Supporting Information

Photocatalytic Formation of P-S Bonds via CdSeS/CdZnS Quantum Dots under Visible Light Irradiation

Xiao-Rui Liu,[a,d,#] Zi-Jun Lei,[a,#] Yue-Yue Zhang,[a] Hui-Ling Lu,[a] Fu-Gang Zhao,[a] Xunshan Liu,[a,c,*], Jian-Hai Zhou,[b,*] Yong-Miao Shen,[a,c,d*] Xiaogang Peng[c]

[a]*School of Chemistry and Chemical Engineering, Zhejiang Sci-Tech University, Zhejiang Key Laboratory of Polymer Surface and Interface Science, Hangzhou 310018, China*

[b]*Najing Technology Corporation Ltd, 428 Qiuyi Road Building No. 3, Binjiang District, Hangzhou, Zhejiang, 310052, People's Republic of China.*

[c]*Key Laboratory of Excited-State Materials of Zhejiang Province, Zhejiang University, Hangzhou 310027, PR China.*

[d]*Zhejiang Sci-Tech University Shengzhou Innovation Research Institute, Shengzhou 312400, PR China.*

[#]*X.-R. L. and Z.-J. L contributed equally.*

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1.General Information

General Remarks. Catalytic reactions were performed under an atmosphere of Ar in a glassware. Glassware was pre-dried in an oven at 100°C for several hours and cooled prior to use. All solvents were purchased from Energy Chemical, Macklin Biochemical or Sinopharm reagents. All chemicals were used directly without any further purification. Analytical TLC was performed with silica gel GF254 plates. For column chromatography, a 200-300 mesh silica gel was employed. Room temperature (r.t.) is 23-25 °C.

Instrumentation. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^{1}H NMR spectra were recorded on Bruker AVANCE III 400 and INOVA instruments with 400 MHz frequencies, and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 with 100 MHz frequencies. ^{31}P NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer with a ^{31}P operating frequency of 162 MHz. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). HRMS was obtained using a Q-TOF instrument equipped with an ESI source. Data collection for crystal structure was performed at room temperature using Mo Kα radiation on a Bruker APEXII diffractometer.

Light source in detail. The light source used for photochemical experiments was a household 3 W fluorescent bulb (**Figure S1**). The reaction vessel is borosilicate glass test tube and no filters were applied.

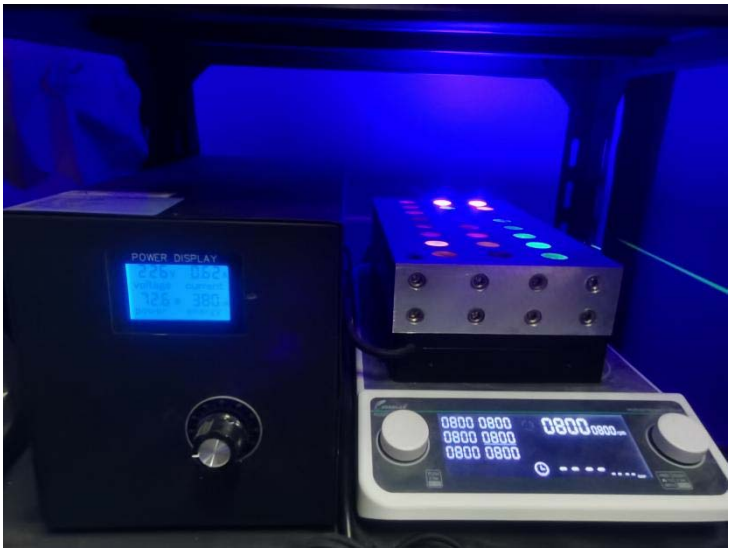


Figure S1. Reaction device

LED fixed lamp (**Figure S2**), 15-40 W (λ = 460 ± 15 nm). Product model: PLS-LED 100. 3W blue LED , purchased from taobao.COM. Manufacturer: Beijing Perfect light Technology Co., Ltd. (China). The reaction vessel is borosilicate glass test tube and no filters were applied. The distance from the light source to the irradiation vessel is 4-5 cm.

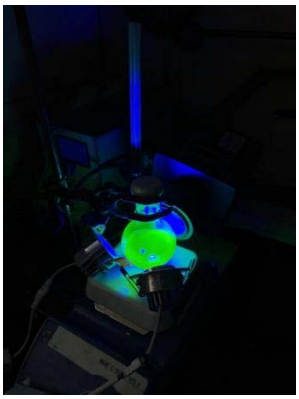


Figure S2. Photoreaction setup for scale-up reaction.

LED fixed lamp (**Figure S3**), 3 W blue LED, purchased from taobao.COM. The reaction vessel is borosilicate glass test tube and no filters were applied. The distance from the light source to the irradiation vessel is 2-3 cm.

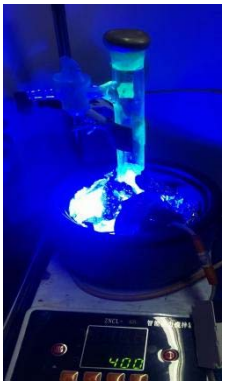


Figure S3. Photoreaction setup for liquid nitrogen deoxygenation reaction.

2. Preparation of CdSeS/CdZnS Quantum Dots

Synthesis of Cadmium Diethyldithiocarbamate ($Cd(DDTC)_2$), Zinc Diethyldithiocarbamate ($Zn(DDTC)_2$), and Se-S-ODE solution. The compound $Cd(Ac)_2{\cdot}2H_2O$ (10 mmol) was dissolved in 100 mL of distilled water, followed by the dropwise addition of $NaDDTC{\cdot}3H_2O$ (20 mmol) dissolved in 60 mL of distilled water under vigorous stirring. The mixture was stirred for an additional 20 minutes to ensure complete precipitation of $Cd(DDTC)_2$. The resulting white precipitate was collected by filtration, washed with distilled water three times and dried under vacuum. The synthesis of $Zn(DDTC)_2$ followed the same procedure, with $Cd(Ac)_2{\cdot}2H_2O$ being replaced by an equal amount of $Zn(Ac)_2{\cdot}2H_2O$. For epitaxial growth of the shells, the shell precursor solutions were prepared with a given molar ratio of $Cd(DDTC)_2$ and $Zn(DDTC)_2$ in dodecane-amine (dodecane : oleylamine = 3 : 1) solution (0.1 mol/L in total). Se-S-ODE (1-octadecene) solution was prepared by dissolving sulfur powder and selenium power in a certain molar ratio (1 mmol in total) with 10mL of ODE by sonication.

Synthesis of CdSeS Core Quantum Dots. In a typical synthesis, CdO (0.13 g, 0.1 mmol) and oleic acid (0.85 g, 0.003 mmol) were loaded into a 25 mL three-neck flask with 5 mL of ODE. After bubbling with argon for 10 min, the mixture was heated to 250 °C. At this point, Se-S-ODE (0.4 mL) was rapidly injected into the reaction flask. After growth for 10 min, the reaction mixture was allowed to cool to 50 °C, add 0.2 mL of

tributylphosphate (TBP) and 0.2 mL of octylamine into the solution, and stir vigorously for 2.5 minutes. Then add 4 mL of hexane and 8 mL of anhydrous methanol, and stir for another 2.5 minutes. After the solution is layered, discard the part without quantum dots and continue with the above procedure. Then, blow away the hexane and methanol with argon at 60°C, and the remaining solution is the ODE solution containing CdSeS quantum dots.

Synthesis of CdSeS/CdZnS Quantum Dots. Take 0.6 mL of oleylamine and 1 mL of CdSeS-ODE solution, and add the corresponding volume of dodecane to make the total volume of the solution reach 6 mL. Bubble with argon gas for 10 minutes and heat to 80℃, then add 0.05 mL of $Cd(DDTC)_2$ solution and 0.05 mL of $Zn(DDTC)_2$ solution, and elevate the temperature to 160℃ for 20 minutes. After that, cool the solution to 80℃ and repeat the steps until the desired emission wavelength of the quantum dots is achieved.

Quantify the QDs. The total number of core/shell ODs was the same with the one of core QDs. The density of CdSe and CdS was 5810 kg/m^3 and 4820 kg/m^3. In our experiment, the proportion of Se and S was 3:1. Thus it was reasonable that the density of bulk of CdSeS was about 5562 kg/m^3. And the size of CdSeS was about 3 nm. Therefor the mass of one CdSeS quantum dot was about 7.9×10^{-20} g. The molecular mass of CdSeS (Se:S = 3:1) in our experiment was about 179. In other words, the molar weight of Cd-Se-S in one quantum dot was about 4.4×10^{-22} mol. In our experiment, if the reaction progress was completely. The total molar weight of Cd-Se-S was about 1 mmol. Combined with Avogadro constant, the total molar weight of CdSeS QDs was 2.2×10^{-5} mol. Considering the dose of CdSeS for core/shell QDs. The total molar weight of core/shell QDs was about 2.2×10^{-6} mol in 20mL tolune. We use 50uL of QDs into the reaction solution (2.0 mL), so the quantum dot concentration in the reaction solution is about 2.75×10^{-8}mol/L. It should be noted that the concentration derived by this computation is approximately and greater than the actual concentration, so that the TON of this reaction must be greater than what we have reported.

3. General Procedure for Synthesis of Products 4 and 6

To two 4 mL vials respectively equipped with a Teflon septum and magnetic stir bar were added **1** or **5** (0.2 mmol per bottle, 0.4 mmol in total), **3** (0.4 mmol per bottle, 0.8 mmol in total), 2 mL toluene (4 mL toluene in total), 0.5 mL DMSO (1 mL DMSO in total), **2** (0.6 mmol per bottle, 1.2 mmol in total), and CdSeS/CdZnS QDs (50 μL per bottle). The solution was purged with argon gas for 15 minutes irradiated with 3W blue LEDs. After 36 hours, add 12 mL of acetonitrile to precipitate and centrifuge to remove the QDs. Take the organic layer for concentration. The crude mixture was subjected to silica gel (ethyl acetate/petroleum ether 1:5) flash column chromatography, anhydrous magnesium sulfate drying, concentration in vacuum and purification to obtain the desired product **4** or **6**.

4. General Procedure for Synthesis of Products 8 and 9

To two 4 mL vials respectively equipped with a Teflon septum and magnetic stir bar were added **1** or **5** (0.2 mmol per bottle, 0.4 mmol in total), TBPB (0.6 mmol per bottle, 1.2 mmol in total), 2 mL toluene (4 mL toluene in total), 0.5 mL DMSO (1 mL DMSO in total), **7** (0.4 mmol per bottle, 0.8 mmol in total), and CdSeS/CdZnS QDs (50 μL per bottle). The solution was purged with argon gas for 15 minutes irradiated with 3W blue LEDs. After 36 hours, add 12 mL of acetonitrile to precipitate and centrifuge to remove the QDs. Take the organic layer for concentration. The crude mixture was subjected to silica gel (ethyl acetate/petroleum ether 1:6) flash column chromatography, anhydrous magnesium sulfate drying, concentration in vacuum and purification to obtain the desired product **8** or **9**.

5. Recycling of Quantum Dots

To verify the low contamination and repeatability of the reaction, we examined it by ICP-OES. The traditional quantum dots and the quantum dots used in our reaction were dried before testing. And before testing, the reaction stock solution was settled by 12 ml acetonitrile and centrifuged to remove the quantum dots in the reaction solution.

To reuse the catalysis of QDs, we need to precipitate nuclear / shell QDs (QDs) from the reaction solution. The crude reaction solution was combined with 50 ml of acetonitrile in a 100 ml centrifuge tube. Subsequently, the tube was inserted into a centrifuge and spun at a speed of 4000 rpm for 3 minutes. The resulting supernatant was discarded, while the obtained precipitate (QDs) was dissolved in toluene.Then put into the reaction to obtain the product **4**, repeat the above operation to obtain the yield of **4** .

Table S1. ICP-OES detection results of quantum dots

Sample number	quantity (g)	constant volume/ V_0 (mL)	Test elements	Test element concentration/C_o (mg/L)	dilution ratio/f	Elemental concentration of the original sample solution/C_1 (mg/L)	Sample element content/C_x (mg/kg)	Percent of sample element content/ W (%)
Z-QDs	0.0348	25	Zn	0.079	1	0.079	56.75	0.006
P-QDs	0.0271	25	Zn	9.341	100	934.100	861715.87	86.2
RL	1ML	25	Zn	0.512	25	12.800	/	/
Z-QDs	0.0348	25	Cd	8.935	100	893.500	641882.18	64.2
P-QDs	0.0271	25	Cd	1.334	100	133.400	123062.73	12.3
RL	1ML	25	Cd	0.008	25	0.200	/	/

Z-QDs: traditional QDs, P-QDs: The QDs used in the reaction, RL: The treated reaction solution.

Table S2. Catalyst recycling

entry	Time(h)	Yield (%)
1	36	91
2	36	90
3	36	>99

6. Absorption and photoluminescence spectra of CdSeS/CdZnS QDs

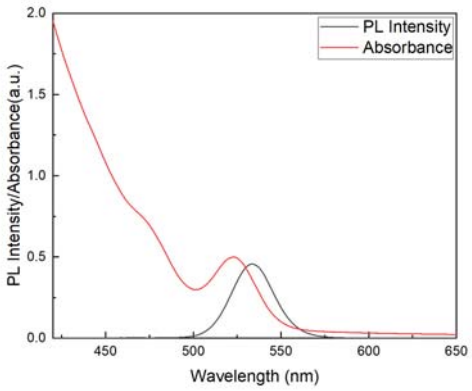


Figure S4a. Absorption and fluorescence spectra of CdSeS/CdZnS QDs

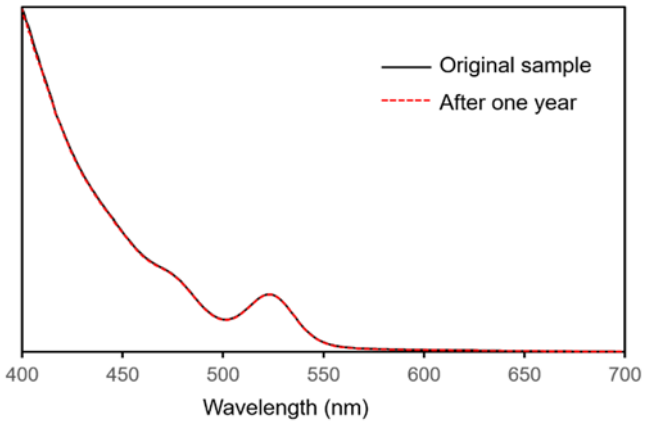


Figure S4b. Stability of CdSeS / CdZnS QDs in toluene

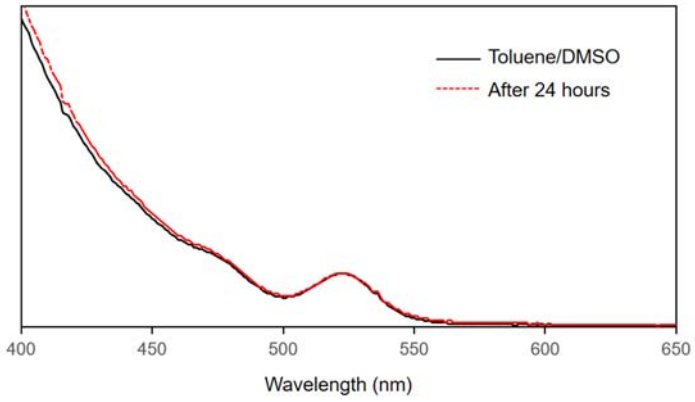
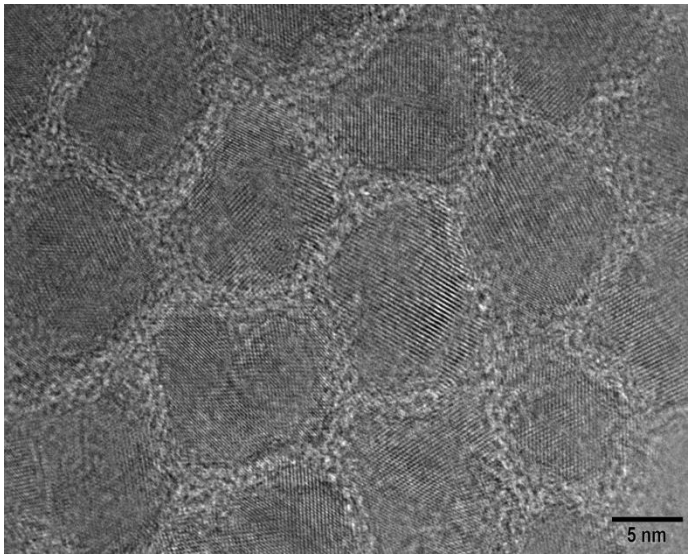
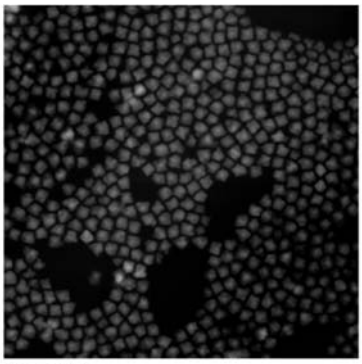


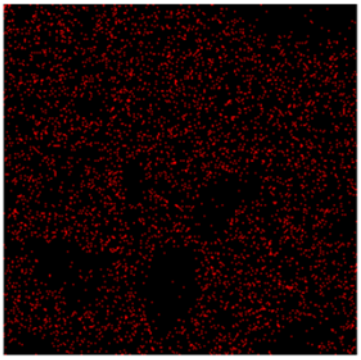
Figure S4c. Stability of CdSeS/CdZnS QDs in toluene/DMSO

7. EDS Mapping Results

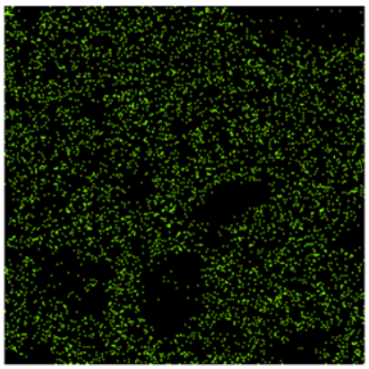




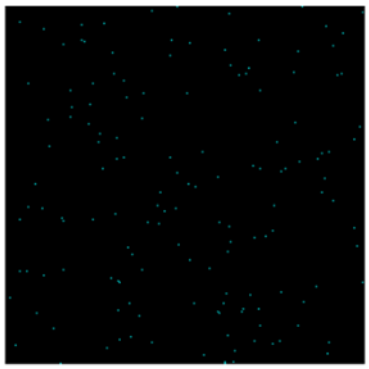
电子图像 1



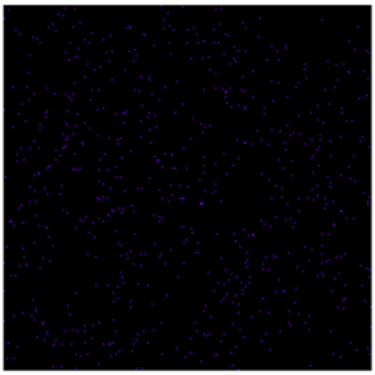
S Ka1



Zn Ka1



Se Ka1



Cd La1

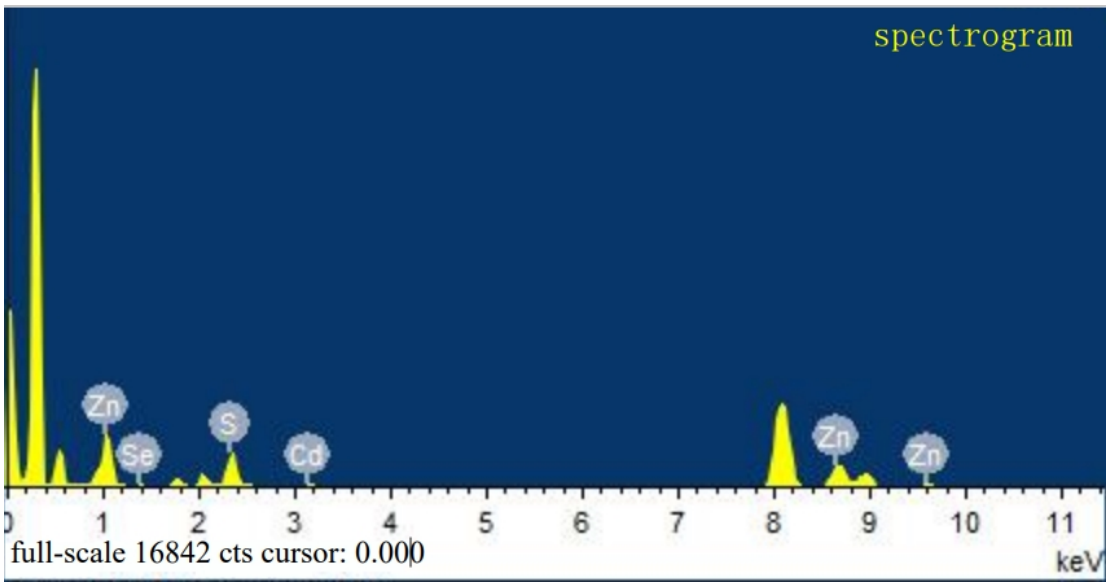


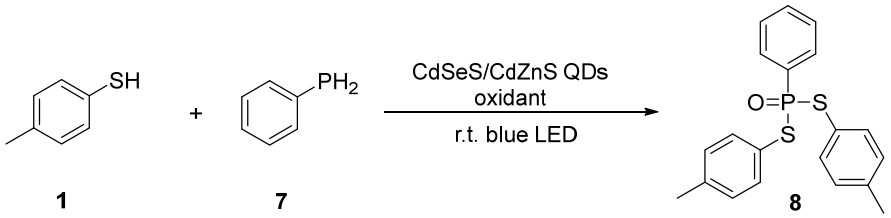
Figure S5. The HRTEM EDS-Mapping diagram of CdSeS/CdZnS QDs

Table S3. The elemental analysis of CdSeS/CdZnS QDs

Element	Weight percentage	Atomic percent
S K	36.36	55.31
Zn K	54.67	40.79
Se K	0.04	0.03
Cd L	8.93	3.87
Total quantity	100.0	

8. Optimization Experiments of Phenylphosphine

Table S4. Selected optimization experiments of phenylphosphine



1 **7** **8**

entry[a]	1 (mmol)	7 (mmol)	Oxidant (mmol)	Solvent(mL)	Oxidant	Yield (%)
1	0.2	0.6	0.4	2 mL toluene	benzophenone	13
2	0.2	0.6	0.4	2 mL dichloromethane	benzophenone	6
3	0.2	0.6	0.4	2 mL heptane	benzophenone	11
4	0.2	0.6	0.4	2 mL toluene/0.5 mL ethanol	benzophenone	10

5	0.2	0.6	0.4	2 mL toluene/0.5 mL DMSO	benzophenone	20
6	0.2	0.6	0.4	2 mL toluene/0.5 mL DMSO	TBPB[d]	37
7	0.2	0.6	0.4	2 mL toluene/0.5 mL DMSO	H_2O_2	24
8	0.2	0.6	0.4	2 mL toluene/0.5 mL DMSO	azobenzene	27
9	0.2	0.6	0.4	2 mL toluene/0.5 mL DMSO	4-hydroxybenzaldehyde	28
10	0.2	0.6	0	2 mL toluene/0.5 mL DMSO	/	19
11	0.4	0.2	0.4	2 mL toluene/0.5 mL DMSO	TBPB	30
12	0.4	0.2	0.6	2 mL toluene/0.5 mL DMSO	TBPB	38
13	0.2	0.4	0.6	2 mL toluene/0.5 mL DMSO	TBPB	62
14[b]	0.2	0.4	0.6	2 mL toluene/0.5 mL DMSO	TBPB	trace
15[c]	0.2	0.4	0.6	2 mL toluene/0.5 mL DMSO	TBPB	trace

[a]Reaction conditions: **1a** (0.2 mmol), **7** (0.4 mmol), 50 μL CdSeS/CdZnS QDs in solvent (2 mL toluene/0.5 mL DMSO) were irradiated with 3 W blue LEDs at room temperature under Ar for 36 h. [b]The reaction was performed in the dark. [c]The reaction wasperformed without photocatalyst. [d]The TBPB is tert-Butyl peroxybenzoate.

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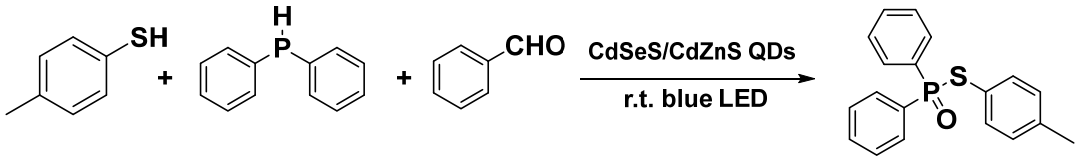
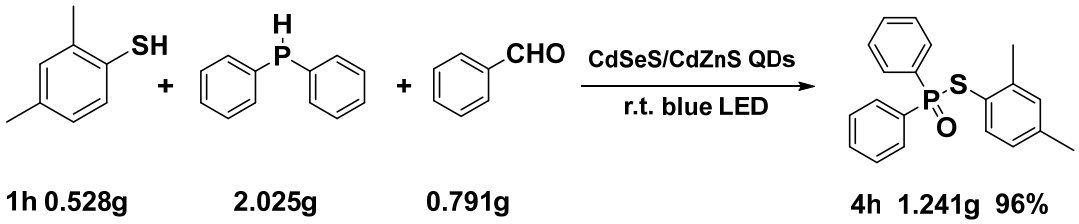
9. Gram-Scale Reaction



1a 0.433g **1.962g** **0.752g** **4a 0.896g 79%**

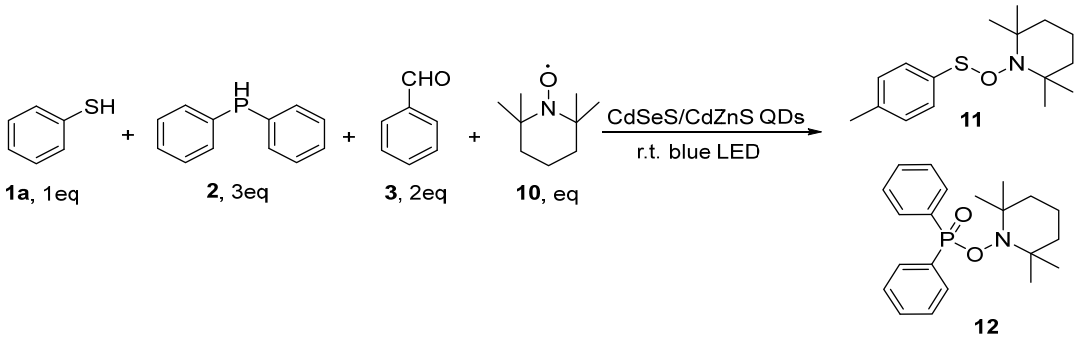
In a 100ml round bottom flask, **1a** (0.433 g, 3.5 mmol), **2** (1.962 g, 10.5 mmol), **3** (0.752 g, 7.1 mmol), and 75 microliters of CdSeS/CdZnS QDs were dissolved in toluene (30ml) and DMSO (7.5 mL). The reaction mixture was mixed with argon for 30 min and reacted at 42 W blue LED for 36h. After the reaction, the reaction

mixture was diluted with acetonitrile and centrifuged to remove CdSeS/CdZnS QDs. It was then extracted with ethyl acetate (3×100 mL), and the combined organic extract was washed with saline (300 mL), dried with anhydrous sodium sulfate and concentrated in vacuo. The crude mixture was directly purified by column chromatography on silica gel (EtOAc : petroleum ether =1:5) by flash column chromatography to obtain the desired product **4a** (**0.896g, 79%**).



In a 100ml round bottom flask, **1h** (0.528 g, 3.8 mmol), **2** (2.025 g, 10.9 mmol), **3** (0.791 g, 7.1 mmol), and 75 microliters of CdSeS/CdZnS QDs were dissolved in toluene (30ml) and DMSO (7.5 mL). The reaction mixture was mixed with argon for 30 min and reacted at 42 W blue LED for 36h. After the reaction, the reaction mixture was diluted with acetonitrile and centrifuged to remove CdSeS/CdZnS QDs. It was then extracted with ethyl acetate (3×100 mL), and the combined organic extract was washed with saline (300 mL), dried with anhydrous sodium sulfate and concentrated in vacuo. The crude mixture was directly purified by column chromatography on silica gel (EtOAc : petroleum ether =1:5) by flash column chromatography to obtain the desired product **4h** (**1.241g, 96%**).

10. The Radical Trapping Experiments



To a 4 mL vial respectively equipped with a Teflon septum and magnetic stir bar were added **1** (0.2 mmol per bottle, 0.4 mmol in total), **3** (0.4 mmol per bottle, 0.8 mmol in total), **10** (TEMPO, 0.3130 g, 2.0 mmol). 2 mL toluene (4 mL toluene in total), 0.5 mL DMSO (1 mL DMSO in total), **2** (0.6 mmol per bottle, 1.2 mmol in total), and CdSeS/CdZnS QDs (50 μL per bottle). The solution was purged with argon gas for 15 minutes irradiated with 3W blue LEDs. After 36 hours, add 12 mL of acetonitrile to precipitate and centrifuge to remove the QDs. Take the organic layer for concentration. The crude mixture was subjected to silica gel (ethyl acetate/petroleum ether 1:5) flash column chromatography, anhydrous magnesium sulfate drying, concentration in vacuum and purification to obtain the desired product **11** and **12**.

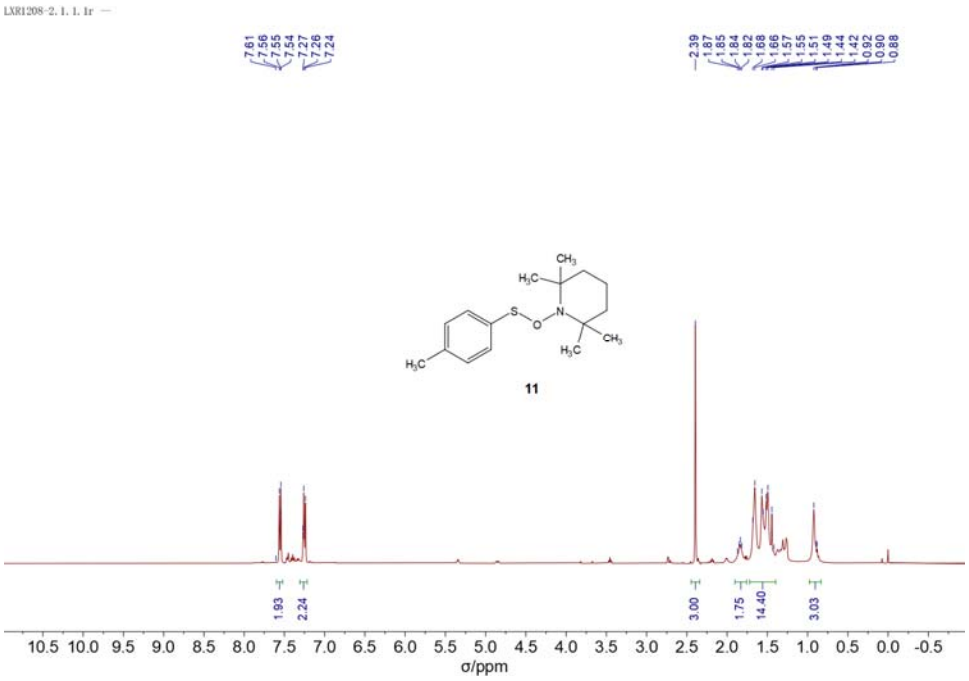


Figure S6. ^{1}H NMR of TEMPO-p-Toluenesulphenol adduct

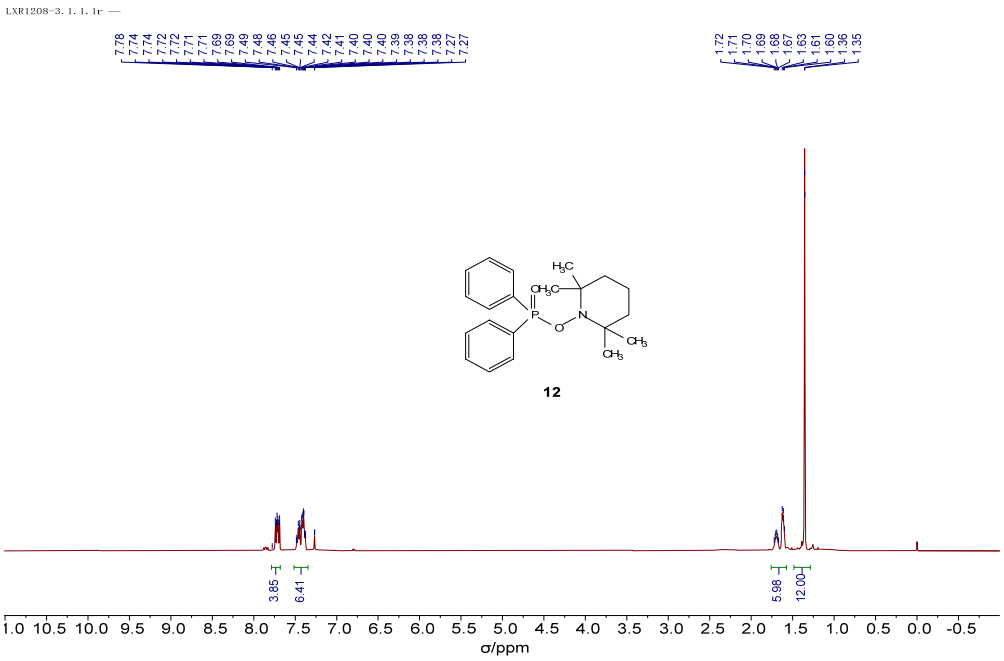
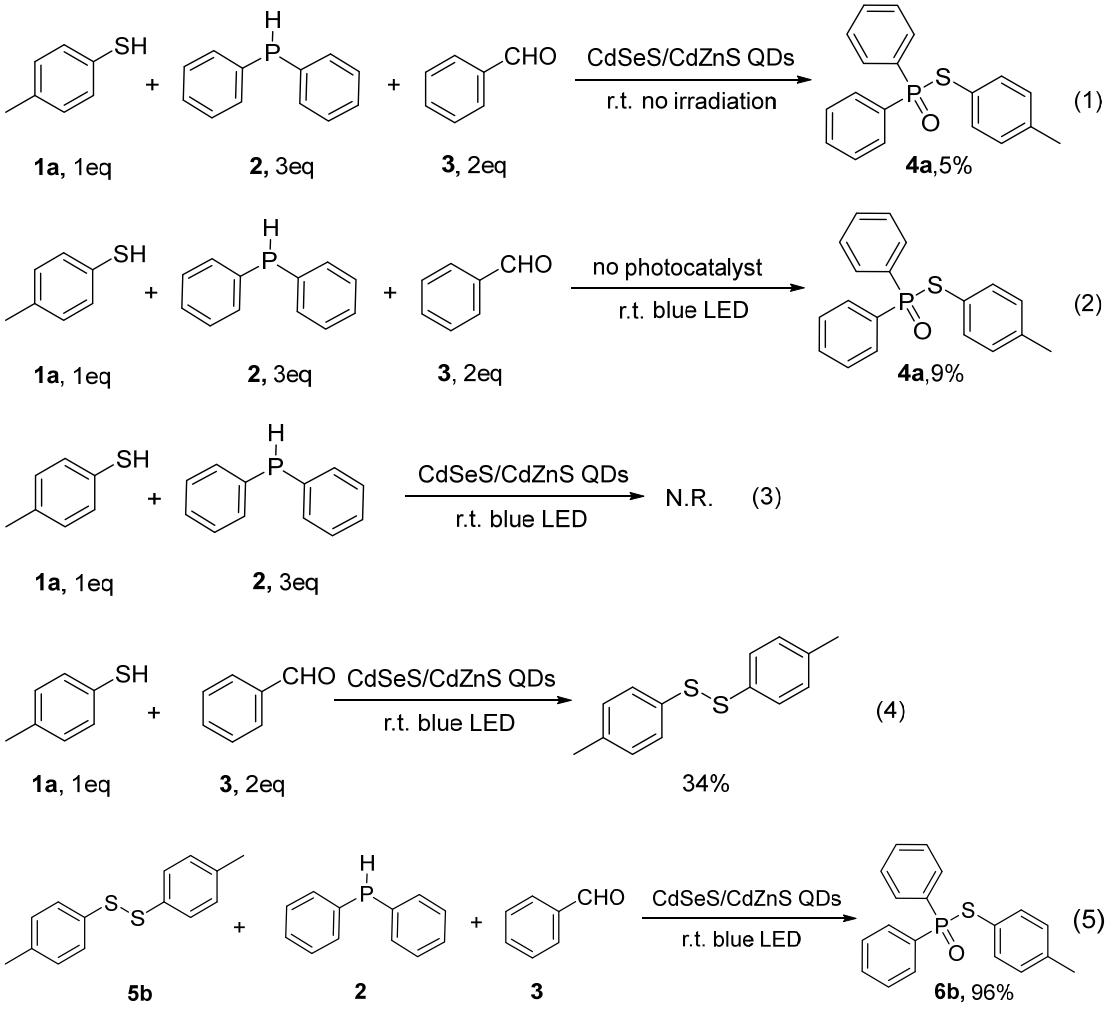


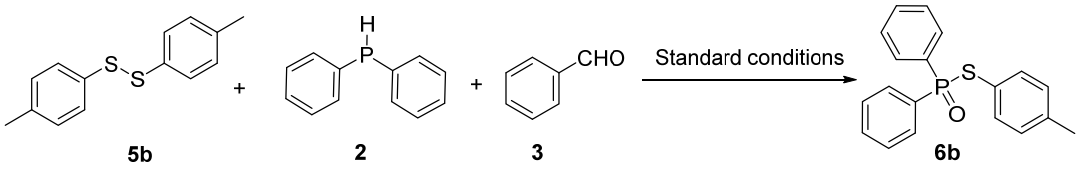
Figure S7. ^{1}H NMR of TEMPO-Diphenylphosphine adduct

11. Preliminary Mechanistic Studies

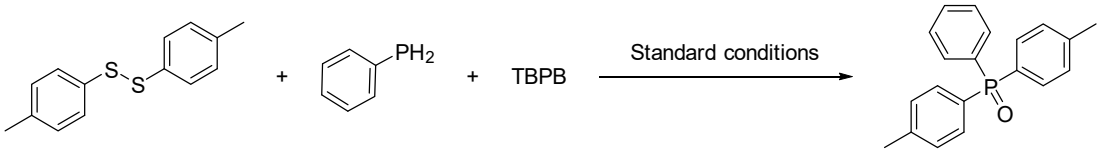
Scheme S1. The controlled experiments



Scheme S2. Other controlled experiments

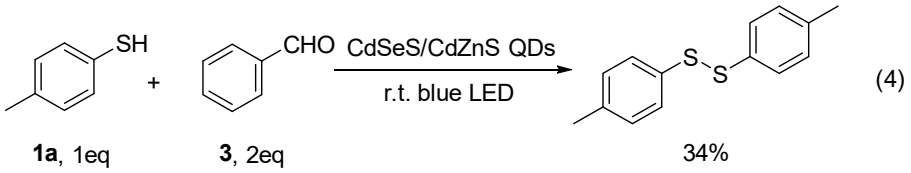


Enter	Variation form standard conditions	Isolated yields(%)
1	None	96
2	No irradiation	trace
3	No photocatalyst	trace
4	In the air	10
5	No irradiation, No photocatalyst, in the oxygen	18



5b **2** **3** **8a**

Enter	Variation form standard conditions	Isolated yields(%)
1	None	62
2	No irradiation	trace
3	No photocatalyst	trace
5	In the air	22



1a, 1eq **3**, 2eq 34%

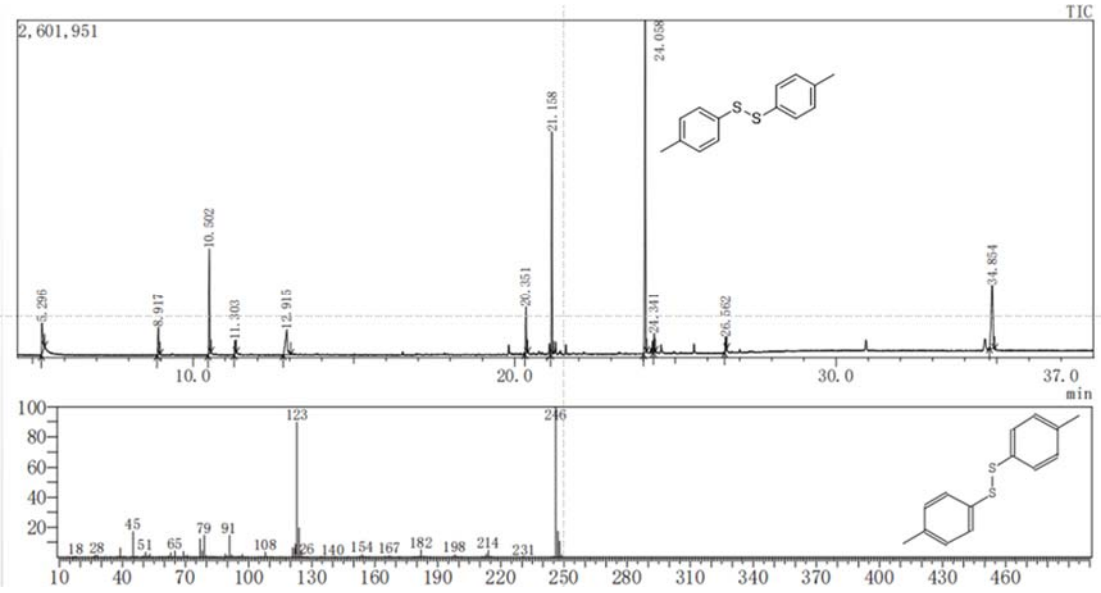
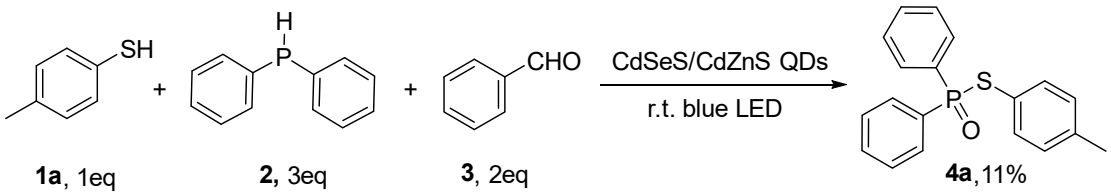


Figure S8. GC-MS plot of benzaldehyde in reaction with p-methylthiophol

12. Liquid Nitrogen Deoxygenation Experiment



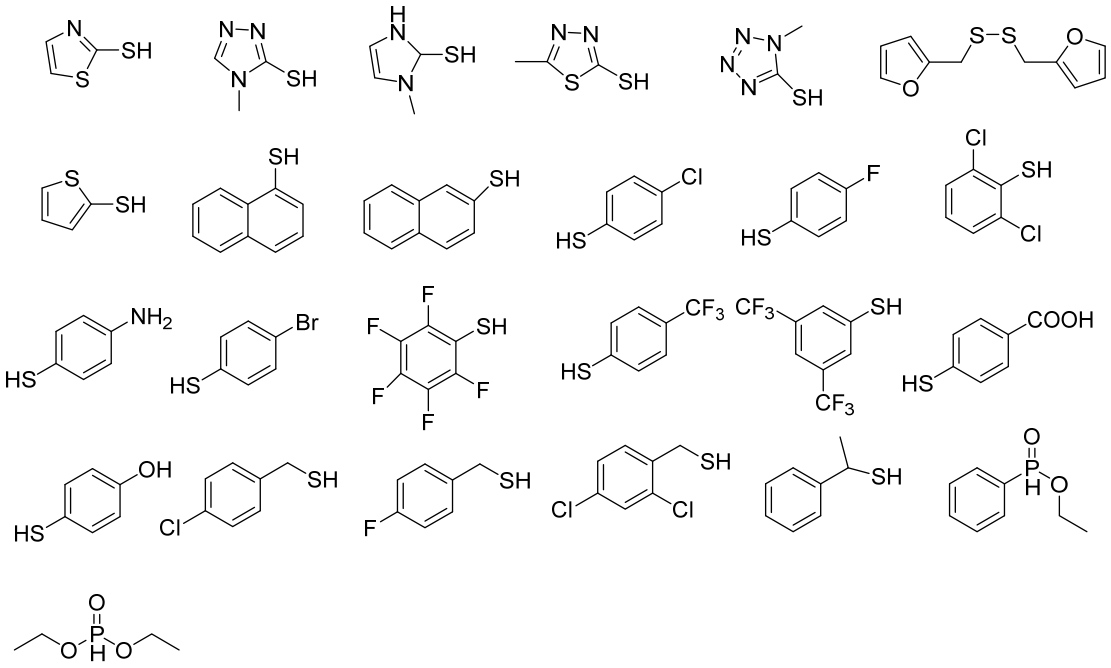
1a, 1eq **2,** 3eq **3**, 2eq **4a**,11%

Figure S8. Synthesize of compound 4a without oxygen

Oxygen was removed by using freezing and thawing protocol. The main operation steps are shown below: A small magnet was added to the schlenk tube, followed by 0.0489 g (0.40 mmol) of **1a**, 0.0844 g (0.80 mmol) of **3**, 0.2312 g (1.21 mmol) of **2**, CdSeS/CdZnS QDs (50 μL), 4 mL of toluene, and 1 mL of

DMSO in the glove box,purged with Argon gas for 15 minutes, sonicate for 5 minutes. Then connect the Schlenk tube to the Schlenk line, making sure the switch is closed, and the bottle is sealed. Open the double inclined valve to connect the catheter to the vacuum line and place the Schlenk tube in a liquid nitrogen dewar until all the solvent is completely frozen. Open the valve and evacuate for 2-3 minutes, then close the valve to isolate the container from the vacuum line. The reaction was then removed from liquid nitrogen to allow the solvent to thaw. Repeat this freezing, pumping, and thawing cycle five times after the solvent is thawed. After the fifth cycle it was filled with argon through the Schlenk line. The Schlenk tube was then placed under blue light for 36 hours. After the reaction was completed, add 12 mL of acetonitrile to precipitate and centrifuge to remove the QDs. Take the organic layer for concentration. The crude mixture was separated to obtain 0.0143g of **4a** with a yield of 11%.

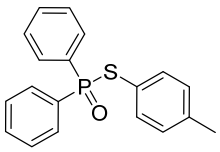
13. Unsuccessful substrates



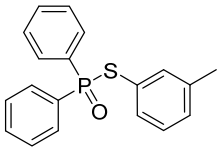
14. Characterization Data

Diphenylphosphine as phosphorus source

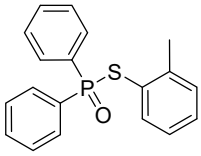
(1) Thiol/mercaptan as substrate



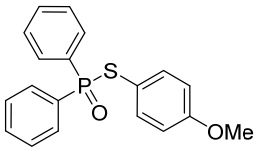
Phosphinothioic acid, P-diphenyl-S-(4-methylphenyl) ester (4a): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography).White solide (87%, 55.4 mg), Mp: 106-108°C. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 – 7.80 (m, 4H), 7.59 – 7.44 (m, 6H), 7.35 (dd, J = 8.2, 1.7 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 2.29 (d, J = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.3, 135.5, 132.3, 131.8, 131.7, 130.0, 128.6, 128.5, 21.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.41.



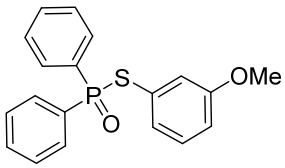
Phosphinothioic acid, P-diphenyl-S-(3-methylphenyl) ester (4b): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (55%, 35.1 mg), Mp: 94-98℃. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.95 – 7.82 (m, 4H), 7.59 – 7.53 (m, 2H), 7.48 (ddt, J = 10.7, 7.4, 2.8 Hz, 4H), 7.36 (s, 1H), 7.23 (t, J = 3.2 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.0, 136.2, 133.2, 132.5, 132.4, 132.4, 132.4, 132.1, 131.8, 131.7, 129.9, 128.9, 128.7, 128.5, 126.9, 125.7, 125.7, 21.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.47.



Phosphinothioic acid, P-diphenyl-S-(2-methylphenyl) ester (4c): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (94%, 61.6 mg), Mp: 70-72℃. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 – 7.79 (m, 4H), 7.56 – 7.50 (m, 2H), 7.46 (dt, J = 7.7, 3.8 Hz, 4H), 7.22 – 7.10 (m, 3H), 7.04 (td, J = 7.4, 1.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 142.9, 136.8, 133.4, 132.4, 131.6, 131.5, 130.8, 129.4, 128.6, 128.5, 127.9, 127.2, 126.5, 125.5, 21.5. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.20.

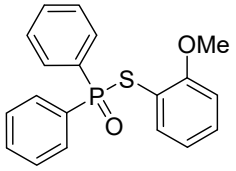


Phosphinothioic acid, P-diphenyl-S-(4-methoxyphenyl) ester (4d): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (52%, 37.7 mg), Mp: 132-134℃. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.90 – 7.80 (m, 4H), 7.53 – 7.47 (m, 2H), 7.44 (ddd, *J* = 8.6, 6.7, 3.6 Hz, 4H), 7.35 – 7.31 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.6, 137.2, 137.1, 133.2, 132.5, 132.3, 132.3, 132.1, 131.7, 131.6, 128.7, 128.6, 128.5, 116.1, 115.9, 114.9, 114.9, 55.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.42.

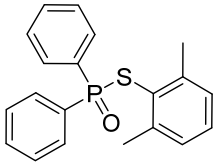


Phosphinothioic acid, P-diphenyl-S-(3-methoxyphenyl) ester (4e): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (26%, 19.4 mg), Mp: 129-138℃. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (ddd, *J* = 12.8, 6.9, 1.4 Hz, 4H), 7.55 – 7.48 (m, 2H), 7.44 (dt, *J* = 7.8, 3.9 Hz, 4H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.04 (t, *J* = 1.4 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.7, 133.1, 132.4, 131.9, 131.8,

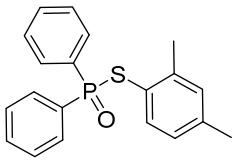
131.7, 131.4, 129.9, 128.7, 128.6, 127.6, 127.1, 126.5, 119.9, 115.9, 55.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.61.



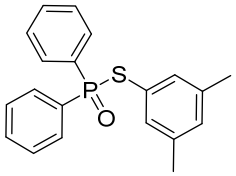
Phosphinothioic acid, P-diphenyl-S-(2-methoxyphenyl) ester (4f): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (62%, 40.5 mg), Mp: 66-67°C. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 – 7.82 (m, 4H), 7.68 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.44 – 7.40 (m, 3H), 7.23 – 7.19 (m, 2H), 6.86 (s, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.5, 159.5, 137.7, 137.7, 133.6, 132.2, 132.2, 131.7, 131.6, 130.8, 130.8, 128.4, 128.3, 121.2, 114.1, 114.1, 111.2, 55.6.^{31}P NMR (162 MHz, Chloroform-d) δ 41.83.



Phosphinothioic acid, P-diphenyl-S-(2,6-dimethylphenyl) ester (4g): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (85%, 59.2 mg), Mp: 98-99°C. The compound data was in agreement with the literature (*Tetrahedron, 2017, 73, 3133-3138*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.69 (m, 4H), 7.56 – 7.49 (m, 2H), 7.42 (td, *J* = 7.8, 3.6 Hz, 4H), 7.14 – 7.08 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 2.29 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 145.2, 133.7, 132.7, 132.3, 132.3, 131.4, 131.3, 129.3, 128.5, 128.5, 128.4, 128.4, 128.1, 127.5, 127.0, 124.6, 22.6. ^{31}P NMR (162 MHz, Chloroform-d) δ 39.86.

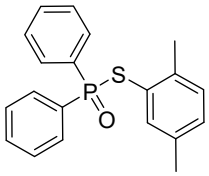


Phosphinothioic acid, P-diphenyl-S-(2,4-dimethylphenyl) ester (4h): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (>99%, 83.2 mg), Mp: 73-76°C. The compound data was in agreement with the literature (*Org. Biomol. Chem., 2018, 16, 30-33*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 (dd, *J* = 12.9, 7.6 Hz, 4H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.43 (dd, *J* = 7.6, 3.5 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 142.9, 139.6, 136.9, 133.5, 132.5, 132.3, 131.6, 131.5, 128.6, 128.5, 128.0, 127.4, 127.4, 127.2, 121.6, 21.4, 21.1. ^{31}P NMR (162 MHz, Chloroform-d) δ 40.99.

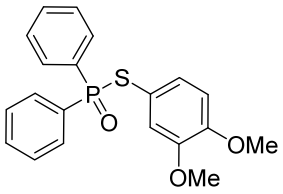


Phosphinothioic acid, P-diphenyl-S-(3,5-dimethylphenyl) ester (4i): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White

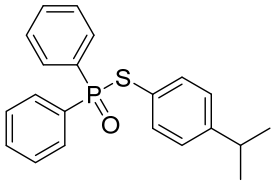
solid (44%, 29.6 mg), Mp: 112-113℃. The compound data was in agreement with the literature (*Tetrahedron 2016, 72, 7594-7598*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (ddt, *J* = 12.9, 6.9, 1.5 Hz, 4H), 7.51 – 7.45 (m, 2H), 7.41 (ddd, *J* = 8.7, 6.7, 3.7 Hz, 4H), 7.15 (t, *J* = 3.3 Hz, 1H), 7.01 (s, 1H), 6.85 (s, 1H), 2.15 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 140.5, 140.2, 138.8, 133.2, 132.3, 132.1, 131.8, 131.7, 130.9, 128.6, 128.5, 127.9, 127.6, 127.2, 125.2, 21.1. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.64.



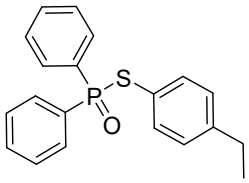
Phosphinothioic acid, P-diphenyl-S-(2,5-dimethylphenyl) ester (4j): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (>99%, 74.1 mg), Mp: 82-85℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 – 7.73 (m, 4H), 7.57 – 7.48 (m, 2H), 7.50 – 7.38 (m, 4H), 7.19 (s, 1H), 6.99 (d, *J* = 10.8 Hz, 1H), 6.89 – 6.76 (m, 1H), 2.28 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.9, 137.5, 136.2, 133.3, 132.4, 132.2, 131.6, 131.5, 130.5, 130.3, 128.6, 128.5, 124.7, 116.3, 115.6, 115.4, 20.9, 20.6. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.55. HRMS (ESI-TOF) for $C_{20}H_{19}OSP$ ($[M+H]^+$): calcd. 339.0967; found: 339.0964.



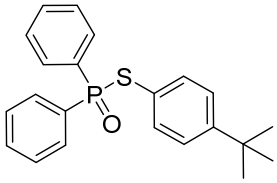
Phosphinothioic acid, P-diphenyl-S-(3,4-methoxyphenyl) ester (4k): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (55%, 42.4 mg), Mp: 134-138℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (ddt, *J* = 7.3, 5.3, 2.6 Hz, 4H), 7.34 (dt, *J* = 5.5, 1.7 Hz, 6H), 7.00 (ddd, *J* = 8.4, 2.2, 1.4 Hz, 1H), 6.90 (dd, *J* = 2.2, 1.0 Hz, 1H), 6.72 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 149.0, 137.8, 137.6, 132.9, 132.8, 129.4, 128.7, 128.6, 125.9, 125.2, 125.1, 116.3, 111.7, 56.0, 55.9. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.55. HRMS (ESI-TOF) for $C_{20}H_{19}O_3SP$ ($[M+H]^+$): calcd. 371.0866; found: 371.0861.



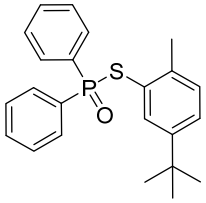
Phosphinothioic acid, P-diphenyl-S-[4-(1-methylethyl)phenyl] ester (4l): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (94%, 65.3 mg), Mp: 109-110℃. The compound data was in agreement with the literature (*Chem-Eur. J., 2021, 27, 14931-14935*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 – 7.80 (m, 4H), 7.50 (dt, *J* = 7.4, 3.7 Hz, 2H), 7.43 (td, *J* = 7.4, 3.3 Hz, 4H), 7.38 – 7.32 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.85 – 2.77 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 150.2, 135.6, 133.1, 132.33, 132.1, 131.7, 131.6, 128.6, 128.5, 127.5, 122.4, 116.4, 115.6, 115.4, 33.8, 23.8. ^{31}P NMR (162 MHz, Chloroform-d) δ 42.01.



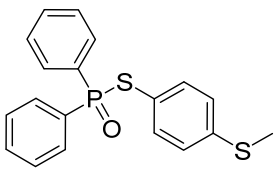
Phosphinothioic acid, P-diphenyl-S-(4-ethylphenyl) ester (4m): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (91%, 64.6 mg), Mp: 84-86°C. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 – 7.68 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.40 (m, 4H), 7.41 – 7.32 (m, 2H), 7.23 – 7.13 (m, 1H), 7.03 – 7.00 (m, 1H), 2.75 (d, J = 7.6 Hz, 1H), 2.54 (q, J = 7.6 Hz, 1H), 1.22 – 1.04 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 148.4, 145.5, 136.8, 135.6, 133.2, 132.4, 131.8, 131.7, 131.5, 129.5, 129.2, 128.9, 128.7, 128.6, 128.5, 128.5, 127.3, 126.5, 122.5, 122.4, 28.5, 15.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.82.



Phosphinothioic acid, P-diphenyl-S-(4-tert-butylphenyl) ester (4n): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (82%, 64.6 mg), Mp: 128-129°C. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (dd, *J* = 12.9, 7.6 Hz, 4H), 7.53 – 7.47 (m, 2H), 7.43 (dd, *J* = 7.6, 3.3 Hz, 4H), 7.33 (s, 2H), 7.22 – 7.19 (m, 2H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 152.4, 135.3, 135.3, 132.3, 132.3, 131.8, 131.7, 128.6, 128.5, 128.1, 128.1, 127.9, 127.8, 127.2, 127.1, 126.4, 34.6, 31.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.92.

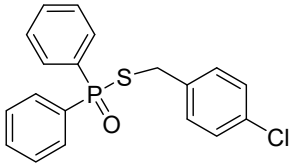


Phosphinothioic acid, P-diphenyl-S-(4-tert-butyl-2-dimethylphenyl) ester (4o): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). Colorless oil (87%, 68.7 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 (dd, *J* = 12.8, 7.6 Hz, 4H), 7.53 – 7.49 (m, 1H), 7.49 – 7.38 (m, 5H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 3H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 149.4, 140.3, 133.9, 133.5, 132.41, 132.2, 131.7, 131.7, 130.5, 128.6, 128.5, 126.5, 124.7, 124.7, 34.2, 31.1, 21.1. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.80. HRMS (ESI-TOF) for $C_{23}H_{25}OSP$ ($[M+H]^+$): calcd. 381.1437; found: 381.1442.

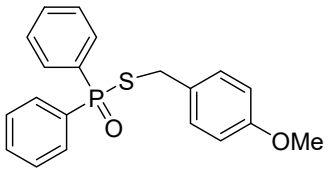


Phosphinothioic acid, P-diphenyl-S-(4-methylthiophenyl) ester (4p): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White

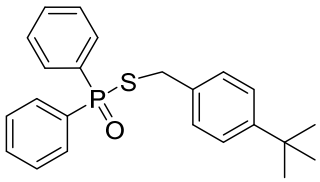
solid (84%, 68.9 mg) Mp: 92-94°C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (dd, *J* = 13.0, 7.6 Hz, 3H), 7.54 – 7.36 (m, 5H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.22 – 7.10 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.39 (d, *J* = 25.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 140.7, 135.8, 132.9, 132.5, 131.7, 131.6, 130.3, 129.5, 128.7, 128.6, 127.6, 127.3, 126.9, 126.5, 15.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 42.06. HRMS (ESI-TOF) for $C_{19}H_{17}OS_2P$ ([M+H]$^+$): calcd. 357.0532; found: 357.0524.



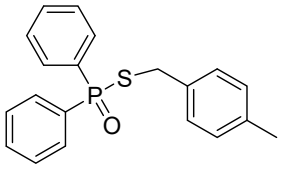
((4-chlorobenzyl) thio) diphenylphosphine oxide (4q): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (21%, 15.7 mg). The compound data was in agreement with the literature (*Adv. Synth Catal., 2020, 362, 1825-1830*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 (ddd, *J* = 12.6, 5.5, 3.4 Hz, 4H), 7.54 – 7.48 (m, 2H), 7.44 (dtdd, *J* = 8.5, 5.2, 4.3, 3.4, 1.6 Hz, 4H), 7.14 (dd, *J* = 14.3, 7.8 Hz, 2H), 7.00 – 6.90 (m, 2H), 3.81 (dd, *J* = 18.7, 13.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.4, 131.7, 131.7, 131.6, 130.5, 129.3, 128.7, 128.6, 128.5, 128.2, 128.0, 127.2, 40.8, 40.5, 40.0. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.90, 35.86.



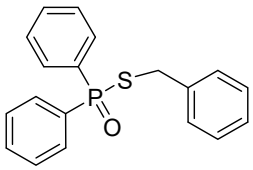
((4-methoxybenzyl) thio) diphenylphosphine oxide (4r): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colourless oil (17%, 11.6 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.96 – 7.86 (m, 4H), 7.50 – 7.46 (m, 2H), 7.40 (td, *J* = 6.5, 5.9, 2.8 Hz, 4H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 4.11 (d, *J* = 11.7 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 134.6, 132.2, 131.8, 131.8, 131.6, 131.5, 131.5, 130.5, 128.6, 128.5, 128.4, 113.9, 55.3, 35.5. ^{31}P NMR (162 MHz, Chloroform-d) δ 80.30, 63.67. HRMS (ESI-TOF) for $C_{20}H_{19}O_2SP$ ([M+H]$^+$): calcd. 355.0917; found: 355.0897.



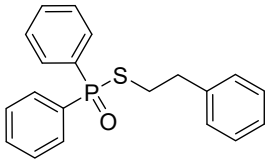
((4-tert-butylbenzyl) thio) diphenylphosphine oxide (4s): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colourless oil (26%, 19.9 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 – 7.76 (m, 4H), 7.52 – 7.39 (m, 6H), 7.18 (dd, *J* = 8.2, 3.5 Hz, 2H), 6.95 (ddd, *J* = 8.5, 4.2, 2.4 Hz, 2H), 3.82 (dd, *J* = 13.5, 3.6 Hz, 2H), 1.26 (d, *J* = 3.7 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 150.0, 132.8, 132.2, 132.0, 131.7, 131.6, 131.5, 130.2, 130.2, 128.6, 128.4, 127.8, 125.0, 40.7, 40.2, 31.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 80.30, 42.06. HRMS (ESI-TOF) for $C_{23}H_{25}OSP$ ([M+H]$^+$): calcd. 381.1437; found: 381.1429.



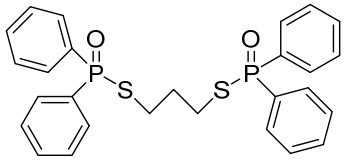
((4-methylbenzyl) thio) diphenylphosphine oxide (4t): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colourless oil (17%, 11.7 mg). The compound data was in agreement with the literature (*Adv. Synth Catal., 2020, 362, 1825-1830*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 – 7.77 (m, 4H), 7.50 – 7.41 (m, 6H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.87 (dd, *J* = 8.1, 2.7 Hz, 2H), 3.83 (t, *J* = 13.6 Hz, 2H), 2.26 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.2, 131.7, 131.6, 131.6, 130.4, 130.4, 128.8, 128.8, 128.6, 128.5, 128.4, 128.32, 127.7, 40.8, 40.3, 21.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 80.29, 42.04.



(Thiobenzyl) diphenylphosphine oxide (4u): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colourless oil (23%, 14.7 mg). The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 – 7.79 (m, 4H), 7.54 (dt, *J* = 7.4, 4.6 Hz, 2H), 7.48 (td, *J* = 7.4, 2.3 Hz, 4H), 7.25 – 7.17 (m, 3H), 7.11 – 6.97 (m, 2H), 3.89 (d, *J* = 13.5 Hz, 2H).^{13}C NMR (101 MHz, Chloroform-d) δ 132.7, 132.2, 131.9, 131.7, 131.6, 131.6, 130.9, 130.6, 129.6, 128.6, 128.5, 128.0, 128.0, 127.2, 127.2, 125.9, 41.2, 40.7. ^{31}P NMR (162 MHz, Chloroform-d) δ 80.27, 42.15.

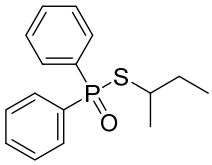


(Thiophenylethyl) diphenylphosphine oxide (4v): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colourless oil (28%, 18.9 mg). The compound data was in agreement with the literature (*Green. Chem., 2017, 19, 1005-1013*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 (dt, *J* = 12.7, 6.3 Hz, 4H), 7.66 – 7.39 (m, 6H), 7.22 (dd, *J* = 16.2, 8.0 Hz, 2H), 7.08 (t, *J* = 6.2 Hz, 2H), 3.15 – 3.00 (m, 2H), 2.91 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.5, 133.8, 132.4, 131.6, 131.5, 128.8, 128.7, 128.5, 126.7, 36.9, 30.5. ^{31}P NMR (162 MHz, Chloroform-d) δ 44.01.

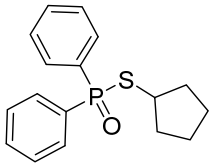


(1,3-propyl dithio) diphenylphosphine oxide (4w): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1 Gradient elution chromatography). Colorless oil (15%, 15.1 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 – 7.82 (m, 8H), 7.46 (dddd, *J* = 12.9, 8.6, 5.3, 2.2 Hz, 12H), 2.95 (dt, *J* = 13.9, 7.1 Hz, 4H), 1.84 (p, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 131.9, 131.5, 131.4, 128.7, 128.6, 30.4, 29.8. ^{31}P NMR (162 MHz, Chloroform-d) δ 63.05. HRMS (ESI-TOF)

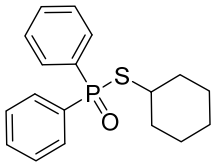
for $C_{23}H_{25}OSP$ ([M+H]$^+$): calcd. 509.0923; found: 509.0925.



(Sec-butylthio) diphenylphosphine oxide (4x): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1 Gradient elution chromatography). White solid (67%, 44.2 mg), Mp:116-117℃. The compound data was in agreement with the literature (*Org. Lett., 2021, 23, 1541-1547.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 – 7.74 (m, 4H), 7.59 – 7.43 (m, 6H), 3.26 (dq, *J* = 10.5, 6.6 Hz, 1H), 1.72 – 1.51 (m, 2H), 1.34 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 134.7, 133.4, 132.2, 132.2, 131.6, 131.5, 131.4, 128.7, 128.5, 43.3, 31.7, 23.3, 11.1. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.94.

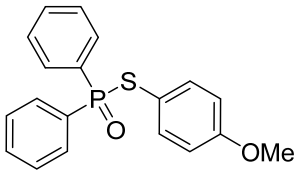


S-cyclopentyl diphenyl thiophosphate (4y): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). White solid (98%, 59.4 mg), Mp: 56-58℃. The compound data was in agreement with the literature (*China, CN112010897 A*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 (dd, J = 13.1, 7.4 Hz, 4H), 7.55 – 7.45 (m, 6H), 3.53 – 3.38 (m, 1H), 1.96 (qd, J = 7.8, 6.8, 3.5 Hz, 2H), 1.74 – 1.56 (m, 4H), 1.51 (dt, J = 11.5, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 140.4, 134.3, 133.3, 132.3, 132.2, 131.6, 131.5, 128.7, 128.6, 127.9, 127.7, 127.7, 127.2, 43.6, 35.5, 29.7, 24.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 42.19.



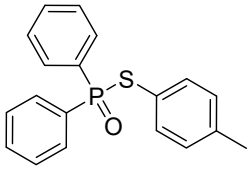
S-cyclohexyl diphenylphosphinothioate (4z): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). White solid (64%, 40.8 mg), Mp:80-82℃. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 (dd, *J* = 13.0, 7.5 Hz, 4H), 7.61 – 7.38 (m, 6H), 3.30 (dq, *J* = 15.8, 10.5, 8.2 Hz, 1H), 2.04 – 1.87 (m, 2H), 1.66 (dd, *J* = 12.1, 5.6 Hz, 2H), 1.59 – 1.45 (m, 3H), 1.32 – 1.24 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.3, 131.5, 131.4, 128.7, 128.6, 44.6, 44.6, 35.6, 35.6, 25.7, 25.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 42.51.

(2) Disulfide as substrate

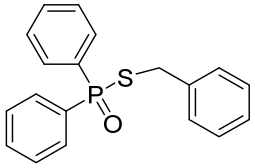


Phosphinothioic acid, P-diphenyl-S-(4-methoxyphenyl) ester (6a): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). white solid (31%, 22.3 mg), Mp: 132-134℃. The compound data was in agreement with the literature (*Org. Lett., 2016,*

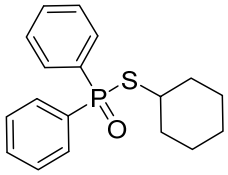
18, 5114-5117.) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 (ddt, *J* = 12.9, 6.9, 1.4 Hz, 4H), 7.51 – 7.39 (m, 6H), 7.36 – 7.31 (m, 2H), 6.79 – 6.68 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.6, 160.5, 137.1, 137.1, 133.2, 132.3, 132.3, 132.1, 131.7, 131.6, 131.5, 128.6, 128.5, 116.0, 114.9, 114.9, 55.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.48.



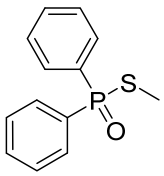
Phosphinothioic acid, P-diphenyl-S-(4-methylphenyl) (6b): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (96%, 63.3 mg), Mp: 106-108°C. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (dd, *J* = 12.8, 7.3 Hz, 4H), 7.54 – 7.35 (m, 6H), 7.31 (d, *J* = 7.7 Hz, 2H), 6.98 (dd, *J* = 8.2, 2.5 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 140.0, 139.3, 135.5, 133.2, 132.3, 132.1, 131.8, 131.7, 130.1, 128.7, 128.5, 128.1, 127.9, 127.2, 122.2, 21.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 41.64.



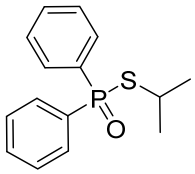
(Thiobenzyl) diphenylphosphine oxide (6c): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colourless oil (25%, 15.9 mg). The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (dd, J = 12.7, 7.5 Hz, 4H), 7.53 – 7.47 (m, 2H), 7.44 (td, J = 7.5, 2.7 Hz, 4H), 7.23 – 7.13 (m, 3H), 7.05 – 6.95 (m, 2H), 3.84 (d, J = 13.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.7, 132.2, 131.9, 131.7, 131.6, 130.9, 130.8, 130.6, 130.5, 128.6, 128.5, 128.0, 128.0, 127.2, 127.2, 41.2, 40.7. ^{31}P NMR (162 MHz, Chloroform-d) δ 42.15, 80.28.



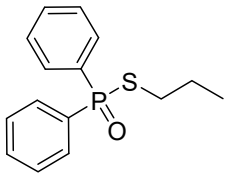
S-cyclohexyl diphenylphosphinothioate (6d): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). White solid (>99%, 66.5 mg), Mp:80-82°C. The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 (dd, *J* = 13.1, 7.5 Hz, 4H), 7.48 (dt, *J* = 15.9, 7.2 Hz, 6H), 3.30 (d, *J* = 10.9 Hz, 1H), 1.95 (d, *J* = 12.8 Hz, 2H), 1.67 (dd, *J* = 12.5, 5.3 Hz, 2H), 1.50 (dd, *J* = 16.2, 8.3 Hz, 3H), 1.27 (t, *J* = 11.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 134.7, 133.6, 132.2, 132.1, 131.5, 131.4, 128.7, 128.5, 35.6, 35.6, 25.8, 25.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 42.00.



(Methylthio) diphenylphosphine oxide (6e): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1 Gradient elution chromatography). Colorless oil (77%, 41.1 mg). The compound data was in agreement with the literature (*Adv. Synth Catal., 2020, 362, 1825-1830*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.96 – 7.82 (m, 1H), 7.64 – 7.44 (m, 5H), 7.36 (qd, *J* = 4.9, 2.6 Hz, 4H), 2.22 (dd, *J* = 11.6, 4.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 137.5, 132.7, 132.5, 132.5, 131.5, 129.2, 128.6, 15.3, 15.1. ^{31}P NMR (162 MHz, Chloroform-d) δ 65.95, 84.12.



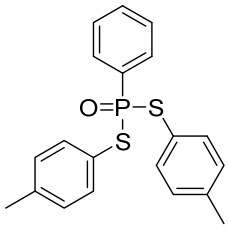
(isopropyl thio) diphenylphosphine oxide (6f): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1 Gradient elution chromatography). White solid (25%, 14.3 mg), Mp:104-106℃. The compound data was in agreement with the literature (*Green. Chem., 2017, 19, 1005-1013*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (tq, *J* = 6.2, 2.7, 2.1 Hz, 4H), 7.42 – 7.32 (m, 6H), 3.27 (dq, *J* = 13.6, 6.7 Hz, 1H), 1.44 (dd, *J* = 6.8, 1.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 138.8, 138.6, 132.8, 132.6, 128.9, 128.5, 128.5, 38.9, 38.7, 25.6, 25.6. ^{31}P NMR (162 MHz, Chloroform-d) δ 61.56, 78.59.



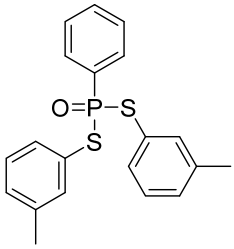
(Propylthio) diphenylphosphine oxide (6g): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1 Gradient elution chromatography). Colorless oil (32%, 17.7 mg). The compound data was in agreement with the literature (*Org. Lett., 2016, 18, 5114-5117.*) ^{1}H NMR (400 MHz, Chloroform-d) δ 8.05 – 7.86 (m, 4H), 7.50 (dddd, J = 11.8, 8.4, 6.1, 2.2 Hz, 6H), 2.93 (dt, J = 13.0, 7.3 Hz, 1H), 1.83 – 1.57 (m, 3H), 1.00 (dt, J = 14.3, 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 131.8, 131.5, 131.4, 128.7, 128.5, 13.4. ^{31}P NMR (162 MHz, Chloroform-d) δ 63.90, 80.89.

Phenylphosphine as phosphorus source

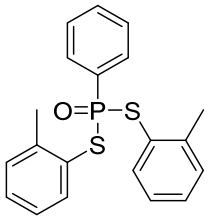
(1) Thiol/mercaptan as substrate



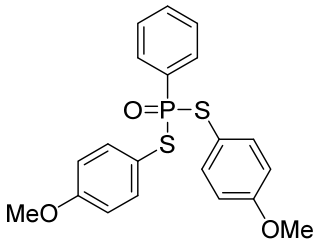
P-phenyl-S-bis(4-methylphenyl) ester (8a): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). Colorless oil (62%, 45.6 mg). The compound data was in agreement with the literature (*Org. Biomol. Chem., 2020, 18, 1567-1571*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (d, *J* = 13.9 Hz, 2H), 7.50 (td, *J* = 7.3, 1.8 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.32 (dd, *J* = 8.2, 2.0 Hz, 3H), 7.09 (dd, *J* = 14.4, 7.8 Hz, 4H), 2.31 (d, *J* = 5.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.7, 135.7, 135.7, 131.8, 131.7, 130.1, 129.9, 128.6, 128.5, 128.3, 21.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 49.81.



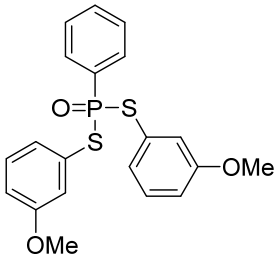
P-phenyl-S-bis(3-methylphenyl) ester (8b): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (57%, 44.1 mg), Mp: 76-80℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.72 (m, 2H), 7.49 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.40 (tt, *J* = 7.4, 4.4 Hz, 2H), 7.25 (d, *J* = 3.7 Hz, 4H), 7.13 (s, 4H), 2.26 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.2, 136.4, 136.3, 132.7, 132.7, 131.8, 131.7, 130.3, 130.3, 129.1, 129.0, 128.4, 128.3, 21.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 49.85. HRMS (ESI-TOF) for $C_{20}H_{19}OS_2P$ ([M+H]$^+$): calcd. 371.0688; found: 371.0696.



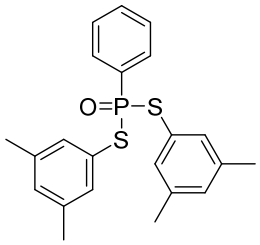
P-phenyl-S-bis(2-methylphenyl) ester (8c): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (68%, 51.4 mg), Mp: 80-84℃. The compound data was in agreement with the literature (*Org. Lett., 2017, 19, 3899-3902*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 (ddd, *J* = 14.0, 8.3, 1.4 Hz, 2H), 7.52 – 7.36 (m, 5H), 7.24 – 7.14 (m, 4H), 7.07 (td, *J* = 7.5, 1.8 Hz, 2H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 143.3, 137.3, 137.2, 132.6, 131.6, 131.5, 130.9, 130.9, 129.8, 129.8, 128.5, 128.3, 126.6, 126.6, 21.5. ^{31}P NMR (162 MHz, Chloroform-d) δ 49.07.



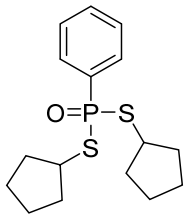
P-phenyl-S-bis(4-methoxyphenyl) ester (8d): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (32%, 25.9 mg), Mp: 134-136℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 – 7.71 (m, 2H), 7.52 – 7.45 (m, 1H), 7.43 – 7.31 (m, 6H), 6.81 (dd, *J* = 19.1, 8.7 Hz, 4H), 3.78 (d, *J* = 11.3 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 137.4, 137.4, 132.7, 132.6, 131.8, 131.7, 128.5, 128.3, 114.9, 114.7, 55.4. ^{31}P NMR (162 MHz, Chloroform-d) δ 50.36. HRMS (ESI-TOF) for $C_{20}H_{19}O_3S_2P$ ([M+H]$^+$): calcd. 403.0586; found: 403.0597.



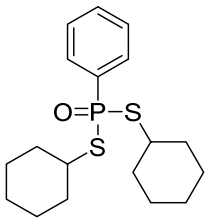
P-phenyl-S-bis(3-methoxyphenyl) ester (8e): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (42%, 34.0 mg), Mp: 88-91℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.76 (m, 1H), 7.55 – 7.32 (m, 2H), 7.19 (dt, *J* = 16.1, 8.0 Hz, 3H), 7.13 – 7.02 (m, 4H), 6.98 (s, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.80 – 6.74 (m, 1H), 3.77 (d, *J* = 1.1 Hz, 3H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.8, 131.9, 131.7, 129.9, 128.6, 128.4, 127.9, 120.2, 119.6, 116.2, 113.2, 112.6, 55.4. ^{31}P NMR (162 MHz, Chloroform-d) δ 49.87. HRMS (ESI-TOF) for $C_{20}H_{19}O_3S_2P$ ([M+H]$^+$): calcd. 403.0586; found: 403.0594.



P-phenyl-S-bis(3,5-dimethylphenyl) ester (8f): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). Yellow solid (31%, 24.3 mg), Mp: 120-123℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (ddd, *J* = 13.9, 8.1, 1.5 Hz, 1H), 7.52 – 7.22 (m, 4H), 7.11 (s, 1H), 7.05 (s, 3H), 6.89 (d, *J* = 33.9 Hz, 2H), 2.25 (d, *J* = 23.2 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 138.9, 133.4, 132.5, 131.8, 131.3, 129.1, 128.2, 127.6, 126.6, 125.2, 21.3, 21.1. ^{31}P NMR (162 MHz, Chloroform-d) δ 49.80. HRMS (ESI-TOF) for $C_{22}H_{23}OS_2P$ ([M+H]$^+$): calcd. 399.1001; found: 399.1010.



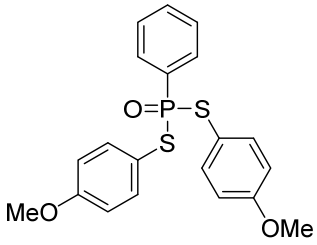
P-phenyl-S-biscyclopentyl ester (8g): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colorless oil (23%, 16.8 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (dt, *J* = 13.3, 6.1 Hz, 2H), 7.49 (d, *J* = 6.1 Hz, 3H), 3.58 (dd, *J* = 10.8, 5.8 Hz, 2H), 2.14 (p, *J* = 7.0 Hz, 2H), 1.95 (dq, *J* = 11.4, 5.8, 5.4 Hz, 2H), 1.71 (tt, *J* = 12.1, 5.5 Hz, 5H), 1.54 (dq, *J* = 14.6, 7.8, 7.1 Hz, 6H), 1.36 – 1.25 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.4, 131.3, 131.2, 128.7, 128.5, 45.2, 35.4, 24.4, 24.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 51.54. HRMS (ESI-TOF) for $C_{16}H_{23}OS_2P$ ([M+H]$^+$): calcd. 327.1001; found: 327.1009.



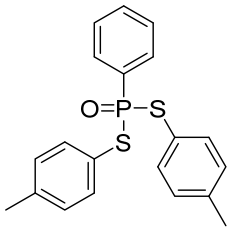
P-phenyl-S-biscyclohexyl ester (8h): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colorless oil (11%, 7.9 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (dd, *J* = 14.2, 7.4 Hz, 2H), 7.64 – 7.45 (m, 3H), 3.41 (d, *J* = 10.7 Hz, 2H), 2.16 – 2.05 (m, 2H), 1.93 – 1.86 (m, 2H), 1.72 (dd, *J* = 9.3, 4.5 Hz, 2H), 1.63 (dd, *J* = 8.6, 4.7 Hz, 2H), 1.59 – 1.48 (m, 4H), 1.46 – 1.24 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.3, 131.1, 130.9, 128.5, 128.4,

46.2, 35.4, 25.9, 25.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 51.84. HRMS (ESI-TOF) for $C_{18}H_{27}OS_2P$ ($[M+H]^+$): calcd. 355.1314; found: 355.1323.

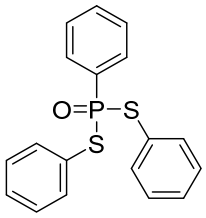
(2) Disulfide as substrate



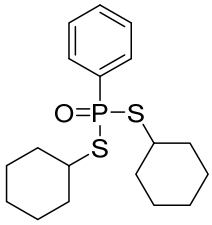
P-phenyl-S-bis(4-methoxyphenyl) ester (9a): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (48%, 38.5 mg), Mp: 134-136℃. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.69 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.27 (m, 6H), 6.81 (ddd, *J* = 19.7, 8.7, 1.9 Hz, 4H), 3.78 (d, *J* = 13.6 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.85, 160.8, 137.4, 137.4, 132.7, 132.6, 132.6, 131.8, 131.7, 128.5, 128.3, 114.9, 114.9, 114.7, 55.4. ^{31}P NMR (162 MHz, Chloroform-d) δ 50.29. HRMS (ESI-TOF) for $C_{20}H_{19}O_3S_2P$ ($[M+H]^+$): calcd. 403.0586; found: 403.0590.



P-phenyl-S-bis(4-methylphenyl) ester (9b): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). Colorless oil (52%, 38.2 mg). The compound data was in agreement with the literature (*Org. Biomol. Chem., 2020, 18, 1567-1571*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (dd, *J* = 13.9, 7.5 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.43 – 7.26 (m, 6H), 7.08 (dd, *J* = 14.9, 8.0 Hz, 4H), 2.31 (d, *J* = 5.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.7, 135.7, 132.7, 131.8, 130.1, 129.8, 128.6, 128.3, 122.6, 21.3. ^{31}P NMR (162 MHz, Chloroform-d) δ 49.94.



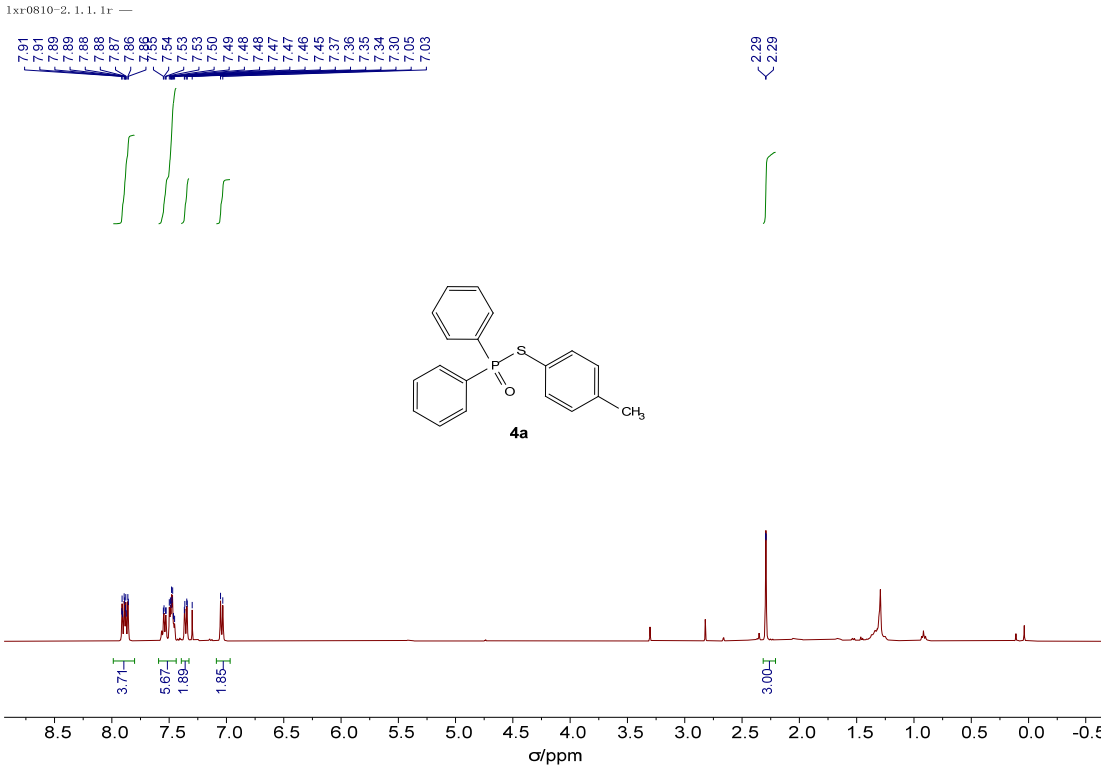
P-phenyl-S-bisphenyl ester (9c): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 Gradient elution chromatography). White solid (58%, 39.5 mg), Mp: 90-95℃. The compound data was in agreement with the literature (*J. Org. Chem., 1965, 30, 3967-3968*) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (dd, *J* = 14.2, 7.7 Hz, 2H), 7.51 – 7.38 (m, 7H), 7.35 – 7.27 (m, 5H), 7.24 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 135.8, 132.7, 131.7, 129.5, 129.3, 129.1, 128.5, 128.4, 127.6, 127.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 49.84.



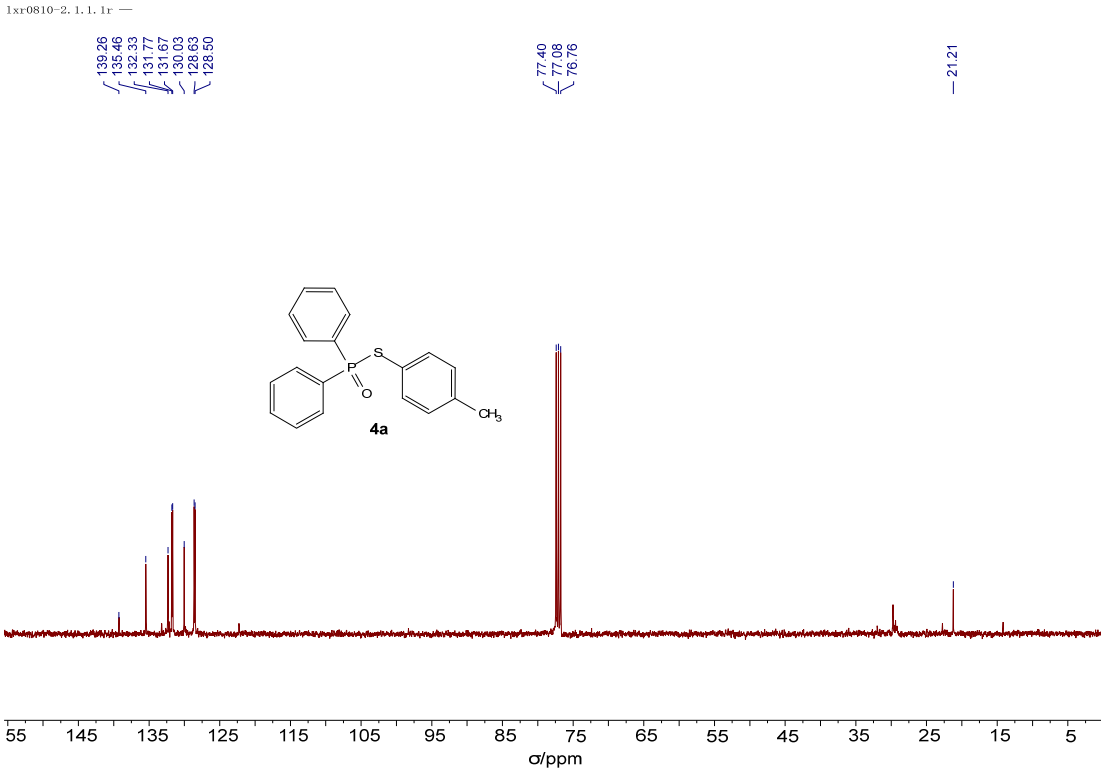
P-phenyl-S-biscyclohexyl ester (9d): The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Colorless oil (23%, 15.7 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (dd, *J* = 14.2, 7.4 Hz, 2H), 7.61 – 7.39 (m, 3H), 3.40 (ddt, *J* = 14.3, 9.8, 5.2 Hz, 2H), 2.16 – 2.02 (m, 2H), 1.93 – 1.84 (m, 2H), 1.75 – 1.25 (m, 16H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.4, 132.3, 131.2, 131.1, 128.6, 128.5, 46.2, 46.2, 35.4, 25.9, 25.4. ^{31}P NMR (162 MHz, Chloroform-d) δ 51.74. HRMS (ESI-TOF) for $C_{18}H_{27}OS_2P$ ($[M+H]^+$): calcd. 355.1314; found: 355.1320.

15. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra

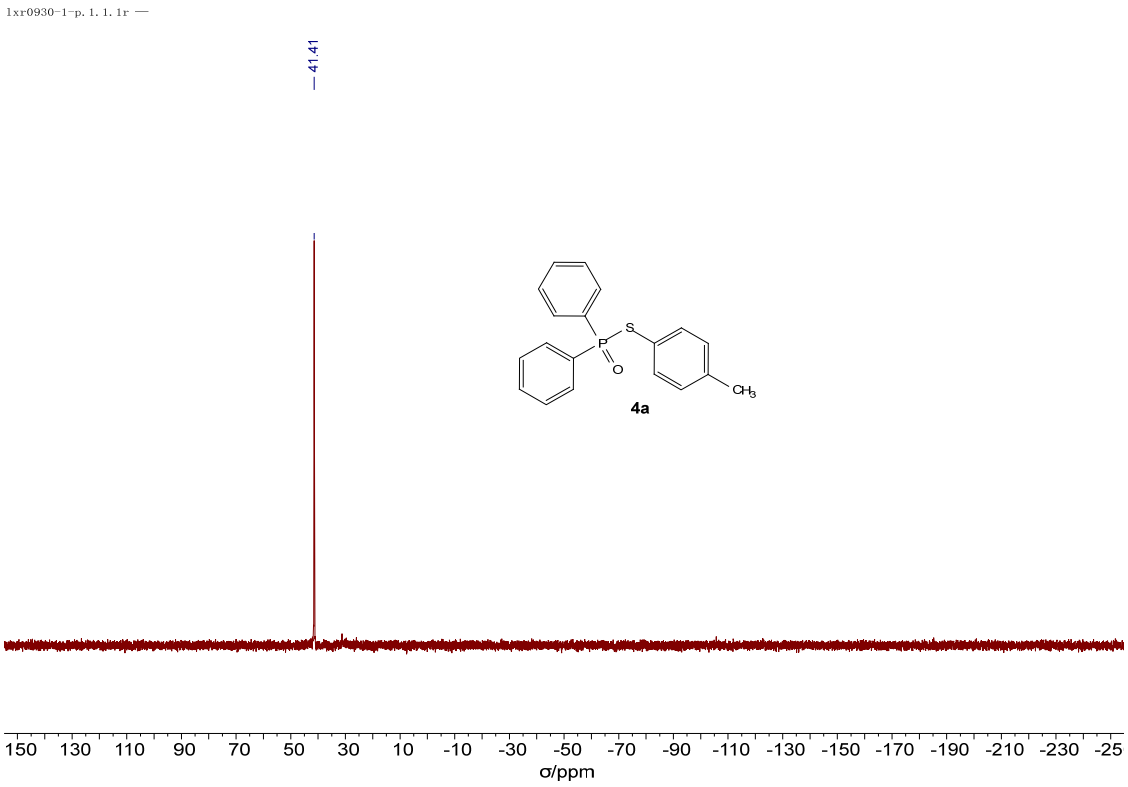
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4a**



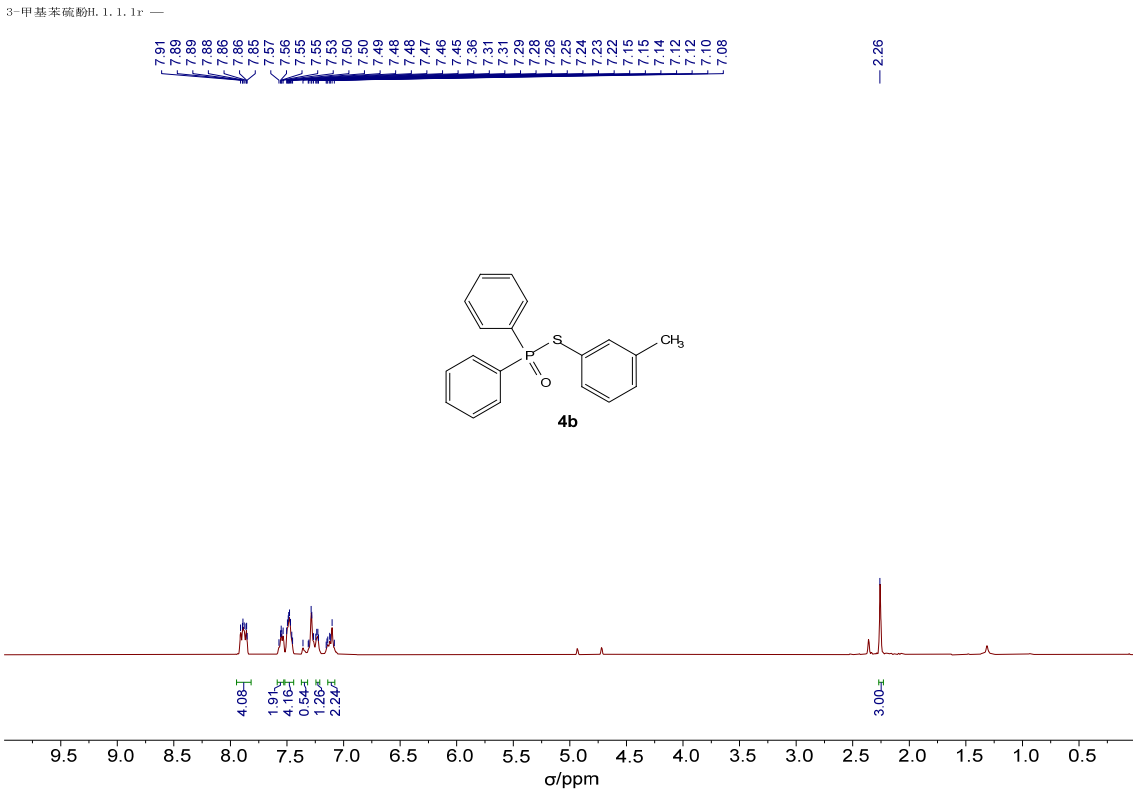
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4a**



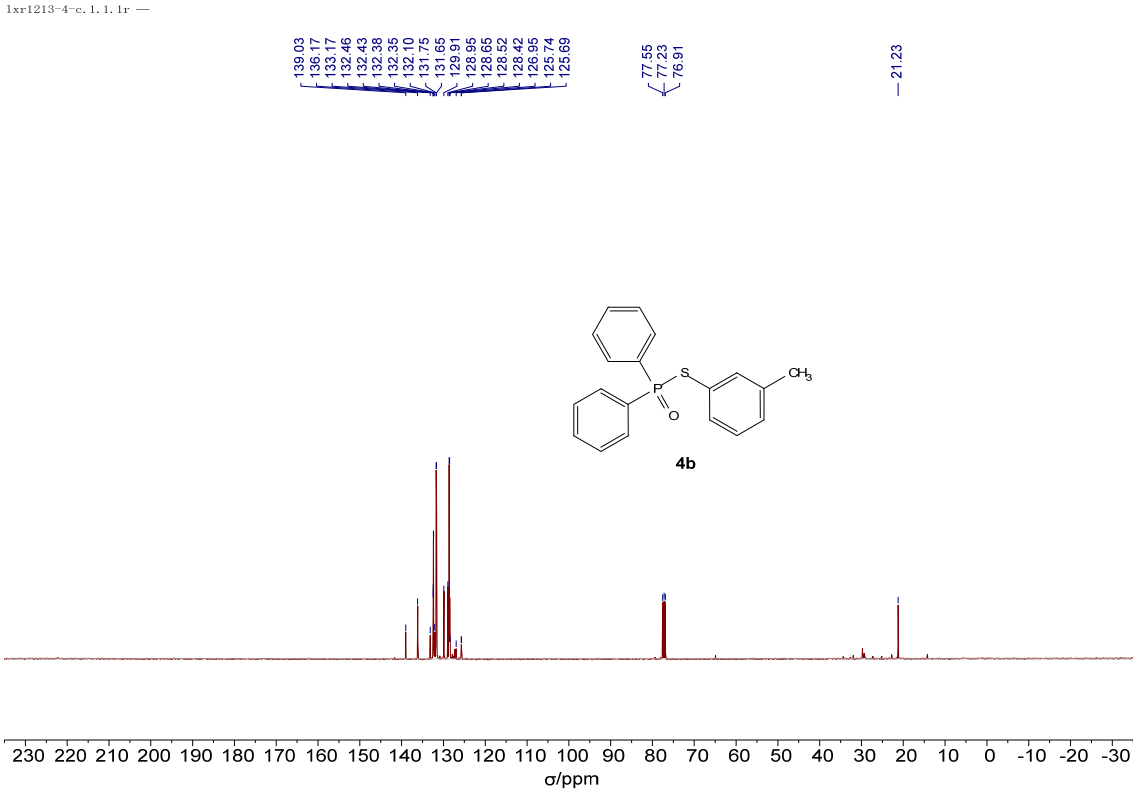
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4a**



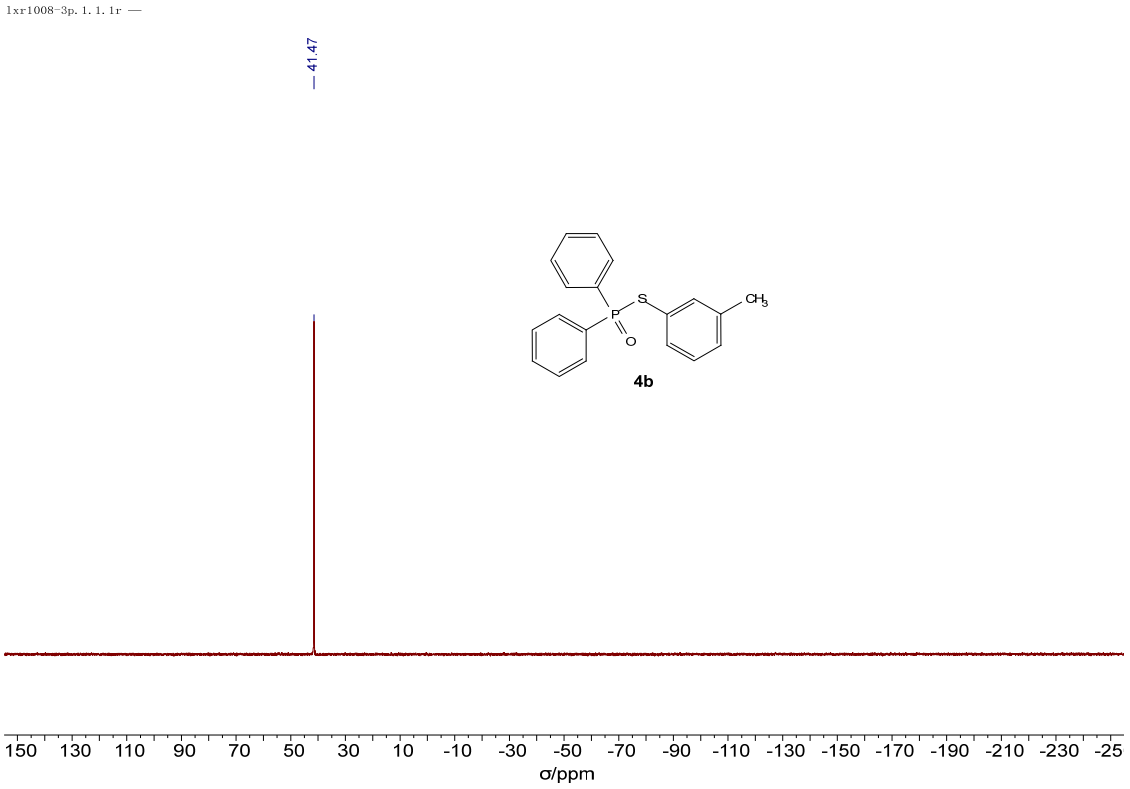
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4b**



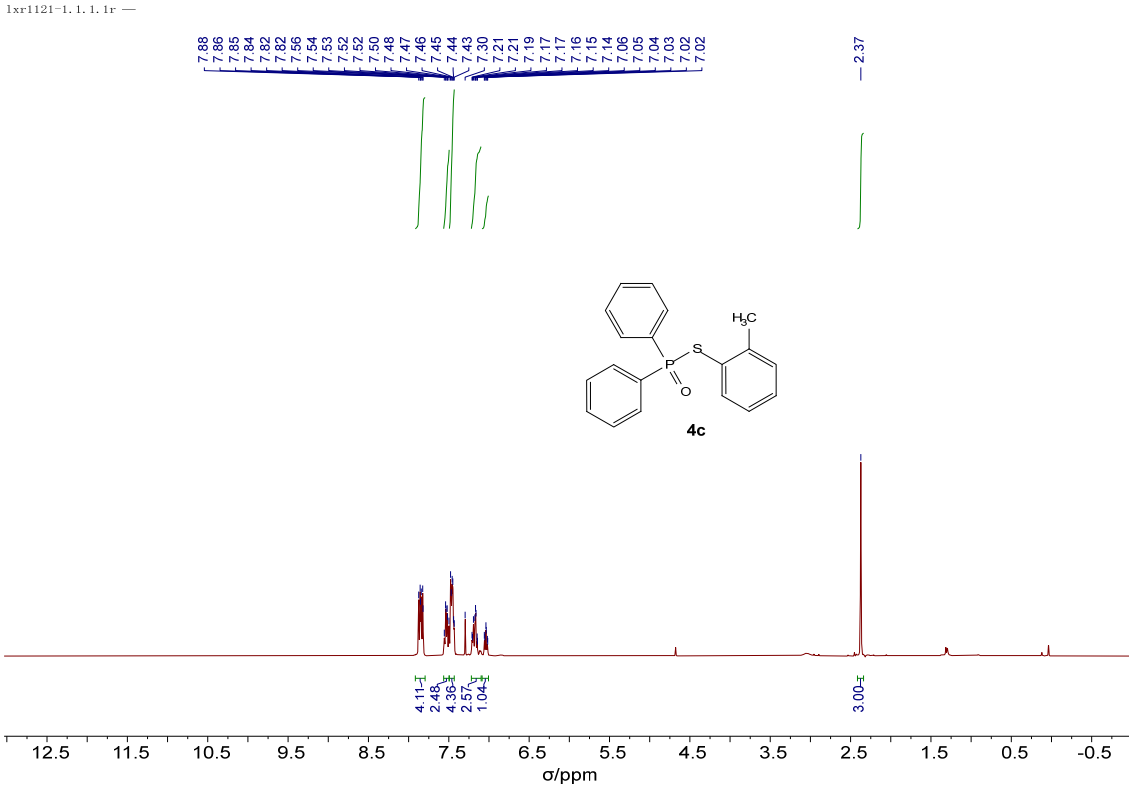
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4b**



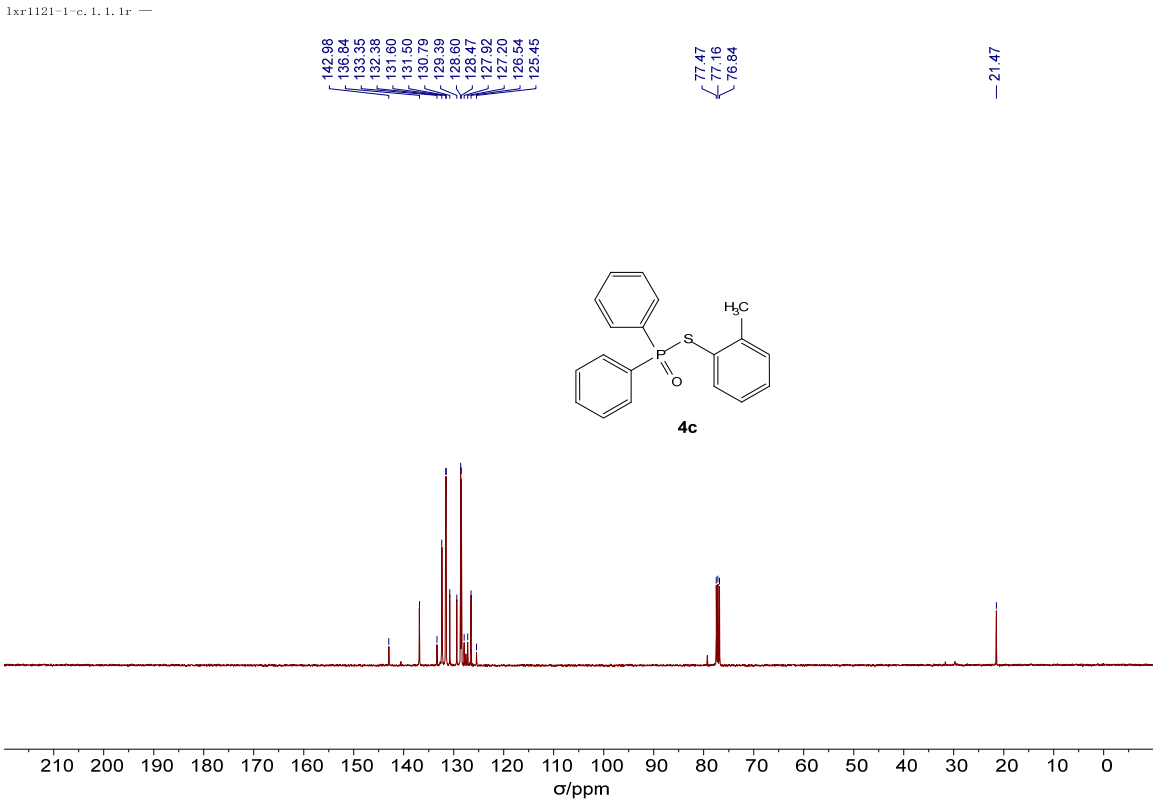
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4b**



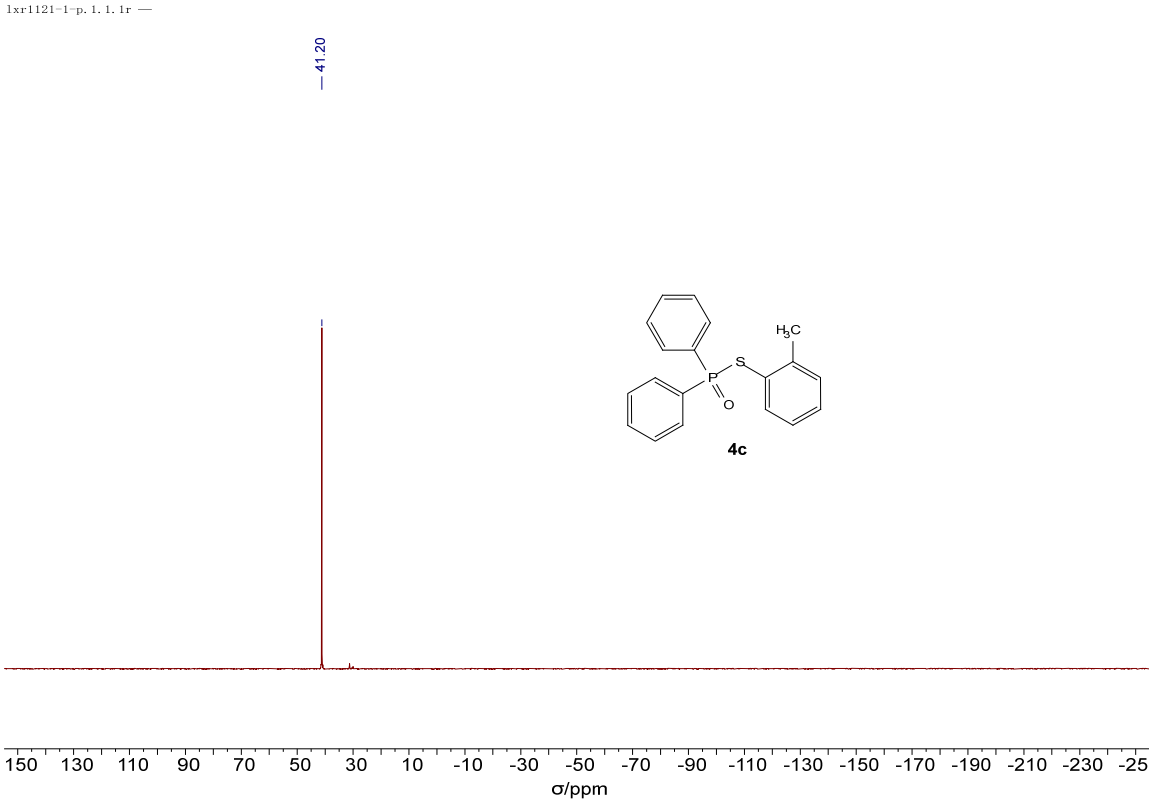
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4c**



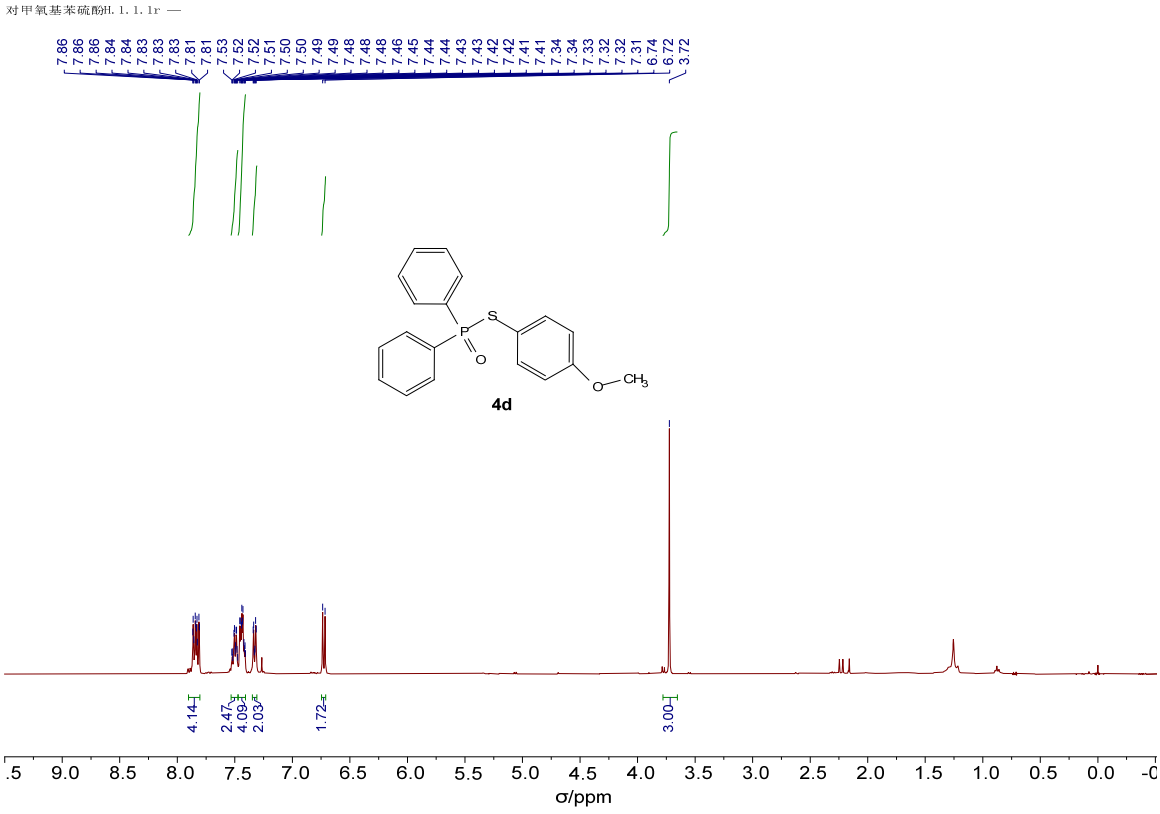
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4c**



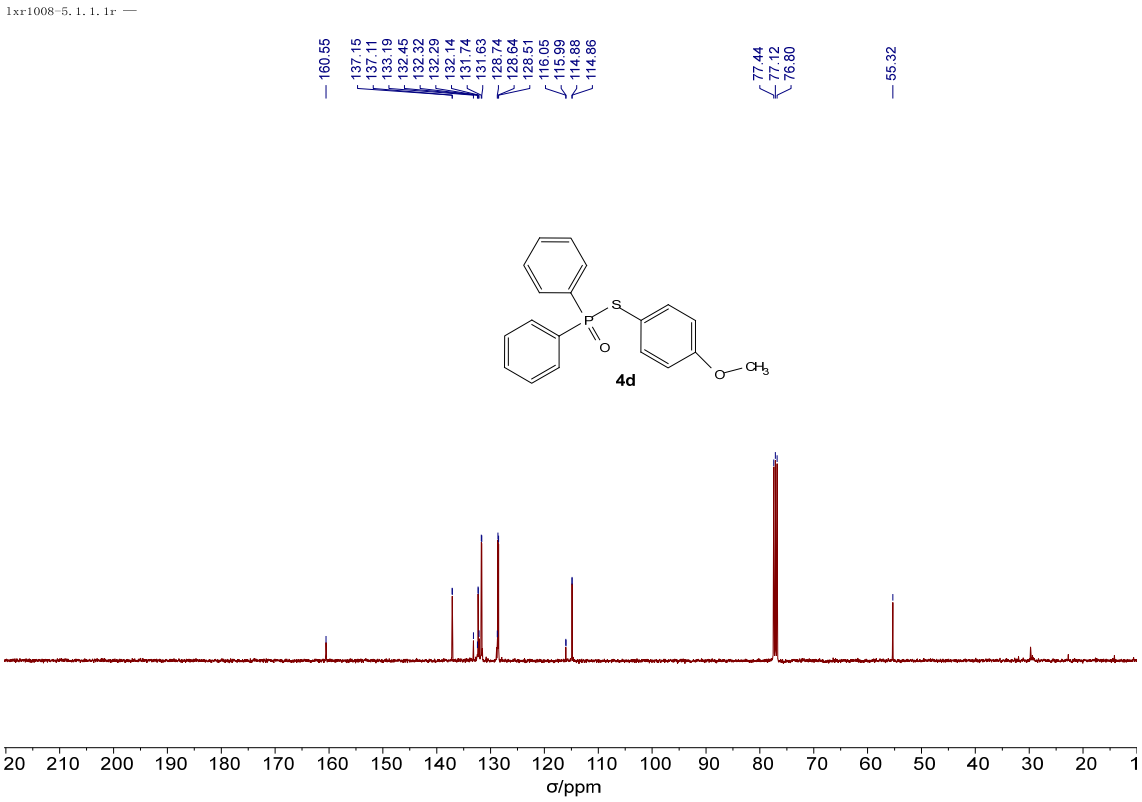
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4c**



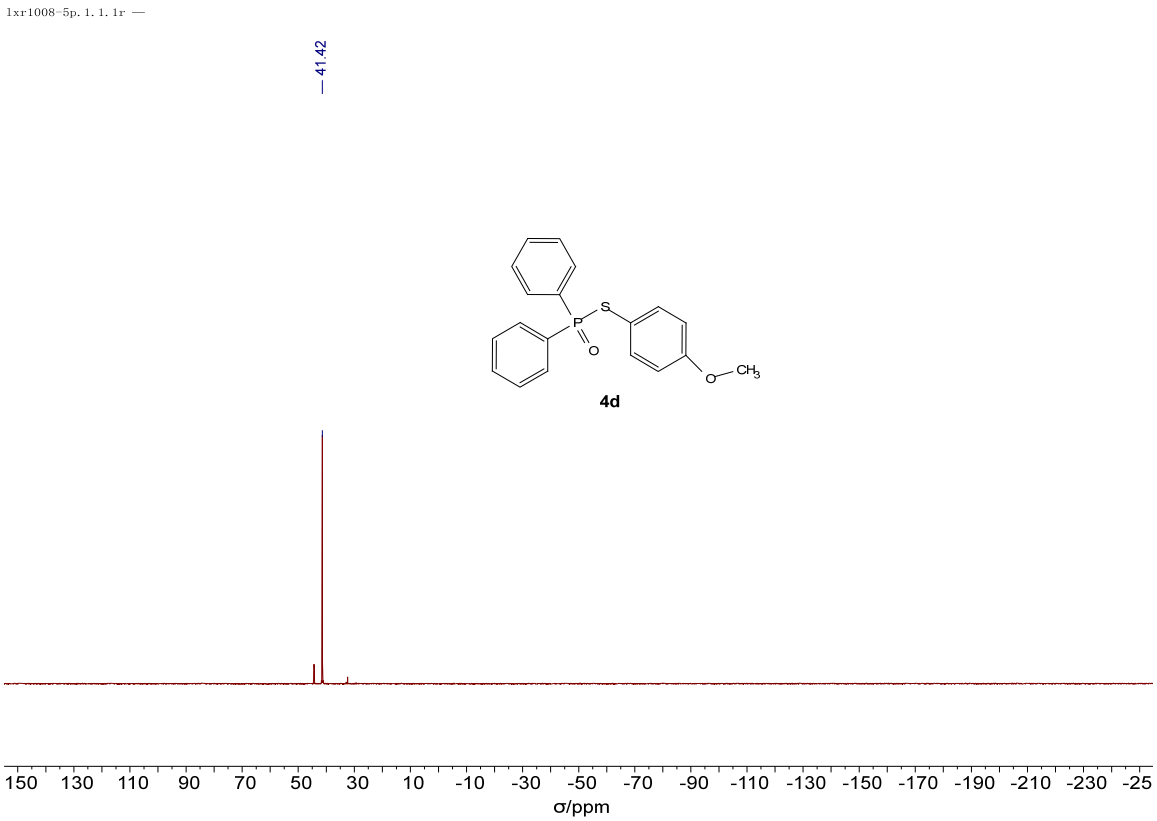
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4d**



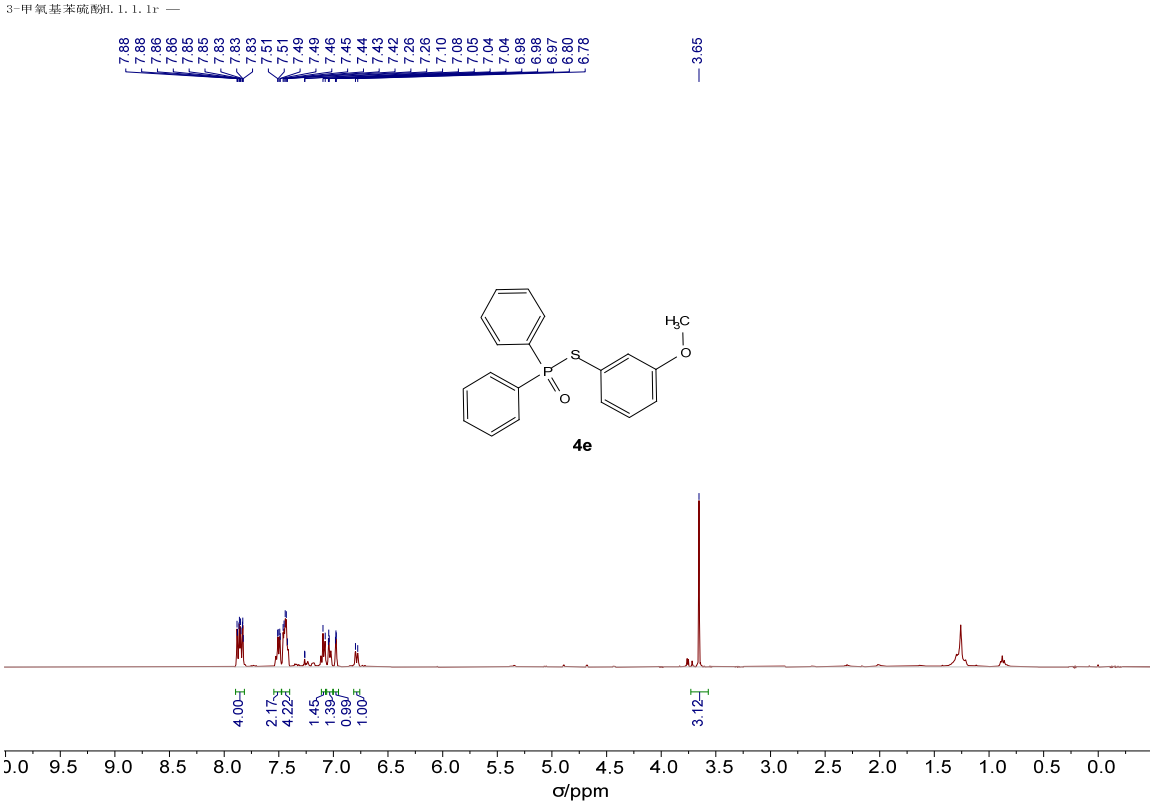
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4d**



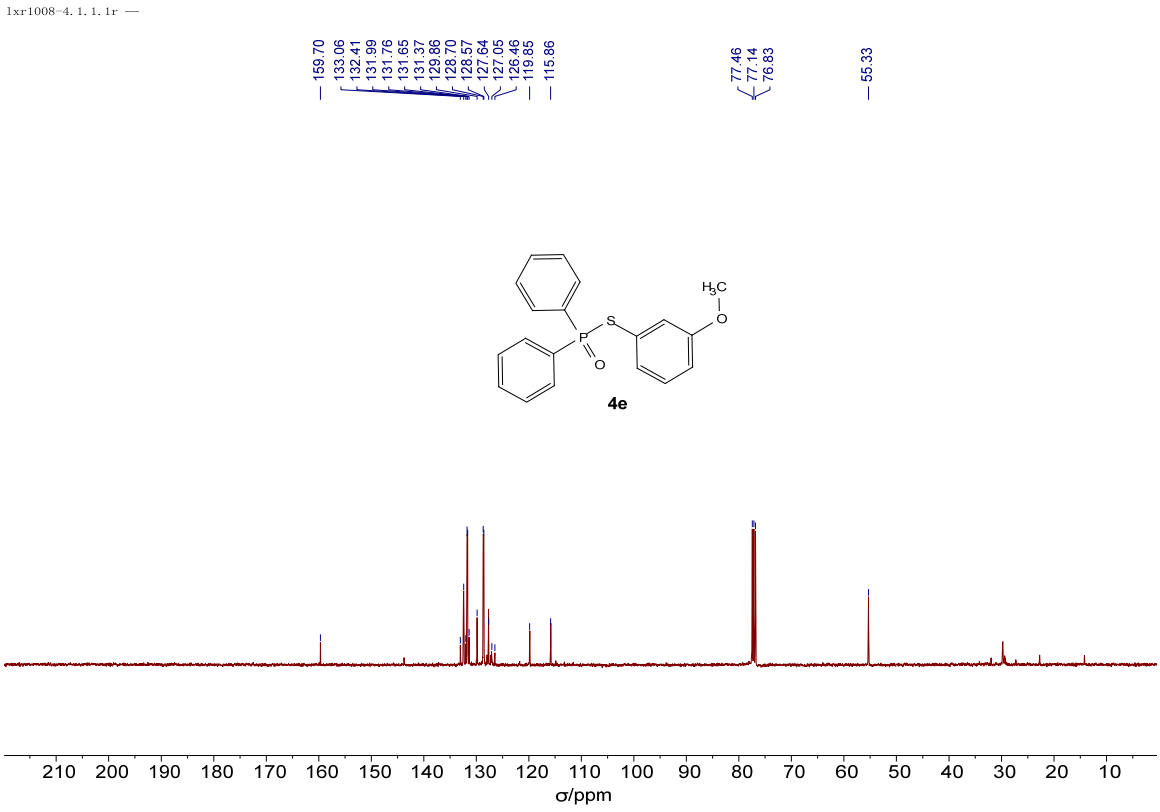
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4d**



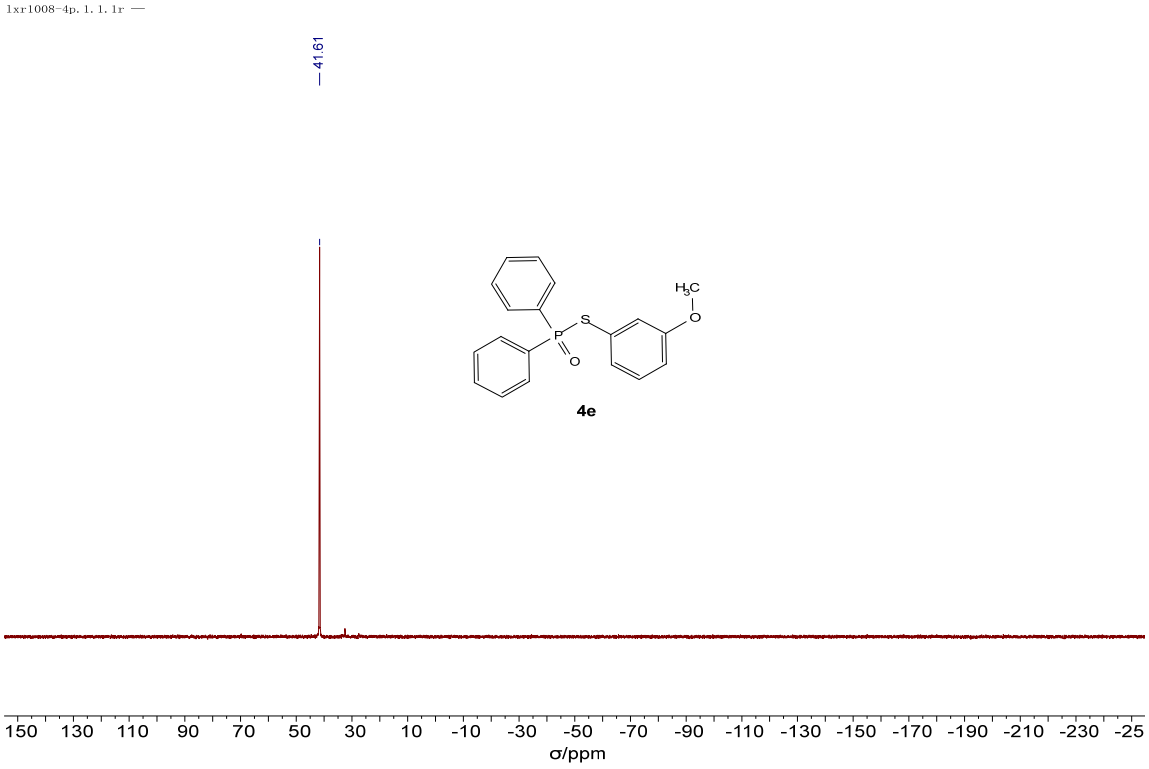
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4e**



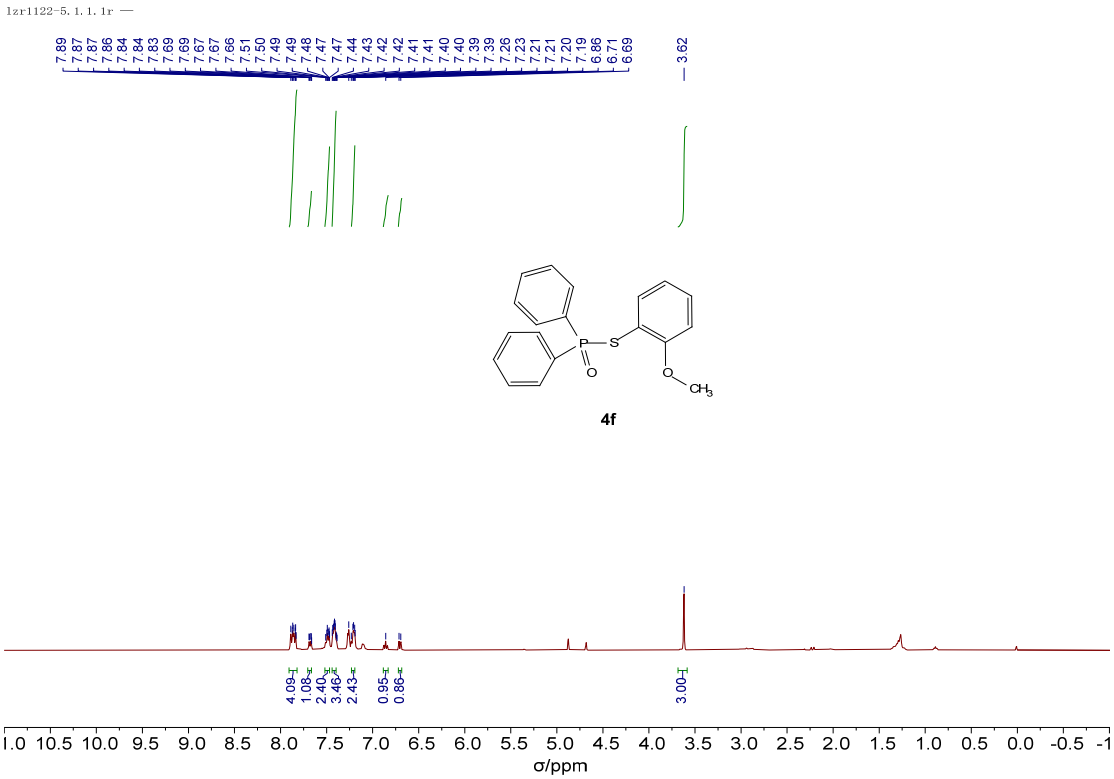
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4e**



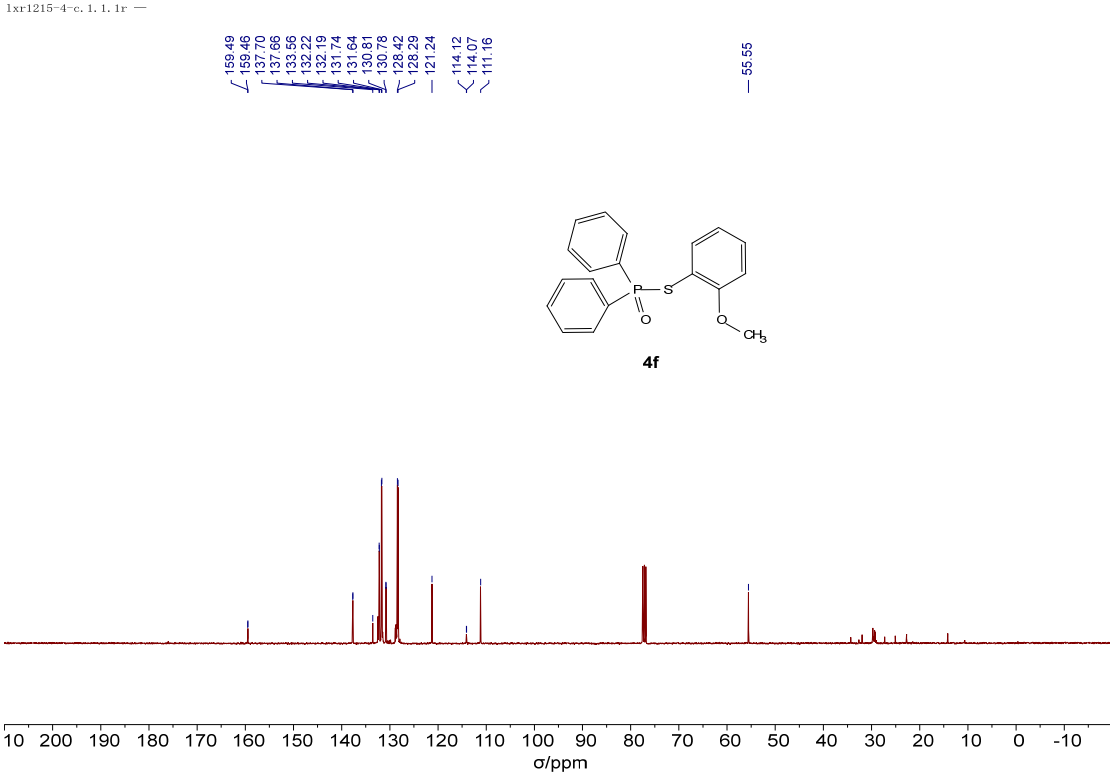
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4e**



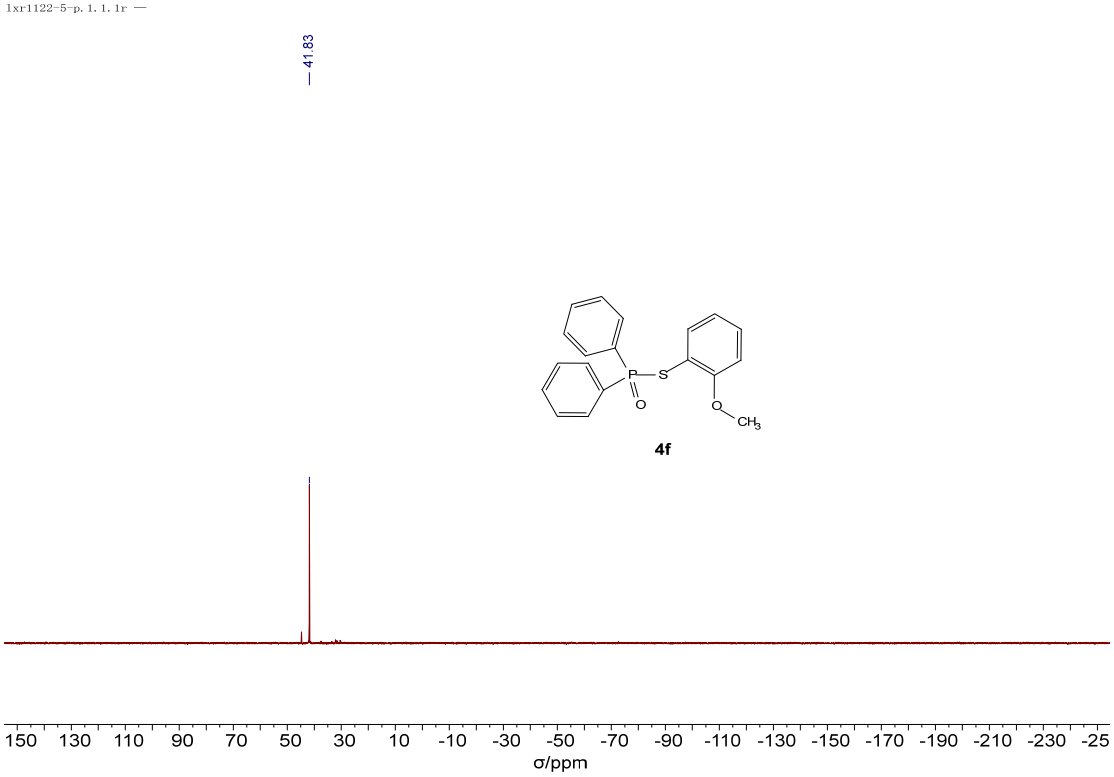
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4f**



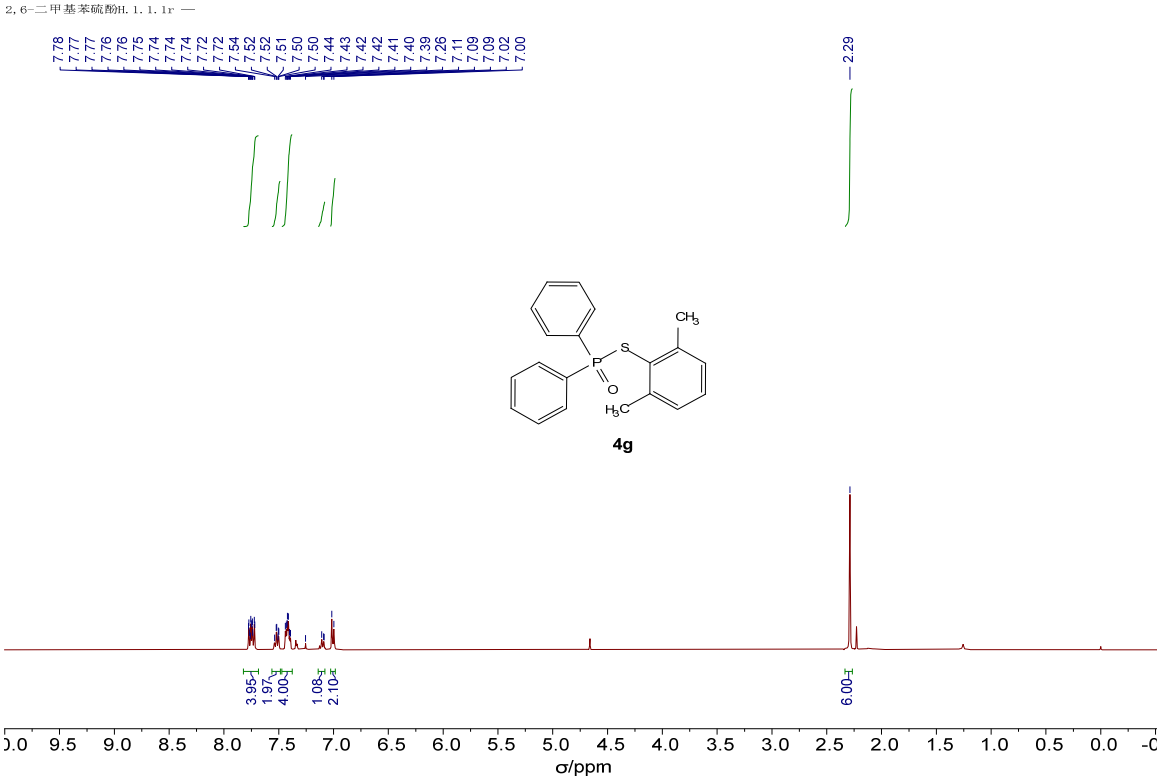
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4f**



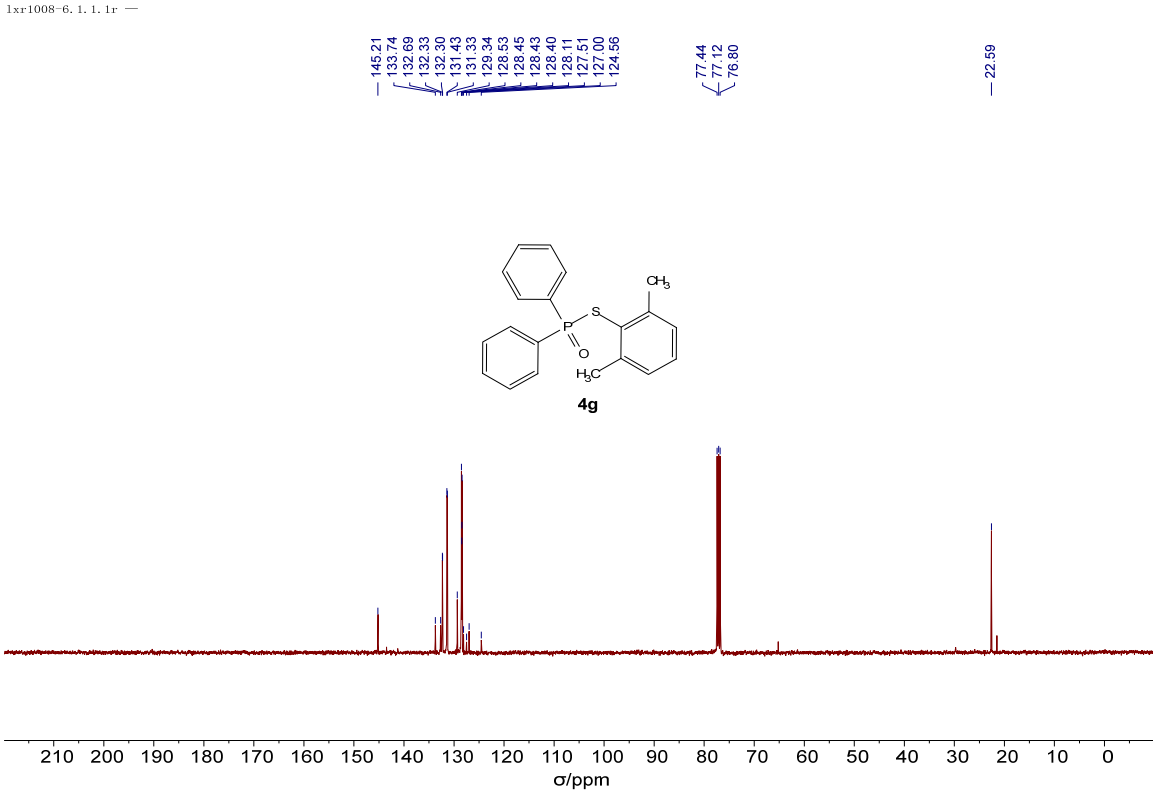
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4f**



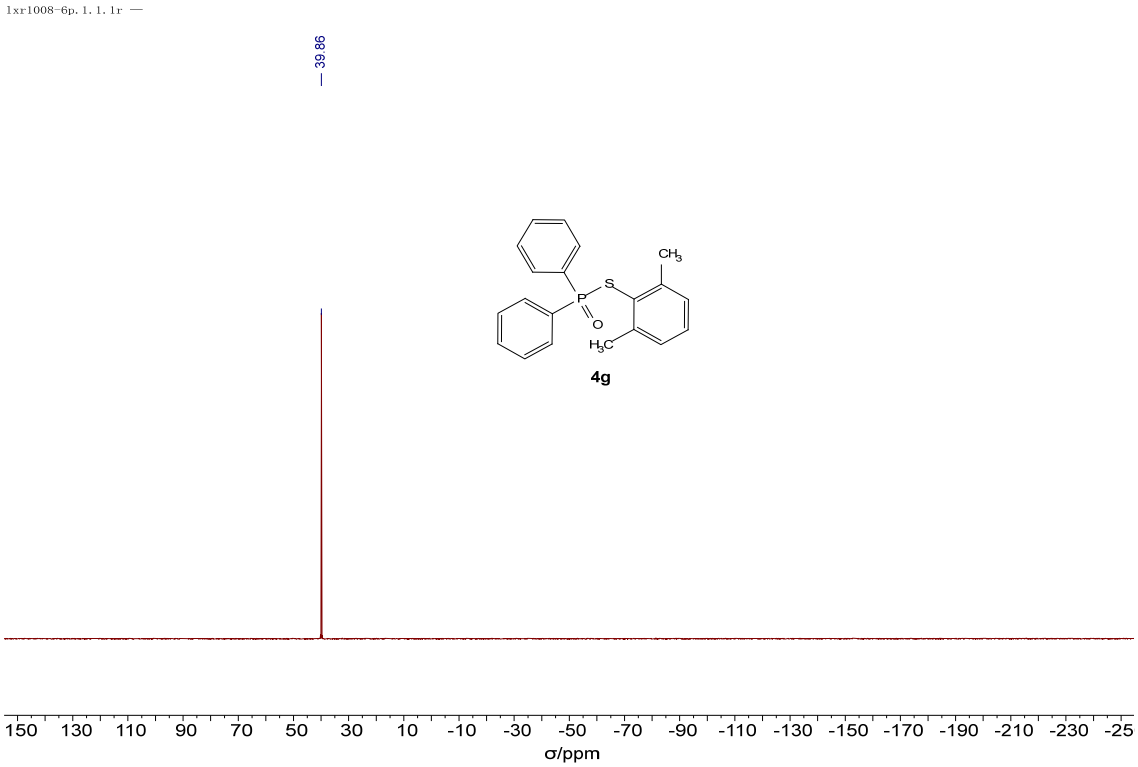
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4g**



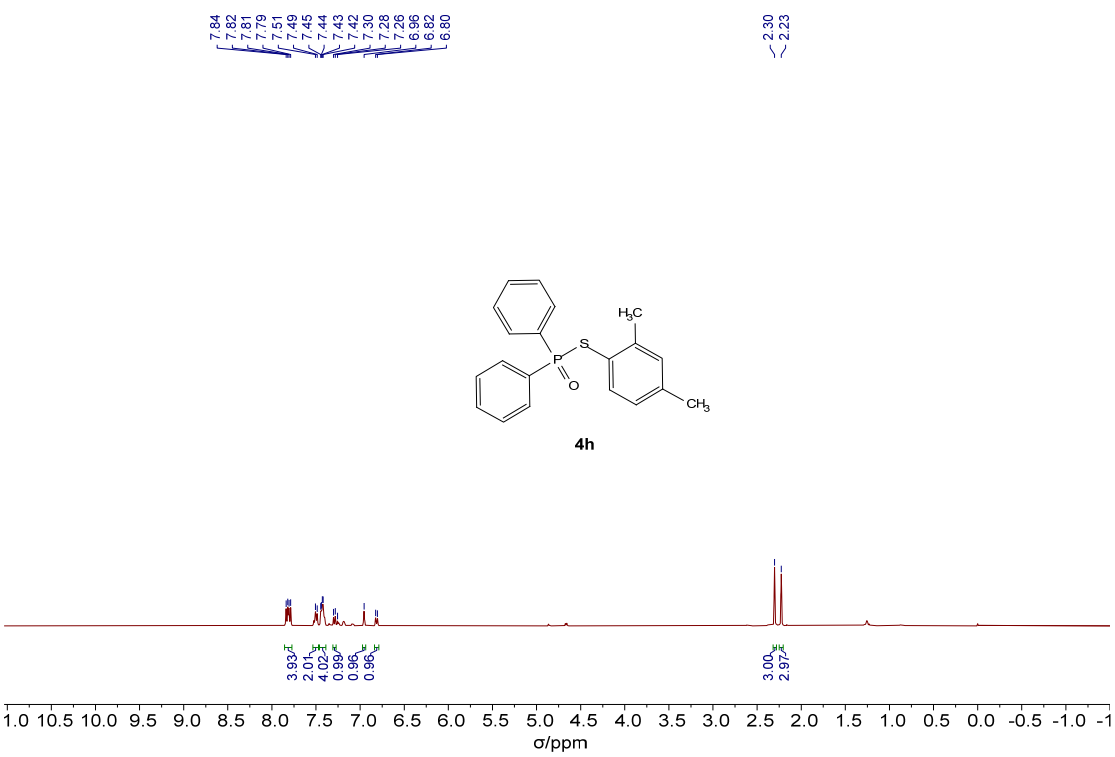
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4g**



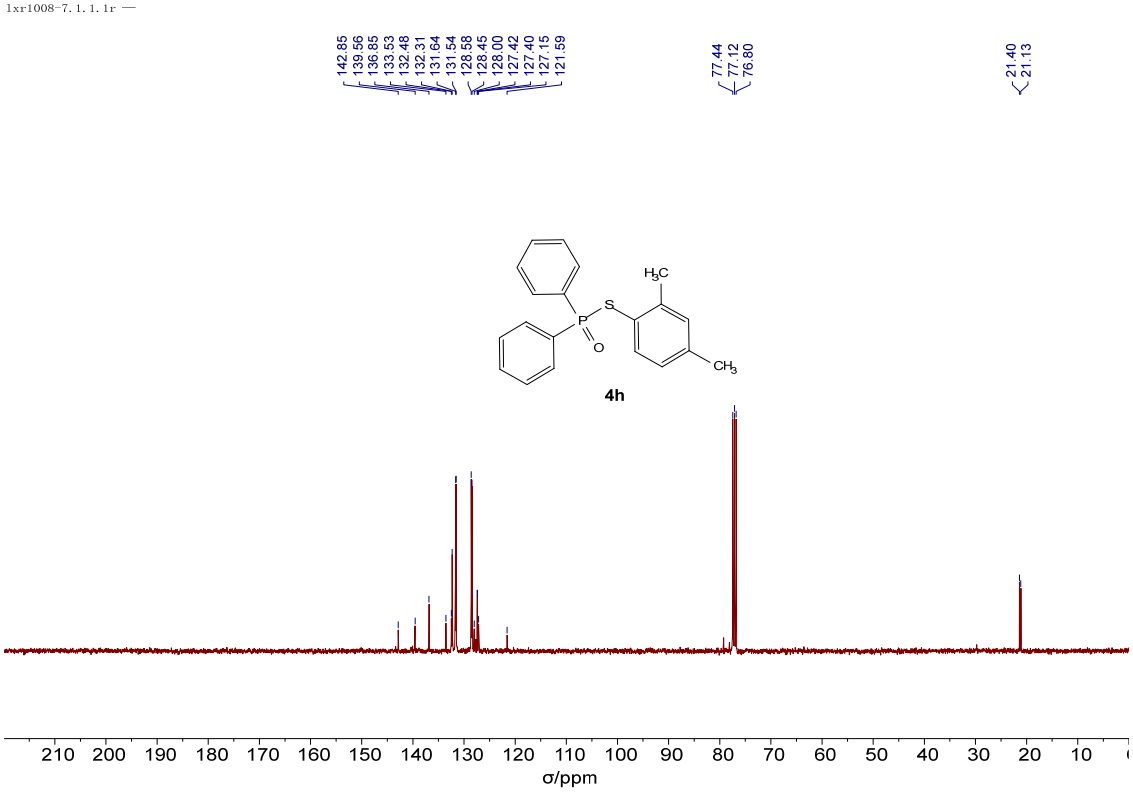
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4g**



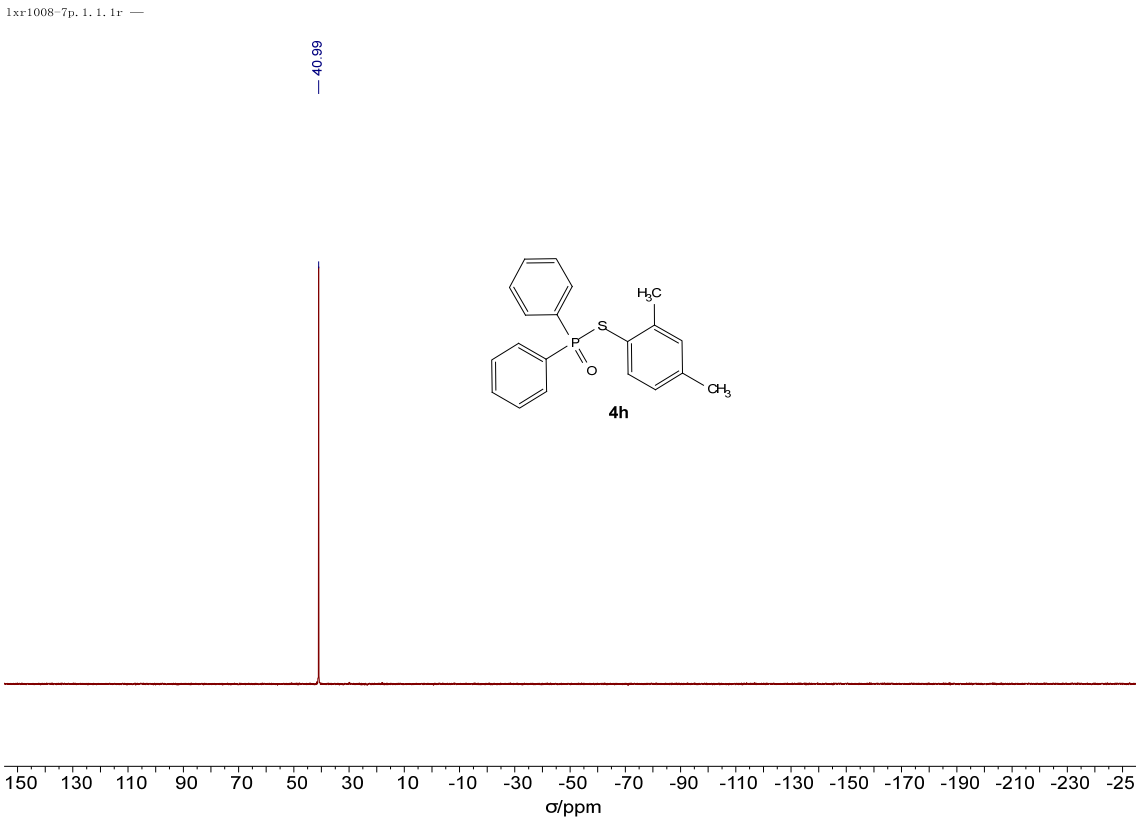
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4h**



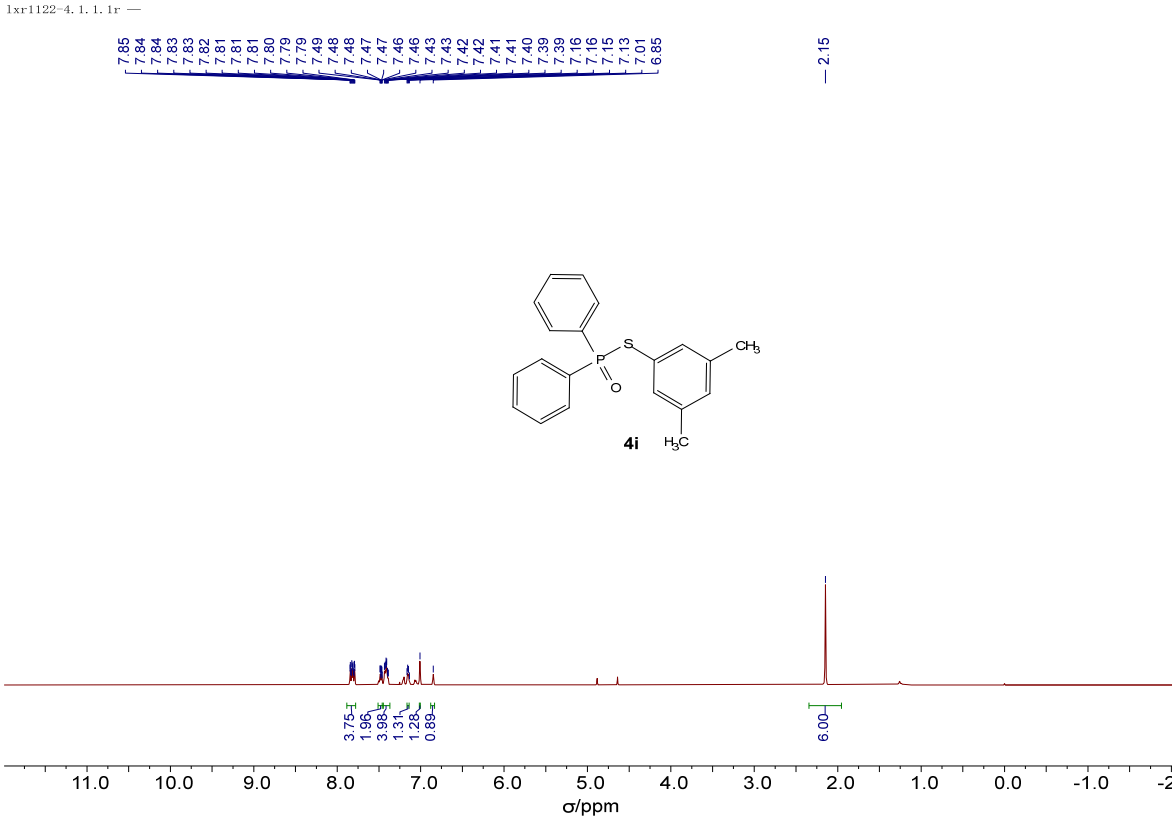
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4h**



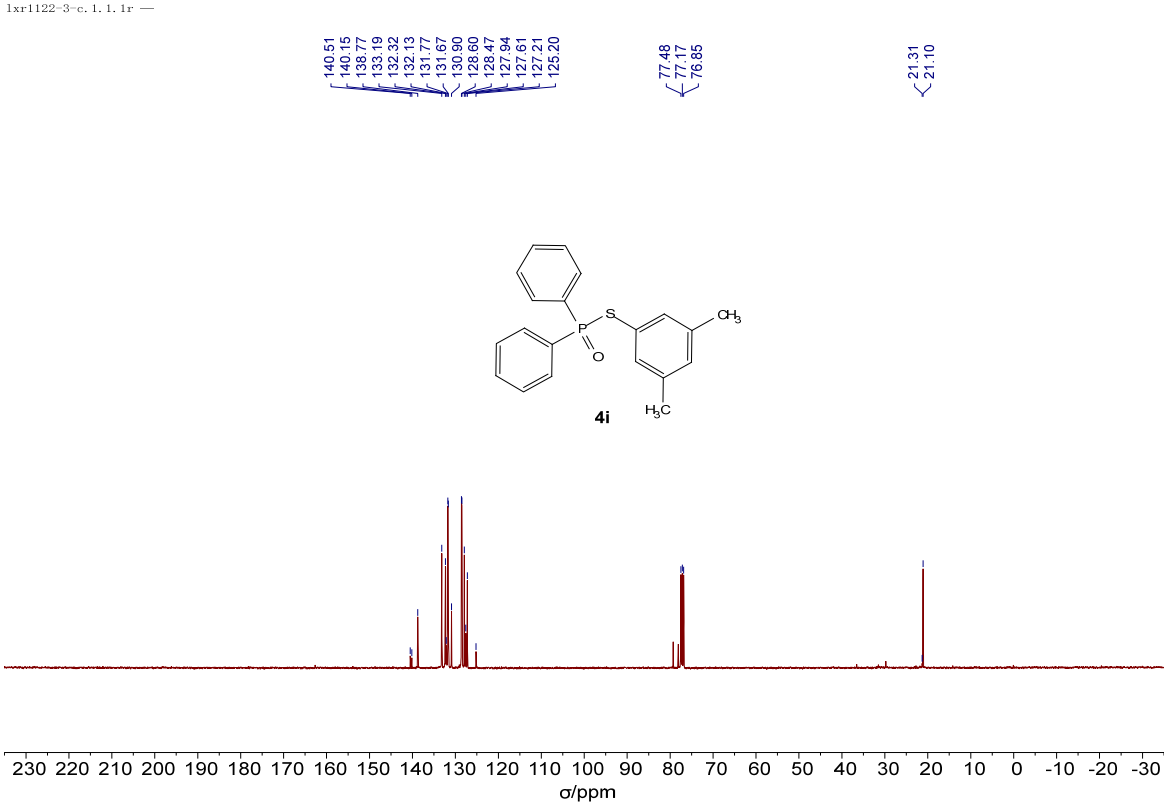
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4h**



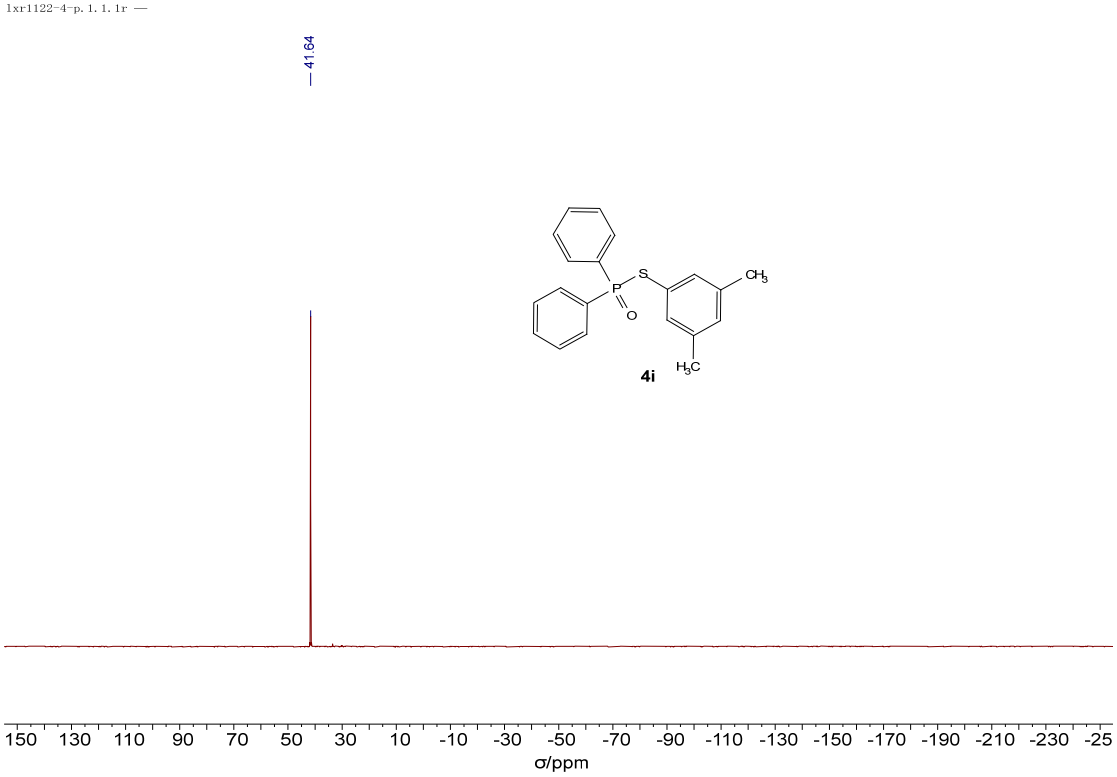
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4i**



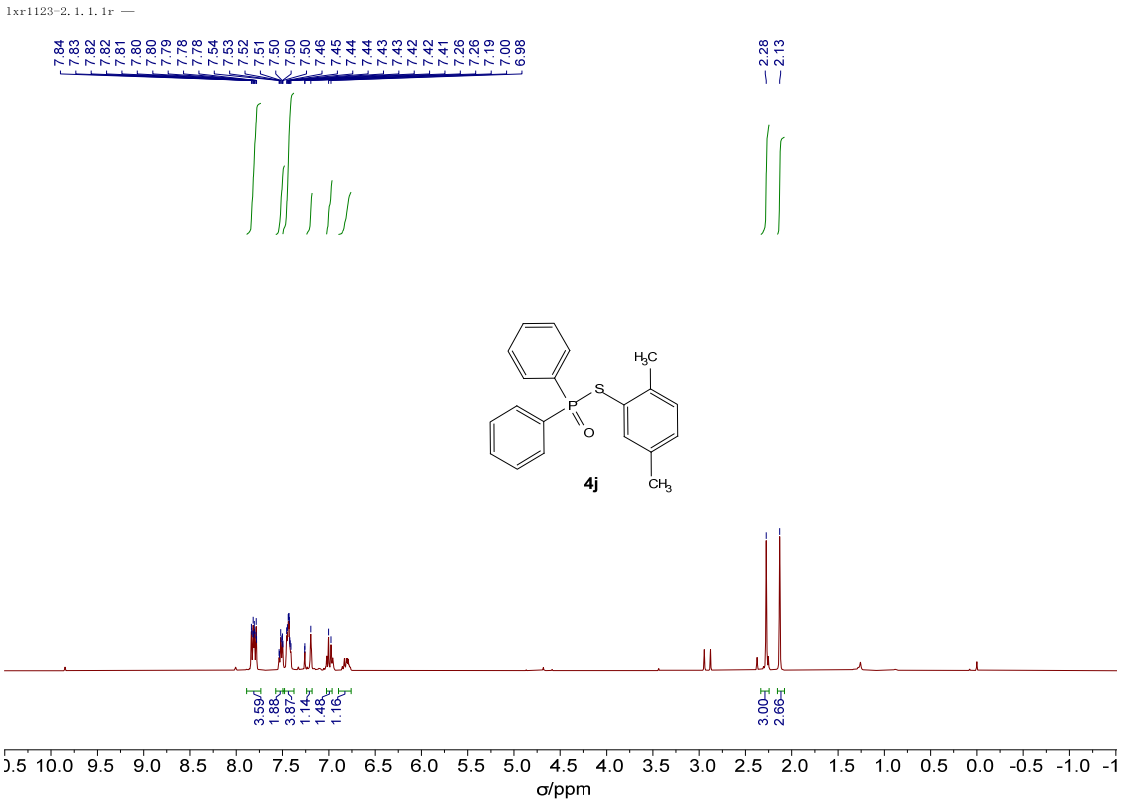
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4i**



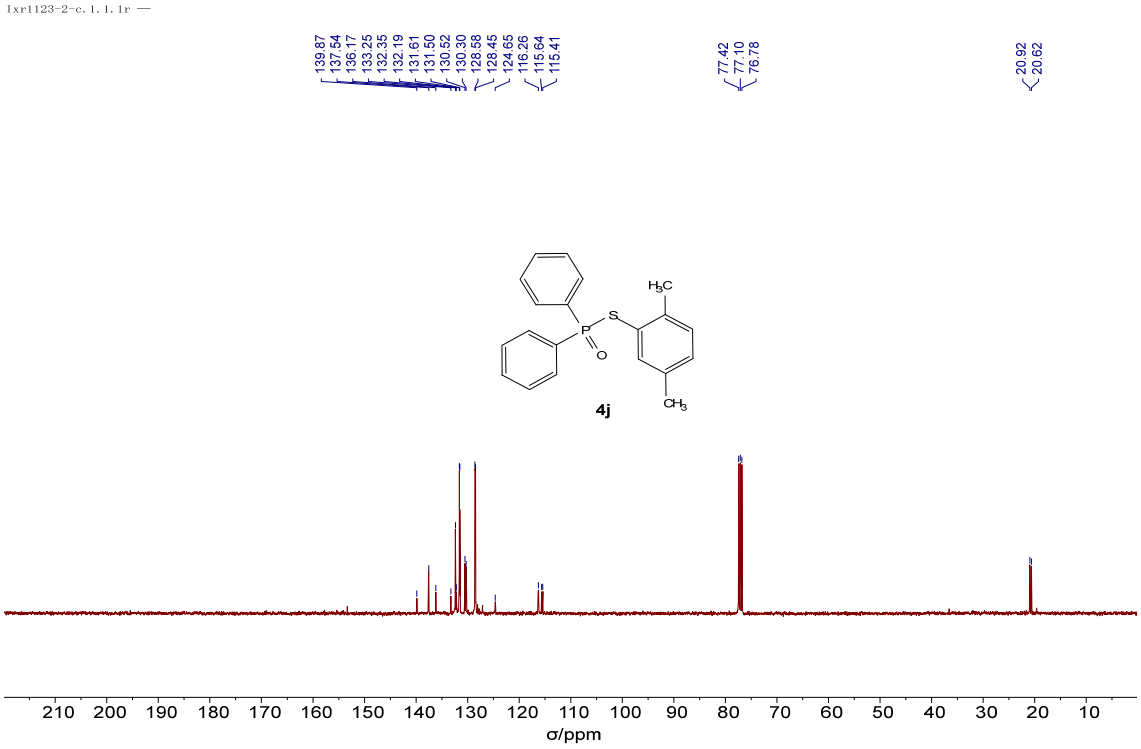
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4i**



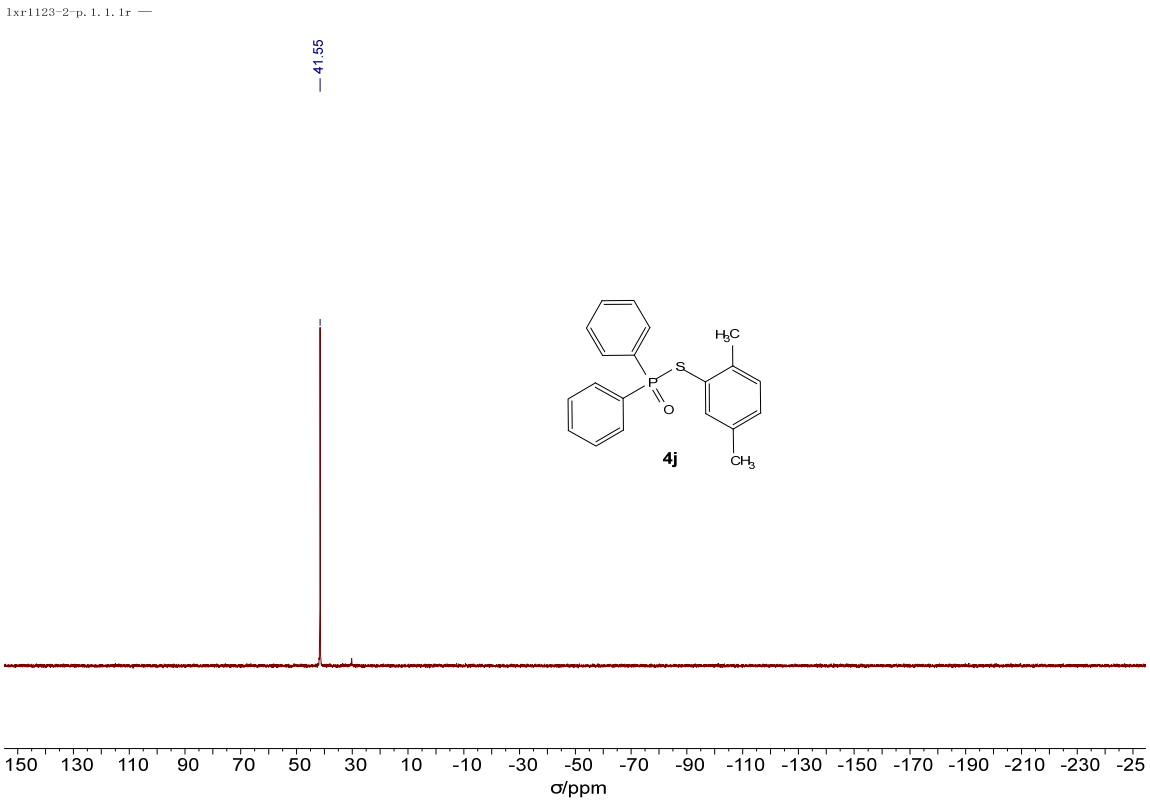
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4j**



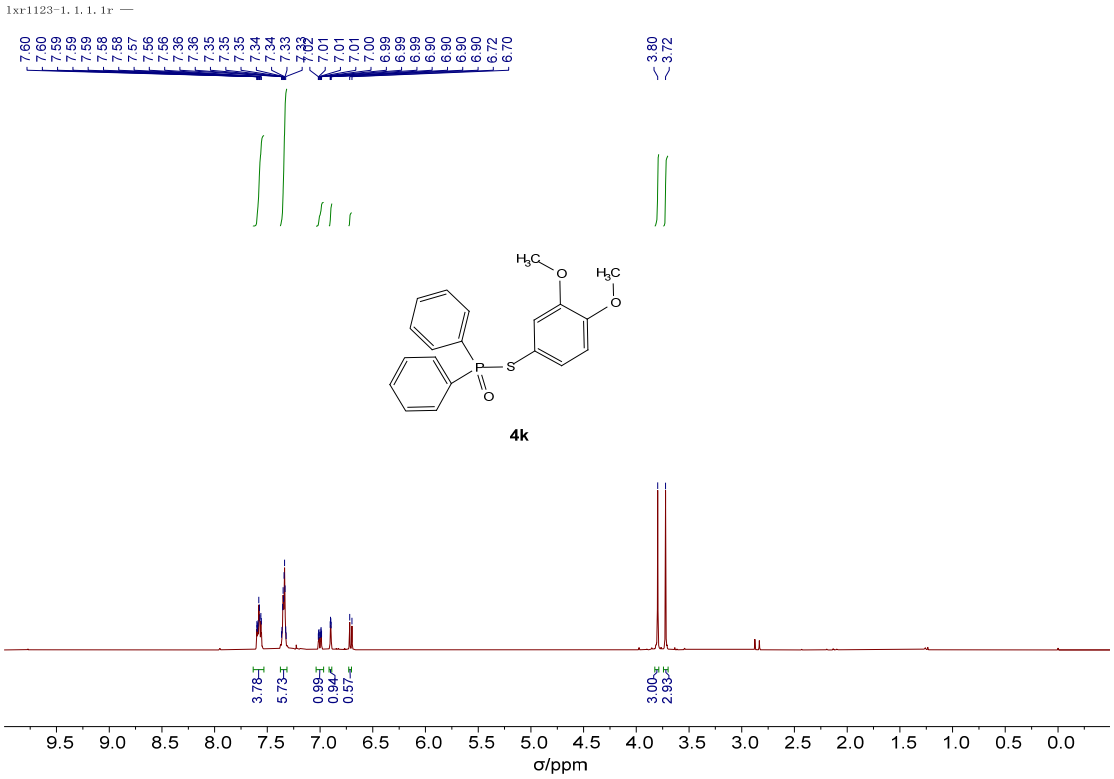
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4j**



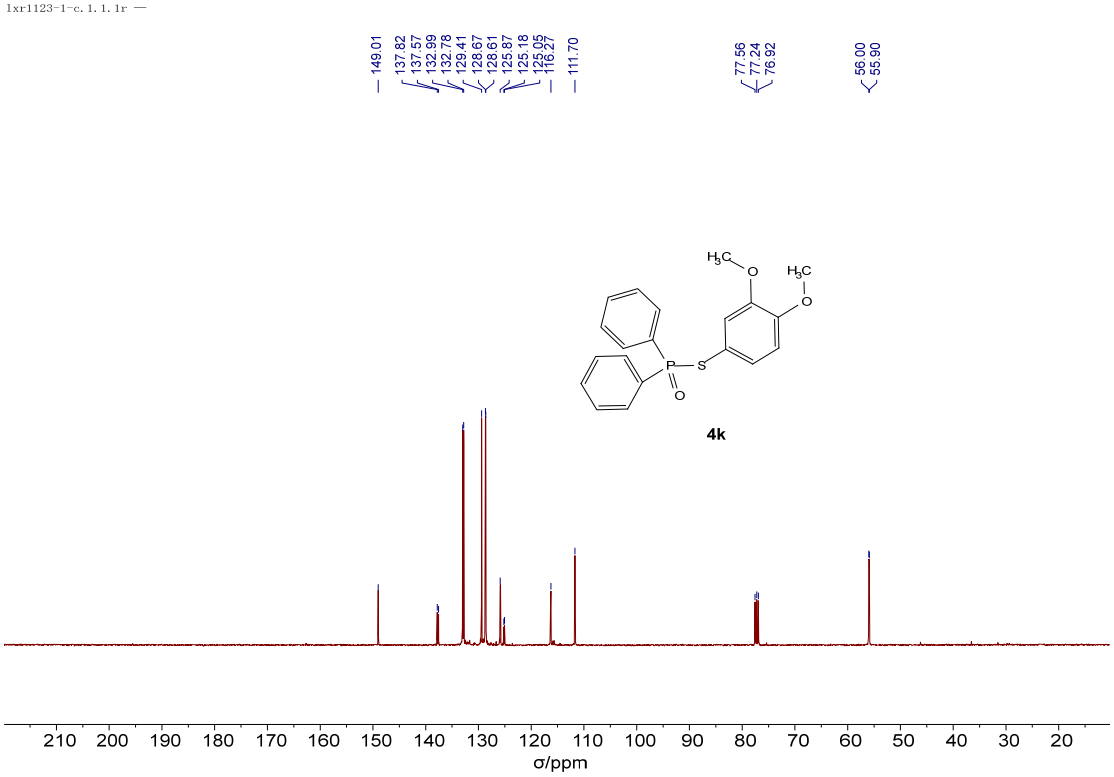
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4j**



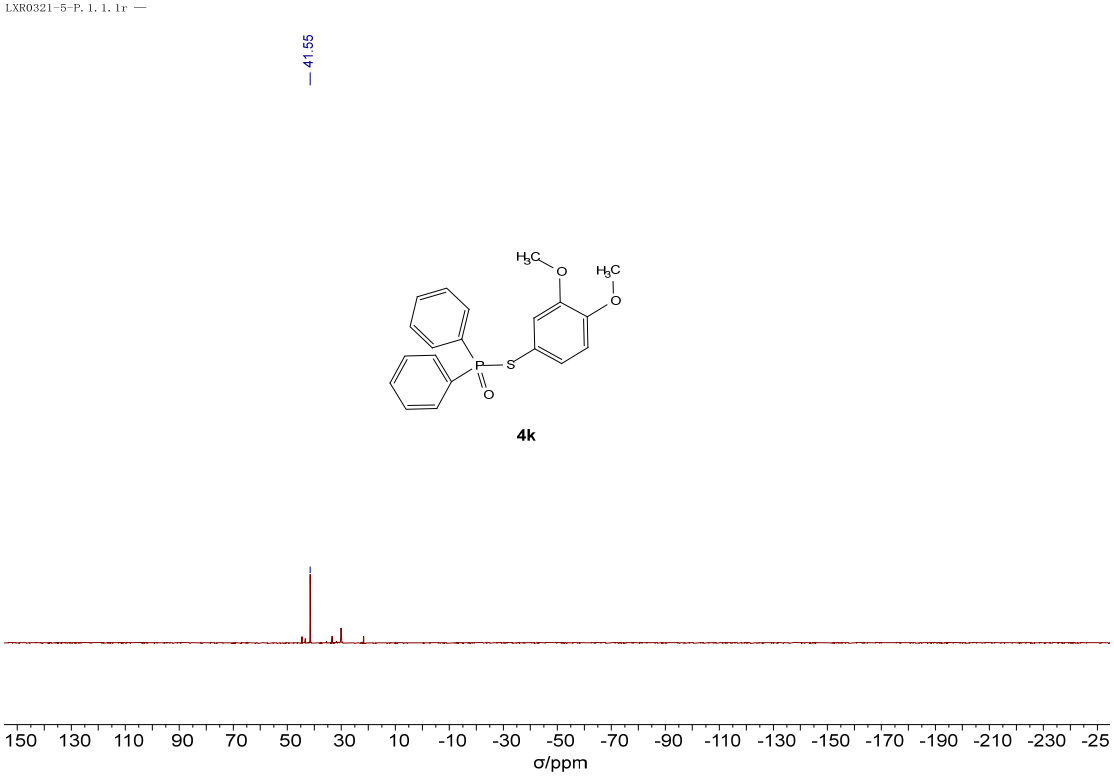
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4k**



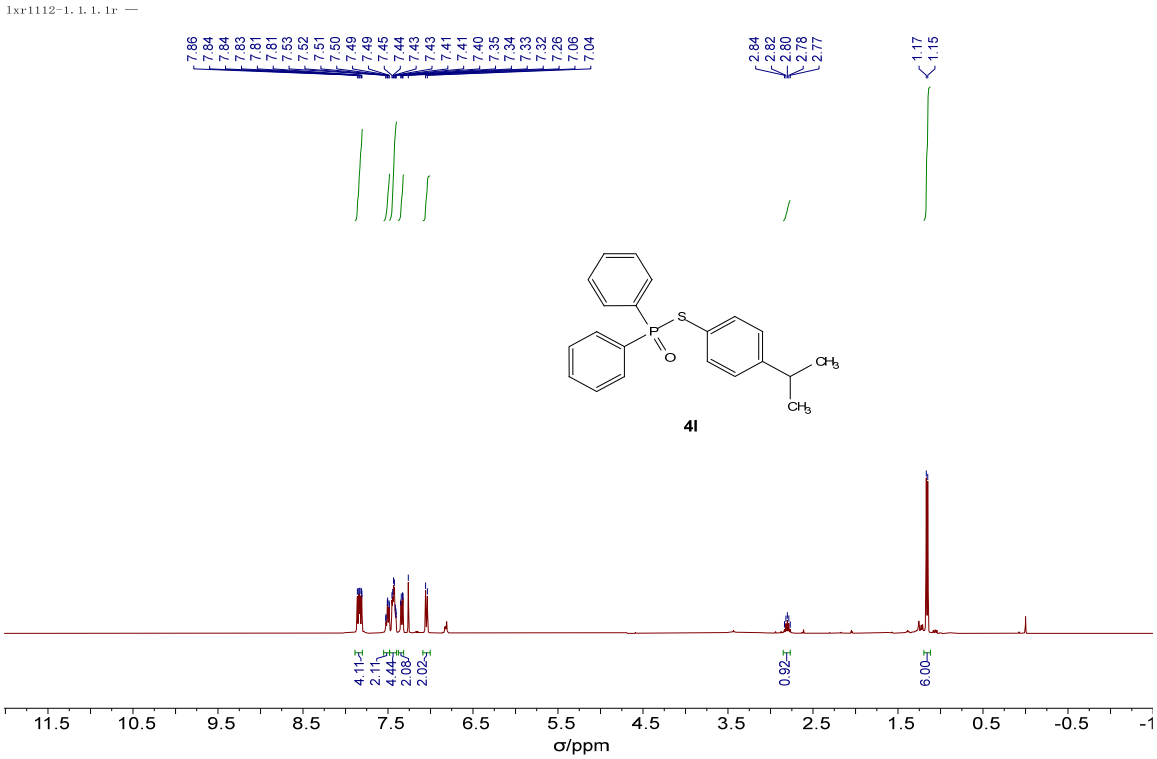
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4k**



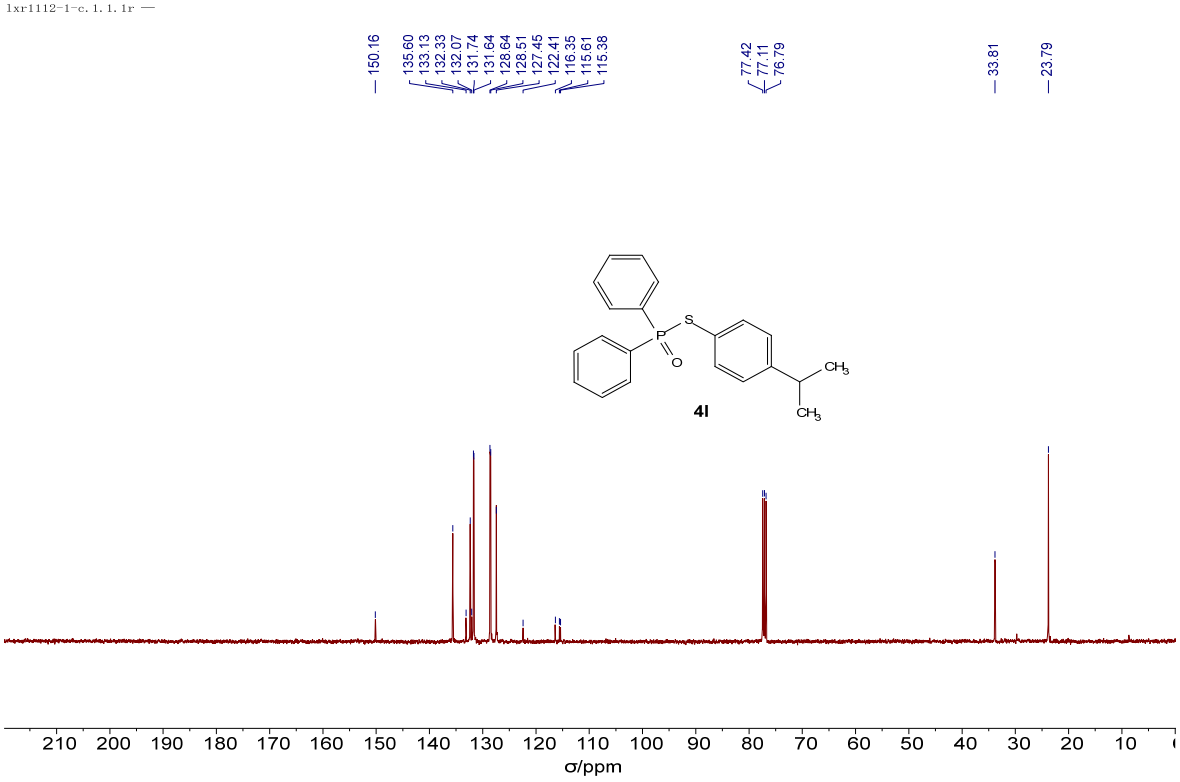
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4k**



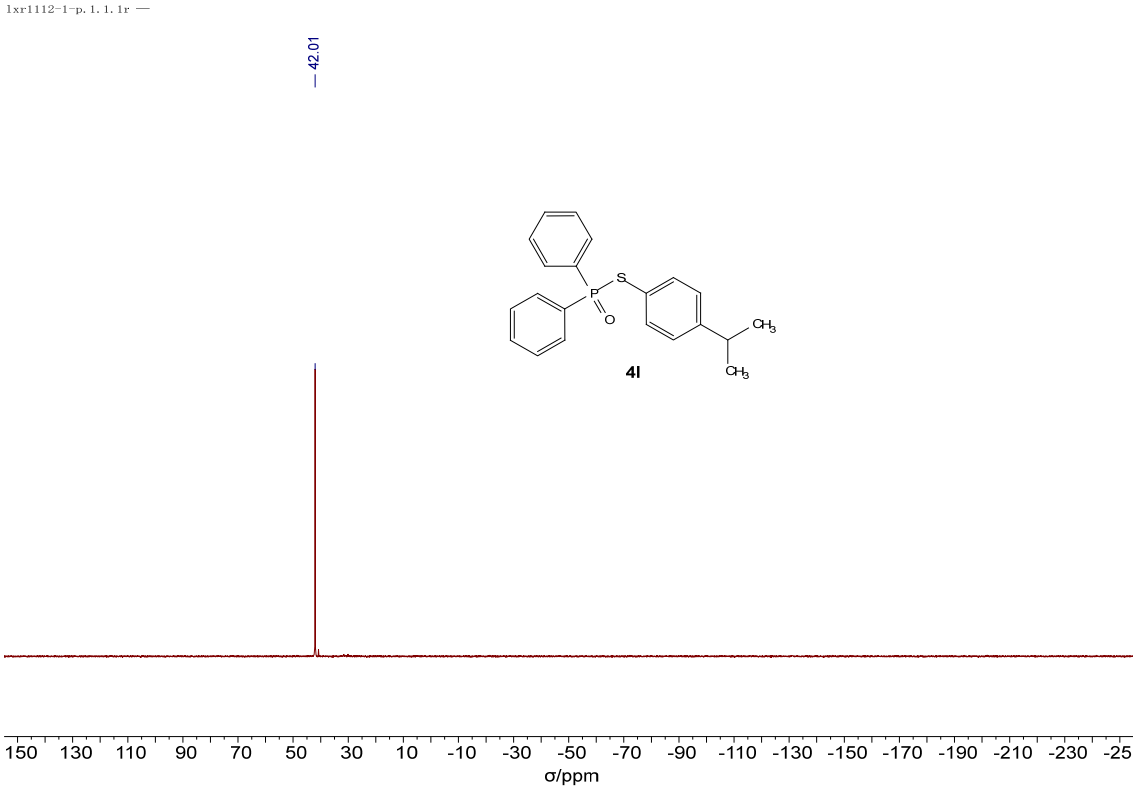
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4l**



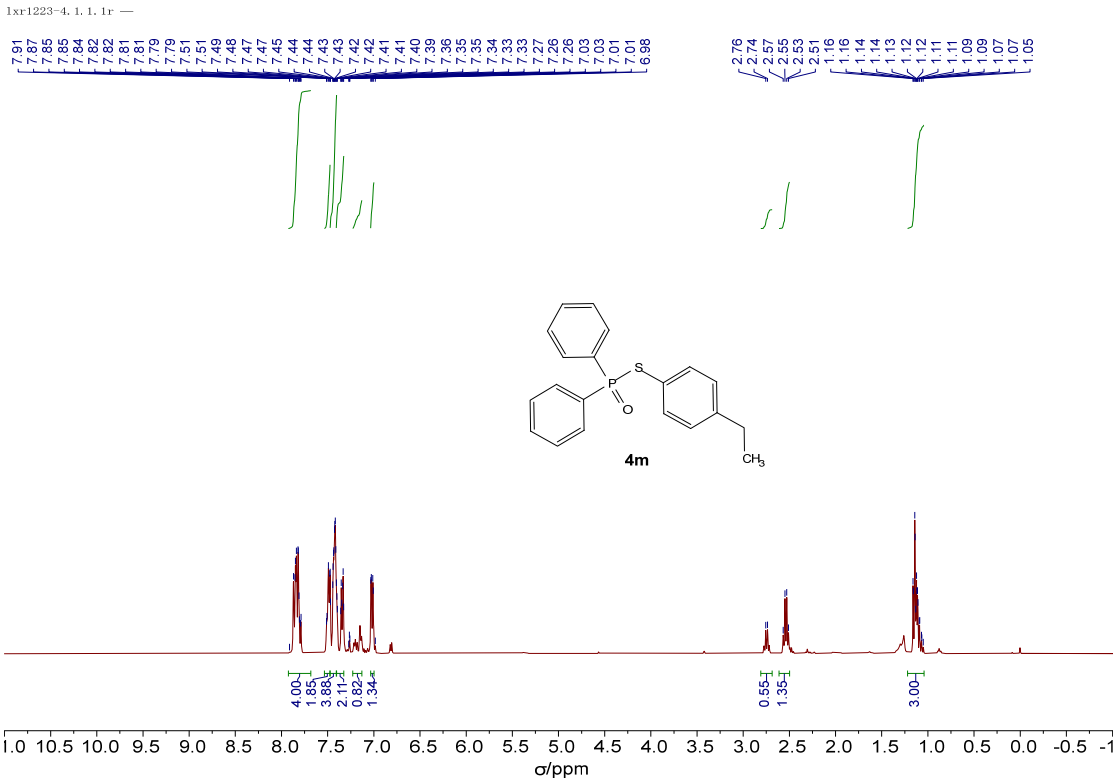
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4l**



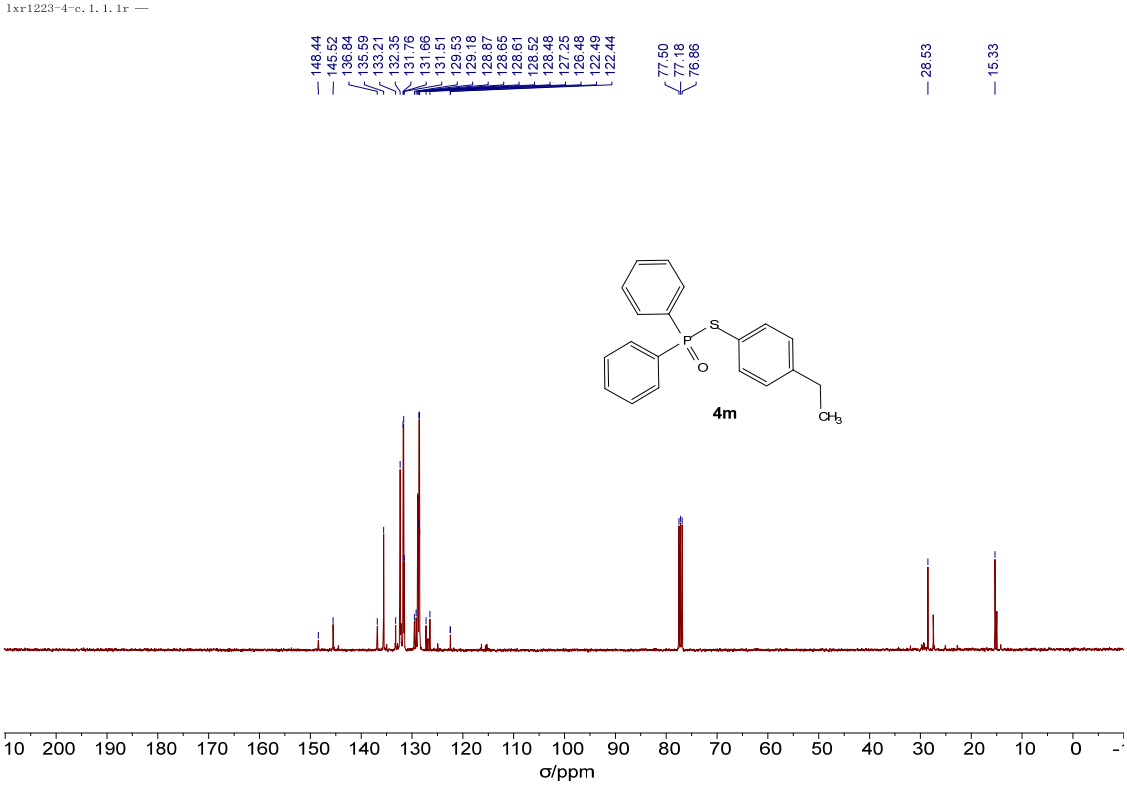
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4l**



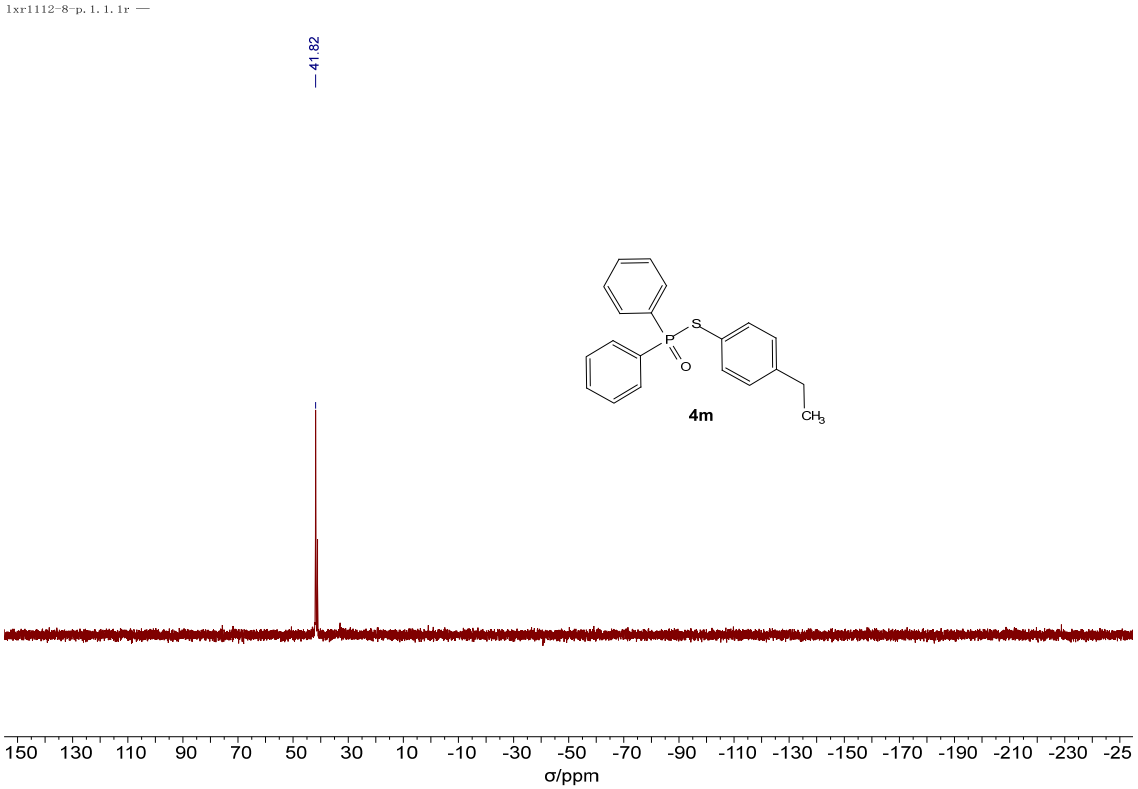
[1]H NMR-spectrum (400MHz，$CDCl_3$) of **4m**



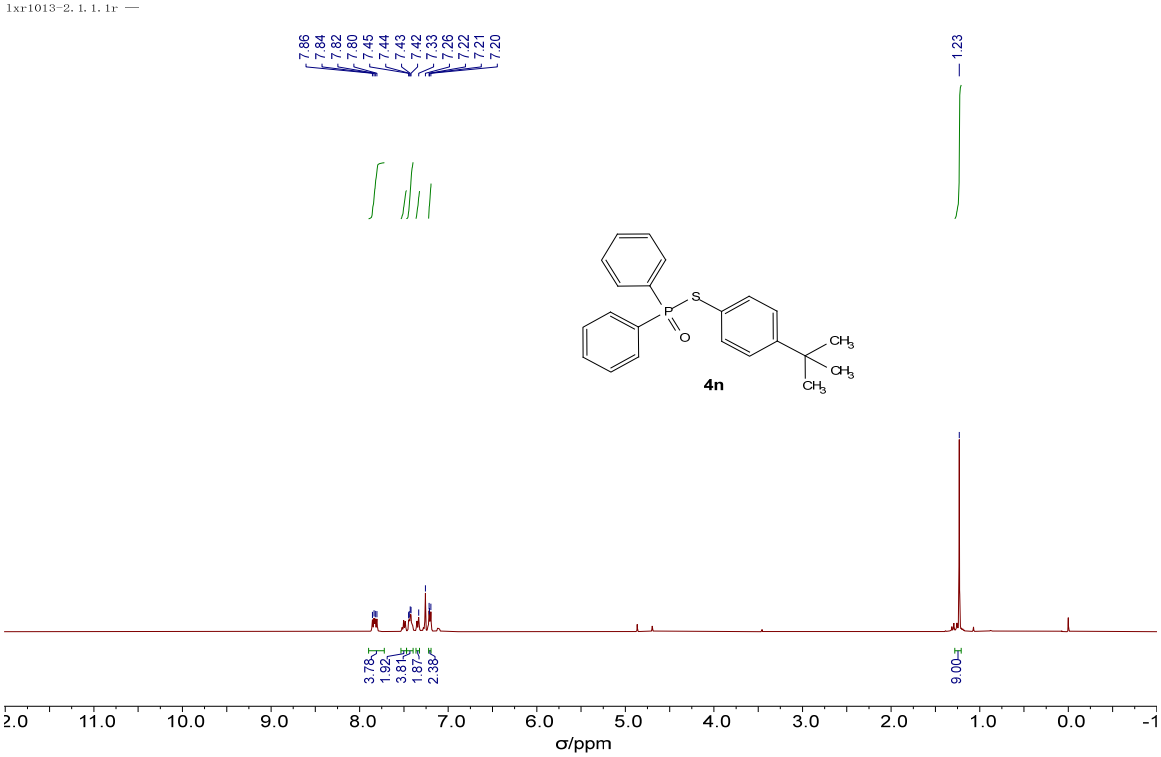
[13]C NMR-spectrum (101MHz，$CDCl_3$) of **4m**



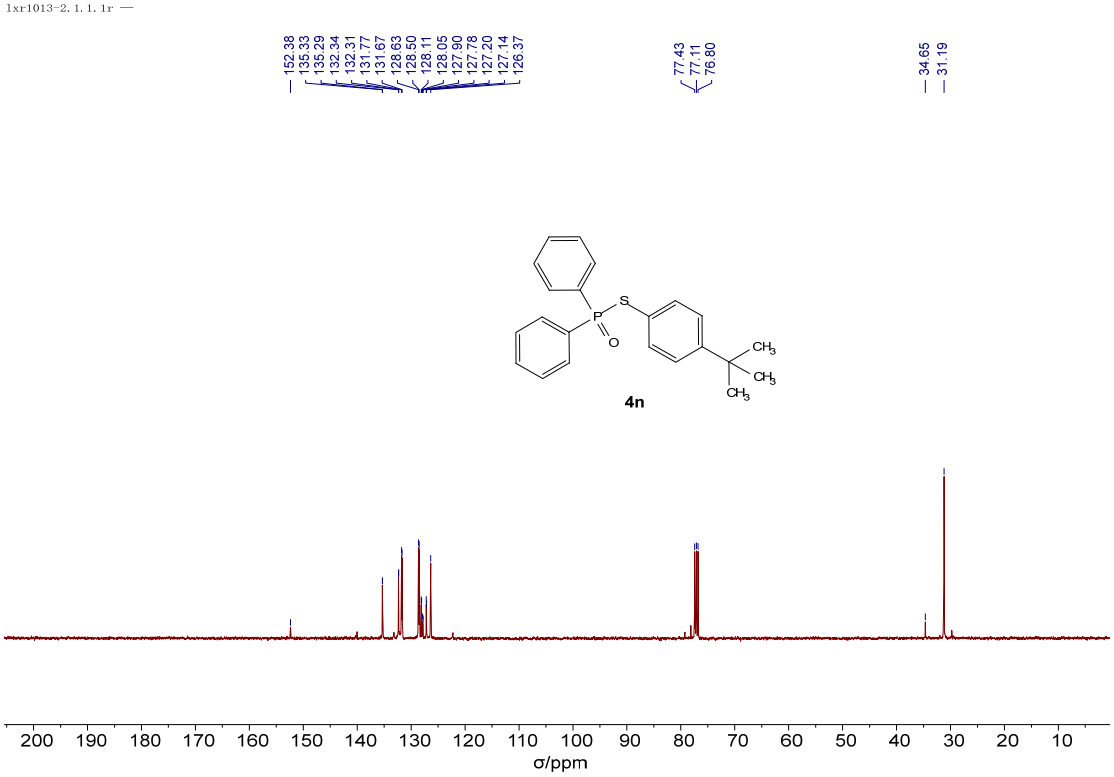
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4m**



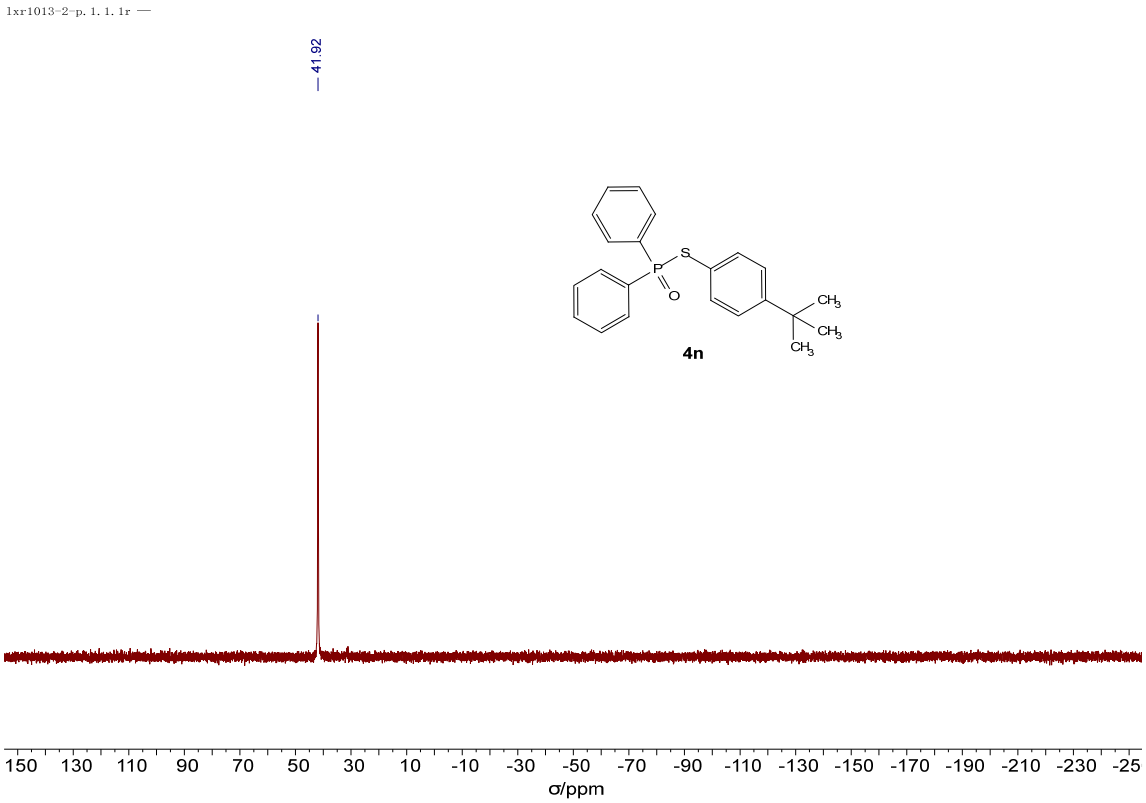
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4n**



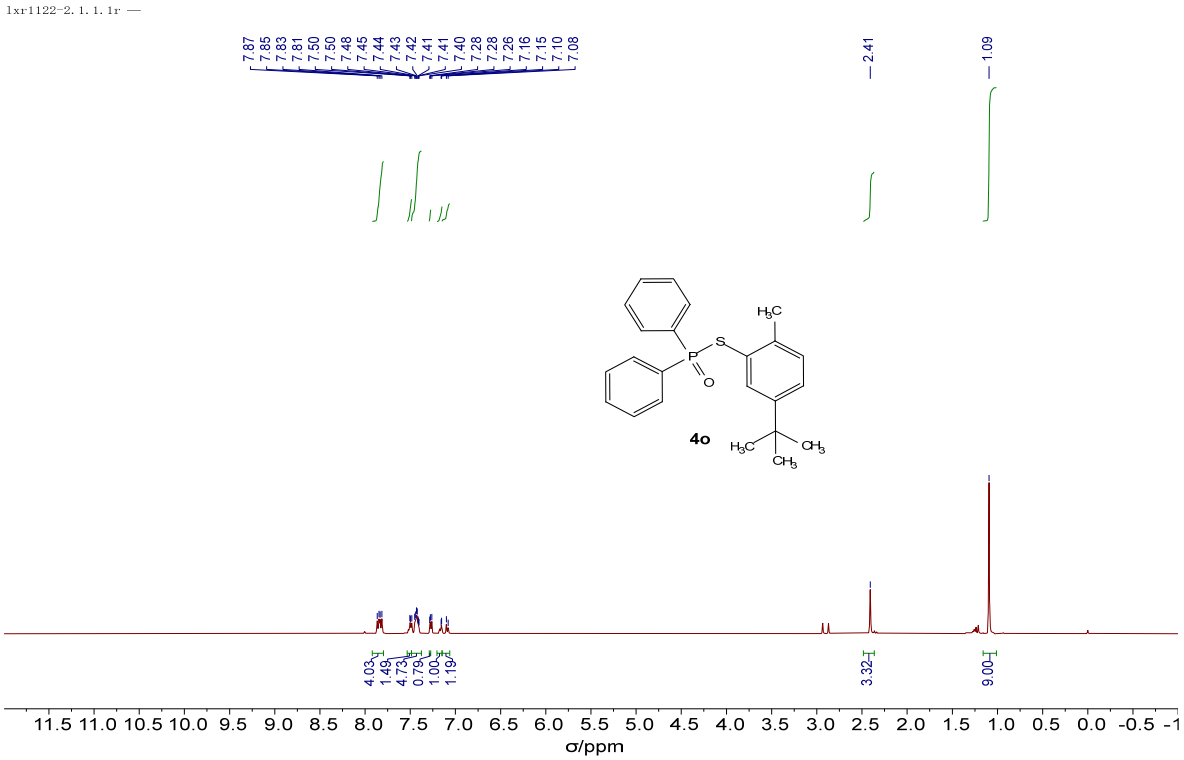
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4n**



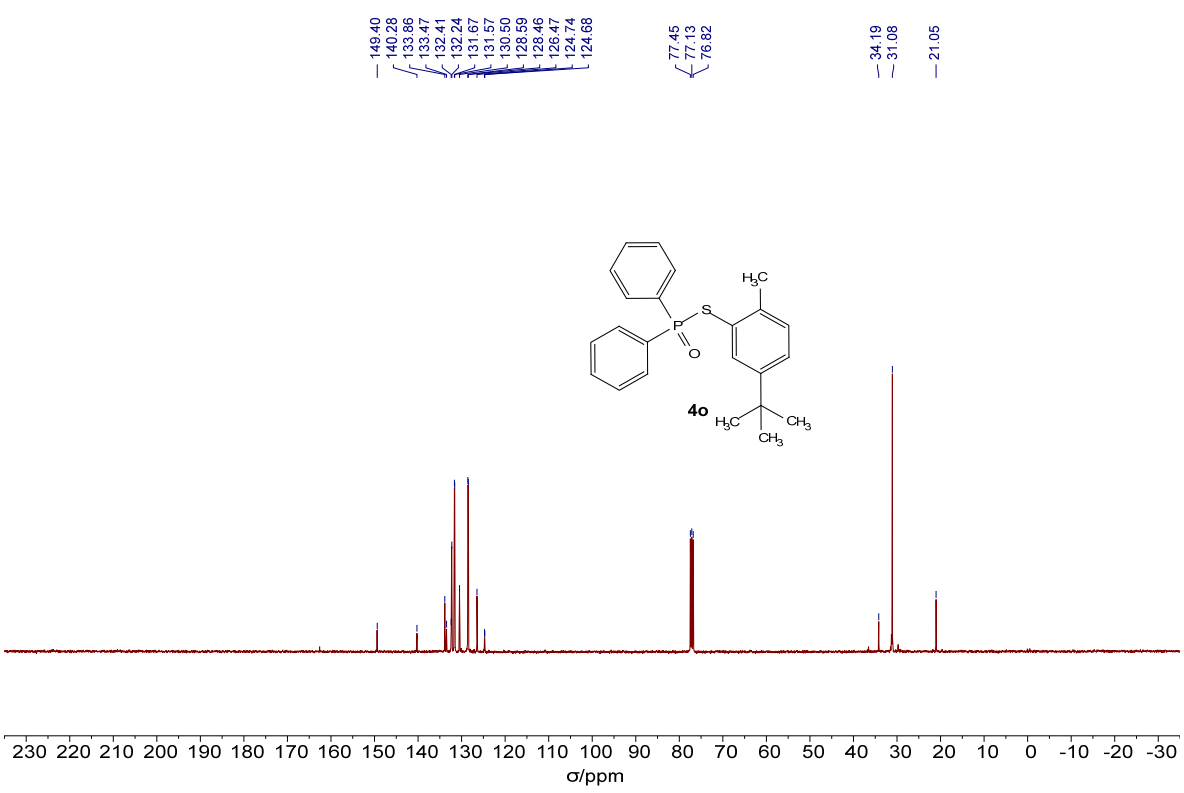
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4n**



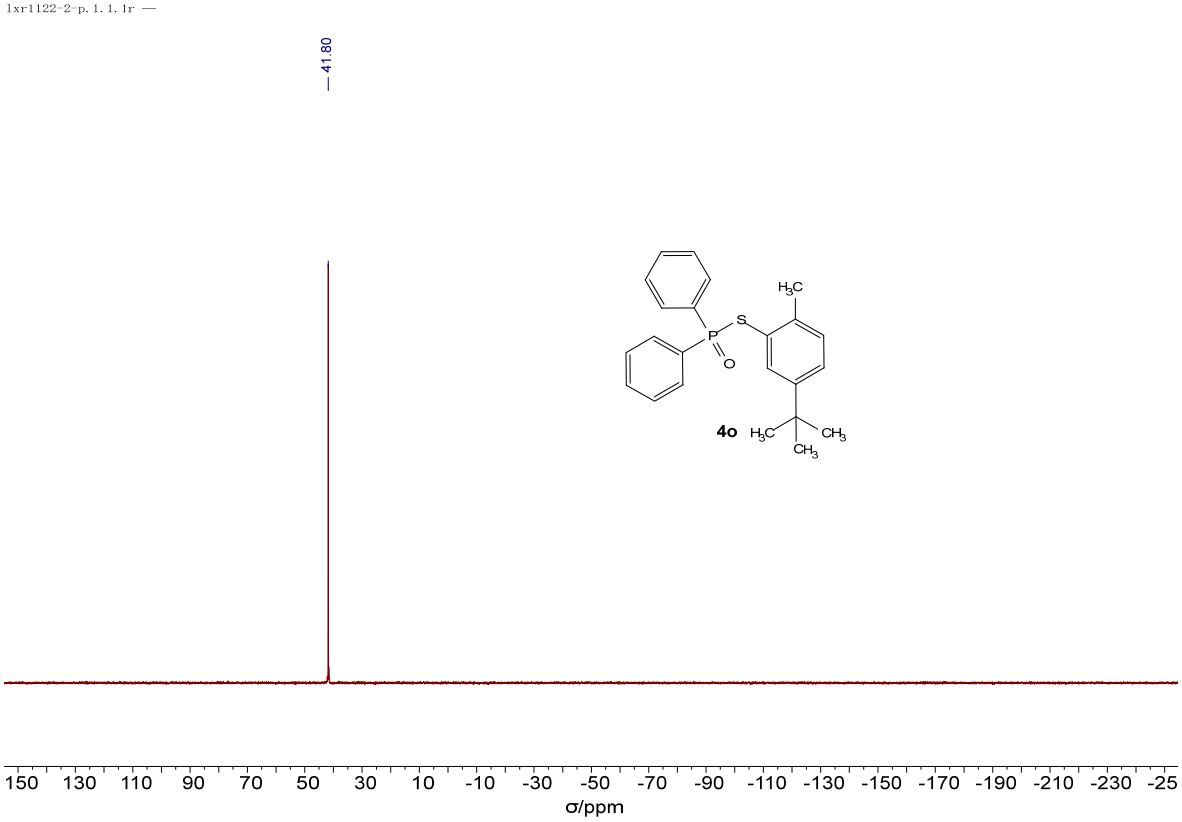
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4o**



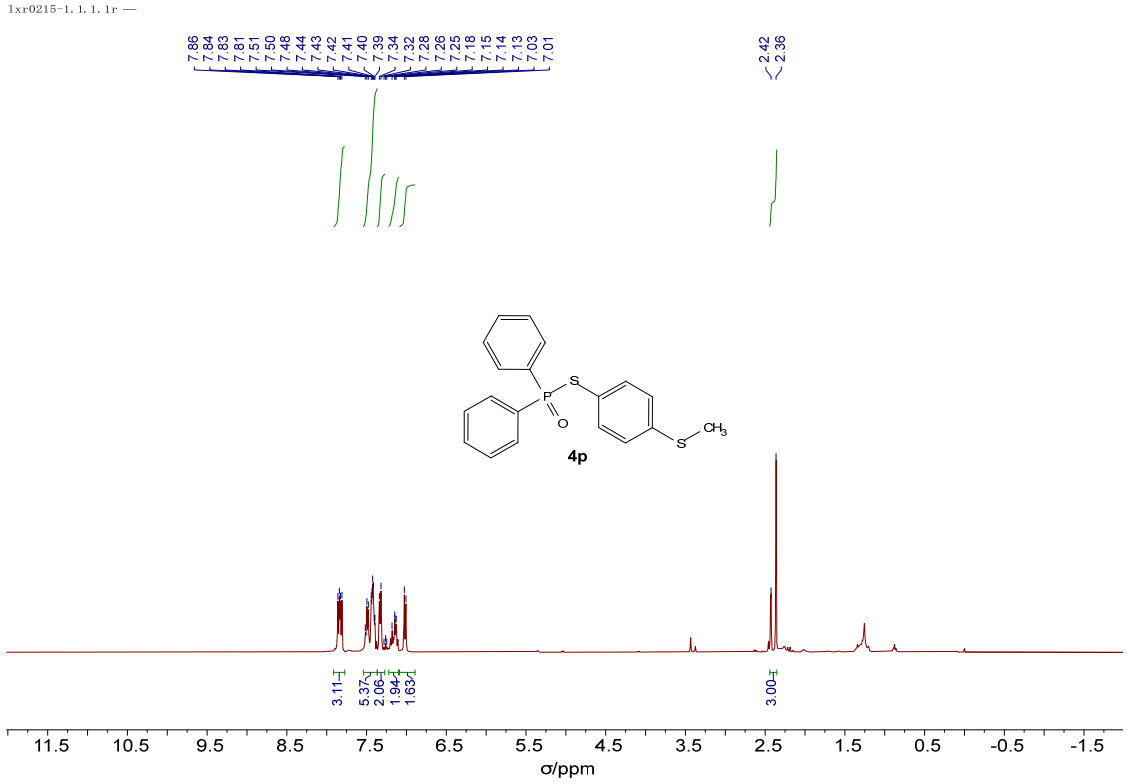
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4o**



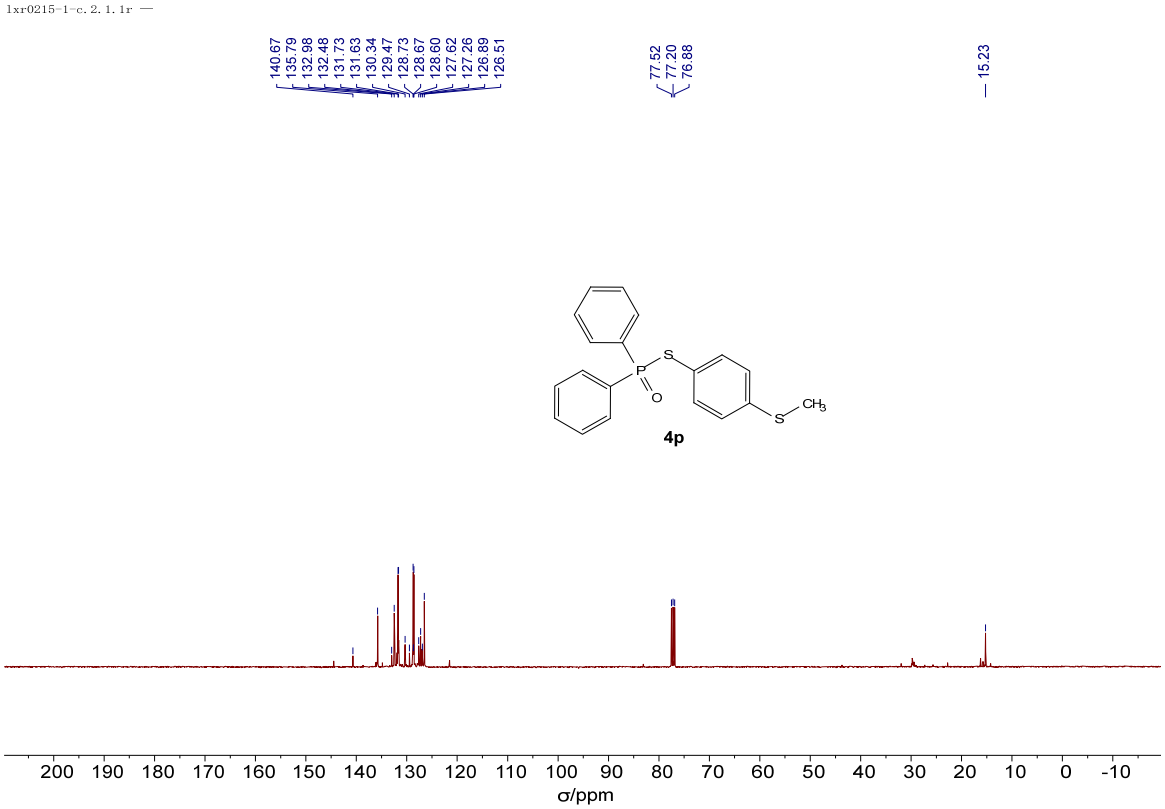
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4o**



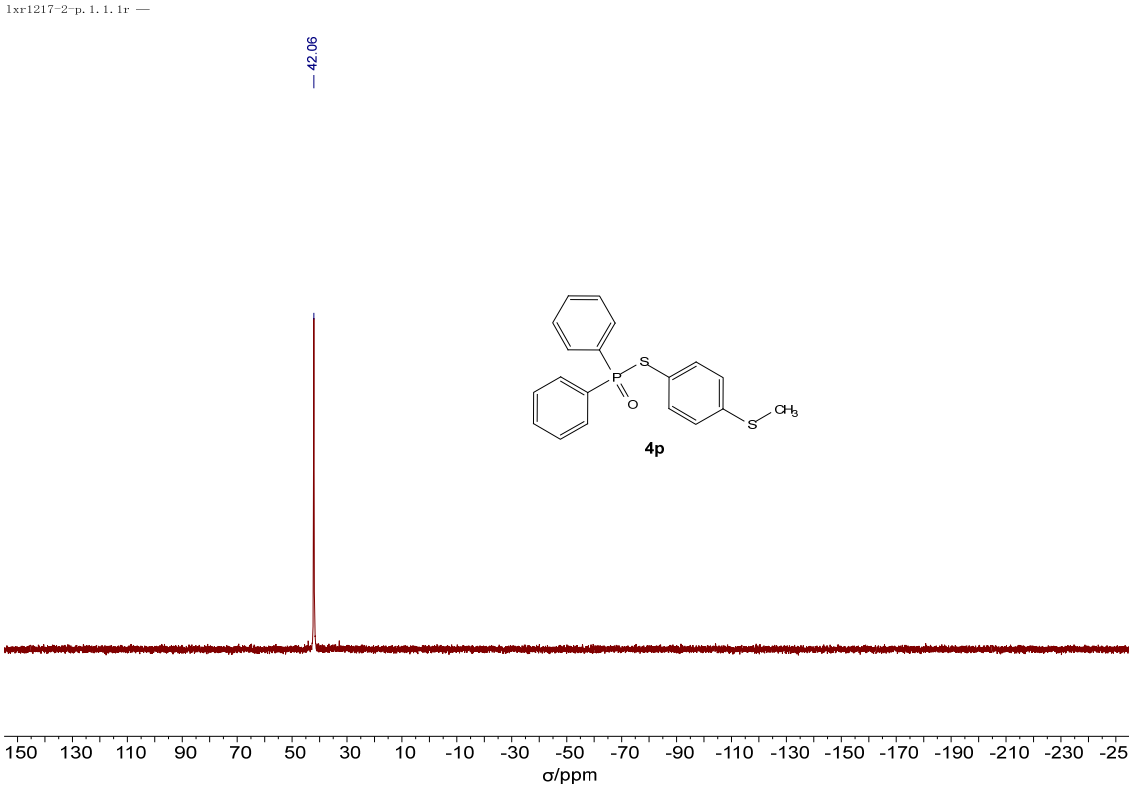
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4p**



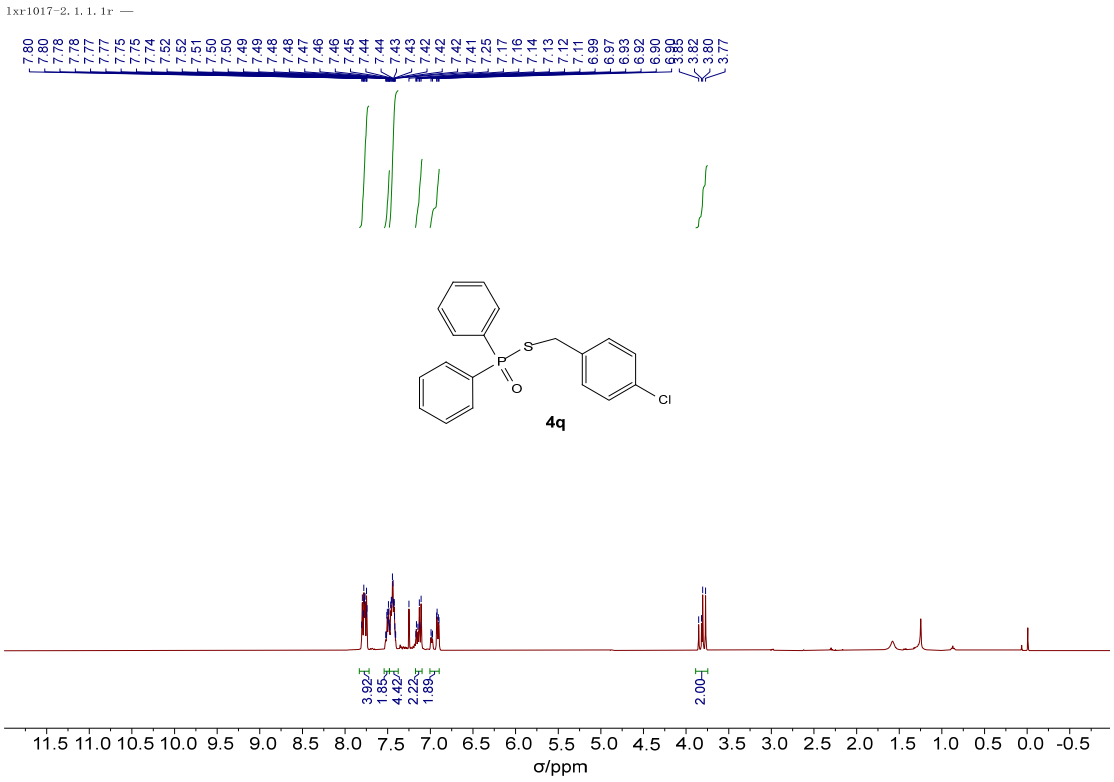
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4p**



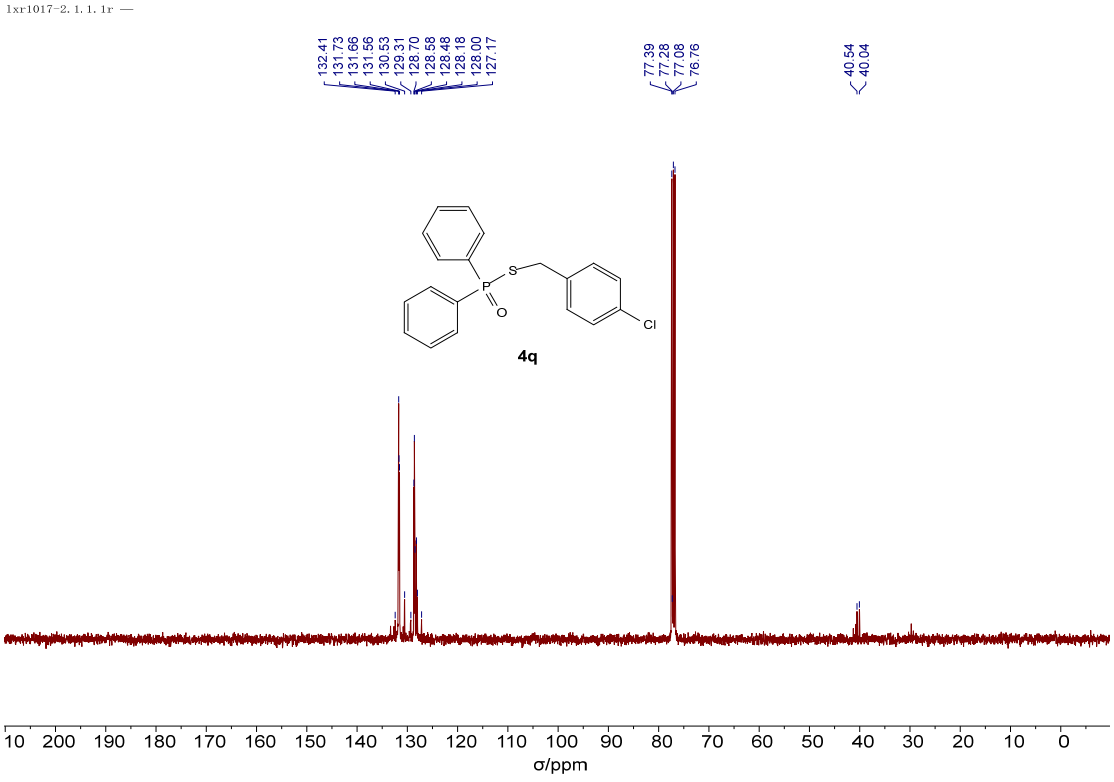
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4p**



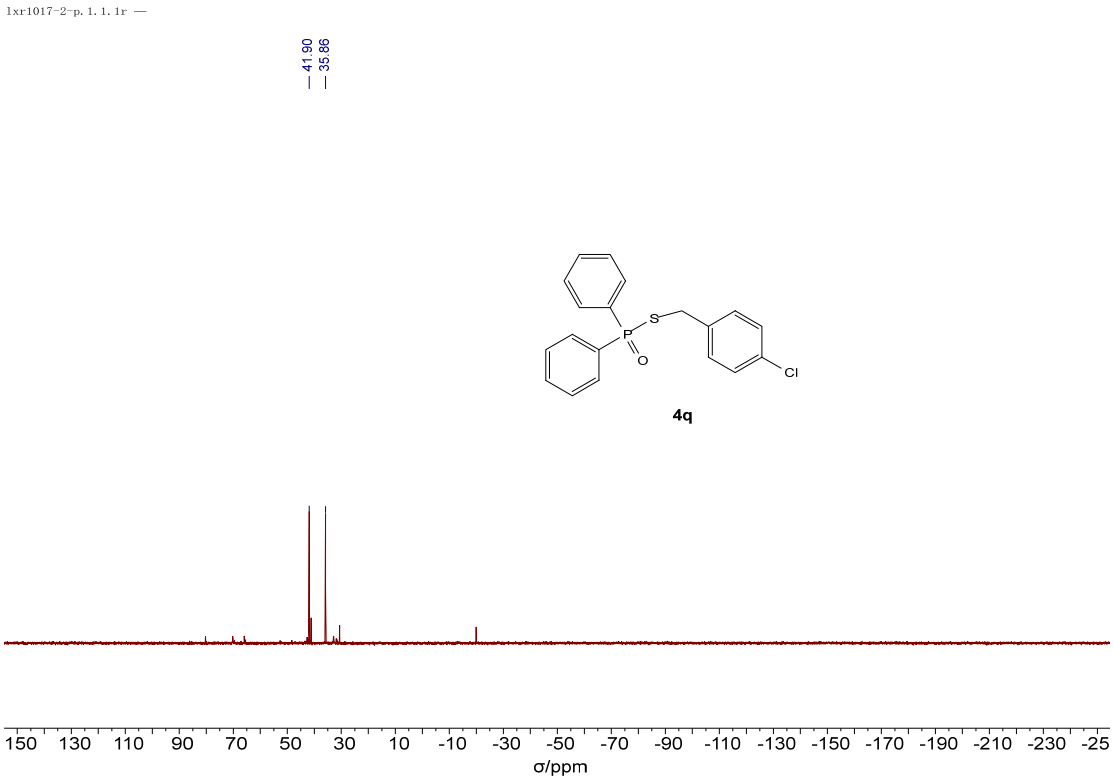
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4q**



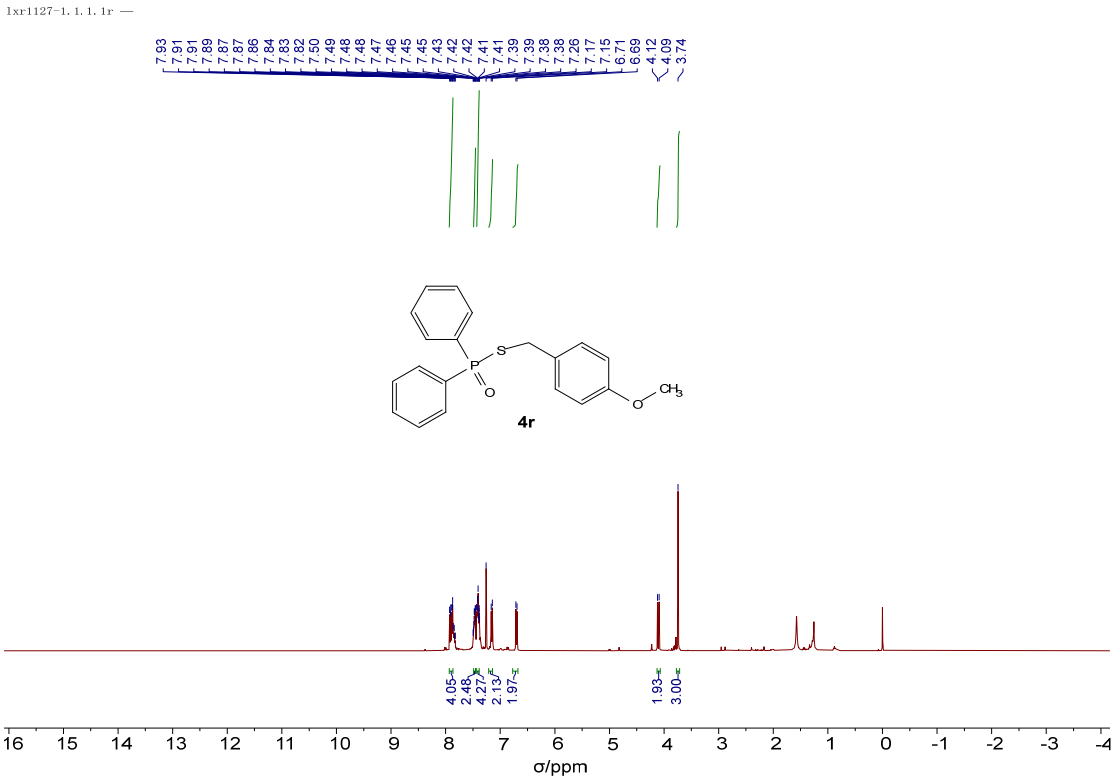
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4q**



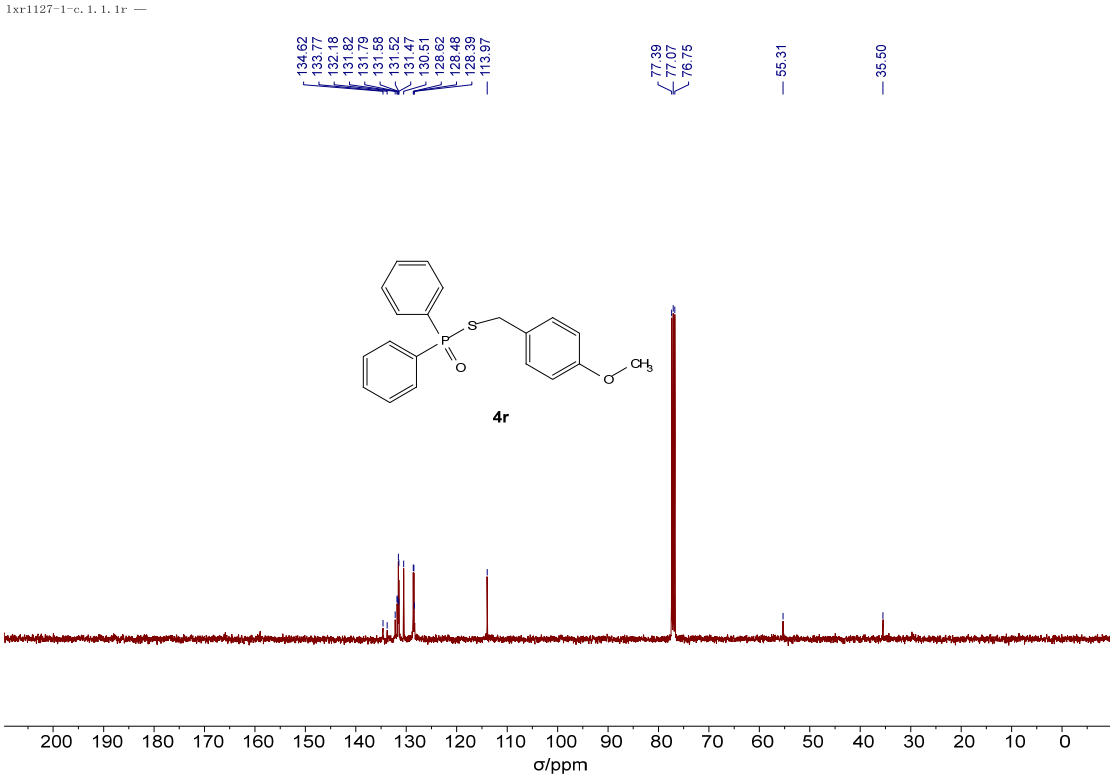
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4q**



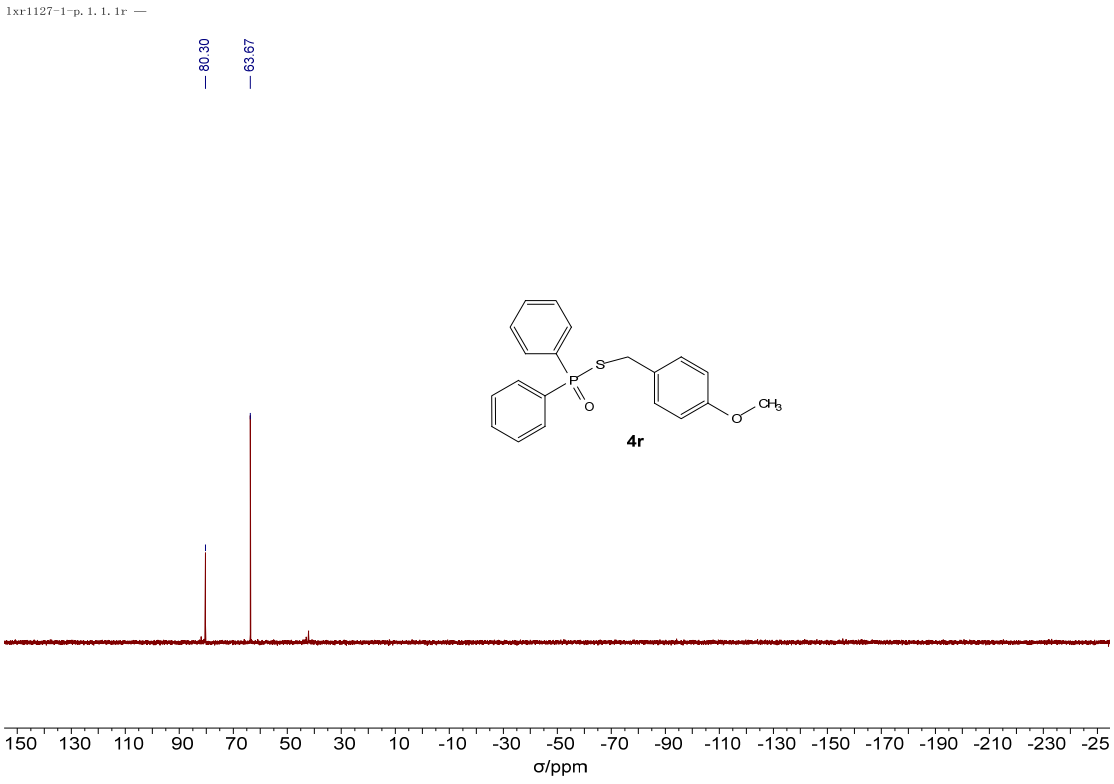
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4r**



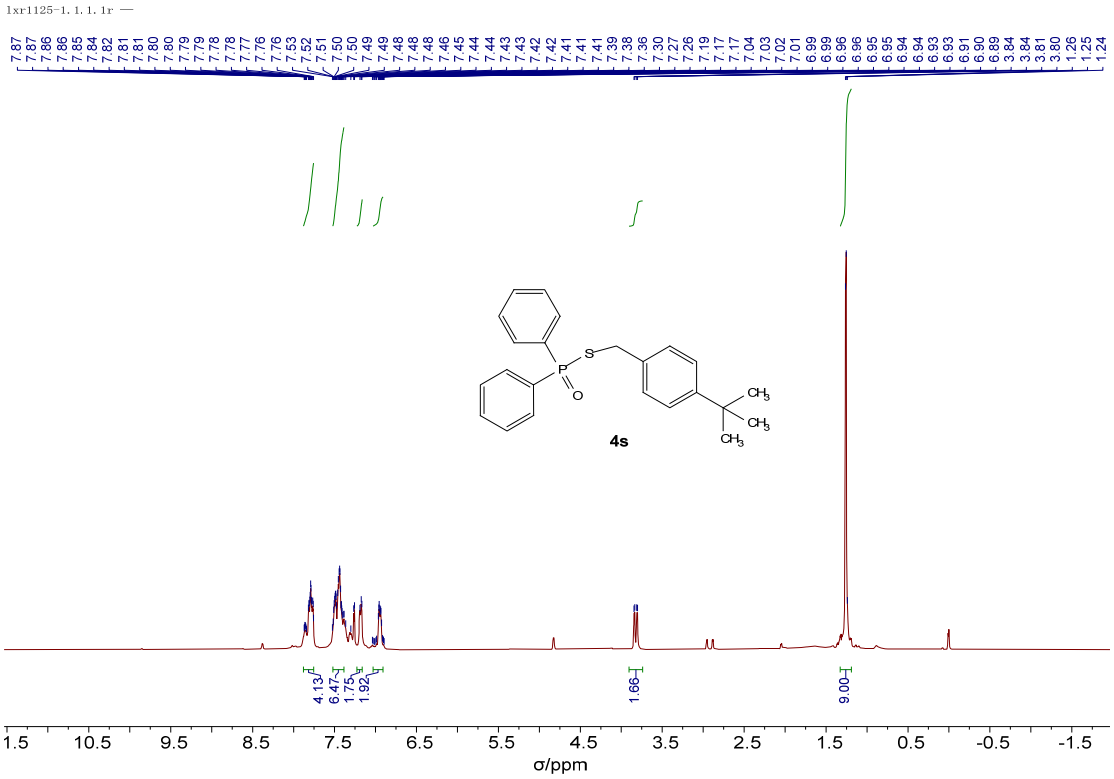
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4r**



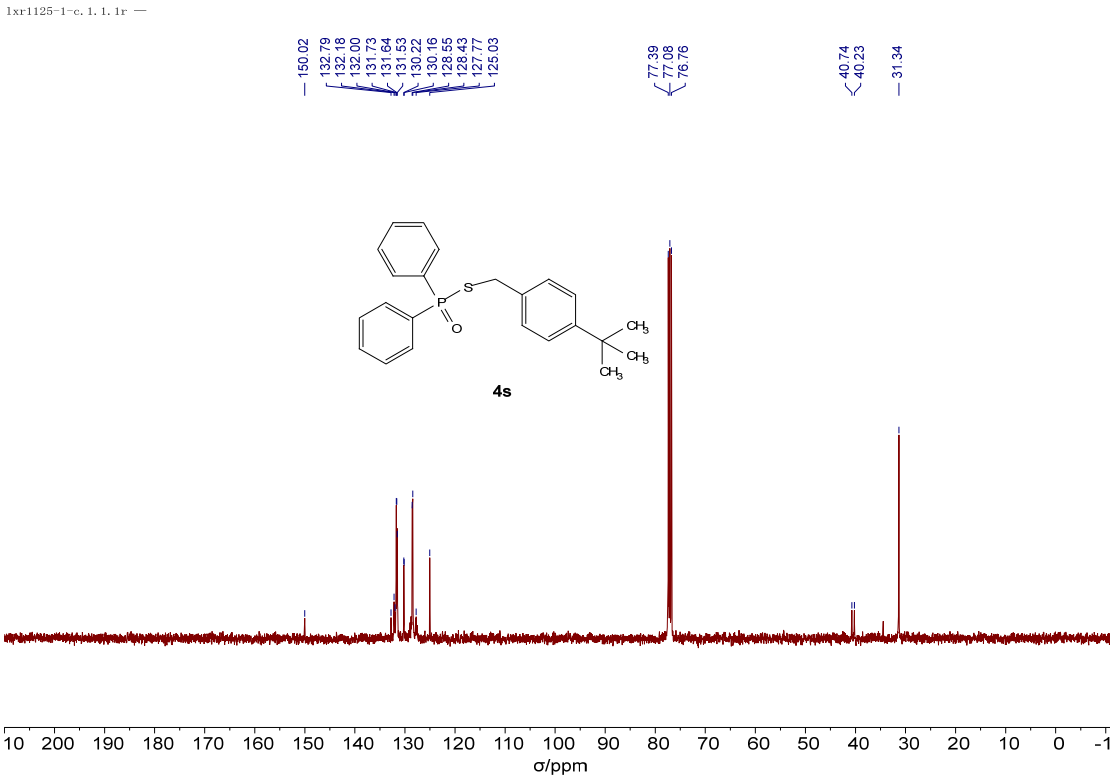
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4r**



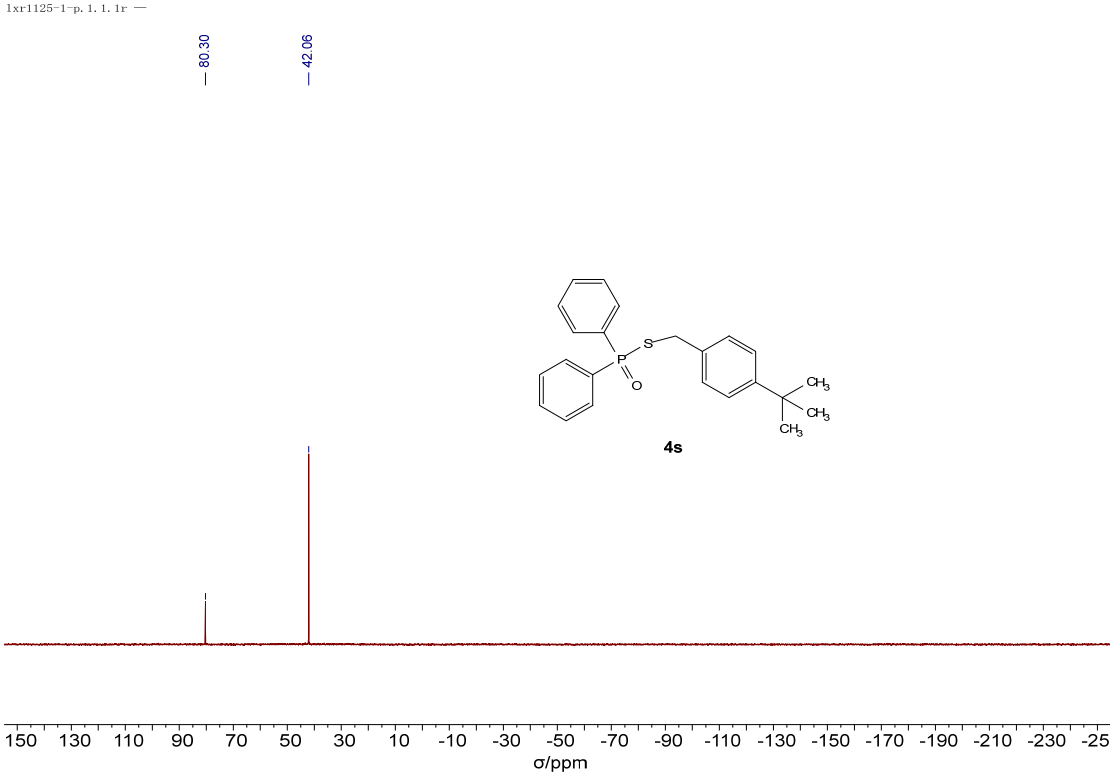
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4s**



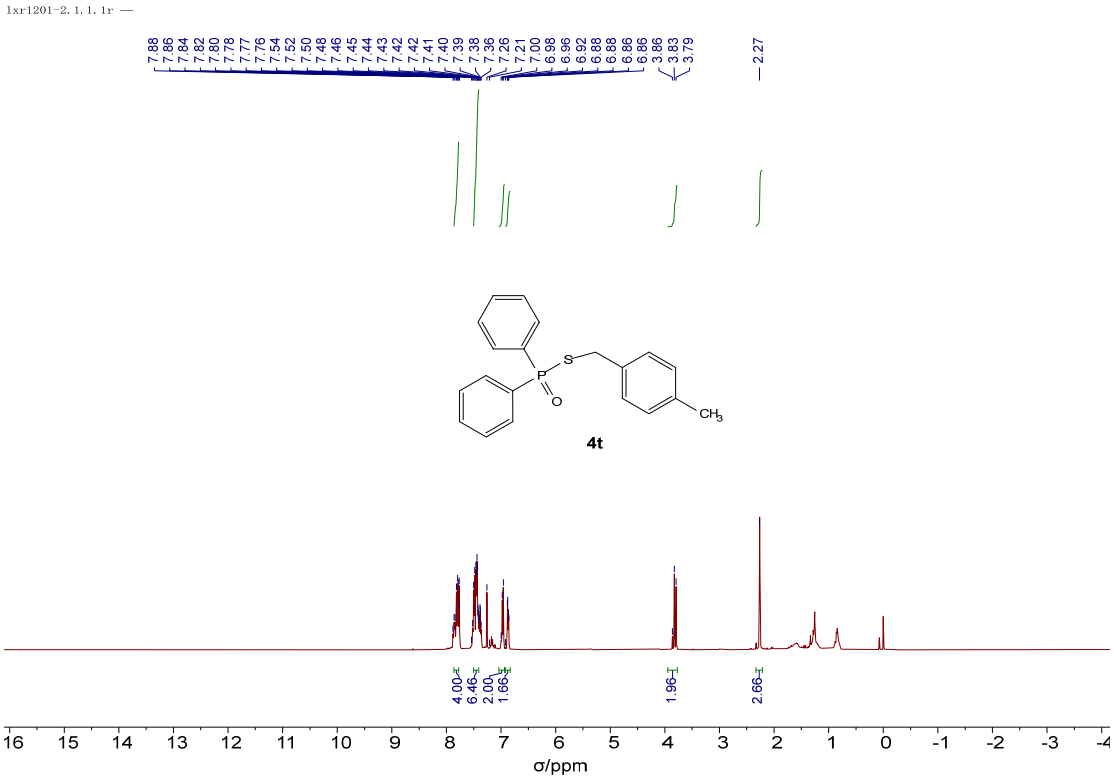
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4s**



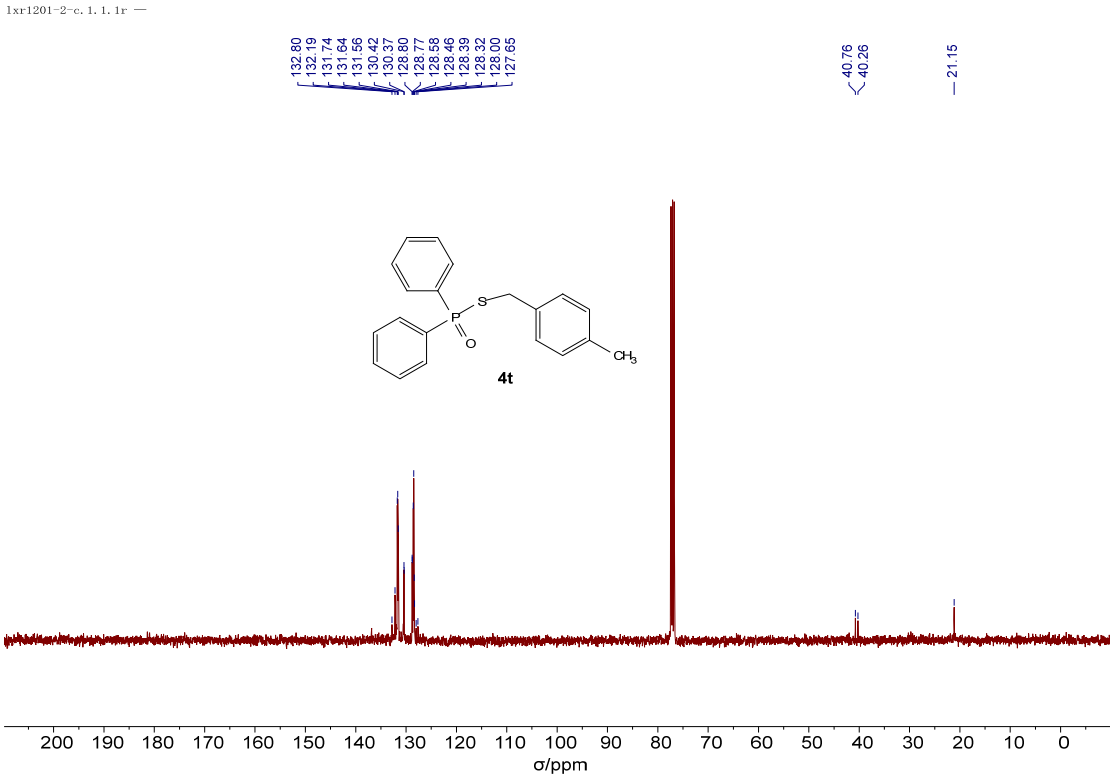
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4s**



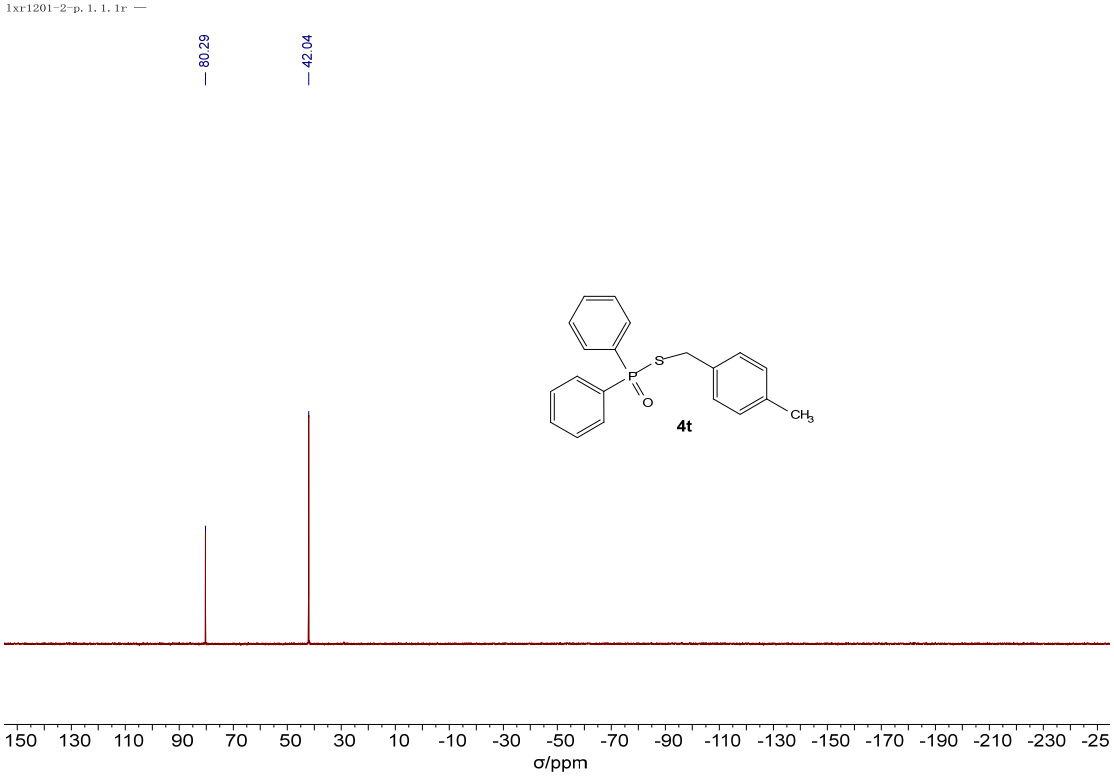
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4t**



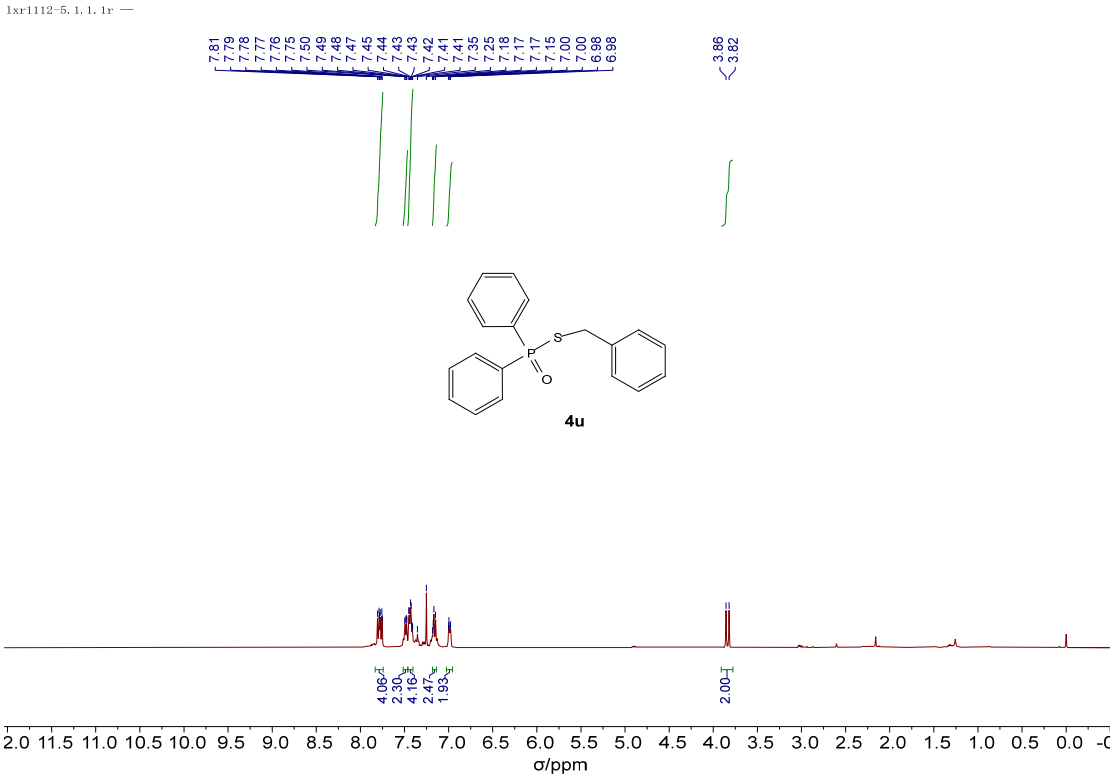
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4t**



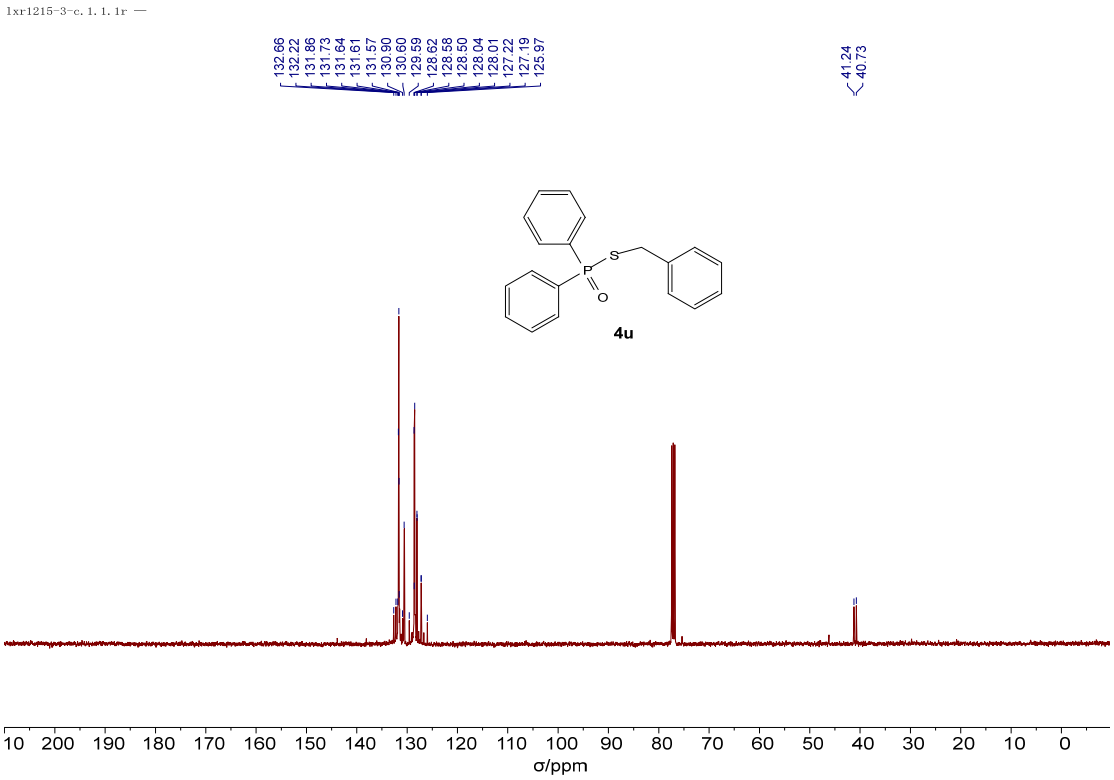
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4t**



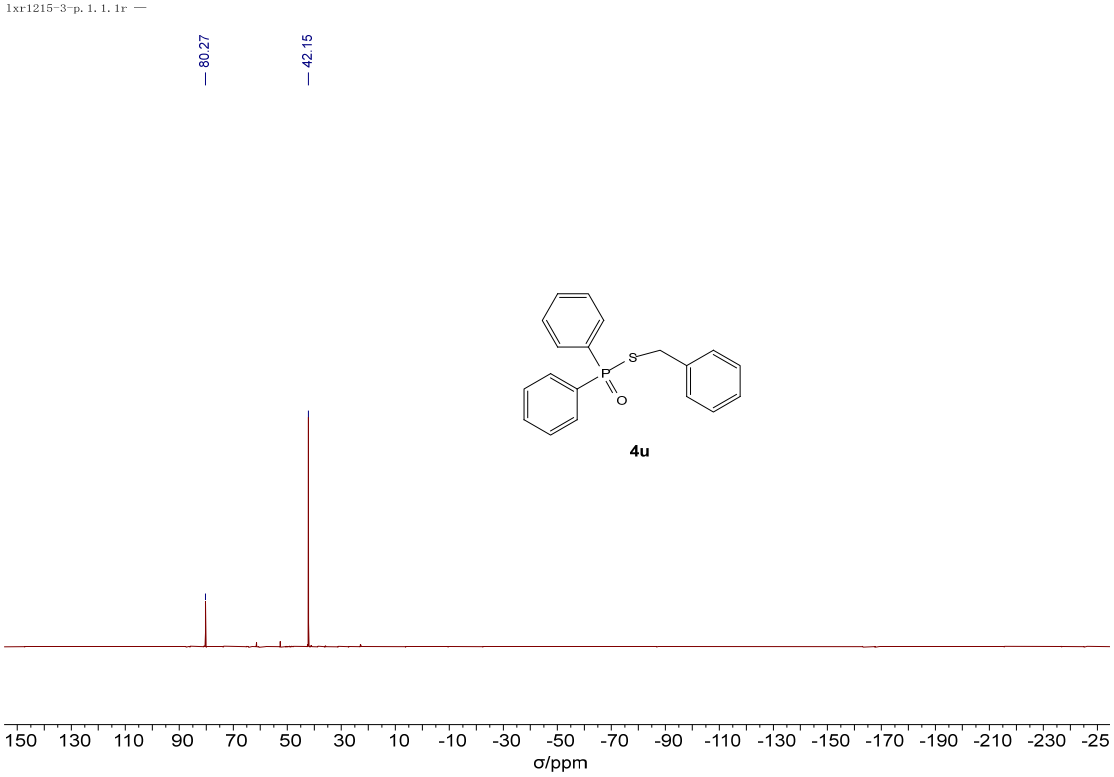
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4u**



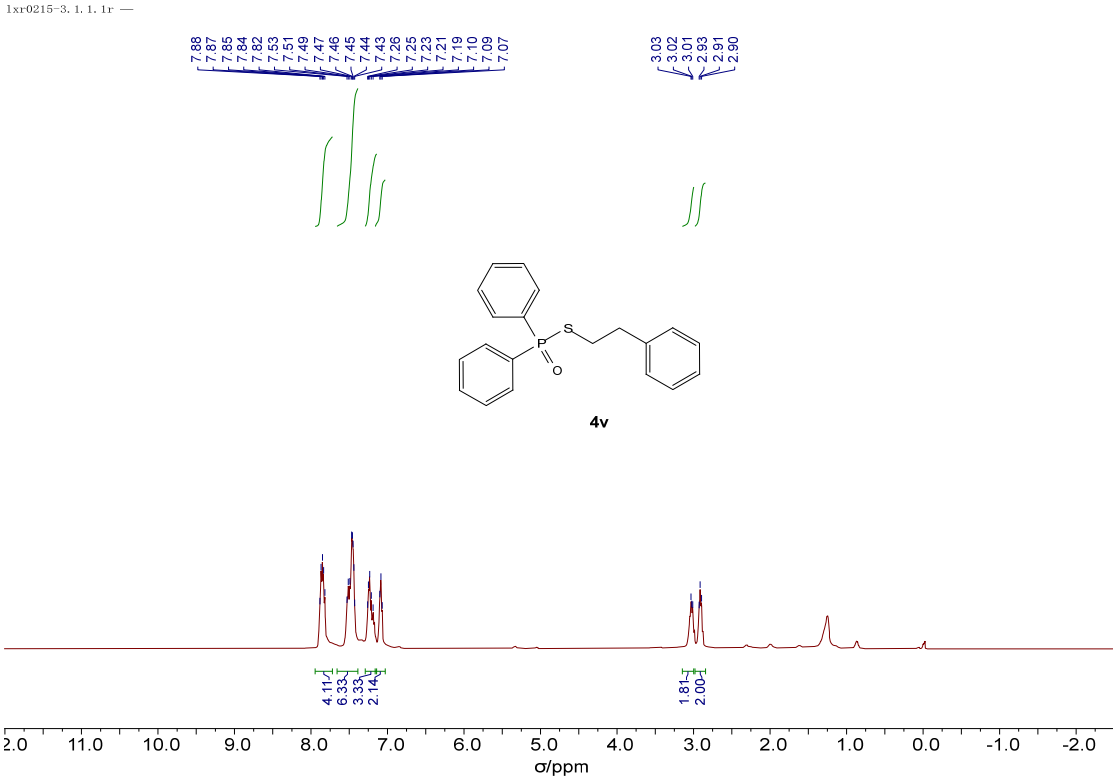
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4u**



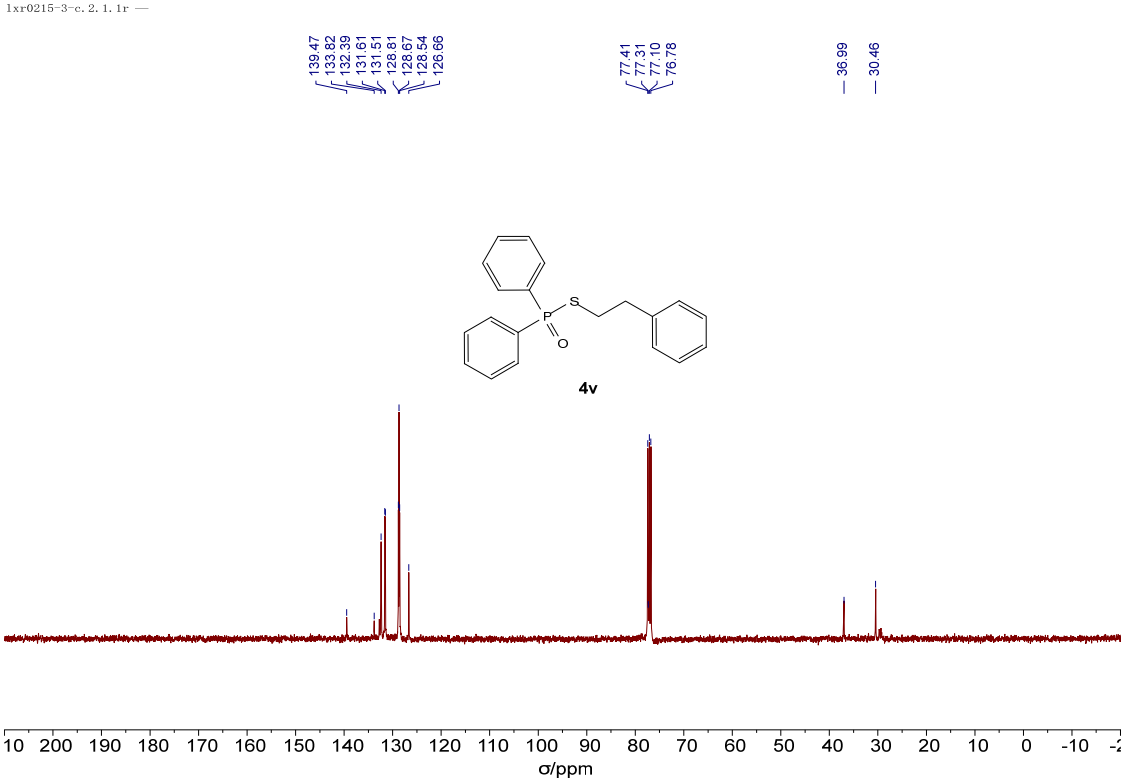
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4u**



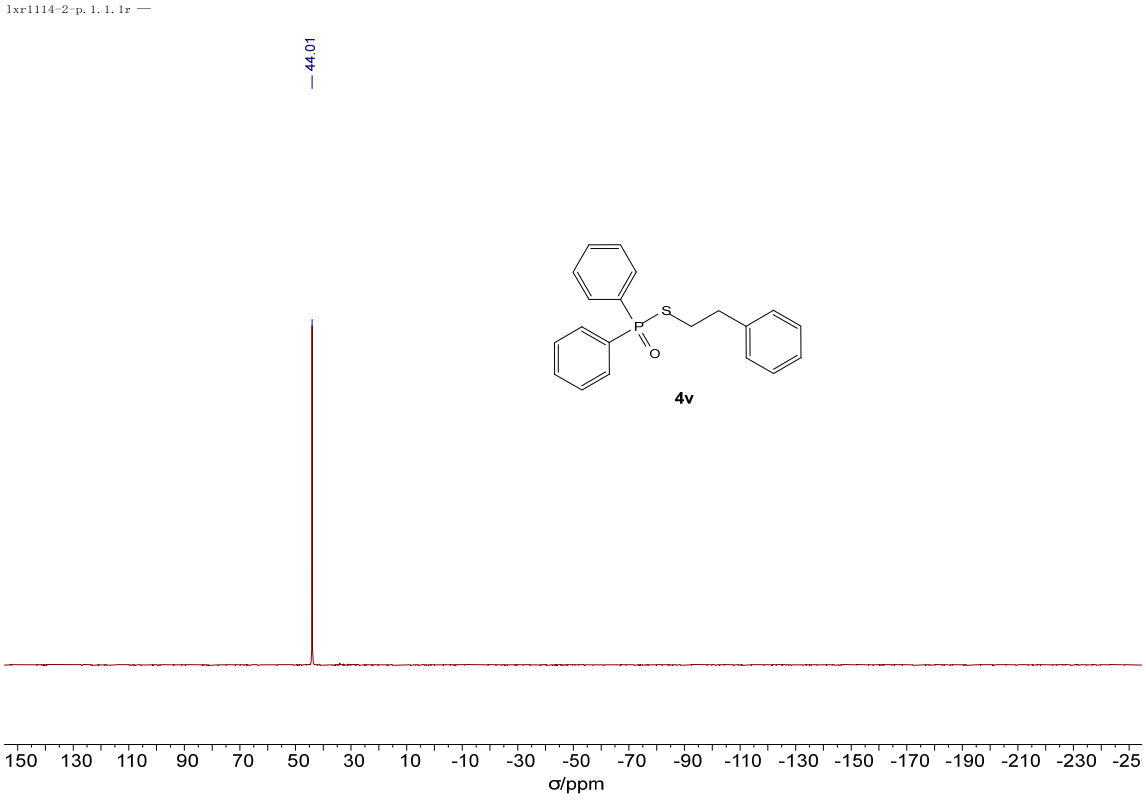
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4v**



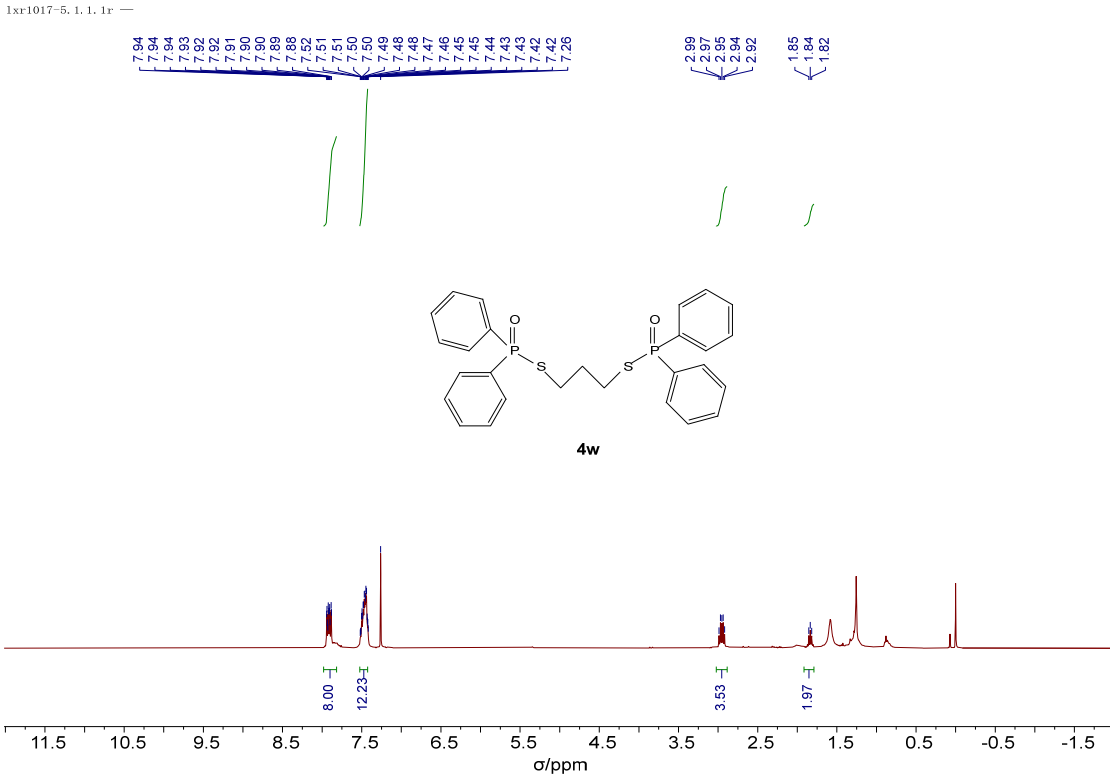
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4v**



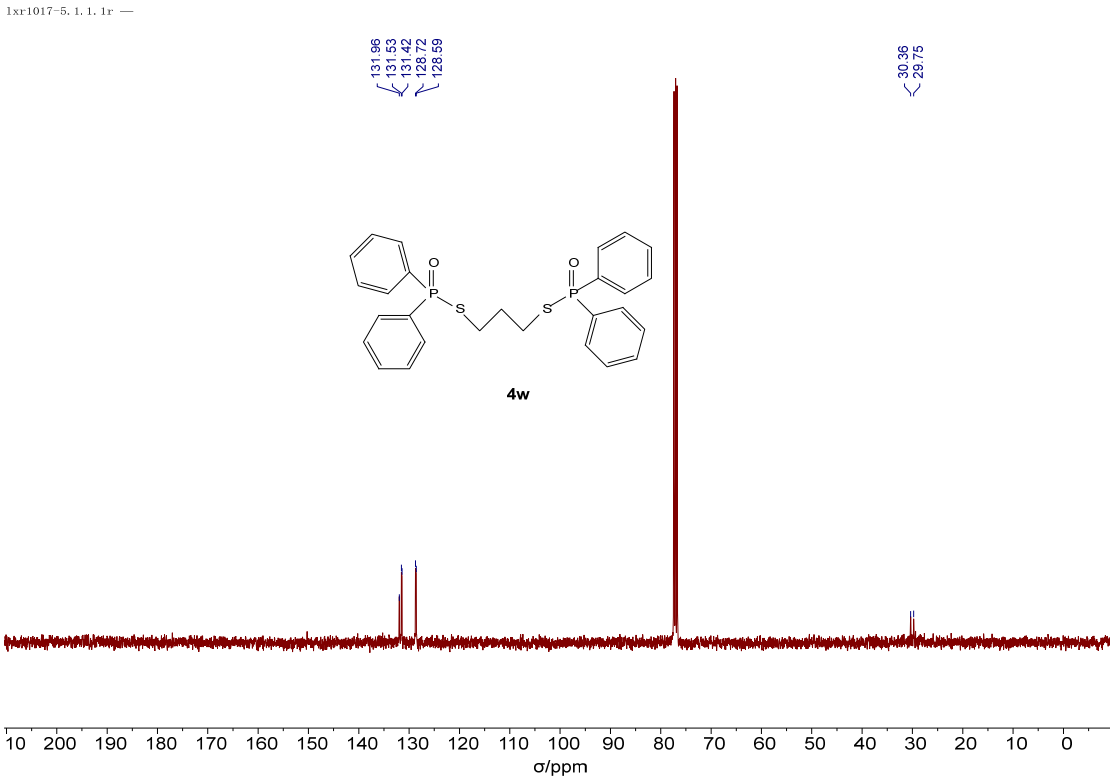
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4v**



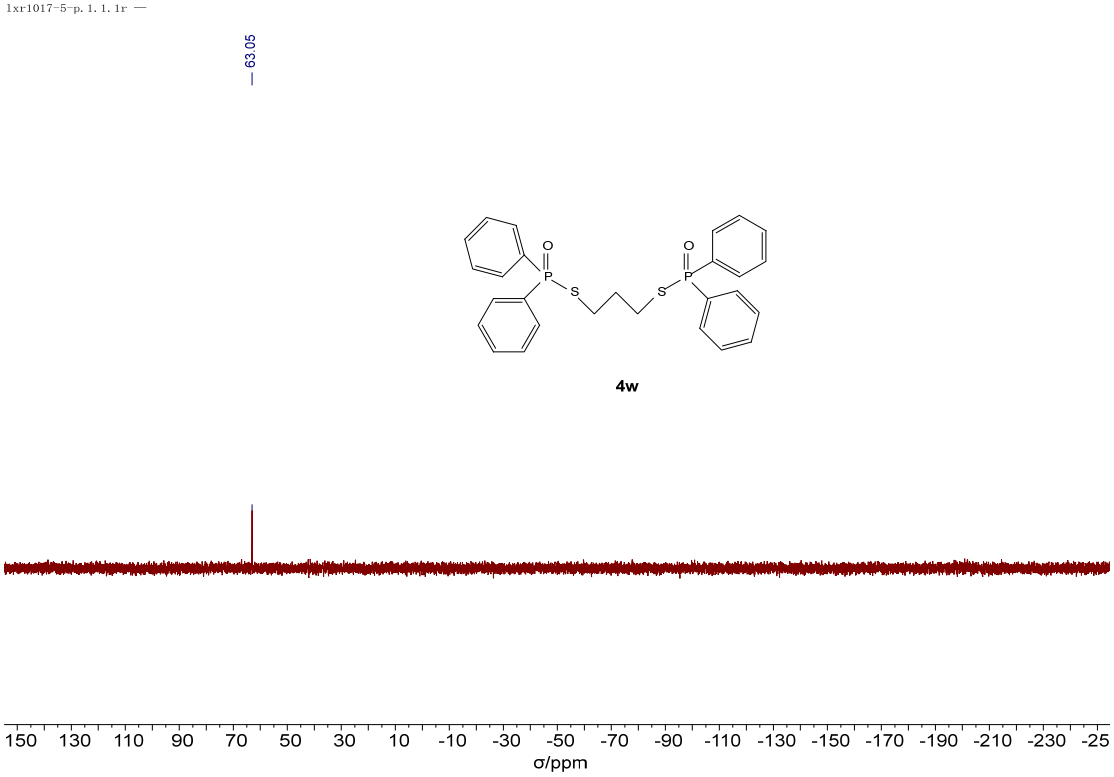
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4w**



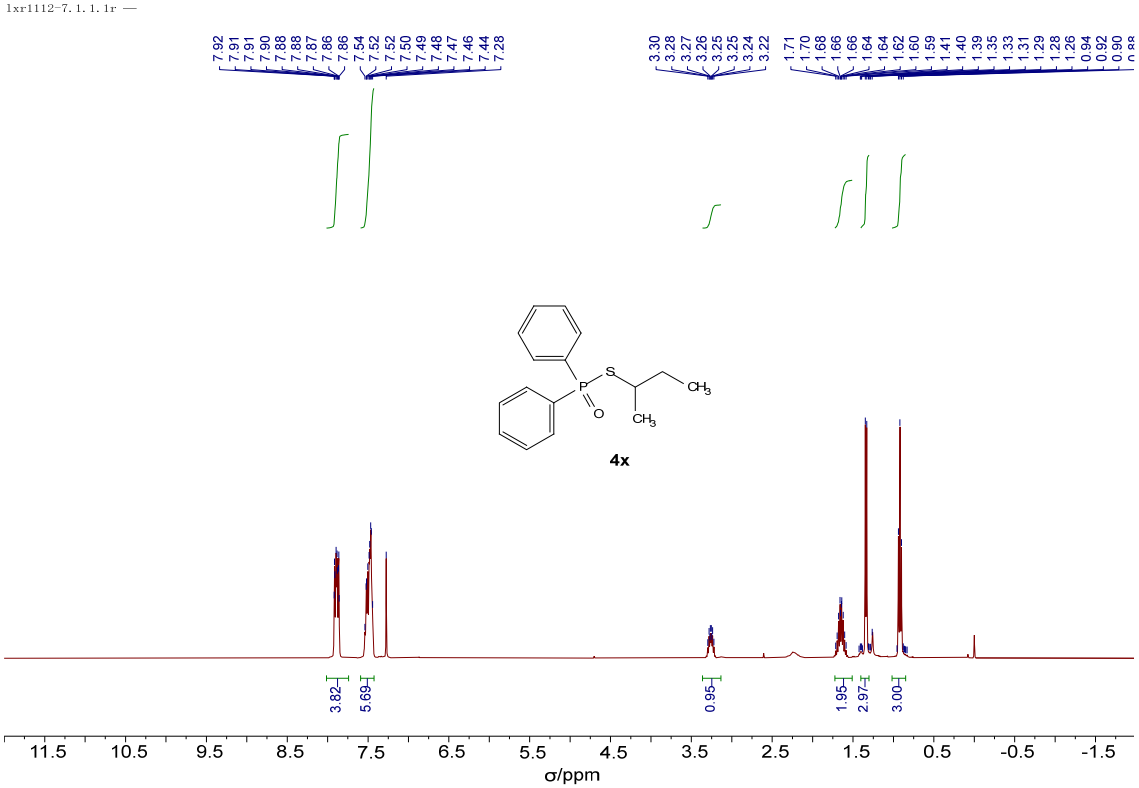
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4w**



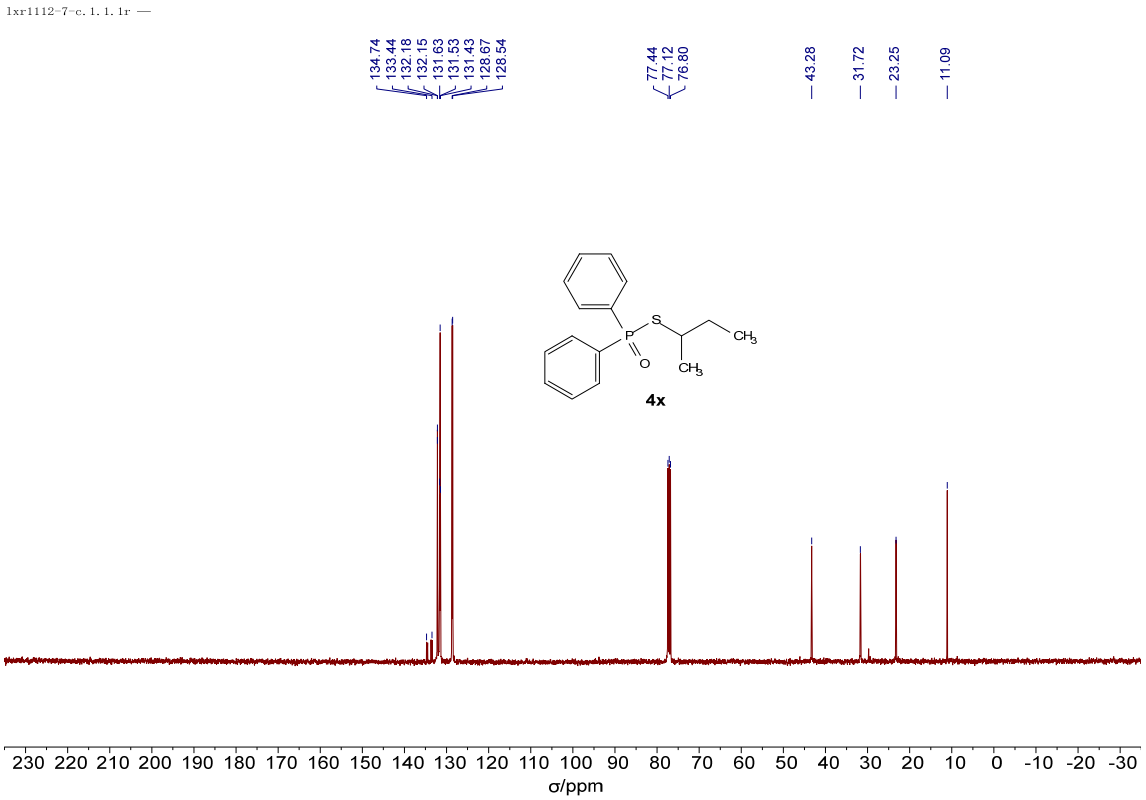
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4w**



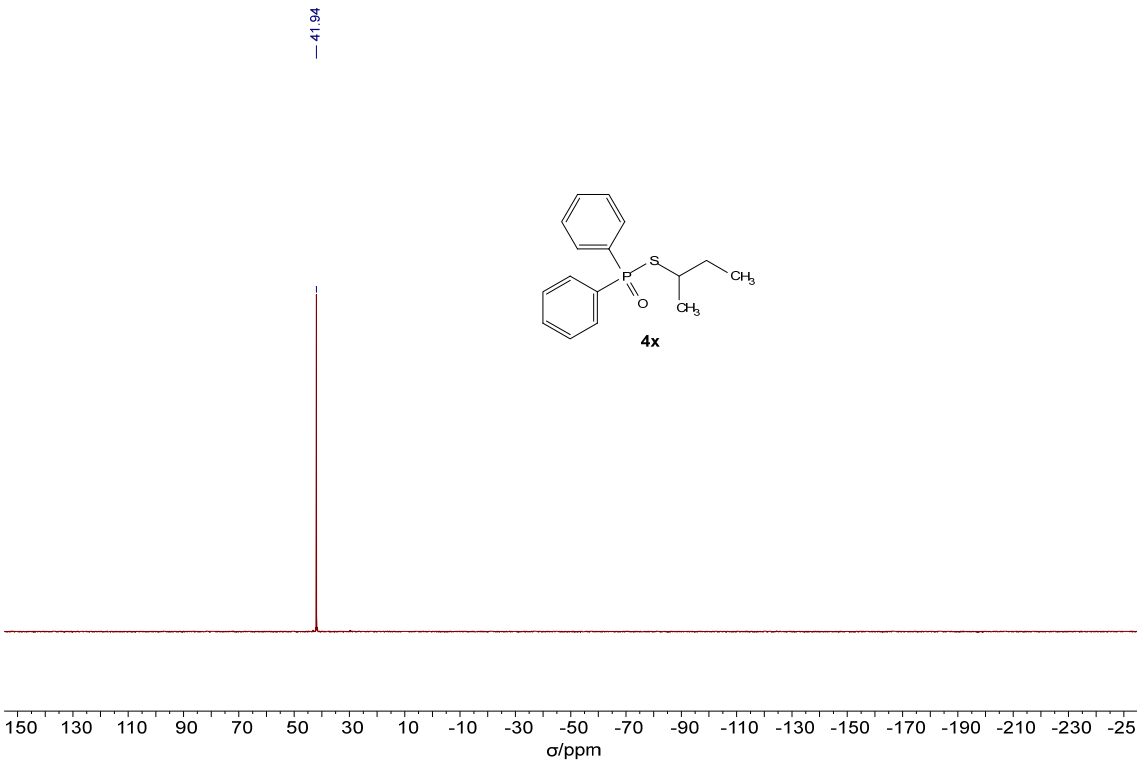
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4x**



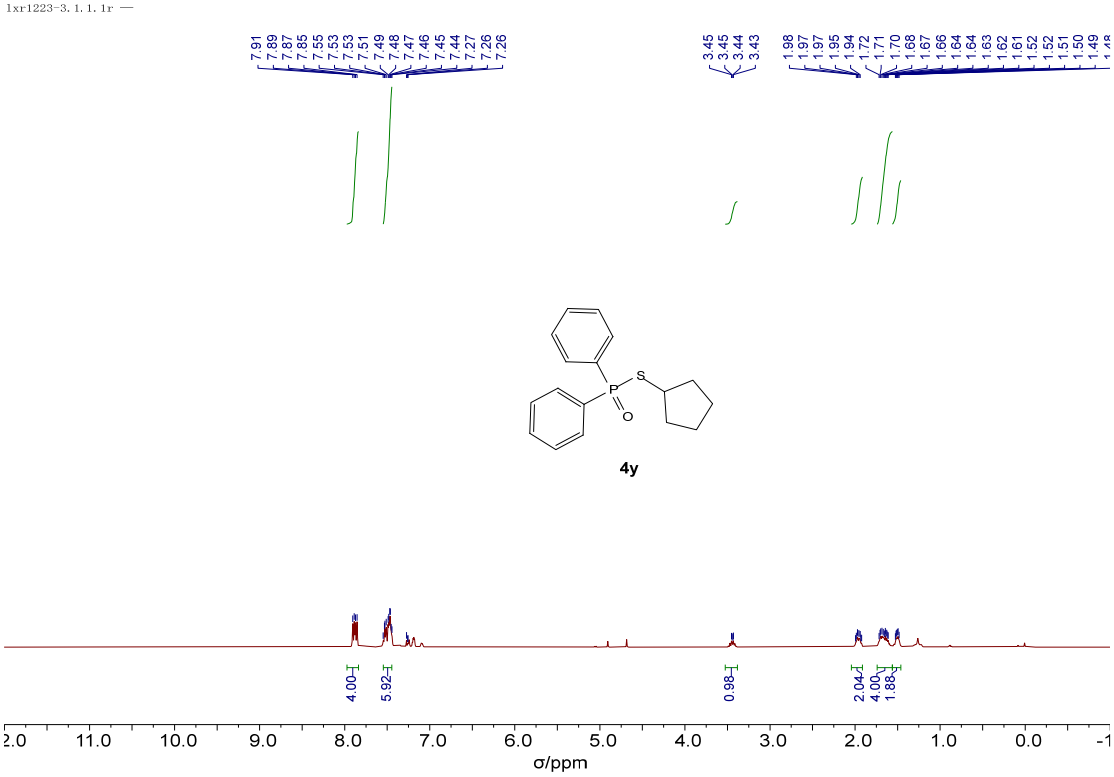
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4x**



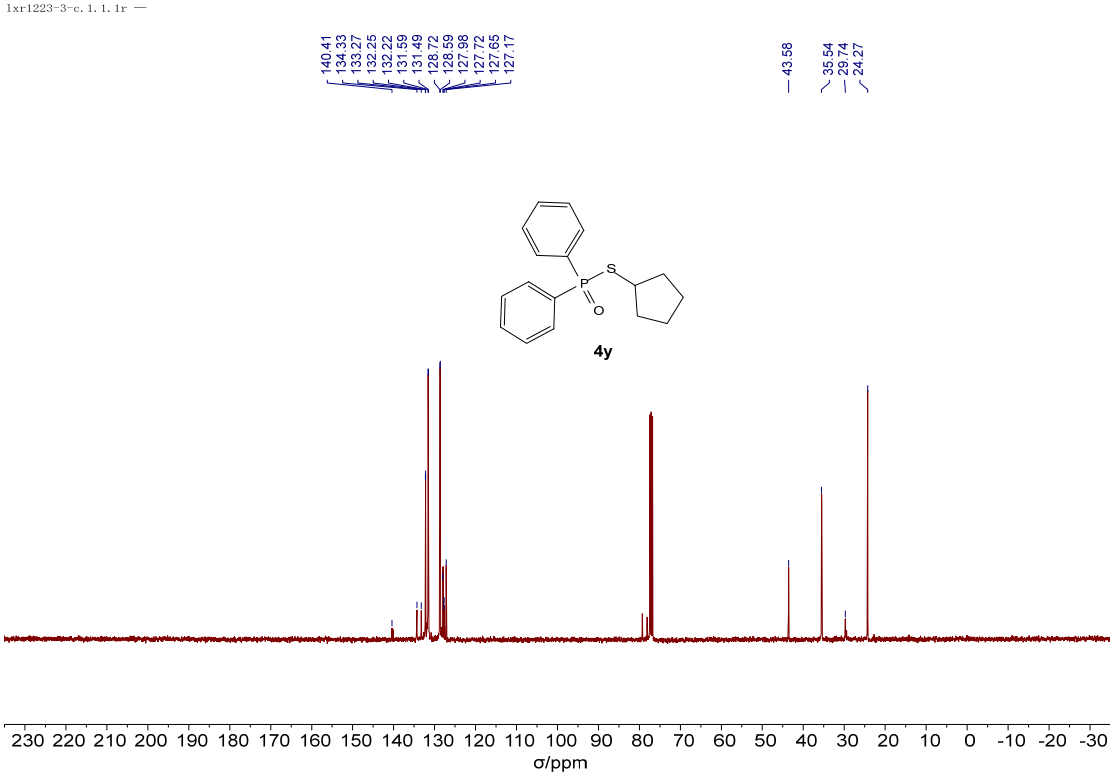
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4x**



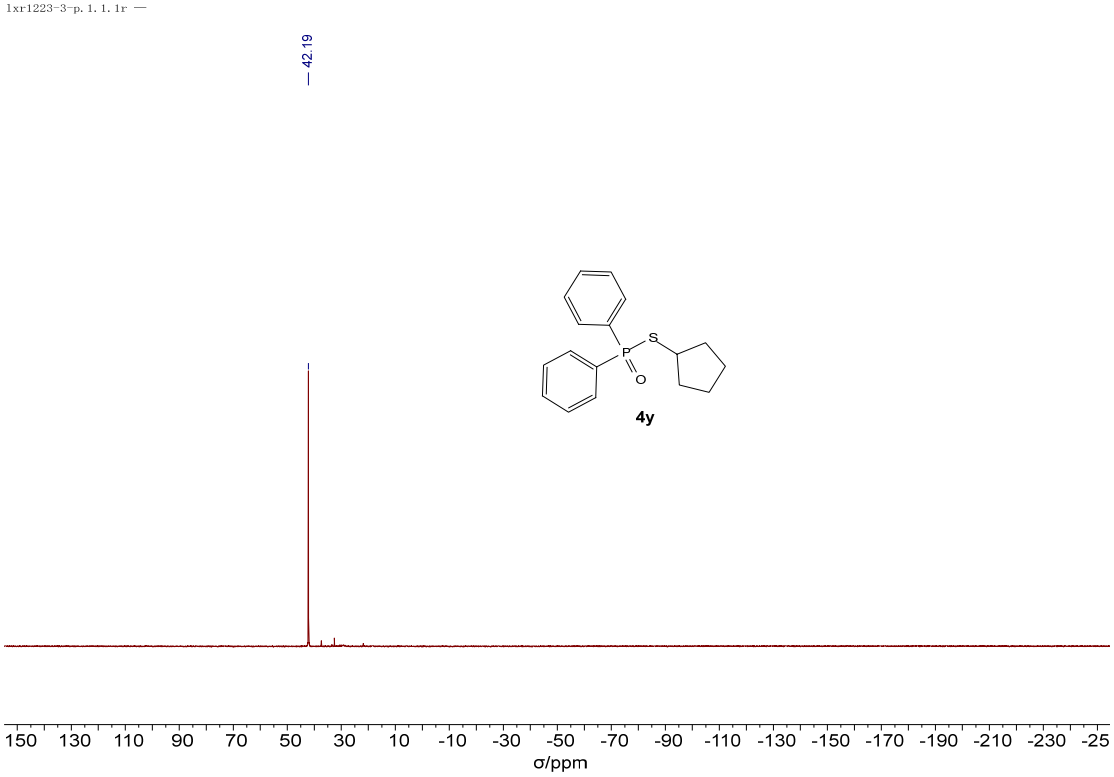
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4y**



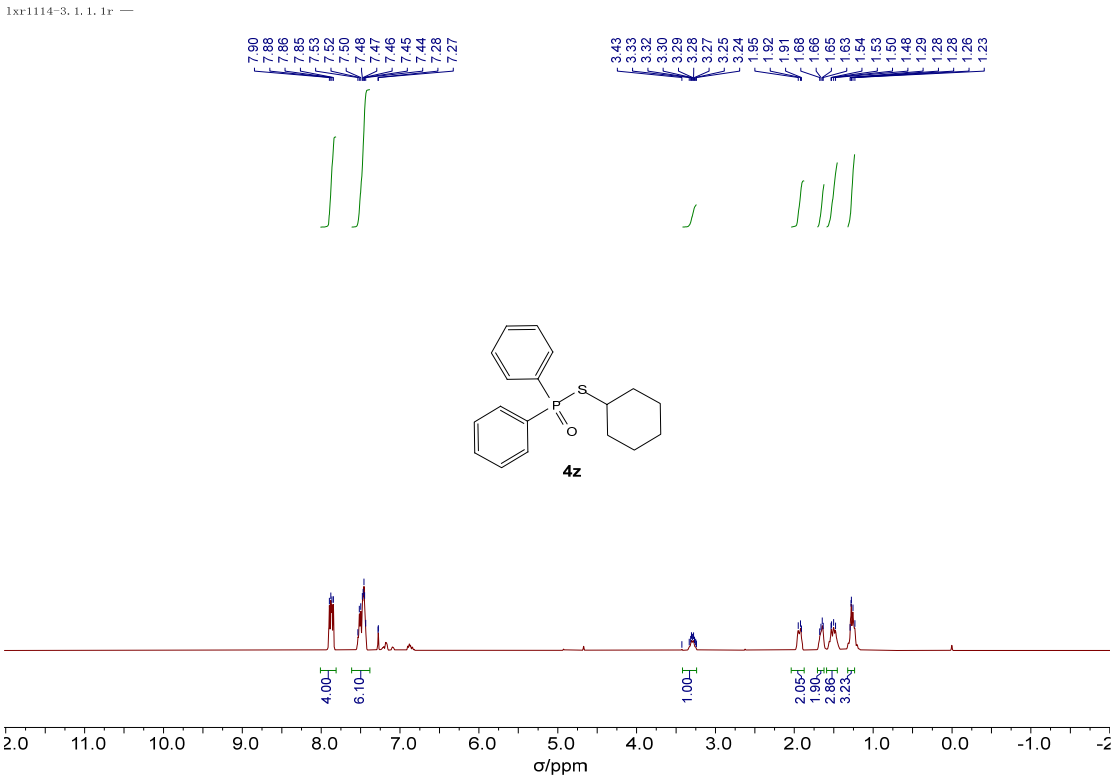
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4y**



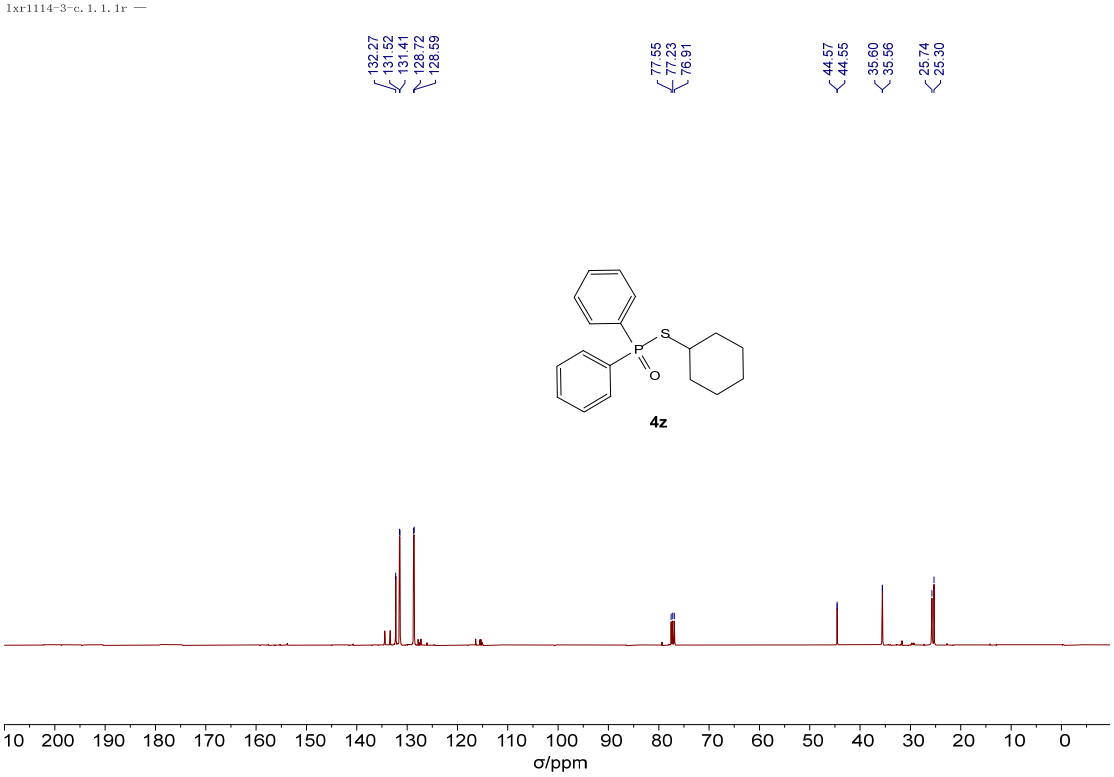
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4y**



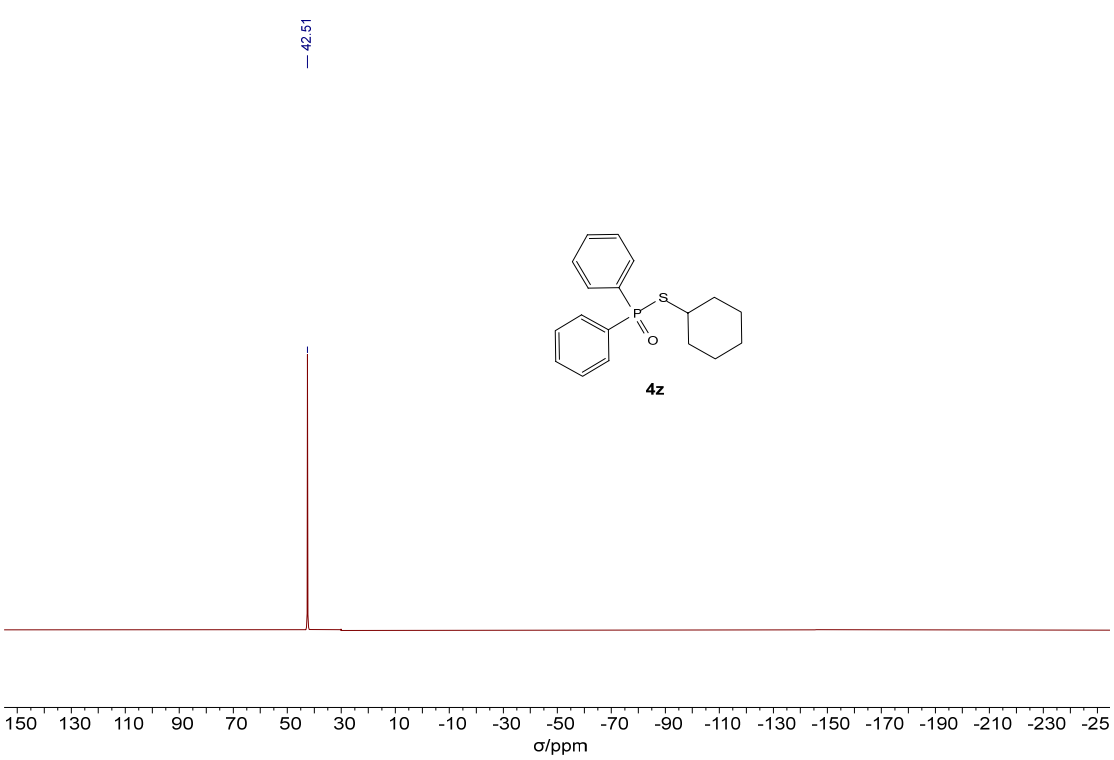
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **4z**



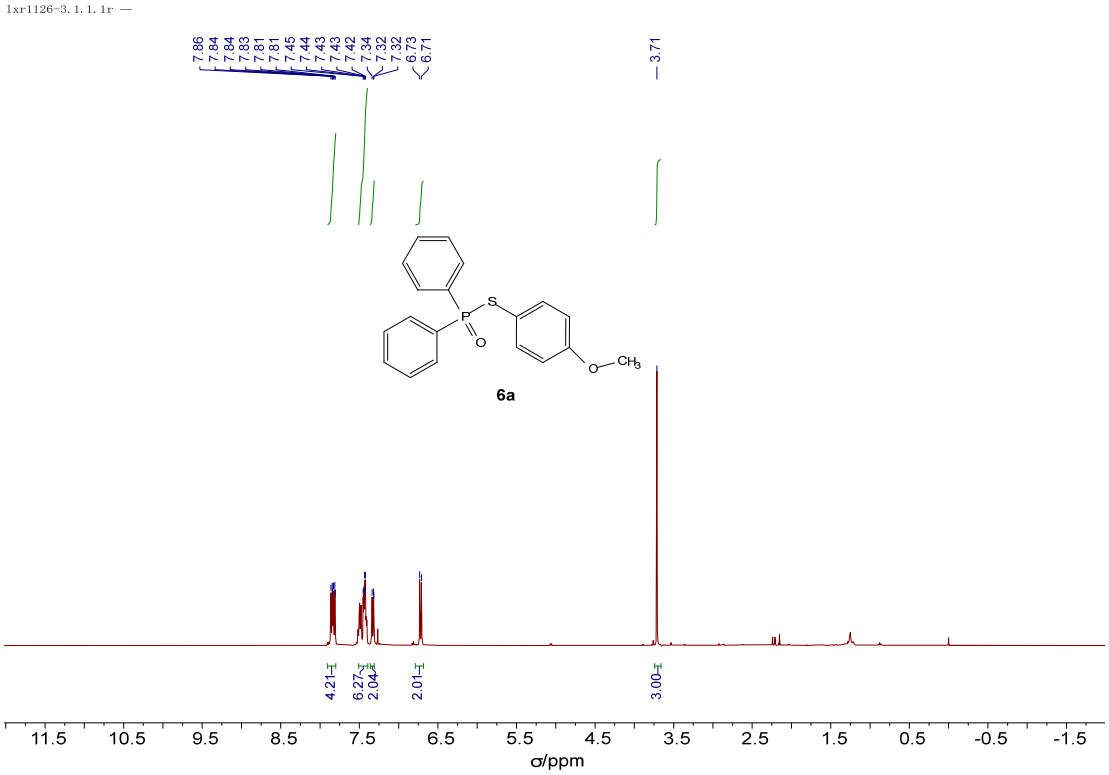
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **4z**



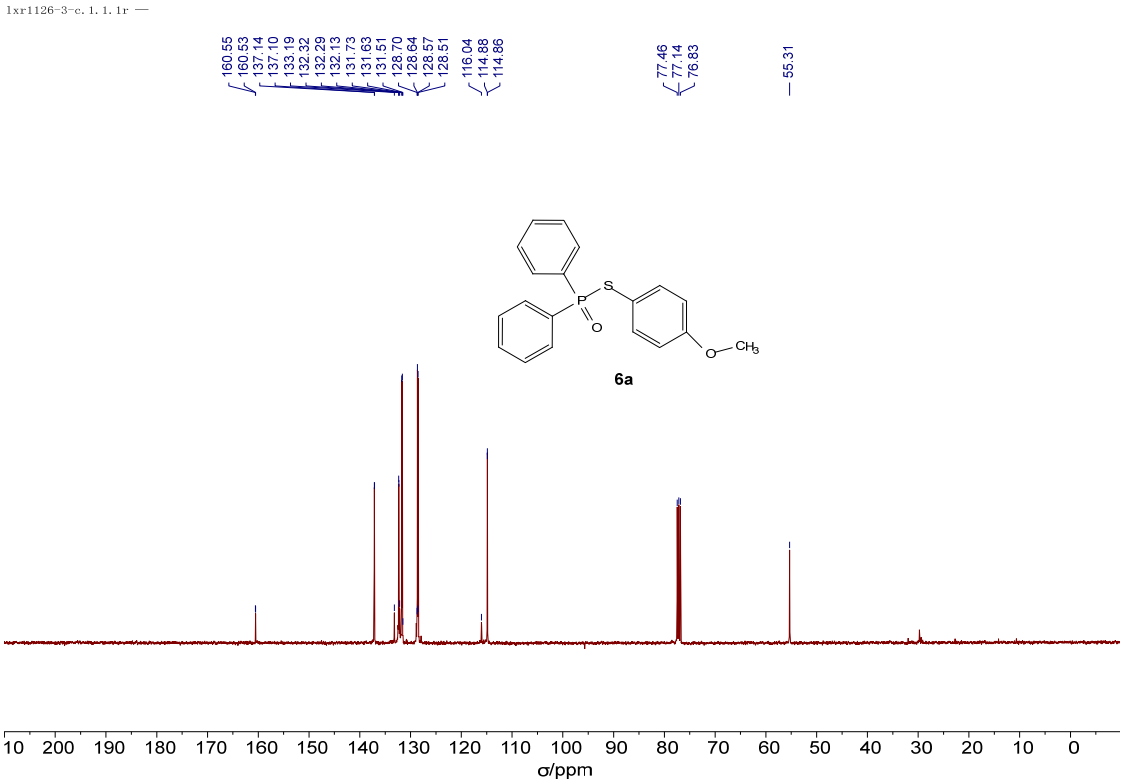
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **4z**



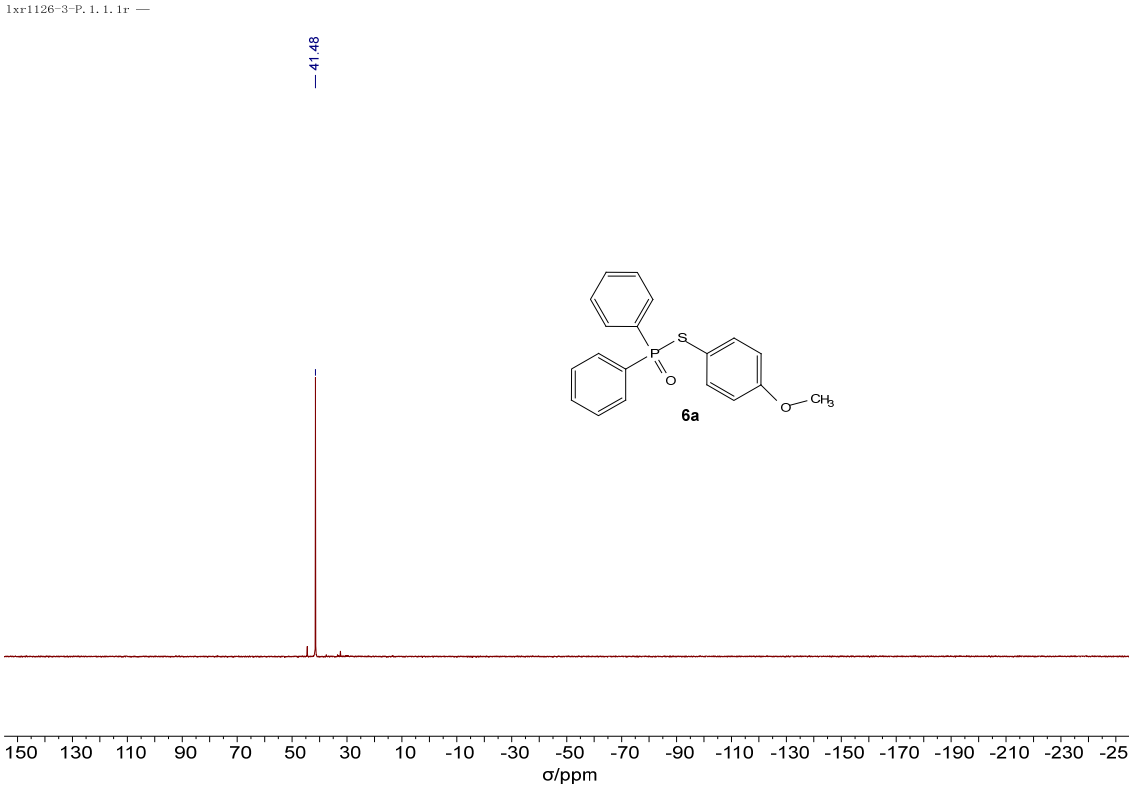
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **6a**



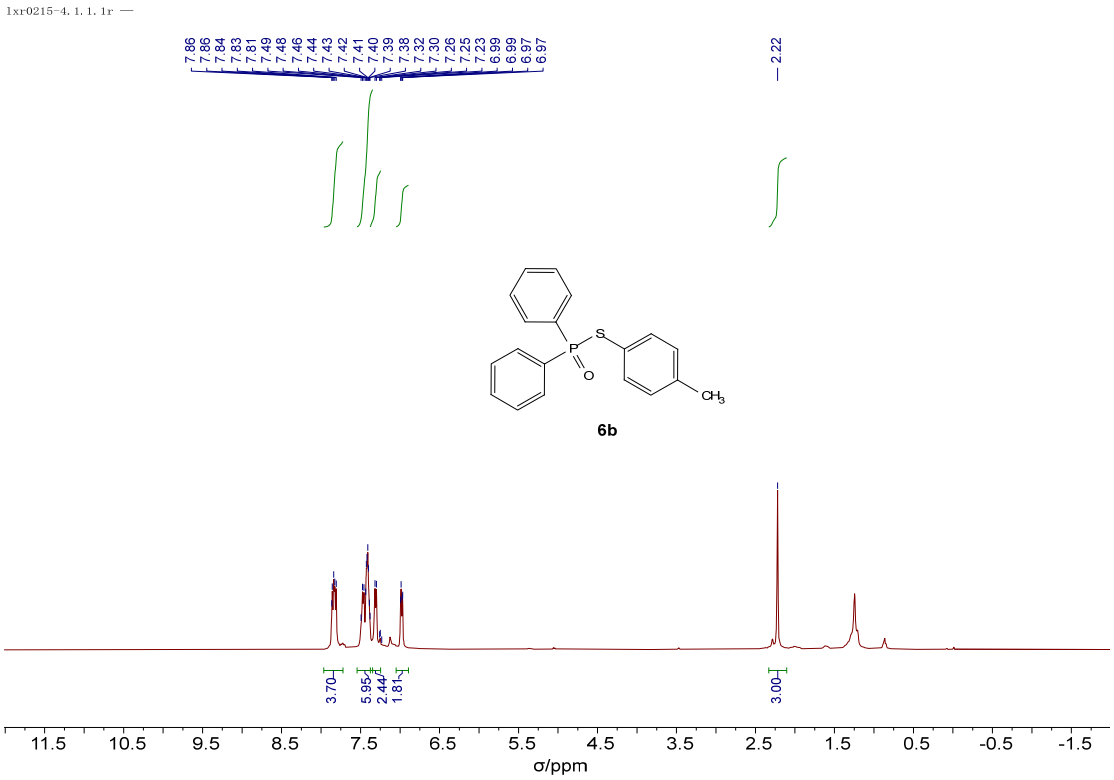
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **6a**



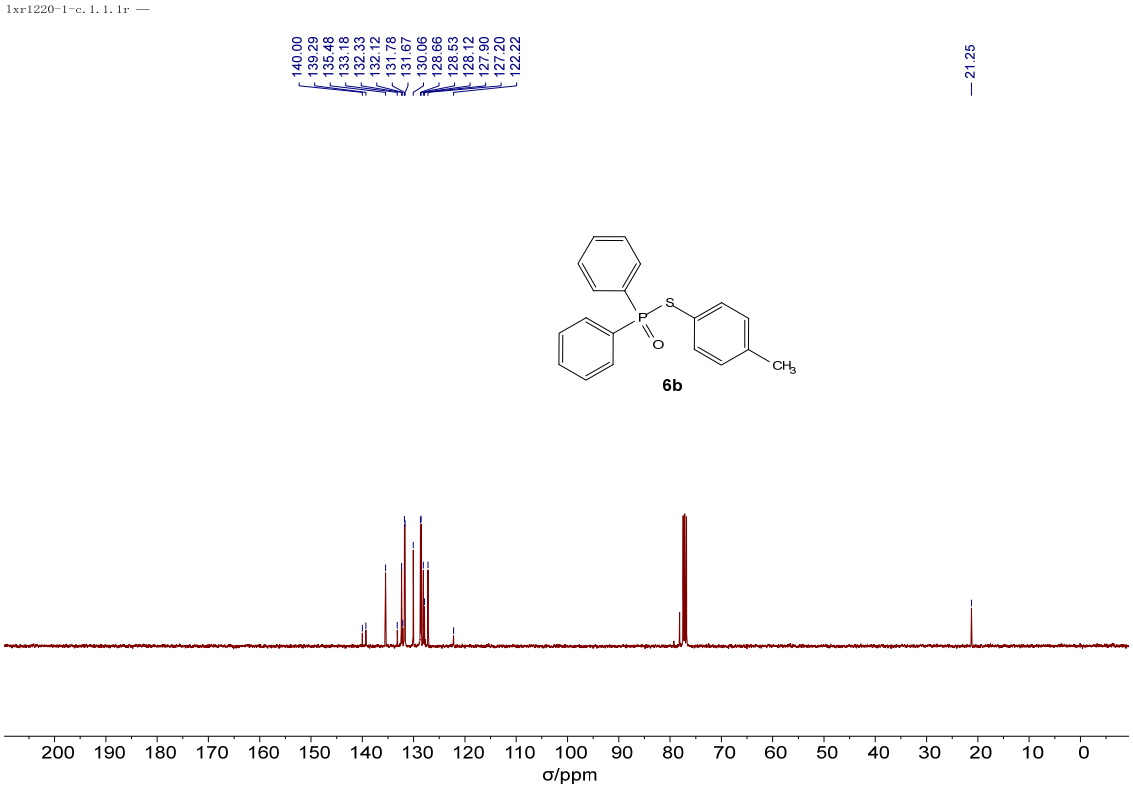
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **6a**



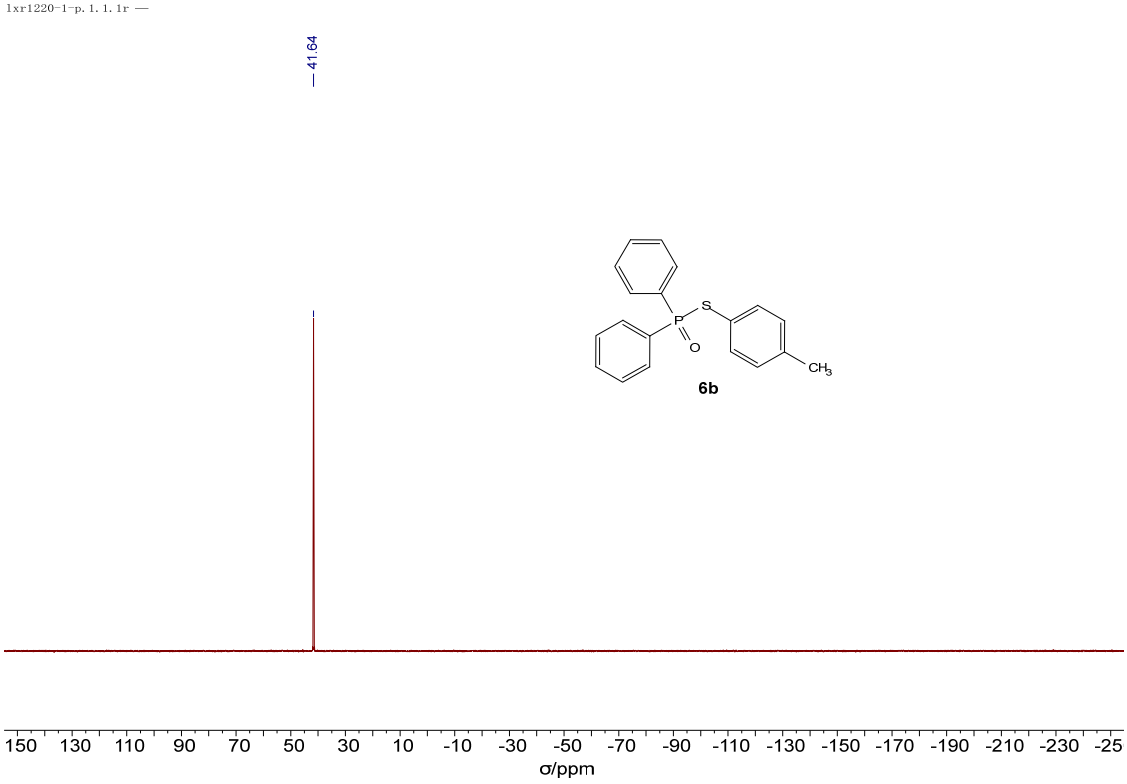
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **6b**



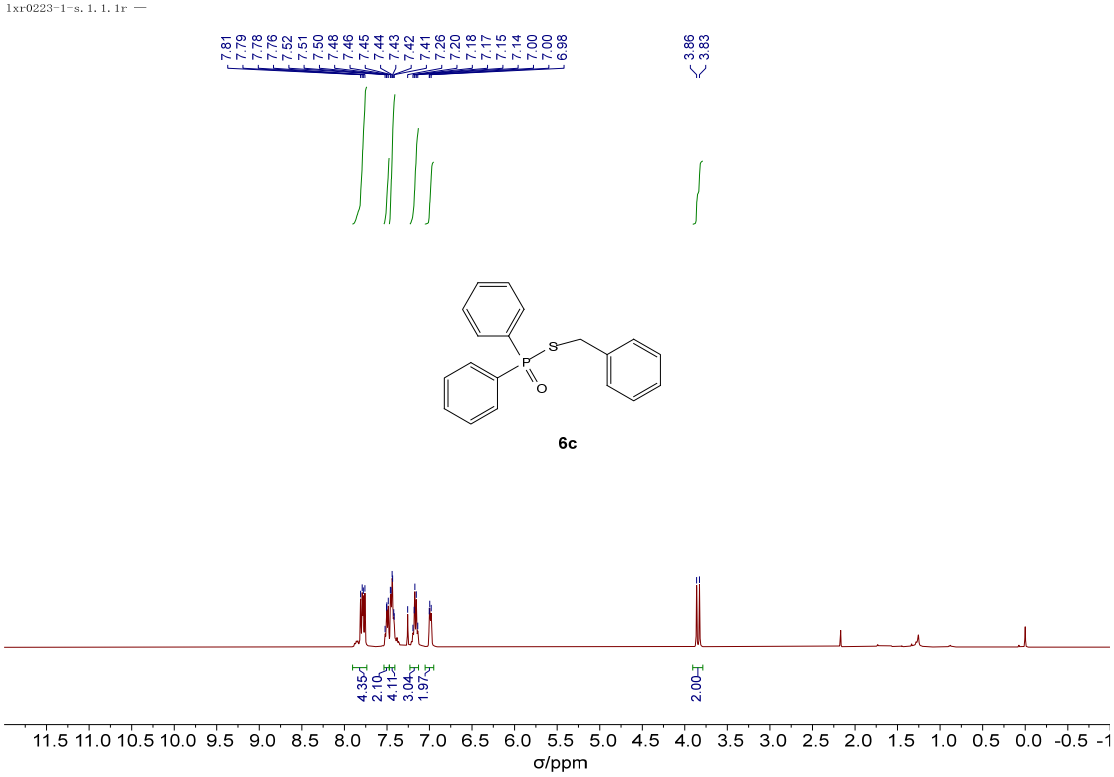
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **6b**



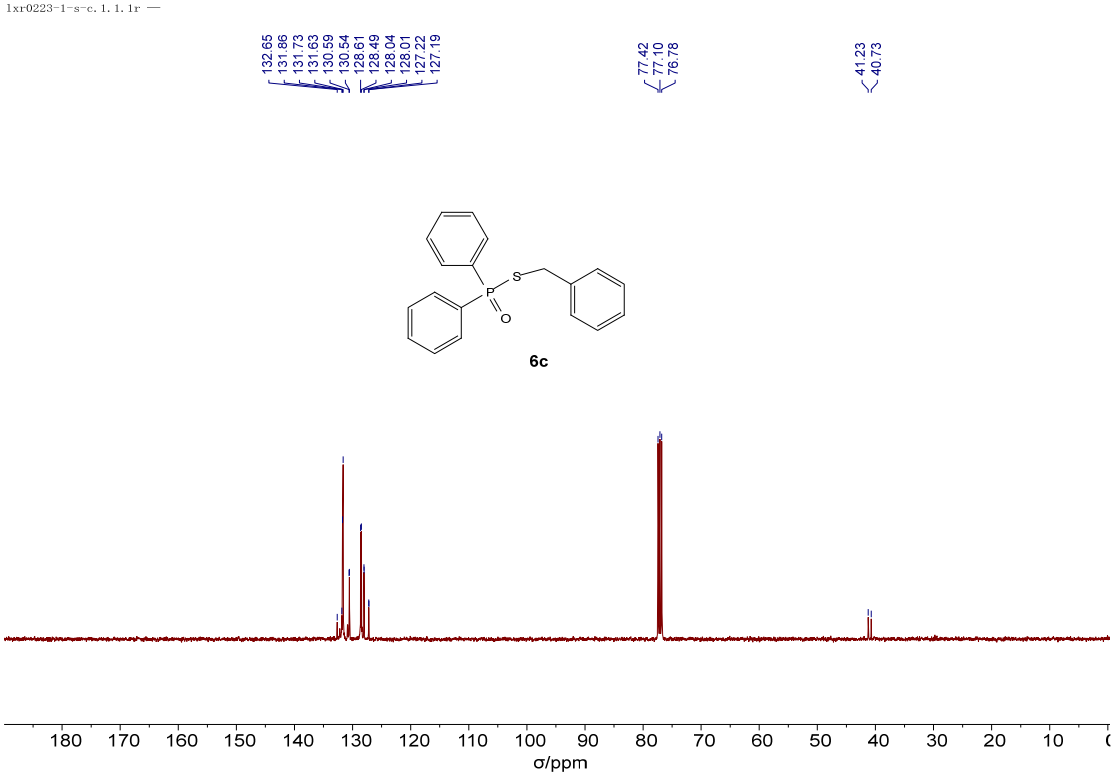
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **6b**



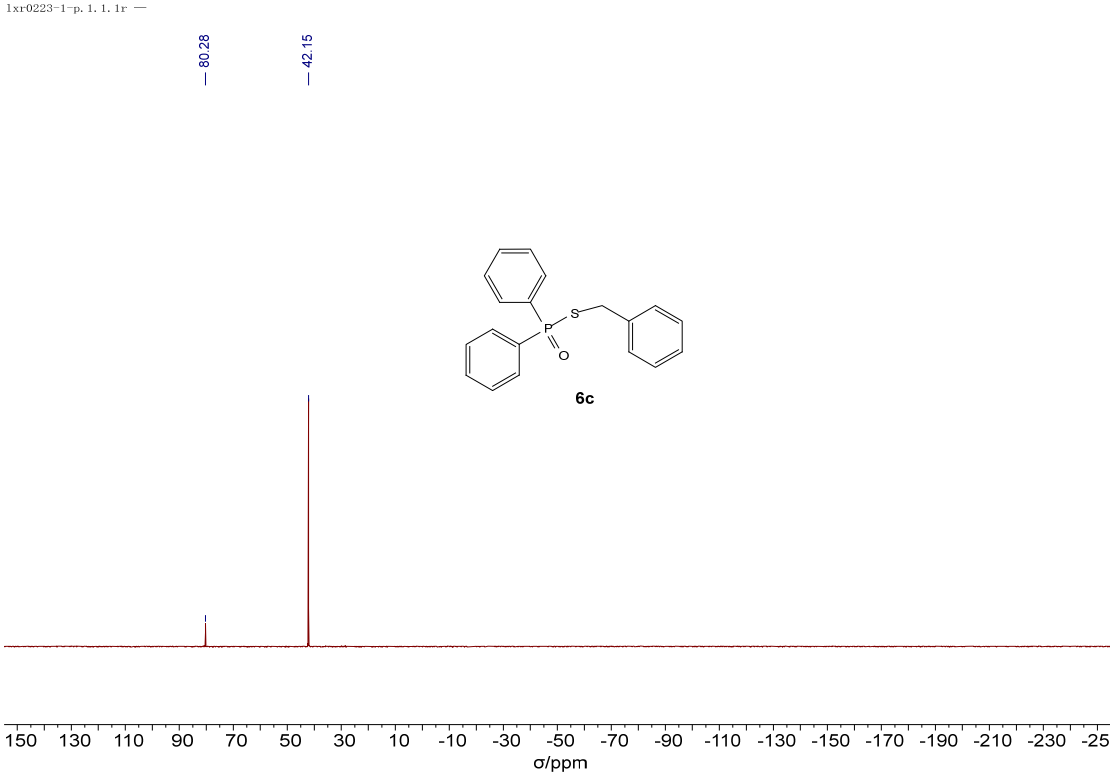
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **6c**



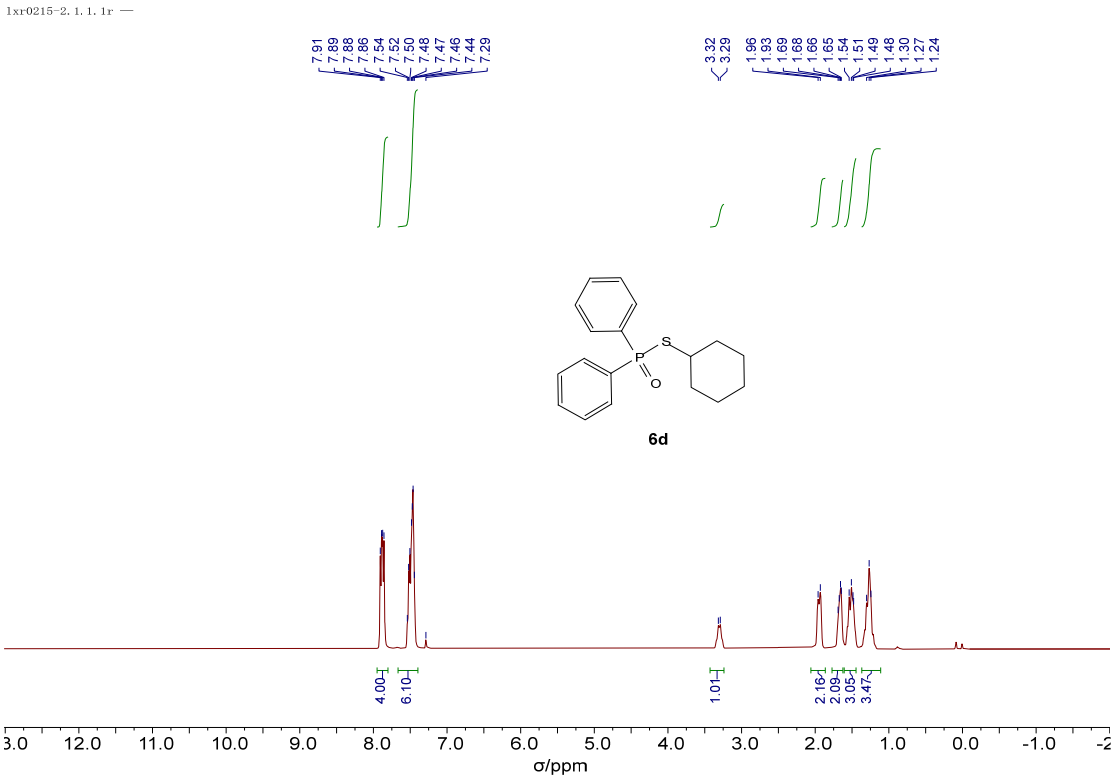
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **6c**



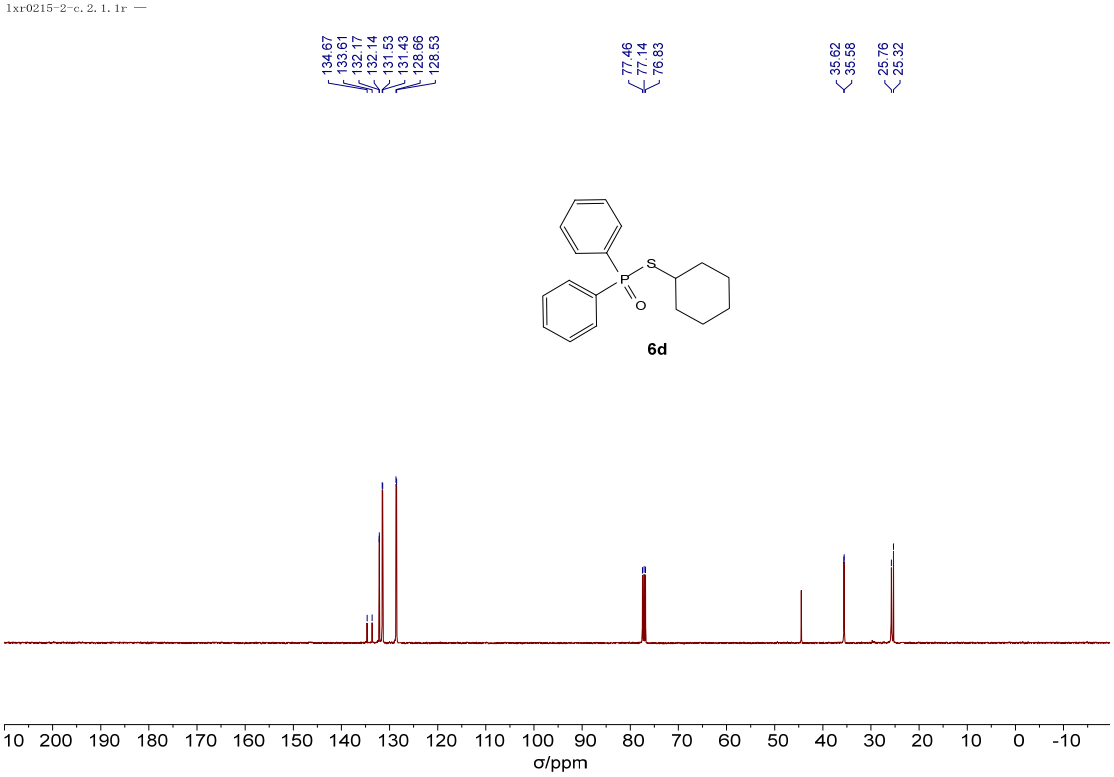
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **6c**



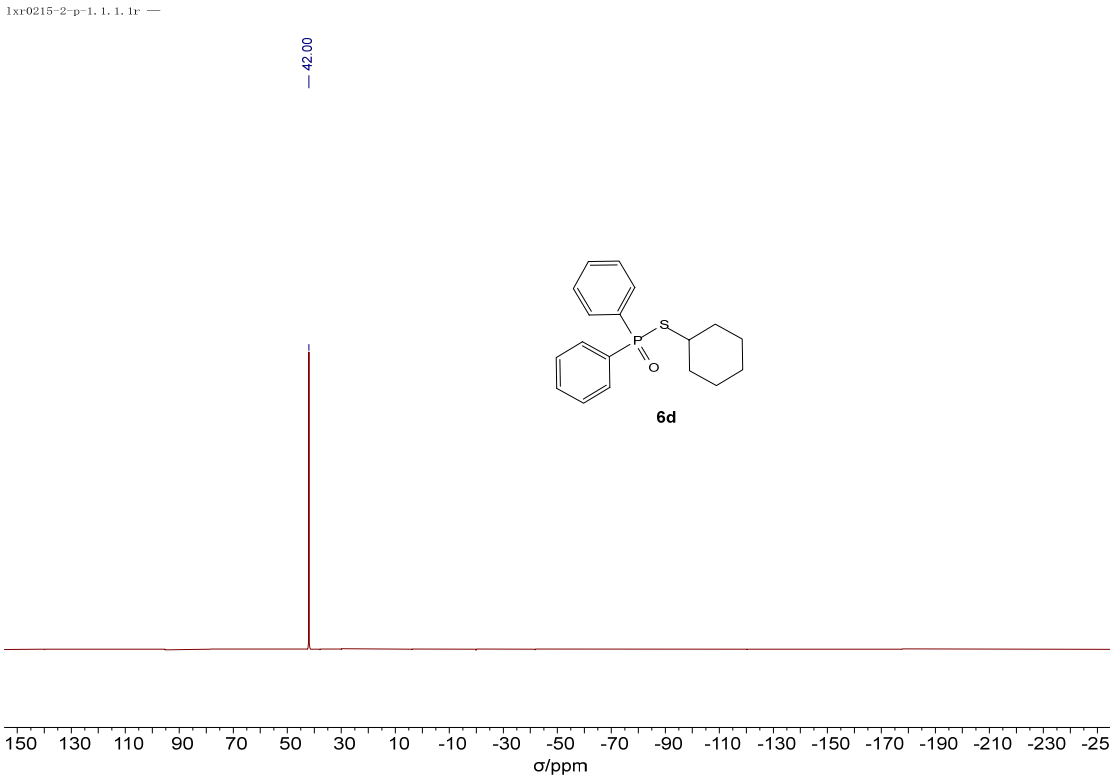
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **6d**



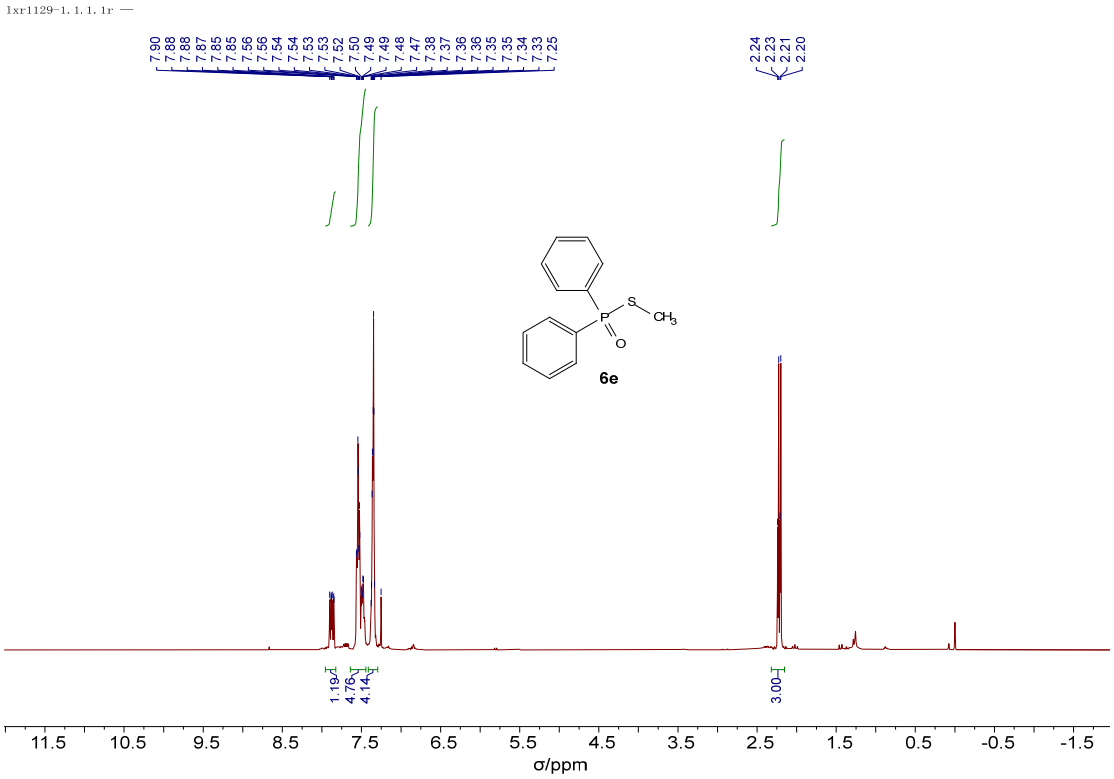
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **6d**



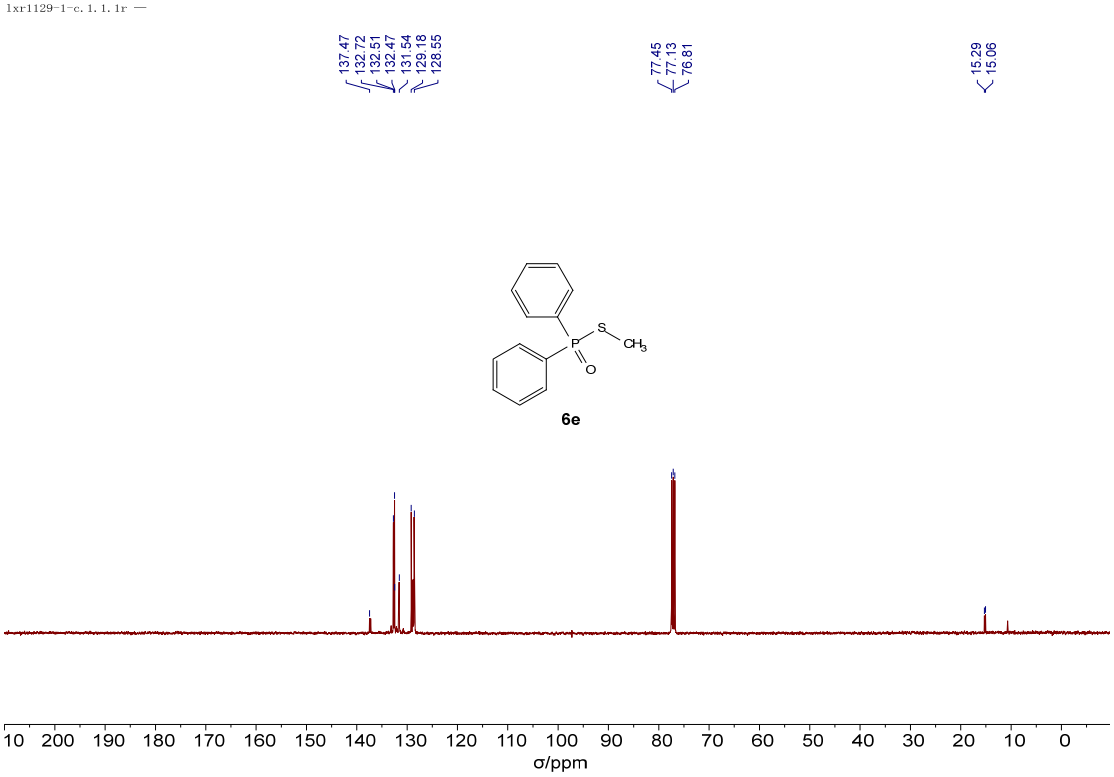
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **6d**



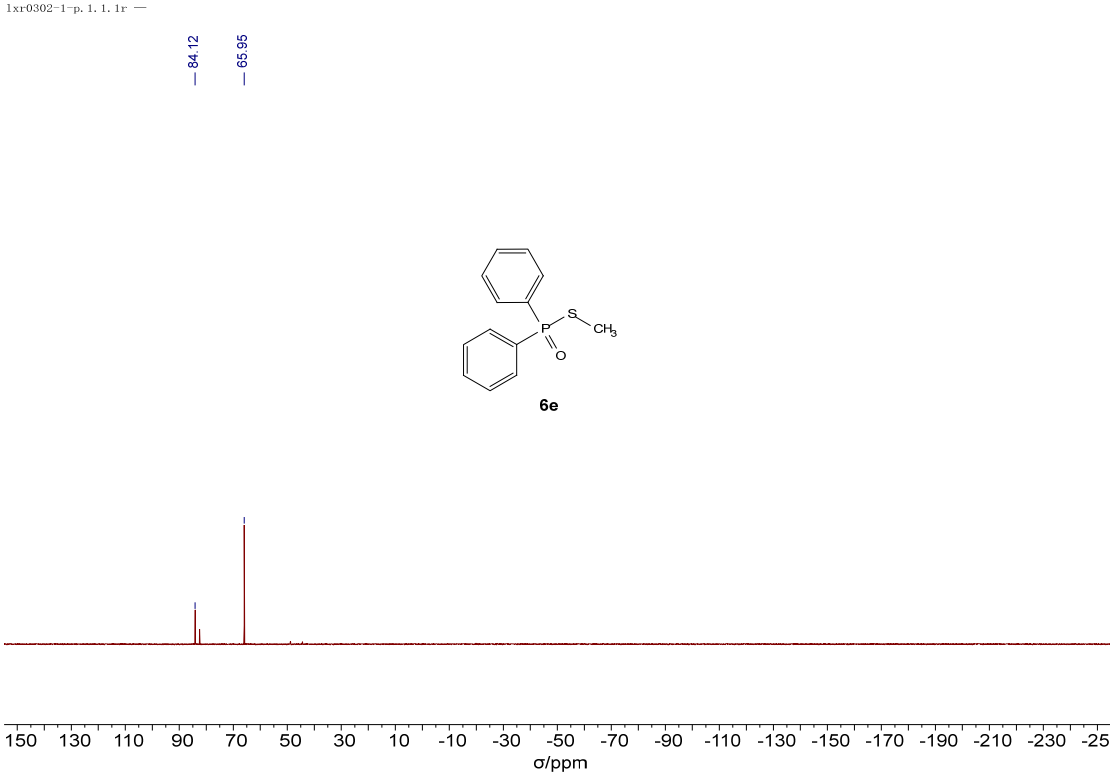
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **6e**



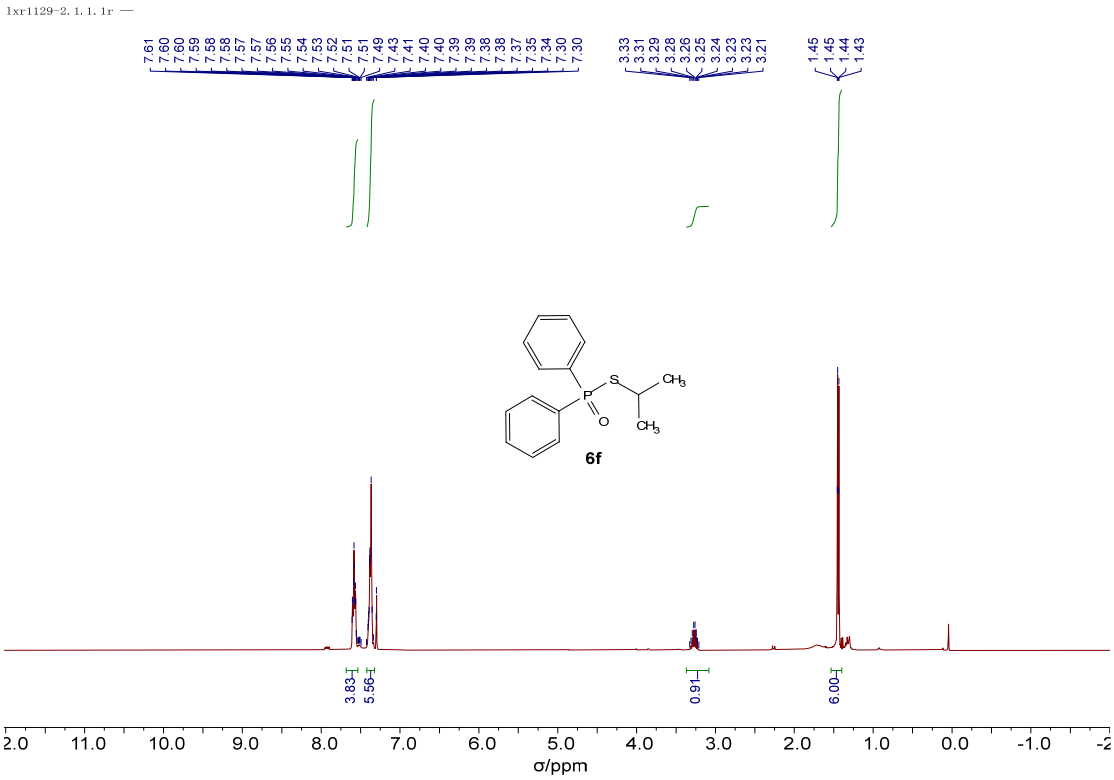
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **6e**



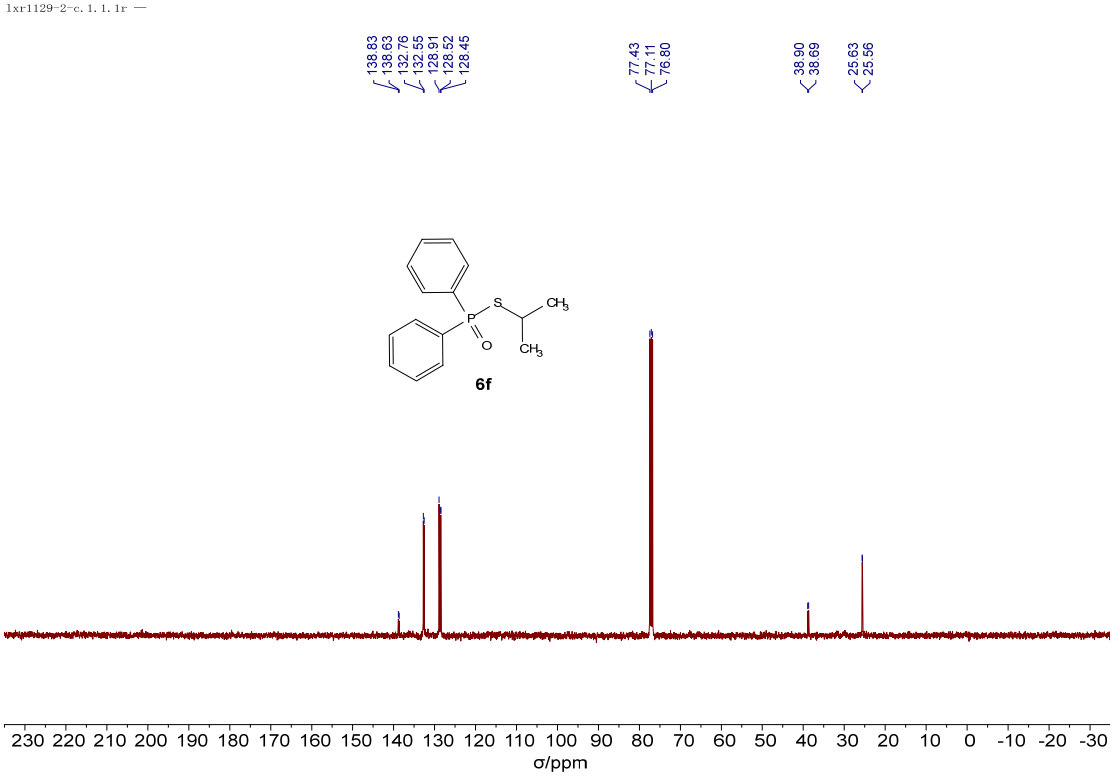
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **6e**



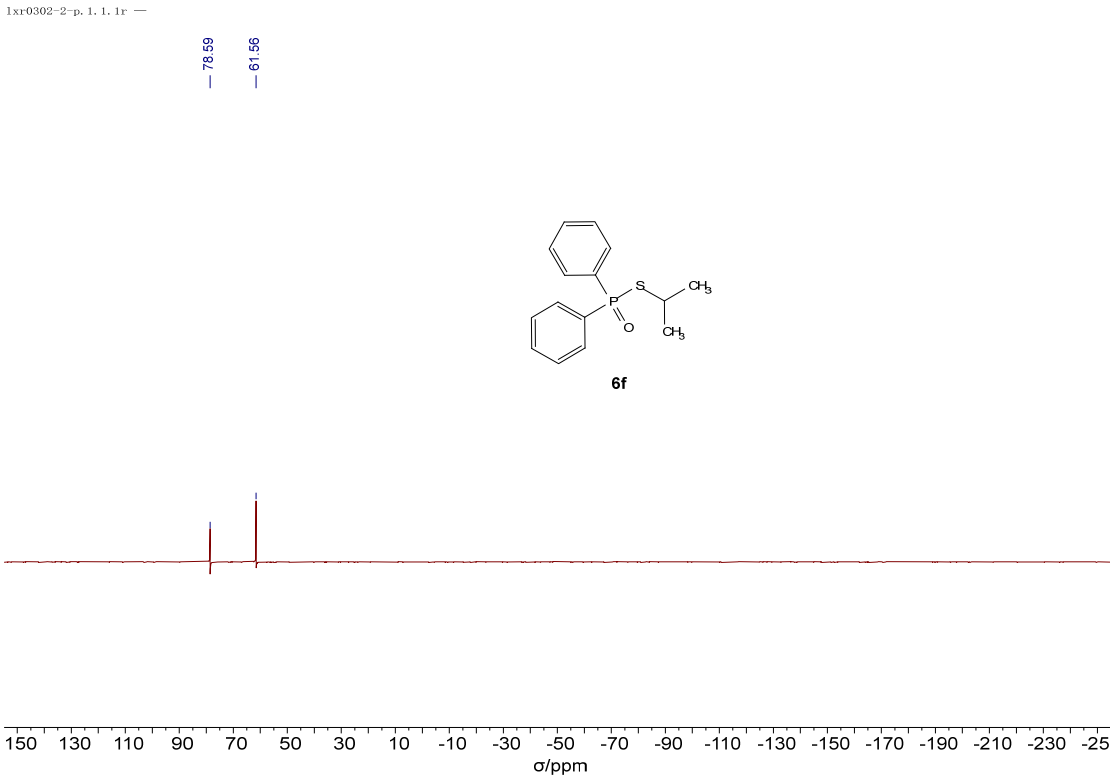
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **6f**



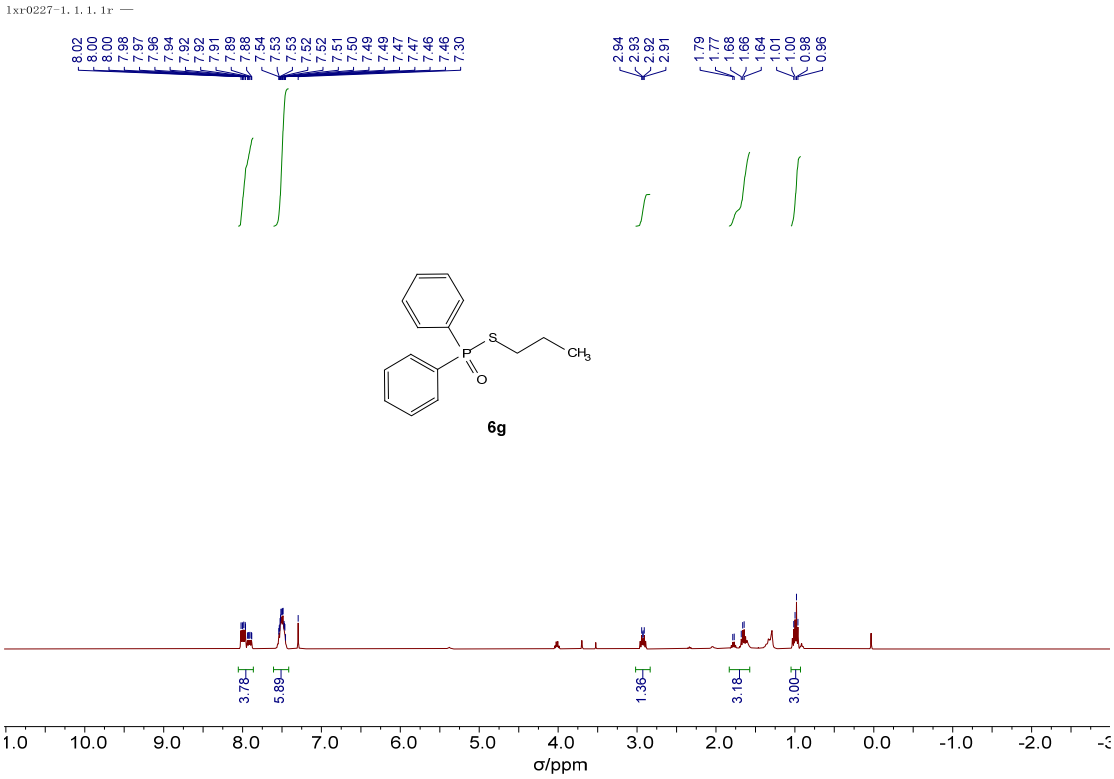
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **6f**



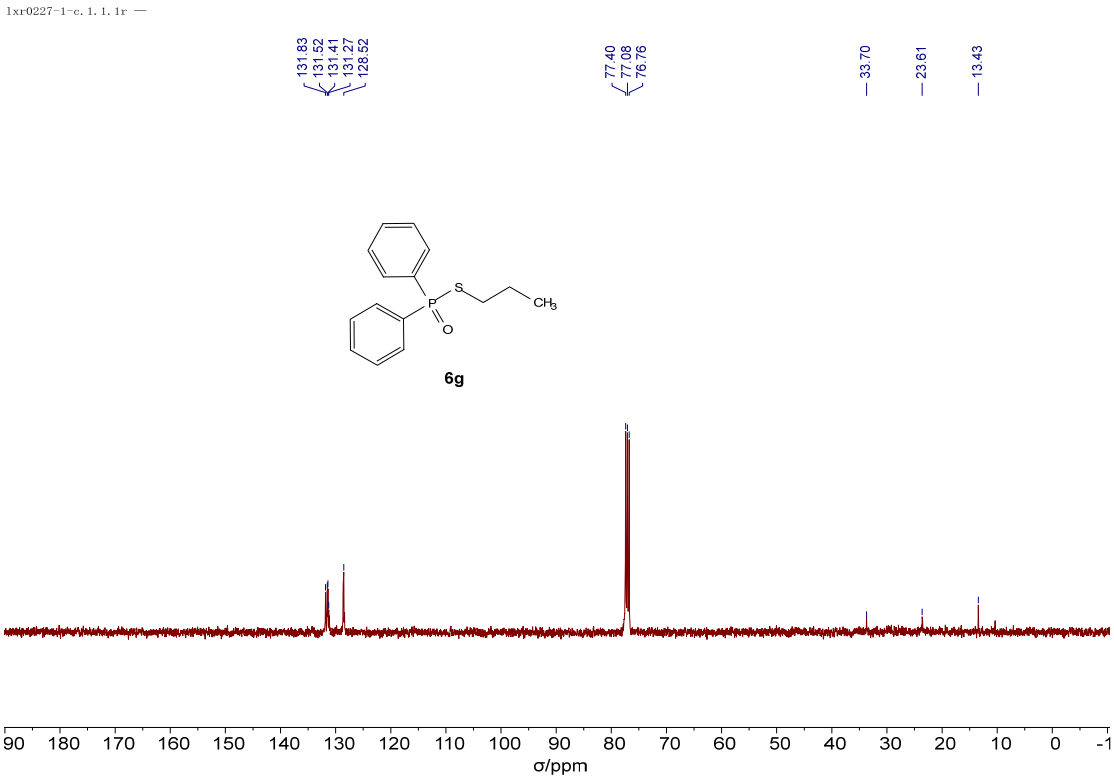
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **6f**



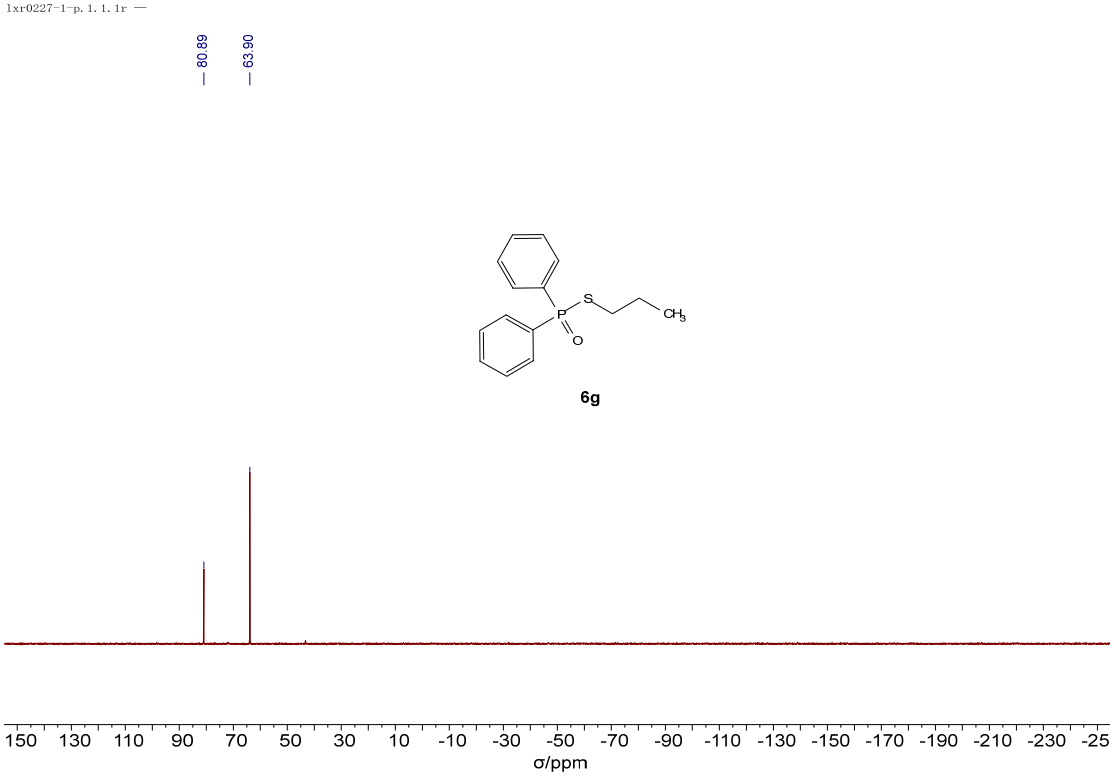
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **6g**



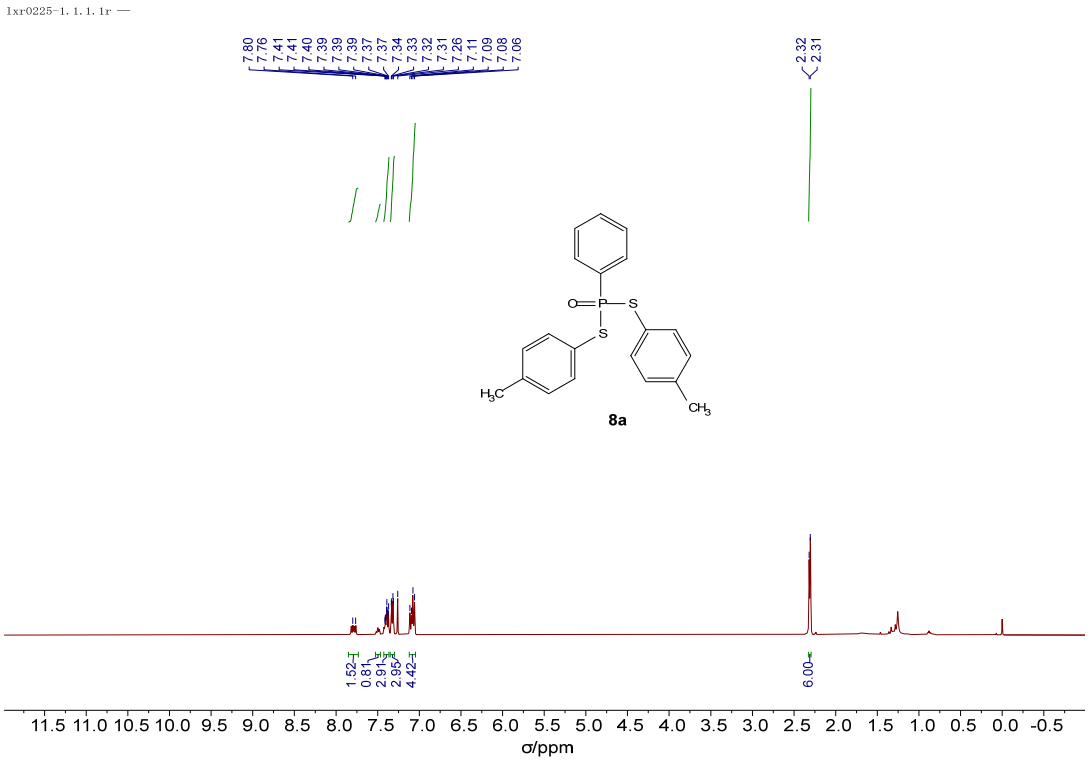
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **6g**



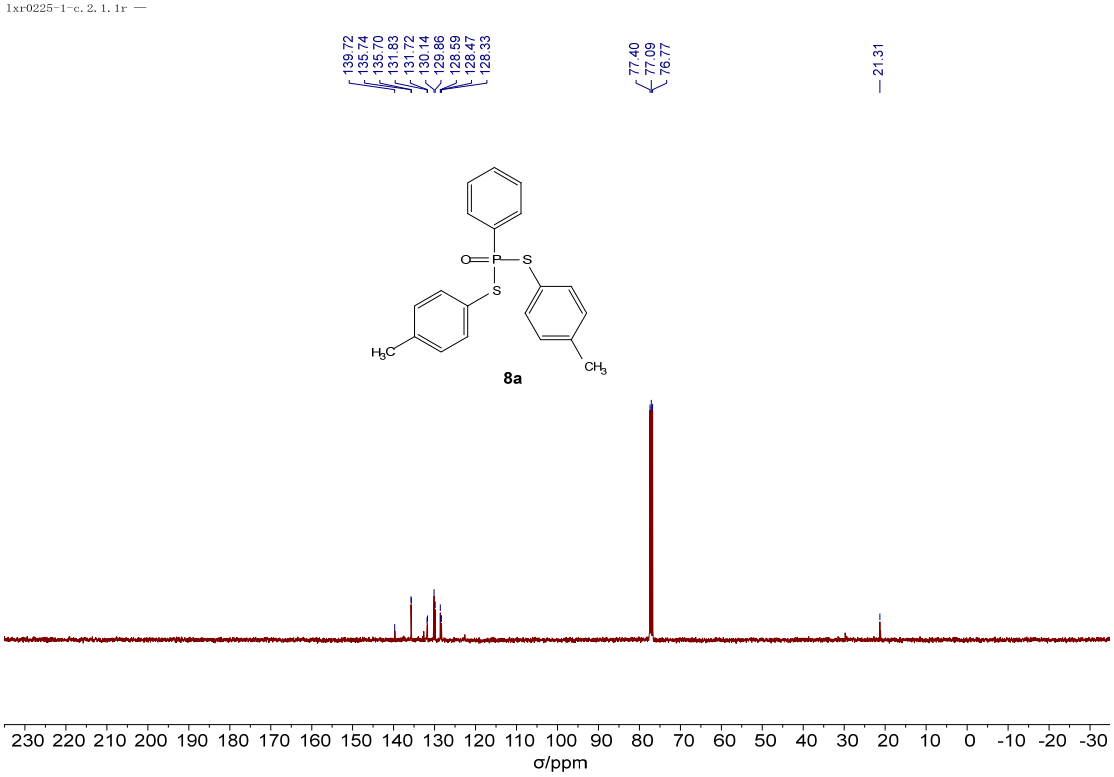
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **6g**



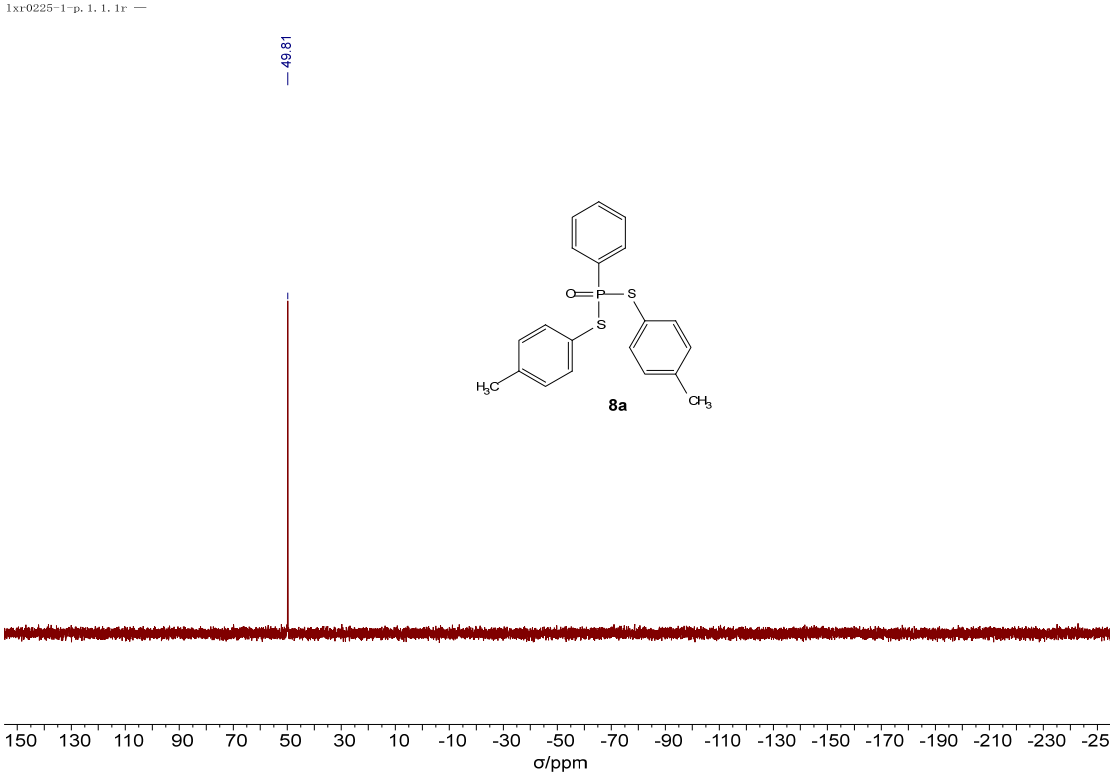
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8a**



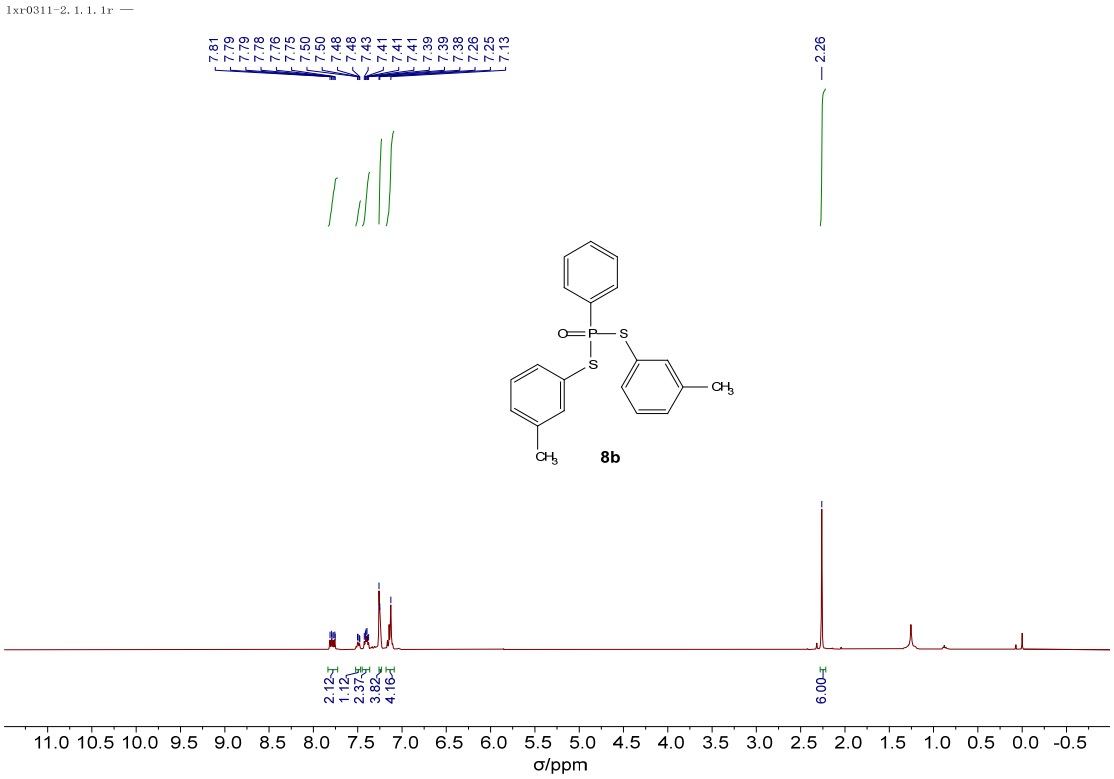
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8a**



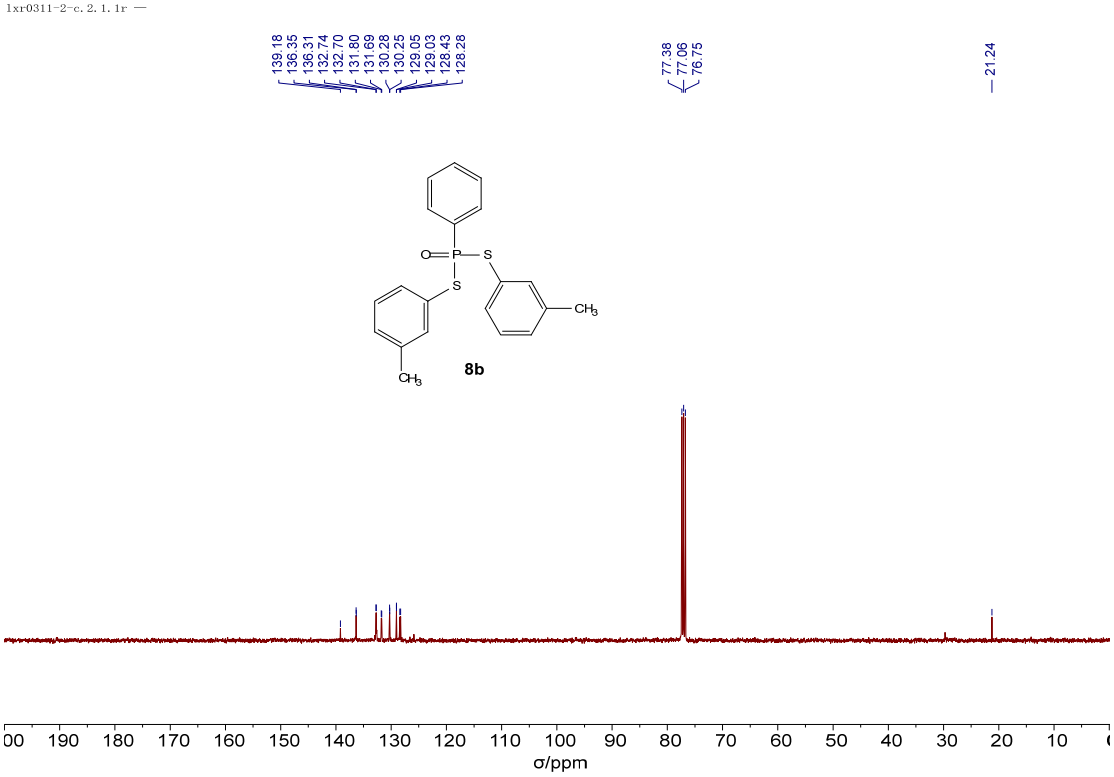
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8a**



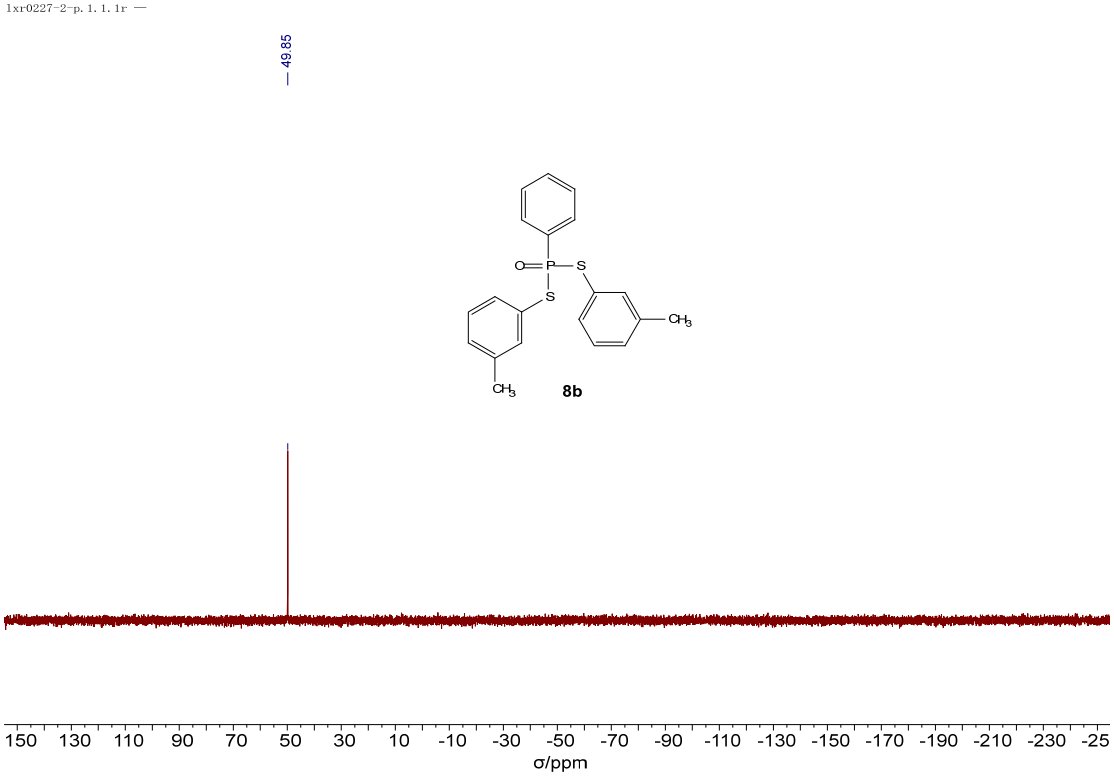
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8b**



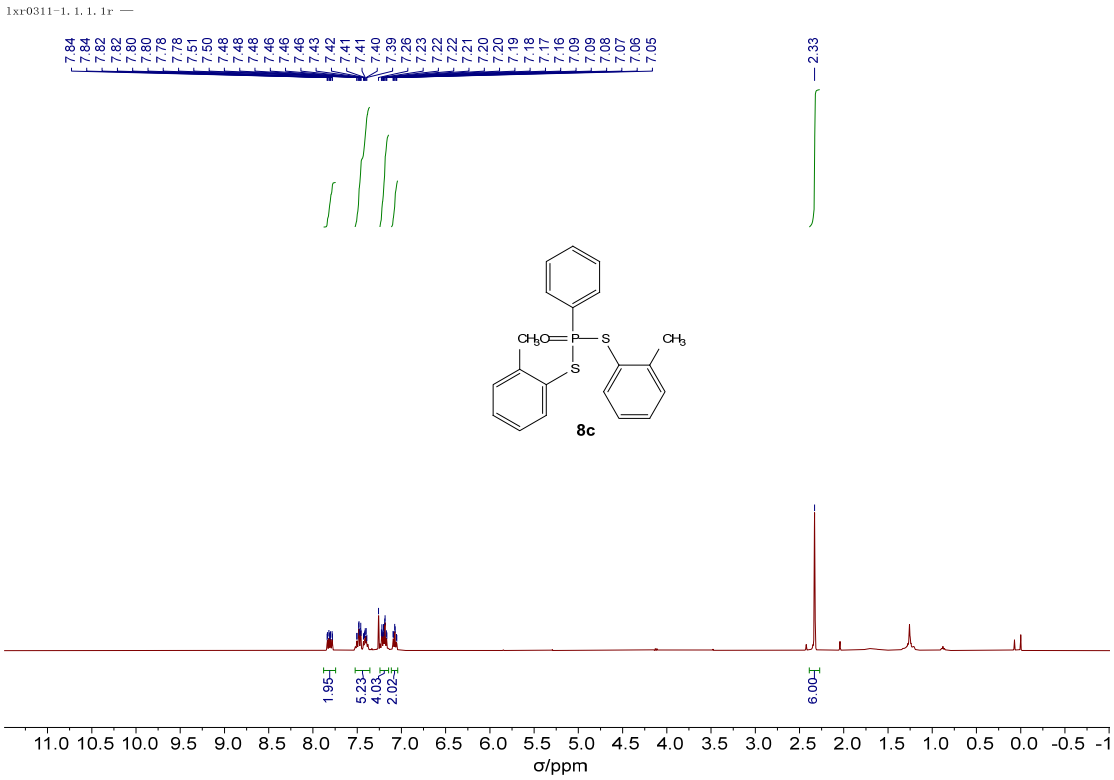
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8b**



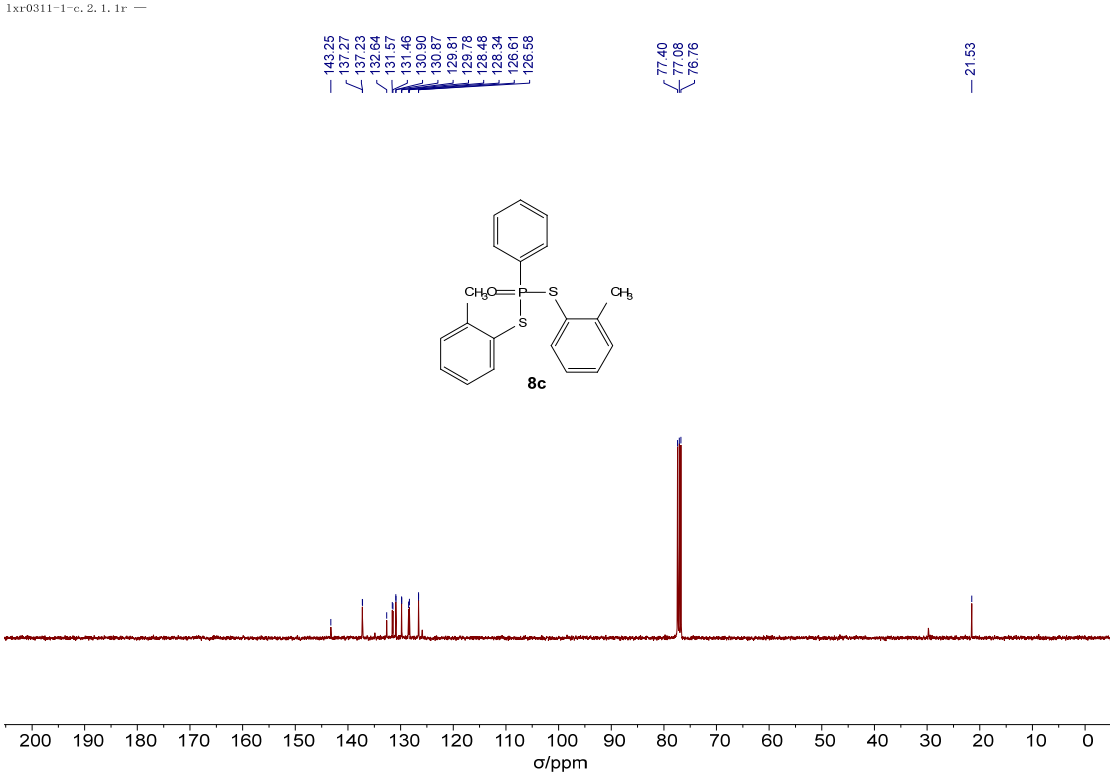
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8b**



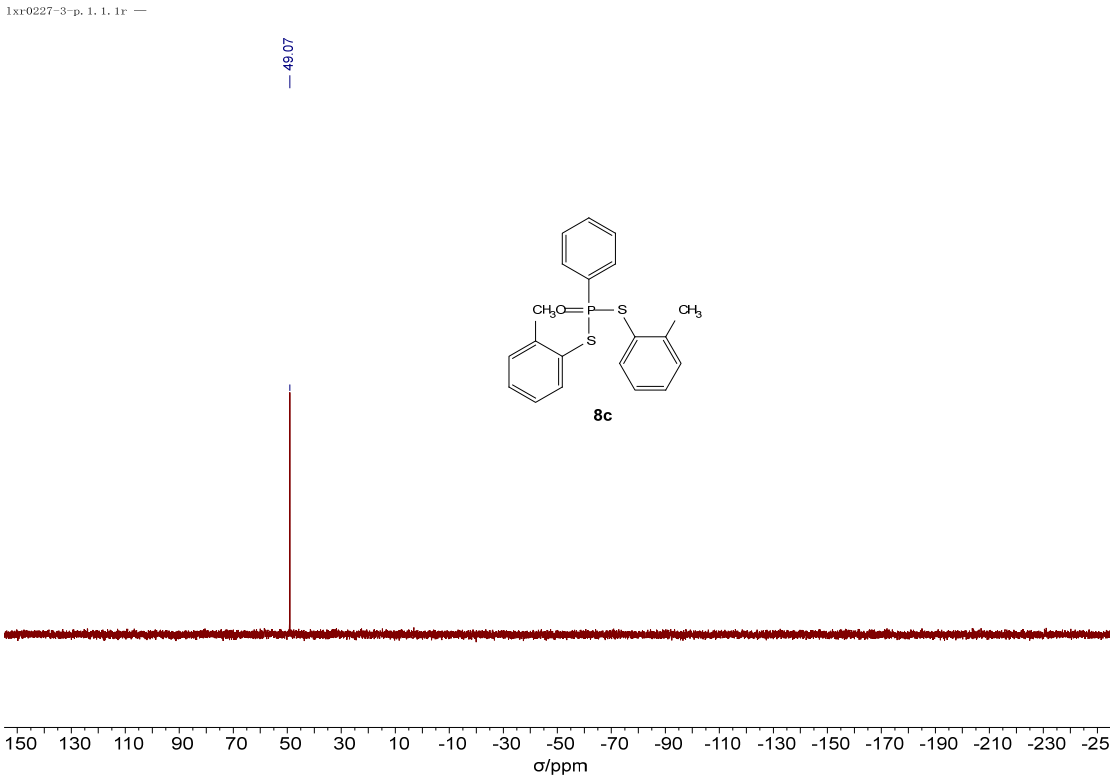
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8c**



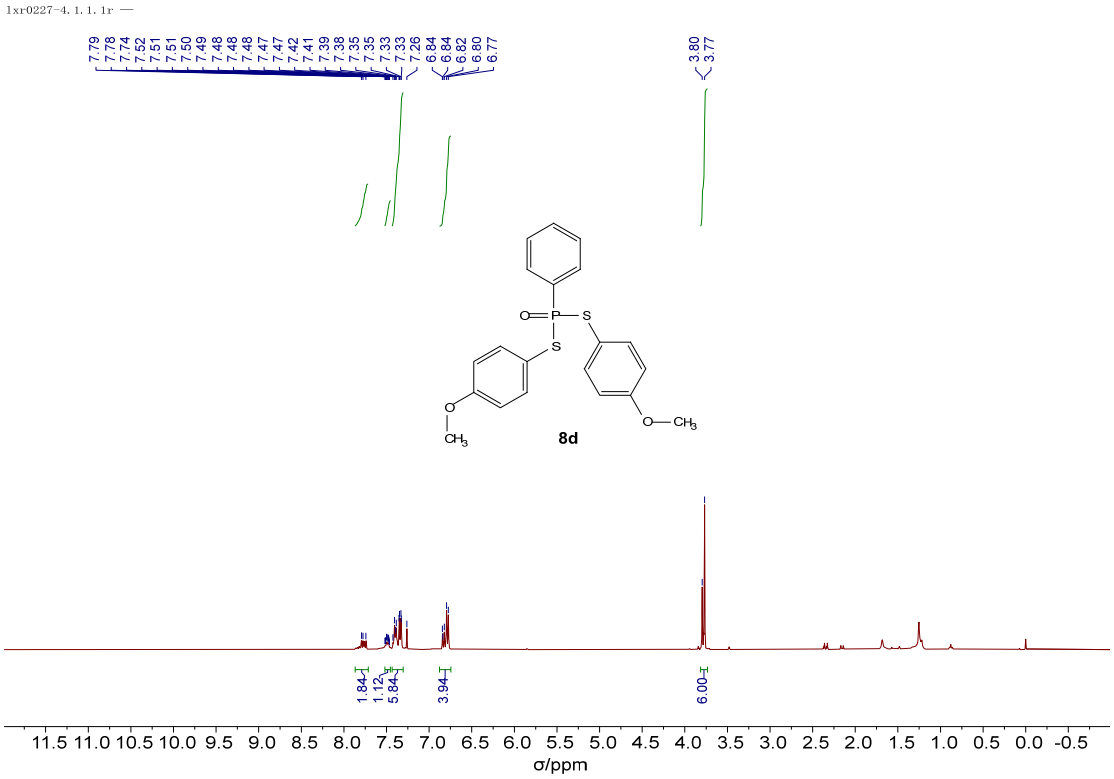
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8c**



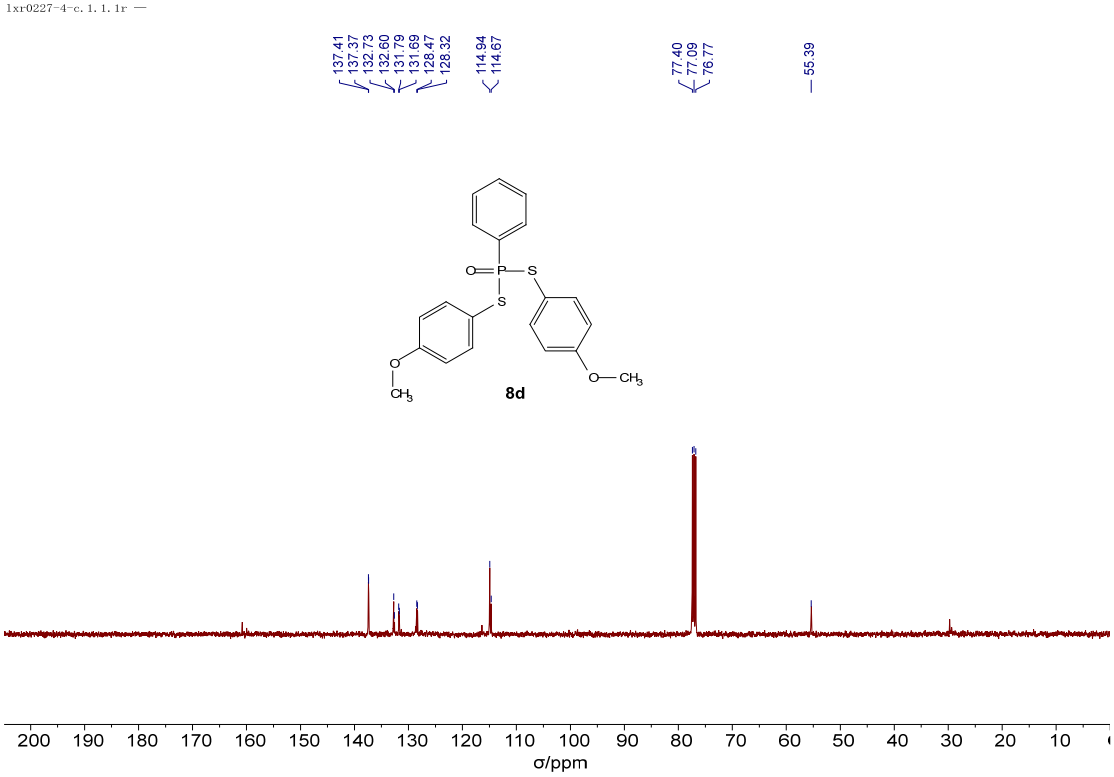
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8c**



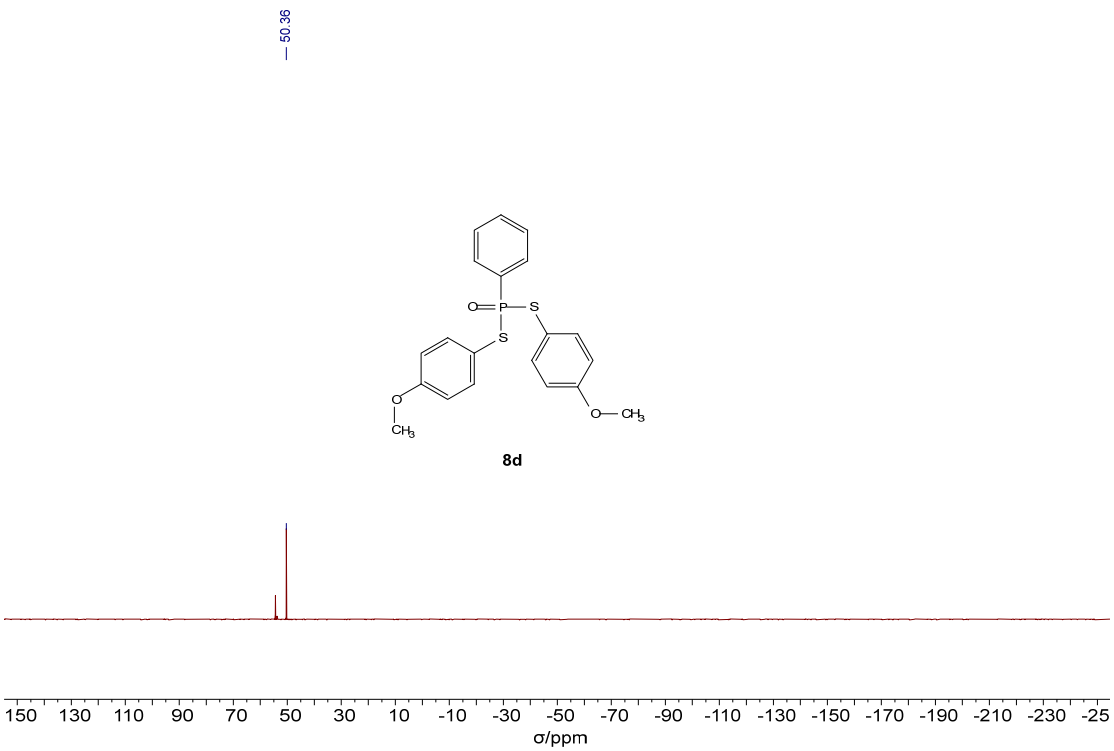
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8d**



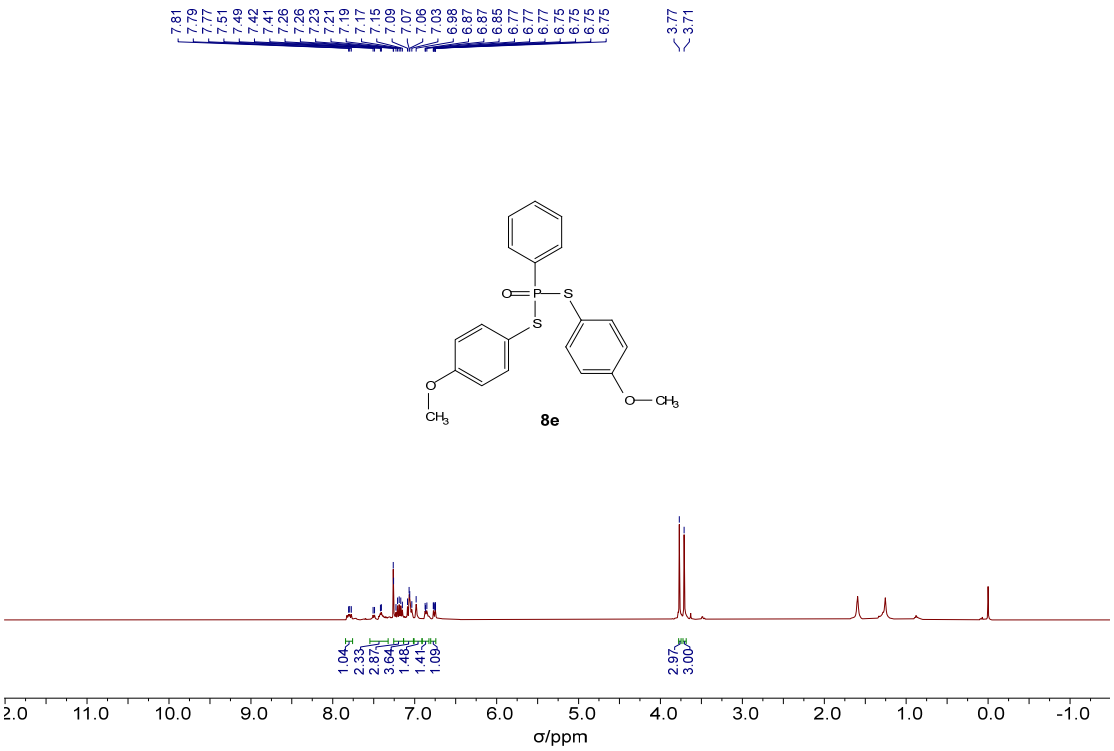
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8d**



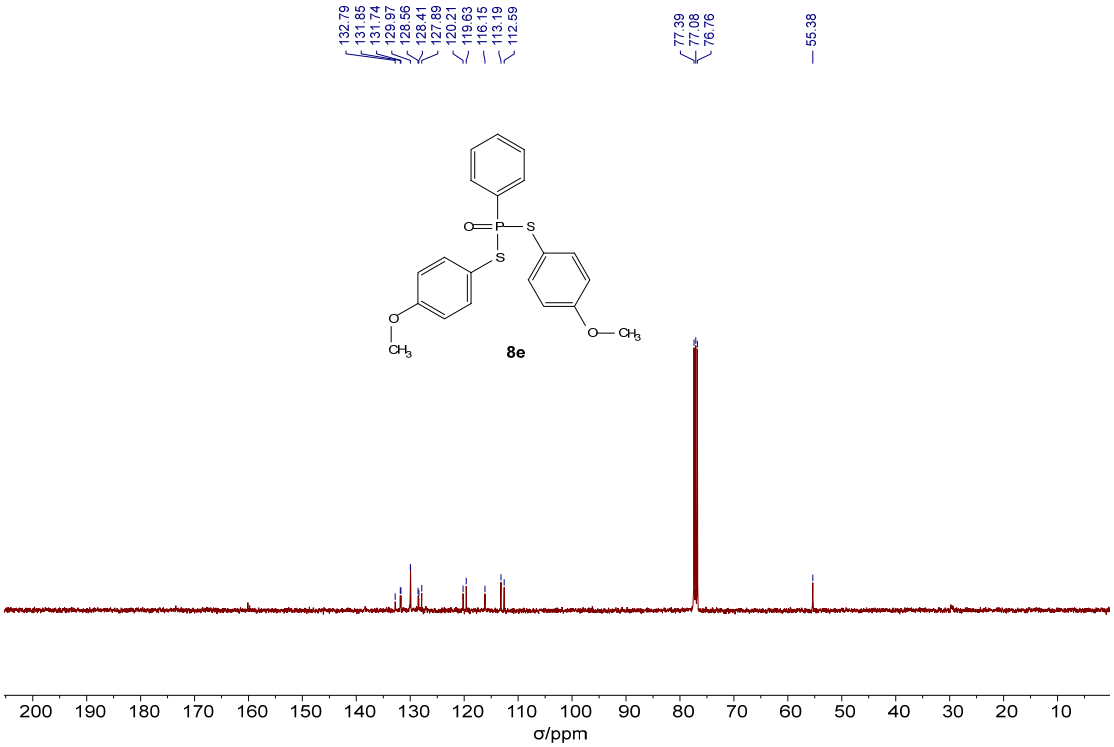
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8d**



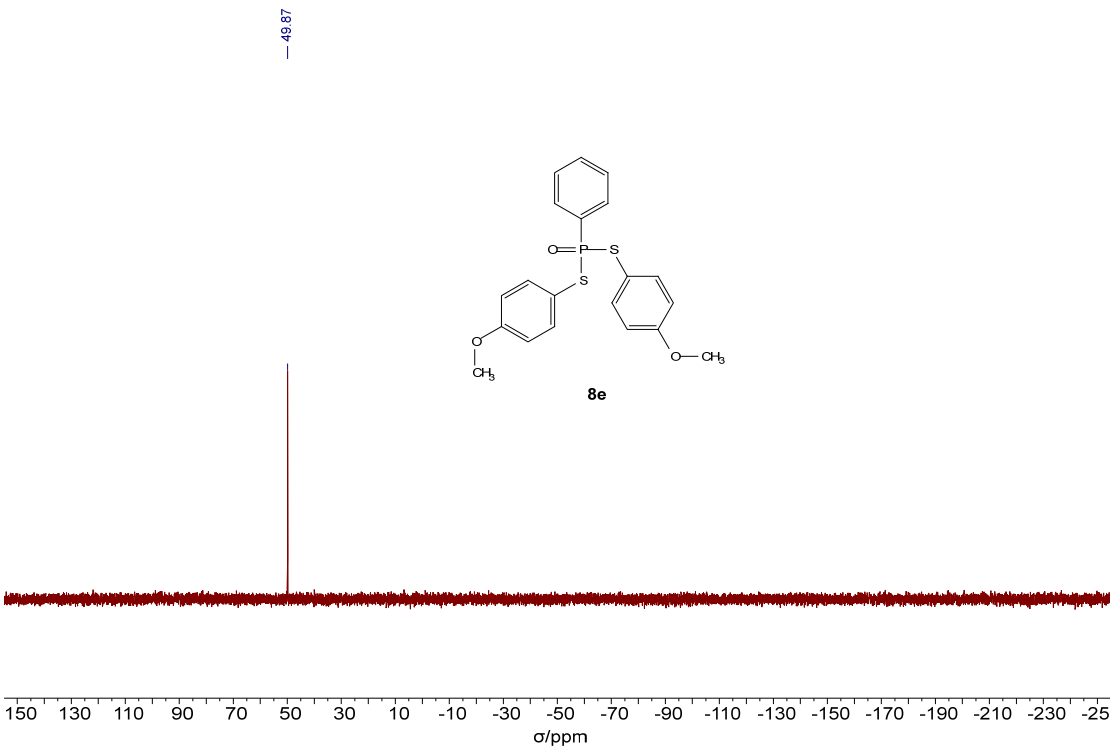
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8e**



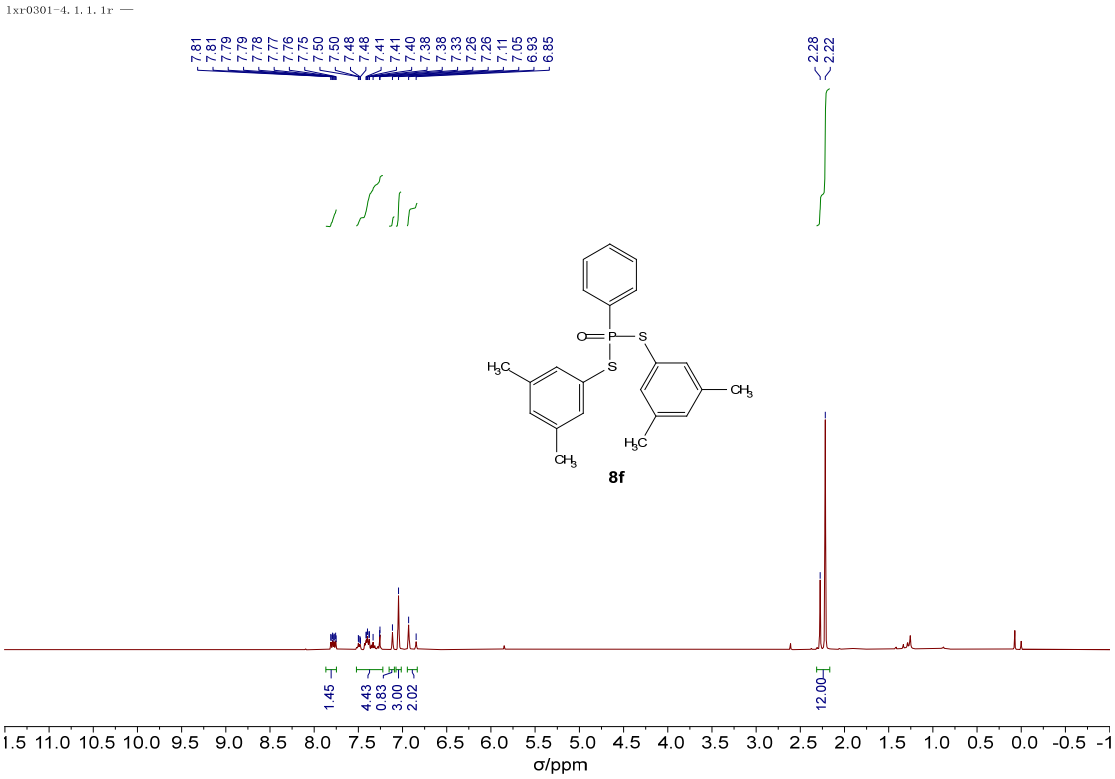
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8e**



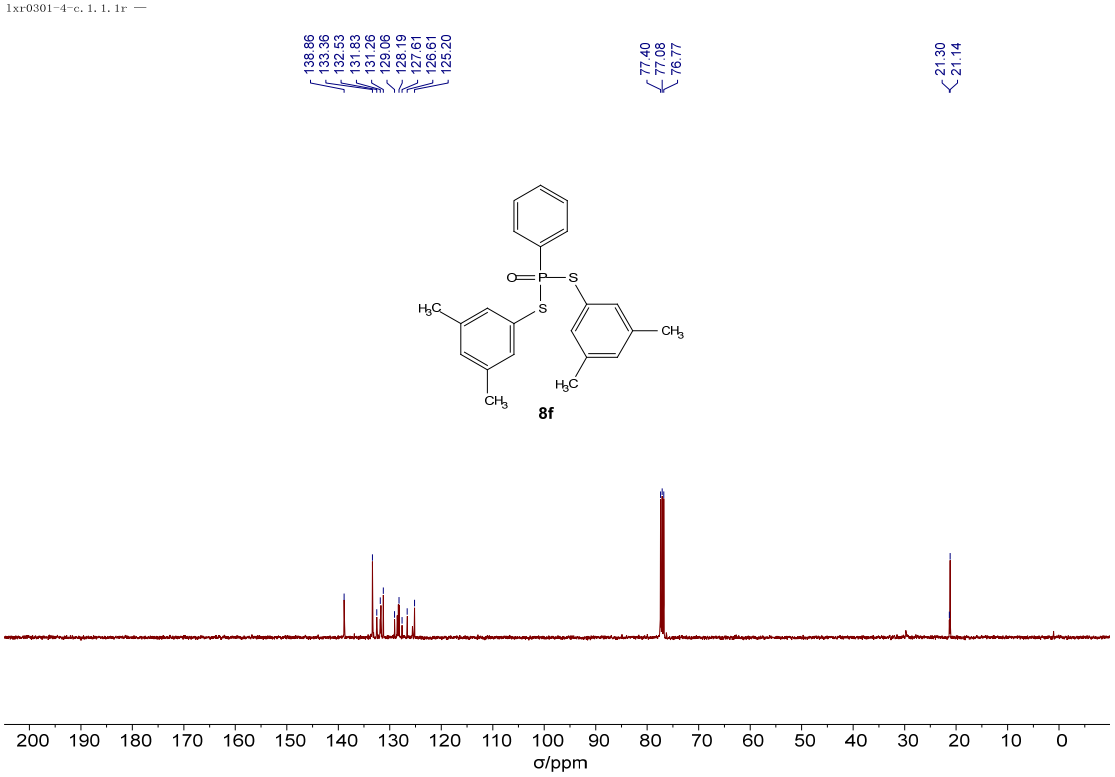
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8e**



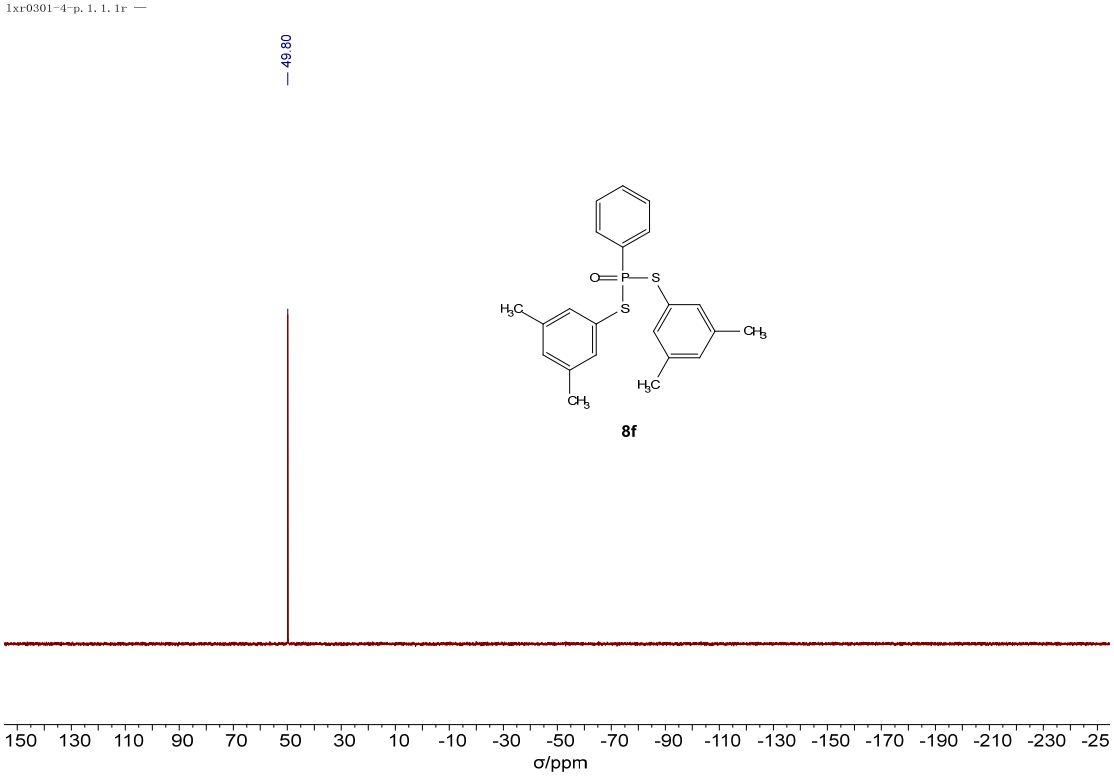
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8f**



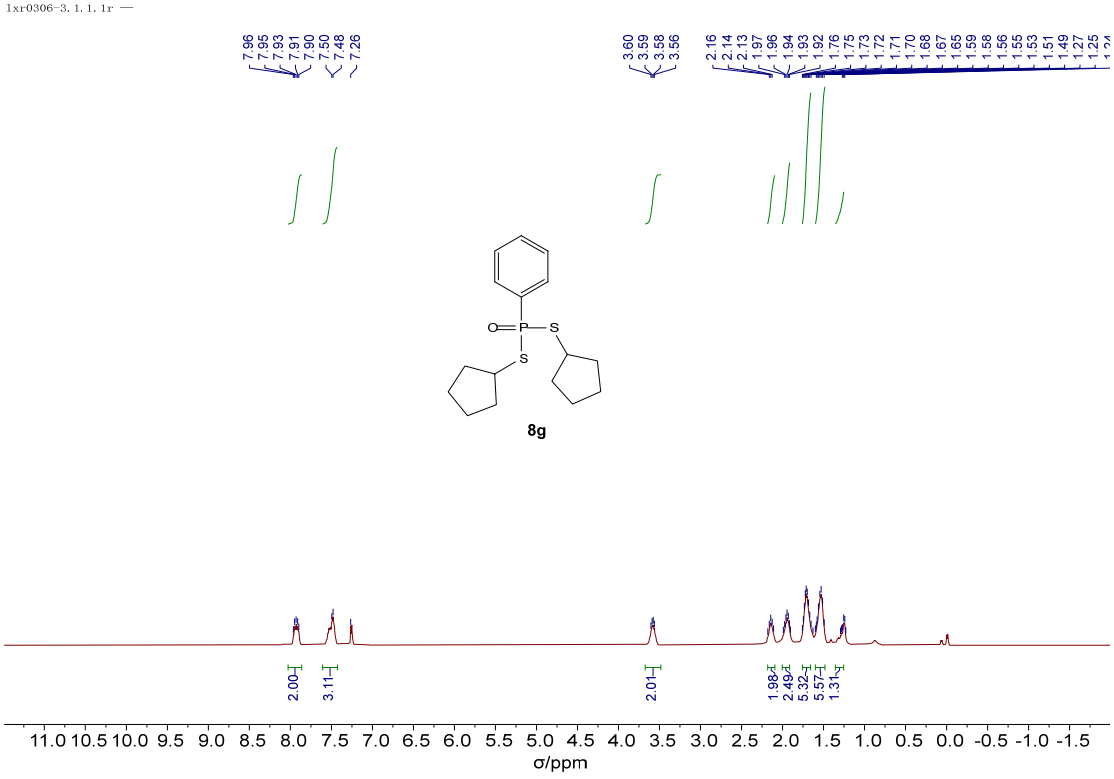
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8f**



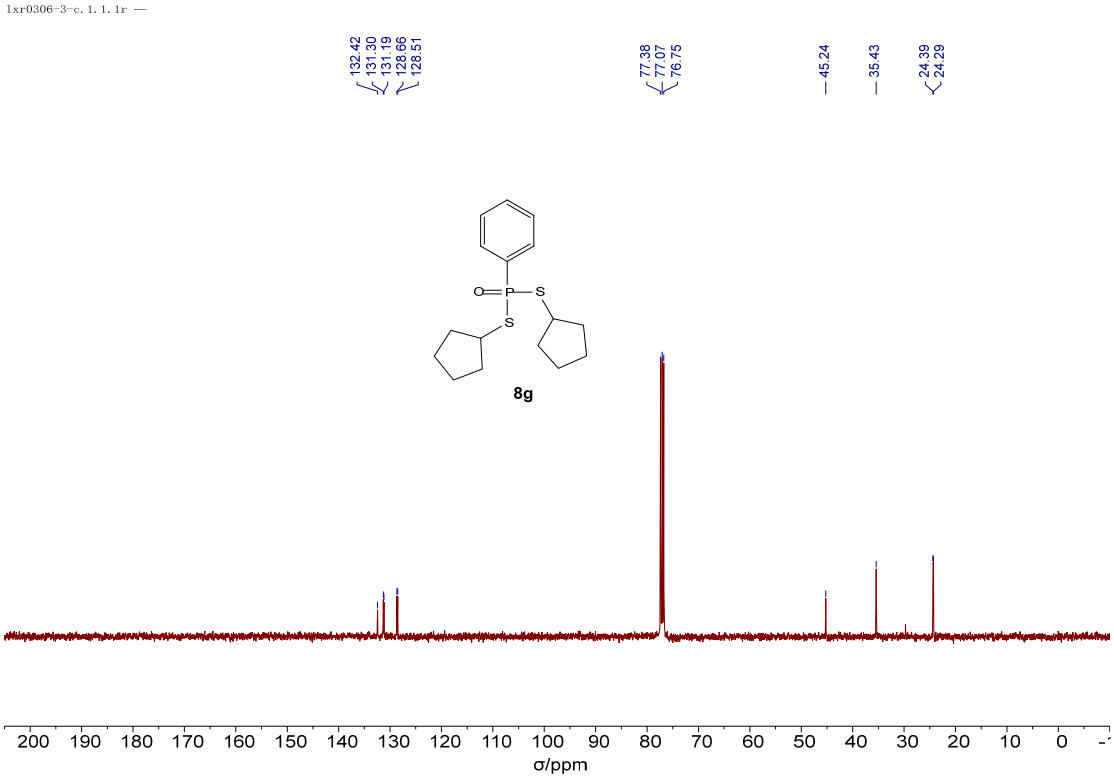
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8f**



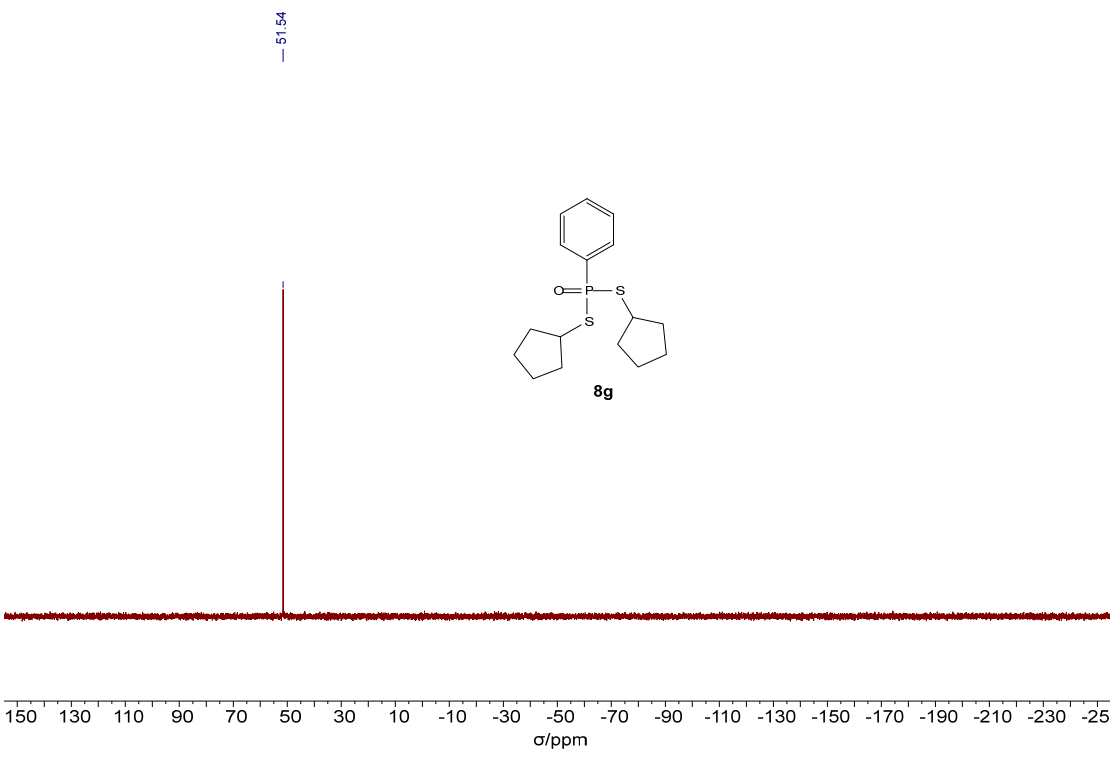
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8g**



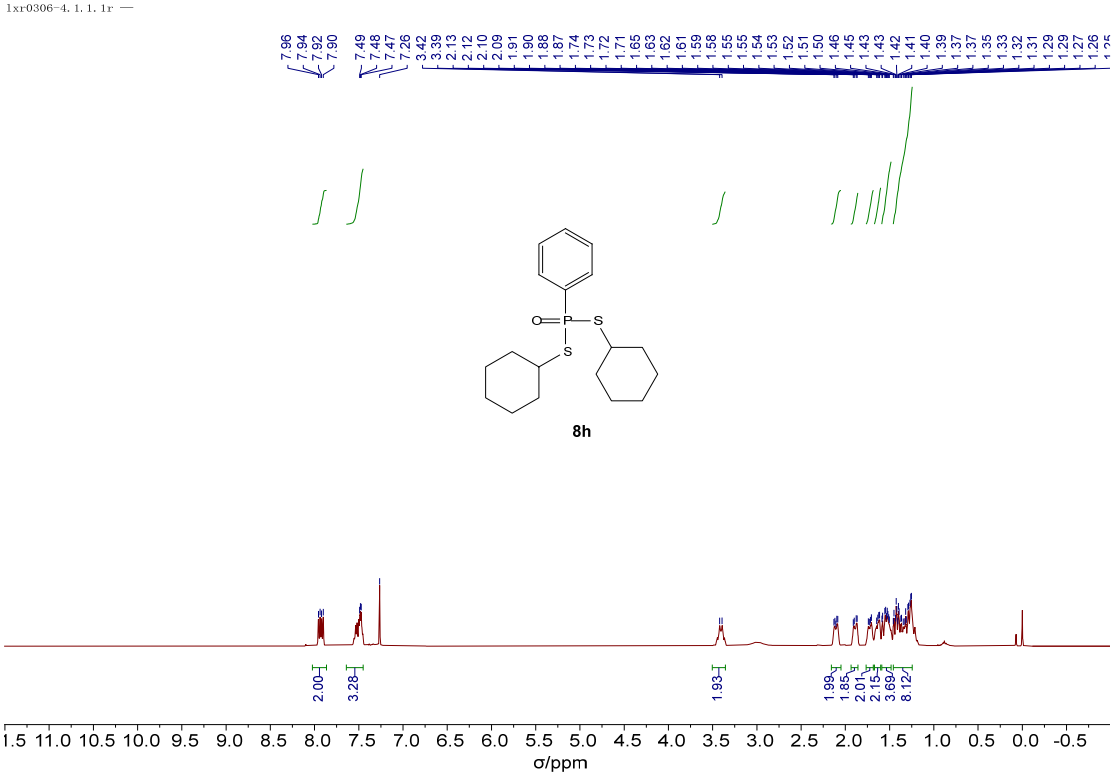
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8g**



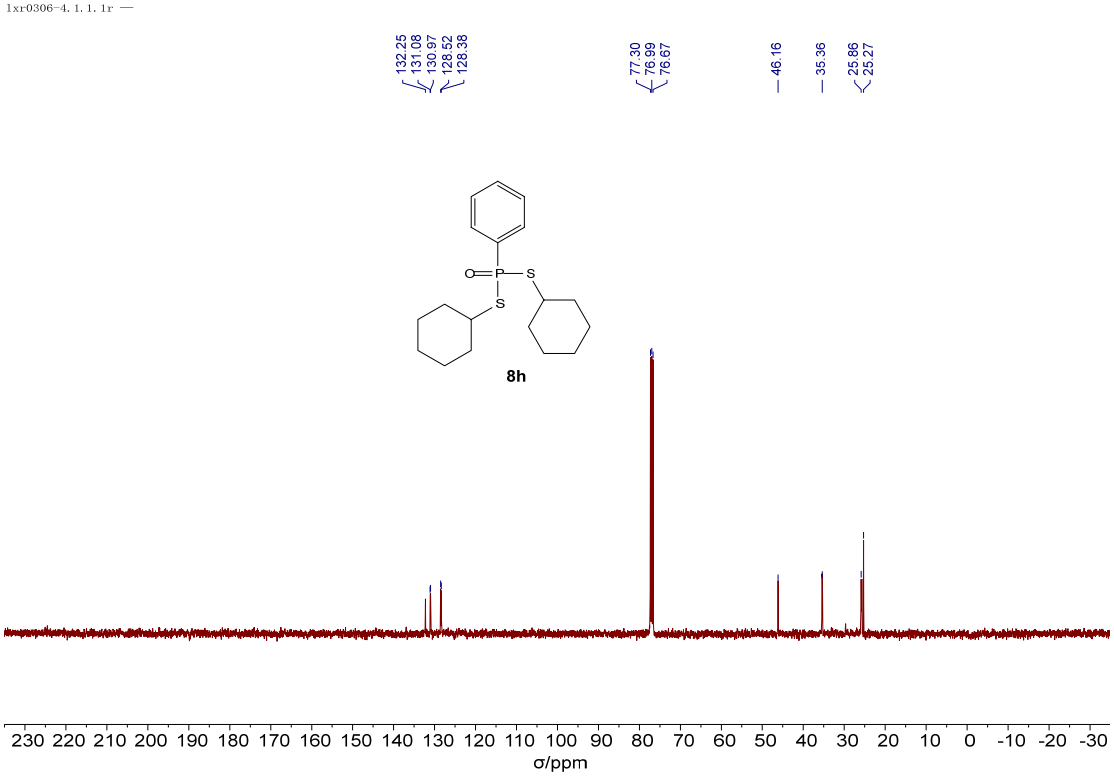
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8g**



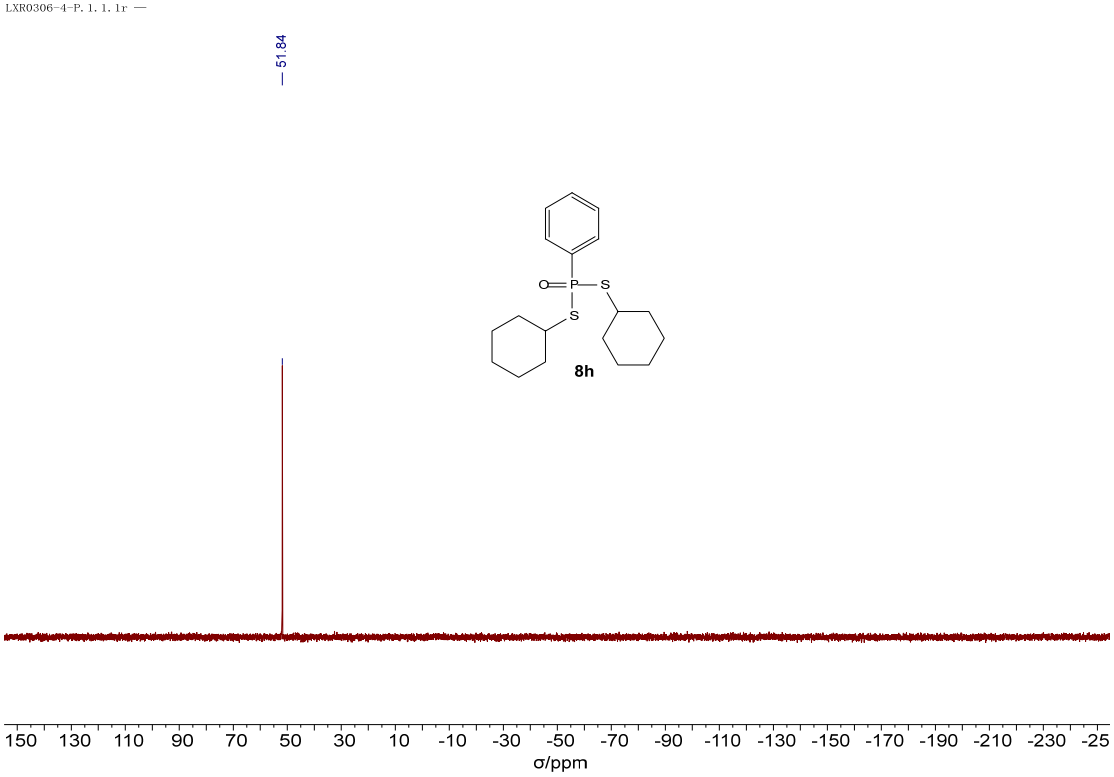
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **8h**



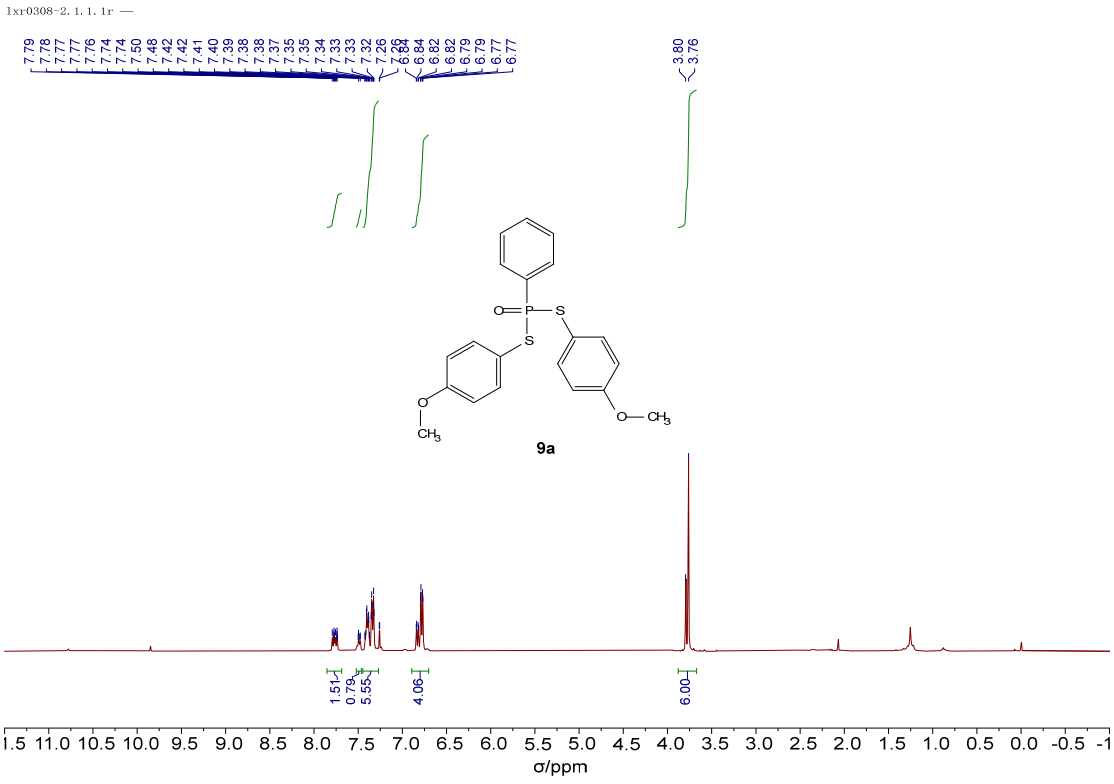
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **8h**



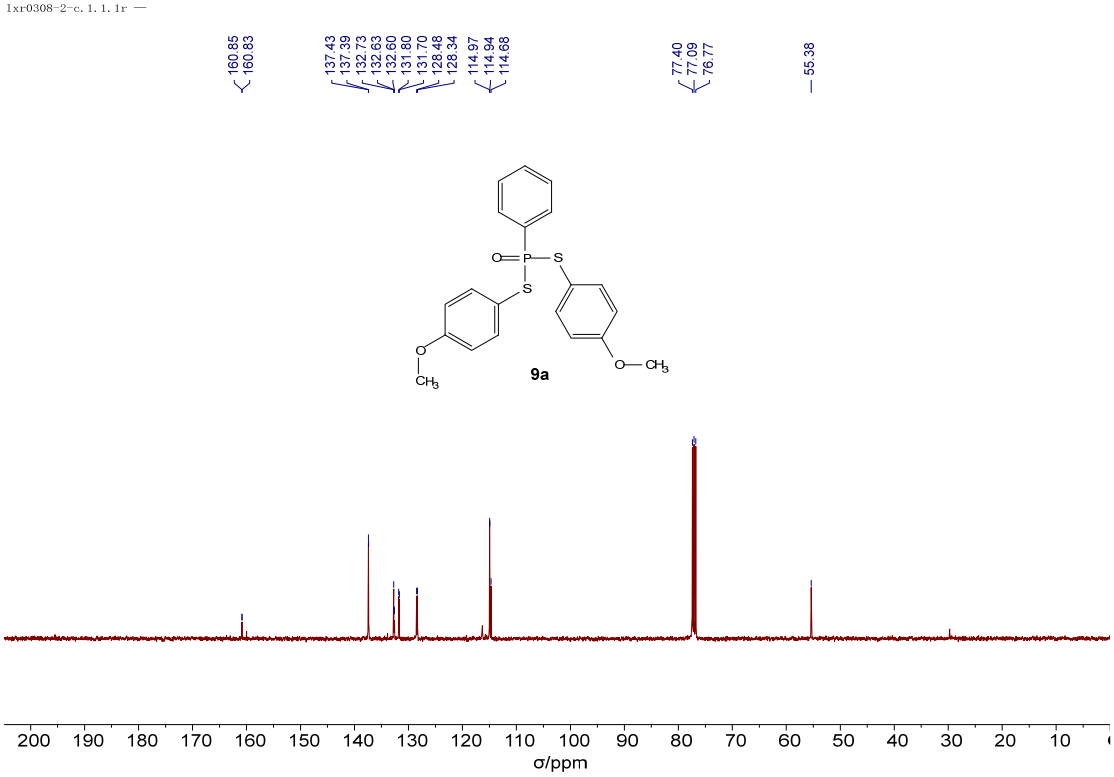
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **8h**



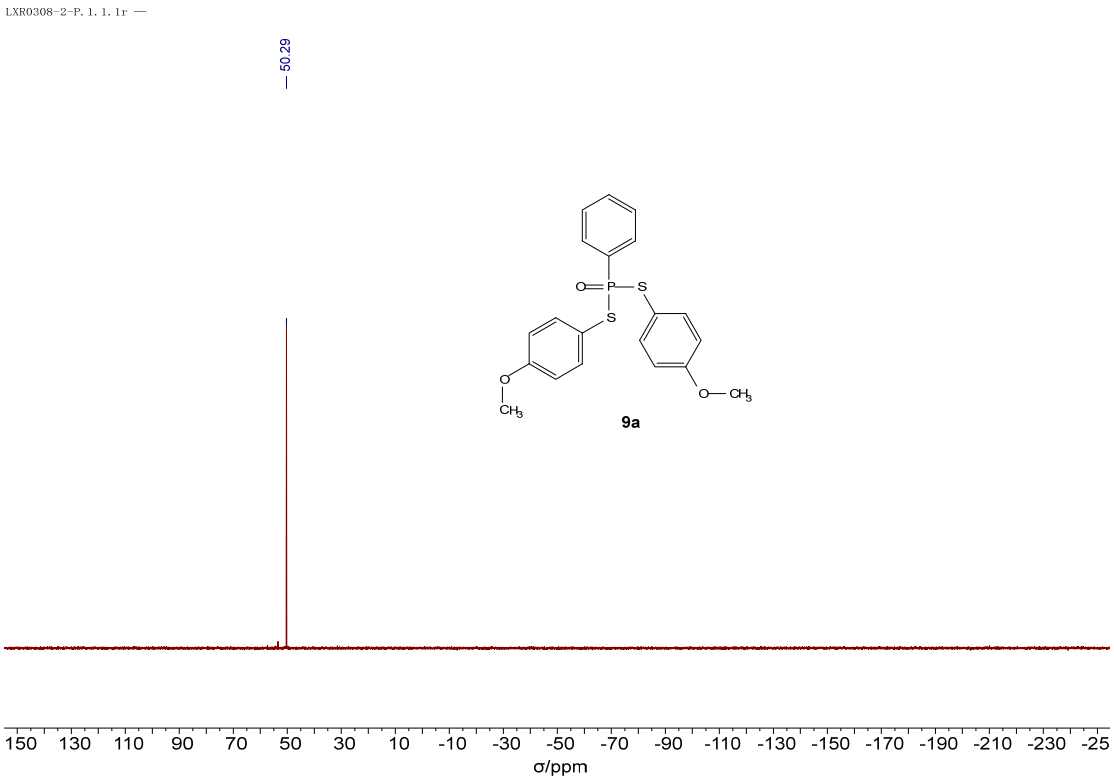
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **9a**



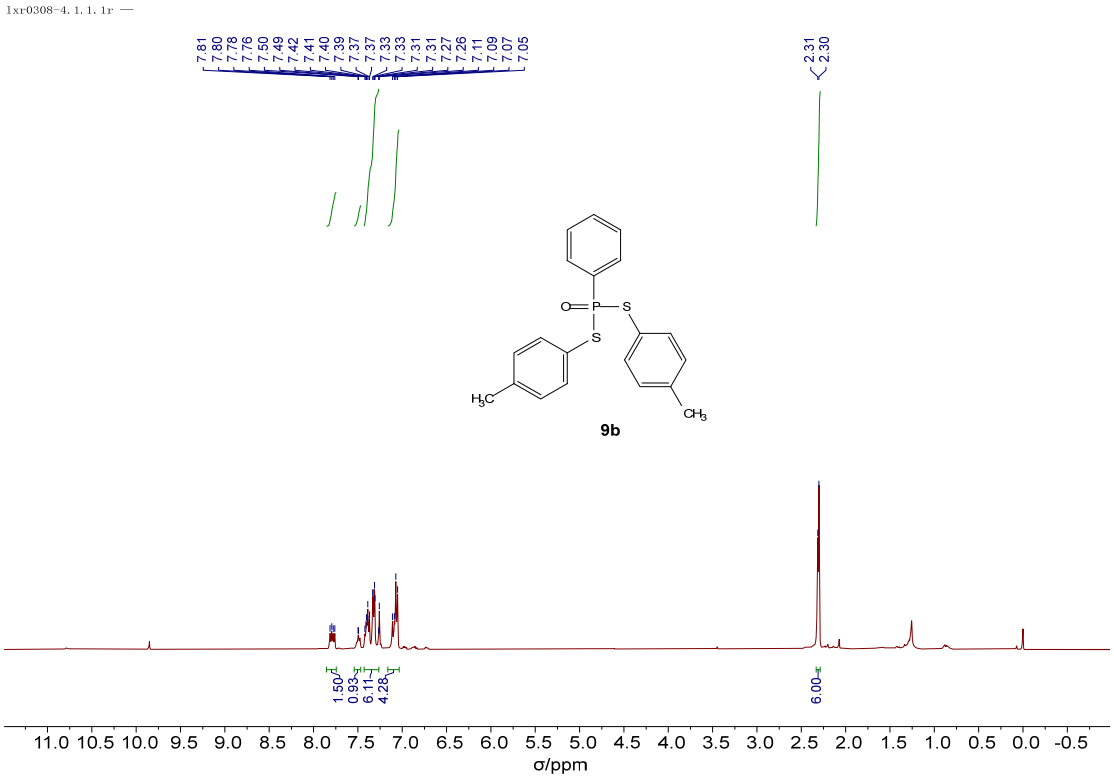
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **9a**



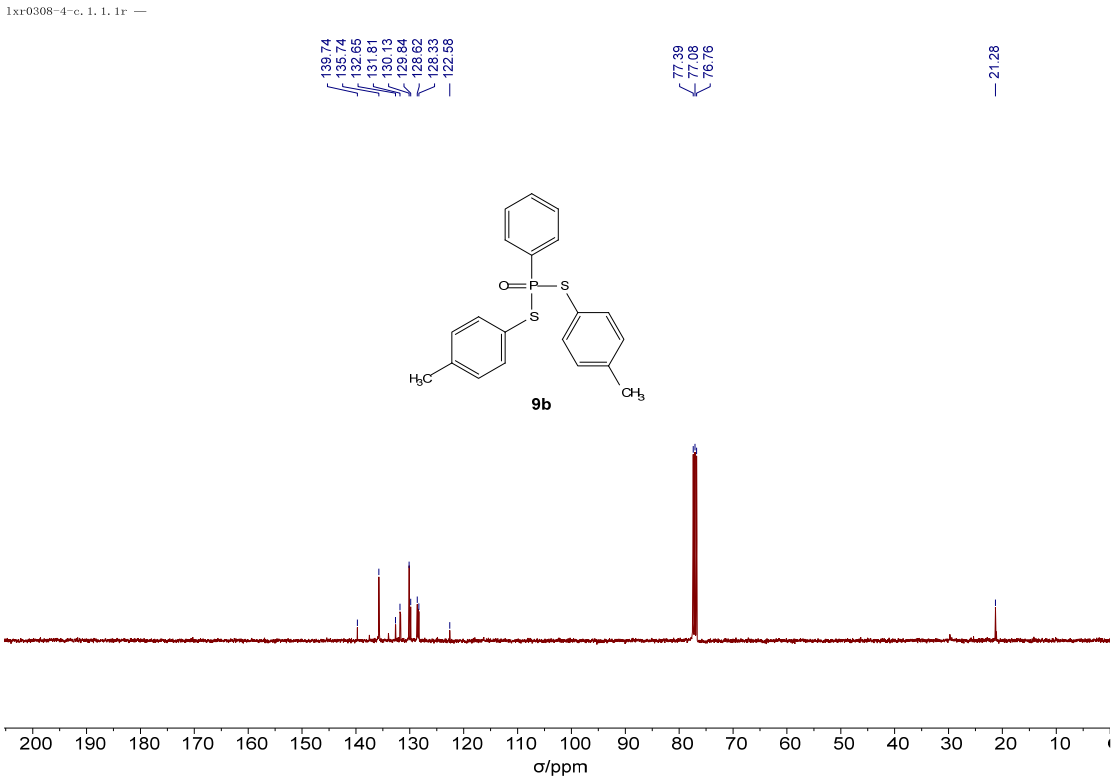
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **9a**



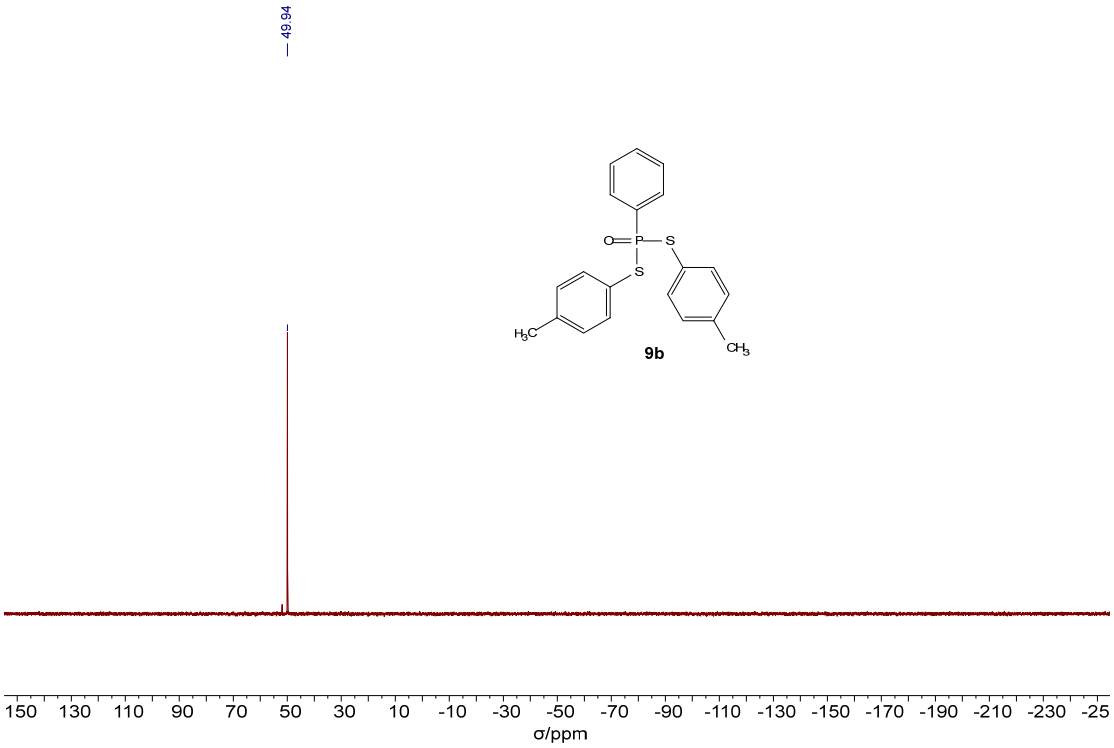
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **9b**



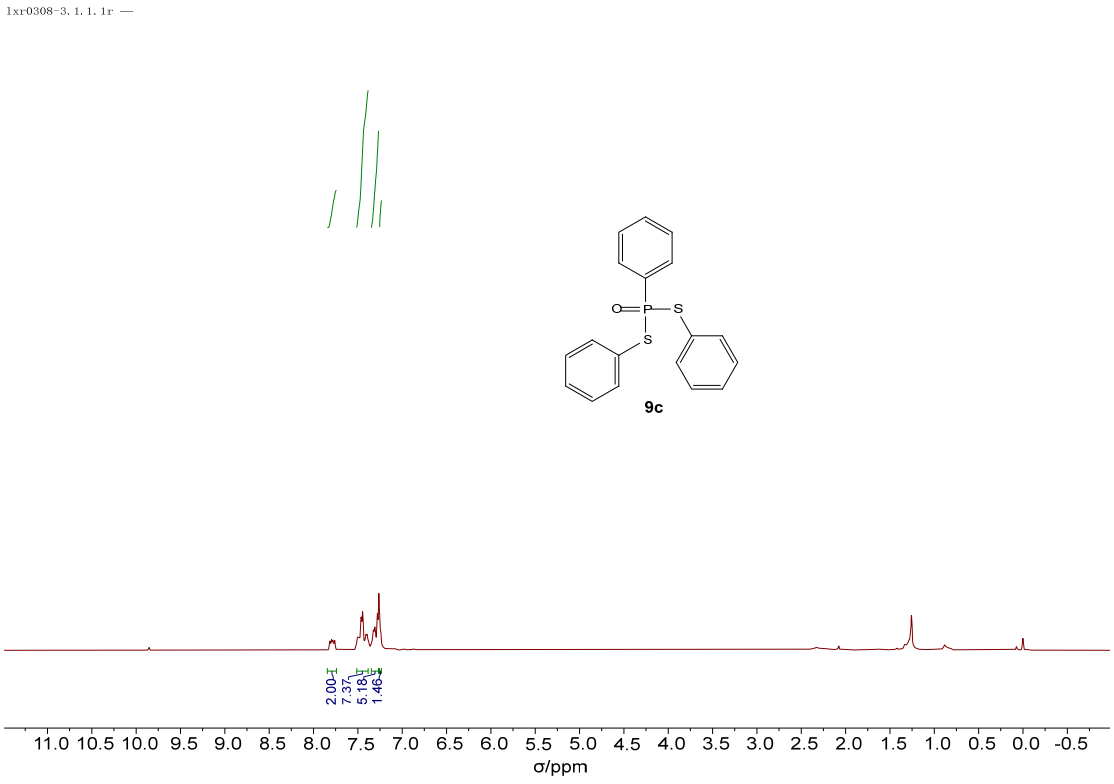
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **9b**



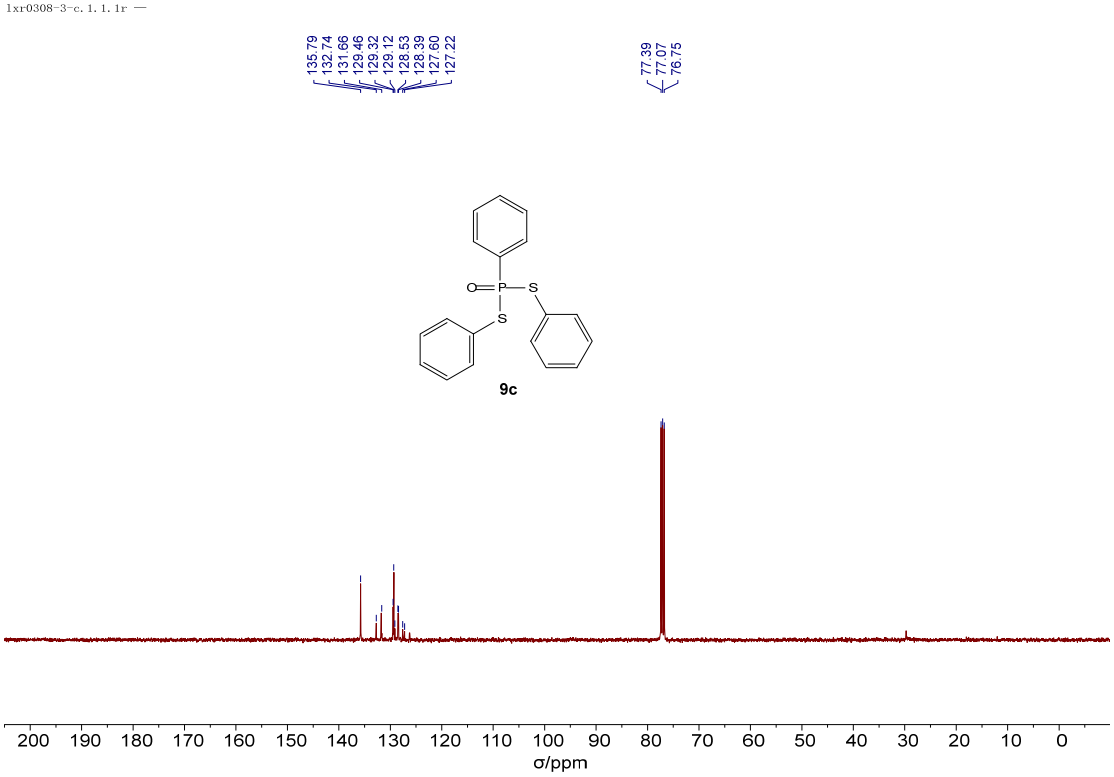
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **9b**



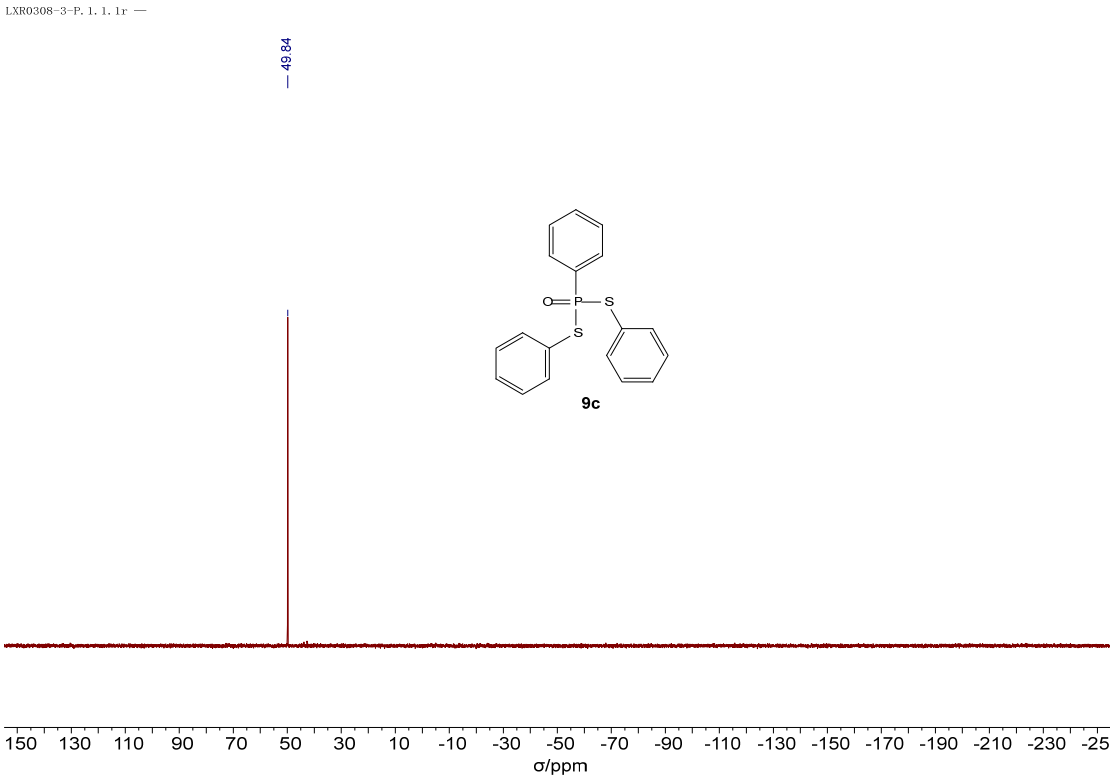
^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **9c**



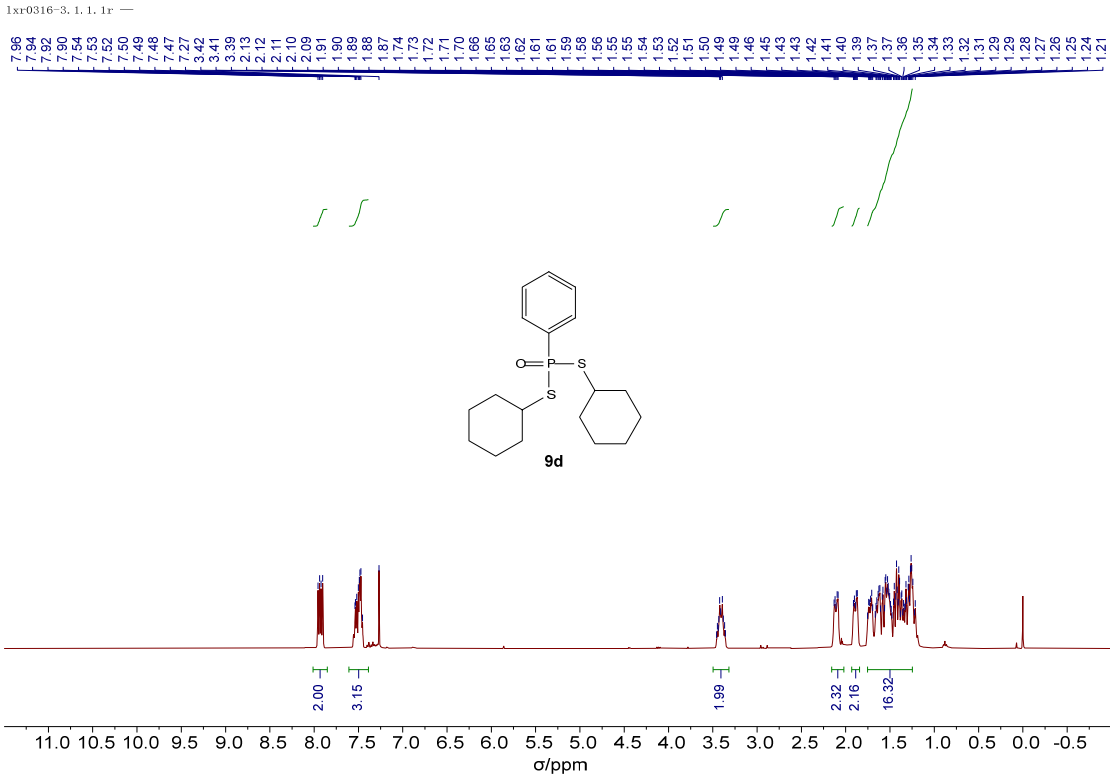
^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **9c**



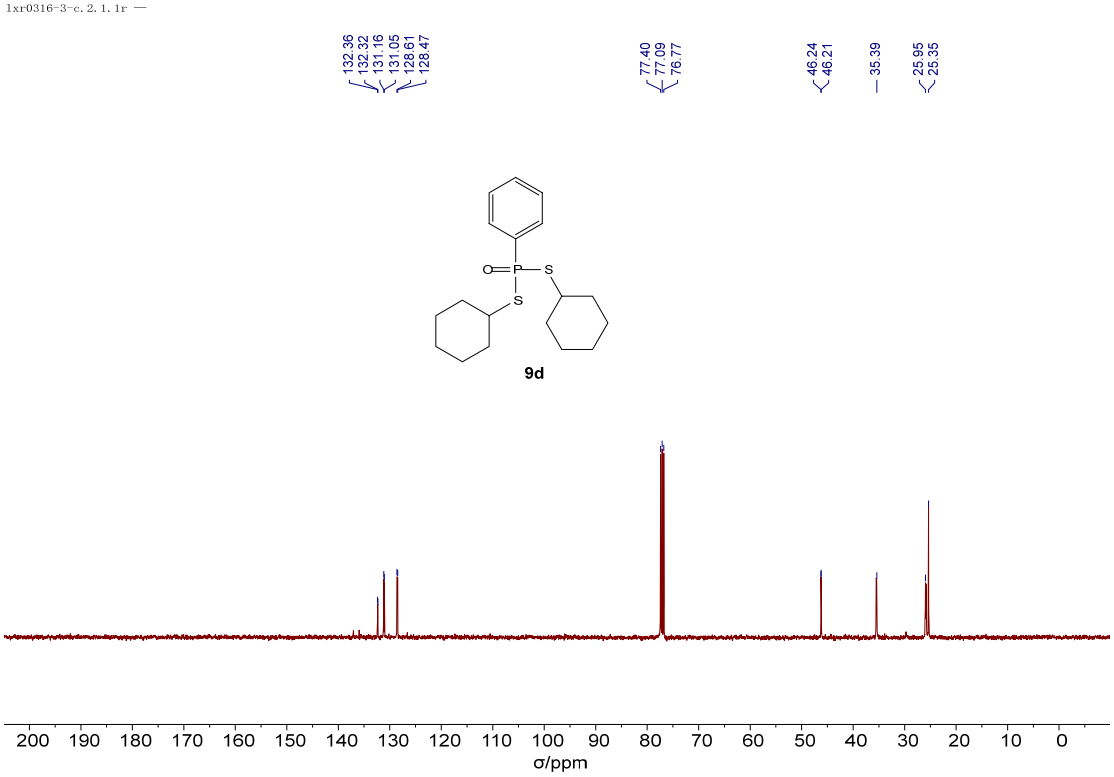
^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **9c**



^{1}H NMR-spectrum (400MHz，$CDCl_3$) of **9d**



^{13}C NMR-spectrum (101MHz，$CDCl_3$) of **9d**



^{31}P NMR-spectrum (162MHz，$CDCl_3$) of **9d**