Additive-free aerobic oxidative difunctionalization of alkenes with P_4S_{10} and alcohols to access β-hydroxy phosphorodithioates

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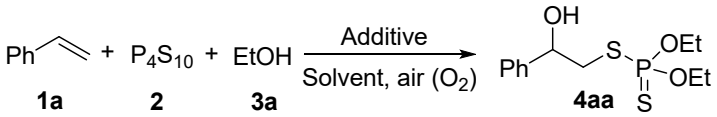
Contents

1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Bidepharm and Energy Chemical Company and used as received without further purification unless otherwise stated. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR were recorded in $CDCl_3$ on a Bruker Avance III spectrometer with TMS as internal standard (500 MHz ^{1}H, 125 MHz ^{13}C, 202 MHz ^{31}P, and 500 MHz ^{19}F) 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). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).

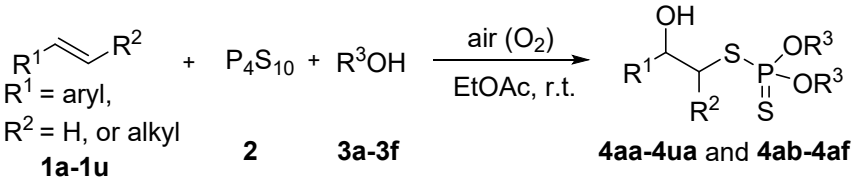
2. The screening of reaction conditions



Entry	Additive	Solvent	**4aa** Yield (%)[b]
1	DBU (100 mol%)	EtOH/EtOAc(1/3)	15
2	Cs_2CO_3 (100 mol%)	EtOH/EtOAc(1/3)	6
3	$CuCl_2$ (20 mol%)	EtOH/EtOAc(1/3)	trace
4	$PdBr_2$ (20 mol%)	EtOH/EtOAc(1/3)	trace
5	$K_2S_2O_8$ (100 mol%)	EtOH/EtOAc(1/3)	73
6	TBHP (100 mol%)	EtOH/EtOAc(1/3)	70
7	Ag_2O (100 mol%)	EtOH/EtOAc(1/3)	52

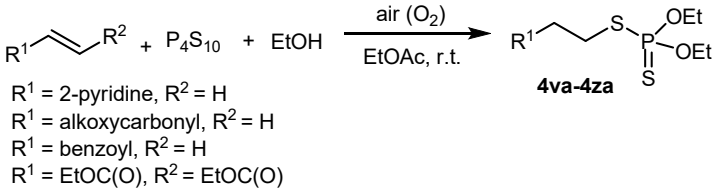
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), **3a** (0.5 mL), Additive (20-100 mol%), EtOAc (2 mL), air (O_2), r.t., 6 h. [b] Isolated yields based on **1a**.

3. General procedure for aerobic oxidative difunctionalization of alkenes with P_4S_{10} and alcohols to access β-hydroxy phosphorodithioates.



Alkene **1** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and ethyl acetate (1.5 mL) were successively added in a 15 mL reaction tube. Then, the alcohol **3** (0.5 mL) was added to the mixture. The reaction mixture was open to air and stirred at room temperature for 6 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 product **4**.

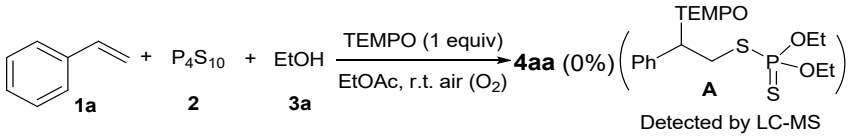
4. The procedure for hydrophosphorodithiolation of alkenes with P_4S_{10} and alcohols to access alkyl phosphorodithioates.



Alkene (**1v-1z**) (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and ethyl acetate (1.5 mL) were successively added in a 15 mL reaction tube. Then, the EtOH **3a** (0.5 mL) was added to the mixture. The reaction mixture was open to air and stirred at room temperature for 6 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 product (**4va-4za**).

5. Preliminary mechanistic studies

5.1 The addition of TEMPO in the model reaction system.



Styrene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and ethyl acetate (1.5 mL) were successively added in a 15 mL reaction tube. Then, the TEMPO (0.2 mmol) and EtOH **3** (0.5 mL) was added to the above mixture. The reaction mixture was open to air and stirred at room temperature for 6 h. After completion of the reaction, the solution was

concentrated in vacuum, no desired product **4aa** was observed and TEMPO-trapped complex **A** was detected by LC-MS (Figure S1). This result indicated that a radical process might be involved in the present transformation.

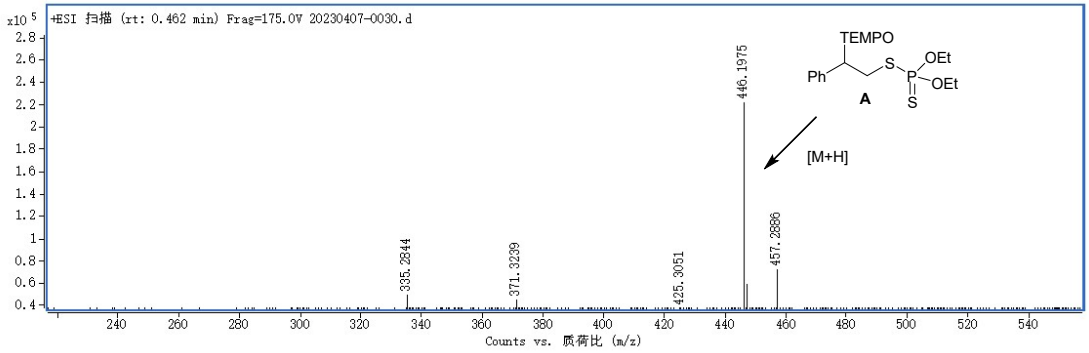
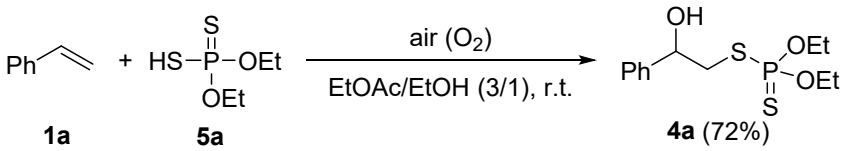


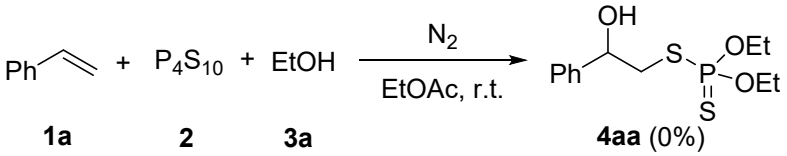
Figure S1

5.2 The reaction of O,O-diethyl S-hydrogen phosphorodithioate 5a with styrene 1a.



Styrene **1a** (0.2 mmol) and ethyl acetate (1.5 mL) were added in a 15 mL reaction tube. Then, O,O-diethyl S-hydrogen phosphorodithioate **5a** (0.2 mmol) and EtOH (0.5 ml) was added to the above mixture. The reaction mixture was open to air and stirred at room temperature for 6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum, the desired product **4aa** was isolated in 72% yield. This result indicated that S-hydrogen phosphorodithioate as a key intermediate might be involved in the present transformation.

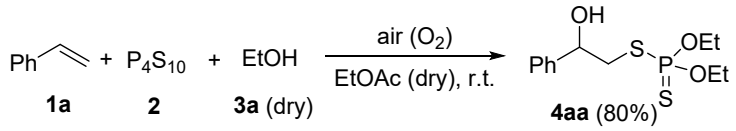
5.3 The model reaction was carried out under N_2.



Styrene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and ethyl acetate (1.5 mL) were successively added in a 15 mL reaction tube under N_2. Then, EtOH **3a** (0.5 mL) was added to the above mixture. The reaction mixture was stirred under N_2 at room temperature for 6 h. After completion of the reaction, the solution was concentrated in vacuum, no desired product **4aa** was detected. This result indicated that air (O_2) is

indispensable for this transformation.

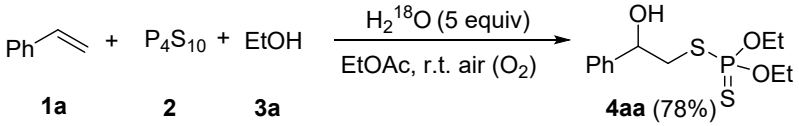
5.4 The model reaction was carried out in dry EtOH and EtOAc with the addition of 4Å MS.



1a **2** **3a** (dry) **4aa** (80%)

Styrene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), 4Å MS (30 mg) and dry ethyl acetate (1.5 mL) were successively added in a 15 mL reaction tube. Then, dry EtOH **3a** (0.5 mL) was added to the above mixture. The reaction mixture was open to air and stirred at room temperature for 6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum, the desired product **4aa** was isolated in 80% yield. This result indicated that water should not take part in this transformation.

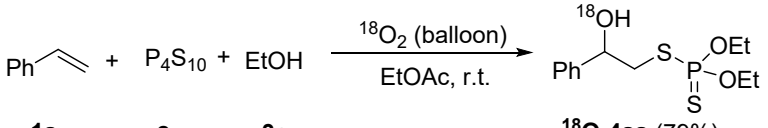
5.5 The model reaction was carried out with the addition of H_2O^{18}.



1a **2** **3a** **4aa** (78%)

Styrene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and dry ethyl acetate (1.5 mL) were successively added in a 15 mL reaction tube. Then, H_2O^{18} (1 mmol) and dry EtOH **3a** (0.5 mL) was added to the above mixture. The reaction mixture was open to air and stirred at room temperature for 6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum, the product **4aa** was detected by LC-MS and was isolated in 78% yield. This result indicated that hydroxyl oxygen atom of product came from dioxygen in air.

5.6 The model reaction was carried out with the addition of $^{18}O_2$.

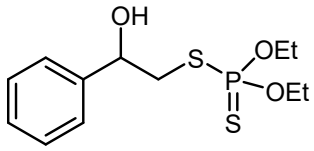


1a **2** **3a** **^{18}O-4aa** (79%)

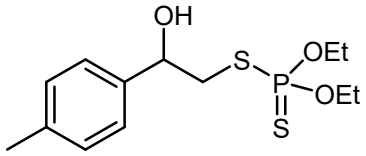
Styrene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and dry ethyl acetate (1.5 mL) were successively added in a 15 mL reaction tube. The reaction tube was protected by $^{18}O_2$ (balloon). Then, EtOH **3a** (0.5 mL) was added to reaction tube by syringe. The reaction was stirred at room temperature for 6 h. After completion of the reaction, the reaction

mixture was concentrated in vacuum, the product ^{18}O-**4aa** was obtained in 79% yield. This result indicated that hydroxyl oxygen atom of product came from dioxygen.

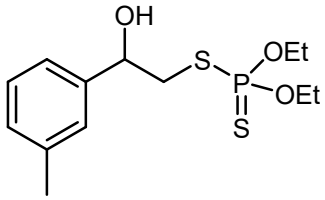
6. Characterization data of products.



***O*,*O*-diethyl *S*-(2-hydroxy-2-phenylethyl) phosphorodithioate(4aa)** Compound **4aa** was obtained in 80% yield (49.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.40 (m, 4H), 7.29-7.32 (m, 1H), 4.93 (d, J = 7.85 Hz, 1H), 4.11-4.25 (m, 4H), 3.24-3.31 (m, 1H), 3.08-3.17 (m, 1H), 2.59 (s, 1H), 1.36 (t, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.0, 128.6 (2C), 128.1, 125.8 (2C), 73.2 (d, J = 3.6 Hz), 64.29 (d, J = 6.1 Hz), 64.26 (d, J = 6.3 Hz), 42.4 (d, J = 3.6 Hz), 15.9 (d, J = 8.3 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.2. ESI HRMS: calculated for $C_{12}H_{19}NaO_3PS_2$ $[M+Na]^+$ 329.0411, found 329.0413.

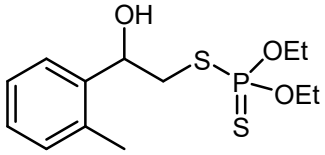


***O*,*O*-diethyl *S*-(2-hydroxy-2-(*p*-tolyl)ethyl) phosphorodithioate (4ba)** Compound **4ba** was obtained in 84% yield (54.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 4.88-4.90 (m, 1H), 4.11-4.24 (m, 4H), 3.22-3.29 (m, 1H), 3.08-3.17 (m, 1H), 2.51 (s, 1H), 2.34 (s, 3H), 1.36 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.0, 137.9, 129.3 (2C), 125.8 (2C), 73.1 (d, J = 3.7 Hz), 64.3 (d, J = 6.1 Hz), 64.2 (d, J = 6.2 Hz), 42.3 (d, J = 3.6 Hz), 21.2, 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.2. ESI HRMS: calculated for $C_{13}H_{21}NaO_3PS_2$ $[M+Na]^+$ 343.0567, found 343.0554.

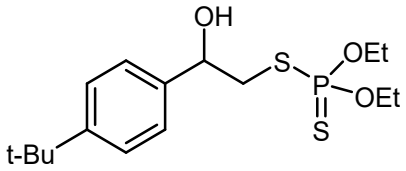


***O*,*O*-diethyl *S*-(2-hydroxy-2-(*m*-tolyl)ethyl) phosphorodithioate (4ca)** Compound **4ca** was obtained in 75% yield (48.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (m, 1H), 7.21 (t, J = 8.8 Hz, 2H), 7.18 (d, J = 7.6 Hz, 1H), 4.88 (dd, J_1=3.7 Hz, J_1=9.0 Hz,1H), 4.12-4.24 (m, 4H), 3.23-3.30 (m, 1H), 3.08-3.17

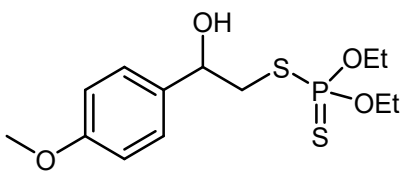
(m, 1H), 2.55 (s, 1H), 2.36 (s, 3H), 1.36 (t, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 141.9, 138.4, 128.9, 128.5, 126.4, 122.9, 73.3 (d, J = 3.6 Hz), 64.3 (d, J = 6.0 Hz), 64.3 (d, J = 6.2 Hz), 42.4 (d, J = 3.6 Hz), 21.5, 15.9 (d, J = 8.8 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.2. ESI HRMS: calculated for $C_{13}H_{21}NaO_3PS_2$ $[M+Na]^+$ 343.0567, found 343.0555.



***O*,*O*-diethyl *S*-(2-hydroxy-2-(*o*-tolyl)ethyl) phosphorodithioate(4da)** Compound **4da** was obtained in 62% yield (39.7 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 7.45 Hz, 1H), 7.25-7.23 (m, 1H), 7.21 (td, J = 1.4, 7.4 Hz, 1H), 7.14 (d, J = 4.1 Hz, 1H), 5.11-5.14 (m, 1H), 4.12-4.25 (m, 4H), 3.22-3.28 (m, 1H), 3.01-3.10 (m, 1H), 2.53 (d, J = 3.15 Hz, 1H), 2.37 (s, 3H), 1.36 (t, J = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 140.0, 134.6, 130.6, 127.9, 126.4, 125.3, 69.8 (d, J = 3.5 Hz), 64.3 (d, J = 6.2 Hz), 64.3 (d, J = 6.3 Hz), 41.2 (d, J = 3.7 Hz), 19.2, 15.9 (d, J = 8.2 Hz), 15.9 (d, J = 8.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.2. ESI HRMS: calculated for $C_{13}H_{21}NaO_3PS_2$ $[M+Na]^+$ 343.0567, found 343.0550.

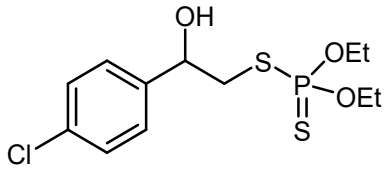


***S*-(2-(4-(*tert*-butyl)phenyl)-2-hydroxyethyl) *O*,*O*-diethyl phosphorodithioate (4ea)** Compound **4ea** was obtained in 70% yield (50.7 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 4.88-4.91 (m, 1H), 4.10-4.23 (m, 4H), 3.22-3.25 (m, 1H), 3.09-3.17 (m, 1H), 2.18 (s, 1H), 1.36 (t, J =7.1 Hz, 6H), 1.31 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 151.2, 139.0, 125.6 (2C), 125.5 (2C), 73.1 (d, J = 3.6 Hz), 64.2 (d, J = 6.2 Hz), 64.2 (d, J = 6.1 Hz), 42.2 (d, J = 3.6 Hz), 34.6, 31.3, 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.0. ESI HRMS: calculated for $C_{16}H_{27}NaO_3PS_2$ $[M+Na]^+$ 385.1037, found 385.1003.

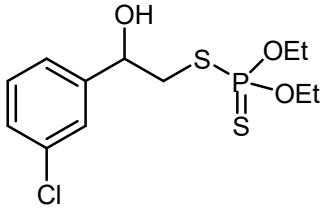


***O*,*O*-diethyl *S*-(2-hydroxy-2-(4-methoxyphenyl)ethyl) phosphorodithioate (4fa)** Compound **4fa** was obtained in 52% yield (35.0 mg) according to the general procedure

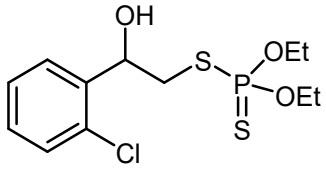
(eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.55 Hz, 2H), 4.91-4.88 (dd, J_1=3.9 Hz, J_1=8.8 Hz,1H), 4.11-4.24 (m, 4H), 3.80 (s, 3H), 3.20-3.27 (m, 1H), 3.08-3.16 (m, 1H), 2.44 (s, 1H), 1.36 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.5, 134.1, 127.1 (2C), 114.0 (2C), 72.9 (d, J = 3.6 Hz), 64.3 (d, J = 6.2 Hz), 64.2 (d, J = 6.3 Hz), 55.3, 42.3 (d, J = 3.6 Hz), 15.9 (d, J = 8.3 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.3. ESI HRMS: calculated for $C_{13}H_{21}NaO_4PS_2$ $[M+Na]^+$ 359.0517, found 359.0504.



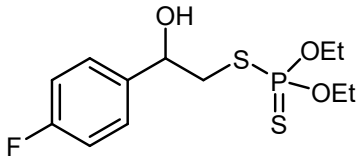
***S*-(2-(4-chlorophenyl)-2-hydroxyethyl) *O*,*O*-diethyl phosphorodithioate (4ga)** Compound **4ga** was obtained in 82% yield (56.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (s, 4H), 4.96-4.89 (m, 1H), 4.12-4.27 (m, 4H), 3.22-3.29 (m, 1H), 3.04-3.13 (m, 1H), 2.66 (d, J = 3.4 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.4, 133.8, 128.7 (2C), 127.2 (2C), 72.5 (d, J = 3.2 Hz), 64.4 (d, J = 6.3 Hz), 64.4 (d, J = 6.5 Hz), 42.5 (d, J = 3.5 Hz), 15.9 (d, J = 8.1 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.4. ESI HRMS: calculated for $C_{12}H_{18}ClNaO_3PS_2$ $[M+Na]^+$ 363.0021, found 363.0015.



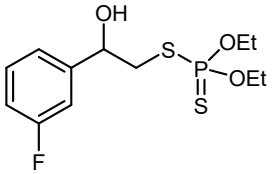
***S*-(2-(3-chlorophenyl)-2-hydroxyethyl) *O*,*O*-diethyl phosphorodithioate (4ha)** Compound **4ha** was obtained in 71% yield (48.5 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.24-7.33 (m, 3H), 4.91 (dd, J_1=3.6 Hz, J_1=8.8 Hz, 1H), 4.13-4.24 (m, 4H), 3.24-3.31 (m, 1H), 3.05-3.14 (m, 1H), 2.71 (s, 1H), 1.38 (t, J = 7.1 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 144.0, 134.6, 129.9, 128.2, 126.1, 124.1, 72.6 (d, J = 3.1 Hz), 64.4 (d, J = 6.2 Hz), 64.4 (d, J = 6.4 Hz), 42.5 (d, J = 3.5 Hz), 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.2. ESI HRMS: calculated for $C_{12}H_{18}ClNaO_3PS_2$ $[M+Na]^+$ 363.0021, found 363.0035.



***S*-(2-(2-chlorophenyl)-2-hydroxyethyl) *O*,*O*-diethyl phosphorodithioate (4ia)** Compound **4ia** was obtained in 65% yield (44.5 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, J_1=3.6 Hz, J_1=8.8 Hz, 1H), 7.36-7.30 (m, 2H), 7.22-7.26 (m, 1H), 5.31 (dd, J_1=3.2 Hz, J_1=8.6 Hz, 1H), 4.10-4.26 (m, 4H), 3.38-3.45 (m, 1H), 3.04-3.12 (m, 1H), 2.78 (s, 1H), 1.37 (dd, J_1=6.9 Hz, J_1=13.9 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.2, 131.7, 129.5, 129.1, 127.4, 127.2, 69.8 (d, J = 3.8 Hz), 64.4 (d, J = 6.2 Hz), 64.3 (d, J = 6.2 Hz) 40.3 (d, J = 3.8 Hz), 15.9 (d, J = 8.3 Hz), 15.9 (d, J = 8.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 94.6. ESI HRMS: calculated for $C_{12}H_{18}ClNaO_3PS_2$ $[M+Na]^+$ 363.0021, found 362.9989.

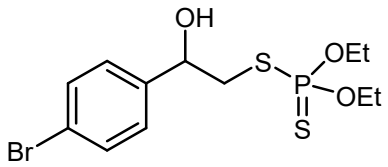


***O*,*O*-diethyl *S*-(2-(4-fluorophenyl)-2-hydroxyethyl) phosphorodithioate (4ja)** Compound **4ja** was obtained in 81% yield (52.5 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.38 (m, 2H), 7.08-7.02 (m, 2H), 4.92 (dd, J_1 = 3.5 Hz, J_2 = 8.8 Hz, 1H), 4.11-4.24 (m, 4H), 3.22-3.29 (m, 1H), 3.06-3.14 (m, 1H), 2.65 (s, 1H), 1.37 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.5 (d, J = 244.9 Hz), 137.7 (d, J = 3.0 Hz), 127.6 (d, J = 8.1 Hz, 2C), 115.5 (d, J = 21.3 Hz, 2C), 72.6 (d, J = 3.35 Hz), 64.4 (d, J = 6.2 Hz), 64.4 (d, J = 6.3 Hz), 42.6 (dd, J_1 = 0.7 Hz, J_2 = 3.3 Hz), 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.4. ^{19}F NMR (500 MHz, $CDCl_3$): -114.1. ESI HRMS: calculated for $C_{12}H_{18}FNaO_3PS_2$ $[M+Na]^+$ 347.0317, found 347.0333.

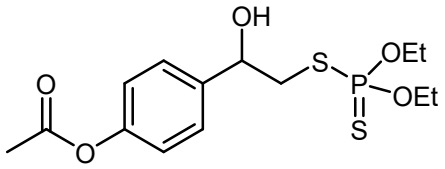


***O*,*O*-diethyl *S*-(2-(3-fluorophenyl)-2-hydroxyethyl) phosphorodithioate (4ka)** Compound **4ka** was obtained in 55% yield (35.6 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.35 (m, 1H), 7.12-7.16 (m, 2H), 6.97-7.01(m, 1H), 4.98-4.90 (m, 1H), 4.11-4.25 (m, 4H), 3.25-3.32 (m, 1H), 3.05-3.14 (m, 1H), 2.68 (d, J = 3.2 Hz, 1H), 1.38 (t, J = 7.1 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.0 (d, J = 245.1 Hz), 144.6(d, J = 6.8 Hz), 130.2 (d, J

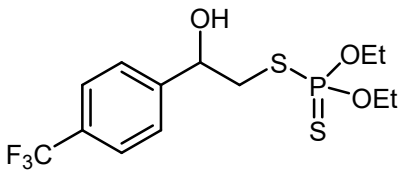
= 8.1 Hz), 121.4 (d, *J* = 2.9 Hz), 114.9 (d, *J* = 21.1 Hz), 112.8 (d, *J* = 22.1 Hz), 72.6 (dd, *J* = 3.0, 1.9 Hz), 64.4 (d, *J* = 6.3 Hz), 64.4 (d, *J* = 6.4 Hz), 42.5 (d, *J* = 3.5 Hz), 15.9 (d, *J* = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.3. ^{19}F NMR (500 MHz, $CDCl_3$): -112.4. ESI HRMS: calculated for $C_{12}H_{18}FNaO_3PS_2$ $[M+Na]^+$ 347.0317, found 347.0327.



***S*-(2-(4-bromophenyl)-2-hydroxyethyl) *O*,*O*-diethyl phosphorodithioate (4la)**
Compound **4la** was obtained in 70 % yield (54.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.89-4.92 (m, 1H), 4.11-4.24 (m, 4H), 3.23-3.29 (m, 1H), 3.04-3.13 (m, 1H), 2.65 (d, *J* = 3.3 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.9, 131.7 (2C), 127.6 (2C), 122.0, 72.6 (d, *J* = 3.2 Hz), 64.4 (d, *J* = 6.3 Hz), 64.4 (d, *J* = 6.4 Hz), 42.5 (d, *J* = 3.5 Hz), 15.9 (d, *J* = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.4. ESI HRMS: calculated for $C_{12}H_{18}BrNaO_3PS_2$ $[M+Na]^+$ 406.9516, found 406.9494.

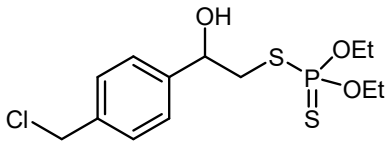


methyl 4-(2-((diethoxyphosphorothioyl)thio)-1-hydroxyethyl)benzoate (4ma)
Compound **4ma** was obtained in 56% yield (40.8 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 4.92-4.94 (m, 1H), 4.11-4.23 (m, 4H), 3.23-3.29 (m, 1H), 3.05-3.14 (m, 1H), 2.66 (d, *J* = 3.1 Hz, 1H), 2.29 (s, 3H), 1.39-1.34 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.4, 150.4, 139.5, 127.0 (2C), 121.7 (2C), 72.7 (d, *J* = 3.3 Hz), 64.4 (d, *J* = 6.3 Hz), 64.3 (d, *J* = 6.3 Hz), 42.4 (d, *J* = 3.5 Hz), 21.1, 15.9 (d, *J* = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.2. ESI HRMS: calculated for $C_{14}H_{21}NaO_5PS_2$ $[M+Na]^+$ 387.0466, found 387.0460.

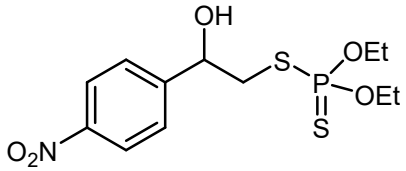


***O*,*O*-diethyl *S*-(2-hydroxy-2-(4-(trifluoromethyl)phenyl)ethyl) phosphorodithioa**

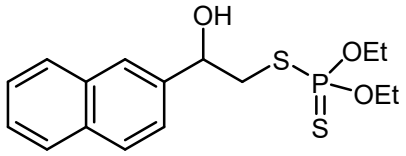
te (4na) Compound **4na** was obtained in 84% yield (63.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 5.05-4.99 (m, 1H), 4.11-4.24 (m, 4H), 3.27-3.34 (m, 1H), 3.08-3.15 (m, 1H), 2.75 (d, J = 2.3 Hz, 1H), 1.37 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.8, 130.3 (d, J = 32.2 Hz), 126.2 (2C), 125.6 (q, J = 3.8 Hz, 2C), 124.0 (q, J = 270.2 Hz), 72.6 (d, J = 3.0 Hz), 64.5 (d, J = 6.4 Hz), 64.5 (d, J = 6.4 Hz), 42.6 (d, J = 3.3 Hz), 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.4. ^{19}F NMR (500 MHz, $CDCl_3$): -62.6. ESI HRMS: calculated for $C_{13}H_{19}F_3O_3PS_2$ $[M+H]^+$ 375.0465, found 375.0449.



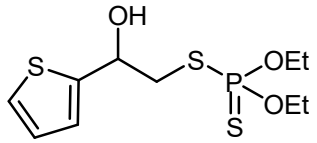
***S*-(2-(4-(chloromethyl) phenyl)-2-hydroxyethyl) *O*,*O*-diethyl phosphorodithioate (4oa)** Compound **4oa** was obtained in 88% yield (62.8 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (s, 4H), 4.93-4.95 (m, 1H), 4.58 (s, 2H), 4.11-4.24 (m, 4H), 3.24-3.31 (m, 1H), 3.08-3.15 (m, 1H), 2.65 (d, J = 2.65 Hz, 1H), 1.37 (t, J = 7.0 Hz, 3H), 1.36 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.2, 137.4, 128.9 (2C), 126.3 (2C), 72.9 (d, J = 3.3 Hz), 64.38 (d, J = 6.3 Hz), 64.35 (d, J = 6.2 Hz), 45.9, 42.4 (d, J = 3.5 Hz), 15.9 (d, J = 8.3 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.3. ESI HRMS: calculated for $C_{13}H_{20}ClNaO_3PS_2$ $[M+Na]^+$ 377.0178, found 377.0177.



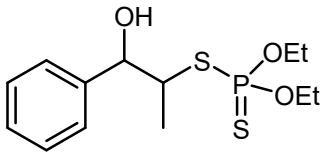
***O*,*O*-diethyl *S*-(2-hydroxy-2-(4-nitrophenyl)ethyl) phosphorodithioate (4pa)** Compound **4pa** was obtained in 54% yield (37.5 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21-8.23 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 5.07-5.09 (m, 1H), 4.13-4.25 (m, 4H), 3.30-3.37 (m, 1H), 3.06-3.15 (m, 1H), 2.90 (d, J = 2.9 Hz, 1H), 1.38 (dd, J_1=7.1 Hz, J_1=12.2 Hz, 6H), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.0, 147.6, 126.8 (2C), 123.8 (2C), 72.3 (d, J = 2.7 Hz), 64.63 (d, J = 6.4 Hz), 64.59 (d, J = 6.5 Hz), 42.5 (d, J = 3.4 Hz), 15.91 (d, J = 8.2 Hz), 15.90 (d, J = 8.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.5. ESI HRMS: calculated for $C_{12}H_{19}NO_5PS_2$ $[M+H]^+$ 352.0442, found 352.0425.



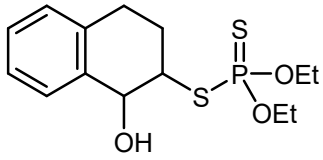
***O*,*O*-diethyl *S*-(2-hydroxy-2-(naphthalen-2-yl)ethyl) phosphorodithioate (4qa)** Compound **4qa** was obtained in 68% yield (48.5 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.85 (m, 4H), 7.46-7.50 (m, 3H), 5.10 (dd, J_1 = 3.7 Hz, J_2 = 8.8 Hz), 4.10-4.24 (m, 4H), 3.33-3.40 (m, 1H), 3.17-3.25 (m, 1H), 2.54 (m, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.3, 133.24, 133.2, 128.5, 128.0, 127.7, 126.3, 126.1, 124.8, 123.6, 73.3 (d, J = 3.5 Hz), 64.35 (d, J = 6.1 Hz), 64.32 (d, J = 6.4 Hz), 42.4 (d, J = 3.6 Hz), 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.3. ESI HRMS: calculated for $C_{16}H_{21}NaO_3PS_2$ $[M+Na]^+$ 379.0567, found 379.0553.



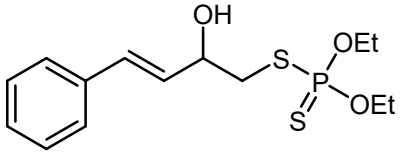
***O*,*O*--diethyl *S*-(2-hydroxy-2-(thiophen-2-yl)ethyl) phosphorodithioate (4ra)** Compound **4ra** was obtained in 37% yield (23.5 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, J_1 = 1.2 Hz, J_2 = 5 Hz, 1H), 7.05-37.02 (m, 1H), 6.99 (dd, J_1 = 3.5 Hz, J_2 = 5.0 Hz, 1H), 5.19 (dd, J_1 = 4.1 Hz, J_2 = 8.2 Hz, 1H), 4.12-4.26 (m, 4H), 3.32-3.39 (m, 1H), 3.21-3.39 (m, 1H), 2.39 (s, 1H), 1.38 (t, J = 7.0 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.6, 126.8, 125.1, 124.2, 69.6 (d, J = 3.6 Hz), 64.38 (d, J = 6.2 Hz), 64.37 (d, J = 6.3 Hz) 42.2 (d, J = 3.55 Hz), 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 94.9. ESI HRMS: calculated for $C_{10}H_{17}NaO_3PS_3$ $[M+Na]^+$ 334.9975, found 334.9972.



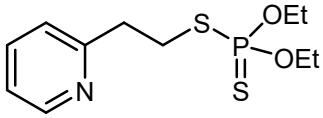
***O*,*O*-diethyl *S*-(1-hydroxy-1-phenylpropan-2-yl) phosphorodithioate (4sa)** Compound **4sa** was obtained in 53% yield (34.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.27-7.29 (m, 1H), 5.10 (d, J = 2.8 Hz, 1H), 4.10-4.26 (m, 4H), 3.67-3.73 (m, 1H), 2.43 (d, J = 2.2 Hz, 1H), 1.36 (t, J = 7.1 Hz, 6H), 1.22 (d, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.6, 128.2 (2C), 127.7, 126.1 (2C), 76.0 (d, J = 3.7 Hz), 64.2 (d, J = 6.5 Hz), 52.2 (d, J = 3.2 Hz), 15.9 (d, J = 8.3 Hz), 15.4 (d, J = 7.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 94.6. ESI HRMS: calculated for $C_{13}H_{21}NaO_3PS_2$ $[M+Na]^+$ 343.0567, found 343.0579.



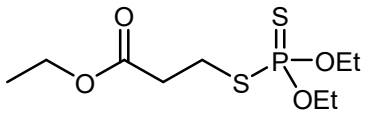
***O*,*O*-diethyl *S*-(1-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl) phosphorodithioate (4ta)** Compound **4ta** was obtained in 72% yield (48.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51-7.47 (m, 1H), 7.20-7.26 (m, 2H), 7.13-7.08 (m, 1H), 4.75-4.77 (m, 1H), 4.15-4.26 (m, 4H), 3.62-3.69 (m, 1H), 2.91-2.94 (m, 2H), 2.42-2.48 (m, 1H), 2.03-2.10 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.4, 135.5, 128.6, 128.6, 127.9, 126.6, 72.6 (d, J = 5.7 Hz), 64.39 (d, J = 6.5 Hz), 64.31 (d, J = 6.4 Hz), 52.5 (d, J = 3.4 Hz), 27.7, 27.5 (d, J = 4.9 Hz), 15.9 (d, J = 8.7 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 93.9. ESI HRMS: calculated for $C_{14}H_{21}NaO_3PS_2$ $[M+Na]^+$ 355.0567, found 355.0560.



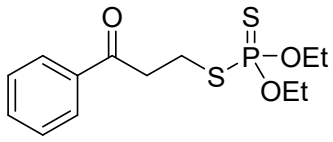
(*E*)-O,O-diethyl *S*-(2-hydroxy-4-phenylbut-3-en-1-yl) phosphorodithioate (4ua) Compound **4ua** was obtained in 50% yield (33.1 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.24-7.26 (m, 1H), 6.67 (d, J = 15.9 Hz, 1H), 6.21 (dd, J_1 = 6.2 Hz, J_2 = 15.9 Hz, 1H), 4.53-4.56 (m, 1H), 4.15-4.22 (m, 4H), 3.18-3.25 (m, 1H), 3.04-3.12 (m, 1H), 1.99 (s, 1H), 1.36 (dt, J_1 = 7.1 Hz, J_2 = 1.8 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.2, 131.9, 129.2, 128.6 (2C), 128.0, 126.6 (2C), 71.6 (d, J = 3.8 Hz), 64.34 (d, J = 6.3 Hz), 64.31 (d, J = 6.3 Hz), 40.7 (d, J = 3.6 Hz), 15.9 (d, J = 8.2 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.3. ESI HRMS: calculated for $C_{14}H_{22}NaO_3PS_2$ $[M+H]^+$ 333.0748, found 333.0748.



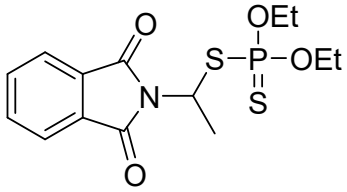
***O*,*O*-diethyl *S*-(2-(pyridin-2-yl)ethyl) phosphorodithioate phosphorodithioate (4va)** Compound **4va** was obtained in 90% yield (52.4 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (d, J = 4.8 Hz ,1H), 7.62 (td, J_1 = 1.8 Hz, J_2 = 7.7 Hz, 1H), 7.20 (d, J = 7.8 Hz ,1H), 7.14-7.17 (m, 1H), 4.09-4.23 (m, 4H), 3.26-3.32 (m, 2H), 3.16 (t, J = 7.6 Hz, 2H), 1.36 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.9, 149.5, 136.5, 123.4, 121.8, 63.9 (d, J = 5.9 Hz), 38.6 (d, J = 5.0 Hz), 32.7 (d, J = 3.8 Hz), 15.9 (d, J = 8.3 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 94.7. ESI HRMS: calculated for $C_{11}H_{19}NO_2PS_2$ $[M+H]^+$ 292.0595, found 292.0604.



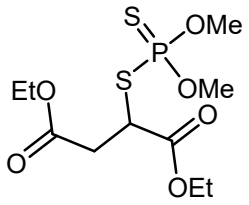
ethyl 3-((diethoxyphosphorothioyl)thio)propanoate (4wa) Compound **4wa** was obtained in 92% yield (53.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=20/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.11-4.23 (m, 6H), 3.09-3.14 (m, 2H), 2.71 (t, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.1, 64.0 (d, J = 6 Hz, 2C), 60.8, 35.2 (d, J = 3.9 Hz), 28.3 (d, J = 4.0 Hz), 15.8 (d, J = 8.3 Hz, 2C), 14.18. ^{31}P NMR (202 MHz, $CDCl_3$): δ 94.1. ESI HRMS: calculated for $C_9H_{20}O_4PS_2$ $[M+H]^+$ 287.0541, found 287.0549.



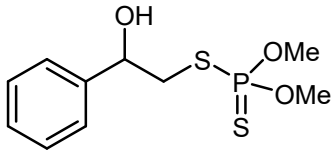
***O*,*O*-diethyl *S*-(3-oxo-3-phenylpropyl) phosphorodithioate (4xa)** Compound **4xa** was obtained in 30% yield (20.4 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=20/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95-7.97 (m, 2H), 7.57-7.60 (m, 1H), 7.48 (t, J = 7.8 Hz, 2H), 4.11-4.23 (m, 4H), 3.42 (t, J = 7.1 Hz, 2H), 3.32-3.29 (m 2H), 1.36 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 197.5, 136.3, 133.5, 128.7 (2C), 128.0 (2C), 64.1 (d, J = 6.2 Hz, 2C), 39.3 (d, J = 3.5 Hz), 27.5 (d, J = 3.8 Hz), 15.9 (d, J = 8.3 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 94.8. ESI HRMS: calculated for $C_{13}H_{19}NaO_3PS_2$ $[M+Na]^+$ 341.0411, found 341.0426.



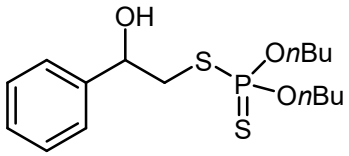
***S*-(1-(1,3-dioxoisoindolin-2-yl)ethyl) *O*,*O*-diethyl phosphorodithioate (4ya)** Compound **4ya** was obtained in 89% yield (67.8 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85-7.88 (m, 2H), 7.77-7.73 (m, 2H), 5.84-5.91 (m, 1H), 4.09-4.23 (m, 3H), 4.95-4.00 (m, 1H), 1.90 (d, J = 7 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.4, 134.3 (2C), 131.7, 123.5 (2C), 64.21 (d, J = 5.9 Hz), 64.20 (d, J = 5.8 Hz), 51.8 (d, J = 3.8 Hz), 22.0 (d, J = 6.7 Hz), 15.8 (d, J = 8.3 Hz), 15.6 (d, J = 8.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 89.4. ESI HRMS: calculated for $C_{14}H_{18}NNaO_4PS_2$ $[M+Na]^+$ 382.0313, found 382.0336.



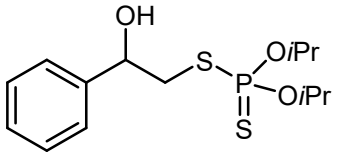
diethyl 2-((dimethoxyphosphorothioyl)thio)succinate (4za) Compound **4za** was obtained in 40% yield (26.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.20-4.24 (m, 2H), 4.09-4.18 (m, 3H), 3.83 (d, J = 5.0 Hz, 3H), 3.80 (d, J = 5.0 Hz, 3H), 3.03 (dd, J_1 = 9.2 Hz, J_2 = 17.5 Hz,1H), 2.90 (dd, J_1 = 5.1 Hz, J_2 = 17.0 Hz, 1H), 1.28 (dt, J_1 = 7.2 Hz, J_2 = 17.7 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.0 (d, J = 5.7 Hz), 169.9, 62.1, 61.1, 54.33 (d, J = 5.6 Hz), 54.32 (d, J = 5.1 Hz), 45.1 (d, J = 3.6 Hz), 37.8 (d, J = 4.3 Hz), 14.1, 14.0. ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.6. ESI HRMS: calculated for $C_{10}H_{20}O_6PS_2$ $[M+H]^+$ 331.0439, found 331.0443.



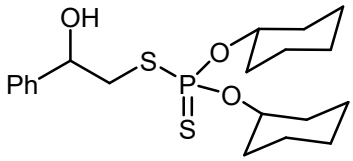
***S*-(2-hydroxy-2-phenylethyl) *O*,*O*-dimethyl phosphorodithioate (4ab)** Compound **4ab** was obtained in 71% yield (39.6 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.41 (m, 4H), 7.30-7.32 (m, 1H), 4.91 (dd, J_1 = 3.8 Hz, J_2 = 8.8 Hz, 1H), 3.79 (d, J = 1.60 Hz, 3H), 3.76 (d, J =1.65 Hz, 3H), 3.23-3.30 (m, 1H), 3.09-3.18 (m, 1H), 2.24 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.8, 128.7 (2C), 128.2, 125.9 (2C), 73.2 (d, J = 3.6 Hz), 54.25 (d, J = 6.2 Hz), 54.20 (d, J = 6.3 Hz), 42.2 (d, J = 3.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.2. ESI HRMS: calculated for $C_{10}H_{15}NaO_3PS_2$ $[M+Na]^+$ 301.0098 found 301.0096.



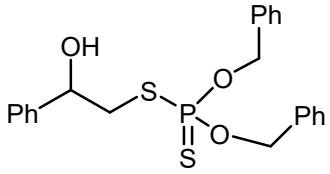
***O*,*O*-dibutyl *S*-(2-hydroxy-2-phenylethyl) phosphorodithioate (4ac)** Compound **4ac** was obtained in 64% yield (46.3 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.40 (m, 4H), 7.29-7.32 (m, 1H), 4.92 (dd, J_1 = 3.7 Hz, J_2 = 8.9 Hz, 1H), 4.03-4.17 (m, 4H), 3.24-3.31 (m, 1H), 3.08-3.17 (m, 1H), 2.58 (s, 1H), 1.64-1.71 (m, 4H), 1.38-1.45 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.0, 128.6 (2C), 128.1, 125.8 (2C), 73.2 (d, J = 3.5 Hz), 68.02 (d, J = 6.7 Hz), 67.98 (d, J = 6.8 Hz), 42.4 (d, J = 3.6 Hz), 32.0 (d, J = 8.1 Hz, 2C), 18.8 (2C), 13.6 (2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.6. ESI HRMS: calculated for $C_{16}H_{27}NaO_3PS_2$ $[M+Na]^+$ 385.1037. found 385.1025.



***S*-(2-hydroxy-2-phenylethyl) *O*,*O*-diisopropyl phosphorodithioate (4ad)** Compound **4ad** was obtained in 64% yield (43.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.41 (m, 4H), 7.30 (t, J = 7.0 Hz 1H), 4.99-4.93 (m, 1H), 4.83-4.90 (m, 2H), 3.26-3.33 (m, 1H), 3.09-3.17 (m, 1H), 2.71 (s, 1H), 1.35-1.38 (m, 12H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.1, 128.6 (2C), 128.1, 125.8 (2C), 73.9 (d, J = 7.0 Hz, 2C), 73.1 (d, J = 3.6 Hz), 42.7 (d, J = 3.6 Hz), 23.75 (d, J = 4.5 Hz), 23.74 (d, J = 4.3 Hz), 23.52 (d, J = 5.4 Hz), 23.50 (d, J = 5.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 92.2. ESI HRMS: calculated for $C_{14}H_{23}NaO_3PS_2$ $[M+Na]^+$ 357.0724. found 357.0710.



***O*,*O*-dicyclohexyl *S*-(2-hydroxy-2-phenylethyl) phosphorodithioate (4ae)** Compound **4ae** was obtained in 75% yield (62.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.40 (m, 4H), 7.28-7.31 (m, 1H), 4.96 (dd, J_1 = 3.5 Hz, J_2 = 9.2 Hz, 1H), 4.55-4.62 (m, 2H), 3.26-3.38 (m, 2H), 3.07-3.16 (m, 1H), 1.95 (s, 4H), 1.73-1.75 (m, 4H), 1.50-1.59 (m, 6H), 1.33-1.40 (m, 4H), 1.24-1.29 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.0, 128.6 (2C), 128.0, 125.8 (2C), 78.7 (d, J = 7.8 Hz, 2C), 73.1 (d, J = 3.4 Hz), 42.7 (d, J = 3.6 Hz), 33.4 (d, J = 3.6 Hz, 2C), 33.2 (d, J = 3.3 Hz), 33.1 (d, J = 3.2 Hz), 25.1(2C), 23.7 (2C), 23.6 (2C). ^{31}P NMR (202 MHz, $CDCl_3$): δ 91.8. ESI HRMS: calculated for $C_{20}H_{31}NaO_3PS_2$ $[M+Na]^+$ 437.1350. found 437.1334.

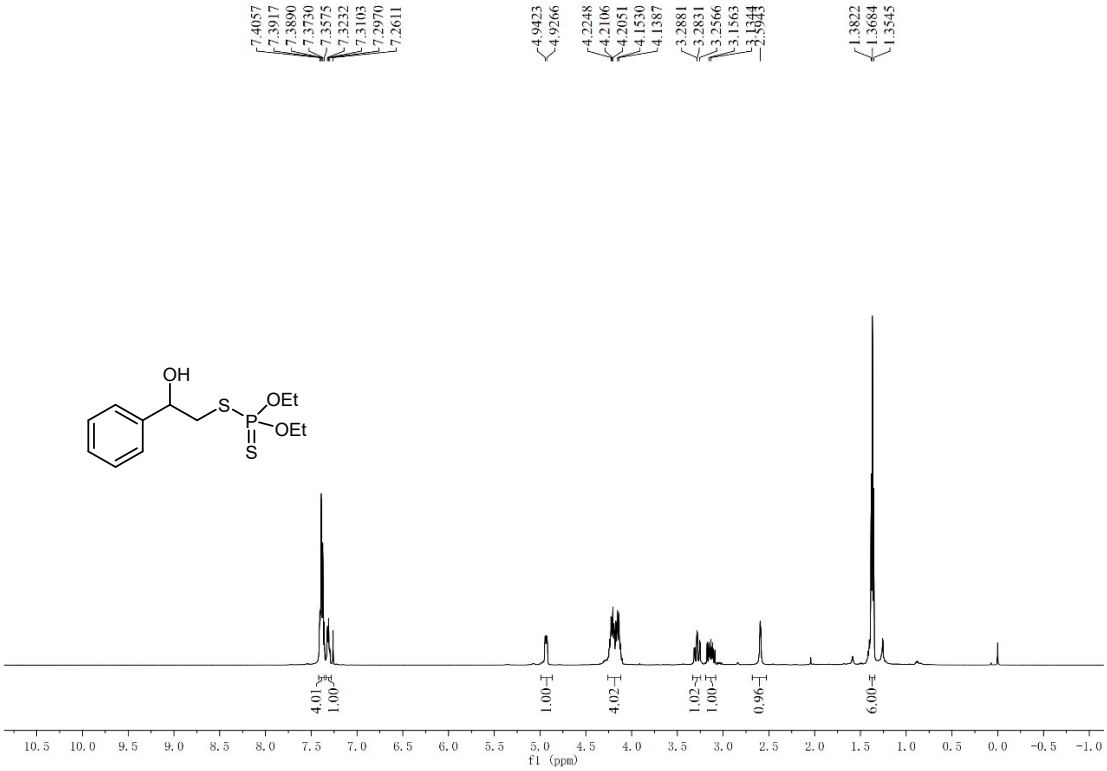


***O*,*O*-dibenzyl *S*-(2-hydroxy-2-phenylethyl) phosphorodithioate (4af)** Compound **4af** was obtained in 85% yield (73.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.39 (m, 12H), 7.25-7.29 (m, 3H), 5.08-5.18 (m, 4H), 4.84-34.79 (m, 1H), 3.18-3.24 (m, 1H), 3.02-3.10 (m, 1H), 2.39 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.8, 135.5 (d, J = 8.4 Hz, 2C), 128.6 (overlapped, 6C), 128.5 (2C), 128.34 (d, J = 3.7 Hz, 4C), 128.1, 125.8 (2C), 73.1 (d, J = 3.7 Hz), 69.64 (d, J = 6.1 Hz), 69.57 (d, J = 6.2 Hz), 42.3 (d, J = 3.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 96.5.

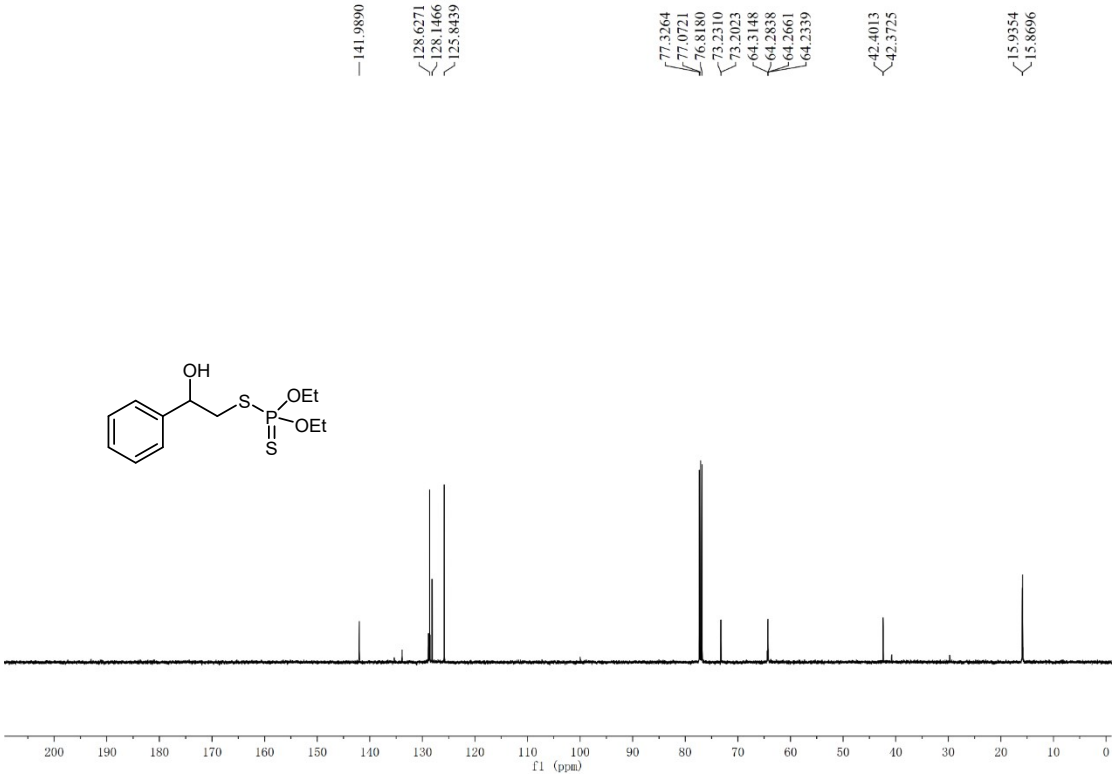
ESI HRMS: calculated for $C_{22}H_{23}NaO_3PS_2$ $[M+Na]^+$ 453.0724. found 453.0714.

7. Copies of NMR spectra for products

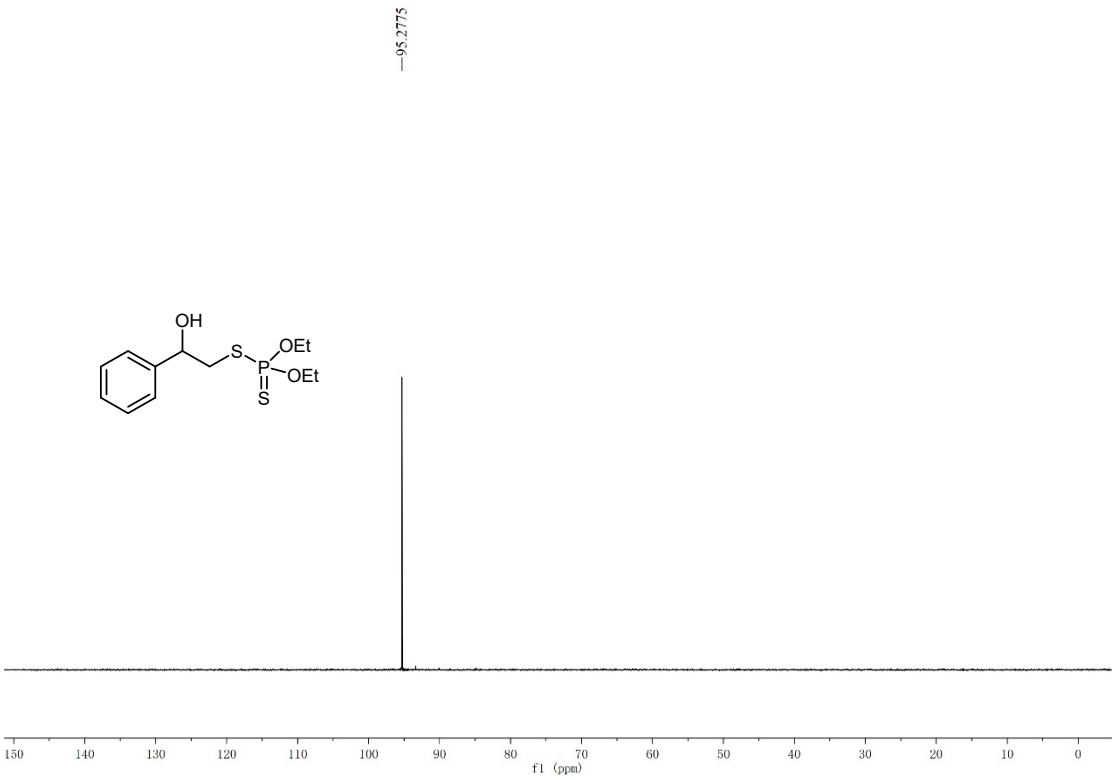
4aa ^{1}H NMR (500 MHz, $CDCl_3$)



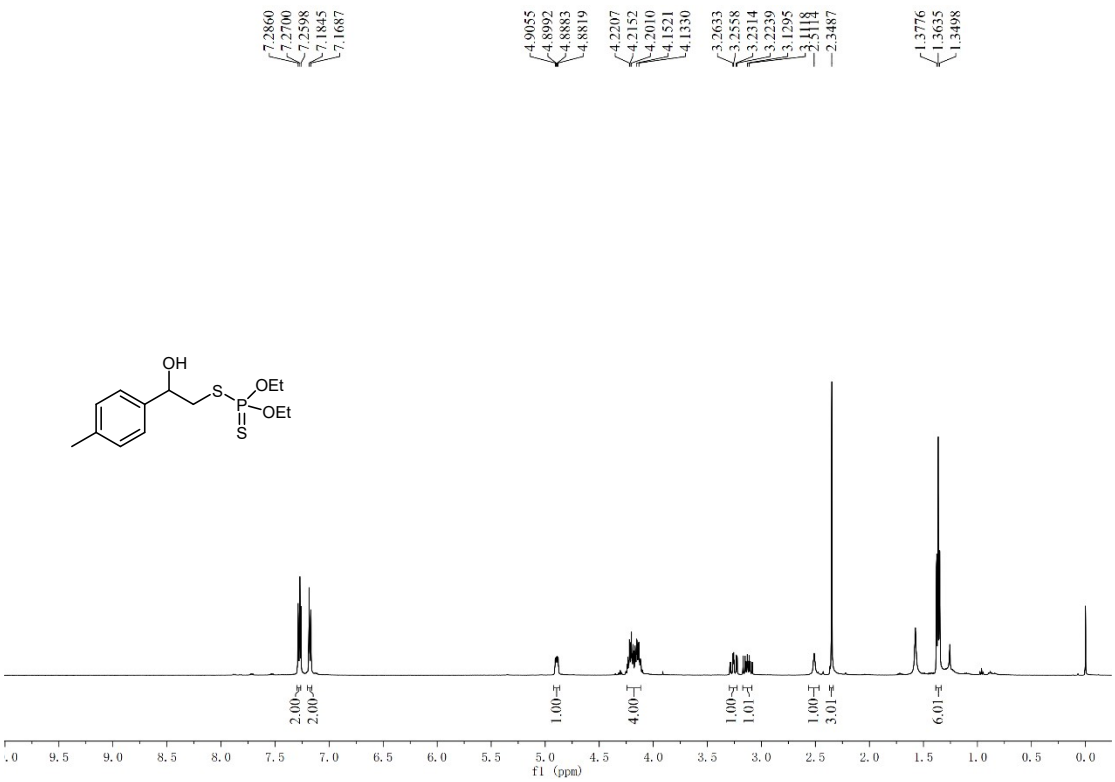
4aa ^{13}C NMR (125MHz, $CDCl_3$)



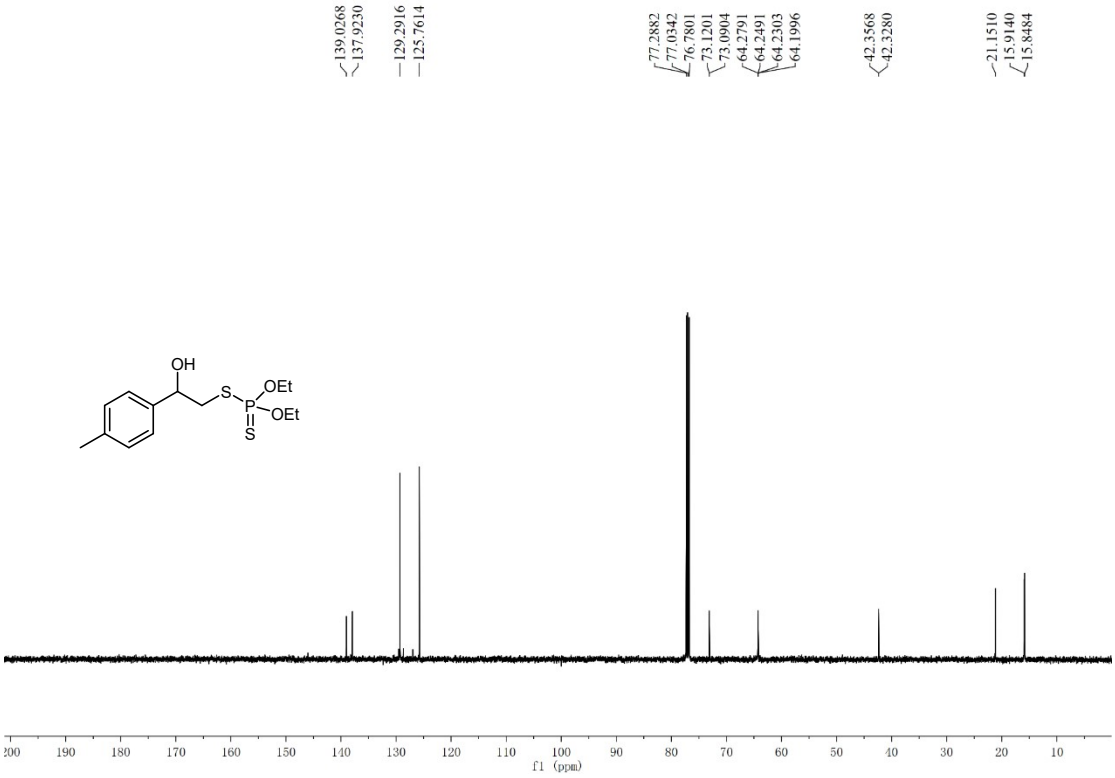
4aa ^{31}P NMR (202 MHz, $CDCl_3$):



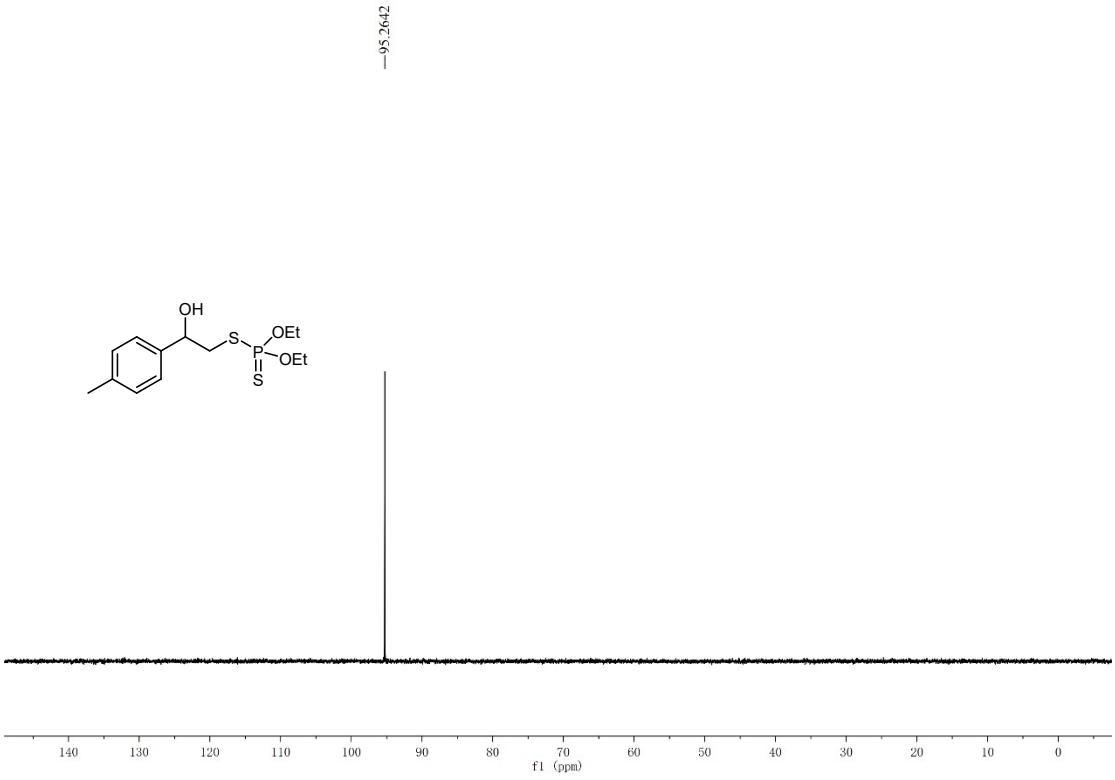
4ba ^{1}H NMR (500 MHz, $CDCl_3$)



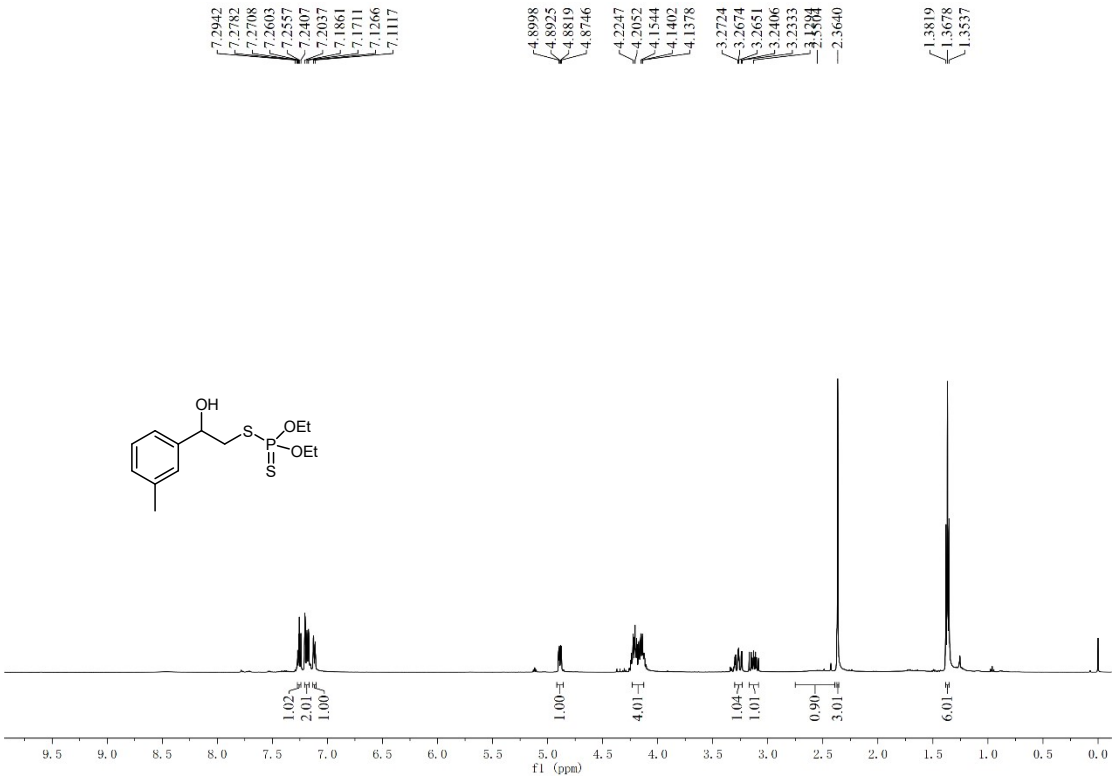
4ba ^{13}C NMR (125 MHz, $CDCl_3$)



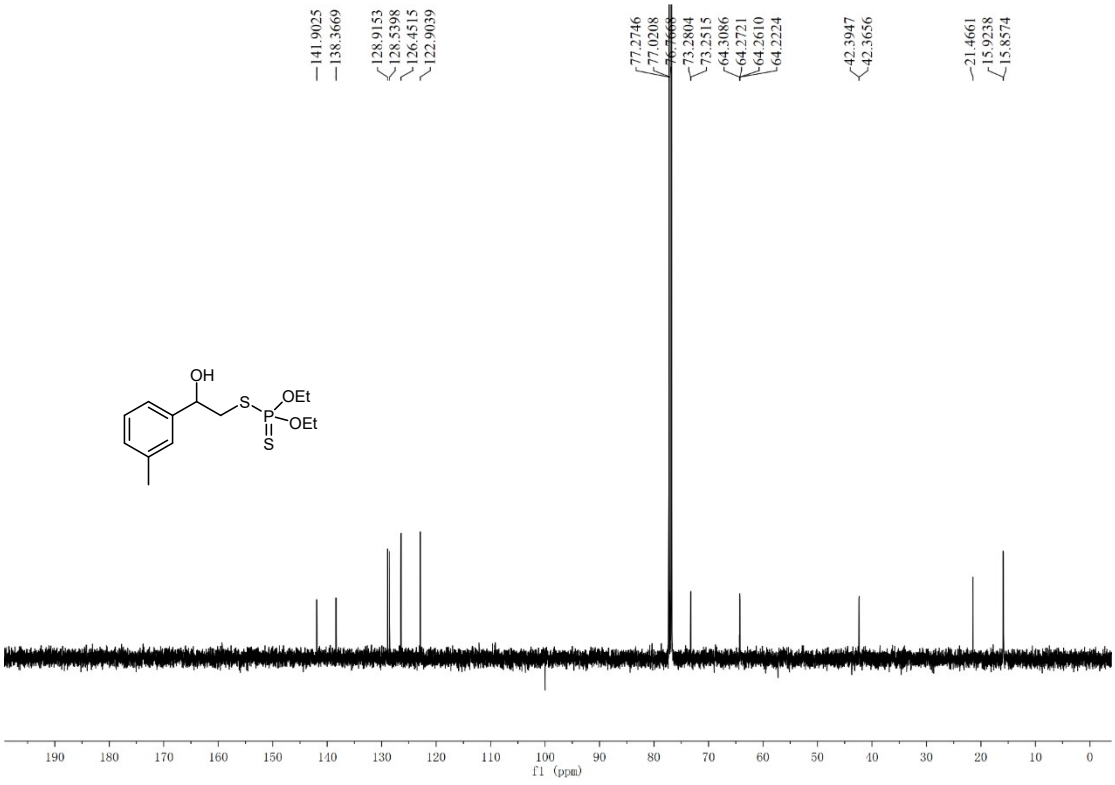
4ba ^{31}P NMR (202 MHz, $CDCl_3$):



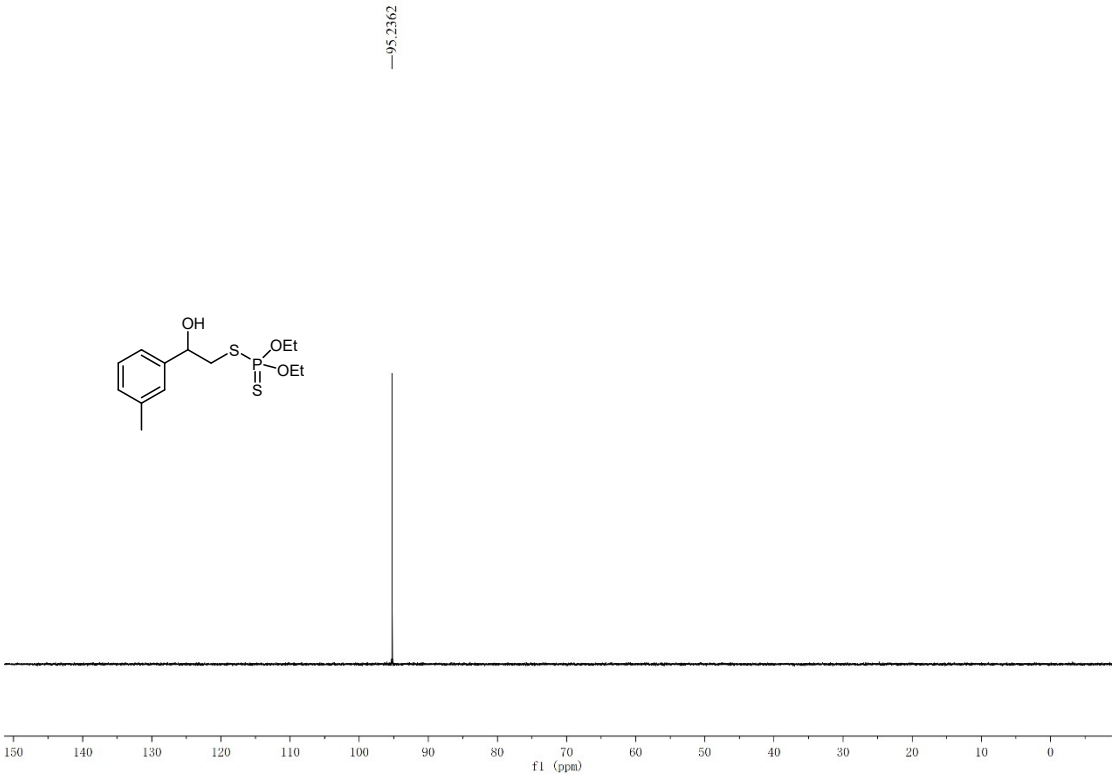
4ca ^{1}H NMR (500 MHz, $CDCl_3$)



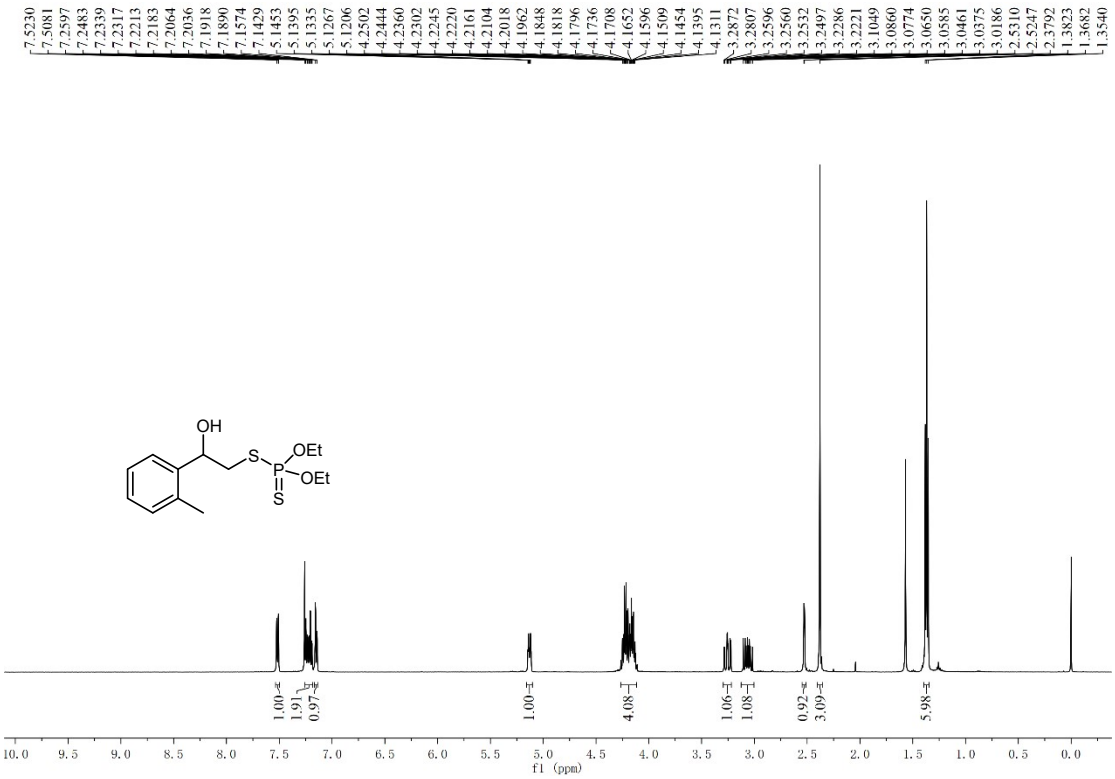
4ca ^{13}C NMR (125 MHz, $CDCl_3$)



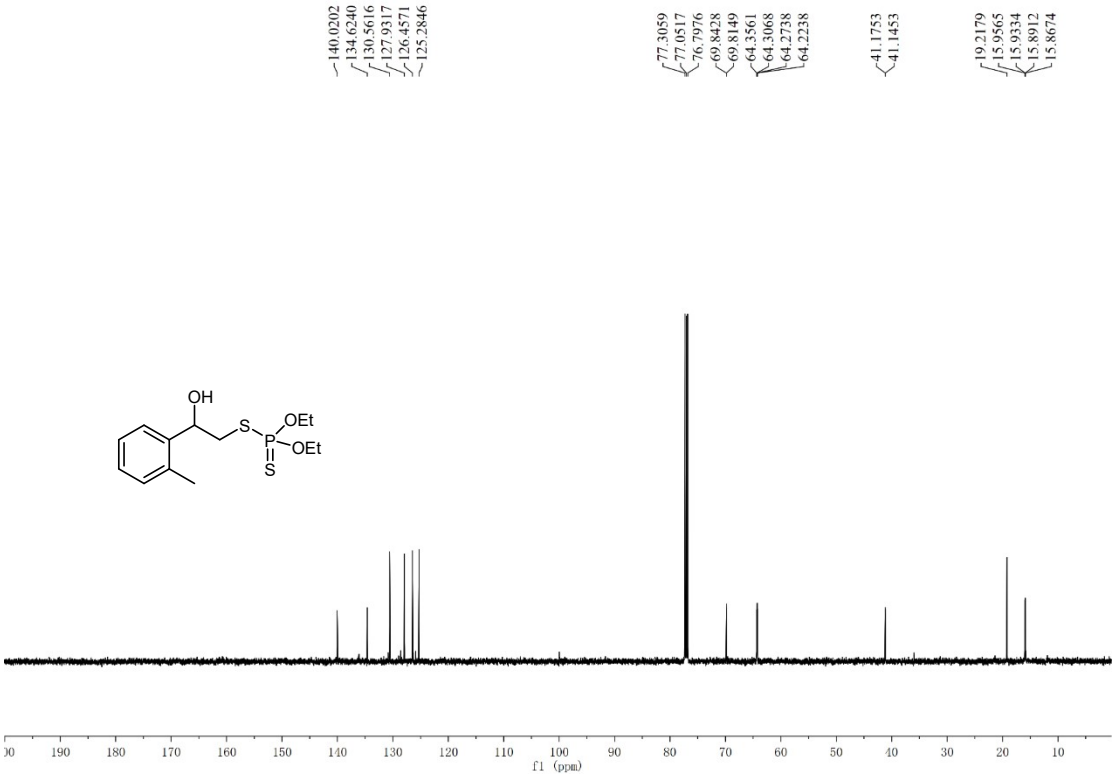
4ca ^{31}P NMR (202 MHz, $CDCl_3$):



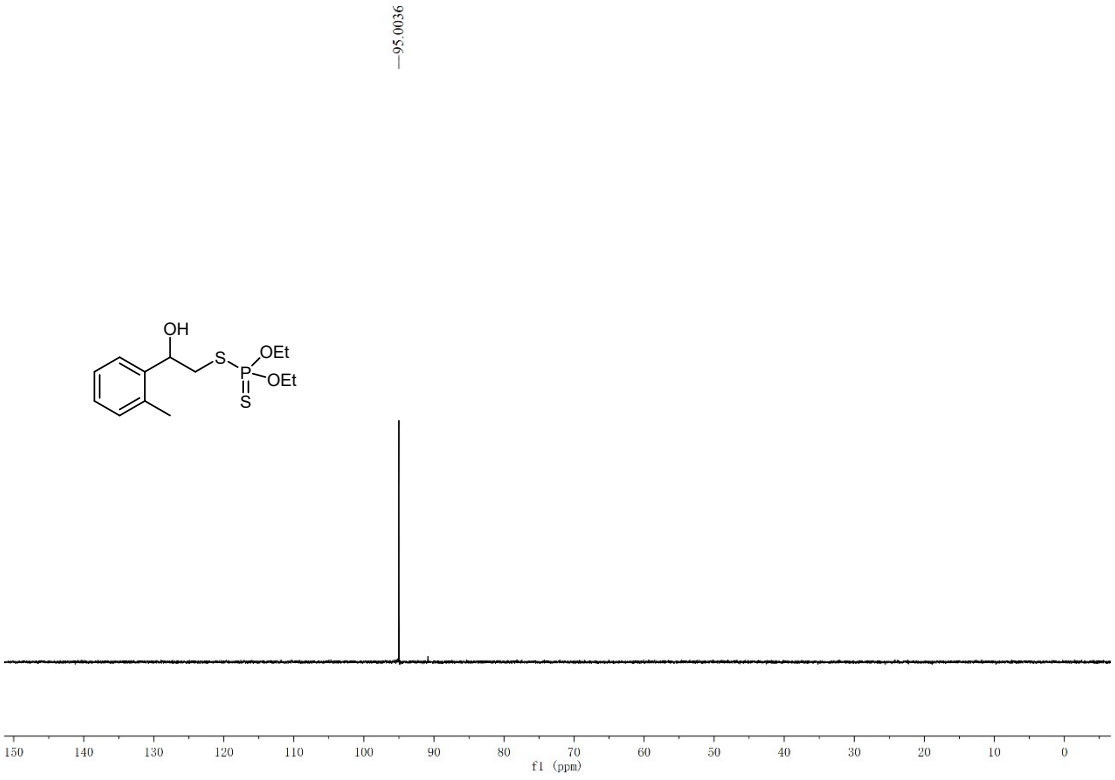
4da ^{1}H NMR (500 MHz, $CDCl_3$)



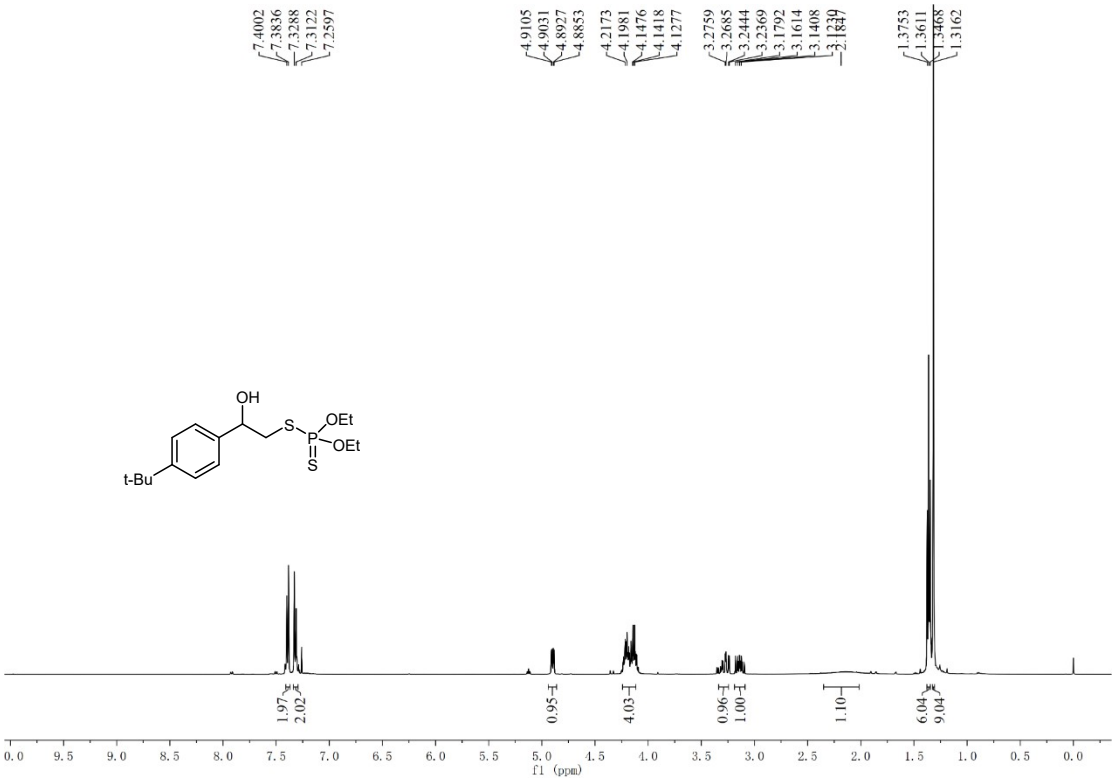
4da ^{13}C NMR (125 MHz, $CDCl_3$)



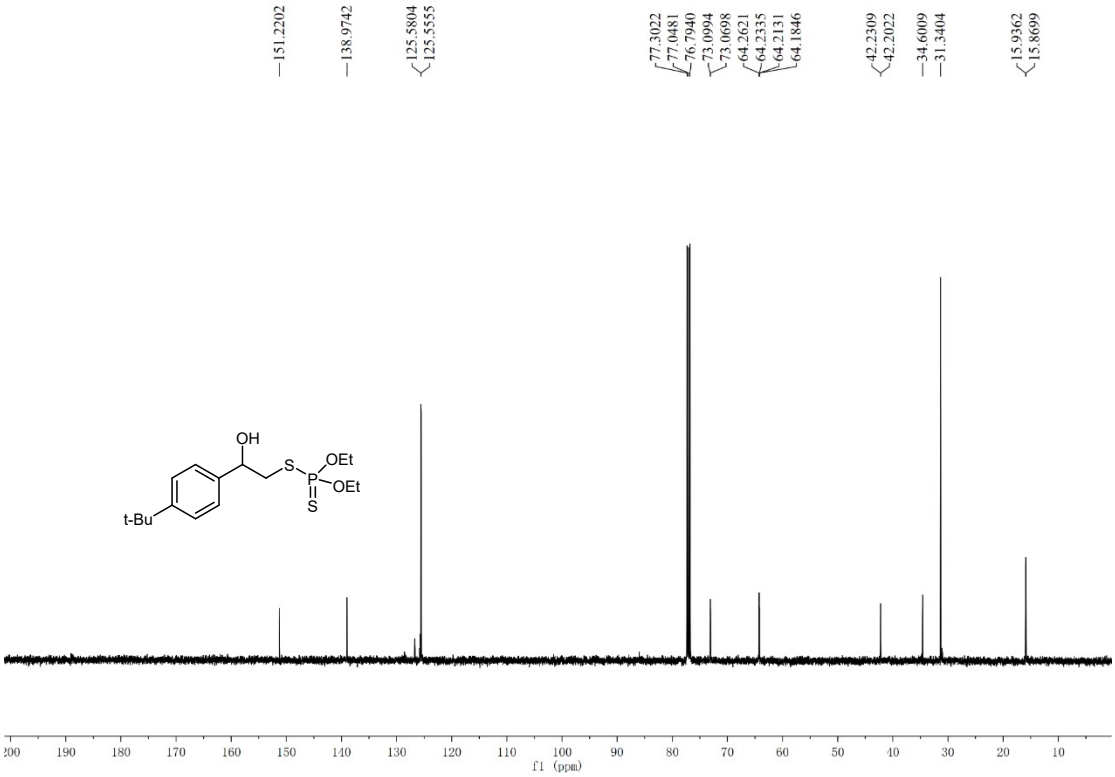
4da ^{31}P NMR (202 MHz, $CDCl_3$):



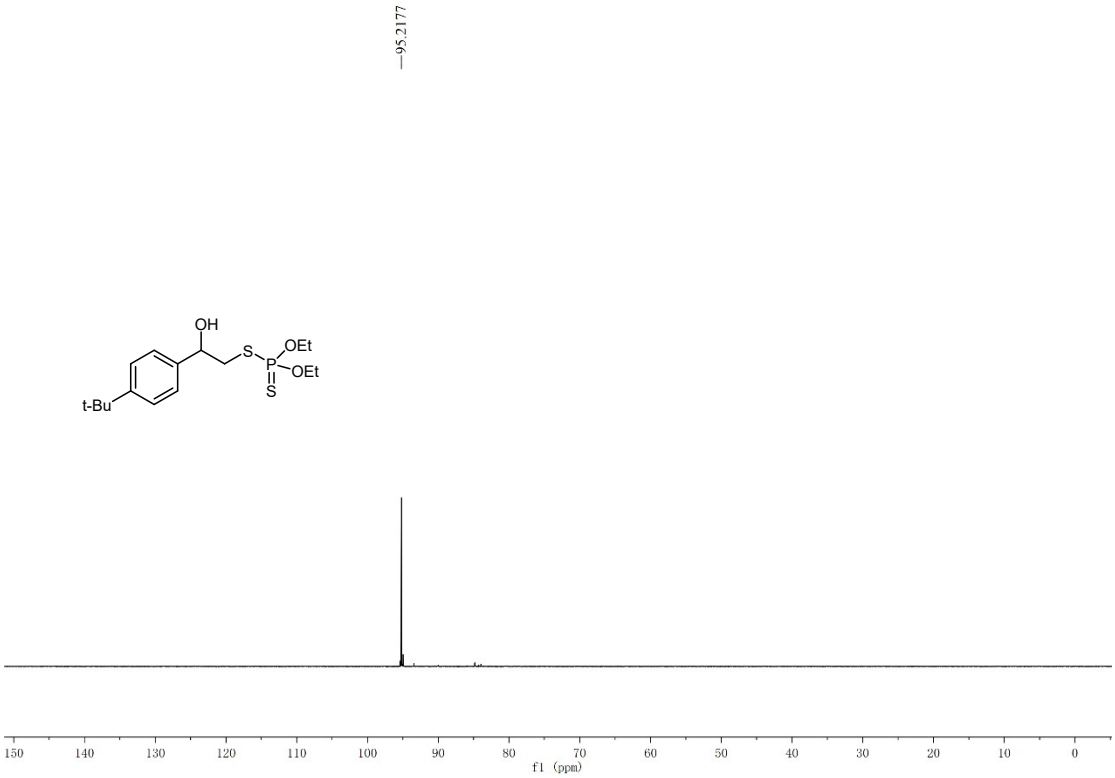
4ea ^{1}H NMR (500 MHz, $CDCl_3$)



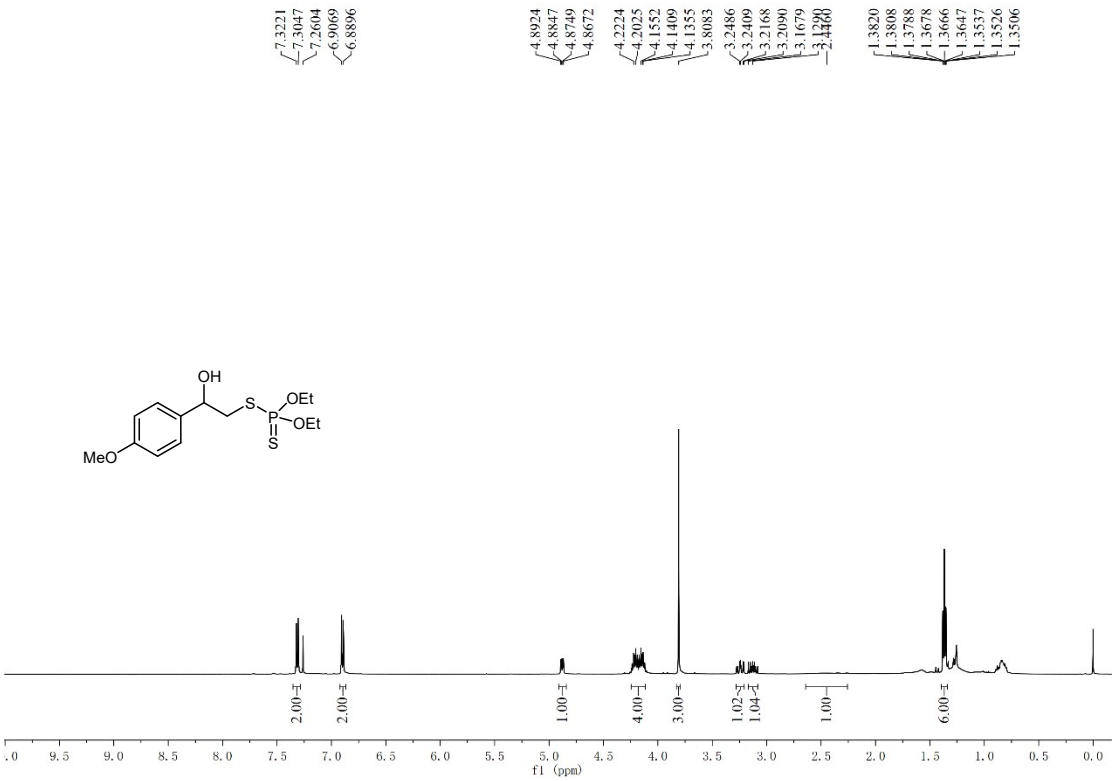
4ea ^{13}C NMR (125 MHz, $CDCl_3$)



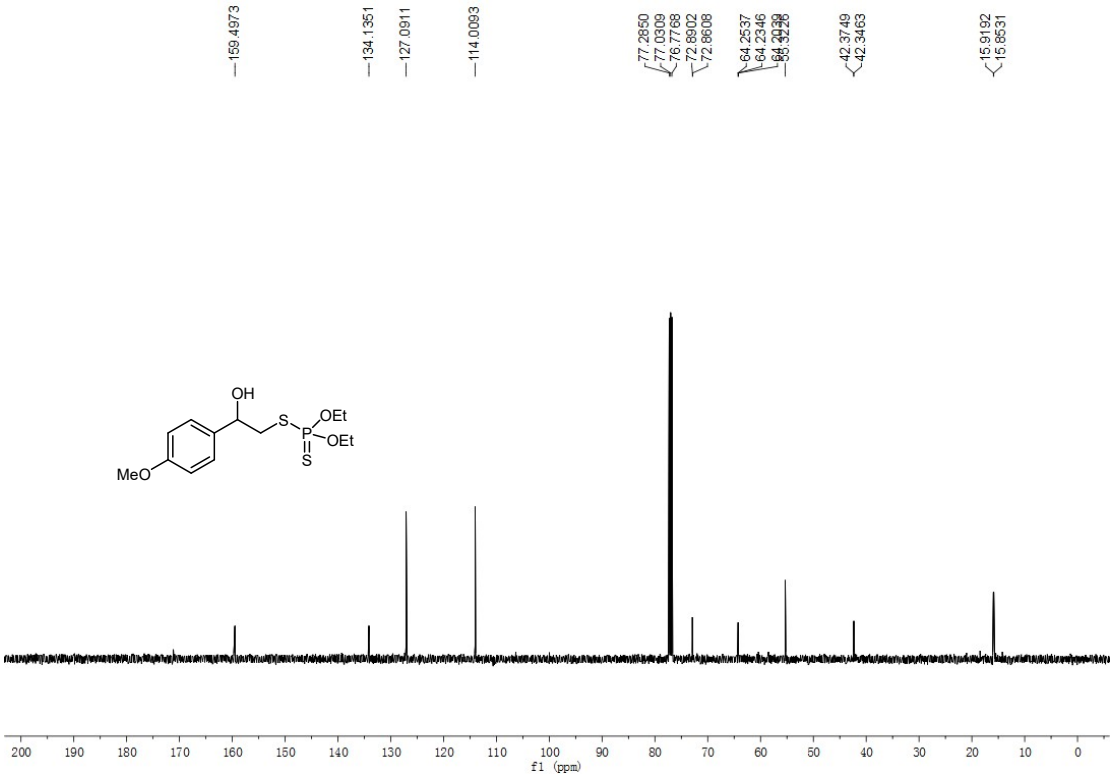
4ea ^{31}P NMR (202 MHz, $CDCl_3$):



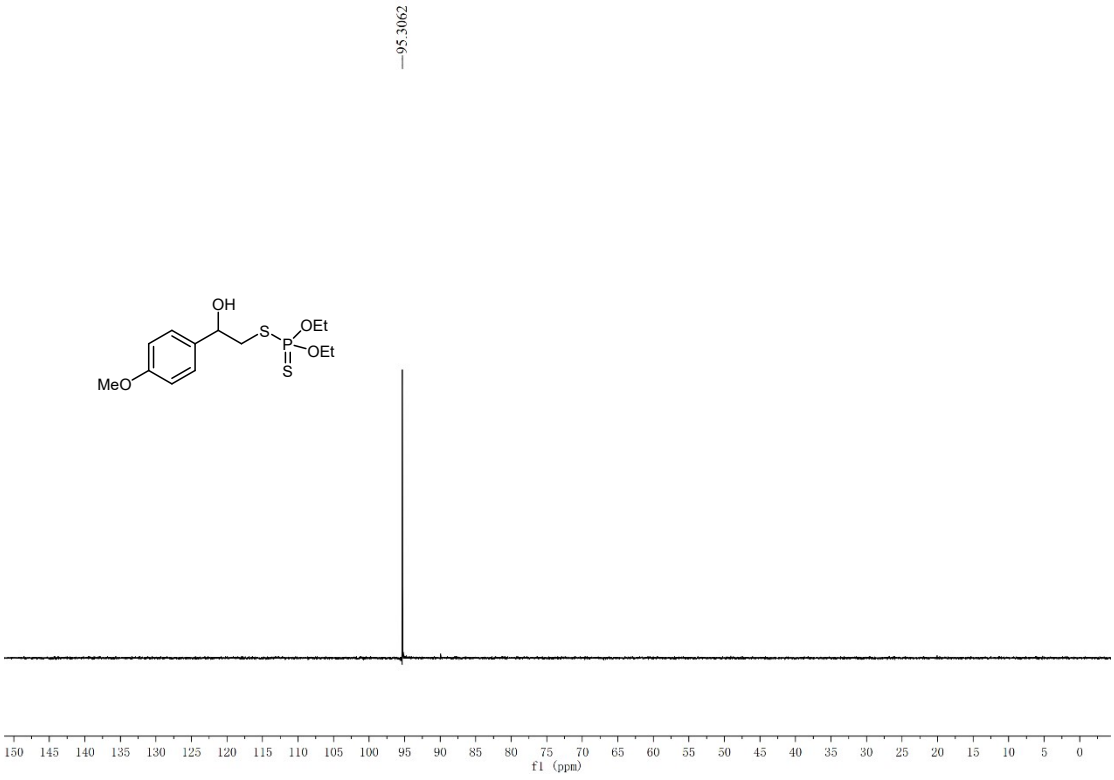
4fa ^{1}H NMR (500 MHz, $CDCl_3$)



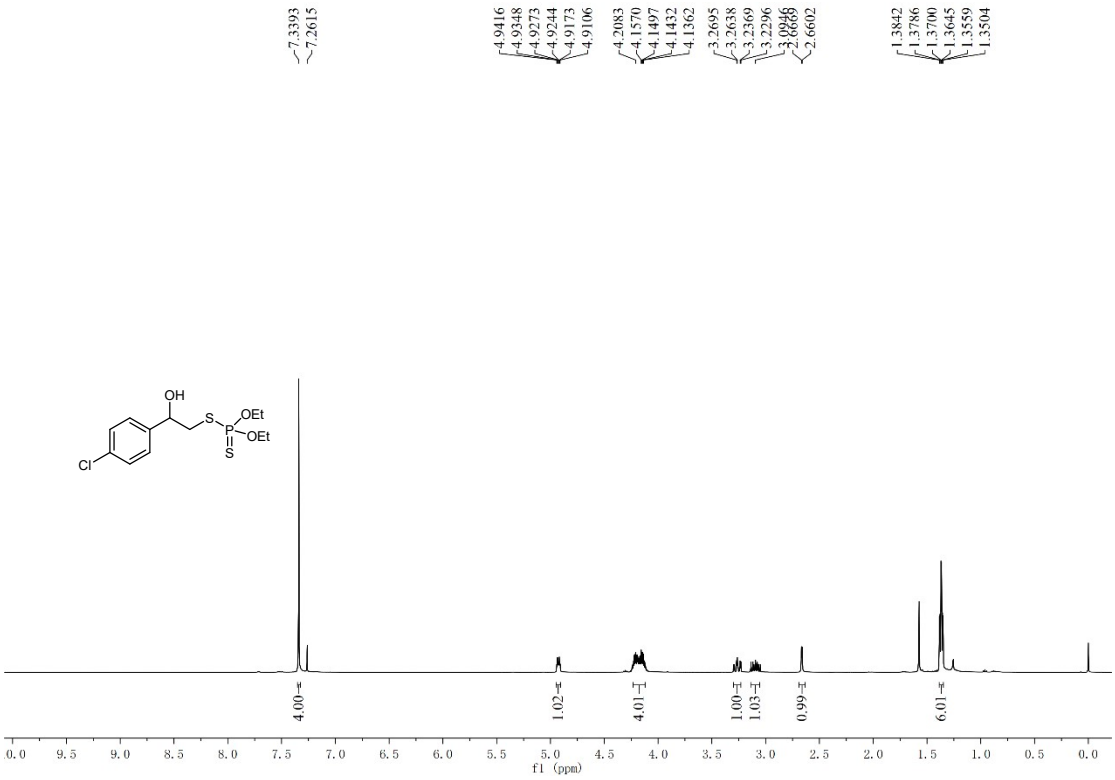
4fa ^{13}C NMR (125 MHz, $CDCl_3$)



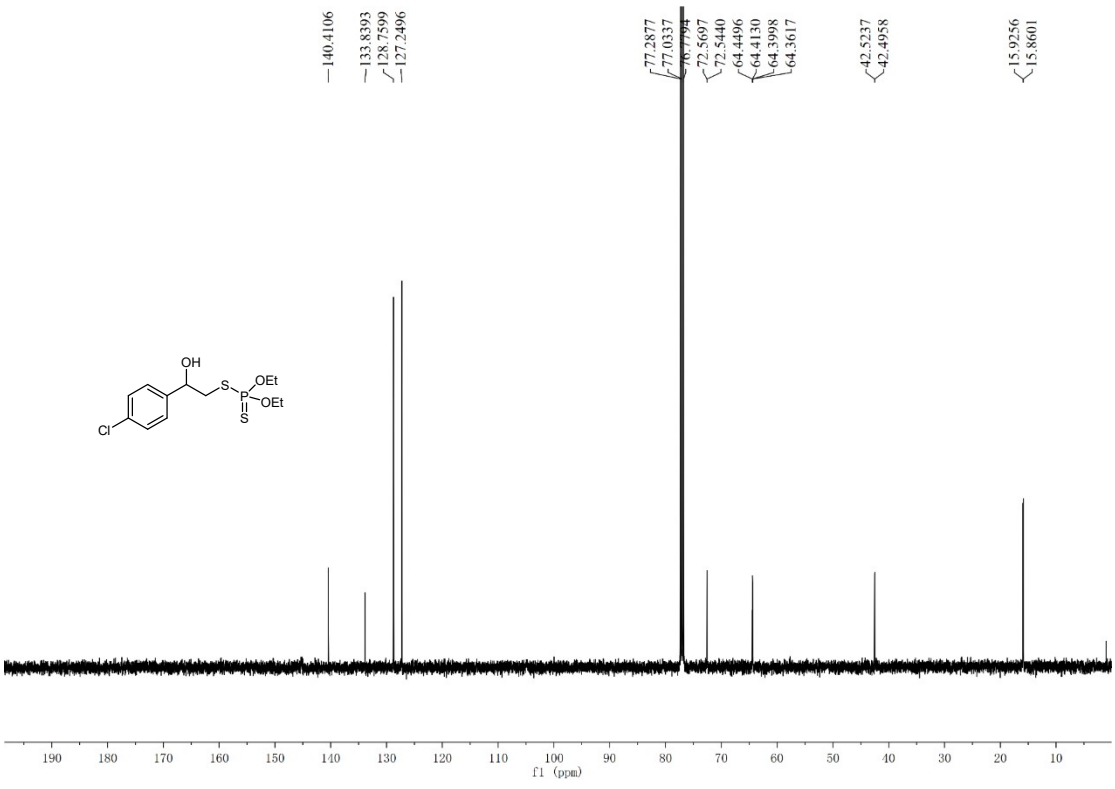
4fa ^{31}P NMR (202 MHz, $CDCl_3$):



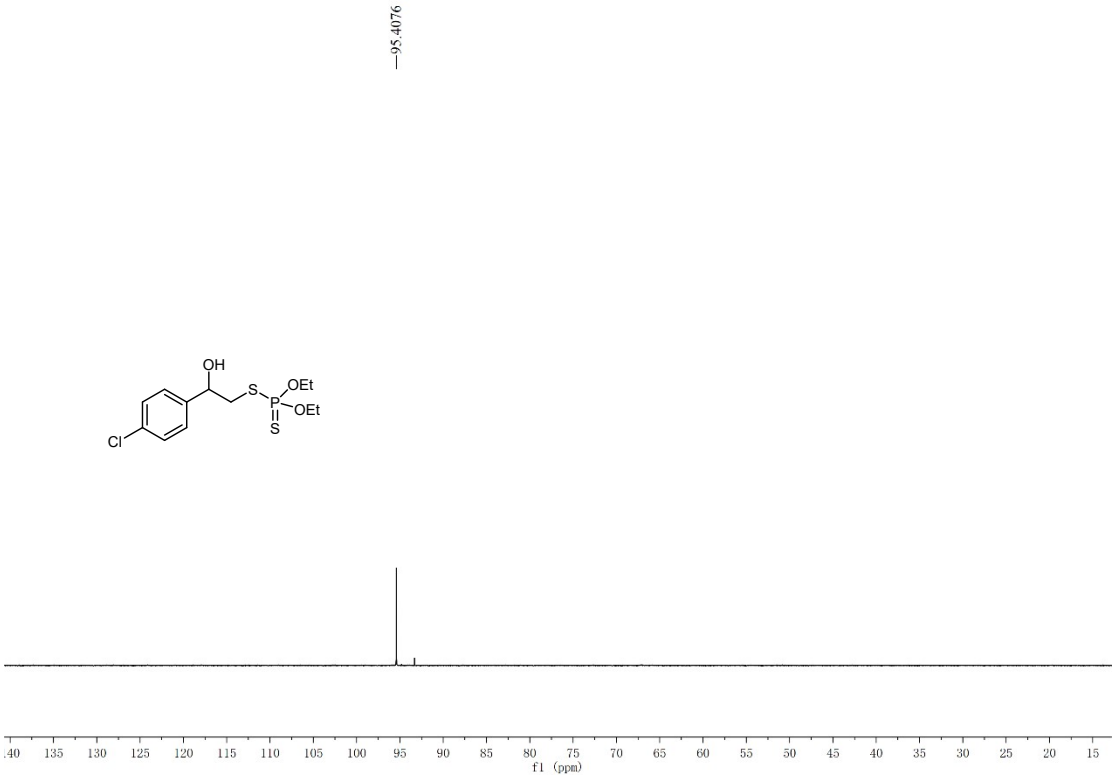
4ga ^{1}H NMR (500 MHz, $CDCl_3$)



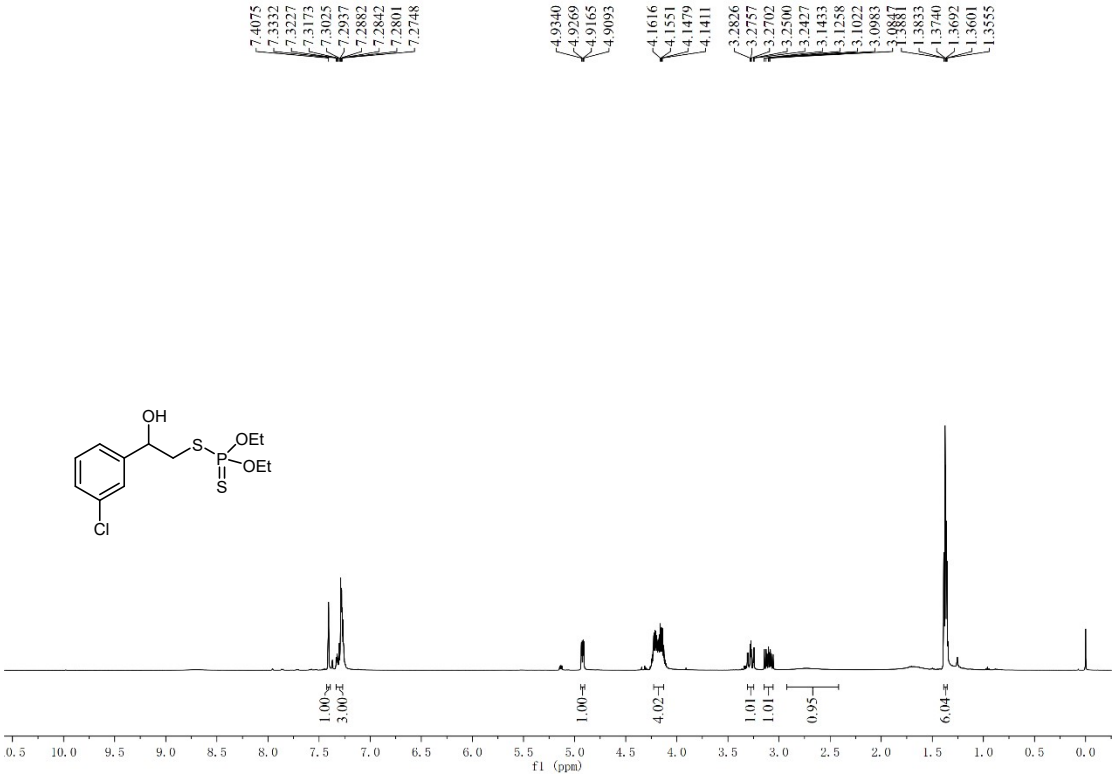
4ga ^{13}C NMR (125 MHz, $CDCl_3$)



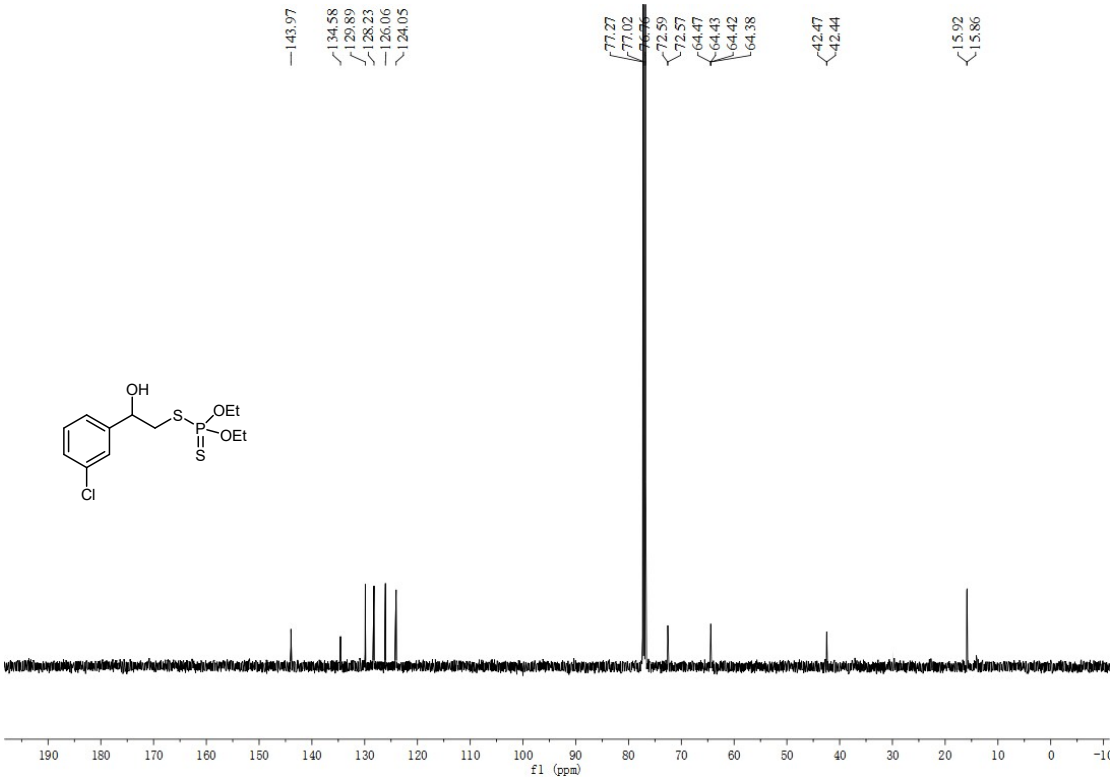
4ga ^{31}P NMR (202 MHz, $CDCl_3$):



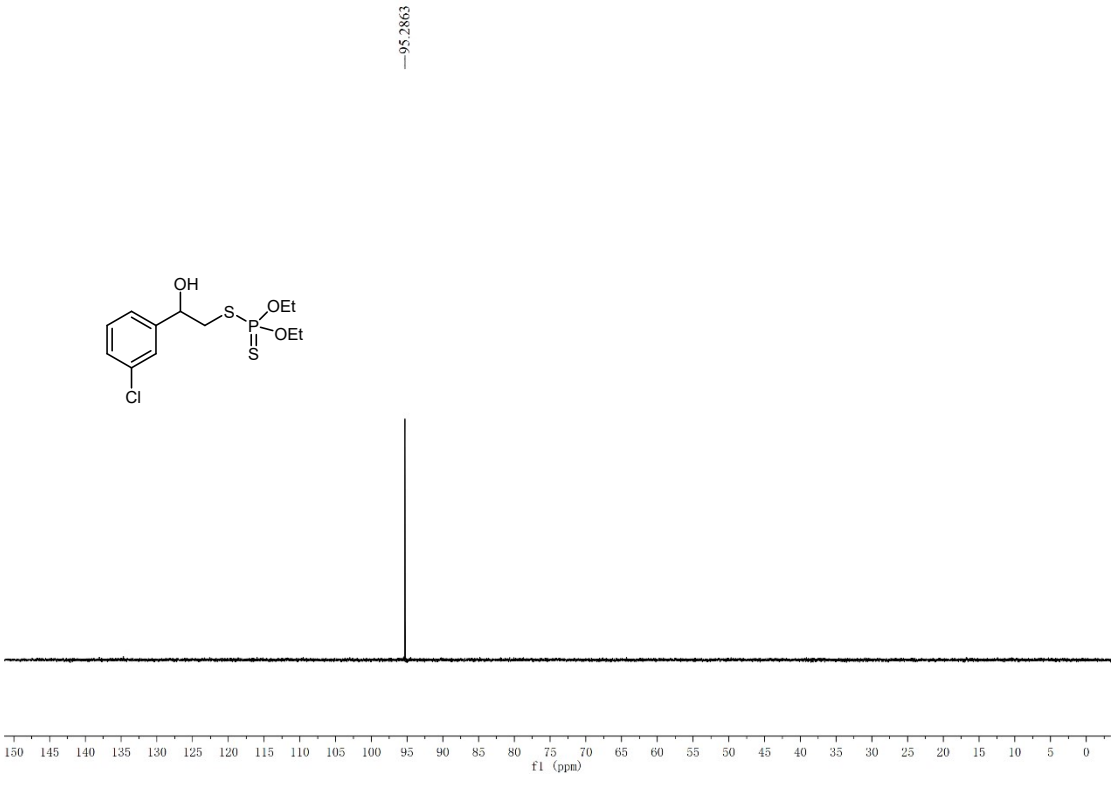
4ha ^{1}H NMR (500 MHz, $CDCl_3$)



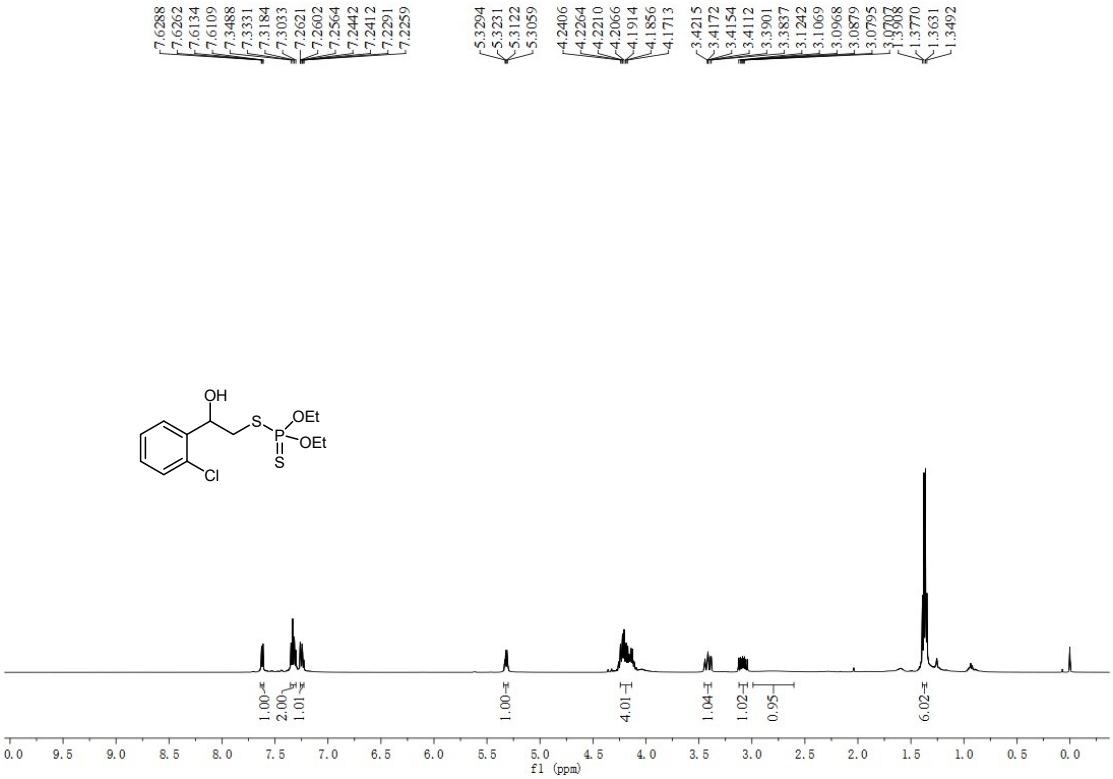
4ha ^{13}C NMR (125 MHz, $CDCl_3$)



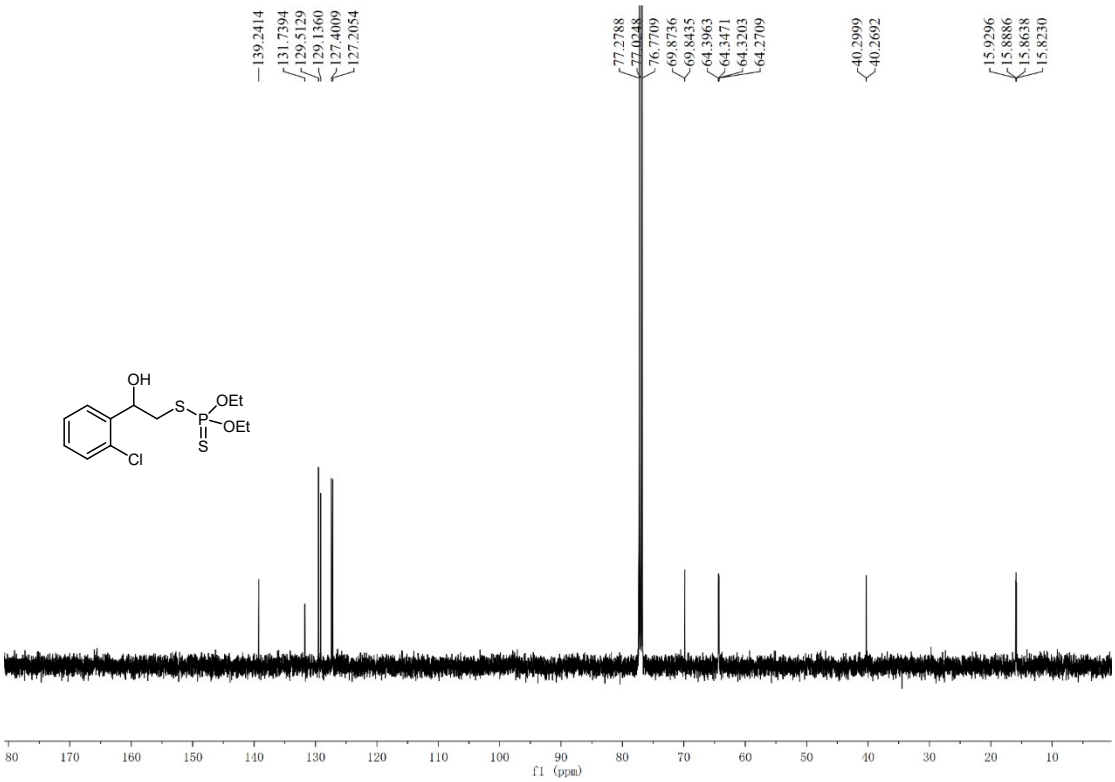
4ha ^{31}P NMR (202 MHz, $CDCl_3$):



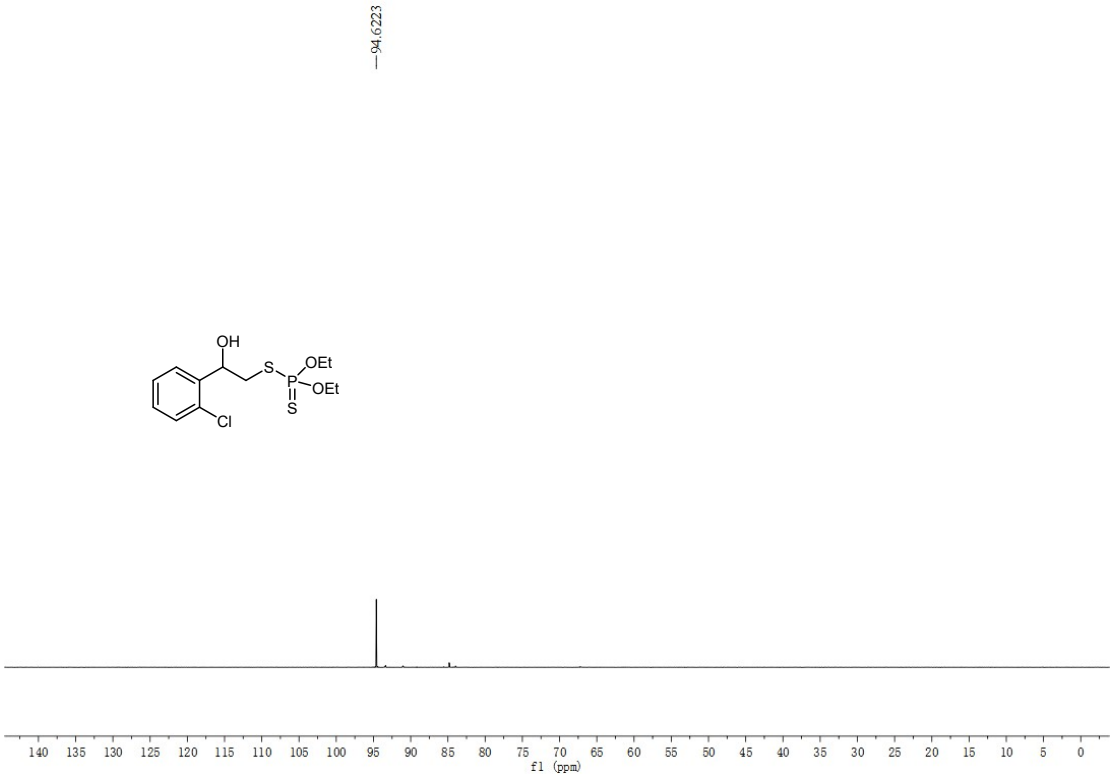
4ia ^{1}H NMR (500 MHz, $CDCl_3$)



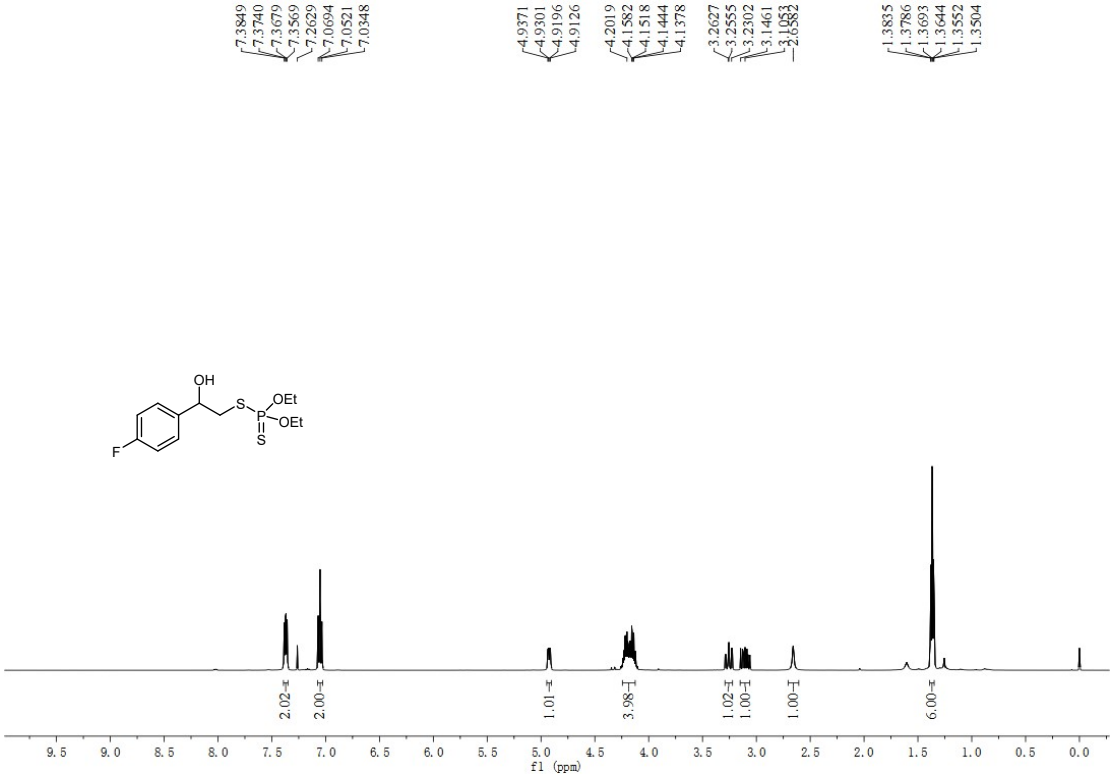
4ia ^{13}C NMR (125 MHz, $CDCl_3$)



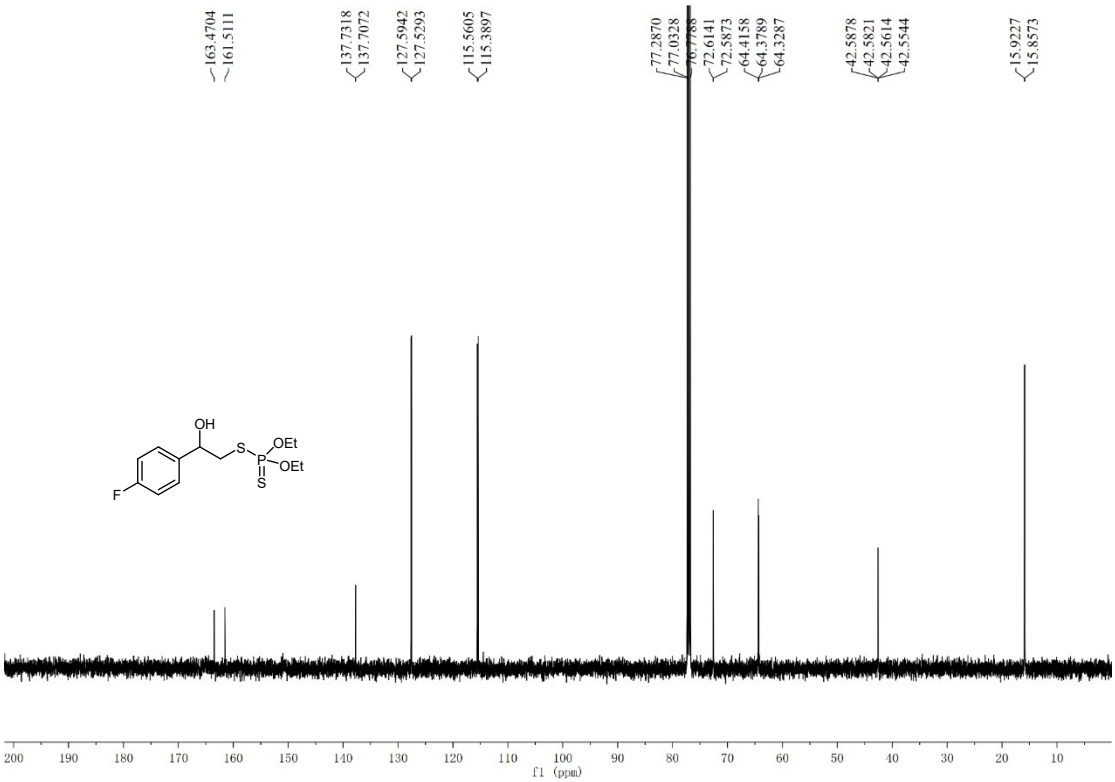
4ia ^{31}P NMR (202 MHz, $CDCl_3$):



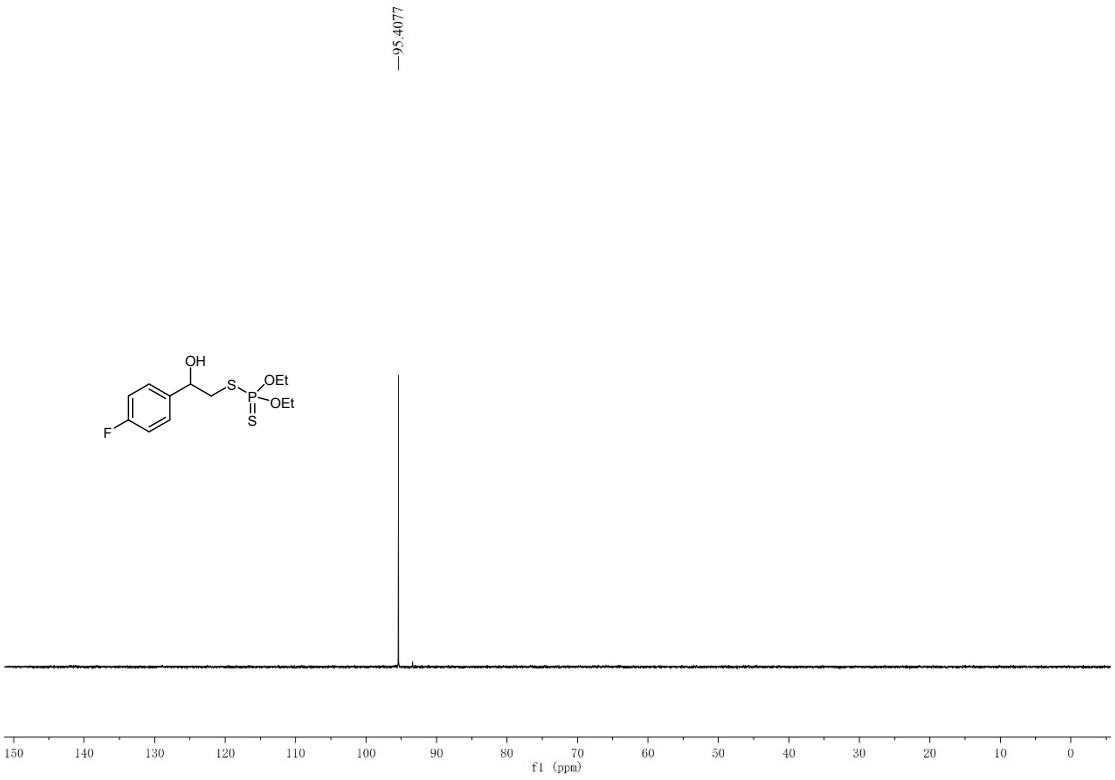
4ja ^{1}H NMR (500 MHz, $CDCl_3$)



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

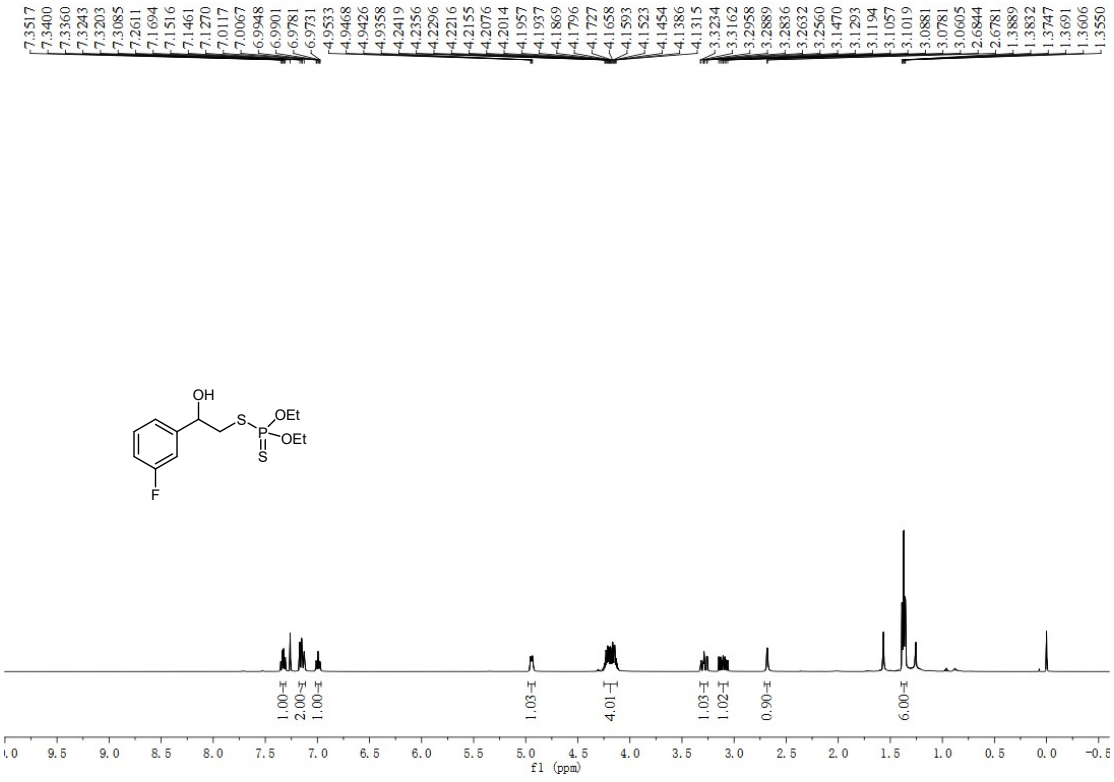


4ja ^{31}P NMR (202 MHz, $CDCl_3$):

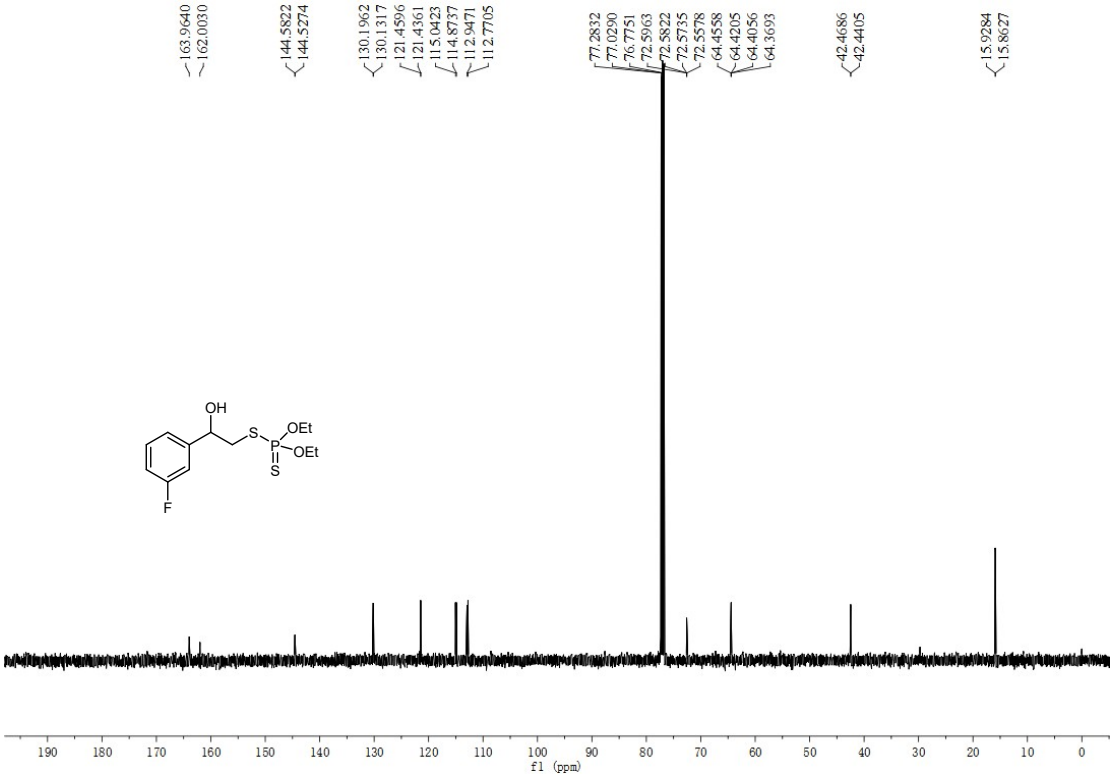


4ja ^{19}F NMR (500 MHz, $CDCl_3$):

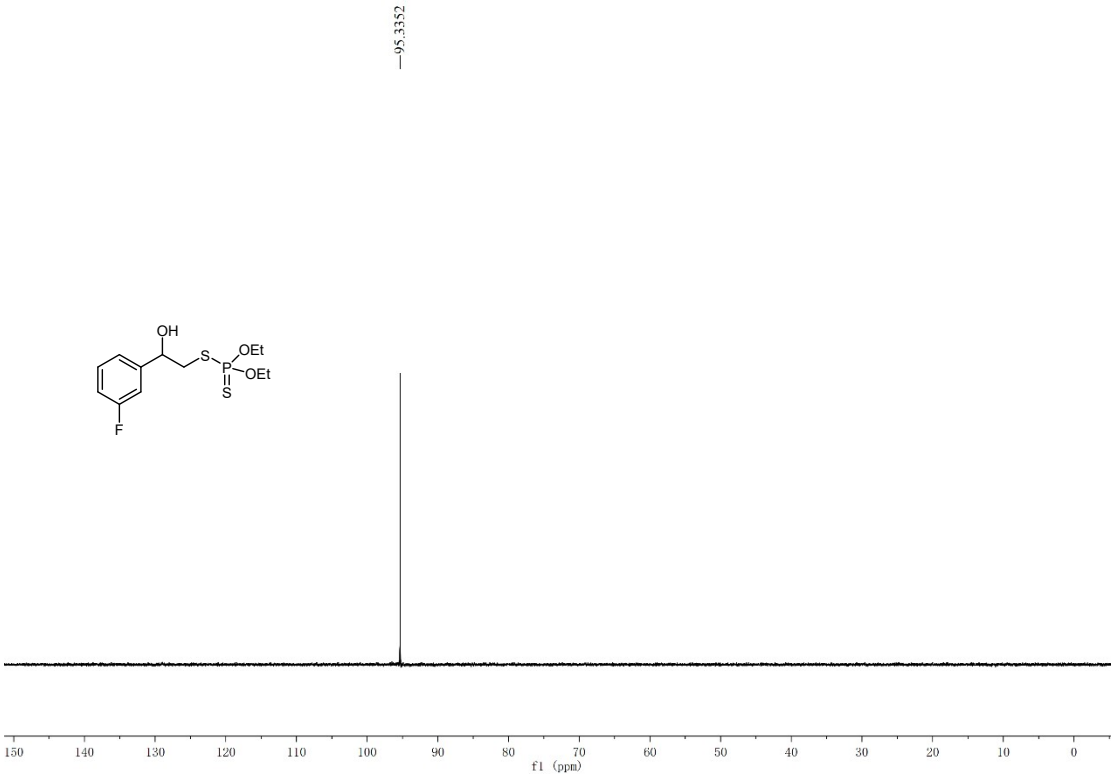
4ka ^{1}H NMR (500 MHz, $CDCl_3$)



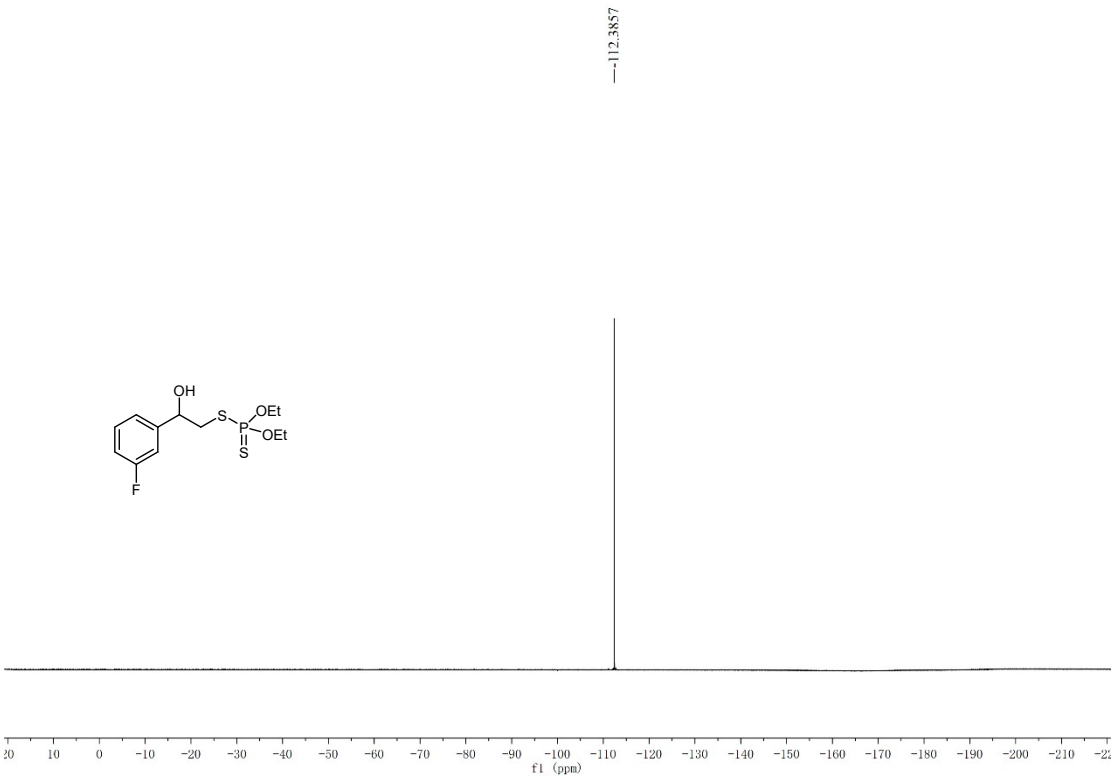
4ka ^{13}C NMR (125 MHz, $CDCl_3$)



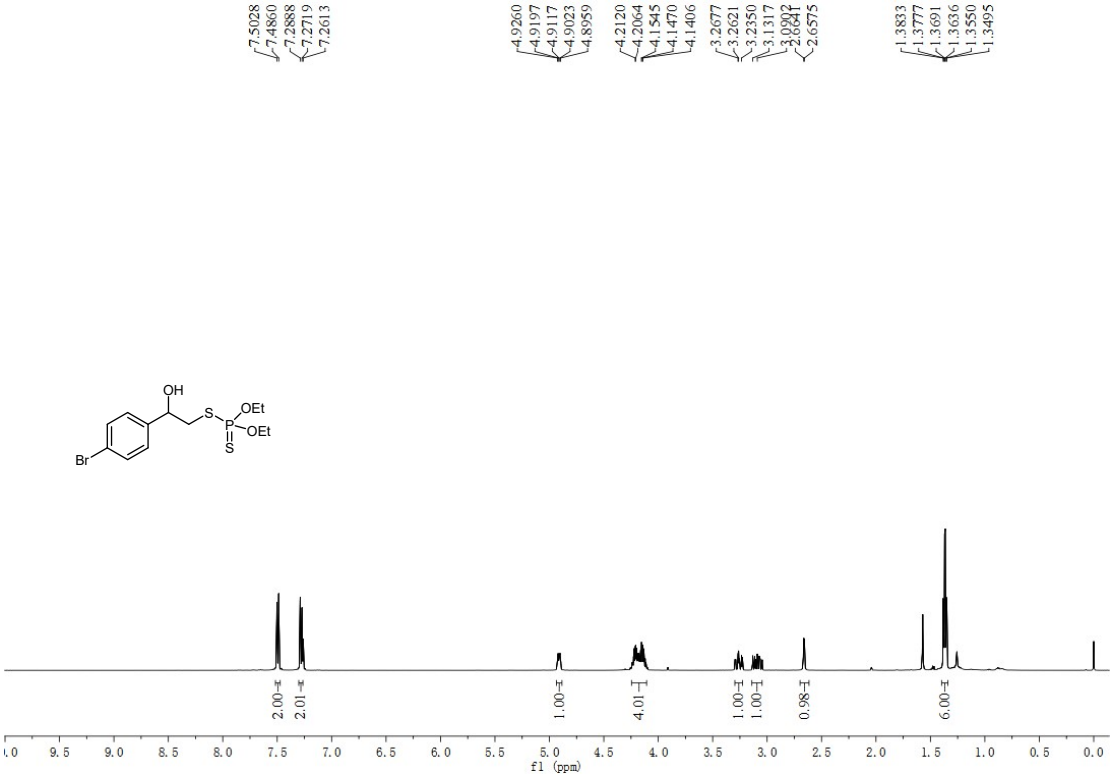
4ka ^{31}P NMR (500 MHz, $CDCl_3$):



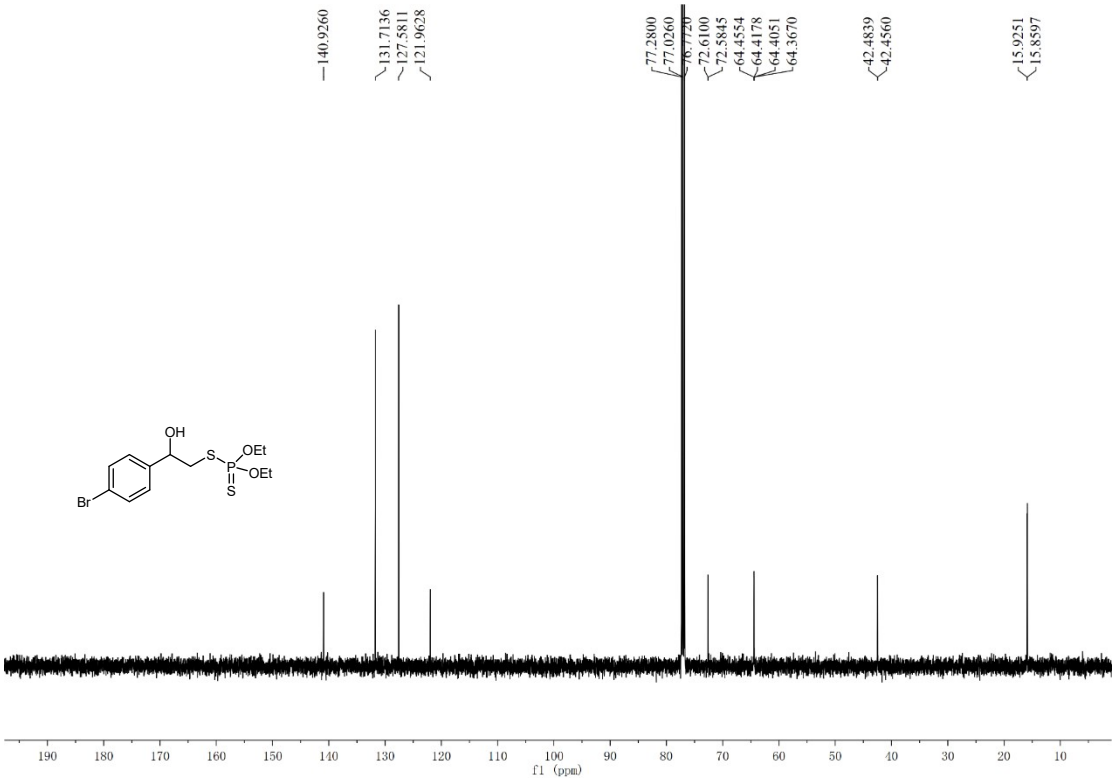
4ka ^{19}F NMR (500 MHz, $CDCl_3$):



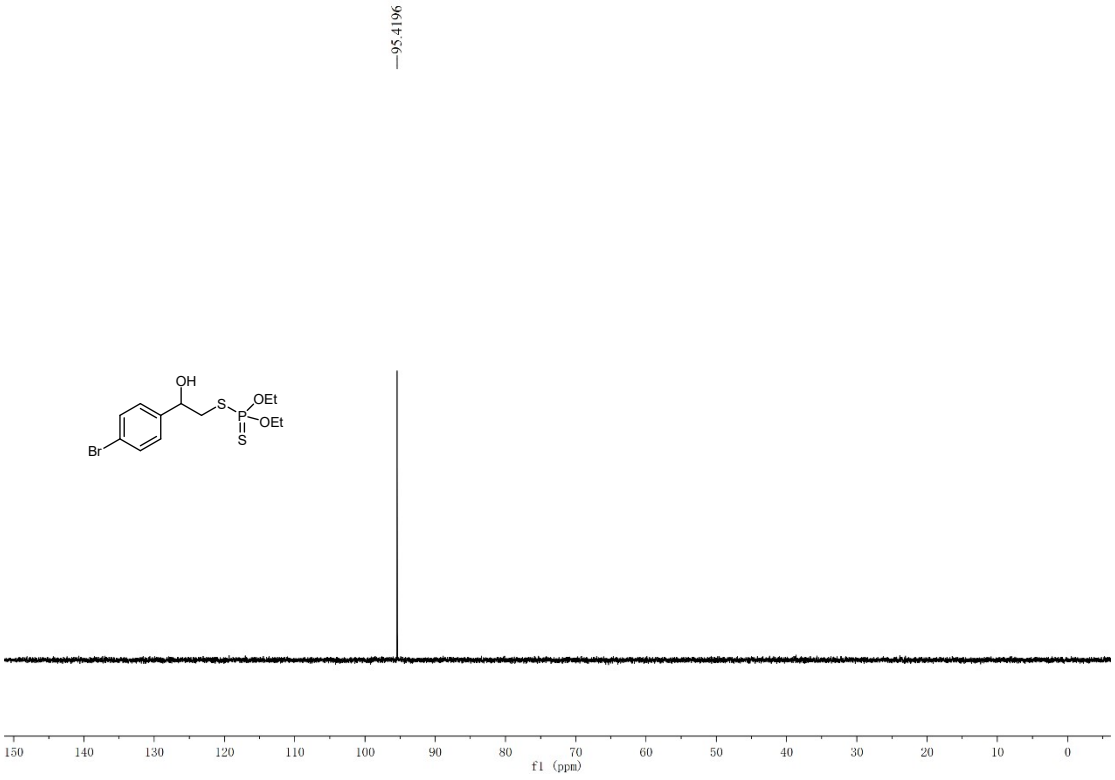
4la ^{1}H NMR (500 MHz, $CDCl_3$)



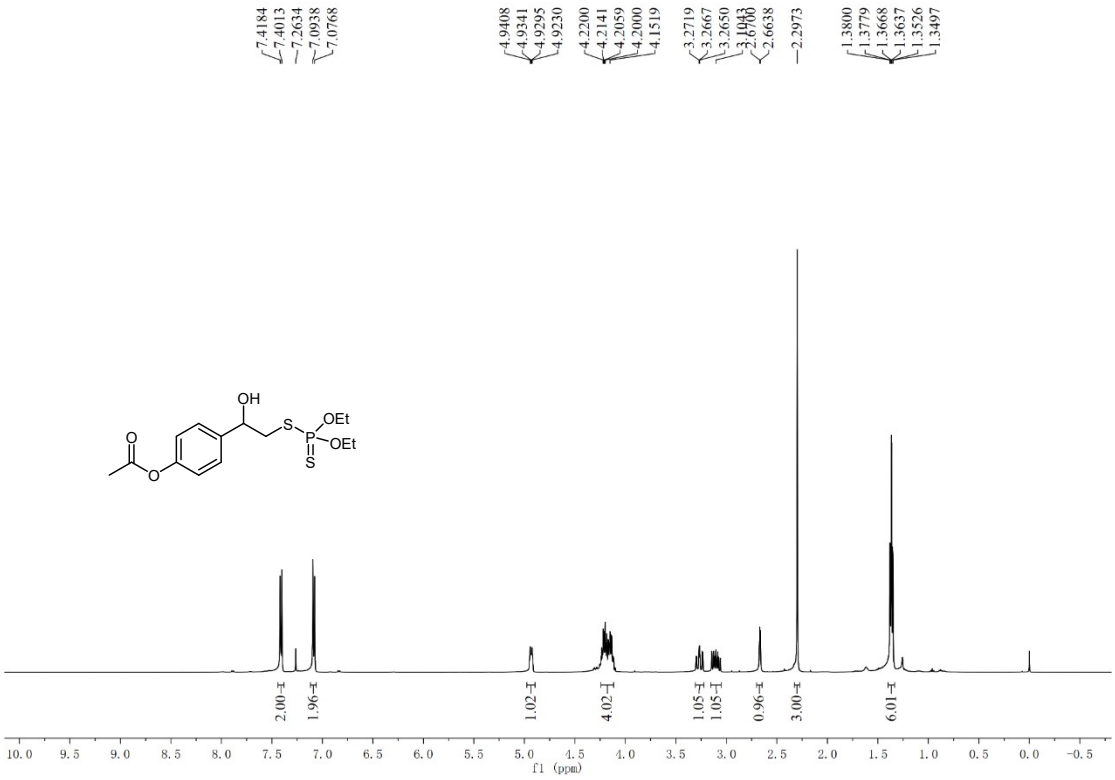
4la^{13}C NMR (125 MHz, $CDCl_3$)



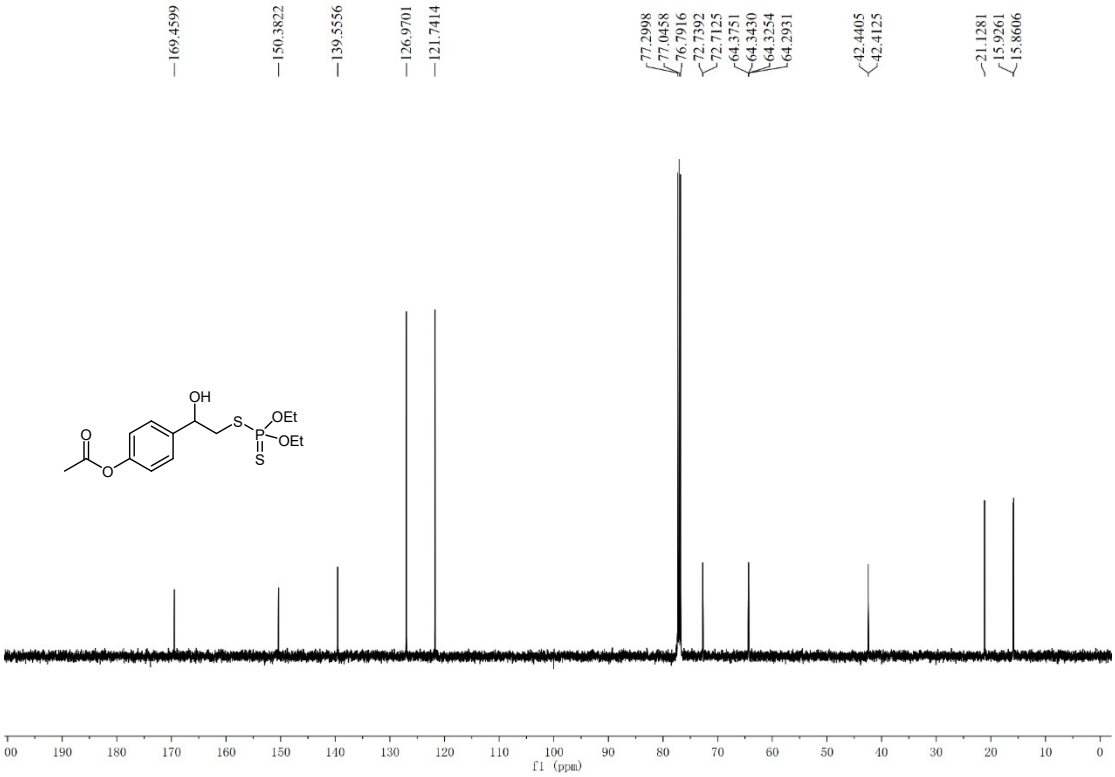
4la ^{31}P NMR (202 MHz, $CDCl_3$):



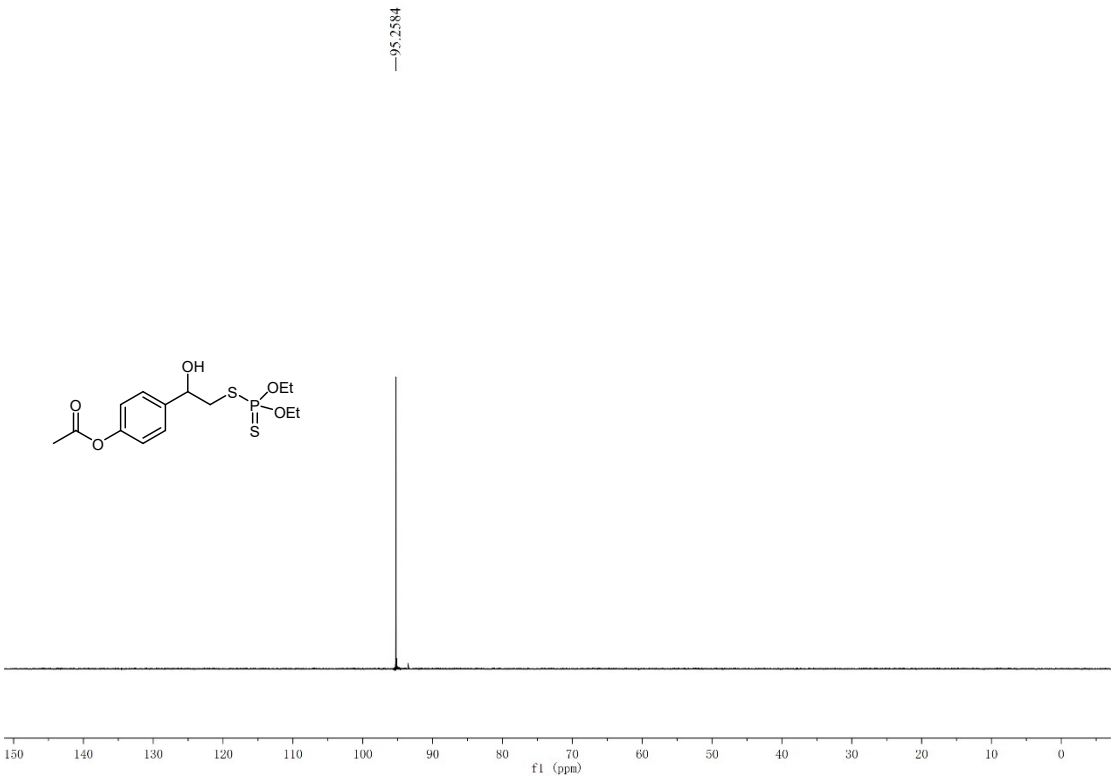
4ma ^{1}H NMR (500 MHz, $CDCl_3$)



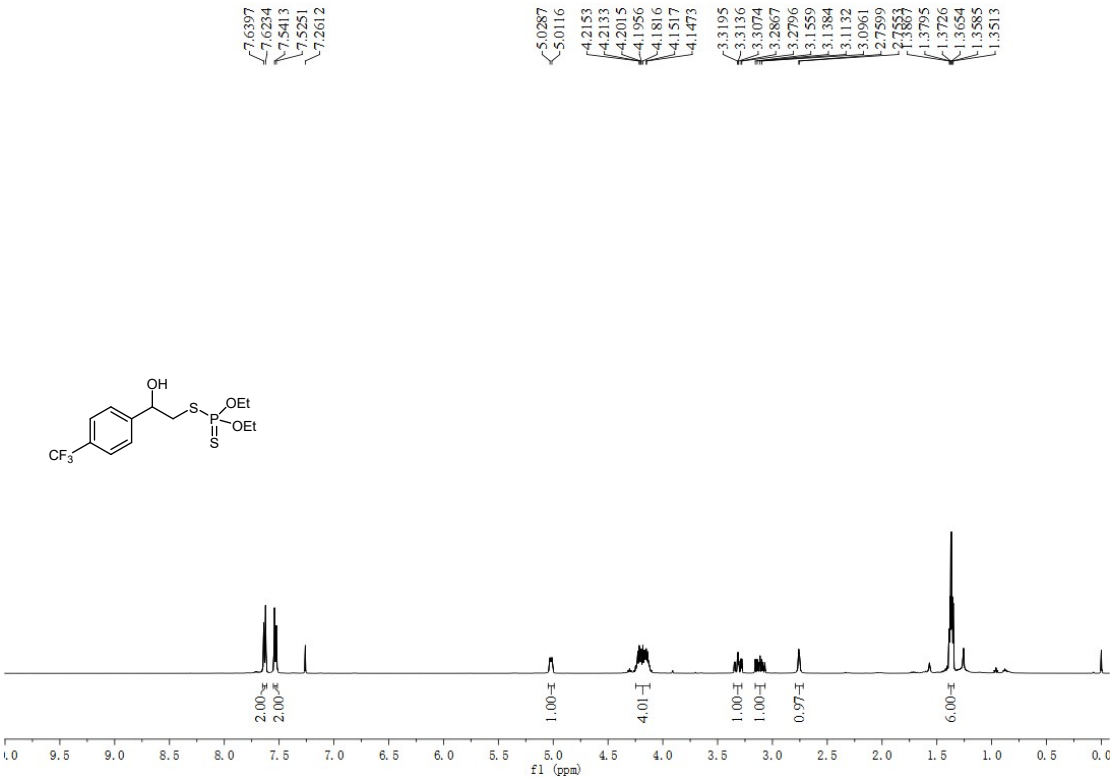
4ma ^{13}C NMR (125 MHz, $CDCl_3$)



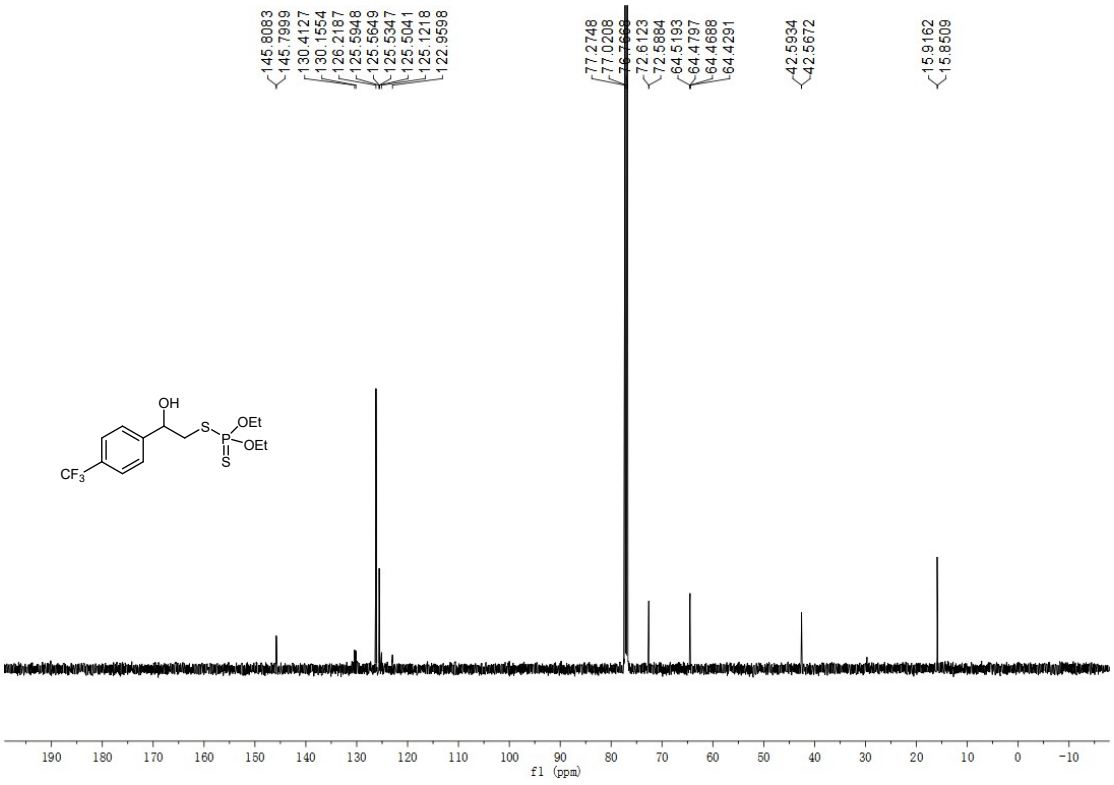
4ma ^{31}P NMR (202 MHz, $CDCl_3$):



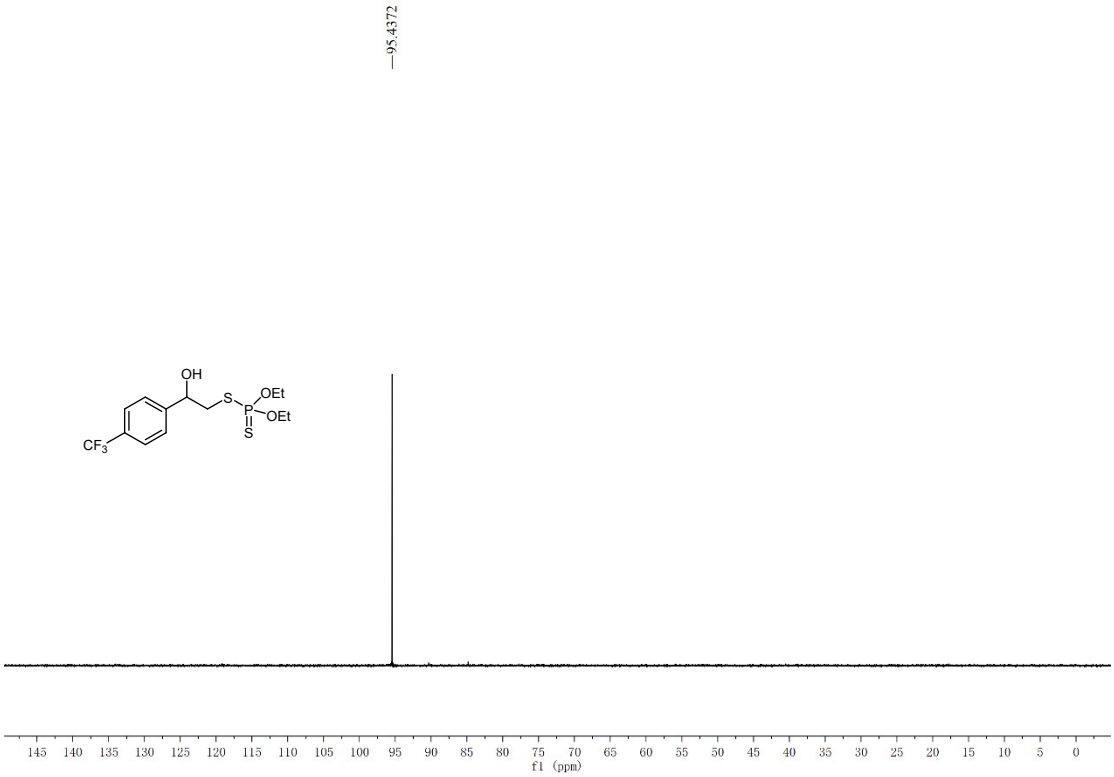
4na ^{1}H NMR (500 MHz, $CDCl_3$)



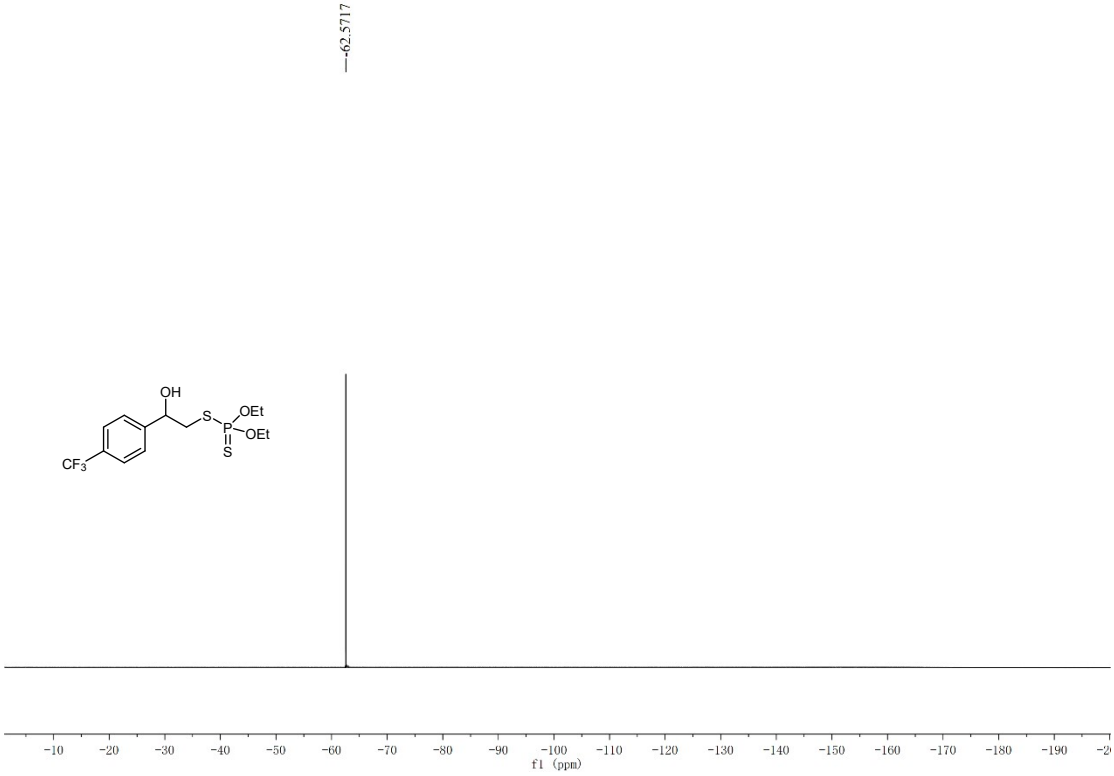
4na ^{13}C NMR (125 MHz, $CDCl_3$)



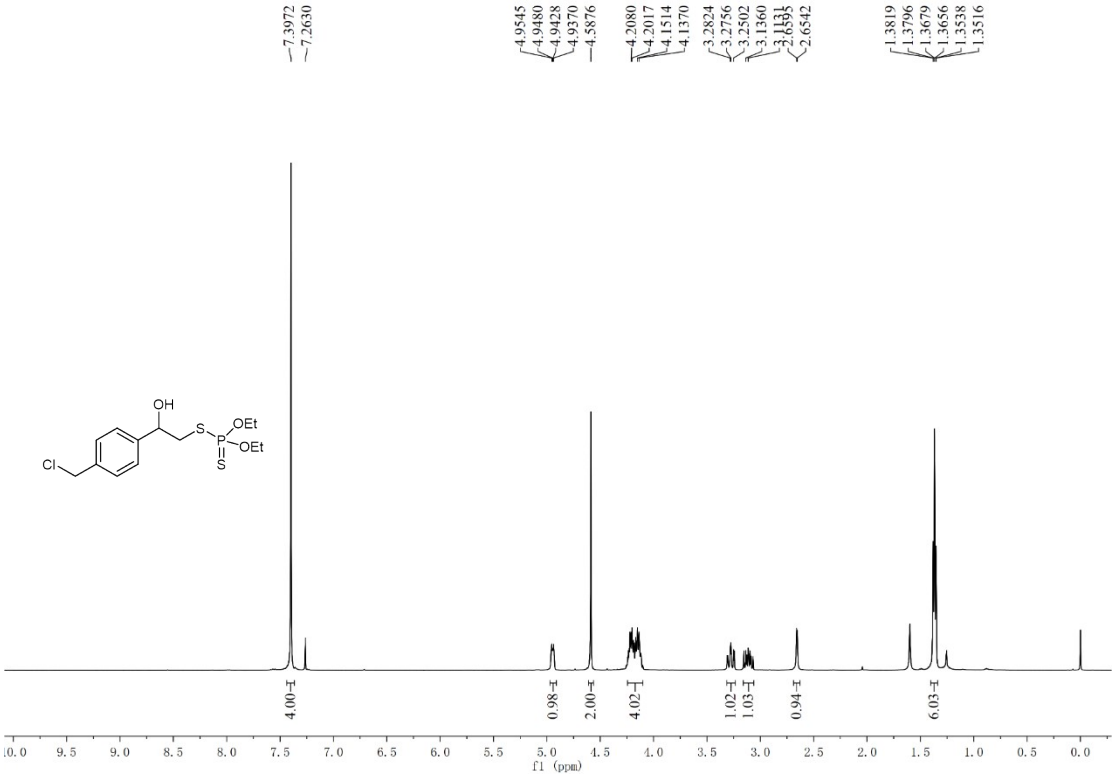
4na ^{31}P NMR (202 MHz, $CDCl_3$):



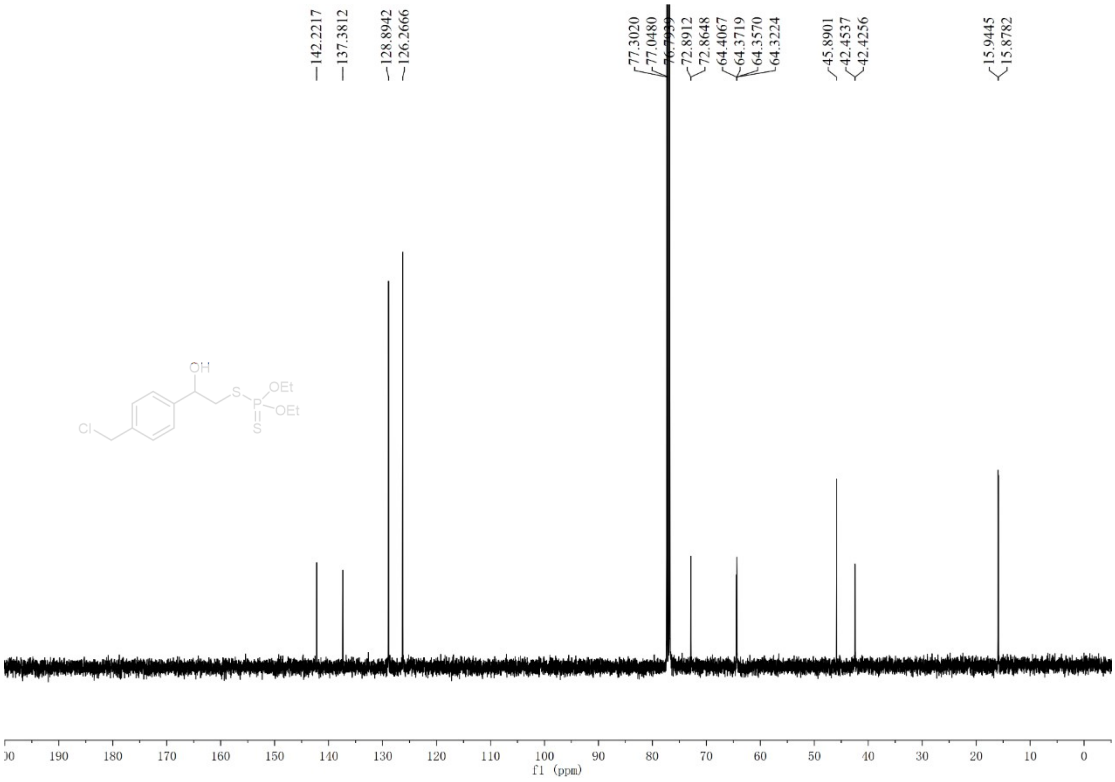
4na ^{19}F NMR (500 MHz, $CDCl_3$):



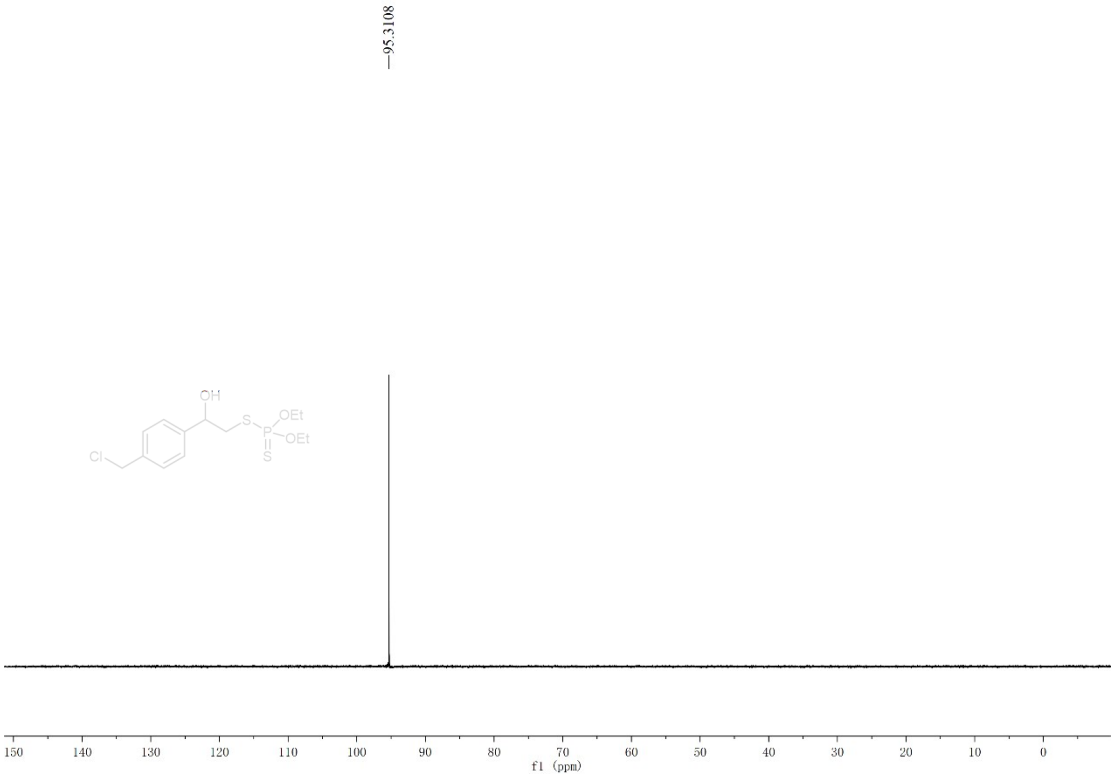
4oa ^{1}H NMR (500 MHz, $CDCl_3$)



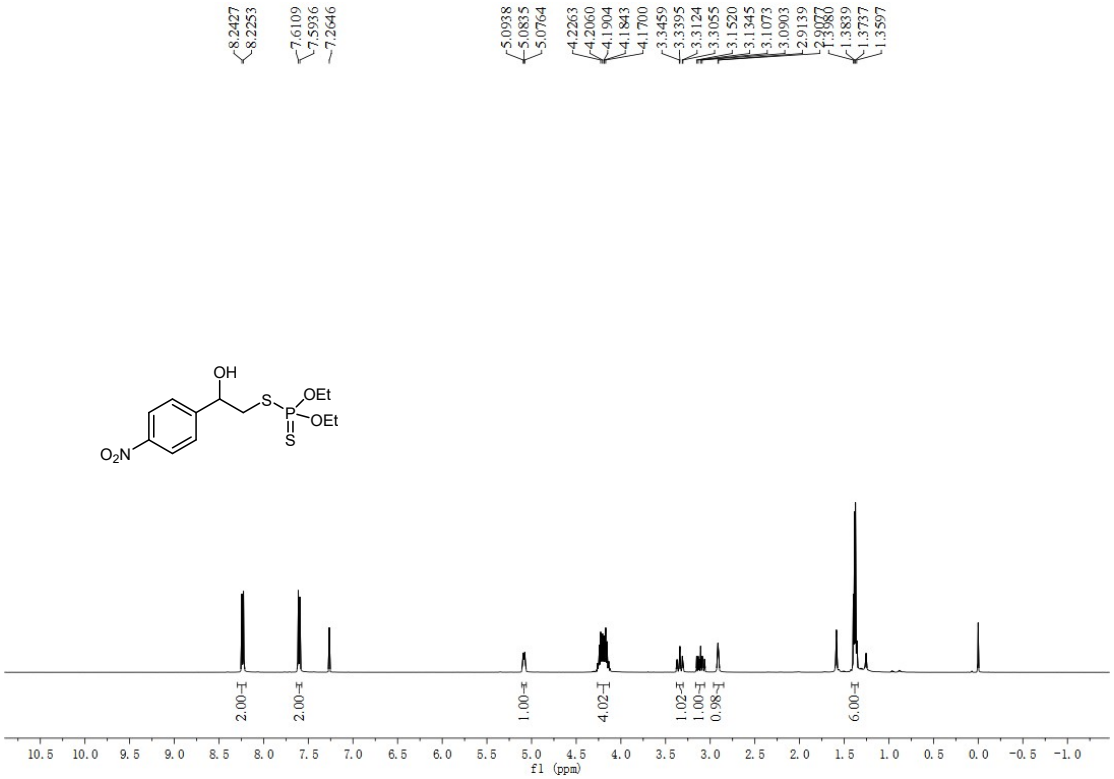
4oa ^{13}C NMR (125 MHz, $CDCl_3$)



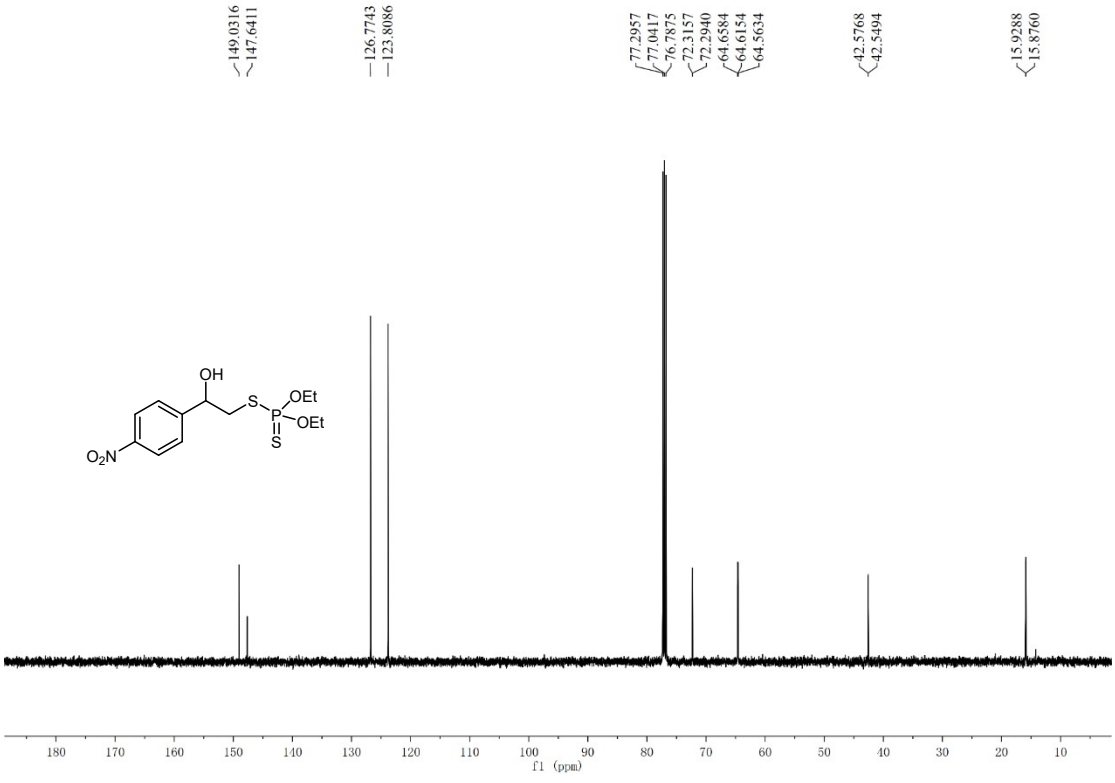
4oa ^{31}P NMR (202 MHz, $CDCl_3$):



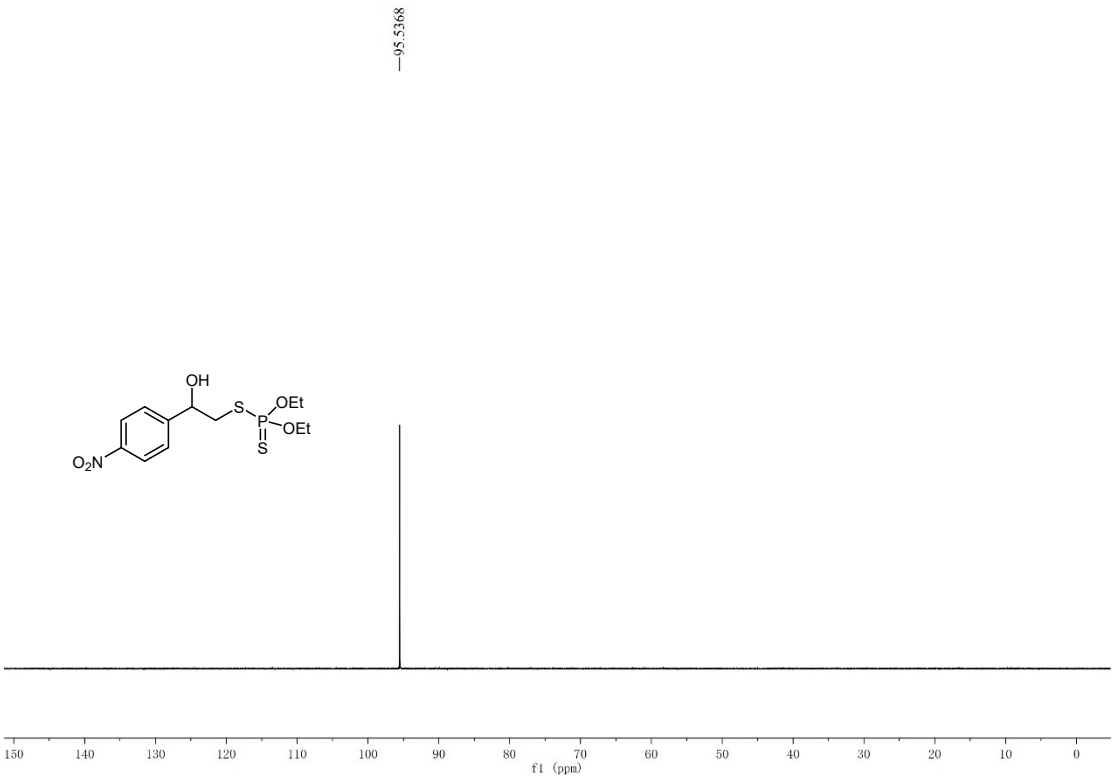
4pa ^{1}H NMR (500 MHz, $CDCl_3$)



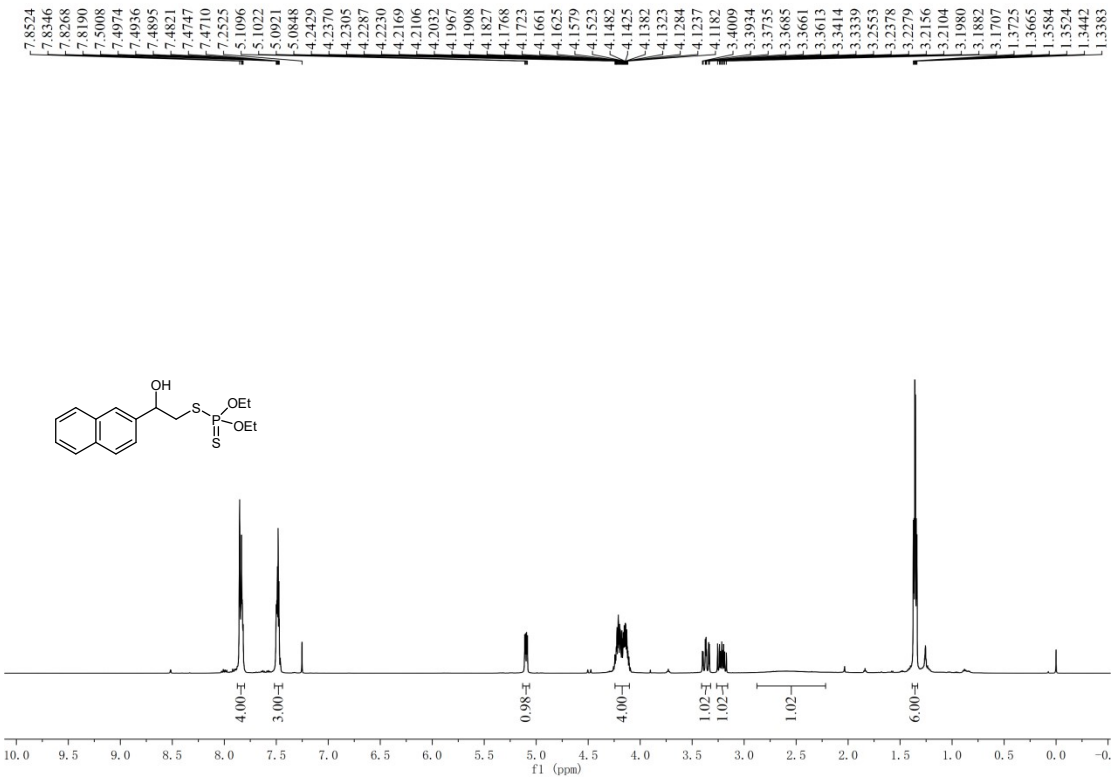
4pa ^{13}C NMR (125 MHz, $CDCl_3$)



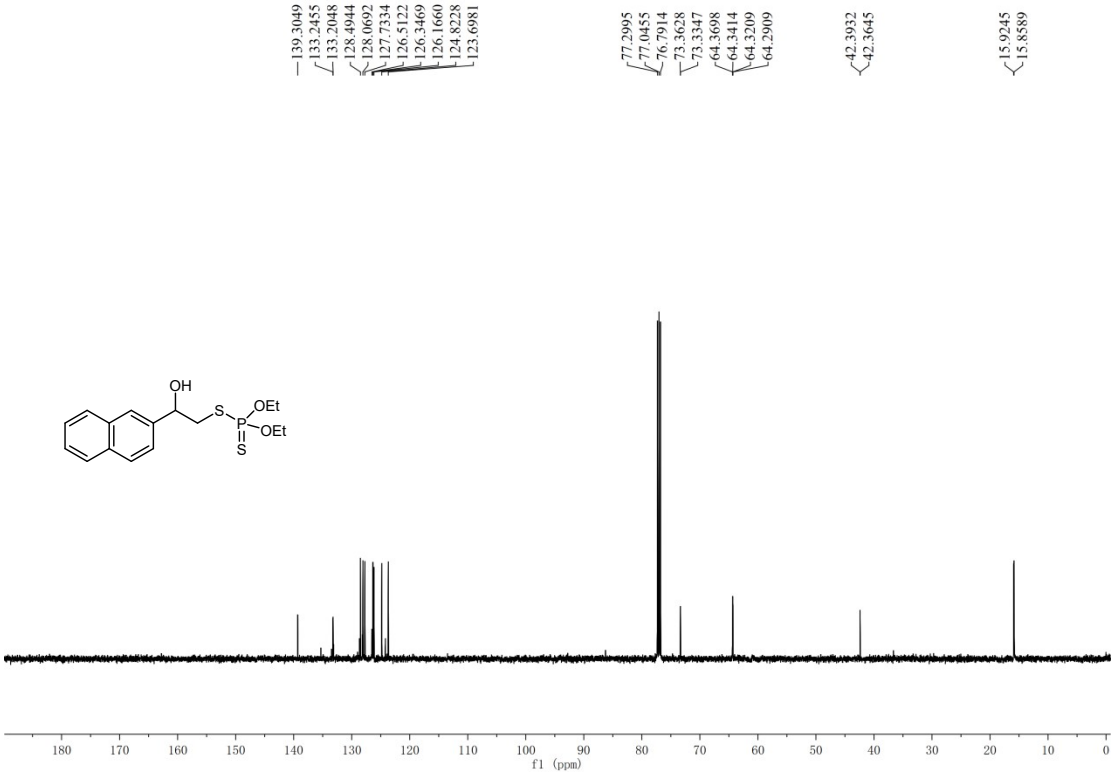
4pa ^{31}P NMR (202 MHz, $CDCl_3$):



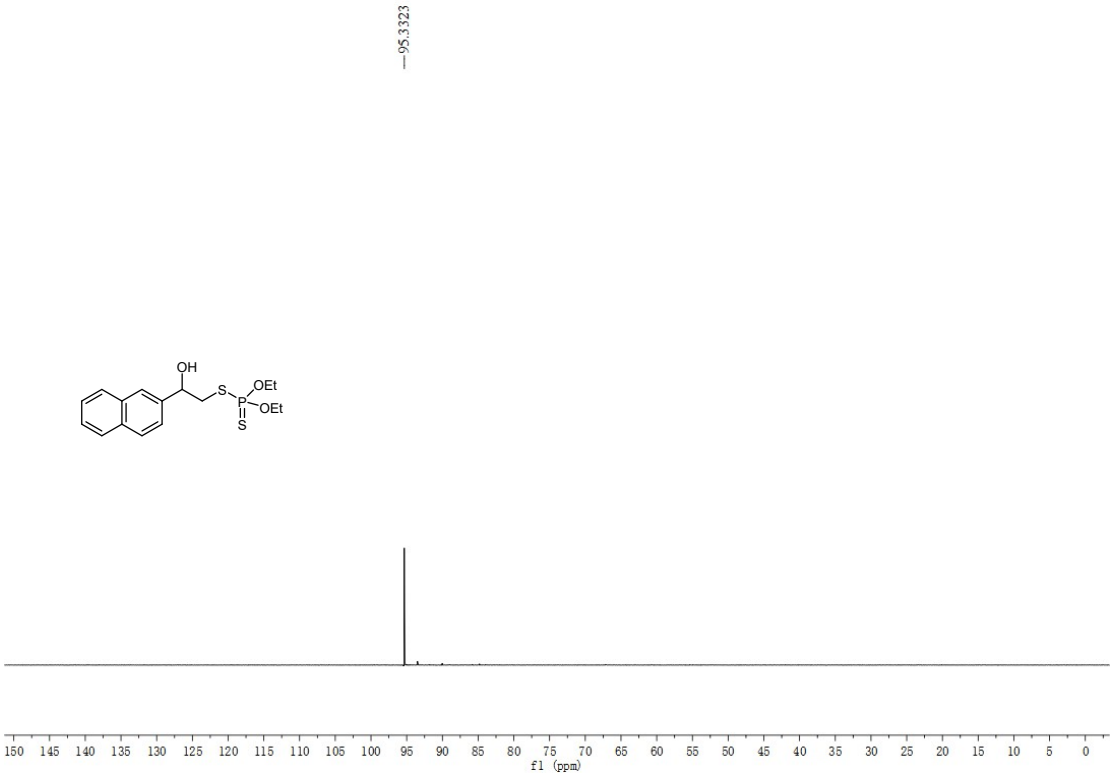
4qa ^{1}H NMR (500 MHz, $CDCl_3$)



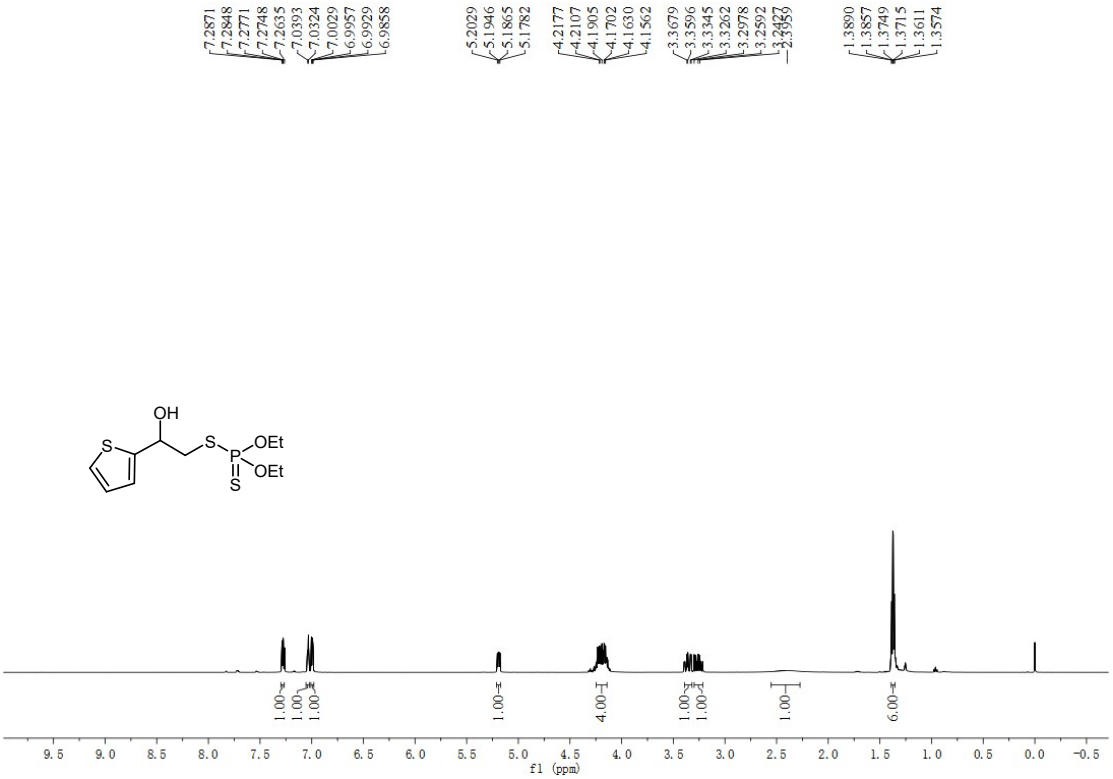
4qa ^{13}C NMR (125 MHz, $CDCl_3$)



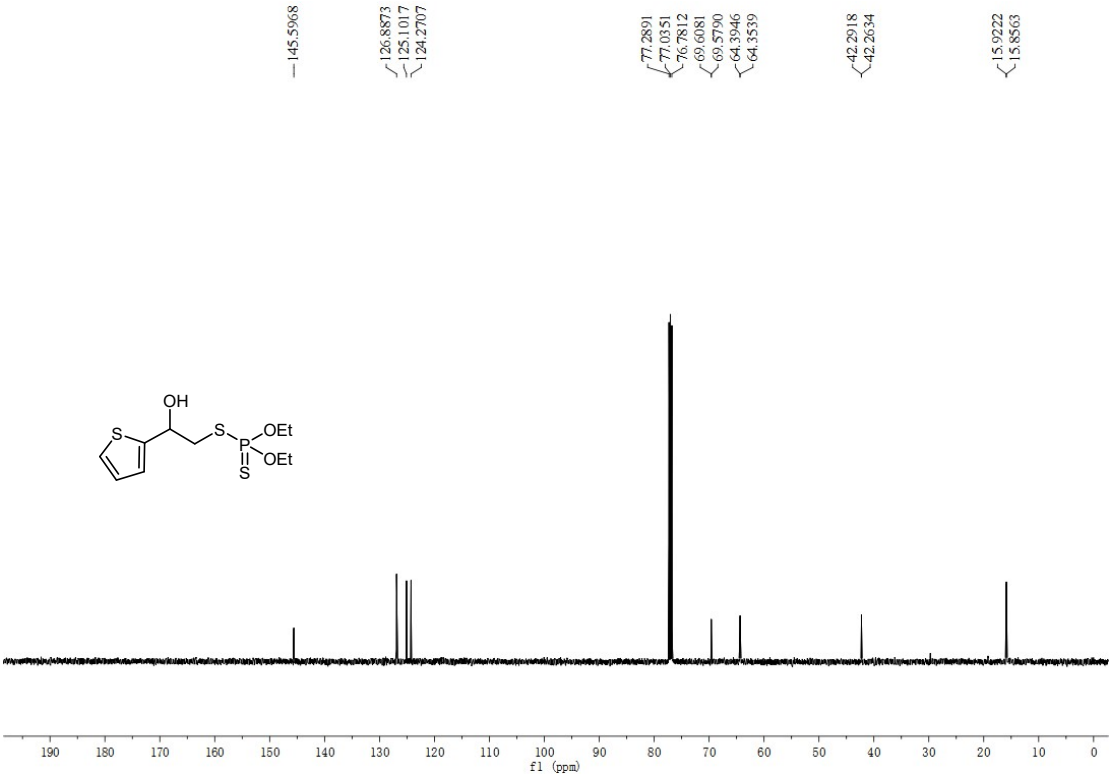
4qa ^{31}P NMR (202 MHz, $CDCl_3$):



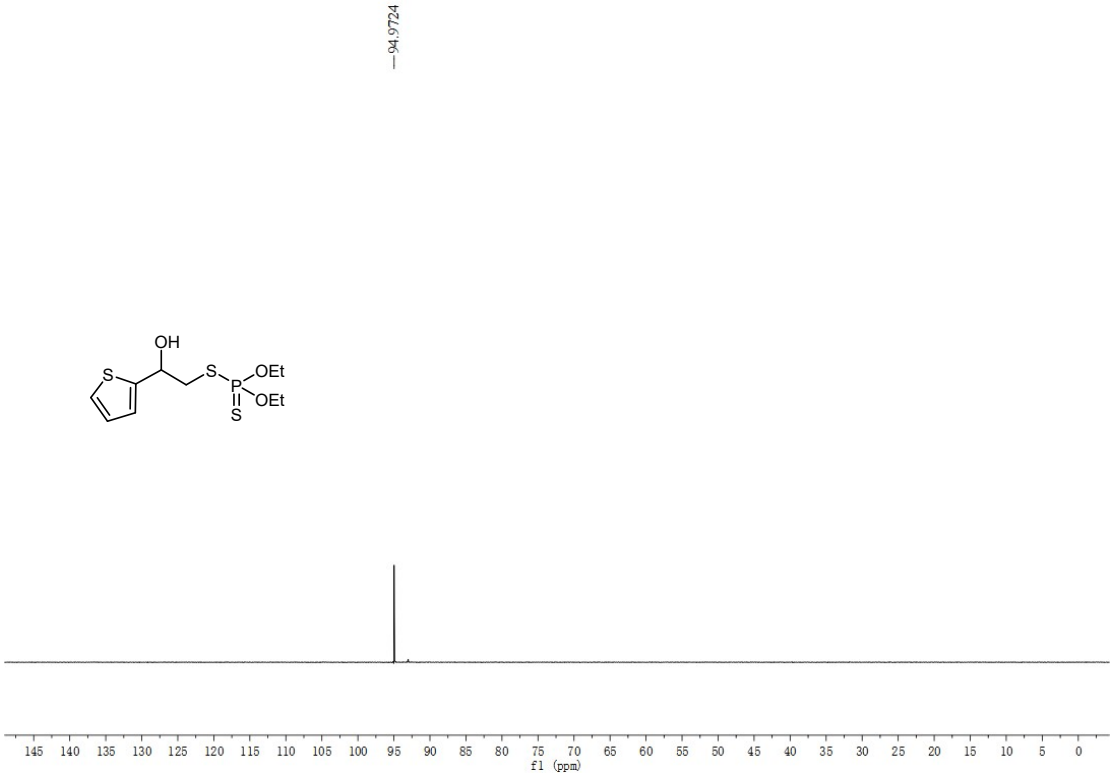
4ra ^{1}H NMR (500 MHz, $CDCl_3$)



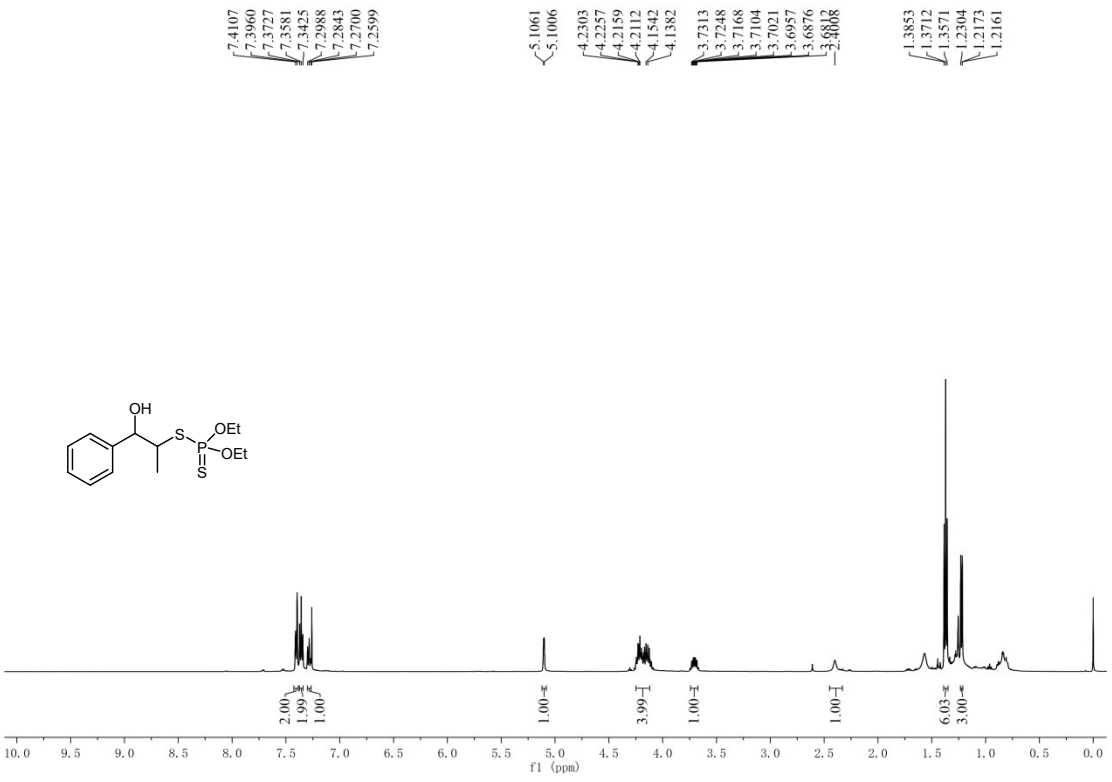
4ra ^{13}C NMR (125 MHz, $CDCl_3$)



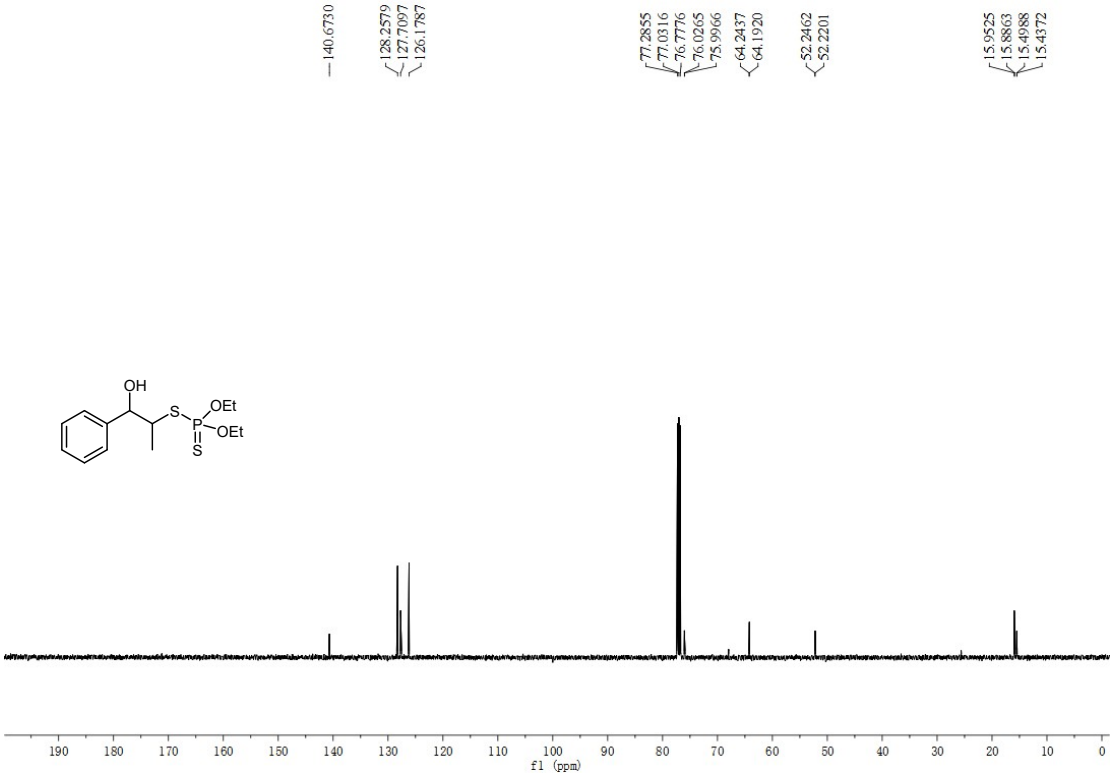
4ra ^{31}P NMR (202 MHz, $CDCl_3$):



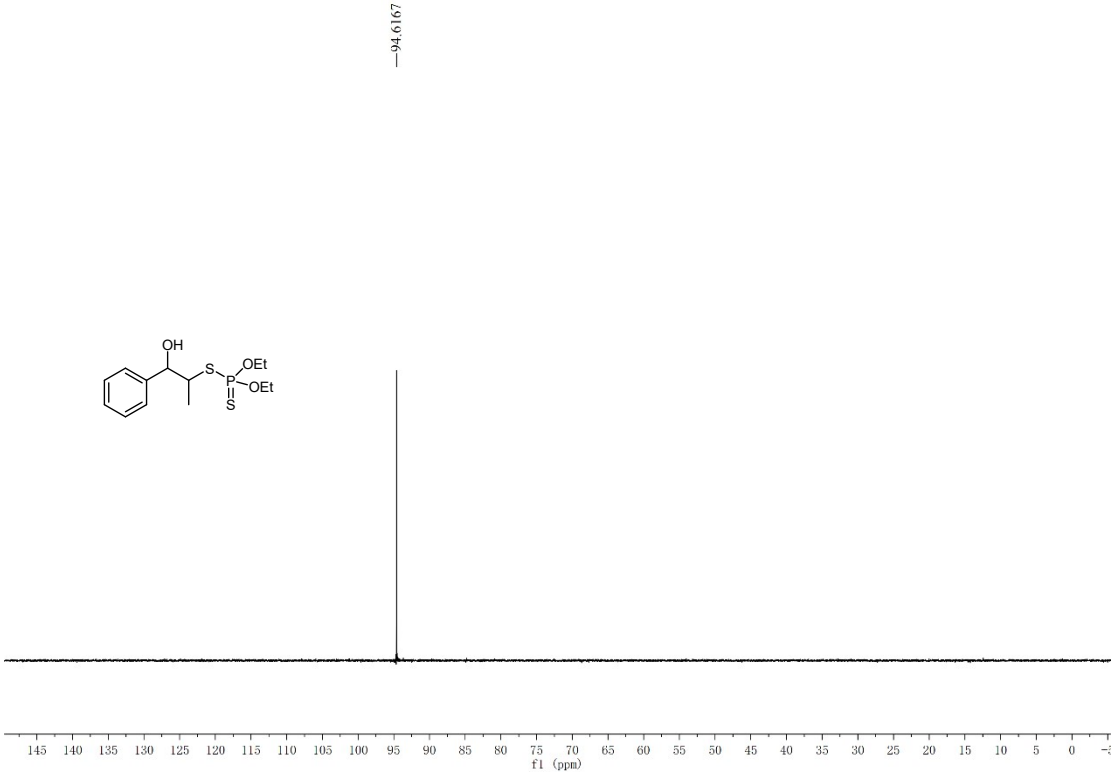
4sa ^{1}H NMR (500 MHz, $CDCl_3$)



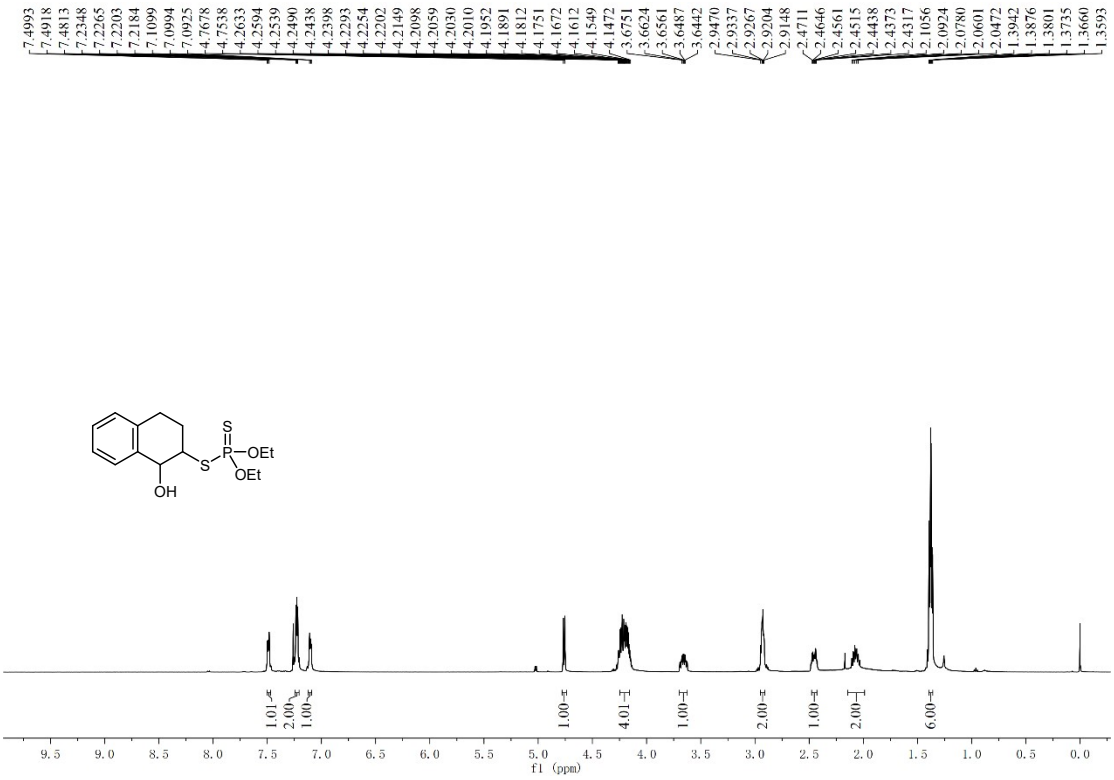
4sa ^{13}C NMR (125 MHz, $CDCl_3$)



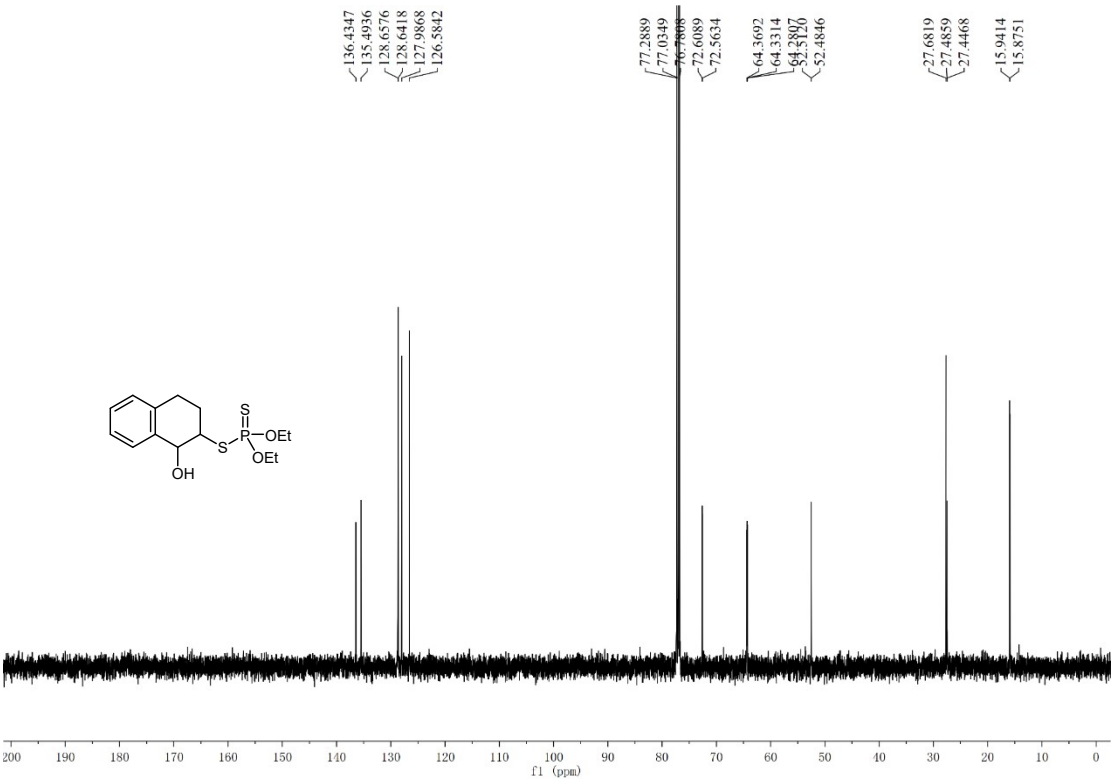
4sa ^{31}P NMR (202 MHz, $CDCl_3$):



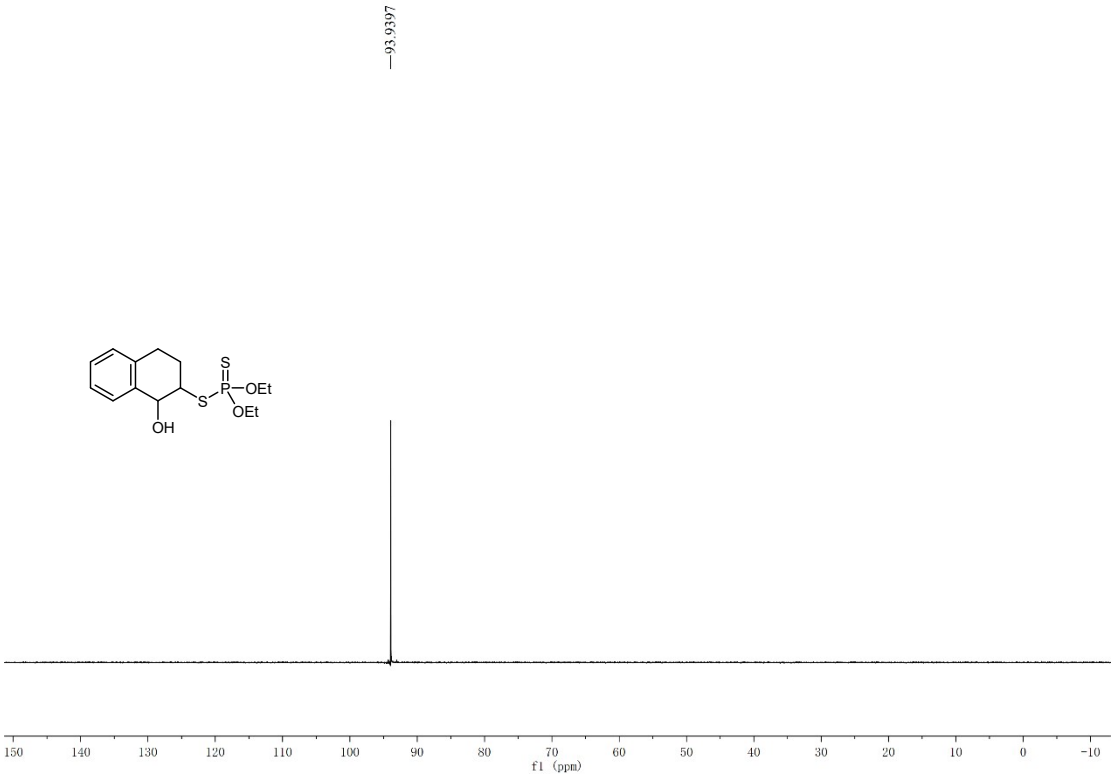
4ta ^{1}H NMR (500 MHz, $CDCl_3$)



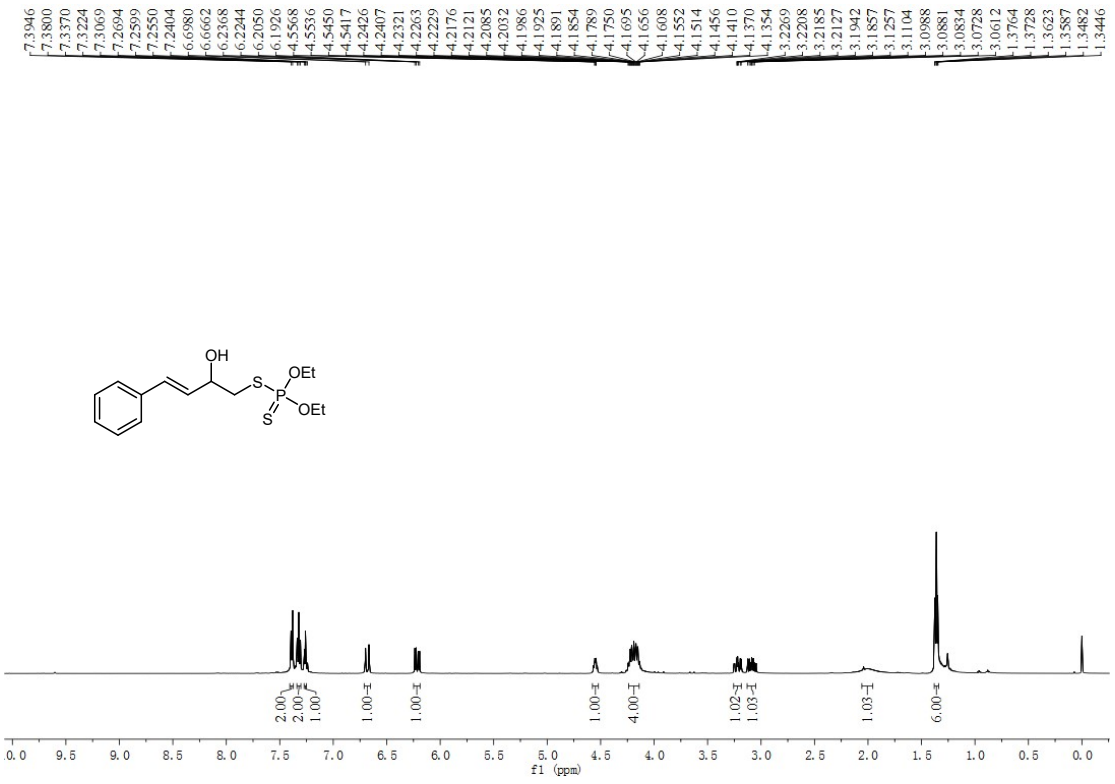
4ta ^{13}C NMR (125 MHz, $CDCl_3$)



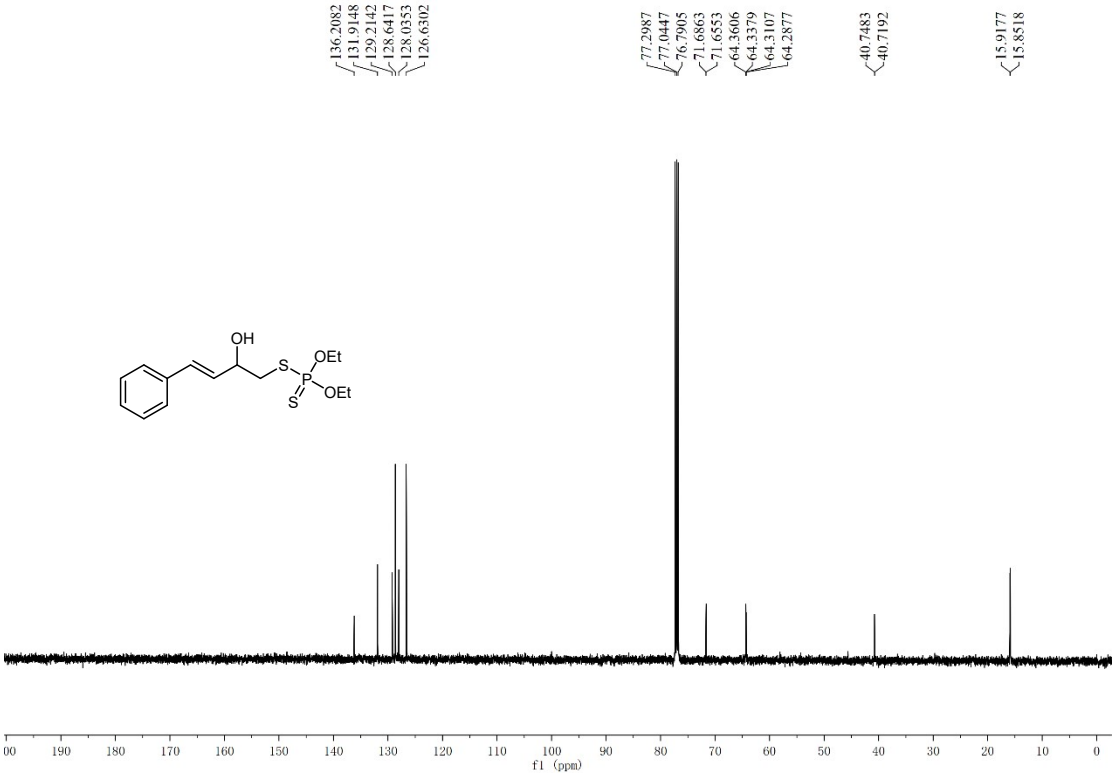
4ta ^{31}P NMR (202 MHz, $CDCl_3$):



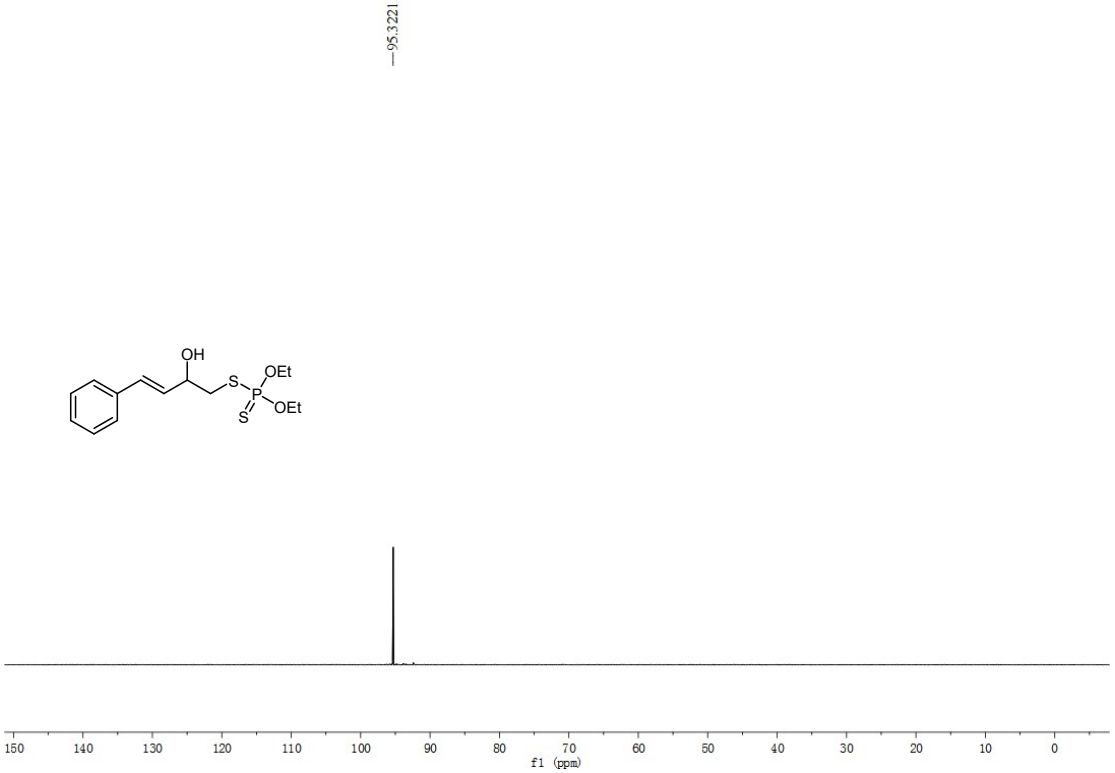
4ua ^{1}H NMR (500 MHz, $CDCl_3$)



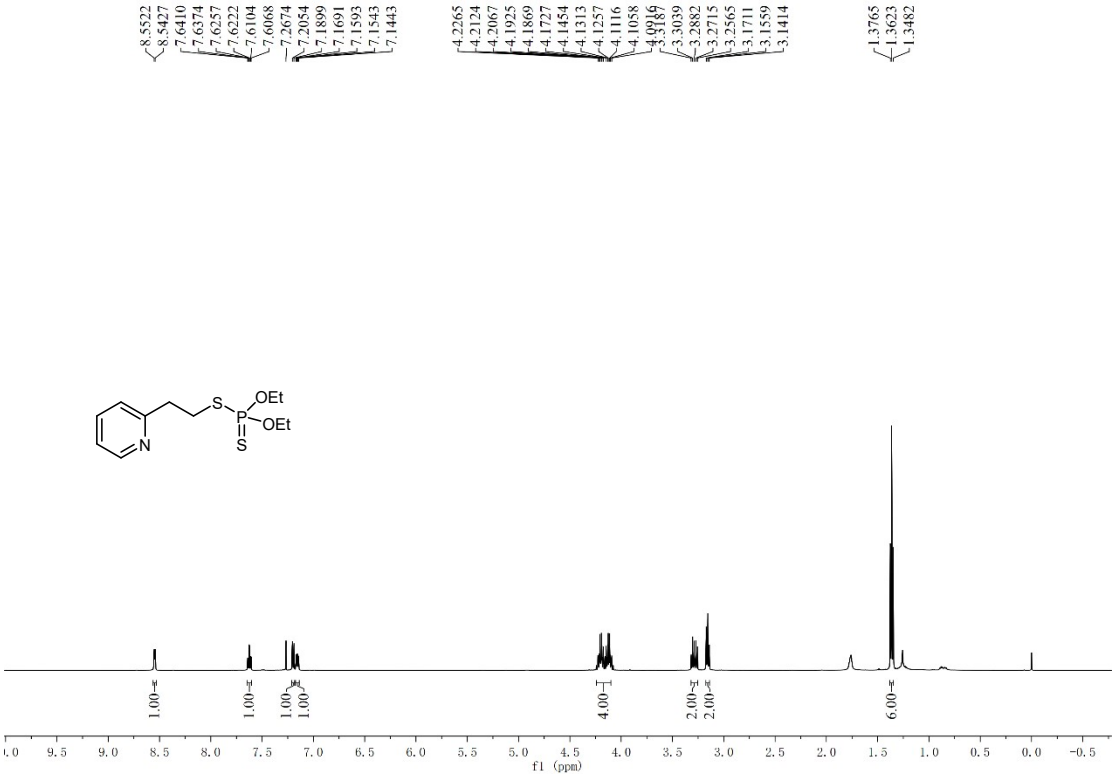
4ua ^{13}C NMR (125 MHz, $CDCl_3$)



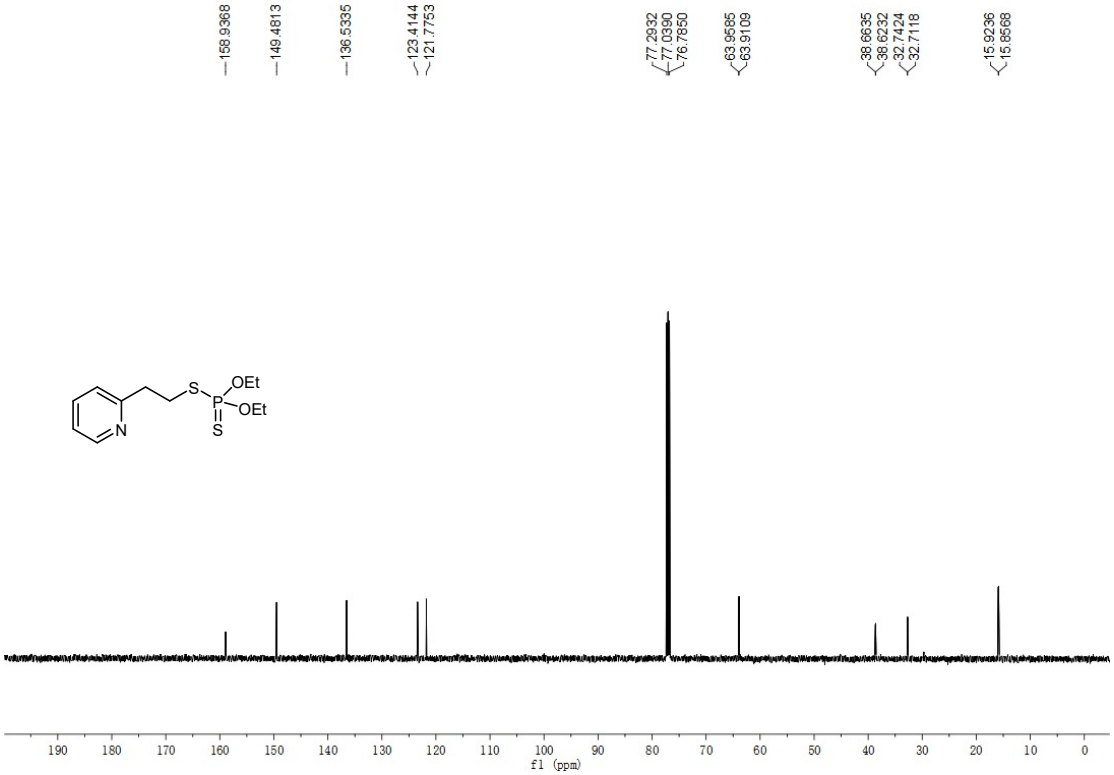
4ua ^{31}P NMR (202 MHz, $CDCl_3$):



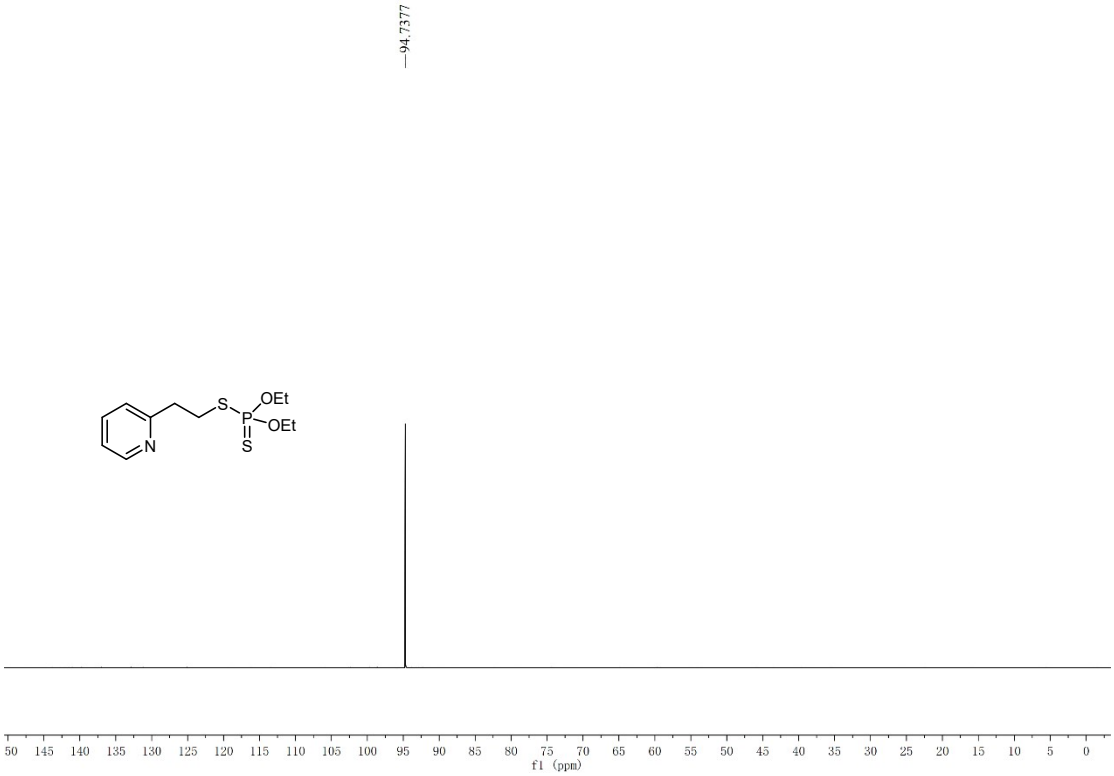
4va ^{1}H NMR (500 MHz, $CDCl_3$)



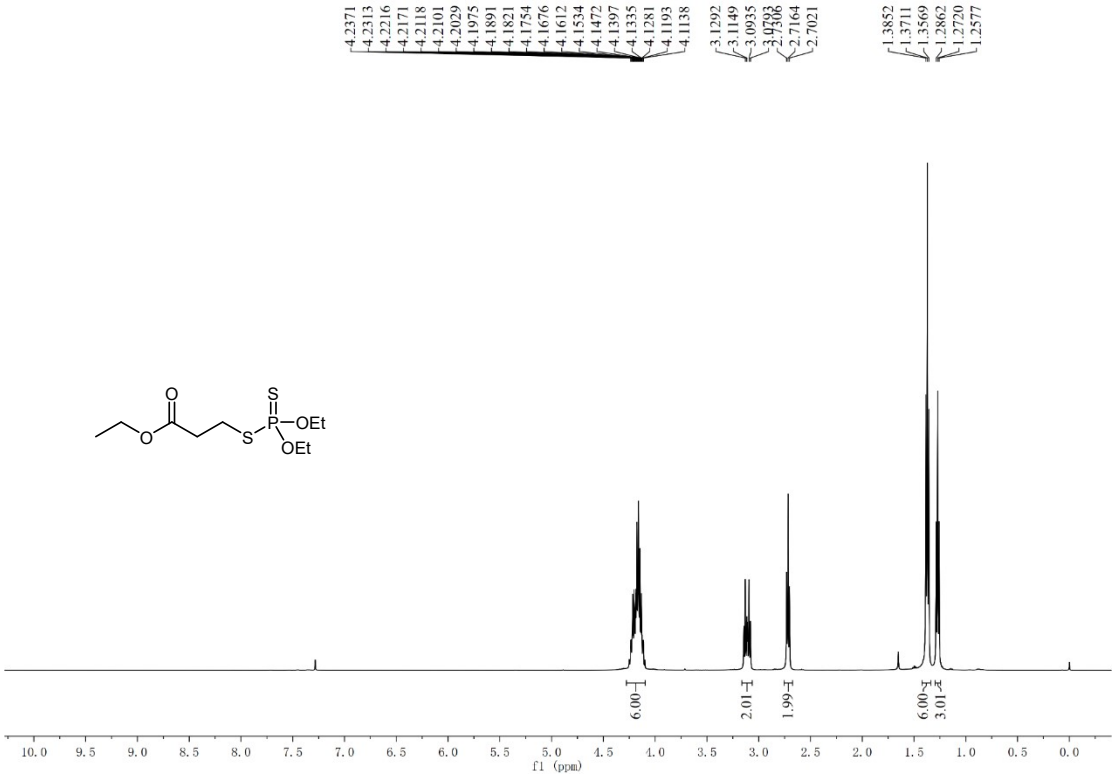
4va ^{13}C NMR (125 MHz, $CDCl_3$)



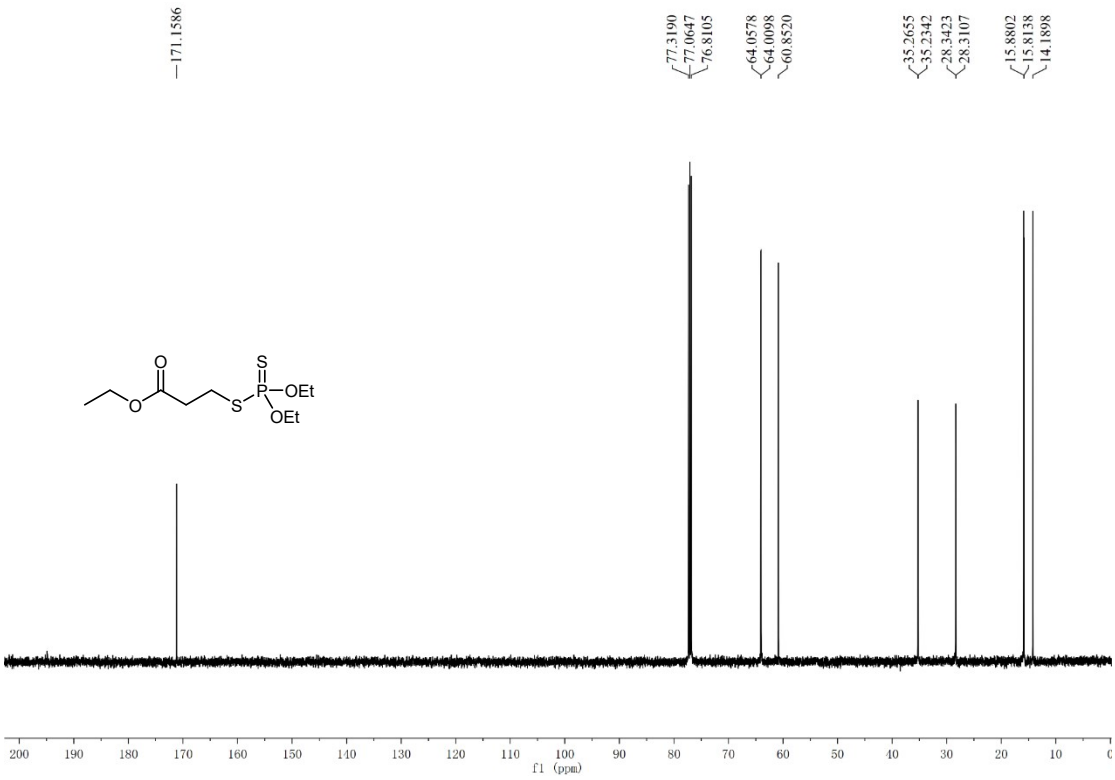
4va ^{31}P NMR (202 MHz, $CDCl_3$):



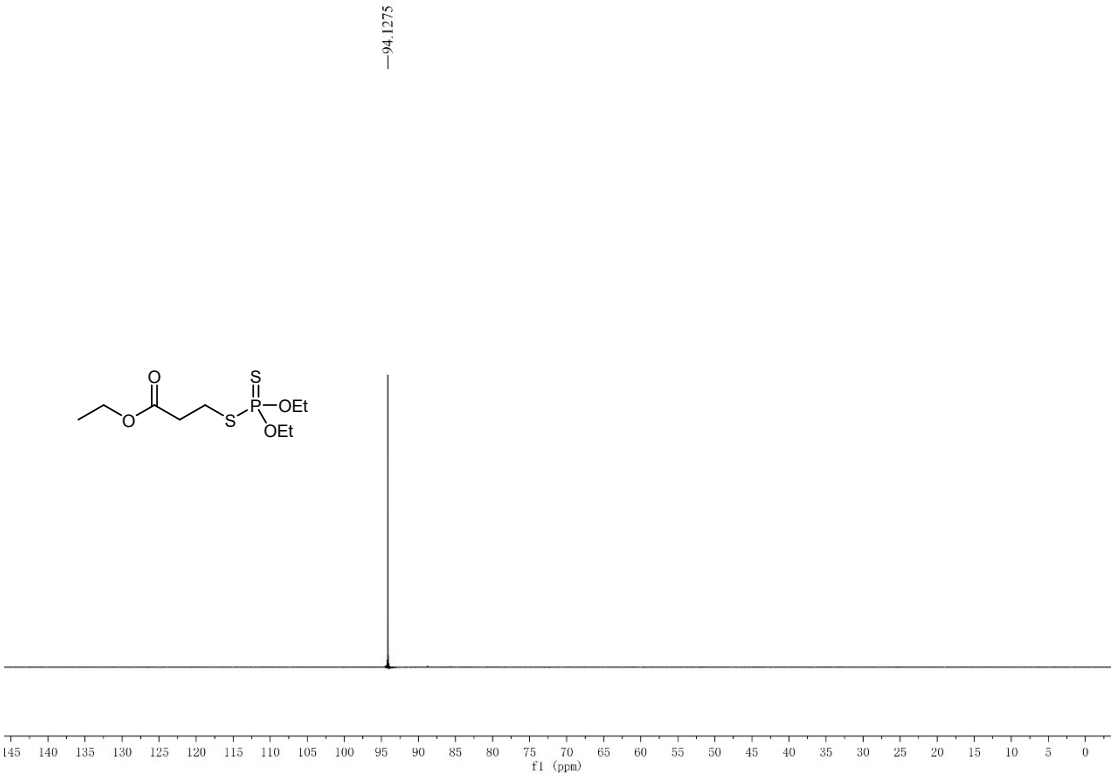
4wa ^{1}H NMR (500 MHz, $CDCl_3$)



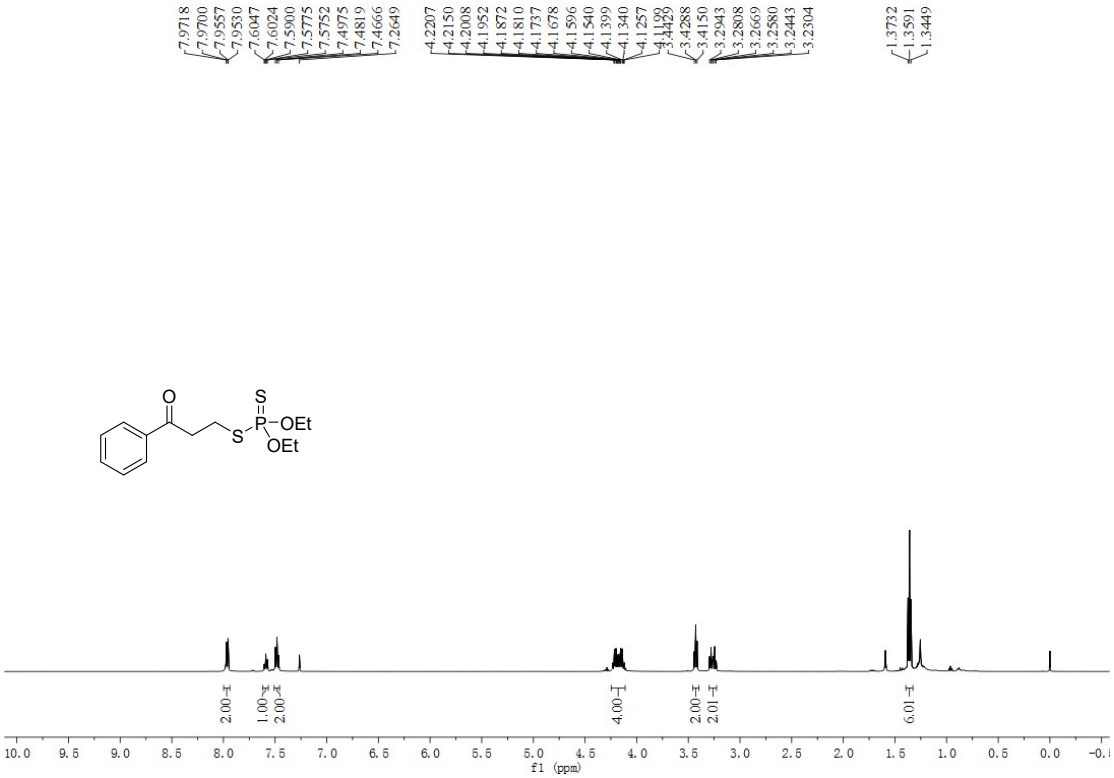
4wa ^{13}C NMR (125 MHz, $CDCl_3$)



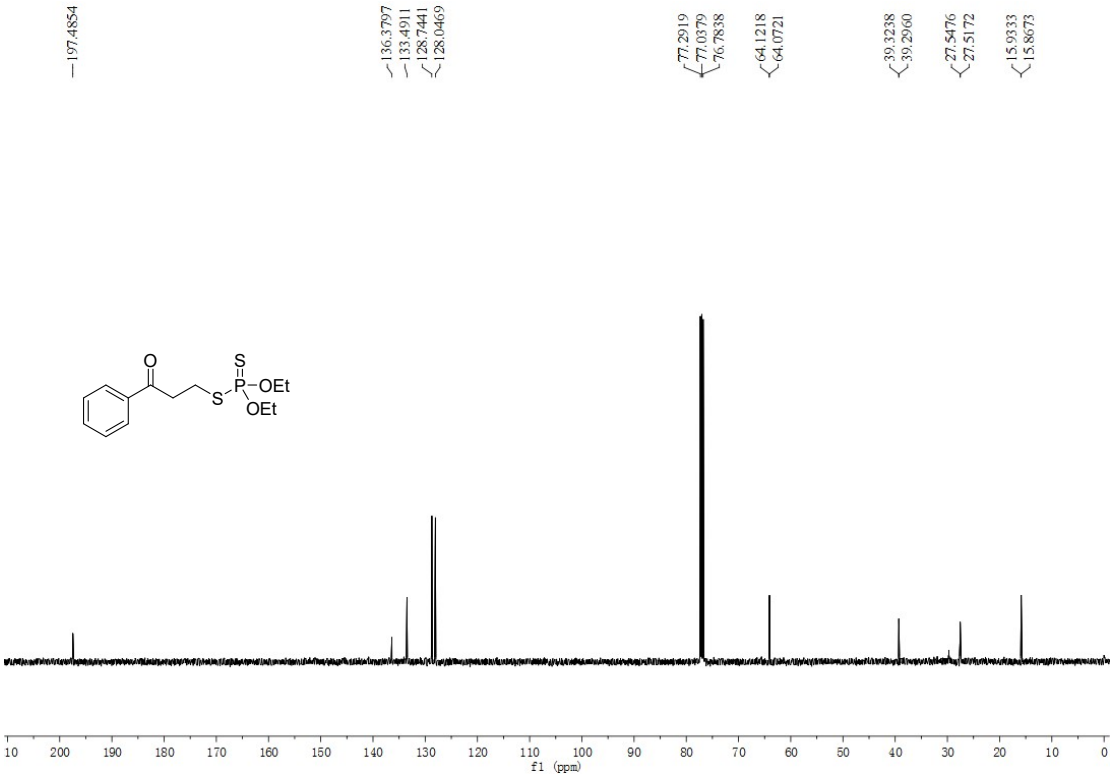
4wa ^{31}P NMR (202 MHz, $CDCl_3$):



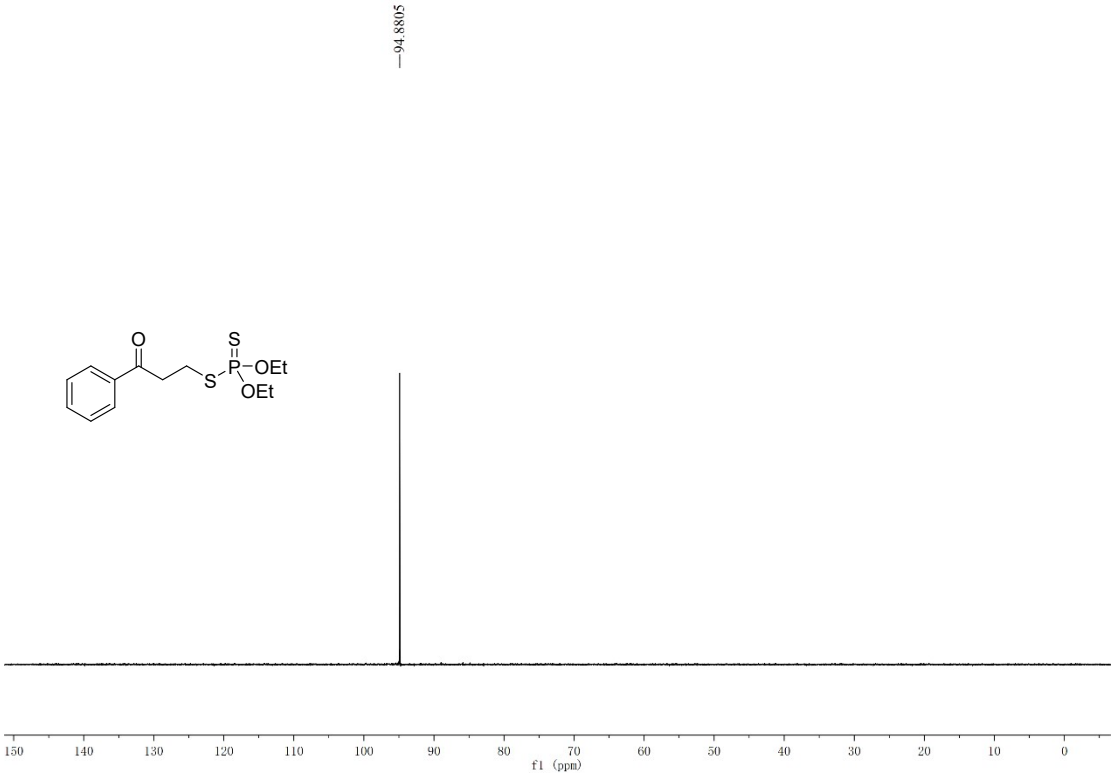
4xa ^{1}H NMR (500 MHz, $CDCl_3$)



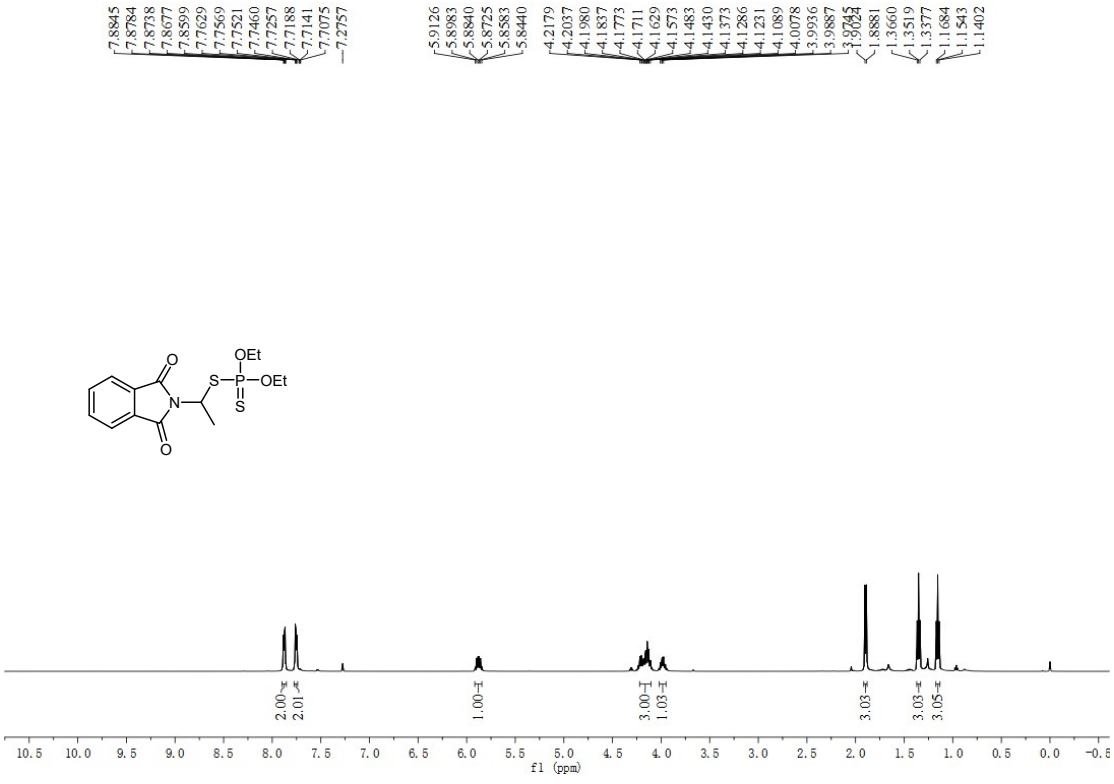
4xa ^{13}C NMR (125MHz, $CDCl_3$)



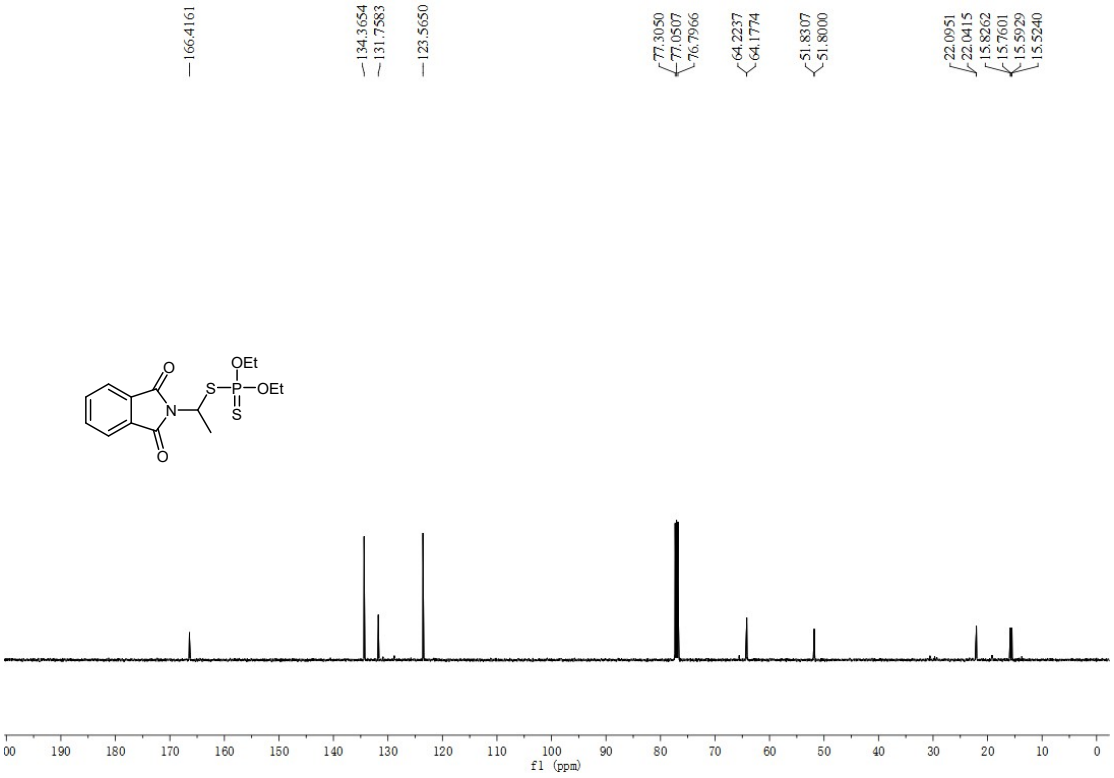
4xa ^{31}P NMR (202 MHz, $CDCl_3$):



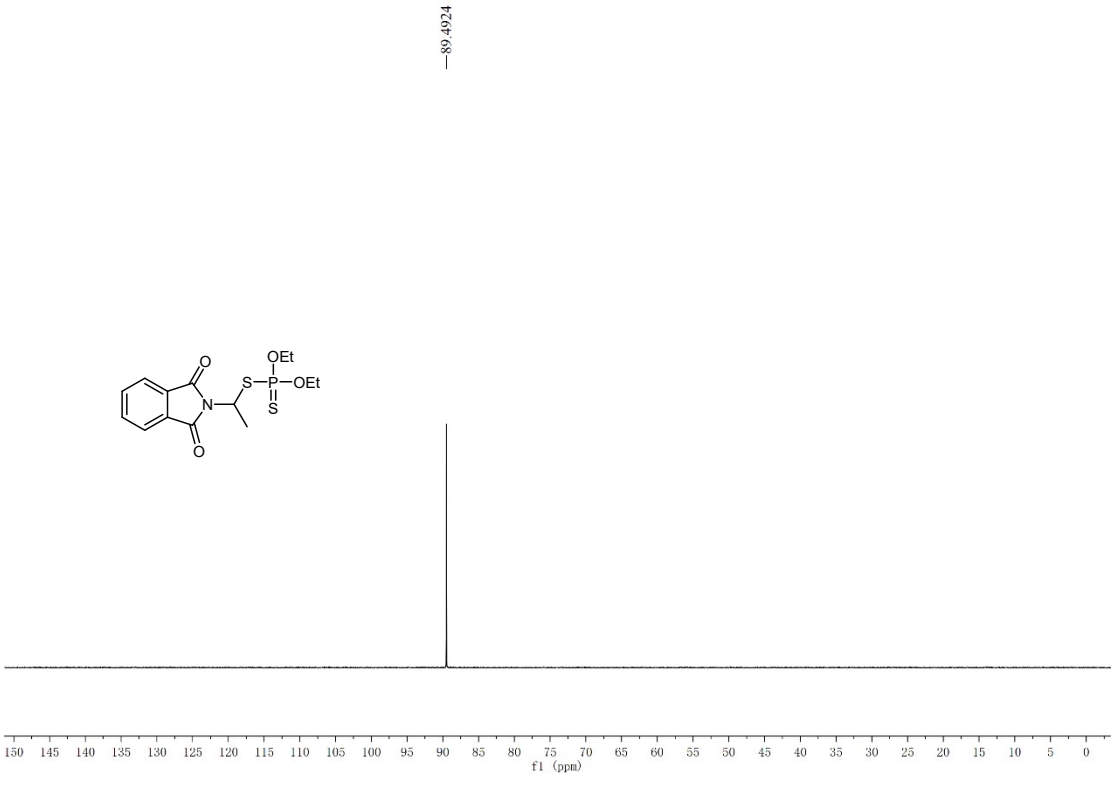
4ya ^{1}H NMR (500 MHz, $CDCl_3$)



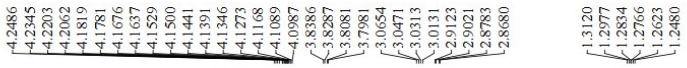
4ya ^{13}C NMR (125MHz, $CDCl_3$)

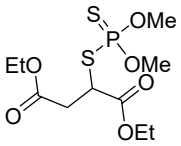


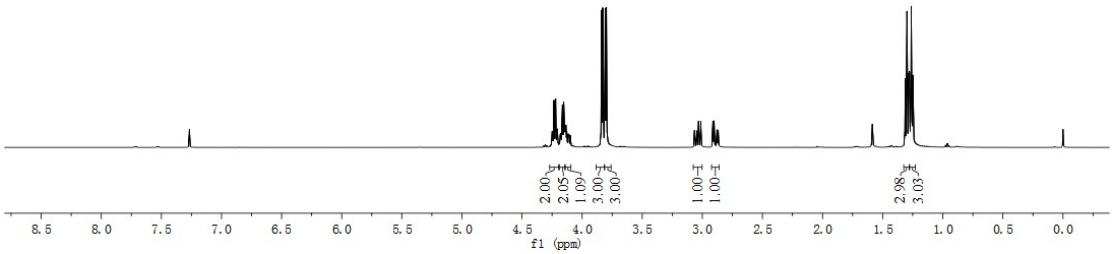
4ya ^{31}P NMR (202 MHz, $CDCl_3$):



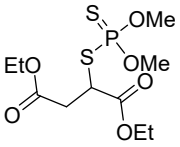
4za ^{1}H NMR (500 MHz, $CDCl_3$)

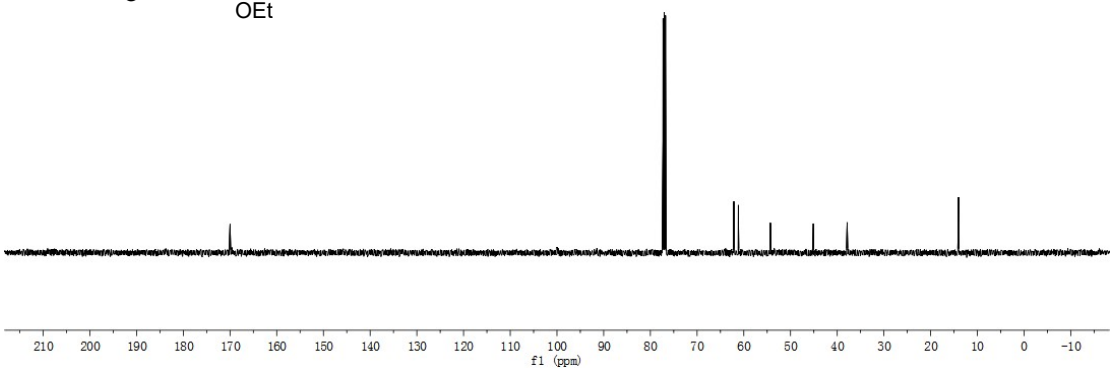




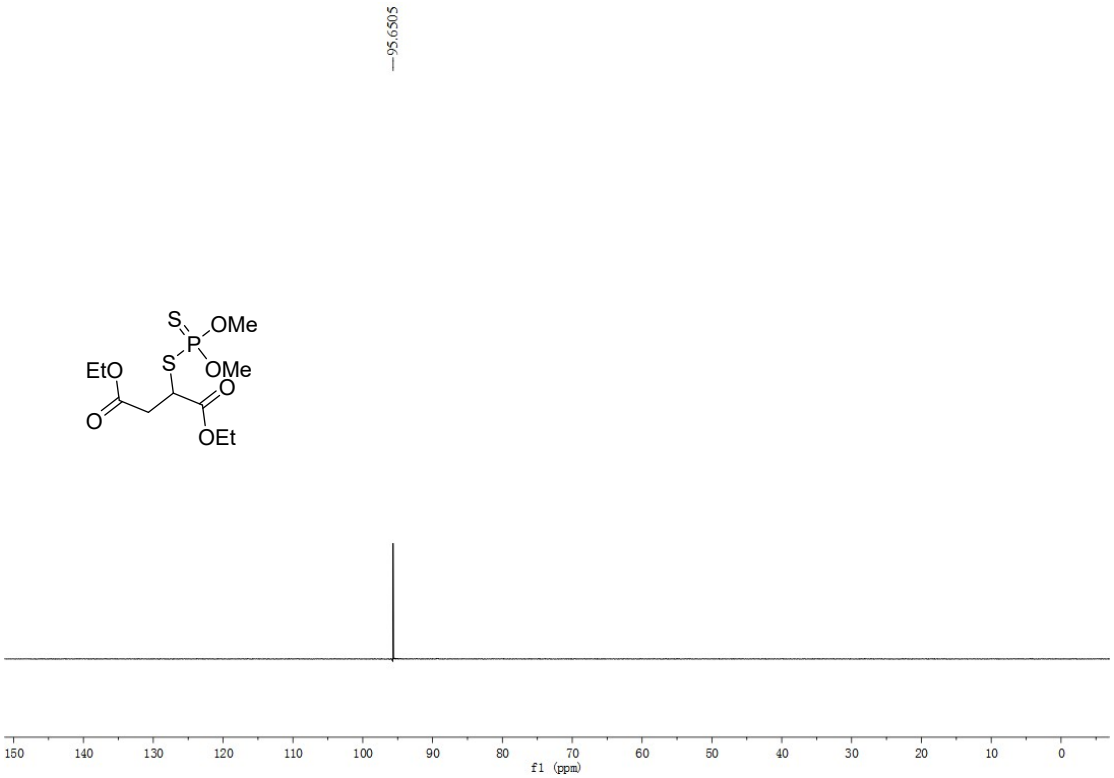


4za ^{13}C NMR (125MHz, $CDCl_3$)

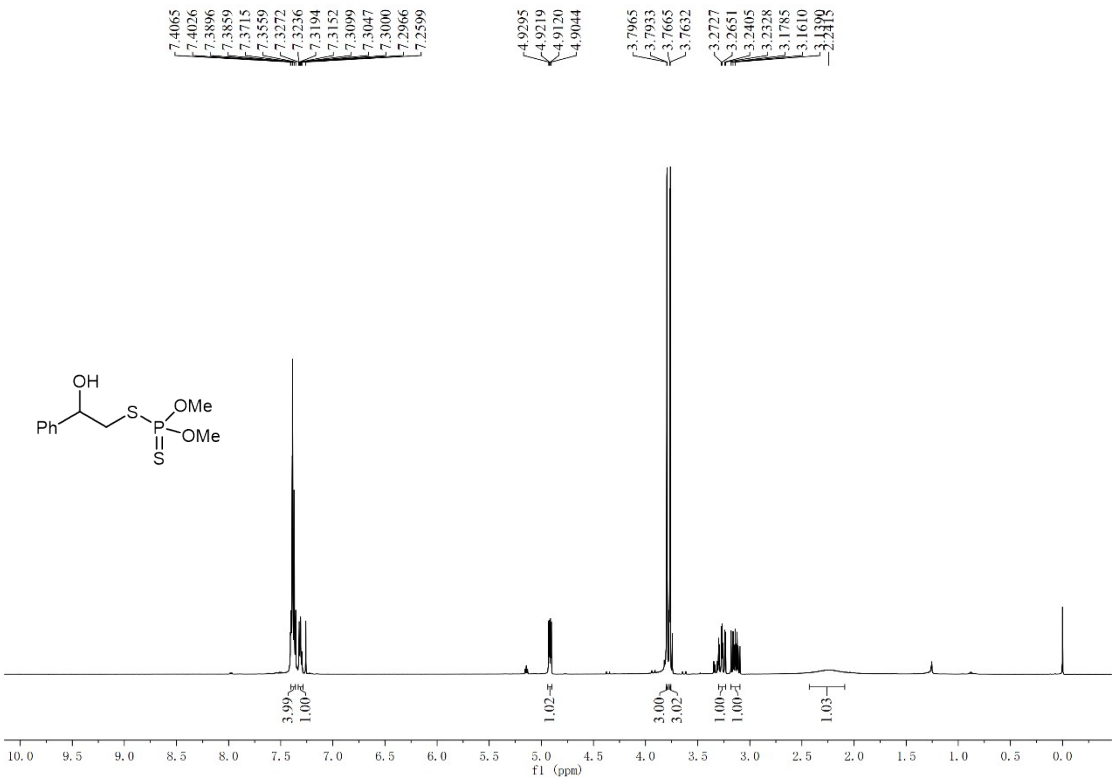




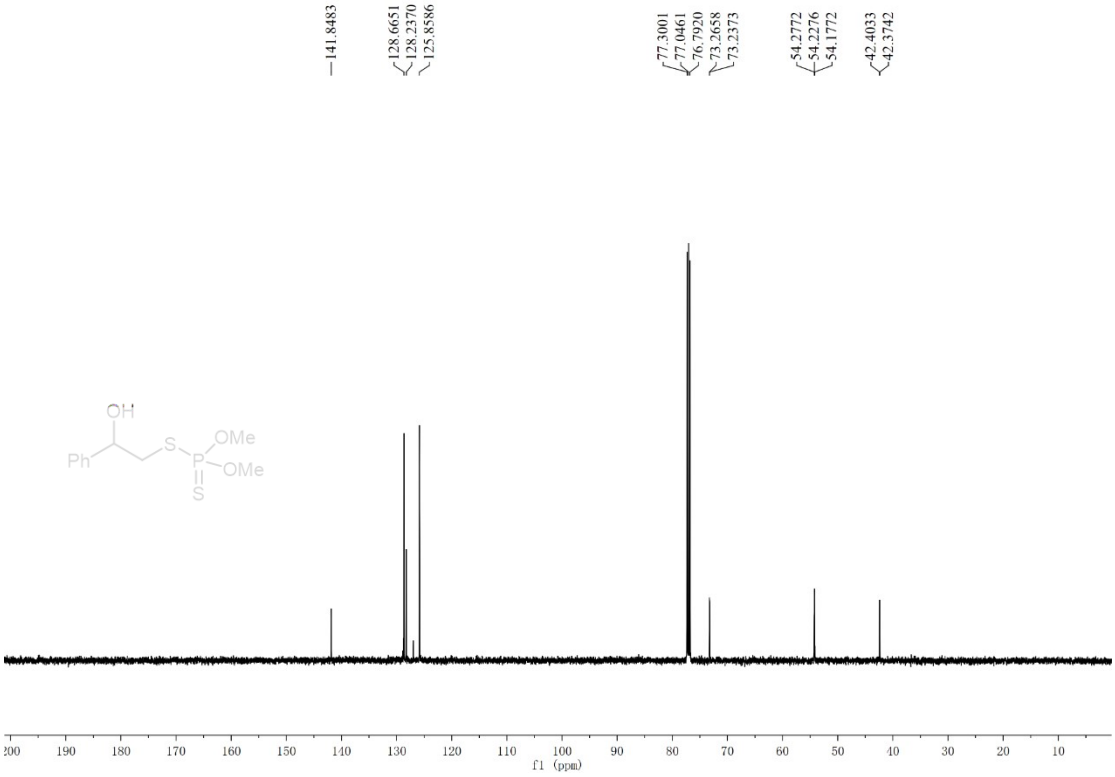
4za ^{31}P NMR (202 MHz, $CDCl_3$):



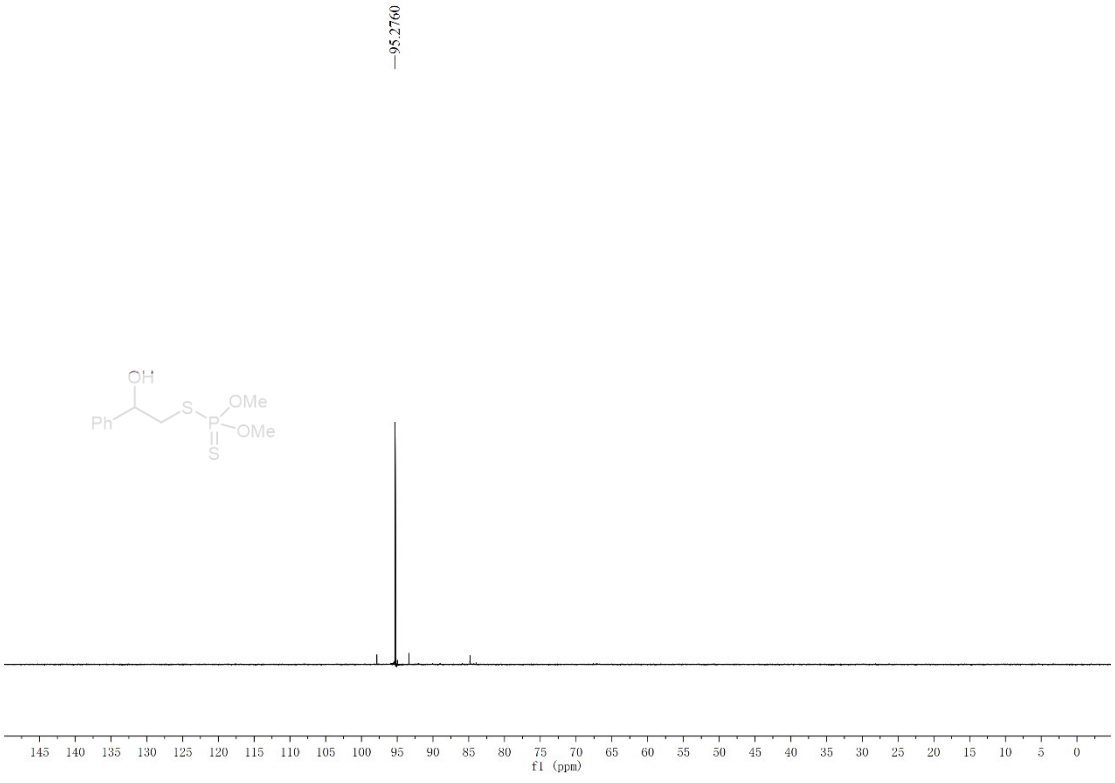
4ab ^{1}H NMR (500 MHz, $CDCl_3$)



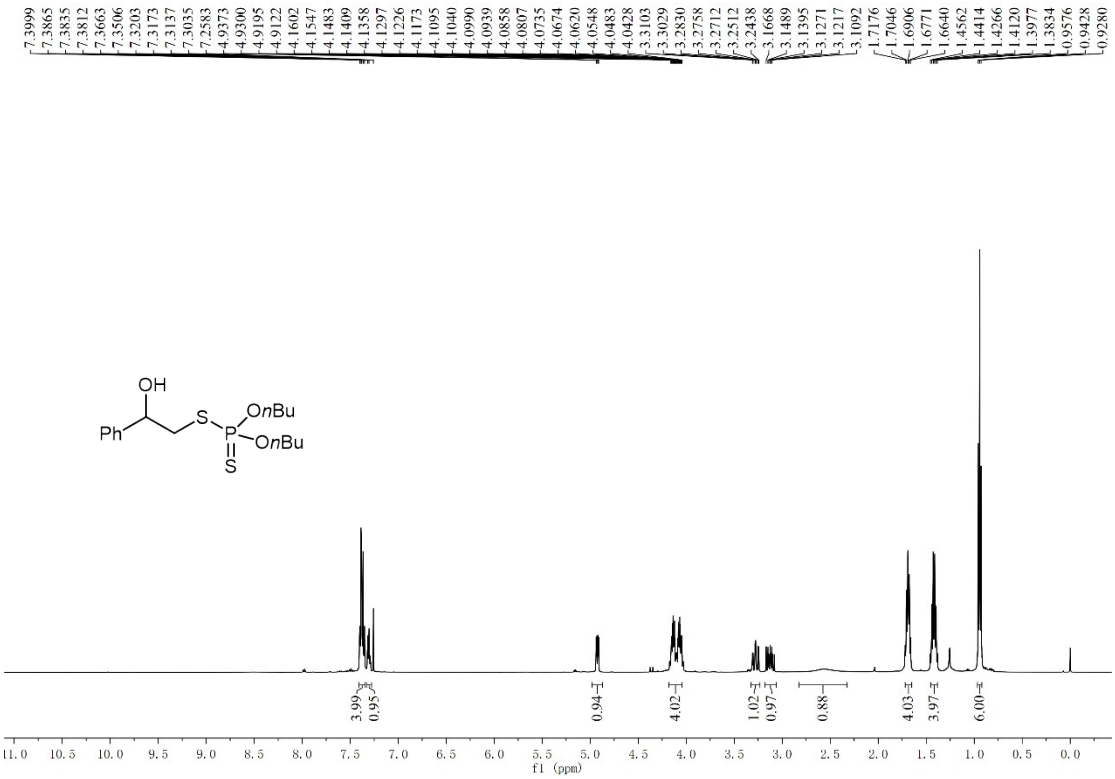
4ab ^{13}C NMR (125 MHz, $CDCl_3$)



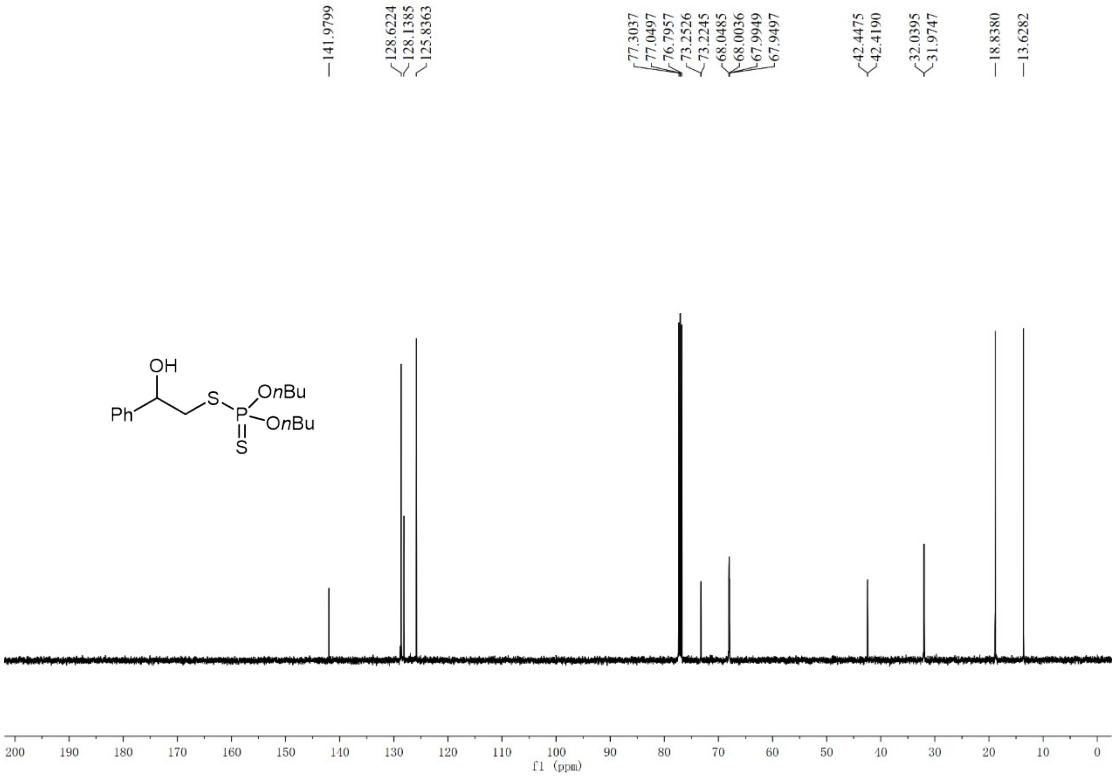
4ab ^{31}P NMR (202 MHz, $CDCl_3$):



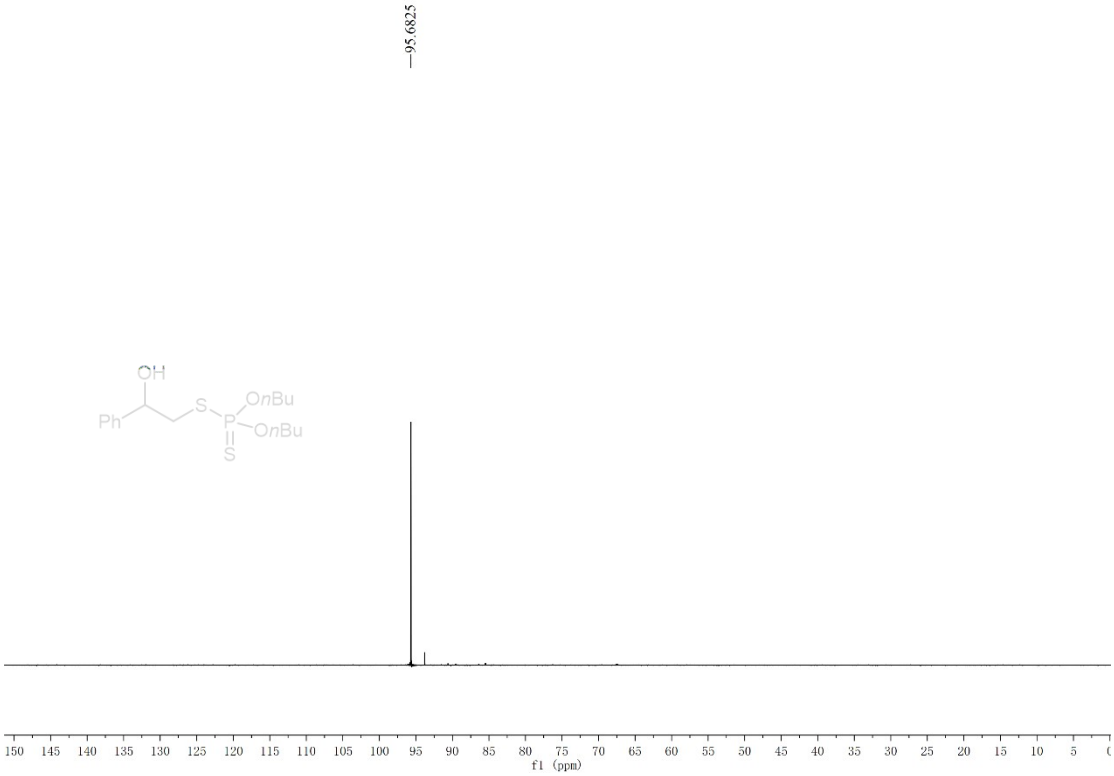
4ac ^{1}H NMR (500 MHz, $CDCl_3$)



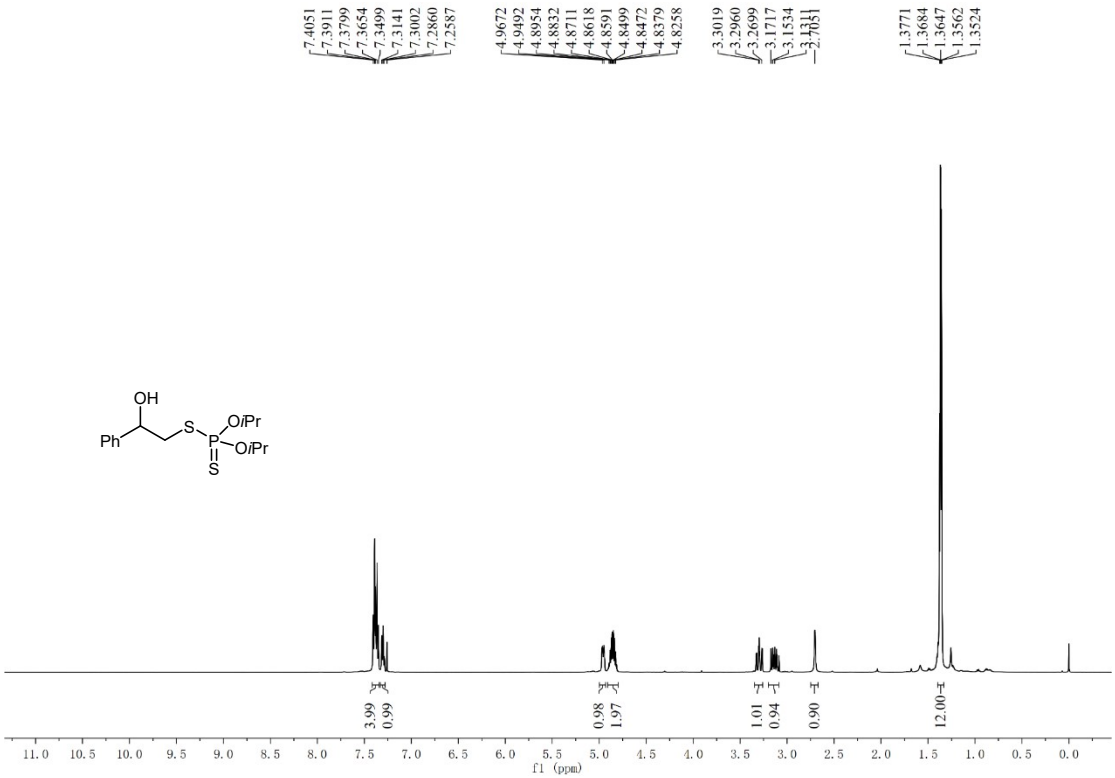
4ac ^{13}C NMR (125 MHz, $CDCl_3$)



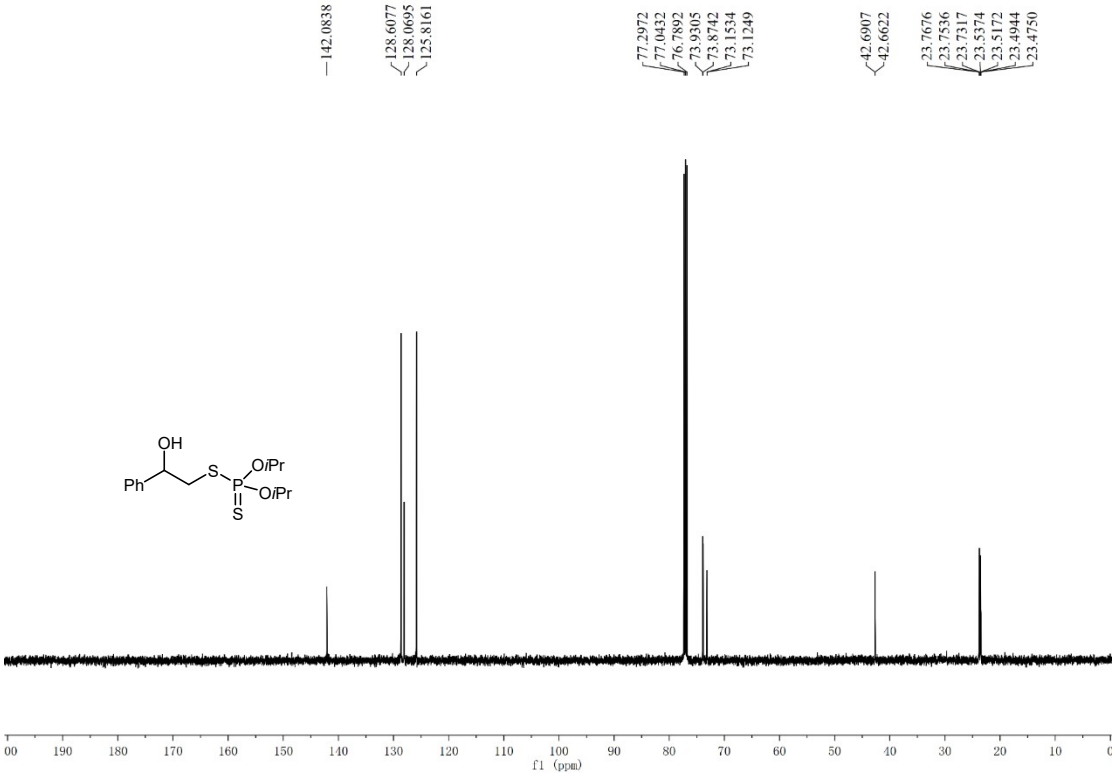
4ac ^{31}P NMR (202 MHz, $CDCl_3$):



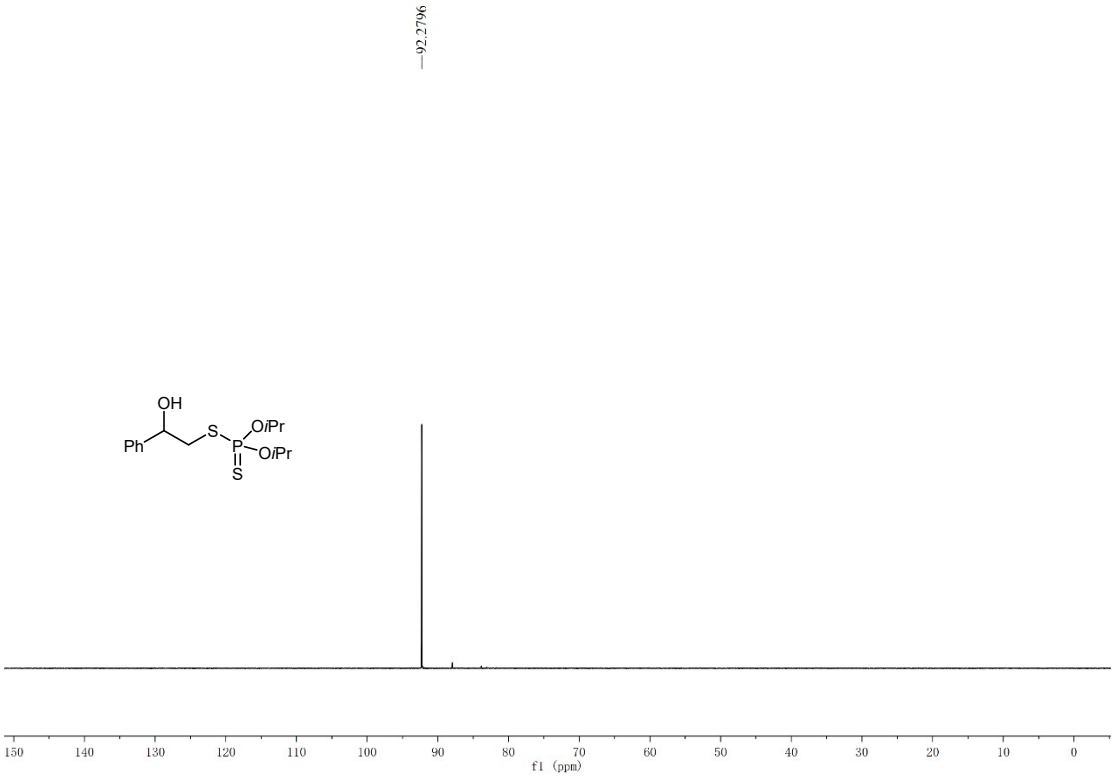
4ad ^{1}H NMR (500 MHz, $CDCl_3$)



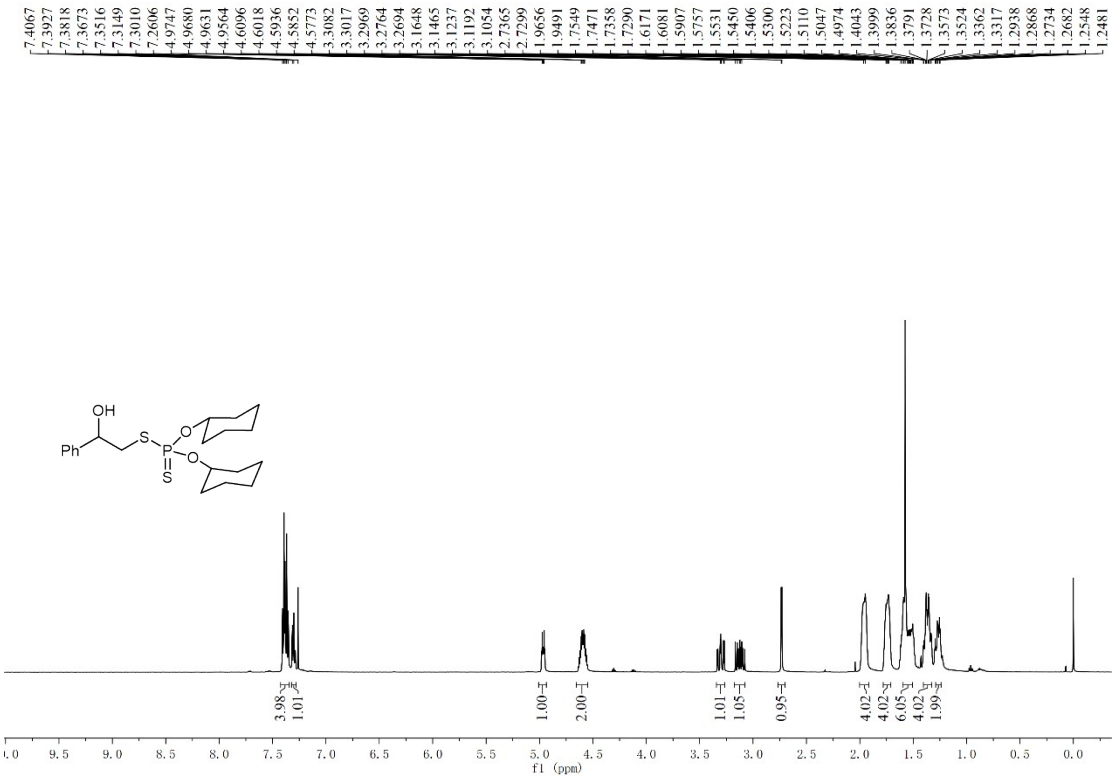
4ad ^{13}C NMR (125 MHz, $CDCl_3$)



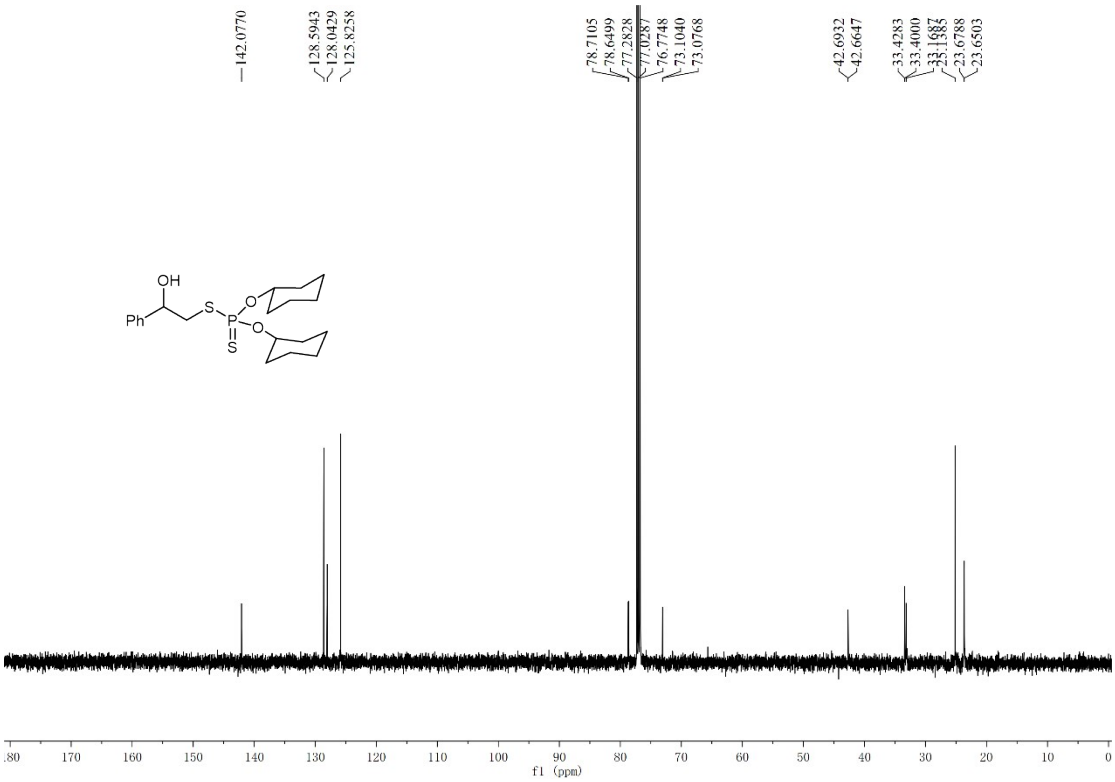
4ad ^{31}P NMR (202 MHz, $CDCl_3$):



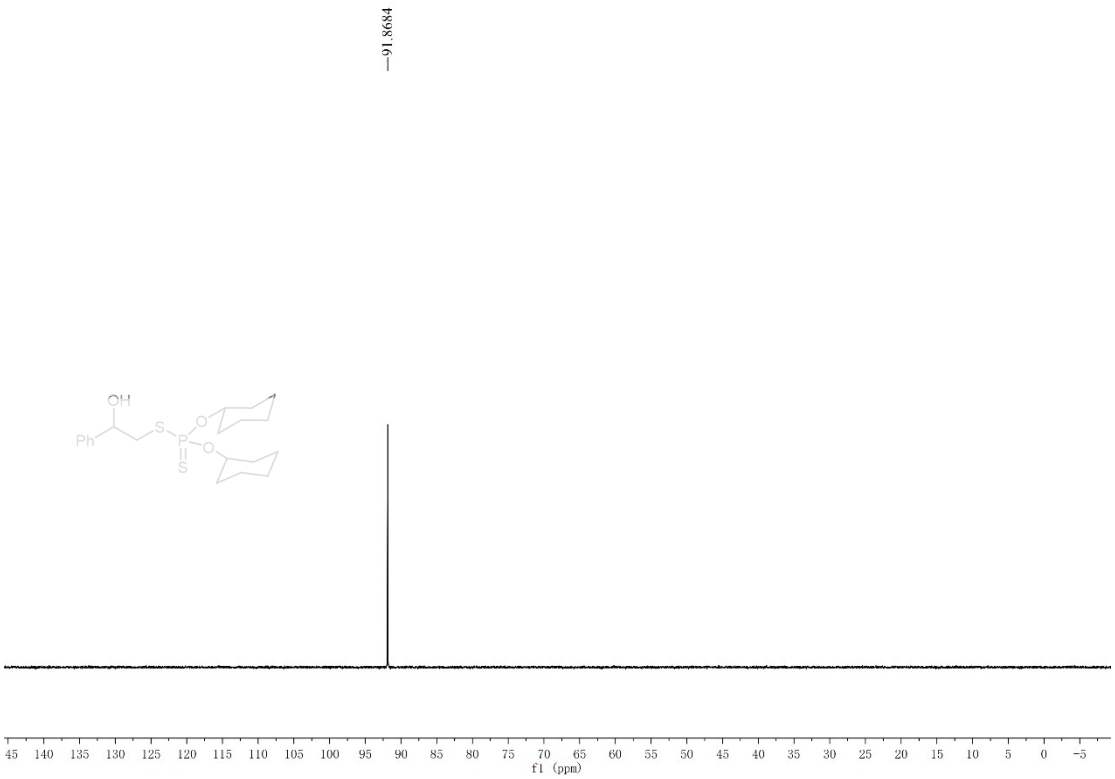
4ae ^{1}H NMR (500 MHz, $CDCl_3$)



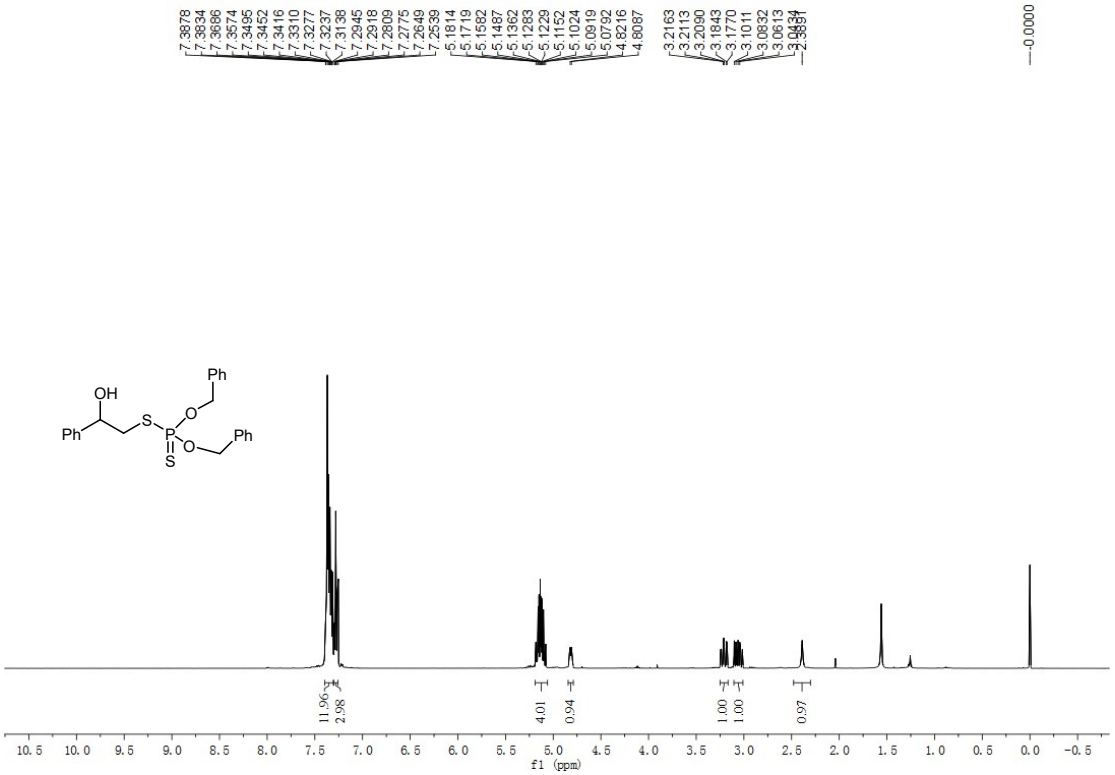
4ae ^{13}C NMR (125 MHz, $CDCl_3$)



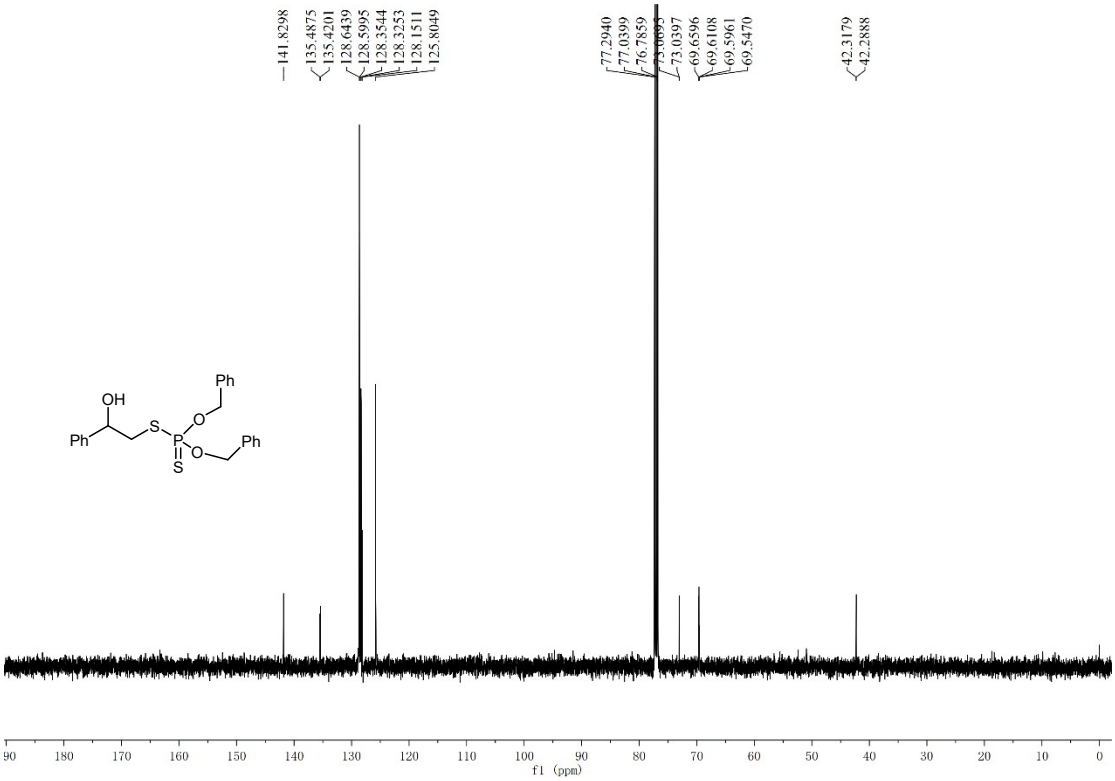
4ae ^{31}P NMR (202 MHz, $CDCl_3$):



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



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



4af ^{31}P NMR (202 MHz, $CDCl_3$):