Supplementary Information

Visible-light-driven multicomponent reactions to access S-alkyl phosphorothioates using elemental sulfur as the sulfur source

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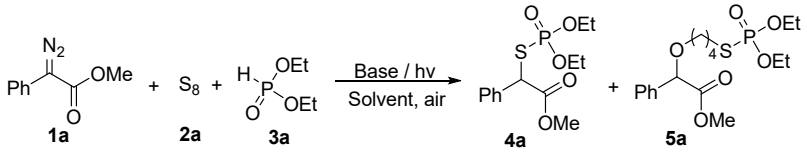
Contents

1. General information All commercially available reagent grade chemicals were purchased from Adamas, Strem, MERYER, Alfa Aesar and Energy Chemical Company and used as received without further purification unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker Avance III 500MHz spectrometer with TMS as internal standard at room temperature, the chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). High-resolution mass spectra (HRMS) were obtained on an LTQ Orbitrap XL mass spectrometry equipped with an ESI source. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

2. Optimization of reaction conditions.

Table S1 Optimization of reactions.[a]

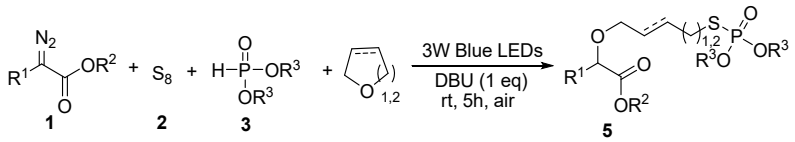


Entry	Base (equiv)	Solvent	**4a** Yield(%)[b]	**5a** Yield(%)[b]
1	DBU (1)	THF	0	92
2	DBU (1)	DMSO	trace[c]	
3	DBU (1)	CH_3OH	0[d]	
4	DBU (1)	1,4-dioxane	62	--
5	CS_2CO_3 (1)	1,4-dioxane	25	--
6	K_2CO_3 (1)	1,4-dioxane	21	--

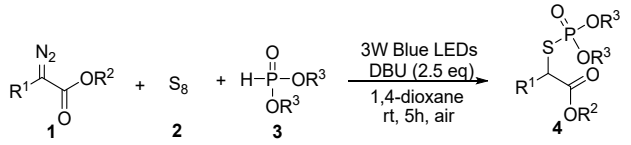
7	NaOH (1)	1,4-dioxane	38	--
8	K_3PO_4 (1)	1,4-dioxane	20	--
9	DABCO (1)	1,4-dioxane	45	--
10	Et_3N (1)	1,4-dioxane	40	--
11	DBU (1.5)	1,4-dioxane	66	--
12	DBU (2)	1,4-dioxane	70	--
13	DBU (2.5)	1,4-dioxane	77	--
14	DBU (3)	1,4-dioxane	72	--

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), **3a** (0.1 mmol), Base (1-3 equiv), Solvent (2 mL), 3 W blue LEDs, rt, 5 h. [b] Isolated yields based on **3a**. [c] methyl 2-methoxy-2-phenylacetate was obtained in 36% yield. [d] sulfoxonium ylide (methyl 2-(dimethyl(oxo)-λ6-sulfaneylidene)-2-phenylacetate) was obtained in 43% yield.

3. General procedure for visible-light-driven multicomponent reactions to access S-alkyl phosphorothioates.



To a mixture of α-diazoesters **1** (0.2 mmol), S_8 **2** (0.2 mmol), H-phosphonates **3** (0.1 mmol) and DBU (0.1 mmol) was added cyclic ether (2 mL). The reaction mixture was open to air and stirred under the irradiation of 3W blue LEDs at room temperature for 5 h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired four-component product **5**.

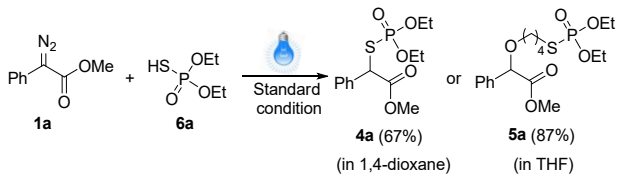


To a mixture of α-diazoesters **1** (0.2 mmol), S_8 **2** (0.2 mmol), H-phosphonates **3**

(0.1 mmol) and DBU (0.25 mmol) was added 1,4-dioxane (2 mL). The reaction mixture was open to air and stirred under the irradiation of 3W blue LEDs at room temperature for 5 h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired three-component product **4**.

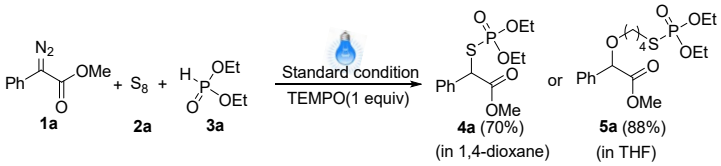
4. Preliminary mechanistic studies

4.1 The reaction of phosphorothioic acid 6a with α-diazoester 1a.



To a mixture of α-diazoester **1a** (0.2 mmol), phosphorothioic acid **6a** (0.1 mmol), and DBU (0.1 or 0.25mmol) was added THF (2 mL) or 1,4-dioxane (2 mL). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 5h. After completion of the reaction, the solution was concentrated in vacuum, the desired product **4a** and **5a** was obtained in 67% and 87% yields, respectively. This result indicated that phosphorothioic acid as a key intermediate might be involved in the present transformations.

4.2 The addition of TEMPO in the model reaction system.



To a mixture of α-diazoester **1a** (0.2 mmol), S_8 **2** (0.2 mmol), diethyl H-phosphonate **3a** (0.1 mmol), TEMPO (0.1 mmol) and DBU (0.1 or 0.25mmol) was added THF (2 mL) or 1,4-dioxane (2 mL). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 5h. After completion of the

reaction, the solution was concentrated in vacuum, the desired product **4a** and **5a** was obtained in 70% and 88% yields, respectively. This result indicated that a radical process might not be involved in the present transformations.

4.3 The procedures for Light On/off experiments.

To a mixture of α-diazoester **1a** (0.4 mmol), S_8 **2** (0.2 mmol), diethyl H-phosphonate **3a** (0.1 mmol), and DBU (0.1 mmol) was added THF (2 mL). The reaction mixture was separately stirred and irradiated by 3 W blue LEDs at room temperature for 1h, 2h, and 3h. The desired product **5a** was isolated in 33%, 64%, and 79%, respectively. Additionally, the reaction mixture was stirred and irradiated by 3 W Blue LEDs at room temperature for 1h, then the reaction mixture was continuously stirred in the dark for 1h, the corresponding product was also obtained in 33.3% yield. Additionally, when the reaction mixture was stirred and irradiated by 3 W blue LEDs at room temperature for 2h, then the reaction mixture was continuously stirred in the dark for 1h, the corresponding product was obtained in 64.1% yield. Additionally, when the reaction mixture was stirred and irradiated by 3 W blue LEDs at room temperature for 3h, then the reaction mixture was continuously stirred in the dark for 1h, the corresponding product **5a** was still obtained in 79% yield. The above results suggested that the continuous visible-light irradiation is necessary for promoting this transformation.

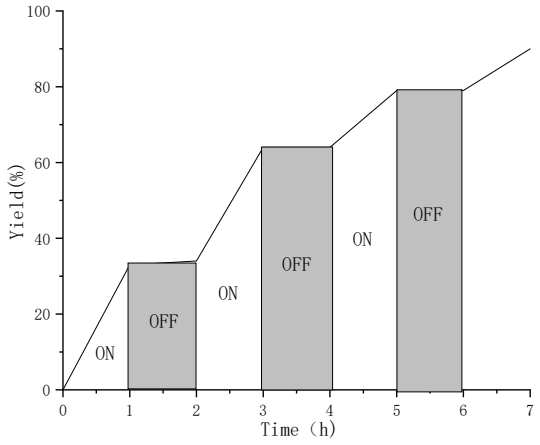
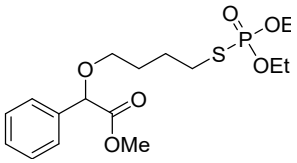
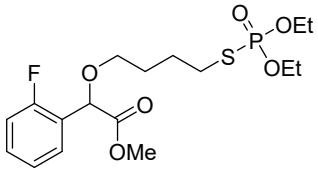


Fig S1. On/off experiments.

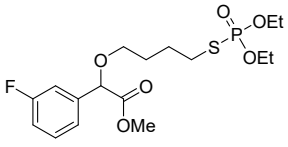
5. Characterization data of products.



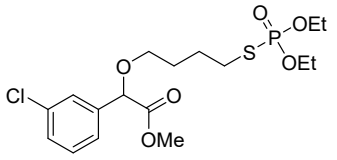
methyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5a), Compound **5a** was obtained in 90% yield (35.0mg) according to the general procedure (5h), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.33-7.38 (m, 3H), 4.86 (s, 1H), 4.09-4.20 (m, 4H), 3.70 (s, 3H), 3.54-3.58 (m, 1H), 3.43-3.48 (m, 1H), 2.83-2.89 (m, 2H), 1.71-1.84 (m, 4H), 1.33-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.84, 135.57, 131.77, 128.76, 122.76, 80.42, 69.21, 63.50 (d, J = 6.3Hz), 52.35, 30.60 (d, J = 3.2Hz), 28.43, 27.54 (d, J = 5.0Hz), 16.6 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{17}H_{28}O_6PS$ $[M+H]^+$ 391.1344, found 391.1344.



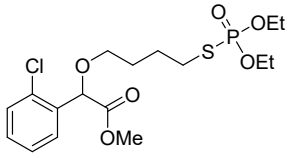
methyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-(2-fluorophenyl)acetate(5b), Compound **5b** was obtained in 92% yield (38.0mg) according to the general procedure (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.44-7.47 (m,1H), 7.30-7.35 (m, 1H), 7.15-7.18 (m, 1H), 7.06-7.09 (m,1H), 5.20 (s, 1H), 4.08-4.21 (m, 4H), 3.72 (s, 3H), 3.59-3.63 (m, 1H), 3.45-3.49 (m, 1H), 2.82-2.2.88 (m, 2H), 1.71-1.83 (m, 4H), 1.34 (t, J = 7.1Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.71, 160.38 (d, J = 246.3 Hz), 130.38 (d, J = 7.5Hz), 128.6 (d, J = 3.75 Hz), 124.50 (d, J = 3.75Hz), 124.06 (d, J = 13.75Hz), 115.53 (d, J = 22.5Hz), 74.01 (d, J = 2.5Hz), 69.36, 63.45 (d, J = 6.25Hz), 52.33, 30.02 (d, J = 5Hz), 28.42, 27.47 (d, J = 6.25Hz), 16.04 (d, J = 7.5Hz). ^{19}F NMR ($CDCl_3$, 500 MHz): -118.5. ESI HRMS: calculated for $C_{17}H_{27}FO_6PS$ $[M+H]^+$ 409.1250, found 409.1257.



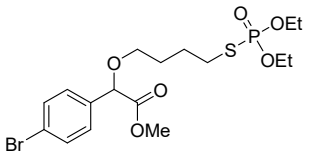
methyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-(3-fluorophenyl)acetate(5c) Compound **5c** was obtained in 94% yield (38.0mg) according to the general procedure (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.30-7.349 (m, 1H), 7.16-7.22 (m, 2H), 7.00-7.04 (m, 1H), 4.85 (s, 1H), 4.10-4.20 (m, 4H), 3.72 (s, 3H), 3.55-3.59 (m, 1H), 3.44-3.48 (m, 1H), 2.84-2.90 (m, 2H), 1.75-1.83 (m, 4H), 1.35-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.81, 162.85 (d, J =246.3Hz), 138.94 (d, J = 7.5Hz), 130.13 (d, J = 7.5Hz), 122.69 (d, J = 2.5 Hz), 115.60 (d, J = 21.3Hz), 113.99 (d, J = 22.5Hz), 80.42 (d, J = 2.5Hz), 69.25, 63.50 (d, J = 6.3Hz), 52.37, 30.62 (d, J = 3.8Hz), 28.44, 27.54 (d, J = 50Hz), 16.05 (d, J = 7.5Hz); ^{19}F NMR ($CDCl_3$, 500 MHz): -114.1. ESI HRMS: calculated for $C_{17}H_{27}FO_6PS$ $[M+H]^+$ 409.1250, found 409.1257.



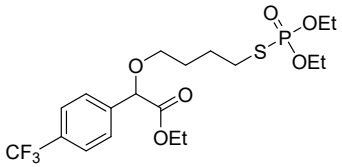
methyl 2-(3-chlorophenyl)-2-(4-((diethoxyphosphoryl)thio)butoxy)acetate(5d) Compound **5d** was obtained in 85% yield (36.0mg) according to the general procedure (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.49 (d, J = 8.4Hz, 2H), 7.32 (d, J = 8.4Hz, 2H), 4.81 (s, 1H), 4.10-4.19 (m, 4H), 3.70 (s, 3H), 3.54-3.58 (m, 1H), 3.42-3.46 (m, 1H), 2.83-2.89 (m, 2H), 1.73-1.83 (m, 4H), 1.33-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.76, 138.48, 134.55, 129.69, 128.85, 127.20, 125.20, 80.40, 69.29, 63.50 (d, J = 5Hz), 52.41, 30.61 (d, J = 3.8Hz), 28.44, 27.53 (d, J = 5Hz), 16.06 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{17}H_{27}ClO_6PS$ $[M+H]^+$ 425.0954, found 425.0959.



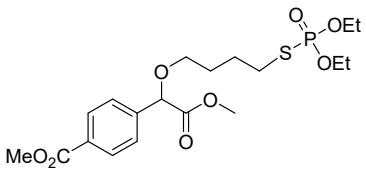
methyl 2-(2-chlorophenyl)-2-(4-((diethoxyphosphoryl)thio)butoxy)acetate(5e) Compound **5e** was obtained in 85% yield (36.0mg) according to the general procedure (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.30-7.31 (m, 3H), 4.82 (s, 1H), 4.12-4.19 (m, 4H), 3.72 (s, 3H), 3.55-3.59 (m, 1H), 3.43-3.48 (m, 1H), 2.84-2.90 (m, 2H), 1.73-1.83 (m, 4H), 1.33-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.77, 138.48, 134.56, 129.88, 128.85, 127.20, 125.20, 80.41, 69.30, 63.50 (d, J = 5Hz), 52.41, 30.61 (d, J = 3.8Hz), 28.44, 27.53 (d, J = 5Hz), 16.05 (d, J = 6.3Hz). ESI HRMS: calculated for$C_{17}H_{27}ClO_6PS$ $[M+H]^+$ 425.0954, found 425.0959.



methyl 2-(4-bromophenyl)-2-(4-((diethoxyphosphoryl)thio)butoxy)acetate(5f) Compound **5f** was obtained in 84% yield (39.0mg) according to the general procedure (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.29-7.32 (m, 3H), 3.72 (s, 3H), 3.56-3.58 (m, 1H), 3.45-3.48 (m, 1H), 2.84-2.90 (m, 2H), 1.73-1.85 (m, 4H), 1.33-1.36 (m, 6H);170.84, 135.57, 131.77, 128.76, 122.76, 80.42, 69.21, 63.49 (d, J = 6.25Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.84, 135.57, 131.77, 128.76, 122.76, 80.42, 69.21, 63.50 (d, J = 6.3Hz), 52.35, 30.60 (d, J = 3.8Hz), 28.43, 27.54 (d, J = 5Hz), 16.06 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{17}H_{27}BrO_6PS$ $[M+H]^+$ 469.0449, found 469.0450.

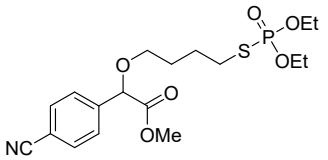


ethyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-(4-(trifluoromethyl)phenyl)acetate (5g), Compound **5g** was obtained in 79% yield (37.0mg) according to the general procedure (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ δ 7.62 (d, J = 8.4Hz, 2H), 7.58 (d, J = 8.4Hz, 2H), 4.89 (s, 1H), 4.08-4.23 (m, 6H), 3.59-3.63 (m, 1H) 3.45-3.49 (m, 1H), 2.85-2.91 (m, 2H), 1.74-1.87 (m, 4H), 1.33-1.36 (m, 6H), 1.23 (t, J = 7.2Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.18, 140.60, 130.86 (d, J = 20.5Hz), 127.32, 125.49 (q, J = 3.8Hz), 123.9 (d, J = 265.1 Hz), 80.56, 69.40, 63.50 (d, J = 6.3Hz), 61.50, 30.61 (t, J = 3.8Hz), 28.45, 27.58 (d, J = 6.3Hz), 16.04 (d, J = 7.5Hz), 14.06; ^{19}F NMR ($CDCl_3$, 500 MHz): -62.7. ESI HRMS: calculated for $C_{19}H_{29}F_3O_6PS$ $[M+H]^+$ 473.1375, found 473.1381.

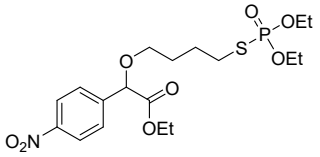


methyl 4-(1-(4-((diethoxyphosphoryl)thio)butoxy)-2-methoxy-2-oxoethyl)benzoate)(5h), Compound **5h** was obtained in 94% yield (42.0mg) according to the general procedure (5h) Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.3 (d, J = 8.3

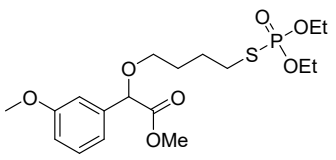
Hz, 2H), 7.53 (d, *J* = 8.3Hz, 2H), 4.92 (s, 1H), 4.15 (m, 4H), 3.92 (s, 3H), 3.71 (s, 3H), 3.57-3.60 (m, 1H), 3.44-3.49 (m, 1H), 2.84-2.90 (m, 2H), 1.75-1.86 (m, 4H), 1.33-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.71, 166.63, 1 41.38, 130.43, 129.86, 127.00, 80.69, 69.36, 63.47 (d, *J* = 6.3Hz), 52.40 (d, *J* = 28.8Hz), 30.61 (d, *J* = 3.8Hz), 28.44, 27.54 (d, *J* = 5Hz), 16.05 (d, *J* = 7. 5Hz). ESI HRMS: calculated for $C_{19}H_{30}O_8PS$ $[M+H]^+$ 449.1399, found 449.1410.



methyl 2-(4-cyanophenyl)-2-(4-((diethoxyphosphoryl)thio)butoxy)acetate(5i), Co mpound **5i** was obtained in 56% yield (23.0mg) according to the general proce dure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.1Hz, 2H), 7.58 (d, *J* = 8.2Hz, 2H), 4.91 (s, 1H), 4.12-4.19 (m, 4H), 3.72 (s, 3H), 3.60-3.6 3 (m, 1H), 3.46-3.49 (m, 1H), 2.85-2.91 (m, 2H), 1.77-1.85 (m, 4H), 1.33-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.31, 141.65, 132.39, 127.65, 118. 47, 112.53, 80.35, 69.62, 63.53 (d, *J* = 5Hz), 52.58, 30.56 (d, *J* = 5Hz), 28.4 2, 27.54 (d, *J* = 5Hz), 16.07 (d, *J* = 7.5Hz). ESI HRMS: calculated for $C_{18}H_{27}NO_6PS$ $[M+H]^+$ 416.1297, found 416.1302.

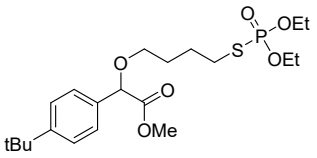


ethyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-(4-nitrophenyl)acetate(5j), Comp ound **5j** was obtained in 52% yield (23.0mg) according to the general procedur e (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.8Hz, 2H), 7. 65 (d, *J* = 8.8Hz, 2H), 4.94 (s, 1H), 4.12-4.20 (m, 6H), 3.64-3.67 (m, 1H), 3. 47-3.52 (m, 1H), 2.86-2.92 (m, 2H), 1.78-1.86 (m, 4H), 1.33-1.37 (m, 6H), 1.2 3 (t, *J* = 7.15Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.74, 148.01, 143.6 9, 127.77, 123.73, 80.25, 69.65, 63.55 (d, *J* = 6.3Hz), 61.75, 30.59 (d, *J* = 3. 8Hz), 28.44, 27.58 (d, *J* = 6.3Hz), 16.08 (d, *J* = 7.5Hz), 14.08. ESI HRMS: calculated for $C_{18}H_{29}NO_8PS$ $[M+H]^+$ 450.1351, found 450.1356.

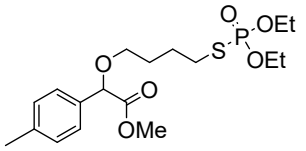


methyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-(3-methoxyphenyl)acetate(5k),

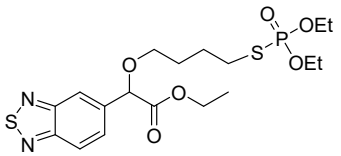
Compound **5k** was obtained in 81% yield (34.0mg) according to the general pr ocedure (5h), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.26-7.28 (m, 1H), 6. 98-7.01 (m, 2H), 6.86-6.88 (m, 1H), 4.82 (s, 1H), 4.09-4.20 (m, 4H), 3.81 (s, 3H), 3.70 (s, 3H), 3.52-3.56 (m, 1H), 3.43-3.47 (m, 1H), 2.83-2.89 (m, 2H), 1. 73-1.83 (m, 4H), 1.33-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.17, 159.82, 137.97, 129.61, 119.53, 114.40, 112.41, 80.99, 69.02, 63.47(d, J = 5H z), 55.28, 52.24, 30.62 (d, J = 3.8Hz), 28.45, 27.55 (d, J = 6.3Hz), 16.05 (d,J = 7.5Hz). ESI HRMS: calculated for $C_{18}H_{30}O_7PS$ $[M+H]^+$ 421.1450, found 421. 1456.



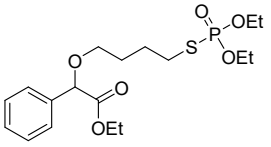
methyl 2-(4-(tert-butyl)phenyl)-2-(4-((diethoxyphosphoryl)thio)butoxy)acetate(5 l), Compound **5l** was obtained in 71% yield (32.0mg) according to the general procedure (5h) Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.33-7.38 (m, 4H), 4. 83 (s, 1H), 4.10-4.19 (m, 4H), 3.71 (s, 3H), 3.52-3.56 (m, 1H), 3.43-3.47 (m, 1H), 2.83-2.88 (m, 2H), 1.74-1.83 (m, 4H), 1.32-1.369 (m, 6H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.49, 151.68, 133.43, 128.84, 125.57, 80.93, 68.98, 63.47 (d, J = 6.3Hz), 52.17, 34.61, 31.29, 30.68 (d, J = 3.8Hz), 28.49, 27.55 (d, J = 3.8Hz), 16.06 (d, J = 7.5Hz). ESI HRMS: calculated for $C_{21}H_{36}O_6PS$ $[M+H]^+$ 447.1970, found 447.1977.



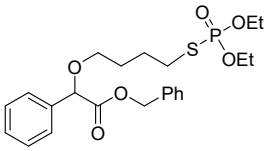
methyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-(p-tolyl)acetate(5m), Compoun d **5m** was obtained in 64% yield (26.0mg) according to the general procedure (5h) Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.31 (d, J = 8.1Hz, 2H), 7.17 (d, J = 8.0Hz, 2H), 4.82 (s, 1H), 4.09-4.20 (m, 4H), 3.69 (s, 3H), 3.51-3.55 (m, 1H), 3.41-3.45 (m, 1H), 2.82-2.88 (m, 2H), 2.34 (s, 3H), 1.71-1.84 (m, 4H), 1.33-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.45, 138.57, 133.55,129. 33, 127.13, 80.95, 68.89, 63.46 (d, J = 5Hz), 52.18, 30.66 (d, J = 3.8Hz), 28.4 8, 27.55 (d, J = 6.3Hz), 21.20, 16.05 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{18}H_{30}O_6PS$ $[M+H]^+$ 405.1501, found 405.1503.



ethyl 2-(benzo[c][1,2,5]thiadiazol-5-yl)-2-(4-((diethoxyphosphoryl)thio)butoxy)acetate (5n), Compound **5n** was obtained in 645% yield (26.0mg) according to the general procedure (5h) Yellow oil. 8.09 (d, J = 0.6 Hz, 1H), 8.00 (d, J = 9.1Hz, 1H), 7.71-7.73 (m, 1H), 5.02 (s,1H), 4.10-4.24 (m, 6H), 3.64-3.68 (m, 1H), 3.51-3.56 (m, 1H), 2.86-2.92 (m, 2H), 1.80-1.87 (m, 4H), 1.33-1.36 (m, 6H), 1.23 (t, J = 7.1Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$):δ 170.06, 154.77, 154.65, 138.42, 128.32, 121.72, 119.91, 80.73, 69.46, 63.51 (d, J = 6.3Hz), 61.64, 30.62 (d, J = 3.8Hz), 28.49, 27.57 (d, J = 6.3Hz), 16.07 (d, J = 7.5Hz), 14.11. ESI HRMS: calculated for $C_{18}H_{28}N_2O_6PS_2$ $[M+H]^+$ 463.1126, found 463.1129.

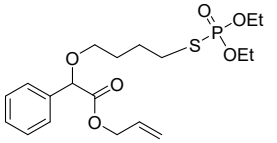


ethyl 2- (4-((diethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5o), Compound **5o** was obtained in 79% yield (32.0mg) according to the general procedure (5h) Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.44 (d, J = 6.8Hz, 2H), 7.31-7.37(m, 3H), 4.83 (s, 1H), 4.11-4.19 (m, 6H), 3.54-3.59 (m, 1H), 3.44-3.48 (m, 1H), 2.83-2.89 (m, 2H), 1.73-1.88 (m, 4H), 1.32-1.36 (m, 6H), 1.21 (t, J = 7.1Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.86, 136.65, 128.57, 128.55, 127.10, 81.15, 68.99, 63.45 (d, J = 6.3Hz), 61.15, 30.67 (d, J = 3.8Hz), 28.49, 27.58, 16.06 (d, J = 7.5Hz), 14.10. ESI HRMS: calculated for $C_{18}H_{30}O_6PS$ $[M+H]^+$ 405.1501, found 405.1509.

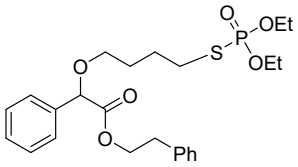


benzyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5p), Compound **5p** was obtained in 79% yield (37.0mg) according to the general procedure (5h) Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.42-7..43 (m, 2H), 7.27-7.36 (m, 6H), 7.19-7.21 (m, 2H), 5.14 (dd, J_1 =12.45Hz, J_2 =25.7Hz, 2H), 4.89 (s, 1H), 4.10-4.17 (m, 4H), 3.53-3.57 (m, 1H), 3.43-3.48 (m, 1H), 2.81-2.87 (m, 2H), 1.72-1.83 (m, 4H), 1.32-1.35 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.70, 13

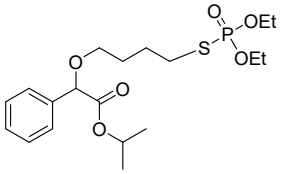
6.45, 136.54, 128.67, 128.59, 128.51, 128.25, 127.95, 127.17, 81.14, 69.06, 66.71, 63.48 (d, J = 6.3Hz), 30.67 (d, J = 3.8Hz), 28.49, 27.56 (d, J = 5Hz),16.07 (d, J = 7.5Hz). ESI HRMS: calculated for $C_{23}H_{32}O_6PS$ $[M+H]^+$ 467.1657, foun d 467.1663.



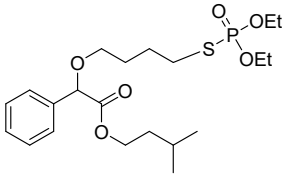
allyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5q), Compound **5q** was obtained in 53% yield (22.0mg) according to the general procedure (5h) Y ellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.43-7.45 (m, 2H), 7.31-7.37 (m, 3H), 5.79-5.87 (m, 1H), 5.16-5.20 (m, 2H), 4.87 (s, 1H), 4.57-4.61 (m, 2H), 4.09-4. 19 (m, 4H), 3.55-3.59 (m, 1H), 3.44-3.48 (m, 1H), 2.83-2.89 (m, 2H), 1.73-1.8 5 (m, 4H), 1.32-1.36 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.52, 136.52, 131.61, 128.67, 128.59, 127.15, 118.42, 81.12, 69.04, 65.55, 63.47 (d, J =6.3H z), 30.67 (d, J = 3.8Hz), 28.49, 27.67 (d, J = 6.3Hz), 16.07 (d, J = 6.25Hz). ESI HRMS: calculated for $C_{19}H_{30}O_6PS$ $[M+H]^+$ 417.1501, found 417.1510.



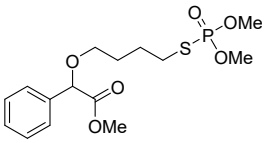
phenethyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5r), Compou nd **5r** was obtained in 53% yield (25.0mg) according to the general procedure (5h) Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.37-7.39 (m, 2H), 7.32-7.34 (m, 3H), 7.19-7.25 (m, 3H), 7.06-7.08 (m, 2H), 4.80 (s, 1H), 4.28-4.36 (m, 2H), 4. 09-4.19 (m, 4H), 3.48-3.52 (m, 1H), 3.38-3.43 (m, 1H), 2.82-2.88 (m, 4H), 1.7 1-1.82 (m, 4H), 1.34 (t, J = 7.05Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1 70.78, 137.48, 136.54, 128.86, 128.59, 128.58, 128.46, 127.14, 126.54, 81.11, 6 9.00, 65.50, 63.47 (d, J = 6.3Hz), 34.94, 30.69 (d, J = 3.8Hz), 28.49, 27.55 (d, J = 6.3Hz), 16.07 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{24}H_{34}O_6PS$ [$M+H]^+$ 481.1821, found 481.1830.



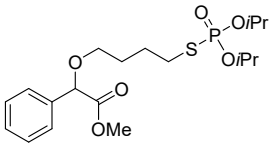
isopropyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5s), Compound **5s** was obtained in 55% yield (23.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.31-7.36 (m, 3H), 5.00-5.05 (m, 1H), 4.11-4.18 (m, 4H), 3.55-3.59 (m, 1H), 3.44-3.48 (m, 1H), 2.84-2.90 (m, 2H), 1.67-1.86 (m, 4H), 1.32-1.36 (m, 6H), 1.24 (d, J = 6.3Hz, 3H), 1.12 (d, J = 6.3Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.44, 136.75, 128.48, 127.04, 81.24, 68.97, 68.72, 63.47 (d, J = 6.3Hz), 30.69 (d, J = 3.8Hz), 28.51, 27.61 (d, J = 5Hz), 21.76, 21.49, 16.07 (d, J = 6.3Hz).ESI HR MS: calculated for $C_{19}H_{32}O_6PS$ $[M+H]^+$ 419.1657, found 419.1663.



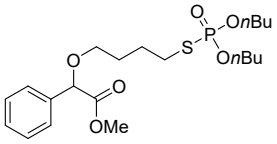
isopentyl 2-(4-((diethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5t), Compound **5t** was obtained in 96% yield (43.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.30-7.36 (m, 3H), 4.83 (s, 1H), 4.09-4.19 (m, 6H), 3.54-3.59 (m, 1H), 3.43-3.48 (m, 1H), 2.83-2.89 (m, 2H), 1.74-1.84 (m, 4H), 1.51-1.55 (m, 1H), 1.43-1.47 (m, 2H), 1.32-1.35 (m, 6H), 0.85 (d, J = 6.6Hz, 3H), 0.83 (d, J = 6.6Hz, 3H); ^{13}CNMR (125 MHz, $CDCl_3$): δ 170.93, 136.69, 128.55, 128.52, 127.08, 81.16, 68.98, 63.80, 63.45 (d, J = 6.3Hz), 37.14, 30.67 (d, J = 5Hz), 28.49, 27.57 (d, J = 5Hz), 24.94, 22.33 (d, J = 8.8Hz), 16.05 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{21}H_{36}O_6PS$ $[M+H]^+$ 447.1970, found 447.1983.



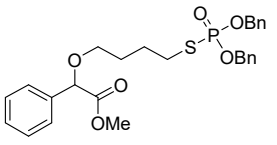
methyl 2-(4-((dimethoxyphosphoryl)thio)butoxy)-2-phenylacetate(5u), Compound **5u** was obtained in 95% yield (34.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.43 (d, J = 6.7Hz, 2H), 7.34-7.36 (m, 3H), 4.86 (s, 1H), 3.79 (d, J = 2.3Hz, 3H), 3.76 (d, J = 2.3Hz, 3H), 3.71 (s, 3H), 3.54-3.58 (m, 1H), 3.43-3.48 (m, 1H), 2.83-2.89 (m, 2H), 1.73-1.84 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.31, 136.51, 128.72, 128.68,127.15, 81.10, 68.99, 53.76 (d, J = 6.3Hz), 52.26, 30.61, 28.43, 27.58 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{15}H_{24}O_6PS$ $[M+H]^+$ 363.1031, found 363.1035.



methyl 2-(4-((diisopropoxyphosphoryl)thio)butoxy)-2-phenylacetate(5v), Compound **5v** was obtained in 98% yield (41.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.32-7.37 (m, 3H), 4.85 (s, 1H), 4.69-4.74 (m, 2H), 3.70 (s, 3H), 3.53-3.57 (m, 1H), 3.43-3.47 (m, 1H), 2.83-2.88 (m, 2H), 1.74-1.82 (m, 4H), 1.32-1.36 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.33, 136.53, 128.68, 128.62, 127.14, 81.10, 72.48 (d, J = 6.3Hz), 69.08, 52.24, 30.80 (d, J = 3.8Hz), 28.56, 27.47 (d, J = 6.3Hz), 23.89 (d, J = 3.8Hz), 23.65 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{19}H_{32}O_6PS$ $[M+H]^+$ 419.1657, found 419.1668.

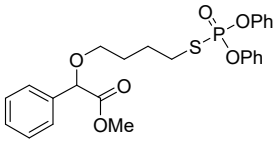


methyl 2-(4-((dibutoxyphosphoryl)thio)butoxy)-2-phenylacetate(5w), Compound **5w** was obtained in 64% yield (29.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.32-7.37 (m, 3H), 4.85 (s, 1H), 4.02-4.12 (m, 4H), 3.71 (s, 3H), 3.53-3.56 (m, 1H), 3.44-3.47 (m, 1H), 2.82-2.86 (m, 2H), 1.71-1.83 (m, 4H), 1.64-1.69 (m, 4H), 1.38-1.43 (m, 4H), 0.91-0.94 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.32, 136.52, 128.68, 128.62, 127.13, 81.11, 69.04, 67.20 (d, J = 6.3Hz), 52.23, 32.18 (d, J = 7.5Hz), 30.60 (d, J = 5Hz), 28.49, 27.54 (d, J = 5Hz), 18.74, 13.58. ESI HRMS: calculated for $C_{21}H_{36}O_6PS$ $[M+H]^+$ 447.1970, found 447.1977.

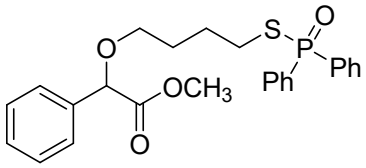


methyl 2-(4-((bis(benzyloxy)phosphoryl)thio)butoxy)-2-phenylacetate(5x), Compound **5x** was obtained in 57% yield (23.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.40-7.42 (m, 2H), 7.30-7.36 (m, 13H), 5.05-5.12 (m, 4H), 4.82 (s, 1H), 3.69 (s, 3H), 3.45-3.49 (m, 1H),3.35-3.49 (m, 1H), 2.77-2.83 (m, 2H), 1.64-1.75 (m, 4H); ^{13}C NMR (125 MHz,$CDCl_3$): 171.31, 136.51, 135.59 (d, J = 7.5Hz), 128.70, 128.64, 128.60, 128.58,128.09, 127.14, 81.09, 68.97, 68.88 (d, J = 5Hz), 52.25, 30.70 (d, J = 3.8Hz),

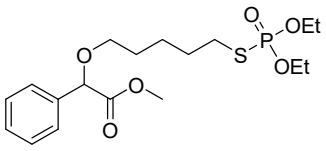
28.42, 27.36 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{27}H_{32}O_6PS$ $[M+H]^+$ 515.1657, found 515.1663.



methyl 2-(4-((diphenoxyphosphoryl)thio)butoxy)-2-phenylacetate(5y), Compound **5y** was obtained in 62% yield (30.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.39-7.41 (m, 2H), 7.31-7.36 (m, 8H), 7.26-7.28 (m, 3H), 7.18-7.21 (m, 2H), 4.81 (s, 1H), 3.69 (s, 3H), 3.45-3.49 (m, 1H), 3.34-3.38 (m, 1H), 2.94-3.00 (m, 2H), 1.64-1.77 (m, 4H); ^{13}CNMR (125 MHz, $CDCl_3$): 171.29, 150.24 (d, J = 8.8Hz), 136.48, 129.82, 128.71, 128.65, 127.13, 125.60, 120.73 (d, J = 5Hz), 81.09, 68.90, 52.25, 31.59 (d,J = 5Hz), 28.27, 27.43 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{25}H_{28}O_6PS$ $[M+H]^+$ 487.1344, found 487.1350.

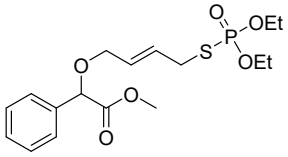


methyl 2-(4-(diphenylphosphorylthio)butoxy)-2-phenylacetate (5z), Compound **5z** was obtained in 22% yield (10.0 mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.84-7.88 (m, 4H), 7.51-7.52 (m,2H), 7.46-7.48 (m, 4H), 7.39-7.40 (m, 2H), 7.33-7.35 (m, 3H), 4.80 (s, 1H), 3.68 (s, 3H), 3.44-3.49 (m, 1H), 3.34-3.38 (m, 1H), 2.79-2.83 (m, 2H), 1.68-1.76(m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 136.5, 133.4 (d, J = 106.3Hz), 132.3 (d, J = 3.8Hz), 131.5 (d, J = 10.0Hz), 128.7, 128.66, 128.62, 127.1, 81.0, 68.9, 52.2, 29.0, 28.5, 27.2 (d, J = 5.0Hz). ESI HRMS: calculated for $C_{25}H_{28}O_4PS$ $[M+H]^+$ 455.1466, found 455.1471.

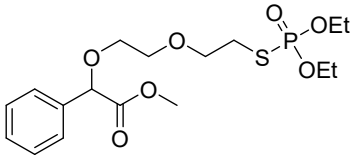


methyl 2-((5-((diethoxyphosphoryl)thio)pentyl)oxy)-2-phenylacetate(5z'), Compound **5z'** was obtained in 66% yield (25.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.32-7.37 (m, 3H), 4.86 (s, 1H), 4.11-4.18 (m, 4H), 3.71 (s, 3H), 3.51-3.54 (m, 1H), 3.42-3.45 (m, 1H), 2.79-2.85 (m, 2H), 1.64-1.72 (m, 4H), 1.47-1.52(m, 2H), 1.

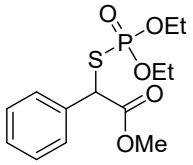
35 (t, J = 7.1Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.40, 136.61, 128.66, 128.62, 127.14, 81.11, 69.57, 63.45(d, J = 6.3Hz), 52.24, 30.76 (d, J = 3.25Hz), 30.59 (d, J = 7.3Hz), 29.03, 25.15, 16.09 (d, J = 6.3Hz). ESI HRMS: calculated for $C_{18}H_{30}O_6PS$ $[M+H]^+$ 405.1501, found 405.1520.



methyl (E)-2-((4-((diethoxyphosphoryl)thio)but-2-en-1-yl)oxy)-2-phenylacetate(5z'') Compound **5z''** was obtained in 26% yield (9.2mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.45 (m, 2H),7.34-7.38 (m, 3H), 5.74-5.76 (m, 2H), 4.92 (s, 1H), 4.08-4.19 (m, 6H), 3.71 (s, 3H), 3.42-3.46 (m, 2H), 1.32-1.35 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.09, 136.14, 128.93, 128.90, 128.83, 128.70, 127.36, 80.17, 64.57, 63.62 (d, J = 7.5Hz), 52.32, 27.51 (d, J = 5Hz), 16.03 (d, J = 7.5Hz). ESI HRMS: calculated for $C_{17}H_{26}O_6PS$ $[M+H]^+$ 389.1188, found 389.1185.

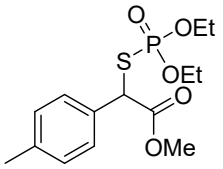


methyl 2-(2-(2-((diethoxyphosphoryl)thio)ethoxy)ethoxy)-2-phenylacetate(5z'''), Compound **5z'''** was obtained in 12% yield (6.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.45 (m, 2H), 7.32-7.37 (m, 3H), 5.00 (s, 1H), 4.13-4.19 (m, 4H), 3.71 (s, 3H), 3.67-3.70 (m, 5H), 3.62-3.64 (m, 1H), 3.04-2.98 (m, 2H), 1.34-1.37(m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$)δ 171.31, 136.51, 128.68, 128.62, 127.13, 81.09, 69.02, 63.47 (d, J = 5Hz), 52.23, 30.65 (d, J = 3.3Hz), 28.47, 27.54 (d, J =5Hz), 16.06 (d, J= 7.5Hz). ESI HRMS: calculated for $C_{17}H_{28}O_7PS$ $[M+H]^+$ 407.1293, found 407.1304.

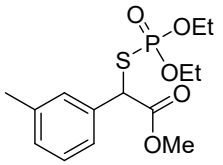


methyl 2-((diethoxyphosphoryl)thio)-2-phenylacetate(4a) Compound **4a** was ob

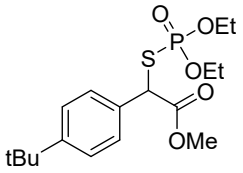
tained in 77% yield (24.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.45-7.47 (m, 2H), 7.31-7.37 (m, 3H), 5.04 (d, J = 11.2Hz, 1H), 4.12-4.18 (m, 1H), 3.96-4.06 (m, 3H), 3.74 (m, 3H), 1.22-1.28 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.42 (d, J = 7.5Hz), 136.16 (d, J = 5Hz), 128.90, 128.66, 128.32, 63.93 (d, J = 6.3Hz), 63.78 (d, J = 5Hz), 53.20, 51.99 (d, J = 2.5Hz), 15.88 (d, J = 3.8Hz), 15.83 (d, J = 3.8Hz), ESI HRMS: calculated for $C_{13}H_{20}O_5PS$ $[M+H]^+$ 319.0769, found 319.0772.



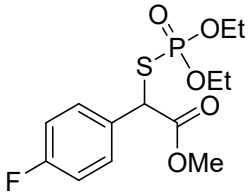
methyl 2-((diethoxyphosphoryl)thio)-2-(p-tolyl)acetate(4b) Compound **4b** was obtained in 64% yield (21.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.34 (d, J = 8.1Hz, 2H), 7.16 (d, J = 7.9Hz, 2H), 5.01 (d, J = 11.1Hz, 1H), 4.13-4.18 (m, 1H), 3.96-4.06 (m, 3H), 3.73 (s, 3H), 2.34 (s, 3H), 1.25-1.27 (m, 6H); ^{13}C NMR (125 MHz $CDCl_3$): δ 170.59 (d, J = 5Hz), 138.63, 133.05 (d, J = 6.3Hz), 129.58, 128.17,63.93 (d, J = 5Hz), 63.78 (d, J = 5Hz), 53.15, 51.76 (d, J = 2.5Hz), 21.16,15.88 (d, J = 3.3Hz), 15.83 (d, J = 5Hz). ESI HRMS: calculated for $C_{14}H_{22}O_5PS$ $[M+H]^+$ 333.0926, found 333.0923.



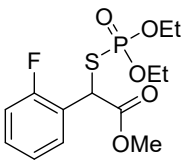
methyl 2-((diethoxyphosphoryl)thio)-2-(m-tolyl)acetate(4c) Compound **4c** was obtained in 72% yield (24.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.21-7.26 (m, 3H), 7.13 (d, J = 6.4Hz, 1H), 5.00 (d, J = 11.1Hz, 1H), 4.14-4.19 (m, 1H), 3.98-4.08 (m, 3H), 3.74 (s, 3H), 2.35 (s, 3H), 1.24-1.29 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.57, 138.7, 135.94, 129.45, 128.86, 128.80, 125.35, 63.90 (d, J = 5Hz), 63.77 (d, J = 6.3Hz), 53.17, 51.99 (d, J = 2.5Hz), 21.34, 15.89 (d, J = 6.3Hz), 15.82 (d, J = 3.8Hz). ESI HRMS: calculated for $C_{14}H_{22}O_5PS$ $[M+H]^+$ 333.0926, found 333.0923.



methyl 2-(4-(tert-butyl)phenyl)-2-((diethoxyphosphoryl)thio)acetate(4d) Compound **4d** was obtained in 65% yield (24.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.37 (m, 4H), 7.31-7.37 (m, 3H), 5.02 (d, J = 10.8Hz, 1H), 4.13-4.16 (m, 1H), 3.96-4.04 (m, 3H),3.74 (s, 3H), 1.30 (s, 9H), 1.21-1.26 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$):δ 170.53, 151.78, 132.96, 127.98, 125.85, 63.85 (d, J = 5.6 Hz), 63.72 (d, J =5.6 Hz), 53.13, 51.67 (d, J = 2.5Hz), 34.63, 31.24, 15.88 (d, J = 2.5Hz), 15.82 (d, J = 2.5Hz). ESI HRMS: calculated for $C_{17}H_{28}O_5PS$ $[M+H]^+$ 375.1395, found 375.1404.

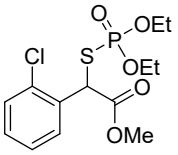


methyl 2-((diethoxyphosphoryl)thio)-2-(4-fluorophenyl)acetate(4e) Compound **4e** was obtained in 50% yield (17.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.43-7.46 (m, 2H), 7.01-7.06(m, 2H), 5.04 (d, J = 11.1Hz, 1H), 4.12-4.19 (m, 1H), 3.95-4.05 (m, 3H), 3.75 (s, 3H), 1.23-1.30 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.28 (d, J = 6.3Hz), 162.77 (d, J = 246.8 Hz), 131.97, 130.19 (d, J = 7.5Hz), 115.84 (d, J = 22.5Hz), 64.02 (d, J = 6.3Hz), 63.83 (d, J = 6.3Hz), 53.26, 51.21,15.87, 15.86 (d, J = 7.5Hz). ^{19}F NMR ($CDCl_3$, 500 MHz): -112.8. ESI HRMS: calculated for $C_{13}H_{19}FO_5PS$ $[M+H]^+$ 337.0675, found 337.0681.

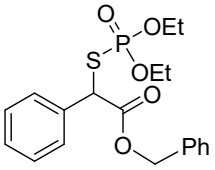


methyl 2-((diethoxyphosphoryl)thio)-2-(2-fluorophenyl)acetate(4f) Compound **4f** was obtained in 50% yield (17.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.50-7.53 (m, 1H), 7.26-7.34(m, 1H), 7.14-7.17 (m, 1H), 7.06-7.09 (m, 1H), 5.35 (d, J = 12.15, 1H), 4.00-4.21 (m, 4H), 3.76 (s, 3H), 1.25-1.30 (m, 6H); ^{13}C NMR (125 MHz, CDC

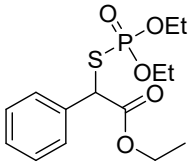
l_3): 169.79 (d, J = 6.3Hz), 160.87 (d, J = 247.7Hz), 130.41 (d, J = 8.8Hz), 129.99 (d, J = 2.5Hz), 124.62 (d, J = 3.3Hz), 123.89 (q, J = 3.7Hz), 115.78 (d, J = 21.3 Hz), 63.97 (d, J = 5Hz), 63.85 (d, J = 6.3Hz), 53.38, 45.07, 15.87 (d, J = 2.5Hz), 15.82 (d, J = 2.5Hz). ^{19}F NMR ($CDCl_3$, 500 MHz): -116.1. ESI HRMS: calculated for $C_{13}H_{19}FO_5PS$ $[M+H]^+$ 337.0675, found 337. 0681.



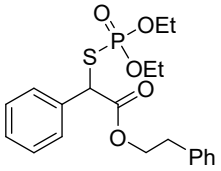
methyl 2-(2-chlorophenyl)-2-((diethoxyphosphoryl)thio)acetate(4g), Compound **4g** was obtained in 57% yield (20.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.54-7.56 (m, 1H), 7.39-7.41 (m, 1H), 7.25-7.30 (m, 2H), 5.54 (d, J = 12.4Hz, 1H), 4.04-4.20 (m, 4H), 3.76 (s, 3H), 1.27-1.31 (m, 6H); ^{13}C NMR (125 MHz, CDCl3): δ 169.90 (d, J = 5.3Hz), 134.23 (d, J = 6.3Hz), 133.66, 130.26, 129.93, 129.81, 127.39, 64.00 (d, J = 5Hz), 63.87 (d, J = 6.3Hz), 53.40, 49.10 (d, J = 2.5Hz), 15.91, 15.85. ESI HRMS: calculated for $C_{13}H_{19}ClO_5PS$ $[M+H]^+$ 353.0379, found 353.0383.



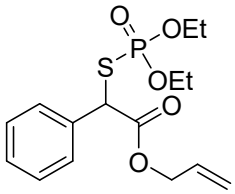
benzyl 2-((diethoxyphosphoryl)thio)-2-phenylacetate(4h), Compound **4h** was obtained in 58% yield (20.0mg) according to the general procedure (5h). Yell ow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.44-7.46 (m, 2H), 7.39-7.41 (m, 6H),7 .25-7.30 (d, J = 6.1Hz, 2H), 5.11-5.20 (m, 2H), 5.07 (d, J = 11.5Hz, 1H),4. 07-4.14 (m, 1H), 3.90-4.03 (m, 3H), 1.18-1.25 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.70 (d, J = 5Hz), 136.16 (d, J = 5Hz), 135.15, 128.86, 128.6 3, 128.52, 128.37, 128.36, 128.05, 67.81, 63.87 (d, J = 5Hz), 63.77 (d, J = 5Hz), 52.15, 15.87 (d, J = 3.8Hz), 15.81 (d, J = 2.5Hz). ESI HRMS: calcul ated for $C_{19}H_{24}O_5PS$ $[M+H]^+$ 395.1082, found 395.1076.



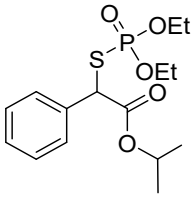
ethyl 2-((diethoxyphosphoryl)thio)-2-phenylacetate(4i) Compound **4i** was obtai ned in 60% yield (20.0mg) according to the general procedure (5h). Yellowoi l. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.45-7.47 (m, 2H), 7.31-7.37 (m, 3H), 5.01 (d, J = 11.2Hz, 1H), 4.13-4.24 (m, 3H), 3.95-4.03 (m, 3H), 1.22-1.27 (m,9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.84 (d, J = 6.3Hz), 136.39 (d, J = 5H z), 128.83, 128.56, 128.32, 63.86 (d, J = 6.3Hz), 63.73 (d, J = 5Hz), 62.28, 52.20 (d, J = 3.8Hz), 15.87 (d, J = 3.8Hz), 15.82 (d, J = 3.8Hz) 13.96. E SI HRMS: calculated for $C_{14}H_{22}O_5PS$ $[M+H]^+$ 333.0926, found 333.0923.



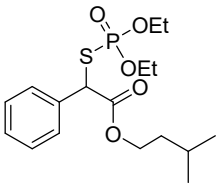
phenethyl 2-((diethoxyphosphoryl)thio)-2-phenylacetate(4j) Compound **4j** wa s obtained in 60% yield (25.0mg) according to the general procedure (5h). Y ellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.40-7.42 (m, 2H), 7.30-7.34 (m, 3 H), 7.19-7.24 (m, 3H), 7.09 (d, J = 6.8Hz, 2H), 5.00 (d, J = 11.3Hz, 1H), 4.29-4.37 (m, 2H), 4.10-4.15 (m, 1H), 3.92-4.03 (m, 3H), 286-2.91 (m, 2H), 1.20-1.25 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.70 (d, J = 6.3Hz), 137.28, 128.88, 128.84, 128.57, 128.50, 128.36, 126.59, 66.65, 63.86 (d, J = 5Hz), 63.73(d, J = 5Hz), 52.25, 34.84, 15.88 (d, J = 2.5Hz), 15.82 (d, J = 2.5Hz). ESI HRMS: calculated for $C_{20}H_{26}O_5PS$ $[M+H]^+$ 409.1239, found 409. 1235.



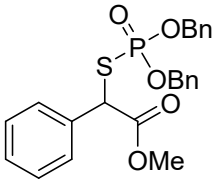
allyl 2-((diethoxyphosphaneyl)thio)-2-phenylacetate(4k) Compound **4k** was o btained in 55% yield (27.0mg) according to the general procedure (5h). Yello w oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.47 (d, J = 6.65Hz, 2H), 7.31-7.36 (m, 3H), 5.85-5.89 (m, 1H), 5.19-5.26 (m, 2H), 5.06 (d, J = 11.3Hz, 1H), 4. 58-4.66 (m, 2H), 4.11-4.19 (m, 1H), 3.94-4.06 (m, 3H), 1.22-1.27 (m, 6H);^{13}C NMR (125 MHz, $CDCl_3$): δ 169.56 (d, J = 6.3Hz), 136.20, 131.30, 128.87, 128.64, 128.35, 118.70, 66.61, 63.91 (d, J = 5Hz), 63.76 (d, J = 6.3Hz),52. 14, 15.89 (d, J = 2.5Hz) 15.83(d, J = 2.5Hz). ESI HRMS: calculated for $C_{15}H_{22}O_5PS$ $[M+H]^+$ 345.0926, found 345.0920.



isopropyl 2-((diethoxyphosphoryl)thio)-2-phenylacetate(4l) Compound **4l** was obtained in 60% yield (25.0mg) according to the general procedure (5h). Yell ow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.46 (d, J = 6.95Hz, 2H), 7.30-7.35 (m, 3H), 4.96-5.04 (m, 1H), 4.98 (d, J = 11.4Hz, 1H), 4.10-4.17 (m, 1H), 3. 94-4.04 (m, 3H), 1.22-1.26 (m, 9H), 1.15 (d, J = 6.3Hz, 3H); ^{13}C NMR (12 5 MHz, $CDCl_3$): δ 169.30 (d, J = 6.3Hz), 136.57 (d, J = 3.75Hz), 128.77, 128.47, 128.28, 70.02, 63.81 (d, J = 5Hz), 63.68 (d, J = 6.25Hz), 52.45 (d, J = 2.5Hz), 21.49 (d, J = 21.25Hz), 15.88 (d, J = 2.5Hz), 15.82(d, J = 2.5 Hz). ESI HRMS: calculated for $C_{15}H_{24}O_5PS$ $[M+H]^+$ 347.1082, found 347.108 1.

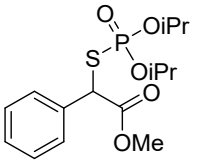


isopentyl 2-((diethoxyphosphoryl)thio)-2-phenylacetate(4m) Compound **4m** w as obtained in 70% yield (26.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.45-7.47 (m, 2H), 7.27-7.35 (m, 3H), 5.01 (d, J = 11.3Hz, 1H), 4.12-4.17 (m, 3H), 3.95-4.03 (m, 3H), 1.55-1.60 (m, 1H), 1.46-1.51 (m, 2H), 1.22-1.26 (m, 6H), 0.85 (t, J = 6.9Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.89, 169.84, 136.46 (d, J= 5Hz), 128.79, 128.54, 128.31, 64.96, 63.84 (d, J = 2.5Hz), 63.71 (d, J = 5Hz), 52.29 (d, J = 2.5Hz), 37.02, 24.91, 22.33, 15.87 (d, J = 2.5Hz), 15.81 (d, J = 2.5Hz). ESI HRMS: calculated for $C_{17}H_{28}O_5PS$ $[M+H]^+$ 375.1395, found 375.1409.

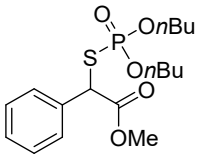


methyl 2-((bis(benzyloxy)phosphoryl)thio)-2-phenylacetate(4n) Compound **4n** was obtained in 57% yield (25.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.39-7.41(m, 2H), 7.29-7.35 (m,11 H), 7.24-7.26 (m, 2H), 5.11-5.15 (m, 1H), 5.00-5.05 (m, 1H), 4.90-5.00 (m,3

H), 3.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.03, 135.90 (d, J = 3. 8Hz), 135.2, 128.95, 128.72, 128.65, 120.60, 128.55, 128.34, 128.20, 128.11,69. 21 (d, J = 5Hz), 69.05 (d, J = 5.3Hz), 53.18, 52.07**.** ESI HRMS: calculated for $C_{23}H_{24}O_5PS$ $[M+H]^+$ 443.1082, found 443.1082.



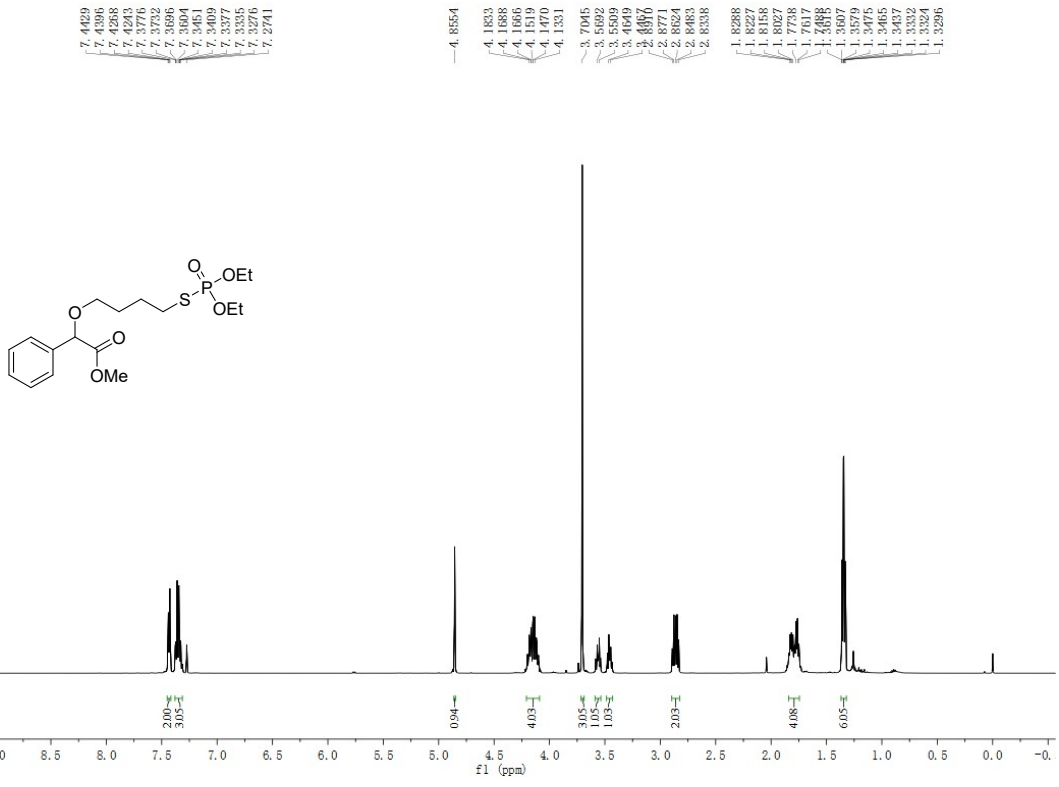
methyl 2-((diisopropoxyphosphoryl)thio)-2-phenylacetate(4o) Compound **4o** w as obtained in 50% yield (17.0mg) according to the general procedure (5h). Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$):δ 7.47 (d, J = 7.0Hz, 2H), 7.30-7.35 (m, 3H), 5.09 (d, J = 11.5Hz, 1H), 4.71-4.76 (m, 1H), 4.51-4.55 (m, 1H),3. 73 (s, 3H), 1.35 (d, J = 6.2Hz, 3H), 1.20-1.25 (m, 9H); ^{13}C NMR (125 MH z, $CDCl_3$):170.60 (d, J = 3.8Hz), 136.41 (d, J = 5Hz), 128.85, 128.55, 128. 37, 73.24 (d, J = 6.3Hz), 73.05 (d, J = 6.3Hz) 53.10, 52.10 (d, J = 2.5Hz), 23.85 (d, J = 3.75Hz), 23.65 (d, J = 5Hz), 23.43 (d, J = 2.5Hz), 23.38(d, J = 2.5Hz). ESI HRMS: calculated for $C_{15}H_{24}O_5PS$ $[M+H]^+$ 347.1082, found 3 47.1074.



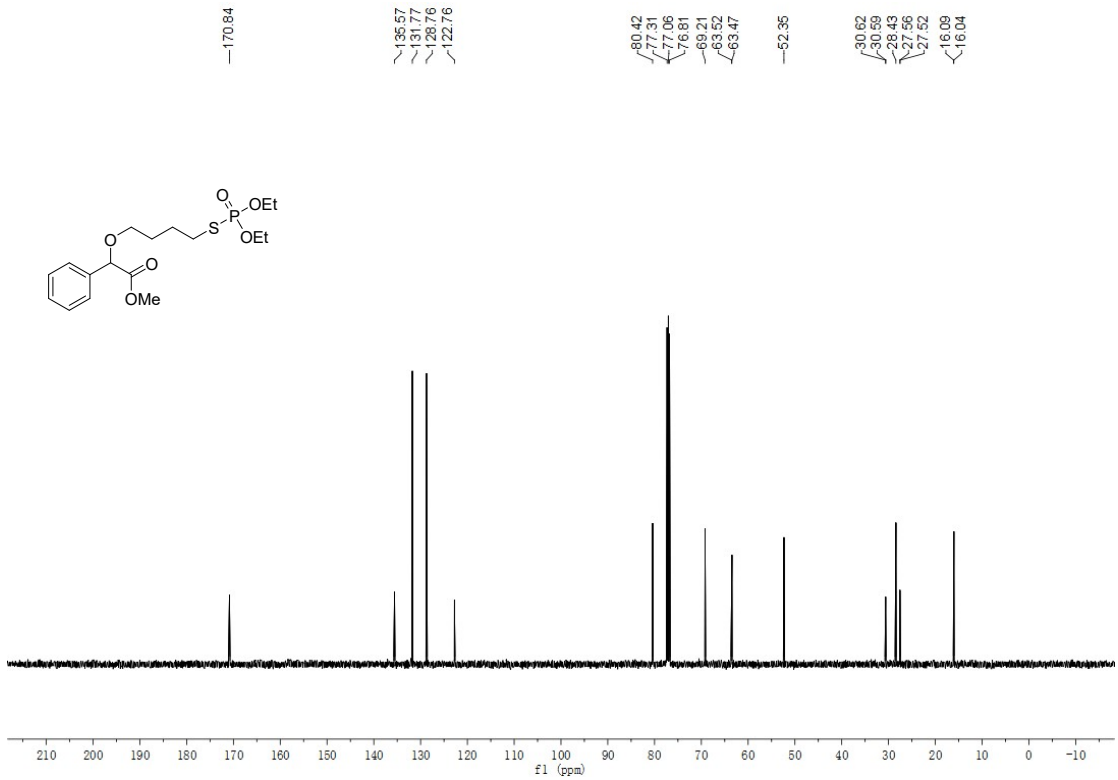
methyl 2-((dibutoxyphosphoryl)thio)-2-phenylacetate(4p) Compound **4p** was obtained in 70% yield (26.0mg) according to the general procedure (5h). Yell ow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.45-7.47 (m, 2H), 7.29-7.36 (m, 3H), 5.05 (d, J = 11.2Hz, 1H), 4.07-4.11 (m, 1H), 3.86-3.95 (m, 3H), 3.73 (s, 3 H), 1.51-1.60 (m, 4H), 1.28-1.37 (m, 4H), 0.86-0.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 170.43 (d, J = 6.3 Hz), 136.31 (d, J = 5Hz), 128.87, 128.61, 128.33, 67.62 (d, J = 5Hz), 67.45 (d, J = 6.3Hz), 53.17, 52.01 (d, J = 2.5 Hz), 31.98 (t, J = 7.5Hz), 18.63 (d, J = 5Hz), 13.55 (d, J = 3.8Hz). ESI HRMS: calculated for $C_{17}H_{28}O_5PS$ $[M+H]^+$ 375.1395, found 375.1389.

6.Copies of NMR spectra for products

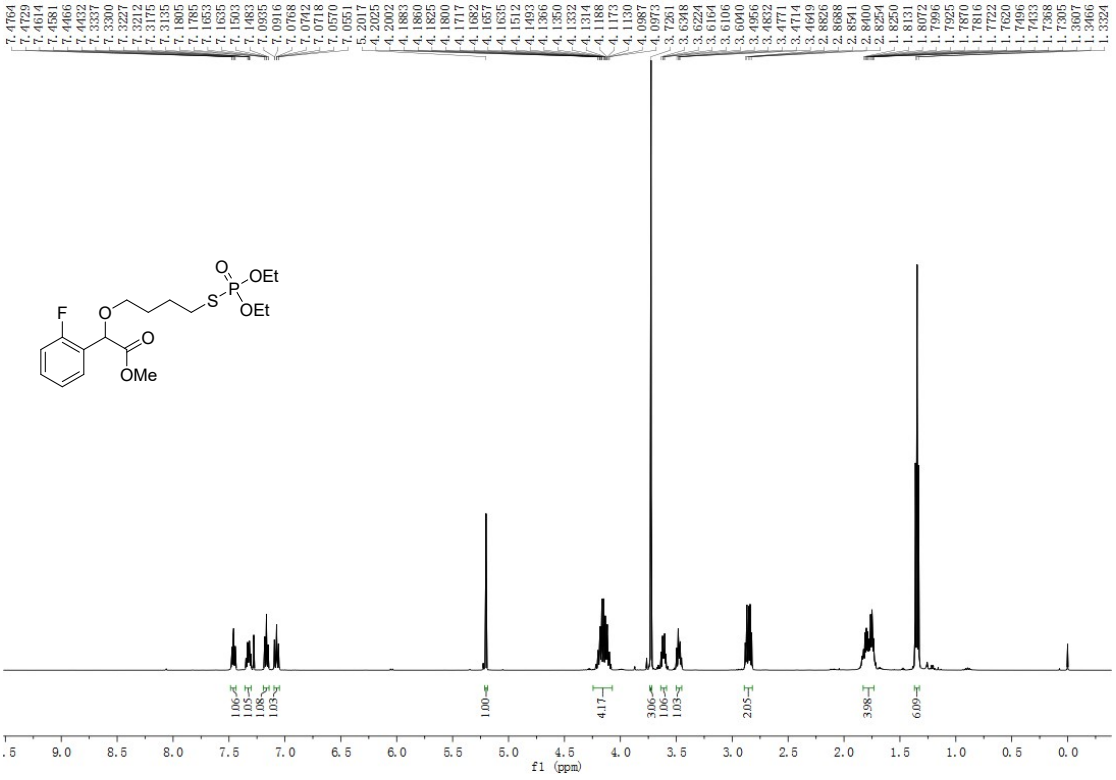
5a ^{1}H NMR (500 MHz, $CDCl_3$)



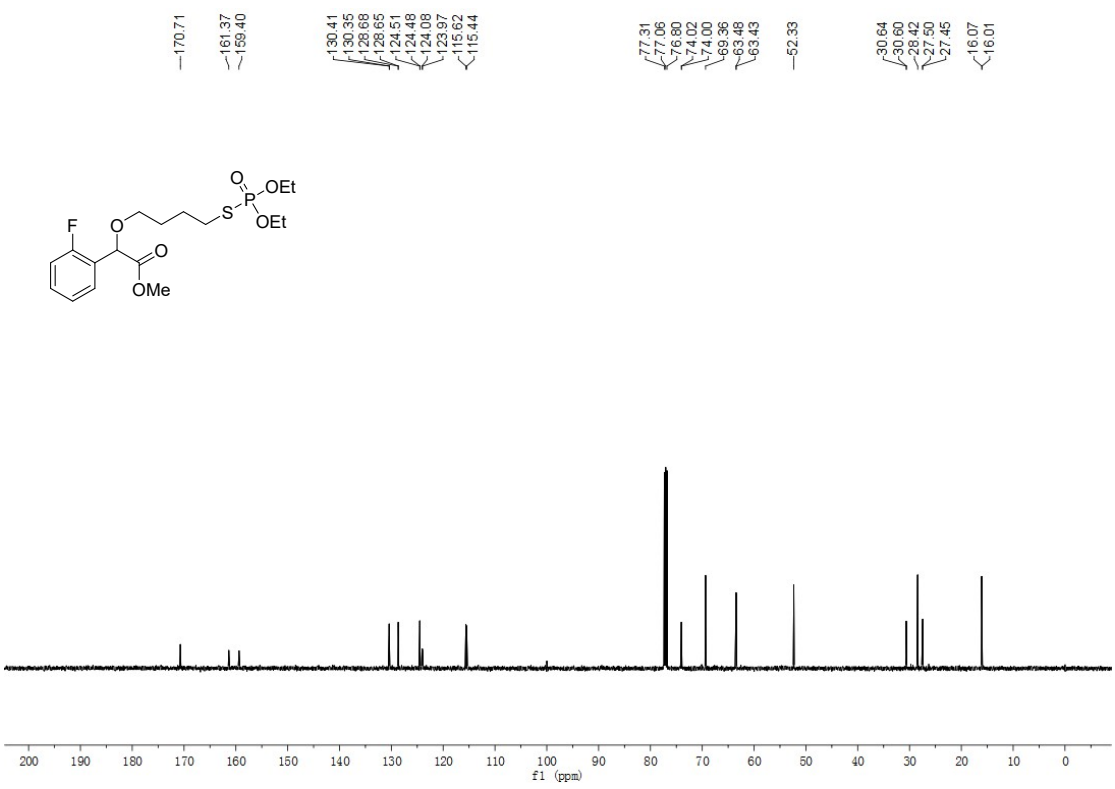
5a ^{13}C NMR (125MHz, $CDCl_3$)



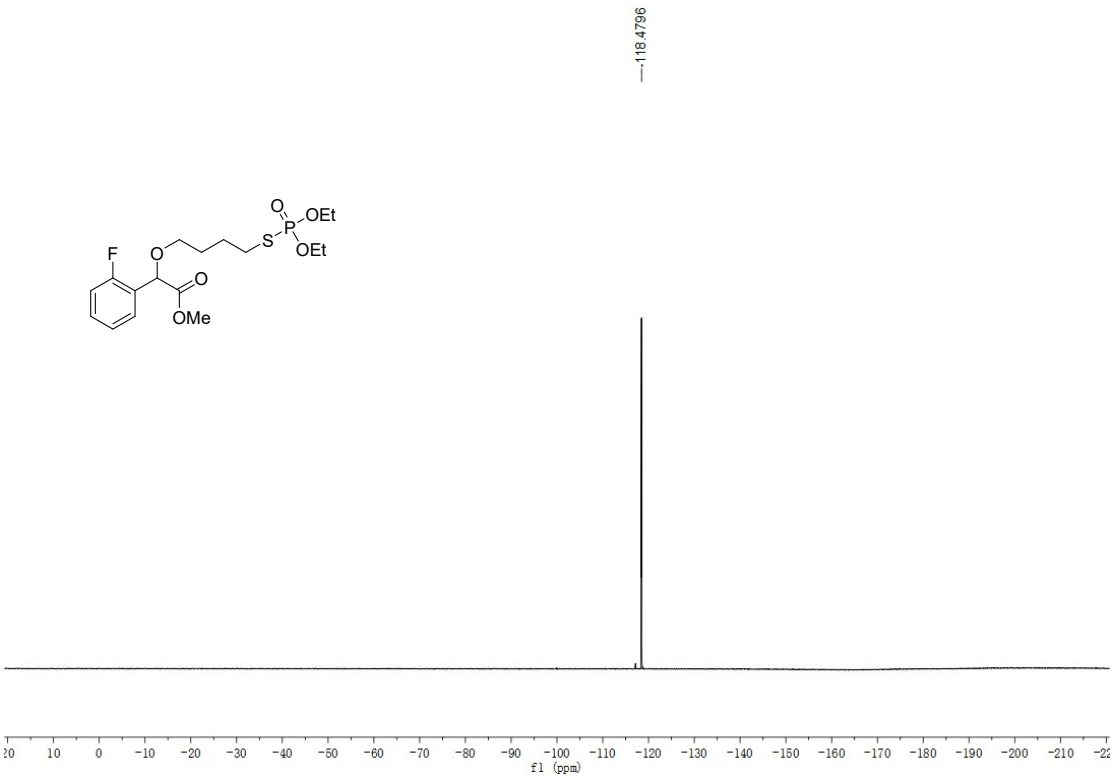
5b ^{1}H NMR (500 MHz, $CDCl_3$)



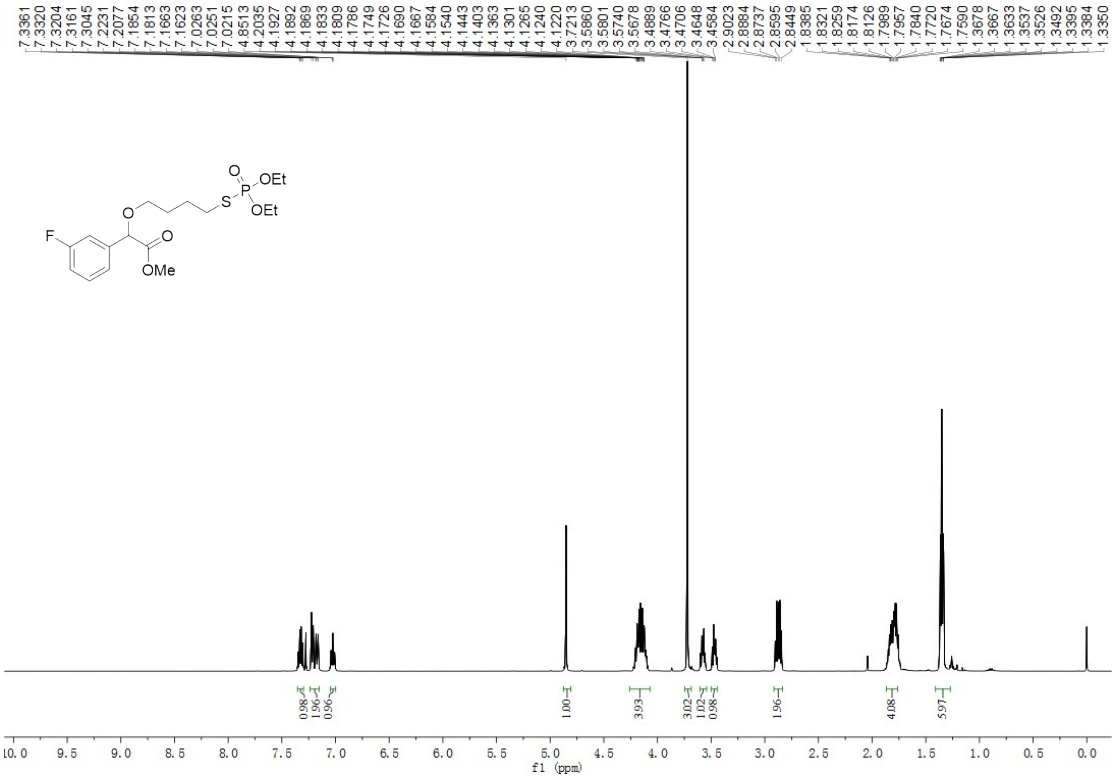
5b ^{13}C NMR (125MHz, $CDCl_3$)



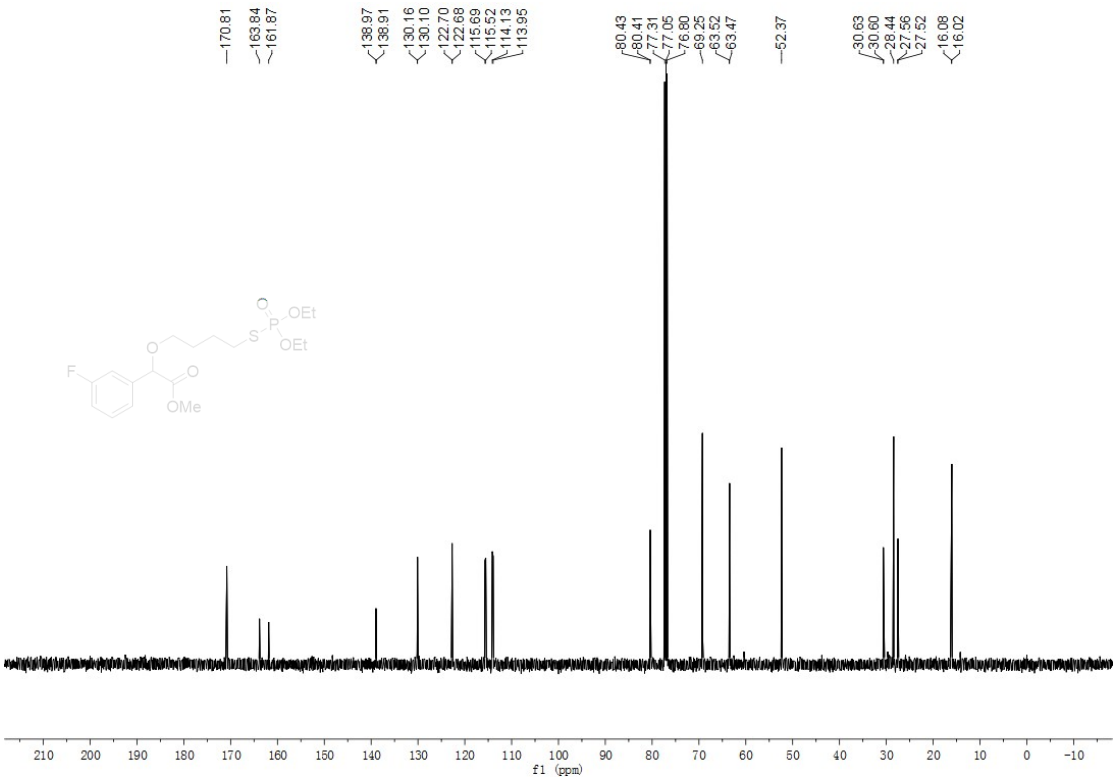
5b ^{19}F NMR (500 MHz, $CDCl_3$)



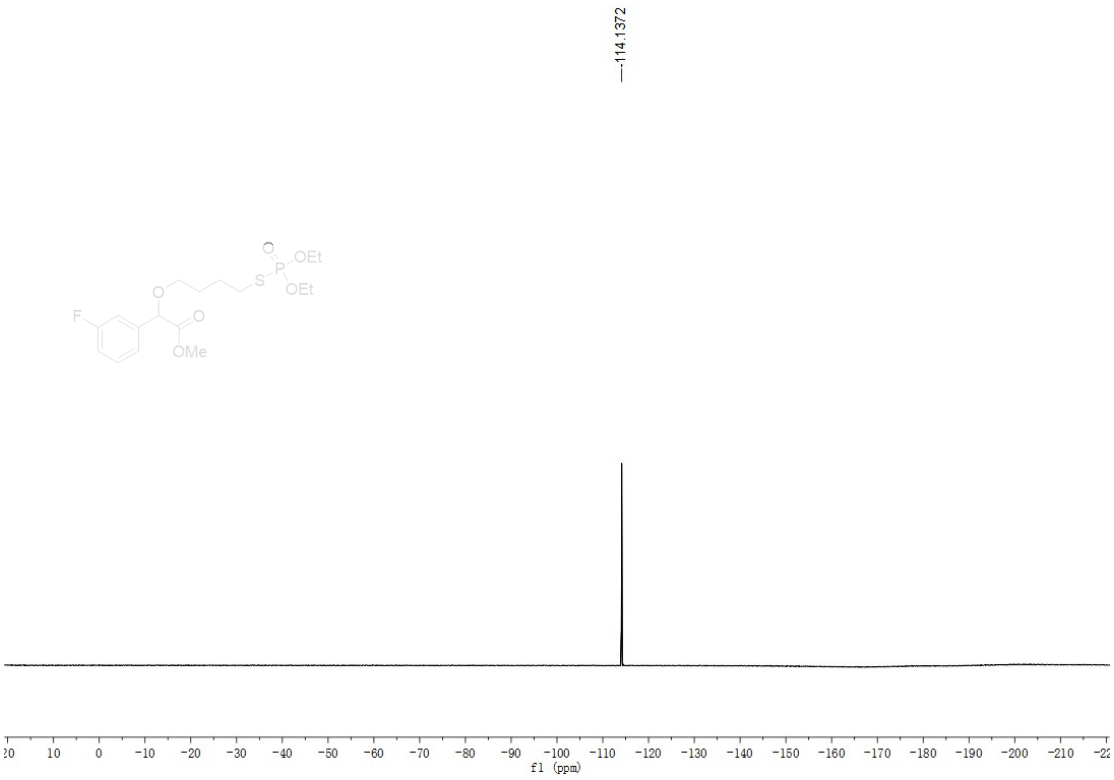
5c ^{1}H NMR (500 MHz, $CDCl_3$)



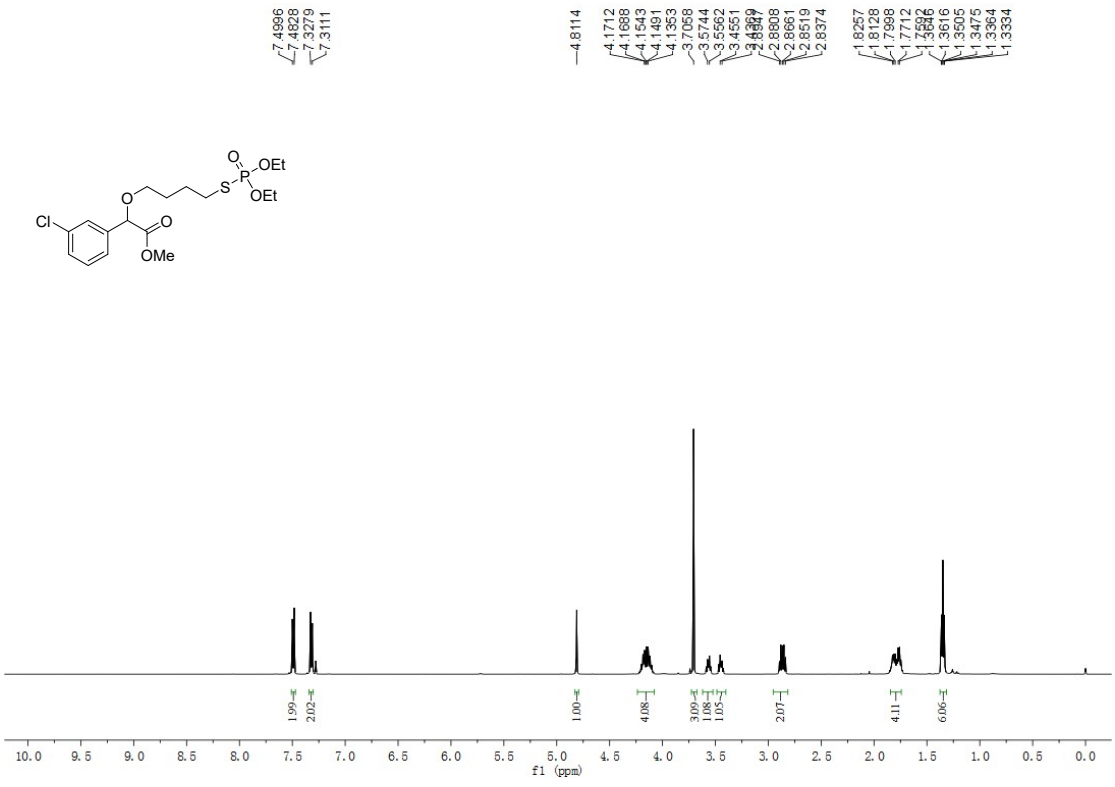
5c ^{13}C NMR (125MHz, $CDCl_3$)



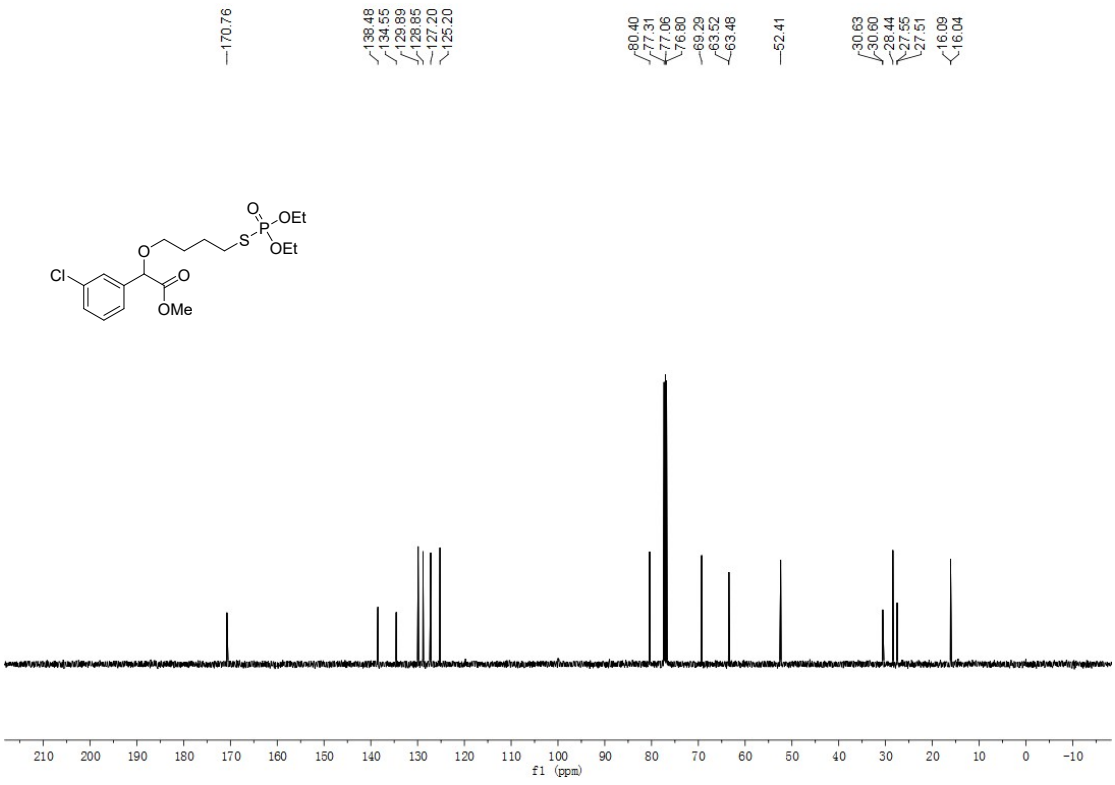
5c ^{19}F NMR (500 MHz, $CDCl_3$)



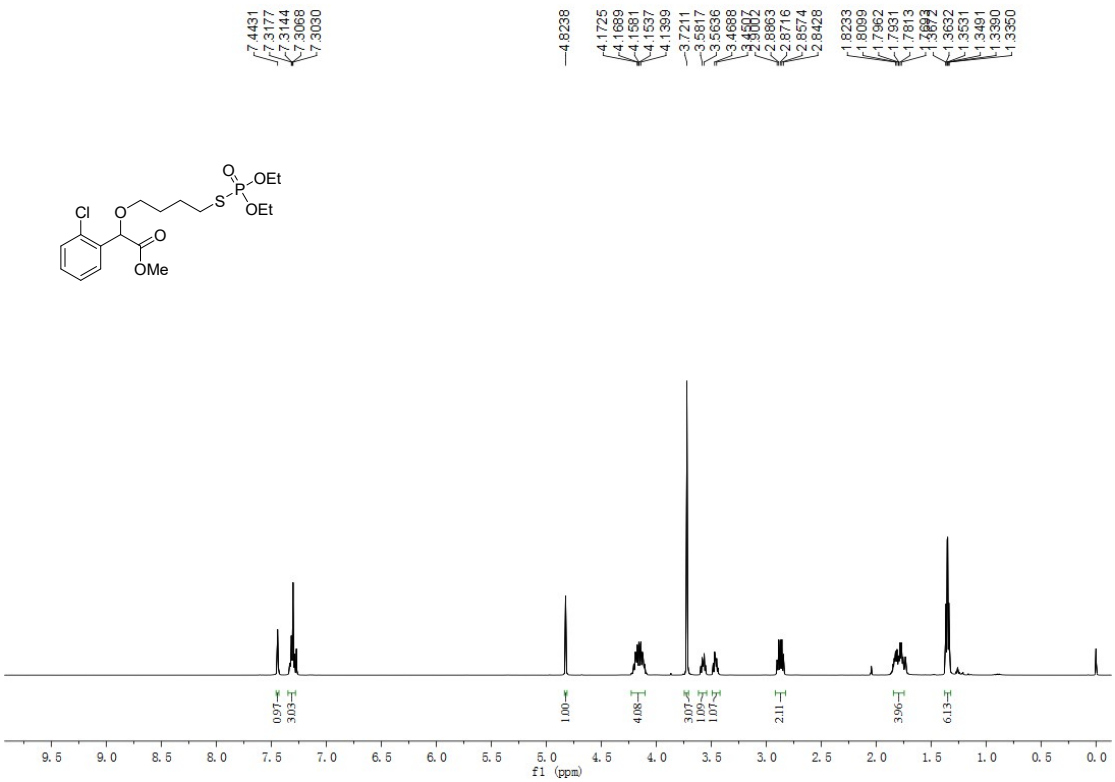
5d ^{1}H NMR (500 MHz, $CDCl_3$)



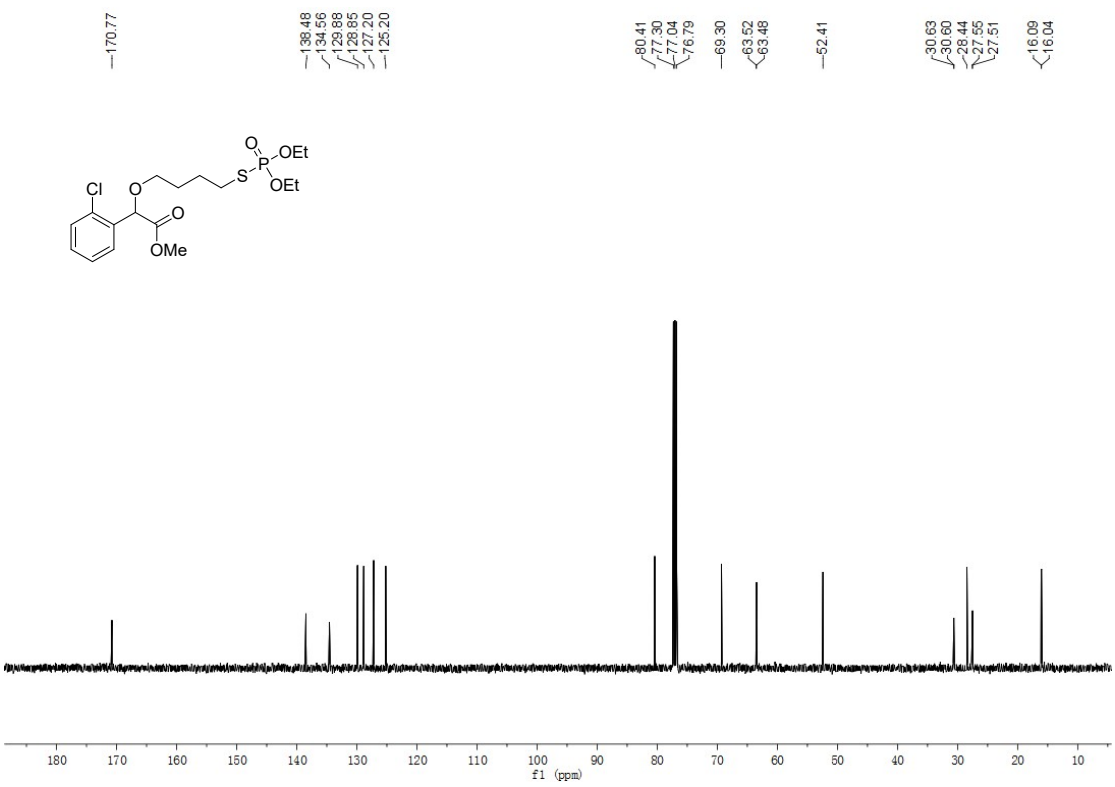
5d ^{13}C NMR (125MHz, $CDCl_3$)



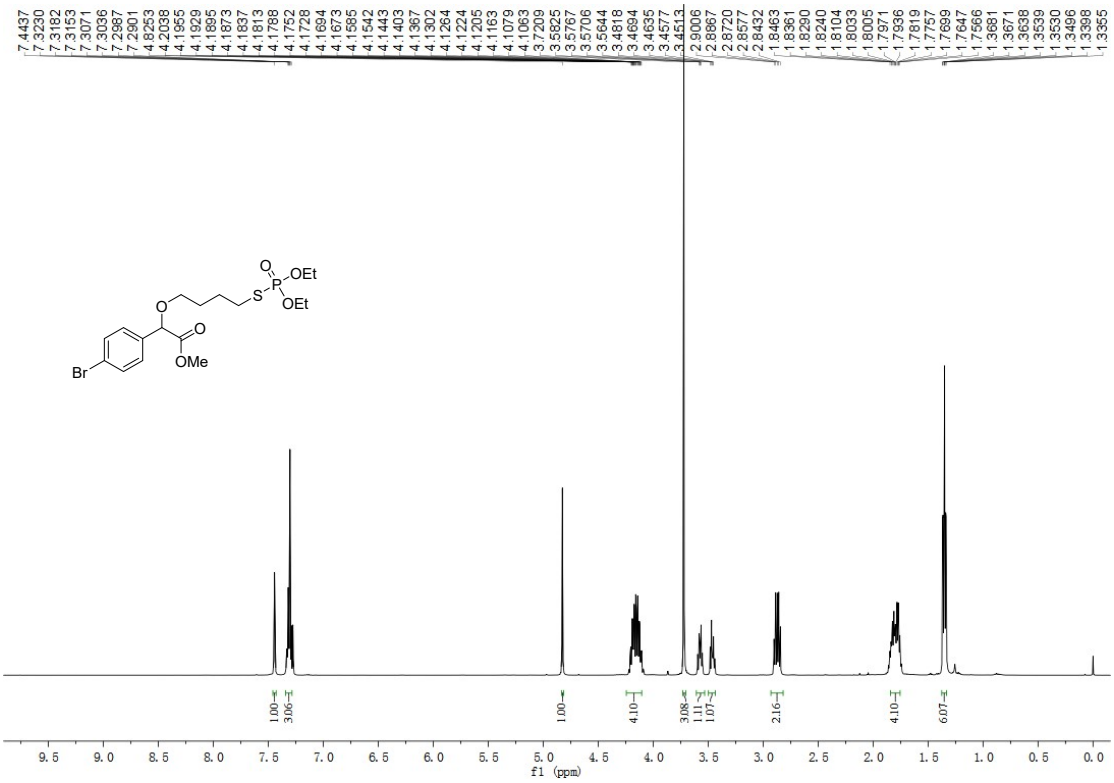
5e ^{1}H NMR (500 MHz, $CDCl_3$)



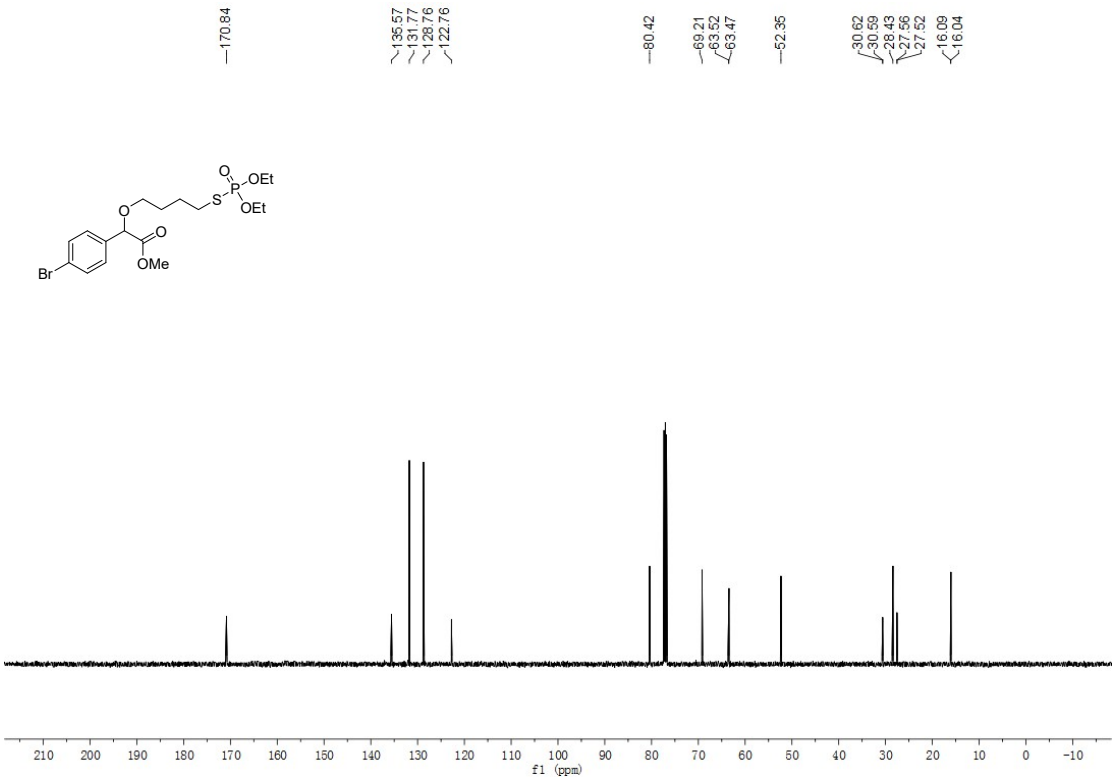
5e ^{13}C NMR (125MHz, $CDCl_3$)



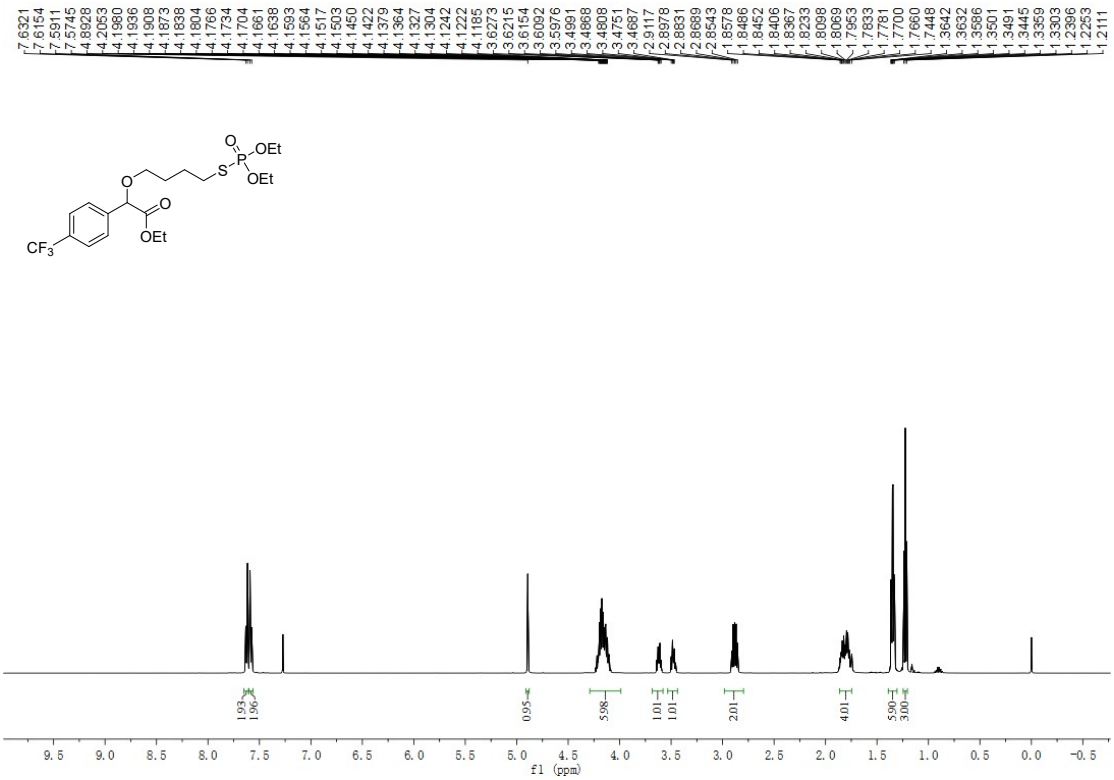
5f ^{1}H NMR (500 MHz, $CDCl_3$)



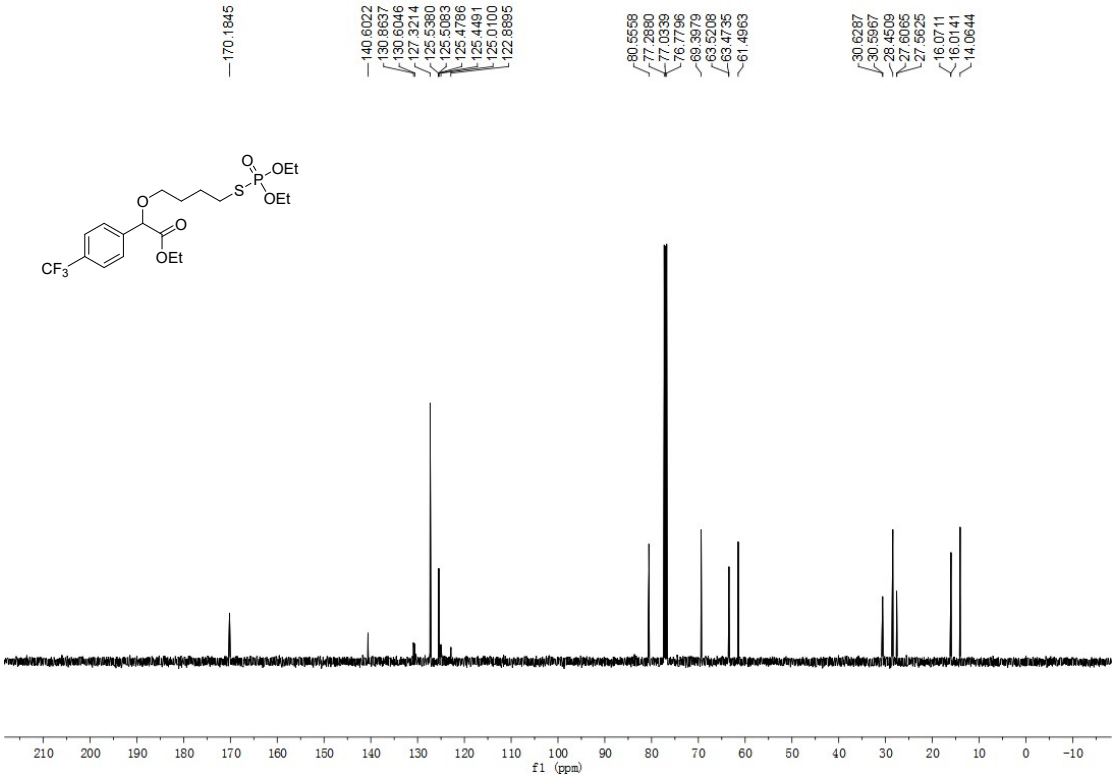
5f ^{13}C NMR (125MHz, $CDCl_3$)



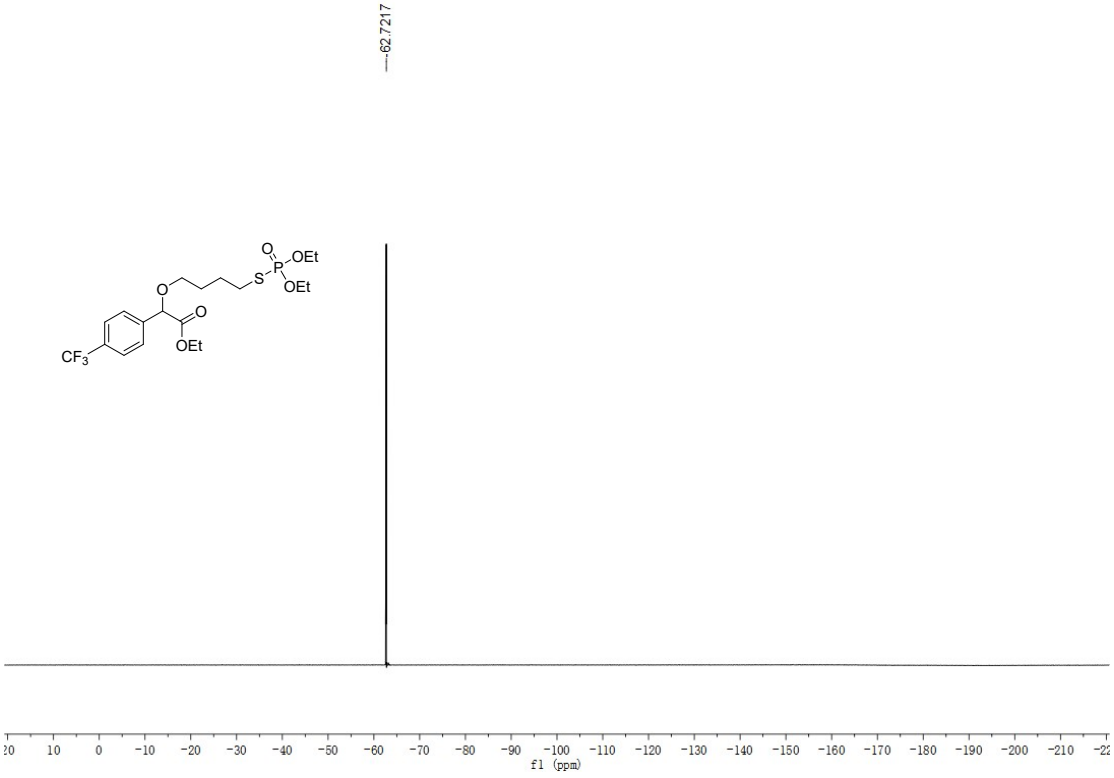
5g ^{1}H NMR (500 MHz, $CDCl_3$)



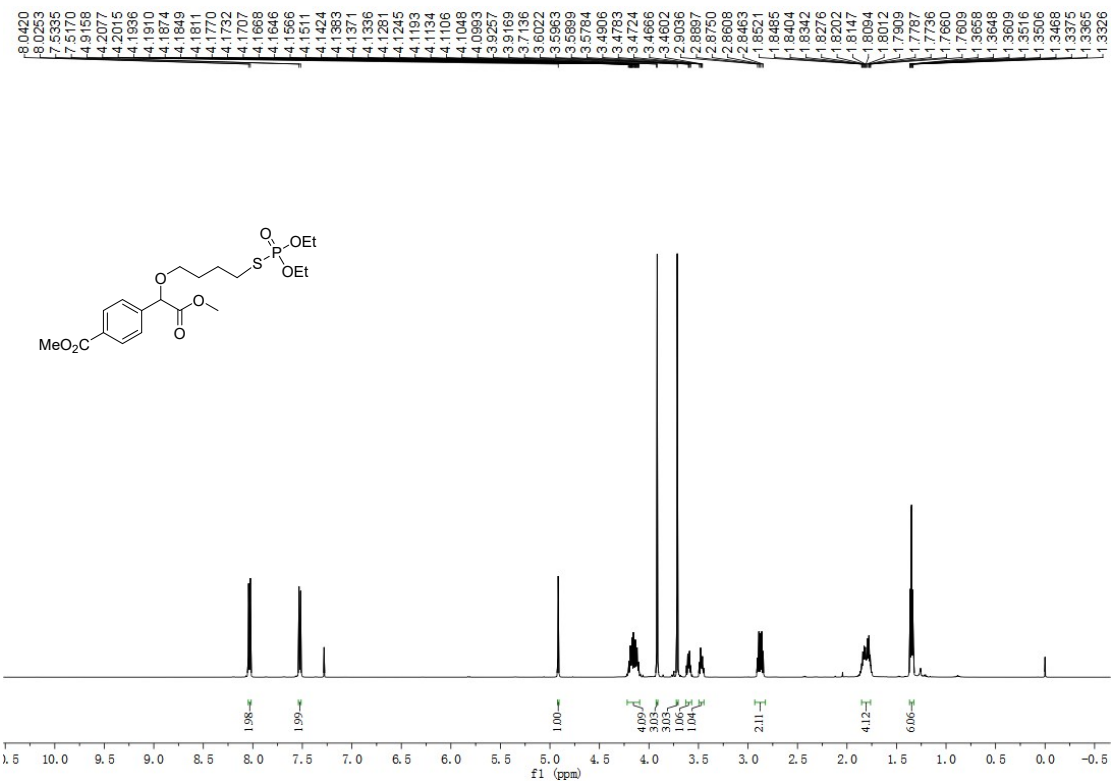
5g ^{13}C NMR (125MHz, $CDCl_3$)



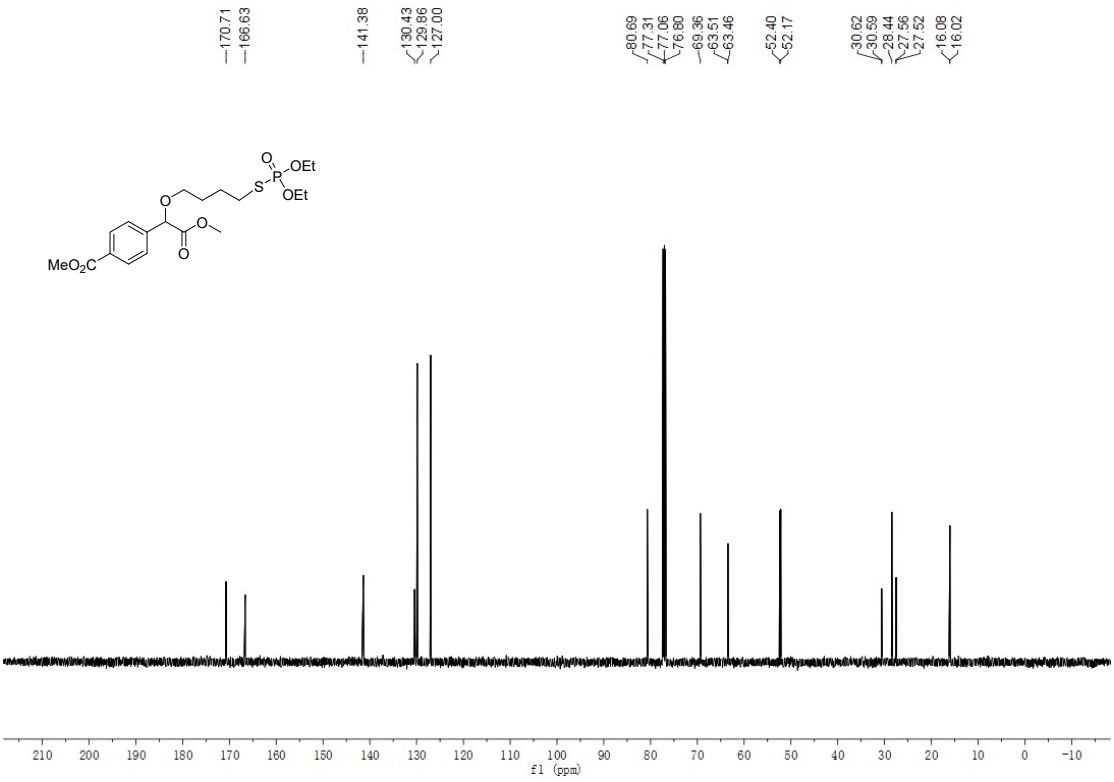
5g ^{19}F NMR (500MHz, $CDCl_3$)



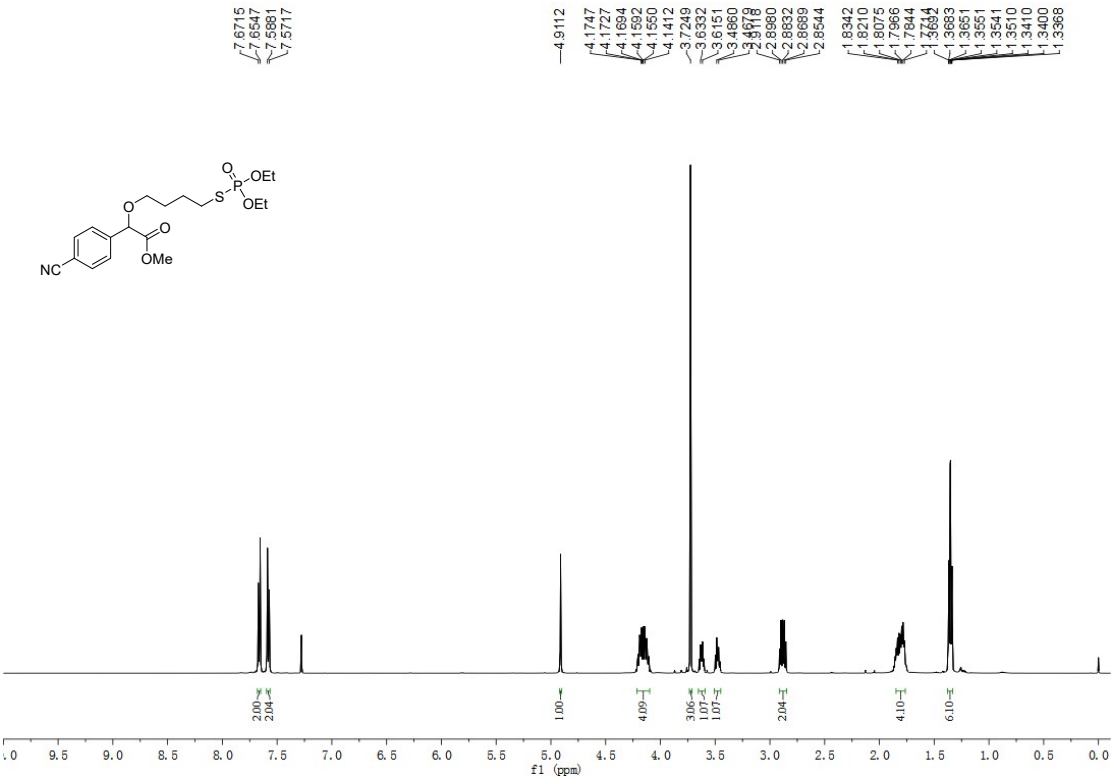
5h ^{1}H NMR (500 MHz, $CDCl_3$)



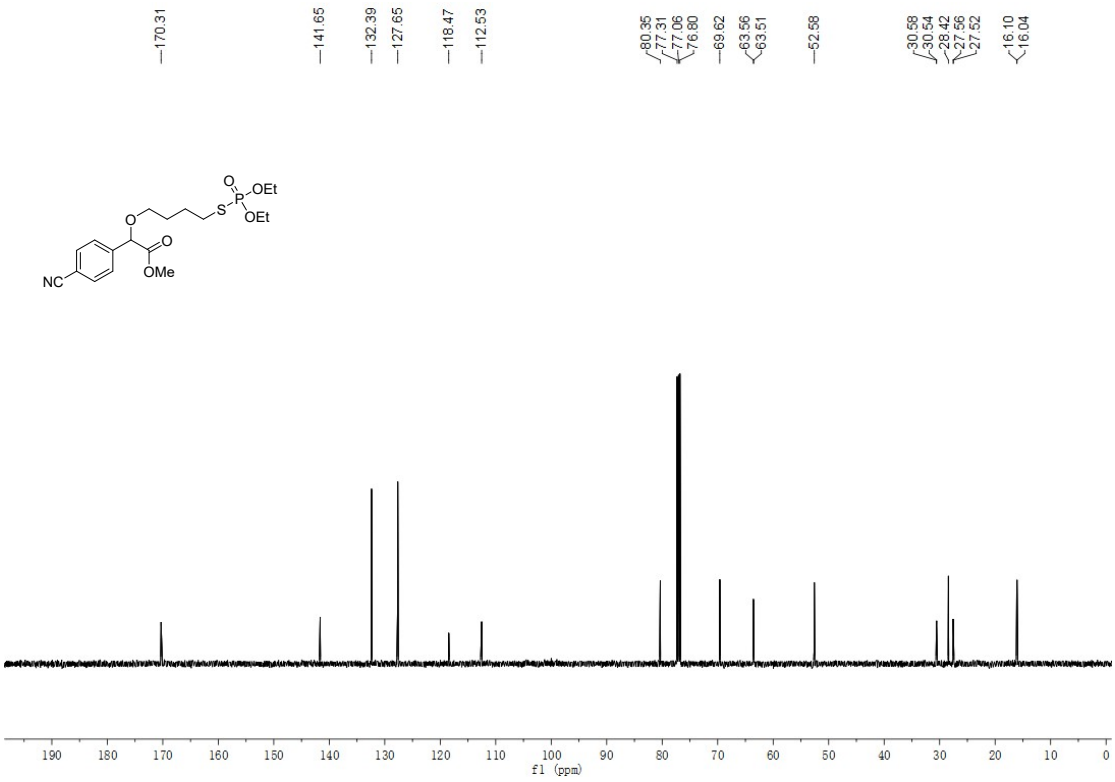
5h ^{13}C NMR (125MHz, $CDCl_3$)



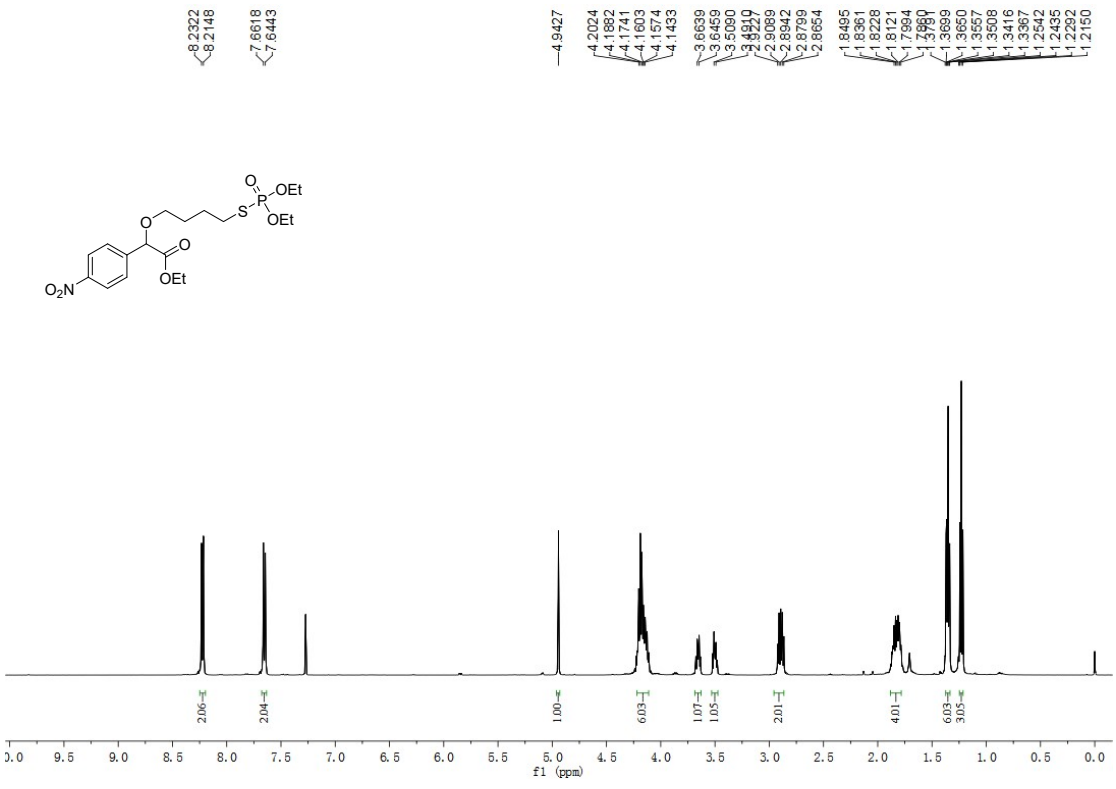
5i ^{1}H NMR (500 MHz, $CDCl_3$)



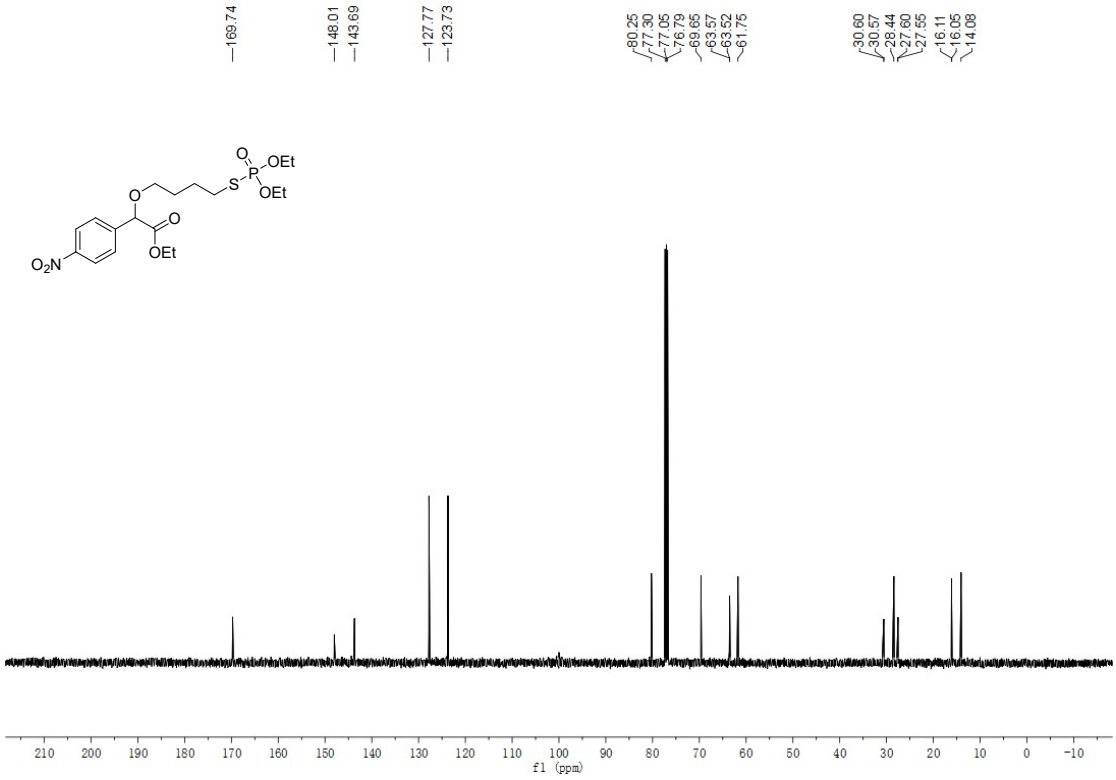
5i ^{13}C NMR (125MHz, $CDCl_3$)



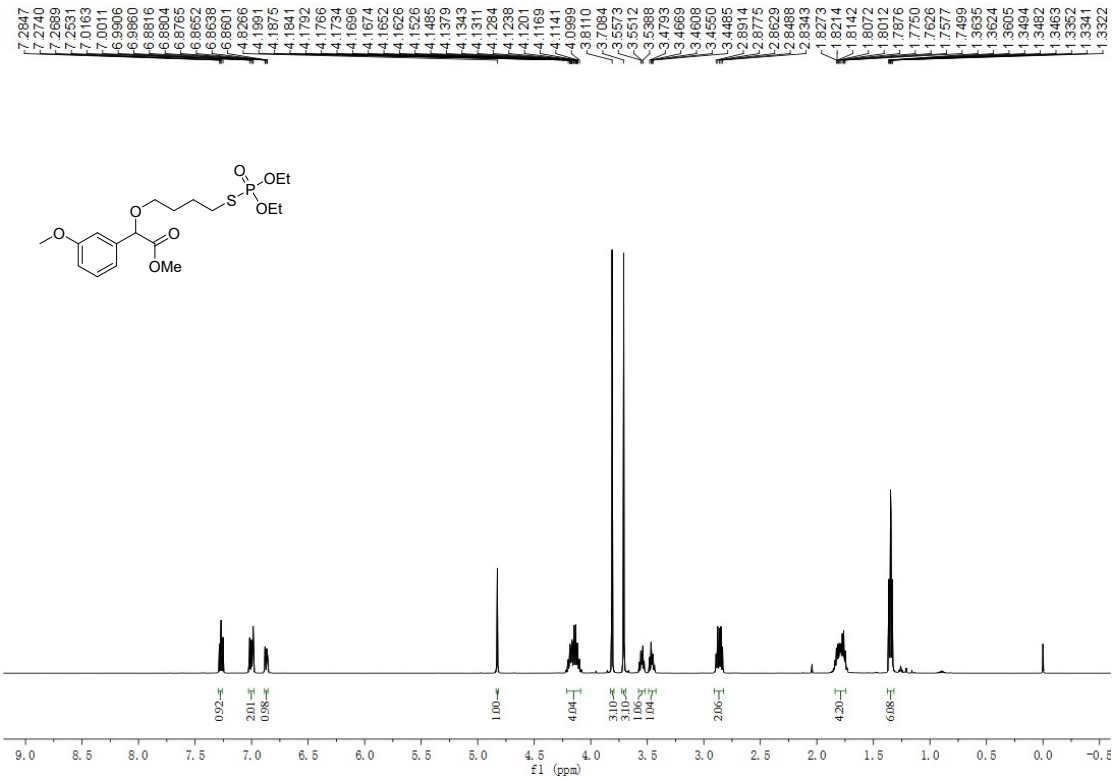
5j ^{1}H NMR (500 MHz, $CDCl_3$)



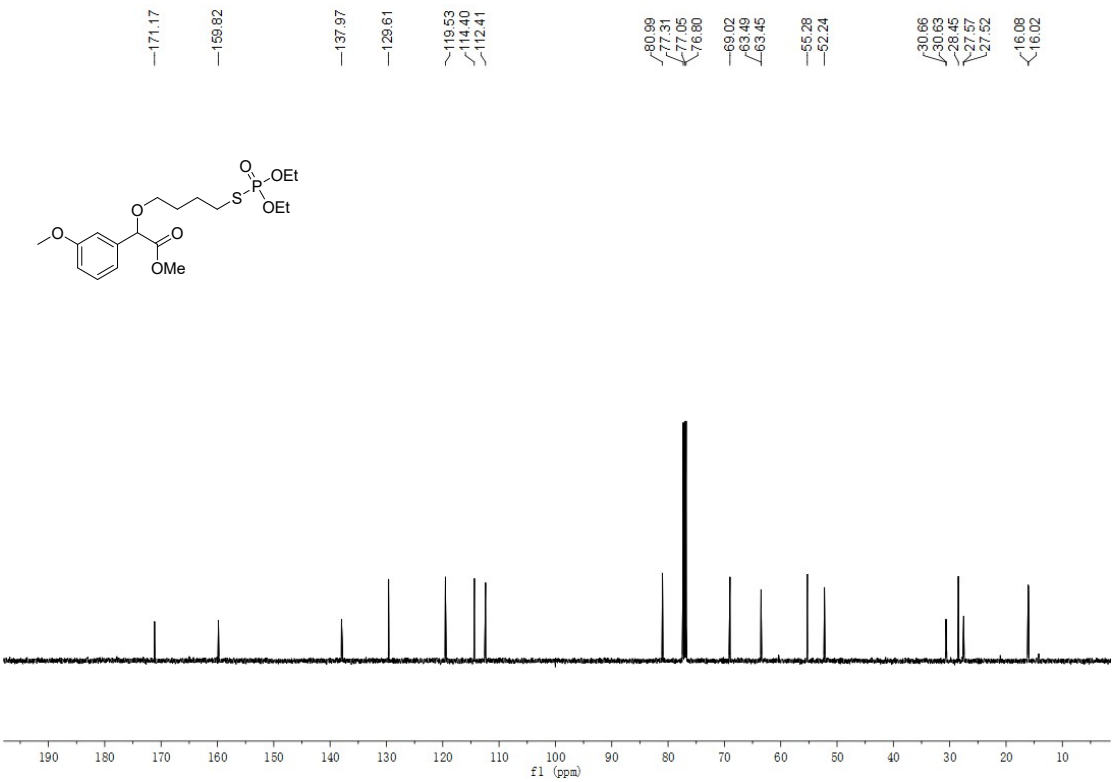
5j ^{13}C NMR (125MHz, $CDCl_3$)



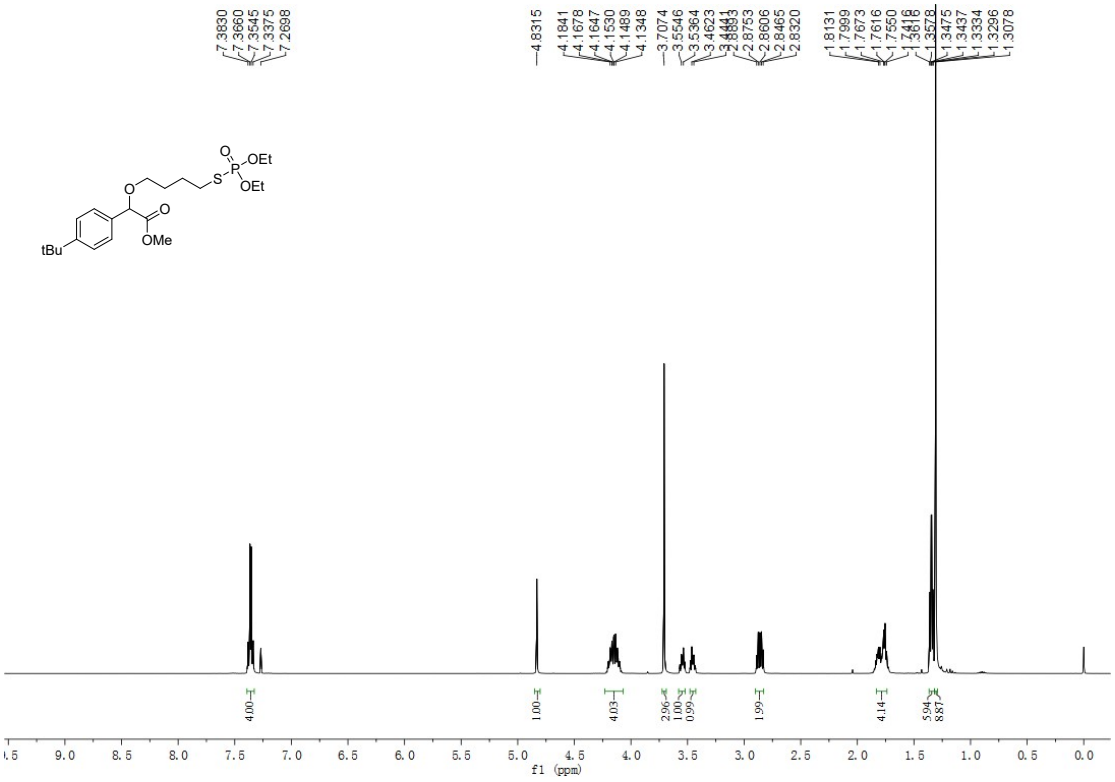
5k ^{1}H NMR (500 MHz, $CDCl_3$)



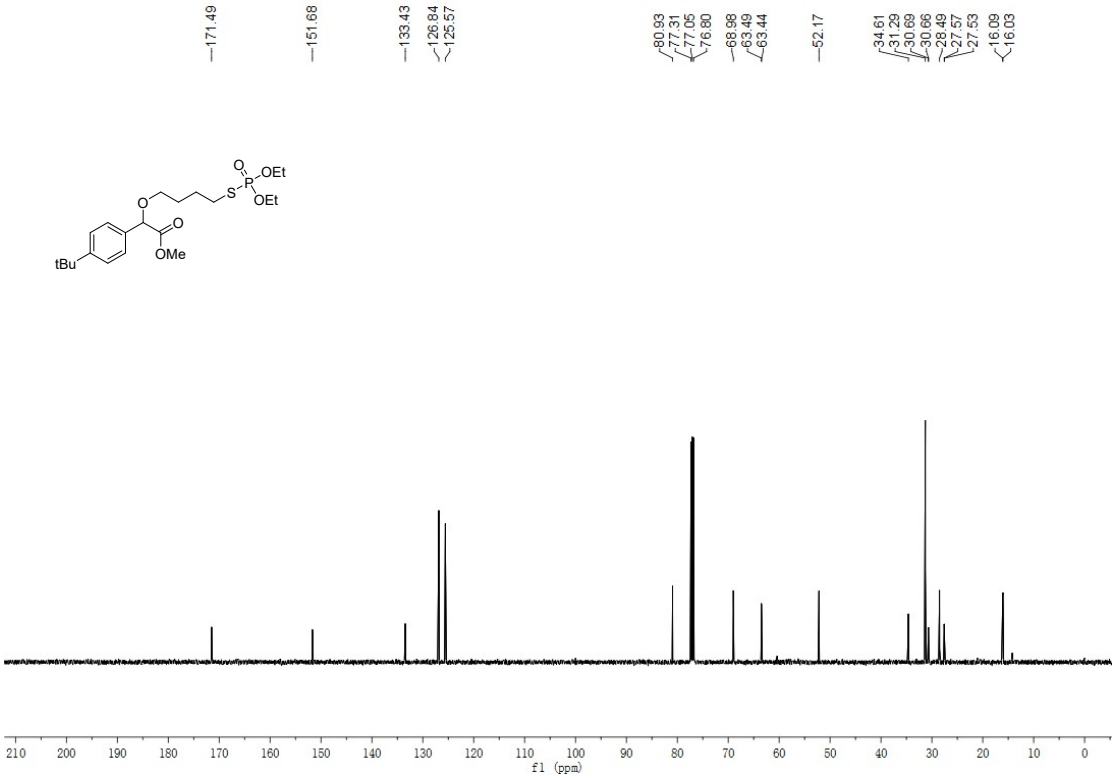
5k ^{13}C NMR (125MHz, $CDCl_3$)



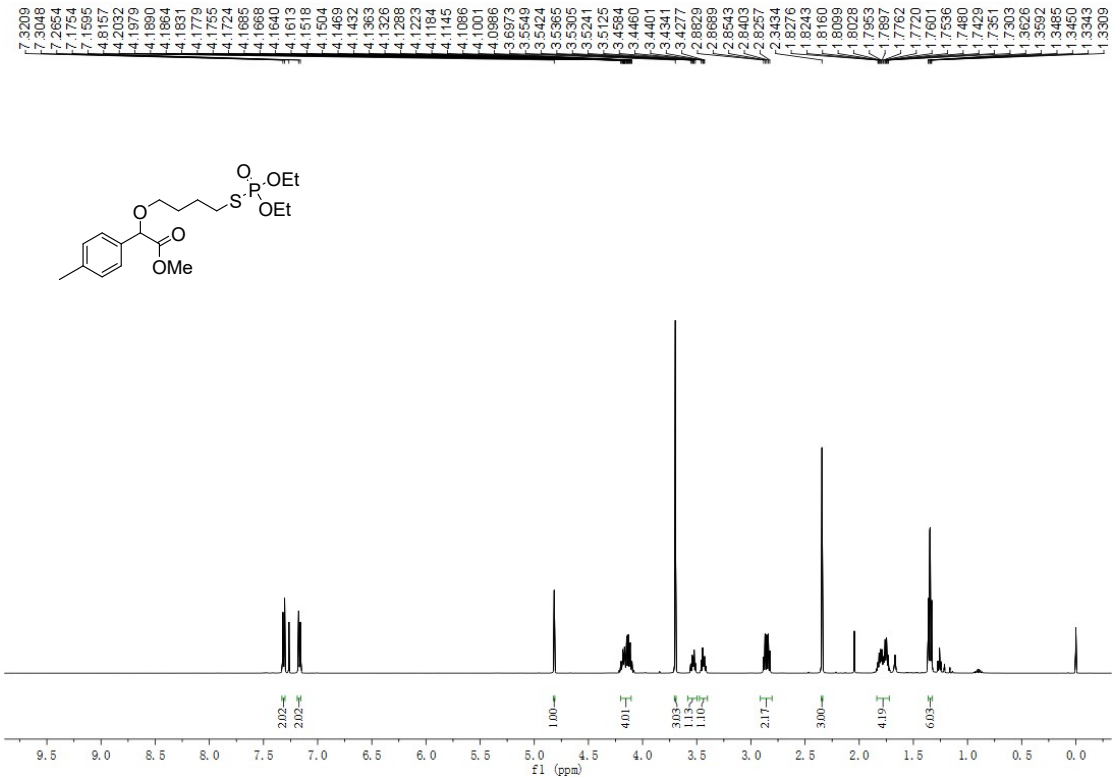
5l ^{1}H NMR (500 MHz, $CDCl_3$)



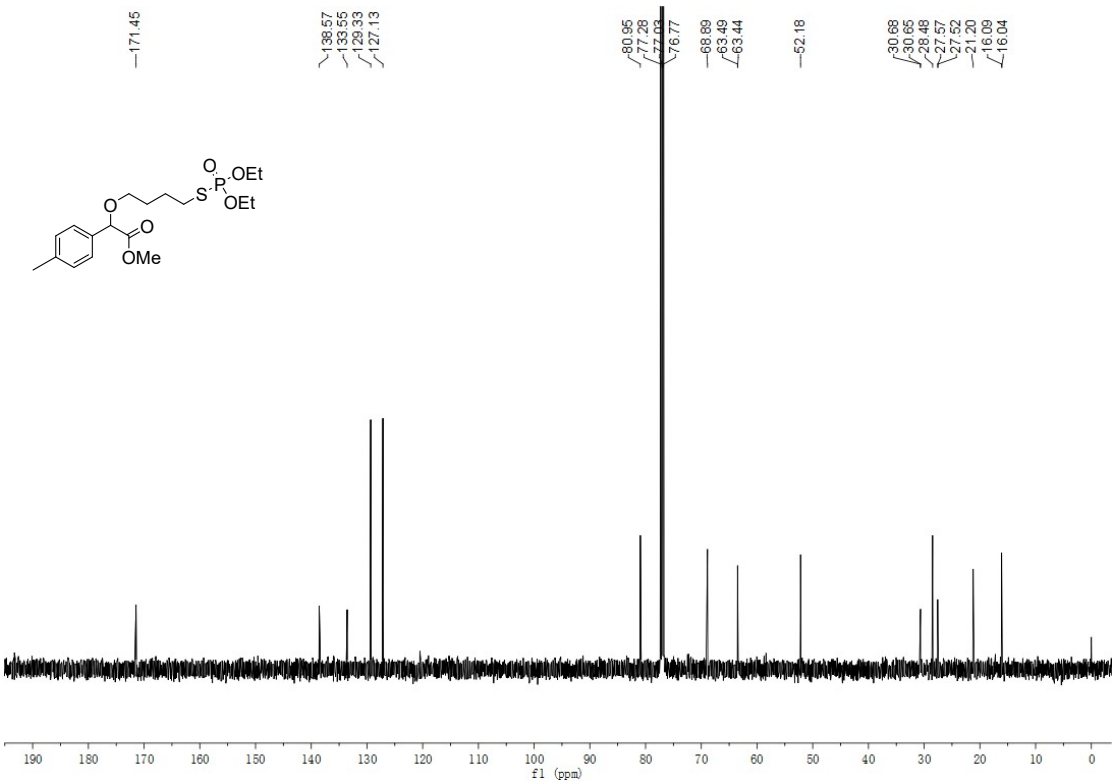
5l ^{13}C NMR (125MHz, $CDCl_3$)



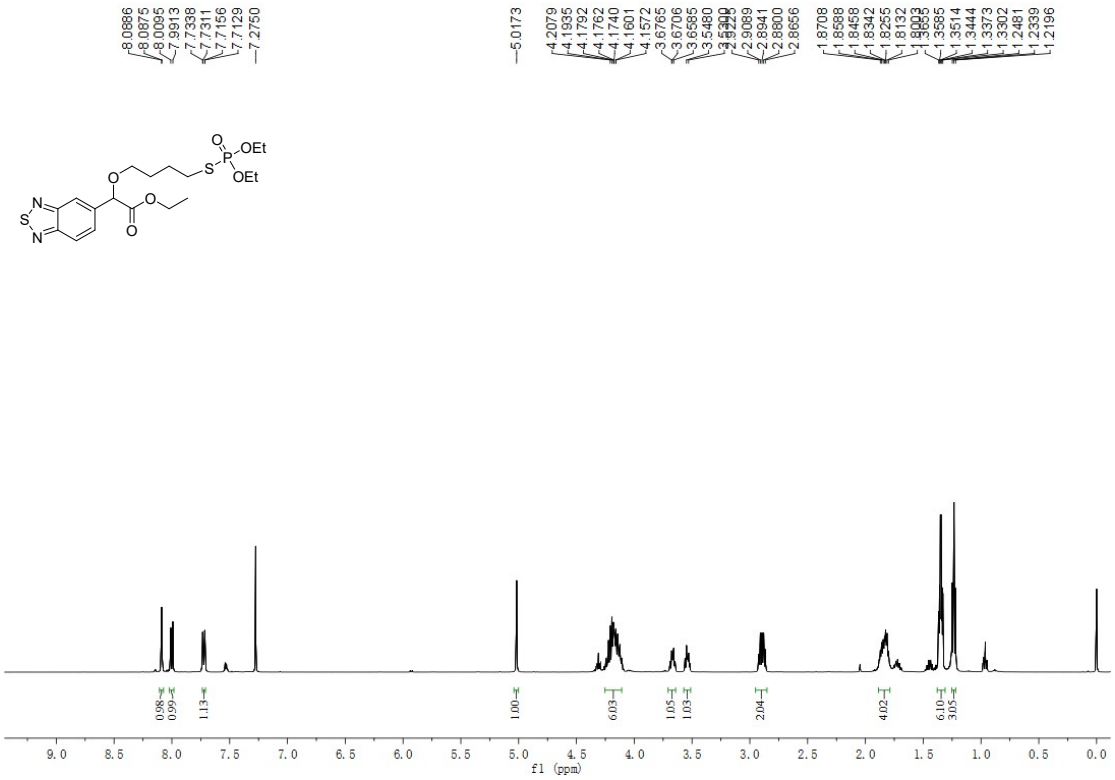
5m ^{1}H NMR (500 MHz, $CDCl_3$)



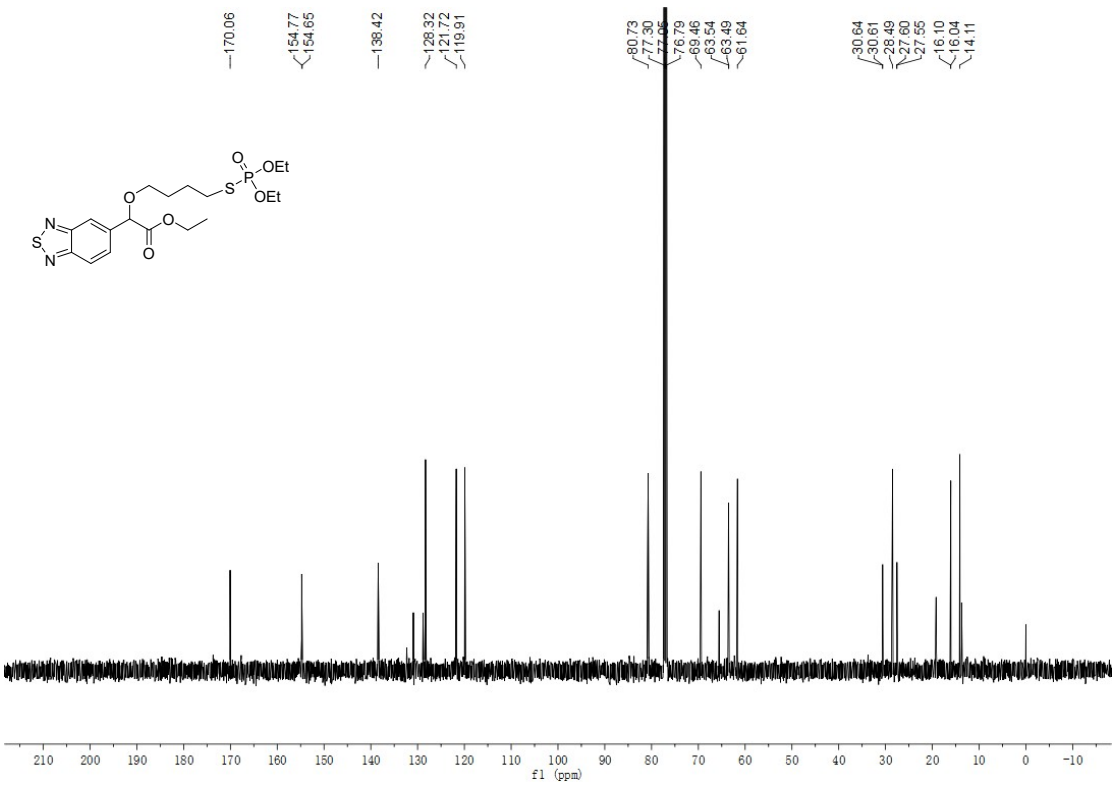
5m ^{13}C NMR (125MHz, $CDCl_3$)



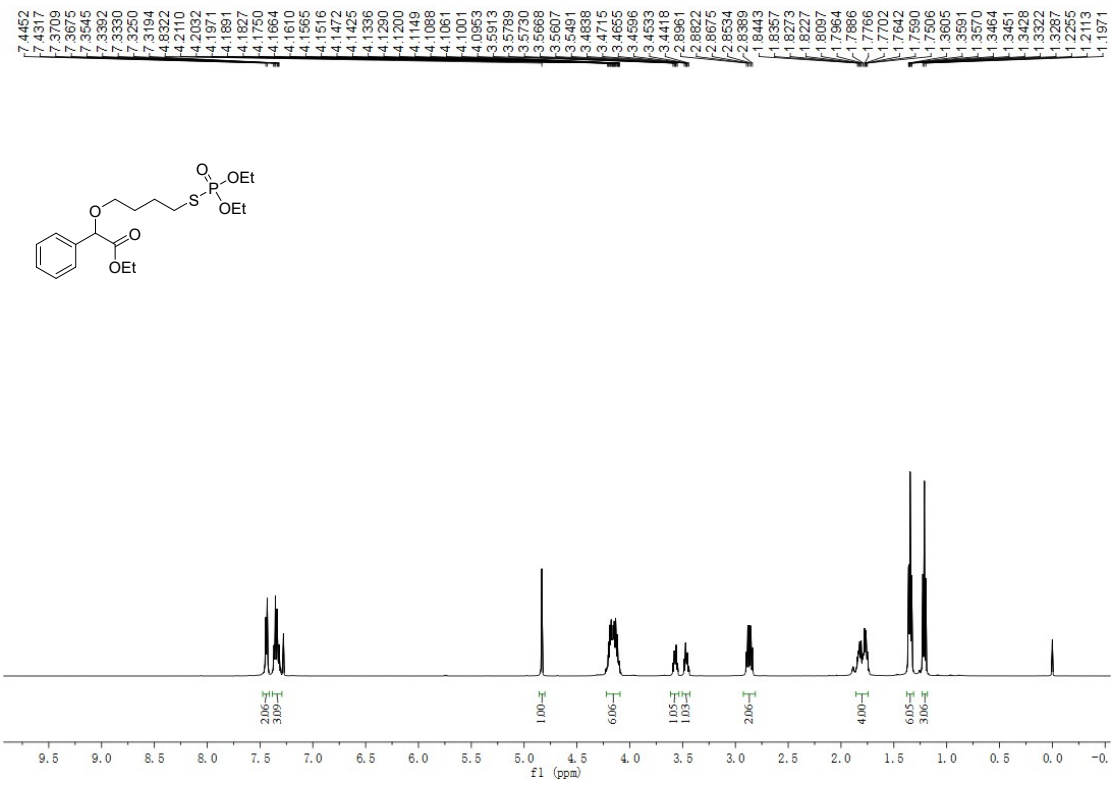
5n ^{1}H NMR (500 MHz, $CDCl_3$)



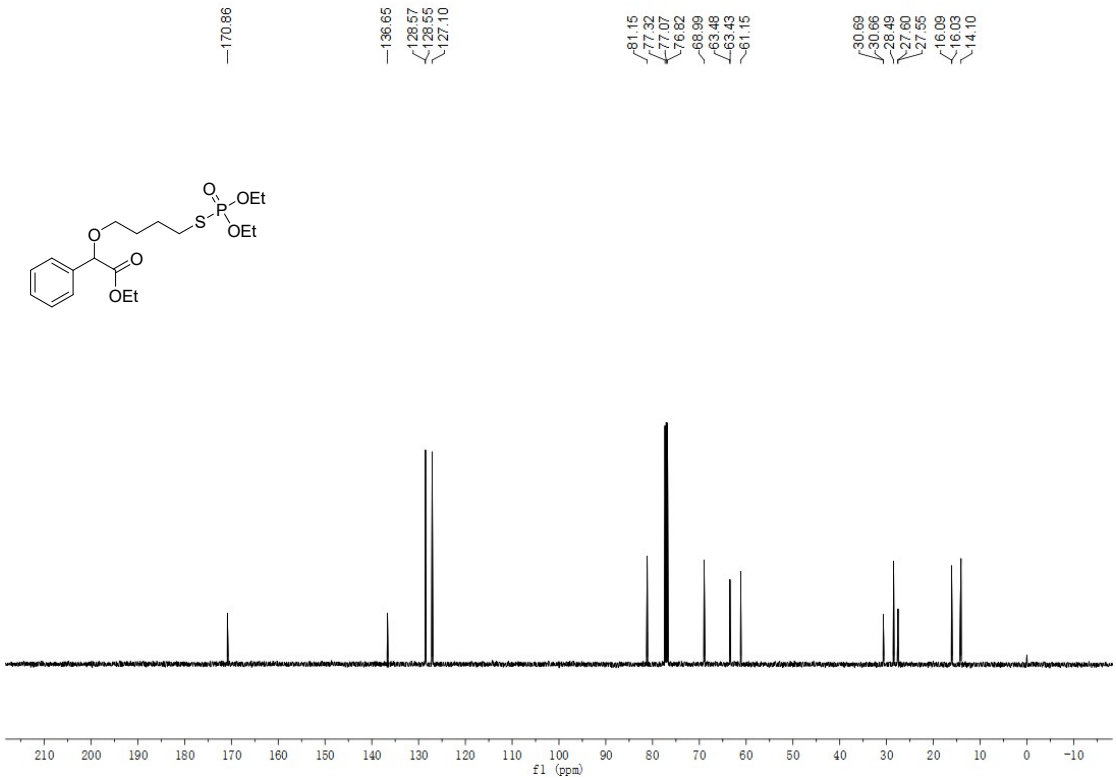
5n ^{13}C NMR (125MHz, $CDCl_3$)



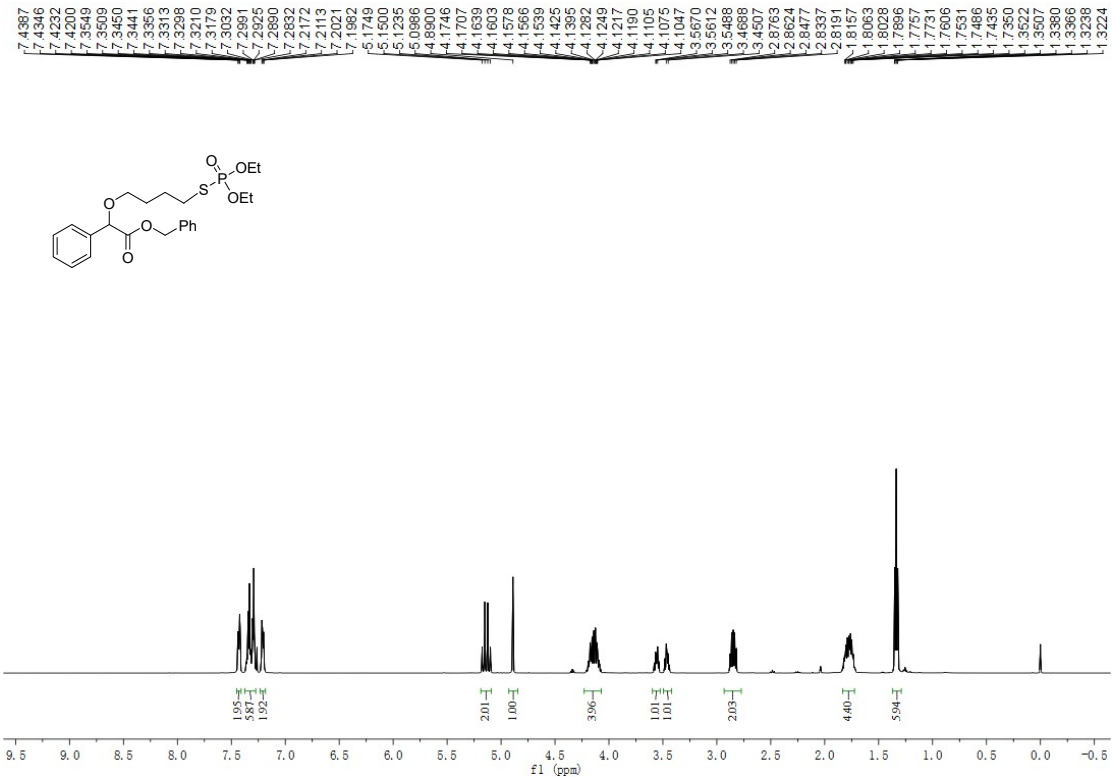
5o ^{1}H NMR (500 MHz, $CDCl_3$)



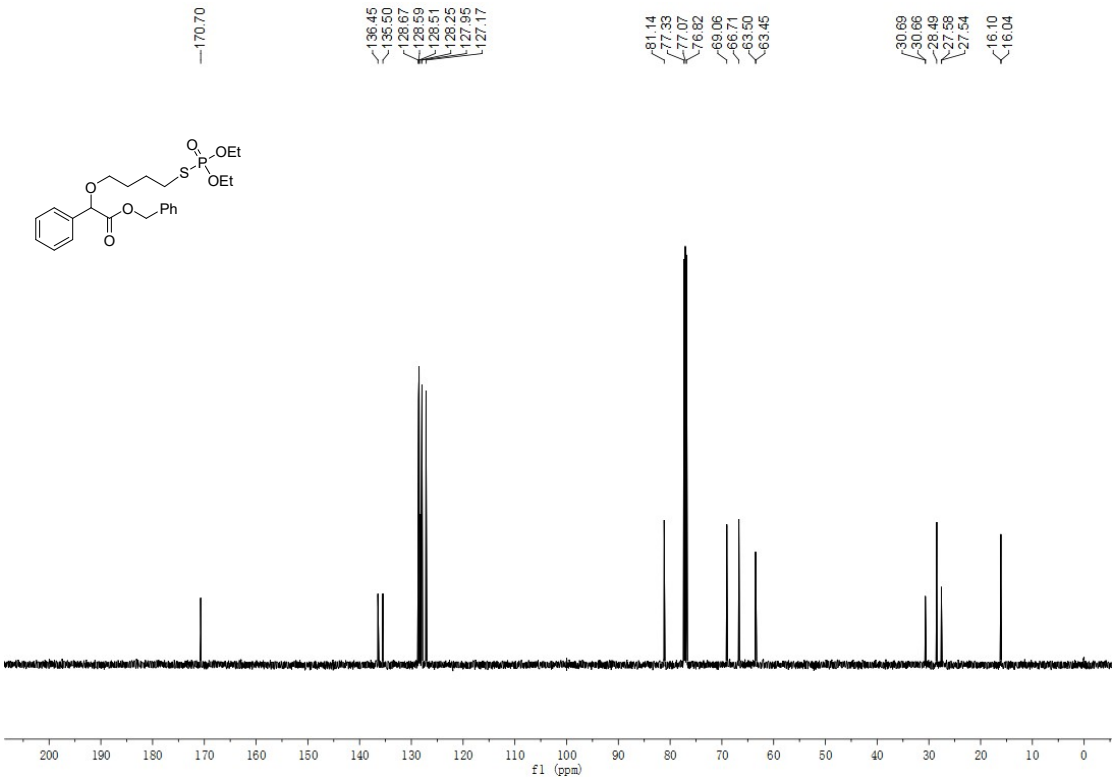
5o ^{13}C NMR (125MHz, $CDCl_3$)



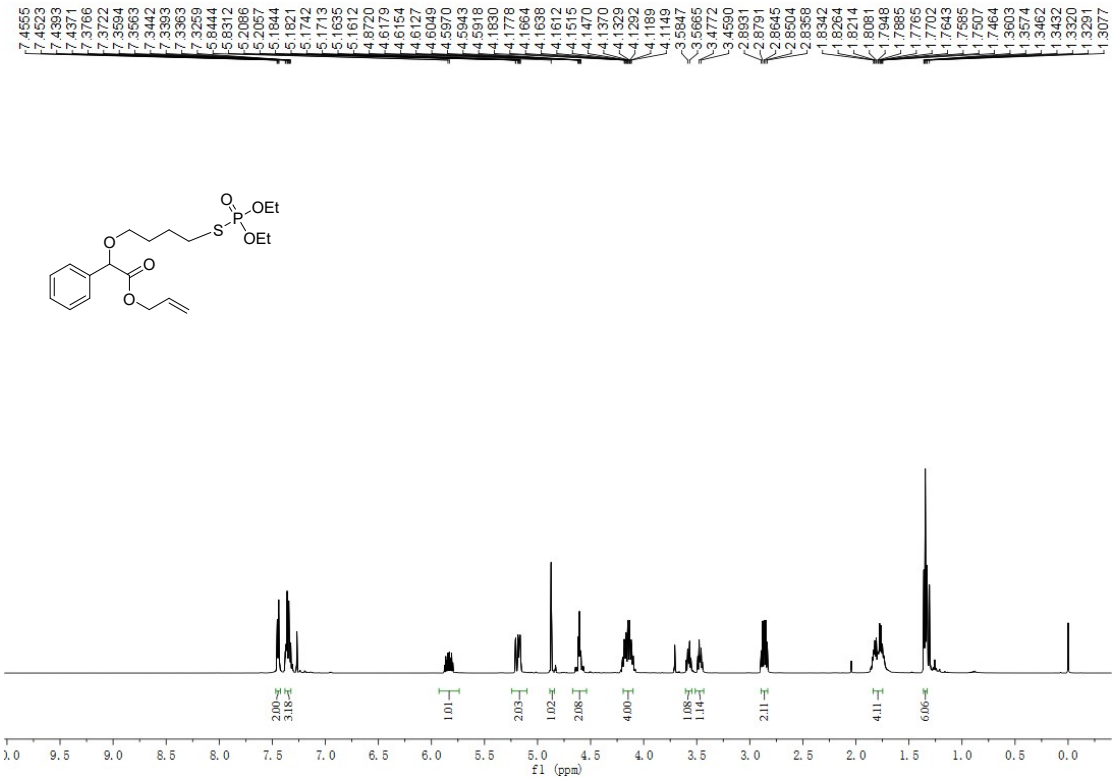
5p ^{1}H NMR (500 MHz, $CDCl_3$)



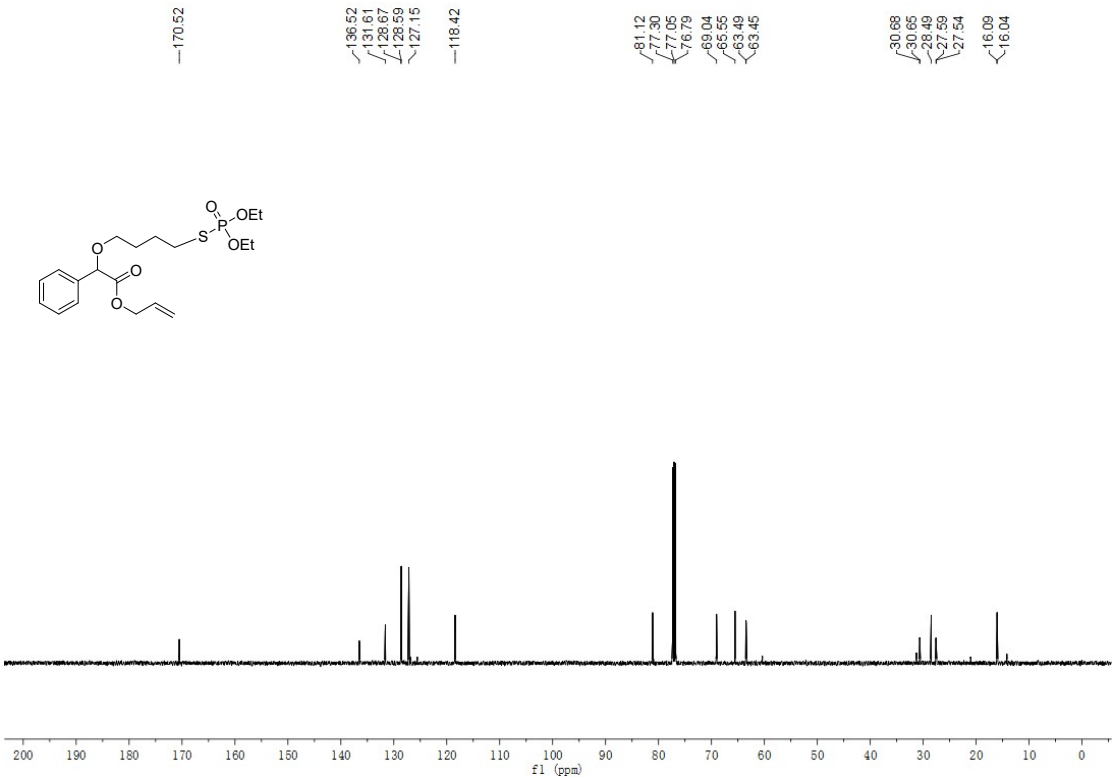
5p ^{13}C NMR (125MHz, $CDCl_3$)



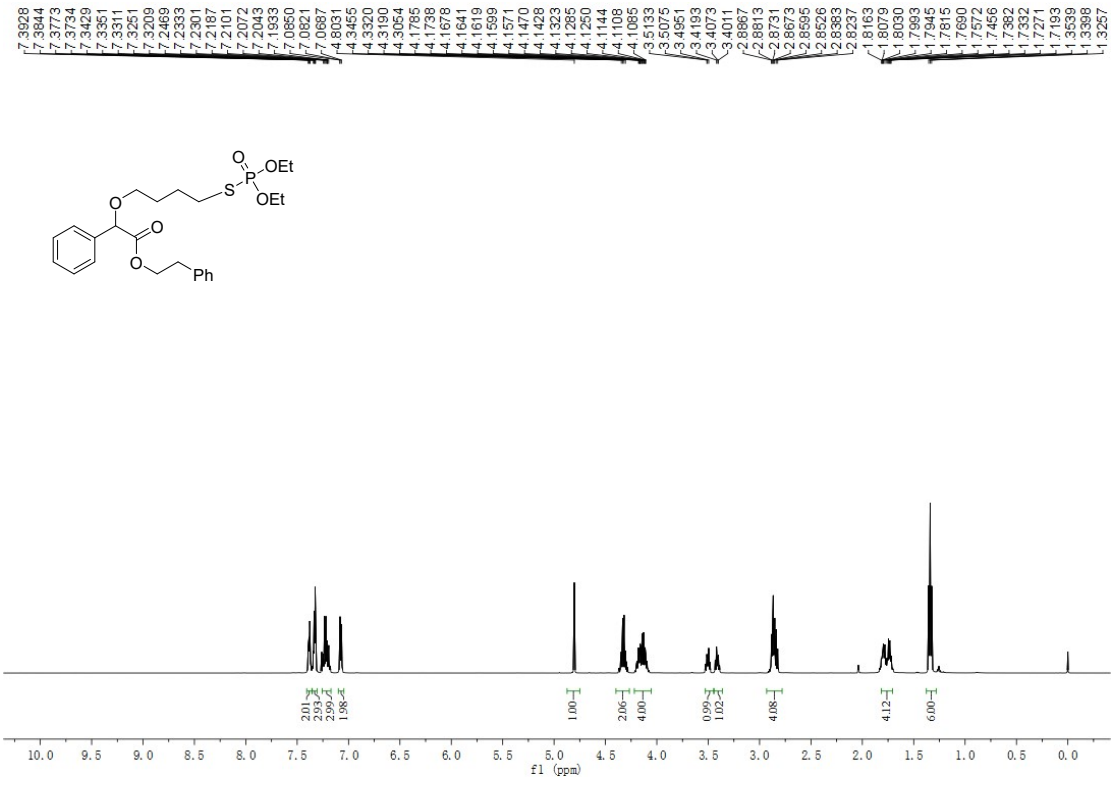
5q ^{1}H NMR (500 MHz, $CDCl_3$)



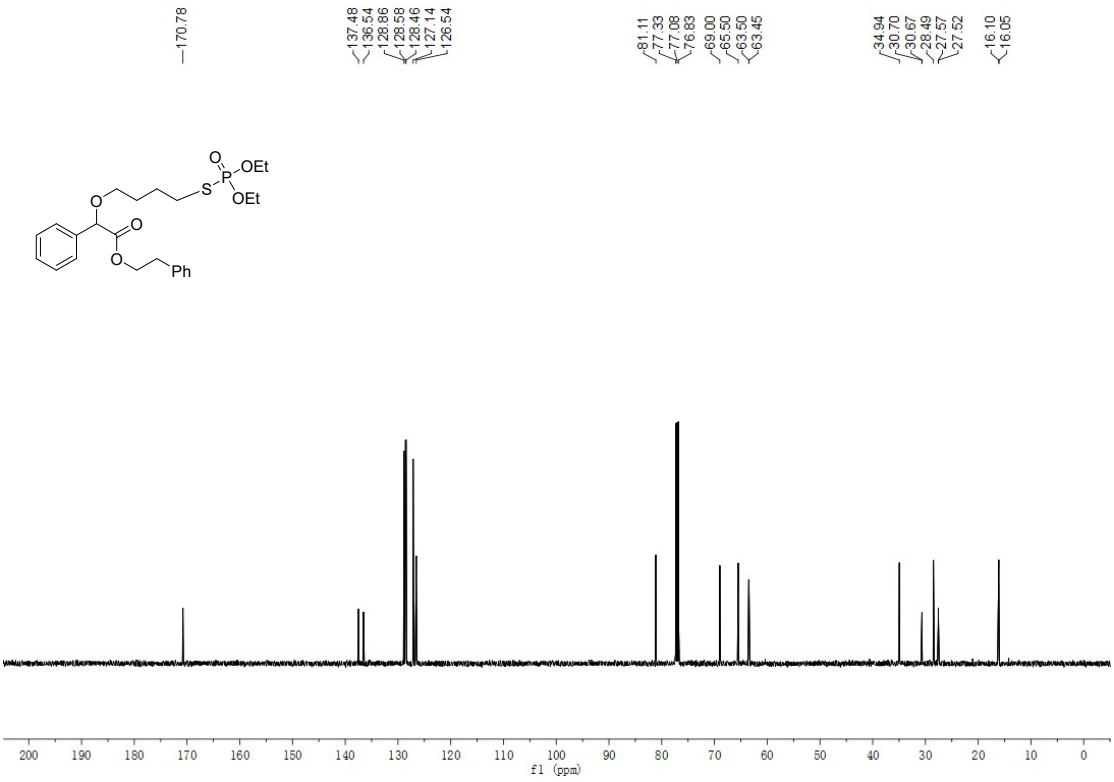
5q ^{13}C NMR (125MHz, $CDCl_3$)



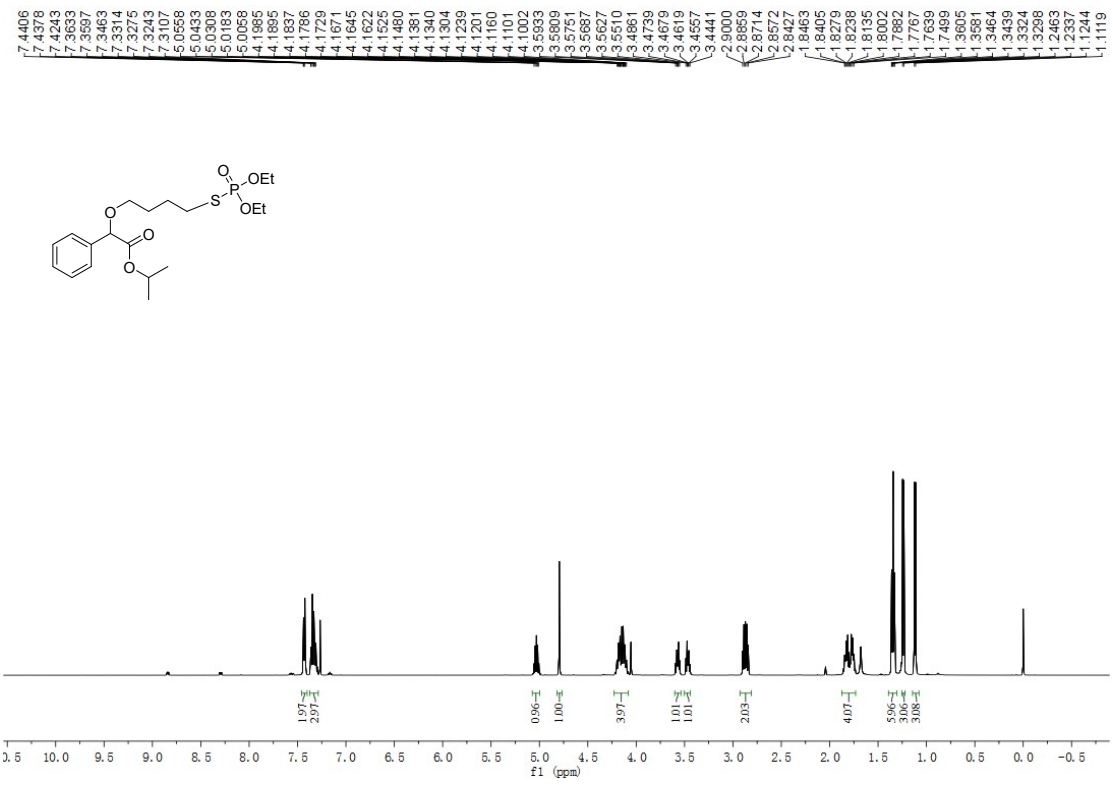
5r ^{1}H NMR (500 MHz, $CDCl_3$)



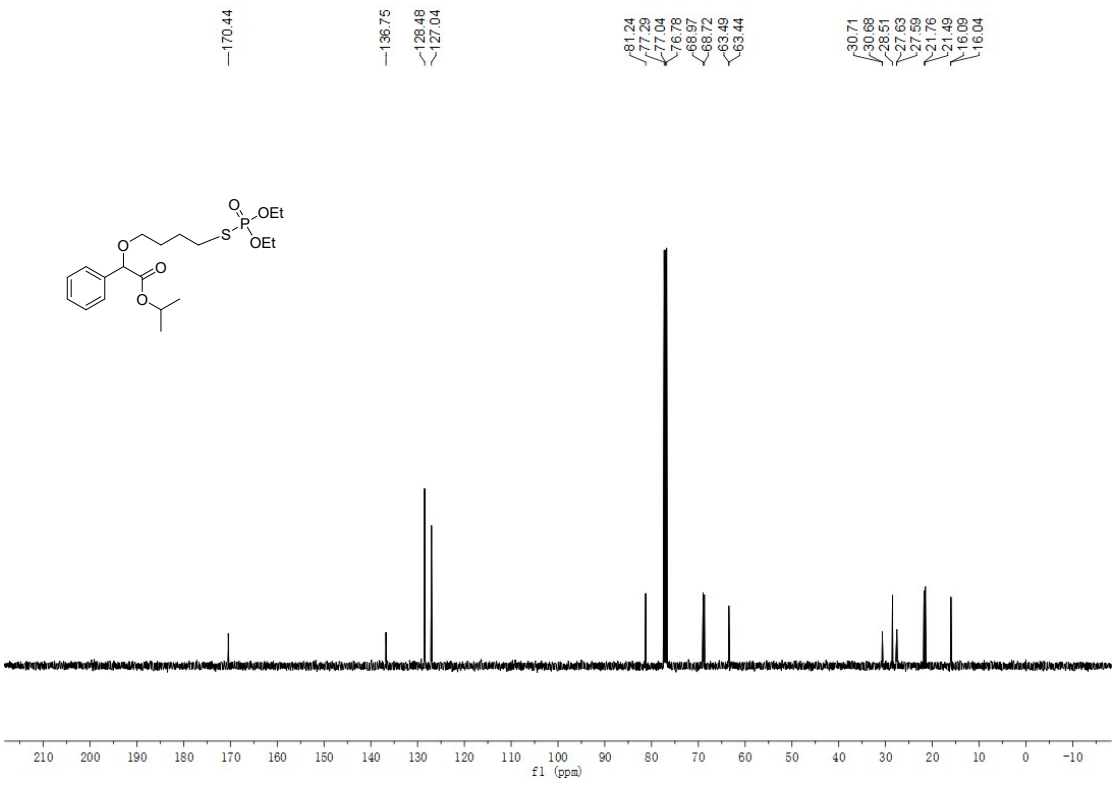
5r ^{13}C NMR (125MHz, $CDCl_3$)



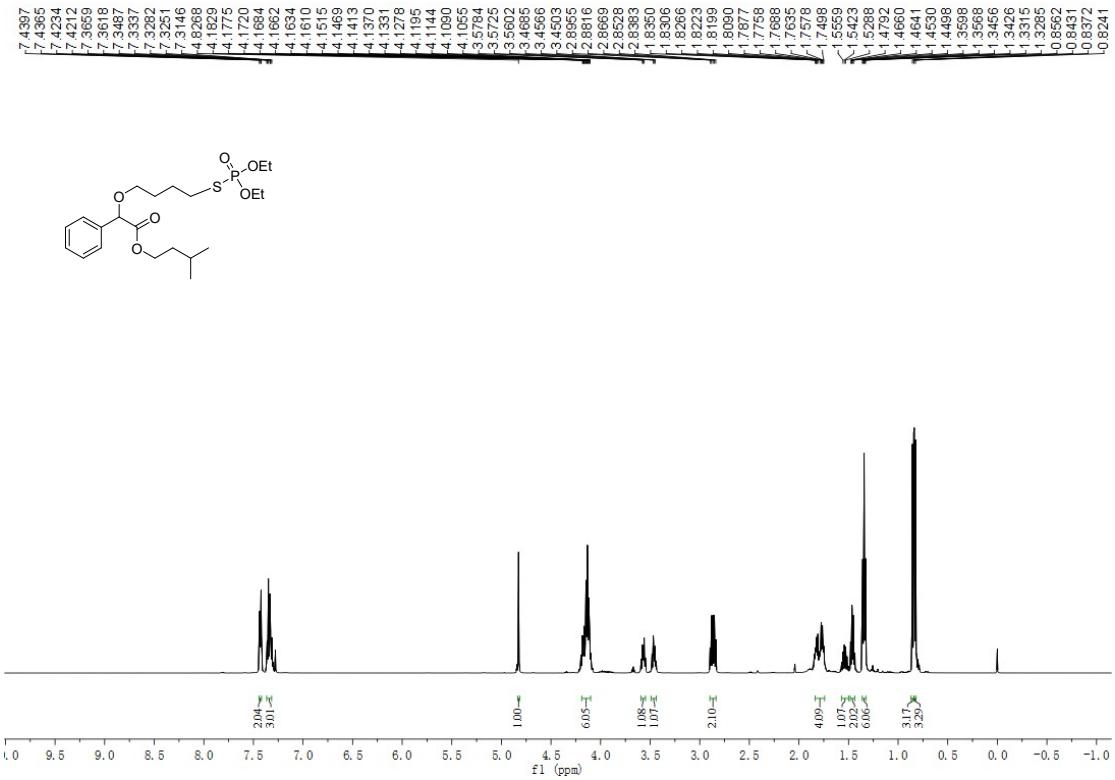
5s ^{1}H NMR (500 MHz, $CDCl_3$)



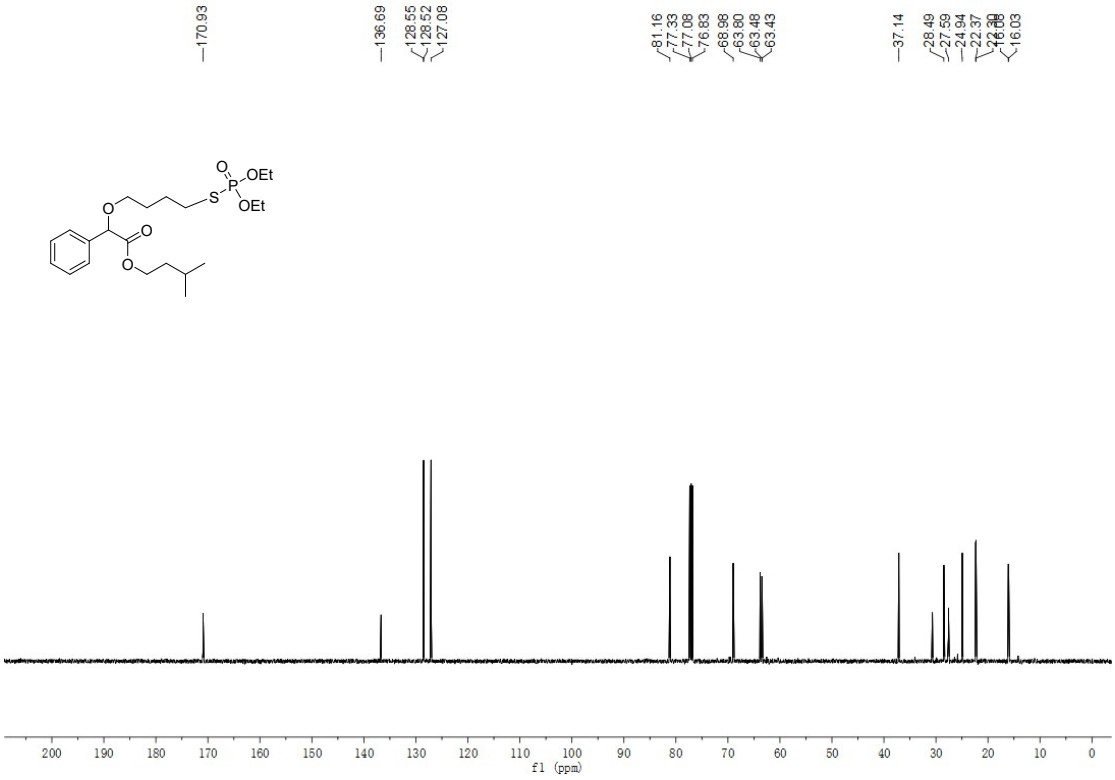
5s ^{13}C NMR (125MHz, $CDCl_3$)



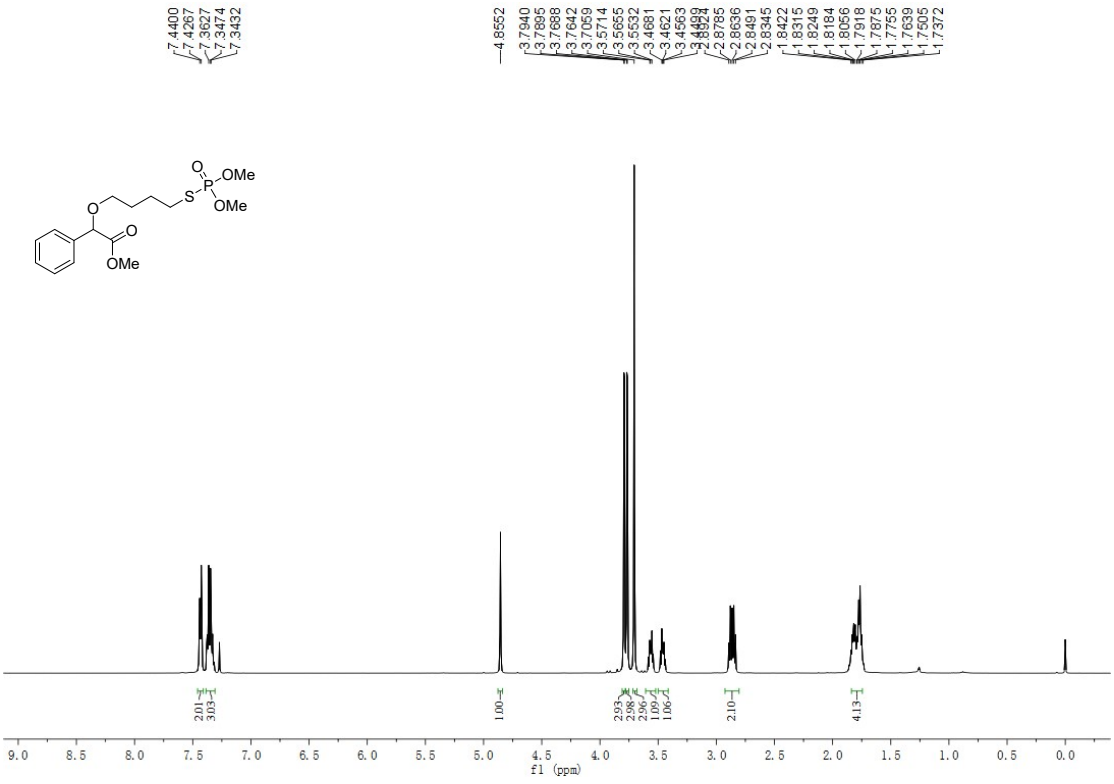
5t ^{1}H NMR (500 MHz, $CDCl_3$)



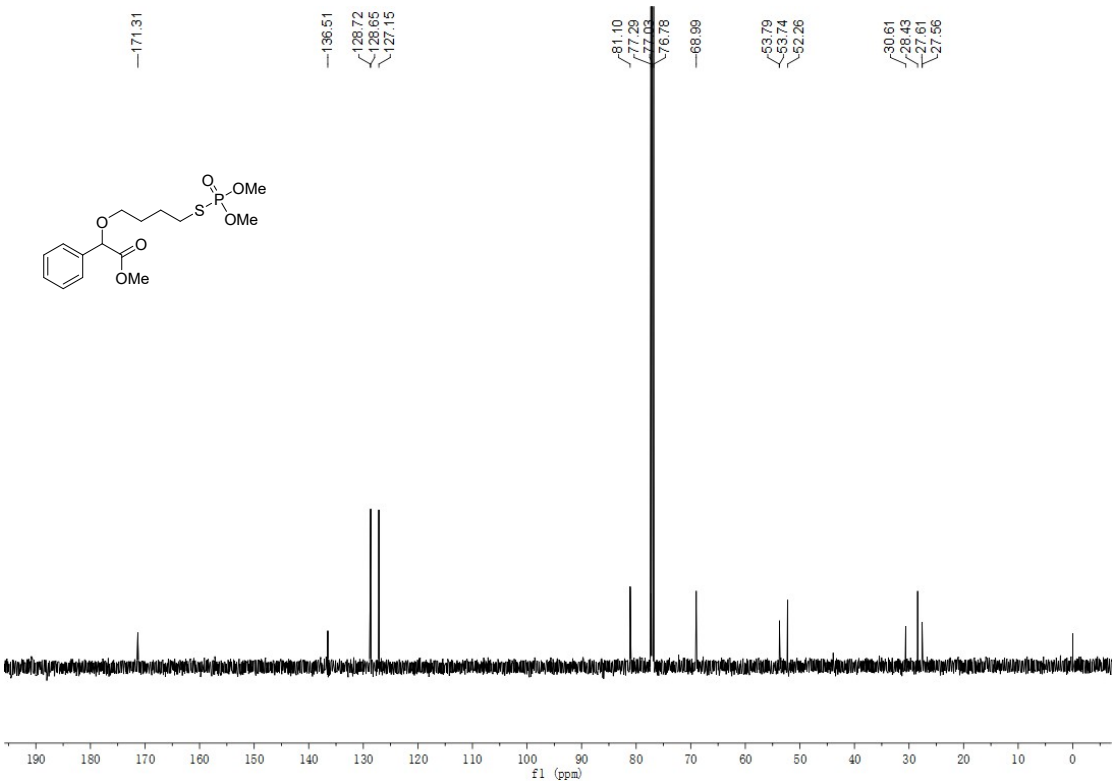
5t ^{13}C NMR (125MHz, $CDCl_3$)



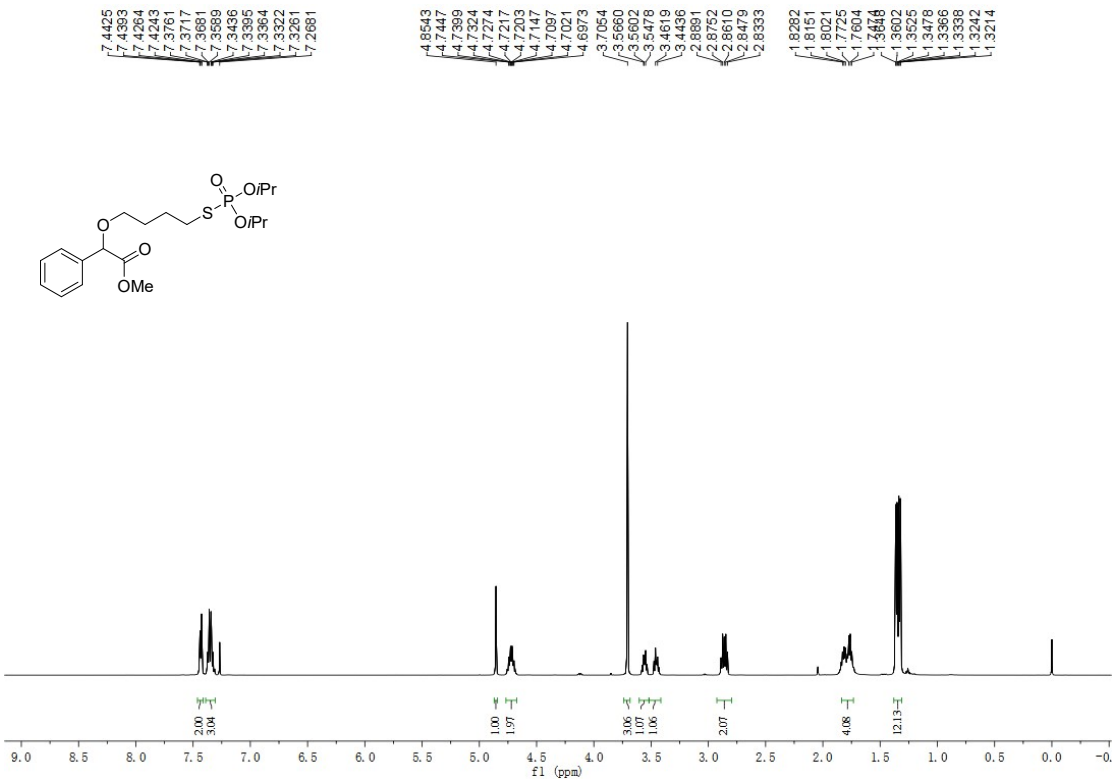
5u ^{1}H NMR (500 MHz, $CDCl_3$)



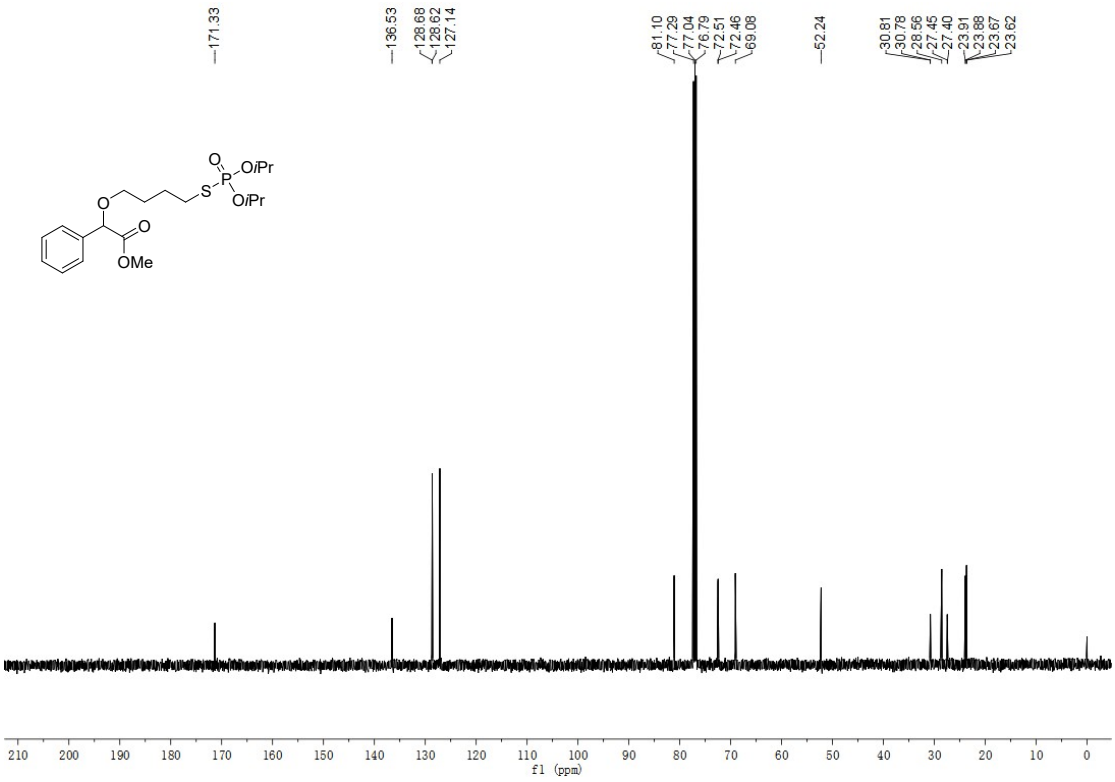
5u ^{13}C NMR (125MHz, $CDCl_3$)



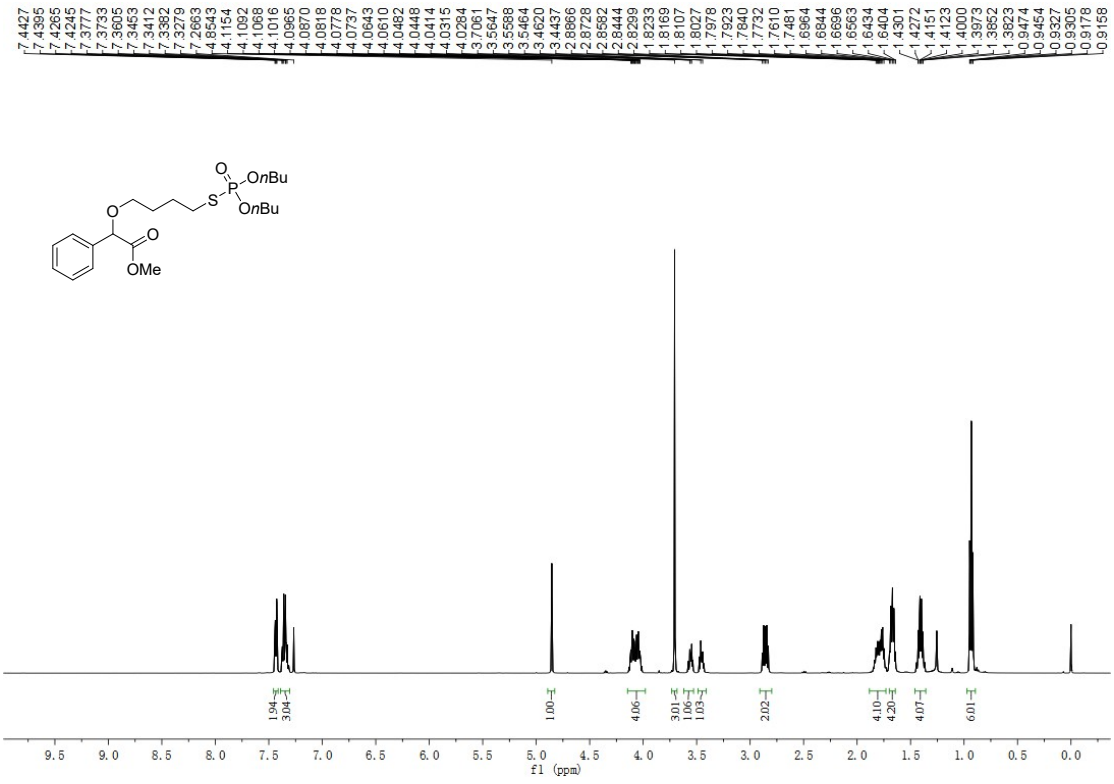
5v ^{1}H NMR (500 MHz, $CDCl_3$)



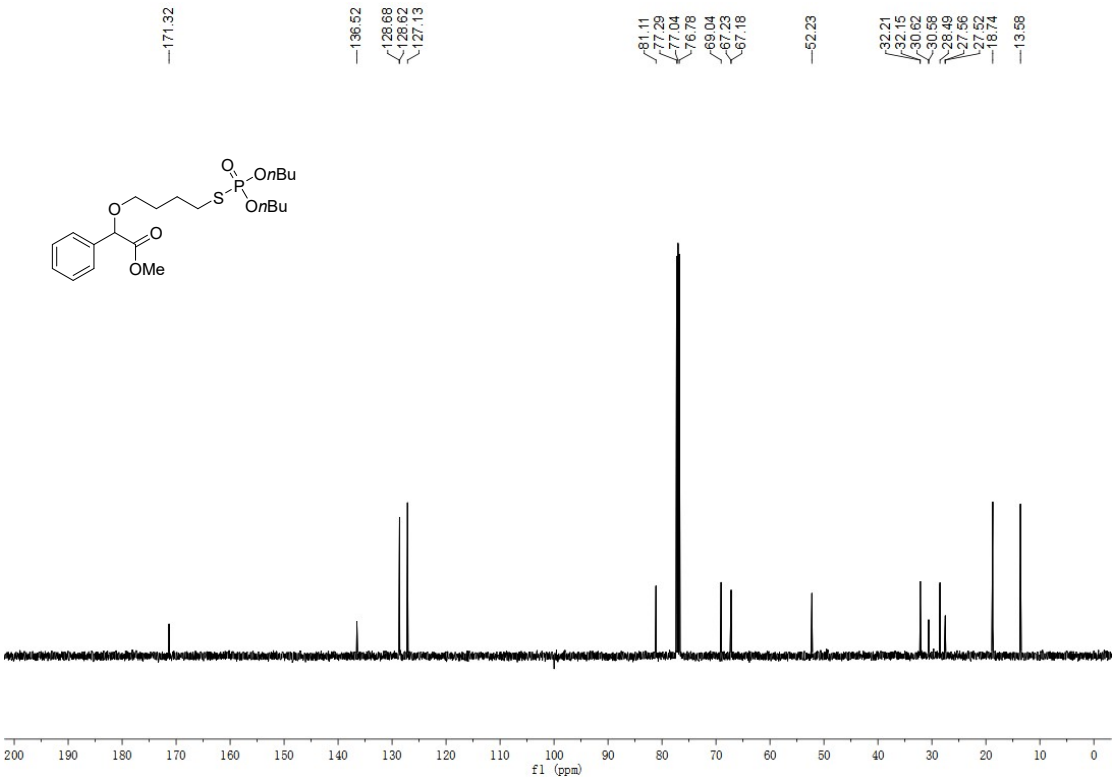
5v ^{13}C NMR (125MHz, $CDCl_3$)



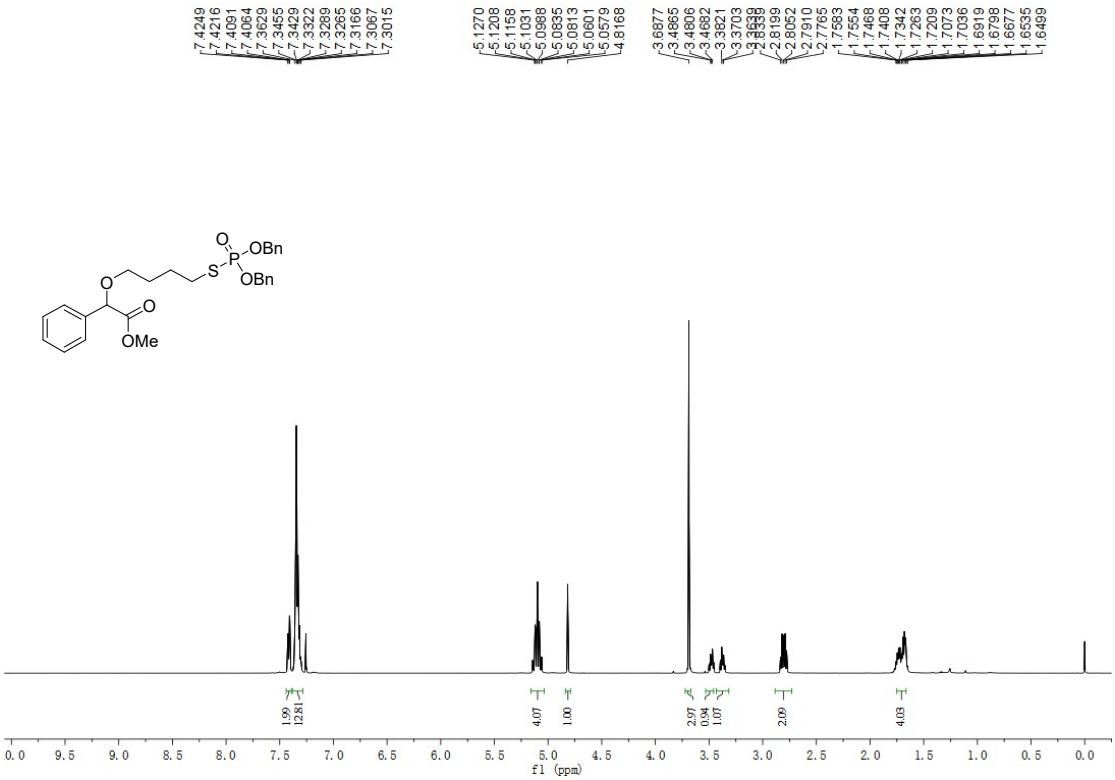
5w ^{1}H NMR (500 MHz, $CDCl_3$)



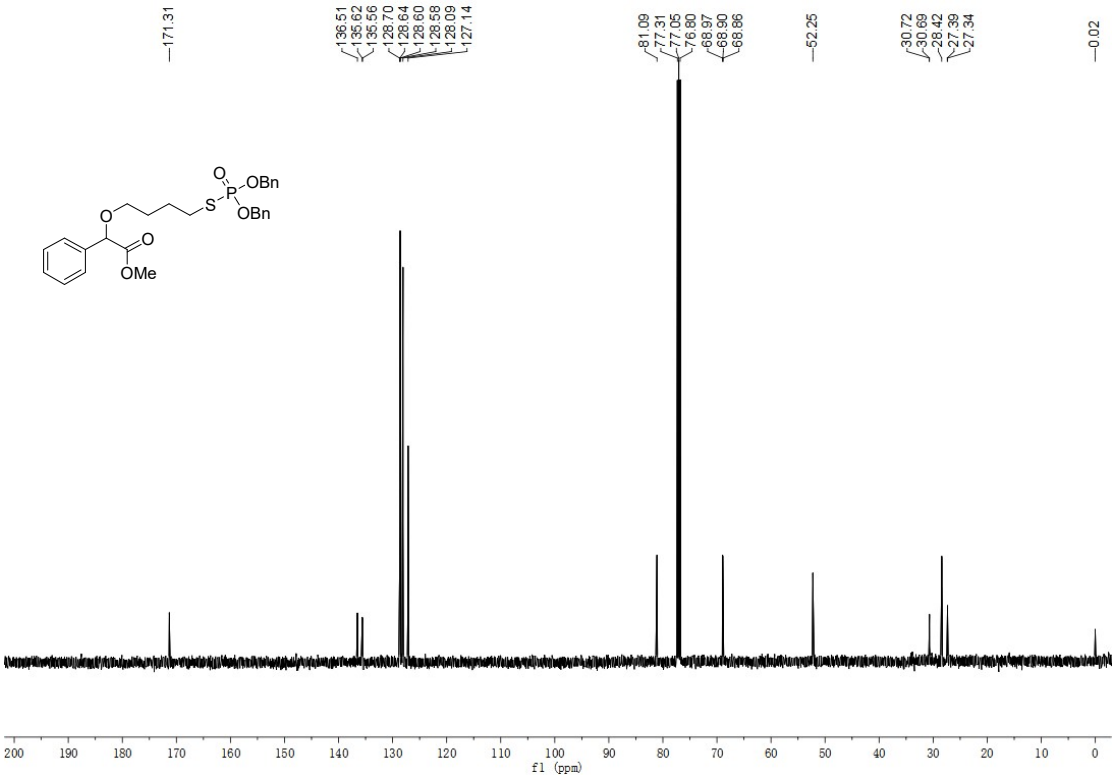
5w ^{13}C NMR (125MHz, $CDCl_3$)



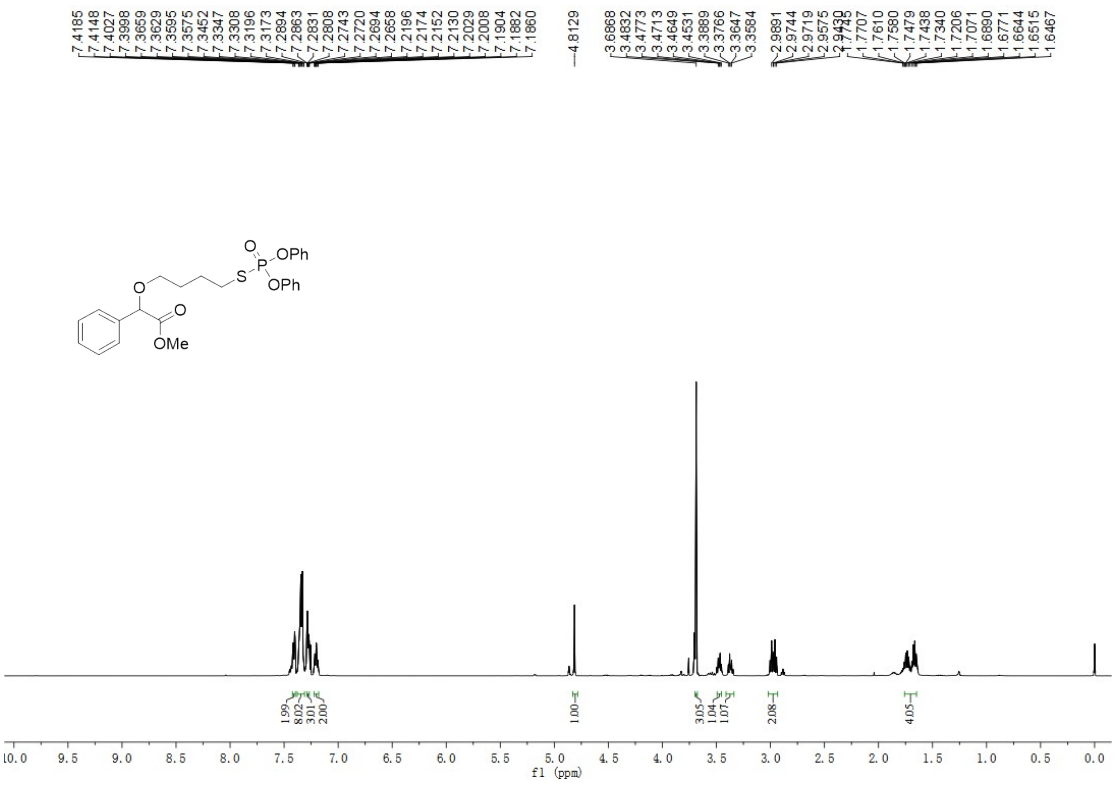
5x ^{1}H NMR (500 MHz, $CDCl_3$)



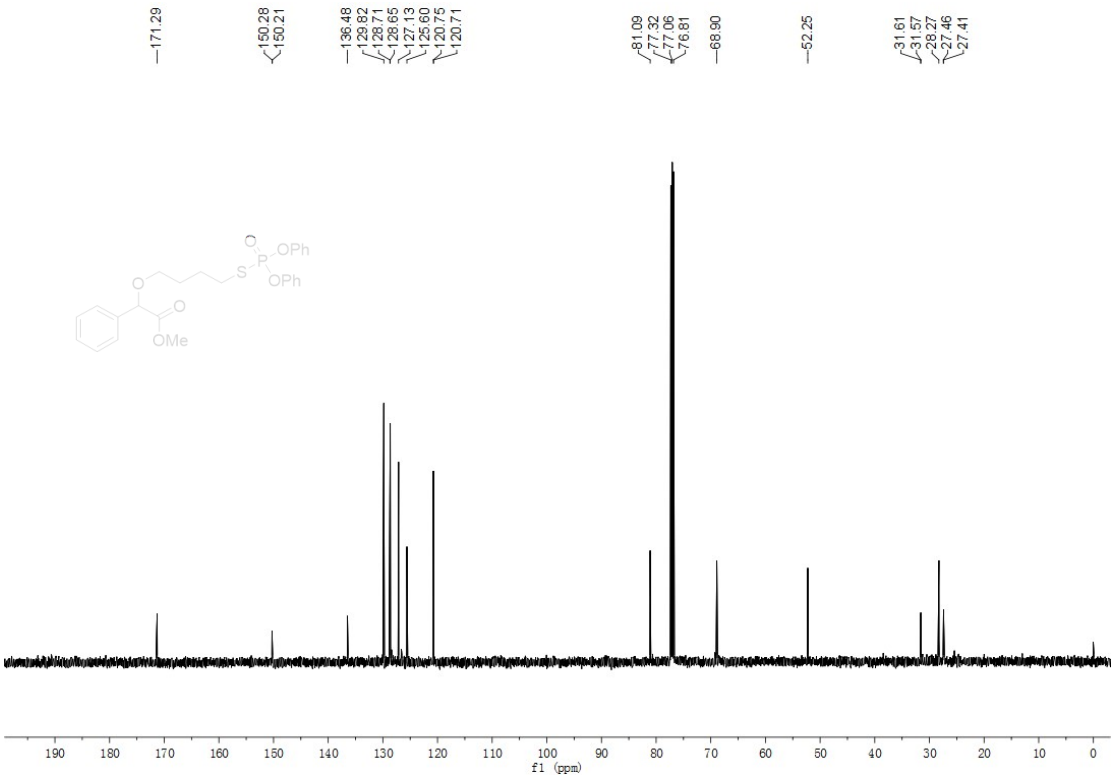
5x ^{13}C NMR (125MHz, $CDCl_3$)



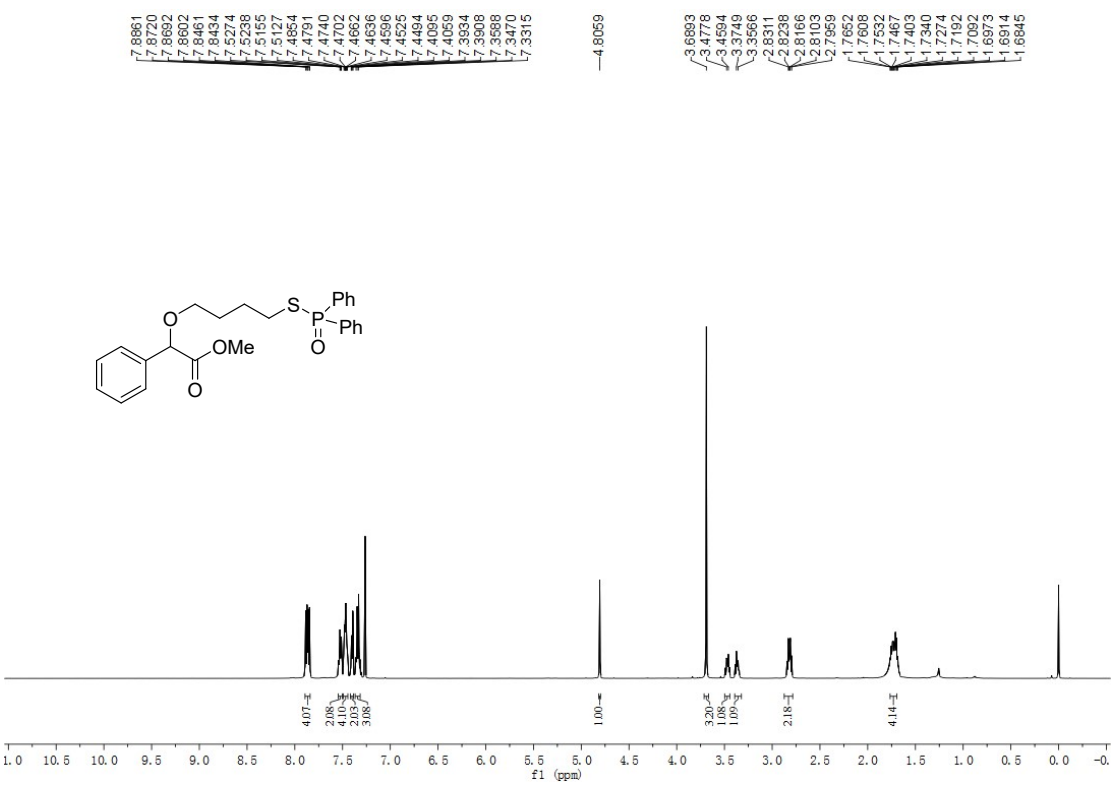
5y ^{1}H NMR (500 MHz, $CDCl_3$)



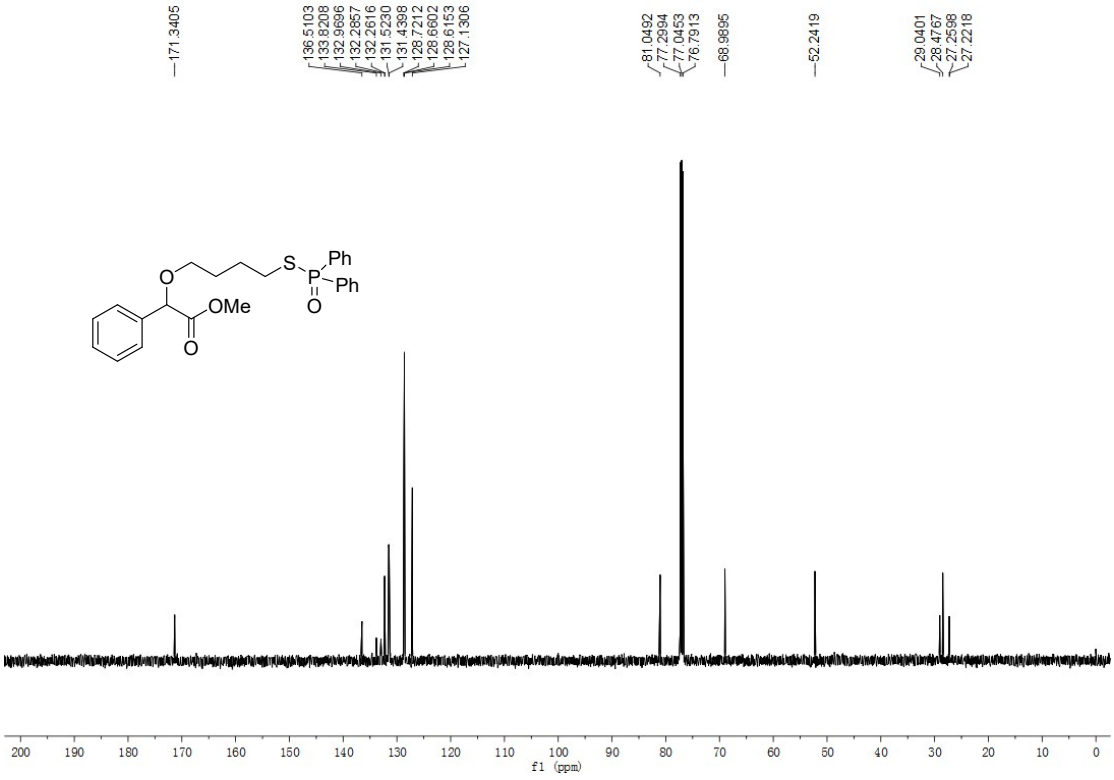
5y ^{13}C NMR (125MHz, $CDCl_3$)



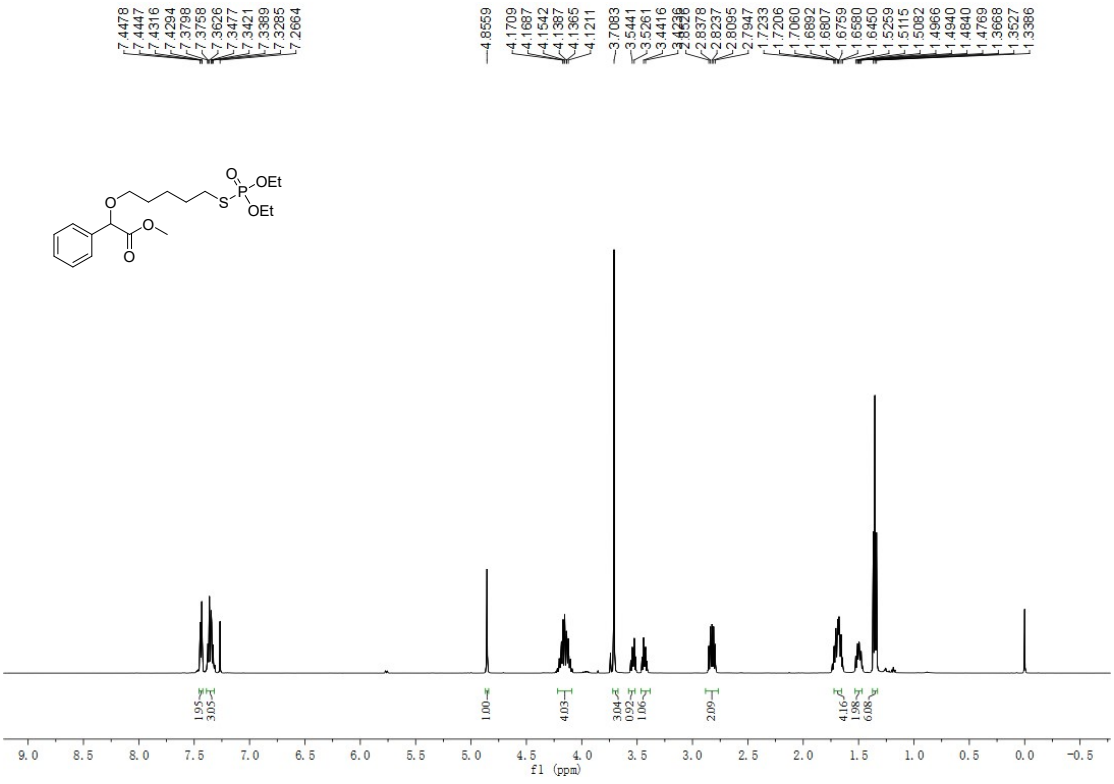
5z ^{1}H NMR (500 MHz, $CDCl_3$)



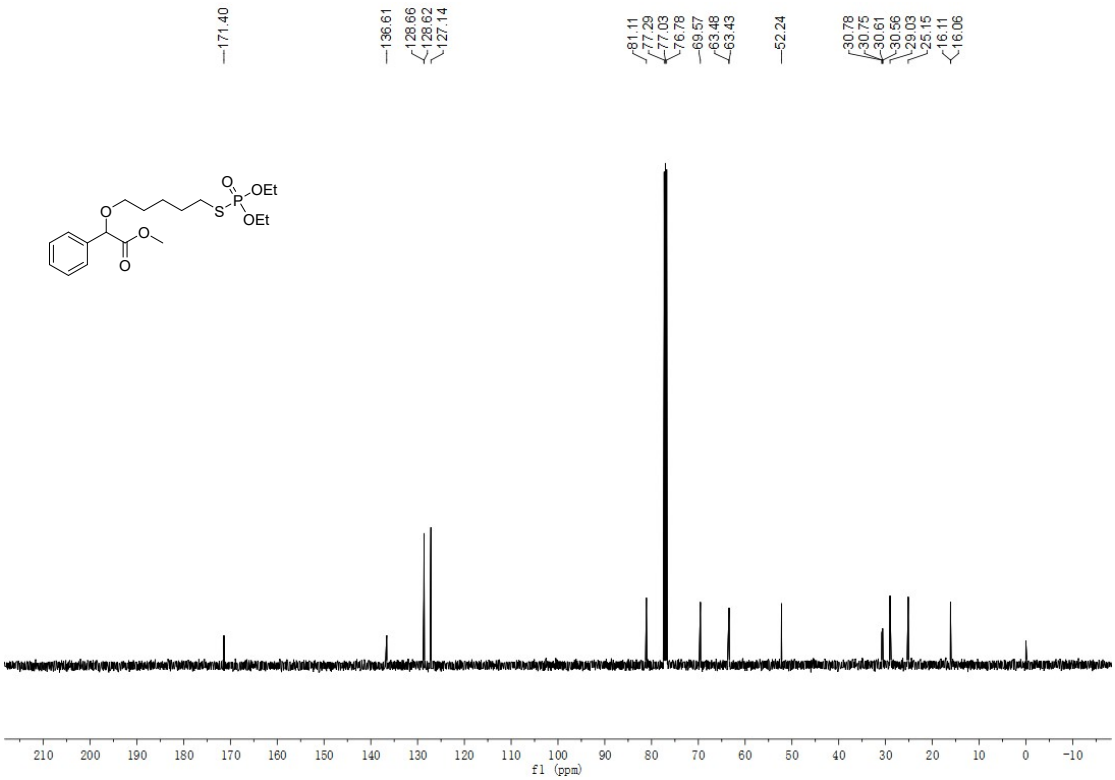
5z ^{13}C NMR (125MHz, $CDCl_3$)



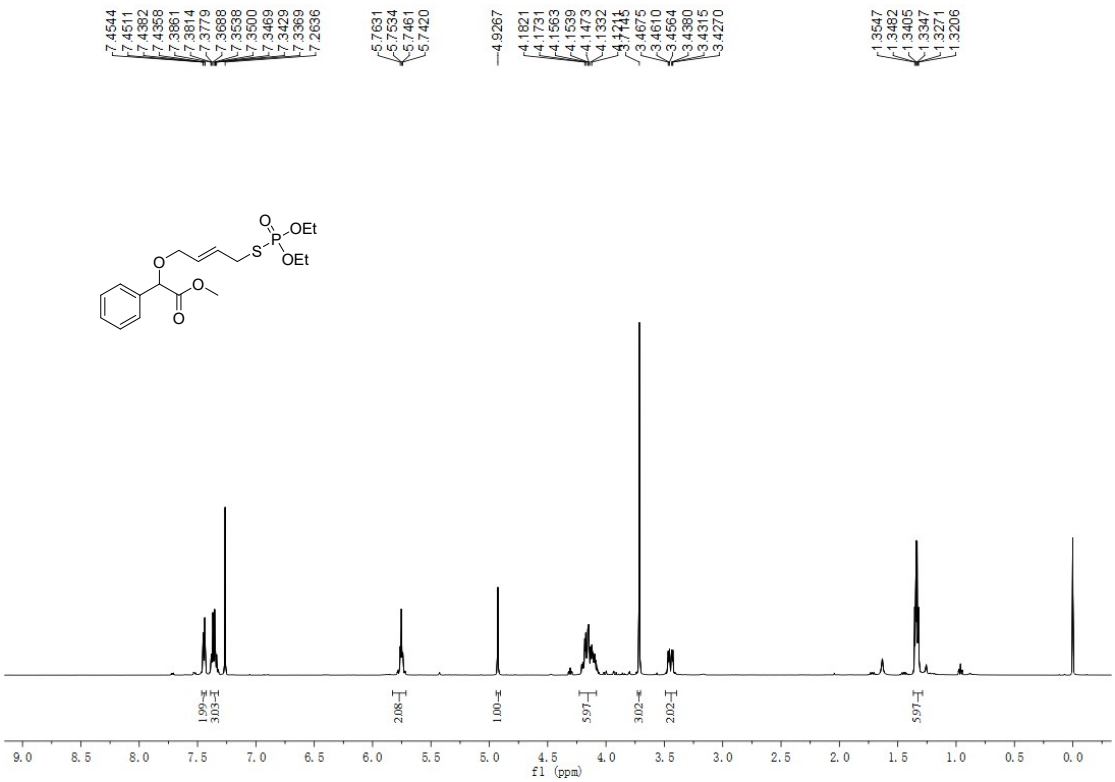
5z' ^{1}H NMR (500 MHz, $CDCl_3$)



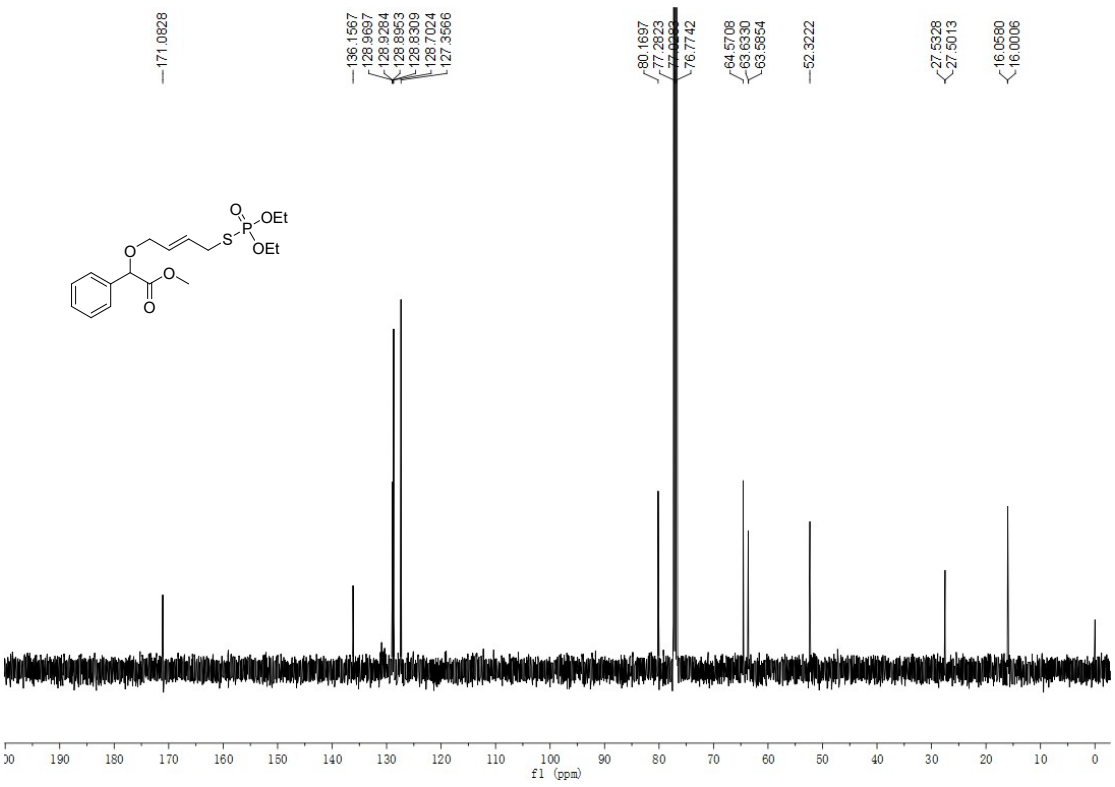
5z' ^{13}C NMR (125MHz, $CDCl_3$)



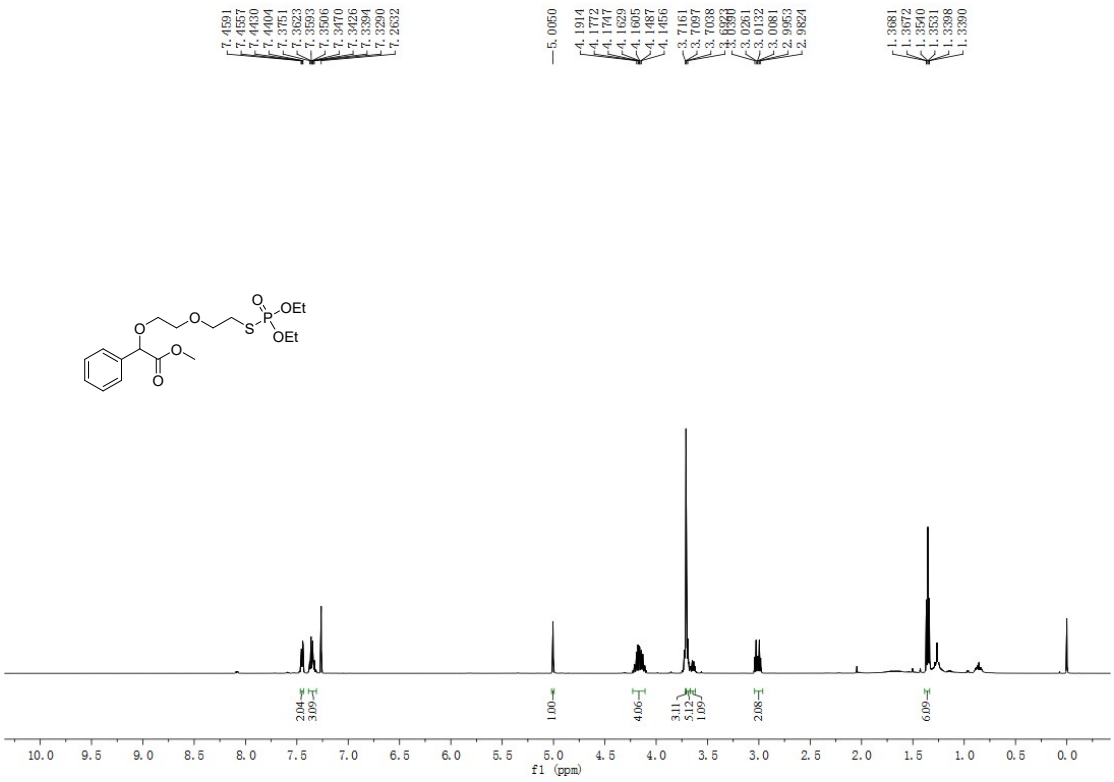
5z'' ^{1}H NMR (500 MHz, $CDCl_3$)



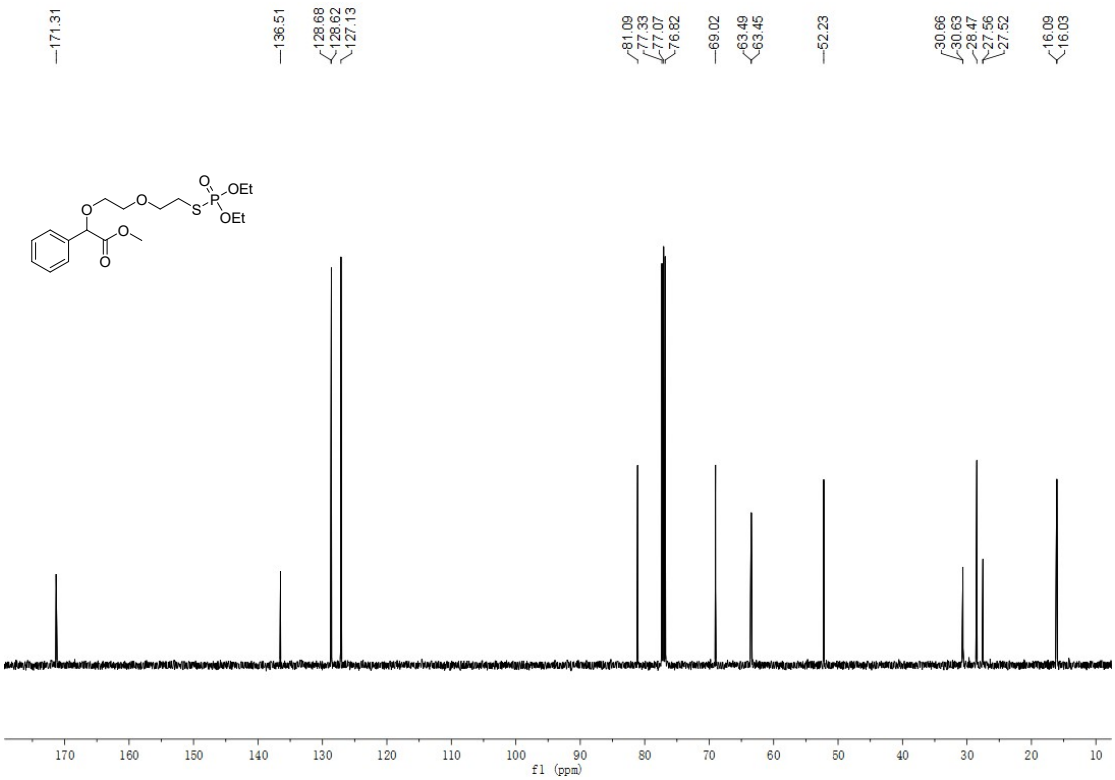
5z'' ^{13}C NMR (125MHz, $CDCl_3$)



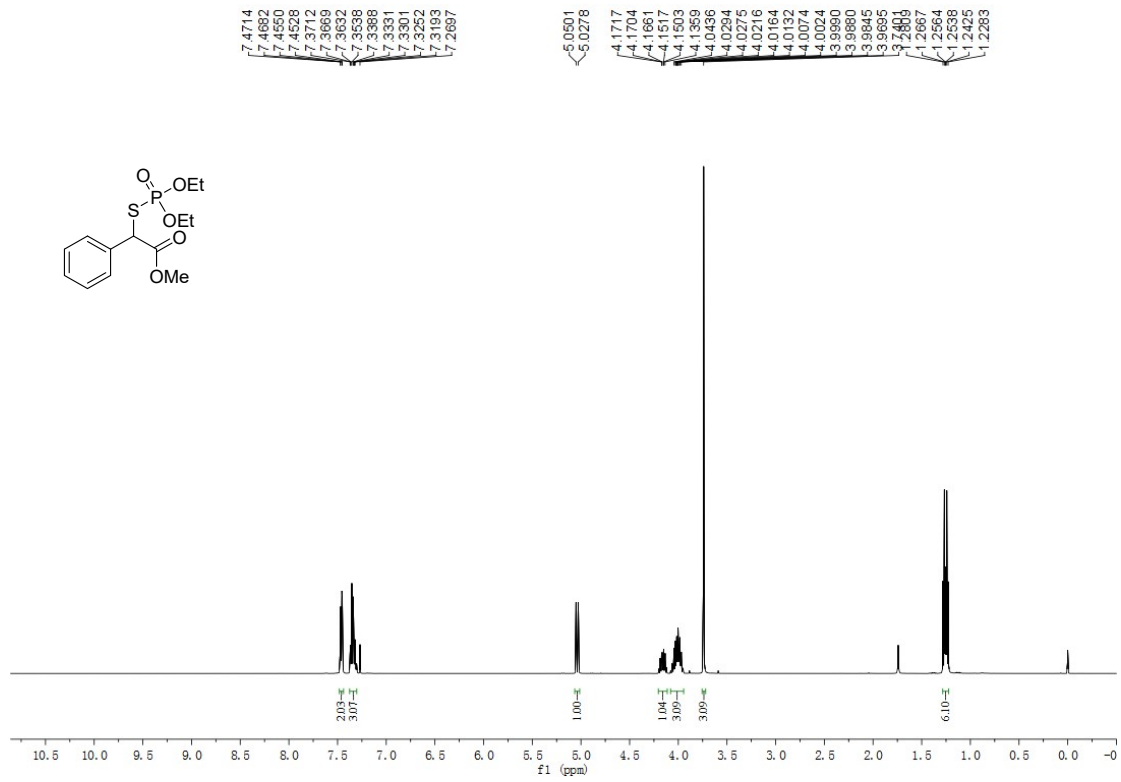
5z''' ^{1}H NMR (500 MHz, $CDCl_3$)



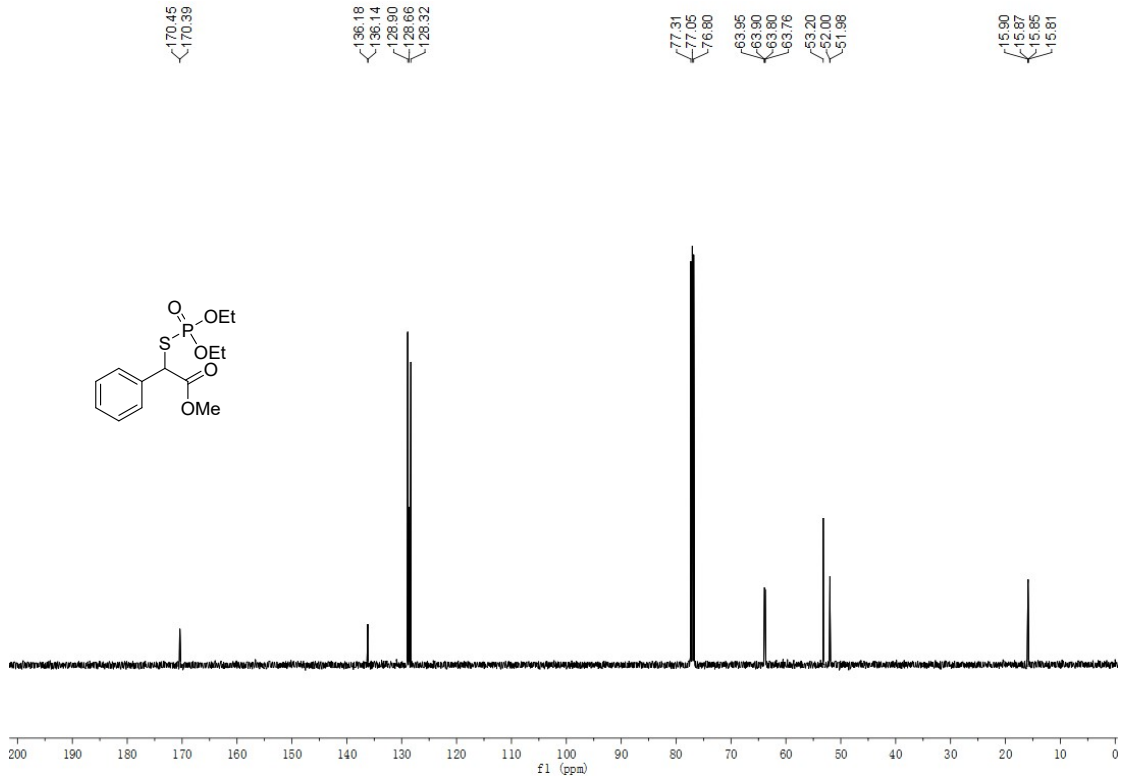
5z''' ^{13}C NMR (125MHz, $CDCl_3$)



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

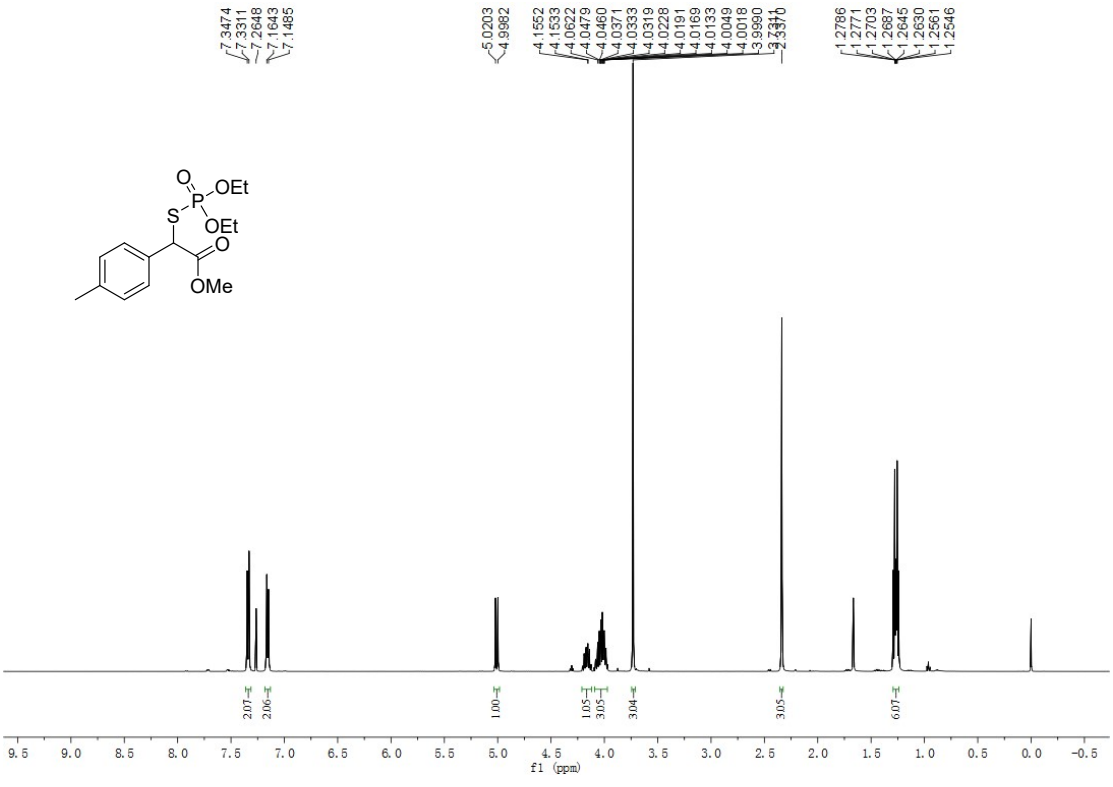


4a^{13}C NMR (125MHz, $CDCl_3$)



4b^{13}C NMR (125MHz, $CDCl_3$)

4b ^{1}H NMR (500 MHz, $CDCl_3$)



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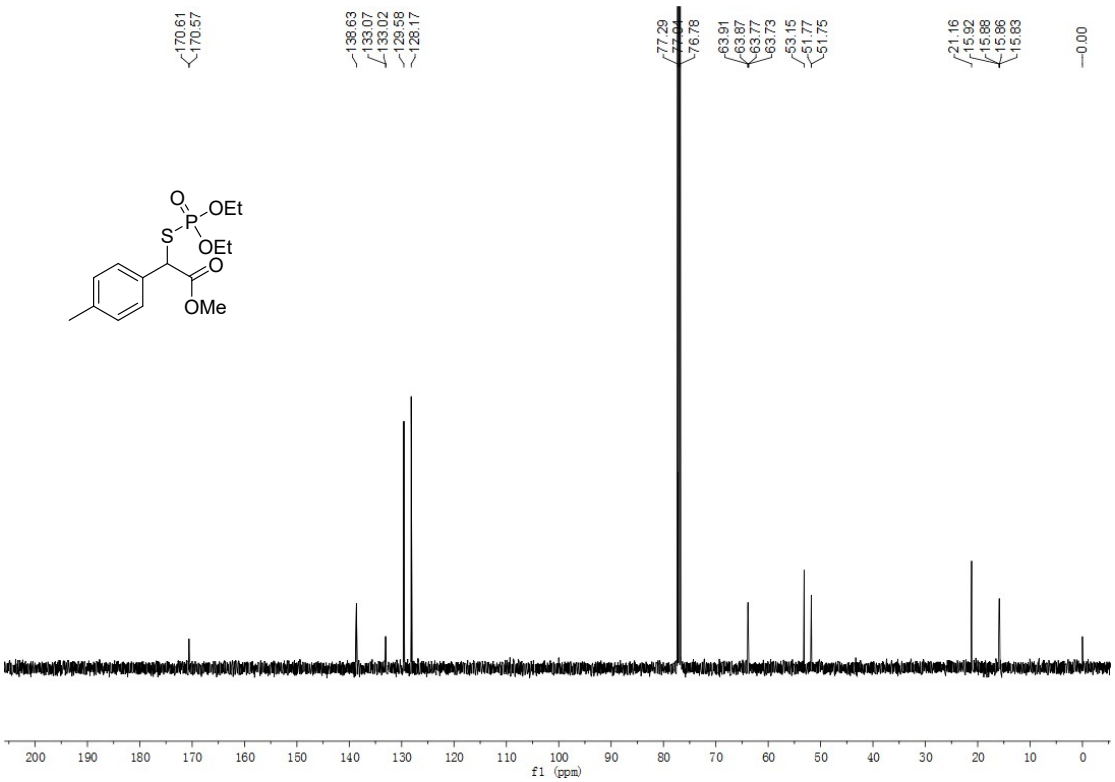
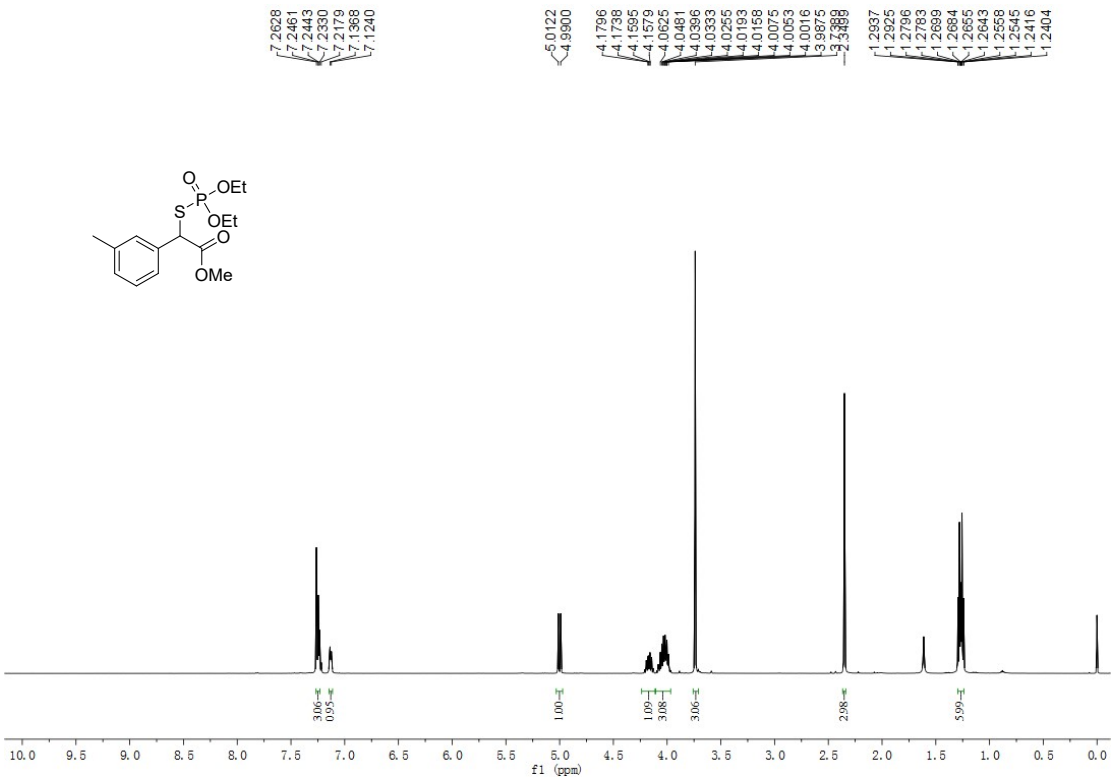
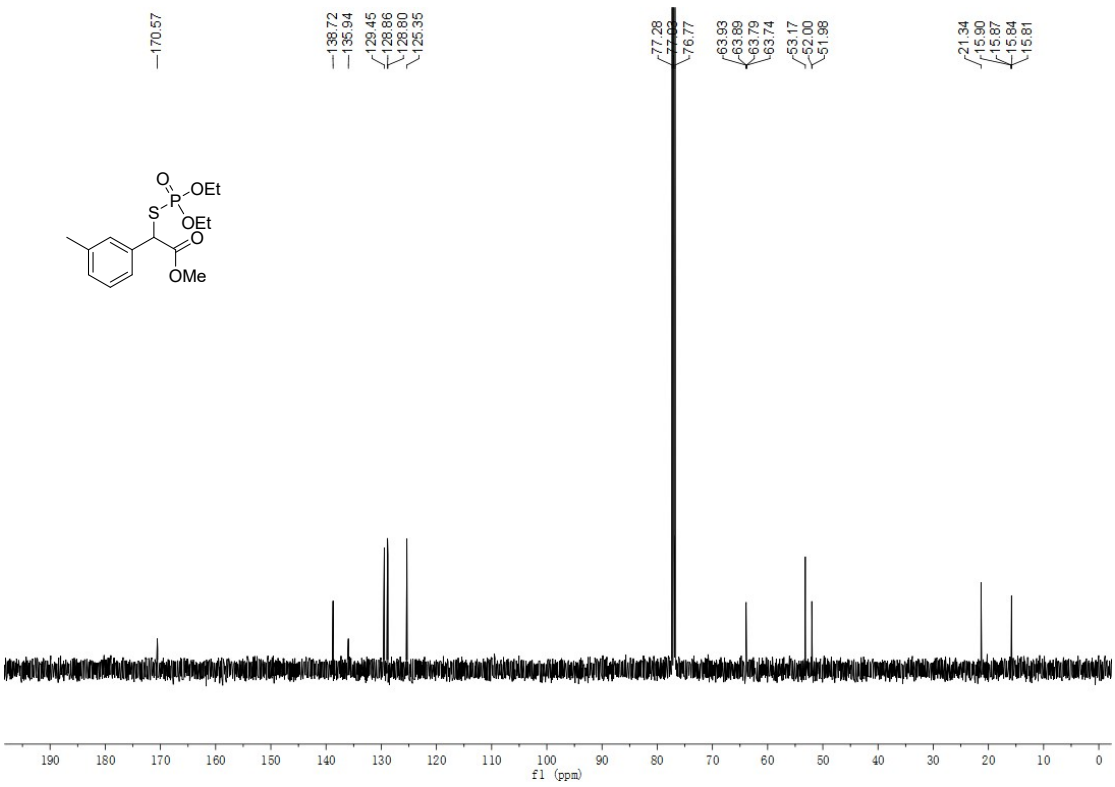


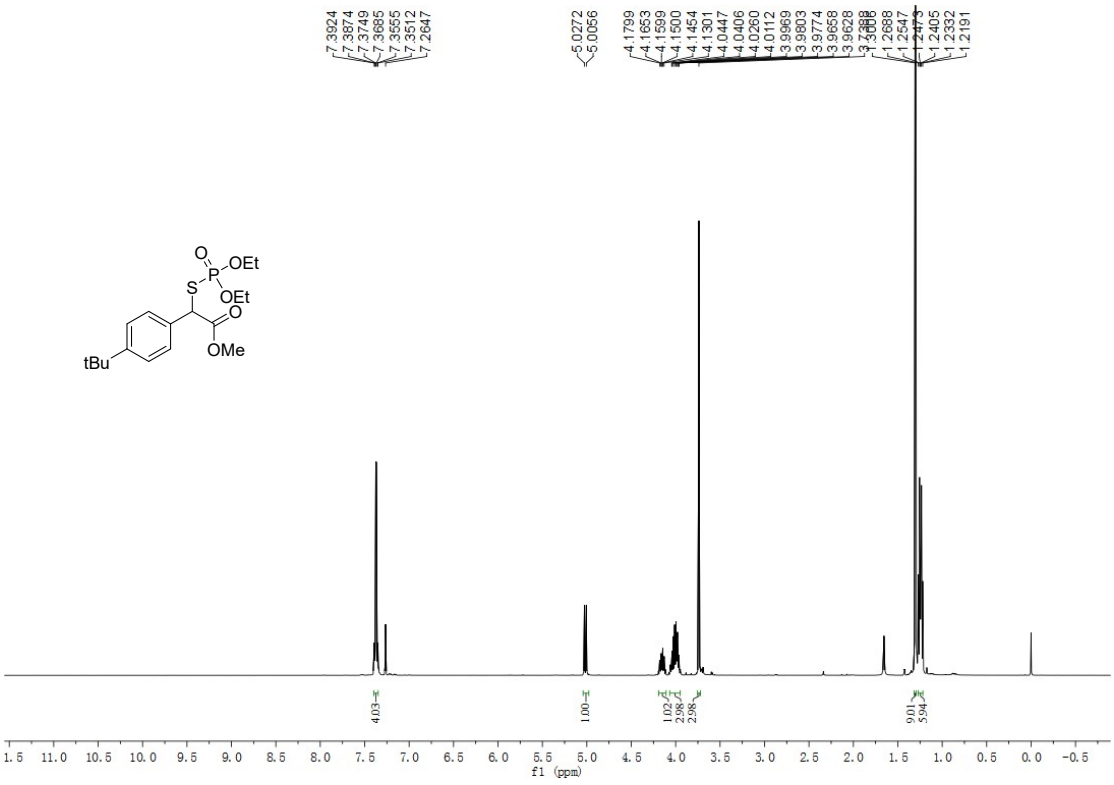
4c ^{1}H NMR (500 MHz, $CDCl_3$)



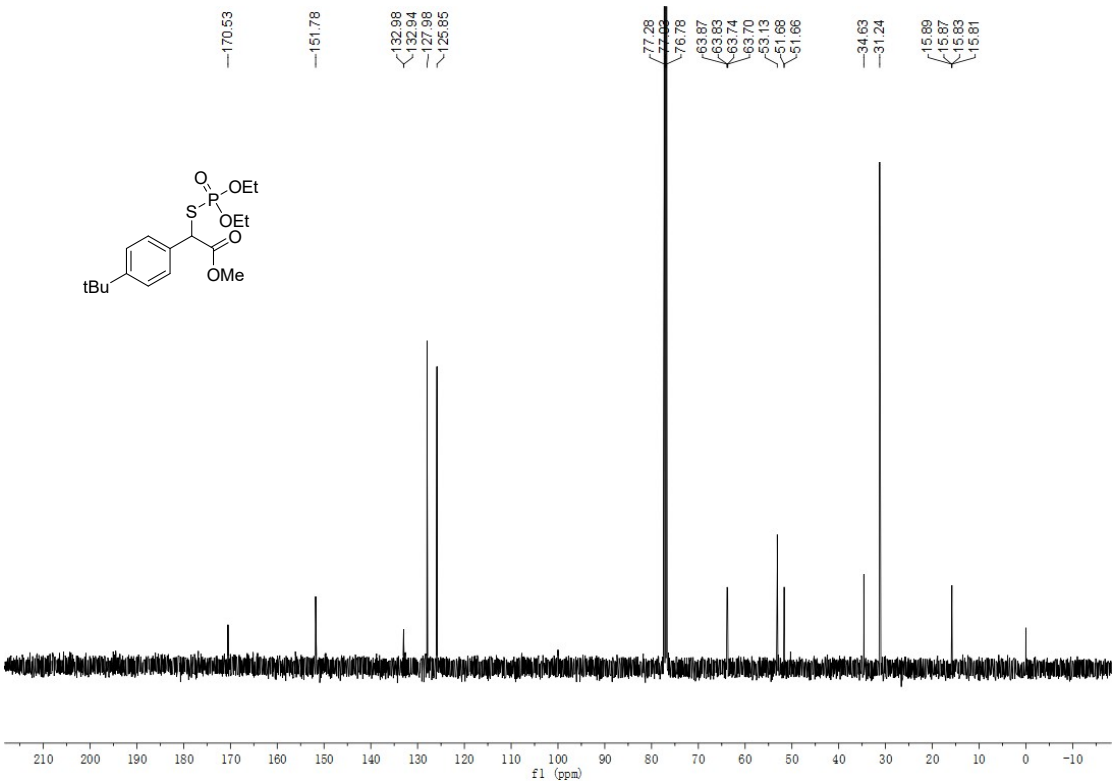
4c ^{13}C NMR (125MHz, $CDCl_3$)



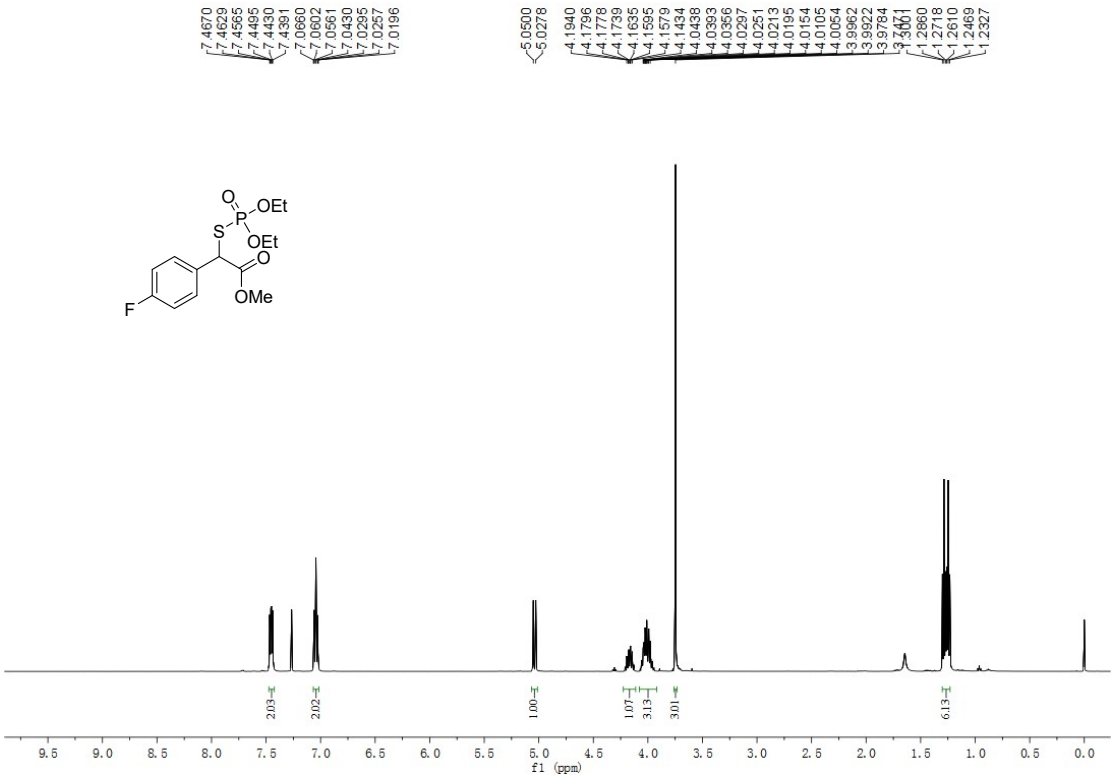
4d ^{1}H NMR (500 MHz, $CDCl_3$)



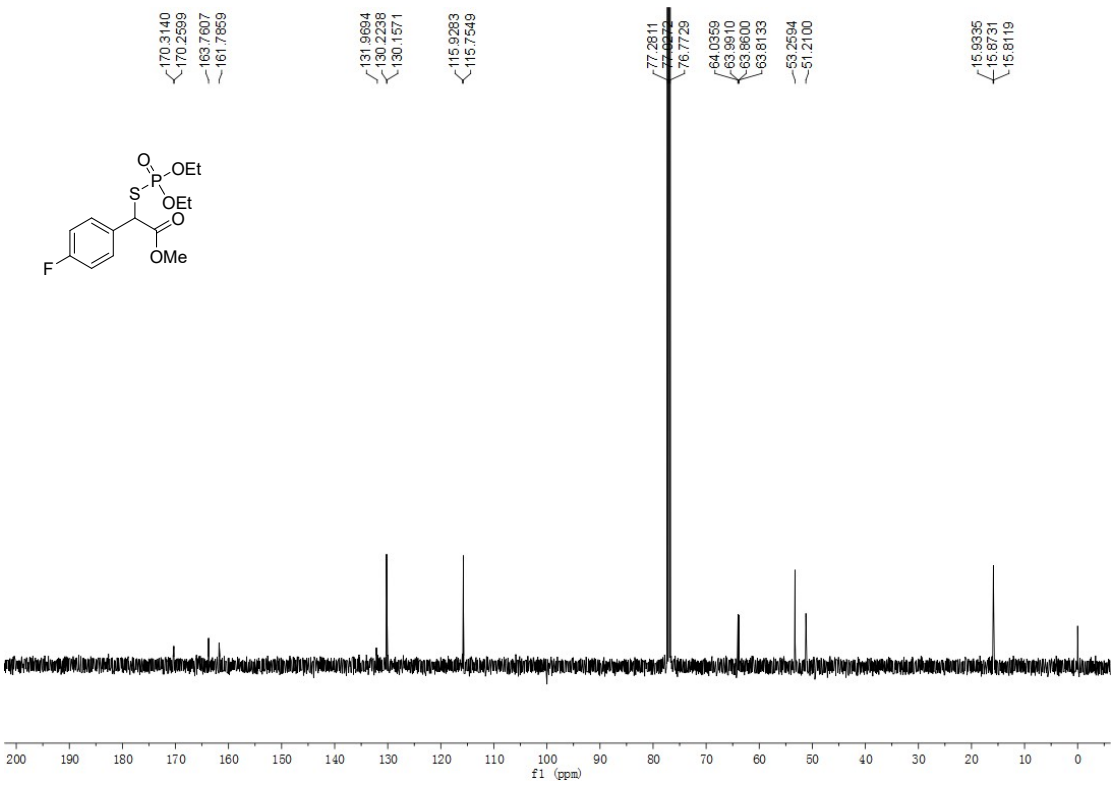
4d ^{13}C NMR (125MHz, $CDCl_3$)



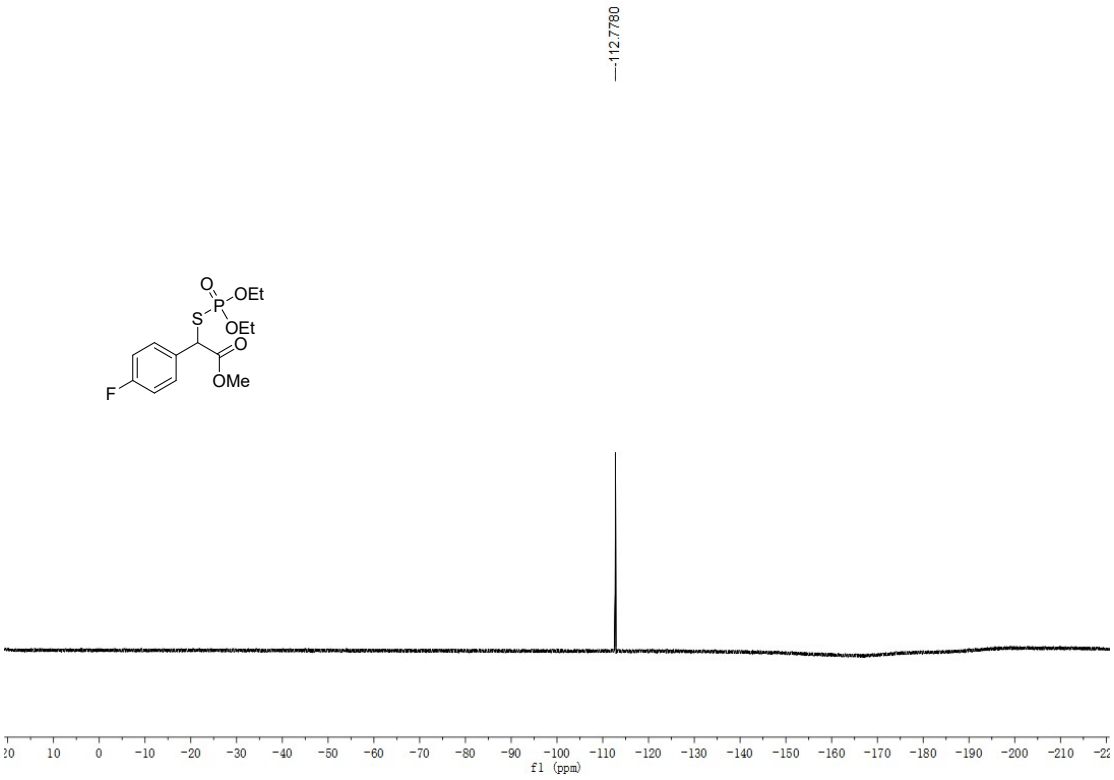
4e ^{1}H NMR (500 MHz, $CDCl_3$)



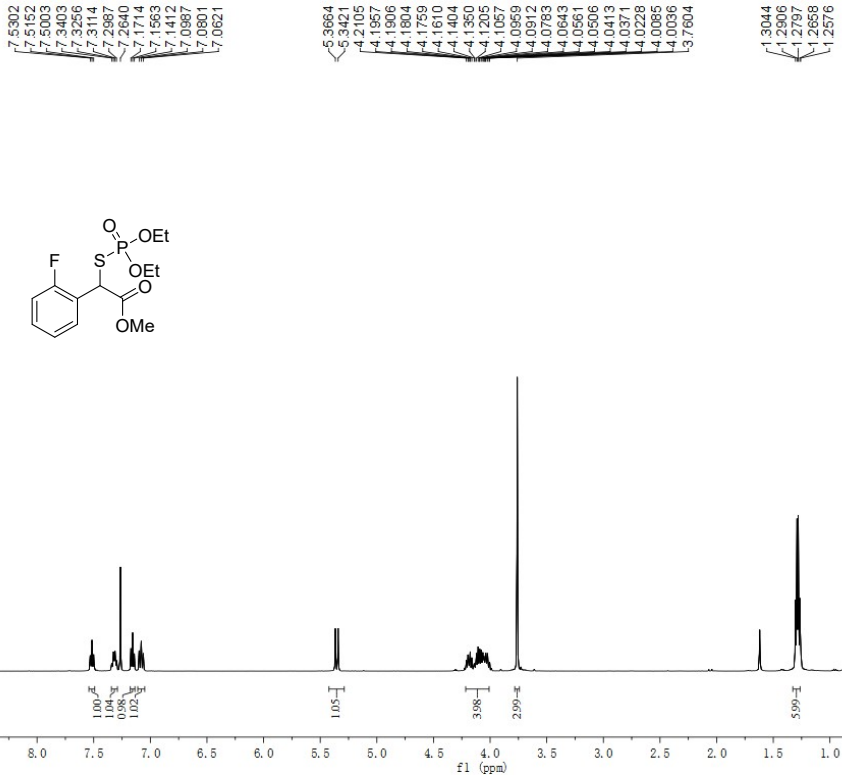
4e ^{13}C NMR (125MHz, $CDCl_3$)



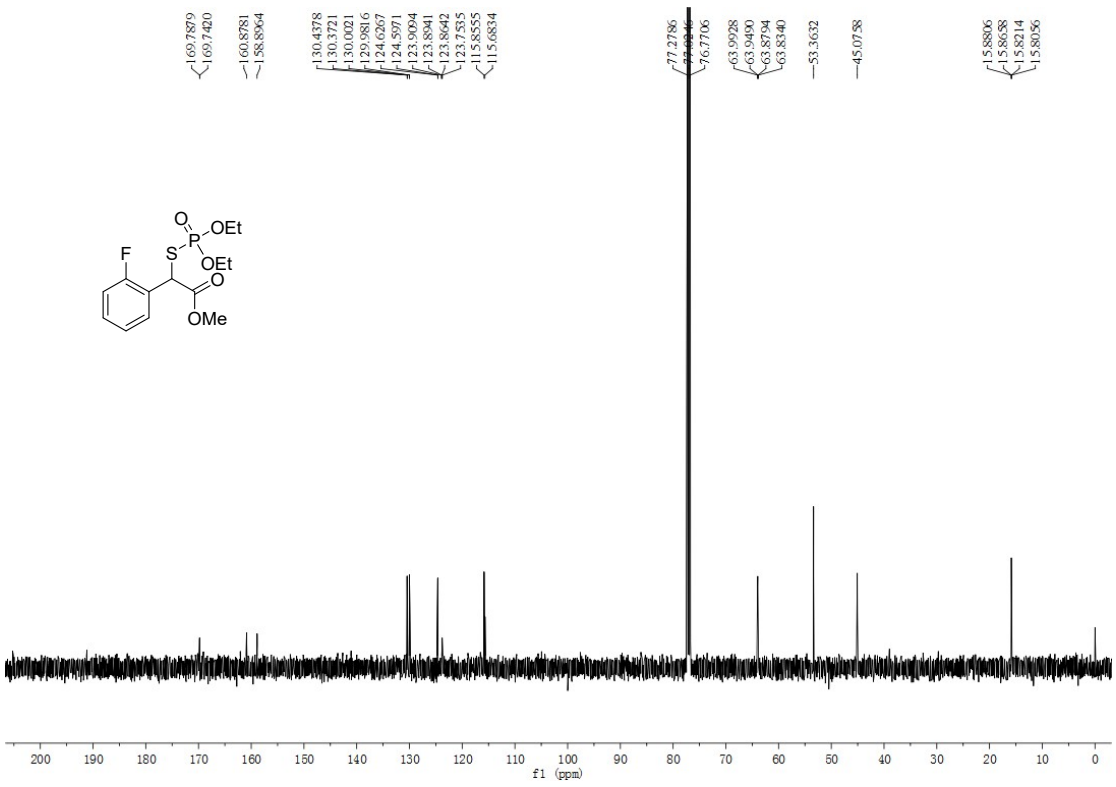
4e ^{19}F NMR (500MHz, $CDCl_3$)



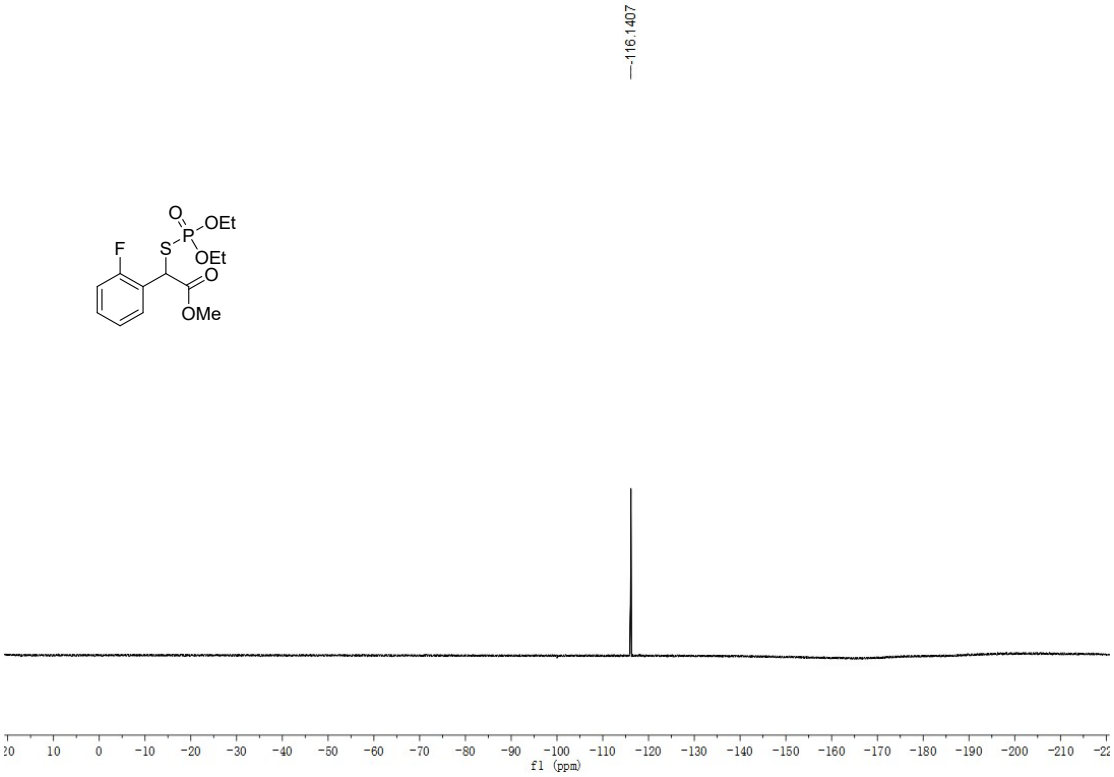
4f ^{1}H NMR (500 MHz, $CDCl_3$)



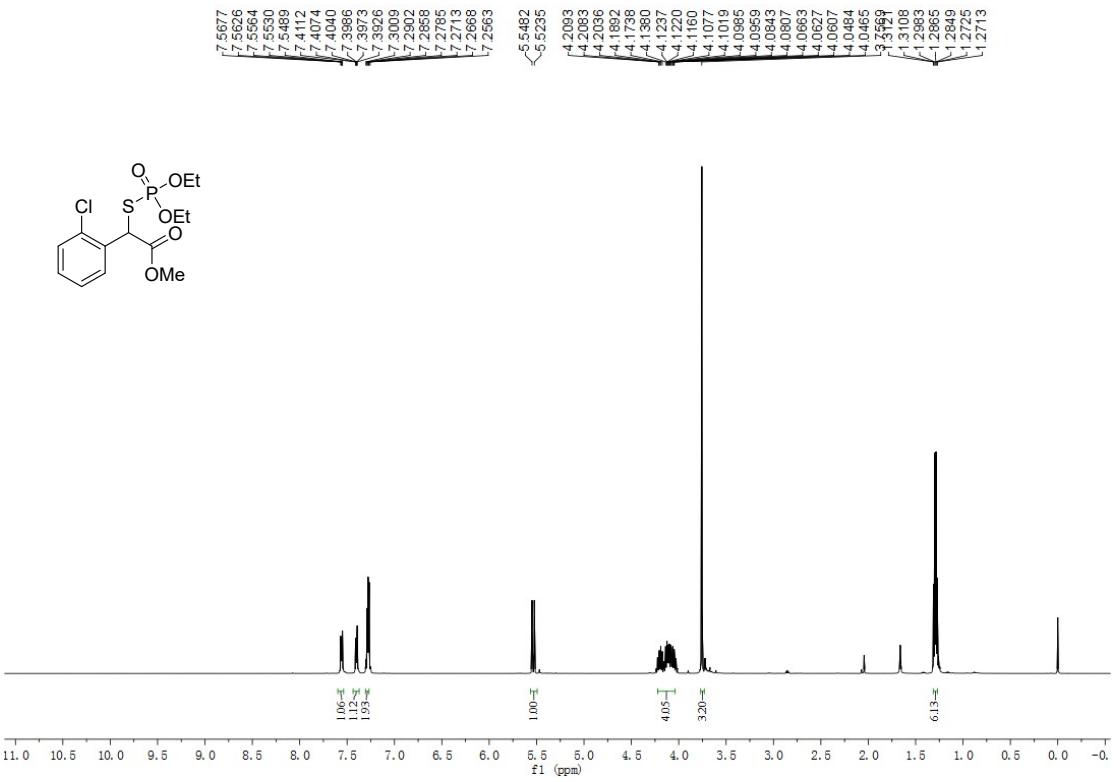
4f ^{13}C NMR (125MHz, $CDCl_3$)



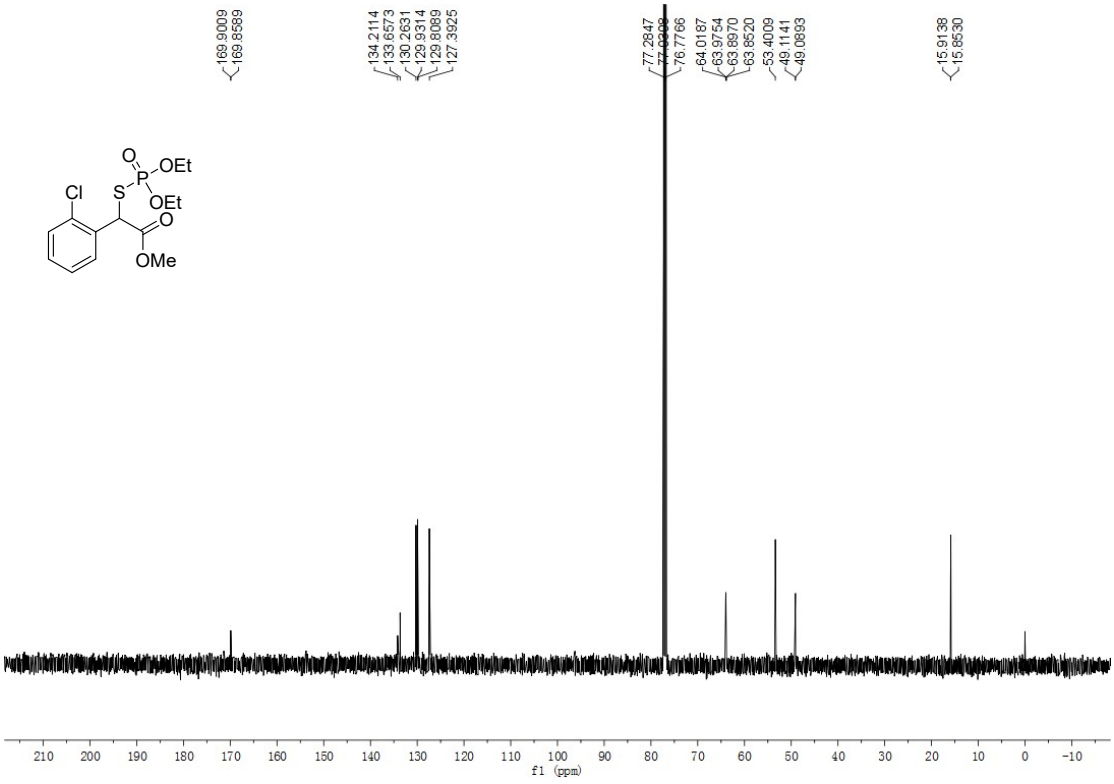
4f ^{19}F NMR (500MHz, $CDCl_3$)



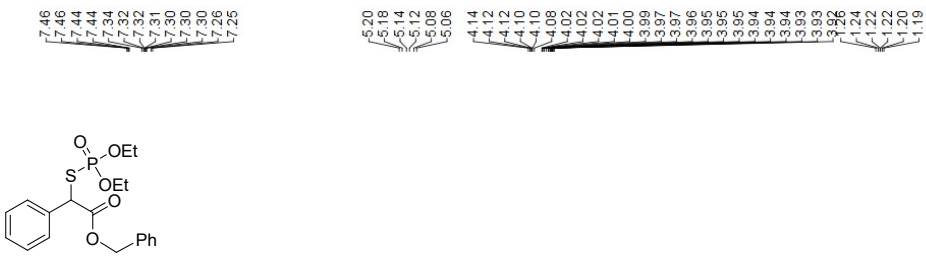
4g ^{1}H NMR (500 MHz, $CDCl_3$)

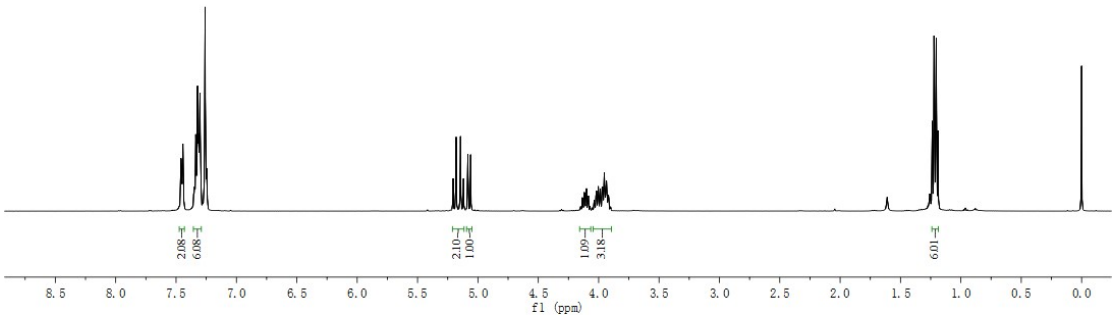


4g^{13}C NMR (125MHz, $CDCl_3$)

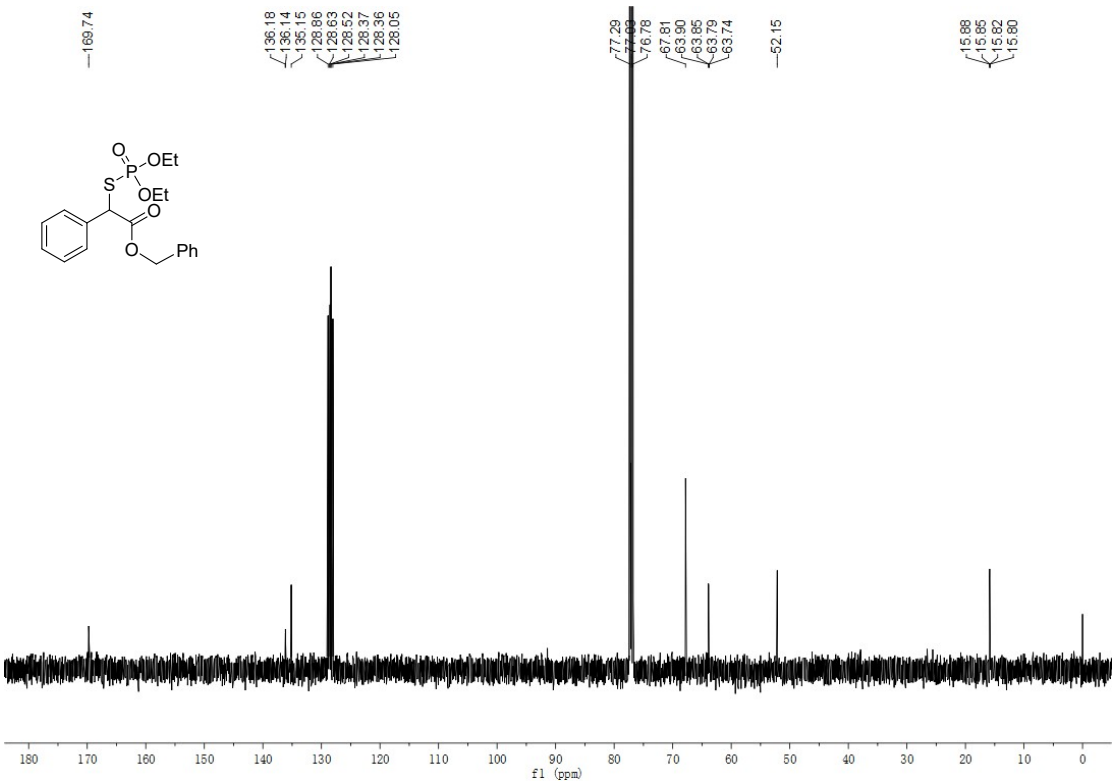


4h ^{1}H NMR (500 MHz, $CDCl_3$)

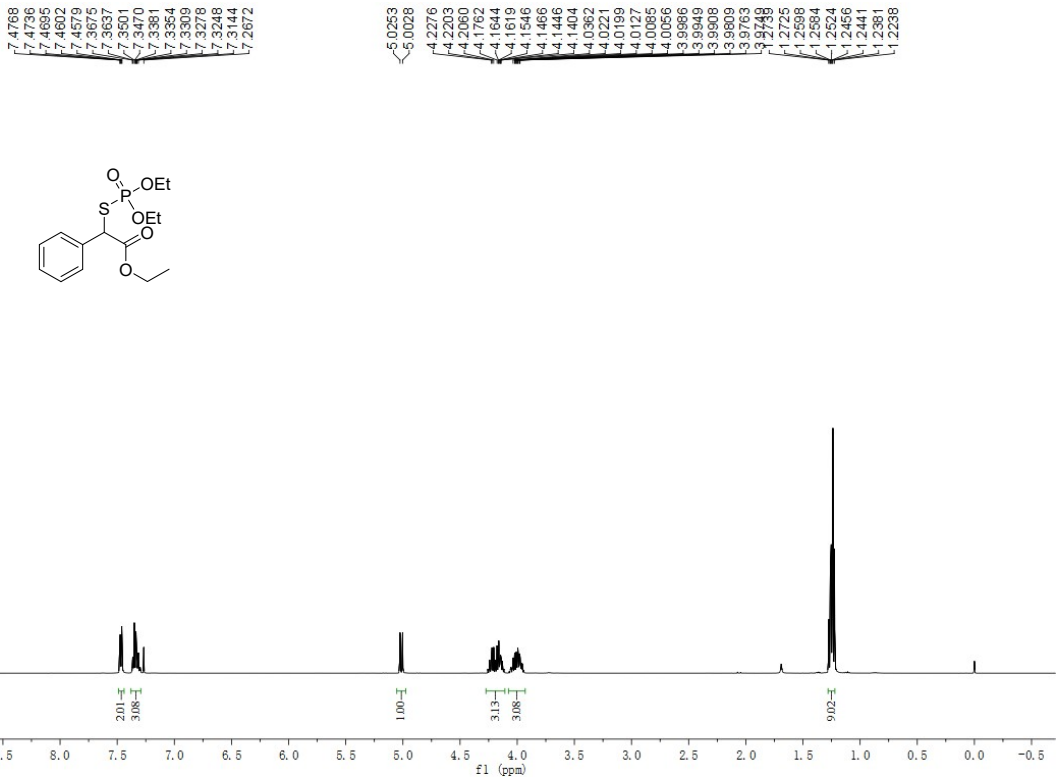




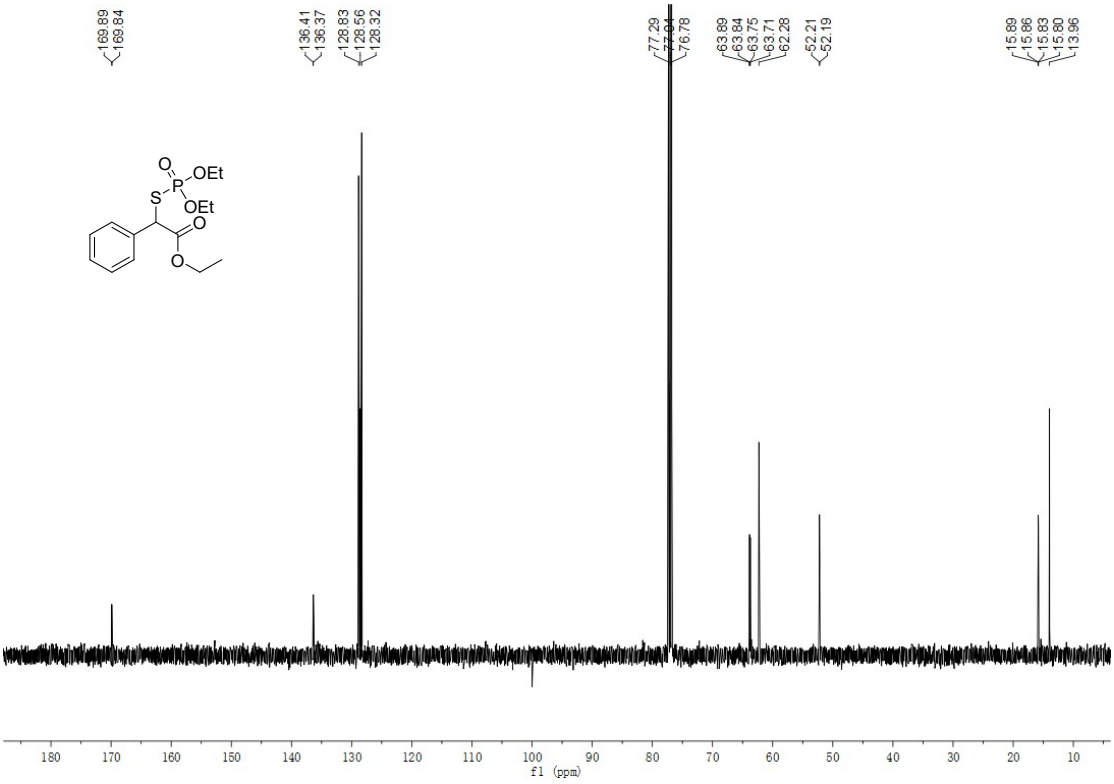
4h ^{13}C NMR (125MHz, $CDCl_3$)



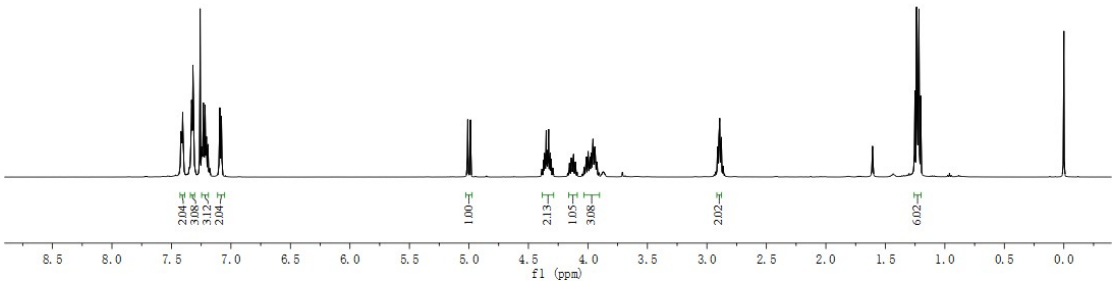
4i ^{1}H NMR (500 MHz, $CDCl_3$)



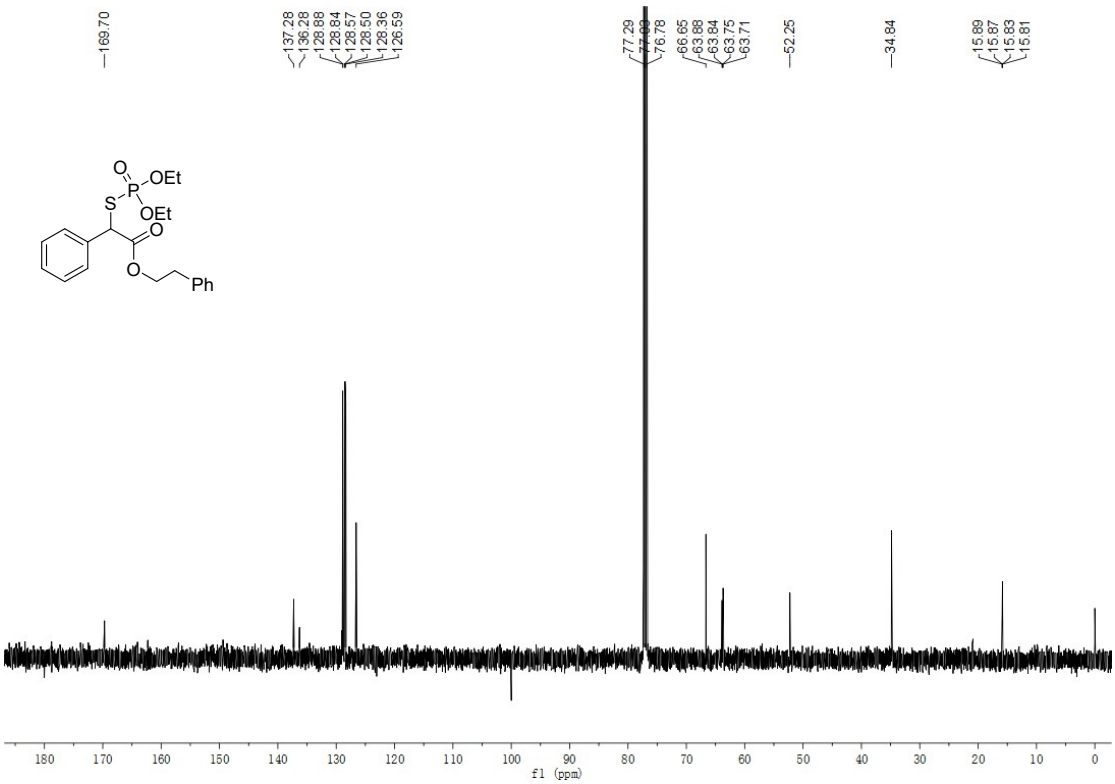
4i ^{13}C NMR (125MHz, $CDCl_3$)



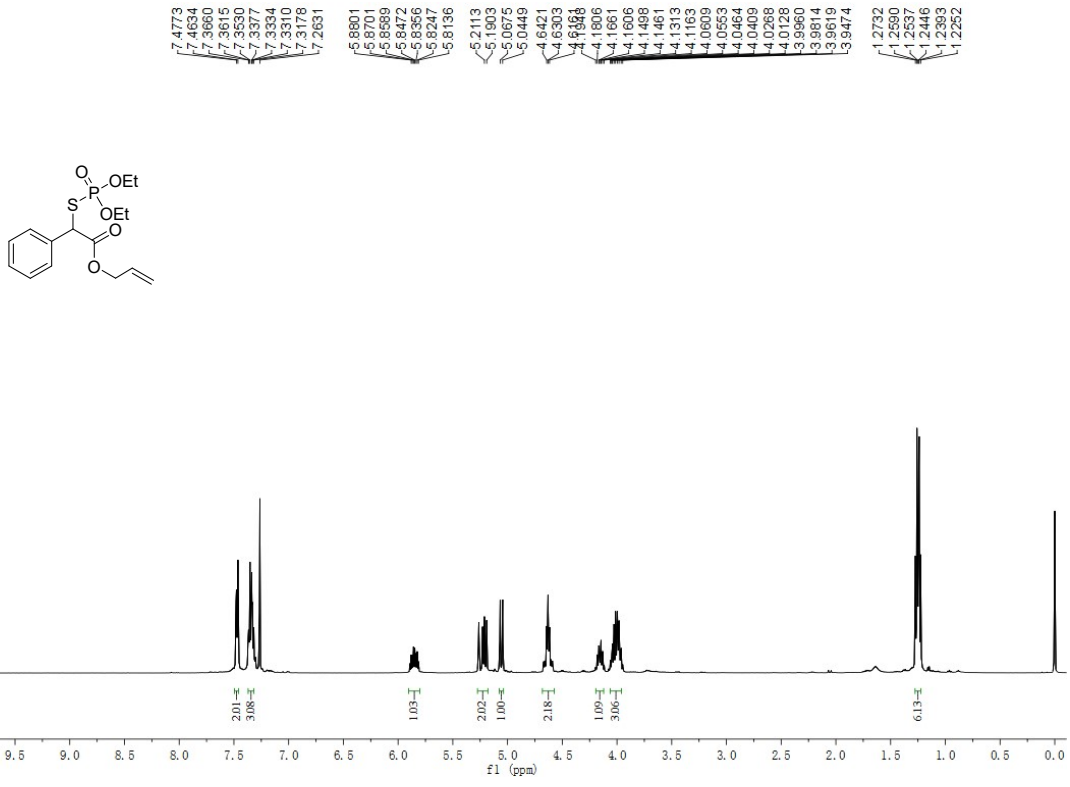
4j ^{1}H NMR (500 MHz, $CDCl_3$)



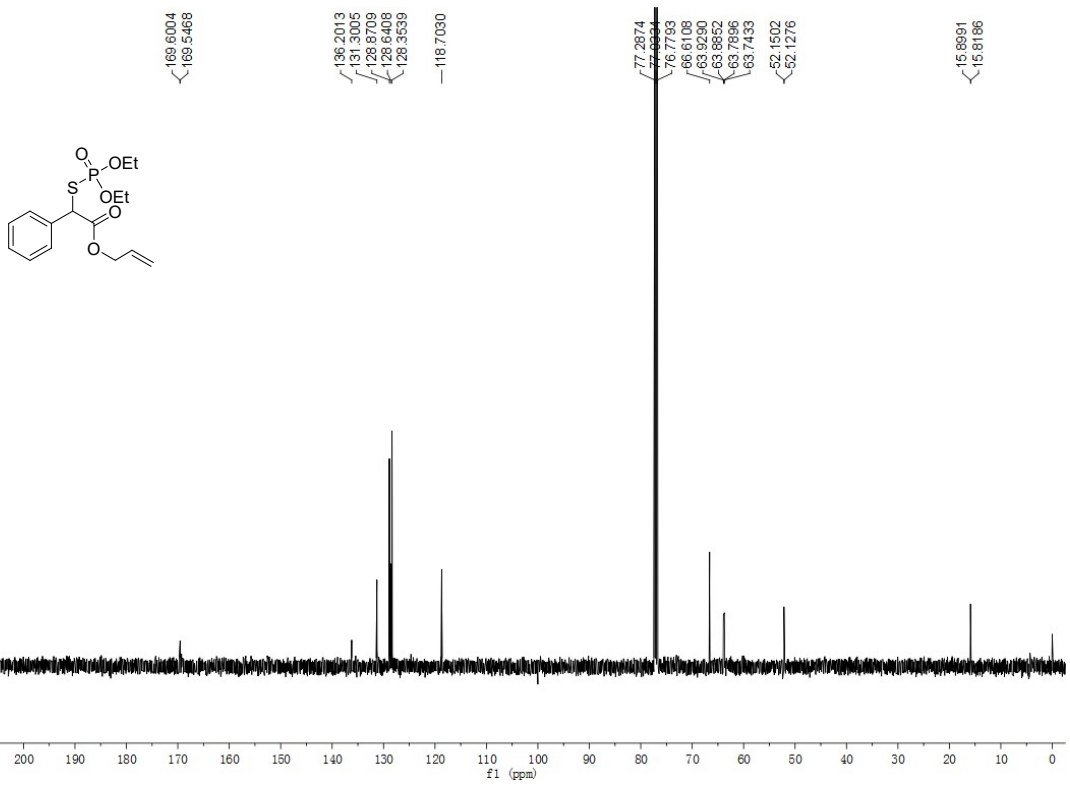
4j ^{13}C NMR (125MHz, $CDCl_3$)



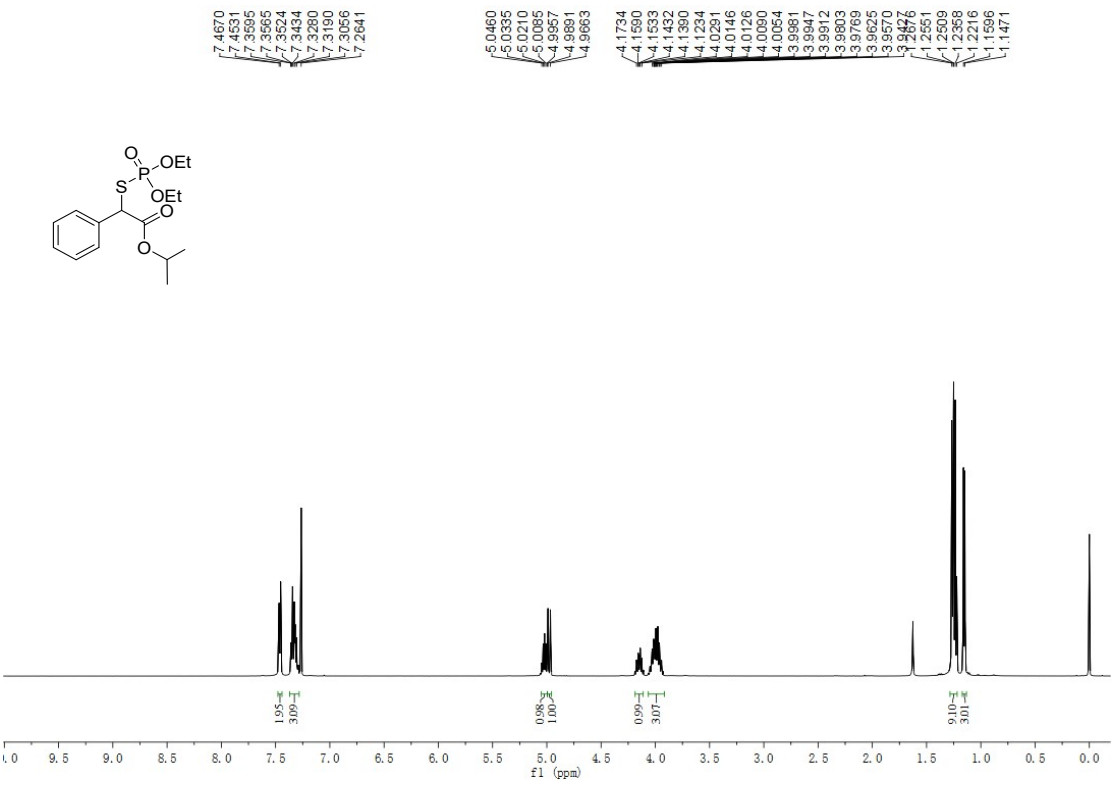
4k ^{1}H NMR (500 MHz, $CDCl_3$)



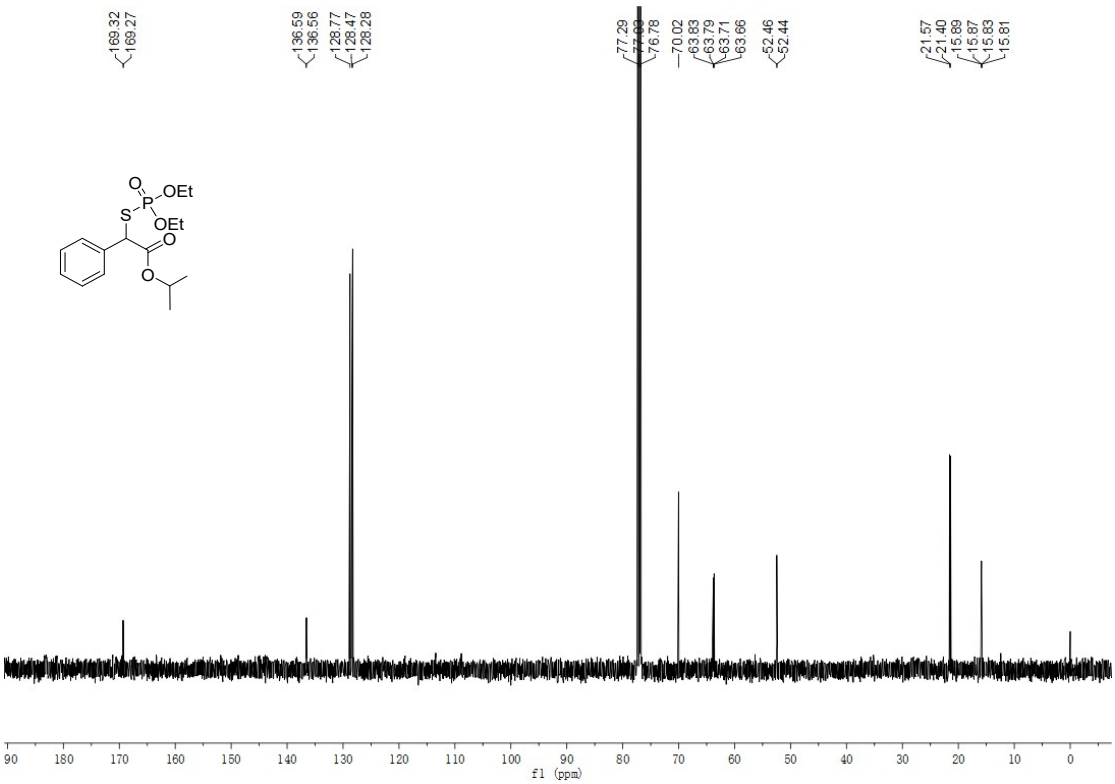
4k ^{13}C NMR (125MHz, $CDCl_3$)



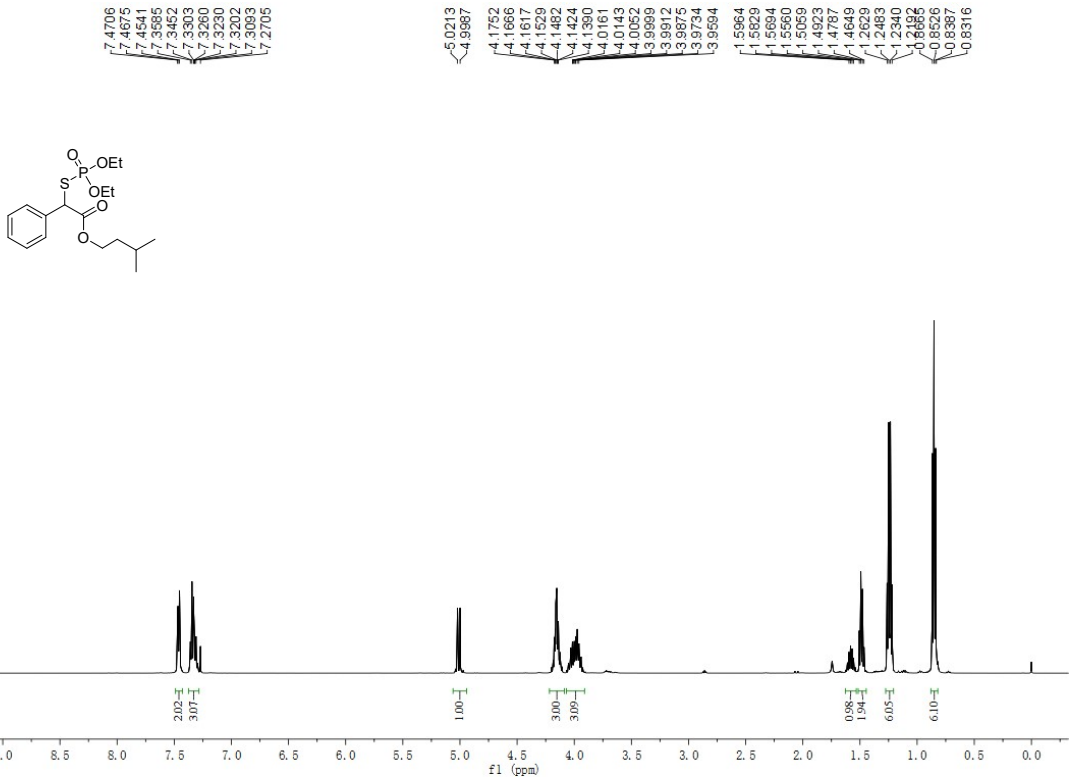
4l ^{1}H NMR (500 MHz, $CDCl_3$)



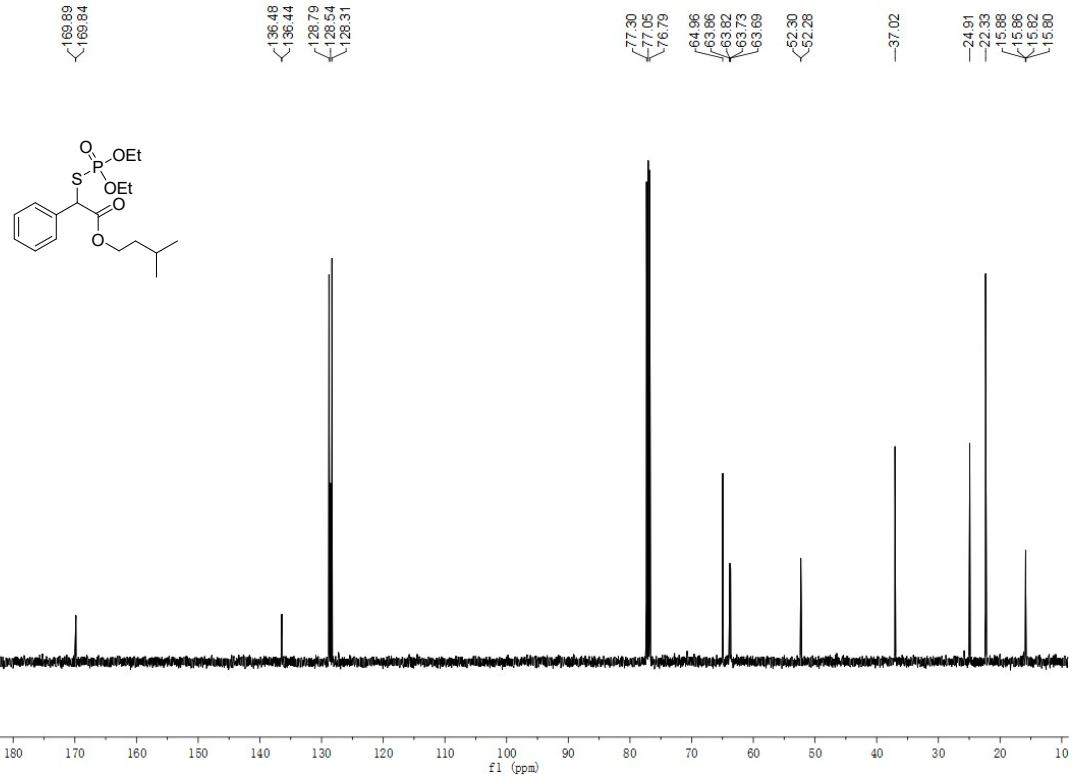
4l ^{13}C NMR (125MHz, $CDCl_3$)



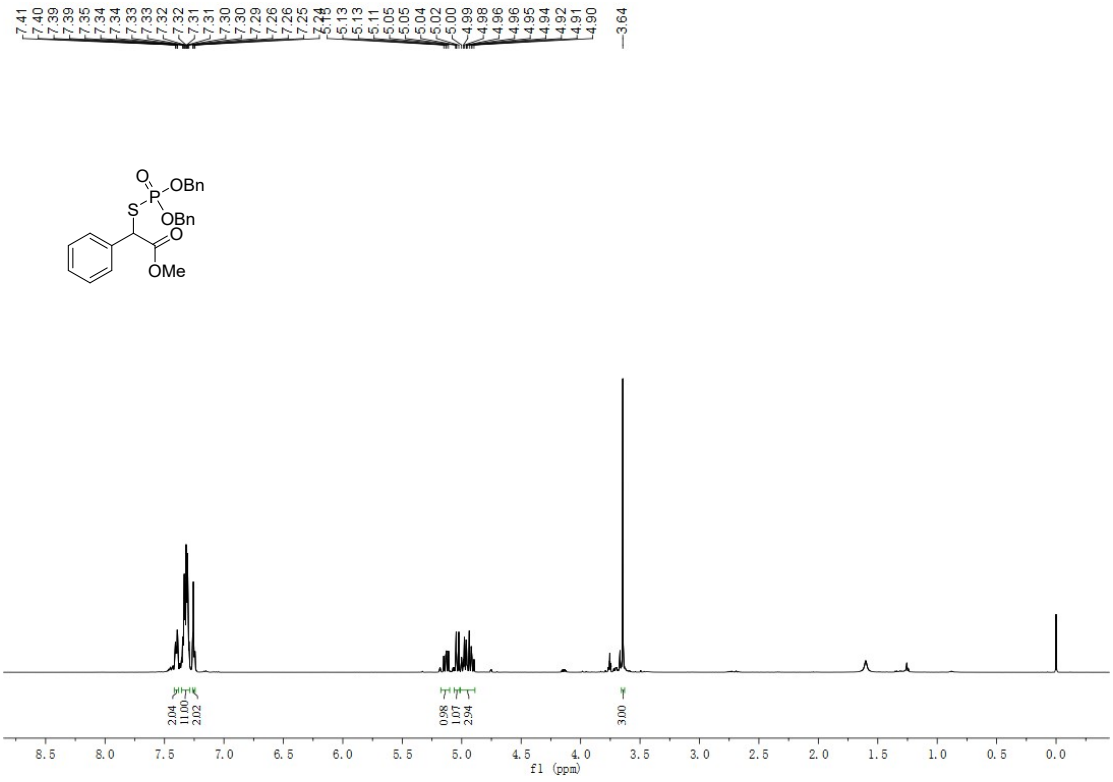
4m ^{1}H NMR (500 MHz, $CDCl_3$)



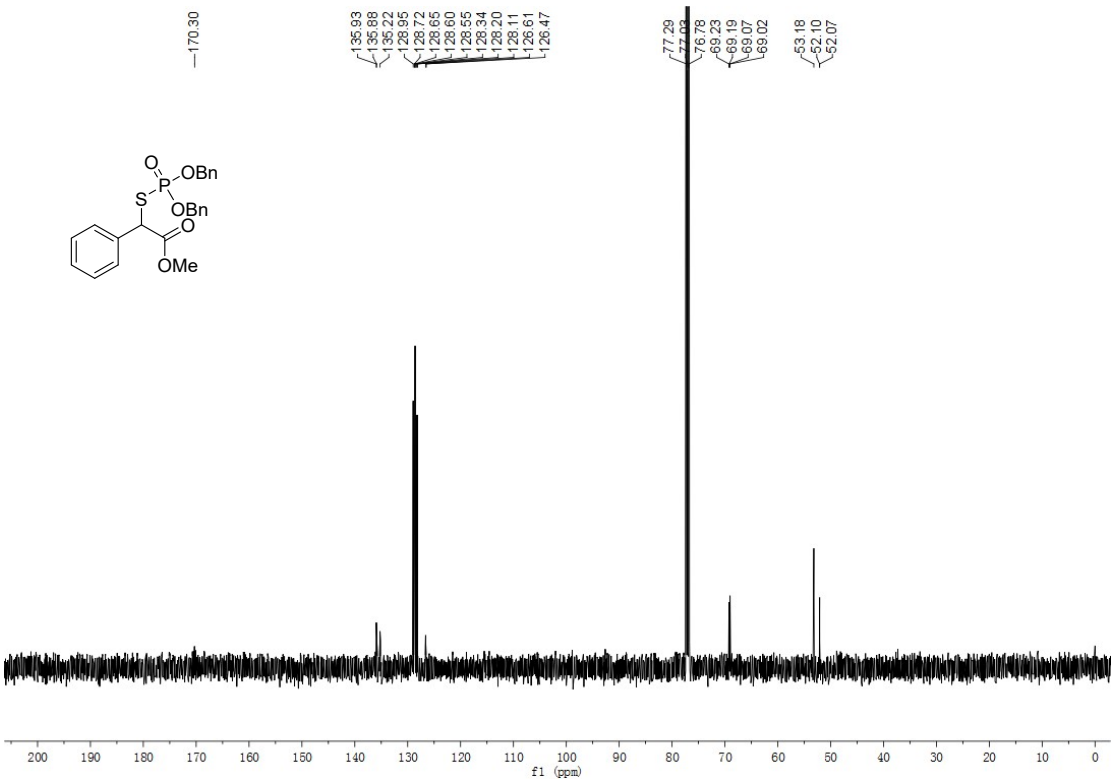
4m ^{13}C NMR (125MHz, $CDCl_3$)



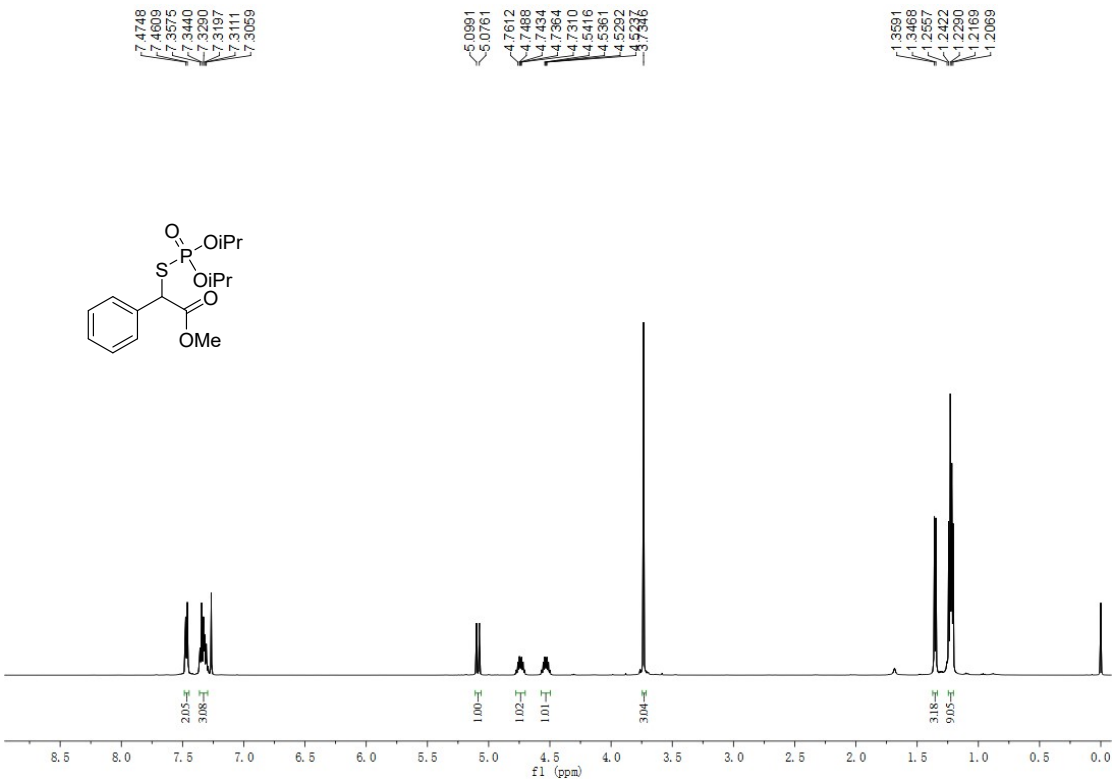
4n ^{1}H NMR (500 MHz, $CDCl_3$)



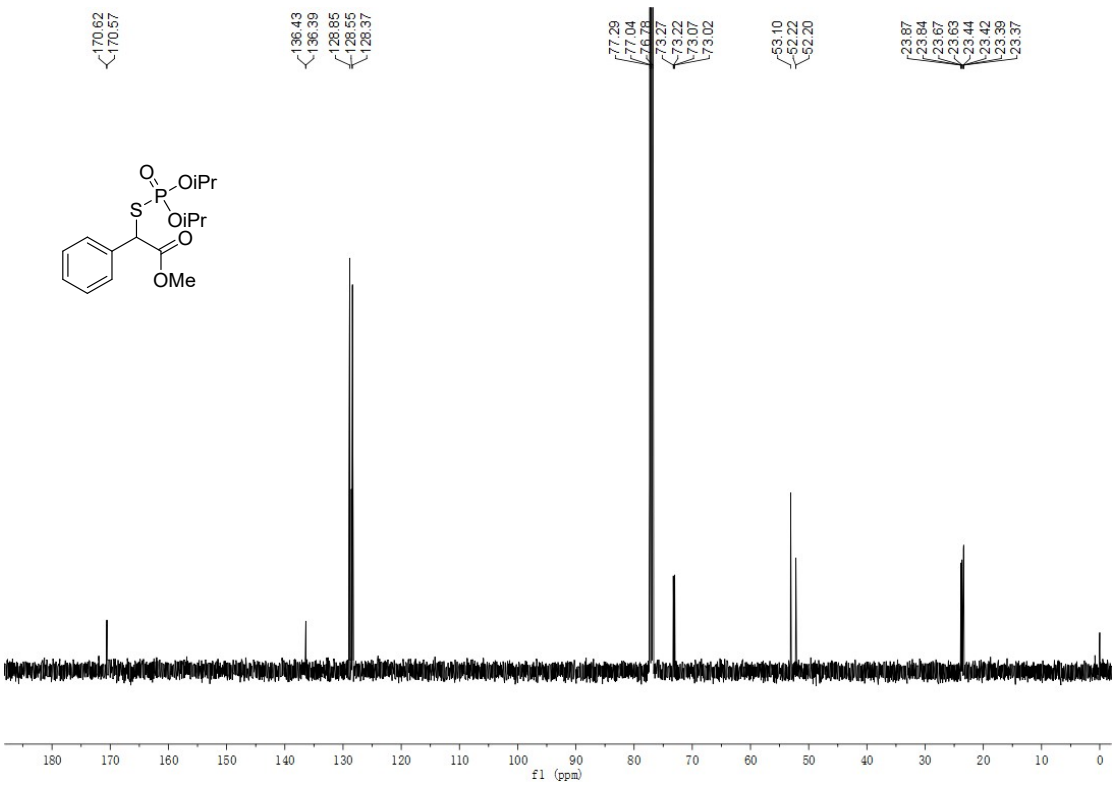
4n ^{13}C NMR (125MHz, $CDCl_3$)



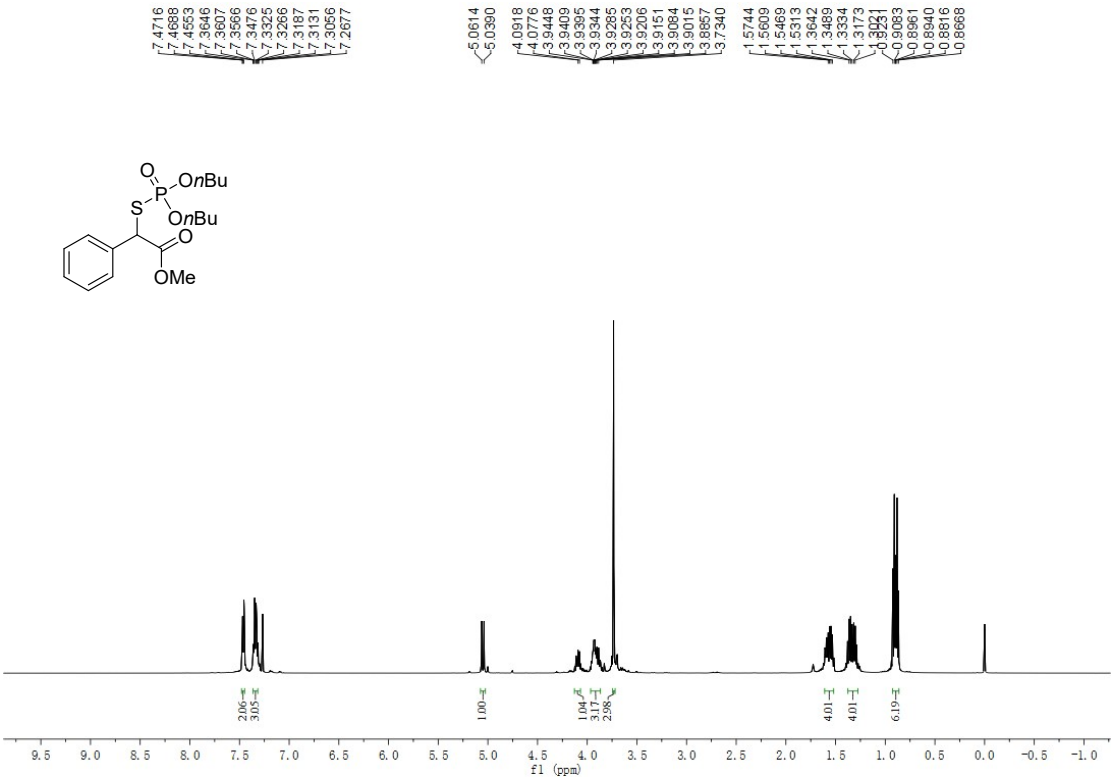
4o ^{1}H NMR (500 MHz, $CDCl_3$)



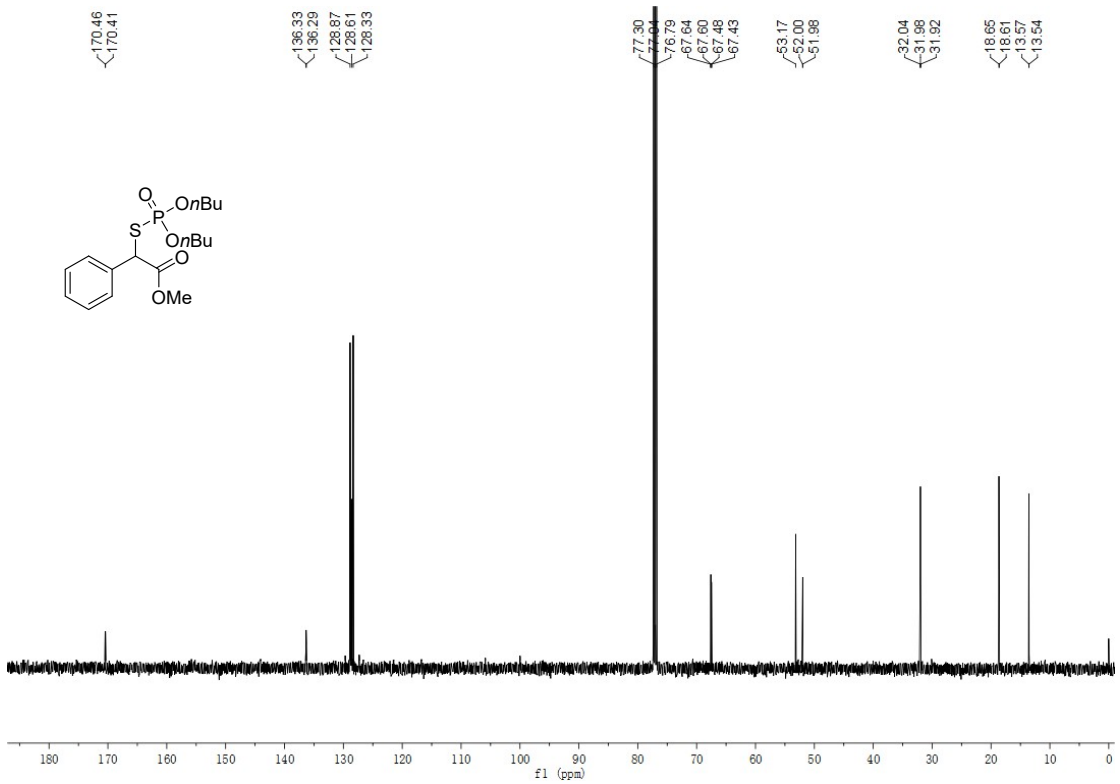
4o ^{13}C NMR (125MHz, $CDCl_3$)



4p ^{1}H NMR (500 MHz, $CDCl_3$)



4p ^{13}C NMR (125MHz, $CDCl_3$)


170.46
170.41
136.33
136.29
128.87
128.61
128.33
77.30
77.04
76.79
67.64
67.60
67.48
67.43
53.17
52.00
51.98
32.04
31.98
31.92
18.65
18.61
13.57
13.54
O
P
S
OnBu
OnBu
O
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)