Supporting Information

Inorganic Ligand-Supported Mo Oxide as a Hydrogen Atom Transfer Photocatalyst for Direct C(sp^2)−H Phosphorylation

Zeqi Jiang,[+a]* Shuangfei Jiang,[+a,b] Jin Gao,[a,b] Junmei Xia,[a] Hongwei Yu,[a] Lixin Ma,[a] Xi Chen,[a] Bo Chen,[a] Xinghua Zhang,[b]* Wenchao Zhu[a]*

a. State Key Laboratory of NBC Protection for Civilian, Beijing, 102205 (P. R. China)

b. School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai, 201418 (P. R. China)

[+] These authors contributed equally to this work

[*] Corresponding authors: Zeqi Jiang (zeqijiang@qq.com); Xinghua Zhang (xhzhang@sit.edu.cn); Wenchao Zhu (15811043200@139.com).

Contents

1. General considerations

Analytical thin layer chromatography was carried out using silica gel GF254, visualized under UV light (at 254 nm). ^{1}H ,^{13}C , ^{31}P and ^{19}F NMR spectra were recorded using a Bruker Avance III HD 600 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm,respectively.Analytical thin layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates , Column chromatography was performed on 200-300 mesh silica gel. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. X-ray diffraction data were collected on SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. FT-IR spectra were recorded on a Agilent 8890-Bruker INVENIO-HYPERION. UV-vis absorption spectra were recorded with a 760CRT UV-vis spectrophotometer. Mass spectral data were collected by GC–MS analysis with a hermo scientific TSQ 9000. High-resolution mass spectra were recorded on a Agilent 1200 Infinity-Agilent 6520 QTOF MS instrument in the ESI mode. Electron paramagnetic resonance spectra were recorded on a Brooke A300 electron paramagnetic resonance spectrometer. Excitation wavelength, Emission wavelength, Fluorescence lifetime and Fluorescence quenching were recorded on a FLS1000 Edinburgh Fluorescence spectrometer.

2. Preparation of catalyst $[N(C_4H_9)_4]_2[Mo_6O_{19}]$

$(NH_4)_6Mo_7O_{24}$•$4H_2O$ (5.0 g, 4 mmol) and $[N(C_4H_9)_4]Br$ (4.0 g, 12 mmol) was dissolved respectively in water (100 mL) and mixed into a beaker to obtained a muddy solution with a lot of white precipitates after stirring for half an hour. Then, the hydrochloric acid was added the into the muddy solution dropwise under stirring, and the appearance of the precipitates changed from white to yellow. It should be noted that the pH of the solution must be controlled between 3.0 and 4.0. After finishing the addition of hydrochloric acid, the yellow muddy solution continued to stir for 3 hours. Finally, the yellow precipitates were filtered out, and the resulting yellow solid was placed in the vacuum drying oven at 50 ℃ for 36 h. (Figure S1).

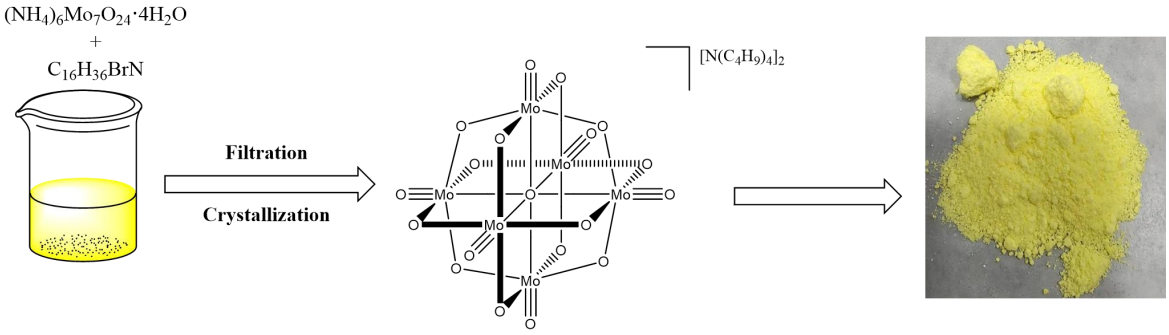


Figure S1. The process of catalyst preparation;

3. FT-IR spectra of catalyst $[N(C_4H_9)_4]_2[Mo_6O_{19}]$

The infrared absorption spectrum of $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ was obtained by KBr pellets method (Figure S2). IR: 949.50 (ν Mo=O, νs), 899.68 (ν Mo=O, νs), 652.77 (ν Mo-O-Mo, νs), 571.09 (ν M-O-Mo, w) cm^{-1}.

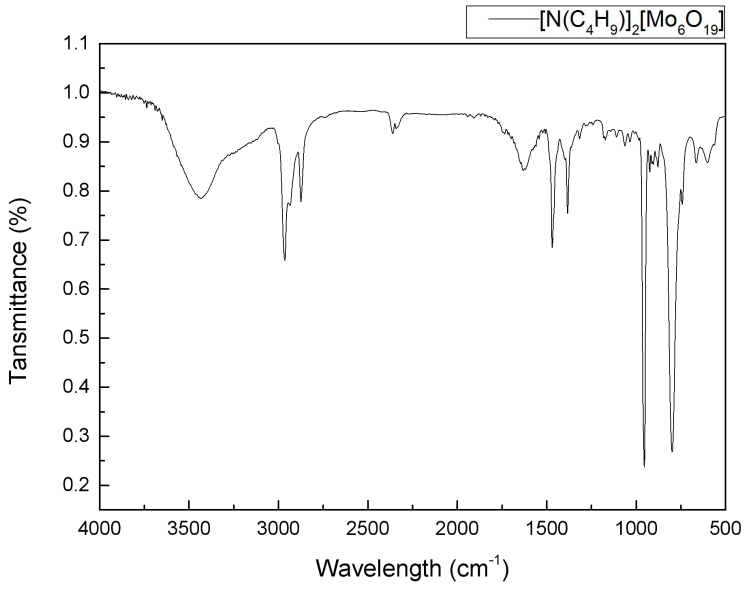


Figure S2. FT-IR spectra of catalysts $[N(C_4H_9)_4]_2[Mo_6O_{19}]$

4. XRD graph of catalyst $[N(C_4H_9)_4]_2[Mo_6O_{19}]$

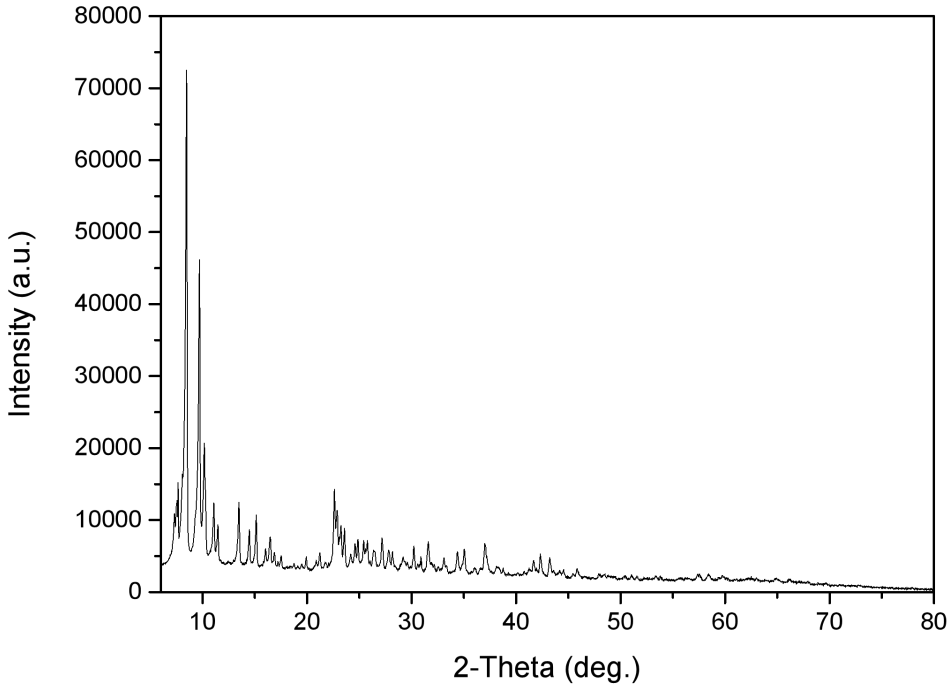


Figure S3. XRD graph of catalysts $[N(C_4H_9)_4]_2[Mo_6O_{19}]$

5. Fluorescence spectrum of catalyst

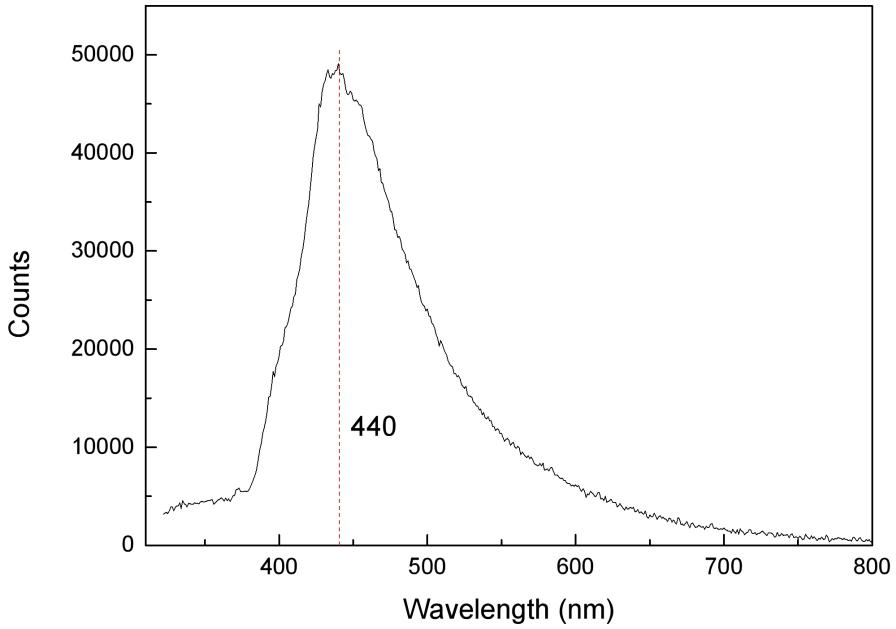


Figure S4. Emission spectrum of catalyst

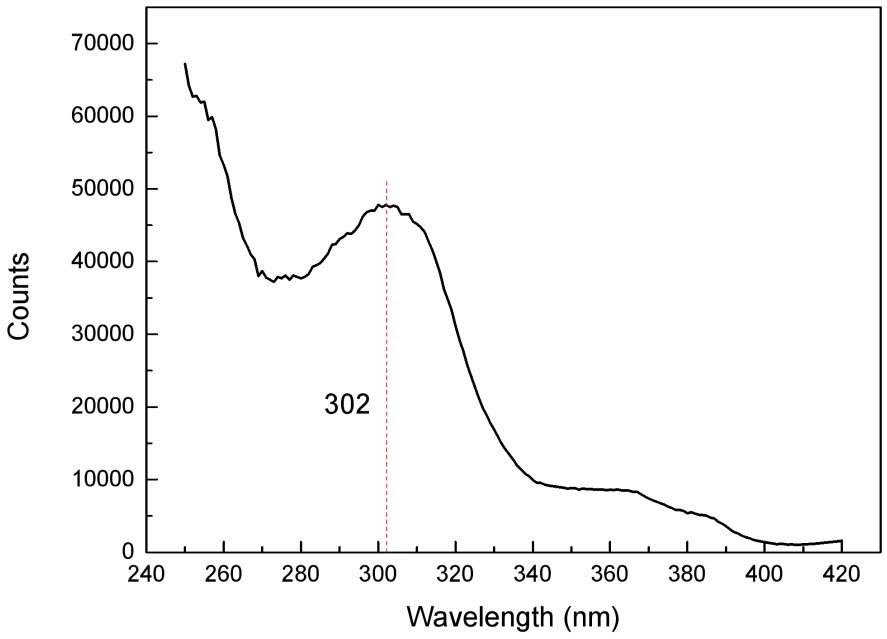
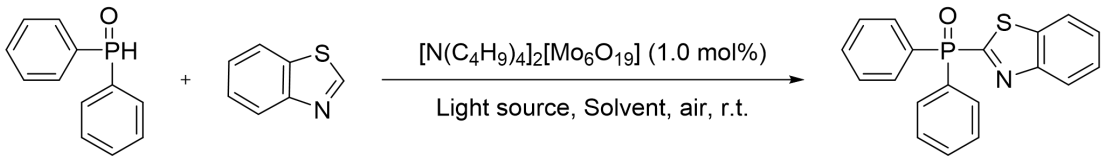


Figure S5. Excitation spectrum of catalyst

6. Experimental Procedure

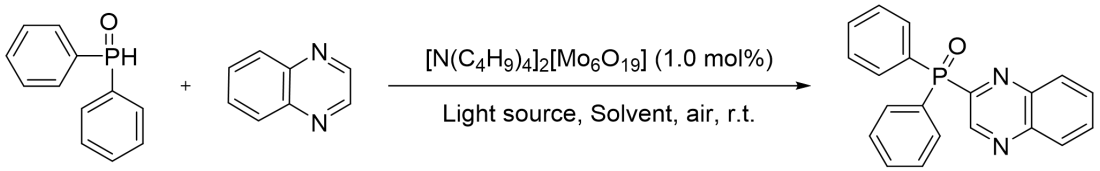
(a) Synthesis of **3a-3aa** according to the following procedure



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

Compound diphenylphosphine oxide **1a** (0.3 mmol), benzothiazole **2a** (0.1 mmol), and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) were added to a glass tube, then 1.5 mL of H_2O:$CHCl_3$=4:1 was added. The glass tube was placed in the photoreactor. Then the reaction mixture was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature in the air atmosphere for 20 h. After completion of the reaction, the mixture was extracted with ethyl acetate and then concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to give the product **3a**.

(b) Synthesis of **5a-5aa** according to the following procedure



1a **4a** **5a**

Compound diphenylphosphine oxide **1a** (0.4 mmol), benzothiazole **2a** (0.2 mmol), and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) were added to a glass tube, then 1.5 mL of H_2O:MeCN=4:1 was added. The glass tube was placed in the photoreactor. Then the reaction mixture was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature in the air atmosphere for 24 h. After completion of the reaction, the mixture was extracted with ethyl acetate and then concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to give the product **5a**.

(c) Photoreactor equipment

The photochemical reactions were carried out in a photoreactor (022-AF2-2029), which is manufactured by Shanghai Shanshi Technology Co., Ltd (Figure S6). The photoreactor was equipped with ten light-emitting elements.Different wavelengths of light can be provided, ranging from 370 nm to 600 nm, each light source can be removed and replaced independently (Figure S7). It can be connected to flowing water or a cryostatic bath, a cryostatic bath DC-2006 (1000 W, 220 V,50 Hz), which is manufactured by Shanghai Billang Instrument Manufacturing Co., Ltd.

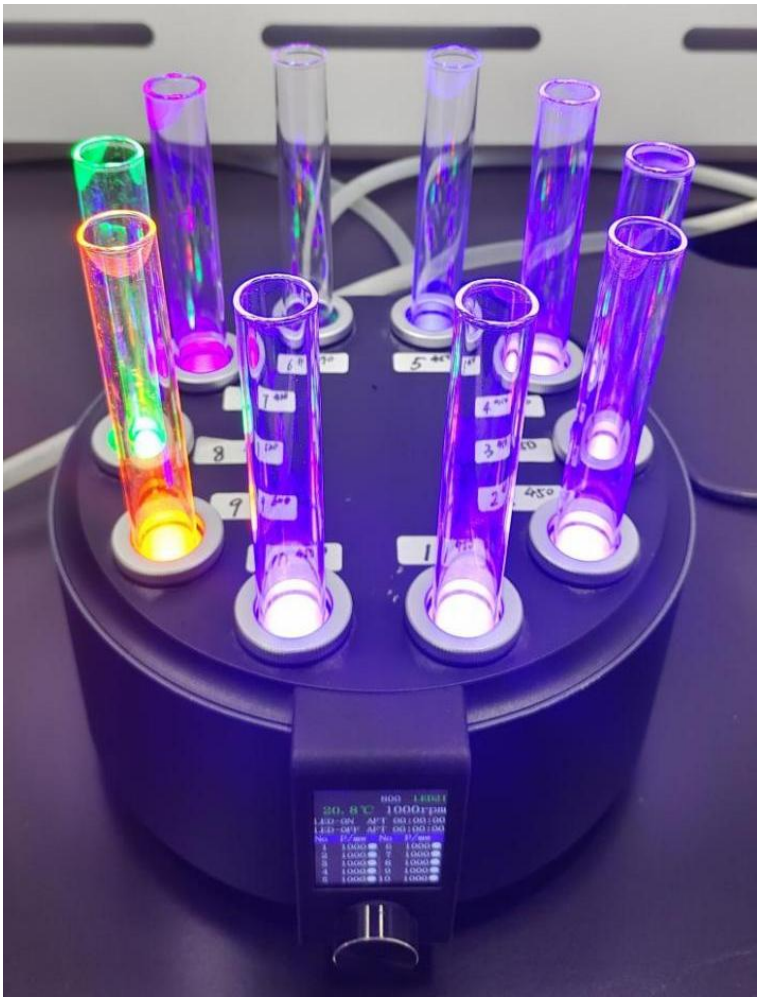


Figure S6. The setup apparatus described in this work

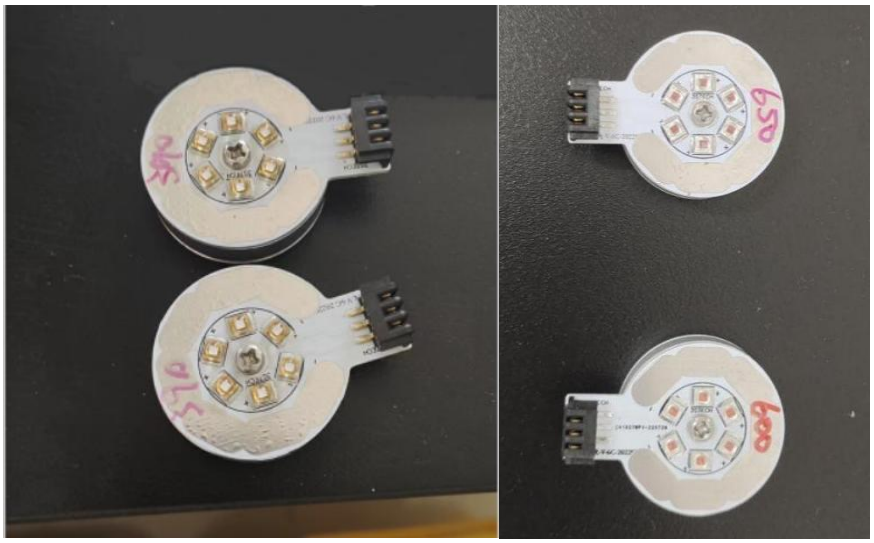
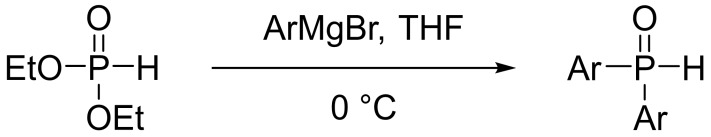
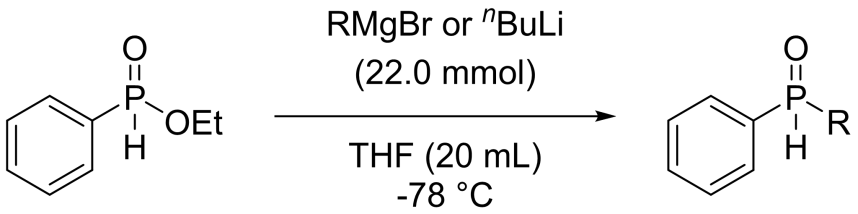


Figure S7. Independent removable replacement light source

7. Preparation of phosphine oxide



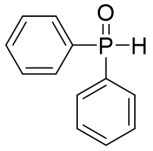
The Grignard reagent (1 mol/L in THF, 32 mmol) was added dropwise to a solution of diethyl phosphonate (10 mmol) and anhydrous THF (20 ml) at 0 ℃ under nitrogen atmosphere. Then the reaction was allowed to warm to room temperature, the resulting mixture was stirred at room temperature for 2 h. Afterwards the mixture should be cooled to 0 ℃, and quenched with aqueous NH_4Cl, extracted with EA (3 × 15 mL). The combined organic layers were washed with aqueous $NaHCO_3$ then dried over Na_2SO_4, filtered, and concentrated *in vacuo*.[1] The product was obtained after purification by column chromatography on silica gel (PE/EA = 1:1).



A flame-dried flask was charged with commercially available Grignard reagent or *n*BuLi solution (22.0 mmol) under argon atmosphere and cooled to -78 °C. The ethyl phosphinate solution was added dropwise over 30 min and the resulting mixture stirred at r.t. for 2 h. The reaction was then quenched with sat. aq. NH_4Cl solution and subsequently extracted with EA (3 × 15 mL) and the combined organic layers were washed with aqueous $NaHCO_3$ then dried over Na_2SO_4, filtered, and concentrated *in vacuo*.[2] The product was obtained after purification by column chromatography on silica gel (PE/EA = 1:1).

The P(O)－H compounds employed in the present paper were listed as follows:

Structures of the P(O) －H compounds



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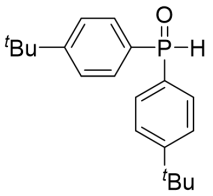

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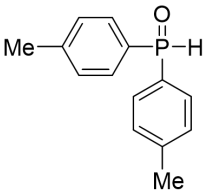

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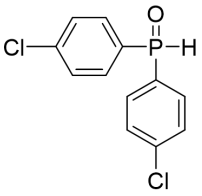

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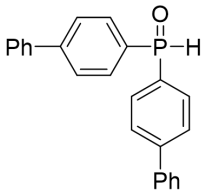

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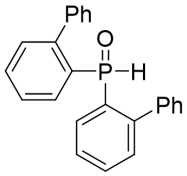

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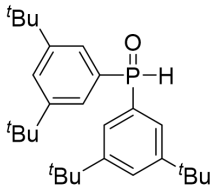

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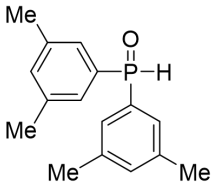

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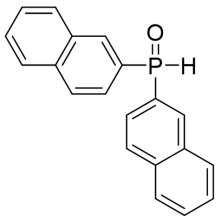

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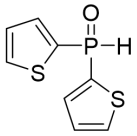

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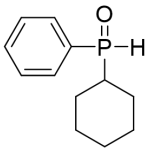

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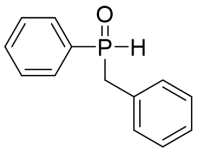

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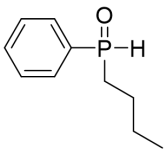

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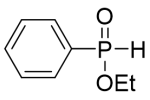

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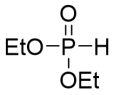

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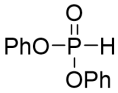

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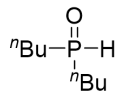

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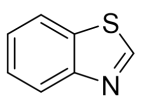
Structures of the thiazol compounds



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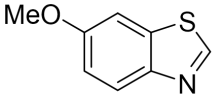

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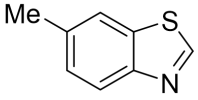

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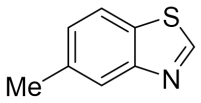

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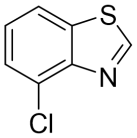

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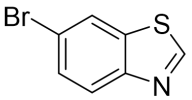

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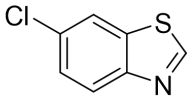

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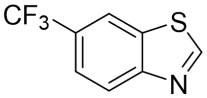

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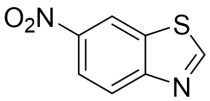

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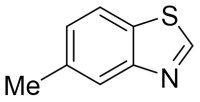

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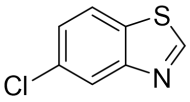

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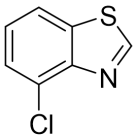

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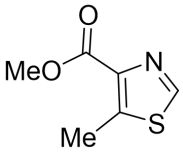

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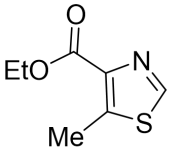

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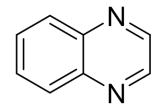
The quinoxaline compounds employed in the present paper were listed as follows:

Structures of the quinoxaline compounds



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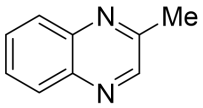

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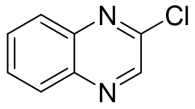

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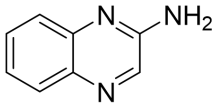

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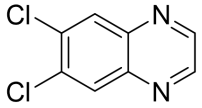

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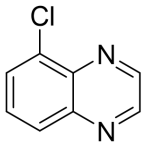

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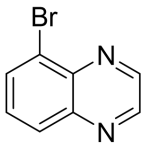
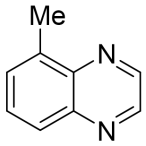
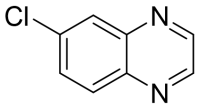


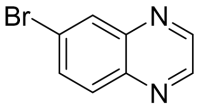
4g



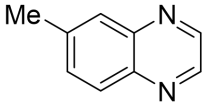
4h



4i

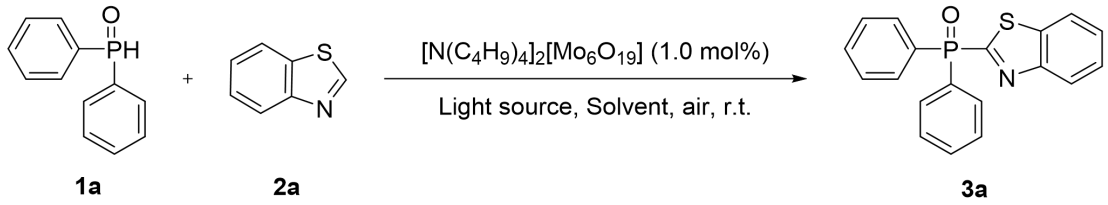


4j



4k

8. Optimization of reaction conditions



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

Table S1. Optimization of amount ratio of the substrates

Entry	Amount ratio	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	1a:2a=1:1	H_2O	20	8000	31
2	1a:2a=2:1	H_2O	20	8000	40
3	**1a:2a=3:1**	**H_2O**	**20**	8000	**52**
4	1a:2a=4:1	H_2O	20	8000	55

[a]Reaction conditions: **1a**, **2a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with 390 nm 8 W LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S2. Optimization of wattage

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	390	H_2O	20	2000	trace
2	390	H_2O	20	4000	trace
3	390	H_2O	20	6000	36
4	390	H_2O	20	8000	52
5	**390**	**H_2O**	**20**	**10000**	**64**
6	390	H_2O	20	12000	60

[a]Reaction conditions: 0.60 mmol **1a**, 0.20 mmol **2a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S3. Optimization of solvents

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	390	H_2O	20	10000	64
2	390	MeCN	20	10000	22
3	390	DCM	20	10000	36
4	390	$CHCl_3$	20	10000	69
5	390	$CHCl_3$:H_2O=1:6	20	10000	84
6	**390**	**$CHCl_3$:H_2O=1:4**	**20**	**10000**	**88**
7	390	$CHCl_3$:H_2O=1:2	20	10000	80
8	390	CH_3OH	20	10000	Trace
9	390	THF	20	10000	0

10	390	DMF	20	10000	0
11	390	Tol	20	10000	0
12	390	1,4-Dioxane	20	10000	0
13	390	MeOH:H_2O=1:4	20	10000	67
14	390	MeCN:H_2O=1:4	20	10000	73
15	390	THF:H_2O=1:4	20	10000	29
16	390	DMSO:H_2O=1:4	20	10000	Trace
17	390	1,4-Dioxane:H_2O=1:4	20	10000	Trace

[a]Reaction conditions: 0.60 mmol **1a**, 0.20 mmol **2a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S4. Optimization of wavelengths

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	370	$CHCl_3$:H_2O=1:4	20	10000	70
2	**390**	**$CHCl_3$:H_2O=1:4**	**20**	**10000**	**88**
3	420	$CHCl_3$:H_2O=1:4	20	10000	75
4	450	$CHCl_3$:H_2O=1:4	20	10000	35
5	490	$CHCl_3$:H_2O=1:4	20	10000	trace
6	520	$CHCl_3$:H_2O=1:4	20	10000	trace
7	600	$CHCl_3$:H_2O=1:4	20	10000	trace

[a]Reaction conditions: 0.60 mmol **1a**, 0.20 mmol **2a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S5. Optimization of the addition amount of the catalyst

Entry	Catalyst (mol%)	Wavelength (nm)	Solvent	Watts (mW)	Yield[b] (%)
1	0.05	390	$CHCl_3$:H_2O=1:4	10000	trace
2	0.5	390	$CHCl_3$:H_2O=1:4	10000	46
3	**1.0**	**390**	**$CHCl_3$:H_2O=1:4**	**10000**	**88**
4	2.0	390	$CHCl_3$:H_2O=1:4	10000	85
5	3.0	390	$CHCl_3$:H_2O=1:4	10000	87

[a]Reaction conditions: 0.60 mmol **1a**, 0.20 mmol **2a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S6. Optimization of reaction time

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	390	$CHCl_3$:H_2O=1:4	4	10000	21
2	390	$CHCl_3$:H_2O=1:4	8	10000	46
3	390	$CHCl_3$:H_2O=1:4	12	10000	60
4	390	$CHCl_3$:H_2O=1:4	16	10000	75
5	**390**	**$CHCl_3$:H_2O=1:4**	**20**	**10000**	**88**

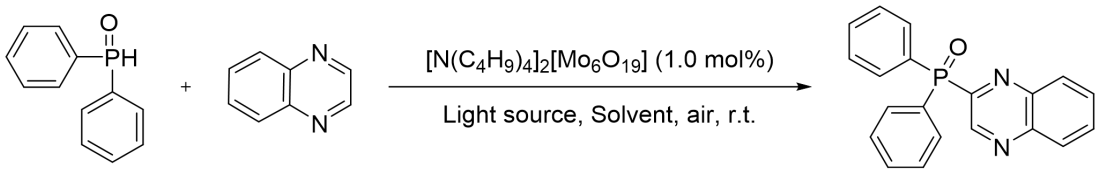
6	390	$CHCl_3$:H_2O=1:4	24	10000	85
7	390	$CHCl_3$:H_2O=1:4	28	10000	77
8	390	$CHCl_3$:H_2O=1:4	32	10000	69

[a]Reaction conditions: 0.60 mmol **1a**, 0.20 mmol **2a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air. [b]Isolated yields.

Table S7. Comparison with other types of catalysts

Entry	Catalyst variety	Solvent	Time (h)	Yield[b] (%)
1	TBADT	$CHCl_3$:H_2O=1:4	20	39
2	**$[N(C_4H_9)_4]_2[Mo_6O_{19}]$**	**$CHCl_3$:H_2O=1:4**	**20**	**88**

[a]Reaction conditions: 0.60 mmol **1a**, 0.20 mmol **2a** and catalyst (1.0 mol%) in 1.5 mL solvent were irradiated with 390 nm 10 W LED lights at room temperature under air. [b]Isolated yields.



1a **4a** **5a**

Table S8. Optimization of amount ratio of the substrates

Entry	Amount ratio	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	1a:4a=1:1	$CHCl_3$:H_2O=1:4	20	10000	66
2	**1a:4a=2:1**	**$CHCl_3$:H_2O=1:4**	**20**	**10000**	**90**
3	1a:4a=3:1	$CHCl_3$:H_2O=1:4	20	10000	91
4	1a:4a=4:1	$CHCl_3$:H_2O=1:4	20	10000	85

[a]Reaction conditions: **1a**, **4a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with 390 nm 10 W LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S9. Optimization of wattage

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	390	$CHCl_3$:H_2O=1:4	20	2000	trace
2	390	$CHCl_3$:H_2O=1:4	20	4000	trace
3	390	$CHCl_3$:H_2O=1:4	20	6000	61
4	390	$CHCl_3$:H_2O=1:4	20	8000	70
5	**390**	**$CHCl_3$:H_2O=1:4**	**20**	**10000**	**90**
6	390	$CHCl_3$:H_2O=1:4	20	12000	85

[a]Reaction conditions: 0.40 mmol **1a**, 0.20 mmol **4a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S10. Optimization of solvents

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	390	H_2O	20	10000	71
2	390	MeCN	20	10000	79
3	390	DCM	20	10000	67
4	390	$CHCl_3$	20	10000	74
5	390	CH_3OH	20	10000	Trace
6	390	THF	20	10000	0
7	390	DMF	20	10000	0
8	390	Tol	20	10000	0
9	390	1,4-Dioxane	20	10000	0
10	390	$CHCl_3$:H_2O=1:4	20	10000	90
11	**390**	**MeCN:H_2O=1:4**	**20**	**10000**	**87**
12	390	THF:H_2O=1:4	20	10000	29
13	390	DCM:H_2O=1:4	20	10000	77
14	390	DMSO:H_2O=1:4	20	10000	Trace
15	390	MeCN:H_2O=1:2	20	10000	84
16	390	MeCN:H_2O=1:6	20	10000	75

[a]Reaction conditions: 0.40 mmol **1a**, 0.20 mmol **4a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S11. Optimization of wavelengths

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	370	MeCN:H_2O=1:4	20	10000	72
2	**390**	**MeCN:H_2O=1:4**	**20**	**10000**	**87**
3	420	MeCN:H_2O=1:4	20	10000	78
4	450	MeCN:H_2O=1:4	20	10000	54
5	490	MeCN:H_2O=1:4	20	10000	trace
6	520	MeCN:H_2O=1:4	20	10000	0
7	600	MeCN:H_2O=1:4	20	10000	0

[a]Reaction conditions: 0.40 mmol **1a**, 0.20 mmol **4a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S12. Optimization of the addition amount of the catalyst

Entry	Catalyst (mol%)	Wavelength (nm)	Solvent	Watts (mW)	Yield[b] (%)
1	0.05	390	MeCN:H_2O=1:4	10000	trace
2	0.5	390	MeCN:H_2O=1:4	10000	52
3	**1.0**	**390**	**MeCN:H_2O=1:4**	**10000**	**87**
4	2.0	390	MeCN:H_2O=1:4	10000	88
5	3.0	390	MeCN:H_2O=1:4	10000	87

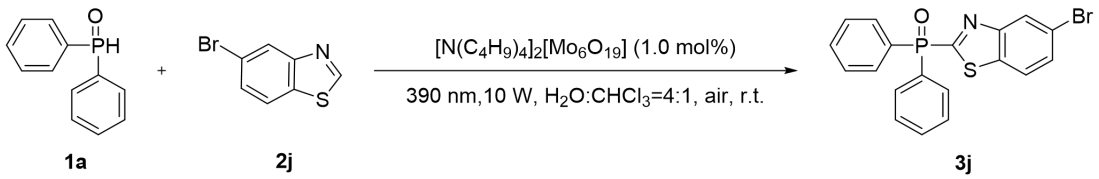
[a]Reaction conditions: 0.40 mmol **1a**, 0.20 mmol **4a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ in 1.5 mL solvent were irradiated with LED lights at room temperature under air for 20 hrs. [b]Isolated yields.

Table S13. Optimization of reaction time

Entry	Wavelength (nm)	Solvent	Time (h)	Watts (mW)	Yield[b] (%)
1	390	MeCN:H_2O=1:4	4	10000	trace
2	390	MeCN:H_2O=1:4	8	10000	44
3	390	MeCN:H_2O=1:4	12	10000	53
4	390	MeCN:H_2O=1:4	16	10000	79
5	**390**	**MeCN:H_2O=1:4**	**20**	**10000**	**87**
6	390	MeCN:H_2O=1:4	24	10000	86
7	390	MeCN:H_2O=1:4	28	10000	83

[a]Reaction conditions: 0.40 mmol **1a**, 0.20 mmol **2a** and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in 1.5 mL solvent were irradiated with LED lights at room temperature under air. [b]Isolated yields.

9. Gram-scale Reactions



1a 2j 3j

Gram-scale synthesis of **3j**:

A test tube equipped with a stirrer bar was charged with the diphenylphosphine **1a** (30 mmol, 3.0 equiv), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (**x** mol%) and 6-bromobenzo[*d*]thiazole **2j** (10 mmol, 1.0 equiv), and then $CHCl_3$:H_2O=1:4 (10 ml) was added into the test tube. Afterwards, the reaction mixture was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature in the air atmosphere for **y** hours. After the reaction was completed, the mixture was extracted with ethyl acetate, then the aqueous and organic phases were separated, the solvent was removed by evaporation under reduced pressure. Subsequently, the crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3j**, and the detailed results are listed as follows :

Table S14. TOF of gram-scale reaction

entry	x (mol%)	y (hours)	weight (g)	yield (%)	TOF (h^{-1})
1	1	48	3.35	71	0.25
2	0.5	48	3.23	68	0.47
3	0.1	72	2.90	60	1.39
4	0.01	96	2.32	56	9.72

[a]Reaction conditions: 30 mmol **1a**, 10 mmol **2j** and **x** mol% $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ in 10 mL solvent (H_2O:$CHCl_3$=4:1) were irradiated with 390 nm LED (10 W) at room temperature under air for y hrs. [b]Isolated yield.

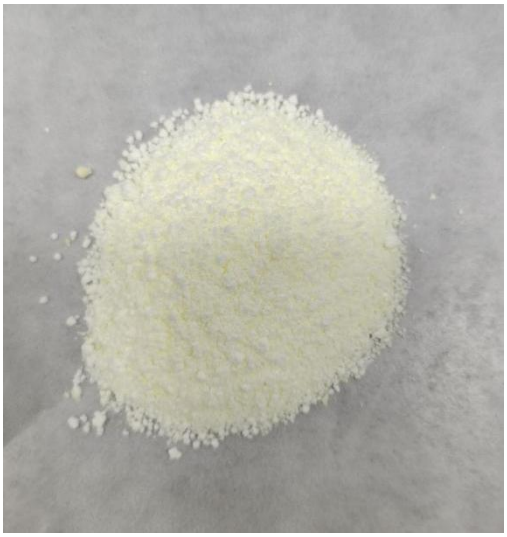
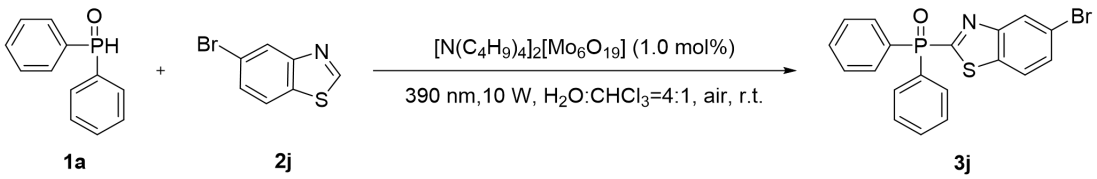


Figure S8. Obtained of product **3j** (2.32 g)

10. Experiments on stability and reusability of catalyst



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

A test tube equipped with a stirrer bar was charged with the diphenylphosphine **1a** (3 mmol, 3.0 equiv), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) and 6-bromobenzo[*d*]thiazole **2j** (1 mmol, 1.0 equiv), and then H_2O:$CHCl_3$=4:1 (5 ml) was added into the test tube. Afterwards, the reaction mixture was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature in the air atmosphere for 20 h. The catalyst was used in six consecutive reaction runs. After each reaction run, the organic phase was extracted by EtOAc, and the remaining aqueous solution and catalyst was used as the reaction system for the next run. It was demonstrated that the reaction could proceed smoothly at least six times without impairing the yields (Figure S9).

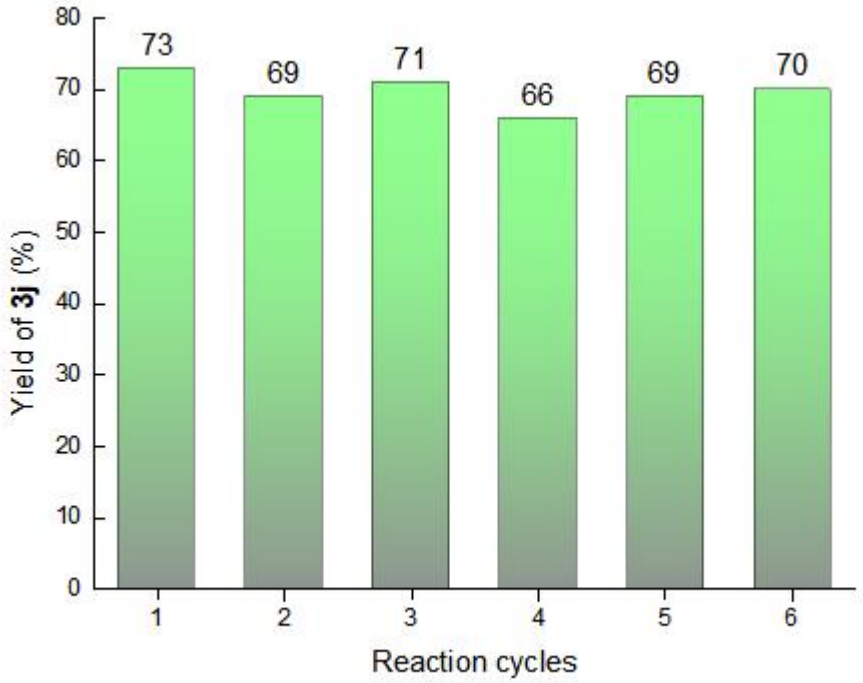


Figure S9. Experiments on reusability of catalyst

To examine the reusability of ***Cat.***, the catalyst was filtered after the addition of ether to the reaction system after each reaction run, and the recycled solid catalyst was used directly for the subsequent reaction run. After that, the structure of the recycled catalyst after six reaction cycles were further investigated by FT-IR spectroscopy (Figure. S10) and XRD graph (Figure. S11).

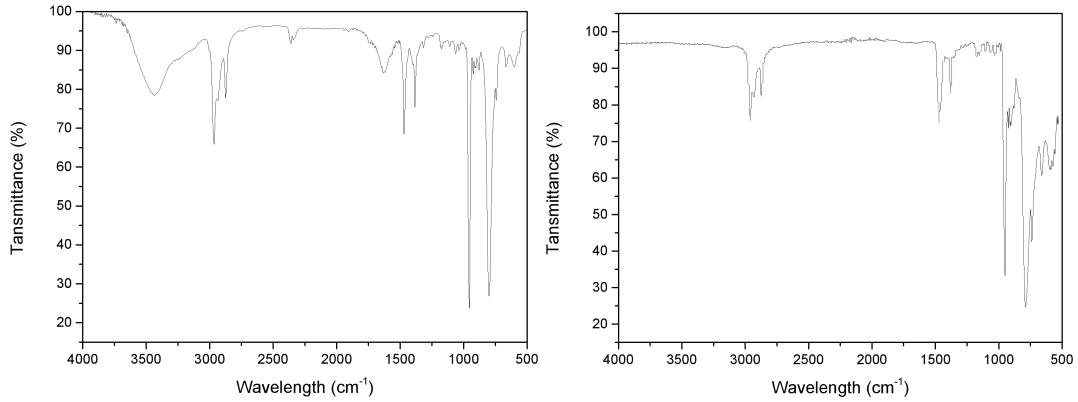


Figure S10. The FT-IR of fresh catalyst (left) and the sixth cycling catalyst (right)

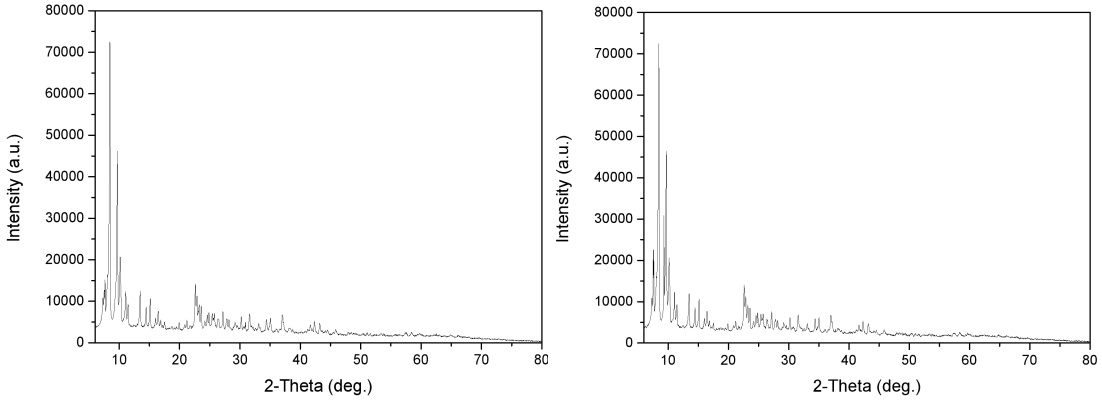
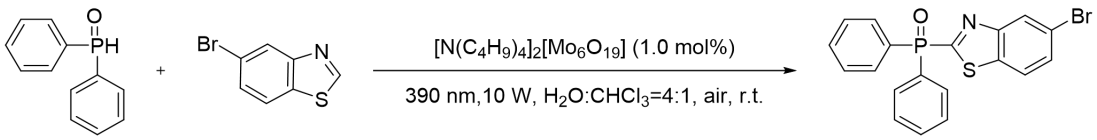


Figure S11. The XRD spectrum of fresh catalyst (left) and the sixth cycling catalyst (right)

11. Reaction under sunlight irradiation



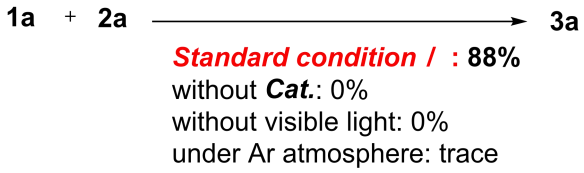
1a **2j** **3j**

A test tube equipped with a stirrer bar was charged with the diphenylphosphine **1a** (3 mmol, 3.0 equiv), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) and 6-bromobenzo[*d*]thiazole **2j** (1 mmol, 1.0 equiv), and then add H_2O:$CHCl_3$=4:1 (5 ml) into the large test tube. Place large tubes on a magnetic stirrer then put this device in sunlight and react for 8 h (9:00 a.m.–17:00 p.m.), 16 h (two consecutive days). After the reaction was complete, the mixture was extracted with ethyl acetate, then the aqueous and organic phases were separated, the solvent was removed by evaporation under reduced pressure. Subsequently, the crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3j**. The experimental picture is shown below (Figure S12).

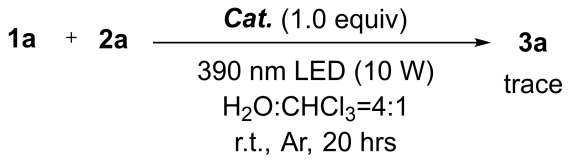
Figure S12. The reaction under sunlight irradiation

12. Experiments on mechanisms

(a) Control experiments

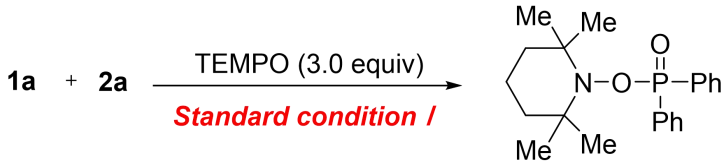


A solution of diphenylphosphine oxide **1a** (0.60 mmol), benzothiazol **2a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%), and TEMPO (0.60 mmol) in H_2O:$CHCl_3$=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. When there was a lack of oxygen, visible light, ***Cat.*** the reaction cannot proceed normally.



A solution of diphenylphosphine oxide **1a** (0.60 mmol), benzothiazol **2a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (0.20 mmol), and TEMPO (0.60 mmol) in H_2O:$CHCl_3$=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature under Ar for 20 h.

(b) Radical trapping experiments



4

HRMS: m/z $(M+H)^+$

Calc: 358.1930, Found: 358.1925

A solution of diphenylphosphine oxide **1a** (0.60 mmol), benzothiazol **2a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%), and TEMPO (0.60 mmol) in H_2O:$CHCl_3$=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. In the radical trapping experiments, a coupling product of phosphoryl radical and TEMPO was detected by HRMS.

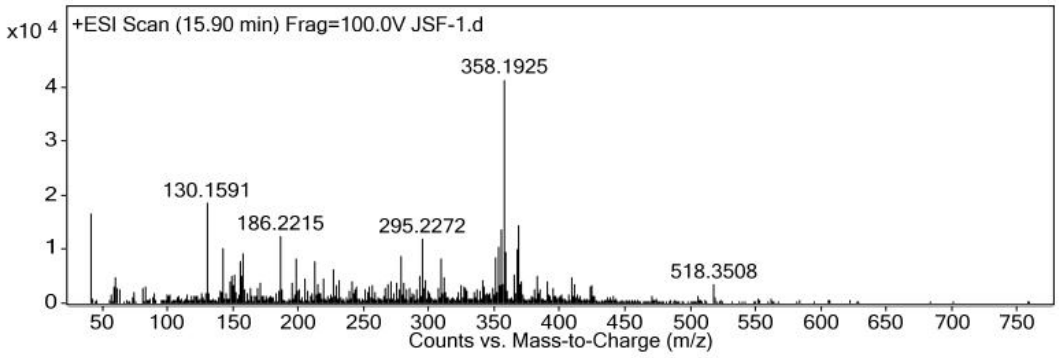
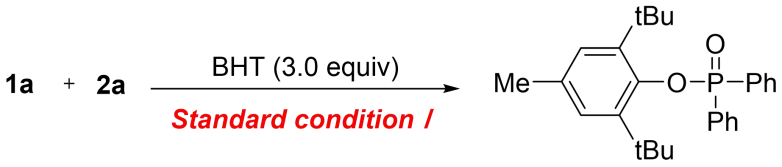


Figure S13. High resolution mass spectrometry of compound **4**



5

HRMS: m/z $(M+H)^+$

Calc: 421.2291, Found: 421.2299

A solution of diphenylphosphine oxide **1a** (0.60 mmol), benzothiazol **2a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%), and BHT (0.60 mmol) in H_2O:$CHCl_3$=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. In the radical trapping experiments, a coupling product of phosphoryl radical and BHT was detected by HRMS.

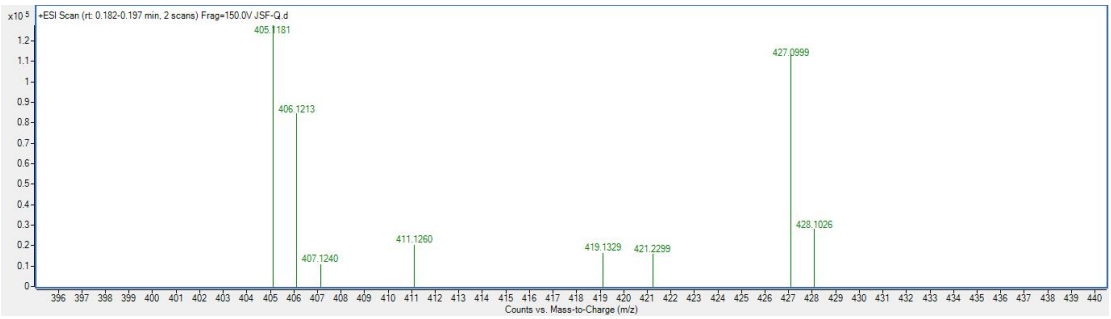
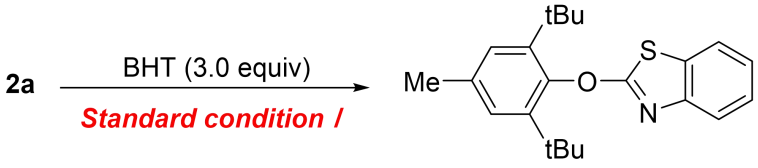


Figure S14. High resolution mass spectrometry of compound **5**



6

HRMS: m/z $(M+H)^+$

Calc: 354.1886, Found: 354.1887

A solution of benzothiazol **2a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%), and

BHT (0.60 mmol) in H_2O:$CHCl_3$=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. In the radical trapping experiments, a coupling product of benzothiazol radical and BHT was detected by HRMS.

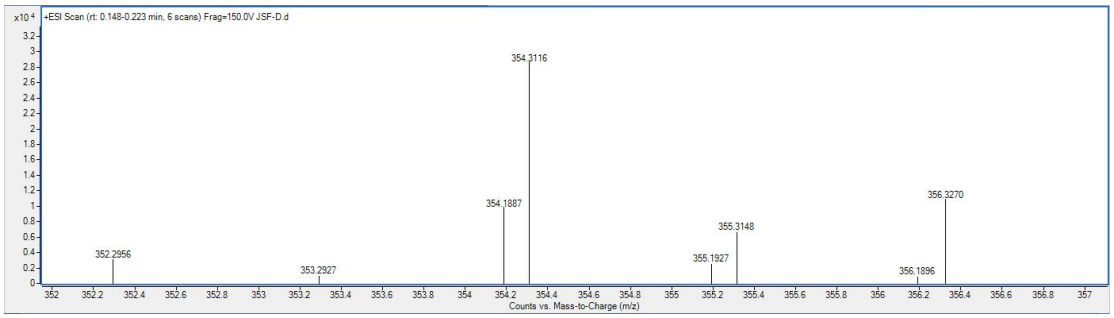


Figure S15. High resolution mass spectrometry of compound **6**

7

HRMS: m/z $(M+H)^+$

Calc: 349.2274, Found: 349.2271

A solution of diphenylphosphine oxide **1a** (0.40 mmol), benzothiazol **4a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%), and BHT (0.60 mmol) in H_2O:MeCN=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. In the radical trapping experiments, a coupling product of quinoxaline radical and BHT was detected by HRMS.

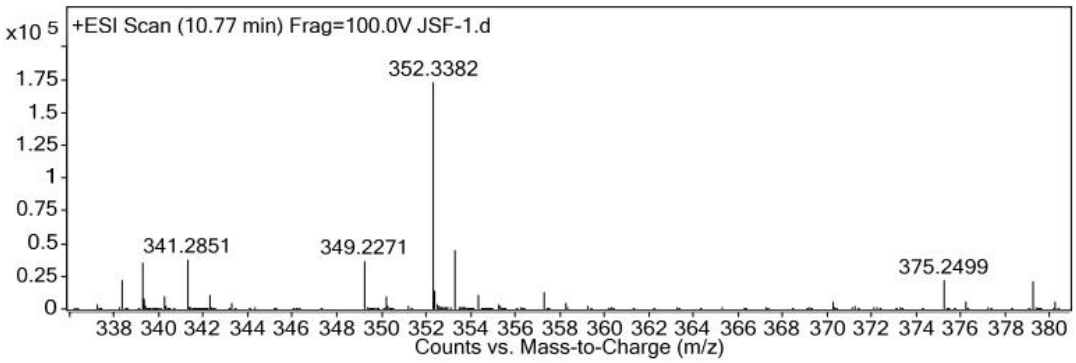
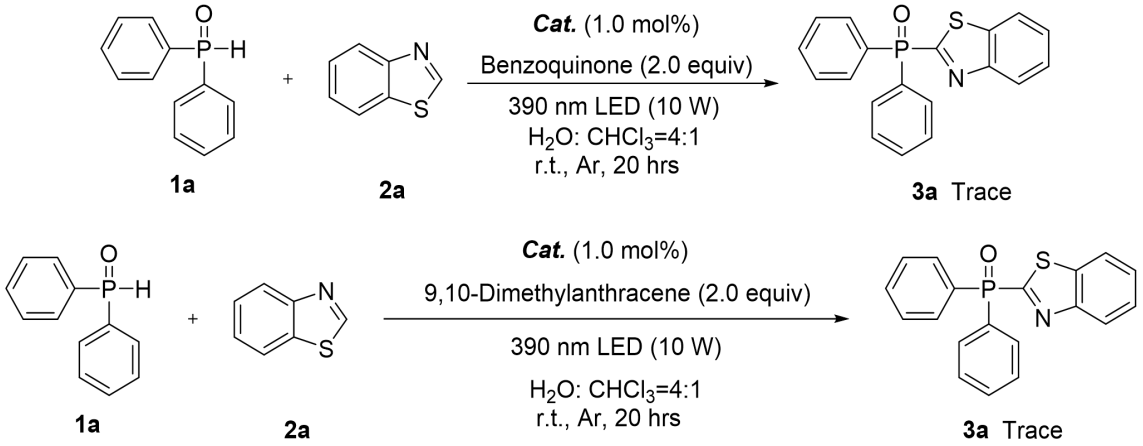


Figure S16. High resolution mass spectrometry of compound **6**

(b) Experiments demonstrating the role of O_2



A solution of diphenylphosphine oxide **1a** (0.60 mmol), benzothiazol **4a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%), and Benzoquinone (0.40 mmol, 2.0 equiv) in H_2O:$CHCl_3$=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. Trace of **3a** was observed by GC-MS.

A solution of diphenylphosphine oxide **1a** (0.60 mmol), benzothiazol **4a** (0.20 mmol), $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%), and 9,10-Dimethylanthracene (0.40 mmol, 2.0 equiv) in H_2O:$CHCl_3$=4:1 (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. Trace of **3a** was observed by GC-MS.

(c)EPR detection of ROS

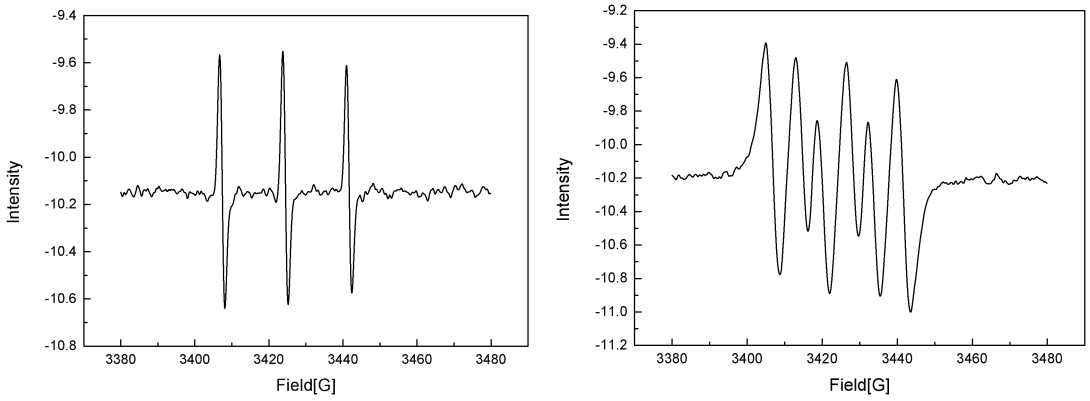


Figure S17. The electron paramagnetic resonance (EPR) spectra

Diphenylphosphine oxide **1a** (0.60 mmol) and benzothiazole **4a** (0.20 mmol), and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) was added to tube equipped with a stir bar, H_2O:$CHCl_3$=4:1 (1.5 mL) was injected in the reaction tube. The reaction mixture was allowed to stir at room temperature under 10 W LED light for 2 h, followed by the addition of 12 μL DMPO and 15 mg TEMP stir at room temperature under 10 W LED light for 10 min. Then, this reaction was taken out by capillary and was analyzed by EPR at room temperature. This result was shown in Figure S17.

(d) Stern-Volmer fluorescence quenching experiments

Stern-Volmer experiments for all the components of the reaction mixture were carried out to monitor the emission intensity of solutions of $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (0.2 mM) containing variable amounts of the quencher in $CHCl_3$. The emmision intensity at 440 nm was collected with excited wavelength of 302 nm in $CHCl_3$ using a Fluorescence spectrometer FLS1000 Edinburgh. The emission intensity of the sample was collected and plots were constructed according to the Stern-Volmer equation $I_0/I = 1 + Kqt_0[Q]$.

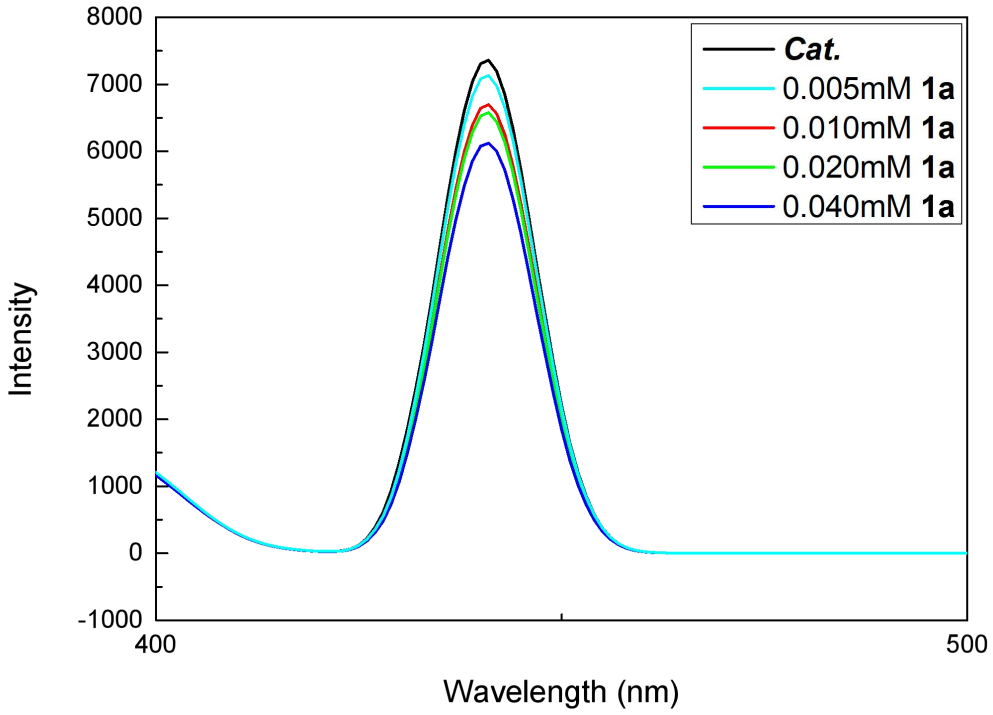


Figure S18. $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ emission quenching with **1a**.

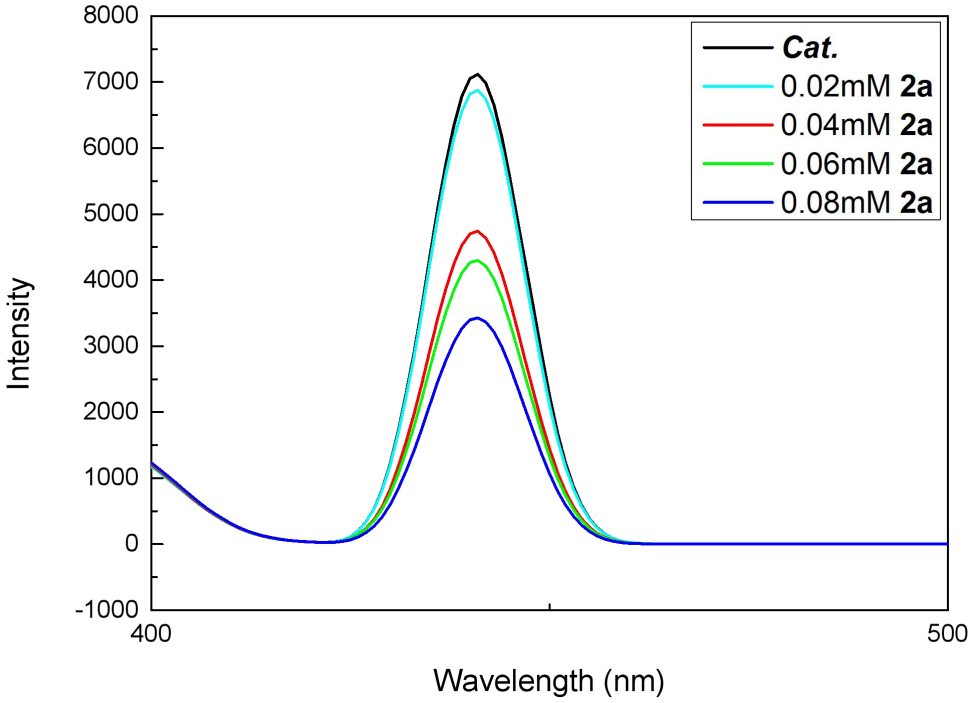


Figure S19. $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ emission quenching with **2a**.

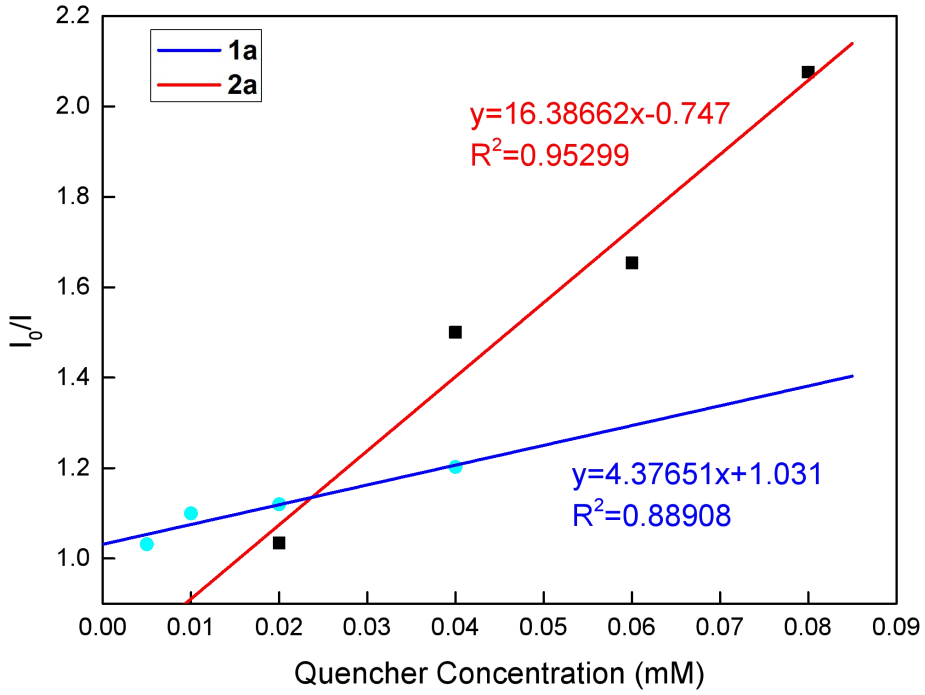


Figure S20. Stern-Volmer quenching studies

(e) Verification of H_2O_2 generation

A solution of diphenylphosphine oxide **1a** (0.60 mmol), benzothiazole **4a** (0.20

mmol), and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in $CHCl_3$ (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 20 h. And then add the starch-KI solution into the reaction solution.

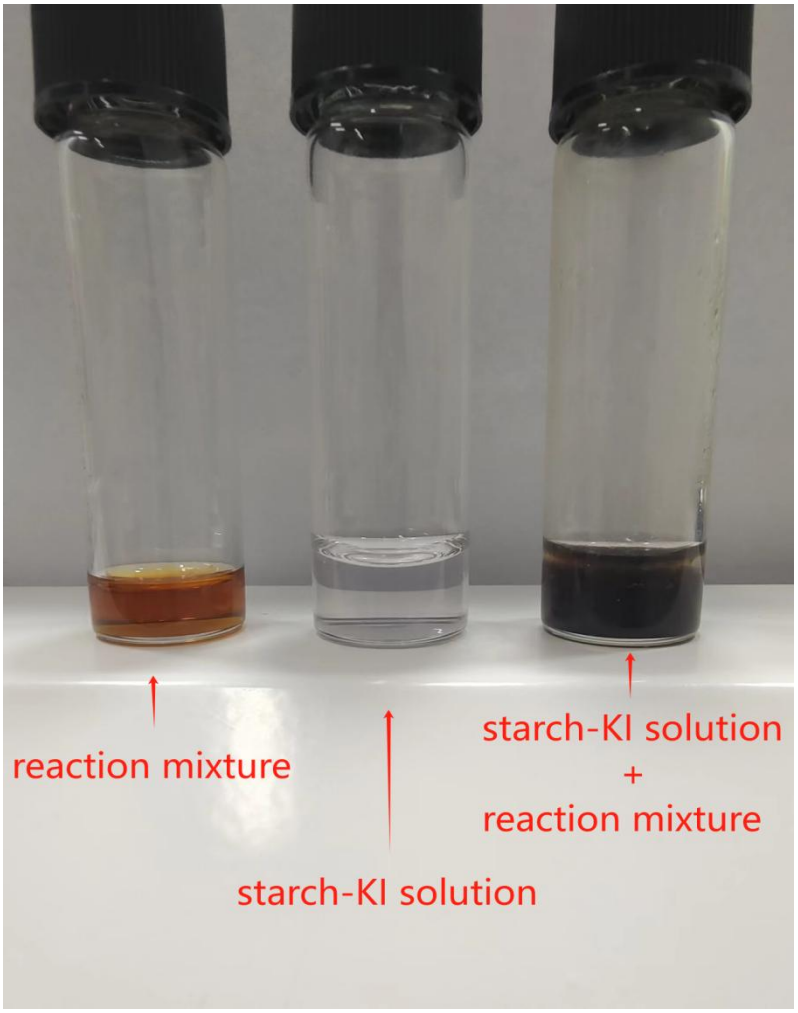


Figure S21. Verification of H_2O_2 generation

(f) Verification of intermediate ***TS2***

A solution of diphenylphosphine oxide **1a** (0.60 mmol), and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0 mol%) in $CHCl_3$ (1.5 mL) was stirred under the irradiation of visible light (390 nm, 10 W) at room temperature for 8 h. A coupling product ***TS2*** of diphenylphosphine oxide and ***Cat.*** was detected by HRMS.

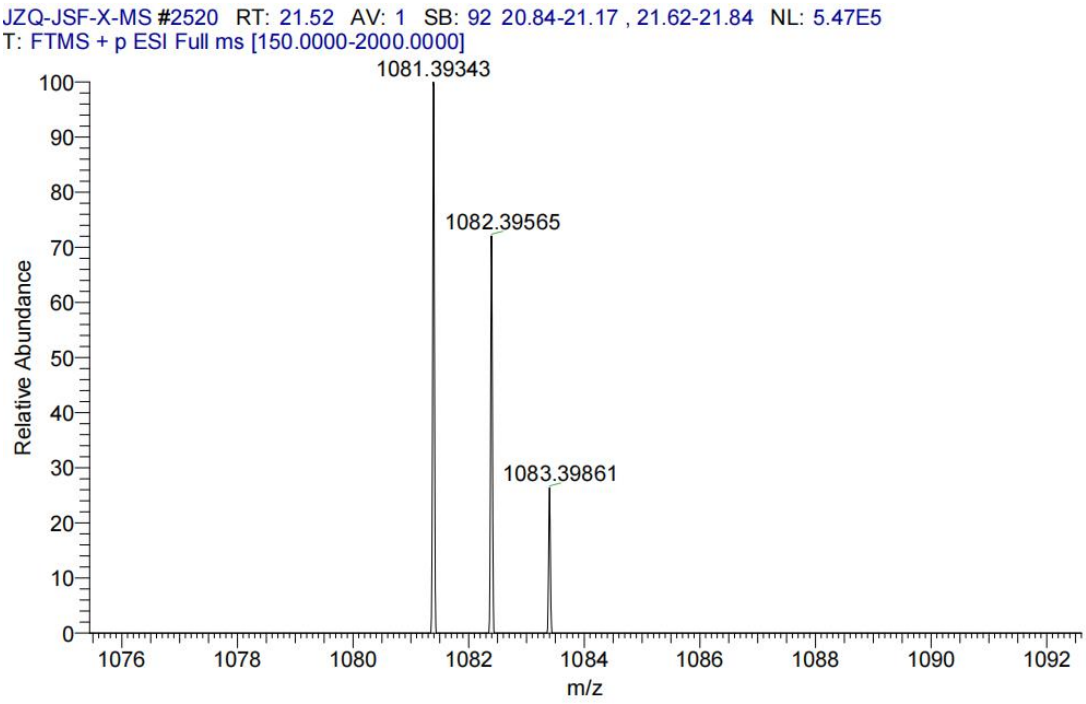


Figure S22. High resolution mass spectrometry of compound ***TS2***

(g) Verification of coupling product of phosphoryl radical and BHT

Diphenylphosphine oxide **1a** (0.60 mmol), benzothiazole **4a** (0.20 mmol), BHT (0.60 mmol) and $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ (1.0% mmol) was added to a tube equipped with a stir bar, H_2O:$CHCl_3$=4:1 (1.5 mL) was injected in the tube. The reaction mixture was allowed to stir at room temperature under 390 nm 8 W LED light for 12 h. After completion of the reaction, the reaction mixture was analyzed by ^{31}P NMR. The results were shown in Figure S23.

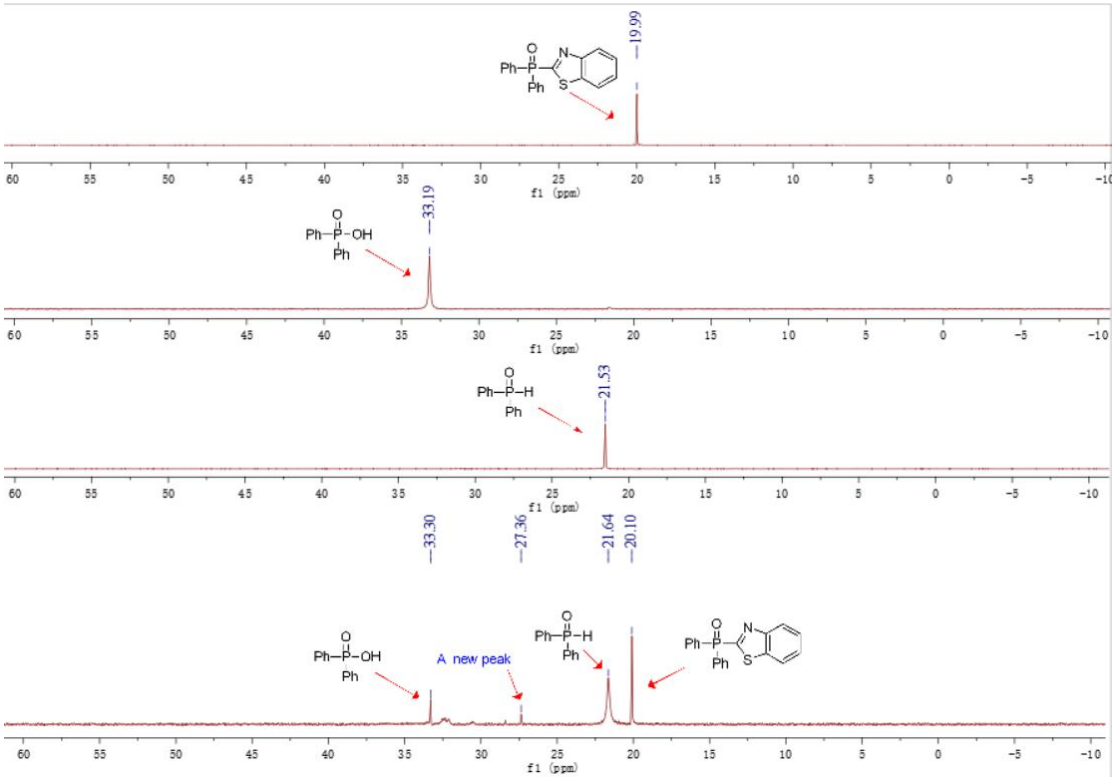
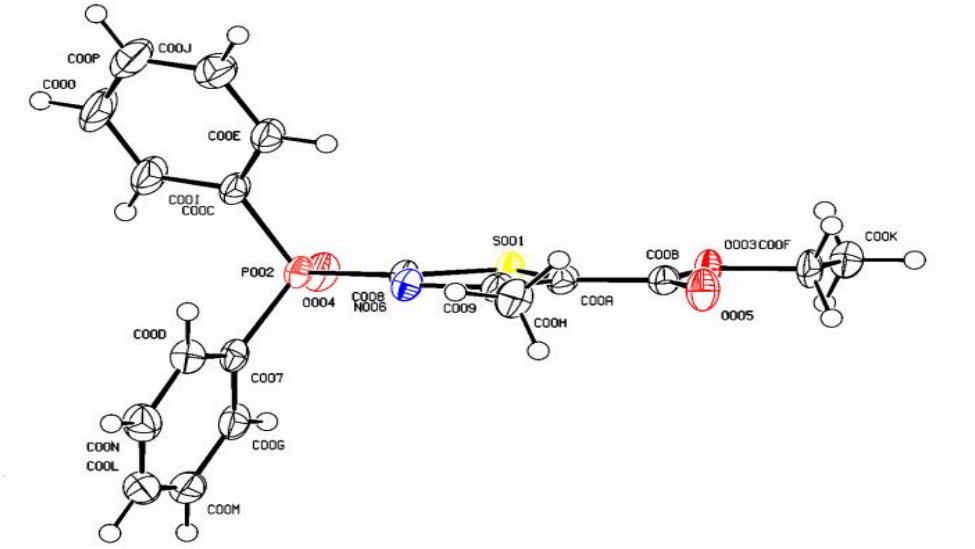


Figure S23. Verification of coupling product of phosphoryl radical and BHT

13. X-ray structure and data

Single crystals of **3o** (Figure S24) were grown by slow evaporation of its EtOAc/PE solution. Single crystal X-ray diffraction data were collected on SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 293 K during data collection. Using Olex2, the structure was solved with the Olex2. Solve structure solution program using Charge Flipping and refined with the Olex2. Refine refinement package using Least Squares minimization. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (**CCDC** 2301193).



Bond precision: C-C = 0.0027 A Wavelength=1.54178

Cell: a=17.3863(7) b=8.7024(3) c=12.2510(5)
alpha=90 beta=102.256(2) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	1811.36(12)	1811.36(12)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H18 N O3 P S	C19 H18 N O3 P S
Sum formula	C19 H18 N O3 P S	C19 H18 N O3 P S
Mr	371.37	371.37
Dx,g cm-3	1.362	1.362
Z	4	4
Mu (mm-1)	2.574	2.574
F000	776.0	776.0
F000'	780.52	
h,k,lmax	21,10,14	21,10,14
Nref	3450	3426
Tmin,Tmax		0.616,0.753
Tmin'		

Correction method= # Reported T Limits: Tmin=0.616 Tmax=0.753
AbsCorr = NONE

Data completeness= 0.993 Theta(max)= 70.122

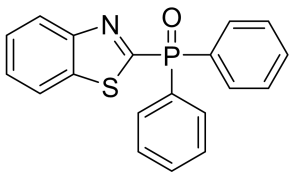
R(reflections)= 0.0370(2988) wR2(reflections)= 0.1023(3426)

S = 1.060 Npar= 228

Figure S24. X-ray structure and data of **3o**

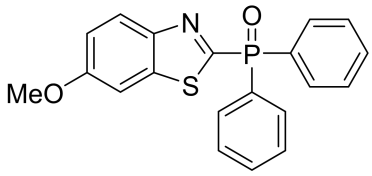
14. Physical data of the compounds

Benzo[*d*]thiazol-2-yldiphenylphosphine oxide (**3a**)



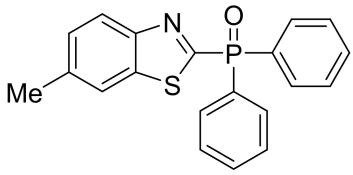
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3a**. White solid (29.5 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 8.03 – 8.00 (m, 1H), 8.00 – 7.94 (m, 4H), 7.59 – 7.53 (m, 3H), 7.52 – 7.47 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.21 (s), 166.37 (s), 155.41 (s), 155.27 (s), 136.79 (s), 132.60 (d, *J* = 2.8 Hz), 131.92 (d, *J* = 10.3 Hz), 131.34 (s), 130.61 (s), 128.62 (d, *J* = 12.9 Hz), 126.61 (d, *J* = 7.7 Hz), 124.74 (s), 122.07 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.99 (s). The data matched the reported[3].

(6-methoxybenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3b**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3b**. White solid (22.7 mg, 62%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.1 Hz, 1H), 7.97 – 7.92 (m, 4H), 7.59 – 7.54 (m, 2H), 7.52 – 7.46 (m, 4H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.14 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.69 (s), 162.83 (s), 158.83 (s), 150.16 (s), 150.02 (s), 138.60 (s), 132.53 (d, *J* = 2.8 Hz), 131.88 (d, *J* = 10.3 Hz), 131.51 (s), 130.79 (s), 128.59 (d, *J* = 12.8 Hz), 125.25 (s), 117.16 (s), 103.30 (s), 55.82 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.02 (s). The data matched the reported[3].

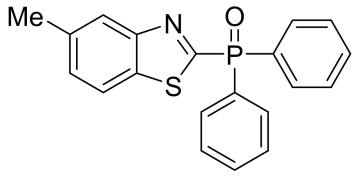
(6-methylbenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3c**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3c**. White solid (29.0 mg, 83%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 8.01 – 7.87 (m, 4H), 7.79 (s, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.52 – 7.41 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.67 (s), 153.52 (s), 137.07 (s), 132.54 (d, *J* = 2.8 Hz), 131.89 (d, *J* = 10.3 Hz), 131.44 (s), 130.72 (s), 128.77 – 128.13 (m), 124.16 (s), 121.56 (s), 76.96

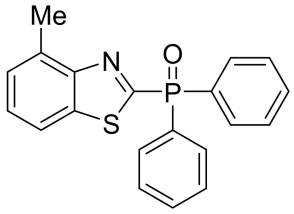
– 76.92 (m), 76.79 (s), 21.61 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.41 (s). The data matched the reported[3].

(5-methylbenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3d**)



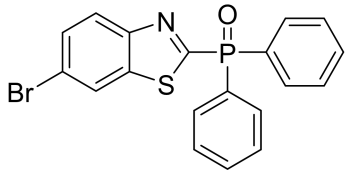
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3d**. White solid (27.6 mg, 79%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 5H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.51 – 7.45 (m, 4H), 7.34 – 7.30 (m, 1H), 2.51 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.98 (s), 166.13 (s), 155.88 (s), 155.74 (s), 136.88 (s), 133.84 (s), 132.53 (d, *J* = 2.8 Hz), 132.01 – 131.78 (m), 131.41 (s), 130.69 (s), 128.68 – 128.34 (m), 124.45 (s), 121.48 (s), 21.40 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.96 (s). The data matched the reported[4].

(4-methylbenzo[d]thiazol-2-yl)diphenylphosphine oxide (**3e**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3e**. White solid (21.3 mg, 61%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 4H), 7.84 – 7.81 (m, 1H), 7.58 – 7.53 (m, 2H), 7.51 – 7.47 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.32 (m, 1H), 2.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.33 (s), 164.48 (s), 155.01 (s), 154.87 (s), 136.65 (s), 134.82 (s), 132.44 (d, *J* = 2.9 Hz), 131.87 (d, *J* = 10.2 Hz), 131.68 (s), 130.96 (s), 128.52 (d, *J* = 12.8 Hz), 126.93 (s), 126.59 (s), 119.37 (s), 18.33 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.31 (s). The data matched the reported[3].

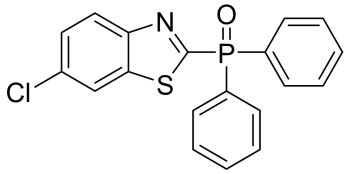
(6-bromobenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3f**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3f**. White solid (27.7 mg, 67%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.9 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.98 – 7.92 (m, 4H), 7.63 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.52 – 7.47 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.06 (s), 167.23 (s), 154.20 (s), 154.06 (s), 138.37 (s), 132.74 (d, *J*

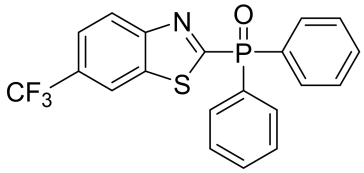
= 2.8 Hz), 131.87 (d, *J* = 10.2 Hz), 130.94 (s), 130.26 (d, *J* = 13.1 Hz), 128.82 – 128.57 (m), 125.73 (s), 124.59 (s), 120.75 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.95 (s). The data matched the reported[3].

(6-chlorobenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3g**)



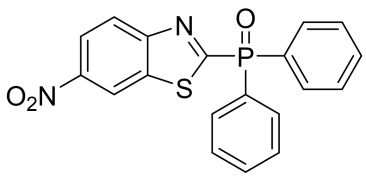
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3g**. White solid (26.6 mg, 72%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 8.01 – 7.91 (m, 5H), 7.58 (tt, *J* = 4.0, 1.3 Hz, 2H), 7.53 – 7.47 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.05 (s), 167.22 (s), 153.92 (s), 153.78 (s), 137.95 (s), 132.94 (s), 132.74 (d, *J* = 2.8 Hz), 131.88 (d, *J* = 10.3 Hz), 131.00 (s), 130.28 (s), 128.76 (t, *J* = 18.3 Hz), 127.66 (s), 125.45 (s), 121.62 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.92 (s). The data matched the reported[4].

diphenyl(6-(trifluoromethyl)benzo[*d*]thiazol-2-yl)phosphine oxide (**3h**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3h**. White solid (32.3 mg, 80%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 8.01 – 7.93 (m, 4H), 7.77 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.53 – 7.48 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.32 (s), 170.50 (s), 157.01 (s), 156.87 (s), 136.74 (s), 132.85 (d, *J* = 2.8 Hz), 131.99 – 131.77 (m), 130.69 (s), 129.96 (s), 128.67 (t, *J* = 16.2 Hz), 125.20 (s), 124.75 (s), 123.81 – 123.39 (m), 122.94 (s), 119.91 (q, *J* = 4.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.00 (s). HRMS: m/z $[M+H]^+$ calcd for $C_{20}H_{14}F_3NOPS^+$: 404.0480, found: 404.0477.

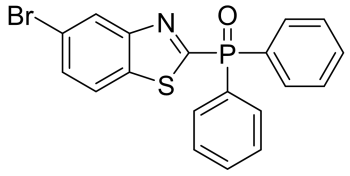
(6-nitrobenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3i**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3i**. White solid (26.6 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (d, *J* = 2.2 Hz, 1H), 8.40 (dd, *J* = 9.1, 2.3 Hz, 1H), 8.28 (d, *J* = 9.1 Hz, 1H), 7.97 (ddd, *J* = 12.8, 5.1, 3.3 Hz, 4H), 7.64 – 7.57 (m, 2H), 7.53 (ddd, *J* = 10.8,

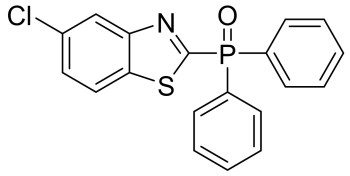
5.4, 2.5 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.60 (s), 172.81 (s), 157.46 (s), 157.33 (s), 144.84 (s), 136.04 (s), 132.04 (d, *J* = 2.9 Hz), 131.03 – 130.80 (m), 129.39 (s), 128.66 (s), 127.95 – 127.70 (m), 124.18 (s), 120.90 (s), 117.82 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.80 (s). The data matched the reported[3].

(5-bromobenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3j**)



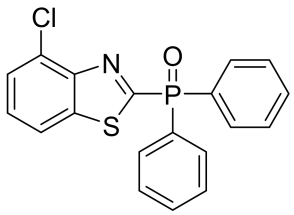
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3j**. White solid (30.1 mg, 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.8 Hz, 1H), 7.95 (ddd, *J* = 12.7, 8.2, 1.2 Hz, 4H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.50 (ddd, *J* = 10.8, 5.4, 2.5 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.41 (s), 168.59 (s), 156.47 (s), 156.33 (s), 135.54 (s), 132.75 (d, *J* = 2.9 Hz), 131.86 (d, *J* = 10.3 Hz), 130.95 (s), 130.23 (s), 129.78 (s), 128.79 – 128.55 (m), 127.49 (s), 123.12 (s), 120.38 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.82 (s). The data matched the reported[3].

(5-chlorobenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3k**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3k**. White solid (28.4 mg, 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.9 Hz, 1H), 7.99 – 7.91 (m, 5H), 7.61 – 7.55 (m, 2H), 7.52 – 7.46 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.62 (s), 168.80 (s), 156.17 (s), 156.03 (s), 135.04 (s), 132.94 – 132.68 (m), 131.88 (d, *J* = 10.2 Hz), 130.98 (s), 130.26 (s), 128.69 (d, *J* = 12.8 Hz), 127.23 (s), 124.39 (s), 122.82 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.85 (s). The data matched the reported[3].

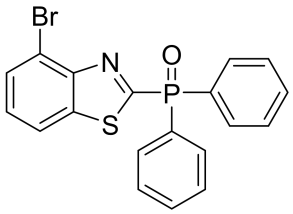
(4-chlorobenzo[d]thiazol-2-yl)diphenylphosphine oxide (**3l**)



The crude product was purified by flash column chromatography on silica gel (3:1, PE/EA) to afford the product **3l**. White solid (23.3 mg, 63%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 4H), 7.90 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.60 – 7.55 (m, 3H),

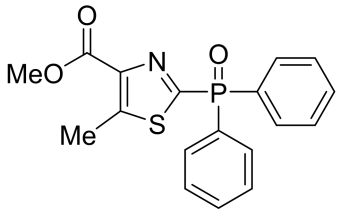
7.53 – 7.49 (m, 4H), 7.41 (t, J = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.55 (s), 152.40 (s), 138.24 (s), 132.64 (d, J = 2.8 Hz), 131.86 (d, J = 10.2 Hz), 131.19 (s), 130.46 (s), 129.66 (s), 128.72 (t, J = 14.2 Hz), 127.09 (s), 126.88 (s), 120.62 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.98 (s). The data matched the reported[3].

(4-bromobenzo[*d*]thiazol-2-yl)diphenylphosphine oxide (**3m**)



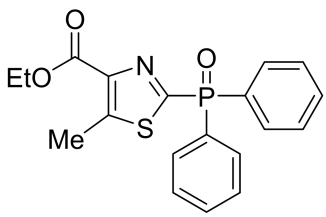
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3m**. White solid (27.2 mg, 66%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 4H), 7.95 – 7.92 (m, 1H), 7.74 (dd, J = 7.7, 0.9 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.53 – 7.48 (m, 4H), 7.33 (t, J = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.08 (s), 167.25 (s), 153.64 (s), 153.50 (s), 137.60 (s), 132.61 (d, J = 2.8 Hz), 131.87 (t, J = 11.3 Hz), 131.19 (s), 130.47 (s), 130.10 (s), 128.64 (dd, J = 12.9, 3.5 Hz), 127.38 (s), 121.25 (s), 118.36 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.72 (s). The data matched the reported[4].

methyl 2-(diphenylphosphoryl)-5-methylthiazole-4-carboxylate (**3n**)



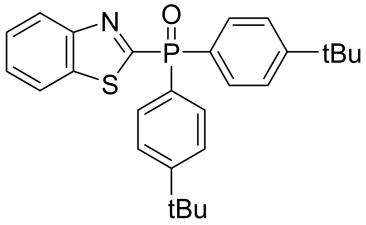
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3n**. White solid (22.5 mg, 63%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 4H), 7.57 (tt, J = 3.9, 1.3 Hz, 2H), 7.51 – 7.45 (m, 4H), 3.87 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.19 (s), 167.36 (s), 163.18 (d, J = 19.1 Hz), 162.06 (s), 132.64 (d, J = 2.8 Hz), 131.80 (d, J = 10.2 Hz), 131.11 (s), 130.39 (s), 128.63 (d, J = 12.9 Hz), 126.88 (s), 52.47 (s), 17.54 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.66 (s). The data matched the reported[3].

ethyl 2-(diphenylphosphoryl)-5-methylthiazole-4-carboxylate (**3o**)



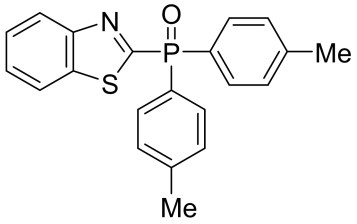
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3o**. White solid (26.4 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.83 (m, 4H), 7.59 – 7.52 (m, 2H), 7.52 – 7.43 (m, 4H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.78 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.96 (s), 167.13 (s), 162.89 (d, *J* = 19.0 Hz), 161.57 (s), 132.60 (d, *J* = 2.8 Hz), 131.89 – 131.66 (m), 131.11 (s), 130.38 (s), 128.73 – 128.48 (m), 127.36 (s), 76.79 (s), 61.61 (s), 17.51 (s), 14.15 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.66 (s). The data matched the reported[3].

benzo[*d*]thiazol-2-ylbis(4-(tert-butyl)phenyl)phosphine oxide (**3p**)



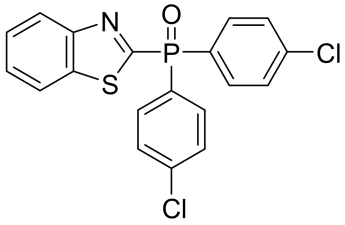
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3p**. White solid (40.2 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.93 – 7.87 (m, 4H), 7.54 – 7.48 (m, 5H), 7.48 – 7.44 (m, 1H), 1.30 (s, 18H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.99 (s), 167.16 (s), 156.01 (d, *J* = 2.8 Hz), 155.40 (s), 155.26 (s), 136.74 (s), 131.77 (d, *J* = 10.6 Hz), 128.13 (s), 127.39 (s), 126.44 (d, *J* = 14.7 Hz), 125.61 (d, *J* = 13.0 Hz), 124.61 (s), 122.00 (s), 35.00 (s), 30.99 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.09 (s). The data matched the reported[3].

benzo[*d*]thiazol-2-yldi-p-tolylphosphine oxide (**3q**)



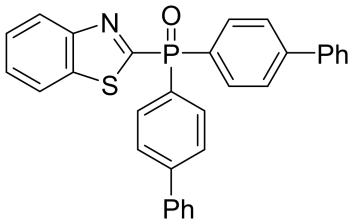
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3q**. White solid (28.0 mg, 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.83 (dd, *J* = 12.5, 8.1 Hz, 4H), 7.53 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.29 (dd, *J* = 8.0, 3.0 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.84 (s), 166.00 (s), 154.40 (s), 154.26 (s), 142.22 (d, *J* = 2.8 Hz), 135.80 (s), 131.06 – 130.83 (m), 128.36 (d, *J* = 13.2 Hz), 127.15 (s), 126.41 (s), 125.50 (d, *J* = 11.3 Hz), 123.69 (s), 121.04 (s), 20.67 (d, *J* = 0.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.81 (s). The data matched the reported[3].

benzo[*d*]thiazol-2-ylbis(4-chlorophenyl)phosphine oxide **3r**)



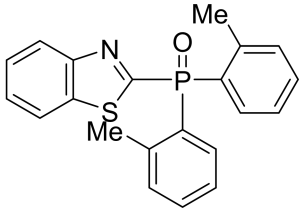
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3r**. White solid (28.1 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.96 (t, *J* = 7.4 Hz, 1H), 7.86 – 7.79 (m, 4H), 7.53 – 7.48 (m, 1H), 7.48 – 7.39 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.08 (s), 164.22 (s), 154.32 (s), 154.17 (s), 138.61 (d, *J* = 3.6 Hz), 135.72 (s), 132.23 (d, *J* = 11.1 Hz), 128.54 (s), 128.15 (d, *J* = 13.5 Hz), 127.80 (s), 125.90 (s), 123.78 (s), 121.17 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.32 (s). The data matched the reported[4].

di([1,1'-biphenyl]-4-yl)(benzo[*d*]thiazol-2-yl)phosphine oxide (**3s**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3s**. White solid (32.1 mg, 66%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 1H), 8.11 – 8.02 (m, 5H), 7.74 (dd, *J* = 8.4, 2.9 Hz, 4H), 7.62 – 7.59 (m, 4H), 7.59 – 7.55 (m, 1H), 7.53 – 7.49 (m, 1H), 7.48 – 7.44 (m, 4H), 7.42 – 7.37 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.29 (s), 166.44 (s), 155.43 (s), 155.28 (s), 145.44 (d, *J* = 2.9 Hz), 139.74 (s), 136.80 (s), 132.42 (d, *J* = 10.5 Hz), 129.80 (s), 129.07 (s), 128.90 (d, *J* = 4.4 Hz), 128.65 (s), 128.19 (d, *J* = 10.4 Hz), 127.46 – 127.01 (m), 126.65 (d, *J* = 8.7 Hz), 124.73 (s), 122.10 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.11 (s). HRMS: m/z $[M+H]^+$ calcd for $C_{31}H_{23}NOPS^+$: 488.1232, found: 488.1232.

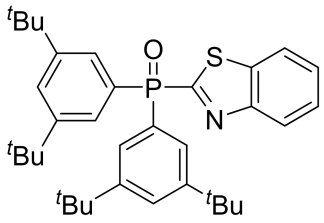
benzo[*d*]thiazol-2-yldi-*o*-tolylphosphine oxide (**3t**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3t**. White solid (28.7 mg, 79%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.57 – 7.40 (m, 6H), 7.29 (dd, *J* = 7.6, 4.7 Hz, 2H), 7.23 – 7.18 (m, 2H), 2.54 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$)

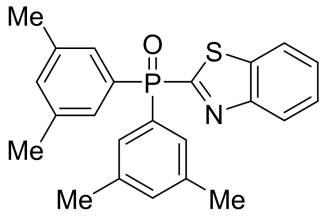
δ 168.05 (s), 167.22 (s), 155.11 (s), 154.96 (s), 143.03 (d, *J* = 9.0 Hz), 137.13 (s), 132.78 (d, *J* = 12.5 Hz), 132.55 (d, *J* = 2.7 Hz), 131.87 (d, *J* = 11.3 Hz), 129.59 (s), 128.88 (s), 126.50 (s), 125.62 (d, *J* = 13.3 Hz), 124.75 (s), 121.98 (s), 21.61 (d, *J* = 4.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.19 (s). The data matched the reported[3].

benzo[*d*]thiazol-2-ylbis(3,5-di-*tert*-butylphenyl)phosphine oxide (**3u**)



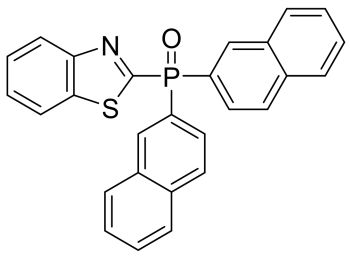
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3u**. White solid (33.5 mg, 57%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 13.3, 1.4 Hz, 4H), 7.61 (s, 2H), 7.52 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 1.30 (s, 36H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.42 (d, *J* = 20.8 Hz), 151.02 (d, *J* = 12.5 Hz), 136.77 (s), 130.37 (s), 129.66 (s), 126.71 (s), 126.46 (s), 126.43 – 126.10 (m), 124.56 (s), 122.01 (s), 35.10 (s), 31.29 (s). ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.01 (s). HRMS: m/z [M+H]+ calcd for $C_{35}H_{47}NOPS^+$: 560.3071, found: 560.3077.

benzo[*d*]thiazol-2-yldi(thiophen-2-yl)phosphine oxide (**3v**)



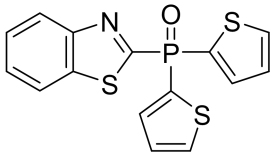
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3v**. White solid (27.8 mg, 71%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.7 Hz, 1H), 8.06 – 7.97 (m, 1H), 7.63 – 7.44 (m, 6H), 7.18 (s, 2H), 2.33 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.21 (s), 155.50 (s), 155.22 (s), 138.36 (d, *J* = 13.5 Hz), 136.83 (s), 134.43 (d, *J* = 3.0 Hz), 131.21 (s), 129.78 (s), 129.37 (d, *J* = 10.3 Hz), 126.45 (d, *J* = 5.6 Hz), 124.73 (s), 122.03 (s), 77.42 (s), 77.00 (s), 76.58 (s), 21.27 (s). ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.50 (s). The data matched the reported[3].

benzo[*d*]thiazol-2-yldi(naphthalen-2-yl)phosphine oxide (**3w**)



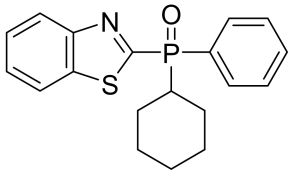
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3w**. White solid (26.1 mg, 60%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 14.7 Hz, 2H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.00 (ddd, *J* = 10.3, 8.5, 1.4 Hz, 2H), 7.95 (dd, *J* = 8.5, 3.4 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.52 (m, 3H), 7.51 (dd, *J* = 11.3, 3.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.16 (s), 166.32 (s), 155.44 (s), 155.30 (s), 136.84 (s), 135.05 (d, *J* = 2.4 Hz), 134.19 (d, *J* = 9.7 Hz), 132.38 (d, *J* = 14.2 Hz), 129.12 (s), 128.57 (t, *J* = 6.3 Hz), 128.33 (s), 127.85 (s), 127.61 (s), 127.02 (s), 126.57 (dd, *J* = 28.1, 8.3 Hz), 124.80 (s), 122.10 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.65 (s). The data matched the reported[4].

benzo[*d*]thiazol-2-yldi(thiophen-2-yl)phosphine oxide (**3x**)



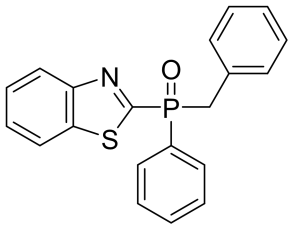
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3x**. White solid (28.4 mg, 82%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.78 (m, 4H), 7.56 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.23 (ddd, *J* = 4.7, 3.7, 2.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.73 (s), 164.76 (s), 154.09 (s), 153.94 (s), 136.70 (d, *J* = 11.2 Hz), 135.85 (s), 134.25 (d, *J* = 5.8 Hz), 131.16 (s), 130.31 (s), 127.45 (d, *J* = 15.5 Hz), 125.86 (d, *J* = 6.5 Hz), 123.88 (s), 121.14 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 6.88 (s). The data matched the reported[4].

benzo[*d*]thiazol-2-yl(cyclohexyl)(phenyl)phosphine oxide (**3y**)



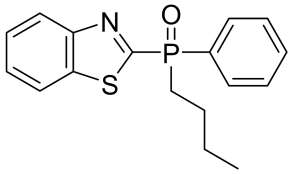
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3y**. White solid (23.2 mg, 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.96 (dddd, *J* = 29.5, 28.0, 5.6, 1.0 Hz, 3H), 7.58 – 7.31 (m, 5H), 2.56 – 2.41 (m, 1H), 1.77 – 1.56 (m, 6H), 1.50 – 1.40 (m, 1H), 1.28 – 1.14 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.67 (s), 166.93 (s), 155.16 (d, *J* = 20.0 Hz), 136.67 (s), 132.13 (d, *J* = 2.7 Hz), 131.29 (d, *J* = 9.1 Hz), 129.93 (s), 129.28 (s), 128.54 (d, *J* = 11.9 Hz), 126.50 (s), 126.30 (s), 124.39 (s), 122.10 (s), 39.18 (s), 38.69 (s), 26.05 (dd, *J* = 17.8, 14.3 Hz), 25.63 (d, *J* = 1.2 Hz), 24.56 (d, *J* = 3.6 Hz), 23.98 (d, *J* = 2.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 32.06 (s). HRMS: m/z $[M+H]^+$ calcd for $C_{19}H_{21}NOPS^+$: 342.1076, found: 342.1071.

benzo[*d*]thiazol-2-yl(benzyl)(phenyl)phosphine oxide (**3z**)



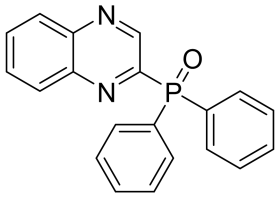
The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3z**. White solid (27.9 mg, 80%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 8.00 – 7.92 (m, 3H), 7.60 – 7.56 (m, 1H), 7.54 – 7.43 (m, 4H), 7.21 – 7.12 (m, 5H), 3.99 (t, *J* = 15.3 Hz, 1H), 3.91 – 3.84 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.16 (s), 166.37 (s), 154.84 (s), 154.70 (s), 136.88 (s), 132.45 (d, *J* = 2.8 Hz), 131.20 (d, *J* = 9.5 Hz), 130.42 (s), 130.11 (dd, *J* = 22.6, 7.1 Hz), 129.73 (s), 128.52 (dd, *J* = 13.4, 7.6 Hz), 127.01 (d, *J* = 3.3 Hz), 126.68 (s), 126.54 (s), 124.46 (s), 122.19 (s), 39.00 (s), 38.55 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.86 (s). HRMS: m/z $[M+H]^+$ calcd for $C_{20}H_{17}NOPS^+$: 350.0763, found: 350.0757.

benzo[*d*]thiazol-2-yl(butyl)(phenyl)phosphine oxide (**3aa**)



The crude product was purified by flash column chromatography on silica gel (2:1, PE/EA) to afford the product **3aa**. White solid (23.0 mg, 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 1H), 8.02 – 7.96 (m, 3H), 7.58 – 7.46 (m, 5H), 2.63 – 2.56 (m, 1H), 2.48 – 2.43 (m, 1H), 1.66 (tt, *J* = 16.8, 7.6 Hz, 2H), 1.48 – 1.41 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.96 (s), 167.18 (s), 154.96 (s), 154.83 (s), 136.77 (s), 132.35 (d, *J* = 2.8 Hz), 131.22 (s), 130.92 (d, *J* = 9.5 Hz), 130.55 (s), 128.72 (d, *J* = 12.2 Hz), 126.64 (s), 126.48 (s), 124.41 (s), 122.18 (s), 30.64 (s), 30.15 (s), 23.89 (d, *J* = 15.7 Hz), 23.12 (d, *J* = 4.3 Hz), 13.54 (s).^{31}P NMR (243 MHz, $CDCl_3$) δ 29.88 (s). HRMS: m/z $[M+H]^+$ calcd for $C_{17}H_{19}NOPS^+$: 316.0919, found: 316.0921.

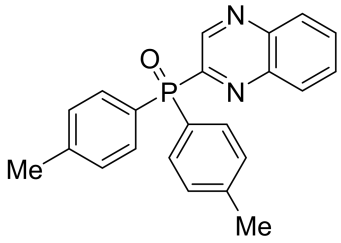
diphenyl(quinoxalin-2-yl)phosphine oxide (**5a**)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5a**. White solid (57.4 mg, 87%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.19 – 8.13 (m, 2H), 8.00 – 7.93 (m, 4H), 7.84 (dddd, *J* = 16.6, 8.2, 6.9, 1.4 Hz, 2H), 7.56 (td, *J* = 7.4, 1.3 Hz, 2H), 7.51 – 7.45 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.64 (s), 151.82 (s), 146.52 (s), 146.37 (s), 142.66 (d, *J* = 2.2

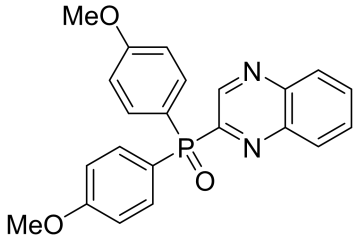
Hz), 142.19 (d, J = 17.1 Hz), 132.19 (dd, J = 23.9, 6.1 Hz), 131.93 (s), 131.77 (s), 131.08 (s), 130.70 (s), 130.19 (s), 129.65 (d, J = 1.6 Hz), 128.52 (d, J = 12.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.39 (s).

quinoxalin-2-yldi-p-tolylphosphine oxide (**5b**)



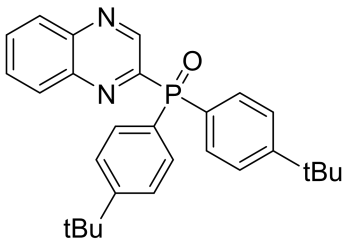
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5b**. White solid (57.9 mg, 81%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.08 (t, J = 9.0 Hz, 2H), 7.79 – 7.71 (m, 6H), 7.22 – 7.18 (m, 4H), 2.31 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.13 (s), 152.31 (s), 146.50 (s), 146.35 (s), 142.77 (d, J = 2.8 Hz), 142.56 (d, J = 2.1 Hz), 142.19 (d, J = 17.0 Hz), 132.13 (d, J = 10.0 Hz), 131.75 (s), 130.55 (s), 130.18 (s), 129.58 (d, J = 1.6 Hz), 129.24 (d, J = 12.7 Hz), 128.63 (s), 127.92 (s), 21.61 (d, J = 0.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.16 (s).

bis(4-methoxyphenyl)(quinoxalin-2-yl)phosphine oxide (**5c**)



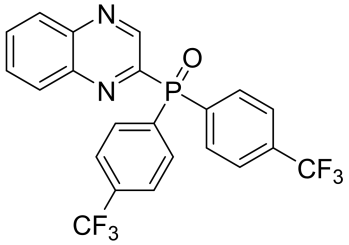
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5c**. White solid (71.8 mg, 92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.17 – 8.08 (m, 2H), 7.81 (ddd, J = 24.7, 13.0, 8.1 Hz, 6H), 6.96 (d, J = 7.2 Hz, 4H), 3.81 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.65 (d, J = 2.8 Hz), 153.34 (s), 152.51 (s), 146.42 (s), 146.27 (s), 142.49 (d, J = 2.0 Hz), 142.14 (d, J = 17.0 Hz), 133.97 (d, J = 11.0 Hz), 131.68 (s), 130.52 (s), 130.10 (s), 129.53 (d, J = 1.4 Hz), 123.08 (s), 122.34 (s), 114.05 (d, J = 13.3 Hz), 55.28 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.13 (s).

bis(4-(tert-butyl)phenyl)(quinoxalin-2-yl)phosphine oxide (**5d**)



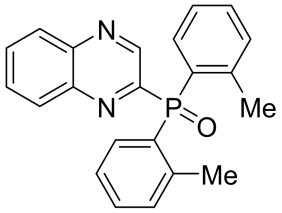
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5d**. White solid (75.1 mg, 85%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.16 (t, *J* = 7.9 Hz, 2H), 7.90 (dd, *J* = 11.7, 8.5 Hz, 4H), 7.82 (dtd, *J* = 16.5, 7.0, 1.3 Hz, 2H), 7.48 (td, *J* = 8.1, 2.8 Hz, 4H), 1.30 (s, 18H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.66 (d, *J* = 2.8 Hz), 153.22 (s), 152.40 (s), 146.34 (s), 146.20 (s), 142.29 (dd, *J* = 20.8, 9.6 Hz), 132.04 – 131.72 (m), 130.57 (s), 130.18 (s), 129.46 (d, *J* = 1.6 Hz), 128.53 (s), 127.82 (s), 125.51 (d, *J* = 12.6 Hz), 31.03 (d, *J* = 5.7 Hz).^{31}P NMR (243 MHz, $CDCl_3$) δ 20.21 (s).

quinoxalin-2-ylbis(4-(trifluoromethyl)phenyl)phosphine oxide (**5e**)



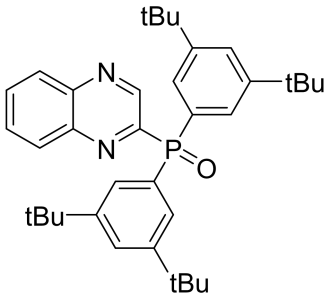
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5e**. White solid (82.9 mg, 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.67 (d, *J* = 5.4 Hz, 1H), 8.21 – 8.12 (m, 6H), 7.88 (dt, *J* = 15.1, 7.0 Hz, 2H), 7.78 – 7.73 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.82 (s), 149.98 (s), 146.31 (s), 146.16 (s), 142.98 (d, *J* = 2.2 Hz), 142.04 (d, *J* = 17.5 Hz), 135.63 (s), 134.95 (s), 134.60 (d, *J* = 2.8 Hz), 134.38 (d, *J* = 2.9 Hz), 134.16 (d, *J* = 2.9 Hz), 133.94 (d, *J* = 2.9 Hz), 132.49 (d, *J* = 9.7 Hz), 131.21 (s), 129.99 (s), 129.80 (d, *J* = 1.7 Hz), 126.08 (s), 125.68 – 125.33 (m), 124.27 (s), 122.46 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 16.76 (s).

quinoxalin-2-yldi-o-tolylphosphine oxide (**5f**)



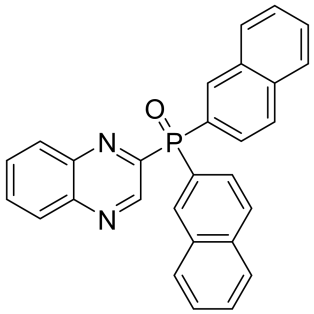
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5f**. White solid (51.5 mg, 72%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.82 – 7.77 (m, 1H), 7.48 – 7.40 (m, 4H), 7.29 (d, *J* = 3.6 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 2.49 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.95 (s), 152.13 (s), 147.07 (s), 146.92 (s), 142.94 (d, *J* = 8.5 Hz), 142.29 (d, *J* = 2.2 Hz), 141.86 (d, *J* = 17.0 Hz), 132.95 (d, *J* = 12.0 Hz), 132.27 (d, *J* = 2.5 Hz), 131.95 – 131.68 (m), 130.56 (s), 130.18 (s), 129.84 (s), 129.42 (d, *J* = 1.6 Hz), 129.15 (s), 125.46 (d, *J* = 12.8 Hz), 21.77 (d, *J* = 4.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.77 (s).

bis(3,5-di-tert-butylphenyl)(quinoxalin-2-yl)phosphine oxide (**5g**)



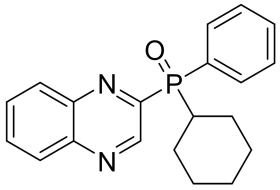
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5g**. White solid (88.6 mg, 80%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.17 – 8.10 (m, 2H), 7.98 (dd, *J* = 12.6, 1.7 Hz, 4H), 7.83 – 7.77 (m, 2H), 7.59 (s, 2H), 1.31 (s, 36H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.07 (s), 153.27 (s), 150.83 (d, *J* = 12.0 Hz), 146.33 (s), 146.19 (s), 142.28 (dd, *J* = 27.7, 9.3 Hz), 131.50 (s), 130.99 (s), 130.57 (s), 130.31 (s), 129.81 (s), 129.55 (d, *J* = 1.1 Hz), 126.20 (dd, *J* = 9.1, 6.4 Hz), 35.09 – 34.79 (m), 31.48 – 30.92 (m); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.90 (s).

di(naphthalen-2-yl)(quinoxalin-2-yl)phosphine oxide (**5h**)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5h**. White solid (61.1 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.60 (d, *J* = 14.2 Hz, 2H), 8.16 (t, *J* = 9.4 Hz, 2H), 8.00 (t, *J* = 9.2 Hz, 2H), 7.94 – 7.87 (m, 4H), 7.86 – 7.76 (m, 4H), 7.54 (dt, *J* = 14.9, 7.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.60 (s), 151.77 (s), 146.52 (s), 146.37 (s), 142.62 (d, *J* = 2.0 Hz), 142.14 (d, *J* = 17.2 Hz), 134.78 (d, *J* = 2.2 Hz), 134.21 (d, *J* = 9.2 Hz), 132.32 (d, *J* = 13.6 Hz), 131.91 (s), 130.68 (s), 130.09 (s), 129.56 (d, *J* = 1.2 Hz), 128.95 (s), 128.75 (s), 128.53 – 128.19 (m), 128.05 (s), 127.73 (s), 127.04 – 126.64 (m); ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.28 (s).

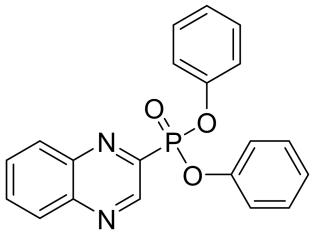
cyclohexyl(phenyl)(quinoxalin-2-yl)phosphine oxide (**5i**)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5i**. colorless oil (37.0 mg, 55%); ^{1}H NMR (600 MHz,

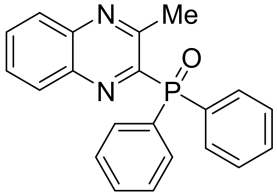
$CDCl_3$) δ 9.50 (s, 1H), 8.25 – 8.20 (m, 1H), 8.18 – 8.13 (m, 1H), 8.08 – 8.01 (m, 2H), 7.89 – 7.82 (m, 2H), 7.51 – 7.45 (m, 3H), 2.74 – 2.66 (m, 1H), 1.84 – 1.76 (m, 2H), 1.68 (dd, *J* = 18.6, 11.1 Hz, 4H), 1.32 (t, *J* = 7.1 Hz, 1H), 1.29 – 1.23 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.62 (d, *J* = 19.5 Hz), 142.68 (d, *J* = 2.2 Hz), 142.25 (d, *J* = 16.2 Hz), 131.84 (d, *J* = 2.7 Hz), 131.70 – 131.37 (m), 130.61 (d, *J* = 10.8 Hz), 130.04 (s), 129.72 (d, *J* = 1.6 Hz), 128.59 – 128.38 (m), 37.50 (s), 37.02 (s), 26.16 (dd, *J* = 16.3, 13.9 Hz), 25.72 (d, *J* = 0.9 Hz), 24.60 (d, *J* = 3.4 Hz), 23.94 (d, *J* = 2.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.60 (s).

diphenyl quinoxalin-2-ylphosphonate (**5j**)



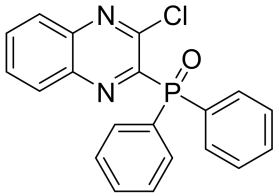
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5j**. colorless oil (50.0 mg, 69%); ^1H NMR (600 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.32 – 8.29 (m, 1H), 8.20 – 8.17 (m, 1H), 7.90 (ddt, *J* = 8.0, 7.1, 4.0 Hz, 2H), 7.34 – 7.28 (m, 8H), 7.17 (ddd, *J* = 5.6, 5.0, 2.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.03 (d, *J* = 7.9 Hz), 146.94 (s), 146.55 (s), 146.35 (s), 145.41 (s), 143.23 (d, *J* = 2.8 Hz), 142.45 (s), 142.30 (s), 132.70 (s), 131.19 (s), 130.44 (d, *J* = 1.5 Hz), 129.87 (s), 129.62 (d, *J* = 2.5 Hz), 125.62 (d, *J* = 0.7 Hz), 120.78 (d, *J* = 4.5 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 1.06 (s).

(3-methylquinoxalin-2-yl)diphenylphosphine oxide (**5l**)



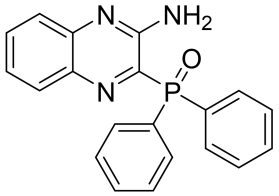
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5l**. White solid (53.7 mg, 78%); ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.77 (m, 5H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.48 (td, *J* = 7.6, 2.8 Hz, 4H), 2.99 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.69 (s), 156.54 (s), 151.90 (s), 151.08 (s), 141.57 (d, *J* = 2.1 Hz), 139.87 (d, *J* = 17.7 Hz), 132.24 – 131.77 (m), 131.23 (s), 129.92 (s), 129.38 (s), 128.40 (dd, *J* = 13.4, 7.2 Hz), 23.66 (d, *J* = 0.8 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.15 (s).

(3-chloroquinoxalin-2-yl)diphenylphosphine oxide (**5m**)



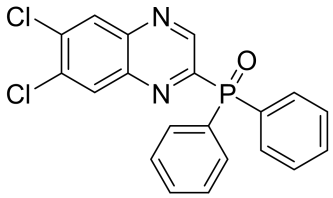
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5m**. White solid (56.1mg, 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.84 – 7.74 (m, 5H), 7.59 (td, *J* = 7.4, 1.3 Hz, 2H), 7.53 – 7.48 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.24 (s), 150.40 (s), 148.83 (s), 148.69 (s), 141.81 (d, *J* = 2.0 Hz), 139.92 (d, *J* = 15.6 Hz), 133.11 (s), 132.29 (d, *J* = 2.8 Hz), 132.19 – 131.99 (m), 130.96 (s), 130.64 (s), 130.30 – 130.04 (m), 128.46 (d, *J* = 12.6 Hz), 128.27 (d, *J* = 1.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.42 (s).

(3-aminoquinoxalin-2-yl)diphenylphosphine oxide (**5n**)



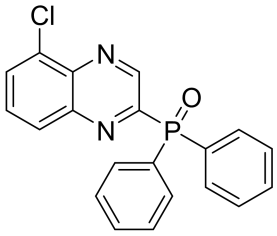
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5n**. White solid (55.9 mg, 81%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 4H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.55 (dd, *J* = 10.7, 4.1 Hz, 2H), 7.47 (td, *J* = 7.6, 3.1 Hz, 4H), 7.37 – 7.33 (m, 1H), 7.10 (ddd, *J* = 224.9, 109.7, 93.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.70 (d, *J* = 19.6 Hz), 141.81 (s), 140.76 (s), 139.93 (s), 137.13 (d, *J* = 17.1 Hz), 132.38 – 132.01 (m), 131.65 (s), 130.95 (s), 129.68 (s), 128.40 (d, *J* = 12.4 Hz), 125.62 (d, *J* = 1.2 Hz), 124.83 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.61 (s).

(6,7-dichloroquinoxalin-2-yl)diphenylphosphine oxide (**5o**)



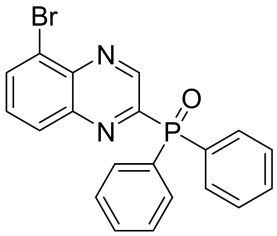
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5o**. White solid (58.1 mg, 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.27 (d, *J* = 2.9 Hz, 2H), 7.92 (dd, *J* = 11.9, 7.6 Hz, 4H), 7.59 – 7.53 (m, 2H), 7.48 (td, *J* = 7.5, 2.7 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.16 (s), 153.35 (s), 147.44 (s), 147.30 (s), 141.33 (d, *J* = 2.0 Hz), 140.68 (d, *J* = 17.3 Hz), 136.84 (s), 135.72 (s), 132.50 (d, *J* = 2.7 Hz), 132.06 (d, *J* = 9.6 Hz), 131.25 (s), 130.55 (s), 130.21 (d, *J* = 1.6 Hz), 128.64 (d, *J* = 12.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.49 (s).

(5-chloroquinoxalin-2-yl)diphenylphosphine oxide (**5p**)



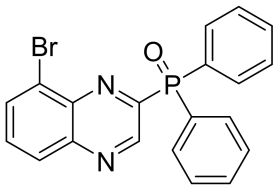
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5p**. White solid (57.5 mg, 79%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.09 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.94 (ddd, *J* = 12.1, 7.9, 1.2 Hz, 5H), 7.76 – 7.72 (m, 1H), 7.56 (td, *J* = 7.4, 1.3 Hz, 2H), 7.50 – 7.46 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.63 (s), 152.82 (s), 146.54 (s), 146.39 (s), 142.81 (d, *J* = 17.1 Hz), 139.22 (d, *J* = 2.3 Hz), 133.32 (d, *J* = 2.4 Hz), 132.19 (d, *J* = 2.8 Hz), 131.97 – 131.77 (m), 131.46 (s), 131.18 (s), 130.49 (s), 130.19 (s), 129.03 (d, *J* = 0.8 Hz), 128.36 (d, *J* = 12.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.44 (s).

(5-bromoquinoxalin-2-yl)diphenylphosphine oxide (**5q**)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5q**. White solid (55.8 mg, 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.15 (ddd, *J* = 8.6, 8.0, 4.5 Hz, 6H), 7.74 – 7.70 (m, 1H), 7.57 – 7.52 (m, 2H), 7.52 – 7.47 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.59 (s), 152.77 (s), 146.94 (s), 146.80 (s), 143.73 (d, *J* = 2.2 Hz), 139.84 (d, *J* = 16.6 Hz), 134.13 (s), 132.30 (d, *J* = 2.8 Hz), 132.11 (d, *J* = 9.4 Hz), 131.68 (s), 130.98 (s), 129.46 (d, *J* = 1.8 Hz), 128.60 (d, *J* = 12.3 Hz), 125.41 (d, *J* = 1.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 17.25 (s).

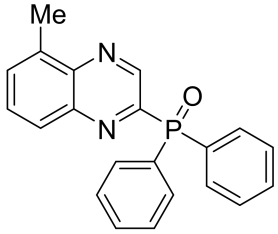
(8-bromoquinoxalin-2-yl)diphenylphosphine oxide (**5q***)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5q***. White solid (7.0 mg, 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.20 – 8.11 (m, 2H), 7.98 – 7.90 (m, 4H), 7.72 – 7.66 (m, 1H), 7.60 – 7.54 (m, 2H), 7.49 (td, *J* = 7.6, 3.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.82 (s), 153.01 (s), 147.04 (s), 146.90 (s), 143.10 (d, *J* = 17.1 Hz), 140.36 (d, *J* = 2.3 Hz), 135.29 (s), 132.44 (d, *J* = 2.8 Hz), 132.11 (d, *J* = 9.6 Hz), 131.39 (s), 130.99

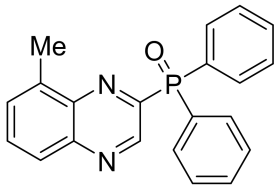
(s), 130.69 (s), 130.04 (s), 128.61 (d, J = 12.4 Hz), 124.47 (d, J = 2.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.44 (s).

(5-methylquinoxalin-2-yl)diphenylphosphine oxide (**5r**)



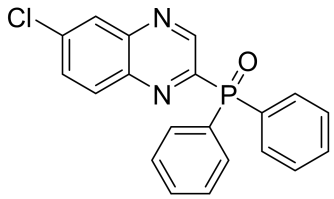
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5r**. White solid (38.1 mg, 83%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.02 – 7.97 (m, 5H), 7.77 – 7.73 (m, 1H), 7.66 (d, J = 7.0 Hz, 1H), 7.55 (td, J = 7.4, 1.3 Hz, 2H), 7.51 – 7.45 (m, 4H), 2.74 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 146.13 (s), 145.98 (s), 142.86 (d, J = 2.4 Hz), 141.30 (d, J = 16.5 Hz), 138.40 (s), 132.28 – 131.97 (m), 131.87 (s), 131.33 (s), 130.60 (s), 128.47 (t, J = 10.8 Hz), 127.43 (d, J = 1.9 Hz), 17.11 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.18 (s).

(8-methylquinoxalin-2-yl)diphenylphosphine oxide (**5r***)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5r***. White solid (19.0 mg, 83%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.00 – 7.92 (m, 5H), 7.72 – 7.67 (m, 2H), 7.57 – 7.52 (m, 2H), 7.48 (td, J = 7.6, 3.0 Hz, 4H), 2.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.96 (s), 151.13 (s), 145.33 (s), 145.18 (s), 142.37 (d, J = 17.0 Hz), 141.92 (d, J = 2.3 Hz), 138.09 (d, J = 1.6 Hz), 132.18 (dd, J = 12.1, 6.2 Hz), 131.92 (s), 131.76 (s), 131.23 (s), 130.44 (s), 128.51 (d, J = 12.3 Hz), 128.04 (s), 17.27 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.56 (s).

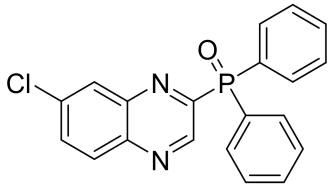
(6-chloroquinoxalin-2-yl)diphenylphosphine oxide (**5s**)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5s**. White solid (32.8 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.16 (d, J = 2.3 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.97 – 7.91 (m, 4H), 7.79 (dd, J = 9.0, 2.3 Hz, 1H), 7.56 (td, J = 7.4, 1.3 Hz, 2H), 7.52 – 7.46 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.66 (s), 152.85 (s), 146.43 (s), 146.28 (s),

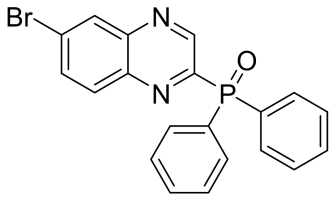
142.07 (d, *J* = 17.4 Hz), 141.00 (d, *J* = 2.3 Hz), 136.53 (s), 132.74 (s), 132.19 (d, *J* = 2.8 Hz), 131.86 (d, *J* = 9.6 Hz), 131.24 (s), 130.69 (d, *J* = 2.0 Hz), 130.55 (s), 128.67 (s), 128.37 (d, *J* = 12.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.35 (s).

(7-chloroquinoxalin-2-yl)diphenylphosphine oxide (**5s***)



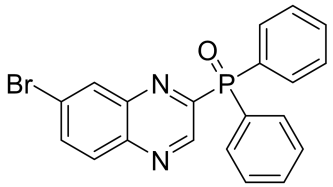
The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5s***. White solid (32.8 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.16 (d, *J* = 2.2 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.97 – 7.90 (m, 4H), 7.76 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.56 (td, *J* = 7.4, 1.2 Hz, 2H), 7.49 (td, *J* = 7.6, 3.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.93 (s), 152.11 (s), 147.37 (s), 147.22 (s), 142.92 (d, *J* = 2.2 Hz), 140.67 (d, *J* = 17.1 Hz), 138.02 (s), 132.39 (d, *J* = 2.8 Hz), 132.09 (d, *J* = 9.6 Hz), 131.91 (s), 131.42 (d, *J* = 18.8 Hz), 130.79 (s), 128.54 (dd, *J* = 11.7, 7.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.53 (s).

(6-bromoquinoxalin-2-yl)diphenylphosphine oxide (**5t**)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5t**. White solid (44.1 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.35 (d, *J* = 2.1 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.97 – 7.91 (m, 5H), 7.57 (td, *J* = 7.4, 1.2 Hz, 2H), 7.49 (td, *J* = 7.6, 3.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.85 (s), 153.03 (s), 146.78 (s), 146.64 (s), 142.55 (d, *J* = 17.3 Hz), 141.47 (d, *J* = 2.2 Hz), 135.48 (s), 132.38 (dd, *J* = 16.7, 1.8 Hz), 132.20 – 132.00 (m), 131.46 (s), 130.97 (d, *J* = 1.8 Hz), 130.76 (s), 128.61 (d, *J* = 12.4 Hz), 124.97 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.37 (s).

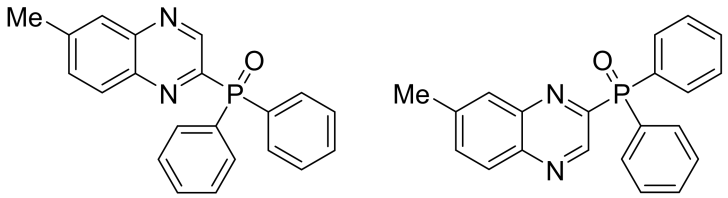
(7-bromoquinoxalin-2-yl)diphenylphosphine oxide (**5t***)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5t***. White solid (29.4 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.35 (d, *J* = 2.1 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.97 – 7.90 (m, 4H), 7.89 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.56 (td, *J* = 7.4, 1.3 Hz, 2H), 7.51 – 7.46 (m,

4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.12 (s), 152.31 (s), 147.34 (s), 147.19 (s), 143.15 (d, *J* = 2.3 Hz), 140.91 (d, *J* = 17.1 Hz), 134.46 (s), 132.42 (d, *J* = 2.8 Hz), 132.21 – 131.89 (m), 131.55 – 131.32 (m), 130.79 (s), 128.61 (d, *J* = 12.4 Hz), 126.40 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.55 (s).

(6-methylquinoxalin-2-yl)diphenylphosphine oxide (**5u**) and (7-methylquinoxalin-2 -yl)diphenylphosphine oxide (**5u***)



The crude product was purified by flash column chromatography on silica gel (1:1, PE/EA) to afford the product **5u**, **5u***. White solid (58.5 mg, 85%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.57 (t, *J* = 3.8 Hz, 1H), 8.04 (dd, *J* = 10.6, 8.8 Hz, 2H), 7.99 – 7.91 (m, 8H), 7.69 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.64 (dt, *J* = 7.9, 3.9 Hz, 1H), 7.54 (tt, *J* = 10.4, 5.2 Hz, 3H), 7.48 (td, *J* = 7.6, 2.9 Hz, 6H), 2.62 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.37 (s), 151.54 (s), 146.56 (s), 146.41 (s), 145.73 (s), 145.58 (s), 143.02 (s), 142.79 (d, *J* = 2.3 Hz), 142.29 (d, *J* = 17.2 Hz), 141.49 (s), 141.25 (d, *J* = 2.3 Hz), 140.84 (d, *J* = 17.2 Hz), 134.38 (s), 133.14 (s), 132.31 – 131.90 (m), 131.29 (d, *J* = 4.6 Hz), 129.71 (d, *J* = 0.7 Hz), 129.12 (d, *J* = 1.8 Hz), 128.86 (d, *J* = 0.8 Hz), 128.41 (dd, *J* = 27.1, 7.1 Hz), 22.09 (s), 21.83 (s); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.43 (s), 20.34 (s).

References

[1] a) J. P. Cao, Y. S. Xue, N. F. Li, J. J. Gong, R. K. Kang and Y. Xu, *J. Am. Chem. Soc.*, 2019, **141**, 19487-19497; b) D. L. Long, R. Tsunashima and L. Cronin, *Angew Chem. Int. Ed. Engl.*, 2010, **49**, 1736-1758; c) E. Derat, D. Kumar, R. Neumann and S. Shaik, *Inorg. Chem.*, 2006, **45**, 8655-8663.

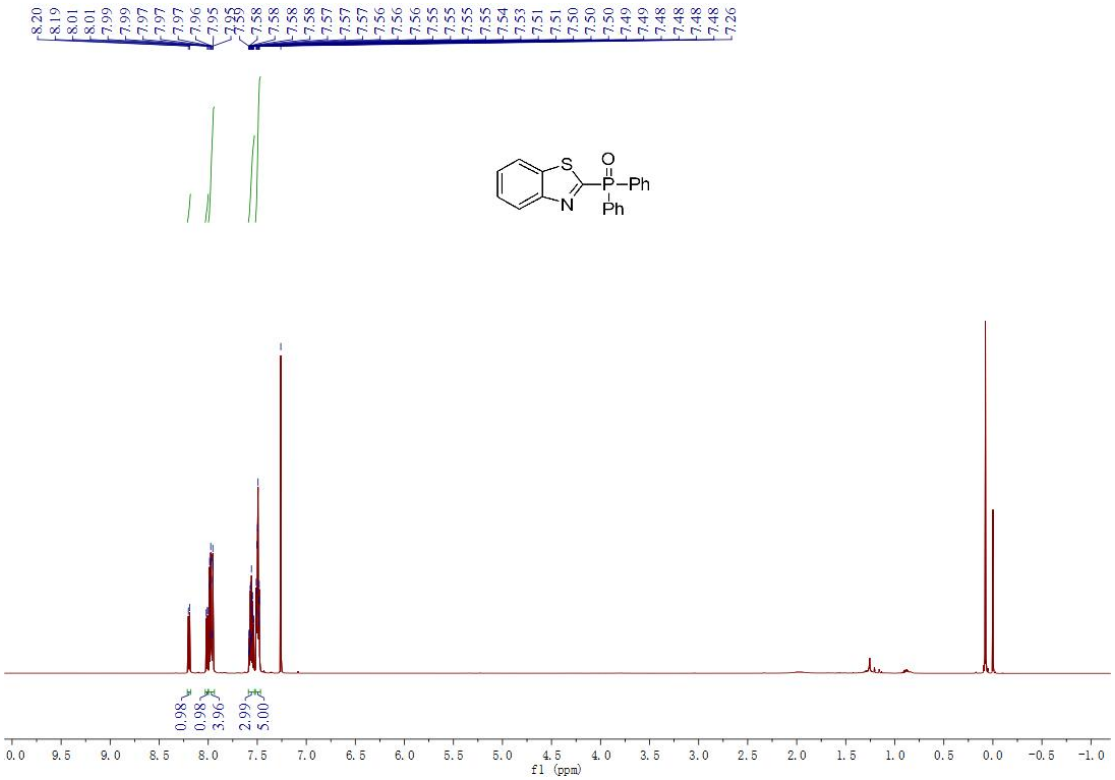
[2] H. Hou, B. Zhou, J. Wang, D. Zhao, D. Sun, X. Chen, Y. Han, C. Yan, Y. Shi and S. Zhu, *Org. Lett*, 2021, ***23***, 2981-2987.

[3] K. Luo, Y.-Z. Chen, W.-C. Yang, J. Zhu and L. Wu, *Org. Lett.*, 2016, **18**, 452-455.

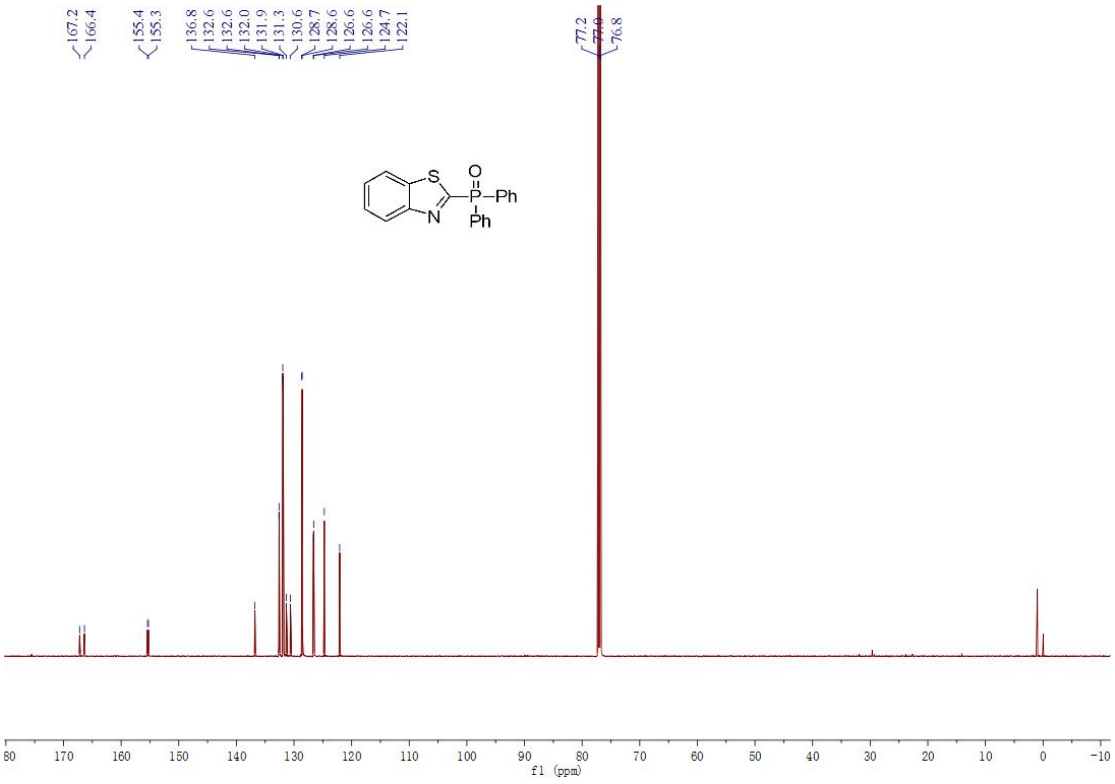
[4] P. Peng, L. Peng, G. Wang, F. Wang, Y. Luo and A. Lei, *Org. Chem. Front.* 2016, **3**, 749-752.

NMR spectra

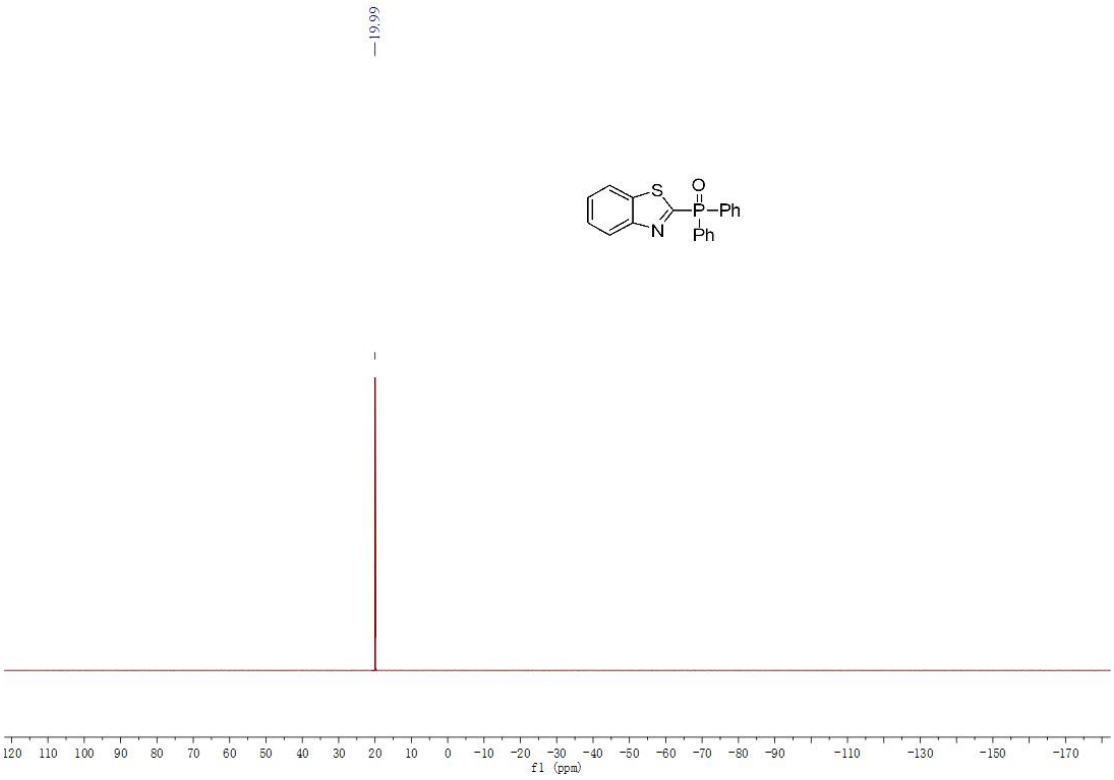
^{1}H NMR Spectrum of **3a**



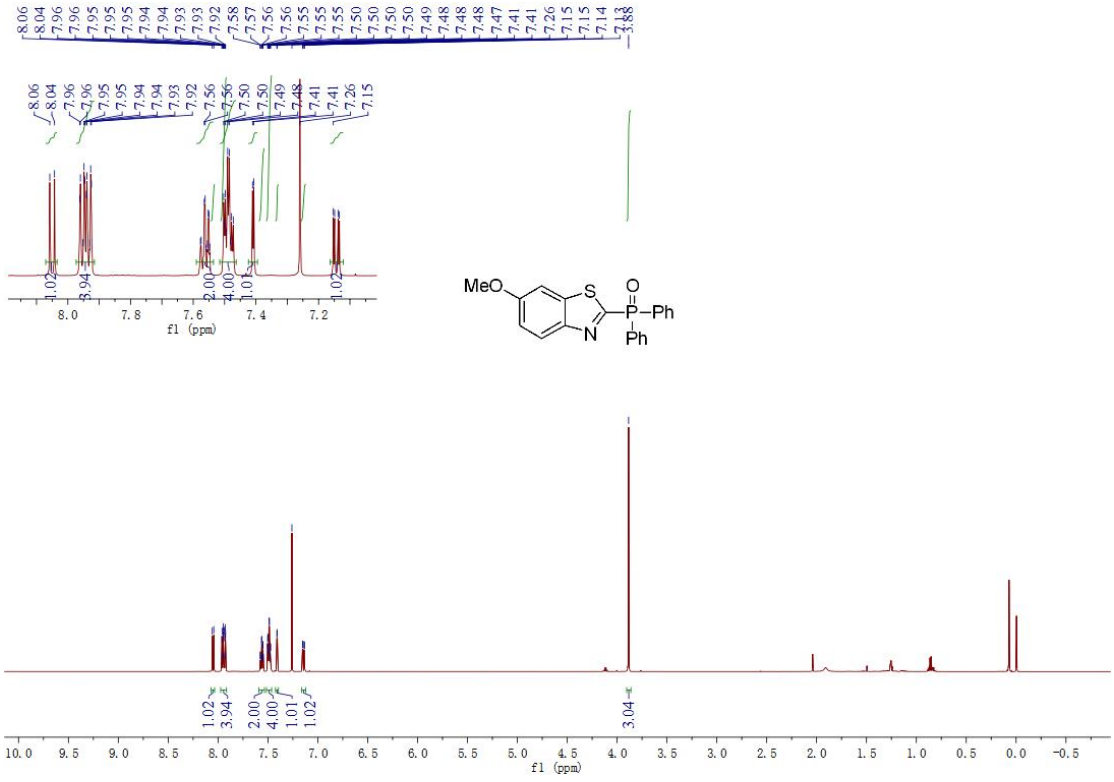
^{13}C NMR Spectrum of **3a**



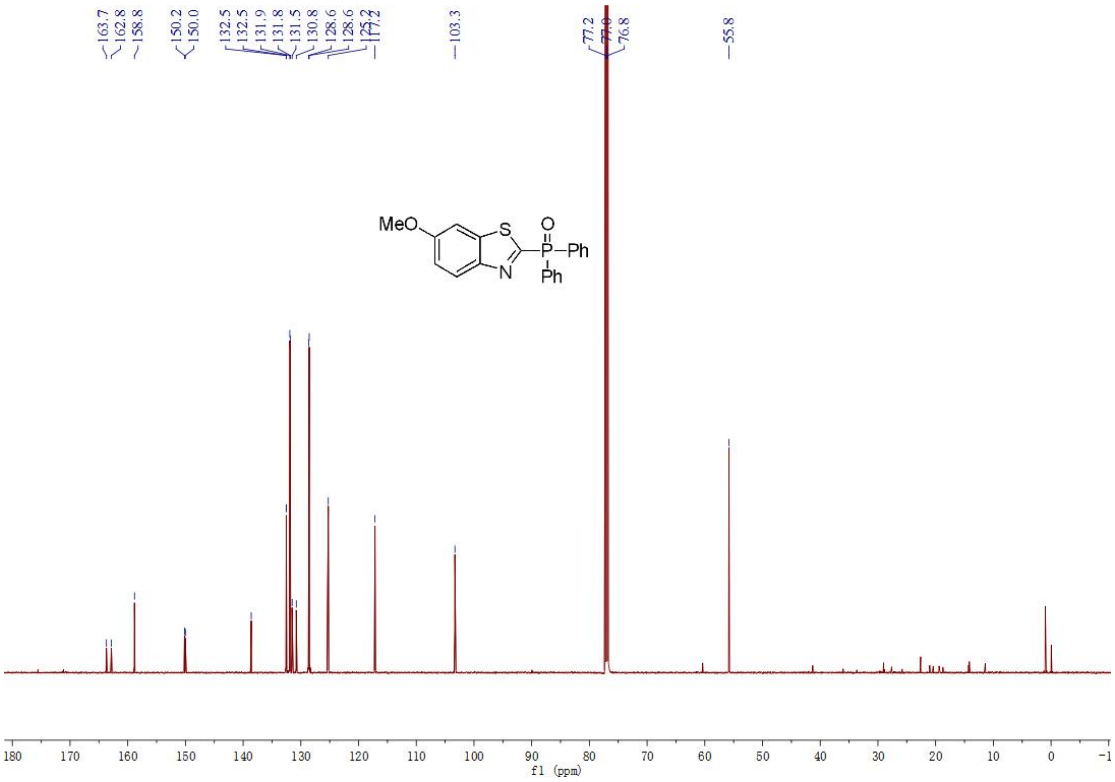
^{31}P NMR Spectrum of **3a**



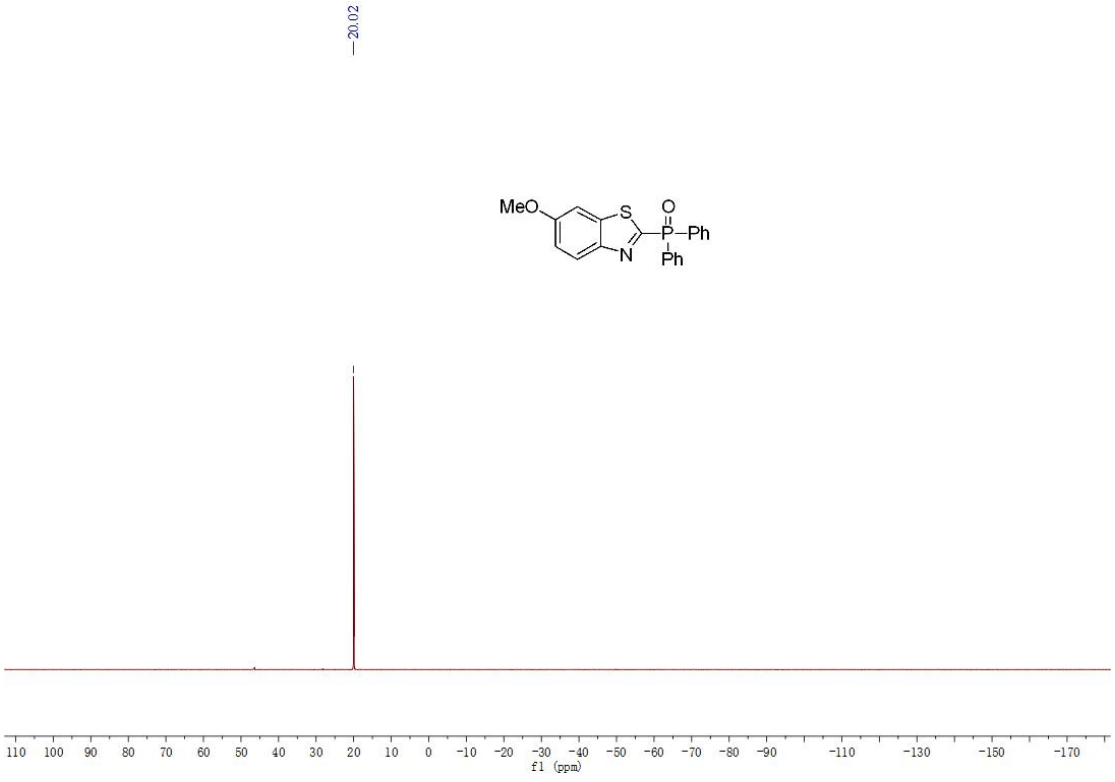
^{1}H NMR Spectrum of **3b**



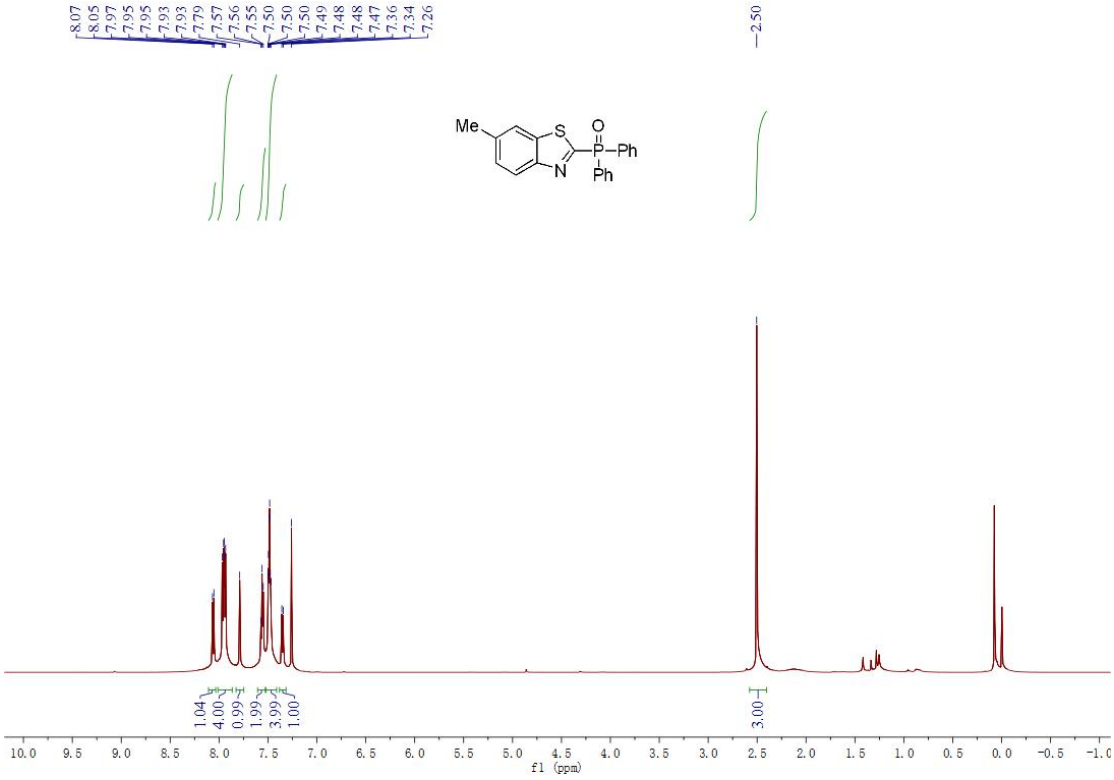
^{13}C NMR Spectrum of **3b**



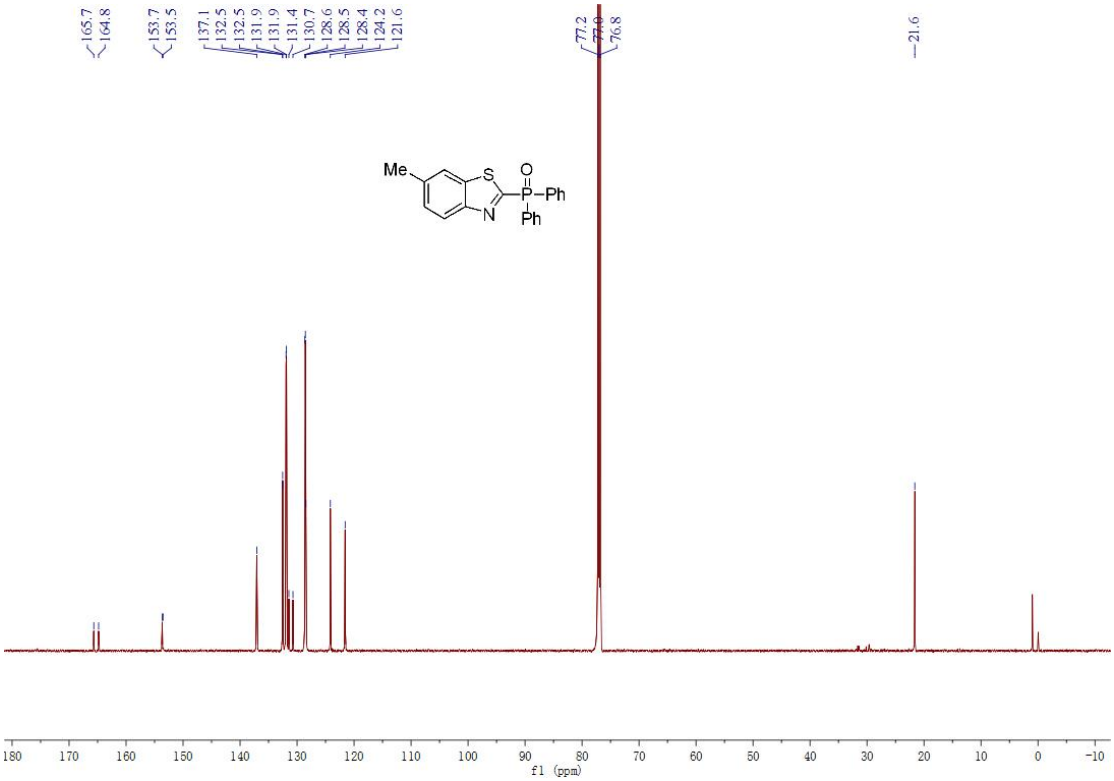
^{31}P NMR Spectrum of **3b**



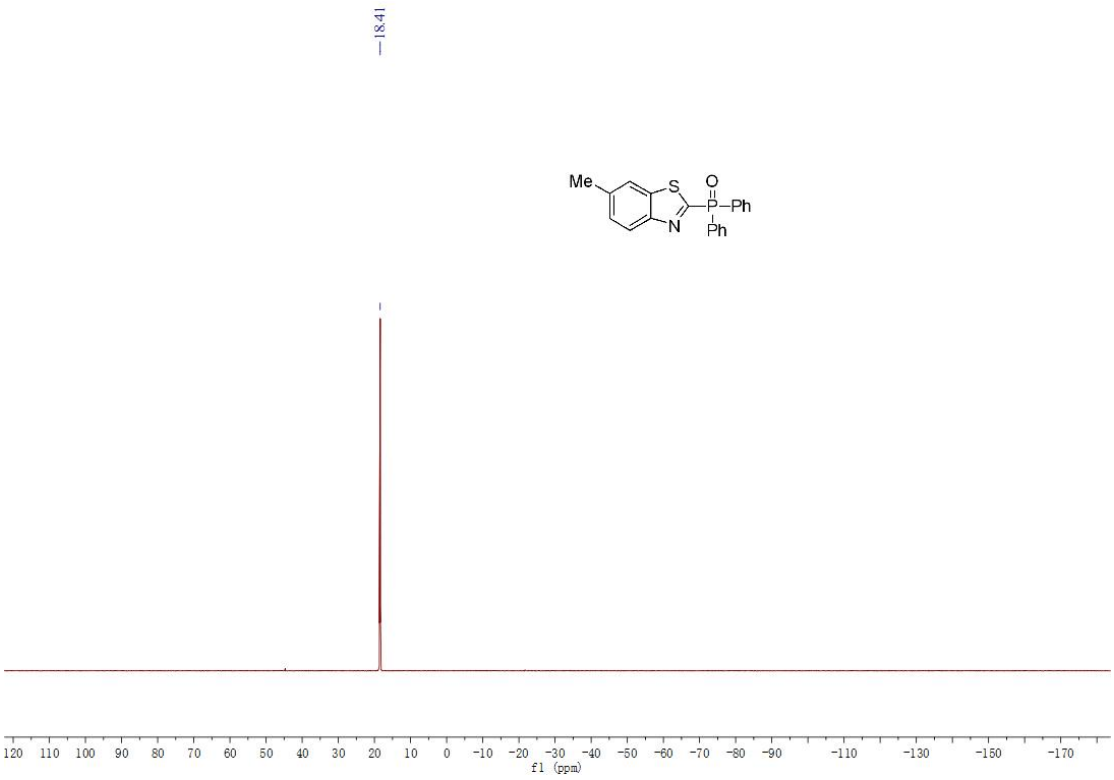
^{1}H NMR Spectrum of **3c**



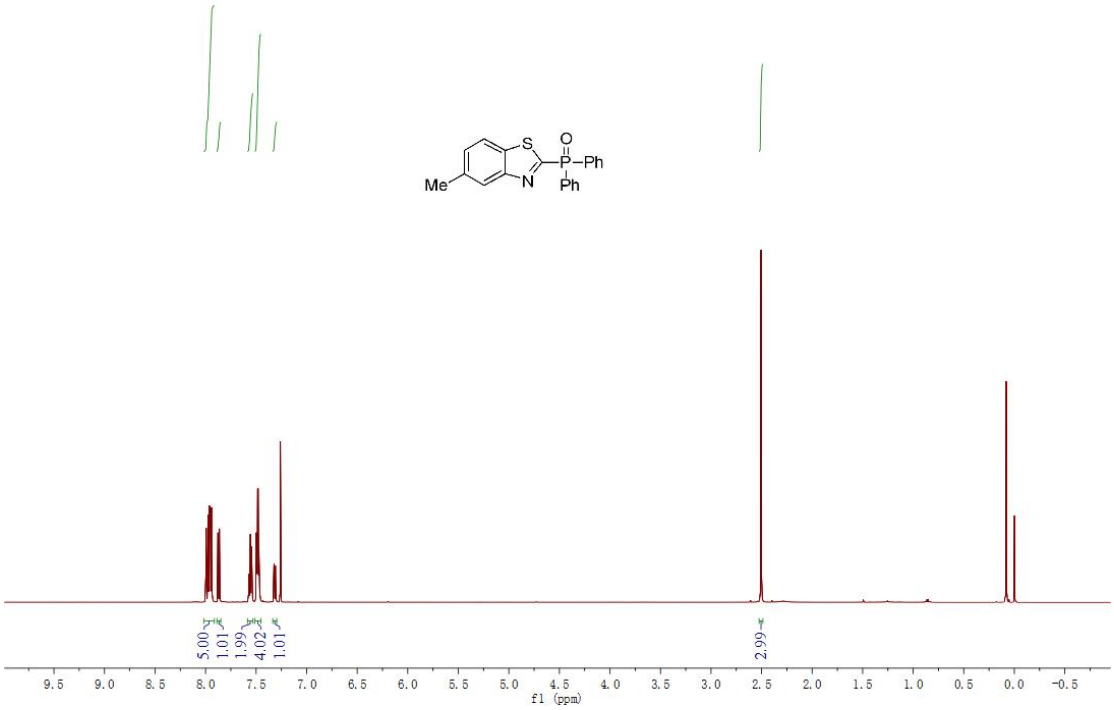
^{13}C NMR Spectrum of **3c**



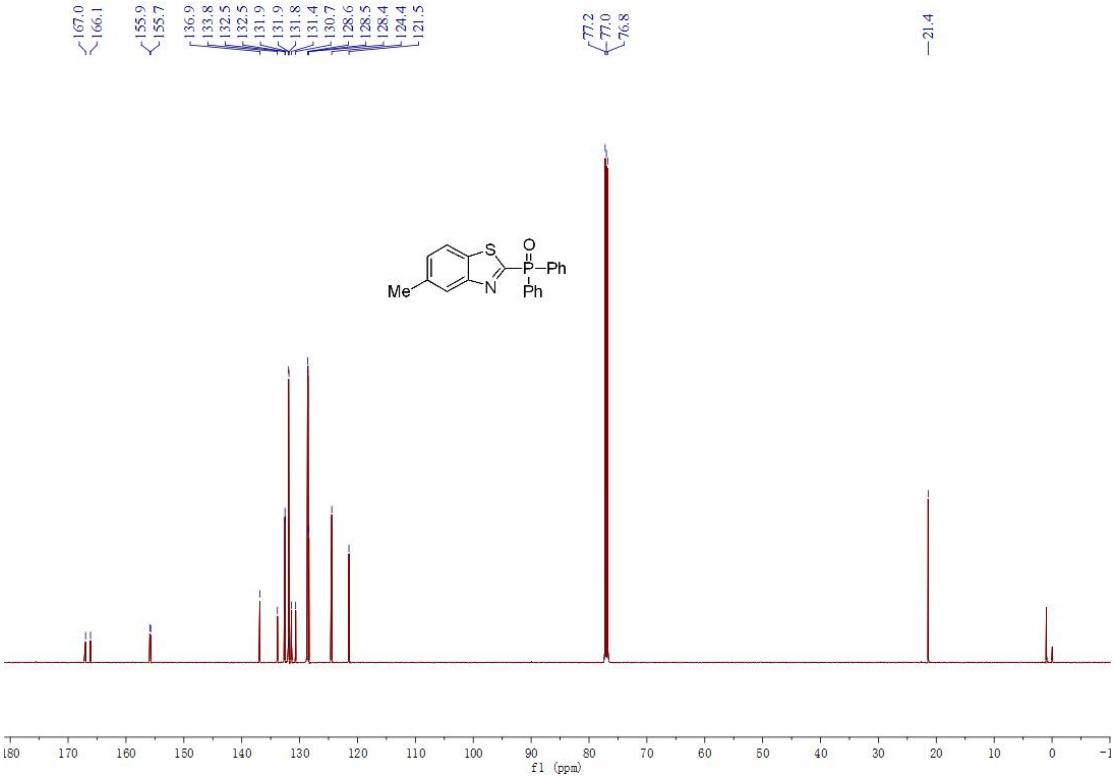
^{31}P NMR Spectrum of **3c**



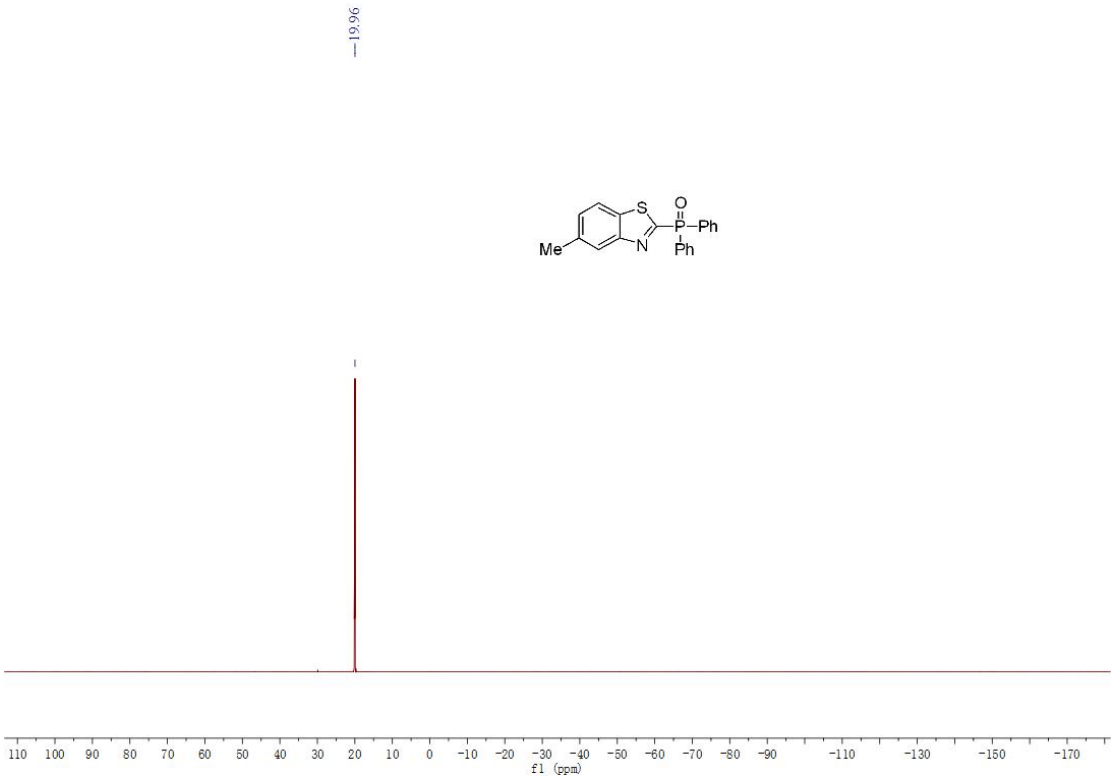
^{1}H NMR Spectrum of **3d**



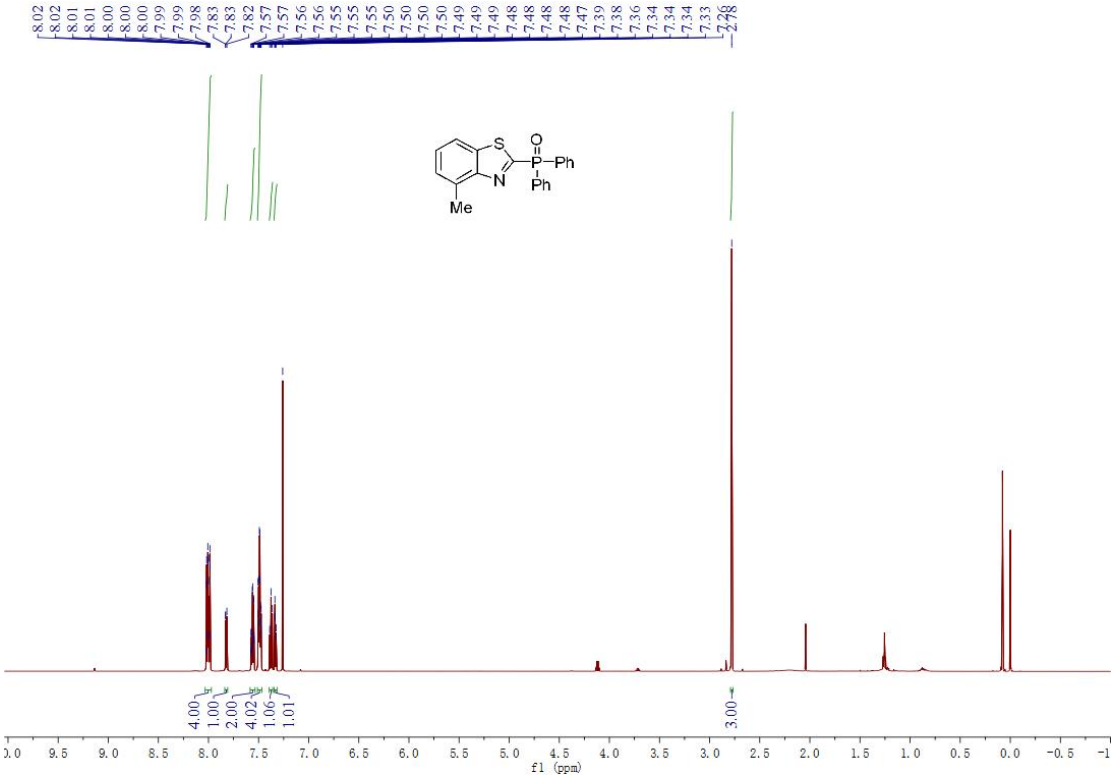
^{13}C NMR Spectrum of **3d**



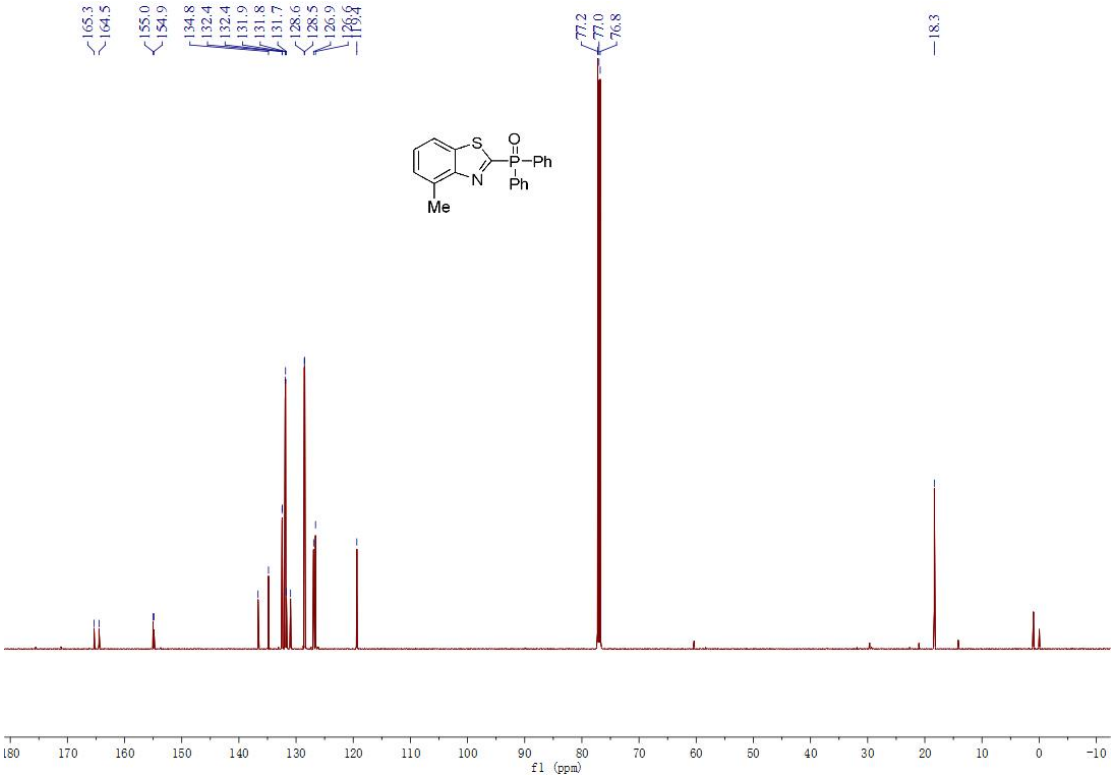
^{31}P NMR Spectrum of **3d**



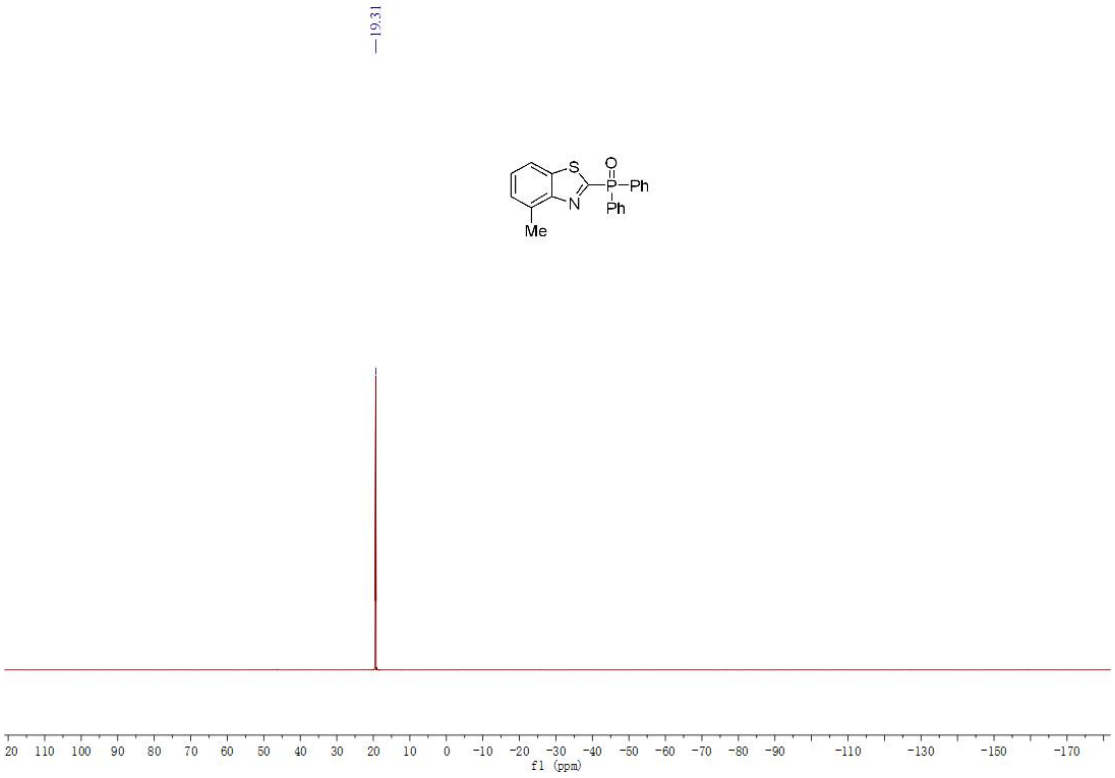
^{1}H NMR Spectrum of **3e**



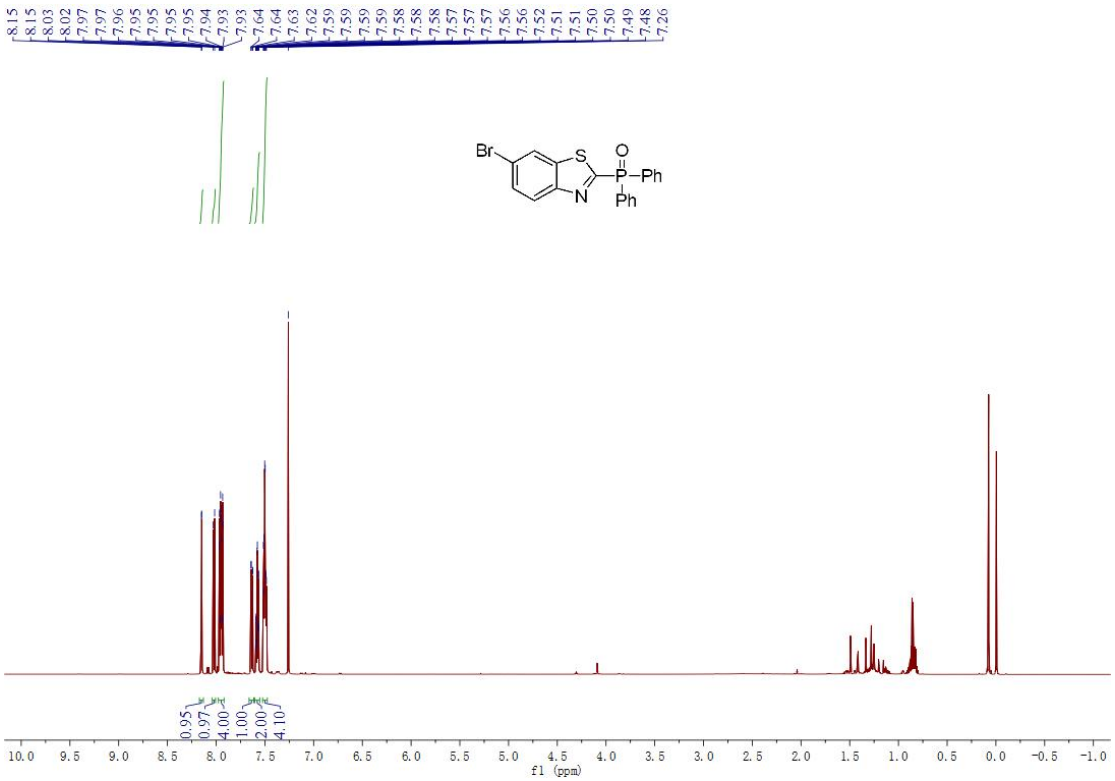
^{13}C NMR Spectrum of **3e**



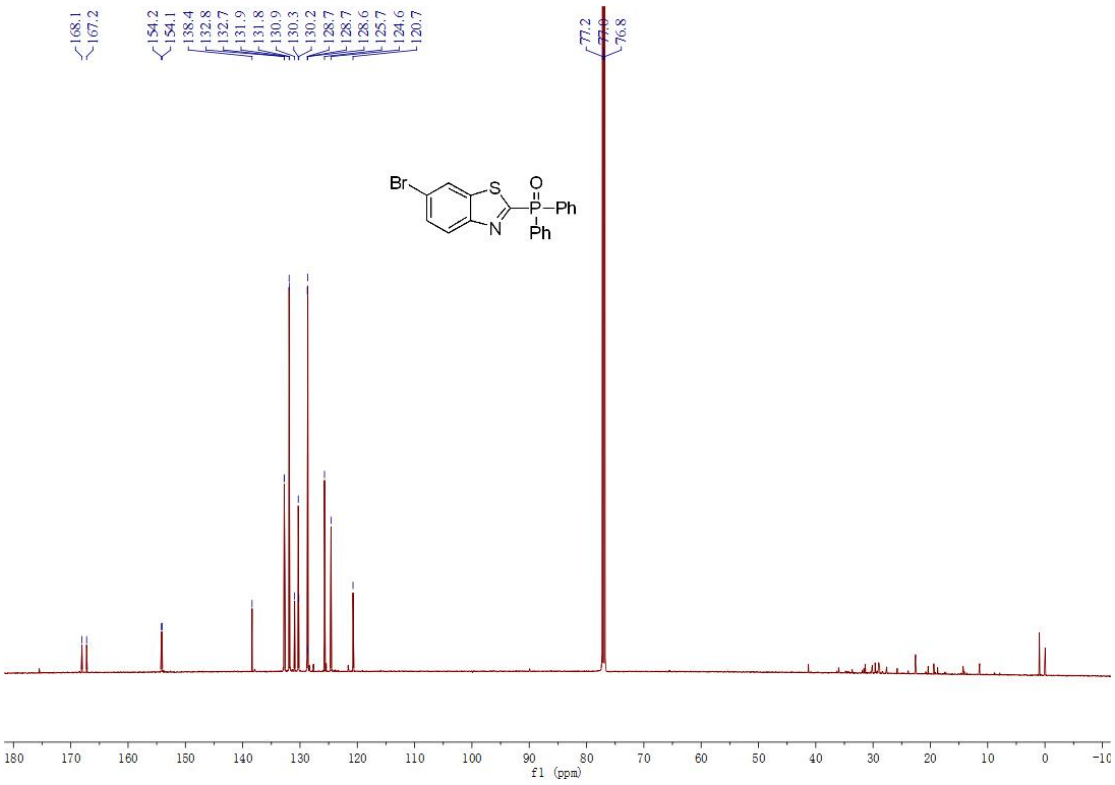
^{31}P NMR Spectrum of **3e**



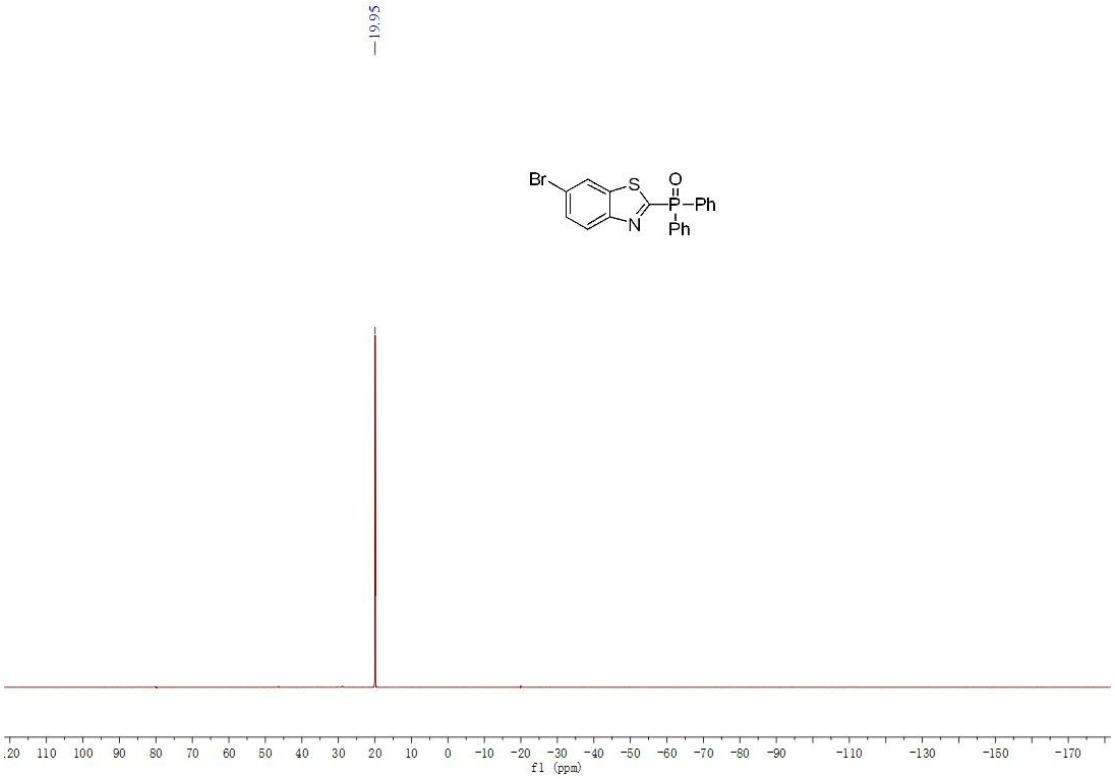
^{1}H NMR Spectrum of **3f**



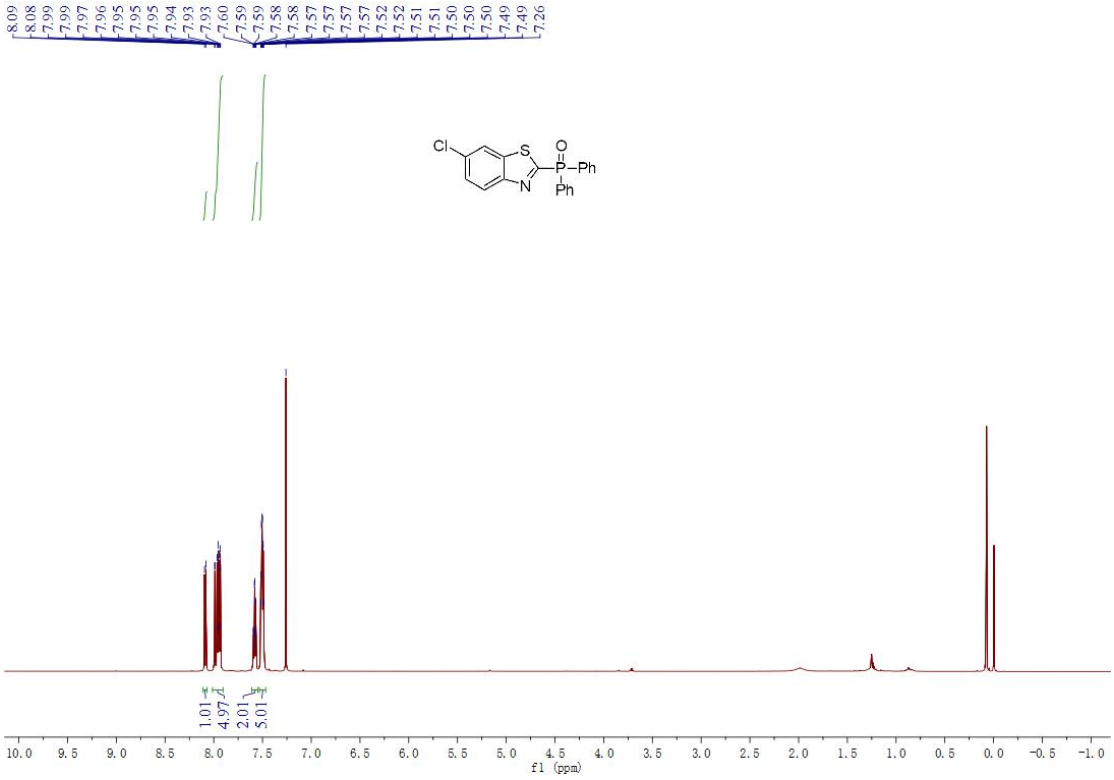
^{13}C NMR Spectrum of **3f**



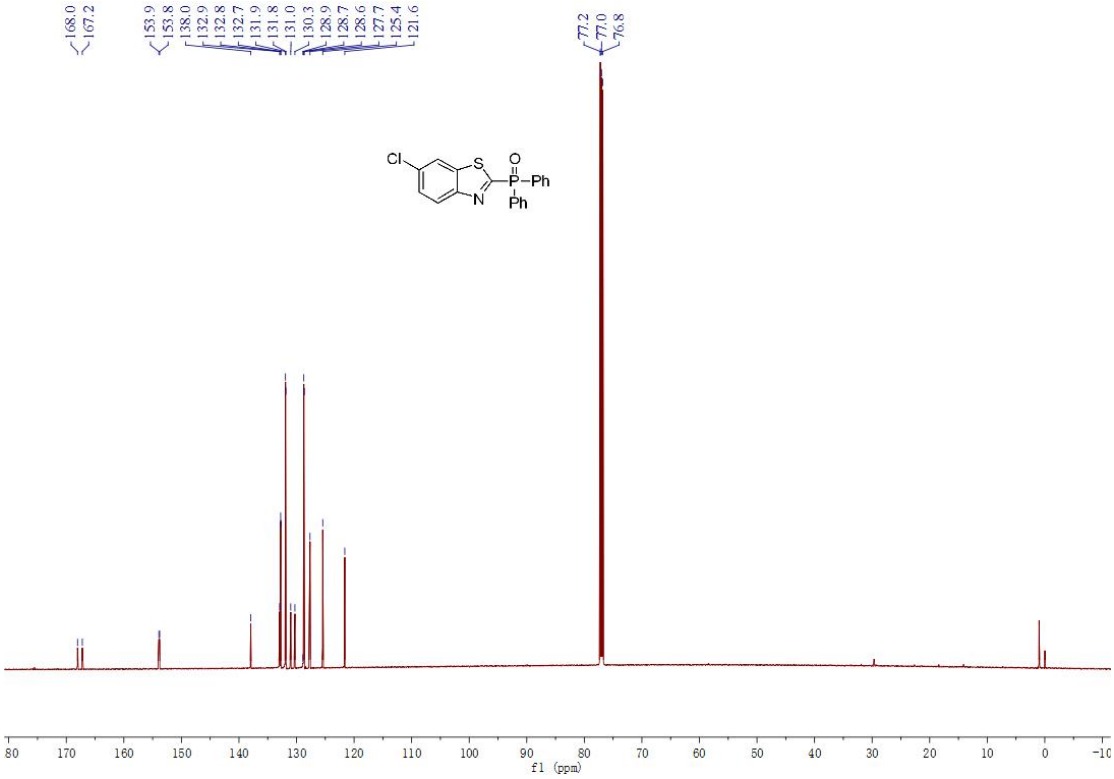
^{31}P NMR Spectrum of **3f**



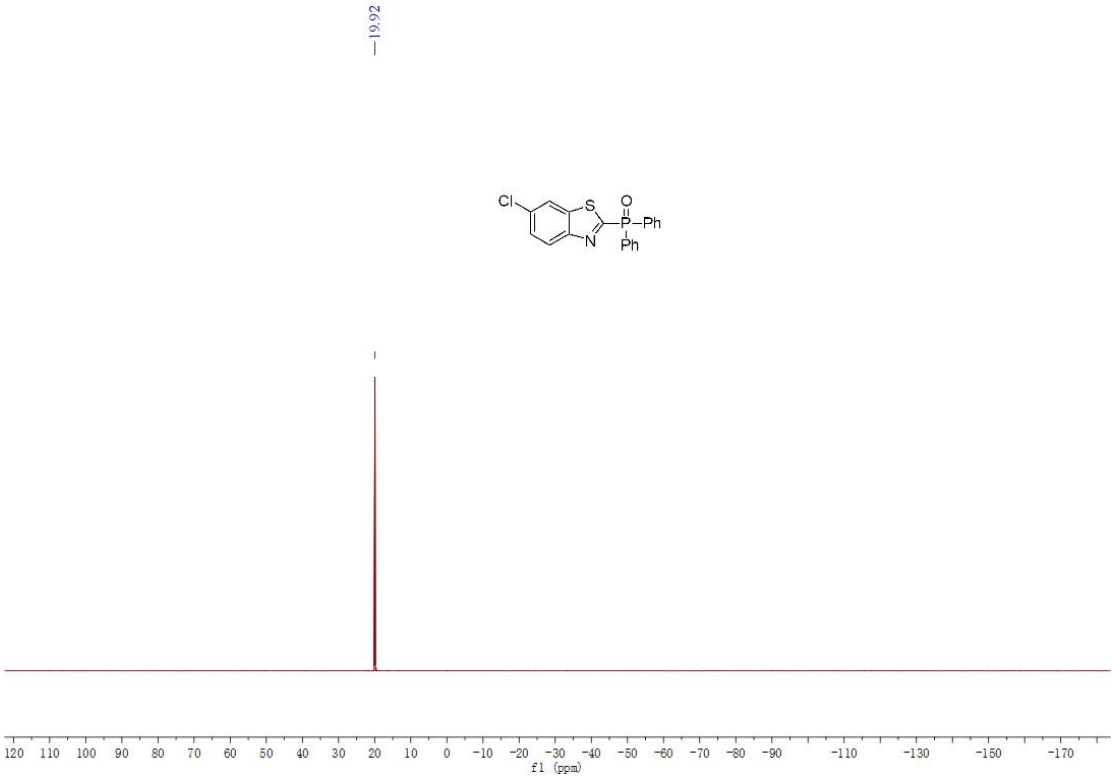
^{1}H NMR Spectrum of **3g**



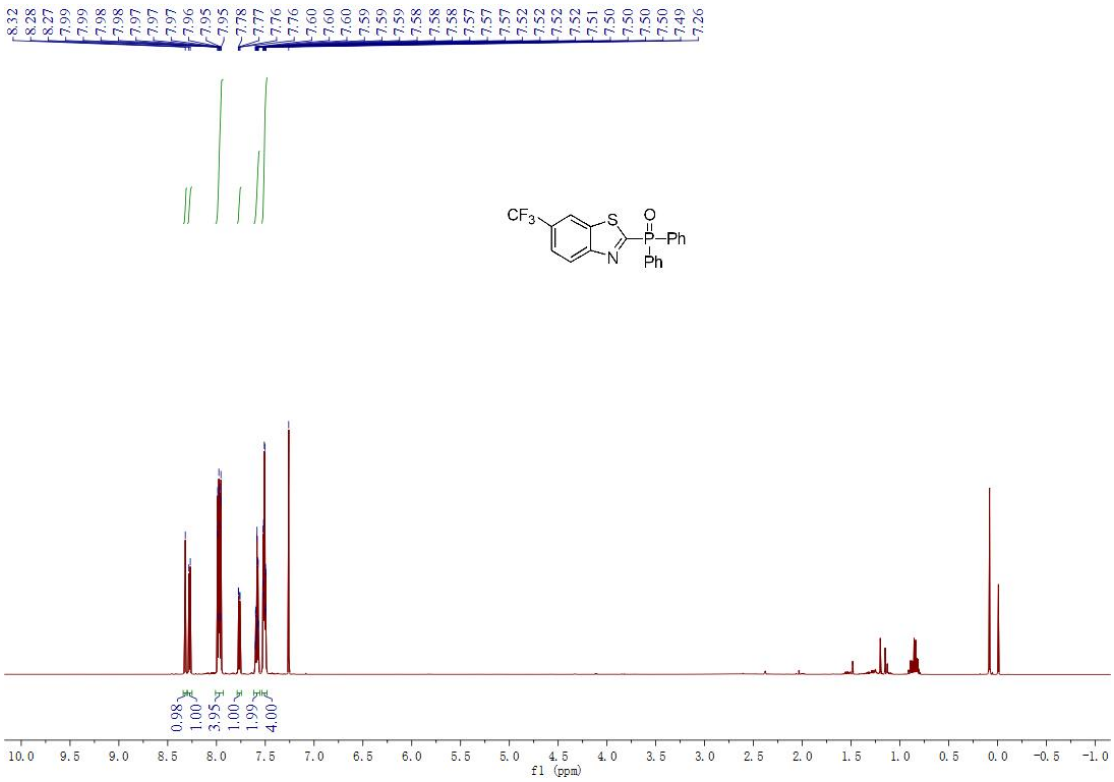
^{13}C NMR Spectrum of **3g**



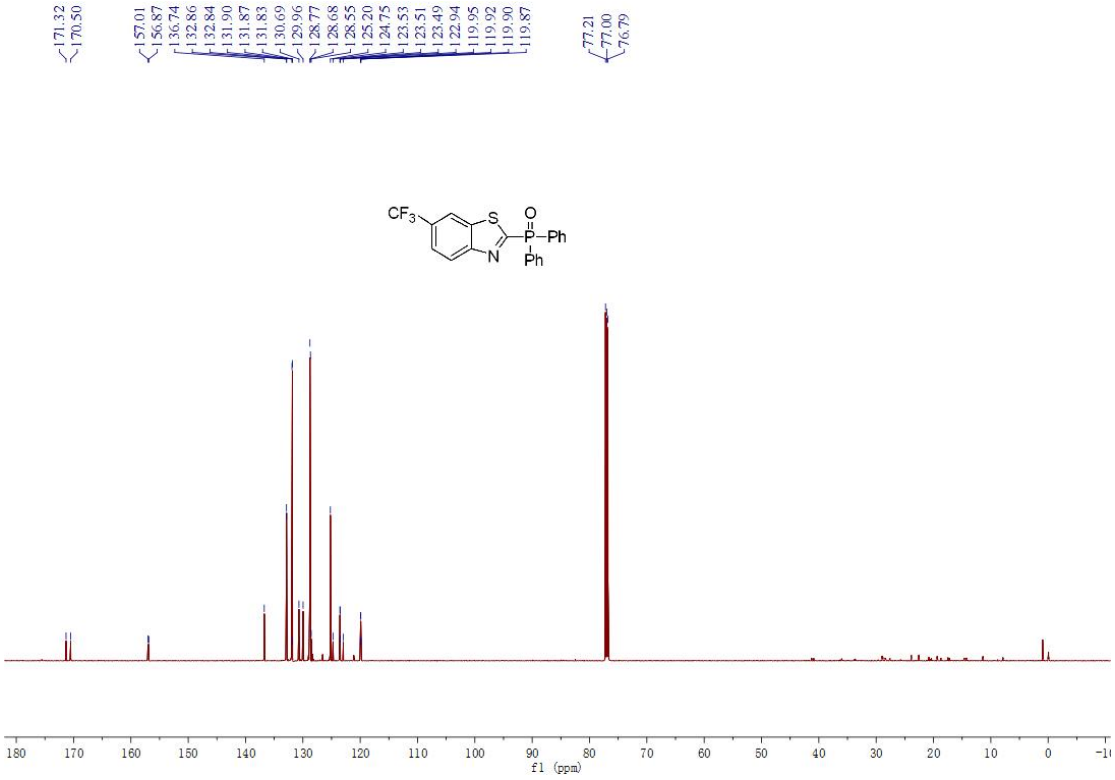
^{31}P NMR Spectrum of **3g**



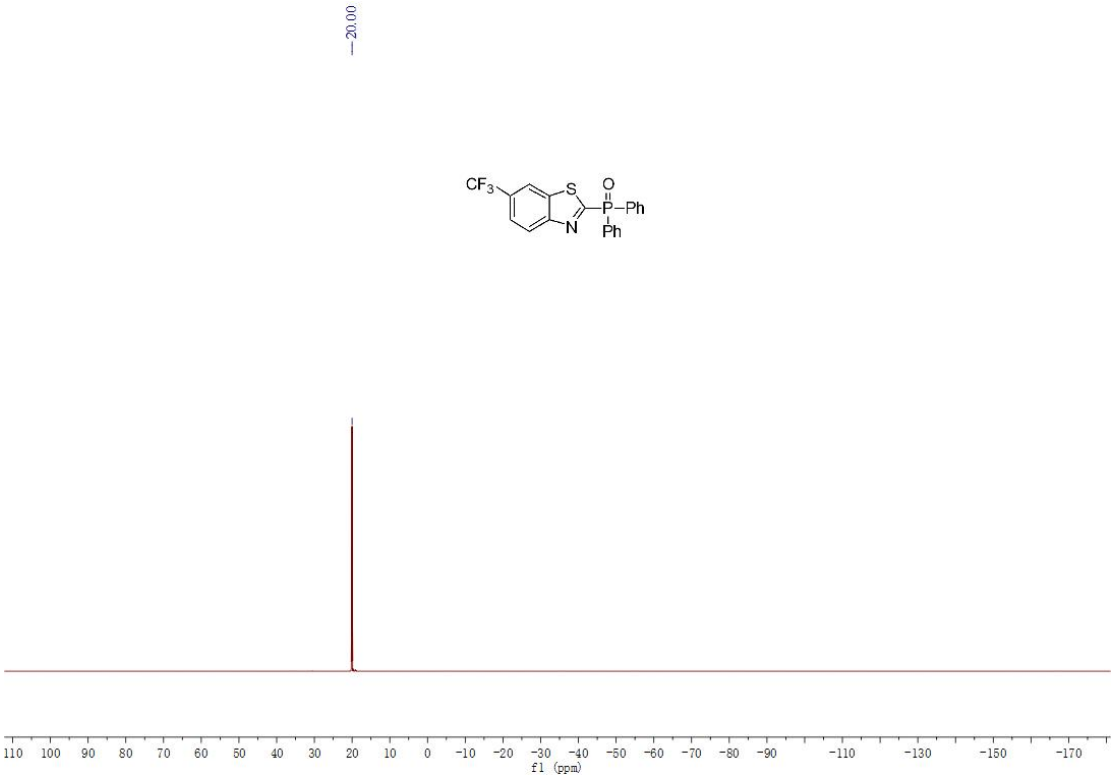
^{1}H NMR Spectrum of **3h**



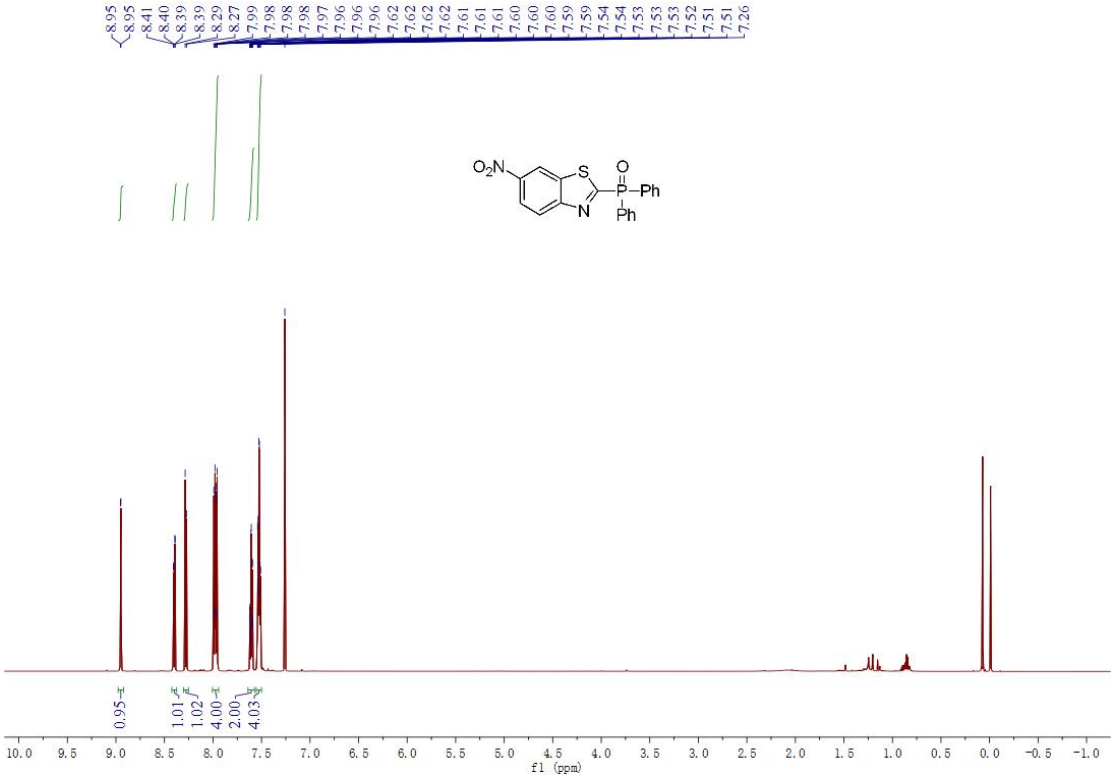
^{13}C NMR Spectrum of **3h**



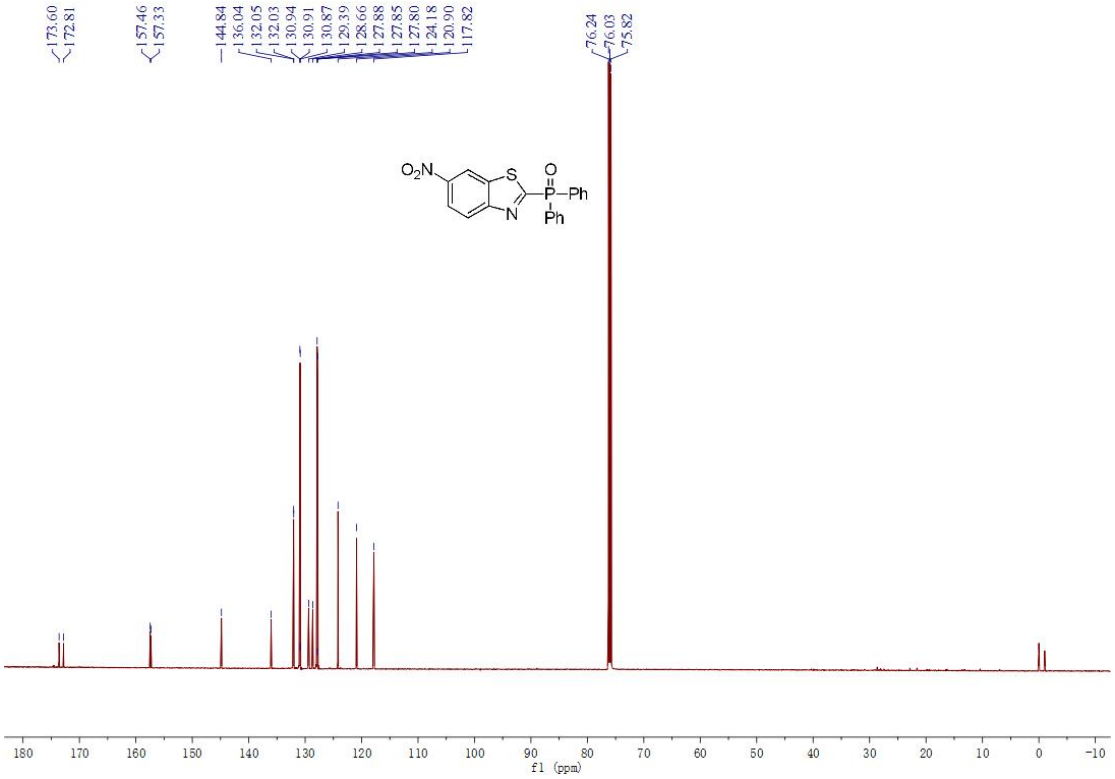
^{31}P NMR Spectrum of **3h**



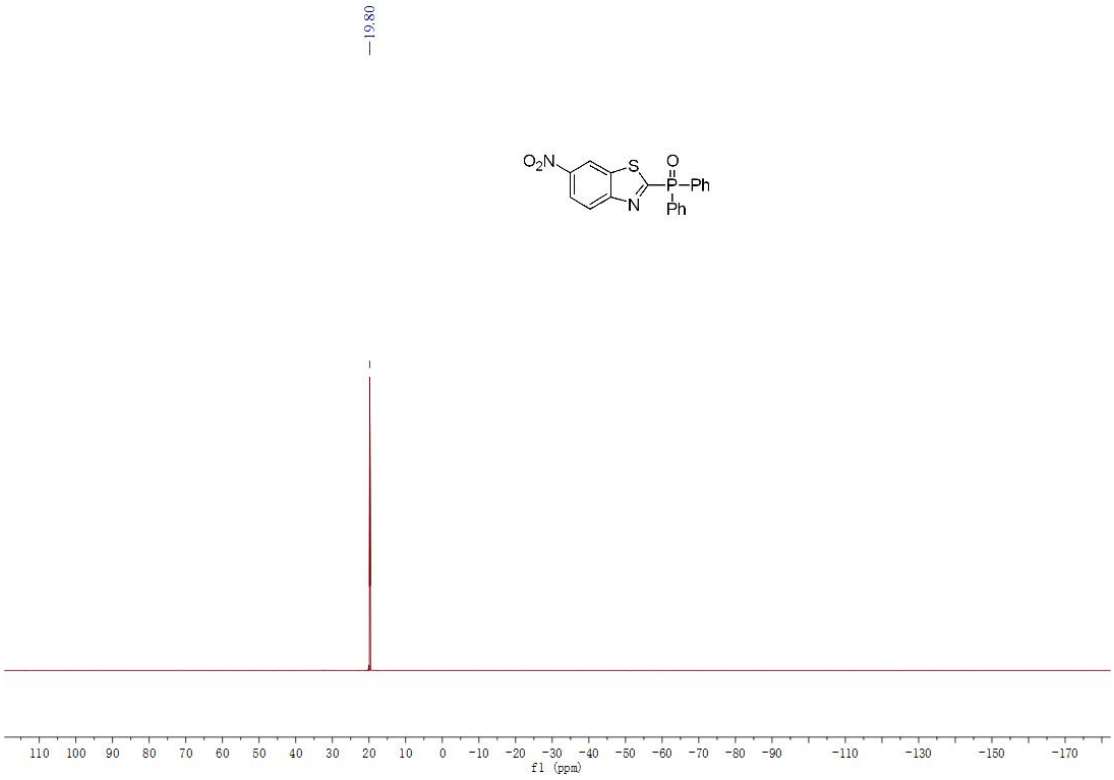
^{1}H NMR Spectrum of **3i**



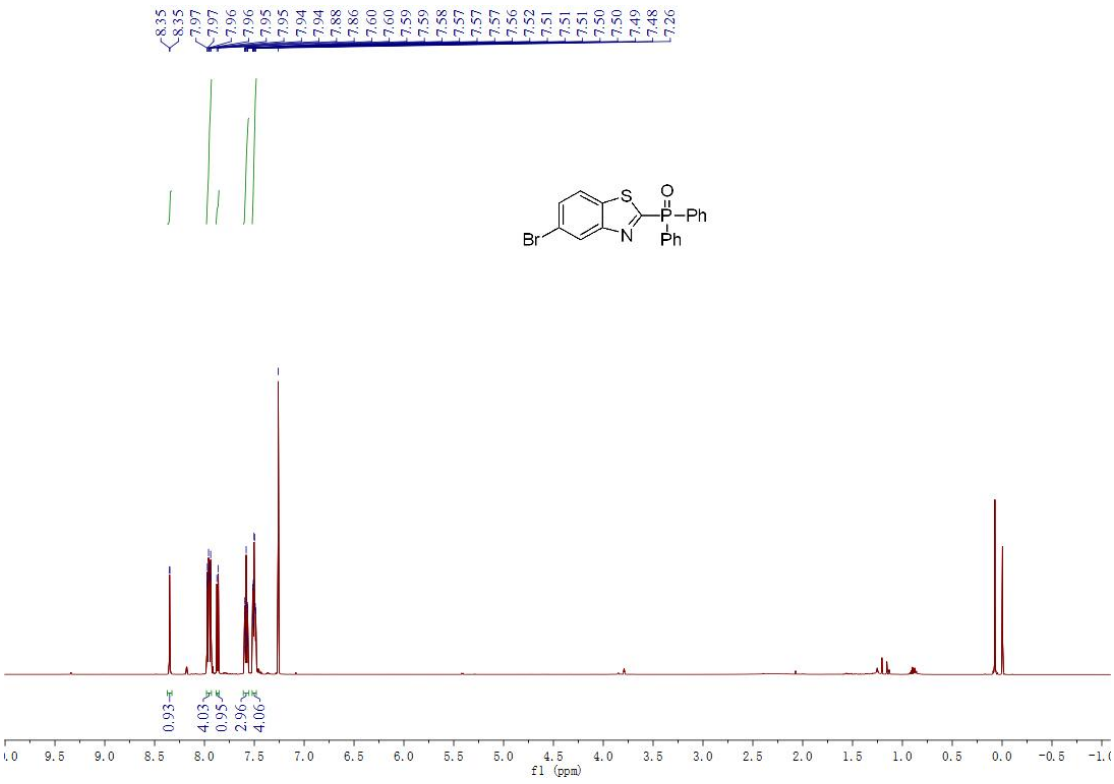
^{13}C NMR Spectrum of **3i**



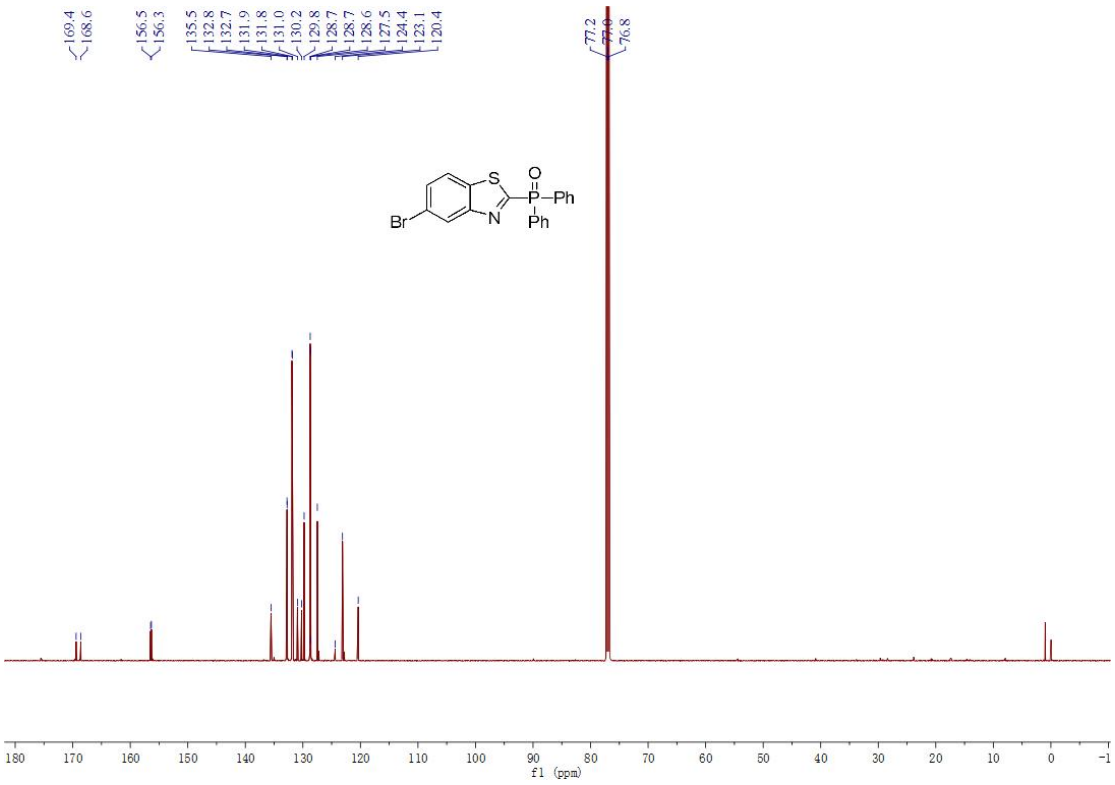
^{31}P NMR Spectrum of **3i**



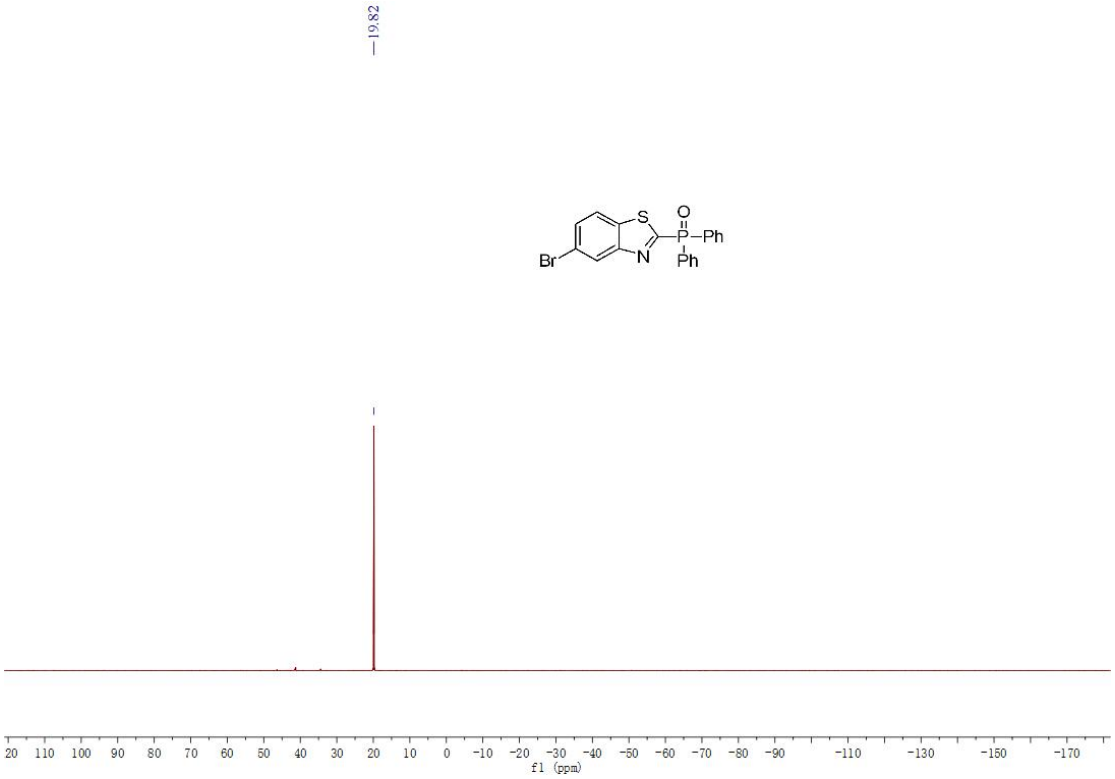
^{1}H NMR Spectrum of **3j**



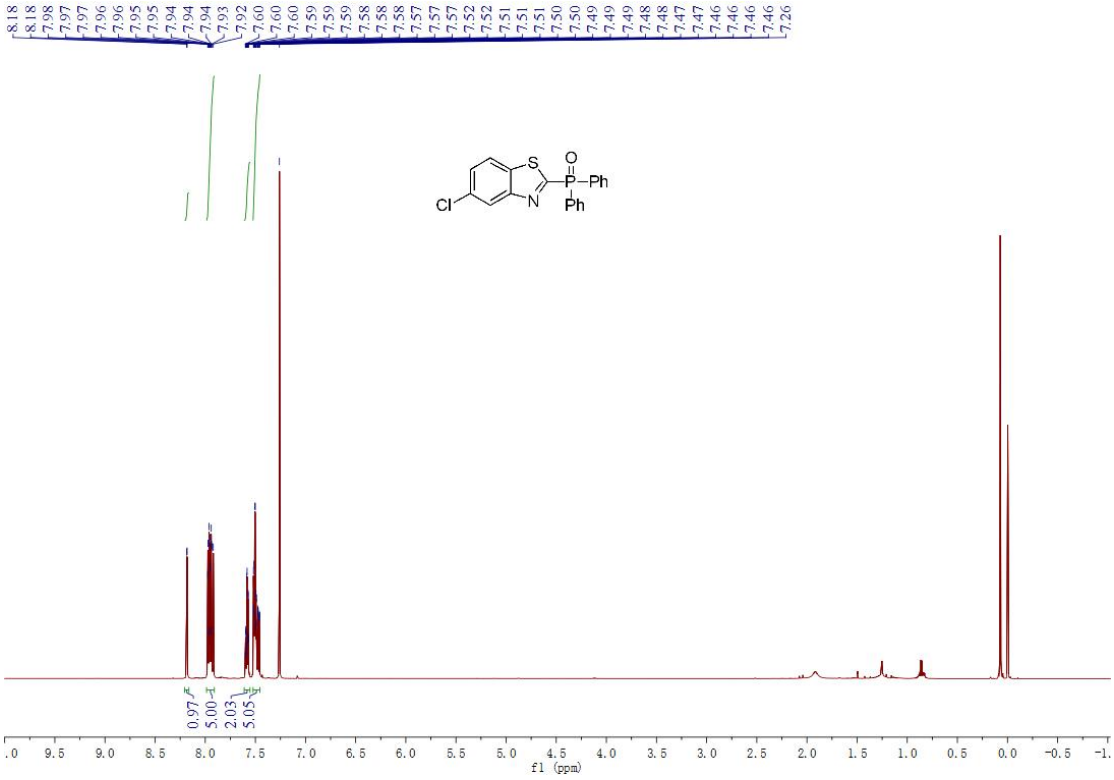
^{13}C NMR Spectrum of **3j**



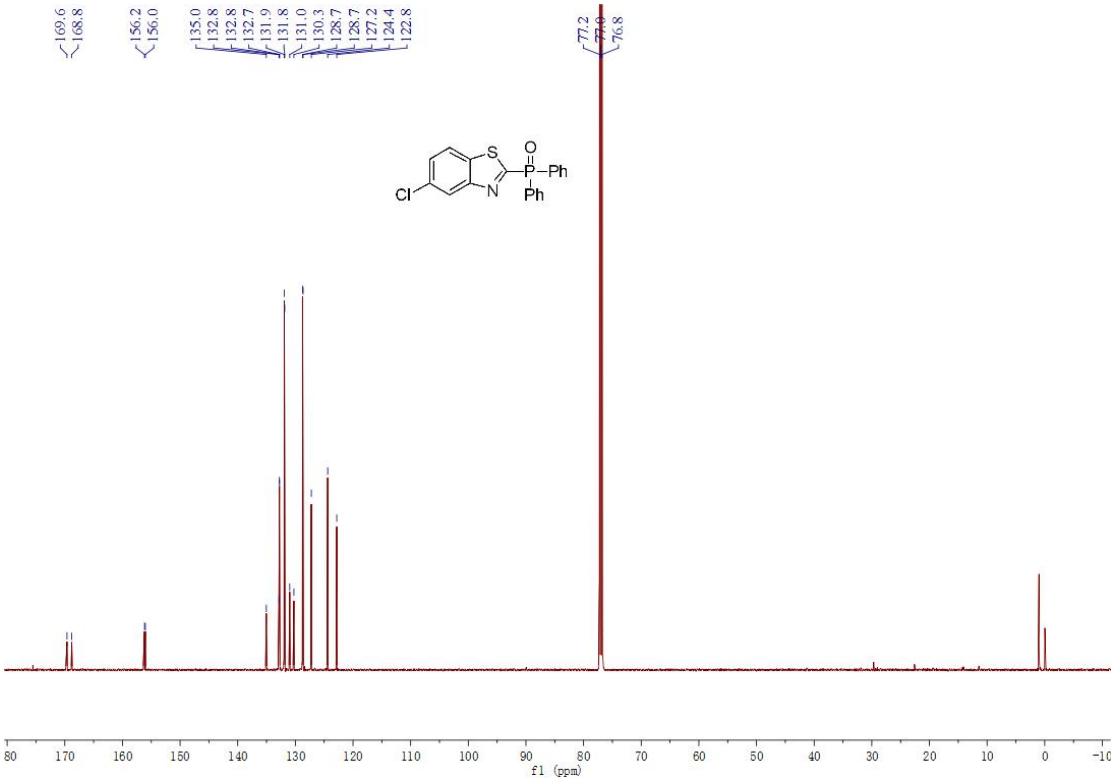
^{31}P NMR Spectrum of **3j**



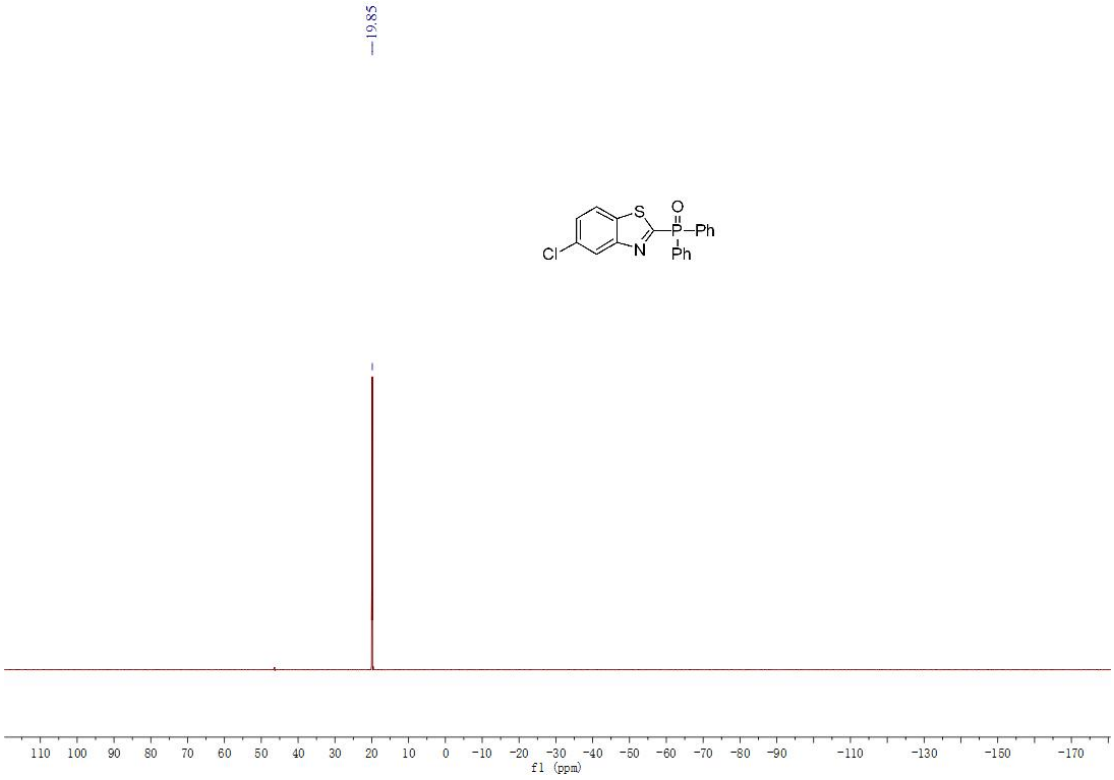
^{1}H NMR Spectrum of **3k**



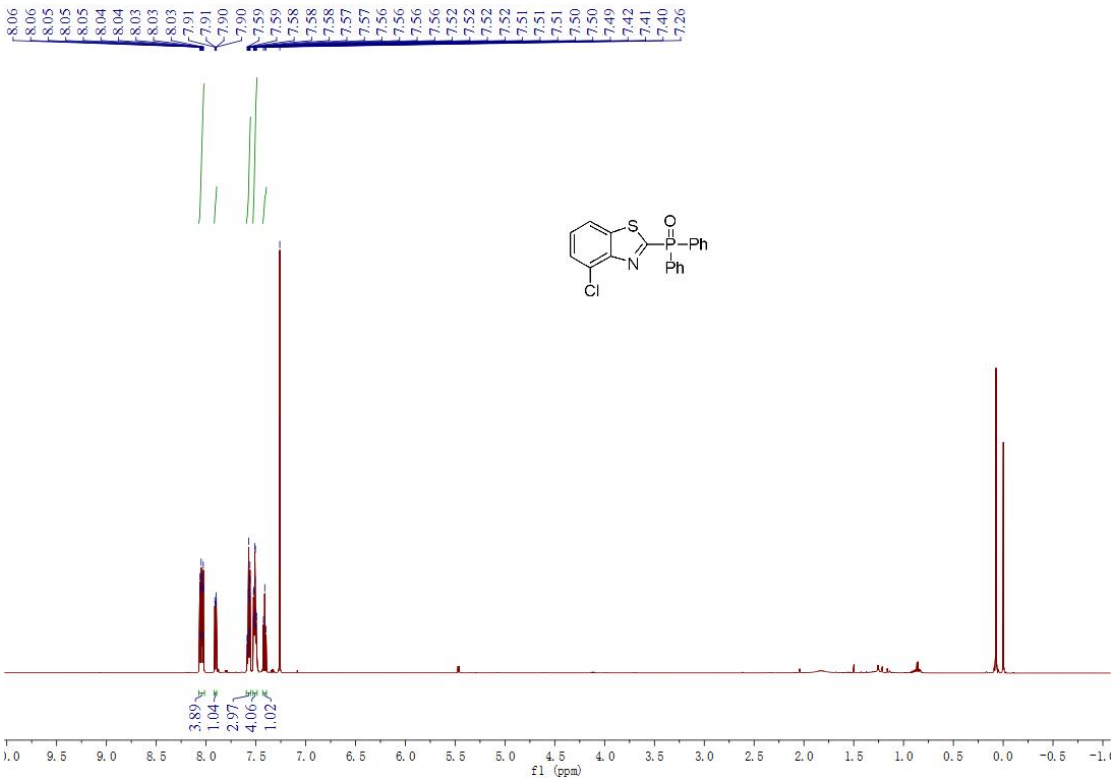
^{13}C NMR Spectrum of **3k**



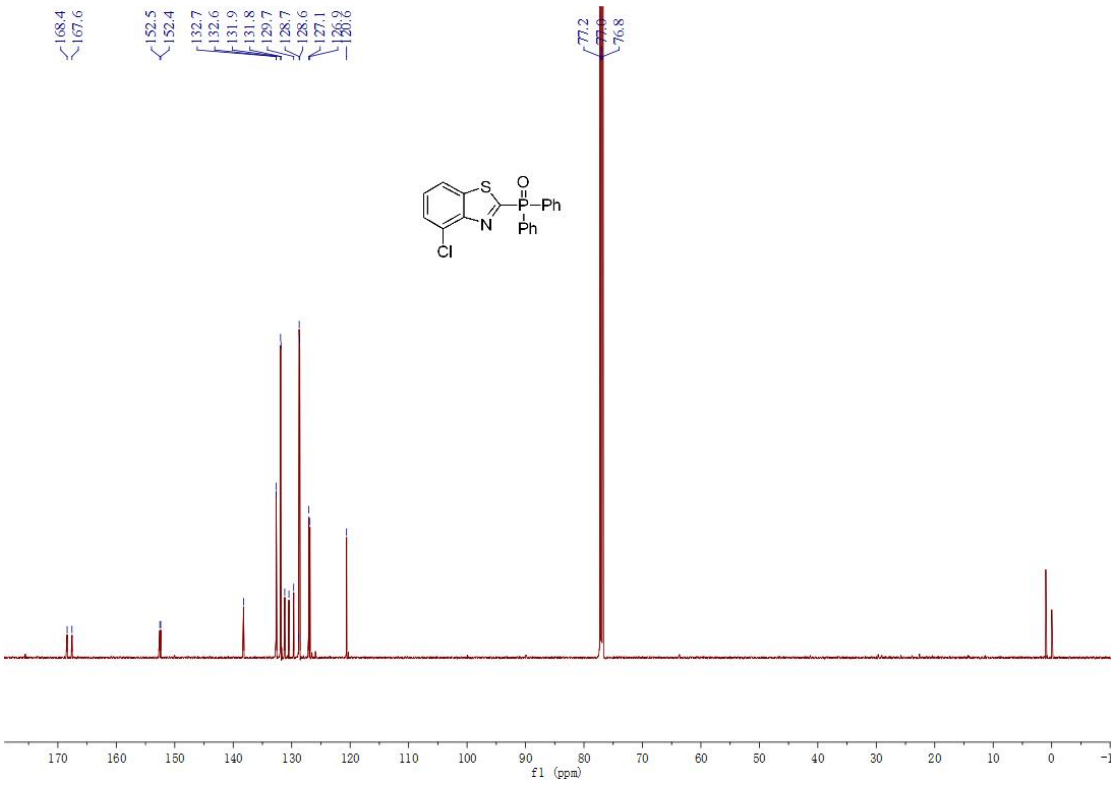
^{31}P NMR Spectrum of **3k**



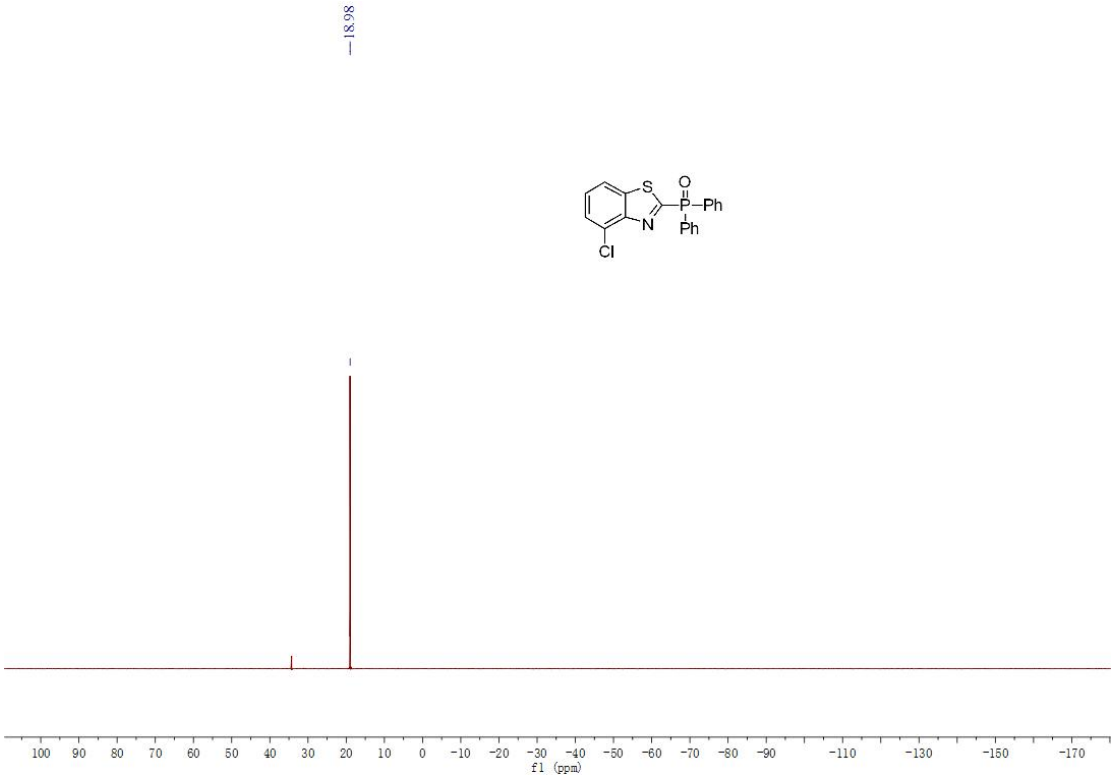
^{1}H NMR Spectrum of **3l**



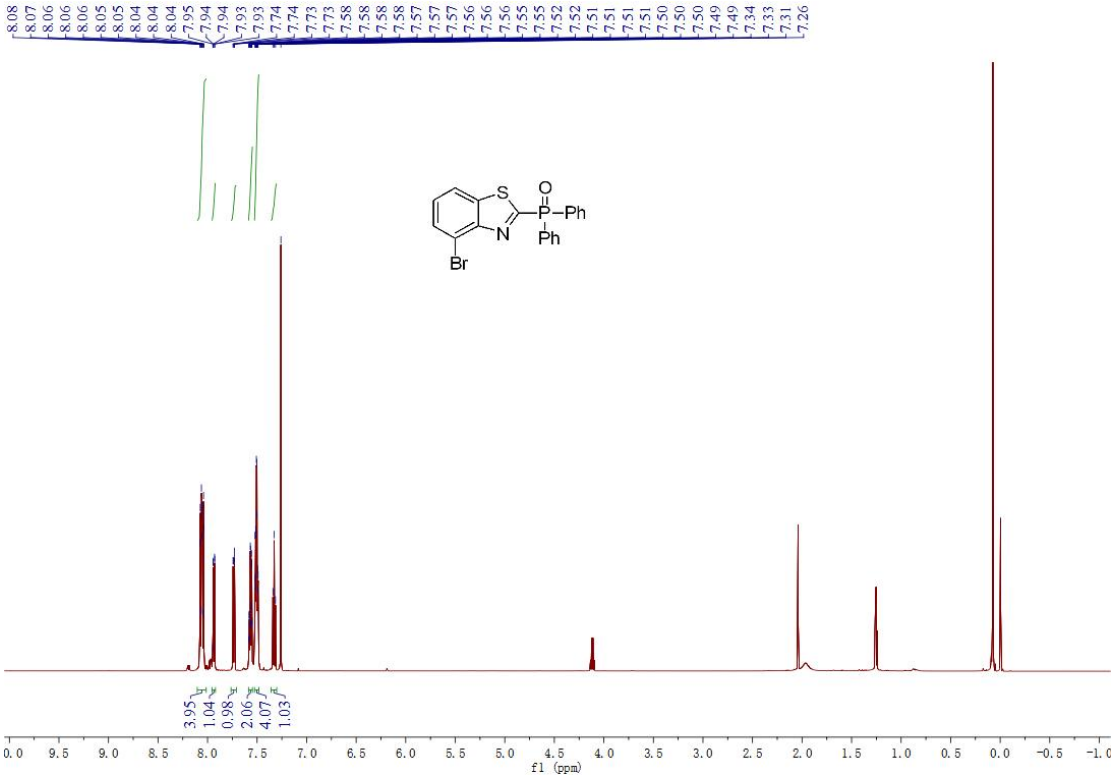
^{13}C NMR Spectrum of **3l**



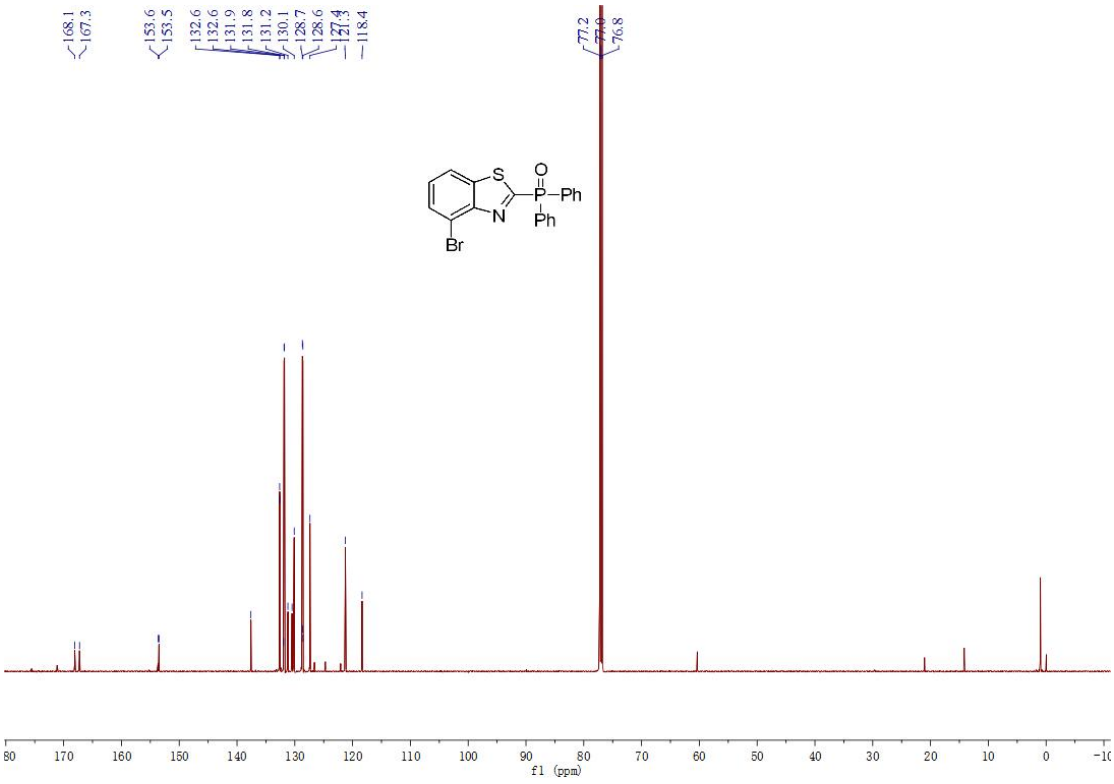
^{31}P NMR Spectrum of **3l**



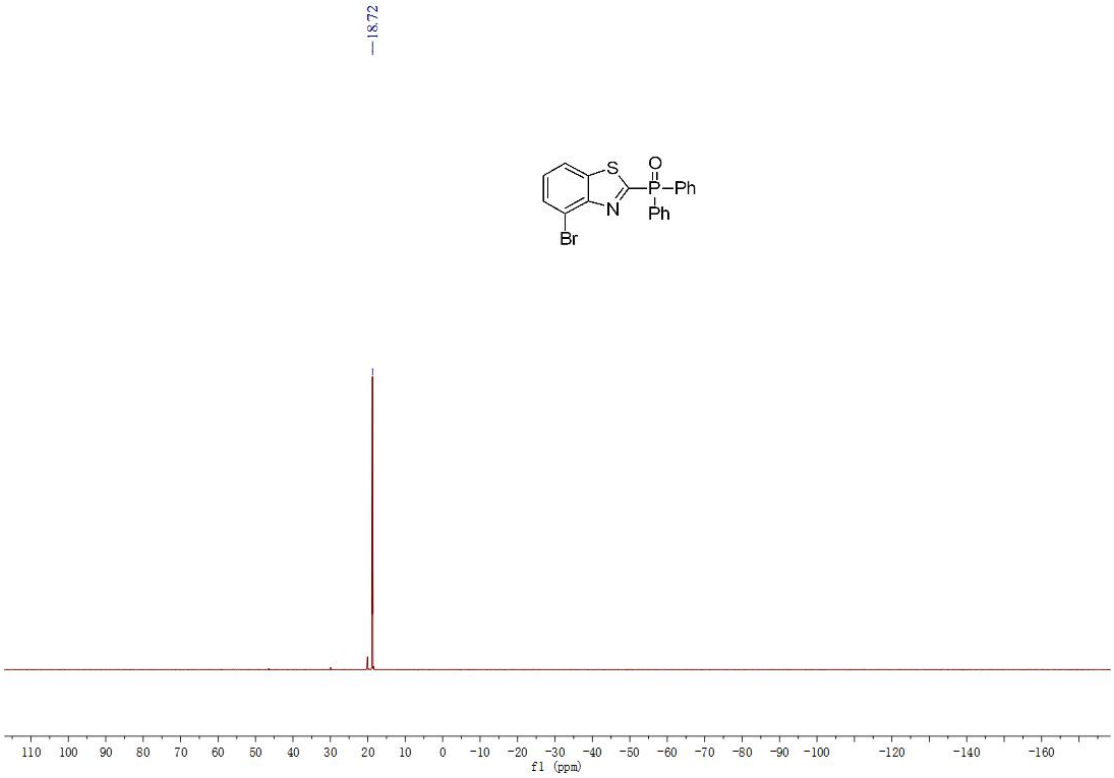
^{1}H NMR Spectrum of **3m**



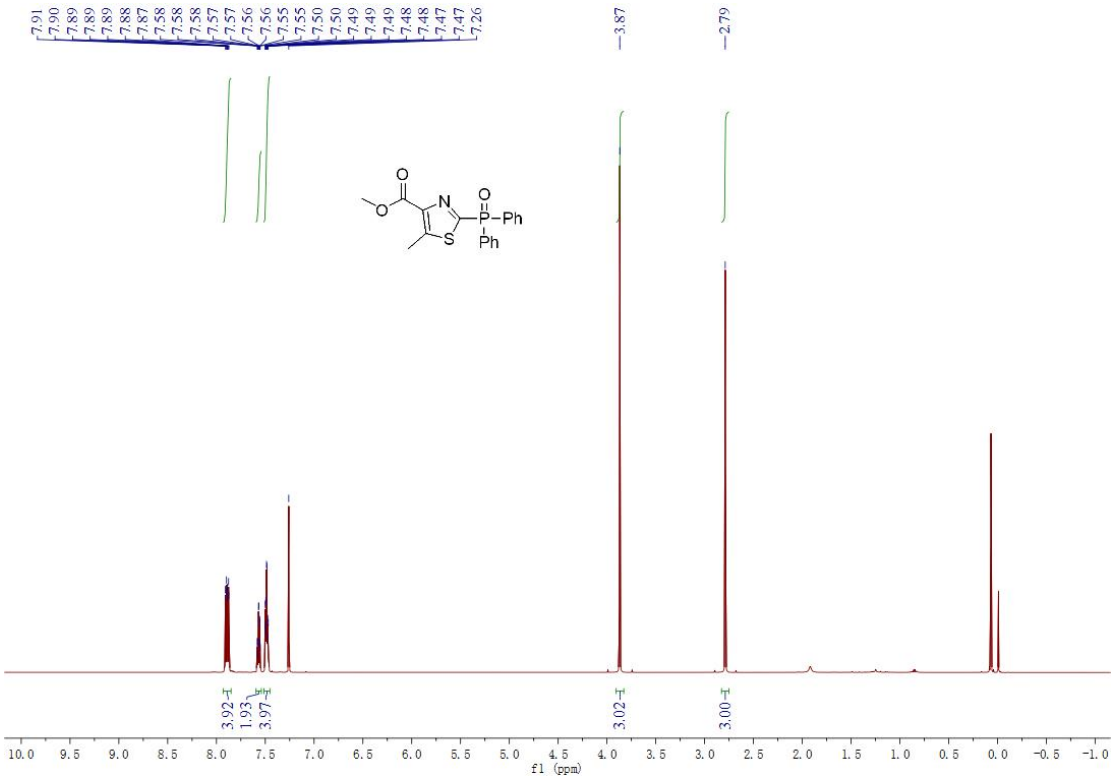
^{13}C NMR Spectrum of **3m**



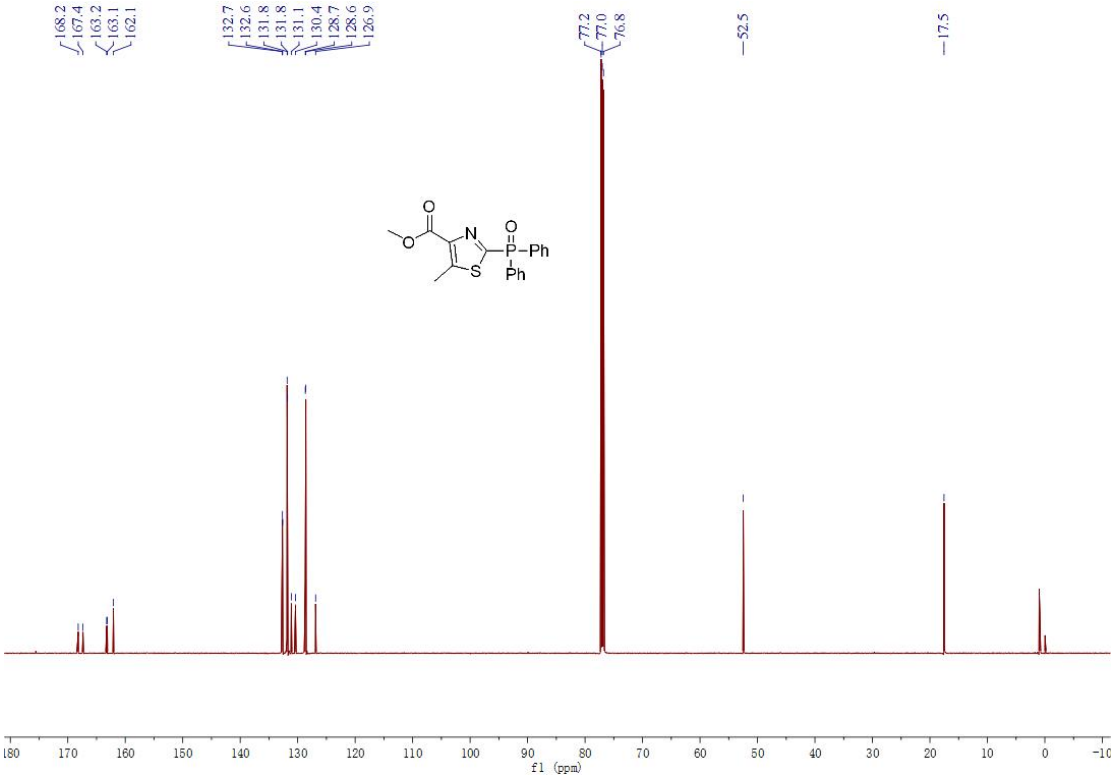
^{31}P NMR Spectrum of **3m**



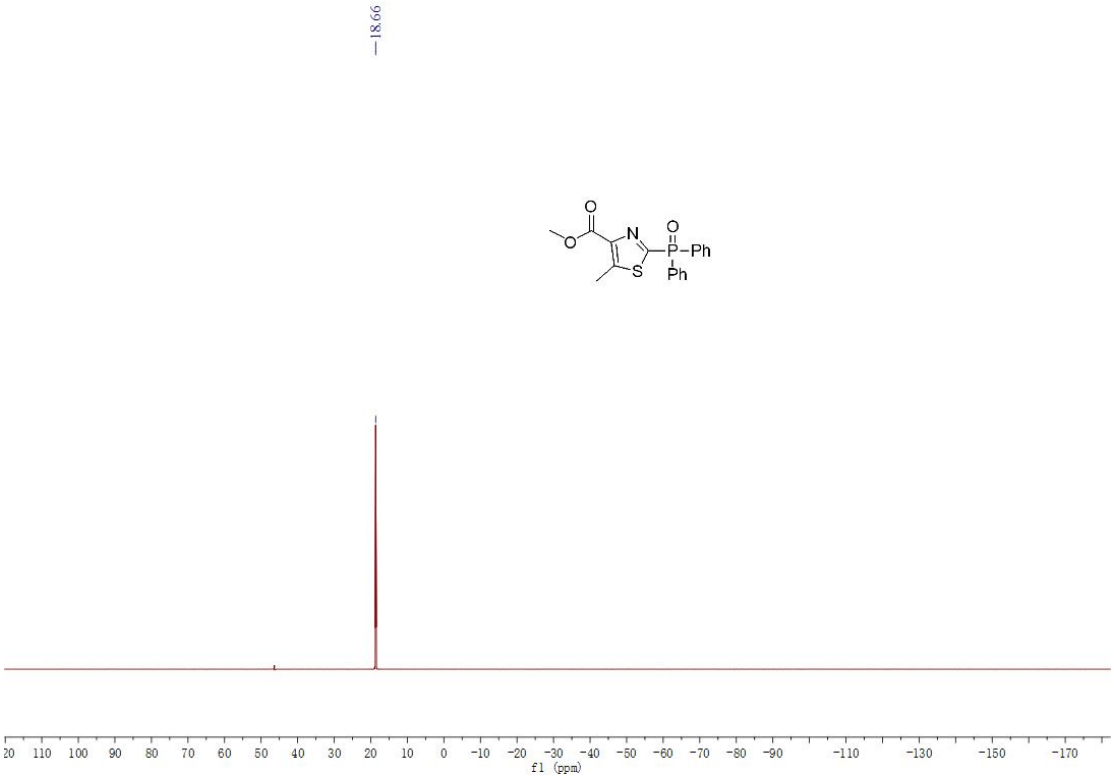
^{1}H NMR Spectrum of **3n**



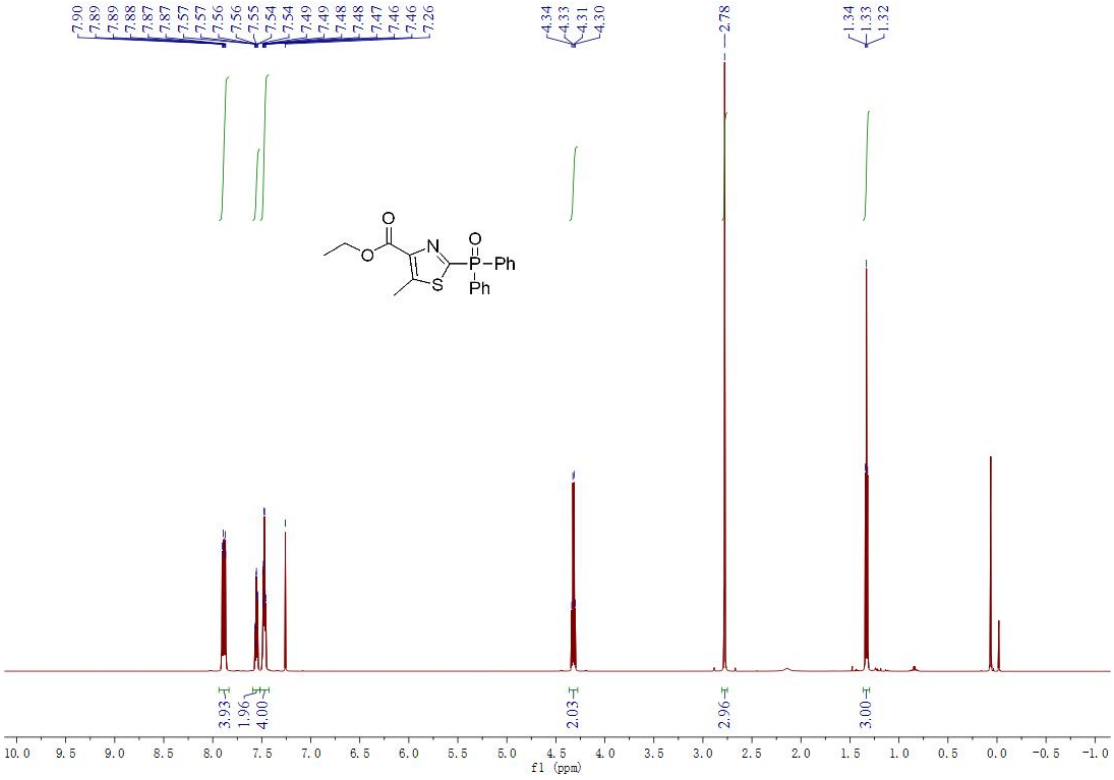
^{13}C NMR Spectrum of **3n**



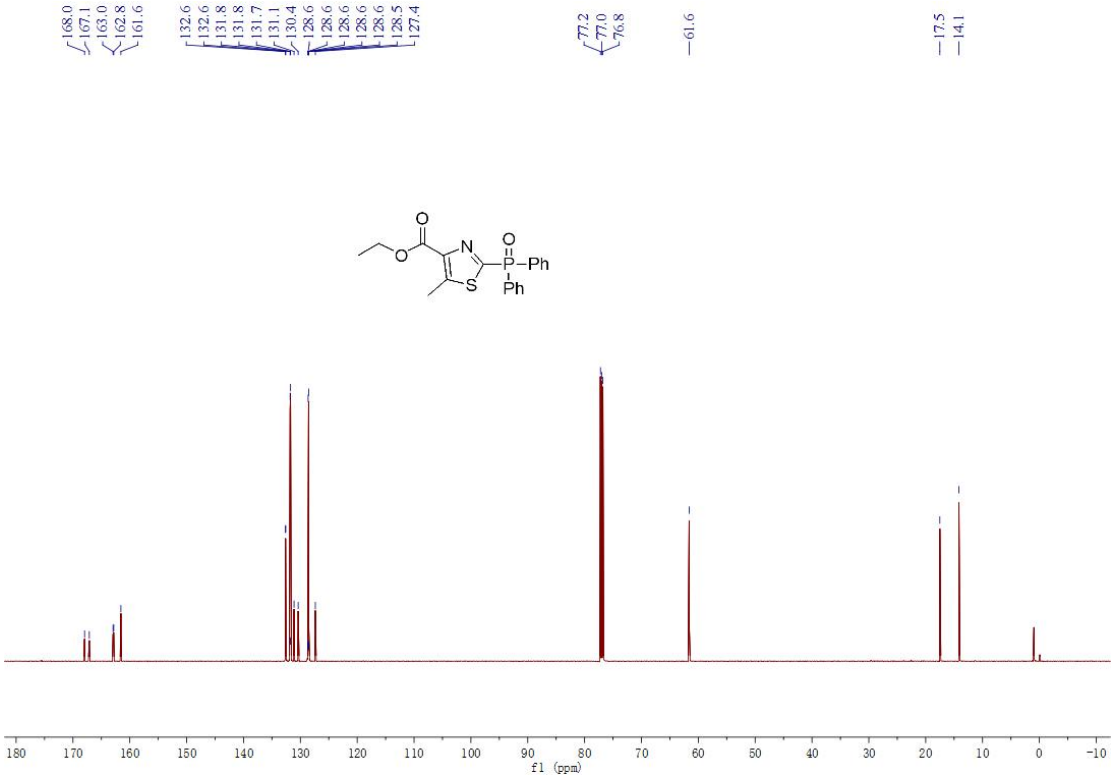
^{31}P NMR Spectrum of **3n**



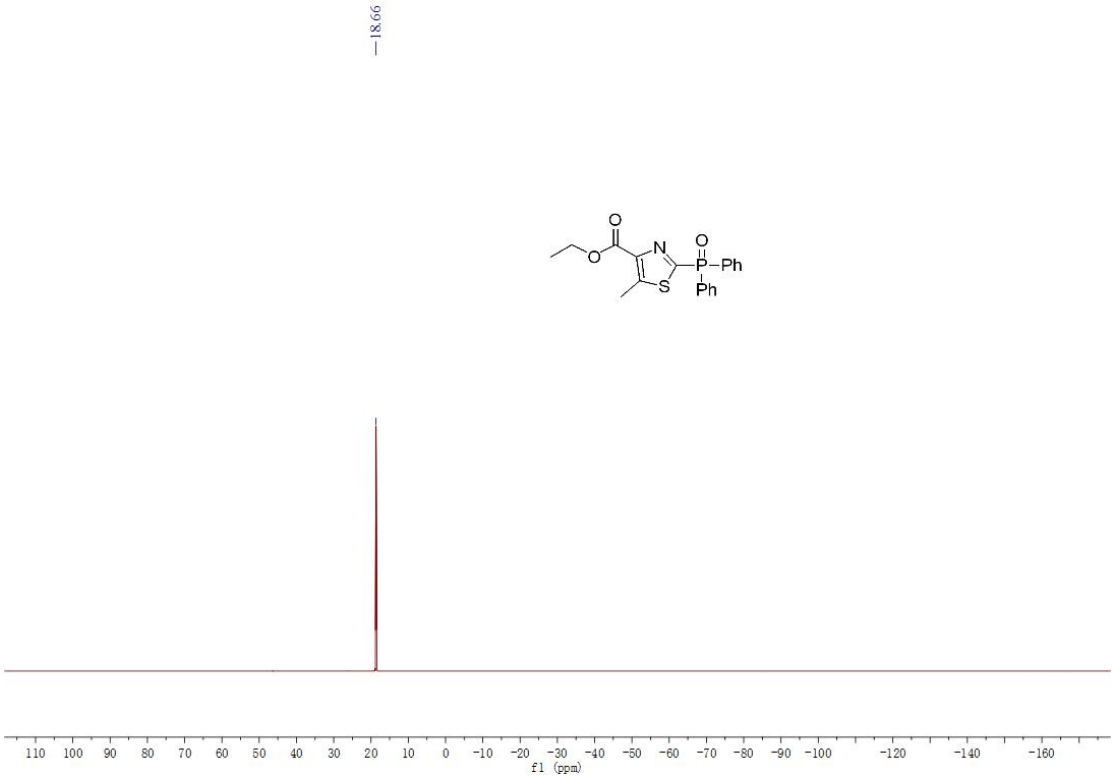
^{1}H NMR Spectrum of **3o**



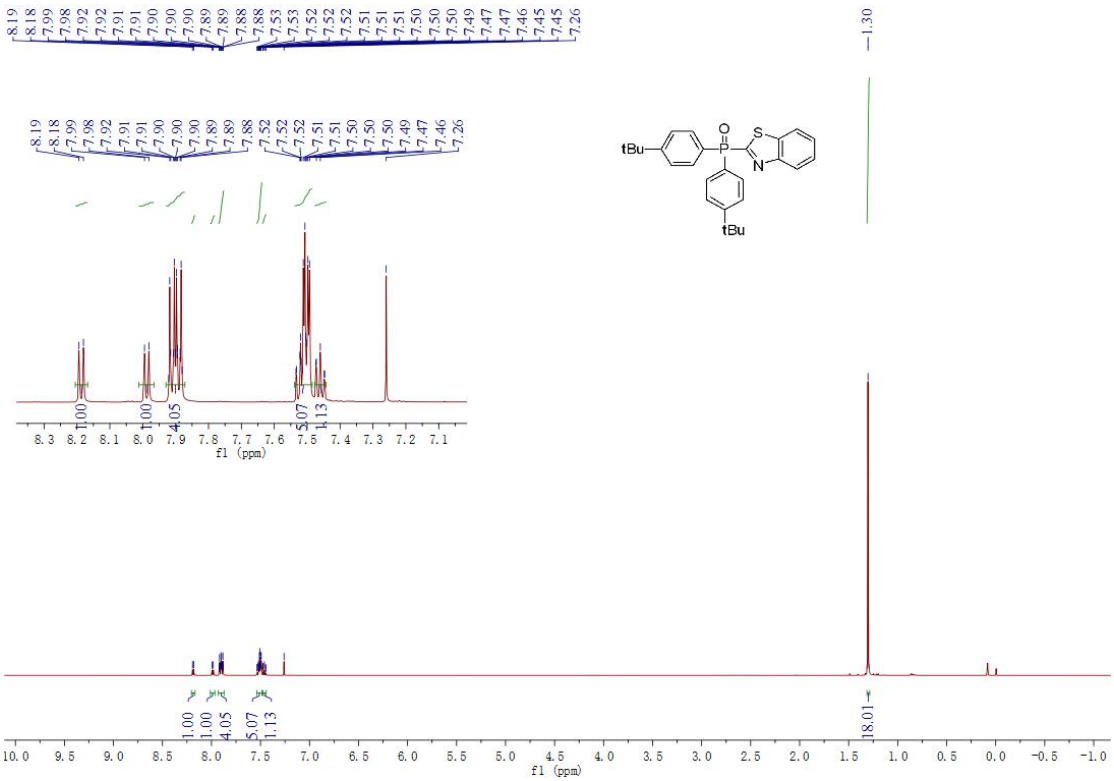
^{13}C NMR Spectrum of **3o**



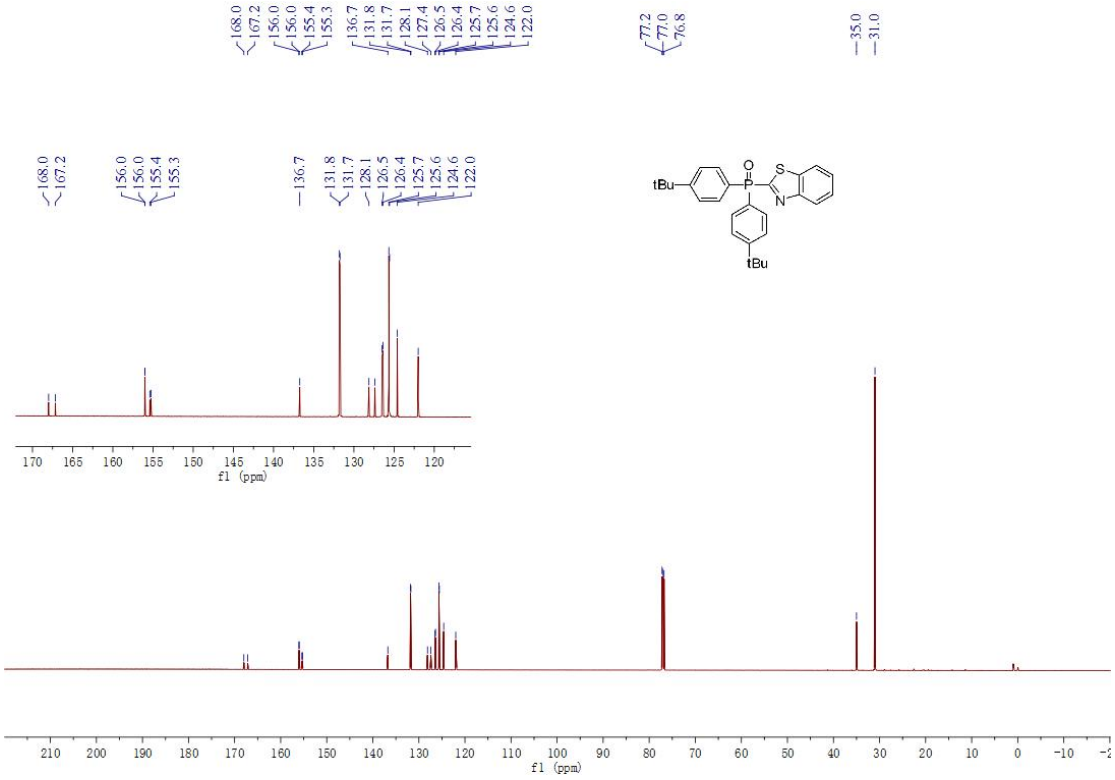
^{31}P NMR Spectrum of **3o**



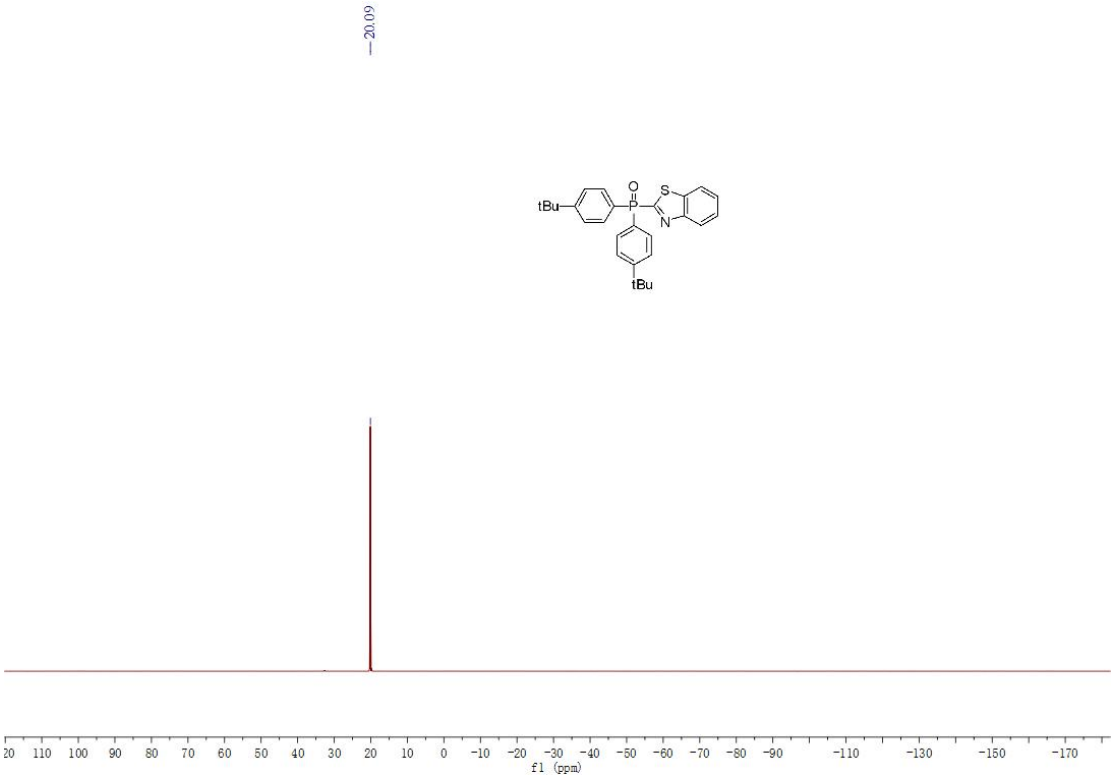
^{1}H NMR Spectrum of **3p**



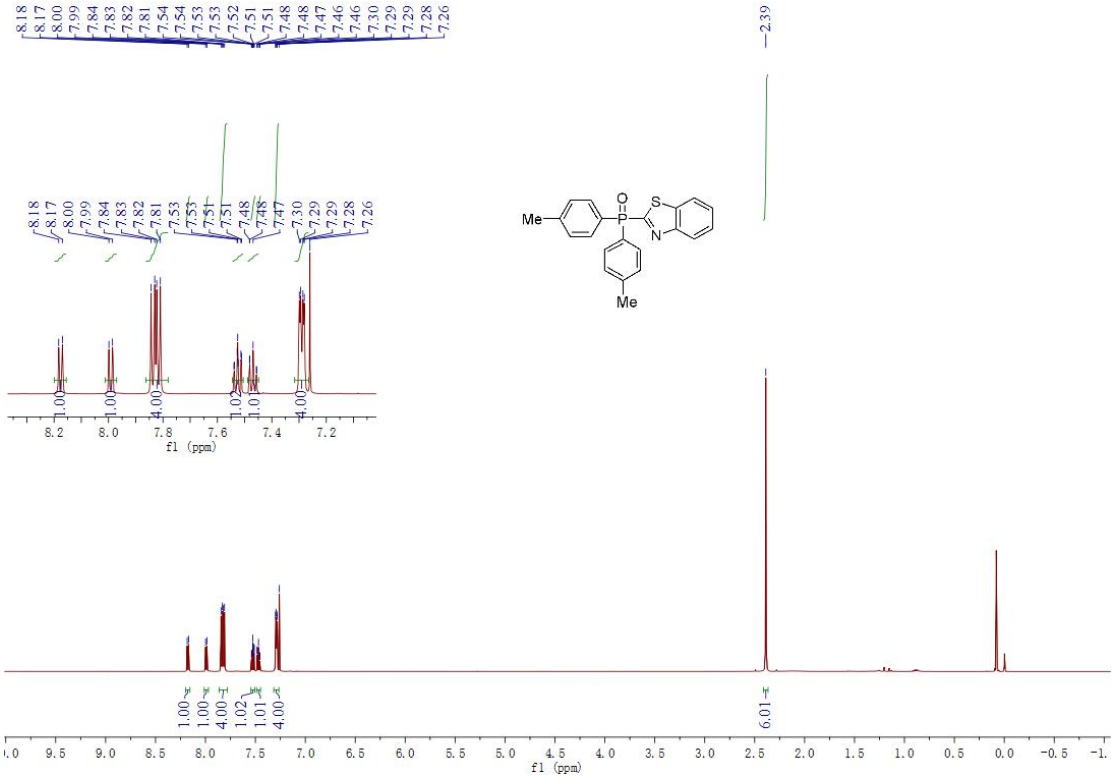
^{13}C NMR Spectrum of **3p**



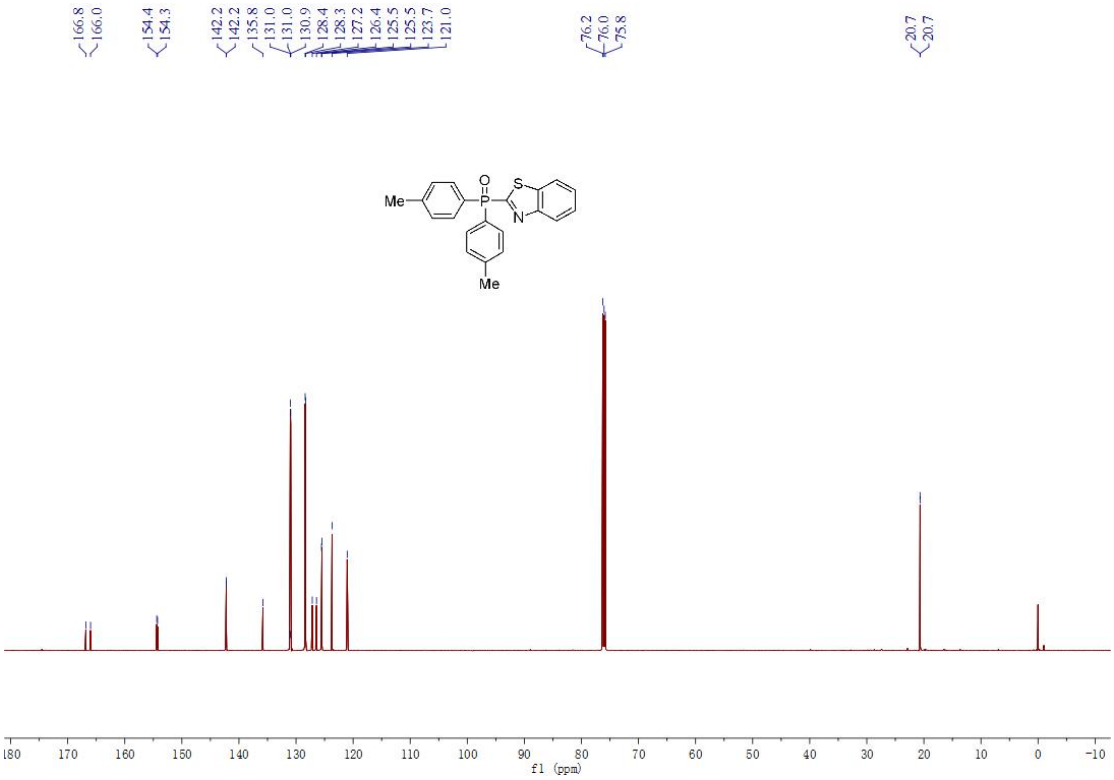
^{31}P NMR Spectrum of **3p**



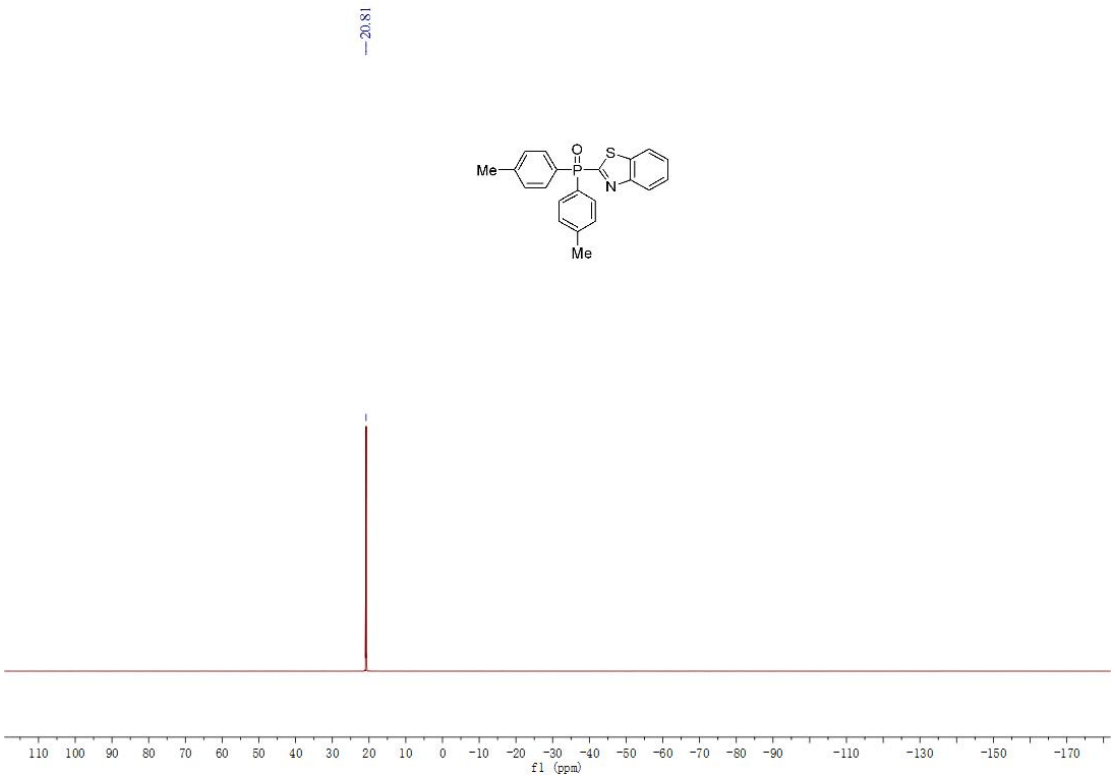
^{1}H NMR Spectrum of **3q**



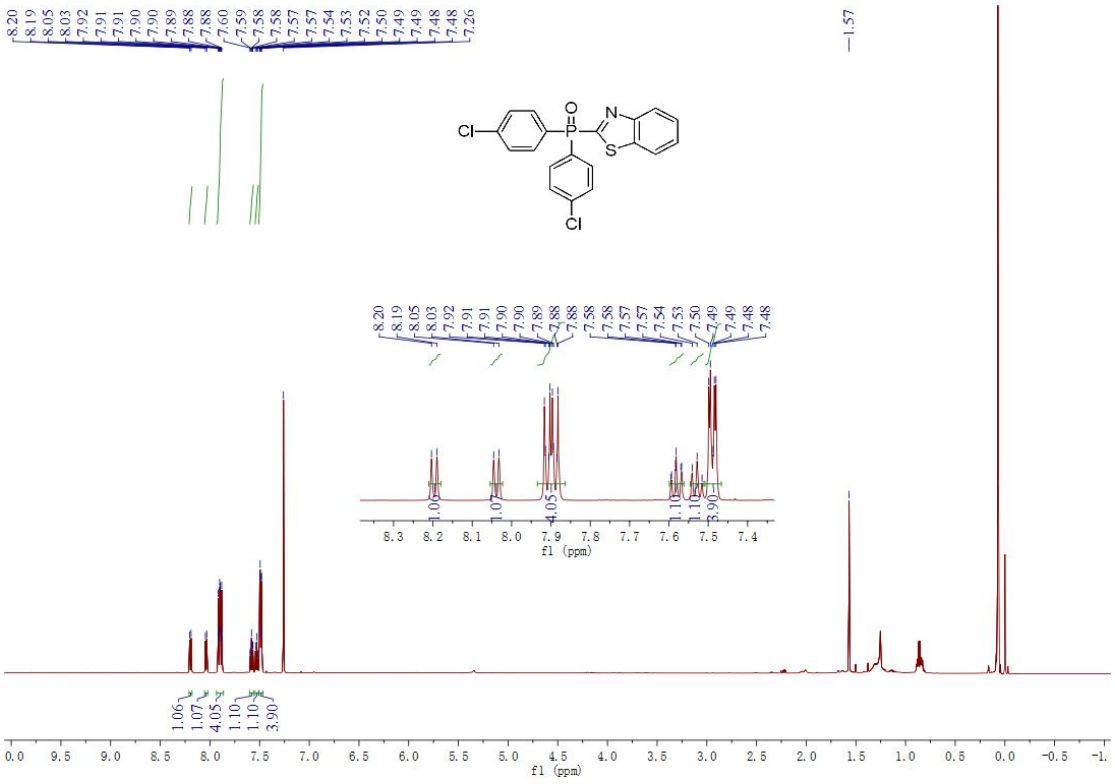
^{13}C NMR Spectrum of **3q**



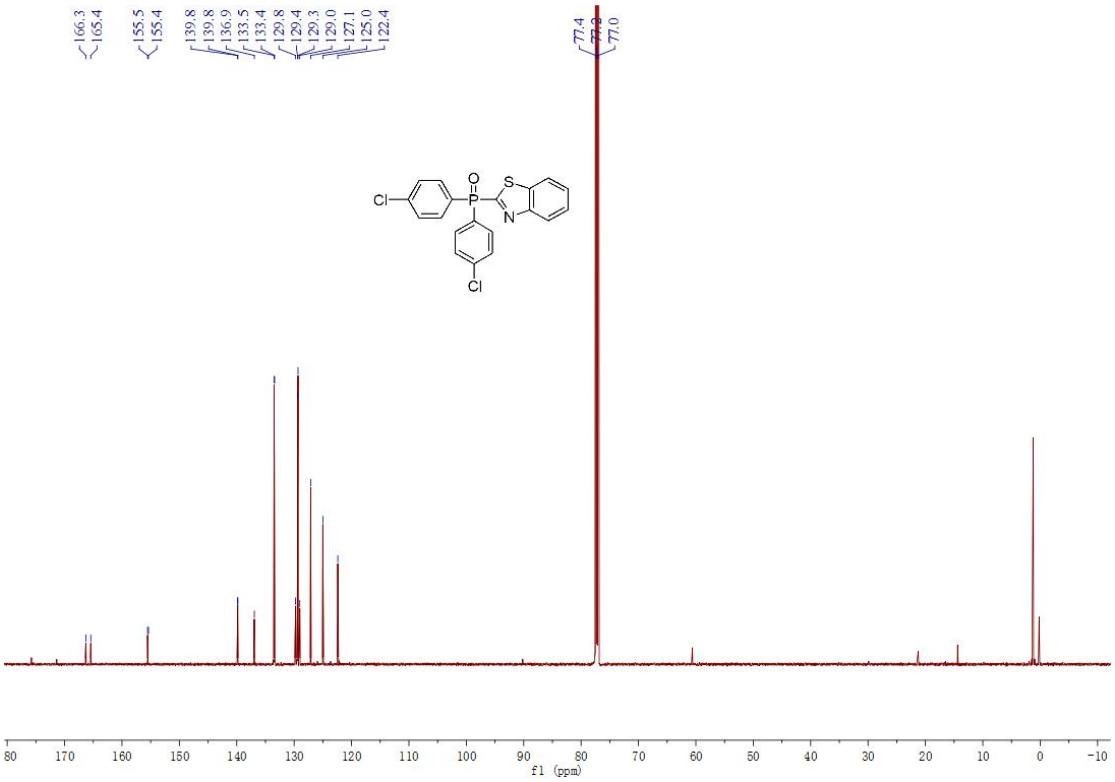
^{31}P NMR Spectrum of **3q**



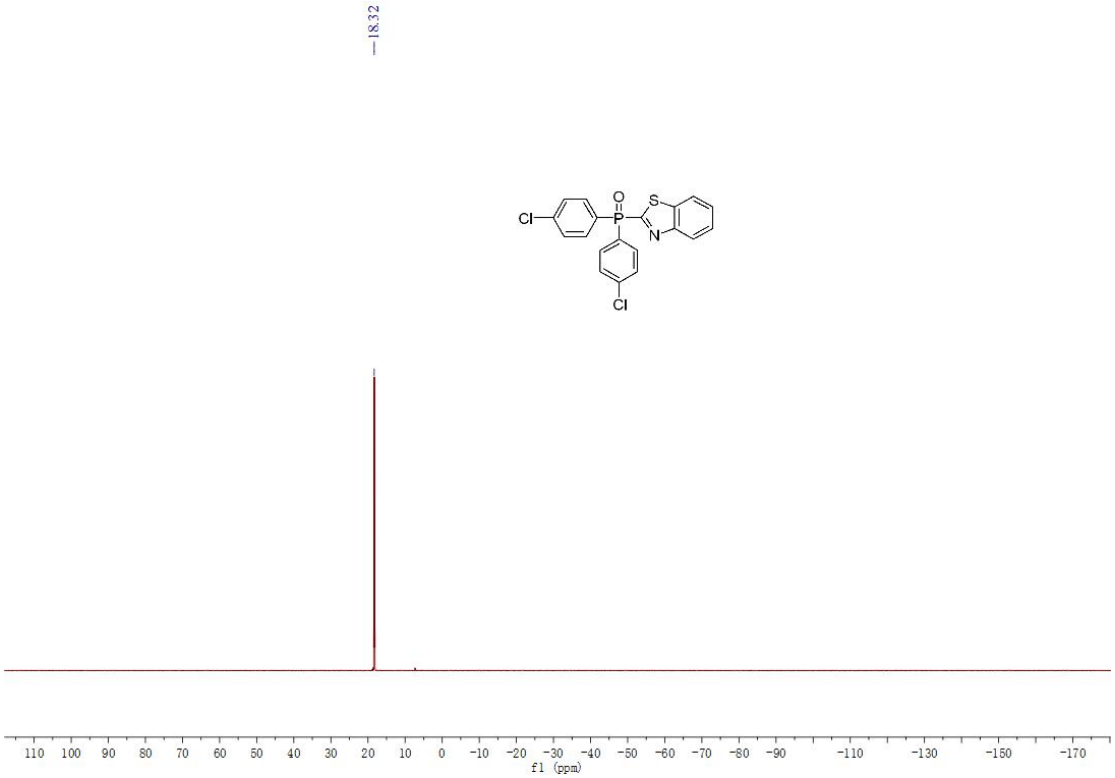
^{1}H NMR Spectrum of **3r**



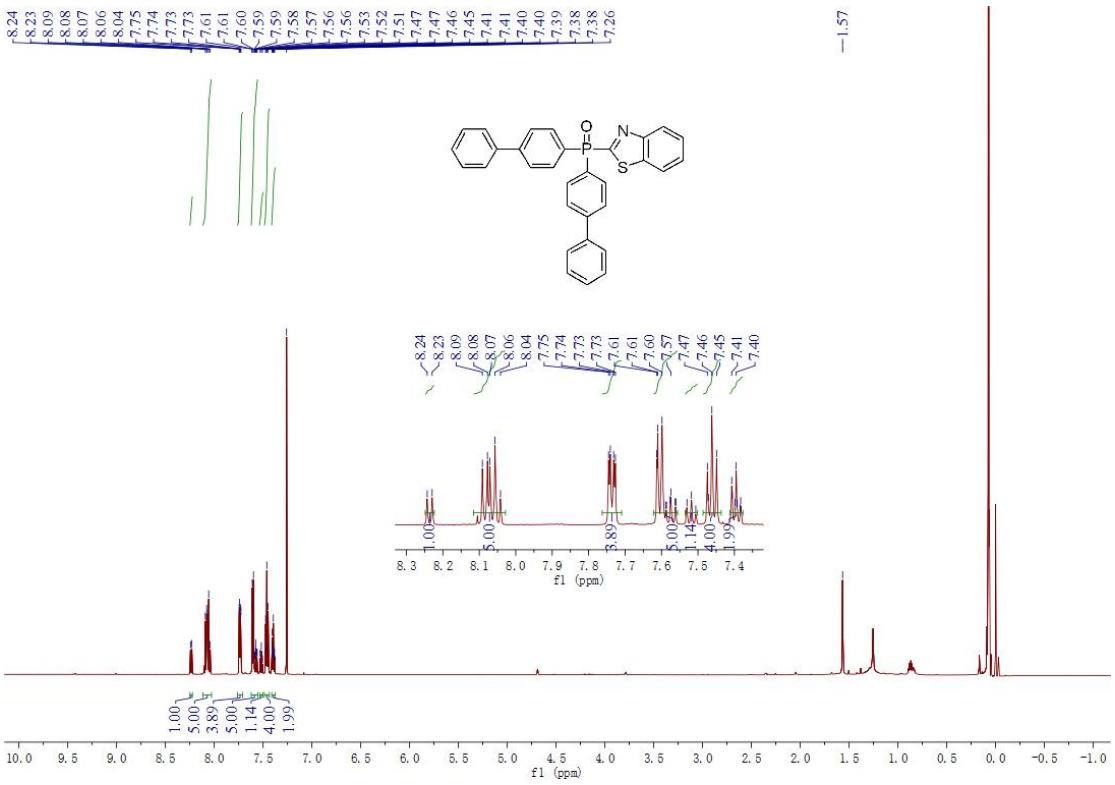
^{13}C NMR Spectrum of **3r**



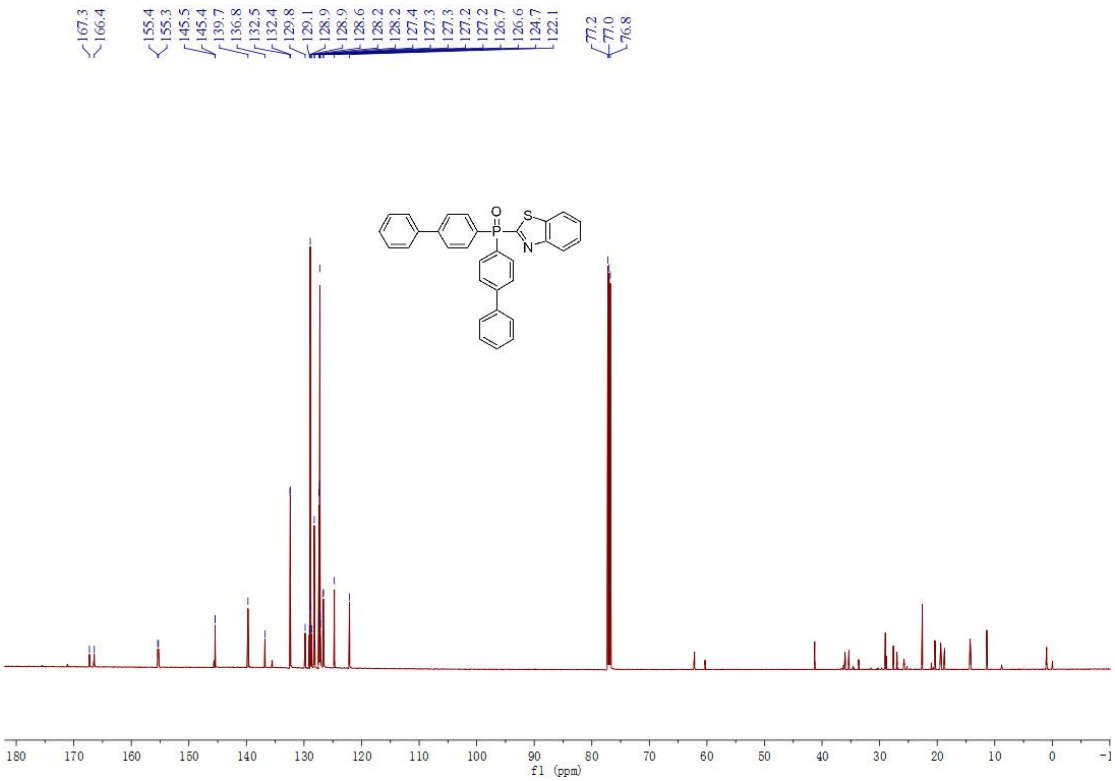
^{31}P NMR Spectrum of **3r**



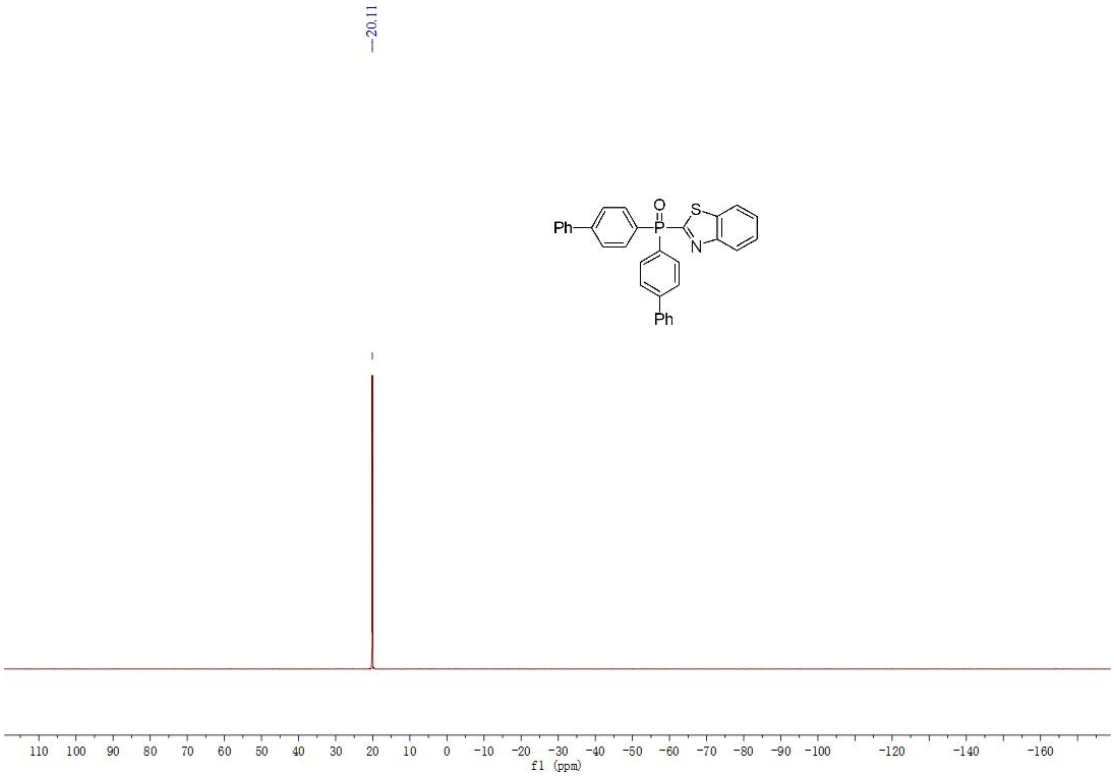
^{1}H NMR Spectrum of **3s**



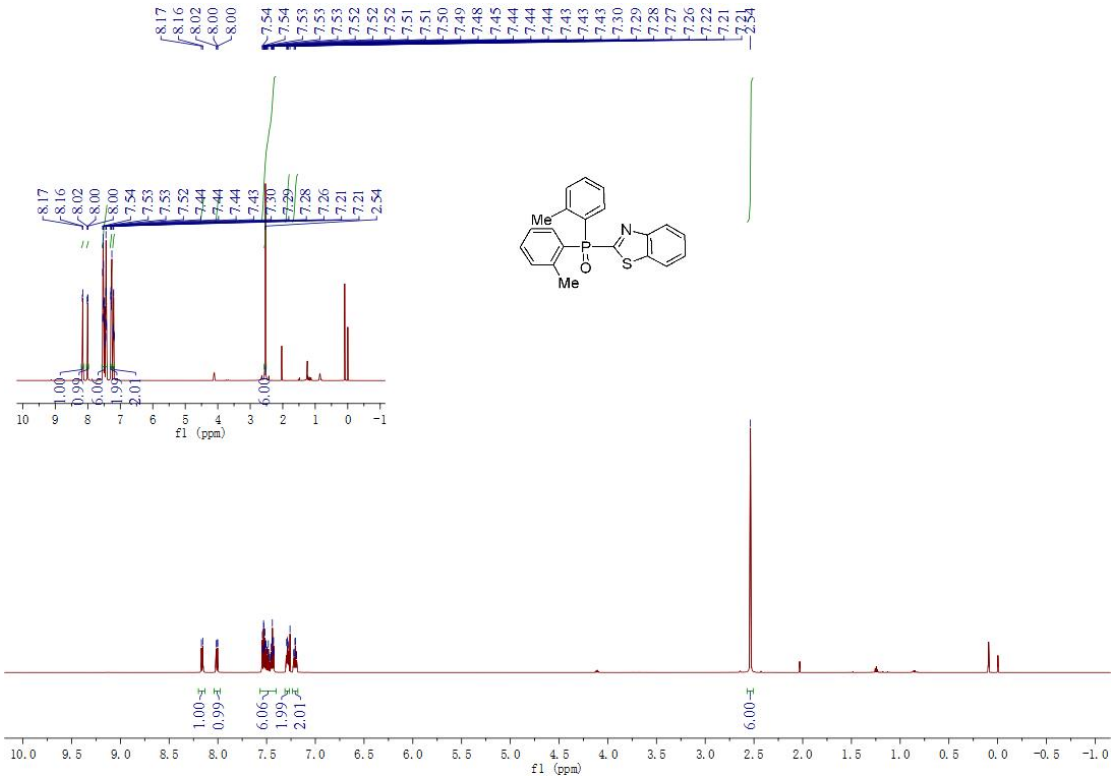
^{13}C NMR Spectrum of **3s**



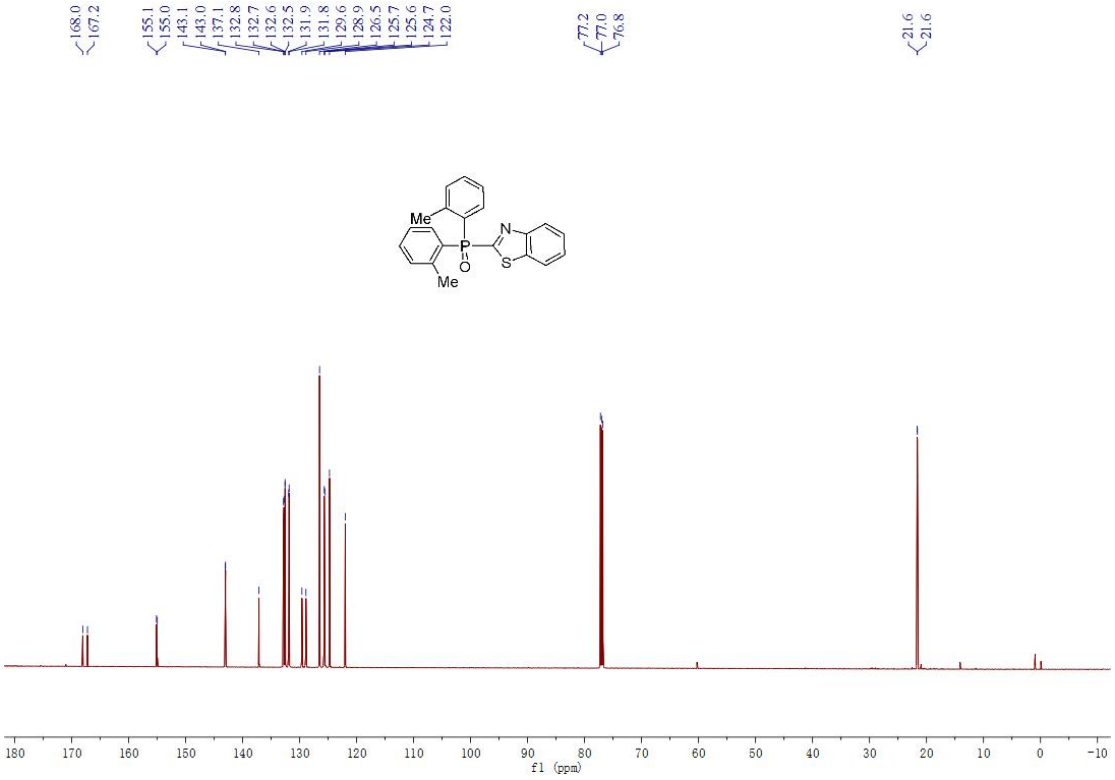
^{31}P NMR Spectrum of **3s**



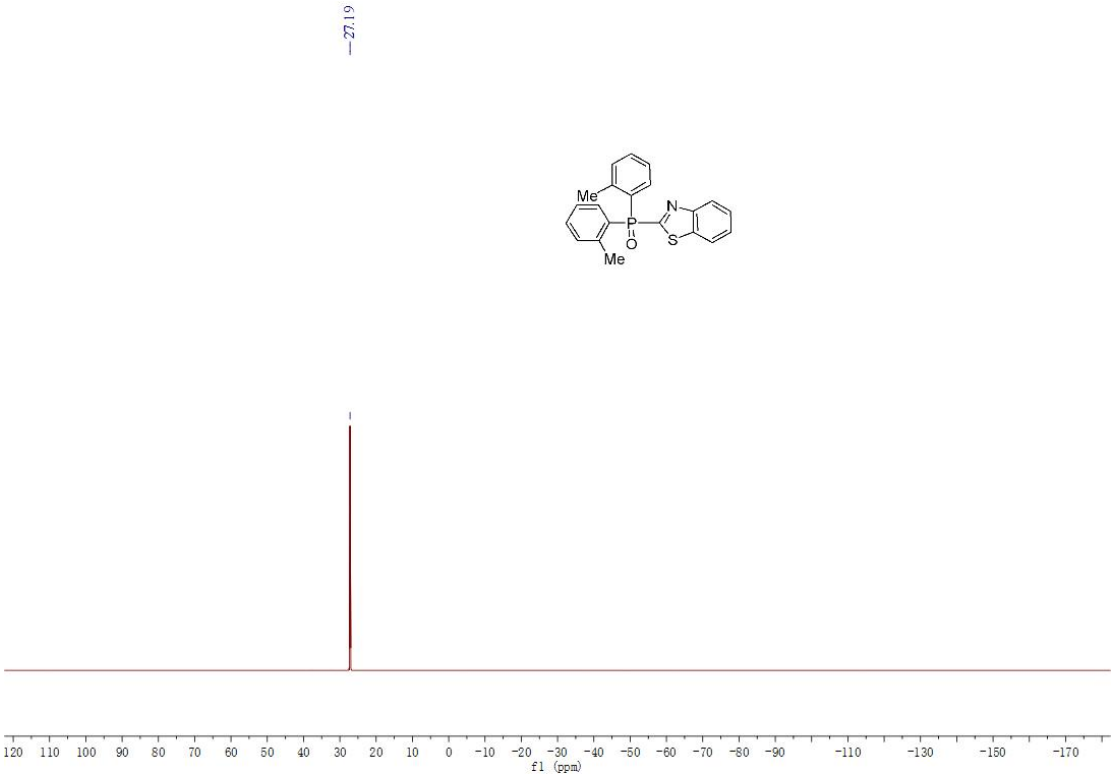
^{1}H NMR Spectrum of **3t**



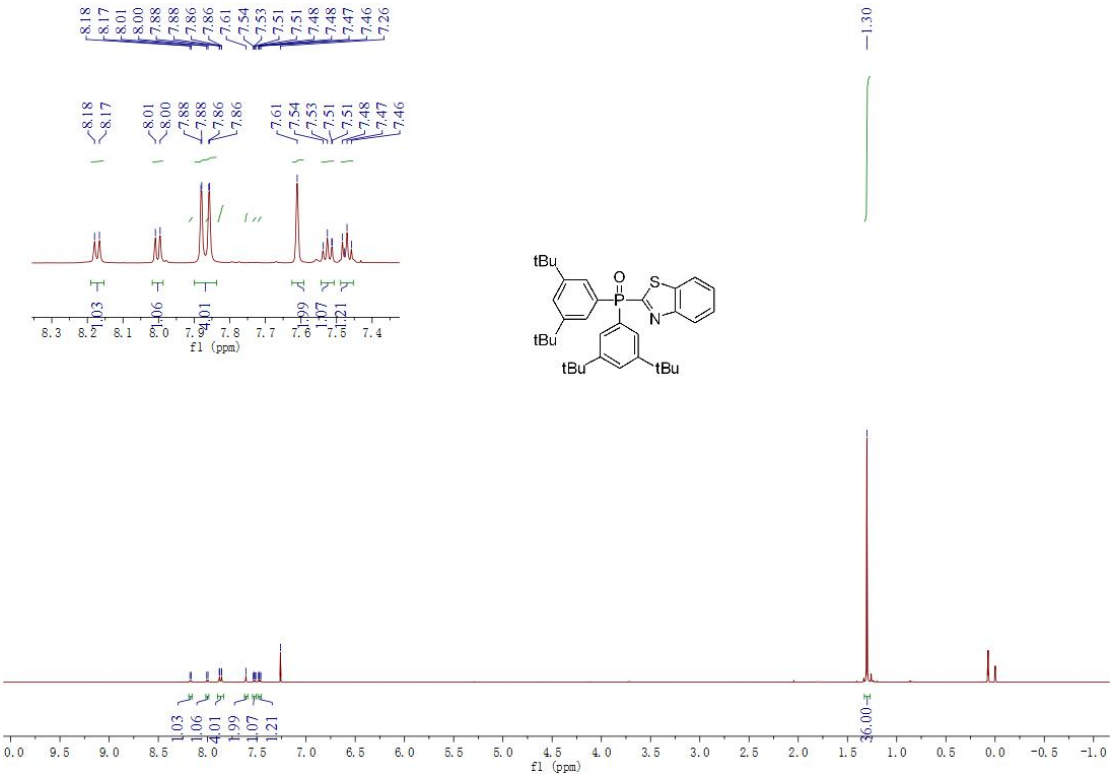
^{13}C NMR Spectrum of **3t**



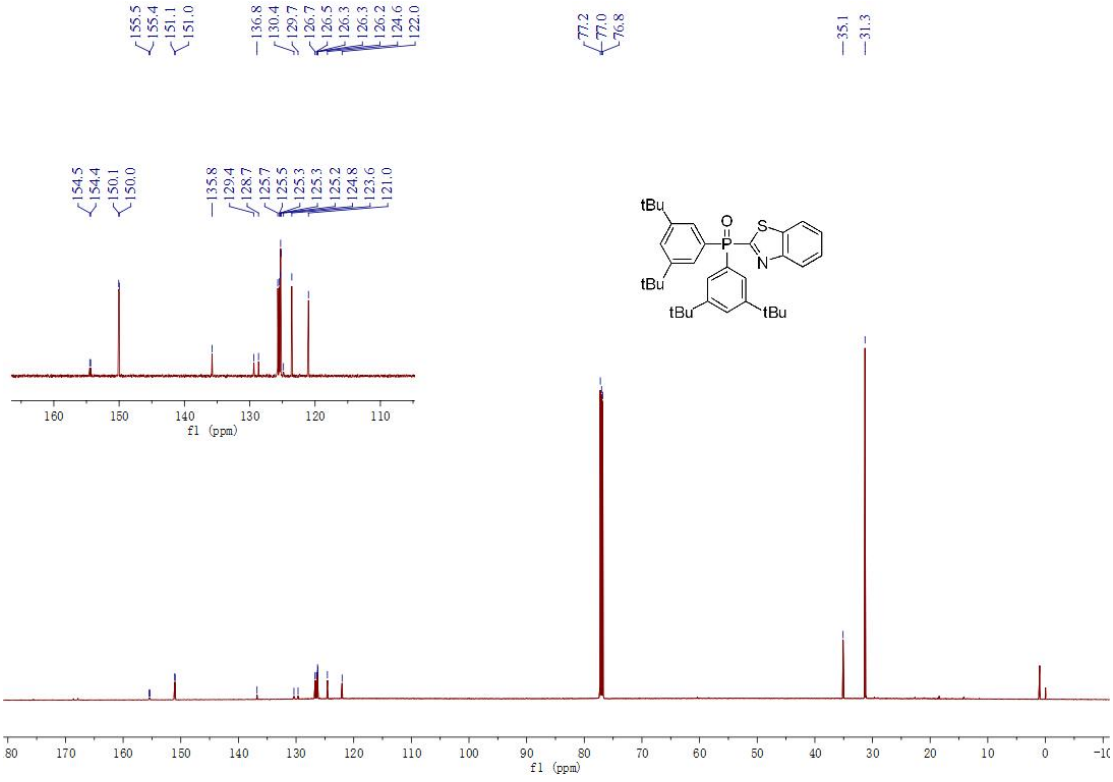
^{31}P NMR Spectrum of **3t**



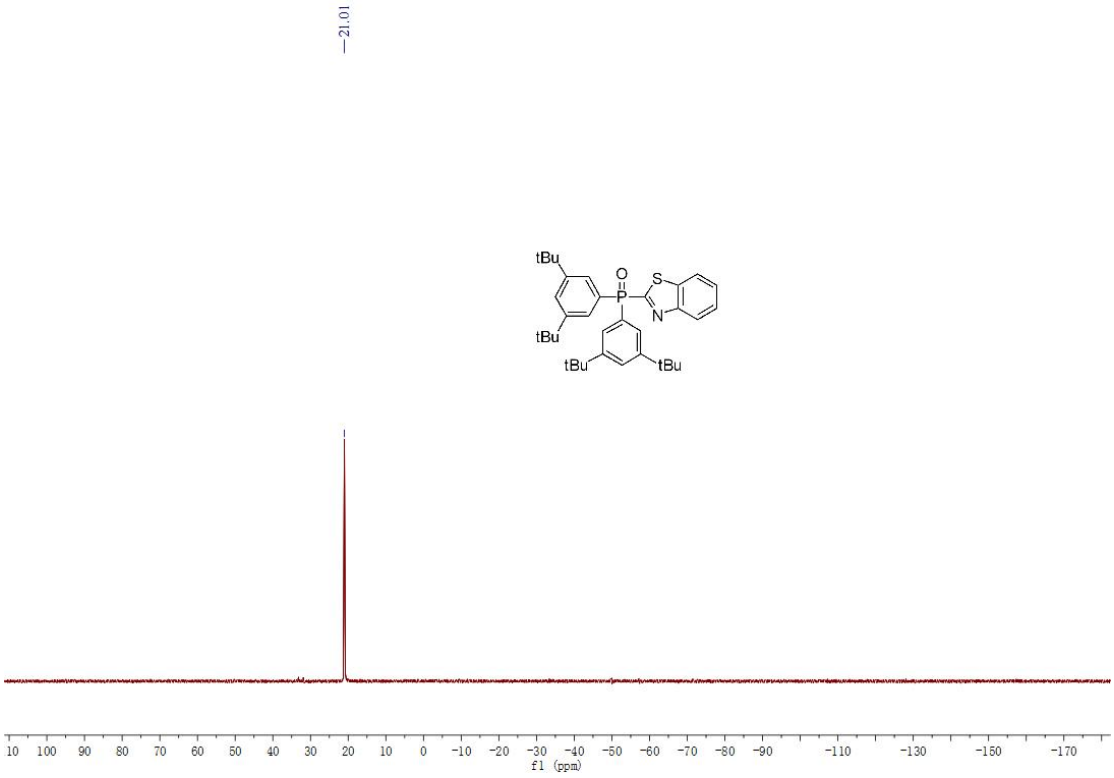
^{1}H NMR Spectrum of **3u**



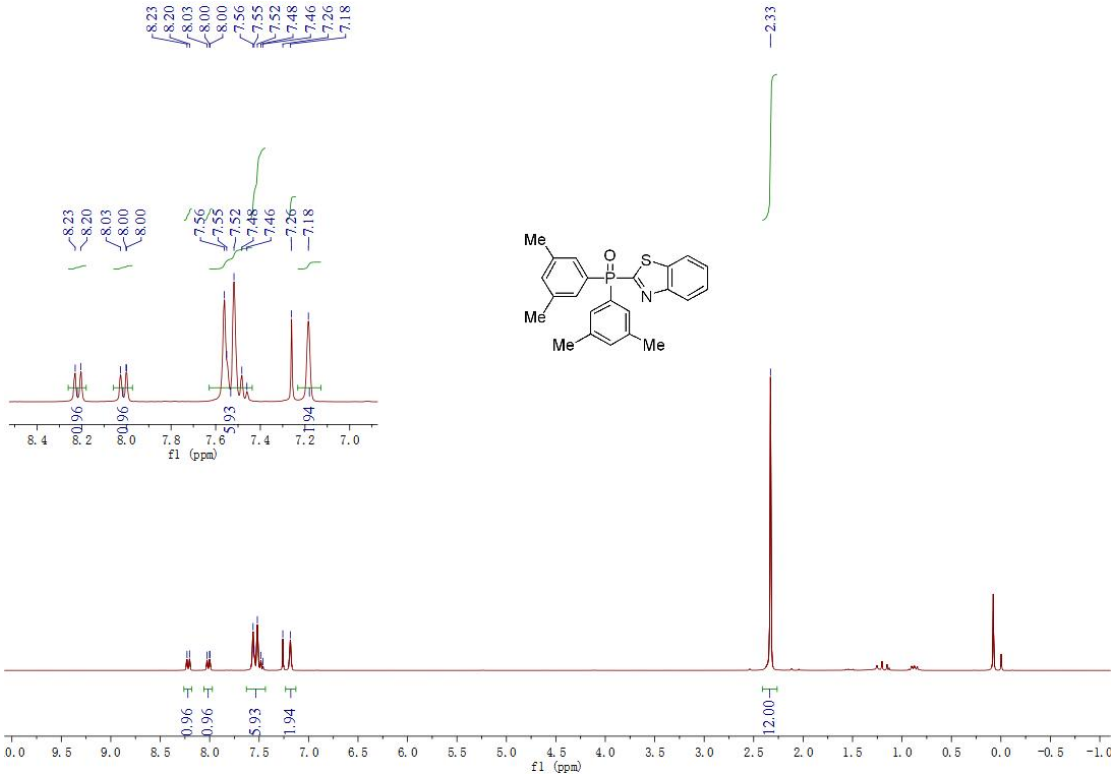
^{13}C NMR Spectrum of **3u**



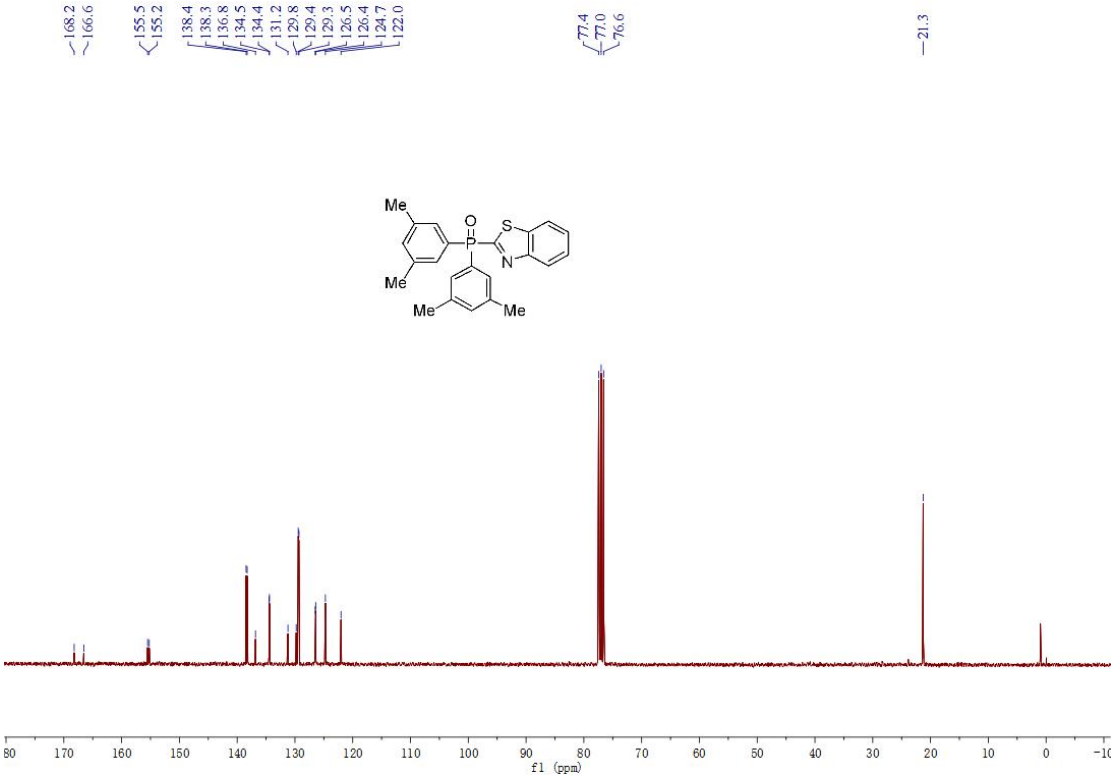
^{31}P NMR Spectrum of **3u**



^{1}H NMR Spectrum of **3v**

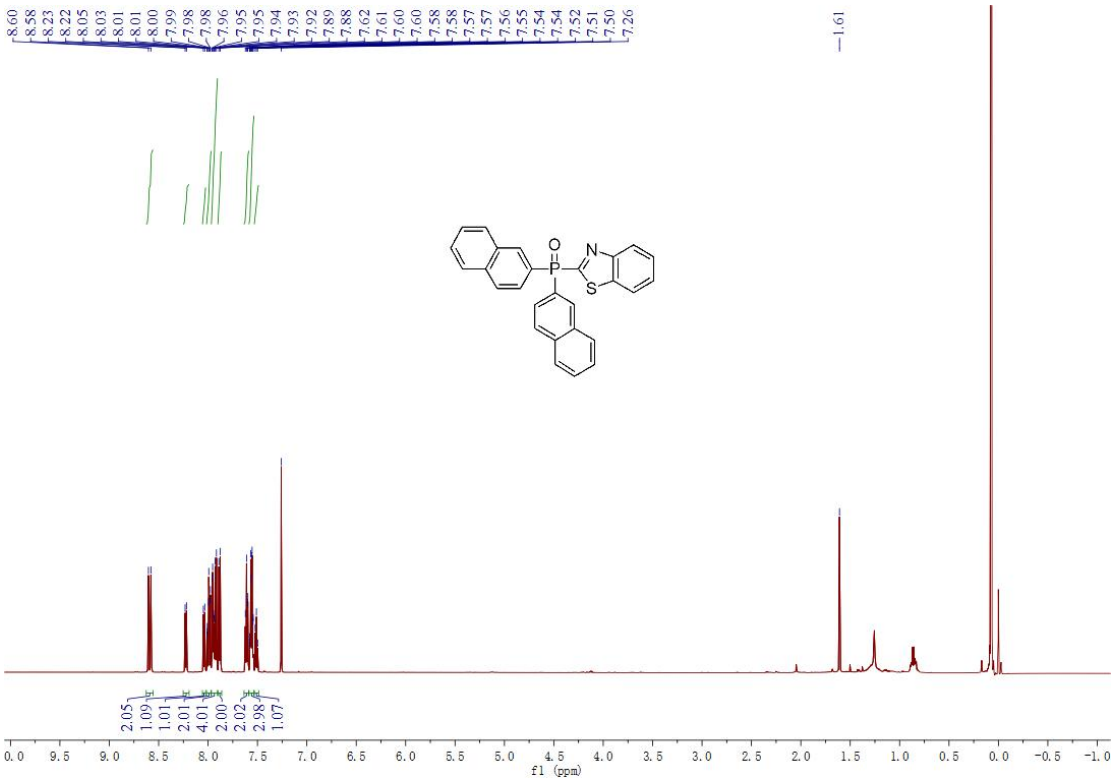


^{13}C NMR Spectrum of **3v**

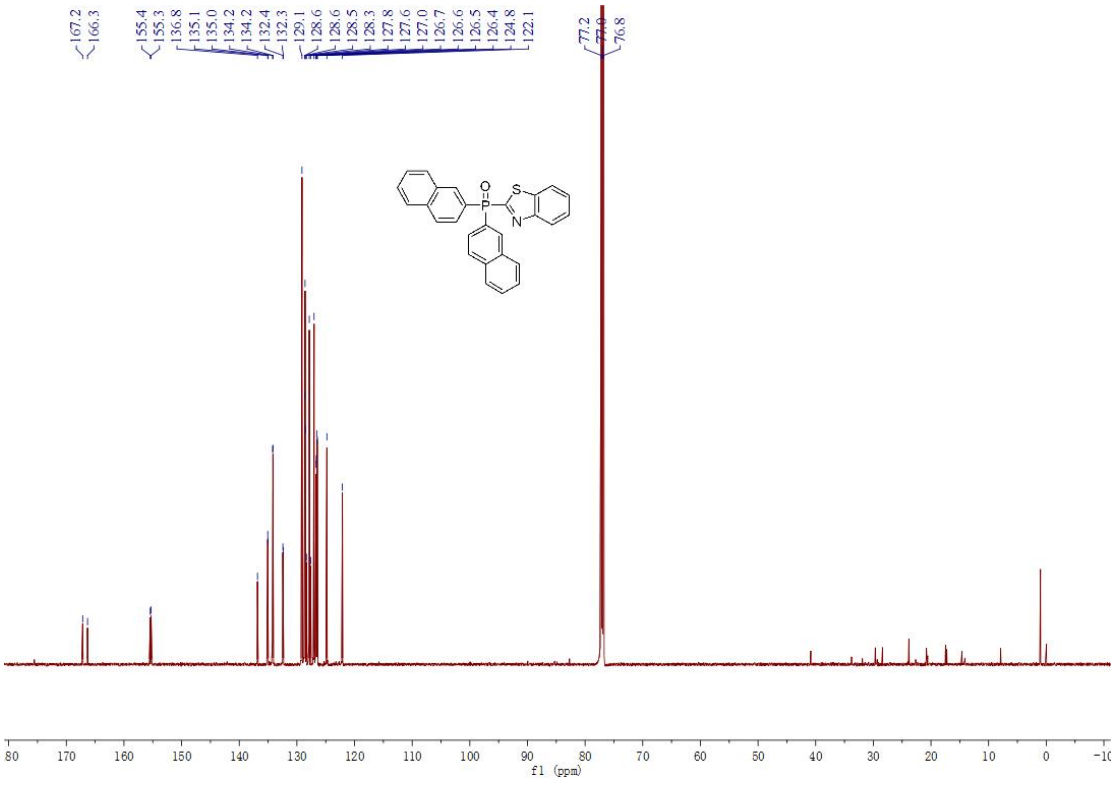


^{31}P NMR Spectrum of **3v**

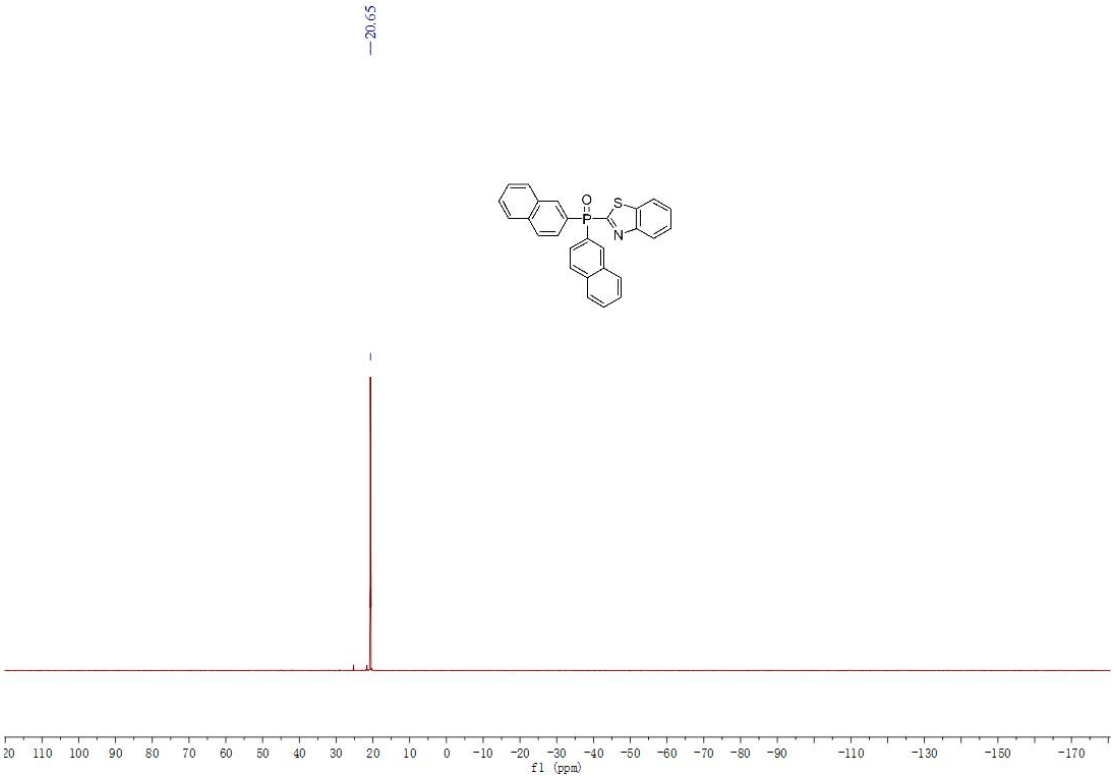
^{1}H NMR Spectrum of **3w**



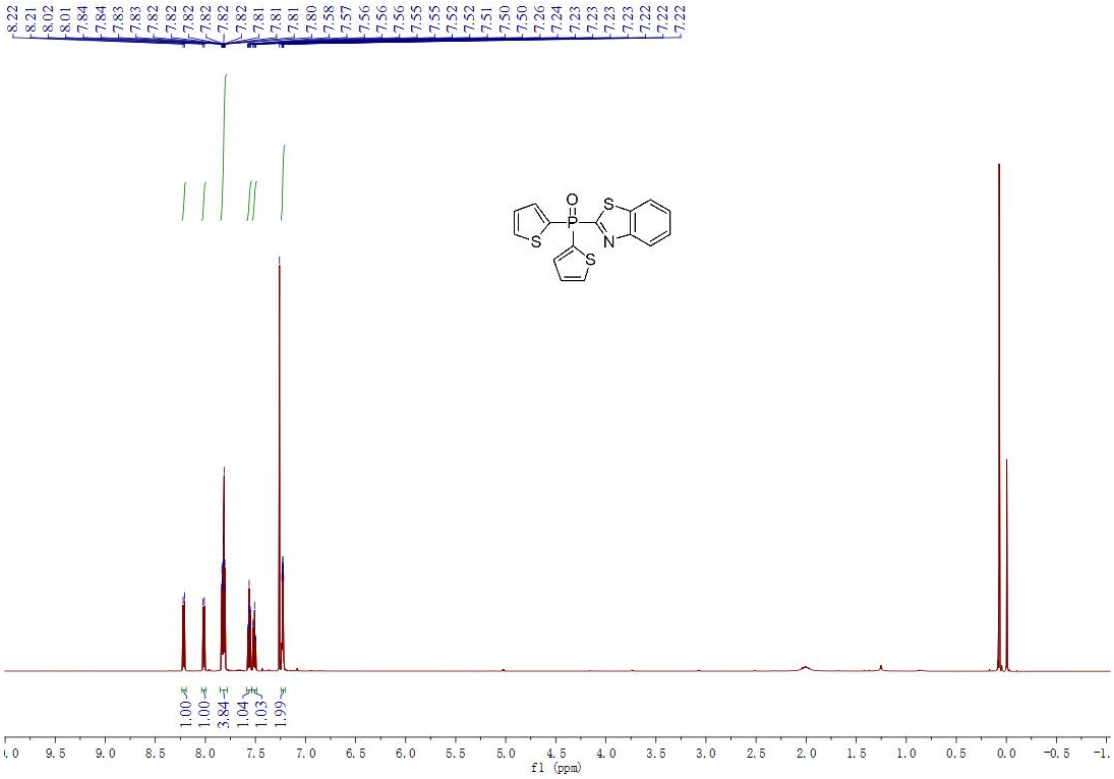
^{13}C NMR Spectrum of **3w**



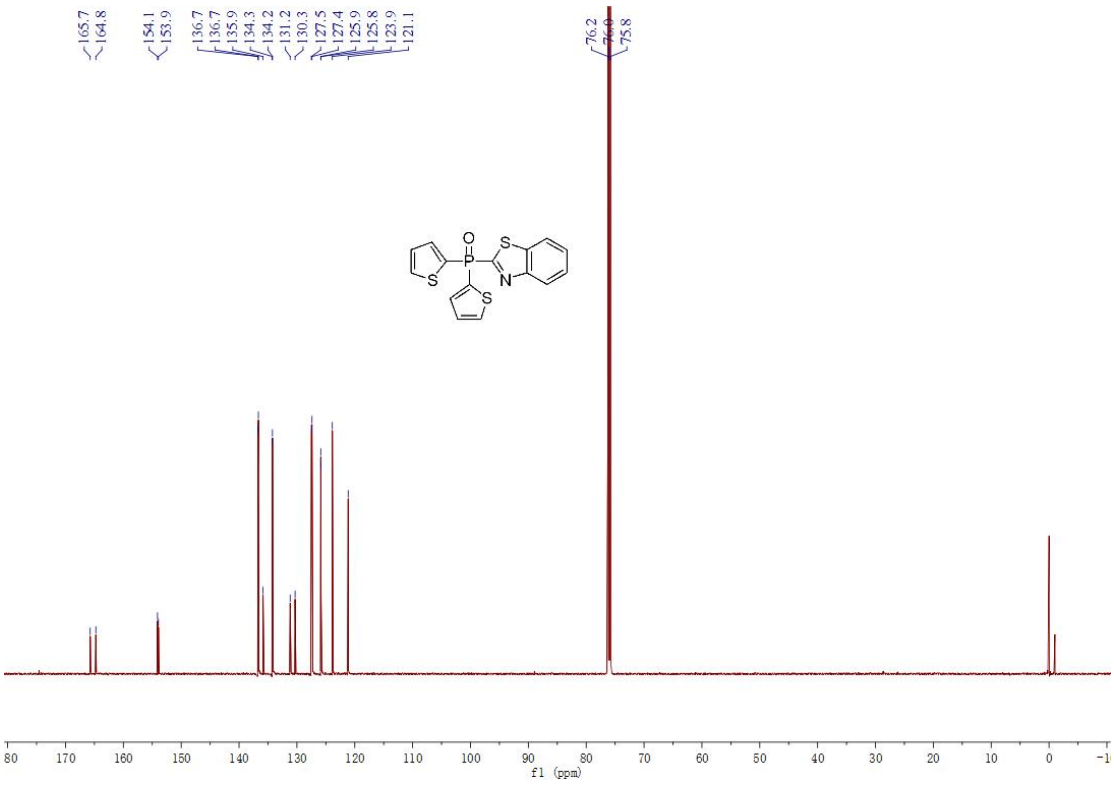
^{31}P NMR Spectrum of **3w**



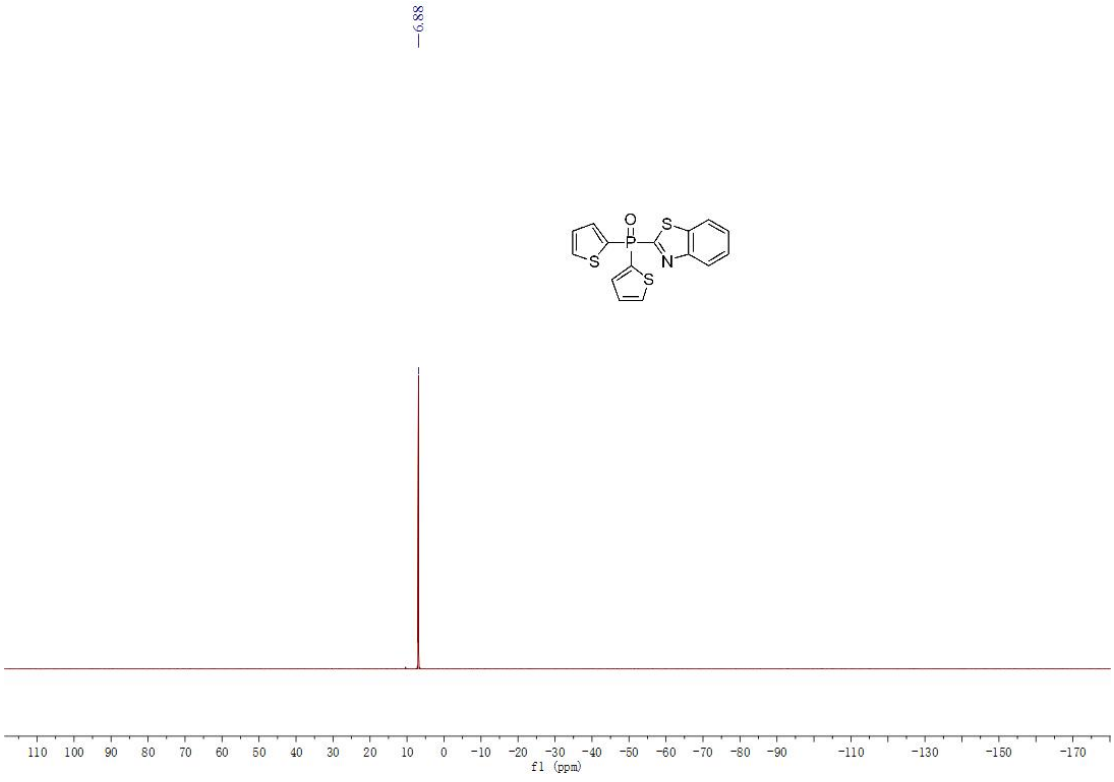
^{1}H NMR Spectrum of **3x**



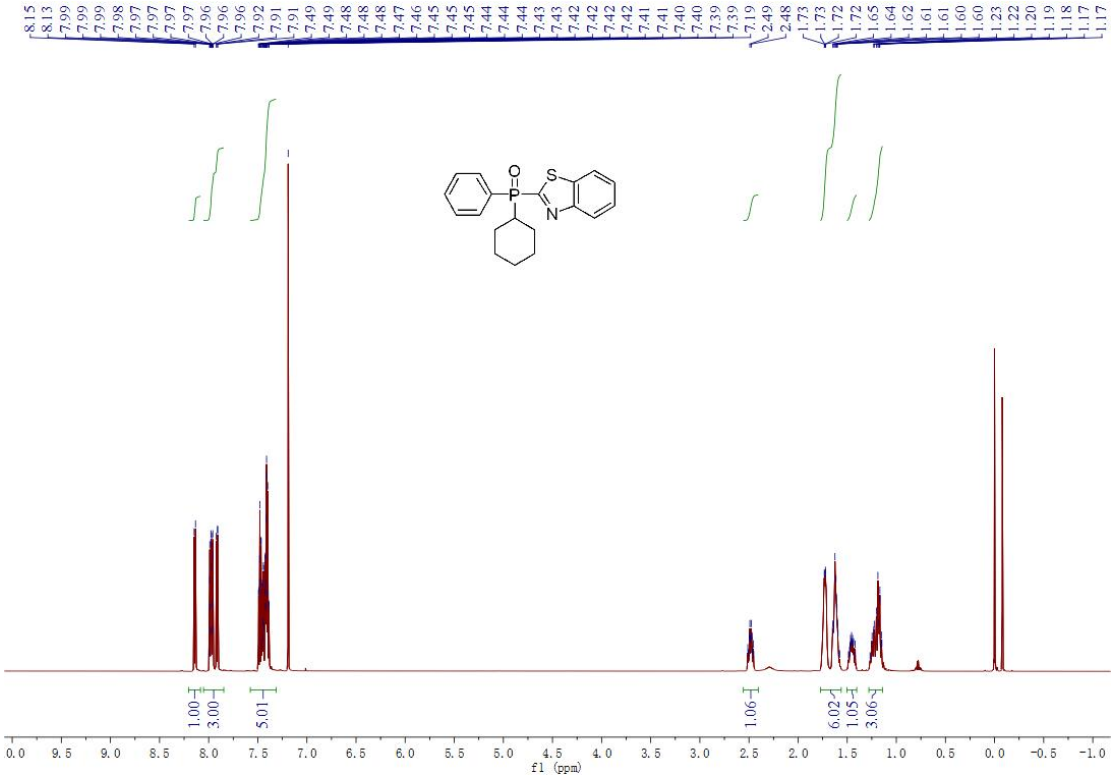
^{13}C NMR Spectrum of **3x**



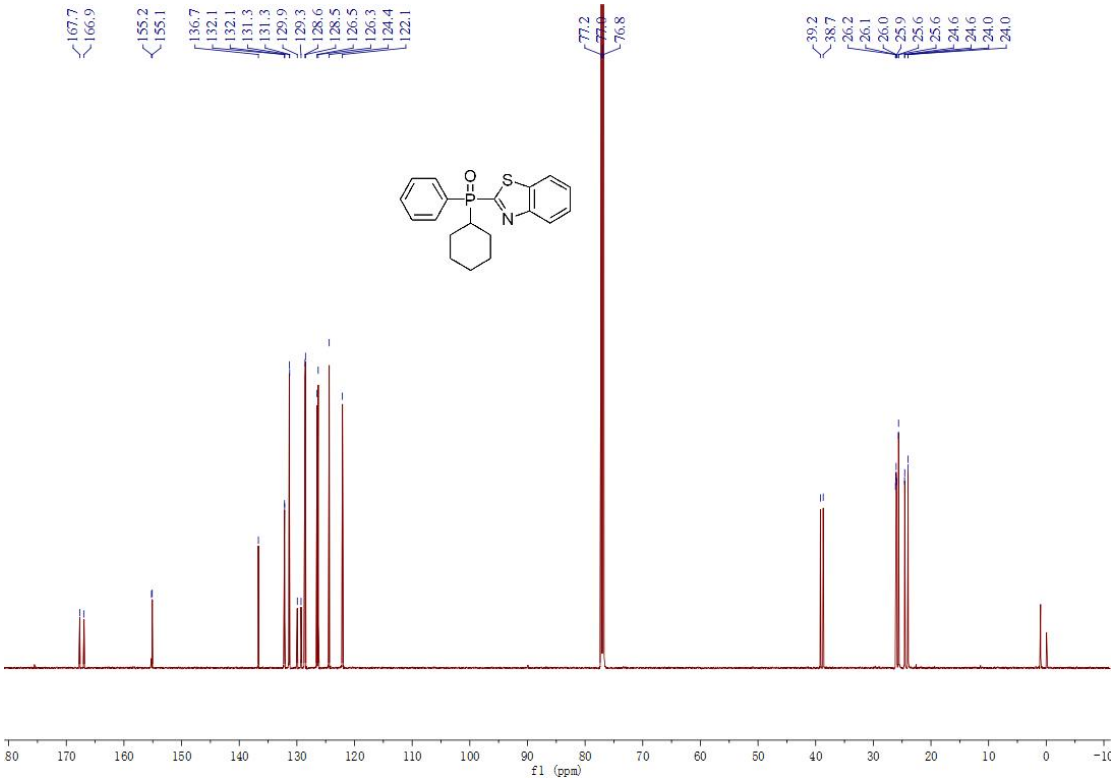
^{31}P NMR Spectrum of **3x**



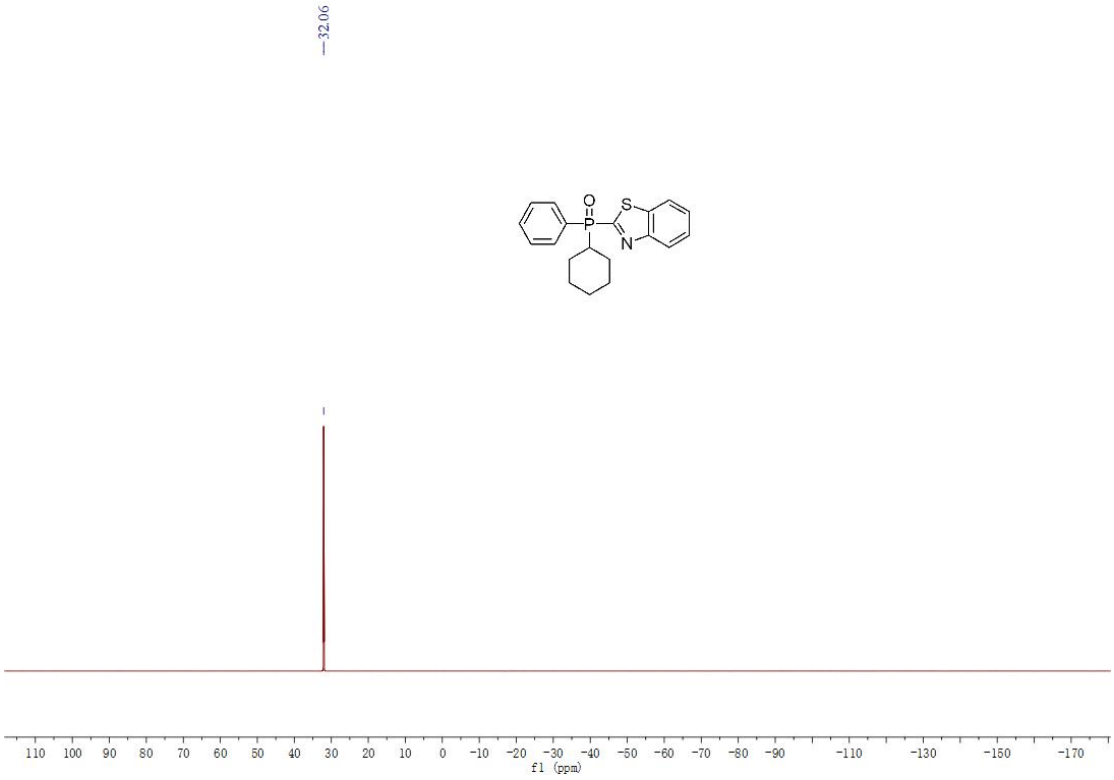
^{1}H NMR Spectrum of **3y**



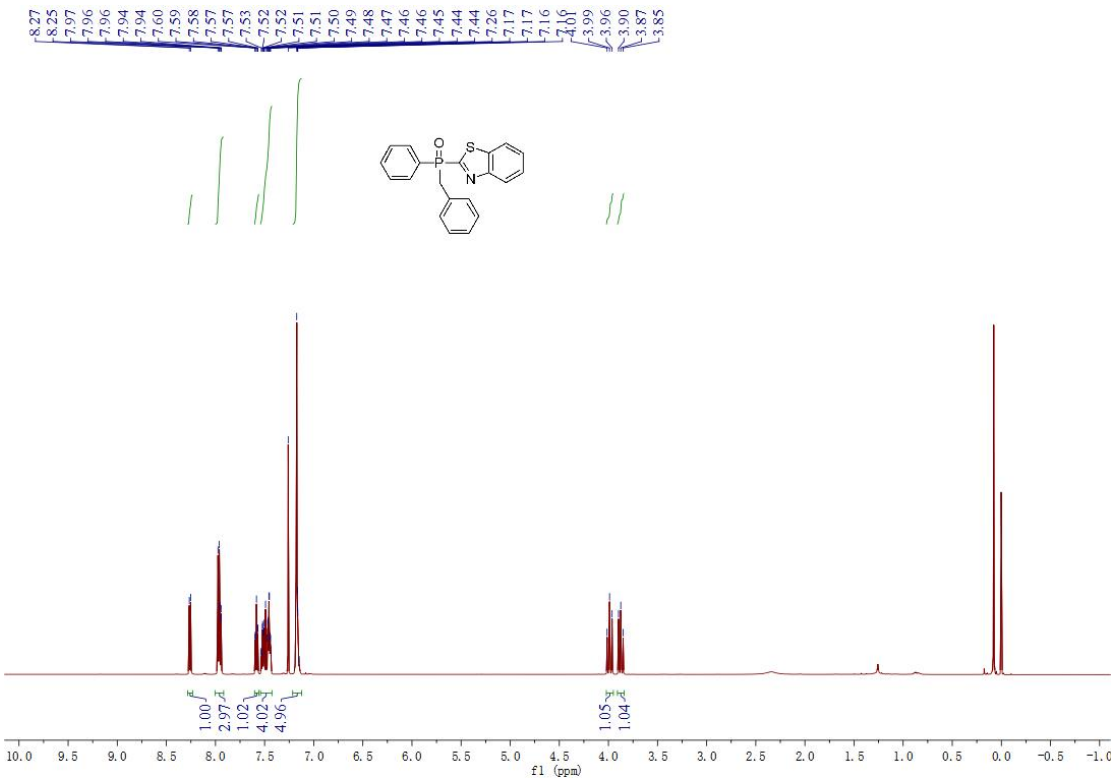
^{13}C NMR Spectrum of **3y**



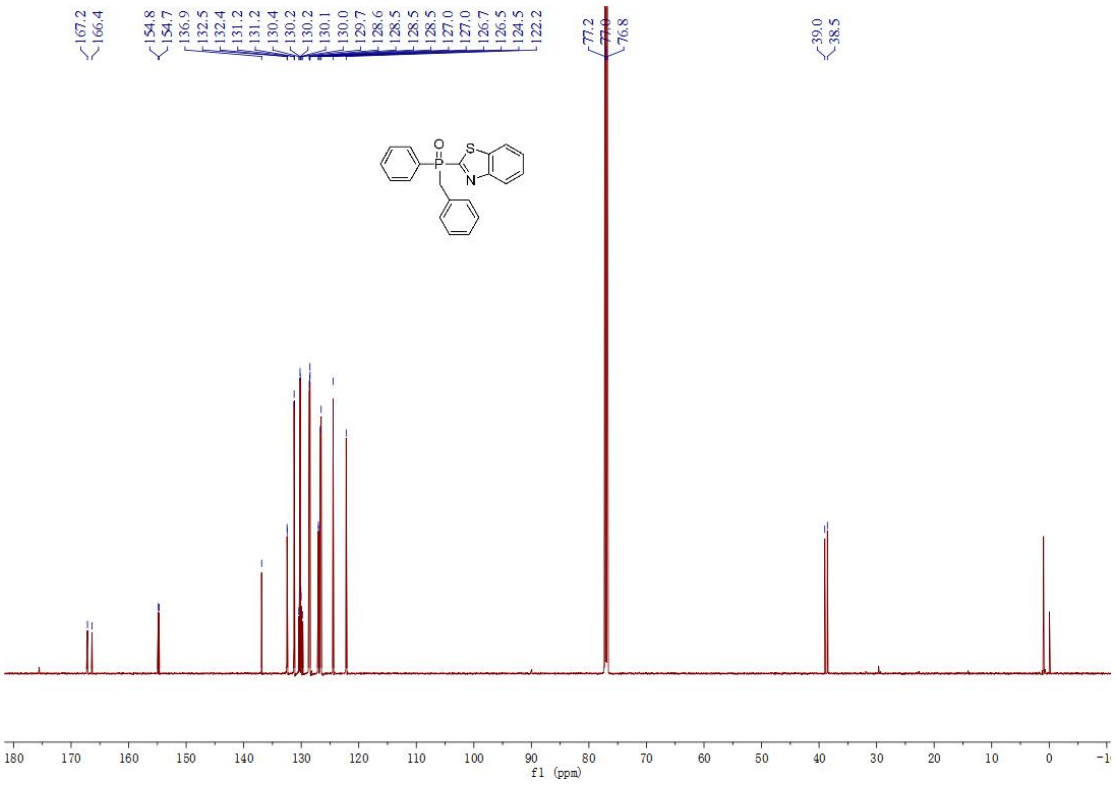
^{31}P NMR Spectrum of **3y**



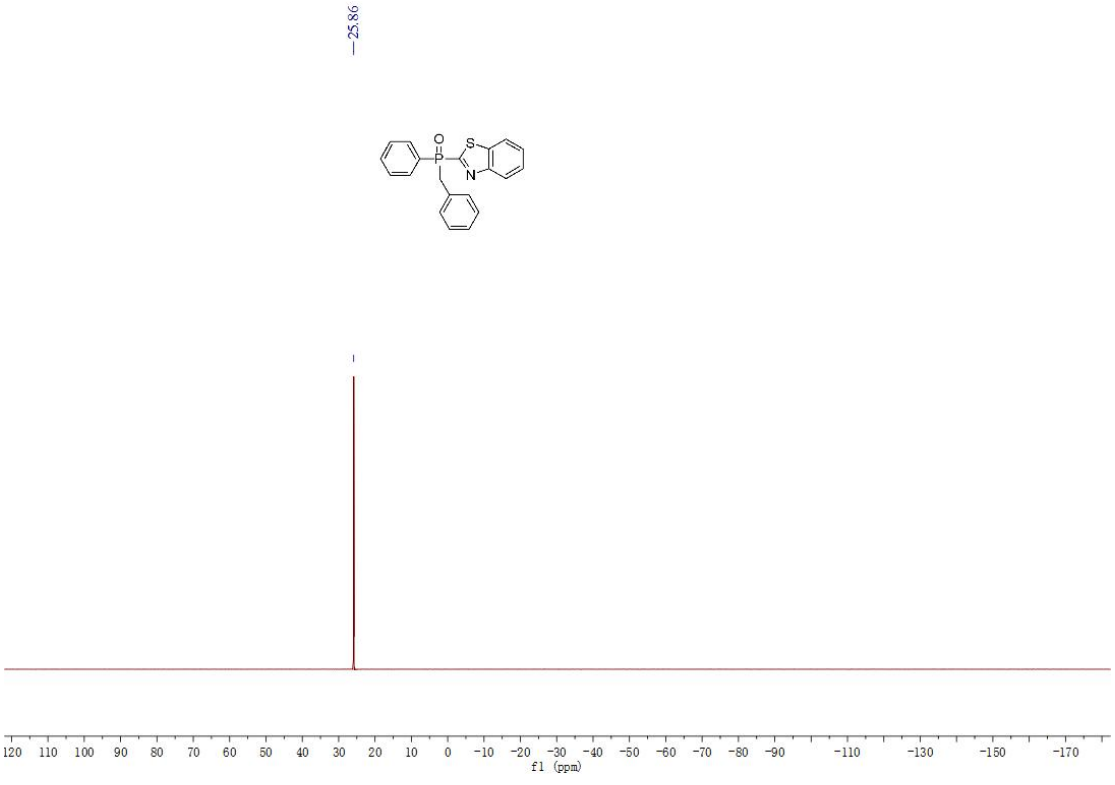
^{1}H NMR Spectrum of **3z**



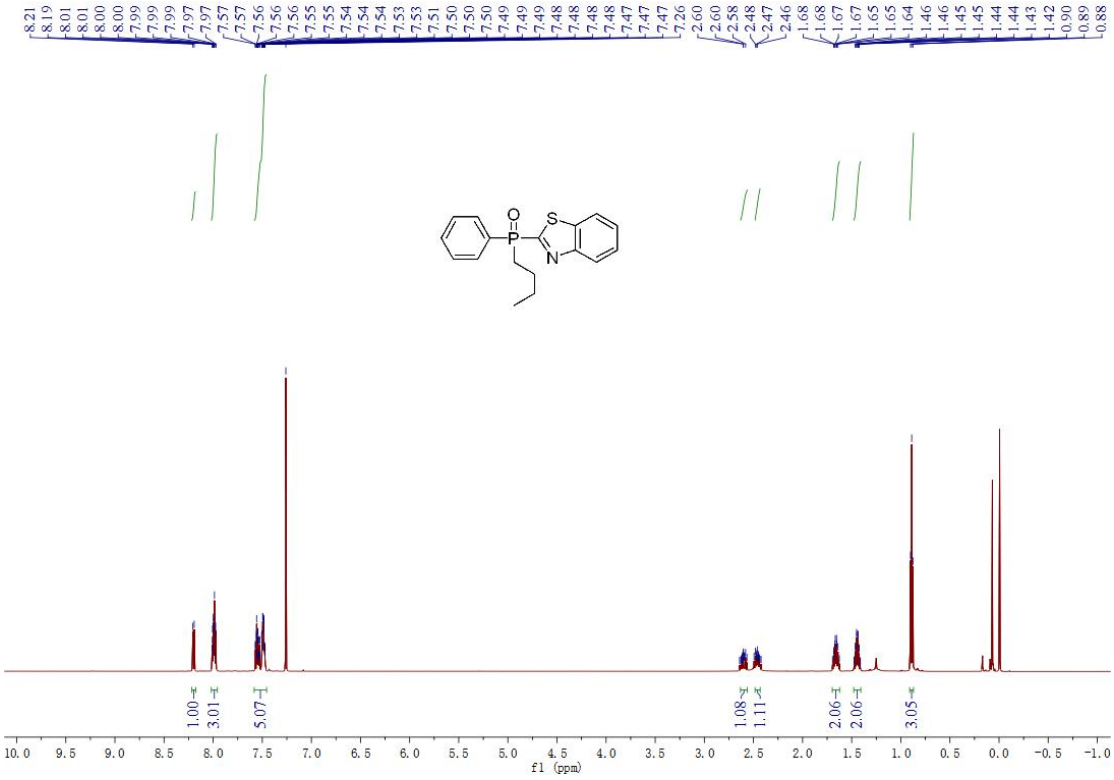
^{13}C NMR Spectrum of **3z**



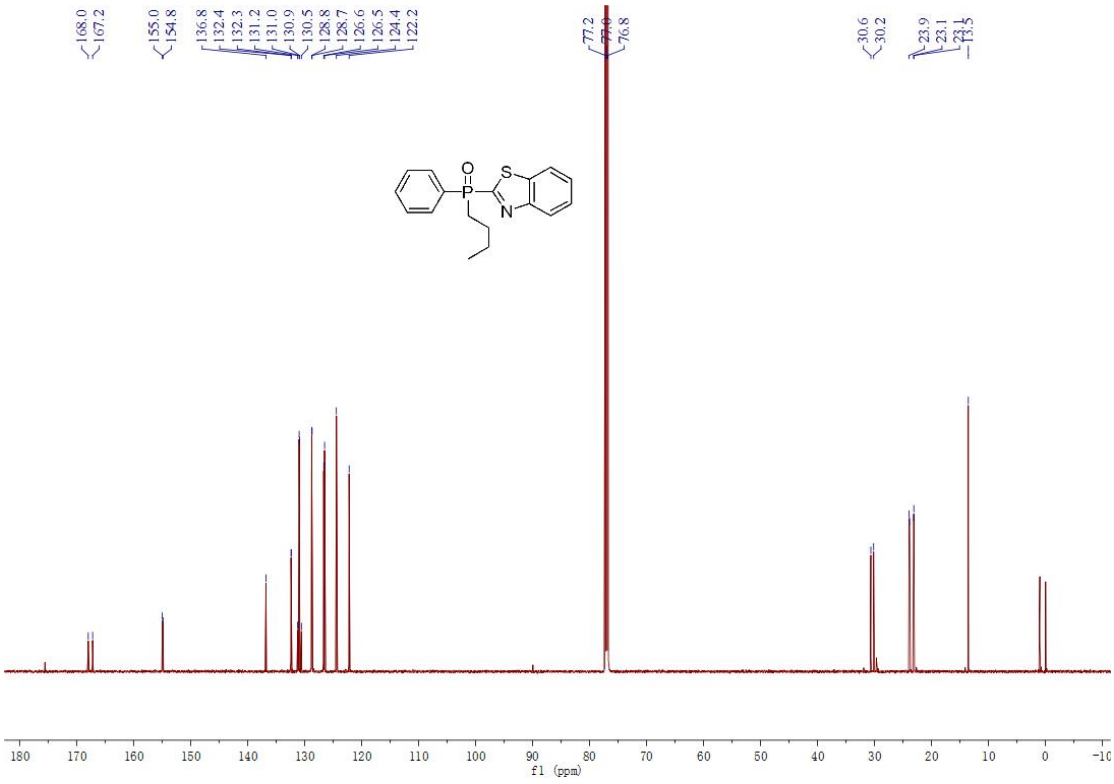
^{31}P NMR Spectrum of **3z**



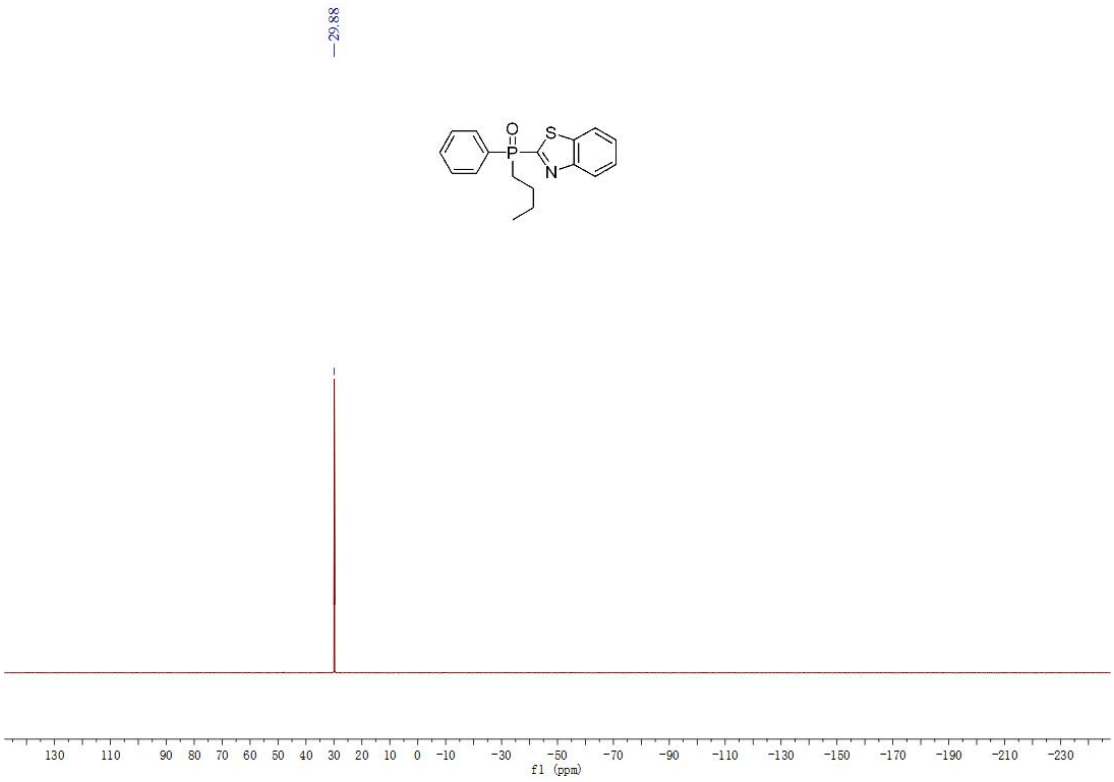
^{1}H NMR Spectrum of **3aa**



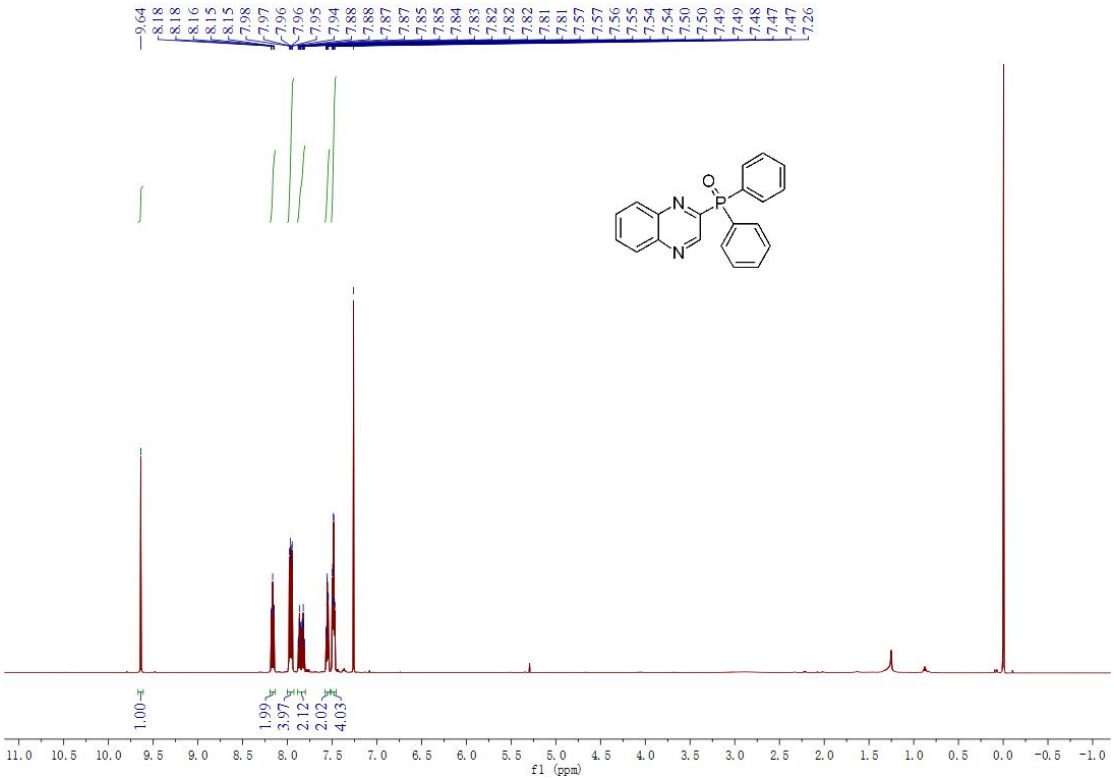
^{13}C NMR Spectrum of **3aa**



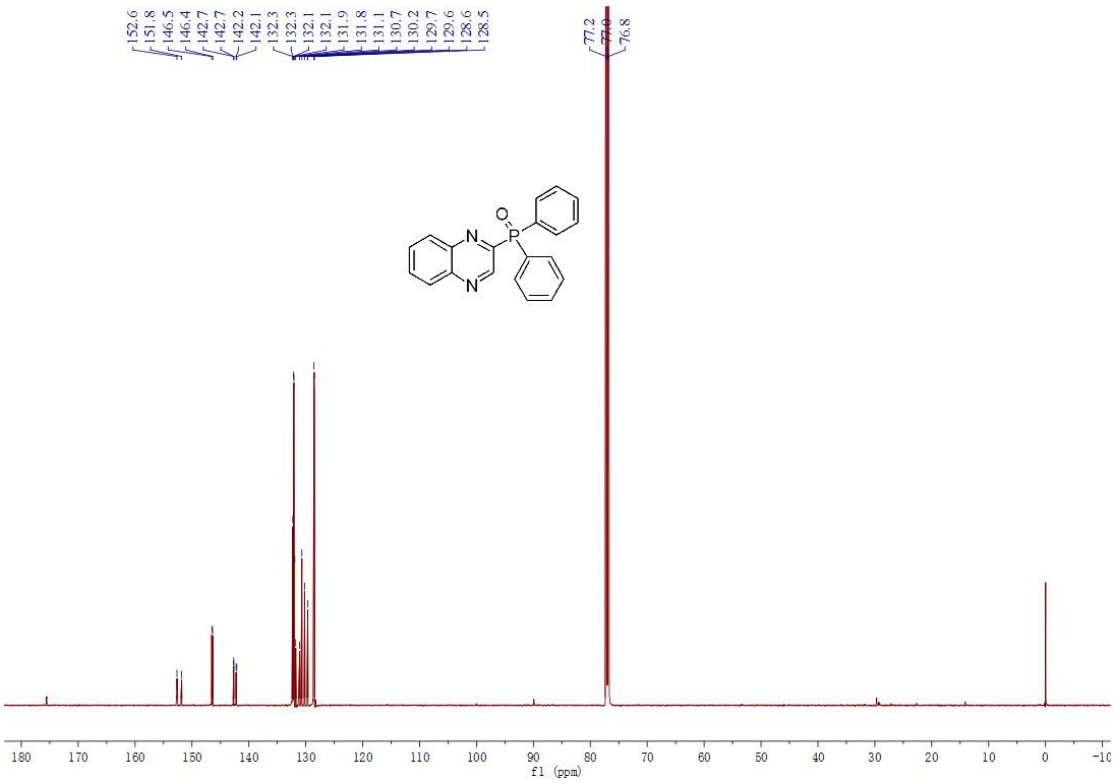
^{31}P NMR Spectrum of **3aa**



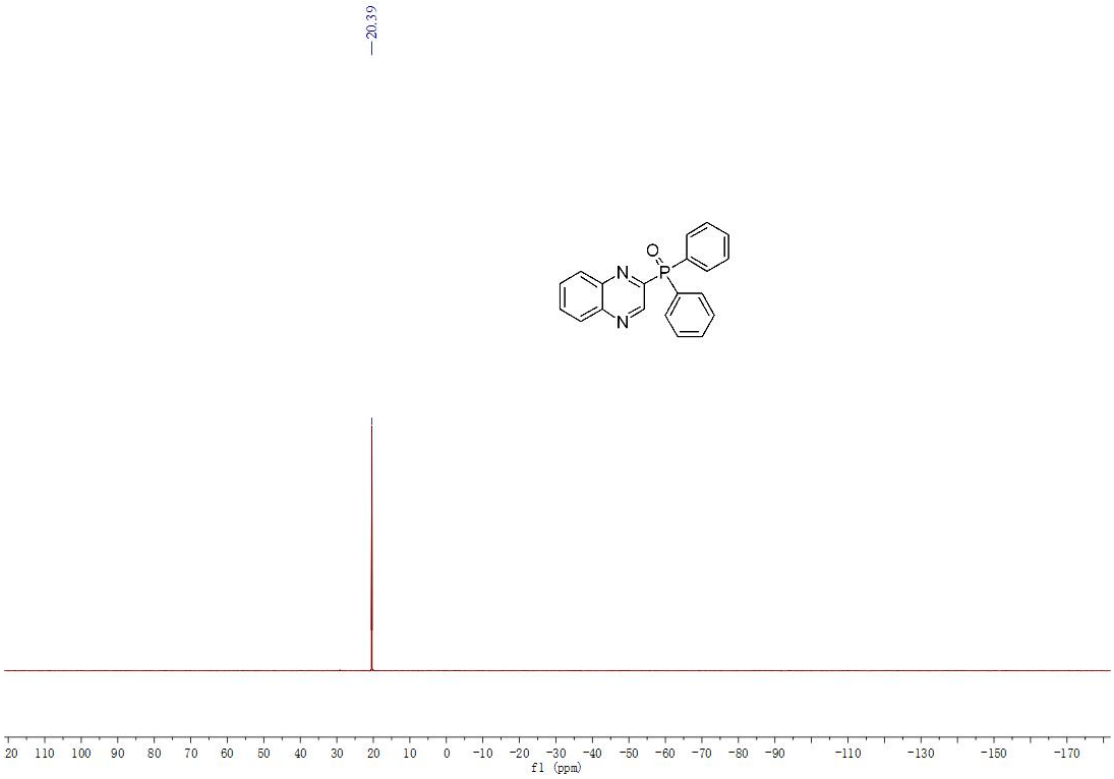
^{1}H NMR Spectrum of **5a**



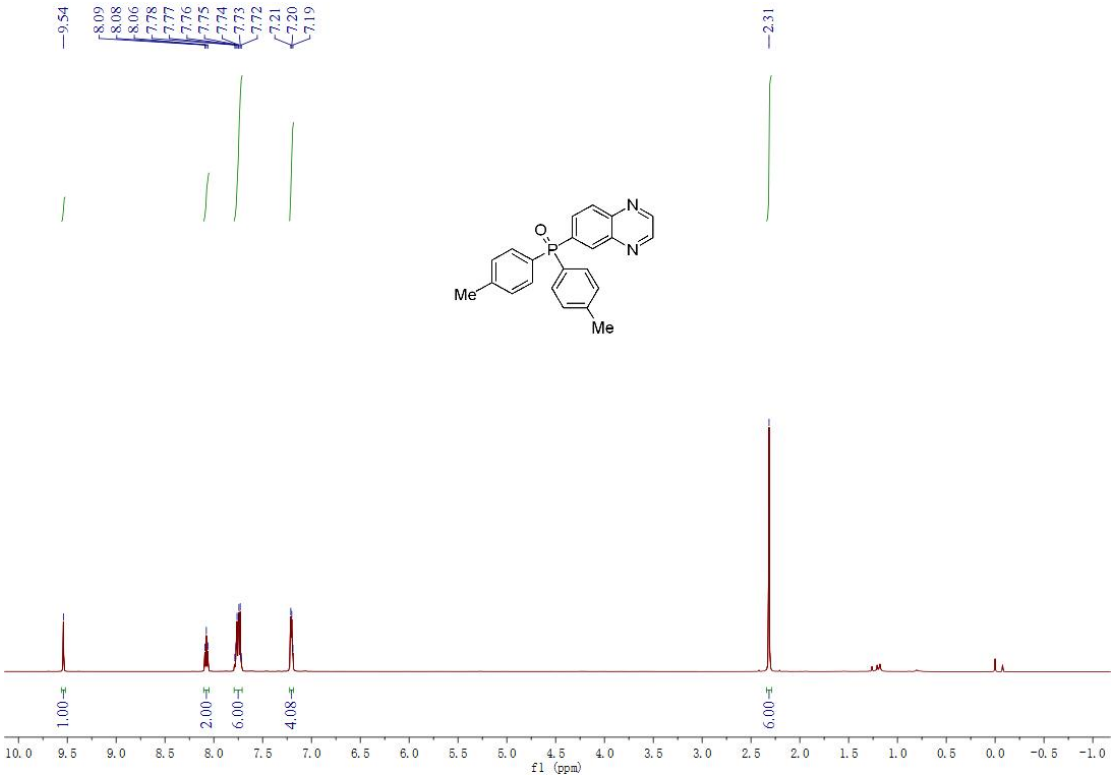
^{13}C NMR Spectrum of **5a**



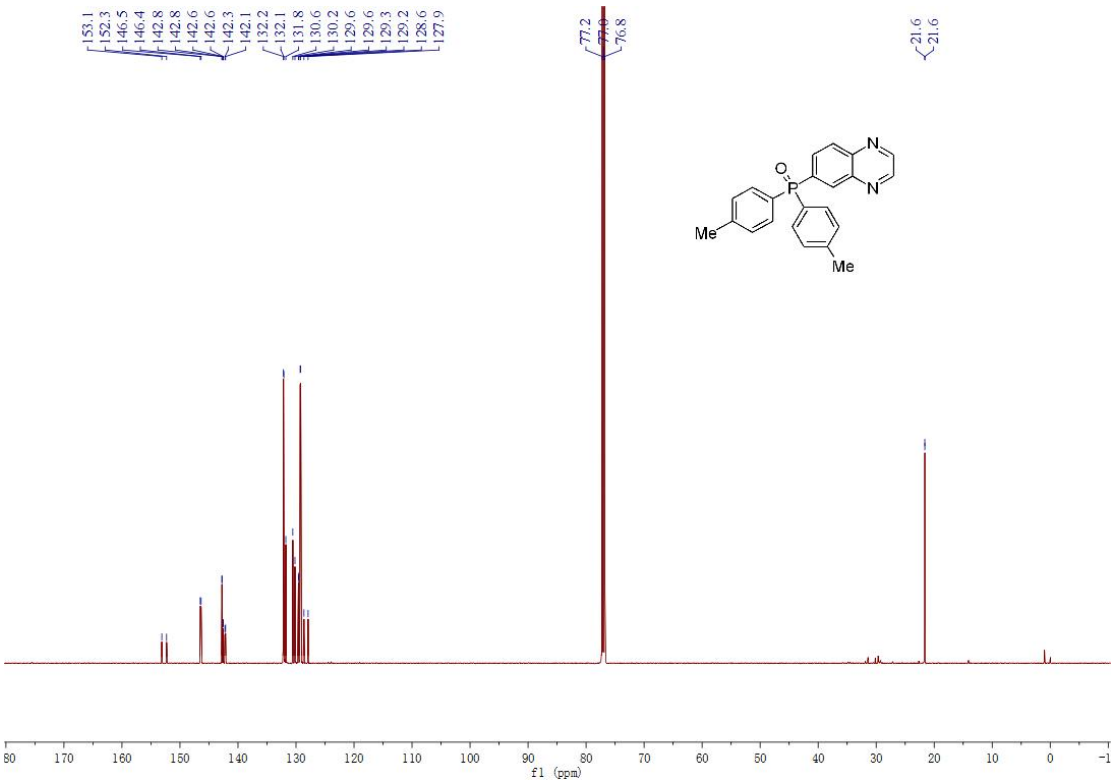
^{31}P NMR Spectrum of **5a**



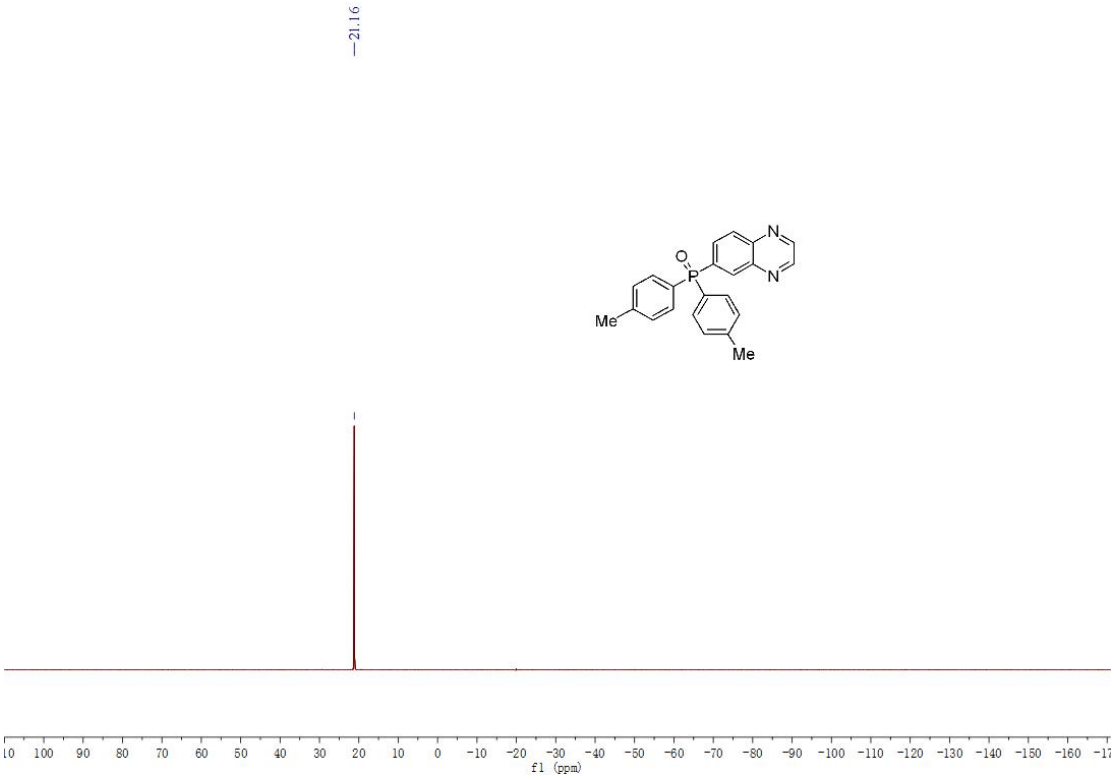
^{1}H NMR Spectrum of **5b**



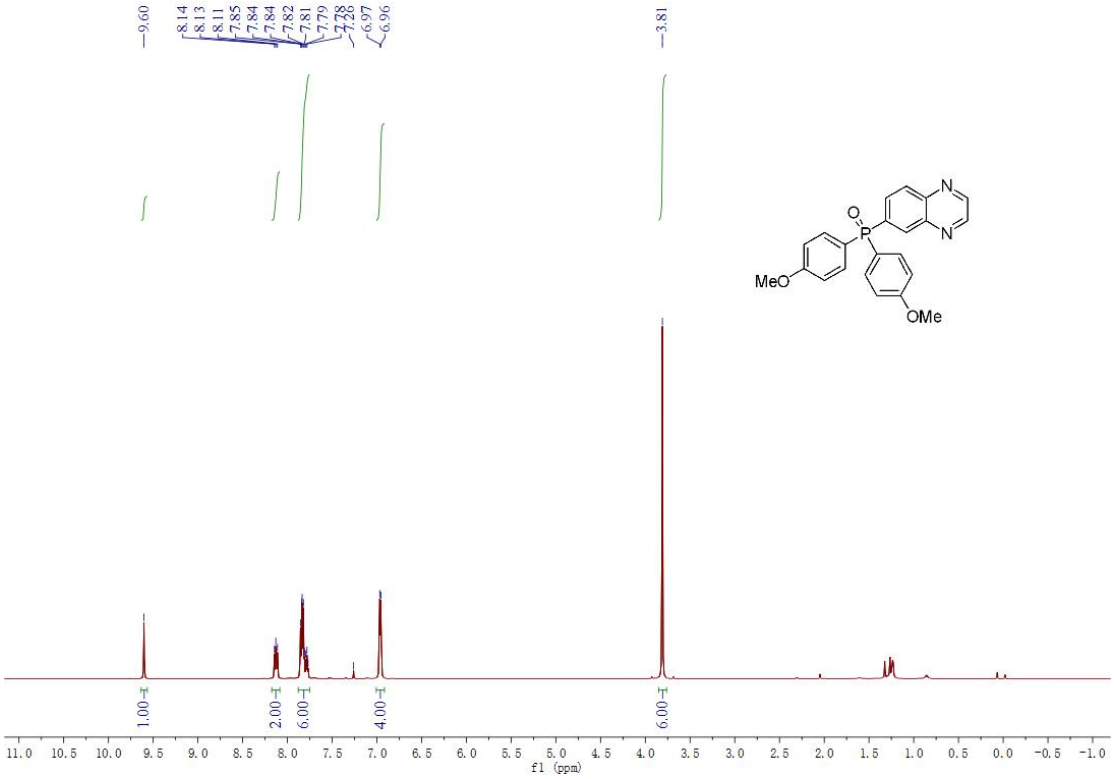
^{13}C NMR Spectrum of **5b**



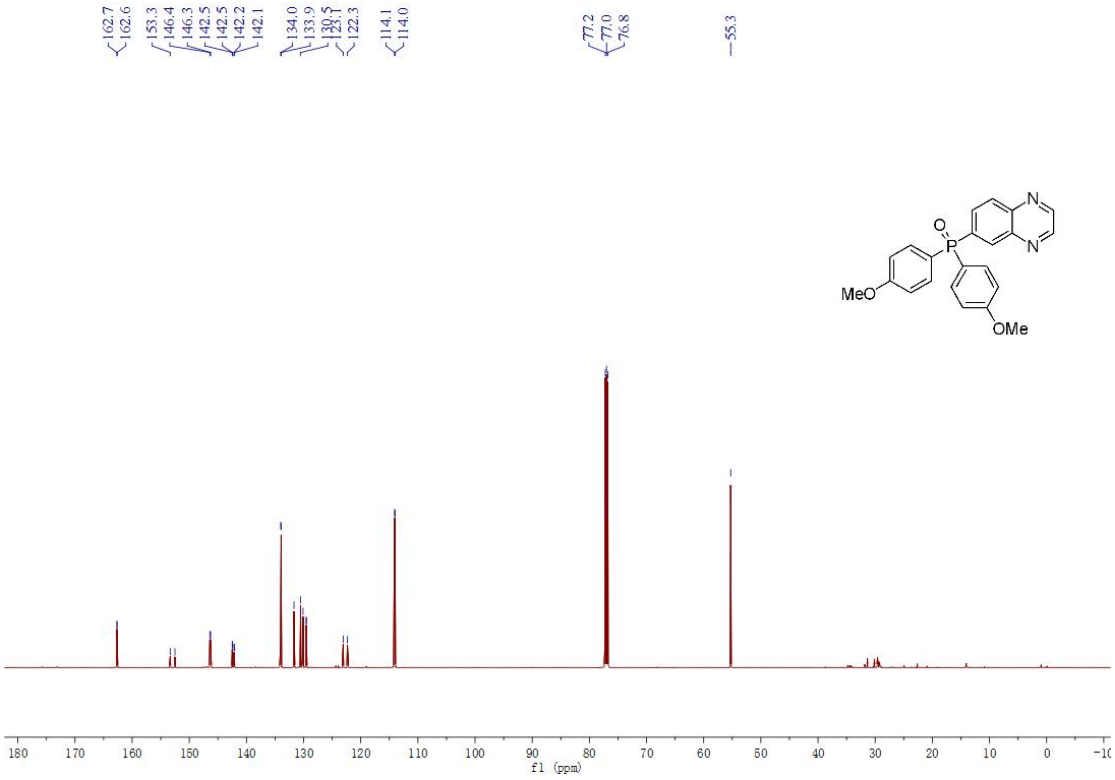
^{31}P NMR Spectrum of **5b**



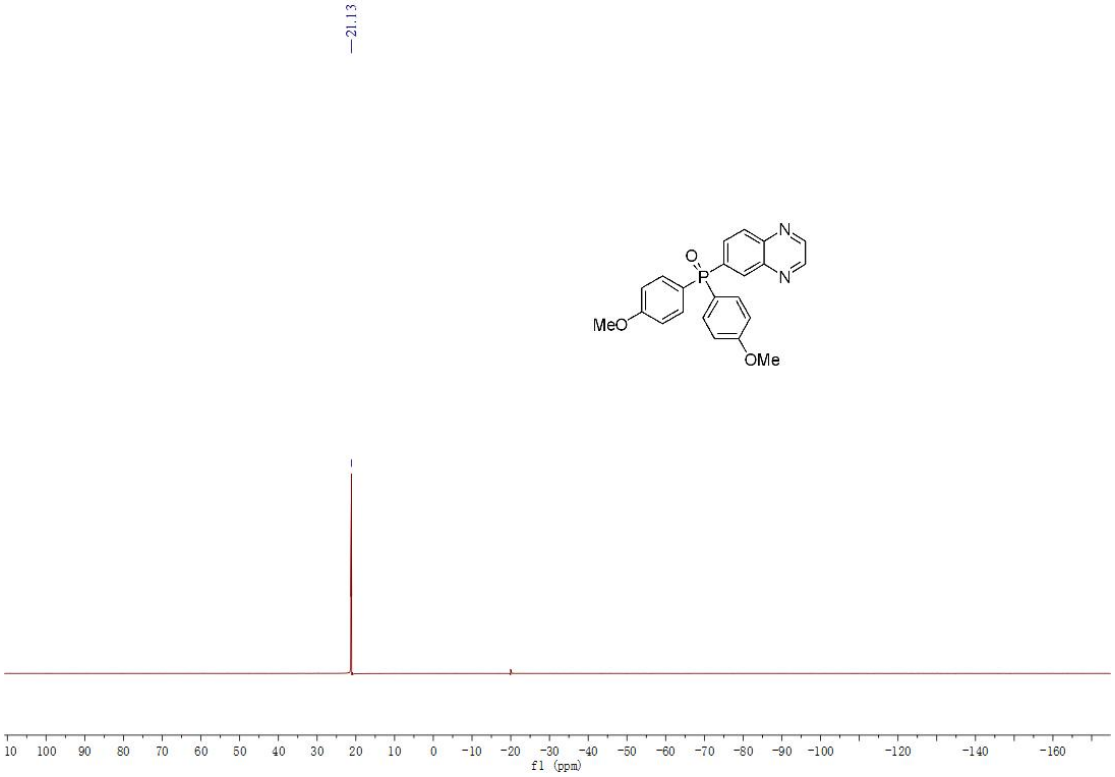
^{1}H NMR Spectrum of **5c**



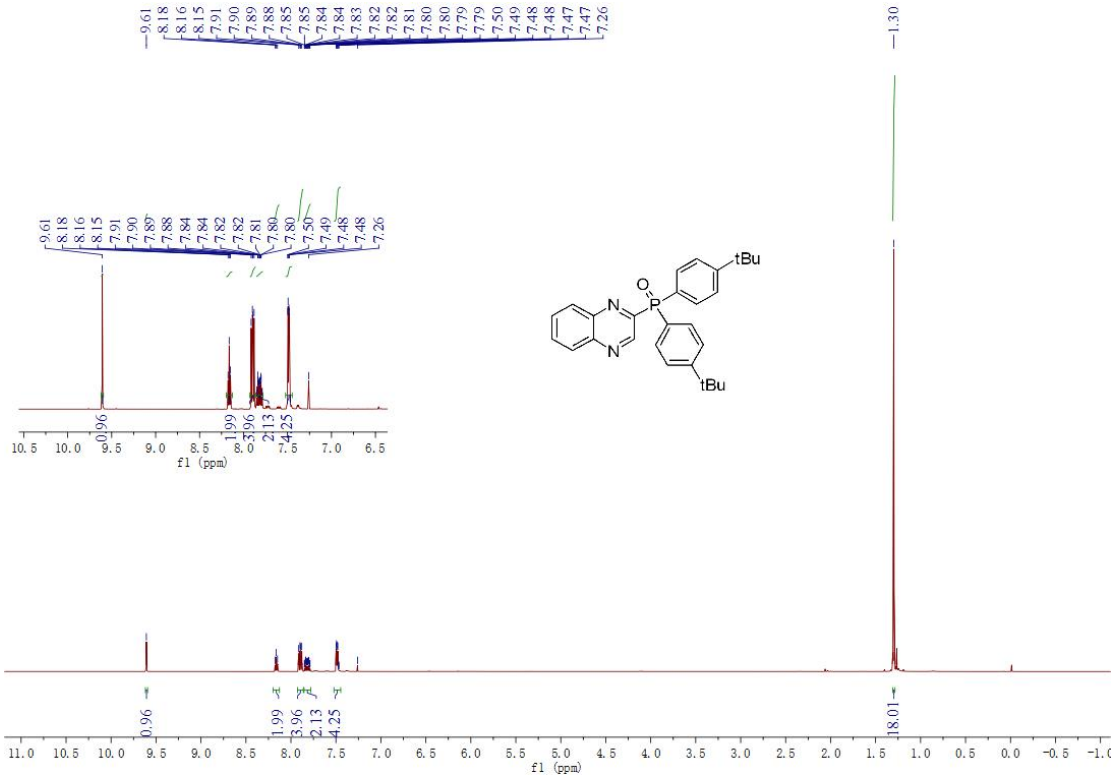
^{13}C NMR Spectrum of **5c**



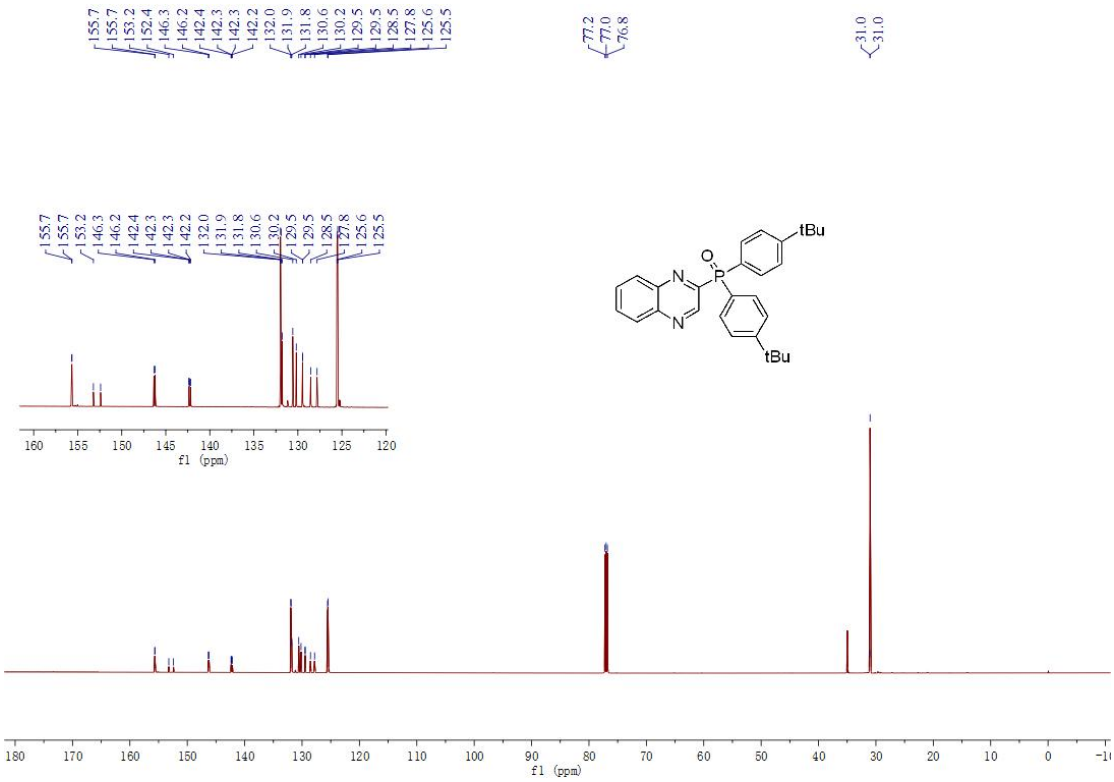
^{31}P NMR Spectrum of **5c**



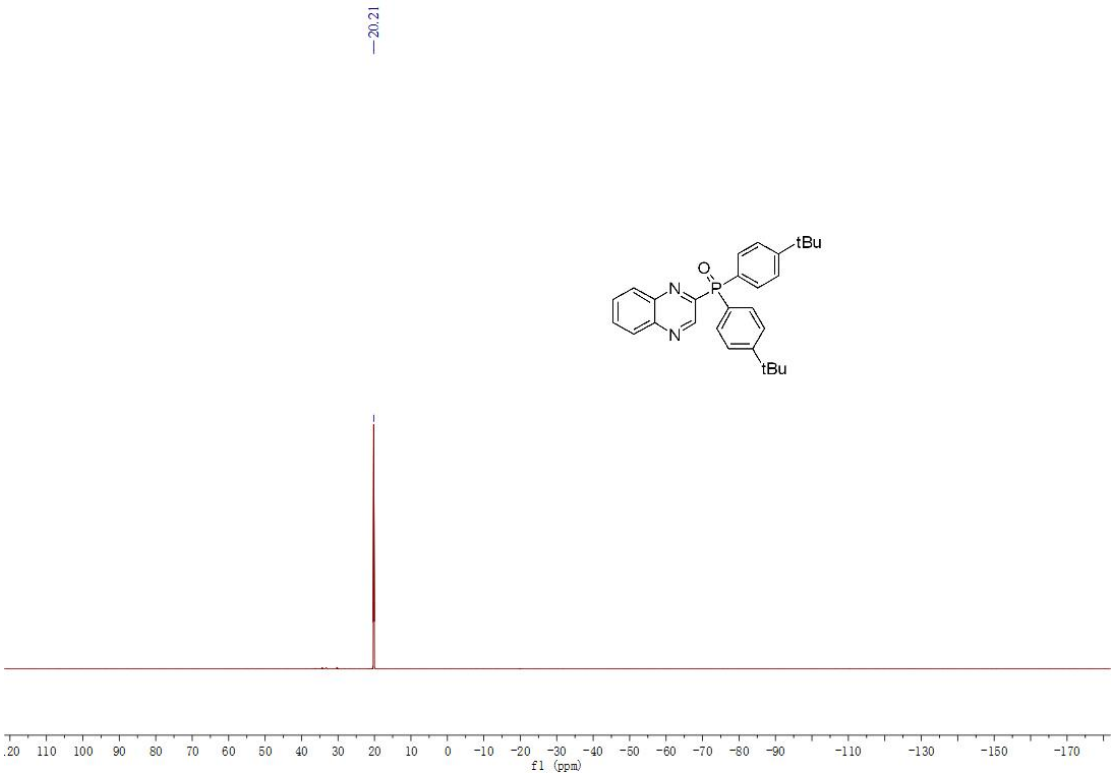
^{1}H NMR Spectrum of **5d**



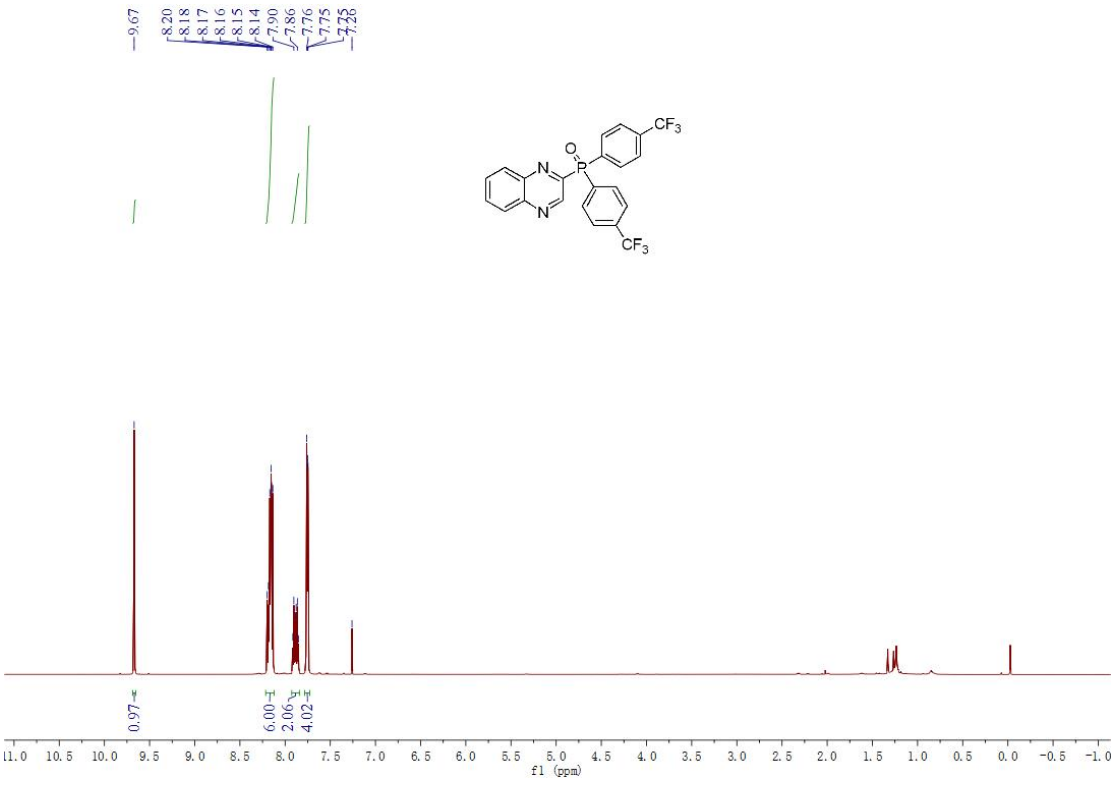
^{13}C NMR Spectrum of **5d**



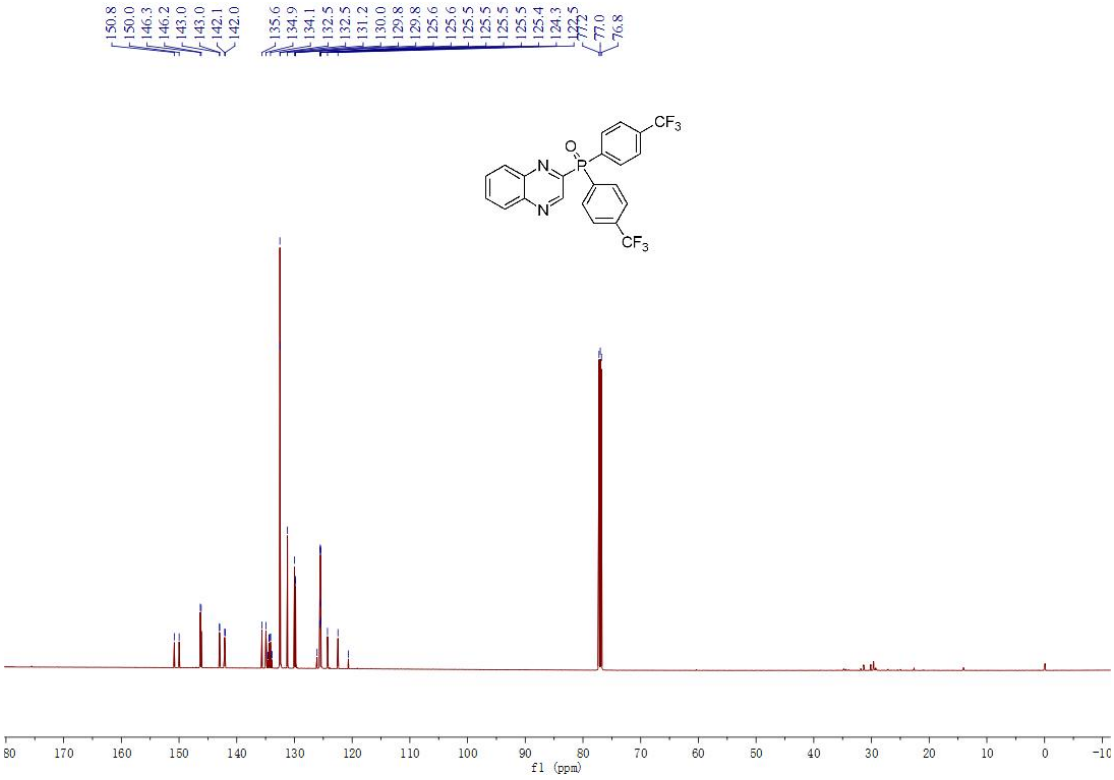
^{31}P NMR Spectrum of **5d**



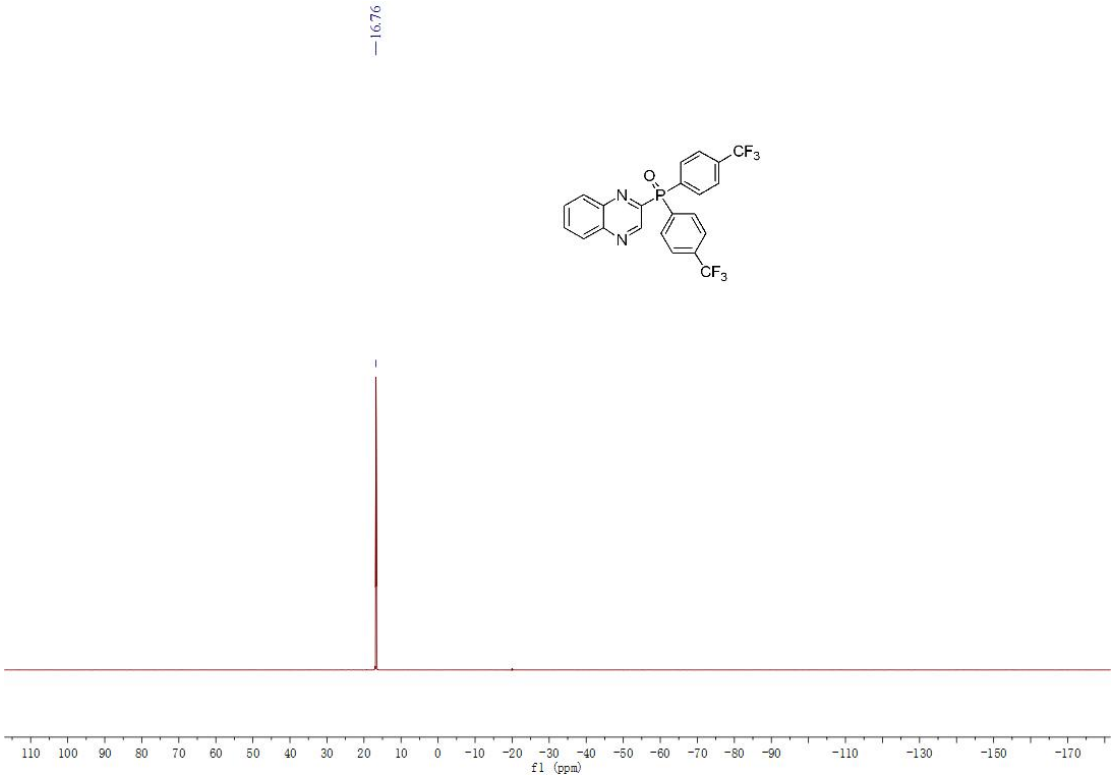
^{1}H NMR Spectrum of **5e**



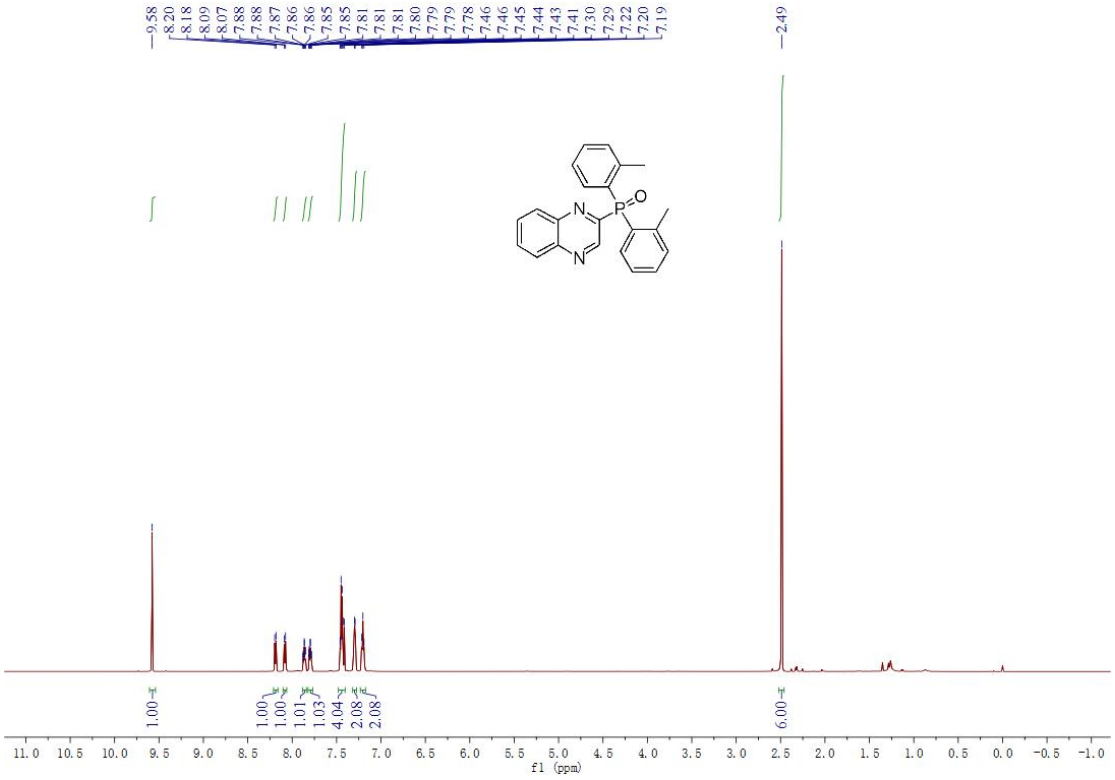
^{13}C NMR Spectrum of **5e**



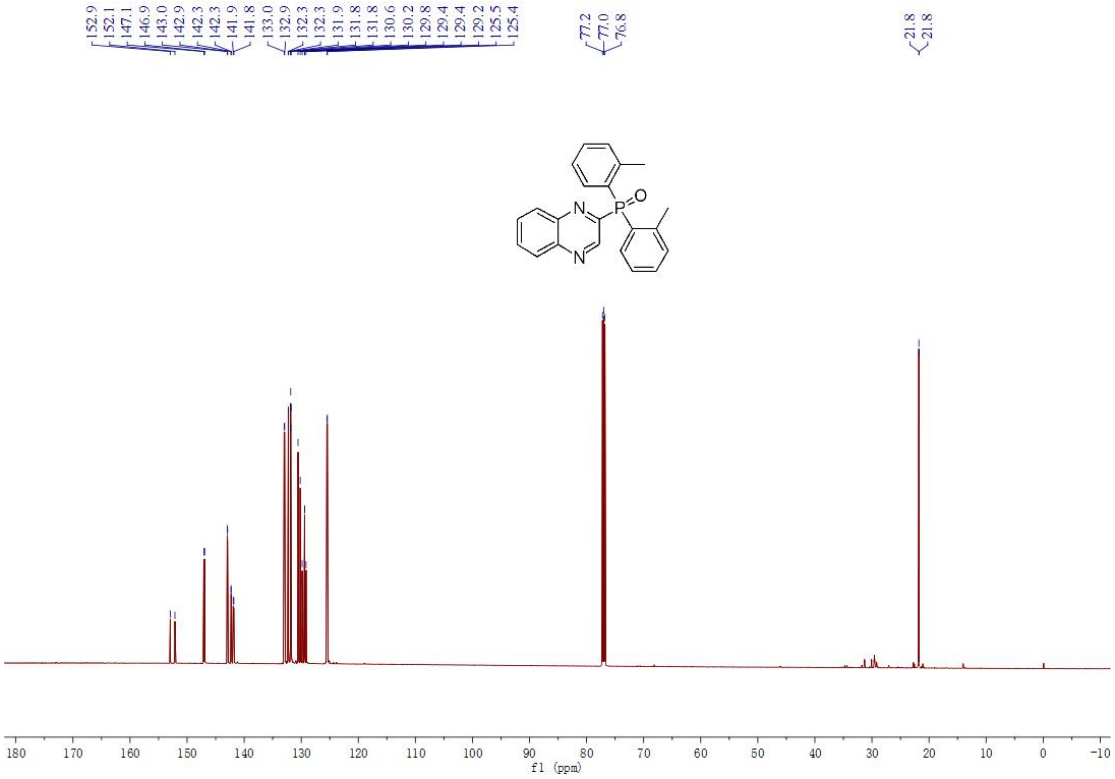
^{31}P NMR Spectrum of **5e**



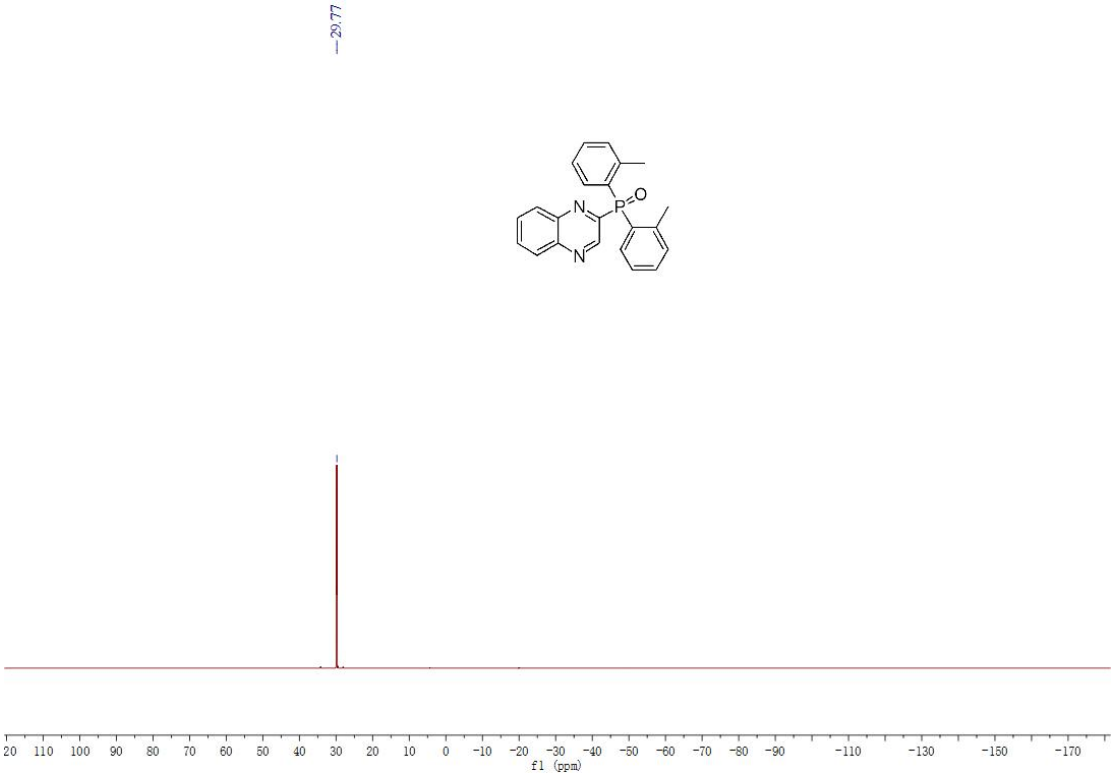
^{1}H NMR Spectrum of **5f**



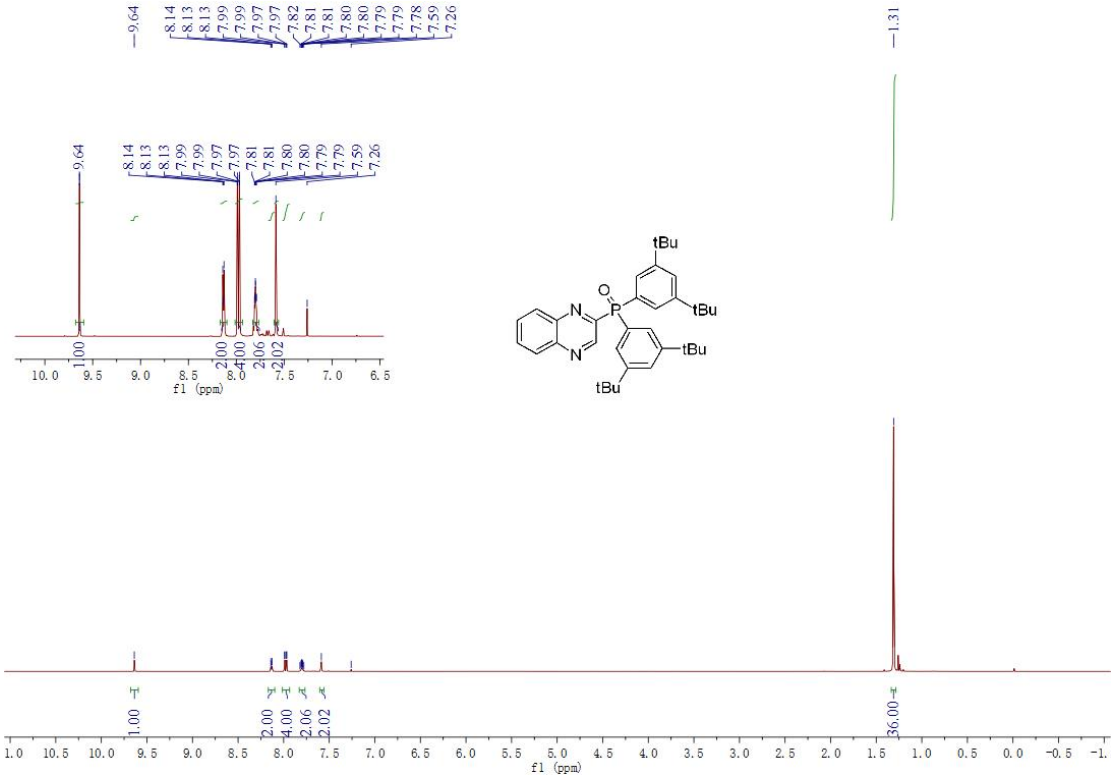
^{13}C NMR Spectrum of **5f**



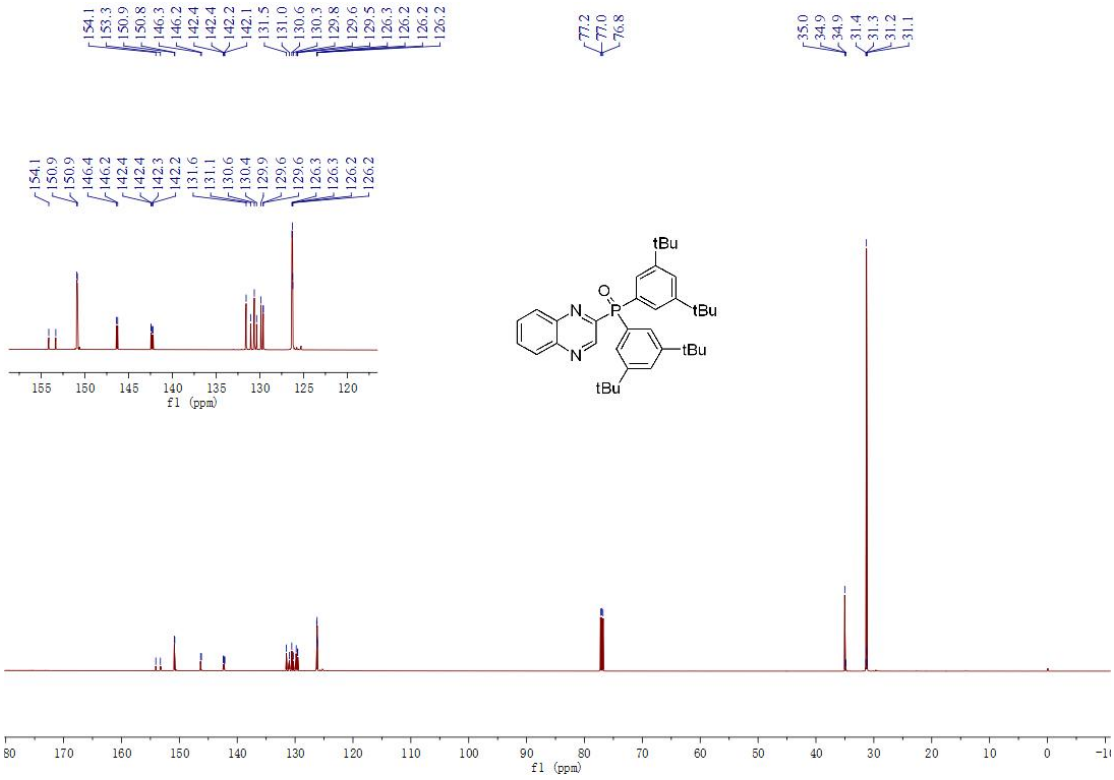
^{31}P NMR Spectrum of **5f**



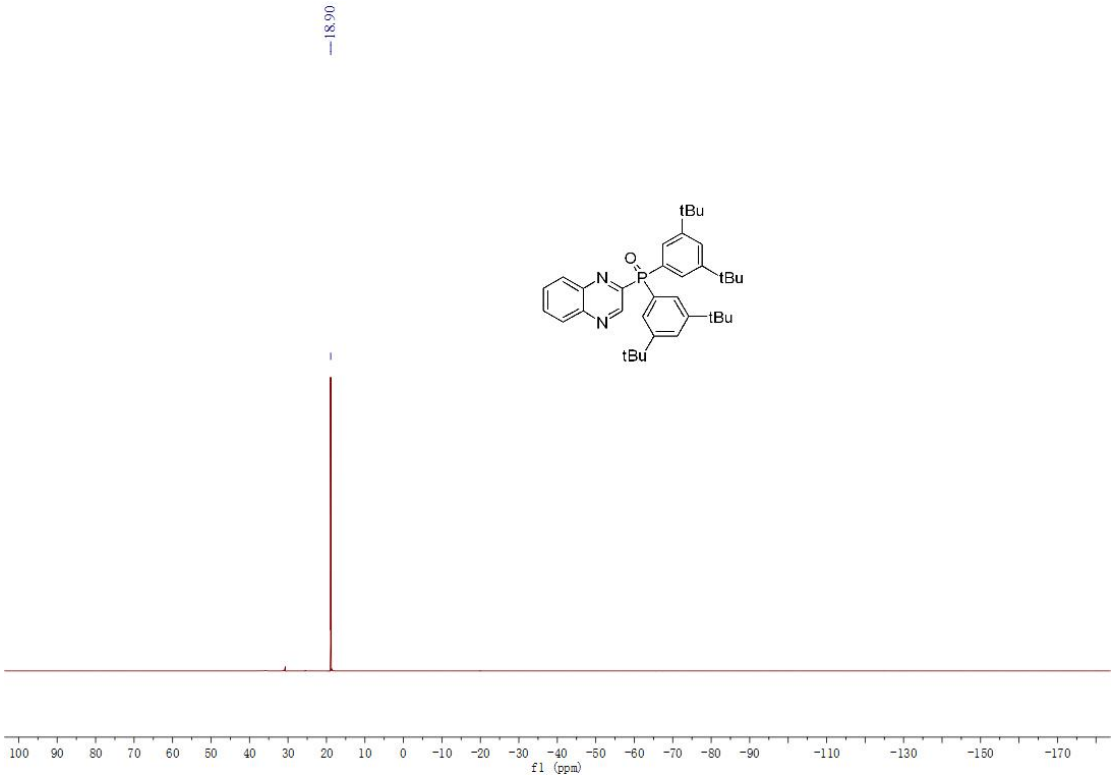
^{1}H NMR Spectrum of **5g**



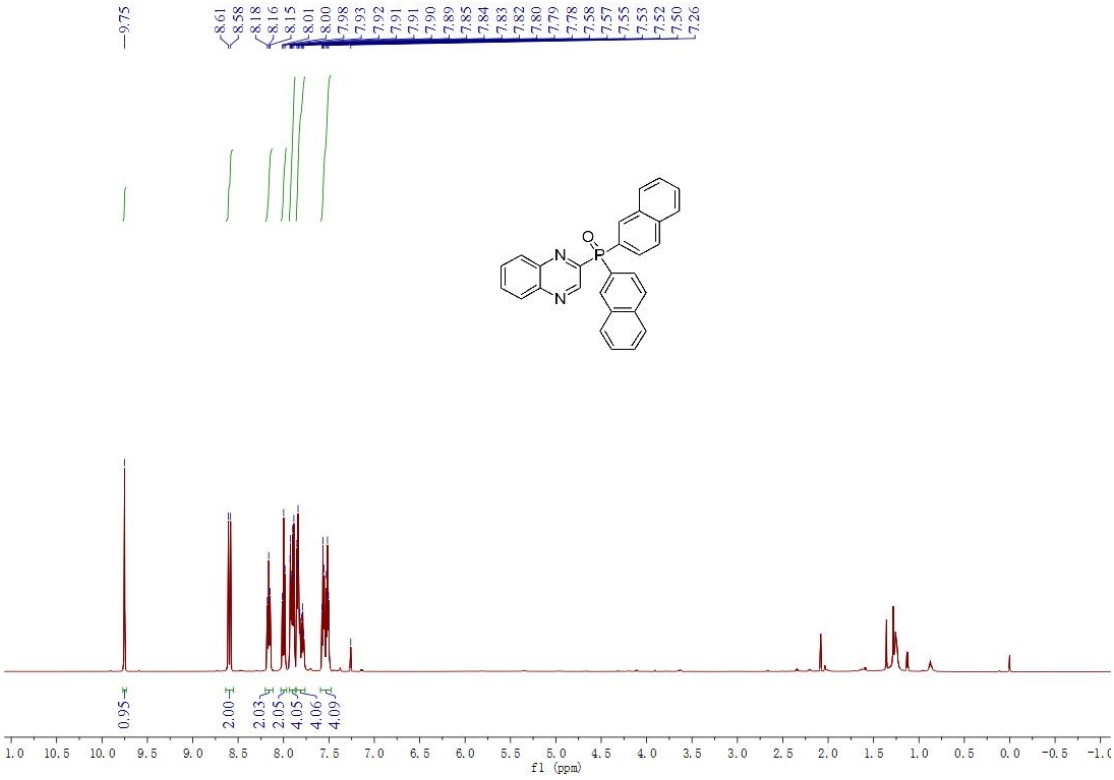
^{13}C NMR Spectrum of **5g**



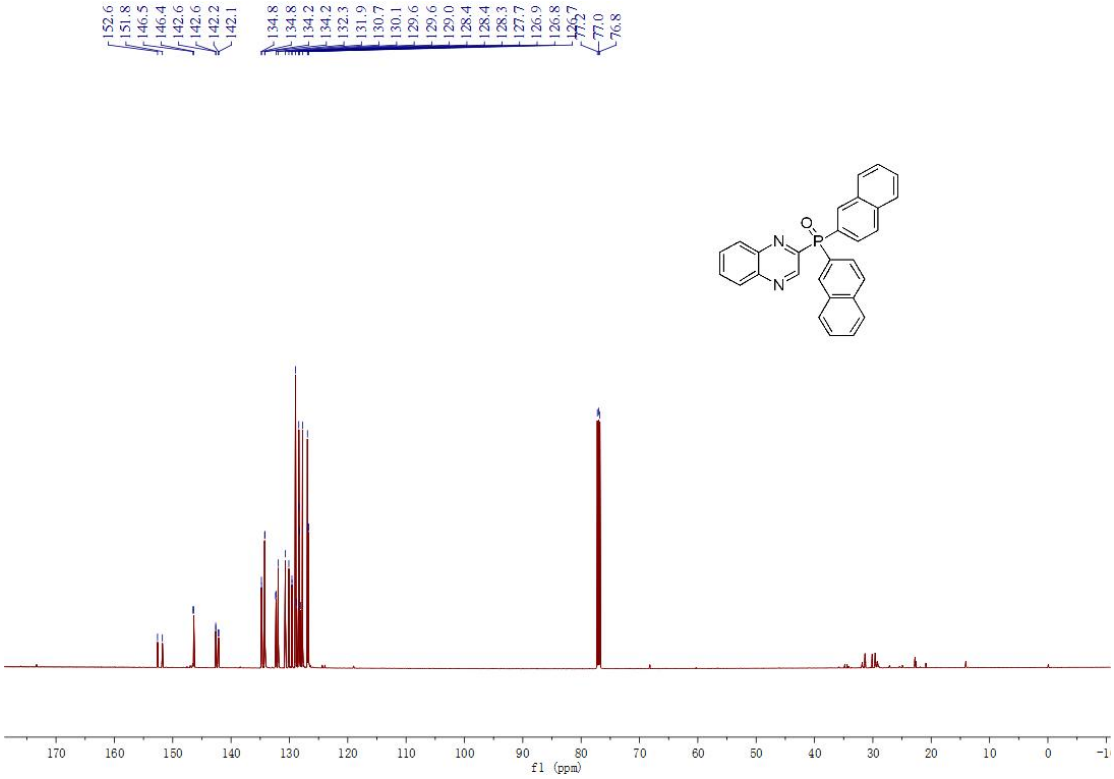
^{31}P NMR Spectrum of **5g**



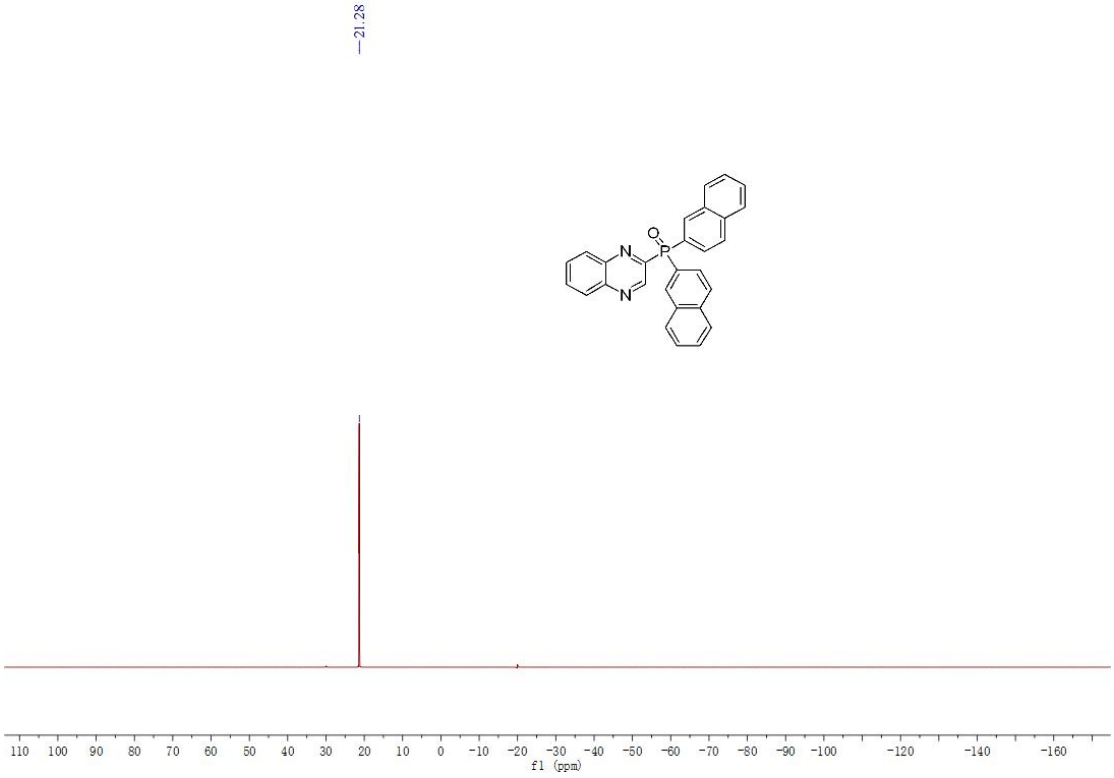
^{1}H NMR Spectrum of **5h**



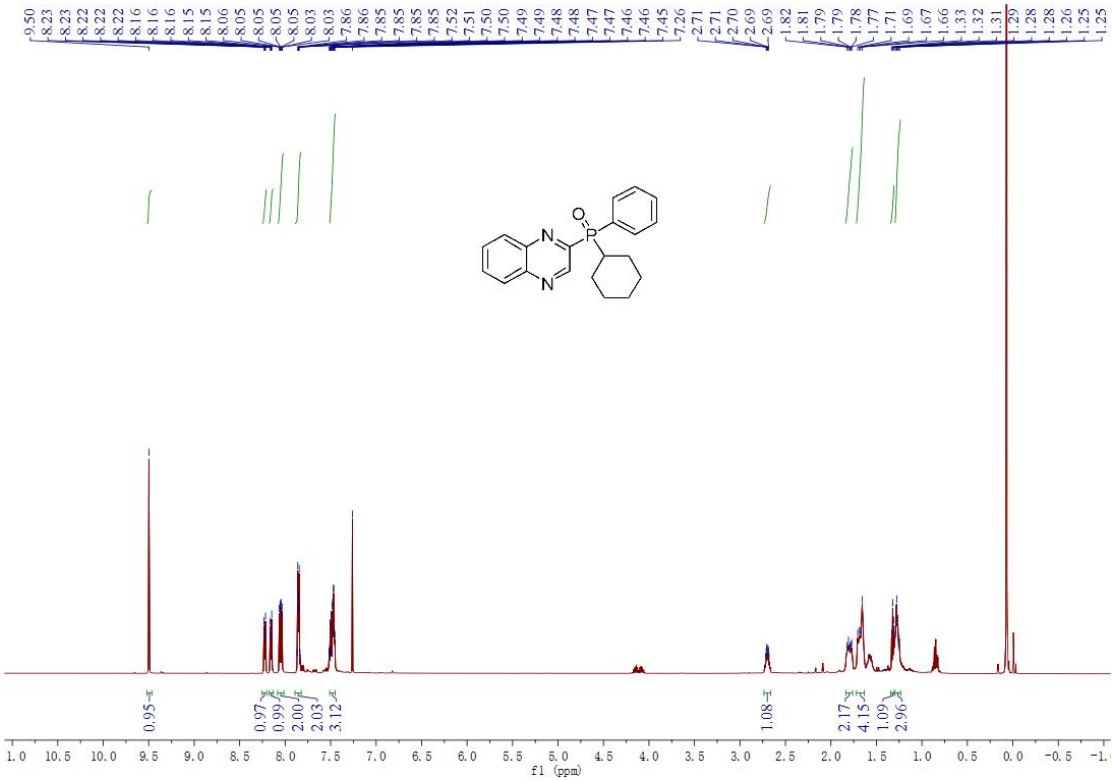
^{13}C NMR Spectrum of **5h**



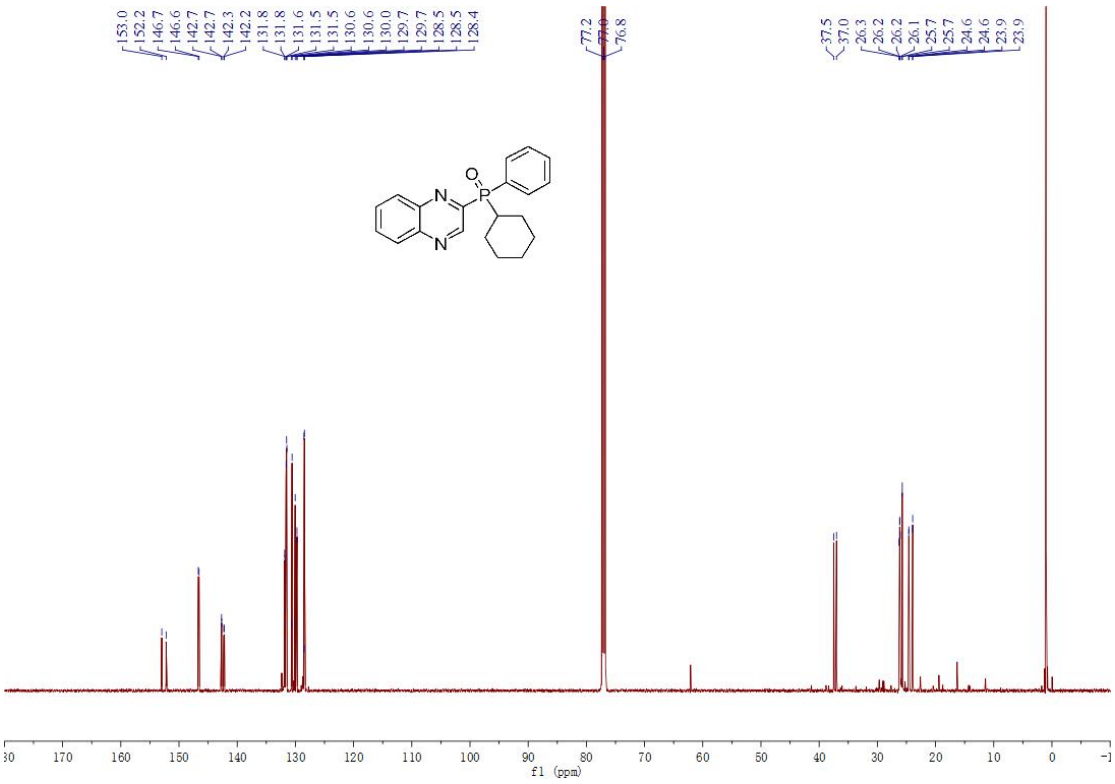
^{31}P NMR Spectrum of **5h**



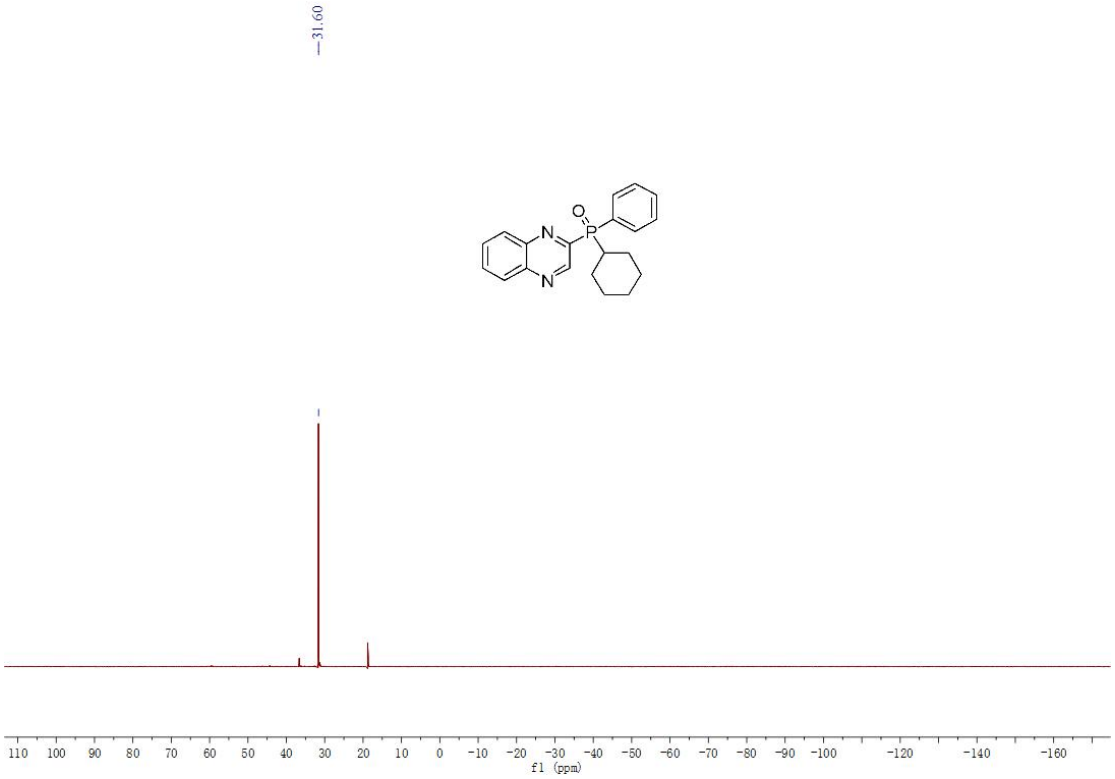
^{1}H NMR Spectrum of **5i**



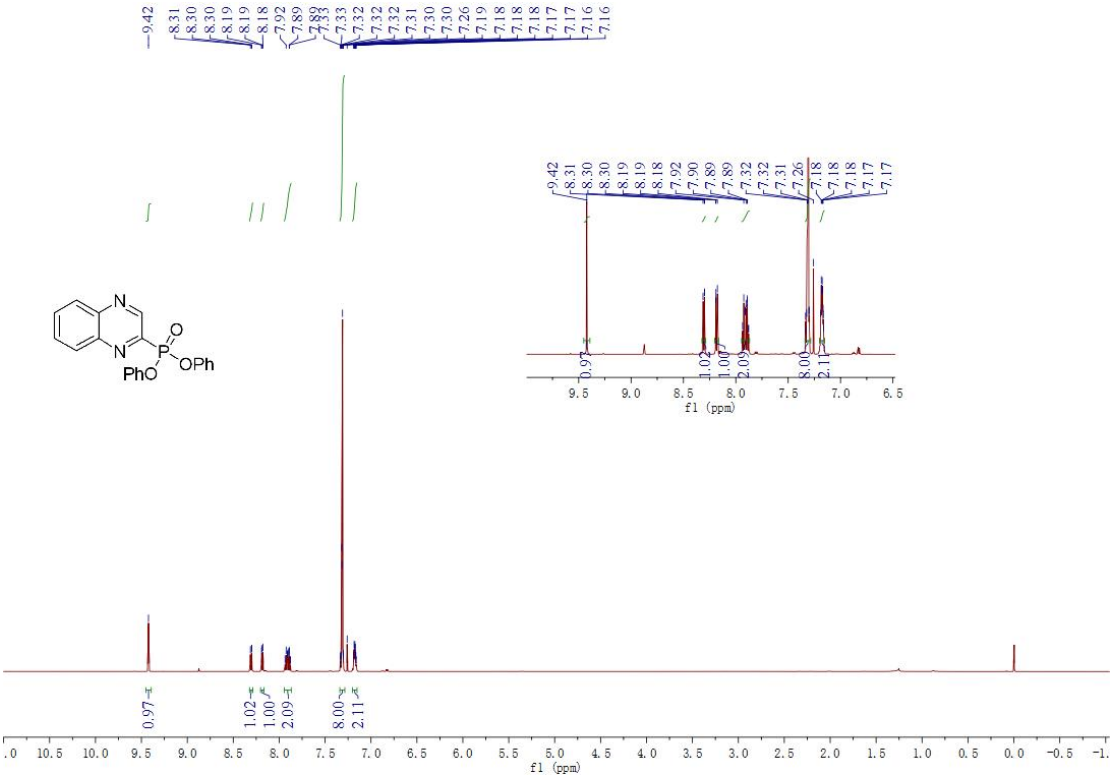
^{13}C NMR Spectrum of **5i**



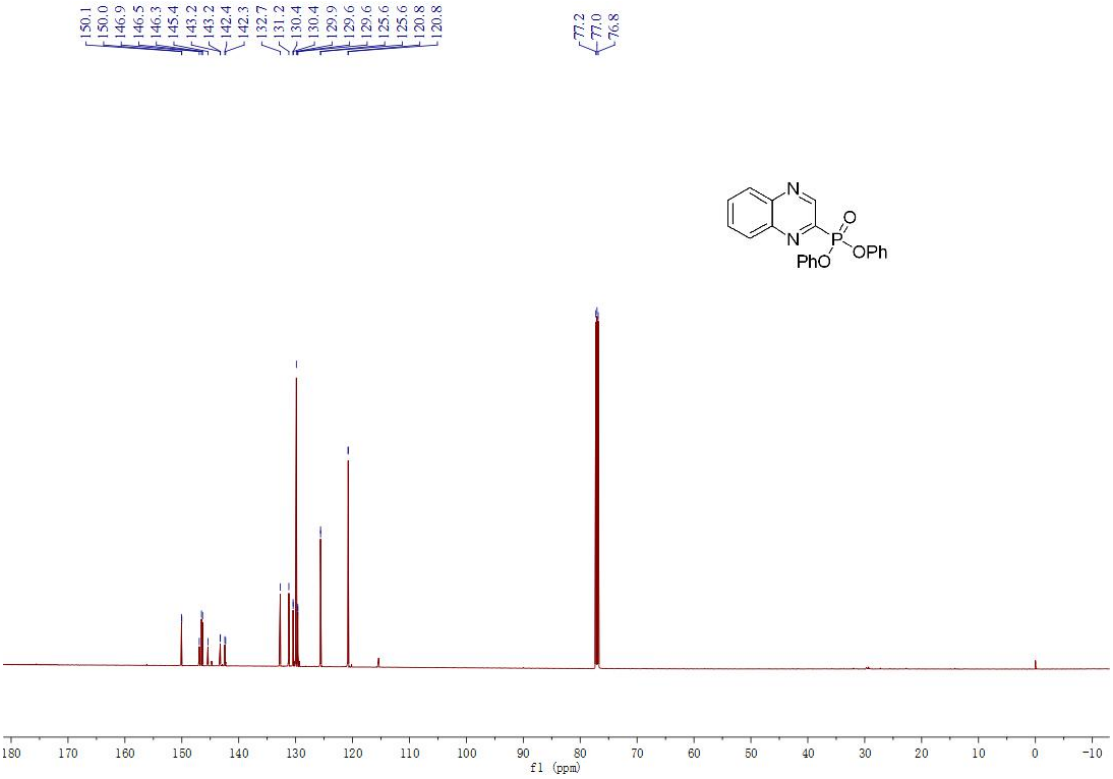
^{31}P NMR Spectrum of **5i**



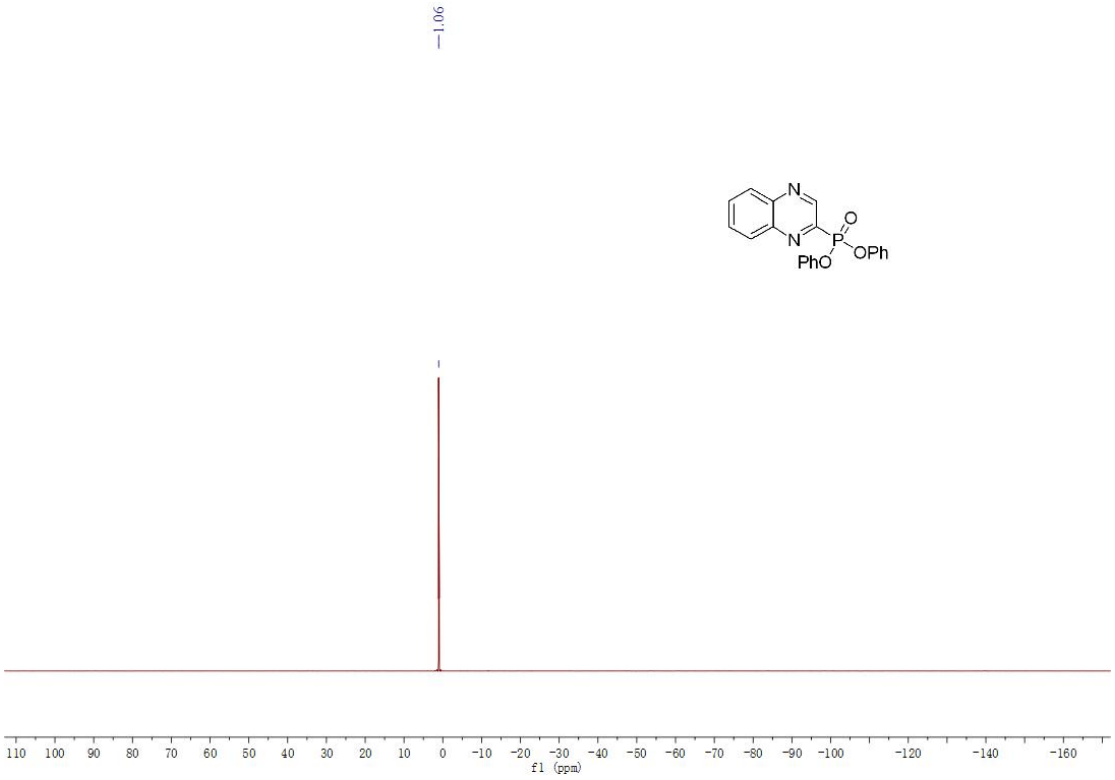
^{1}H NMR Spectrum of **5j**



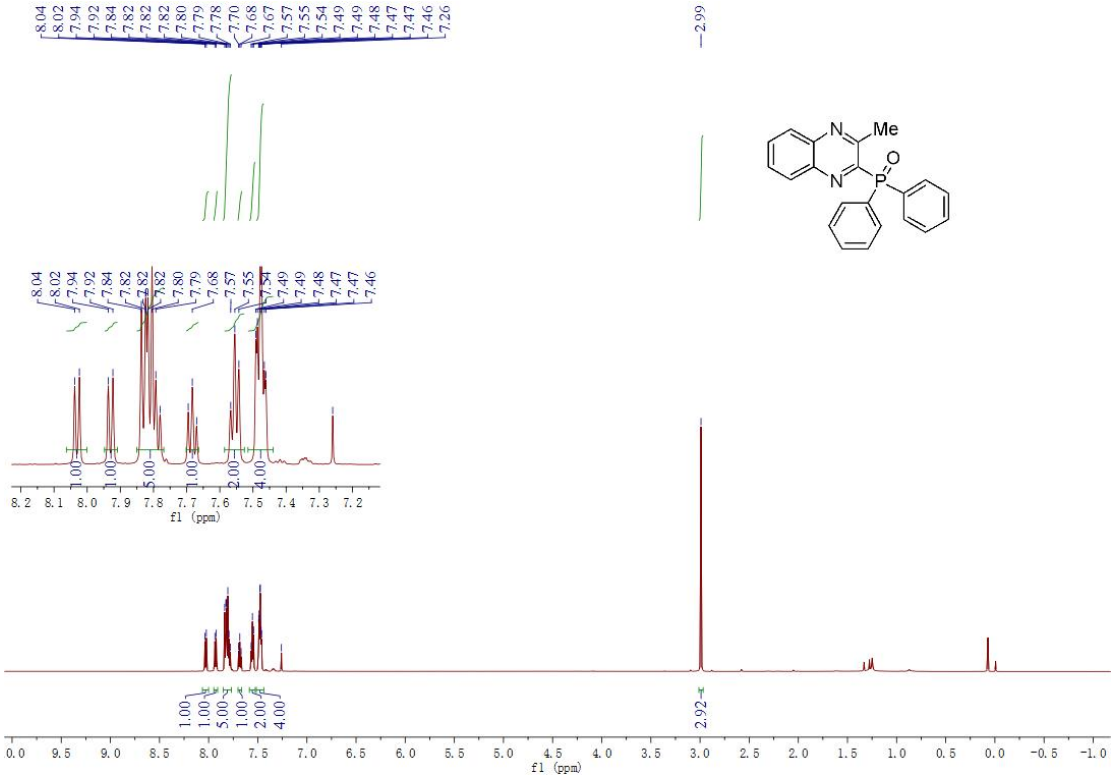
^{13}C NMR Spectrum of **5j**



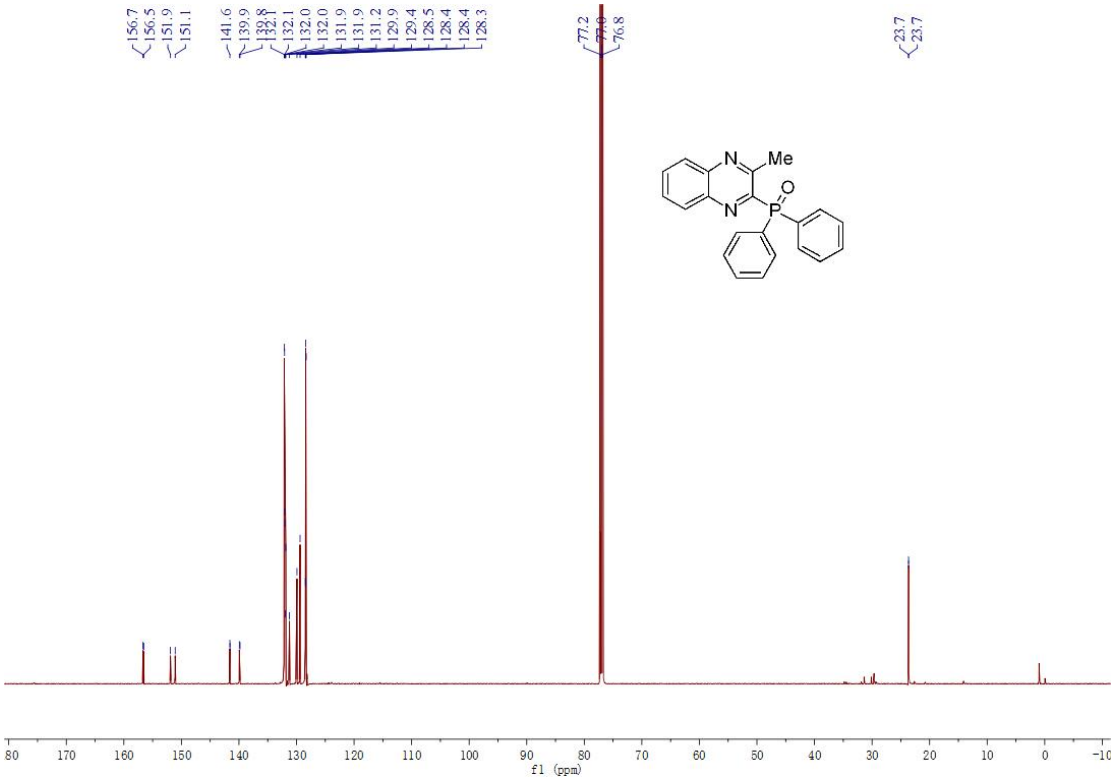
^{31}P NMR Spectrum of **5j**



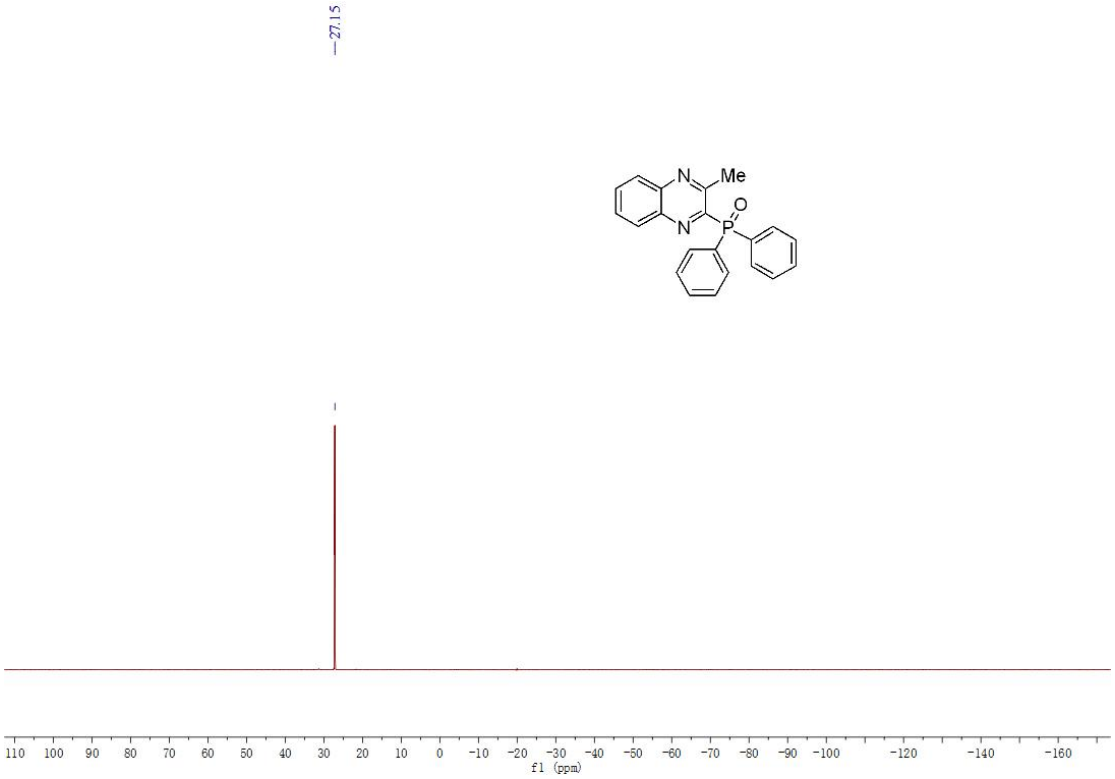
^{1}H NMR Spectrum of **5l**



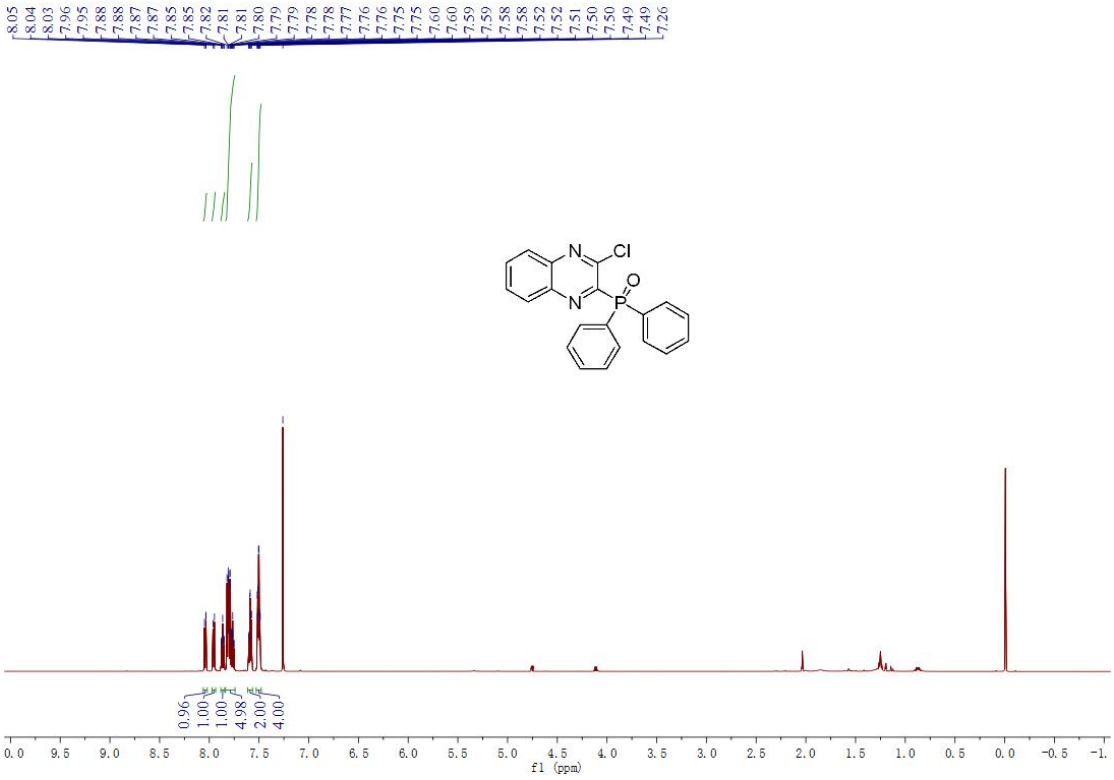
^{13}C NMR Spectrum of **5l**



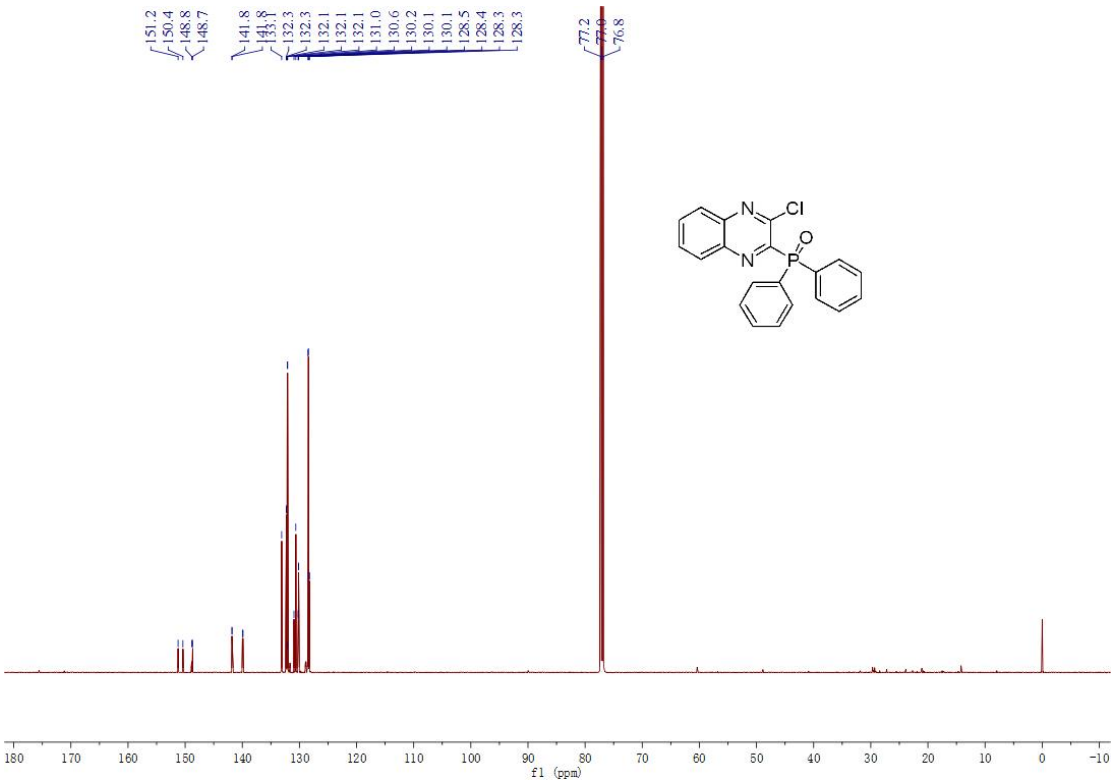
^{31}P NMR Spectrum of **5l**



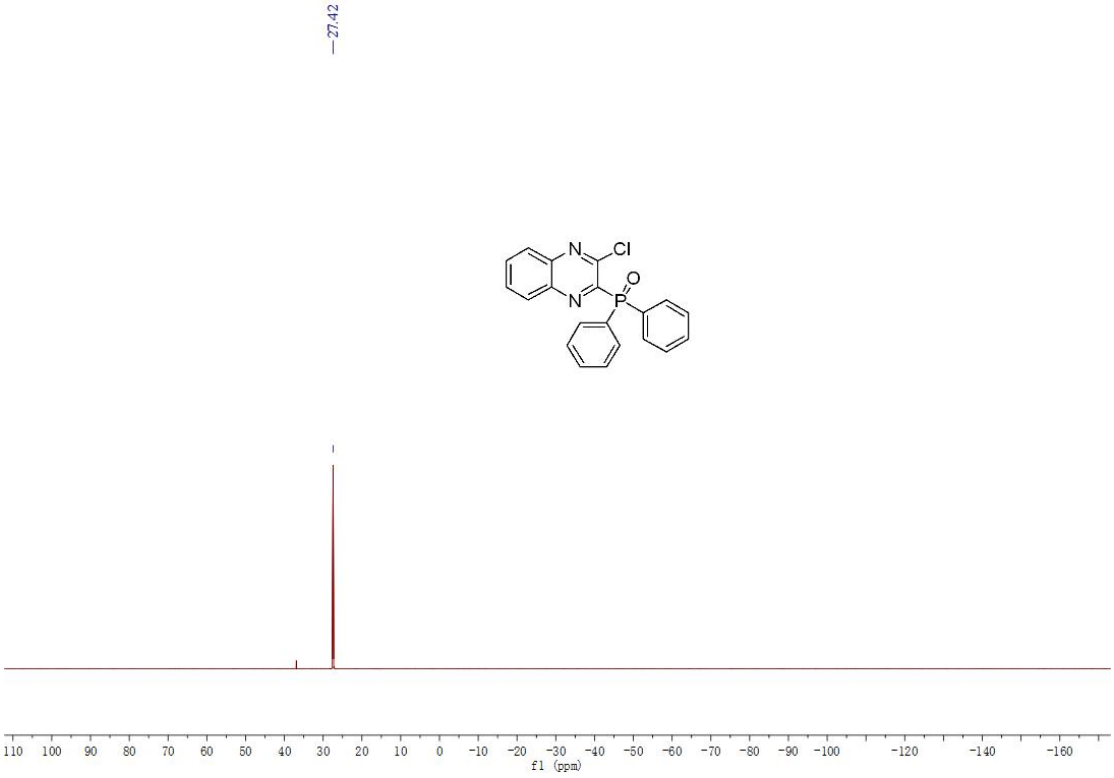
^{1}H NMR Spectrum of **5m**



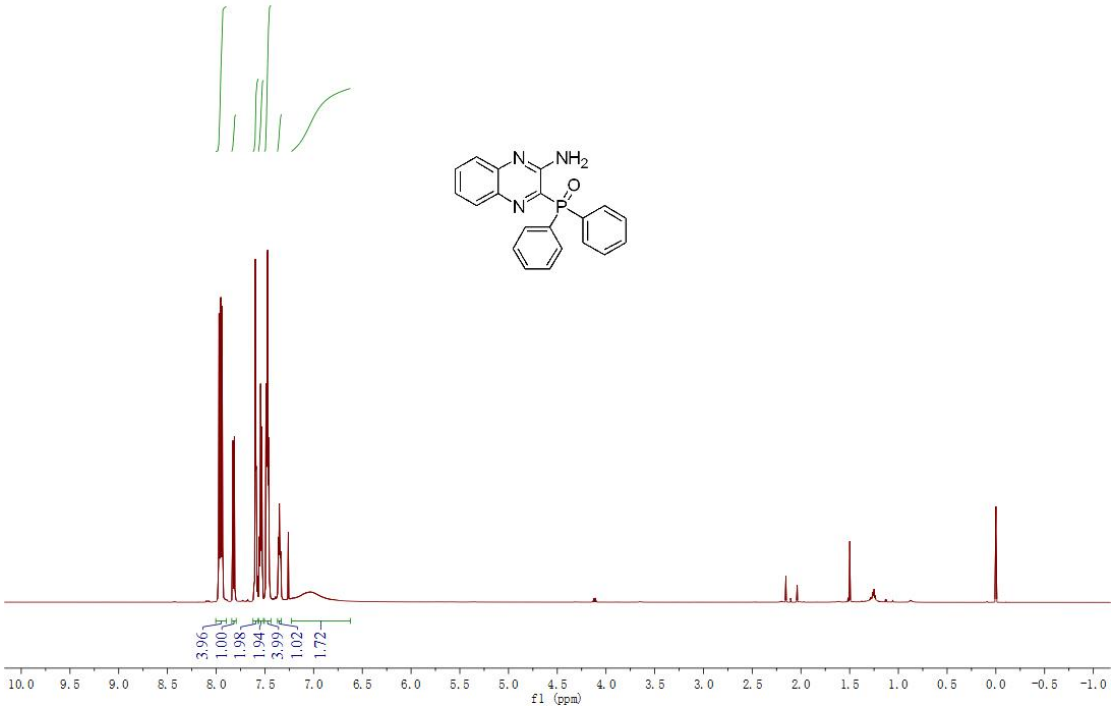
^{13}C NMR Spectrum of **5m**



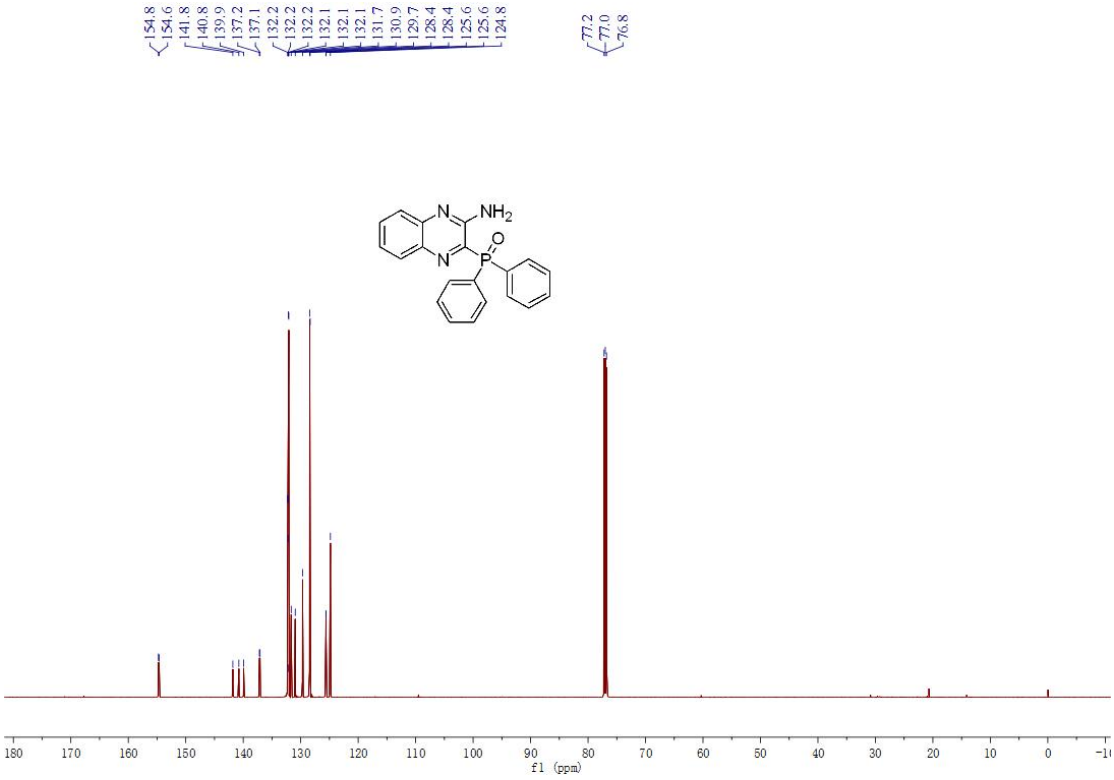
^{31}P NMR Spectrum of **5m**



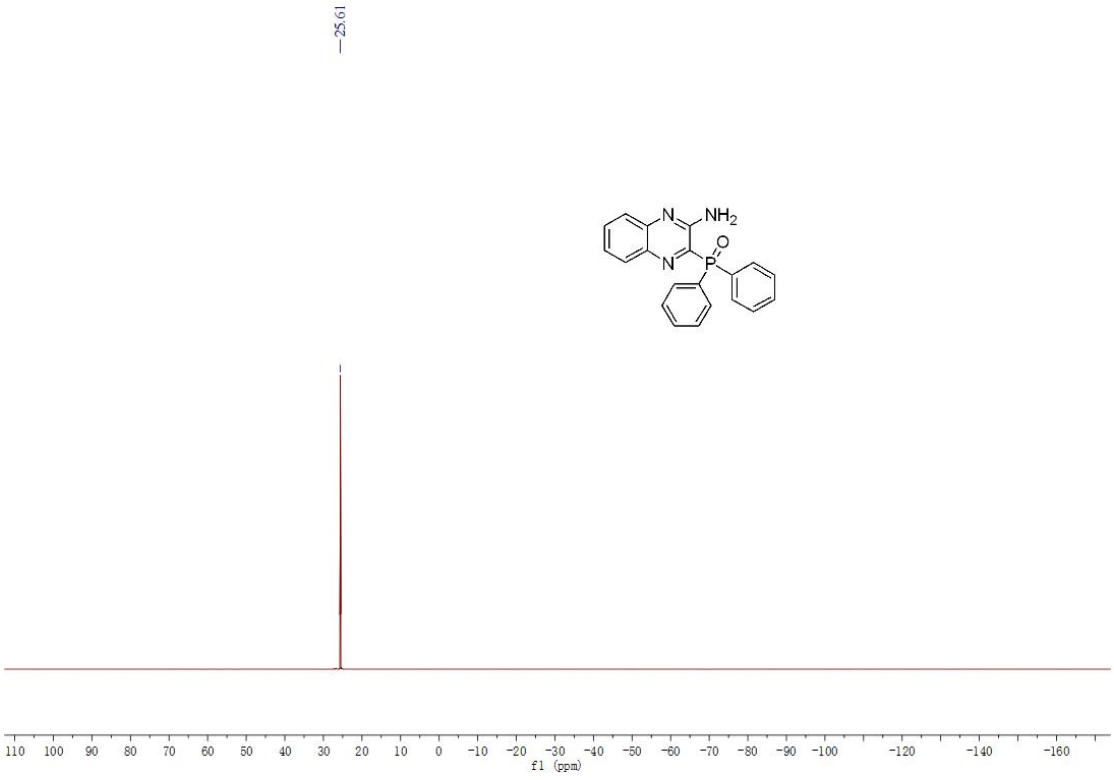
^{1}H NMR Spectrum of **5n**



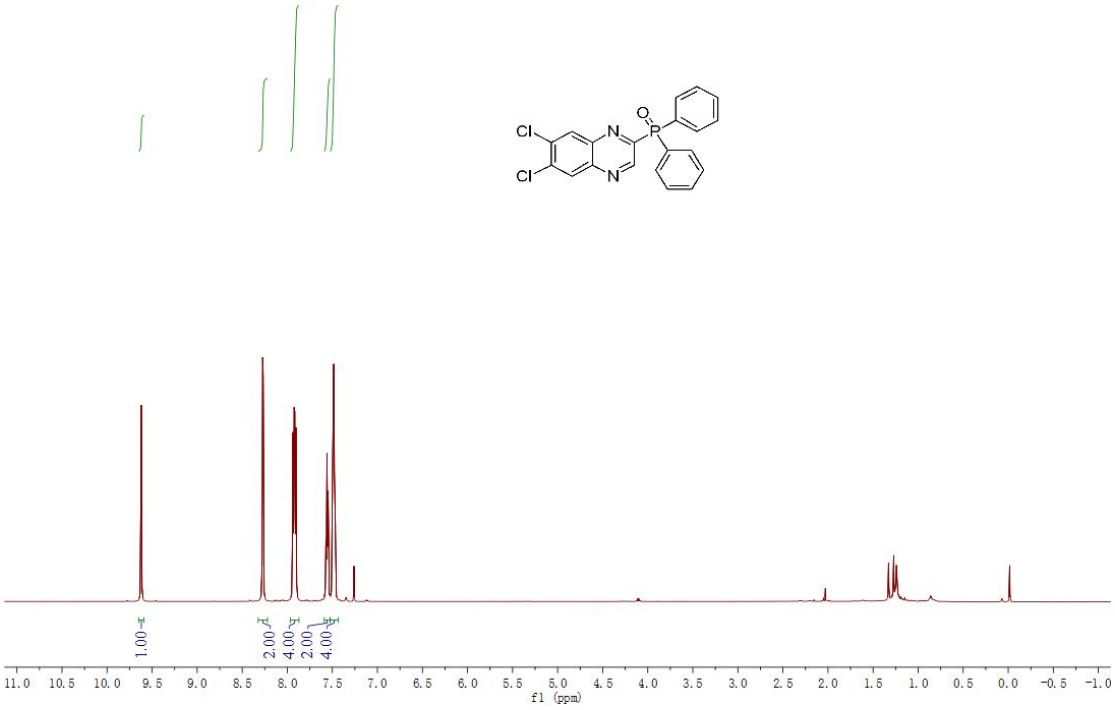
^{13}C NMR Spectrum of **5n**



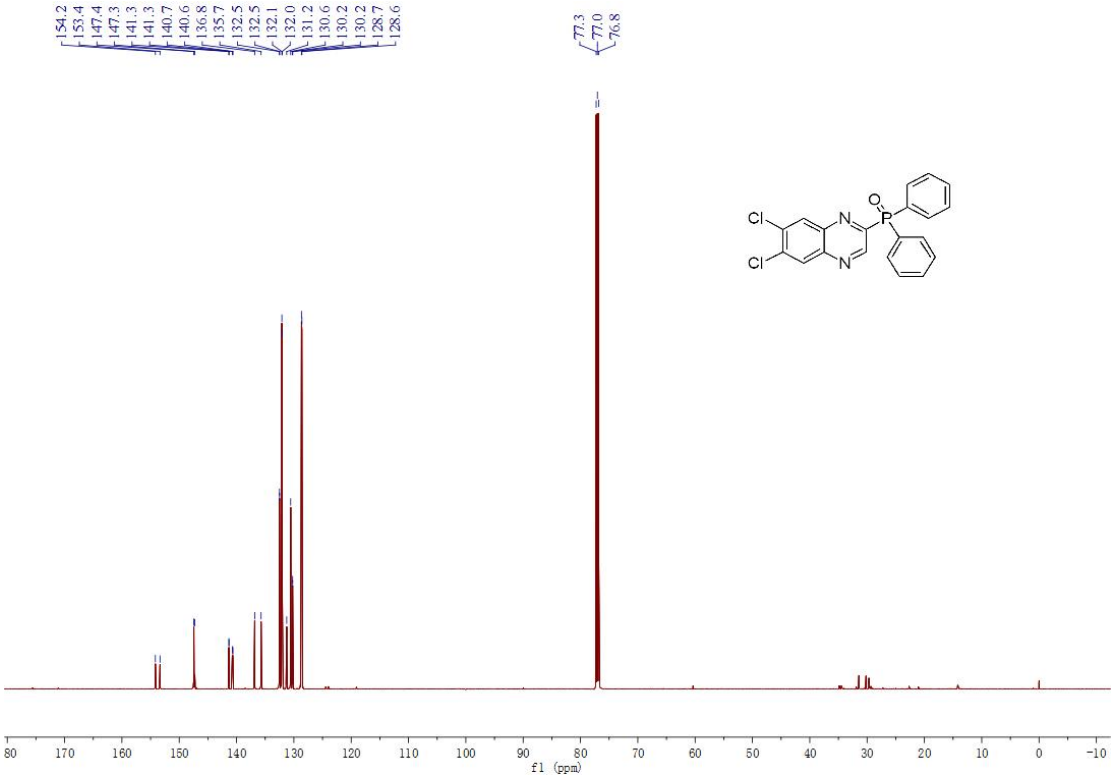
^{31}P NMR Spectrum of **5n**



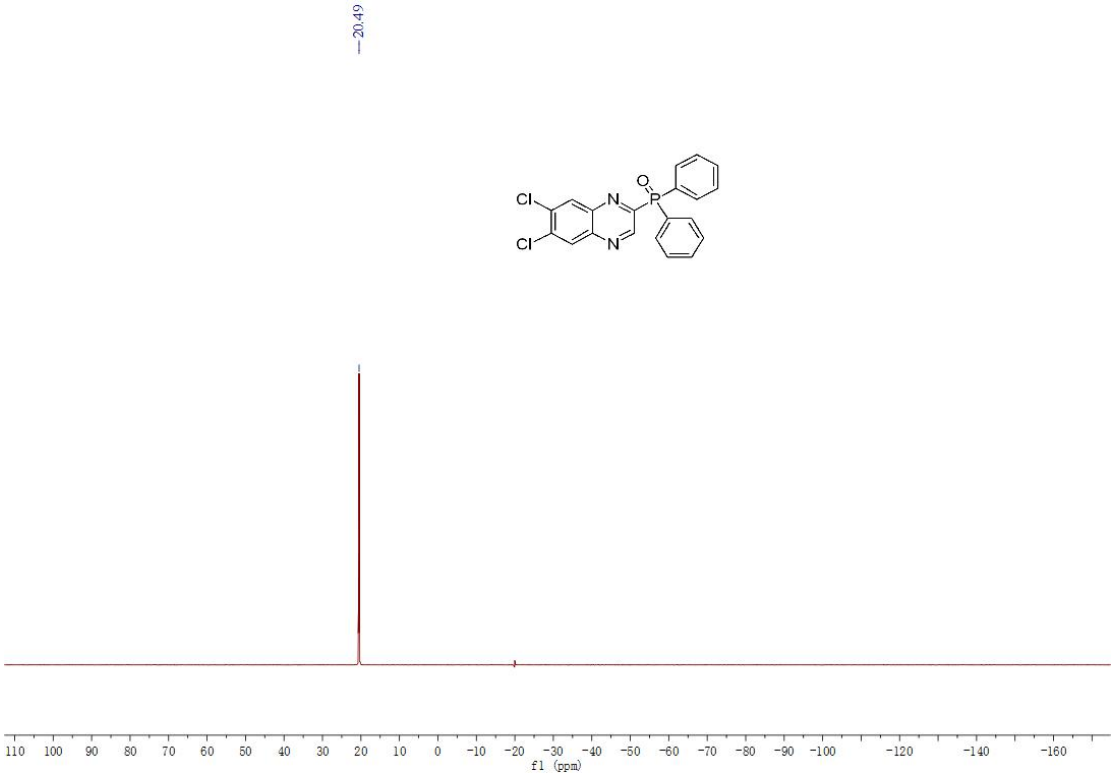
^{1}H NMR Spectrum of **5o**



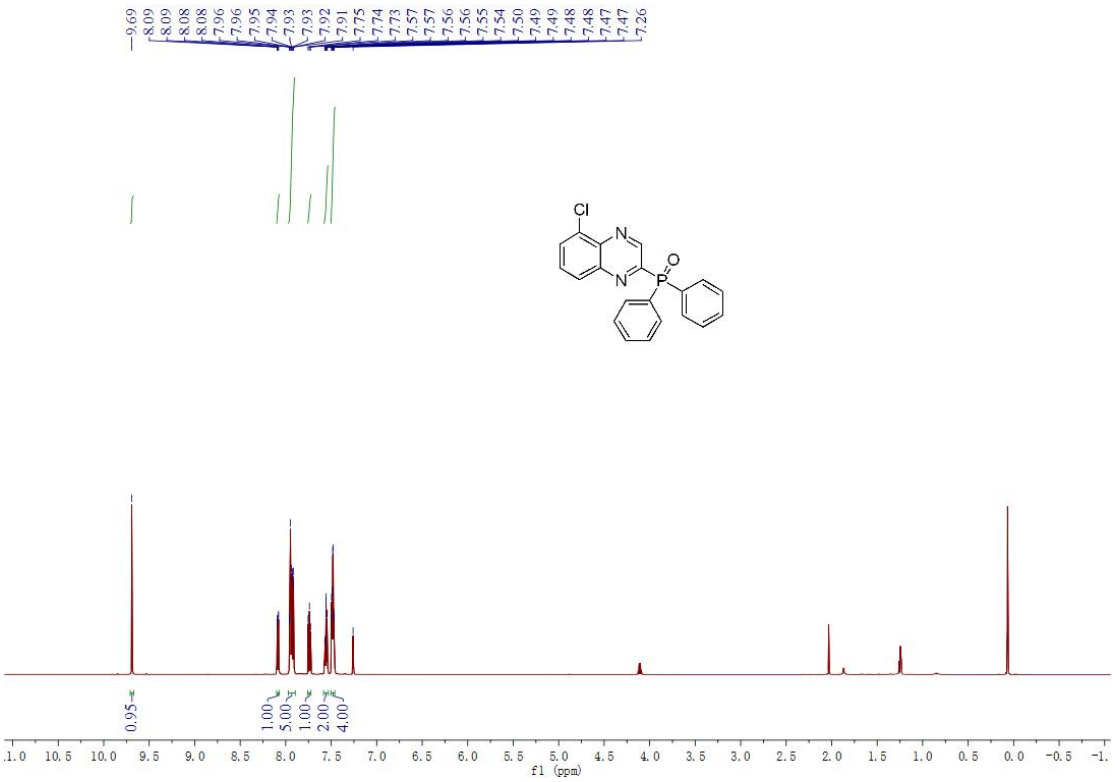
^{13}C NMR Spectrum of **5o**



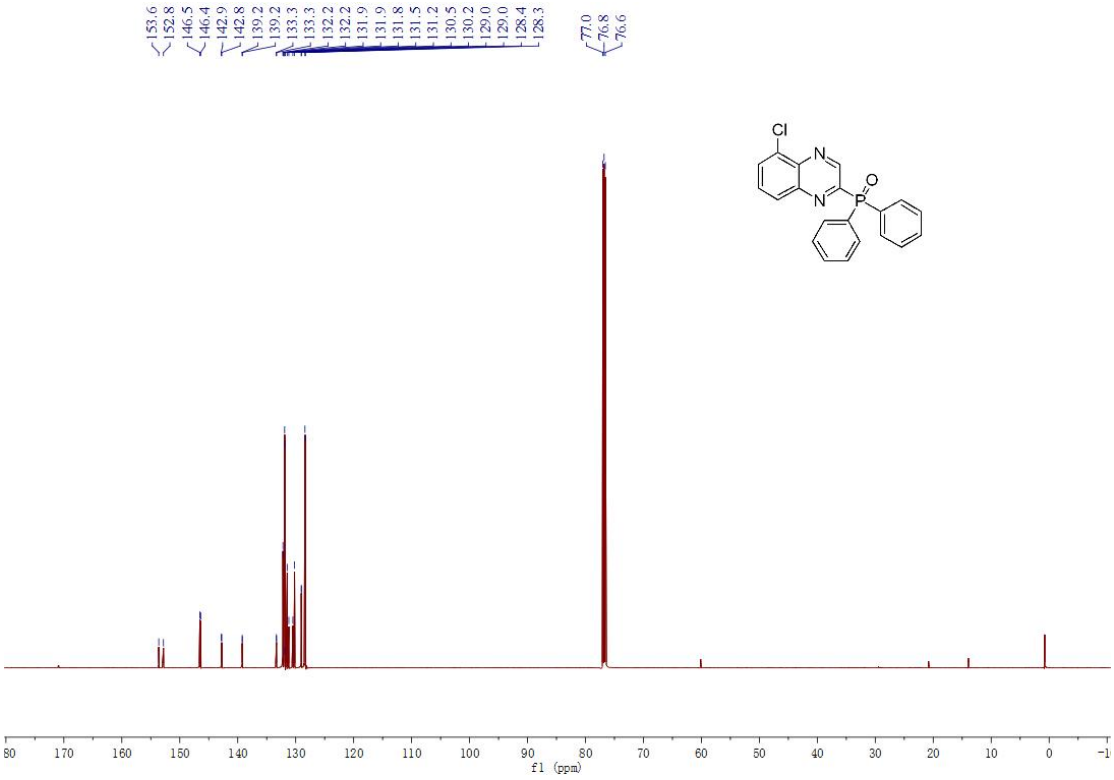
^{31}P NMR Spectrum of **5o**



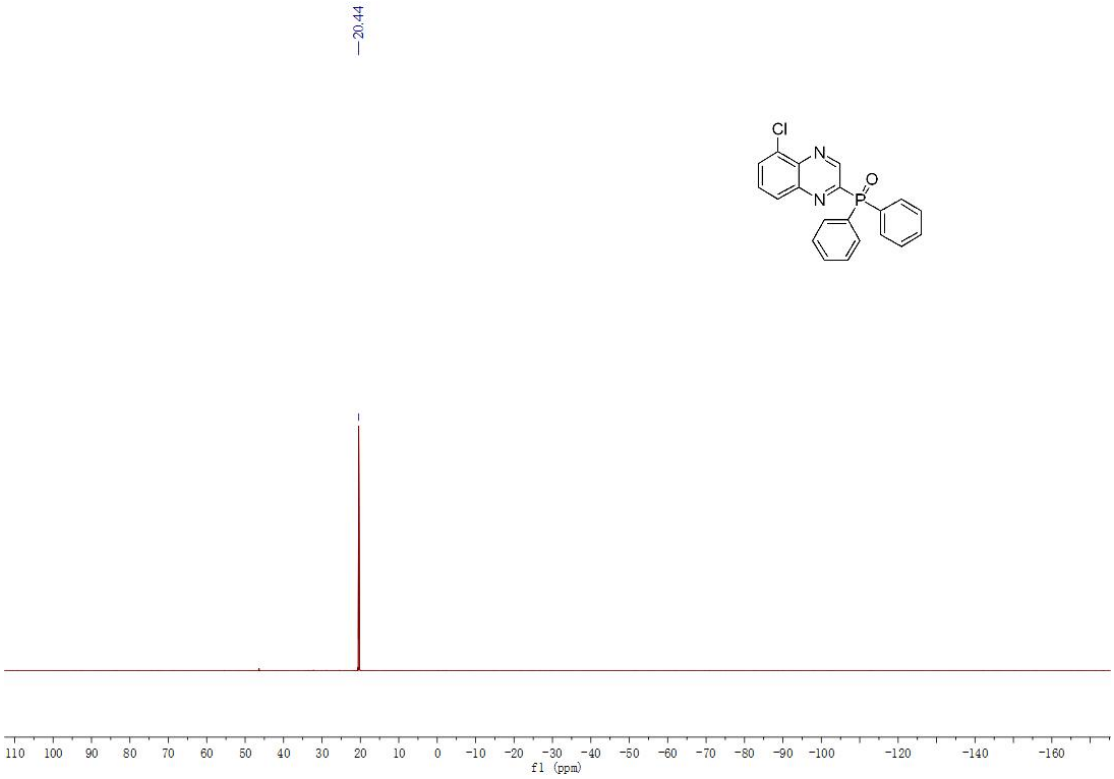
^{1}H NMR Spectrum of **5p**



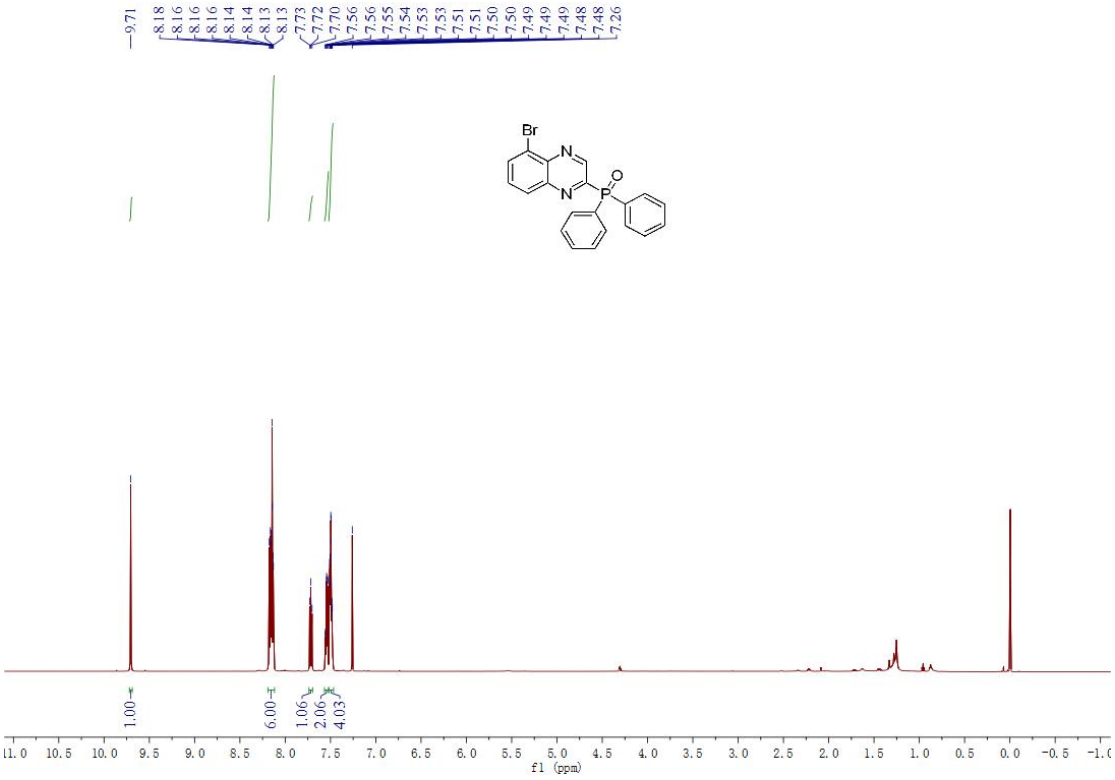
^{13}C NMR Spectrum of **5p**



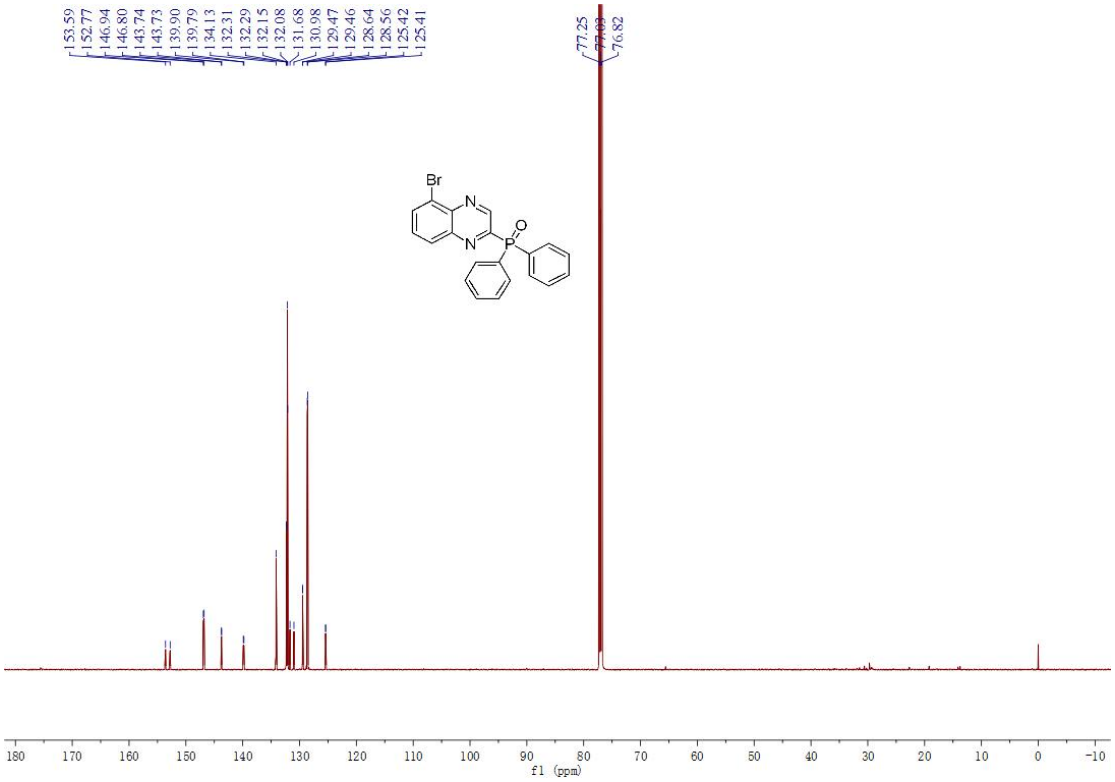
^{31}P NMR Spectrum of **5p**



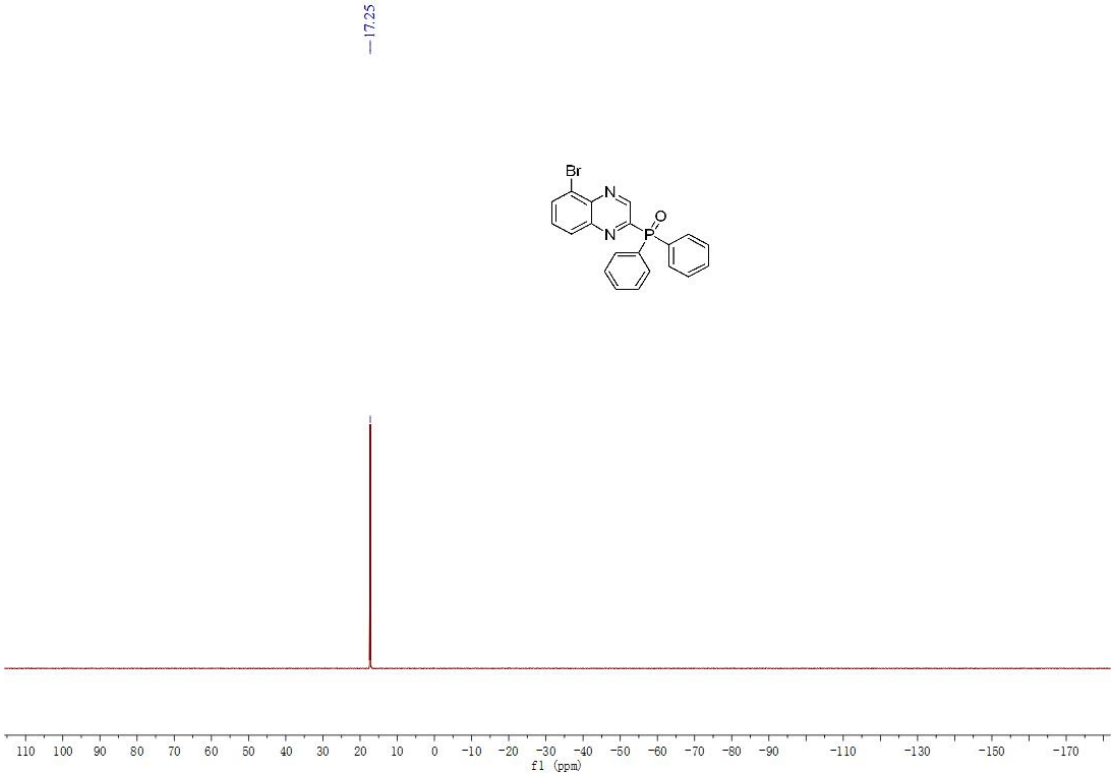
^{1}H NMR Spectrum of **5q**



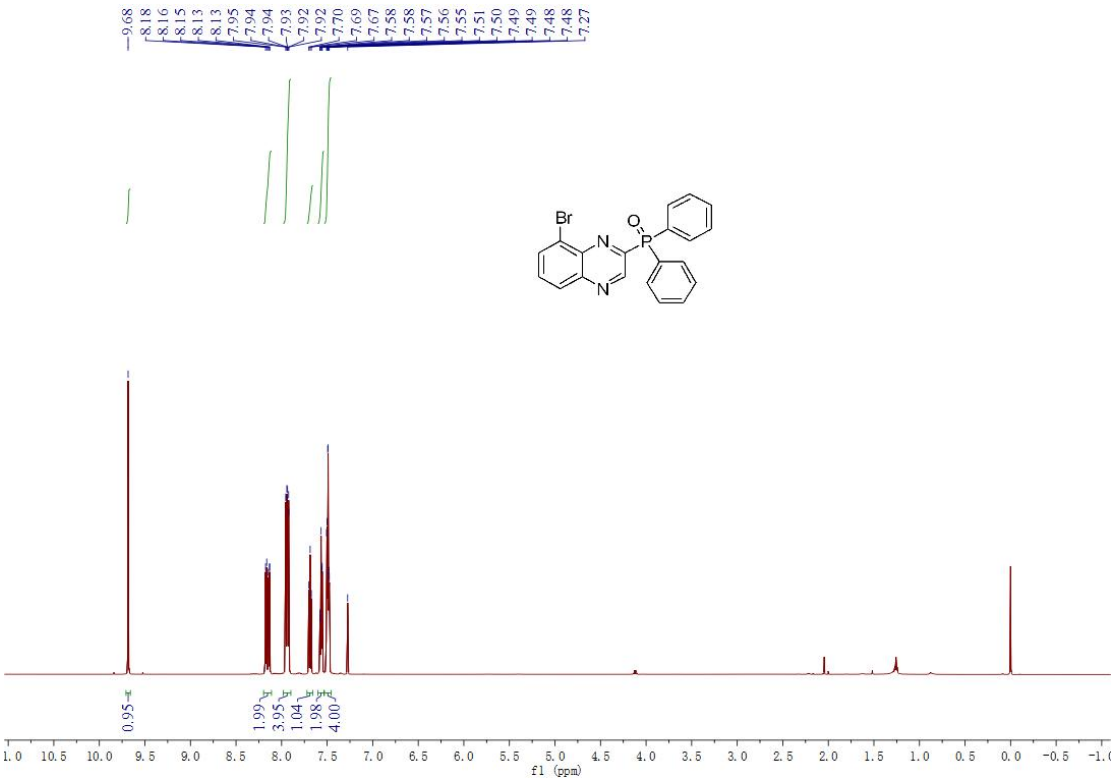
^{13}C NMR Spectrum of **5q**



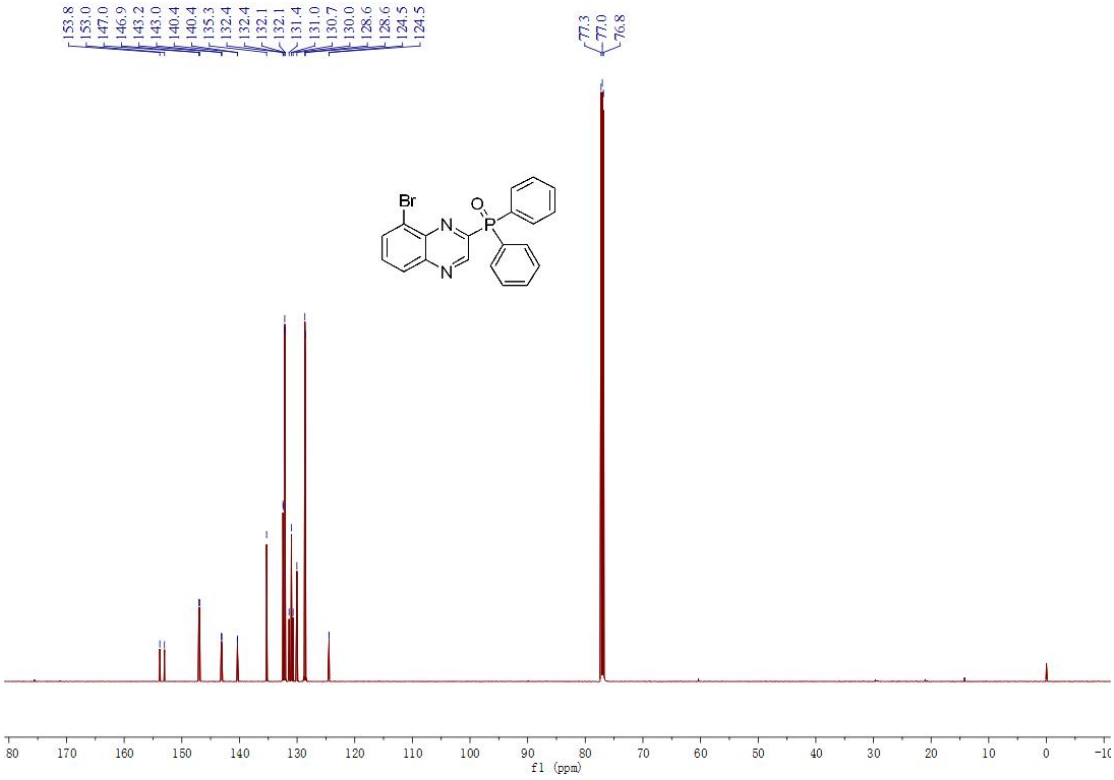
^{31}P NMR Spectrum of **5q**



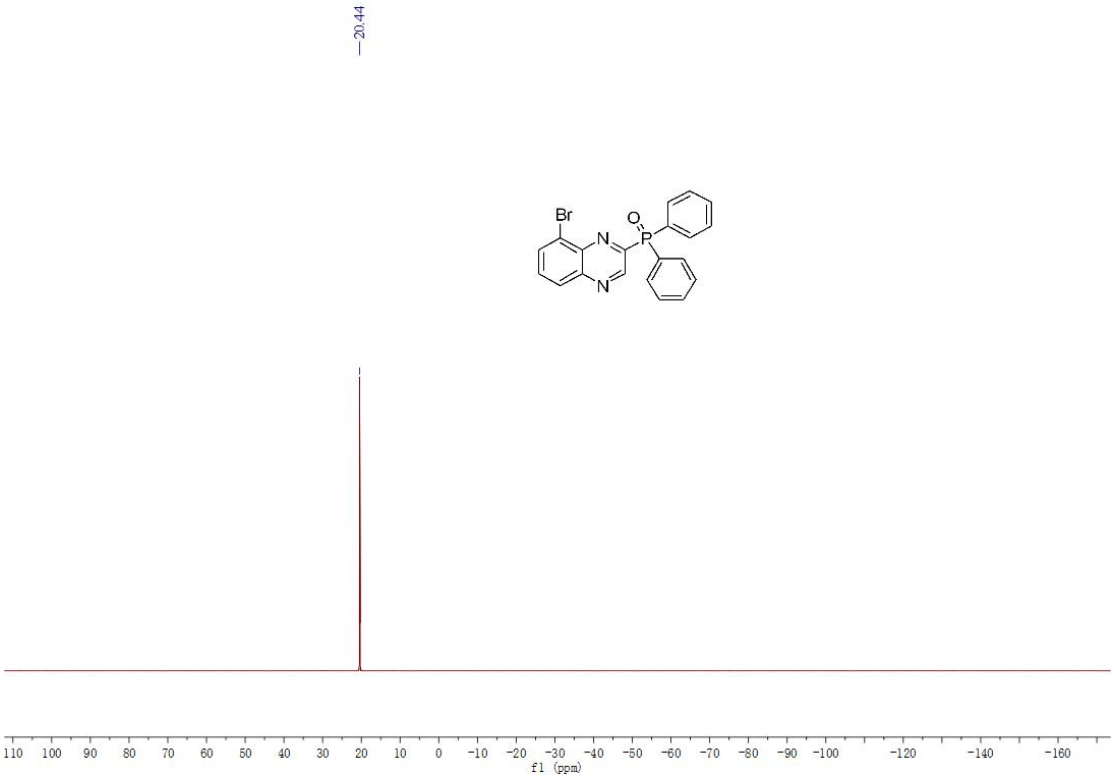
^{1}H NMR Spectrum of **5q***



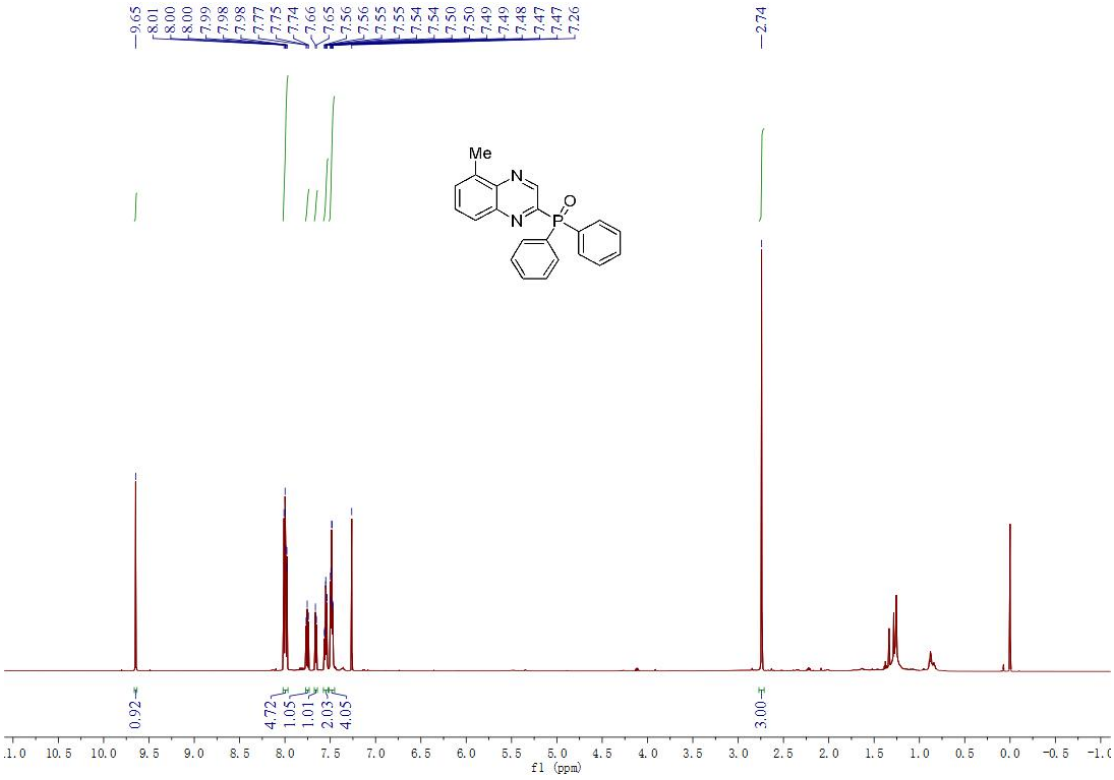
^{13}C NMR Spectrum of **5q***



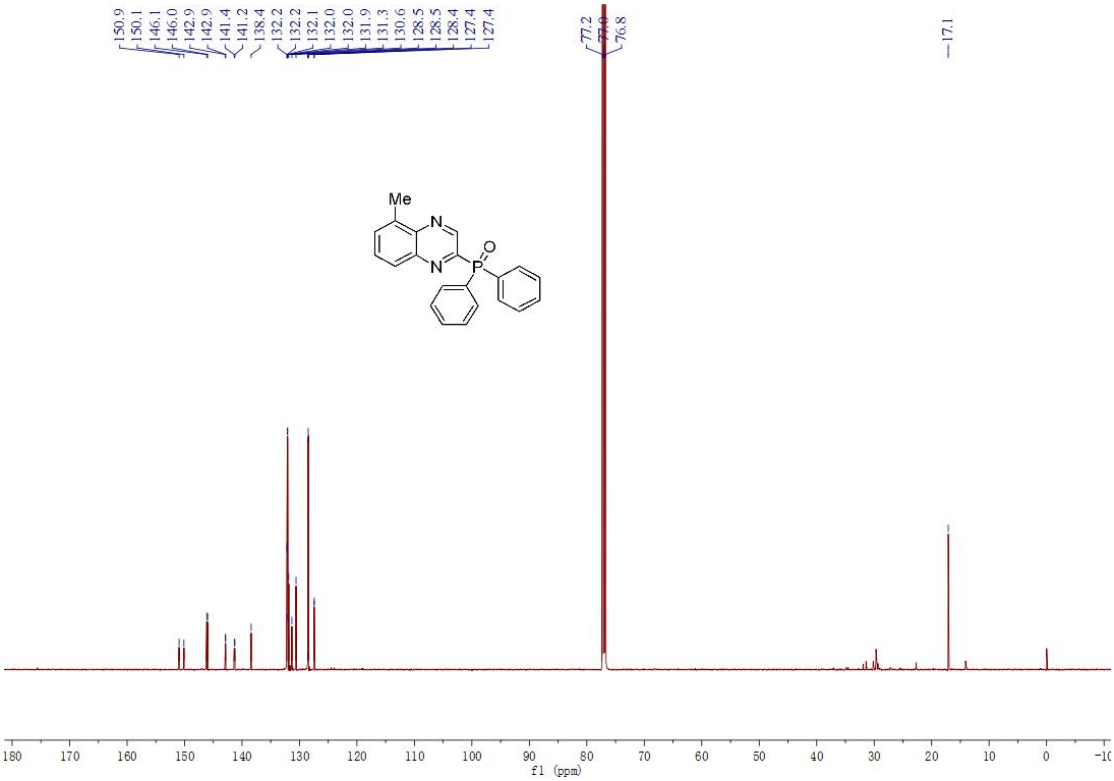
^{31}P NMR Spectrum of **5q***



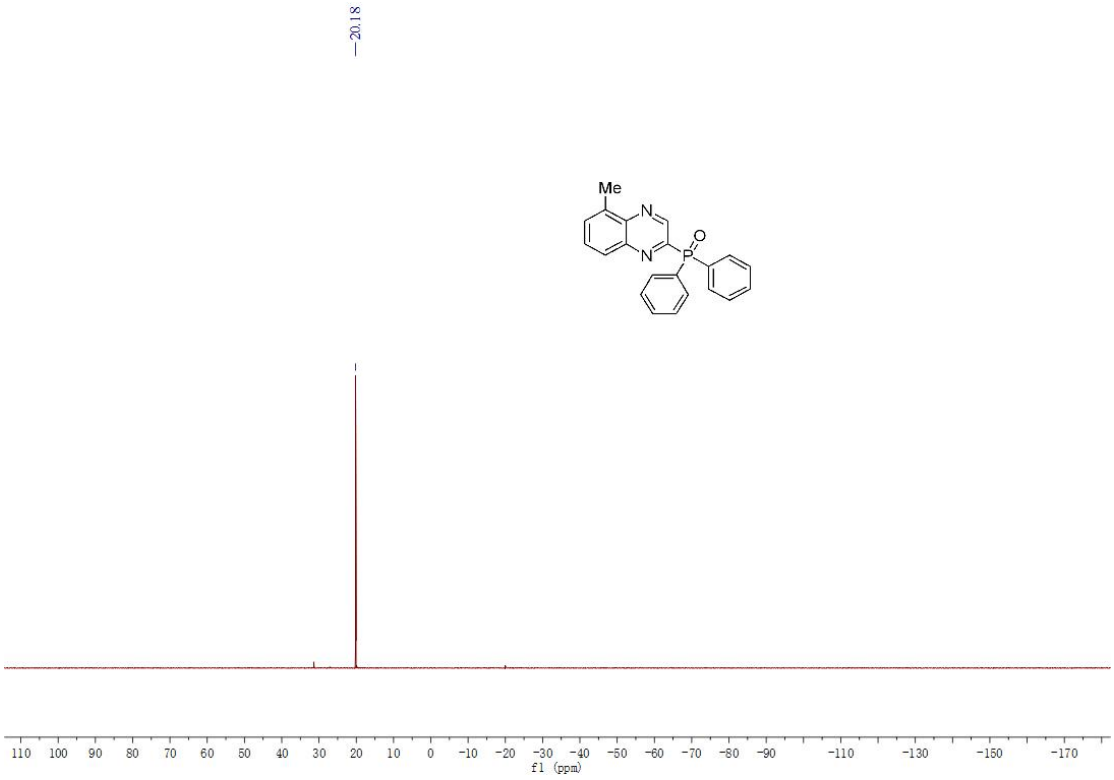
^{1}H NMR Spectrum of **5r**



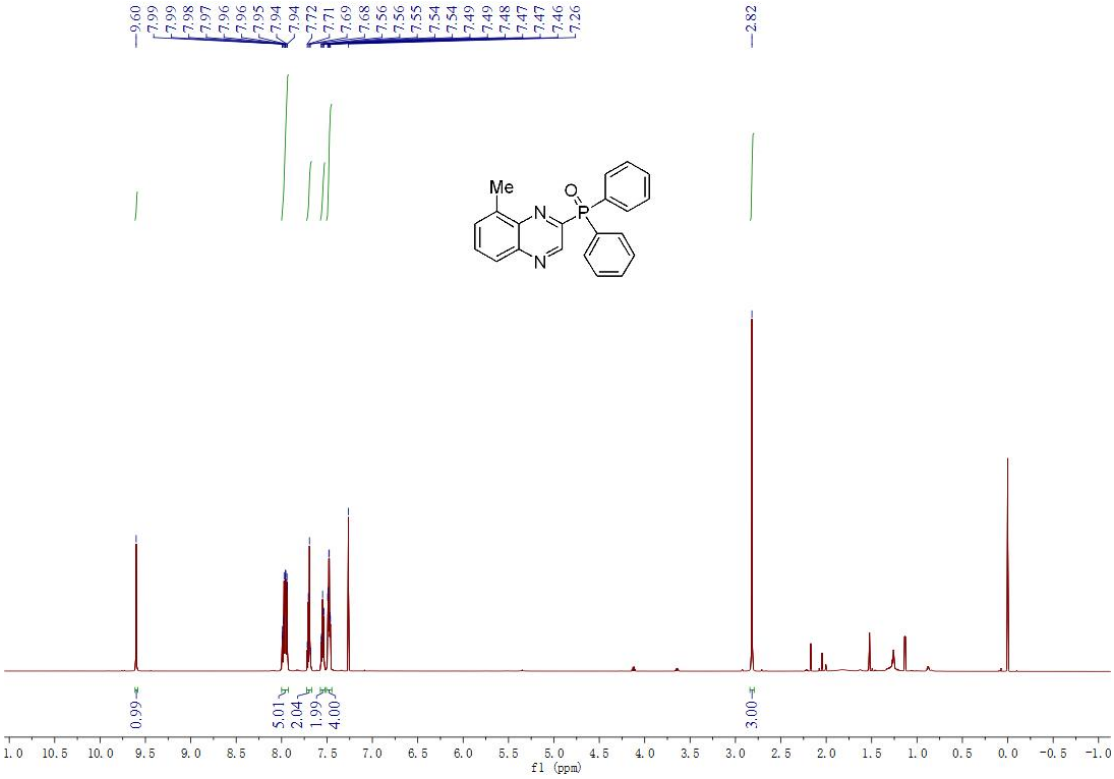
^{13}C NMR Spectrum of **5r**



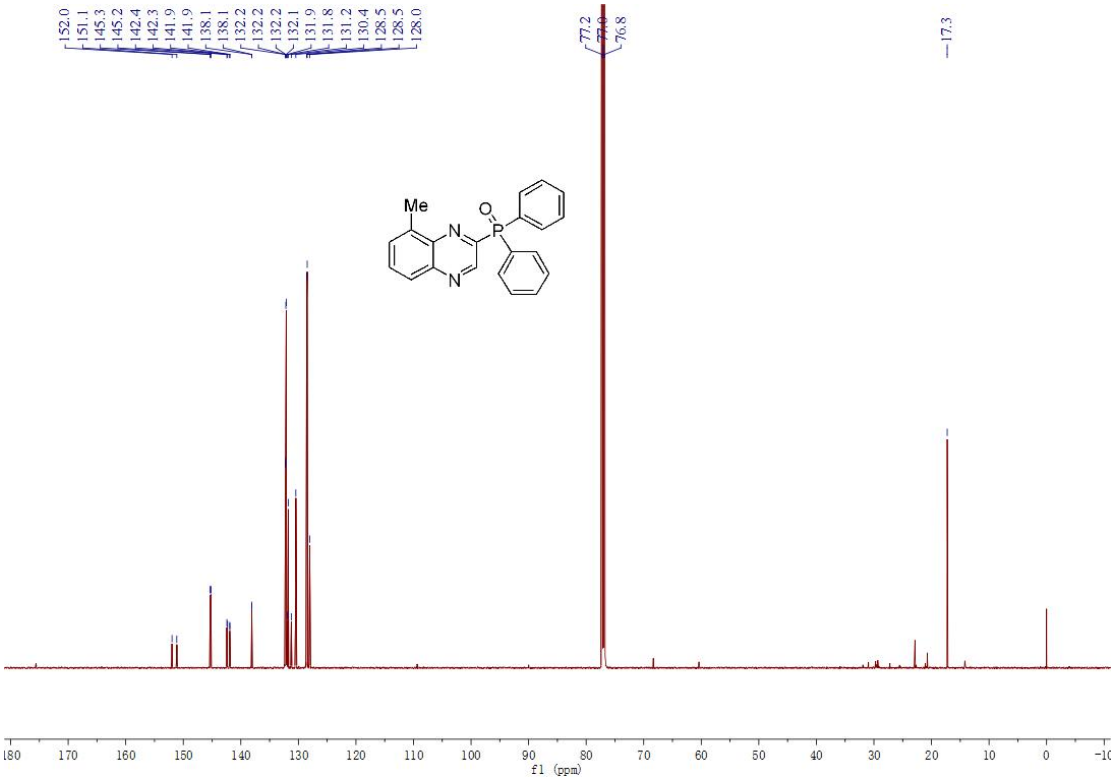
^{31}P NMR Spectrum of **5r**



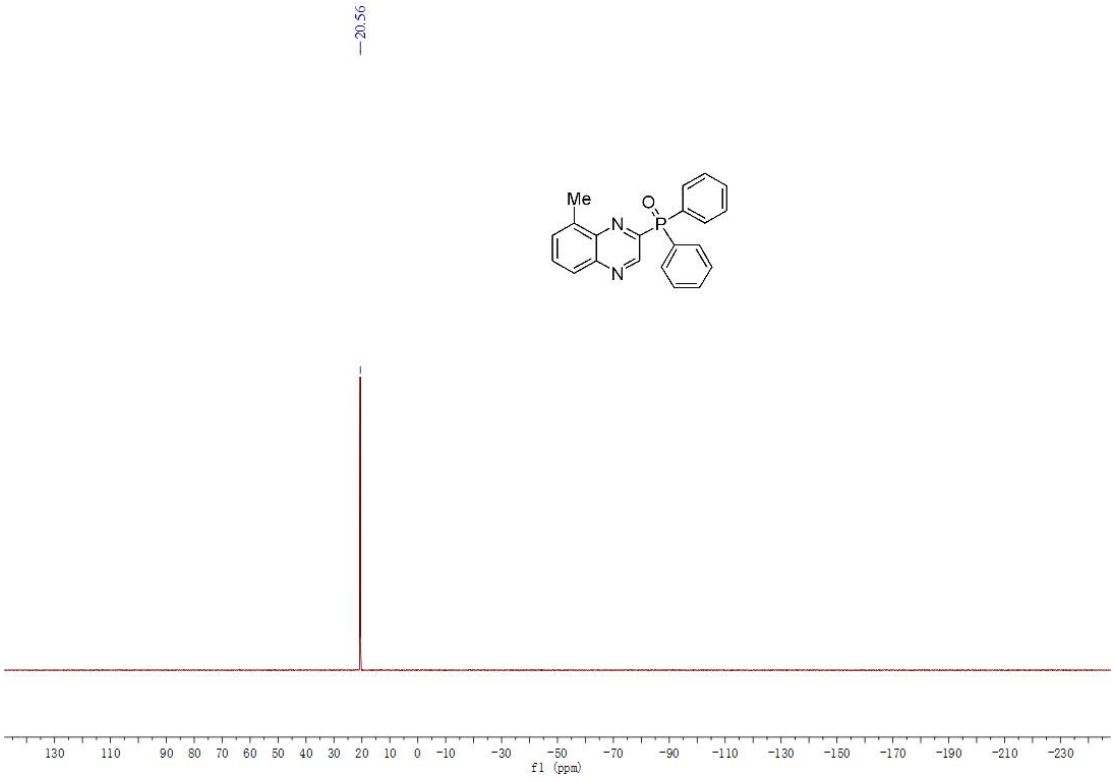
^{1}H NMR Spectrum of **5r***



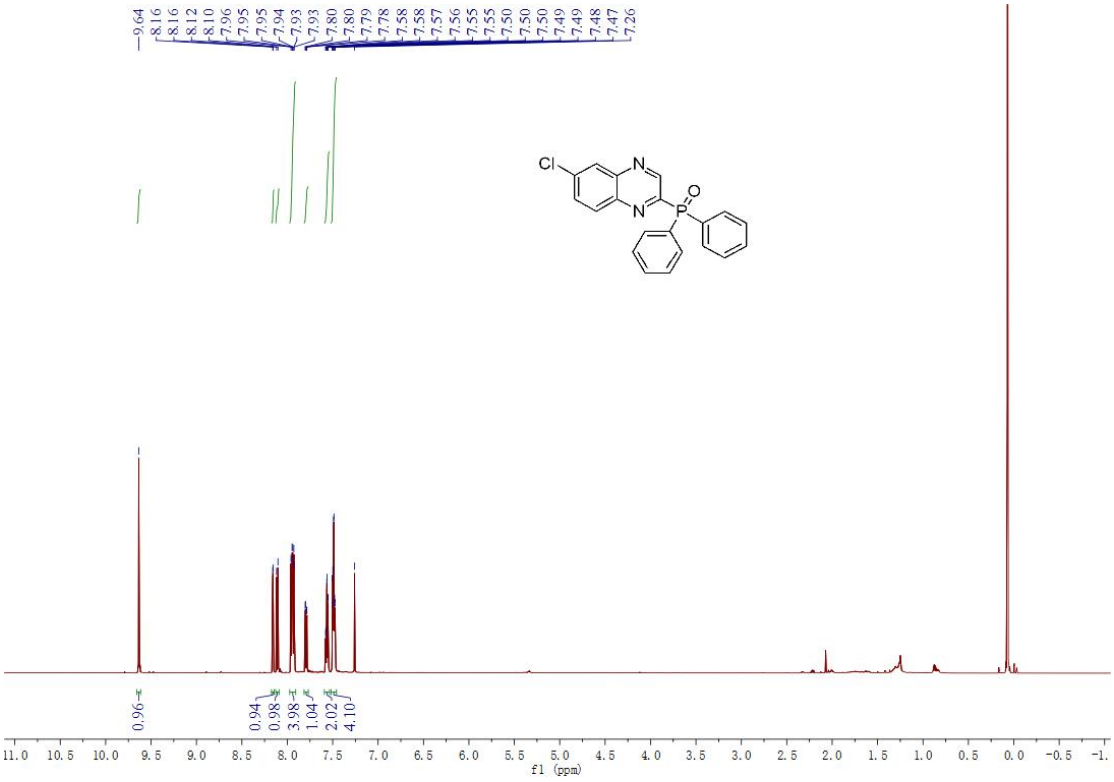
^{13}C NMR Spectrum of **5r***



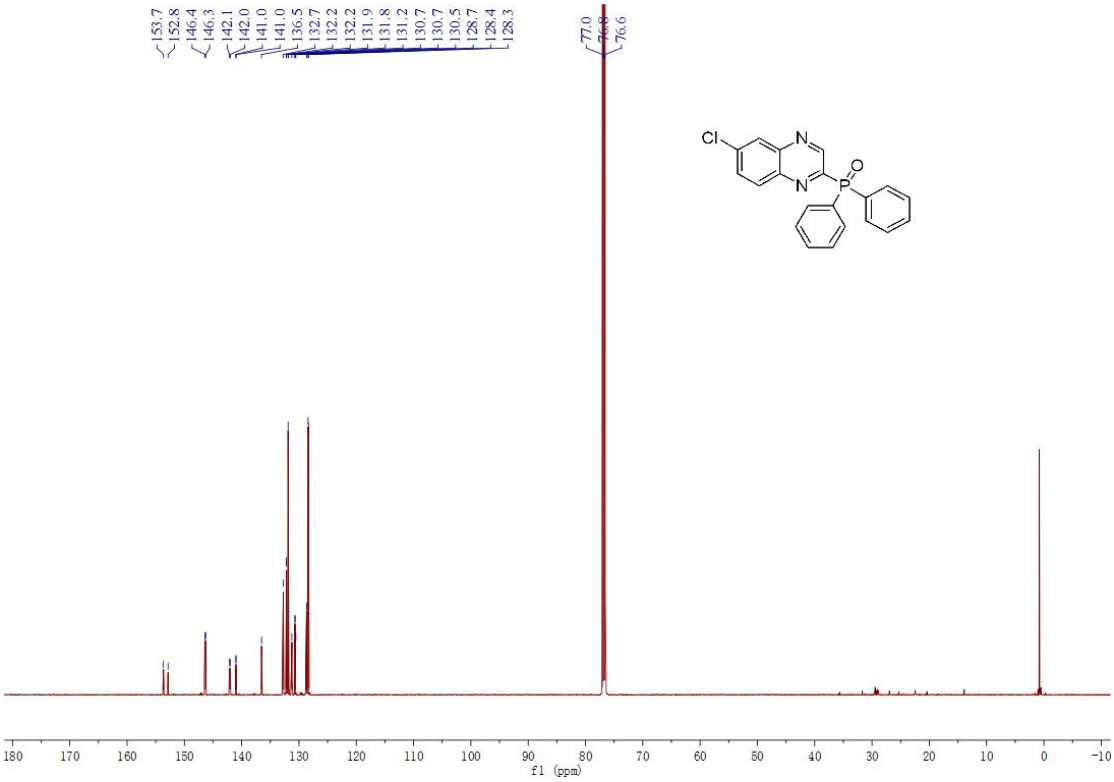
^{31}P NMR Spectrum of **5r***



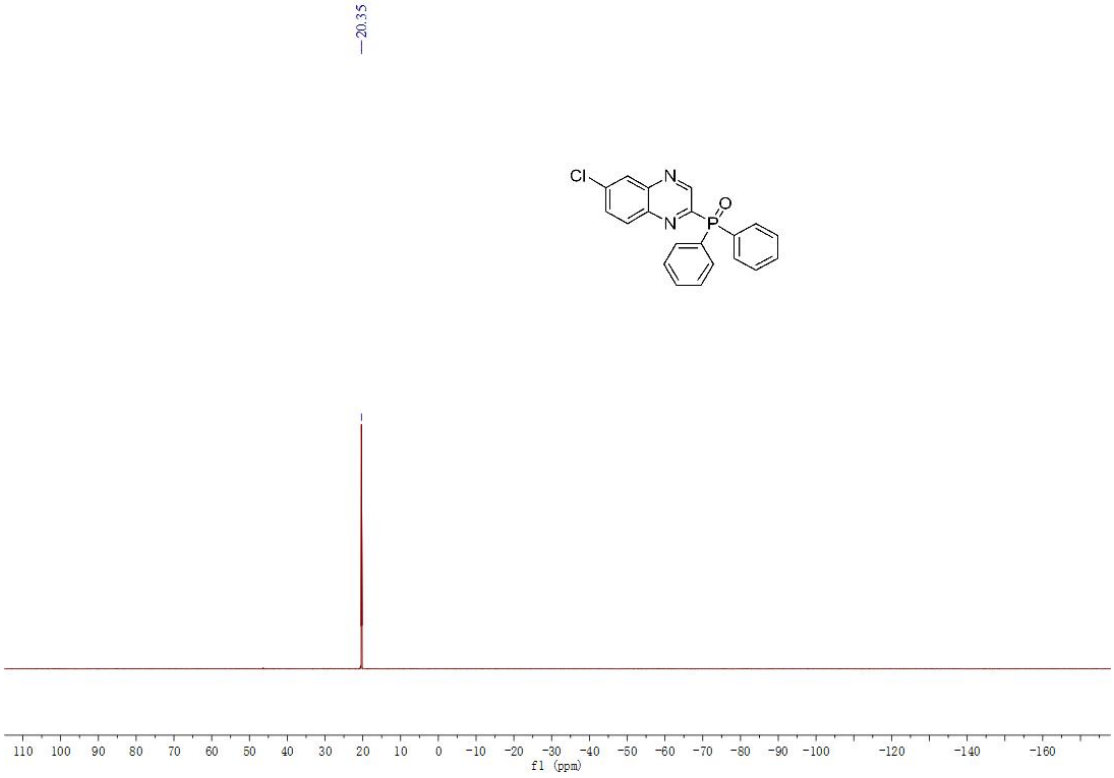
^{1}H NMR Spectrum of **5s**



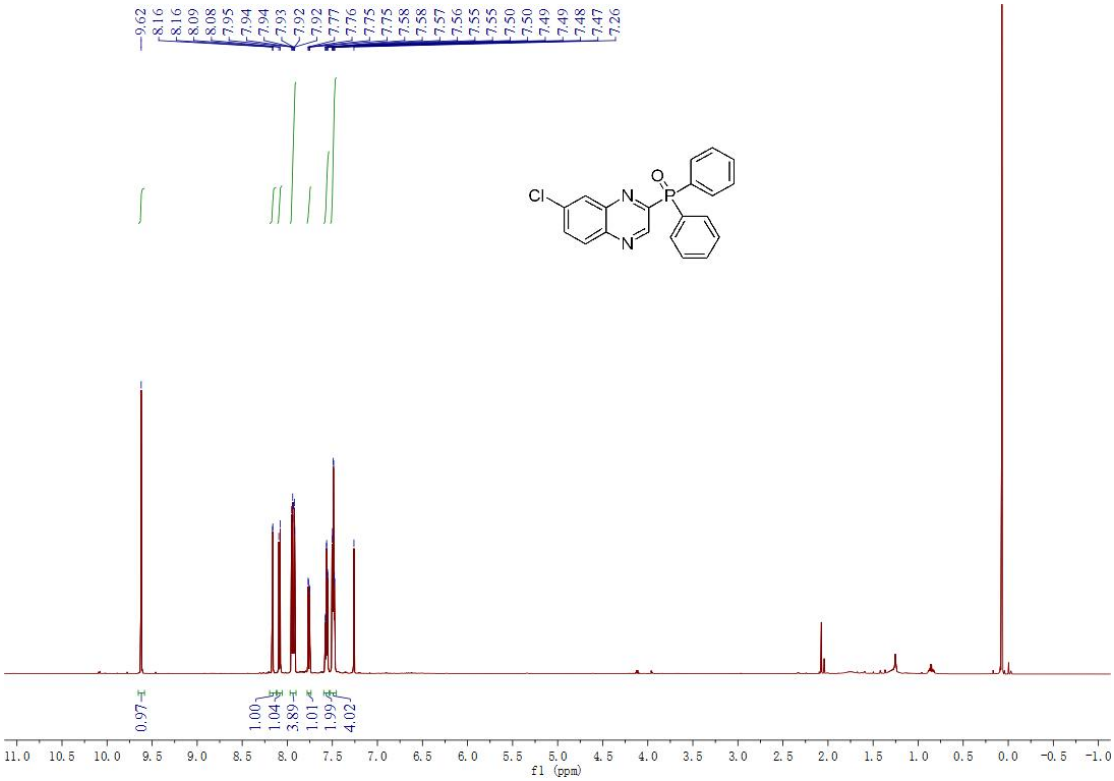
^{13}C NMR Spectrum of **5s**



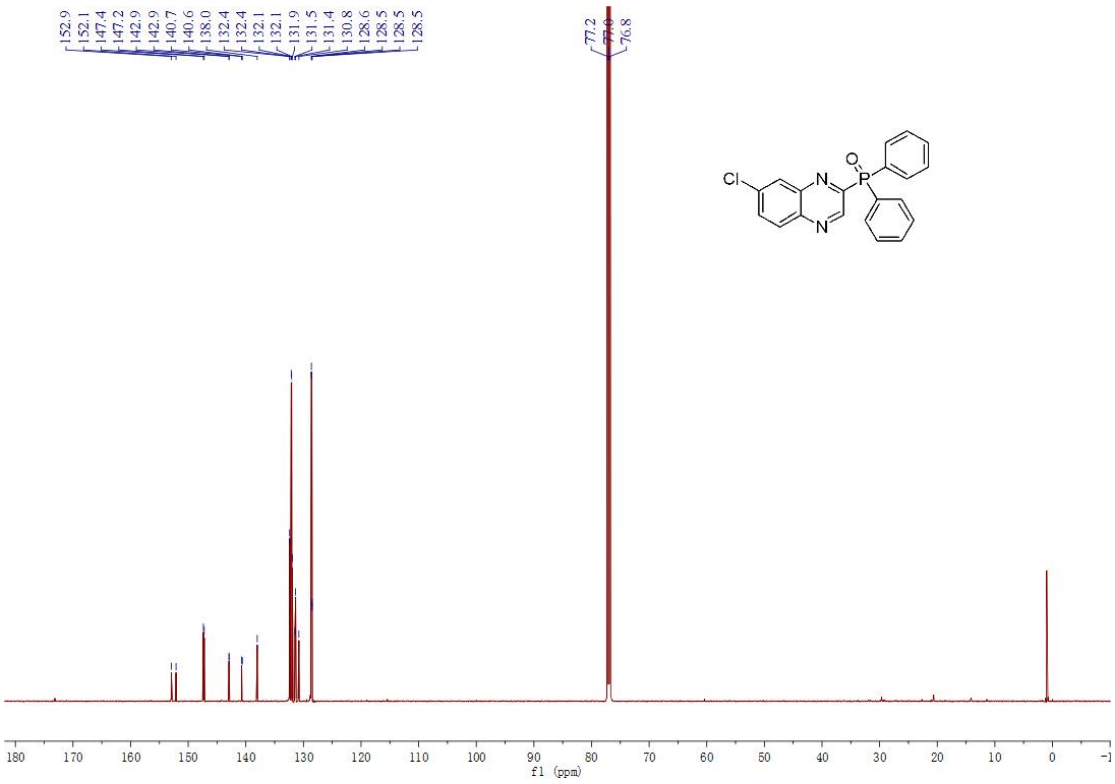
^{31}P NMR Spectrum of **5s**



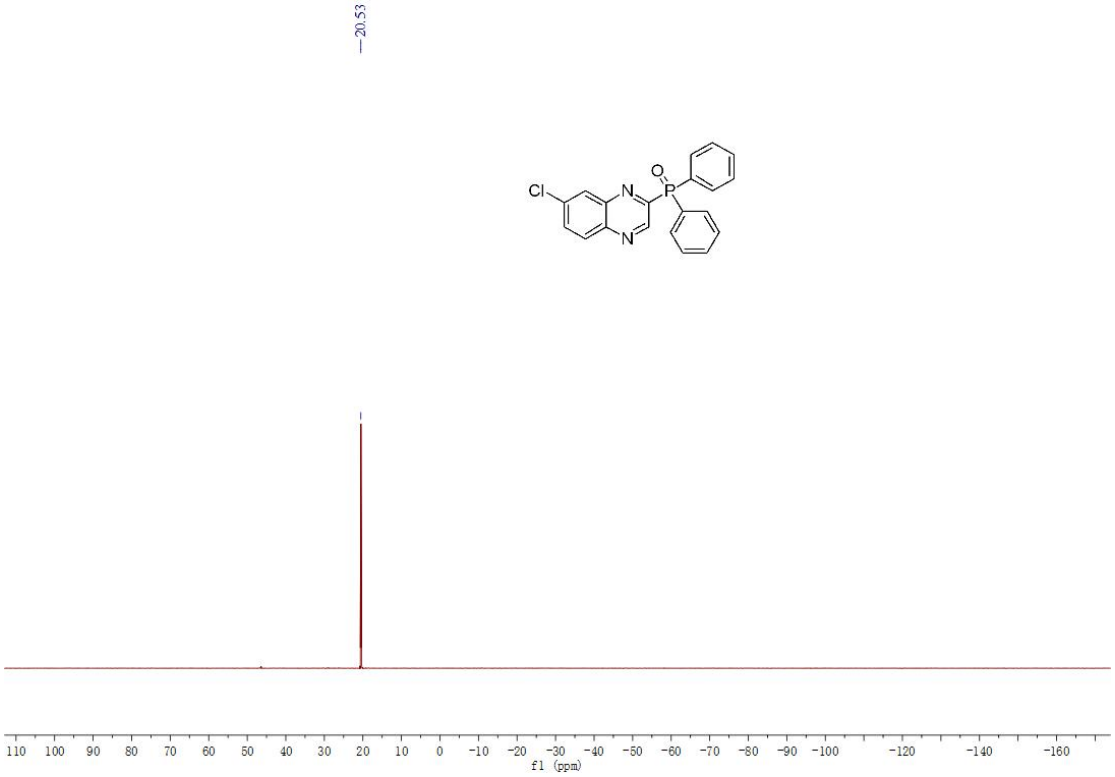
^{1}H NMR Spectrum of **5s***



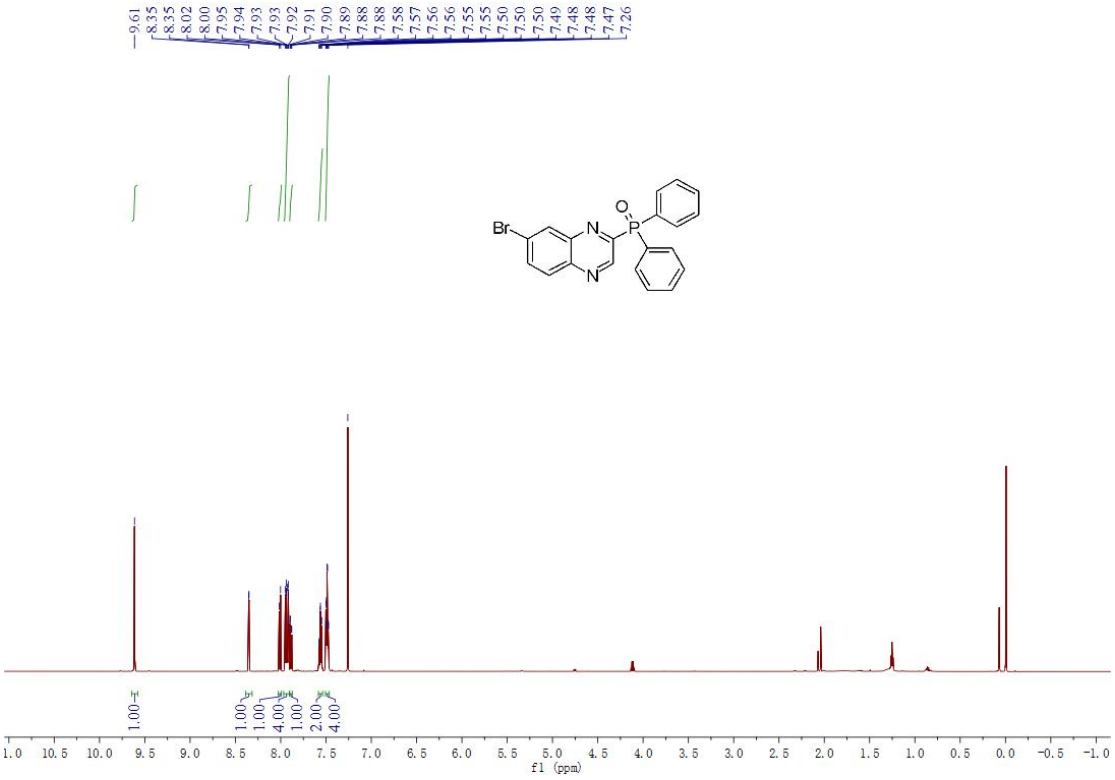
^{13}C NMR Spectrum of **5s***



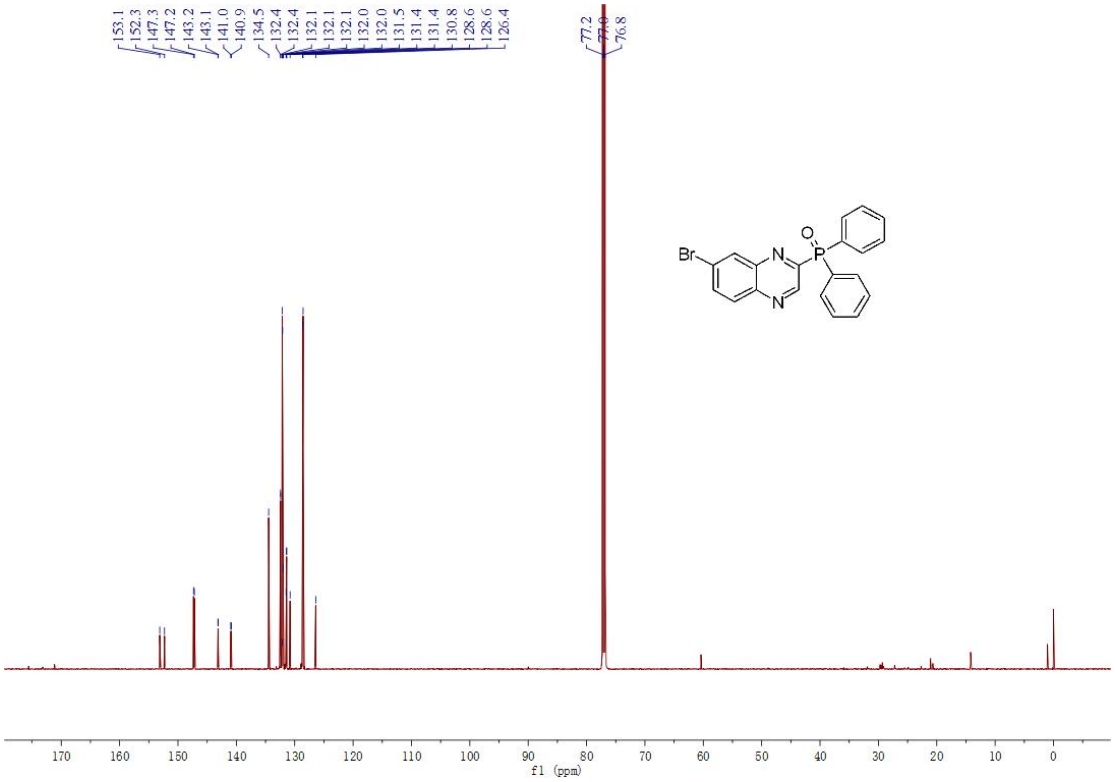
^{31}P NMR Spectrum of **5s***



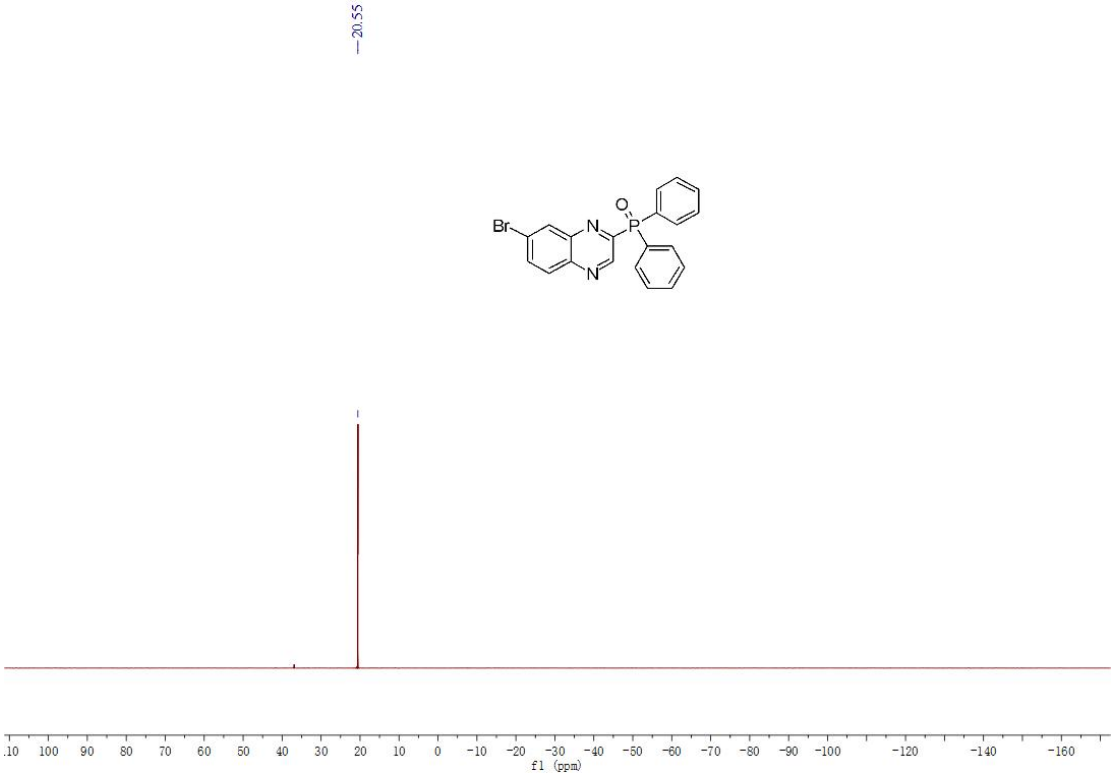
^{1}H NMR Spectrum of **5t**



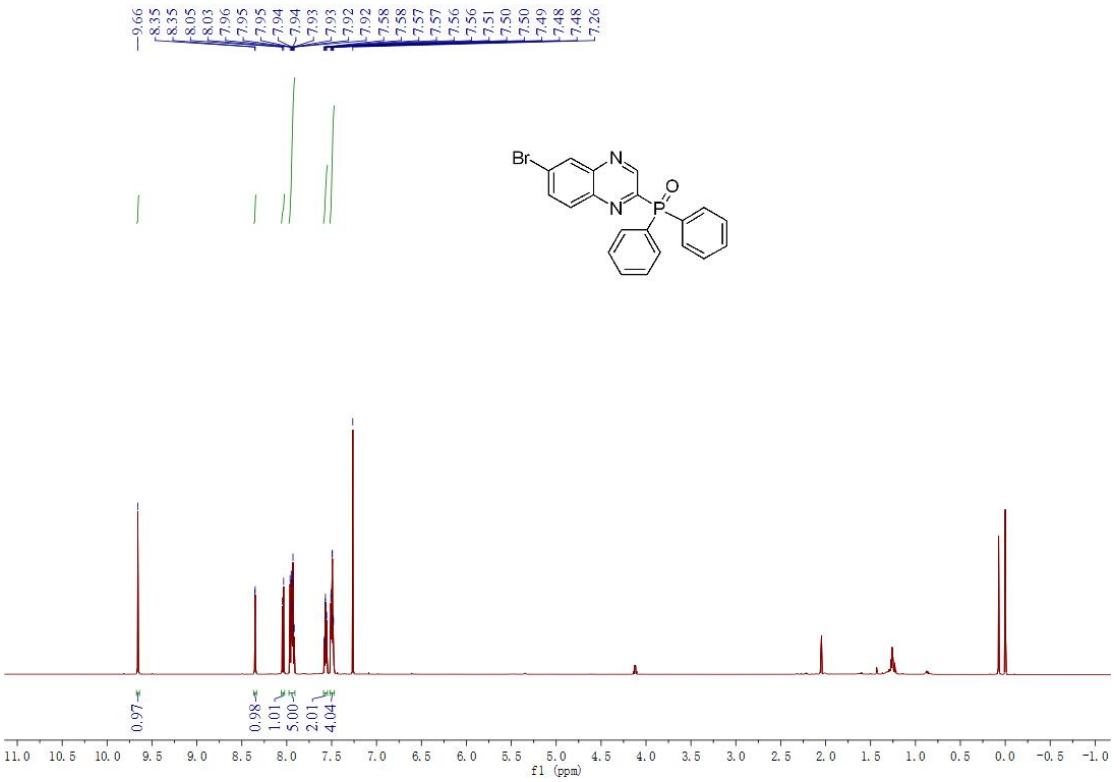
^{13}C NMR Spectrum of **5t**



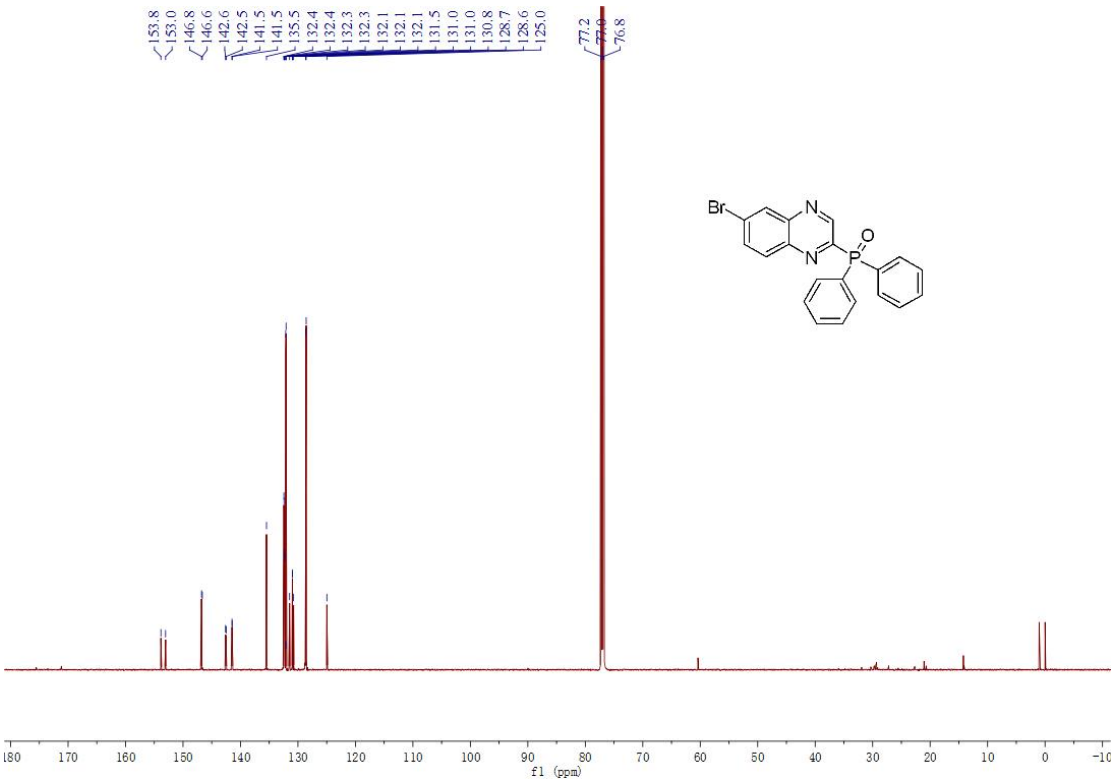
^{31}P NMR Spectrum of **5t**



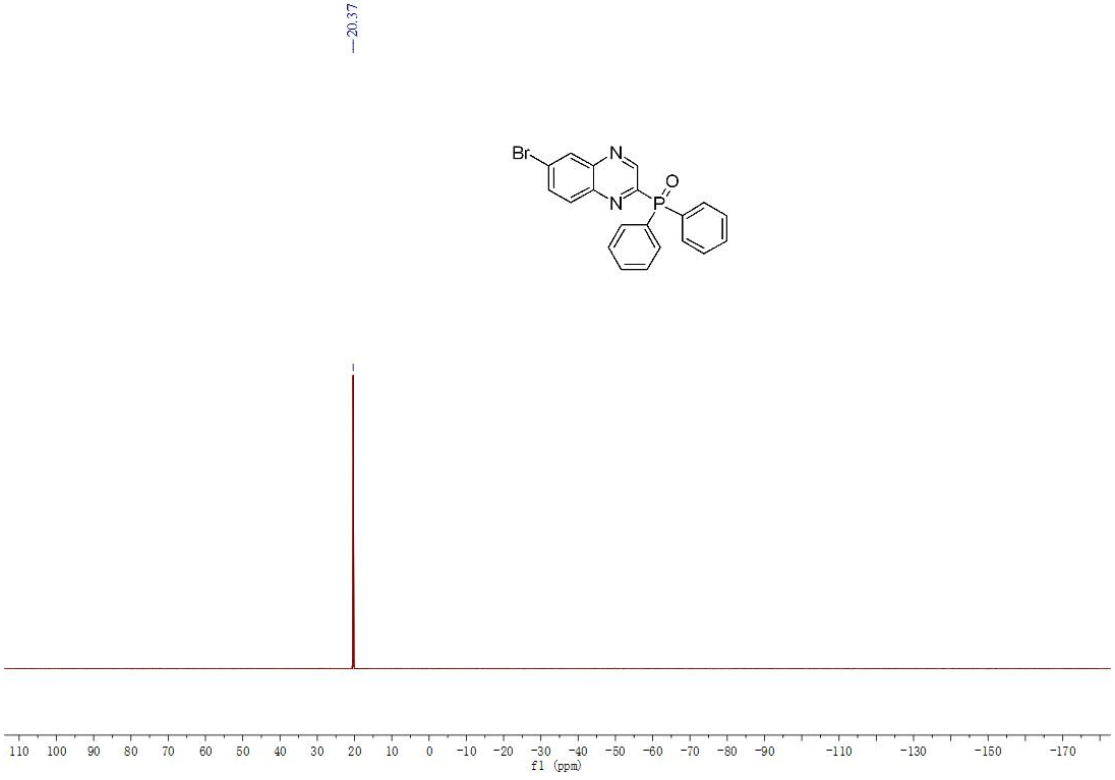
^{1}H NMR Spectrum of **5t***



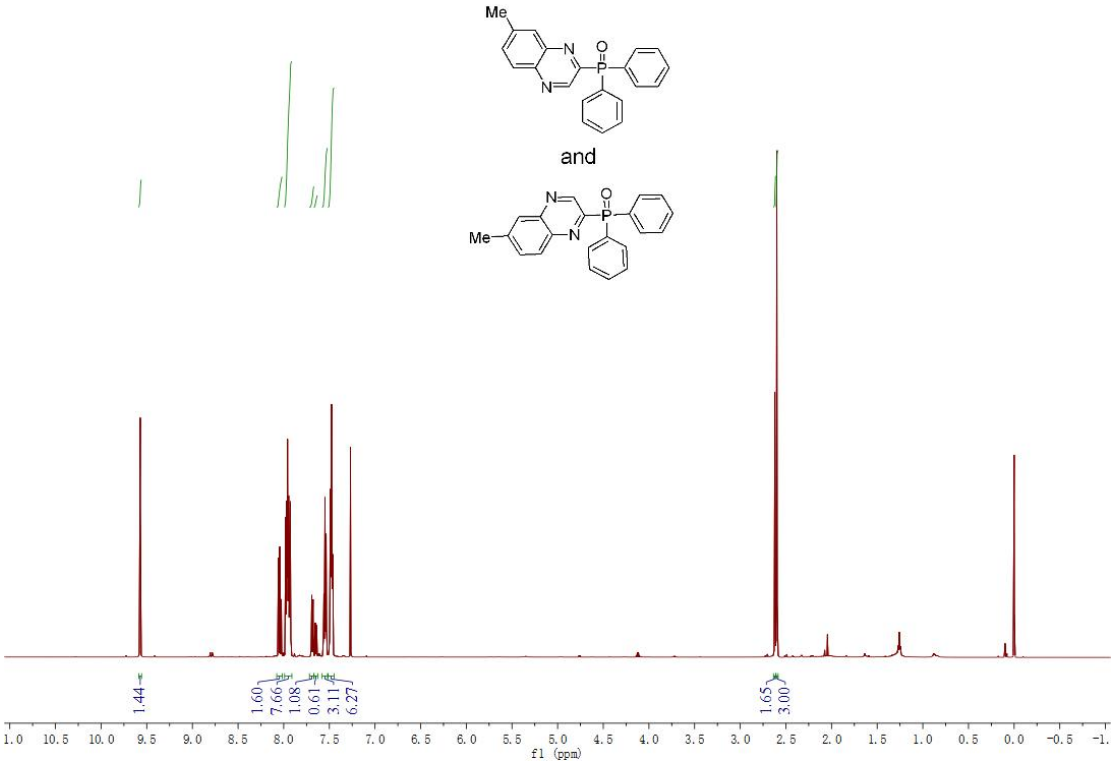
^{13}C NMR Spectrum of **5t***



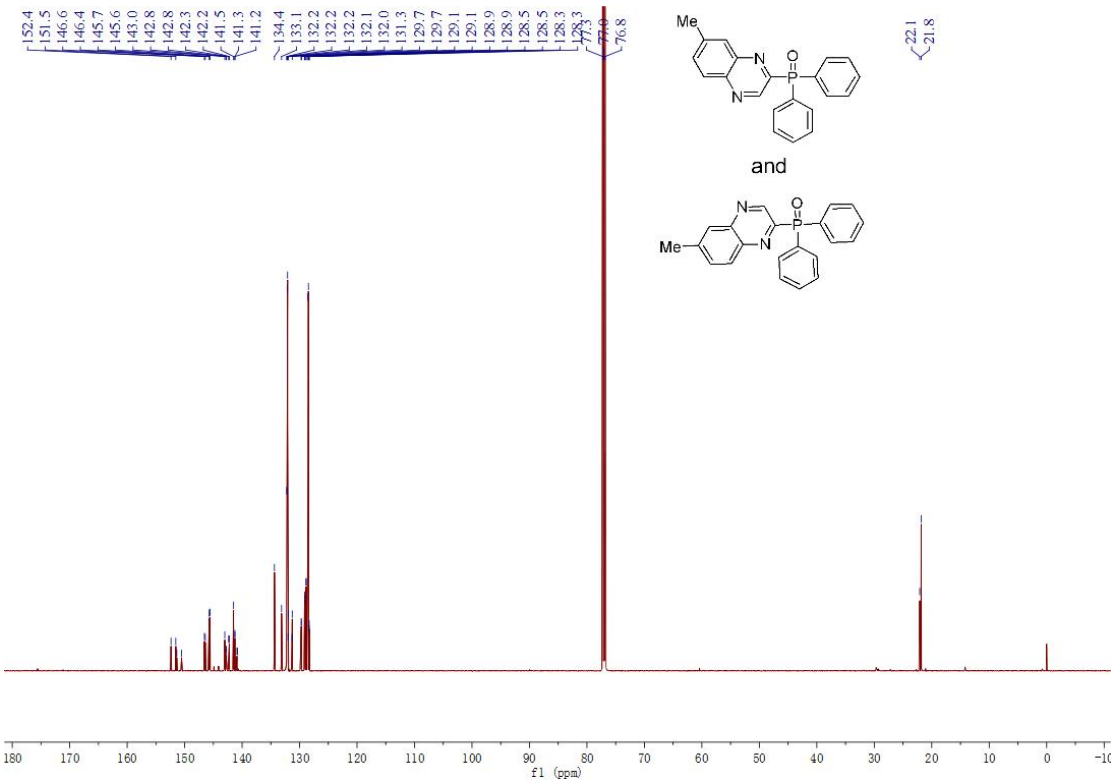
^{31}P NMR Spectrum of **5t***



^{1}H NMR Spectrum of **5u**



^{13}C NMR Spectrum of **5u**



^{31}P NMR Spectrum of **5u**