Electronic Supplementary Information

Metal-free Catalytic Nucleophilic Substitution of Primary Alcohols with Secondary Phosphine Oxides

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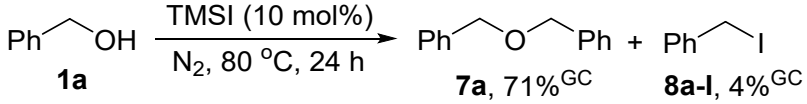
1. General information

Unless otherwise noted, all chemicals were purchased and used without further purification and all reactions were carried out in sealed Schlenk tubes under N_2 and then monitored by TLC and/or GC-MS. ^{1}H、^{13}C and ^{31}P NMR spectra were measured on a JNM-ECZ600R/S3 (Jeol, Japan) (600、151 and 243 MHz for ^{1}H、^{13}C and ^{31}P NMR, respectively) using $CDCl_3$ as the solvent. Chemical shifts for ^{1}H、^{13}C and ^{31}P NMR were referred to internal Me_4Si (0 ppm) as the standard. Mass spectra were measured on an Agilent GC-MS-7890A/5975C Plus spectrometer (EI). HRMS were recorded on a LC-TOF spectrometer (Xevo G2-XS QTof) using ESI techniques. ^{18}O contents of ^{18}O-benzyl alcohol was measured on an Agilent HRGC spectrometer (8890-7250) using EI techniques at Zhejiang University.

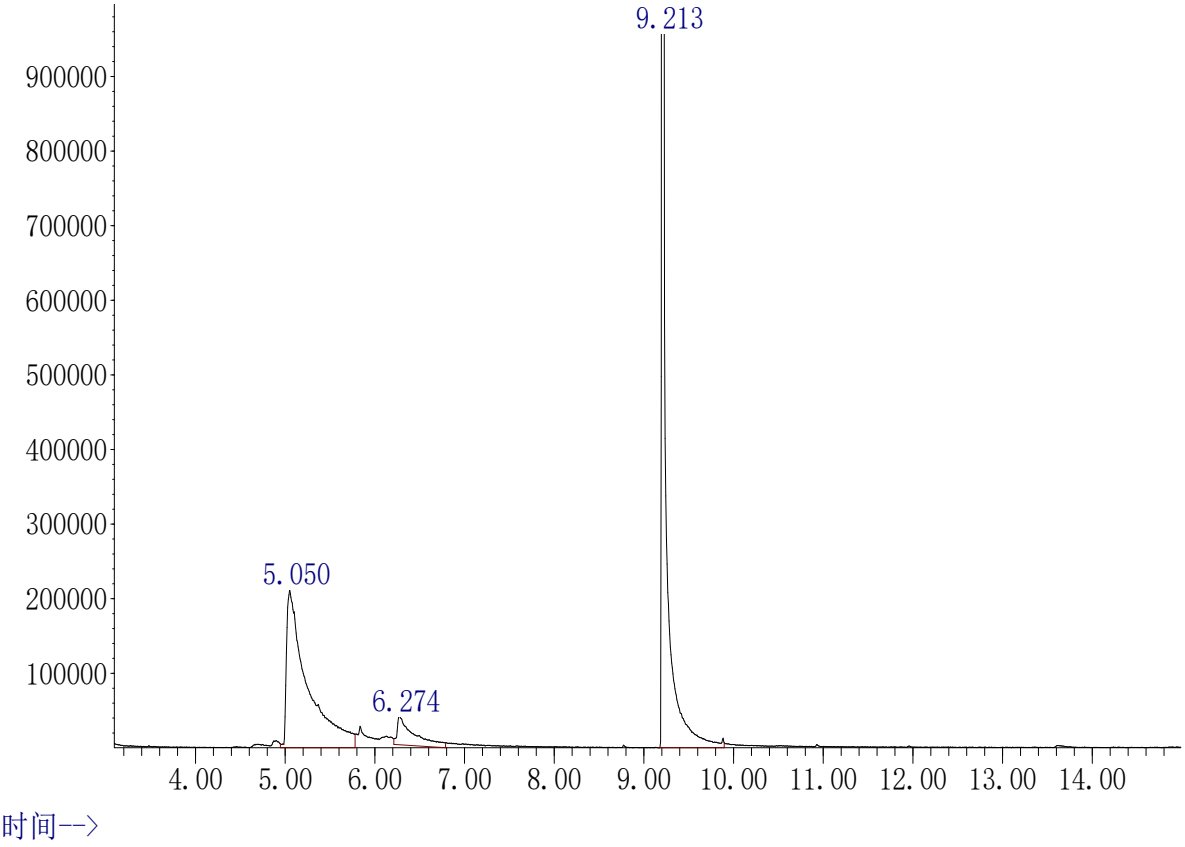
2. Control experiments for Mechanistic Studies

2.1 The reaction of benzyl alcohol (1a) and TMSI (Eq. 5 in the text)



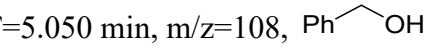
Detailed Procedure: The mixture of benzyl alcohol **1a** (62.1 μL, 0.60 mmol), TMSI (7.1 μL, 0.05 mmol) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 24 h. The reaction mixture was analyzed by GC-MS, showing the generation of **7a** and **8a-I** in 71% and 4% yield, respectively.

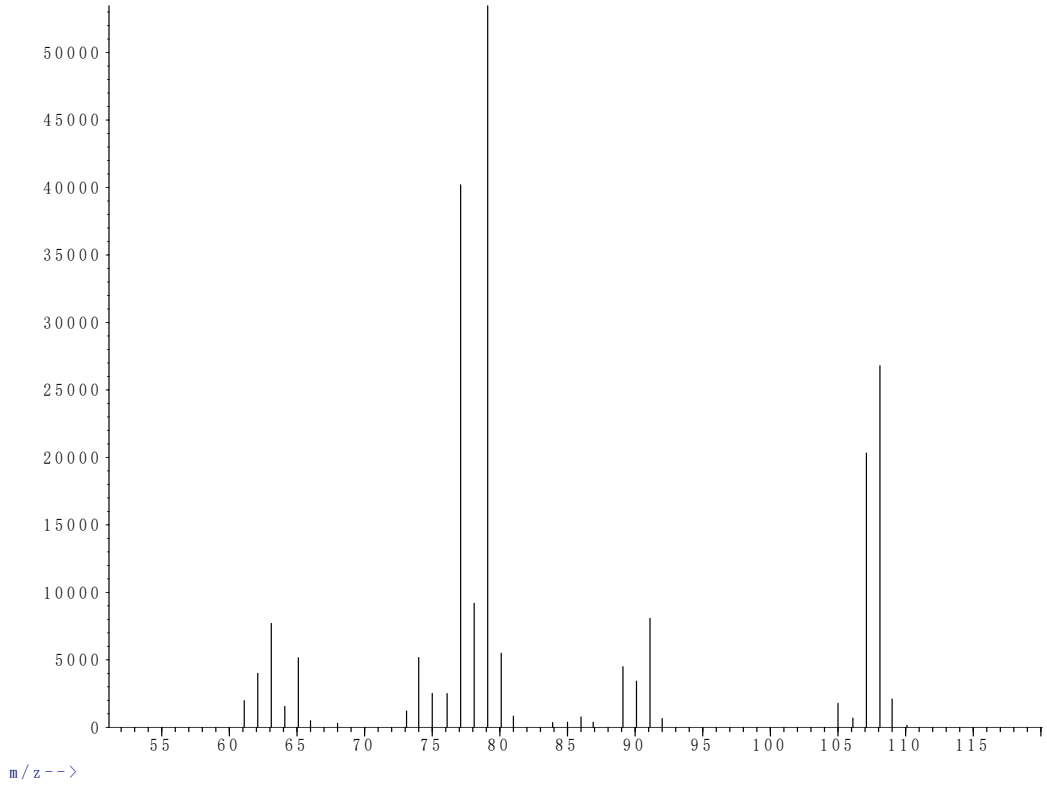
GC spectra

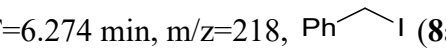


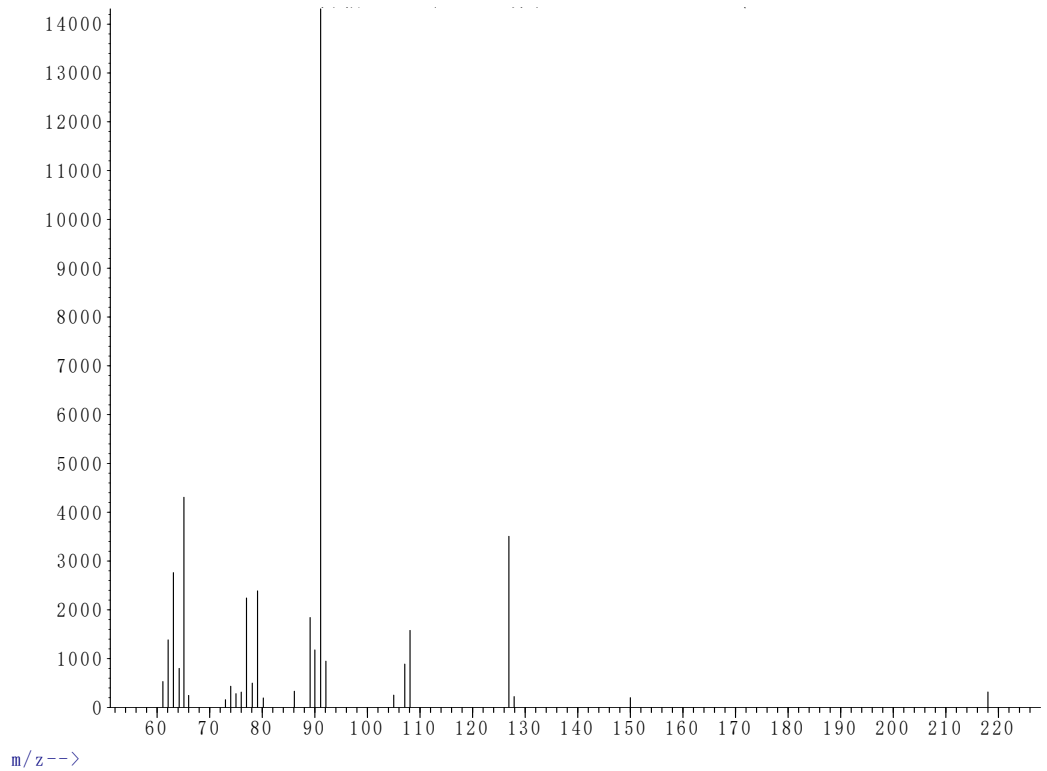
Run	Time /min	Start scanning	Peak scanning	Stop scanning	Peak type	Hight	Correction area	Correction maximum%	Total %
1	5.050	256	270	370	M	212372	33978668	34.91%	**24.915**
2	6.274	430	438	509	M	38160	5059223	5.20%	**3.710**
3	9.213	836	843	937	M	7119292	97338456	100.00%	**71.375**

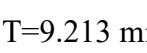
MS Spectra

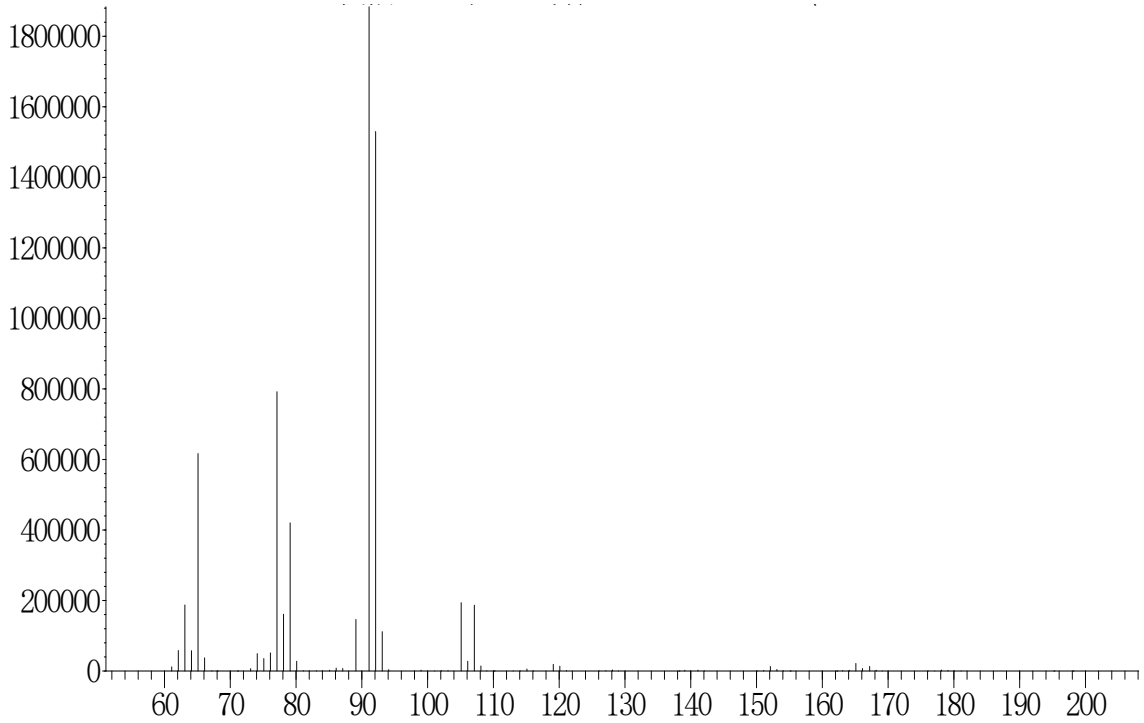
T=5.050 min, m/z=108,  (**1a**)



T=6.274 min, m/z=218,  (**8a-I**)

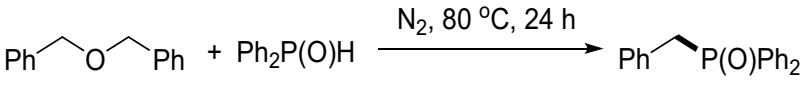


T=9.213 min, m/z=198,  (**7a**)



Results and Discussion: Benzyl alcohol **1a** is converted to dibenzyl ether **7a** and benzyl iodine **8a-I** under standard conditions, and it is preliminarily hypothesized that dibenzyl ether **7a** and benzyl iodine **8a-I** may be the key intermediates

2.2 The reaction of dibenzyl ether (7a) and diphenylphosphine oxide (2a) (Eq. 6 in the text)



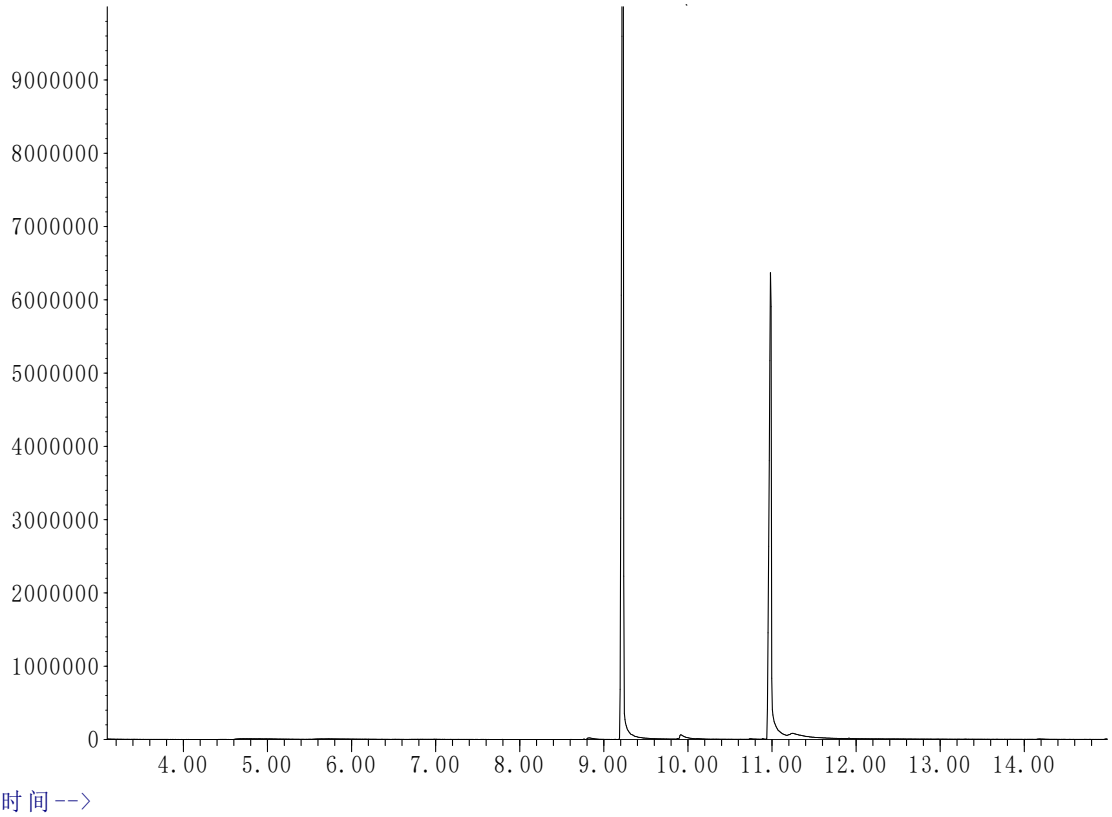
7a 0.30 mmol

2a 0.50 mmol

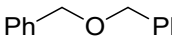
3aa, 0% yield

Detailed Procedure: The mixture of dibenzyl ether **7a** (57 μL, 0.30 mmol), diphenylphosphine oxide **2a** (101.1 mg, 0.50 mmol) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 24 h. The reaction mixture was analyzed by TLC/GC-MS.

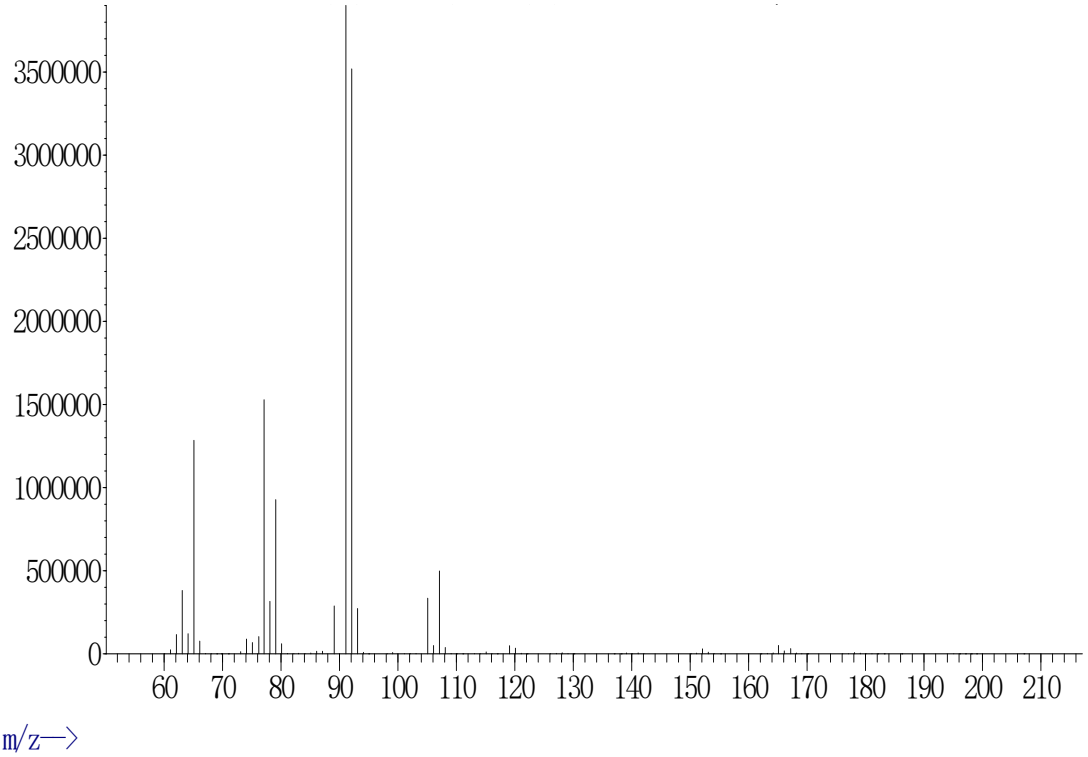
GC spectra



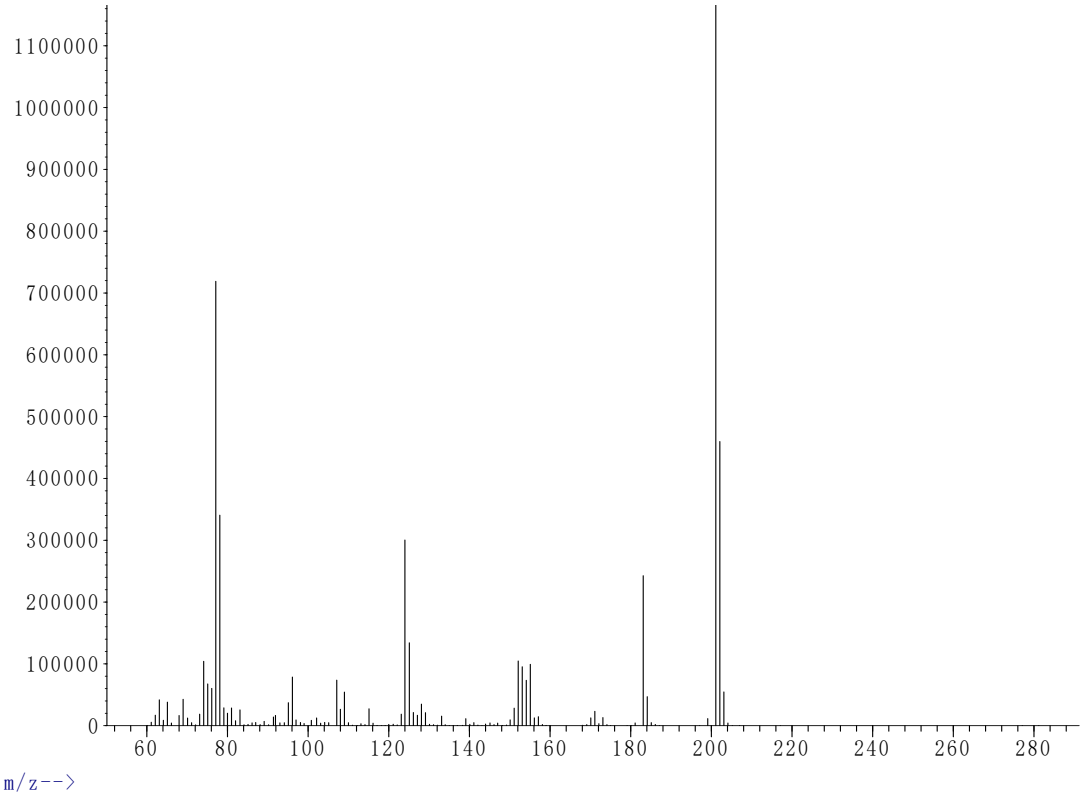
MS Spectra

T=9.230 min, m/z=198, 

(7a)

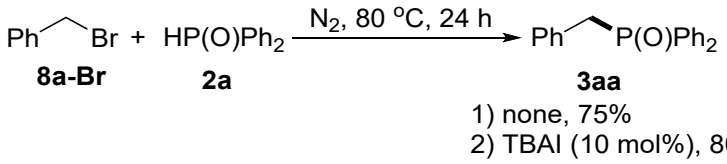


T=10.974 min, m/z=202, $Ph_2P(O)H$ (**2a**)



Results and Discussion: The reaction of dibenzyl ether **7a** and diphenylphosphine oxide **2a** failed to produce the target product **3aa.** Therefore, dibenzyl ether **7a** is not the key reaction intermediate.

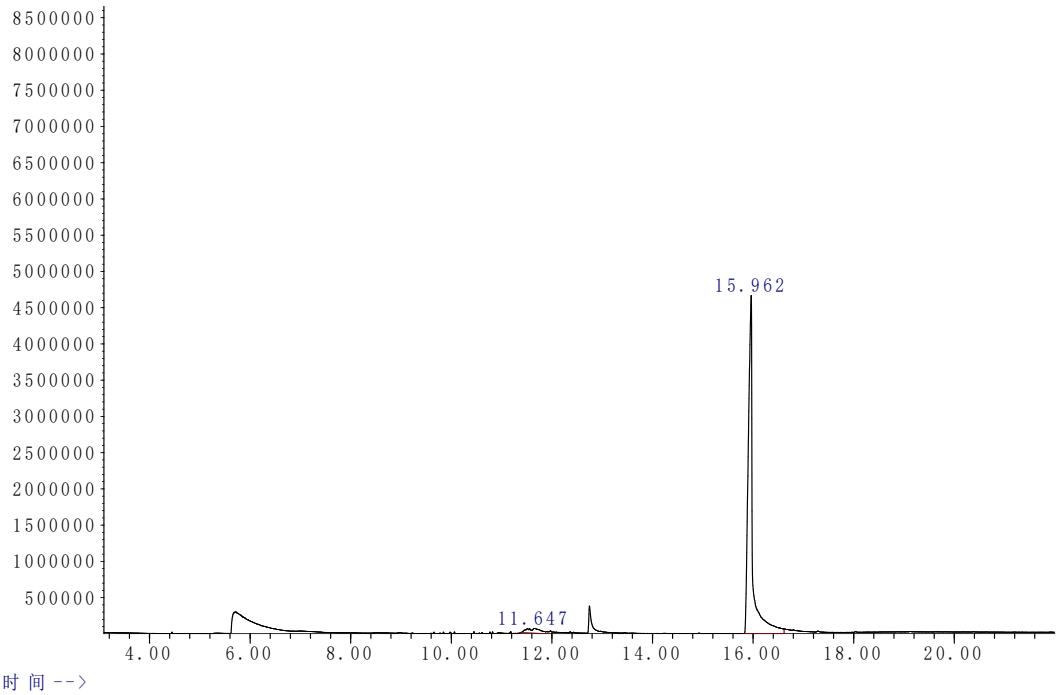
2.3 The reaction of benzyl bromide (8a-Br) and diphenylphosphine oxide (2a) (Eq. 7 in the text)



Detailed Procedure: The mixture of benzyl bromide **8a-Br** (71.3 μL, 0.60 mmol), diphenylphosphine oxide **2a** (101.1 mg, 0.50 mmol) and TBAI (0 or 10 mol%) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 24 h. The reaction mixture was analyzed by TLC/GC-MS, and then purified by flash column chromatography on silica gel using dichloromethane and methanol (0~ 1/1) as the eluent, giving **3aa** in 75% or 80% isolated yield.

GC spectra

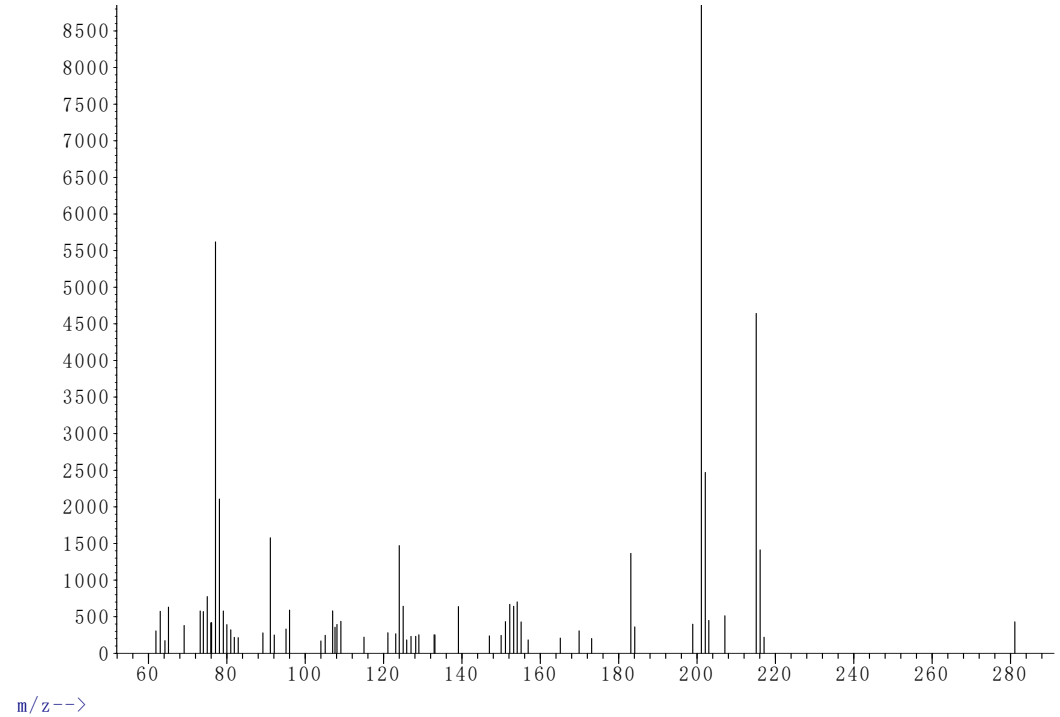
TBAI (0 mol%):

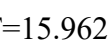


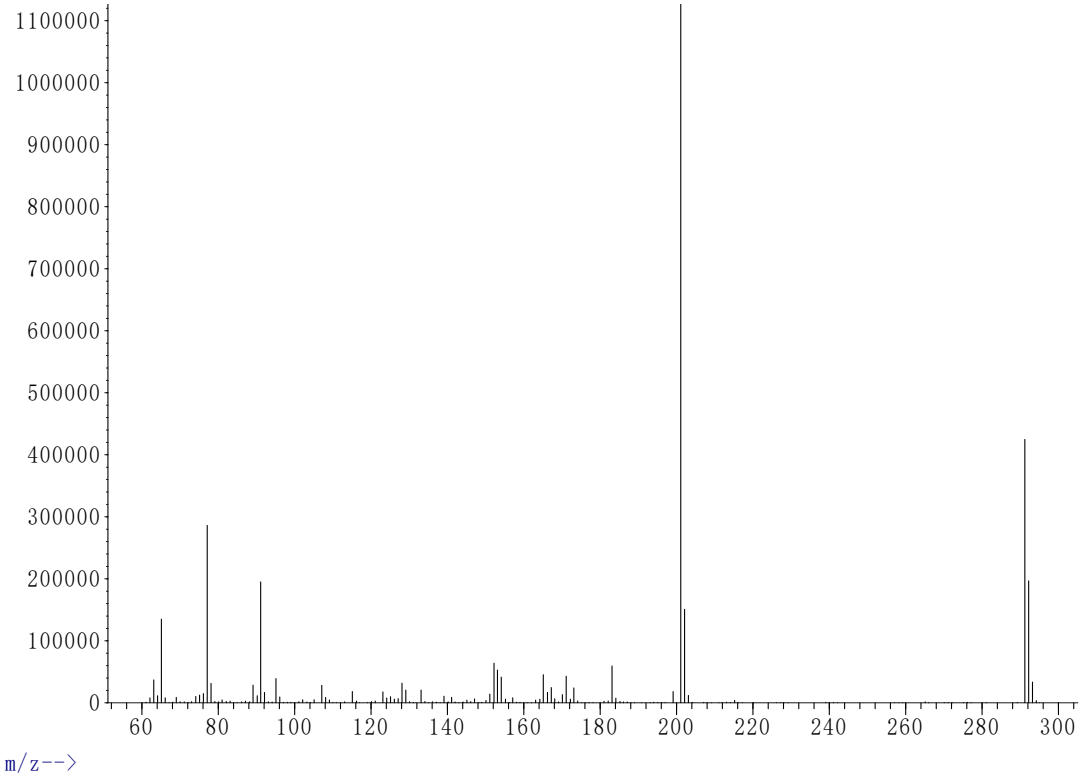
Run	Time /min	Start scanning	Peak scanning	Stop scanning	Peak type	Hight	Correction area	Correction maximum%	Total %
1	11.647	1821	1882	1932	M	69876	12009854	4.15%	**3.985**
2	15.962	2798	2831	2974	M	4719049	289404309	96.015%	**96.015**

MS Spectra

T=11.647 min, m/z=202, $Ph_2P(O)H$ (**2a**)

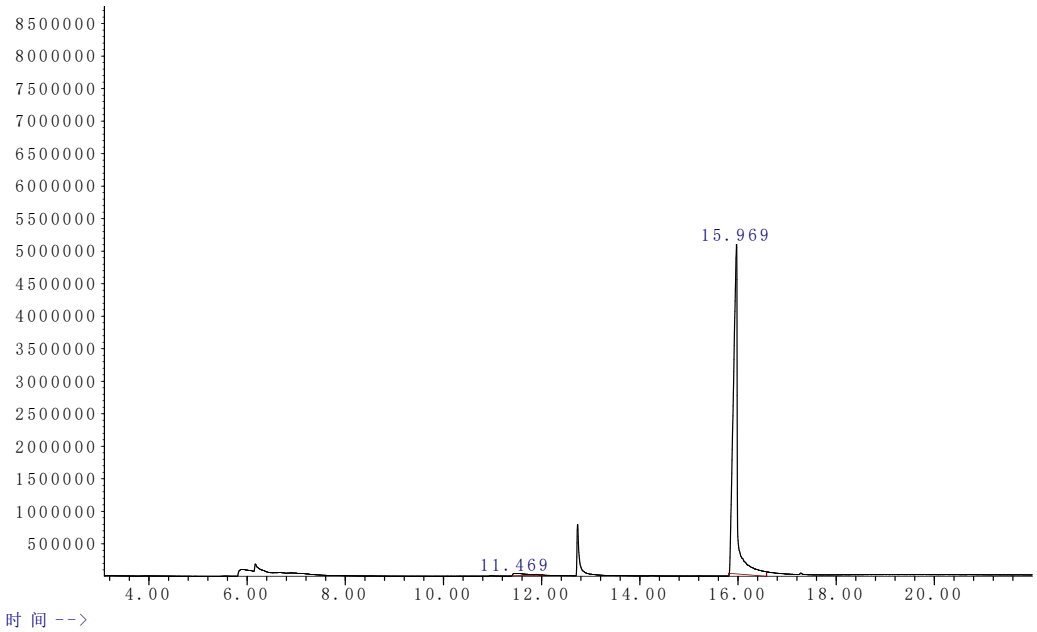


T=15.962 min, m/z=292,  (**3aa**)



GC spectra

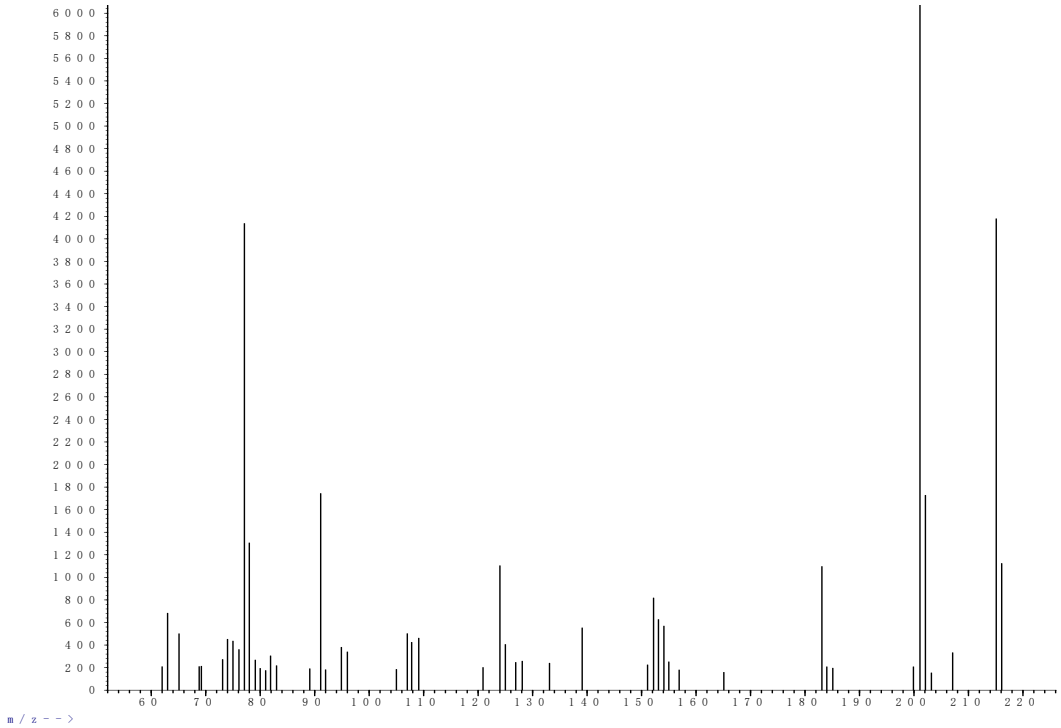
TBAI (10 mol%):

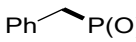


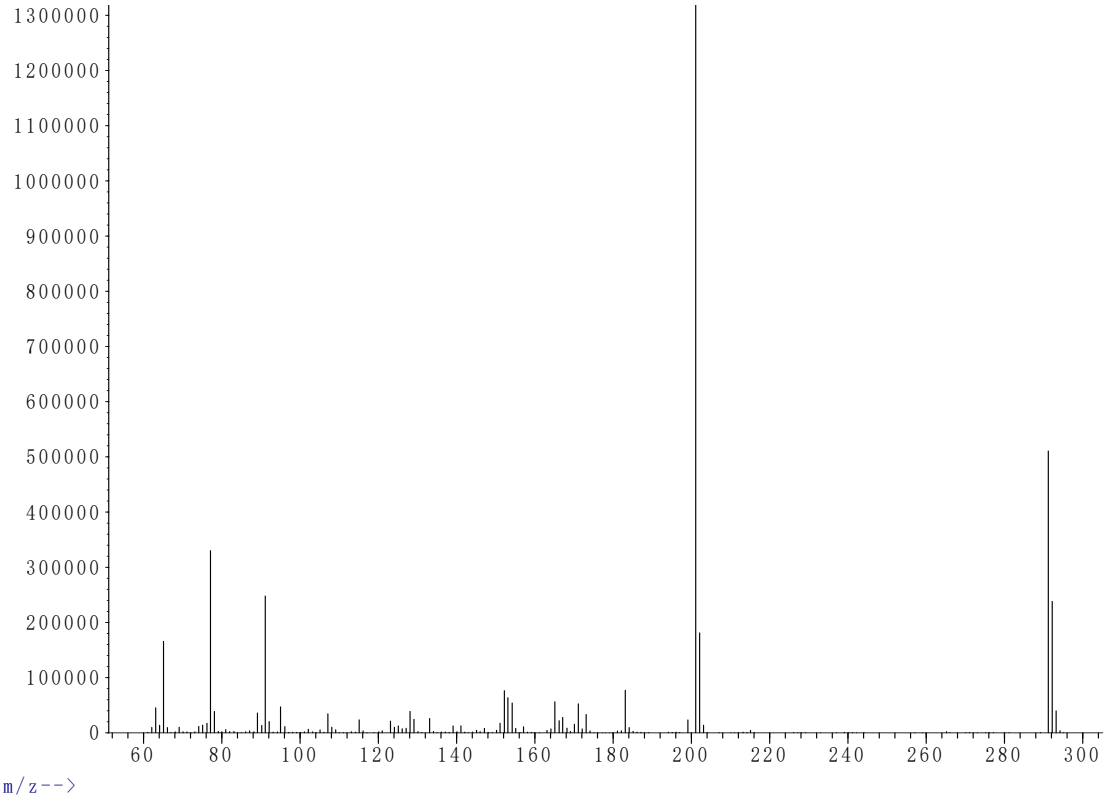
Run	Time /min	Start scanning	Peak scanning	Stop scanning	Peak type	Hight	Correction area	Correction maximum%	Total %
1	11.469	1823	1843	1964	M	42086	7413146	2.36%	**2.301**
2	15.969	2798	2832	2967	M	5079017	314737801	100.00%	**97.699**

MS Spectra

T=11.496 min, m/z=202, $Ph_2P(O)H$ (**2a**)



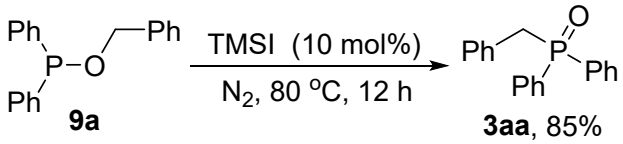
T=15.969 min, m/z=292,  (**3aa**)



Results and Discussion: Benzyl iodide (**8a-I**) generated from the reaction of

$PhCH_2Br$ (**8a-Br**) with TBAI can react smoothly with diphenylphosphine oxide (**2a**) to give the target product **3aa**, therefore, benzyl iodine **8a-I** may be the key reaction intermediate.

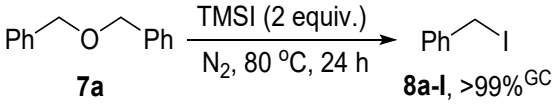
2.4 The MA rearrangement of benzyl diphenylphosphinite (9a) (Eq. 8 in the text)



(8)

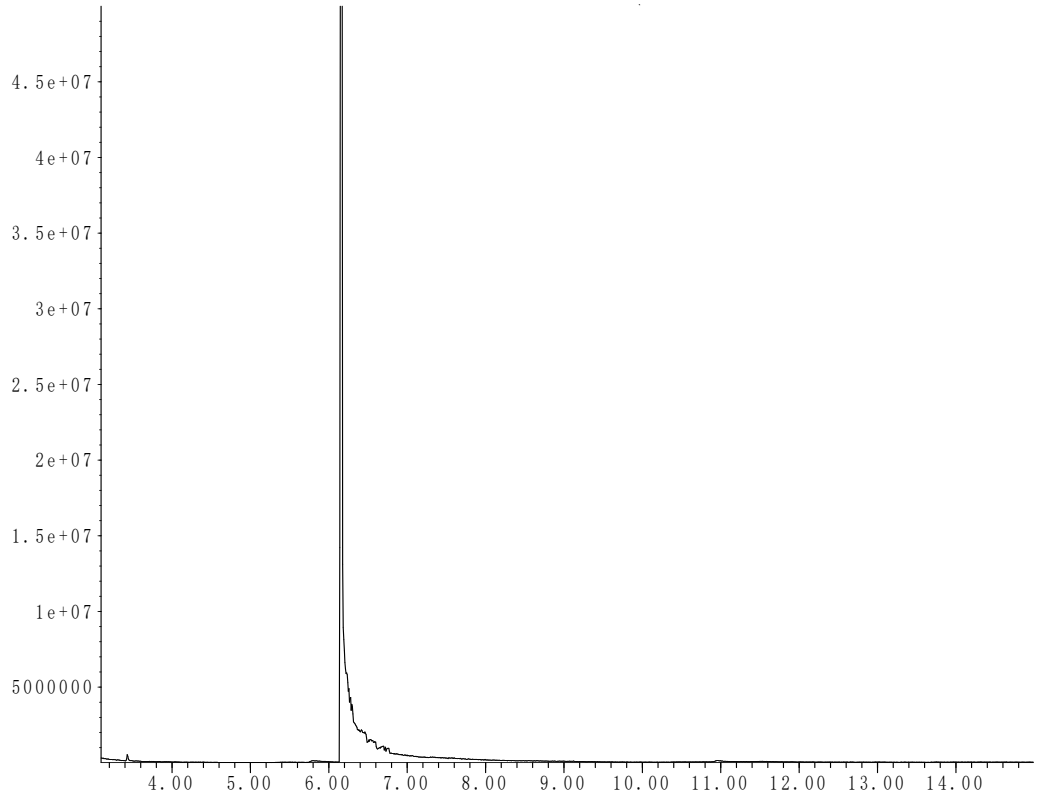
Detailed Procedure: The mixture of benzyl diphenylphosphinite (**9a**) (58.4 mg, 0.20 mmol), TMSI (2.8 μL, 10 mol%, 0.020 mmol) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 12 h. The reaction mixture was analyzed by TLC/GC-MS, and then purified by flash column chromatography on silica gel using dichloromethane and methanol (0~ 1/1) as the eluent, giving **3aa** in 85% isolated yield.

2.5 The reaction of dibenzyl ether (7a) and TMSI (Eq. 9 in the text)

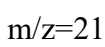


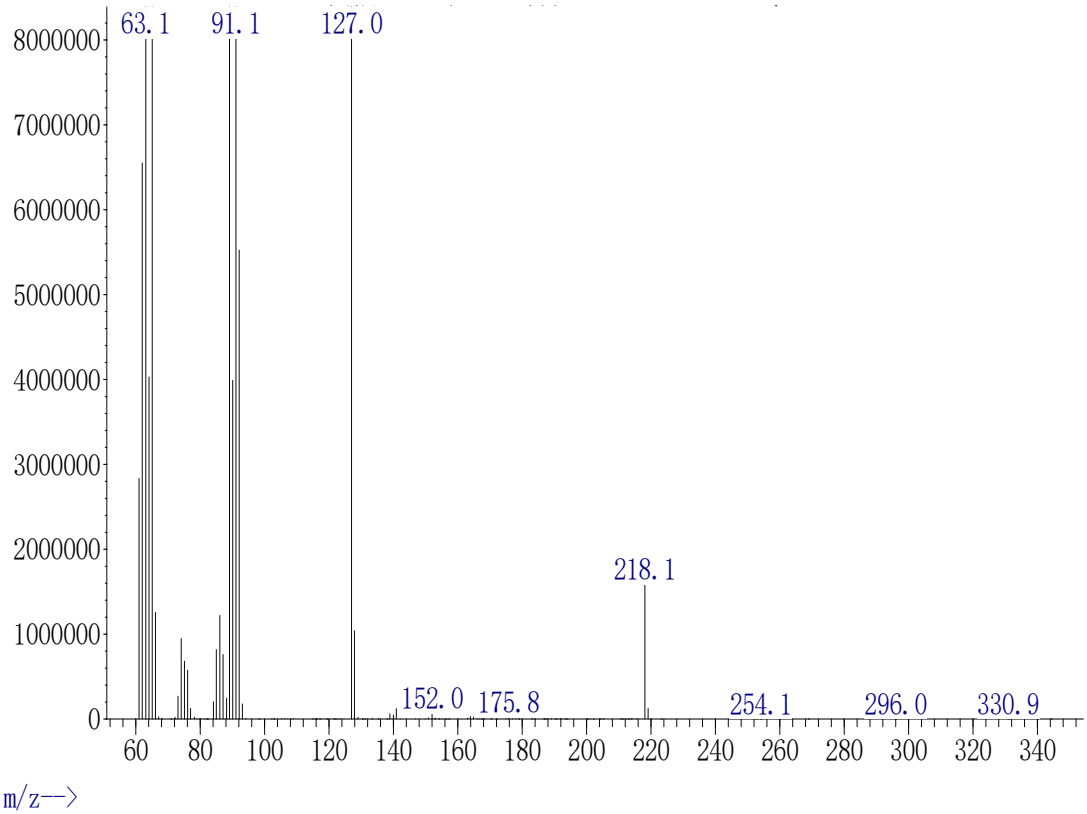
Detailed Procedure: The mixture of dibenzyl ether **7a** (57 μL, 0.30 mmol), TMSI (85.4 μL, 0.60 mmol) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 24 h. The reaction mixture was analyzed by TLC/GC-MS.

GC spectra:



MS Spectra

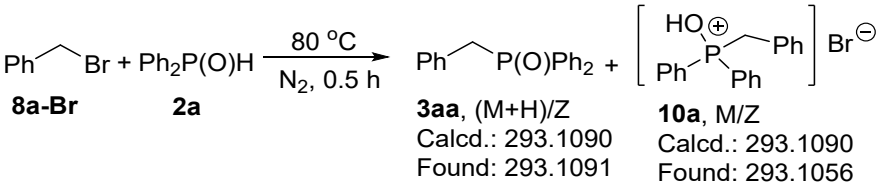
T=6.162 min, m/z=218,  (**8a-I**)



Results and Discussion: The reaction of dibenzyl ether **7a** with TMSI proceed

smoothly to produce benzyl iodine **8a-I** intermediate. Therefore, the initial formation of unwanted ethers from alcohols (Eq. 5) does not affect the reaction outcome at all.

2.5 The observation of possible intermediate 10a (Eq. 10 in the text)



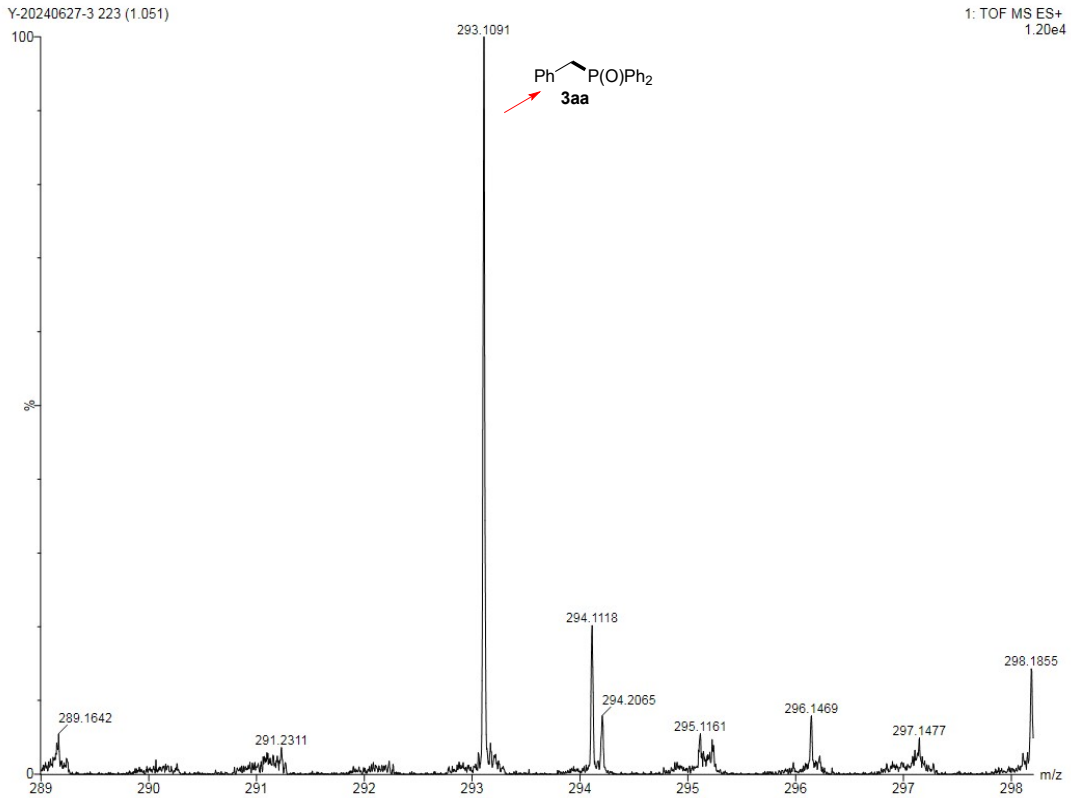
8a-Br **2a**

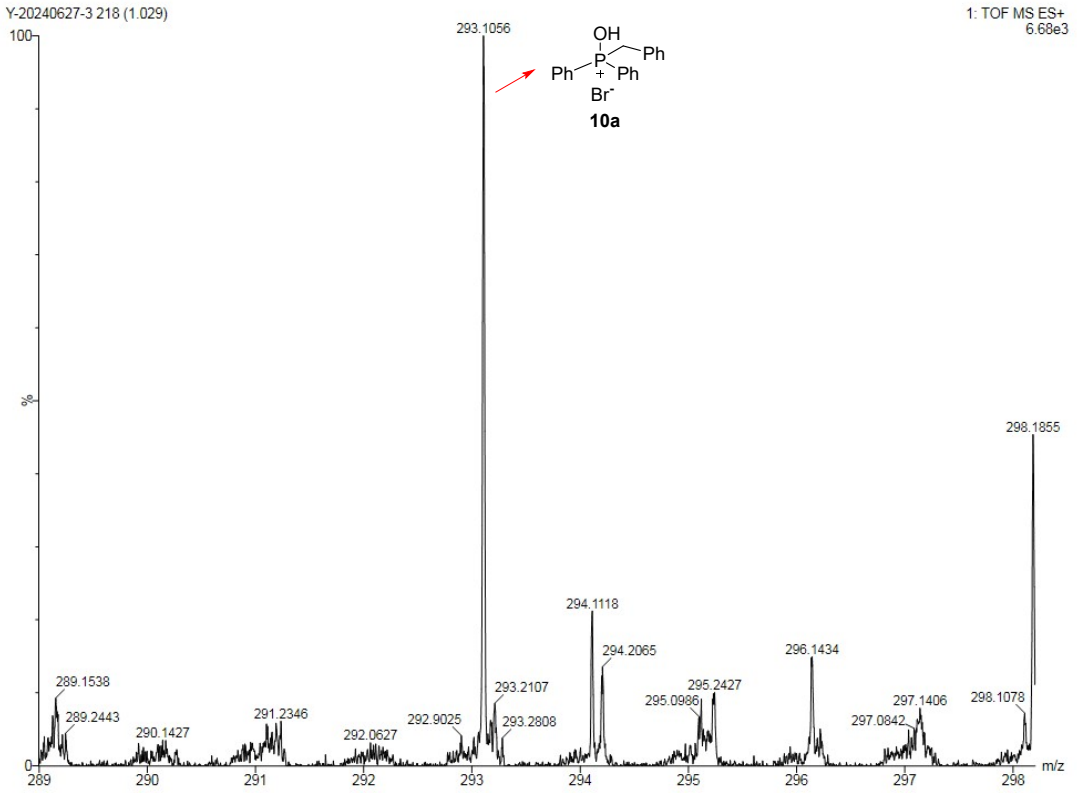
3aa, (M+H)/Z
Calcd.: 293.1090
Found: 293.1091

10a, M/Z
Calcd.: 293.1090
Found: 293.1056

Detailed Procedure: The mixture of benzyl bromide **8a-Br** (71.3 μL, 0.60 mmol), diphenylphosphine oxide **2a** (101.1 mg, 0.50 mmol) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 0.5 h. After cooling, the reaction mixture was directly analyzed by HRMS, showing the signals of both 293.1091 and 293.1056.

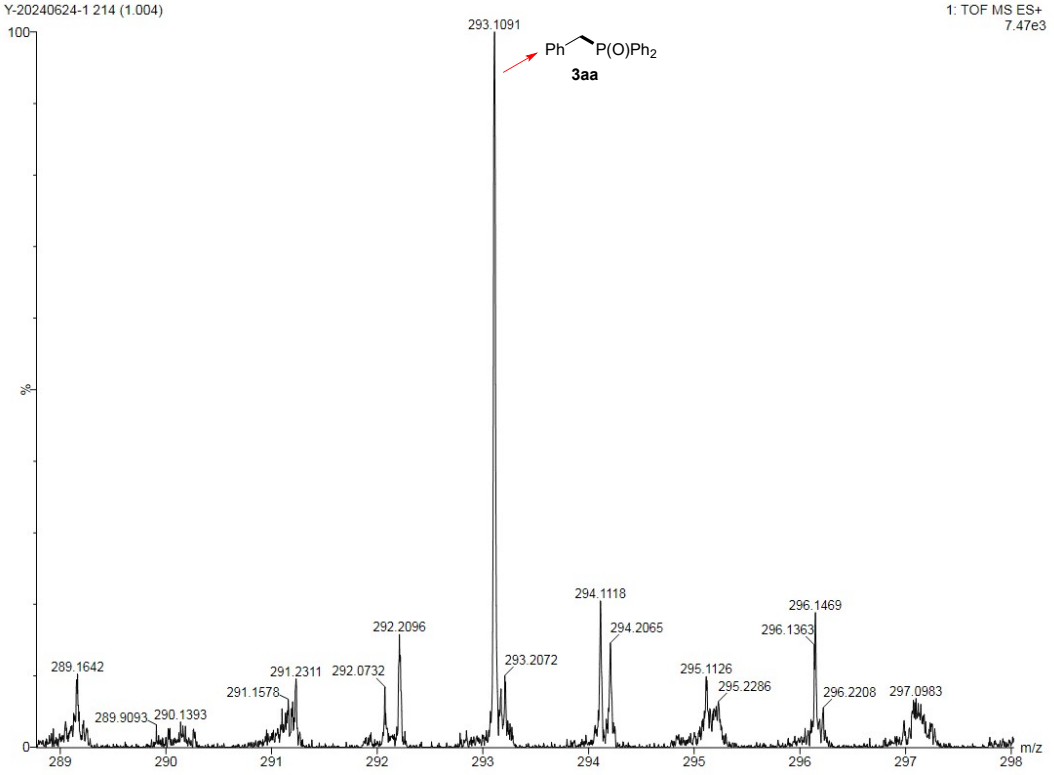
HRMS spectra



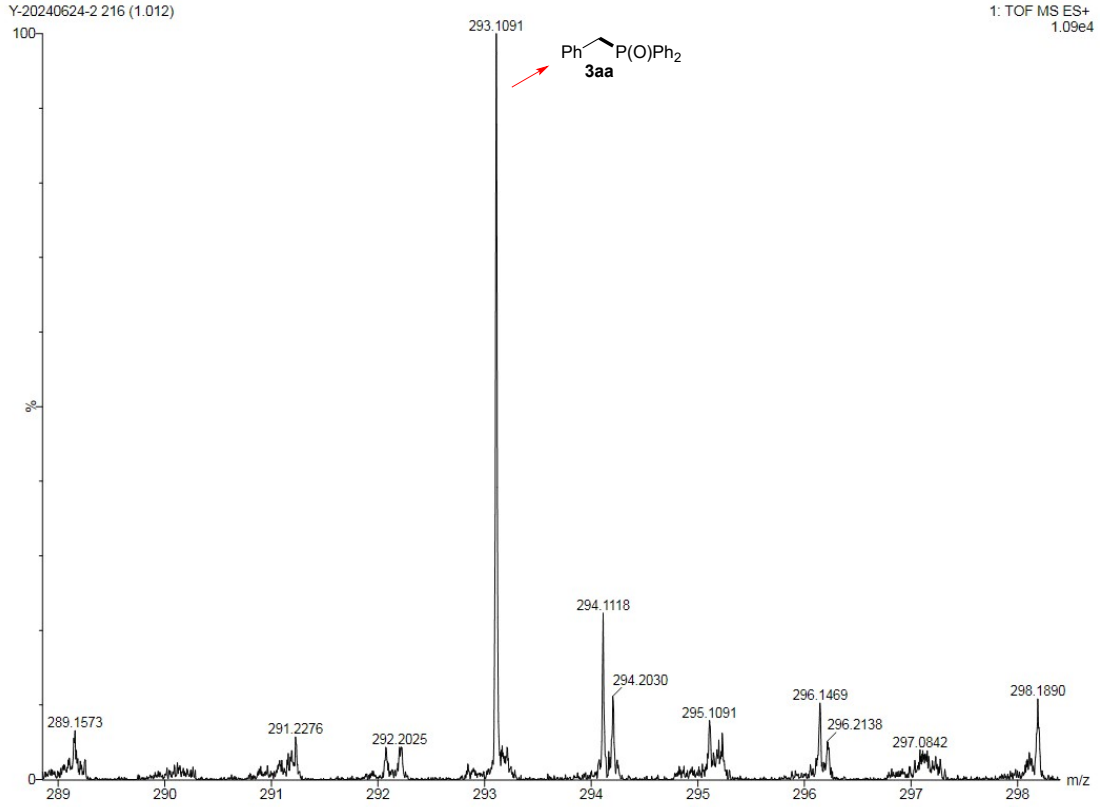


Previous results: The (M+H) peaks (293.1091) of **3aa** have been previously detected for some times during the condition screening (Table 1, runs 4-7 and 9-11 in the text, see below).

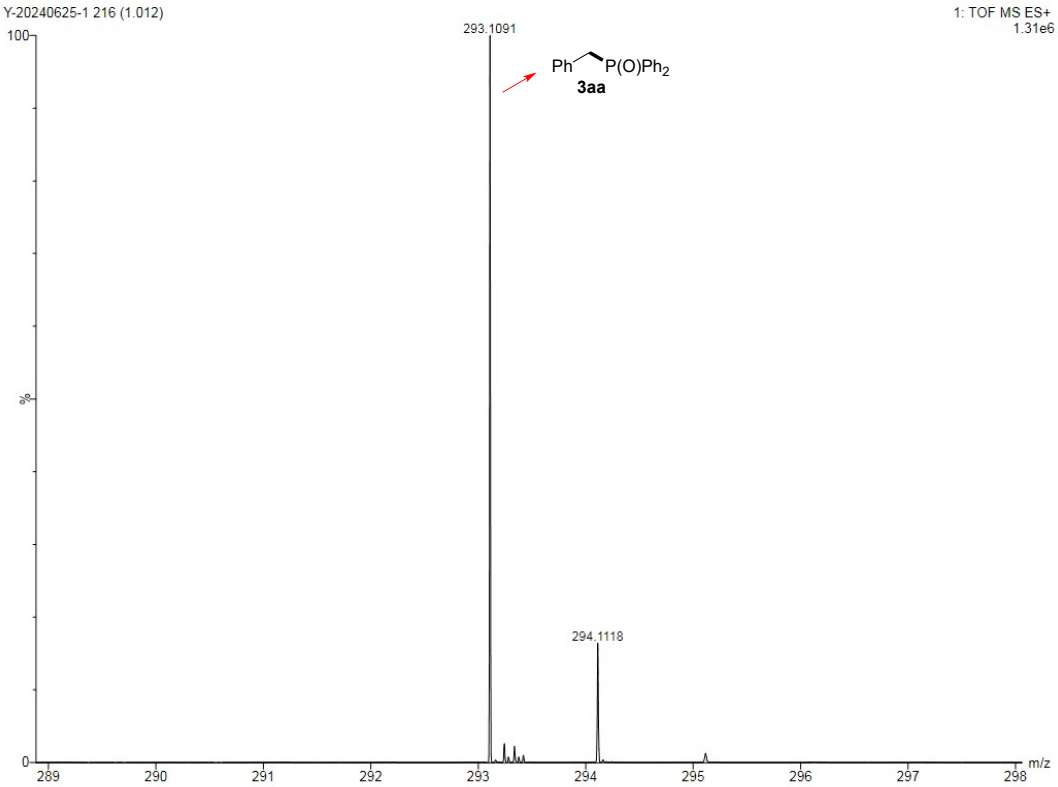
HRMS spectrum of 3aa (Table 1, run 4 in the text)



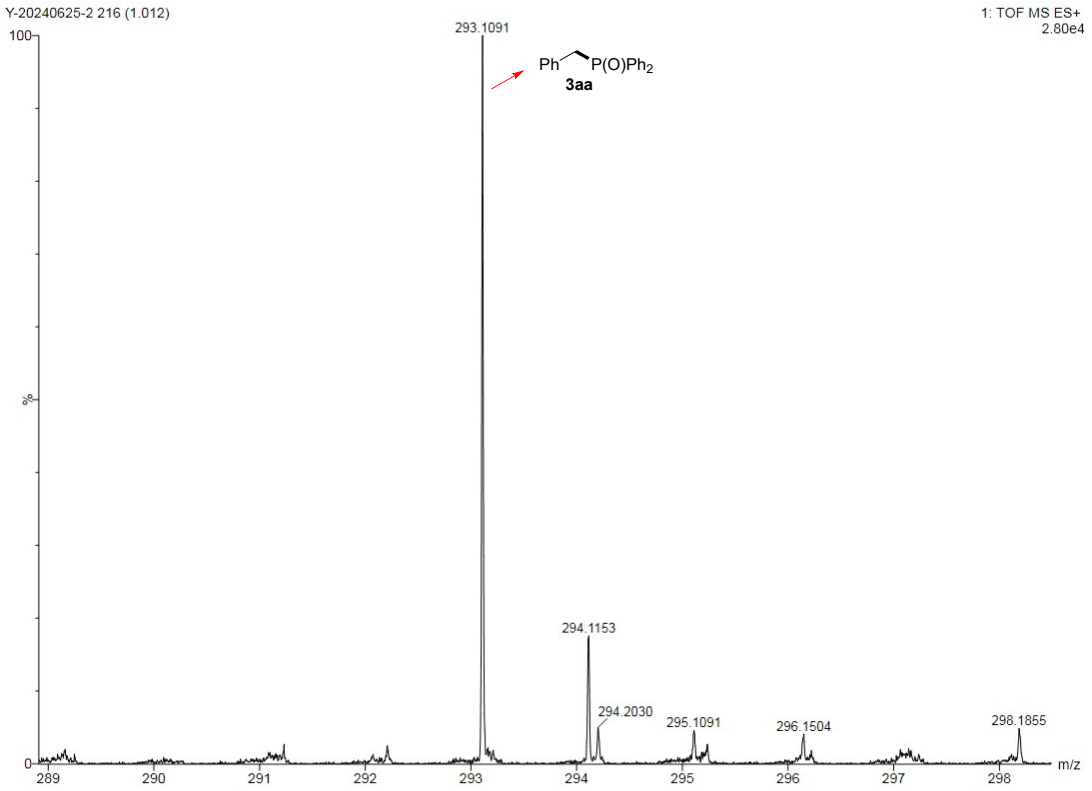
HRMS spectrum of 3aa (Table 1, run 5 in the text)



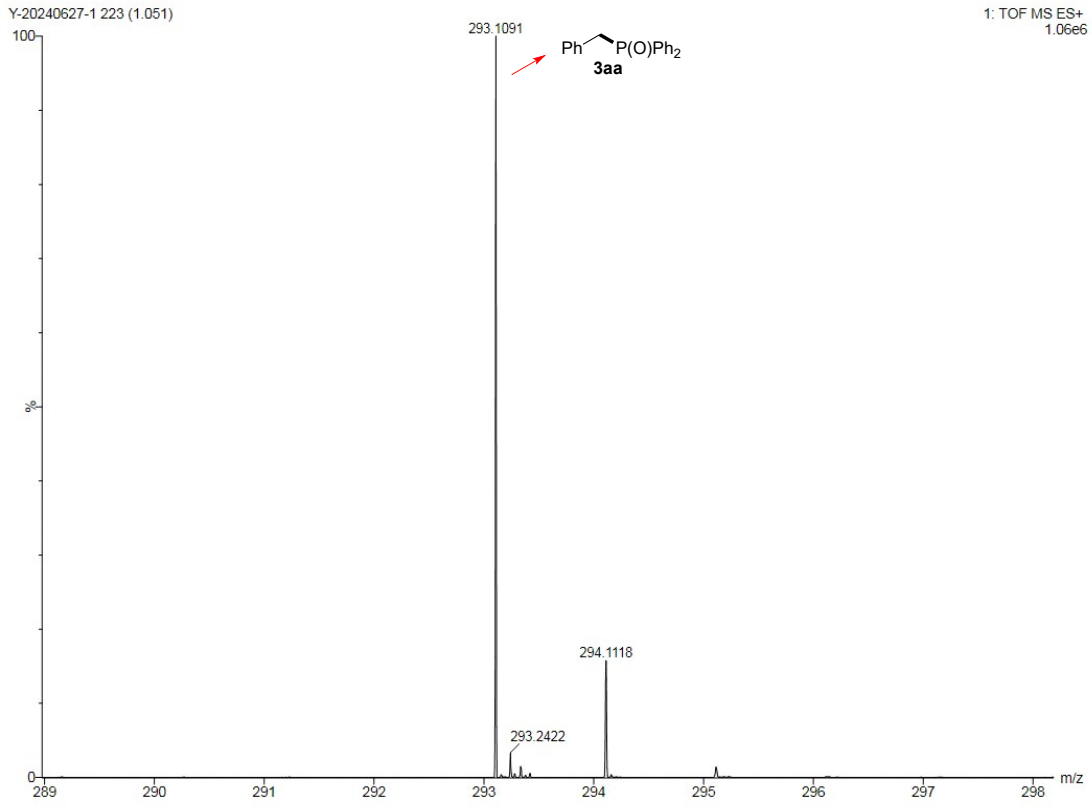
HRMS spectrum of 3aa (Table 1, run 6 in the text)



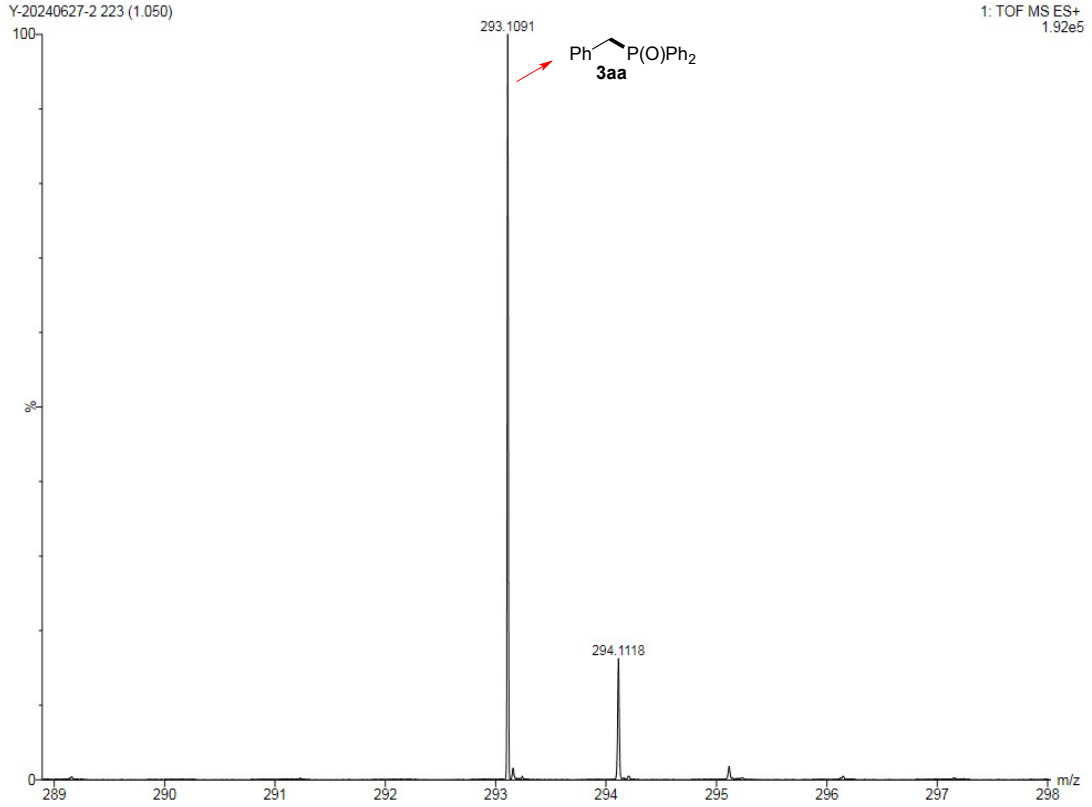
HRMS spectrum of 3aa (Table 1, run 7 in the text)



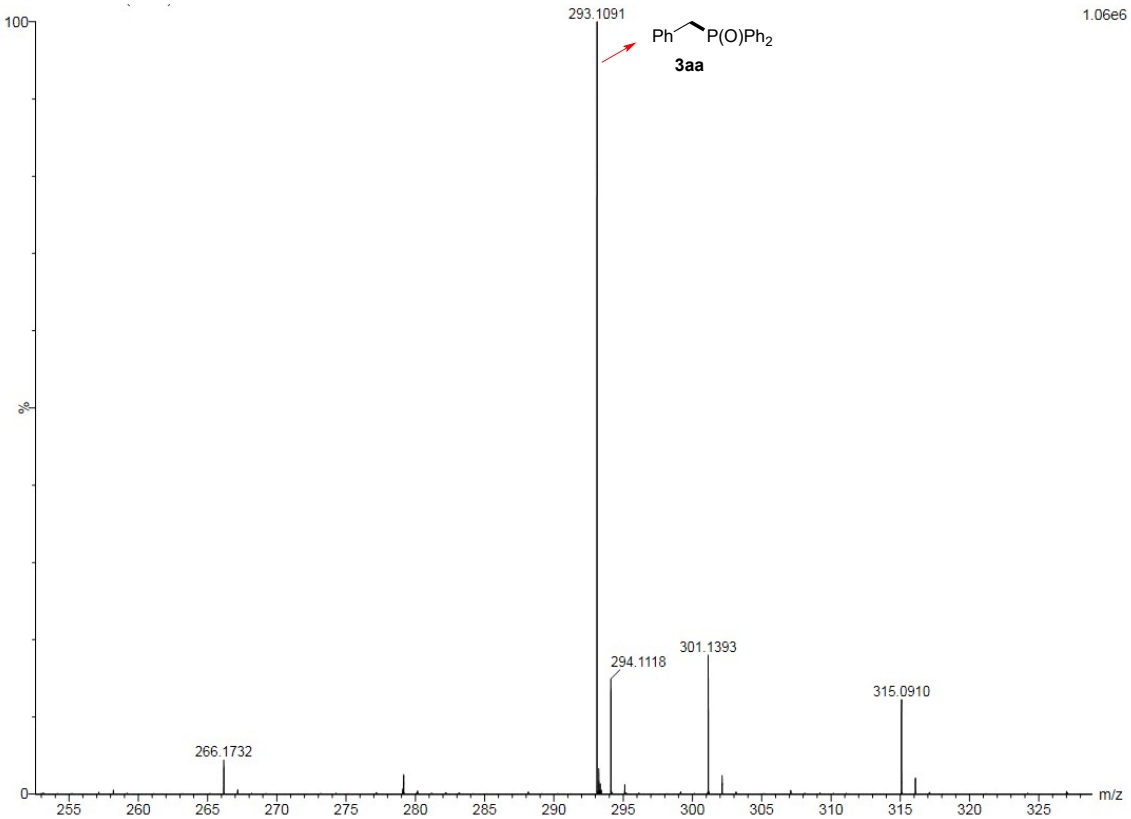
HRMS spectrum of 3aa (Table 1, run 9 in the text)



HRMS spectrum of 3aa (Table 1, run 10 in the text)



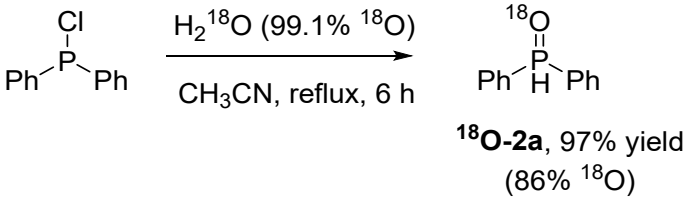
HRMS spectrum of 3aa (Table 1, run 11 in the text)



Results and Discussion: Both signals of 293.1091 and 293.1056 were detected by HRMS during the mixture. The peak of 293.1091 which has been previously detected for some times during the condition screening (as shown above) has been identified as the target product **3aa**. Therefore, it is hypothesized that 293.1056 may be the signal of the possible intermediate **10a**.

2.6 The reaction of benzyl alcohol and ^{18}O-diphenylphosphine oxide (^{18}O-2a) (Eq. 11 in the text)

2.6.1 The synthesis of ^{18}O-diphenylphosphine oxide (^{18}O-2a):



$H_2{}^{18}O$ (99.1 % ^{18}O) (1 mL) was added to a solution of chlorodiphenylphosphine (1.8 mL, 10 mmol) in anhydrous acetonitrile (10 mL) and the mixture was refuxed for 6h., The reaction mixture was then concentrated under reduced pressure.The residue was extracted with CH_2Cl_2 (10 mLx3) and dried over $MgSO_4$. The solvent was removed in vacuo to give ^{18}O-diphenylphosphine oxide as a colorless oil in 97% yield. ^{18}O-**2a** was determined to be containing 86 atom% ^{18}O by HRMS analysis. This method is known in the literature: Shioji, K.; Matsumoto, A.; Takao, M.; Kurauchi, Y.; Shigetomi, T.; Yokomori, Y.; Okuma, K. *B. Chem. Soc. Jpn.* **2007**, *80*, 4, 743-746.

The Specification of $H_2{}^{18}O$

安耐吉化学 Energy Chemical

ISO9001/ISO14001/ISO45001认证企业

ZS/QA-4001-2024（A4）

产品质量检测报告

报告日期：2022-12-29

中 文 名 重氧水

英 文 名 Heavy-oxygen water

规　　格 98 atom % 18O

CAS 编码 14314-42-2

分 子 量 20.02

分 子 式 18OH2

$H_2{}^{18}O$

产品编号 E090044

批　　号 TODHRRDW

检测日期 2022-12-26

复检日期 2025-12-25

储存条件 室温

检查项	规格要求	实测结果
外观	无色液体	无色透明液体
含量	≥ 98.0 atom % 18O	99.10 atom % 18O
O-17	≤ 1 atom %	< 1 atom %
O-16	≤ 2 atom %	< 2 atom %
结论		

报告人：胡沈锦　　批准人：梁砚荣

Anhui Senrise Technology Co.,Ltd 安徽贤开科技股份有限公司 质量检验专用章

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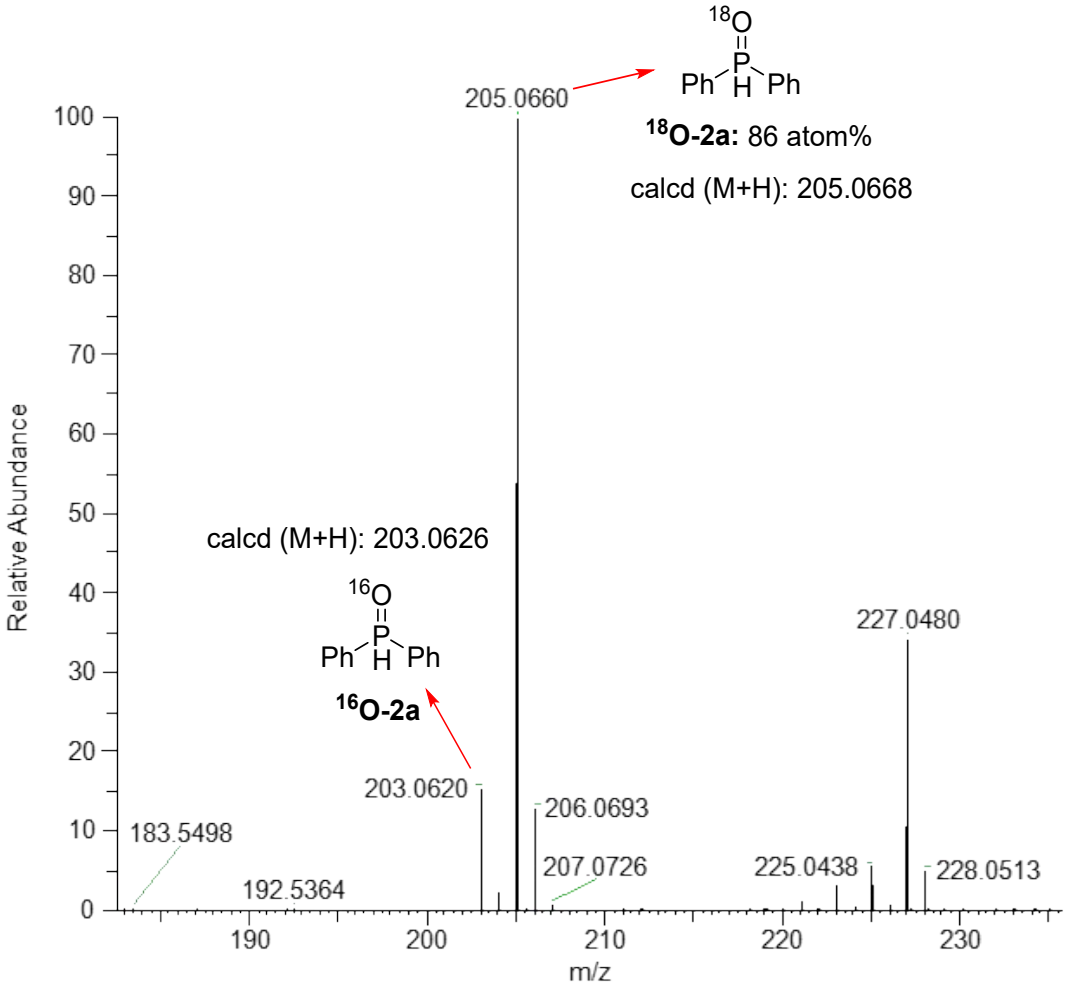
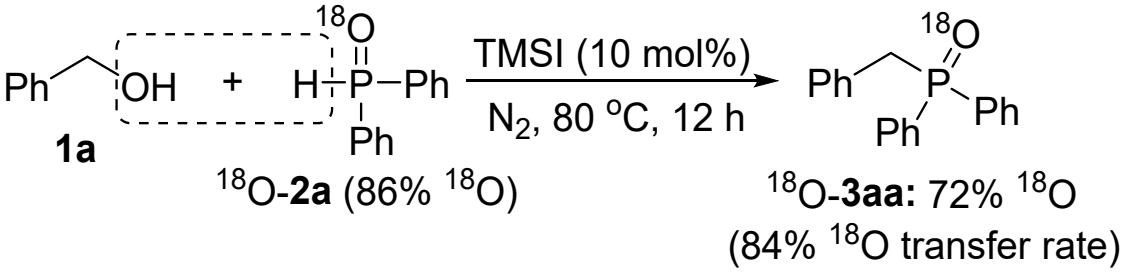
HRMS spectra of the product 2a



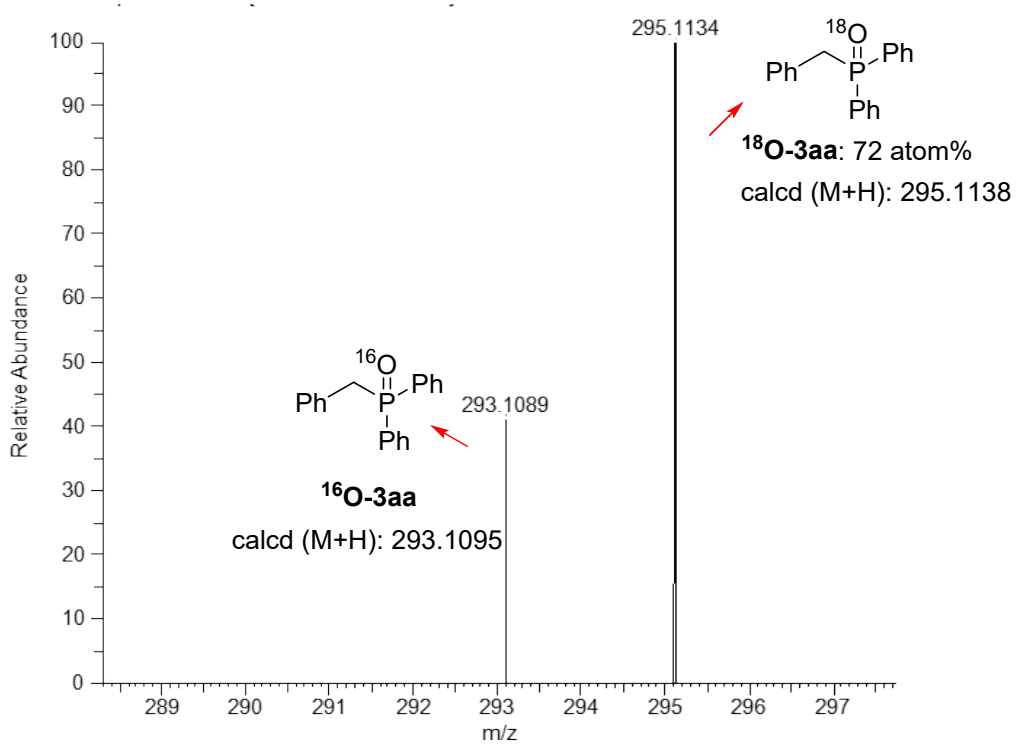
Scan Number	m/z	Relative
114	205.0659	100.00
114	203.0620	16.49

^{18}O-2a: 100.00/(100.00+16.49) = 86%

2.4.2 Detailed Procedure for the reaction of benzyl alcohol and ^{18}O-diphenylphosphine oxide (^{18}**O-2a)**: The mixture of benzyl alcohol **1a** (62.1 μL, 0.60 mmol), ^{18}O-diphenylphosphine oxide (**^{18}O-2a**) (102.0 mg, 0.5 mmol) and TMSI (7.1 μL, 0.05 mmol) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 12 h. After cooling, then the isotope analysis of the product **^{18}O-3aa** by HRMS showed that ^{18}O-**3aa** should contain 72 atom% ^{18}O.



HRMS spectra



Spectrum List 44 - 7

Scan Number	m/z	Relative
44	293.1089	38.90
44	295.1134	100.00

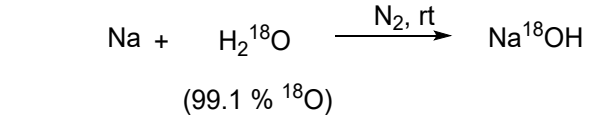
^{18}O-3aa: 100.00/(100.00+38.90) = 72%

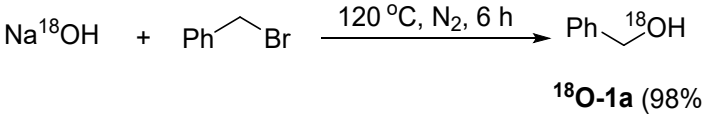
Results and Discussion: The reaction of **1a** and **^{18}O-2a** (86 atom% ^{18}O) under standard conditions afforded the target **^{18}O-3aa** (72 atom% ^{18}O), suggesting that the byproduct water is generated through the dehydroxylation of alcohols **1a** and dehydrogenation of secondary P(O)-H compounds **2a.** Therefore, these results suggested 1) the reaction majorly proceeded with retention of P-O bond, and 2) the alcohol's OH group majorly worked as the leaving group, which consists well with

the supposal that the reaction most possibly starts with a TMSI-promoted transformation of alcohols **1** to iodides **8** as the key intermediate, followed by C-P bond formation of **8** and **2**.

2.7 The reaction of ^{18}O-benzyl alcohol (^{18}O-1a) and diphenylphosphine oxide (2a) (Eq. 12 in text)

2.7.1 The Synthesis of ^{18}O-benzyl alcohol (^{18}O-1a):

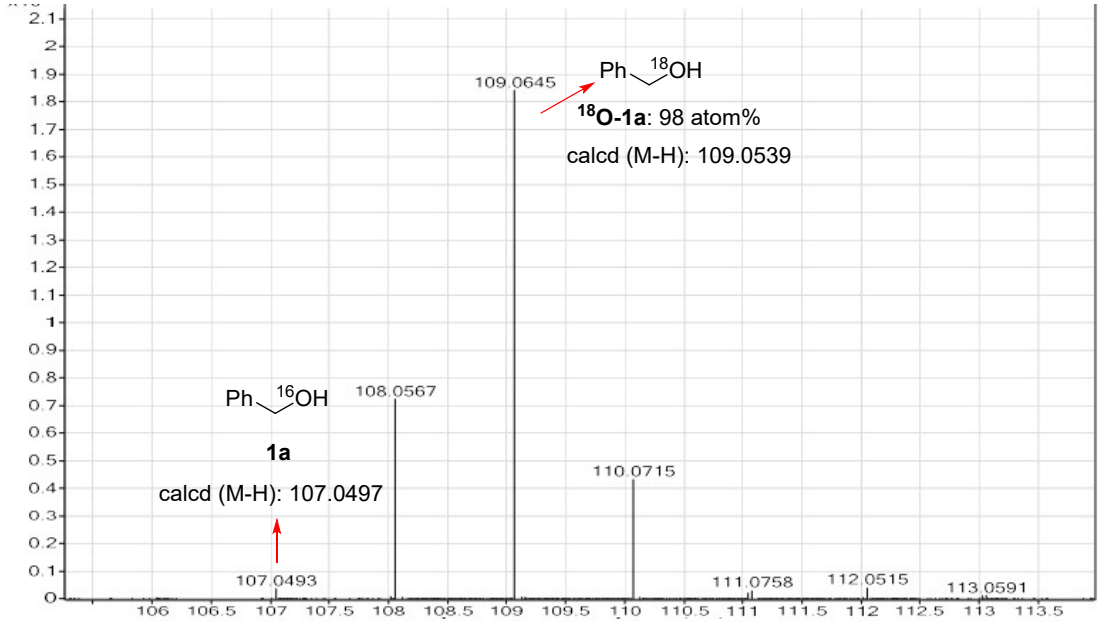




^{18}O-1a (98% ^{18}O)

To a 25 mL Schlenk tube containing a magnetic stir bar was added $H_2{}^{18}O$ (99 atom%) (1mL) under nitrogen. Subsequently, sodium (0.368g, 1.2 mmol, 4 equiv) was introduced. Then benzyl bromide (0.48 mL, 4 mmol) was added and refluxed at 120 °C for 6 h. Finally, the mixture is extracted with ethyl acetate, concentrated under reduced pressure and then purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate (v/v) = 10:1) to afford ^{18}O-benzyl alcohol. Then the isotope analysis of the product **^{18}O-1a** by HRGC showed that ^{18}O-**1a** should contain 98 atom% ^{18}O.

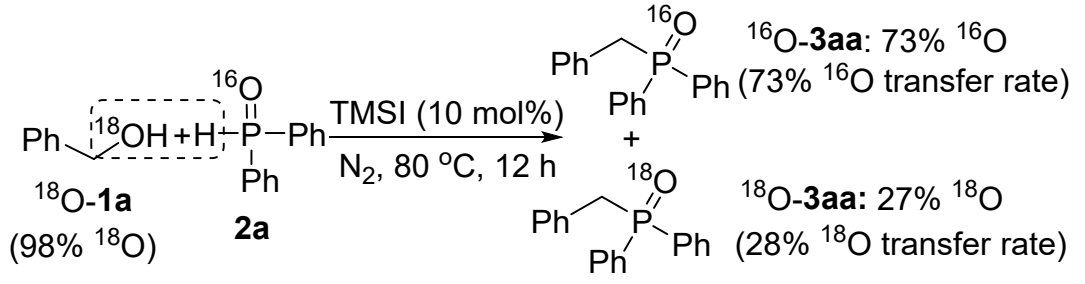
HRGC spectra



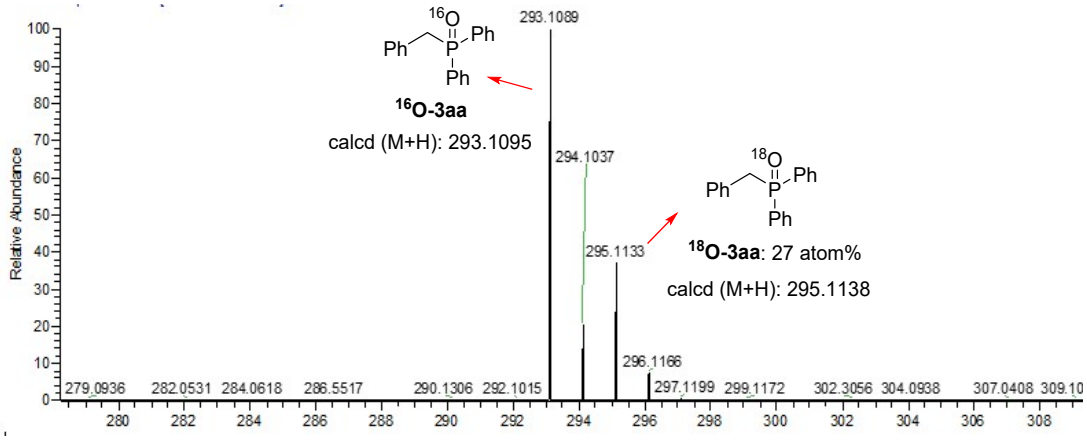
1	m/z	Abund	Abund % (Norm)	Max Abund
2	107.0493	34909.36		34909.36
3	108.0567	722203.5		722203.5
4	109.0645	1841064.25		1841064.25

^{18}O-1a: 1841064.25/(34909.36+1841064.25)= 98%

2.7.2 Detailed Procedure for the reaction of ^{18}O-benzyl alcohol (^{18}O-1a) and diphenylphosphine oxide (2a): The mixture of ^{18}O-benzyl alcohol (**^{18}O-1a**) (63.2 μL, 0.60 mmol), diphenylphosphine oxide **2a** (101.0 mg, 0.5 mmol) and TMSI (7.1 μL, 0.05 mmol) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 80 °C for 12 h. After cooling, the reaction mixture was directly analyzed by HRMS, showing that ^{18}O-**3aa** should contain 27 atom% ^{18}O.



HRMS spectra



	m/z	NL
1	293.1089	3.90E+08
2	295.1133	1.45E+08

^{18}O-3aa:1.45/(3.90+1.45) = 27%

Results and Discussion: The reaction of **^{18}O-1a** (98 atom% ^{18}O) with **2a** under standard conditions gave the target **^{18}O-3aa** (27 atom% ^{18}O) in high yield, revealing that the byproduct water can partially generated through the dehydroxylation of secondary P(O)-H compounds **2a** and dehydrogenation of benzyl alcohols **1a**. Therefore, another reaction pathway may be involved in the reaction. However, as only 27 atom% ^{18}O-**3aa** was obtained using 98 atom% ^{18}O-**1a** (Eq. 12), which corresponds to only 28% ^{18}O transfer rate, this process (Scheme 2, path a) should be a minor pathway in the reaction mechanism.

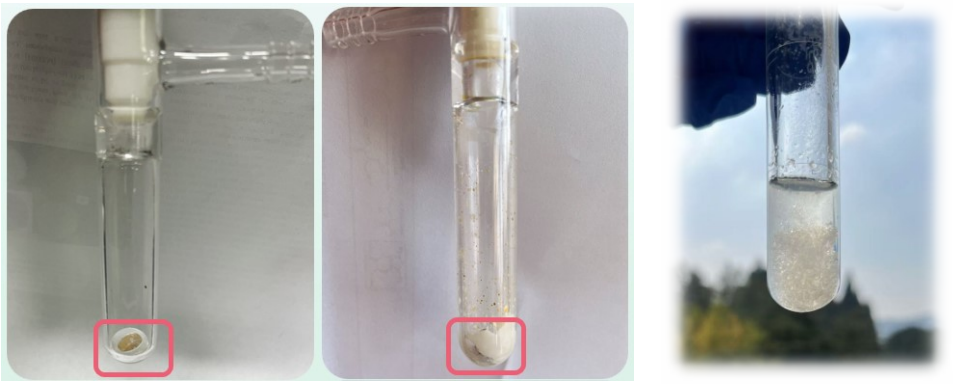
3. Typical Procedure and Characterization of the Products

Typical procedure for the Catalytic Dehydrative Substitution of Primary Alcohols (CH_2–OH) with P(O)–H Compounds: The mixture of **1a** (62.1 μL, 0.60 mmol), **2a** (101.1 mg, 0.50 mmol) and TMSI (7.1μL, 10 mol%) sealed under N_2 in a 10 mL Schlenk tube was heated at 80 °C for 12 h. Then the reaction mixture was analyzed by TLC/GC-MS and purified by washing the reaction mixture with a mixed solvent of ethyl acetate/petroleum ether (1:1) after the reaction under column chromatography-free conditions, giving **3aa** in 90% isolated yield. The product can also be directly purified by recrystallizing with a mixed solvent of MeOH/water (v/v 1/1) in 84% yield (> 99% purity).

Typical Prcedure for Gram Scale Reaction of 1a and 2a for the Synthesis of 3aa (Eq. 1, run 1 in the text): The mixture of **1a** (1.3 g, 12 mmol), **2a** (2.0 g, 10 mmol) and TMSI (142.3 μL, 1.0 mol, 10 mol%) was sealed under N_2 in a 25 mL Schlenk tube was heated at 100 °C for 24 h. Then the reaction mixture was analyzed by TLC/GC-MS and purified by washing the reaction mixture with a mixed solvent of ethyl acetate/petroleum ether (1:1) after the reaction under column chromatography-free conditions, giving **3aa** in 82% isolated yield.

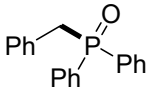
(Eq. 1, run 2 in the text): The mixture of **1a** (1.3 g, 12 mmol), **2a** (2.0 g, 10 mmol) and TMSI (142.3 μL, 1.0 mol, 10 mol%) and toluene (2.0 mL) was sealed under N_2 in a 25 mL Schlenk tube was heated at 100 °C for 24 h. Then the reaction mixture was analyzed by TLC/GC-MS. The solvent was evaporated by a rotary evaporator, and the residue was purified by washing the reaction mixture with a mixed solvent of ethyl acetate/petroleum ether (1:1) after the reaction under column chromatography-free conditions, giving **3aa** in 84% isolated yield.

Note: *Benefiting for the obvious experimental phenomenon that the reaction mixture changes from liquid at the beginning (Figure 1A) to solid at the end (Figure 1B), the column chromatography-free isolation and purification of the target products was achieved (Figure 1C), making the method much greener and practical.*

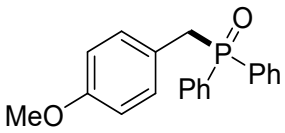


A) At the beginning of the reaction B) After the reaction C) Recrystallization

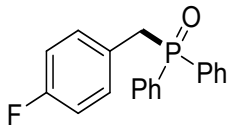
Figure 1 . The obvious experimental phenomenon



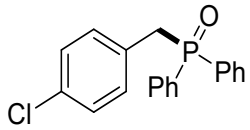
Benzyldiphenylphosphine Oxide(3aa), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 4H), 7.51 – 7.47 (m, 2H), 7.44 – 7.37 (m, 4H), 7.18 – 7.16 (m, 3H), 7.10 (dd, J = 5.4, 1.8 Hz, 2H), 3.64 (d, J = 13.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.3 (d, J = 98.9 Hz), 131.91, 131.3 (d, J = 8.8 Hz), 130.2 (d, J = 4.8 Hz), 128.6, 128.6, 128.5, 126.9, 38.2 (d, J = 66.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.18. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.



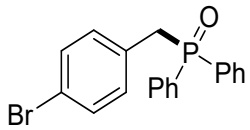
(4-Methoxybenzyl)Diphenylphosphine Oxide(3ab), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.40 (m, 4H), 7.02 (dd, J = 8.4, 2.4 Hz, 2H), 6.79 – 6.68 (m, 2H), 3.74 (s, 3H), 3.60 (d, J = 13.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 132.4 (d, J = 98.5 Hz), 131.9, 131.3, 131.23, 131.19, 122.9 (d, J = 7.8 Hz), 114.0, 55.3, 37.2 (d, J = 67.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.23. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.



(4-Fluorobenzyl)Diphenylphosphine Oxide(3ac), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 4H), 7.52 (t, J = 7.2 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.12 – 7.03 (m, 2H), 6.87 (t, J = 8.4 Hz, 2H), 3.62 (d, J = 13.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0 (d, J = 248.0 Hz), 132.1 (d, J = 99.2 Hz), 132.0 (d, J = 1.8 Hz), 131.7 (dd, J = 7.5, 5.4 Hz), 131.2 (d, J = 8.9 Hz), 128.7 (d, J = 11.6 Hz), 126.89 (dd, J = 7.8, 2.8 Hz), 115.4 (d, J = 21.7 Hz), 37.3 (d, J = 66.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.98. This compound is known in the literature: F. J. Wang, M. L. Qu, F. Chen, Q. Xu, M. Shi, *Chem. Commun*., **2012**, *48*, 8580-8582.

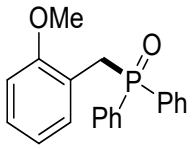


(4-Chlorobenzyl)Diphenylphosphine Oxide(3ad), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 4H), 7.56 – 7.50 (m, 2H), 7.48 – 7.42 (m, 4H), 7.16 (d, J = 8.4 Hz, 2H), 7.04 (dd, J = 8.4, 2.4 Hz, 2H), 3.61 (d, J = 13.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.9 (d, J = 2.9 Hz), 132.1 (d, J = 2.1 Hz), 132.0 (d, J = 99.7 Hz), 131.5 (d, J = 4.7 Hz), 131.2 (d, J = 8.9 Hz), 129.8 (d, J = 8.2 Hz), 128.7 (d, J = 11.7 Hz), 128.6 (d, J = 2.4 Hz), 37.5 (d, J = 66.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.82. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.

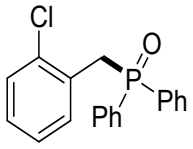


(4-Bromobenzyl)Diphenylphosphine Oxide(3ae), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (ddd, J = 11.2, 5.4, 3.2 Hz, 4H), 7.57 – 7.50 (m, 2H), 7.49 – 7.41 (m, 4H), 7.31 (d, J = 8.4 Hz, 2H), 6.98 (dd, J = 8.4, 2.4 Hz, 2H), 3.60 (d, J = 13.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.1, 132.0 (d, J = 99.5 Hz), 131.8 (d, J = 4.6 Hz), 131.6, 131.2 (d, J = 8.9 Hz), 130.3 (d, J = 8.2 Hz), 128.7 (d, J = 11.7 Hz), 121.1, 37.6 (d, J = 66.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.68. This compound is known in

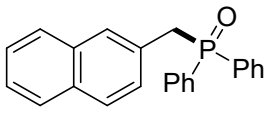
the literature: F. J. Wang, M. L. Qu, F. Chen, Q. Xu, M. Shi, *Chem. Commun*., **2012**, *48*, 8580-8582.



(2-Methylbenzyl)Diphenylphosphine Oxide(3af), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 4H), 7.51 – 7.44 (m, 2H), 7.44 – 7.37 (m, 4H), 7.37 – 7.32 (m, 1H), 7.19 – 7.10 (m, 1H), 6.86 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 3.76 (d, J = 14.4 Hz, 2H), 3.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9 (d, J = 5.4 Hz), 132.6 (d, J = 98.9 Hz), 131.8 (d, J = 4.5 Hz), 131.7 (d, J = 1.8 Hz), 131.3 (d, J = 9.0 Hz), 128.293 (d, J = 3.0 Hz), 128.290 (d, J = 11.6 Hz), 120.6 (d, J = 2.2 Hz), 119.7 (d, J = 8.2 Hz), 110.2, 54.9, 31.1 (d, J = 67.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.58. This compound is known in the literature: P.-Y. Renard, P. Vayron, C. Mioskowski, *Org. Lett.*, **2003**, *5*, 1661 - 1664.

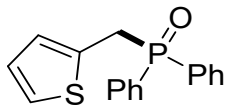


(2-Chlorobenzyl)Diphenylphosphine Oxide(3ag), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.74 (m, 4H), 7.63 (d, J = 7.8 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.54 – 7.50 (m, 4H), 7.31 (d, J = 7.8 Hz, 1H), 7.24 (dd, J = 14.4, 7.2 Hz, 1H), 7.19 (dd, J = 10.2, 4.8 Hz, 1H), 3.96 (d, J = 13.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.4 (d, J = 6.7 Hz), 132.2 (d, J = 99.8 Hz), 132.1, 132.0, 131.2 (d, J = 9.1 Hz), 129.8 (d, J = 7.2 Hz), 129.5, 128.6 (d, J = 11.7 Hz), 128.4, 126.9, 34.7 (d, J = 66.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.11. This compound is known in the literature: L. Liu, Y. Y. Tang, K. Y. Wang, T. Z. Huang, T. Q. Chen, *J. Org. Chem.,* **2021**, *86*, 4159−4170.

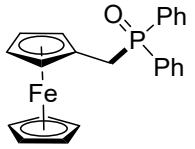


(Naphthalen-2-Ylmethyl)Diphenylphosphine Oxide(3ah), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 5H), 7.68 – 7.65 (m, 2H), 7.57 (s, 1H), 7.53 – 7.48 (m, 2H), 7.46 – 7.39 (m, 6H), 7.23 (d, J = 8.4 Hz, 1H), 3.82 (d, J = 13.8 Hz, 2H).

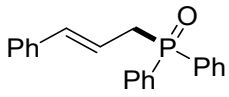
^{13}C NMR (151 MHz, $CDCl_3$) δ 133.4 (d, J = 2.0 Hz), 132.7, 132.2 (d, J = 41.8 Hz), 131.97, 131.94, 131.3 (d, J = 9.1 Hz), 129.1 (d, J = 6.9 Hz), 128.8 (d, J = 8.3 Hz), 128.6 (d, J = 11.7 Hz), 128.3 (d, J = 3.9 Hz), 128.0, 127.7 (d, J = 12.2 Hz), 126.1, 125.8, 38.44 (d, J = 66.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.07. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.



Diphenyl(Thiophen-2-Ylmethyl)Phosphine Oxide(3ai), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 4H), 7.53 – 7.51 (m, 2H), 7.46 – 7.42 (m, 4H), 7.08 (dd, J = 6.6, 1.2 Hz, 1H), 6.85 (dt, J = 5.4, 3.2 Hz, 2H), 3.88 (d, J = 13.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.1, 132.0 (d, J = 8.6 Hz), 131.8 (d, J = 99.7 Hz), 131.3 (d, J = 9.4 Hz), 128.7 (d, J = 11.6 Hz), 127.9 (d, J = 6.4 Hz), 127.1 (d, J = 2.0 Hz), 125.0 (d, J = 1.9 Hz), 32.7 (d, J = 68.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.14. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.

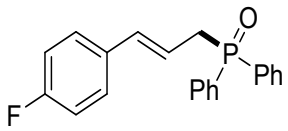


(Ferrocenylmethyl)Diphenylphosphine Oxide(3aj), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 4H), 7.51 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 5.4 Hz, 4H), 4.05 (d, J = 44.4 Hz, 10H), 3.43 (d, J = 12.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.4 (d, J = 98.0 Hz), 131.8, 131.3 (d, J = 8.7 Hz), 128.5 (d, J = 11.4 Hz), 69.9, 69.0, 68.1, 33.4 (d, J = 67.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 28.96. This compound is known in the literature: F. J. Wang, M. L. Qu, F. Chen, Q. Xu, M. Shi, *Chem. Commun*., **2012**, *48*, 8580-8582. Unknown NMR (151 MHz,) δ.

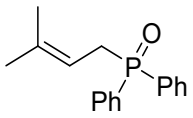


Cinnamyldiphenylphosphine Oxide(3ak), white solid. ^{1}H NMR (600 MHz, $CDCl_3$)

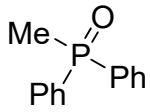
*δ*7.82 – 7.70 (m, 4H), 7.57 – 7.52 (m, 2H), 7.50 – 7.43 (m, 4H), 7.30 – 7.22 (m, 4H), 7.22 – 7.17 (m, 1H), 6.42 (dd, *J* = 15.6, 4.2 Hz, 1H), 6.18 (ddd, *J* = 15.2, 13.8, 7.8 Hz, 1H), 3.30 (ddd, *J* = 14.4, 7.8, 1.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 136.8, 135.7 (d, *J* = 12.1 Hz), 132.5 (d, *J* = 98.8 Hz), 132.0 (d, *J* = 2.1 Hz), 131.2 (d, *J* = 9.1 Hz), 128.7 (d, *J* = 11.7 Hz), 128.6, 127.7, 126.3, 118.5 (d, *J* = 9.4 Hz), 35.7 (d, *J* = 68.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) *δ* 30.67. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.



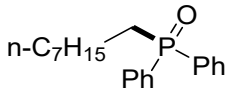
(E)-(3-(4-Fluorophenyl)Allyl)Diphenylphosphine Oxide(3al), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.80 – 7.71 (m, 4H), 7.57 – 7.52 (m, 2H), 7.50 – 7.46 (m, 4H), 7.20 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.94 (t, *J* = 8.4 Hz, 2H), 6.39 (dd, *J* = 15.6, 4.2 Hz, 1H), 6.16 – 6.02 (m, 1H), 3.28 (dd, *J* = 14.4, 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 162.3 (d, *J* = 246.9 Hz), 134.5 (d, *J* = 12.0 Hz), 132.9 (d, *J* = 35.1 Hz), 132.1 (d, *J* = 10.7 Hz), 131.1 (d, *J* = 9.4 Hz), 128.8 (d, *J* = 11.8 Hz), 127.8 (d, *J* = 7.8 Hz), 118.2 (d, *J* = 10.1 Hz), 115.5 (d, *J* = 21.6 Hz), 35.5 (d, *J* = 68.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) *δ* 30.68. HRMS (ESI) for $C_{21}H_{19}FOP$ (M+H): Calcd: 337.1158; found: 337.1154.



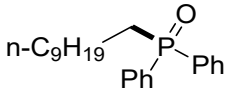
(3-Methylbut-2-en-1-yl)Diphenylphosphine Oxide(3am), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.78 – 7.70 (m, 4H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.49 – 7.43 (m, 4H), 5.31 – 5.10 (m, 1H), 3.08 (dd, *J* = 14.4, 7.8 Hz, 2H), 1.66 (d, *J* = 4.2 Hz, 3H), 1.44 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 137.7 (d, *J* = 12.2 Hz), 132.9 (d, *J* = 97.9 Hz), 131.8, 131.1 (d, *J* = 9.0 Hz), 128.6 (d, *J* = 11.5 Hz), 112.3 (d, *J* = 8.6 Hz), 30.9 (d, *J* = 70.6 Hz), 25.9, 18.1. ^{31}P NMR (243 MHz, $CDCl_3$) *δ* 31.64. This compound is known in the literature: C. Tejo, J. H. Pang, D. Y. Ong, M. Oi, M. Uchiyama, R. Takita, S. Chiba, *Chem. Commun*., **2018**, *54*, 1782 - 1785.



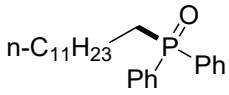
Methyldiphenylphosphine Oxide(3ao), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 4H), 7.55 – 7.44 (m, 6H), 2.03 (d, J = 13.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.1 (d, J = 101.3 Hz), 131.9 (d, J = 2.2 Hz), 130.6 (d, J = 9.8 Hz), 128.7 (d, J = 11.8 Hz), 16.7 (d, J = 73.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.6. This compound is known in the literature: C.-K. Li, Z.-K. Tao, A. Shoberu, W. Zhang, J.-P. Zou, *Org. Lett.*, **2022**, *24*, 6083 – 6087.



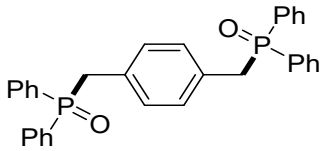
Octyldiphenylphosphine Oxide(3ap), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 4H), 7.54 – 7.44 (m, 6H), 2.31 – 2.20 (m, 2H), 1.62 (tt, J = 16.2, 8.4 Hz, 2H), 1.42 – 1.35 (m, 2H), 1.32 – 1.17 (m, 8H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.2 (d, J = 97.8 Hz), 131.7, 130.9 (d, J = 9.3 Hz), 128.7 (d, J = 11.5 Hz). 31.9, 31.1 (d, J = 14.6 Hz), 30.1, 29.6, 29.1, 22.7, 21.5 (d, J = 3.8 Hz) 14.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 33.24. This compound is known in the literature: C. K. Li, Z. K. Tao, A. Shoberu, W. Zhang, J. P. Zou, *Org. Lett.*, **2022**, *24*, 6083–6087.



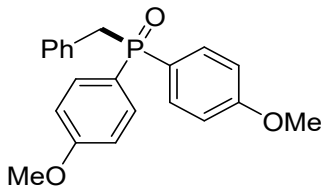
Decyldiphenylphosphine Oxide(3aq), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 4H), 7.54 – 7.49 (m, 2H), 7.49 – 7.43 (m, 4H), 2.29 – 2.21 (m, 2H), 1.68 – 1.55 (m, 2H), 1.43 – 1.34 (m, 2H), 1.31 – 1.18 (m, 12H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.3 (d, J = 97.7 Hz), 131.7, 130.9 (d, J = 9.4 Hz), 128.7 (d, J = 11.5 Hz), 31.9, 31.1 (d, J = 14.6 Hz), 30.1, 29.6, 29.4, 29.3, 29.2, 22.7, 21.5 (d, J = 3.8 Hz), 14.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 33.24. This compound is known in the literature: C. K. Li, Z. K. Tao, A. Shoberu, W. Zhang, J. P. Zou, *Org. Lett.*, **2022**, *24*, 6083–6087.



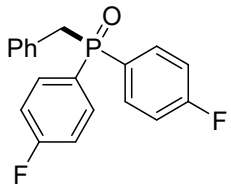
Dodecyldiphenylphosphine Oxide(3ar), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 4H), 7.55 – 7.49 (m, 2H), 7.49 – 7.44 (m, 4H), 2.27 – 2.25 (m, 2H), 1.69 – 1.57 (m, 2H), 1.38 (dd, J = 14.4, 7.8 Hz, 2H), 1.28 – 1.17 (m, 16H), 0.94 – 0.84 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.2 (d, J = 97.8 Hz), 131.7 (d, J = 1.9 Hz), 130.9 (d, J = 9.1 Hz), 128.7 (d, J = 11.5 Hz), 32.0, 31.1 (d, J = 14.9 Hz), 30.0, 29.7, 29.64, 29.56, 29.5, 29.4, 29.2, 22.8, 21.5 (d, J = 3.8 Hz), 14.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 33.45. This compound is known in the literature: C. K. Li, Z. K. Tao, A. Shoberu, W. Zhang, J. P. Zou, *Org. Lett.*, **2022**, *24*, 6083–6087.



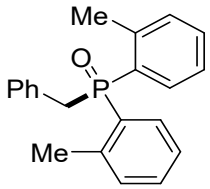
(1,4-Phenylenebis(Methylene))bis(Diphenylphosphine Oxide) (3au), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (dd, J = 10.2, 8.4 Hz, 8H), 7.53 – 7.44 (m, 4H), 7.39 (t, J = 6.6 Hz, 8H), 6.93 (s, 4H), 3.56 (d, J = 13.8 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.7 (d, J = 99.7 Hz), 131.7, 131.2 (d, J = 8.9 Hz), 130.2, 1230.0 (d, J = 3.0 Hz), 128.4 (d, J = 11.8 Hz), 38.0 (d, J = 67.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.33. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.



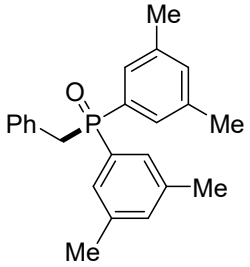
Benzylbis(4-Methoxyphenyl)Phosphine Oxide(3ba), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 4H), 7.21 – 7.16 (m, 3H), 7.12 – 7.05 (m, 2H), 6.94 – 6.91 (m, 4H), 3.83 (s, 6H), 3.58 (d, J = 13.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 133.1 (d, J = 10.4 Hz), 131.7 (d, J = 7.5 Hz), 130.2 (d, J = 5.3 Hz), 128.4, 126.7, 123.7 (d, J = 105.5 Hz), 114.1 (d, J = 12.6 Hz), 55.4, 38.7 (d, J = 67.3 Hz).. ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.32. This compound is known in the literature: L. Liu, Y. Y. Tang, K. Y. Wang, T. Z. Huang, T. Q. Chen, *J. Org. Chem.,* **2021**, *86*, 4159−4170.



Benzylbis(4-Fluorophenyl)Phosphine Oxide(3ca), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.22 – 7.19 (m, 3H), 7.16 – 7.13 (m, 4H), 7.10 – 7.05 (m, 2H), 3.63 (d, J = 13.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1 (d, J = 253.8 Hz), 133.8 – 133.6 (m), 130.7 (d, J = 7.7 Hz), 130.2 (d, J = 5.1 Hz), 128.6 (d, J = 1.8 Hz), 128.3 (d, J = 2.3 Hz), 127.6 (d, J = 2.2 Hz), 127.1 (s), 116.1 (dd, J = 21.1, 12.8 Hz), 38.4 (d, J = 67.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.19. This compound is known in the literature: N. Li, F. Chen, G. H. Wang, Q. L. Zeng, *Monatsh. Chem*., **2020**, *151*, 99 - 106.

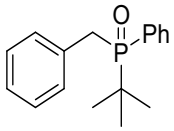


Benzyldi-O-Tolylphosphine Oxide(3da), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.38 (td, J = 7.8, 1.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 2H), 7.18 – 7.13 (m, 5H), 7.04 (dd, J = 4.8, 2.4 Hz, 2H), 3.74 (d, J = 13.2 Hz, 2H), 2.21 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4 (d, J = 8.0 Hz), 131.8 (d, J = 6.8 Hz), 131.7 (d, J = 36.1 Hz), 131.5, 131.3 (d, J = 7.6 Hz), 131.2 (s), 130.4 (d, J = 5.2 Hz), 128.3, 126.8, 125.6 (d, J = 12.2 Hz), 37.5 (d, J = 66.2 Hz), 21.1 (d, J = 3.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 32.07. This compound is known in the literature: L. Liu, Y. Y. Tang, K. Y. Wang, T. Z. Huang, T. Q. Chen, *J. Org. Chem.,* **2021**, *86*, 4159−4170.

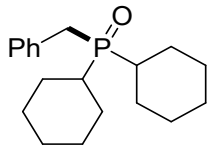


Benzylbis(3,5-Dimethylphenyl)Phosphine Oxide(3ea), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 138.2 (d, J = 12.0 Hz), 133.5, 132.2 (d, J = 98.1 Hz), 131.6 (d, J = 7.6

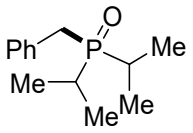
Hz), 130.3 (d, J = 5.3 Hz), 128.8 (d, J = 9.1 Hz), 128.4, 126.7, 38.2 (d, J = 65.9 Hz), 21.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.70. This compound is known in the literature: N. Li, F. Chen, G. H. Wang, Q. L. Zeng, *Monatsh. Chem*., **2020**, *151*, 99 - 106.



Benzyl(tert-butyl)(phenyl)Phosphine Oxide(3fa), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.65 (m, 2H), 7.51 – 7.40 (m, 3H), 7.30-7.26 (m, 2H), 7.19 (t, J = 7.8 Hz, 2H), 7.16 – 7.10 (m, 1H), 3.51 (t, J = 14.4 Hz, 1H), 3.42 (dd, J = 14.4, 9.6 Hz, 1H), 1.15 (d, J = 14.4 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.1 (d, J = 7.6 Hz), 132.0 (d, J = 7.6 Hz), 131.5 (d, J = 2.0 Hz), 130.2 (d, J = 4.9 Hz), 129.8 (d, J = 87.8 Hz), 128.5, 128.1 (d, J = 10.4 Hz), 126.6, 33.5 (d, J = 67.9 Hz), 31.4 (d, J = 59.0 Hz), 24.82 (s). ^{31}P NMR (243 MHz, $CDCl_3$) δ 46.99. This compound is known in the literature: L. Liu, Y. Y. Tang, K. Y. Wang, T. Z. Huang, T. Q. Chen, *J. Org. Chem.,* **2021**, *86*, 4159−4170.



Benzyldicyclohexylphosphine Oxide(3ga), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.30 (m, 4H), 7.24 (t, J = 6.6 Hz, 1H), 3.08 (d, J = 12.6 Hz, 2H), 1.95 – 1.65 (m, 12H), 1.46 – 1.09 (m, 10H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.0 (d, J = 6.9 Hz), 129.9 (d, J = 4.9 Hz), 128.7, 126.7, 36.2 (d, J = 63.7 Hz), 32.2 (d, J = 55.4 Hz), 26.7 (dd, J = 12.3, 6.0 Hz), 26.0, 25.8 (dd, J = 14.4, 2.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 49.07. This compound is known in the literature: S. Montel, T. Z. Jia, P. J. Walsh, *Org. Lett*., **2014**, *16*, 130 – 133.



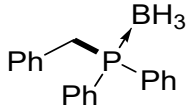
Benzyldiisopropylphosphine Oxide(3ha), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.25 – 7.23 (m, 1H), 3.13 (d, J = 12.6 Hz, 2H), 2.10 – 1.97 (m, 2H), 1.16 (dt, J = 15.2, 7.2 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.7, 129.9 (d,

J = 4.7 Hz), 128.8, 126.8, 31.9 (d, *J* = 56.1 Hz), 25.7 (d, *J* = 63.8 Hz), 16.1 (d, *J* = 19.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 55.29. HRMS (ESI) for $C_{13}H_{22}OP$ (M+H): Calcd: 225.1408; found: 225.1405.

Detailed Procedures for One-pot Synthesis of Phosphine Borane Complex 5a (Eq. 3 in the text).

The mixture of **1a** (62.1 μL, 0.60 mmol), **2a** (101.1 mg, 0.50 mmol) and TMSI (7.1μL, 10 mol%) sealed under N_2 in a 25 mL Schlenk tube was heated at 80 °C for 12 h. Then the reaction mixture was analyzed by TLC/GC-MS and purified by washing the reaction mixture with a mixed solvent of ethyl acetate/petroleum ether (1:1) after the reaction under column chromatography-free conditions to give phosphine oxide **3aa**

To phosphine oxide **3aa** was added dry THF (1 mL), triethoxyl hydrosilane (1.5 mmol, 3.0 equiv.), and titanium (IV) isopropoxide (14.2 mg, 10 mol%) under nitrogen. The reaction mixture was heated at 80 °C for 1 h and cooled to room temperature, then BH_3•SMe_2 (150 μL, 1.5 mmol, 3.0 equiv.) and dry 1,4-dioxane (1 mL) were added through the septum, and the mixture was stirred for an additional 4 hours at ambient temperature. Then, the reaction mixture was filtered through a short celite pad and washed with DCM (10 mL × 3). The solvent was removed under vacuum and the residue was purified by silica gel column chromatography with hexane/ethyl acetate as eluent to give the desired product **5a**.

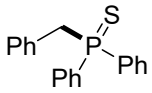


Phosphine borane complex 5a, white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.49 (td, *J* = 7.2, 1.2 Hz, 2H), 7.41 (td, *J* = 7.8, 2.4 Hz, 4H), 7.20 – 7.11 (m, 3H), 7.00 – 6.90 (m, 2H), 3.60 (d, *J* = 12.0 Hz, 2H), 1.28 – 0.55 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.8 (d, *J* = 9.0 Hz), 131.9, 131.4, 130.4 (d, *J* = 4.6 Hz), 128.8 (d, *J* = 10.0 Hz), 128.78 (d, *J* = 54.1 Hz), 128.2, 127.1, 34.2 (d, *J* = 32.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.62 (m). This compound is known in the literature: R. F. Cheng, C. J. Li, *Angew. Chem. Int. Ed*., **2023**, *62*, e202301730.

Detailed Procedures for One-pot Synthesis of Phosphine Sulfide 6a (Eq. 4 in the text).

The mixture of **1a** (62.1 μL, 0.60 mmol), **2a** (101.1 mg, 0.50 mmol) and TMSI (7.1μL, 10 mol%) sealed under N_2 in a 25 mL Schlenk tube was heated at 80 °C for 12 h. Then the reaction mixture was analyzed by TLC/GC-MS and purified by washing the reaction mixture with a mixed solvent of ethyl acetate/petroleum ether (1:1) after the reaction under column chromatography-free conditions to give phosphine oxide **3aa**

To phosphine oxide **3aa** was added dry THF (1 mL), triethoxyl hydrosilane (1.5 mmol, 3.0 equiv.), and titanium (IV) isopropoxide (14.2 mg, 10 mol%) under nitrogen. The reaction mixture was heated at 80 °C for 1 h and cooled to room temperature, then S_8 (64.0 mg, 2.0 mmol, 4.0 equiv.) and dry 1,4-dioxane (1 mL) were added into the tube and the resulting mixture was stirred for another 12 hrs.Then the reaction mixture was filtered through a short celite pad and washed with DCM(10 mL × 3). The solvent was removed under vacuum and the residue was purified by silica gel column chromatography with hexane/ethyl acetate as eluent to give thedesired product **6a**.



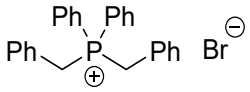
Benzyldiphenylphosphine sulfide(6a), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 4H), 7.53 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 7.21 – 7.11 (m, 3H), 7.02 – 6.95 (m, 2H), 3.83 (d, J = 13.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.1 (d, J = 80.0 Hz), 131.6, 131.5, 130.7 (d, J = 7.4 Hz), 130.5 (d, J = 5.5 Hz), 128.5 (d, J = 12.0 Hz), 127.9 (d, J = 2.4 Hz), 127.1 (d, J = 2.9 Hz), 40.9 (d, J = 50.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 42.79. This compound is known in the literature: R. F. Cheng, C. J. Li, *Angew. Chem. Int. Ed*., **2023**, *62*, e202301730.

Detailed Procedures for One-pot Synthesis of a Phosphine Ligand (Eq. 2 in the text).

The mixture of **1a** (62.1 μL, 0.60 mmol), **2a** (101.1 mg, 0.50 mmol) and TMSI

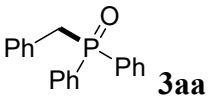
(7.1μL, 10 mol%) sealed under N_2 in a 25 mL Schlenk tube was heated at 80 °C for 12 h. Then the reaction mixture was analyzed by TLC/GC-MS and purified by washing the reaction mixture with a mixed solvent of ethyl acetate/petroleum ether (1:1) after the reaction under column chromatography-free conditions to give phosphine oxide **3aa**

To phosphine oxide **3aa** was added dry THF (1 mL), triethoxyl hydrosilane (1.5 mmol, 3.0 equiv.), and titanium (IV) isopropoxide (14.2 mg, 10 mol%) under nitrogen. The reaction mixture was then heated at 80 °C for 1 h and cooled to room temperature to give the crude benzyldiphenylphosphine **7a**. Since **7a** is air-sensitive and not isolable by usual procedures, benzyl bromide (171 mg, 1 mmol, 2.0 equiv.) was added to **7a** and then heated at 80 °C under nitrogen for 1 h. The target dibenzyldiphenylphosphonium bromide $[PPh_2(CH_2Ph)_2]Br$ **10a** was obtained in 84% yield by filtration and wash with ethyl acetate.



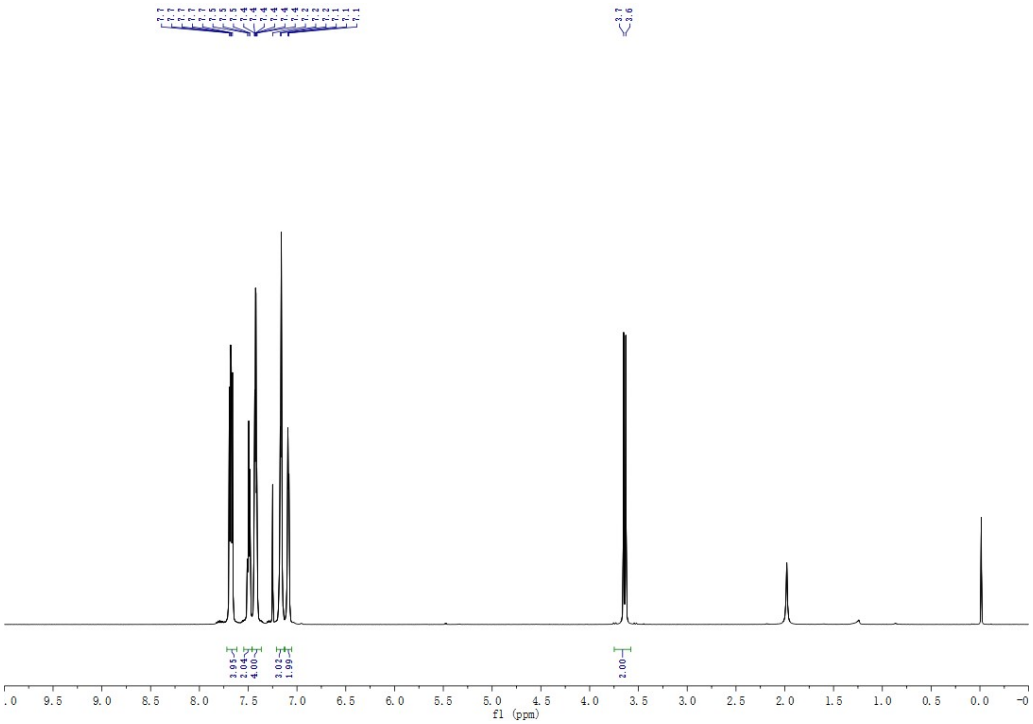
Dibenzyldiphenylphosphonium Bromide(10a), white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.65 (dd, J = 12.0, 8.4 Hz, 4H), 7.56 – 7.49 (m, 4H), 7.17 – 7.11 (m, 2H), 7.05 (t, J = 7.2 Hz, 4H), 7.00 (dd, J = 7.2, 1.8 Hz, 4H), 4.95 (d, J = 14.4 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.82 (d, J = 2.0 Hz), 134.43 (d, J = 8.7 Hz), 130.90 (d, J = 5.5 Hz), 129.70 (d, J = 12.5 Hz), 128.86 (d, J = 2.5 Hz), 128.21 (d, J = 3.7 Hz), 127.58 (d, J = 8.6 Hz), 116.66 (d, J = 82.5 Hz), 29.51 (d, J = 45.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.3. This compound is known in the literature: X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. Cao, L. B. Han, *Green Chem.,* **2018**, *20*, 3408–3413.

4. Copies of the ^{1}H、^{13}C and ^{31}P NMR Spectra of the Products

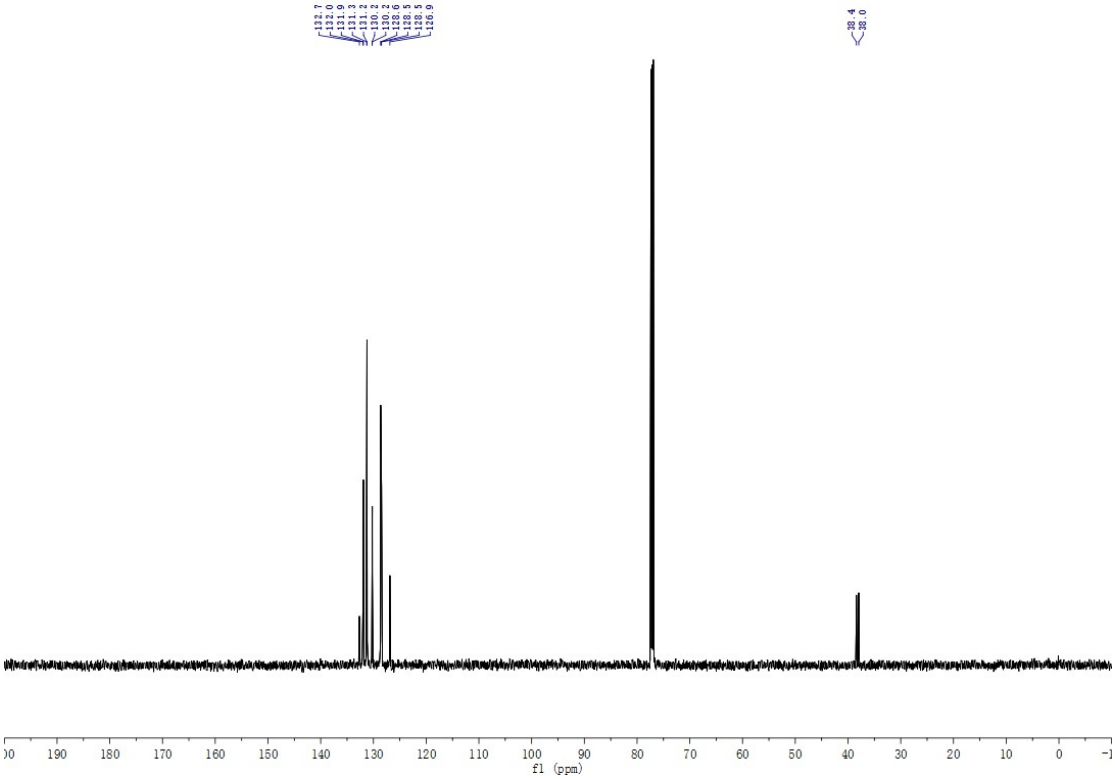


3aa

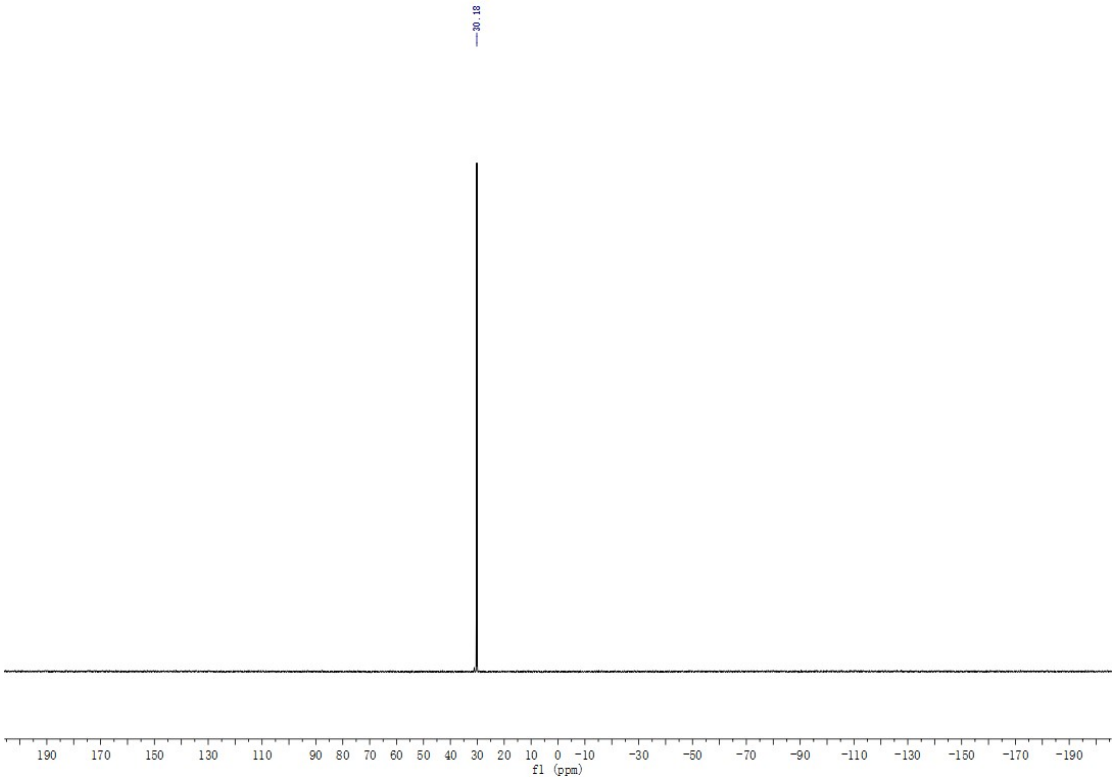
^{1}H NMR (600 MHz, $CDCl_3$)

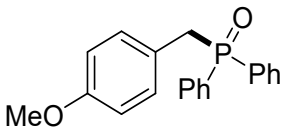


^{13}C NMR (151 MHz, $CDCl_3$)



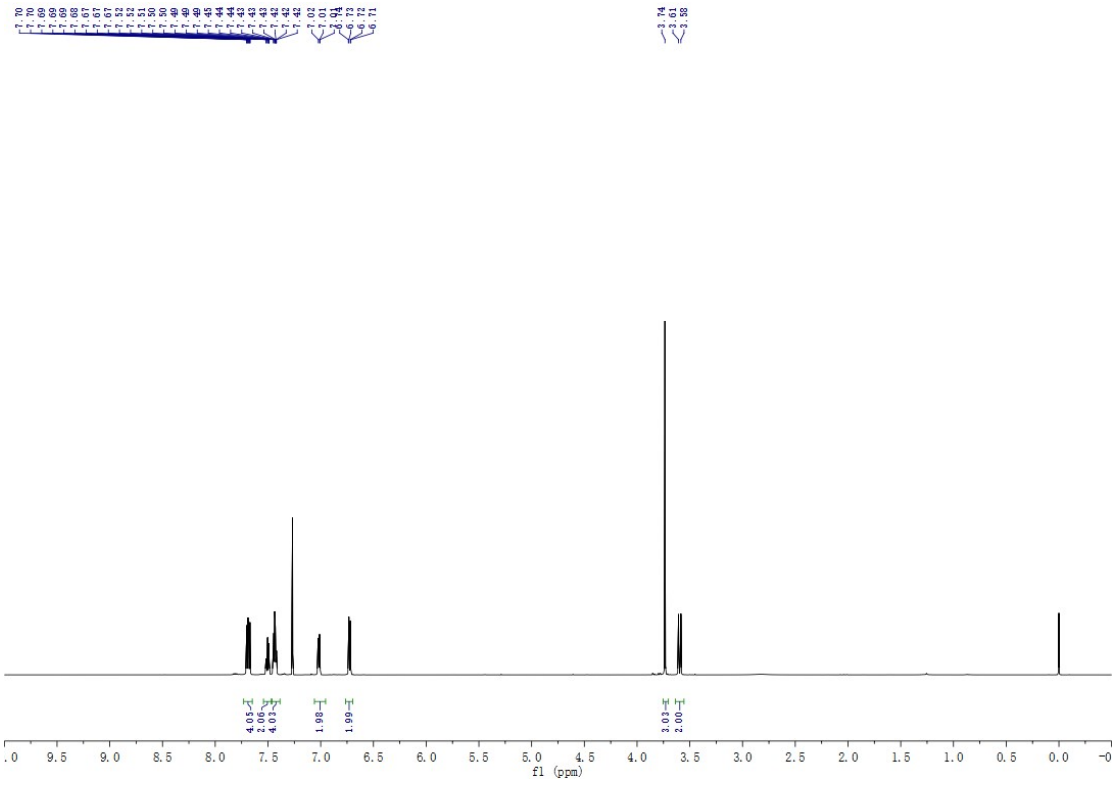
^{31}P NMR (243 MHz, $CDCl_3$)



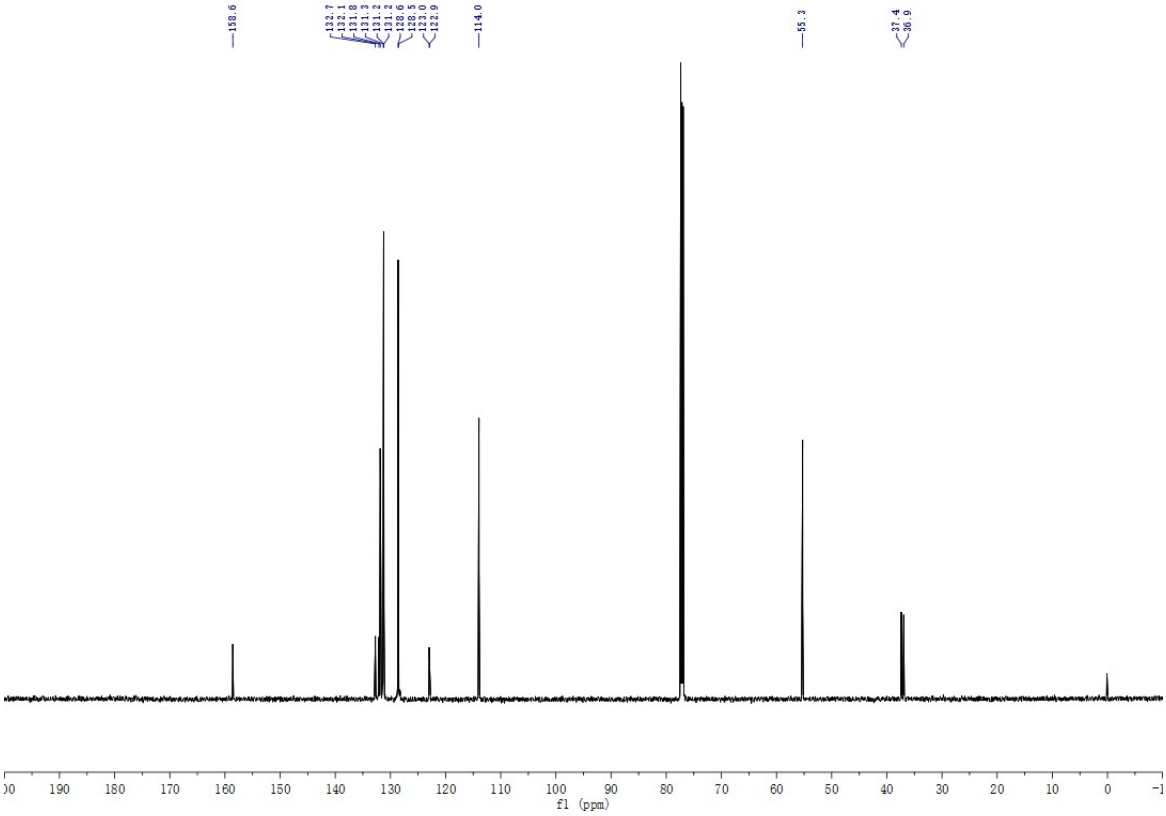


3ab

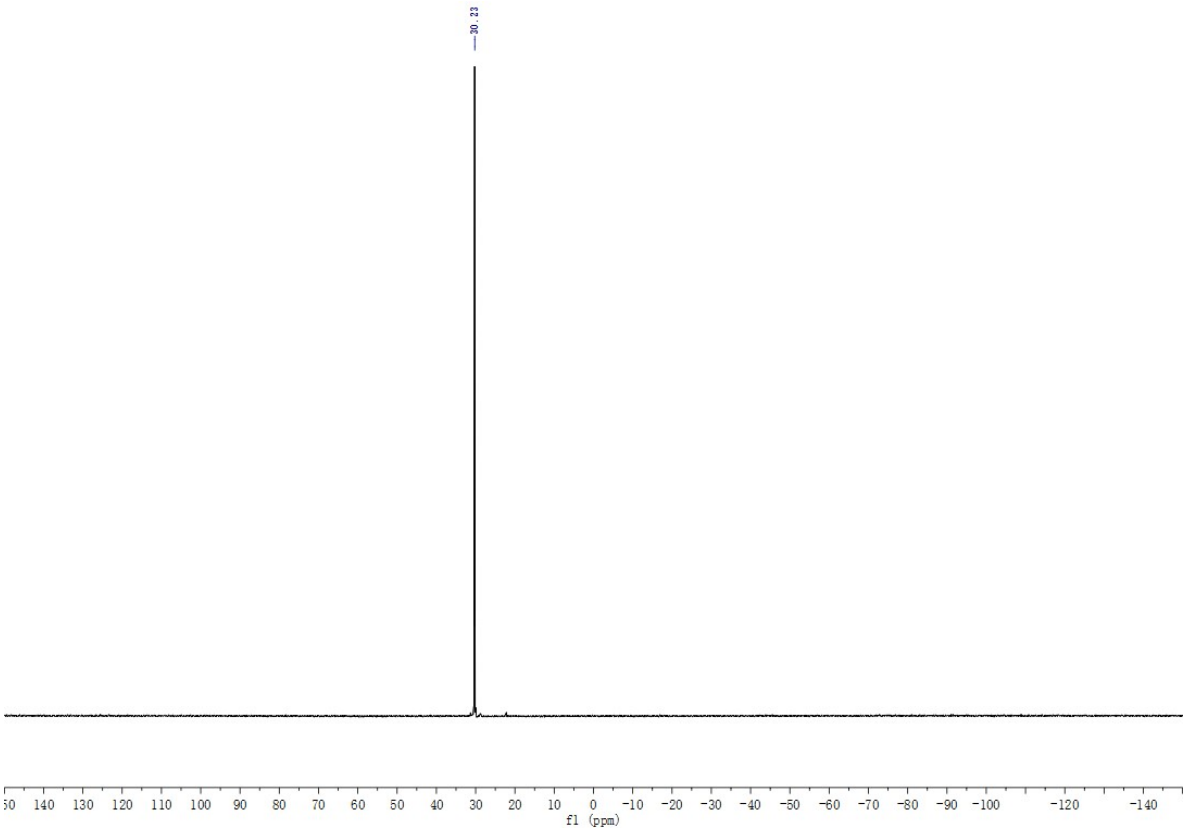
^{1}H NMR (600 MHz, $CDCl_3$)

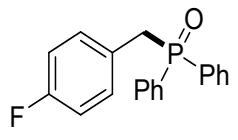


^{13}C NMR (151 MHz, $CDCl_3$)



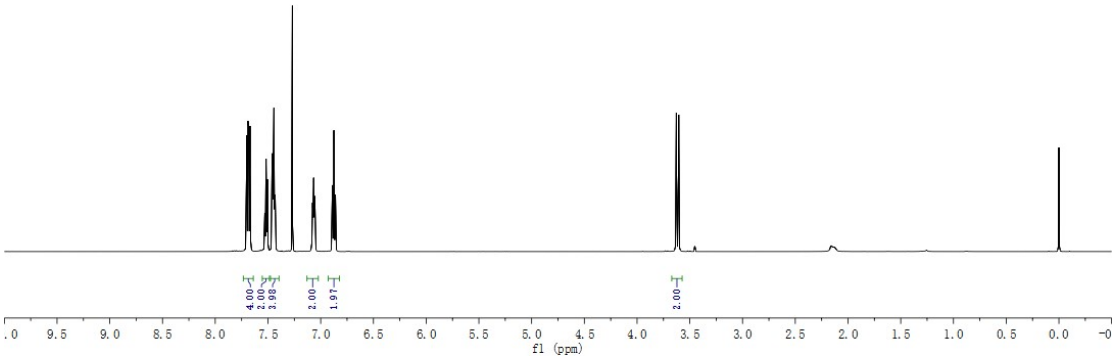
^{31}P NMR (243 MHz, $CDCl_3$)



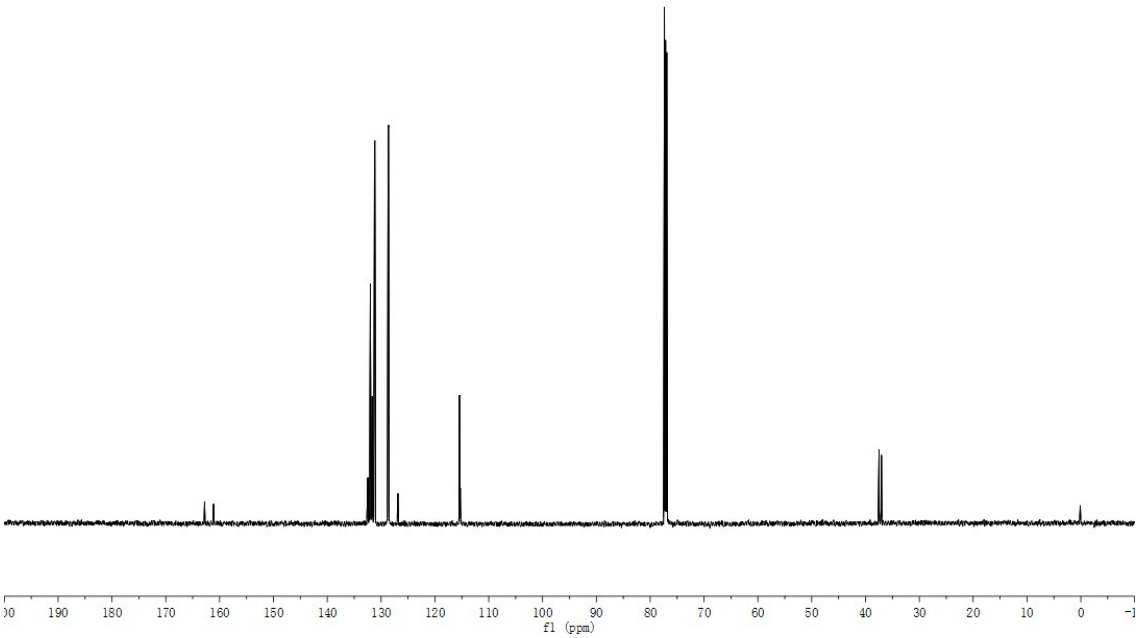


3ac

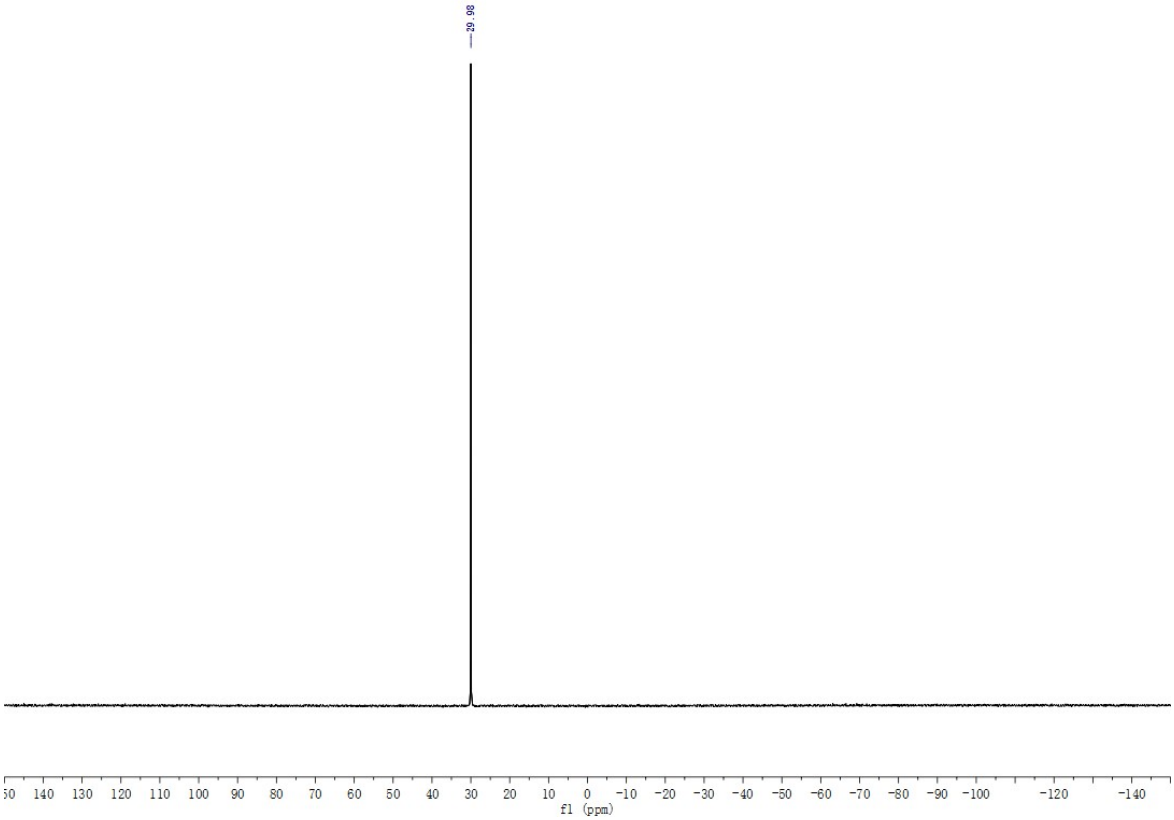
^{1}H NMR (600 MHz, $CDCl_3$)

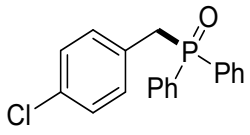


^{13}C NMR (151 MHz, $CDCl_3$)



^{31}P NMR (243 MHz, $CDCl_3$)





3ad

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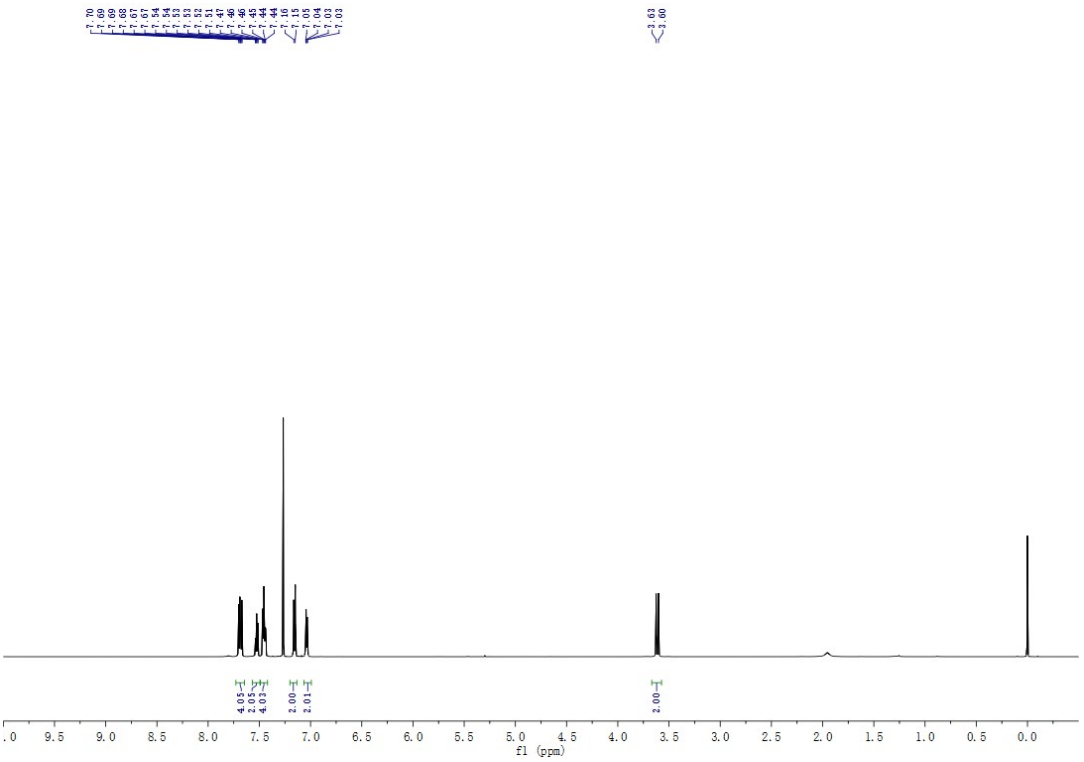
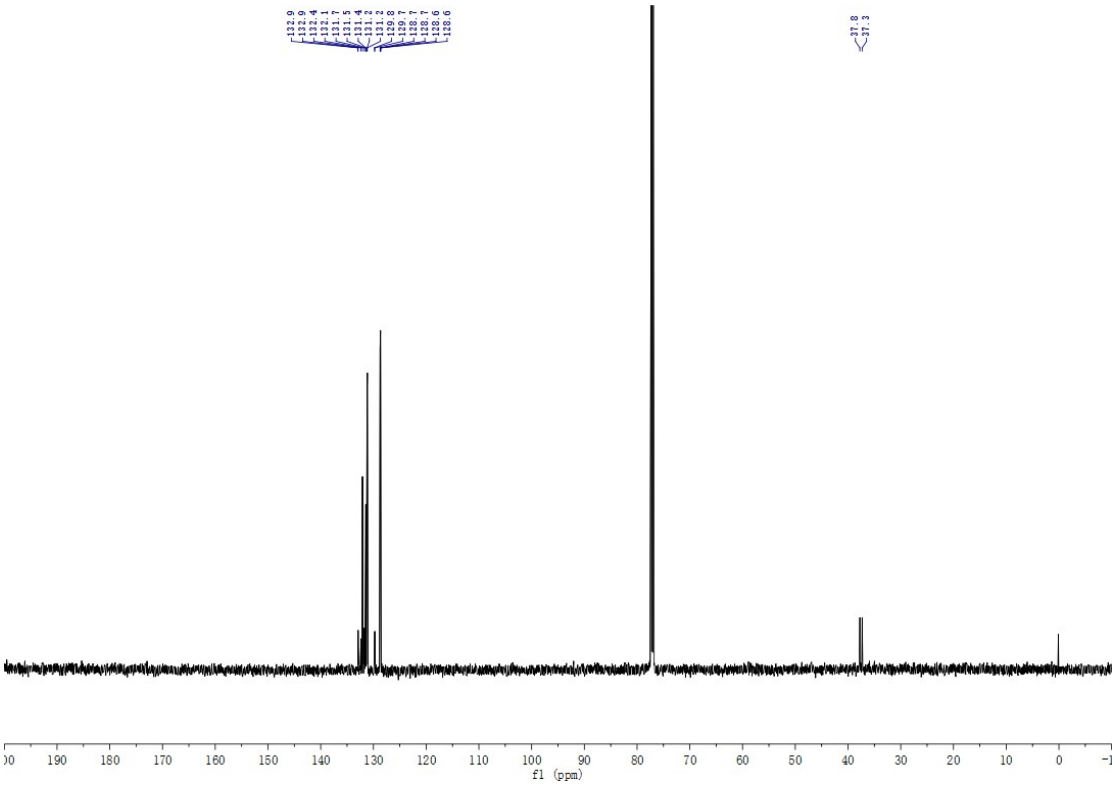
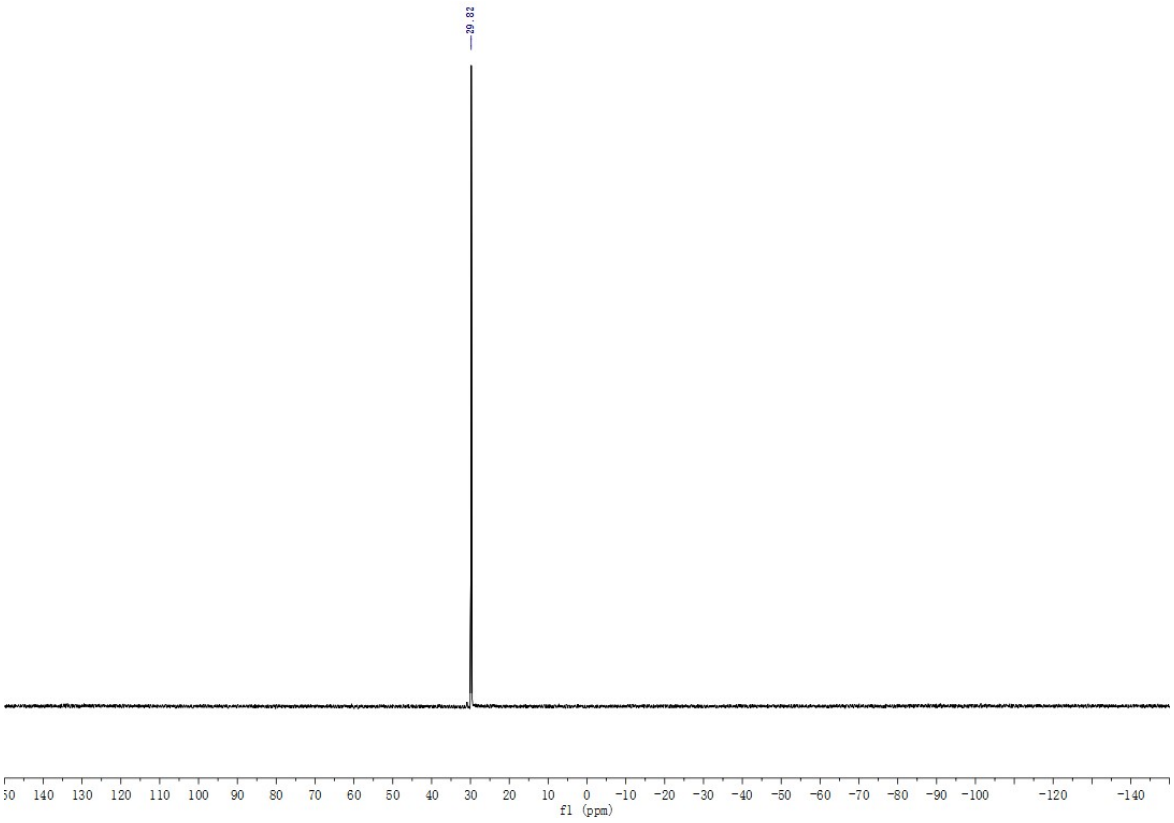
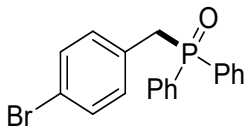


^{13}C NMR (151 MHz, $CDCl_3$)



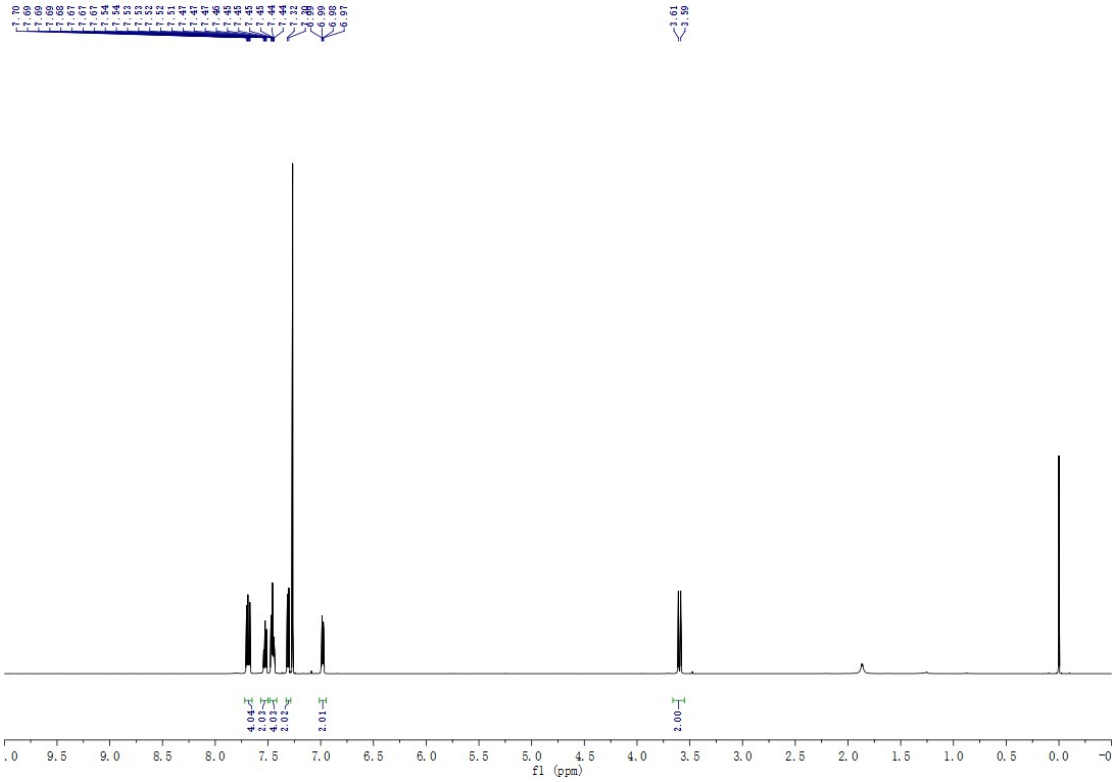
^{31}P NMR (243 MHz, $CDCl_3$)



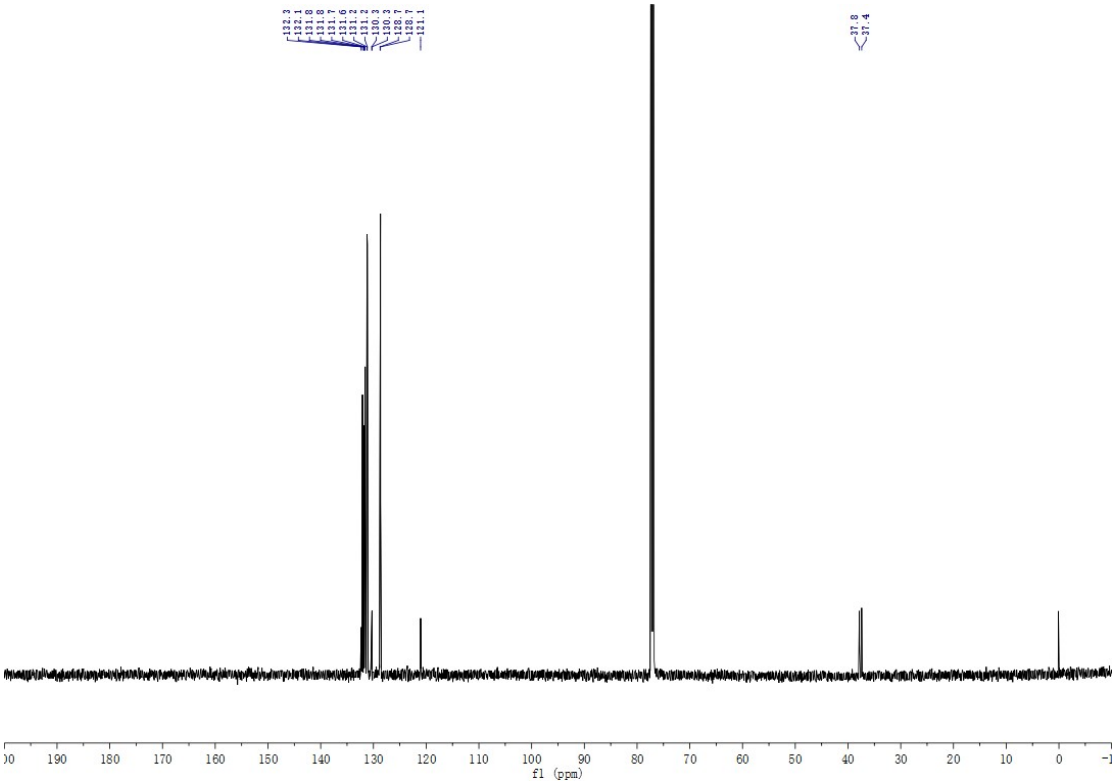


3ae

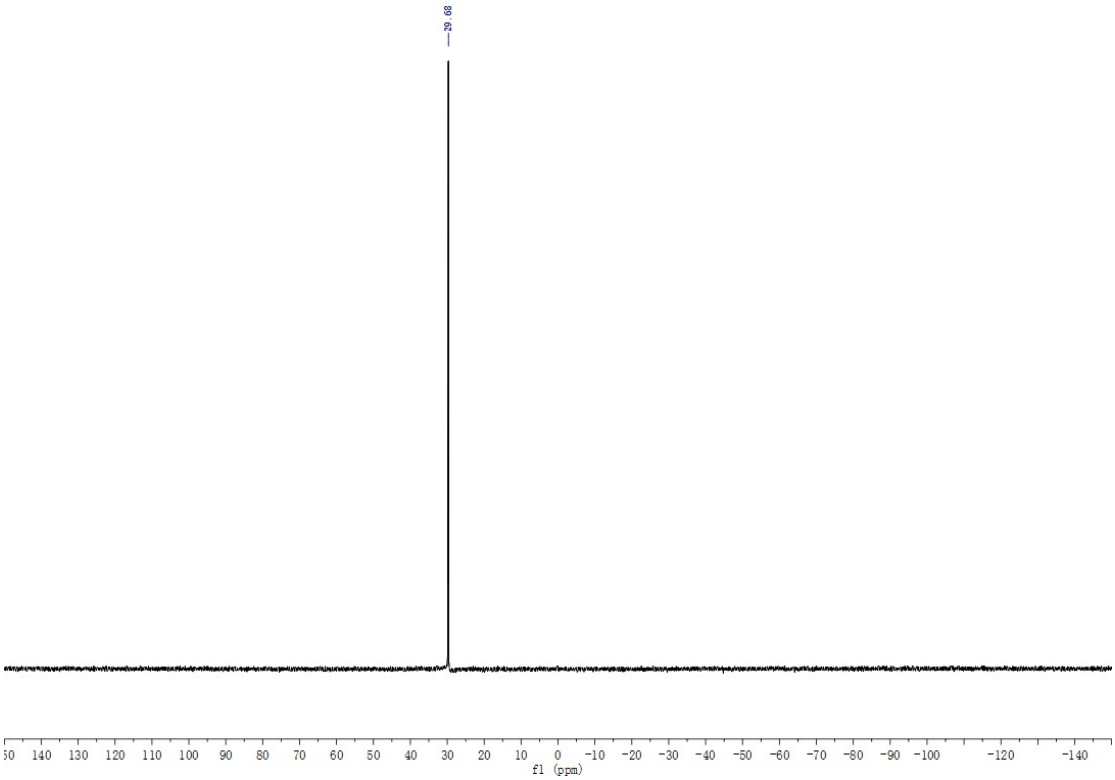
^{1}H NMR (600 MHz, $CDCl_3$)

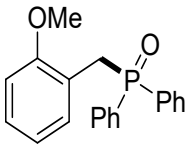


^{13}C NMR (151 MHz, $CDCl_3$)



^{31}P NMR (243 MHz, $CDCl_3$)





3af

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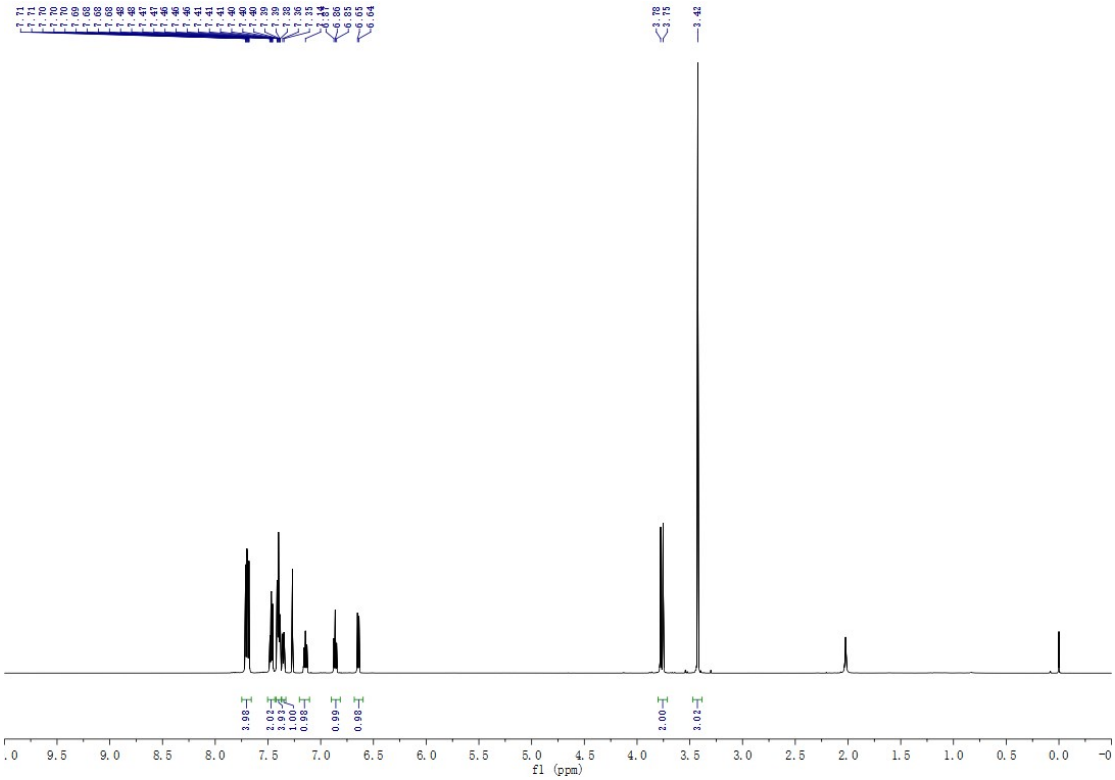
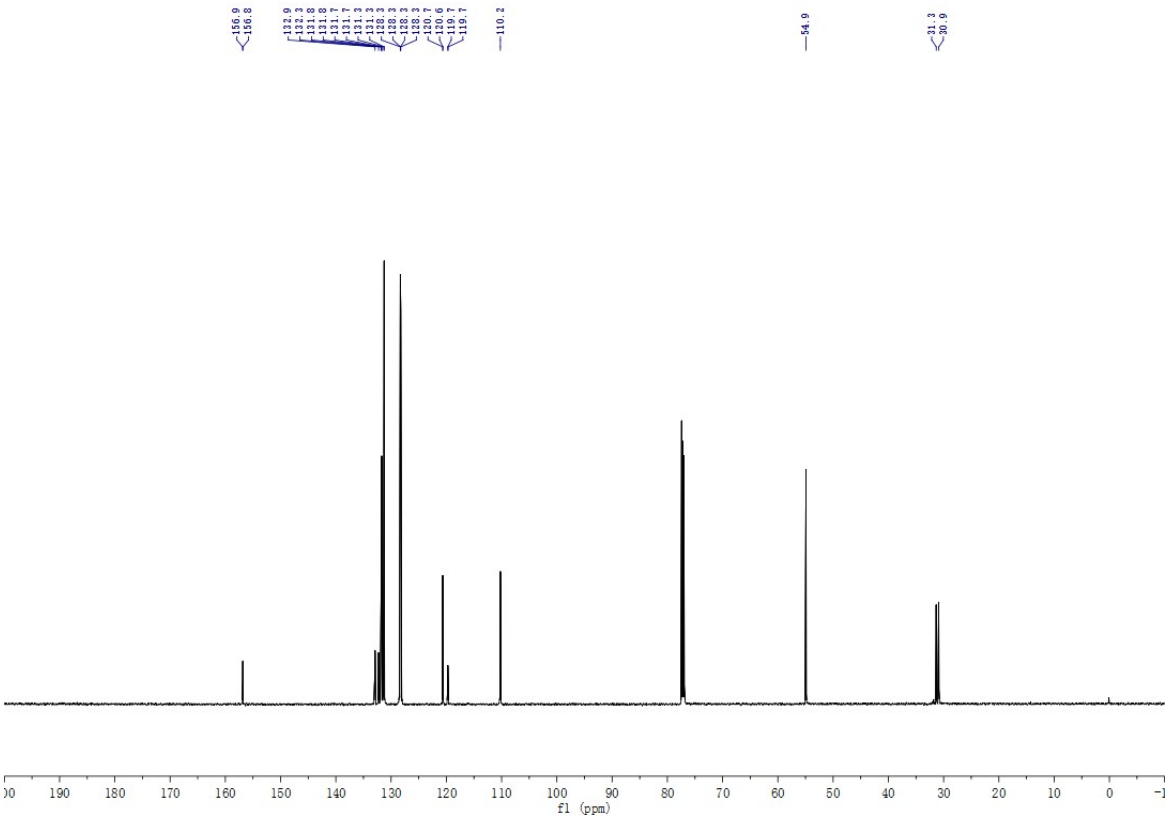
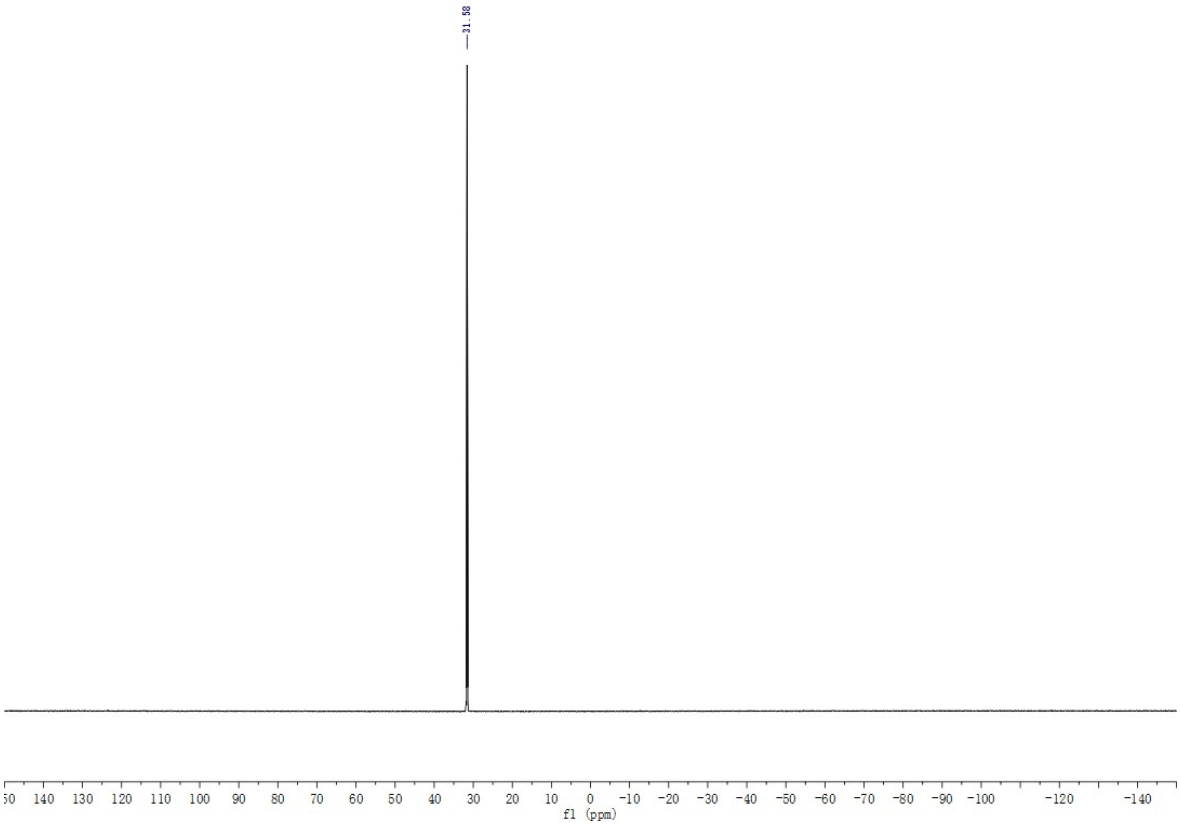
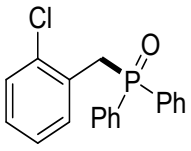


^{13}C NMR (151 MHz, $CDCl_3$)



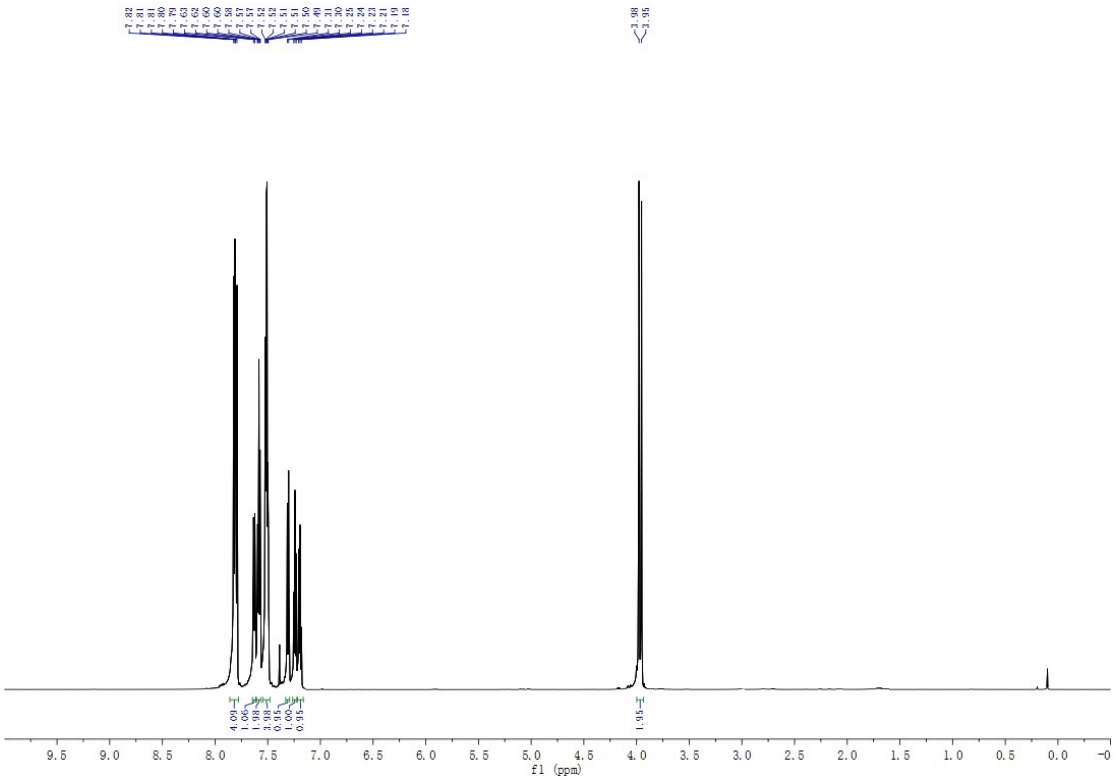
^{31}P NMR (243 MHz, $CDCl_3$)



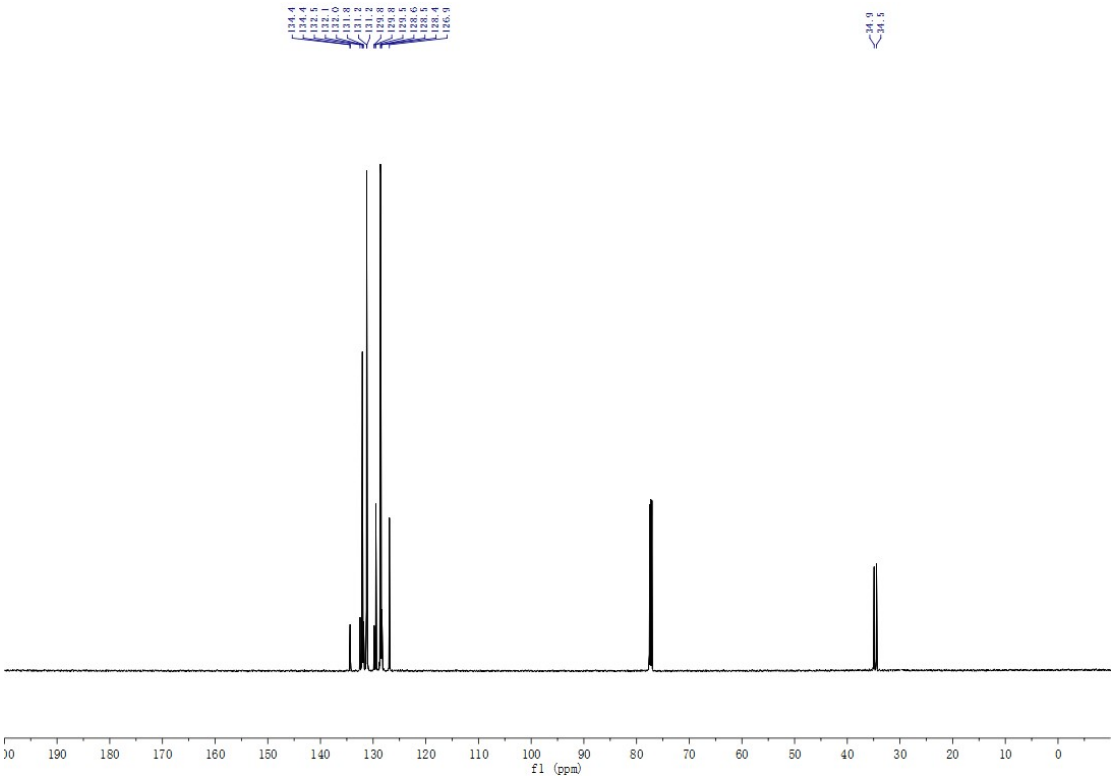


3ag

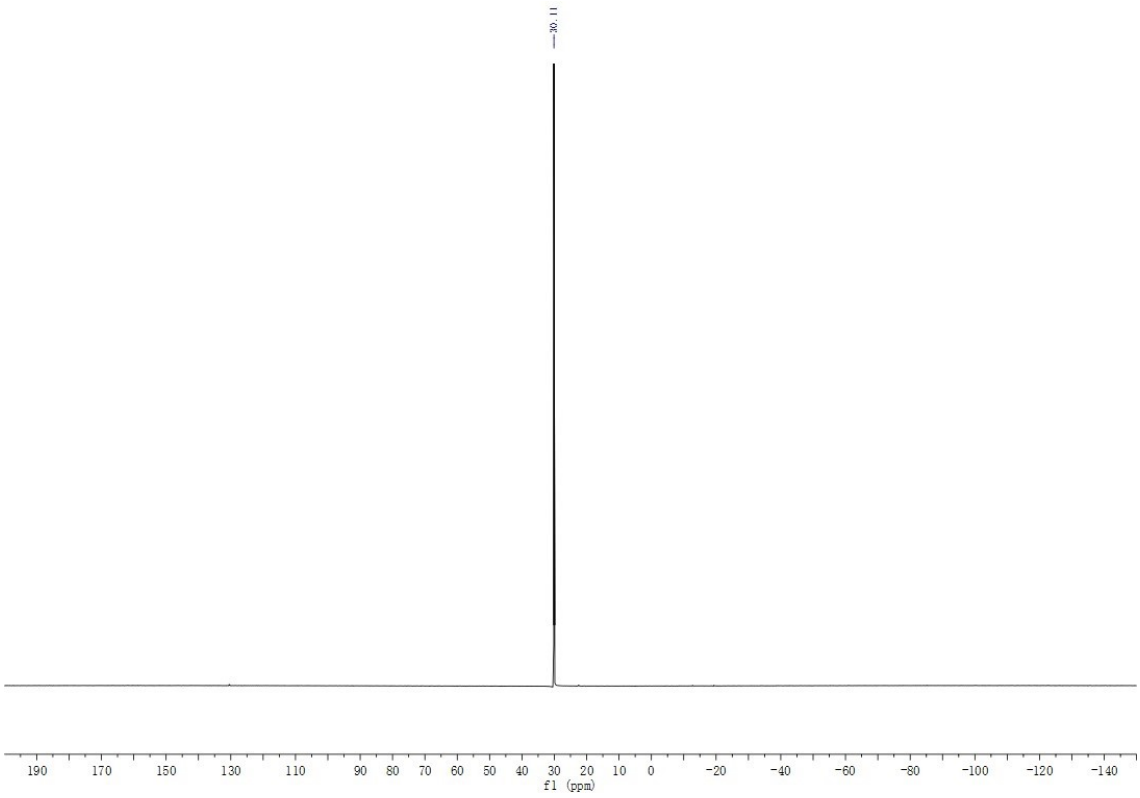
^{1}H NMR (600 MHz, $CDCl_3$)

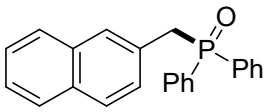


^{13}C NMR (151 MHz, $CDCl_3$)



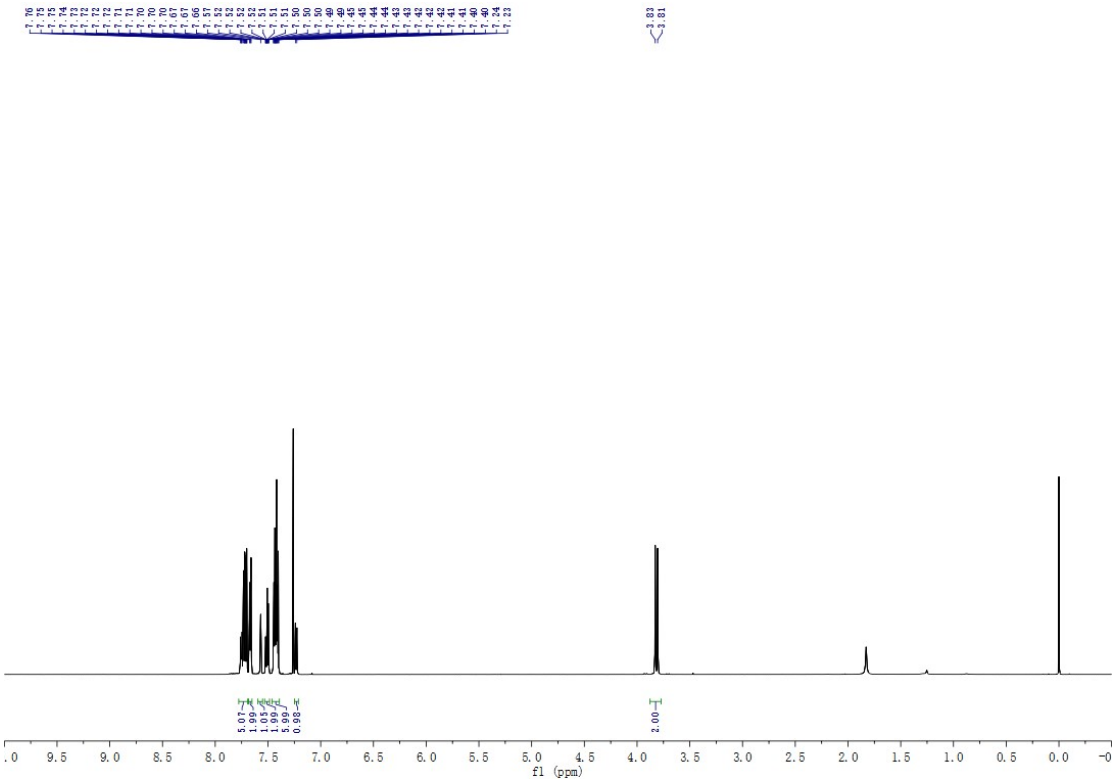
^{31}P NMR (243 MHz, $CDCl_3$)



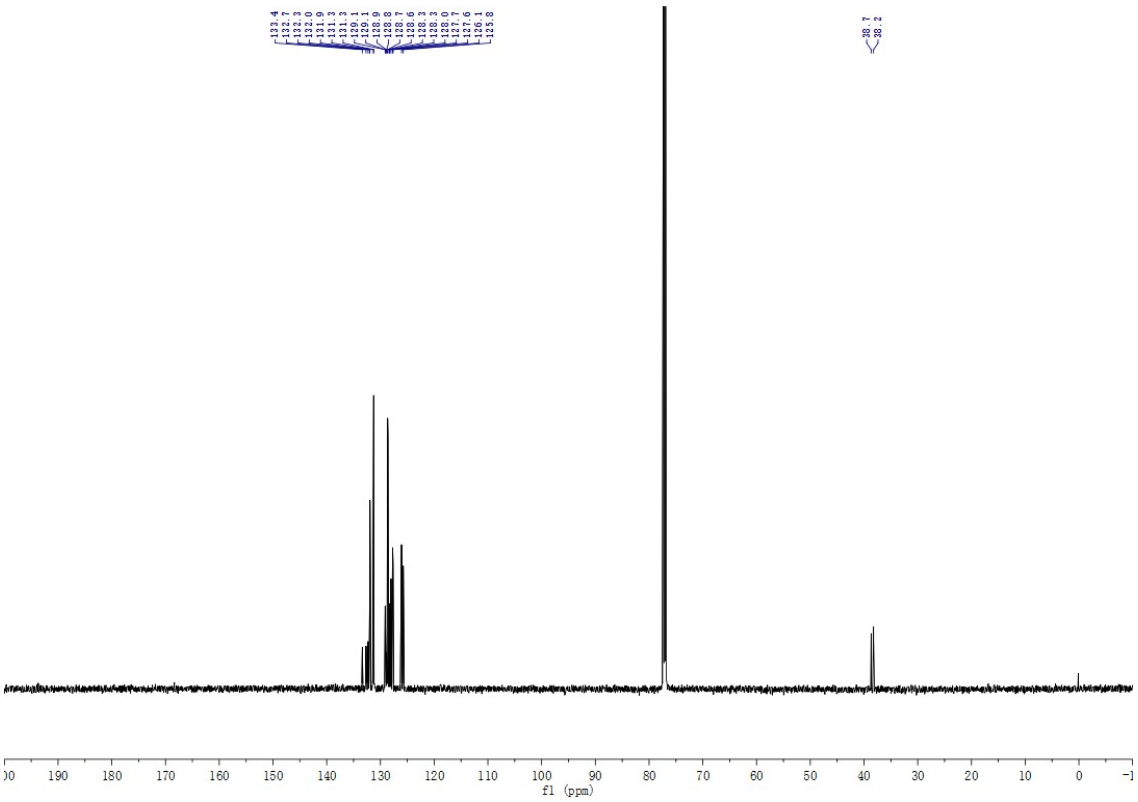


3ah

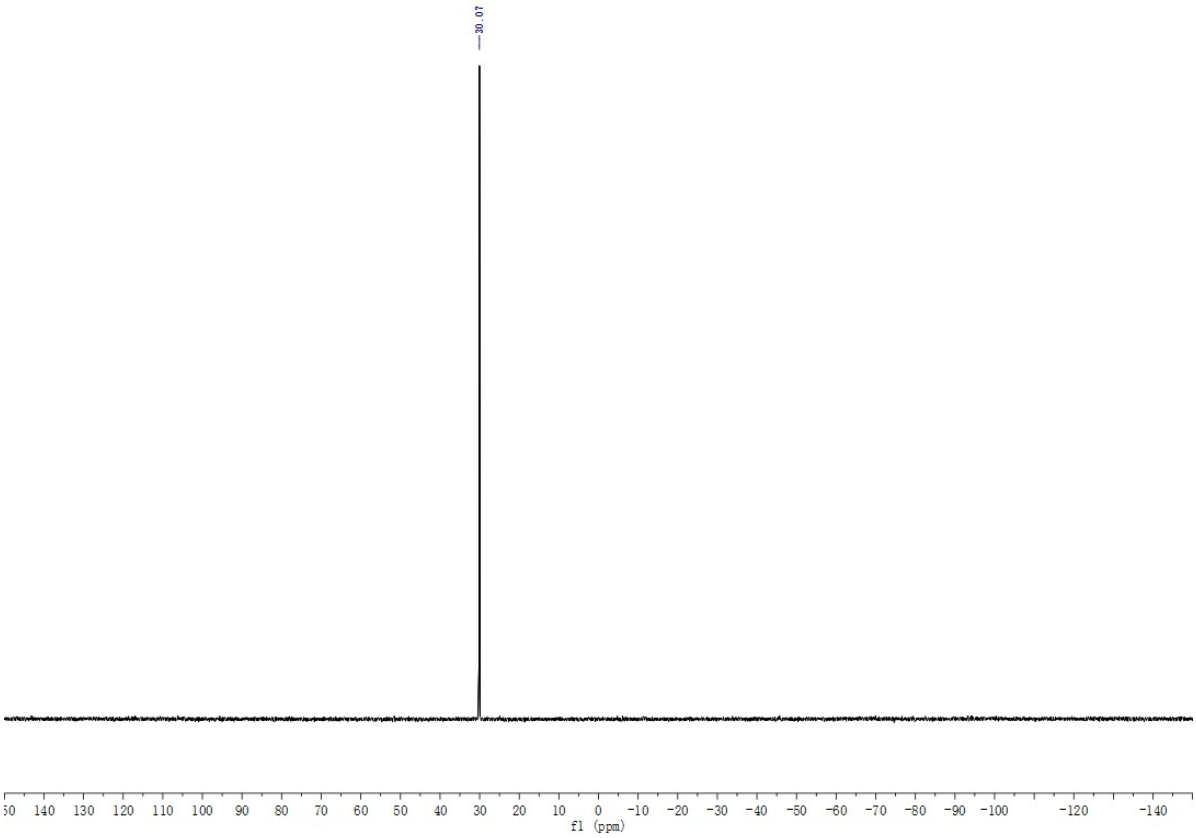
^{1}H NMR (600 MHz, $CDCl_3$)

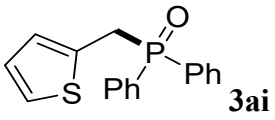


^{13}C NMR (151 MHz, $CDCl_3$)



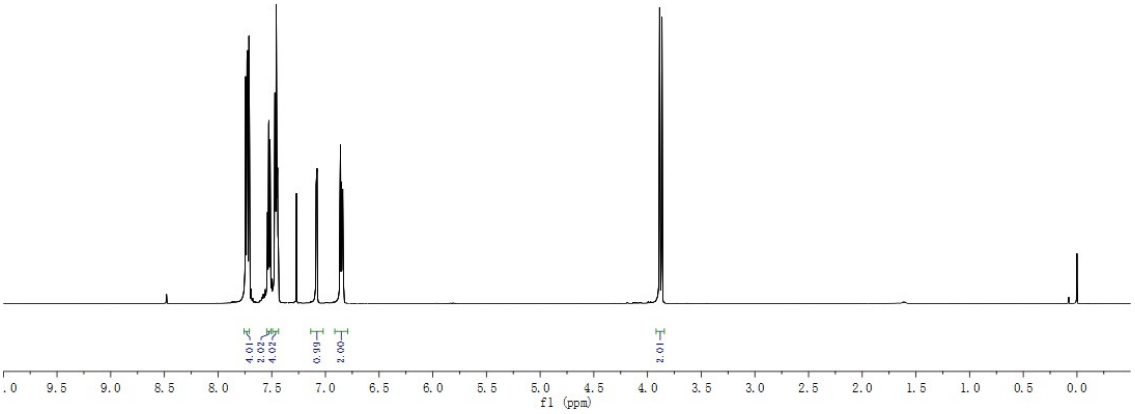
^{31}P NMR (243 MHz, $CDCl_3$)



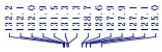


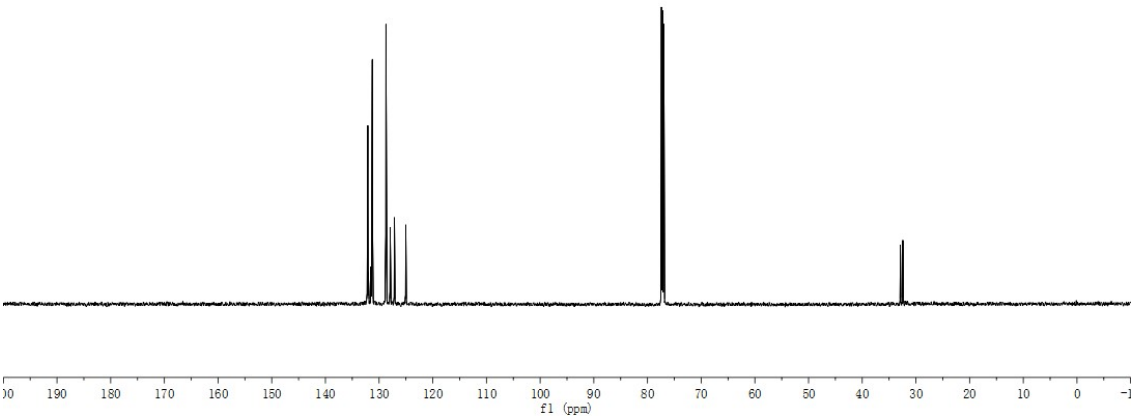
3ai

^{1}H NMR (600 MHz, $CDCl_3$)

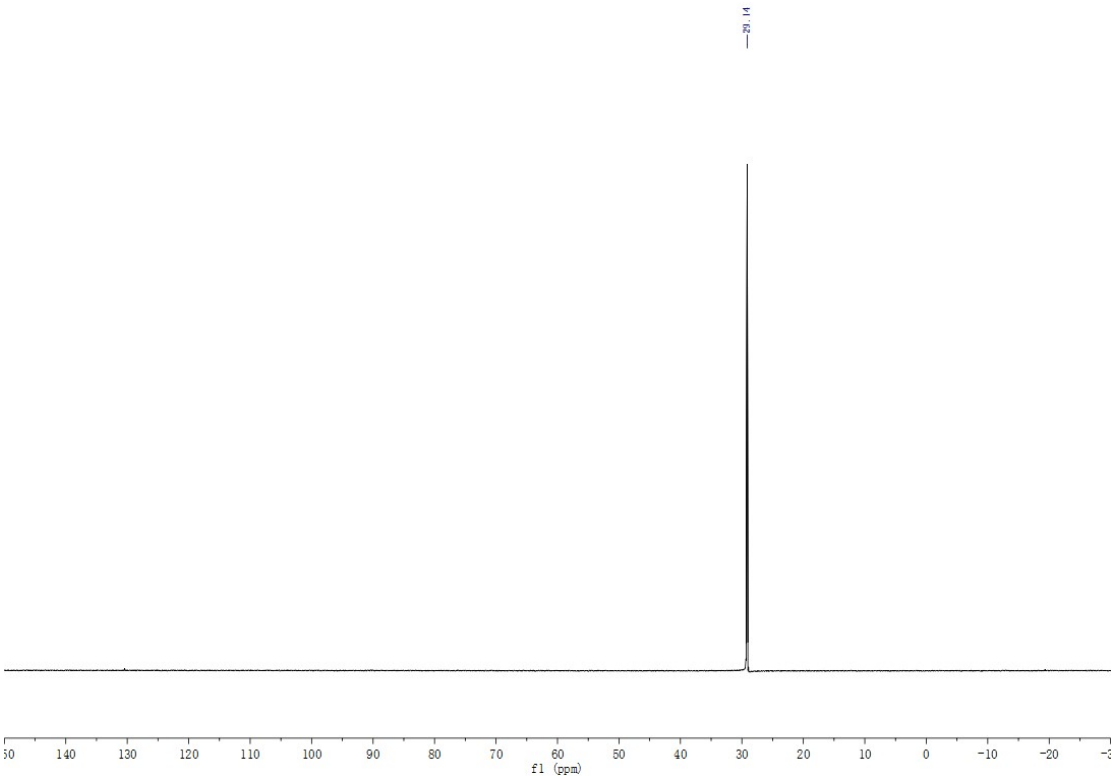


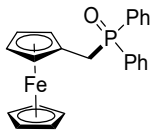
^{13}C NMR (151 MHz, $CDCl_3$)





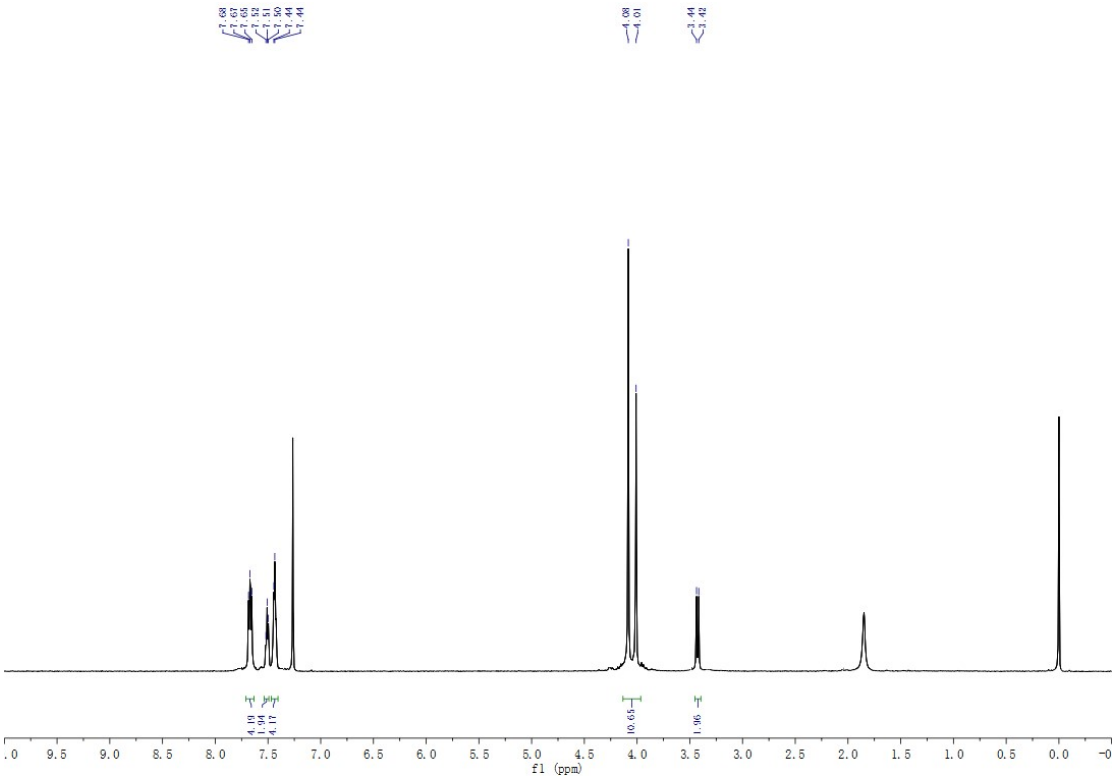
^{31}P NMR (243 MHz, $CDCl_3$)



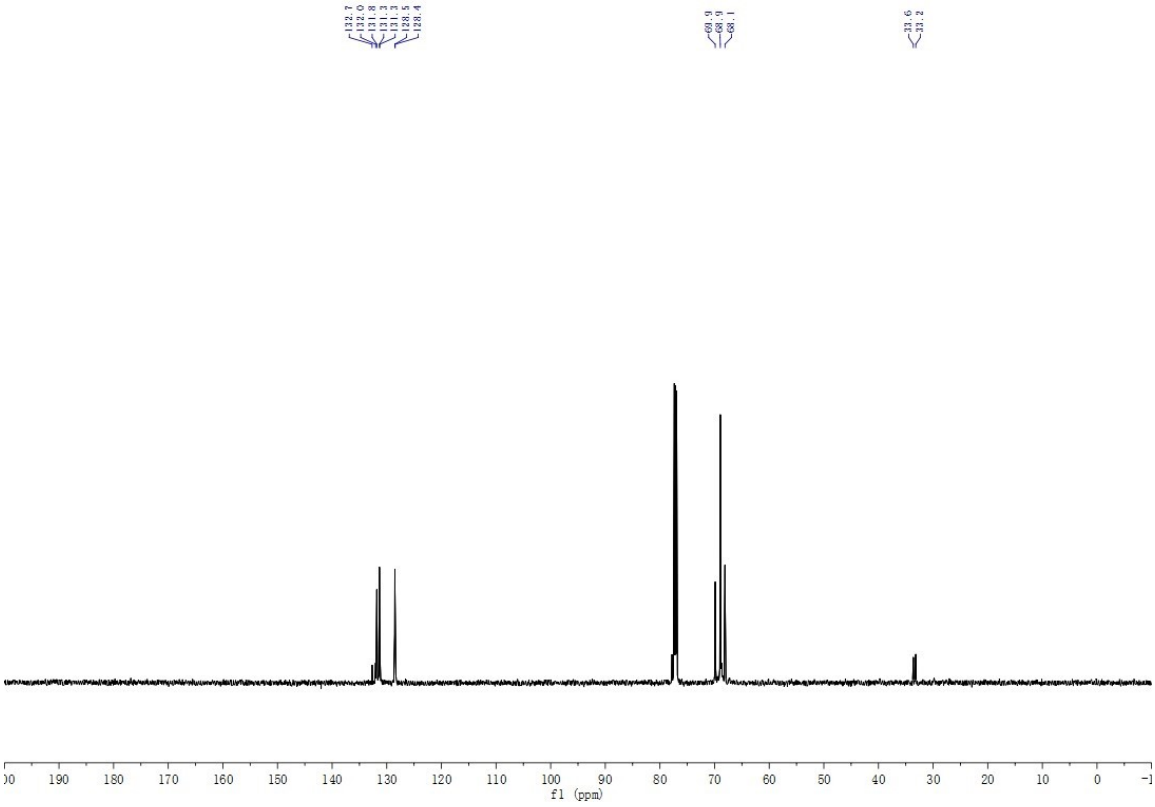


3aj

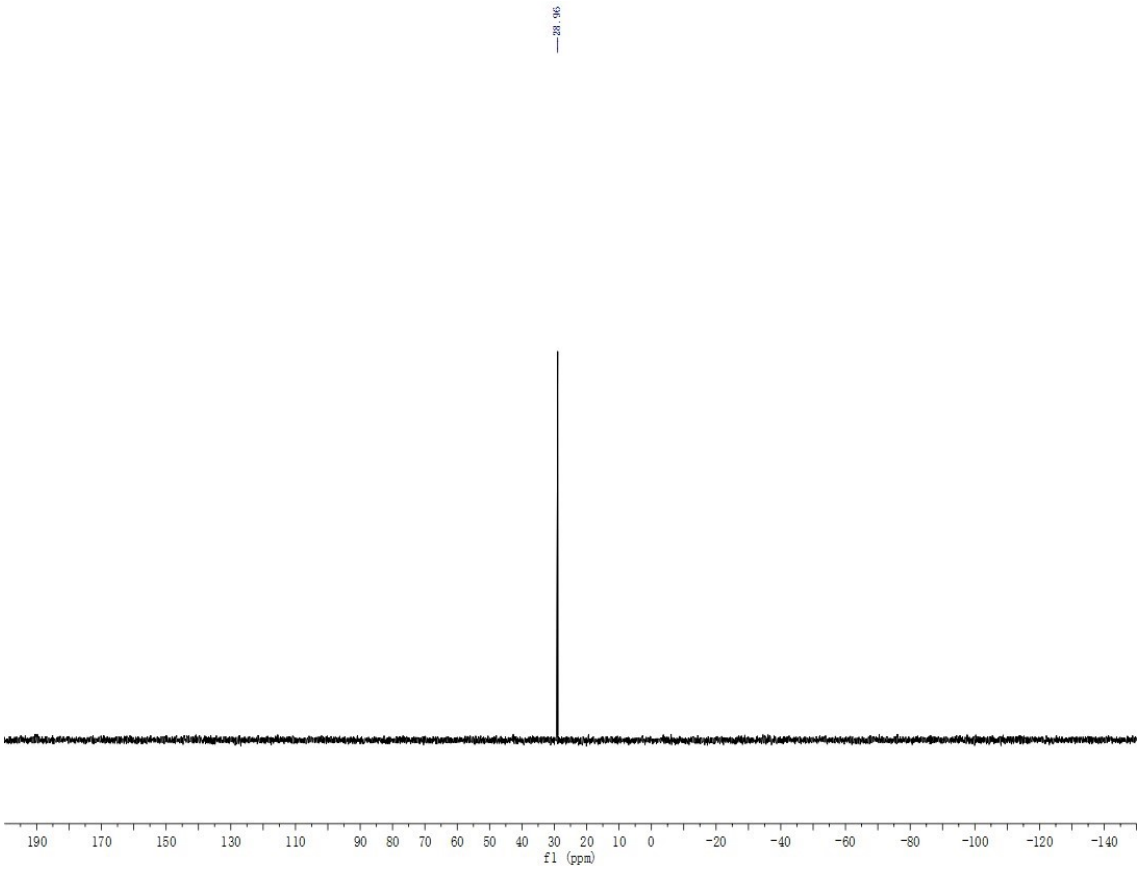
^{1}H NMR (600 MHz, $CDCl_3$)

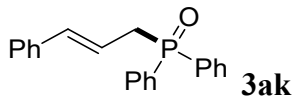


^{13}C NMR (151 MHz, $CDCl_3$)



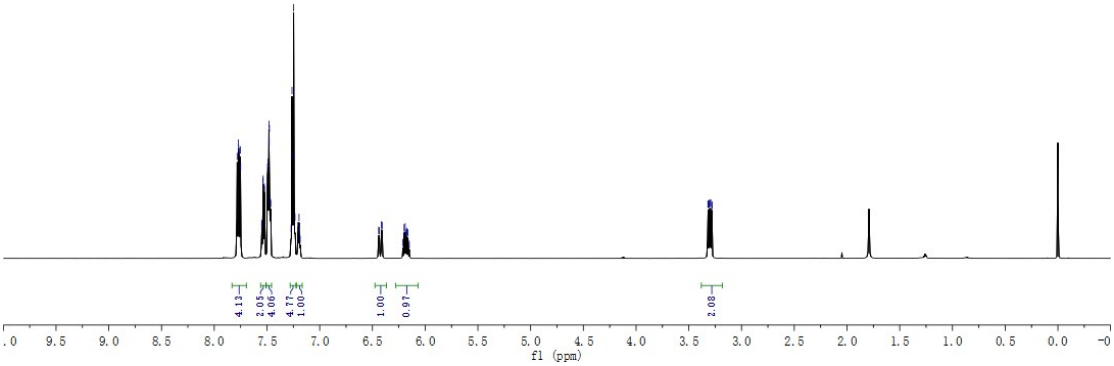
^{31}P NMR (243 MHz, $CDCl_3$)



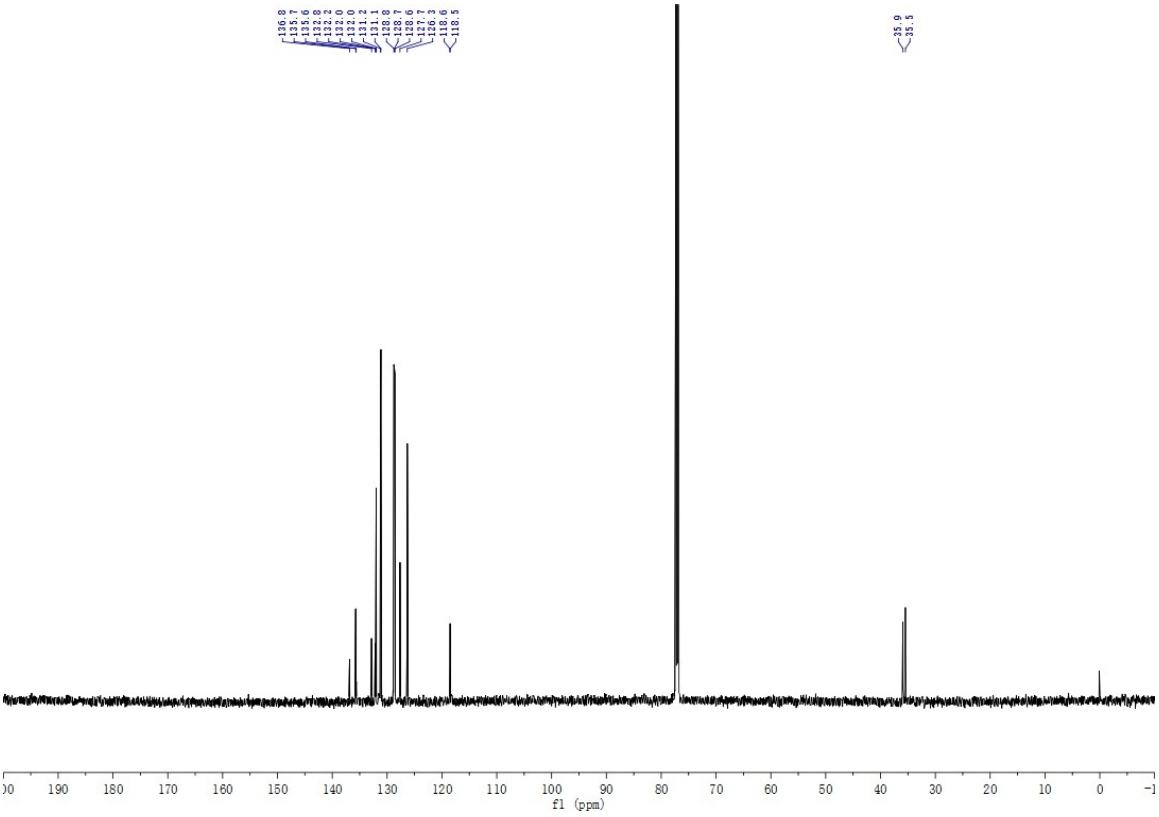


3ak

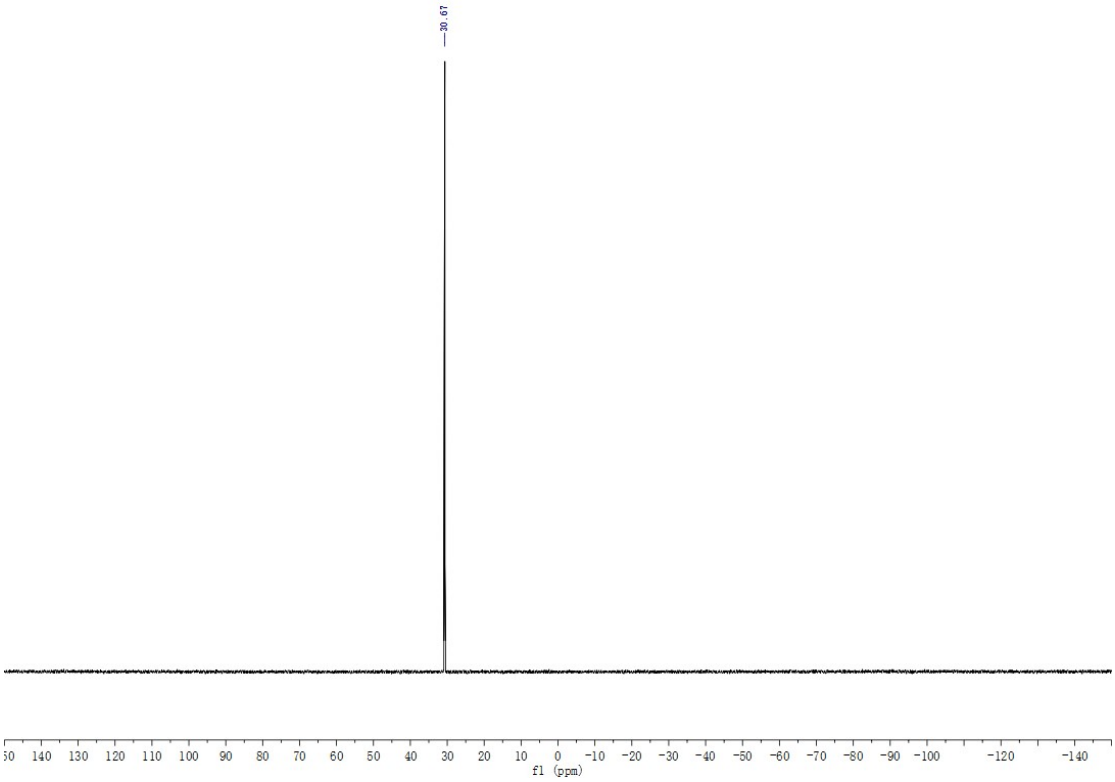
^{1}H NMR (600 MHz, $CDCl_3$)

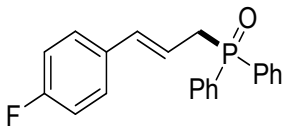


^{13}C NMR (151 MHz, $CDCl_3$)



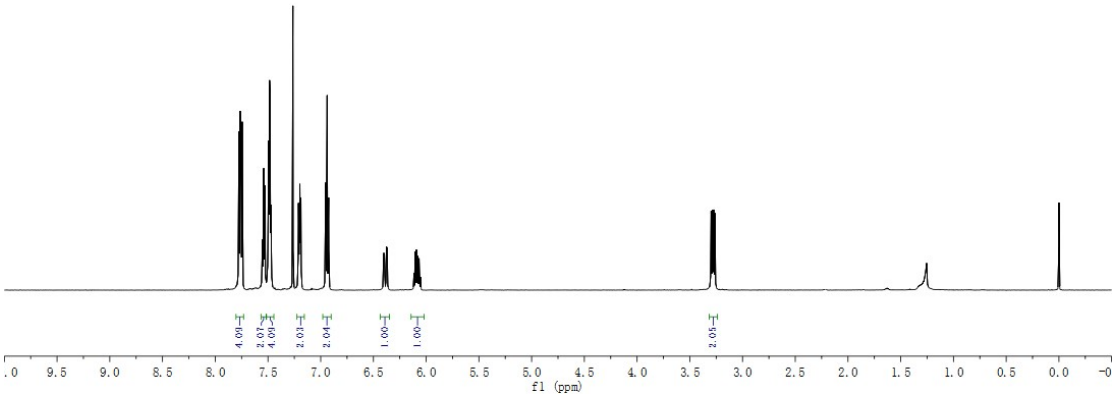
^{31}P NMR (243 MHz, $CDCl_3$)



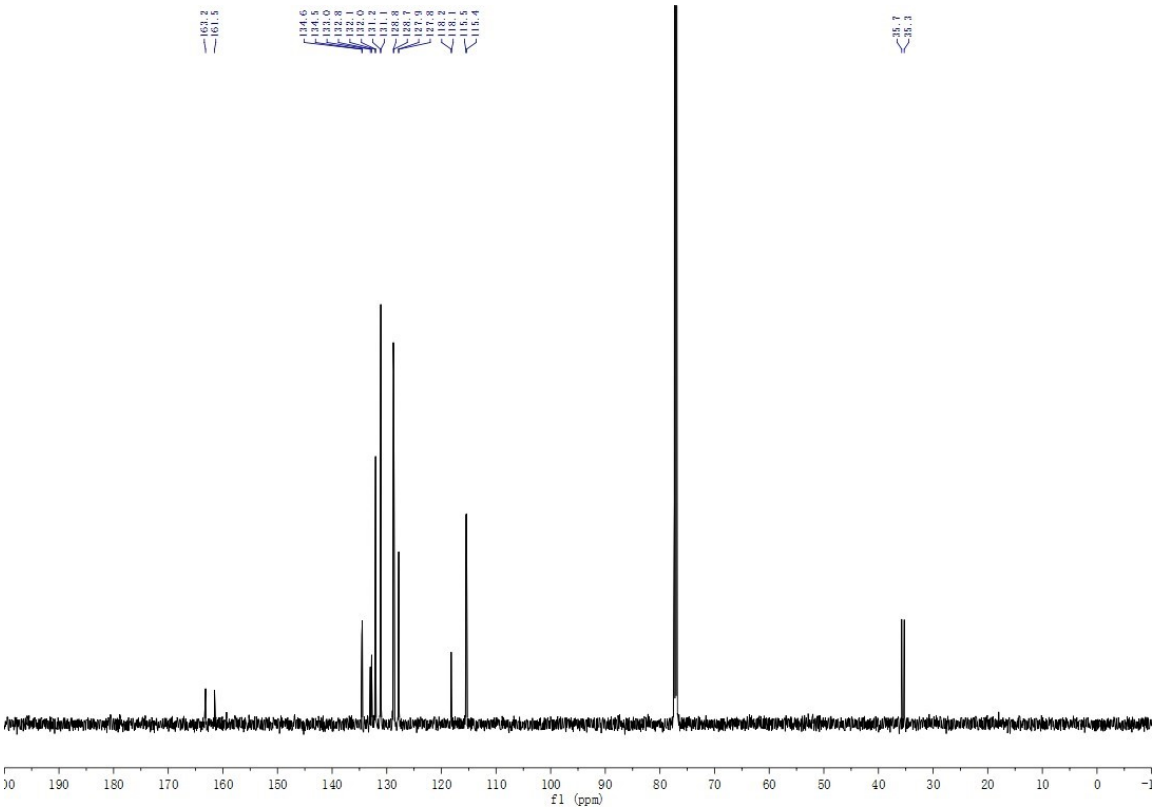


3al

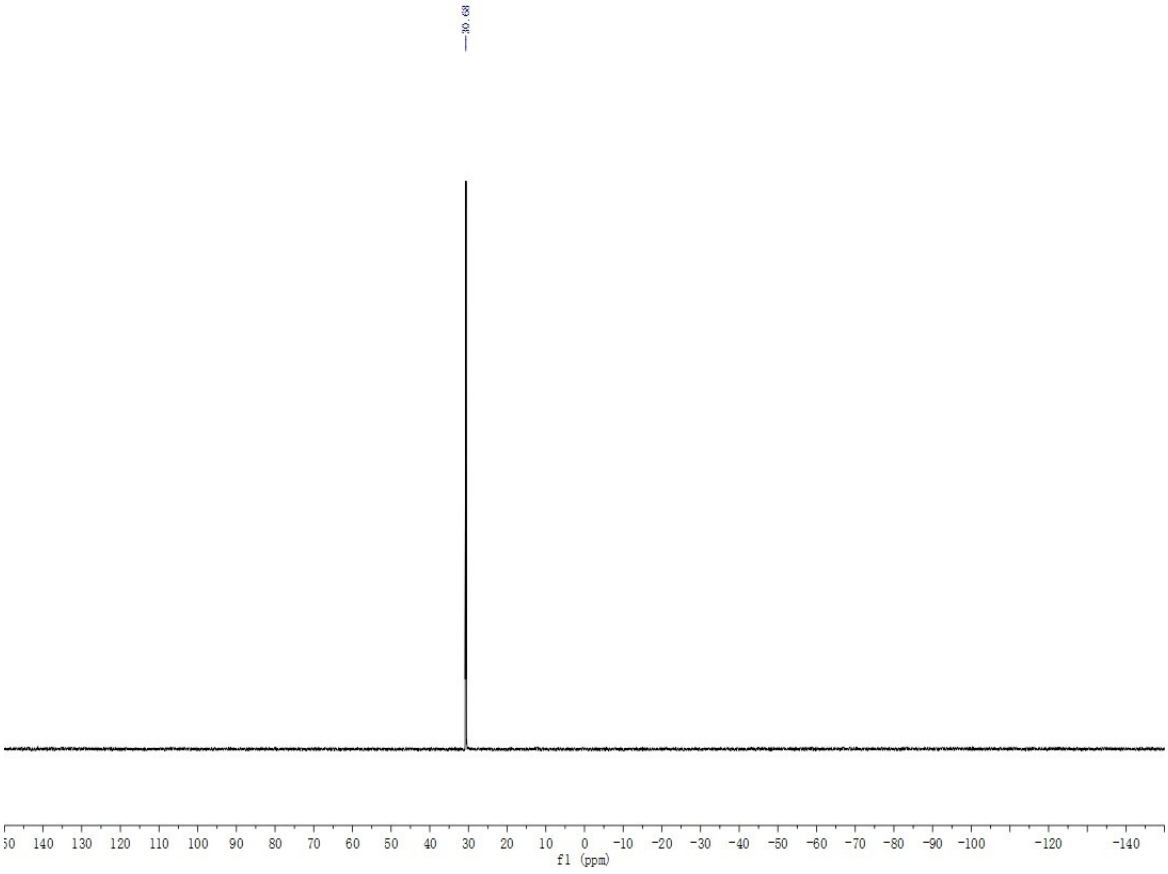
^{1}H NMR (600 MHz, $CDCl_3$)

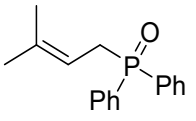


^{13}C NMR (151 MHz, $CDCl_3$)



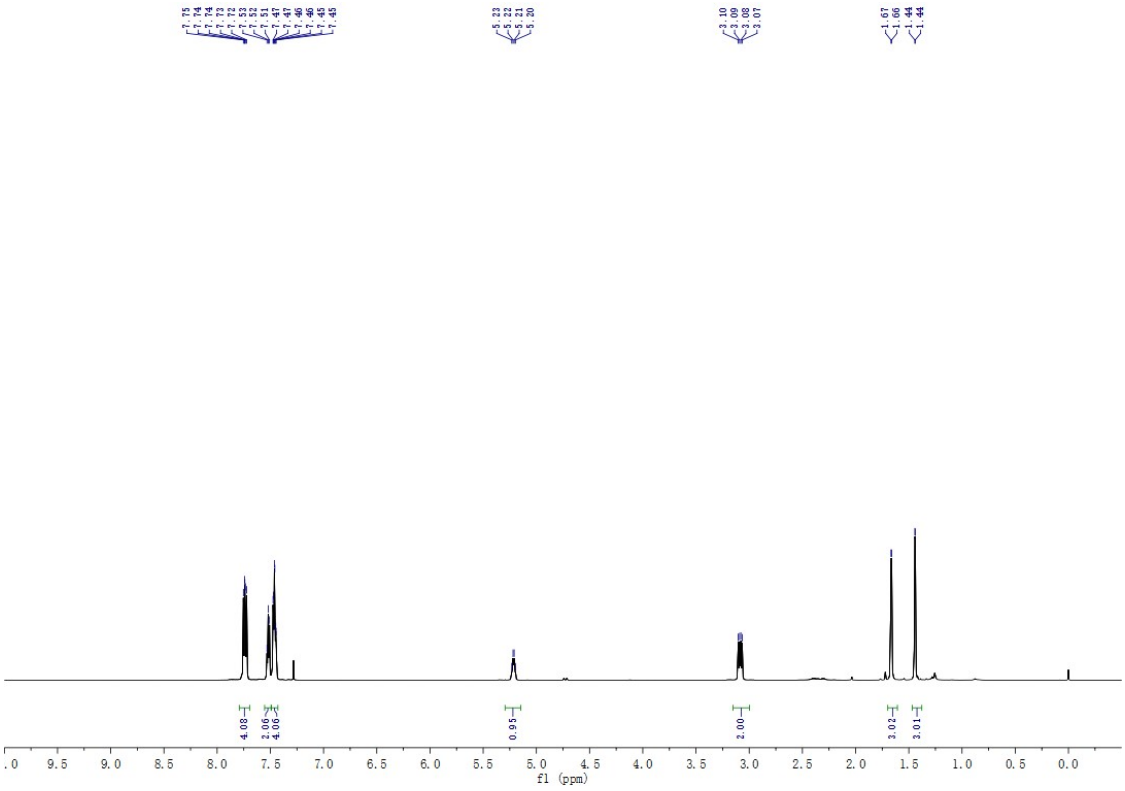
^{31}P NMR (243 MHz, $CDCl_3$)



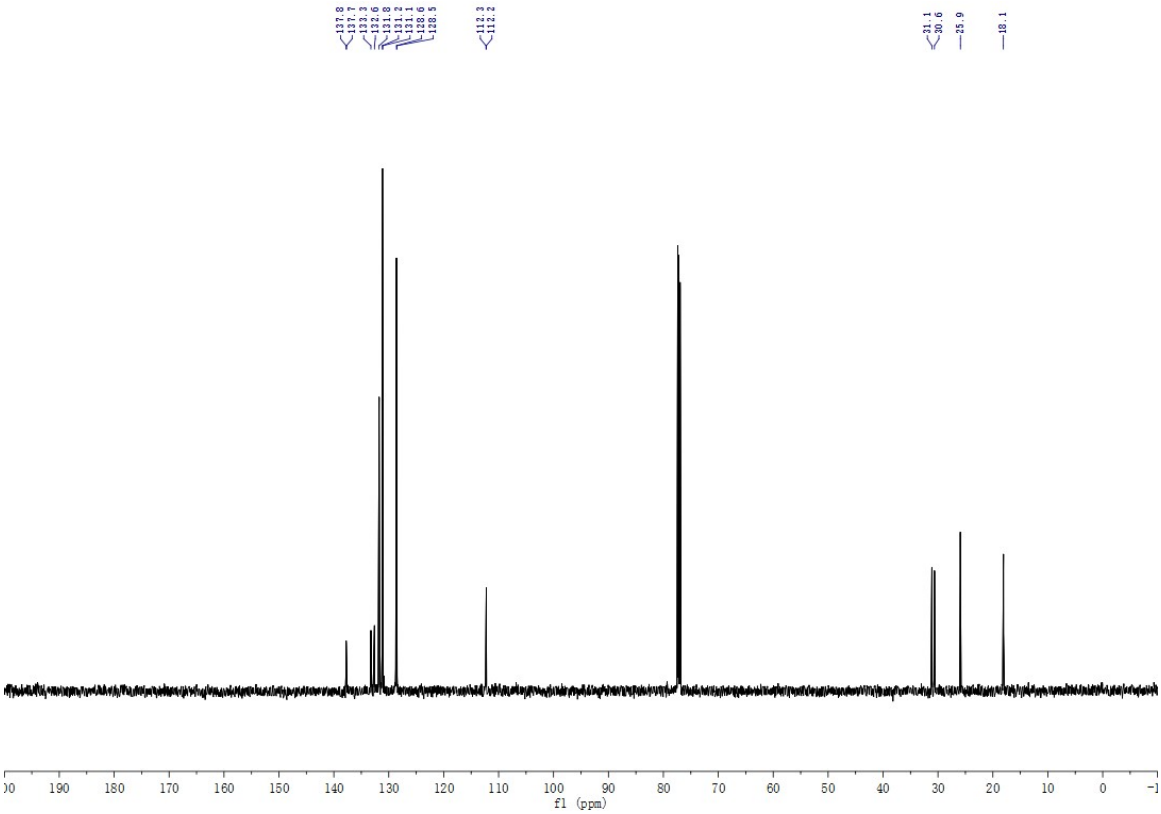


3am

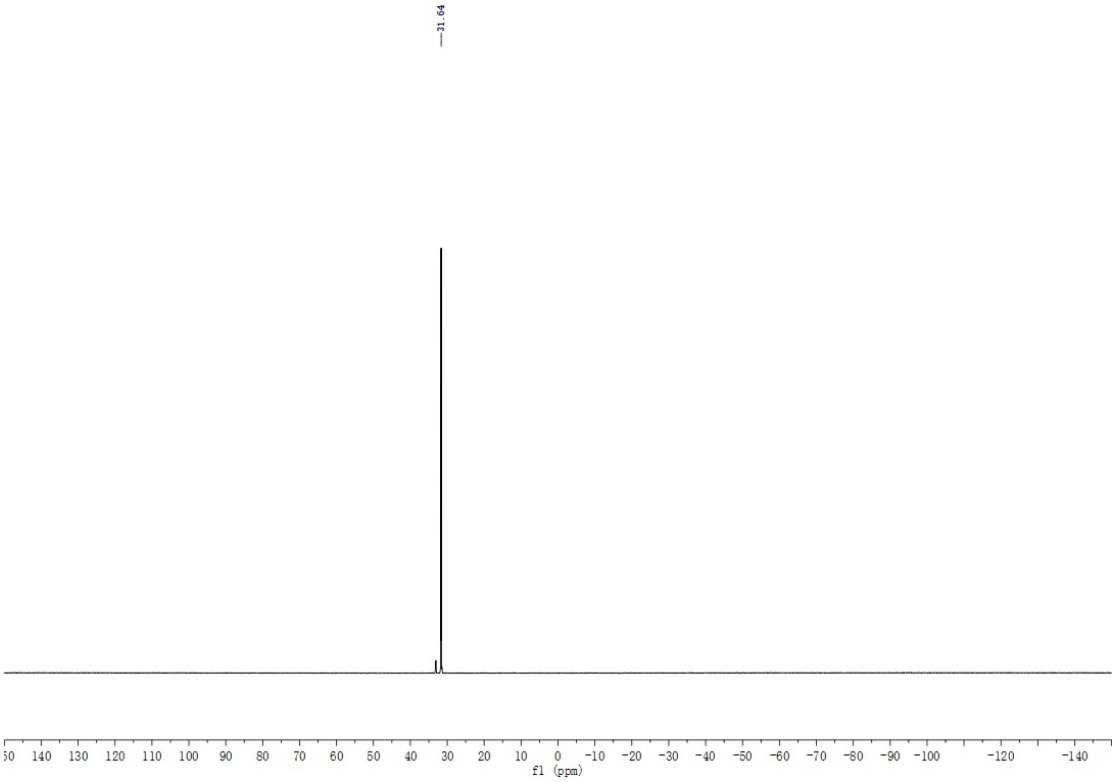
^{1}H NMR (600 MHz, $CDCl_3$)

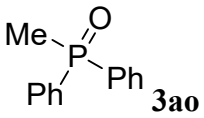


^{13}C NMR (151 MHz, $CDCl_3$)



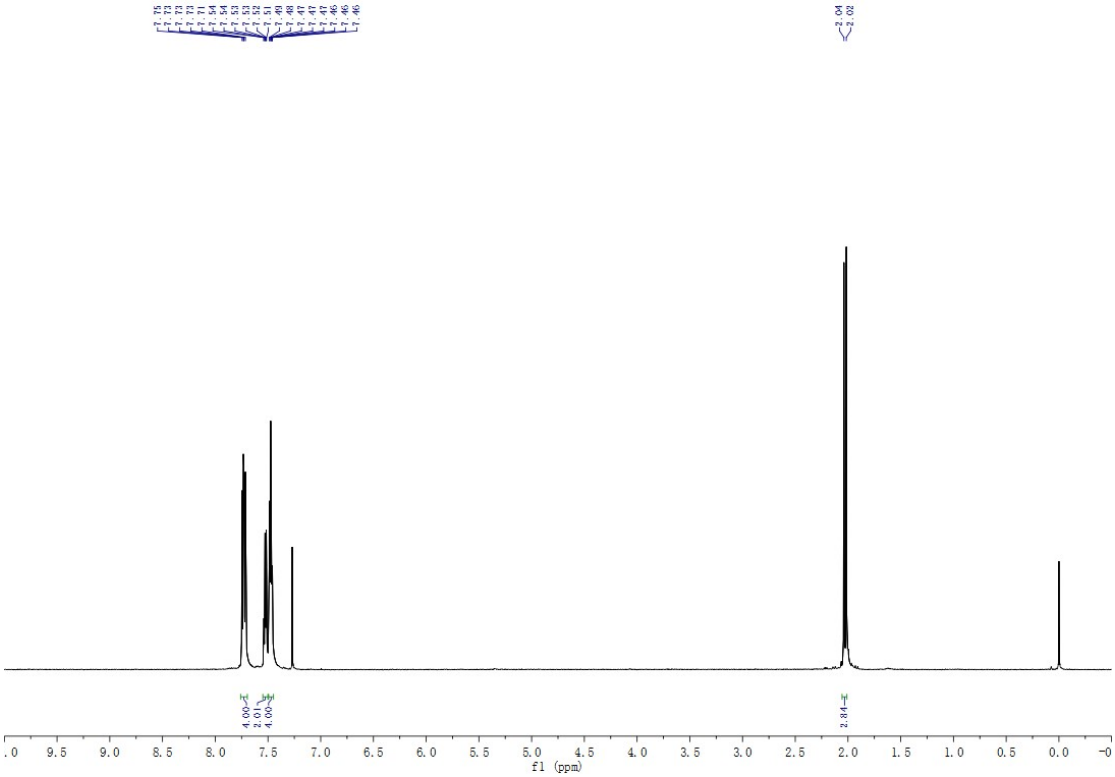
^{31}P NMR (243 MHz, $CDCl_3$)



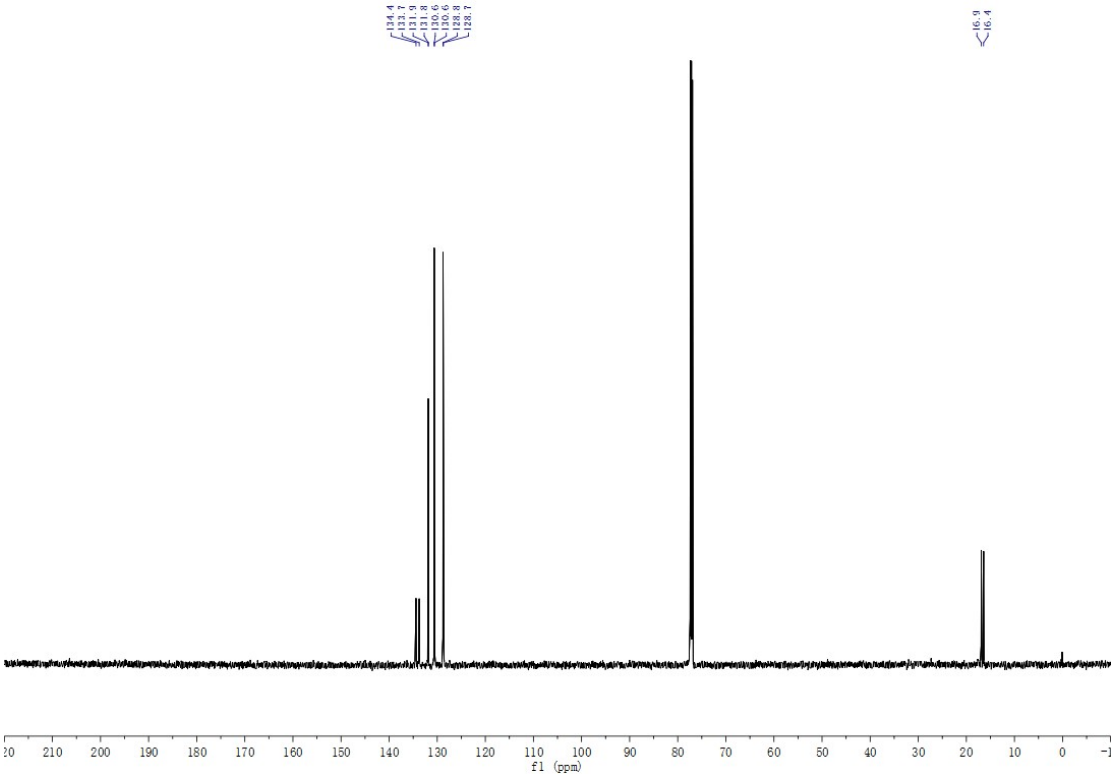


3ao

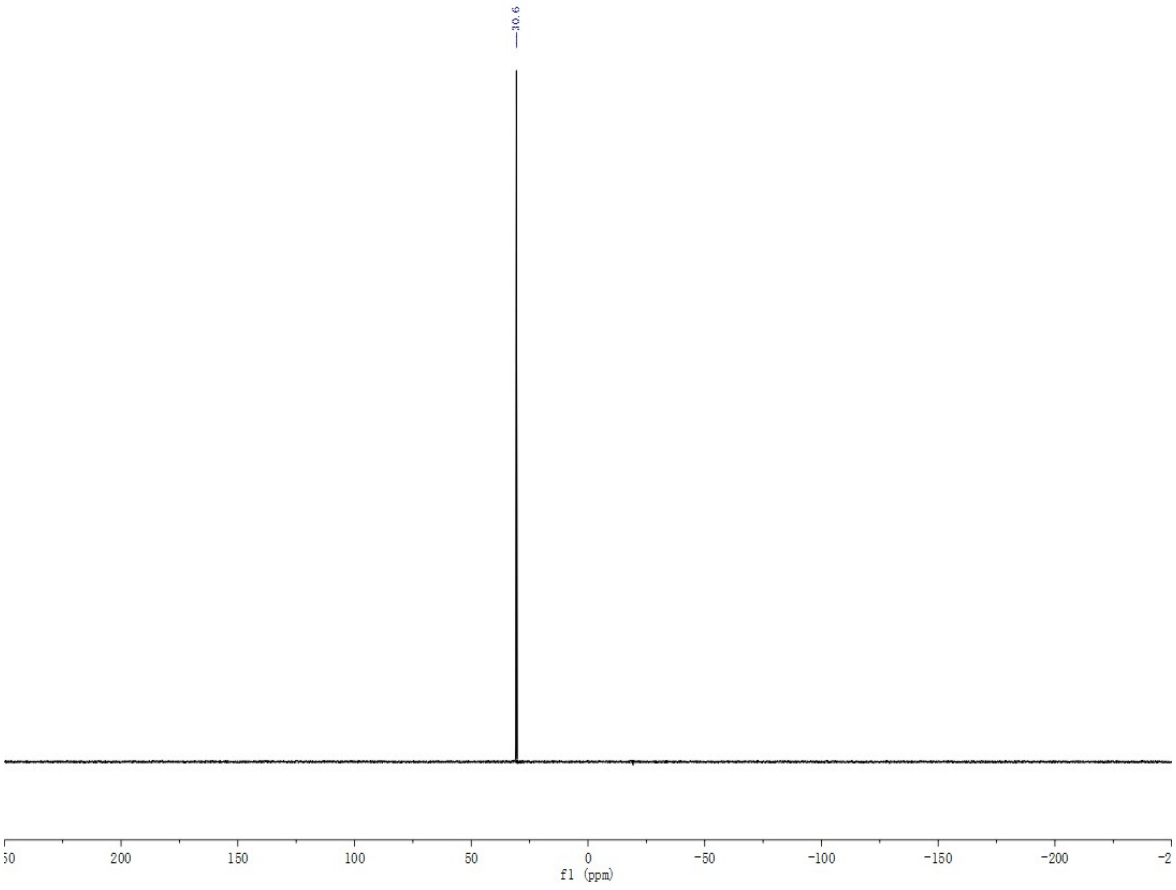
^{1}H NMR (600 MHz, $CDCl_3$)

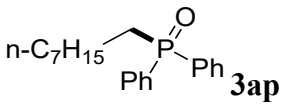


^{13}C NMR (151 MHz, $CDCl_3$)



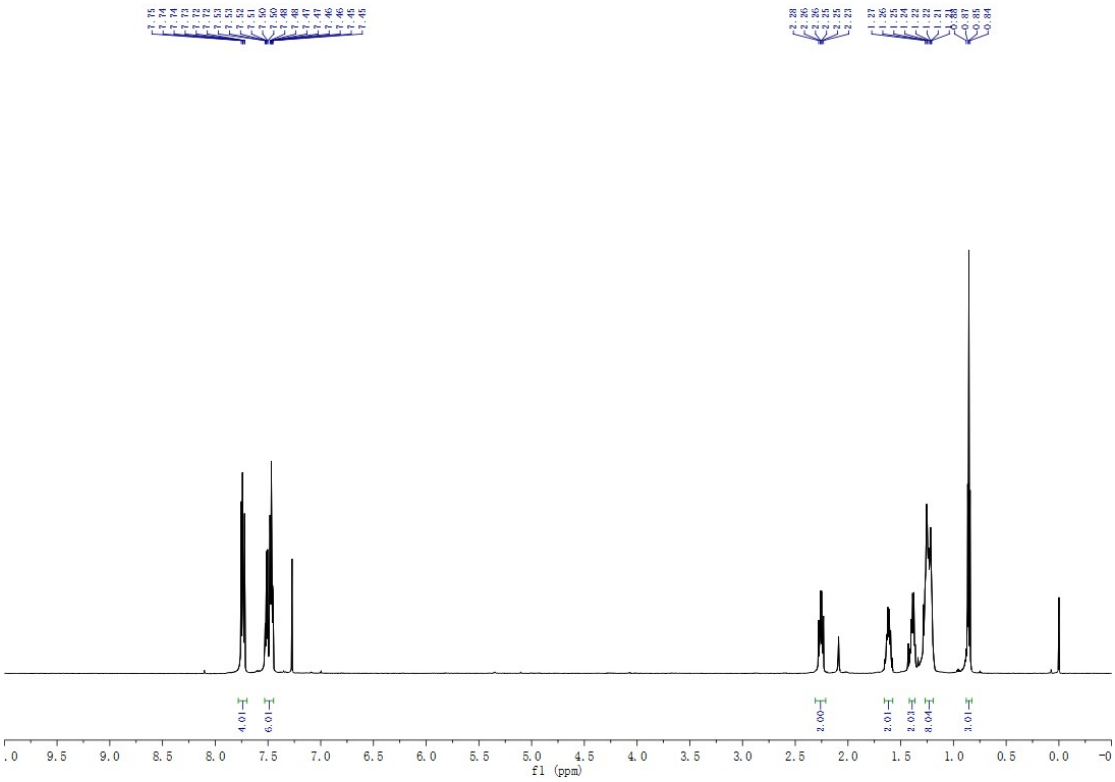
^{31}P NMR (243 MHz, $CDCl_3$)



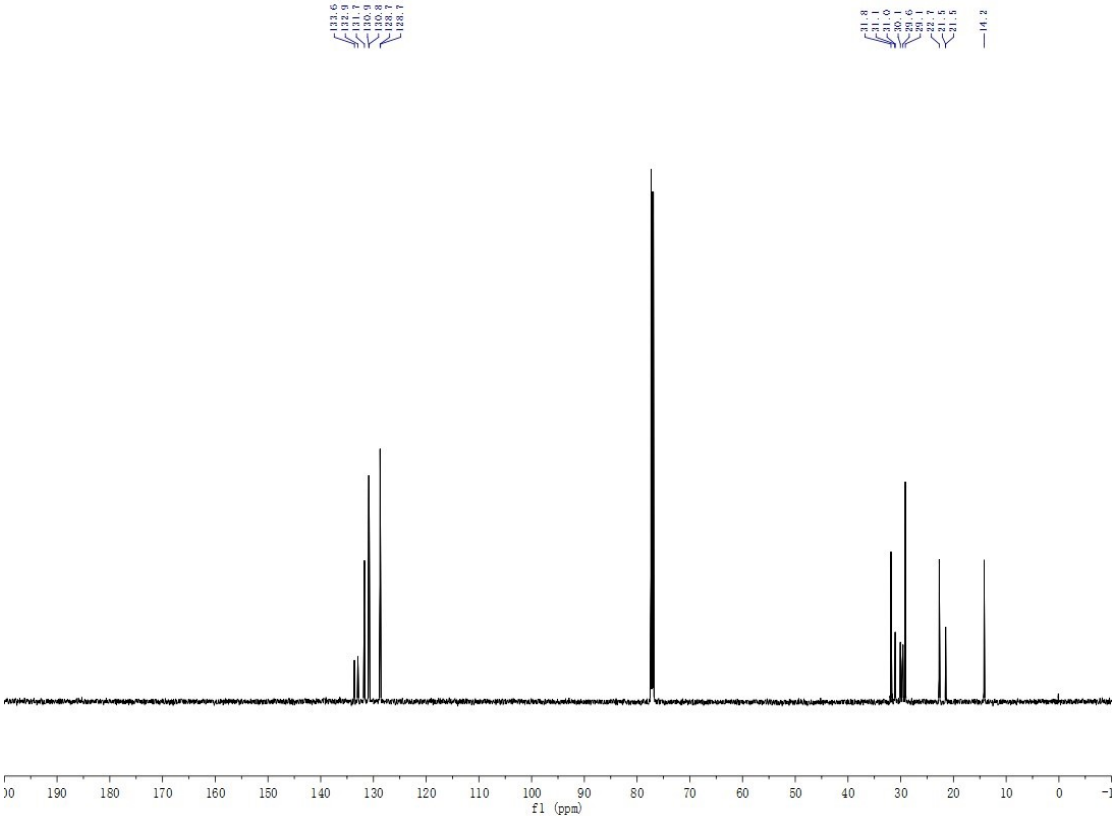


3ap

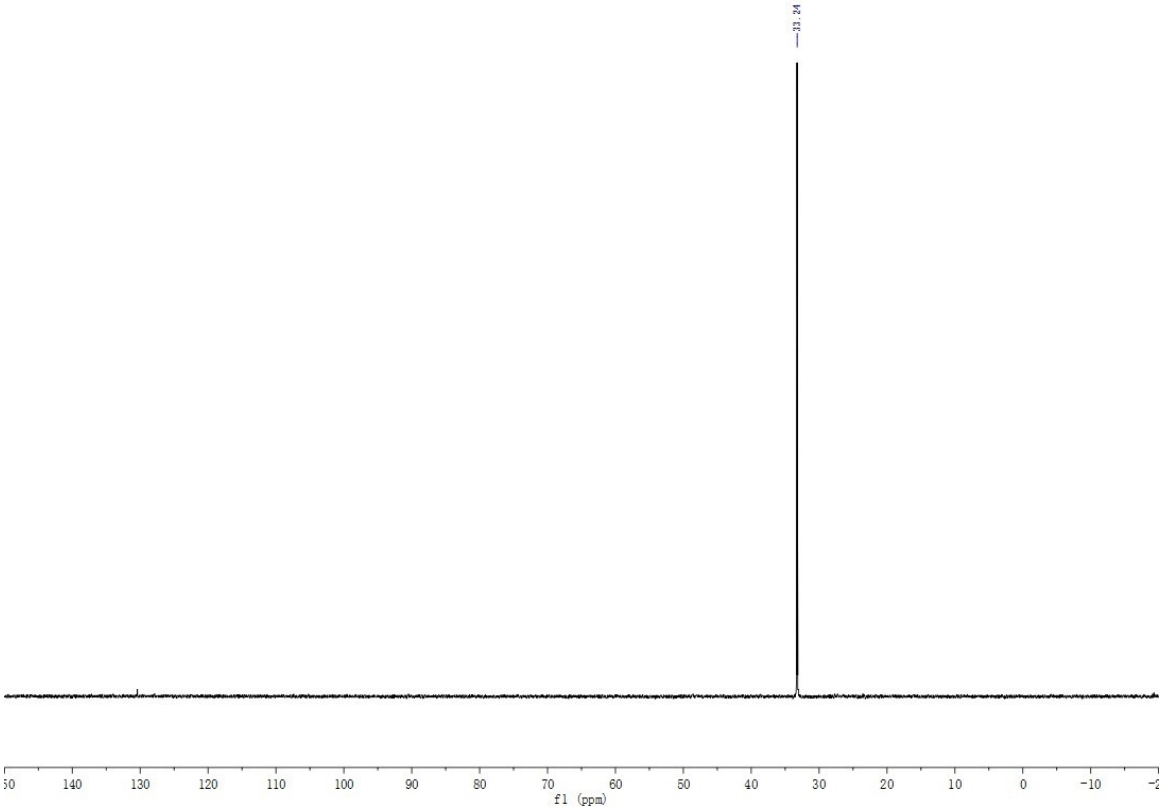
^{1}H NMR (600 MHz, $CDCl_3$)

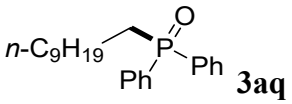


^{13}C NMR (151 MHz, $CDCl_3$)



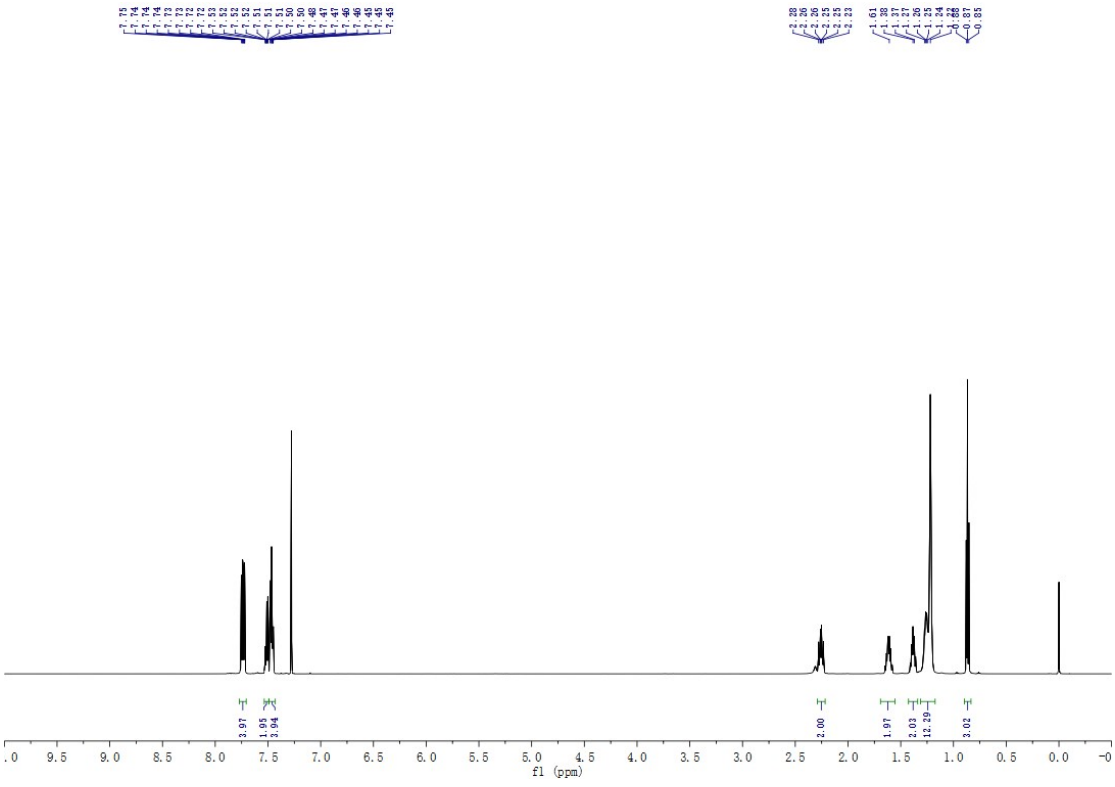
^{31}P NMR (243 MHz, $CDCl_3$)



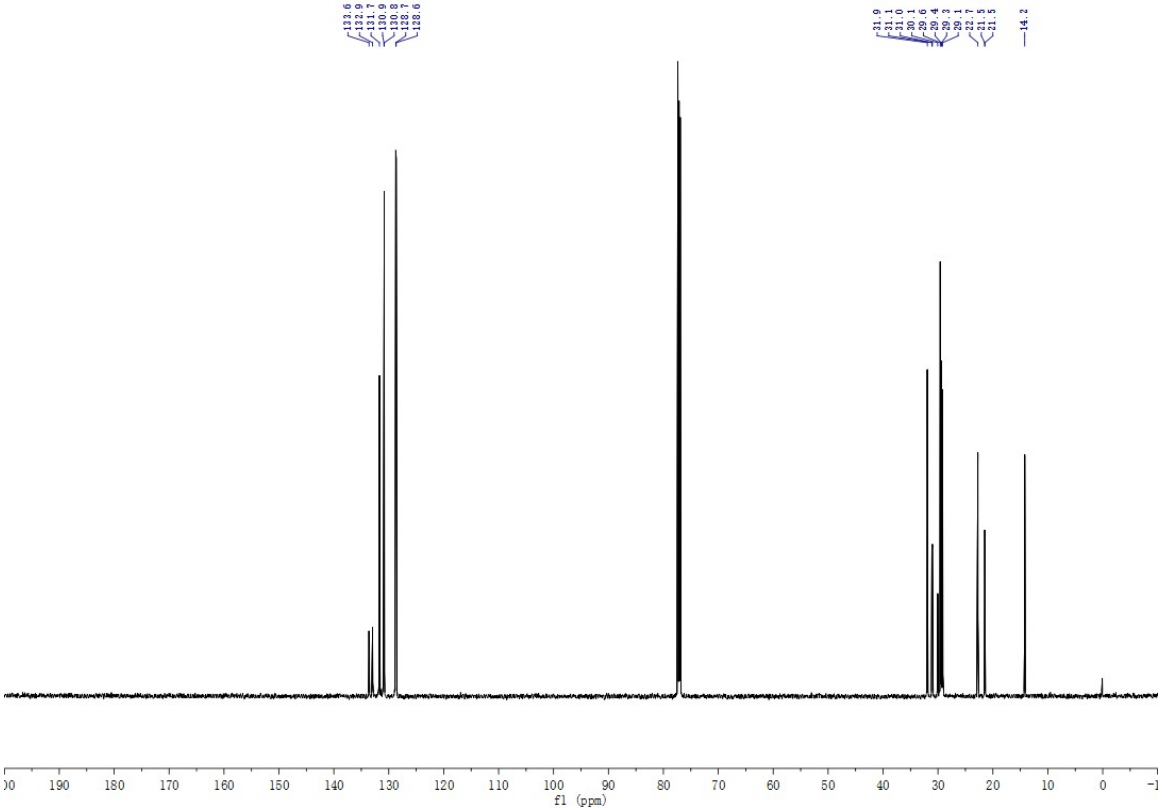


3aq

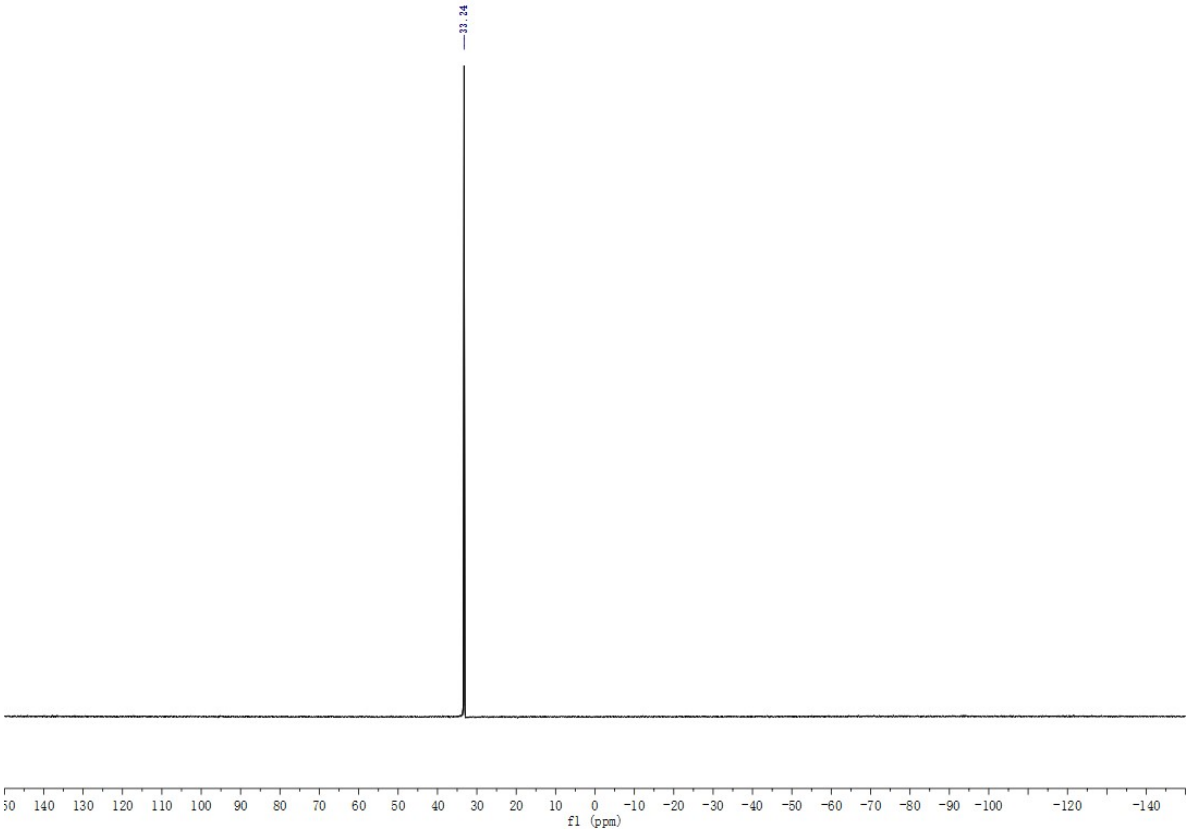
^{1}H NMR (600 MHz, $CDCl_3$)

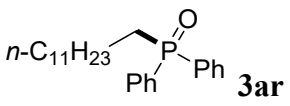


^{13}C NMR (151 MHz, $CDCl_3$)



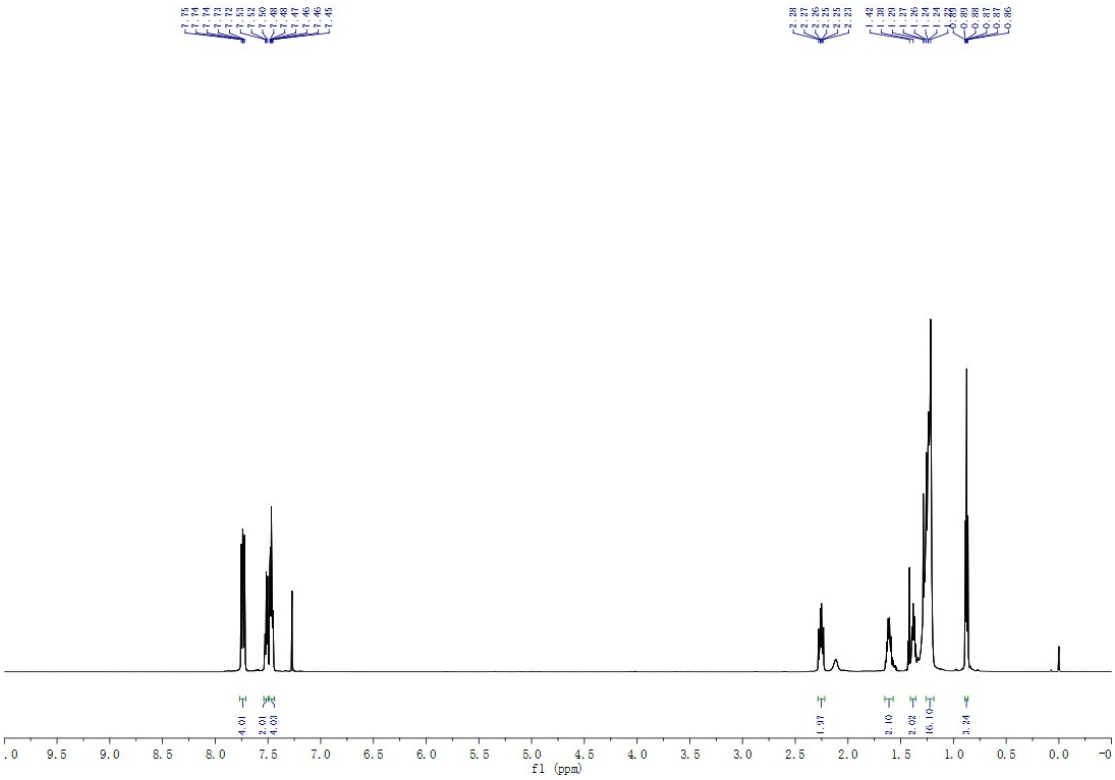
^{31}P NMR (243 MHz, $CDCl_3$)



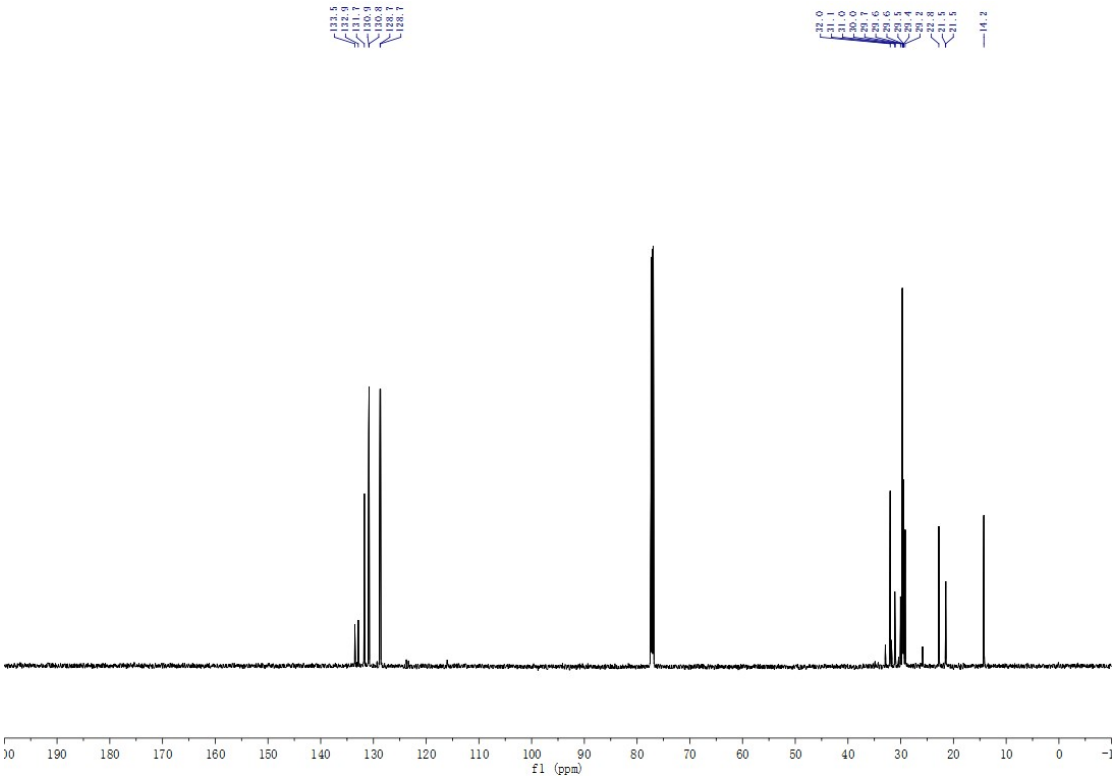


3ar

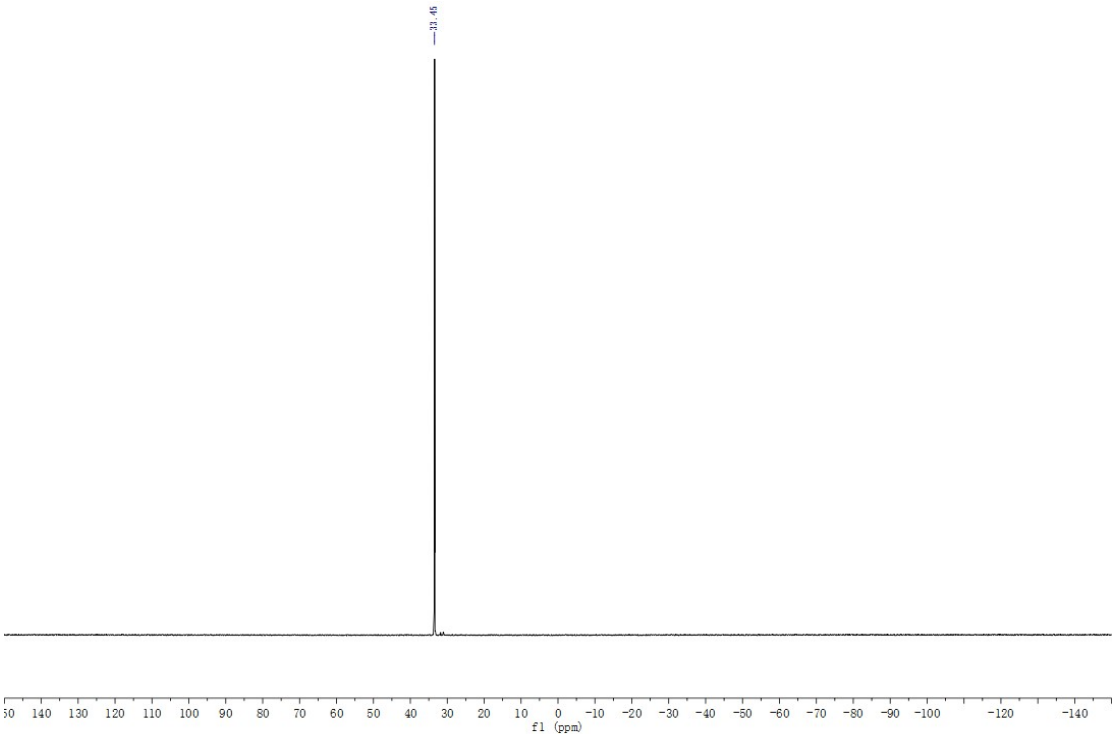
^{1}H NMR (600 MHz, $CDCl_3$)

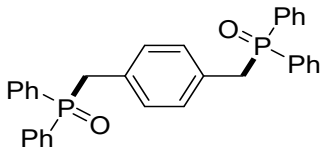


^{13}C NMR (151 MHz, $CDCl_3$)



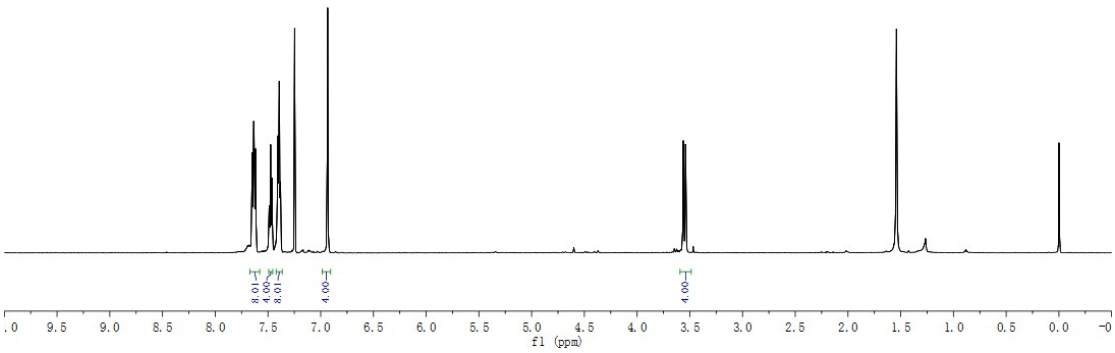
^{31}P NMR (243 MHz, $CDCl_3$)



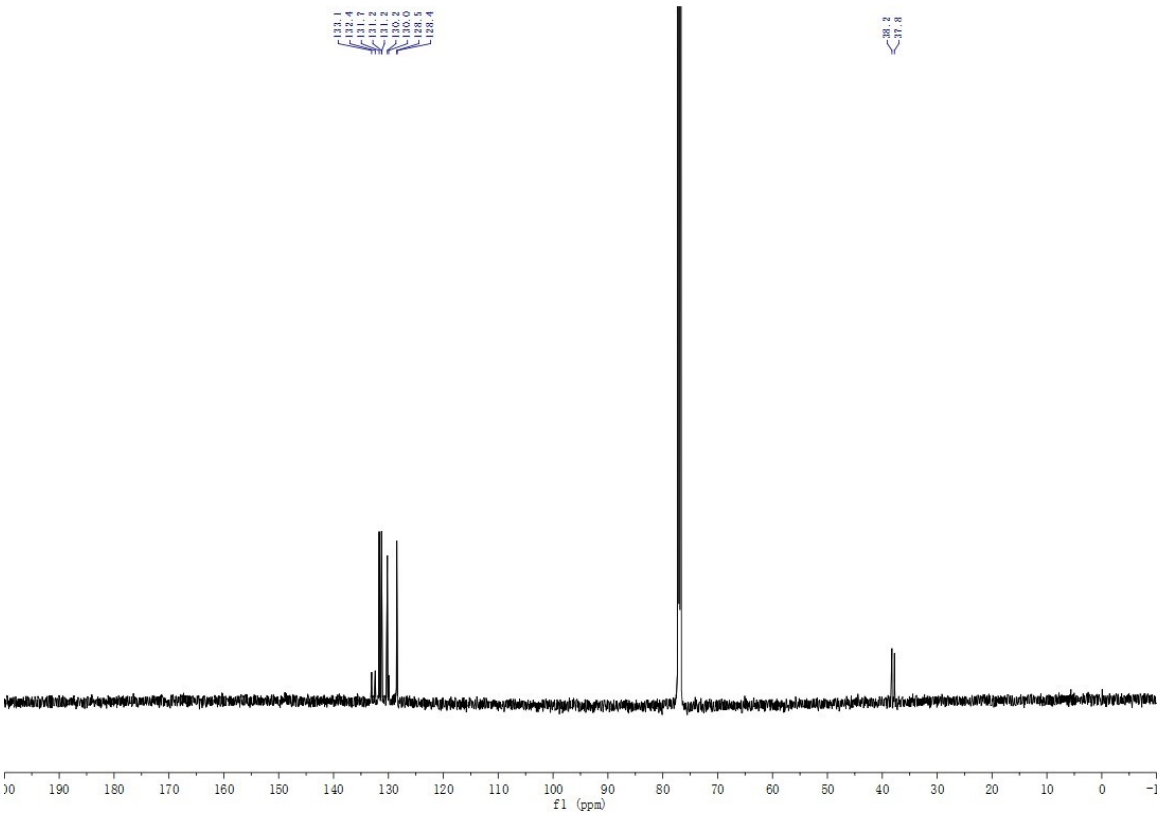


3au

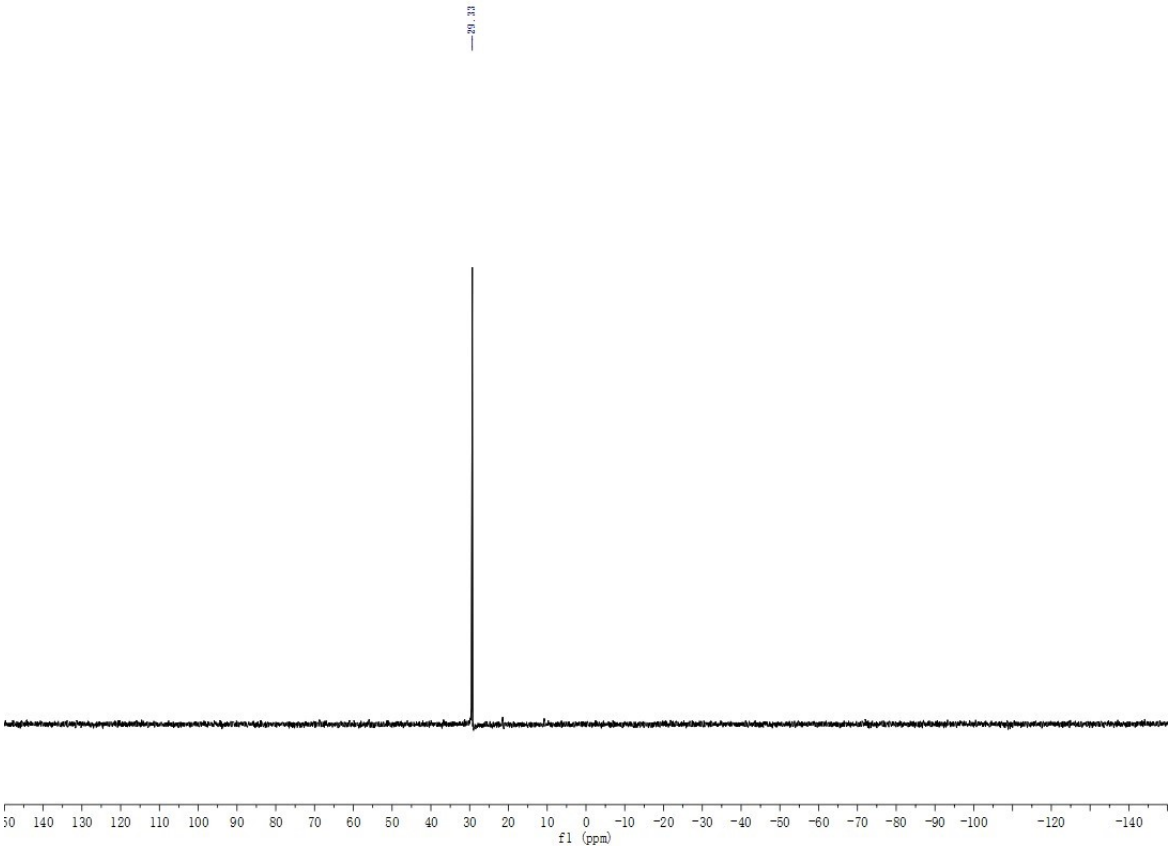
^{1}H NMR (600 MHz, $CDCl_3$)

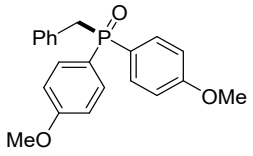


^{13}C NMR (151 MHz, $CDCl_3$)



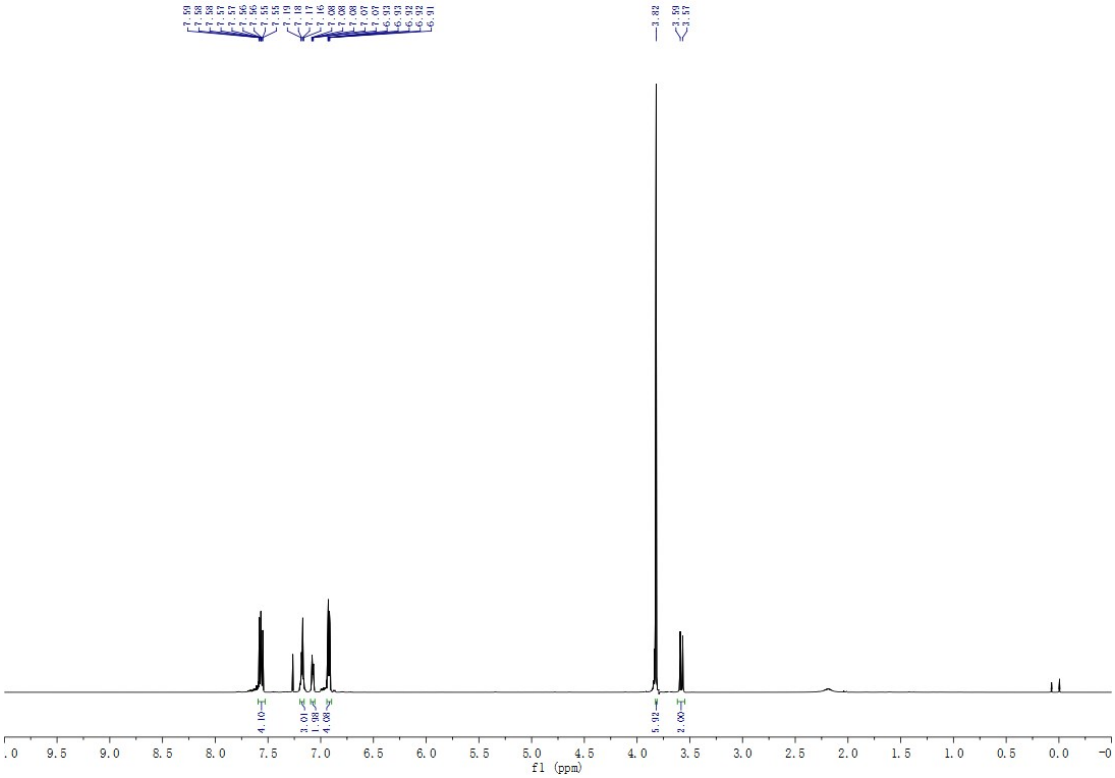
^{31}P NMR (243 MHz, $CDCl_3$)



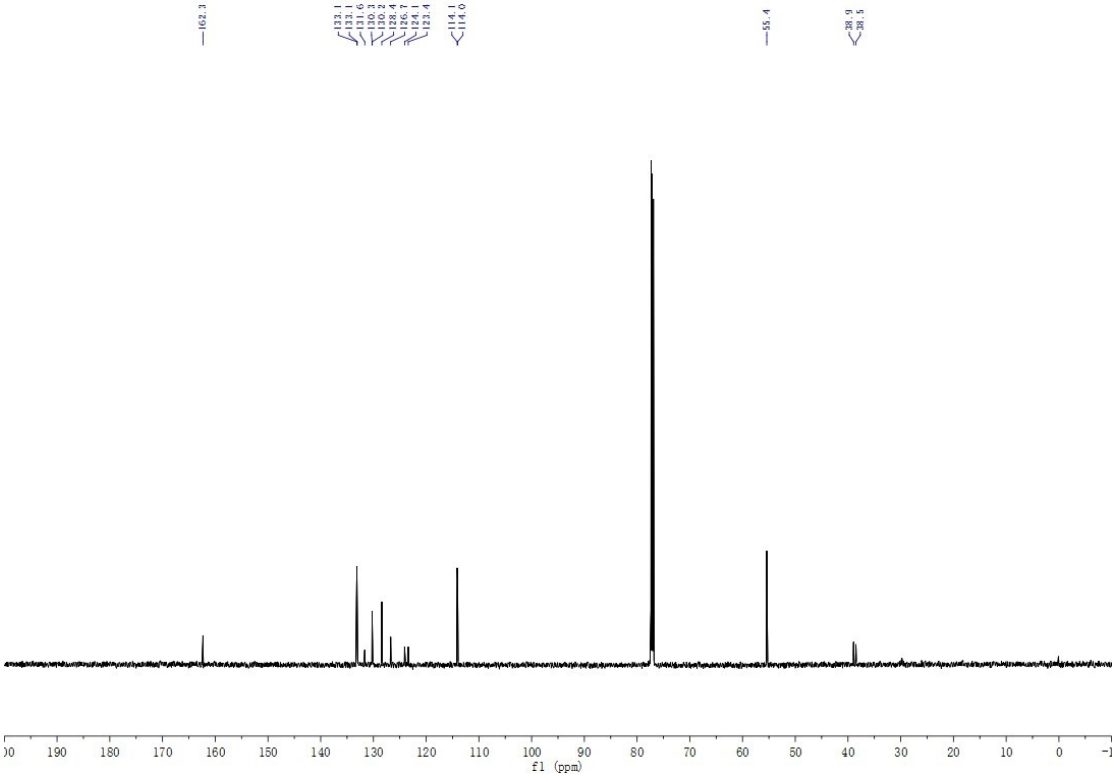


3ba

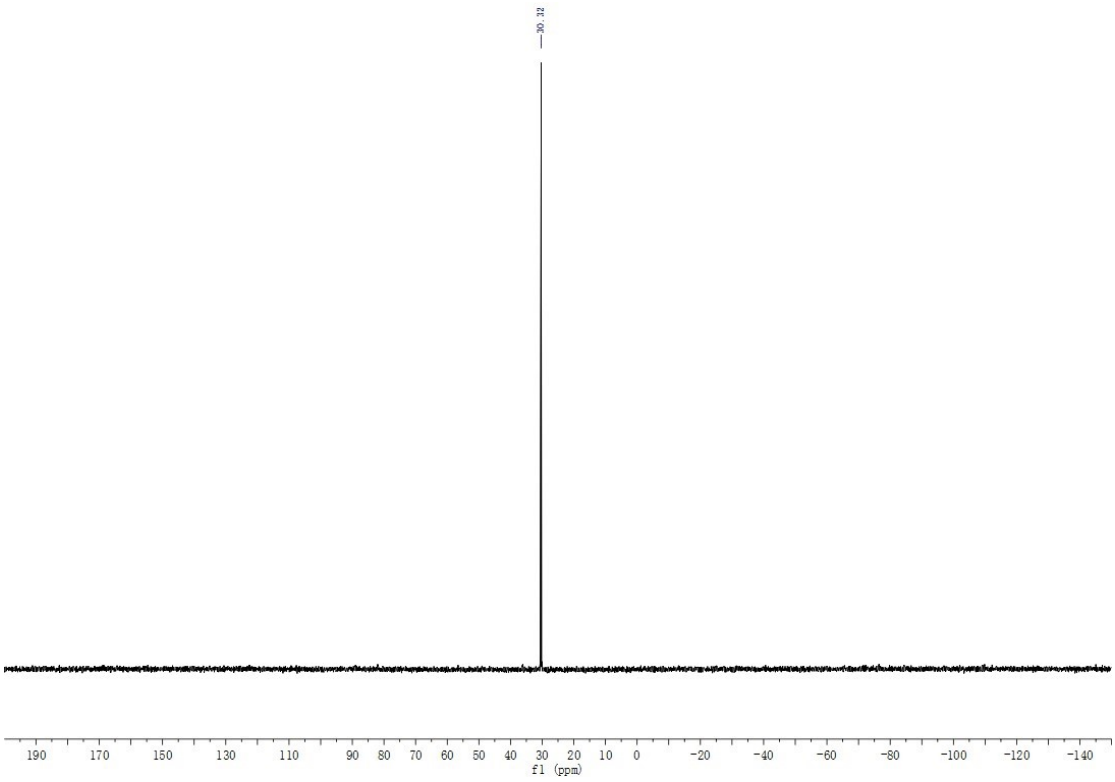
^{1}H NMR (600 MHz, $CDCl_3$)

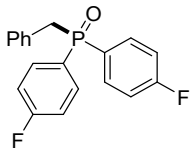


^{13}C NMR (151 MHz, $CDCl_3$)



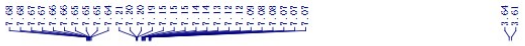
^{31}P NMR (243 MHz, $CDCl_3$)

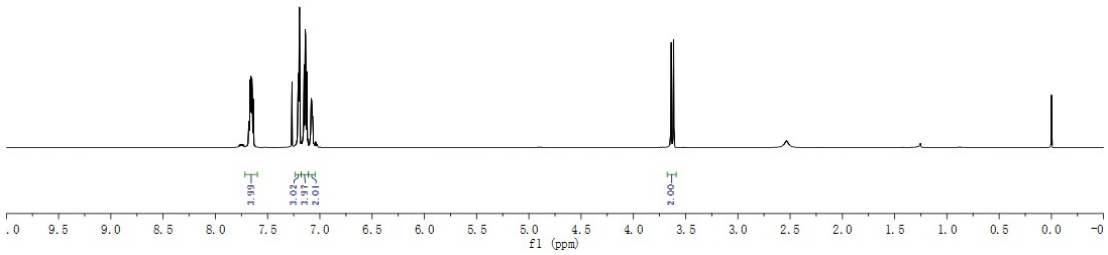




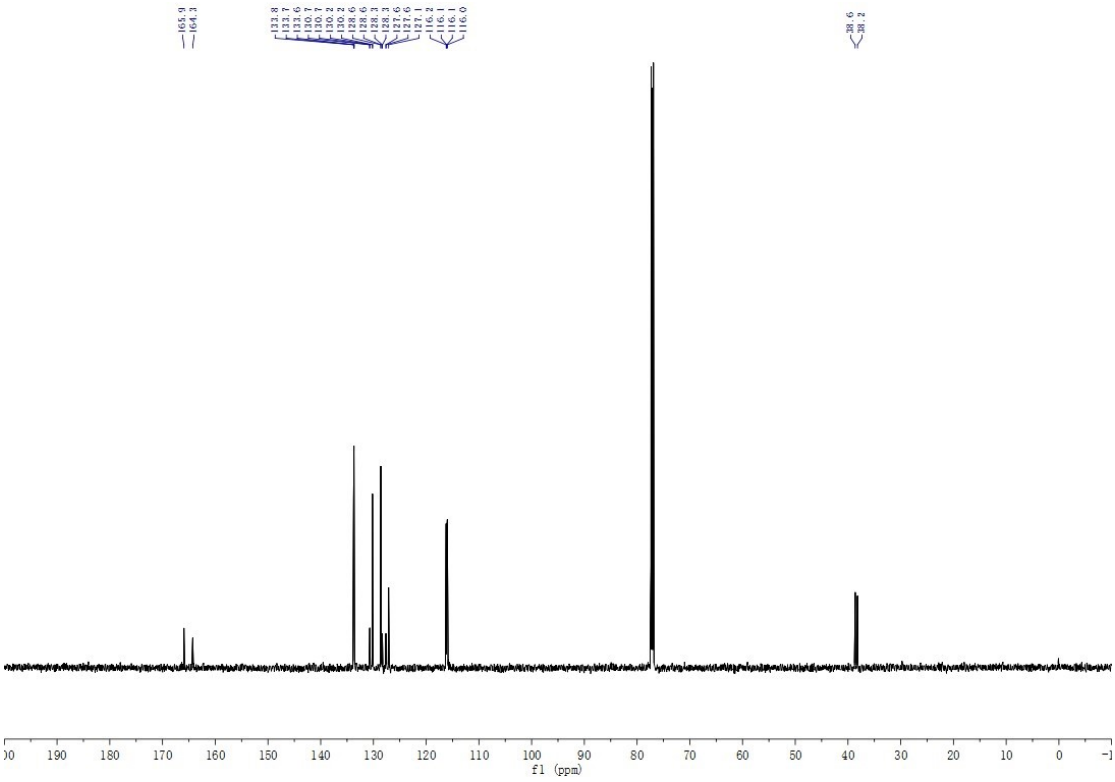
3ca

^{1}H NMR (600 MHz, $CDCl_3$)

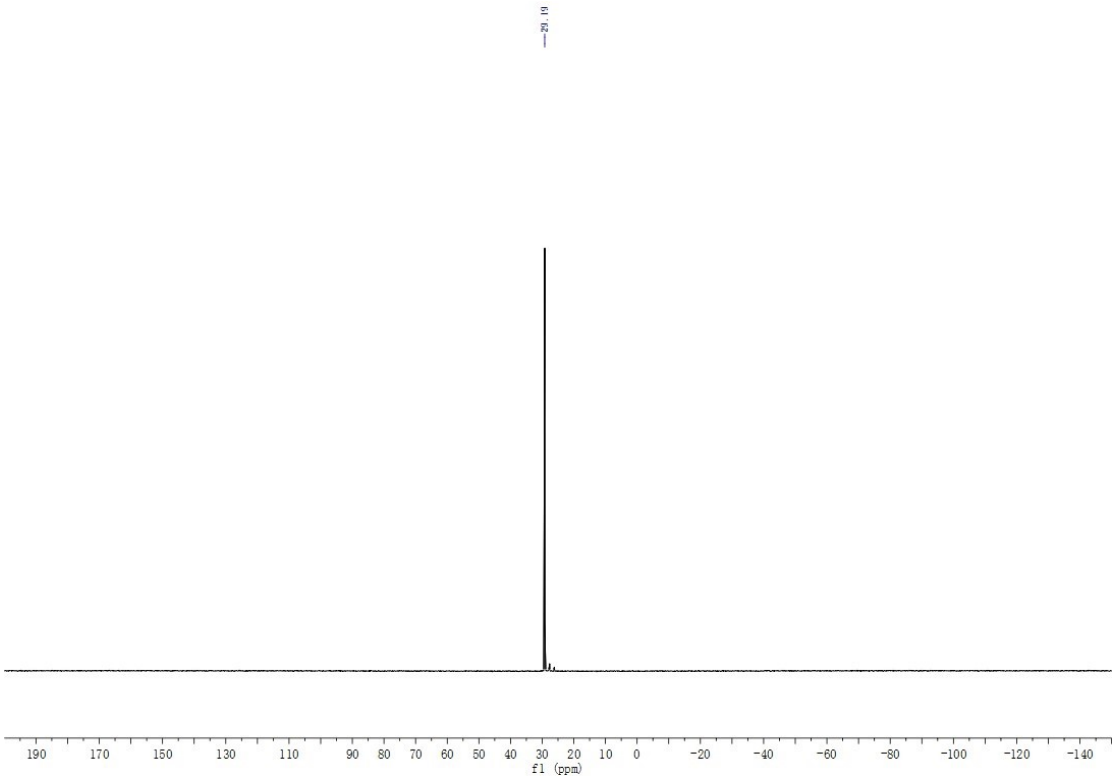


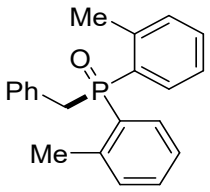


^{13}C NMR (151 MHz, $CDCl_3$)



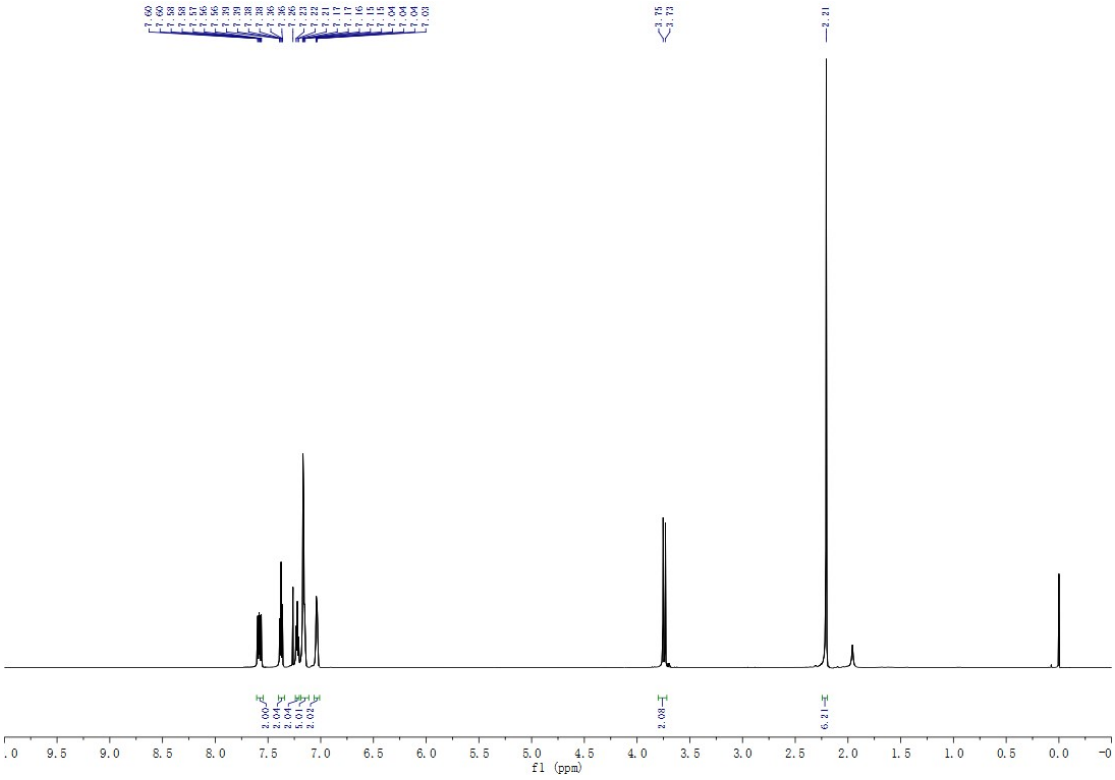
^{31}P NMR (243 MHz, $CDCl_3$)



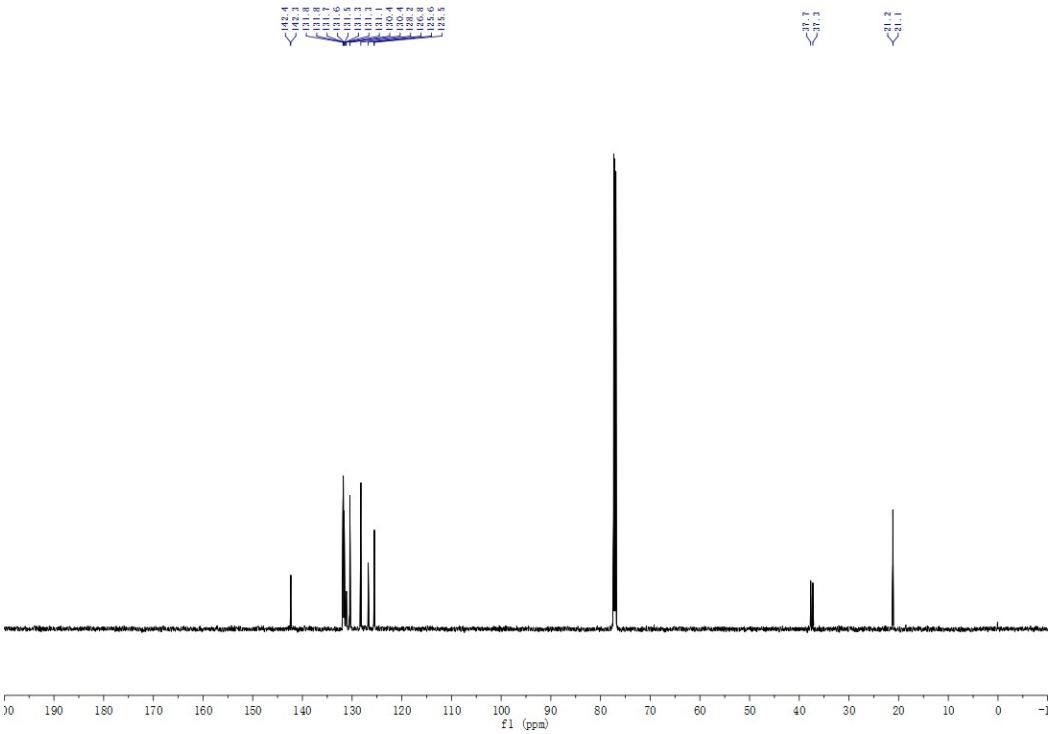


3da

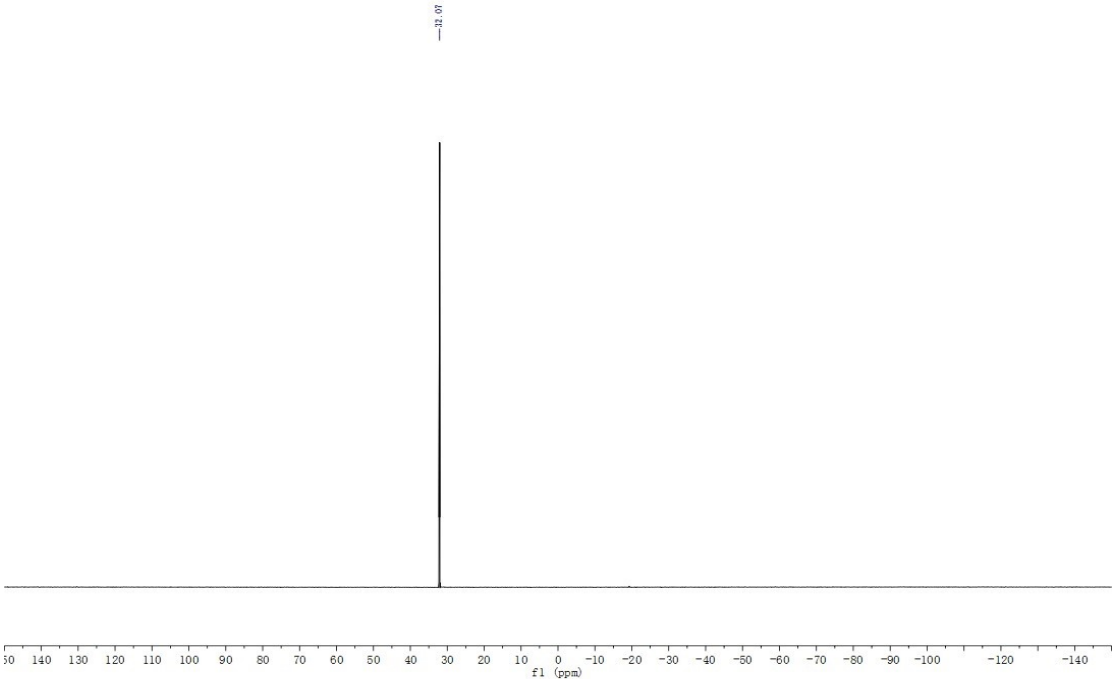
^{1}H NMR (600 MHz, $CDCl_3$)

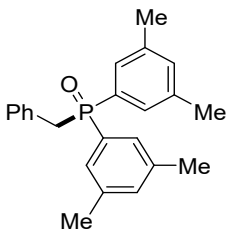


^{13}C NMR (151 MHz, $CDCl_3$)



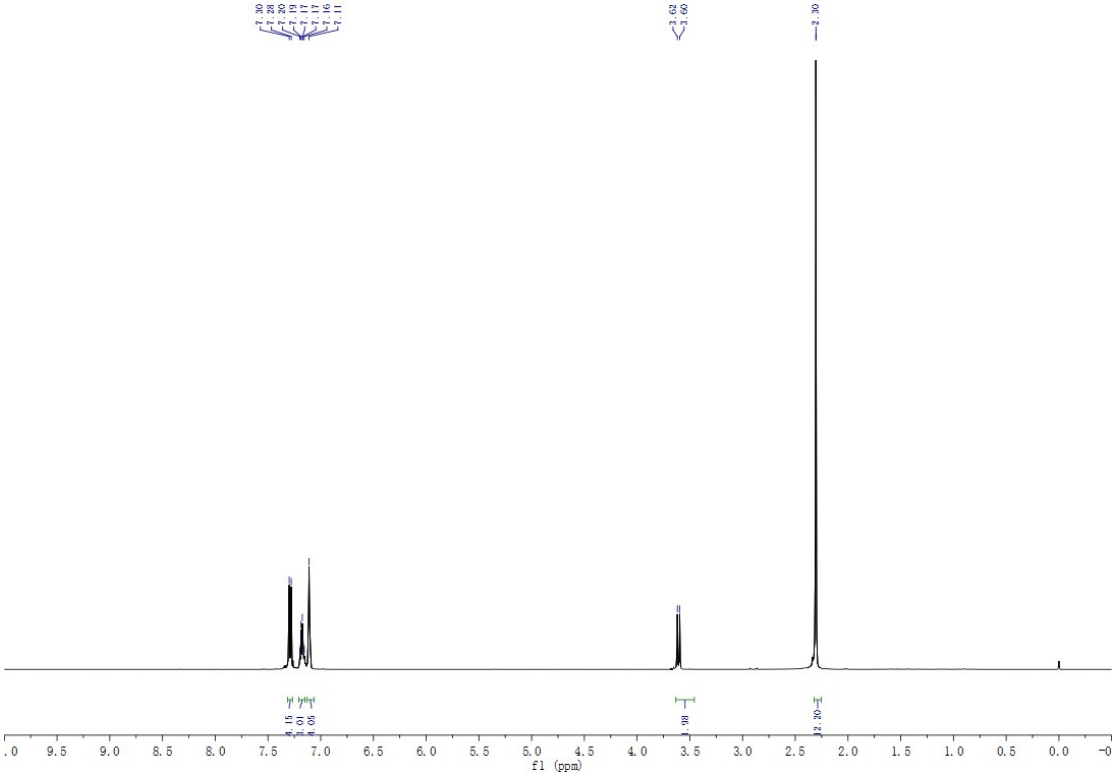
^{31}P NMR (243 MHz, $CDCl_3$)



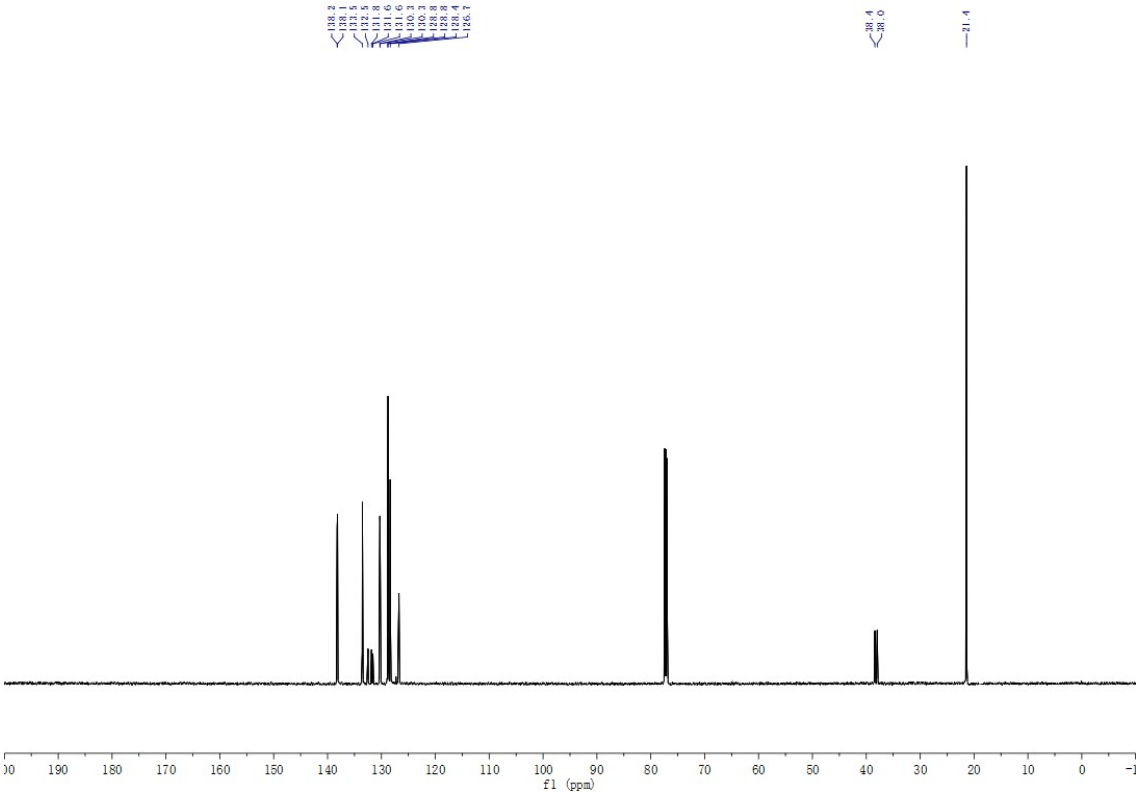


3ea

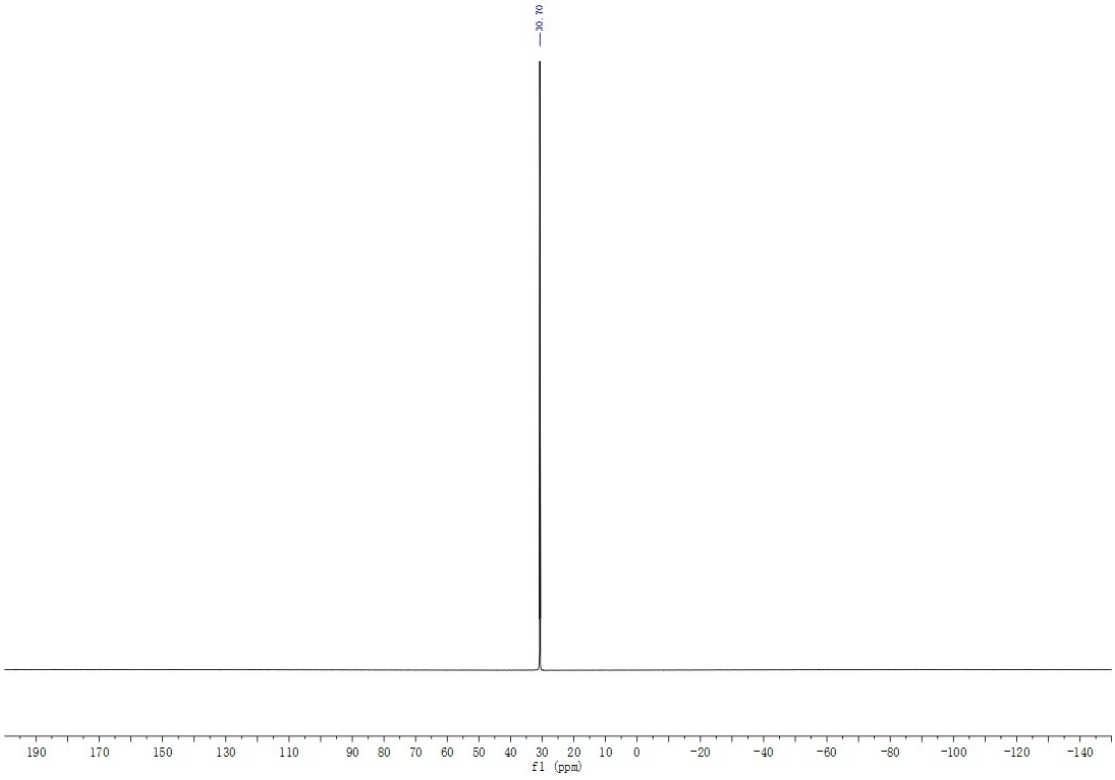
^{1}H NMR (600 MHz, $CDCl_3$)

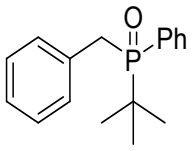


^{13}C NMR (151 MHz, $CDCl_3$)



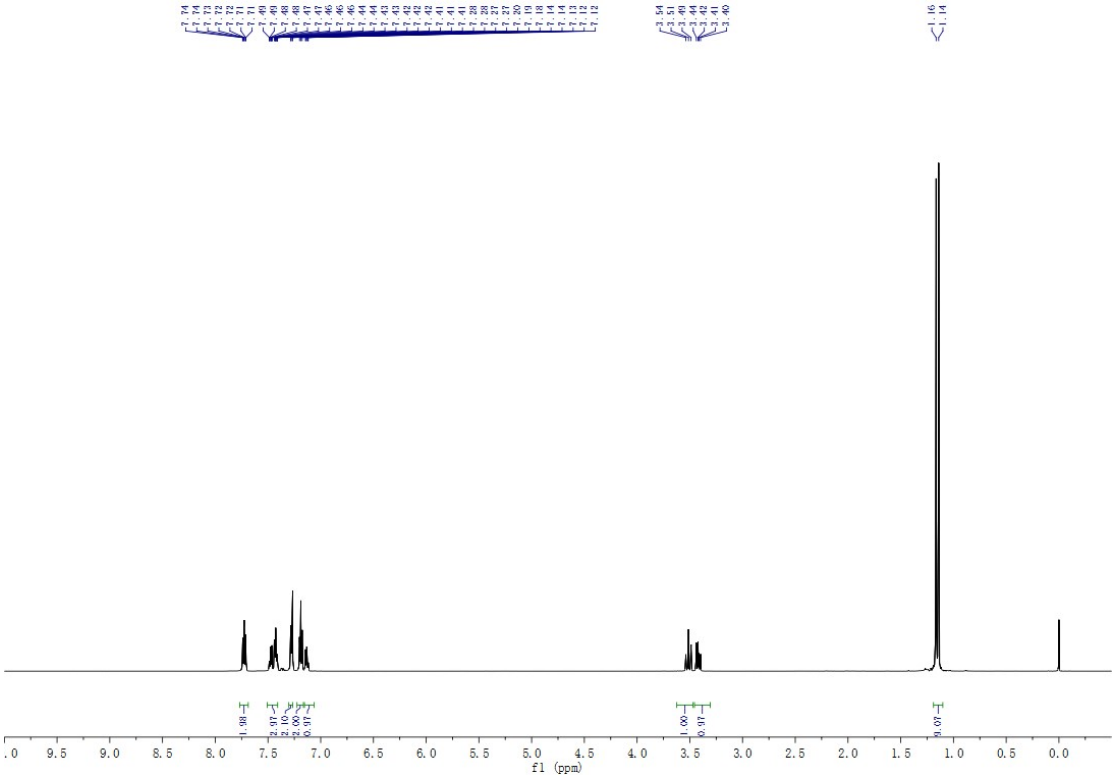
^{31}P NMR (243 MHz, $CDCl_3$)



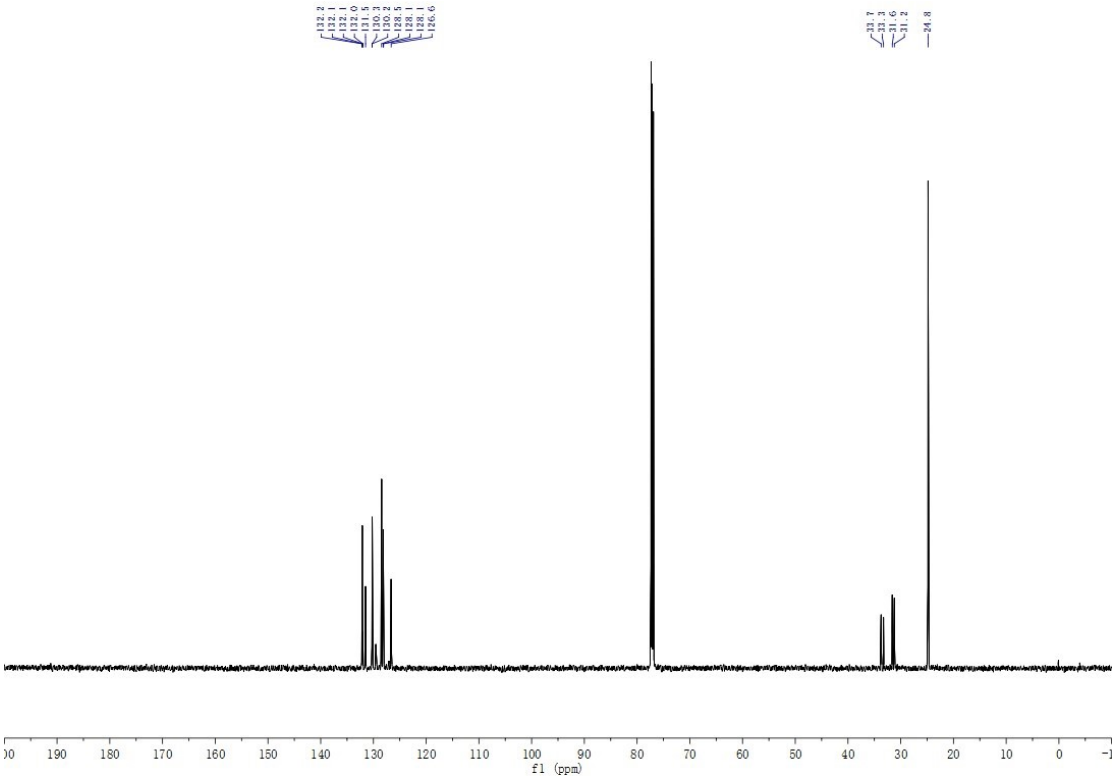


3fa

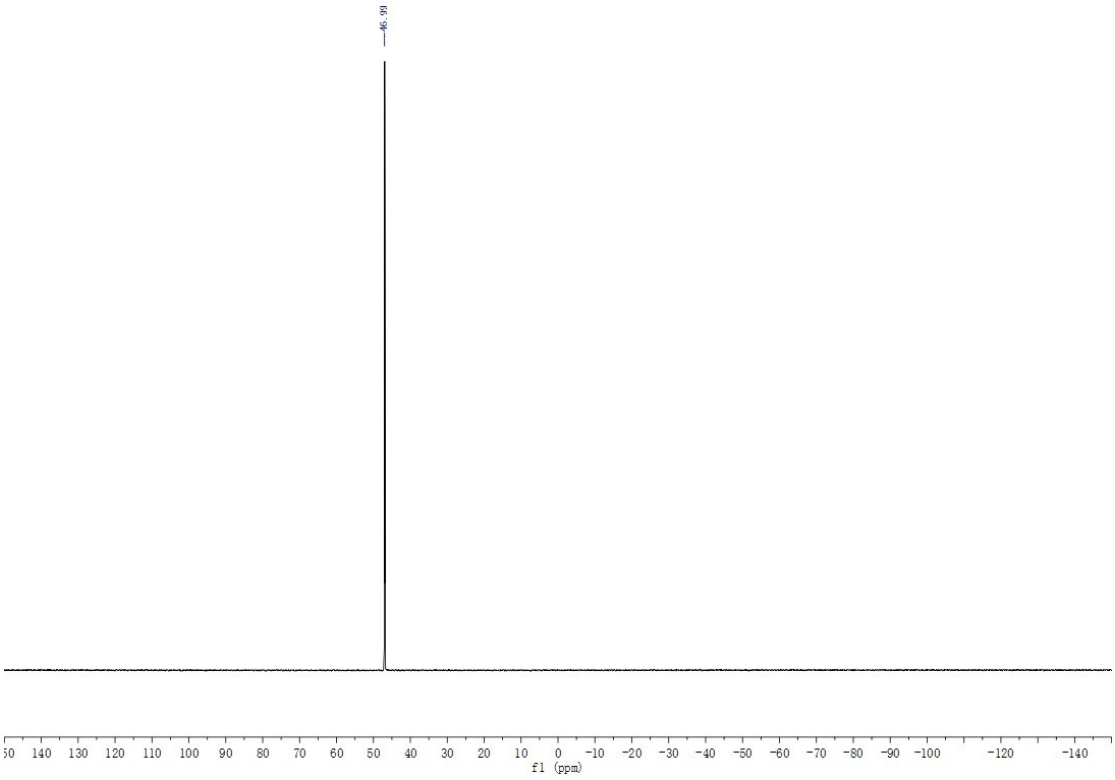
^{1}H NMR (600 MHz, $CDCl_3$)

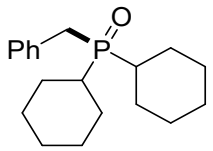


^{13}C NMR (151 MHz, $CDCl_3$)



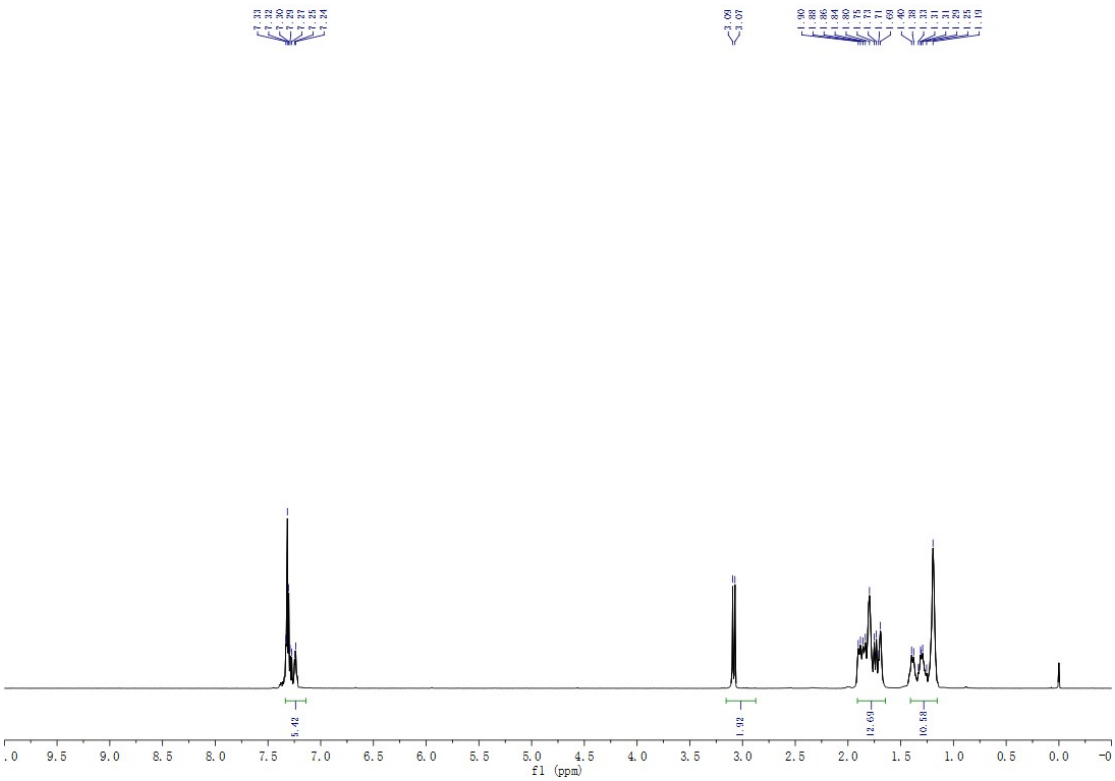
^{31}P NMR (243 MHz, $CDCl_3$)



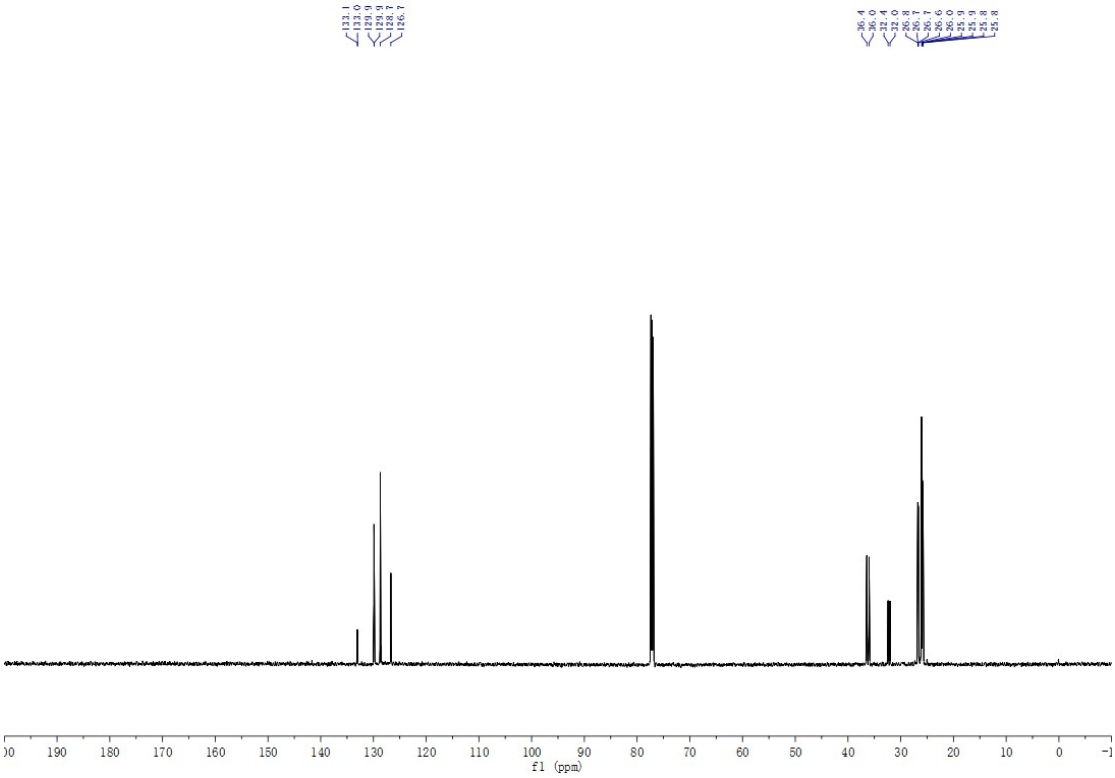


3ga

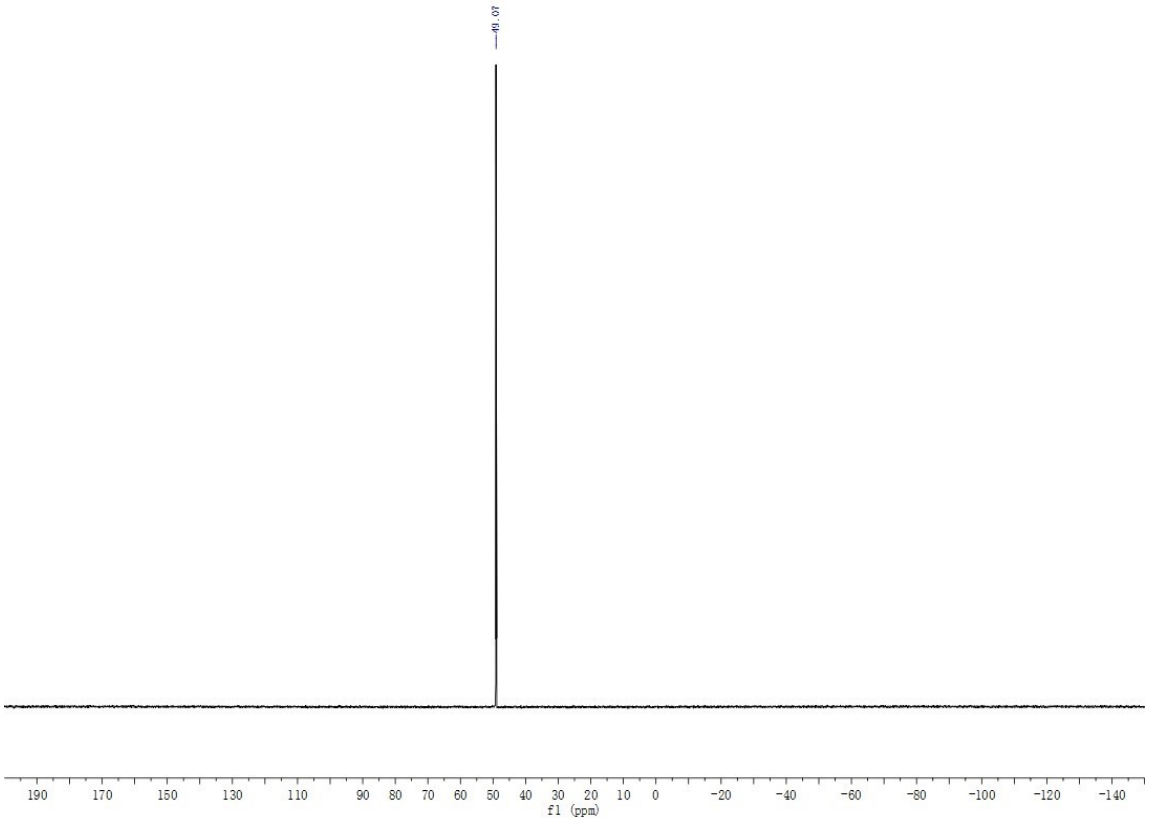
^{1}H NMR (600 MHz, $CDCl_3$)

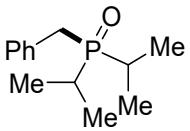


^{13}C NMR (151 MHz, $CDCl_3$)



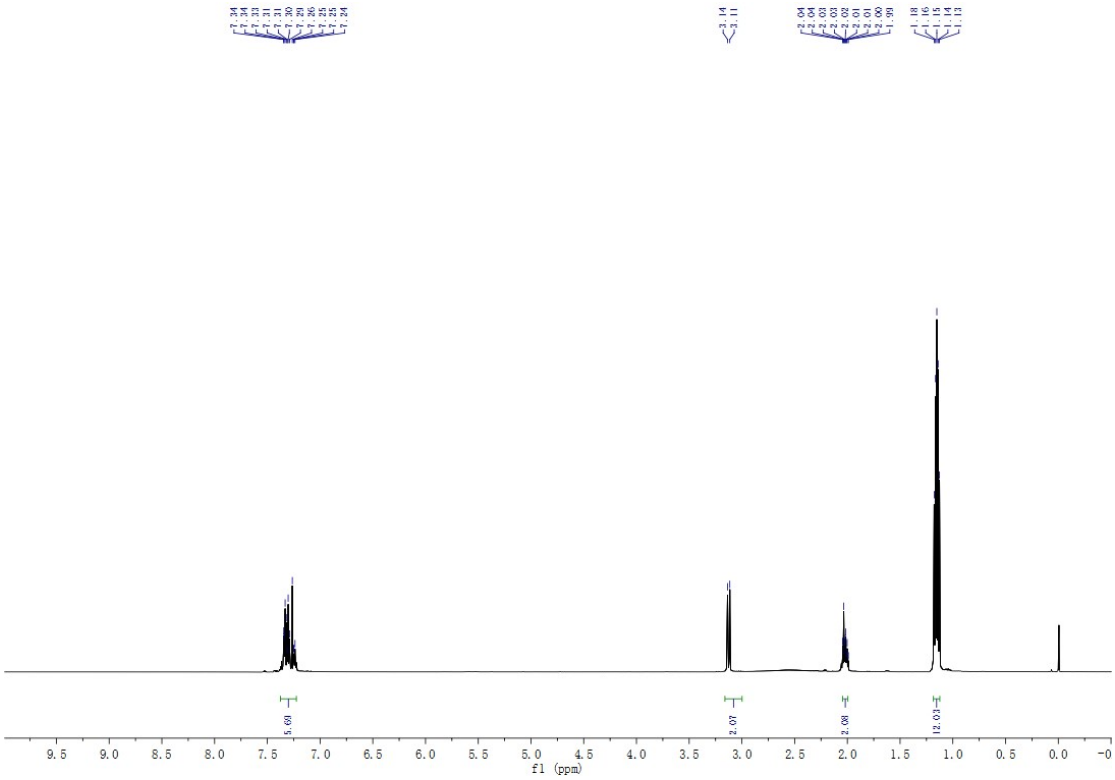
^{31}P NMR (243 MHz, $CDCl_3$)



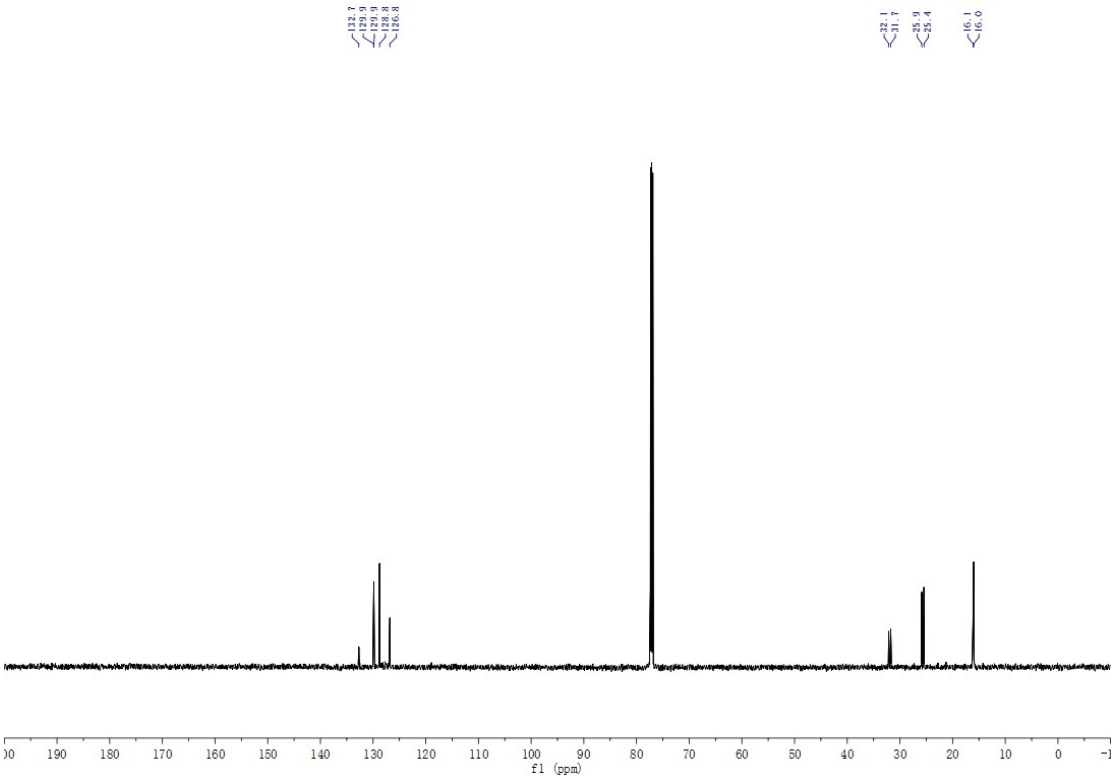


3ha

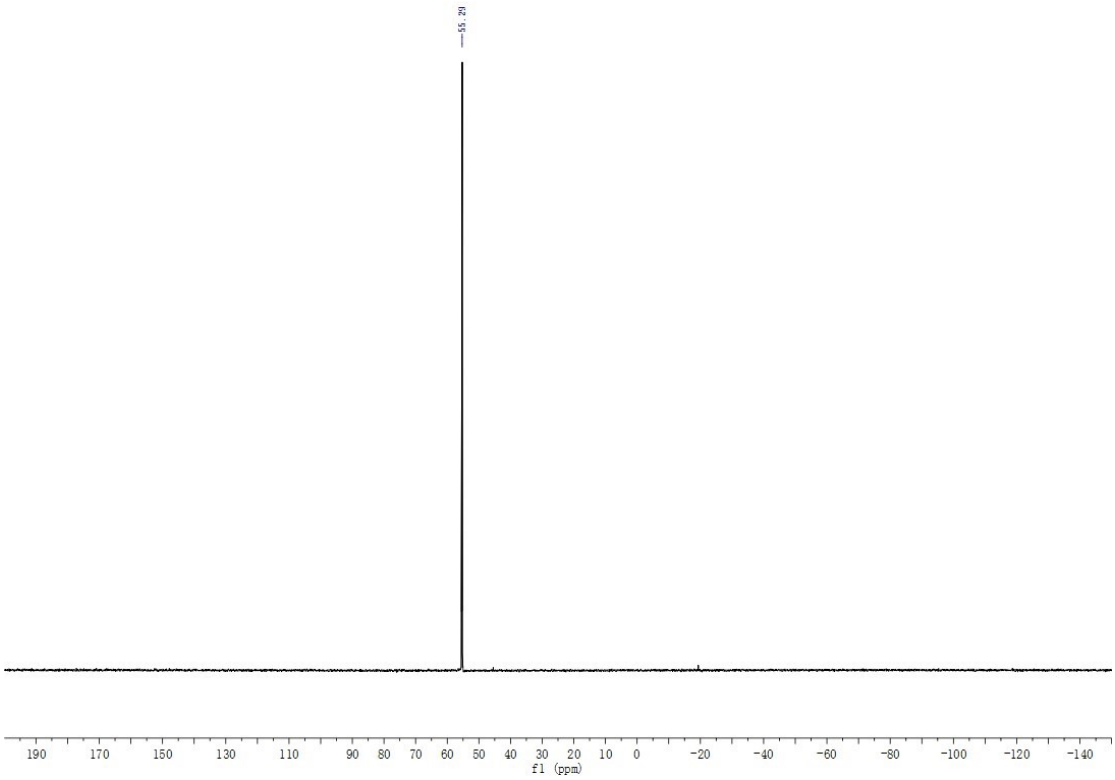
^{1}H NMR (600 MHz, $CDCl_3$)

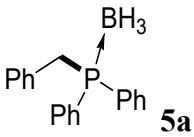


^{13}C NMR (151 MHz, $CDCl_3$)



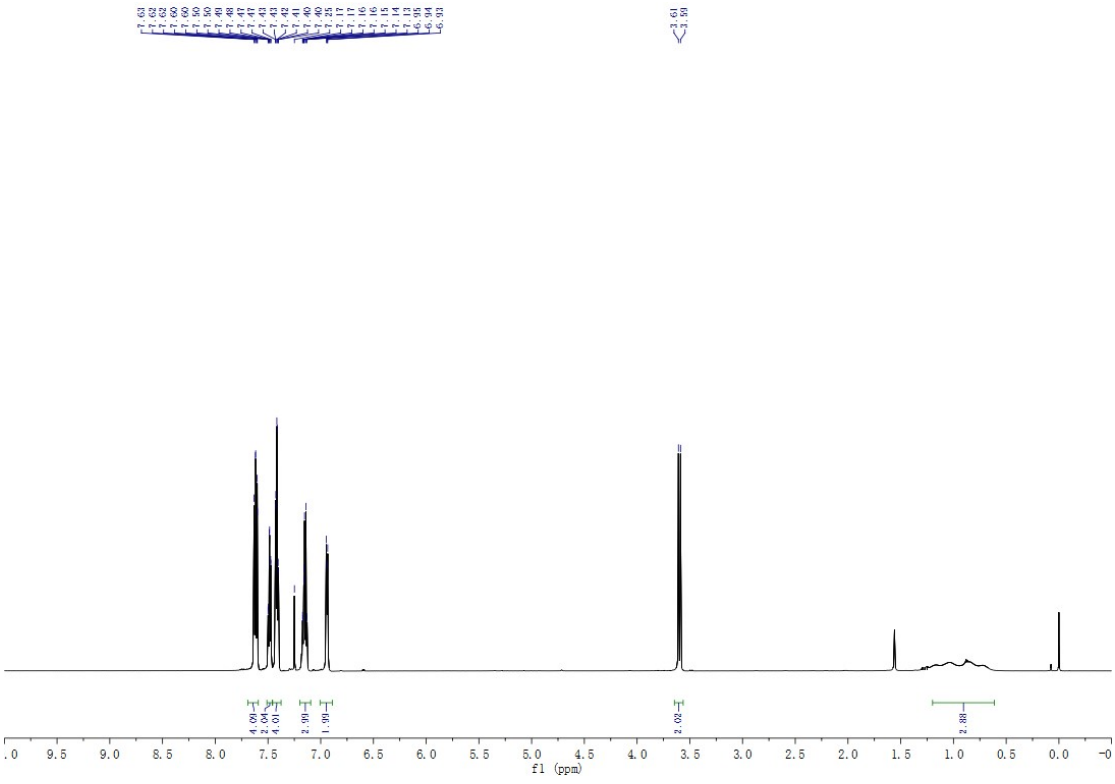
^{31}P NMR (243 MHz, $CDCl_3$)



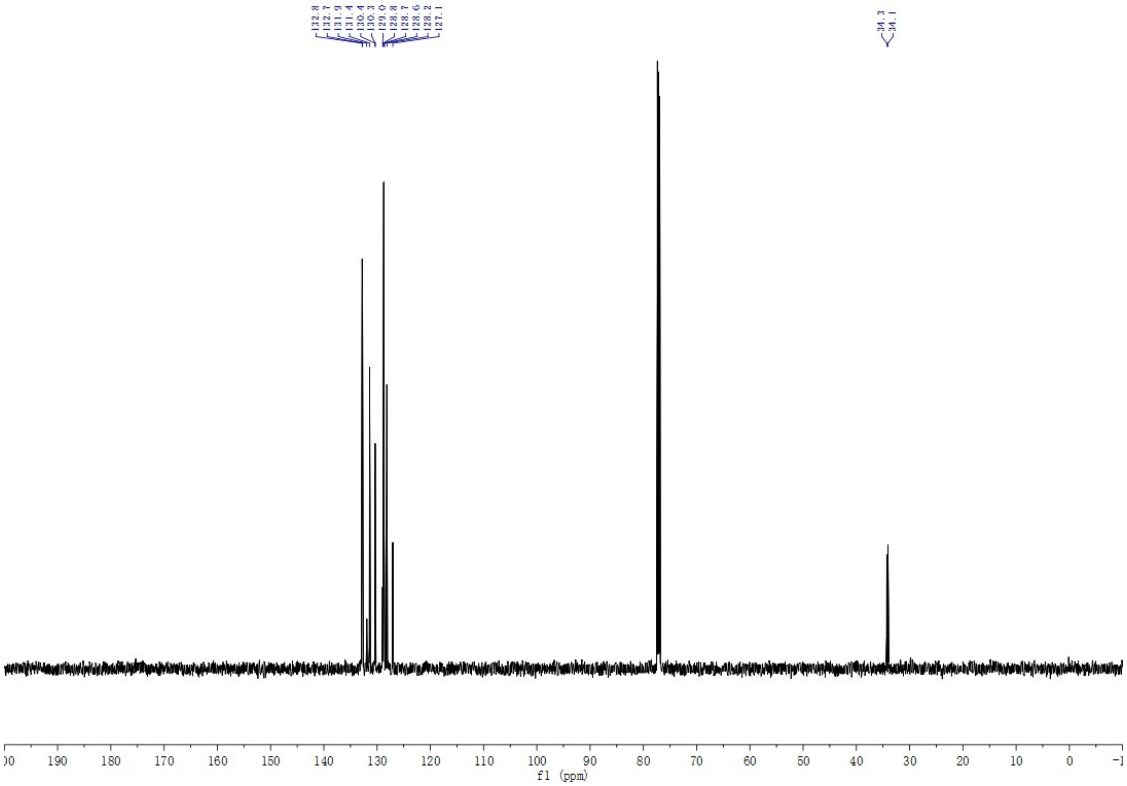


5a

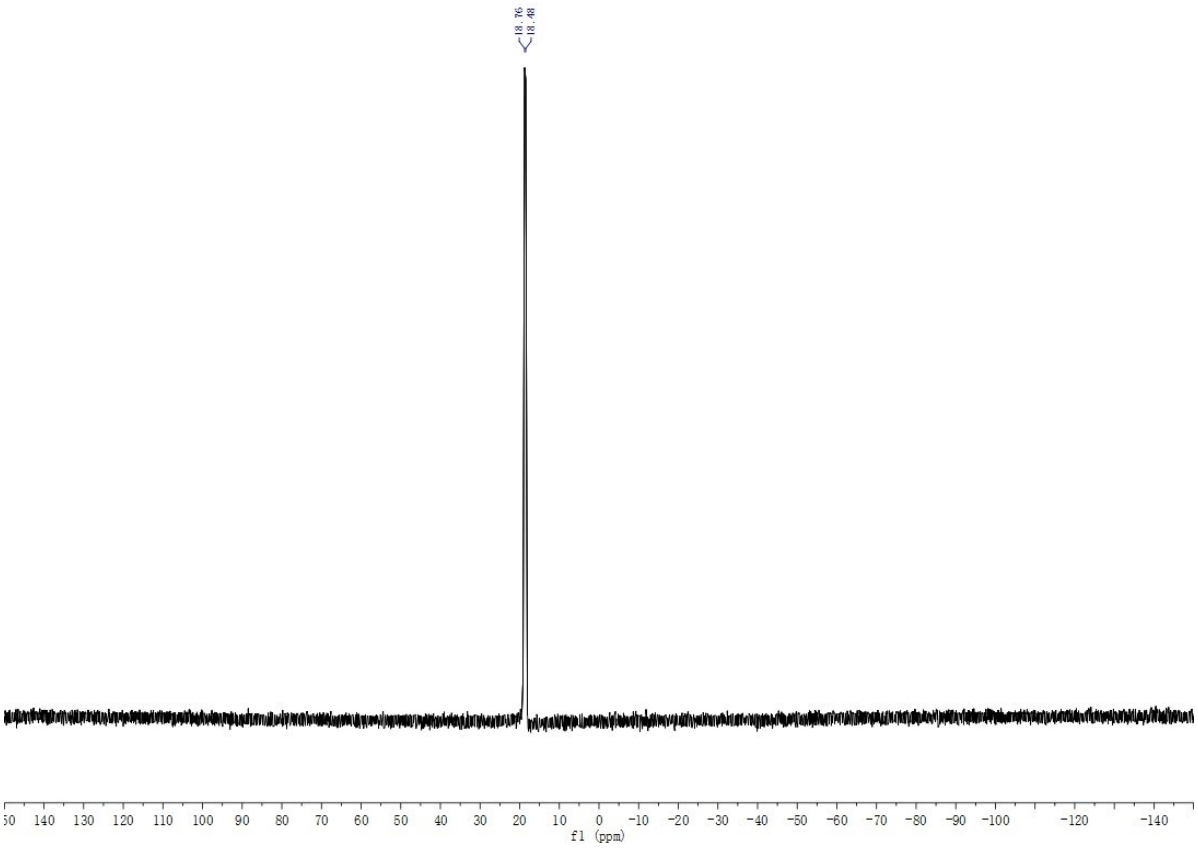
^{1}H NMR (600 MHz, $CDCl_3$)

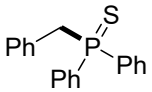


^{13}C NMR (151 MHz, $CDCl_3$)



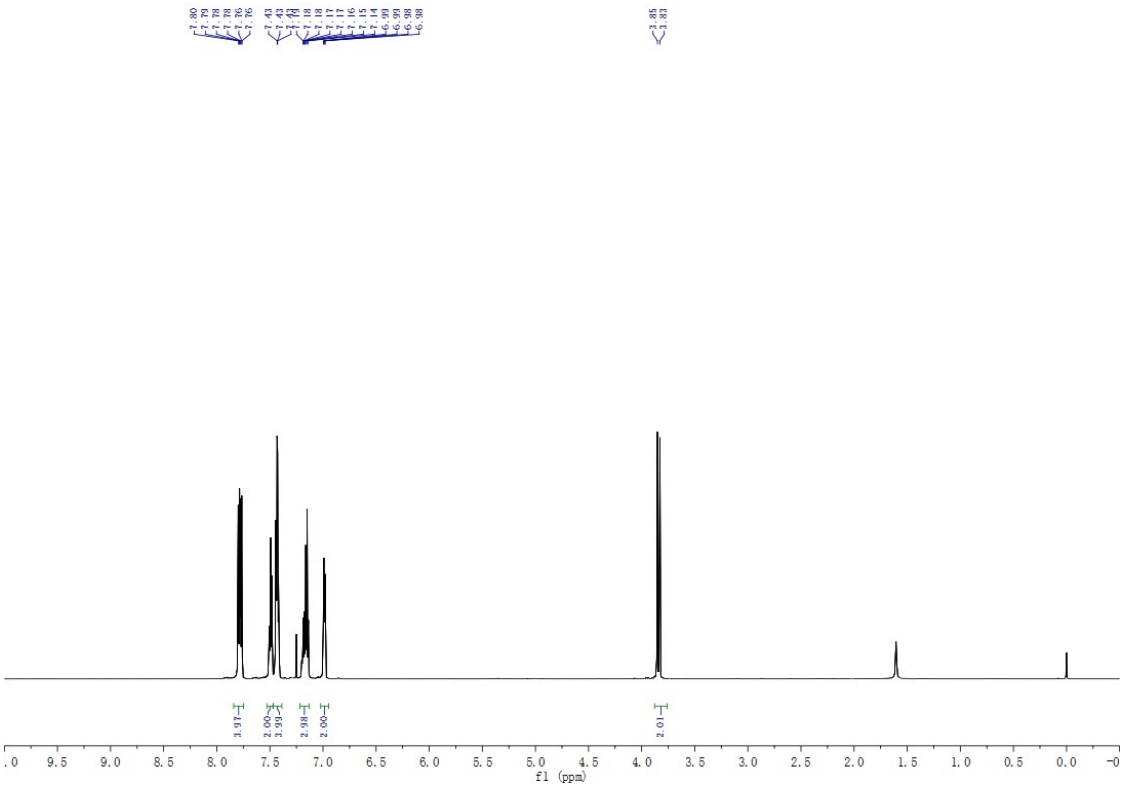
^{31}P NMR (243 MHz, $CDCl_3$)



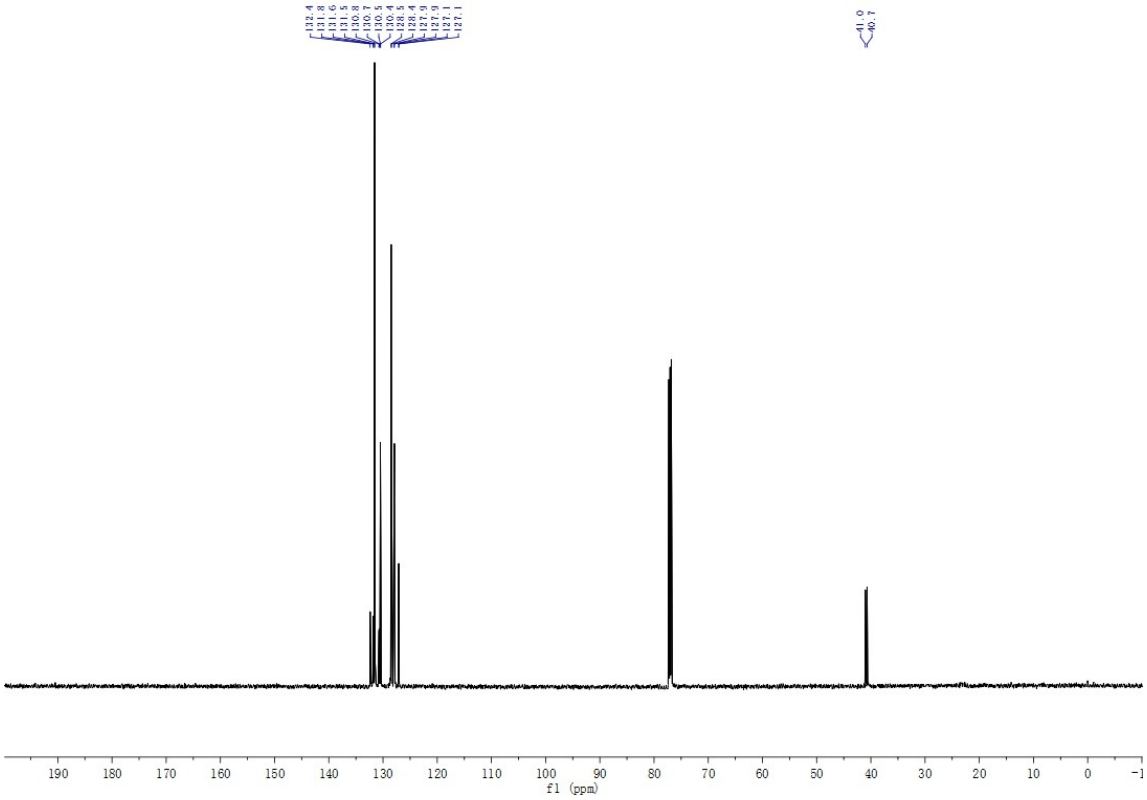


6a

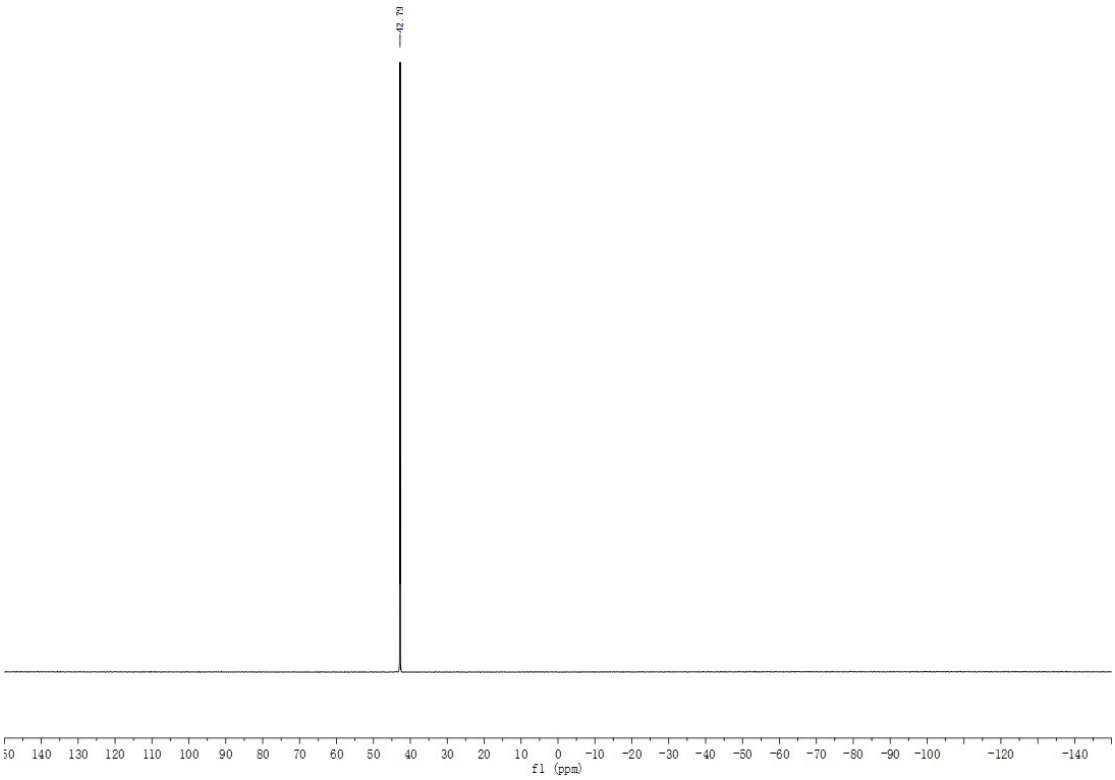
^{1}H NMR (600 MHz, $CDCl_3$)

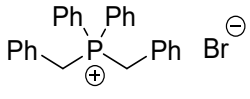


^{13}C NMR (151 MHz, $CDCl_3$)



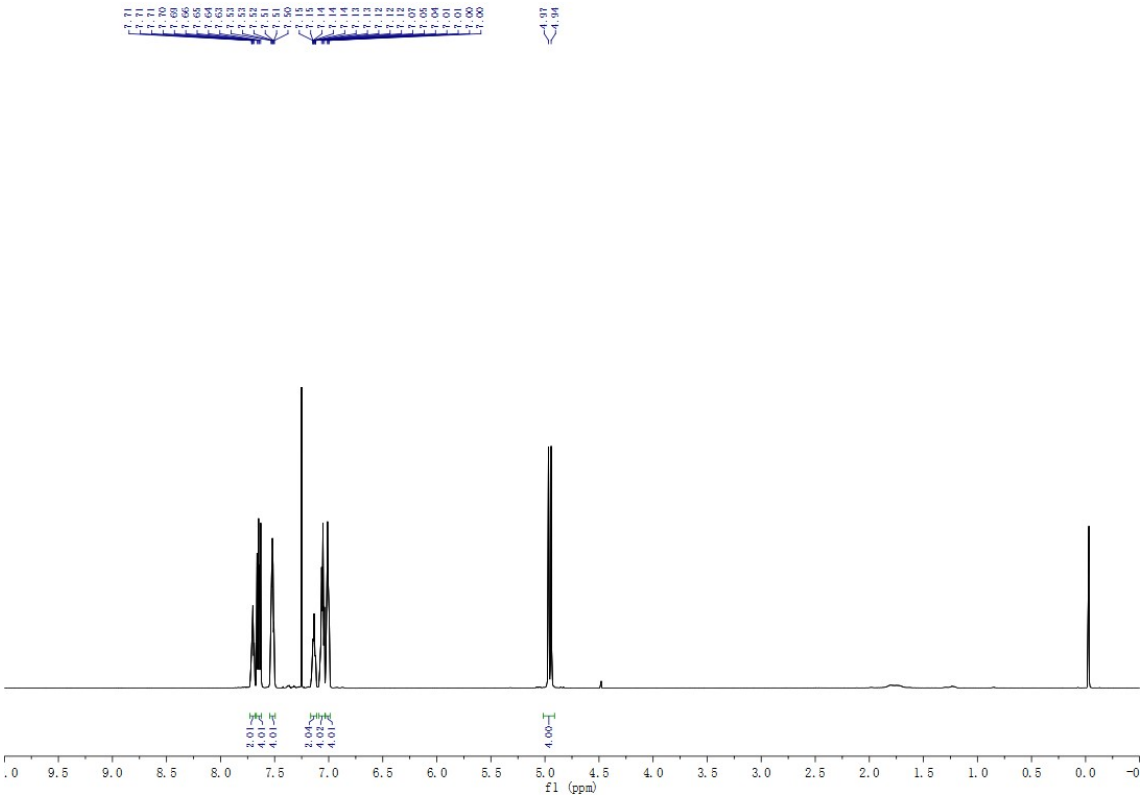
^{31}P NMR (243 MHz, $CDCl_3$)



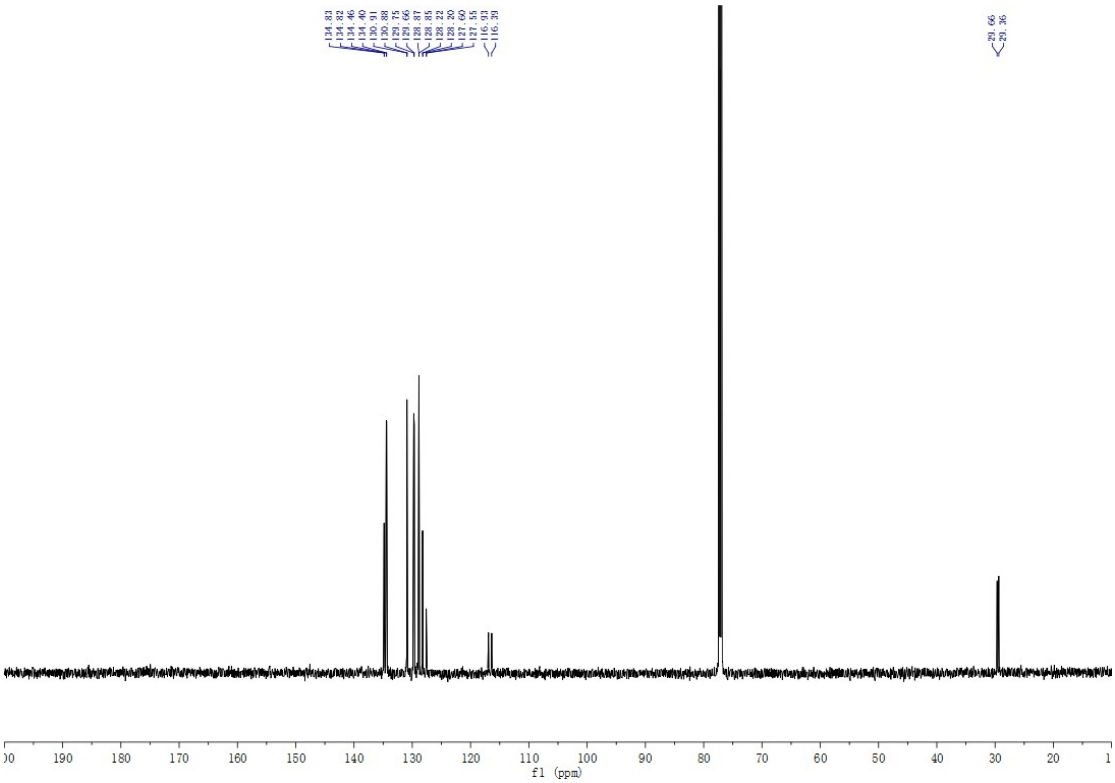


10a

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



^{31}P NMR (243 MHz, $CDCl_3$)