Supporting Information for

Nickel-Catalysed Enantioselective Reaction of Secondary Phosphine Oxides and Activated Vinylcyclopropanes

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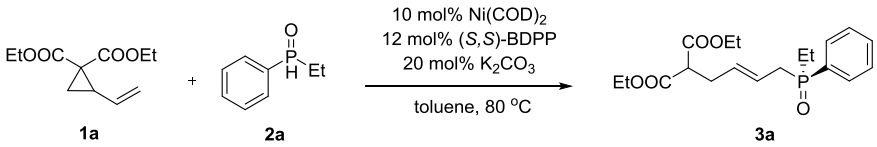
1. General Information

Reactions were performed in a glovebox filled with N_2 using dry and deoxygenated solvents. Toluene were distilled over sodium and deoxygenated with N_2 and other solvents were used directly from commercial sources. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 or 300-400 meshes) was used for column chromatography. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded in $CDCl_3$, CD_3COCD_3 or CD_2Cl_2 solution on Bruker Aescend TM 500 MHz instruments and spectral data were reported in ppm. The residual solvent peak was used as an internal reference: proton ($CDCl_3$ δ 7.26) and carbon ($CDCl_3$ δ 77.0), proton (CD_3COCD_3 δ 2.05) and carbon (CD_3COCD_3 δ 206.26), proton (CD_2Cl_2 δ 5.32) and carbon (CD_2Cl_2 δ 53.26). High-resolution mass spectral analysis (HRMS) data were measured by means of the ESI technique. Enantiomer excess was determined by HPLC analysis employing Darcel Chiracel columns (AD-H, OD-H, IF and IH) and ^{n}hexane/^{i}PrOH as eluents. Optical rotations were measured by Perkin-Elmer-343 polarimeter. Vinylcyclopropanes were prepared according to references 1 and 2, phosphine oxides were prepared according to references 3 and 4.

2. Optimization of reaction conditions.

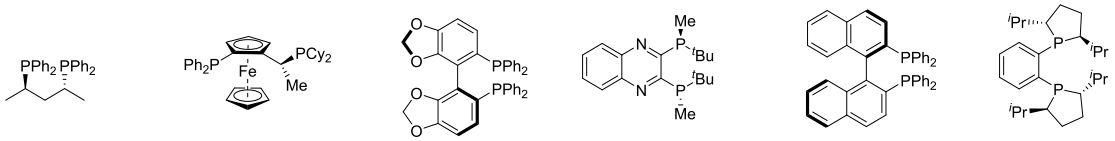
Table S1. Optimization of reaction conditions[a].



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

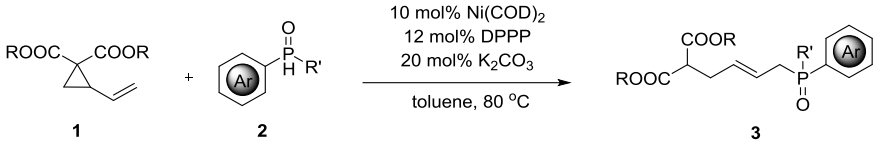
Entry	Base	Ligand	Solvent	Yield(%)[b]	Ee(%)
1	K_2CO_3	**L1**	Toluene	67	81
2	K_2CO_3	**L2**	Toluene	No reaction	-
3	K_2CO_3	**L3**	Toluene	81	0
4	K_2CO_3	**L4**	Toluene	86	0
5	K_2CO_3	**L5**	Toluene	Trace	4
6	K_2CO_3	**L6**	Toluene	79	0
7	K_2CO_3	**L1**	DCE	24	76
8	K_2CO_3	**L1**	Mesitylene	68	65
9	K_2CO_3	**L1**	MeCN	78	68
10	K_2CO_3	**L1**	1,4-Dioxane	80	63
11	K_2CO_3	**L1**	THF	57	81
12[c]	K_2CO_3	**L1**	Toluene	75	69
13[d]	K_2CO_3	**L1**	Toluene	84(70)	90
14[d]	KOAc	**L1**	Toluene	86	89
15[d]	NaOAc	**L1**	Toluene	79	89
16[d]	LiOAc	**L1**	Toluene	79	90
17[d]	Na_2CO_3	**L1**	Toluene	85	89
18[d]	Cs_2CO_3	**L1**	Toluene	81	89

[a]Reaction conditions: **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.05 mmol, 1.0 equiv.), $Ni(COD)_2$ (10 mol%), ligand (12 mol%), K_2CO_3 (20 mol%), solvent (0.5 mL) at 80 °C. Ee value determined by chiral HPLC. [b]Determined by ^{31}P NMR spectra using trimethyl phosphate as internal standard, in brackets is the separation yield. [c]$Ni(COD)_2$ (5 mol%), ligand (6 mol%). [d]**2a** (0.1 mmol, 2.0 equiv.) at room temperature.



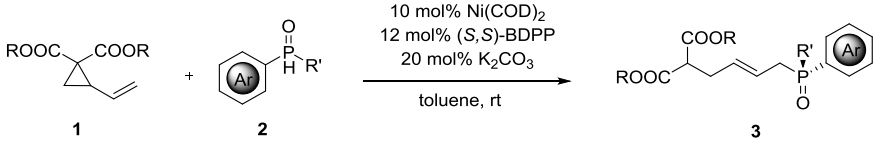
L1 **L2** **L3** **L4** **L5** **L6**

3. General procedure for the synthesis of racemic products.



To a 4 mL vial were added $Ni(COD)_2$ (10 mol%, 1.4 mg), DPPP (12 mol%, 2.50 mg), and toluene (0.5 mL) in a N_2 flushed glove box. Then the mixture was stirred for 10 minutes followed by the addition of K_2CO_3 (20 mol%, 1.4 mg), vinylcyclopropanes **1** (1.2 equiv, 0.06 mmol) and SPOs **2** (1.0 equiv, 0.05 mmol). The vial was capped, removed from the glove box, and the system was stirred at 80 °C until disappearance of **2** by TLC. The reaction mixture was cooled to room temperature and subjected to silica gel column chromatography directly for purification.

4. General procedure for the synthesis of chiral products.



To a 4 mL vial were added $Ni(COD)_2$ (10 mol%, 2.8 mg), (*S*, *S*)-BDPP (12 mol%, 5.2 mg), and toluene (1.0 mL) in a N_2 flushed glove box. Then the mixture was stirred for 10 minutes followed by the addition of K_2CO_3 (20 mol%, 2.8 mg), vinylcyclopropanes **1** (1.0 equiv, 0.1 mmol) and SPOs **2** (2.0 equiv, 0.2 mmol). The vial was capped, removed from the glove box, and the system was stirred at 10 °C (**2b**), 25 °C (**2a**, **2c-2d**, **2h-2j**, **2l-2w**), 60 °C (**2e**, **2g**, **2k**) or 80 °C (**2f**) until disappearance of **2** by TLC. The reaction mixture was cooled to room temperature, S_8 (2.5 equiv, 8.0 mg); Et_2NH (2.5 equiv, 18.2 mg) (**2a-2j**, **2l-2n**, **2p-2w**) or 30% H_2O_2 aqueous solution (20 μL) (**2k**, **2o**) were added to the mixture and stirred for 1 h to remove the remaining SPOs. The reaction mixture was then subjected to silica gel column chromatography directly for purification.

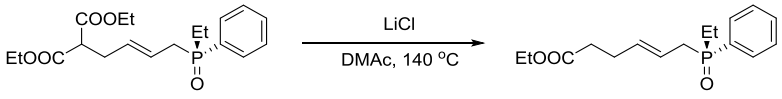
5. Synthetic applications.

5.1 3 mmol-scale synthesis.

1a (3.0 mmol) **2a** (6.0 mmol) **3a** 71% yield, 90% ee

To a 100 mL Schlenk reaction bottle were added $Ni(COD)_2$ (10 mol%, 82.5 mg), ligand (*S*, *S*)-BDPP (12 mol%, 158.5 mg), and toluene (30 mL) in a N_2 flushed glove box. Then the mixture was stirred for 30 minutes followed by the addition of K_2CO_3 (20 mol%, 82.8 mg), vinylcyclopropanes **1** (1.0 equiv, 3.0 mmol) and SPOs **2** (2.0 equiv, 6.0 mmol). The 100 mL Schlenk reaction bottle was capped, removed from the glove box, and the system was stirred at 25 °C until disappearance of 2 by TLC (9 days). The reaction mixture was cooled to room temperature, S_8 (2.5 equiv, 0.24 g) and Et_2NH (2.5 equiv, 0.55 g) were added to the mixture and stirred 2 h to remove the remaining SPO. Then, the reaction mixture was concentrated *in vacuo*. Purification by silica gel column chromatography with 95:5 EtOAc/MeOH afford the desired product **3a** in 71% yield (0.78 g) with 90% ee.

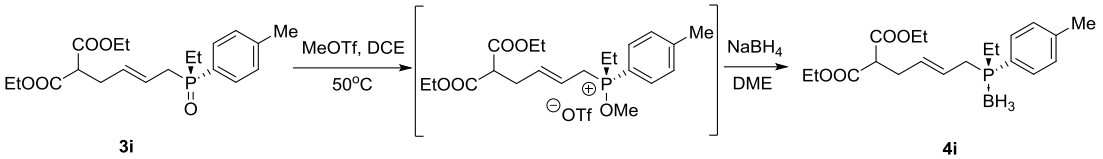
5.2 Decarboxylation.



3a 90% ee **4a** 46% yeild, 90% ee

According to reference 5, a 4 mL vial was charged with tertiary phosphine oxide **3a** (0.1 mmol), LiCl (2.0 equiv, 8.5 mg) and DMAc (0.5 mL). The solution was heated at 140 °C for 6 h. The reaction mixture was cooled to room temperature and diluted with EtOAc (5 mL) and water (5 mL). The organic phase was separated and washed with additional water (5 mL x 2) and the organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography with 95:5 EtOAc/MeOH afford the desired product **3a** in 45% yield (13.3 mg) with 90% ee.

5.3 Reduction to P-stereogenic phosphine (III).



3i

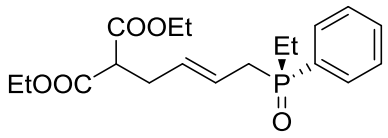
90% ee

4i

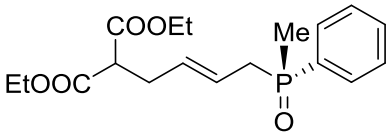
58% yield, 89% ee

According to reference 6, to a stirred solution of MeOTf (0.12 mmol) in DME (0.2 mL) in a 4 mL vial, tertiary phosphine oxide **3i** (0.1 mmol) in DME (0.2 mL) was added dropwise at room temperature. The reaction was heated at 50 °C overnight. After cooling to room temperature, a dispersion of $NaBH_4$ (0.3 mmol) in diglyme (0.5 mL) was added dropwise to the vial. The reaction mixture was stirred for additional 3 hours at 50 °C before being cooled to room temperature and diluted with DCM (5 mL). Water was then added dropwise to quench the remaining $NaBH_4$. The mixture was washed with water (5 mL x 3) and the organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography with 90:10 PE/EtOAc afford the desired product **4i** in 58% yield (21.9 mg) with 89% ee.

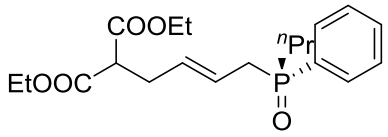
6. Spectroscopic data of products.



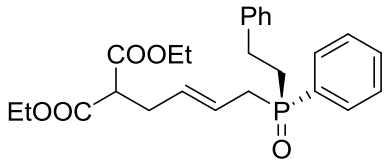
(**3a**) Colorless oil, R_f = 0.34 (ethyl acetate/methanol = 5:1), 70% yield (25.6 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.67 (ddd, *J* = 10.8, 8.2, 1.5 Hz, 2H), 7.56 – 7.45 (m, 3H), 5.66 – 5.38 (m, 2H), 4.25 – 4.08 (m, 4H), 3.31 (t, *J* = 7.5 Hz, 1H), 2.73 (dd, *J* = 14.8, 6.0 Hz, 2H), 2.58 (ddt, *J* = 7.7, 6.1, 2.8 Hz, 2H), 2.08 – 1.96 (m, 1H), 1.94 – 1.81 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.11 (dt, *J* = 17.1, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.74 (d, *J* = 2.6 Hz), 131.67 (d, *J* = 2.7 Hz), 131.60 (d, *J* = 11.4 Hz), 131.53 (d, *J* = 92.8 Hz), 130.54 (d, *J* = 8.6 Hz), 128.56 (d, *J* = 11.3 Hz), 122.31 (d, *J* = 8.6 Hz), 61.44, 51.69 (d, *J* = 3.3 Hz), 34.67 (d, *J* = 65.2 Hz), 31.70 (d, *J* = 2.3 Hz), 21.41 (d, *J* = 70.3 Hz), 14.03, 5.28 (d, *J* = 5.2 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.9. **HRMS** (ESI) calcd for $C_{19}H_{27}O_5PNa^+$ $[M+Na]^+$ 389.1488, Found 389.1490. The enantiomeric excess was determined by Daicel Chiralcel OD-H (90% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 8.25 min, *t* (minor) = 6.99 min. $[\alpha]_D^{20}$ = -8.5 (*c* = 0.2, acetone).



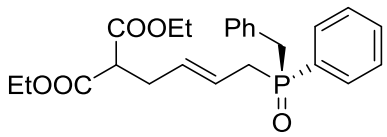
(**3b**) Colorless oil, R_f = 0.31 (Ethyl acetate/methanol = 5:1), 79% yield (27.8 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 2H), 7.50 (dtt, *J* = 14.7, 7.0, 4.3 Hz, 3H), 5.51 (m, 2H), 4.17 (dtt, *J* = 10.8, 7.2, 3.8 Hz, 4H), 3.32 (t, *J* = 7.4 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.59 (dq, *J* = 7.0, 3.8, 3.2 Hz, 2H), 1.68 (d, *J* = 12.8 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.72 (d, *J* = 2.6 Hz), 133.26 (d, *J* = 96.1 Hz), 131.77 (d, *J* = 10.1 Hz), 131.72 – 131.71 (d, *J* = 1.3 Hz), 130.10 (d, *J* = 9.0 Hz), 128.58 (d, *J* = 11.5 Hz), 122.43 (d, *J* = 8.8 Hz), 61.44, 51.71 (d, *J* = 3.4 Hz), 36.81 (d, *J* = 67.0 Hz), 31.72 (d, *J* = 2.4 Hz), 14.72 (d, *J* = 70.9 Hz), 14.04. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 35.1. **HRMS** (ESI) calcd for $C_{18}H_{26}O_5P^+$ $[M+H]^+$ 353.1512, Found 353.1515. The enantiomeric excess was determined by Daicel Chiralcel OD-H (91% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 9.60 min, *t* (minor) = 8.70 min. $[\alpha]_D^{20}$ = -3.9 (*c* = 0.3, acetone).



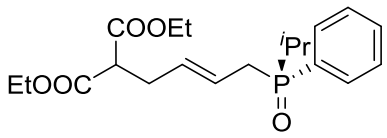
(**3c**) Colorless oil, R_f = 0.37 (Ethyl acetate/methanol = 7:1), 81% yield (30.8 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 – 7.61 (m, 2H), 7.49 (dtt, *J* = 14.3, 6.6, 4.0 Hz, 3H), 5.62 – 5.37 (m, 2H), 4.26 – 4.04 (m, 4H), 3.30 (t, *J* = 7.4 Hz, 1H), 2.71 (dd, *J* = 14.9, 6.1 Hz, 2H), 2.57 (dq, *J* = 7.2, 3.3 Hz, 2H), 2.05 – 1.90 (m, 1H), 1.84 (tdd, *J* = 14.7, 10.1, 5.0 Hz, 1H), 1.75 – 1.57 (m, 1H), 1.56 – 1.41 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 6H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.72 (d, *J* = 1.5 Hz), 132.18 (d, *J* = 91.9 Hz), 131.58, 131.53 (d, *J* = 9.1 Hz), 130.48 (d, *J* = 8.7 Hz), 128.51 (d, *J* = 11.3 Hz), 122.42 (dd, *J* = 8.7, 2.7 Hz), 61.41, 51.73 (d, *J* = 3.2 Hz), 35.27 (d, *J* = 65.0 Hz), 31.72 (d, *J* = 2.3 Hz), 30.64 (d, *J* = 69.2 Hz), 15.60 (d, *J* = 14.9 Hz), 15.00 (d, *J* = 4.1 Hz), 14.04. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 37.6. **HRMS** (ESI) calcd for $C_{20}H_{30}O_5P^+$ $[M+H]^+$ 381.1825, Found 381.1837. The enantiomeric excess was determined by Daicel Chiralcel OD-H (87% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 17.28 min, *t* (minor) = 13.48 min. $[\alpha]_D^{20}$ = -5.9 (*c* = 0.3, acetone).



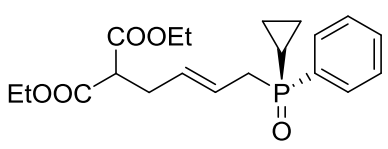
(**3d**) Colorless oil, R_f = 0.56 (Ethyl acetate/methanol = 7:1), 58% yield (25.7 mg), **^{1}H NMR** (500 MHz, Methylene Chloride-d_2) δ 7.69 (ddt, *J* = 9.6, 6.8, 1.5 Hz, 2H), 7.58 – 7.47 (m, 4H), 7.26 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.20 – 7.15 (m, 3H), 5.57 – 5.39 (m, 2H), 4.11 (ddtd, *J* = 17.9, 10.8, 7.0, 3.4 Hz, 5H), 3.30 (t, *J* = 7.5 Hz, 1H), 2.93 (dddd, *J* = 14.2, 12.6, 7.9, 5.1 Hz, 1H), 2.80 – 2.62 (m, 4H), 2.55 (dp, *J* = 7.9, 2.3 Hz, 2H), 2.31 (dtd, *J* = 14.8, 12.3, 5.0 Hz, 1H), 2.15 (dddd, *J* = 14.8, 12.1, 8.8, 4.8 Hz, 1H), 1.21 (td, *J* = 7.1, 3.5 Hz, 6H). **^{13}C NMR** (126 MHz, Methylene Chloride-d_2) δ 169.04, 141.84 (d, *J* = 14.3 Hz), 132.83 (d, *J* = 92.5 Hz), 130.93 (d, *J* = 8.7 Hz), 128.96 (d, *J* = 11.1 Hz), 128.88, 128.48, 126.59, 122.80 (d, *J* = 8.7 Hz), 61.76, 52.11 (d, *J* = 3.2 Hz), 35.76 (d, *J* = 65.1 Hz), 32.13 (d, *J* = 2.3 Hz), 30.98 (d, *J* = 67.1 Hz), 27.72 (d, *J* = 3.4 Hz), 14.25. **^{31}P NMR** (202 MHz, Methylene Chloride-d_2) δ 35.8. **HRMS** (ESI) calcd for $C_{25}H_{32}O_5P^+$ $[M+H]^+$ 443.1982, Found 443.1993. The enantiomeric excess was determined by Daicel Chiralcel OD-H (78% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 13.43 min, *t* (minor) = 10.41 min. $[\alpha]_D^{20}$ = +4.1 (*c* = 0.2, acetone).



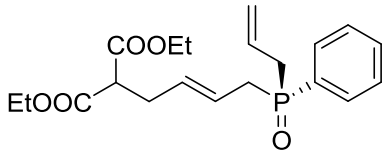
(**3e**) White solid, R_f = 0.52 (Ethyl acetate/methanol = 7:1), 65% yield (27.8 mg), **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.73 (ddd, *J* = 10.8, 8.2, 1.4 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.44 (m, 2H), 7.23 – 7.11 (m, 5H), 5.60 – 5.46 (m, 2H), 4.20 – 4.04 (m, 4H), 3.47 (t, *J* = 14.7 Hz, 1H), 3.42 – 3.32 (m, 2H), 2.83 – 2.74 (m, 2H), 2.54 – 2.46 (m, 2H), 1.20 (td, *J* = 7.1, 3.1 Hz, 6H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 169.43, 134.01 (d, *J* = 92.5 Hz), 133.83 (d, *J* = 7.8 Hz), 132.31 (d, *J* = 2.7 Hz), 132.29 (d, *J* = 11.5 Hz), 132.02 (d, *J* = 8.6 Hz), 131.08 (d, *J* = 5.1 Hz), 129.19 (d, *J* = 11.1 Hz), 129.04 (d, *J* = 2.5 Hz), 127.28 (d, *J* = 2.8 Hz), 123.82 (d, *J* = 9.0 Hz), 61.88, 52.58 (d, *J* = 3.2 Hz), 37.74 (d, *J* = 63.3 Hz), 35.18 (d, *J* = 65.7 Hz), 32.71 (d, *J* = 2.2 Hz), 14.53. **^{31}P NMR** (202 MHz, Acetone-d_6) δ 32.4. **HRMS** (ESI) calcd for $C_{24}H_{30}O_5P^+$ $[M+H]^+$ 429.1825, Found 429.1828. The enantiomeric excess was determined by Daicel Chiralcel OD-H (66% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 35.80 min, *t* (minor) = 26.26 min. $[\alpha]_D^{20}$ = -1.7 (*c* = 0.3, acetone).



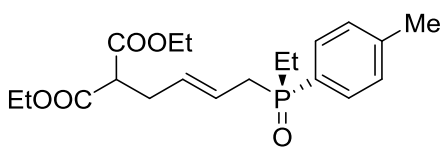
(**3f**) Colorless oil, R_f = 0.34 (Ethyl acetate/methanol = 7:1), 48% yield (18.3 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.75 – 7.61 (m, 2H), 7.49 (dtd, *J* = 14.4, 7.1, 2.0 Hz, 3H), 5.50 (m, 2H), 4.26 – 4.06 (m, 4H), 3.28 (t, *J* = 7.4 Hz, 1H), 2.89 – 2.68 (m, 2H), 2.55 (ddd, *J* = 8.3, 5.7, 2.8 Hz, 2H), 2.18 – 2.01 (m, *J* = 7.4, 6.9 Hz, 1H), 1.34 – 1.18 (m, 10H), 1.03 (dd, *J* = 16.3, 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.72 (d, *J* = 2.3 Hz), 131.50, 131.46 (d, *J* = 14.0 Hz), 131.00 (d, *J* = 8.1 Hz), 130.83 (d, *J* = 90.0 Hz), 128.38 (d, *J* = 10.8 Hz), 122.36 (d, *J* = 8.4 Hz), 61.39, 51.73 (d, *J* = 3.0 Hz), 32.25 (d, *J* = 63.1 Hz), 31.72 (d, *J* = 2.1 Hz), 27.31 (d, *J* = 69.6 Hz), 15.54 (d, *J* = 2.5 Hz), 14.90 (d, *J* = 3.0 Hz), 14.03. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 43.1. **HRMS** (ESI) calcd for $C_{20}H_{30}O_5P^+$ $[M+H]^+$ 381.1825, Found 381.1826. The enantiomeric excess was determined by Daicel Chiralcel OD-H (62% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 7.72 min, *t* (minor) = 6.30 min. $[\alpha]_D^{20}$ = -0.2 (*c* = 0.5, acetone).



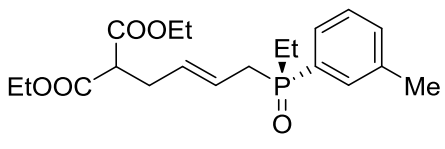
(**3g**) Colorless oil, R_f = 0.36 (Ethyl acetate/methanol = 7:1), 66% yield (25.0 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.92 – 7.65 (m, 2H), 7.64 – 7.40 (m, 3H), 5.67 – 5.35 (m, 2H), 4.16 (ttd, *J* = 10.9, 7.1, 3.7 Hz, 4H), 3.30 (t, *J* = 7.5 Hz, 1H), 2.92 – 2.67 (m, 2H), 2.62 – 2.49 (m, 2H), 1.24 (td, *J* = 7.1, 1.3 Hz, 6H), 1.11 – 0.98 (m, 2H), 0.96 – 0.75 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.74 (d, *J* = 2.4 Hz), 133.02 (d, *J* = 98.4 Hz), 131.56 (d, *J* = 2.7 Hz), 131.36 (d, *J* = 11.7 Hz), 130.40 (d, *J* = 8.7 Hz), 128.44 (d, *J* = 11.3 Hz), 122.56 (d, *J* = 8.5 Hz), 61.41, 51.76 (d, *J* = 3.4 Hz), 35.72 (d, *J* = 69.0 Hz), 31.75 (d, *J* = 2.2 Hz), 14.04, 5.82 (d, *J* = 101.6 Hz), 2.40 (dd, *J* = 73.3, 4.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 36.1. **HRMS** (ESI) calcd for $C_{20}H_{28}O_5P^+$ $[M+H]^+$ 379.1669, Found 379.1675. The enantiomeric excess was determined by Daicel Chiralcel OD-H (46% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 17.88 min, *t* (minor) = 15.92 min. $[\alpha]_D^{20}$ = -12.5 (*c* = 0.2, acetone).



(**3h**) Colorless oil, R_f = 0.40 (Ethyl acetate/methanol = 7:1), 67% yield (25.3 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.79 – 7.61 (m, 2H), 7.63 – 7.41 (m, 3H), 5.76 (dddd, *J* = 17.5, 12.7, 8.8, 6.2 Hz, 1H), 5.54 (dq, *J* = 5.9, 2.9 Hz, 2H), 5.27 – 5.07 (m, 2H), 4.25 – 4.05 (m, 4H), 3.33 (t, *J* = 7.4 Hz, 1H), 2.82 (m, 4H), 2.60 (dt, *J* = 8.3, 3.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.72 (d, *J* = 2.4 Hz), 131.97 (d, *J* = 11.8 Hz), 131.78 (d, *J* = 2.8 Hz), 131.60 (d, *J* = 93.8 Hz), 130.65 (d, *J* = 8.5 Hz), 128.50 (d, *J* = 11.4 Hz), 127.26 (d, *J* = 8.9 Hz), 122.07 (d, *J* = 8.8 Hz), 120.76 (d, *J* = 11.5 Hz), 61.44, 51.71 (d, *J* = 3.3 Hz), 35.06 (d, *J* = 65.7 Hz), 34.07 (d, *J* = 66.0 Hz), 31.74 (d, *J* = 2.2 Hz), 14.04. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.9. **HRMS** (ESI) calcd for $C_{20}H_{28}O_5P^+$ $[M+H]^+$ 379.1669, Found 379.1685. The enantiomeric excess was determined by Daicel Chiralcel OD-H (56% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 8.83 min, *t* (minor) = 7.57 min. $[\alpha]_D^{20}$ = -5.1 (*c* = 0.5, acetone).

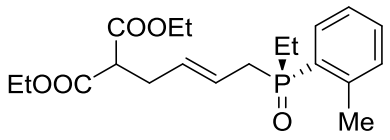


(**3i**) Colorless oil, R_f = 0.29 (Ethyl acetate/methanol = 7:1), 76% (28.9 mg) yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 2H), 7.30 – 7.26 (m, 2H), 5.60 – 5.39 (m, 2H), 4.26 – 4.07 (m, 4H), 3.31 (t, *J* = 7.5 Hz, 1H), 2.75 – 2.64 (m, 2H), 2.57 (dq, *J* = 8.0, 3.3, 2.4 Hz, 2H), 2.39 (s, 3H), 1.96 (m, 1H), 1.84 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 6H), 1.08 (dt, *J* = 17.0, 7.7 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.72 (d, *J* = 2.8 Hz), 142.02 (d, *J* = 2.8 Hz), 131.34 (d, *J* = 11.4 Hz), 130.54 (d, *J* = 8.8 Hz), 129.27 (d, *J* = 11.6 Hz), 128.26 (d, *J* = 95.1 Hz), 122.56 (d, *J* = 8.6 Hz), 61.39, 51.70 (d, *J* = 3.2 Hz), 34.84 (d, *J* = 65.2 Hz), 31.71 (d, *J* = 2.2 Hz), 21.50, 21.46 (d, *J* = 70.4 Hz), 14.02, 5.29 (d, *J* = 5.0 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.6. **HRMS** (ESI) calcd for $C_{20}H_{30}O_5P^+$ $[M+H]^+$ 381.1825, Found 381.1829. The enantiomeric excess was determined by Daicel Chiralcel IF (90% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210, *t* (major) = 27.12 min, *t* (minor) = 31.82 min. $[\alpha]_D^{20}$ = -9.4 (*c* = 1.2, acetone).

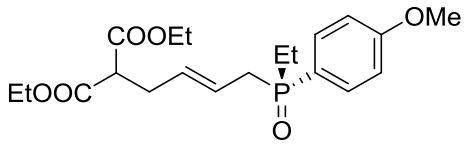


(**3j**) Colorless oil, R_f = 0.32 (Ethyl acetate/methanol = 7:1), 67% yield (25.6 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 11.3 Hz, 1H), 7.45 – 7.29 (m, 3H), 5.59 – 5.44 (m, 2H), 4.26 – 4.08 (m, 4H), 3.31 (t, *J* = 7.5 Hz, 1H), 2.70 (dd, *J* = 14.8, 6.0 Hz, 2H), 2.61 – 2.54 (m, 2H), 2.39 (s, 3H), 2.09 – 1.96 (m, 1H), 1.86 (m, 1H), 1.24 (t,

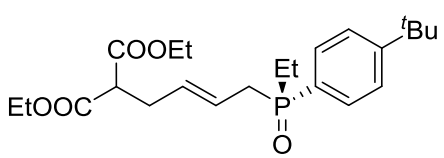
J = 7.1 Hz, 6H), 1.10 (dt, *J* = 17.1, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.73 (d, *J* = 3.0 Hz), 138.47 (d, *J* = 11.0 Hz), 132.41 (d, *J* = 2.8 Hz), 131.48 (d, *J* = 92.4 Hz), 131.46 (d, *J* = 11.2 Hz), 131.28 (d, *J* = 8.2 Hz), 128.37 (d, *J* = 11.9 Hz), 127.31 (d, *J* = 9.0 Hz), 122.47 (d, *J* = 8.6 Hz), 61.40, 51.74 (d, *J* = 3.1 Hz), 34.77 (d, *J* = 65.0 Hz), 31.72 (d, *J* = 2.2 Hz), 21.45 (d, *J* = 70.3 Hz), 21.35, 14.03, 5.31 (d, *J* = 5.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.6. **HRMS** (ESI) calcd for $C_{20}H_{30}O_5P^+$ $[M+H]^+$ 381.1825, Found 381.1829. The enantiomeric excess was determined by Daicel Chiralcel OD-H (87% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 7.44 min, *t* (minor) = 6.33 min. $[\alpha]_D^{20}$ = -7.6 (*c* = 0.6, acetone).



(**3k**) Colorless oil, R_f = 0.35 (Ethyl acetate/methanol = 5:1), 39% yield (14.8 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.54 (ddd, *J* = 12.1, 7.6, 1.4 Hz, 1H), 7.39 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.30 – 7.21 (m, 2H), 5.51 (m, 2H), 4.16 (ddp, *J* = 10.8, 7.2, 3.6 Hz, 5H), 3.29 (t, *J* = 7.5 Hz, 1H), 2.87 – 2.72 (m, 2H), 2.63 (d, *J* = 1.3 Hz, 3H), 2.56 (qd, *J* = 4.7, 1.9 Hz, 2H), 2.13 – 1.91 (m, 2H), 1.24 (td, *J* = 7.1, 1.2 Hz, 6H), 1.13 (dt, *J* = 17.1, 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.75, 141.60 (d, *J* = 8.1 Hz), 131.92 (d, *J* = 10.4 Hz), 131.77 (d, *J* = 9.7 Hz), 131.61 (d, *J* = 2.6 Hz), 131.30 (d, *J* = 11.5 Hz), 129.53 (d, *J* = 90.1 Hz), 125.57 (d, *J* = 11.3 Hz), 122.69 (d, *J* = 8.3 Hz), 61.42, 51.78 (d, *J* = 3.0 Hz), 34.51 (d, *J* = 64.5 Hz), 31.73 (d, *J* = 2.2 Hz), 21.61 (d, *J* = 70.2 Hz), 21.55 (d, *J* = 3.1 Hz), 14.05, 5.55 (d, *J* = 5.0 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 42.3. **HRMS** (ESI) calcd for $C_{20}H_{30}O_5P^+$ $[M+H]^+$ 381.1825, Found 381.1826. The enantiomeric excess was determined by Daicel Chiralcel IH (64% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 30.44 min, *t* (minor) = 27.22 min. $[\alpha]_D^{20}$ = -9.3 (*c* = 0.3, acetone).

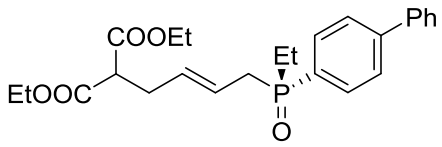


(**3l**) Colorless oil, R_f = 0.35 (Ethyl acetate/methanol = 5:1), 72% yield (28.6 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 10.4, 8.7 Hz, 2H), 6.97 (dd, *J* = 8.8, 2.2 Hz, 2H), 5.55 – 5.42 (m, 2H), 4.24 – 4.07 (m, 5H), 3.83 (s, 3H), 3.30 (t, *J* = 7.5 Hz, 1H), 2.67 (dd, *J* = 14.9, 6.0 Hz, 2H), 2.56 (ddt, *J* = 7.4, 5.4, 2.6 Hz, 2H), 1.96 (ddq, *J* = 15.3, 12.9, 7.6 Hz, 1H), 1.83 (ddq, *J* = 15.2, 9.6, 7.7 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 6H), 1.08 (dt, *J* = 17.1, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.71 (d, *J* = 3.2 Hz), 162.23 (d, *J* = 2.8 Hz), 132.32 (d, *J* = 9.7 Hz), 131.33 (d, *J* = 11.4 Hz), 122.60 (d, *J* = 8.5 Hz), 122.58 (d, *J* = 98.8 Hz), 114.10 (d, *J* = 12.3 Hz), 61.39, 55.24, 51.71 (d, *J* = 3.2 Hz), 34.95 (d, *J* = 65.5 Hz), 31.70 (d, *J* = 2.2 Hz), 21.56 (d, *J* = 70.7 Hz), 14.00, 5.27 (d, *J* = 5.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.5. **HRMS** (ESI) calcd for $C_{20}H_{29}O_6PNa^+$ $[M+Na]^+$ 419.1594, Found 419.1595. The enantiomeric excess was determined by Daicel Chiralcel OD-H (88% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 8.78 min, *t* (minor) = 7.69 min. $[\alpha]_D^{20}$ = -12.7 (*c* = 1.2, acetone).

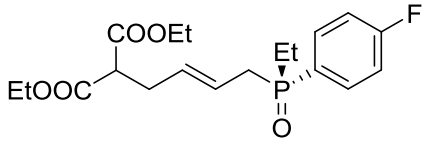


(**3m**) Colorless oil, R_f = 0.32 (Ethyl acetate/methanol = 7:1), 66% yield (27.8 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 10.5, 8.4 Hz, 2H), 7.48 (dd, *J* = 8.4, 2.5 Hz, 2H), 5.52 (m, 2H), 4.25 – 4.08 (m, 4H), 3.32 (t, *J* = 7.5 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.59 (qd, *J* = 4.8, 1.9 Hz, 2H), 1.98 (ddq, *J* = 15.3, 13.0, 7.6 Hz, 1H), 1.85 (ddq, *J* = 15.2, 9.6, 7.6 Hz, 1H), 1.33 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 6H), 1.10 (dt, *J* = 17.0, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.75 (d, *J* = 2.2 Hz),

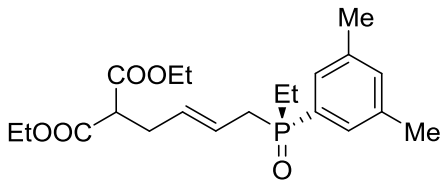
155.02 (d, *J* = 2.8 Hz), 131.28 (d, *J* = 11.4 Hz), 130.39 (d, *J* = 8.9 Hz), 128.36 (d, *J* = 95.0 Hz), 125.53 (d, *J* = 11.4 Hz), 122.70 (d, *J* = 8.3 Hz), 61.42 (d, *J* = 2.4 Hz), 51.71 (d, *J* = 3.2 Hz), 34.92, 34.84 (d, *J* = 65.1 Hz), 31.75 (d, *J* = 2.2 Hz), 31.08, 21.41 (d, *J* = 70.6 Hz), 14.04, 5.34 (d, *J* = 5.0 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.2. **HRMS** (ESI) calcd for $C_{23}H_{36}O_5P^+$ $[M+H]^+$ 423.2295, Found 423.2298. The enantiomeric excess was determined by Daicel Chiralcel AD-H (80% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 6.29 min, *t* (minor) = 6.94 min. $[\alpha]_D^{20}$ = -11.6 (*c* = 0.8, acetone).



(**3n**) White solid, R_f = 0.35 (Ethyl acetate/methanol = 4:1), 84% yield (37.2 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 – 7.66 (m, 4H), 7.66 – 7.55 (m, 2H), 7.49 – 7.41 (m, 2H), 7.42 – 7.33 (m, 1H), 5.53 (m, 2H), 4.24 – 4.02 (m, 4H), 3.33 (t, *J* = 7.5 Hz, 1H), 2.83 – 2.69 (m, 2H), 2.66 – 2.54 (m, 2H), 2.03 (ddq, *J* = 15.3, 12.9, 7.6 Hz, 1H), 1.91 (ddq, *J* = 15.2, 9.5, 7.7 Hz, 1H), 1.22 (td, *J* = 7.1, 4.2 Hz, 6H), 1.13 (dt, *J* = 17.2, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.71 (d, *J* = 2.4 Hz), 144.45 (d, *J* = 2.8 Hz), 139.82, 131.64 (d, *J* = 11.5 Hz), 131.05 (d, *J* = 8.8 Hz), 130.03 (d, *J* = 93.8 Hz), 128.88, 128.07, 127.20 (d, *J* = 11.4 Hz), 127.19, 122.29 (d, *J* = 8.5 Hz), 61.42, 51.66 (d, *J* = 3.2 Hz), 34.72 (d, *J* = 65.3 Hz), 31.69, 21.47 (d, *J* = 70.5 Hz), 13.99 (d, *J* = 1.6 Hz), 5.29 (d, *J* = 5.2 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 40.0. **HRMS** (ESI) calcd for $C_{25}H_{32}O_5P^+$ $[M+H]^+$ 443.1982, Found 443.1986. The enantiomeric excess was determined by Daicel Chiralcel OD-H (87% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 10.59 min, *t* (minor) = 8.86 min. $[\alpha]_D^{20}$ = -11.0 (*c* = 0.4, acetone).

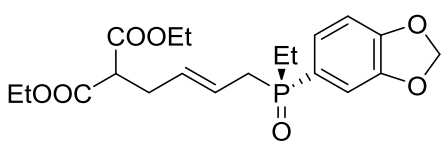


(**3o**) Colorless oil, R_f = 0.31 (Ethyl acetate/methanol = 4:1), 64% yield (24.6 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.76 – 7.57 (m, 2H), 7.17 (td, *J* = 8.7, 2.0 Hz, 2H), 5.49 (m, 2H), 4.24 – 4.07 (m, 4H), 3.30 (t, *J* = 7.4 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.58 (tdd, *J* = 7.8, 4.0, 2.2 Hz, 2H), 2.00 (ddq, *J* = 15.2, 12.8, 7.6 Hz, 1H), 1.86 (ddq, *J* = 15.2, 9.5, 7.6 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 5H), 1.10 (dt, *J* = 17.2, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.69 (d, *J* = 3.1 Hz), 164.90 (dd, *J* = 252.7, 3.1 Hz), 133.04 (t, *J* = 9.3 Hz), 131.78 (d, *J* = 11.5 Hz), 127.49 (dd, *J* = 94.7, 3.3 Hz), 122.18 (d, *J* = 8.7 Hz), 115.92 (dd, *J* = 21.3, 12.2 Hz), 61.45, 51.66 (d, *J* = 3.2 Hz), 34.85 (d, *J* = 65.6 Hz), 31.69 (d, *J* = 2.3 Hz), 21.59 (d, *J* = 70.6 Hz), 14.03, 5.25 (d, *J* = 5.3 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.0. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -107.30. **HRMS** (ESI) calcd for $C_{19}H_{26}FO_5PNa^+$ $[M+Na]^+$ 407.1394, Found 407.1397. The enantiomeric excess was determined by Daicel Chiralcel OD-H (82% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 17.20 min, *t* (minor) = 16.23 min. $[\alpha]_D^{20}$ = -7.2 (*c* = 0.6, acetone).

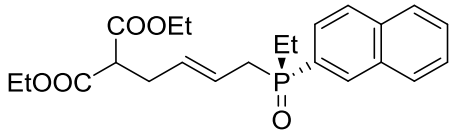


(**3p**) Colorless oil, R_f = 0.37 (Ethyl acetate/methanol = 7:1), 58% yield (22.9 mg), **^{1}H NMR** (500 MHz, Methylene Chloride-d_2) δ 7.25 (dd, *J* = 11.0, 1.7 Hz, 2H), 7.16 (s, 1H), 5.54 – 5.43 (m, 2H), 4.13 (dtdd, *J* = 9.4, 6.9, 4.6, 2.4 Hz, 5H), 3.30 (t, *J* = 7.5 Hz, 1H), 2.70 – 2.60 (m, 2H), 2.58 – 2.51 (m, 2H), 2.36 (s, 6H), 1.94 (ddq, *J* = 15.2, 12.9, 7.7 Hz, 1H), 1.81 (ddq, *J* = 15.1, 9.5, 7.7 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 6H), 1.05 (dt, *J* = 16.9, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Methylene Chloride-d_2) δ 169.09 (d, *J* = 2.2 Hz), 138.69 (d, *J* = 11.6 Hz), 133.50 (d, *J* = 2.9 Hz), 132.48 (d, *J* = 91.8 Hz), 131.55 (d, *J* = 11.2 Hz), 128.50 (d, *J* = 8.7 Hz), 123.20 (d, *J* = 8.7 Hz), 61.76, 52.24 (d, *J* = 3.2 Hz), 35.15 (d, *J*

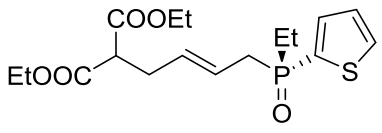
= 64.6 Hz), 32.16 (d, *J* = 2.2 Hz), 22.01 (d, *J* = 70.1 Hz), 21.40, 14.26, 5.56 (d, *J* = 5.2 Hz). **^{31}P NMR** (202 MHz, Methylene Chloride-d_2) δ 38.1. **HRMS** (ESI) calcd for $C_{21}H_{32}O_5P^+$ $[M+Na]^+$ 395.1982, Found 395.1982. The enantiomeric excess was determined by Daicel Chiralcel OD-H (88% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 14.45 min, *t* (minor) = 12.26 min. $[\alpha]_D^{20}$ = -7.0 (*c* = 1.1, acetone).



(**3q**) Colorless oil, R_f = 0.39 (Ethyl acetate/methanol = 5:1), 68% yield (27.9 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.18 (ddd, *J* = 11.4, 7.9, 1.5 Hz, 1H), 7.07 (dd, *J* = 10.3, 1.5 Hz, 1H), 6.89 (dd, *J* = 7.9, 2.2 Hz, 1H), 6.02 (s, 2H), 5.49 (m, 2H), 4.22 – 4.08 (m, 4H), 3.31 (t, *J* = 7.4 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.58 (qd, *J* = 4.6, 2.7 Hz, 2H), 1.95 (ddq, *J* = 15.2, 13.0, 7.6 Hz, 1H), 1.81 (ddq, *J* = 15.3, 9.5, 7.7 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 6H), 1.09 (dt, *J* = 17.1, 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.70 (d, *J* = 3.0 Hz), 150.54 (d, *J* = 2.8 Hz), 148.03 (d, *J* = 16.9 Hz), 131.46 (d, *J* = 11.5 Hz), 125.71 (d, *J* = 9.4 Hz), 124.59 (d, *J* = 96.4 Hz), 122.45 (d, *J* = 8.5 Hz), 109.99 (d, *J* = 11.3 Hz), 108.72 (d, *J* = 13.9 Hz), 101.51, 61.40, 51.70 (d, *J* = 3.2 Hz), 34.95 (d, *J* = 65.6 Hz), 31.70 (d, *J* = 2.2 Hz), 21.59 (d, *J* = 70.8 Hz), 14.01, 5.27 (d, *J* = 5.3 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.7. **HRMS** (ESI) calcd for $C_{20}H_{27}O_7PNa^+$ $[M+Na]^+$ 433.1387, Found 433.1391. The enantiomeric excess was determined by Daicel Chiralcel OD-H (87% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 28.65 min, *t* (minor) = 25.79 min. $[\alpha]_D^{20}$ = -5.7 (*c* = 1.4, acetone).

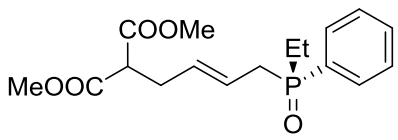


(**3r**) White solid, R_f = 0.32 (Ethyl acetate/methanol = 5:1), 73% yield (30.4 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 12.6 Hz, 1H), 8.01 – 7.81 (m, 3H), 7.65 – 7.48 (m, 3H), 5.62 – 5.45 (m, 2H), 4.20 – 4.04 (m, 4H), 3.30 (t, *J* = 7.4 Hz, 1H), 2.80 (dd, *J* = 14.9, 6.3 Hz, 2H), 2.56 (dt, *J* = 7.2, 3.2 Hz, 2H), 2.08 (ddq, *J* = 15.3, 13.1, 7.6 Hz, 1H), 1.95 (ddq, *J* = 15.3, 9.2, 7.7 Hz, 1H), 1.21 (td, *J* = 7.1, 2.1 Hz, 6H), 1.12 (dt, *J* = 17.2, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.68 (d, *J* = 3.0 Hz), 134.54 (d, *J* = 2.4 Hz), 133.04 (d, *J* = 7.4 Hz), 132.55 (d, *J* = 12.0 Hz), 131.57 (d, *J* = 11.4 Hz), 128.76, 128.69 (d, *J* = 92.4 Hz), 128.29 (d, *J* = 11.0 Hz), 127.99, 127.74, 126.90, 125.06 (d, *J* = 10.2 Hz), 122.36 (d, *J* = 8.7 Hz), 61.37, 51.65 (d, *J* = 3.2 Hz), 34.83 (d, *J* = 65.1 Hz), 31.68 (d, *J* = 2.2 Hz), 21.51 (d, *J* = 70.3 Hz), 13.99, 5.32 (d, *J* = 5.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.6. **HRMS** (ESI) calcd for $C_{23}H_{30}O_5P^+$ $[M+H]^+$ 417.1825, Found 417.1832. The enantiomeric excess was determined by Daicel Chiralcel OD-H (84% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 254 nm, *t* (major) = 11.15 min, *t* (minor) = 9.72 min. $[\alpha]_D^{20}$ = -15.9 (*c* = 1.5, acetone).

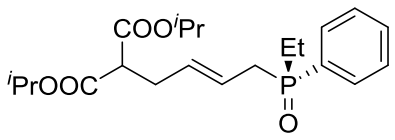


(**3s**) Colorless oil, R_f = 0.32 (Ethyl acetate/methanol = 5:1), 91% yield (33.6 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.68 (ddd, *J* = 4.9, 3.8, 1.1 Hz, 1H), 7.51 (ddd, *J* = 6.4, 3.6, 1.1 Hz, 1H), 7.18 (ddd, *J* = 5.0, 3.5, 1.7 Hz, 1H), 5.62 – 5.44 (m, 2H), 4.22 – 4.08 (m, 4H), 3.32 (t, *J* = 7.4 Hz, 1H), 2.85 – 2.69 (m, 2H), 2.58 (dh, *J* = 5.9, 1.8 Hz, 2H), 2.00 (ddq, *J* = 15.3, 12.8, 7.7 Hz, 1H), 1.88 (ddq, *J* = 15.3, 10.5, 7.7 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 6H), 1.14 (dt, *J* = 17.9, 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.64 (d, *J* = 1.8 Hz), 134.95 (d, *J* = 8.2 Hz), 132.62 (d, *J* = 3.8 Hz), 132.16 (d, *J* = 97.6 Hz), 131.97 (d, *J* = 12.0 Hz), 128.22 (d, *J* = 12.7 Hz), 61.39, 51.64

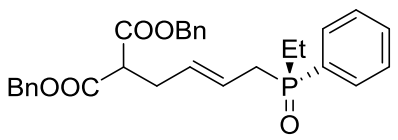
(d, *J* = 3.5 Hz), 35.86 (d, *J* = 68.8 Hz), 31.67 (d, *J* = 2.3 Hz), 23.23 (d, *J* = 73.6 Hz), 13.99, 5.34 (d, *J* = 5.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 36.3. **HRMS** (ESI) calcd for $C_{17}H_{25}O_5PSNa^+$ $[M+H]^+$ 395.1053, Found 395.1041. The enantiomeric excess was determined by Daicel Chiralcel OD-H (90% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 12.42 min, *t* (minor) = 9.84 min. $[\alpha]_D^{20}$ = -16.5 (*c* = 1.6, acetone).



(**3t**) Colorless oil, R_f = 0.30 (Ethyl acetate/methanol = 5:1), 67% yield (22.8 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.72 – 7.60 (m, 2H), 7.54 – 7.40 (m, 3H), 5.59 – 5.40 (m, 2H), 3.70 (d, *J* = 1.1 Hz, 6H), 3.34 (t, *J* = 7.5 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.57 (qd, *J* = 6.0, 5.6, 3.5 Hz, 2H), 2.00 (ddq, *J* = 15.3, 13.0, 7.6 Hz, 1H), 1.86 (ddq, *J* = 15.3, 9.5, 7.6 Hz, 1H), 1.10 (dt, *J* = 17.1, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.06 (d, *J* = 2.3 Hz), 131.62 (d, *J* = 92.8 Hz), 131.61 (d, *J* = 2.8 Hz), 131.26 (d, *J* = 11.5 Hz), 130.51 (d, *J* = 8.7 Hz), 128.52 (d, *J* = 11.1 Hz), 122.56 (d, *J* = 8.7 Hz), 52.53, 51.35 (d, *J* = 3.4 Hz), 34.68 (d, *J* = 64.9 Hz), 31.76 (d, *J* = 2.2 Hz), 21.49 (d, *J* = 70.3 Hz), 5.29 (d, *J* = 5.3 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.5. **HRMS** (ESI) calcd for $C_{17}H_{24}O_5P^+$ $[M+H]^+$ 339.1356, Found 339.1360. The enantiomeric excess was determined by Daicel Chiralcel OD-H (90% ee), *n*-Hexanes/IPA = 80/20, 1 mL/min, λ = 210 nm, *t* (major) = 13.07 min, *t* (minor) = 10.60 min. $[\alpha]_D^{20}$ = -6.7 (*c* = 0.8, acetone).

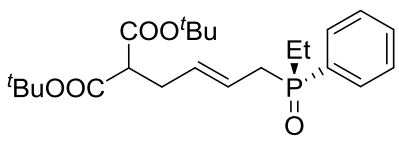


(**3u**) Colorless oil, R_f = 0.32 (Ethyl acetate/methanol = 7:1), 71% yield (28.1 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.75 – 7.60 (m, 2H), 7.54 – 7.40 (m, 3H), 5.49 (m, 2H), 4.99 (heptd, *J* = 6.3, 2.2 Hz, 2H), 3.22 (t, *J* = 7.5 Hz, 1H), 2.76 – 2.62 (m, 2H), 2.61 – 2.49 (m, 2H), 1.99 (ddq, *J* = 15.3, 12.9, 7.7 Hz, 1H), 1.86 (ddq, *J* = 15.3, 9.6, 7.7 Hz, 1H), 1.19 (dt, *J* = 6.0, 2.7 Hz, 11H), 1.08 (dt, *J* = 17.2, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.23 (d, *J* = 1.7 Hz), 131.69 (d, *J* = 92.5 Hz), 131.68 (d, *J* = 11.5 Hz), 131.57 (d, *J* = 2.8 Hz), 130.51 (d, *J* = 8.4 Hz), 128.48 (d, *J* = 11.1 Hz), 122.17 (d, *J* = 8.6 Hz), 68.84 (d, *J* = 2.2 Hz), 52.00 (d, *J* = 3.2 Hz), 34.74 (d, *J* = 65.1 Hz), 31.59 (d, *J* = 2.2 Hz), 21.54 (d, *J* = 8.2 Hz), 21.36 (d, *J* = 70.3 Hz), 5.24 (d, *J* = 5.2 Hz).**^{31}P NMR** (202 MHz, Chloroform-*d*) δ 37.6. **HRMS** (ESI) calcd for $C_{21}H_{32}O_5P^+$ $[M+Na]^+$ 395.1982, Found 395.1987. The enantiomeric excess was determined by Daicel Chiralcel OD-H (92% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 12.61 min, *t* (minor) = 10.54 min. $[\alpha]_D^{20}$ = -9.2 (*c* = 1.6, acetone).

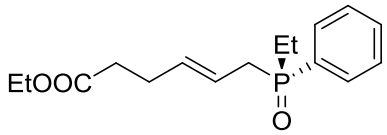


(**3v**) Colorless oil, R_f = 0.35 (Ethyl acetate/methanol = 7:1), 64% yield (31.4 mg), **^{1}H NMR** (500 MHz, Methylene Chloride-d_2) δ 7.76 – 7.60 (m, 2H), 7.57 – 7.45 (m, 3H), 7.41 – 7.19 (m, 10H), 5.56 – 5.40 (m, 2H), 5.22 – 5.04 (m, 4H), 3.45 (t, *J* = 7.5 Hz, 1H), 2.72 – 2.52 (m, 4H), 1.95 (m, 1H), 1.88 – 1.76 (m, 1H), 1.05 (dt, *J* = 17.0, 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, Methylene Chloride-d_2) δ 168.75, 135.96, 132.81 (d, *J* = 91.7 Hz), 131.83 (d, *J* = 2.5 Hz), 131.36 (d, *J* = 11.2 Hz), 130.96 (d, *J* = 8.5 Hz), 128.90, 128.81, 128.68, 128.53, 123.34 (d, *J* = 8.6 Hz), 67.46, 52.16 (d, *J* = 3.1 Hz), 35.07 (d, *J* = 64.8 Hz), 32.16 (d, *J* = 1.9 Hz), 22.01 (d, *J* = 70.1 Hz), 5.52 (d, *J* = 5.0 Hz). **^{31}P NMR** (202 MHz, Methylene Chloride-d_2) δ 37.9. **HRMS** (ESI) calcd for $C_{29}H_{31}O_5PNa^+$ $[M+Na]^+$ 513.1801, Found 513.1804. The enantiomeric excess was determined by Daicel Chiralcel OD-

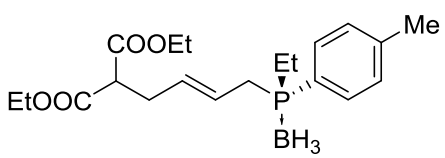
H (89% ee), *n*-Hexanes/IPA = 70/30, 1 mL/min, λ = 210 nm, *t* (major) = 15.65 min, *t* (minor) = 12.33 min. $[\alpha]_D^{20}$ = -7.0 (*c* = 1.6, acetone).



(**3w**) Colorless oil, R_f = 0.45 (Ethyl acetate/methanol = 10:1), 62% yield (26.3 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.76 – 7.59 (m, 2H), 7.56 – 7.40 (m, 3H), 5.49 (m, 2H), 3.09 (t, *J* = 7.5 Hz, 1H), 2.70 (dd, *J* = 14.9, 5.3 Hz, 2H), 2.55 – 2.39 (m, 2H), 2.01 (m, 1H), 1.93 – 1.81 (m, 1H), 1.41 (s, 18H), 1.09 (dt, *J* = 17.1, 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.10, 132.07 (d, *J* = 11.6 Hz), 131.56 (d, *J* = 2.7 Hz), 131.76 (d, *J* = 92.0 Hz), 130.54 (d, *J* = 8.7 Hz), 128.48 (d, *J* = 11.1 Hz), 121.78 (d, *J* = 8.5 Hz), 81.47 (d, *J* = 2.3 Hz), 53.57 (d, *J* = 3.1 Hz), 34.80 (d, *J* = 65.2 Hz), 31.69 (d, *J* = 2.2 Hz), 27.86, 21.31 (d, *J* = 70.3 Hz), 5.25 (d, *J* = 5.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.5. **HRMS** (ESI) calcd for $C_{23}H_{35}O_5PNa^+$ $[M+Na]^+$ 445.2114, Found 445.2125. The enantiomeric excess was determined by Daicel Chiralcel OD-H (89% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 8.38 min, *t* (minor) = 7.40 min. $[\alpha]_D^{20}$ = -8.18 (*c* = 0.6, acetone).



(**4a**) Colorless oil, R_f = 0.42 (Ethyl acetate/methanol = 5:1), 46% yield (13.5 mg), **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 10.7, 7.4 Hz, 2H), 7.59 – 7.44 (m, 3H), 5.56 – 5.39 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.72 (dd, *J* = 15.0, 6.7 Hz, 2H), 2.30 (m, 4H), 2.02 (dp, *J* = 22.4, 7.7 Hz, 1H), 1.89 (dp, *J* = 16.0, 7.9 Hz, 1H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.12 (dt, *J* = 16.2, 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.83, 134.33 (d, *J* = 11.4 Hz), 131.80 (d, *J* = 92.4 Hz), 131.58 (d, *J* = 2.7 Hz), 130.61 (d, *J* = 8.6 Hz), 128.49 (d, *J* = 11.3 Hz), 120.18 (d, *J* = 8.5 Hz), 60.34, 34.72 (d, *J* = 65.4 Hz), 33.77 (d, *J* = 3.2 Hz), 27.85 (d, *J* = 2.3 Hz), 21.53 (d, *J* = 70.0 Hz), 14.21, 5.34 (d, *J* = 5.0 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.7. **HRMS** (ESI) calcd for $C_{16}H_{24}O_3P^+$ $[M+H]^+$ 295.1458, Found 295.1457. The enantiomeric excess was determined by Daicel Chiralcel OD-H (90% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 14.32 min, *t* (minor) = 12.65 min. $[\alpha]_D^{20}$ = -6.81 (*c* = 0.9, acetone).



(**4i**) Colorless oil, R_f = 0.48 (Petroleum ether/ Ethyl acetate = 3:1), 58% yield (21.9 mg), **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.67 (dd, *J* = 9.9, 8.1 Hz, 2H), 7.35 (dd, *J* = 8.1, 2.1 Hz, 2H), 5.63 – 5.41 (m, 2H), 4.29 – 4.02 (m, 4H), 3.37 (t, *J* = 7.4 Hz, 1H), 2.78 – 2.63 (m, 2H), 2.52 (ddd, *J* = 9.5, 4.9, 1.9 Hz, 2H), 2.40 (s, 3H), 1.99 (ddq, *J* = 15.2, 12.6, 7.7 Hz, 1H), 1.89 (ddq, *J* = 15.0, 8.8, 7.7 Hz, 1H), 1.22 (td, *J* = 7.1, 1.8 Hz, 6H), 1.01 (dt, *J* = 16.8, 7.6 Hz, 3H), 0.82 – 0.33 (m, 2H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 169.41, 142.62 (d, *J* = 2.4 Hz), 133.29 (d, *J* = 8.7 Hz), 132.01 (d, *J* = 10.1 Hz), 130.36 (d, *J* = 9.7 Hz), 125.78 (d, *J* = 52.3 Hz), 124.53 (d, *J* = 6.5 Hz), 61.91, 52.60 (d, *J* = 2.9 Hz), 32.57 (d, *J* = 2.1 Hz), 30.66 (d, *J* = 34.6 Hz), 21.59, 17.87 (d, *J* = 37.3 Hz), 14.54, 7.26 (d, *J* = 1.1 Hz). **^{31}P NMR** (202 MHz, Acetone-d_6) δ 16.4 (d, *J* = 72.3 Hz). **^{11}B NMR** (160 MHz, Acetone-d_6) δ -41.06 (qd, *J* = 96.5, 96.1, 58.5 Hz). **HRMS** (ESI) calcd for $C_{20}H_{32}BO_4PNa^+$ $[M+Na]^+$ 401.2023, Found 401.2018. The enantiomeric excess was determined by Daicel Chiralcel IF (89% ee), *n*-Hexanes/IPA = 90/10, 1 mL/min, λ = 210 nm, *t* (major) = 13.13 min, *t* (minor) = 14.12 min. $[\alpha]_D^{20}$ = -6.37 (*c* = 2.1, acetone).

7. Supplementary references

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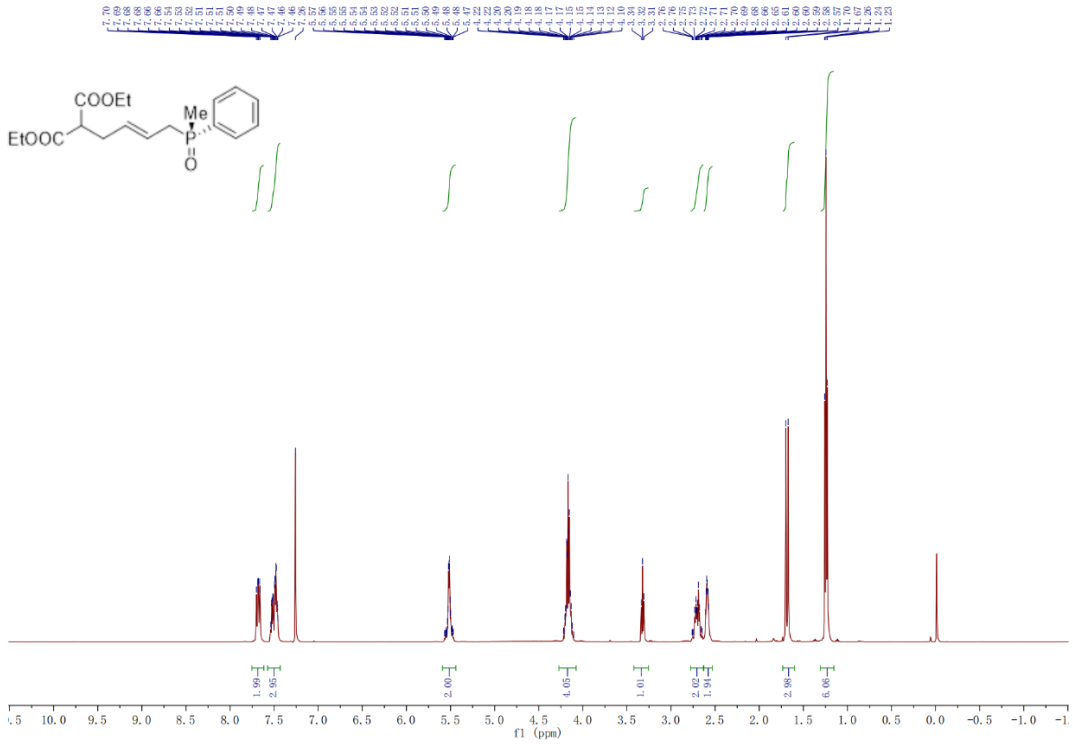
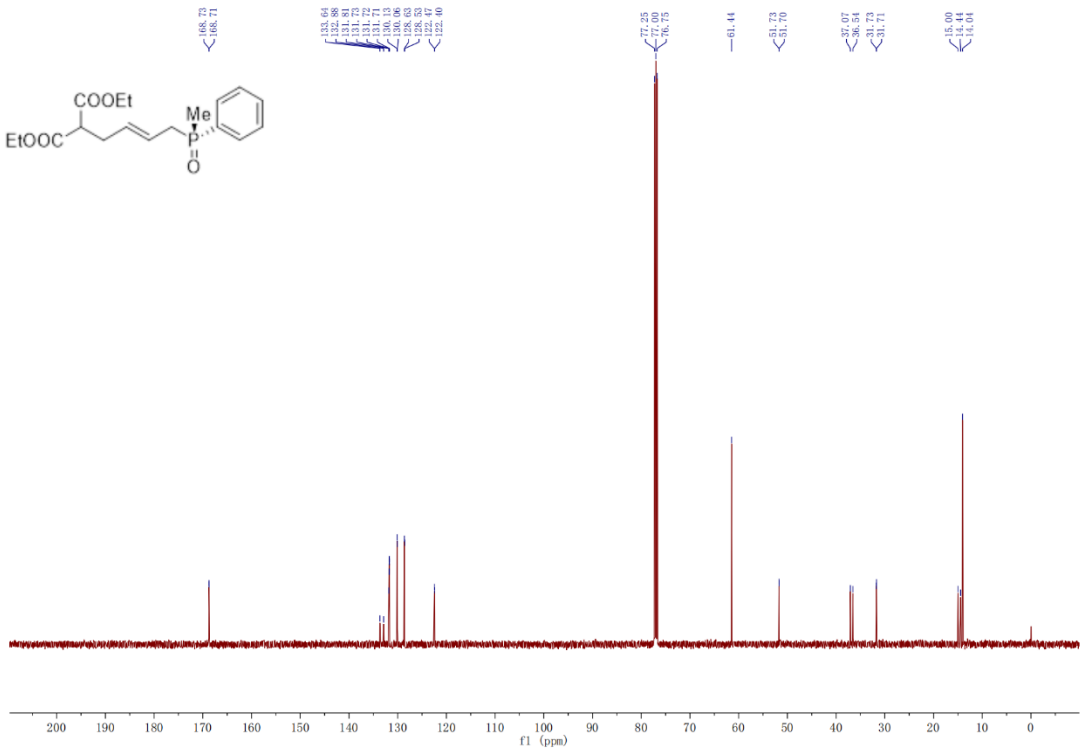
4. Ieki, R.; Kani, Y.; Tsunoi, S.; Shibata, I., Transition-Metal-Free Coupling Reaction of Vinylcyclopropanes with Aldehydes Catalyzed by Tin Hydride. *Chem.–Eur. J.* **2015,** *21* (16), 6295-6300.
5. Abele, S.; Inauen, R.; Funel, J.-A.; Weller, T., Design and Scale-Up of a Practical Enantioselective Route to 5-Phenylbicyclo[2.2.2]oct-5-en-2-one. *Org. Process Res. Dev.* **2012,** *16* (1), 129-140.
6. Rajendran, K. V.; Gilheany, D. G., Simple unprecedented conversion of phosphine oxides and sulfides to phosphine boranes using sodium borohydride. *Chem. Commun.* **2012,** *48* (6), 817-819.

8. Copies of NMR Spectroscopic data

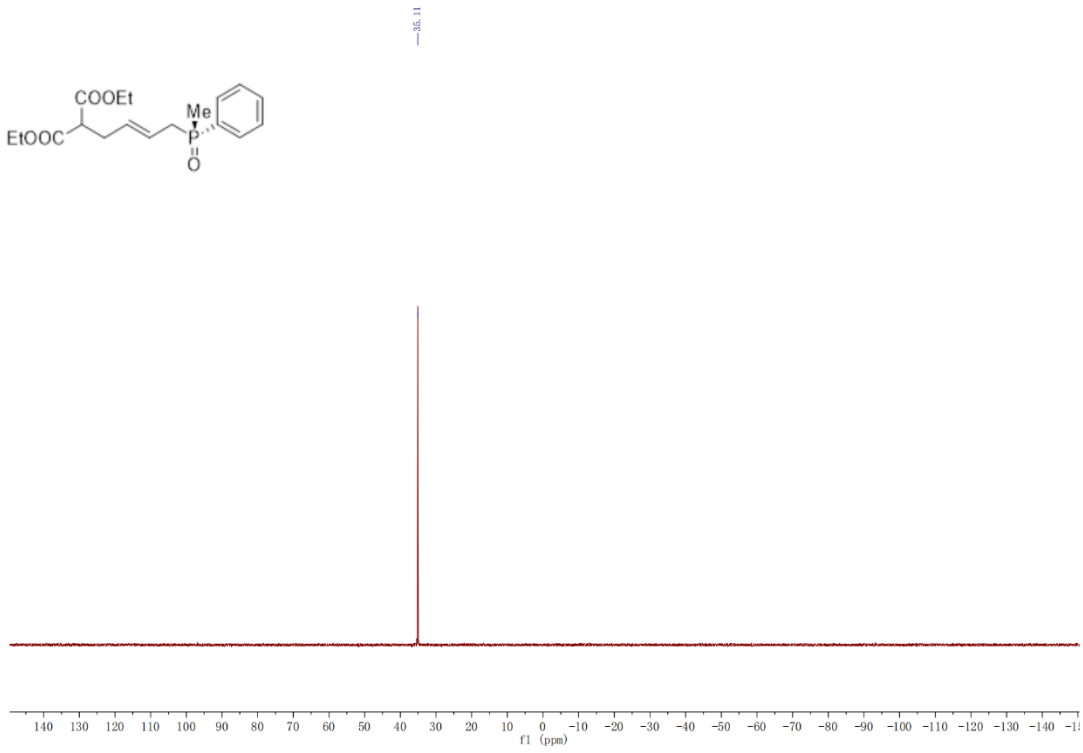
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3a**



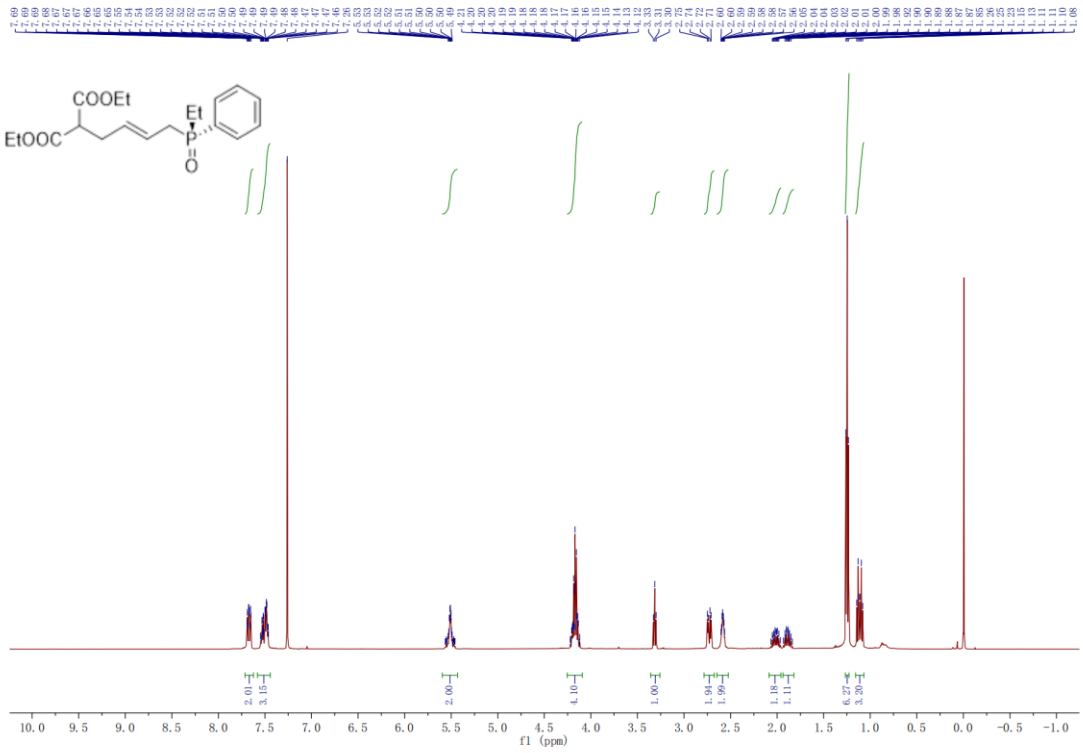
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3a**



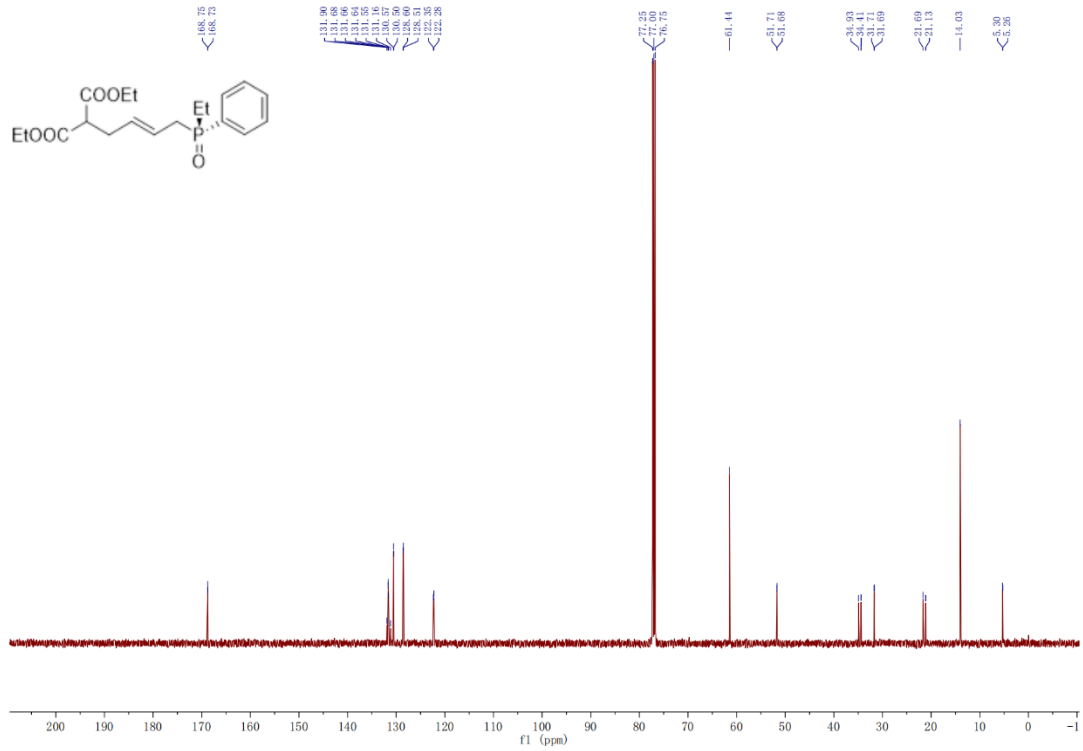
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3a**



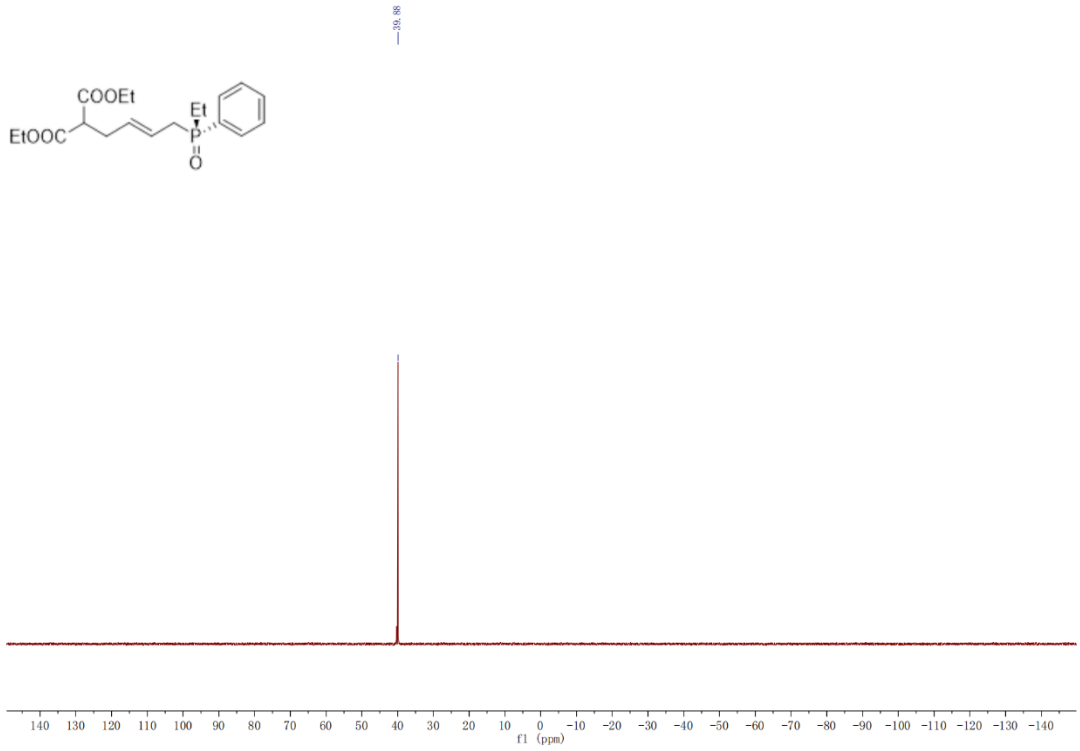
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3b**



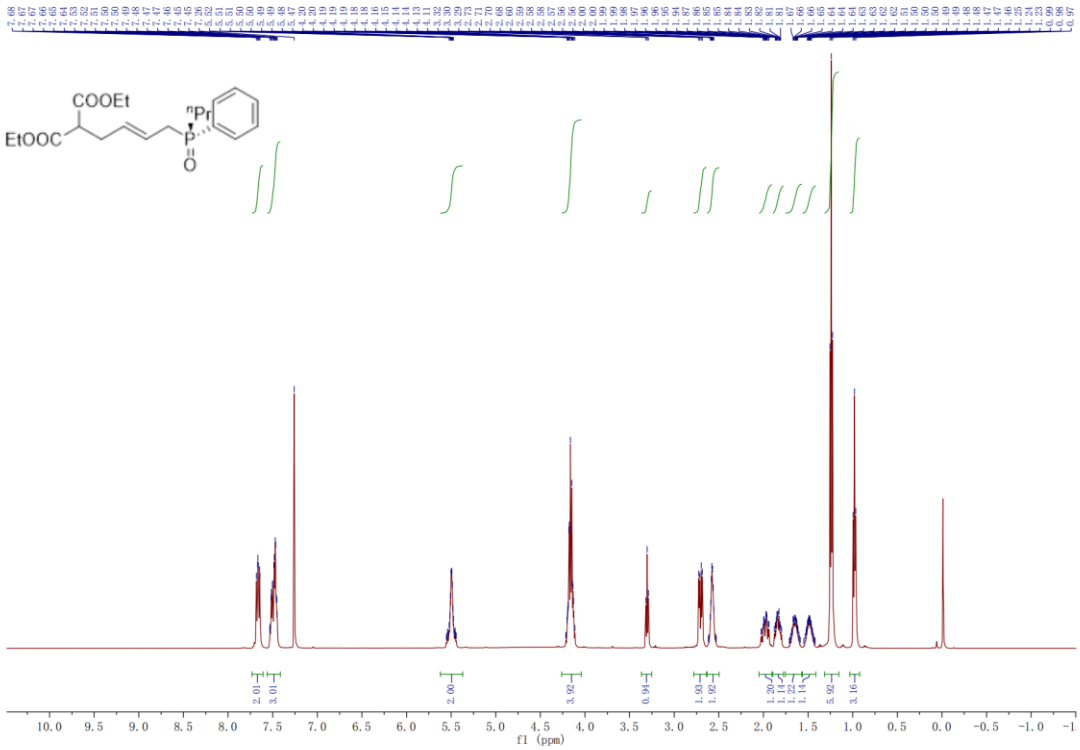
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3b**



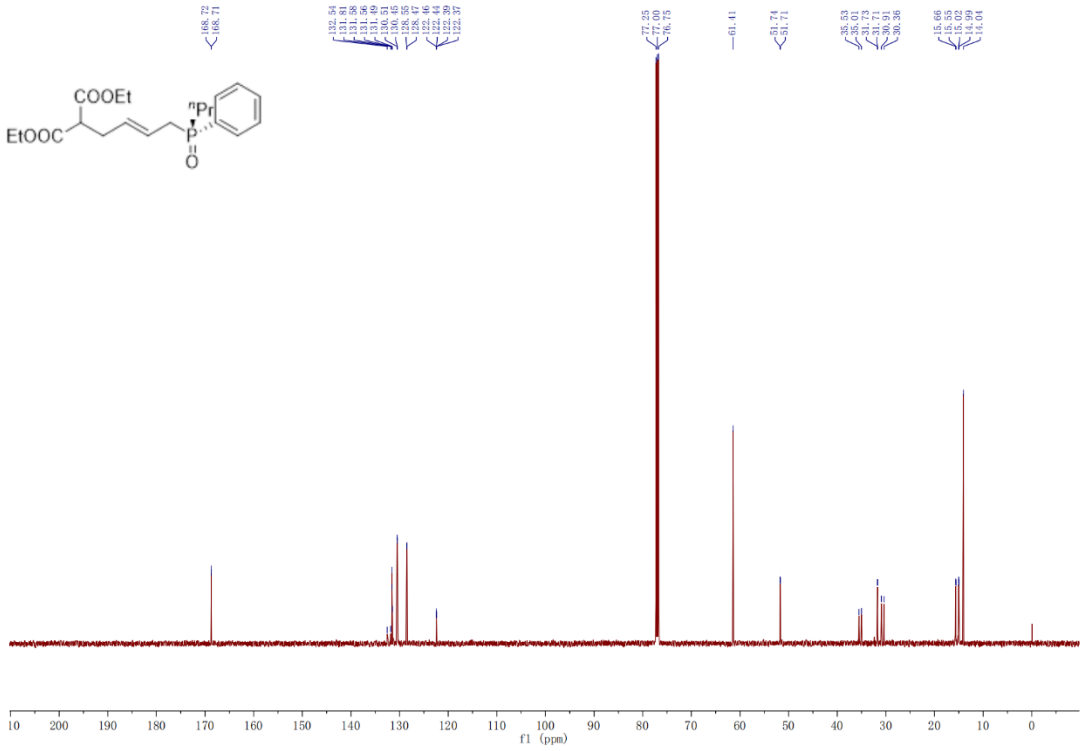
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3b**



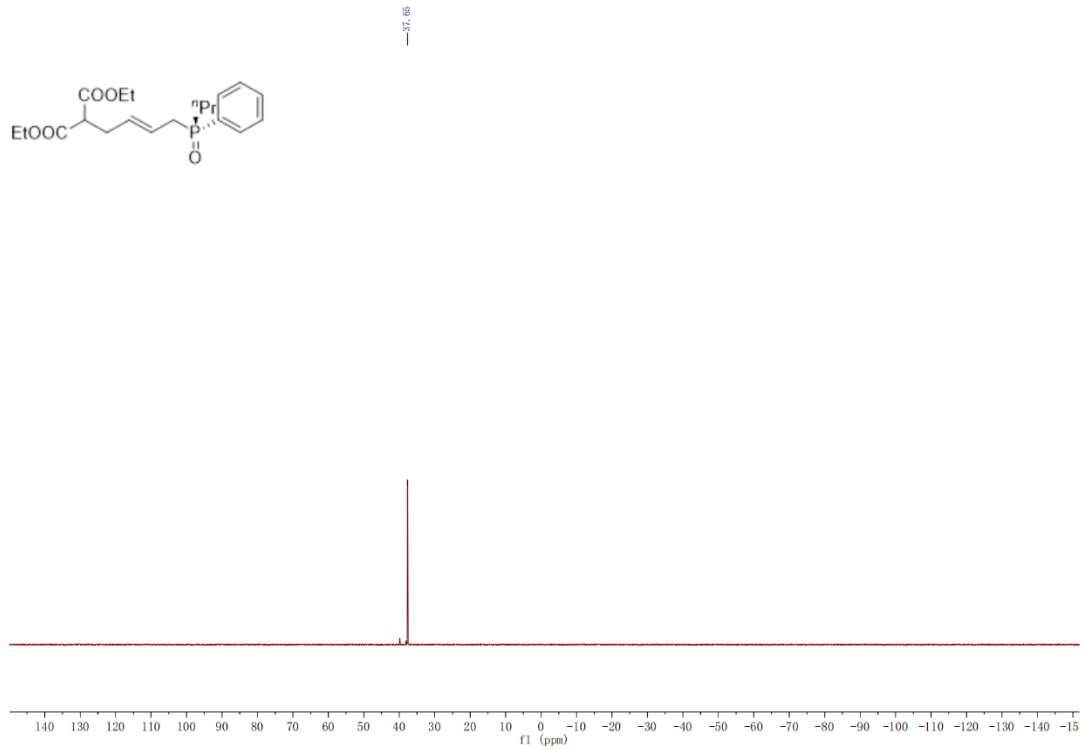
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3c**



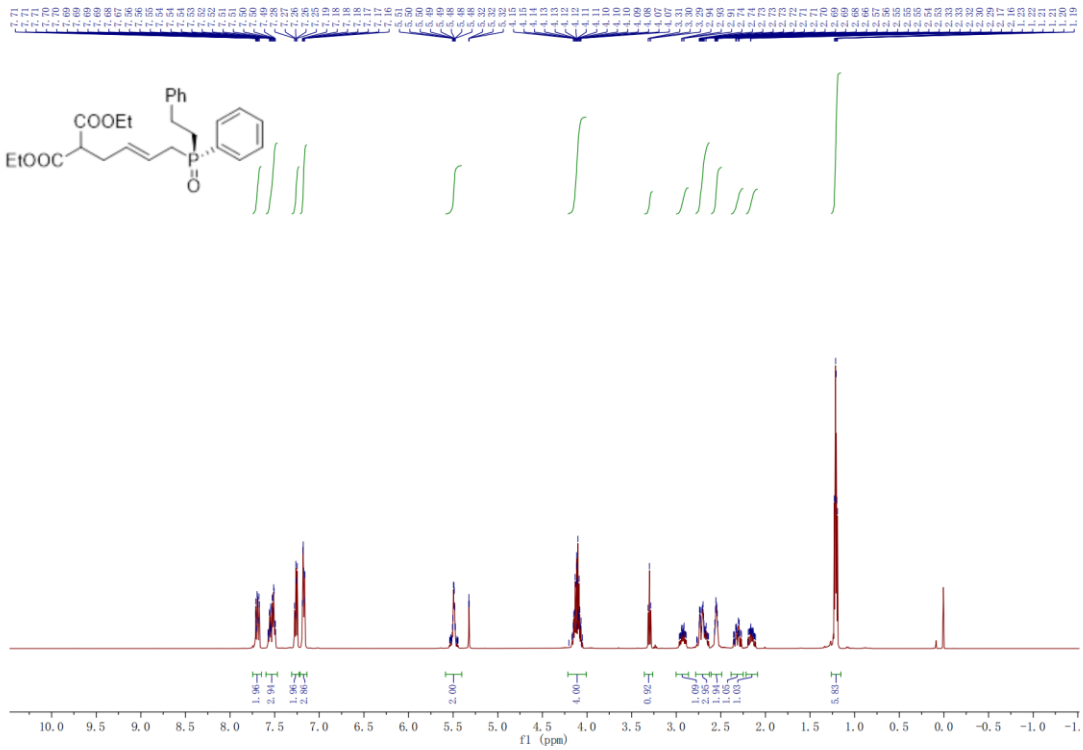
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3c**



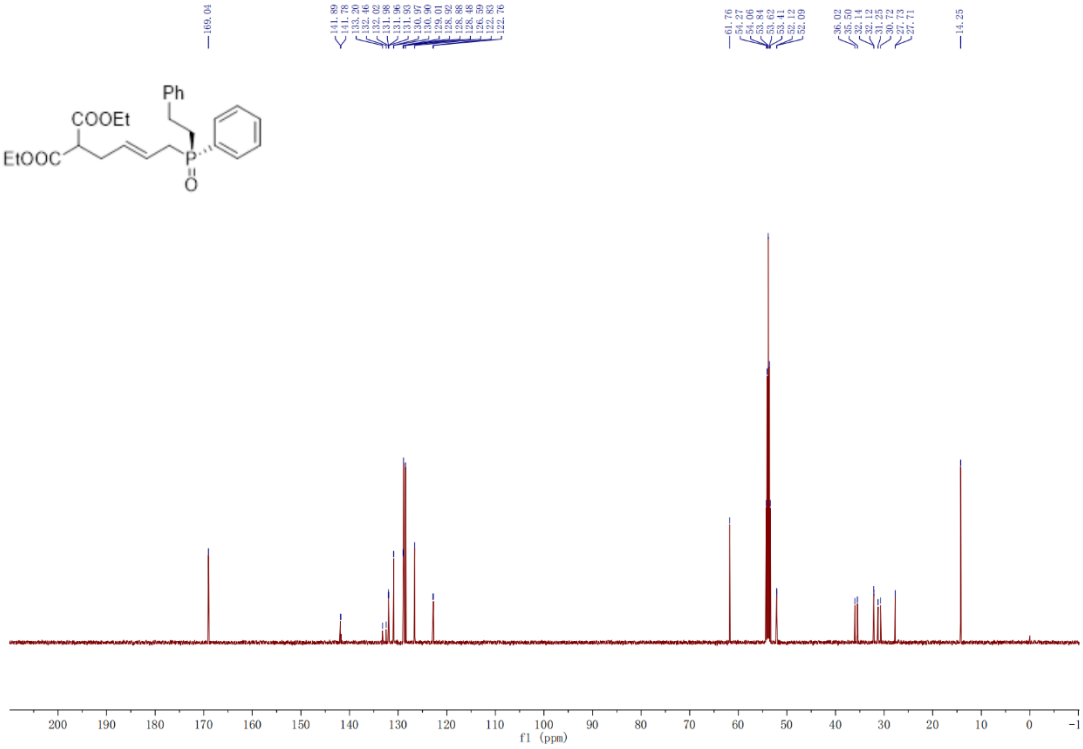
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3c**



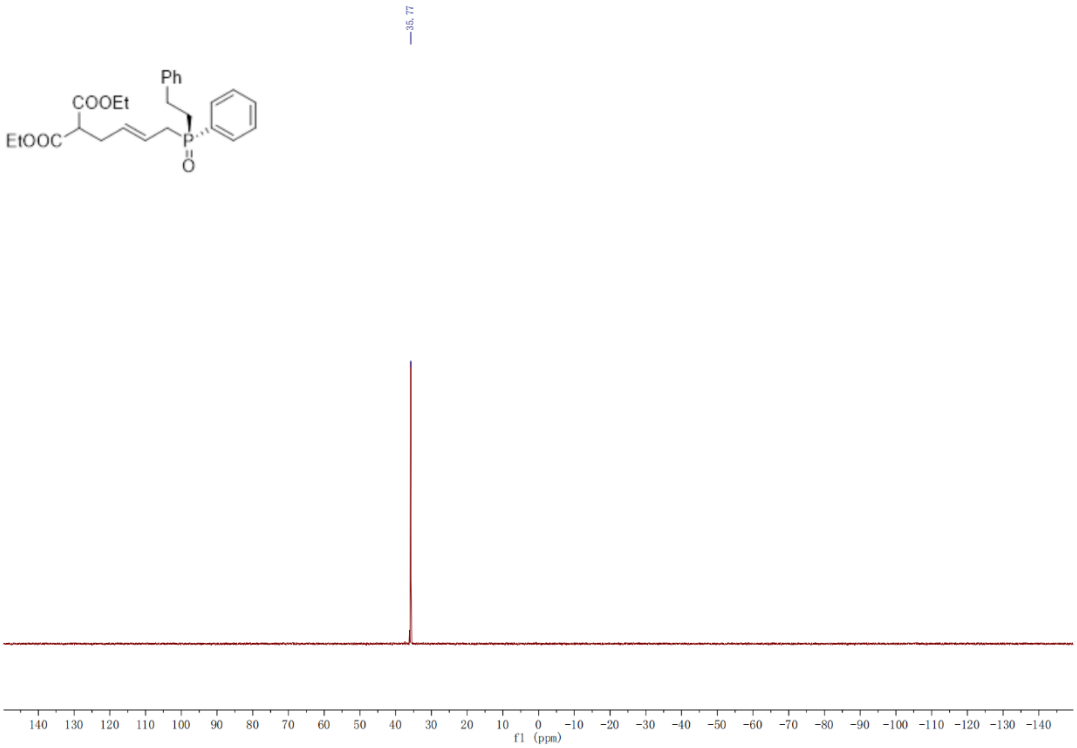
^{1}H NMR spectra (500 MHz, CD_2Cl_2) of **3d**



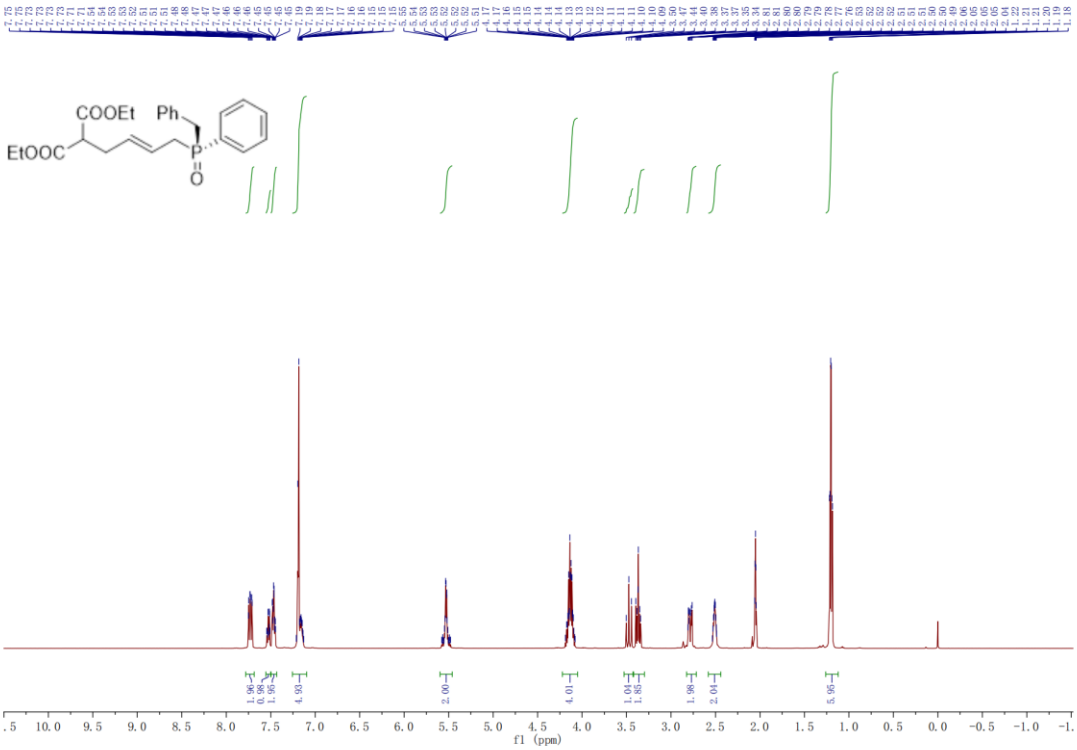
^{13}C NMR spectra (126 MHz, CD_2Cl_2) of **3d**



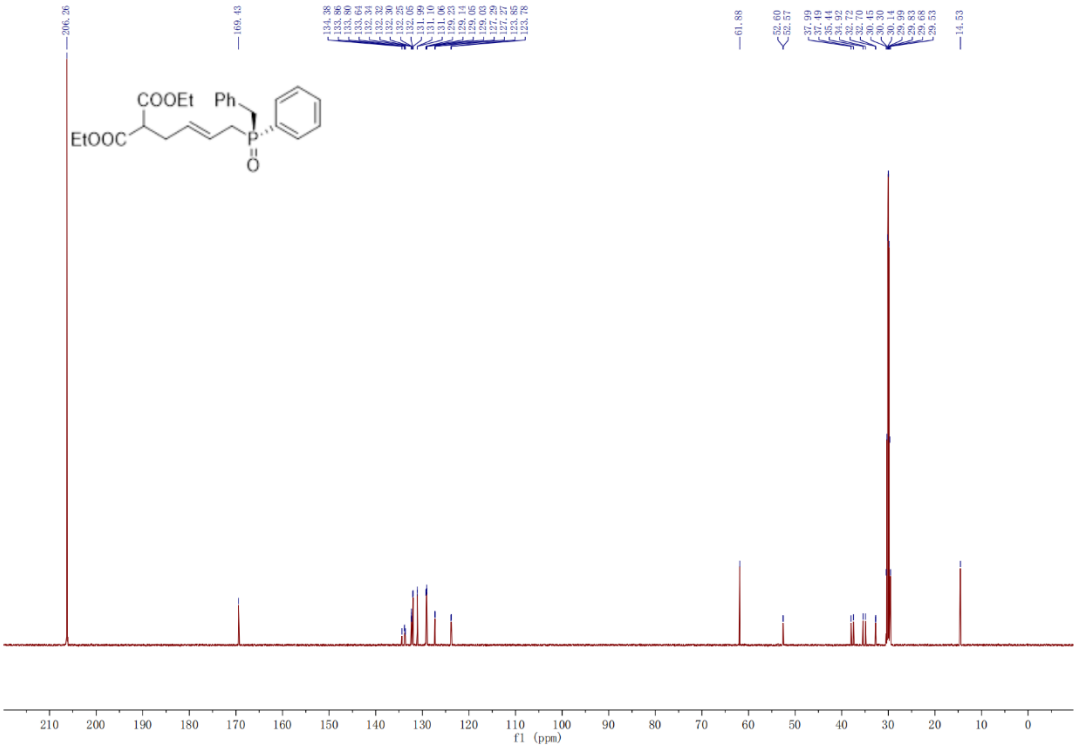
^{31}P NMR spectra (202 MHz, CD_2Cl_2) of **3d**



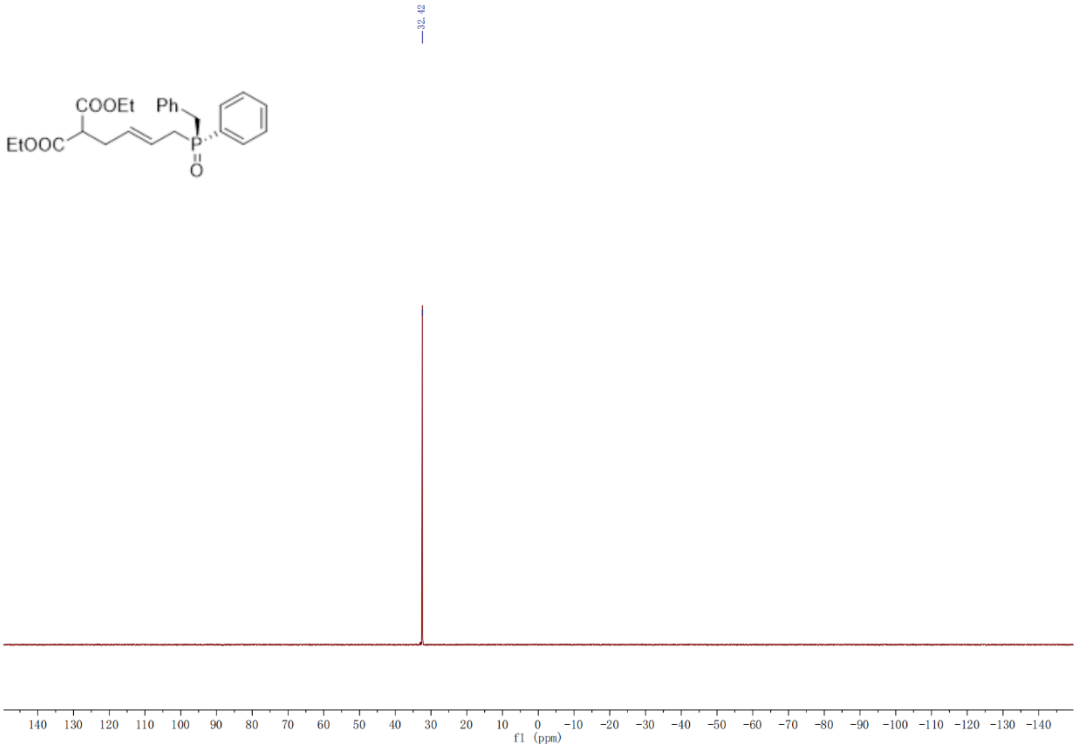
^{1}H NMR spectra (500 MHz, CD_3COCD_3) of **3e**



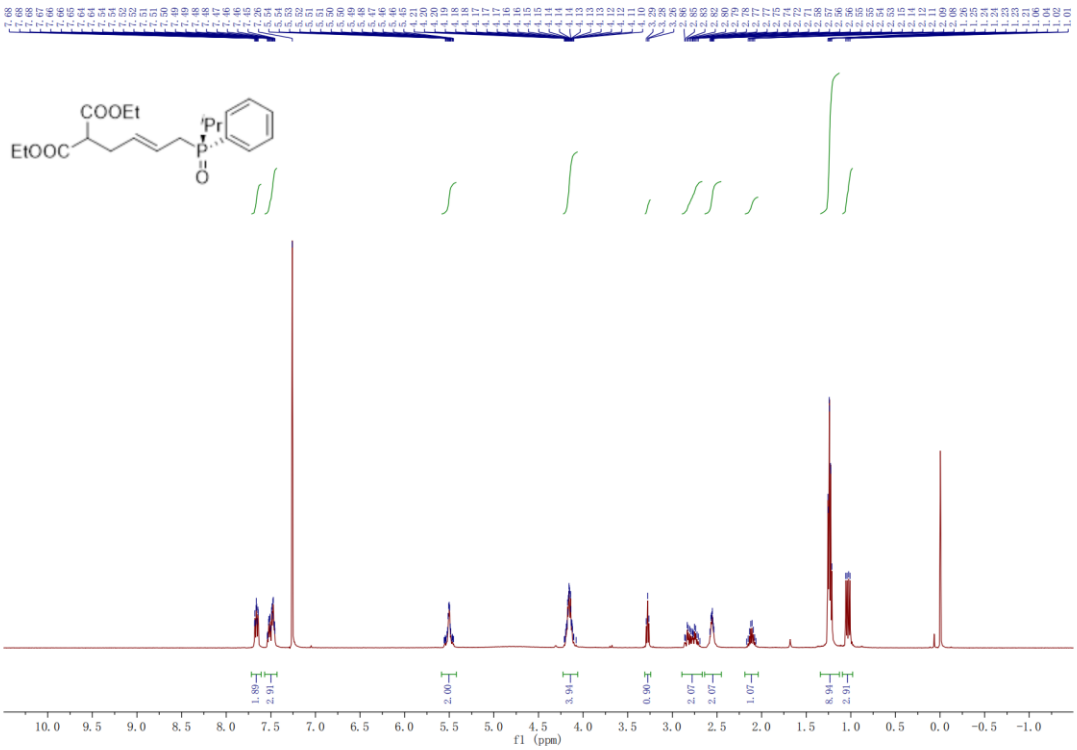
^{13}C NMR spectra (126 MHz, CD_3COCD_3) of **3e**



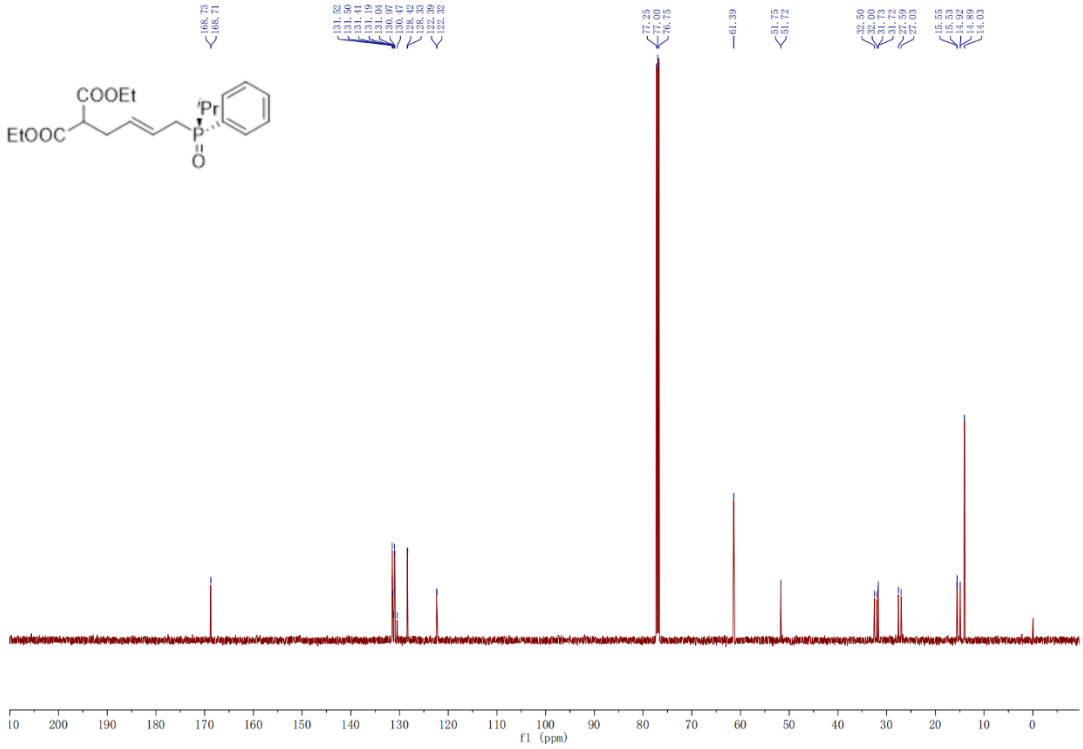
^{31}P NMR spectra (202 MHz, CD_3COCD_3) of **3e**



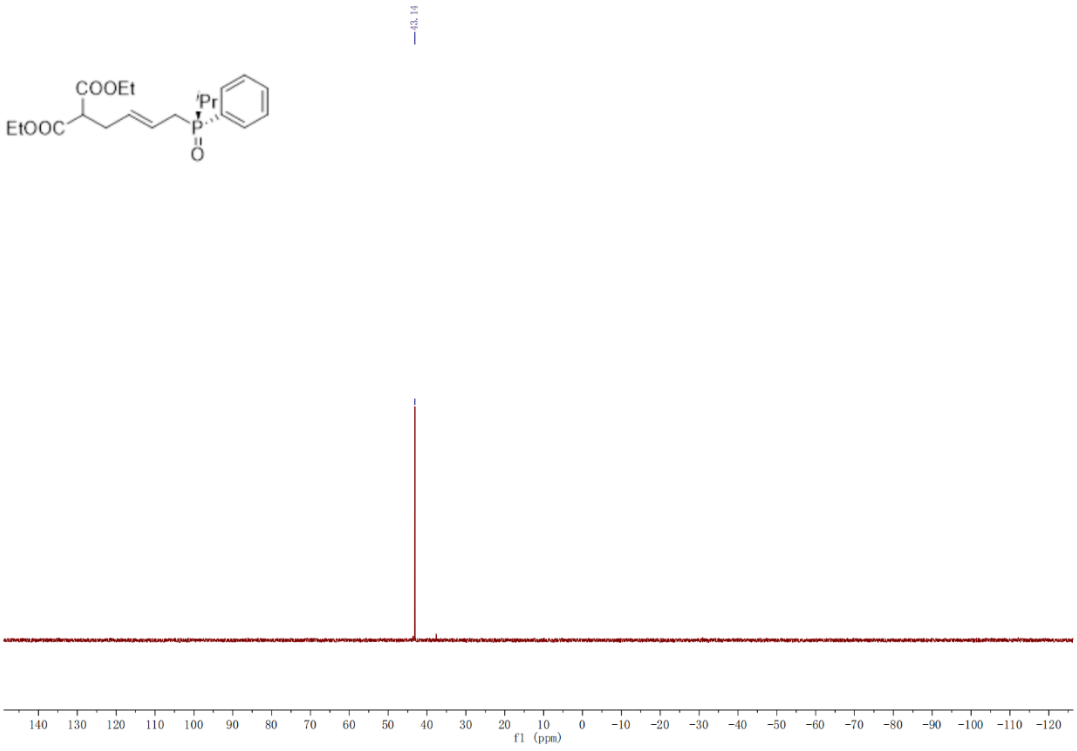
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3f**



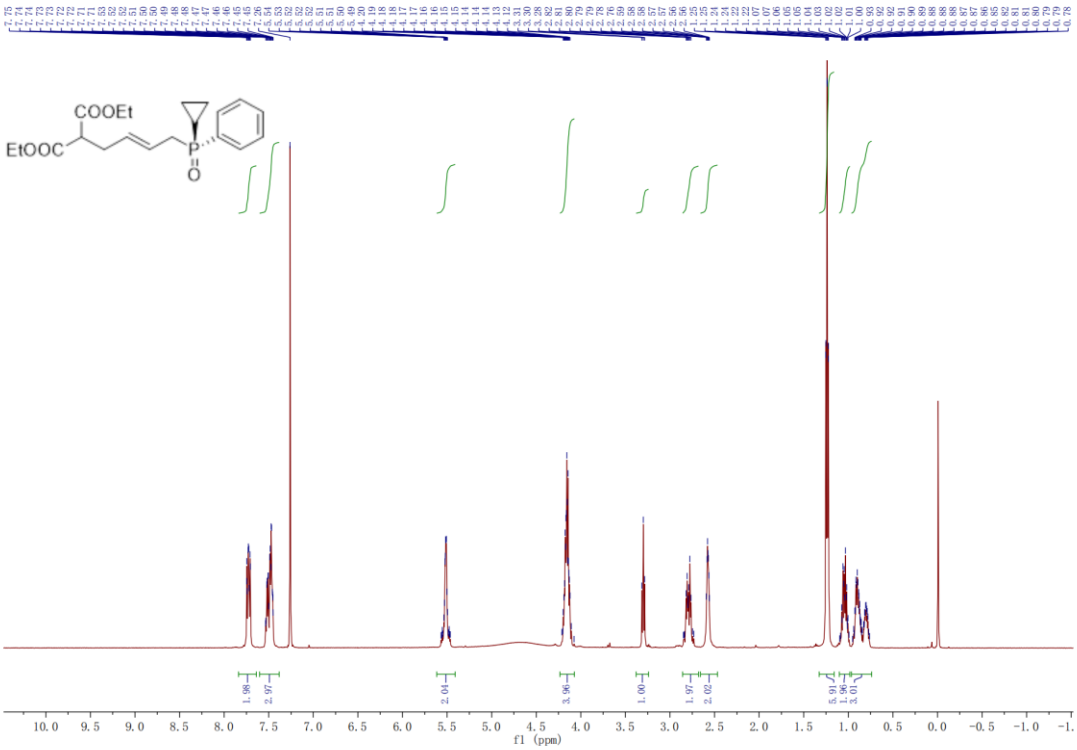
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3f**



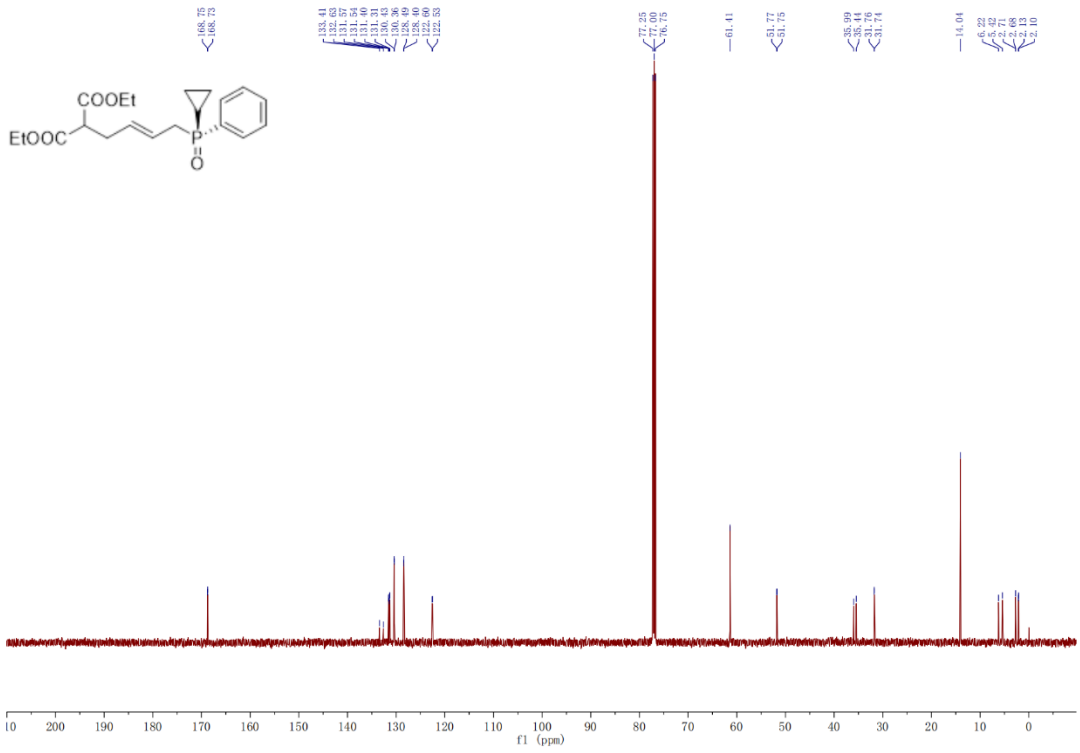
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3f**



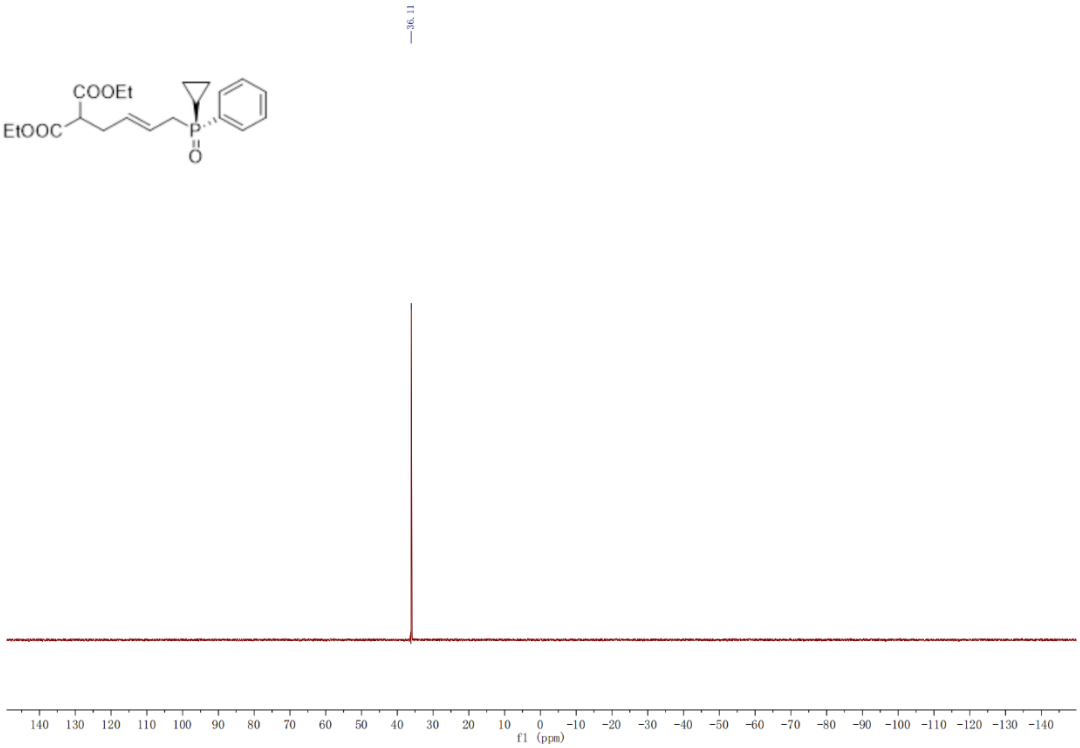
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3g**



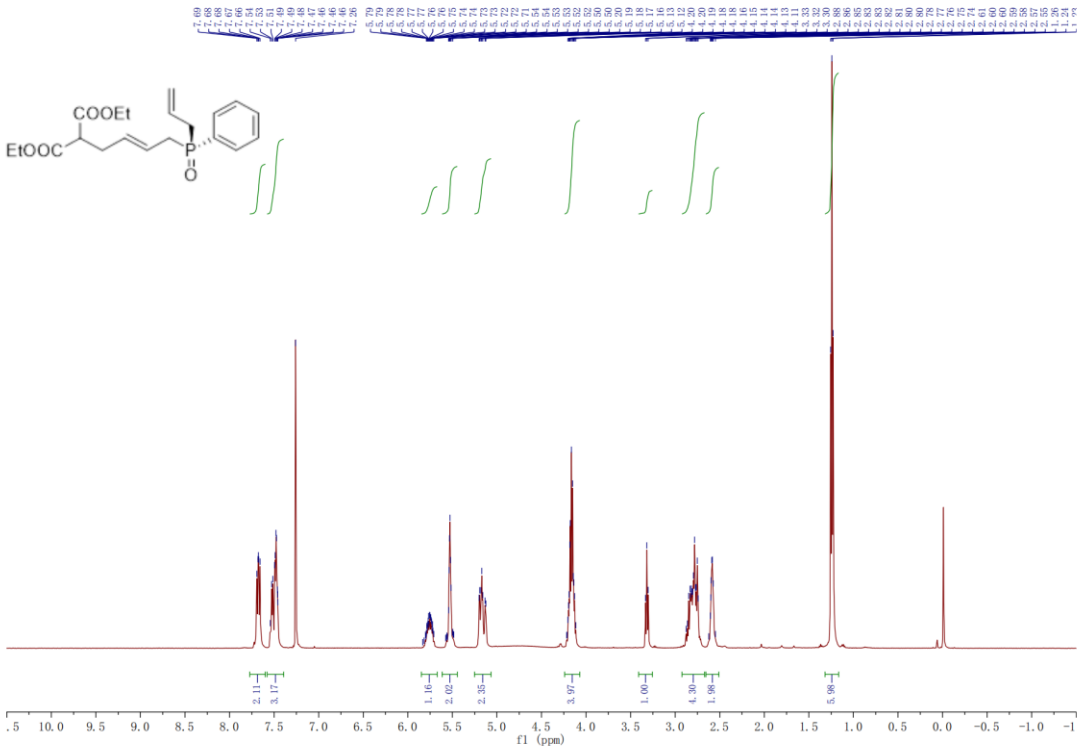
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3g**



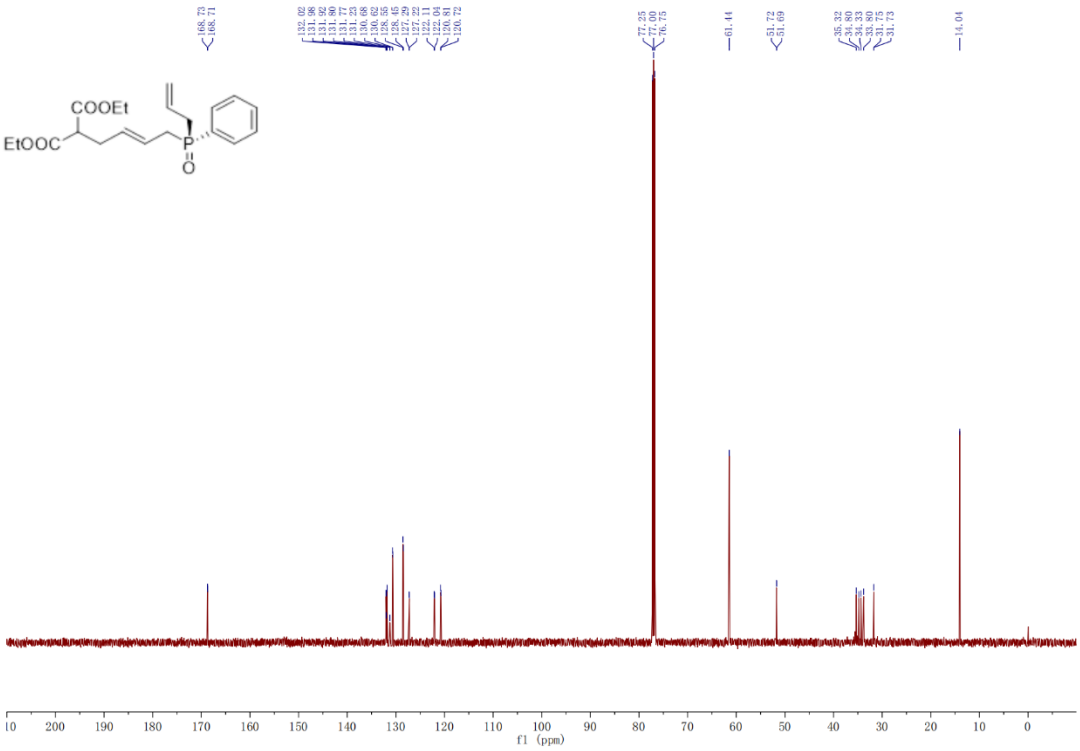
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3g**



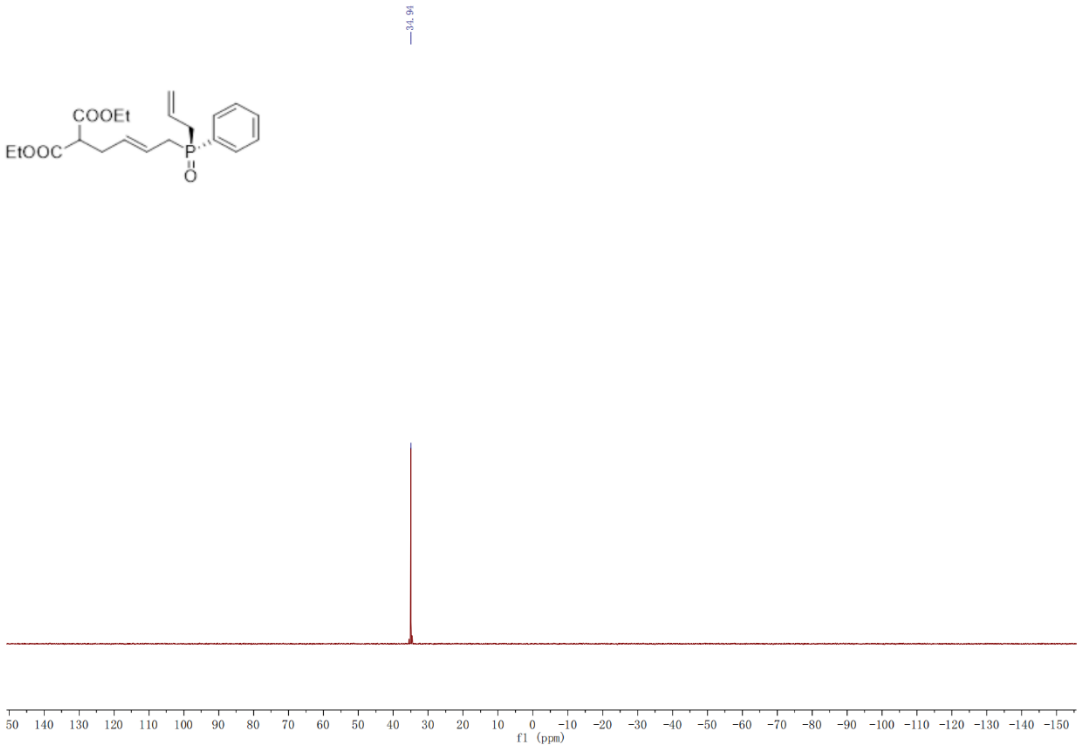
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3h**



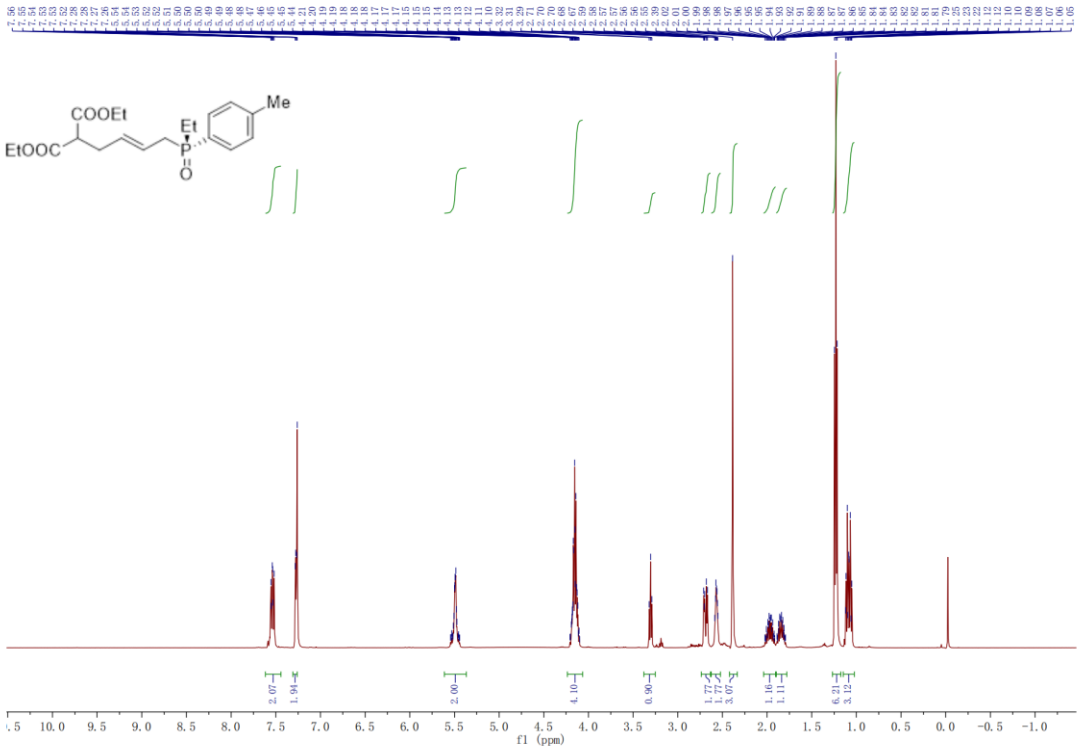
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3h**



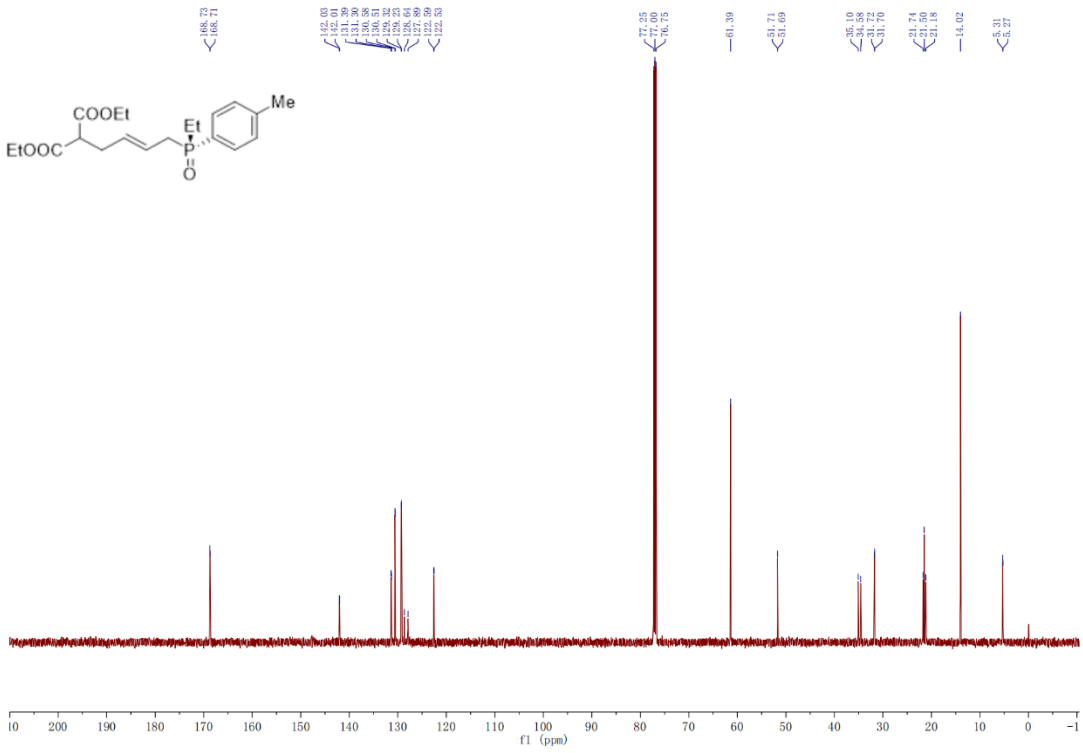
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3h**



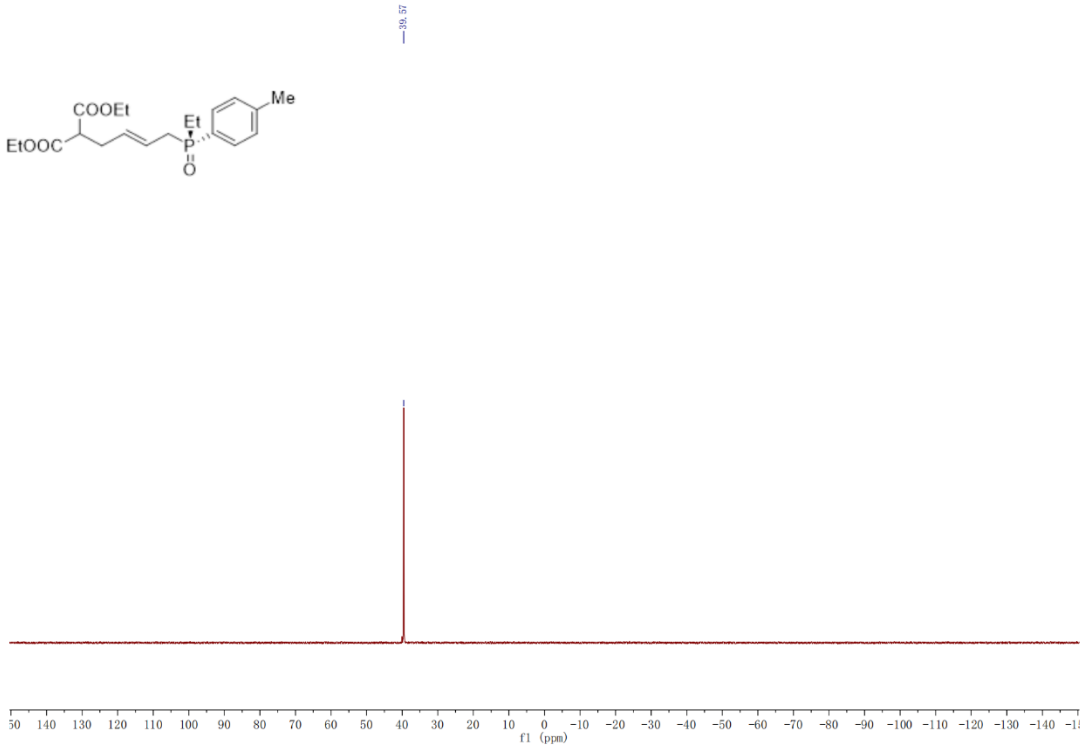
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3i**



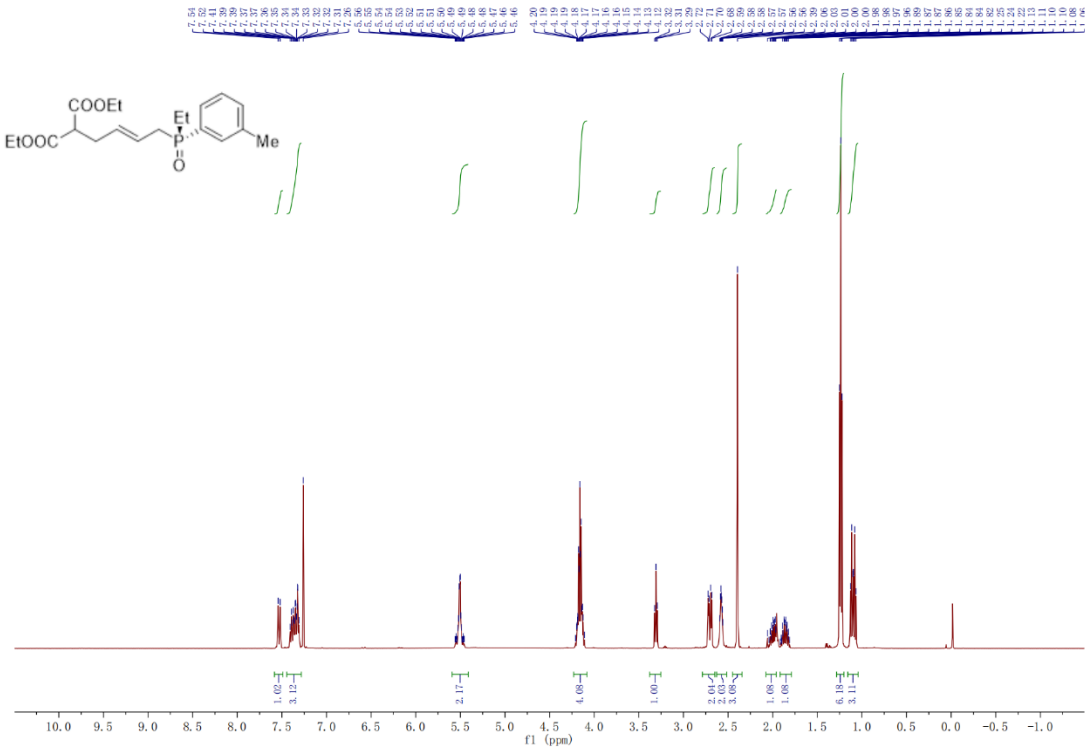
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3i**



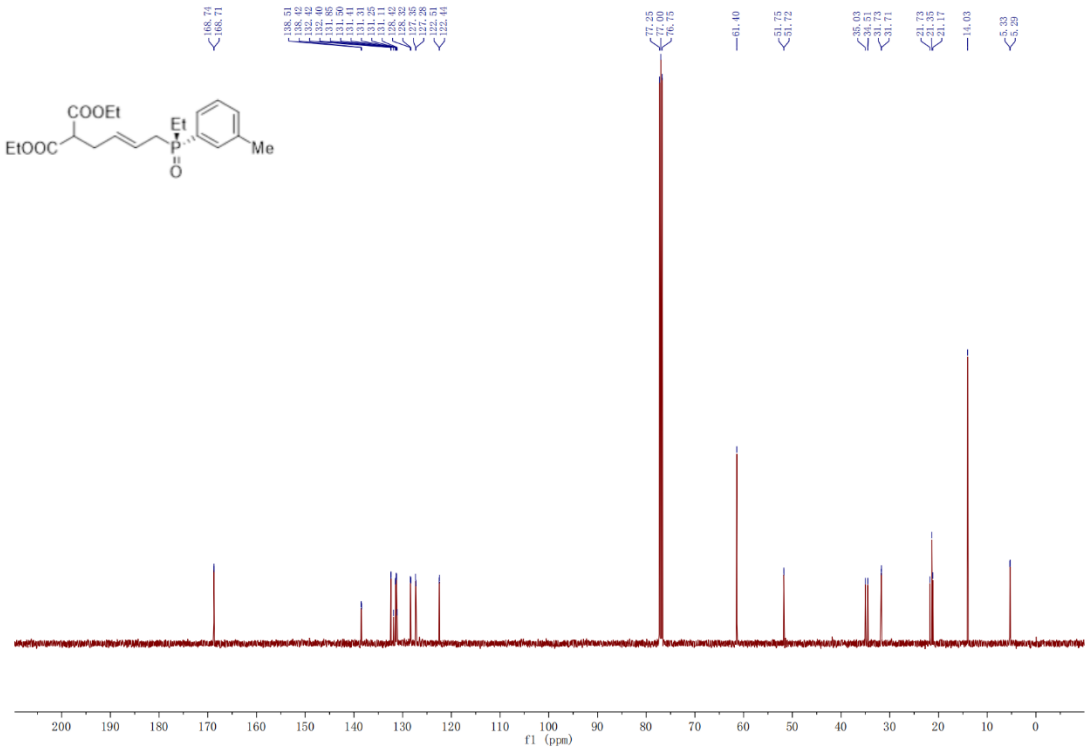
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3i**



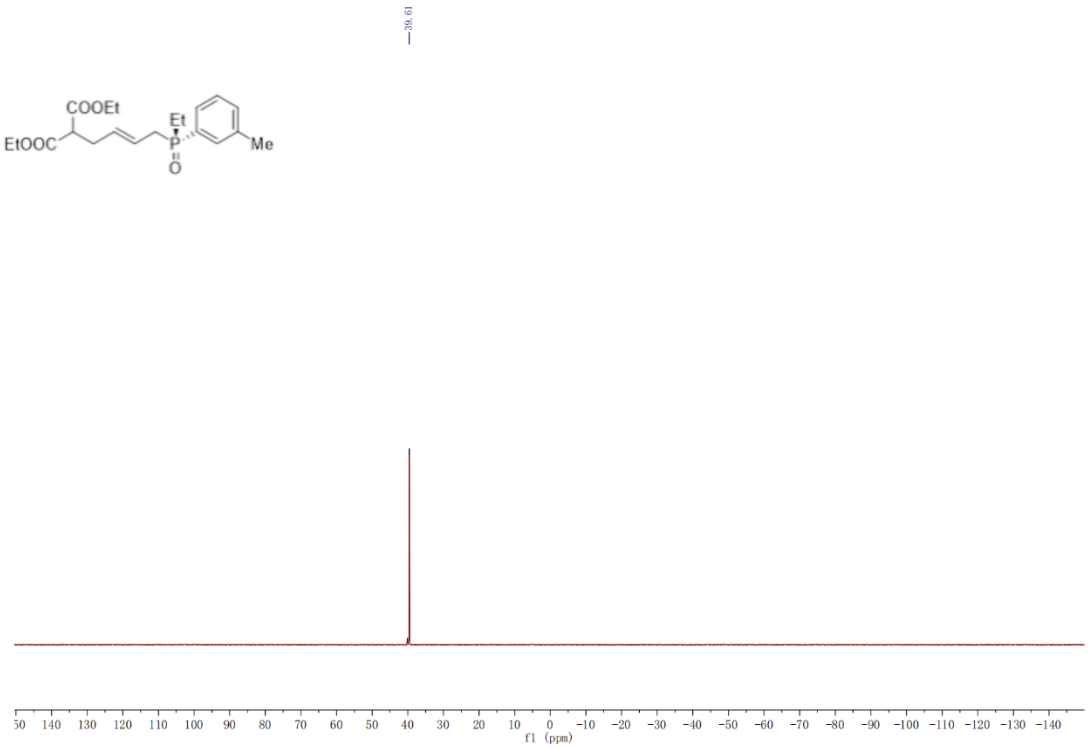
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3j**



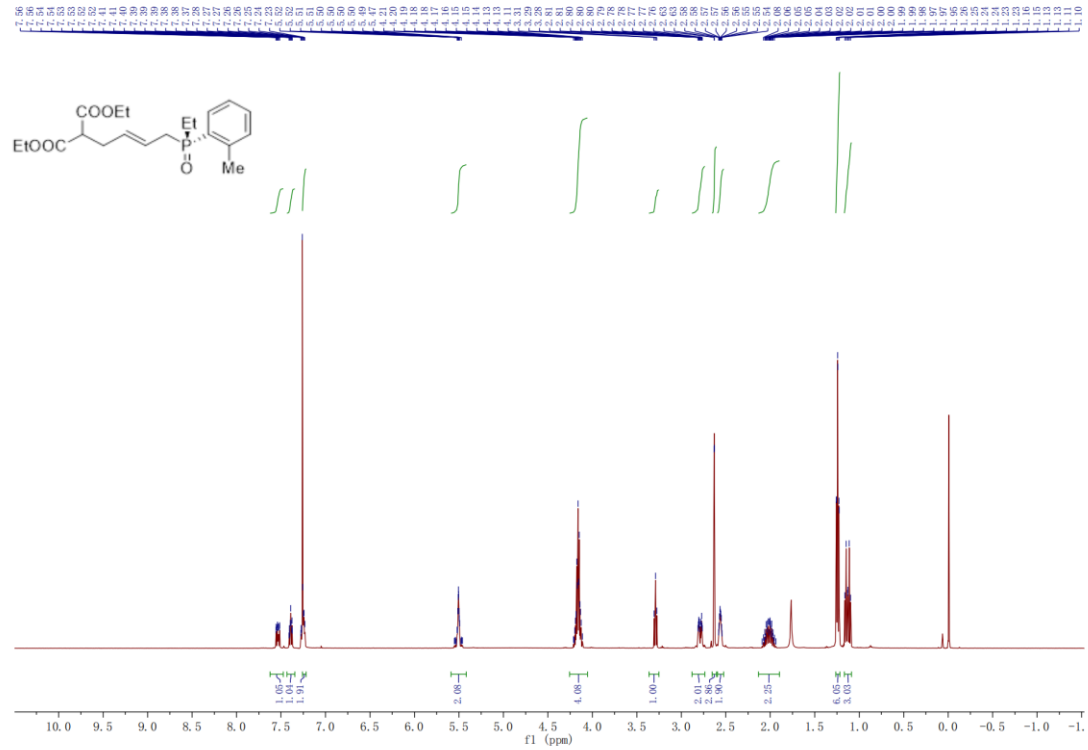
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3j**



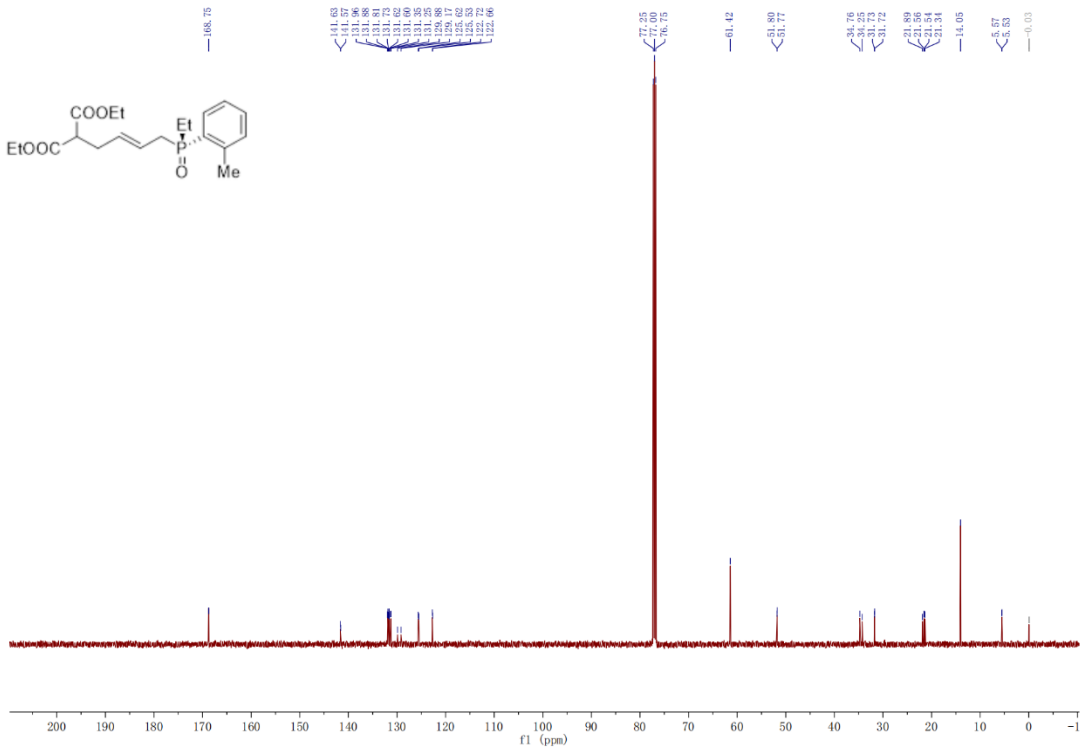
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3j**



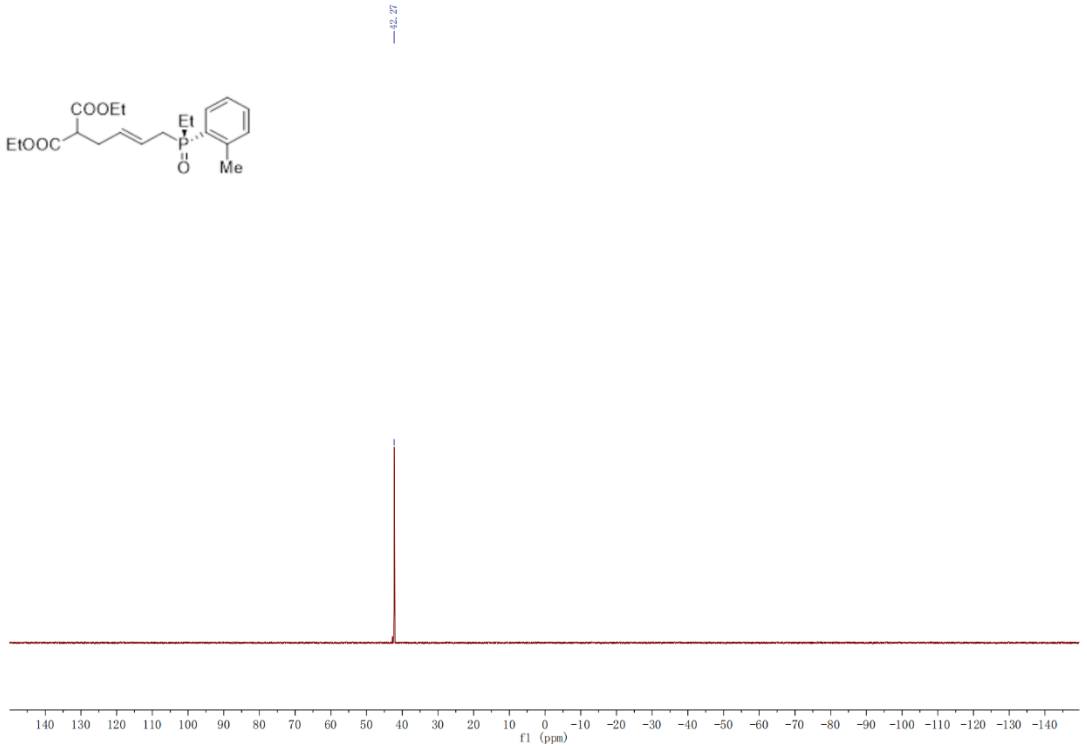
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3k**



^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3k**



^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3k**



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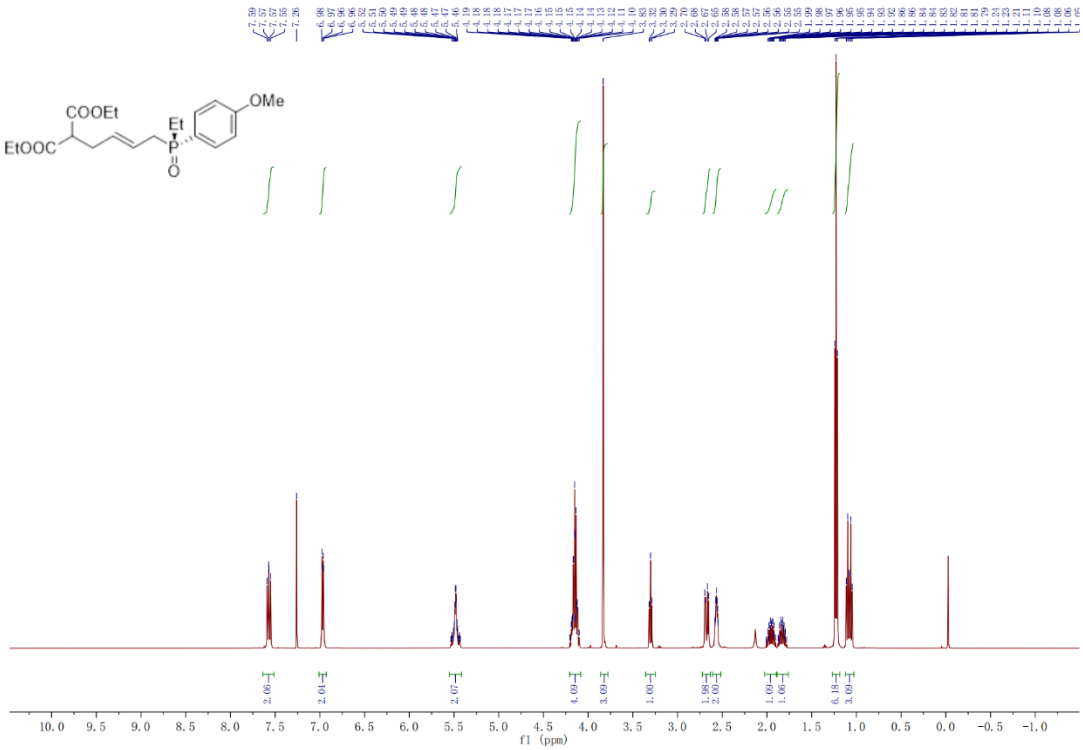

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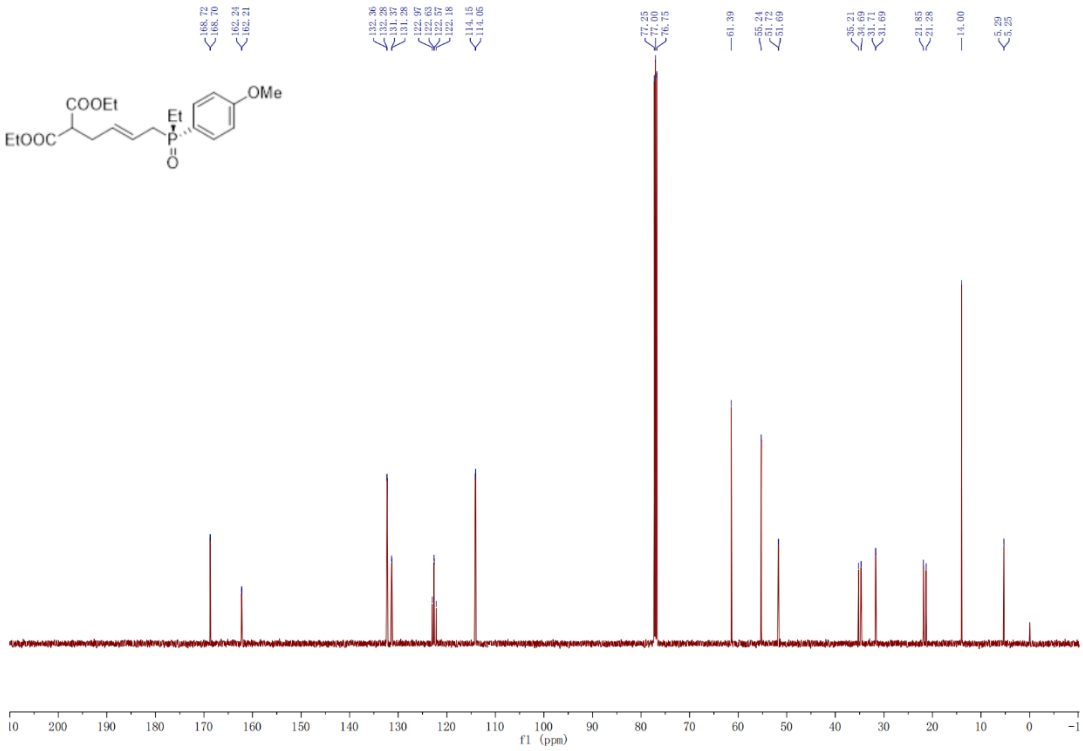
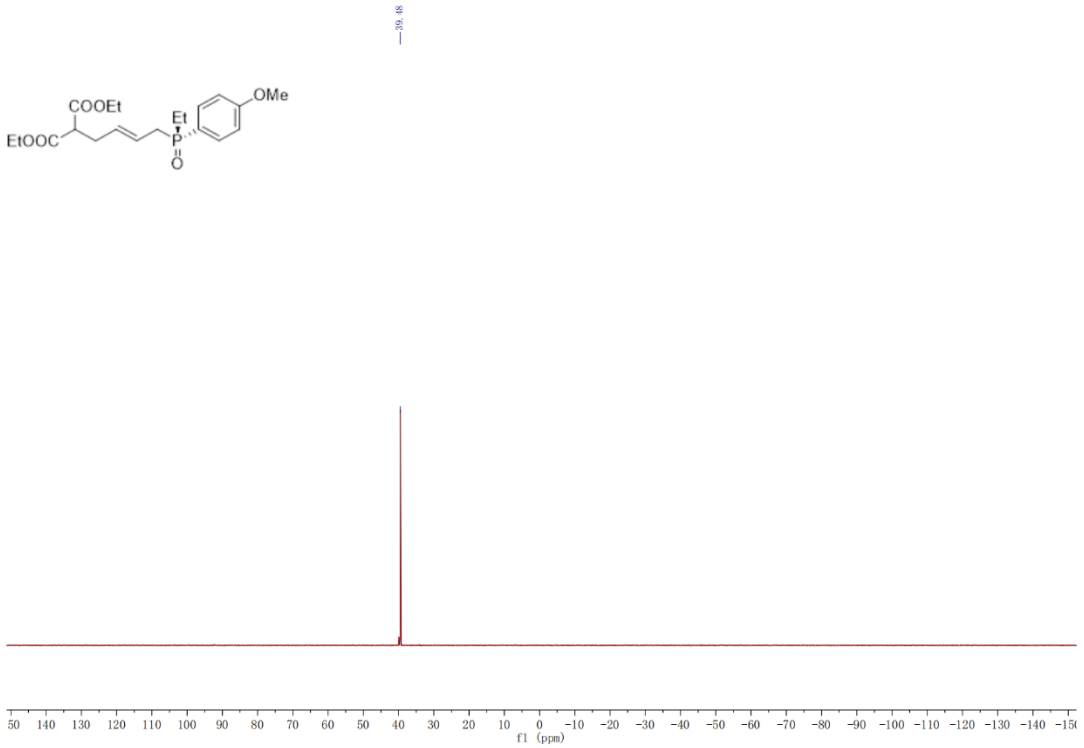
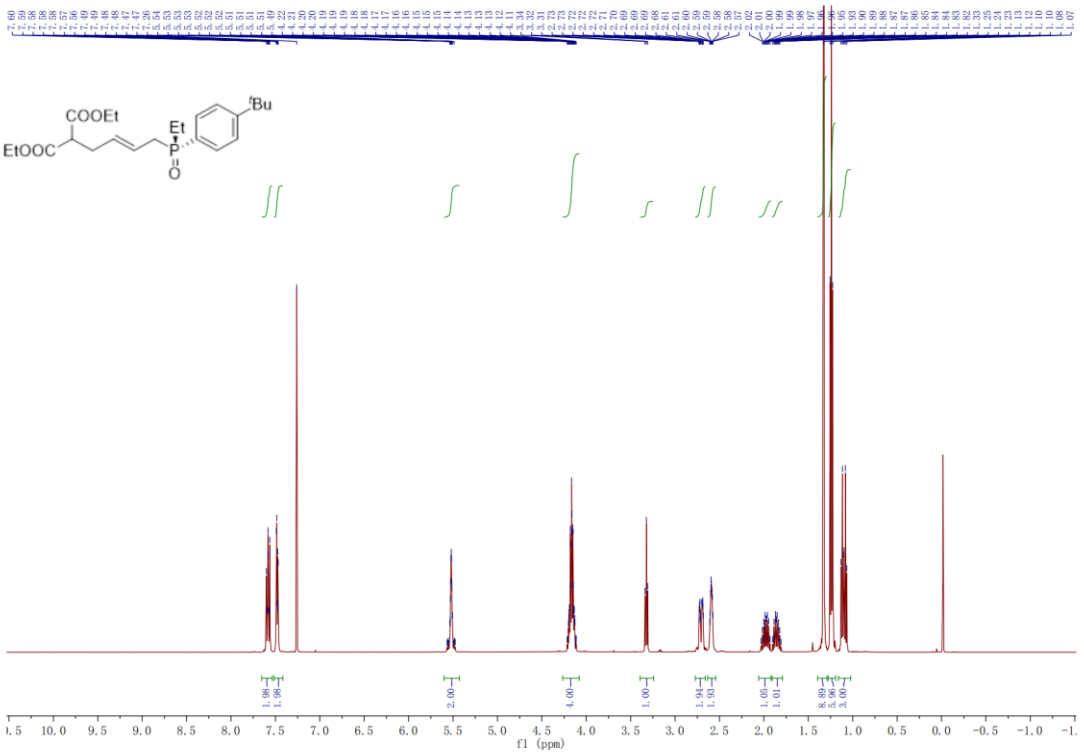


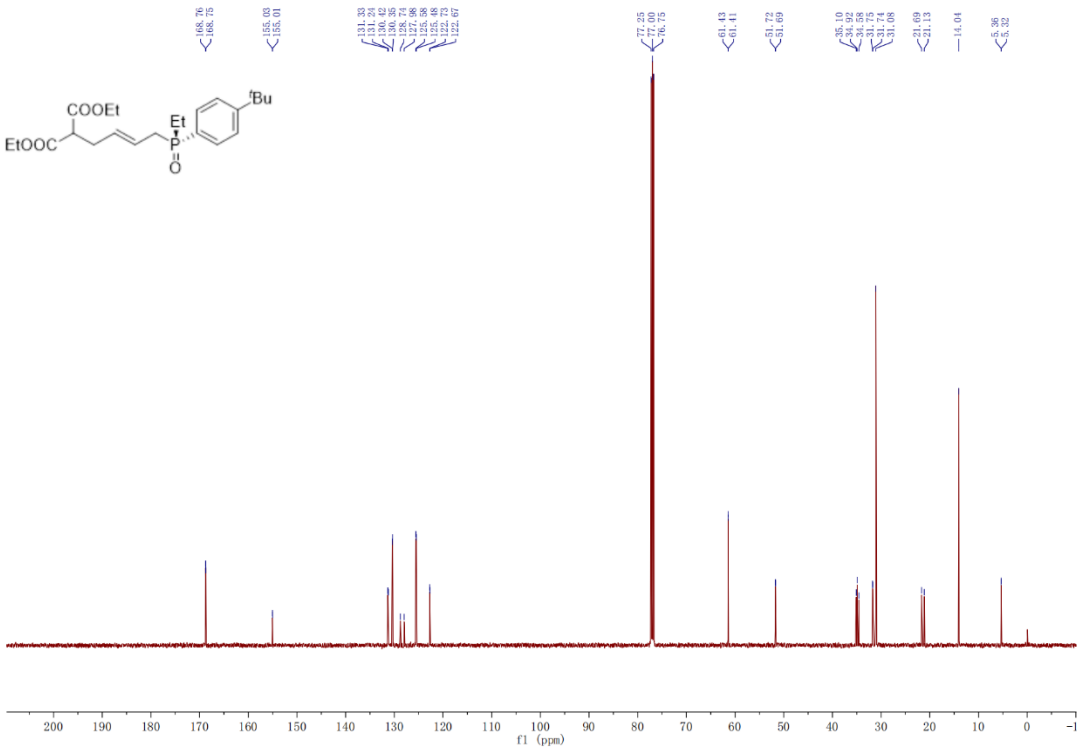
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3l**



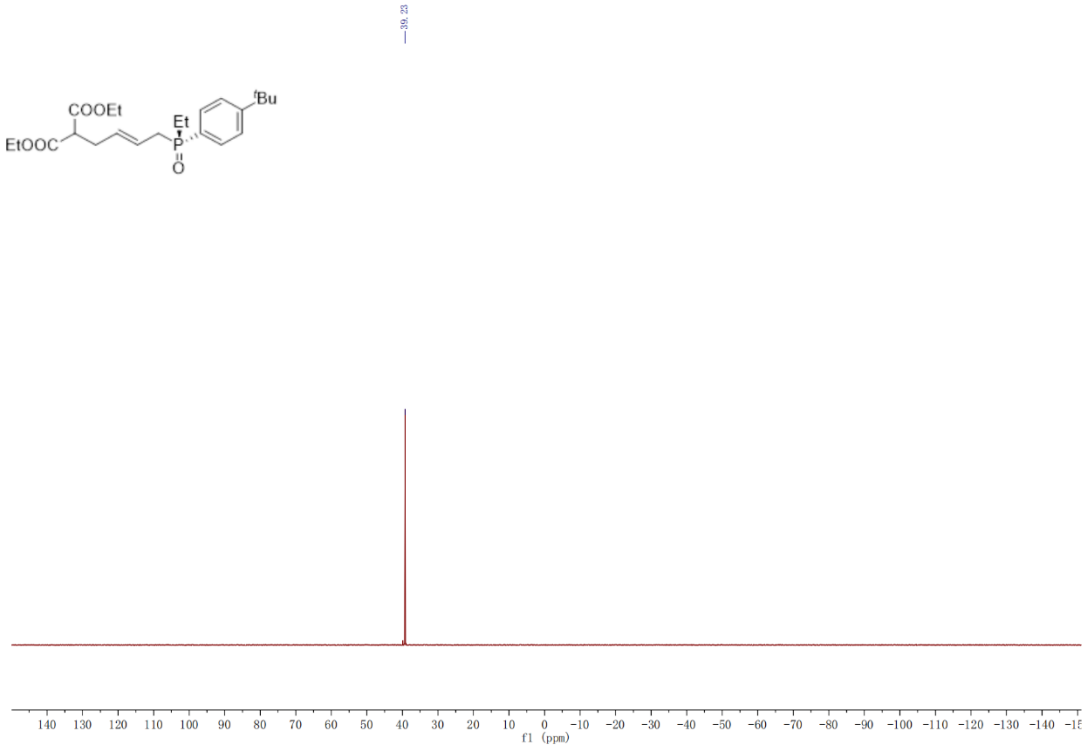
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3m**



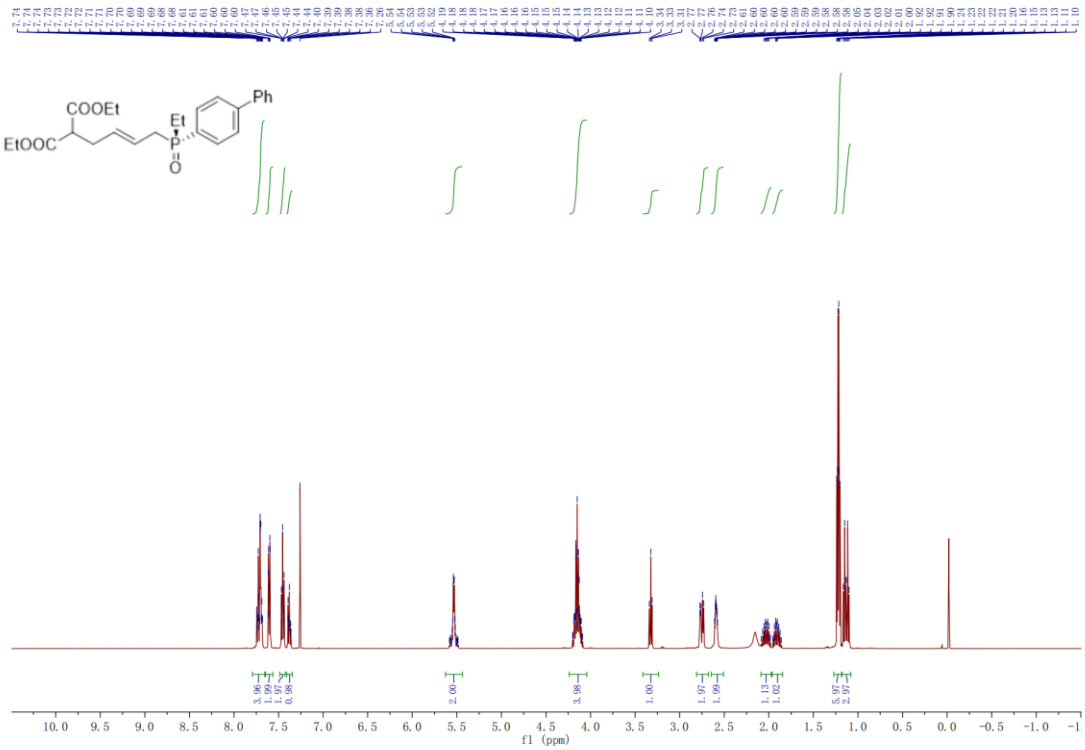
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3m**



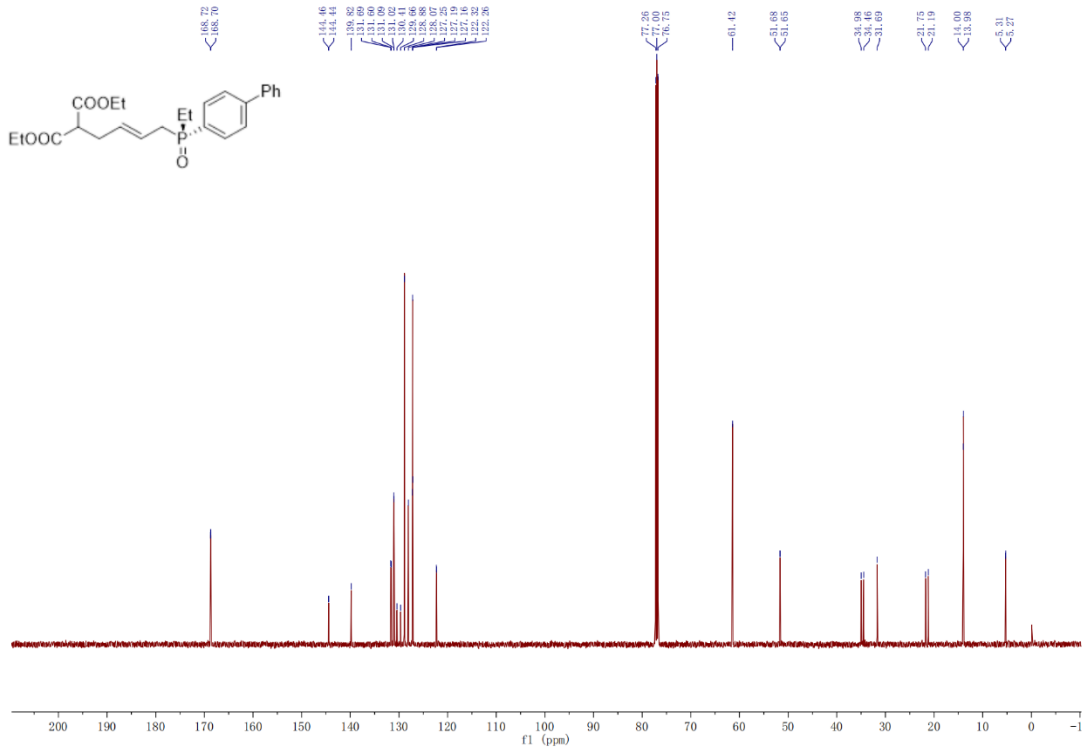
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3m**



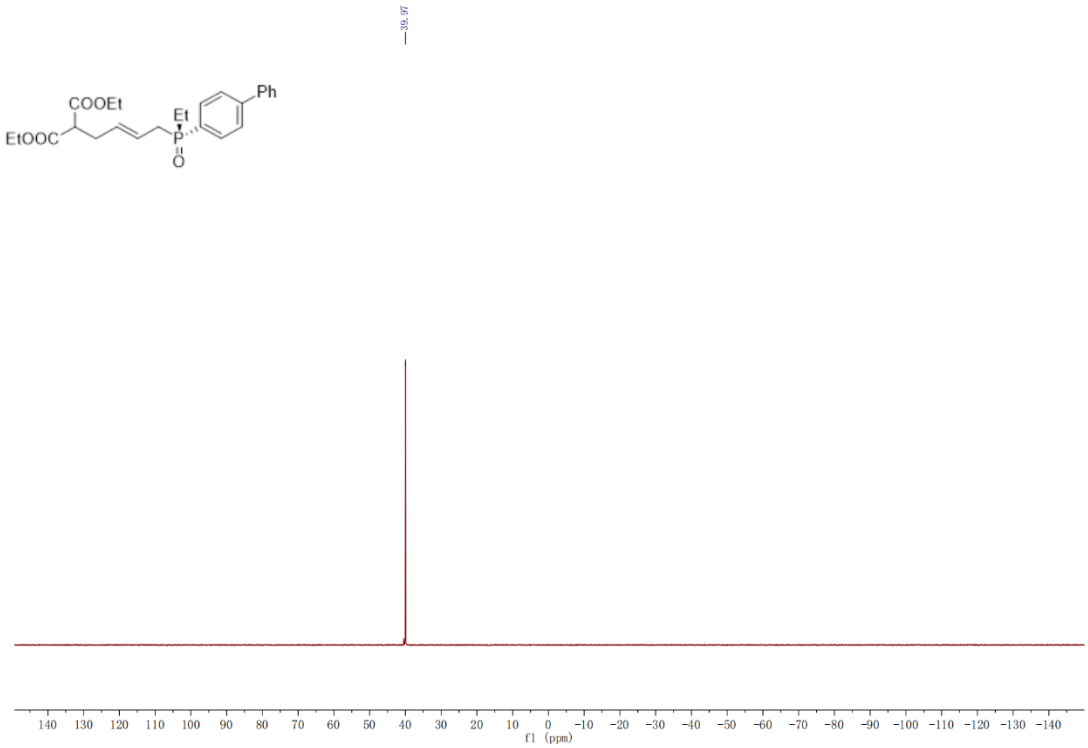
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3n**



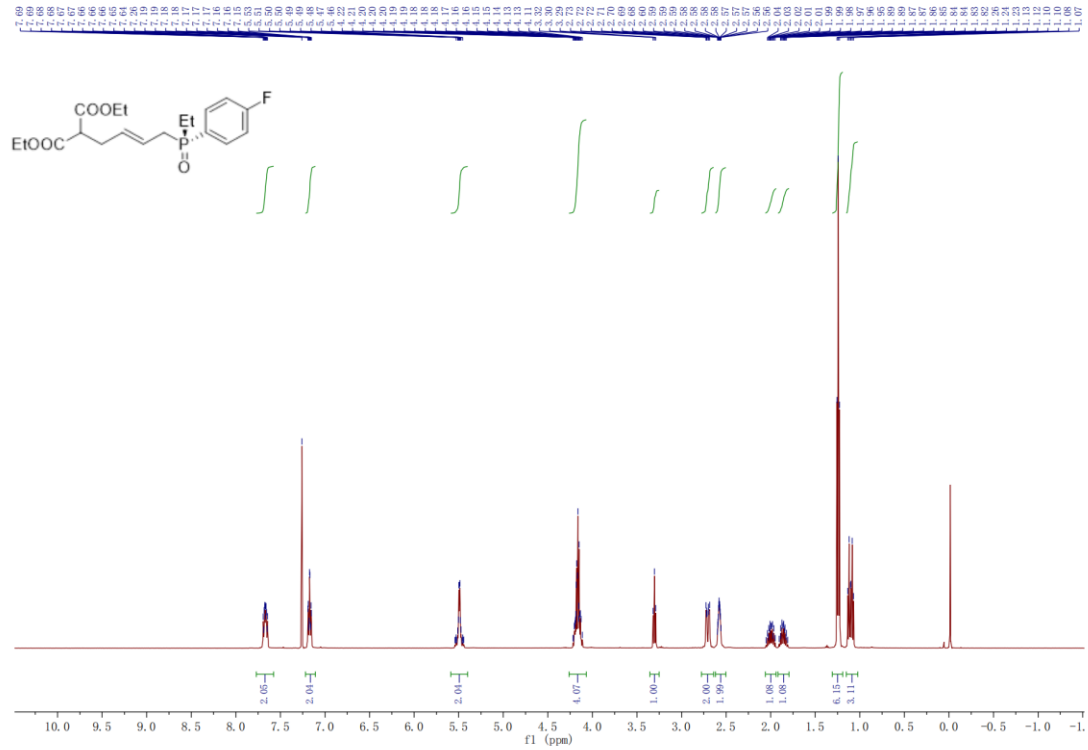
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3n**



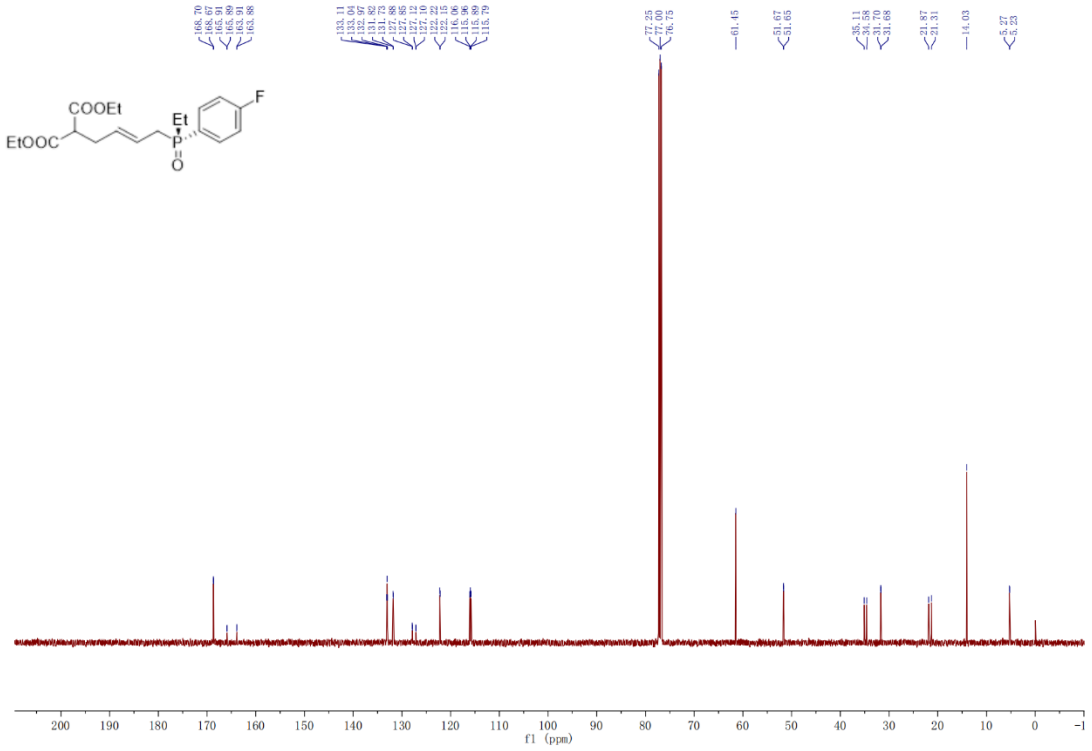
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3n**



^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3o**



^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3o**



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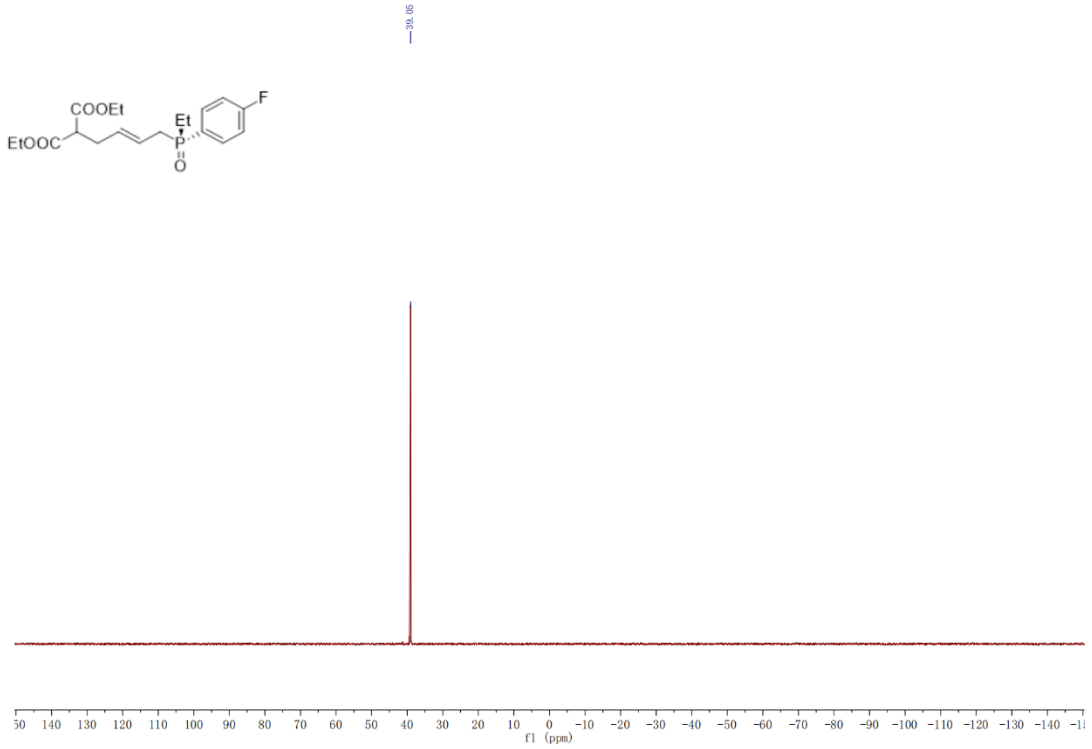
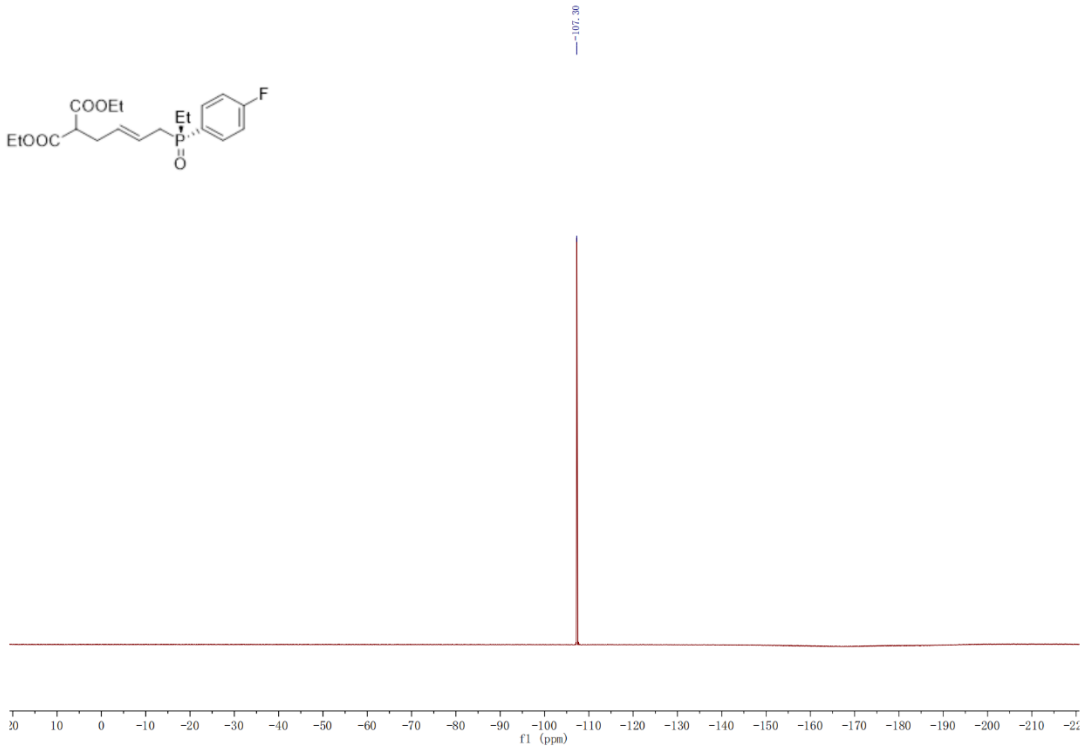
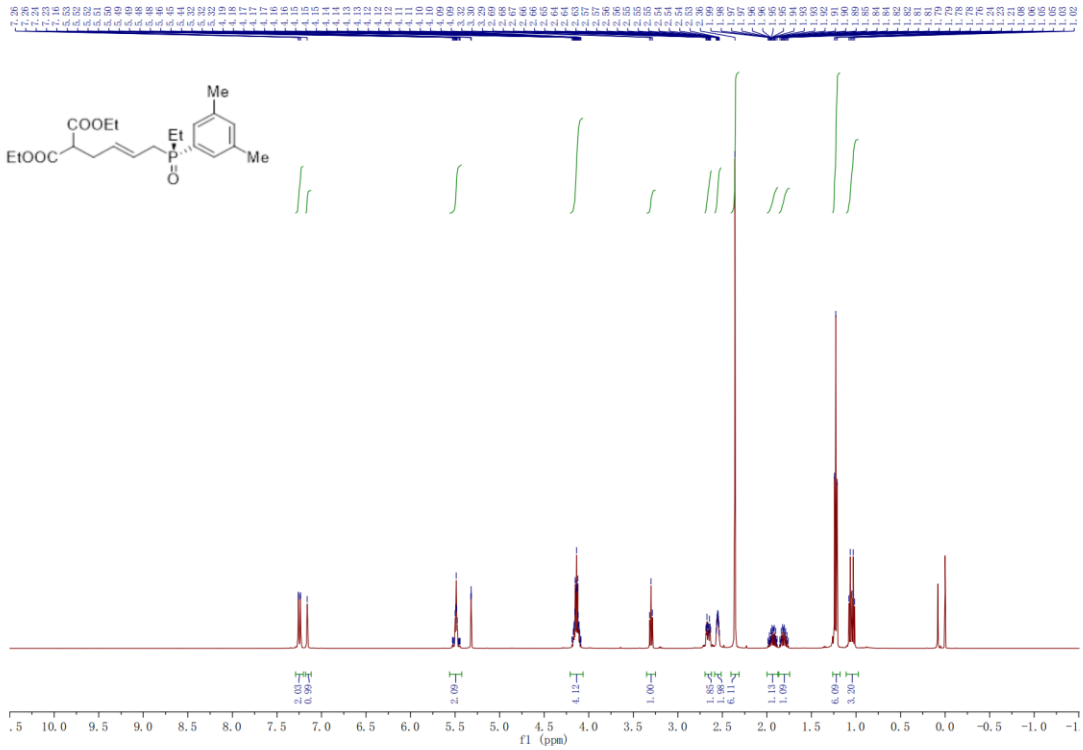


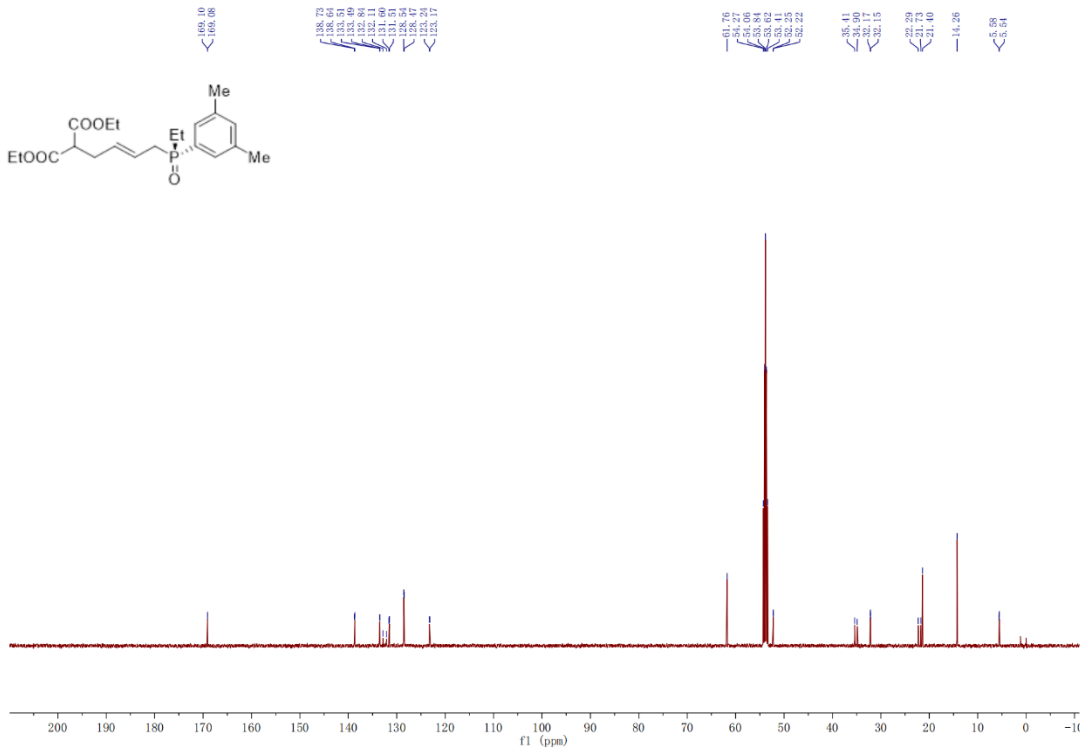
^{19}F NMR spectra (471 MHz, $CDCl_3$) of **3o**



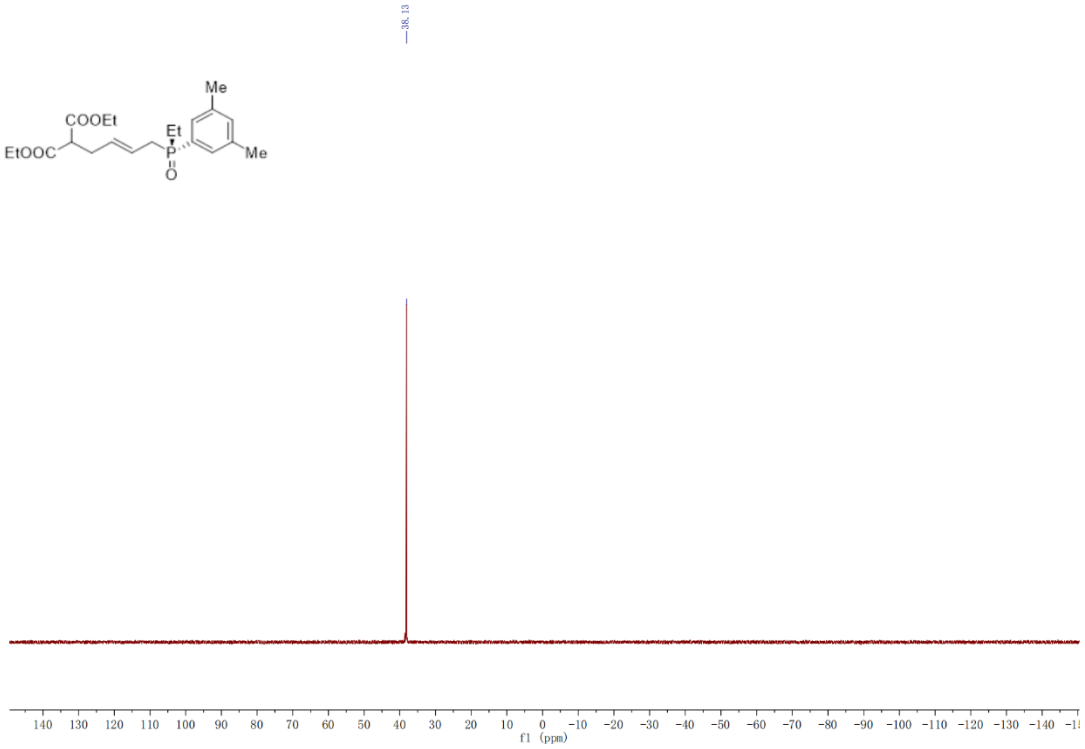
^{1}H NMR spectra (500 MHz, CD_2Cl_2) of **3p**



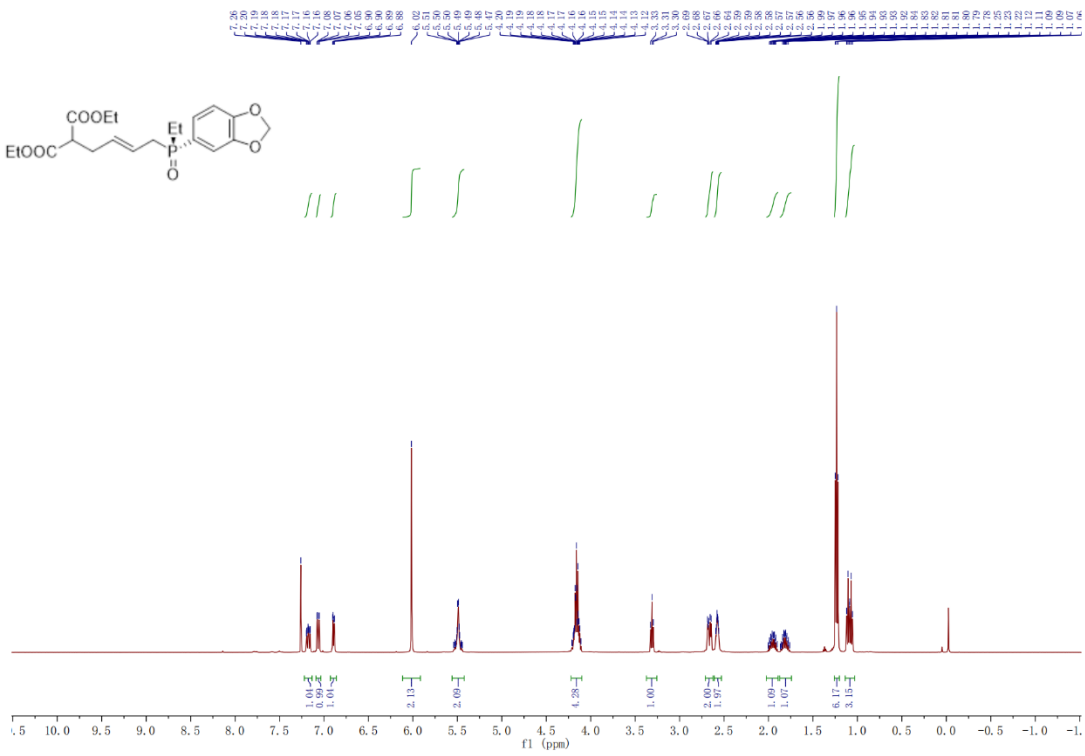
^{13}C NMR spectra (126 MHz, CD_2Cl_2) of **3p**



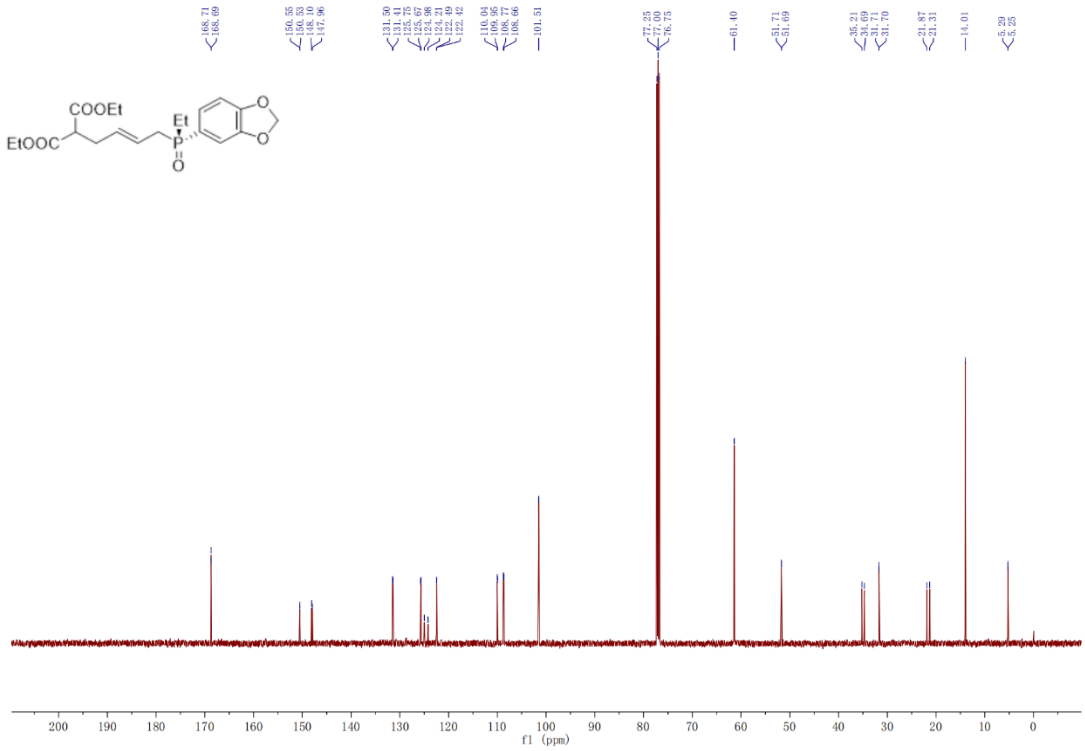
^{31}P NMR spectra (202 MHz, CD_2Cl_2) of **3p**



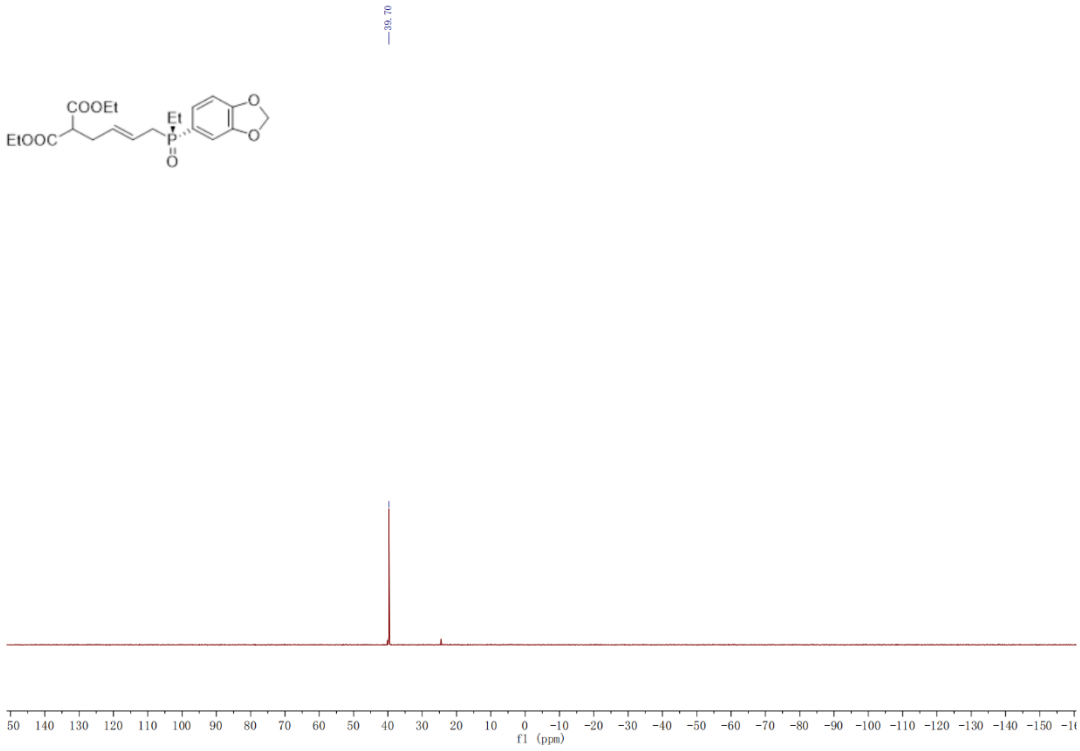
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3q**



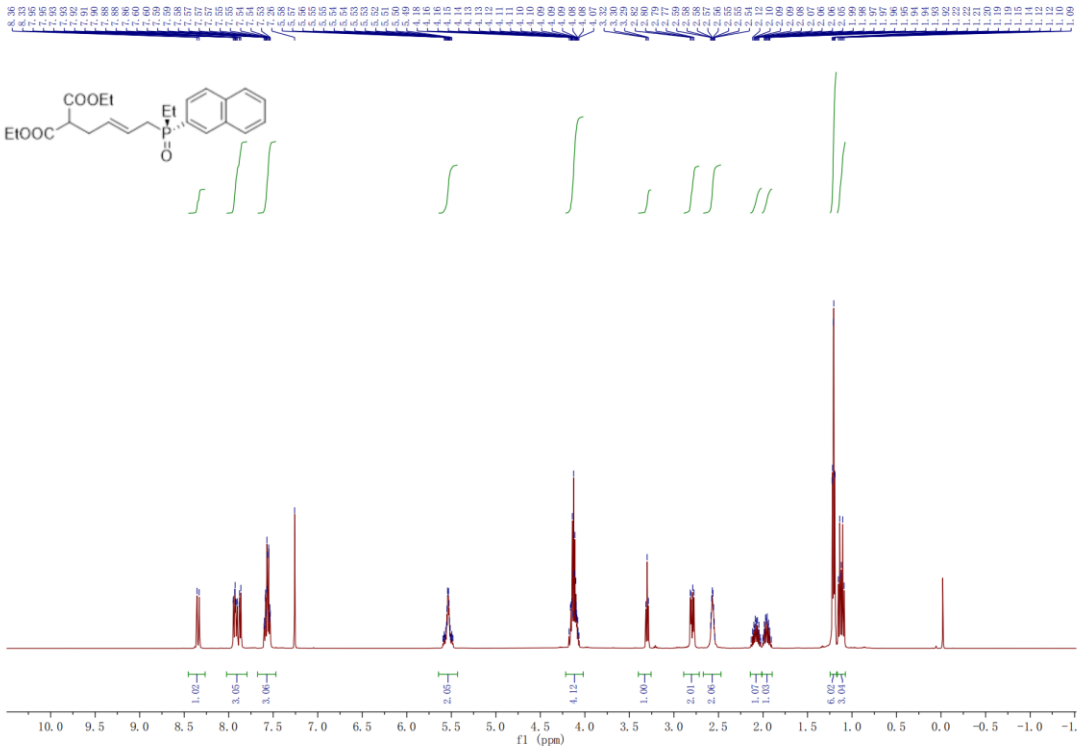
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3q**



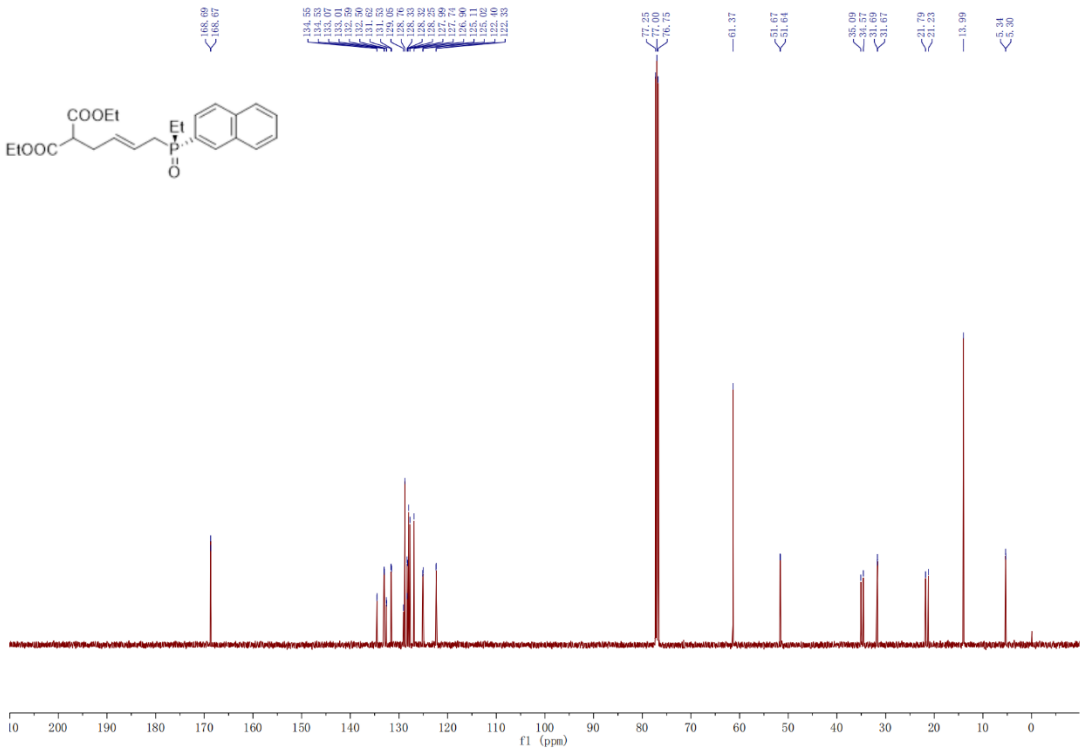
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3o**



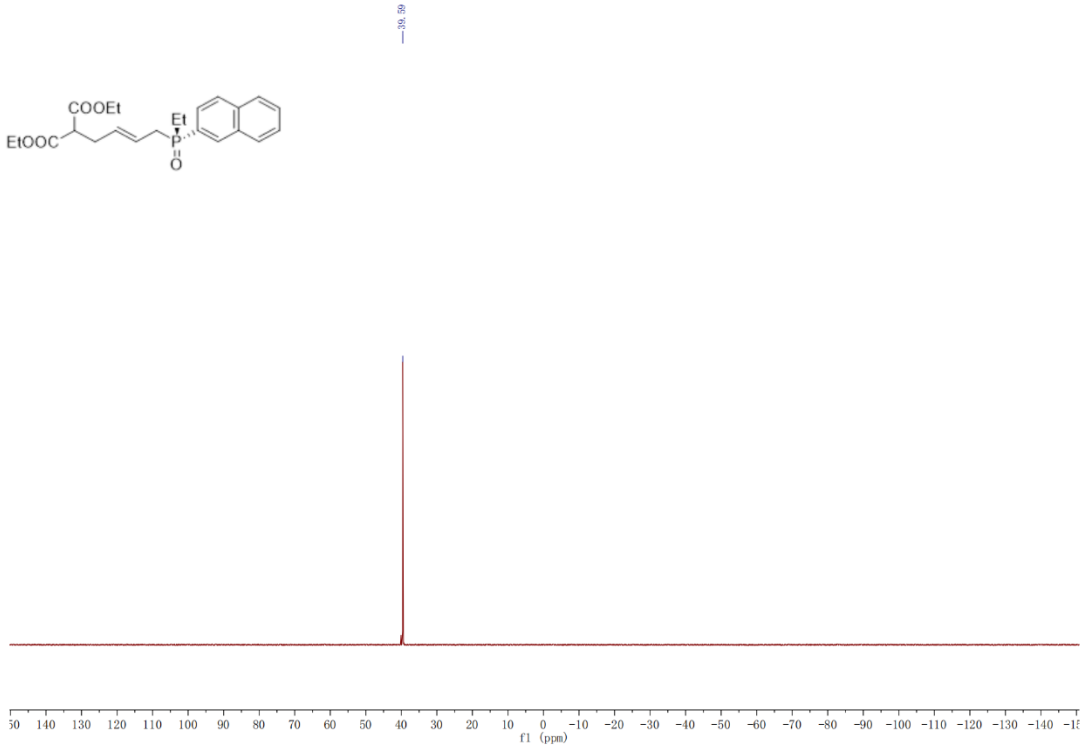
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3r**



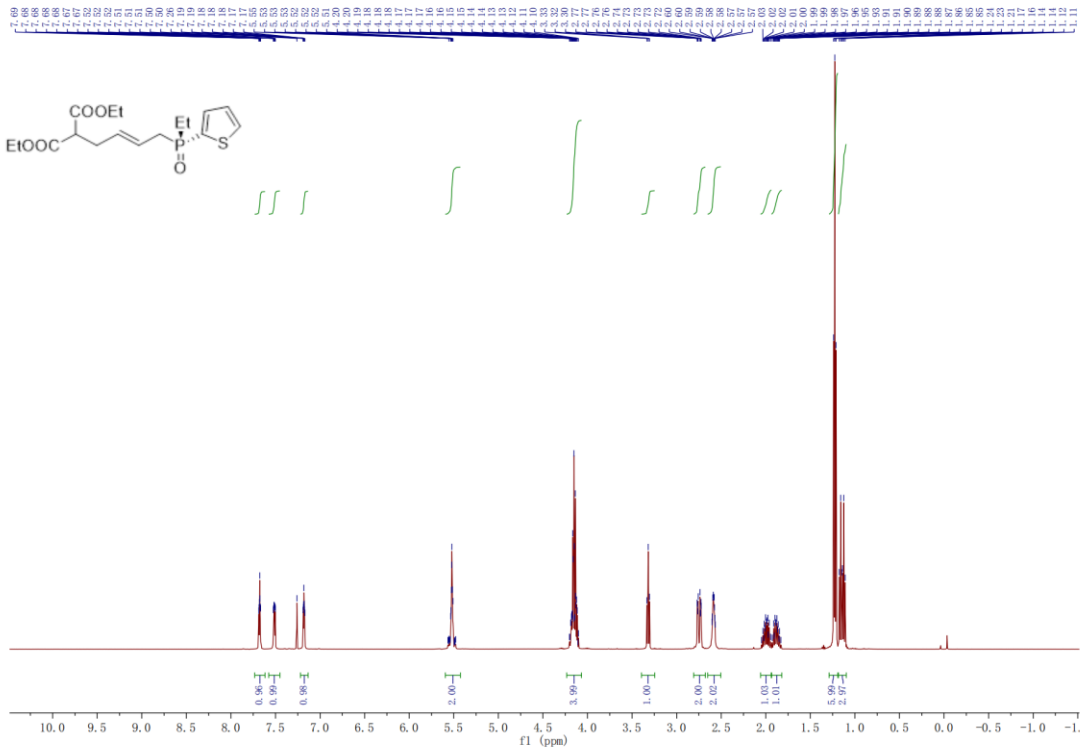
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3r**



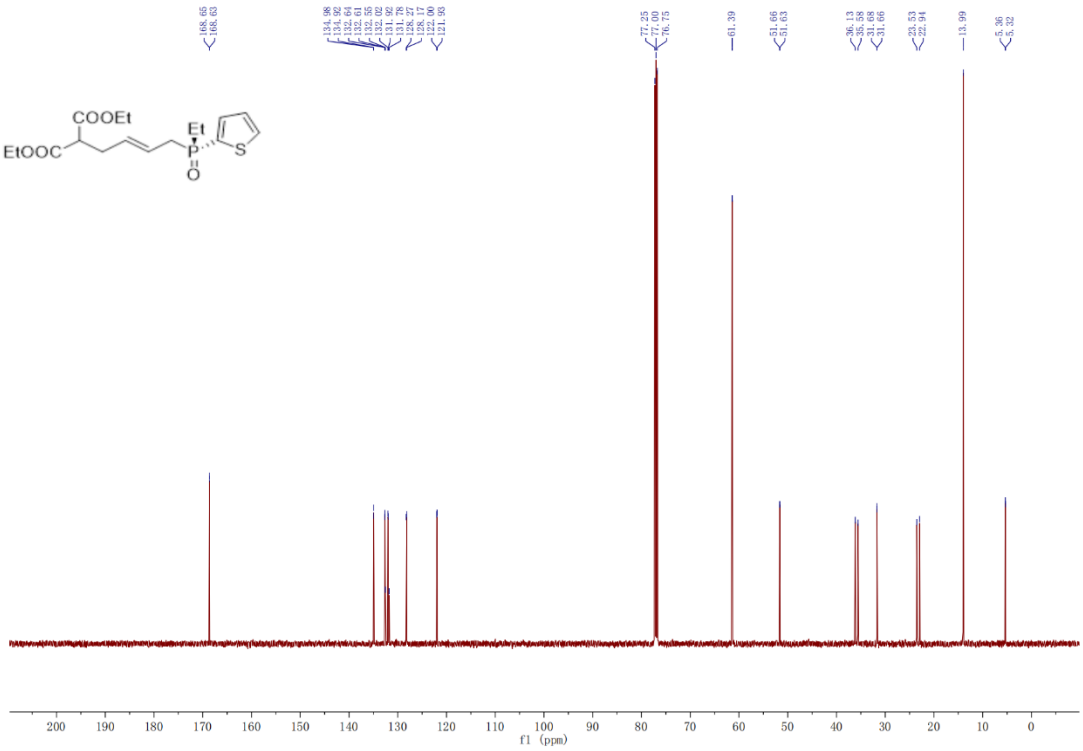
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3r**



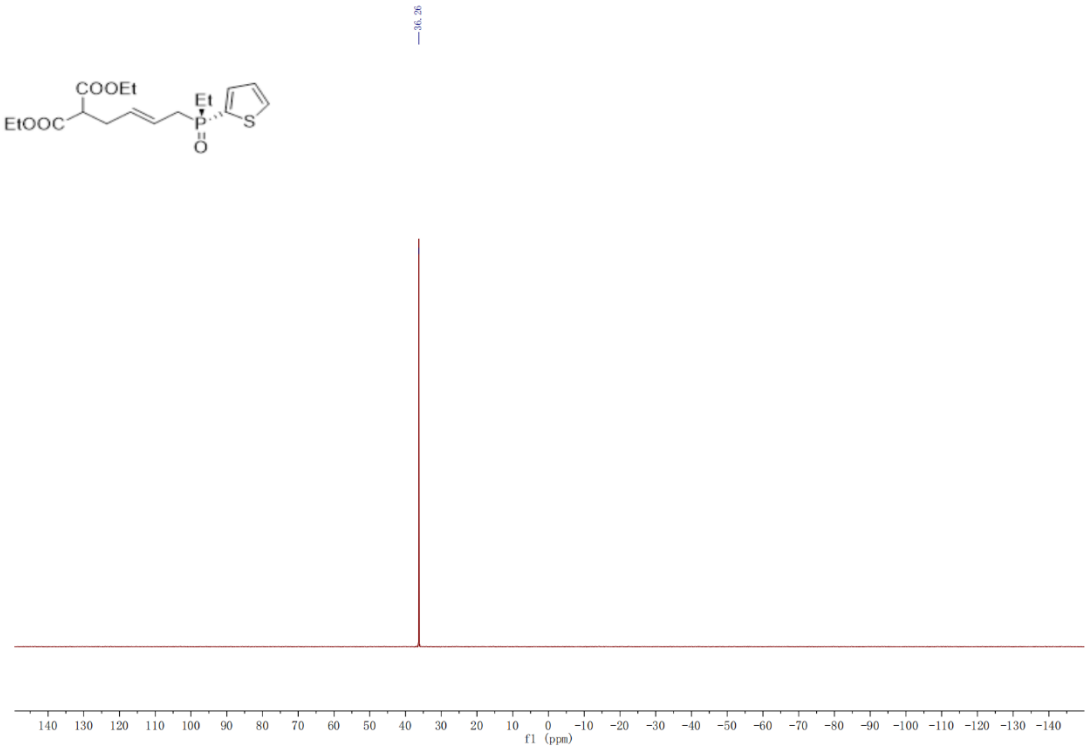
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3s**



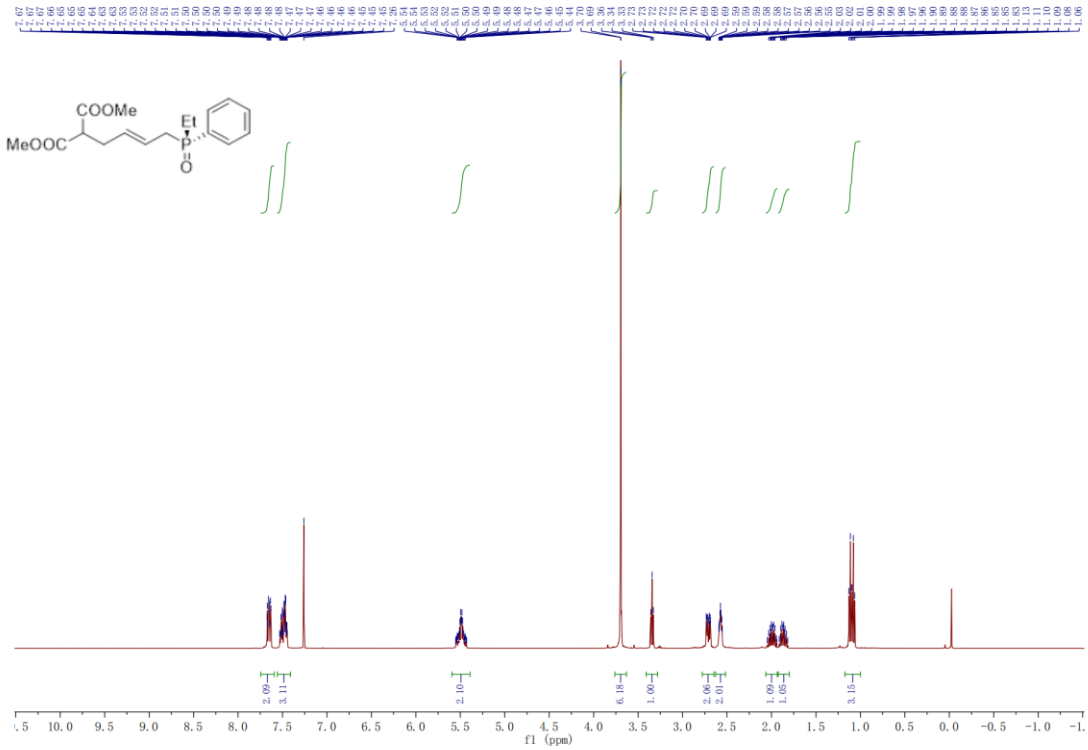
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3s**



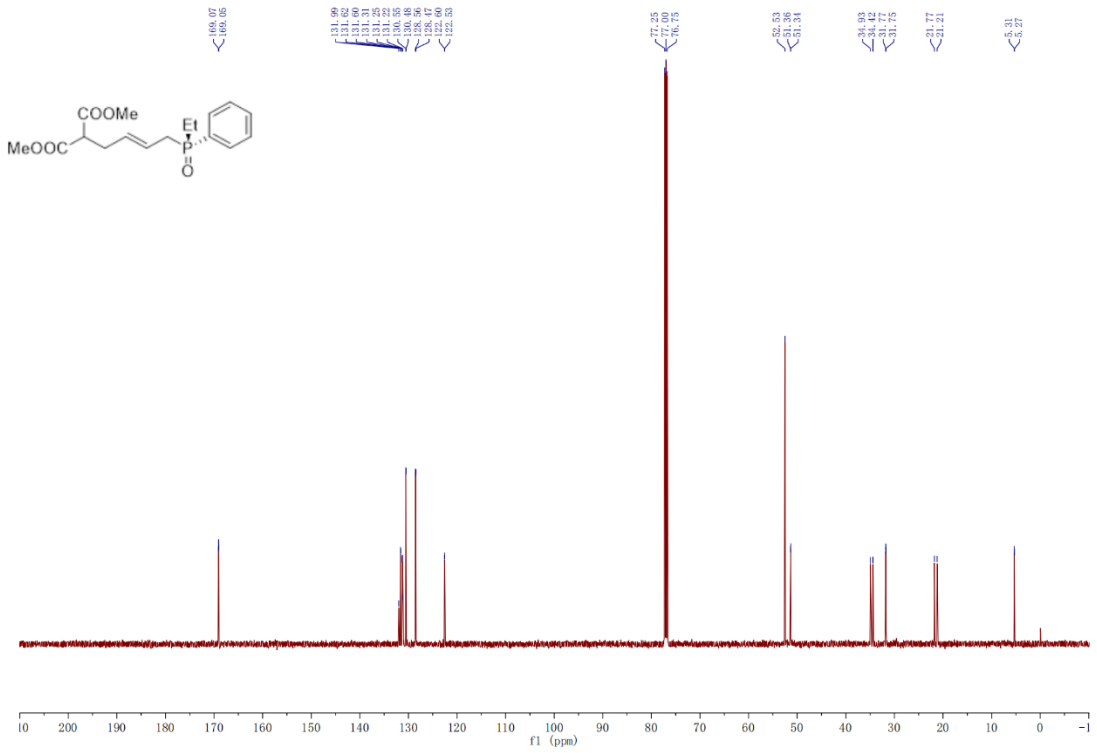
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3s**



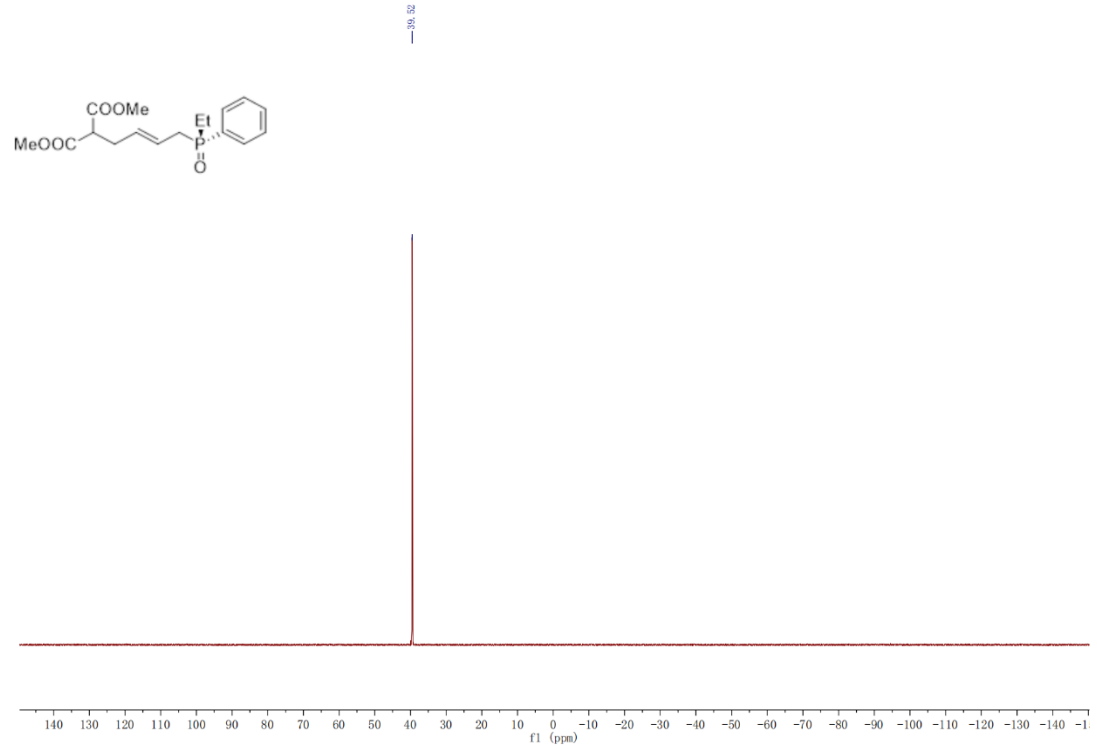
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3t**



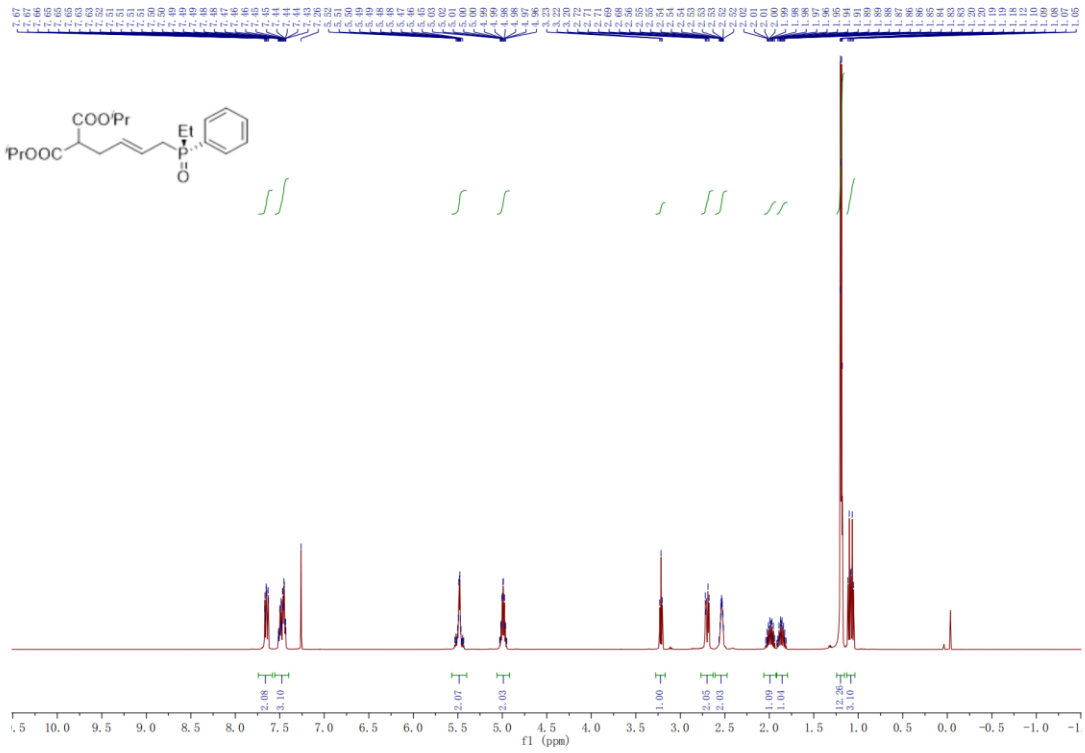
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3t**



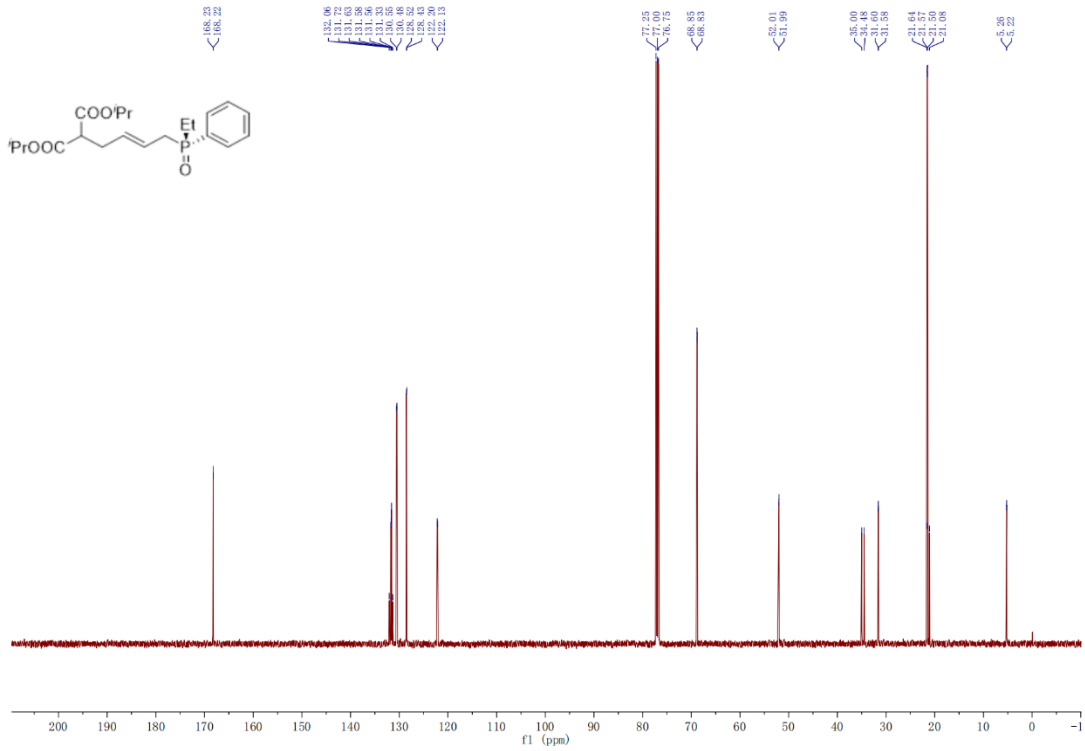
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3t**



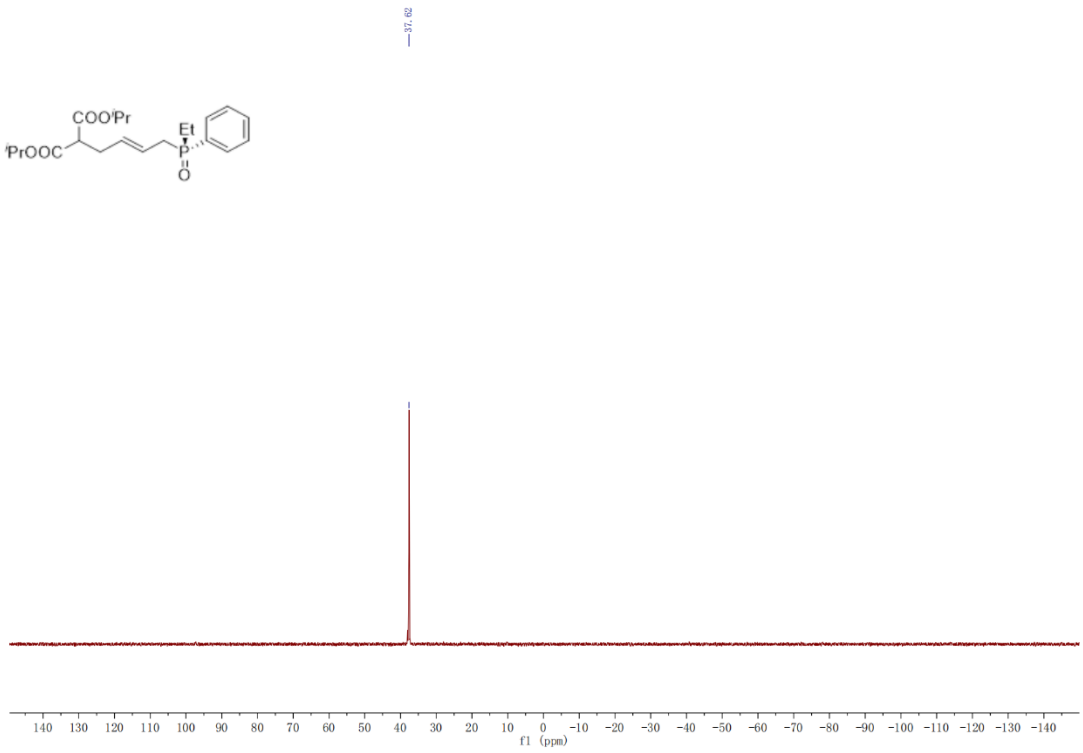
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3u**



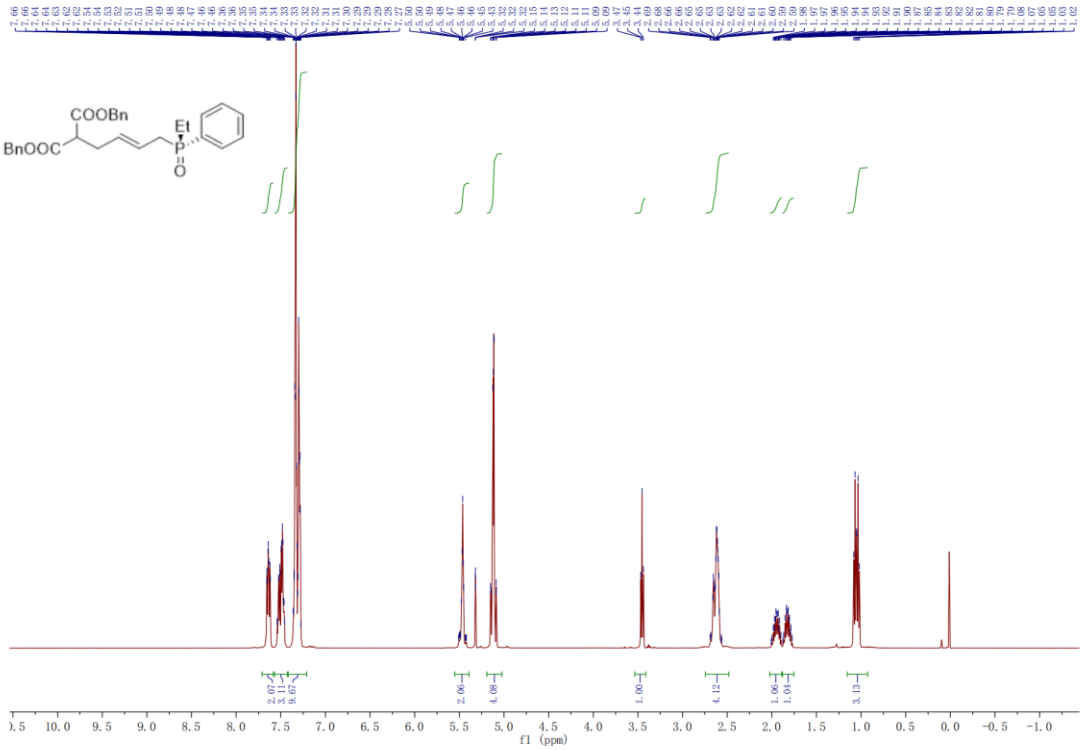
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3u**



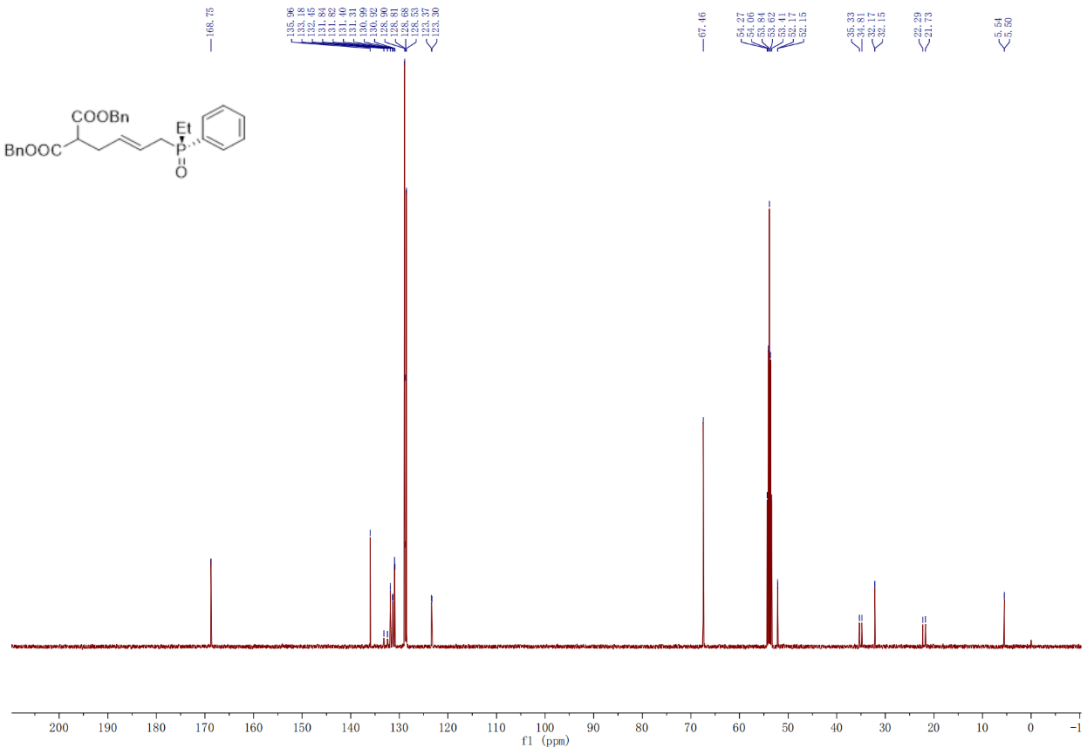
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3u**



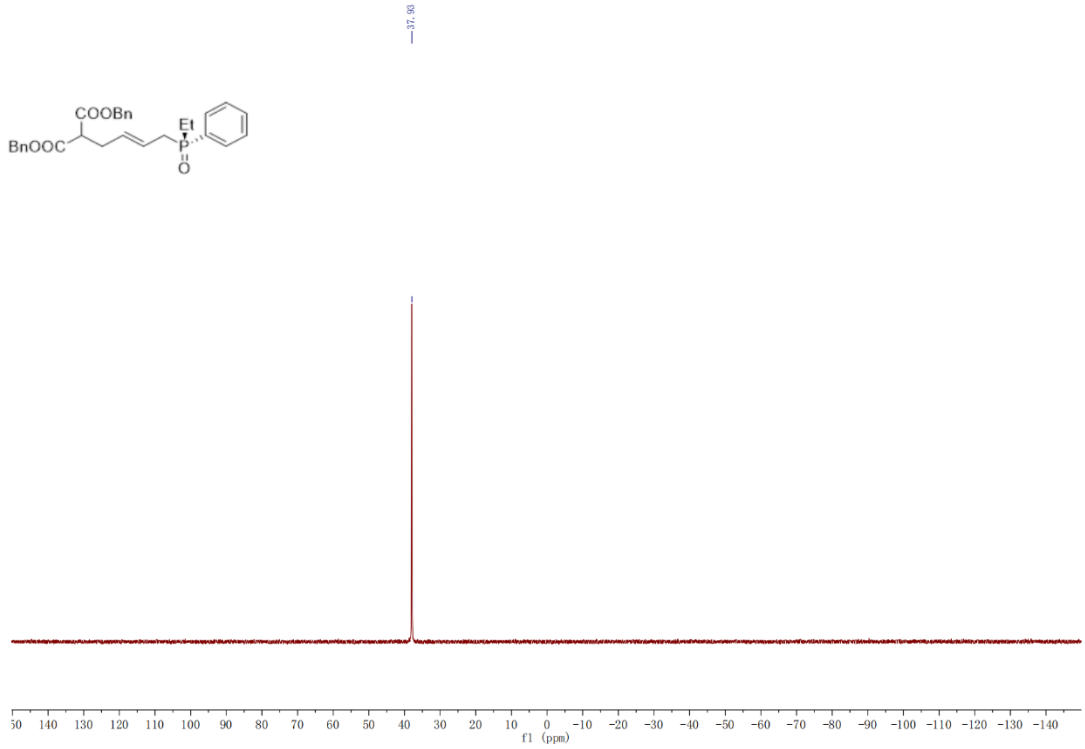
^{1}H NMR spectra (500 MHz, CD_2Cl_2) of **3v**



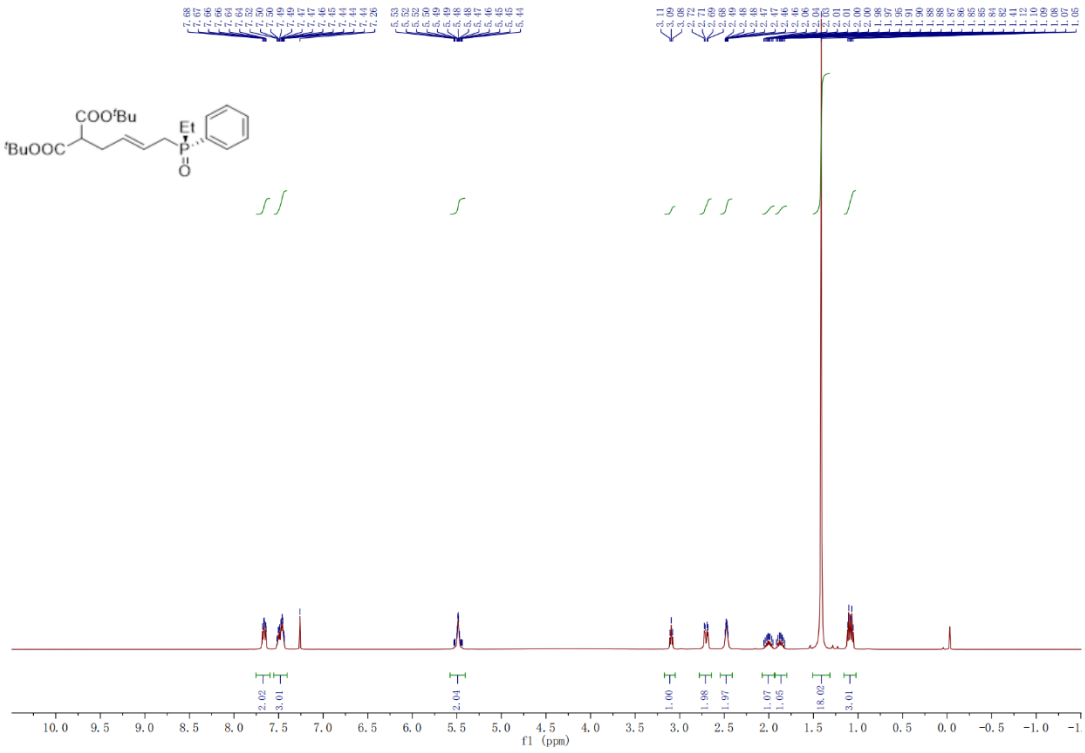
^{13}C NMR spectra (126 MHz, CD_2Cl_2) of **3v**



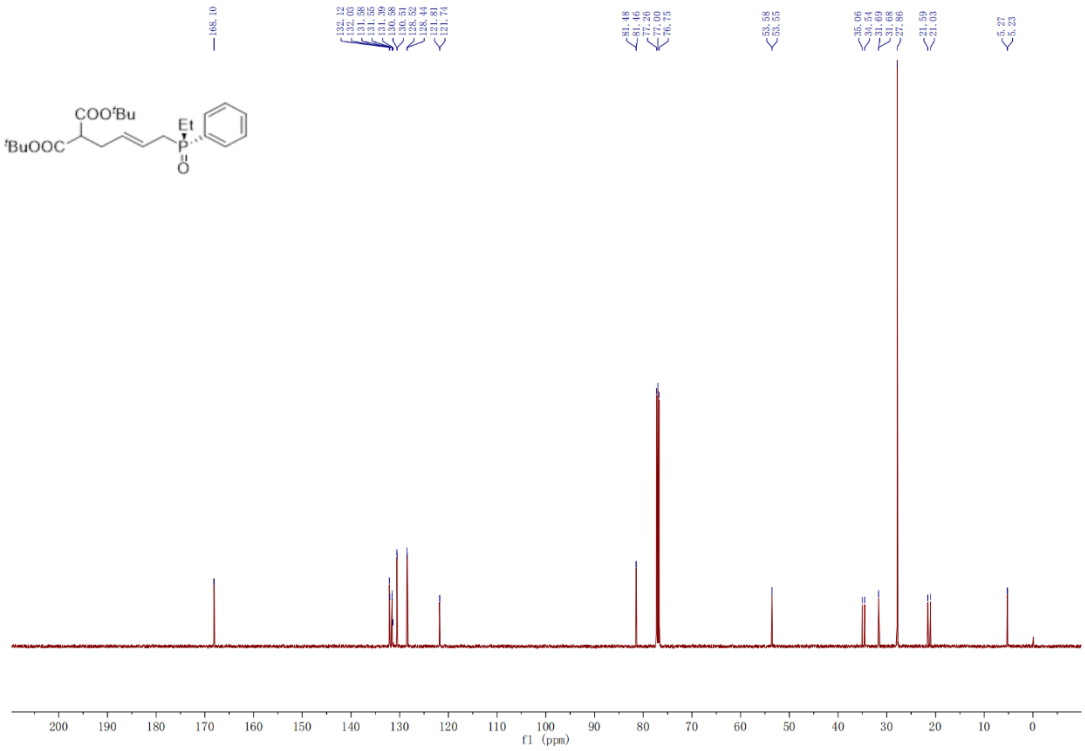
^{31}P NMR spectra (202 MHz, CD_2Cl_2) of **3v**



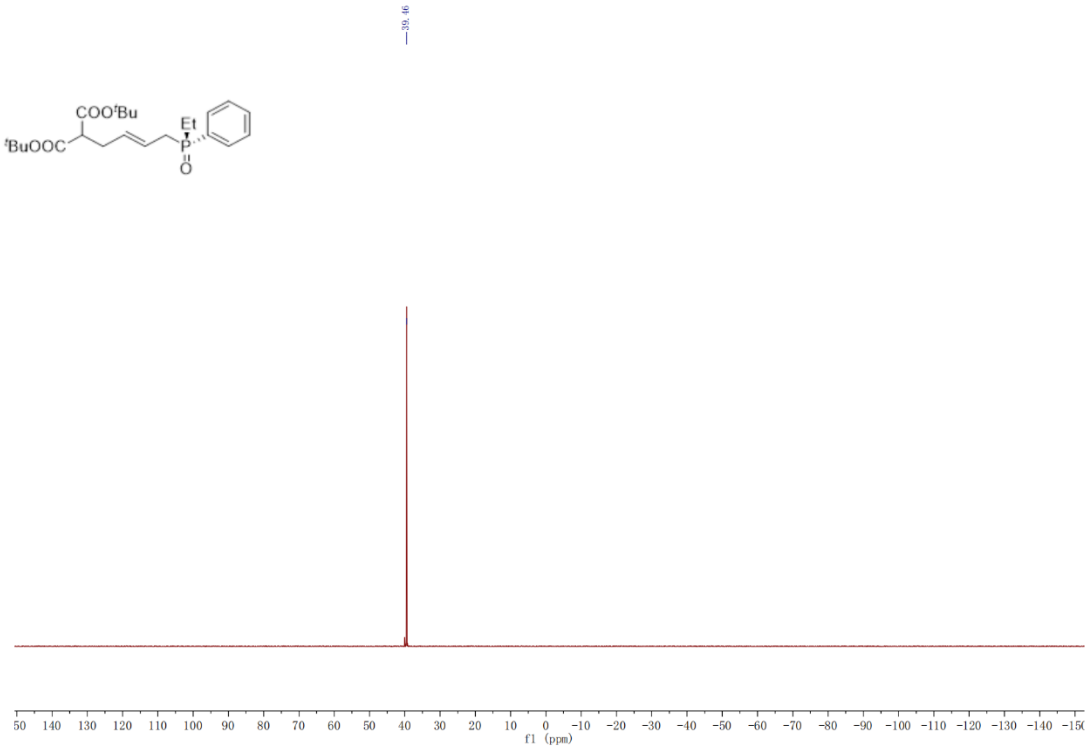
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3w**



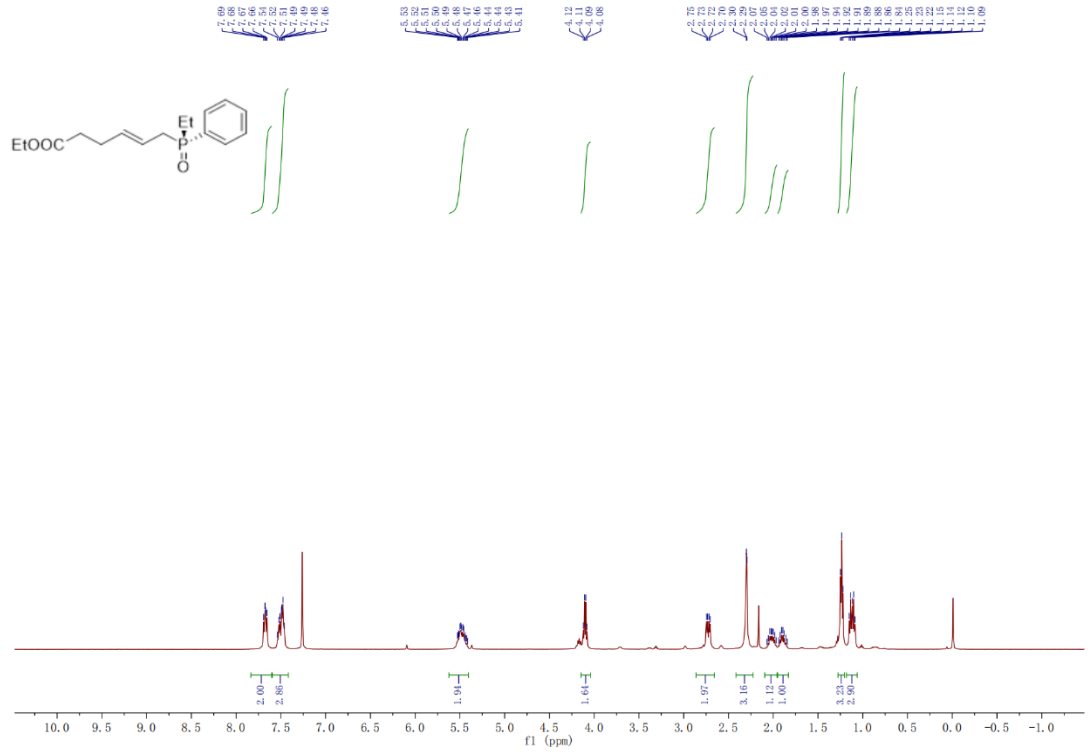
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **3w**



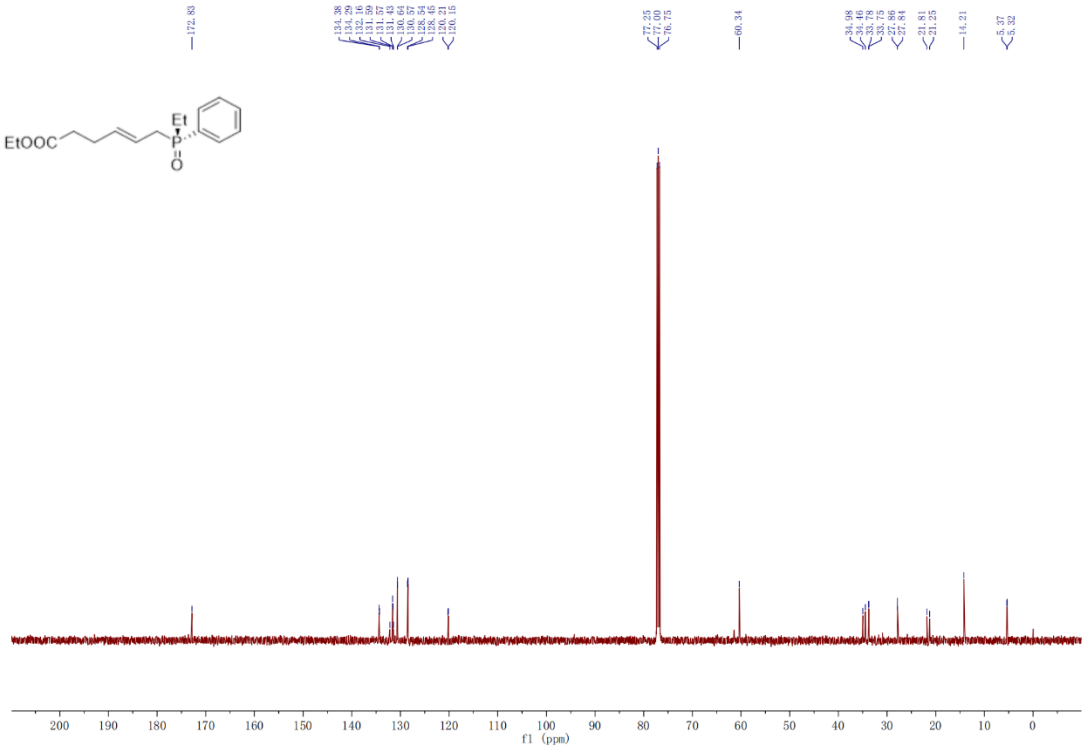
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **3w**



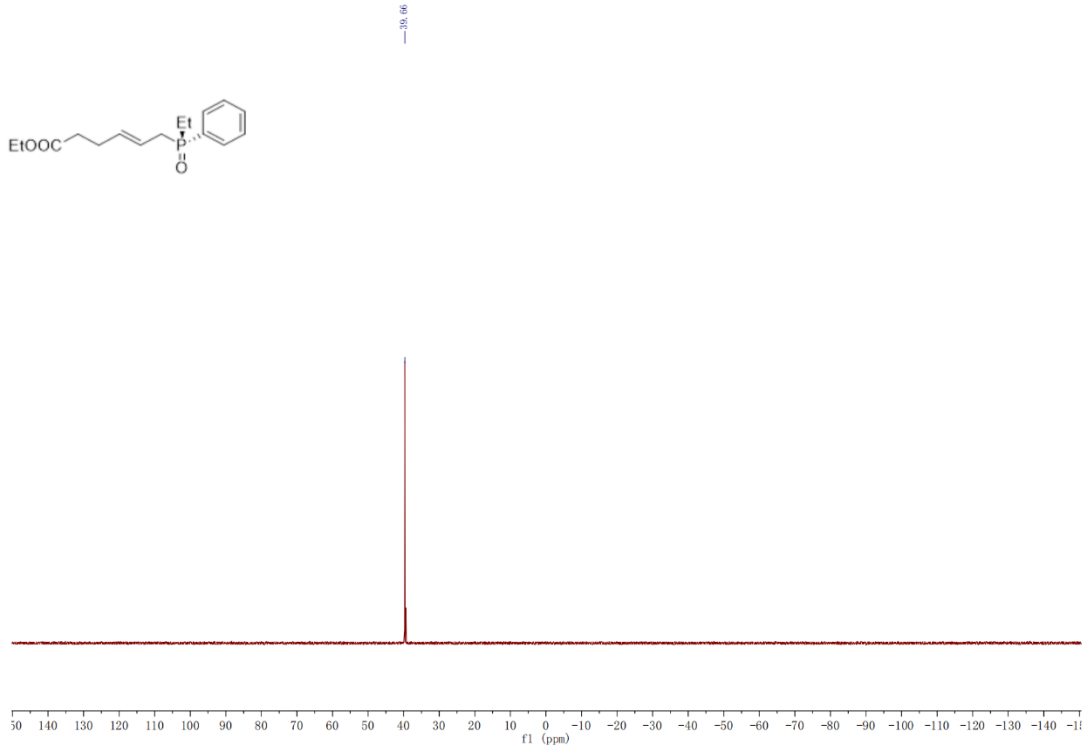
^{1}H NMR spectra (500 MHz, $CDCl_3$) of **4a**



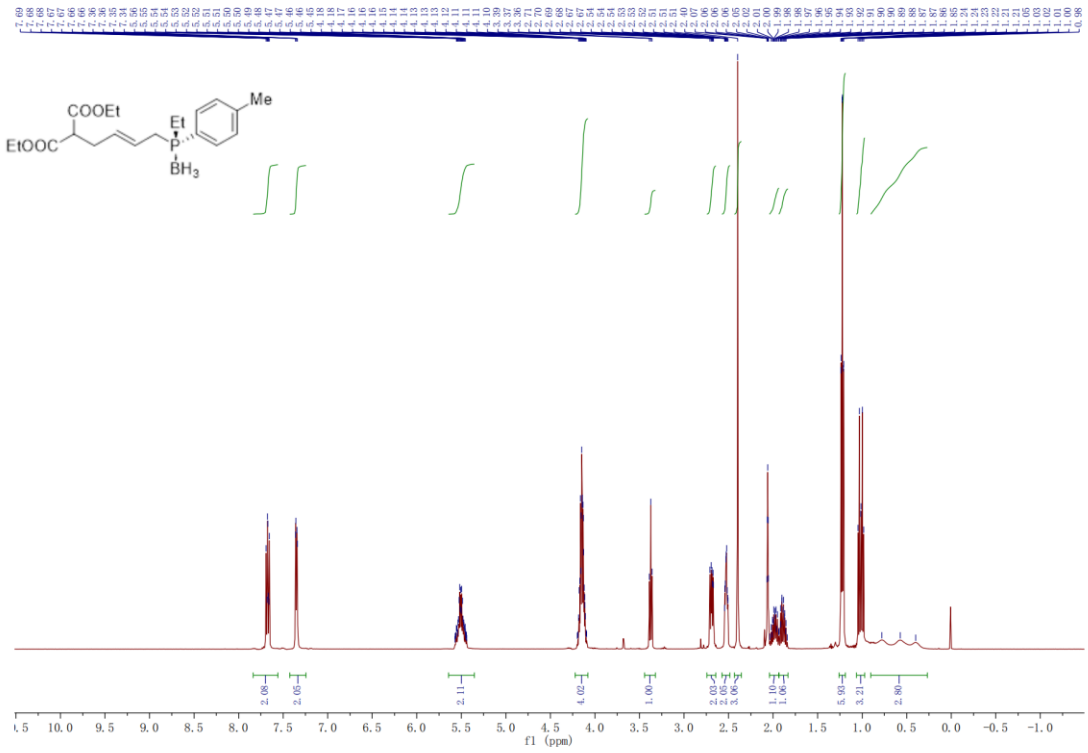
^{13}C NMR spectra (126 MHz, $CDCl_3$) of **4a**



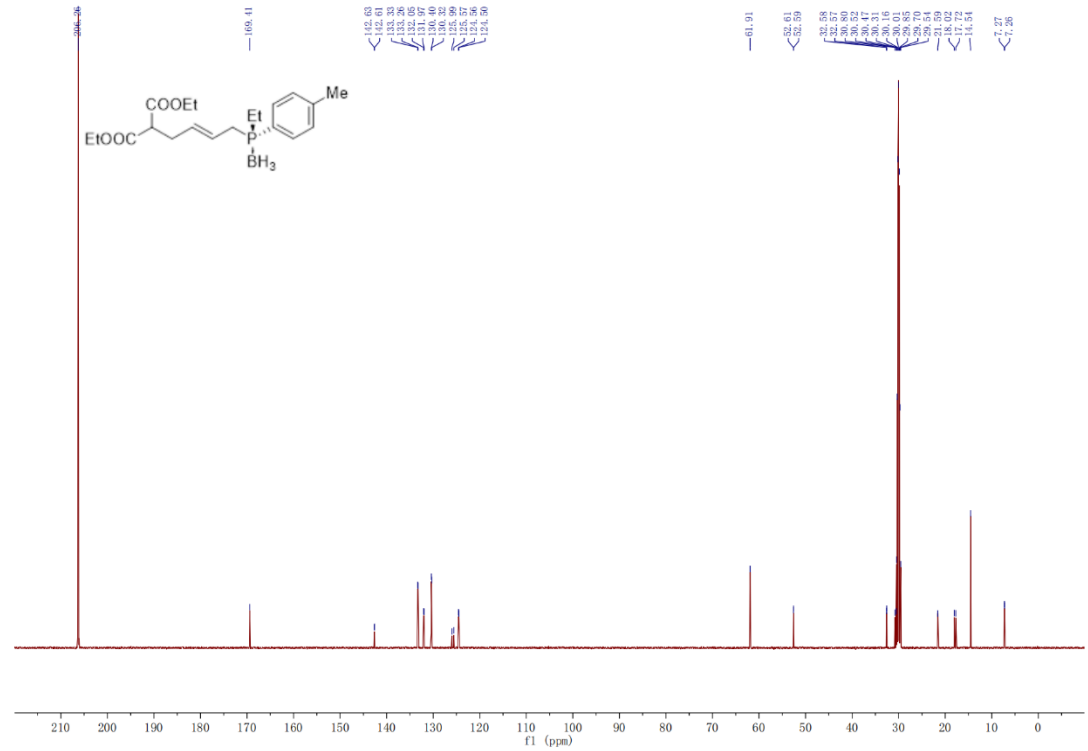
^{31}P NMR spectra (202 MHz, $CDCl_3$) of **4a**



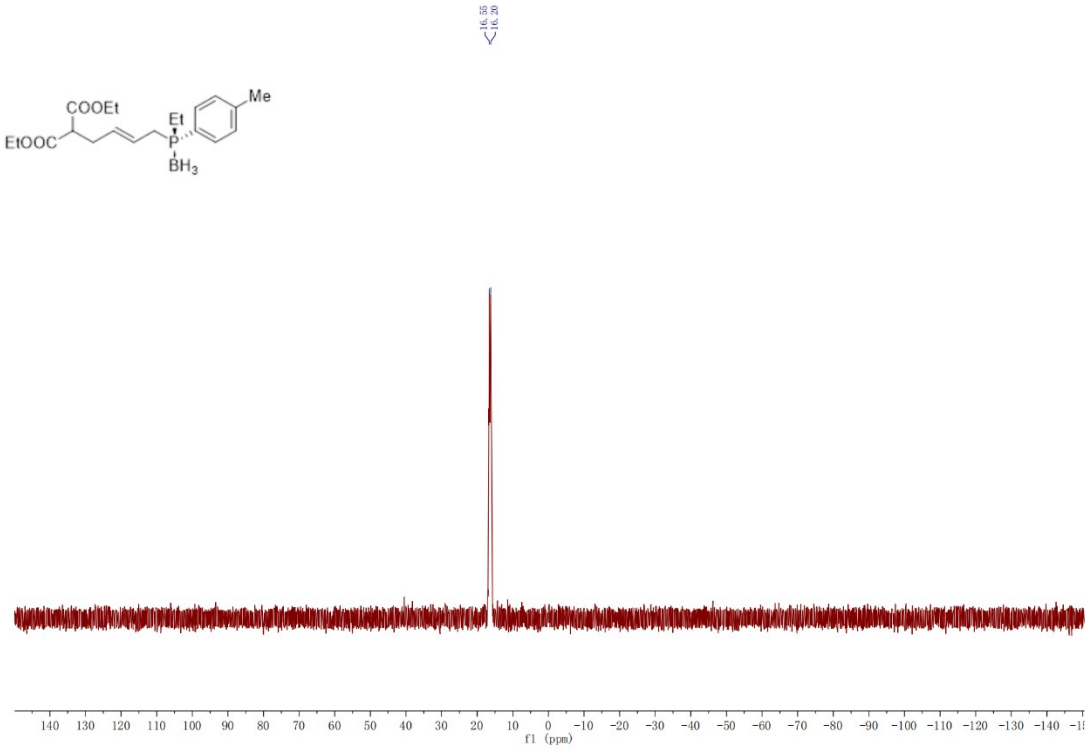
^{1}H NMR spectra (500 MHz, CD_3COCD_3) of **4i**



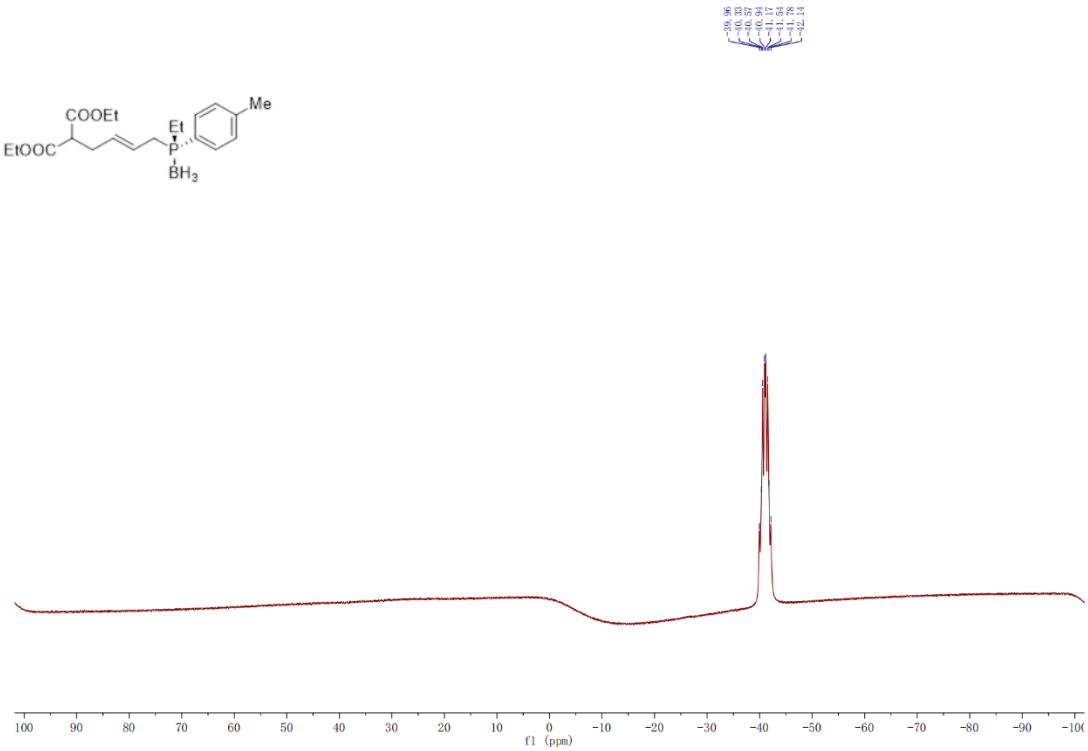
^{13}C NMR spectra (126 MHz, CD_3COCD_3) of **4i**



^{31}P NMR spectra (202 MHz, CD_3COCD_3) of **4i**

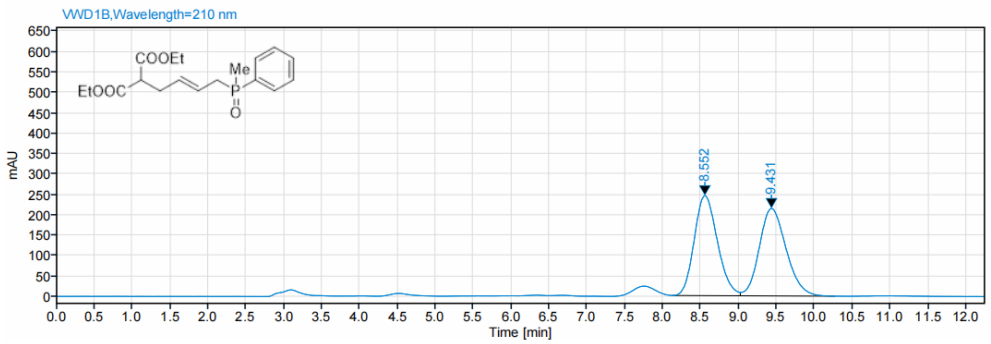


^{11}B NMR spectra (160 MHz, CD_3COCD_3) of **4i**



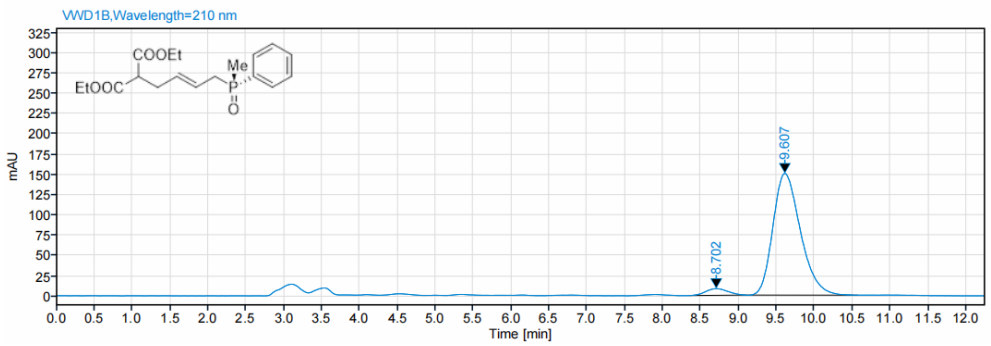
9. HPLC Spectra data

HPLC spectra data of **3a**



Signal: VWD1B,Wavelength=210 nm

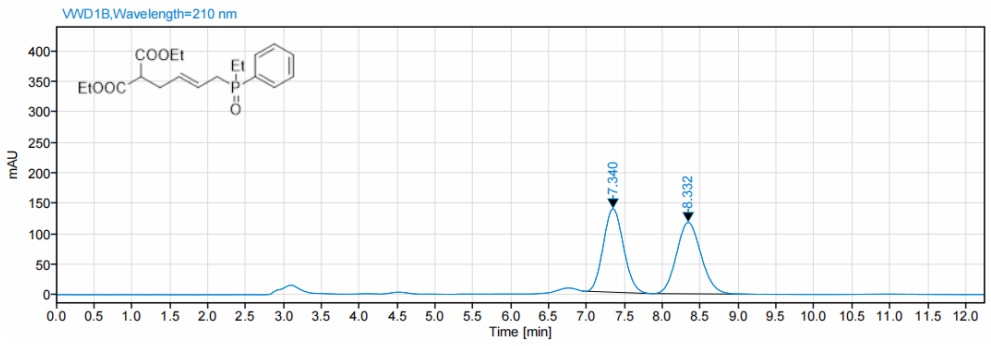
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.552	MM m	0.90	5204.94	245.05	49.65	
9.431	MM m	1.25	5278.49	214.44	50.35	
		Sum	**10483.43**			



Signal: VWD1B,Wavelength=210 nm

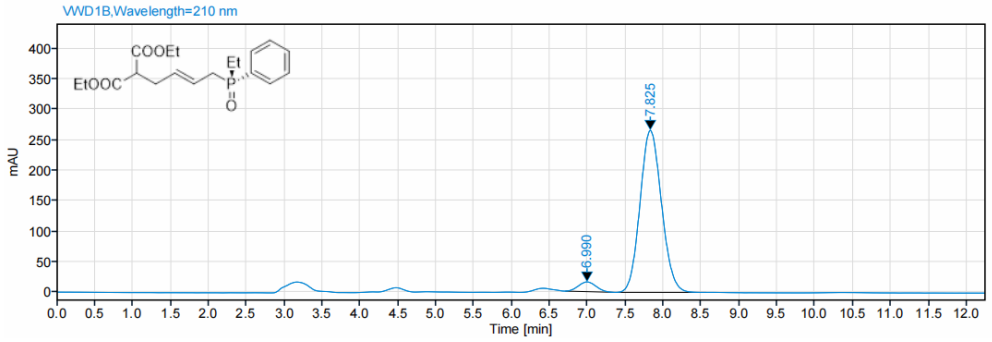
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.702	MM m	0.74	166.22	8.19	4.21	
9.607	MM m	1.48	3778.91	149.87	95.79	
		Sum	**3945.13**			

HPLC spectra data of **3b**



Signal: VWD1B,Wavelength=210 nm

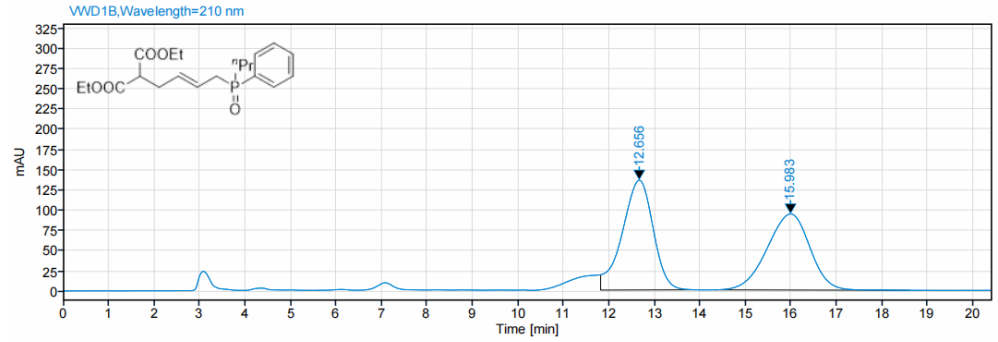
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.340	MM m	0.90	2537.66	136.85	48.99	
8.332	MM m	1.29	2641.92	117.07	51.01	
		Sum	**5179.59**			



Signal: VWD1B,Wavelength=210 nm

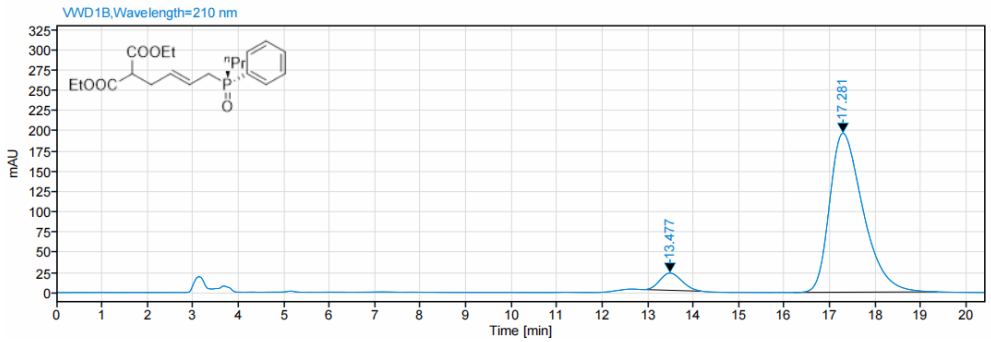
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.990	MM m	0.66	258.10	15.92	4.70	
7.825	MM m	1.19	5233.15	265.74	95.30	
		Sum	**5491.25**			

HPLC spectra data of **3c**



Signal: VWD1B,Wavelength=210 nm

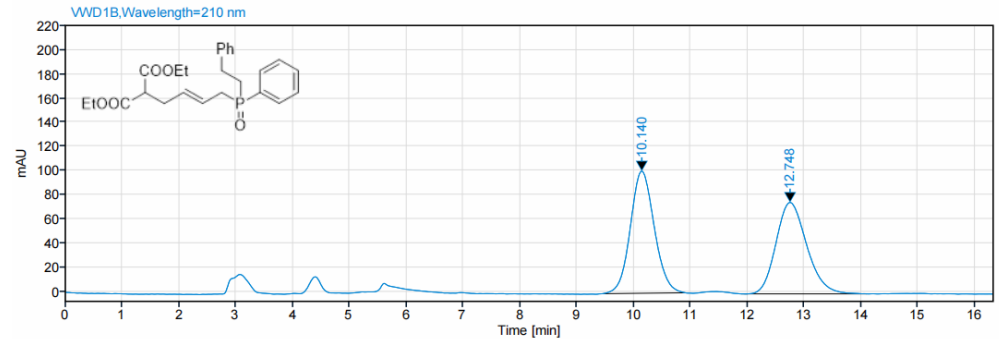
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.656	MM m	2.09	6393.50	135.50	51.02	
15.983	MM m	4.30	6138.63	93.92	48.98	
		Sum	**12532.13**			



Signal: VWD1B,Wavelength=210 nm

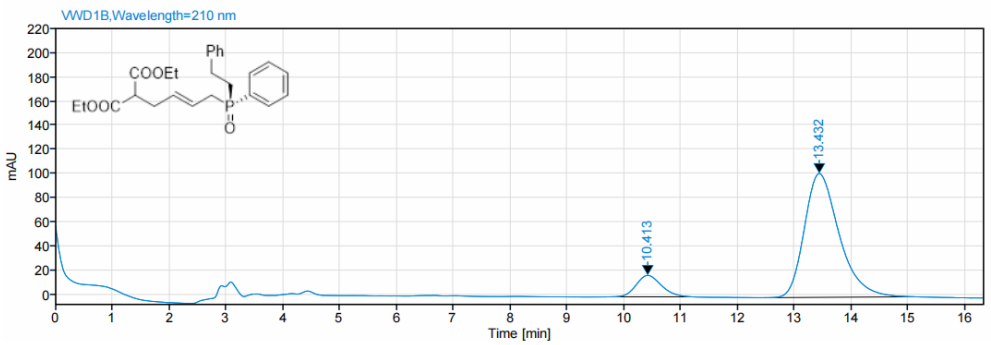
RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.477	MM m	1.27	713.17	21.31	6.65	
17.281	MM m	3.15	10017.16	196.23	93.35	
		Sum	**10730.33**			

HPLC spectra data of **3d**



Signal: VWD1B,Wavelength=210 nm

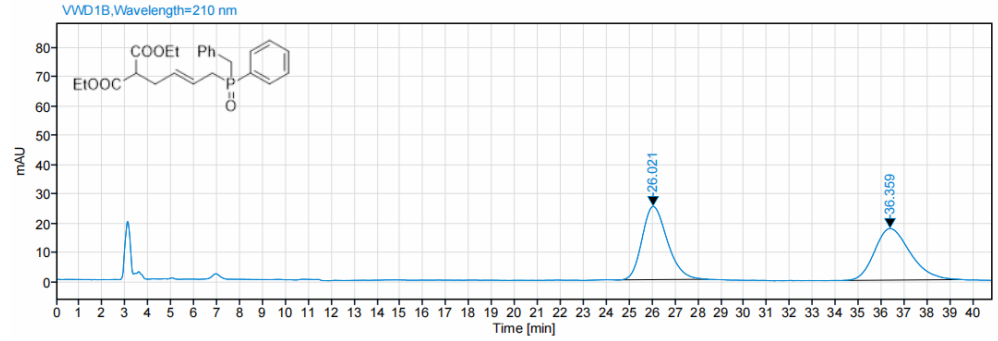
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.140	MM m	1.46	2962.35	101.14	51.01	
12.748	MM m	2.21	2845.48	75.70	48.99	
		Sum	**5807.83**			



Signal: VWD1B,Wavelength=210 nm

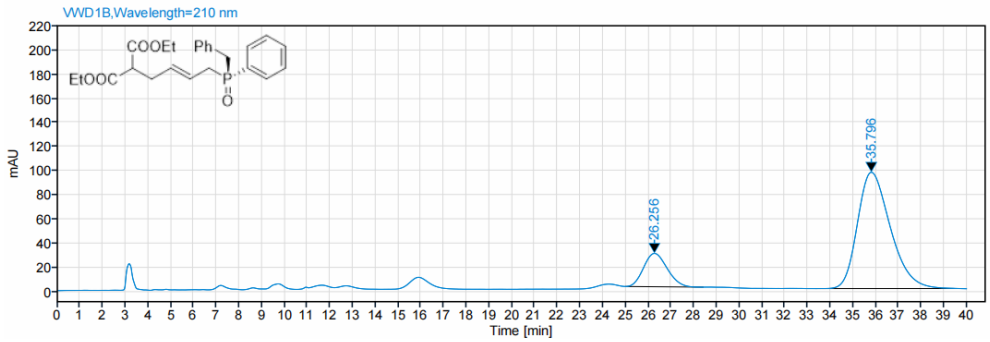
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.413	MM m	1.43	546.09	17.73	11.11	
13.432	MM m	2.66	4368.26	102.50	88.89	
		Sum	**4914.35**			

HPLC spectra data of **3e**



Signal: VWD1B,Wavelength=210 nm

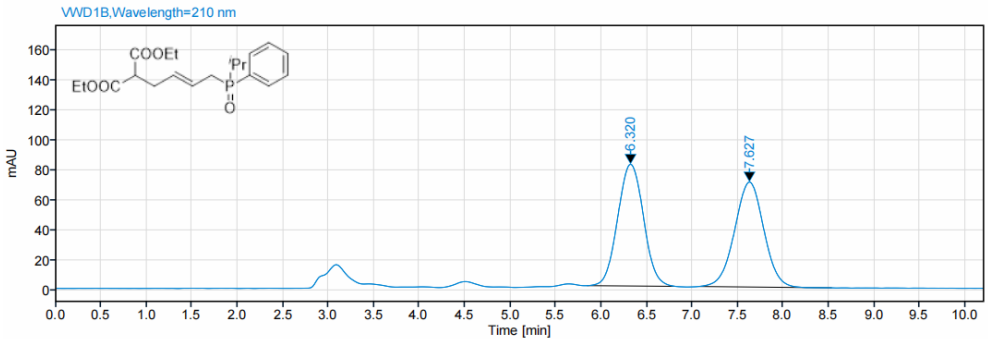
RT [min]	Type	Width [min]	Area	Height	Area%	Name
26.021	MM m	4.08	1911.17	24.95	50.06	
36.359	MM m	5.19	1906.29	17.60	49.94	
		Sum	**3817.47**			



Signal: VWD1B,Wavelength=210 nm

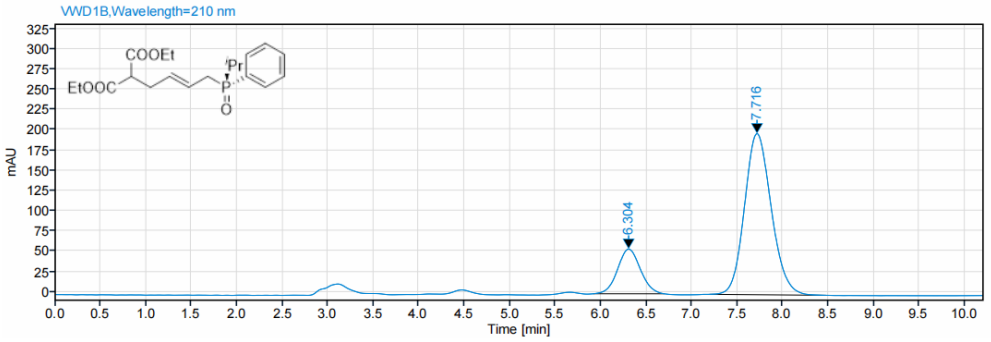
RT [min]	Type	Width [min]	Area	Height	Area%	Name
26.256	MM m	3.45	1983.18	27.58	17.02	
35.796	MM m	6.34	9670.04	96.30	82.98	
		Sum	**11653.22**			

HPLC spectra data of **3f**



Signal: VWD1B,Wavelength=210 nm

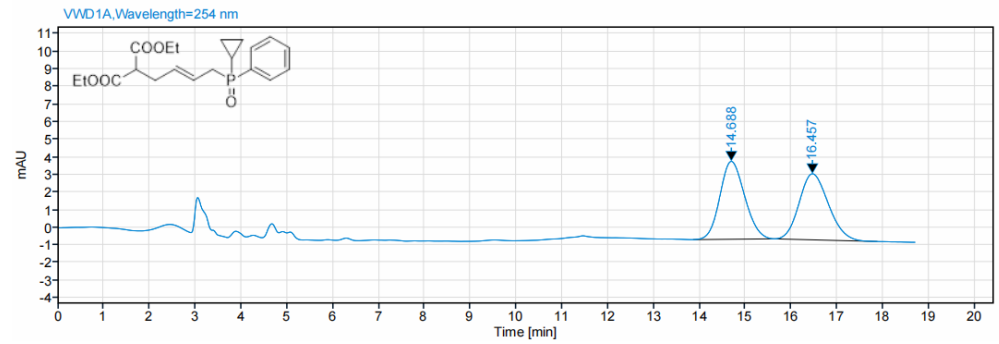
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.320	MM m	0.97	1599.68	80.99	50.64	
7.627	MM m	1.46	1559.22	69.87	49.36	
		Sum	**3158.91**			



Signal: VWD1B,Wavelength=210 nm

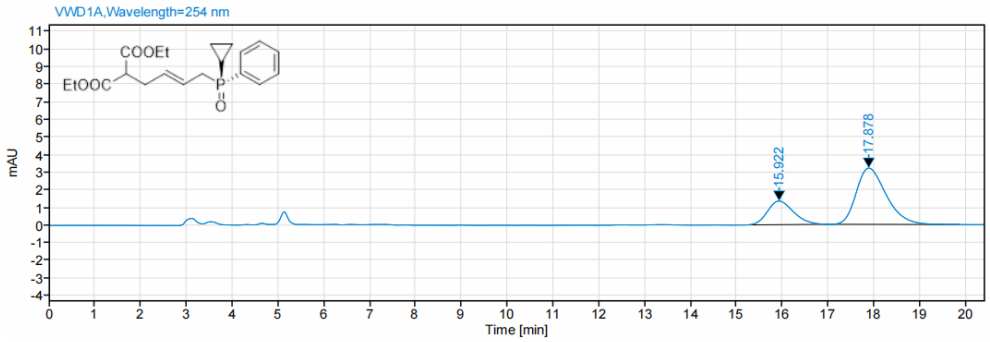
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.304	MM m	0.78	964.03	55.16	19.17	
7.716	MM m	1.28	4064.36	198.82	80.83	
		Sum	**5028.39**			

HPLC spectra data of **3g**



Signal: VWD1A,Wavelength=254 nm

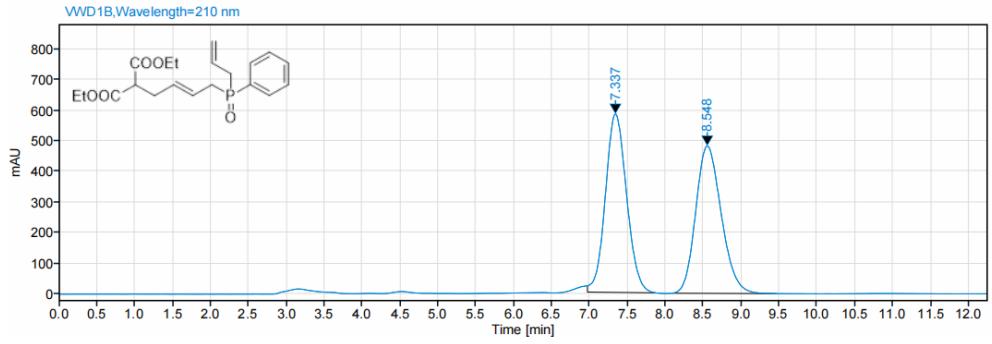
RT [min]	Type	Width [min]	Area	Height	Area%	Name
14.688	MM m	1.76	166.38	4.43	50.05	
16.457	MM m	2.26	166.03	3.75	49.95	
		Sum	**332.42**			



Signal: VWD1A,Wavelength=254 nm

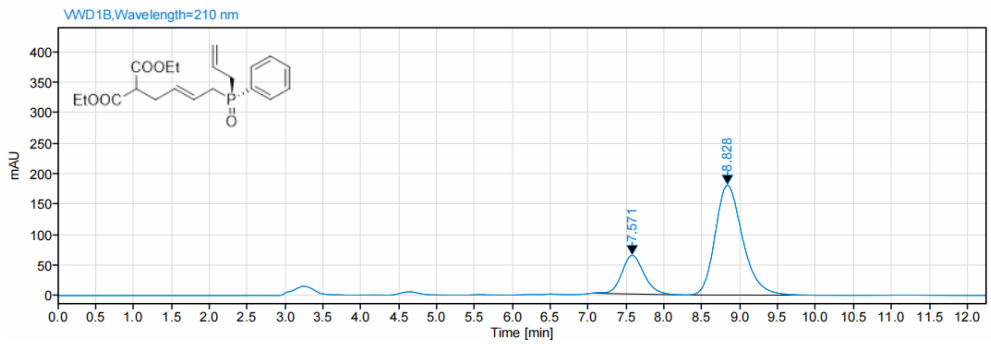
RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.922	MM m	1.79	52.99	1.34	26.71	
17.878	MM m	2.87	145.36	3.20	73.29	
		Sum	**198.35**			

HPLC spectra data of **3h**



Signal: VWD1B,Wavelength=210 nm

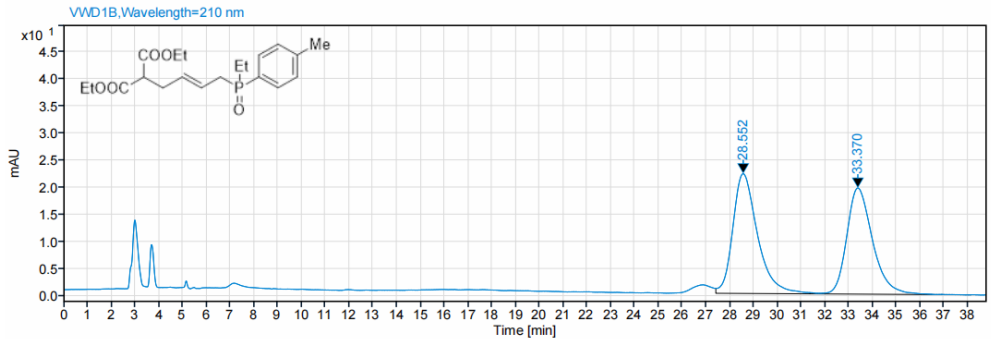
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.337	MM m	0.90	11332.27	582.13	50.13	
8.548	MM m	1.38	11275.59	481.17	49.87	
		Sum	**22607.86**			



Signal: VWD1B,Wavelength=210 nm

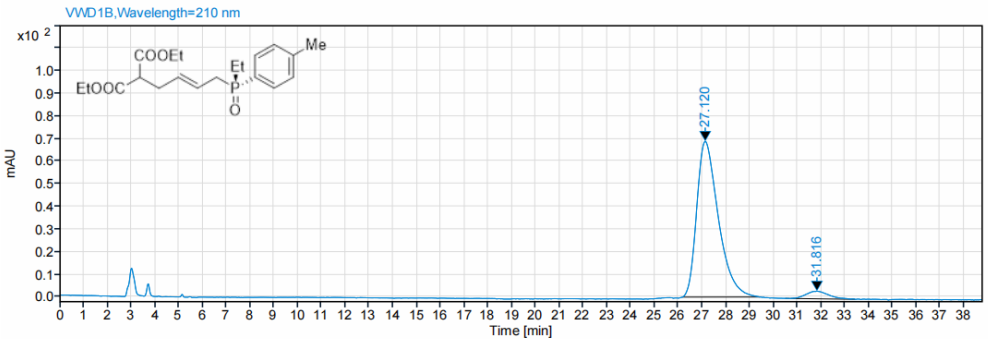
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.571	MM m	1.20	1294.68	63.29	22.20	
8.828	MM m	1.80	4538.32	180.26	77.80	
		Sum	**5833.00**			

HPLC spectra data of **3i**



Signal: VWD1B,Wavelength=210 nm

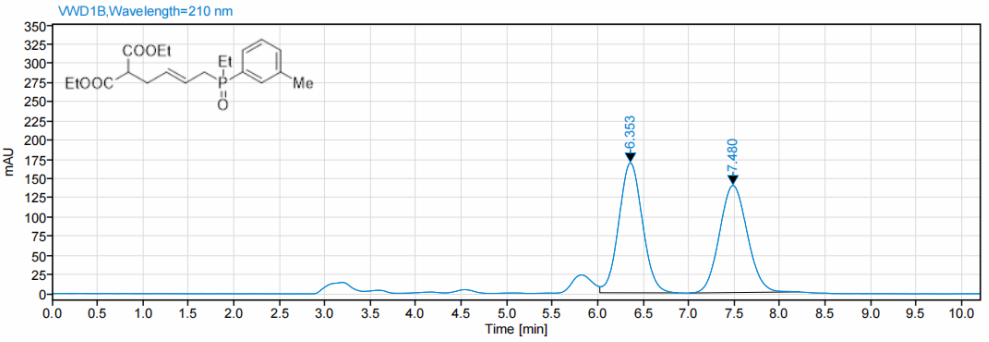
RT [min]	Type	Width [min]	Area	Height	Area%	Name
28.552	MM m	3.97	1598.50	22.14	51.96	
33.370	MM m	6.78	1477.89	19.62	48.04	
		Sum	**3076.39**			



Signal: VWD1B,Wavelength=210 nm

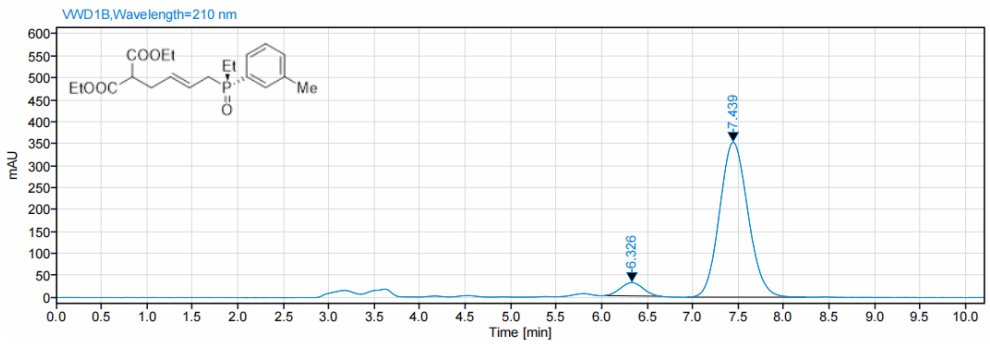
RT [min]	Type	Width [min]	Area	Height	Area%	Name
27.120	MM m	3.27	4347.19	68.86	95.14	
31.816	MM m	2.94	222.03	3.35	4.86	
		Sum	**4569.22**			

HPLC spectra data of **3j**



Signal: VWD1B,Wavelength=210 nm

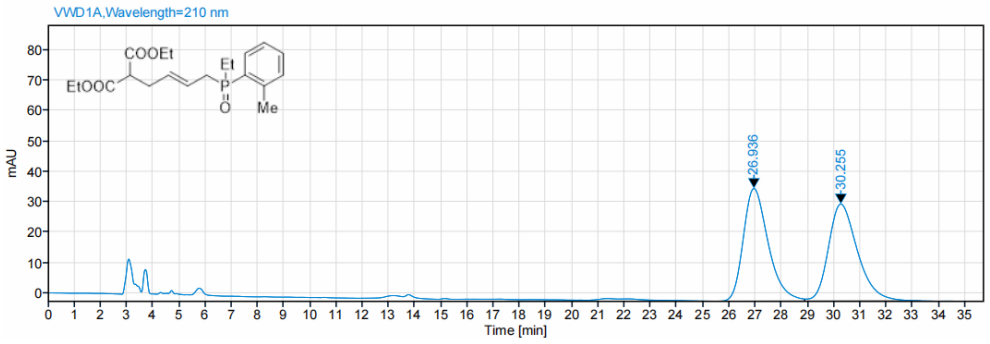
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.353	MM m	0.86	3061.19	169.15	50.77	
7.480	MM m	1.21	2968.57	139.53	49.23	
		Sum	**6029.77**			



Signal: VWD1B,Wavelength=210 nm

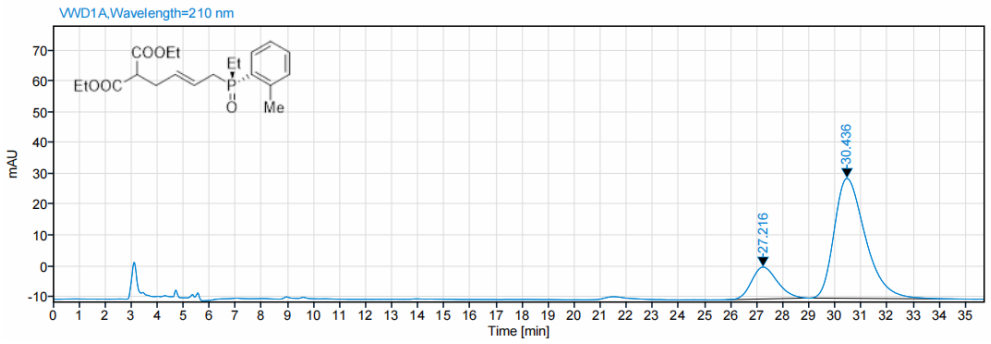
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.326	MM m	0.62	519.09	30.42	6.35	
7.439	MM m	1.30	7651.73	352.62	93.65	
		Sum	**8170.82**			

HPLC spectra data of **3k**



Signal: VWD1A,Wavelength=210 nm

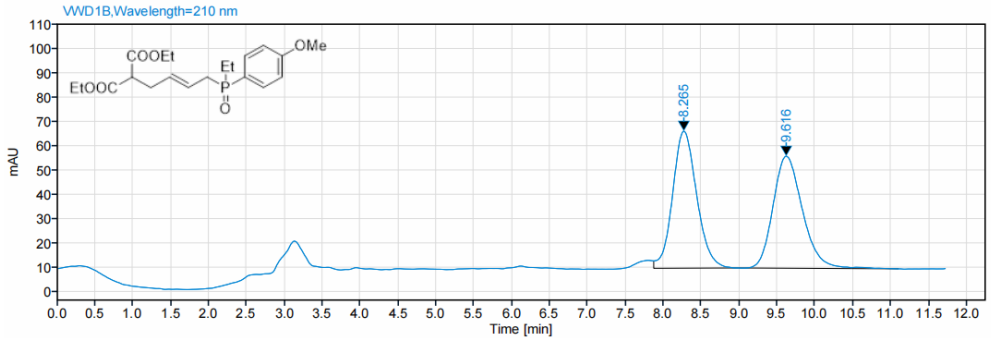
RT [min]	Type	Width [min]	Area	Height	Area%	Name
26.936	MM m	3.48	2449.05	37.02	49.96	
30.255	MM m	4.44	2453.42	31.87	50.04	
		Sum	**4902.48**			



Signal: VWD1A,Wavelength=210 nm

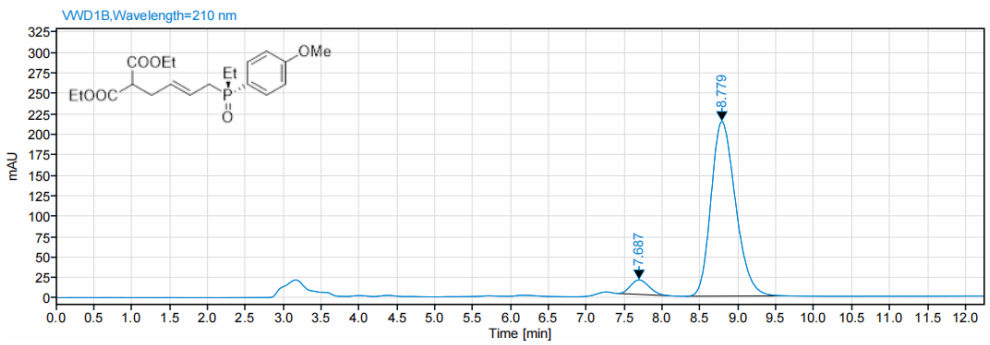
RT [min]	Type	Width [min]	Area	Height	Area%	Name
27.216	MM m	3.10	709.51	10.36	17.98	
30.436	MM m	5.80	3235.59	38.93	82.02	
		Sum	**3945.10**			

HPLC spectra data of **3l**



Signal: VWD1B,Wavelength=210 nm

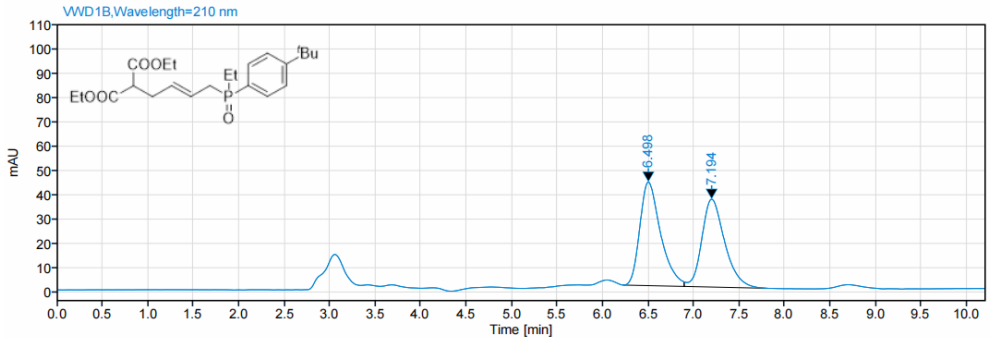
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.265	MM m	1.12	1242.12	56.18	50.04	
9.616	MM m	2.11	1240.17	45.95	49.96	
		Sum	**2482.30**			



Signal: VWD1B,Wavelength=210 nm

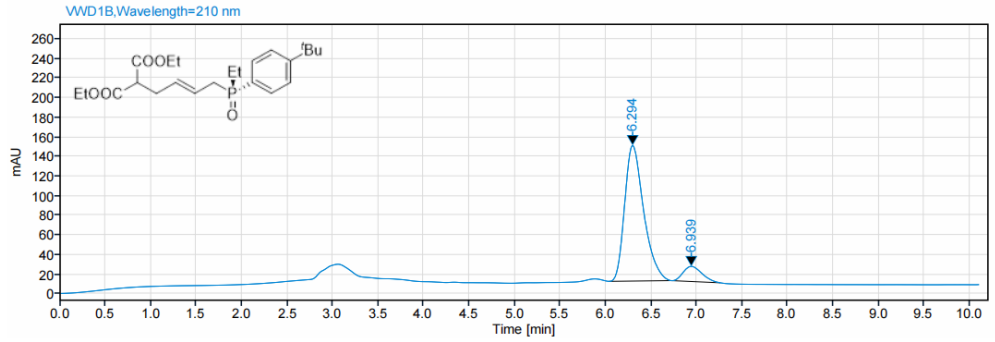
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.687	MM m	0.70	303.15	17.72	5.94	
8.779	MM m	1.36	4800.40	213.30	94.06	
		Sum	**5103.56**			

HPLC spectra data of **3m**



Signal: VWD1B,Wavelength=210 nm

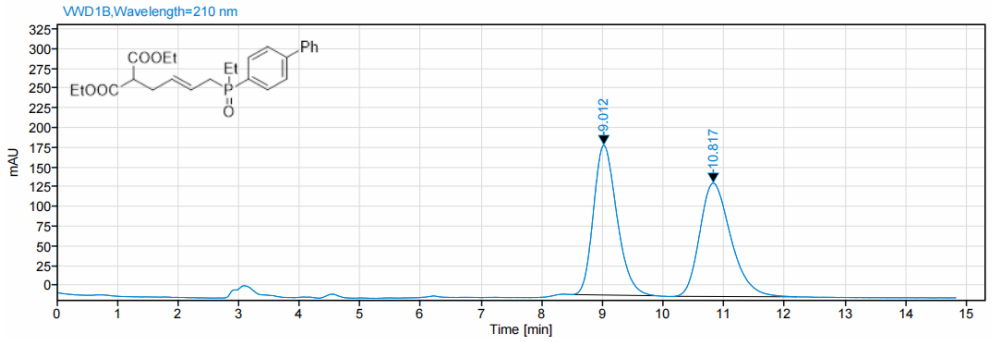
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.498	MM m	0.67	674.46	42.49	51.65	
7.194	MM m	0.91	631.49	36.05	48.35	
		Sum	**1305.95**			



Signal: VWD1B,Wavelength=210 nm

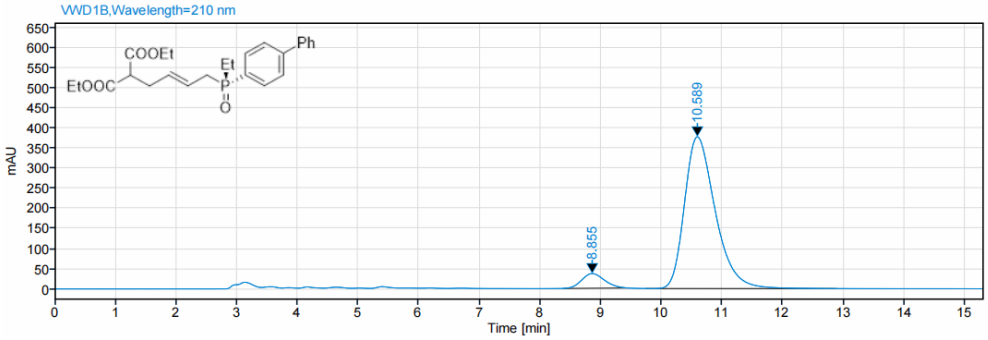
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.294	MM m	0.69	2008.64	138.21	90.07	
6.939	MM m	0.54	221.43	15.42	9.93	
		Sum	**2230.07**			

HPLC spectra data of **3n**



Signal: VWD1B,Wavelength=210 nm

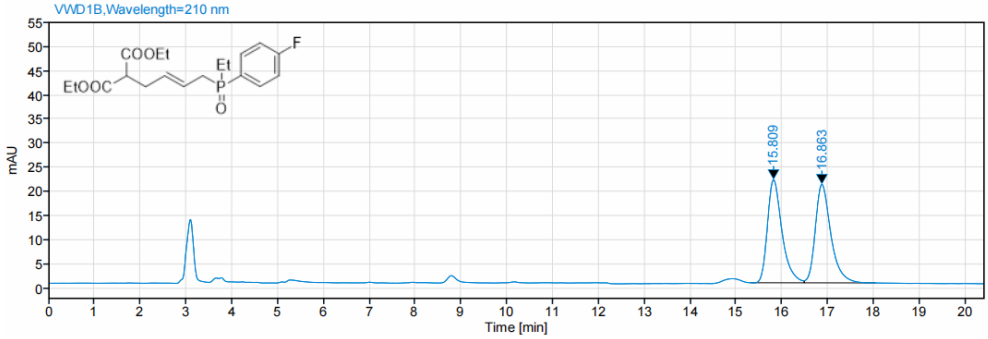
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.012	MM m	1.43	5096.54	189.56	49.86	
10.817	MM m	2.01	5124.59	143.62	50.14	
		Sum	**10221.13**			



Signal: VWD1B,Wavelength=210 nm

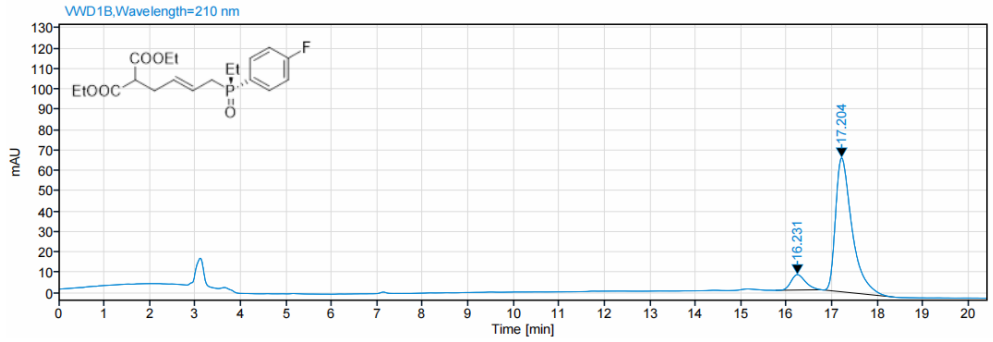
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.855	MM m	1.08	952.63	36.48	6.70	
10.589	MM m	3.15	13264.92	377.00	93.30	
		Sum	**14217.55**			

HPLC spectra data of **3o**



Signal: VWD1B,Wavelength=210 nm

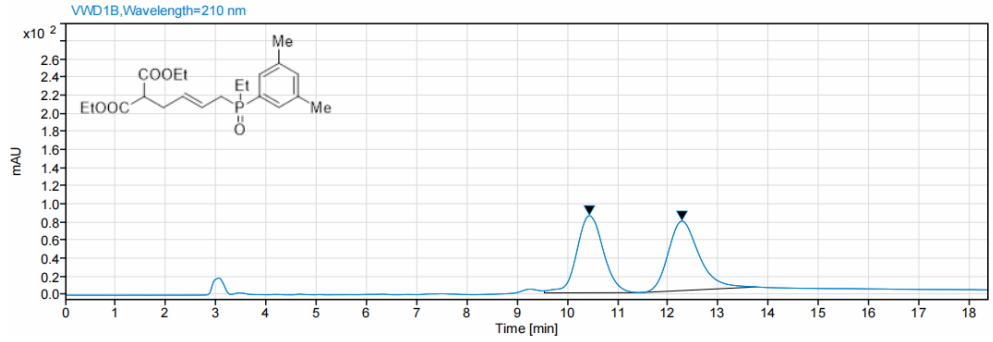
RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.809	MM m	1.17	469.86	21.33	49.47	
16.863	MM m	1.56	479.98	20.38	50.53	
		Sum	**949.84**			



Signal: VWD1B,Wavelength=210 nm

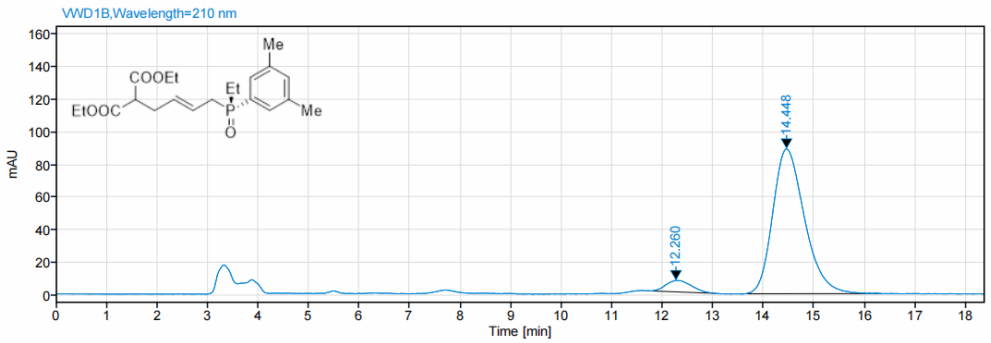
RT [min]	Type	Width [min]	Area	Height	Area%	Name
16.231	MM m	1.00	167.19	7.56	9.16	
17.204	MM m	1.65	1658.58	65.78	90.84	
		Sum	**1825.78**			

HPLC spectra data of **3p**



Signal: VWD1B,Wavelength=210 nm

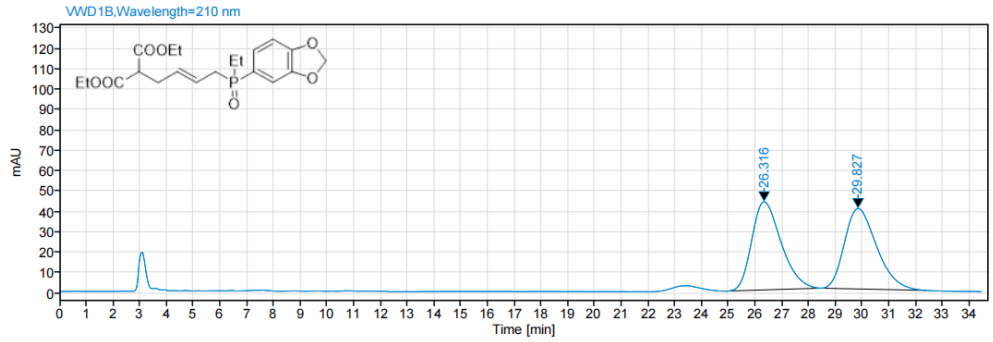
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.424	MM m	1.89	3143.74	85.24	49.03	
12.268	MM m	2.34	3268.67	76.85	50.97	
		Sum	**6412.41**			



Signal: VWD1B,Wavelength=210 nm

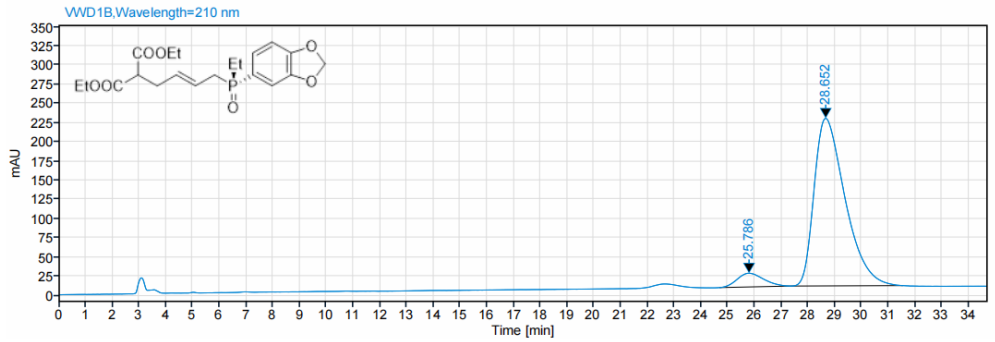
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.260	MM m	1.35	246.84	6.98	5.98	
14.448	MM m	2.91	3878.27	88.80	94.02	
		Sum	**4125.12**			

HPLC spectra data of **3q**



Signal: VWD1B,Wavelength=210 nm

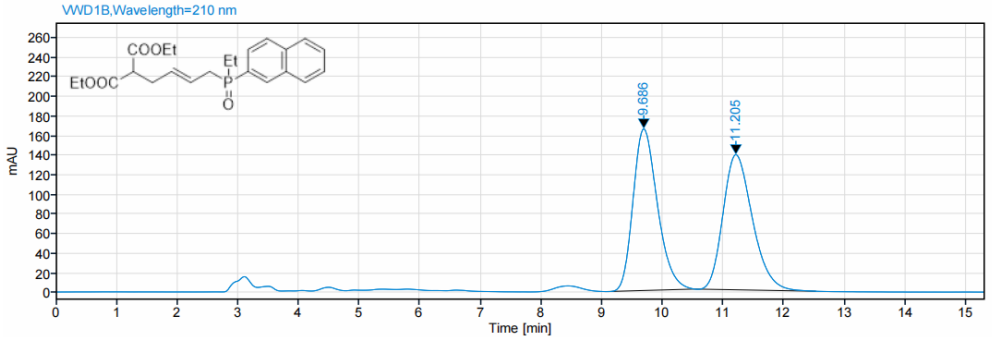
RT [min]	Type	Width [min]	Area	Height	Area%	Name
26.316	MM m	3.54	3304.23	43.32	49.96	
29.827	MM m	3.94	3308.91	39.54	50.04	
		Sum	**6613.14**			



Signal: VWD1B,Wavelength=210 nm

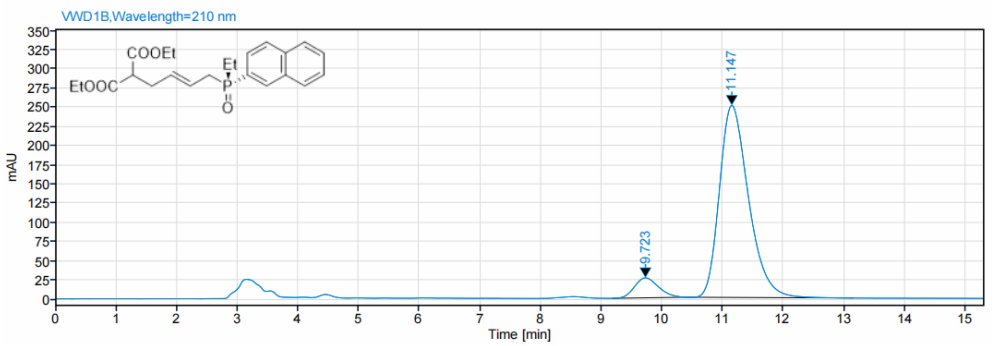
RT [min]	Type	Width [min]	Area	Height	Area%	Name
25.786	MM m	2.64	1223.76	17.84	6.51	
28.652	MM m	4.23	17563.00	218.32	93.49	
		Sum	**18786.76**			

HPLC spectra data of **3r**



Signal: VWD1B,Wavelength=210 nm

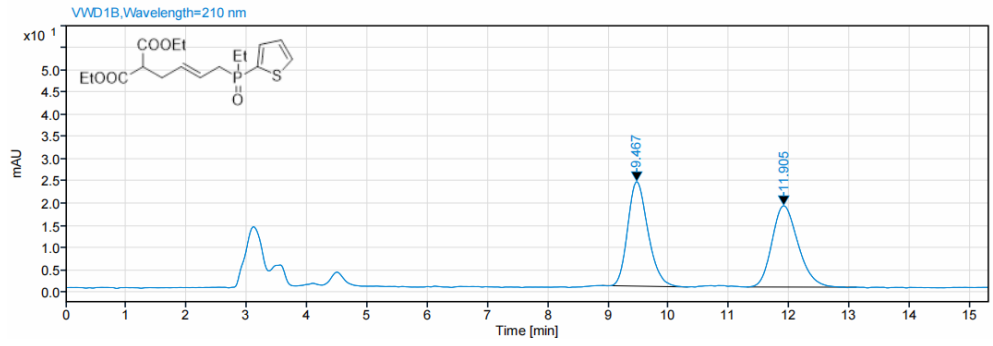
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.686	MM m	1.48	4602.74	164.67	49.79	
11.205	MM m	2.00	4640.68	137.63	50.21	
		Sum	**9243.43**			



Signal: VWD1B,Wavelength=210 nm

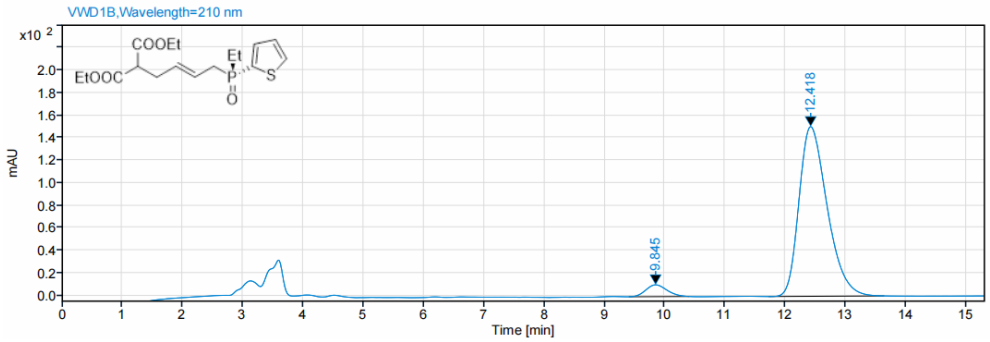
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.723	MM m	1.19	711.56	25.98	7.86	
11.147	MM m	2.79	8345.67	250.17	92.14	
		Sum	**9057.23**			

HPLC spectra data of **3s**



Signal: VWD1B,Wavelength=210 nm

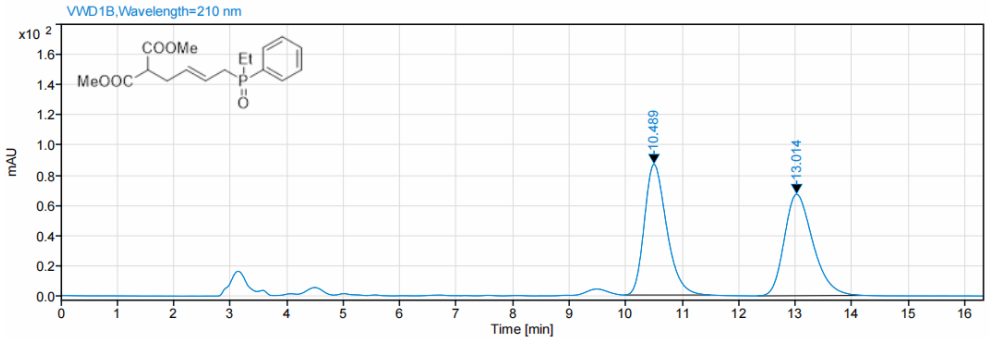
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.467	MM m	1.43	550.03	23.44	50.01	
11.905	MM m	1.82	549.88	18.25	49.99	
		Sum	**1099.91**			



Signal: VWD1B,Wavelength=210 nm

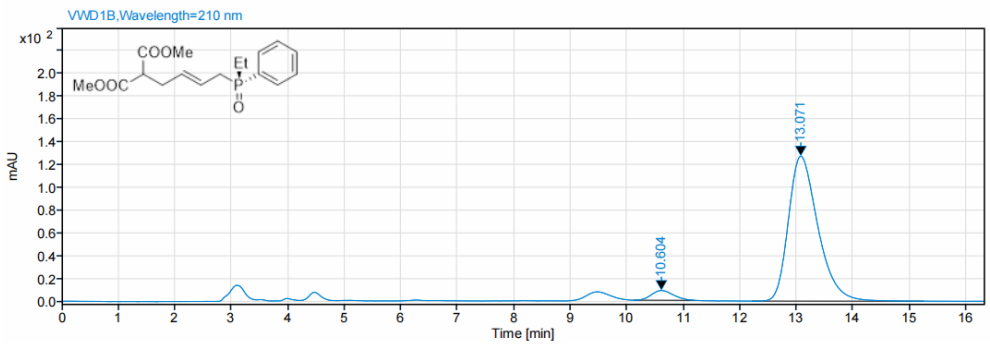
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.845	MM m	1.00	255.71	10.48	4.97	
12.418	MM m	1.92	4892.80	150.66	95.03	
		Sum	**5148.51**			

HPLC spectra data of **3t**



Signal: VWD1B,Wavelength=210 nm

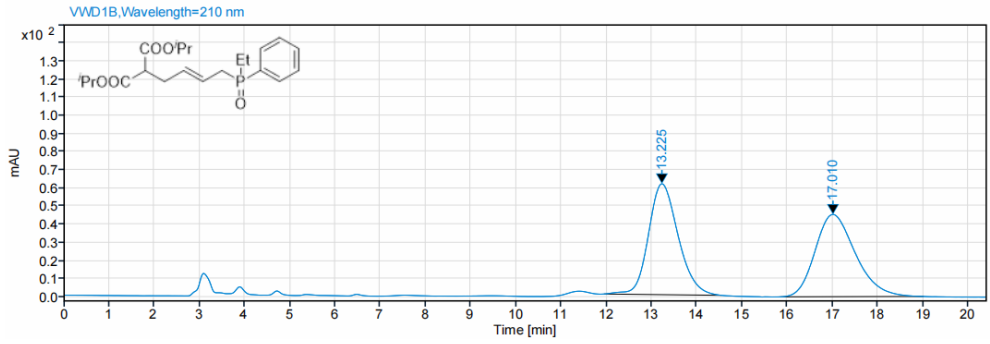
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.489	MM m	1.52	2363.50	86.22	50.09	
13.014	MM m	1.91	2355.03	66.92	49.91	
		Sum	**4718.53**			



Signal: VWD1B,Wavelength=210 nm

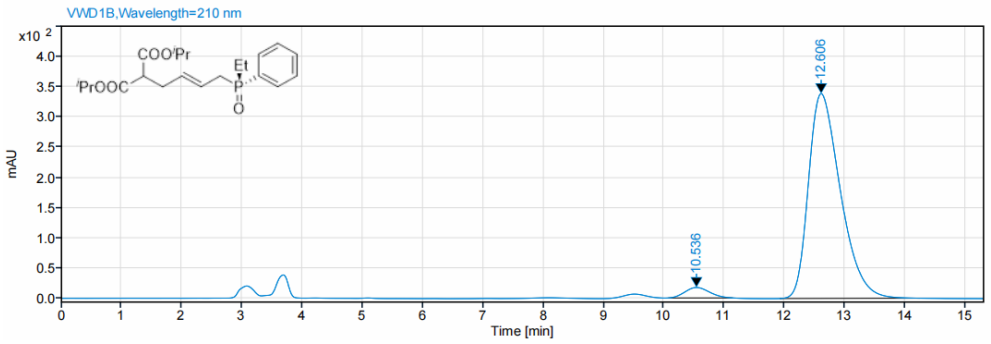
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.604	MM m	1.08	228.73	8.53	4.73	
13.071	MM m	3.04	4604.72	127.10	95.27	
		Sum	**4833.45**			

HPLC spectra data of **3u**



Signal: VWD1B,Wavelength=210 nm

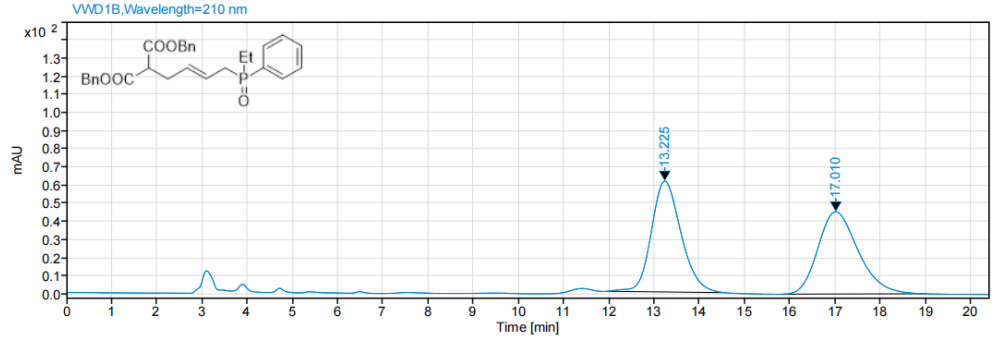
RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.225	MM m	2.60	2788.55	61.07	49.88	
17.010	MM m	3.18	2802.27	45.31	50.12	
		Sum	**5590.82**			



Signal: VWD1B,Wavelength=210 nm

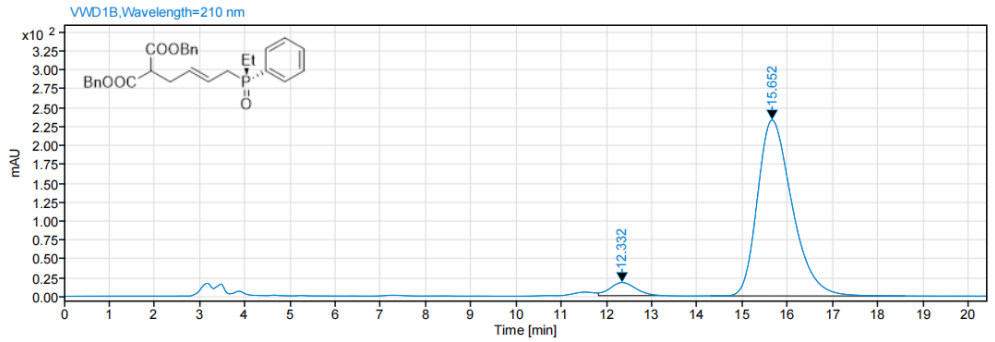
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.536	MM m	1.07	489.72	17.23	3.79	
12.606	MM m	2.33	12419.86	337.75	96.21	
		Sum	**12909.57**			

HPLC spectra data of **3v**



Signal: VWD1B,Wavelength=210 nm

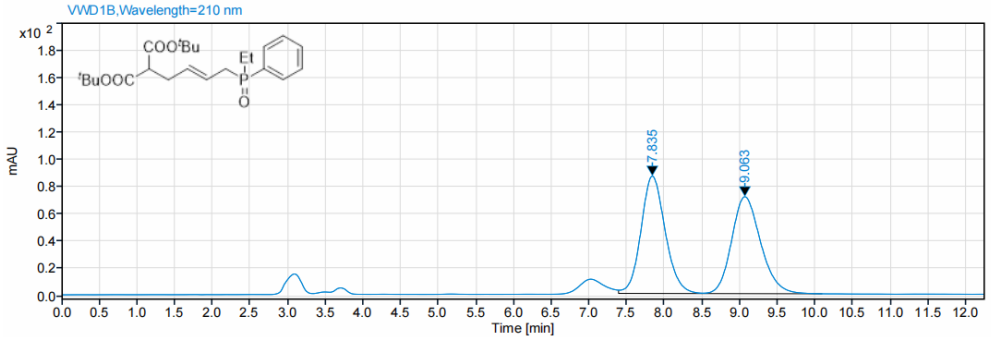
RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.225	MM m	2.60	2788.55	61.07	49.88	
17.010	MM m	3.18	2802.27	45.31	50.12	
		Sum	**5590.82**			



Signal: VWD1B,Wavelength=210 nm

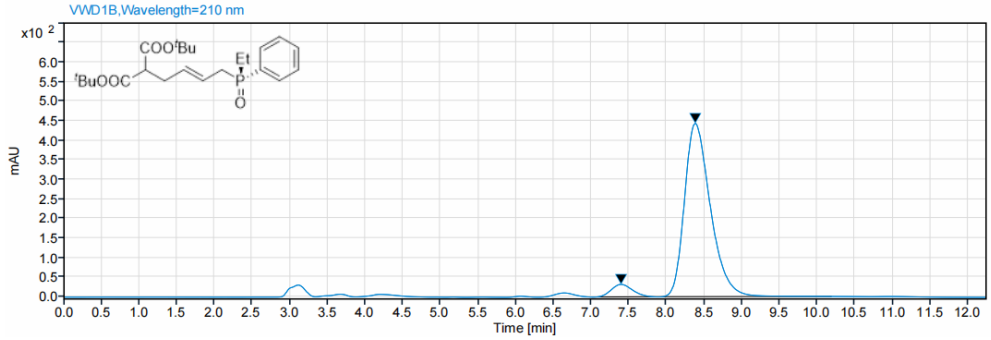
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.332	MM m	1.43	693.99	17.37	5.32	
15.652	MM m	4.30	12359.27	232.71	94.68	
		Sum	**13053.26**			

HPLC spectra data of **3w**



Signal: VWD1B,Wavelength=210 nm

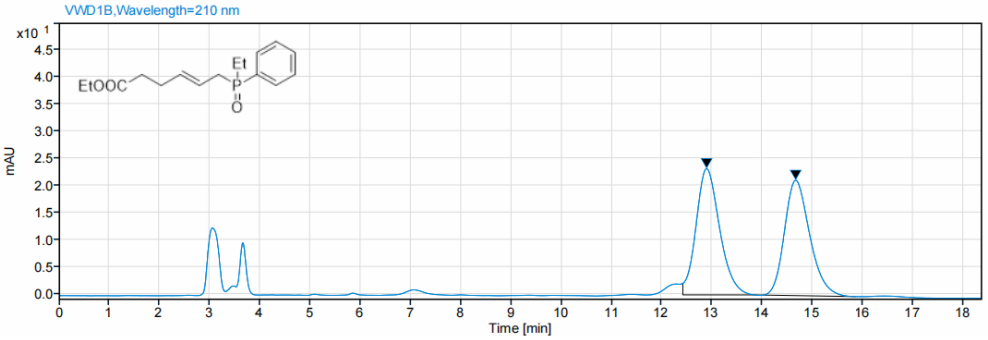
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.835	MM m	1.10	1926.19	85.94	50.30	
9.063	MM m	1.61	1903.47	70.97	49.70	
		Sum	**3829.67**			



Signal: VWD1B,Wavelength=210 nm

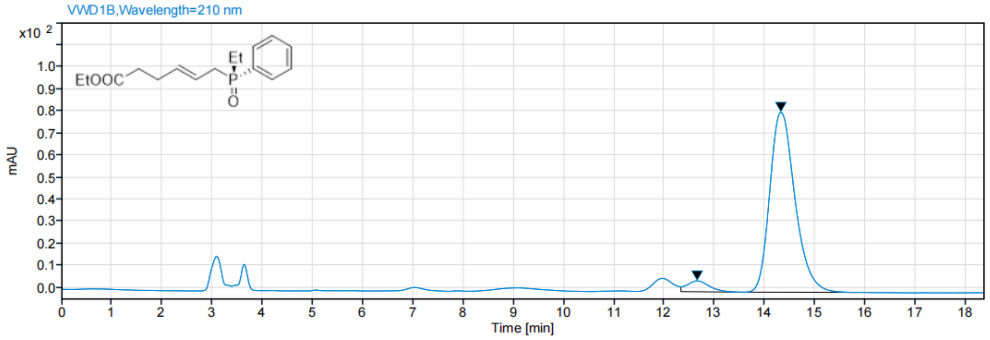
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.395	MM m	0.81	624.28	31.95	5.57	
8.380	MM m	2.37	10592.20	442.63	94.43	
		Sum	**11216.48**			

HPLC spectra data of **4a**



Signal: VWD1B,Wavelength=210 nm

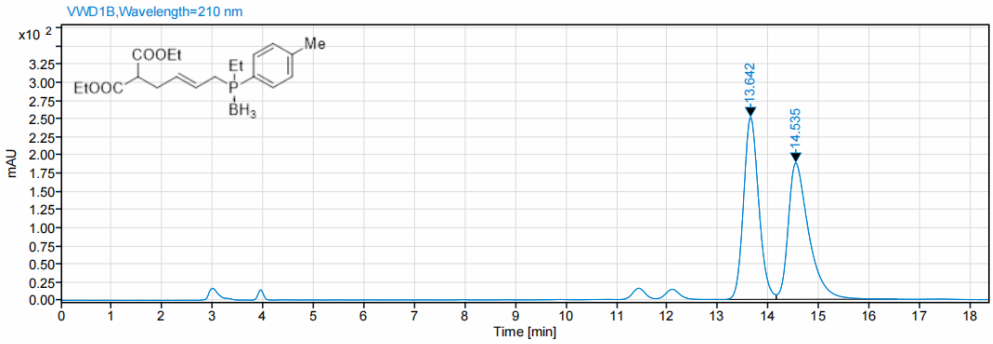
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.888	MM m	1.41	762.29	23.34	50.57	
14.661	MM m	2.03	745.11	21.32	49.43	
		Sum	**1507.40**			



Signal: VWD1B,Wavelength=210 nm

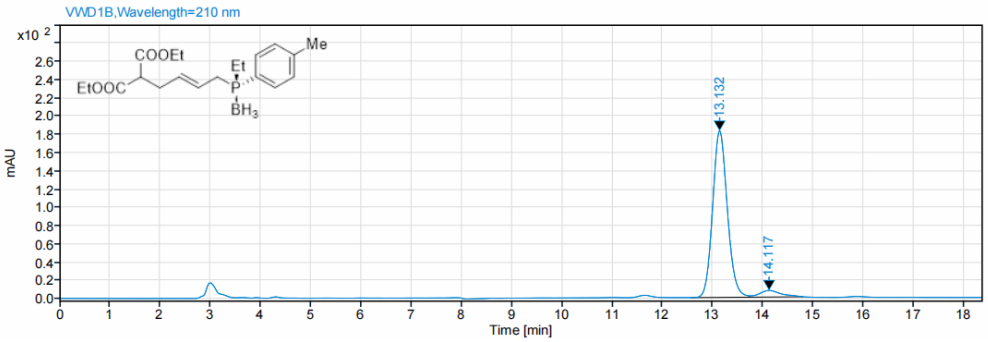
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.649	MM m	1.16	153.09	4.92	5.11	
14.316	MM m	2.37	2842.81	81.53	94.89	
		Sum	**2995.89**			

HPLC spectra data of **4i**



Signal: VWD1B,Wavelength=210 nm

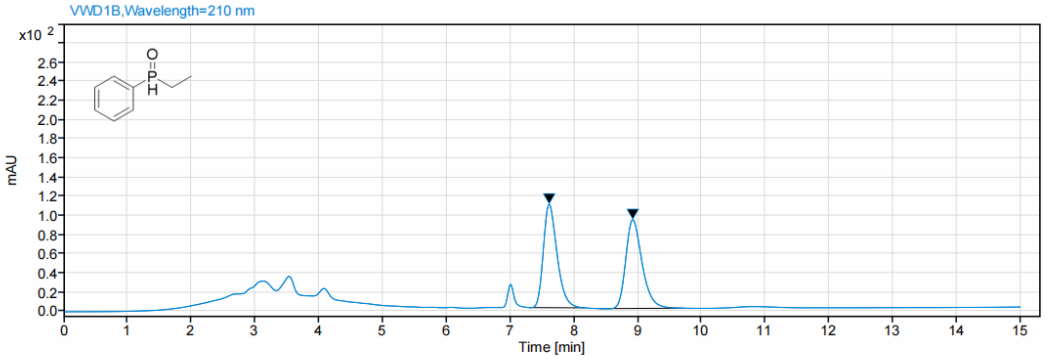
RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.642	MM m	1.26	5207.53	250.26	49.67	
14.535	MM m	2.39	5277.05	187.48	50.33	
		Sum	**10484.58**			



Signal:	VWD1B,Wavelength=210 nm					
RT [min]	**Type**	**Width [min]**	**Area**	**Height**	**Area%**	**Name**
13.132	MM m	1.16	3703.15	182.14	94.51	
14.117	MM m	1.08	215.30	7.20	5.49	
		Sum	**3918.45**			

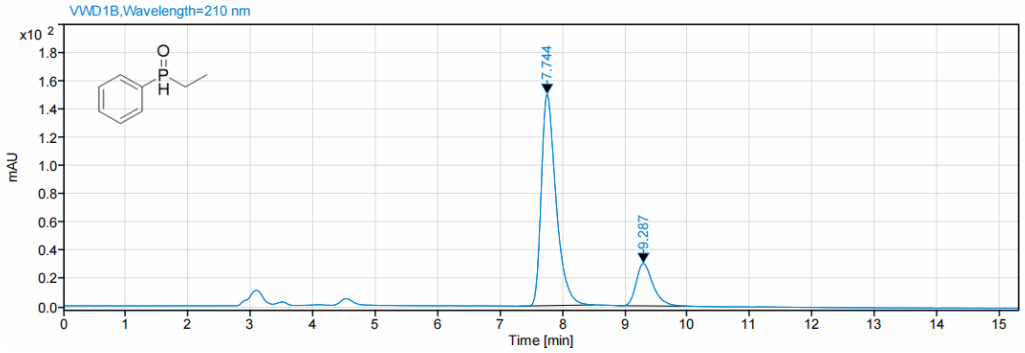
HPLC spectra data of **2a**

HPLC chart for **2a** before the reaction



Signal:	VWD1B,Wavelength=210 nm					
RT [min]	**Type**	**Width [min]**	**Area**	**Height**	**Area%**	**Name**
7.605	MM m	0.88	1615.24	107.98	49.47	
8.916	MM m	1.33	1650.09	92.64	50.53	
		Sum	**3265.33**			

HPLC chart for **2a** after the reaction



Signal: VWD1B,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.744	MM m	1.21	2450.14	149.18	81.41	
9.287	MM m	1.21	559.64	29.87	18.59	
		Sum	**3009.78**			