Metal-free hydrophosphorodithiolation of alkynes with P_4S_{10} and alcohols leading to vinyl phosphorodithioates

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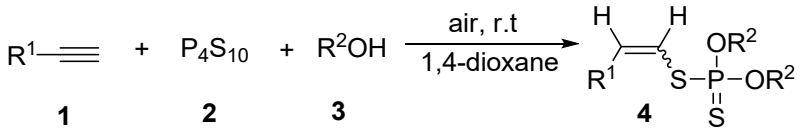
Contents

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 471 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. General procedure for hydrophosphorodithiolation of alkynes with P_4S_{10} and alcohols leading to vinyl phosphorodithioates.



Alkyne **1** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and alcohol **3** (0.5 mL) were successively added in a 15 mL reaction tube. Then, 1,4-dioxane (1.5 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**.

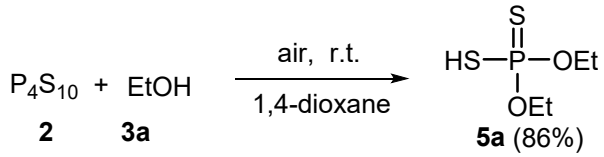
3. Gram-scale reaction

Phenylacetylene (**1a**) (5 mmol), P_4S_{10} **2** (5 mmol), and EtOH **3a** (6 mL) were successively added in a 100 mL reaction tube. Then, 1,4-dioxane (18 mL) was added to the mixture. The reaction mixture was open to air and stirred at room temperature for 12 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 (**4a**) in 84% yield (1.21g).

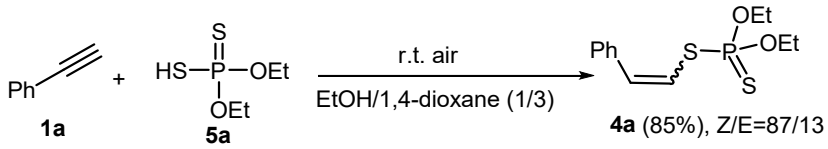
4. Preliminary mechanistic studies

4.1 The reaction of P_4S_{10} with EtOH.



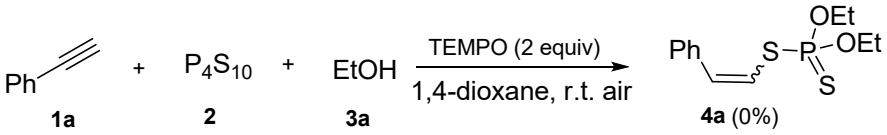
P_4S_{10} **2** (0.2 mmol) and EtOH (0.5 ml) were added in a 15 mL reaction tube. Then, 1,4-dioxane (1.5 mL) was added to the above mixture. The reaction mixture was open to air and stirred at room temperature for 6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum, the desired product **5a** was obtained in 86% yield.

4.2 The reaction of O,O-diethyl S-hydrogen phosphorodithioate 5a with phenylacetylene 1a.



Phenylacetylene **1a** (0.2 mmol) and EtOH (0.5 ml) were added in a 15 mL reaction tube. Then, O,O-diethyl S-hydrogen phosphorodithioate **5a** (0.2 mmol) and 1,4-dioxane (1.5 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 **4a** was isolated in 85% yield. This result indicated that S-hydrogen phosphorodithioate as a key intermediate might be involved in the present transformation.

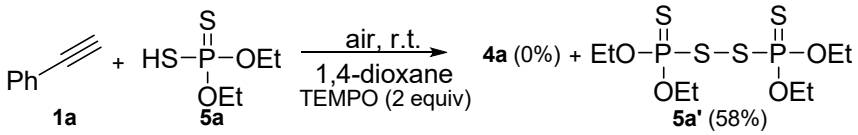
4.3 The addition of TEMPO in the model reaction system.



Phenylacetylene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and EtOH **3** (0.5 mL) were successively added in a 15 mL reaction tube. Then, TEMPO (0.4 mmol) and 1,4-dioxane (1.5 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

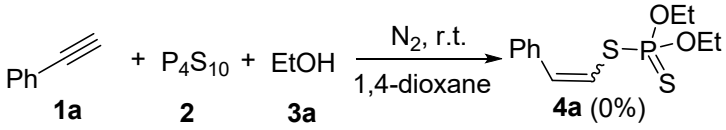
was concentrated in vacuum, no desired product **4a** was observed. This result indicated that a radical process might be involved in the present transformation.

4.4 The addition of TEMPO in the reaction system of phenylacetylene 1a with intermediate 5a.



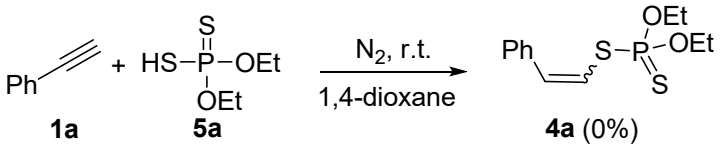
Phenylacetylene **1a** (0.2 mmol), O,O-diethyl S-hydrogen phosphorodithioate **5a**, and EtOH **3** (0.5 mL) were successively added in a 15 mL reaction tube. Then, TEMPO (0.4 mmol) and 1,4-dioxane (1.5 mL) was added to the above mixture. The reaction mixture was open to air and stirred at room temperature for 6 h. After completion of the reaction, the solution was concentrated in vacuum, the corresponding disulfide of O,O-diethyl phosphorodithioate (**5a'**) was obtained in 58% yield and none of product **4a** was observed. This result indicated that a radical process might be involved in the present transformation.

4.5 The model reaction was carried out under N_2.



Phenylacetylene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and EtOH **3a** (0.5 mL) were successively added in a 15 mL reaction tube under N_2. Then, 1,4-dioxane (1.5 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 **4a** was detected. This result indicated that air (O_2) is indispensable for this transformation.

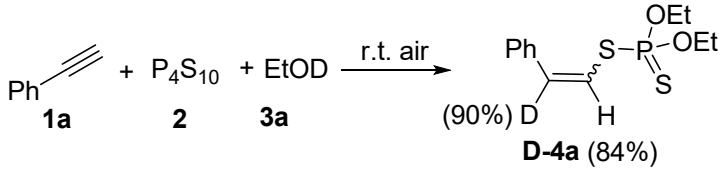
4.6 The reaction of phenylacetylene 1a and intermediate 5a was carried out under N_2.



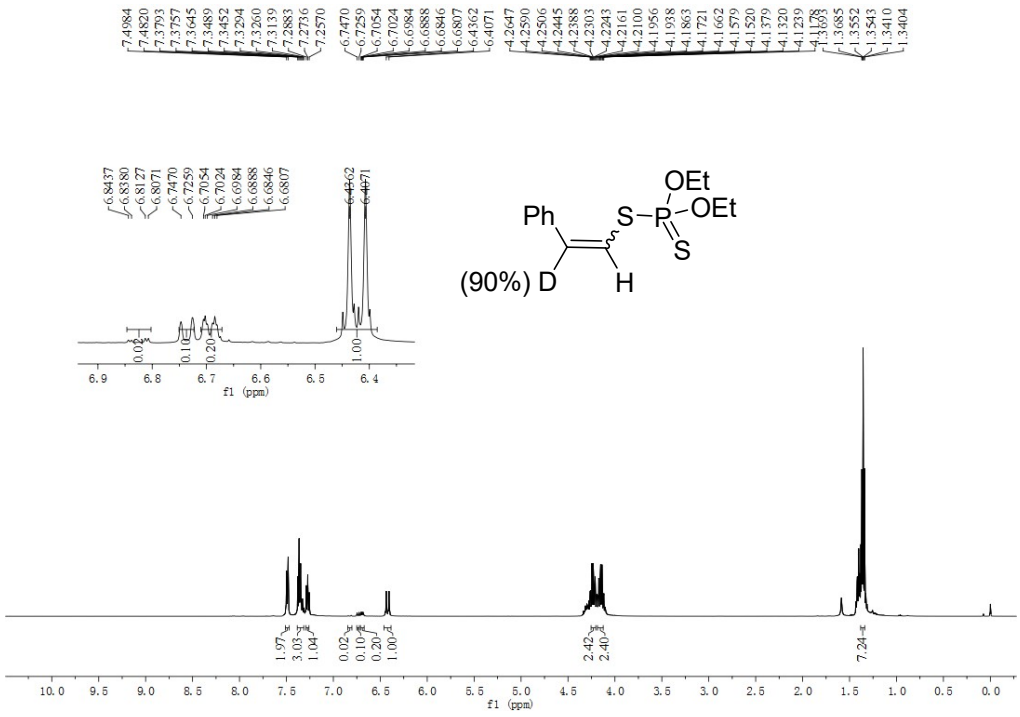
Phenylacetylene **1a** (0.2 mmol), O,O-diethyl S-hydrogen phosphorodithioate **5a**

(0.2 mmol) and EtOH (0.5 ml) were added in a 15 mL reaction tube under N_2. Then, 1,4-dioxane (1.5 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 **4a** was detected. This result indicated that air (O_2) is indispensable for this transformation.

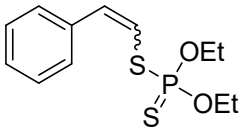
4.7 The model reaction was carried out in EtOD.



Phenylacetylene **1a** (0.2 mmol), P_4S_{10} **2** (0.2 mmol), and EtOD (1.5 mL) were successively added in a 15 mL reaction tube. Then, 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 D-**4a** was isolated in 84% yield. This result indicated that water should not take part in this transformation.

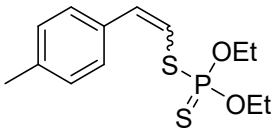


5. Characterization data of products



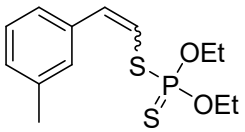
***O,O*-diethyl *S*-styryl phosphorodithioate (4a)**

4a (Z/E = 83:17) was obtained in 88% yield (51.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J = 7.8 Hz, 2H), 7.31-7.39 (m, 3H), 7.29 (d, J = 7.3Hz, 1H), 6.84 (dd, J_1 = 2.7 Hz, J_2 = 15.6 Hz, 0.2H for E), 6.74 (d, J = 10.6 Hz, 1H for Z), 6.70 (dd, J_1 = 8.7 Hz, J_2 = 15.6 Hz, 0.2H for E), 6.44 (dd, J_1 = 10.5 Hz, J_2 = 14.5 Hz, 1H for Z), 4.21-4.30 (m, 2.4H), 4.10-4.19 (m, 2.4H), 1.32-1.40 (m, 7.2 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.7 (d, J = 11.7 Hz), 135.8 (d, J = 1.6 Hz), 135.6 (d, J = 1.3 Hz), 131.5 (d, J = 9.9 Hz), 128.9 (d, J = 1.6 Hz), 128.7, 128.4, 127.9, 126.4, 117.8 (d, J = 4.0 Hz), 116.7 (d, J = 6.0 Hz), 64.3 (d, J = 5.3 Hz), 64.2, 15.9 (d, J = 10.1 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.6, 88.5. ESI HRMS: calculated for $C_{12}H_{18}O_2PS_2$ $[M+H]^+$ 289.0486. found 289.0487.



***O,O*-diethyl *S*-(4-methylstyryl) phosphorodithioate (4b)**

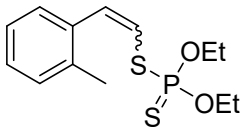
4b (Z/E = 80:20) was obtained in 78% yield (47.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 7.9 Hz, 2H for Z), 7.26 (d, J = 7.9 Hz, 0.5H for E), 7.17 (d, J = 7.9 Hz, 2H for Z), 7.14 (d, J = 7.9 Hz, 0.5H for E), 6.81 (dd, J_1 = 2.9 Hz, J_2 = 15.5 Hz, 0.25H for E), 6.71 (d, J = 10.5 Hz, 1H for Z), 6.64 (dd, J_1 = 8.4 Hz, J_2 = 15.5 Hz, 0.25H for E), 6.37 (dd, J_1 = 10.5 Hz, J_2 = 14.4 Hz, 1H for Z), 4.20-4.27 (m, 2.5H), 4.11-4.19 (m, 2.5H), 2.35 (s, 3H for Z), 2.34 (s, 0.75H for E), 1.33-1.39 (m, 7.5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.5, 137.8, 137.1 (d, J = 11.4 Hz),132.8, 131.6 (d, J = 9.9 Hz), 131.5, 129.4, 129.1, 128.9 (d, J = 1.6 Hz), 126.3 (d, J = 1.0 Hz), 116.6 (d, J = 4.3 Hz), 115.2 (d, J = 6.3 Hz), 64.3 (d, J = 5.3 Hz), 64.2 (d, J = 5.7 Hz), 21.3, 21.2, 15.9 (d, J = 10.1 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.8, 88.6. ESI HRMS: calculated for $C_{13}H_{20}O_2PS_2$ $[M+H]^+$ 303.0642. found 303.0644.



***O,O*-diethyl *S*-(3-methylstyryl) phosphorodithioate (4c)**

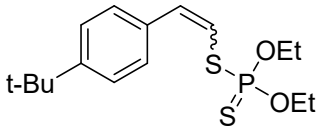
4c (Z/E = 80:20) was obtained in 84% yield (51.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.30 (m, 2H for Z), 7.25 (d, J = 7.8 Hz, 1H for Z), 7.22 (d, J = 7.5Hz, 0.25 H for E), 7.16 (d, J = 8.7 Hz, 0.5H for E), 7.10 (d, J = 8.7 Hz, 1.25H), 6.81(dd, J_1 = 2.9 Hz, J_2 = 15.5 Hz, 0.25H for E), 6.71 (d, J = 10.5 Hz, 1H for Z), 6.64 (dd, J_1 = 8.4 Hz, J_2 = 15.5 Hz, 0.25H for E), 6.37 (dd, J_1 = 10.5 Hz, J_2 = 14.4 Hz, 1H for Z), 4.20-4.27 (m, 2.5H), 4.11-4.19 (m, 2.5H), 2.35(s, 3H for Z), 2.34 (s, 0.75H for E), 1.33-1.39 (m, 7.5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.4, 138.0, 137.0 (d, J = 11.4 Hz), 135.7 (d, J = 1.5 Hz), 135.6 (d, J = 1.3 Hz), 131.6

(d, J = 9.8 Hz), 129.5 (d, J = 1.5 Hz), 129.2, 128.7, 128.6, 128.3, 127.0 (d, J = 1.0 Hz), 125.9 (d, J = 1.8 Hz), 123.6, 117.5 (d, J = 4.1 Hz), 116.3 (d, J = 6.1 Hz), 64.3 (d, J = 5.3 Hz), 64.2 (d, J = 5.8 Hz), 21.5, 21.4, 15.9 (d, J = 10.4 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 89.1, 88.5. ESI HRMS: calculated for $C_{13}H_{20}O_2PS_2$ $[M+H]^+$ 303.0642. found 303.0642.



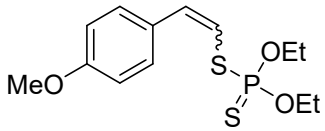
***O,O*-diethyl *S*-(2-methylstyryl) phosphorodithioate (4d)**

4d (Z/E = 83:17) was obtained in 92% yield (56.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): 7.39-7.41 (m, 1H), 7,14-7.21 (m, 3.8H), 7.07 (dd, J_1 = 3.1 Hz, J_2 = 15.4 Hz, 0.2H for E), 6.86 (d, J = 10.2 Hz, 1H for Z), 6.60 (dd, J_1 = 8.7 Hz, J_2 = 15.4 Hz, 0.2H for E), 6.51 (dd, J_1 = 10.2 Hz, J_2 = 15.4 Hz, 1H for Z), 4.25-4.31 (m, 0.8H), 4.17-4.23 (m, 2H), 4.09-4.14 (m, 2H), 2.34 (s, 0.6H for E), 2.27 (s, 3H for Z), 1.38-1.35 (m, 7.5H), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.2, 135.4 (d, J = 1.1 Hz), 135.2 (d, J = 11.6 Hz),135.0 (d, J = 1.4 Hz), 134.6 (d, J = 1.1 Hz), 130.9 (d, J = 10.3 Hz), 130.5, 130.1, 128.4 (d, J = 1.6 Hz), 128.3, 128.1, 126.2, 125.8, 125.6, 119.3 (d, J = 3.7 Hz), 117.6 (d, J = 6.1 Hz), 64.9 (d, J = 5.4 Hz), 64.2 (d, J = 5.4 Hz), 19.8, 15.8 (d, J = 8.3 Hz), 15.8 (d, J = 8.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 89.2, 88.7. ESI HRMS: calculated for $C_{13}H_{20}O_2PS_2$ $[M+H]^+$ 303.0642. found 303.0649.



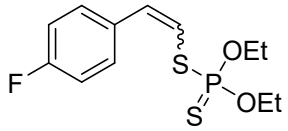
***S*-(4-(*tert*-butyl)styryl) *O,O*-diethyl phosphorodithioate (4e)**

4e (Z/E = 78:22) was obtained in 78% yield (54.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 8.3 Hz, 2H for Z), 7.38 (d, J = 8.4 Hz, 2H for Z), 7.35 (d, J = 8.4 Hz, 0.56 H for E), 7.30 (d, J = 8.5 Hz, 0.56H for E), 6.83 (dd, J_1 = 2.9 Hz, J_2 = 15.5 Hz, 0.28H for E), 6.73 (d, J = 10.5 Hz, 1H for Z), 6.66 (dd, J_1 = 8.5 Hz, J_2 = 15.5 Hz, 0.28H for E), 6.38 (dd, J_1 = 10.5 Hz, J_2 = 14.5 Hz, 1H for Z), 4.18-4.26 (m, 2.56H), 4.11-4.17 (m, 2.56H), 1.33-1.38 (m, 7.68H), 1.31 (s, 9H), 1.31 (s, 2.52H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.7, 151.0, 137.0 (d, J = 11.5 Hz), 133.1 (d, J = 1.6 Hz), 132.8 (d, J = 1.3 Hz), 131.4 (d, J = 9.8 Hz), 128.7 (d, J = 1.6 Hz), 126.2 (d, J = 0.7 Hz), 125.7, 125.3, 116.7 (d, J =4.1 Hz), 115.5 (d, J = 6.4 Hz), 64.3 (d, J = 5.3 Hz), 64.2 (d, J = 5.5 Hz), 34.6, 31.2, 15.9 (d, J = 9.9 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.8, 88.6. ESI HRMS: calculated for $C_{16}H_{26}O_2PS_2$ $[M+H]^+$ 345.1112. found 345.1108.



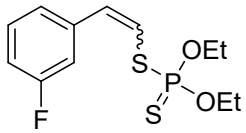
***O,O*-diethyl *S*-(4-methoxystyryl) phosphorodithioate (4f)**

4f (Z/E = 77:23) was obtained in 63% yield (40.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.8 Hz, 2H for Z), 7.30 (d, J = 8.8 Hz, 0.6 H for E), 6.86-6.90 (m, 2H for Z), 6.85-6.86 (m, 0.6H for E), 6.78 (dd, J_1 =3.2 Hz, J_2 = 15.4 Hz, 0.30H for E), 6.71 (d, J = 10.5 Hz, 1H for Z), 6.50 (dd, J_1 = 8.0 Hz, J_2 = 15.5 Hz, 0.3H for E), 6.26 (dd, J_1 = 10.5 Hz, J_2 = 13.9 Hz, 1H for Z), 4.21-4.28 (m, 2.6H), 4.11-4.19 (m, 2.6H), 3.18 (s, 3H for Z), 3.80 (s, 0.9H for E), 1.33-1.39 (m, 7.8H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.9, 159.2, 137.3 (d, J = 10.8 Hz), 131.4 (d, J = 9.8 Hz), 130.4 (d, J = 1.7 Hz), 128.7 (d, J = 1.8 Hz), 128.3 (d, J =1.4 Hz), 127.8 (d, J = 0.8 Hz), 115.0 (d, J = 4.4 Hz), 114.1, 113.8, 113.4 (d, J = 6.5 Hz), 64.2 (d, J = 5.3 Hz), 64.1 (d, J = 5.5 Hz), 55.3, 55.3, 15.9 (d, J = 8.3 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 89.1, 88.5. ESI HRMS: calculated for $C_{13}H_{20}O_3PS_2$ $[M+H]^+$ 319.0591. found 319.0592.



***O,O*-diethyl *S*-(4-fluorostyryl) phosphorodithioate (4g)**

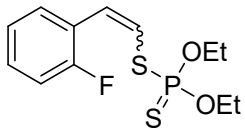
4g (Z/E = 80:20) was obtained in 70% yield (43.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.48 (m, 2H for Z), 7.31-7.34 (m, 0.5H for E), 7.02-7.07 (m, 2H for Z), 7.00-7.02 (m, 0.5H for E), 6.80 (dd, J_1 = 2.8 Hz, J_2 = 15. 5 Hz, 0.25H for E), 6.71 (d, J = 10.5 Hz, 1H for Z), 6.61 (dd, J_1 = 8.8 Hz, J_2 = 15.5 Hz, 0.25H for E), 6.40 (dd, J_1 = 10.5 Hz, J_2 = 14.3 Hz, 1H for Z), 4.20-4.28 (m, 2.5H), 4.11-4.19 (m, 2.5H), 1.34-1.39 (m, 7.5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.0 (d, J = 247.2 Hz), 135.6 (d, J = 11.9 Hz), 132.11 (dd, J = 1.3 Hz, 3.3 Hz), 131.8 (dd, J = 1.3 Hz, 3.4 Hz), 130.6 (dd, J = 1.7 Hz, 8.1 Hz), 130.4 (d, J = 10 Hz), 128.0 (d, J = 8.2 Hz), 116.50 (dd, J = 2.3 Hz, 6.0 Hz), 115.8 (d, J = 21.6 Hz), 115.4 (d, J = 21.4 Hz), 64.4 (d, J = 5.5 Hz), 64.3 (d, J = 5.6 Hz), 15.8 (d, J = 8.3 Hz), 15.8 (d, J = 8.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): -112.7, -112.9. ^{31}P NMR (202 MHz, $CDCl_3$): 88.7, 88.2. ESI HRMS: calculated for $C_{13}H_{17}FO_2PS_2$ $[M+H]^+$ 307.0392. found 307.0387.



***O,O*-diethyl *S*-(3-fluorostyryl) phosphorodithioate (4h)**

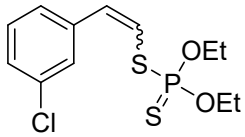
4h (Z/E = 77:23) was obtained in 85% yield (52.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.34 (m, 1H), 7.28-7.30 (m, 0.3H), 7.20-7.35 (m, 2H), 7.11 (d, J = 7.7 Hz, 0.3H), 7.04-7.06 (m, 0.3H), 6.95-6.99 (m, 1.3H), 6.71-6.78 (m, 0.6H for E), 6.68 (d, J = 10.6 Hz, 1H for Z), 6.50 (dd, J_1 = 10.6 Hz, J_2 = 14.9 Hz, 1H for Z), 4.20-4.28 (m, 2.6H), 4.12-4.19 (m, 2.6H), 1.35-1.39 (m, 7.8 H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 163.4 (d, J = 246.1 Hz), 162.6 (d, J = 245.8 Hz), 138.1 (d, J = 1.1 Hz, 7.7 Hz), 137.7 (d, J = 1.2 Hz, 8.1 Hz), 134.8 (d, J = 2.6 Hz, 12.1 Hz), 130.3 (d, J = 8.3 Hz), 130.0 (d, J = 2.5 Hz, 10.1 Hz), 129.9 (d, J = 8.5 Hz), 124.6, 122.2 (d, J = 2.5 Hz), 119.8 (d, J = 3.9 Hz), 118.9 (d, J = 5.6 Hz), 115.47 (dd, J = 1.7 Hz, 22.3 Hz), 115.17 (d, J = 21.3 Hz), 114.75 (d, J = 21.3 Hz), 112.84 (d, J = 22.7 Hz), 64.4 (d, J = 5.5 Hz), 64.3 (d, J = 5.6 Hz), 15.8 (d, J = 8.3 Hz), 15.8 (d, J = 8.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): -112.7, -112.9. ^{31}P NMR (202 MHz, $CDCl_3$): 88.2, 88.1. ESI HRMS: calculated for $C_{13}H_{17}FO_2PS_2$ $[M+H]^+$ 307.0392. found 307.0394.



***O,O*-diethyl *S*-(2-fluorostyryl) phosphorodithioate (4i)**

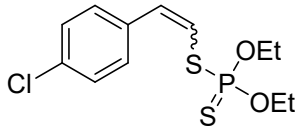
4i (Z/E = 72:28) was obtained in 82% yield (50.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (t, J = 7.65 Hz, 1H for Z), 7.41 (t, J = 7.7 Hz, 0.4H for E), 7.23-7.29 (m, 1.4H), 7.09-7.16 (m, 1.4H), 7.02-7.07 (m, 1.4H), 6.95 (dd, J_1 = 2.6 Hz, J_2 = 15.8 Hz, 0.4H for E), 6.87 (d, J = 10.6 Hz, 1H for Z), 6.82 (dd, J_1 = 9.1 Hz, J_2 = 15.5 Hz, 0.4H for E), 6.55 (dd, J_1 = 10.6 Hz, J_2 = 14.2 Hz, 1H for Z), 4.20-4.28 (m, 2.8H), 4.12-4.19 (m, 2.8H), 1.35-1.40 (m, 8.4H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 160.0 (d, J = 249 Hz), 129.7 (d, J = 8.4 Hz), 129.6 (d, J = 8.5 Hz), 129.5 (t, J = 9.8 Hz), 128.9 (dd, J = 3.0 Hz, 12.2 Hz), 127.5 (d, J = 2.6 Hz), 124.3 (d, J = 3.6 Hz), 123.8 (d, J = 3.7 Hz), 123.7 (dd, J = 5.6 Hz, 10.3 Hz), 123.5 (dd, J = 1.2 Hz, 12.8 Hz), 120.6 (dd, J = 1.4 Hz, 3.9 Hz), 120.0 (dd, J = 6.0 Hz, 6.0 Hz), 115.9 (d, J = 21.9 Hz), 115.5 (d, J = 21.9 Hz), 64.4 (d, J = 5.3 Hz), 64.3 (d, J = 7.1 Hz), 15.9 (d, J = 7.7 Hz), 15.8 (d, J = 8.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): -115.4, -117.2. ^{31}P NMR (202 MHz, $CDCl_3$): 88.1, 87.9. ESI HRMS: calculated for $C_{13}H_{17}FO_2PS_2$ $[M+H]^+$ 307.0392. found 307.0392.



***S*-(3-chlorostyryl) *O,O*-diethyl phosphorodithioate (4j)**

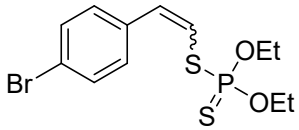
4j (Z/E = 74:26) was obtained in 86% yield (55.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.33 (s, 0.4H), 7.29 (t, J = 7.9 Hz,1H), 7.21-7.26 (m, 2H), 6.74-6.75 (m, 0.7H for E), 6.64 (d, J = 10.6 Hz, 1H for Z), 6.38 (dd, J_1 = 10.6 Hz, J_2 = 14.8 Hz, 1H for Z), 4.20-4.28 (m, 2.7H), 4.12-4.19 (m, 2.7H), 1.35-1.39 (m, 8.1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 137.6 (d, J = 1.4 Hz,), 137.3 (d, J = 1.3 Hz), 134.7, 134.5 (d, J = 11.9 Hz), 134.3, 129.9, 129.8 (d, J = 10.1 Hz), 129.6, 128.7 (d, J = 1.6 Hz), 128.2, 127.8, 126.9 (d, J = 1.5 Hz), 126.2, 124.5, 120.0 (d, J = 3.9 Hz), 117.9 (d, J = 5.7 Hz), 64.5 (d, J = 5.5 Hz), 64.4 (d, J = 5.6 Hz), 15.8 (d, J = 8.4 Hz), 15.8 (d, J = 8.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.2, 88.1. ESI HRMS: calculated for $C_{13}H_{17}ClO_2PS_2$ $[M+H]^+$

323.0096. found 323.0093.



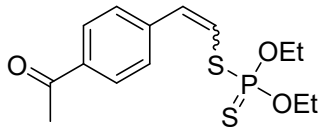
_S_-(4-chlorostyryl) _O,O_-diethyl phosphorodithioate (4k)

4k (Z/E = 80:20) was obtained in 62% yield (40.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 8.5 Hz, 2H), 7.26-7.27 (m, 1H), 7.23-7.25 (m, 1H), 7.21-7.22 (m, 1H), 6.70 (dd, J_1 = 2.2 Hz, J_2 = 15.6 Hz, 0.25H for E), 6.64 (d, J = 8.7 Hz, 0.25H for E), 6.60 (d, J = 9.9 Hz, 1H for Z), 6.38 (dd, J_1 = 10.5 Hz, J_2 = 14.6 Hz, 1H for Z), 4.11-4.20 (m, 2.5H),4.08-4.11 (m, 2.5H), 1.23-1.32 (m, 7.5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 135.0 (d, J = 11.8 Hz), 134.3 (d, J = 1.4 Hz), 134.1, 134.1 (d, J = 1.3 Hz), 133.5, 130.12 (d, J = 9.8 Hz), 130.1 (d, J = 1.6 Hz), 128.9, 128.6, 127.5, 118.9 (d, J = 4.0 Hz), 117.9 (d, J = 5.8 Hz), 64.4 (d, J = 5.6 Hz), 64.4 (d, J = 5.7 Hz), 15.9 (d, J = 9.7 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.5, 88.1. ESI HRMS: calculated for $C_{13}H_{17}ClO_2PS_2$ $[M+H]^+$ 323.0096. found 323.0099.



_S_-(4-bromostyryl) _O,O_-diethyl phosphorodithioate (4l)

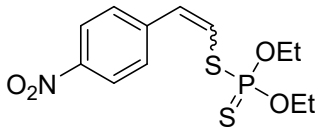
4l (Z/E = 80:20) was obtained in 86% yield (63.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 8.45 Hz, 2H for Z), 7.45 (d, J = 8.45 Hz, 0.5H for E), 7.35 (d, J = 8.4 Hz, 2H for Z), 7.22 (d, J = 8.4 Hz, 0.5H for E), 6.68-6.76 (m, 0.5H for E), 6.67 (d, J = 10.5 Hz, 1H for Z), 6.49 (dd, J_1 = 10.5 Hz, J_2 = 14.6 Hz, 1H for Z), 4.21-4.26 (m, 2.5H), 4.12-4.18 (m, 2.5H), 1.39-1.40 (m, 7.5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 135.0 (d, J = 12.0 Hz,), 134.7 (d, J = 1.4 Hz), 134.5 (d, J = 1.3 Hz), 131.9, 131.5, 130.4 (d, J = 1.6 Hz,), 130.1 (d, J = 10.0 Hz), 127.8, 122.2, 121.7, 119.1 (d, J = 3.9 Hz), 118.1 (d, J = 5.7 Hz), 64.4 (d, J = 5.4 Hz), 64.3 (d, J = 5.6 Hz), 15.8 (d, J = 8.4 Hz), 15.7 (d, J = 8.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$):88.4, 88.1. ESI HRMS: calculated for $C_{13}H_{17}BrO_2PS_2$ $[M+H]^+$ 366.9591. found 366.9592.



_S_-(4-acetylstyryl) _O,O_-diethyl phosphorodithioate (4m)

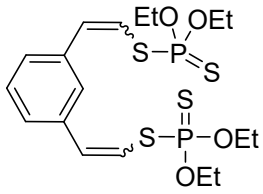
4m (Z/E = 70:30) was obtained in 50% yield (51.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.2 Hz, 2H for Z), 7.92 (d, J = 8.2 Hz, 0.9H for E), 7.57 (d, J = 8.2 Hz, 2H for Z), 7.43 (d, J = 8.2 Hz, 0.9H for Z),

6.90 (dd, J_1 = 9.6 Hz, J_2 = 15.1 Hz, 0.45H for E), 6.82 (d, J = 15.8 Hz, 0.45H for E), 6.85 (d, J = 10.7 Hz, 1H for Z), 6.60 (dd, J_1 = 10.7 Hz, J_2 = 15.1 Hz, 1H for Z), 4.21-4.30 (m, 2.9H), 4.13-4.19 (m, 2.5H), 2.60 (s, 3H for Z), 2.59 (s, 1.4H for E), 1.35-1.40 (m, 8.7H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 197.4, 197.3, 140.2 (d, J = 1.3 Hz, overlapped), 136.4, 135.9, 134.1 (d, J = 12.2 Hz), 129.9 (d, J = 9.9 Hz),128.9 (d, J = 1.6 Hz), 128.8, 128.4, 126.3, 121.4 (d, J = 3.7 Hz), 121.0 (d, J = 5.1 Hz), 64.4 (d, J = 5.5 Hz), 64.5 (d, J = 5.5 Hz), 26.6, 26.6, 15.9 (d, J = 8.5 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.1, 88.0. ESI HRMS: calculated for $C_{14}H_{20}O_3PS_2$ $[M+H]^+$ 331.0591. found 331.0591.



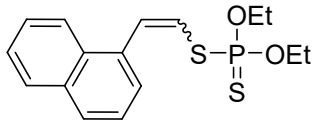
***O,O*-diethyl *S*-(4-nitrostyryl) phosphorodithioate (4n)**

4n (Z/E = 77:23) was obtained in 40% yield (27.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 8.21-8.23 (m, 2H for Z), 8.18-8.20 (m, 0.6H for E), 7.63 (d, J = 8.7 Hz, 2H for E), 7.49 (d, J = 8.7 Hz, 0.6H for Z), 7.02 (dd, J_1 = 10.8 Hz, J_2 = 15.7 Hz, 0.3H for E), 6.85 (dd, J_1 = 2.2 Hz, J_2 = 15.9 Hz, 0.3H for E), 6.70-6.78 (m, 2H for Z), 4.23-4.29 (m, 2.6H), 4.14-4.22 (m, 2.6H), 1.36-1.39 (m, 7.8H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 147.1, 146.6, 142.0 (d, J = 1 Hz, overlapped), 132.1 (d, J = 12.5 Hz,), 129.4 (d, J = 1.6 Hz), 128.4 (d, J = 10.1 Hz), 126.7, 124.2, 124.1 (d, J = 4.6 Hz), 123.9 (d, J = 3.5 Hz), 123.7, 64.7 (d, J = 5.8 Hz), 64.6 (d, J = 5.8 Hz), 15.9 (d, J = 8.0 Hz), 15.8 (d, J = 8.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 87.8, 87.5. ESI HRMS: calculated for $C_{12}H_{16}NNaO_4PS_2$ $[M+Na]^+$ 356.0156. found 356.0163.



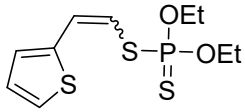
***S,S'*-(1,3-phenylenebis(ethene-2,1-diyl)) *O,O,O',O'*-tetraethyl bis(phosphorodithioate) (4o)**

4o (Z/E = 77:23) was obtained in 48% yield (48.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 0.6H for E), 7.26-7.24 (m, 4H for Z), 6.83 (dd, J_1 = 2.5 Hz, J_2 = 15.6 Hz, 0.3H for E), 6.71-6.76 (m, 2.3H), 6.45 (dd, J_1 = 10.5 Hz, J_2 = 14.3 Hz, 2H for Z), 4.22-4.27 (m, 4.6H), 4.13-4.18 (m, 4.6H), 1.35-1.40 (m, 13.8H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 136.0 (d, J = 3.2 Hz,), 135.8 (d, J = 1.2 Hz), 130.9 (d, J = 9.9 Hz), 130.7 (d, J = 9.9 Hz), 129.0, 128.8, 128.5, 128.3 (d, J = 1.2 Hz), 126.8, 125.6, 118.8 (d, J = 4.0 Hz), 117.9 (d, J = 5.5 Hz), 64.4 (d, J = 5.3 Hz), 64.3 (d, J = 5.8 Hz), 15.9 (d, J = 10.4 Hz), 15.8 (d, J = 8.4 Hz), ^{31}P NMR (202 MHz, $CDCl_3$): 88.5, 88.4. ESI HRMS: calculated for $C_{18}H_{29}O_4P_2S_4$ $[M+H]^+$ 499.0424. found 499.0428.



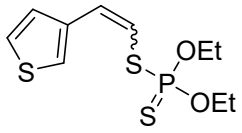
***O,O*-diethyl *S*-(2-(naphthalen-1-yl)vinyl) phosphorodithioate (4p)**

4p (Z/E = 87:13) was obtained in 78% yield (53.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.0 (d, J = 8.3 Hz, 0.15H for E), 7.91-7.94 (m, 1H for Z), 7.84-7.86 (m,1H for Z), 7.80 (d, J = 8.2 Hz, 1H for Z), 7.56-7.61 (m, 0.15H for E), 7.43-7.56 (m, 4.8H), 7.33 (d, J = 10.1 Hz, 1H for Z), 6.75 (dd, J_1 = 8.9 Hz, J_2 = 15.3 Hz, 0.15H for E), 6.70 (dd, J_1 = 10.1 Hz, J_2 = 12.9 Hz, 1H for Z), 4.24-4.30 (m, 0.6H for E), 4.16-4.21 (m, 2H for Z), 4.06-4.12 (m, 2H for Z), 1.37-1.39 (m, 0.9H for E), 1,32 (t, J = 7.1 Hz, 6H for Z). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 134.4 (d, J = 11.7 Hz,), 133.6, 133.5, 132.5, 131.2, 130.2 (d, J = 10.4 Hz), 128.8, 128.7, 128.6, 128.5, 126.6 (d, J = 1.3 Hz), 126.4, 126.2,126.0, 125.9, 125.1, 124.2, 124.1, 123.5, 121.2 (d, J = 3.6 Hz), 118.9 (d, J = 5.9 Hz), 64.3 (d, J = 8.0 Hz), 64.2 (d, J = 5.4 Hz), 15.9 (d, J = 8.3 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 89.1, 88.5. ESI HRMS: calculated for $C_{16}H_{21}O_2PS_2$ $[M+H]^+$ 339.0642. found 339.0636.



***O,O*-diethyl *S*-(2-(thiophen-2-yl)vinyl) phosphorodithioate (4q)**

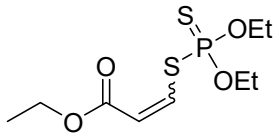
4q (Z/E = 69:31) was obtained in 73% yield (43.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 5 Hz, 1H for Z), 7.21 (d, J = 4.8 Hz, 0.45H for E), 7.17 (d, J = 3.5 Hz, 1H for Z), 7.02-7.04 (m, 1H for Z), 6.92-6.98 (m, 2.35H), 6.49 (dd, J_1 = 8.5 Hz, J_2 = 15.2 Hz, 0.45H for E), 6.26 (dd, J_1 = 10.2 Hz, J_2 = 15.2 Hz, 1H for Z), 4.22-4.34 (m, 2.9H), 4.11-4.21 (m, 2.9H), 1.34-1.40 (m, 8.7H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.4, 139.1 (d, J = 1.3 Hz), 130.5 (d, J = 12.0 Hz), 129.4 (d, J = 1.4 Hz,), 127.5, 127.1 (d, J = 1.5 Hz,), 126.8, 126.6 (d, J = 1.6 Hz,), 125.6 (d, J = 11.0 Hz), 125.5, 115.2 (d, J = 6.3 Hz), 114.8 (d, J = 4.8 Hz,), 64.4 (d, J = 5.3 Hz), 64.3 (d, J =5.5 Hz,), 15.8 (d, J = 8.4 Hz), 15.9 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.1, 87.6. ESI HRMS: calculated for $C_{10}H_{16}O_2PS_3$ $[M+H]^+$ 295.0050. found 295.0044.



***O,O*-diethyl *S*-(2-(thiophen-3-yl)vinyl) phosphorodithioate (4r)**

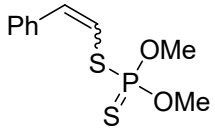
4r (Z/E = 87:13) was obtained in 92% yield (54.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.50 (m, 1H for Z), 7.33 (d, J = 6.8 Hz, 1H for Z), 7.29-7.31 (m, 1H for Z), 7.28-7.29 (m, 0.15H for E), 7.19-7.20 (m, 0.3H

for E), 6.70 (dd, J_1 = 3.1 Hz, J_2 = 15.4 Hz, 0.15H for E), 6.73 (d, J = 10.3 Hz, 1H for Z), 6.53 (dd, J_1 = 8.5 Hz, J_2 = 15.4 Hz, 0.15H for E), 6.30 (dd, J_1 = 10.3 Hz, J_2 = 13.5 Hz, 1H for Z), 4.21-4.28 (m, 2.3H), 4.12-4.19 (m, 2.5H), 1.34-1.39 (m, 6.9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.3 (d, J = 1.8 Hz), 137.0 (d, J = 1.6 Hz,), 131.5 (d, J = 11.9 Hz), 128.3 (d, J = 1.3 Hz), 126.5, 125.9 (d, J = 10.4 Hz), 125.4, 125.2 (d, J = 2.2 Hz), 124.7, 123.3 (d, J = 1.8 Hz), 116.3 (d, J = 4.5 Hz), 116.0 (d, J =6.4 Hz), 64.3 (d, J = 5.5 Hz), 64.3 (d, J = 5.5 Hz,), 15.9 (d, J = 8.5 Hz), 15.8 (d, J = 8.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 88.7, 87.9. ESI HRMS: calculated for $C_{10}H_{16}O_2PS_3$ $[M+H]^+$ 295.0050. found 295.0052.



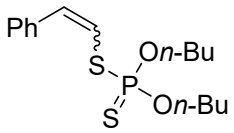
ethyl 3-((diethoxyphosphorothioyl)thio)acrylate (4s)

4s (Z/E = 89:11) was obtained in 98% yield (54.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (t, J = 14.6 Hz, 0.12H for E), 7.35 (dd, J_1 = 10.1 Hz, J_2 = 19.5 Hz, 1H for E), 6.12 (dd, J_1 = 1.2 Hz, J_2 = 15.5 Hz, 0.15H for E), 6.10 (d, J = 10.1 Hz, 1H for Z), 4.16-4.25 (m, 4.48H), 4.12-4.16 (m, 2.24H), 1.36 (t, J = 7.1 Hz, 6.72H), 1.30 (t, J = 7.1 Hz, 3.36H), . $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7, 164.3, 140.4 (d, J = 1.5 Hz), 139.3 (d, J = 3.8 Hz), 122.0 (d, J = 11.6 Hz), 117.9 (d, J = 8.5 Hz), 64.7 (d, J = 5.5 Hz), 64.5 (d, J = 5.5 Hz), 60.7, 60.6, 15.9 (d, J = 8.2 Hz), 15.7 (d, J = 8.3 Hz), 14.2, 14.2. ^{31}P NMR (202 MHz, $CDCl_3$): 91.4. ^{31}P NMR (202 MHz, $CDCl_3$): 91.4. ESI HRMS: calculated for $C_9H_{17}NaO_4PS_2$ $[M+Na]^+$ 307.0204. found 307.0206.



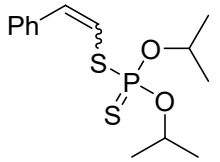
***O,O*-dimethyl *S*-styryl phosphorodithioate (4t)**

4t (Z/E = 74:26) was obtained in 58% yield (30.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J = 7.8 Hz, 2H), 7.25-7.38 (m, 4.8H), 6.84 (dd, J_1 = 2.9 Hz, J_2 = 15.5 Hz, 0.35H for E), 6.75 (d, J = 10.5 Hz, 1H for Z), 6.65 (dd, J_1 = 8.6 Hz, J_2 = 15.5 Hz, 0.35H for E), 6.36 (dd, J_1 = 10.5 Hz, J_2 = 14.3 Hz, 1H for Z), 3.85 (s, 1 H for E), 3.82 (s, 1H for E), 3.81 (s, 3H for E), 3.78 (s, 3H for E). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 137.2 (d, J = 11.7 Hz), 135.7, 135.5 (d, J = 1 Hz), 132.0 (d, J = 9.8 Hz), 128.9 (d, J = 1.6 Hz), 128.7, 128.5, 128.4, 128.0, 126.4, 117.3 (d, J = 4.2 Hz), 116.1 (d, J = 6.2 Hz), 54.2 (d, J = 4.9 Hz), 54.2 (d, J = 5.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 93.6. ESI HRMS: calculated for $C_{10}H_{14}O_2PS_2$ $[M+H]^+$ 261.0173. found 261.0175. ESI HRMS: calculated for $C_{10}H_{14}O_2PS_2$ $[M+H]^+$ 261.0173. found 261.0175.



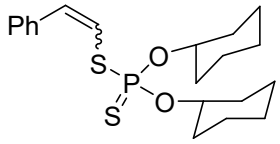
***O,O*-dibutyl *S*-styryl phosphorodithioate (4u)**

4u (Z/E = 87:13) was obtained in 52% yield (36.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 7.8 Hz, 2H), 7.31-7.37 (m, 2.75H), 7.28 (d, J = 7.2 Hz, 1H), 6.82 (dd, J_1 = 2.7 Hz, J_2 = 15.5 Hz, 0.15H for E), 6.73 (d, J = 10.5 Hz, 1H for Z), 6.69 (dd, J_1 = 8.8 Hz, J_2 = 15.5 Hz, 0.15H for E), 6.41 (dd, J_1 = 10.5 Hz, J_2 = 14.4 Hz, 1H for Z), 4.13-4.19 (m, 2.3H), 4.08-4.09 (m, 2.3H), 1.65-1.69 (m, 6H), 1.37-1.42 (m, 6H), 0.91 (t, J = 7.35 Hz, 6.9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.6 (d, J = 11.7 Hz), 135.9, 135.6 (d, J = 1.2 Hz), 131.5 (d, J = 9.8 Hz), 128.9 (d, J = 1.5 Hz), 128.7, 128.4, 127.8, 126.3, 117.9 (d, J = 4.1 Hz), 116.8 (d, J = 5.9 Hz), 68.0 (d, J = 5.9 Hz), 67.9 (d, J = 7.5 Hz), 32.0 (d, J = 7.2 Hz), 31.9 (d, J = 8.2 Hz), 18.8, 18.8, 13.6, 13.5. ^{31}P NMR (202 MHz, $CDCl_3$): 88.9, 88.8. ESI HRMS: calculated for $C_{16}H_{26}O_2PS_2$ $[M+H]^+$ 345.1112. found 345.1114.



***O,O*-diisopropyl *S*-styryl phosphorodithioate (4v)**

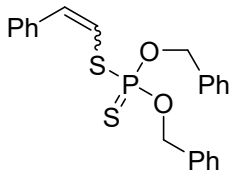
4v (Z/E = 87:13) was obtained in 68% yield (43.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 7.8 Hz, 2H for Z), 7.35 (t, J = 7.6 Hz, 2H for Z), 7.32 (d, J = 7.9 Hz, 0.35H for E), 7.27 (d, J = 7.3 Hz, 1H for Z), 7.25 (d, J = 3.5 Hz, 0.4H for E), 6.78-6.82 (m, 0.15H for E), 6.73-6.76 (m, 0.15H for E), 6.70 (d, J = 10.6 Hz, 1H for Z), 6.69 (dd, J_1 = 10.6 Hz, J_2 = 15 Hz, 1H for E), 4.79-4.93 (m, 2.3H), 1.36-1.39 (m, 7.8H), 1.33 (d, J = 6.2 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.0, 135.7 (d, J = 1.2 Hz), 130.7 (d, J = 9.8 Hz), 128.8 (d, J = 1.6 Hz), 128.7, 128.3, 128.2, 127.7, 126.3, 118.7 (d, J = 4.0 Hz), 117.7 (d, J = 6.3 Hz), 73.9 (d, J = 5.9 Hz), 73.8 (d, J = 6.1 Hz), 23.8 (d, J = 4.6 Hz), 23.7 (d, J = 4.6 Hz), 23.4 (d, J = 5.1 Hz), 23.3 (d, J = 5.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 85.3, 85.1. ESI HRMS: calculated for $C_{14}H_{21}NaO_2PS_2$ $[M+Na]^+$ 339.0618. found 339.0620.



***O,O*-dicyclohexyl *S*-styryl phosphorodithioate (4w)**

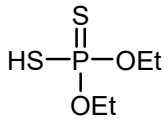
4w (Z/E = 80:20) was obtained in 63% yield (50.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 7.75 Hz, 2H), 7.31-7.37 (m,

3H), 7.24-7.27 (m, 1.25H), 6.75-6.86 (m, 0.5H for E), 6.71 (d, J = 10.6 Hz, 1H for Z), 6.48 (dd, J_1 = 8.9 Hz, J_2 = 14.9 Hz, 1H for Z), 4.55-4.62 (m, 2.5H), 1.90-1.98 (m, 5H), 1.69-1.74 (m, 5H), 1.48-1.62 (m, 10H), 1.12-1.38 (m, 10H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 136.1 (d, J = 1.3 Hz), 135.8 (d, J = 1.3 Hz), 135.7, 130.7 (d, J = 9.8 Hz), 128.8 (d, J = 1.6 Hz), 128.7, 128.3, 128.2, 127.7, 126.3, 118.8 (d, J = 4.0 Hz), 117.8 (d, J = 5.8 Hz), 78.6 (d, J = 6.5 Hz), 78.6 (d, J = 7.1 Hz), 33.4 (d, J = 4.1 Hz), 33.0 (d, J = 4.4 Hz), 25.1, 25.1, 23.6 (d, J = 3.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 85.1, 85.0. ESI HRMS: calculated for $C_{20}H_{29}NaO_2PS_2$ $[M+Na]^+$ 419.1244. found 419.1240.



***O,O*-dibenzyl *S*-styryl phosphorodithioate (4x)**

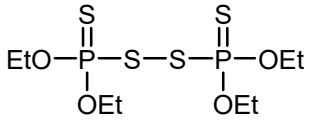
4x (Z/E = 83:17) was obtained in 75% yield (62.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=200/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.41-7.45 (m, 3H), 7.27-7.37 (m, 15H), 6.69-6.72 (m, 1.2H), 6.51-6.56 (m, 0.2H for E), 6.37 (dd, J_1 = 10.5 Hz, J_2 = 14.4 Hz, 1H for Z), 5.17 (t, J = 11.3 Hz, 2.4H), 5.07 (t, J = 9.9 Hz, 2.4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 135.5 (d, J = 1.5 Hz), 135.2 (d, J = 9.0 Hz), 133.0, 132.1 (d, J = 10.1 Hz), 130.1, 129.7, 129.0, 128.9 (d, J = 1.6 Hz), 128.6, 128.6, 128.5, 128.4, 128.4 (d, J = 1.8 Hz), 128.3, 128.2, 128.1, 127.9, 126.5 (d, J = 1.0 Hz), 117.3 (d, J = 4.2 Hz), 115.9 (d, J = 6.6 Hz), 69.6 (d, J = 5.2 Hz), 69.5 (d, J = 5.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): 90.1, 89.8. ESI HRMS: calculated for $C_{22}H_{21}NaO_2PS_2$ $[M+Na]^+$ 435.0618. found 435.0619.



***O,O*-diethyl S-hydrogen phosphorodithioate (5a)[1]**

5a Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 4.11-4.24 (m, 4H), 2.95 (s, 1H), 1.39 (t, J = 7.1 Hz, 3H).

[1] M. Stankiewicz, J. Nycz and J. Rachon, Reductive cleavage of the halogen-phosph orus and sulfur-phosphorus bonds with alkali metals. *Heteroat. Chem.,* 2002**, *13***, 330-339.



disulfide of O,O-diethyl phosphorodithioate (5a') [2]

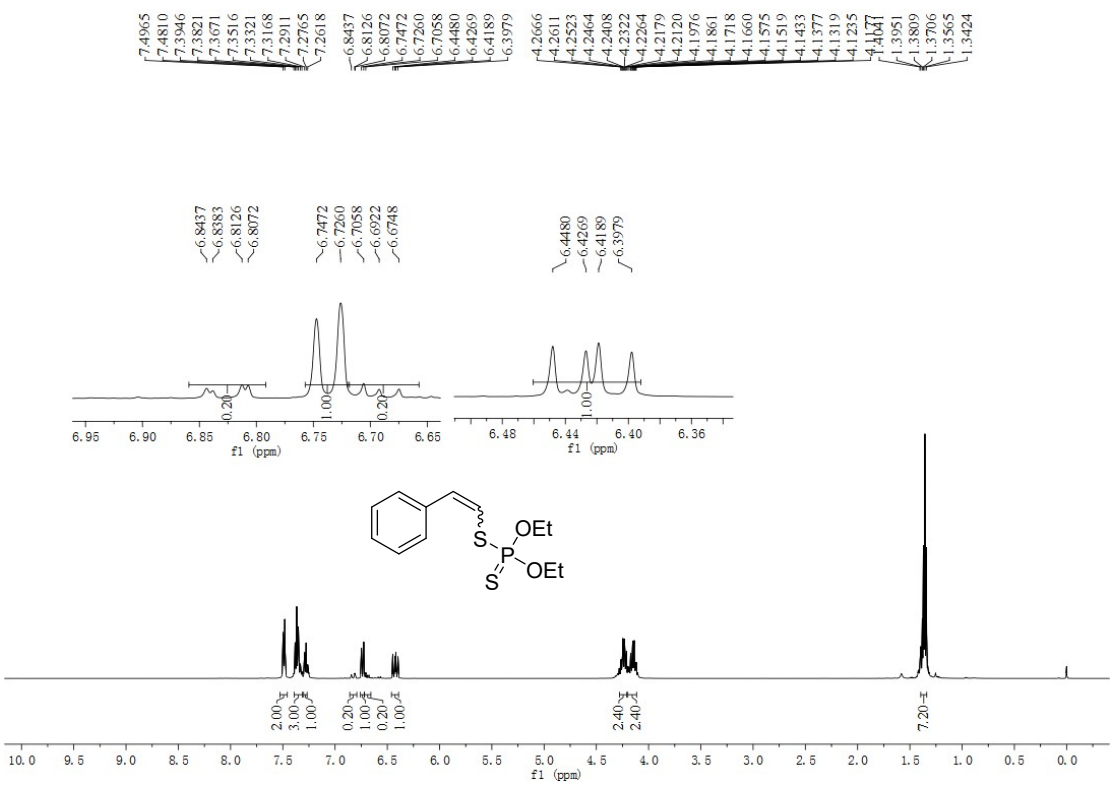
5a' was obtained in 58% yield (42.0 mg) according to the general procedure (eluent ratio for column chromatography: petroleum ether/EtOAc=100/1), Yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 4.28-4.35 (m, 4H), 4.16-4.26 (m, 4H), 1.38-1.42 (m, 12H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 64.8 (d, J = 5.4 Hz), 15.9 (d, J = 8.5 Hz), 15.8 (d, J = 8.4 Hz). ESI HRMS: calculated for $C_8H_{21}O_4P_2S_4$ $[M+H]^+$ 370.9798, found 370.9763.

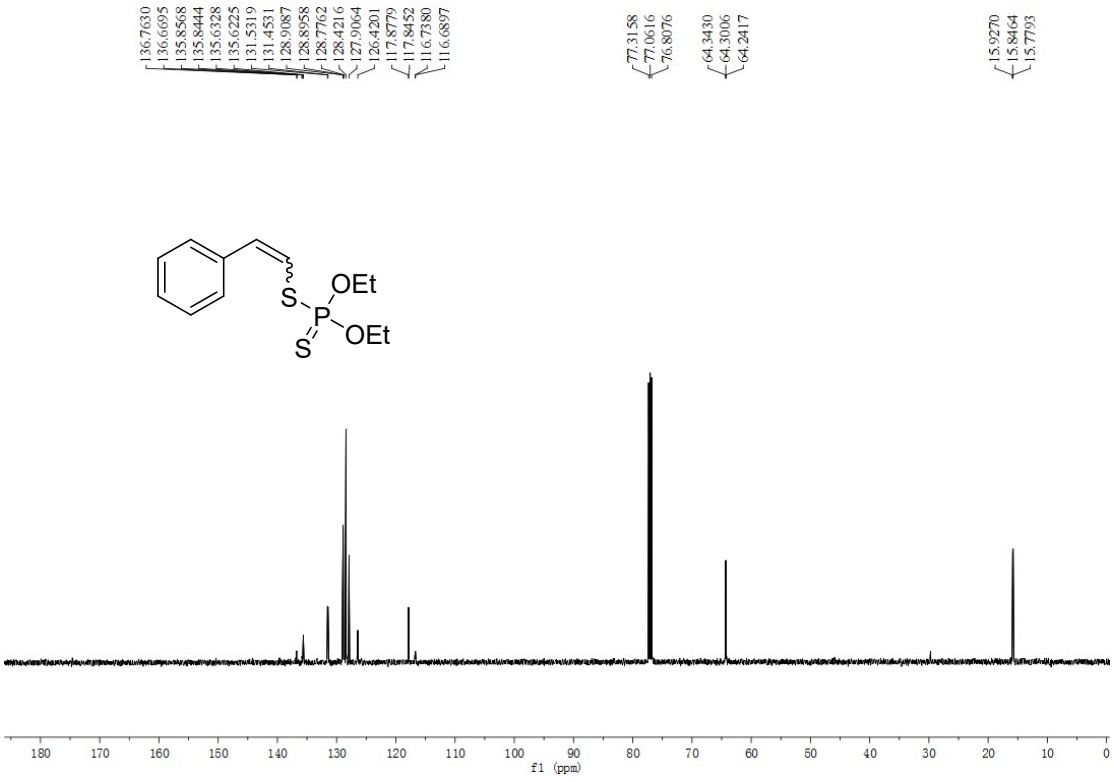
[2] M. B. Gazizov, R. A. Khairullin, N. G. Aksenov and O. G. Sinyashin, Reactions of O,O-dialkyldithiophosphoric acids with N-tert-butyl-2-bromo-2-methylpropanimine a nd its salts. *Tetrahedron Lett.,* 2015, ***56***, 4993-4996.

6.Copies of NMR spectra for products

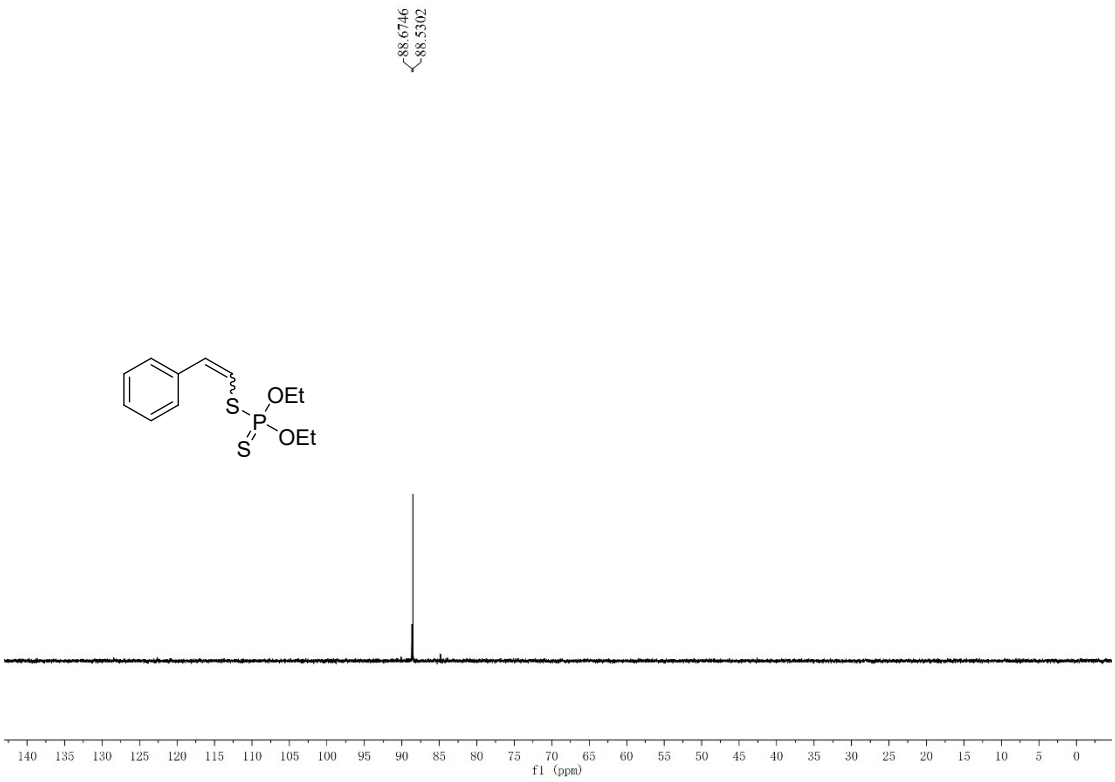
4a ^{1}H NMR (500 MHz, $CDCl_3$)



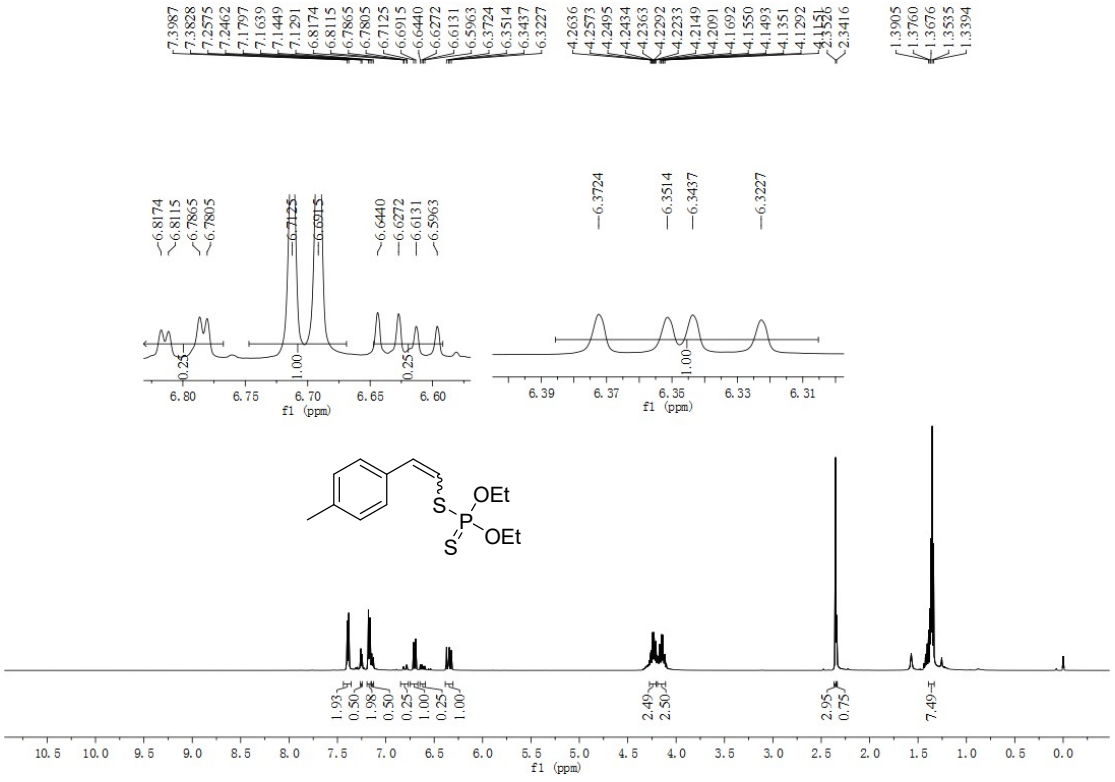
4a ^{13}C NMR (125MHz, $CDCl_3$)



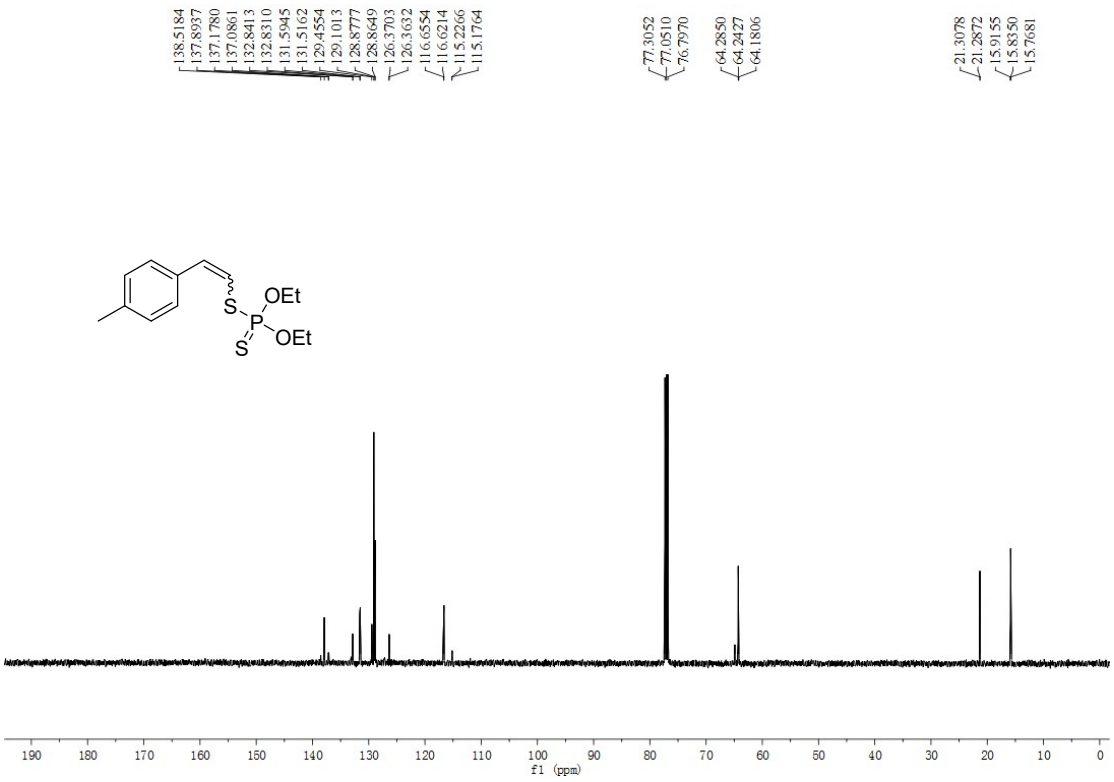
4a ^{31}P NMR (202 MHz, $CDCl_3$)



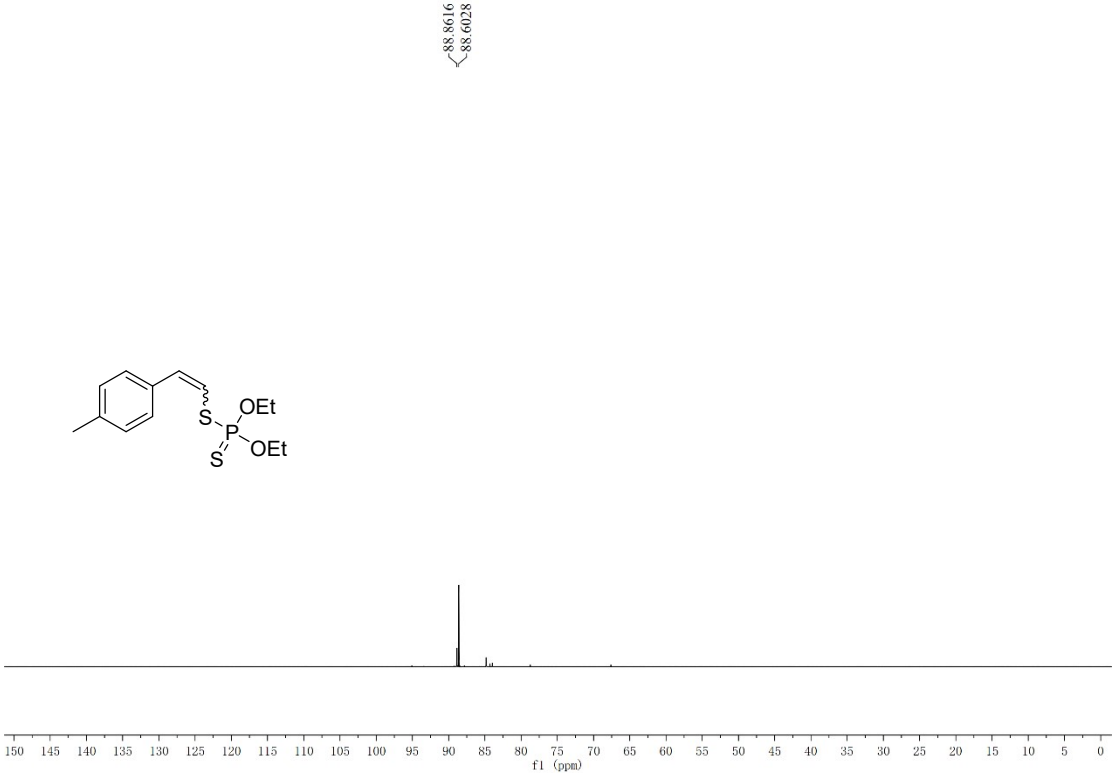
4b ^{1}H NMR (500 MHz, $CDCl_3$)



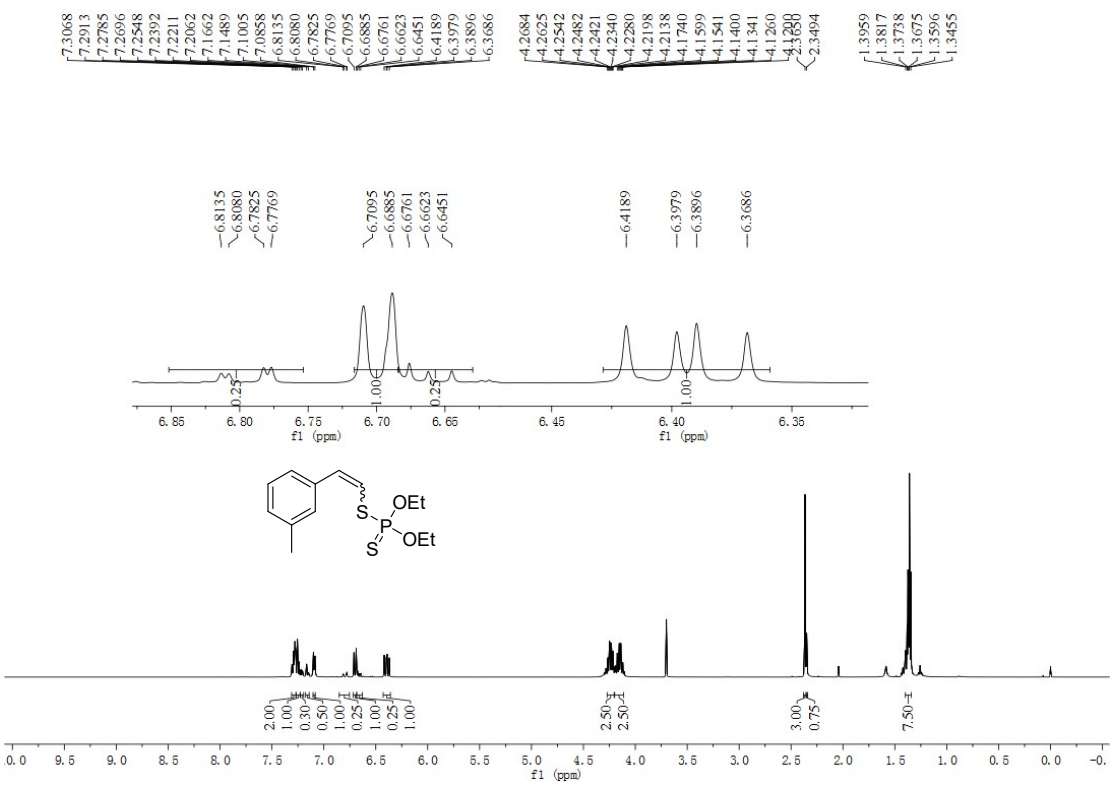
4b ^{13}C NMR (125MHz, $CDCl_3$)



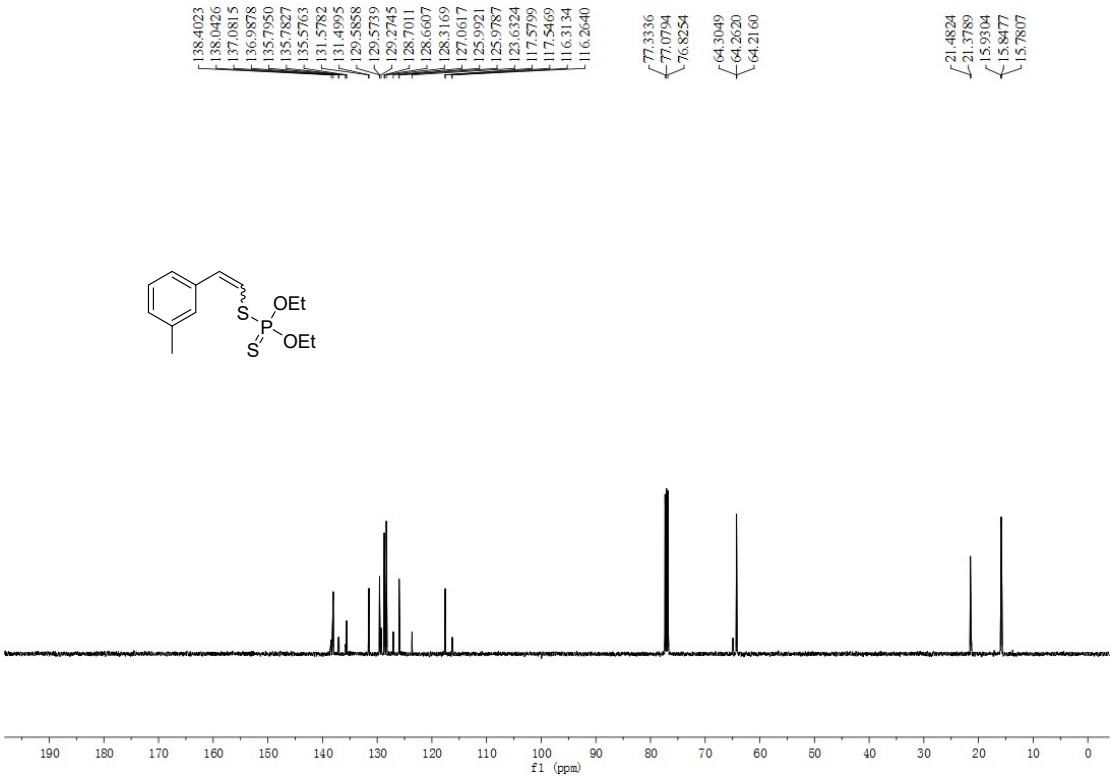
4b ^{31}P NMR (202 MHz, $CDCl_3$)



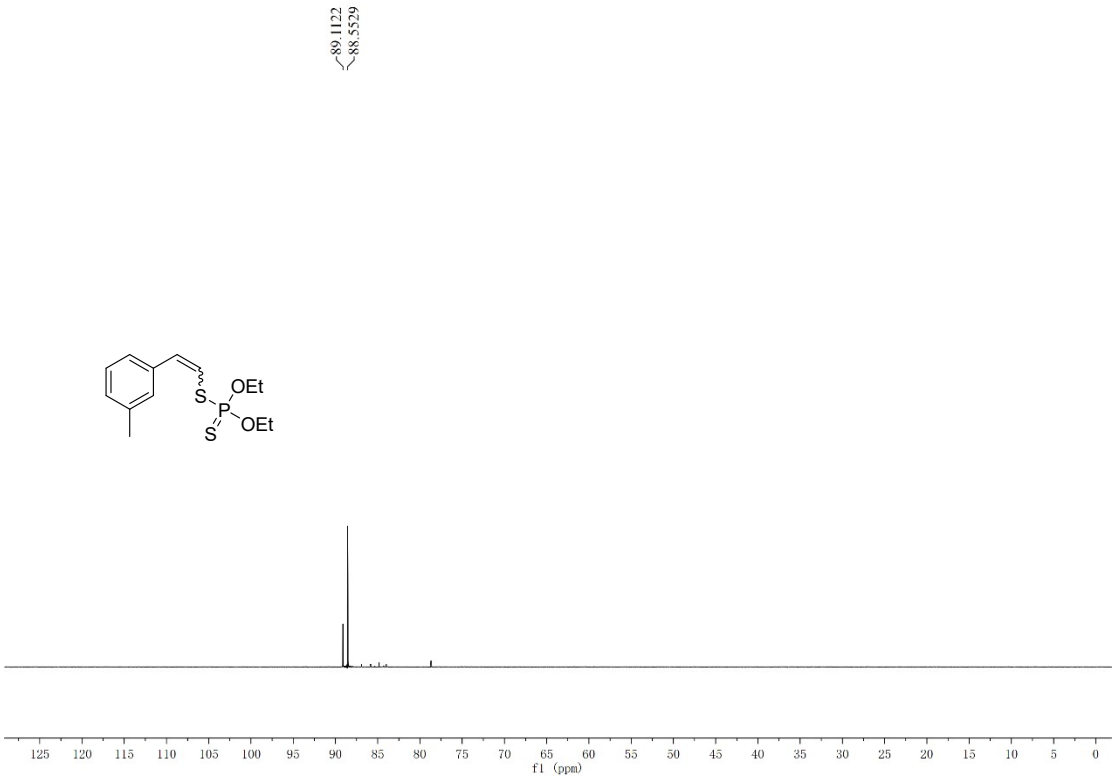
4c ^{1}H NMR (500 MHz, $CDCl_3$)



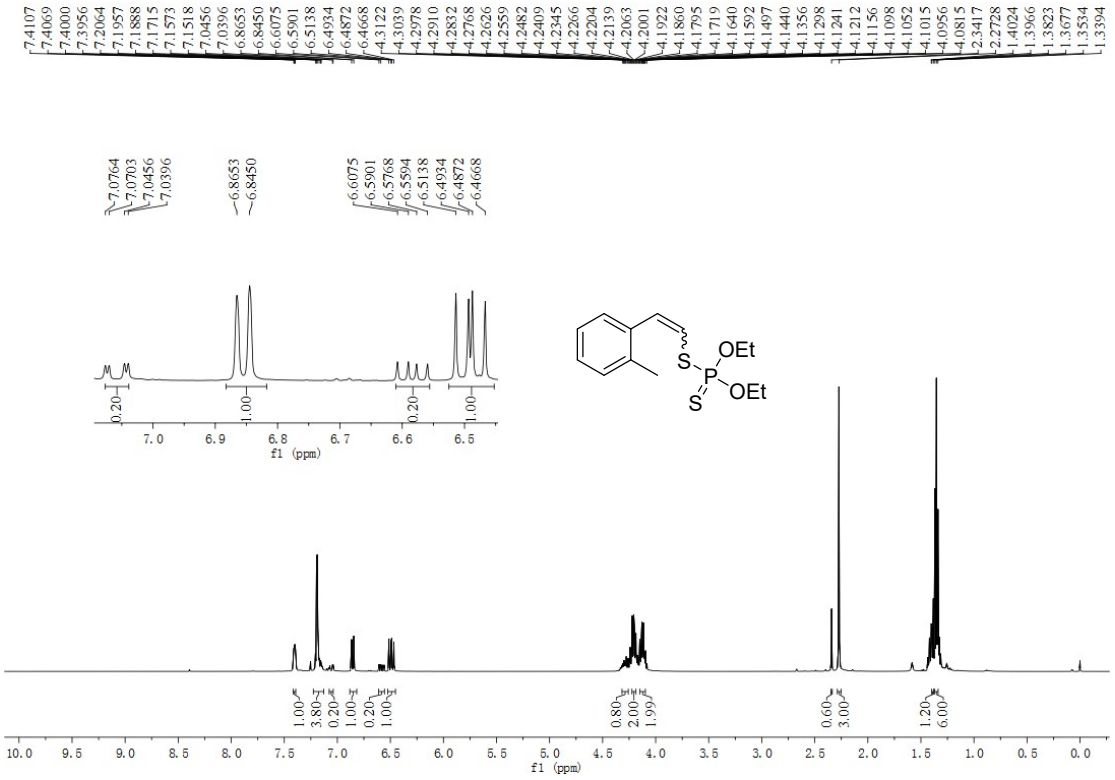
4c ^{13}C NMR (125MHz, $CDCl_3$)



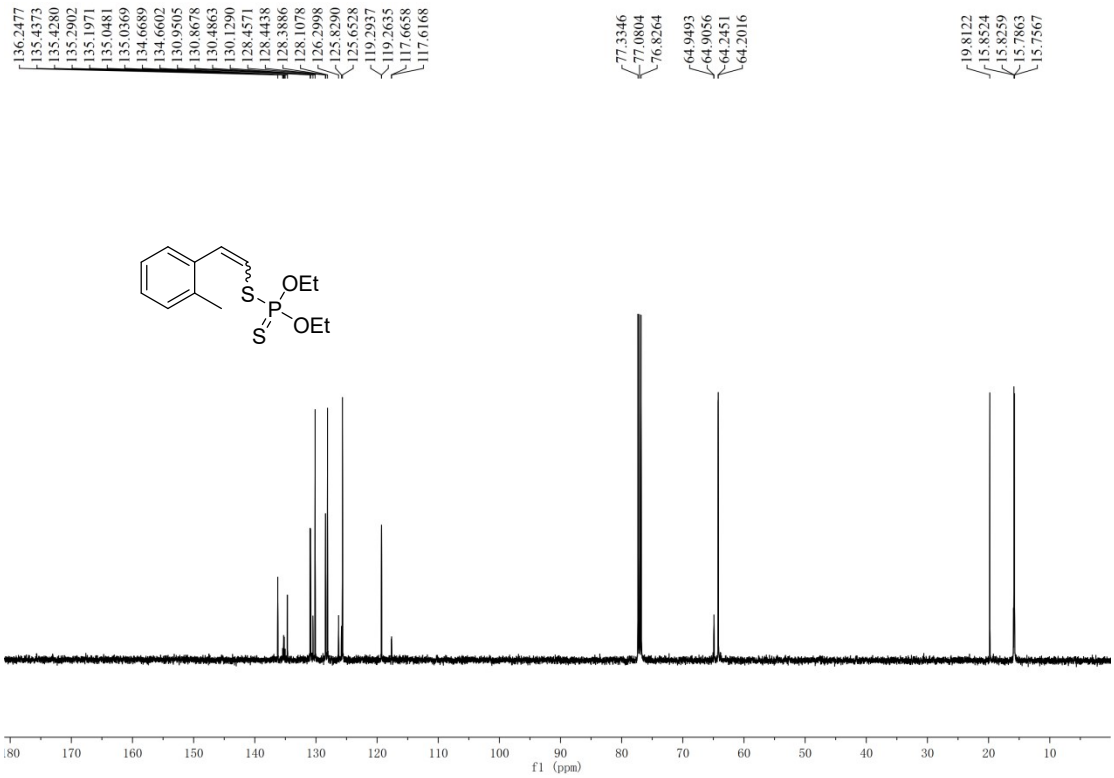
4c ^{31}P NMR (202 MHz, $CDCl_3$)



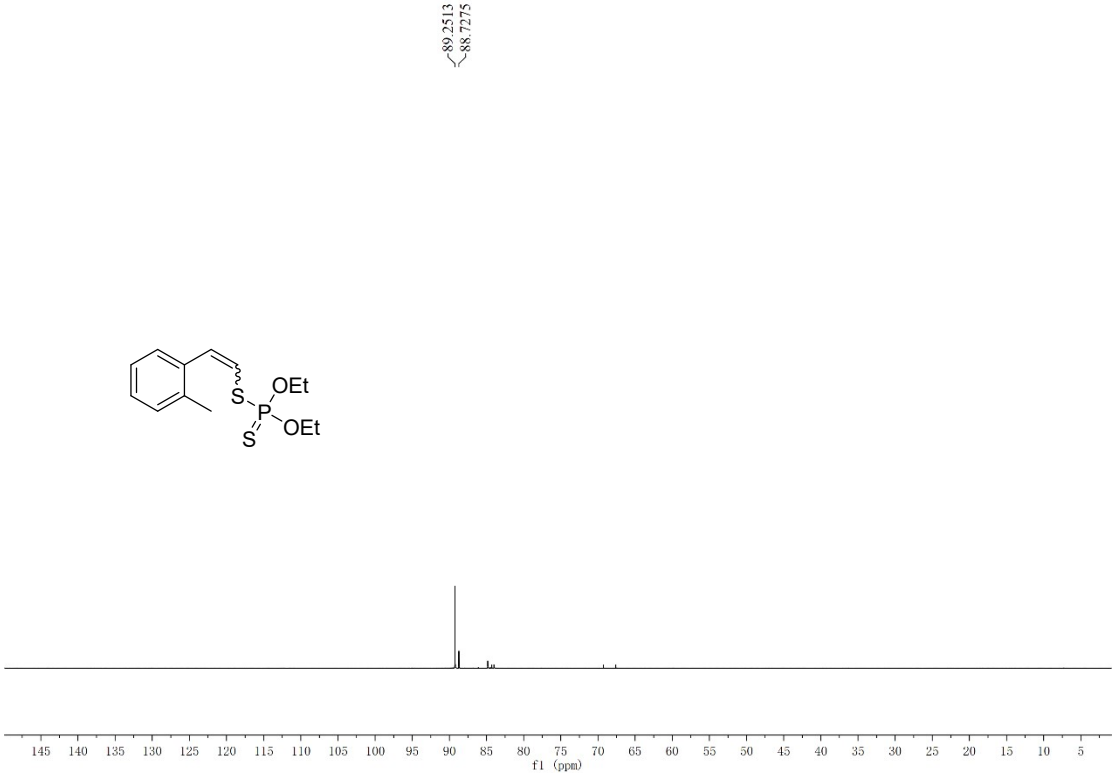
4d ^{1}H NMR (500 MHz, $CDCl_3$)



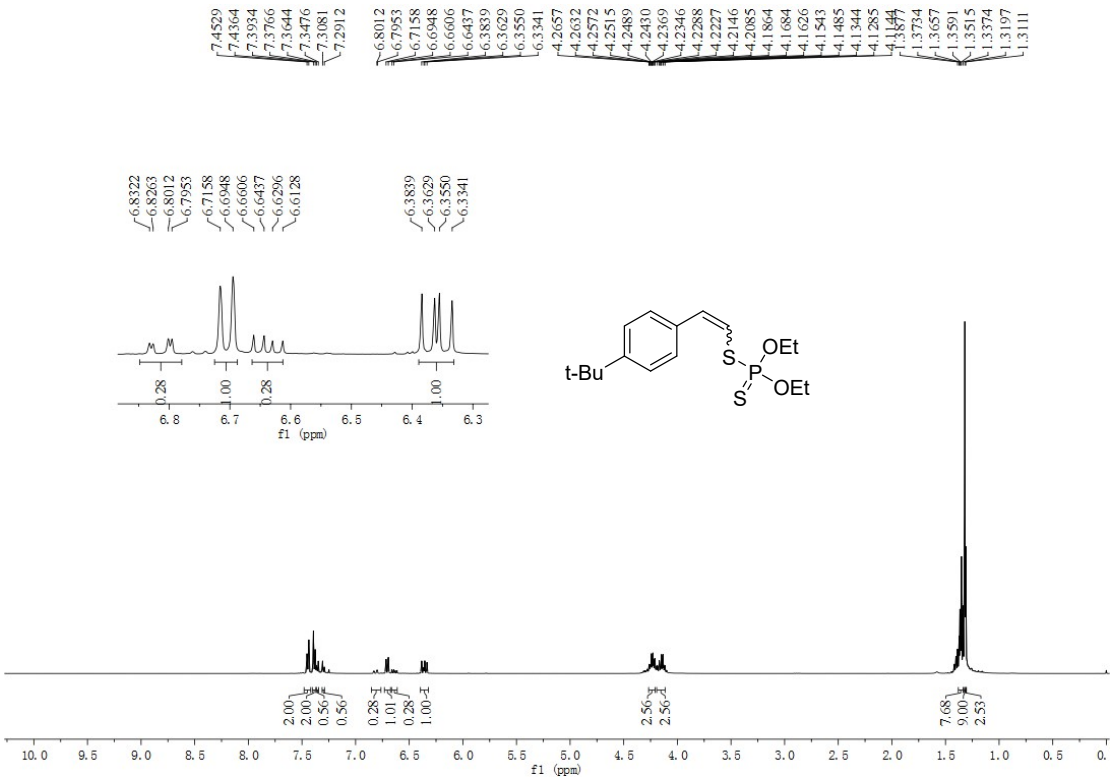
4d ^{13}C NMR (125MHz, $CDCl_3$)



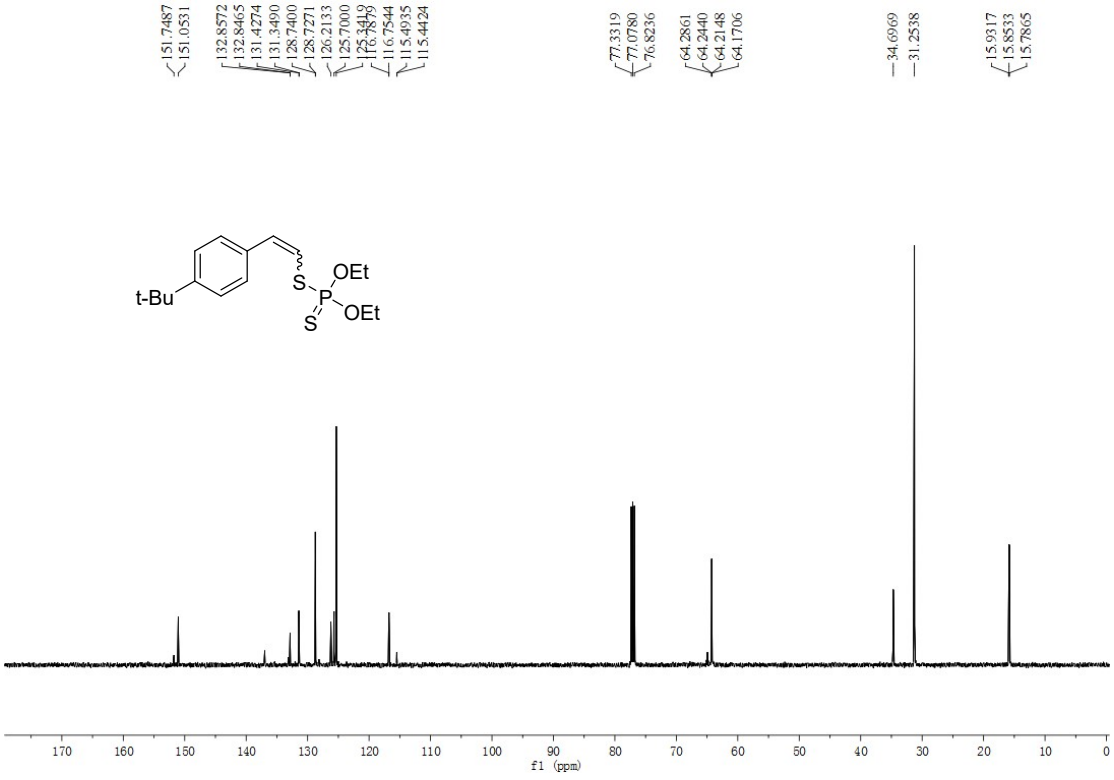
4d ^{31}P NMR (202 MHz, $CDCl_3$)



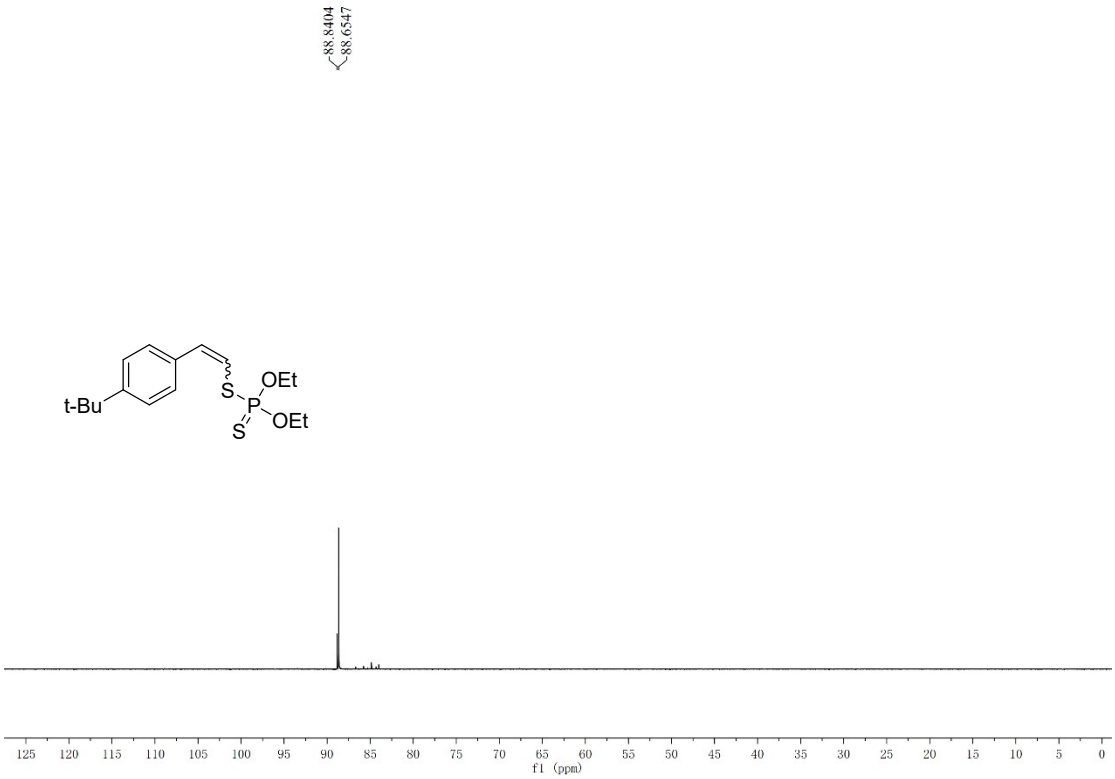
4e ^{1}H NMR (500 MHz, $CDCl_3$)



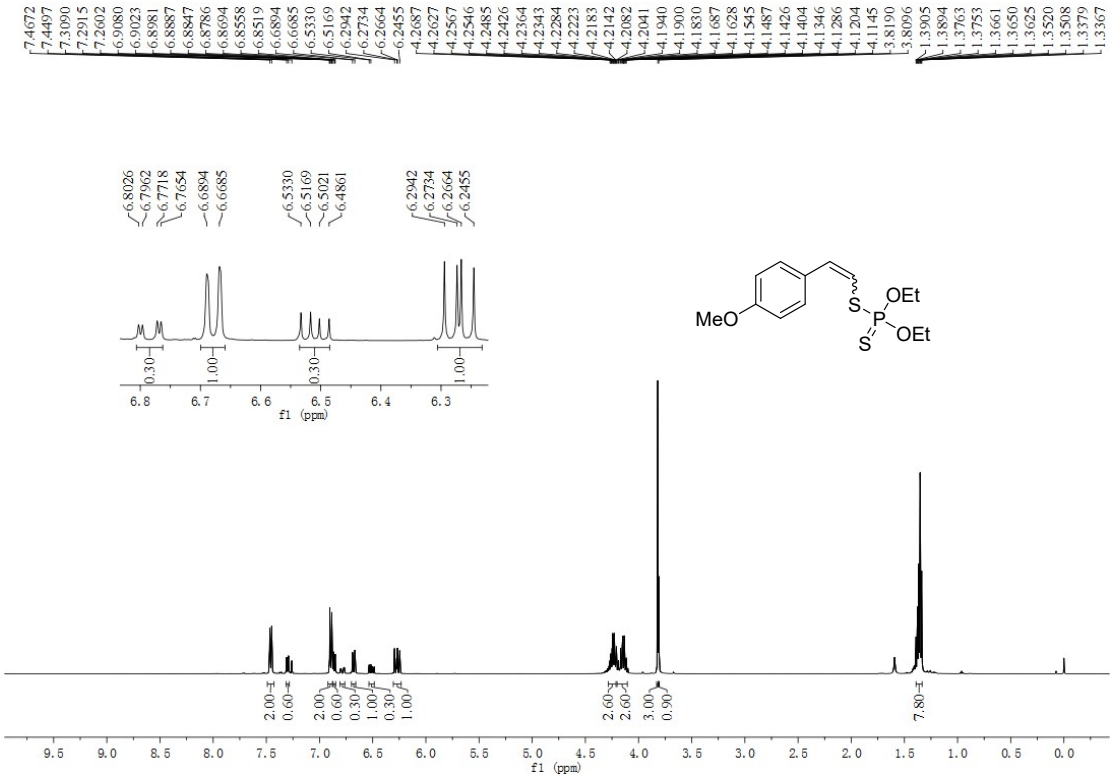
4e ^{13}C NMR (125MHz, $CDCl_3$)



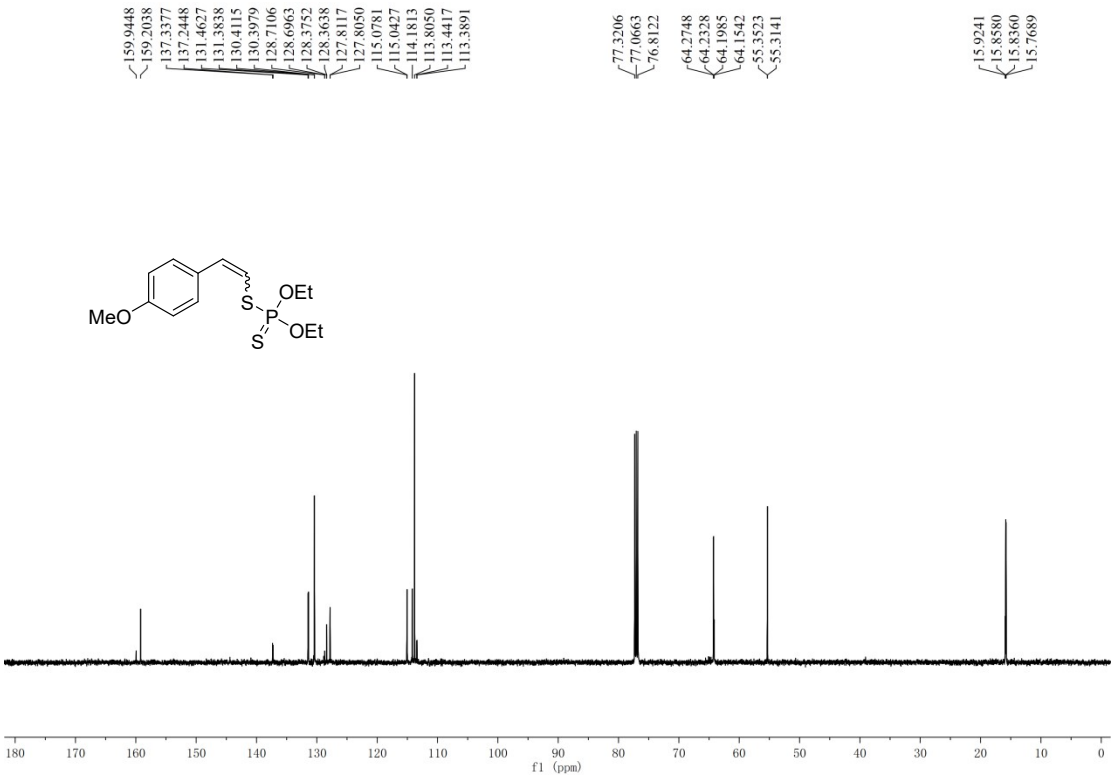
4e ^{31}P NMR (202 MHz, $CDCl_3$)



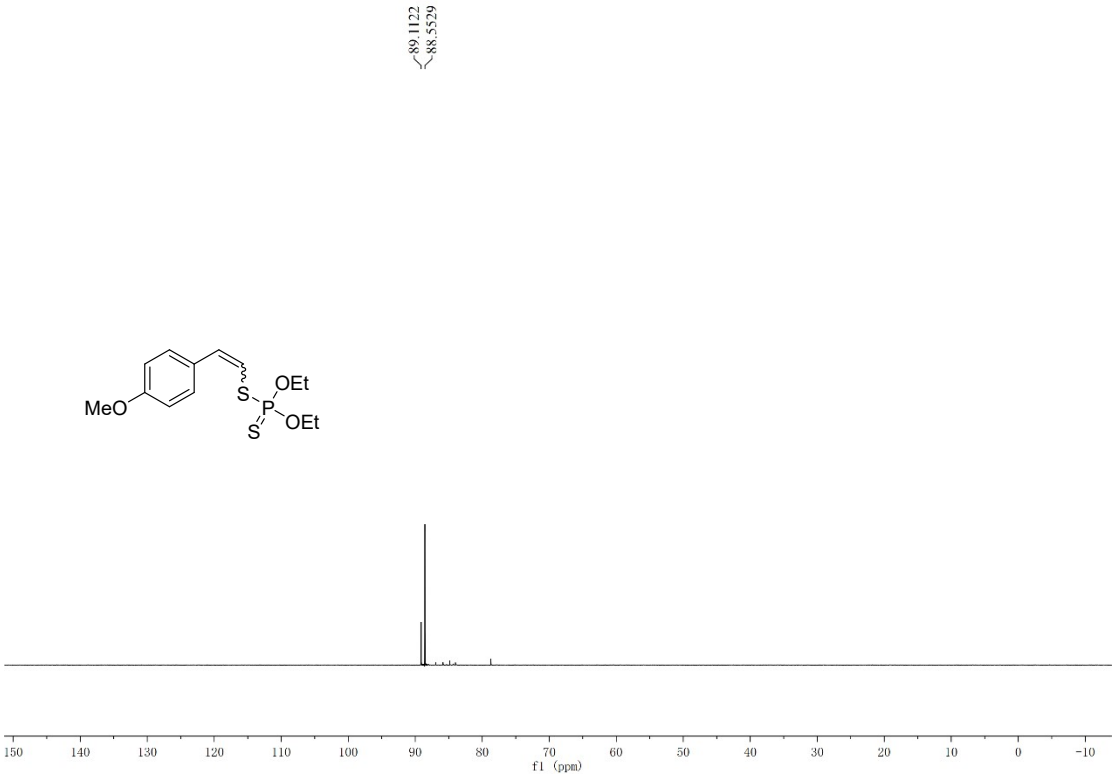
4f ^{1}H NMR (500 MHz, $CDCl_3$)



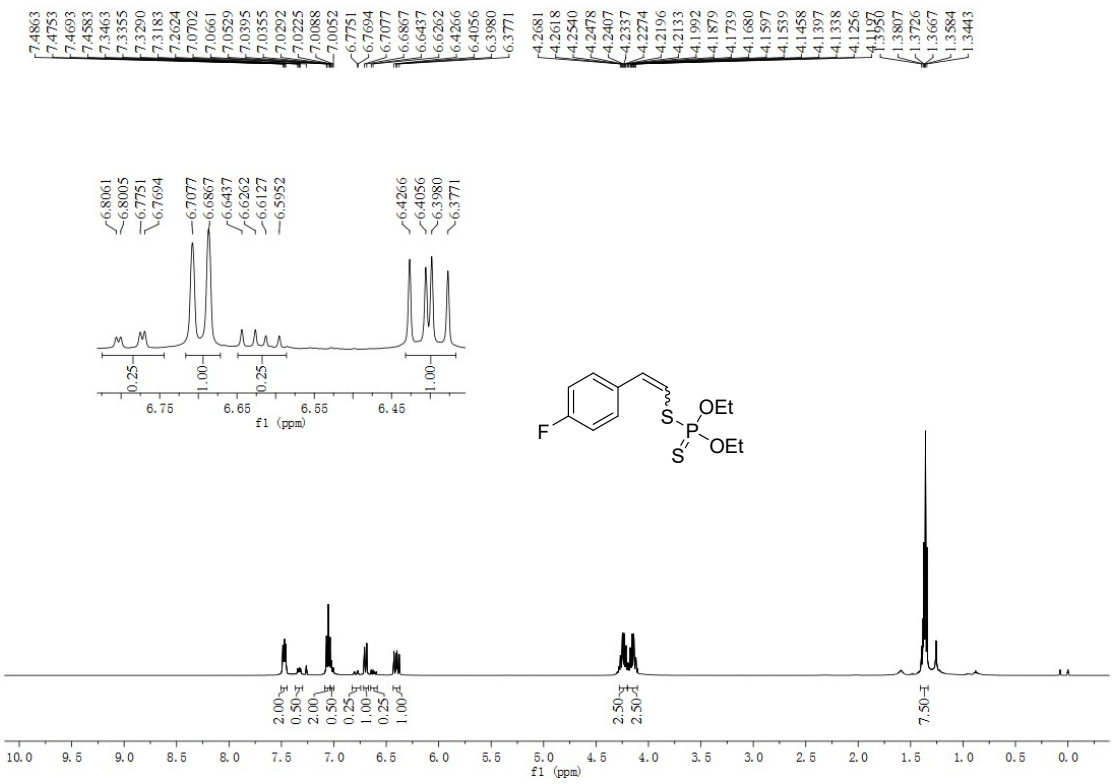
4f ^{13}C NMR (125MHz, $CDCl_3$)



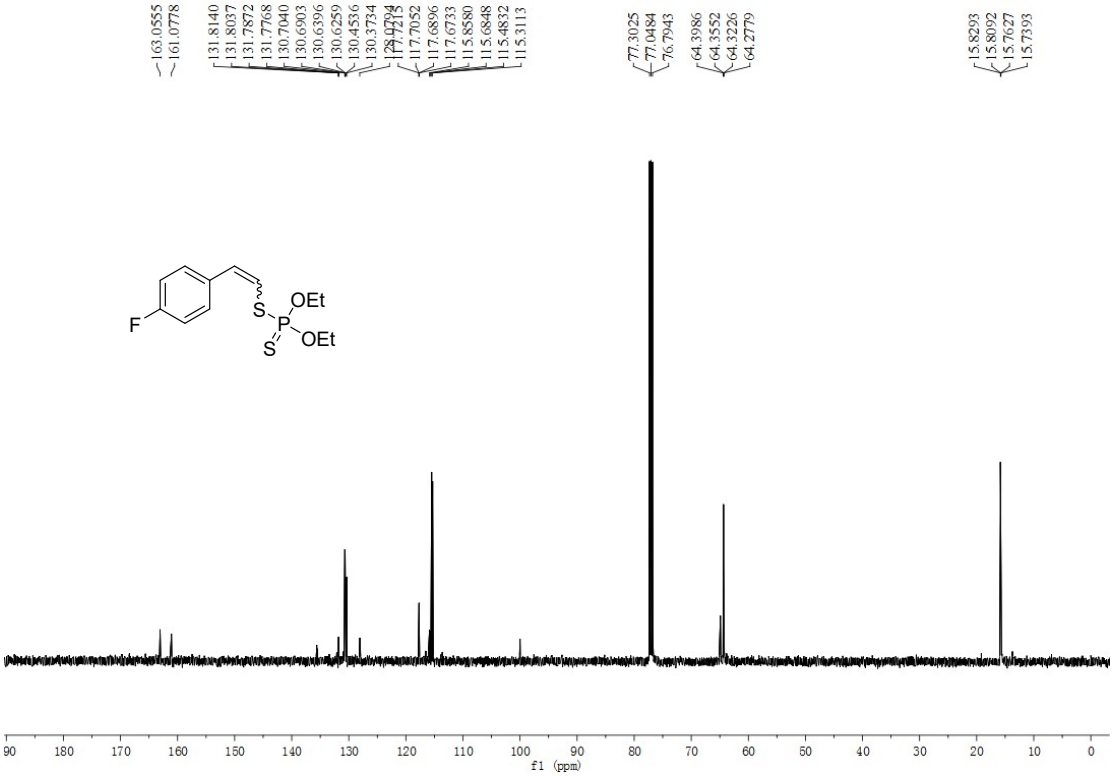
4f ^{31}P NMR (202 MHz, $CDCl_3$)



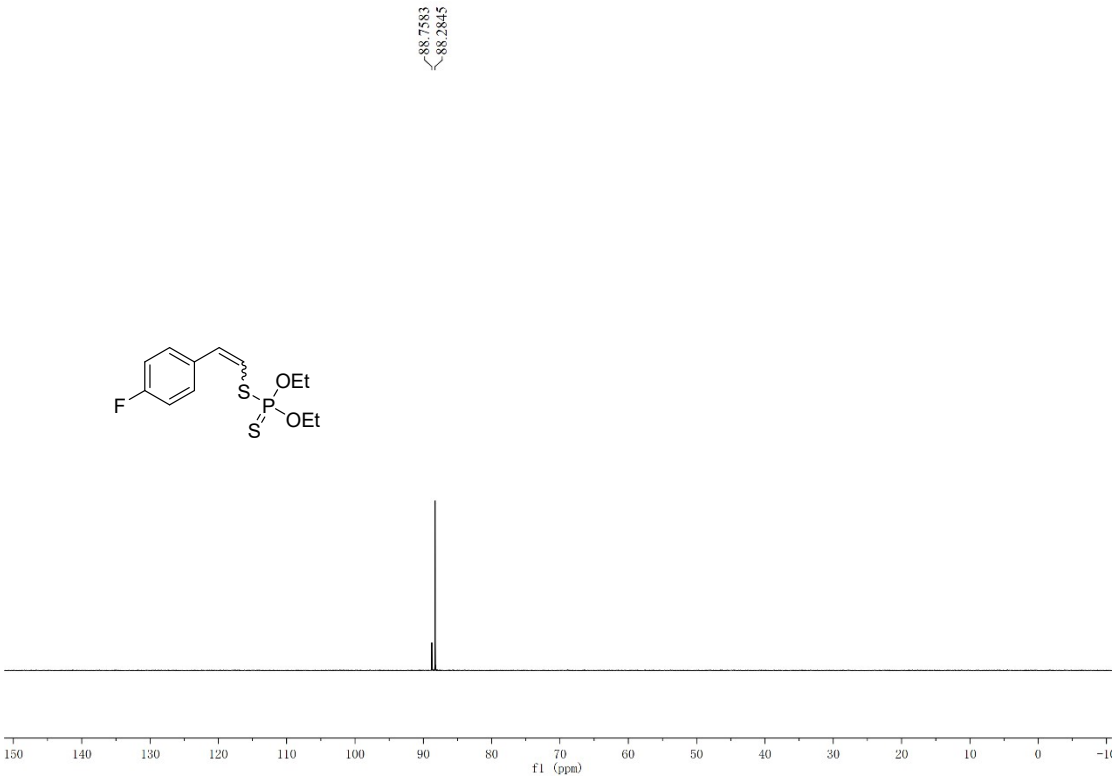
4g ^{1}H NMR (500 MHz, $CDCl_3$)



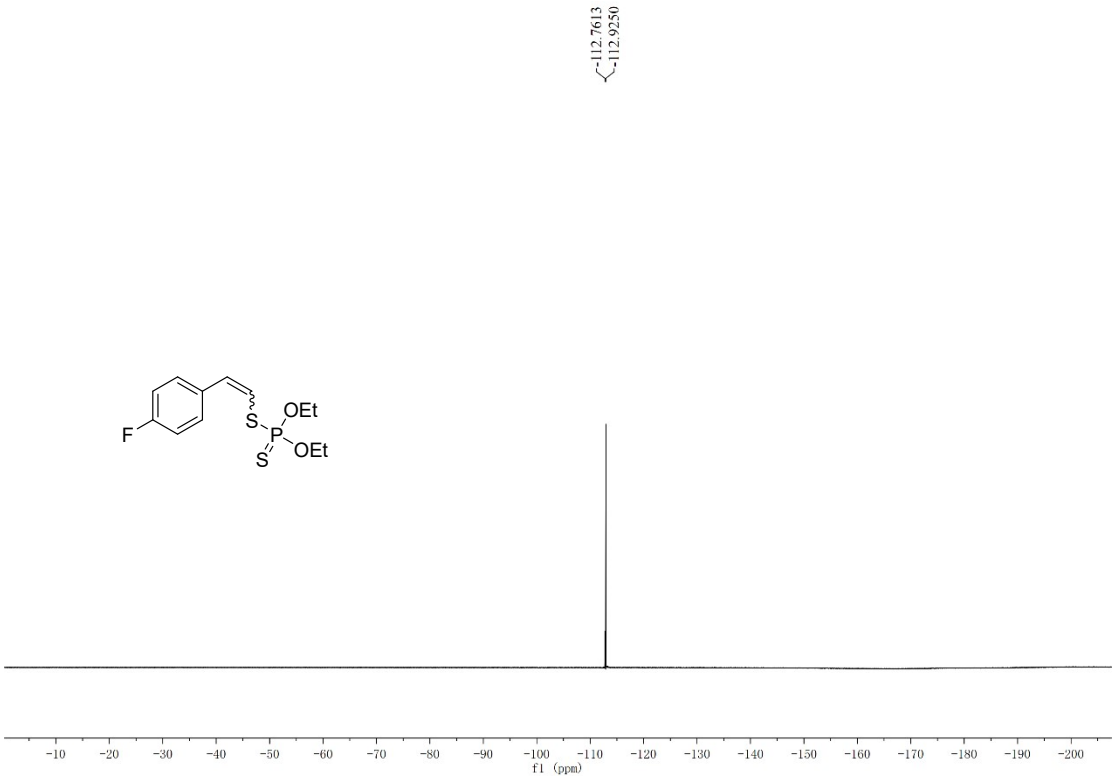
4g ^{13}C NMR (125MHz, $CDCl_3$)



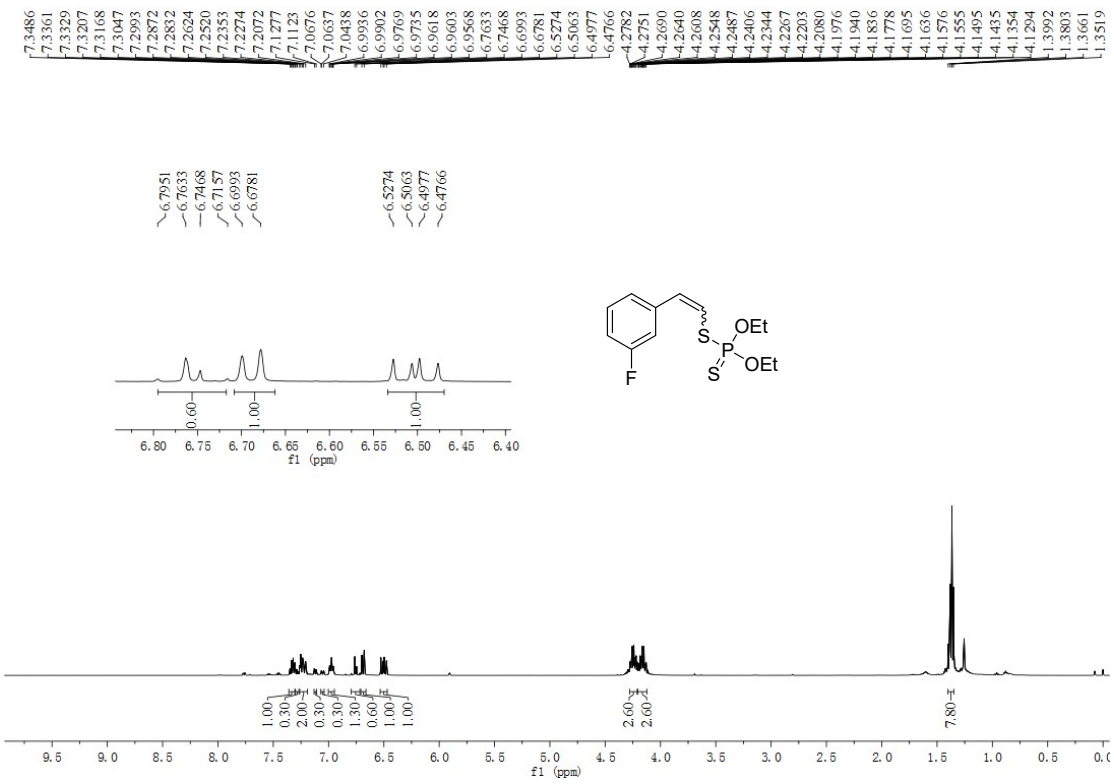
4g ^{31}P NMR (202 MHz, $CDCl_3$)



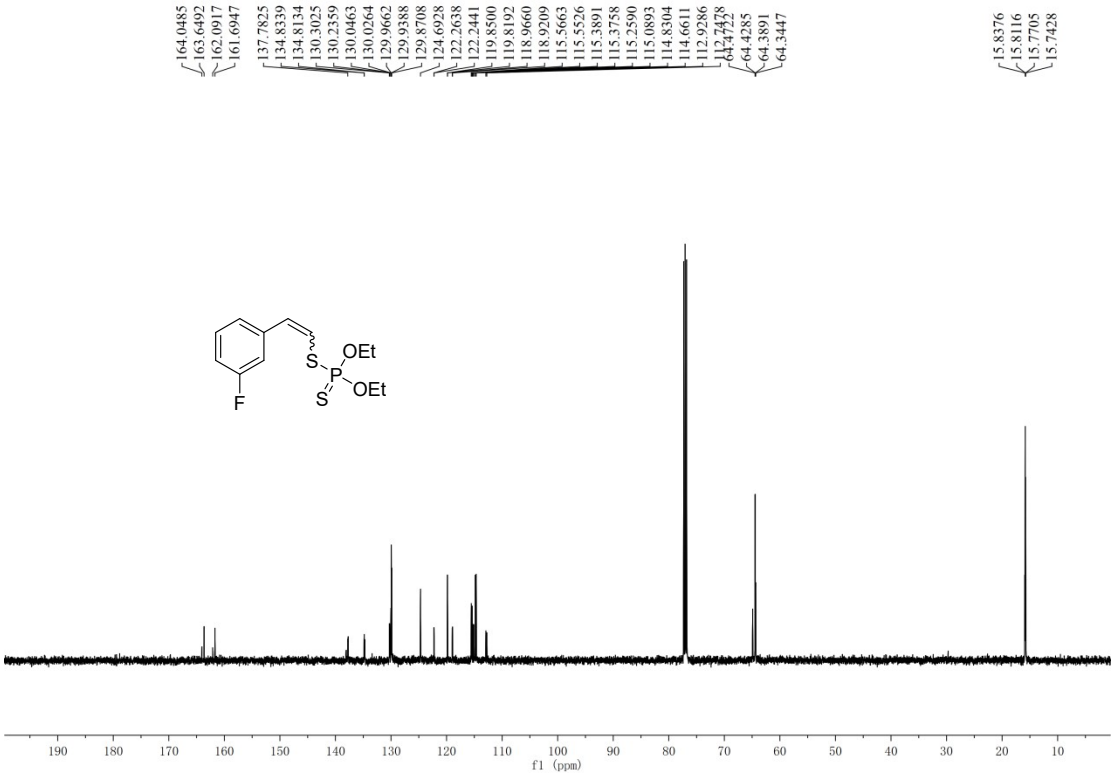
4g ^{19}F NMR (471 MHz, $CDCl_3$)



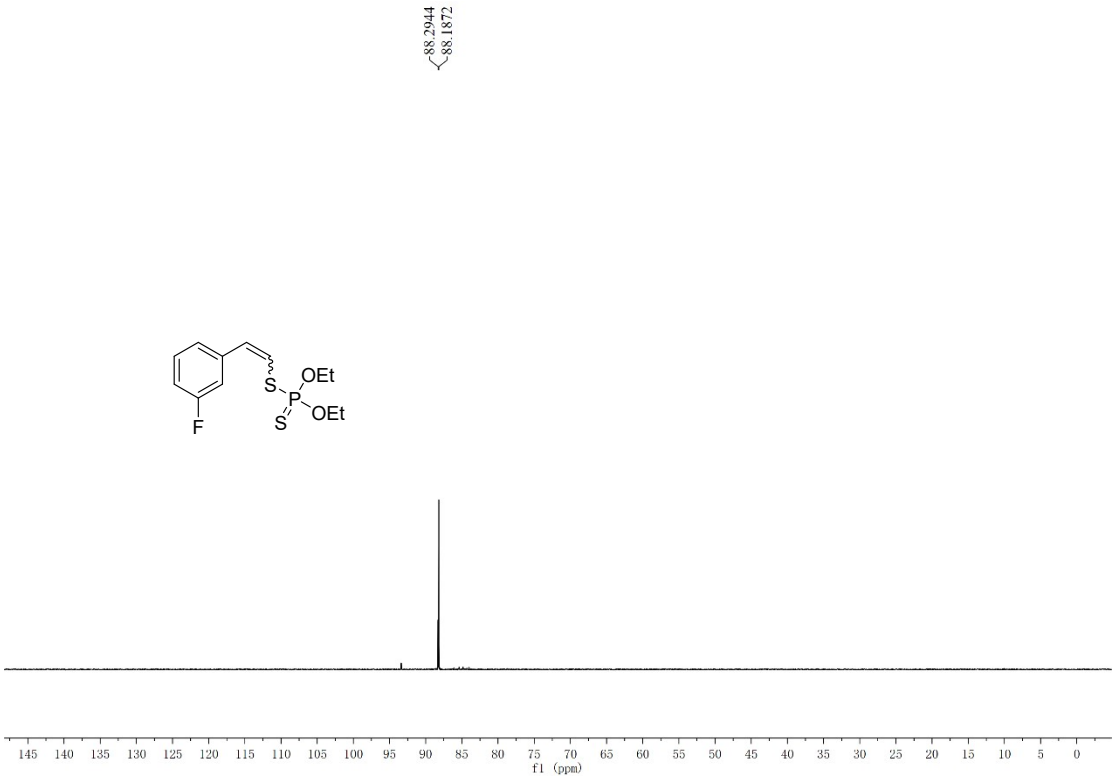
4h ^{1}H NMR (500 MHz, $CDCl_3$)



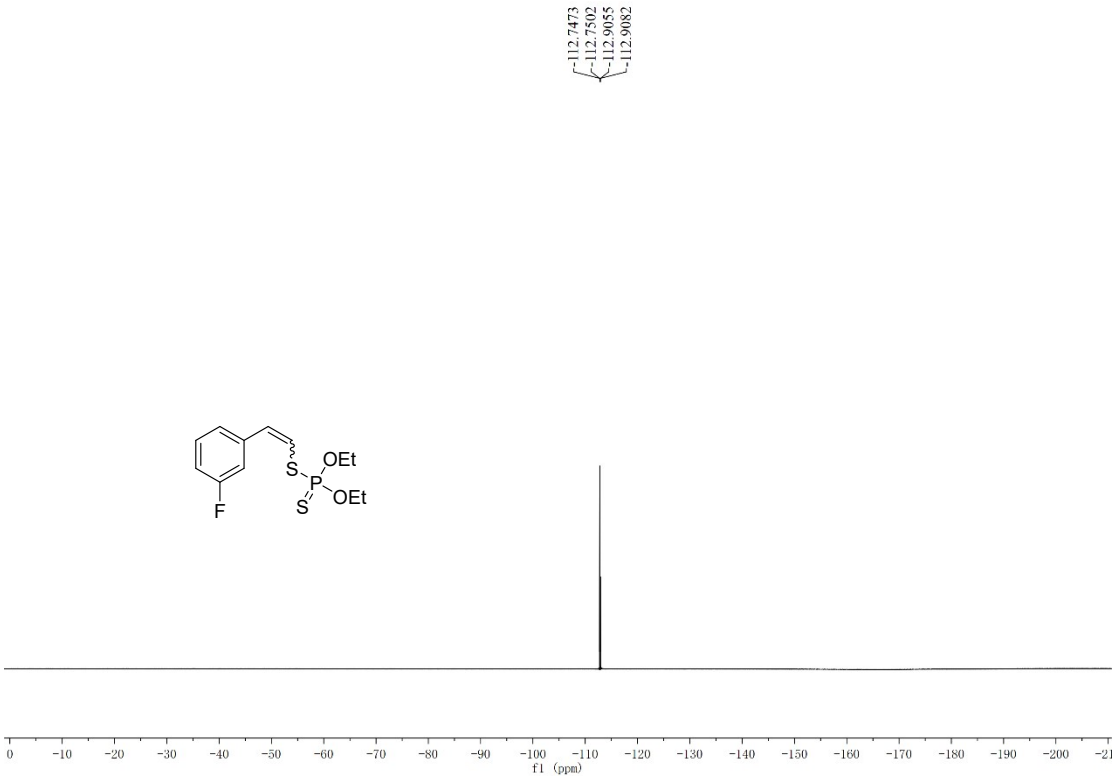
4h ^{13}C NMR (125MHz, $CDCl_3$)



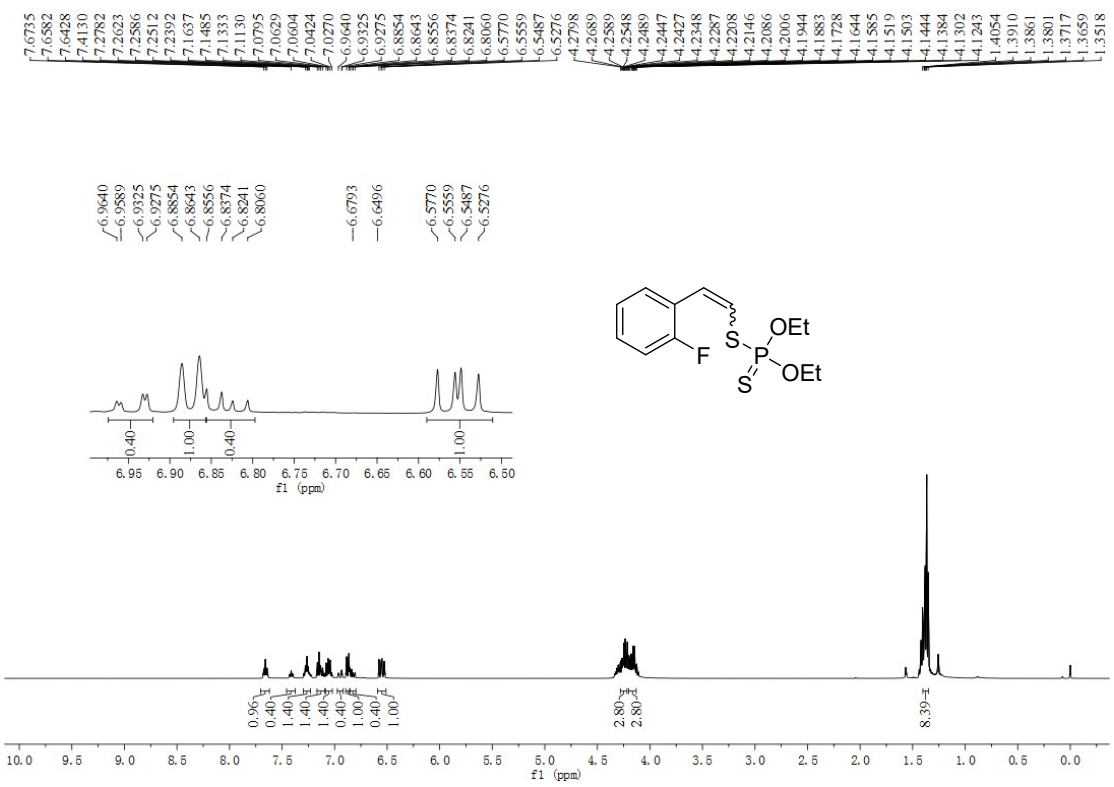
4h ^{31}P NMR (202 MHz, $CDCl_3$)



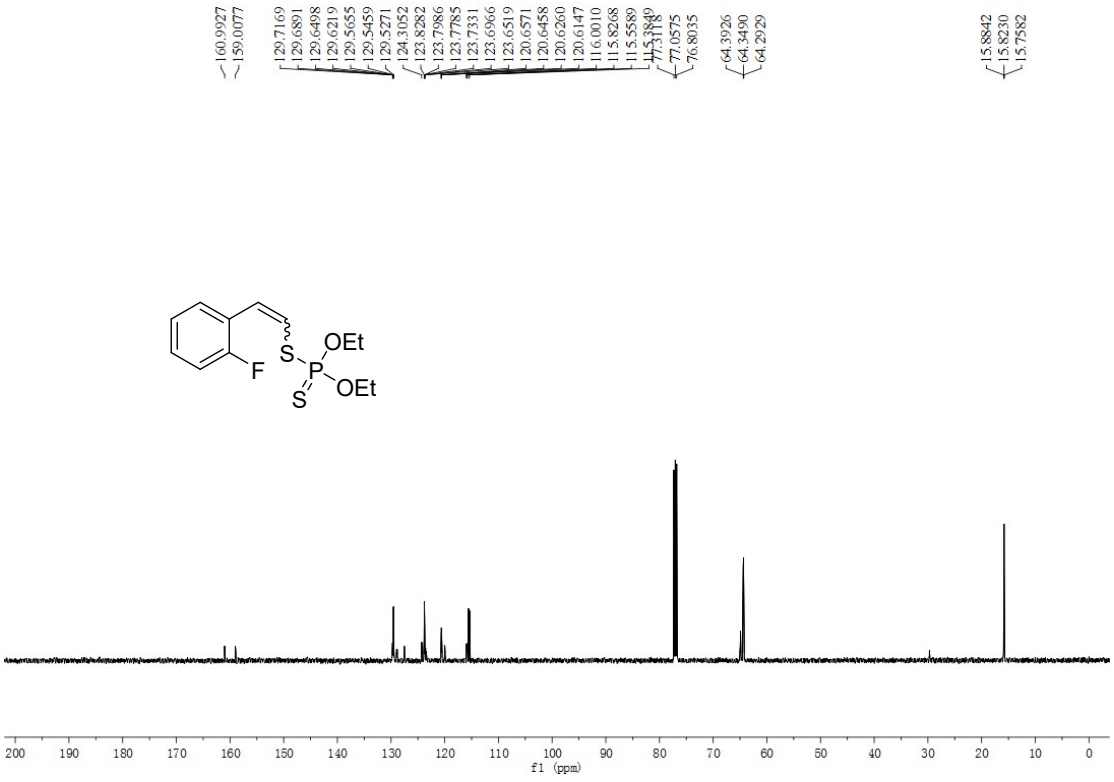
4h ^{19}F NMR (471 MHz, $CDCl_3$)



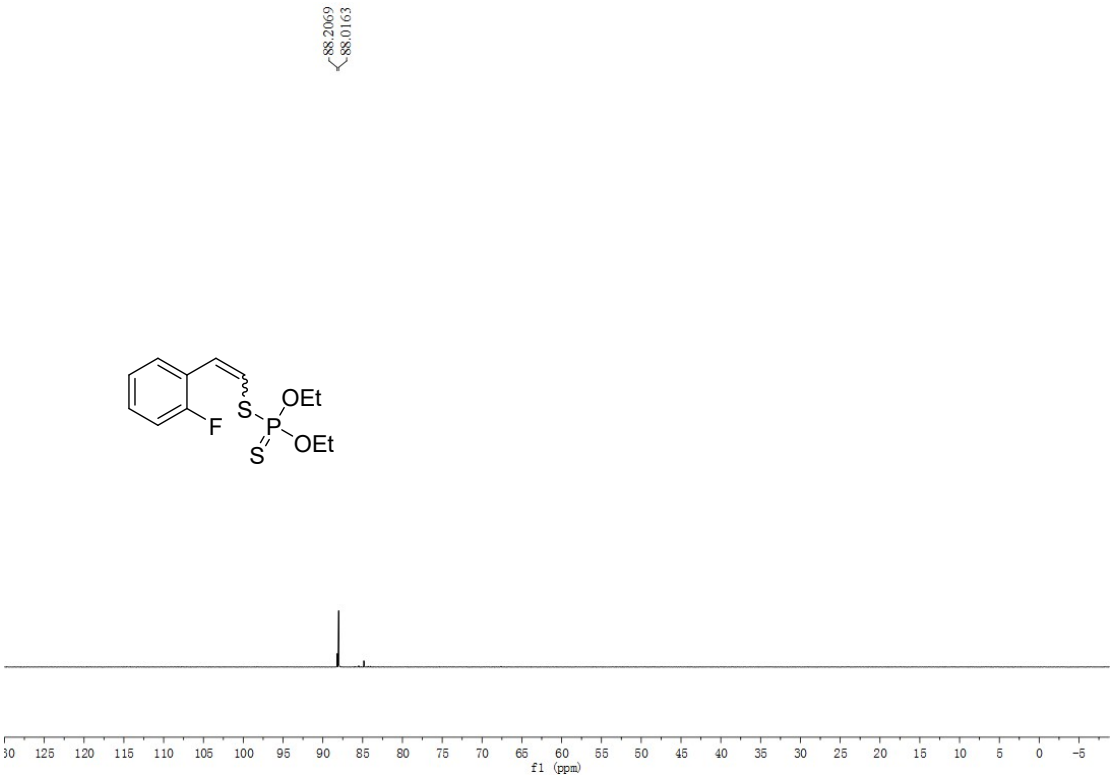
4i ^{1}H NMR (500 MHz, $CDCl_3$)



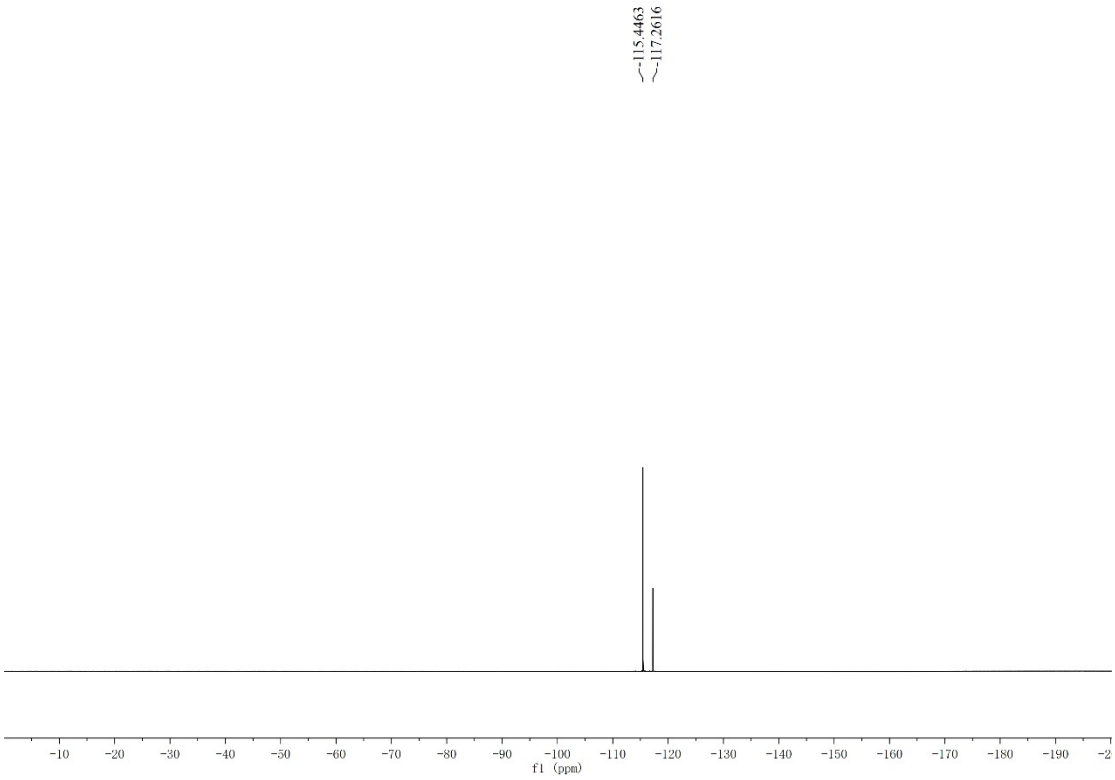
4i ^{13}C NMR (125MHz, $CDCl_3$)



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



4i ^{19}F NMR (471 MHz, $CDCl_3$)



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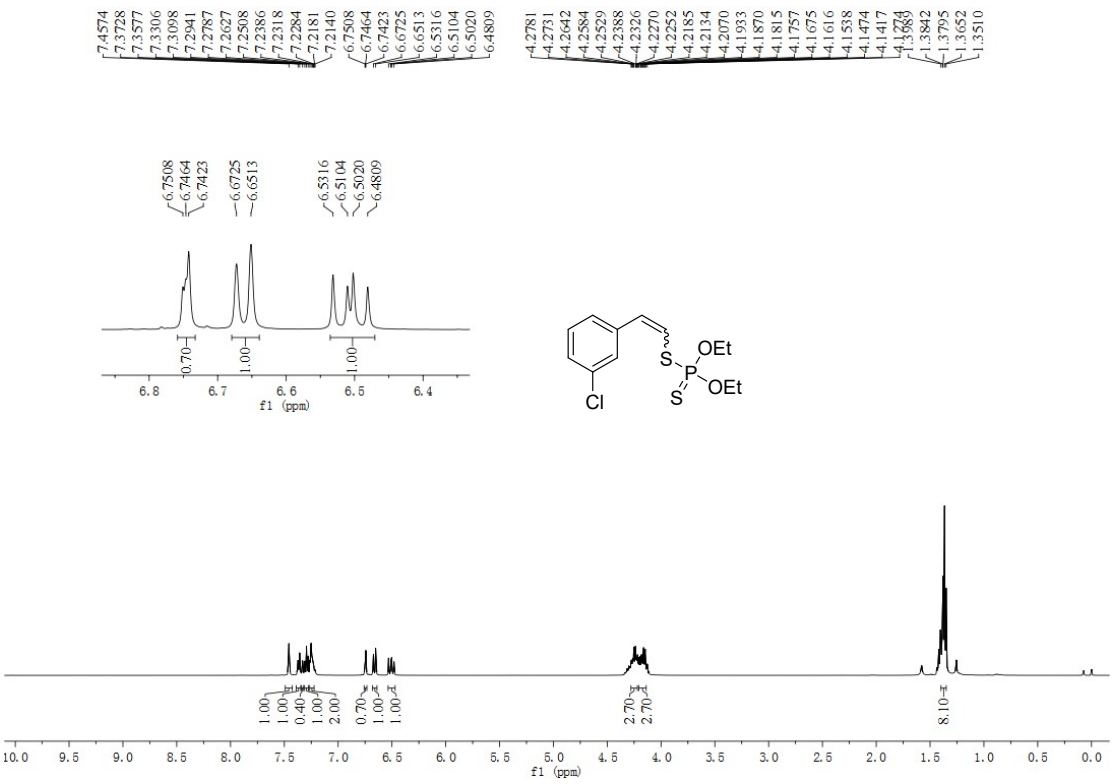

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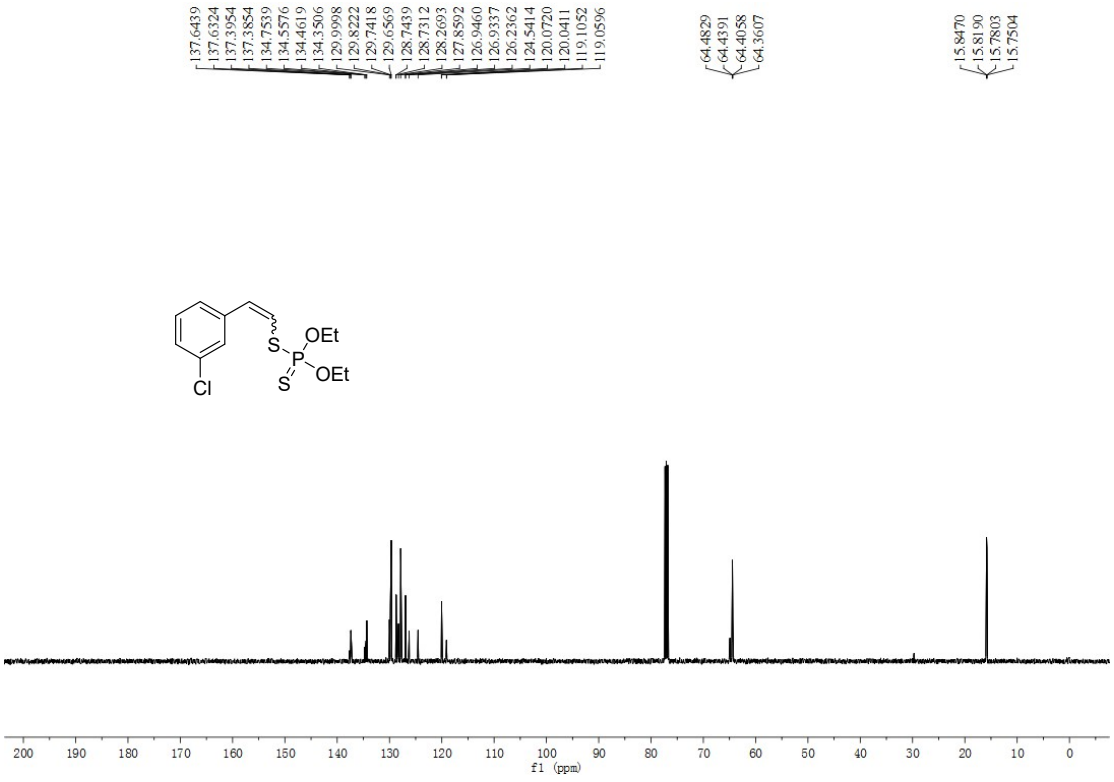

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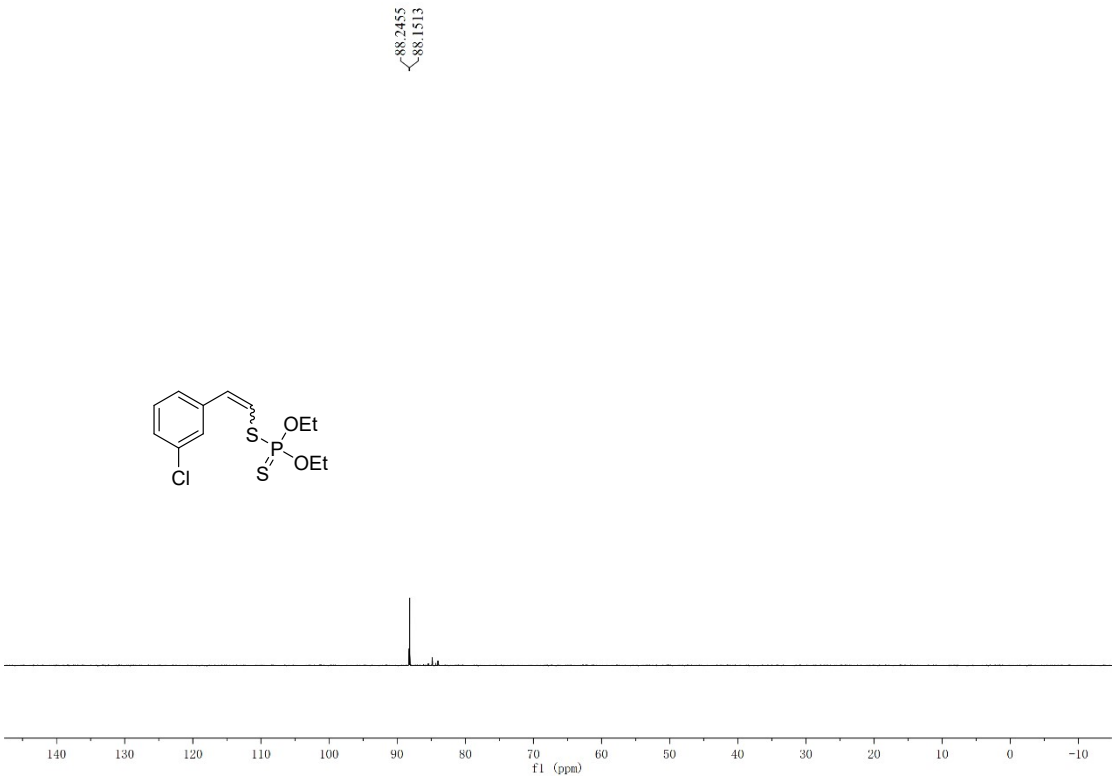

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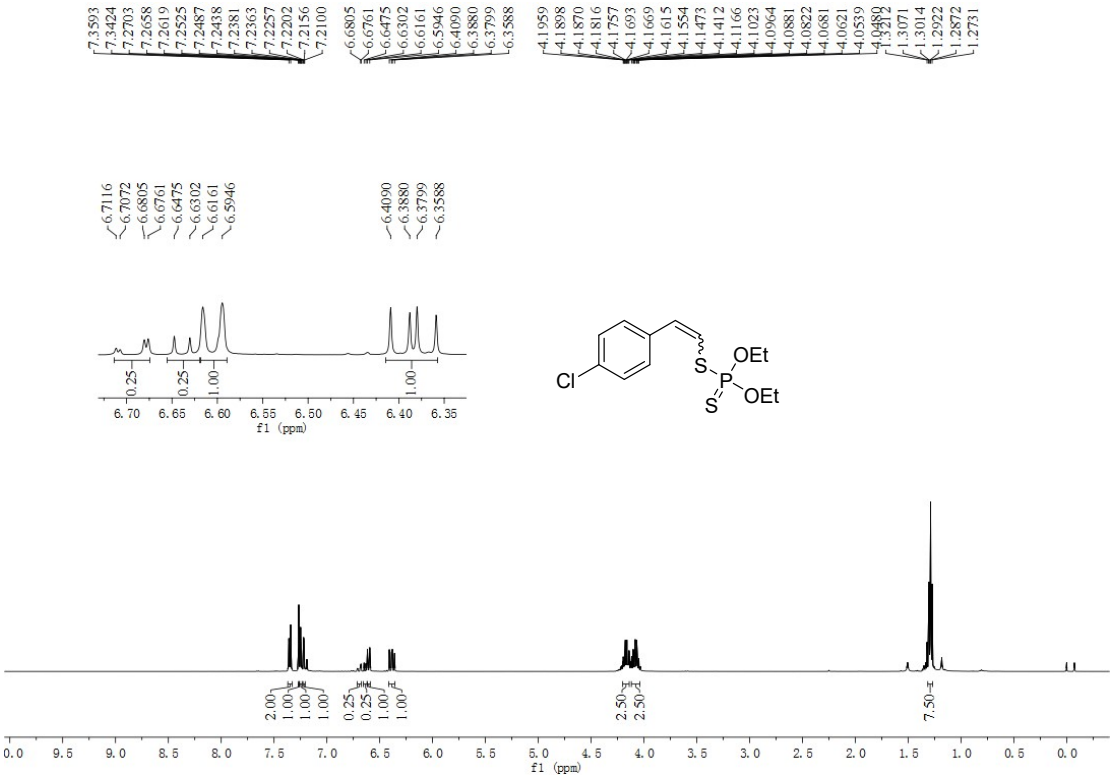
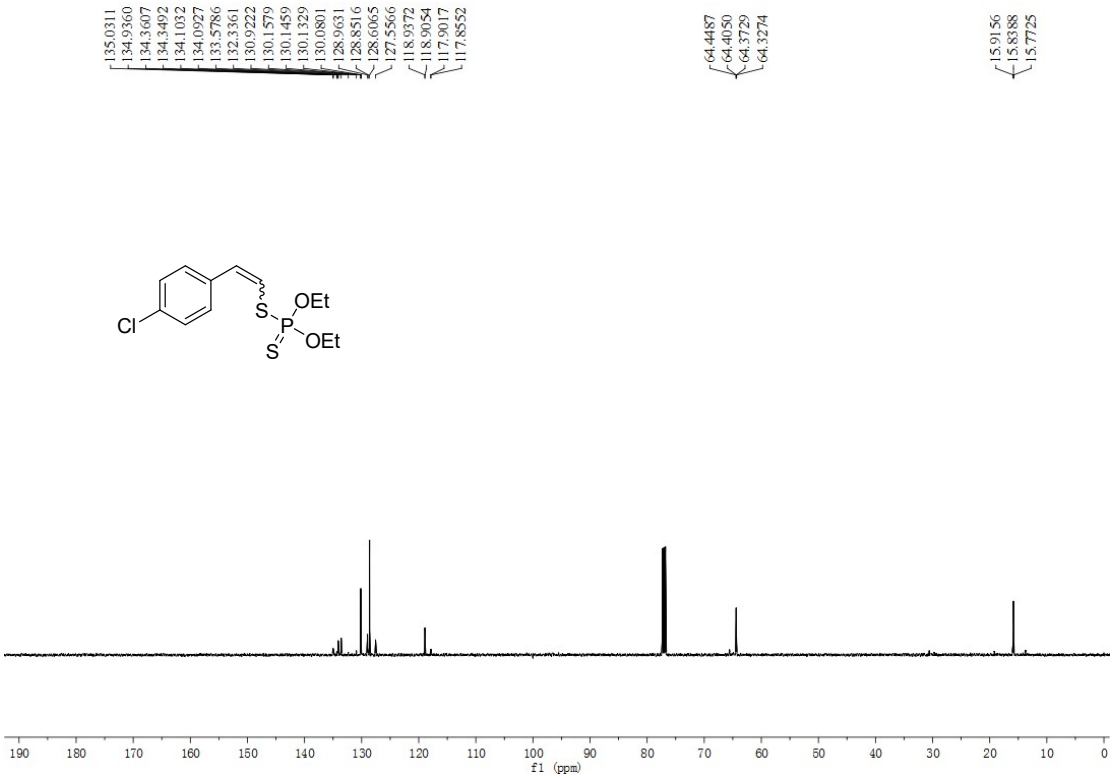
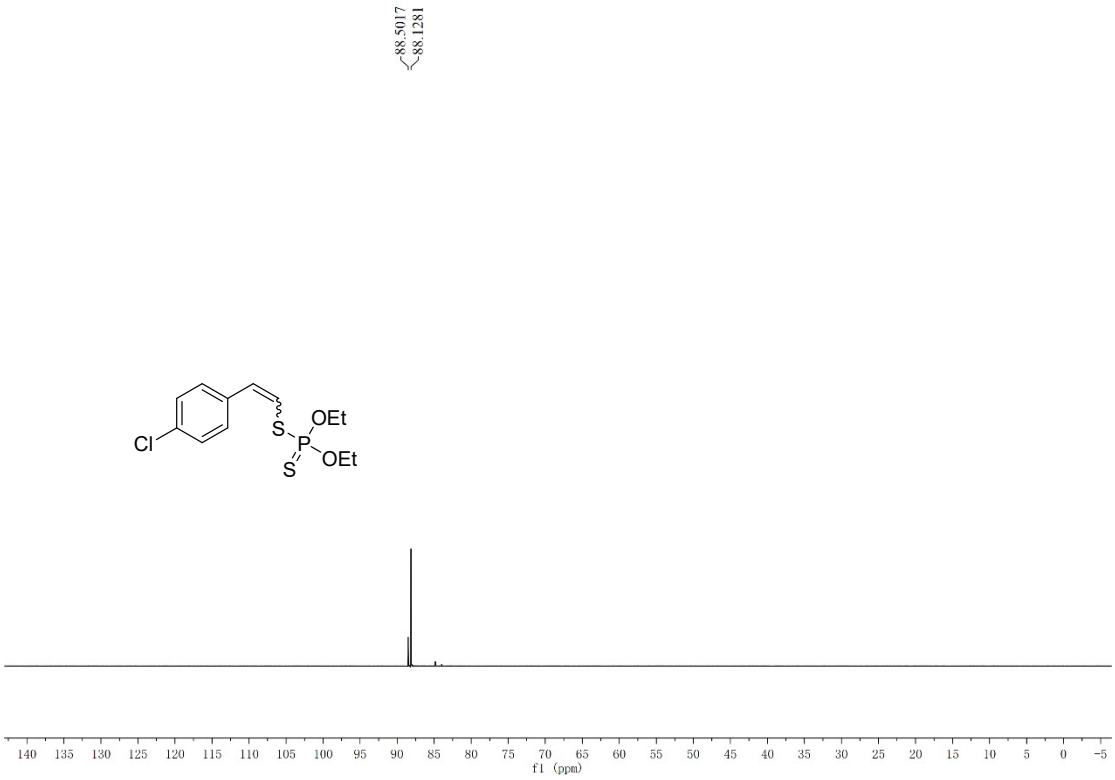


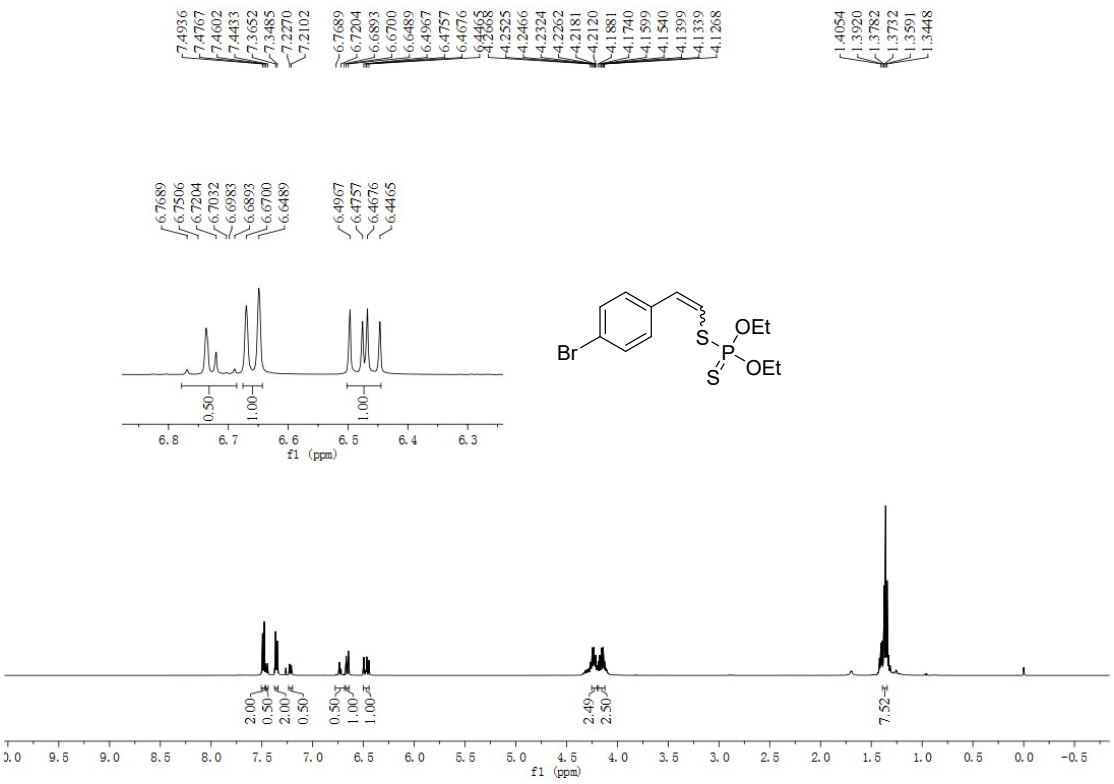
4k ^{13}C NMR (125MHz, $CDCl_3$)



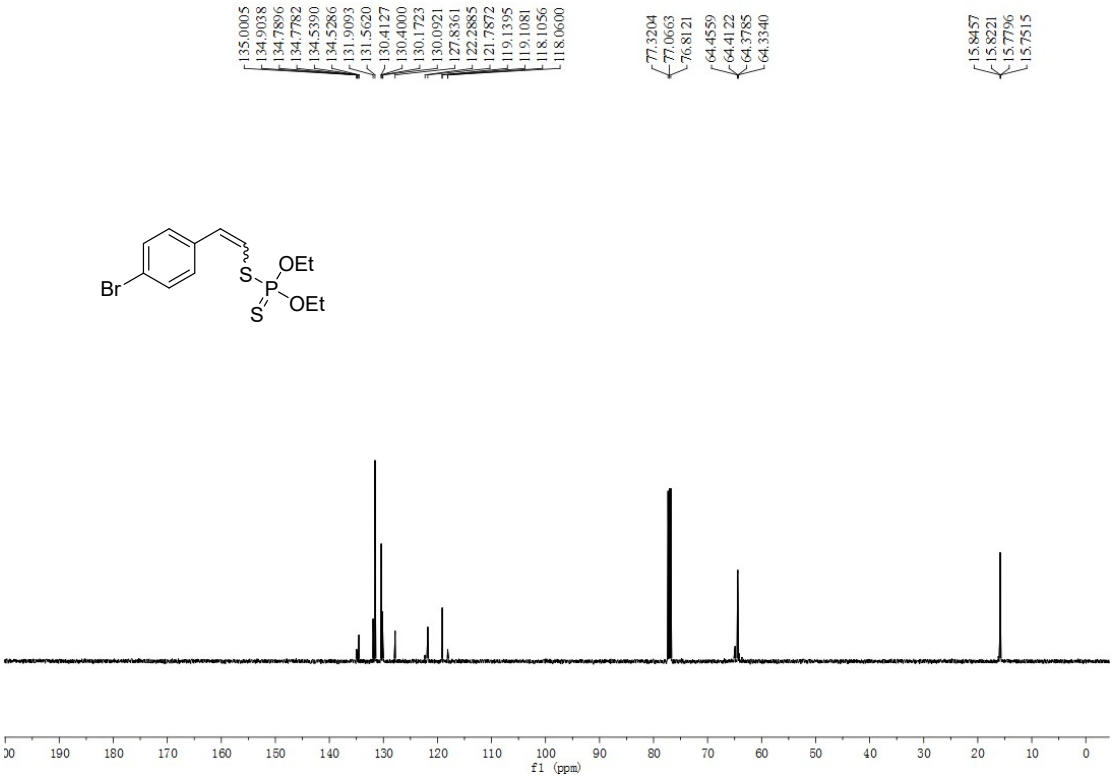
4k ^{31}P NMR (202 MHz, $CDCl_3$)



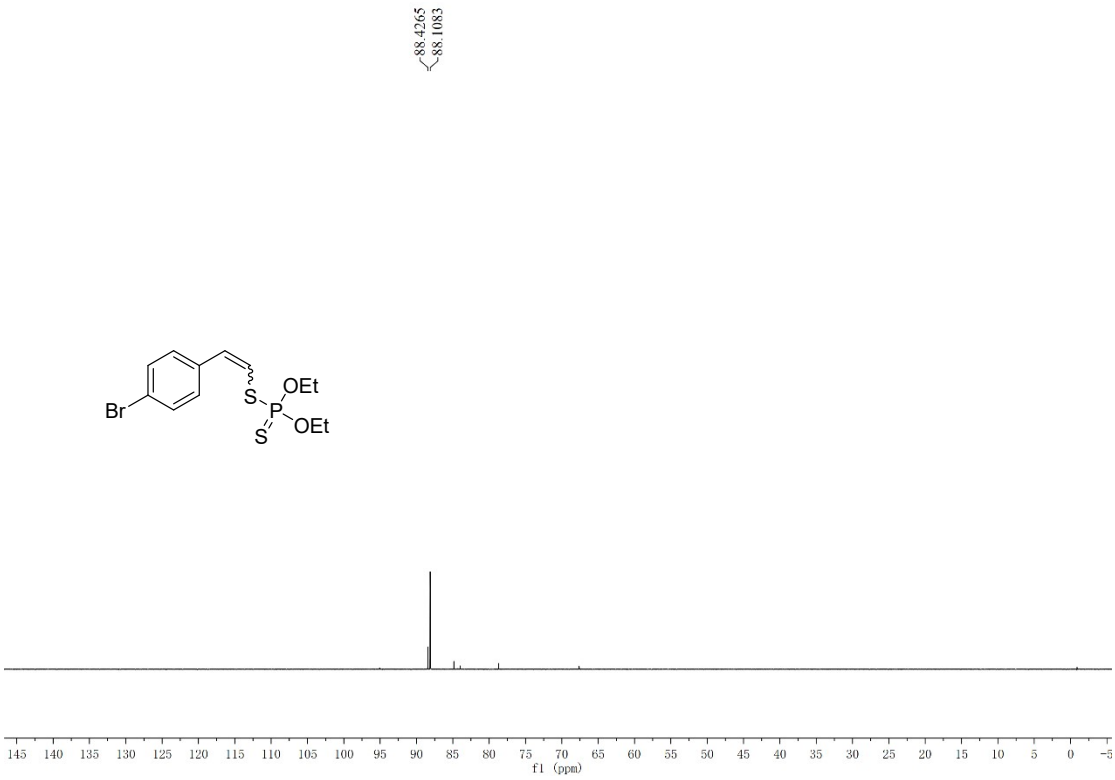
4l ^{1}H NMR (500 MHz, $CDCl_3$)



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



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



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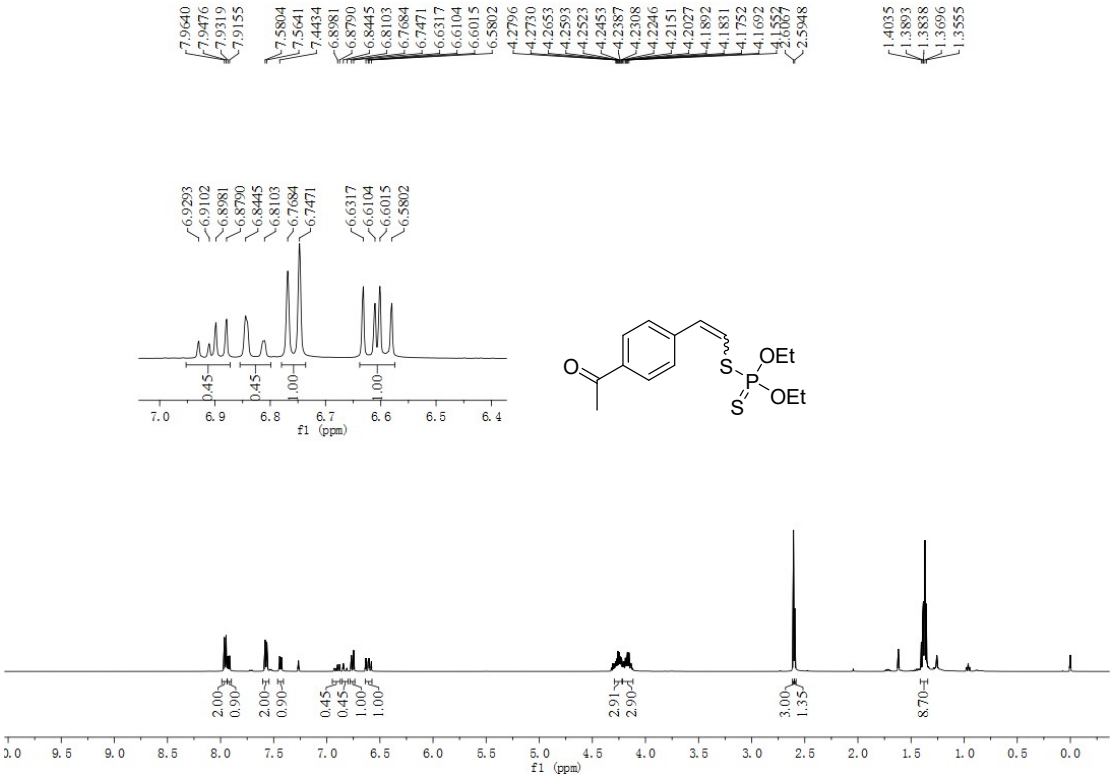
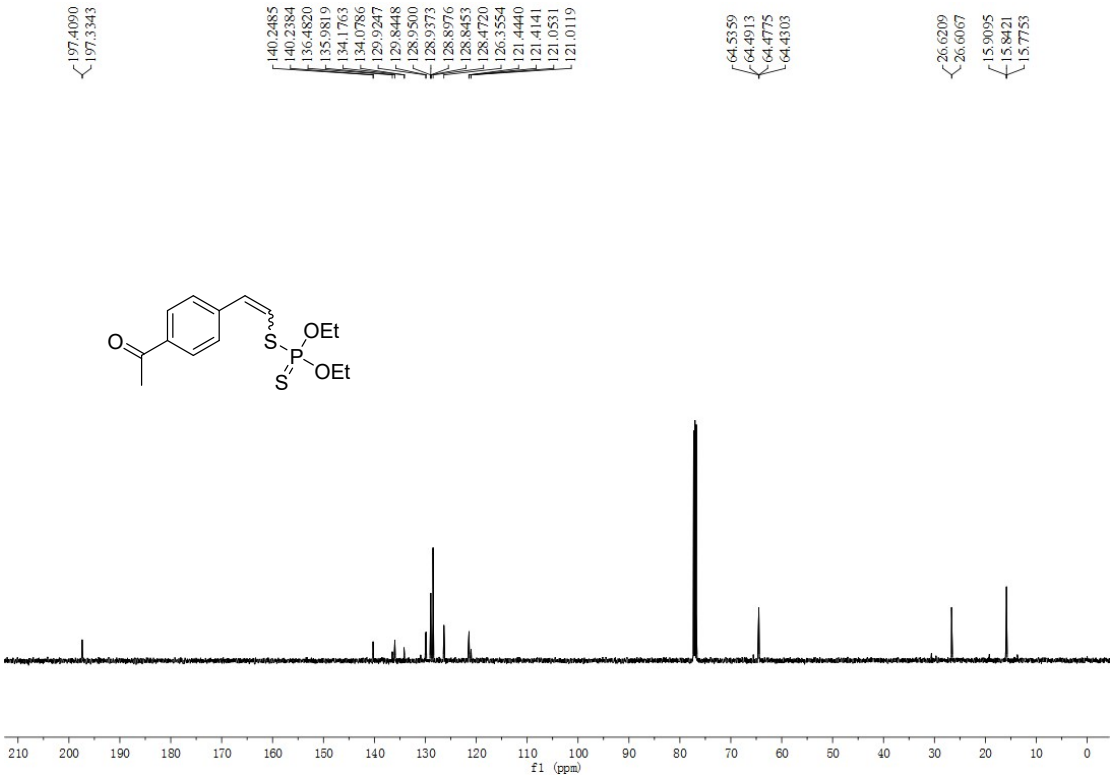
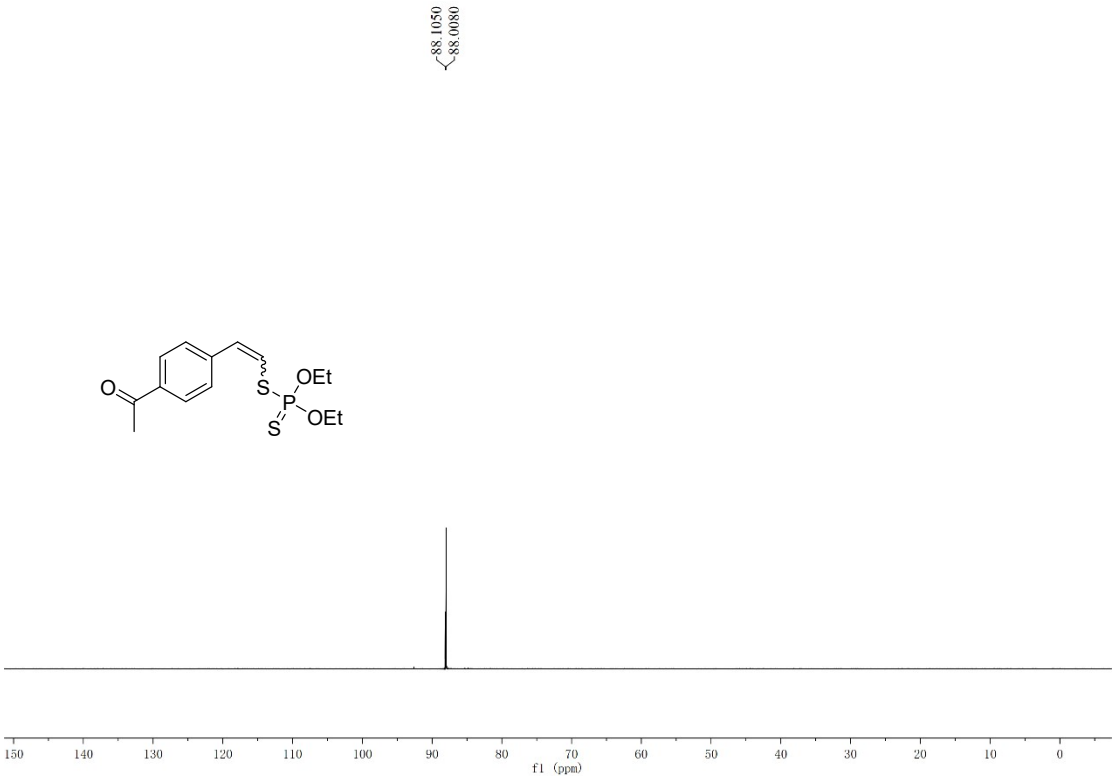


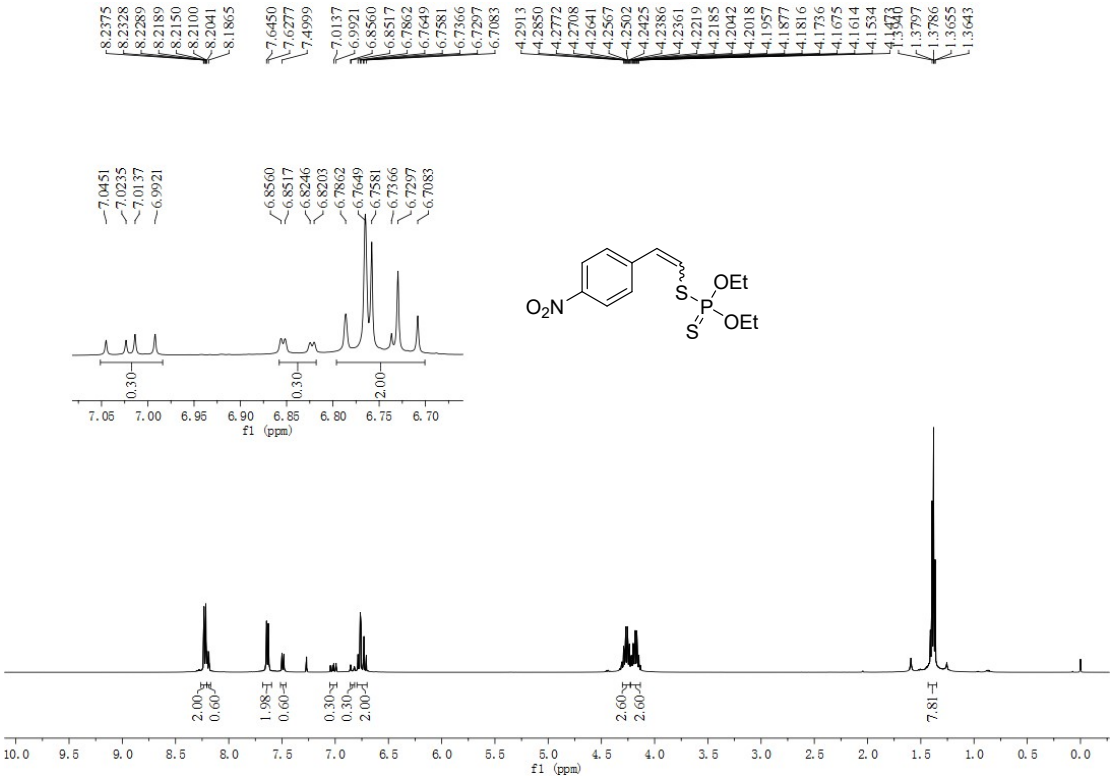
4m ^{13}C NMR (125MHz, $CDCl_3$)



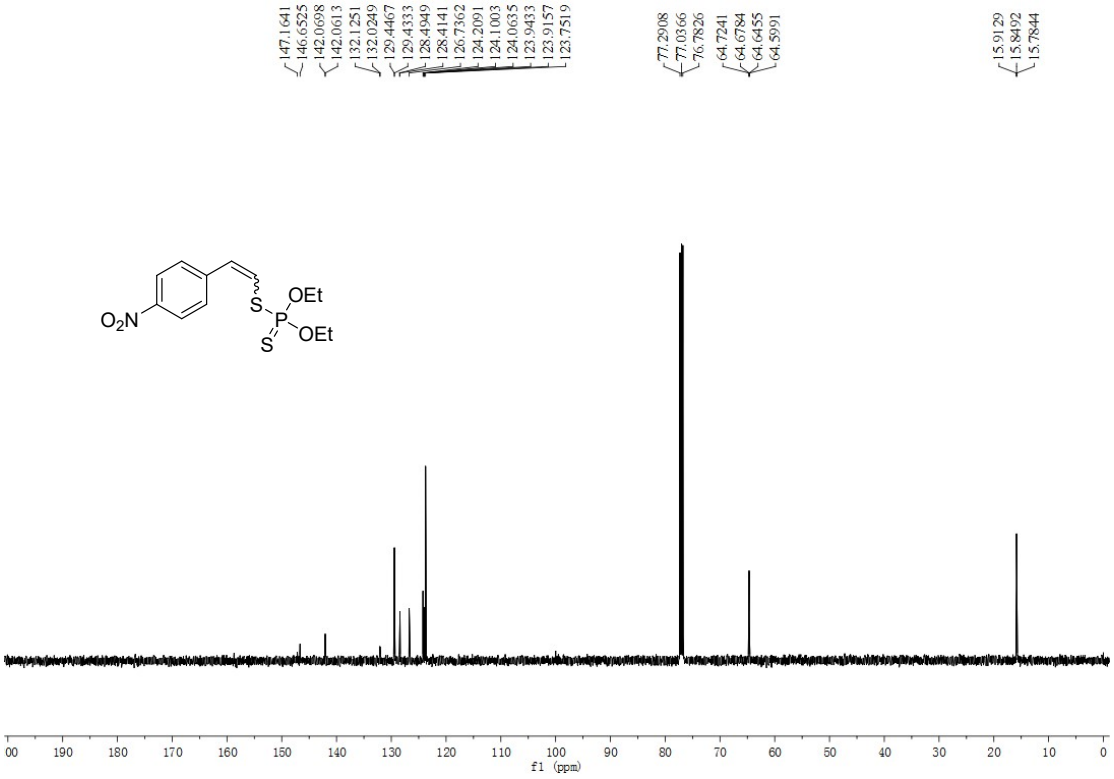
4m ^{31}P NMR (202 MHz, $CDCl_3$)



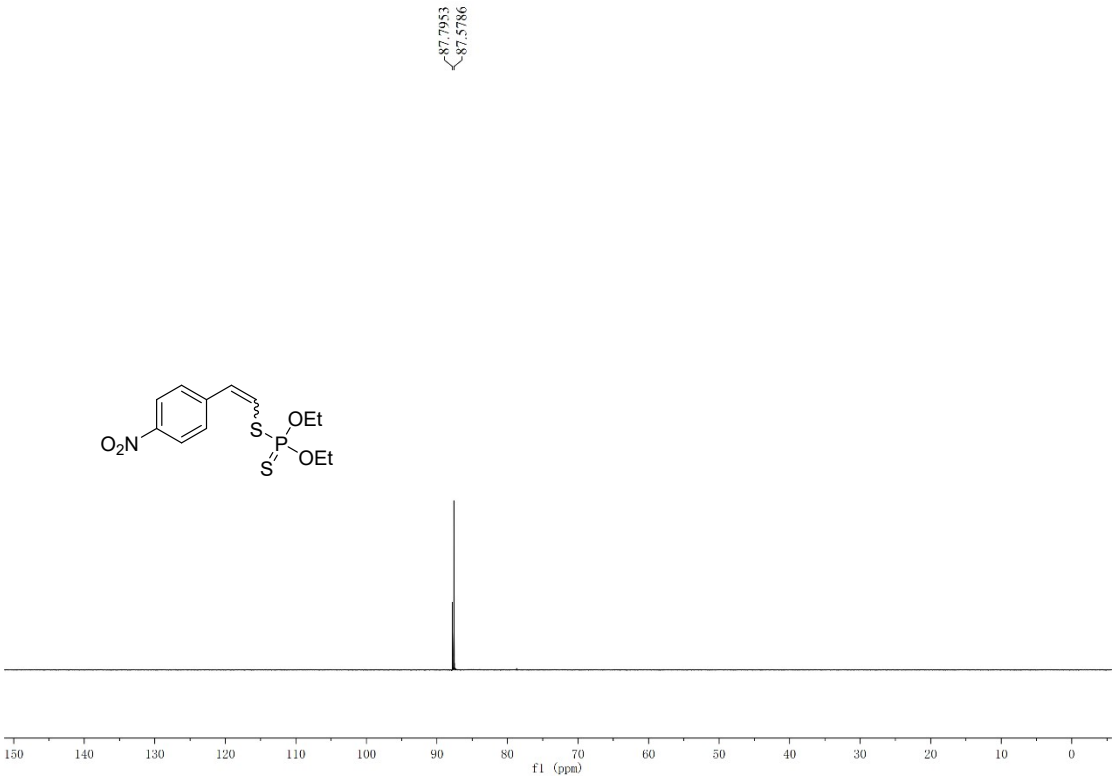
4n ^{1}H NMR (500 MHz, $CDCl_3$)



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



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



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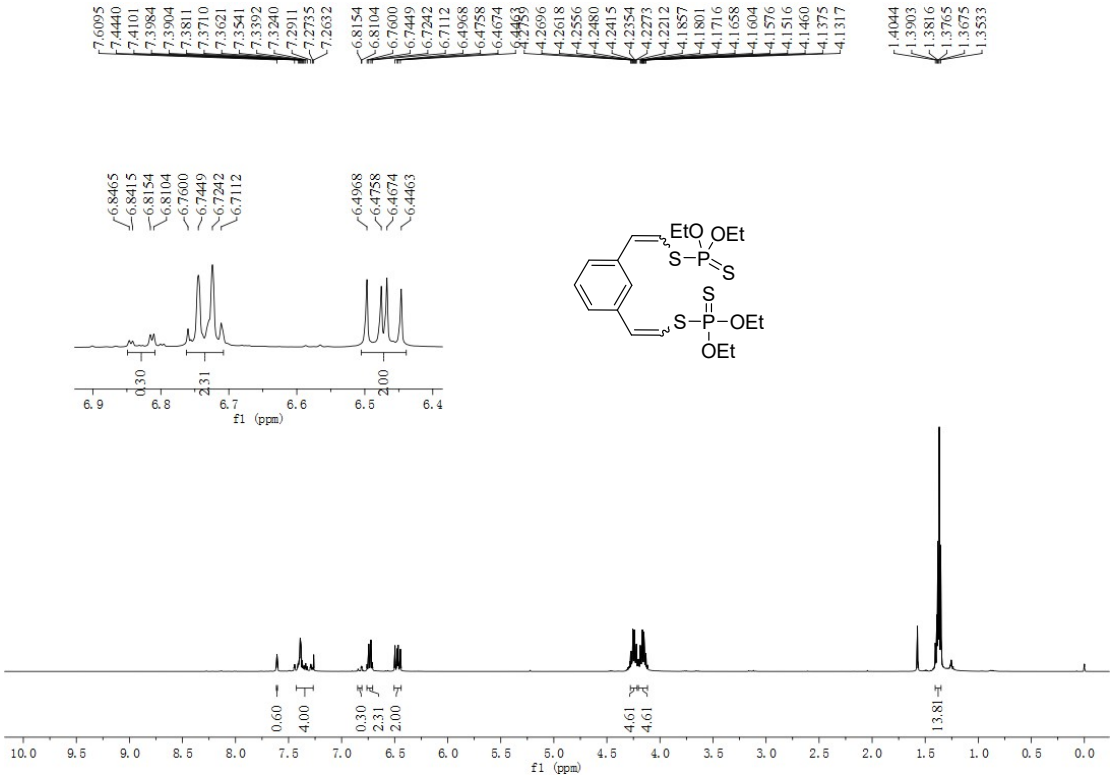

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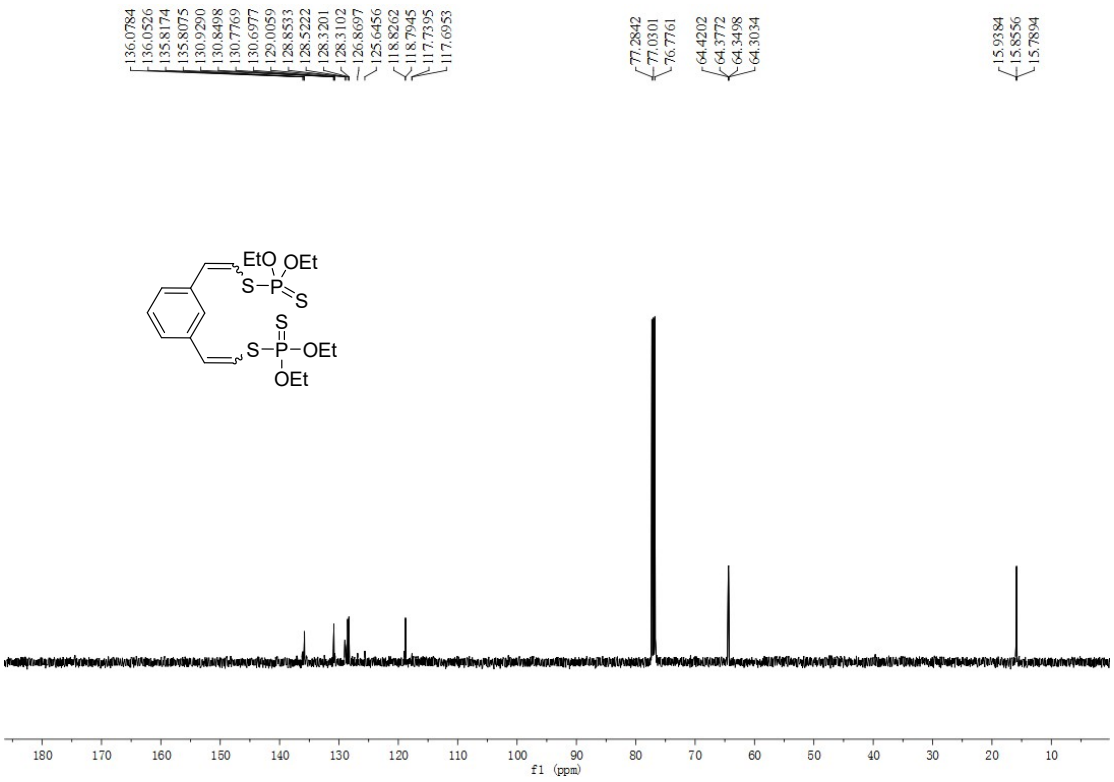
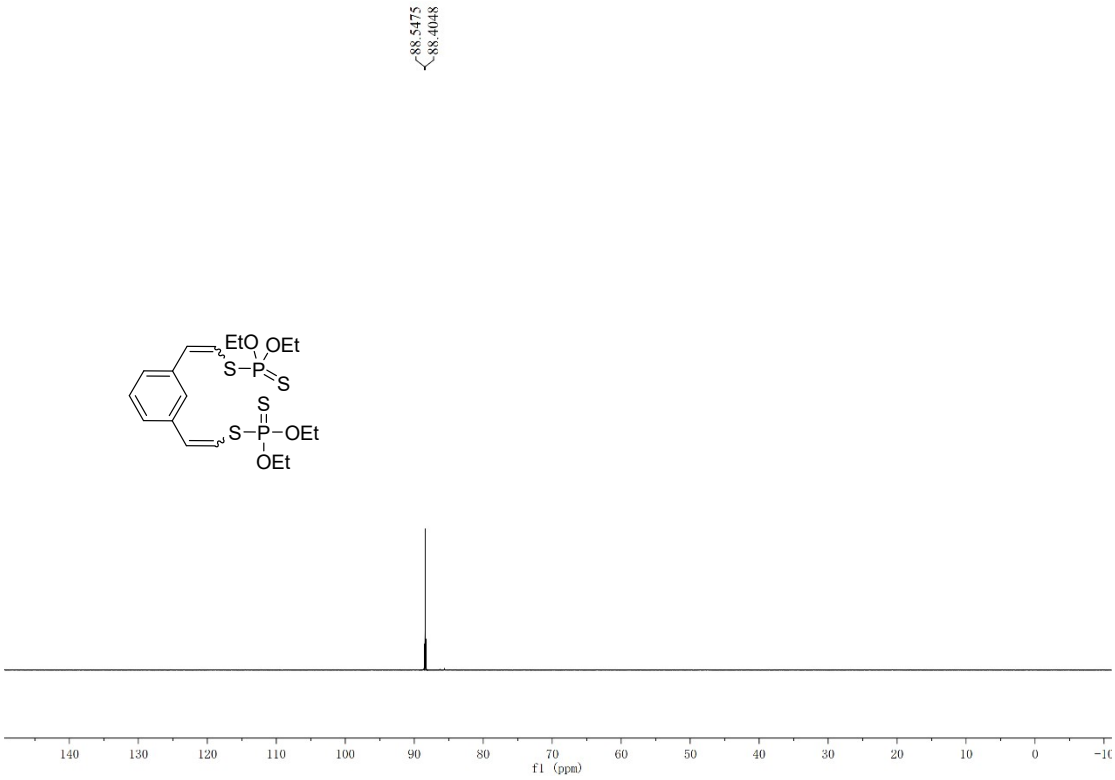


4o ^{31}P NMR (202 MHz, $CDCl_3$)



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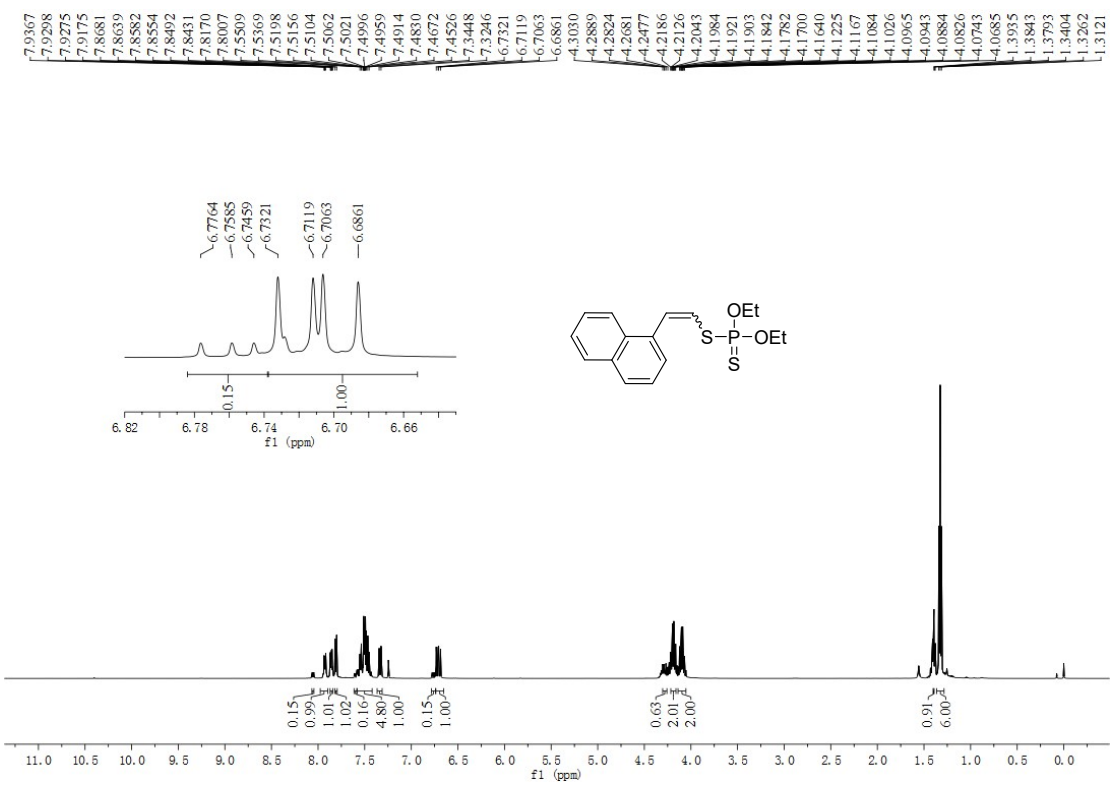
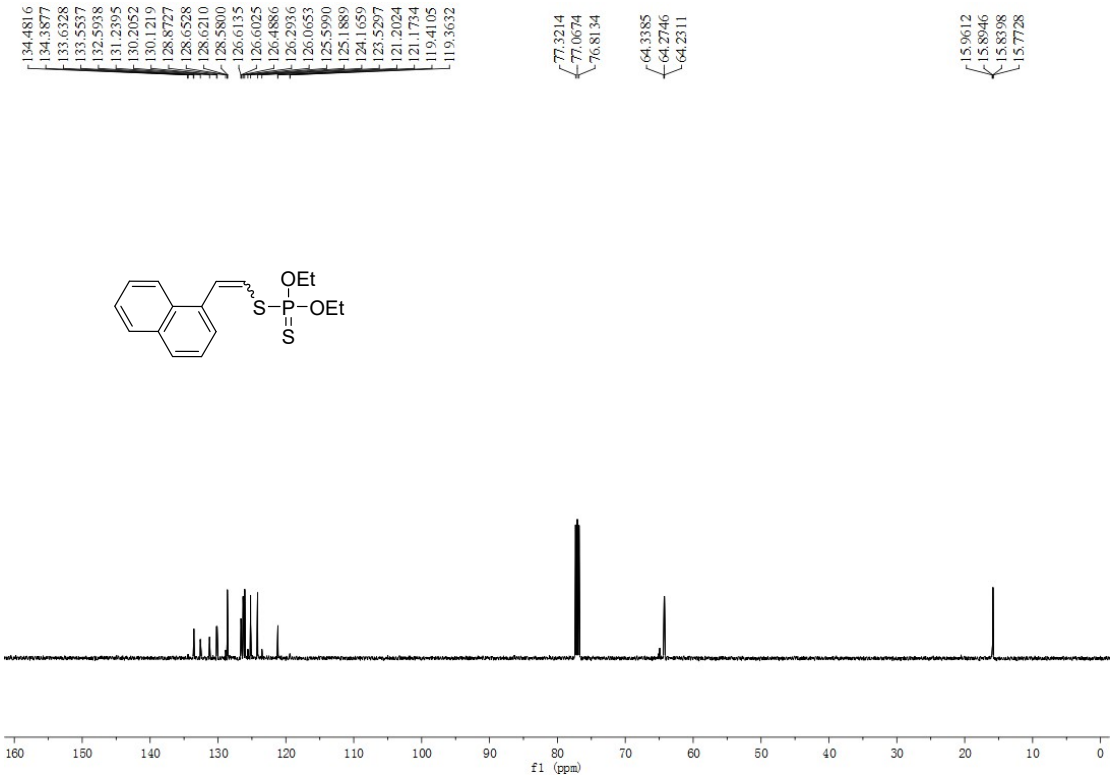
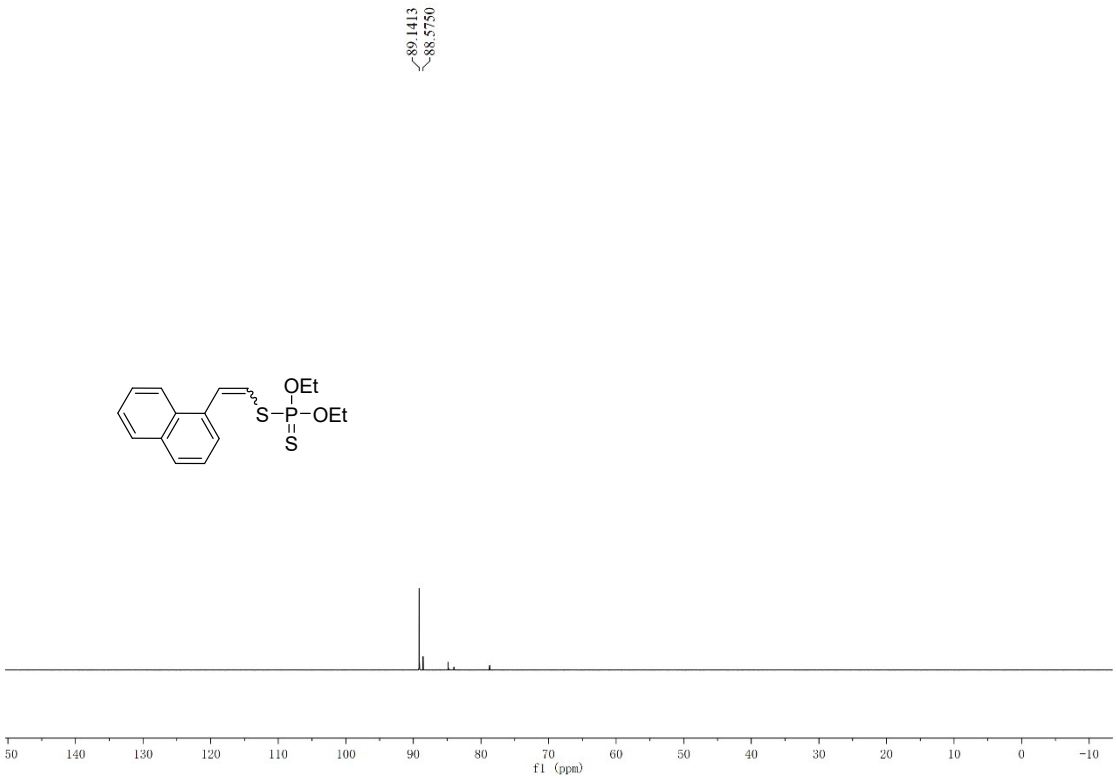


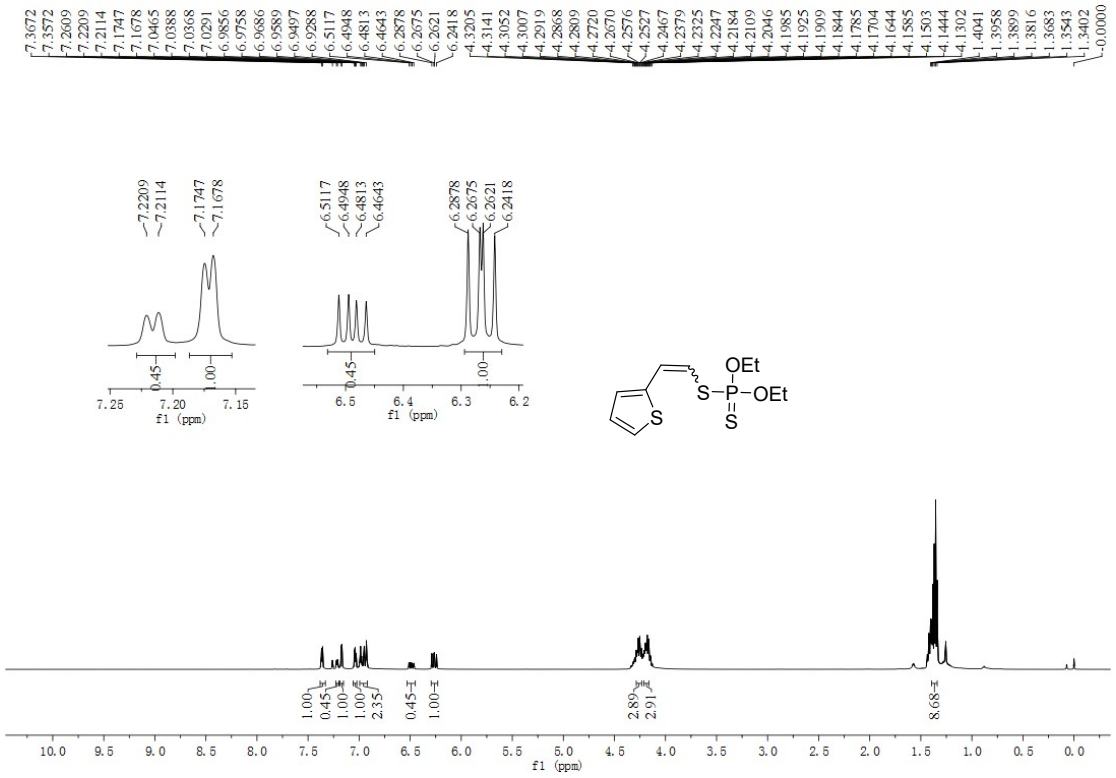
4p ^{13}C NMR (125MHz, $CDCl_3$)



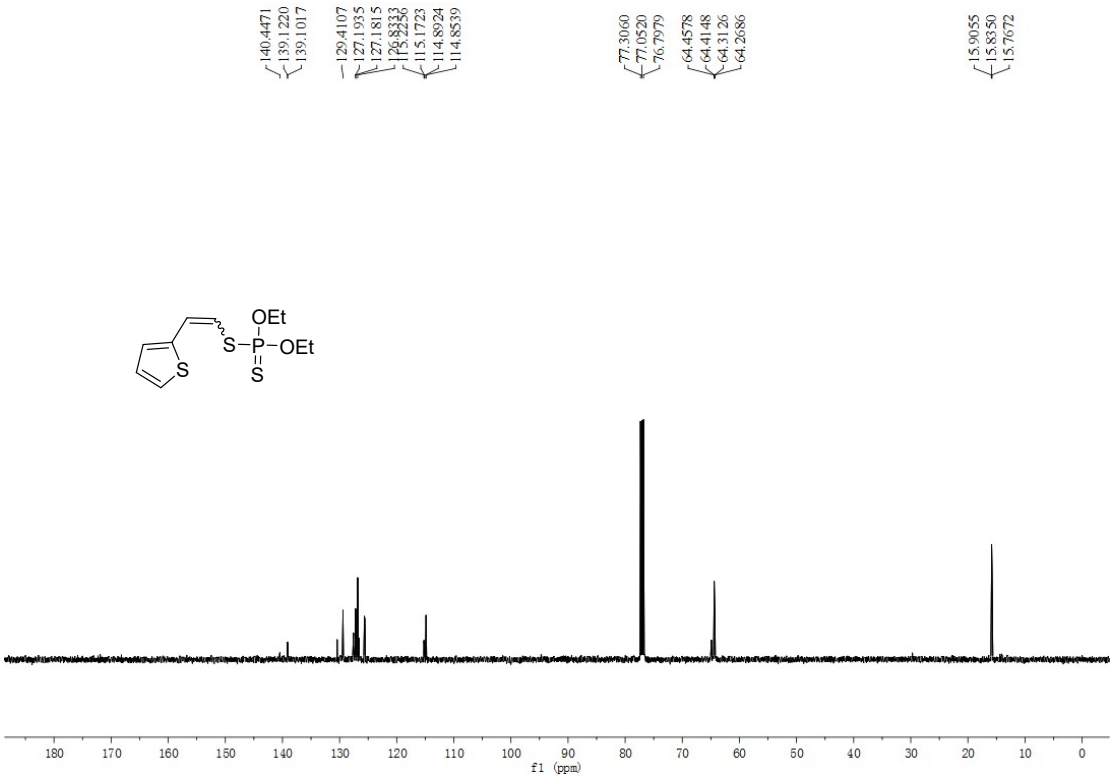
4p ^{31}P NMR (202 MHz, $CDCl_3$)



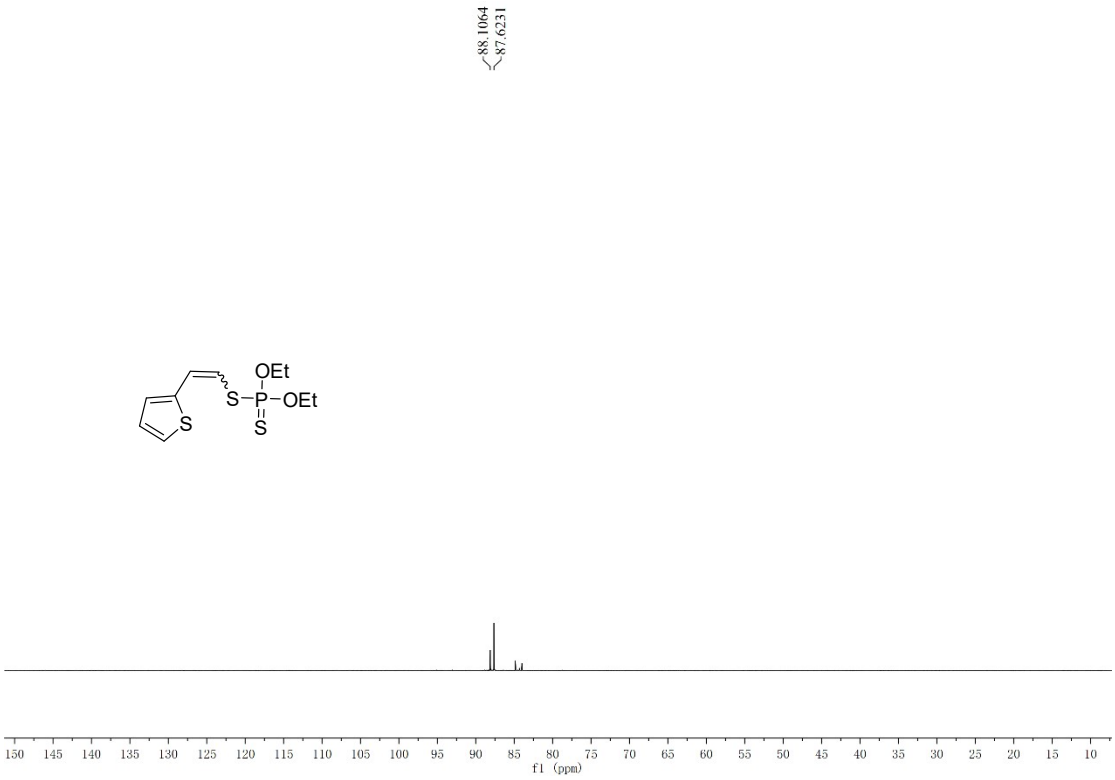
4q ^{1}H NMR (500 MHz, $CDCl_3$)



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



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



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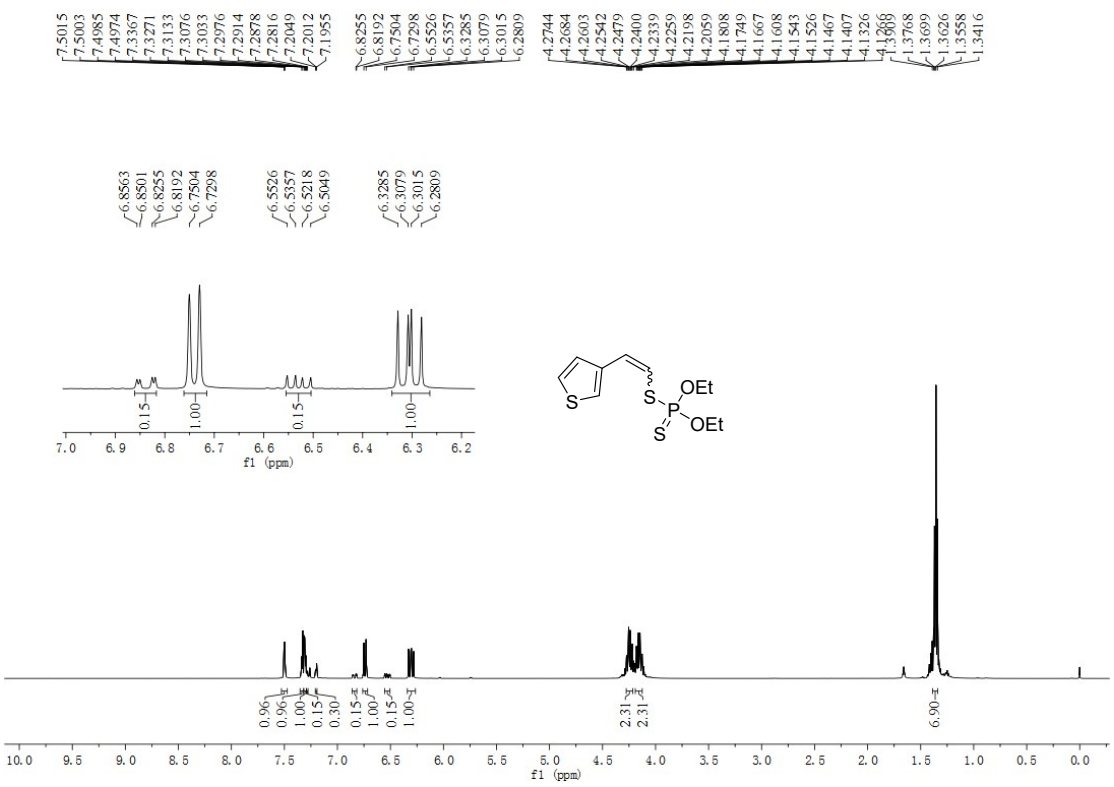

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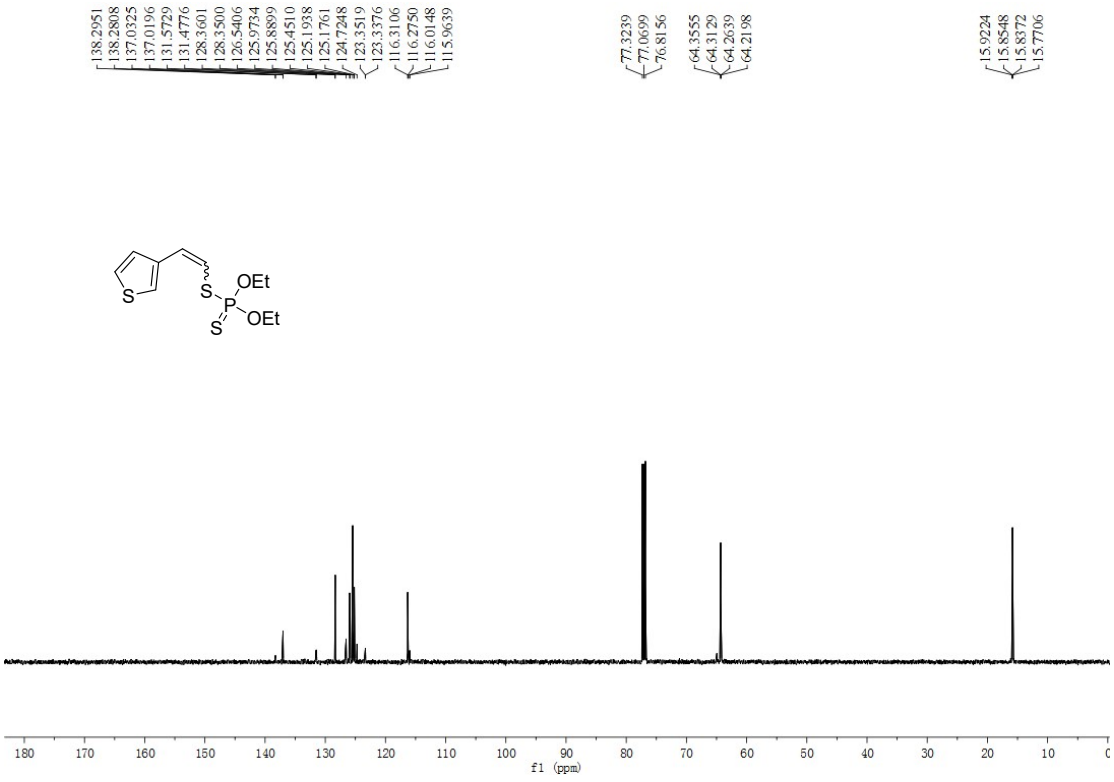
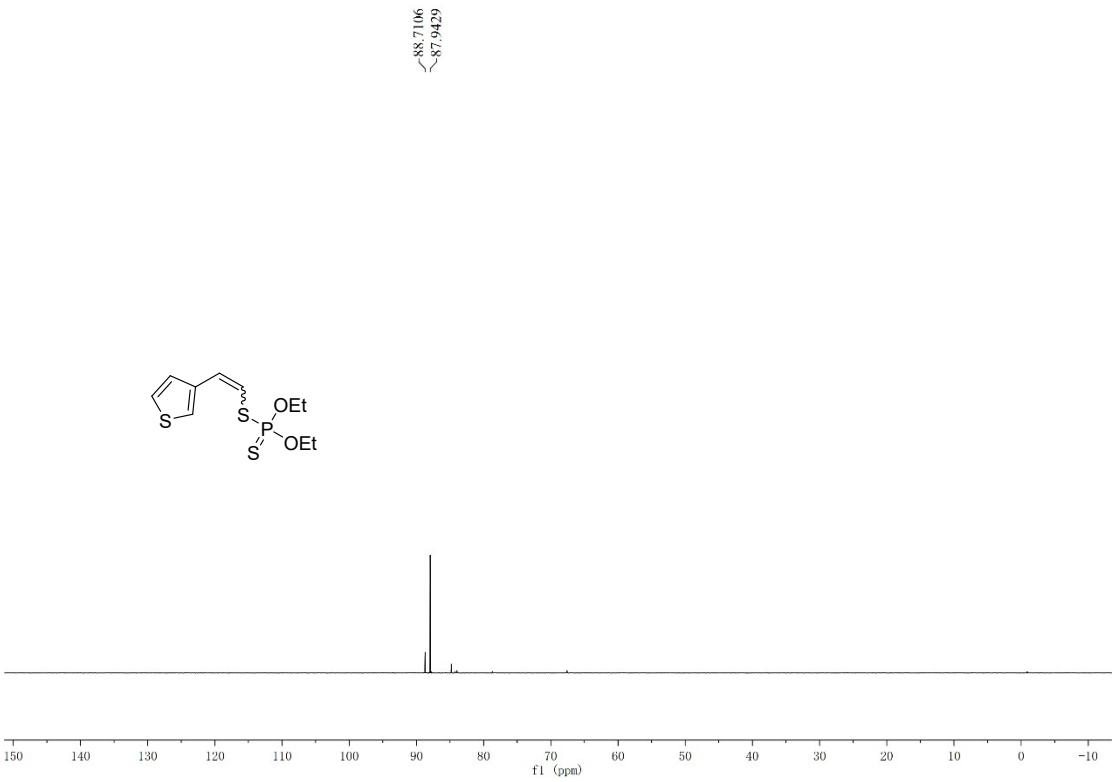
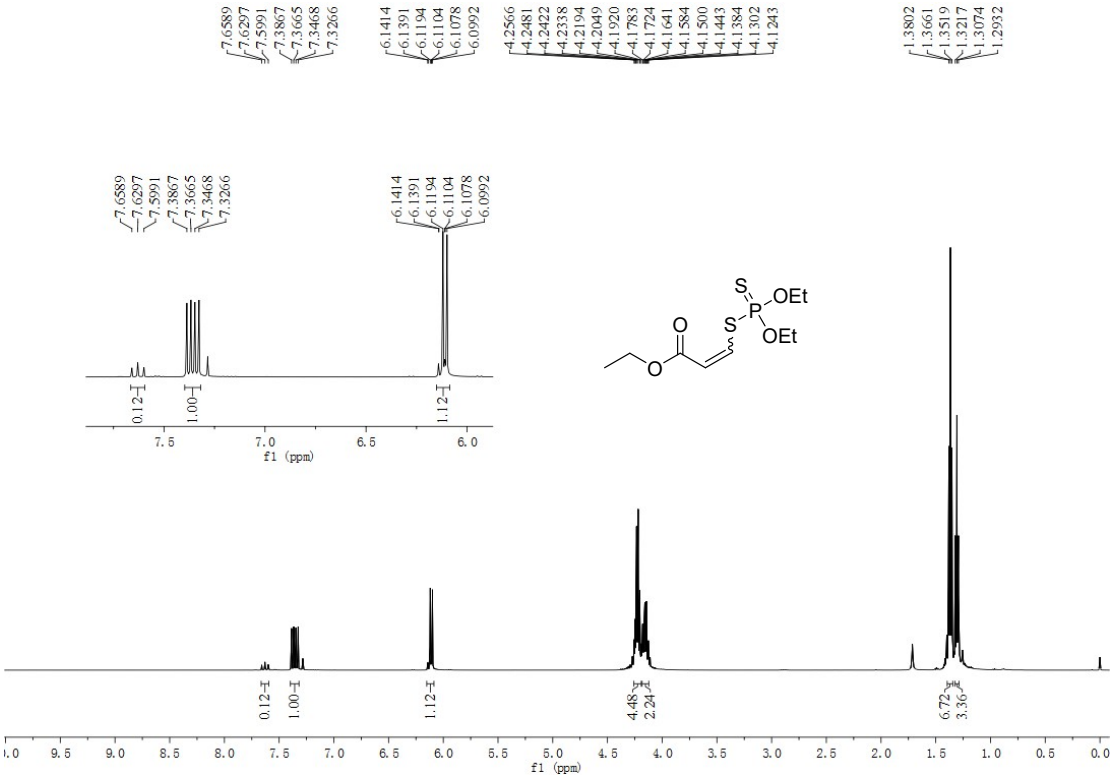


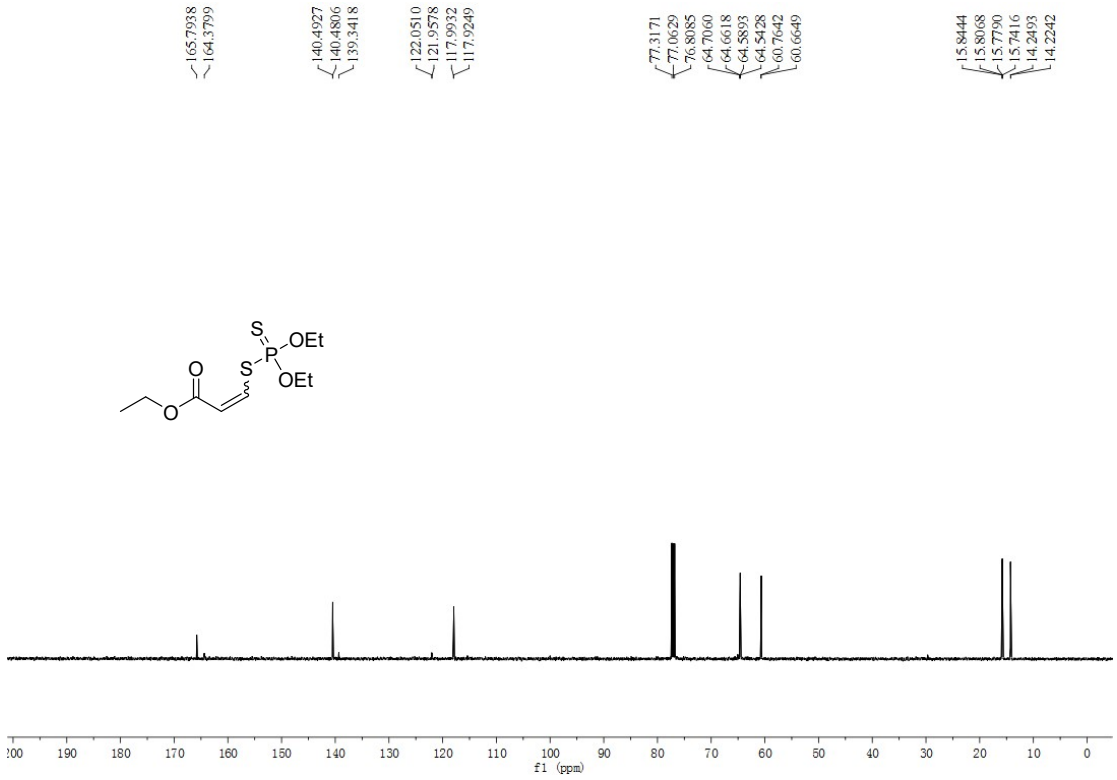
4r ^{31}P NMR (202 MHz, $CDCl_3$)



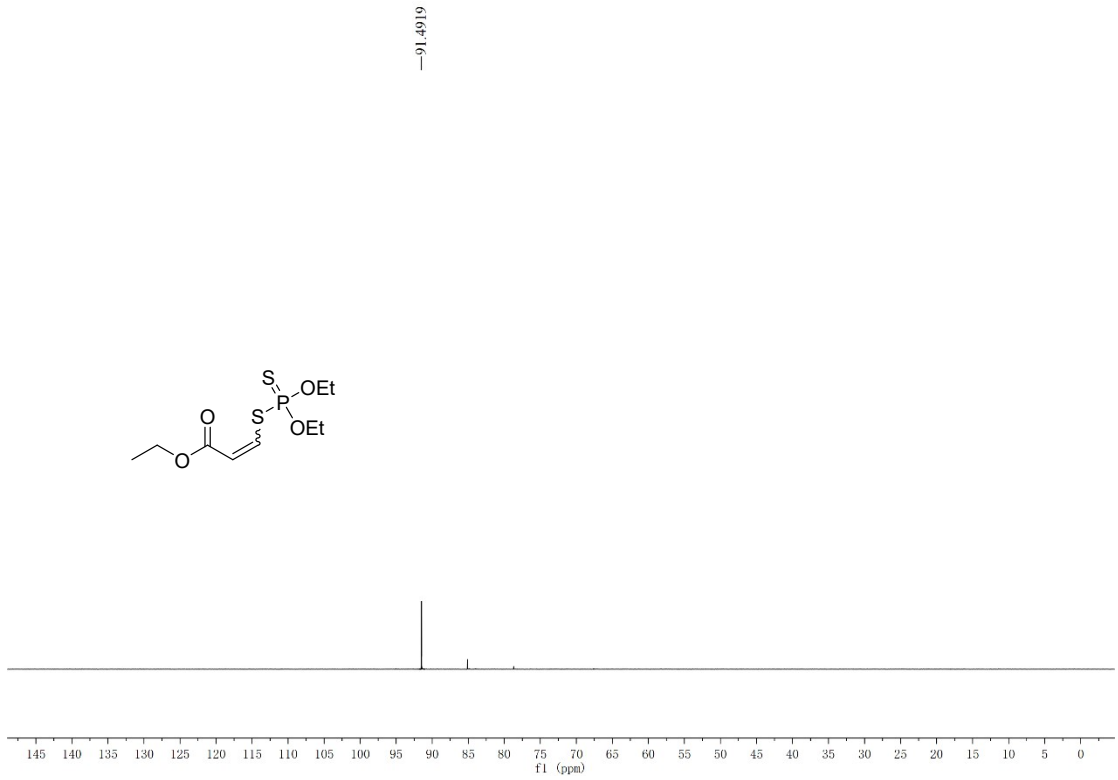
4s ^{1}H NMR (500 MHz, $CDCl_3$)



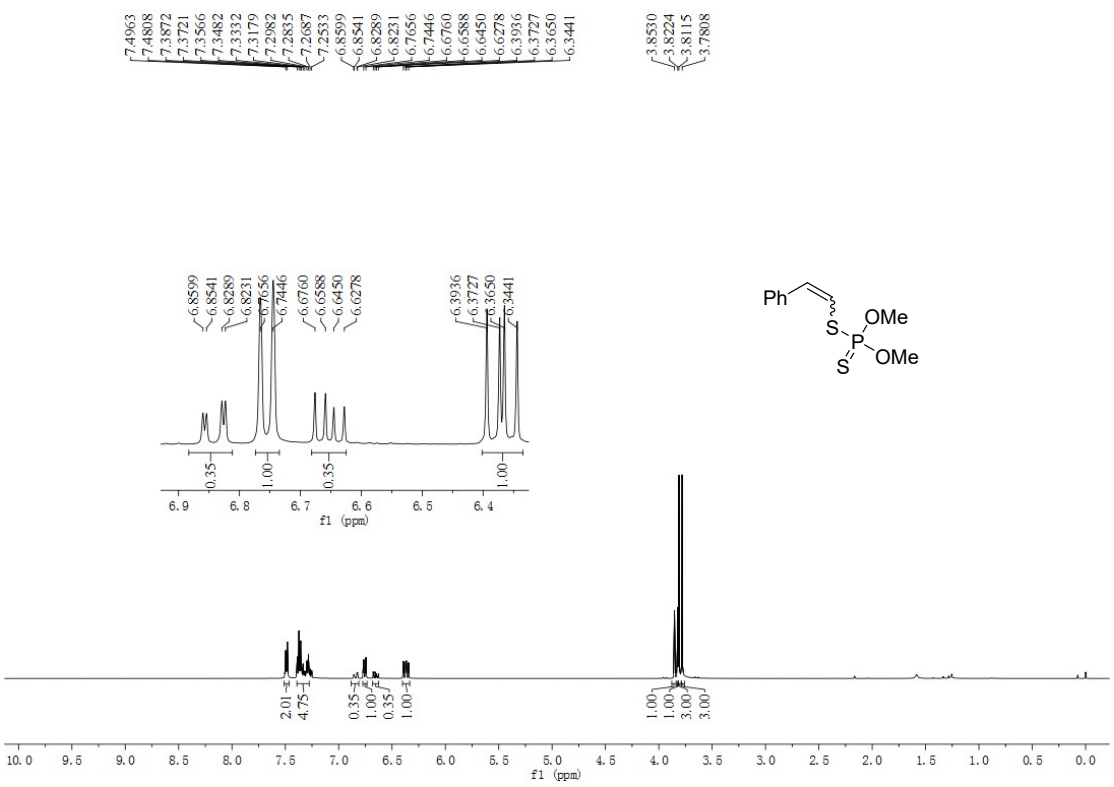
4s ^{13}C NMR (125MHz, $CDCl_3$)



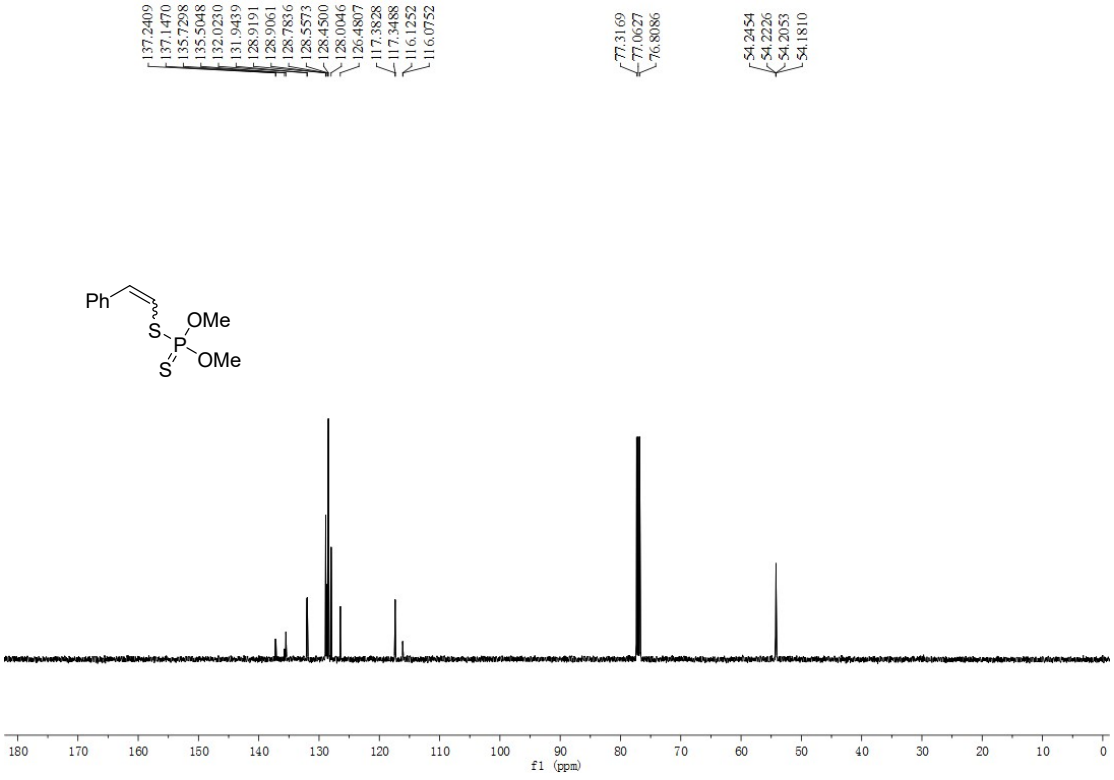
4s ^{31}P NMR (202 MHz, $CDCl_3$)



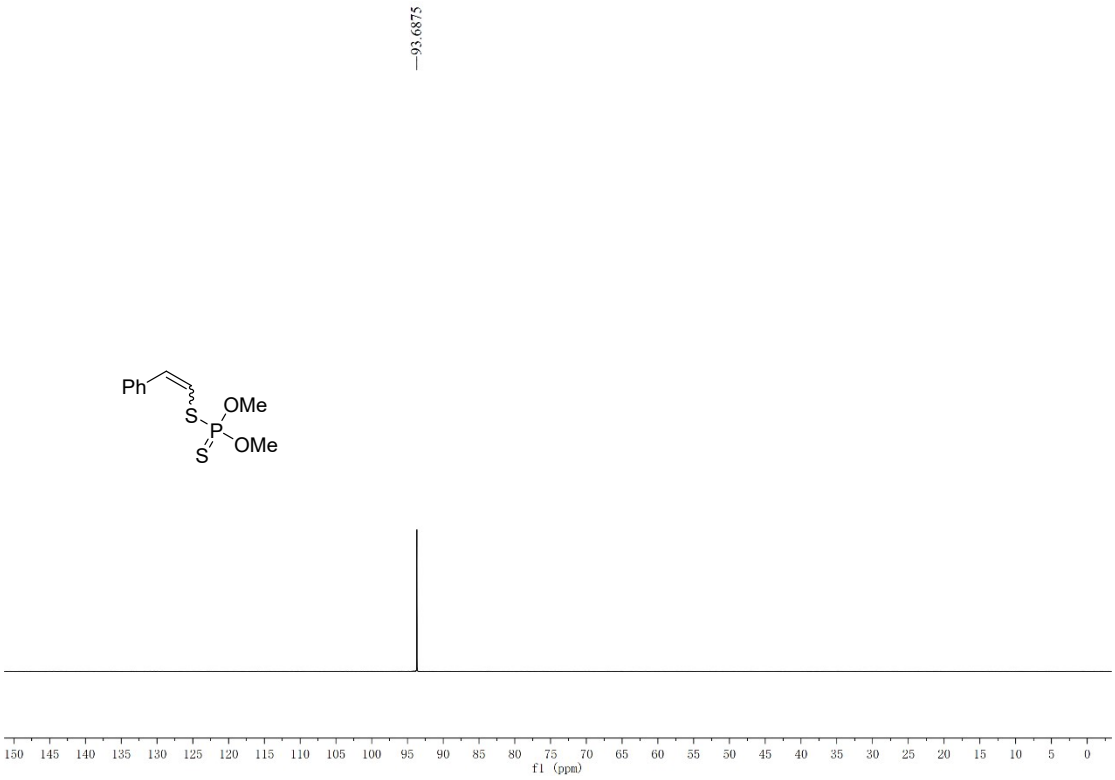
4t ^{1}H NMR (500 MHz, $CDCl_3$)



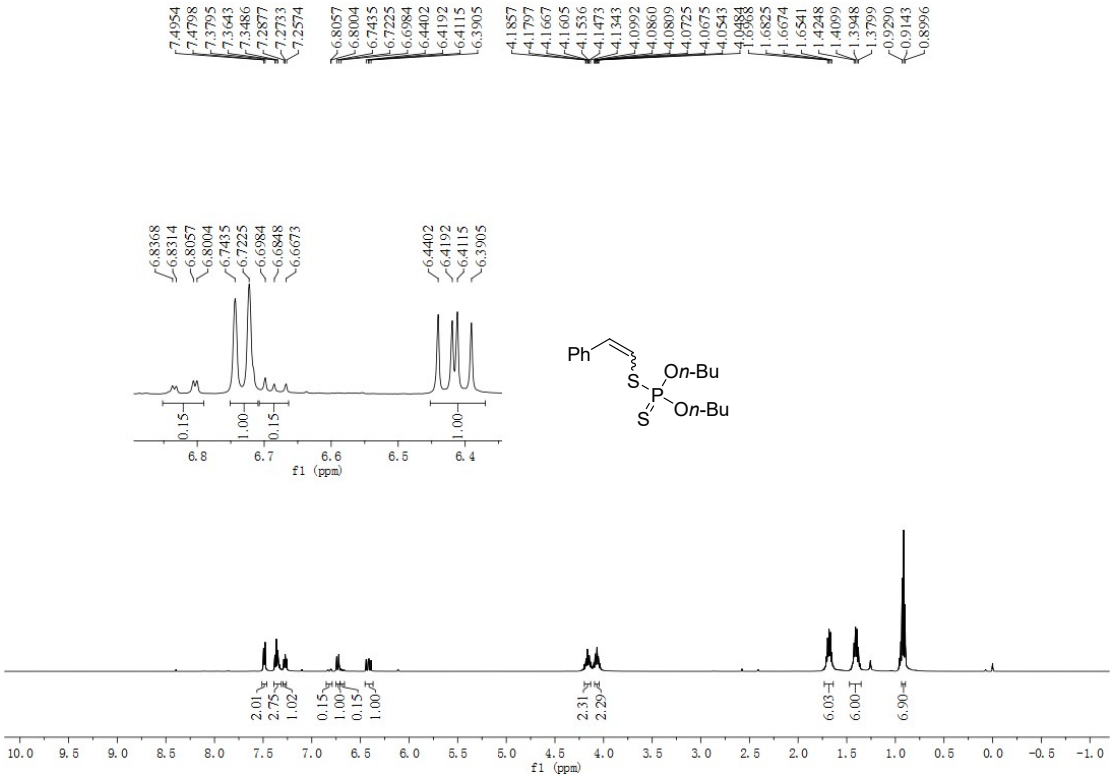
4t ^{13}C NMR (125MHz, $CDCl_3$)



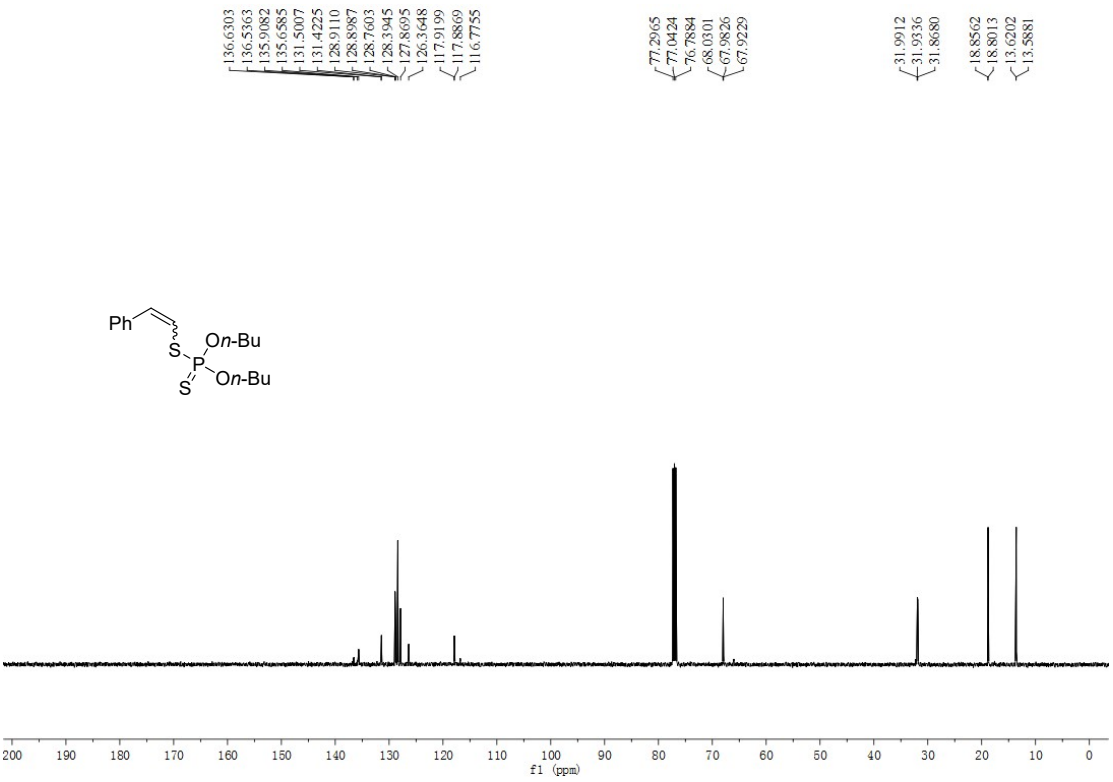
4t ^{31}P NMR (202 MHz, $CDCl_3$)



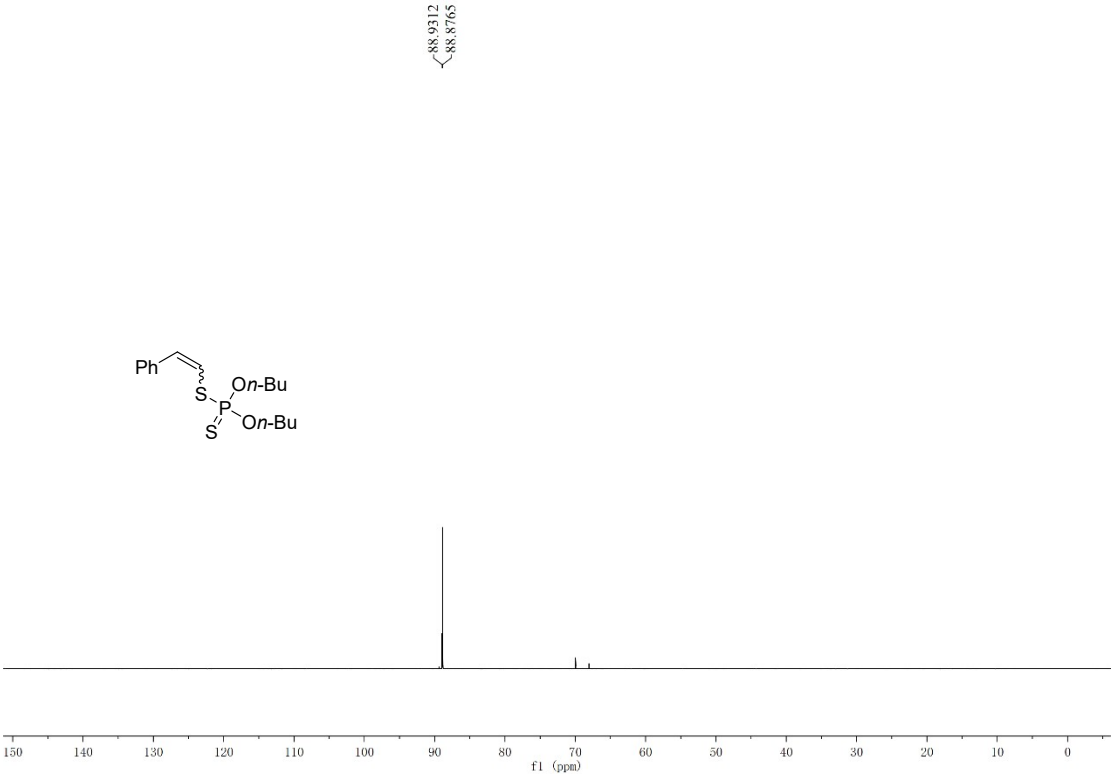
4u ^{1}H NMR (500 MHz, $CDCl_3$)



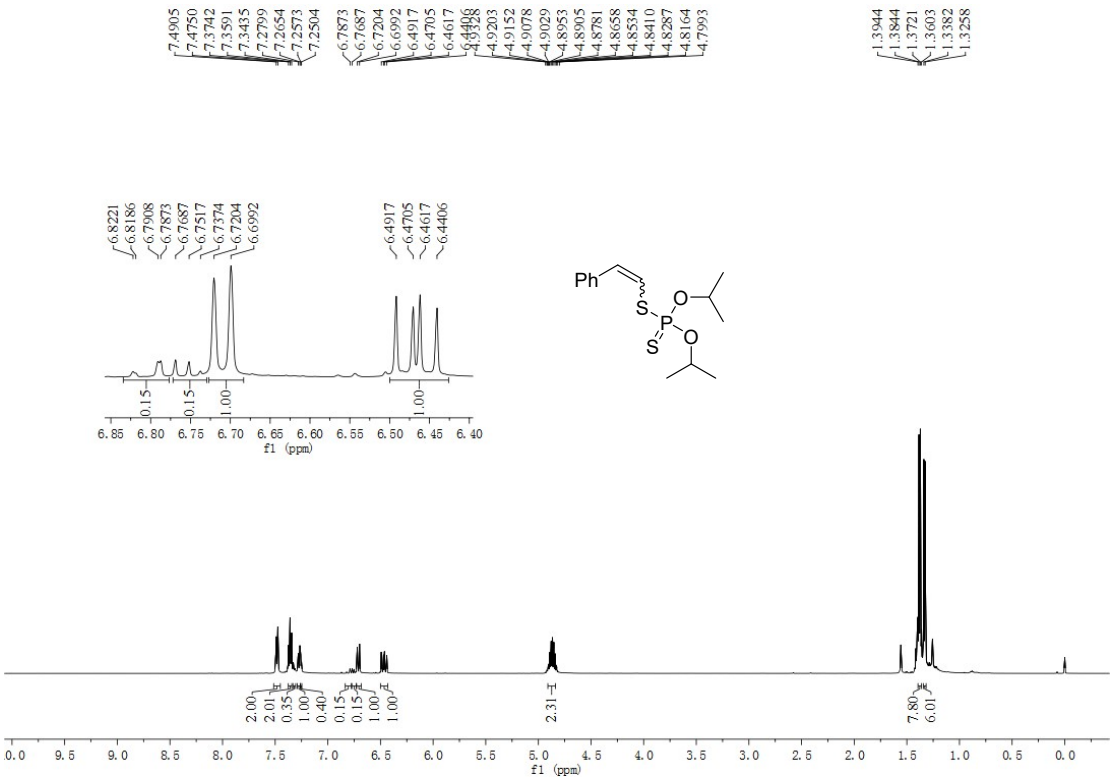
4u ^{13}C NMR (125MHz, $CDCl_3$)



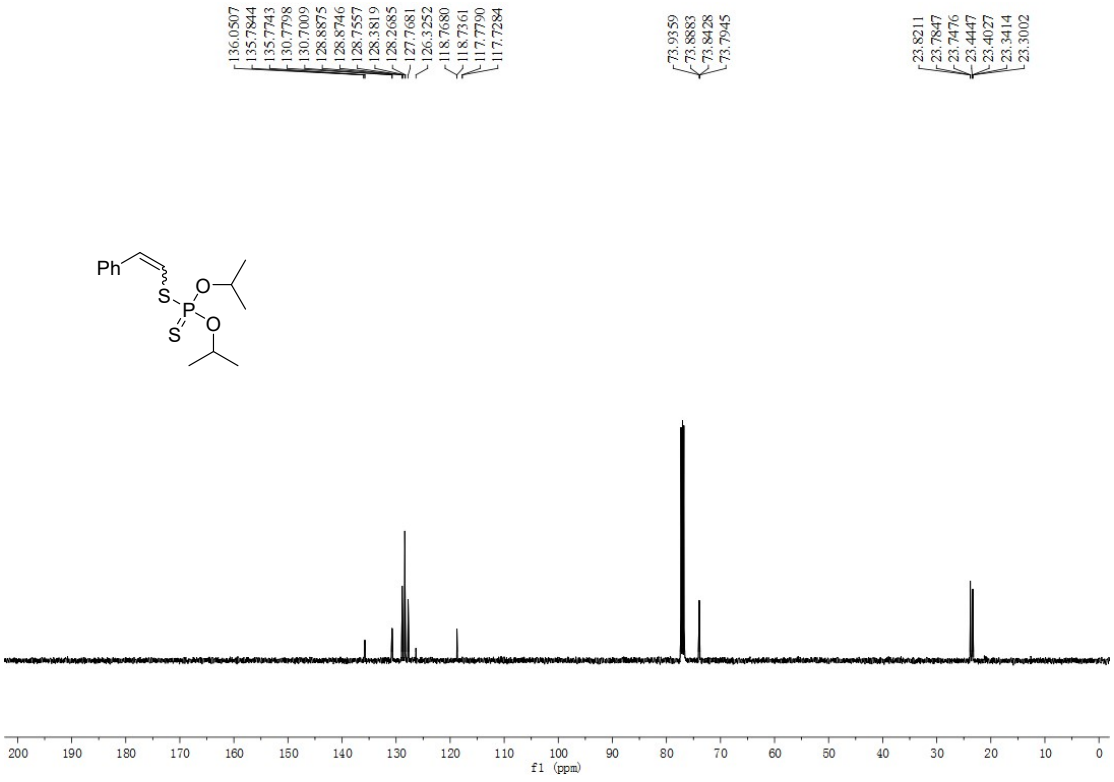
4u ^{31}P NMR (202 MHz, $CDCl_3$)



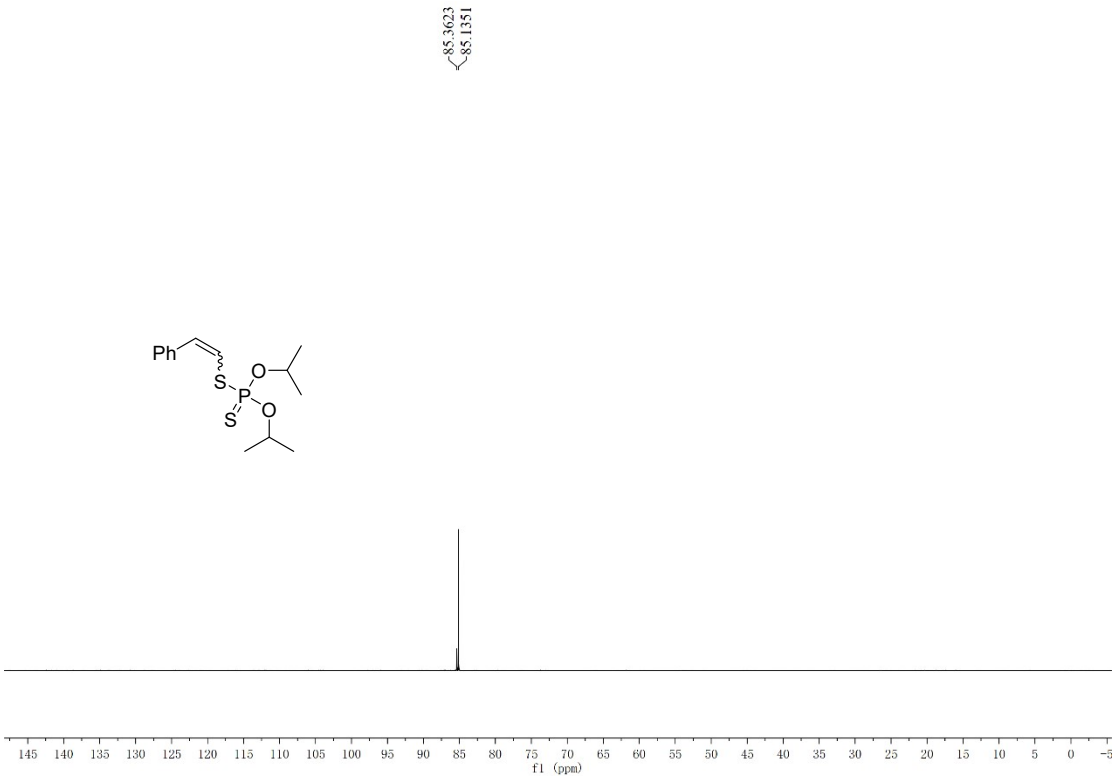
4v ^{1}H NMR (500 MHz, $CDCl_3$)



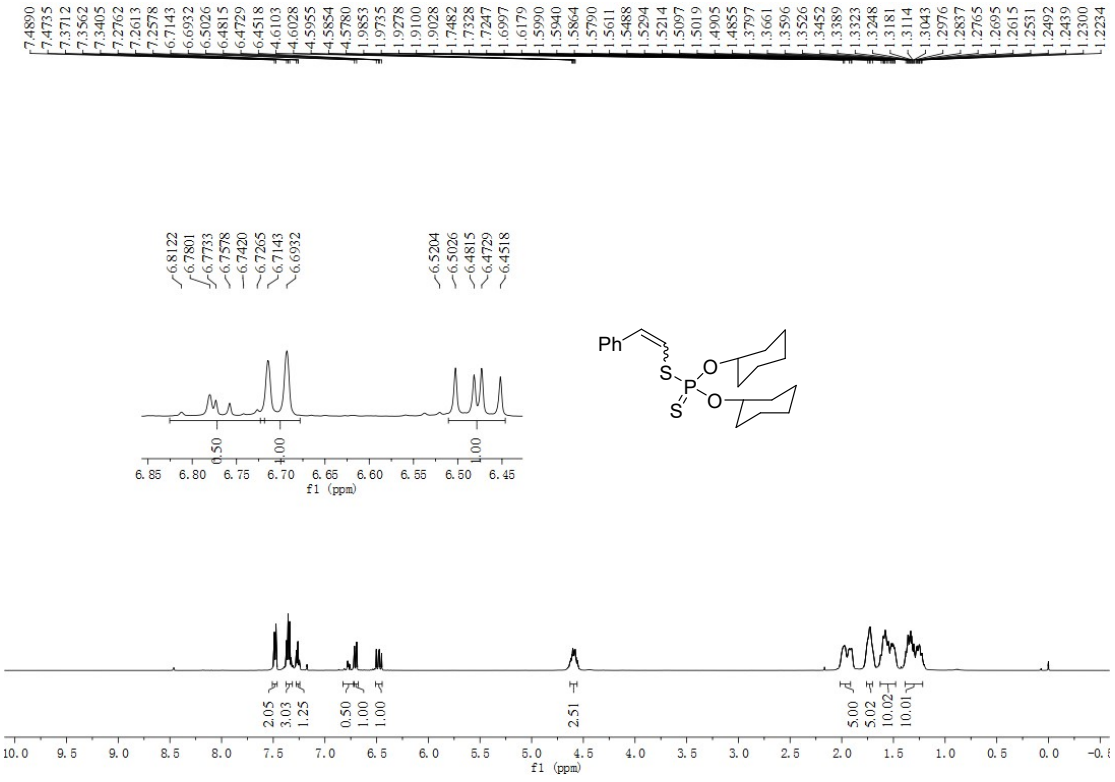
4v ^{13}C NMR (125MHz, $CDCl_3$)



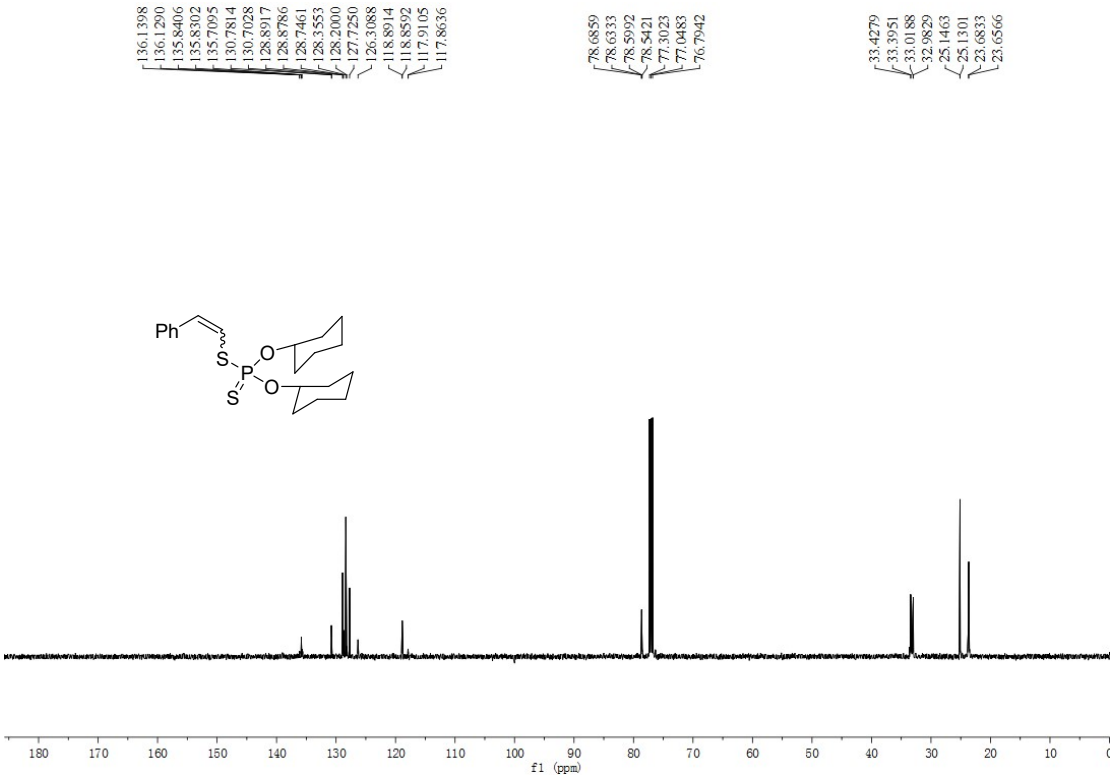
4v ^{31}P NMR (202 MHz, $CDCl_3$)



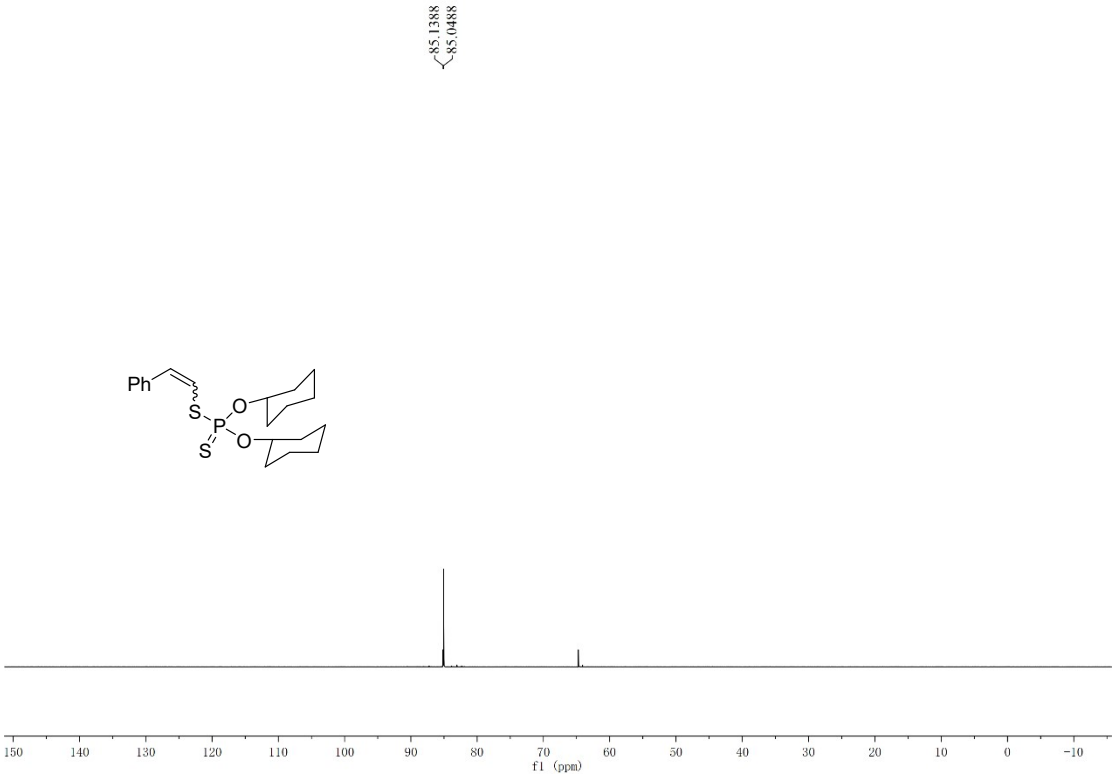
4w ^{1}H NMR (500 MHz, $CDCl_3$)



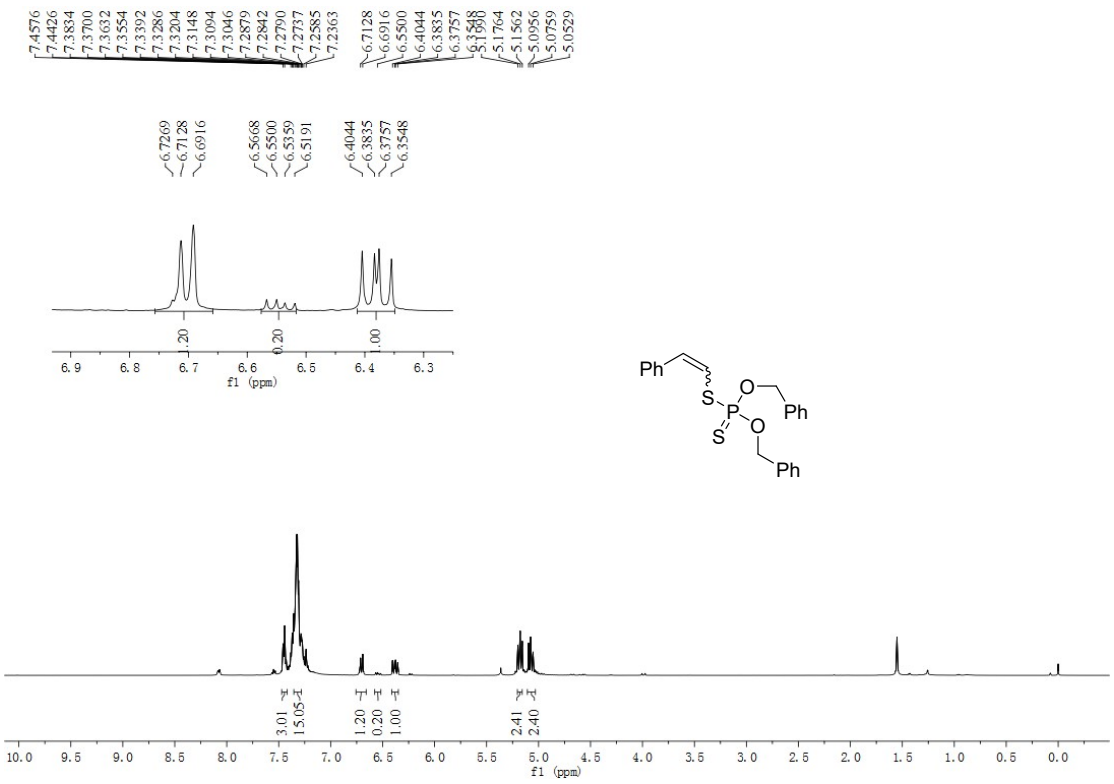
4w ^{13}C NMR (125MHz, $CDCl_3$)



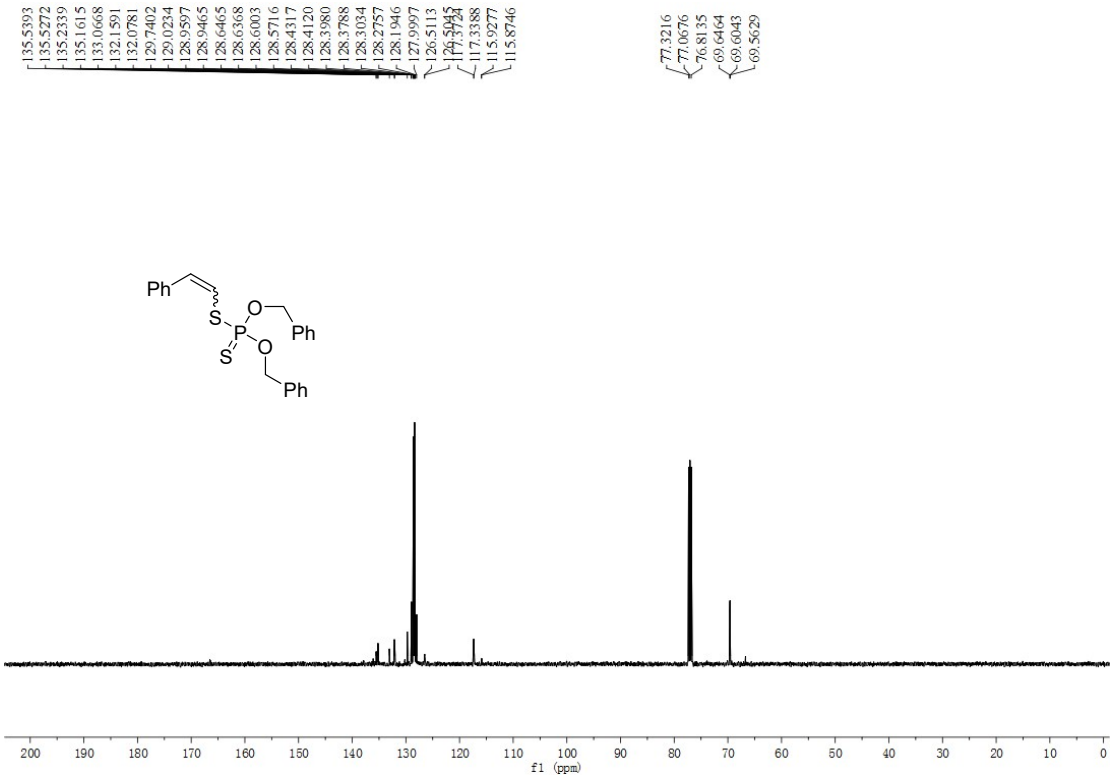
4w ^{31}P NMR (202 MHz, $CDCl_3$)



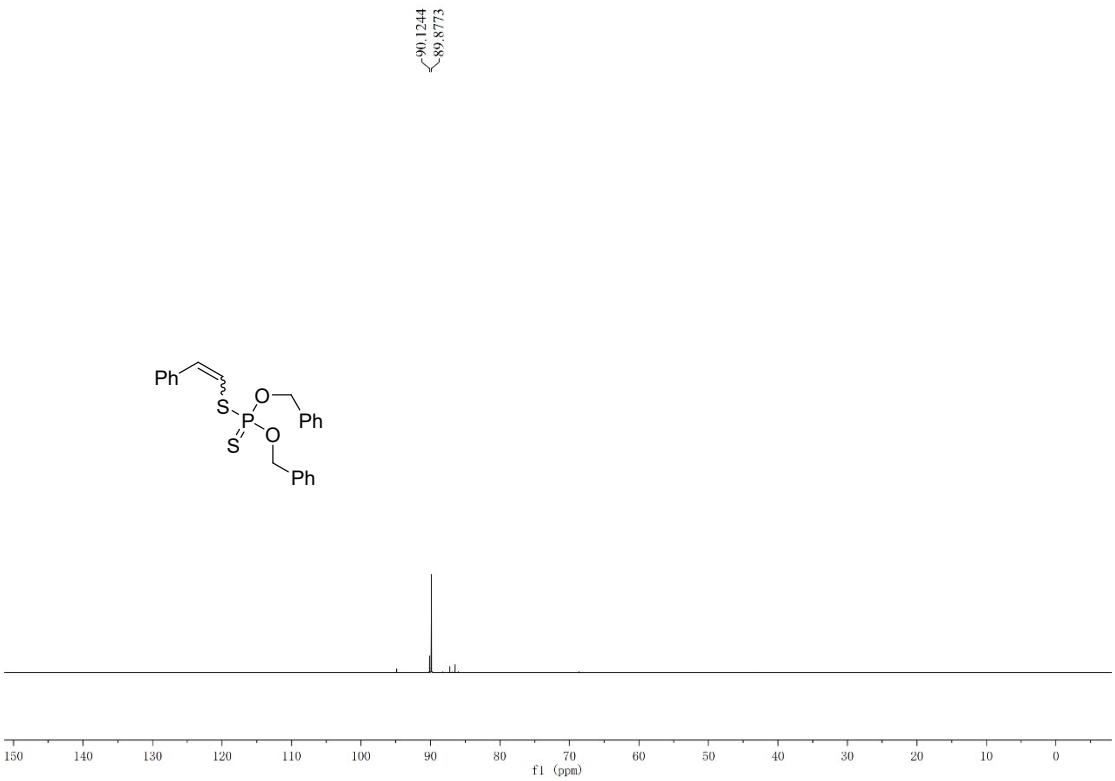
4x ^{1}H NMR (500 MHz, $CDCl_3$)



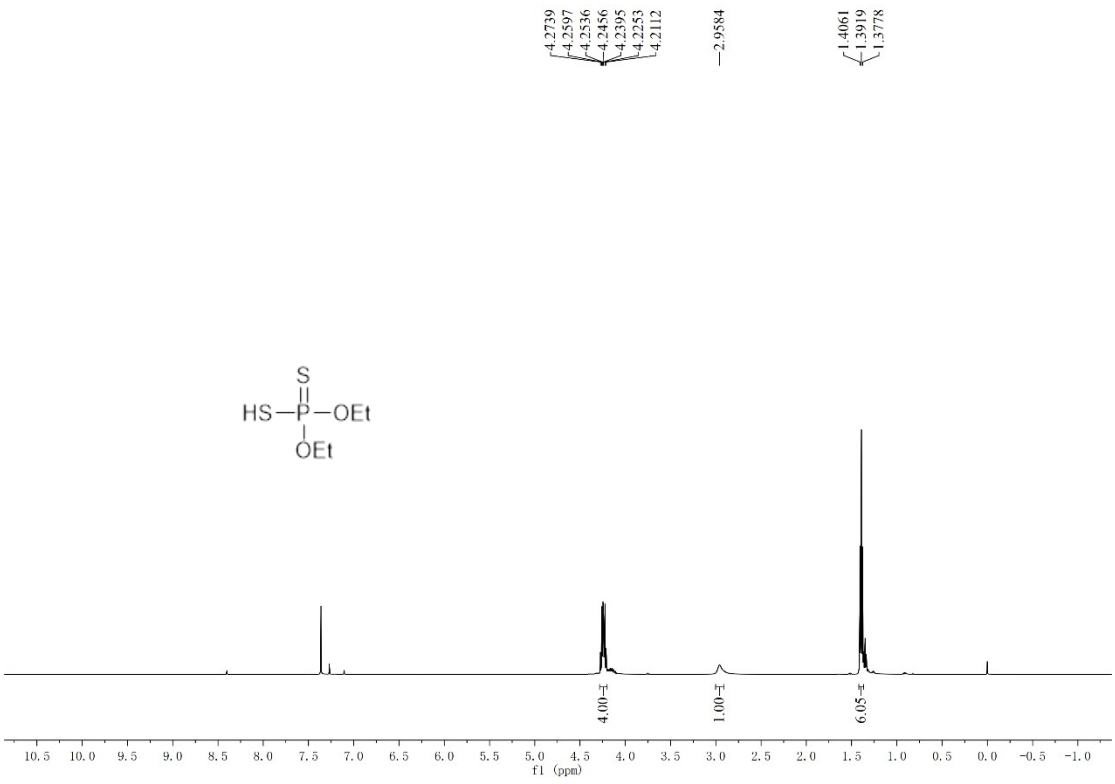
4x ^{13}C NMR (125MHz, $CDCl_3$)



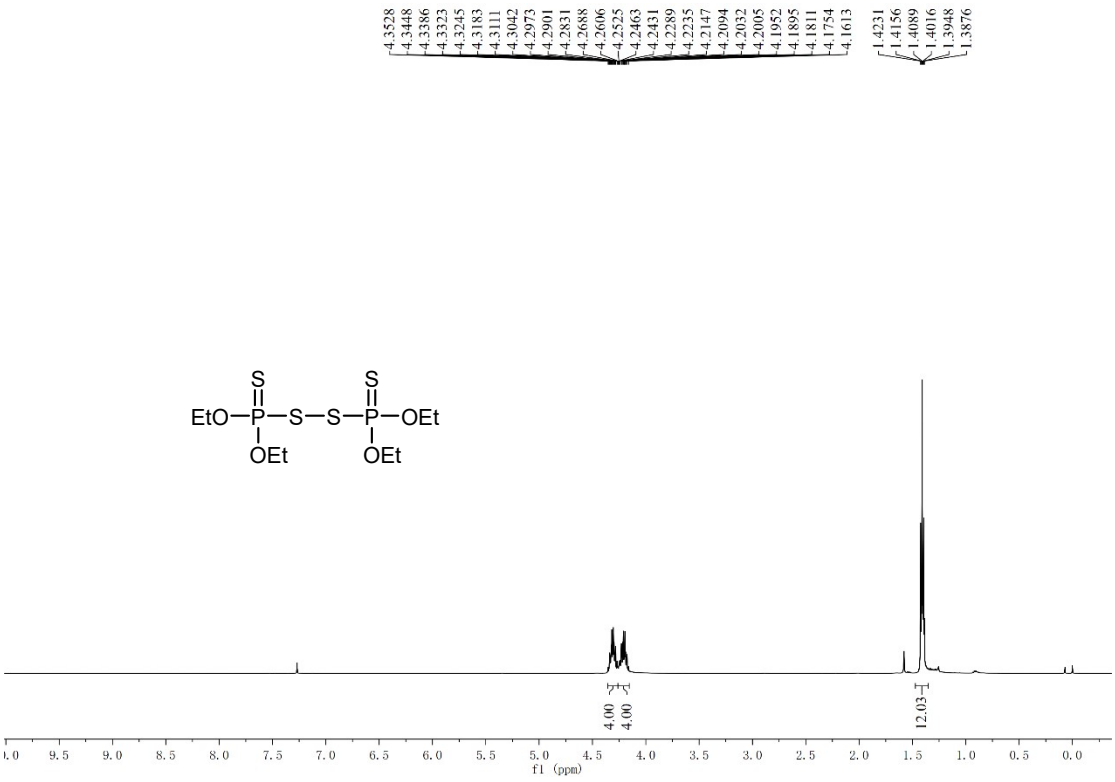
4x ^{31}P NMR (202 MHz, $CDCl_3$)



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



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



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