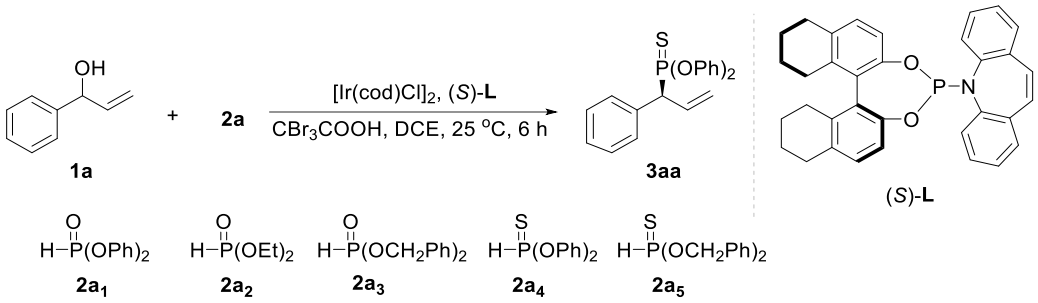
Supporting Information

1. General information

All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques under nitrogen or inside a glove box under nitrogen. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a JEOL (400 MHz) instrument. ^{1}H and $^{13}C\{1H\}$ NMR chemical shifts are reported relative to tetramethylsilane signal or residual proton solvent signals. Solvent purification was carried out using a solvent purification system (Vigor VSPS-5). Dichloroethane was distilled over CaH_2 under nitrogen. All other chemicals were used as received from the suppliers (Aldrich, Alfa, J&K, and Chemical Reagent Companies of China).

2. Optimization of reaction conditions

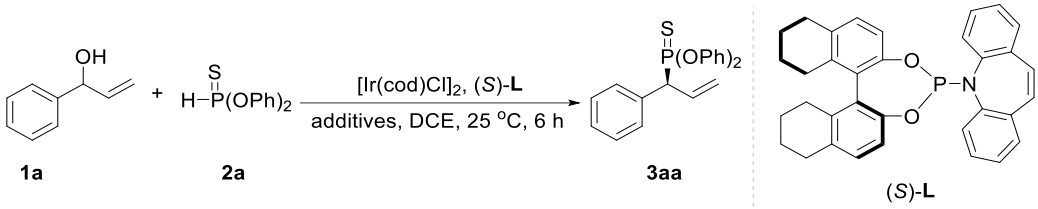
Table S1. Initial Screening of Conditions



Entry[a]	**2a**	B/L	Yiled (%)[b]	ee (%)[c]
1	**$2a_1$**	>100:1	57	75
2	**$2a_2$**	-	Trace	-
3	**$2a_3$**	-	Trace	-
4	**$2a_4$**	>100:1	69	90
5	**$2a_5$**	-	Trace	-

[a]Reaction conditions unless otherwise noted: **1a** (0.4 mmol), **2a** (0.2 mmol), $[Ir(cod)Cl]_2$ (2.5 mol%), (*S*)-**L** (10 mol%), CBr_3COOH (25 mol%), DCE (2 mL), 25 °C, under N_2 for 6 h. [b]Isolated yields. [c]The ee was determined by chiral HPLC.

Table S2. The Impact of Additives

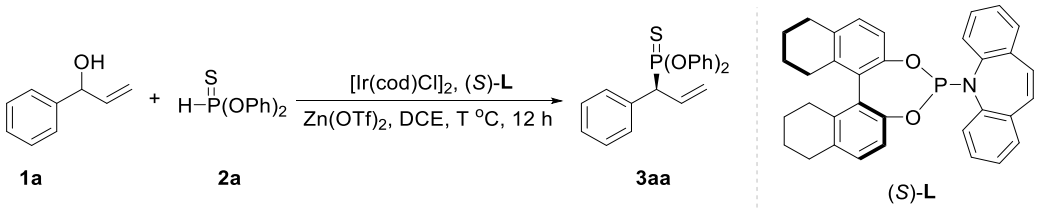


1a **2a** **3aa** (*S*)-**L**

Entry[a]	additives	B/L	Yiled (%)[b]	ee (%)[c]
1	CBr_3COOH	>100:1	69	90
2	TFA	>100:1	61	84
3	$4\text{-}NO_2PhSO_3H$	-	Trace	-
4	CF_3COOH	>100:1	76	84
5	(*R*)-CPA	>100:1	52	82
6[d]	$Sc(OTf)_3$	-	Trace	-
7[d]	$Zn(OTf)_2$	>100:1	62	97
8[d]	$Fe(OTf)_2$	>100:1	54	93
9[d]	$Yb(OTf)_3$	>100:1	55	96
10[d]	$Ca(OTf)_2$	-	Trace	-
11[d]	$Cu(OTf)_2$	-	Trace	-

[a]Reaction conditions unless otherwise noted: **1a** (0.4 mmol), **2a** (0.2 mmol), $[Ir(cod)Cl]_2$ (2.5 mol%), (*S*)-**L** (10 mol%), additives (25 mol%), DCE (2 mL), 25 °C, under N_2 for 6 h. [b]Isolated yields. [c]The ee was determined by chiral HPLC. [d]additives (20mol%).

Table S3. The Impact of Reaction Temperature

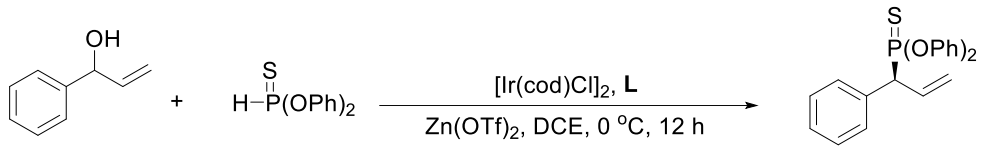


1a **2a** **3aa** (*S*)-**L**

Entry[a]	T °C	B/L	Yiled (%)[b]	ee (%)[c]
1	25	>100:1	65	97
2	0	>100:1	89	98
3	-10	>100:1	75	97
4	-20	>100:1	36	93

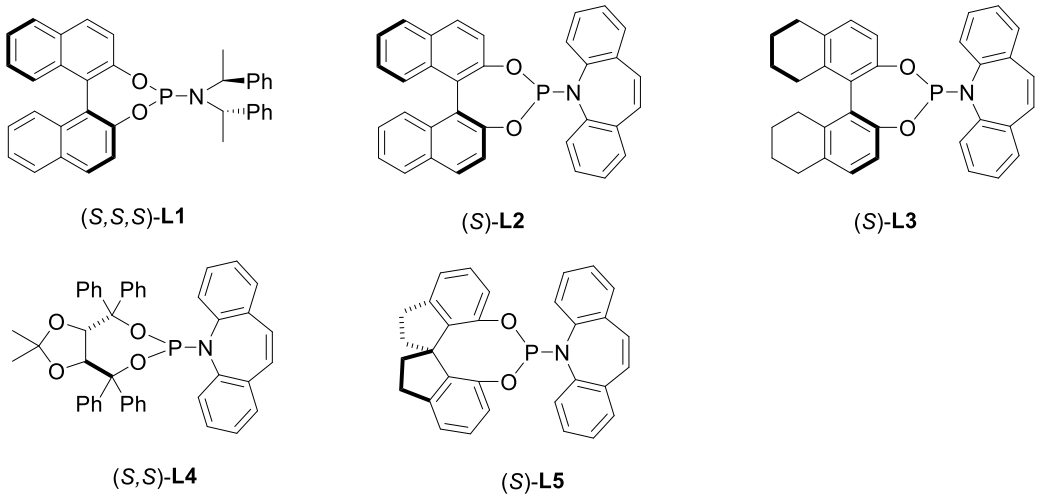
[a]Reaction conditions unless otherwise noted: **1a** (0.4 mmol), **2a** (0.2 mmol), $[Ir(cod)Cl]_2$ (2.5 mol%), (*S*)-**L** (10 mol%), $Zn(OTf)_2$ (20 mol%), DCE (2 mL), T °C , under N_2 for 12 h. [b]Isolated yields. [c]The ee was determined by chiral HPLC.

Table S4. The effect of ligand



1a **2a** **3aa**

Entry[a]	Ligand	B/L	Yiled (%)[b]	ee (%)[c]
1	**L1**	-	Trace	-
2	**L2**	>100:1	73	98
3	L3	>100:1	89	98
4	**L4**	-	Trace	-
5	**L5**	-	Trace	-

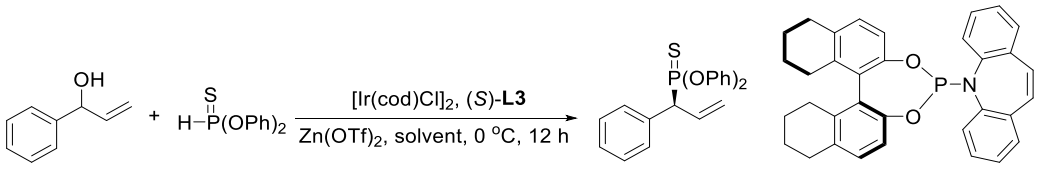


(*S,S,S*)-**L1** (*S*)-**L2** (*S*)-**L3**

(*S,S*)-**L4** (*S*)-**L5**

[a]Reaction conditions unless otherwise noted: **1a** (0.4 mmol), **2a** (0.2 mmol), $[Ir(cod)Cl]_2$ (2.5 mol%), ligand (10 mol%), $Zn(OTf)_2$ (20 mol%), DCE (2 mL), 0 °C , under N_2 for 12 h. [b]Isolated yields. [c]The ee was determined by chiral HPLC.

Table S5. The Effect of the Solvent



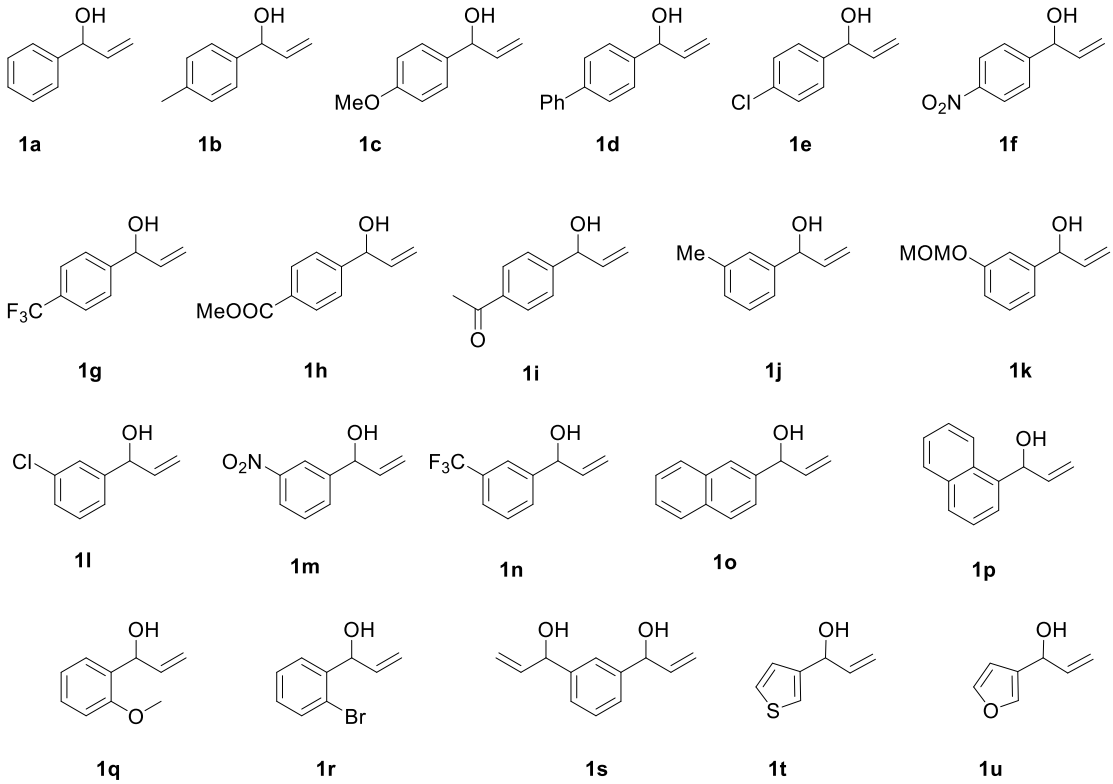
1a **2a** **3aa** (*S*)-**L3**

Entry[a]	solvent	B/L	Yiled (%)[b]	ee (%)[c]
1	DCE	>100:1	89	98
2	DCM	>100:1	93	99

[a]Reaction conditions unless otherwise noted: **1a** (0.4 mmol), **2a** (0.2 mmol), $[Ir(cod)Cl]_2$ (2.5 mol%), (*S*)-**L3** (10 mol%), $Zn(OTf)_2$ (20 mol%), solvent (2 mL), 0 °C , under N_2 for 12 h. [b]Isolated yields. [c]The ee was determined

by chiral HPLC.

3. General Procedure for Preparing Racemic Allylic Alcohols



1a **1b** **1c** **1d** **1e** **1f**

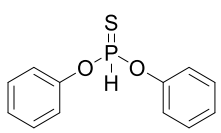
1g **1h** **1i** **1j** **1k**

1l **1m** **1n** **1o** **1p**

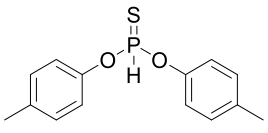
1q **1r** **1s** **1t** **1u**

(**1a, 1b, 1f, 1g, 1h, 1l, 1k, 1n, 1m, 1q, 1r, 1t**)[1], (**1c, 1d, 1j**)[2], **1m**[3], **1e**[4], **1i**[5], **1l**[6] were prepared according to the literature.

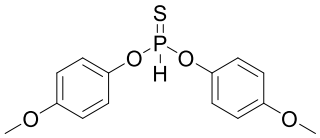
4. General Procedure for Synthesizing Secondary Phosphine Sulfides



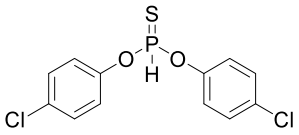
2a



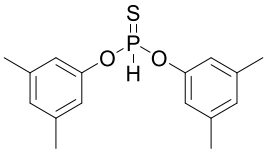
2b



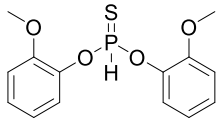
2c



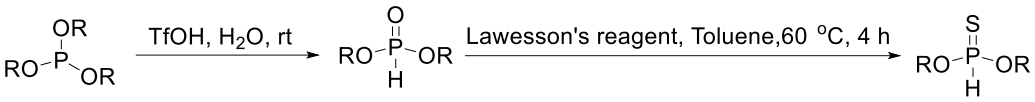
2d



2e



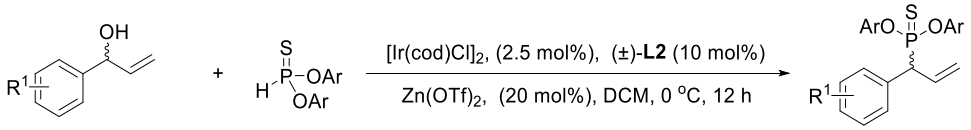
2f



I **II** **2**

Compound **I** was synthesized following the procedure described below; for experimental details, see reference 7. Compound **I** (2.3 mmol) was dissolved in trifluoromethanesulfonic acid (4 μL, 2 mol%) and water (1 equiv., 41.4 μL) in a round-bottom flask under an air atmosphere. The mixture was stirred at room temperature and monitored by TLC until the starting material was completely consumed. The crude product was purified by flash column chromatography (DCM) to obtain compound II. Next, compound **II** (10.0 mmol, 1.0 equiv.) was treated with Lawesson's reagent (2.8 g, 7 mmol, 0.7 equiv.) in anhydrous toluene (40 mL). The yellow solution was heated at 60 °C for 4 hours with continuous stirring. then cooled to room temperature. After removing the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/DCM = 25:1 to 5:1) to yield the target phosphine sulfides (**2a-2f**) as colorless oils.

5. General Procedure for the Synthesis of Racemic Allylic Phosphine Sulfides

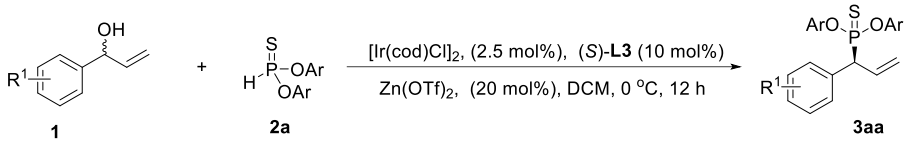


1 **2a** **3aa**

A 10 mL Schlenk tube equipped with a magnetic stir bar was charged inside a glovebox with $[Ir(cod)Cl]_2$ (0.005 mmol), rac-**L2** (0.02 mmol), and DCM (1 mL). The mixture was stirred at room temperature for 15 minutes to allow for preactivation. Substrate **1** (0.4 mmol) and $Zn(OTf)_2$ (0.04 mmol) were added sequentially, followed by an additional 0.5 mL of DCM. The tube was then removed from the glovebox and cooled to 0 °C for 5 minutes. Under a nitrogen atmosphere, substrate **2a** (0.2 mmol) and DCM (1.5 mL) were added to the reaction mixture. The reaction was maintained at 0 °C with continuous stirring for 12 hours. After warming to room temperature, the mixture was filtered through a Celite pad, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography to yield the target products.

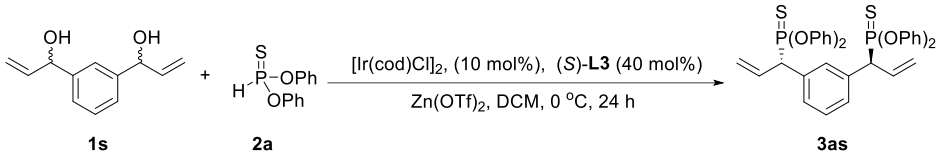
6. General Procedures for Allylic Phosphine Sulfides

6.1 General Procedure A:



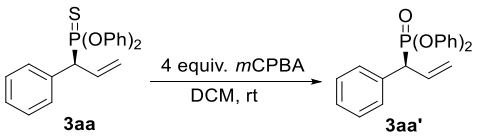
In a nitrogen-filled glove box, a 10 mL Schlenk tube equipped with a magnetic stir bar was sequentially charged with $[Ir(cod)Cl]_2$ (0.005 mmol), chiral ligand **L3** (0.02 mmol), and 1 mL anhydrous dichloromethane (DCM). The mixture was stirred at 25°C for 15 minutes to complete Iridium-ligand coordination. Substrate **1** (0.4 mmol) and $Zn(OTf)_2$ (0.04 mmol) were then added sequentially, followed by 0.5 mL DCM. The tube was quickly removed from the glove box and cooled to 0 °C for 5 min. Under strict nitrogen protection, substrate **2a** (0.2 mmol) and 1.5 mL DCM were injected using a syringe. The reaction proceeded at 0 °C for 12 h. After warming to room temperature, the mixture was filtered through a Celite pad and concentrated under reduced pressure. The residue was purified by gradient flash column chromatography to isolate the desired products (**3aa**-**3ua**).

6.2 General procedure B:



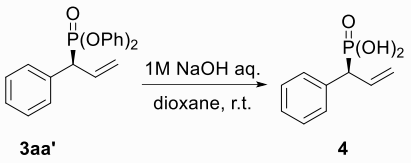
In a nitrogen-filled glove box, a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $[Ir(cod)Cl]_2$ (0.01 mmol), chiral ligand **L3** (0.04 mmol), and 1 mL DCM. The mixture was stirred at 25 °C for 15 min to achieve catalyst-ligand preactivation. Subsequently, substrate **1** (0.1 mmol), $Zn(OTf)_2$ (0.2 mmol), and 0.5 mL DCM were added sequentially. The reaction vessel was rapidly transferred out of the glove box and cooled to 0 °C for 5 min. Under strict nitrogen protection, substrate **2a** (0.1 mmol) and 1.5 mL DCM were introduced via syringe. The reaction was stirred vigorously at 0 °C for 24 hours. followed by gradual warming to ambient temperature. The mixture was filtered through a Celite pad to remove metallic residues, and the filtrate was concentrated under reduced pressure. Purification via gradient silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 5:1) afforded product **3as** in 17% yield (>20:1 dr, 99.9% ee).

7. Product Transformation.



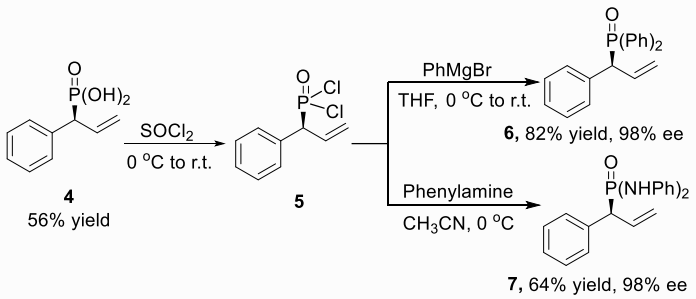
A mixture of compound **3aa** (73.3 mg, 0.2 mmol) and *m*-CPBA (138.1 mg, 0.8 mmol) in anhydrous DCM (3 mL) was added to a 10 mL Schlenk tube equipped with a magnetic stir bar under ambient conditions. The reaction was allowed to proceed at room temperature for 1 hour with vigorous stirring. Once complete, the mixture was washed sequentially with saturated $NaHCO_3$ solution (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered,

and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a gradient eluent of petroleum ether/acetone (from 10:1 to 2:1), yielding the desired product **3aa'** in 90% yield (99% ee).



3aa' **4**

According to the literature[8], to a solution of compound **3aa'** (350.3 mg, 1.0 mmol) in dioxane (5 mL) were added aqueous NaOH (1 M, 5 mL). The mixture was stirred at room temperature for 2 h, after which the dioxane was removed under reduced pressure. The resulting mixture was diluted with water (4 mL), adjusted to pH 6, and washed with dichloromethane (DCM). The aqueous phase was then acidified to pH 2 and stored at 0 °C overnight. The crystals formed were collected by suction filtration, washed with diethyl ether (Et_2O), and dried under vacuum to afford product **4** as colorless crystals (108.9 mg, 55%).

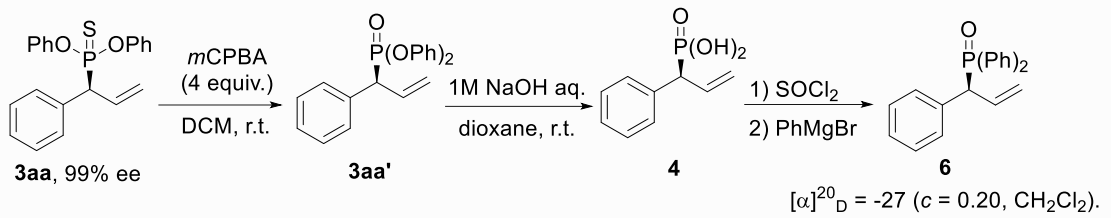


According to the literature[9], a 10 mL Schlenk flask was charged with compound **4** (39.4 mg, 0.2 mmol). Thionyl chloride ($SOCl_2$, 0.5 mL) was then added dropwise at 0 °C. The resulting colorless solution was stirred at room temperature for 2 hours, and then concentrated under reduced pressure at room temperature to produce dichloride 5, which was used directly in the next step without further purification.

According to literature[10], compound **5** (0.2 mmol) was placed in a 10 mL Schlenk flask equipped with a magnetic stir bar. Tetrahydrofuran (2 mL) was added, and the mixture was cooled to 0 °C. Phenylmagnesium bromide (PhMgBr, 0.8 mmol) was added dropwise with stirring. The reaction mixture was then slowly warmed to room temperature and stirred overnight under an argon atmosphere. After completion, the reaction was quenched by the addition of a saturated NH_4Cl solution (3 mL). The mixture was extracted with dichloromethane (3 × 5 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. After filtration and concentration under reduced pressure, the residue was purified by flash column chromatography to afford the desired product **6** in 82% yield with 98% ee.

According to literature[11], to a solution of compound **5** (0.2 mmol) in CH_3CN (2 mL), a solution of aniline (0.84 mmol) in CH_3CN (10 mL) was added dropwise at 0 °C. After stirring for 12 h, the solvent was removed under reduced pressure. The resulting residue was washed with distilled water and dried, affording product **7** in 64% yield with 98% ee.

8. Assignment of Absolute Configuration of Chiral Products[12]

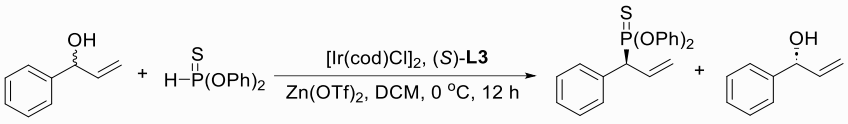


3aa, 99% ee **3aa'** **4** **6**

$[\alpha]^{20}_{D}$ = -27 (*c* = 0.20, CH_2Cl_2).

The reaction product **3aa** was converted to compound **6**, whose specific optical rotation was measured to be -27° (*c* = 0.20, CH_2Cl_2). This data aligns with the optical rotation direction of the (S)-configured compound reported in the literature[12], confirming the absolute configuration of product **3aa** as *S*.

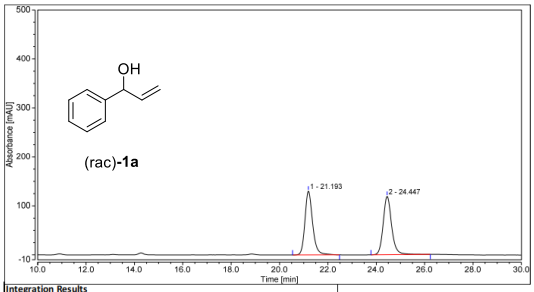
9. Key Evidence Supporting the Kinetic Resolution Mechanism[12-16]



rac-**1a** 2 equiv. **2a** 1 equiv. **3aa** 92% yield, 99% ee (*R*)-**1a**

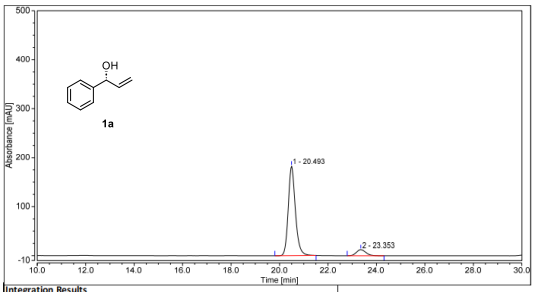
The remaining starting material (*R*)-**1a** was isolated from the reaction mixture, and its enantiomeric excess was measured to be 86% ee. These results suggest that the reaction displays features characteristic of a kinetic resolution process, consistent with the reported literature [12-16]. Thus, the reaction mechanism can be further deduced.

The ee of **1a** was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 99/01, flow = 0.5 mL/min. Retention times: 20.49 min, 23.35 min. 86% ee. $[\alpha]^{20}_{D}$ = +28 (*c* = 0.20, CH_2Cl_2).



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %
1	21.193	47.962	49.66	52.24
2	24.447	48.624	50.34	47.76
Total:		96.587	100.00	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %
1	20.493	62.865	91.82	93.72
2	23.353	5.603	8.18	6.28
Total:		68.468	100.00	100.00

10. Characterization Data of Phosphine Sulfides

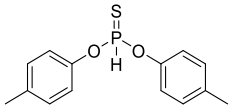
***O,O*-Diphenyl phosphonothioate (2a)** (CAS: 58045-33-3): colorless liquid, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.33 (d, $J_{H\text{-}P}$ = 669.7 Hz, 1H), 7.40 (t, J = 8.0 Hz, 4H), 7.32-7.19 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 130.2, 126.2, 121.6 (d, $J_{C\text{-}P}$ = 5.2 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 65.14.

HRMS (ESI): *m/z* calc. for $C_{12}H_{11}O_2PSNa^+$ [M+Na]$^+$: 273.0110, found: 273.0108.



2b

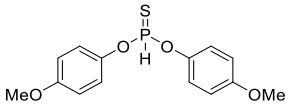
***O,O*-Di-p-tolyl phosphonothioate (2b):** colorless liquid, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.22 (d, $J_{H\text{-}P}$ = 664.9 Hz, 1H), 7.18 (d, J = 8.3 Hz, 4H), 7.10-7.04 (m, 4H), 2.35 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 147.9 (d, $J_{C\text{-}P}$ = 10.3 Hz), 135.6 (d, $J_{C\text{-}P}$ = 1.9 Hz), 130.5 (d, $J_{C\text{-}P}$ = 1.8 Hz), 121.1 (d, $J_{C\text{-}P}$ = 5.2 Hz), 29.9.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 65.66.

HRMS (ESI): *m/z* calc. for $C_{14}H_{15}O_2PSNa^+$ [M+Na]$^+$: 301.0423, found: 301.0423.



2c

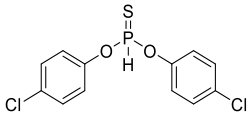
***O,O*-Bis(4-methoxyphenyl) phosphonothioate (2c)** (CAS: 29134-76-7): white solid, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.14 (d, $J_{H\text{-}P}$ = 664.8 Hz, 1H), 7.10-7.04 (m, 4H), 6.89-6.82 (m, 4H), 3.77 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 157.3 (d, $J_{C\text{-}P}$ = 1.9 Hz), 143.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 122.3 (d, $J_{C\text{-}P}$ = 4.9 Hz), 114.9 (d, $J_{C\text{-}P}$ = 1.8 Hz), 55.7.

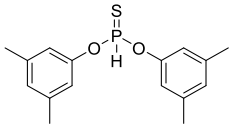
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 67.06.

HRMS (ESI): *m/z* calc. for $C_{14}H_{15}O_4PSNa^+$ [M+Na]$^+$: 333.0321, found: 333.0317.



2d

***O,O*-Bis(4-chlorophenyl) phosphonothioate (2d)** (CAS 55526-70-0): colorless liquid, 40% yield.



2e

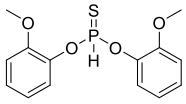
***O,O*-Bis(3,5-dimethylphenyl) phosphonothioate (2e):** colorless liquid, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): δ 8.19 (d, $J_{H\text{-}P}$ = 662.3 Hz, 1H), 6.87 (d, J = 2.1 Hz, 2H), 6.81 (s, 4H), 2.32 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.03 (d, $J_{C\text{-}P}$ = 10.2 Hz), 139.91, 127.60 (d, $J_{C\text{-}P}$ = 2.1 Hz), 118.90 (d, $J_{C\text{-}P}$ = 5.3 Hz), 21.40

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 65.12.

HRMS (ESI): *m/z* calc. for $C_{16}H_{19}O_2PSNa^+$ $[M+Na]^+$: 329.0736, found: 329.0734.



2f

***O,O*-Bis(2-methoxyphenyl) phosphonothioate (2f):** colorless liquid, 70% yield.

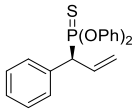
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.52 (d, J_{H-P} = 689.7 Hz, 1H), 7.31-7.22 (m, 2H), 7.23-7.10 (m, 2H), 7.02-6.89 (m, 4H), 3.82 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 151.0 (d, J_{C-P} = 4.1 Hz), 139. 7 (d, J_{C-P} = 10.3 Hz), 126.6, 123.1 (d, J_{C-P} = 4.6 Hz), 121.1, 113.0, 56.1.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 68.17.

HRMS (ESI): *m/z* calc. for $C_{14}H_{25}O_4PSNa^+$ $[M+Na]^+$: 333.0321, found: 333.0319.

11. Characterization Data of products



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

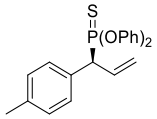
***O,O*-Diphenyl (*S*)-(1-phenylallyl)phosphonothioate (*S*)-3aa**: light yellow liquid, 93% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 9.9 min [(*R*)-enantiomer], 11.7 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -8.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.58 (dd, *J* = 7.6, 2.6 Hz, 2H), 7.46-7.30 (m, 5H), 7.24-7.15 (m, 3H), 7.15-7.06 (m, 3H), 6.59 (dd, *J* = 7.9, 1.9 Hz, 2H), 6.54-6.41 (m, 1H), 5.50 (d, *J* = 4.7 Hz, 1H), 5.47 (dd, *J* = 6.6, 5.0 Hz, 1H), 4.48 (dd, *J* = 23.8, 8.8 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.7, 150.6 (d, J_{C-P} = 19.6 Hz), 135.0 (d, J_{C-P} = 6.3 Hz), 132.8 (d, J_{C-P} = 6.3 Hz), 129.9 (d, J_{C-P} = 7.4 Hz), 129.6 (d, J_{C-P} = 19.2 Hz), 128.9 (d, J_{C-P} = 3.4 Hz), 128.0 (d, J_{C-P} = 3.8 Hz), 125.5 (d, J_{C-P} = 20.7 Hz), 122.2 (d, J_{C-P} = 4.6 Hz), 122.0 (d, J_{C-P} = 4.4 Hz), 120.4 (d, J_{C-P} = 15.7 Hz), 56.8 (d, J_{C-P} = 106.9 Hz).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.67.

HRMS (ESI): *m/z* calc. for $C_{21}H_{19}O_2PSNa^+$ $[M+Na]^+$: 389.0736, found: 357.0839.



(*S*)-**3ab**

***O,O*-Diphenyl (*S*)-(1-(p-tolyl)allyl)phosphonothioate (*S*)-3ab:** light yellow liquid, 85% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.25 mL/min. Retention times: 26.6 min [(*R*)-enantiomer], 31.0 min [(*S*)-enantiomer]. 98% ee. $[\alpha]^{20}_D$ = -4.0 (*c* = 0.200, CH_2Cl_2).

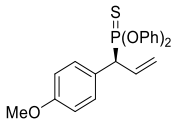
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.43 (dd, *J* = 8.1, 2.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.21-7.14 (m, 5H), 7.12-7.00 (m, 3H), 6.62 (dd, *J* = 8.0, 1.8 Hz, 2H), 6.49-6.35 (m, 1H), 5.51-5.28 (m, 2H), 4.41 (dd, *J* = 23.5, 8.8 Hz, 1H), 2.36 (d, *J* = 2.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.7 (d, J_{C-P} = 6.4 Hz), 150.6 (d, J_{C-P} = 6.5 Hz), 137.7 (d, J_{C-P} = 4.0 Hz), 132.8 (d, J_{C-P} = 5.9 Hz), 131.9 (d, J_{C-P} = 6.3 Hz), 129.7, 129.5 (d, J_{C-P} = 2.9 Hz), 129.5 (d, J_{C-P} = 17.6 Hz), 125.4

(d, $J_{C\text{-}P}$ = 18.1 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.3 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.2 Hz), 120.2 (d, $J_{C\text{-}P}$ = 15.4 Hz), 56.5 (d, $J_{C\text{-}P}$ = 106.8 Hz), 21.3.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.94.

HRMS (ESI): *m/z* calc. for $C_{22}H_{21}O_2PSNa^+$ $[M+Na]^+$: 403.0892, found: 403.0898.



(*S*)-**3ac**

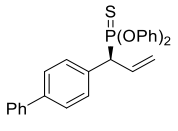
***O,O*-Diphenyl (*S*)-(1-(4-methoxyphenyl)allyl)phosphonothioate (*S*)-3ac:** light yellow liquid, 84% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 12.2 min [R)-enantiomer], 15.0 min [(*S*)-enantiomer]. 97% ee. $[\alpha]^{20}_D$ = -4.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.56-7.44 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.23 -7.15 (m, 3H), 7.14-7.04 (m, 3H), 6.98-6.89 (m, 2H), 6.66-6.62 (m, 2H), 6.51-6.36 (m, 1H), 5.51-5.35 (m, 2H), 4.42 (dd, *J* = 23.7, 8.7 Hz, 1H), 3.84 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 159.4 (d, $J_{C\text{-}P}$ = 3.4 Hz), 150.6 (d, $J_{C\text{-}P}$ = 4.3 Hz), 150.6 (d, $J_{C\text{-}P}$ = 18.2 Hz), 132.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 130.8 (d, $J_{C\text{-}P}$ = 7.0 Hz), 129.5 (d, $J_{C\text{-}P}$ = 15.5 Hz), 126.8 (d, $J_{C\text{-}P}$ = 6.4 Hz), 125.4 (d, $J_{C\text{-}P}$ = 18.0 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.3 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.2 Hz), 120.1 (d, $J_{C\text{-}P}$ = 15.5 Hz), 114.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 55.9 (d, $J_{C\text{-}P}$ = 107.3 Hz), 55.4.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.92.

HRMS (ESI): *m/z* calc. for $C_{22}H_{21}O_3PSNa^+$ $[M+Na]^+$: 419.0841, found: 419.0846.



(*S*)-**3ad**

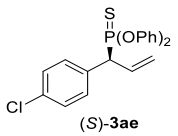
***O,O*-Diphenyl (*S*)-(1-([1,1'-biphenyl]-4-yl)allyl)phosphonothioate (*S*)-3ad**: white solid, 86% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow =0.5 mL/min. Retention times: 11.5 min [(*R*)-enantiomer], 18.2 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = 17.0 (*c* 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.72-7.61 (m, 6H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42-7.32 (m, 3H), 7.26-7.17 (m, 3H), 7.13 (d, *J* = 7.8 Hz, 3H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.60-6.43 (m, 1H), 5.59-5.45 (m, 2H), 4.54 (dd, *J* = 23.6, 8.8 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 150.6 (d, $J_{C\text{-}P}$ = 18.1 Hz), 140.8 (d, $J_{C\text{-}P}$ = 3.9 Hz), 140.7, 134.0 (d, $J_{C\text{-}P}$ = 6.5 Hz), 132.7 (d, $J_{C\text{-}P}$ = 5.9 Hz), 130.2 (d, $J_{C\text{-}P}$ = 7.0 Hz), 129.6 (d, $J_{C\text{-}P}$ = 17.5 Hz), 129.0, 127.6, 127.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 127.2, 125.5 (d, $J_{C\text{-}P}$ = 19.5 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.3 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.2 Hz), 120.5 (d, $J_{C\text{-}P}$ = 15.3 Hz), 56.5 (d, $J_{C\text{-}P}$ = 106.9 Hz.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.40.

HRMS (ESI): *m/z* calc. for $C_{27}H_{23}O_2PSNa^+$ $[M+Na]^+$: 465.1049, found: 465.1064.



(*S*)-**3ae**

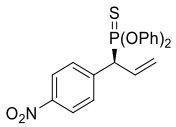
***O,O*-Diphenyl (*S*)-(1-(4-chlorophenyl)allyl)phosphonothioate (*S*)-3ae**: light yellow liquid, 94% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 10.1 min [(*R*)-enantiomer], 11.5 min [(*S*)-enantiomer]. 99.5% ee. $[\alpha]^{20}_D$ = -5.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.54 (t, J = 2.3 Hz, 1H), 7.50-7.43 (m, 1H), 7.36-7.30 (m, 4H), 7.27-7.17 (m, 3H), 7.16-7.11 (m, 1H), 7.06 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.70 (dd, *J* = 7.8, 1.9 Hz, 2H), 6.49-6.31 (m, 1H), 5.52-5.41 (m, 2H), 4.42 (dd, *J* = 23.4, 8.8 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.5 (d, $J_{C\text{-}P}$ = 11.3 Hz), 137.1 (d, $J_{C\text{-}P}$ = 6.3 Hz), 134.5 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.1 (d, $J_{C\text{-}P}$ = 6.2 Hz), 130.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 7.2 Hz), 129.6 (d, $J_{C\text{-}P}$ = 11.1 Hz), 128.1 (d, $J_{C\text{-}P}$ = 3.7 Hz), 127.9 (d, $J_{C\text{-}P}$ = 7.0 Hz), 125.6 (d, $J_{C\text{-}P}$ = 13.2 Hz), 122.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 121.8 (d, $J_{C\text{-}P}$ = 4.3 Hz), 120.9 (d, $J_{C\text{-}P}$ = 15.2 Hz), 56.4 (d, $J_{C\text{-}P}$ = 107.6 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 89.25.

HRMS (ESI): *m/z* calc. for $C_{21}H_{18}{}^{35}ClO_2PSNa^+$ $[M+Na]^+$: 423.0346, found: 423.0362; *m/z* calc. for $C_{21}H_{18}{}^{37}ClO_2PSNa^+$ $[M+Na]^+$: 425.0316, found: 425.0336.



(*S*)-**3af**

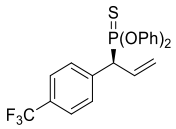
***O,O*-Diphenyl (*S*)-(1-(4-nitrophenyl)allyl)phosphonothioate (*S*)-3af**: light yellow liquid, 70% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 90/10, flow = 1 mL/min. Retention times: 7.4 min [(*R*)-enantiomer], 10.7 min [(*S*)-enantiomer]. 99.5% ee. $[\alpha]^{20}_D$ = -4.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.31-8.20 (m, 2H), 7.78-7.64 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.26-7.10 (m, 4H), 7.06-6.95 (m, 2H), 6.79-6.68 (m, 2H), 6.53-6.32 (m, 1H), 5.59-5.36 (m, 2H), 4.56 (dd, *J* = 23.5, 8.8 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.3 (d, $J_{C\text{-}P}$ = 11.4 Hz), 150.2 (d, $J_{C\text{-}P}$ = 11.3 Hz), 147.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 142.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 131.4 (d, $J_{C\text{-}P}$ = 7.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 6.8 Hz), 129.7 (d, $J_{C\text{-}P}$ = 3.5 Hz), 125.8 (d, $J_{C\text{-}P}$ = 6.2 Hz), 123.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 121.7 (d, $J_{C\text{-}P}$ = 4.6 Hz), 56.6 (d, $J_{C\text{-}P}$ = 107.4 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 87.66.

HRMS (ESI): *m/z* calc. for $C_{21}H_{18}NO_4PSNa^+$ $[M+Na]^+$: 434.0586, found: 434.0585.



(*S*)-**3ag**

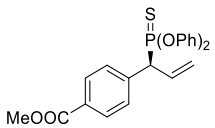
***O,O*-Diphenyl (*S*)-(1-(4-(trifluoromethyl)phenyl)allyl)phosphonothioate (*S*)-3ag**: light yellow liquid, 79% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 97/03, flow = 0.3 mL/min. Retention times: 16.2 min [(*R*)-enantiomer], 18.4 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -7.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.74-7.58 (m, 4H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.24-7.17 (m, 3H), 7.17-7.08 (m, 1H), 7.08-6.98 (m, 2H), 6.69-6.61 (m, 2H), 6.53-6.35 (m, 1H), 5.58-5.37 (m, 2H), 4.52 (dd, *J* = 23.6, 8.8 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.43 (d, $J_{C\text{-}P}$ = 3.5 Hz), 150.32 (d, $J_{C\text{-}P}$ = 3.1 Hz), 139.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 6.6 Hz), 130.1 (d, $J_{C\text{-}P}$ = 6.9 Hz), 129.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.0 Hz), 122.0 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.7 (d, $J_{C\text{-}P}$ = 4.3 Hz), 121.1 (d, $J_{C\text{-}P}$ = 15.4 Hz), 56.6 (d, $J_{C\text{-}P}$ = 107.5 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 88.91.

HRMS (ESI): *m/z* calc. for $C_{22}H_{18}F_3O_2PSNa^+$ $[M+Na]^+$: 457.0609, found: 457.0608.



(*S*)-**3ah**

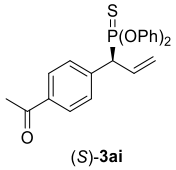
Methyl (*S*)-4-(1-(diphenoxyphosphorothioyl)allyl)benzoate (*S*)-3ah: light yellow liquid, 88% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 21.4 min [(*R*)-enantiomer], 24.3 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = 4.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.08 (d, *J* = 8.0 Hz, 2H), 7.63 (dd, *J* = 8.3, 2.6 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.24-7.16 (m, 3H), 7.15-7.07 (m, 1H), 7.06-6.99 (m, 2H), 6.72-6.61 (m, 2H), 6.53-6.35 (m, 1H), 5.54-5.38 (m, 2H), 4.51 (dd, *J* = 23.6, 8.8 Hz, 1H), 3.94 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 166.9, 150.5 (d, $J_{C\text{-}P}$ = 4.9 Hz), 150.3 (d, $J_{C\text{-}P}$ = 4.4 Hz), 140.3 (d, $J_{C\text{-}P}$ = 6.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 6.2 Hz), 130.0 (d, $J_{C\text{-}P}$ = 2.4 Hz), 129.8 (d, $J_{C\text{-}P}$ = 6.9 Hz), 129.6 (d, $J_{C\text{-}P}$ = 9.7 Hz), 125.6 (d, $J_{C\text{-}P}$ = 12.3 Hz), 122.0 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.7 (d, $J_{C\text{-}P}$ = 4.3 Hz), 121.0 (d, $J_{C\text{-}P}$ = 14.9 Hz), 56.8 (d, $J_{C\text{-}P}$ = 107.1 Hz), 52.3.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 89.02.

HRMS (ESI): *m/z* calc. for $C_{23}H_{21}O_4PSNa^+$ [M+Na]$^+$: 447.0790, found: 447.0807.



(*S*)-**3ai**

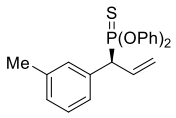
***O,O*-Diphenyl (*S*)-(1-(4-acetylphenyl)allyl)phosphonothioate (*S*)-3ai**: light yellow liquid, 95% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 25.9 min [R)-enantiomer], 28.4 min [(*S*)-enantiomer]. 99.6% ee. $[\alpha]^{20}_D$ = 10.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.01 (d, *J* = 8.0 Hz, 2H), 7.67 (dd, *J* = 8.4, 2.6 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 3H), 7.11 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.07-6.98 (m, 2H), 6.71 (dd, *J* = 8.0, 1.8 Hz, 2H), 6.55-6.37 (m, 1H), 5.55- 5.42 (m, 2H), 4.54 (dd, *J* = 23.5, 8.8 Hz, 1H), 2.63 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 197.8, 150.5 (d, $J_{C\text{-}P}$ = 5.6 Hz), 150.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 140.6 (d, $J_{C\text{-}P}$ = 6.6 Hz), 136.5 (d, $J_{C\text{-}P}$ = 3.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 6.4 Hz), 130.0 (d, $J_{C\text{-}P}$ = 6.3 Hz), 129.6, 128.7, 125.6, 122.0, 121.8 (d, $J_{C\text{-}P}$ = 4.1 Hz), 121.1 (d, $J_{C\text{-}P}$ = 15.6 Hz), 56.8 (d, $J_{C\text{-}P}$ = 106.8 Hz), 26.8 (d, $J_{C\text{-}P}$ = 6.5 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 88.89.

HRMS (ESI): *m/z* calc. for $C_{23}H_{21}O_3PSNa^+$ [M+Na]$^+$: 431.0841, found: 431.0840.



(*S*)-**3aj**

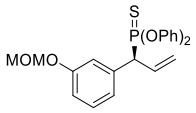
***O,O*-Diphenyl (*S*)-(1-(m-tolyl)allyl)phosphonothioate (*S*)-3aj**: light yellow liquid, 95% yield. The ee was determined on a Daicel Chiralpak ID column with hexane/2-propanol = 99/01, flow = 0.15 mL/min. Retention times: 34.7 min [(*R*)-enantiomer], 37.7 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -8.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.42-7.27 (m, 5H), 7.25-7.15 (m, 4H), 7.15-7.07 (m, 3H), 6.64 (dd, *J* = 7.9, 1.9 Hz, 2H), 6.56-6.38 (m, 1H), 5.55-5.37 (m, 2H), 4.44 (dd, *J* = 23.5, 8.9 Hz, 1H), 2.40 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.6, 150.6 (d, $J_{C\text{-}P}$ = 22.8 Hz), 138.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 134.9 (d, $J_{C\text{-}P}$ = 6.1 Hz), 132.9 (d, $J_{C\text{-}P}$ = 6.1 Hz), 130.5 (d, $J_{C\text{-}P}$ = 7.4 Hz), 129.5 (d, $J_{C\text{-}P}$ = 18.6 Hz), 128.7, 126.8 (d, $J_{C\text{-}P}$ = 6.8 Hz), 125.4 (d, $J_{C\text{-}P}$ = 20.0 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.2 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.2 Hz), 120.3 (d, $J_{C\text{-}P}$ = 15.3 Hz), 56.8 (d, $J_{C\text{-}P}$ = 106.6 Hz), 21.6.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.79.

HRMS (ESI): *m/z* calc. for $C_{22}H_{21}O_2PSNa^+$ [M+Na]$^+$: 403.0892, found: 403.0902.



(*S*)-**3ak**

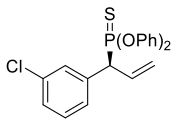
***O,O*-Diphenyl (*S*)-(1-(3-(methoxymethoxy)phenyl)allyl)phosphonothioate (*S*)-3ak**: Colorless liquid, 90% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 13.2 min [(*R*)-enantiomer], 14.4 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -8.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.31 (t, *J* = 7.8 Hz, 3H), 7.28-7.20 (m, 1H), 7.24-7.12 (m, 4H), 7.12-7.00 (m, 4H), 6.63 (dd, *J* = 7.9, 1.9 Hz, 2H), 6.51-6.32 (m, 1H), 5.52-5.38 (m, 2H), 5.16 (s, 2H), 4.41 (dd, *J* = 23.5, 8.9 Hz, 1H), 3.44 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 157.5 (d, $J_{C\text{-}P}$ = 3.2 Hz), 150.6, 150.6 (d, $J_{C\text{-}P}$ = 23.6 Hz), 136.5 (d, $J_{C\text{-}P}$ = 6.2 Hz), 132.6 (d, $J_{C\text{-}P}$ = 6.4 Hz), 129.8 (d, $J_{C\text{-}P}$ = 3.1 Hz), 129.5 (d, $J_{C\text{-}P}$ = 18.4 Hz), 125.4 (d, $J_{C\text{-}P}$ = 21.1 Hz), 123.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.4 Hz), 120.5 (d, $J_{C\text{-}P}$ = 15.5 Hz), 117.9 (d, $J_{C\text{-}P}$ = 7.1 Hz), 115.7 (d, $J_{C\text{-}P}$ = 3.8 Hz), 94.6, 56.8 (d, $J_{C\text{-}P}$ = 106.9 Hz), 56.1.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.29.

HRMS (ESI): *m/z* calc. for $C_{23}H_{23}O_4PSNa^+$ $[M+Na]^+$: 449.0947, found: 449.0955.



(*S*)-**3al**

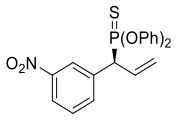
***O,O*-Diphenyl (*S*)-(1-(3-chlorophenyl)allyl)phosphonothioate (*S*)-3al**: light yellow liquid, 95% yield. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 11.4 min [(*R*)-enantiomer], 13.0 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -15.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.52 (t, *J* = 2.3 Hz, 1H), 7.45-7.44 (m, 1H), 7.35-7.27 (m, 4H), 7.24-7.15 (m, 3H), 7.15-7.09 (m, 1H), 7.04 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.69 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.53-6.35 (m, 1H), 5.53-5.35 (m, 2H), 4.40 (dd, *J* = 23.4, 8.8 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.5 (d, $J_{C\text{-}P}$ = 11.3 Hz), 137.1 (d, $J_{C\text{-}P}$ = 6.4 Hz), 134.5 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.1 (d, $J_{C\text{-}P}$ = 6.7 Hz), 130.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 7.2 Hz), 129.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 128.1 (d, $J_{C\text{-}P}$ = 3.7 Hz), 127.9 (d, $J_{C\text{-}P}$ = 6.8 Hz), 125.6 (d, $J_{C\text{-}P}$ = 1.9 Hz), 125.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 122.0 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.8 (d, $J_{C\text{-}P}$ = 4.4 Hz), 120.9 (d, $J_{C\text{-}P}$ = 15.3 Hz), 56.4 (d, $J_{C\text{-}P}$ = 107.6 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 89.22.

HRMS (ESI): *m/z* calc. for $C_{21}H_{18}{}^{35}ClO_2PSNa^+$ $[M+Na]^+$: 423.0346, found: 423.0354; *m/z* calc. for $C_{21}H_{18}{}^{37}ClO_2PSNa^+$ $[M+Na]^+$: 425.0316, found: 425.0334.



(*S*)-**3am**

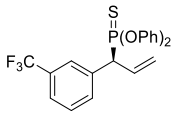
***O,O*-Diphenyl (*S*)-(1-(3-nitrophenyl)allyl)phosphonothioate (*S*)-3am**: light yellow liquid, 77% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 90/10, flow = 0.5 mL/min. Retention times: 14.1 min [(*R*)-enantiomer], 16.7 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -13.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.40 (q, *J* = 2.3 Hz, 1H), 8.24-8.22 (m, 1H), 7.91 (m, 1H), 7.63-7.53 (m, 1H), 7.31 (t, J = 7.9 Hz, 2H), 7.26-7.10 (m, 4H), 7.05-6.96 (m, 2H), 6.80-6.72 (m, 2H), 6.53-6.34 (m, 1H), 5.60-5.36 (m, 2H), 4.55 (dd, *J* = 23.2, 8.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.4 (d, $J_{C\text{-}P}$ = 10.6 Hz), 150.2, 148.4, 137.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 135.7 (d, $J_{C\text{-}P}$ = 6.4 Hz), 131.4 (d, $J_{C\text{-}P}$ = 6.6 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.2 Hz), 125.7 (d, $J_{C\text{-}P}$ = 7.7 Hz), 124.7 (d, $J_{C\text{-}P}$ = 7.3 Hz), 122.9 (d, $J_{C\text{-}P}$ = 3.4 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.6 Hz), 121.6 (d, $J_{C\text{-}P}$ = 4.7 Hz), 56.3 (d, $J_{C\text{-}P}$ = 107.9 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 87.85.

HRMS (ESI): *m/z* calc. for $C_{21}H_{18}NO_4PSNa^+$ [M+Na]$^+$: 434.0586, found: 434.0583.



(*S*)-**3an**

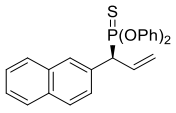
***O,O*-Diphenyl (*S*)-(1-(3-(trifluoromethyl)phenyl)allyl)phosphonothioate (*S*)-3an**: light yellow liquid, 83% yield. The ee was determined on a Daicel Chiralpak OJH column with hexane/2-propanol = 99/01, flow = 0.2 mL/min. Retention times: 54.6 min [(*R*)-enantiomer], 59.9 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -11.0 (*c* = 0.200, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.85-7.70 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.20 (dd, *J* = 8.6, 7.1 Hz, 3H), 7.15-7.07 (m, 1H), 7.07-6.98 (m, 2H), 6.76-6.64 (m, 2H), 6.52-6.33 (m, 1H), 5.61-5.36 (m, 2H), 4.50 (dd, *J* = 23.4, 8.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 136.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 133.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 6.4 Hz), 129.6 (d, $J_{C\text{-}P}$ = 11.4 Hz), 129.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 126.6 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.6 (d, $J_{C\text{-}P}$ = 14.3 Hz), 124.7 (q, $J_{C\text{-}F}$ = 4.0 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.6 Hz), 121.7 (d, $J_{C\text{-}P}$ = 4.1 Hz), 121.1 (d, $J_{C\text{-}P}$ = 15.0 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 88.76.

HRMS (ESI): *m/z* calc. for $C_{22}H_{18}F_3O_2PSNa^+$ [M+Na]$^+$: 457.0609, found: 457.0603.



(*S*)-**3ao**

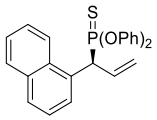
***O,O*-Diphenyl (*S*)-(1-(naphthalen-2-yl)allyl)phosphonothioate (*S*)-3ao**: light yellow liquid, 92% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 14.9 min [(*R*)-enantiomer], 18.6 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -19.0 (*c* = 0.200, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.04 (dd, *J* = 3.7, 1.8 Hz, 1H), 7.94-7.85 (m, 3H), 7.79-7.72 (m, 1H), 7.56-7.50 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.27-7.04 (m, 6H), 6.77-6.66 (m, 2H), 6.66-6.51 (m, 1H), 5.58-5.55 (m, 1H), 5.54-5.46 (m, 1H), 4.68 (dd, *J* = 23.5, 8.7 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.7 (d, $J_{C\text{-}P}$ = 4.6 Hz), 150.5 (d, $J_{C\text{-}P}$ = 4.4 Hz), 133.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.3 Hz), 132.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 132.5 (d, $J_{C\text{-}P}$ = 7.2 Hz), 129.6 (d, $J_{C\text{-}P}$ = 18.0 Hz), 129.0 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.4 (d, $J_{C\text{-}P}$ = 2.0 Hz), 128.0 (d, $J_{C\text{-}P}$ = 29.8 Hz), 127.5 (d, $J_{C\text{-}P}$ = 5.5 Hz), 126.4 (d, $J_{C\text{-}P}$ = 9.7 Hz), 125.5 (d, $J_{C\text{-}P}$ = 19.1 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.3 Hz), 120.7 (d, $J_{C\text{-}P}$ = 15.4 Hz), 57.0 (d, $J_{C\text{-}P}$ = 106.9 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.21.

HRMS (ESI): *m/z* calc. for $C_{25}H_{21}O_2PSNa^+$ [M+Na]$^+$: 439.0892, found: 439.0893.



(*S*)-**3ap**

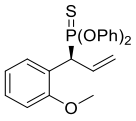
***O,O*-Diphenyl (*S*)-(1-(naphthalen-1-yl)allyl)phosphonothioate (*S*)-3ap**: light yellow liquid, 84% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 10.6 min [(*R*)-enantiomer], 12.5 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -120.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.35 (d, *J* = 8.6 Hz, 1H), 8.21-8.07 (m, 1H), 7.95 (dd, *J* = 18.3, 8.2 Hz, 2H), 7.71-7.50 (m, 3H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.23-7.10 (m, 4H), 7.12-7.03 (m, 1H), 6.74-6.57 (m, 1H), 6.57-6.36 (m, 2H), 5.69-5.38 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.6 (d, $J_{C\text{-}P}$ = 22.6 Hz), 150.6, 134.3, 133.4 (d, $J_{C\text{-}P}$ = 5.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 7.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 5.9 Hz), 129.5 (d, $J_{C\text{-}P}$ = 32.3 Hz), 128.5 (d, $J_{C\text{-}P}$ = 4.2 Hz), 127.6 (d, $J_{C\text{-}P}$ = 7.2 Hz), 126.3 (d, $J_{C\text{-}P}$ = 76.0 Hz), 125.6 (d, $J_{C\text{-}P}$ = 10.0 Hz), 125.3, 123.2, 122.2 (d, $J_{C\text{-}P}$ = 4.3 Hz), 121.7 (d, $J_{C\text{-}P}$ = 4.6 Hz), 120.6 (d, $J_{C\text{-}P}$ = 15.2 Hz), 50.3 (d, $J_{C\text{-}P}$ = 108.6 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 91.27.

HRMS (ESI): *m/z* calc. for $C_{25}H_{21}O_2PSNa^+$ [M+Na]$^+$: 439.0892, found: 439.0898.



(*S*)-**3aq**

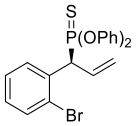
***O,O*-Diphenyl (*S*)-(1-(2-methoxyphenyl)allyl)phosphonothioate (*S*)-3aq**: light yellow liquid, 80% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 99/01, flow = 0.3 mL/min. Retention times: 34.4 min [(*R*)-enantiomer], 36.9 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -53.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.78-7.73 (m, 1H), 7.37-7.29 (m, 3H), 7.22-7.16 (m, 3H), 7.10 (m, 3H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.96-6.91 (m, 1H), 6.69-6.62 (m, 2H), 6.47-6.31 (m, 1H), 5.53-5.40 (m, 2H), 5.25 (dd, *J* = 24.3, 8.6 Hz, 1H), 3.85 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 157.1 (d, $J_{C\text{-}P}$ = 7.9 Hz), 150.8 (d, $J_{C\text{-}P}$ = 4.7 Hz), 150.7 (d, $J_{C\text{-}P}$ = 4.8 Hz), 132.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 130.0 (d, $J_{C\text{-}P}$ = 5.6 Hz), 129.4 (d, $J_{C\text{-}P}$ = 15.2 Hz), 128.8 (d, $J_{C\text{-}P}$ = 3.6 Hz), 125.3 (d, $J_{C\text{-}P}$ = 19.9 Hz), 123.4 (d, $J_{C\text{-}P}$ = 6.2 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.8 (d, $J_{C\text{-}P}$ = 4.4 Hz), 120.8 (d, $J_{C\text{-}P}$ = 3.5 Hz), 120.2 (d, $J_{C\text{-}P}$ = 15.7 Hz), 111.1 (d, $J_{C\text{-}P}$ = 2.1 Hz), 55.9, 47.4 (d, $J_{C\text{-}P}$ = 108.4 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 91.92.

HRMS (ESI): *m/z* calc. for $C_{22}H_{21}O_3PSNa^+$ [M+Na]$^+$: 419.0841, found: 419.0850.



(*S*)-**3ar**

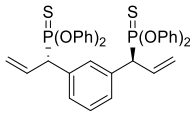
***O,O*-Diphenyl (*S*)-(1-(2-bromophenyl)allyl)phosphonothioate (*S*)-3ar**: colorless liquid, 92% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 99/01, flow = 0.25 mL/min. Retention times: 59.8 min [(*R*)-enantiomer], 62.4 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -42.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.94-7.86 (m, 1H), 7.69-7.63 (m, 1H), 7.39-7.28 (m, 3H), 7.21-7.12 (m, 4H), 7.12-7.03 (m, 3H), 6.68-6.60 (m, 2H), 6.38-6.23 (m, 1H), 5.50-5.38 (m, 2H), 5.24 (dd, *J* = 24.7, 8.4 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 150.4 (d, $J_{C\text{-}P}$ = 2.3 Hz), 134.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 133.4 (d, $J_{C\text{-}P}$ = 1.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 5.2 Hz), 129.5 (d, $J_{C\text{-}P}$ = 15.7 Hz), 129.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.7 (d, $J_{C\text{-}P}$ = 3.4 Hz), 125.9 (d, $J_{C\text{-}P}$ = 10.8 Hz), 125.5 (d, $J_{C\text{-}P}$ = 23.8 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.7 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.0 (d, $J_{C\text{-}P}$ = 15.5 Hz), 54.4 (d, $J_{C\text{-}P}$ = 109.6 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 89.84.

HRMS (ESI): *m/z* calc. for $C_{21}H_{18}{}^{79}BrO_2PSNa^+$ [M+Na]$^+$: 466.9841, found: 466.9857; *m/z* calc. for $C_{21}H_{18}{}^{81}BrO_2PS$ [M+Na]$^+$: 468.9820, found: 468.9838;



(*S*,*S*)-**3as**

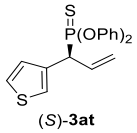
***O,O,O′,O′*-Tetraphenyl ((1*S*,1'*S*)-1,3-phenylenebis(prop-2-ene-1,1-diyl))bis(phosphonothioate) (*S*,*S*)-3as**: light yellow liquid, 17% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 13.8 min [(R)-enantiomer], 29.5 min [(*S*)-enantiomer]. 99.9% ee. dr = 20:1. $[\alpha]^{20}_{D}$ = -9.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.80 (s, 1H), 7.62-7.55 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 4H), 7.22-7.11 (m, 6H), 7.11-7.03 (m, 6H), 6.74-6.66 (m, 4H), 6.53-6.34 (m, 2H), 5.52-5.36 (m, 4H), 4.51 (dd, *J* = 23.6, 8.7 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 136.3-135.1 (m), 132.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.4-130.6 (m), 129.5 (d, $J_{C\text{-}P}$ = 14.8 Hz), 129.4-129.2 (m), 129.1, 125.4 (d, $J_{C\text{-}P}$ = 18.7 Hz), 122.0 (d, $J_{C\text{-}P}$ = 17.5 Hz), 120.6 (d, $J_{C\text{-}P}$ = 16.0 Hz), 56.9 (d, $J_{C\text{-}P}$ = 107.2 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 90.05.

HRMS (ESI): *m/z* calc. for $C_{36}H_{32}O_4P_2S_2Na^+$ [M+Na]$^+$: 677.1109, found: 677.1108.



(*S*)-**3at**

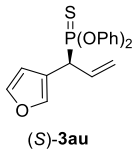
***O,O*-Diphenyl (*S*)-(1-(thiophen-3-yl)allyl)phosphonothioate (*S*)-3at**: light yellow liquid, 90% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 11.7 min [R)-enantiomer], 13.1 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = 15.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.48-7.40 (m, 1H), 7.39-7.27 (m, 4H), 7.27-7.17 (m, 3H), 7.17-7.05 (m, 3H), 6.72-6.61 (m, 2H), 6.47-6.30 (m, 1H), 5.52-5.36 (m, 2H), 4.65 (dd, *J* = 23.6, 8.6 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.6 (d, $J_{C\text{-}P}$ = 24.3 Hz), 150.6, 134.3 (d, $J_{C\text{-}P}$ = 6.3 Hz), 132.4 (d, $J_{C\text{-}P}$ = 6.4 Hz), 129.6 (d, $J_{C\text{-}P}$ = 15.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 125.7 (d, $J_{C\text{-}P}$ = 21.5 Hz), 125.4, 124.1 (d, $J_{C\text{-}P}$ = 10.0 Hz), 122.1 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.2 Hz), 120.3 (d, $J_{C\text{-}P}$ = 15.0 Hz), 52.3 (d, $J_{C\text{-}P}$ = 109.6 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 89.44.

HRMS (ESI): *m/z* calc. for $C_{19}H_{17}O_2PS_2Na^+$ [M+Na]$^+$: 395.0300, found: 395.0309.



(*S*)-**3au**

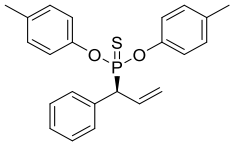
***O,O*-Diphenyl (*S*)-(1-(furan-3-yl)allyl)phosphonothioate (*S*)-3au**: yellow viscous solid, 96% yield. The ee was determined on double Daicel Chiralpak ADH column in series, hexane/2-propanol = 99/01, flow = 0.25 mL/min. Retention times: 84.2 min [(*R*)-enantiomer], 87.1 min [(*S*)-enantiomer]. 99.5% ee. $[\alpha]^{20}_{D}$ = -3.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.61-7.54 (m, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.35-7.24 (m, 4H), 7.21-7.10 (m, 2H), 7.09-7.03 (m, 2H), 6.90-6.82 (m, 2H), 6.63 (q, *J* = 1.3 Hz, 1H), 6.37-6.14 (m, 1H), 5.55-5.28 (m, 2H), 4.39 (dd, *J* = 23.4, 8.3 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.6 (d, $J_{C\text{-}P}$ = 1.5 Hz), 150.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 143.1, 141.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 6.7 Hz), 129.6 (d, $J_{C\text{-}P}$ = 6.9 Hz), 125.5 (d, $J_{C\text{-}P}$ = 8.3 Hz), 122.0 (d, $J_{C\text{-}P}$ = 4.4 Hz), 121.9 (d, $J_{C\text{-}P}$ = 4.3 Hz), 120.4 (d, $J_{C\text{-}P}$ = 14.8 Hz), 118.7 (d, $J_{C\text{-}P}$ = 6.6 Hz), 111.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 47.9 (d, $J_{C\text{-}P}$ = 111.6 Hz).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 89.63.

HRMS (ESI): *m/z* calc. for $C_{19}H_{17}O_3PSNa^+$ $[M+Na]^+$: 379.0528, found: 379.0527.



(*S*)-**3ay**

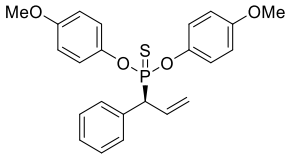
***O,O*-Di-p-tolyl (*S*)-(1-phenylallyl)phosphonothioate (*S*)-3ay**: light yellow liquid, 89% yield. The ee was determined on double Daicel Chiralpak ADH column in series, hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 12.5 min [(*R*)-enantiomer], 16.1 min [(*S*)-enantiomer]. 97% ee. $[\alpha]^{20}_D$ = -7.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.66-7.54 (m, 2H), 7.47-7.34 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.06-6.94 (m, 4H), 6.57-6.39 (m, 3H), 5.61-5.37 (m, 2H), 4.47 (dd, *J* = 23.8, 8.8 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 148.4, 148.4 (d, $J_{C\text{-}P}$ = 24.2 Hz), 135.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 134.9 (d, $J_{C\text{-}P}$ = 1.7 Hz), 132.9 (d, $J_{C\text{-}P}$ = 6.1 Hz), 130.1, 129.8 (d, $J_{C\text{-}P}$ = 8.8 Hz), 128.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 127.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 121.8 (d, $J_{C\text{-}P}$ = 4.3 Hz), 121.5 (d, $J_{C\text{-}P}$ = 4.2 Hz), 120.3 (d, $J_{C\text{-}P}$ = 15.5 Hz), 56.6 (d, $J_{C\text{-}P}$ = 106.9 Hz), 20.9.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 91.08.

HRMS (ESI): *m/z* calc. for $C_{23}H_{23}O_2PSNa^+$ $[M+Na]^+$: 417.1049, found: 417.1050.



(*S*)-**3az**

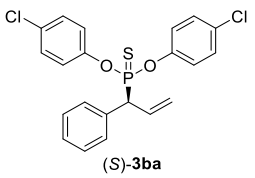
***O,O*-Bis(4-methoxyphenyl) (*S*)-(1-phenylallyl)phosphonothioate (*S*)-3az**: light yellow liquid, 85% yield. The ee was determined on double Daicel Chiralpak ADH column in series, hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 22.4 min [(*R*)-enantiomer], 35.6 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -7.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.63-7.52 (m, 2H), 7.49-7.34 (m, 3H), 7.07-6.97 (m, 2H), 6.91-6.81 (m, 2H), 6.74-6.64 (m, 2H), 6.52-6.38 (m, 3H), 5.54-5.39 (m, 2H), 4.44 (dd, *J* = 23.7, 8.8 Hz, 1H), 3.78 (s, 3H), 3.72 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 156.9 (d, $J_{C\text{-}P}$ = 21.3 Hz), 144.1 (d, $J_{C\text{-}P}$ = 8.6 Hz), 144.1 (d, $J_{C\text{-}P}$ = 31.0 Hz), 135.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 132.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 129.8 (d, $J_{C\text{-}P}$ = 7.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 127.9 (d, $J_{C\text{-}P}$ = 3.3 Hz), 122.9 (d, $J_{C\text{-}P}$ = 4.1 Hz), 122.6 (d, $J_{C\text{-}P}$ = 4.1 Hz), 120.3(d, $J_{C\text{-}P}$ = 15.3 Hz), 114.4 (d, $J_{C\text{-}P}$ = 20.1 Hz), 56.5 (d, $J_{C\text{-}P}$ = 106.5 Hz), 55.6 (d, $J_{C\text{-}P}$ = 7.6 Hz).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 92.18.

HRMS (ESI): *m/z* calc. for $C_{23}H_{23}O_4PSNa^+$ $[M+Na]^+$: 449.0947, found: 449.0948.



(*S*)-**3ba**

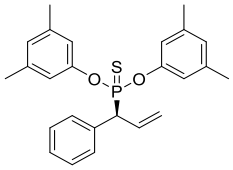
***O,O*-Bis(4-chlorophenyl) (*S*)-(1-phenylallyl)phosphonothioate (*S*)-3ba**: light yellow liquid, 83% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 11.9 min [(*R*)-enantiomer], 14.7 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_D$ = -5.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.56-7.51 (m, 2H), 7.48-7.35 (m, 3H), 7.34-7.27 (m, 2H), 7.21-7.10 (m, 2H), 7.06-6.97 (m, 2H), 6.51-6.34 (m, 3H), 5.57-5.36 (m, 2H), 4.46 (dd, *J* = 24.0, 8.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 148.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 148.9 (d, $J_{C\text{-}P}$ = 25.5 Hz), 134.5(d, $J_{C\text{-}P}$ = 6.3 Hz), 132.3 (d, $J_{C\text{-}P}$ = 6.2 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 130.9(d, $J_{C\text{-}P}$ = 2.0 Hz), 129.8(d, $J_{C\text{-}P}$ = 8.7 Hz), 129.5 128.9 (d, $J_{C\text{-}P}$ = 3.1 Hz), 128.2(d, $J_{C\text{-}P}$ = 3.8 Hz), 123.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 123.1 (d, $J_{C\text{-}P}$ = 4.2 Hz), 120.7 (d, $J_{C\text{-}P}$ = 15.7 Hz), 56.7(d, $J_{C\text{-}P}$ = 106.3 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 91.66.

HRMS (ESI): *m/z* calc. for $C_{21}H_{17}{}^{35}Cl_2O_2PSNa^+$ $[M+Na]^+$: 456.9956, found: 456.9970; *m/z* calc. for $C_{21}H_{17}{}^{37}Cl_2O_2PSNa^+$ $[M+Na]^+$: 458.9927, found: 458.9945.



(*S*)-**3ca**

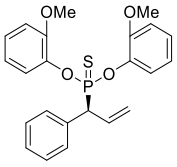
***O,O*-Bis(3,5-dimethylphenyl) (*S*)-(1-phenylallyl)phosphonothioate (*S*)-3ca**: light yellow liquid, 94% yield. The ee was determined on a Daicel Chiralpak ADH column with hexane/2-propanol = 95/05, flow = 0.2 mL/min. Retention times: 17.9 min [(*R*)-enantiomer], 19.4 min [(*S*)-enantiomer]. 99.5% ee. $[\alpha]^{20}_D$ = -8.0 (*c* = 0.200, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.63-7.54 (m, 2H), 7.47-7.38 (m, 3H), 6.86 (s, 1H), 6.76 (s, 3H), 6.57-6.40 (m, 1H), 6.21 (s, 2H), 5.56-5.43 (m, 2H), 4.45 (dd, *J* = 23.7, 8.7 Hz, 1H), 2.32 (s, 6H), 2.20 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.5 (d, $J_{C\text{-}P}$ = 6.4 Hz), 150.5(d, $J_{C\text{-}P}$ = 29.0 Hz), 139.2 (d, $J_{C\text{-}P}$ = 24.9 Hz), 135.2(d, $J_{C\text{-}P}$ = 6.2 Hz), 133.0 (d, $J_{C\text{-}P}$ = 6.3 Hz), 129.9 (d, $J_{C\text{-}P}$ = 7.1 Hz), 128.8(d, $J_{C\text{-}P}$ = 2.9 Hz), 127.9(d, $J_{C\text{-}P}$ = 3.4 Hz), 127.1(d, $J_{C\text{-}P}$ = 24.6 Hz), 120.1 (d, $J_{C\text{-}P}$ = 15.1 Hz), 119.7(d, $J_{C\text{-}P}$ = 4.3 Hz), 119.5(d, $J_{C\text{-}P}$ = 4.3 Hz), 56.8 (d, $J_{C\text{-}P}$ = 106.9 Hz), 21.4(d, $J_{C\text{-}P}$ = 8.5 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 89.99.

HRMS (ESI): *m/z* calc. for $C_{25}H_{27}O_2PSNa^+$ $[M+Na]^+$: 445.1362, found: 445.1368.



(*S*)-**3da**

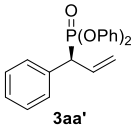
***O,O*-Bis(2-methoxyphenyl) (*S*)-(1-phenylallyl)phosphonothioate (*S*)-3da**: light yellow liquid, 89% yield. The ee was determined on double Daicel Chiralpak ADH column in series, hexane/2-propanol = 95/05, flow = 0.5 mL/min. Retention times: 17.2 min [(*R*)-enantiomer], 19.4 min [(*S*)-enantiomer]. 99.7% ee. $[\alpha]^{20}_D$ = -7.0 (*c* = 0.200, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.67-7.61 (m, 2H), 7.45-7.32 (m, 3H), 7.22-7.06 (m, 3H), 6.98-6.94 (m, 1H), 6.92-6.85 (m, 2H), 6.81-6.75 (m, 1H), 6.69-6.54 (m, 2H), 5.51-5.40 (m, 2H), 4.63 (dd, *J* = 23.1, 8.4 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 151.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.5 (d, $J_{C\text{-}P}$ = 4.2 Hz), 140.3 (d, $J_{C\text{-}P}$ = 2.3 Hz), 140.2(d, $J_{C\text{-}P}$ = 2.7 Hz), 135.7 (d, $J_{C\text{-}P}$ = 6.7 Hz), 133.3 (d, $J_{C\text{-}P}$ = 6.9 Hz), 130.2(d, $J_{C\text{-}P}$ = 7.1 Hz), 128.6(d, $J_{C\text{-}P}$ = 2.6 Hz), 127.6 (d, $J_{C\text{-}P}$ = 3.4 Hz), 125.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 123.3(d, $J_{C\text{-}P}$ = 4.0 Hz), 123.1(d, $J_{C\text{-}P}$ = 4.0 Hz), 119.9(d, $J_{C\text{-}P}$ = 15.4 Hz), 112.7 (d, $J_{C\text{-}P}$ = 17.1 Hz), 57.6(d, $J_{C\text{-}P}$ = 107.2 Hz), 55.8 (d, $J_{C\text{-}P}$ = 13.8 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 92.43.

HRMS (ESI): *m/z* calc. for $C_{23}H_{23}O_4PSNa^+$ $[M+Na]^+$: 449.0947, found: 449.0952.



3aa'

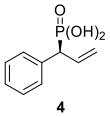
Diphenyl (*S*)-(1-phenylallyl)phosphonate 3aa: white solid, 91% yield. The ee was determined on a Daicel Chiralpak IF column with hexane/2-propanol = 90/10, flow = 0.5 mL/min. Retention times: 9.9 min [(*R*)-enantiomer], 11.6 min [(*S*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -13.0 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.49 (dd, *J* = 7.5, 2.3 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.35-7.27 (m, 3H), 7.25-7.05 (m, 6H), 6.95-6.81 (m, 2H), 6.49-6.25 (m, 1H), 5.52-5.35 (m, 2H), 4.26 (dd, *J* = 25.1, 8.4 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 50.6 (d, $J_{C\text{-}P}$ = 16.1 Hz), 150.6 (d, $J_{C\text{-}P}$ = 3.7 Hz), 134.7(d, $J_{C\text{-}P}$ = 7.6 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.4 Hz), 129.7 (d, $J_{C\text{-}P}$ = 13.7 Hz), 129.5(d, $J_{C\text{-}P}$ = 7.5 Hz), 129.0 (d, $J_{C\text{-}P}$ = 2.4 Hz), 127.8 (d, $J_{C\text{-}P}$ = 3.3 Hz), 125.7(d, $J_{C\text{-}P}$ = 12.2 Hz), 120.8(d, $J_{C\text{-}P}$ = 4.4 Hz), 120.6(d, $J_{C\text{-}P}$ = 4.3 Hz), 120.3 (d, $J_{C\text{-}P}$ = 14.2 Hz), 50.2(d, $J_{C\text{-}P}$ = 138.0 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 18.29.

HRMS (ESI): *m/z* calc. for $C_{21}H_{29}O_3PSNa^+$ $[M+Na]^+$: 373.0964, found: 373.0982.



4

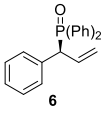
(*S*)-(1-Phenylallyl)phosphonic acid 4: white solid, 56% yield.

^{1}H NMR (400 MHz, MeOD, 298 K) δ (ppm): 5.92-5.84 (m, 1H), 5.81-5.72 (m, 2H), 5.66-5.59 (m, 1H), 5.54-5.49 (m, 1H), 5.19-5.17 (m, 1H), 4.81-4.70 (m, 1H), 3.89-3.81 (m, 1H), 2.92-2.83 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, MeOD, 298 K) δ (ppm): 118.0 (d, $J_{C\text{-}P}$ = 14.0 Hz), 118.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 123.5 (d, $J_{C\text{-}P}$ = 18.0 Hz), 125.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 126.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.5 (d, $J_{C\text{-}P}$ = 7.0 Hz), 123.2 (d, $J_{C\text{-}P}$ = 8.0 Hz), 148.7(d, $J_{C\text{-}P}$ = 10.0 Hz).

^{31}P{^{1}H} NMR (162 MHz, MeOD, 298 K) δ (ppm): 17.02.

HRMS (ESI): *m/z* calc. for $C_9H_{10}O_3P^-$ $[M-H]^-$: 197.0373, found: 197.0367.

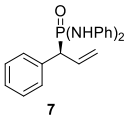


6

(*S*)-Diphenyl(1-phenylallyl)phosphine oxide 6: white solid, 82% yield. The ee was determined on Daicel Chiralpak ADH column with Hexane/iPropanol = 80/20, flow = 0.5 mL/min. Retention times: 24.52 min [(R)-enantiomer], 24.61 min [(S)-enantiomer]. 98% ee. $[\alpha]^{20}_{D}$ = -37 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): δ (ppm) 7.94-7.82 (m, 2H), 7.52 (dd, *J* = 17.1, 9.0 Hz, 5H), 7.40-7.10 (m, 8H), 6.24 (td, *J* = 16.8, 9.1 Hz, 1H), 5.15 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.04 (dd, *J* = 17.0, 3.4 Hz, 1H), 4.26 (t, *J* = 9.2 Hz, 1H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 31.85 (s).



7

white solid, 64% yield. The ee was determined on Daicel Chiralpak IF-3 column with Hexane/iPropanol = 80/20, flow = 0.5 mL/min. Retention times: 21.18 min [(R)-enantiomer], 26.62 min [(S)-enantiomer]. 98% ee. $[\alpha]^{20}_{D}$ = -15 (*c* = 0.200, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): δ (ppm) 7.52 (s, 1H), 7.49-7.41 (m, 1H), 7.36-7.27 (m, 4H), 7.27-7.14 (m,

4H), 7.14-7.09 (m, 1H), 7.07-6.98 (m, 2H), 6.67-6.72 (m, 2H), 6.39-6.45 (m, 1H), 5.54-5.35 (m, 2H), 4.40 (dd, J = 23.4, 8.8 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.98-149.85 (m), 134.93 (d, $J_{C\text{-}P}$ = 6.3 Hz), 132.65 (d, $J_{C\text{-}P}$ = 6.3 Hz), 129.75 (d, $J_{C\text{-}P}$ = 7.4 Hz), 129.45 (d, $J_{C\text{-}P}$ = 19.2 Hz), 128.75 (d, $J_{C\text{-}P}$ = 3.4 Hz), 127.90 (d, $J_{C\text{-}P}$ = 3.8 Hz), 125.38 (d, $J_{C\text{-}P}$ = 20.7 Hz), 121.93 (dd, $J_{C\text{-}P}$ = 24.0, 4.5 Hz), 120.33 (d, $J_{C\text{-}P}$ = 15.7 Hz), 56.72 (d, $J_{C\text{-}P}$ = 106.9 Hz).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm): 24.82.

12. References

[1] M. Lafrance, M. Roggen and E. M. Carreira, *Angew. Chem. Int. Ed.* **2012**, *51*, 3470-3473.

[2] D. E. Latham, K. Polidano and J. M. J. Williams, L. C. Morrill, *Org. Lett.* **2019**, *21*, 7914-7918.

[3] N. Marion, R. Gealageas and S. P. Nolan, *Org. Lett.* **2007**, *9*, 2653-2656.

[4] Y. Pan, Y. You, D. He, F. Chen, X. Chang, M. Y. Jin and X. Xing, *Org. Lett*. **2020**, *22*, 7278-7283.

[5] R. J. Lundgren and B. N. Thomas, *Chem. Commun.* **2016**, *52*, 958-961.

[6] S. J. Chen, G. P. Lu and C. Cai, *Synthesis* **2015**, *47*, 976-984.

[7] C.-Y. Li, Q. Wang, J.-Q. Zhang, J.-J. Ye, J. Xie, Q. Xu and L.-B. Han, *GreenChem*., **2019**, *21*, 2916.

[8] E. C. Y. Woon, A. Zervosen, E. Sauvage, K. J. Simmons, M. Živec, S. R. Inglis, C. W. G. Fishwick, S. Gobec, *ACS Med. Chem. Lett.* **2011***, 2,* 3, 219–223

[9] Y. Ishibashi and M. Kitamura, *Chem. Commun., 2009, 6985-6987*.

[10] E. Korzeniowska, A. E. Kozioł, E. Łastawiecka, A. Flis and M. Stankevič, *Tetrahedron* **2017**, *73* (34), 5153-5162.

[11] D. Zhao, C. Nimphius, M. Lindale and F. Glorius, *Org. Lett.* **2013***, 15,* 17, *4504–4507*.

[12] Z.-H. Wu, H.-Y. Wang, H.-L. Yang, L.-H. Wei, T. Hayashi and W.-L. Duan, *Angew. Chem. Int. Ed.* **2022**, *61*, e202213904 (3 of 5).

[13] M. Lafrance, M. Roggen and E. M. Carreira, *Org. Lett.*, **2012**, 51, 3470-3473.

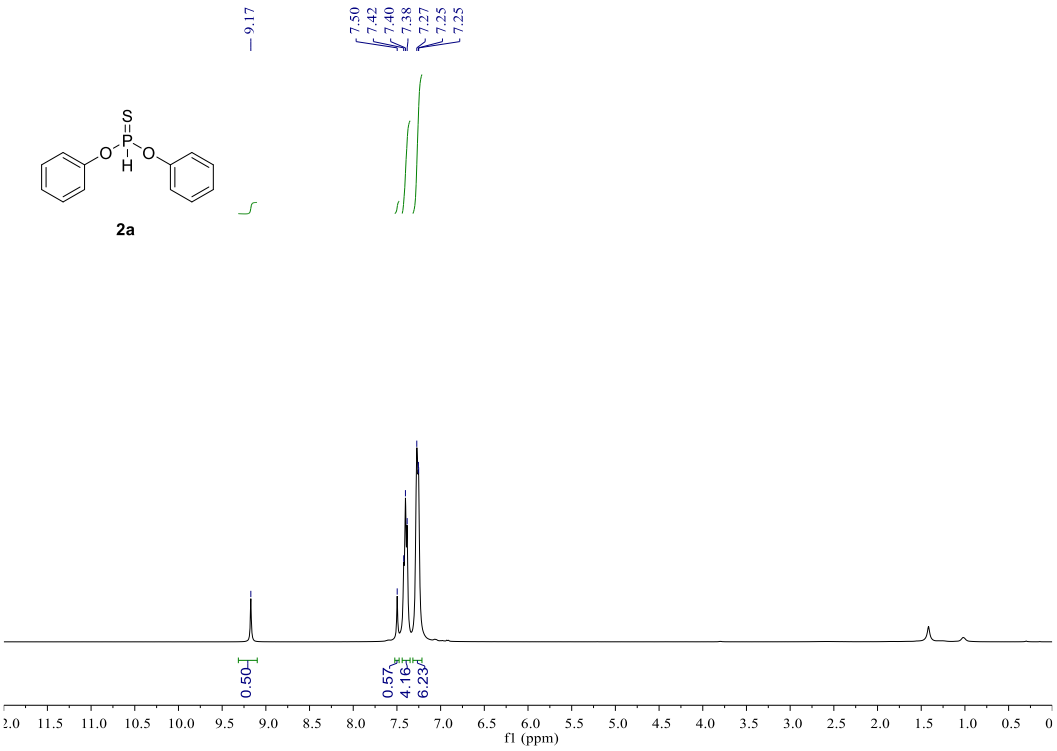
[14] S. L. Rössler, S. Krautwald and E. M. Carreira, *J. Am. Chem. Soc*., **2017**, 139, 3603-3606.

[15] A. Gallen, A. Riera, X. Verdaguer and A. Grabulosa, *Catal. Sci. Technol.*, 2019, **9**, 5504-5561.

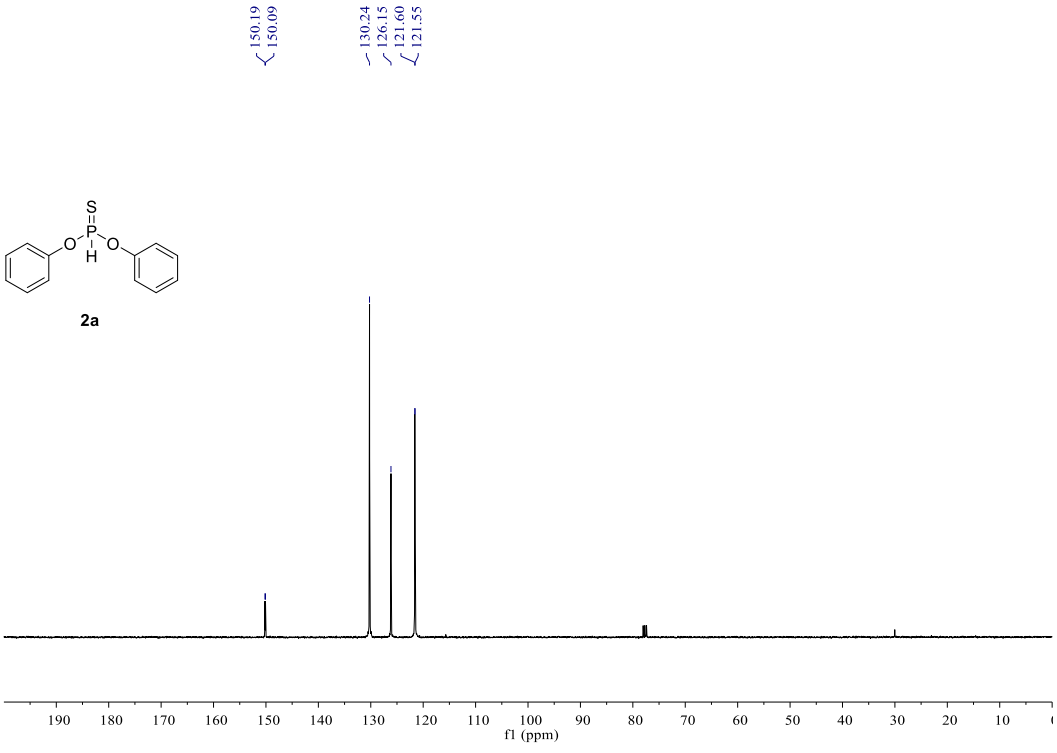
[16] P. W. N. M. van Leeuwen, I. Cano and Z. Freixa, *ChemCatChem*, 2020, **12**, 3982-3994.53

13. Traces of ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR and ^{31}P spectra

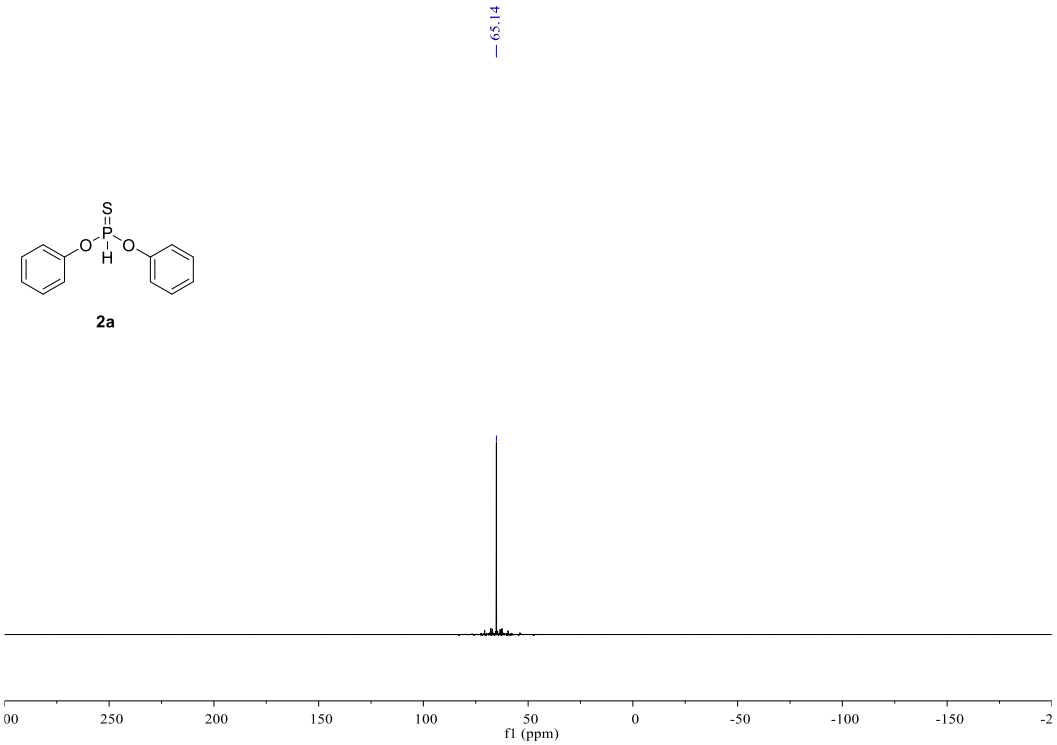
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



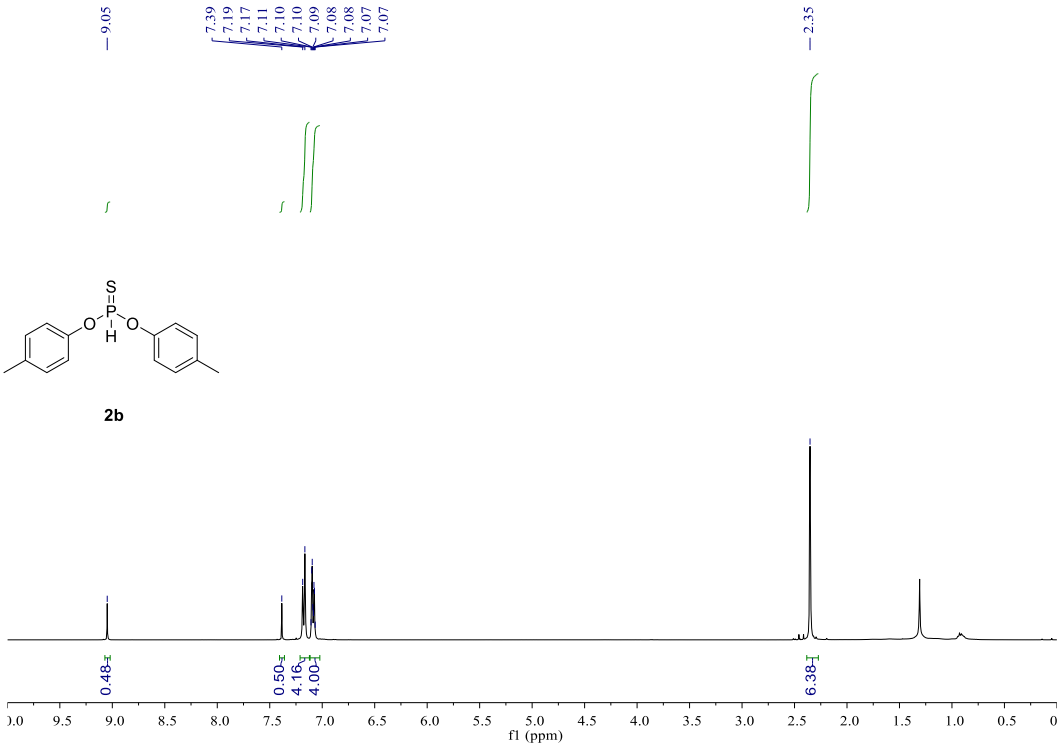
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2a**



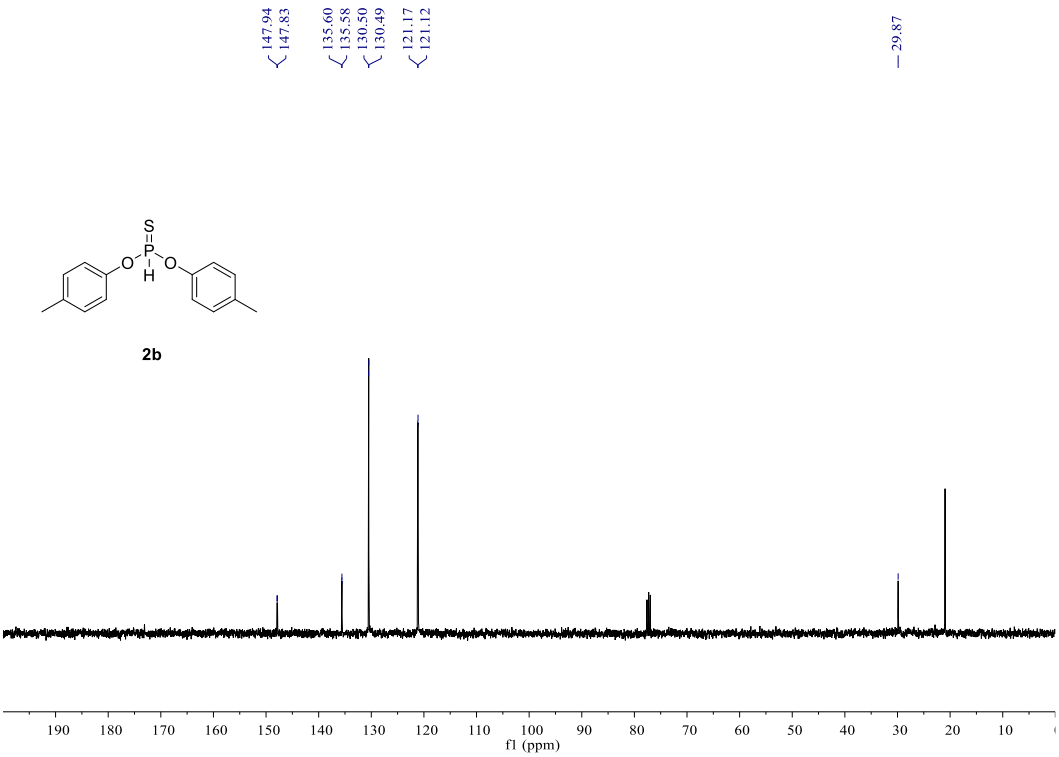
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **2a**



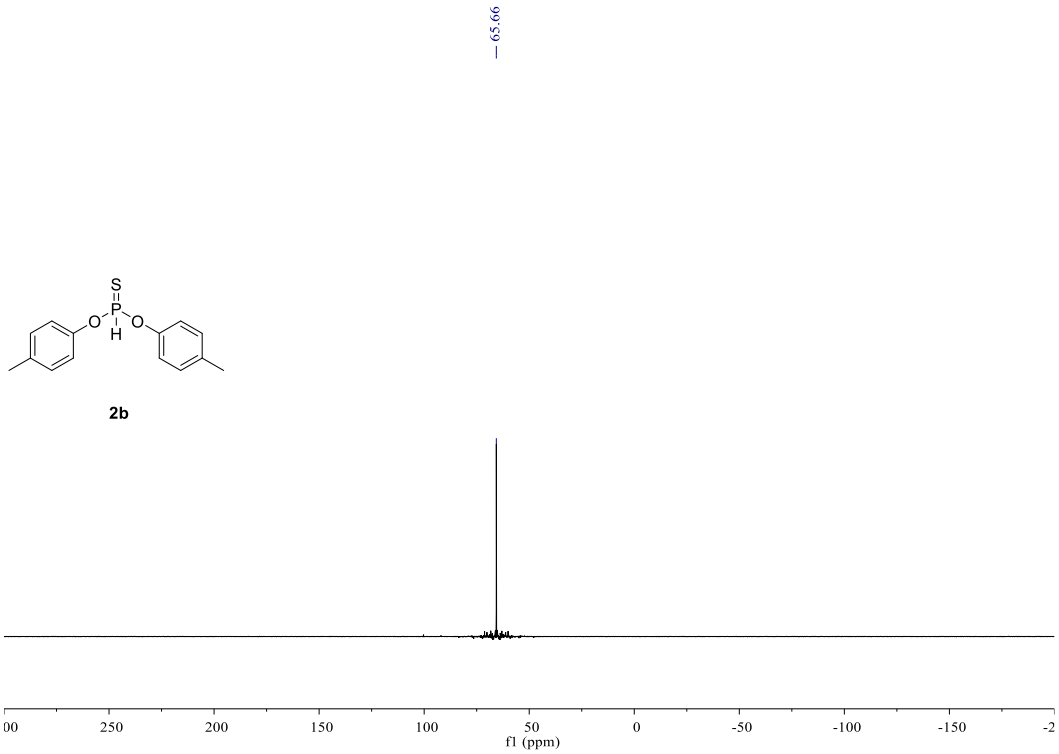
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



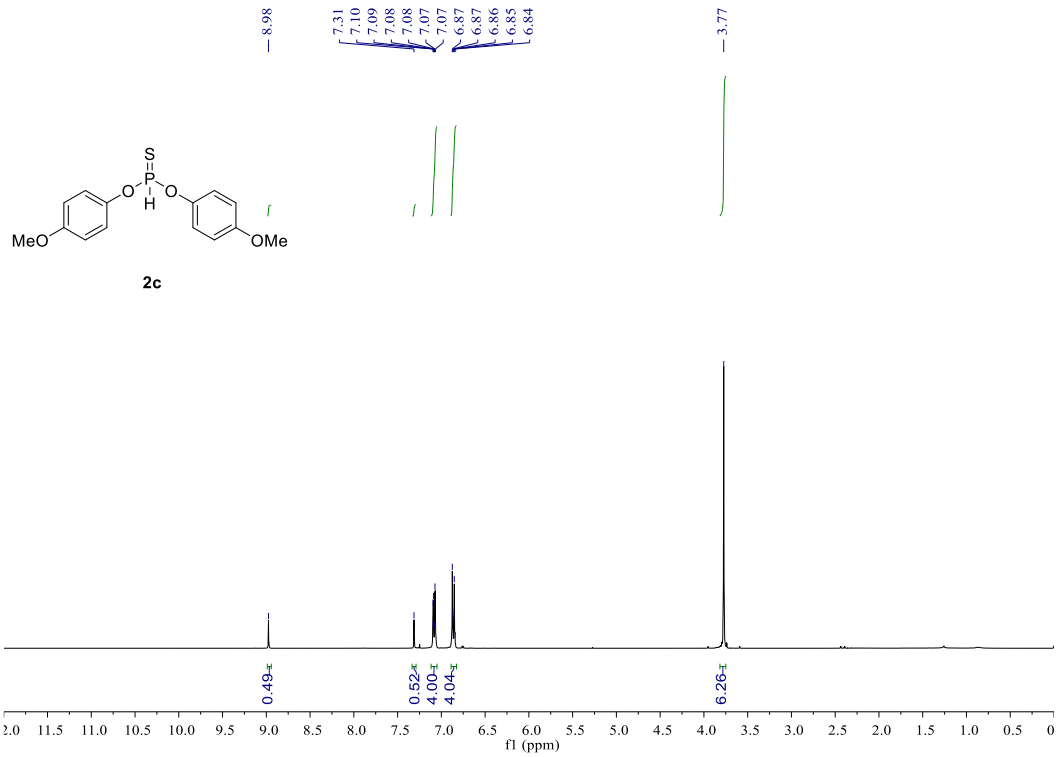
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2b**



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **2b**

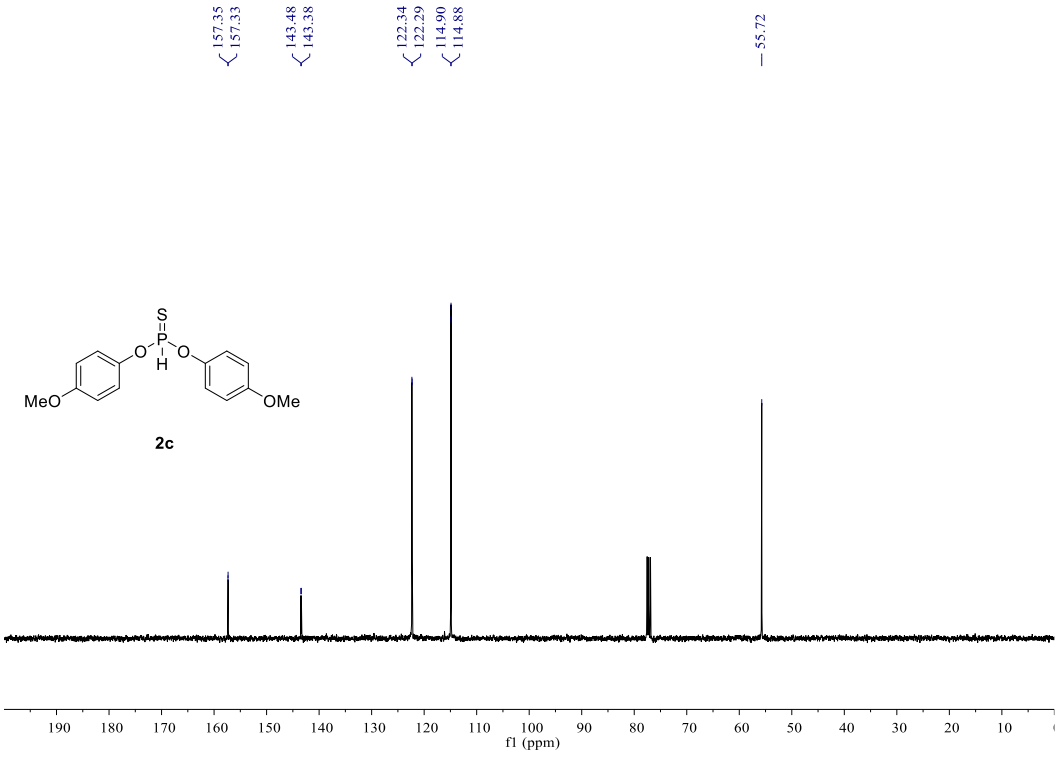


^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



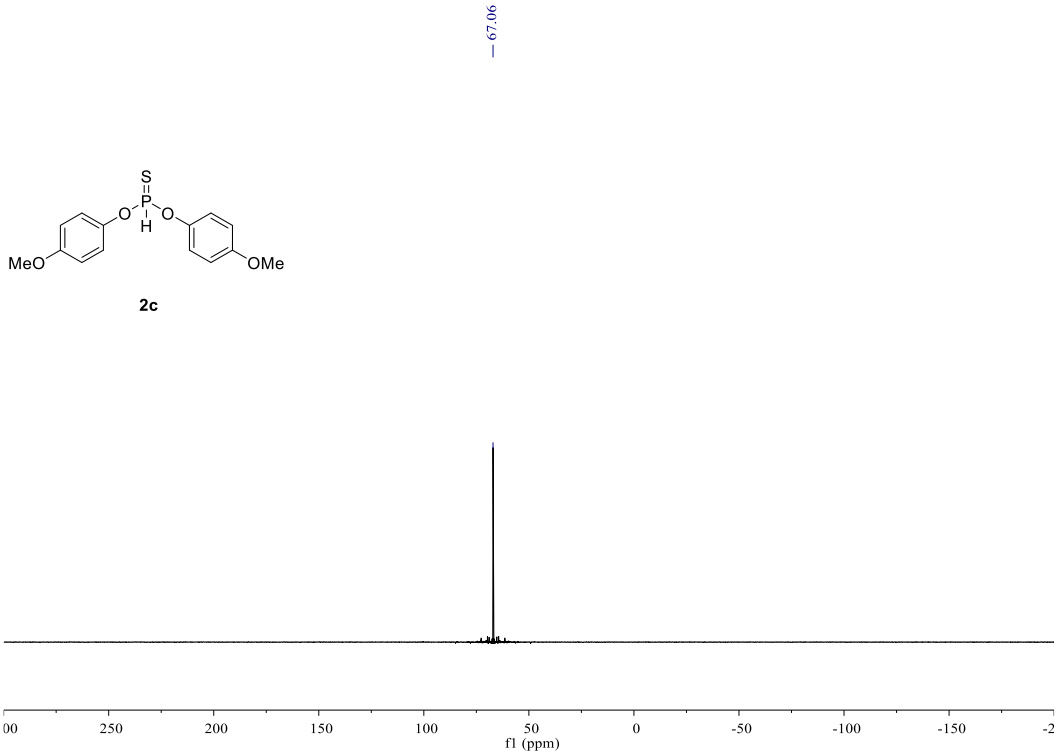
2c

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2c**

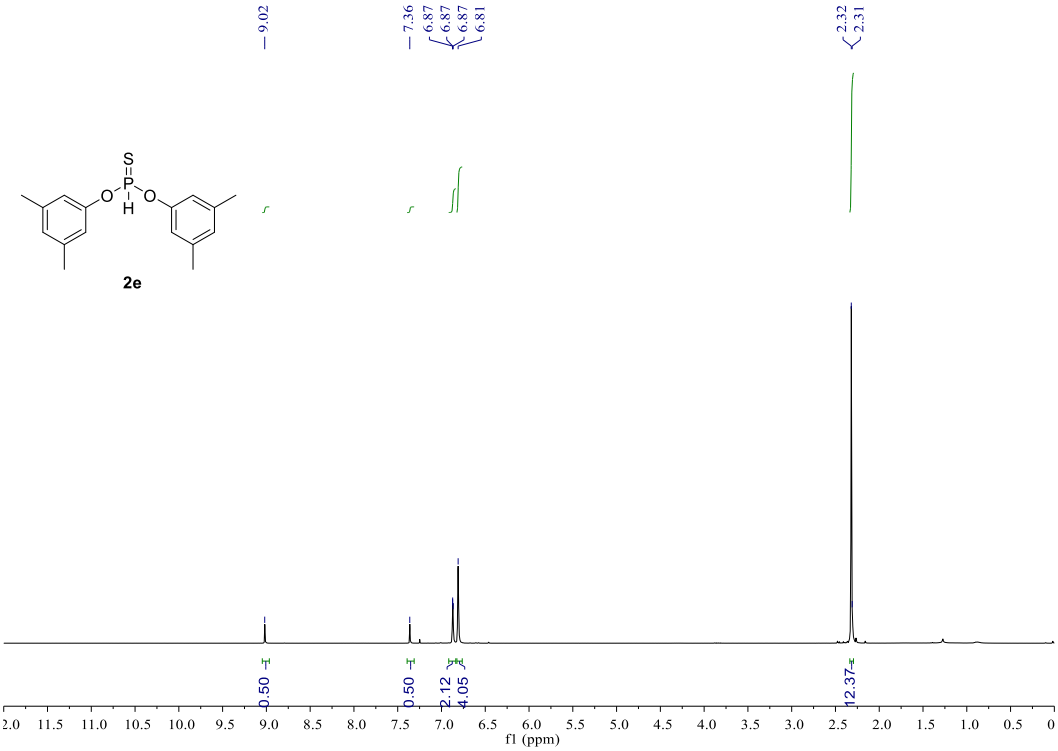


2c

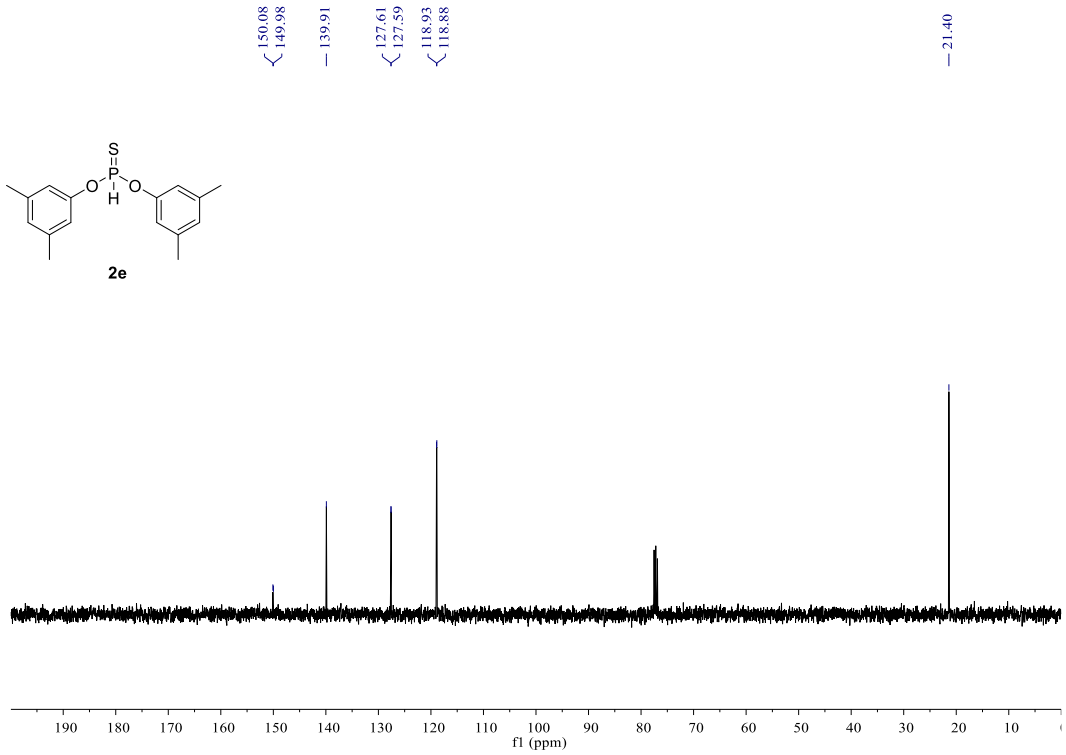
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **2c**



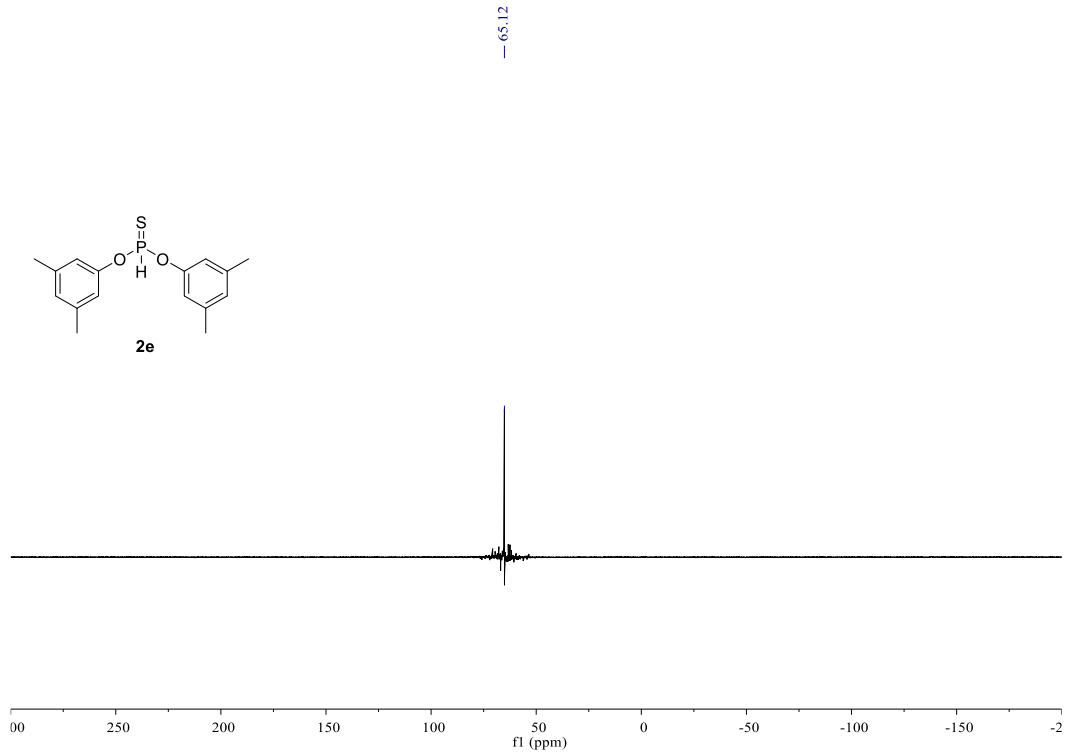
^{1}H NMR (400 MHz, $CDCl_3$) of **2e**



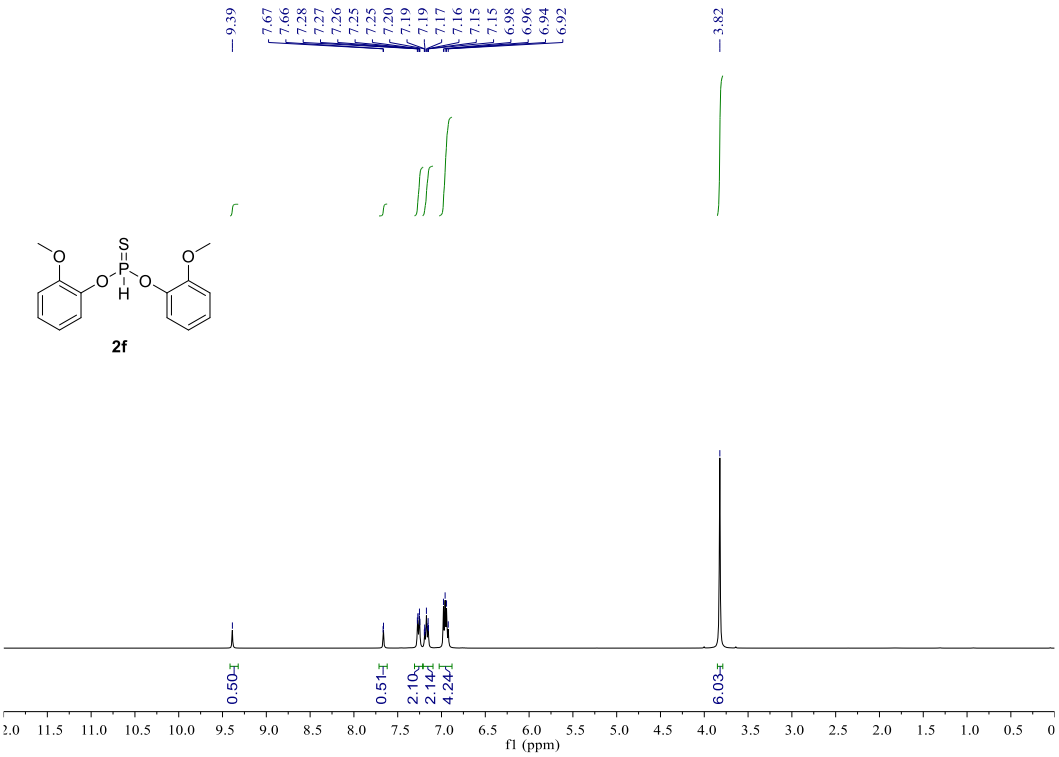
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2e**



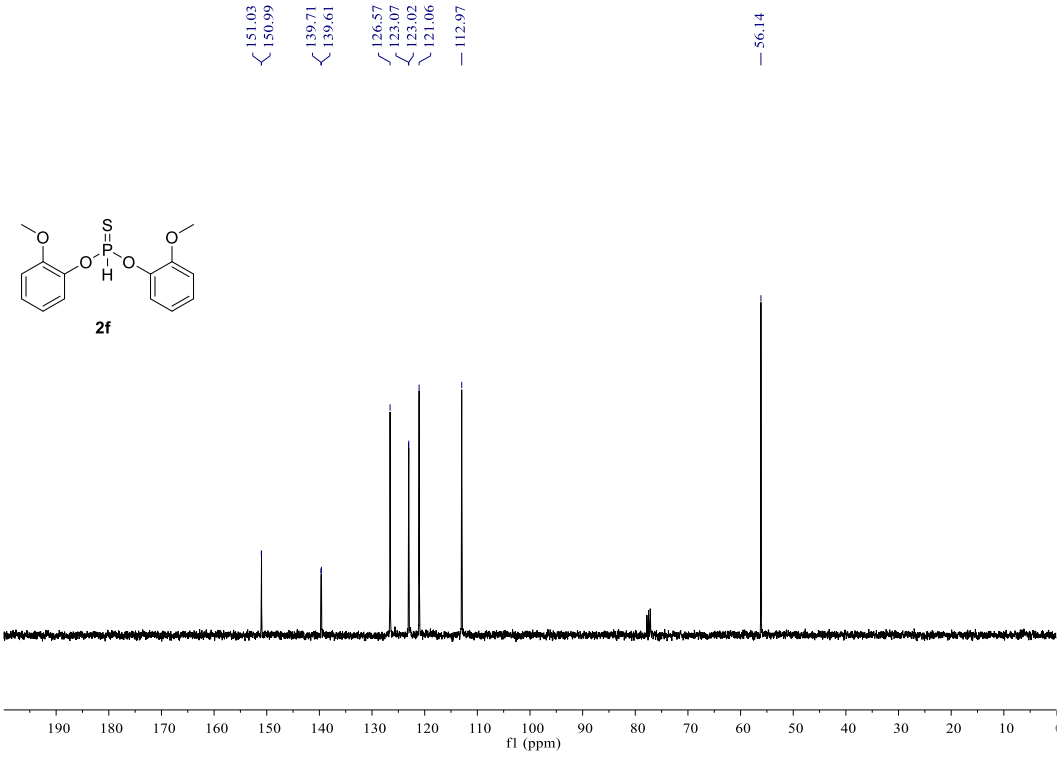
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **2e**



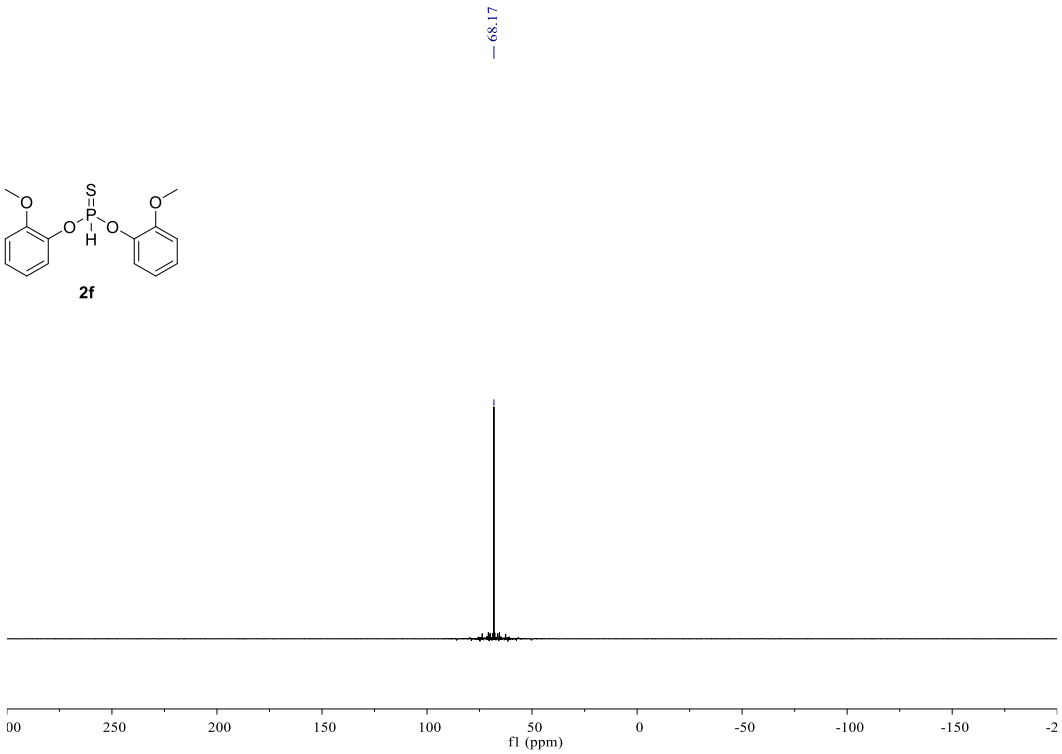
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2f**

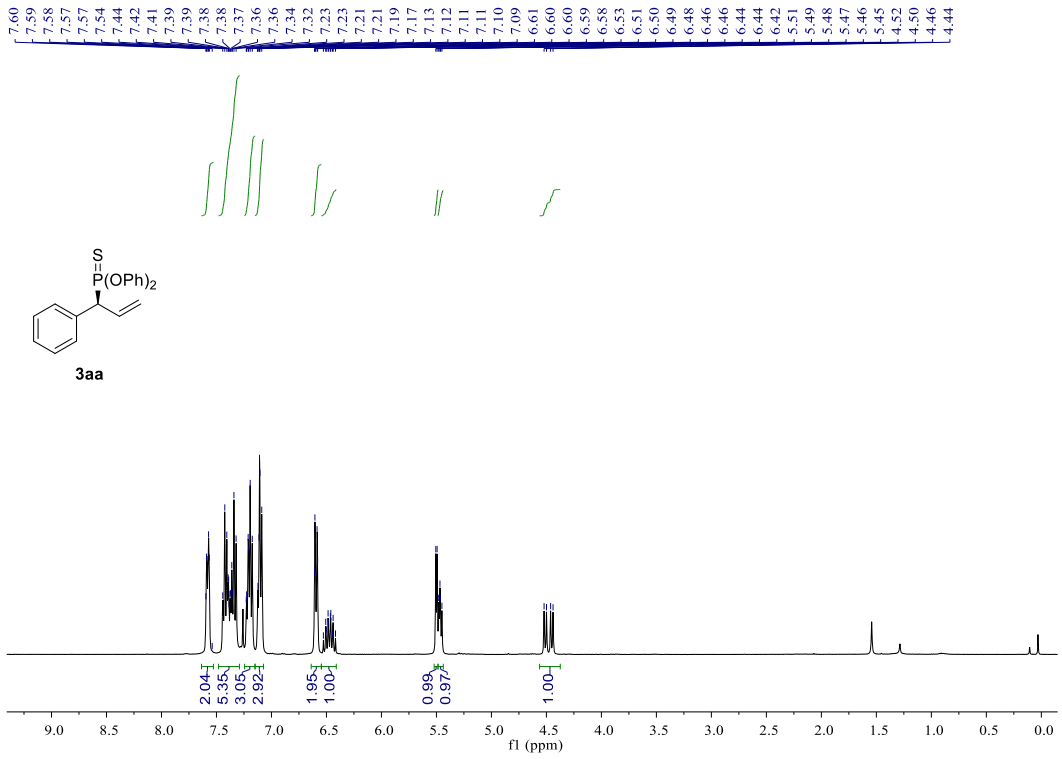


$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **2f**



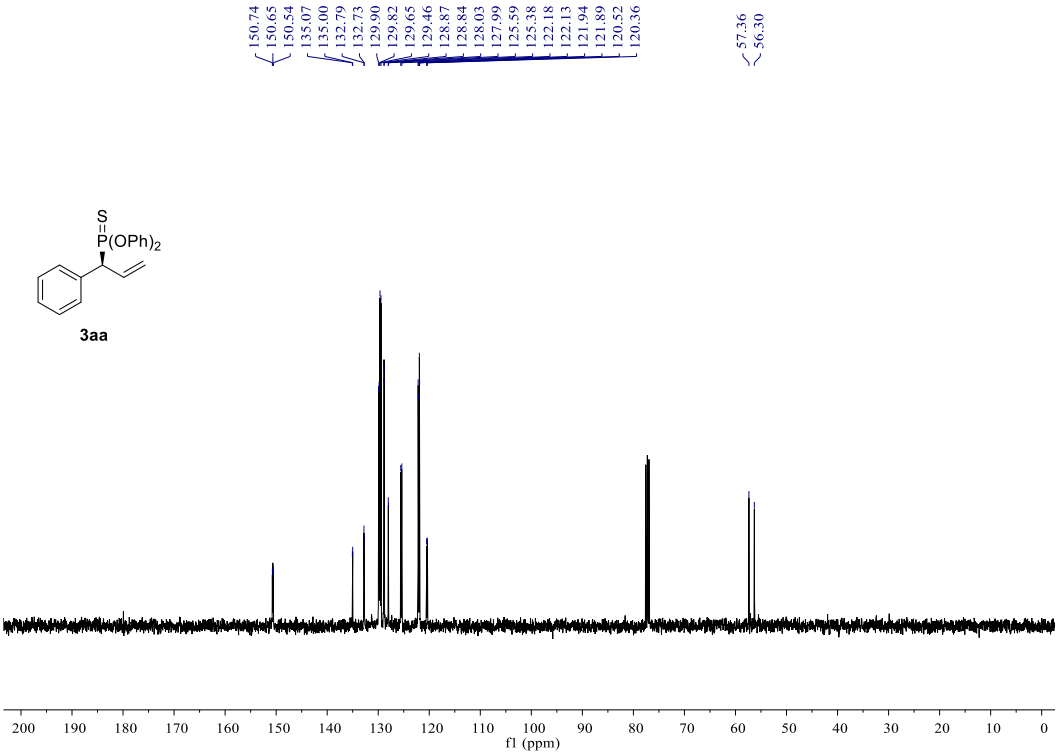
2f

^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**

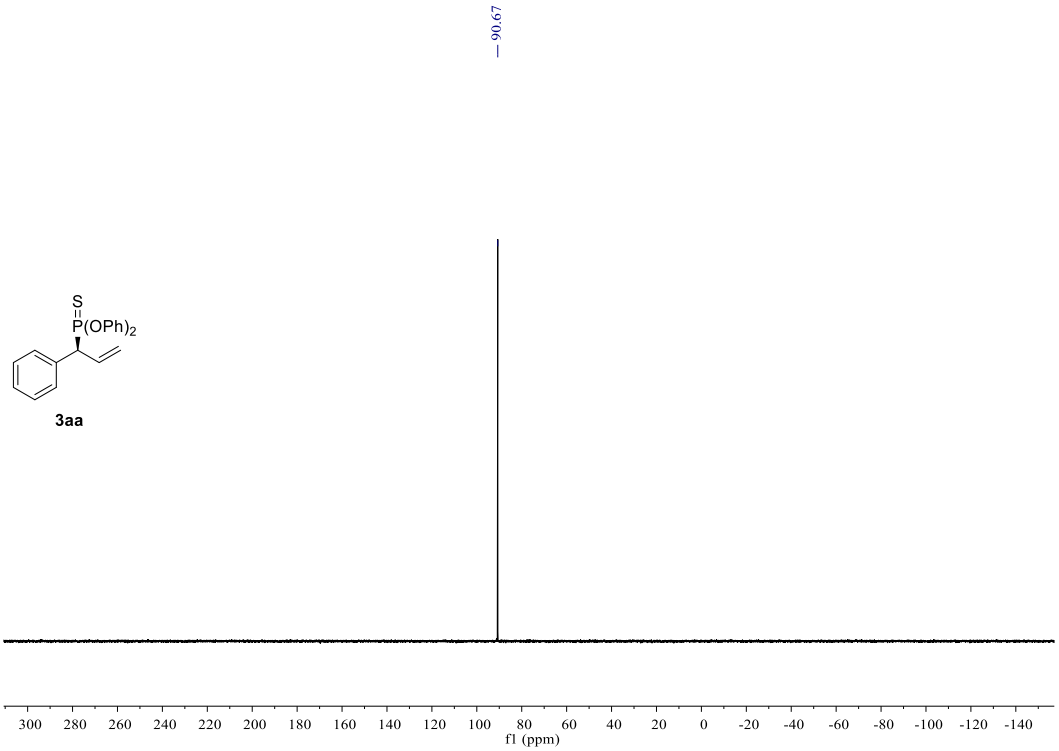


3aa

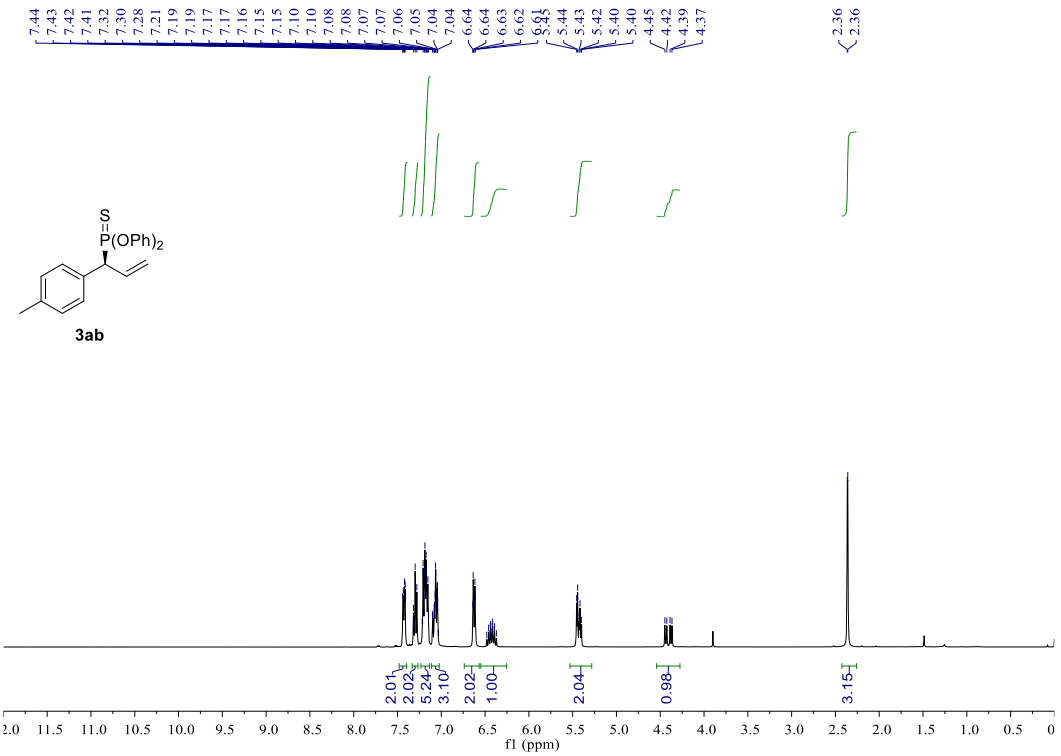
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3aa**



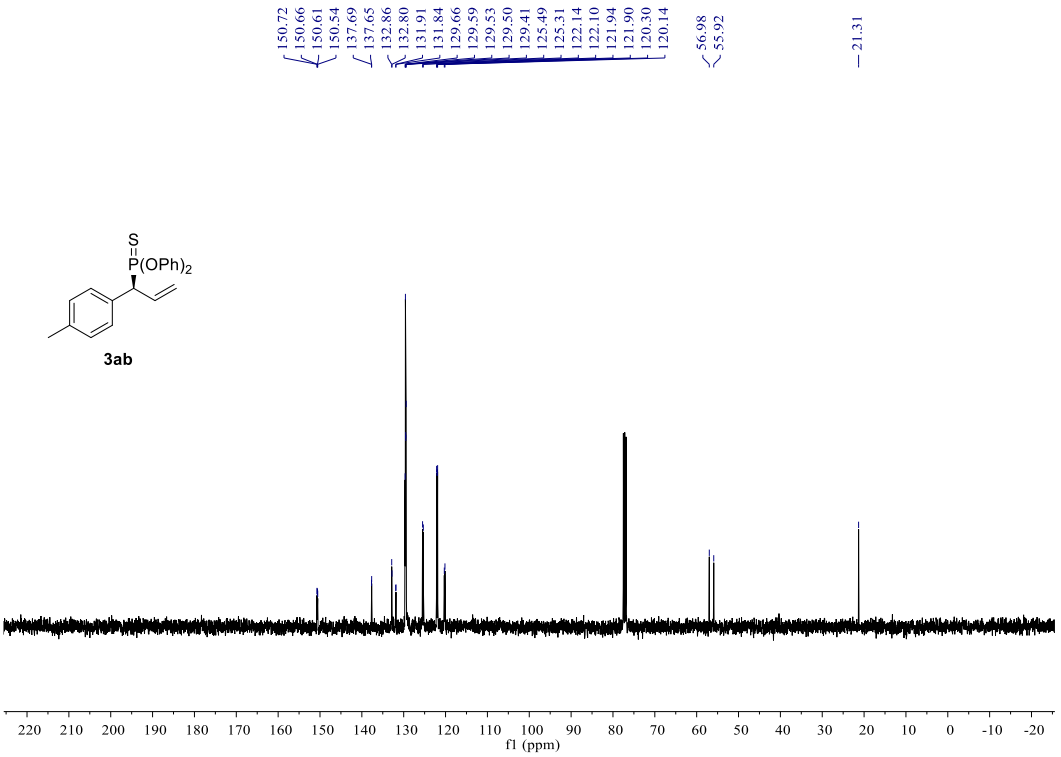
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3aa**



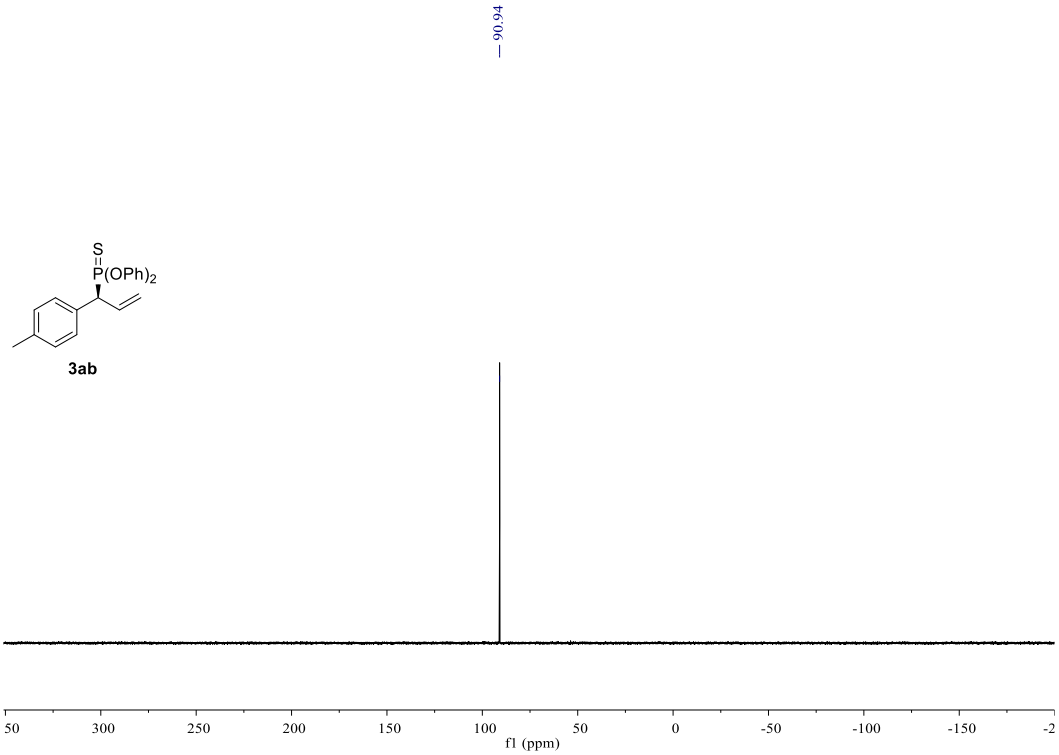
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



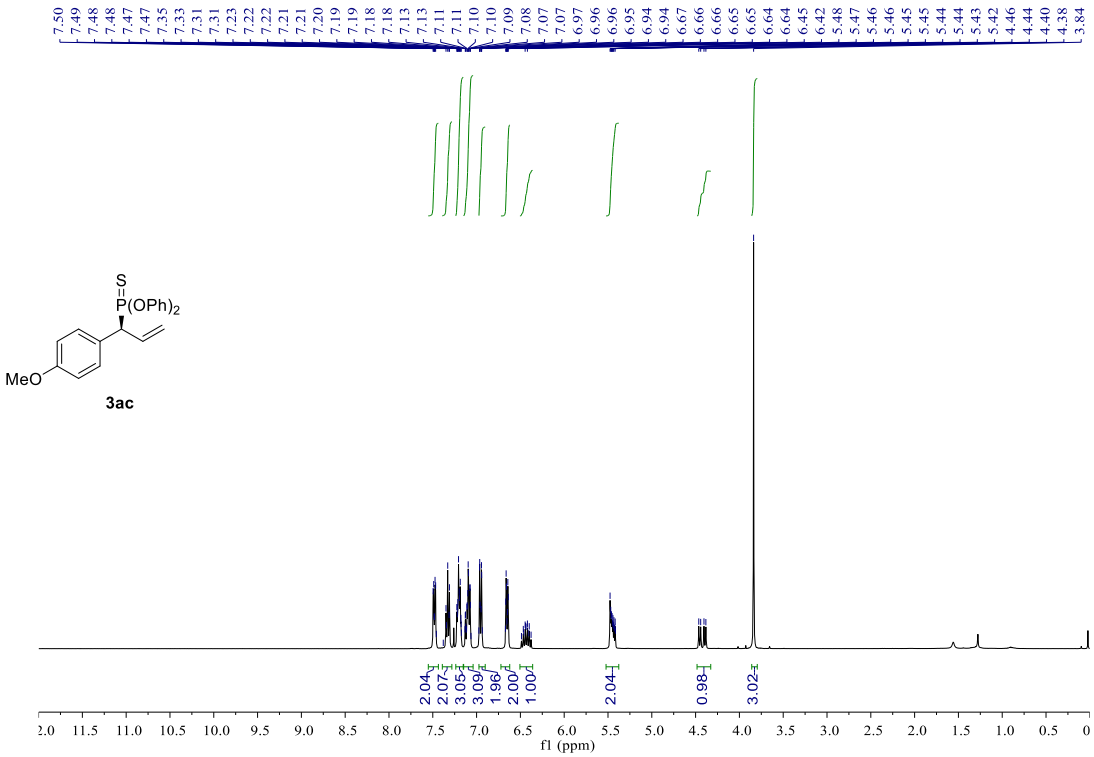
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3ab**



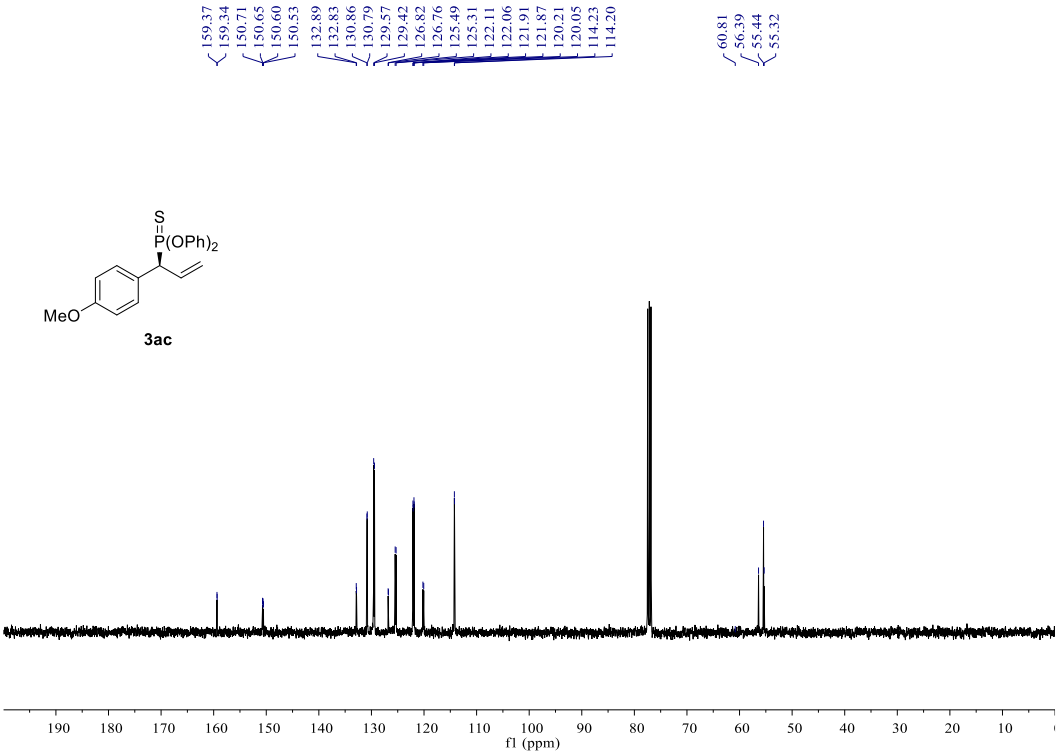
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ab**



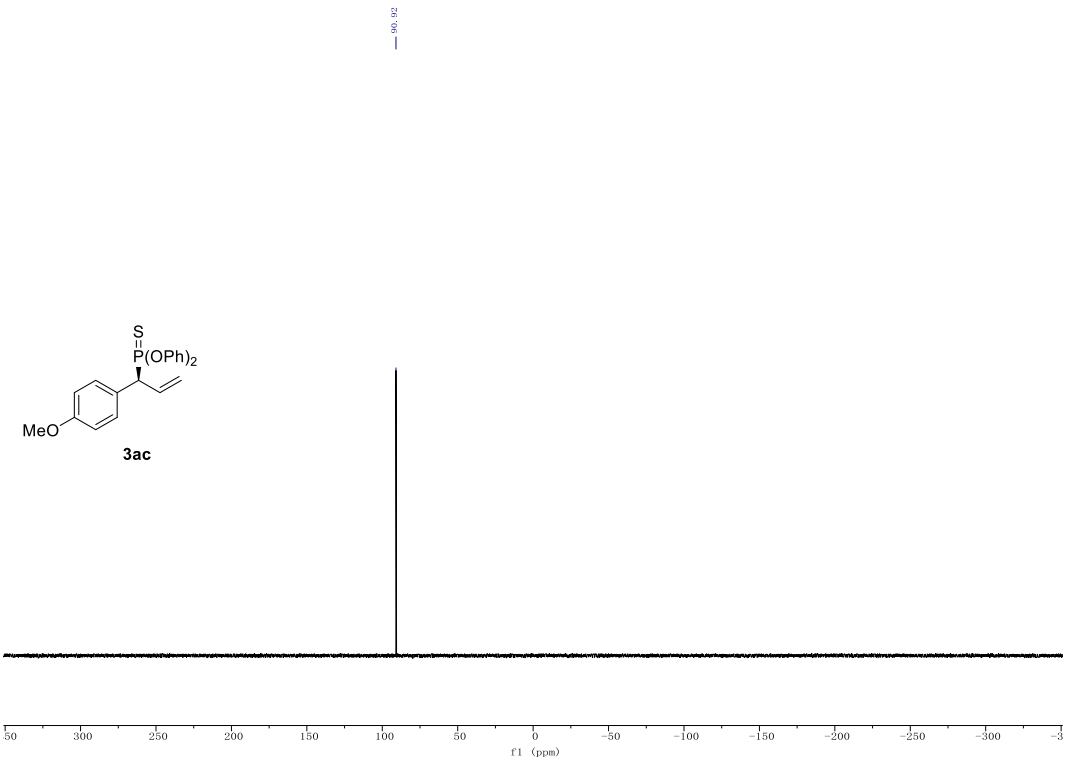
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



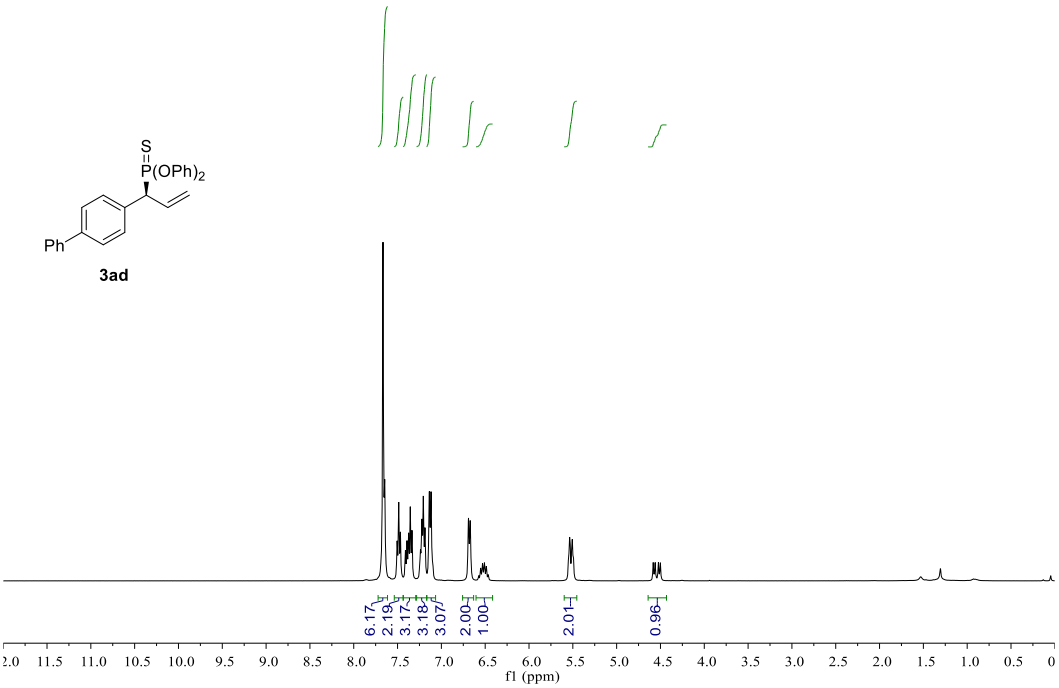
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ac**



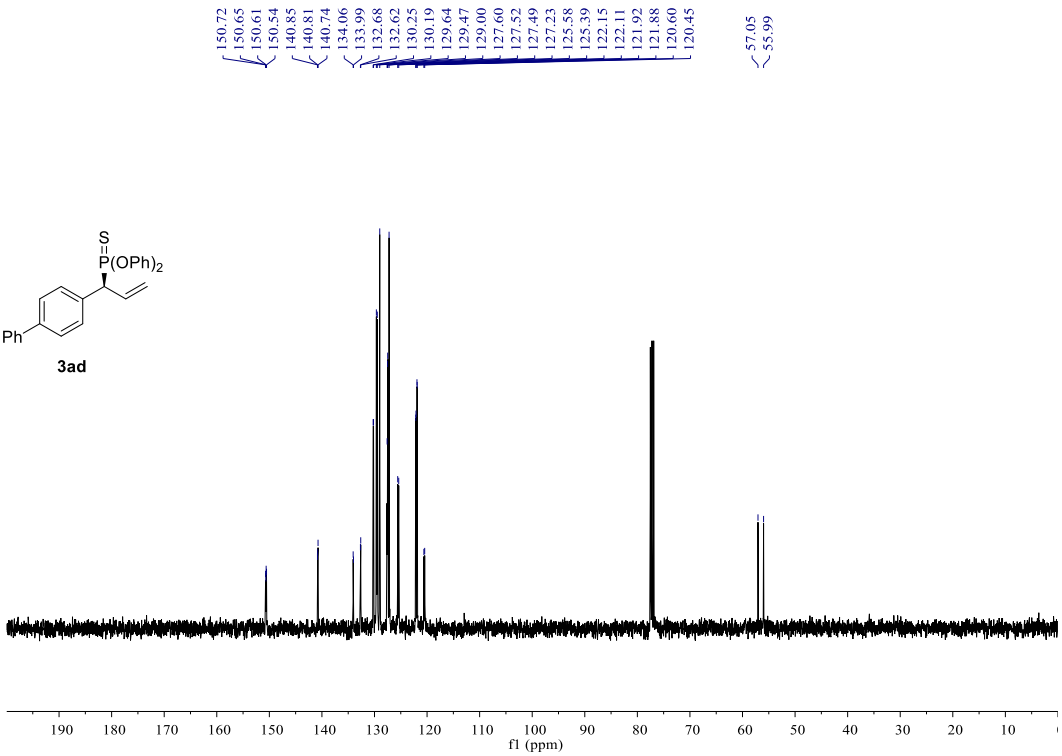
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ac**



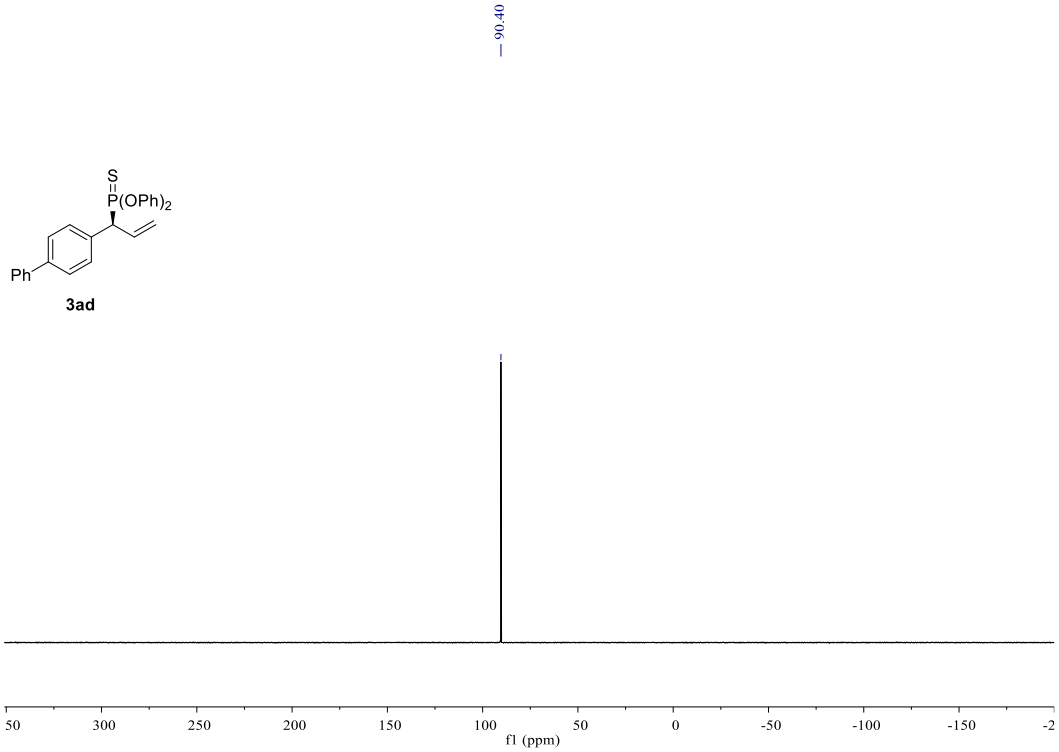
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



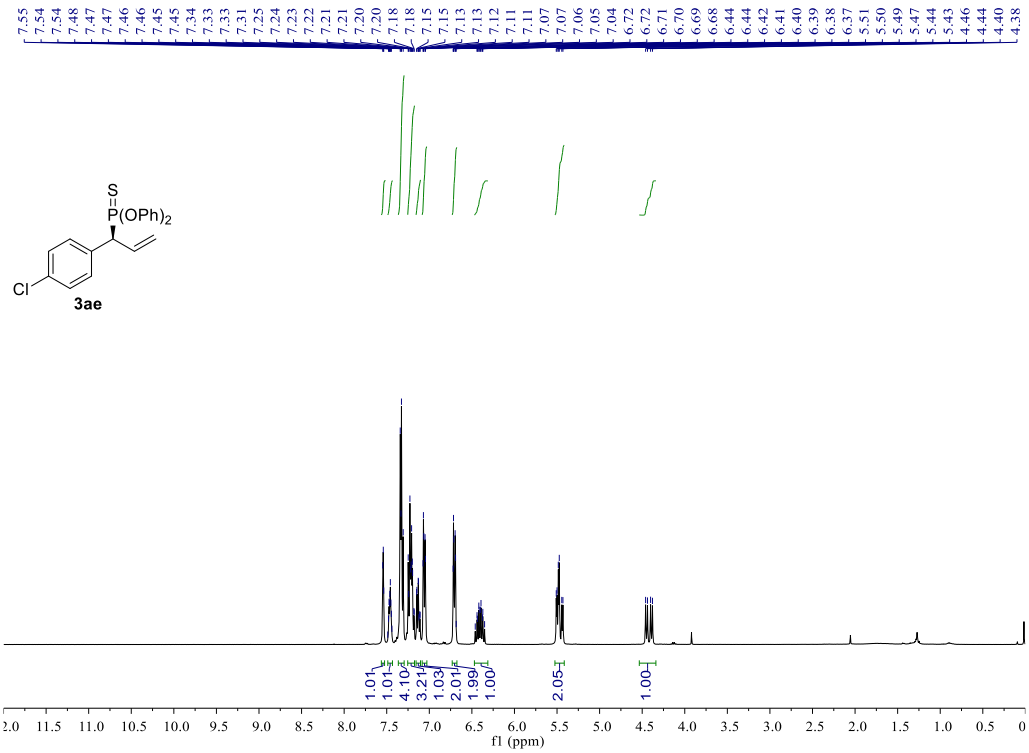
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3ad**



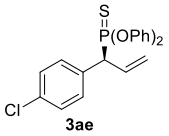
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ad**



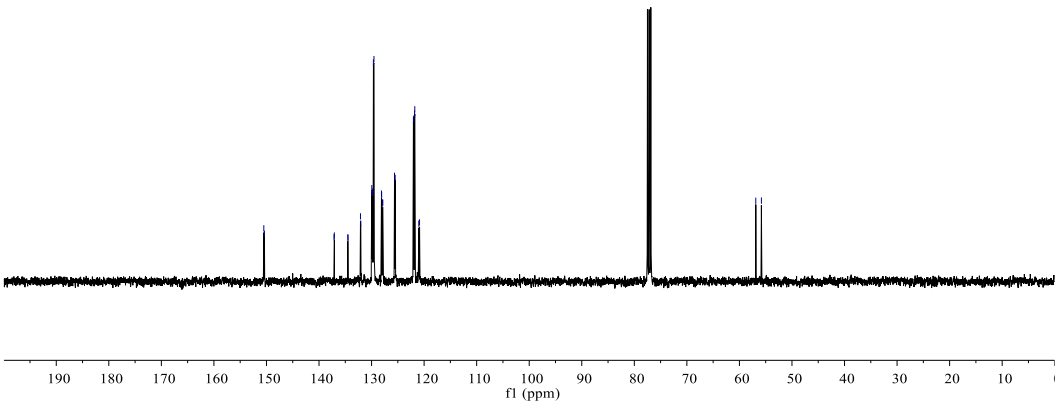
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



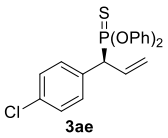
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ae**



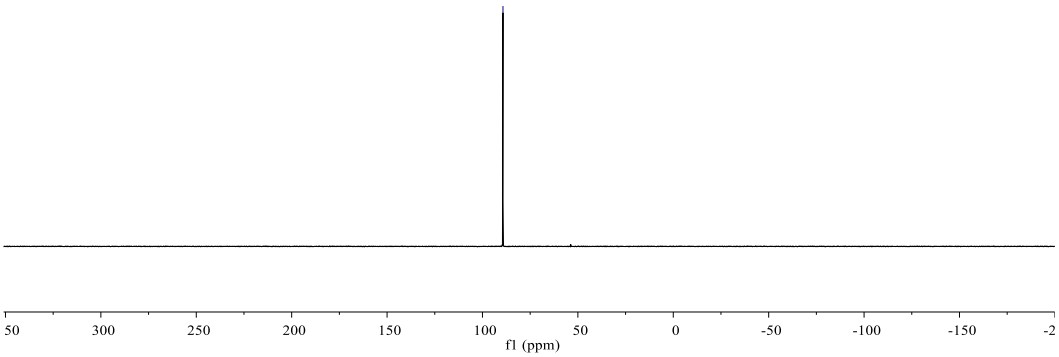
3ae



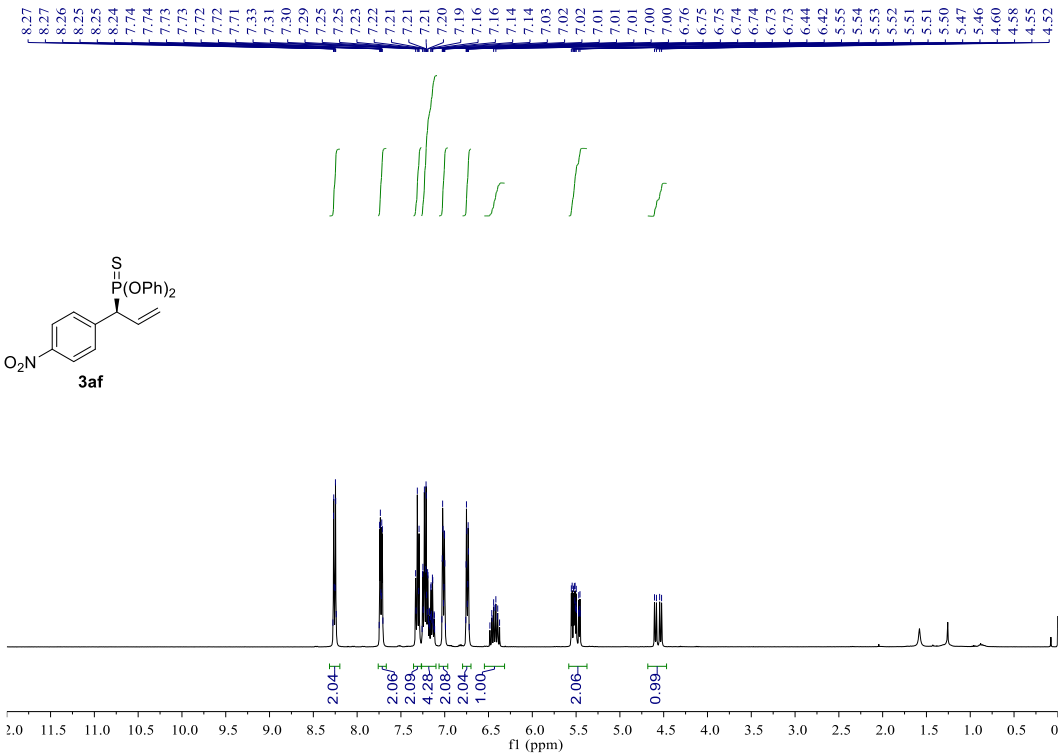
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ae**



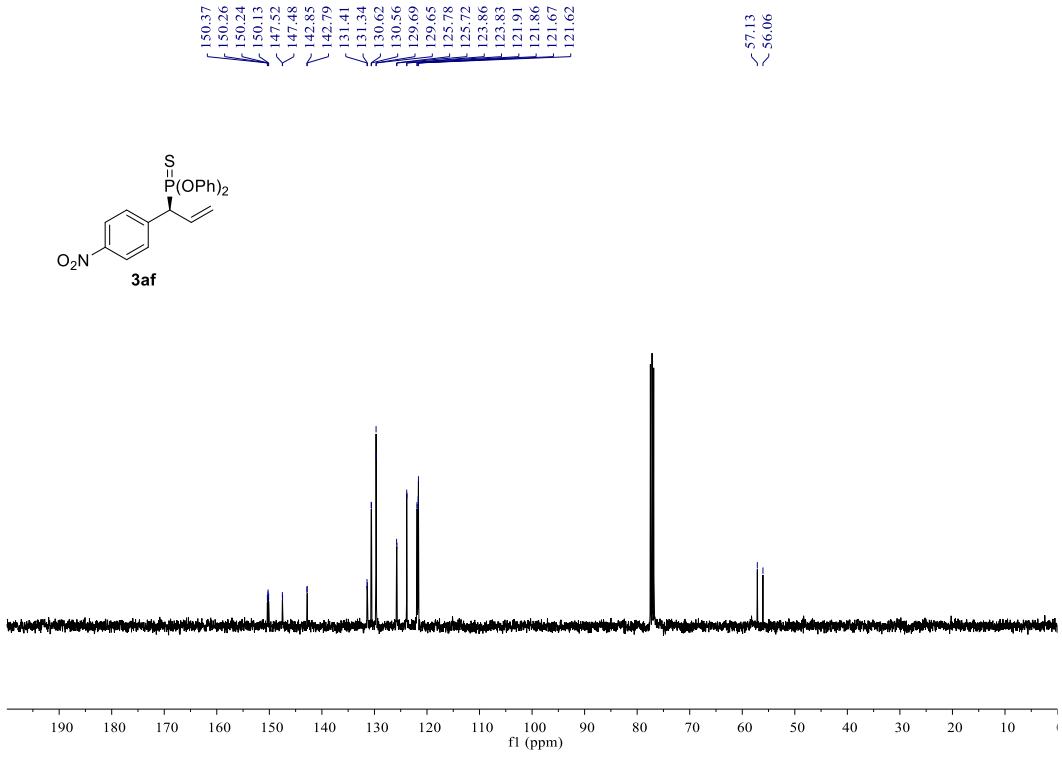
3ae



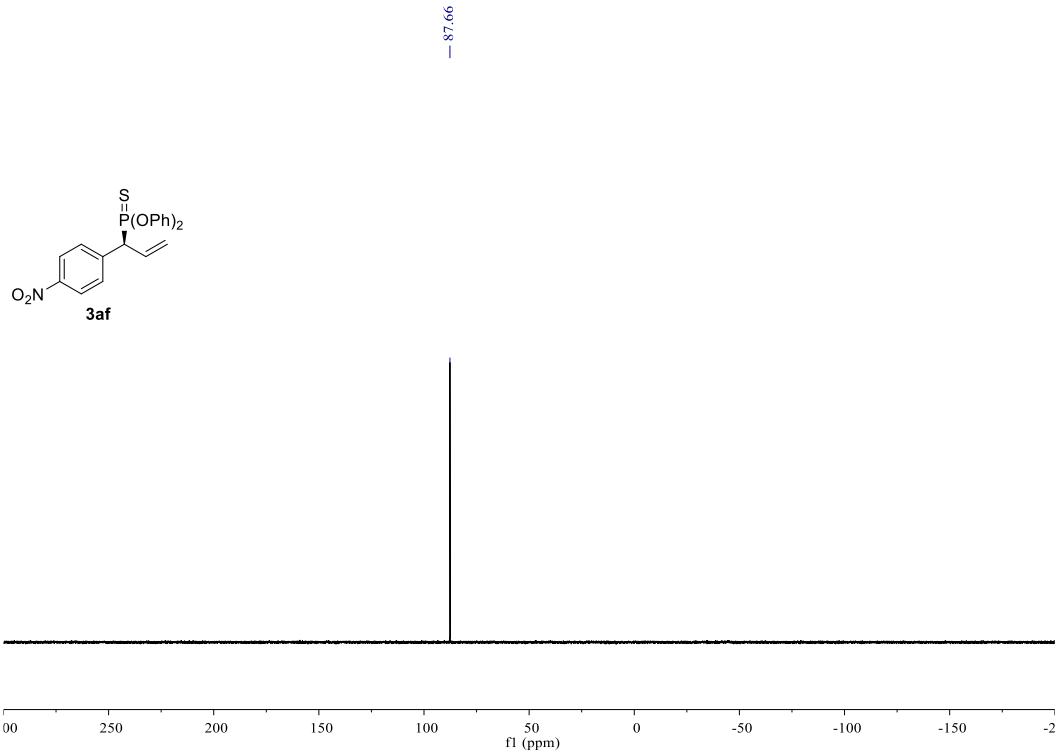
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



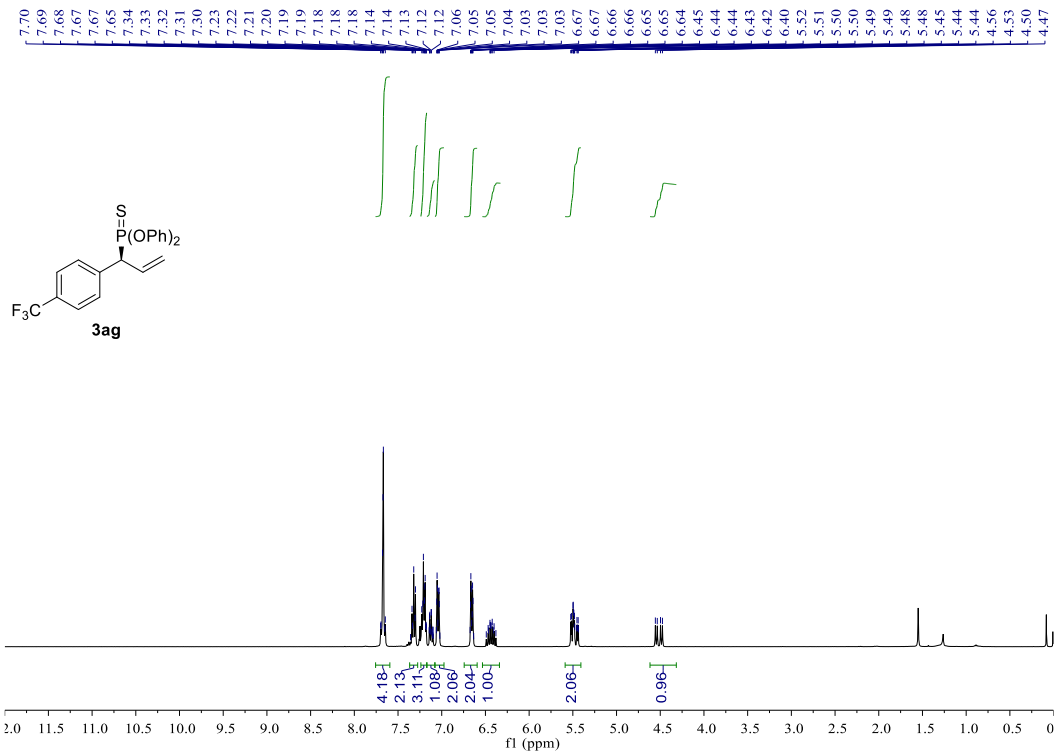
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3af**



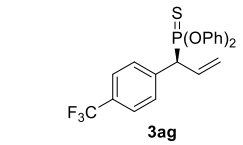
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3af**



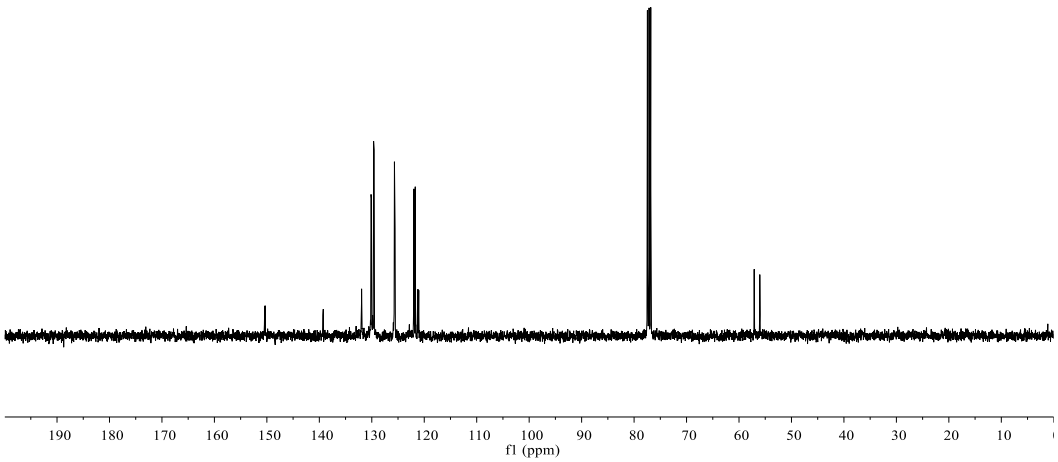
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



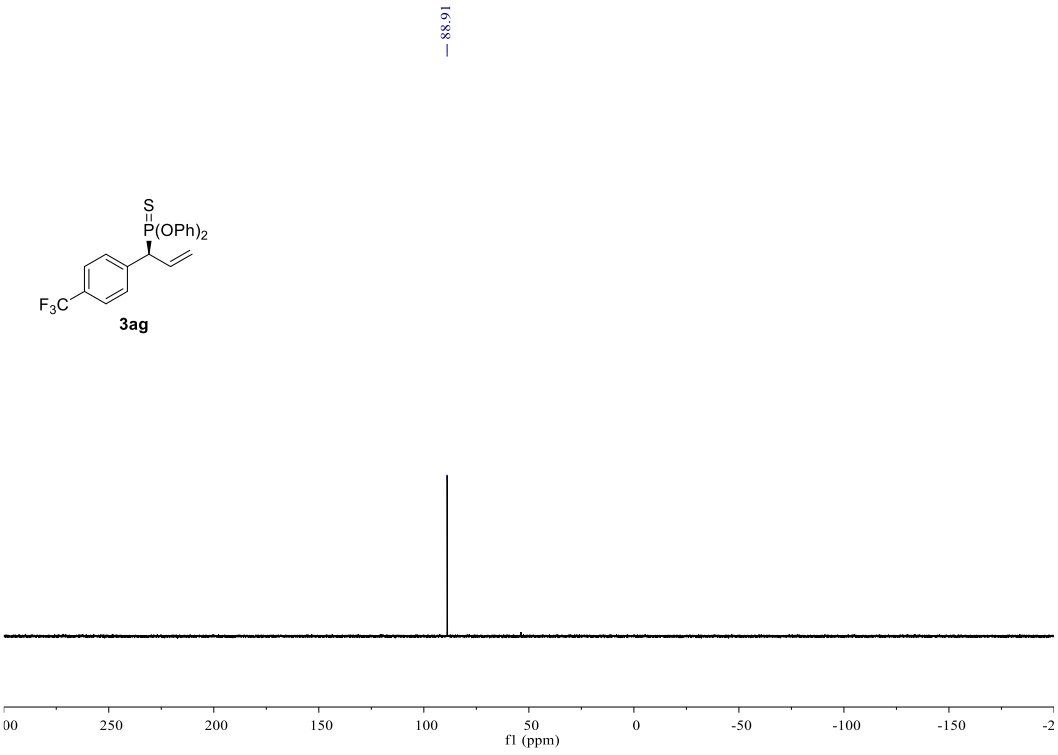
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ag**



3ag

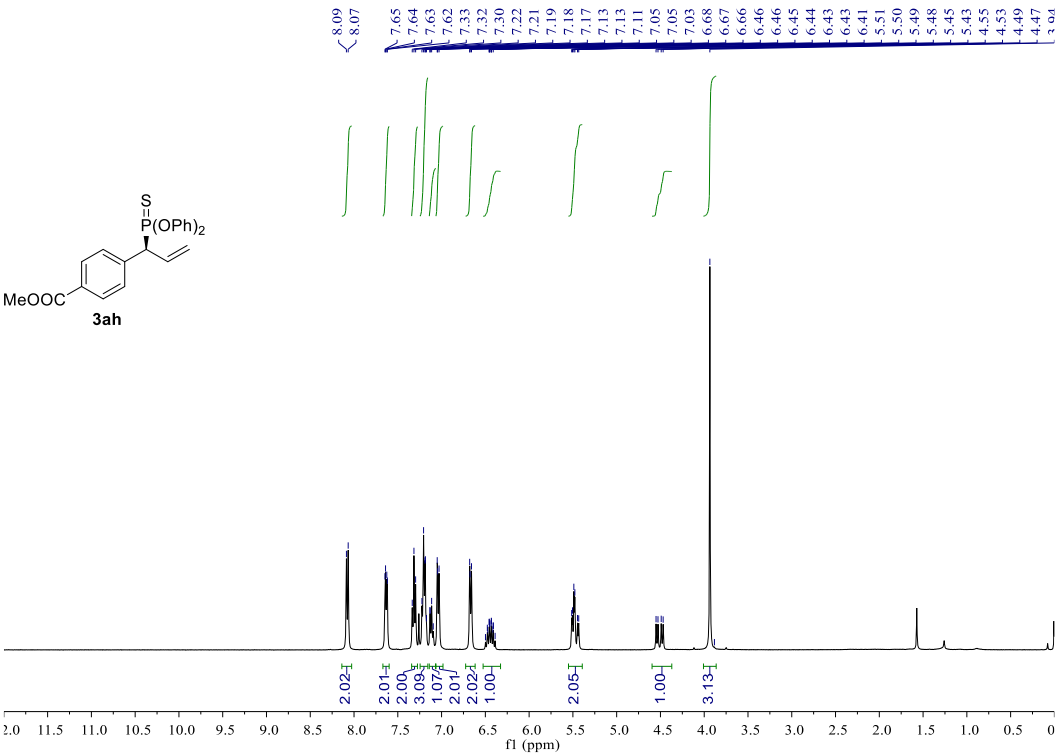


$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ag**

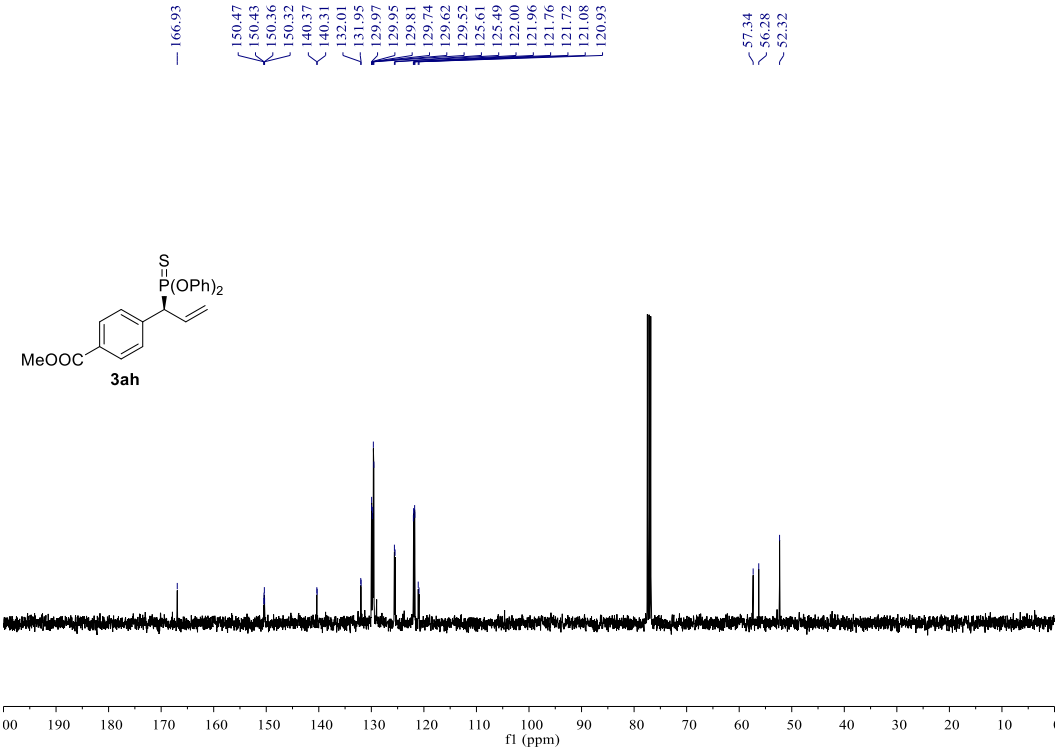


3ag

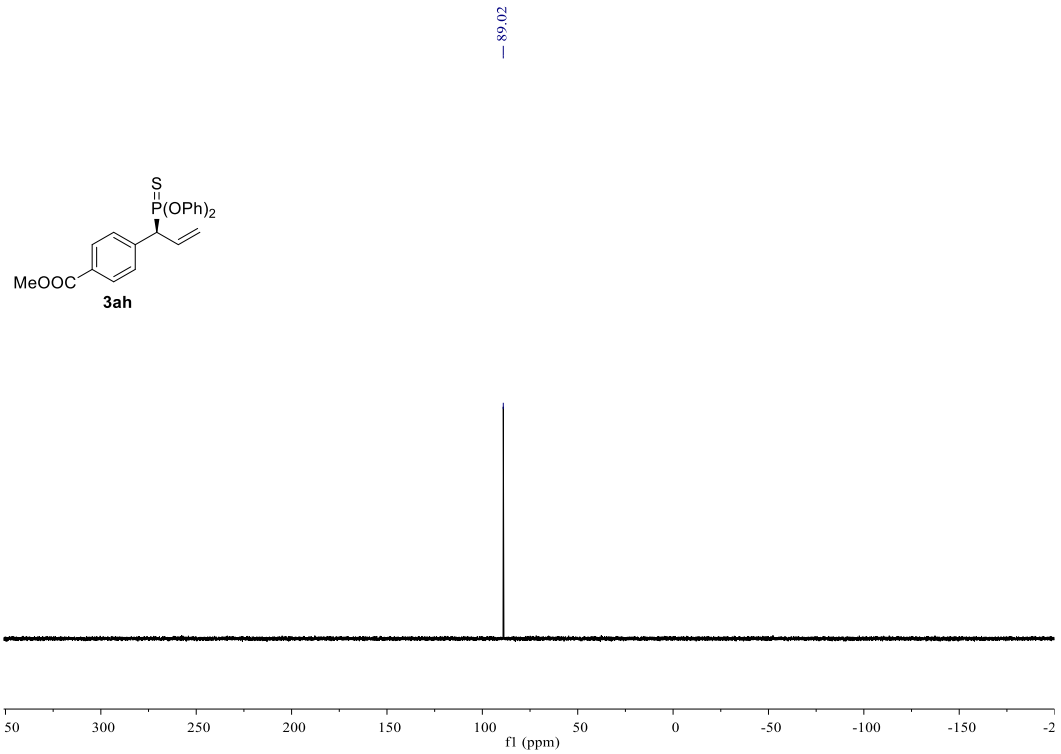
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



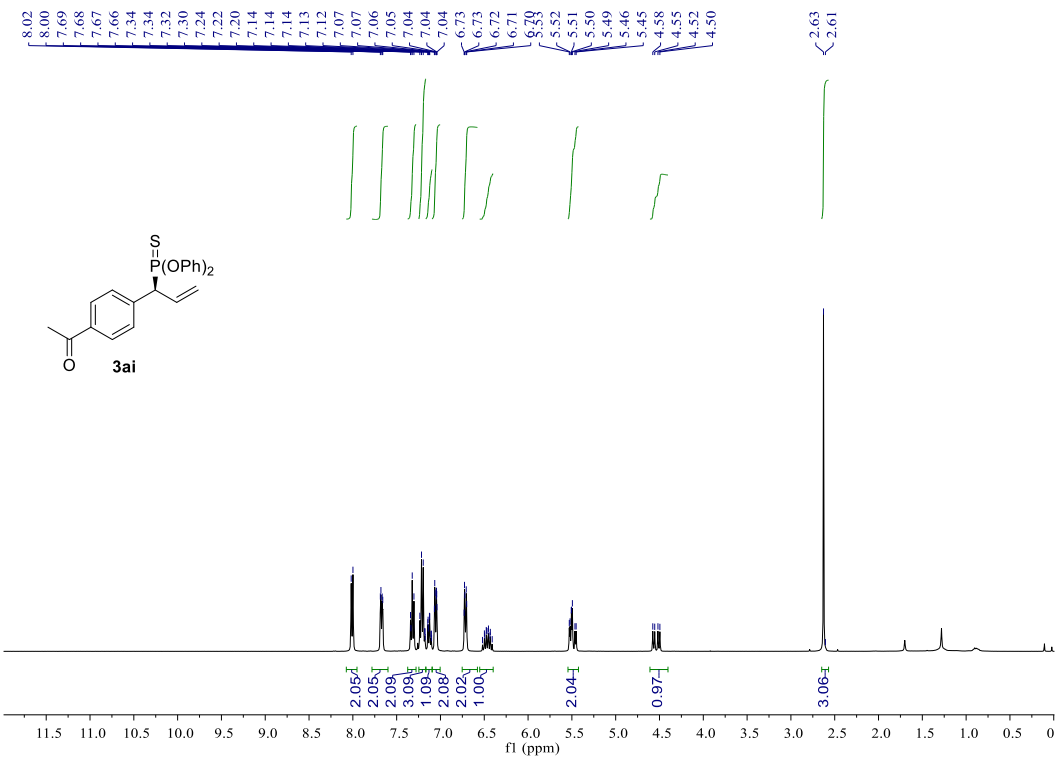
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ah**



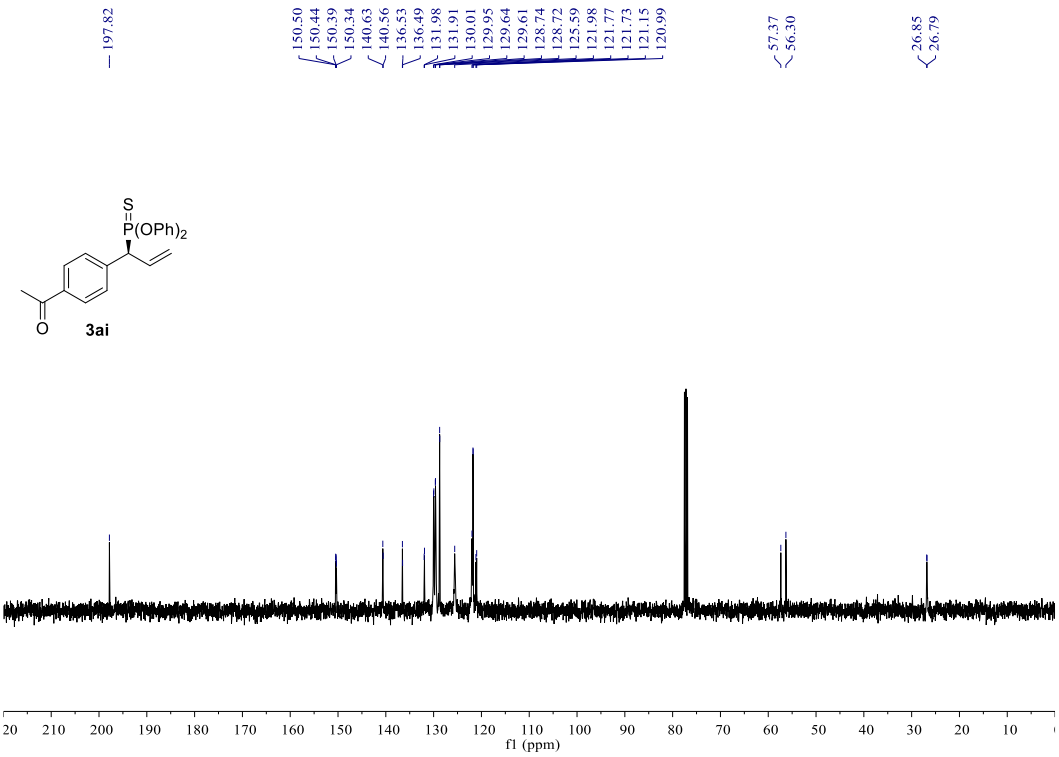
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ah**



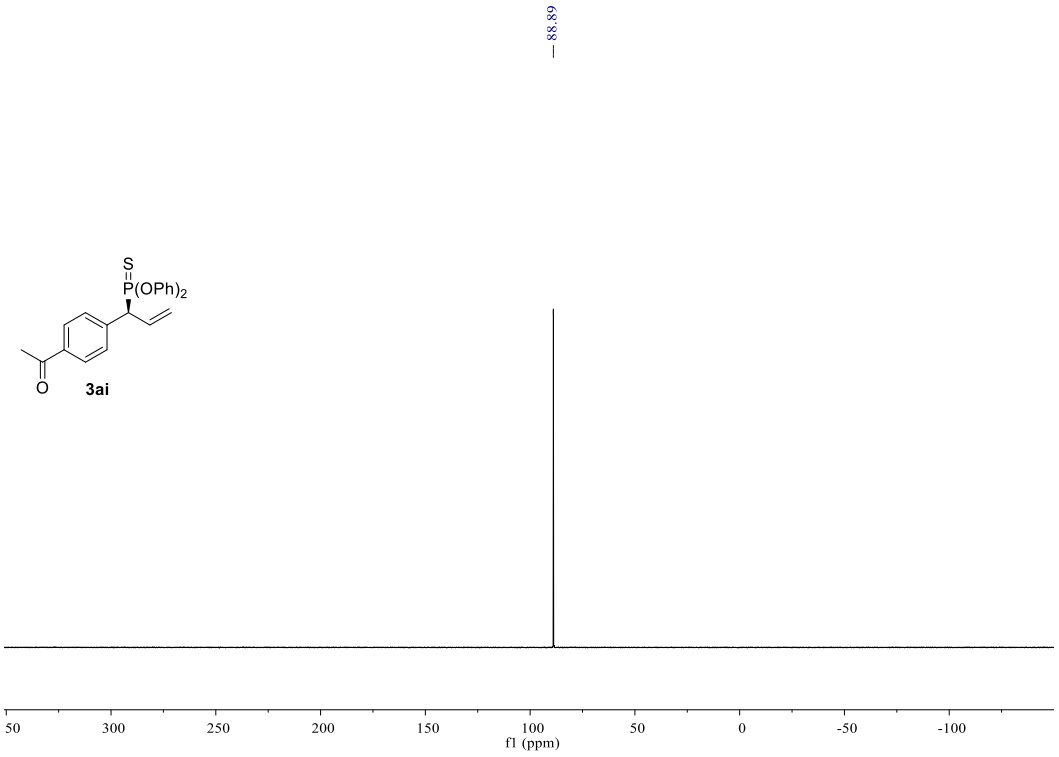
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



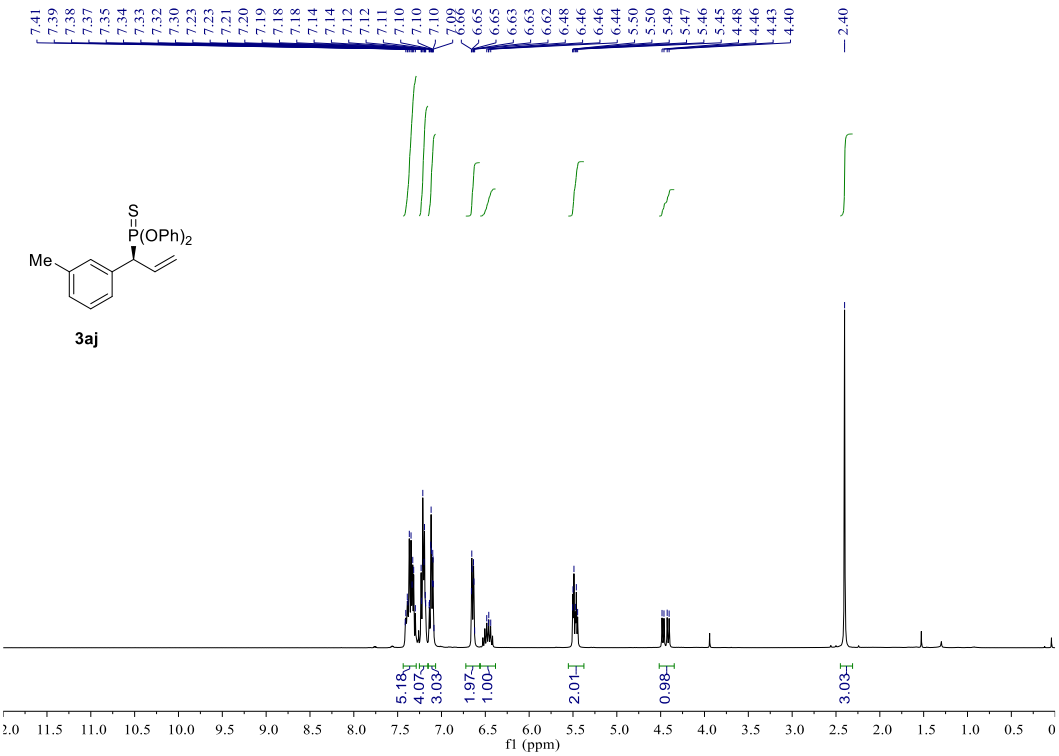
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ai**



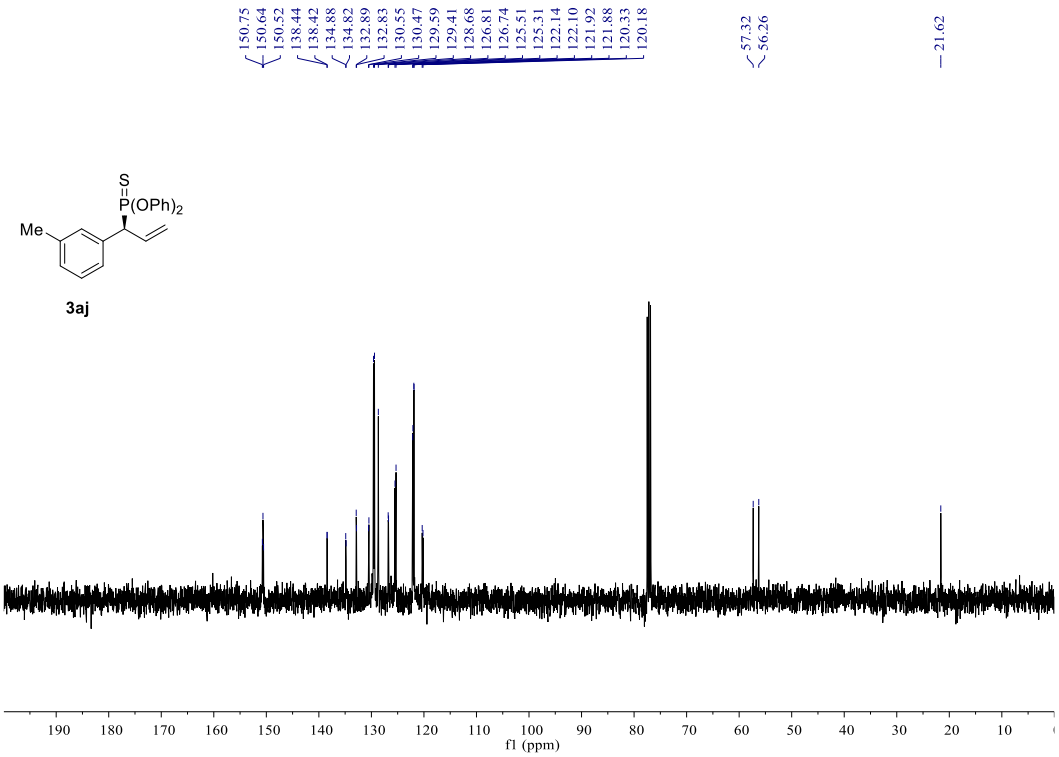
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ai**



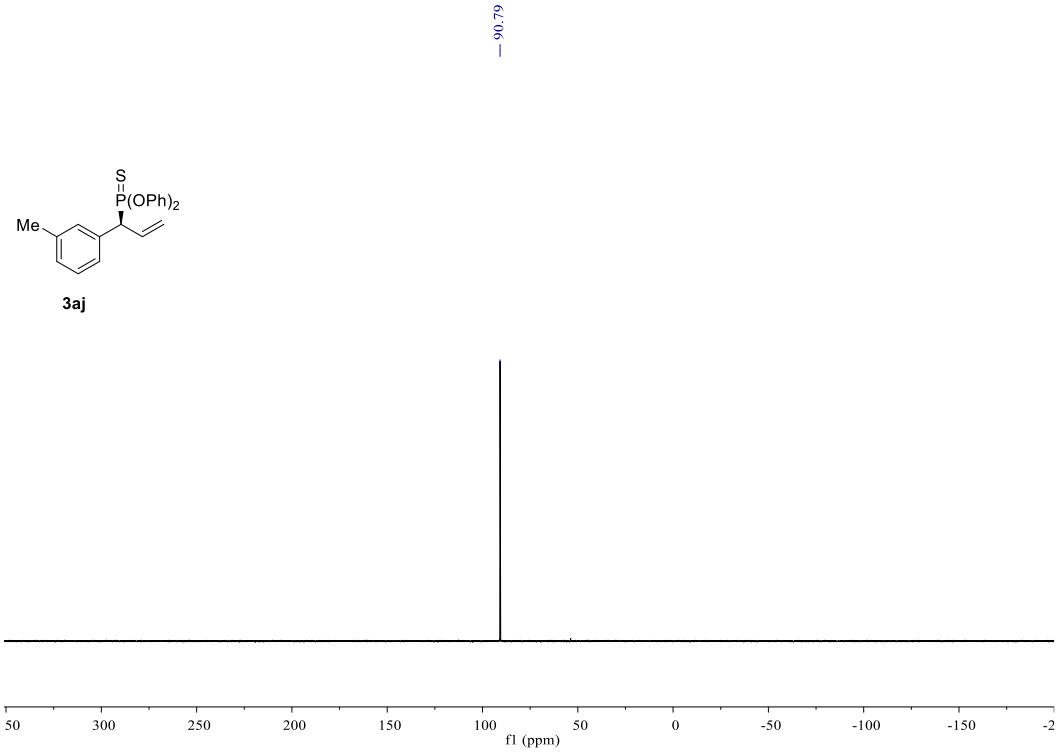
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



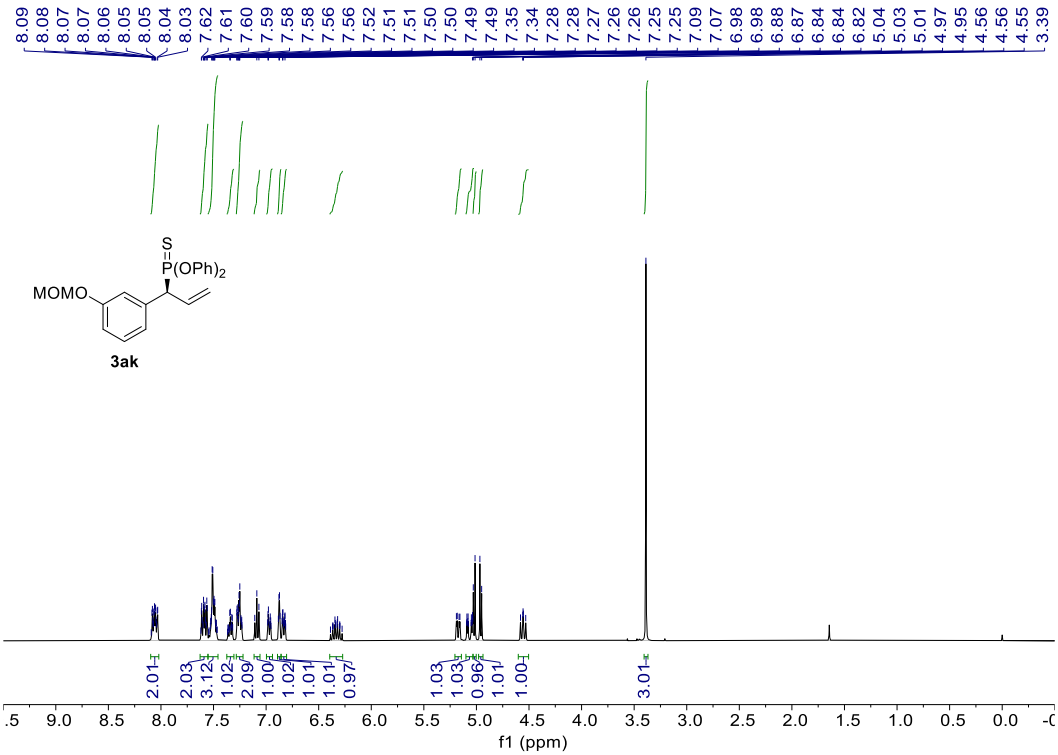
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3aj**



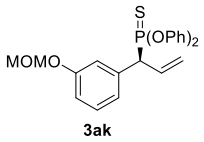
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3aj**



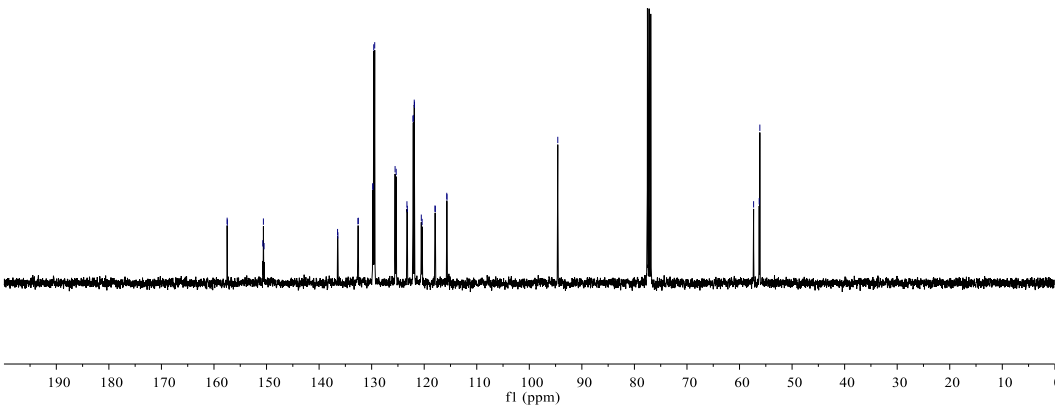
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**



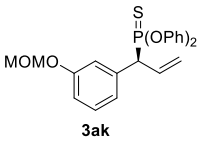
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ak**



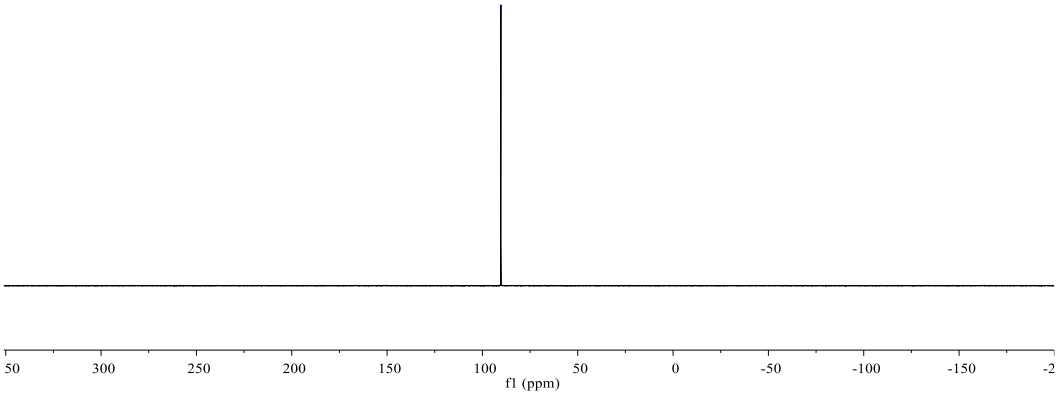
3ak



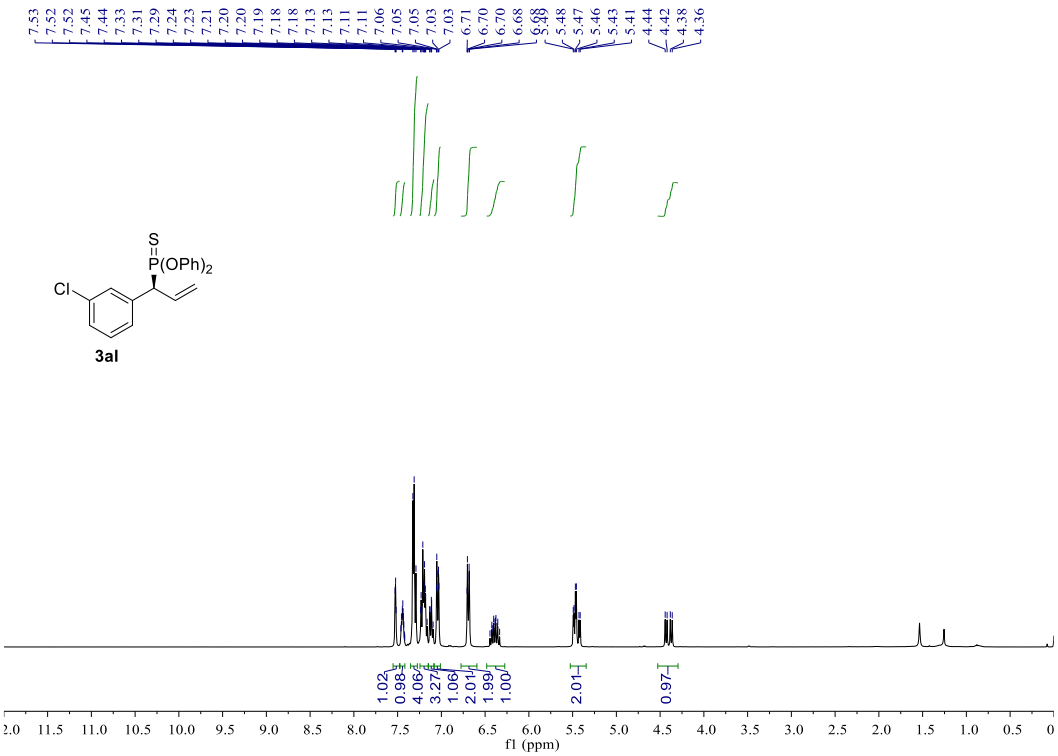
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ak**



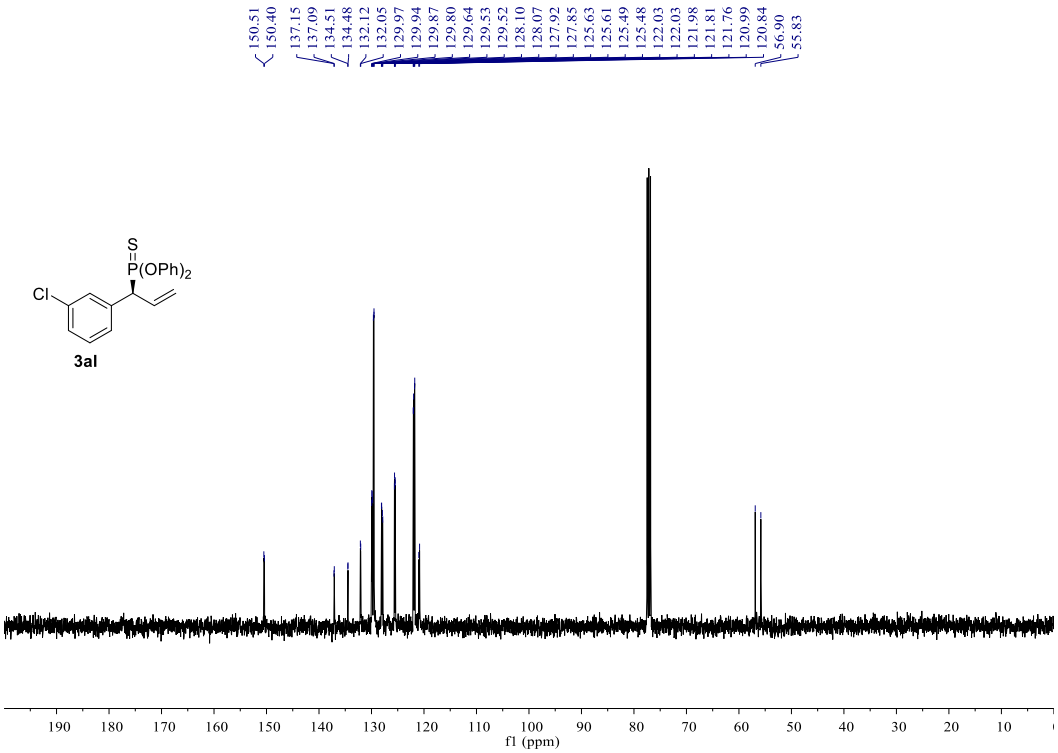
3ak



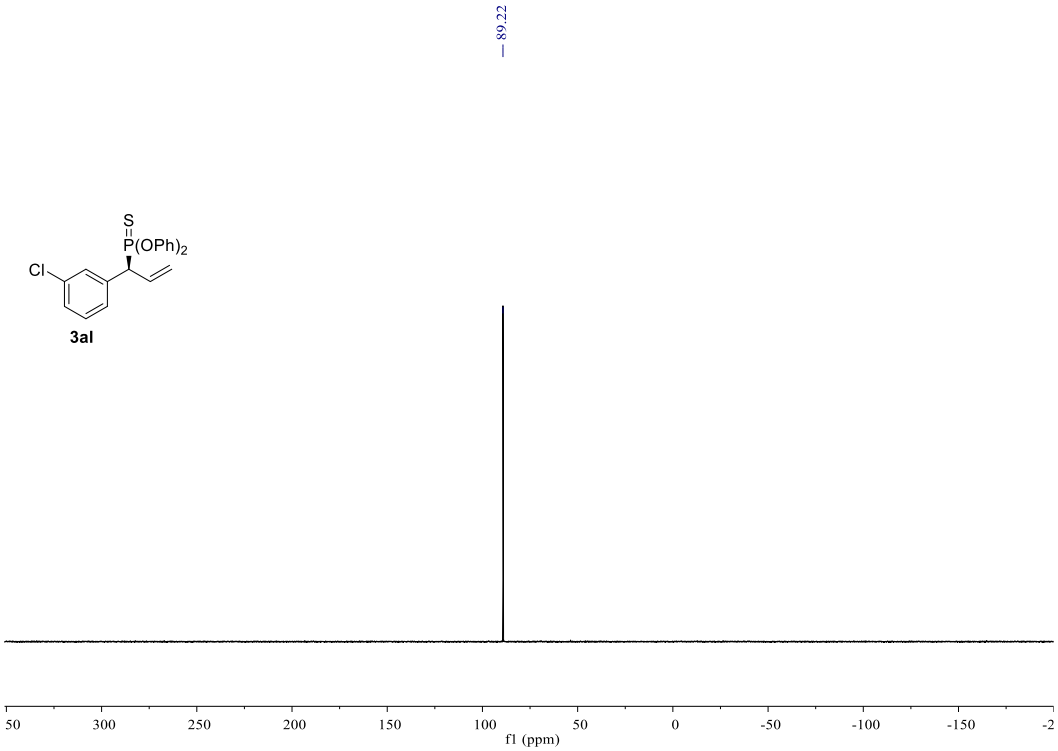
^{1}H NMR (400 MHz, $CDCl_3$) of **3al**



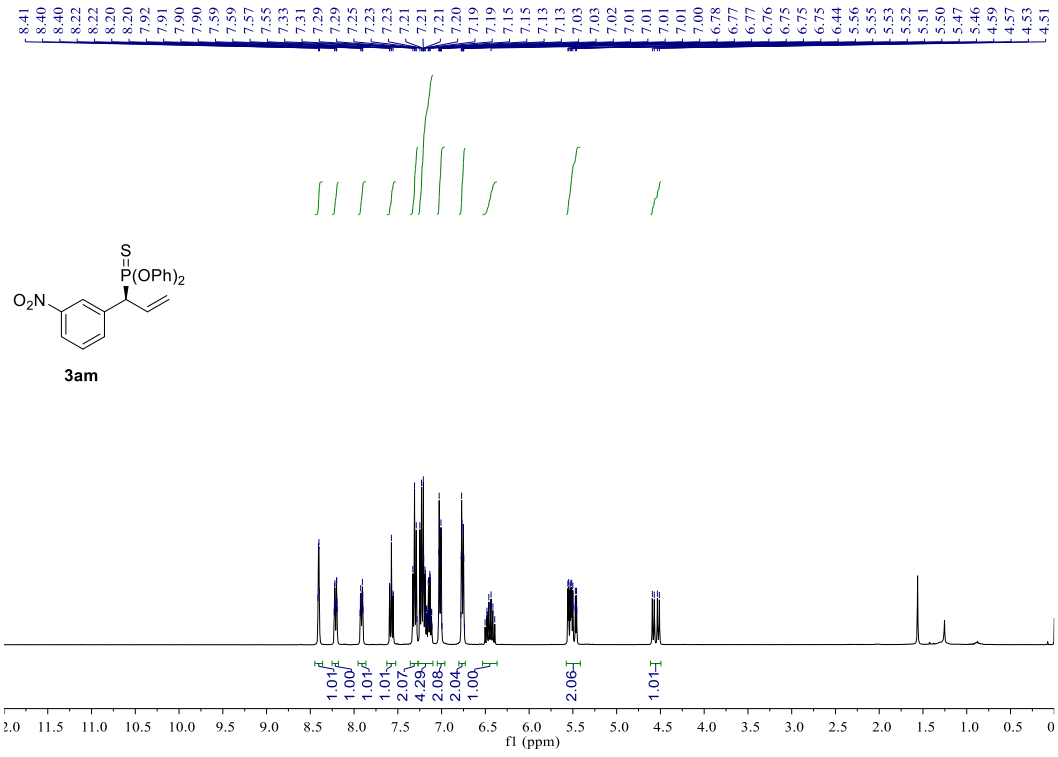
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3al**



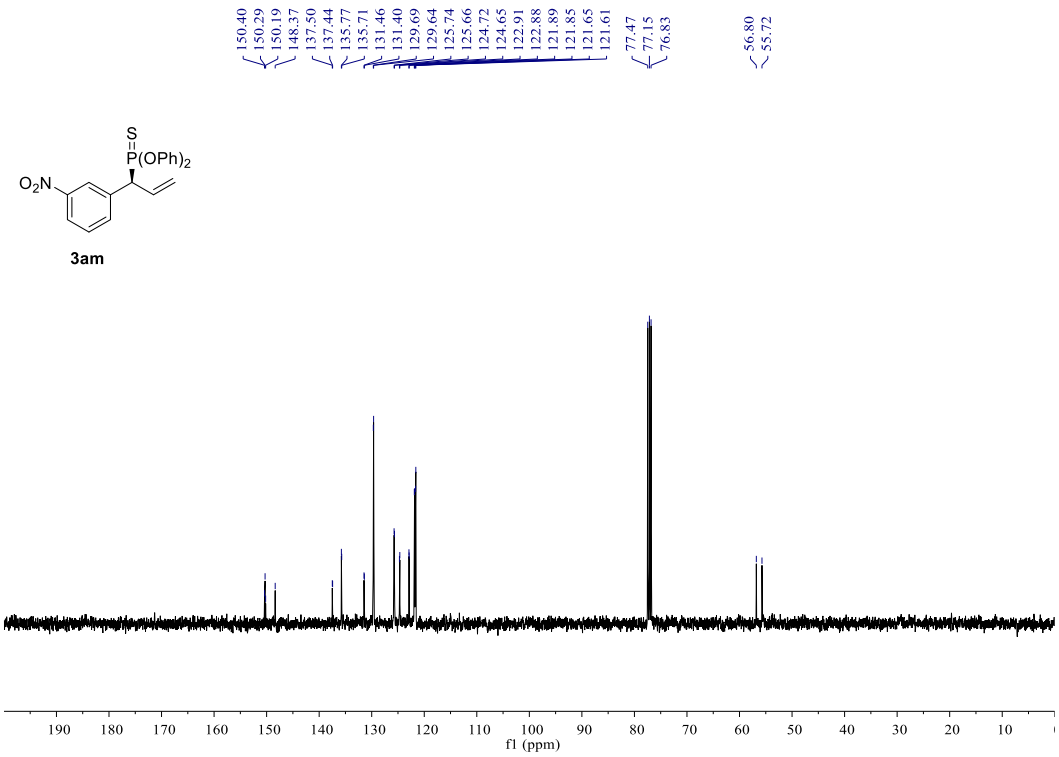
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3al**



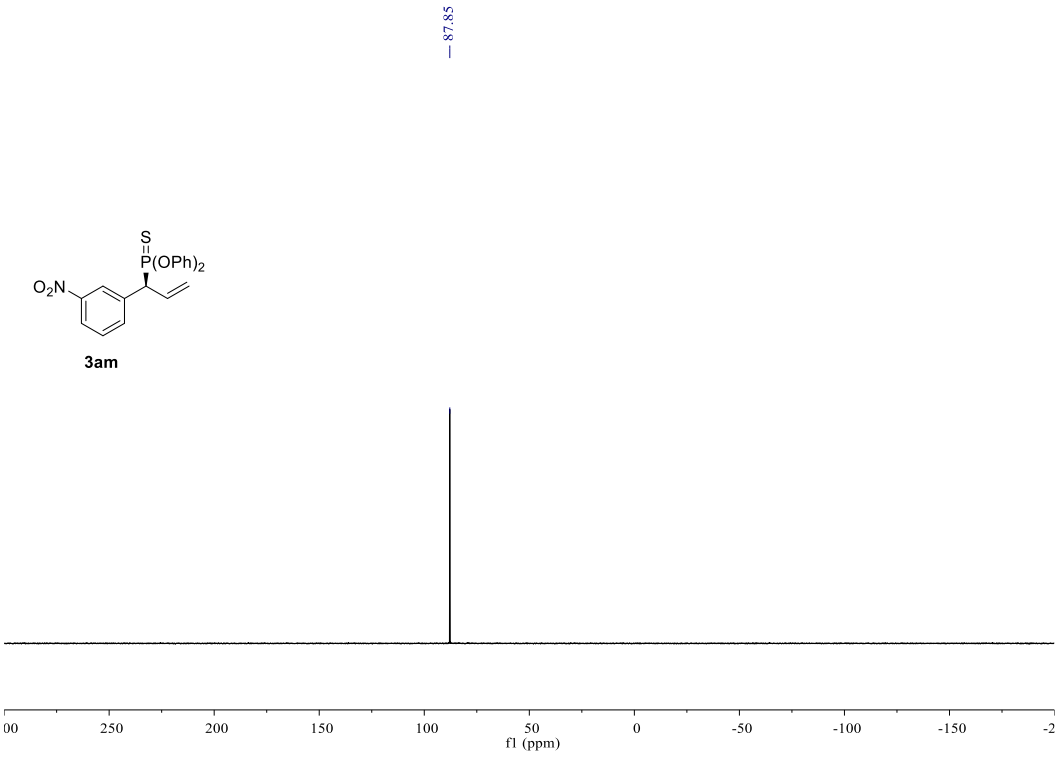
^{1}H NMR (400 MHz, $CDCl_3$) of **3am**



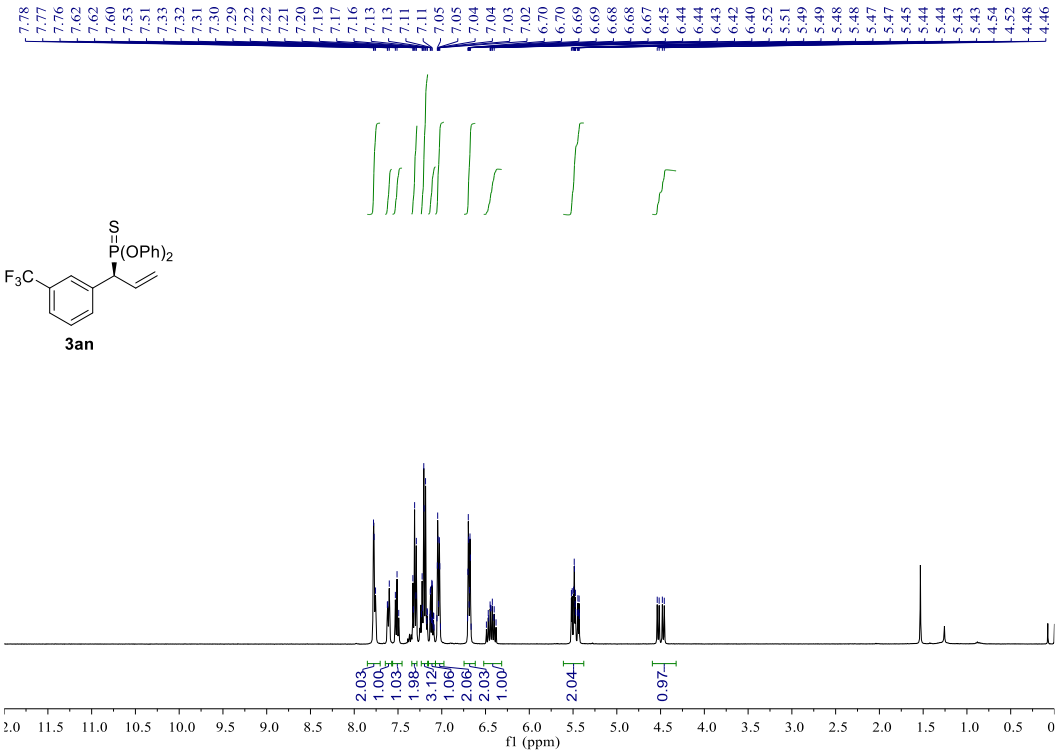
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3am**



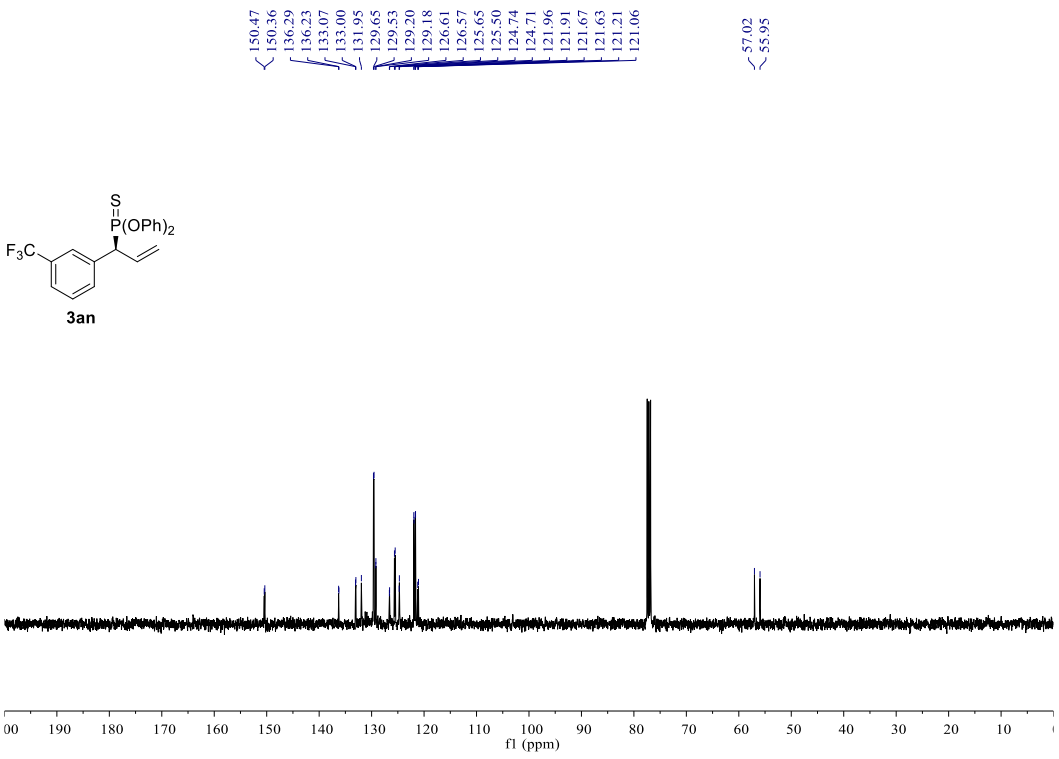
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3am**



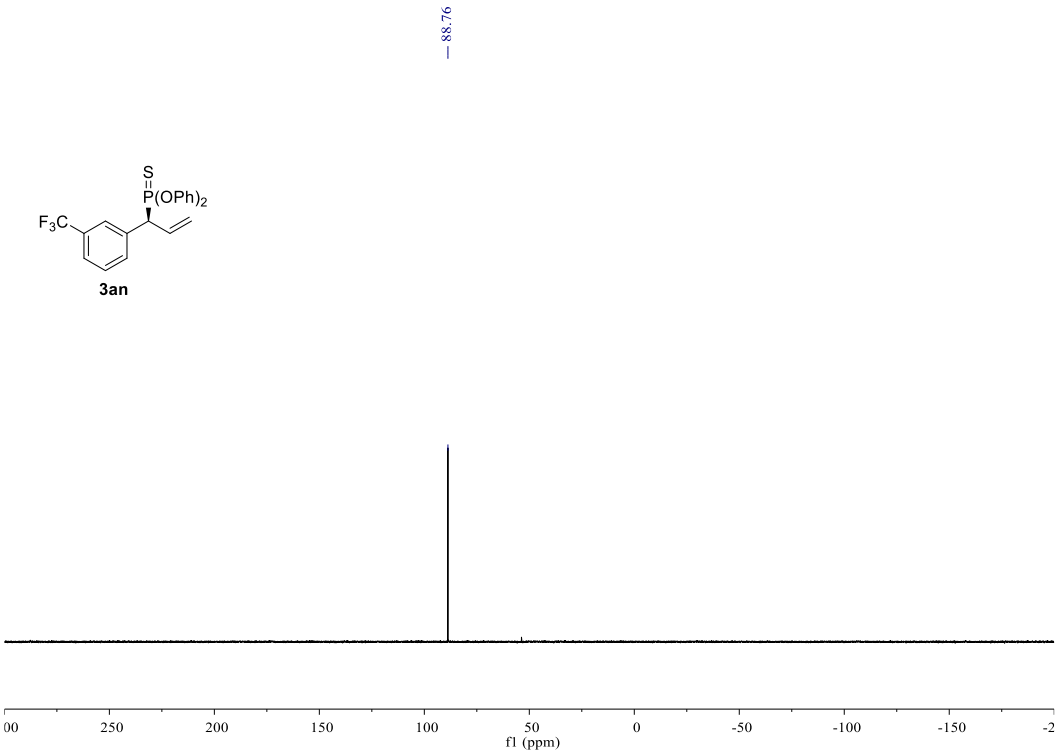
^{1}H NMR (400 MHz, $CDCl_3$) of **3an**



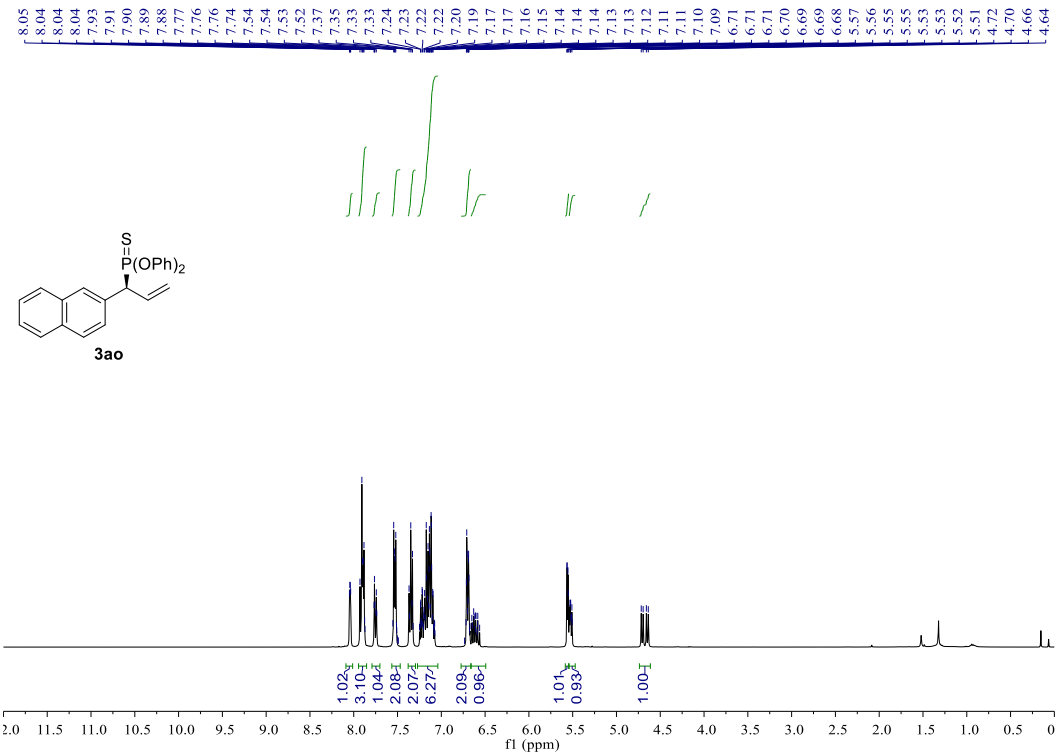
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3an**



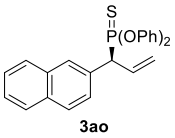
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3an**



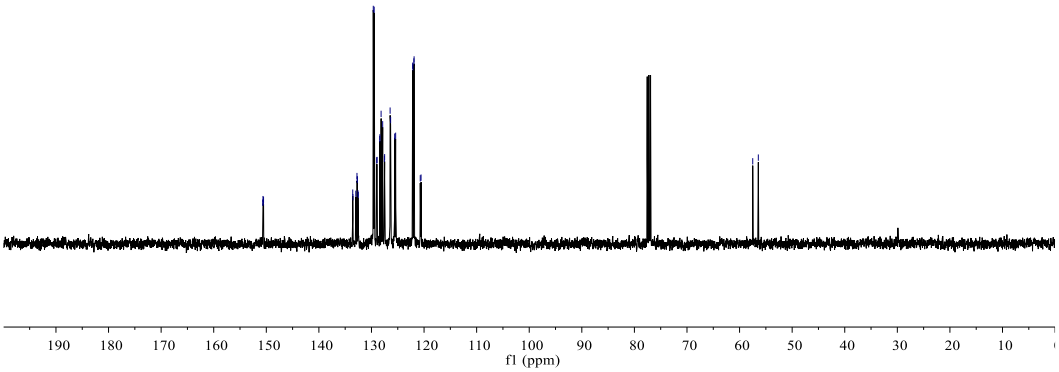
^{1}H NMR (400 MHz, $CDCl_3$) of **3ao**



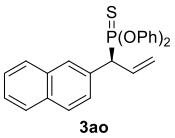
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ao**



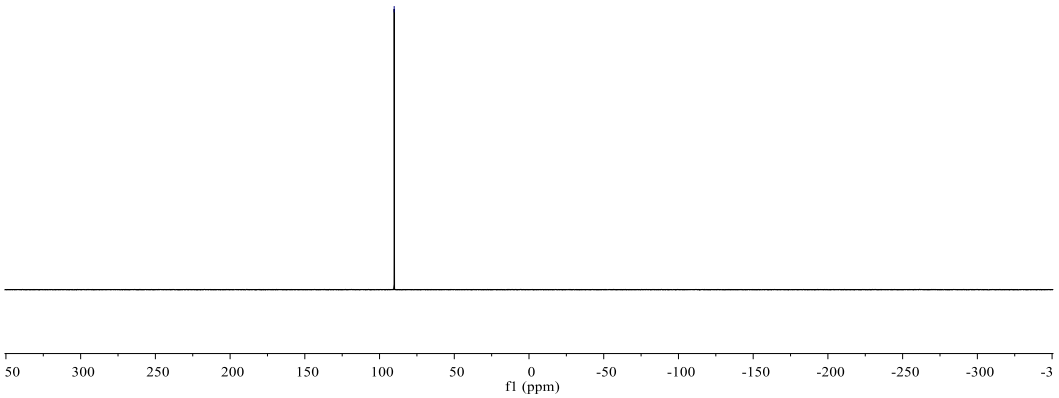
3ao



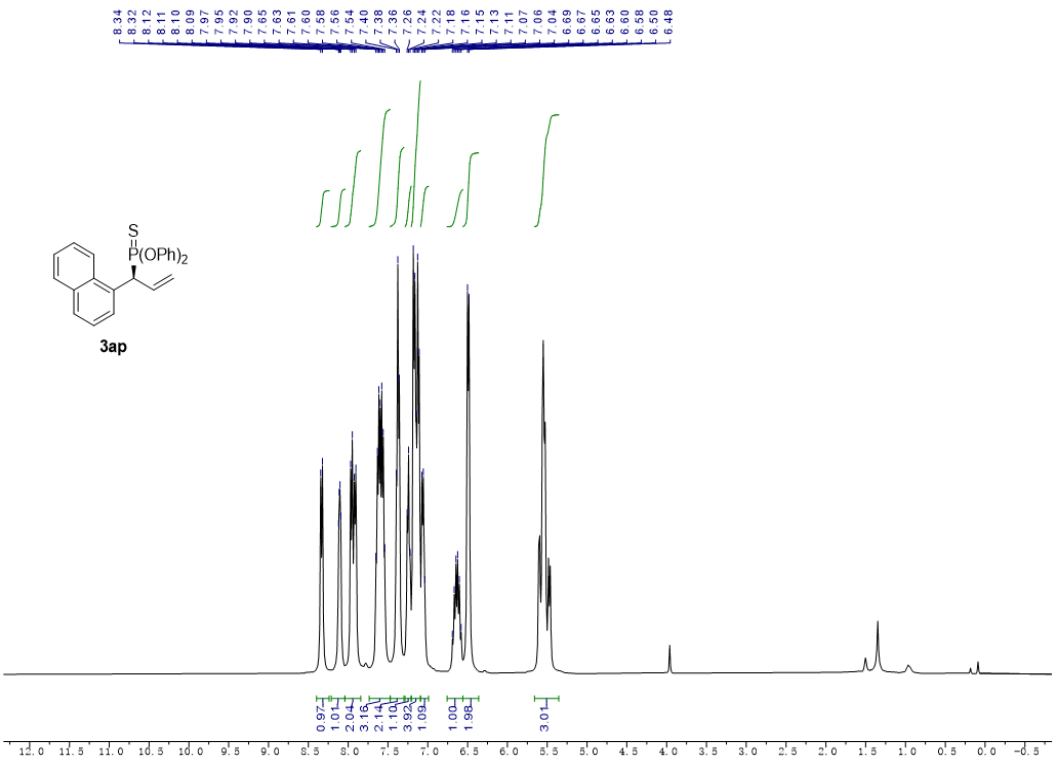
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ao**



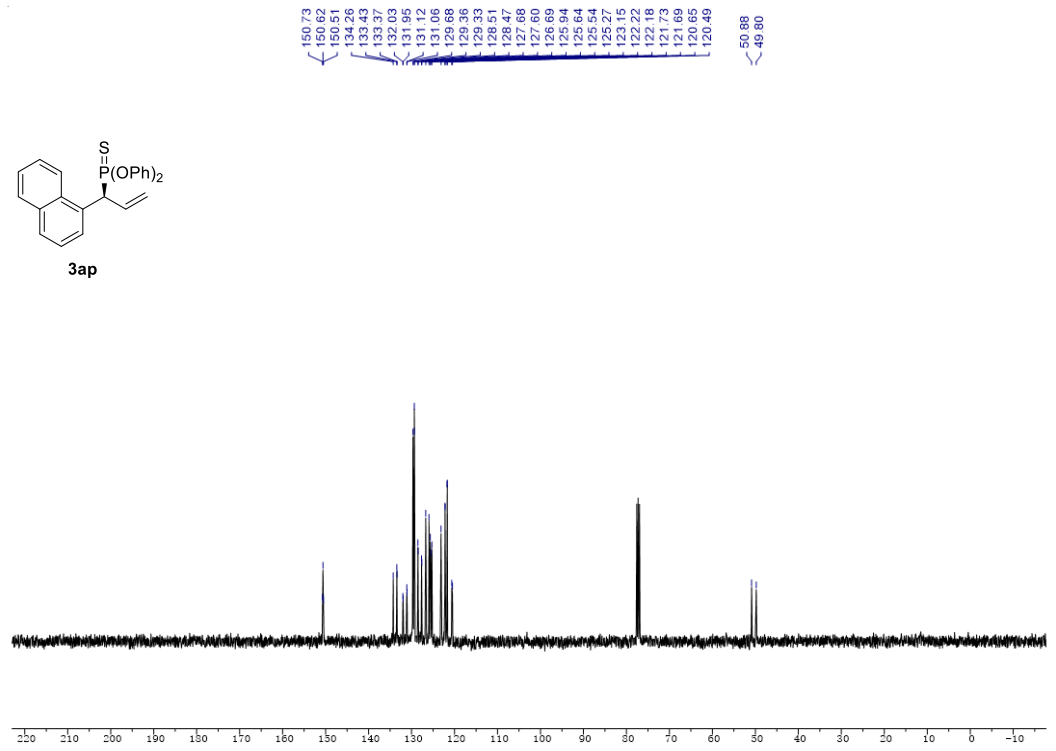
3ao



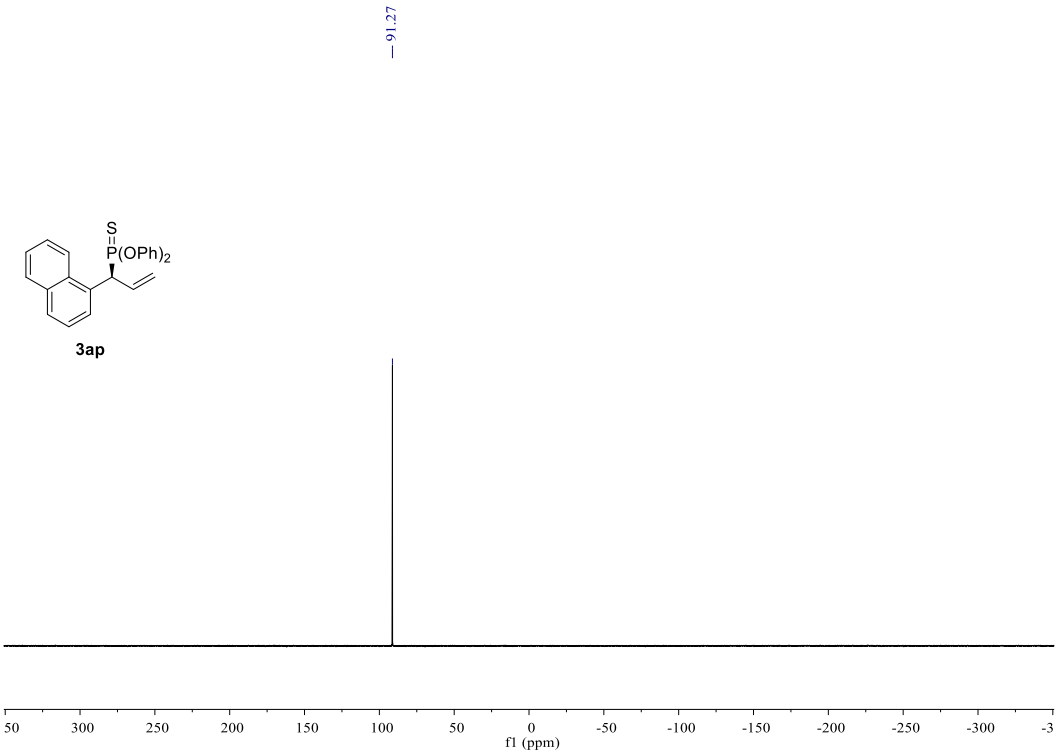
^{1}H NMR (400 MHz, $CDCl_3$) of **3ap**



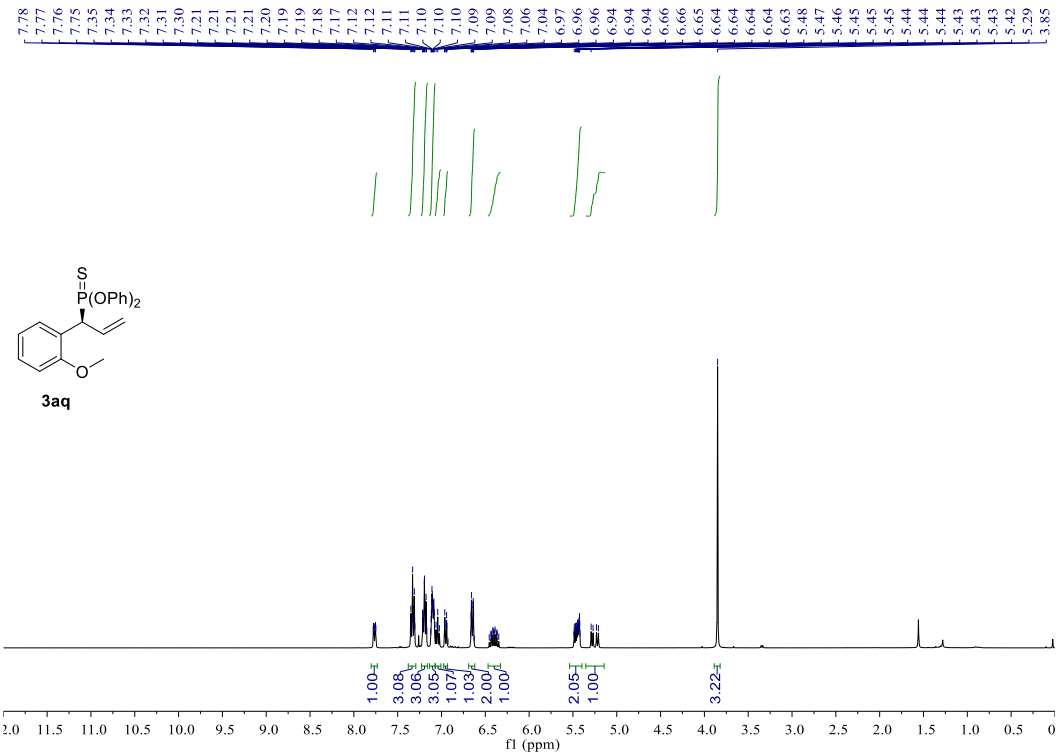
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ap**



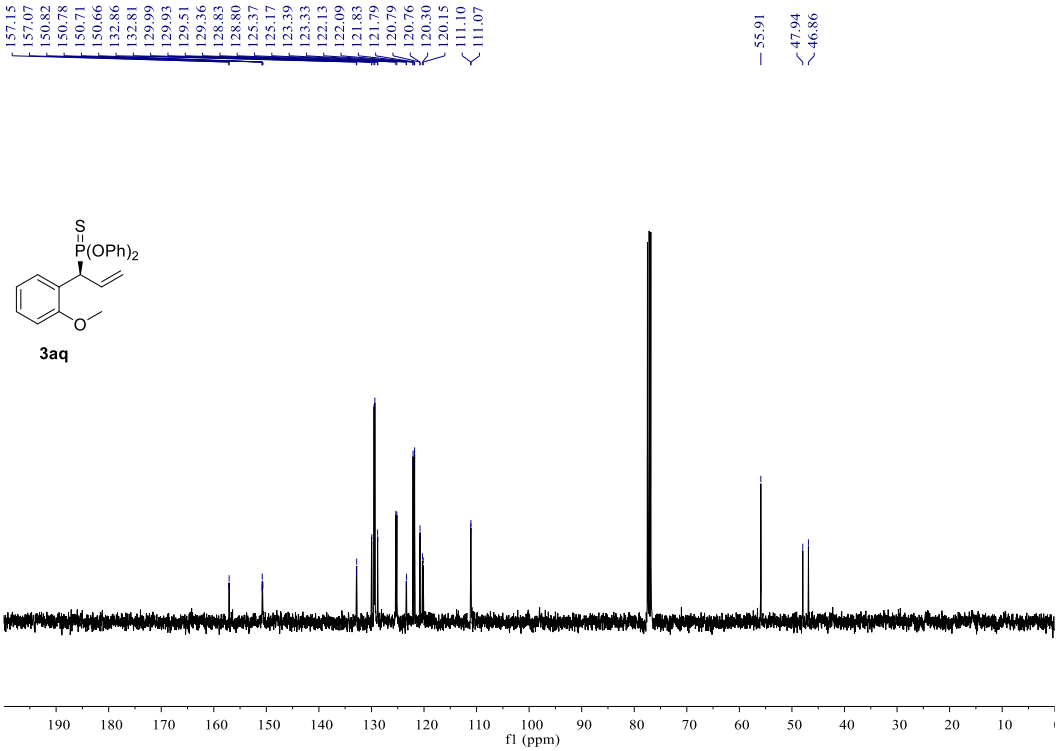
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ap**



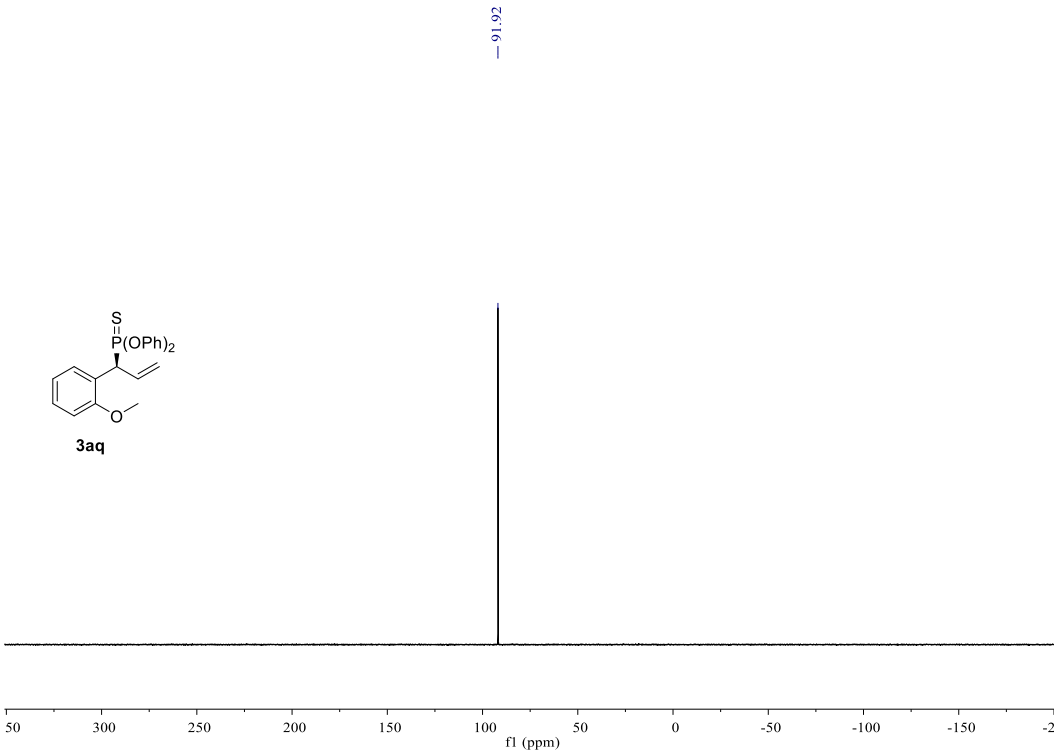
^{1}H NMR (400 MHz, $CDCl_3$) of **3aq**



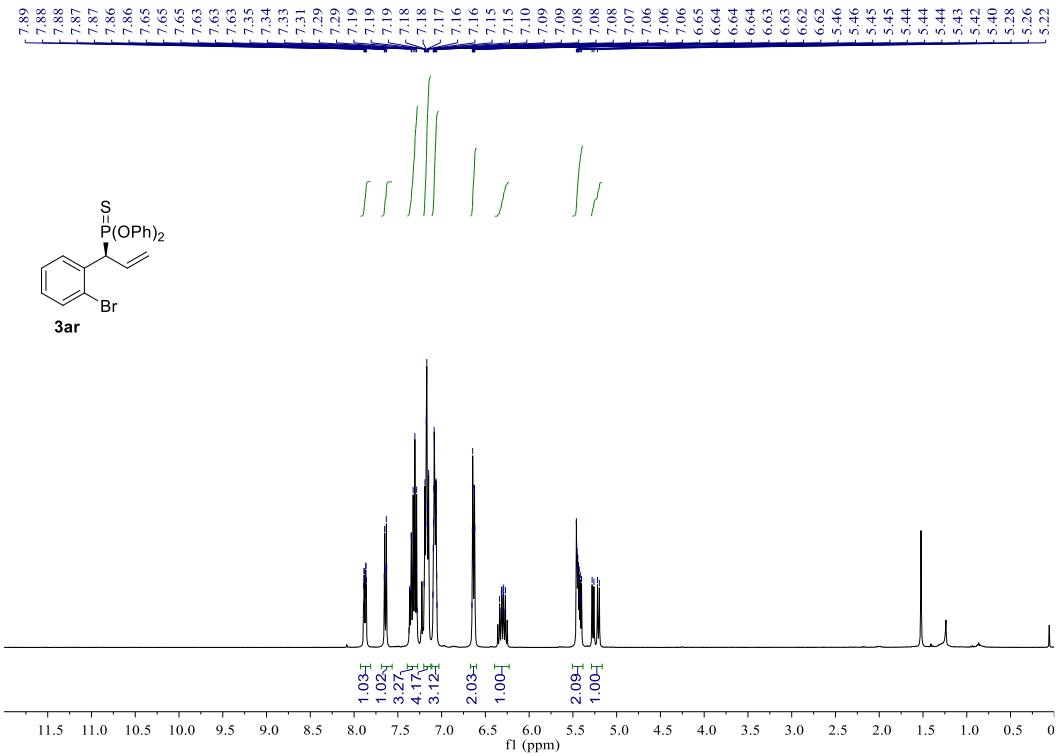
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3aq**



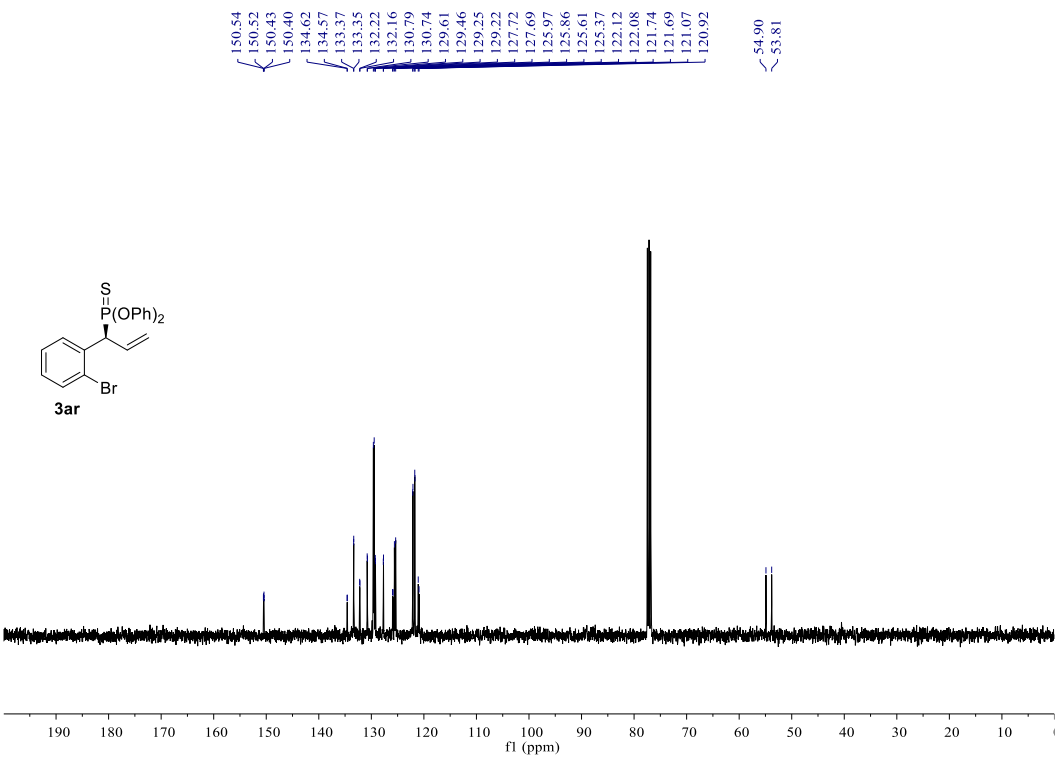
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3aq**



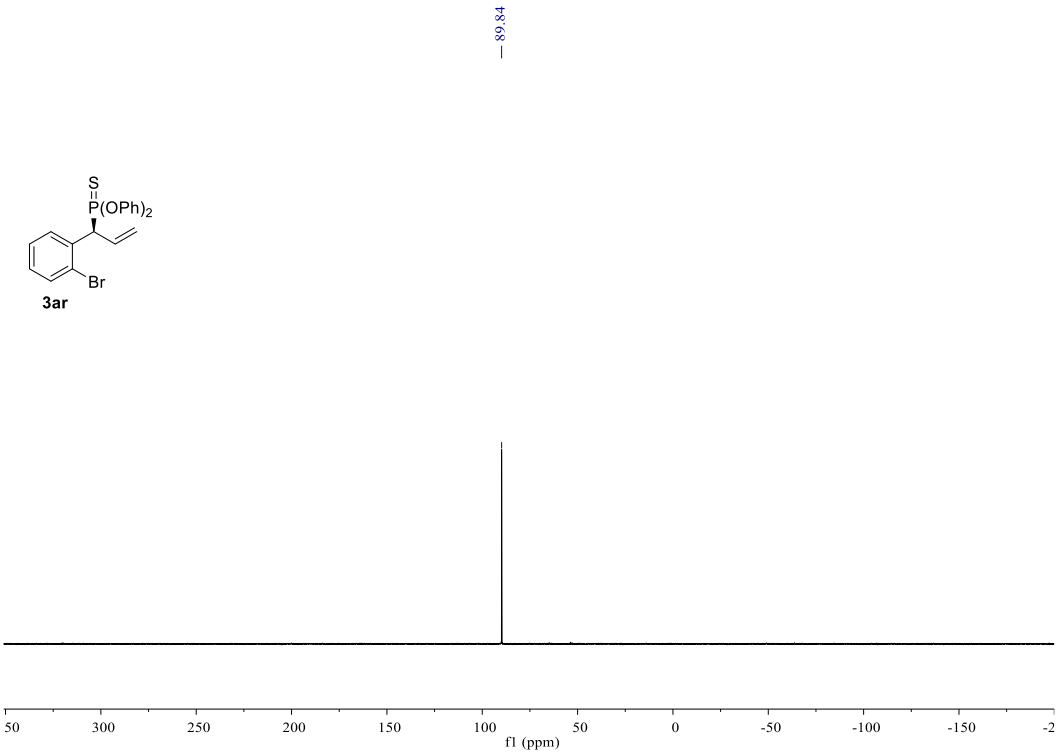
^{1}H NMR (400 MHz, $CDCl_3$) of **3ar**



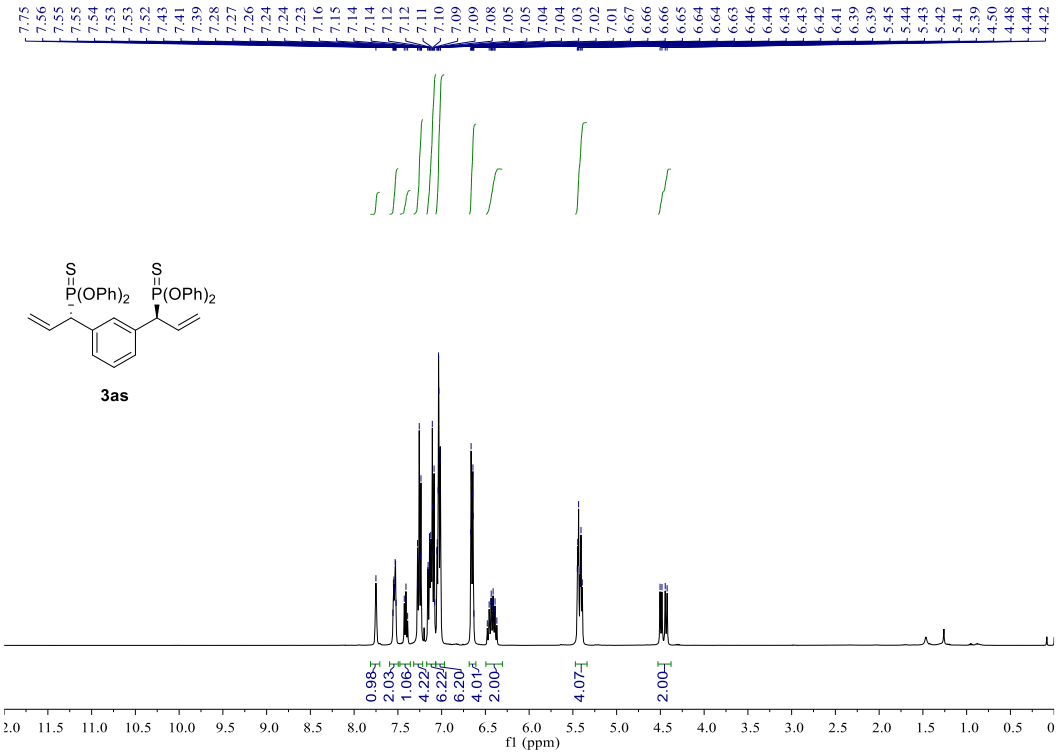
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3ar**



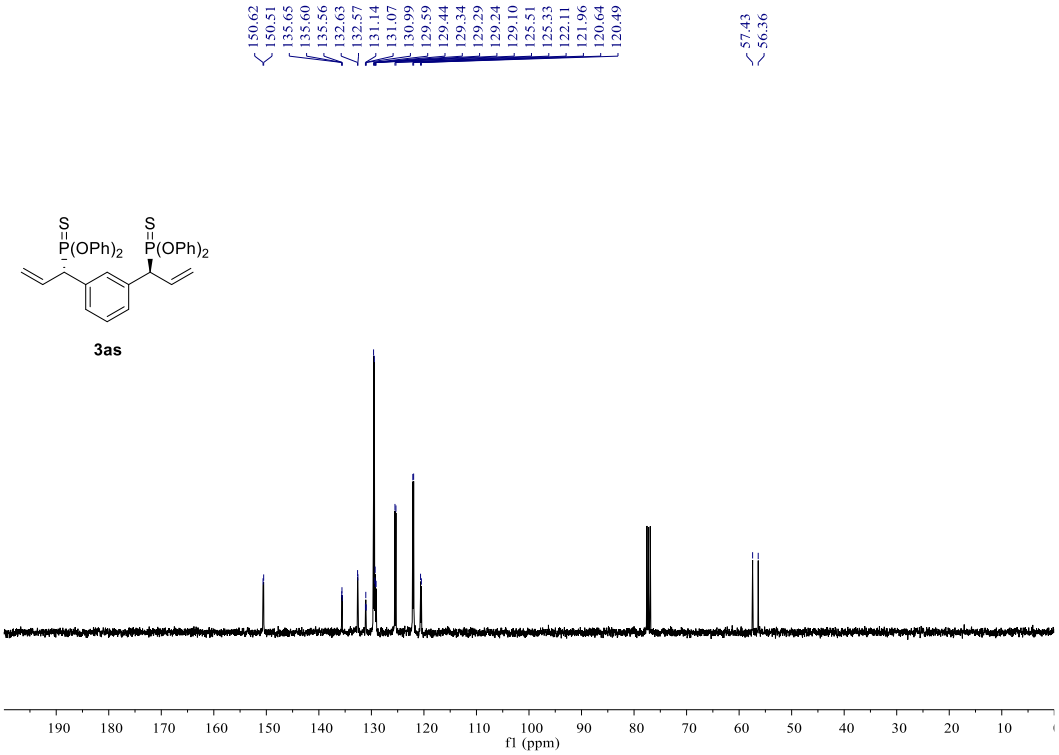
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ar**



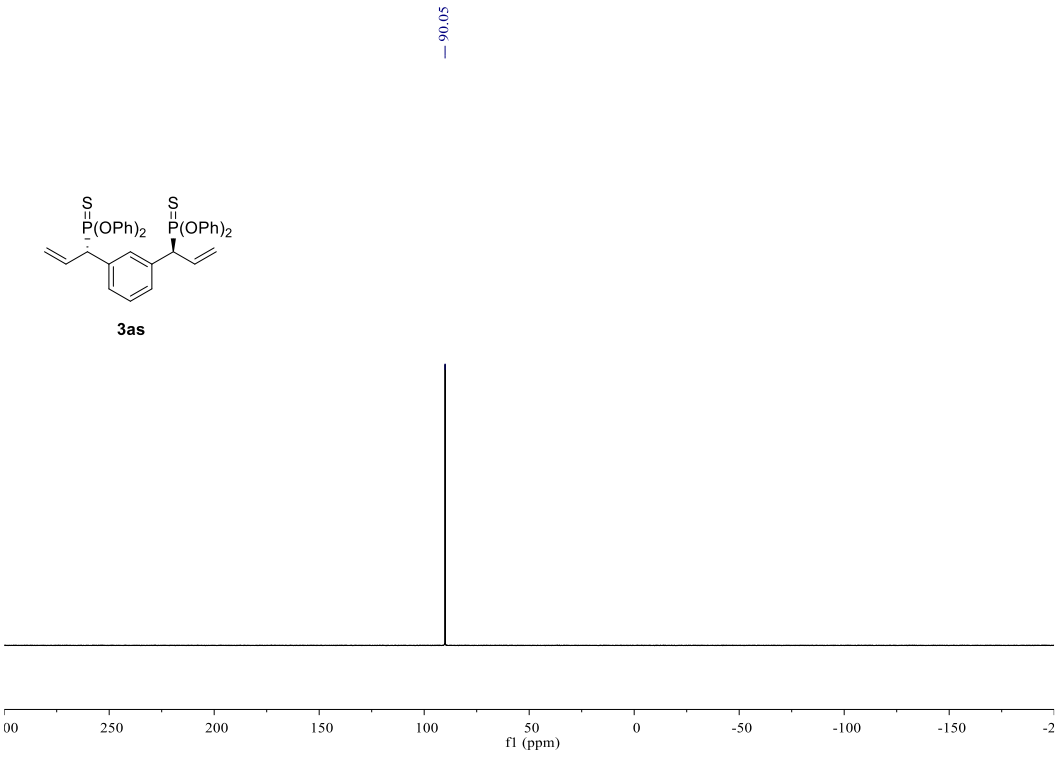
^{1}H NMR (400 MHz, $CDCl_3$) of **3as**



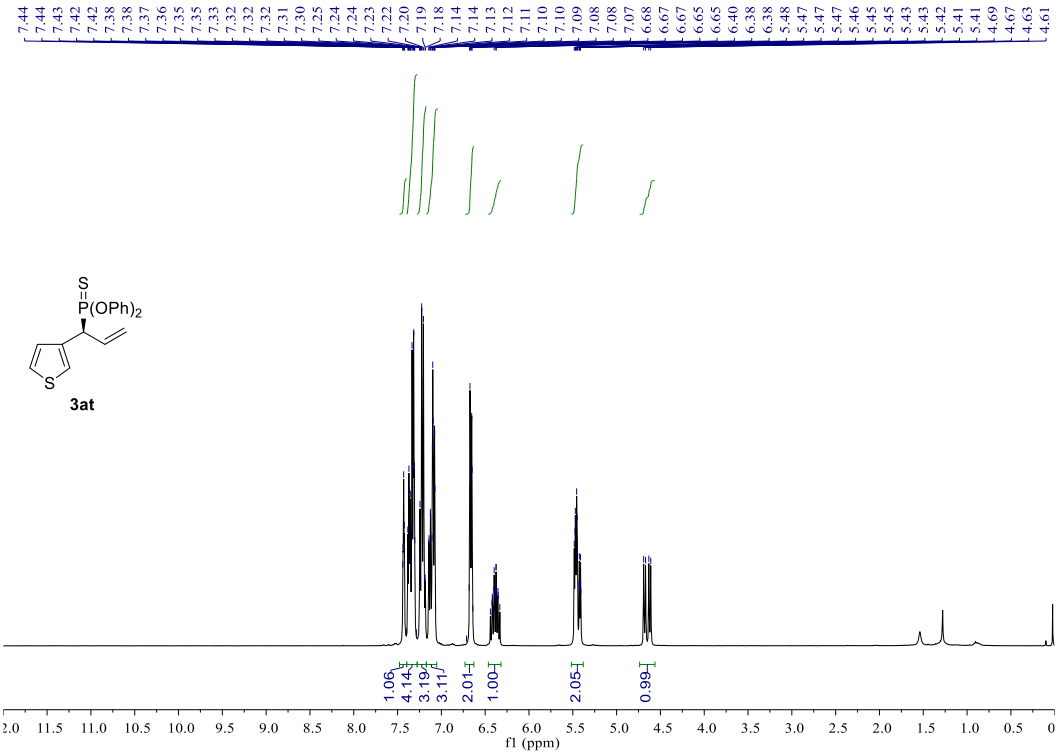
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3as**



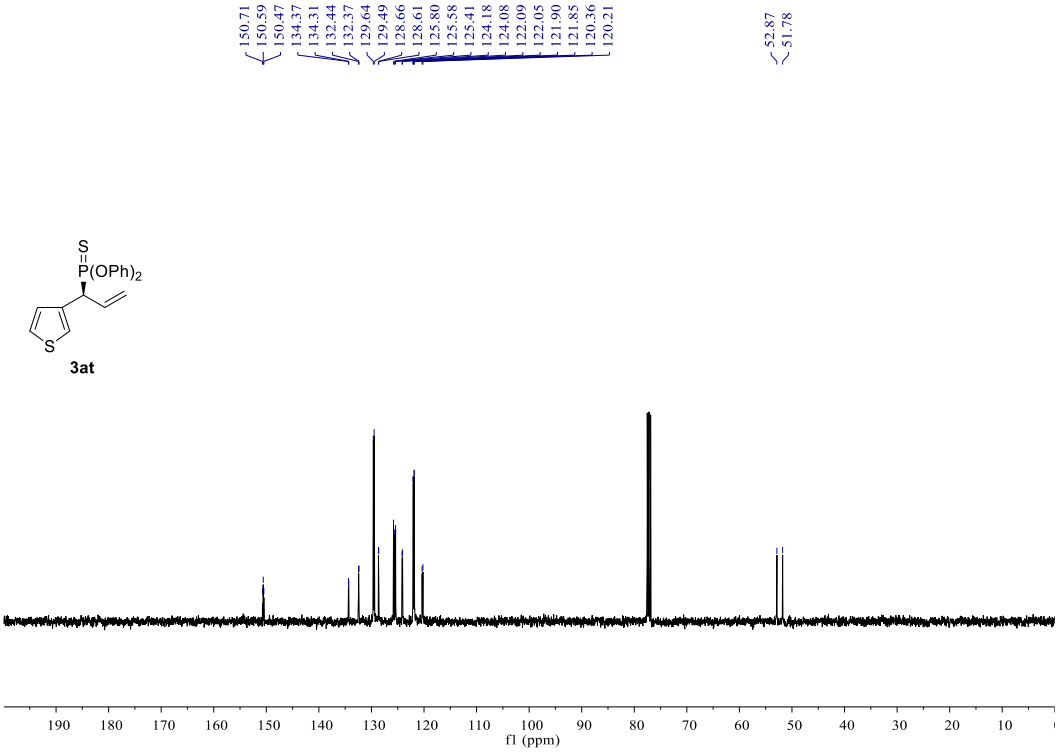
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3as**



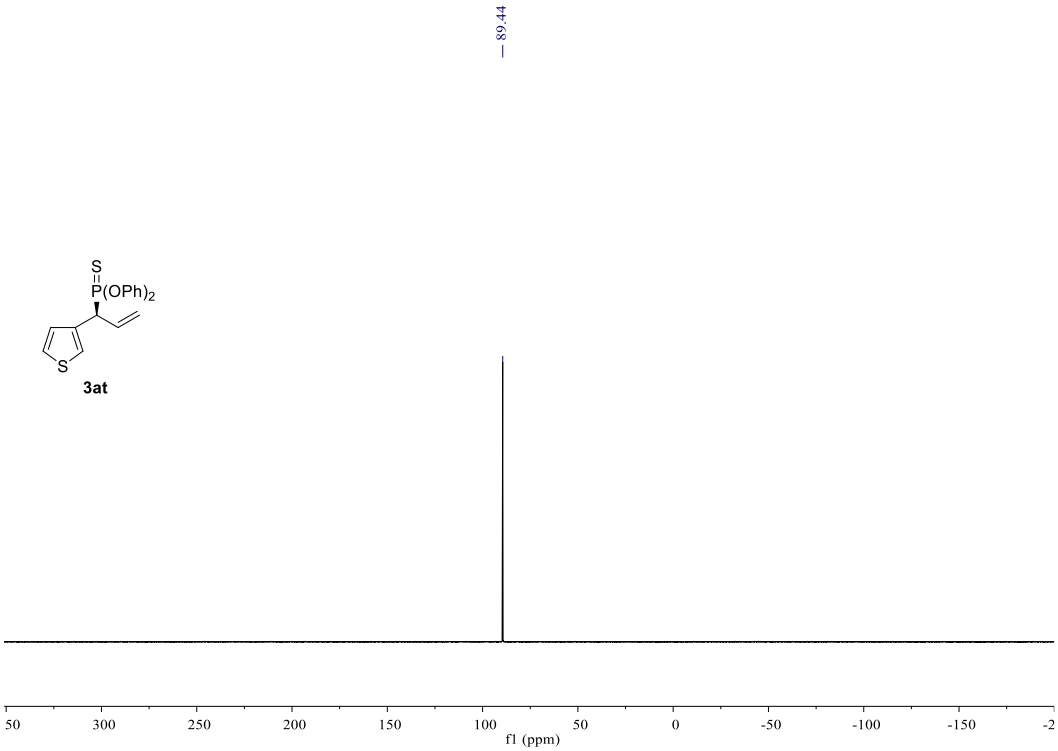
^{1}H NMR (400 MHz, $CDCl_3$) of **3at**



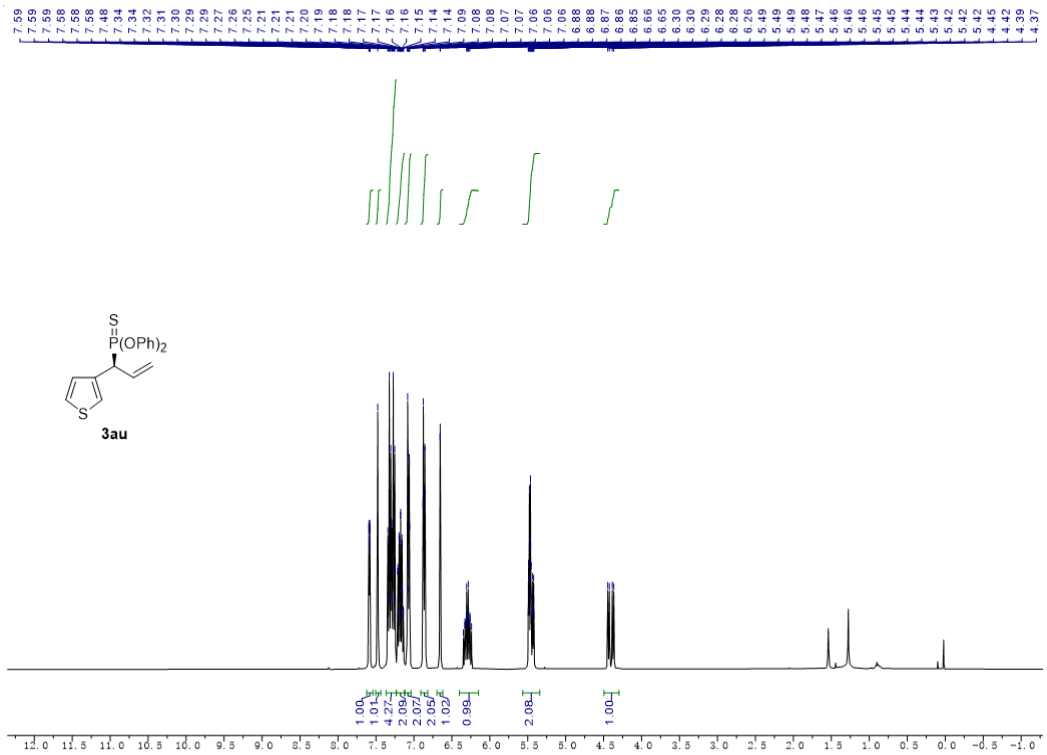
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3at**



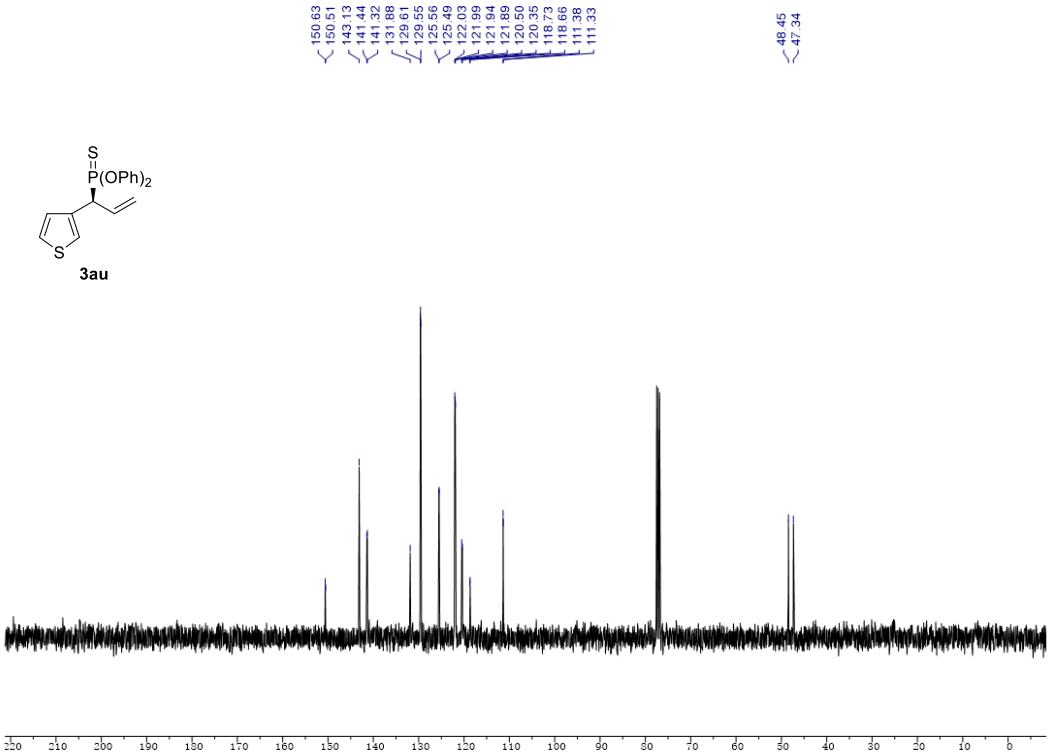
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3at**



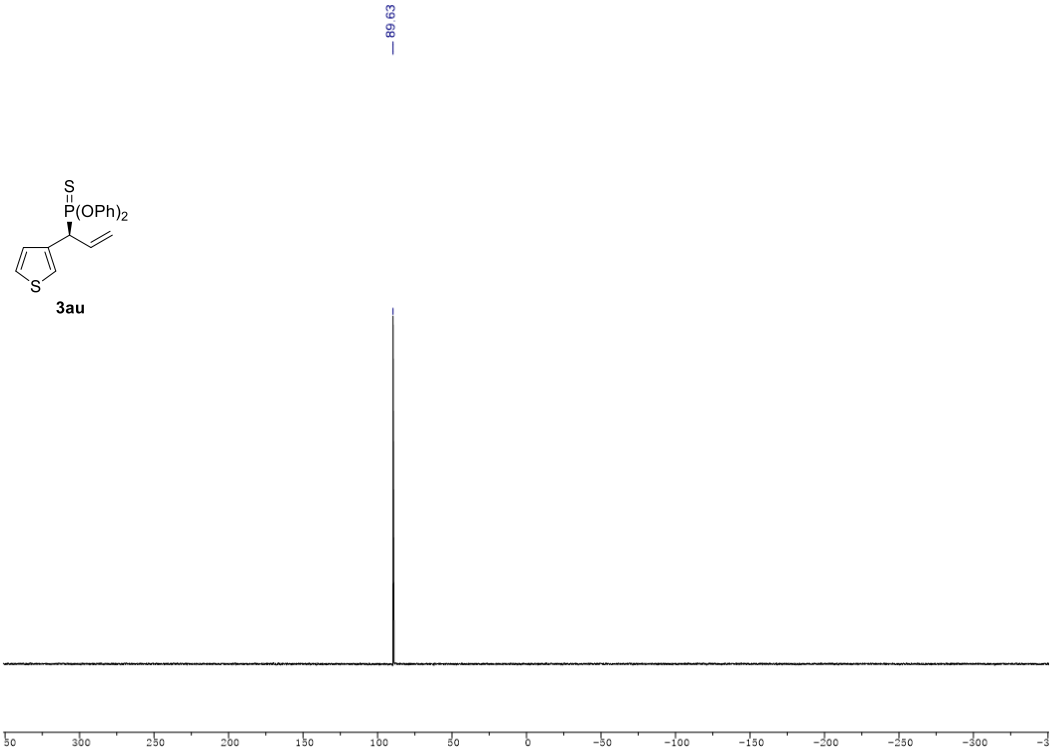
^{1}H NMR (400 MHz, $CDCl_3$) of **3au**



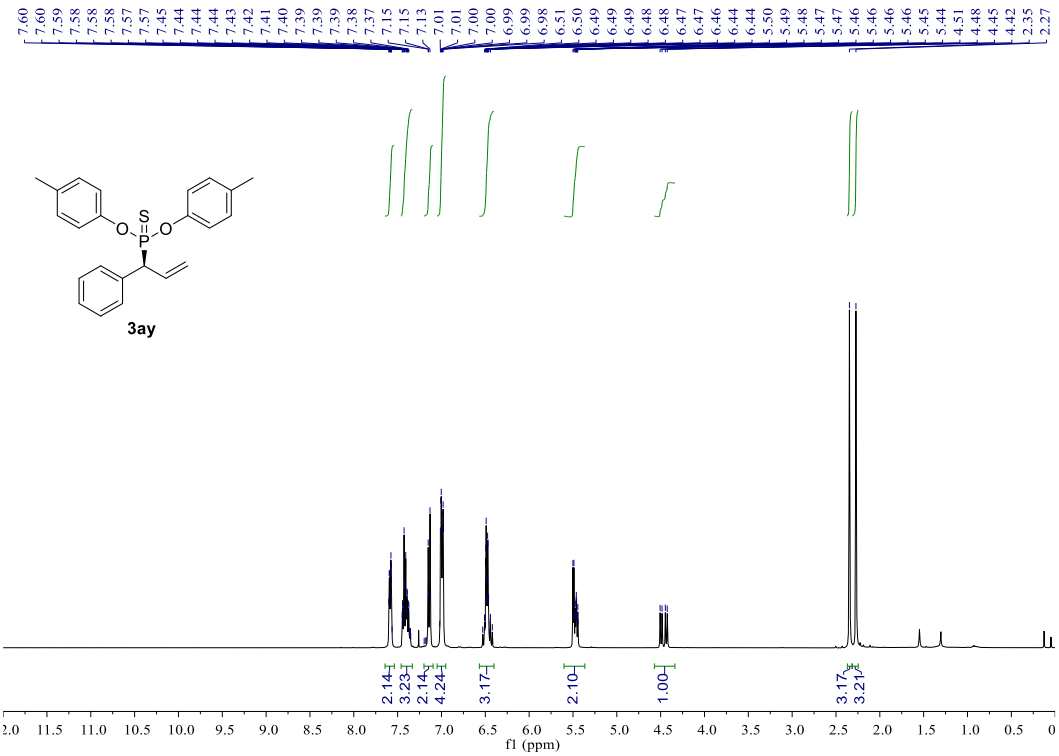
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3au**



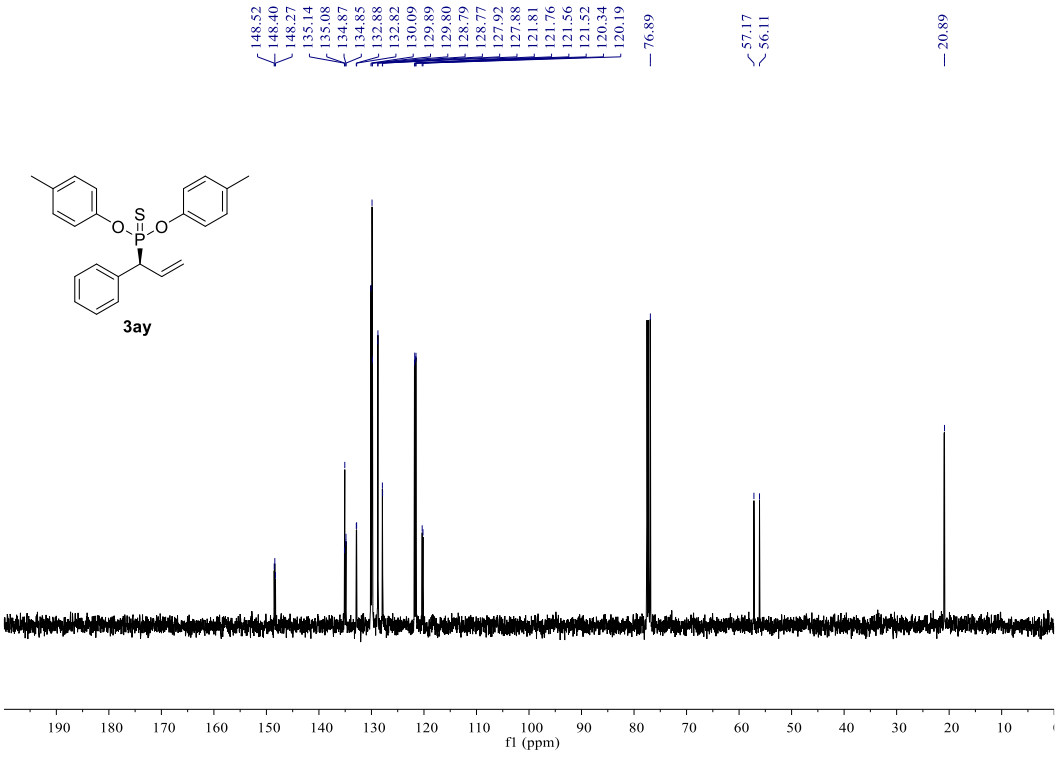
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3au**



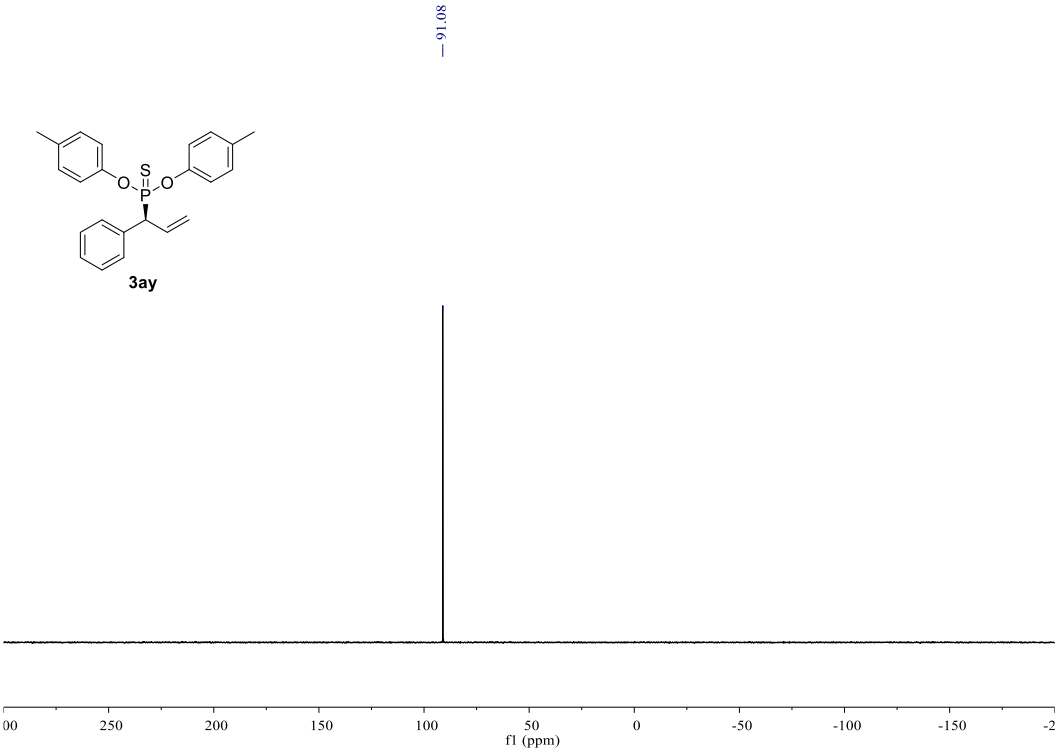
^{1}H NMR (400 MHz, $CDCl_3$) of **3ay**



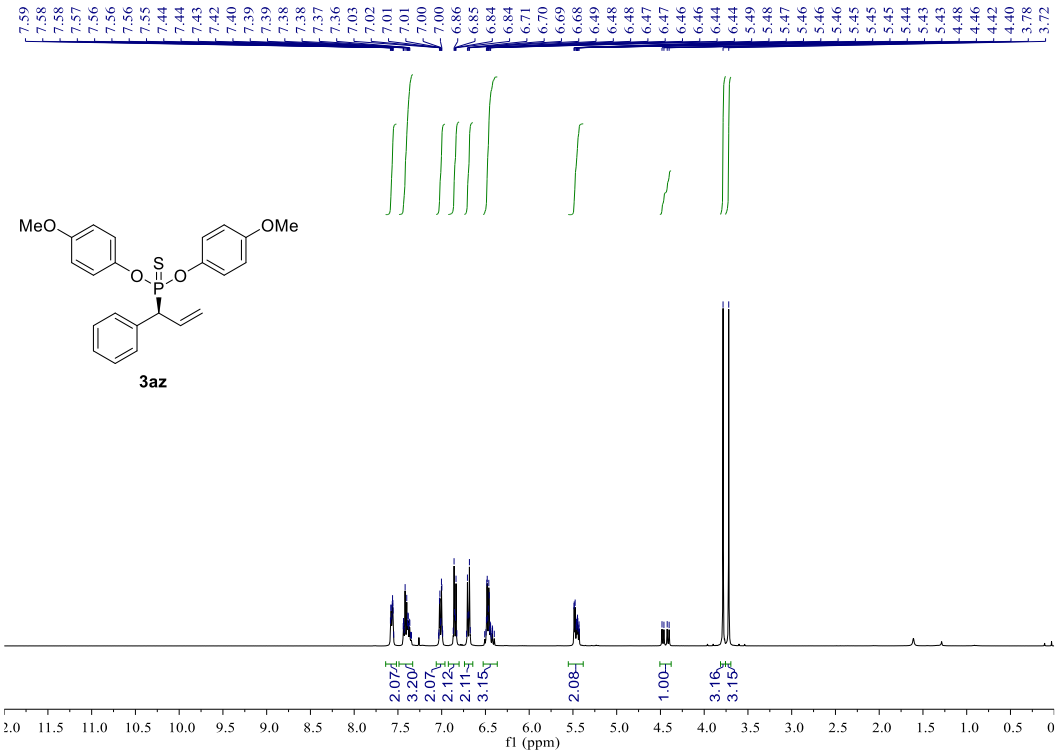
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3ay**



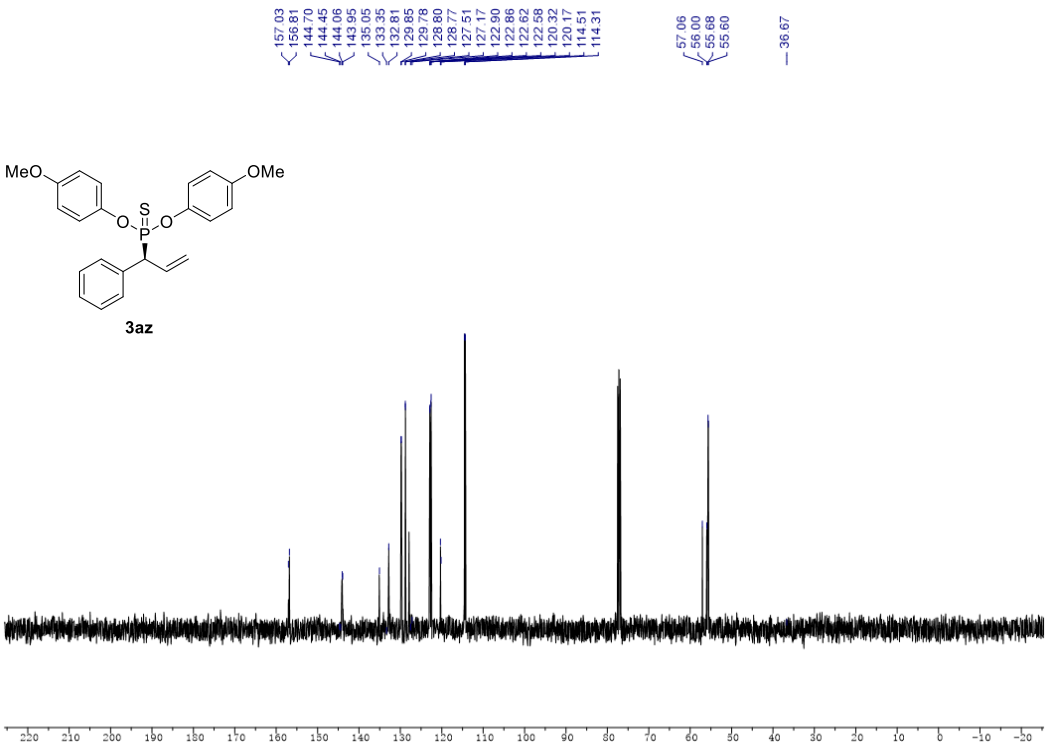
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ay**



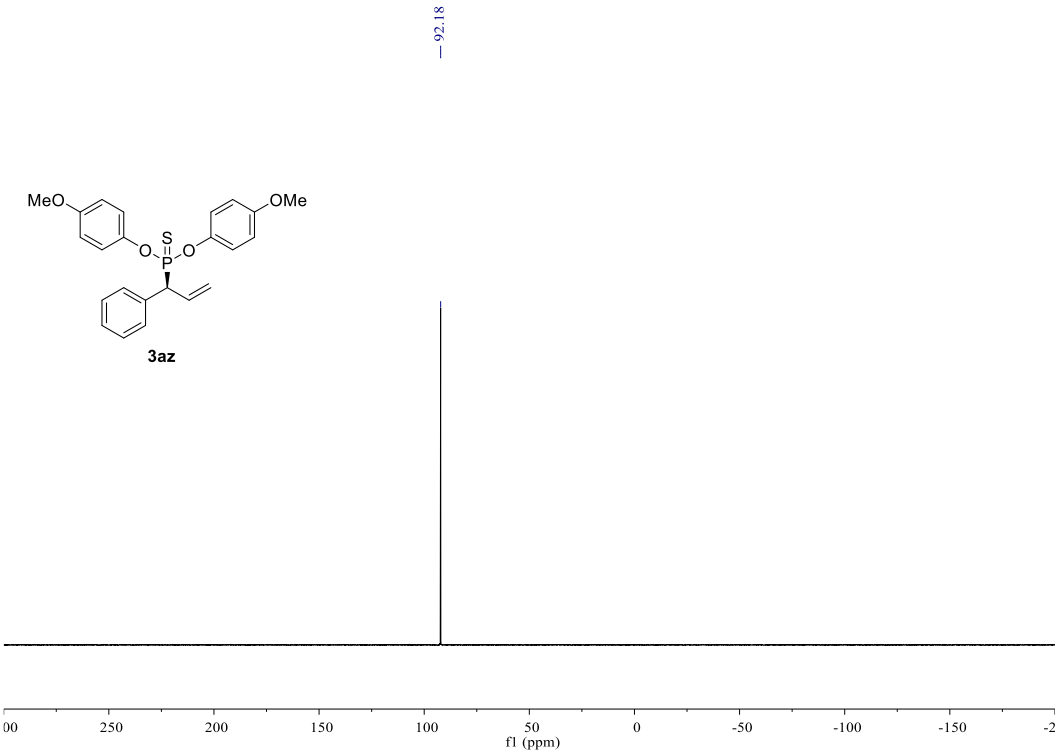
^{1}H NMR (400 MHz, $CDCl_3$) of **3az**



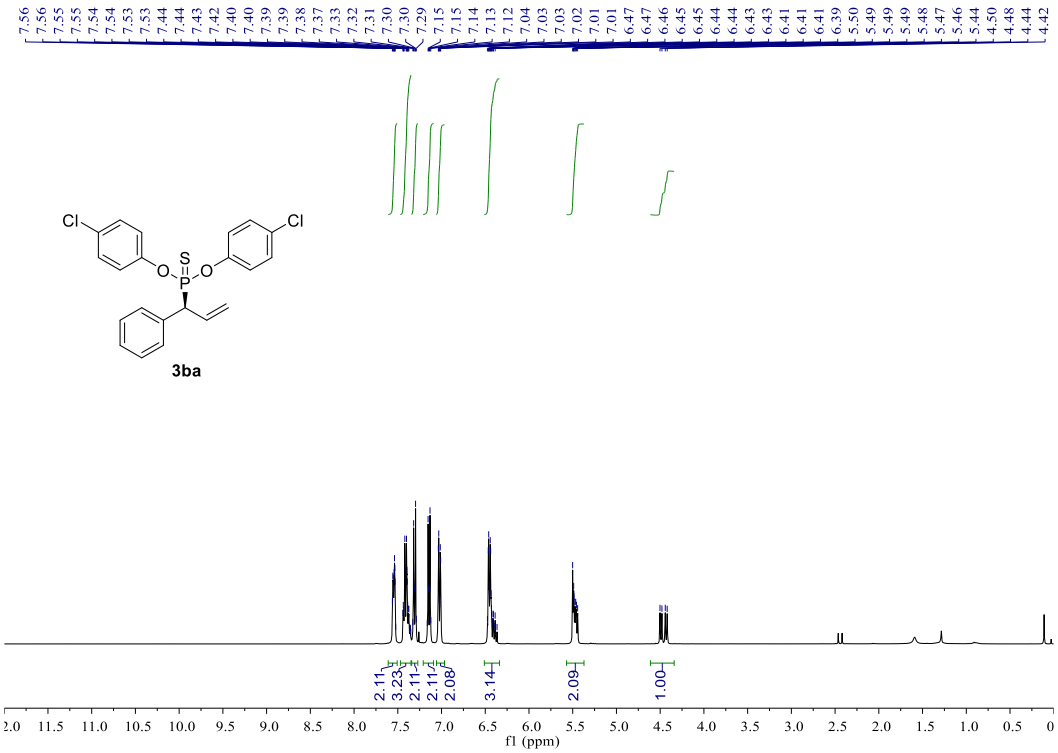
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3az**



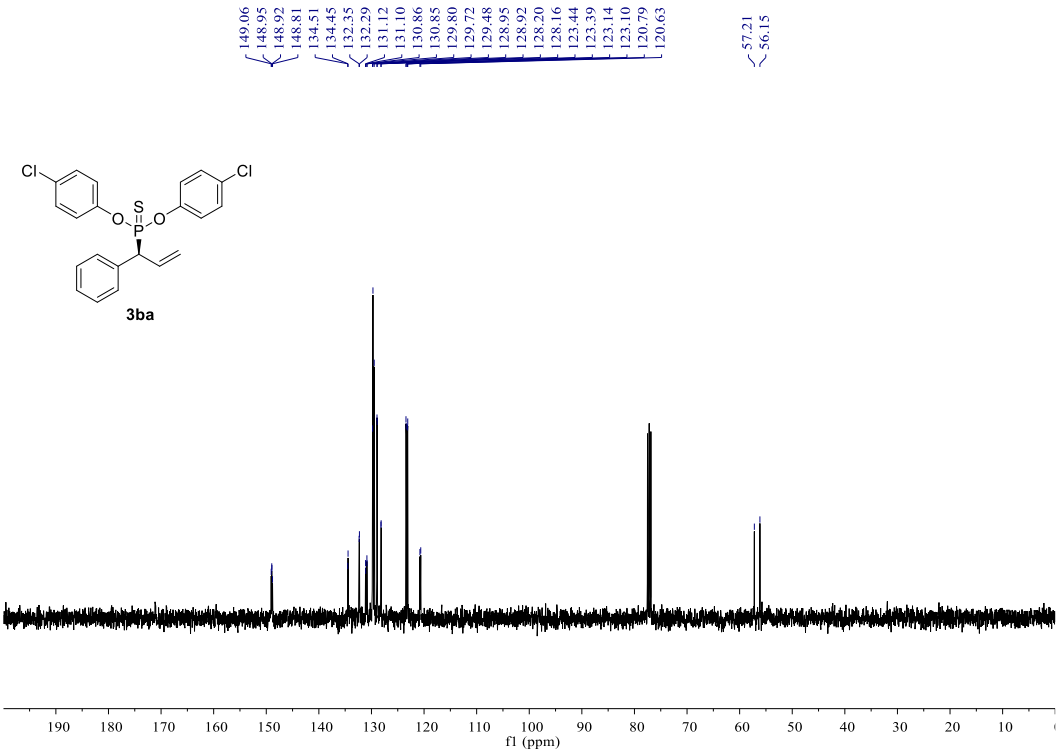
$^{13}P\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3az**



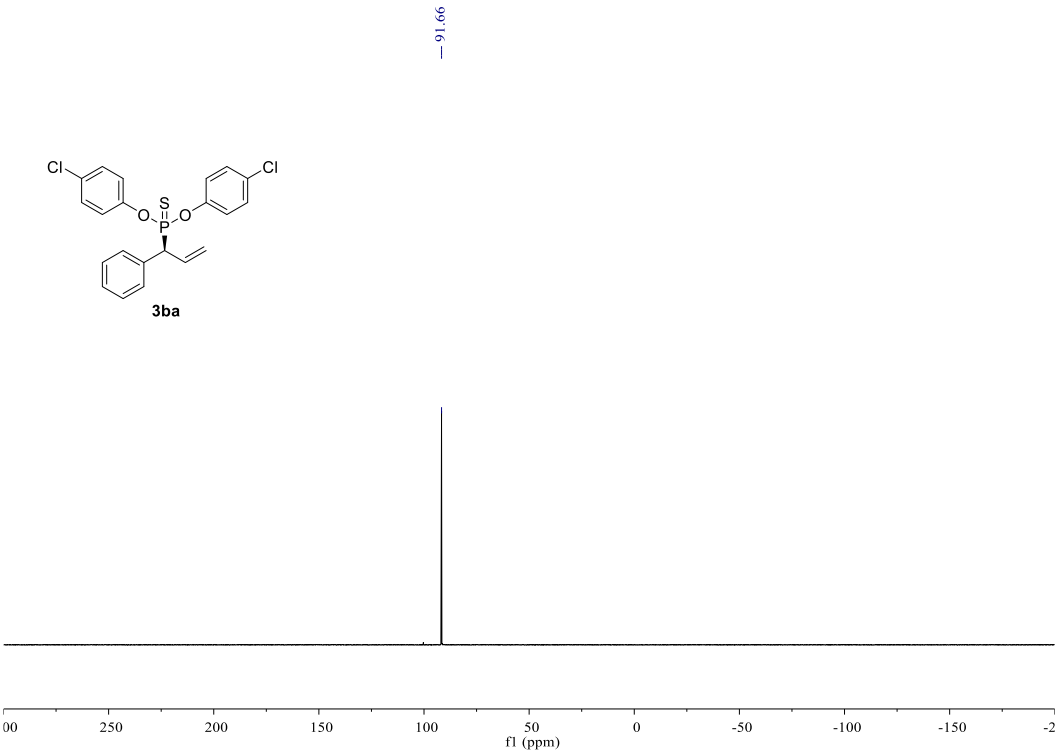
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



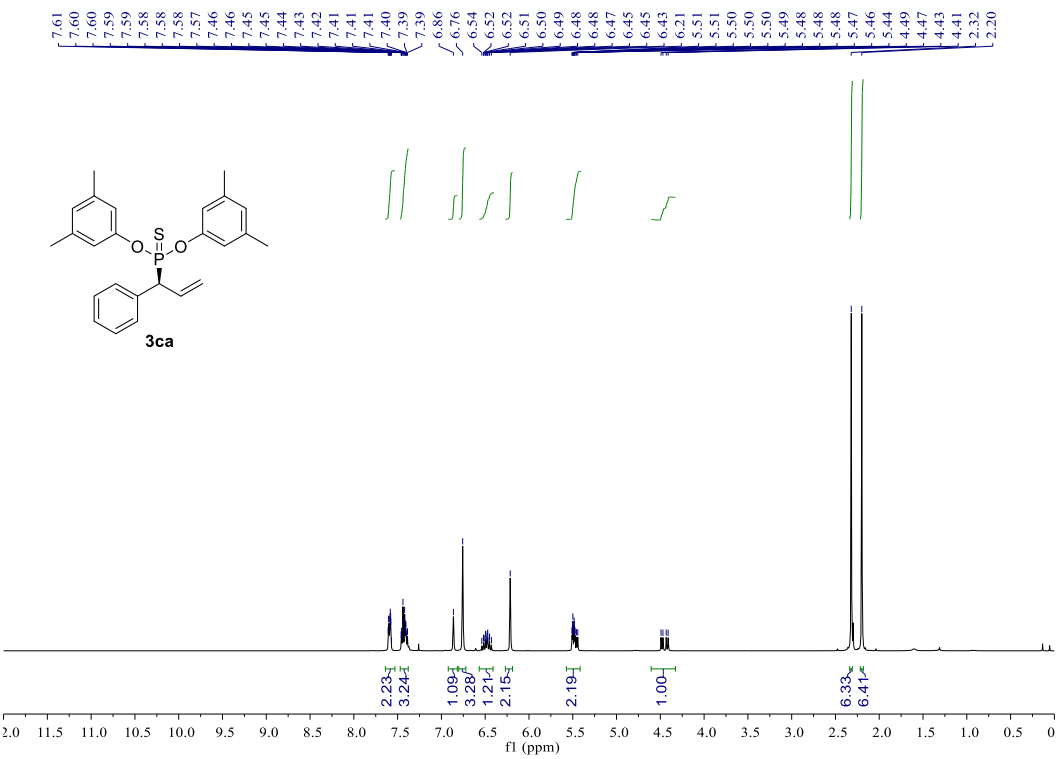
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3ba**



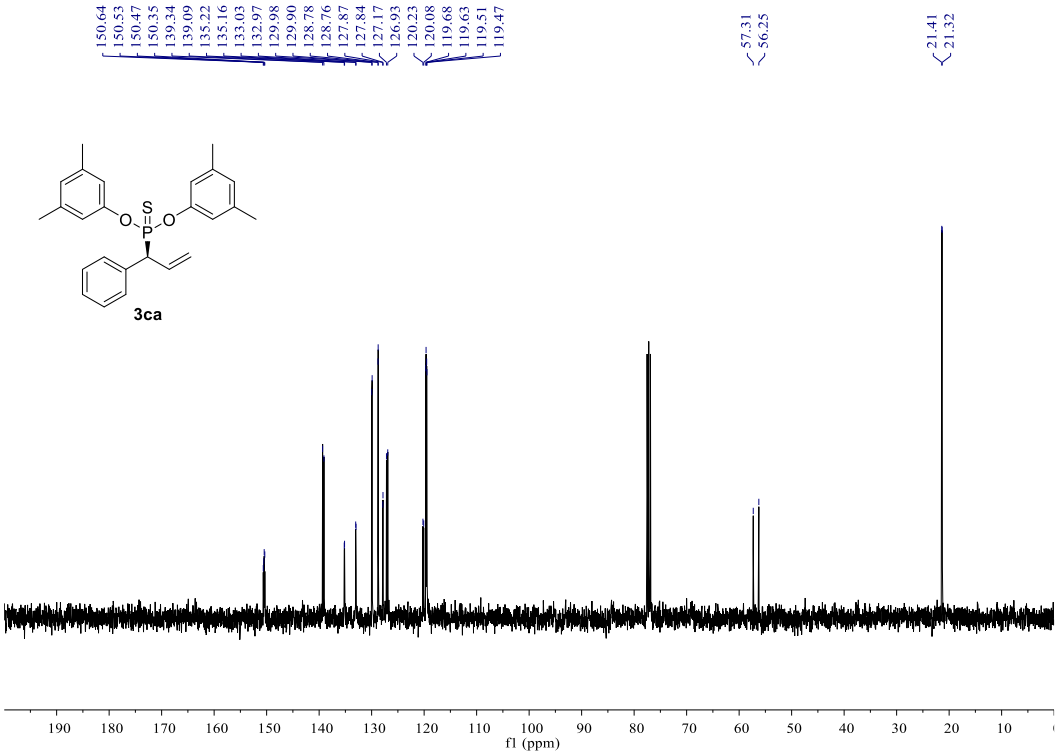
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ba**



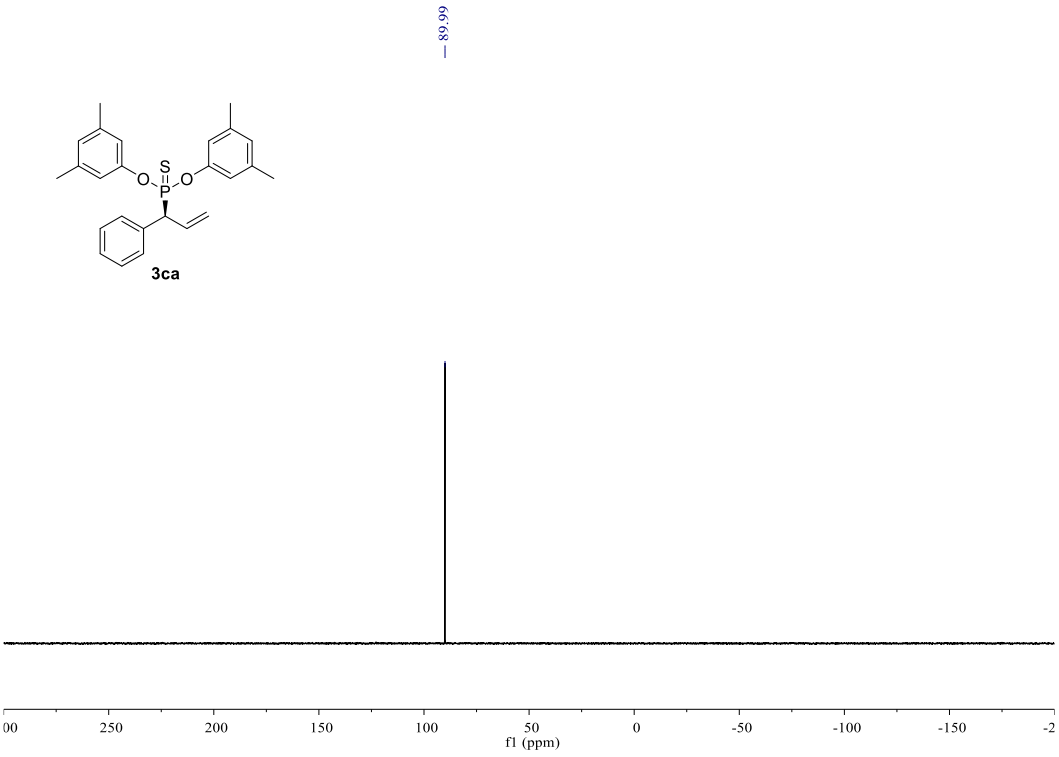
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



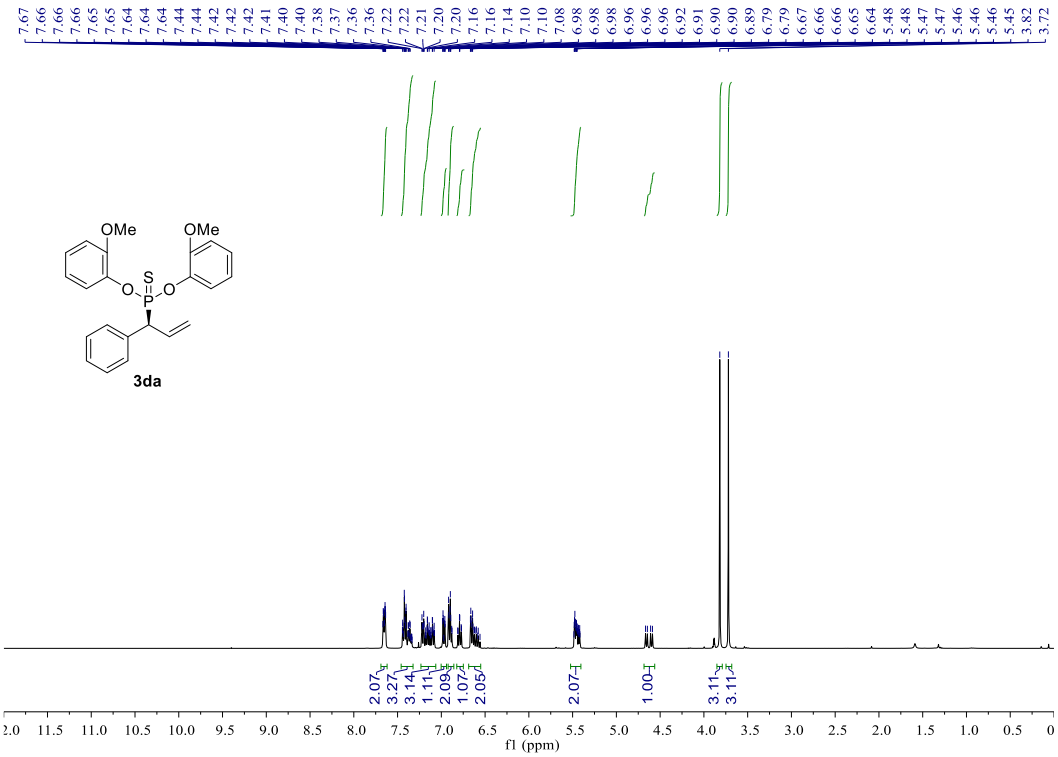
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3ca**



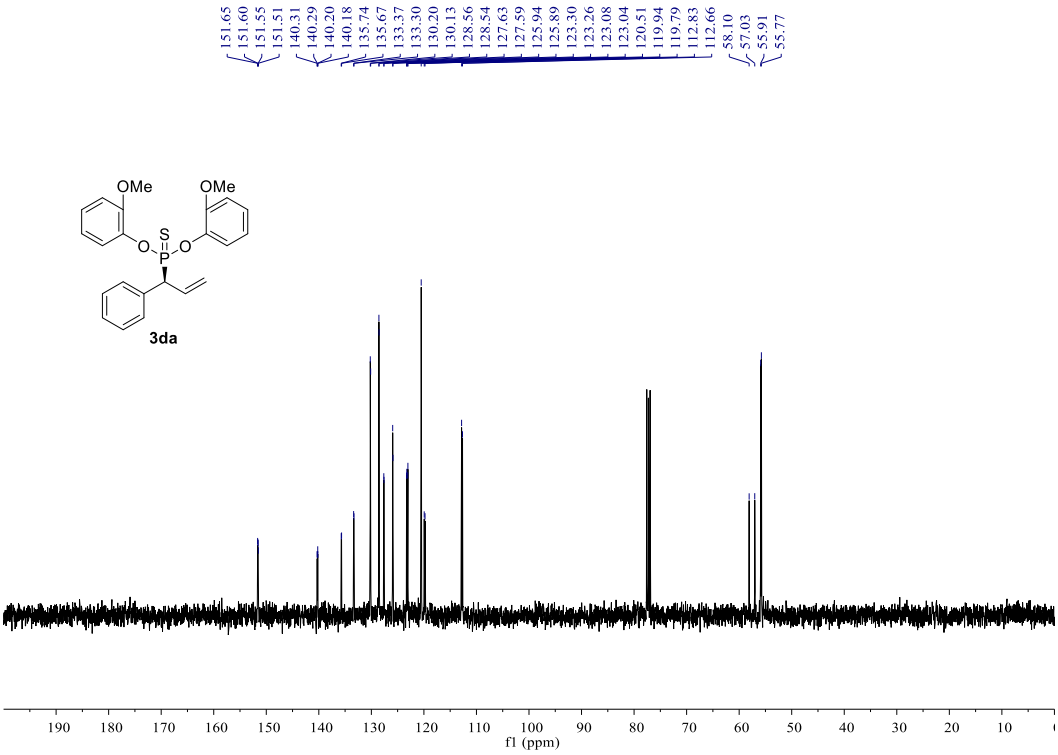
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3ca**



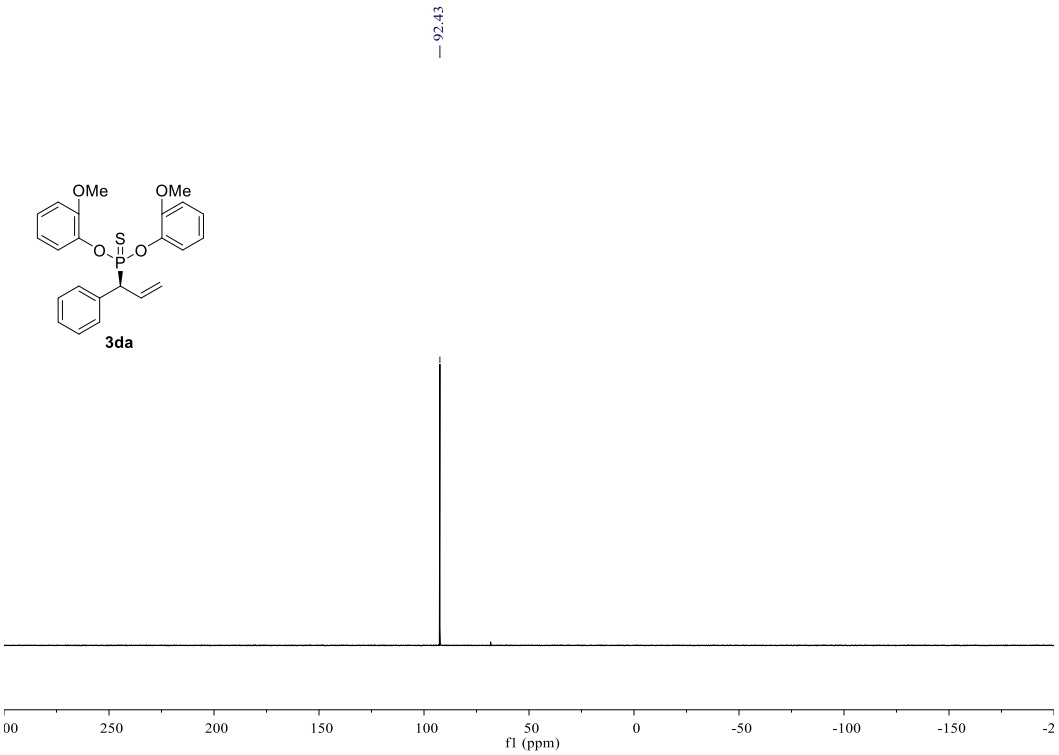
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



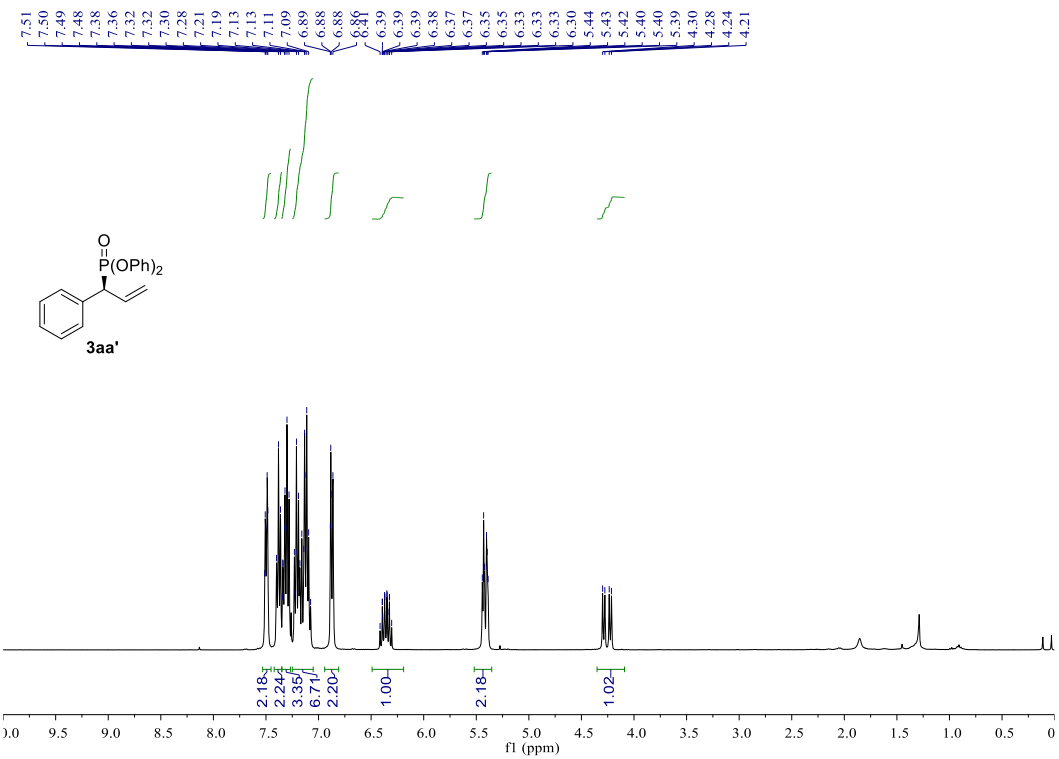
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3da**



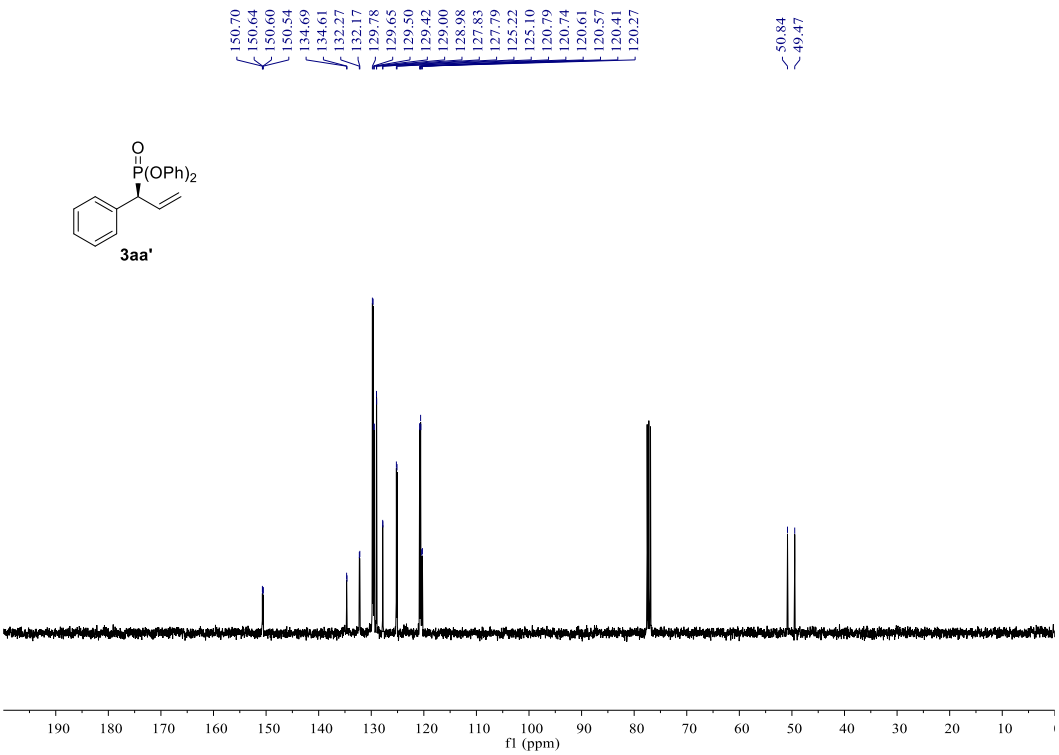
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3da**



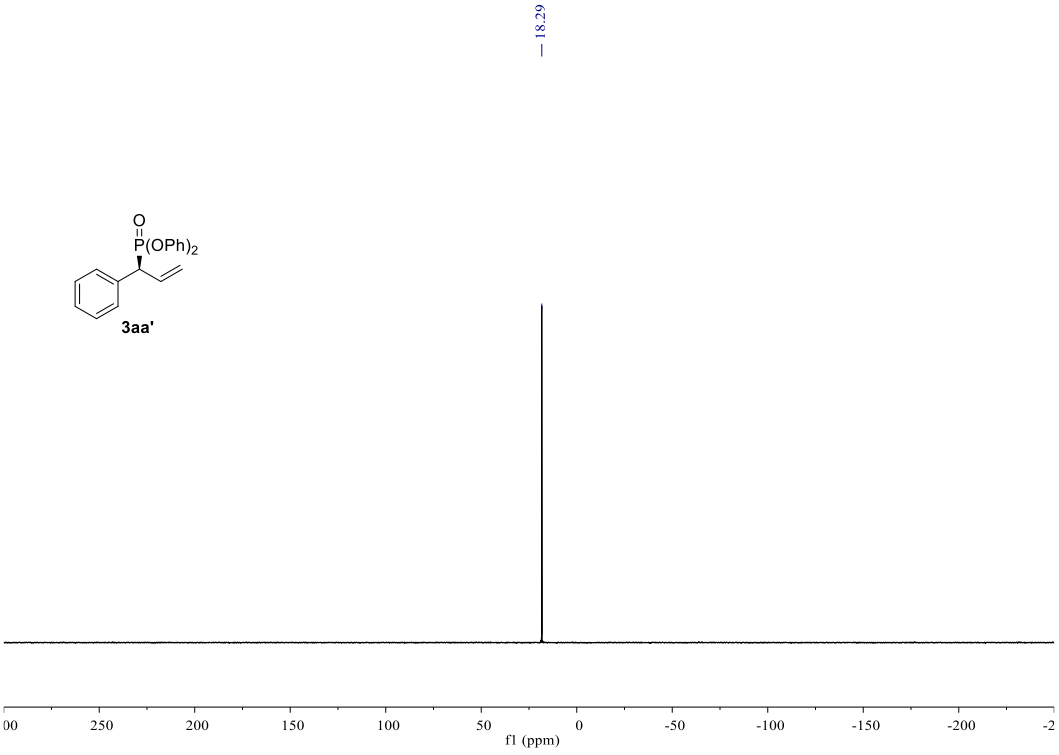
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa′**



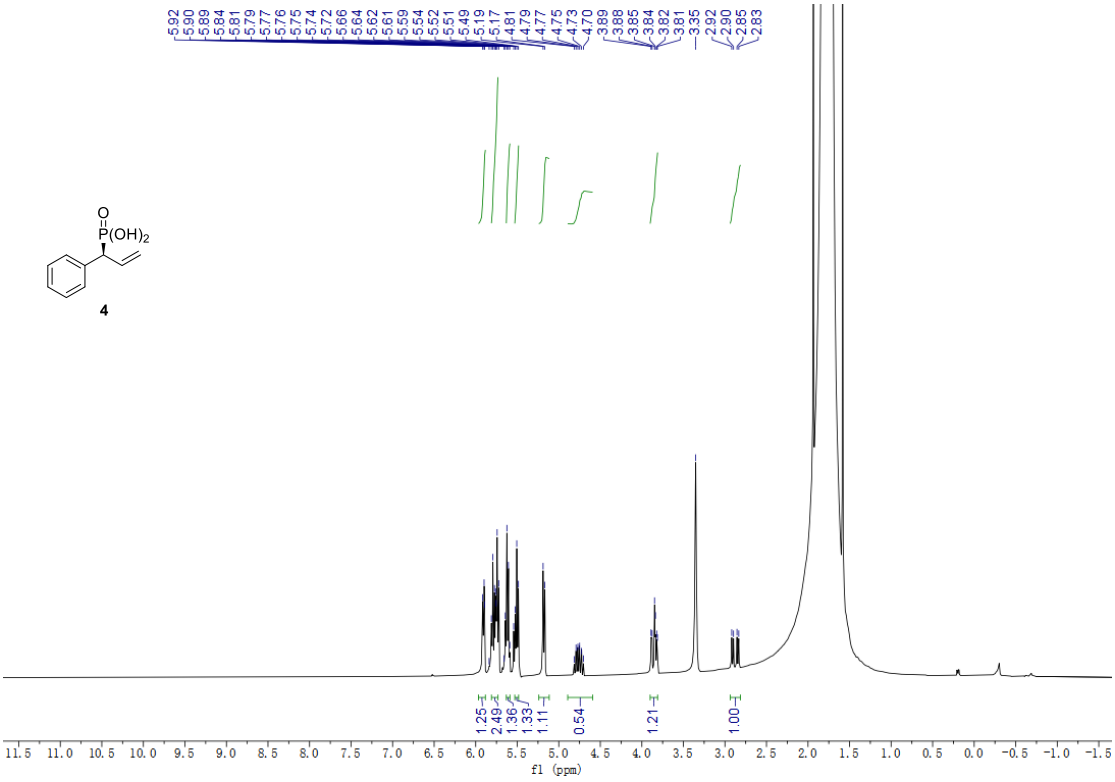
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3aa′**



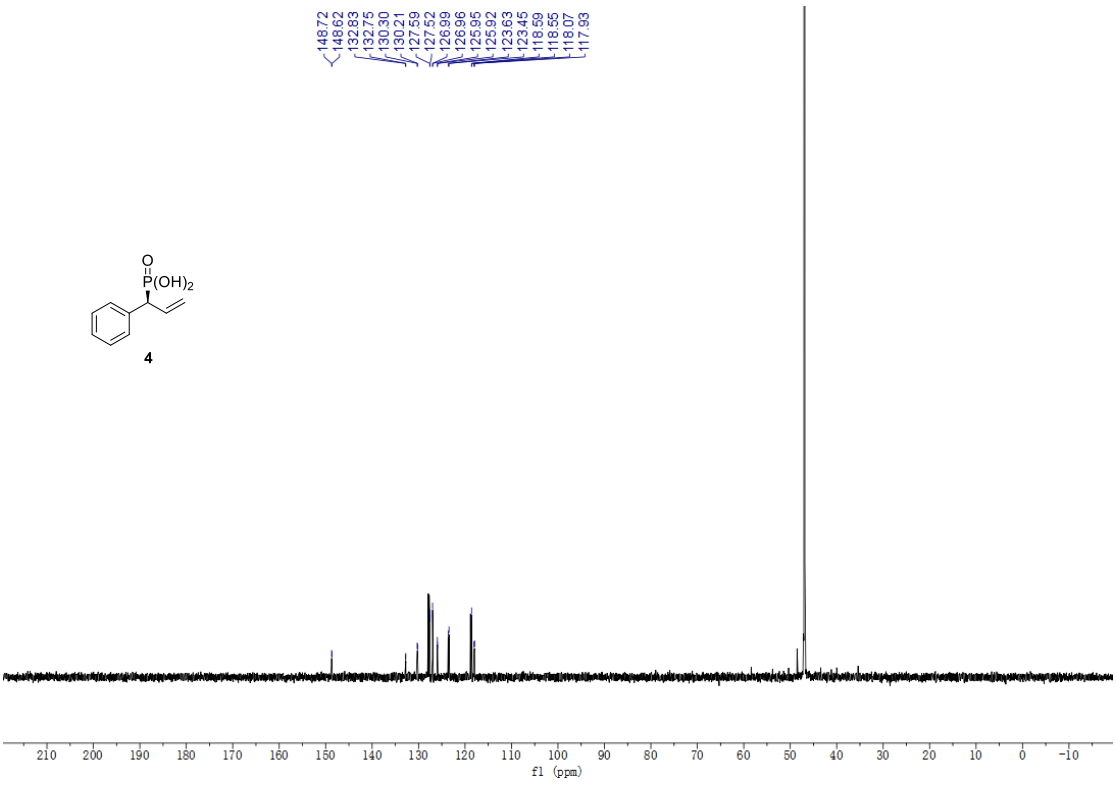
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **3aa′**



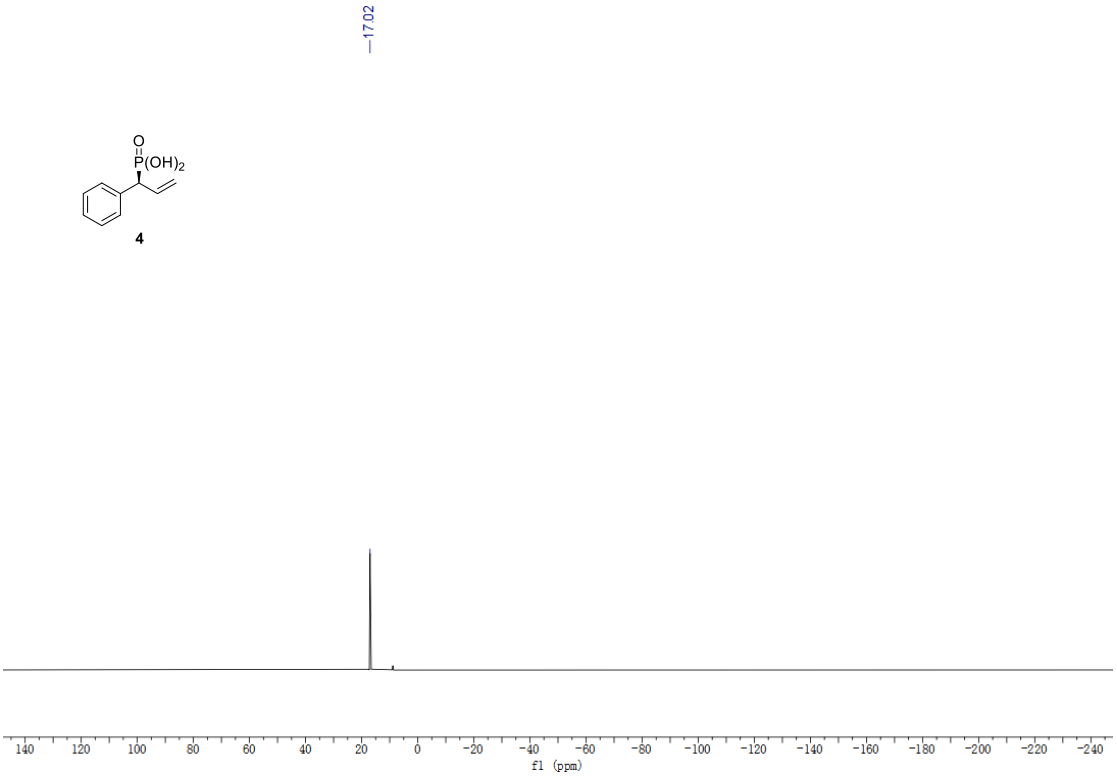
^{1}H NMR (400 MHz, MeOD) of **4**



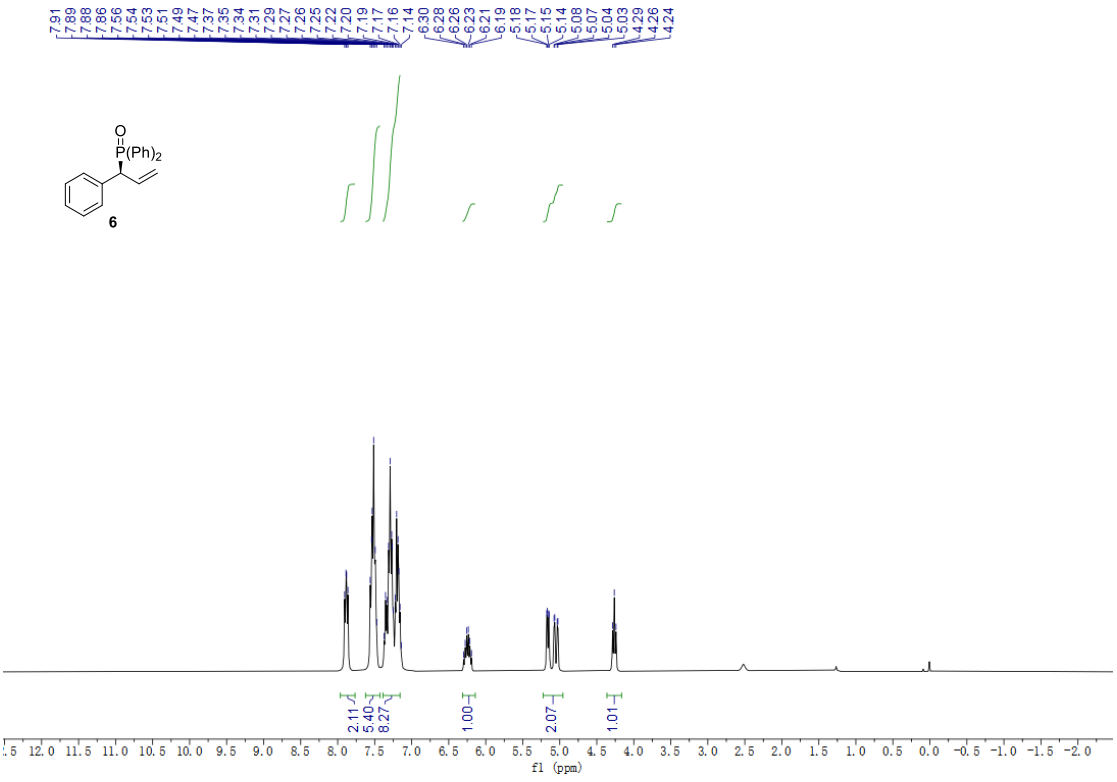
^{13}C{^{1}H} NMR (100 MHz, MeOD) of **4**



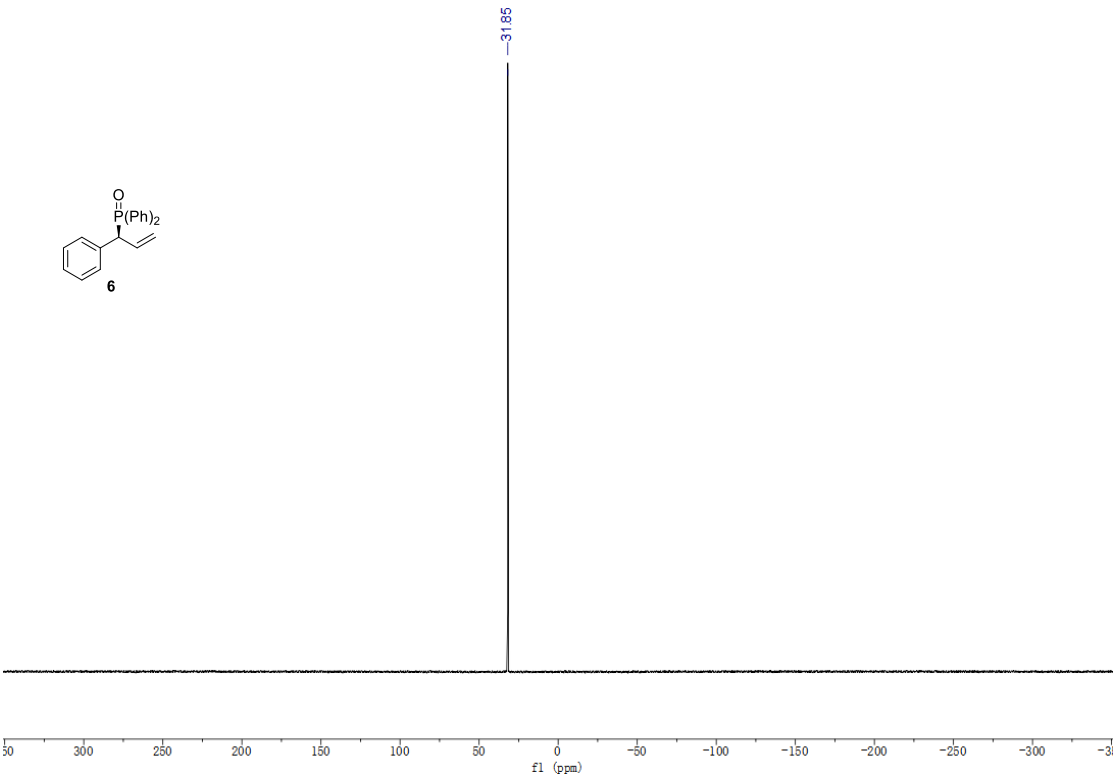
$^{31}P\{^{1}H\}$ NMR (162 MHz, MeOD) **4**



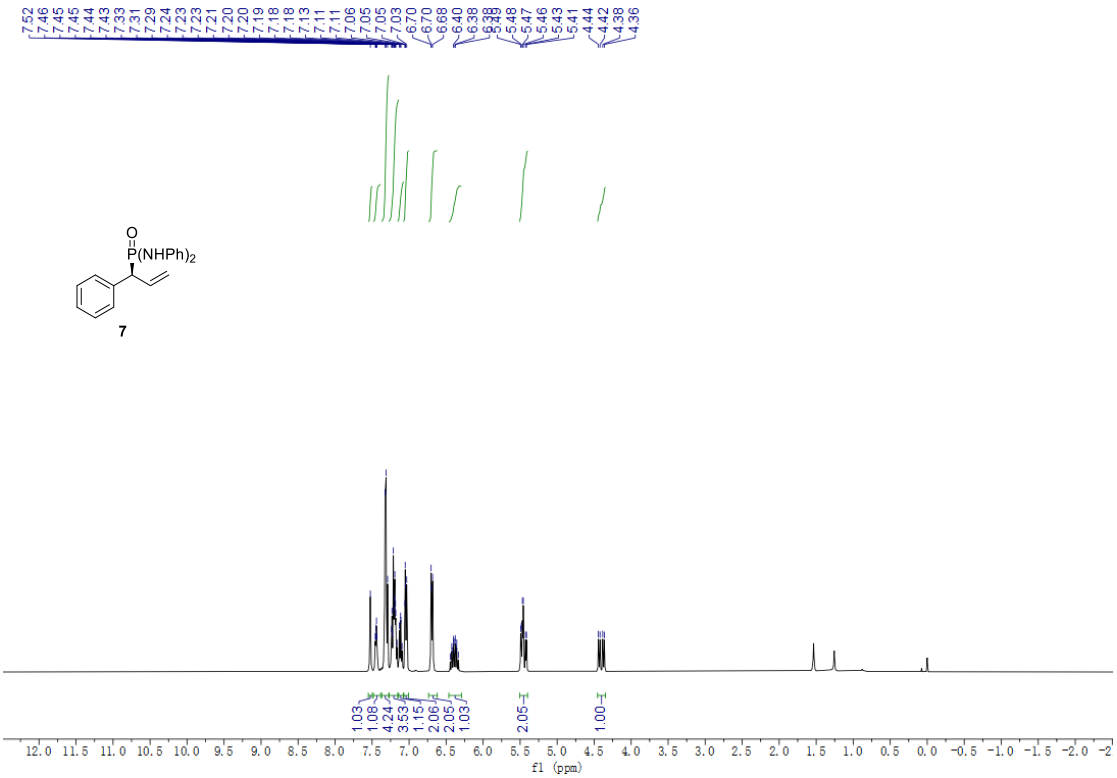
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



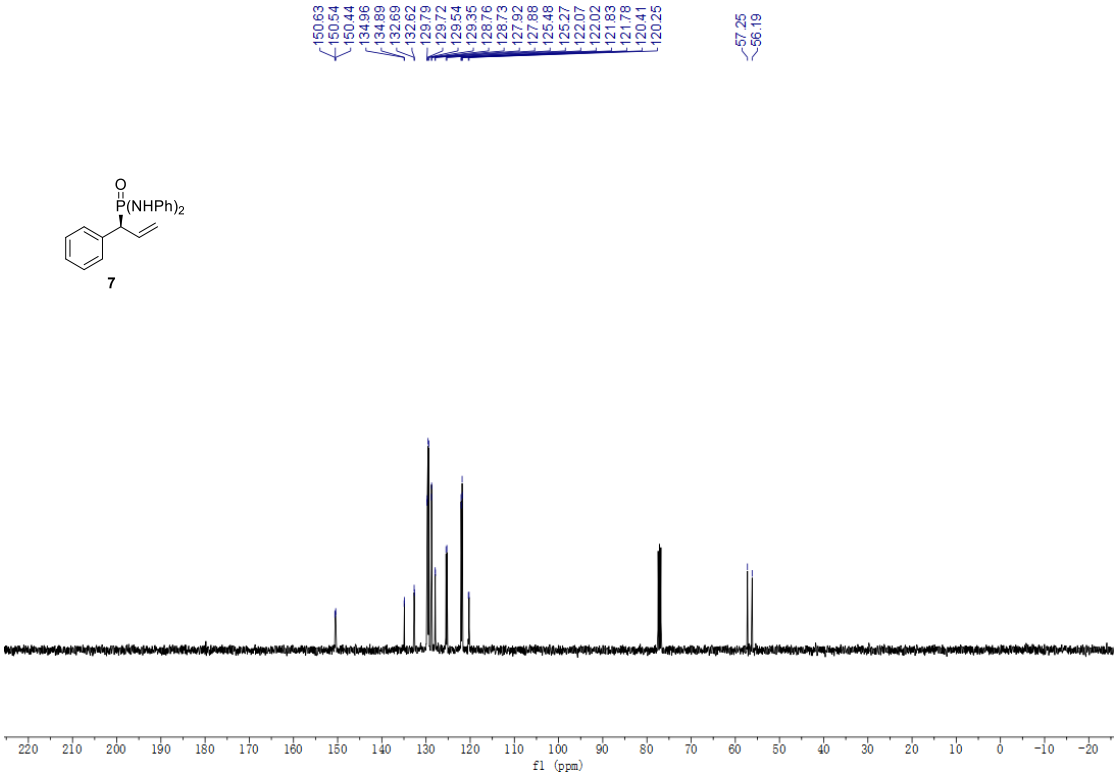
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **6**



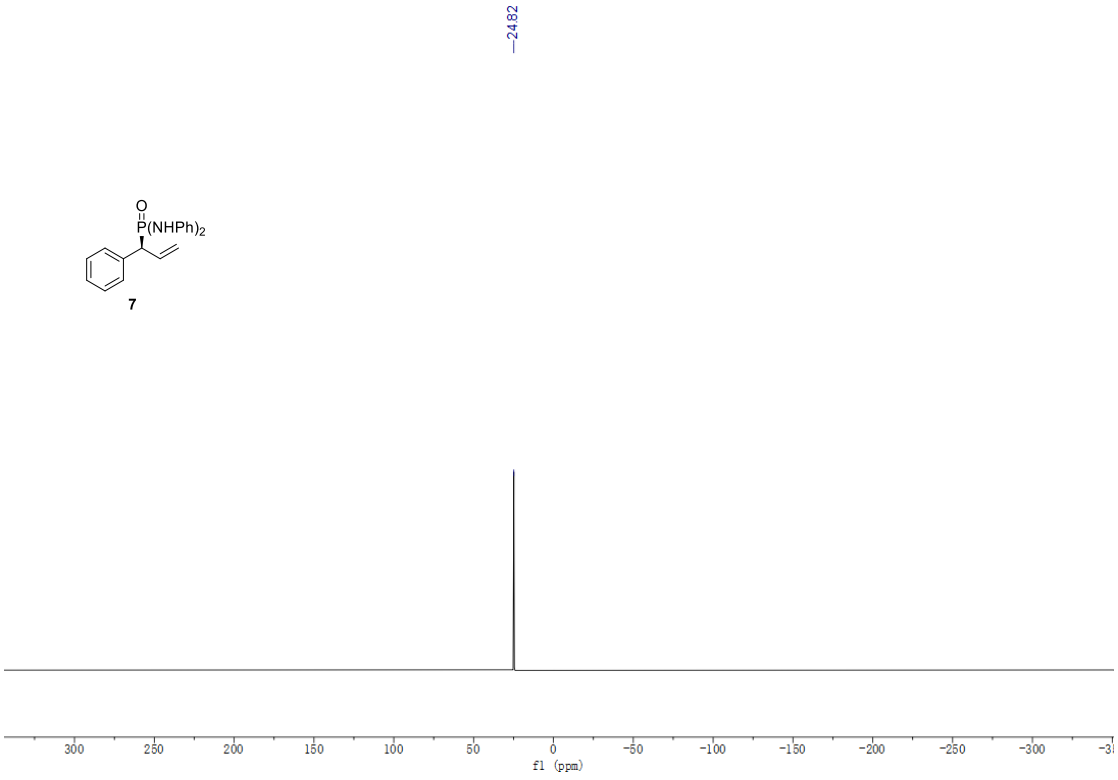
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



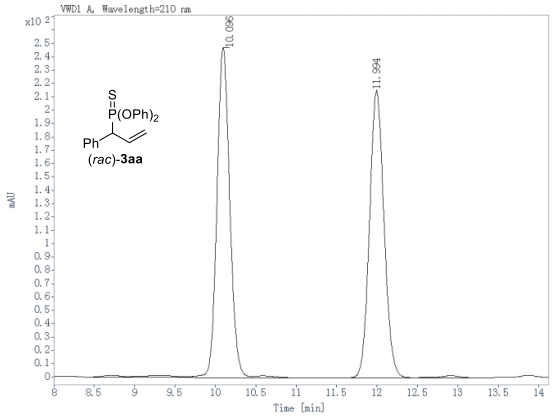
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **7**



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) **7**

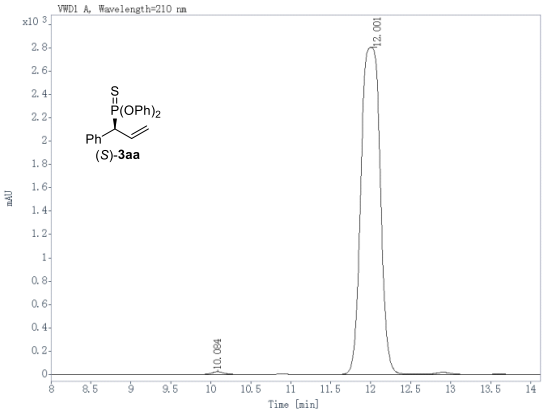


14. Traces of HPLC spectra



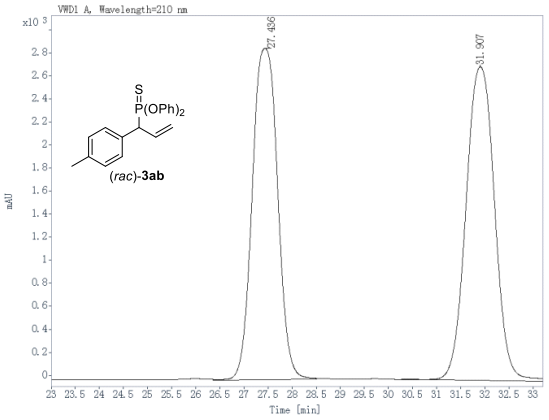
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
10.096	2802.14233	50.75
11.994	2719.05835	49.25
Total	5521.20068	100.00



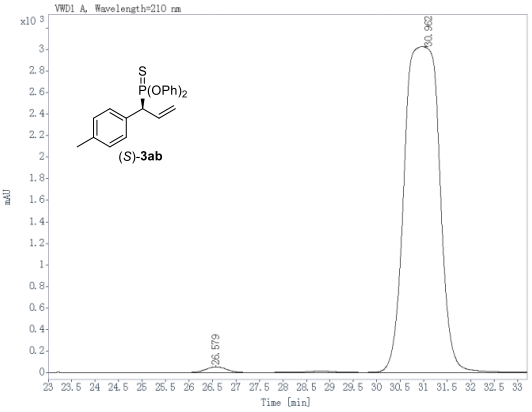
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
10.084	259.73410	0.55
12.001	47013.55469	99.45
Total	47273.28879	100.00



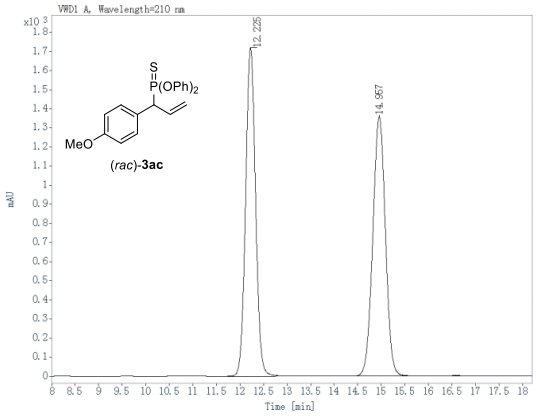
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
27.436	105116.22656	48.43
31.907	111910.71875	51.57
Total	217026.94531	100.00



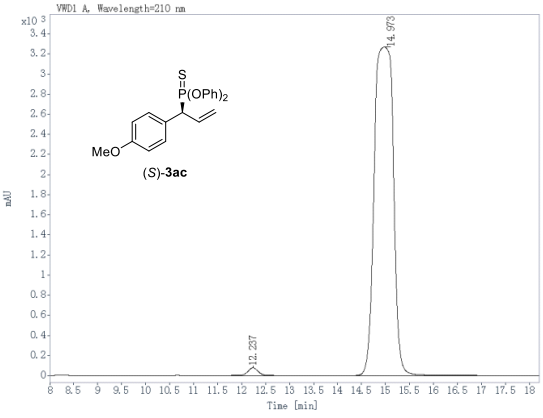
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
26.579	1644.76904	1.03
30.962	157729.14063	98.97
Total	159373.90967	100.00



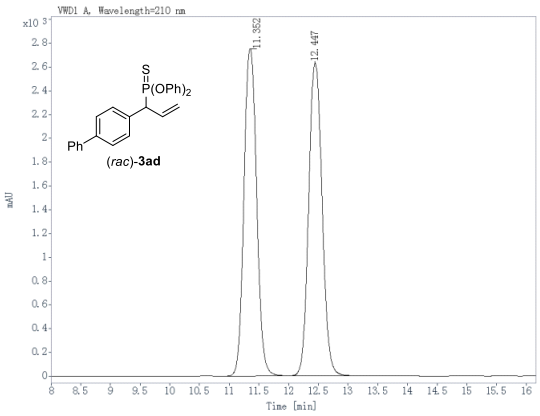
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
12.225	25255.73633	49.83
14.957	25432.30859	50.17
Total	50688.04492	100.00



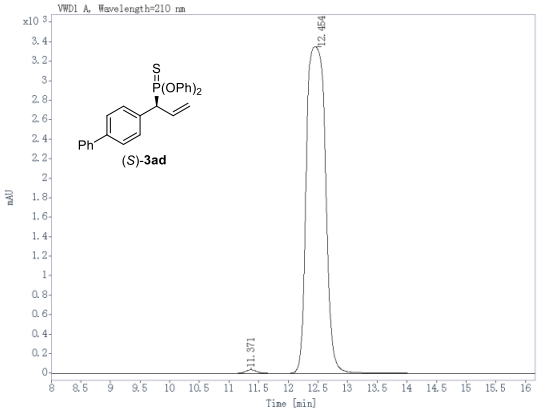
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
12.237	1179.55823	1.29
14.973	90588.95313	98.71
Total	91768.51135	100.00



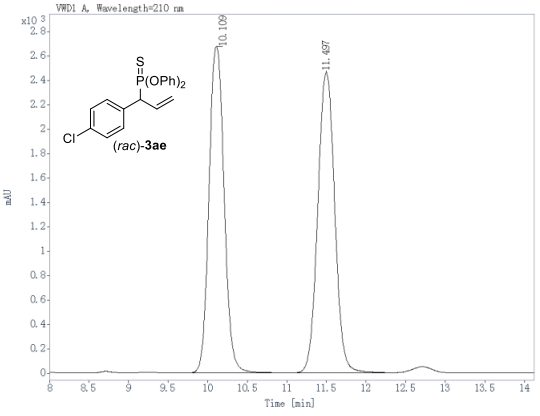
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.352	40874.92188	49.62
12.447	41498.66797	50.38
Total	82373.58984	100.00



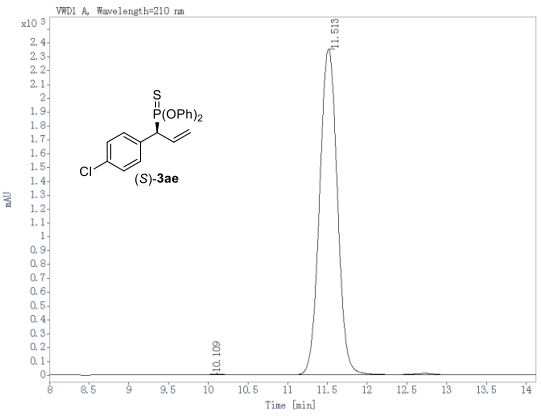
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.371	537.01013	0.72
12.454	74547.88281	99.28
Total	75084.89294	100.00



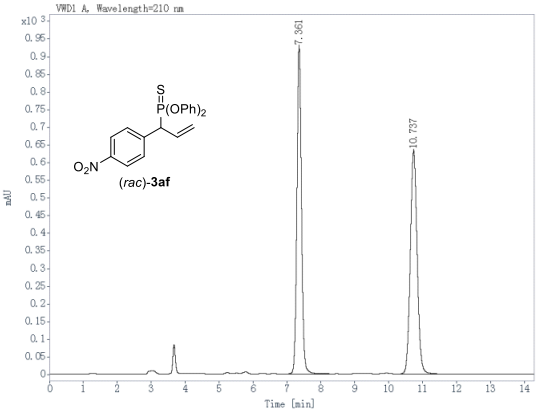
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
10.109	35634.53125	49.19
11.497	36807.11328	50.81
Total	72441.64453	100.00



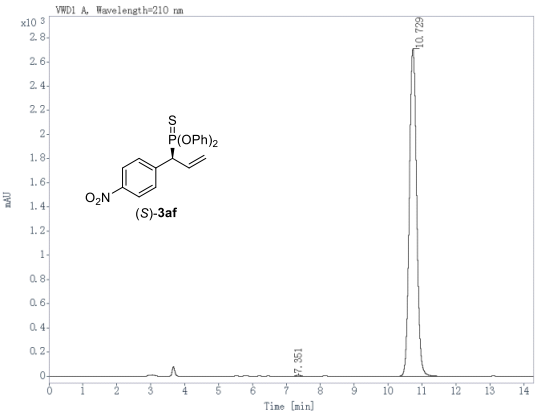
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
10.109	102.11623	0.28
11.513	36966.05859	99.72
Total	37068.17482	100.00



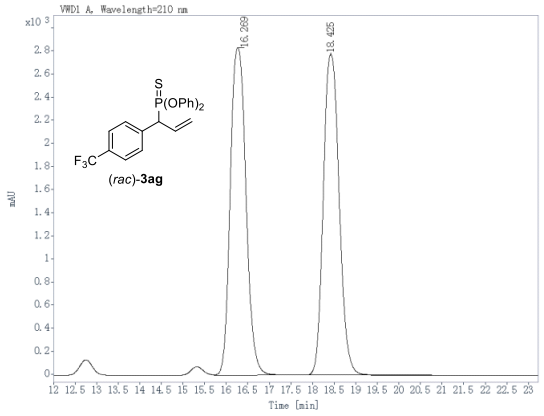
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
7.361	8792.19727	49.82
10.737	8853.98926	50.18
Total	17646.18652	100.00



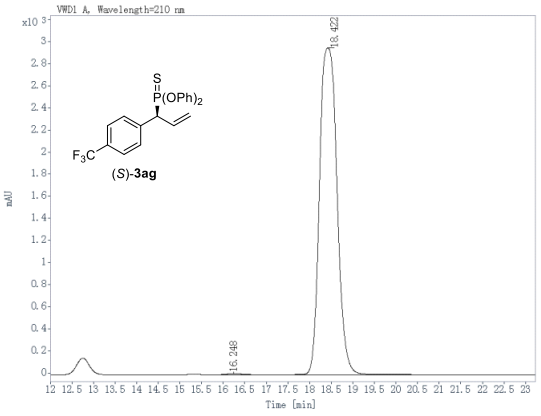
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
7.351	104.66718	0.26
10.729	40482.70313	99.74
Total	40587.37030	100.00



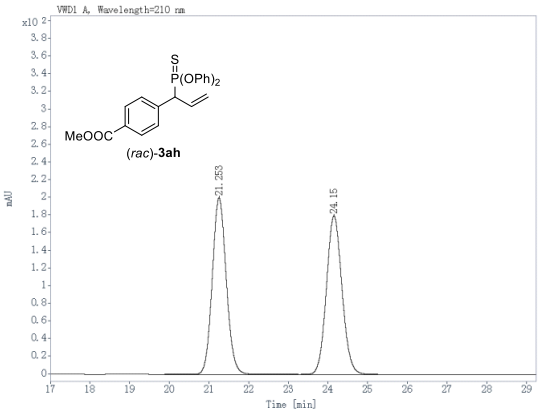
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
16.269	71564.97656	50.22
18.425	70927.08594	49.78
Total	142492.06250	100.00



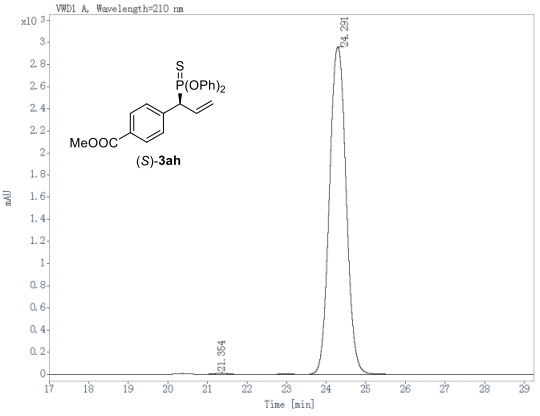
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
16.248	277.34583	0.33
18.422	83143.40625	99.67
Total	83420.75208	100.00



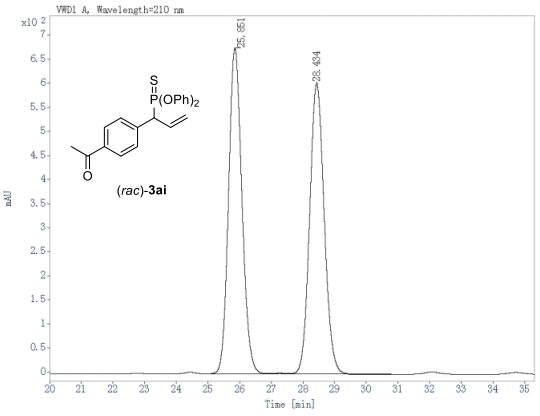
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
21.253	4947.87451	50.08
24.150	4931.72900	49.92
Total	9879.60352	100.00



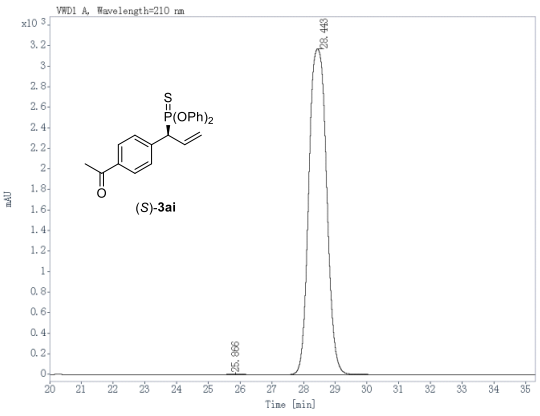
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
21.354	298.20679	0.34
24.291	87036.57813	99.66
Total	87334.78491	100.00



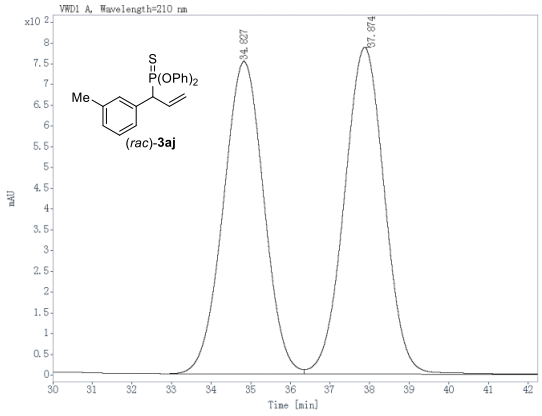
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
25.851	19921.85156	50.77
28.434	19314.80859	49.23
Total	39236.66016	100.00



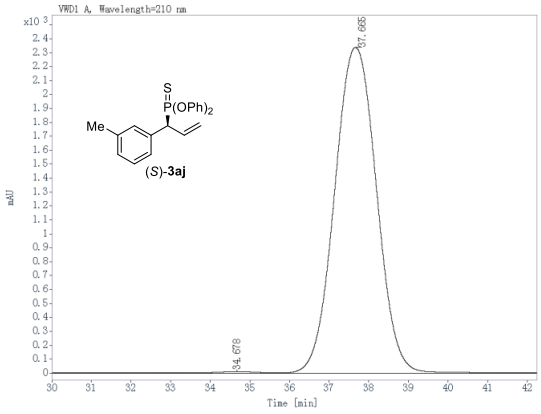
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
25.866	208.15497	0.17
28.443	123280.25781	99.83
Total	123488.41278	100.00



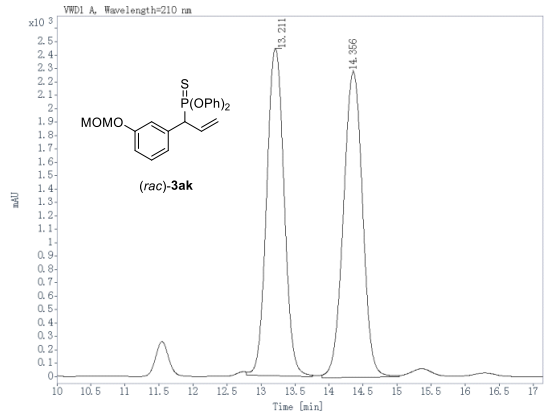
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
34.827	53443.57422	49.10
37.874	55403.10156	50.90
Total	108846.67578	100.00



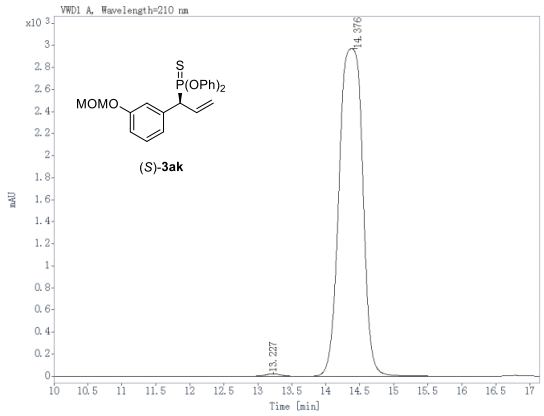
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
34.678	905.69104	0.51
37.665	176075.46875	99.49
Total	176981.15979	100.00



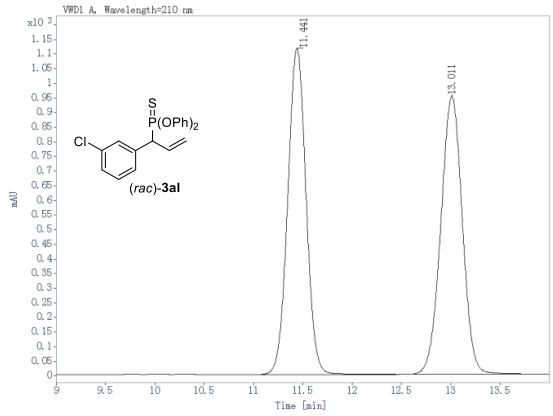
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
13.211	43549.55078	49.35
14.356	44694.13672	50.65
Total	88243.68750	100.00



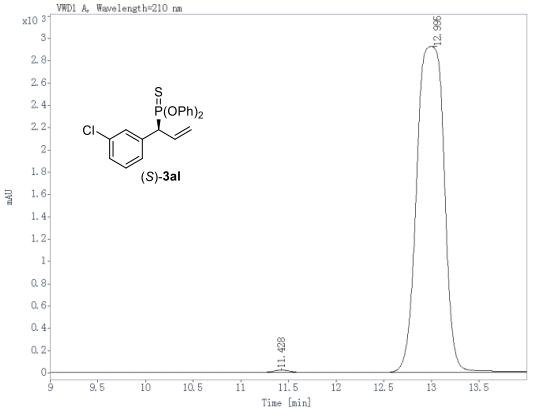
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
13.227	404.23917	0.56
14.376	71572.89844	99.44
Total	71977.13760	100.00



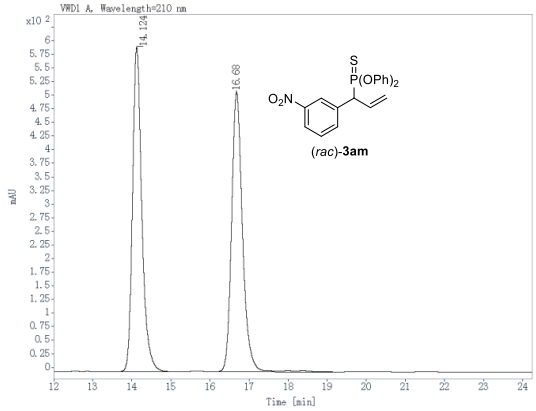
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.441	14399.20020	49.54
13.011	14669.29492	50.46
Total	29068.49512	100.00



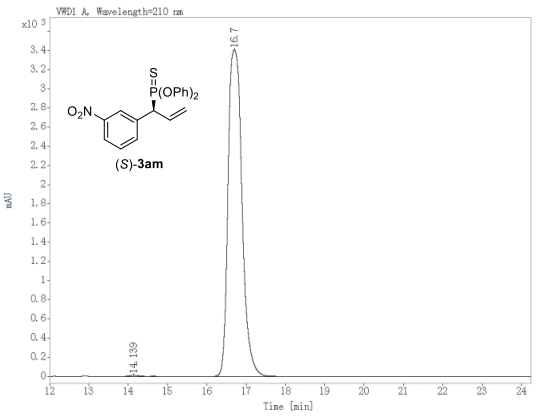
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.428	305.04926	0.51
12.995	59188.24219	99.49
Total	59493.29144	100.00



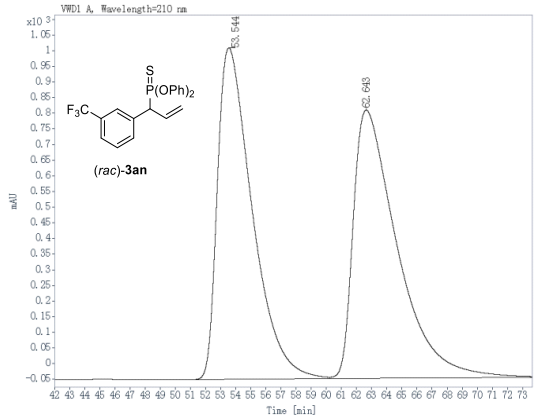
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
14.124	9871.97461	49.67
16.680	10003.87305	50.33
Total	19875.84766	100.00



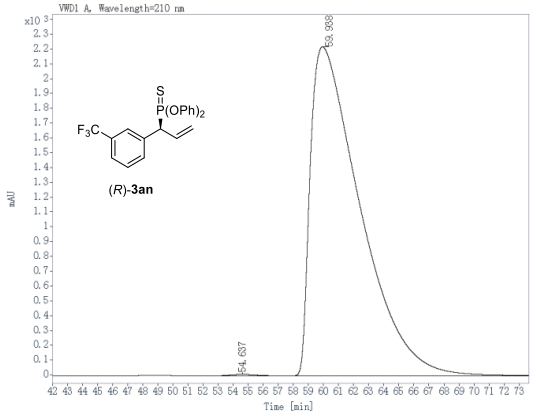
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
14.139	263.74466	0.31
16.700	84053.75781	99.69
Total	84317.50247	100.00



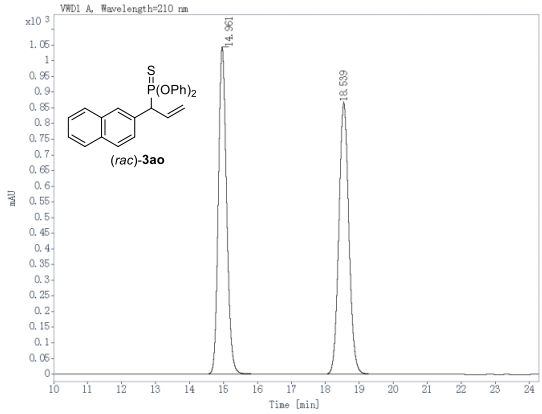
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
53.544	169294.84375	49.37
62.643	173604.75000	50.63
Total	342899.59375	100.00



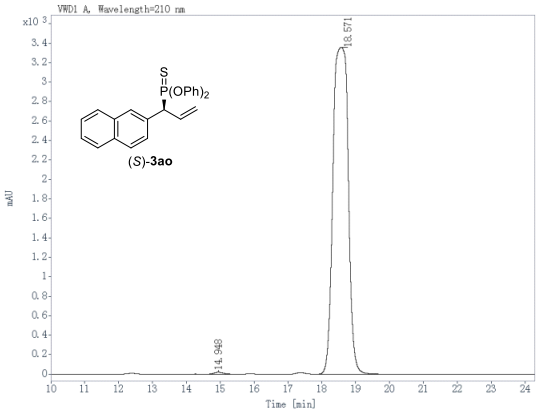
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
54.637	1617.18530	0.31
59.938	512205.15625	99.69
Total	513822.34155	100.00



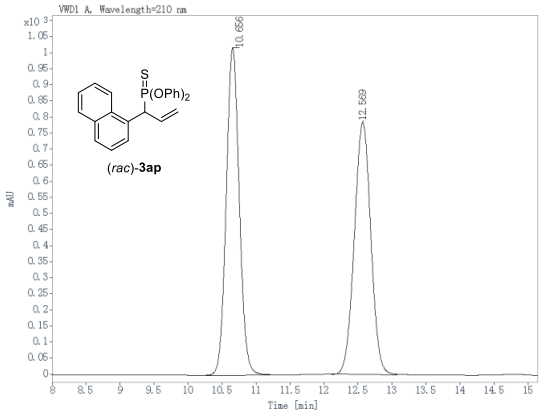
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
14.961	17706.15234	49.76
18.539	17880.38086	50.24
Total	35586.53320	100.00



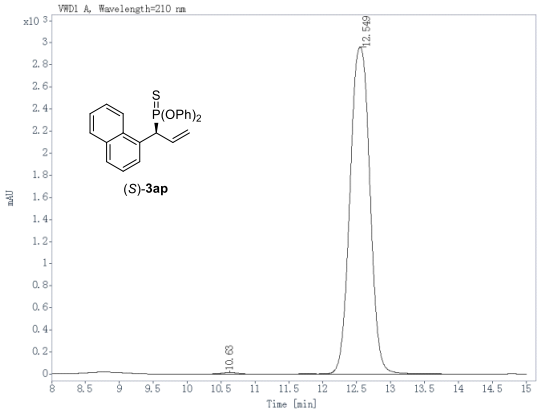
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
14.948	448.34784	0.42
18.571	105344.53906	99.58
Total	105792.88690	100.00



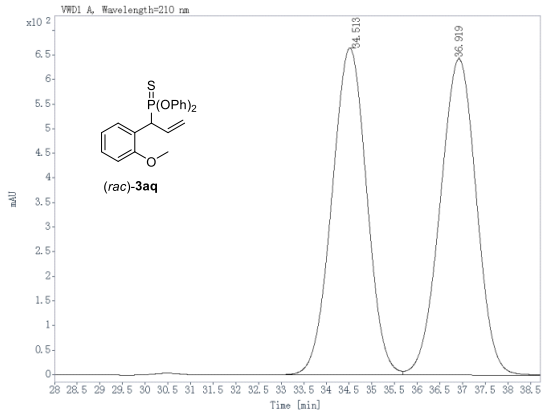
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
10.656	13604.98242	50.64
12.569	13263.35352	49.36
Total	26868.33594	100.00



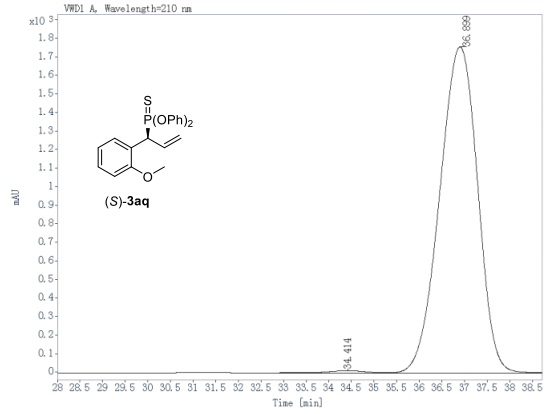
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
10.630	262.99637	0.43
12.549	60372.85547	99.57
Total	60635.85184	100.00



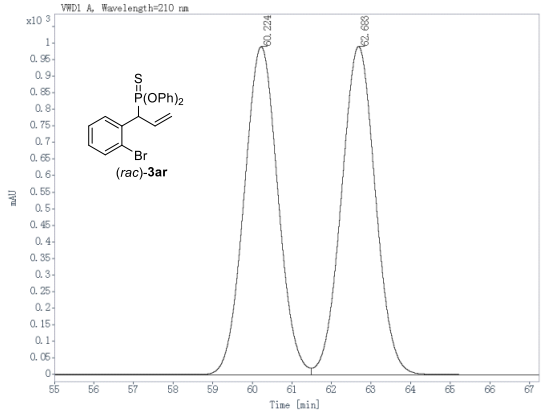
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
34.513	35488.13672	49.89
36.919	35637.58984	50.11
Total	71125.72656	100.00



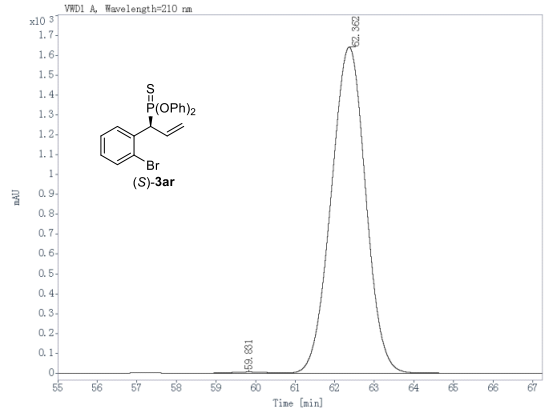
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
34.414	740.79761	0.71
36.899	103053.50000	99.29
Total	103794.29761	100.00



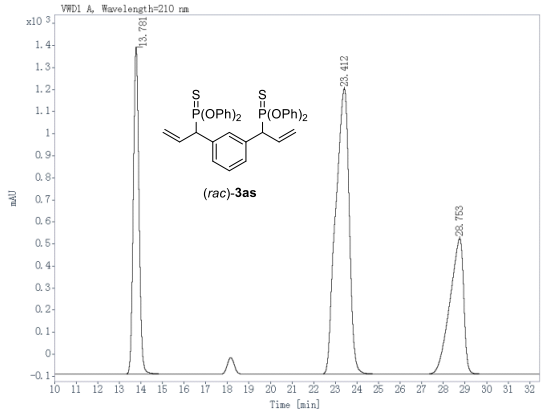
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
60.224	58877.97656	49.94
62.683	59023.25781	50.06
Total	117901.23438	100.00



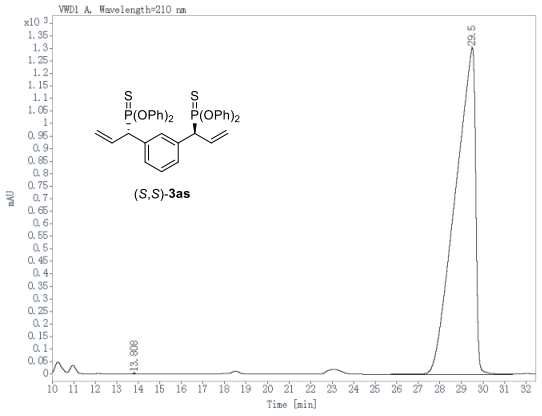
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
59.831	354.63492	0.36
62.362	99378.71875	99.64
Total	99733.35367	100.00



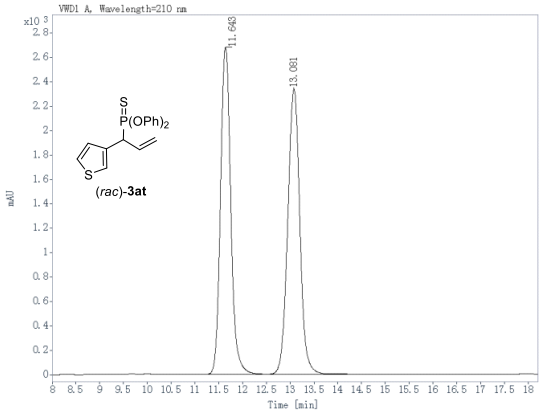
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
13.781	27104.59375	24.49
23.412	56088.51563	50.67
28.753	27495.59766	24.84
Total	110688.70703	100.00



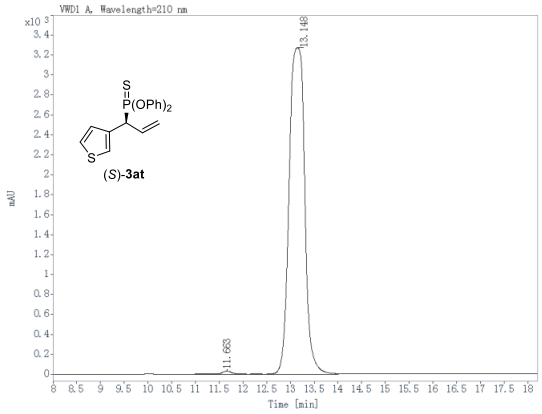
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
13.808	38.43256	0.05
29.500	84908.74219	99.95
Total	84947.17474	100.00



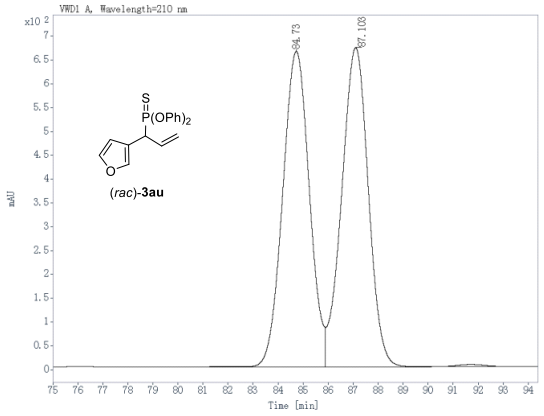
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.643	40302.08594	49.30
13.081	41441.21875	50.70
Total	81743.30469	100.00



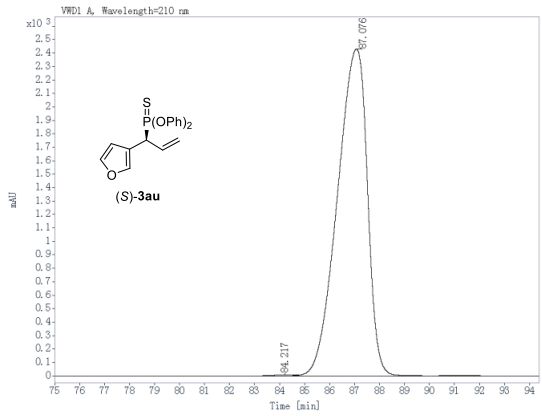
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.663	501.33557	0.67
13.148	74534.82813	99.33
Total	75036.16370	100.00



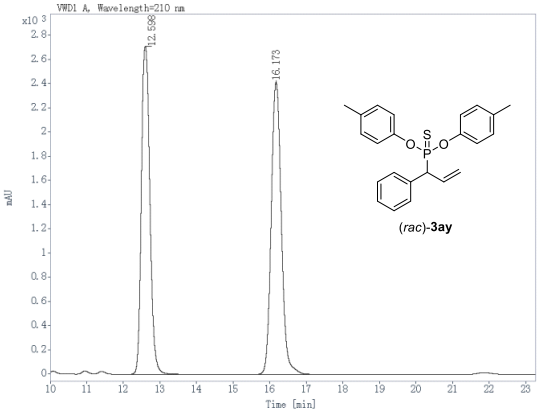
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
84.730	49067.14453	49.54
87.103	49977.42188	50.46
Total	99044.56641	100.00



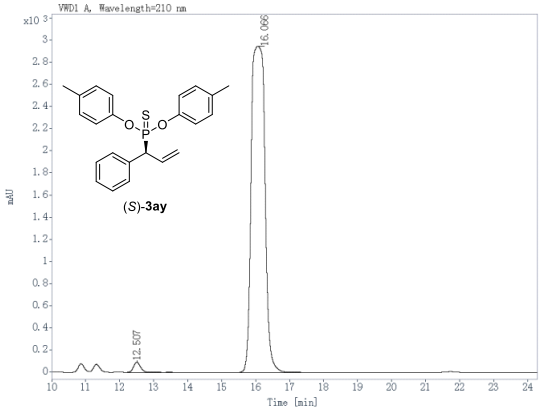
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
84.217	484.05841	0.24
87.076	202840.29688	99.76
Total	203324.35529	100.00



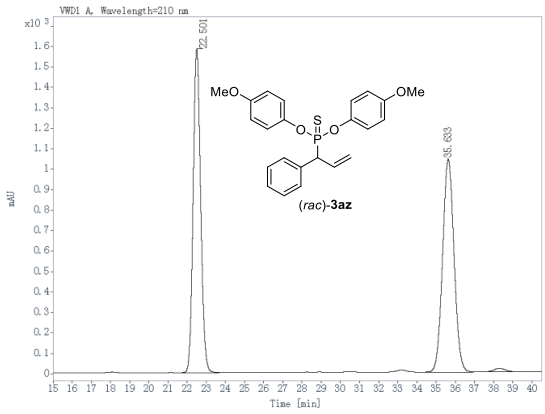
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
12.598	43661.82813	48.55
16.173	46269.21875	51.45
Total	89931.04688	100.00



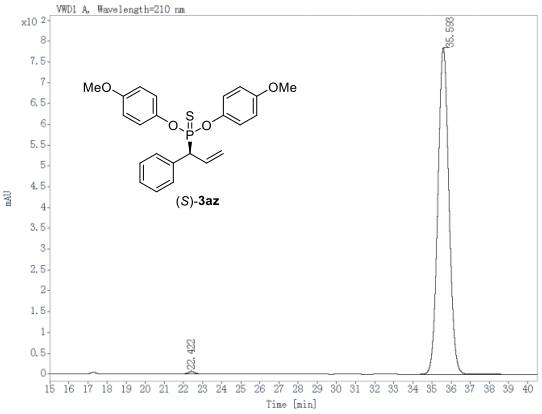
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
12.507	1364.60754	1.63
16.066	82486.15625	98.37
Total	83850.76379	100.00



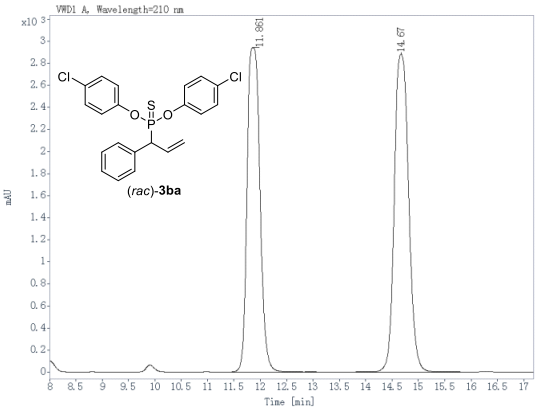
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
22.501	43142.34766	49.47
35.633	44073.41797	50.53
Total	87215.76563	100.00



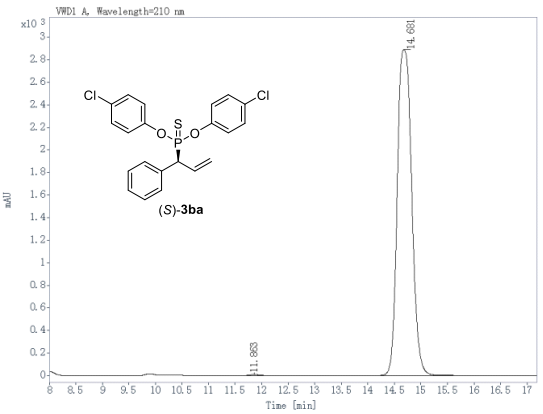
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
22.422	215.57002	0.68
35.593	31448.45898	99.32
Total	31664.02901	100.00



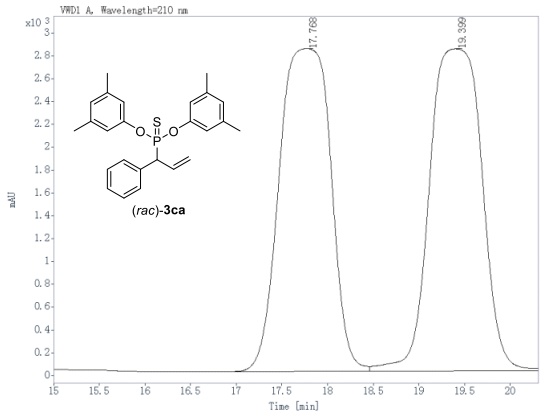
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.861	49870.79297	47.79
14.670	54476.63281	52.21
Total	104347.42578	100.00



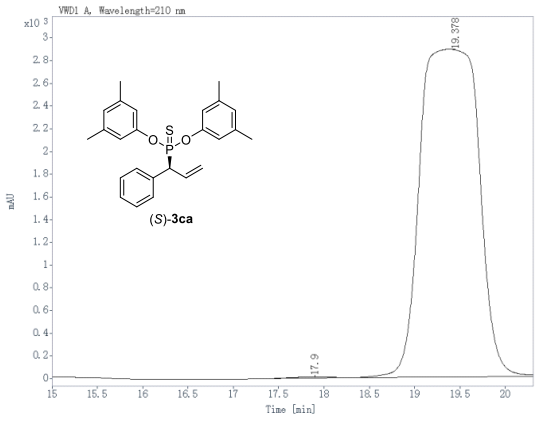
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
11.863	160.26137	0.29
14.681	54684.89844	99.71
Total	54845.15981	100.00



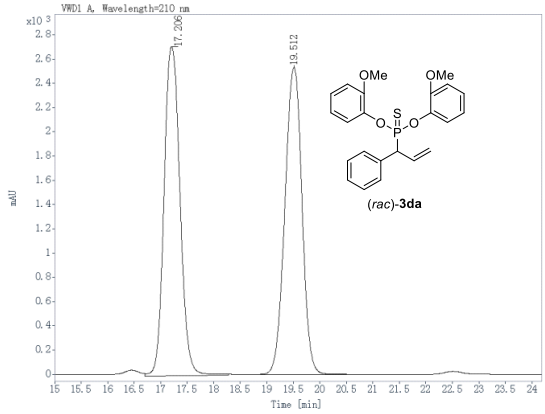
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
17.768	110374.49219	49.55
19.399	112377.17188	50.45
Total	222751.66406	100.00



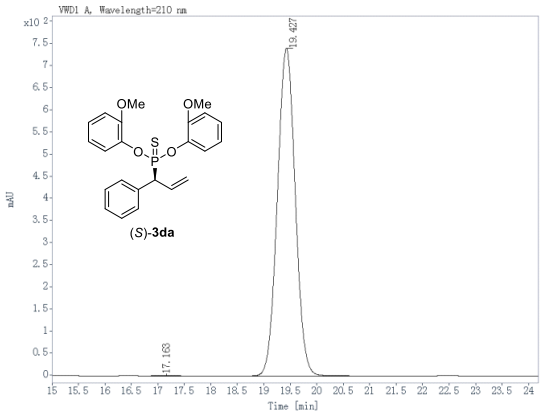
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
17.900	321.35754	0.25
19.378	129580.93750	99.75
Total	129902.29504	100.00



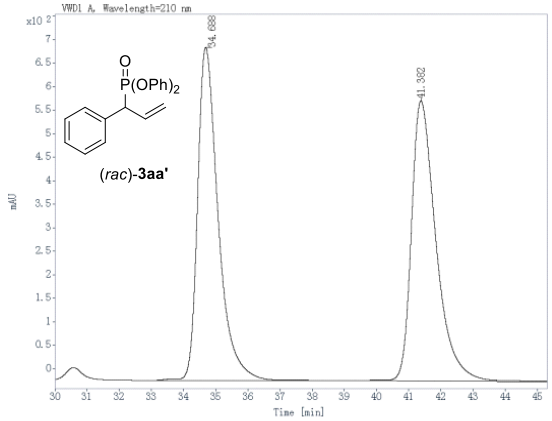
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
17.206	56634.89453	49.94
19.512	56763.48438	50.06
Total	113398.37891	100.00



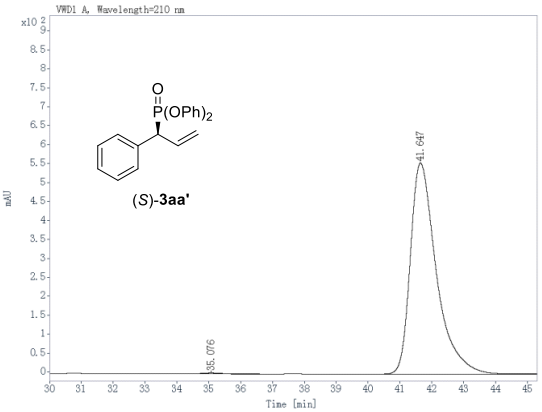
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
17.163	22.49222	0.13
19.427	17416.67578	99.87
Total	17439.16800	100.00



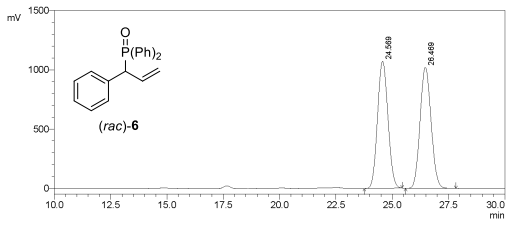
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
34.688	31541.68945	49.89
41.382	31681.99805	50.11
Total	63223.68750	100.00



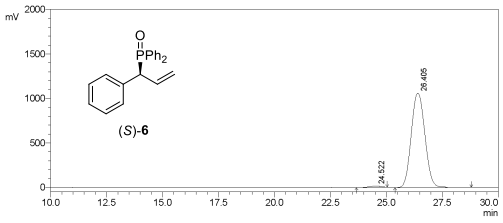
VWD1 A, Wavelength=210 nm

Rt(min)	Area	%Area
35.076	138.90266	0.44
41.647	31721.34961	99.56
Total	31860.25227	100.00



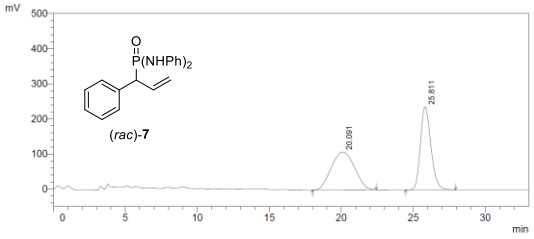
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Area %
1	24.569	34678625	49.885
2	26.469	34837935	50.115
Sum		69516561	100.000



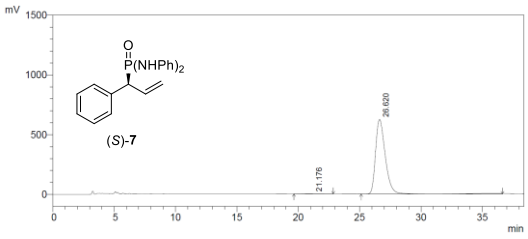
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Area %
1	24.522	533259	1.180
2	26.405	44672357	98.820
Sum		45205617	100.000



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Area %
1	20.091	12006099	50.041
2	25.811	11986555	49.959
Sum		23992654	100.000



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Area %
1	21.176	220051	0.640
2	26.620	34145860	99.360
Sum		34365911	100.000