 (d, J_{C-P} = 135.0 Hz), 127.4, 125.9 (d, J_{C-P} = 10.5 Hz), 124.0 (d, J_{C-P} = 9.0 Hz), 123.5, 122.6, 119.8 (d, J_{C-P} = 13.5 Hz), 118.0 (d, J_{C-P} = 10.5 Hz), 110.5 (d, J_{C-P} = 132.0 Hz), 51.8 (d, J_{C-P} = 6.0 Hz), 40.7.

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 37.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}NaO_5P^+$ 405.0862, found 405.0864.

(*S*)-4-Bromo-2-((5-bromo-2-hydroxyphenyl)(methoxy)phosphoryl)phenyl 3,3-dimethyl butanoate (3ba)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1b** (42.0 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^{o}C for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ba** as a yellow solid (48.2 mg, 93% yield, 93% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.62 (Pet/EtOAc, 2/1, v/v). m.p: 95.6-96.4 ^{o}C.

HPLC analysis: 93% ee (IC, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 7.9 min (major), 6.2 min (minor).

$[\alpha]_D^{22}$ = -134.8 (*c* 0.62, $CHCl_3$).

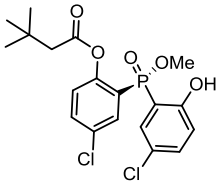
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.83 (s, 1H), 8.07 (dd, *J* = 12.4, 2.4 Hz, 1H), 7.71 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.49 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.21 (dd, *J* = 14.8, 2.4 Hz, 1H), 7.09 (dd, *J* = 8.4, 6.0 Hz, 1H), 6.87 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.82 (d, *J* = 11.6 Hz, 3H), 2.47 (d, *J* = 14.8 Hz, 1H), 2.31 (d, *J* = 14.4 Hz, 1H), 1.06 (s, 9H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 169.5, 162.3 (d, J_{C-P} = 5.0 Hz), 152.0 (d, J_{C-P} = 4.0 Hz), 138.3, 137.5, 135.6 (d, J_{C-P} = 6.0 Hz), 133.5 (d, J_{C-P} = 11.0 Hz), 125.9 (d, J_{C-P} = 9.0 Hz), 124.7 (d, J_{C-P} = 145.0 Hz), 120.3 (d, J_{C-P} = 10.0 Hz), 119.2 (d, J_{C-P} = 15.0 Hz), 113.0, 111.6 (d, J_{C-P} = 17.0 Hz), 52.3 (d, J_{C-P} = 5.0 Hz), 47.0, 31.0, 29.6.

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 33.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}Br_2NaO_5P^+$ 540.9386, found 540.9377.

(*S*)-4-chloro-2-((5-chloro-2-hydroxyphenyl)(methoxy)phosphoryl)phenyl 3,3-dimethylbutanoate (3ca)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1c** (33.2 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ca** as a yellow solid (40.0 mg, 93% yield, 91% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.59 (Pet/EtOAc, 2/1, v/v). m.p: 92.6-93.2 ^oC.

HPLC analysis: 91% ee (IC, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 5.8 min (minor), 7.3 min (major).

$[\alpha]_D^{22}$ = -125.6 (*c* 0.60, $CHCl_3$).

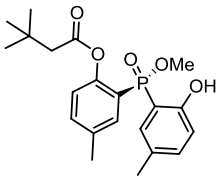
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.80 (s, 1H), 7.92 (dd, *J* = 12.4, 2.4 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.14 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.06 (dd, *J* = 14.8, 2.4 Hz, 1H), 6.92 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.82 (d, *J* = 11.6 Hz, 3H), 2.47 (d, *J* = 14.4 Hz, 1H), 2.31 (d, *J* = 14.4 Hz, 1H), 1.06 (s, 9H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 169.6, 161.8 (d, J_{C-P} = 5.0 Hz), 151.4, 135.5 (d, J_{C-P} = 2.0 Hz), 134.5 (d, J_{C-P} = 3.0 Hz), 132.7 (d, J_{C-P} = 6.0 Hz), 131.6 (d, J_{C-P} = 15.0 Hz), 130.5 (d, J_{C-P} = 11.0 Hz), 125.5 (d, J_{C-P} = 9.0 Hz), 124.9 (d, J_{C-P} = 21.0 Hz), 124.1 (d, J_{C-P} = 106.0 Hz), 119.8 (d, J_{C-P} = 11.0 Hz), 111.7 (d, J_{C-P} = 133 Hz), 52.3 (d, J_{C-P} = 6.0 Hz), 47.0, 31.0, 29.6.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 33.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}Cl_2NaO_5P^+$ 453.0396, found 453.0398.

(*S*)-2-((2-Hydroxy-5-methylphenyl)(methoxy)phosphoryl)-4-methylphenyl 3,3-dimethyl butanoate (3da)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxy-5-methylphenyl)phosphinate **1c** (29.2 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ca** as a white solid (36.3 mg, 93% yield, 93% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.58 (Pet/EtOAc, 2/1, v/v). m.p: 102.9-103.4 ^oC.

HPLC analysis: 93% ee (IC, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 12.3 min (major), 14.1 min (minor).

$[\alpha]_D^{22}$ = -112.5 (*c* 0.53, $CHCl_3$).

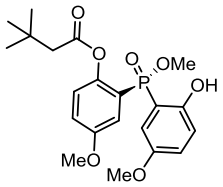
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 10.74 (s, 1H), 7.74 (dd, *J* = 13.2, 2.4 Hz, 1H), 7.37 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.20 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.04 (dd, *J* = 8.4, 6.0 Hz, 1H), 6.88-6.85 (m, 2H), 3.77 (d, *J* = 11.4 Hz, 3H), 2.44 (d, *J* = 15.0 Hz, 1H), 2.41 (s, 3H), 2.23 (d, *J* = 14.4 Hz, 1H), 2.17 (s, 3H), 1.05 (s, 9H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 170.2, 161.1 (d, J_{C-P} = 5.3 Hz), 150.8 (d, J_{C-P} = 4.2 Hz), 136.1, 135.6 (d, J_{C-P} = 11.3 Hz), 134.9, 133.2 (d, J_{C-P} = 5.3 Hz), 131.2 (d, J_{C-P} = 9.9 Hz), 128.8 (d, J_{C-P} = 13.2 Hz), 123.8 (d, J_{C-P} = 8.9 Hz), 122.7 (d, J_{C-P} = 144.5 Hz), 117.8 (d, J_{C-P} = 10.5 Hz), 110.1 (d, J_{C-P} = 132.3 Hz), 51.7 (d, J_{C-P} = 5.4 Hz), 46.9, 30.9, 29.7, 21.0, 20.5.

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 37.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{27}NaO_5P^+$ 413.1488, found 413.1492.

(*S*)-2-((2-Hydroxy-5-methoxyphenyl)(methoxy)phosphoryl)-4-methoxyphenyl 3,3- dimethyl butanoate (3ea)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxy-5-methoxyphenyl)phosphinate **1d** (32.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3da** as a white solid (38.4 mg, 91% yield, 90% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.48 (Pet/EtOAc, 2/1, v/v). m.p: 108.4-110.2 ^oC.

HPLC analysis: 90% ee (IC, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 34.2 min (major), 19.2 min (minor).

$[\alpha]_D^{22}$ = -198.5 (*c* 0.47, $CHCl_3$).

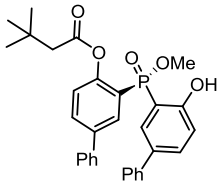
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.46 (s, 1H), 7.42 (dd, *J* = 13.6, 2.4 Hz, 1H), 7. 08-7.00 (m, 3H), 6.91 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.59 (dd, *J* = 15.6, 2.8 Hz, 1H), 3.85 (s, 3H), 3.79 (d, *J* = 11.6 Hz, 3H), 3.66 (s, 3H), 2.43 (d, *J* = 14.8 Hz, 1H), 2.24 (d, *J* = 14.4 Hz, 1H), 1.05 (s, 9H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 170.5, 157.4 (d, J_{C-P} = 5.0 Hz), 156.9 (d, J_{C-P} = 14.0 Hz), 152.5 (d, J_{C-P} = 17.0 Hz), 146.2, 125.2 (d, J_{C-P} = 10.0 Hz), 124.3, 122.9, 122.5 (d, J_{C-P} = 2.0 Hz), 119.8 (d, J_{C-P} = 2.0 Hz), 119.1 (d, J_{C-P} = 11.0 Hz), 117.4 (d, J_{C-P} = 6.0 Hz), 114.5 (d, J_{C-P} = 11.0 Hz), 110.2 (d, J_{C-P} = 133.0 Hz), 56.0 (d, J_{C-P} = 2.0 Hz), 51.9, 51.9, 46.9, 30.8, 29.7.

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 36.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{27}NaO_7P^+$ 445.1387, found 445.1391.

(*S*)-3-((4-Hydroxy-[1,1'-biphenyl]-3-yl)(methoxy)phosphoryl)-[1,1'-biphenyl]-4-yl 3,3- dimethyl butanoate (3fa)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(4-hydroxy-[1,1'-biphenyl]-3-yl)phosphinate **1e** (41.6 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ea** as a white solid (46.3 mg, 90% yield, 95% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.56 (Pet/EtOAc, 2/1, v/v). m.p: 110.5-111.4 ^oC.

HPLC analysis: 95% ee (IA, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 8.6 min (major), 7.8 min (minor).

$[\alpha]_D^{22}$ = -309.4 (*c* 0.51, $CHCl_3$).

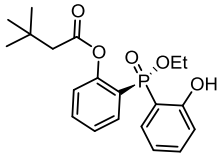
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 11.01 (s, 1H), 8.20 (dd, *J* = 12.6, 2.4 Hz, 1H), 7.79 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.66 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.60-7.59 (m, 2H), 7.47 (td, *J* = 7.8, 1.8 Hz, 2H), 7.42-7.36 (m, 6H), 7.28 (tt, *J* = 6.6, 1.2 Hz, 1H), 7.26-7.24 (m, 1H), 7.07 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.85 (d, *J* = 11.4 Hz, 3H), 2.48 (d, *J* = 14.4 Hz, 1H), 2.30 (d, *J* = 14.4 Hz, 1H), 1.06 (s, 9H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 170.1, 162.8 (d, J_{C-P} = 6.0 Hz), 152.2 (d, J_{C-P} = 5.0 Hz), 139.8 (d, J_{C-P} = 46.0 Hz), 139.2 (d, J_{C-P} = 12.0 Hz), 134.1 (d, J_{C-P} = 2.0 Hz), 133.2, 133.0 (d, J_{C-P} = 3.0 Hz), 131.7 (d, J_{C-P} = 5.0 Hz), 129.9 (d, J_{C-P} = 11.0 Hz), 129.1, 128.9, 128.1, 127.4, 127.2, 126.8, 124.4 (d, J_{C-P} = 9.0 Hz), 124.0, 122.6, 118.5 (d, J_{C-P} = 10.0 Hz), 110.9 (d, J_{C-P} = 132.0 Hz), 52.0 (d, J_{C-P} = 5.0 Hz), 47.0, 31.0, 29.7.

^{31}**P NMR** (243 MHz, $CDCl_3$): δ 37.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{31}NaO_5P^+$ 537.1081, found 537.1080.

(*S*)-2-(Ethoxy(2-hydroxyphenyl)phosphoryl)phenyl 3,3-dimethylbutanoate (3ga)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl ethyl bis(2-hydroxyphenyl)phosphinate **1f** (27.8 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3fa** as a white solid (35.0 mg, 93% yield, 94% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.55 (Pet/EtOAc, 2/1, v/v). m.p: 108.8-110.6 ^oC.

HPLC analysis: 94% ee (IA, 2-propanol/*n*-hexane = 30/70, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 8.5 min (major), 9.9 min (minor).

$[\alpha]_D^{22}$ = -77.9 (*c* 0.42, $CHCl_3$).

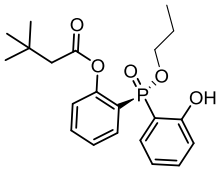
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.03 (s, 1H), 7.96 (ddd, *J* = 12.4, 7.6, 1.6 Hz, 1H), 7.59-7.55 (m, 1H), 7.42-7.37 (m, 1H), 7.34 (tdd, *J* = 7.6, 2.8, 1.2 Hz, 1H), 7.15 (ddd, *J* = 8.0, 5.6, 0.8 Hz, 1H), 7.08 (ddd, *J* = 14.8, 7.6, 1.6 Hz, 1H), 6.95 (ddd, *J* = 8.4, 5.6, 0.8 Hz, 1H), 6.80 (tdd, *J* = 7.2, 2.8, 0.8 Hz, 1H), 4.31-4.21 (m, 1H), 4.09-3.99 (m, 1H), 2.46 (d, *J* = 14.4 Hz, 1H), 2.26 (d, *J* = 14.8 Hz, 1H), 1.38 (t, *J* = 6.8 Hz, 3H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 163.1 (d, J_{C-P} = 6.0 Hz), 153.1 (d, J_{C-P} = 4.0 Hz), 135.0 (d, J_{C-P} = 3.0 Hz), 134.1 (d, J_{C-P} = 2.0 Hz), 133.0 (d, J_{C-P} = 5.0 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 125.6 (d, J_{C-P} = 12.0 Hz), 124.0 (d, J_{C-P} = 8.0 Hz), 123.5 (d, J_{C-P} = 146.0 Hz), 119.6 (d, J_{C-P} = 13.0 Hz), 117.9 (d, J_{C-P} = 9.0 Hz), 111.4 (d, J_{C-P} = 133.0 Hz), 61.7 (d, J_{C-P} = 5.0 Hz), 46.9, 30.9, 29.7, 16.4 (d, J_{C-P} = 7.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 35.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{25}NaO_5P^+$ 399.1332, found 399.1339.

(*S*)-2-((2-Hydroxyphenyl)(propoxy)phosphoryl)phenyl 3,3-dimethylbutanoate (3ha)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), propyl bis(2-hydroxyphenyl)phosphinate **1g** (29.2 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ga** as a white solid (35.5 mg, 91% yield, 94% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.57 (Pet/EtOAc, 2/1, v/v). m.p: 102.9-103.4 ^oC.

HPLC analysis: 94% ee (IA, 2-propanol/*n*-hexane = 5/95, flow rate = 0.4 mL/min; λ = 256 nm) t_R = 23.7 min (major), 28.4 min (minor).

$[\alpha]_D^{22}$ = -76.3 (*c* 0.52, $CHCl_3$).

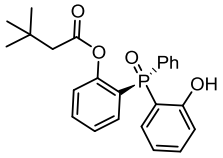
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.03 (s, 1H), 7.96 (ddd, *J* = 12.0, 7.6, 1.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.39 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.34 (tdd, *J* = 7.2, 2.8, 0.8 Hz, 1H), 7.16 (ddd, *J* = 8.4, 5.6, 1.2 Hz, 1H), 7.06 (ddd, *J* = 14.8, 8.0, 2.0 Hz, 1H), 6.97-6.94 (m, 1H), 6.82-6.78 (m, 1H), 4.20-4.12 (m, 1H), 3.93-3.86 (m, 1H), 2.45 (d, *J* = 14.4 Hz, 1H), 2.25 (d, *J* = 14.4 Hz, 1H), 1.79-1.72 (m, 2H), 1.04 (s, 9H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 163.1 (d, J_{C-P} = 5.0 Hz), 153.2 (d, J_{C-P} = 5.0 Hz), 135.0 (d, J_{C-P} = 3.0 Hz), 134.1 (d, J_{C-P} = 3.0 Hz), 132.9 (d, J_{C-P}= 4.0 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 125.6 (d, J_{C-P} = 12.0 Hz), 124.0 (d, J_{C-P} = 8.0 Hz), 123.5 (d, J_{C-P} = 146.0 Hz), 119.6 (d, J_{C-P} = 14.0 Hz), 117.9 (d, J_{C-P} = 10.0 Hz), 111.3 (d, J_{C-P} = 132.0 Hz), 67.0 (d, J_{C-P} = 6.0 Hz), 46.9, 30.9, 29.7, 23.9 (d, J_{C-P} = 7.0 Hz), 10.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 35.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{27}NaO_5P^+$ 413.1488, found 413.1489.

(*S*)-2-((2-hydroxyphenyl)(phenyl)phosphoryl)phenyl 3,3-dimethylbutanoate (3ia)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), bis(2-hydroxyphenyl)(phenyl)phosphine oxide **1h** (31.0 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 3,3-dimethylbutanoyl chloride **2a** (14.9 μL, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ha** as a white solid (34.3 mg, 84% yield, 12% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.45 (Pet/EtOAc, 2/1, v/v). m.p: 134.9-136.4 ^oC.

HPLC analysis: 12% ee (IC, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 16.1 min (major), 23.2 min (minor).

$[\alpha]_D^{22}$ = -18.3 (*c* 0.42, $CHCl_3$).

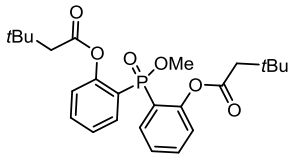
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 11.19 (s, 1H), 7.74-7.71 (m, 2H), 7.62-7.57 (m, 2H), 7.50 (td, *J* = 7.8, 3.0 Hz 2H), 7.42-7.38 (m, 2H), 7.28-7.26 (m, 2H), 7.03 (ddd, *J* = 13.8, 7.8, 1.8 Hz 1H), 6.98 (dd, *J* = 8.4, 4.8 Hz 1H), 6.83 (td, *J* = 7.2, 2.4 Hz 1H), 1.93 (dd, *J* = 17.4, 14.4 Hz 2H), 0.95 (s, 9H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 169.6, 163.9 (d, J_{C-P} = 3.0 Hz), 153.0 (d, J_{C-P} = 1.0 Hz), 134.5 (d, J_{C-P} = 2.0 Hz), 134.3 (d, J_{C-P} = 2.0 Hz), 134.2 (d, J_{C-P} = 5.0 Hz), 132.6 (d, J_{C-P} = 3.0 Hz), 131.7 (d, J_{C-P} = 107.0 Hz), 131.7 (d, J_{C-P} = 11.0 Hz), 131.4 (d, J_{C-P} = 10.0 Hz), 129.0 (d, J_{C-P} = 13.0 Hz), 125.7 (d, J_{C-P} = 12.0 Hz), 124.3 (d, J_{C-P} = 7.0 Hz), 124.2 (d, J_{C-P} = 103.0 Hz), 119.2 (d, J_{C-P} = 13.0 Hz), 118.8 (d, J_{C-P} = 8.0 Hz), 110.9 (d, J_{C-P} = 106.0 Hz), 46.6, 30.6, 29.5.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 37.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{25}NaO_4P^+$ 431.1383, found 431.1388.

(methoxylphosphoryl)bis(2,1-phenylene) bis(3,3-dimethylbutanoate) (4aa)



R_f = 0.24 (Pet/EtOAc, 2/1, v/v). m.p: 132.9-133.5 ^oC.

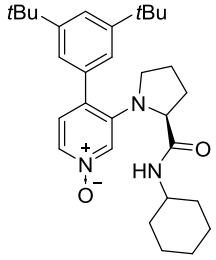
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.00 (ddd, *J* = 13.2, 7.6, 1.6 Hz 2H), 7.60-7.55 (m, 2H), 7.36 (tdd, *J* = 7.6, 2.8, 1.2 Hz 2H), 7.12 (ddd, *J* = 8.0, 5.6, 0.8 Hz 2H), 3.67 (d, *J* = 11.6 Hz 3H), 2.15 (dd, *J* = 34.8, 14.4 Hz 4H), 1.01 (s, 18H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 170.0, 152.4 (d, J_{C-P} = 3.5 Hz), 134.1 (d, J_{C-P} = 6.1 Hz), 133.8 (d, J_{C-P} = 2.1 Hz), 125.6 (d, J_{C-P} = 12.2 Hz), 123.9 (d, J_{C-P} = 140.1 Hz), 123.8 (d, J_{C-P} = 8.0 Hz), 51.7 (d, J_{C-P} = 5.7 Hz), 47.0, 30.7, 29.6.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 25.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{33}NaO_6P^+$ 483.1907, found 483.1908.

(*S*)-3-(2-(Cyclohexylcarbamoyl)pyrrolidin-1-yl)-4-(3,5-di-tert-butylphenyl)pyridine 1-oxide (C2l)



Light yellow solid, m. p. = 111.2-113.5 ℃.

R_f = 0.21 (DCM/MeOH, 20/1, v/v).

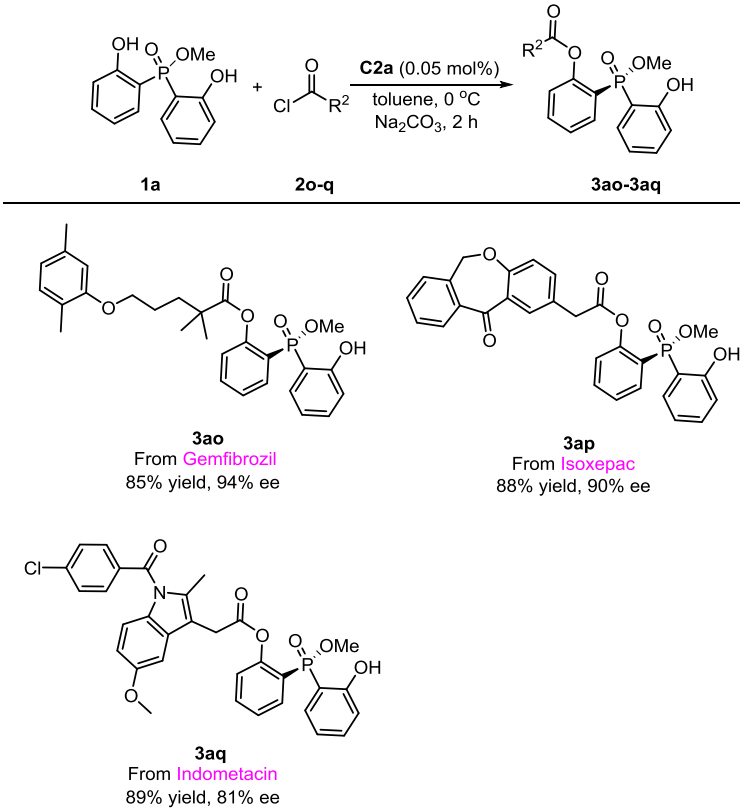
$[\alpha]_D^{25}$ = -31.0 (c = 0.50, $CHCl_3$).

^{1}**H NMR** (400 MHz, $CDCl^3$) δ 8.07 (d, *J* = 1.6 Hz, 1H), 7.83 (dd, *J* = 6.4, 1.6 Hz, 1H), 7.41 (t, *J* = 2.0 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 2H), 7.07 (d, *J* = 6.4 Hz, 1H), 6.16 (d, *J* = 8.4 Hz, 1H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.56-3.68 (m, 1H), 3.07-3.19 (m, 1H), 2.74-2.87 (m, 1H), 2.17-2.27 (m, 1H), 1.79-1.96 (m, 2H), 1.66-1.78 (m, 3H), 1.49-1.65 (m, 3H), 1.34 (s, 18H), 1.22-1.31 (m, 2H), 0.82-1.08 (m, 3H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 170.6, 151.5, 144.7, 137.5, 131.2, 130.7, 128.8, 127.9, 122.6, 122.0, 63.1, 53.0, 47.9, 35.1, 33.18, 33.16, 31.6, 31.2, 25.5, 24.9, 24.82, 24.80.

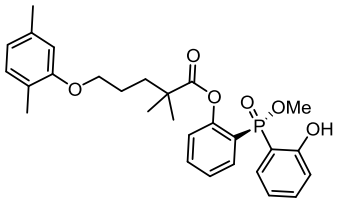
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{44}N_3O_2^+$ 478.3428; found 478.3426.

Late-stage functionalization of drugs.[a]



[a]Reaction conditions unless specified otherwise: **1a** (0.1 mmol), **2o-2q** (0.1 mmol), **C2a** (0.05 mol%), and Na_2CO_3 (1.0 equiv) in toluene (1 mL) at 0 ℃ for 2 h. Isolated yields are reported. The ee values are determined by chiral HPLC analysis.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl 5-(2,5-dimethylphenoxy)-2,2- dimethyl pentanoate (3ao)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl chloride **2o** (26.8 mg, 0.1 mmol) was added in mixture at 0 °C for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ao** as a white solid (42.2 mg, 85% yield, 93% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.45 (Pet/EtOAc, 2/1, v/v). m.p: 107.9-108.4 °C.

HPLC analysis: 93% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 25.8 min (major), 23.4 min (minor).

$[\alpha]_D^{22}$ = -176.3 (*c* 0.32, $CHCl_3$).

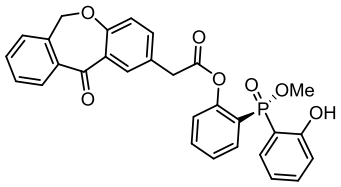
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.83 (s, 1H), 7.87 (ddd, *J* = 13.2, 8.0, 2.0 Hz, 1H), 7.61-7.56 (m, 1H), 7.40 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.34 (tdd, *J* = 7.6, 2.8, 1.2 Hz, 1H), 7.12-7.07 (m, 2H), 7.00-6.94 (m, 2H), 6.85-6.81 (m, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.61 (br, 1H), 3.94-3.92 (m, 2H), 3.77 (d, *J* = 11.6 Hz, 3H), 2.30 (s, 3H), 2.15 (s, 3H), 1.83-1.77 (m, 4H), 1.34 (s, 3H), 1.29 (m, 3H).

^{13}**C NMR** (150 MHz, $CDCl_3$): δ 176.0, 163.3 (d, J_{C-P} = 4.4 Hz), 157.0, 153.6 (d, J_{C-P} = 3.2 Hz), 136.6, 135.2, 134.5, 133.8 (d, J_{C-P} = 6.3 Hz), 131.6 (d, J_{C-P} = 10.8 Hz), 130.4, 125.7 (d, J_{C-P} = 12.0 Hz), 124.0 (d, J_{C-P} = 7.8 Hz), 123.7, 122.5 (d, J_{C-P} = 144.5 Hz), 120.8, 119.7 (d, J_{C-P} = 13.2 Hz), 118.1 (d, J_{C-P} = 9.6 Hz), 112.1, 110.4 (d, J_{C-P} = 132.3 Hz), 67.9, 51.8 (d, J_{C-P} = 5.6 Hz), 42.7, 37.0, 25.0, 25.0 (d, J_{C-P} = 43.5 Hz), 21.5, 15.9.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 39.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{33}NaO_6P^+$ 519.1907, found 519.1904.

(*S*)-2-((2-Hydroxyphenyl)(methoxy)phosphoryl)phenyl-2-(11-oxo-6,11-dihydrodibenzo [b,e]oxepin-2-yl)acetate (3ap)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetyl chloride **2p** (28.6 mg, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3ap** as a white solid (45.2 mg, 88% yield, 88% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.46 (Pet/EtOAc, 2/1, v/v). m.p: 112.9-114.4 ^oC.

HPLC analysis: 88% ee (AD-H, 2-propanol/*n*-hexane = 30/70, flow rate = 0.8 mL/min; λ = 256 nm) t_R = 33.1 min (major), 46.9 min (minor).

$[\alpha]_D^{22}$ = -121.3 (*c* 0.32, $CHCl_3$).

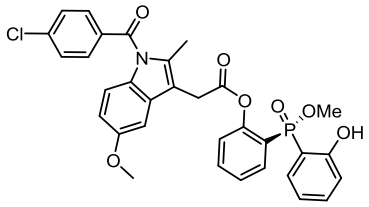
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 11.04 (s, 1H), 8.10 (d, *J* = 2.4 Hz, 1H), 7.95 (ddd, *J* = 12.6, 7.8, 1.8 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.58-7.54 (m, 2H), 7.48-7.44 (m, 2H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.37-7.34 (m, 2H), 7.14 (dd, *J* = 8.4, 5.4 Hz, 1H), 7.09-7.01 (m, 3H), 6.86-6.83 (m, 1H), 5.17 (s, 2H), 3.90 (d, *J* = 16.8 Hz, 1H), 3.81 (d, *J* = 11.4 Hz, 3H), 3.75 (d, *J* = 16.8 Hz, 1H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 190.9, 169.4, 163.2 (d, J_{C-P} = 5.0 Hz), 160.7, 153.0 (d, J_{C-P} = 3.0 Hz), 140.6, 136.7, 135.6, 135.4 (d, J_{C-P} = 2.0 Hz), 134.4 (d, J_{C-P} = 2.0 Hz), 132.9 (d, J_{C-P} = 5.0 Hz), 132.9 (d, J_{C-P} = 4.0 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 129.5 (d, J_{C-P} = 20.0 Hz), 127.9, 126.9, 126.0 (d, J_{C-P} = 12.0 Hz), 125.3, 124.0 (d, J_{C-P} = 9.0 Hz), 123.0 (d, J_{C-P} = 146.0 Hz), 121.2, 119.9 (d, J_{C-P} = 14.0 Hz), 118.1 (d, J_{C-P} = 10.0 Hz), 110.5 (d, J_{C-P} = 133.0 Hz), 73.7, 51.9 (d, J_{C-P} = 5.0 Hz), 39.6.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 37.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}NaO_7P^+$ 537.1074, found 537.1075.

(*S*)-2-((2-hydroxyphenyl)(methoxy)phosphoryl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (3aq)



Prepared according to general procedure E using chiral ArPNO **C2a** (24 μL, 0.005 mmol, 0.05 mol%), methyl bis(2-hydroxyphenyl)phosphinate **1a** (26.4 mg, 0.1 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol), were added in toluene (2 mL). Then, the 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetyl chloride **2q** (37.5 mg, 0.1 mmol) was added in mixture at 0 ^oC for 2 h. Purification by flash column chromatography using gradient elution to give the title product **3aq** as a white solid (53.7 mg, 89% yield, 80% ee). The eluents were pure Pet and Pet/EtOAc (10/1, v/v), respectively.

R_f = 0.46 (Pet/EtOAc, 2/1, v/v). m.p: 130.9-131.4 ^oC.

HPLC analysis: 80% ee (IA, 2-propanol/*n*-hexane = 20/80, flow rate = 0.6 mL/min; λ = 256 nm) t_R = 34.5 min (major), 42.2 min (minor).

$[\alpha]_D^{22}$ = -66.1 (*c* 0.32, $CHCl_3$).

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 11.15 (s, 1H), 7.95 (ddd, *J* = 12.4, 7.6, 1.6 Hz, 1H), 7.66-7.62 (m, 2H), 7.58-7.54 (m, 1H), 7.49-7.42 (m, 3H), 7.36 (tdd, *J* = 7.6, 2.8, 1.2 Hz, 1H), 7.11-7.05 (m, 2H), 7.03-6.99 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.85 (tdd, *J* = 7.2, 2.8, 0.8 Hz, 1H), 6.67 (d, *J* = 8.8, 2.4 Hz, 1H), 3.95 (d, *J* = 16.4 Hz, 1H), 3.83-3.79 (m, 6H), 3.75 (d, *J* = 16.4 Hz, 1H), 2.34 (s, 3H)

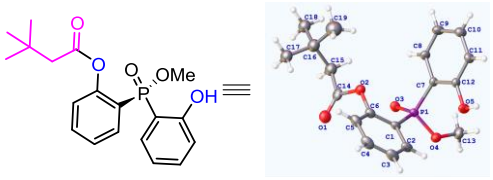
^{13}**C NMR** (100 MHz, $CDCl_3$): δ 168.8, 168.5, 163.3 (d, J_{C-P} = 5.0 Hz), 156.3, 153.2 (d, J_{C-P} = 5.0 Hz), 139.4, 136.5, 135.4, 134.5, 134.0, 132.9 (d, J_{C-P} = 4.0 Hz), 131.7 (d, J_{C-P} = 10.0 Hz), 131.3, 131.0, 130.7, 129.3, 126.1 (d, J_{C-P} = 12.0 Hz), 124.1 (d, J_{C-P} = 9.0 Hz), 123.0 (d, J_{C-P} = 146.0 Hz), 119.9 (d, J_{C-P} = 13.0 Hz), 118.1 (d, J_{C-P} = 10.0 Hz), 115.1, 112.1, 111.8, 110.6 (d, J_{C-P} = 133.0 Hz), 101.3, 55.9, 51.9 (d, J_{C-P} = 5.0 Hz), 29.9 (d, J_{C-P} = 14.0 Hz), 13.5.

^{31}**P NMR** (162 MHz, $CDCl_3$): δ 37.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{27}ClNaO_7P^+$ 626.1106, found 626.1115.

X-ray data of (*S*)-3aa

Figure S1. X-Ray crystal structure of **(*S*)-3aa** (The crystal was obtained by slow evaporation of **(*S*)-3aa** in a mixture of EtOAc/CH_2Cl_2). (CCDC:2290776)



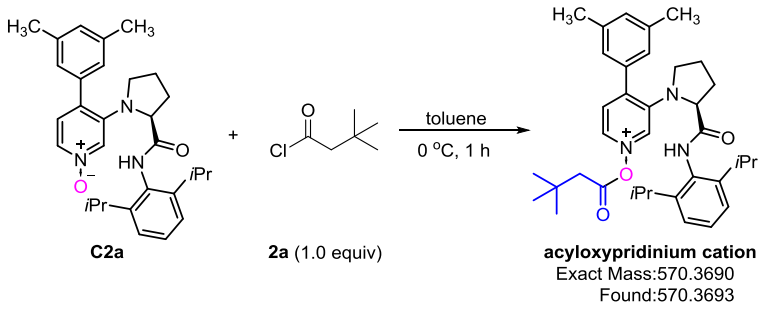
(*S*)-3aa (*S*)-3aa

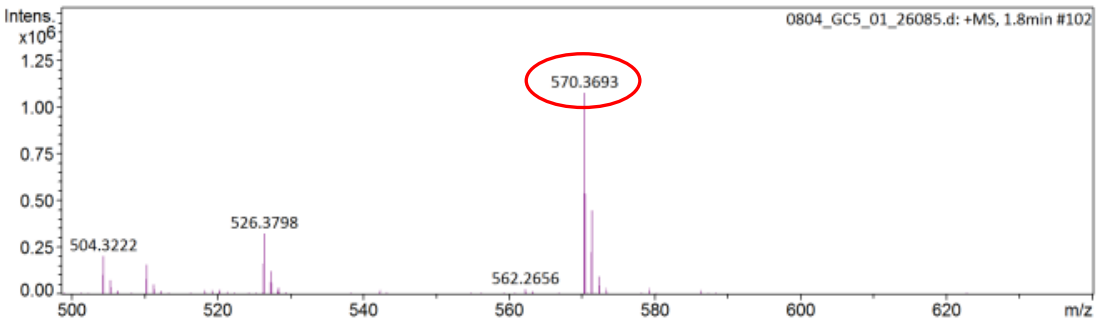
Table S2. Crystal data and structure refinement for (*S*)-3aa.

Identification code	**(*S*)-3aa**
Empirical formula	$C_{19}H_{23}O_5P$
Formula weight	362.34
Temperature/K	298.1(2)
Crystal system	triclinic
Space group	P1
a/Å	9.0660(2)
b/Å	9.2370(2)
c/Å	12.8726(2)
α/°	92.325(2)
β/°	96.687(2)
γ/°	115.494(2)
Volume/Å^3	961.45(4)
Z	2
ρ_{calc}g/cm^3	1.252
μ/mm^{-1}	1.482
F(000)	384.0
Crystal size/mm^3	0.16 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.95 to 142.484
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	52356
Independent reflections	6625 [R_{int} = 0.0761, R_{sigma} = 0.0300]
Data/restraints/parameters	6625/514/512
Goodness-of-fit on F^2	1.117
Final R indexes [I>=2σ (I)]	R_1 = 0.0640, wR_2 = 0.1841
Final R indexes [all data]	R_1 = 0.0667, wR_2 = 0.1892
Largest diff. peak/hole / e Å^{-3}	0.54/-0.33
Flack parameter	-0.01(3)

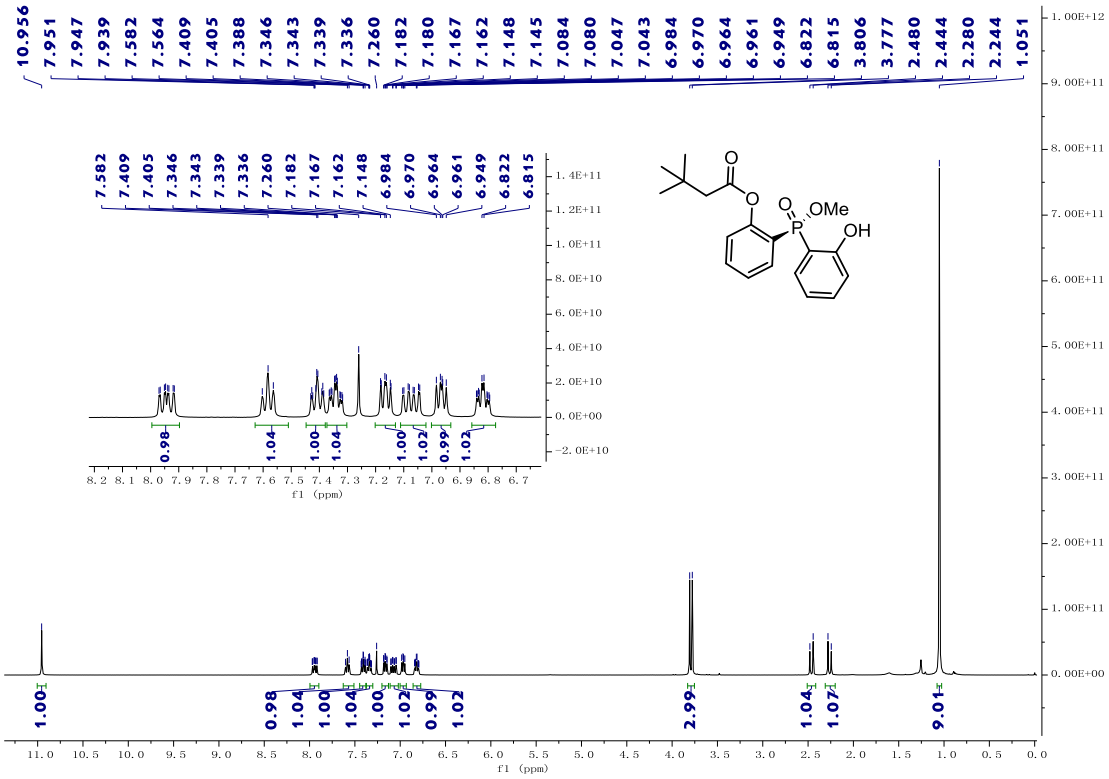
HRMS analysis

Figure S2. The mixture of **C2a** and acyl chloride **2a** in toluene at 0 °C for 1 h.

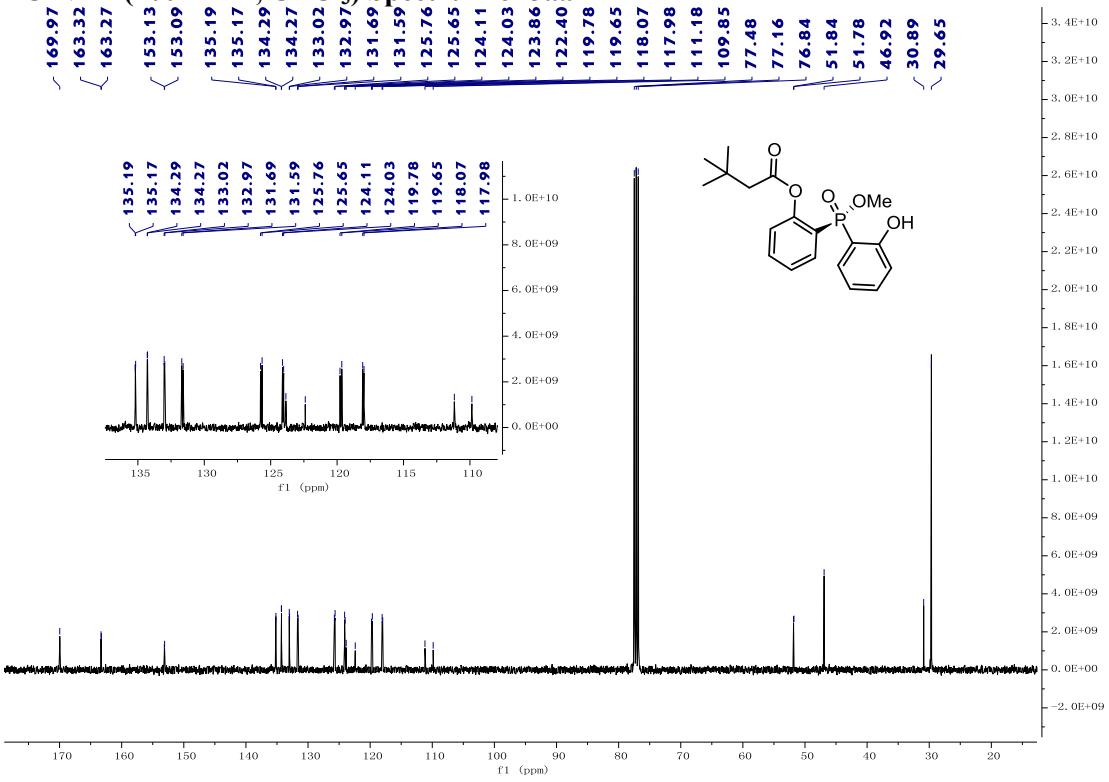




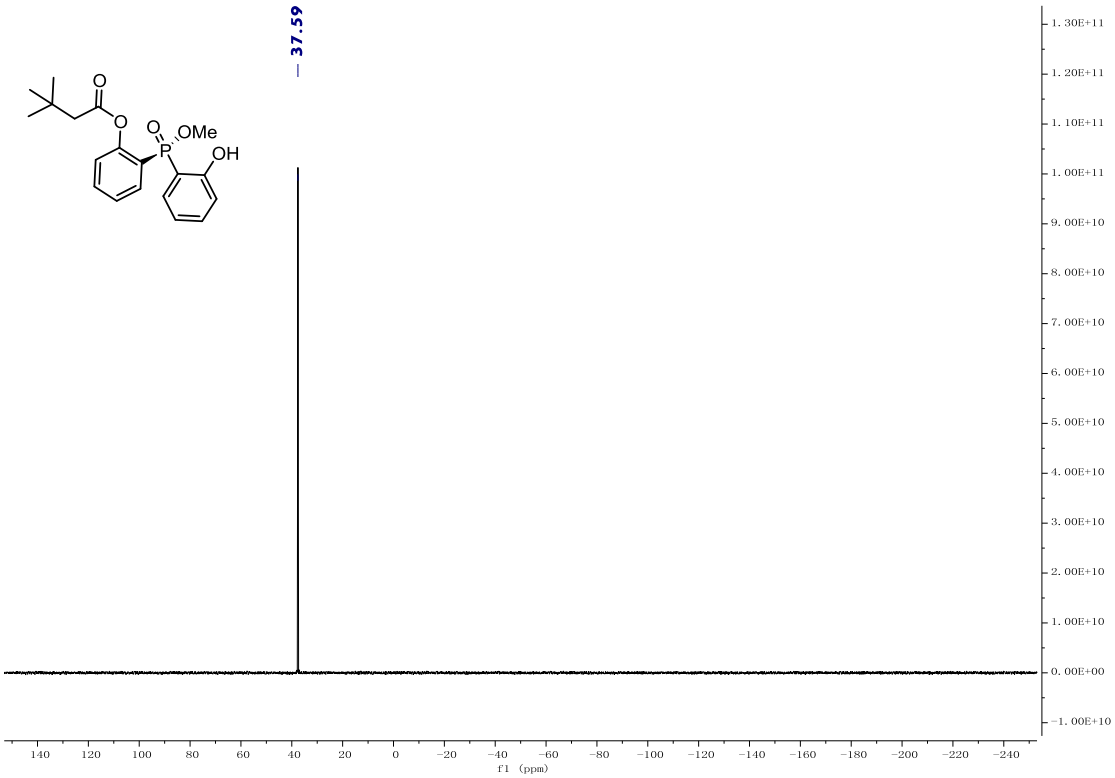
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3aa



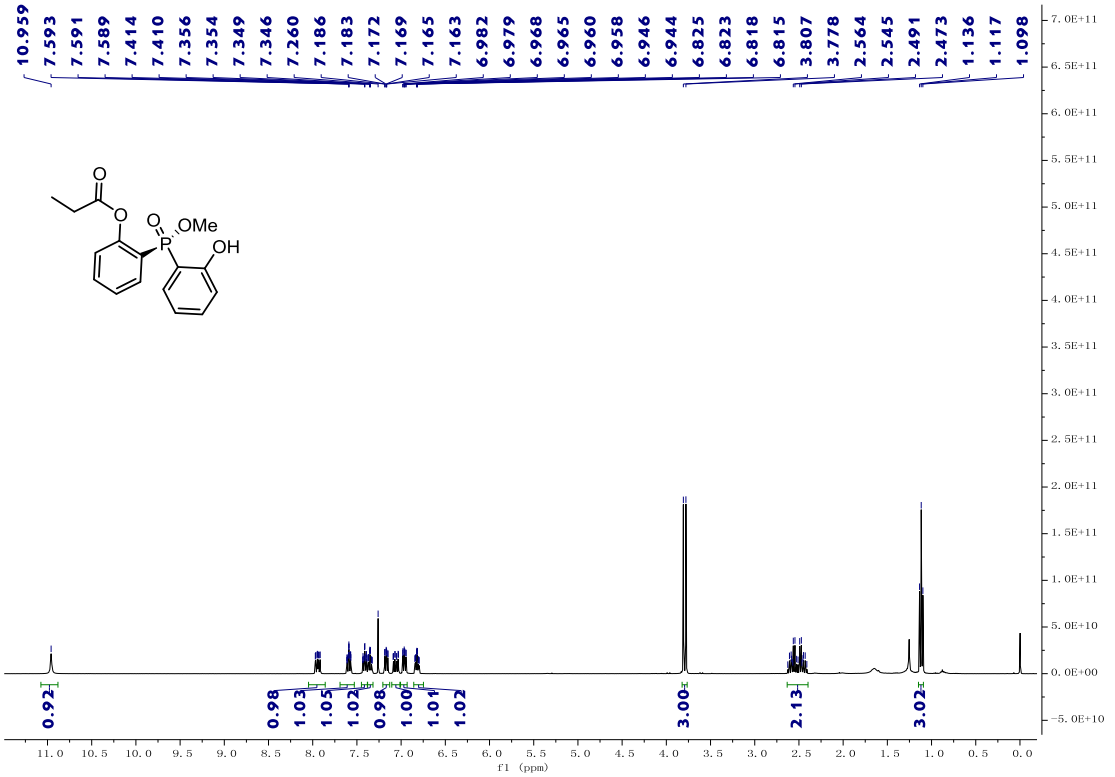
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3aa



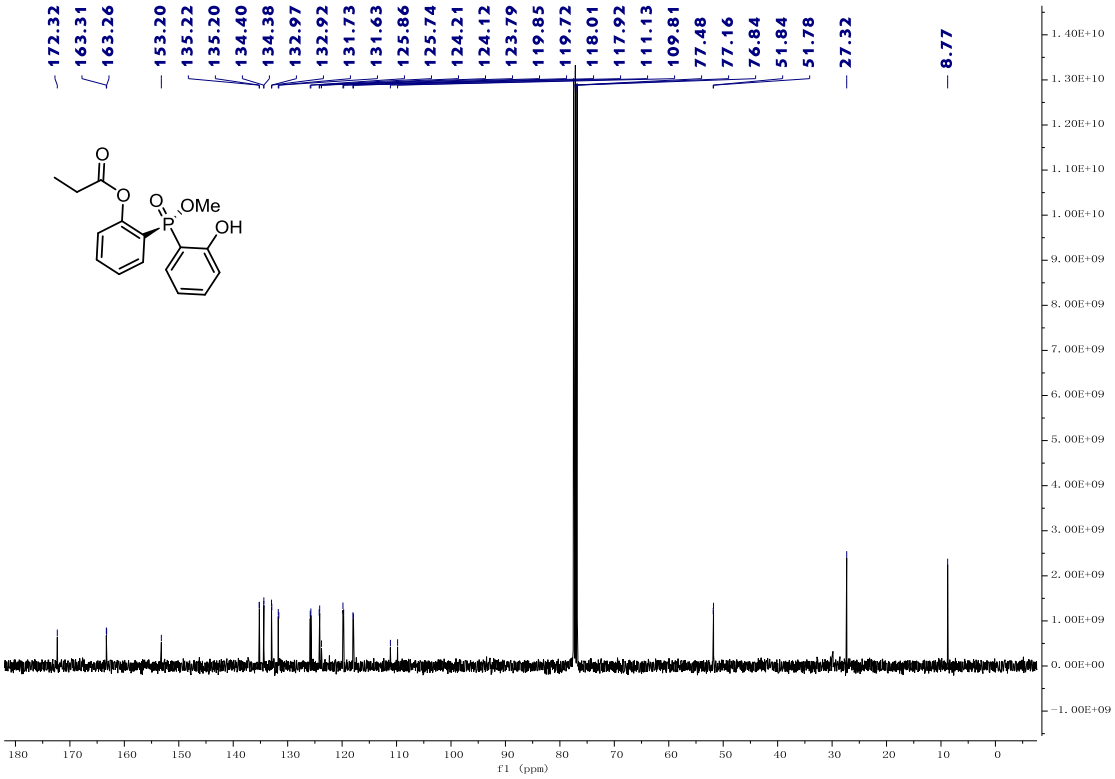
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3aa



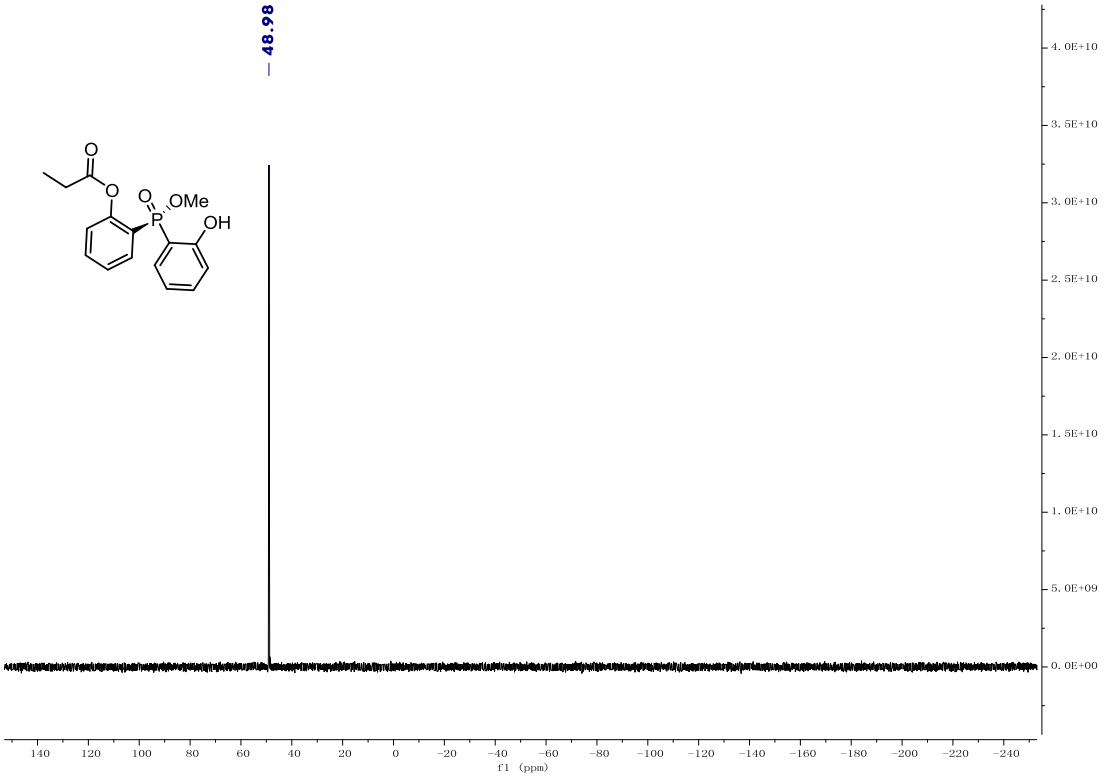
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ab



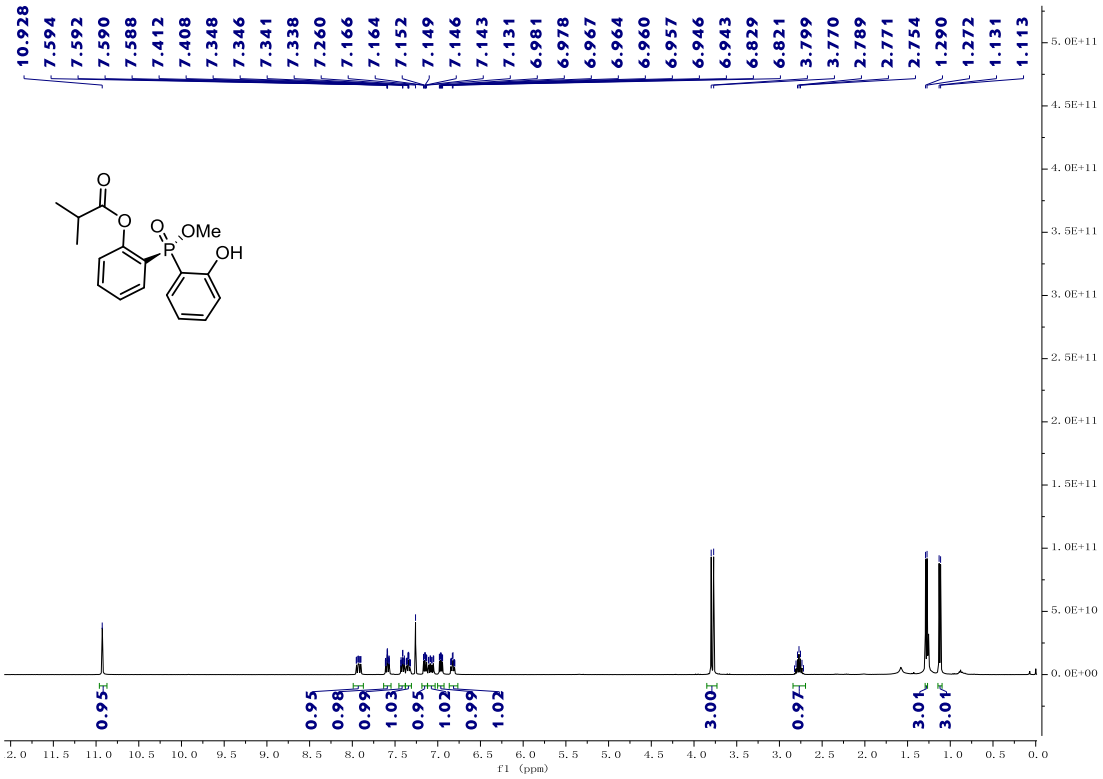
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ab



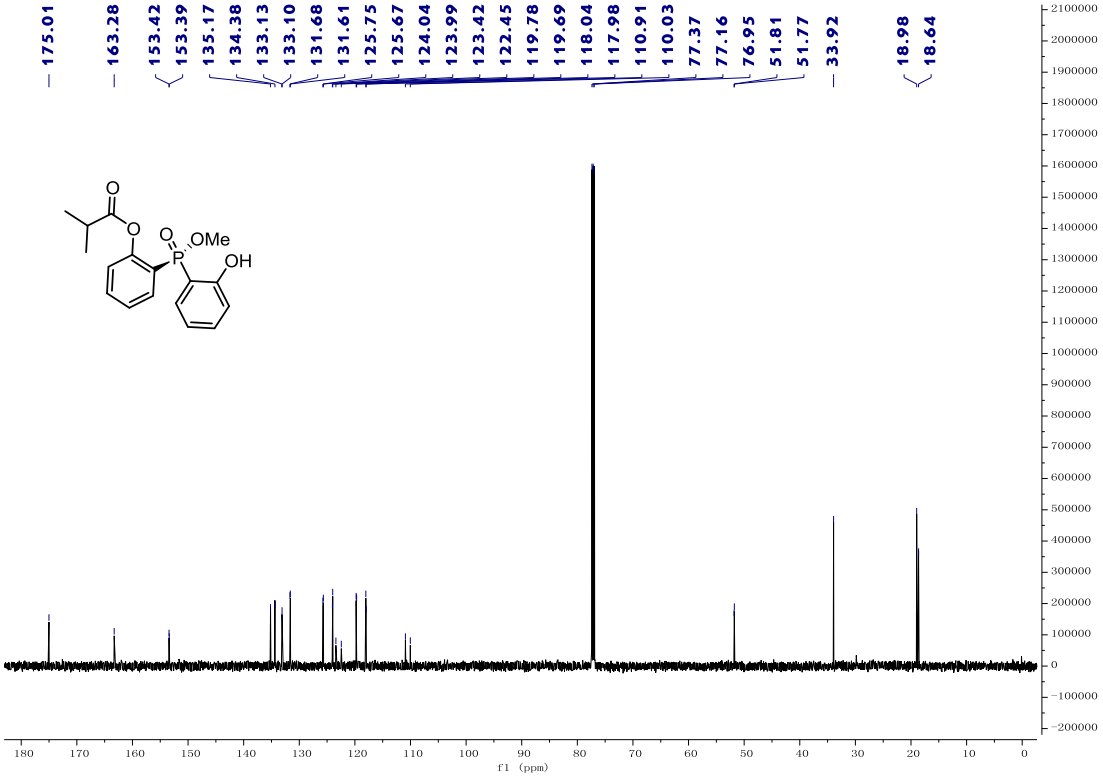
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ab



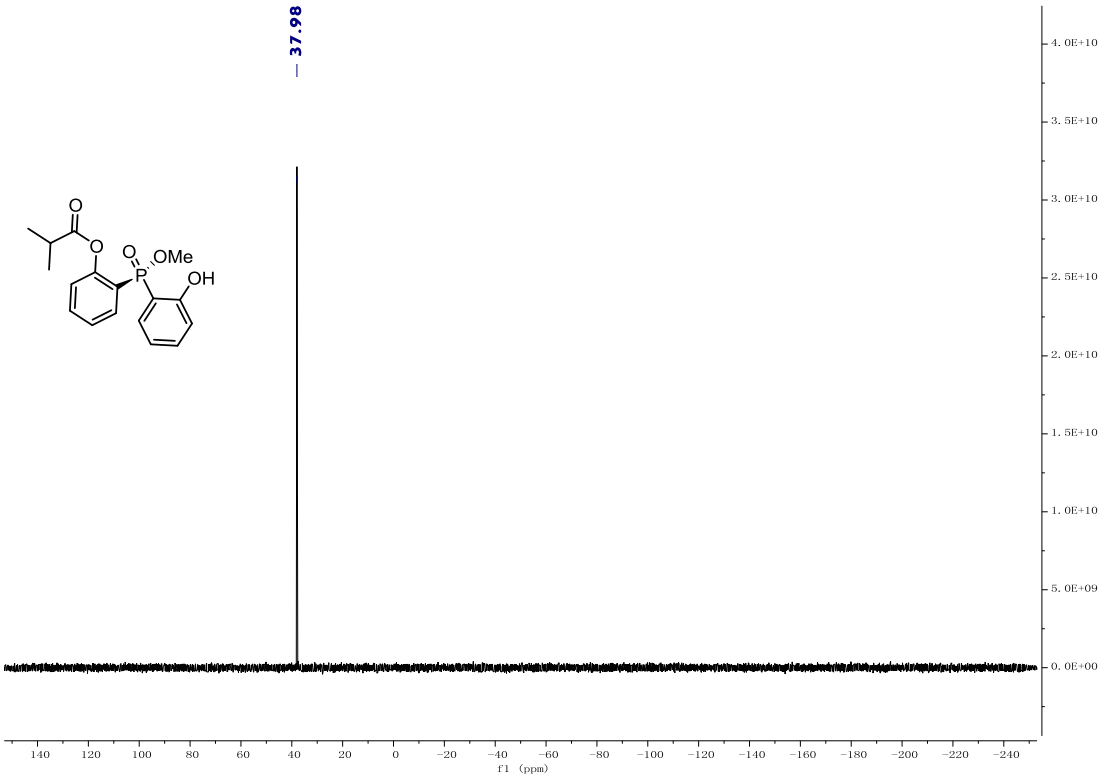
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ac



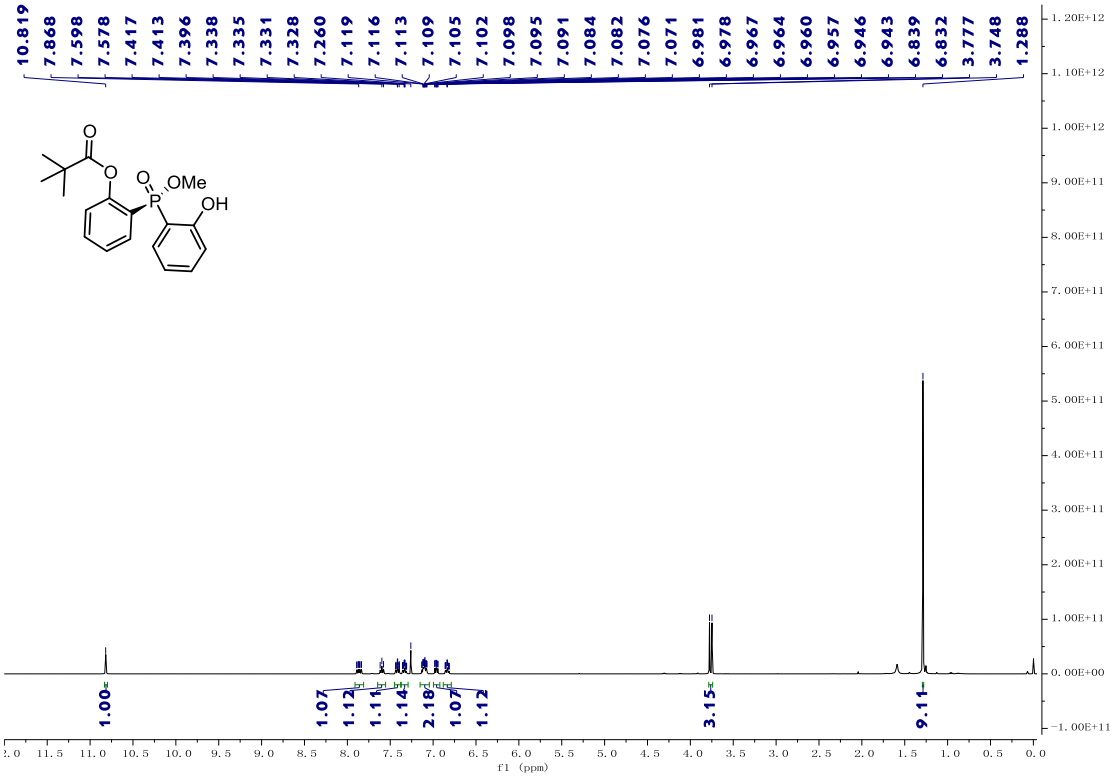
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3ac



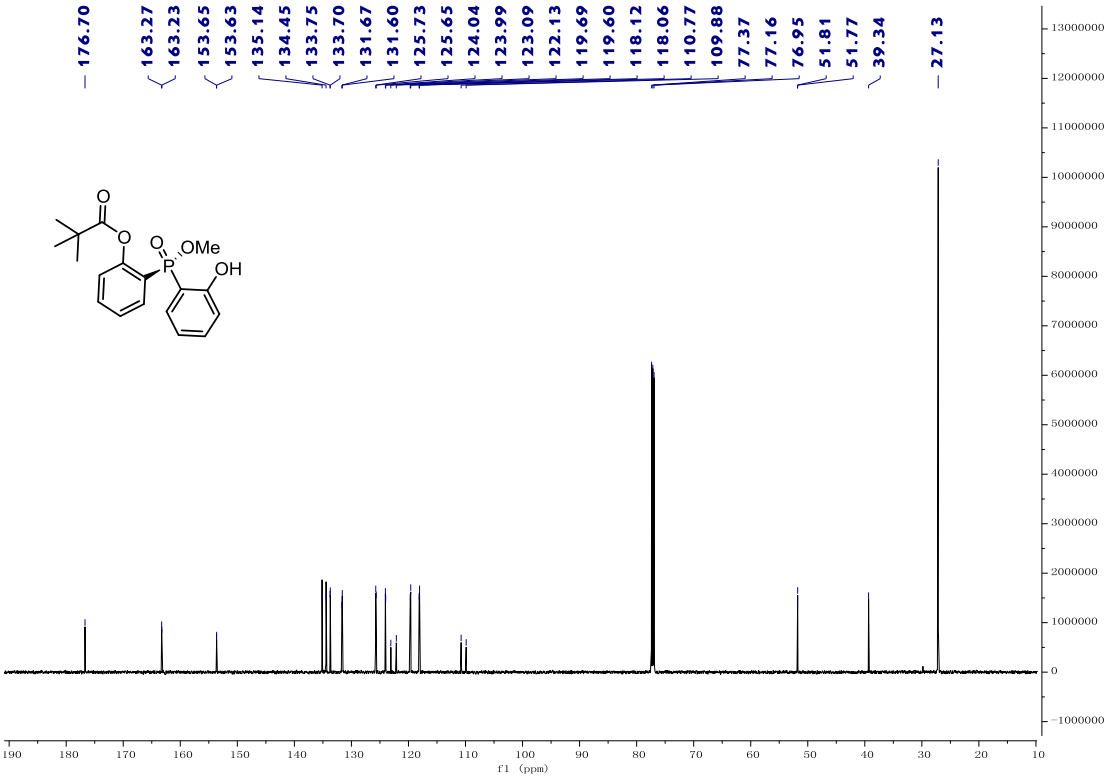
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ac



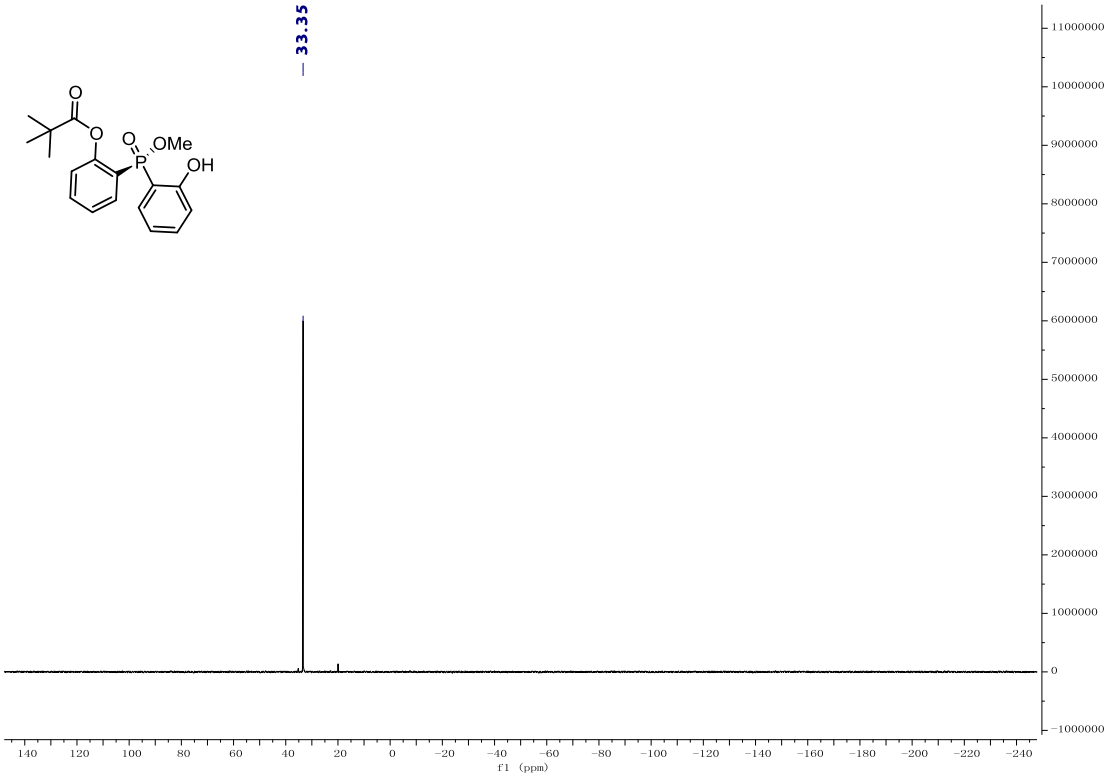
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ad



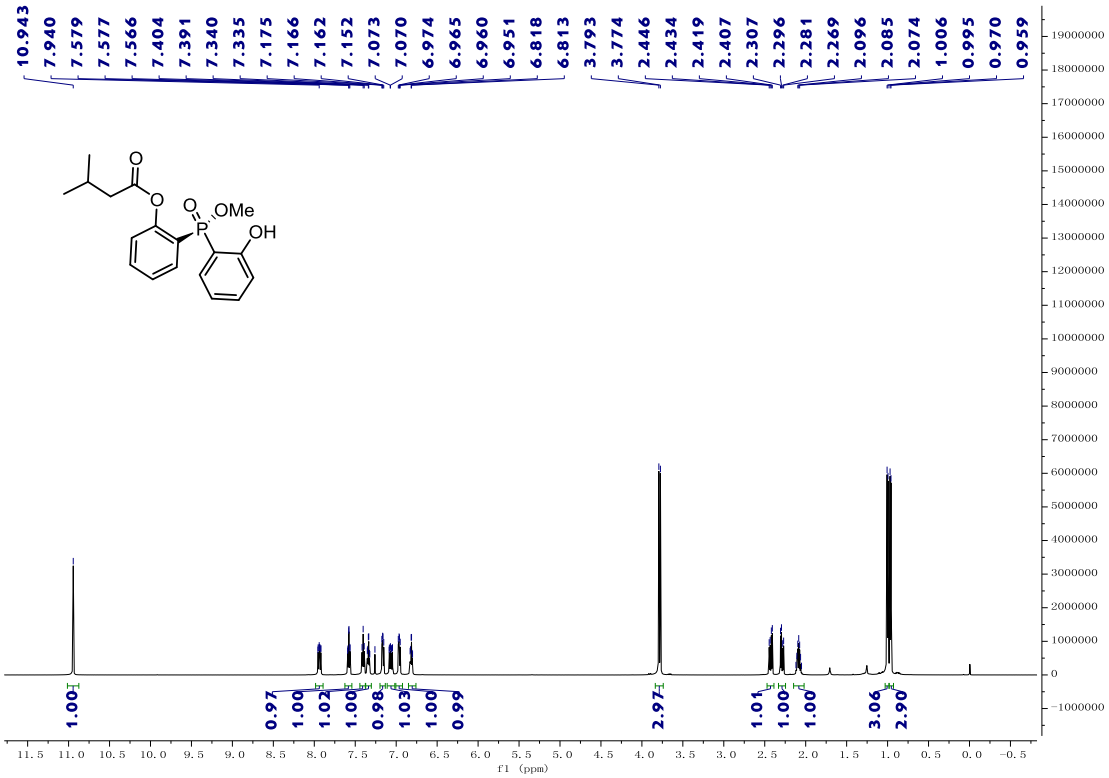
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3ad



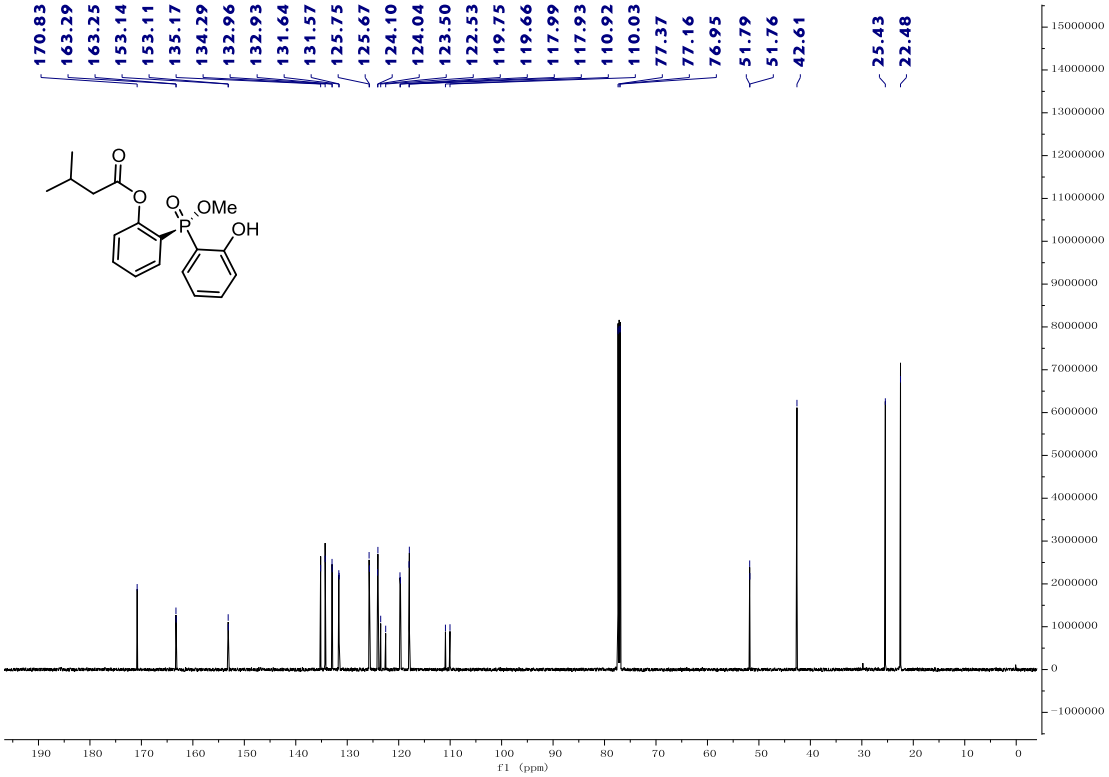
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3ad



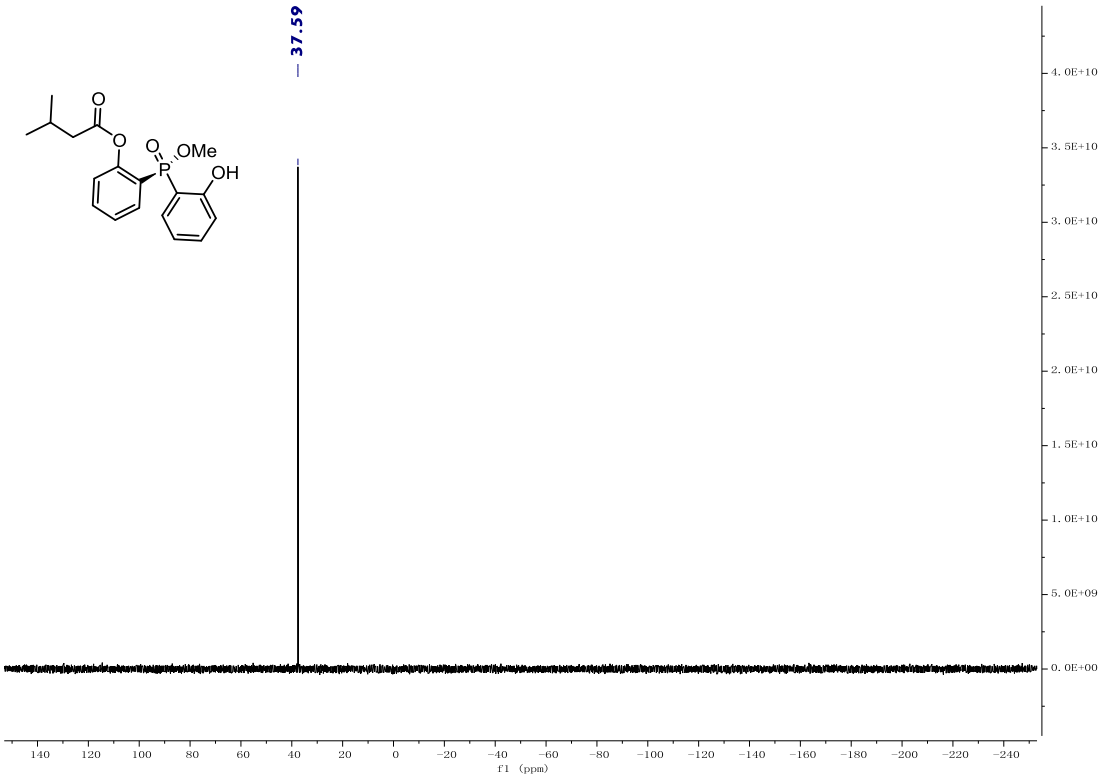
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3ae



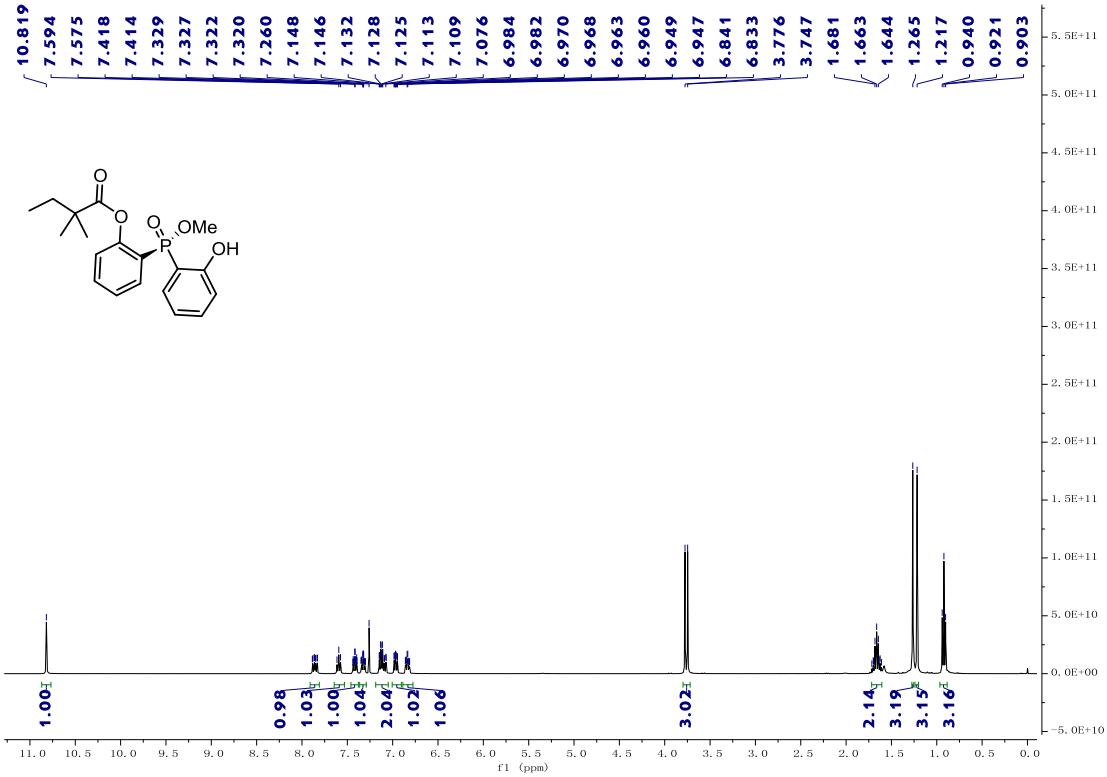
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3ae



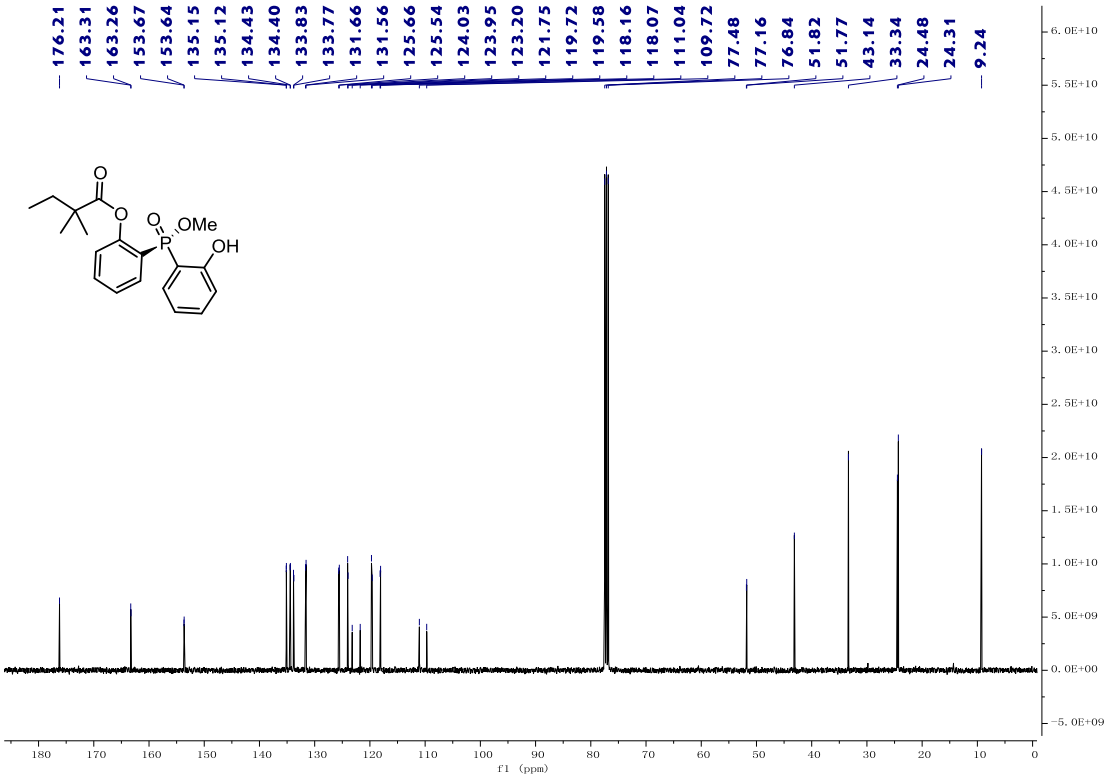
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3ae



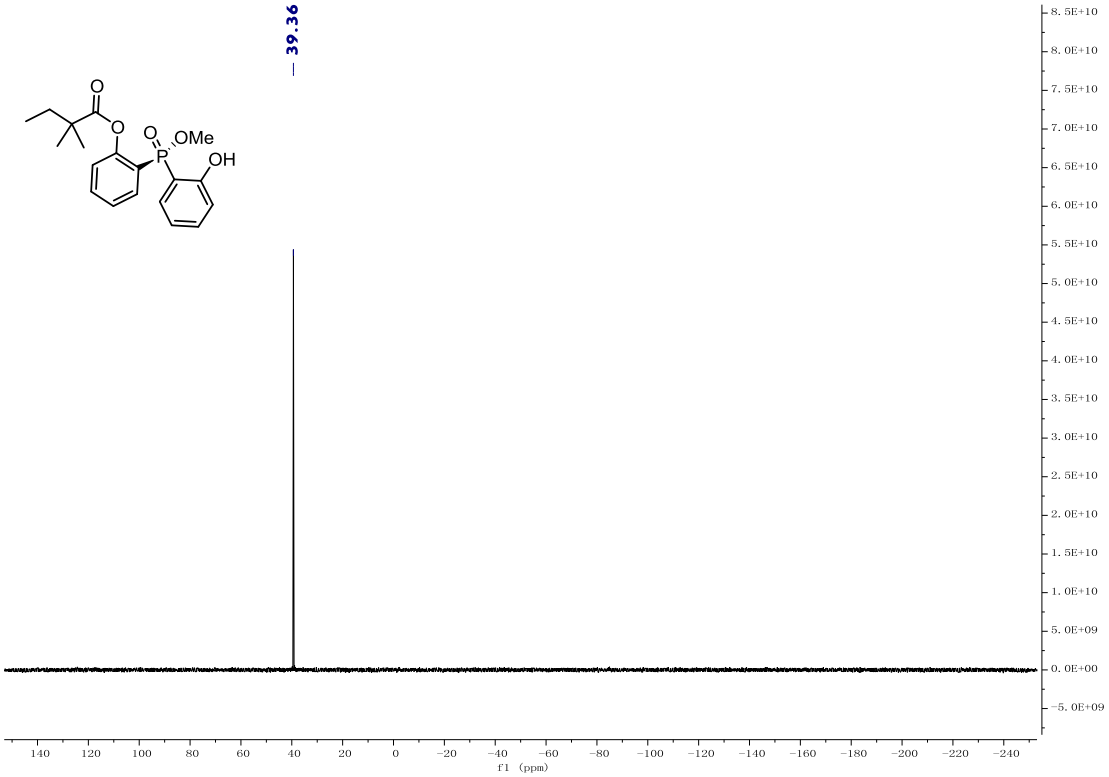
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3af



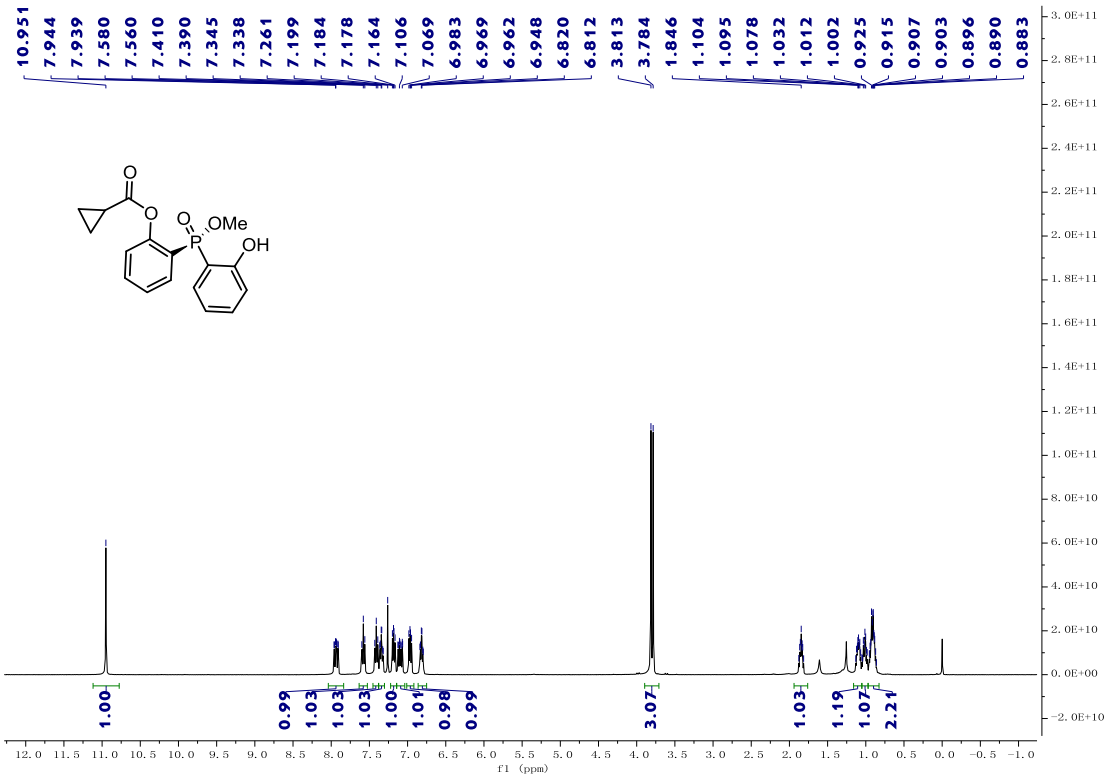
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3af



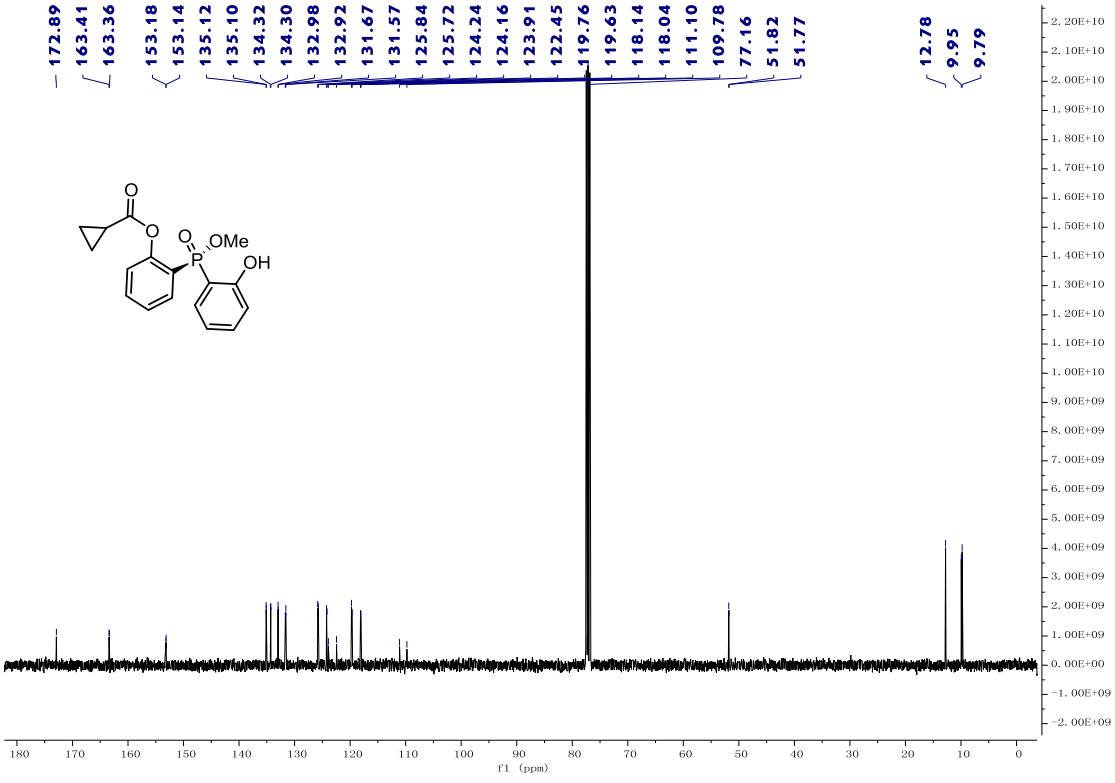
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3af



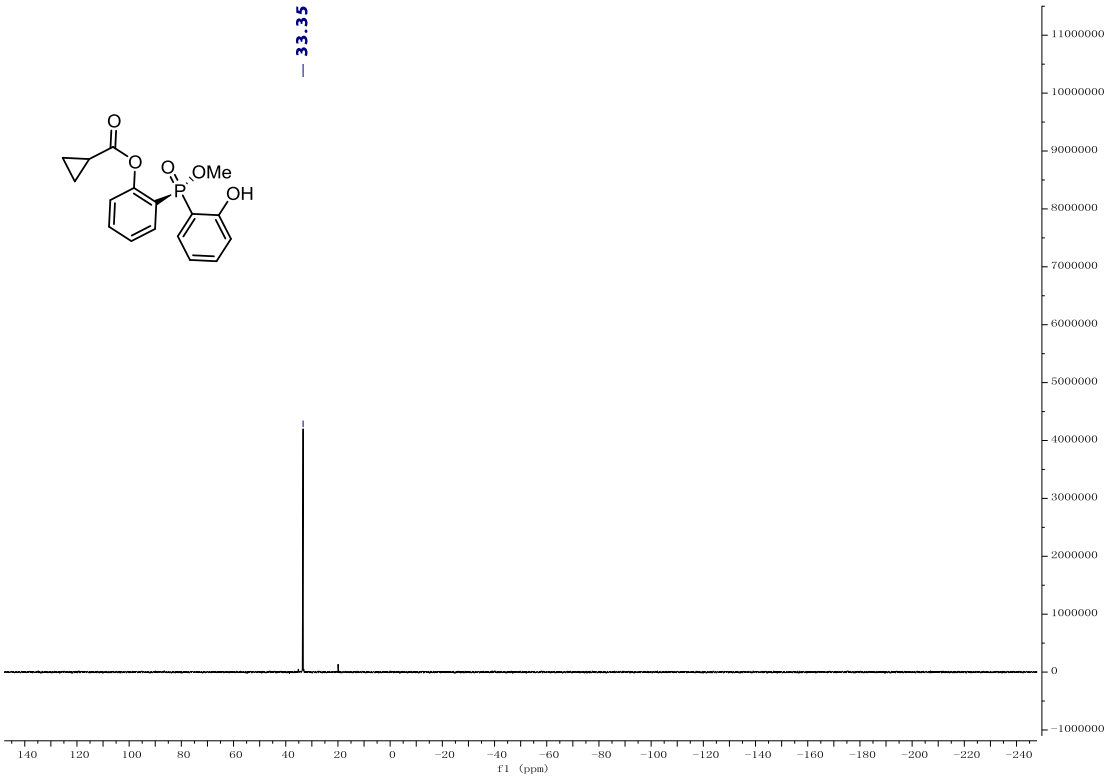
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ag



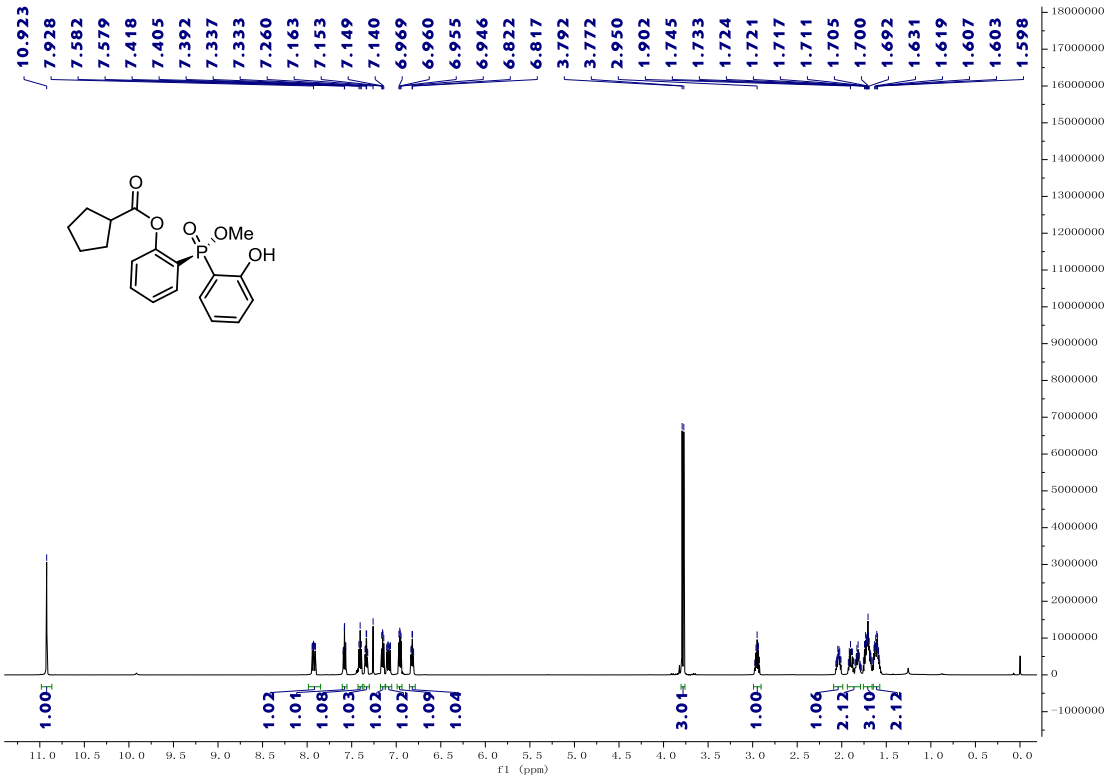
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ag



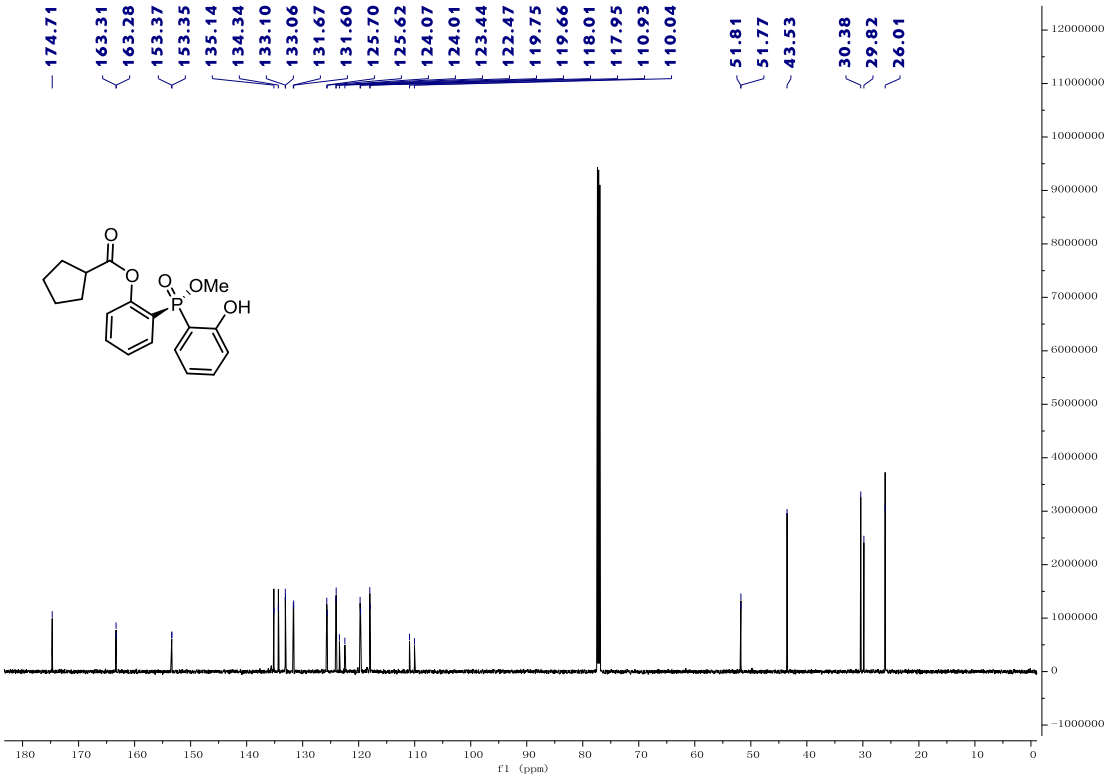
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3ag



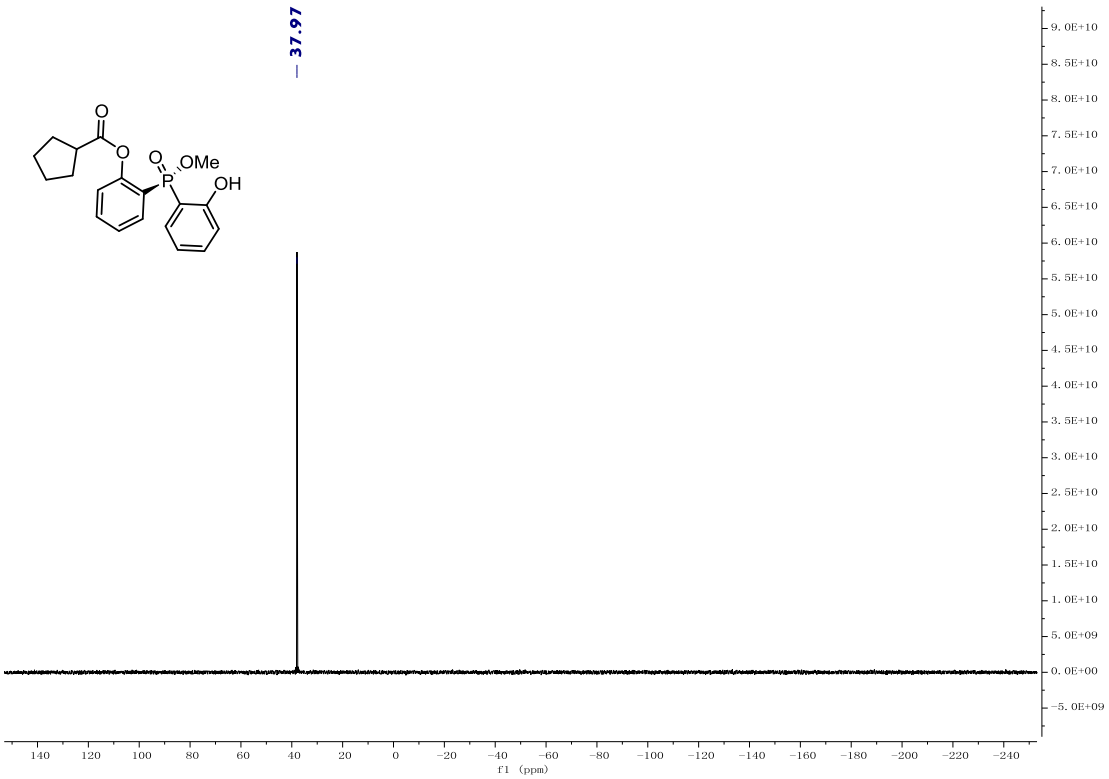
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3ah



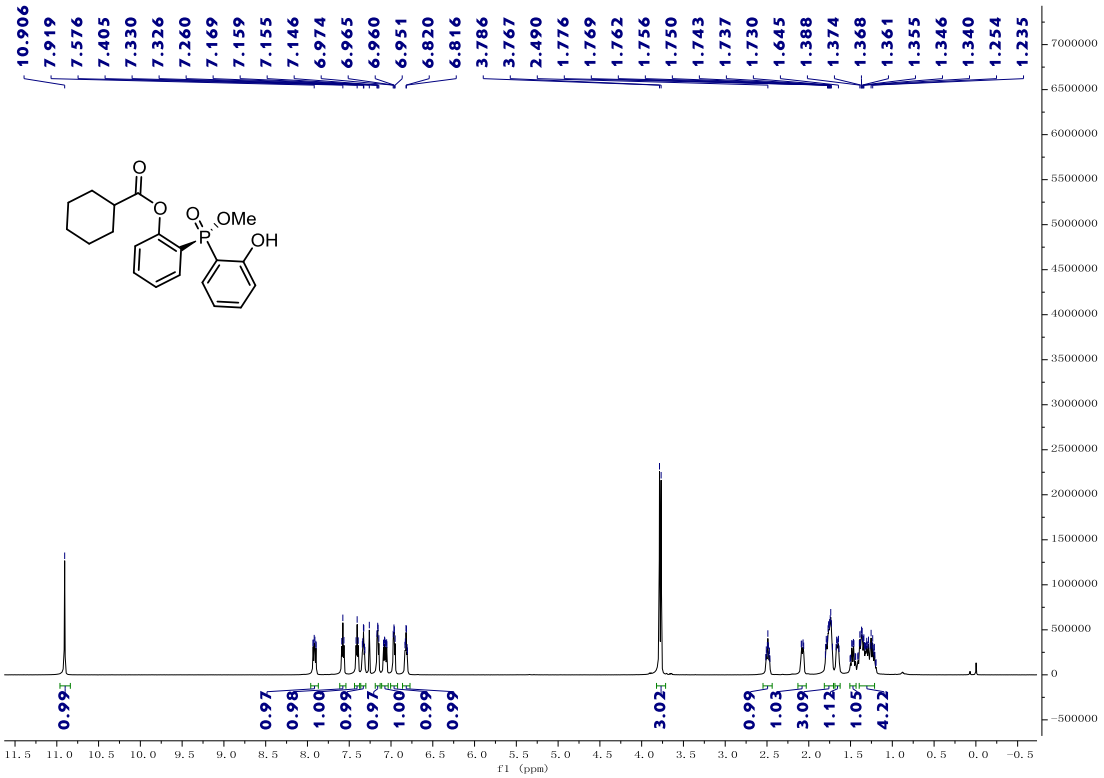
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3ah



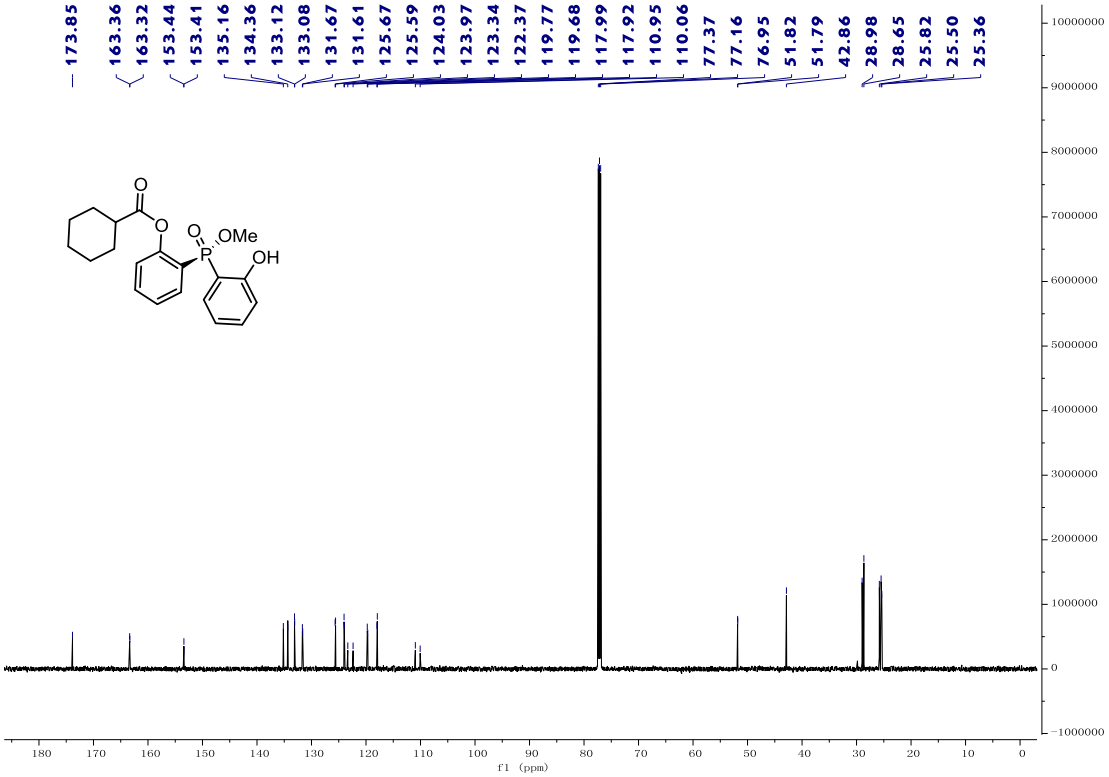
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ah



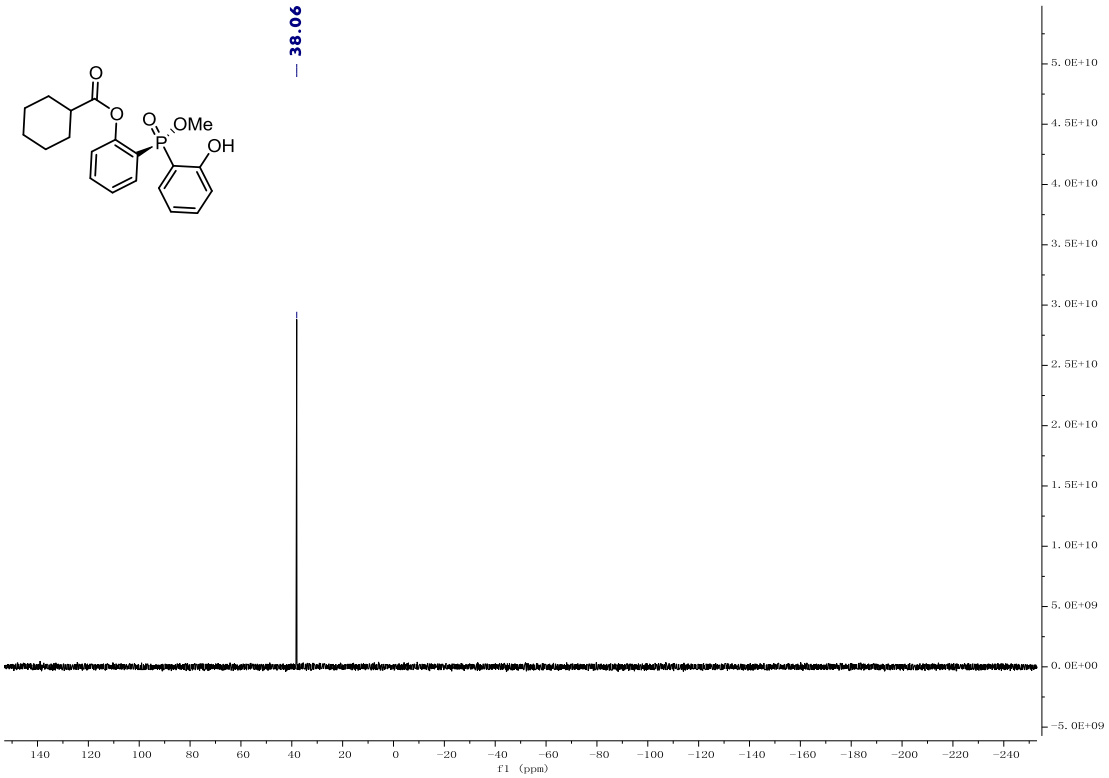
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3ai



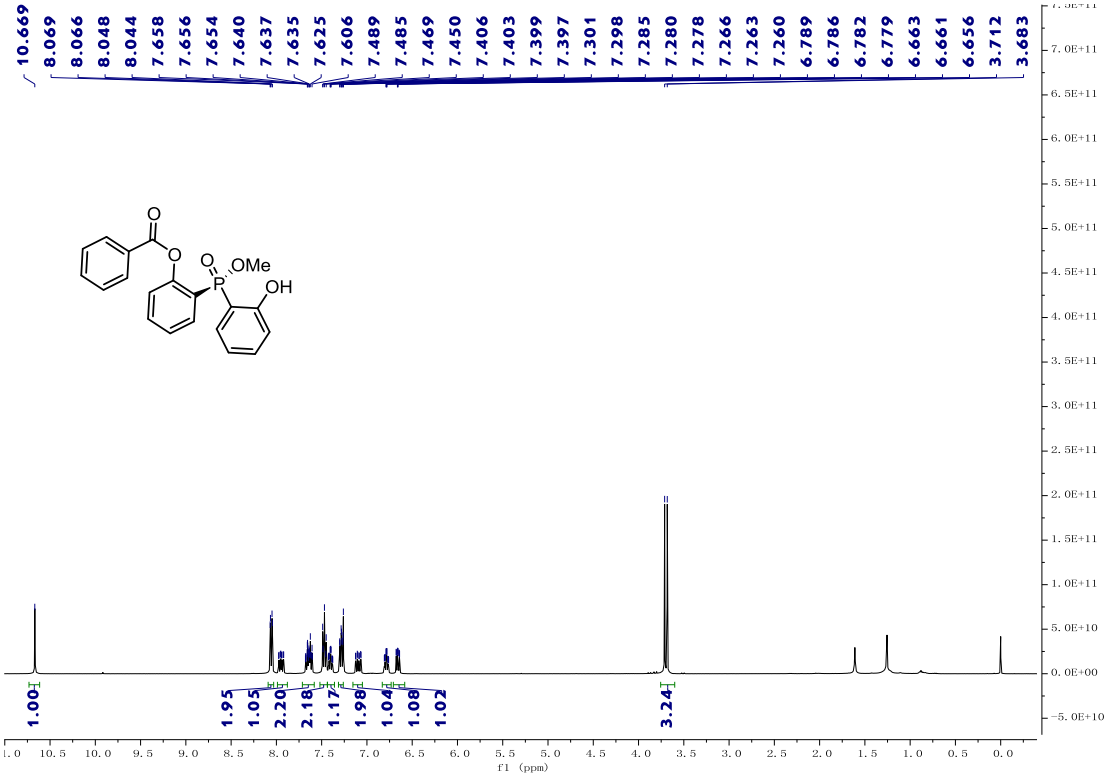
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3ai



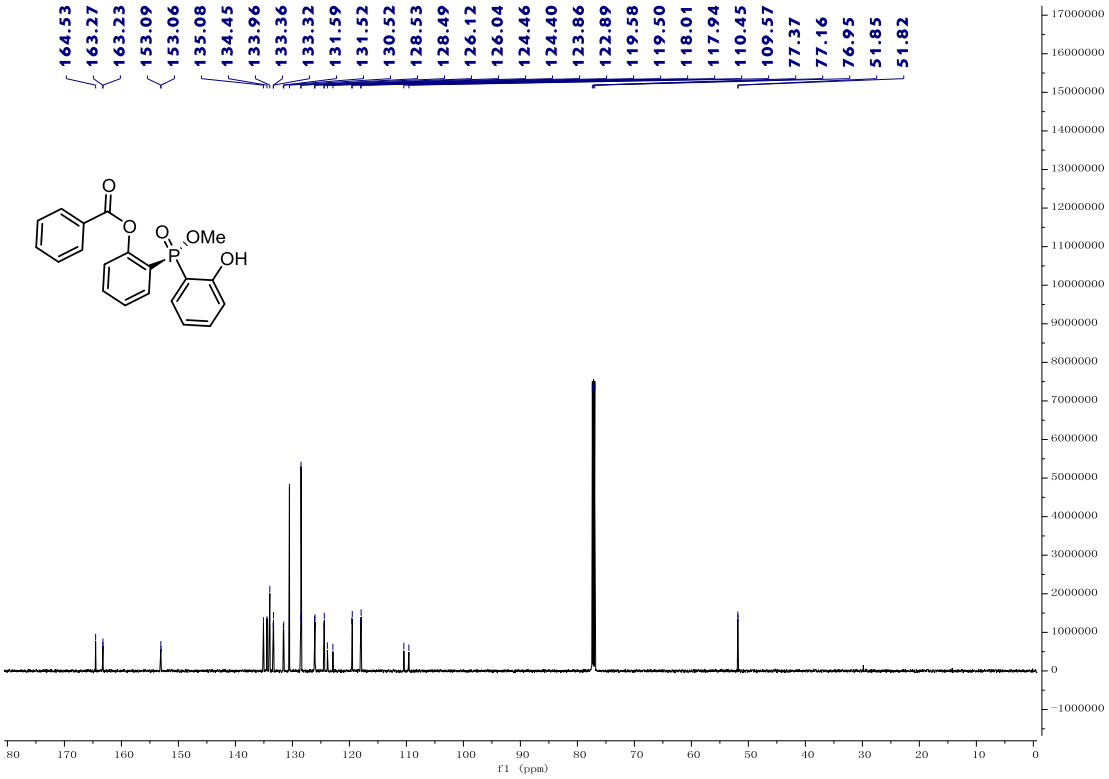
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ai



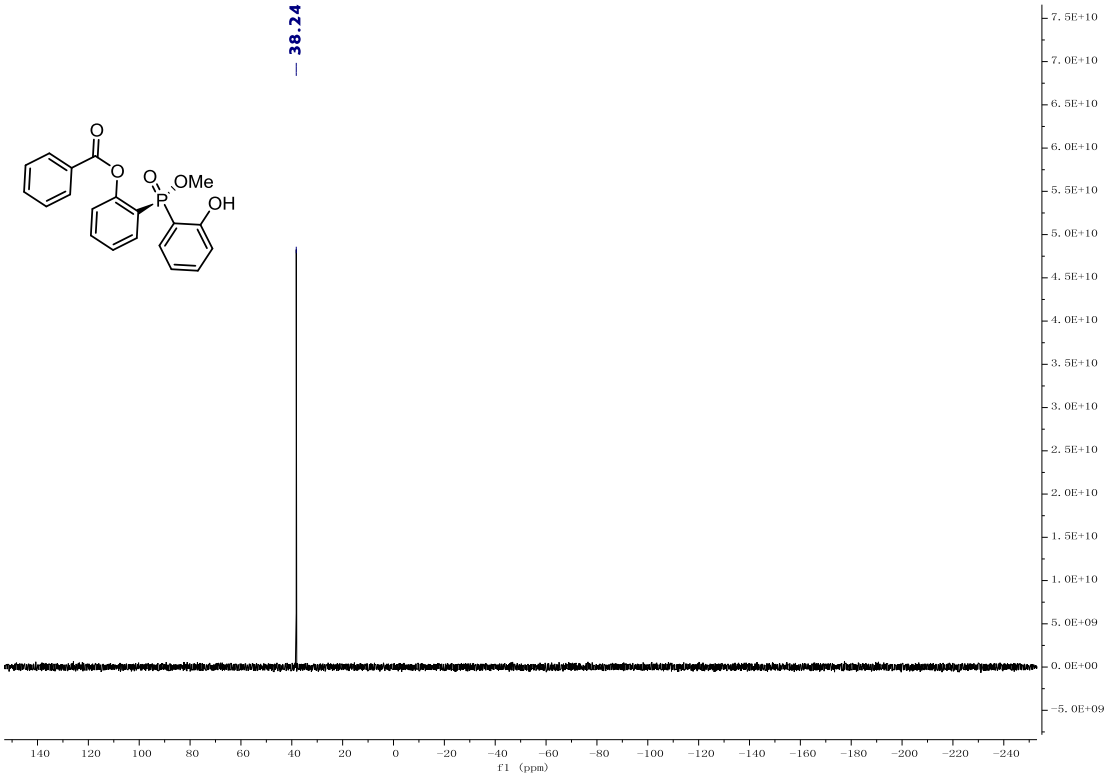
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3aj



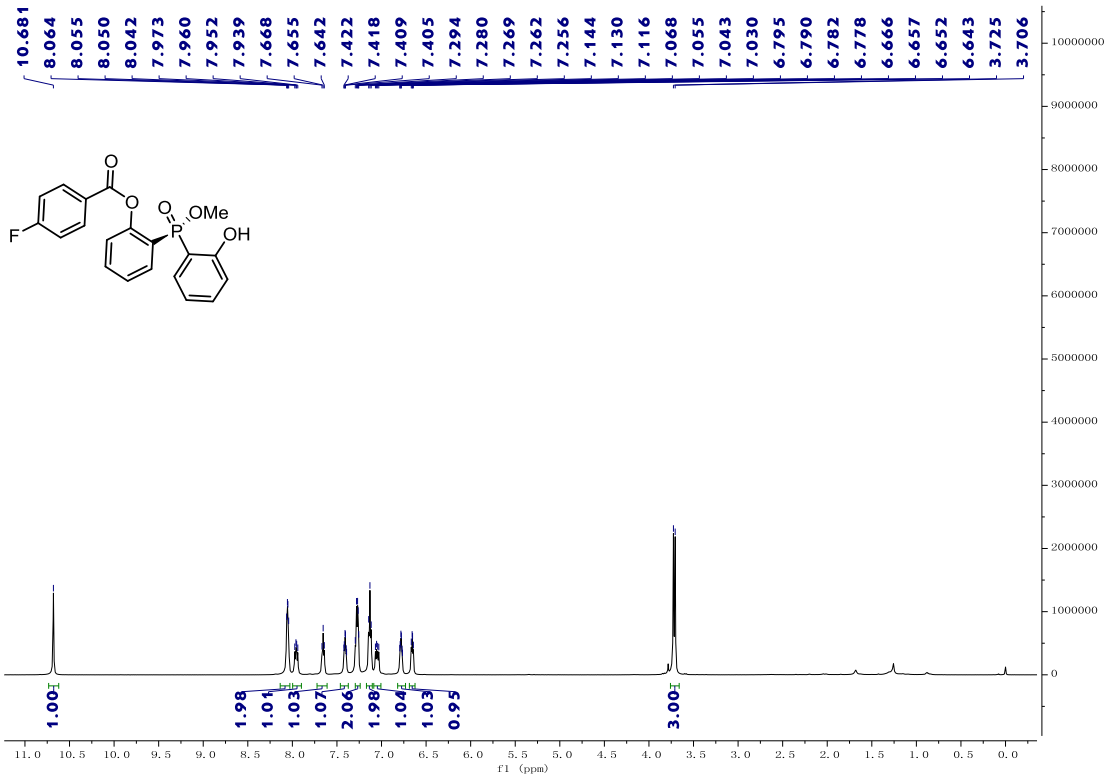
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3aj



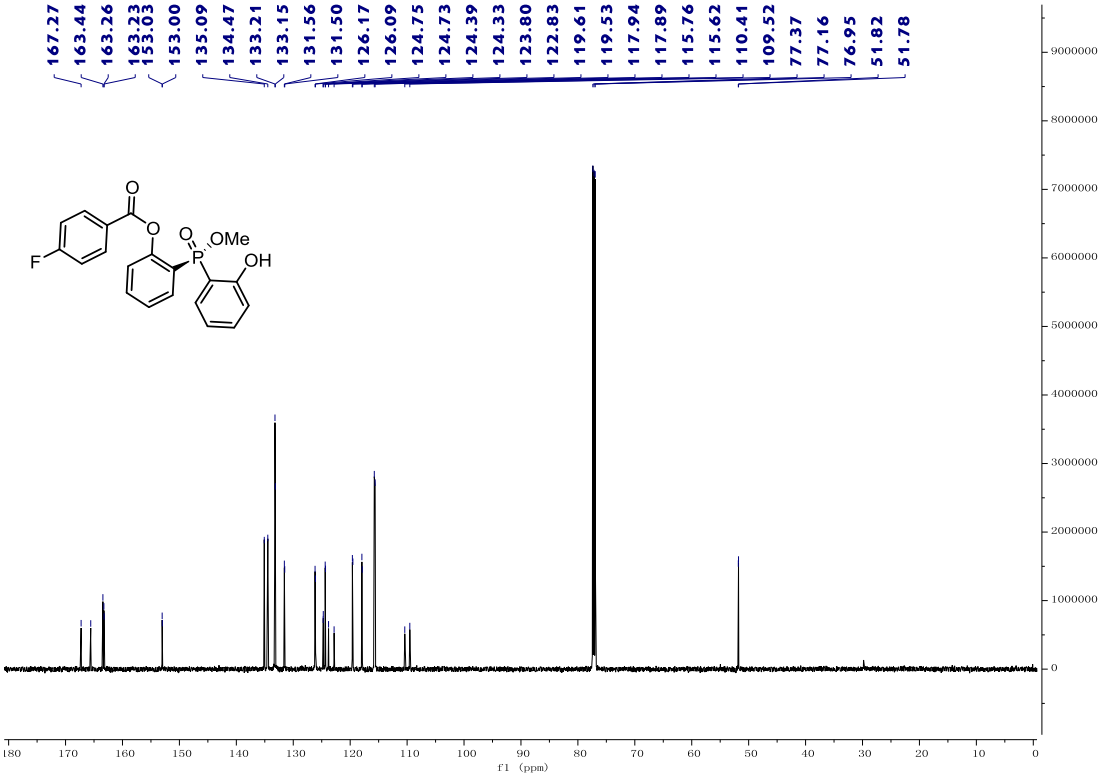
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3aj



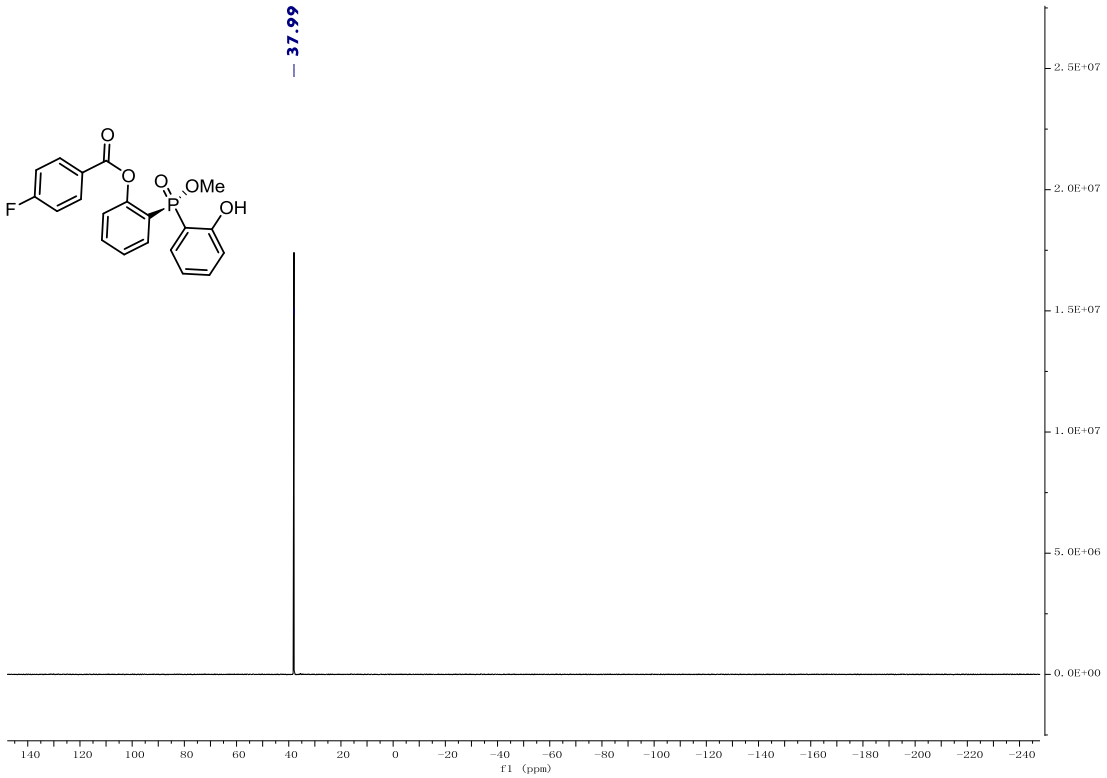
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3ak



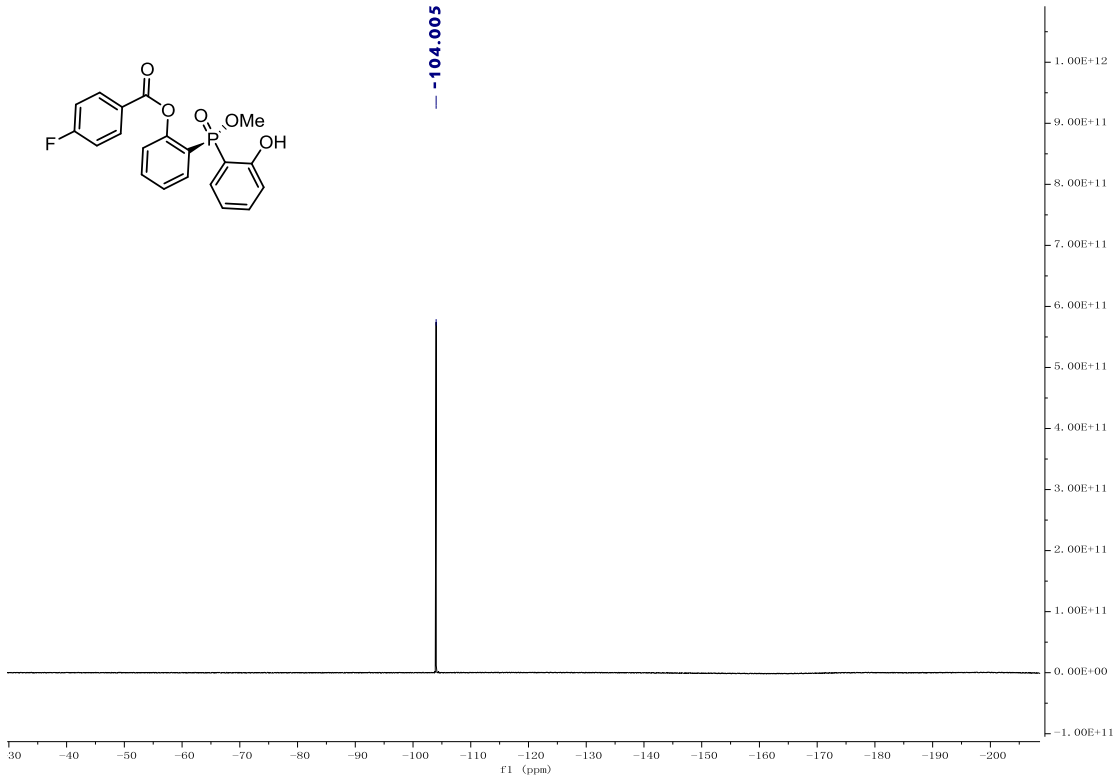
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3ak



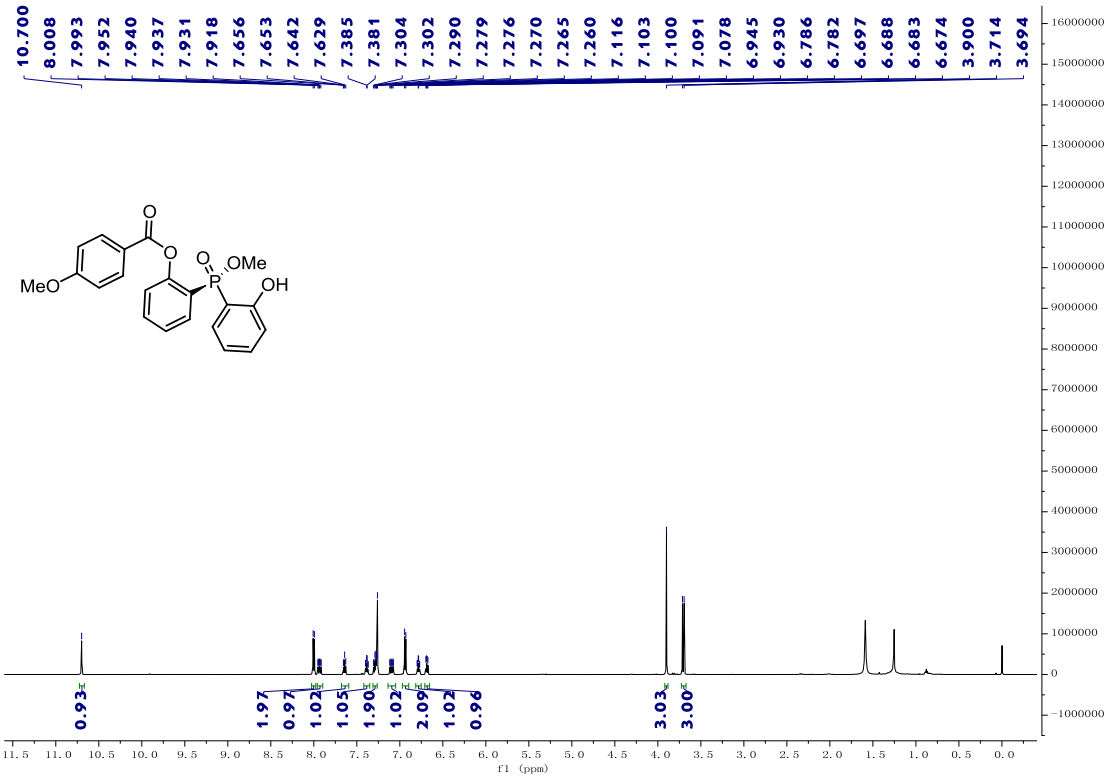
^{31}P-NMR(242 MHZ, $CDCl_3$) Spectrum of 3ak



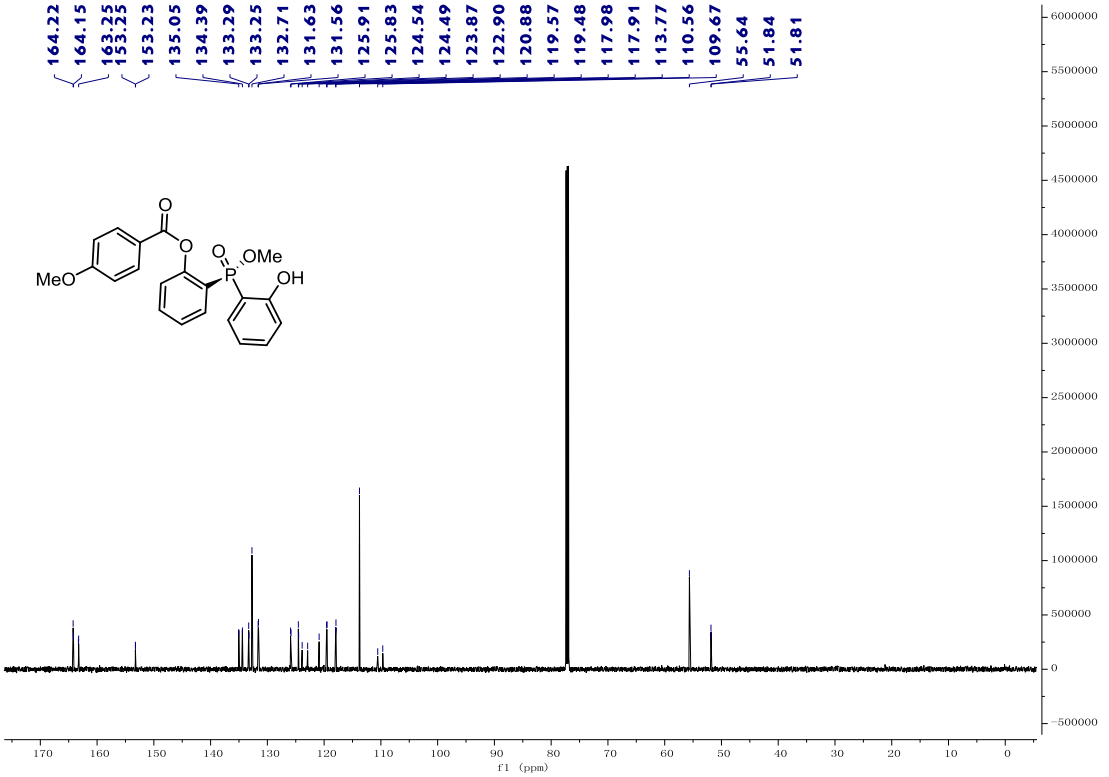
^{19}F-NMR(376 MHZ, $CDCl_3$) Spectrum of 3ak



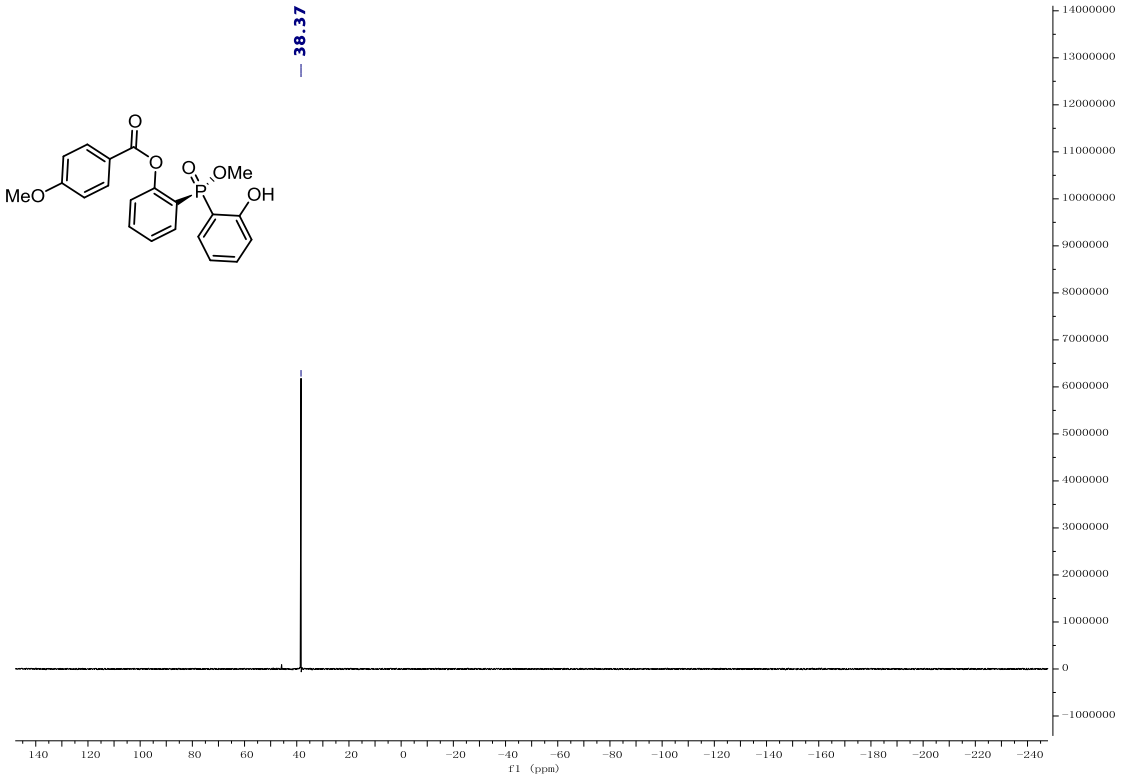
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3al



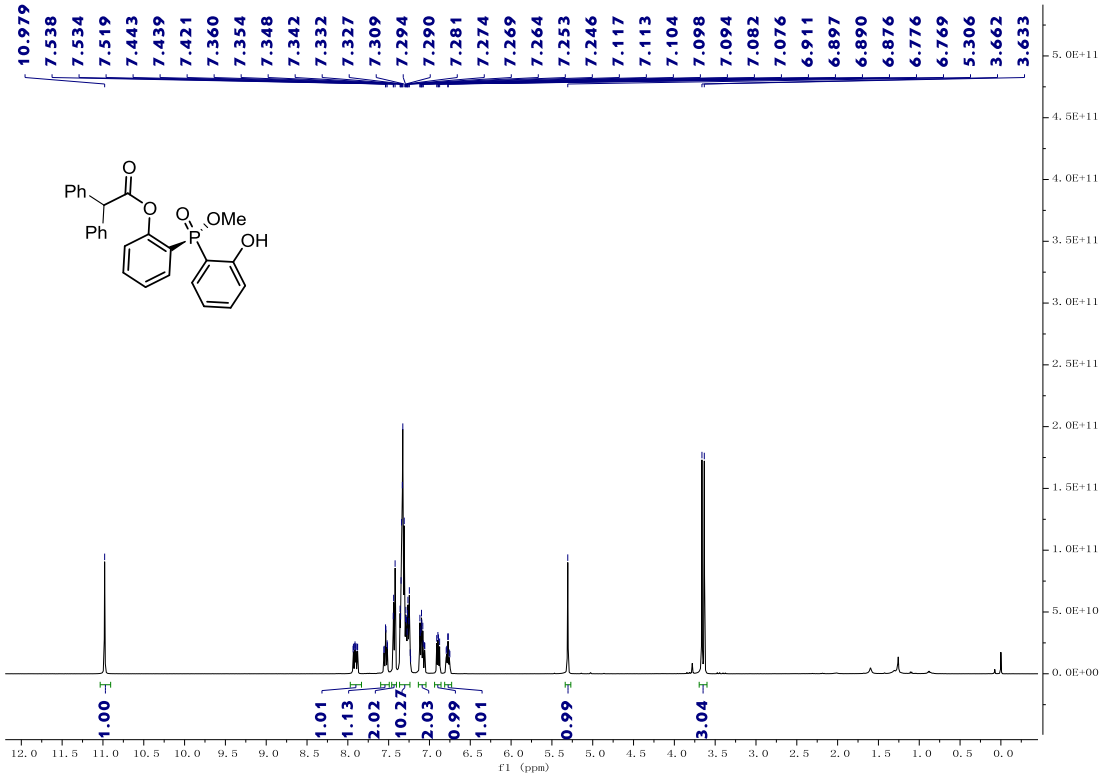
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3al



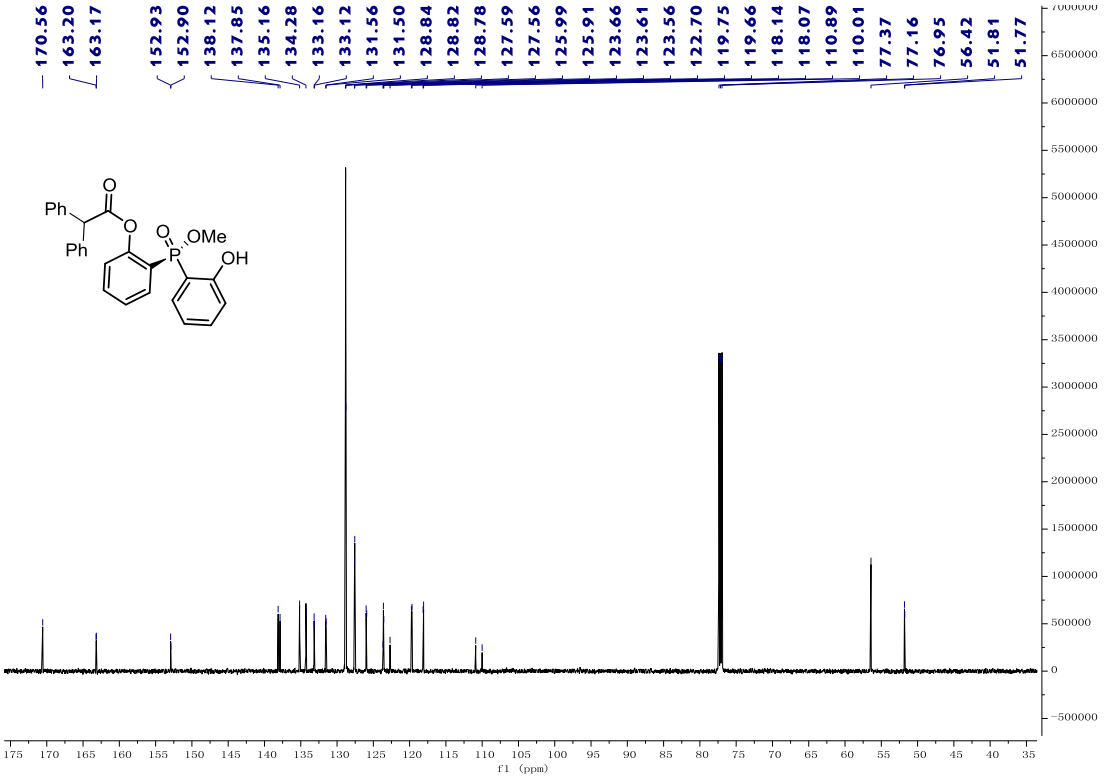
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3al



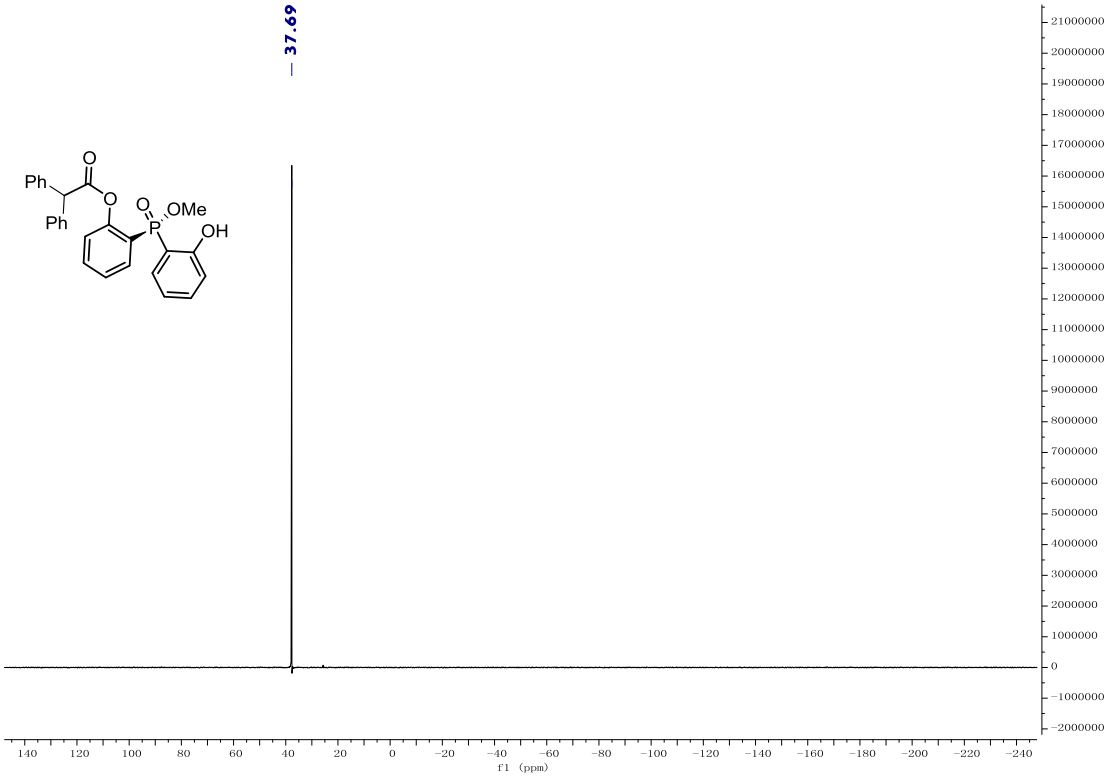
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3am



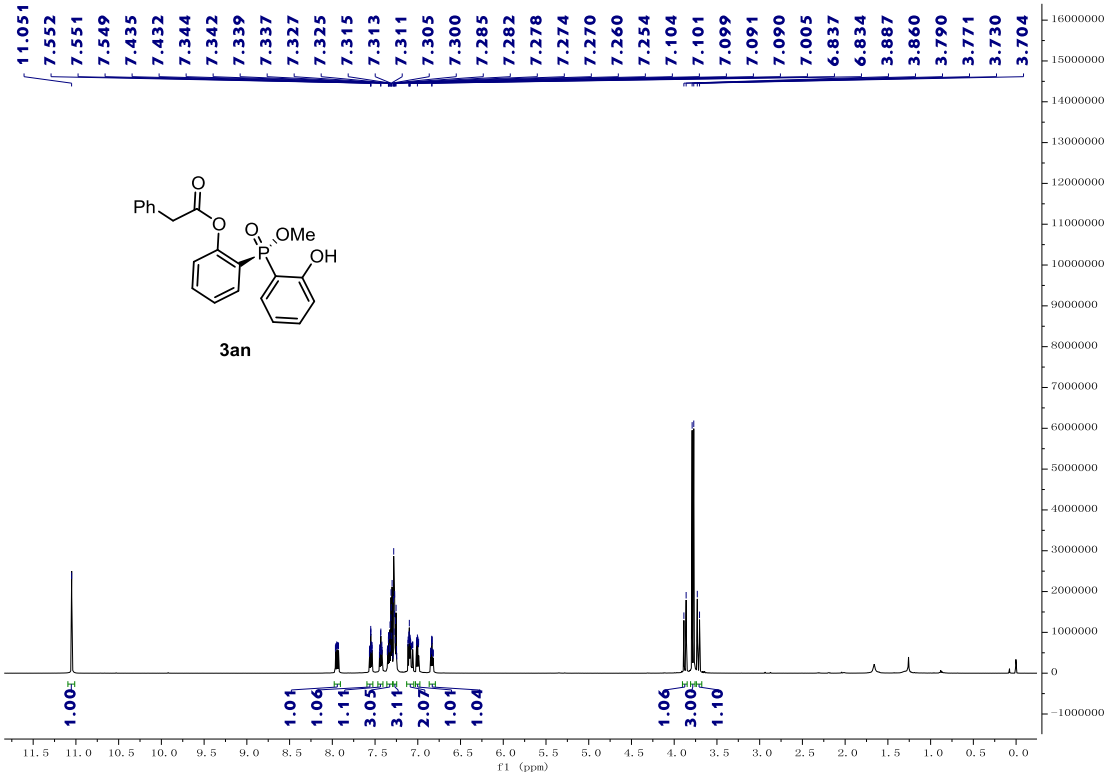
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3am



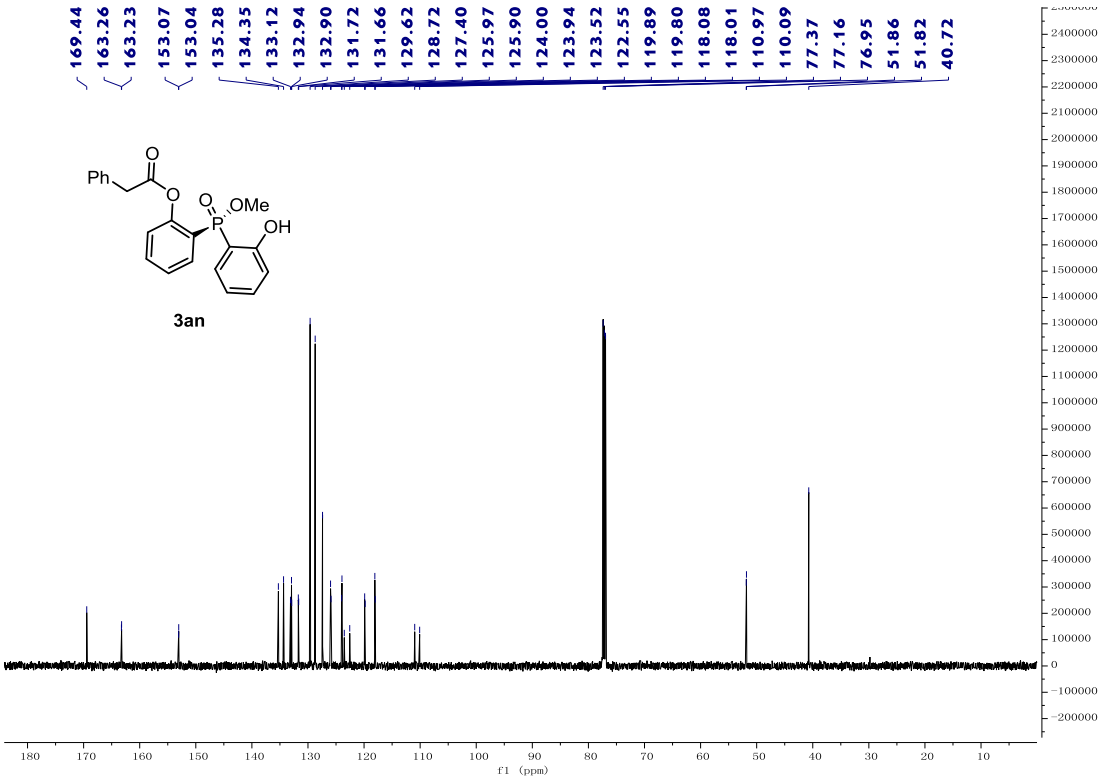
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3am



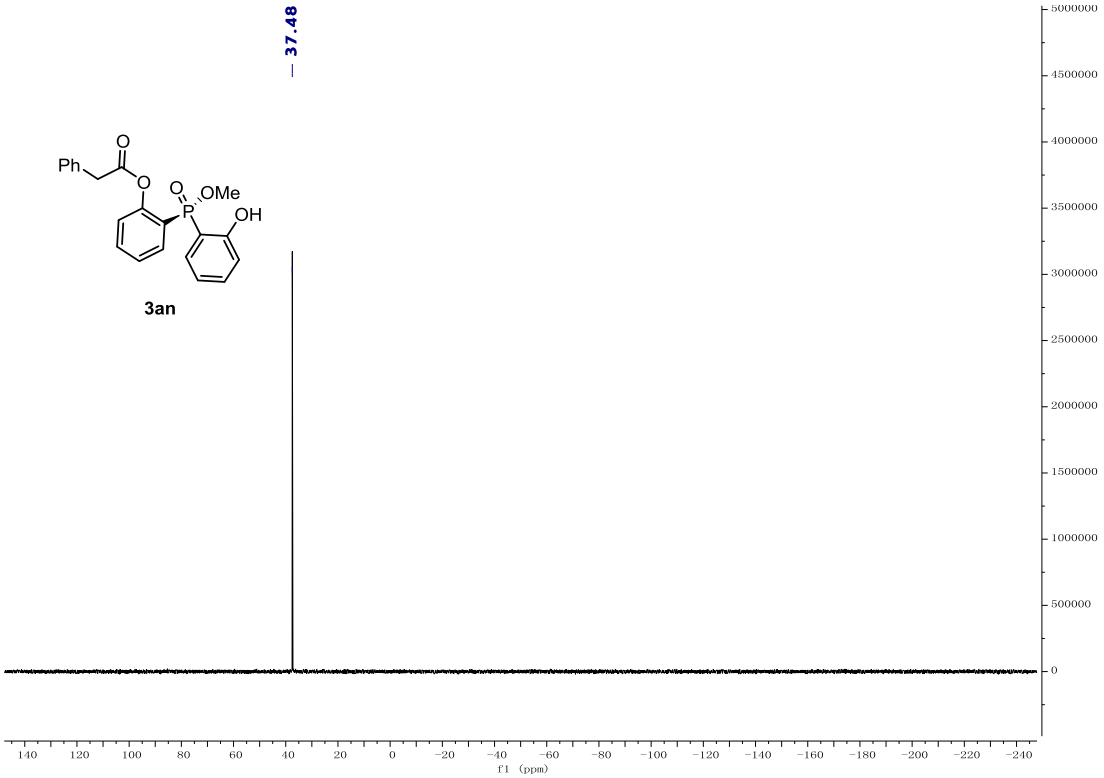
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3an



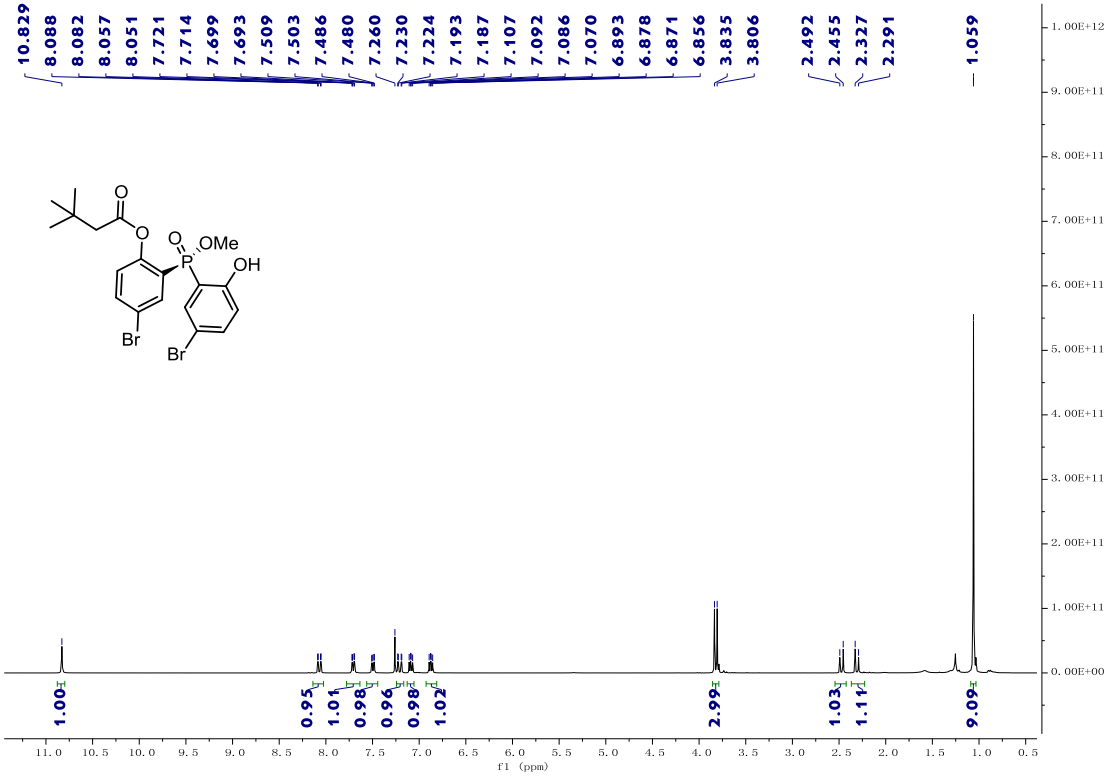
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3an



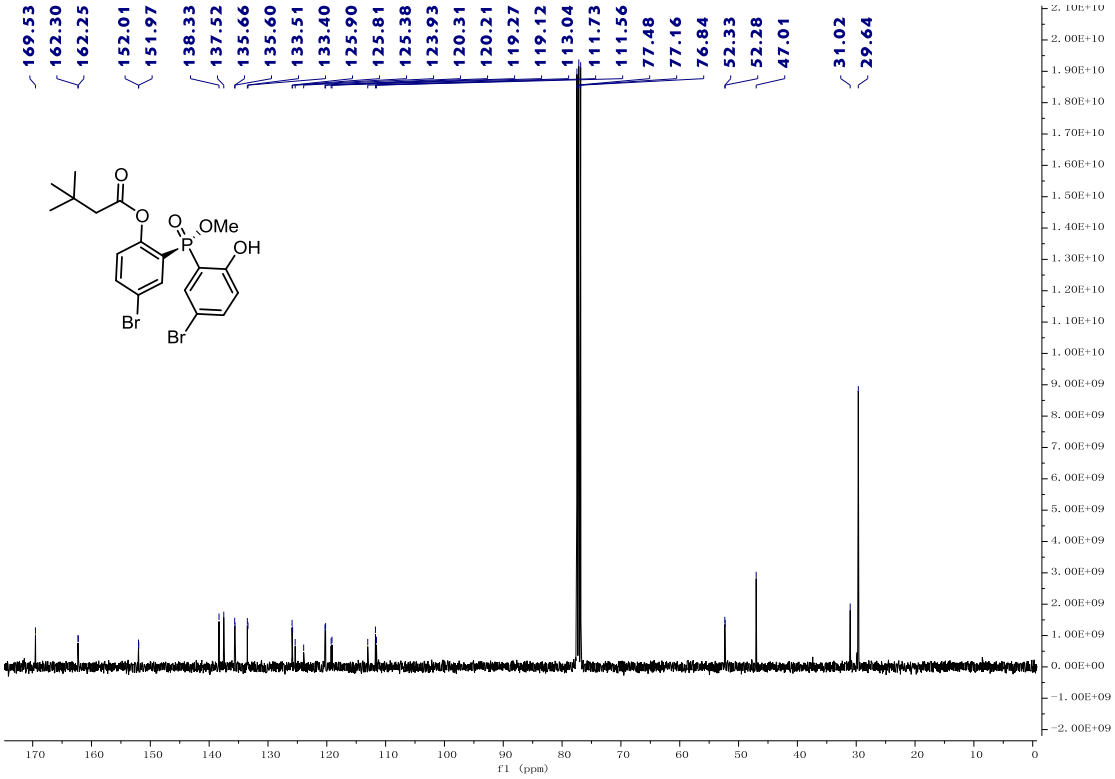
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3an



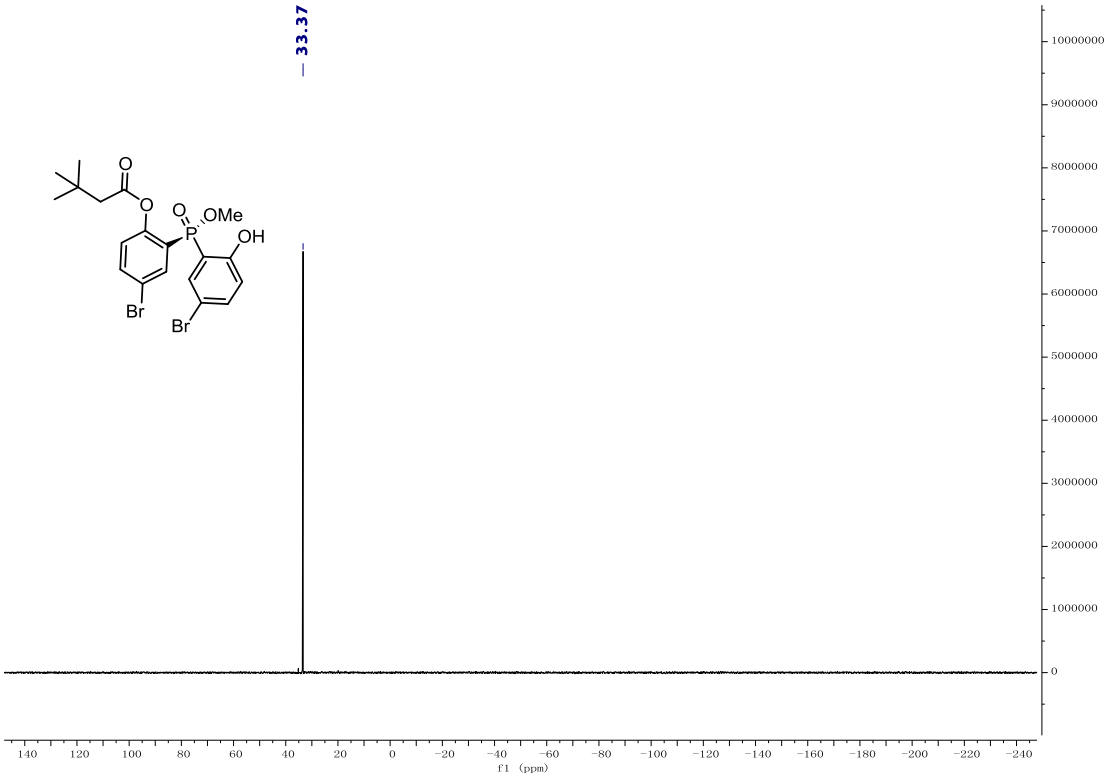
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ba



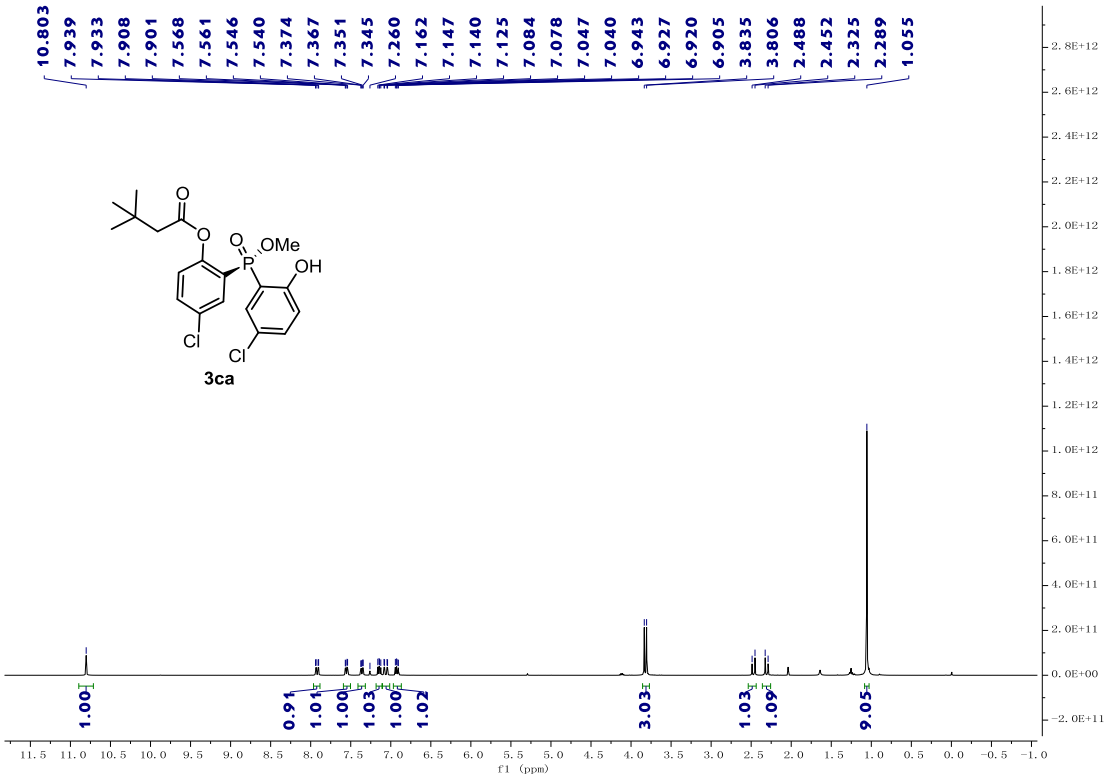
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ba



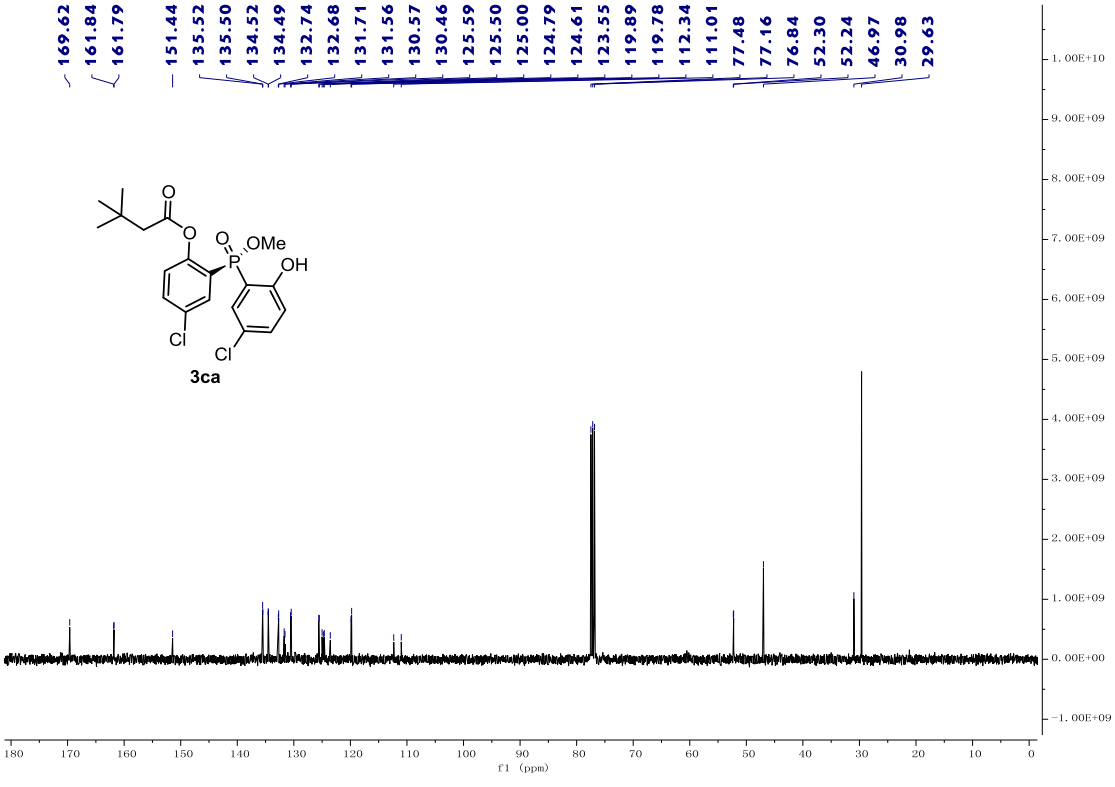
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3ba



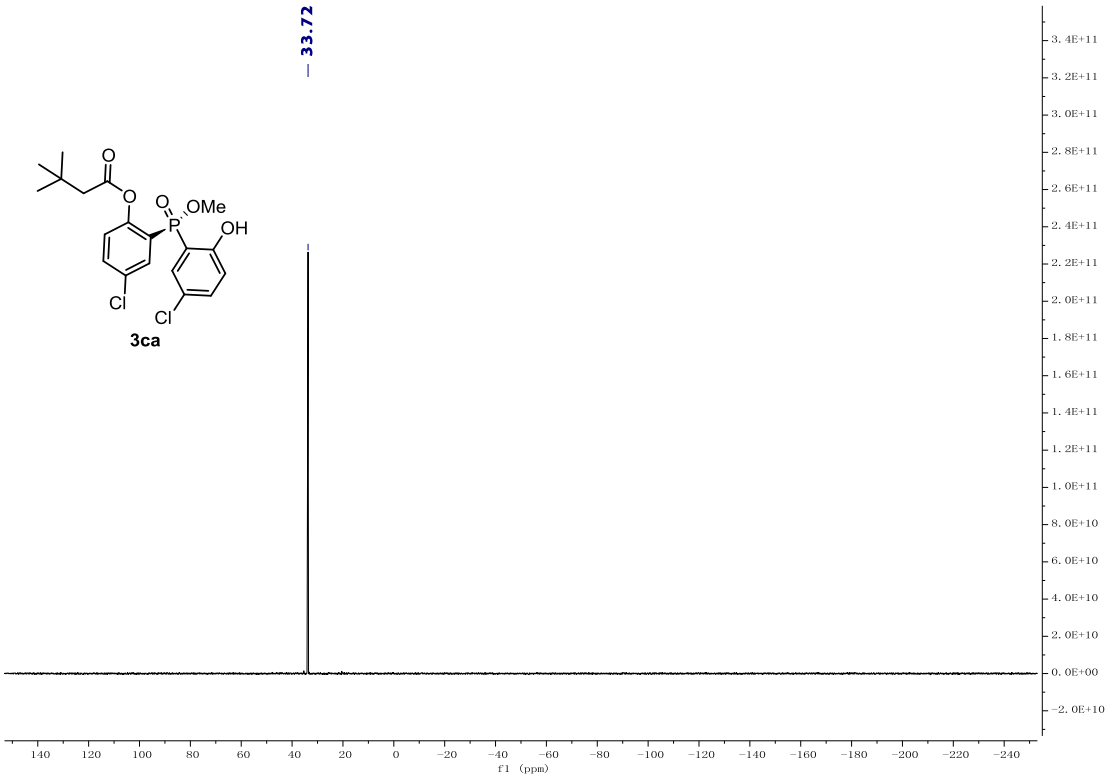
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ca



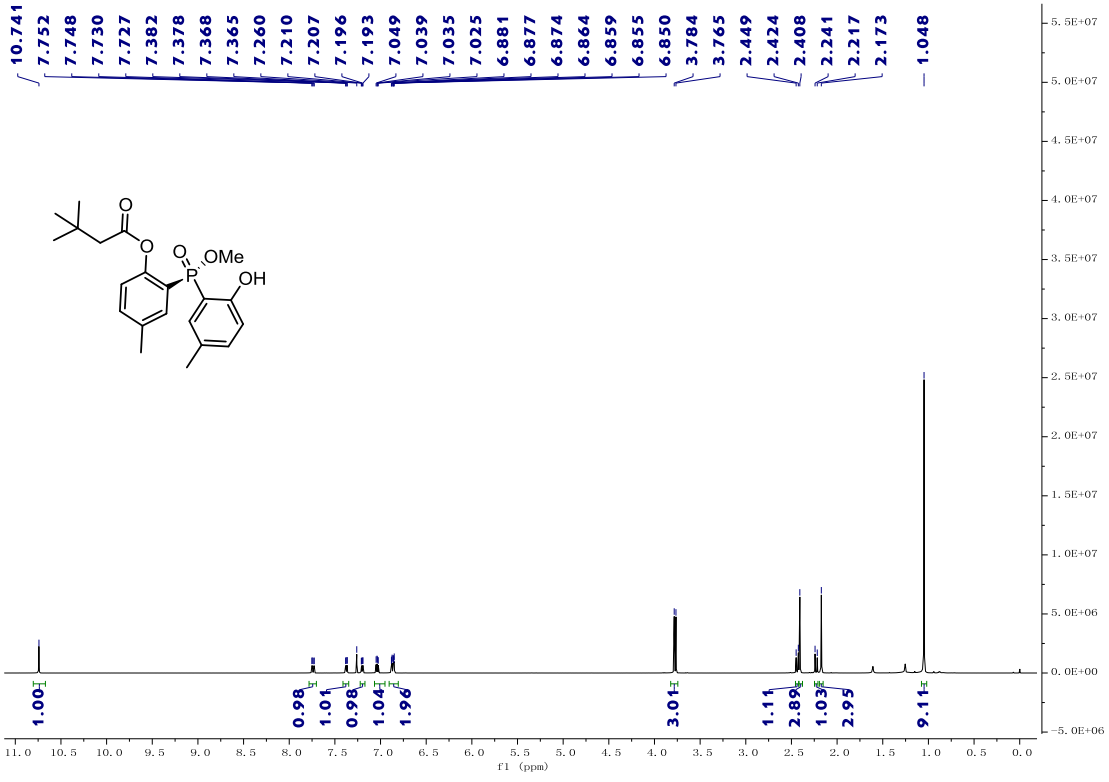
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ca



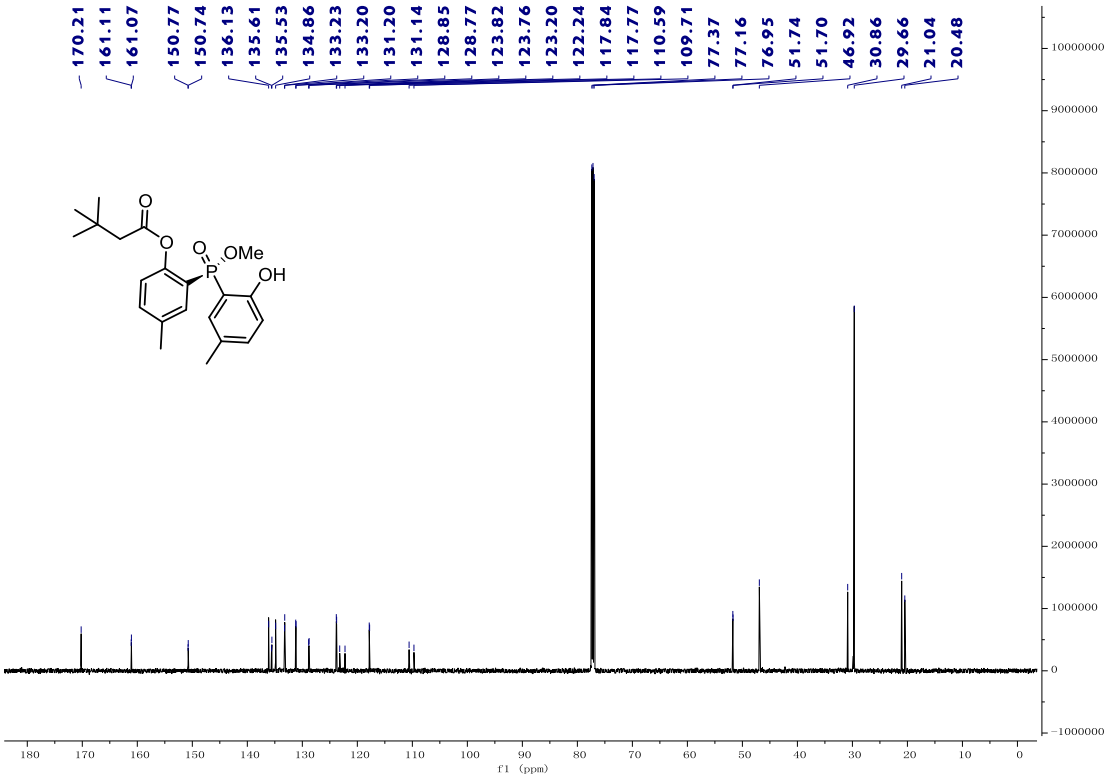
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ca



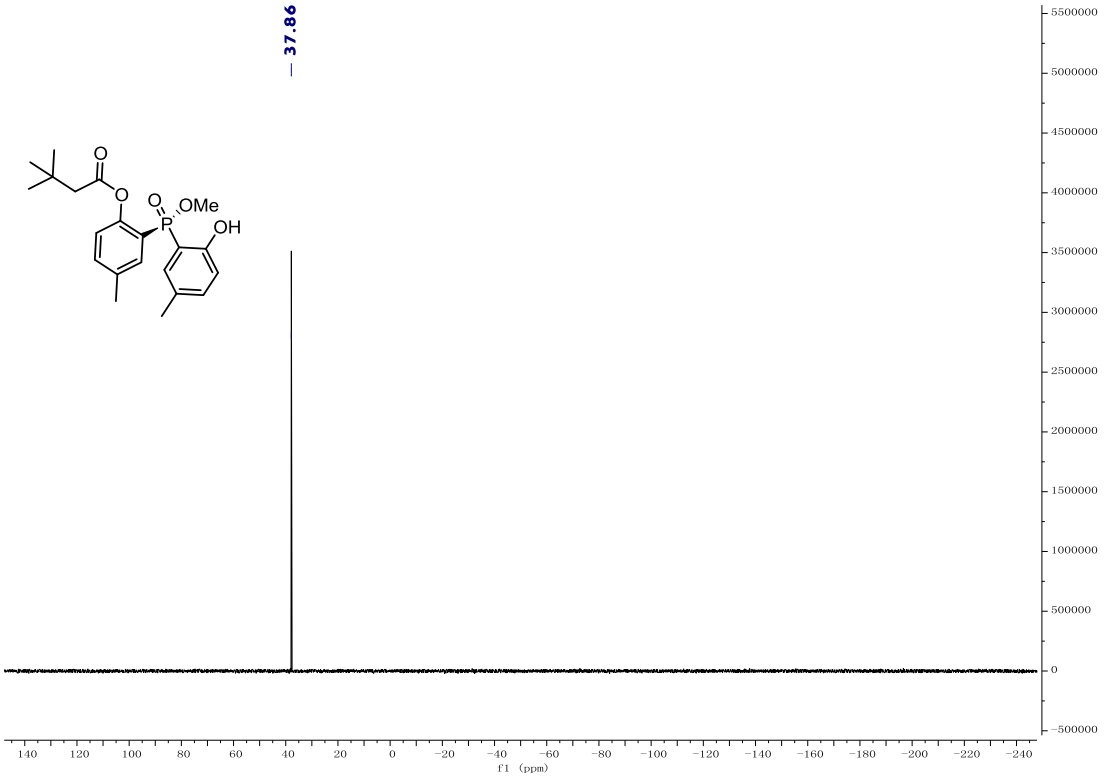
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3da



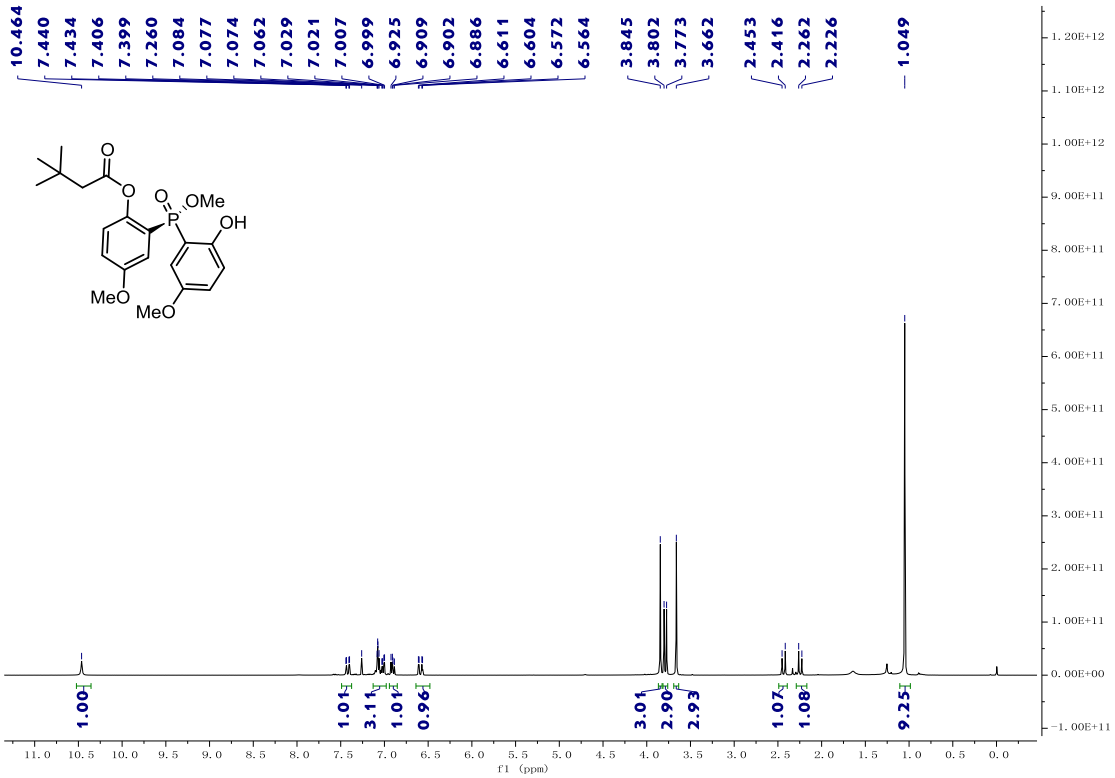
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3da



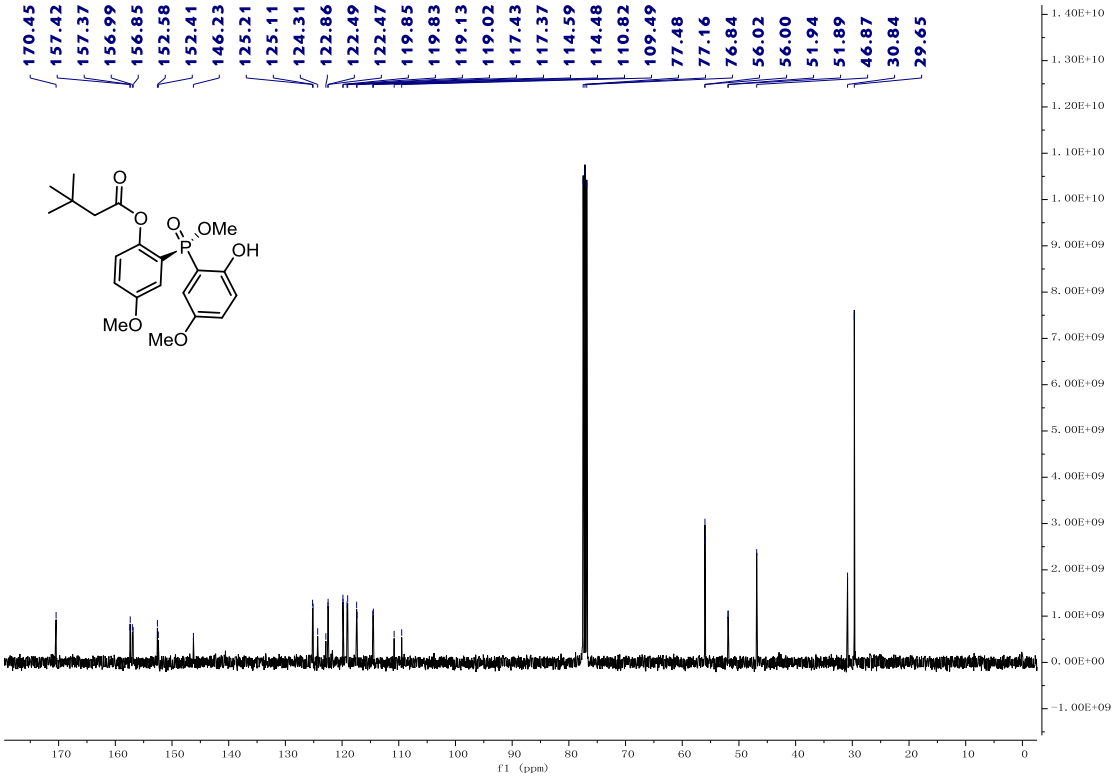
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3da



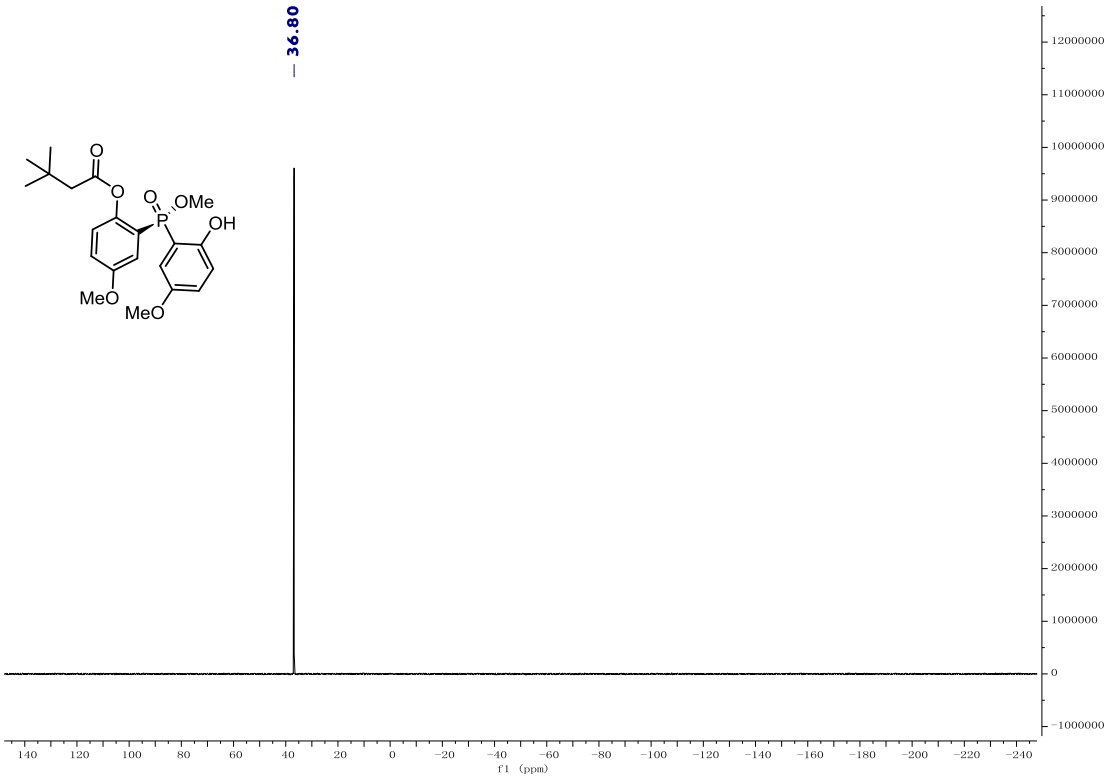
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ea



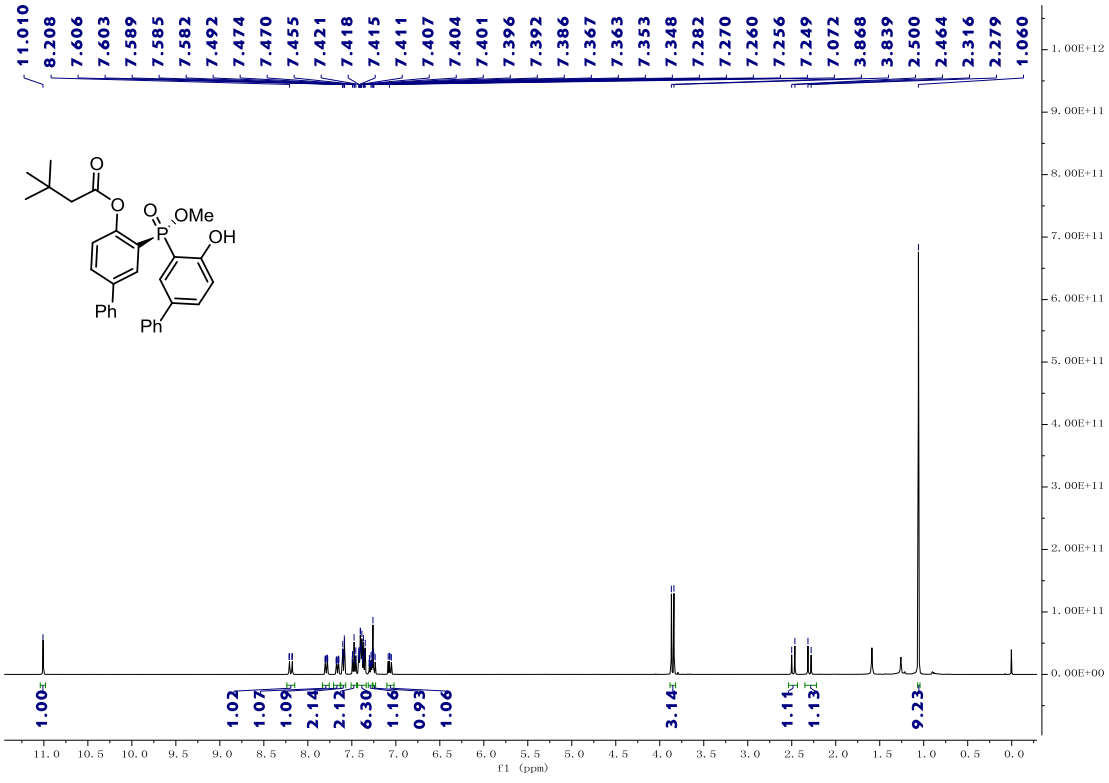
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ea



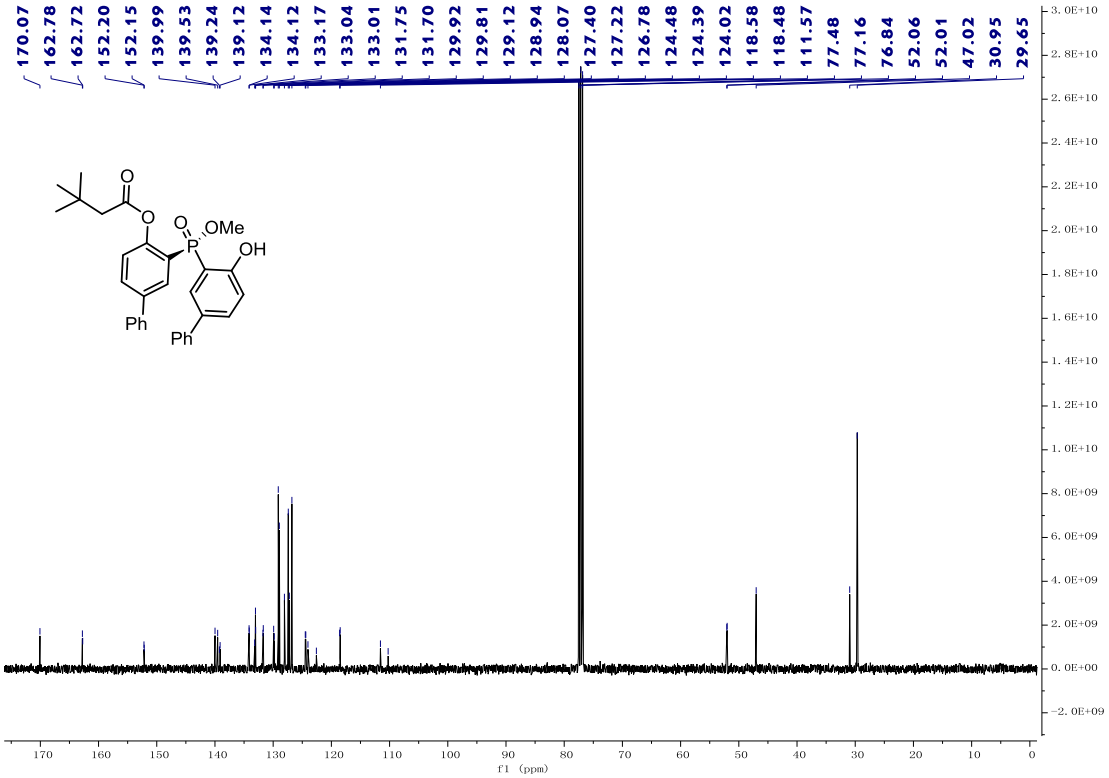
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3ea



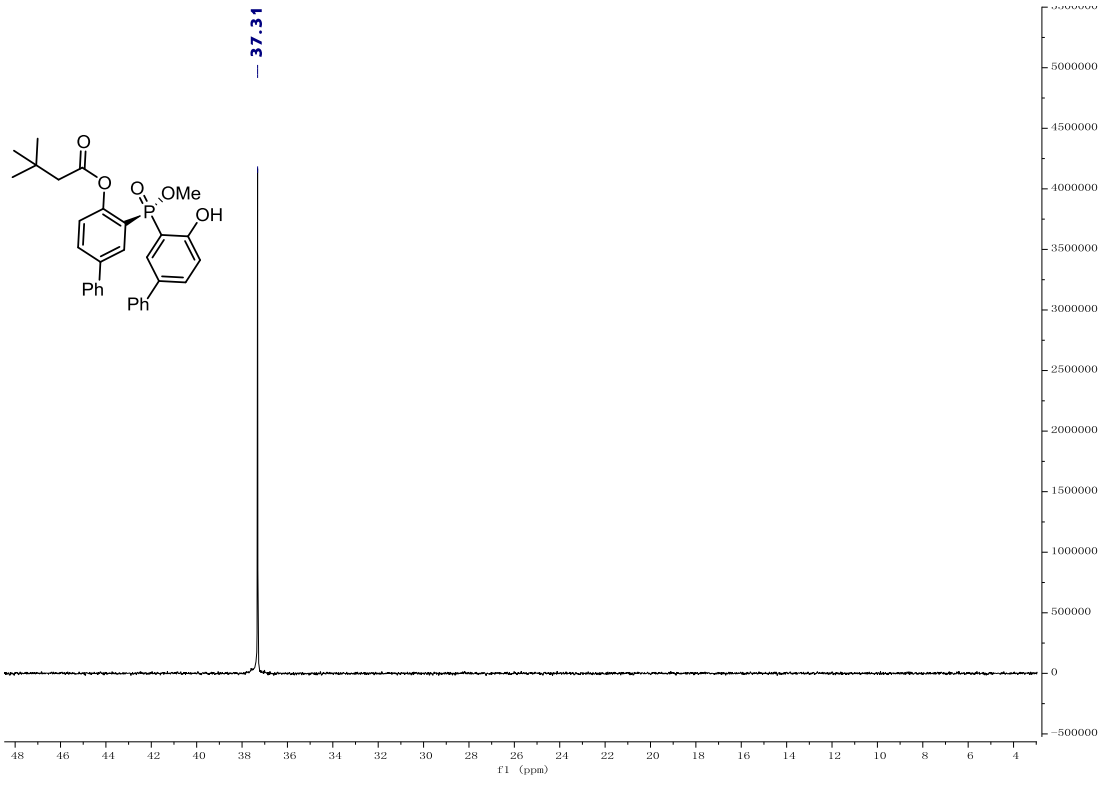
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3fa



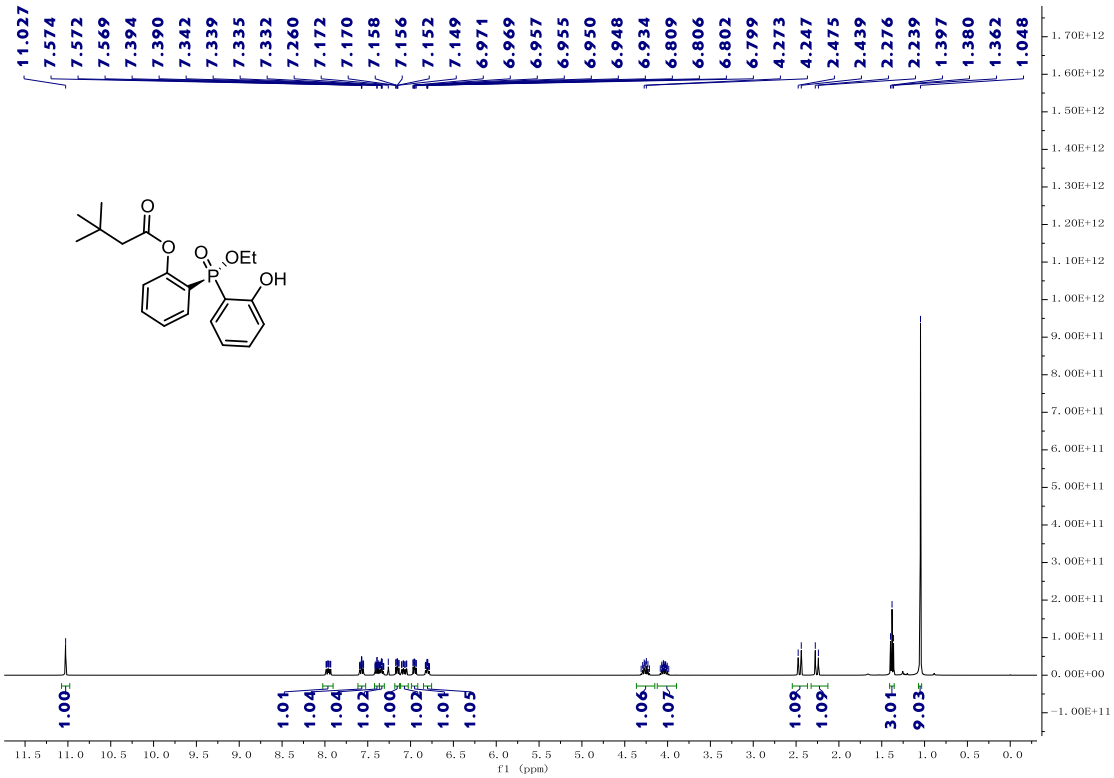
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3fa



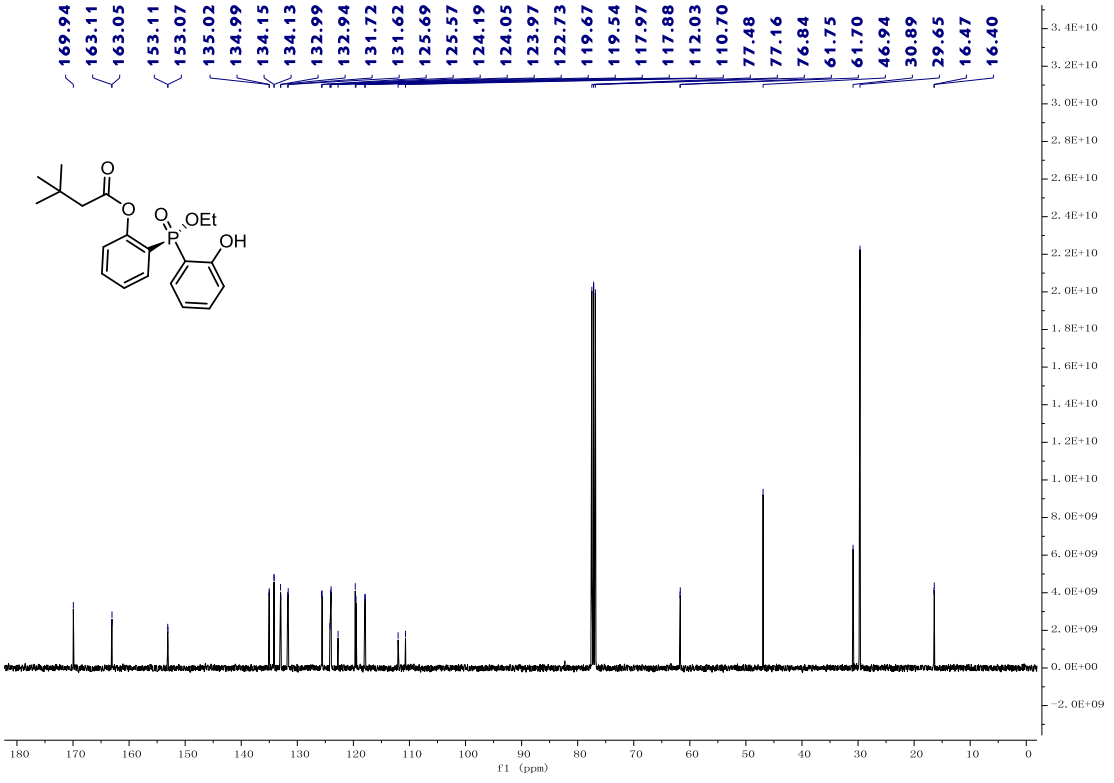
^{31}P-NMR(243 MHZ, $CDCl_3$) Spectrum of 3fa



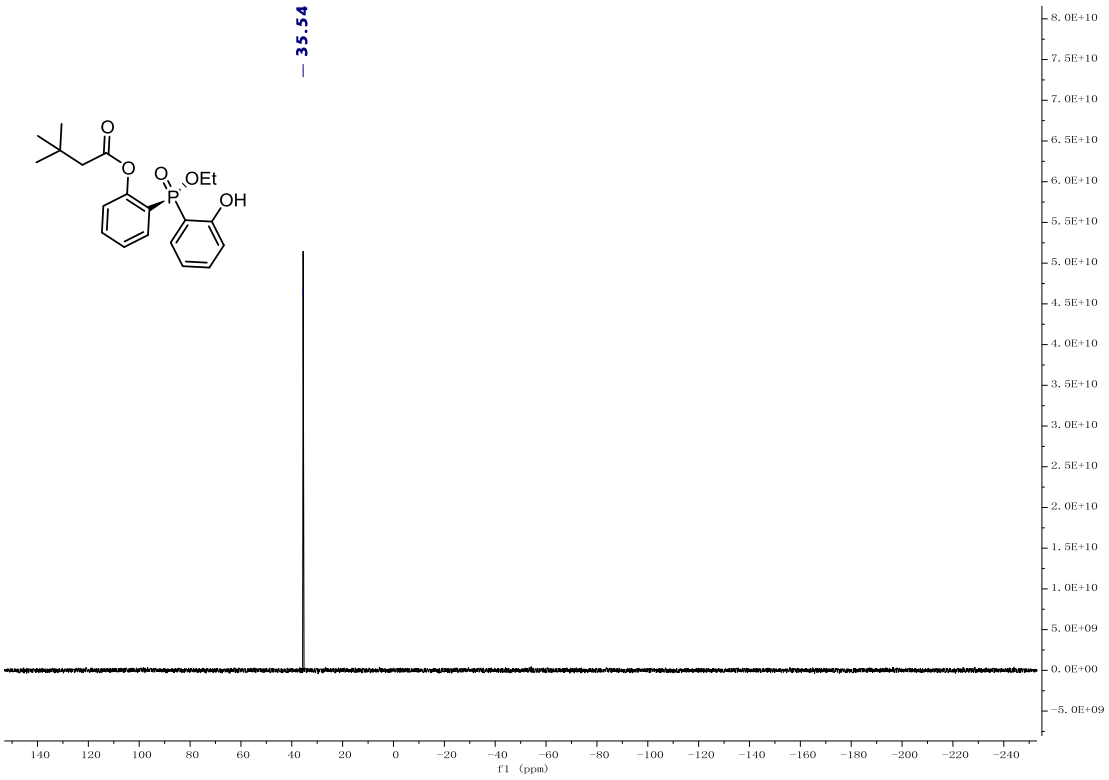
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ga



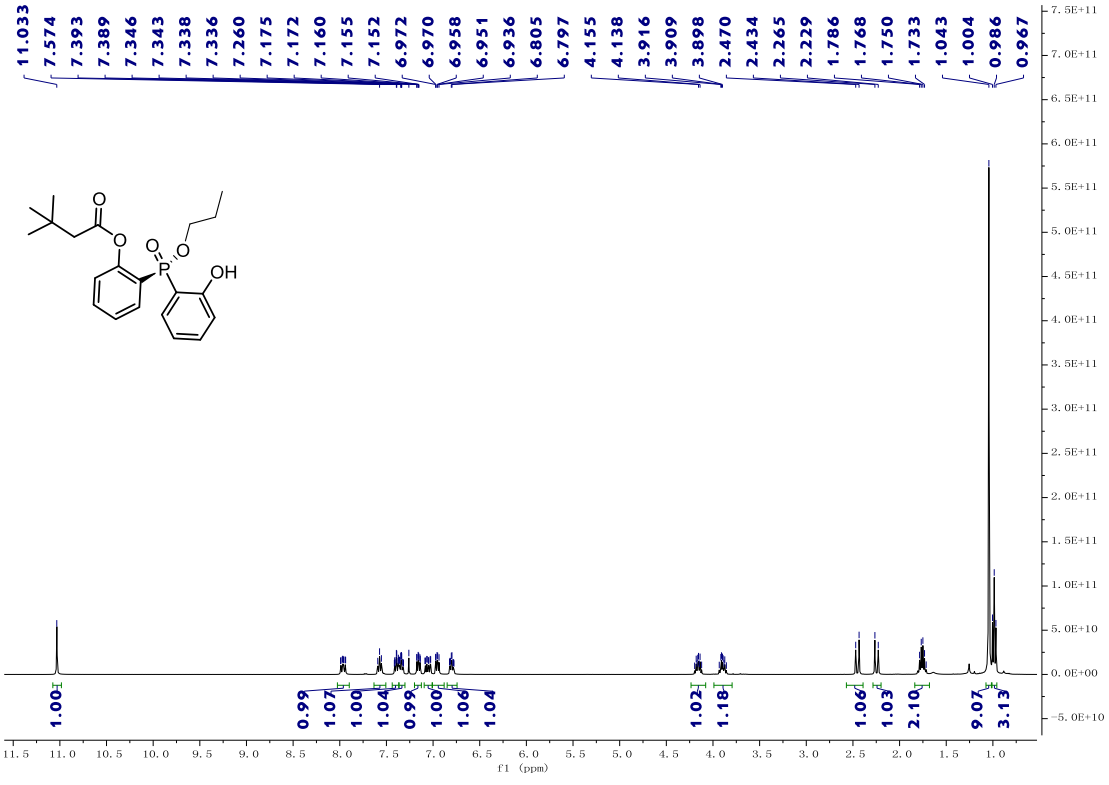
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ga



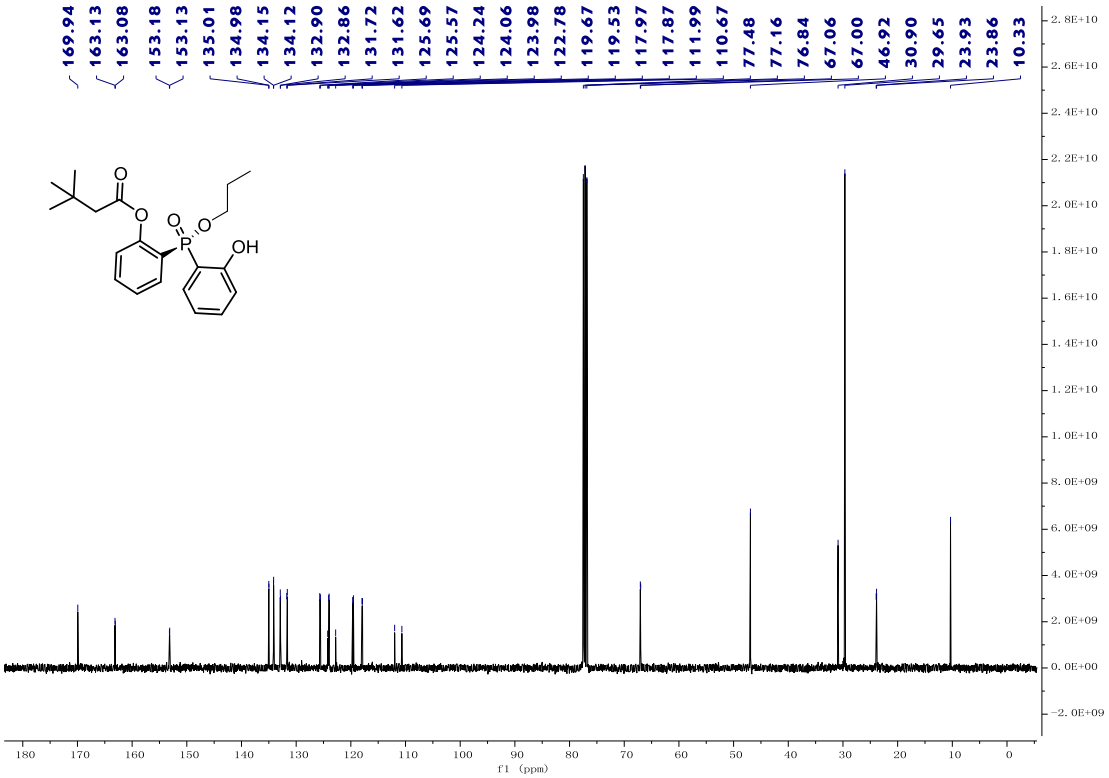
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ga



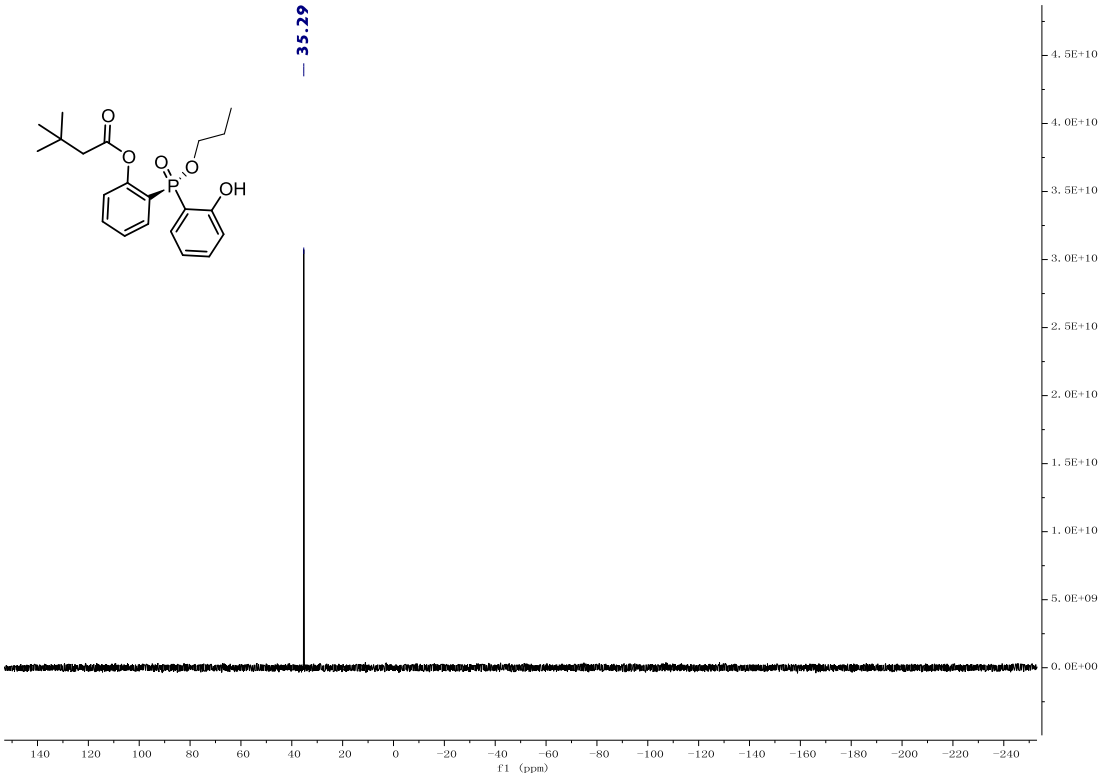
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ha



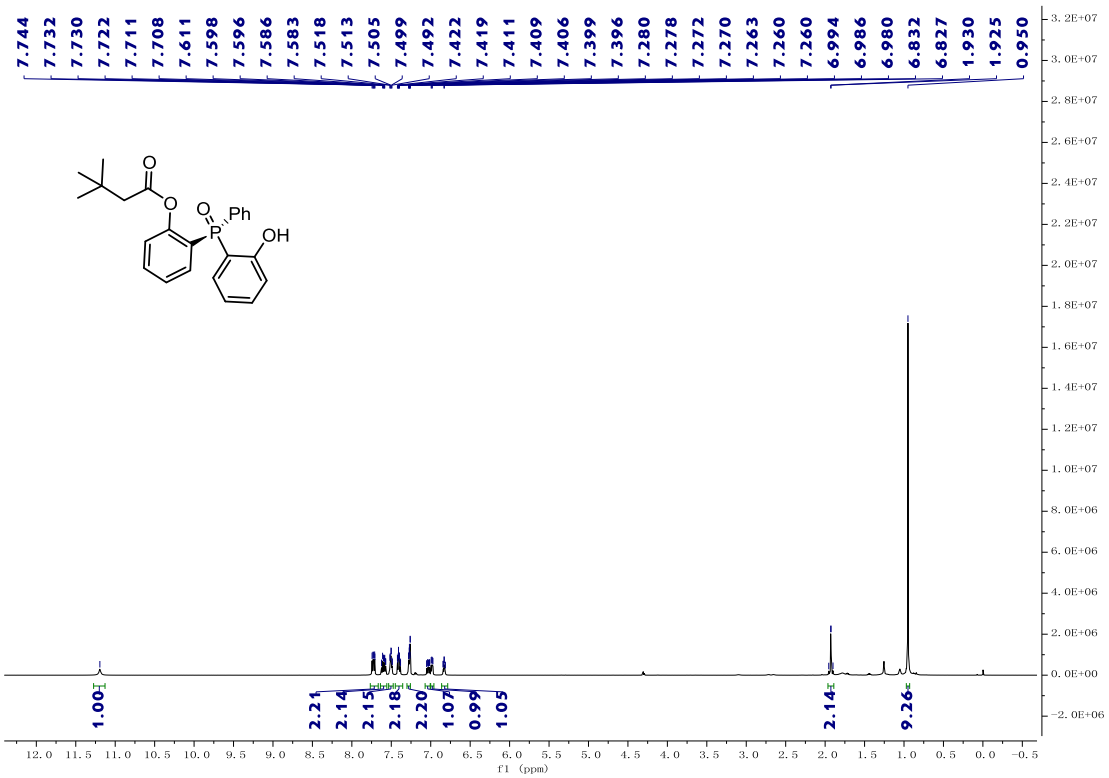
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ha



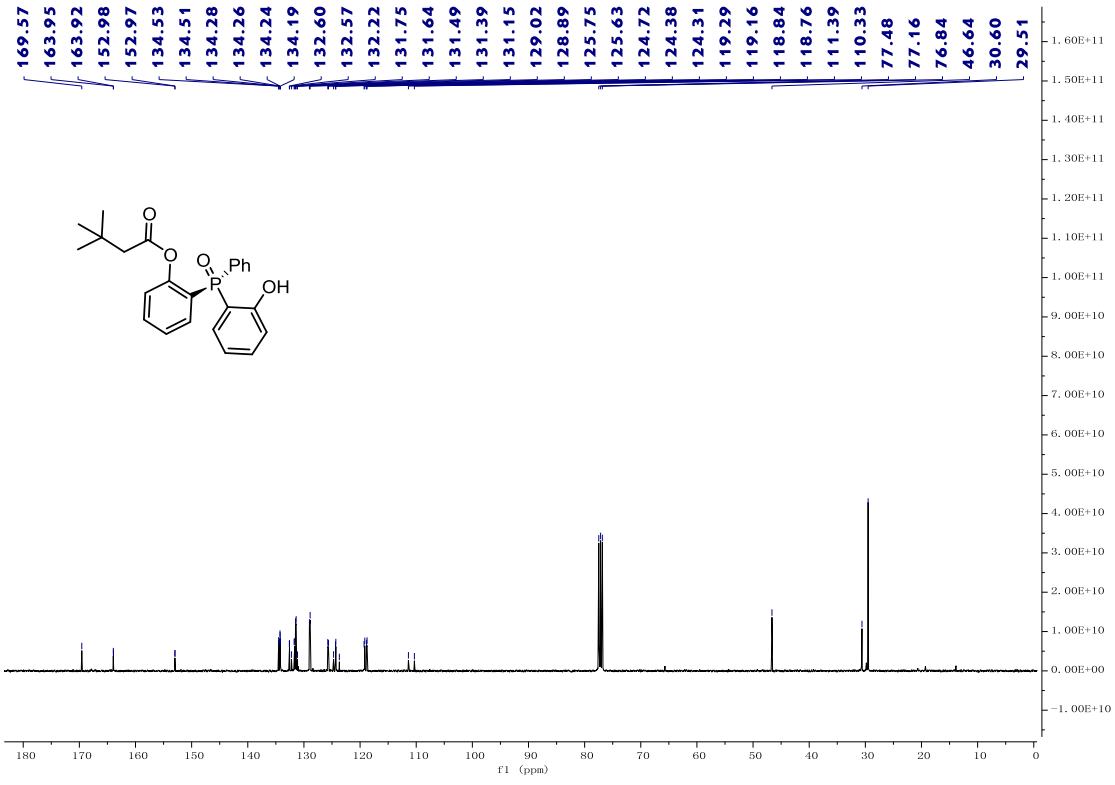
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ha



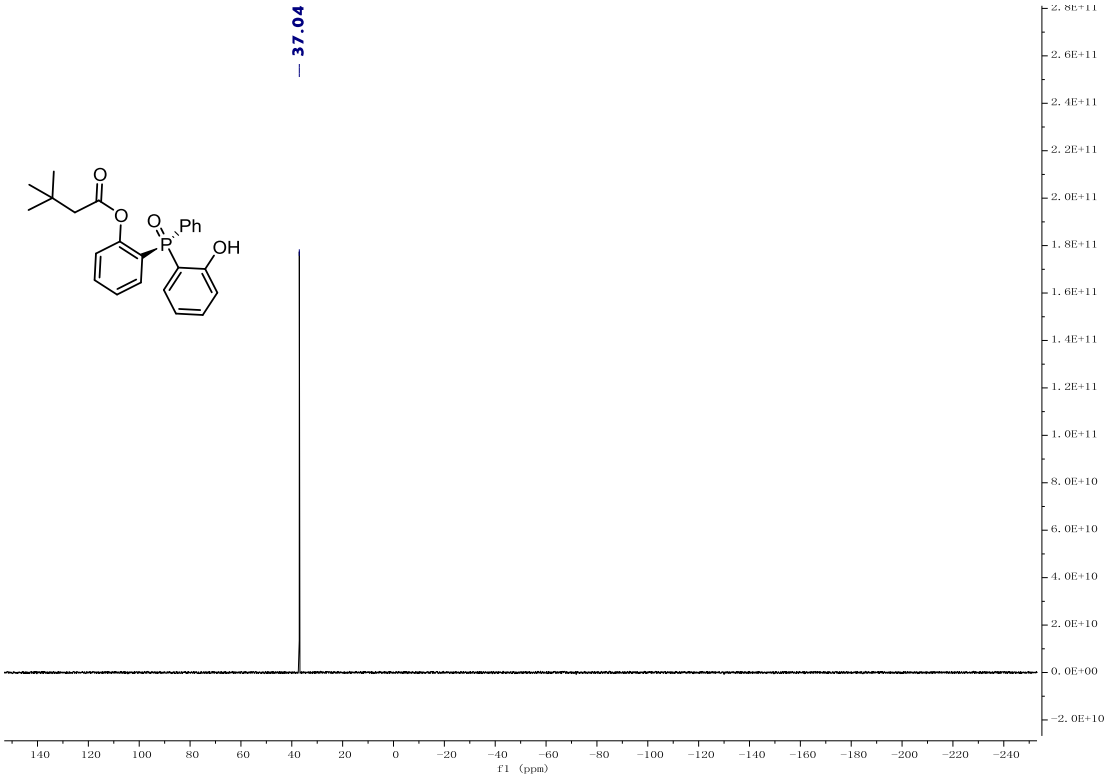
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3ia



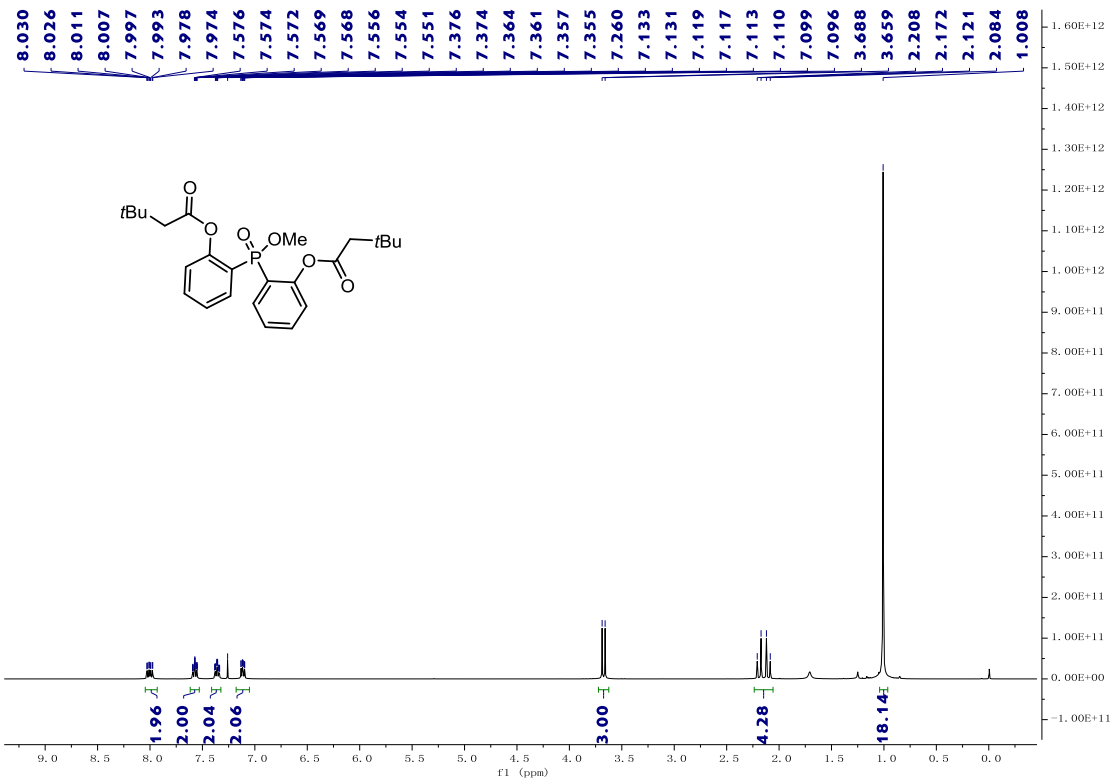
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ia



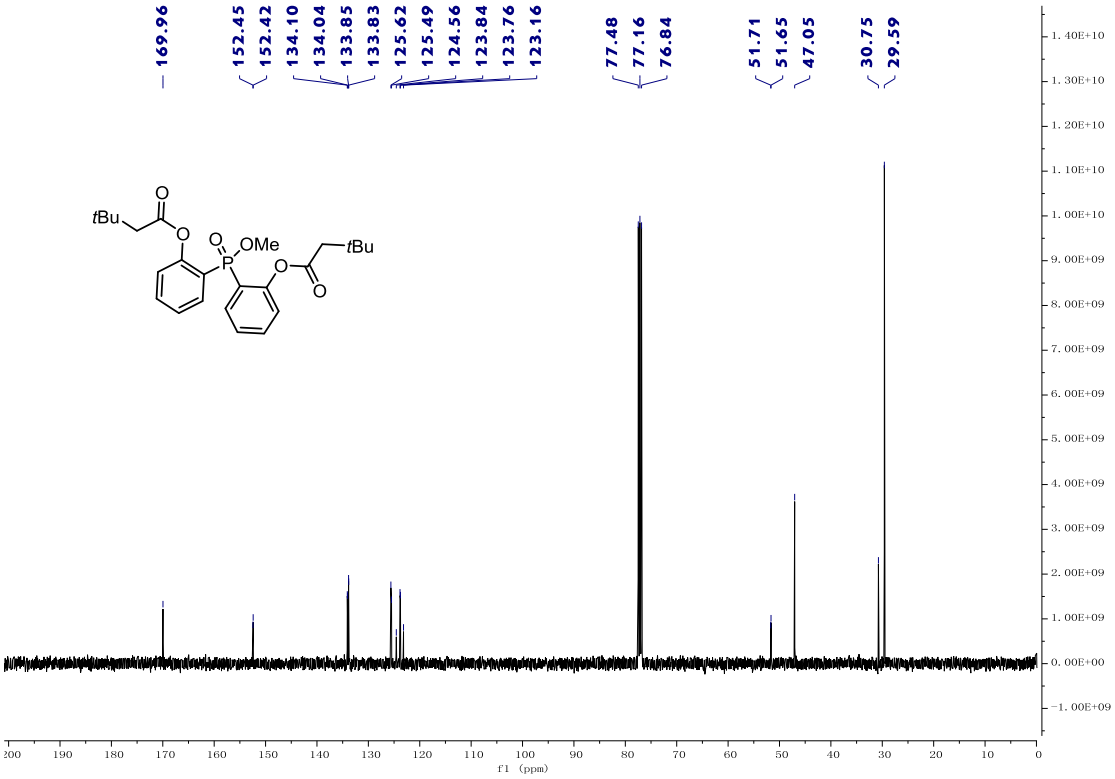
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ia



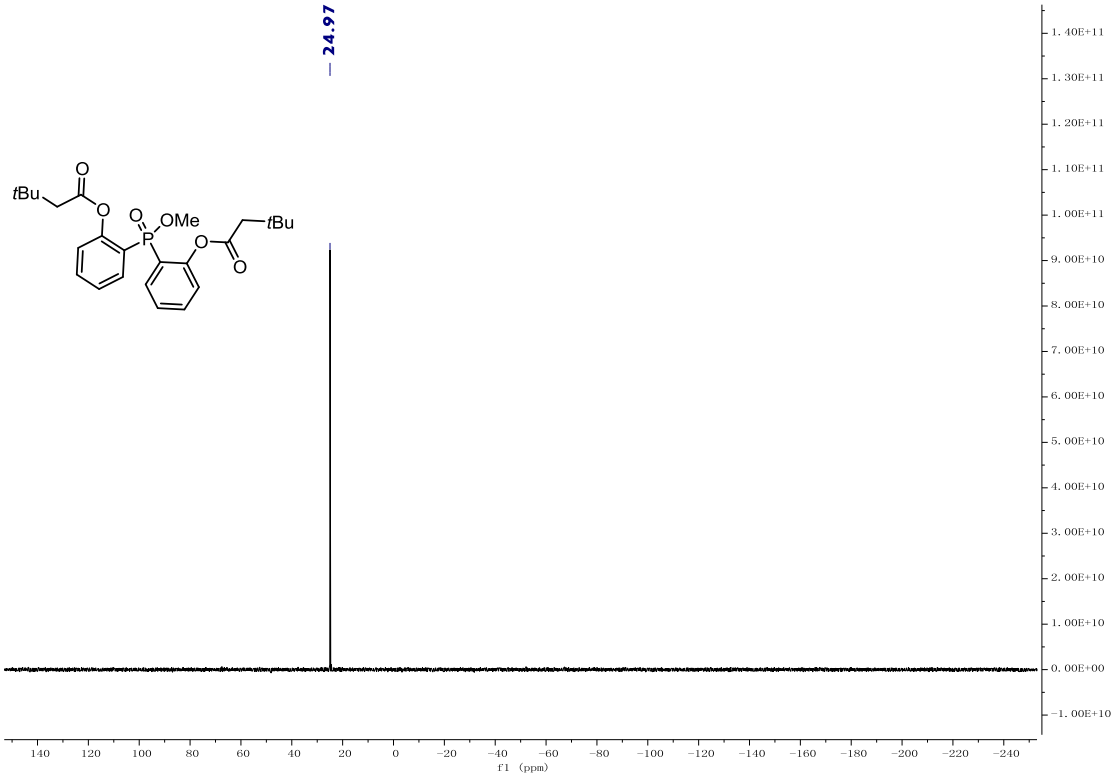
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 4aa



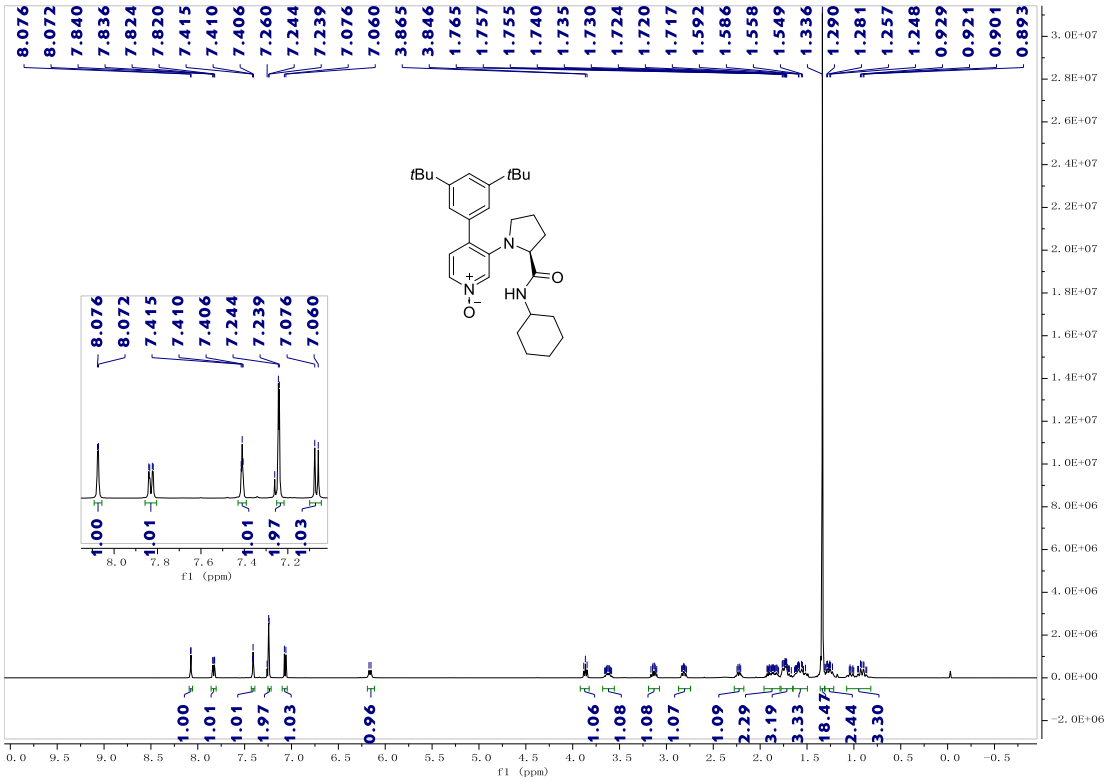
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 4aa



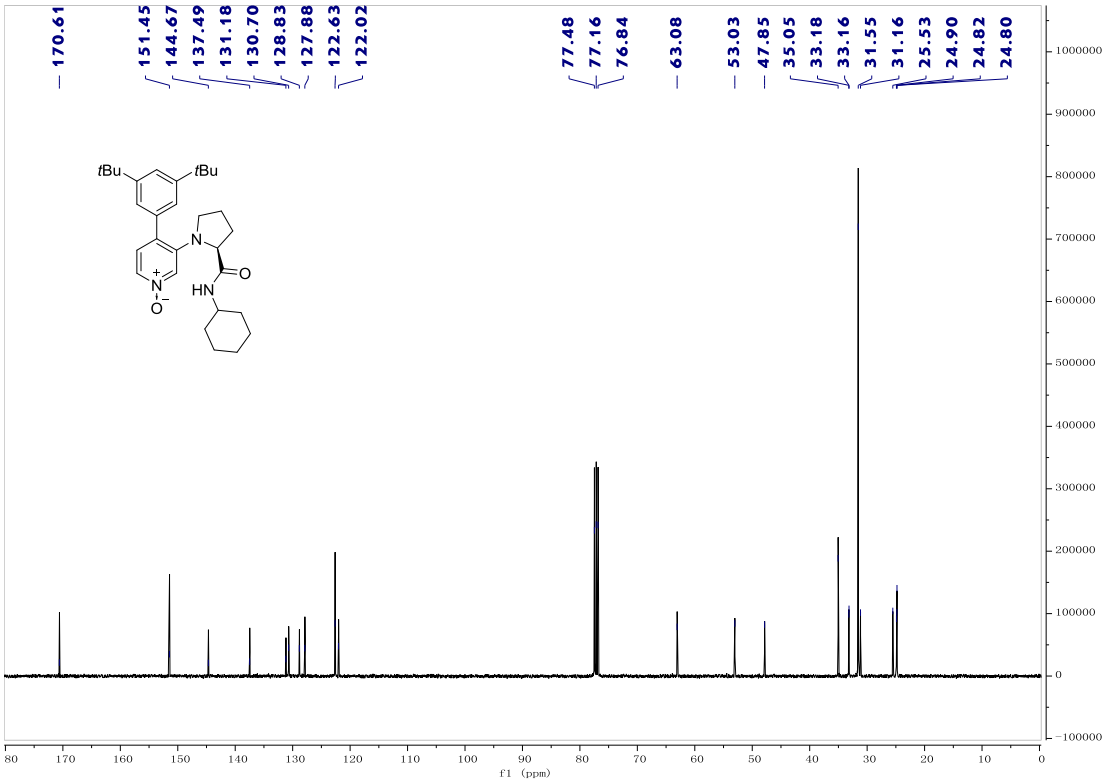
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 4aa



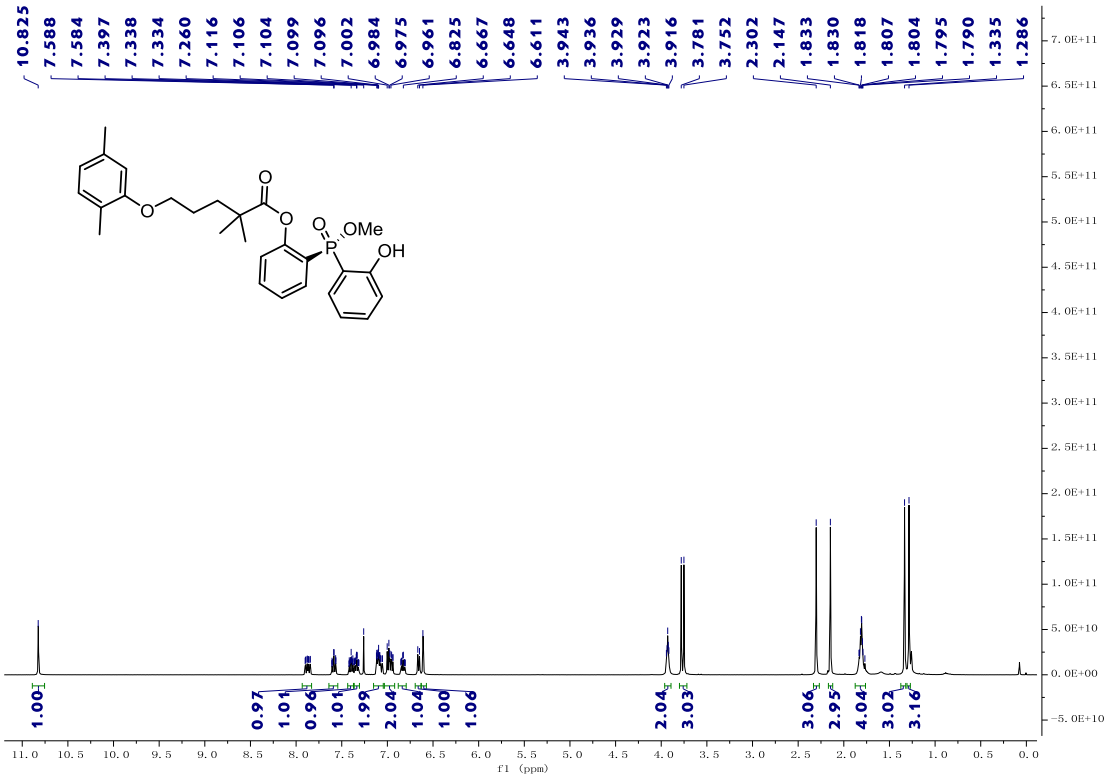
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of C2l



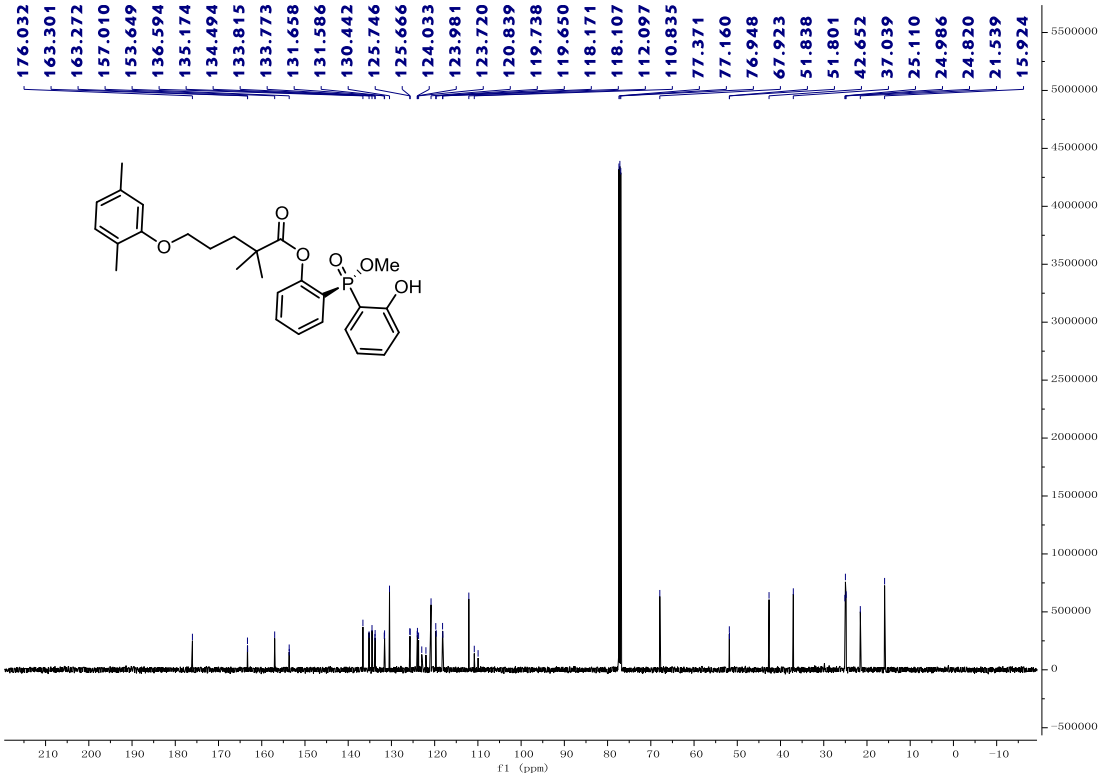
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of C2l



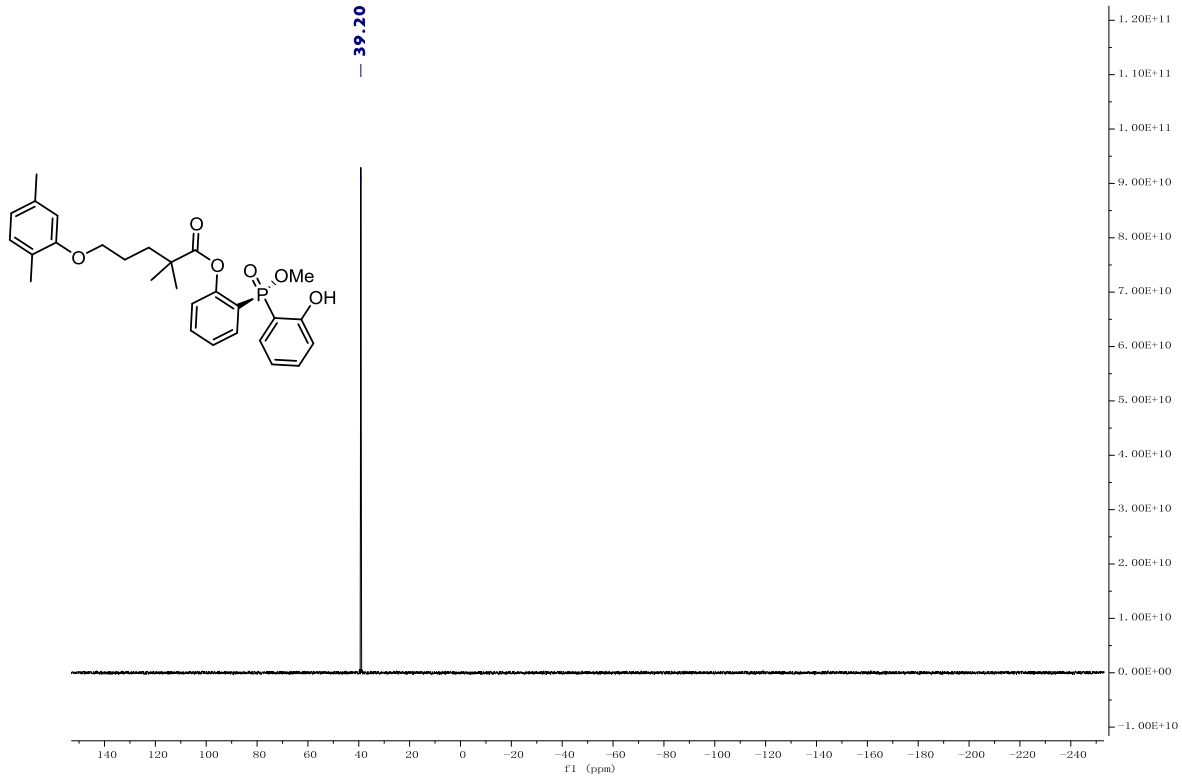
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3ao



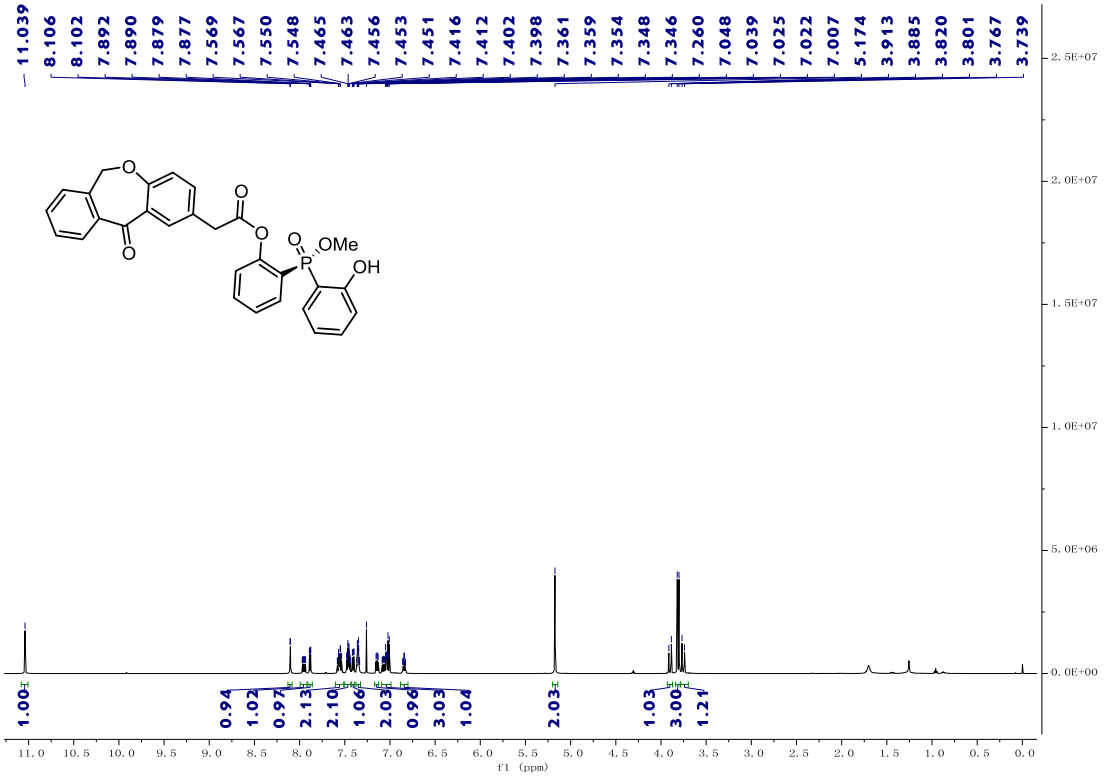
^{13}C-NMR(150 MHZ, $CDCl_3$) Spectrum of 3ao



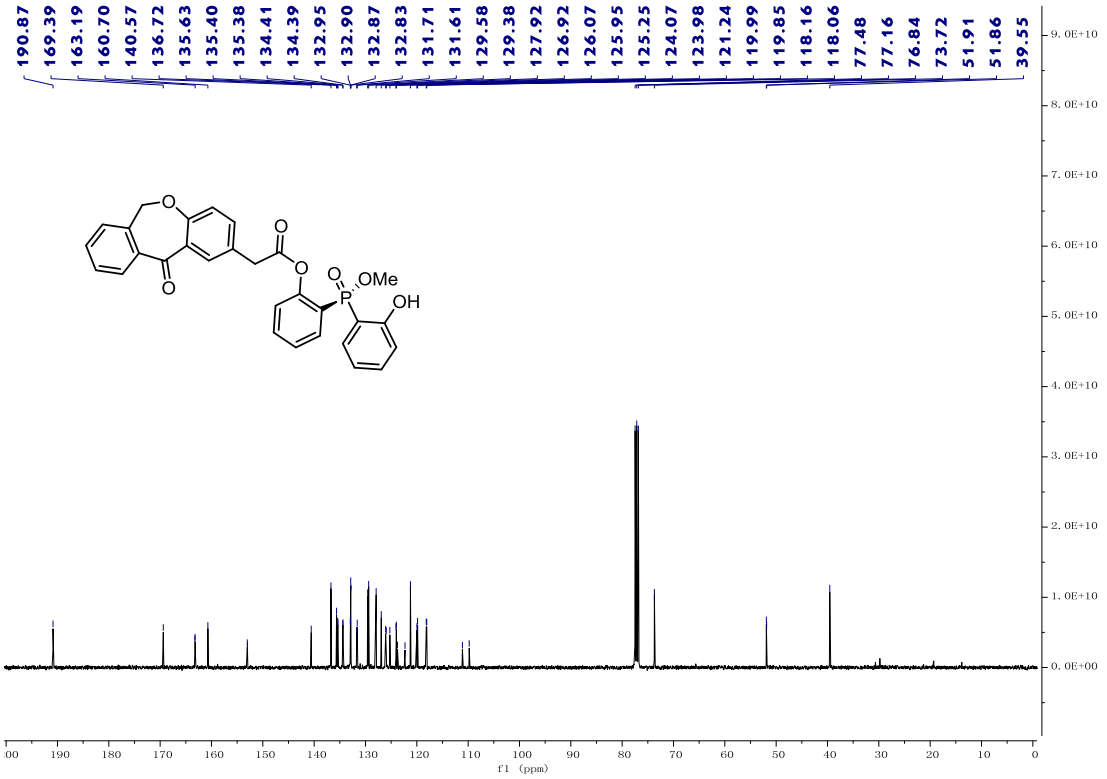
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ao



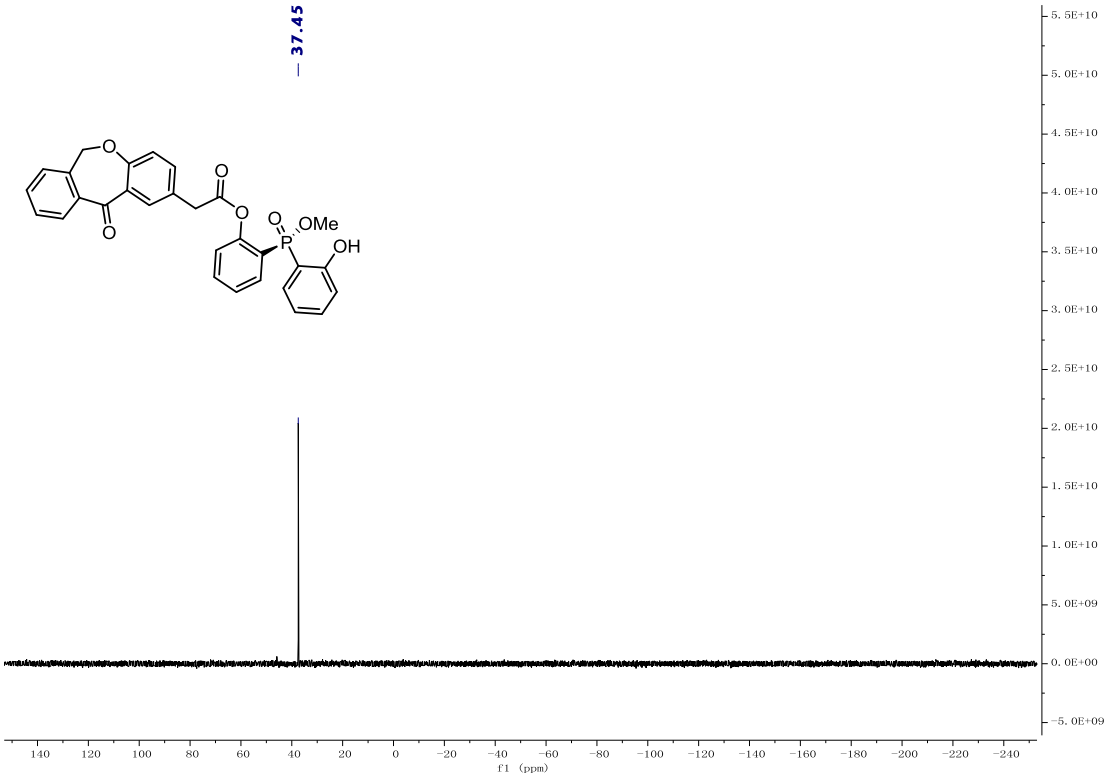
^{1}H-NMR(600 MHZ, $CDCl_3$) Spectrum of 3ap



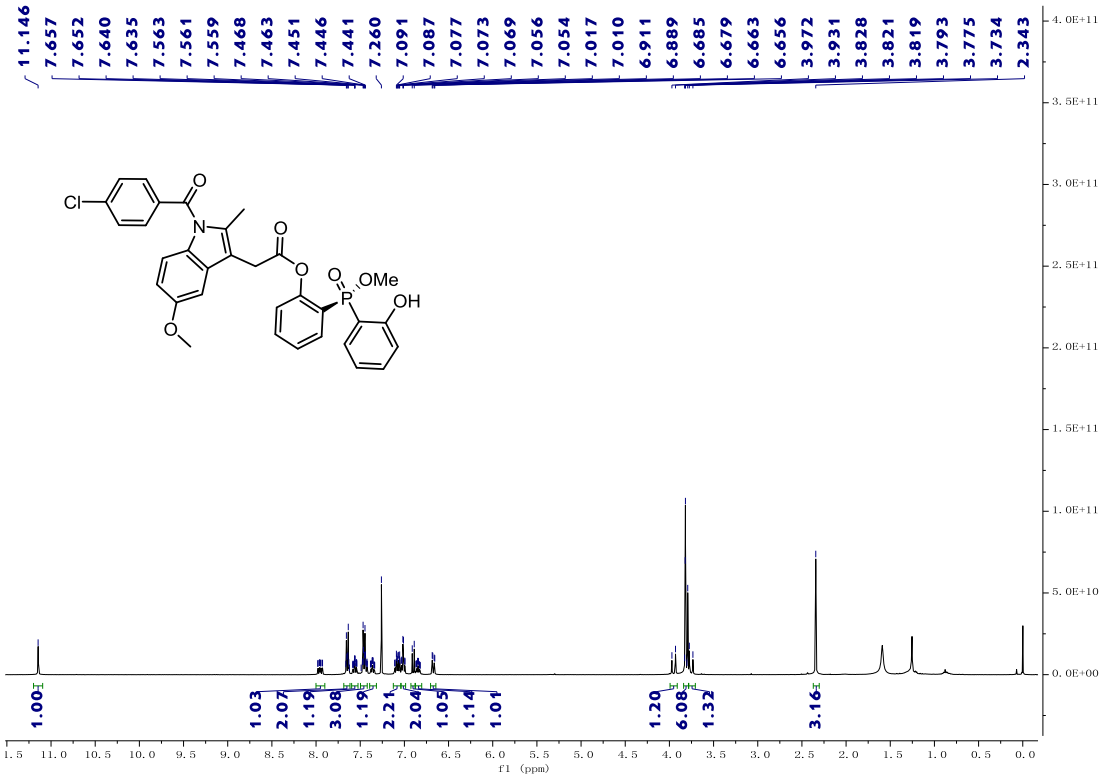
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3ap



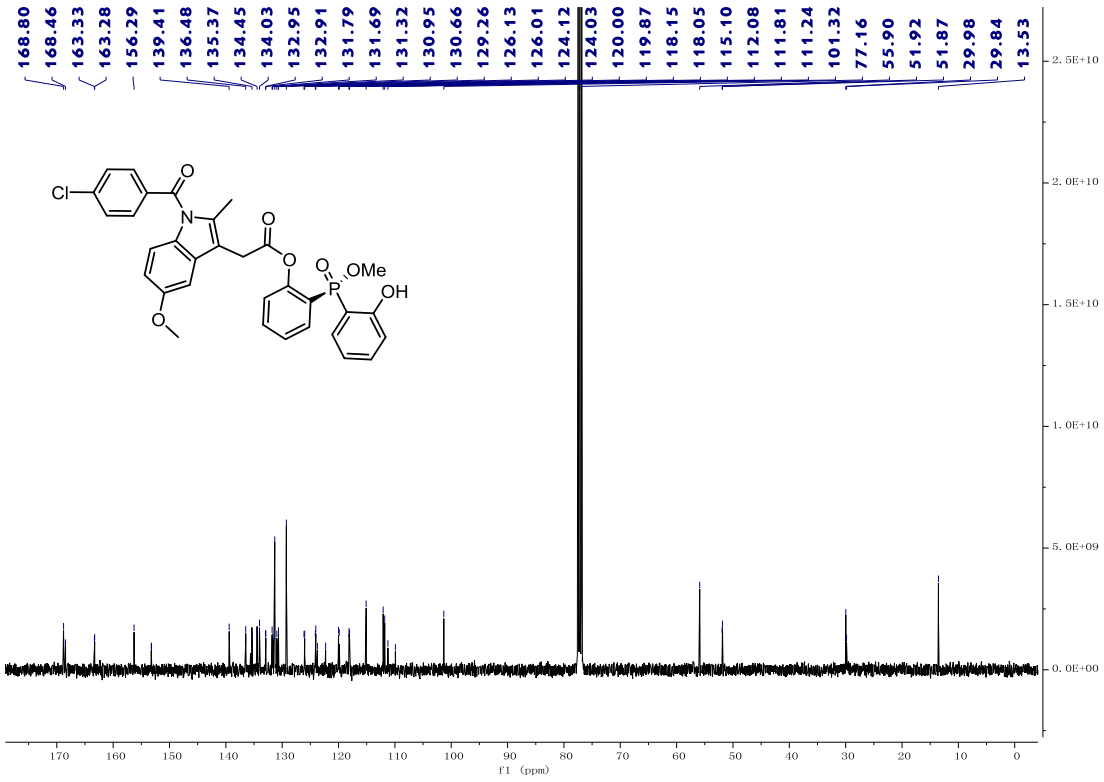
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3ap



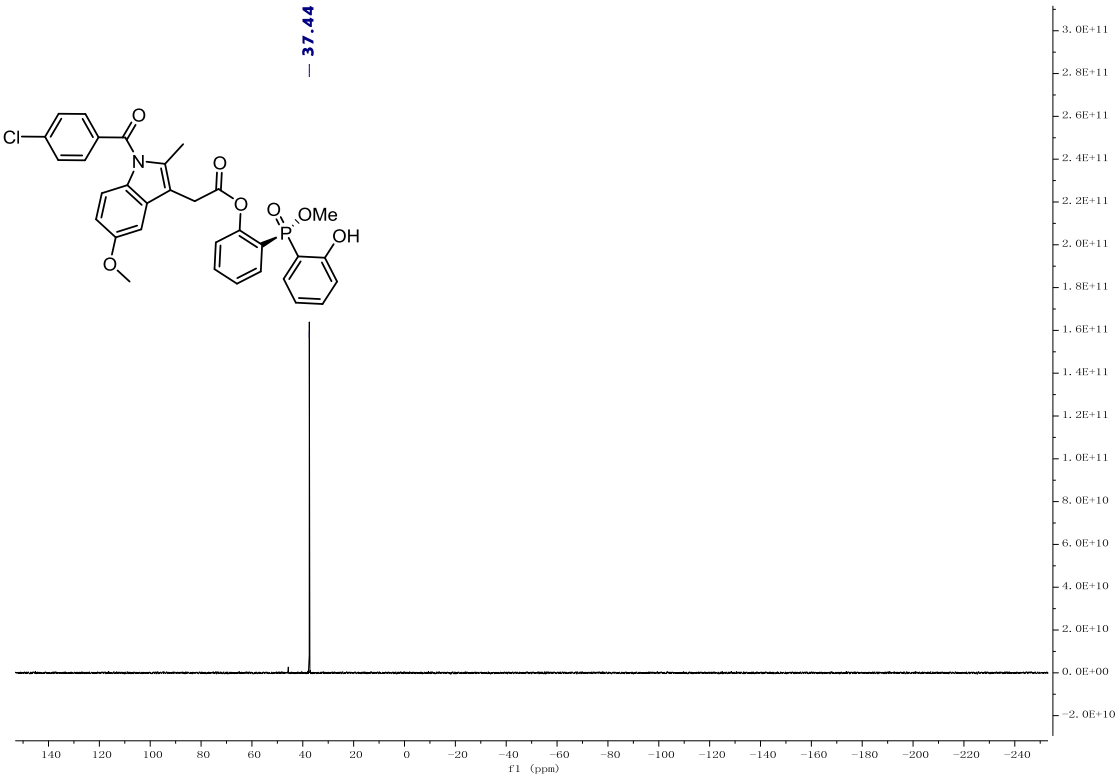
^{1}H-NMR(400 MHZ, $CDCl_3$) Spectrum of 3aq



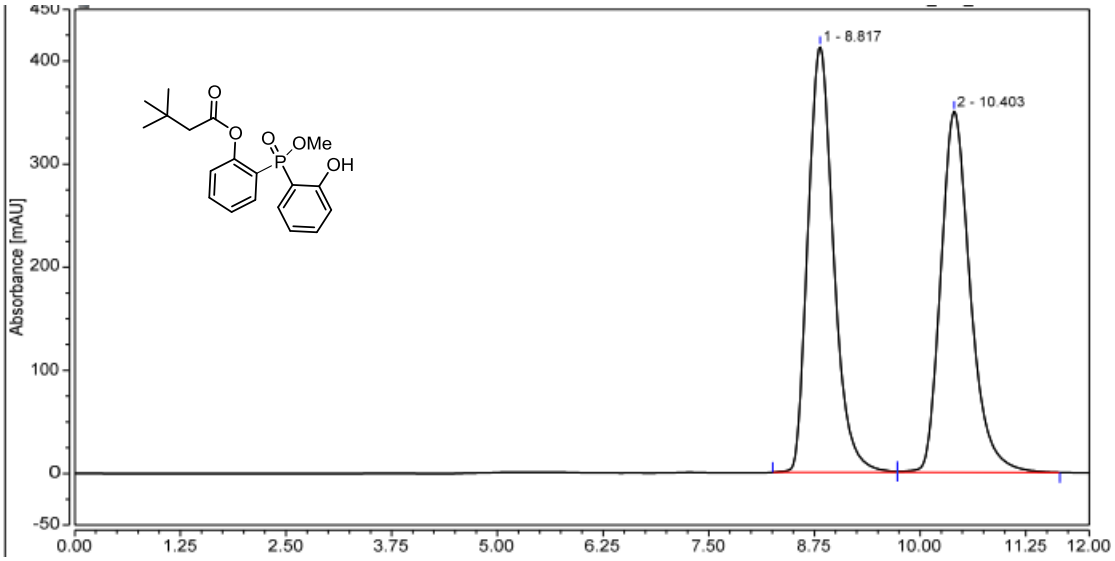
^{13}C-NMR(100 MHZ, $CDCl_3$) Spectrum of 3aq



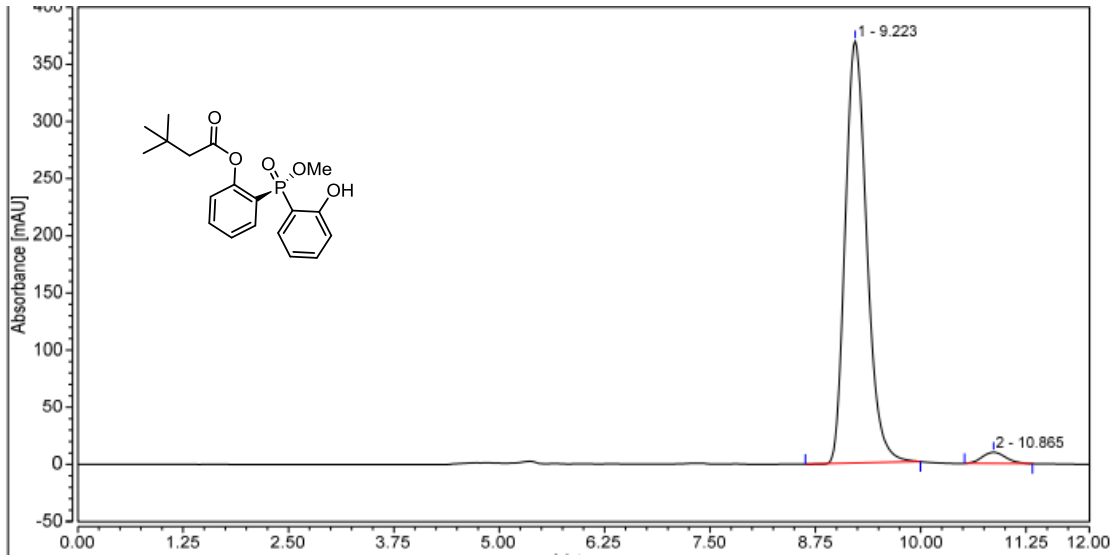
^{31}P-NMR(162 MHZ, $CDCl_3$) Spectrum of 3aq



HPLC spectra of 3aa

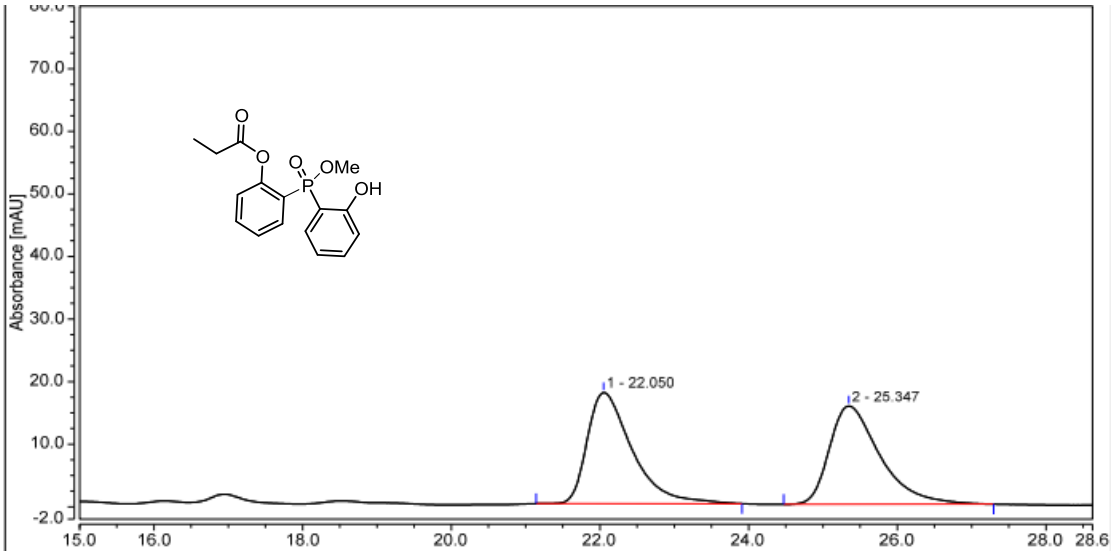


Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	8.817	145.216	412.821	50.55	54.11
2	10.403	142.050	350.133	49.45	45.89
Total:		**287.266**	**762.955**	**100.00**	**100.00**

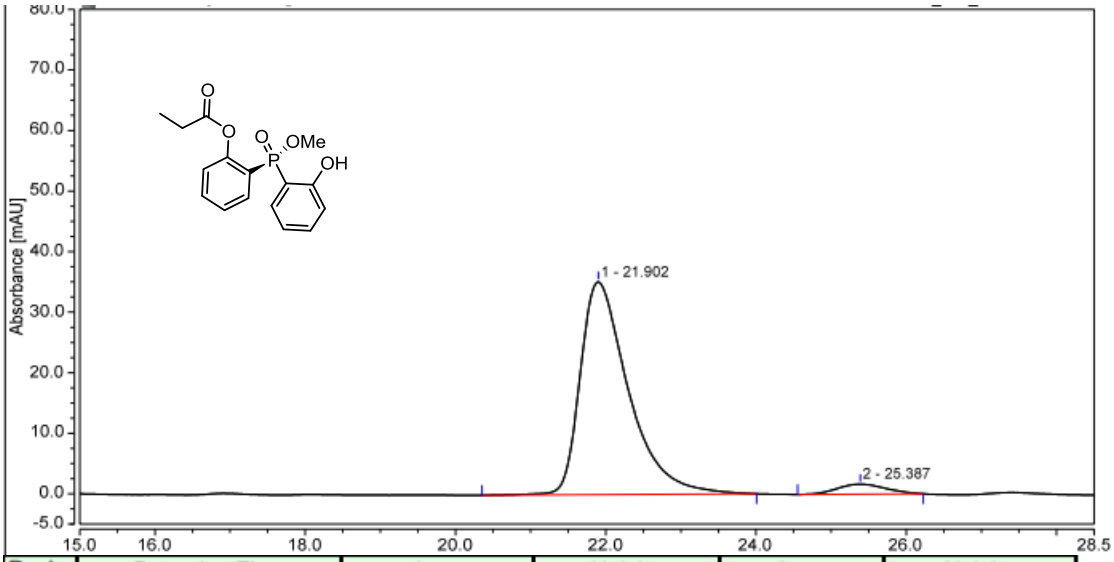


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.223	109.182	369.411	97.16	97.41
2	10.865	3.197	9.828	2.84	2.59
Total:		**112.379**	**379.239**	**100.00**	**100.00**

HPLC spectra of 3ab

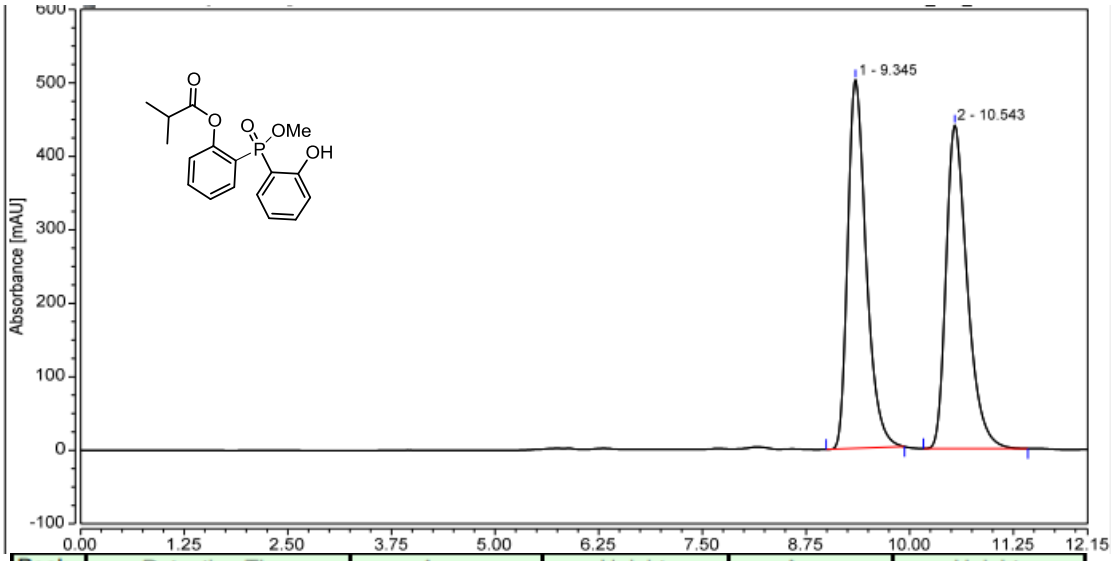


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	22.050	12.511	17.762	49.88	53.02
2	25.347	12.572	15.739	50.12	46.98
Total:		**25.083**	**33.501**	**100.00**	**100.00**

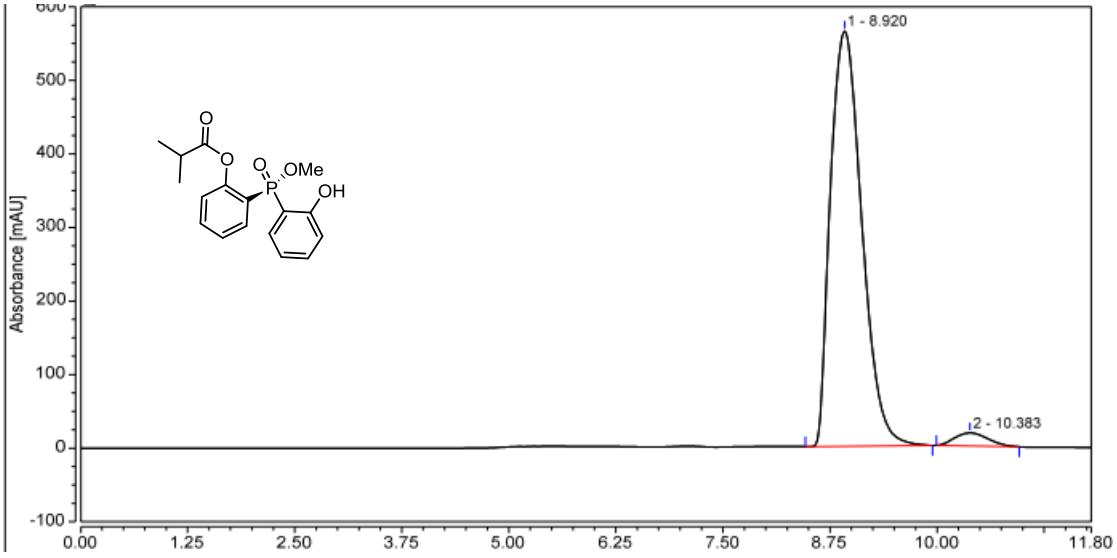


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.902	26.258	35.141	95.40	95.46
2	25.387	1.265	1.670	4.60	4.54
Total:		**27.523**	**36.811**	**100.00**	**100.00**

HPLC spectra of 3ac

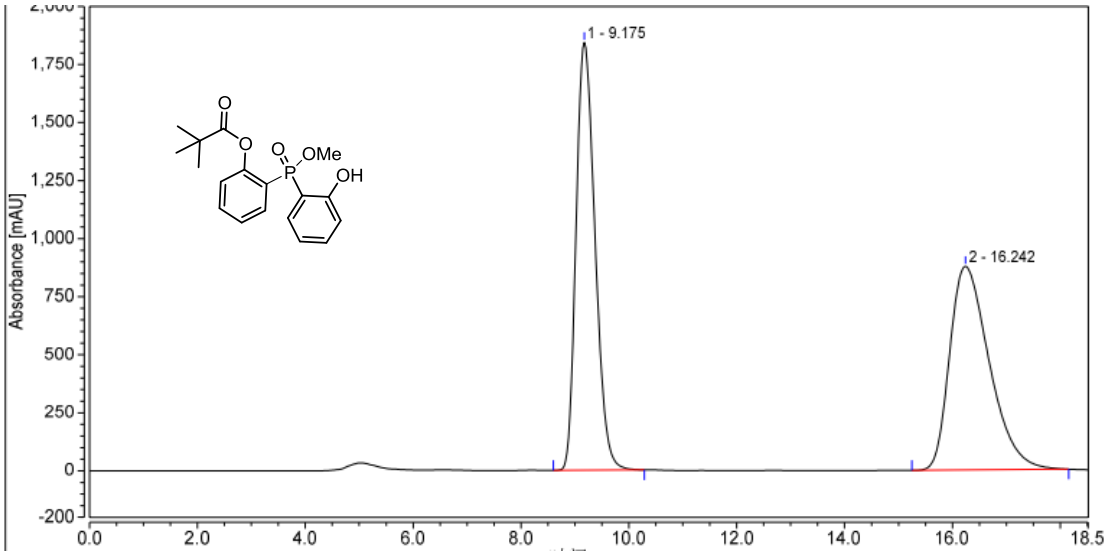


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.345	129.502	501.673	49.67	53.26
2	10.543	131.248	440.190	50.33	46.74
Total:		**260.750**	**941.863**	**100.00**	**100.00**

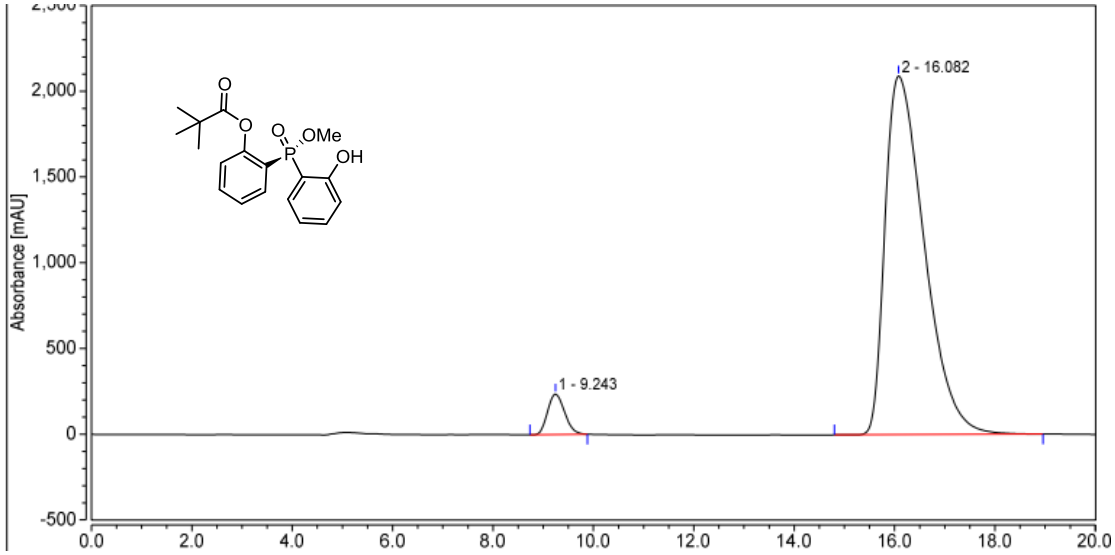


Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	8.920	239.387	564.307	96.77	96.95
2	10.383	8.000	17.767	3.23	3.05
Total:		**247.387**	**582.073**	**100.00**	**100.00**

HPLC spectra of 3ad

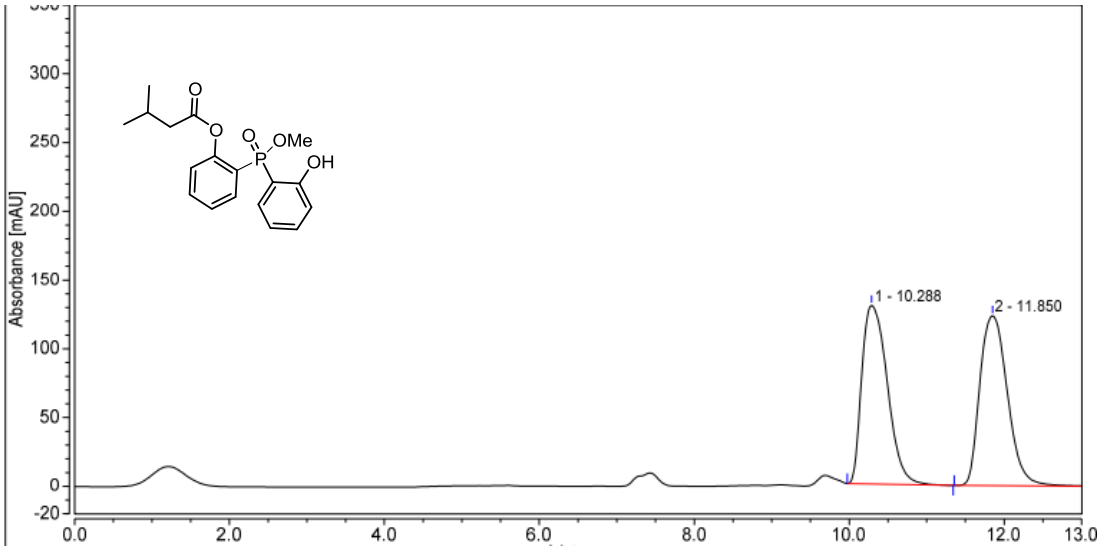


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	9.175	747.199	1842.141	50.02	67.74
2	16.242	746.460	877.450	49.98	32.26
Total:		**1493.659**	**2719.591**	**100.00**	**100.00**

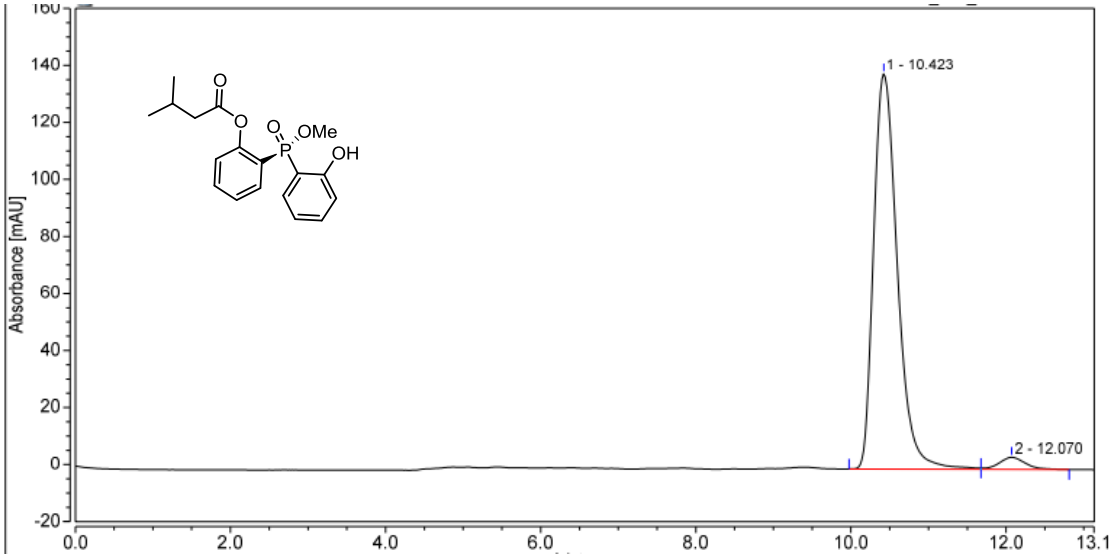


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	9.243	92.666	236.196	4.67	10.14
2	16.082	1891.595	2092.129	95.33	89.86
Total:		**1984.260**	**2328.325**	**100.00**	**100.00**

HPLC spectra of 3ae

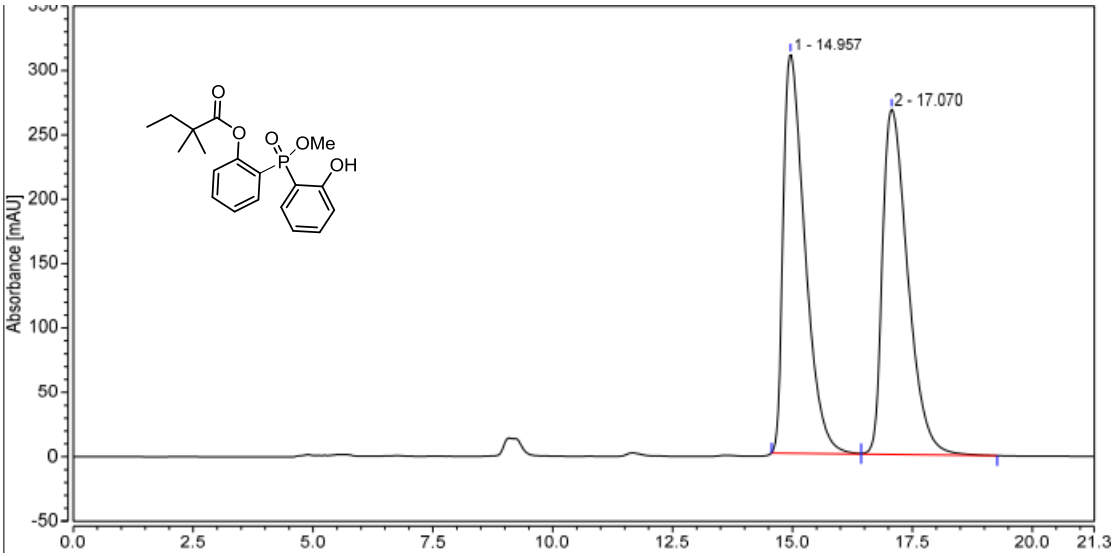


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	10.288	49.630	129.906	49.30	51.28
2	11.850	51.038	123.445	50.70	48.72
Total:		**100.668**	**253.350**	**100.00**	**100.00**

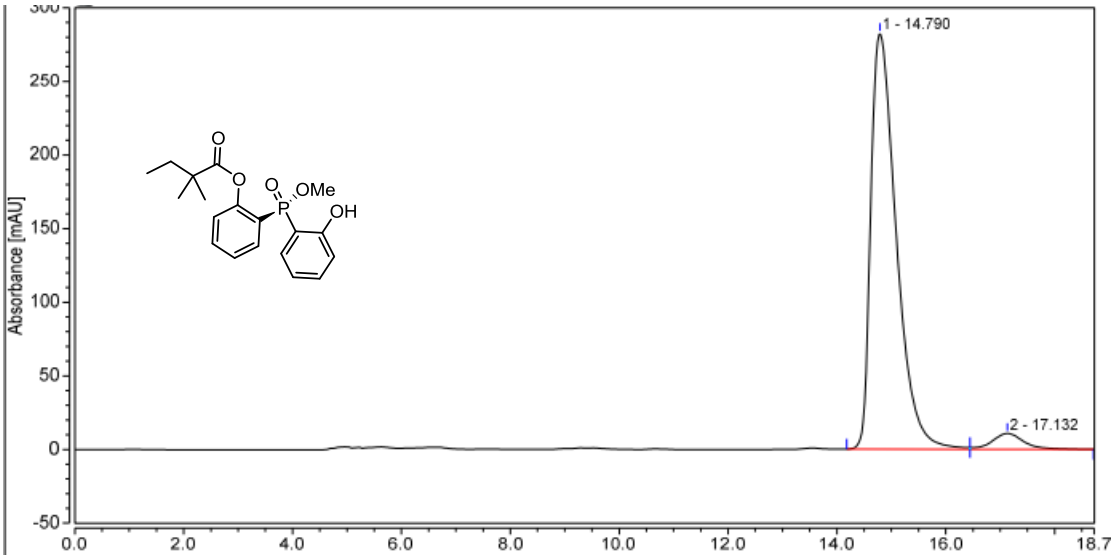


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	10.423	49.026	138.606	96.78	97.05
2	12.070	1.632	4.216	3.22	2.95
Total:		**50.658**	**142.821**	**100.00**	**100.00**

HPLC spectra of 3af

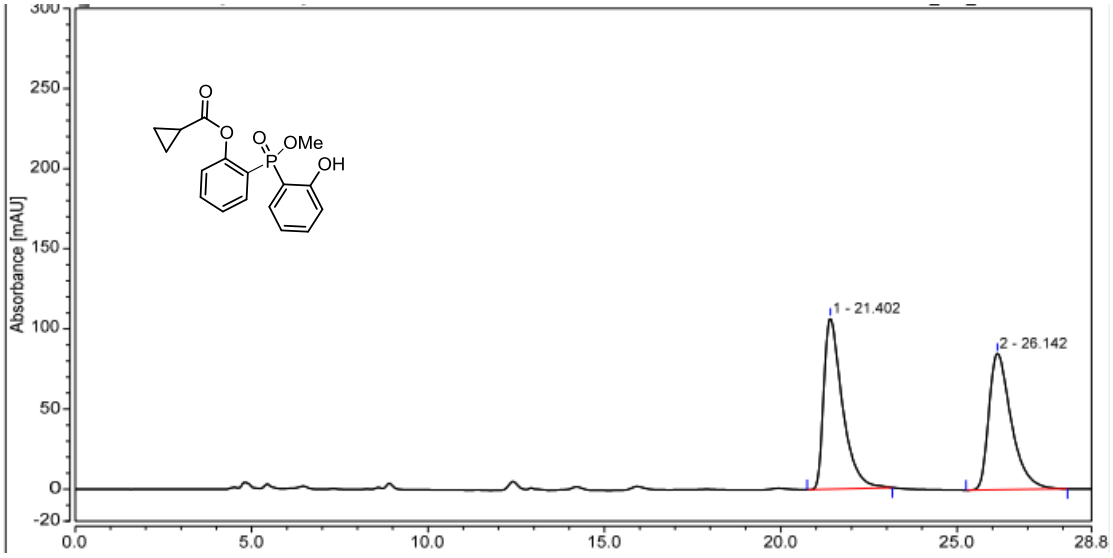


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.957	162.727	310.186	49.77	53.63
2	17.070	164.225	268.210	50.23	46.37
Total:		**326.952**	**578.395**	**100.00**	**100.00**

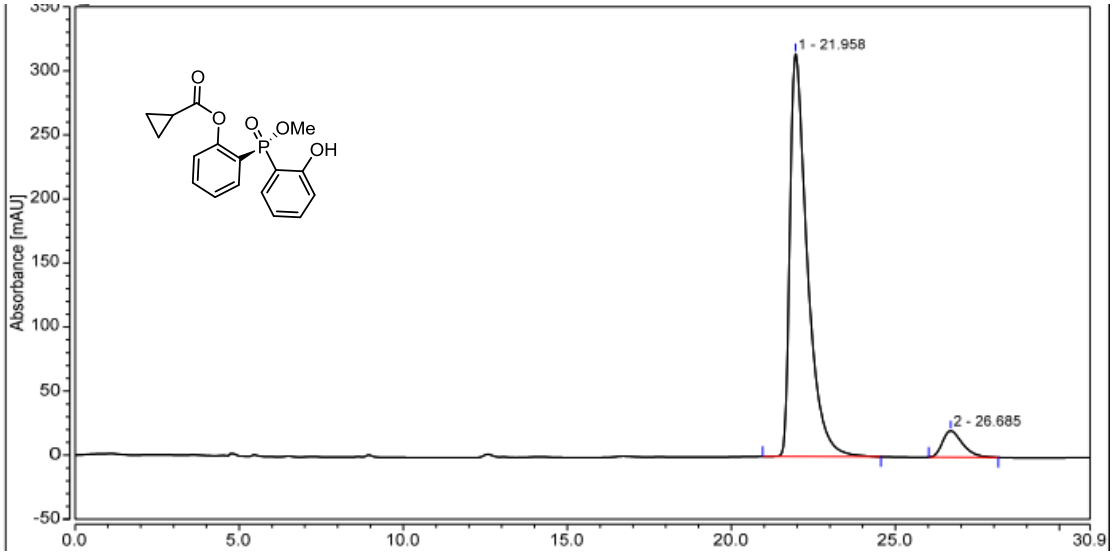


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.790	153.251	282.334	95.51	96.35
2	17.132	7.198	10.707	4.49	3.65
Total:		**160.449**	**293.041**	**100.00**	**100.00**

HPLC spectra of 3ag

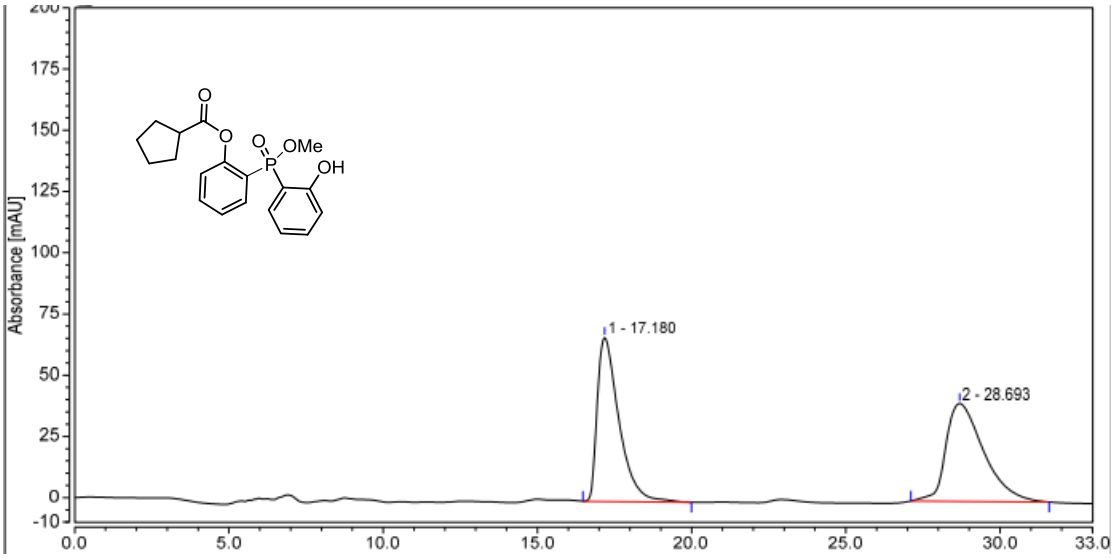


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.402	65.534	106.664	51.09	55.63
2	26.142	62.743	85.061	48.91	44.37
Total:		**128.277**	**191.725**	**100.00**	**100.00**

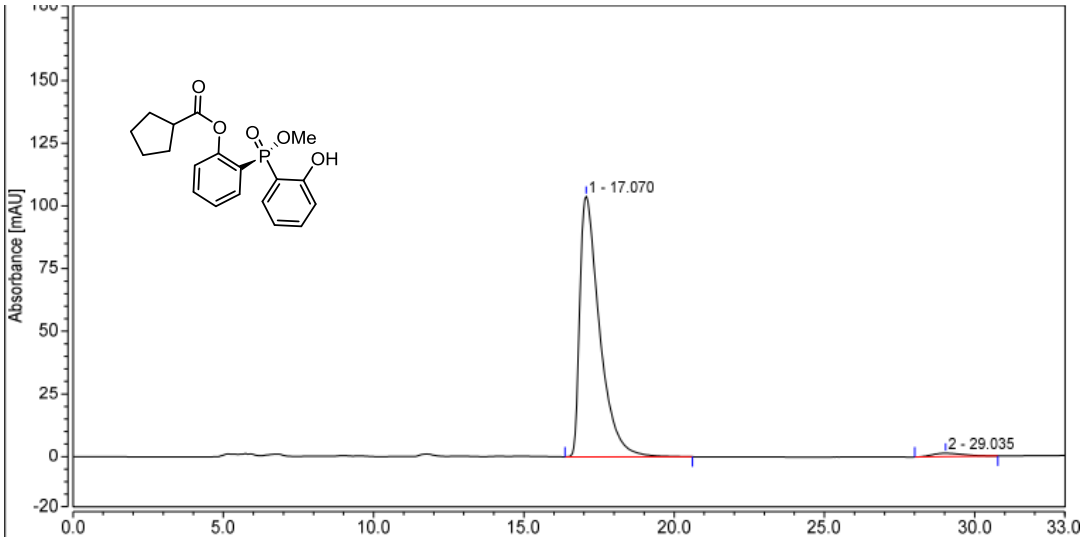


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.958	192.571	314.305	92.86	93.83
2	26.685	14.801	20.661	7.14	6.17
Total:		**207.371**	**334.965**	**100.00**	**100.00**

HPLC spectra of 3ah

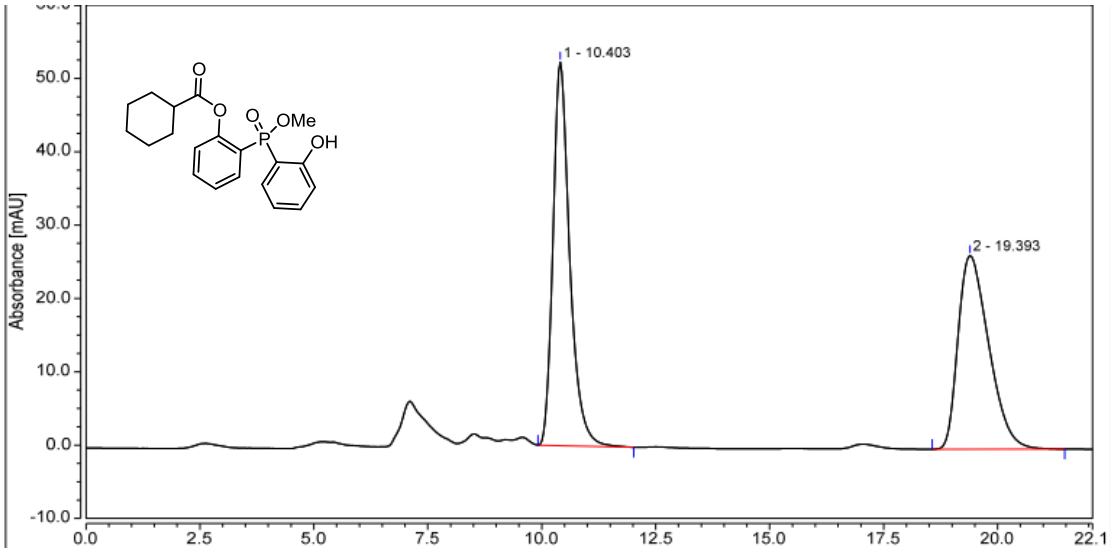


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	17.180	54.614	66.925	49.01	62.62
2	28.693	56.817	39.955	50.99	37.38
Total:		**111.431**	**106.880**	**100.00**	**100.00**

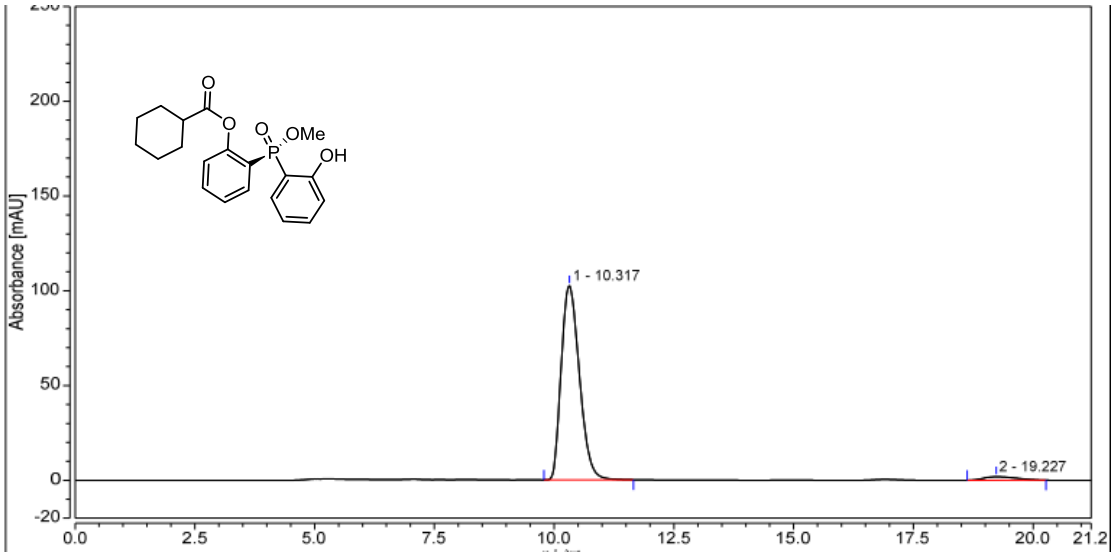


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	17.070	79.264	103.969	97.91	98.70
2	29.035	1.690	1.371	2.09	1.30
Total:		**80.955**	**105.340**	**100.00**	**100.00**

HPLC spectra of 3ai

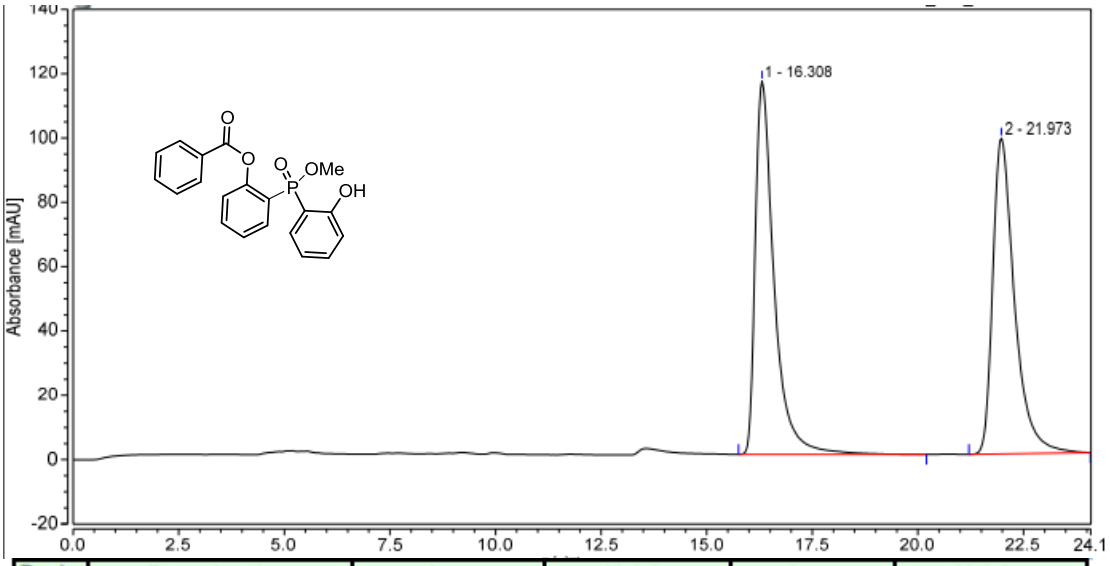


Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	10.403	22.273	52.279	51.93	66.46
2	19.393	20.621	26.389	48.07	33.54
Total:		**42.894**	**78.669**	**100.00**	**100.00**

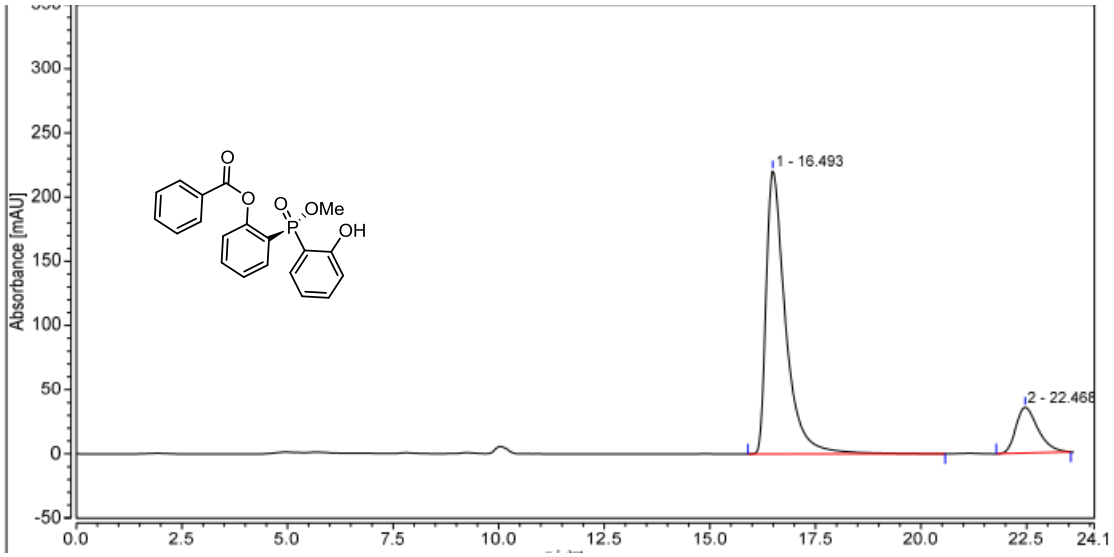


Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	10.317	45.254	102.499	96.87	98.24
2	19.227	1.463	1.837	3.13	1.76
Total:		**46.717**	**104.336**	**100.00**	**100.00**

HPLC spectra of 3aj

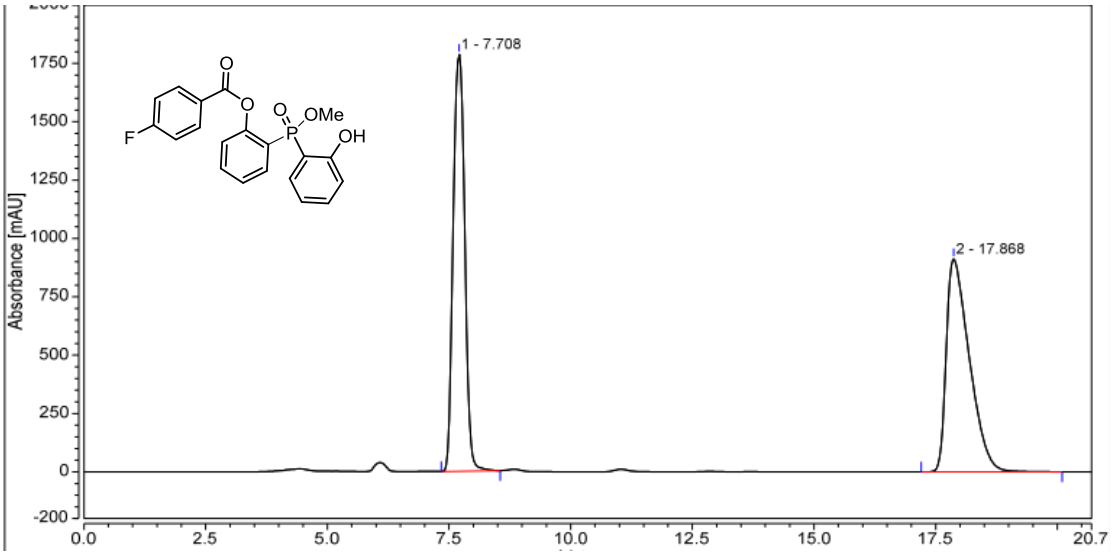


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	16.308	60.066	116.080	50.54	54.17
2	21.973	58.784	98.223	49.46	45.83
Total:		**118.850**	**214.303**	**100.00**	**100.00**

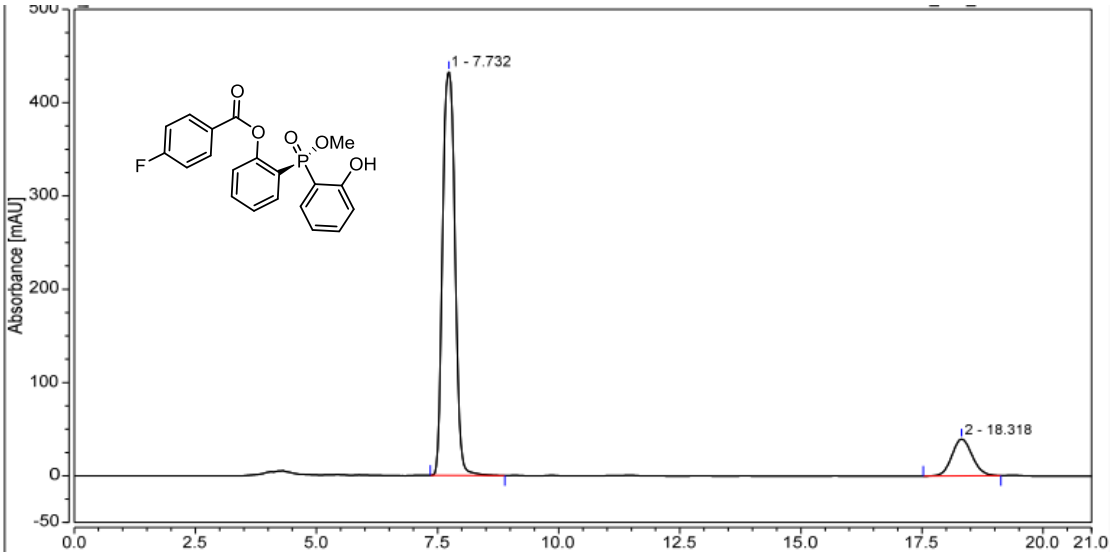


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.493	117.476	220.711	84.33	86.08
2	22.468	21.822	35.702	15.67	13.92
Total:		**139.298**	**256.413**	**100.00**	**100.00**

HPLC spectra of 3ak

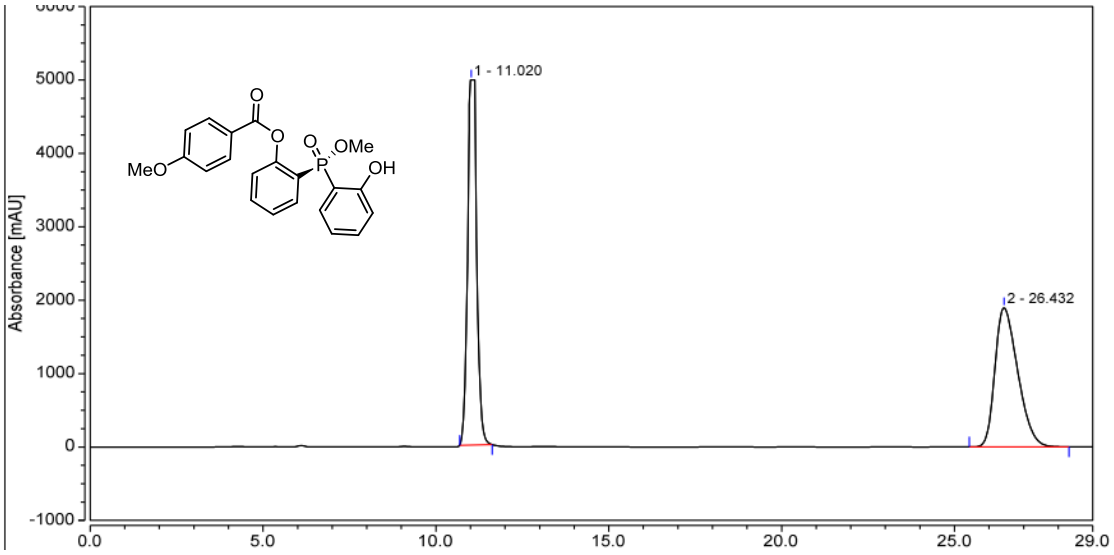


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.708	492.807	1786.569	49.59	66.17
2	17.868	500.875	913.493	50.41	33.83
Total:		**993.682**	**2700.062**	**100.00**	**100.00**

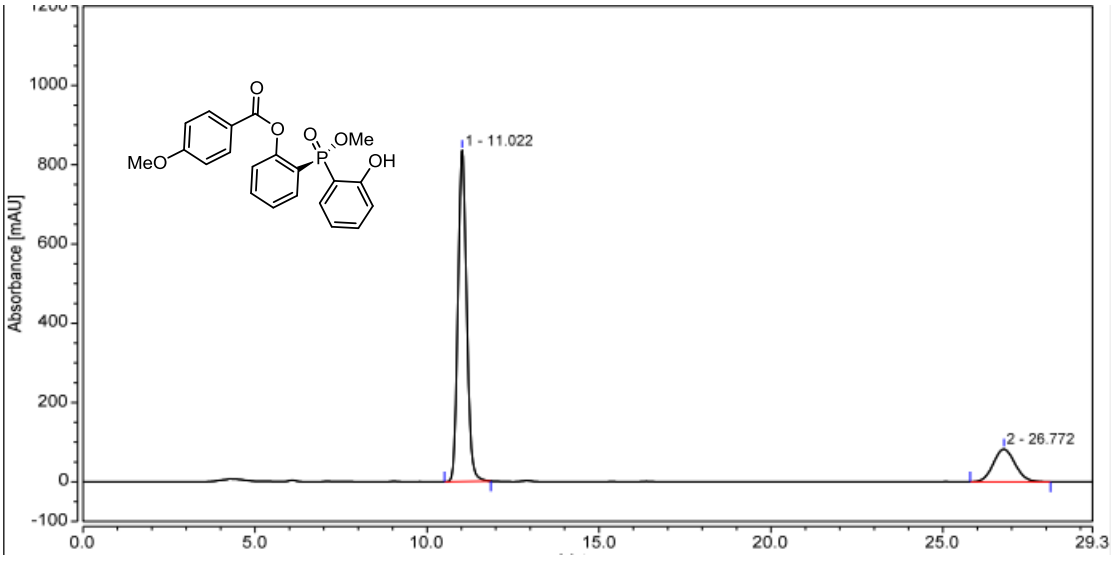


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.732	127.936	433.119	86.98	91.67
2	18.318	19.158	39.348	13.02	8.33
Total:		**147.094**	**472.467**	**100.00**	**100.00**

HPLC spectra of 3al

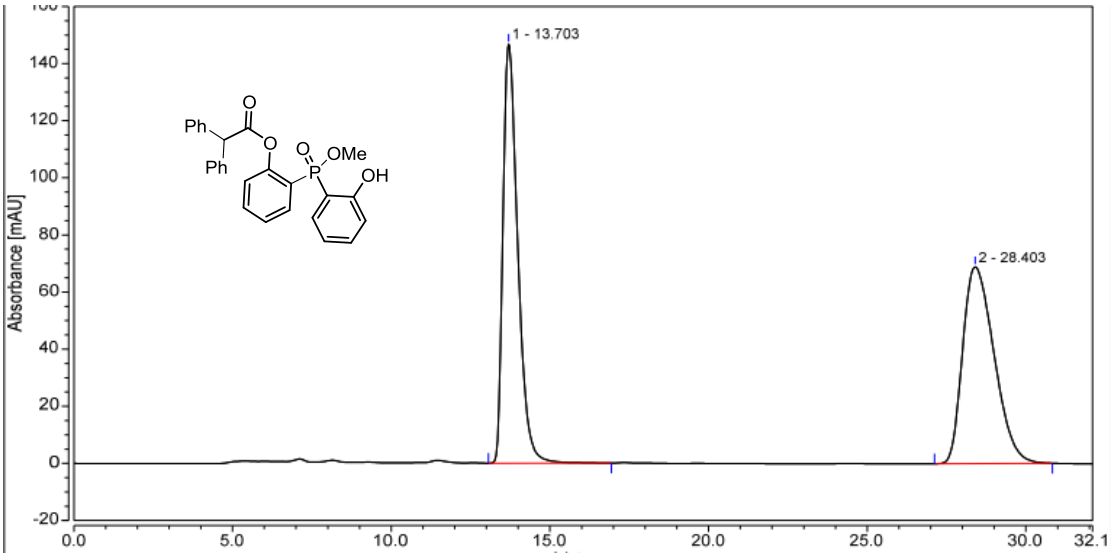


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.020	1520.027	4974.117	51.15	72.40
2	26.432	1451.738	1896.628	48.85	27.60
Total:		**2971.765**	**6870.745**	**100.00**	**100.00**

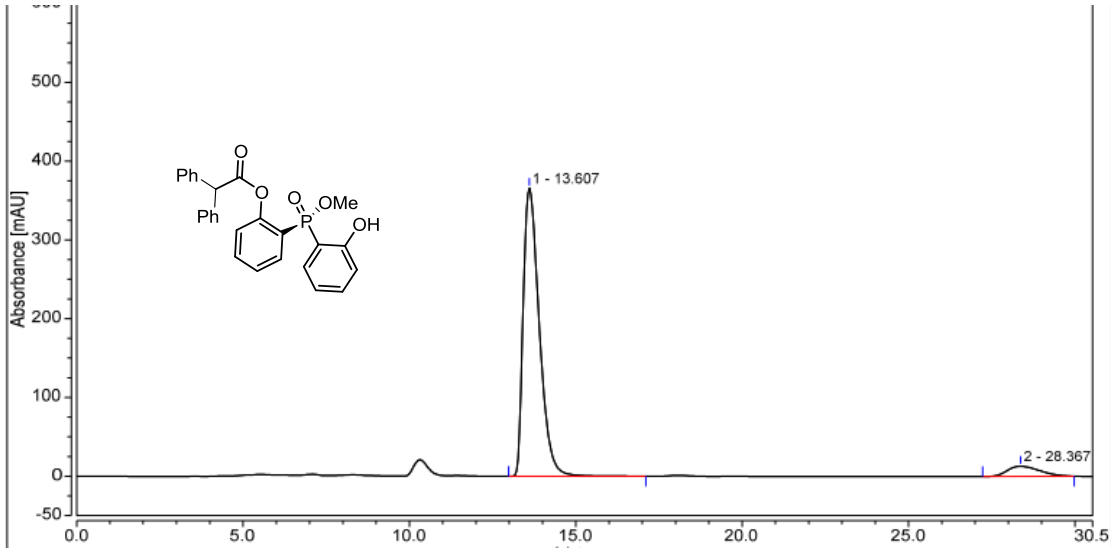


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.022	245.076	835.225	80.05	90.99
2	26.772	61.070	82.692	19.95	9.01
Total:		**306.146**	**917.917**	**100.00**	**100.00**

HPLC spectra of 3am

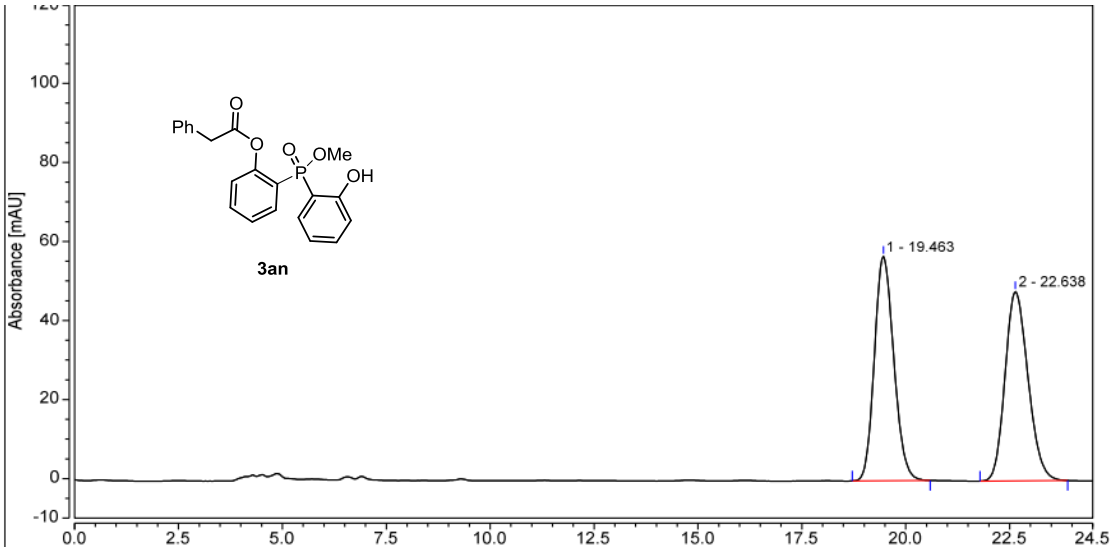


Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	13.703	79.472	146.759	50.11	68.05
2	28.403	79.132	68.900	49.89	31.95
Total:		**158.604**	**215.659**	**100.00**	**100.00**

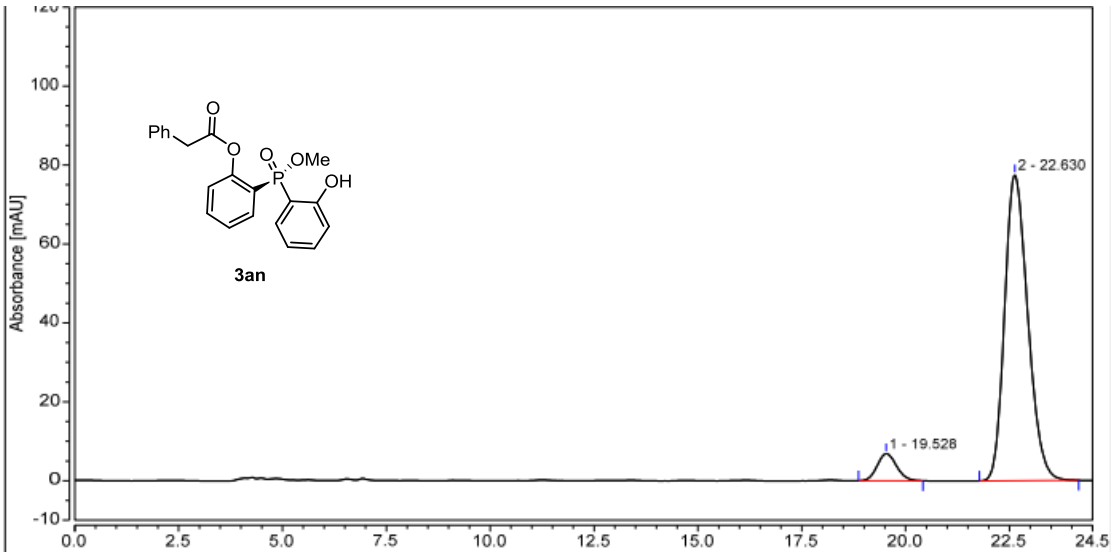


Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	13.607	204.549	365.631	93.42	96.60
2	28.367	14.397	12.863	6.58	3.40
Total:		**218.946**	**378.494**	**100.00**	**100.00**

HPLC spectra of 3an

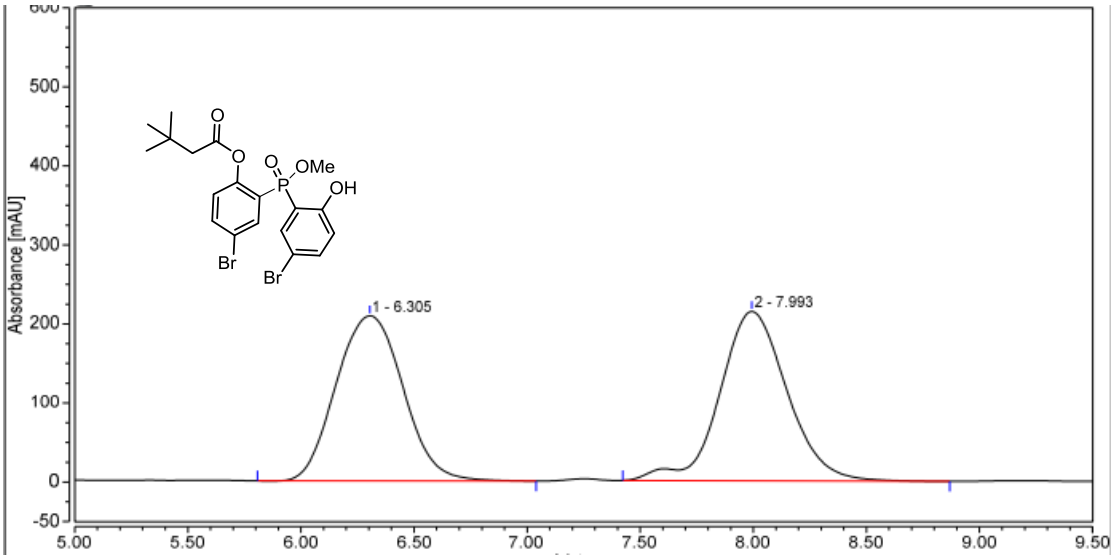


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.463	30.771	56.760	49.96	54.24
2	22.638	30.820	47.878	50.04	45.76
Total:		**61.591**	**104.638**	**100.00**	**100.00**

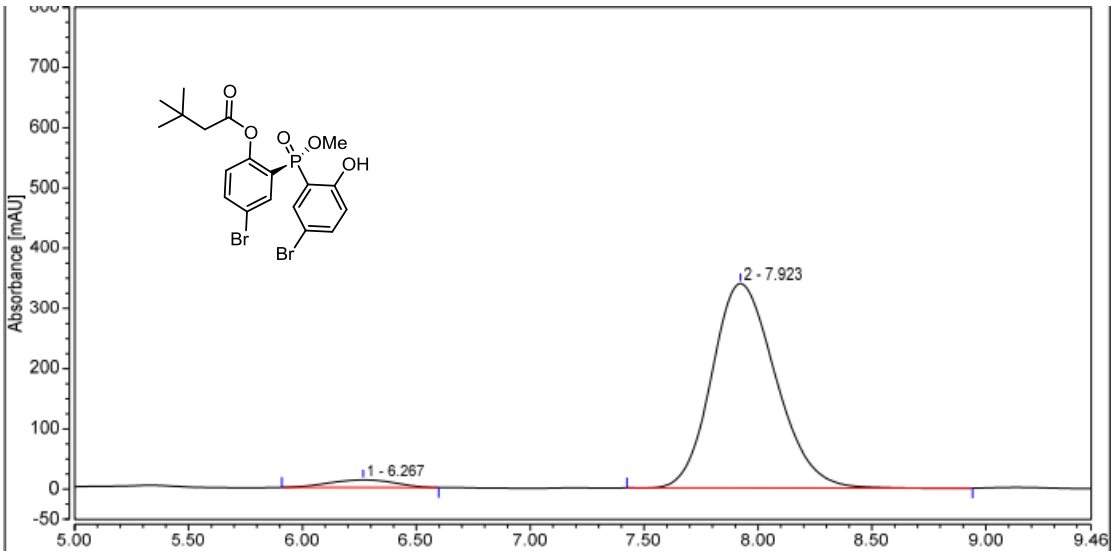


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.528	3.727	6.879	6.91	8.15
2	22.630	50.228	77.541	93.09	91.85
Total:		**53.955**	**84.421**	**100.00**	**100.00**

HPLC spectra of 3ba

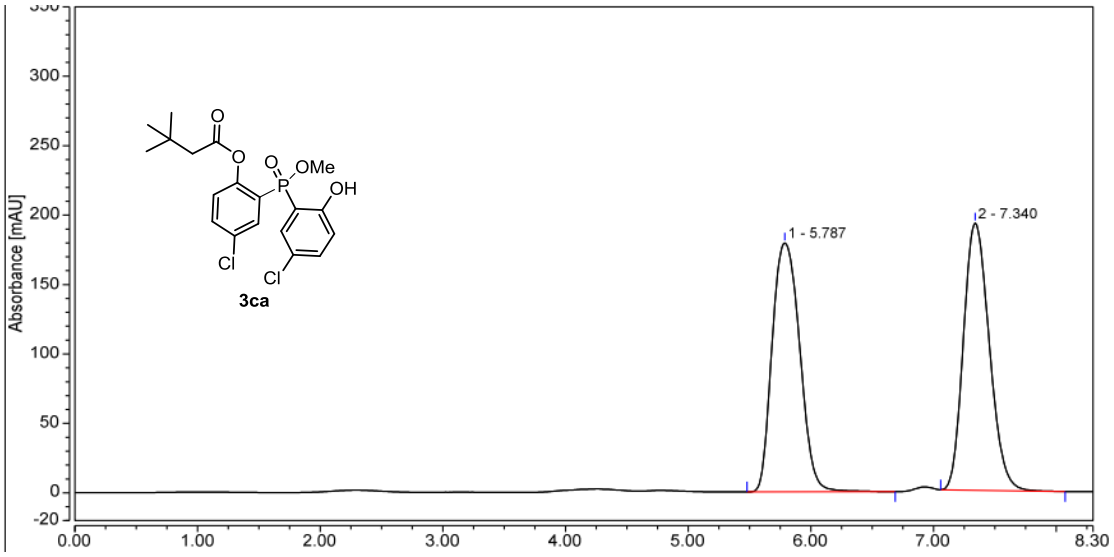


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	6.305	71.892	208.872	49.25	49.38
2	7.993	74.073	214.117	50.75	50.62
Total:		**145.965**	**422.989**	**100.00**	**100.00**

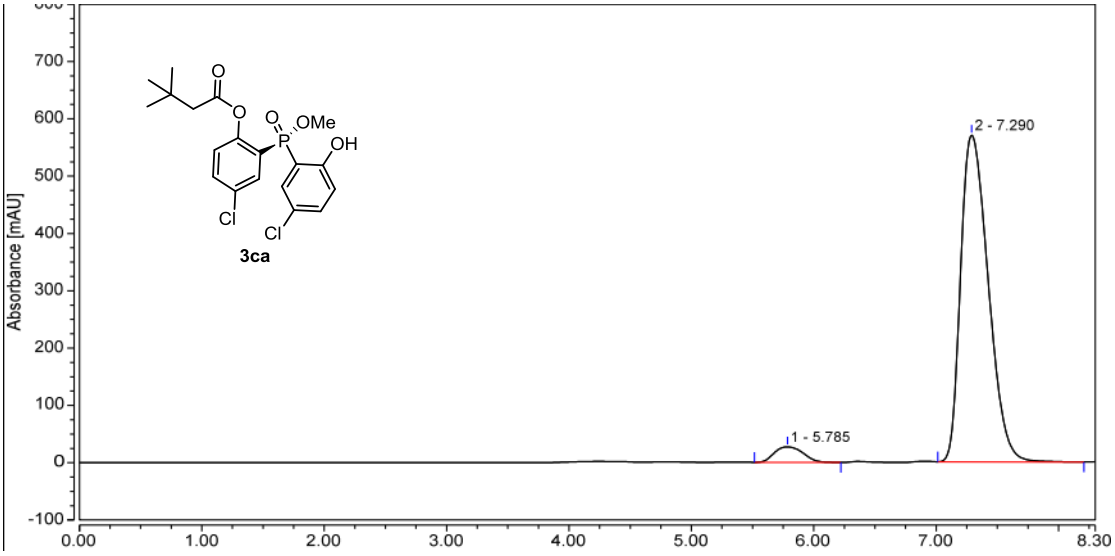


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	6.267	4.190	12.489	3.66	3.55
2	7.923	110.413	339.323	96.34	96.45
Total:		**114.603**	**351.812**	**100.00**	**100.00**

HPLC spectra of 3ca

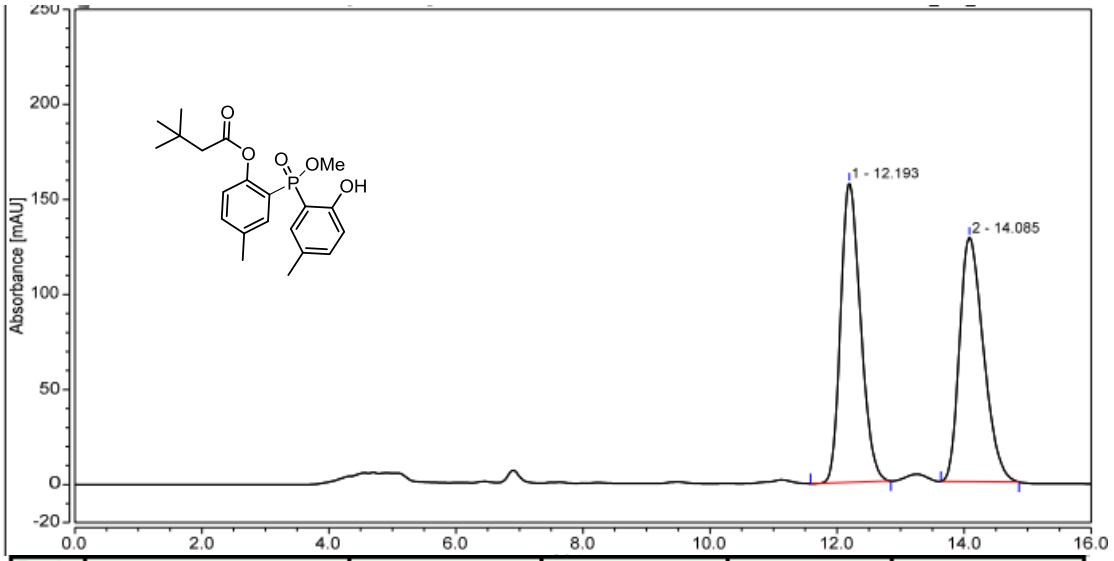


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	5.787	46.835	179.347	49.89	48.25
2	7.340	47.047	192.383	50.11	51.75
Total:		**93.882**	**371.730**	**100.00**	**100.00**

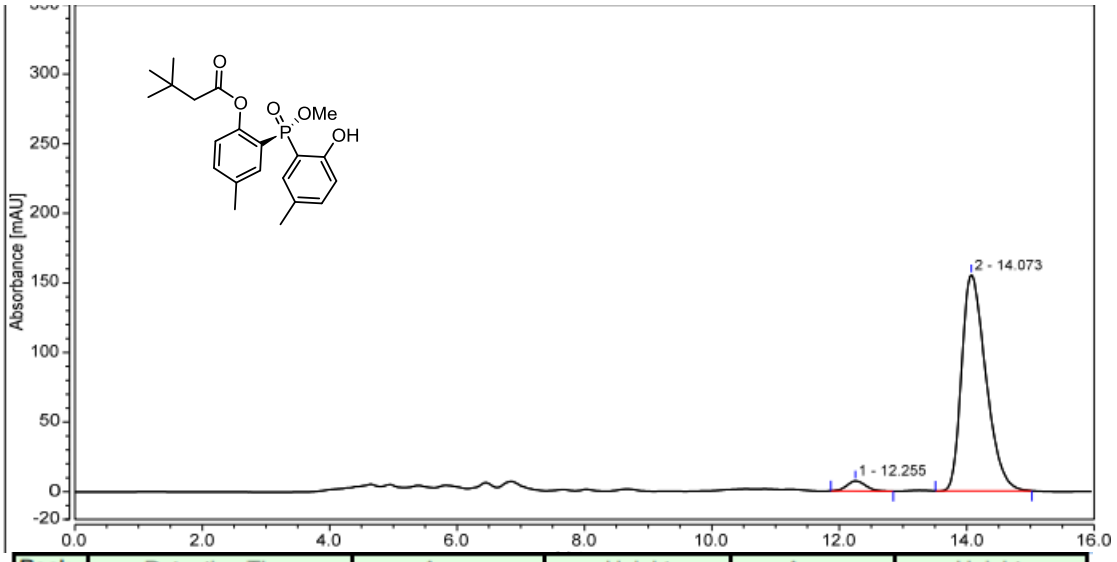


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	5.785	7.315	26.823	4.68	4.49
2	7.290	148.978	570.087	95.32	95.51
Total:		**156.293**	**596.909**	**100.00**	**100.00**

HPLC spectra of 3da

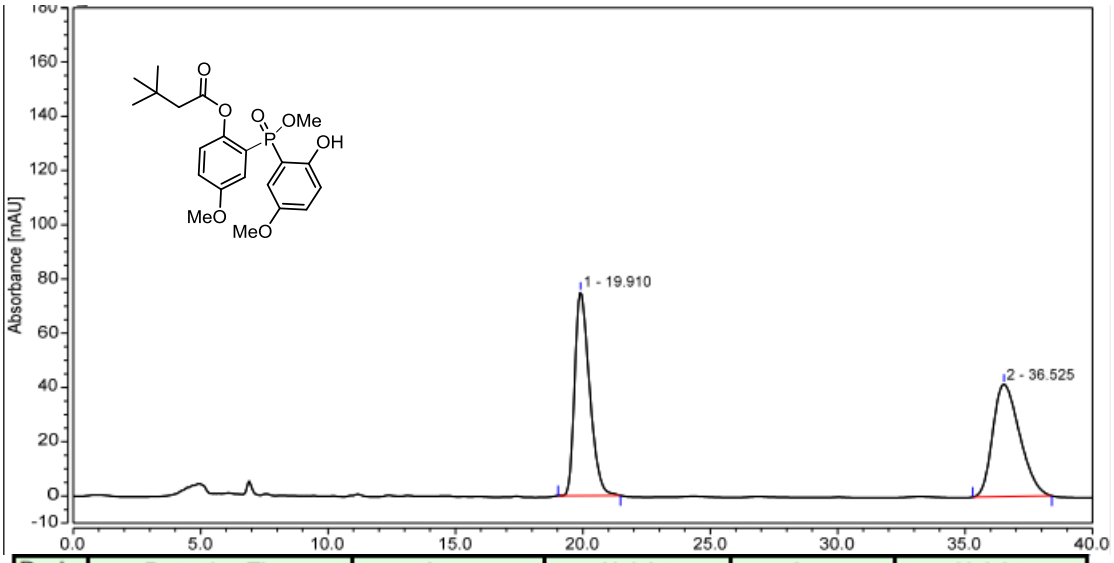


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.193	57.144	157.419	50.39	55.07
2	14.085	56.255	128.446	49.61	44.93
Total:		**113.399**	**285.866**	**100.00**	**100.00**

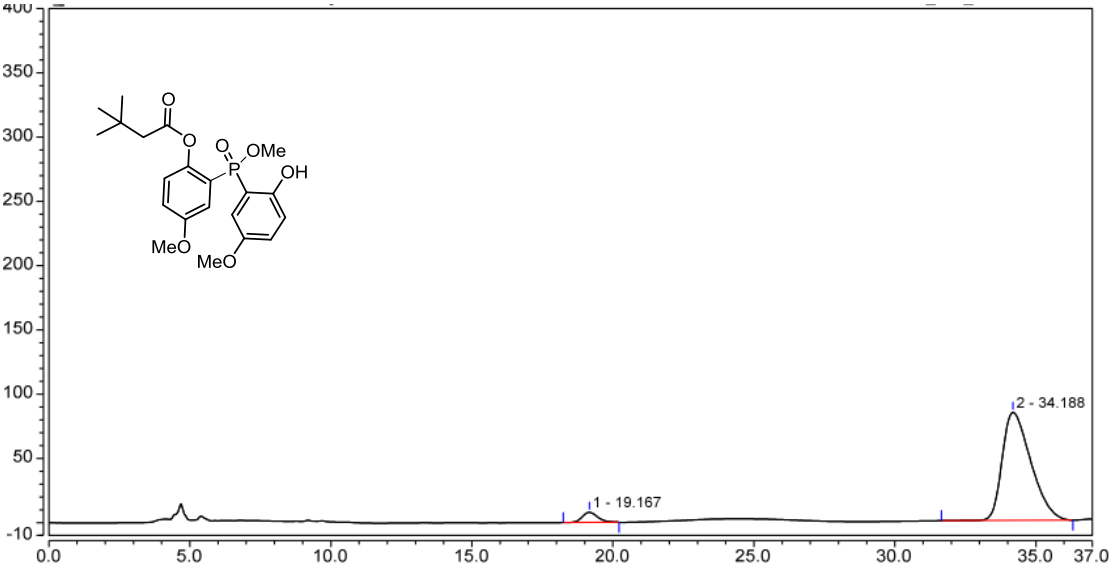


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.255	2.459	7.209	3.46	4.44
2	14.073	68.621	155.294	96.54	95.56
Total:		**71.080**	**162.502**	**100.00**	**100.00**

HPLC spectra of 3ea

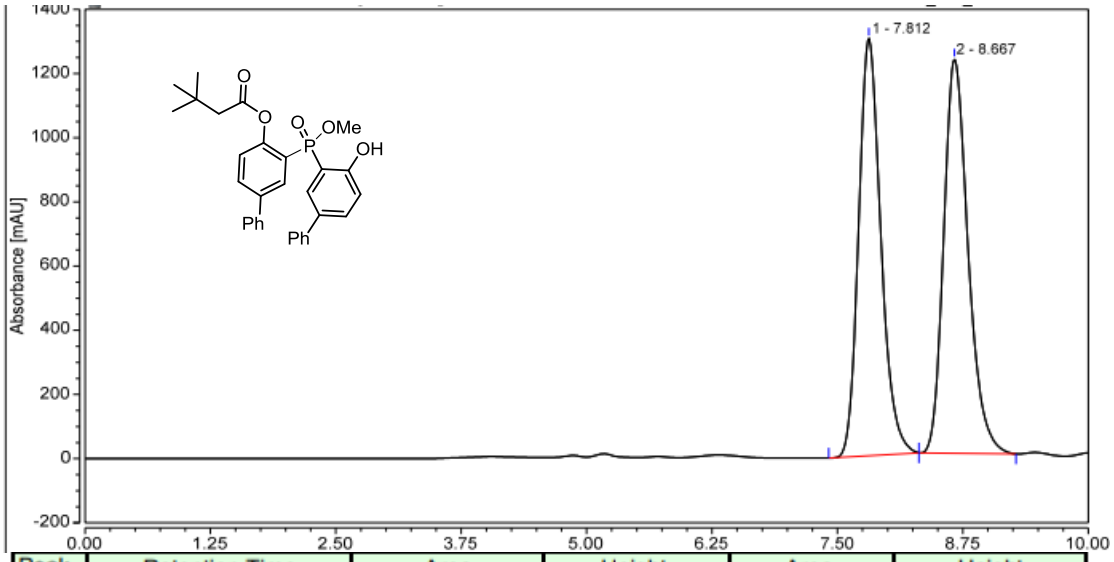


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.910	50.761	74.968	49.91	64.42
2	36.525	50.952	41.413	50.09	35.58
Total:		**101.713**	**116.382**	**100.00**	**100.00**

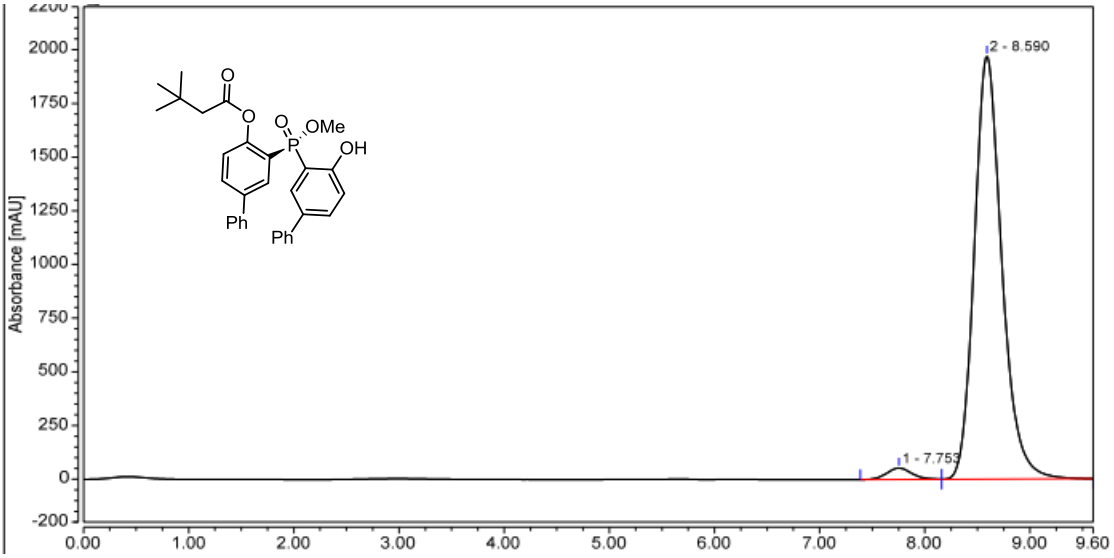


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.167	5.081	7.916	4.87	8.60
2	34.188	99.257	84.078	95.13	91.40
Total:		**104.338**	**91.994**	**100.00**	**100.00**

HPLC spectra of 3fa

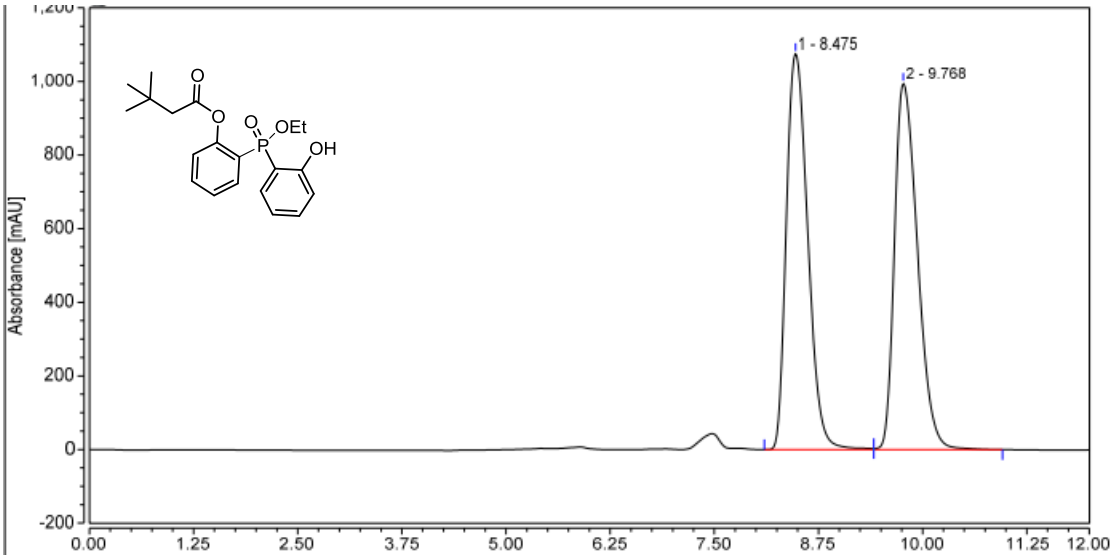


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.812	333.766	1301.912	49.13	51.46
2	8.667	345.575	1228.134	50.87	48.54
Total:		**679.341**	**2530.046**	**100.00**	**100.00**

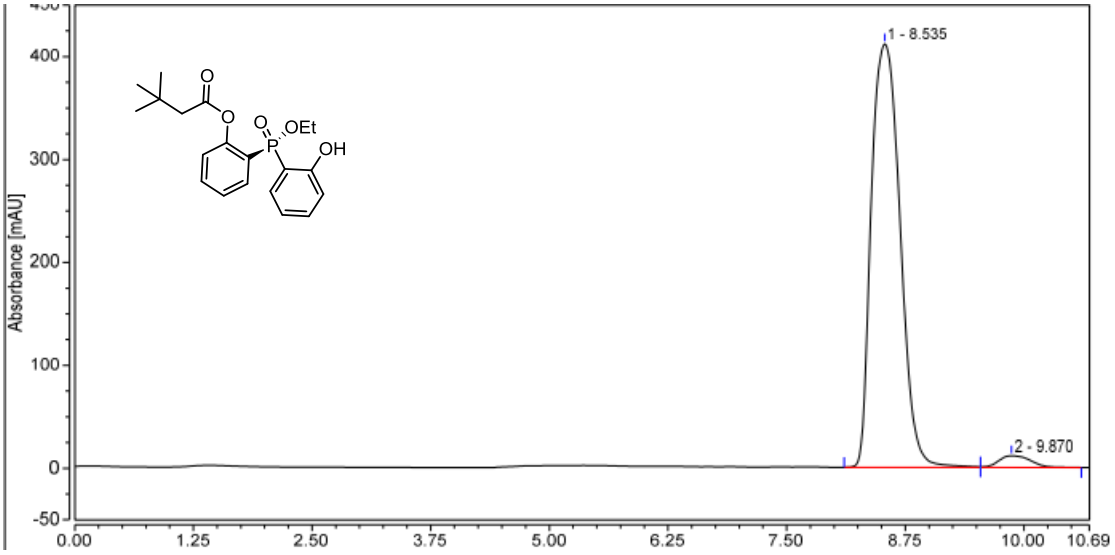


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.753	14.627	52.897	2.39	2.61
2	8.590	598.476	1970.241	97.61	97.39
Total:		**613.103**	**2023.138**	**100.00**	**100.00**

HPLC spectra of 3ga

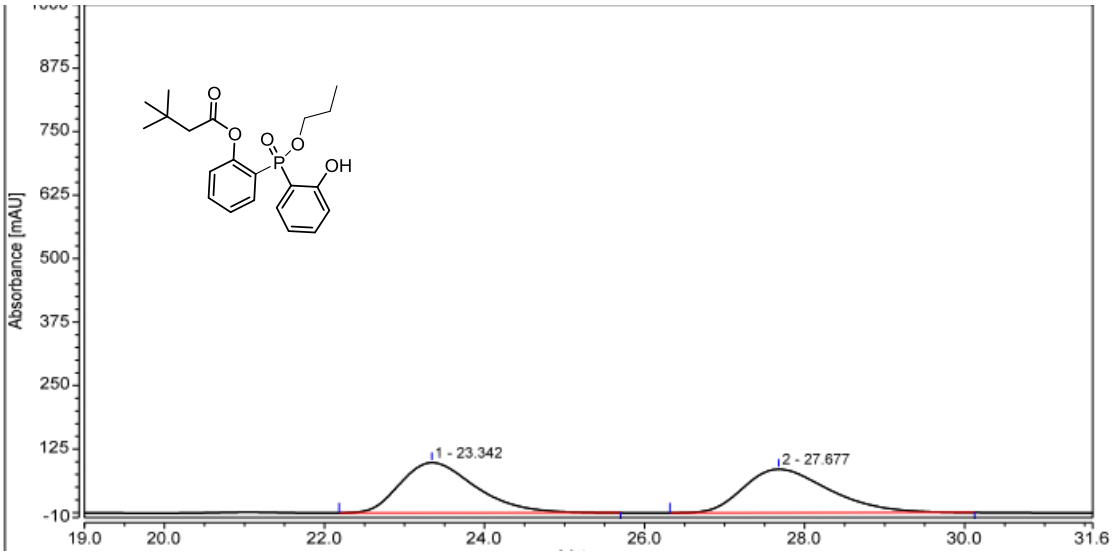


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	8.475	320.181	1076.675	50.14	51.96
2	9.768	318.370	995.472	49.86	48.04
Total:		**638.552**	**2072.147**	**100.00**	**100.00**

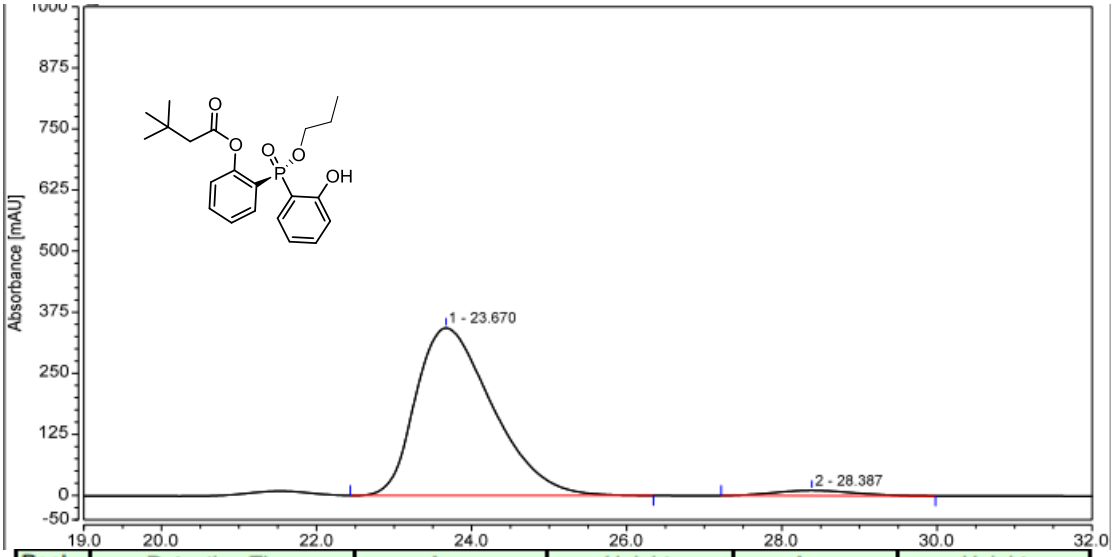


Peak	Retention time min	Area mAU*min	Height mAU	Area %	Height %
1	8.535	144.459	411.427	97.02	97.32
2	9.870	4.444	11.347	2.98	2.68
Total:		**148.903**	**422.774**	**100.00**	**100.00**

HPLC spectra of 3ha

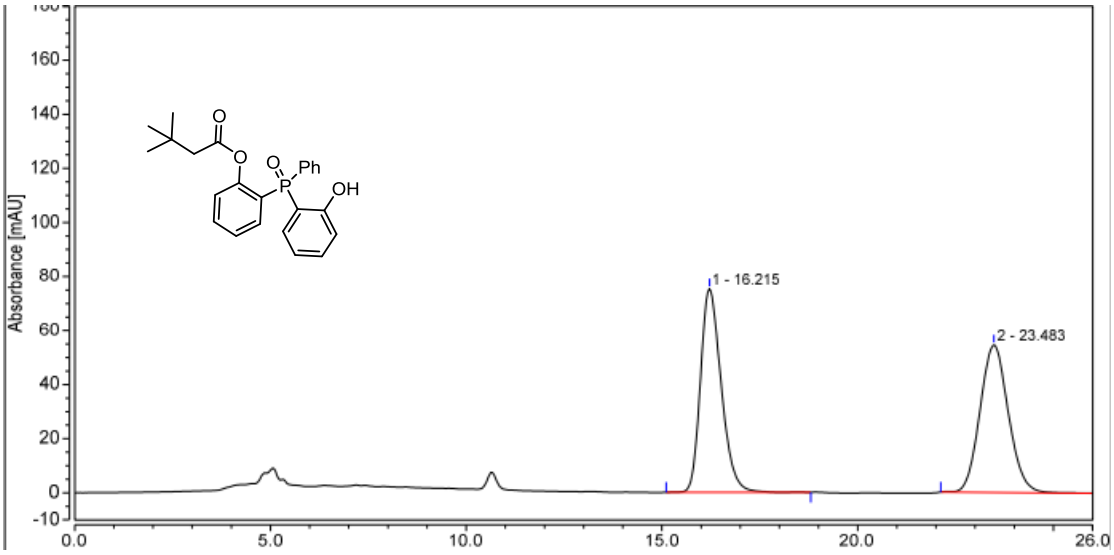


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	23.342	108.940	99.031	50.22	53.56
2	27.677	107.975	85.865	49.78	46.44
Total:		**216.915**	**184.896**	**100.00**	**100.00**

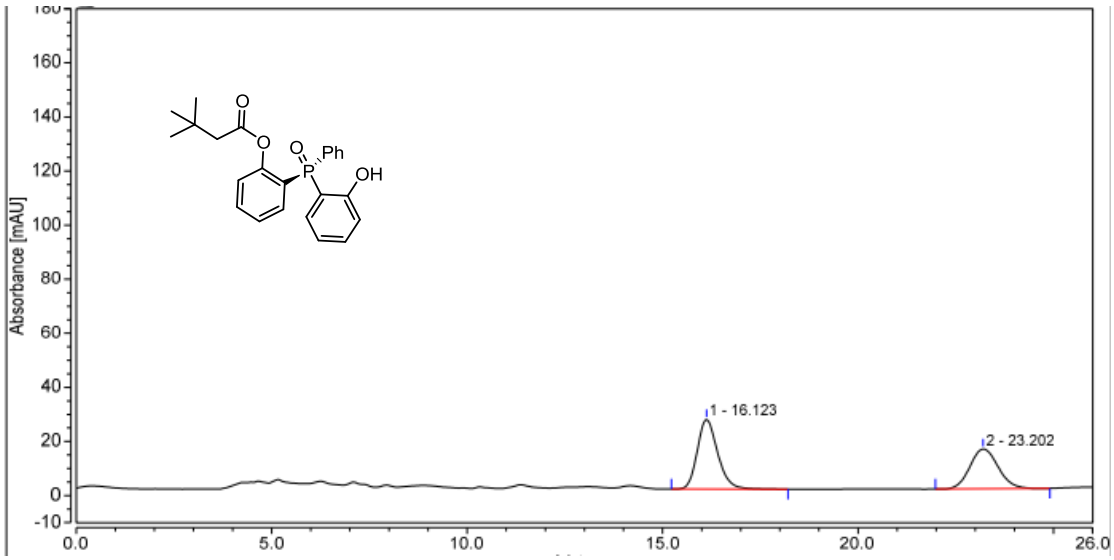


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	23.670	393.133	342.589	96.80	96.94
2	28.387	12.993	10.831	3.20	3.06
Total:		**406.125**	**353.421**	**100.00**	**100.00**

HPLC spectra of 3ia

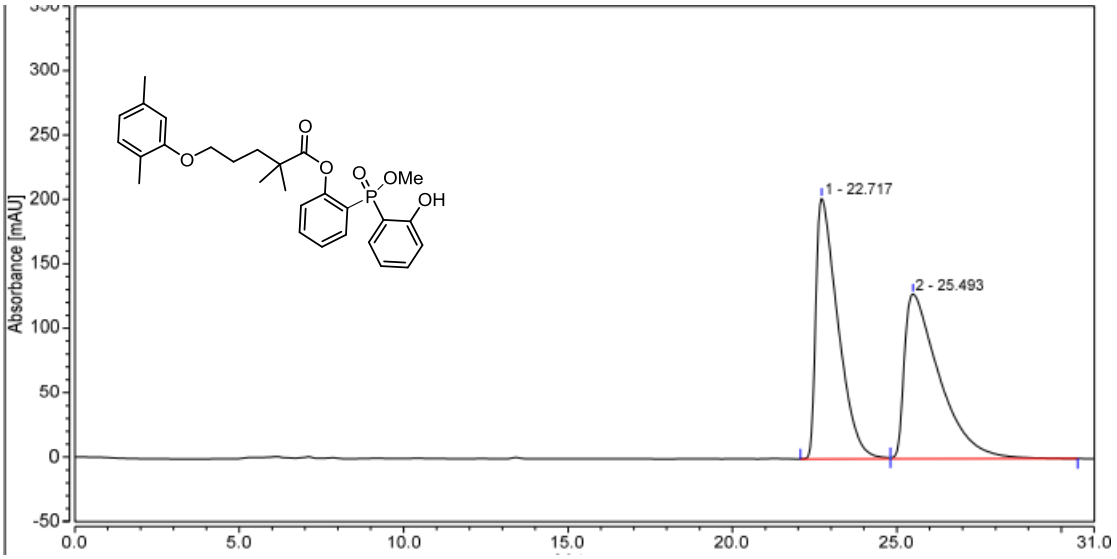


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.215	46.191	75.280	50.18	57.98
2	23.483	45.858	54.553	49.82	42.02
Total:		**92.049**	**129.833**	**100.00**	**100.00**

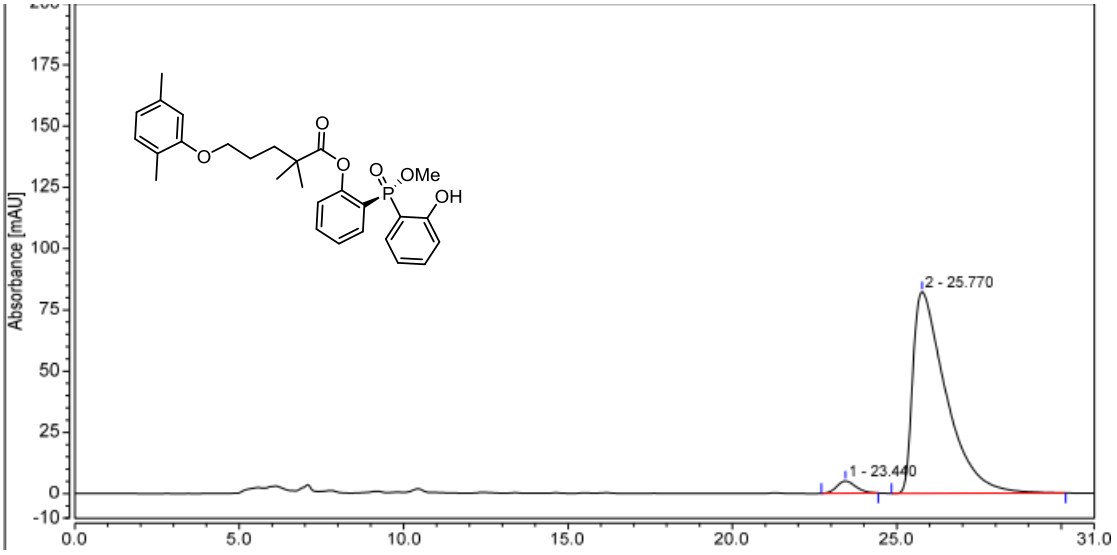


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.123	15.587	25.708	55.90	63.67
2	23.202	12.296	14.667	44.10	36.33
Total:		**27.882**	**40.374**	**100.00**	**100.00**

HPLC spectra of 3ao

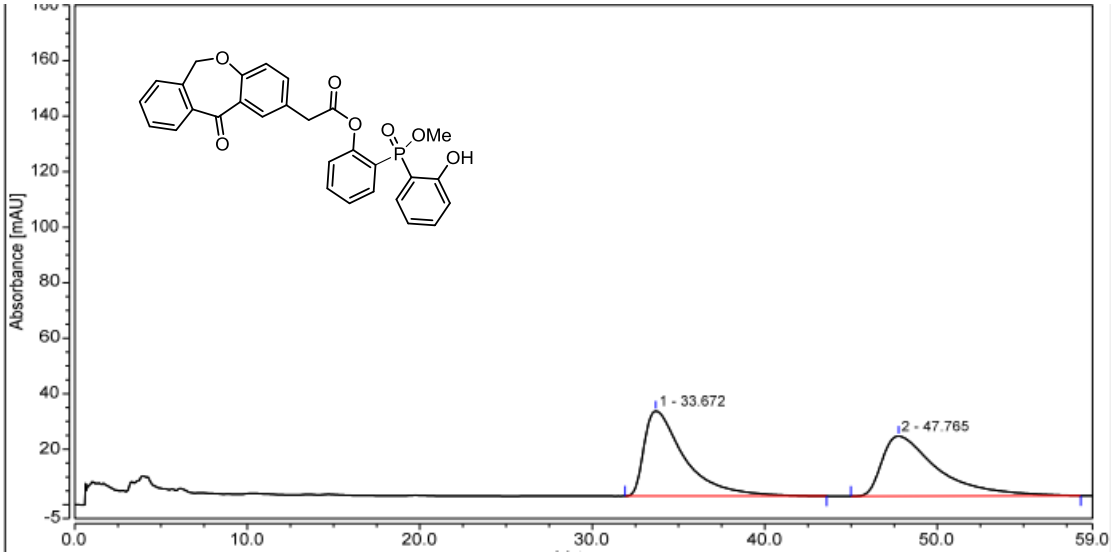


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	22.717	157.199	202.185	49.86	61.25
2	25.493	158.083	127.888	50.14	38.75
Total:		**315.282**	**330.073**	**100.00**	**100.00**

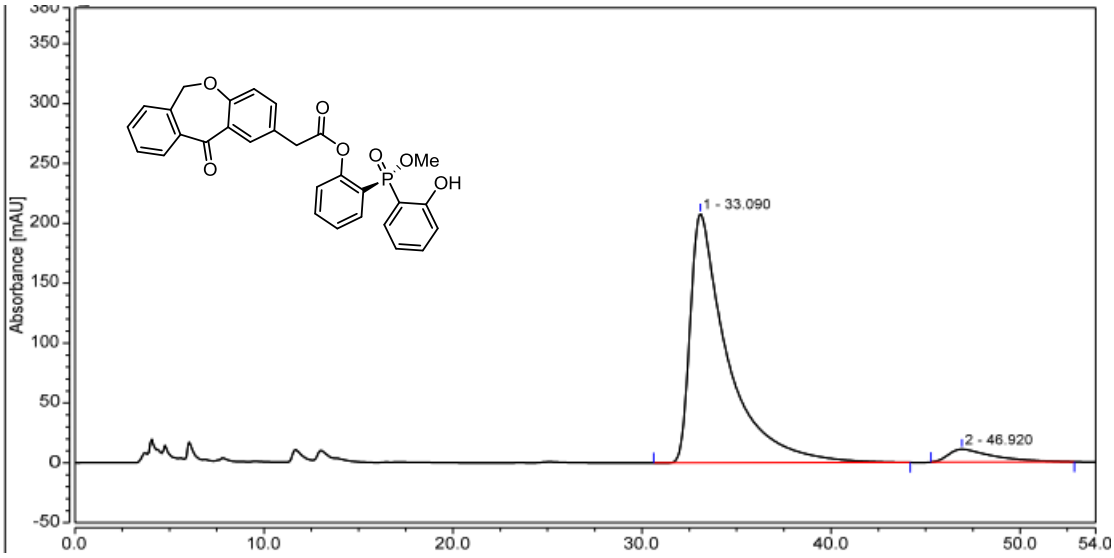


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	23.440	3.357	4.992	3.37	5.72
2	25.770	96.243	82.279	96.63	94.28
Total:		**99.599**	**87.271**	**100.00**	**100.00**

HPLC spectra of 3ap

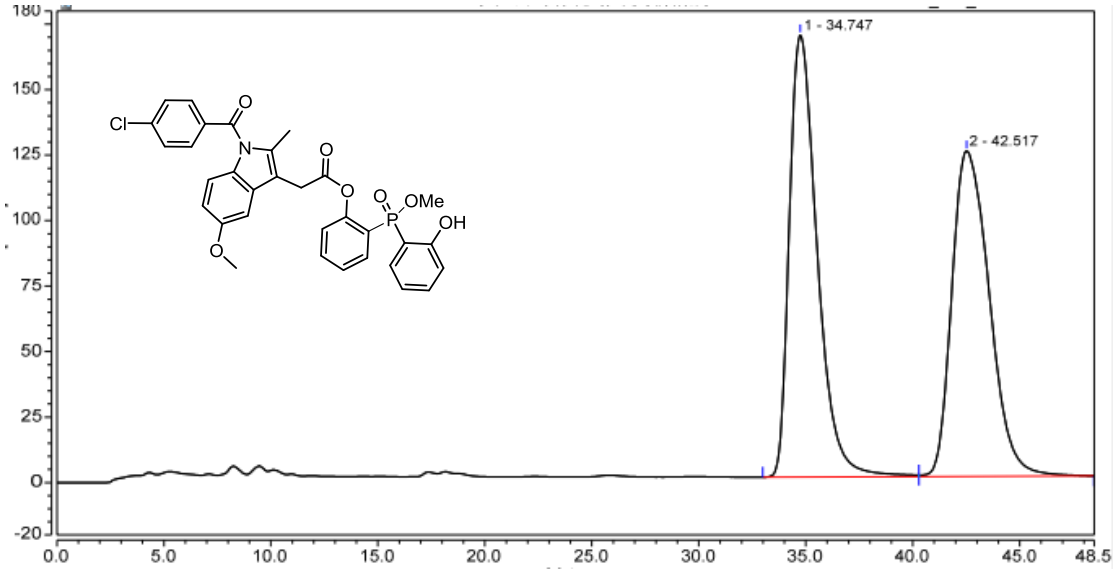


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	33.672	83.207	30.632	50.15	58.55
2	47.765	82.695	21.687	49.85	41.45
Total:		**165.902**	**52.320**	**100.00**	**100.00**

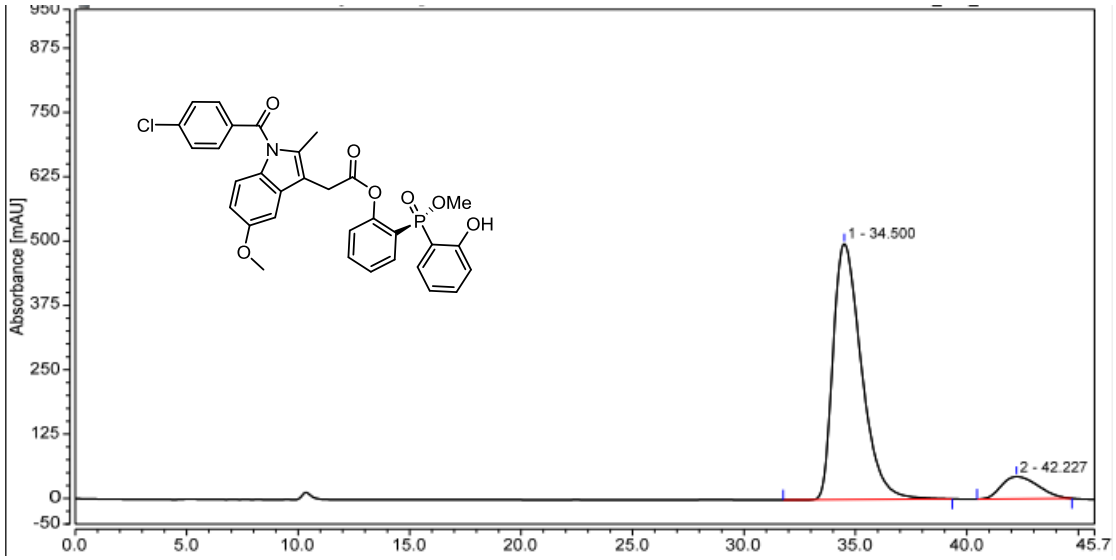


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	33.090	475.858	207.765	94.15	95.07
2	46.920	29.573	10.772	5.85	4.93
Total:		**505.431**	**218.537**	**100.00**	**100.00**

HPLC spectra of 3aq



Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	34.747	254.794	168.784	50.25	57.59
2	42.517	252.232	124.298	49.75	42.41
Total:		**507.026**	**293.082**	**100.00**	**100.00**



Peak	Retention min	Area mAU*min	Height mAU	Area %	Height %
1	34.500	730.331	496.823	89.86	92.01
2	42.227	82.437	43.135	10.14	7.99
Total:		**812.769**	**539.958**	**100.00**	**100.00**

Reference

[1] M.-S. Xie, Y.-F. Zhang, M. Shan, X.-X. Wu, G.-R. Qu and H.-M. Guo, Chiral DMAP-*N*-oxides as Acyl Transfer Catalysts: Design, Synthesis, and Application in Asymmetric Steglich Rearrangement, *Angew. Chem., Int. Ed.*, 2019, **58**, 2839-2843.

[2] M.-S. Xie, M. Shan, N. Li, Y.-G. Chen, X.-B. Wang, X. Cheng, Y. Tian, X.-X. Wu, Y. Deng, G.-R. Qu and H.-M. Guo, Chiral 4-Aryl-pyridine-*N*-oxide Nucleophilic Catalysts: Design, Synthesis, and Application in Acylative Dynamic Kinetic Resolution. *ACS Catal*., 2022, **12**, 877-891.