Supporting Information for

Alkylaluminium-Catalyzed Regioselective Hydrophosphinylation of *α,β*-unsaturated Ketones into *γ*-Ketophosphine Oxides

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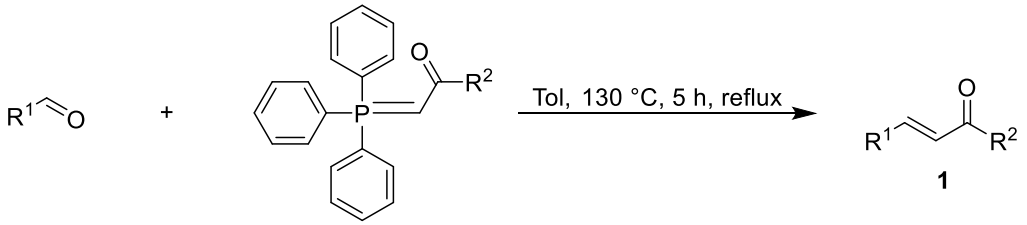
1. General considerations

All air-sensitive reactions and product manipulations were conducted under a dry nitrogen atmosphere, utilizing standard Schlenk techniques or working in glove boxes with strict air and moisture exclusion. All solvents were refluxed over the appropriate drying agent and distilled prior to use. Commercially available chemicals were purchased from *J&K* chemical or Aldrich and used as received. TLC analysis was performed on silica gel plates coated with glass and visualized by UV lamp (254 nm). column chromatography was performed on silica gel (400-500 mesh). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker Avance III 400 MHz spectrometer. Melting points were measured in sealed glass tubes. CCDC-2426265-2426268 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

2. Experimental Section

a）Preparation of *α,β*-unsaturated ketones

α,β-unsaturated ketones **1** was synthesised following a reported procedure.[1] Using a similar approach. General procedure for of *α,β*-unsaturated ketones synthesis:



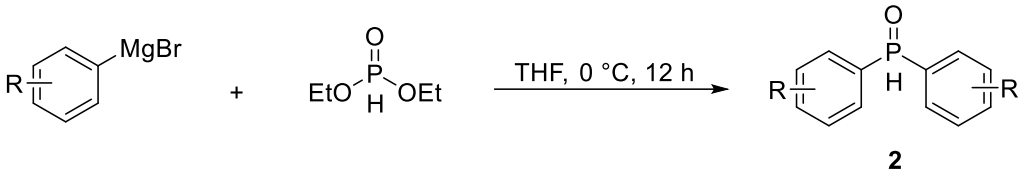
Scheme S2.1 Synthesis of *α,β*-unsaturated ketones

1-(triphenylphosphoranylidene)-2-ketone (40 mmol, 1.33 equivalents) was added to a solution of aldehyde (30 mmol, 1.0 equivalent) in toluene (50 mL) at room temperature. The reaction mixture was refluxed at 130 °C for 5 hours. Afterward, the mixture was extracted with EtOAc and H_2O. The combined organic layers were washed with brine, followed by water, and then dried over sodium sulfate. The resulting solution was concentrated under vacuum, and the residue was purified by column

chromatography using a mixture of petroleum ether and ethyl acetate (in a ratio ranging from 15:1 to 10:1, v/v).

b）Preparation of diarylphosphine oxides

diarylphosphine oxides was synthesised following a reported procedure.[2] Using a similar approach. General procedure for of diarylphosphine oxides synthesis:



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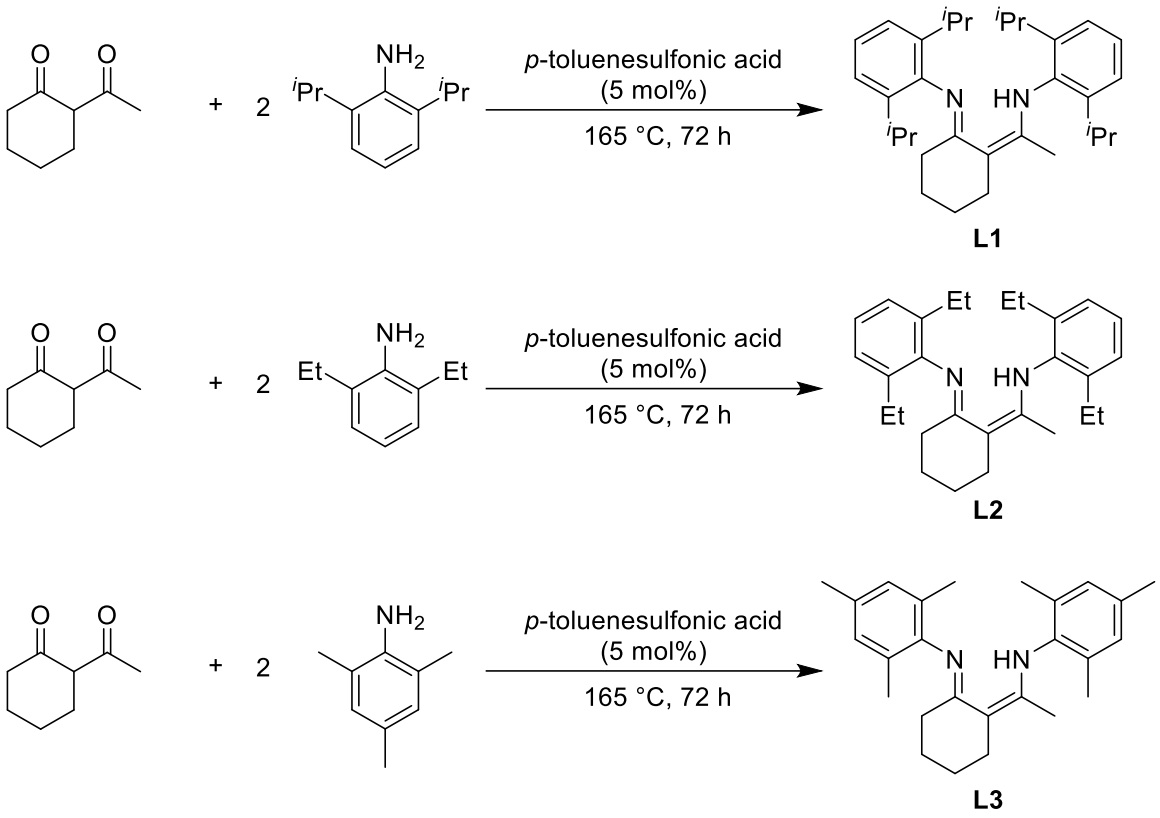
Scheme S2.2 Synthesis of diarylphosphine oxides

Dissolving 10 mmol of diethylphosphite in 10 mL of THF, which was then added slowly dropwise to 35 mmol of aryl magnesium bromide while maintaining the mixture in an ice-water bath. The reaction was stirred at room temperature for 12 hours until completion. The reaction was quenched with saturated aqueous NH_4Cl in an ice-water bath and stirring was continued for 0.5 h at room temperature, then the mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine and subsequently dried over sodium sulfate. Final purification was achieved through column chromatography using a mixture of petroleum ether and ethyl acetate, with the ratio varying from 5:1 to 1:1 (v/v).

c）Synthesis of L1-L3



Scheme S2.3 Synthesis of **L1-L3**

Ligands **L1-L3** were synthesized using a similar approach. 2-acetylcyclohexanone (50 mmol) and aniline (100 mmol) were added to a solution of dry toluene (80 mL) and *p*-toluenesulfonic acid (2.5 mmol) was added as a catalyst. The mixture was heated under reflux conditions and the water formed was removed by azeotropy using a Dean-Stark apparatus for 72 h. Toluene was evaporated to give a brown solid. The crude product was washed by ice ethanol to white or yellow, and then recrystallized by ice ethyl acetate to obtain white or yellow solid.

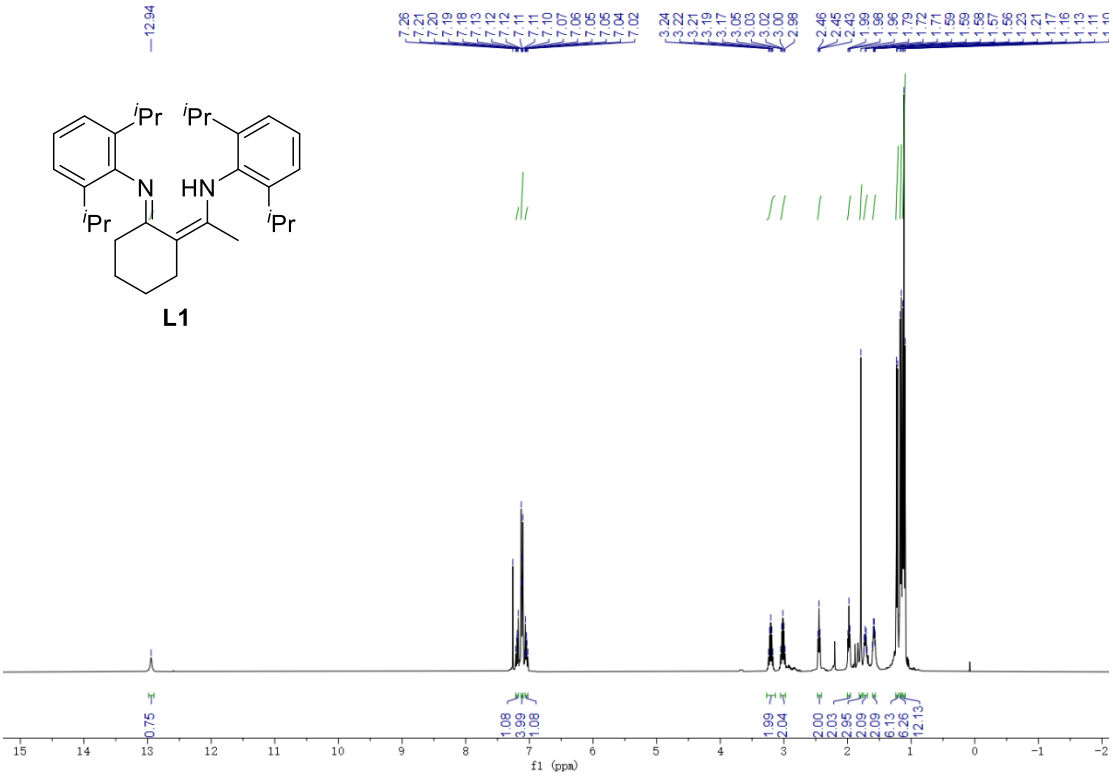
d）^{1}H and ^{13}C NMR data and spectra of L1-L3

Ligand **L1.** 11.93 g, 52% yield; white solid; m.p. 164.4 – 166.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.94 (s, 1H), 7.23 – 6.96 (m, 6H), 3.27 – 3.11 (m, 2H), 3.09 – 2.96 (m, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 1.98 (t, *J* = 6.3 Hz, 2H), 1.79 (s, 3H), 1.76 – 1.69 (m, 2H), 1.62 – 1.54 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.16 (d, *J* = 6.9 Hz, 6H), 1.11 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 155.2, 145.9, 145.0, 139.2, 136.7, 126.4,

123.1, 123.1, 122.9, 97.1, 77.4, 77.1, 76.7, 28.2, 28.1, 27.9, 26.8, 24.8, 23.9, 23.9, 23.6, 23.3, 22.1, 19.1.

Ligand **L2.** 13.25 g, 66% yield; light yellow solid; m.p. 160.3 – 162.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.02 (s, 1H), 7.12 – 6.98 (m, 6H), 2.72 – 2.60 (m, 2H), 2.60 – 2.49 (m, 4H), 2.49 – 2.45 (m, 2H), 2.45 – 2.38 (m, 2H), 1.98 (t, J = 6.4 Hz, 2H), 1.78 (s, 3H), 1.76 – 1.68 (m, 2H), 1.64 – 1.54 (m, 2H), 1.20 – 1.15 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 155.1, 146.4, 141.3, 138.6, 134.5, 125.9, 125.9, 125.6, 122.8, 97.5, 28.0, 26.9, 24.6, 24.5, 24.2, 23.9, 22.3, 18.5, 14.7, 14.2, 13.9.

Ligand **L3.** 10.72 g, 57% yield; yellow solid; m.p. 167.2 – 170.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.96 (s, 1H), 6.85 (d, J = 10.2 Hz, 4H), 2.45 (t, J = 6.3 Hz, 2H), 2.27 (s, 6H), 2.16 (s, 6H), 2.06 (s, 6H), 1.97 (t, J=6.4 Hz, 2H), 1.77 (s, 3H), 1.74 – 1.68 (m, 2H), 1.63 – 1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 155.0, 145.1, 137.5, 135.2, 134.8, 131.5, 128.6, 128.4, 128.3, 97.5, 27.7, 26.9, 23.9, 22.4, 20.9, 20.7, 19.5, 18.5, 18.5, 17.9.



FigureS2.1 ^{1}H NMR spectrum of **L1** (400 MHz, $CDCl_3$).

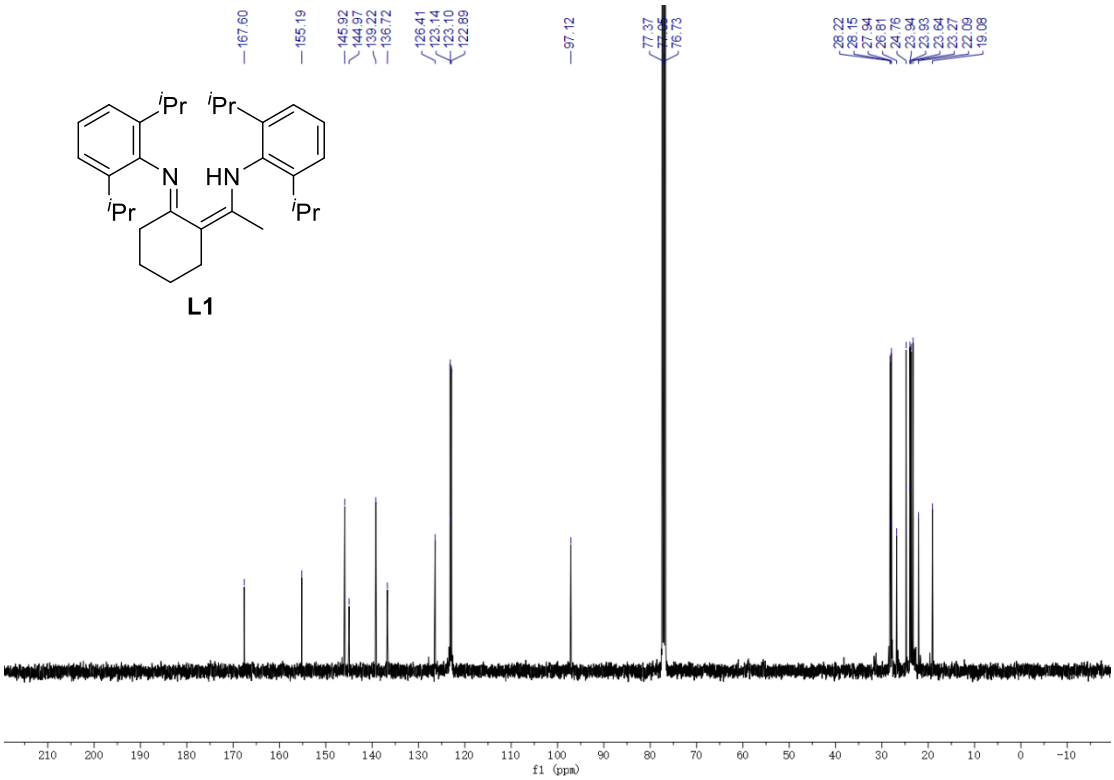


Figure S2.2 ^{13}C NMR spectrum of **L1** (101 MHz, $CDCl_3$).

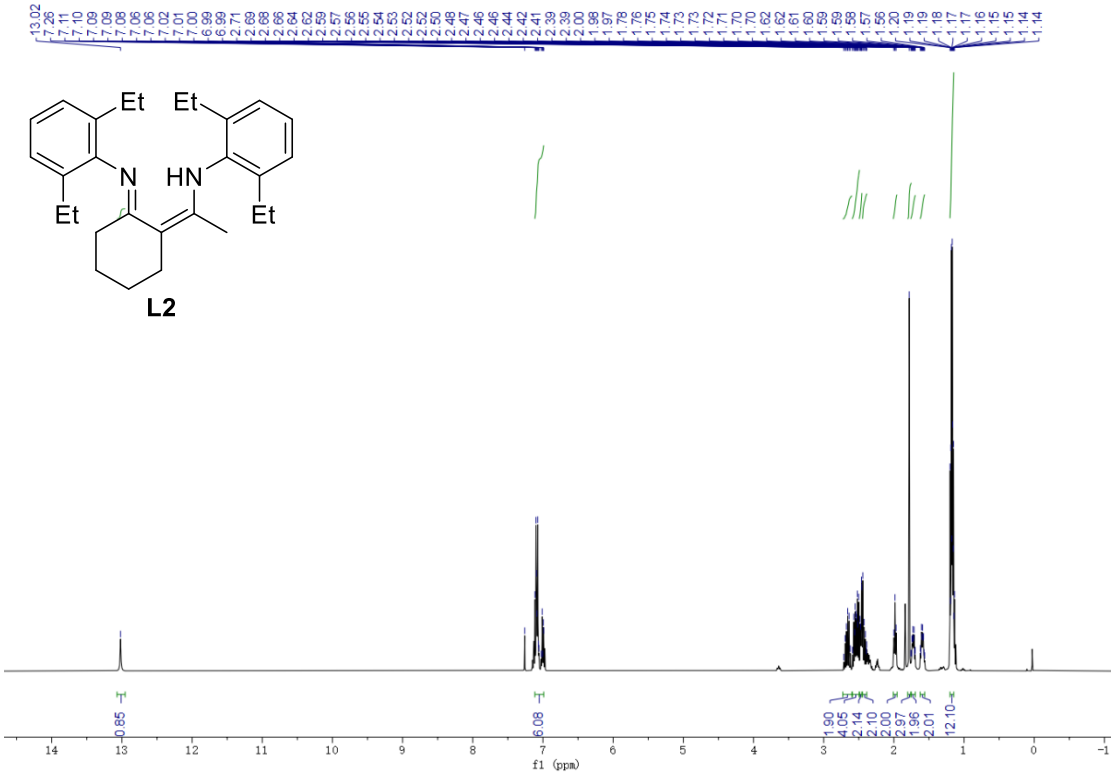


Figure S2.3 ^{1}H NMR spectrum of **L2** (400 MHz, $CDCl_3$).

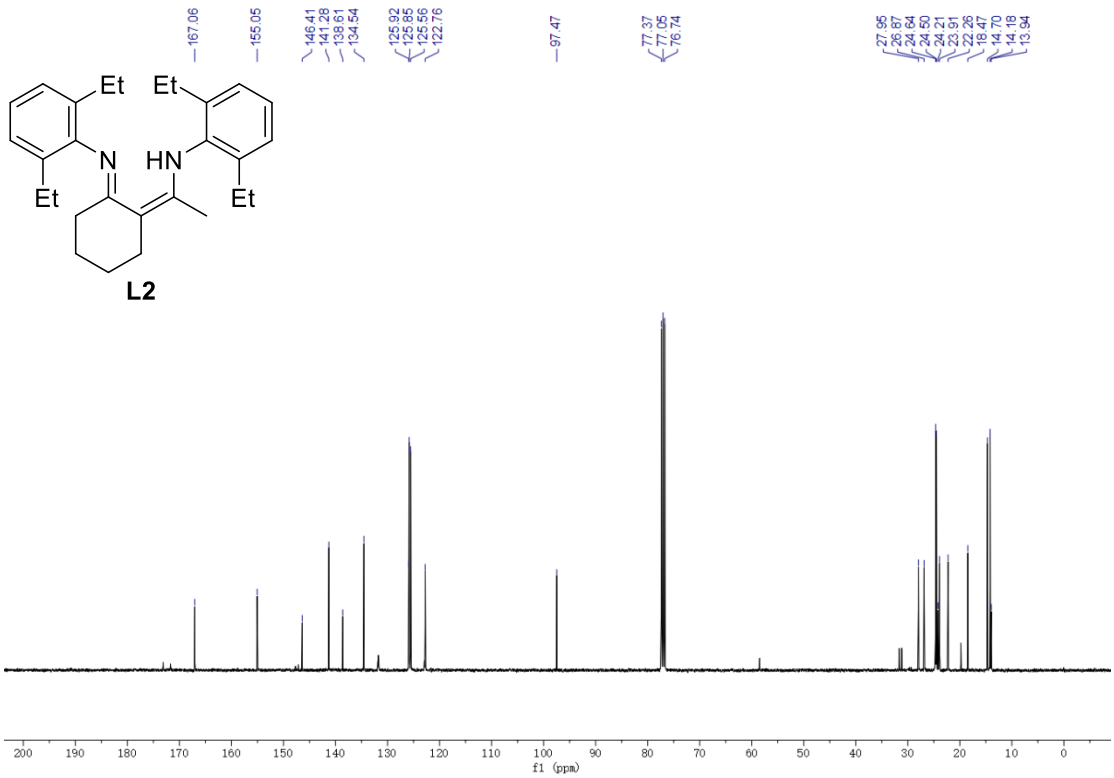


Figure S2.4 ^{13}C NMR spectrum of **L2** (101 MHz, $CDCl_3$).

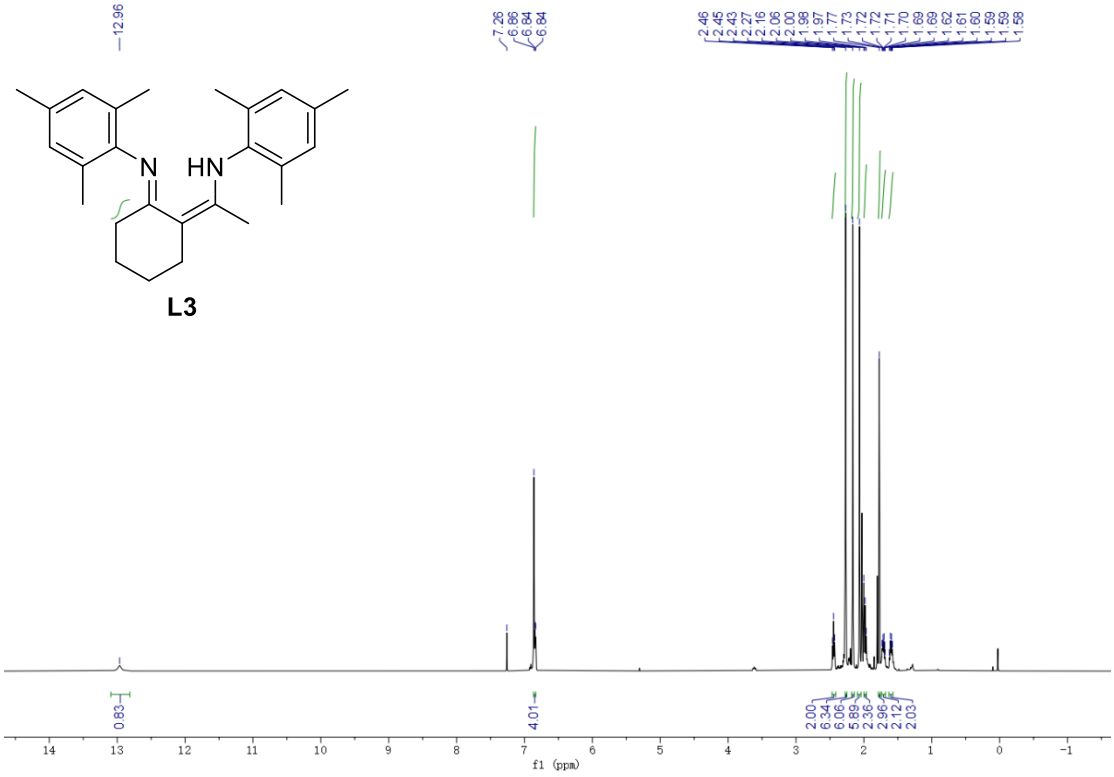


Figure S2.5 ^{1}H NMR spectrum of **L3** (400 MHz, $CDCl_3$).

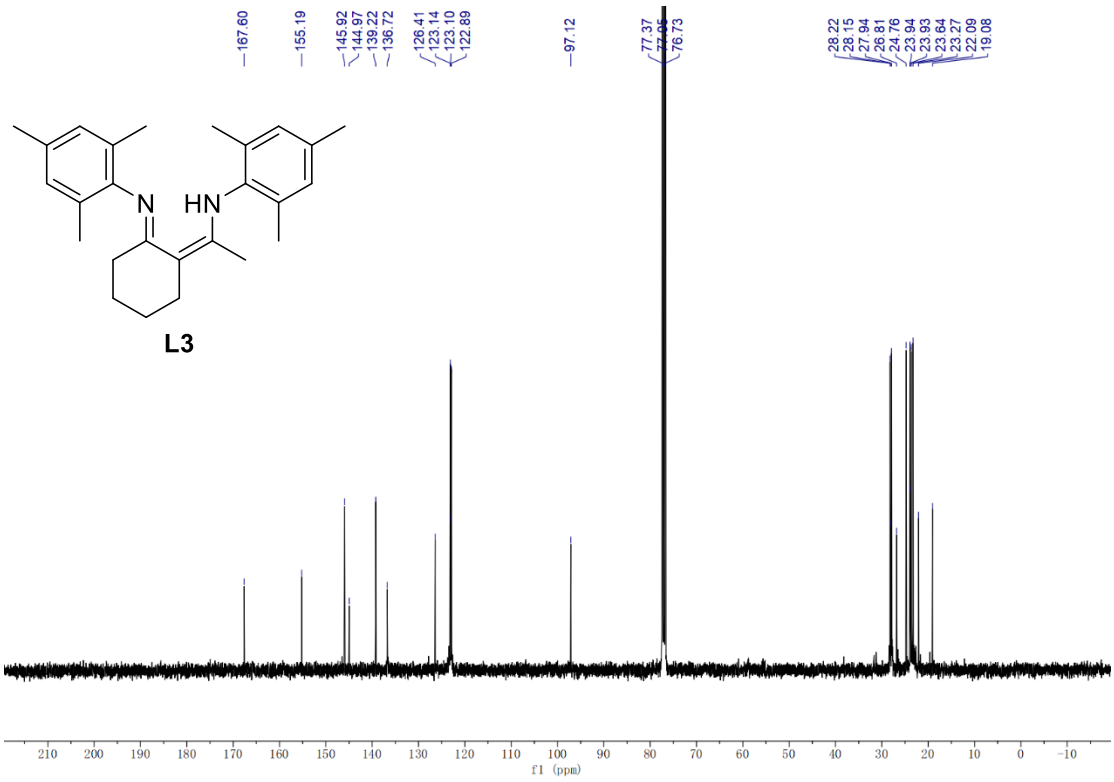
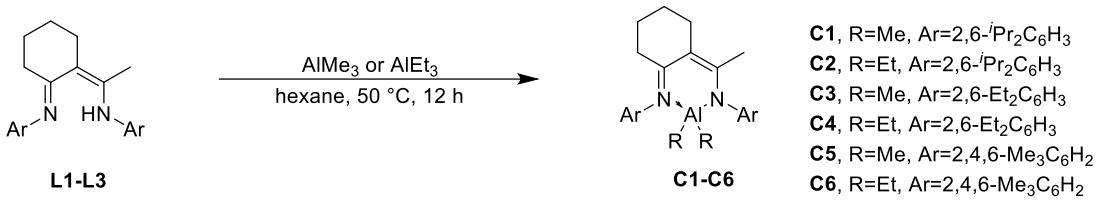


Figure S2.6 ^{13}C NMR spectrum of **L3** (101 MHz, $CDCl_3$).

e）Synthesis of C1-C6

Compounds **C1**–**C6** were synthesised following a similar procedure. Under a nitrogen atmosphere, ligand **L1**–**L3** (1.0 mmol) was dissolved in 10 mL of dry *n*-hexane in a flame-dried Schlenk flask and cooled to 0 °C using an ice bath. Subsequently, a 1.0 mL *n*-hexane solution of trimethylaluminium or triethylaluminium (1.0 mmol/mL, 1.0 mmol) was added dropwise over 5 minutes under continuous stirring. After the addition was complete, the reaction mixture was slowly warmed to room temperature and then heated to 50 °C, and stirred at this temperature for 12 hours. Upon completion of the reaction, the solvent was partially evaporated under reduced pressure to concentrate the solution to approximately 5 mL. The concentrated solution was then placed at –15 °C for 24 hours to allow crystallisation. The resulting yellow crystalline solids (**C1**–**C6**) were collected by filtration, washed with cold n-hexane, and dried under vacuum.



Scheme S2.4 Synthesis of **C1-C6.**

f）^{1}H and ^{13}C NMR data and spectra of C1-C6

Compound **C1**. 0.345 g, 64% yield; white solid; m.p. 181.1 – 184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 6H), 3.30 – 3.12 (m, 4H), 2.46 (t, *J* = 6.4 Hz, 2H), 2.06 (t, *J* = 6.6 Hz, 2H), 1.84 (s, 3H), 1.72 – 1.64 (m, 2H), 1.54 – 1.46 (m, 2H), 1.23 (t, *J* = 6.6 Hz, 12H), 1.15 – 1.08 (m, 12H), -1.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 167.7, 143.5, 143.1, 140.2, 140.1, 125.4, 124.8, 123.1, 123.0, 101.5, 30.9, 27.7, 27.0, 26.8, 24.4, 23.8, 23.6, 23.6, 22.1, 21.1, 20.5.

Compound **C2**. 0.266 g, 49% yield; light yellow solid; m.p. 173.4 – 176.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 6H), 3.33 – 3.21 (m, 4H), 2.42 (t, *J* = 6.3 Hz, 2H), 2.11 (t, *J* = 6.6 Hz, 2H), 1.85 (s, 3H), 1.69 – 1.61 (m, 2H), 1.55 – 1.46 (m, 2H), 1.28 (t, *J* = 6.9 Hz, 12H), 1.17 – 1.11 (m, 12H), 0.72 (t, *J* = 8.0 Hz, 6H), -0.29 – -0.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.0, 144.3, 143.8, 141.1, 141.0, 126.2, 125.8, 123.9, 123.8, 103.0, 31.4, 28.3, 27.6, 27.4, 25.1, 24.6, 24.5, 24.3, 22.7, 21.8, 21.2, 9.2.

Compound **C3**. 0.389 g, 85% yield; yellow solid; m.p. 116.6 – 118.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.01 (m, 6H), 2.73 – 2.60 (m, 4H), 2.57 – 2.48 (m, 4H), 2.46 (t, *J* = 6.2 Hz, 2H), 2.04 (t, *J* = 6.6 Hz, 2H), 1.83 (s, 3H), 1.72 – 1.65 (m, 2H), 1.57 – 1.48 (m, 2H), 1.27 - 1.16 (m, 12H), -1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 166.8, 141.4, 141.3, 138.1, 138.0, 124.8, 124.6, 124.5, 100.2, 30.4, 28.7, 27.6, 22.9, 22.7, 22.2, 21.3, 18.9, 13.1, 13.1, -10.8.

Compound **C4**. 0.350 g, 72% yield; yellow solid; m.p. 79.2 – 83.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.07 (m, 6H), 2.77 – 2.63 (m, 4H), 2.61 – 2.51 (m, 4H), 2.44 (t, *J* = 6.3 Hz, 2H), 2.07 (t, *J* = 6.6 Hz, 2H), 1.84 (s, 3H), 1.70 – 1.63 (m, 2H), 1.57 – 1.50 (m, 2H), 1.26 – 1.19 (m, 12H), 0.59 (t, *J* = 8.0 Hz, 6H), -0.45 – -0.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.2, 142.7, 142.7, 139.2, 139.0, 125.8, 125.6, 125.5, 102.5, 31.2,

28.6, 23.8, 23.6, 23.2, 22.3, 19.8, 14.2, 14.1, 9.1.

Compound **C5**. 0.381 g, 88% yield; yellow solid; m.p. 136.9 – 139.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 4.8 Hz, 4H), 2.45 (t, J = 6.3 Hz, 2H), 2.27 (d, J = 2.4 Hz, 6H), 2.14 (d, J = 2.7 Hz, 12H), 2.01 (t, J = 6.6 Hz, 2H), 1.79 (s, 3H), 1.69 – 1.63 (m, 2H), 1.57 – 1.50 (m, 2H), -1.15(s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.5, 140.0, 139.8, 133.7, 133.4, 132.5, 132.4, 128.1, 128.1, 99.8, 30.1, 27.7, 22.3, 21.5, 19.8, 19.8, 18.0, 17.8, -10.0.

Compound **C6**. 0.243 g, 53% yield; yellow solid; m.p. 81.7 – 84.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, J = 5.7 Hz, 4H), 2.43 (t, J = 6.2 Hz, 2H), 2.26 (d, J = 2.5 Hz, 6H), 2.18 (d, J = 4.4 Hz, 12H), 2.04 (t, J = 6.6 Hz, 2H), 1.80 (s, 3H), 1.68 – 1.61 (m, 2H), 1.57 – 1.50 (m, 2H), 0.62 (t, J = 8.0 Hz, 6H), -0.36 – -0.52 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 166.7, 140.3, 140.2, 133.6, 133.4, 132.4, 132.3, 128.1, 128.1, 101.1, 29.9, 27.7, 22.2, 21.5, 19.8, 17.9, 17.7, 8.0.

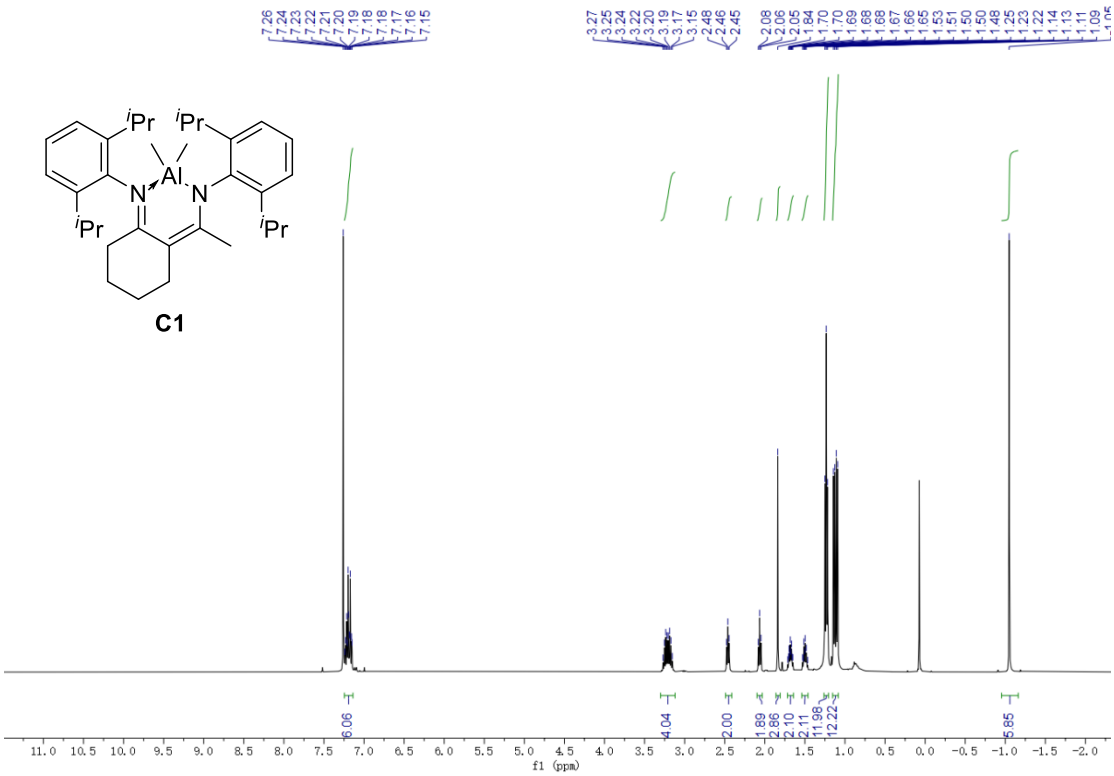


Figure S2.7 ^{1}H NMR spectrum of **C1** (400 MHz, $CDCl_3$).

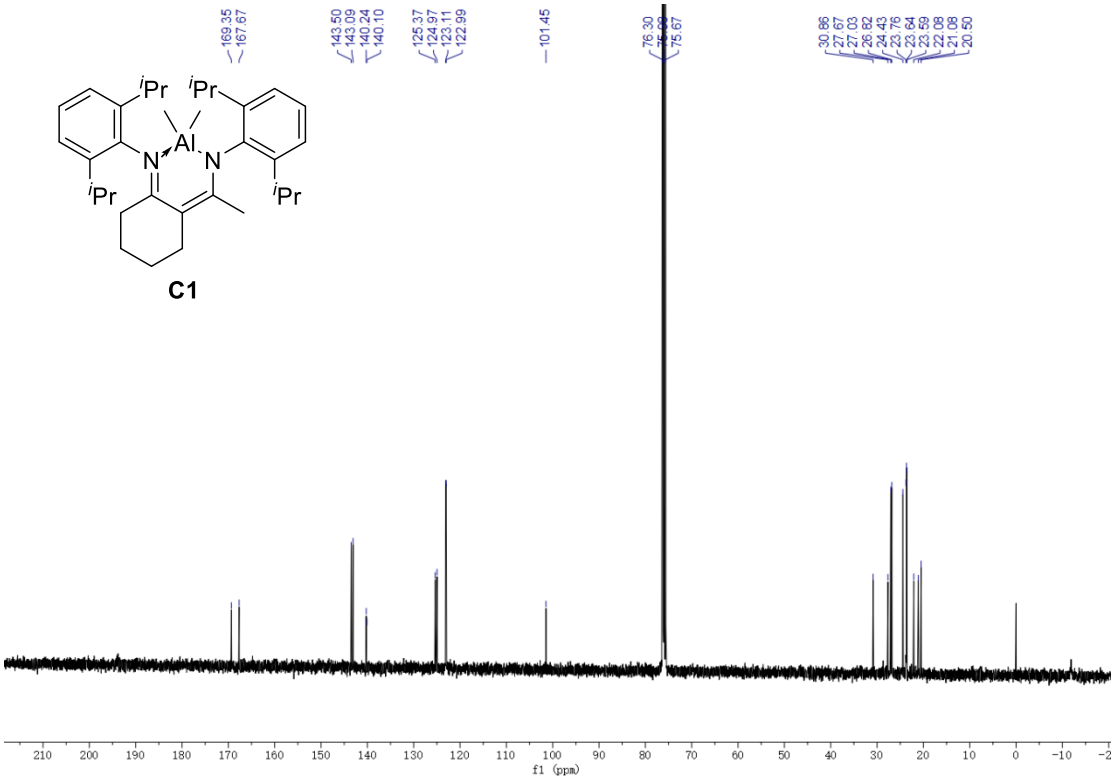


Figure S2.8^{13}C NMR spectrum of **C1** (101 MHz, $CDCl_3$).

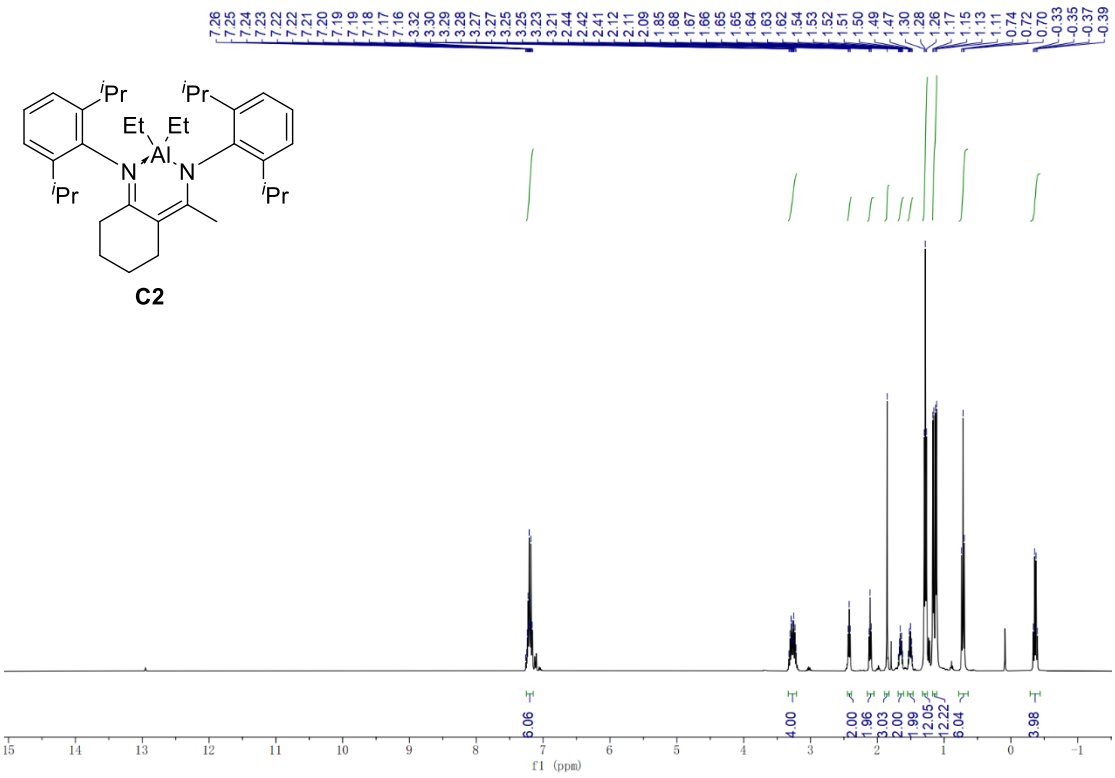


Figure S2.9 ^{1}H NMR spectrum of **C2** (400 MHz, $CDCl_3$).

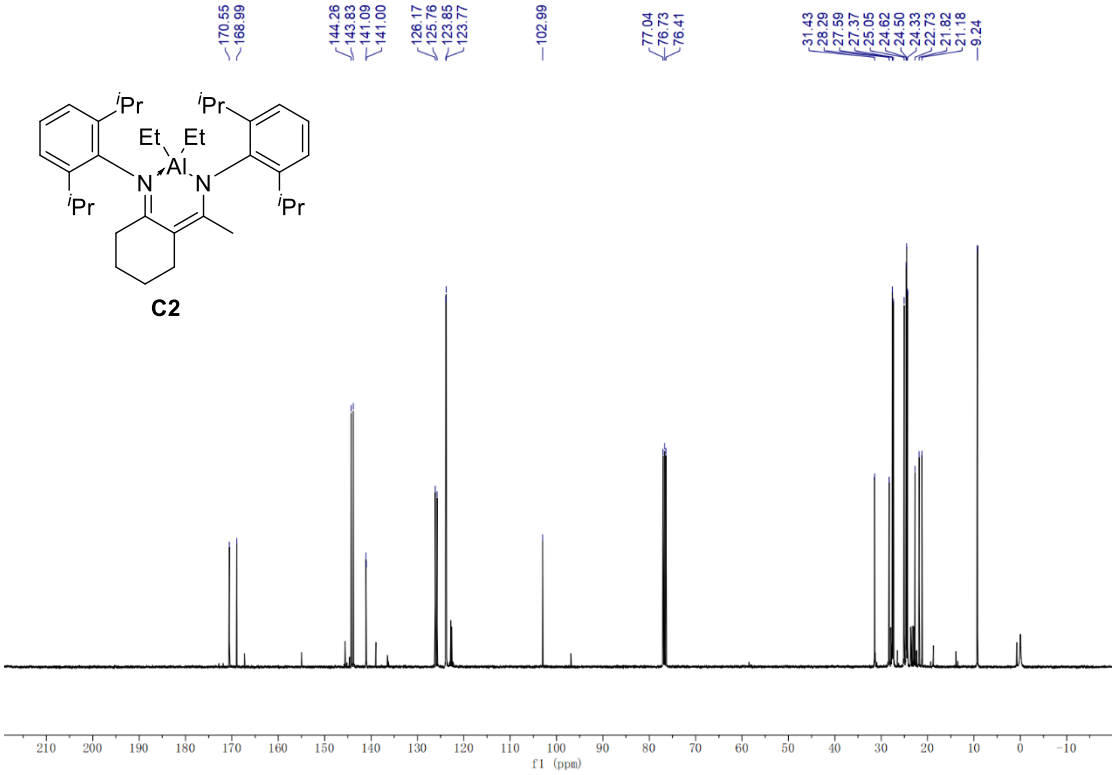


Figure S2.10 ^{13}C NMR spectrum of **C2** (101 MHz, $CDCl_3$).

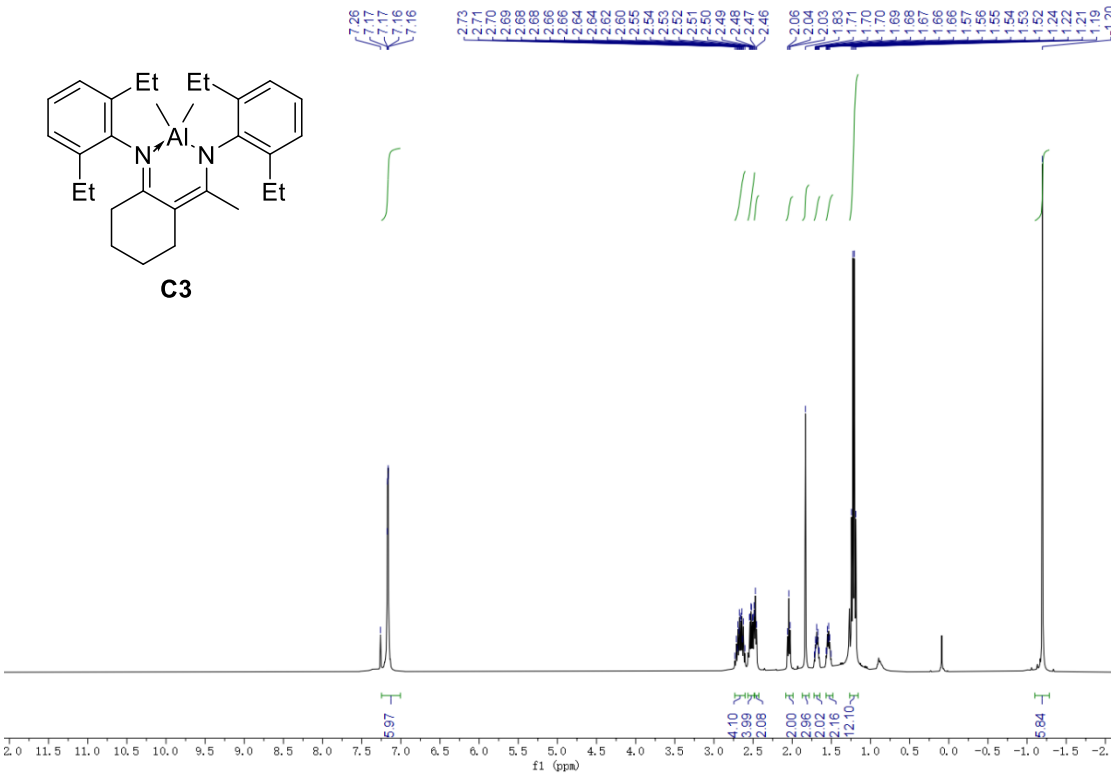


Figure S2.11 ^{1}H NMR spectrum of **C3** (400 MHz, $CDCl_3$).

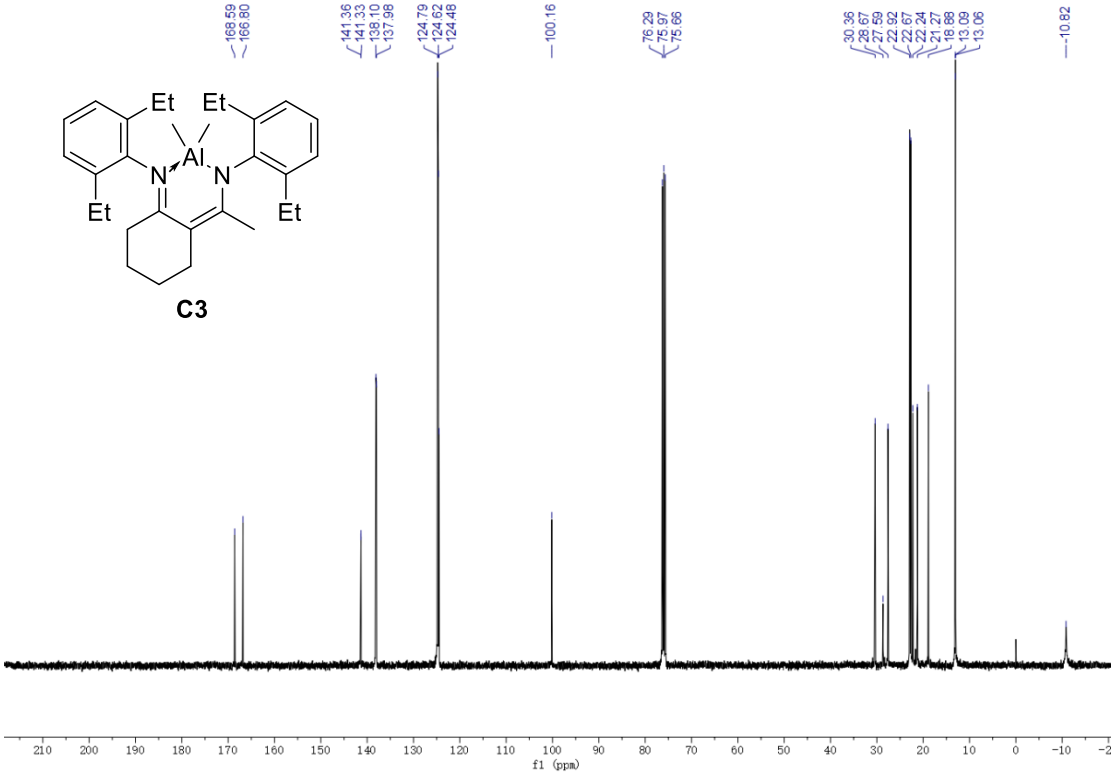


Figure S2.12 ^{13}C NMR spectrum of **C3** (101 MHz, $CDCl_3$).

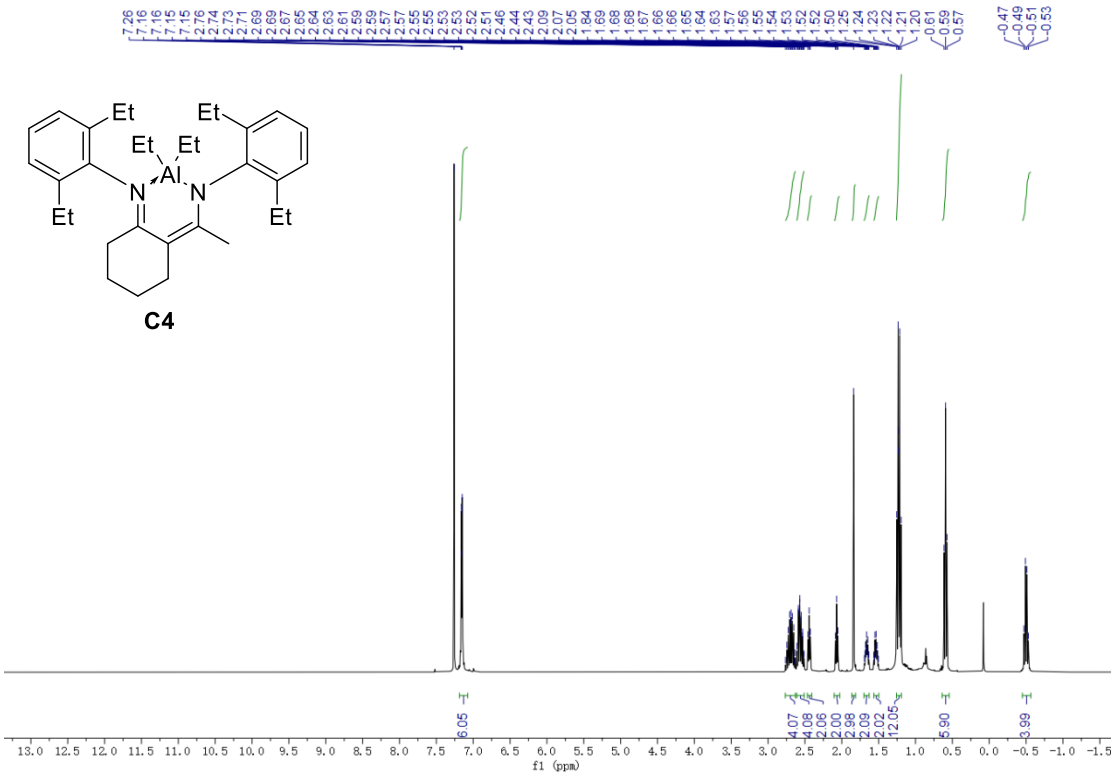


Figure S2.13 ^{1}H NMR spectrum of **C4** (400 MHz, $CDCl_3$).

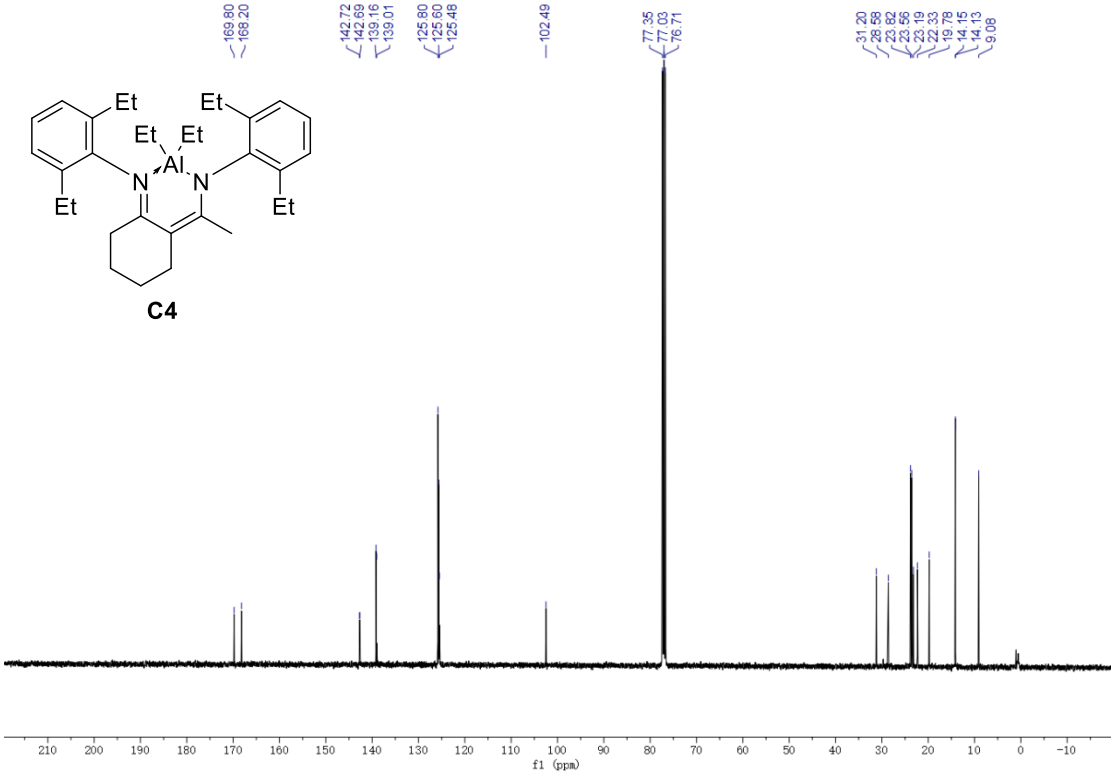


Figure S2.14 ^{13}C NMR spectrum of **C4** (101 MHz, $CDCl_3$).

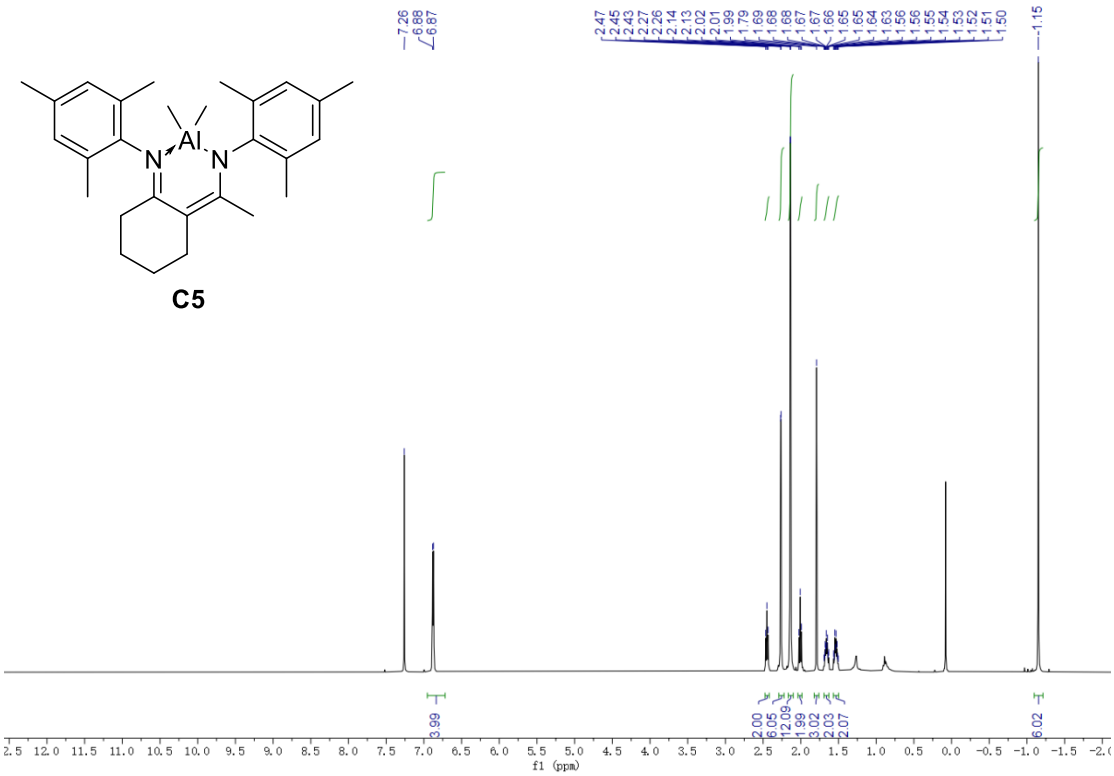


Figure S2.15 ^{1}H NMR spectrum of **C5** (400 MHz, $CDCl_3$).

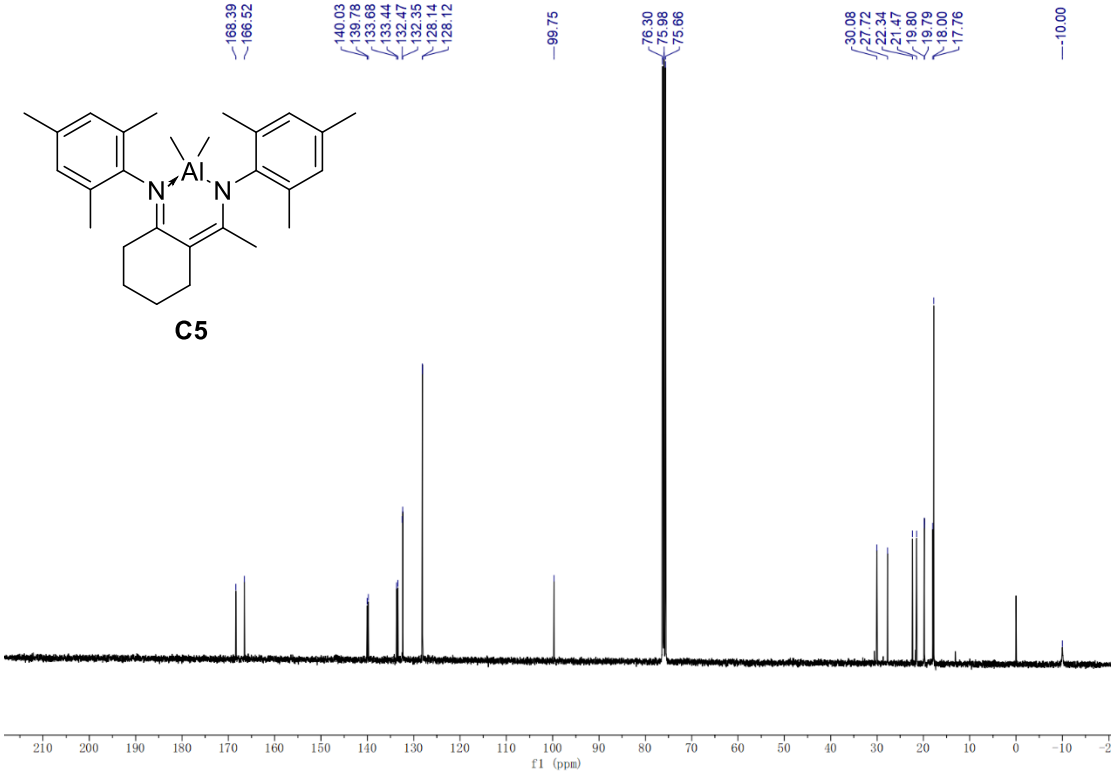


Figure S2.16 ^{13}C NMR spectrum of **C5** (101 MHz, $CDCl_3$).

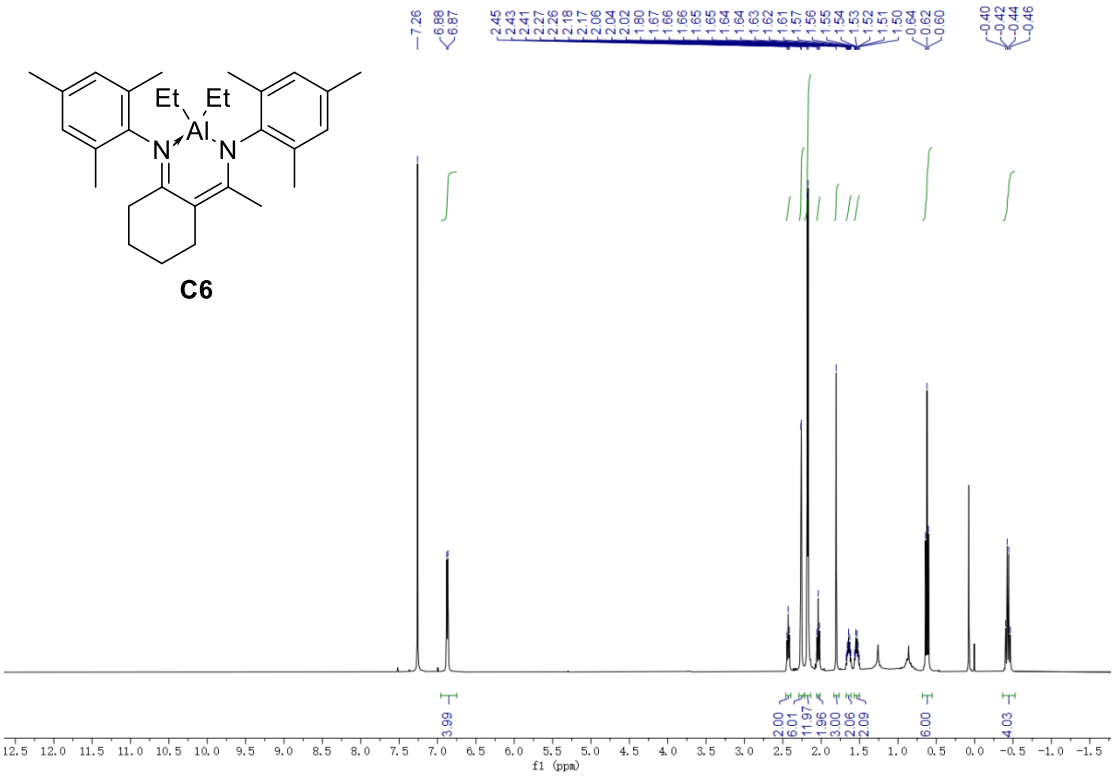


Figure S2.17 ^{1}H NMR spectrum of **C6** (400 MHz, $CDCl_3$).

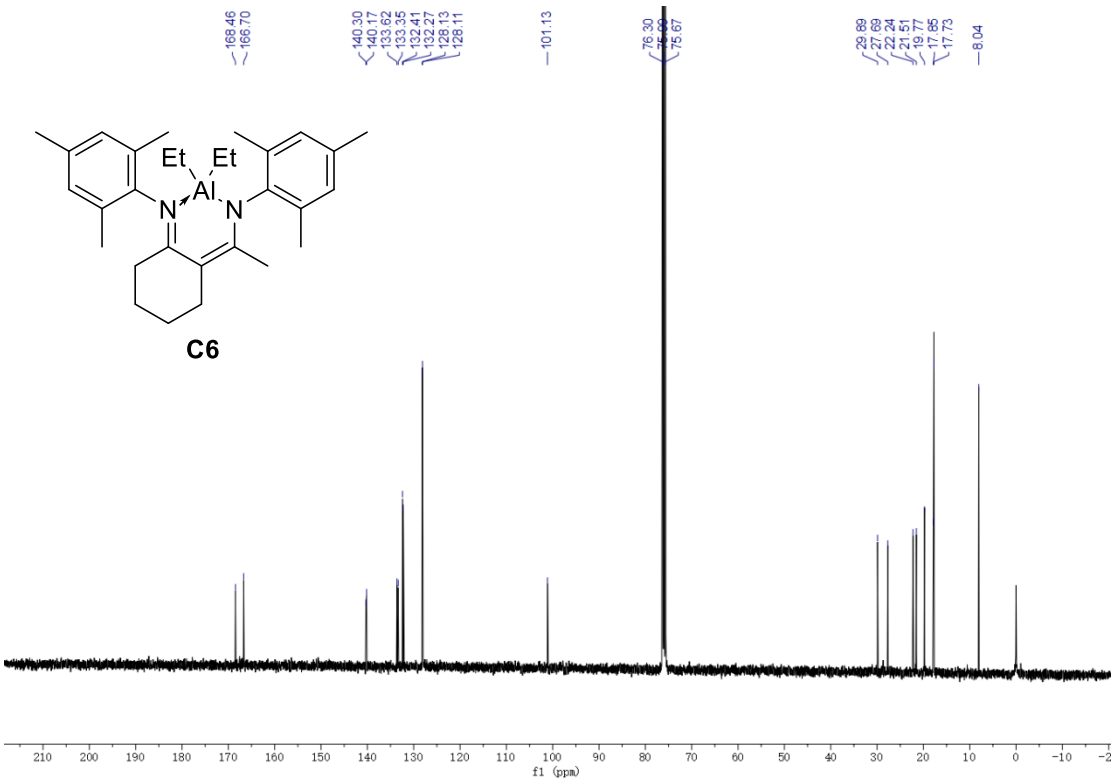


Figure S2.18 ^{13}C NMR spectrum of **C6** (101 MHz, $CDCl_3$).

g）Single crystal X-ray structure and refinement

The single-crystal structures of **C2**, **C3**, and **C5** were successfully obtained from the *n*-hexane mother liquor. Additionally, the single-crystal structure of the catalytic product **3w** was obtained from ethyl acetate. The crystal data were collected on a Rigaku Oxford diffractometer. Selected data collection parameters and other crystallographic results are summarized in **Table S2.1** and **Table S2.2**. Structure solution by direct methods was achieved through the use of the SHELXT program, and the structural model refined by full matrix least-squares on F^2 using SHELXL by using the Olex2 software.[3-5] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The molecular structures of **C2**, **C3** and **3w** are shown in Figures **S2.19–S2.21.**

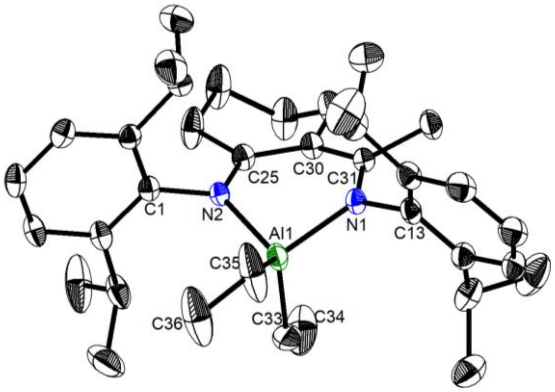


Figure S2.19 Molecular structure of **C2**. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity.

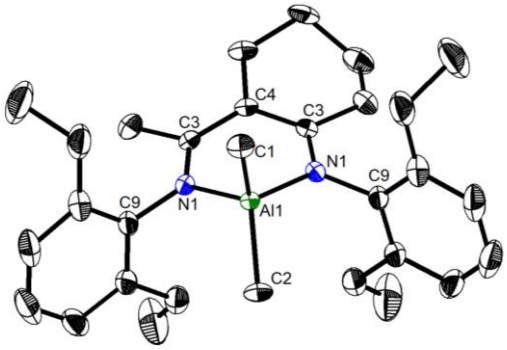


Figure S2.20 Molecular structure of **C3**. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity.

Table S2.1 Crystal data and structure refinement for **C2**, **C3** and **C5**.

Identification code	**C2**	**C3**	**C5**
CCDC	2426265	2426266	2426267
Empirical formula	$C_{36}H_{55}AlN_2$	$C_{30}H_{43}AlN_2$	$C_{28}H_{39}AlN_2$
Formula weight	542.8	458.64	430.59
Temperature/K	293(2)	99.99(10)	99.9(2)
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	Aem2	$P2_12_12_1$
a/Å	10.4055(4)	15.6163(7)	16.5787(4)
b/Å	25.6624(12)	22.5091(9)	20.7155(4)
c/Å	12.8303(6)	7.7370(5)	29.8150(6)
α/°	90	90	90
β/°	103.621(4)	90	90
γ/°	90	90	90
Volume/Å^3	3329.7(3)	2719.6(2)	10239.5(4)
Z	4	4	16
ρ_{calc}g/cm^3	1.083	1.12	1.117
μ/mm^{-1}	0.086	0.094	0.096
F(000)	1192	1000	3744
Crystal size/mm^3	0.34 × 0.21 × 0.15	0.13 × 0.12 × 0.1	0.15 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.572 to 61.97	7.242 to 62.162	3.932 to 61.676
Index ranges	-14 ≤ h ≤ 11, -35 ≤ k ≤ 37, -15 ≤ l ≤ 18	-19 ≤ h ≤ 21, -31 ≤ k ≤ 28, -10 ≤ l ≤ 9	-22 ≤ h ≤ 19, -27 ≤ k ≤ 26, -35 ≤ l ≤ 42
Reflections collected	23020	8882	66871
Independent reflections	8301 [R_{int} = 0.0917, R_{sigma} = 0.1008]	3279 [R_{int} = 0.0436, R_{sigma} = 0.0350]	24858 [R_{int} = 0.0424, R_{sigma} = 0.0621]
Data/restraints/parameters	8301/41/393	3279/20/182	24858/0/1153
Goodness-of-fit on F^2	1.102	1.079	1.04
Final R indexes [I>=2σ (I)]	R_1 = 0.0797, wR_2 = 0.2132	R_1 = 0.0636, wR_2 = 0.1627	R_1 = 0.0461, wR_2 = 0.1108
Final R indexes [all data]	R_1 = 0.1147, wR_2 = 0.2340	R_1 = 0.0670, wR_2 = 0.1645	R_1 = 0.0692, wR_2 = 0.1184
Largest diff. peak/hole / e Å^{-3}	0.84/-0.62	0.36/-0.24	0.48/-0.23

Table S2.2 Crystal data and structure refinement for **3w**.

Identification code	**3w**
CCDC	2426268
Empirical formula	$C_{25}H_{27}O_2P$
Formula weight	390.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.7275(3)
b/Å	20.7047(12)
c/Å	17.3578(11)
α/°	90
β/°	91.347(6)
γ/°	90
Volume/Å^3	2057.8(2)
Z	2
ρ_{calc}g/cm^3	1.26
μ/mm^{-1}	0.151
F(000)	832
Crystal size/mm^3	0.33 × 0.27 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.044 to 51.358
Index ranges	-6 ≤ h ≤ 6, -25 ≤ k ≤ 25, -18 ≤ l ≤ 21
Reflections collected	12550
Independent reflections	7069 [R_{int} = 0.0483, R_{sigma} = 0.0718]
Data/restraints/parameters	7069/1875/984
Goodness-of-fit on F^2	1.107
Final R indexes [I>=2σ (I)]	R_1 = 0.1083, wR_2 = 0.2806
Final R indexes [all data]	R_1 = 0.1171, wR_2 = 0.2867
Largest diff. peak/hole / e Å^{-3}	1.31/-0.72

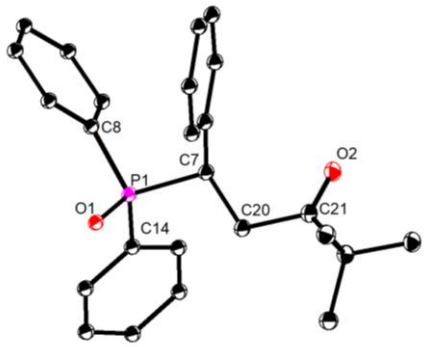


Figure S2.21 Molecular structure of **3w**. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity.

h）Comparison of Catalytic Performance with Previously Reported Complexes

Based on the optimisation studies presented in Table 1 of the main text, the optimal reaction conditions were identified as employing catalyst **C5** in toluene at 80 °C for 3 hours. Under these conditions, we further evaluated the catalytic performance of several related aluminium complexes previously synthesised by our group (**Fig. S2.22**), in order to compare their activities with that of **C5**. Unless otherwise specified, reactions were conducted under nitrogen atmosphere using **1a** (1 mmol), **2a** (1.2 equiv., 1.2 mmol), with stirring at the indicated temperature. The corresponding yields of the isolated products are summarised in **Table S2.3**.

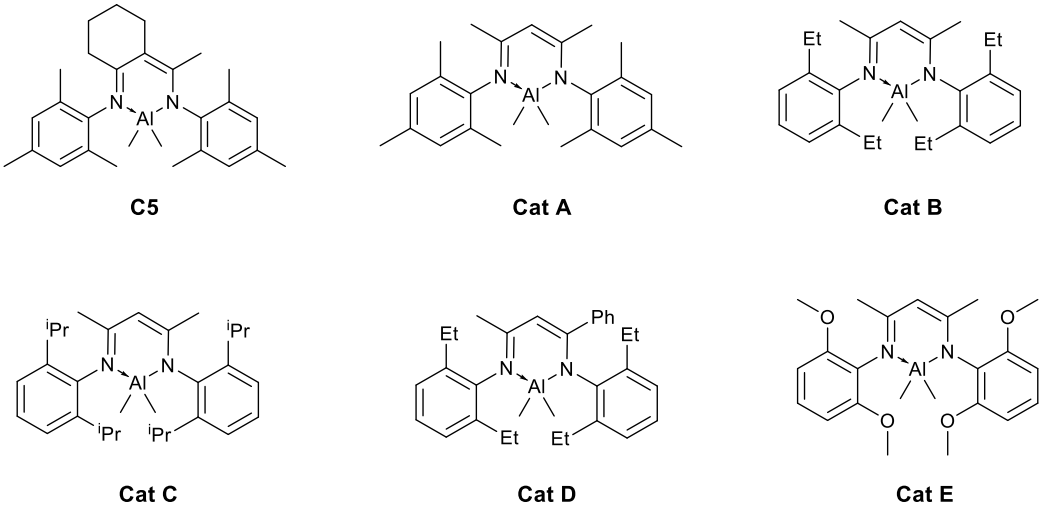
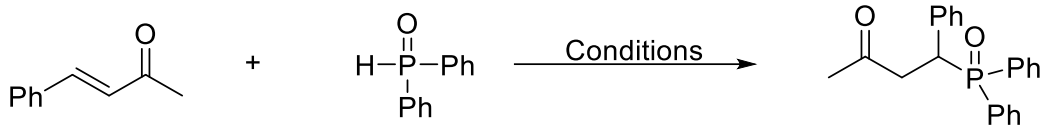


Figure S2.22 Comparative catalytic efficiencies of aluminium complexes in the hydrophosphinylation of *α,β*-unsaturated ketones

Table S2.3 Comparative catalytic efficiencies of aluminium complexes.[a]

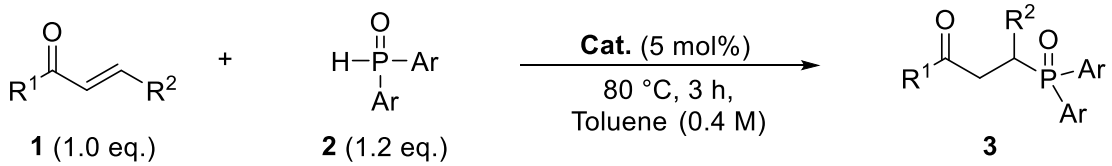


1a **2a** **3a**

entry	Cat. (mol%)	solvent	T (°C)	t (h)	yield (%)[b]
1	**C5 (5)**	**Tol**	**80**	**3**	**96**
2	Cat A	Tol	80	3	95
3	Cat B	Tol	80	3	81
4	Cat C	Tol	80	3	79
5	Cat D	Tol	80	3	83
6	Cat E	Tol	80	3	89

[a] Experimental conditions: 1a (1 mmol), 2a (1.2 equiv., 1.2 mmol), catalyst (mol%), and solvent (2.5 mL) stirred at the indicated temperature under nitrogen. [b] Isolated yields.

i）General Procedure for the Alkylaluminium-Catalyzed Hydrophosphinylation of *α,β*-Unsaturated Ketones



1 (1.0 eq.) **2** (1.2 eq.) **3**

Scheme S2.5 Synthesis of **3**

Under a nitrogen atmosphere, all operations were carried out either in a glovebox or using standard Schlenk techniques. *α,β*-Unsaturated ketone (1.0 mmol) and diarylphosphine oxide (1.2 mmol) were sequentially added to a flame-dried 10 mL Schlenk flask equipped with a magnetic stir bar. Subsequently, the catalyst (5 mol%) was added as a solid. Finally, distilled toluene (2.5 mL) was introduced via syringe under nitrogen protection. The reaction mixture was stirred and heated in an oil bath at 80 °C for 3 hours. Upon completion, the reaction mixture was allowed to cool to room temperature. The solvent was then removed under reduced pressure to afford a yellow crude product. The crude product was purified by flash column chromatography on silica gel using a mixture of dichloromethane and methanol (30:1, v/v) as the eluent, affording the desired product as a white or pale yellow powder.

j） Detailed Procedure for the Gram Synthesis of 3a and 3x

Under the atmosphere of nitrogen, 10 mmol **1a** (1.462 g) or **1x** (2.083 g) and 12 mmol (2.424 g) of **2a** were added to a 100 mL Schlenk reaction flask, followed by 1 mmol% **C5** (0.043 g), and finally 25 mL of redistilled toluene. The resulting solution was reacted under an oil bath at 80 °C for 24 h. After the solution was cooled, the solvent was drained to give a white crude product. The crude product was separated by column chromatography, dichloromethane: methanol=30:1, to obtain a white powder. **3a** was obtained with 2.96 g in 85% yield as white solid, **3x** was obtained with 3.56 g in 87% yield as white solid.

3. NMR data and spectra of *γ*-Ketophosphine Oxides

4-(Diphenylphosphoryl)-4-phenylbutan-2-one (**3a**). 96% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 7.61 – 7.48 (m, 3H), 7.48 – 7.37 (m, 2H), 7.36 – 7.26 (m, 3H), 7.26 – 7.20 (m, 2H), 7.19 – 7.09 (m, 3H), 4.22 (ddd, J = 10.2, 7.3, 2.9 Hz, 1H), 3.33 (ddd, J = 17.9, 10.1, 5.3 Hz, 1H), 2.94 (ddd, J = 18.0, 11.2, 2.9 Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4 (d, $J_{C–P}$ = 12.6 Hz), 135.9 (d, $J_{C–P}$ = 5.7 Hz), 132.0 (d, $J_{C–P}$ = 2.9 Hz), 131.9, 131.4 (d, $J_{C–P}$ = 2.9 Hz), 131.3 (d, $J_{C–P}$ = 8.5 Hz), 131.0 (d, $J_{C–P}$ = 2.9 Hz), 131.0 (d, $J_{C–P}$ = 8.9 Hz), 129.7 (d, $J_{C–P}$ = 5.6 Hz), 128.9 (d, $J_{C–P}$ = 11.3 Hz), 128.4 (d, $J_{C–P}$ = 1.9 Hz), 128.1 (d, $J_{C–P}$ = 11.8 Hz), 127.1 (d, $J_{C–P}$ = 2.5 Hz), 43.6, 41.1 (d, $J_{C–P}$ = 68.9 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.60.

4-(Diphenylphosphoryl)-4-(2-tolyl)butan-2-one (**3b**). 98% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.68 (d, J = 7.9 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.32 (d, J = 1.6 Hz, 1H), 7.24 – 7.11 (m, 5H), 7.10 – 7.03 (m, 1H), 6.89 (d, J = 7.5 Hz, 1H), 4.35 (ddd, J = 10.3, 7.5, 2.8 Hz, 1H), 3.30 (ddd, J = 18.0, 10.1, 5.1 Hz, 1H), 2.88 (ddd, J = 18.1, 11.1, 2.8 Hz, 1H), 1.98 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5 (d, $J_{C–P}$ = 13.1 Hz), 137.3 (d, $J_{C–P}$ = 6.4 Hz), 134.3 (d, $J_{C–P}$ = 5.7 Hz), 132.3, 132.2 (d, $J_{C–P}$ = 2.7 Hz), 131.7 (d, $J_{C–P}$ = 8.3 Hz), 131.5 (d, $J_{C–P}$ = 2.8 Hz), 131.2 (d, $J_{C–P}$ = 23.5 Hz), 130.9 (d, $J_{C–P}$ = 9.3 Hz), 130.1 (d, $J_{C–P}$ = 2.1 Hz), 129.0 (d, $J_{C–P}$ = 11.2 Hz), 128.8, 127.8 (d, $J_{C–P}$ = 11.7 Hz), 127.1 (d, $J_{C–P}$ = 2.7 Hz), 126.3 (d, $J_{C–P}$ = 2.4 Hz), 44.4, 36.1 (d, $J_{C–P}$ = 68.7 Hz), 30.5, 19.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.14.

4-(Diphenylphosphoryl)-4-(3-tolyl)butan-2-one (**3c**). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.57 – 7.49 (m, 3H), 7.45 – 7.38 (m, 2H), 7.34 – 7.29 (m, 1H), 7.25 – 7.19 (m, 2H), 7.09 – 7.00 (m, 3H), 6.95 – 6.88 (m, 1H), 4.11 (ddd, J = 10.3, 7.5, 2.9 Hz, 1H), 3.24 (ddd, J = 17.9, 10.1, 5.4 Hz, 1H), 2.86 (ddd, J = 18.0, 11.3, 3.0 Hz, 1H), 2.97 – 2.87 (m, 1H), 2.19 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5 (d, $J_{C–P}$ = 12.7 Hz), 137.9 (d, $J_{C–P}$ = 2.1 Hz), 135.6 (d, $J_{C–P}$ = 5.5 Hz), 132.0 (d, $J_{C–P}$ = 2.8 Hz), 131.9 (d, $J_{C–P}$ = 5.4 Hz), 131.4, 131.3 (d, $J_{C–P}$ = 8.6 Hz), 131.1 (d, $J_{C–P}$ = 8.8 Hz), 131.0, 130.5 (d, $J_{C–P}$ = 5.6 Hz), 128.9 (d, $J_{C–P}$ = 11.2 Hz), 128.2 (d, $J_{C–P}$ = 2.0 Hz), 128.0 (d,

J_{C-P} = 11.8 Hz), 127.9 (d, J_{C-P} = 2.6 Hz), 126.8 (d, J_{C-P} = 5.8 Hz), 43.5, 41.0 (d, J_{C-P} = 68.6 Hz), 30.7, 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.53.

4-(Diphenylphosphoryl)-4-(4-tolyl)butan-2-one (**3d**). 91% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.80 (m, 2H), 7.62 – 7.38 (m, 5H), 7.36 – 7.28 (m, 1H), 7.26 – 7.20 (m, 2H), 7.20 – 7.11 (m, 2H), 6.96 (d, J = 7.8 Hz, 2H), 4.12 (ddd, J = 10.2, 7.4, 2.9 Hz, 1H), 3.21 (ddd, J = 17.8, 10.2, 5.4 Hz, 1H), 2.84 (ddd, J = 17.9, 11.1, 2.9 Hz, 1H), 2.22 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5 (d, J_{C-P} = 12.9 Hz), 136.7 (d, J_{C-P} = 2.6 Hz), 132.7 (d, J_{C-P} = 5.6 Hz), 132.1 (d, J_{C-P} = 2.1 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 131.2 (d, J_{C-P} = 7.9 Hz), 131.0 (d, J_{C-P} = 8.8 Hz), 129.6 (d, J_{C-P} = 5.7 Hz), 129.1 (d, J_{C-P} = 1.9 Hz), 128.8 (d, J_{C-P} = 11.3 Hz), 128.1 (d, J_{C-P} = 11.8 Hz), 43.6, 40.7 (d, J_{C-P} = 69.1 Hz), 30.7, 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.40.

4-(Diphenylphosphoryl)-4-(4-Chlorophenyl)butan-2-one (**3e**). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.60 – 7.49 (m, 3H), 7.50 – 7.42 (m, 2H), 7.39 – 7.32 (m, 1H), 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 2H), 7.13 (d, J = 8.5 Hz, 2H), 4.20 (ddd, J = 10.1, 7.2, 2.9 Hz, 1H), 3.27 (ddd, J = 18.1, 10.2, 5.1 Hz, 1H), 2.92 (ddd, J = 18.1, 11.0, 2.9 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0 (d, J_{C-P} = 12.7 Hz), 134.6 (d, J_{C-P} = 5.5 Hz), 133.0 (d, J_{C-P} = 2.9 Hz), 132.1 (d, J_{C-P} = 2.8 Hz), 131.8, 131.6 (d, J_{C-P} = 3.0 Hz), 131.2 (d, J_{C-P} = 8.6 Hz), 131.0 (d, J_{C-P} = 5.8 Hz), 130.9 (d, J_{C-P} = 8.8 Hz), 130.7 (d, J_{C-P} = 4.7 Hz), 130.0 (d, J_{C-P} = 11.3 Hz), 128.5 (d, J_{C-P} = 2.1 Hz), 128.3 (d, J_{C-P} = 11.8 Hz), 43.6, 40.4 (d, J_{C-P} = 68.6 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.15.

4-(Diphenylphosphoryl)-4-(4-fluorophenyl)butan-2-one (**3f**). 92% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (ddd, J = 10.8, 7.9, 1.6 Hz, 2H), 7.52 – 7.43 (m, 3H), 7.41 – 7.34 (m, 2H), 7.27 (d, J = 6.0 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.18 (dd, J = 3.1, 1.3 Hz, 2H), 6.84 – 6.73 (m, 2H), 4.13 (ddd, J = 10.1, 7.1, 2.9 Hz, 1H), 3.20 (ddd, J = 18.0, 10.3, 5.1 Hz, 1H), 2.84 (ddd, J = 18.1, 10.9, 2.9 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2 (d, J_{C-P} = 12.8 Hz), 161.9 (dd, J_{C-F} = 246.1, 2.6 Hz), 132.1 (d, J_{C-P} = 2.9 Hz), 131.9, 131.7 (s), 131.6 (d, J_{C-P} = 2.8 Hz), 131.2 (d, J_{C-P} = 8.5 Hz), 131.2 (d, J_{C-P} = 13.4 Hz), 130.9 (d, J_{C-P} = 8.8 Hz), 129.0 (d, J_{C-P} = 11.3 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 115.4 (d, J_{C-P}

= 1.9 Hz), 115.2 (d, J_{C-P} = 2.0 Hz), 43.7, 40.2 (d, J_{C-P} = 69.1 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.38. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.20.

4-(Diphenylphosphoryl)-4-(4-bromophenyl)butan-2-one (3g). 88% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddt, J = 10.9, 6.6, 1.6 Hz, 2H), 7.56 – 7.34 (m, 5H), 7.33 – 7.26 (m, 1H), 7.24 – 7.20 (m, 3H), 7.18 (dd, J = 3.0, 1.2 Hz, 1H), 7.12 (dd, J = 8.5, 1.9 Hz, 2H), 4.11 (ddd, J = 10.1, 7.1, 2.8 Hz, 1H), 3.19 (ddd, J = 18.1, 10.2, 5.1 Hz, 1H), 2.84 (ddd, J = 18.1, 11.0, 2.8 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0 (d, J_{C-P} = 12.7 Hz), 135.1 (d, J_{C-P} = 5.6 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 131.8, 131.7 (d, J_{C-P} = 2.5 Hz), 131.5 (d, J_{C-P} = 1.9 Hz), 131.4 (d, J_{C-P} = 5.7 Hz), 131.2 (d, J_{C-P} = 8.5 Hz), 130.9 (d, J_{C-P} = 8.9 Hz), 130.7 (d, J_{C-P} = 3.9 Hz), 129.0 (d, J_{C-P} = 11.4 Hz), 128.3 (d, J_{C-P} = 11.8 Hz), 121.3 (d, J_{C-P} = 3.2 Hz), 43.6, 40.5 (d, J_{C-P} = 68.4 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.96.

4-(Diphenylphosphoryl)-4-(4-hydroxyphenyl)butan-2-one (3h). 98% yield, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 8.07 – 7.89 (m, 2H), 7.73 – 7.64 (m, 2H), 7.60 – 7.51 (m, 3H), 7.42 – 7.28 (m, 3H), 7.16 – 7.05 (m, 2H), 6.57 – 6.47 (m, 2H), 4.35 (ddd, J = 10.9, 7.5, 3.1 Hz, 1H), 3.13 (ddd, J = 16.9, 11.3, 5.9 Hz, 1H), 2.60 (ddd, J = 16.7, 9.4, 3.0 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 210.8 (d, J_{C-P} = 14.3 Hz), 161.2 (d, J_{C-P} = 2.2 Hz), 138.3 (d, J_{C-P} = 43.0 Hz), 137.3 (d, J_{C-P} = 49.8 Hz), 136.9 (d, J_{C-P} = 2.7 Hz), 136.4 (d, J_{C-P} = 2.7 Hz), 136.0 (d, J_{C-P} = 4.6 Hz), 135.9 (d, J_{C-P} = 4.5 Hz), 135.8 (d, J_{C-P} = 5.6 Hz), 134.0 (d, J_{C-P} = 11.0 Hz), 133.3 (d, J_{C-P} = 11.4 Hz), 131.1 (d, J_{C-P} = 5.9 Hz), 120.0 (d, J_{C-P} = 1.9 Hz), 48.0, 44.3 (d, J_{C-P} = 69.0 Hz), 35.4. ^{31}P NMR (162 MHz, DMSO-d_6) δ 31.67.

4-(Diphenylphosphoryl)-4-(4-methoxyphenyl)butan-2-one (3i). 95% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddt, J = 9.7, 6.4, 1.7 Hz, 2H), 7.51 – 7.35 (m, 5H), 7.30 – 7.24 (m, 1H), 7.19 – 7.10 (m, 4H), 6.69 – 6.58 (m, 2H), 4.09 (ddd, J = 10.3, 7.4, 2.9 Hz, 1H), 3.64 (s, 3H), 3.20 (ddd, J = 17.8, 10.3, 5.3 Hz, 1H), 2.82 (ddd, J = 17.9, 10.8, 2.9 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5 (d, J_{C-P} = 13.0 Hz), 157.6 (d, J_{C-P} = 2.2 Hz), 131.1 (d, J_{C-P} = 7.5 Hz), 130.9 (d, J_{C-P} = 2.8 Hz), 130.4 (d, J_{C-P} = 2.9 Hz), 130.3 (d, J_{C-P} = 8.5 Hz), 130.1, 130.0 (d, J_{C-P} = 8.8 Hz), 129.7 (d, J_{C-P} = 5.6 Hz),

127.8 (d, $J_{C–P}$ = 11.3 Hz), 127.1 (d, $J_{C–P}$ = 11.7 Hz), 126.6 (d, $J_{C–P}$ = 5.6 Hz), 112.8 (d, $J_{C–P}$ = 1.9 Hz), 54.1, 42.7, 39.2 (d, $J_{C–P}$ = 69.5 Hz), 29.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.57.

4-(4-(Dimethylamino)phenyl)-4-(diphenylphosphoryl)butan-2-one (3j). 77% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (ddd, J = 10.2, 7.6, 1.8 Hz, 2H), 7.47 – 7.36 (m, 5H), 7.29 – 7.23 (m, 1H), 7.17 (dd, J = 7.5, 2.8 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.56 – 6.41 (m, 2H), 4.06 (ddd, J = 10.4, 7.6, 2.9 Hz, 1H), 3.18 (ddd, J = 17.5, 10.3, 5.5 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.78 (s, 6H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8 (d, $J_{C–P}$ = 13.1 Hz), 149.6 (d, $J_{C–P}$ = 1.9 Hz), 132.4 (d, $J_{C–P}$ = 3.4 Hz), 131.8 (d, $J_{C–P}$ = 2.8 Hz), 131.5 (d, $J_{C–P}$ = 10.6 Hz), 131.4 (d, $J_{C–P}$ = 8.5 Hz), 131.3, 131.2 (d, $J_{C–P}$ = 8.8 Hz), 130.4 (d, $J_{C–P}$ = 5.6 Hz), 128.8 (d, $J_{C–P}$ = 11.1 Hz), 128.0 (d, $J_{C–P}$ = 11.6 Hz), 123.0 (d, $J_{C–P}$ = 5.7 Hz), 112.5 (d, $J_{C–P}$ = 1.8 Hz), 43.7, 40.5, 40.2 (d, $J_{C–P}$ = 69.9 Hz), 30.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.63.

4-(Diphenylphosphoryl)-4-(4-nitrophenyl)butan-2-one (3k). 98% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.87 (ddt, J = 11.0, 6.5, 1.6 Hz, 2H), 7.50 (dddd, J = 12.4, 6.6, 4.6, 3.3 Hz, 3H), 7.45 – 7.37 (m, 4H), 7.33 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 4.27 (ddd, J = 10.0, 7.0, 2.8 Hz, 1H), 3.27 (ddd, J = 18.5, 10.3, 5.0 Hz, 1H), 2.92 (ddd, J = 18.5, 10.9, 2.8 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5 (d, $J_{C–P}$ = 12.3 Hz), 146.9 (d, $J_{C–P}$ = 2.9 Hz), 144.1 (d, $J_{C–P}$ = 5.4 Hz), 132.4 (d, $J_{C–P}$ = 2.7 Hz), 132.0 (d, $J_{C–P}$ = 2.8 Hz), 131.3, 131.2 (d, $J_{C–P}$ = 8.6 Hz), 130.7 (d, $J_{C–P}$ = 9.0 Hz), 130.6 (d, $J_{C–P}$ = 5.5 Hz), 130.2 (d, $J_{C–P}$ = 16.3 Hz), 129.1 (d, $J_{C–P}$ = 11.4 Hz), 128.5 (d, $J_{C–P}$ = 11.9 Hz), 123.4 (d, $J_{C–P}$ = 1.9 Hz), 43.5, 41.2 (d, $J_{C–P}$ = 66.6 Hz), 30.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.54.

4-(Diphenylphosphoryl)-4-(4-(trifluoromethyl)phenyl)butan-2-one (3l). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (ddt, J = 11.0, 6.5, 1.7 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.43 – 7.31 (m, 6H), 7.30 – 7.25 (m, 1H), 7.20 – 7.14 (m, 2H), 4.22 (ddd, J = 10.1, 7.1, 2.9 Hz, 1H), 3.25 (ddd, J = 18.3, 10.2, 5.1 Hz, 1H), 2.89 (ddd, J = 18.3, 11.1, 2.9 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8 (d, $J_{C–P}$ = 12.5 Hz), 140.4 (d, $J_{C–P}$ = 5.3 Hz), 132.3 (d, $J_{C–P}$ = 2.8 Hz), 131.7 (d, $J_{C–P}$ = 2.9 Hz), 131.5 (d, $J_{C–P}$ = 13.9 Hz), 131.2 (d, $J_{C–P}$ = 8.5 Hz), 130.8 (d, $J_{C–P}$ = 8.9 Hz), 130.5 (d, $J_{C–P}$ = 9.1 Hz), 130.0 (d, $J_{C–P}$ = 5.6 Hz), 129.4, 129.0 (d, $J_{C–P}$ = 11.5 Hz), 128.3 (d, $J_{C–P}$ = 11.8 Hz), 125.2, 124.0 (d, $J_{C–P}$ =

272.1 Hz), 43.5, 41.0 (d, $J_{C–P}$ = 67.8 Hz), 30.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.03. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.61.

4-(1-(Diphenylphosphoryl)-3-oxobutyl)benzonitrile (3m). 96% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (ddt, *J* = 10.8, 8.0, 1.2 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.42 – 7.34 (m, 6H), 7.32 – 7.26 (m, 1H), 7.21 – 7.14 (m, 2H), 4.23 – 4.16 (m, 1H), 3.24 (ddd, *J* = 18.5, 10.2, 5.1 Hz, 1H), 2.90 (ddd, *J* = 18.5, 11.0, 2.8 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6 (d, $J_{C–P}$ = 12.4 Hz), 141.9 (d, $J_{C–P}$ = 5.5 Hz), 132.4 (d, $J_{C–P}$ = 2.6 Hz), 132.0 (d, $J_{C–P}$ = 1.9 Hz), 131.9 (d, $J_{C–P}$ = 2.8 Hz), 131.4, 131.2 (d, $J_{C–P}$ = 8.5 Hz), 130.7 (d, $J_{C–P}$ = 8.9 Hz), 130.5 (d, $J_{C–P}$ = 5.5 Hz), 130.3 (d, $J_{C–P}$ = 21.1 Hz), 129.1 (d, $J_{C–P}$ = 11.5 Hz), 128.4 (d, $J_{C–P}$ = 12.0 Hz), 118.6 (d, $J_{C–P}$ = 1.6 Hz), 111.0 (d, $J_{C–P}$ = 2.6 Hz), 43.4, 41.3 (d, $J_{C–P}$ = 66.8 Hz), 30.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.73.

4-(Diphenylphosphoryl)-4-(naphthalen-2-yl)butan-2-one (3n). 87% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.71 (t, *J* = 2.1 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.28 (m, 8H), 7.16 (q, *J* = 1.4 Hz, 1H), 7.09 (ddd, *J* = 8.6, 6.7, 3.0 Hz, 2H), 4.32 (ddd, *J* = 10.2, 7.4, 2.9 Hz, 1H), 3.34 (ddd, *J* = 18.0, 10.1, 5.3 Hz, 1H), 2.94 (ddd, *J* = 18.0, 11.1, 2.9 Hz, 1H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2 (d, $J_{C–P}$ = 12.7 Hz), 132.6 (d, $J_{C–P}$ = 5.6 Hz), 132.2 (d, $J_{C–P}$ = 1.9 Hz), 131.4 (d, $J_{C–P}$ = 1.8 Hz), 131.1, 131.0 (d, $J_{C–P}$ = 2.8 Hz), 130.9, 130.4 (d, $J_{C–P}$ = 2.8 Hz), 130.3 (d, $J_{C–P}$ = 8.5 Hz), 130.1, 130.0 (d, $J_{C–P}$ = 9.0 Hz), 127.9 (d, $J_{C–P}$ = 11.3 Hz), 127.7 (d, $J_{C–P}$ = 6.8 Hz), 127.1 (d, $J_{C–P}$ = 11.8 Hz), 127.0 (d, $J_{C–P}$ = 1.5 Hz), 126.9, 126.7 (d, $J_{C–P}$ = 4.9 Hz), 126.5, 124.8 (d, $J_{C–P}$ = 14.3 Hz), 42.8, 40.2 (d, $J_{C–P}$ = 68.6 Hz), 29.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.32.

4-(Diphenylphosphoryl)-4-(pyridin-2-yl)butan-2-one (3o). 91% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.31 (m, 1H), 7.81 – 7.73 (m, 2H), 7.52 (ddd, *J* = 11.4, 8.3, 1.4 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.41 (dt, *J* = 8.5, 3.3 Hz, 2H), 7.33 (td, *J* = 7.9, 1.8 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.96 – 6.91 (m, 1H), 4.45 (td, *J* = 10.9, 3.0 Hz, 1H), 3.61 (ddd, *J* = 18.0, 10.5, 5.7 Hz, 1H), 2.92 (ddd, *J* = 18.0, 10.4, 3.0 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5 (d, $J_{C–P}$ = 13.0 Hz), 155.6 (d, $J_{C–P}$ = 5.2 Hz), 149.1 (d, $J_{C–P}$ = 2.1 Hz), 136.0 (d, $J_{C–P}$ = 2.2 Hz), 132.0 (d, $J_{C–P}$ = 2.8 Hz), 131.9, 131.7 (d, $J_{C–P}$ = 2.9 Hz), 131.4 (d, $J_{C–P}$ = 18.4 Hz), 131.4, 130.7 (d, $J_{C–P}$ = 50.7 Hz), 128.7

(d, J_{C-P} = 11.6 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 124.8 (d, J_{C-P} = 3.8 Hz), 121.9 (d, J_{C-P} = 2.5 Hz), 44.4 (d, J_{C-P} = 65.4 Hz), 41.7, 30.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.39.

4-(Diphenylphosphoryl)-4-(thiophen-2-yl)butan-2-one (3p). 82% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (ddd, *J* = 10.9, 8.0, 1.6 Hz, 2H), 7.53 – 7.39 (m, 5H), 7.32 (td, *J* = 7.3, 1.5 Hz, 1H), 7.27 – 7.20 (m, 2H), 6.98 (d, *J* = 3.8 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 4.51 (ddd, *J* = 10.6, 8.0, 2.9 Hz, 1H), 3.20 (ddd, *J* = 17.8, 10.2, 5.0 Hz, 1H), 2.86 (ddd, *J* = 17.8, 10.3, 2.9 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0 (d, J_{C-P} = 12.3 Hz), 137.5 (d, J_{C-P} = 6.3 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 131.7 (d, J_{C-P} = 2.8 Hz), 131.5 (d, J_{C-P} = 3.5 Hz), 131.3 (d, J_{C-P} = 8.6 Hz), 131.1 (d, J_{C-P} = 8.8 Hz), 130.5 (d, J_{C-P} = 9.5 Hz), 128.9 (d, J_{C-P} = 11.3 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 127.3 (d, J_{C-P} = 6.5 Hz), 126.8 (d, J_{C-P} = 2.6 Hz), 124.9 (d, J_{C-P} = 2.9 Hz), 44.4, 36.6 (d, J_{C-P} = 70.5 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.49.

4-(diphenylphosphoryl)-4-(furan-2-yl)butan-2-one (3q). 74% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (ddd, *J* = 11.2, 8.2, 1.5 Hz, 2H), 7.51 (m, 3H), 7.47 – 7.38 (m, 3H), 7.32 (m, 2H), 7.18 – 7.09 (m, 1H), 6.14 (dd, *J* = 3.3, 1.9 Hz, 1H), 5.96 (d, *J* = 3.3 Hz, 1H), 4.46 (ddd, J = 10.7, 10.7, 3.2 Hz, 1H), 3.22 (ddd, J = 18.0, 10.5, 5.5 Hz, 1H), 2.96 (ddd, J = 18.0, 10.0, 3.2 Hz, 1H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9 (d, J_{C-P} = 12.1 Hz), 148.9 (d, J_{C-P} = 6.5 Hz), 141.8 (d, J_{C-P} = 3.0 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 131.9 (d, J_{C-P} = 2.8 Hz), 131.4, 131.3, 130.9 (d, J_{C-P} = 18.7 Hz), 130.6 (d, J_{C-P} = 6.5 Hz), 128.8 (d, J_{C-P} = 11.5 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 110.8 (d, J_{C-P} = 2.7 Hz), 108.7 (d, J_{C-P} = 6.1 Hz), 40.8, 35.9 (d, J_{C-P} = 70.1 Hz), 30.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.18.

4-Cyclohexyl-4-(diphenylphosphoryl)butan-2-one (3r). 61% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.66 (m, 4H), 7.44 – 7.27 (m, 6H), 3.19 – 3.03 (m, 1H), 2.72 – 2.63 (m, 2H), 2.07 – 1.95 (m, 1H), 1.85 (s, 3H), 1.59 (ddd, *J* = 33.0, 12.9, 2.6 Hz, 3H), 1.50 – 1.41 (m, 2H), 1.09 – 0.83 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2 (d, J_{C-P} = 8.2 Hz), 132.3 (d, J_{C-P} = 9.1 Hz), 131.4 (d, J_{C-P} = 10.3 Hz), 130.5 (d, J_{C-P} = 5.2 Hz), 130.5, 130.0 (d, J_{C-P} = 8.6 Hz), 129.8 (d, J_{C-P} = 8.8 Hz), 127.6 (d, J_{C-P} = 22.1 Hz), 127.6, 36.9, 36.7 (d, J_{C-P} = 1.7 Hz), 35.6 (d, J_{C-P} = 71.8 Hz), 31.9 (d, J_{C-P} = 12.8 Hz), 28.8, 28.4 (d, J_{C-P} = 2.7 Hz), 25.6, 25.1 (d, J_{C-P} = 29.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.60.

4-(Diphenylphosphoryl)nonan-2-one (3s). 75% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.68 (m, 4H), 7.45 – 7.33 (m, 6H), 3.09 (tdd, J = 10.5, 7.4, 3.9 Hz, 1H), 2.71 (ddd, J = 19.5, 15.9, 3.8 Hz, 1H), 2.60 – 2.53 (m, 1H), 1.91 (s, 3H), 1.54 (tdd, J = 14.4, 9.5, 4.5 Hz, 1H), 1.40 (ddd, J = 13.8, 9.2, 4.7 Hz, 1H), 1.24 – 1.14 (m, 1H), 1.13 – 0.98 (m, 5H), 0.76 – 0.65 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0 (d, $J_{C–P}$ = 9.8 Hz), 130.7 (d, $J_{C–P}$ = 2.2 Hz), 130.7 (d, $J_{C–P}$ = 7.3 Hz), 130.7 (d, $J_{C–P}$ = 1.9 Hz), 130.0, 129.9 (d, $J_{C–P}$ = 1.9 Hz), 129.9, 127.7 (d, $J_{C–P}$ = 2.2 Hz), 127.6 (d, $J_{C–P}$ = 2.4 Hz), 40.8, 30.6, 30.5 (d, $J_{C–P}$ = 72.8 Hz), 29.0, 27.5 (d, $J_{C–P}$ = 2.1 Hz), 26.3 (d, $J_{C–P}$ = 10.8 Hz), 21.3, 12.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.75.

4-(Diphenylphosphoryl)-6-phenylhex-5-en-2-one (3t). 65% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (ddd, J = 11.0, 8.1, 1.6 Hz, 2H), 7.69 (ddd, J = 11.1, 8.1, 1.5 Hz, 2H), 7.49 – 7.31 (m, 6H), 7.18 – 7.07 (m, 5H), 6.30 (dd, J = 15.9, 4.2 Hz, 1H), 5.98 (ddd, J = 15.8, 9.2, 6.4 Hz, 1H), 3.95 – 3.80 (m, 1H), 2.91 (ddd, J = 17.7, 9.8, 5.3 Hz, 1H), 2.83 – 2.72 (m, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2 (d, $J_{C–P}$ = 12.8 Hz), 135.6 (d, $J_{C–P}$ = 2.8 Hz), 134.2 (d, $J_{C–P}$ = 11.5 Hz), 131.0 (d, $J_{C–P}$ = 2.9 Hz), 131.1, 130.8 (d, $J_{C–P}$ = 2.9 Hz), 130.4 (d, $J_{C–P}$ = 8.8 Hz), 130.2 (d, $J_{C–P}$ = 8.7 Hz), 129.9 (d, $J_{C–P}$ = 21.8 Hz), 127.8(d, $J_{C–P}$ = 11.4 Hz), 127.4, 127.4 (d, $J_{C–P}$ = 11.7 Hz), 126.7, 125.3 (d, $J_{C–P}$ = 1.7 Hz), 122.3 (d, $J_{C–P}$ = 7.4 Hz), 40.7, 37.9 (d, $J_{C–P}$ = 70.2 Hz), 29.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.47.

4-(Diphenylphosphoryl)-6-phenylhex-5-yn-2-one (3u). 58% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.79 (m, 4H), 7.55 – 7.37 (m, 6H), 7.19 – 7.04 (m, 5H), 4.11 (ddd, J = 16.8, 10.5, 3.0 Hz, 1H), 3.09 (ddd, J = 17.5, 9.5, 3.0 Hz, 1H), 2.80 (ddd, J = 17.5, 10.5, 5.2 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3 (d, $J_{C–P}$ = 11.8 Hz), 132.4 (d, $J_{C–P}$ = 7.1 Hz), 132.4, 132.2 (d, $J_{C–P}$ = 8.6 Hz), 131.6, 131.5, 131.5 (d, $J_{C–P}$ = 6.2 Hz), 130.5 (d, $J_{C–P}$ = 14.7 Hz), 129.5, 128.7 (d, $J_{C–P}$ = 11.9 Hz), 128.4 (d, $J_{C–P}$ = 11.8 Hz), 128.2, 122.6 (d, $J_{C–P}$ = 3.4 Hz), 85.7 (d, $J_{C–P}$ = 8.5 Hz), 85.2 (d, $J_{C–P}$ = 7.7 Hz), 41.9, 30.2, 29.3 (d, $J_{C–P}$ = 71.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.72.

3-(Diphenylphosphoryl)-1-phenylhexan-1-one (3v). 91% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.71 (m, 6H), 7.43 (d, J = 11.0 Hz, 4H), 7.32 (d, J = 6.8 Hz, 5H), 3.38 (tt, J = 6.4, 3.0 Hz, 1H), 3.29 – 3.07 (m, 2H), 1.55 (dddd, J = 24.4, 14.0, 7.7, 4.3 Hz, 2H), 1.27 – 1.04 (m, 2H), 0.69 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

197.6 (d, J_{C-P} = 10.9 Hz), 136.4, 133.4, 132.8 (d, J_{C-P} = 20.5 Hz), 131.9, 131.7 (d, J_{C-P} = 4.7 Hz), 131.7, 131.0 (d, J_{C-P} = 1.5 Hz), 130.9 (d, J_{C-P} = 1.4 Hz), 128.8 (d, J_{C-P} = 1.5 Hz), 128.7 (d, J_{C-P} = 1.6 Hz), 128.6, 128.1, 37.1, 31.5 (d, J_{C-P} = 73.1 Hz), 30.9 (d, J_{C-P} = 2.1 Hz), 21.0 (d, J_{C-P} = 11.0 Hz), 14.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.35.

1-(Diphenylphosphoryl)-4,4-dimethyl-1-phenylpentan-3-one (3w). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (ddd, J = 10.7, 7.6, 1.9 Hz, 2H), 7.52 – 7.40 (m, 3H), 7.39 – 7.30 (m, 2H), 7.23 (ddd, J = 7.2, 5.9, 1.6 Hz, 3H), 7.14 (ddd, J = 8.5, 6.7, 3.0 Hz, 2H), 7.10 – 6.99 (m, 3H), 4.20 (ddd, J = 9.7, 6.6, 2.7 Hz, 1H), 3.40 (ddd, J = 17.8, 10.1, 4.7 Hz, 1H), 2.76 (ddd, J = 17.8, 11.5, 2.7 Hz, 1H), 0.80 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5 (d, J_{C-P} = 12.1 Hz), 135.1 (d, J_{C-P} = 5.4 Hz), 131.2 (d, J_{C-P} = 36.7 Hz), 130.9 (d, J_{C-P} = 2.6 Hz), 130.3 (d, J_{C-P} = 3.3 Hz), 130.3 (d, J_{C-P} = 8.4 Hz), 130.3 (d, J_{C-P} = 31.1 Hz), 129.9 (d, J_{C-P} = 8.8 Hz), 128.9 (d, J_{C-P} = 5.8 Hz), 127.8 (d, J_{C-P} = 11.3 Hz), 127.2 (d, J_{C-P} = 1.9 Hz), 127.0 (d, J_{C-P} = 11.8 Hz), 126.0 (d, J_{C-P} = 2.4 Hz), 43.1, 40.1 (d, J_{C-P} = 69.4 Hz), 36.5, 24.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.14.

3-(Diphenylphosphoryl)-1,3-diphenylpropan-1-one (3x). 98% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.85 (m, 2H), 7.76 (d, J = 7.7 Hz, 2H), 7.52 – 7.34 (m, 6H), 7.28 (dq, J = 12.7, 7.4, 5.3 Hz, 5H), 7.15 (dd, J = 8.0, 2.9 Hz, 2H), 7.05 (dt, J = 14.2, 7.2 Hz, 3H), 4.40 (ddd, J = 9.9, 6.7, 2.4 Hz, 1H), 3.94 (ddd, J = 18.2, 10.3, 4.4 Hz, 1H), 3.31 (ddd, J = 18.2, 11.3, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7 (d, J_{C-P} = 13.2 Hz), 136.4, 136.0 (d, J_{C-P} = 5.6 Hz), 133.4, 132.1 (d, J_{C-P} = 25.7 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 2.9 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 131.2, 131.0 (d, J_{C-P} = 8.9 Hz), 129.9 (d, J_{C-P} = 5.6 Hz), 129.0 (d, J_{C-P} = 11.3 Hz), 128.6, 128.3 (d, J_{C-P} = 2.0 Hz), 128.1, 128.0, 127.1 (d, J_{C-P} = 2.6 Hz), 41.1 (d, J_{C-P} = 69.0 Hz), 39.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.24.

3-(Diphenylphosphoryl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (3y). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 2H), 7.75 (dd, J = 7.7, 2.1 Hz, 2H), 7.40 (ddt, J = 11.5, 5.5, 2.0 Hz, 6H), 7.30 – 7.16 (m, 7H), 6.66 – 6.52 (m, 2H), 4.35 (ddd, J = 10.4, 6.9, 2.4 Hz, 1H), 3.88 (ddd, J = 18.0, 10.4, 4.3 Hz, 1H), 3.59 (s, 3H), 3.26 (ddd, J = 18.0, 10.9, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8 (d, J_{C-P} = 13.5 Hz), 158.6 (d, J_{C-P} = 2.3 Hz), 136.5, 133.3, 132.3 (d, J_{C-P} = 23.5 Hz), 132.0 (d, J_{C-P} = 2.8 Hz), 131.4 (d, J_{C-P} = 2.9 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 131.2, 131.0 (d, J_{C-P} = 8.8 Hz), 130.9 (d,

J_{C-P} = 5.8 Hz), 128.9 (d, J_{C-P} = 11.1 Hz), 128.6, 128.1 (d, J_{C-P} = 11.6 Hz), 128.1, 127.8 (d, J_{C-P} = 5.8 Hz), 113.8 (d, J_{C-P} = 2.2 Hz), 55.1, 40.2 (d, J_{C-P} = 70.1 Hz), 39.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.22.

3-(Diphenylphosphoryl)-3-(4-fluorophenyl)-1-phenylpropan-1-one (3z). 94% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (ddd, J = 10.7, 7.4, 2.0 Hz, 2H), 7.79 – 7.69 (m, 2H), 7.52 – 7.36 (m, 6H), 7.34 – 7.24 (m, 5H), 7.22 – 7.19 (m, 2H), 6.76 (t, J = 8.7 Hz, 2H), 4.38 (ddd, J = 10.6, 6.8, 2.4 Hz, 1H), 3.89 (ddd, J = 18.1, 10.5, 4.2 Hz, 1H), 3.28 (ddd, J = 18.1, 10.8, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6 (d, J_{C-P} = 13.3 Hz), 160.9 (dd, J_{C-F} = 246.1, 2.6 Hz), 135.3, 132.4, 131.1 (d, J_{C-P} = 3.0 Hz), 130.8 (d, J_{C-P} = 3.3 Hz), 130.7, 130.7, 130.6 (d, J_{C-P} = 2.8 Hz), 130.4, 130.3 (d, J_{C-P}= 2.3 Hz), 130.3, 130.2, 129.9 (d, J_{C-P} = 29.1 Hz), 129.9 (d, J_{C-P} = 9.0 Hz), 128.0 (d, J_{C-P} = 11.2 Hz), 127.3 (d, J_{C-P} = 52.1 Hz), 127.2 (d, J_{C-P} = 11.8 Hz), 114.2 (dd, J_{C-F} = 21.3, 1.9 Hz), 39.3 (d, J_{C-P} = 69.4 Hz), 38.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.30

3-(Diphenylphosphoryl)-3-(4-chlorophenyl)-1-phenylpropan-1-one (3aa). 95% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 2H), 7.80 – 7.70 (m, 2H), 7.43 (dddd, J = 12.7, 6.5, 3.3, 1.6 Hz, 6H), 7.34 – 7.19 (m, 7H), 7.08 – 6.98 (m, 2H), 4.37 (ddd, J = 10.5, 6.8, 2.4 Hz, 1H), 3.88 (ddd, J = 18.1, 10.5, 4.3 Hz, 1H), 3.28 (ddd, J = 18.2, 10.8, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4 (d, J_{C-P} = 13.2 Hz), 135.2, 133.6 (d, J_{C-P} = 5.6 Hz), 132.5, 132.0 (d, J_{C-P} = 2.9 Hz), 131.1 (d, J_{C-P} = 2.7 Hz), 130.8 (d, J_{C-P} = 25.6 Hz), 130.6 (d, J_{C-P} = 2.7 Hz), 130.1 (d, J_{C-P} = 16.1 Hz), 130.1 (d, J_{C-P} = 1.8 Hz), 129.9 (d, J_{C-P} = 9.0 Hz), 129.7, 128.0 (d, J_{C-P} = 11.3 Hz), 127.6, 127.5 (d, J_{C-P} = 2.0 Hz), 127.2 (d, J_{C-P} = 11.8 Hz), 127.1, 39.5 (d, J_{C-P} = 68.9 Hz), 38.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.75.

3-(Diphenylphosphoryl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (3ab). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (td, J = 8.2, 7.7, 3.6 Hz, 2H), 7.75 (d, J = 8.6 Hz, 2H), 7.47 – 7.35 (m, 5H), 7.27 (dd, J = 25.6, 7.5 Hz, 3H), 7.16 (dt, J = 7.8, 3.8 Hz, 2H), 7.04 (dt, J = 14.8, 7.2 Hz, 3H), 6.75 (d, J = 8.5 Hz, 2H), 4.40 (ddd, J = 9.9, 6.7, 2.3 Hz, 1H), 3.89 (ddd, J = 18.0, 10.4, 4.3 Hz, 1H), 3.72 (s, 3H), 3.24 (ddd, J = 17.9, 11.4, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1 (d, J_{C-P} = 13.2 Hz), 162.6, 135.1 (d, J_{C-P} = 5.6 Hz), 131.2 (d, J_{C-P} = 30.3 Hz), 130.9 (d, J_{C-P} = 2.8 Hz), 130.3, 130.3 (d, J_{C-P} = 6.3 Hz), 130.1, 129.9 (d, J_{C-P} = 8.9 Hz), 129.4, 128.8 (d, J_{C-P} = 5.8 Hz), 128.5, 127.9 (d, J_{C-P} = 11.1

Hz), 127.2 (d, $J_{C–P}$ = 2.0 Hz), 127.0 (d, $J_{C–P}$ = 11.8 Hz), 126.0(d, $J_{C–P}$ = 2.5 Hz), 112.6, 54.4, 40.1 (d, $J_{C–P}$ = 69.2 Hz), 37.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.35.

3-(Diphenylphosphoryl)-1-(4-fluorophenyl)-3-phenylpropan-1-one (3ac). 92% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 2H), 7.78 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.49 – 7.35 (m, 5H), 7.32 – 7.23 (m, 3H), 7.16 (dd, *J* = 7.2, 3.1 Hz, 2H), 7.10 – 6.99 (m, 3H), 6.96 (t, *J* = 8.7 Hz, 2H), 4.37 (ddd, *J* = 9.8, 6.9, 2.6 Hz, 1H), 3.89 (ddd, *J* = 18.0, 10.3, 4.7 Hz, 1H), 3.29 (ddd, *J* = 18.0, 11.1, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2 (d, $J_{C–P}$ = 13.4 Hz), 164.8 (d, $J_{C–F}$ = 255.4 Hz), 134.9 (d, $J_{C–P}$ = 5.5 Hz), 131.9 (d, $J_{C–P}$ = 2.8 Hz), 131.0 (d, $J_{C–P}$ = 2.9 Hz), 130.9, 130.4 (d, $J_{C–P}$ = 2.8 Hz), 130.3 (d, $J_{C–P}$ = 8.5 Hz), 130.1, 130.0 (d, $J_{C–P}$ = 8.9 Hz), 129.8 (d, $J_{C–P}$ = 9.4 Hz), 128.8 (d, $J_{C–P}$ = 5.7 Hz), 127.9 (d, $J_{C–P}$ = 11.2 Hz), 127.3 (d, $J_{C–P}$ = 2.0 Hz), 127.1 (d, $J_{C–P}$ = 11.8 Hz), 126.1 (d, $J_{C–P}$ = 2.5 Hz), 114.6 (d, $J_{C–P}$ = 21.9 Hz), 40.2 (d, $J_{C–P}$ = 69.0 Hz), 37.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.15. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.56.

1-(Diphenylphosphoryl)-3-(4-chlorophenyl)-3-phenylpropan-1-one (3ad). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.57 – 7.41 (m, 5H), 7.40 – 7.28 (m, 5H), 7.23 (dd, *J* = 7.9, 2.6 Hz, 2H), 7.18 – 7.03 (m, 3H), 4.43 (ddd, *J* = 9.9, 6.9, 2.6 Hz, 1H), 3.95 (ddd, *J* = 18.0, 10.3, 4.8 Hz, 1H), 3.36 (ddd, *J* = 18.0, 11.1, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7 (d, $J_{C–P}$ = 13.2 Hz), 139.9, 135.8 (d, $J_{C–P}$ = 5.5 Hz), 134.7, 132.1 (d, $J_{C–P}$ = 2.9 Hz), 131.9, 131.5 (d, $J_{C–P}$ = 2.8 Hz), 131.3 (d, $J_{C–P}$ = 8.4 Hz), 131.1, 131.0 (d, $J_{C–P}$ = 9.0 Hz), 129.8 (d, $J_{C–P}$ = 5.6 Hz), 129.5, 129.0 (d, $J_{C–P}$ = 11.3 Hz), 128.9, 128.4 (d, $J_{C–P}$ = 1.9 Hz), 128.1 (d, $J_{C–P}$ = 11.8 Hz), 127.2 (d, $J_{C–P}$ = 2.5 Hz), 41.2 (d, $J_{C–P}$ = 68.9 Hz), 39.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.02.

4-(Di-p-tolylphosphoryl)-4-phenylbutan-2-one (3ae). 95% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.23 (tt, *J* = 8.1, 3.5 Hz, 6H), 7.12 – 7.01 (m, 3H), 6.95 (dd, *J* = 8.0, 2.8 Hz, 2H), 4.09 (ddd, *J* = 10.3, 7.5, 2.9 Hz, 1H), 3.23 (ddd, *J* = 17.9, 10.2, 5.3 Hz, 1H), 2.85 (ddd, *J* = 17.9, 11.1, 2.9 Hz, 1H), 2.33 (s, 3H), 2.17 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5 (d, $J_{C–P}$ = 12.8 Hz), 141.4 (d, $J_{C–P}$ = 2.8 Hz), 140.7 (d, $J_{C–P}$ = 2.9 Hz), 135.1 (d, $J_{C–P}$ = 5.5 Hz), 130.3 (d, $J_{C–P}$ = 8.8 Hz), 130.0 (d, $J_{C–P}$ = 9.2 Hz), 128.7 (d, $J_{C–P}$ = 5.7 Hz), 128.6 (d, $J_{C–P}$ = 11.6 Hz), 127.9 (d, $J_{C–P}$ = 11.0 Hz), 127.8 (d, $J_{C–P}$ = 12.2 Hz), 127.3 (d, $J_{C–P}$ = 2.0 Hz), 126.9 (d, $J_{C–P}$ = 5.6 Hz), 126.0 (d, $J_{C–P}$ =

2.5 Hz), 42.7, 40.3 (d, J_{C-P} = 68.8 Hz), 29.6, 20.6 (d, J_{C-P} = 1.3 Hz), 20.4 (d, J_{C-P} = 1.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.96.

4-(Bis(4-chlorophenyl)phosphoryl)-4-phenylbutan-2-one (3af). 97% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 10.4, 8.4 Hz, 2H), 7.49 – 7.38 (m, 2H), 7.32 – 7.19 (m, 4H), 7.17 – 6.99 (m, 5H), 4.12 (ddd, J = 10.0, 7.1, 2.9 Hz, 1H), 3.23 (ddd, J = 18.0, 9.8, 5.5 Hz, 1H), 2.85 (ddd, J = 18.1, 11.8, 3.0 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9 (d, J_{C-P} = 12.7 Hz), 139.0 (d, J_{C-P} = 3.3 Hz), 138.3 (d, J_{C-P} = 3.4 Hz), 135.3, 132.7 (d, J_{C-P} = 9.4 Hz), 132.3 (d, J_{C-P} = 9.6 Hz), 130.1 (d, J_{C-P} = 18.3 Hz), 129.7 (d, J_{C-P} = 5.8 Hz), 129.4 (d, J_{C-P} = 11.8 Hz), 129.2 (d, J_{C-P} = 12.2 Hz), 128.6 (d, J_{C-P} = 2.0 Hz), 128.6 (d, J_{C-P} = 12.3 Hz), 127.5 (d, J_{C-P} = 2.5 Hz), 43.5, 40.9 (d, J_{C-P} = 69.8 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.76.

4-(Bis(4-methoxyphenyl)phosphoryl)-4-phenylbutan-2-one (3ag). 95% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.34 – 7.26 (m, 4H), 7.21 – 7.10 (m, 3H), 7.02 (dd, J = 8.9, 2.3 Hz, 2H), 6.78 – 6.68 (m, 2H), 4.12 (ddd, J = 10.5, 7.8, 3.0 Hz, 1H), 3.85 (s, 3H), 3.73 (s, 3H), 3.29 (ddd, J = 17.8, 10.2, 5.4 Hz, 1H), 2.95 (ddd, J = 17.9, 11.2, 2.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6 (d, J_{C-P} = 12.8 Hz), 162.5 (d, J_{C-P} = 2.9 Hz), 161.9 (d, J_{C-P} = 2.9 Hz), 136.2 (d, J_{C-P} = 5.5 Hz), 133.1 (d, J_{C-P} = 9.7 Hz), 132.9 (d, J_{C-P} = 10.1 Hz), 129.7 (d, J_{C-P} = 5.5 Hz), 128.3 (d, J_{C-P} = 1.9 Hz), 127.0 (d, J_{C-P} = 2.5 Hz), 123.3 (d, J_{C-P} = 48.1 Hz), 122.3 (d, J_{C-P} = 42.8 Hz), 114.4 (d, J_{C-P} = 12.2 Hz), 113.6 (d, J_{C-P} = 12.7 Hz), 55.4, 55.2, 43.7, 41.6 (d, J_{C-P} = 69.3 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.78.

4-(Bis(4-ethylphenyl)phosphoryl)-4-phenylbutan-2-one (3ah). 51% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 10.5, 7.9 Hz, 2H), 7.30 – 7.20 (m, 6H), 7.13 – 7.02 (m, 3H), 6.98 (dd, J = 8.2, 2.8 Hz, 2H), 4.10 (ddd, J = 10.3, 7.5, 2.9 Hz, 1H), 3.24 (ddd, J = 17.8, 10.3, 5.3 Hz, 1H), 2.86 (ddd, J = 17.9, 11.0, 2.9 Hz, 1H), 2.63 (q, J = 7.6 Hz, 2H), 2.48 (q, J = 7.6 Hz, 2H), 1.87 (s, 3H), 1.18 (t, J = 7.6 Hz, 3H), 1.06 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6 (d, J_{C-P} = 12.8 Hz), 147.5 (d, J_{C-P} = 2.7 Hz), 146.9 (d, J_{C-P} = 2.8 Hz), 135.1 (d, J_{C-P} = 5.5 Hz), 130.4 (d, J_{C-P} = 8.8 Hz), 130.1 (d, J_{C-P} = 9.2 Hz), 128.7 (d, J_{C-P} = 5.6 Hz), 128.0 (d, J_{C-P} = 13.2 Hz), 127.4 (d, J_{C-P} = 11.7 Hz), 127.3 (d, J_{C-P}

= 1.9 Hz), 127.0 (d, $J_{C–P}$ = 7.7 Hz), 126.6 (d, $J_{C–P}$ = 12.1 Hz), 126.0 (d, $J_{C–P}$ = 2.5 Hz), 42.6, 40.3 (d, $J_{C–P}$ = 68.6 Hz), 29.6, 27.8, 27.7, 14.1, 14.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.93.

4-(Di-o-tolylphosphoryl)-4-phenylbutan-2-one (3ai). 53% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 10.7, 6.9 Hz, 1H), 7.45 – 7.32 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 3H), 7.16 – 7.00 (m, 5H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.85 (dd, *J* = 7.7, 4.4 Hz, 1H), 4.36 (ddd, *J* = 9.8, 6.8, 2.5 Hz, 1H), 3.40 (ddd, *J* = 18.2, 10.1, 4.3 Hz, 1H), 3.15 (ddd, *J* = 18.2, 10.7, 2.5 Hz, 1H), 2.28 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8 (d, $J_{C–P}$ = 12.6 Hz), 142.2 (d, $J_{C–P}$ = 7.4 Hz), 140.8 (d, $J_{C–P}$ = 8.4 Hz), 135.6 (d, $J_{C–P}$ = 5.0 Hz), 131.6 (d, $J_{C–P}$ = 5.5 Hz), 131.4 (d, $J_{C–P}$ = 5.1 Hz), 130.8 (d, $J_{C–P}$ = 2.5 Hz), 130.4, 130.3 (d, $J_{C–P}$ = 2.2 Hz), 130.2 (d, $J_{C–P}$ = 6.2 Hz), 130.1 (d, $J_{C–P}$ = 10.1 Hz), 129.5, 128.6 (d, $J_{C–P}$ = 5.8 Hz), 127.3 (d, $J_{C–P}$ = 1.9 Hz), 126.0 (d, $J_{C–P}$ = 2.4 Hz), 124.5 (d, $J_{C–P}$ = 11.3 Hz), 124.0 (d, $J_{C–P}$ = 12.1 Hz), 43.5, 38.5 (d, $J_{C–P}$ = 69.4 Hz), 29.8, 20.3 (d, $J_{C–P}$ = 4.1 Hz), 20.0 (d, $J_{C–P}$ = 3.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.17.

4-(Di-m-tolylphosphoryl)-4-phenylbutan-2-one (3aj). 74% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 11.2 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.37 – 7.20 (m, 4H), 7.17 – 7.00 (m, 7H), 4.11 (ddd, *J* = 10.2, 7.3, 2.9 Hz, 1H), 3.25 (ddd, *J* = 17.8, 10.3, 5.3 Hz, 1H), 2.84 (ddd, *J* = 17.9, 11.0, 2.9 Hz, 1H), 2.33 (s, 3H), 2.10 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4 (d, $J_{C–P}$ = 12.8 Hz), 138.8 (d, $J_{C–P}$ = 11.1 Hz), 137.9 (d, $J_{C–P}$ = 11.7 Hz), 136.0 (d, $J_{C–P}$ = 5.5 Hz), 132.8 (d, $J_{C–P}$ = 2.9 Hz), 132.2 (d, $J_{C–P}$ = 2.9 Hz), 132.0 (d, $J_{C–P}$ = 8.1 Hz), 131.8 (d, $J_{C–P}$ = 3.3 Hz), 131.8 (d, $J_{C–P}$ = 8.2 Hz), 130.8 (d, $J_{C–P}$ = 2.1 Hz), 129.8 (d, $J_{C–P}$ = 5.6 Hz), 128.7 (d, $J_{C–P}$ = 12.0 Hz), 128.3 (d, $J_{C–P}$ = 2.0 Hz), 128.1 (d, $J_{C–P}$ = 8.9 Hz), 127.9 (d, $J_{C–P}$ = 6.7 Hz), 127.8 (d, $J_{C–P}$ = 3.6 Hz), 127.1 (d, $J_{C–P}$ = 2.5 Hz), 43.5, 41.2 (d, $J_{C–P}$ = 68.3 Hz), 30.6, 21.5, 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.94.

4-(Bis(3,5-dimethylphenyl)phosphoryl)-4-phenylbutan-2-one (3ak). 53% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 11.1, 1.7 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.13 – 7.01 (m, 4H), 6.94 (dd, *J* = 11.6, 1.6 Hz, 2H), 6.86 (s, 1H), 4.08 (ddd, *J* = 10.3, 7.4, 2.9 Hz, 1H), 3.23 (ddd, *J* = 17.8, 10.3, 5.2 Hz, 1H), 2.83 (ddd, *J* = 17.9, 10.9, 2.9 Hz, 1H), 2.30 (s, 6H), 2.09 (s, 6H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6 (d, $J_{C–P}$ = 12.9 Hz), 138.5 (d, $J_{C–P}$ = 11.9 Hz), 137.6 (d, $J_{C–P}$ = 12.4 Hz), 136.2 (d, $J_{C–P}$ = 5.5 Hz), 133.7 (d, $J_{C–P}$ = 2.9 Hz), 133.1 (d, $J_{C–P}$ = 2.9 Hz), 131.7 (d, $J_{C–P}$ = 7.3 Hz), 130.8 (d, $J_{C–P}$ = 12.6 Hz),

129.8 (d, J_{C-P} = 5.6 Hz), 128.9 (d, J_{C-P} = 8.6 Hz), 128.7 (d, J_{C-P} = 8.8 Hz), 128.2 (d, J_{C-P} = 1.9 Hz), 127.0 (d, J_{C-P} = 2.4 Hz), 43.6, 41.2 (d, J_{C-P} = 68.0 Hz), 30.6, 21.4, 21.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.11.

4-(Di(naphthalen-2-yl)phosphoryl)-4-phenylbutan-2-one (3am). 31% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 12.7 Hz, 1H), 8.01 (d, J = 13.2 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.86 – 7.80 (m, 2H), 7.65 (q, J = 8.0 Hz, 3H), 7.56 – 7.47 (m, 2H), 7.45 – 7.28 (m, 5H), 7.06 (dt, J = 13.1, 6.9 Hz, 3H), 4.39 (ddd, J = 10.2, 7.2, 2.9 Hz, 1H), 3.33 (ddd, J = 17.9, 10.2, 5.2 Hz, 1H), 2.94 (ddd, J = 18.0, 11.2, 2.9 Hz, 1H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3 (d, J_{C-P} = 12.8 Hz), 135.9 (d, J_{C-P} = 5.6 Hz), 134.7 (d, J_{C-P} = 2.2 Hz), 134.4 (d, J_{C-P} = 2.5 Hz), 133.7 (d, J_{C-P} = 7.5 Hz), 133.3 (d, J_{C-P} = 7.8 Hz), 132.7 (d, J_{C-P} = 12.4 Hz), 132.3 (d, J_{C-P} = 12.8 Hz), 129.8 (d, J_{C-P} = 5.8 Hz), 129.2 (d, J_{C-P} = 6.1 Hz), 128.9 (d, J_{C-P} = 17.7 Hz), 128.9, 128.8, 128.5 (d, J_{C-P} = 1.9 Hz), 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.2 (d, J_{C-P} = 2.5 Hz), 127.1, 126.7, 125.8 (d, J_{C-P} = 10.0 Hz), 43.7, 41.0 (d, J_{C-P} = 68.9 Hz), 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.00.

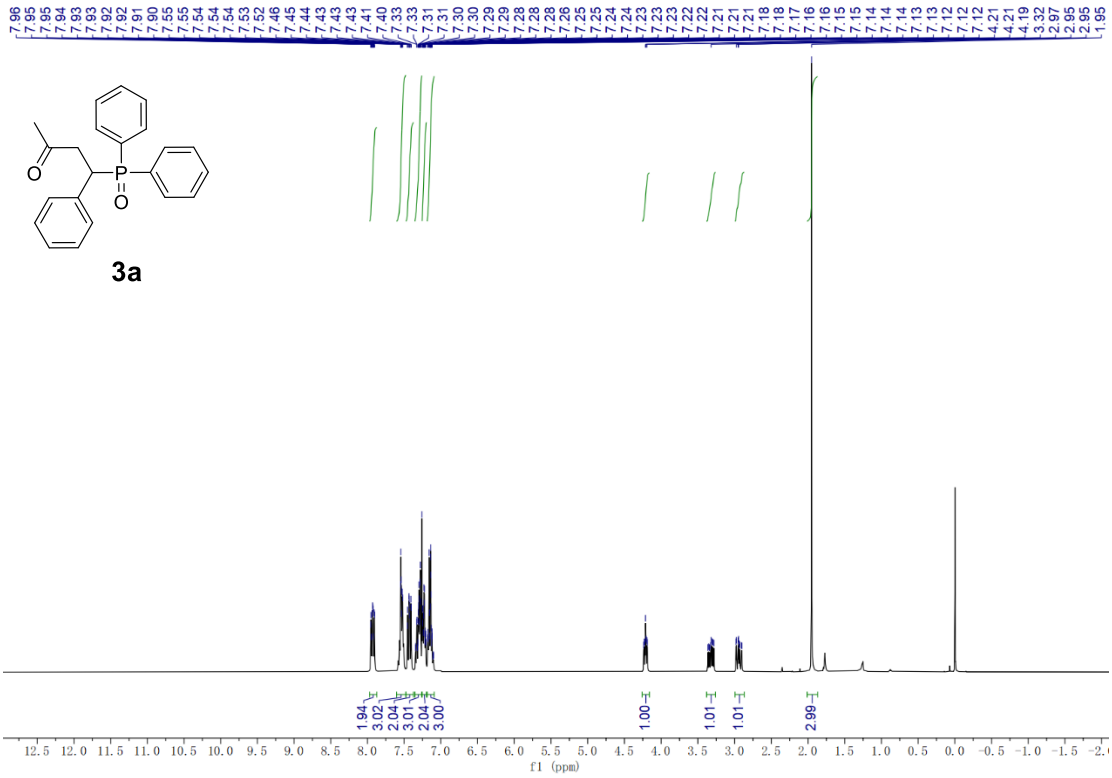


Figure S3.1 ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$).

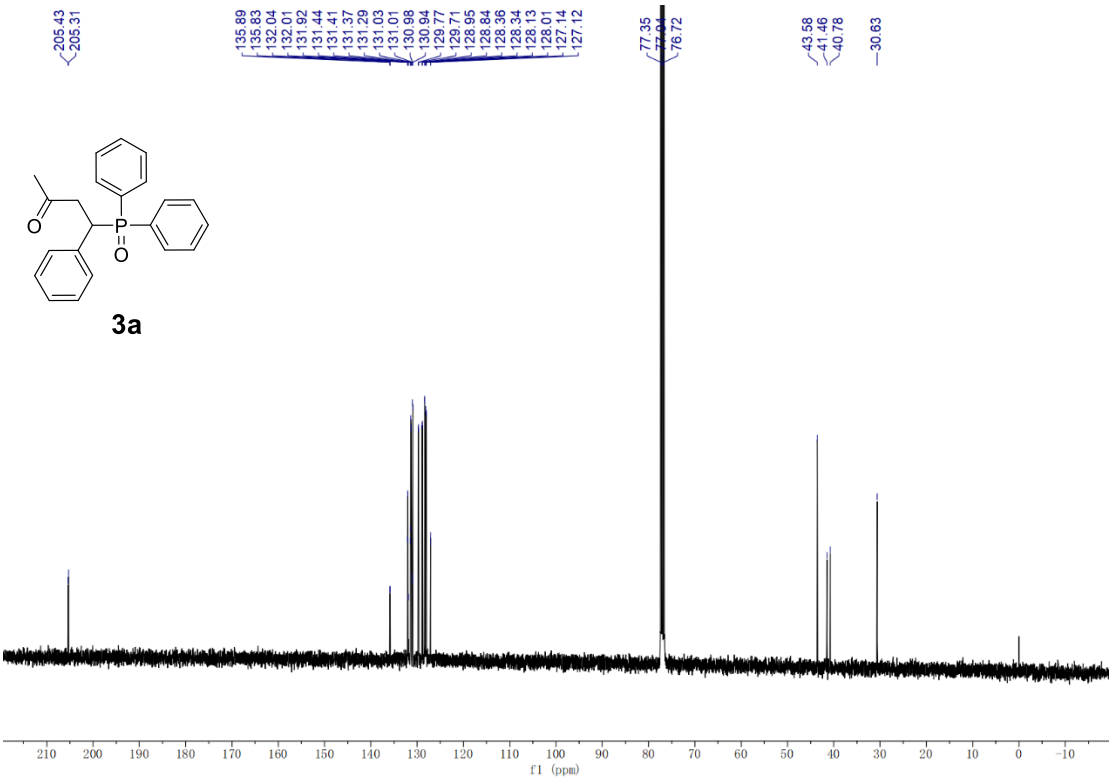


Figure S3.2 ^{13}C NMR spectrum of **3a** (101 MHz, $CDCl_3$).

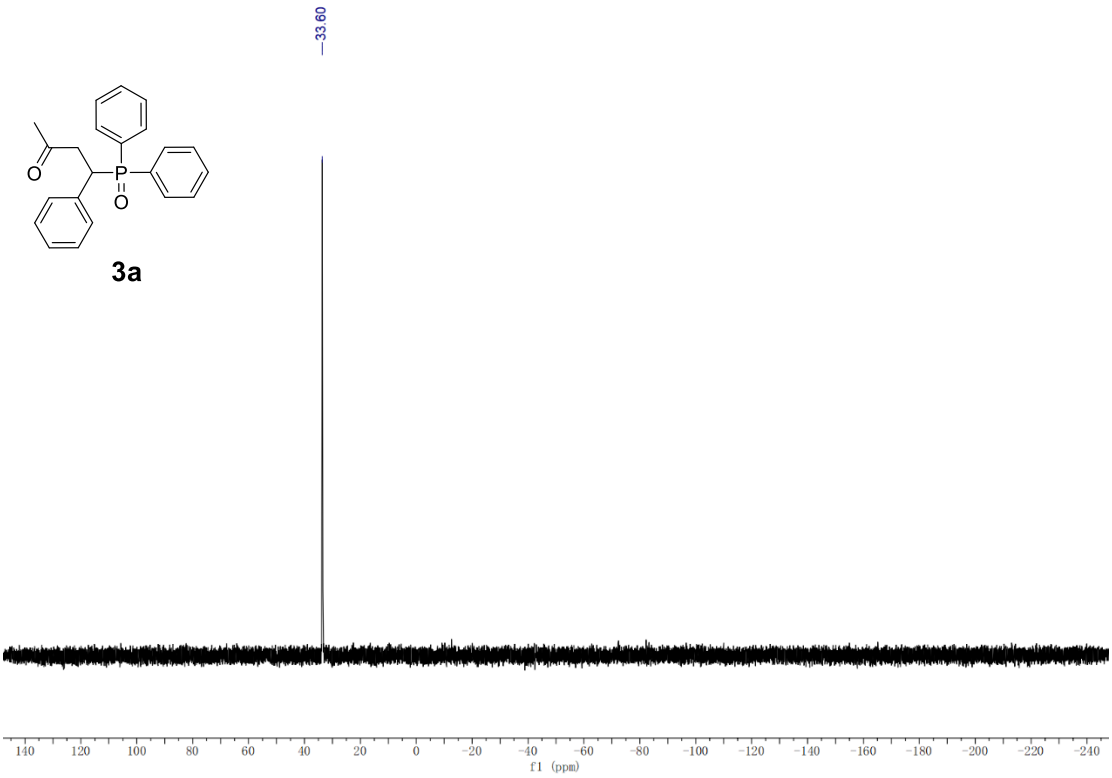


Figure S3.3 ^{31}P NMR spectrum of **3a** (162 MHz, $CDCl_3$).

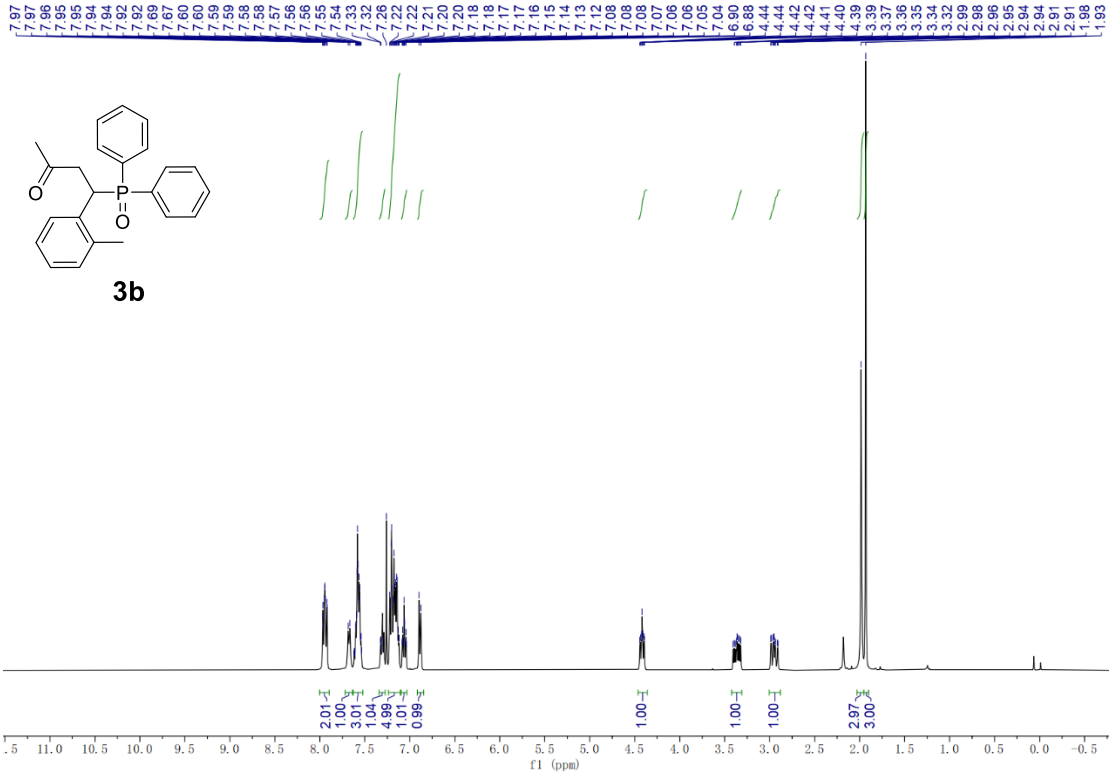


Figure S3.4 ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$).

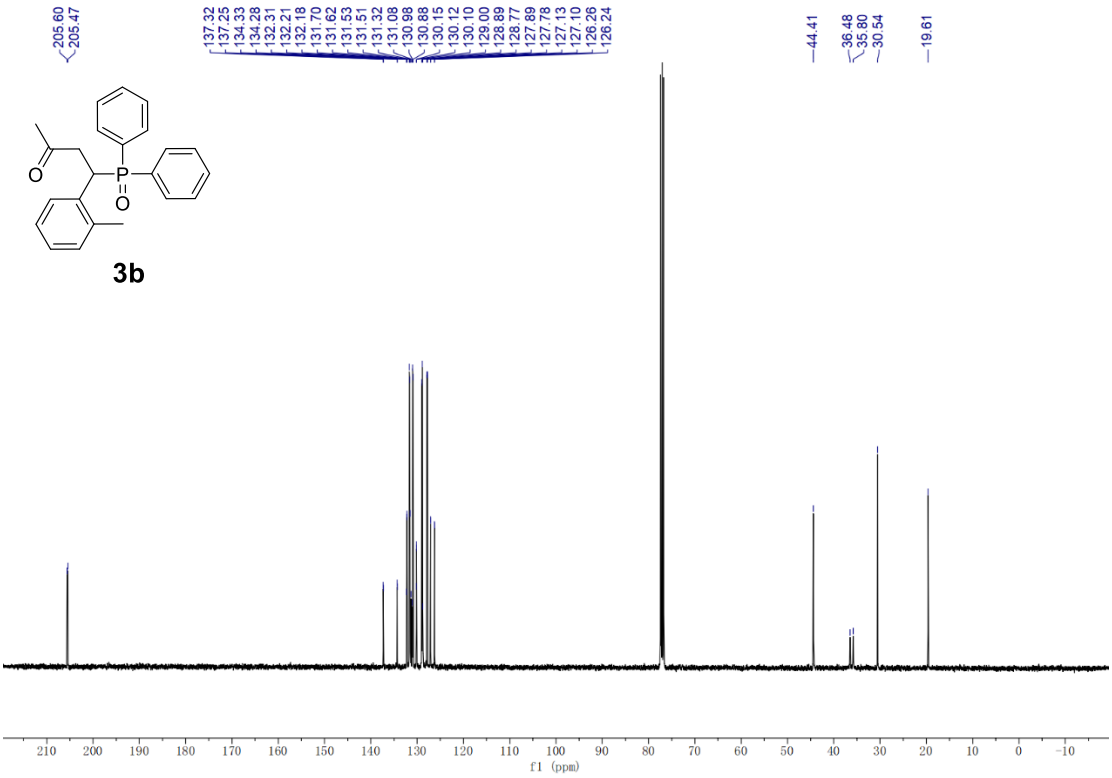


Figure S3.5 ^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$).

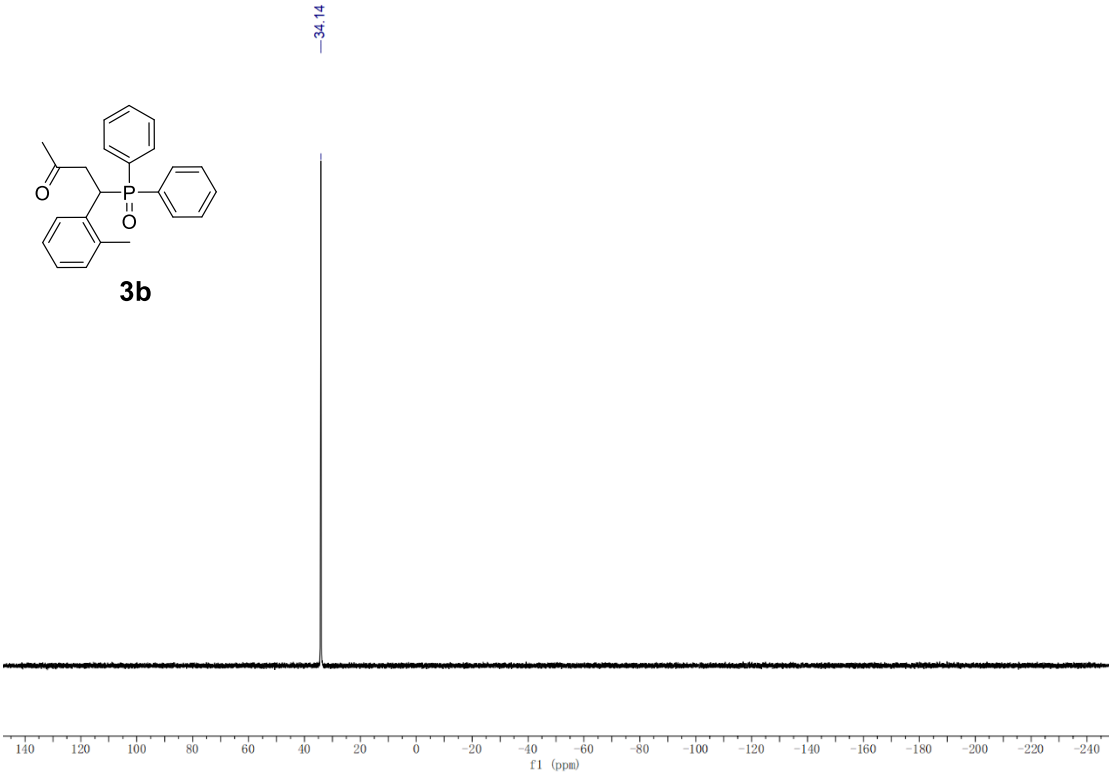


Figure S3.6 ^{31}P NMR spectrum of **3b** (162 MHz, $CDCl_3$).

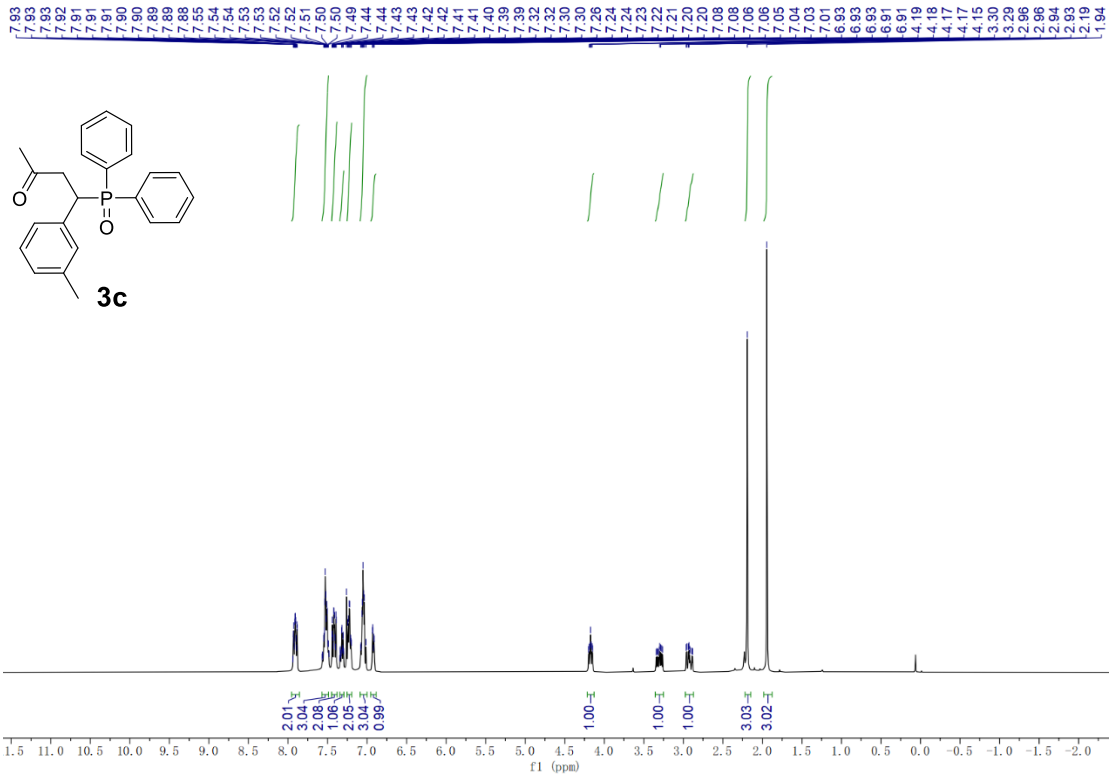


Figure S3.7 ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$).

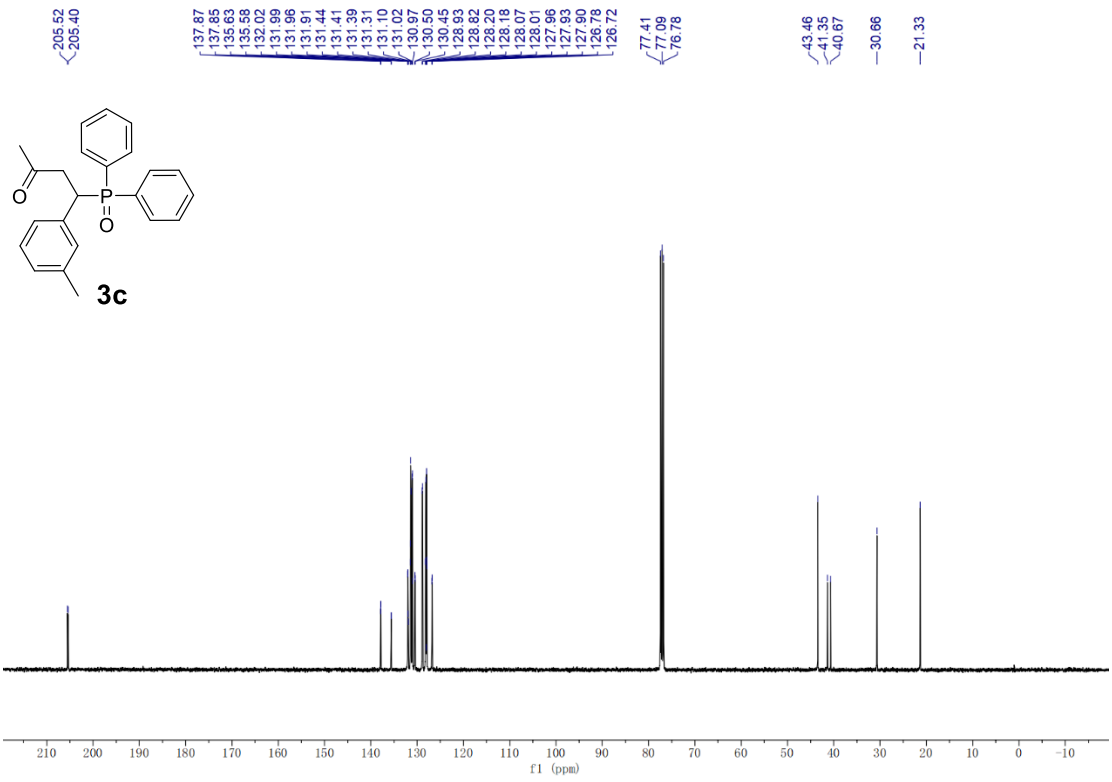


Figure S3.8 ^{13}C NMR spectrum of **3c** (101 MHz, $CDCl_3$).

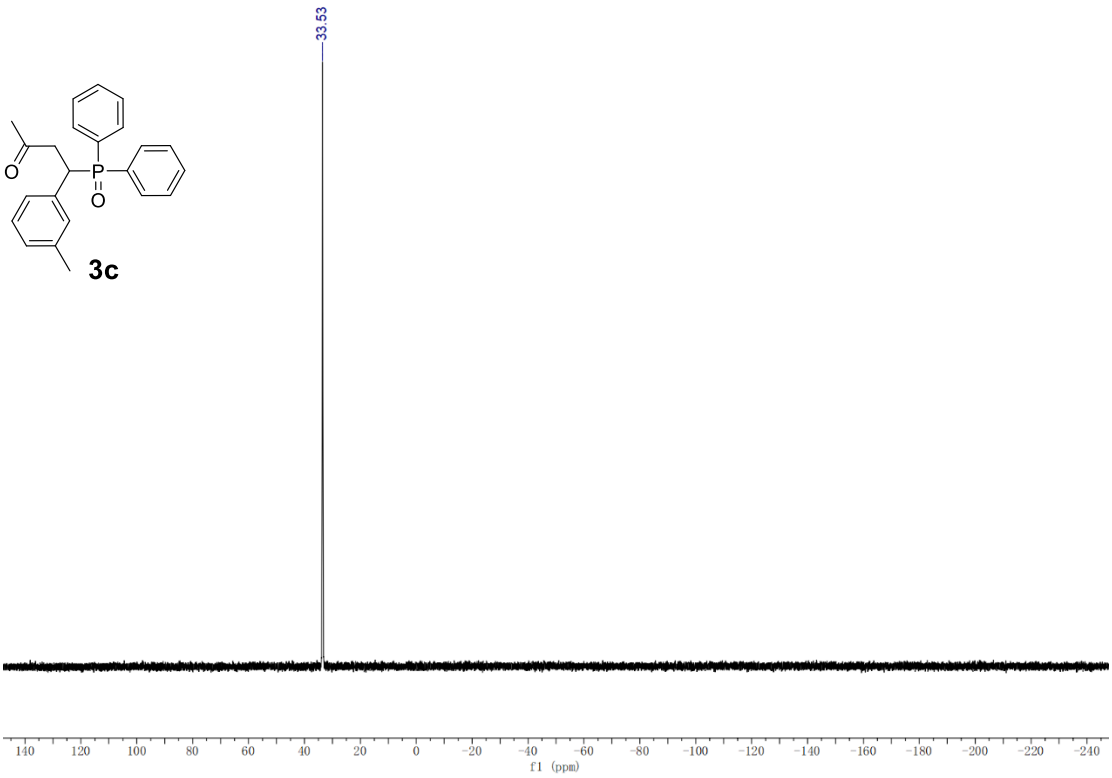


Figure S3.9 ^{31}P NMR spectrum of **3c** (162 MHz, $CDCl_3$).

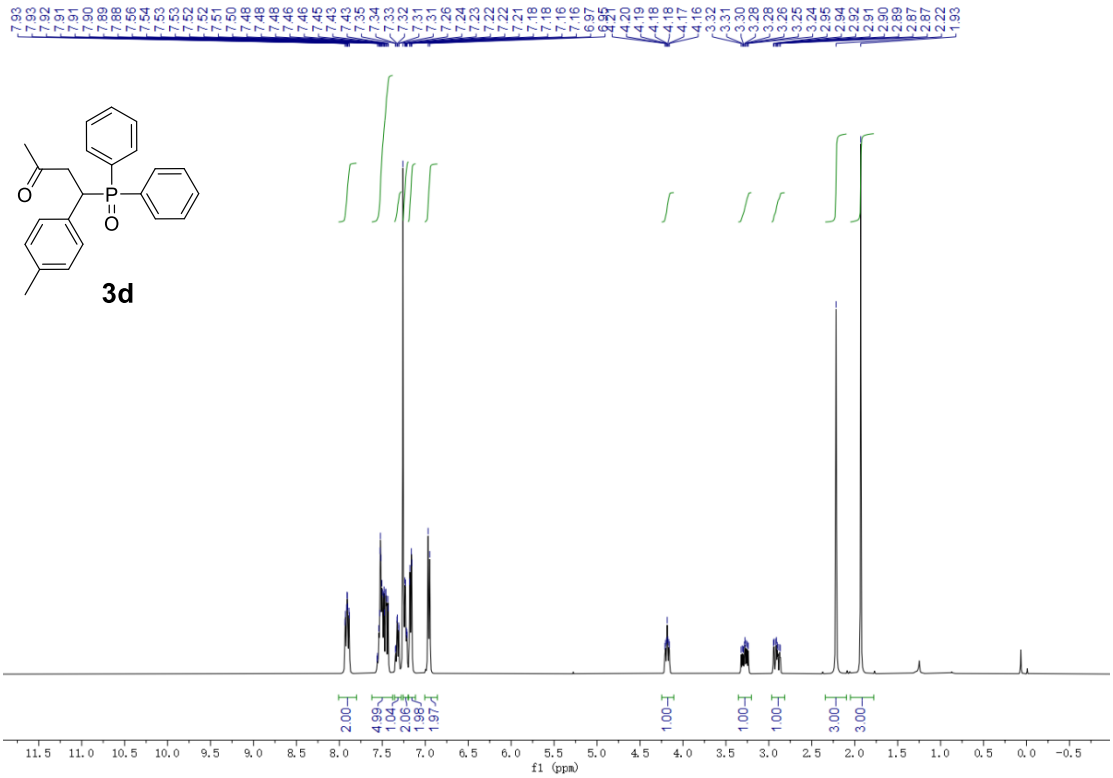


Figure S3.10 ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$).

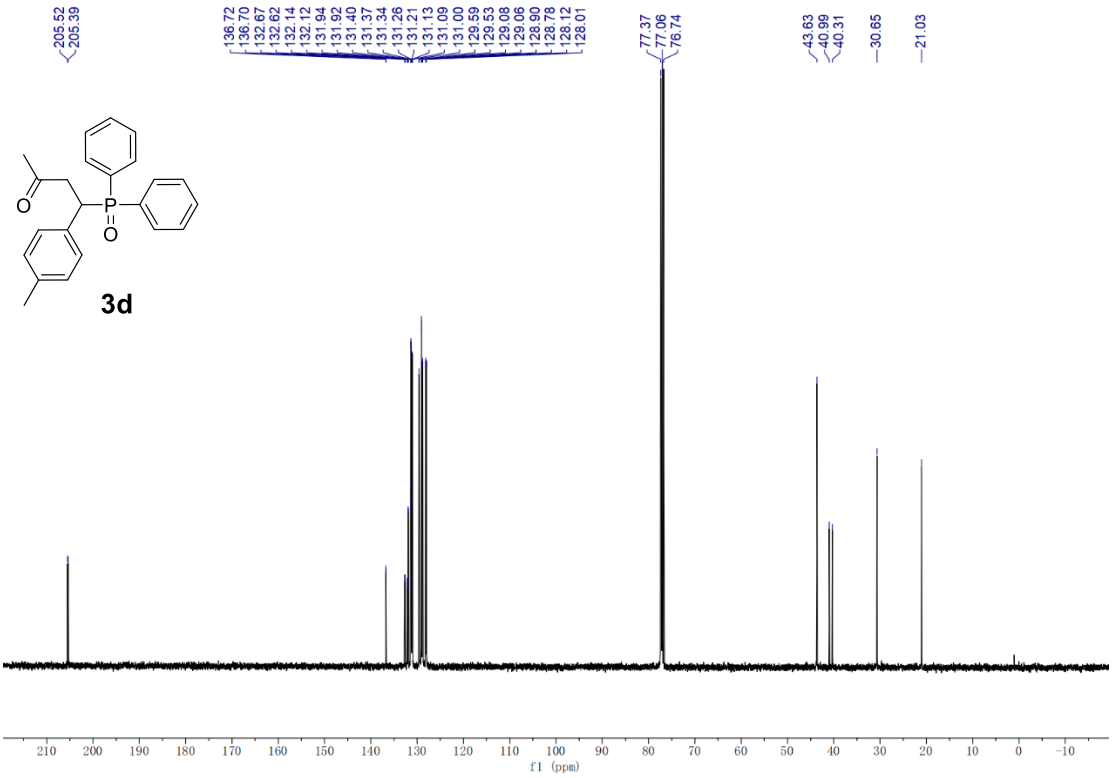


Figure S3.11 ^{13}C NMR spectrum of **3d** (101 MHz, $CDCl_3$).

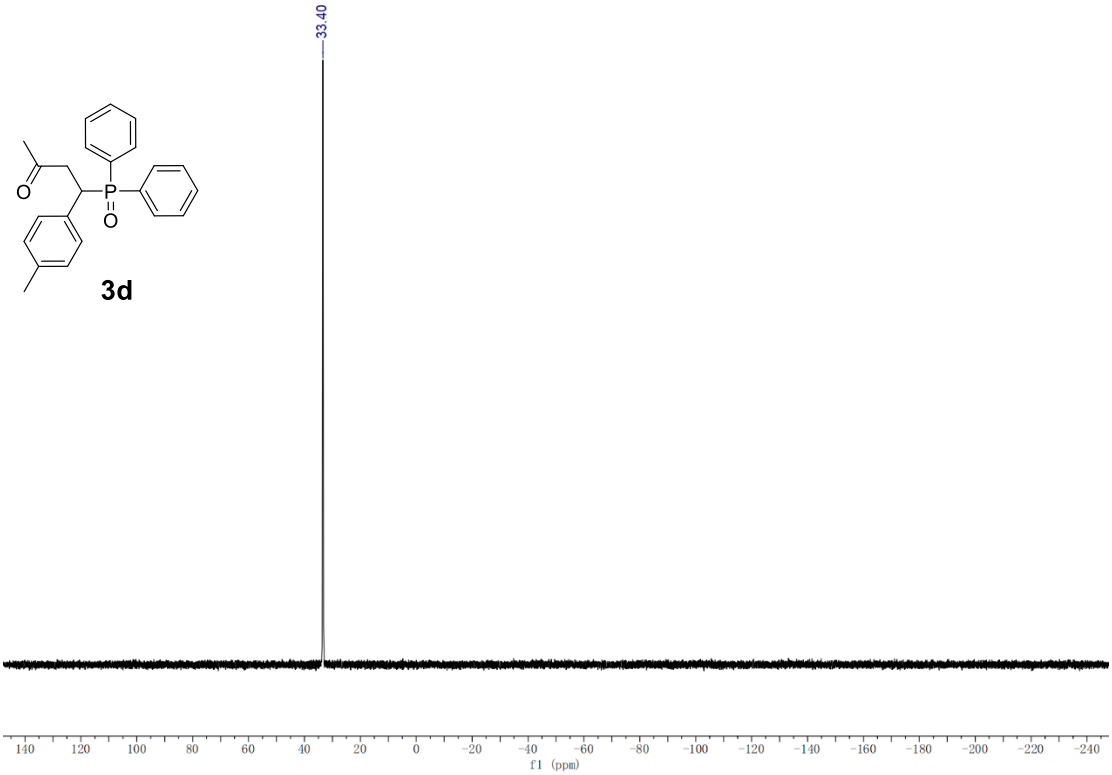


Figure S3.12 ^{31}P NMR spectrum of **3d** (162 MHz, $CDCl_3$).

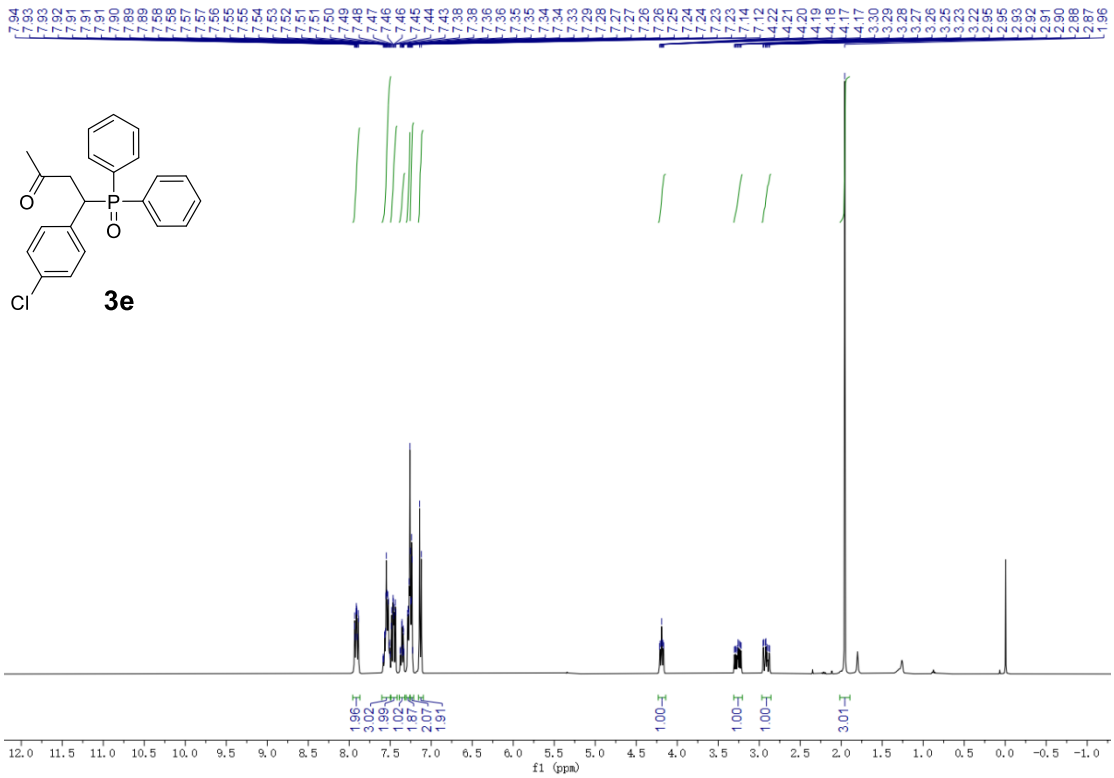


Figure S3.13 ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$).

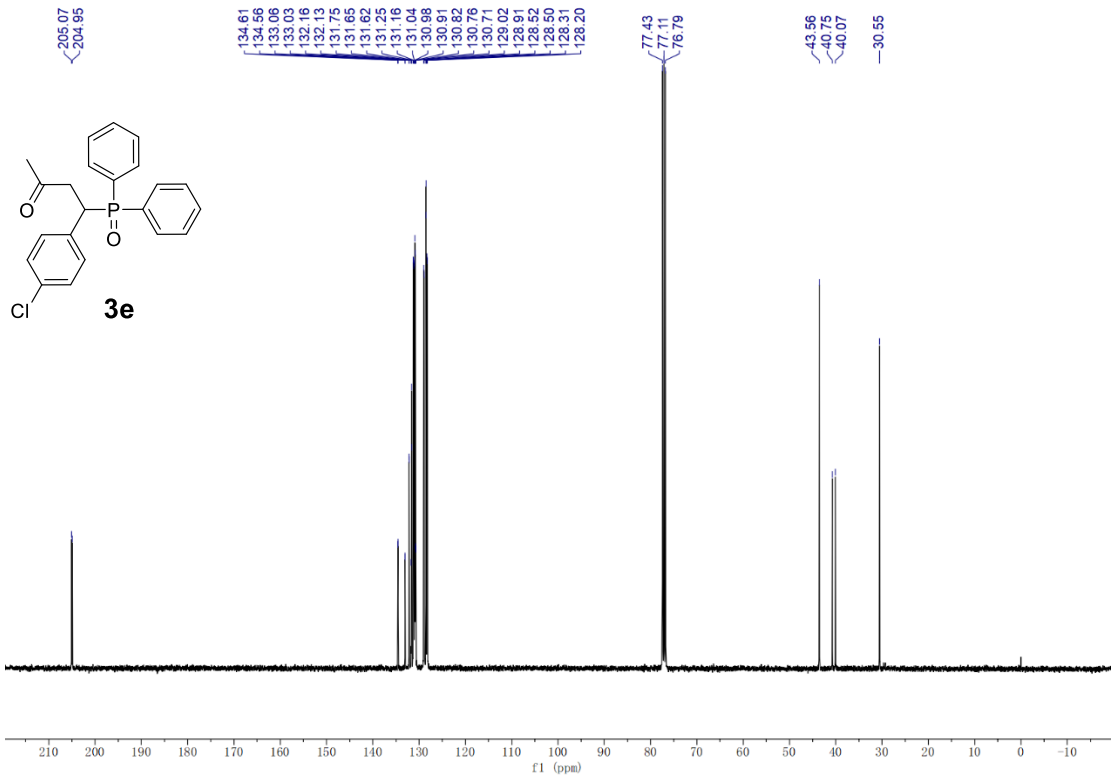


Figure S3.14 ^{13}C NMR spectrum of **3e** (101 MHz, $CDCl_3$).

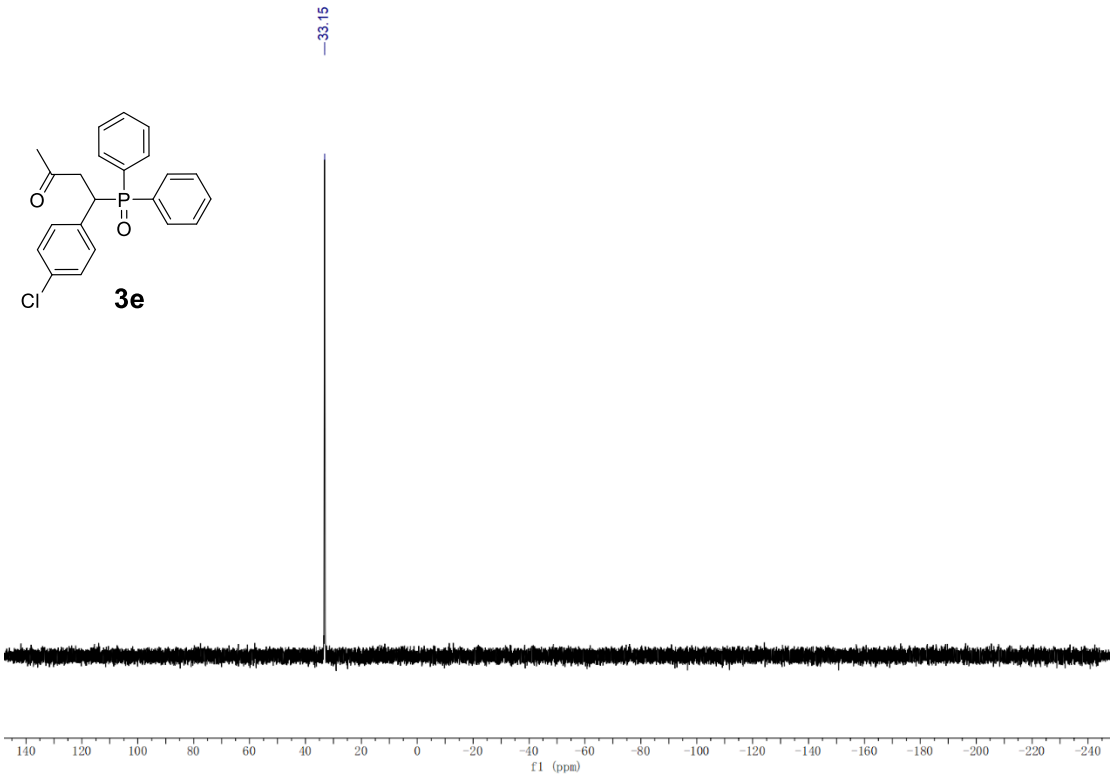


Figure S3.15 ^{31}P NMR spectrum of **3e** (162 MHz, $CDCl_3$).

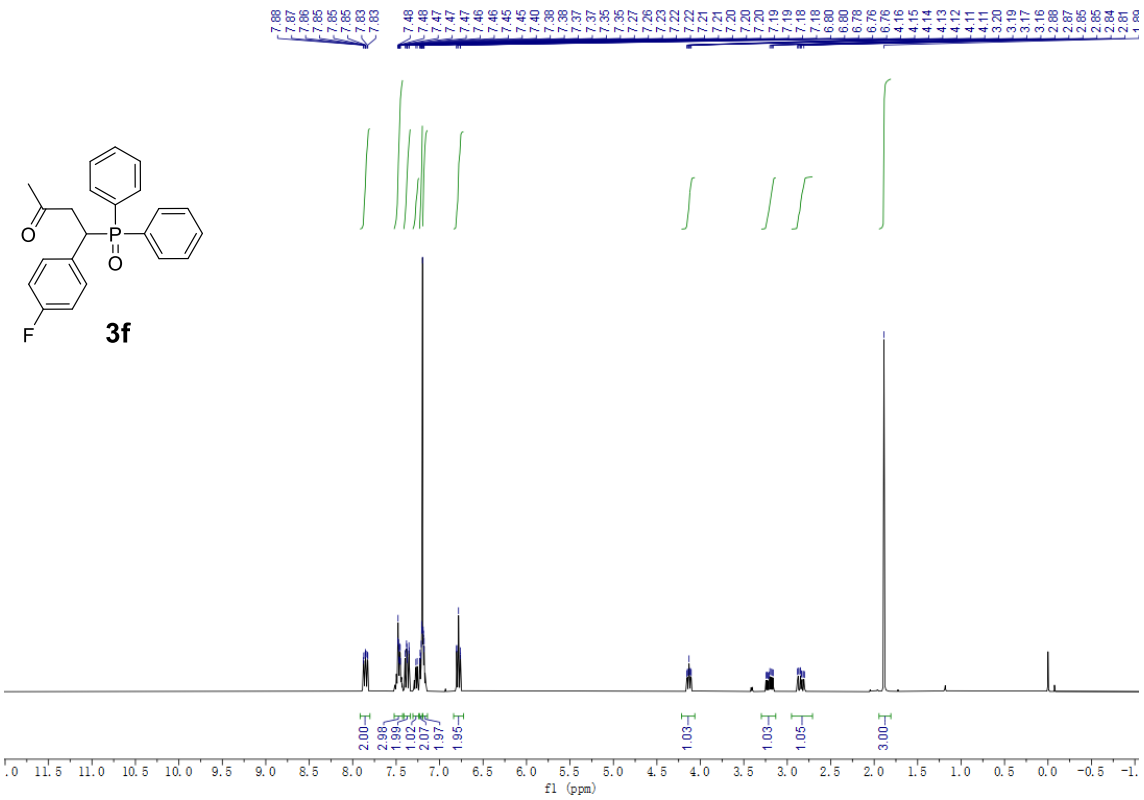


Figure S3.16 ^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$).

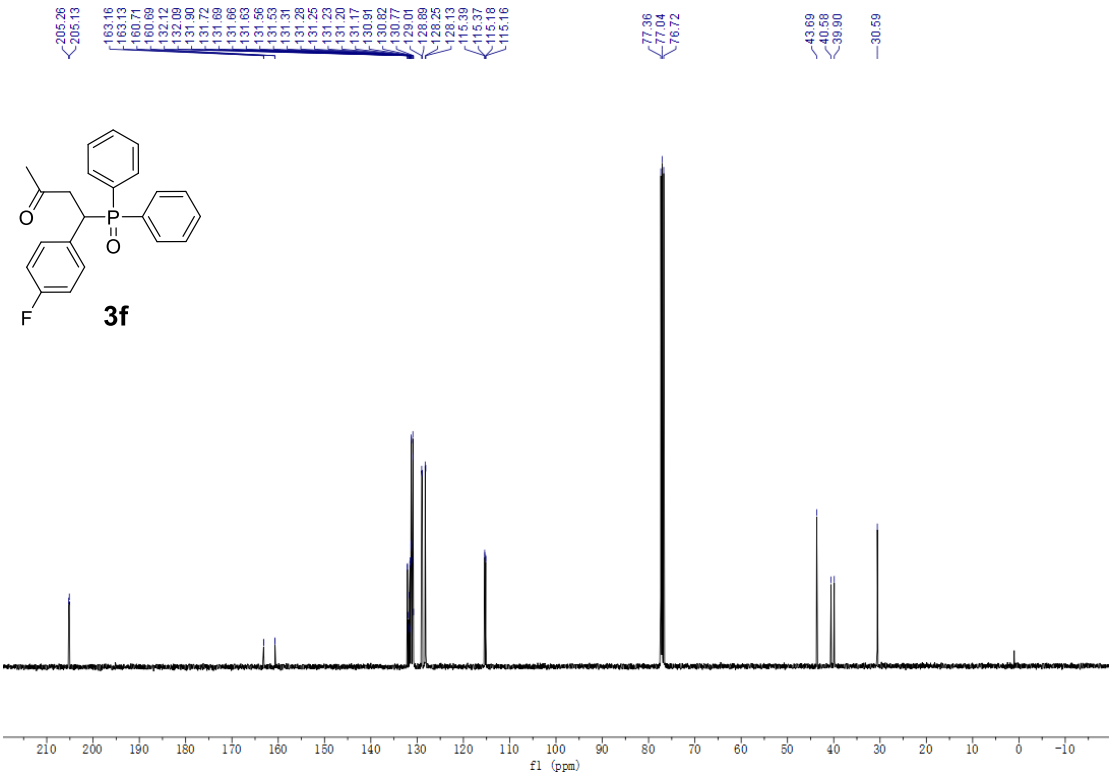


Figure S3.17 ^{13}C NMR spectrum of **3f** (101 MHz, $CDCl_3$).

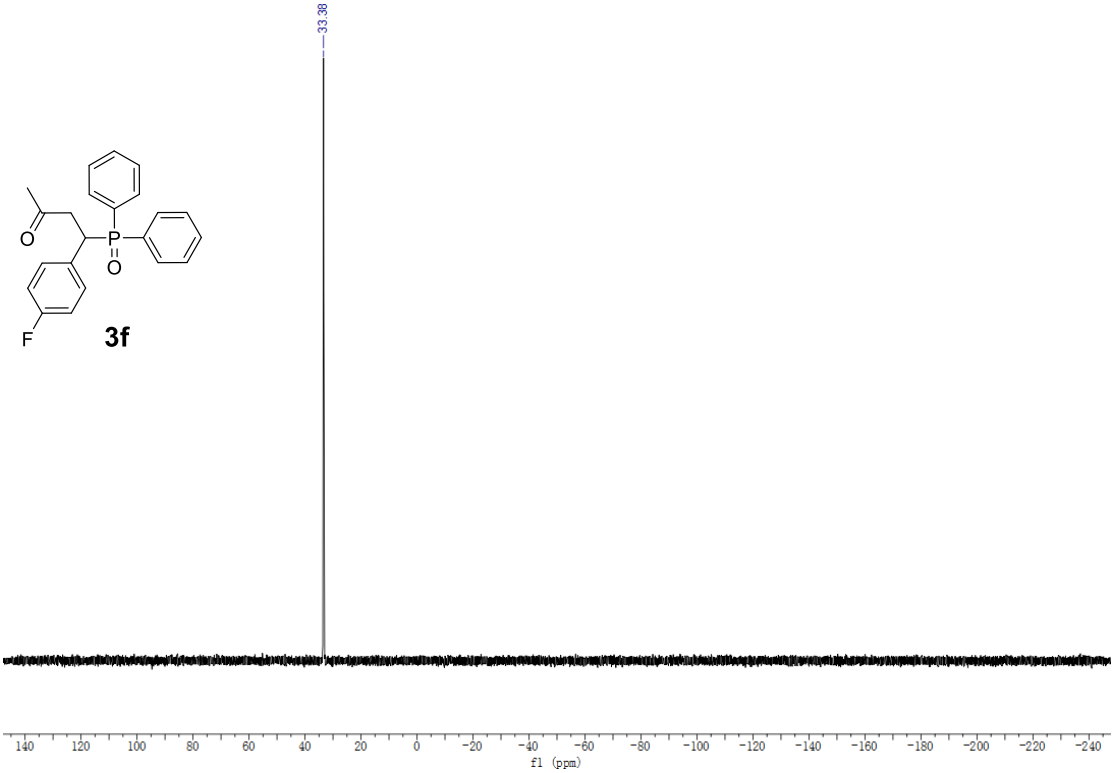


Figure S3.18 ^{31}P NMR spectrum of **3f** (162 MHz, $CDCl_3$).

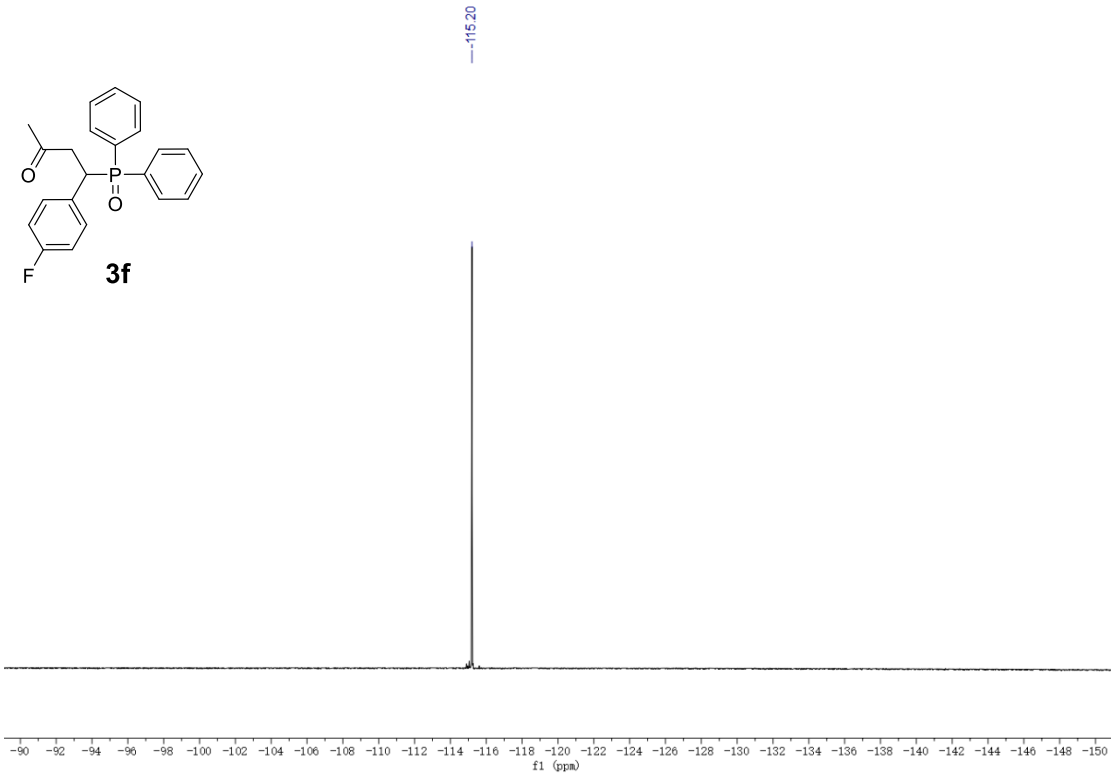


Figure S3.19 ^{19}F NMR spectrum of **3f** (376 MHz, $CDCl_3$).

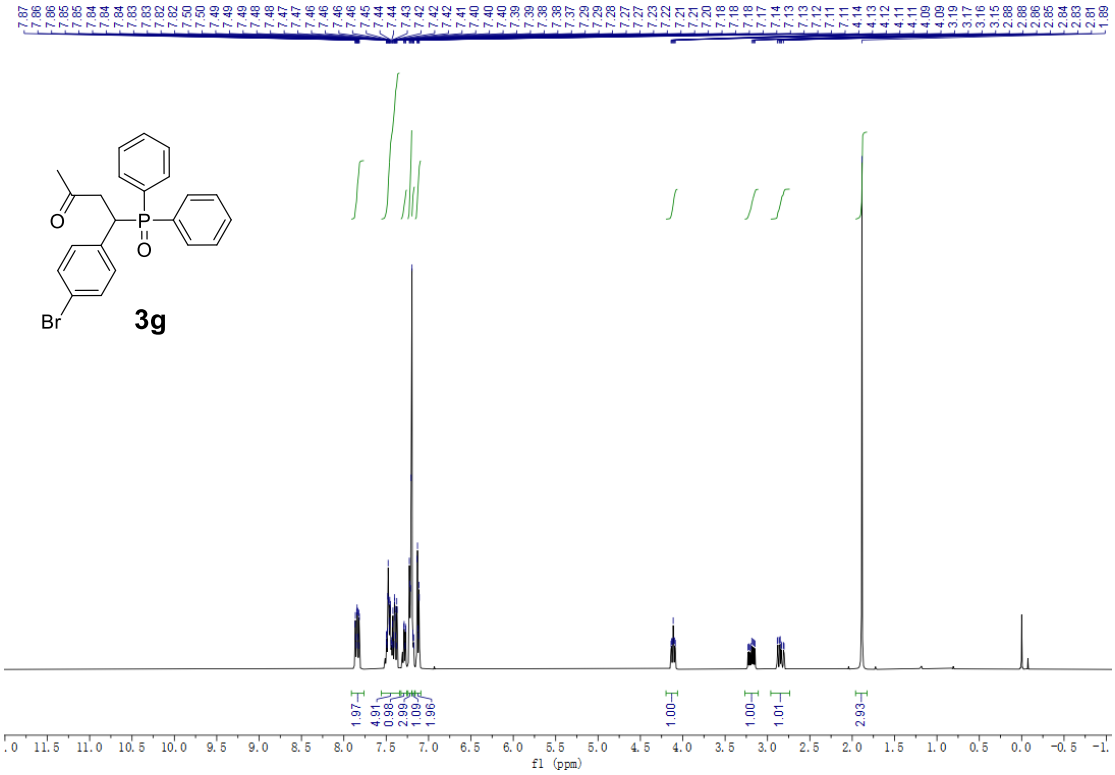


Figure S3.20 ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$).

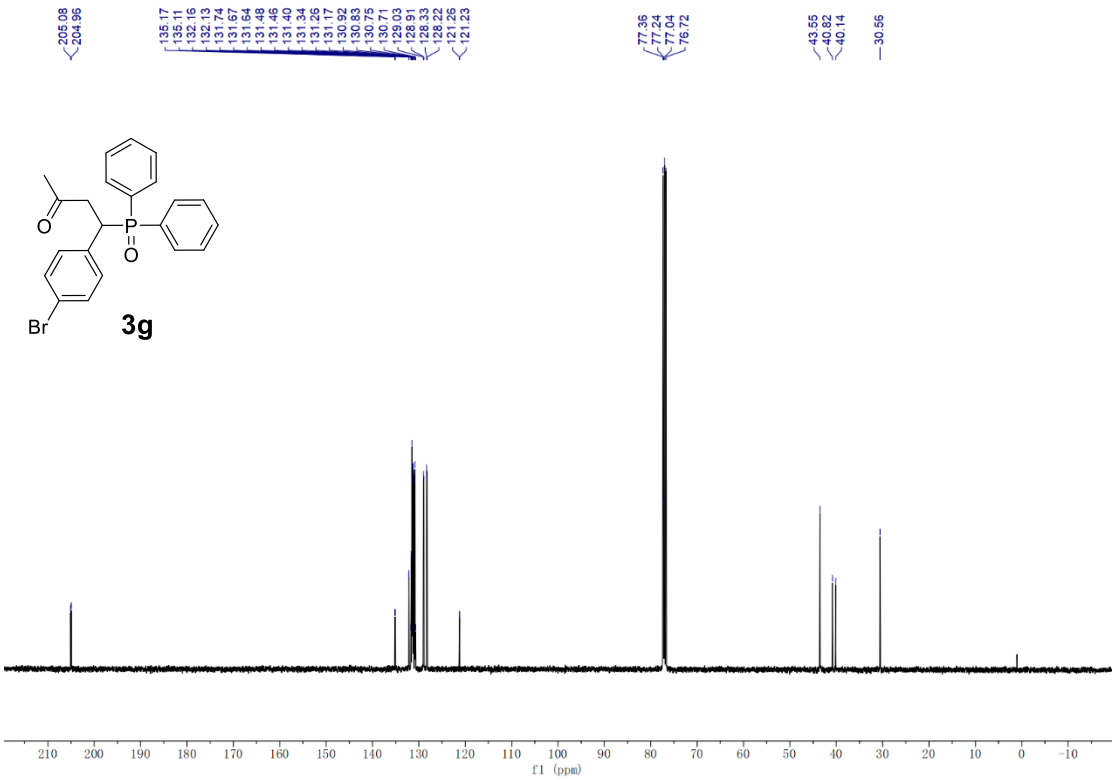


Figure S3.21 ^{13}C NMR spectrum of **3g** (101 MHz, $CDCl_3$).

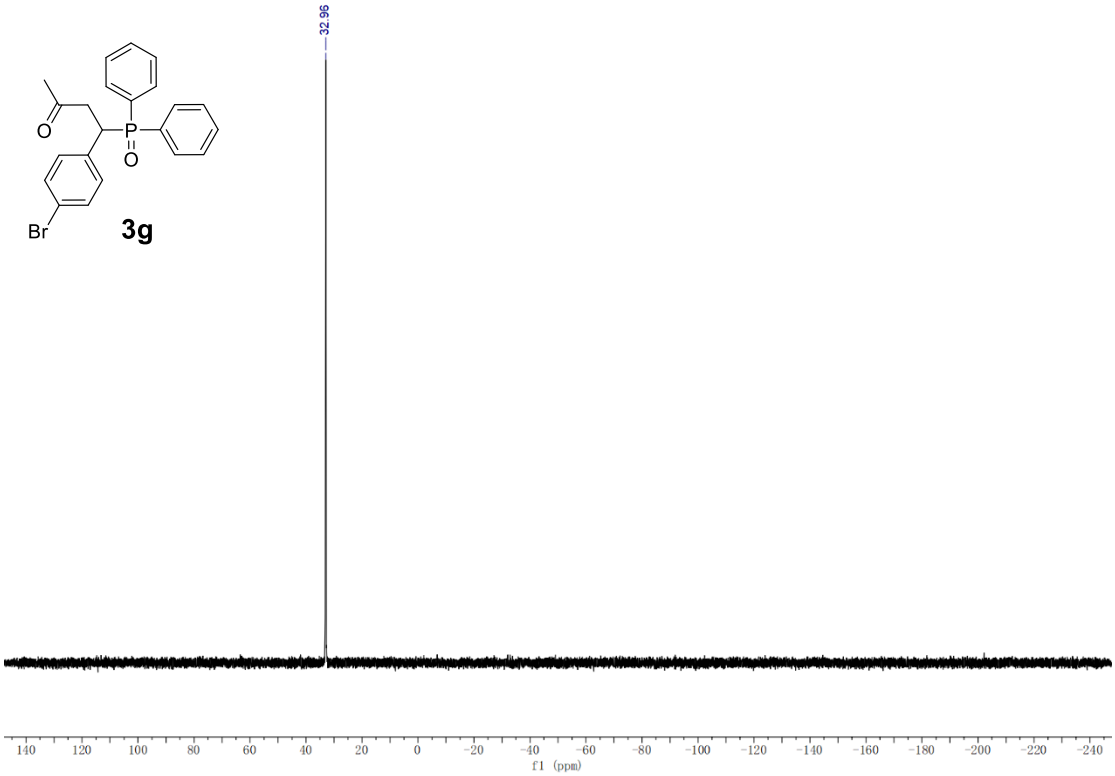


Figure S3.22 ^{31}P NMR spectrum of **3g** (162 MHz, $CDCl_3$).

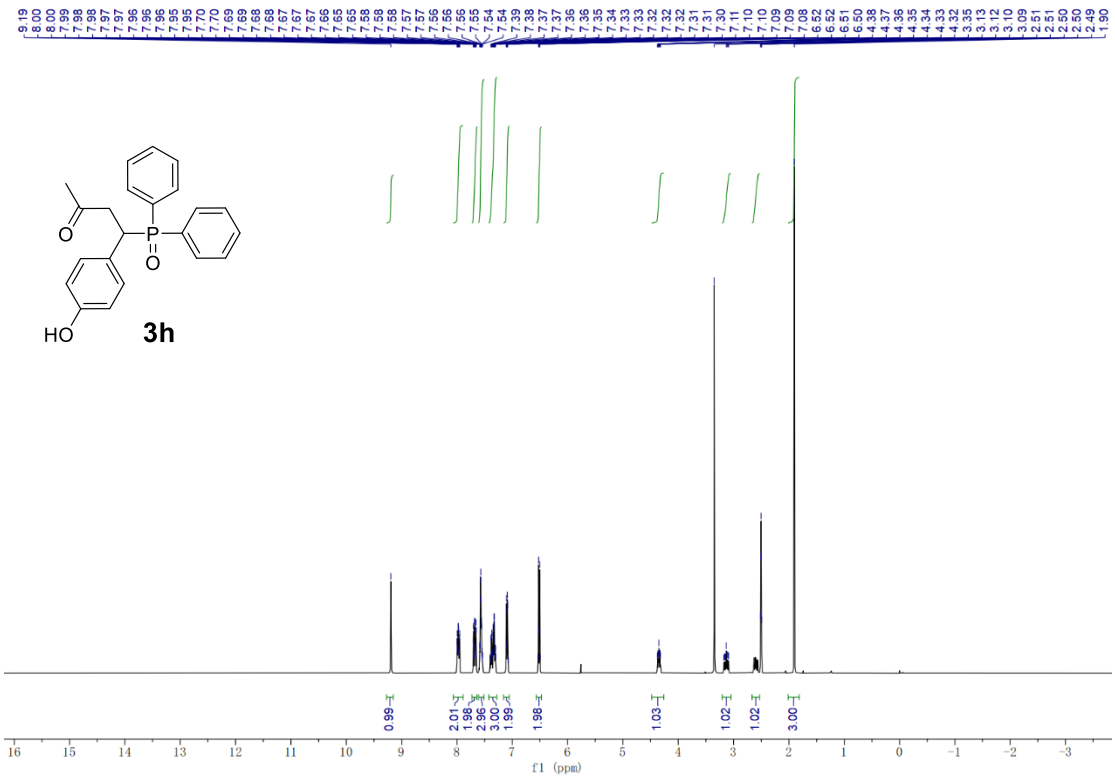


Figure S3.23 ^{1}H NMR spectrum of **3h** (400 MHz, DMSO-d_6).

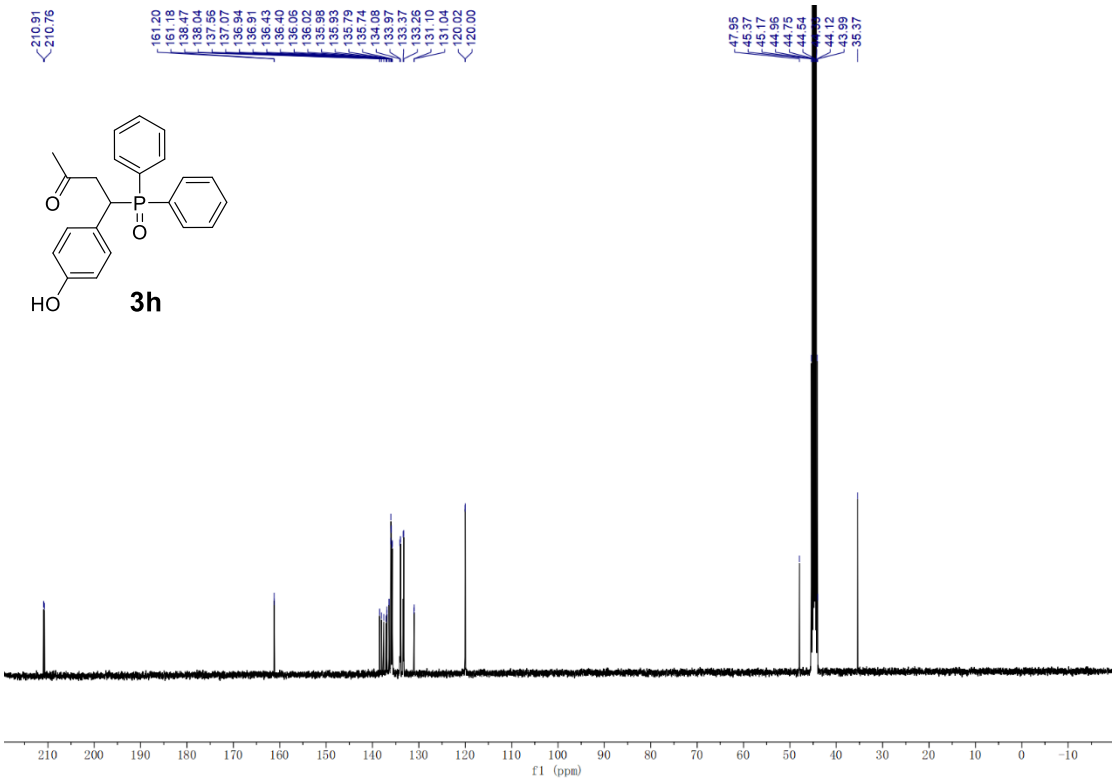


Figure S3.24 ^{13}C NMR spectrum of **3h** (101 MHz, DMSO-d_6).

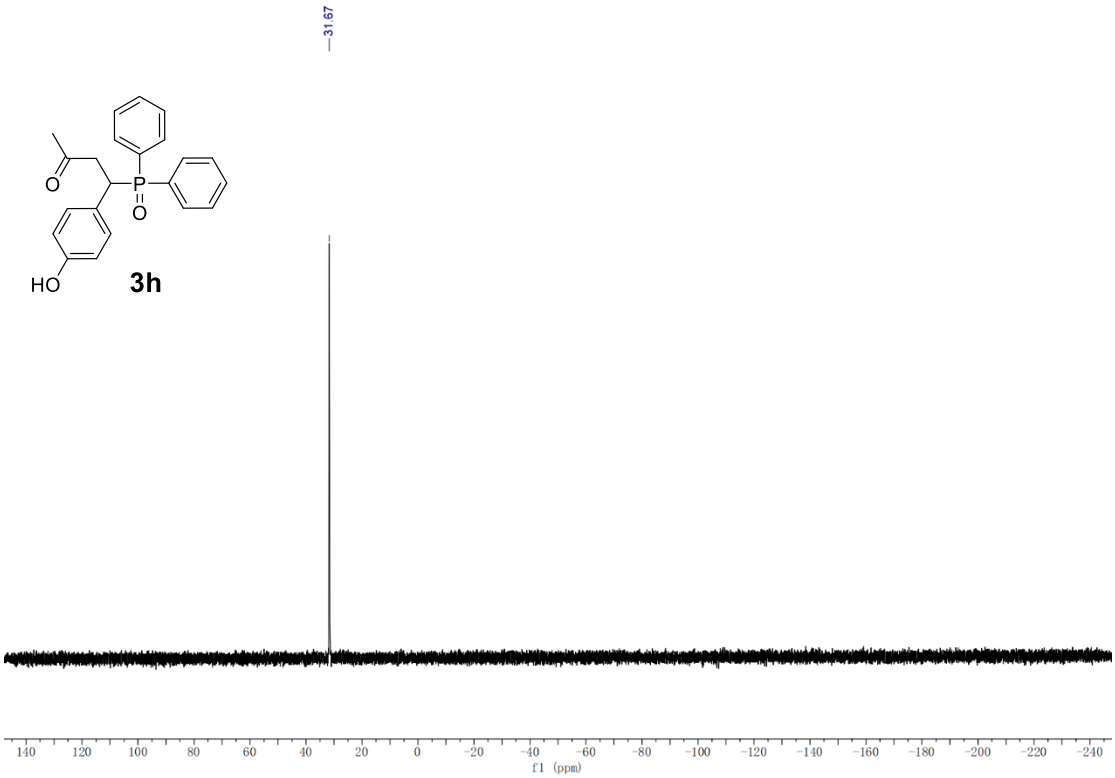


Figure S3.25 ^{31}P NMR spectrum of **3h** (162 MHz, DMSO-d_6).

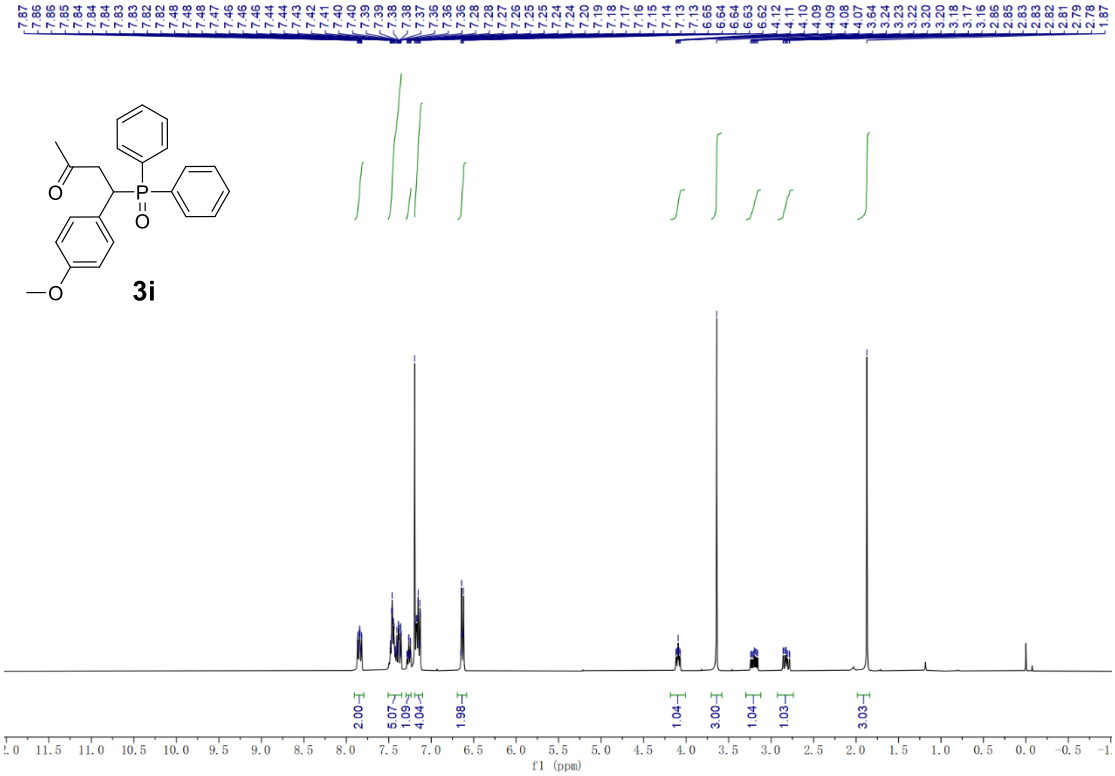


Figure S3.26 ^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$).

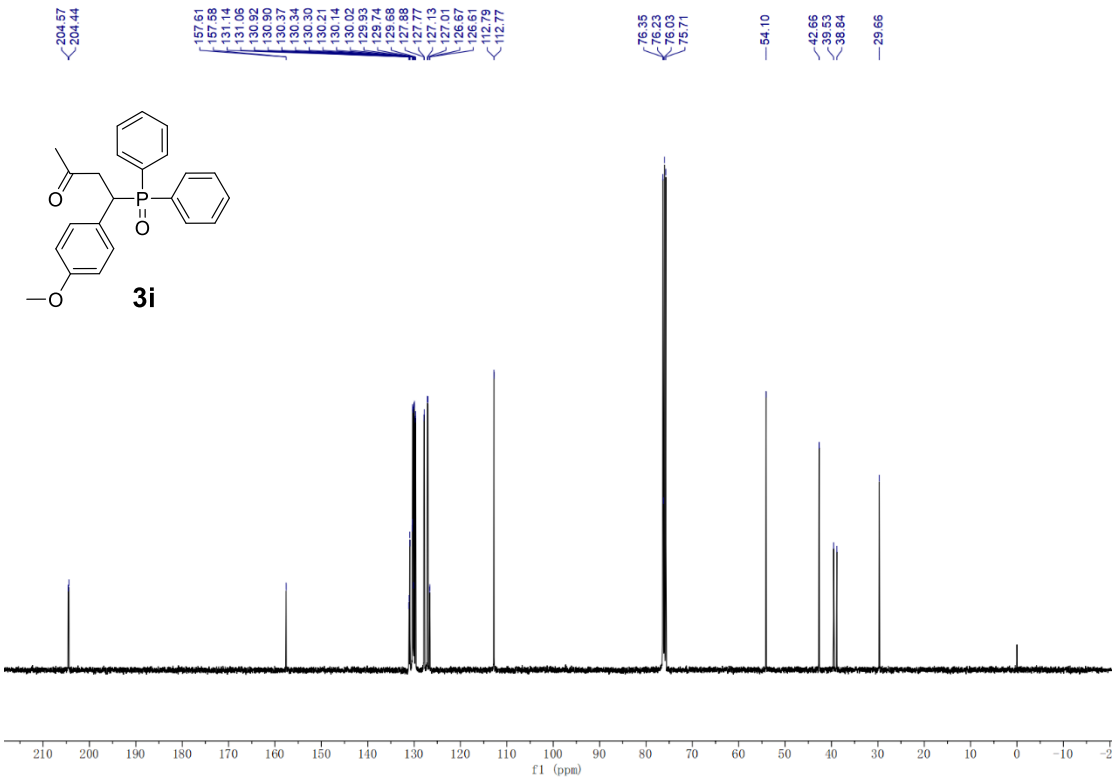


Figure S3.27 ^{13}C NMR spectrum of **3i** (101 MHz, $CDCl_3$).

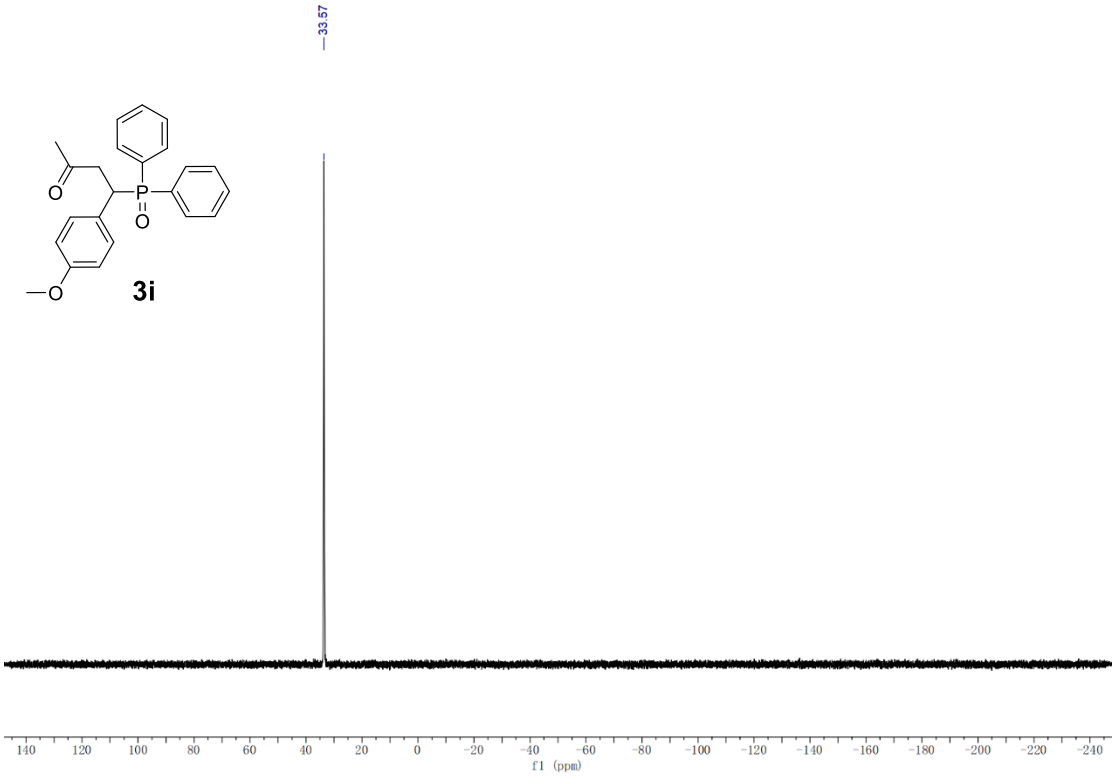


Figure S3.28 ^{31}P NMR spectrum of **3i** (162 MHz, $CDCl_3$).

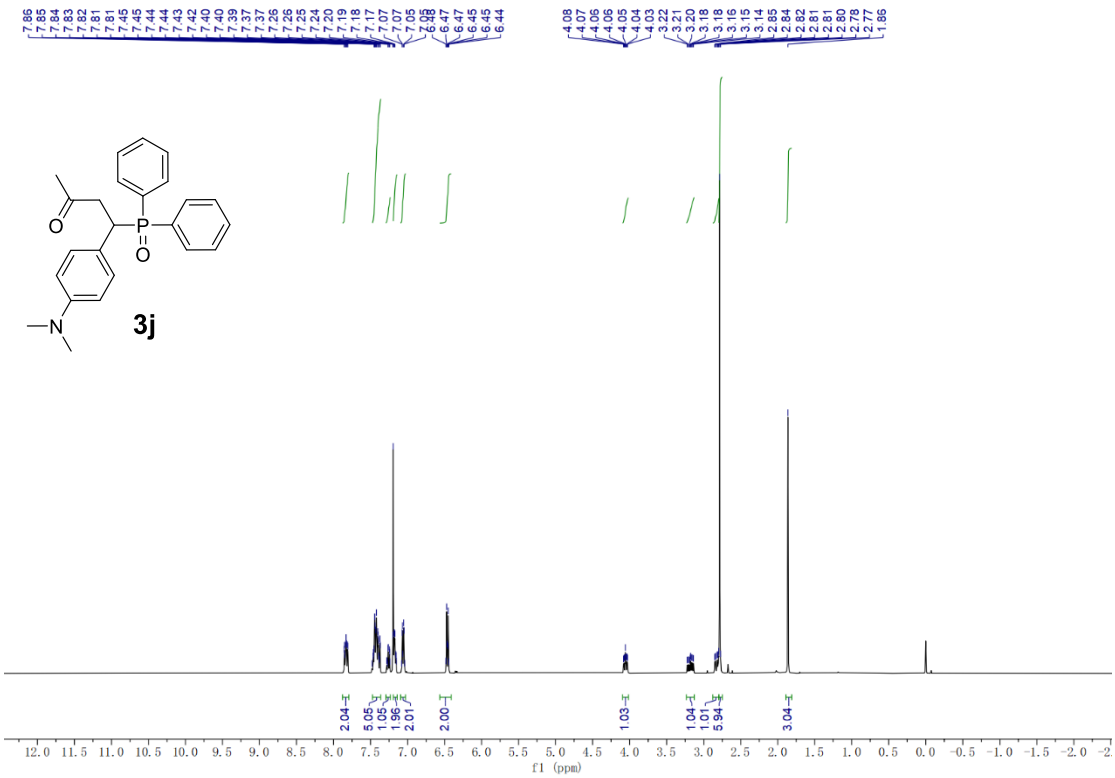


Figure S3.29 ^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$).

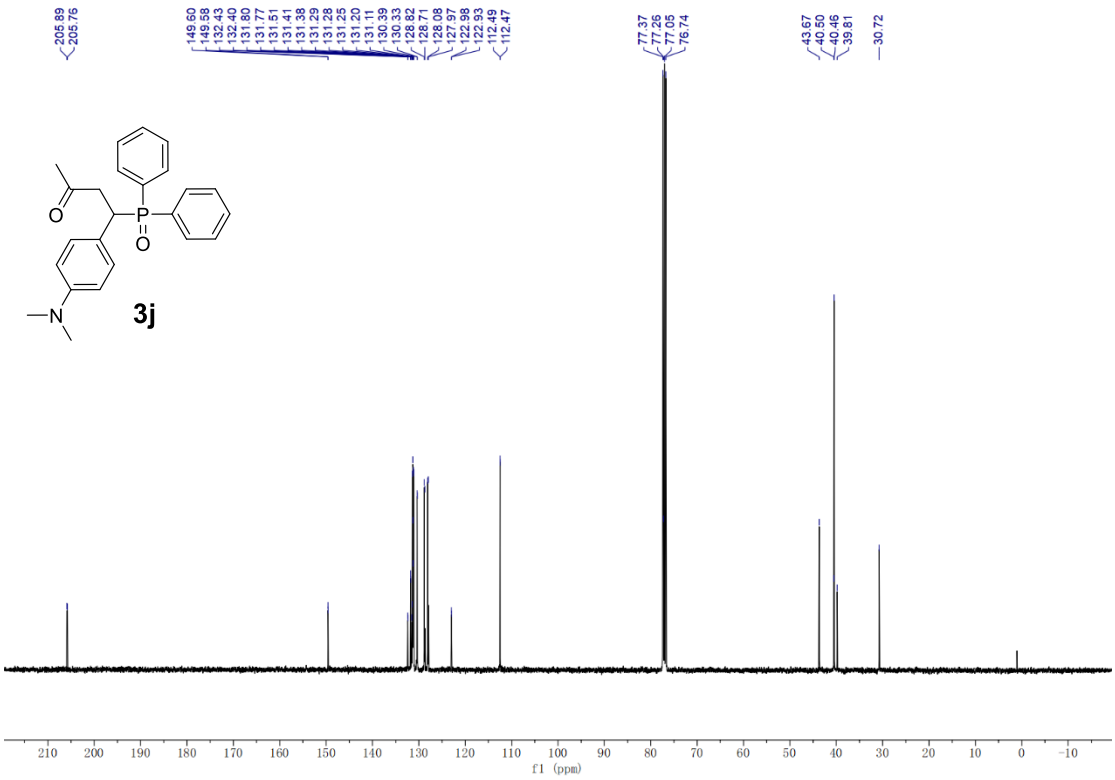


Figure S3.30 ^{13}C NMR spectrum of **3j** (101 MHz, $CDCl_3$).

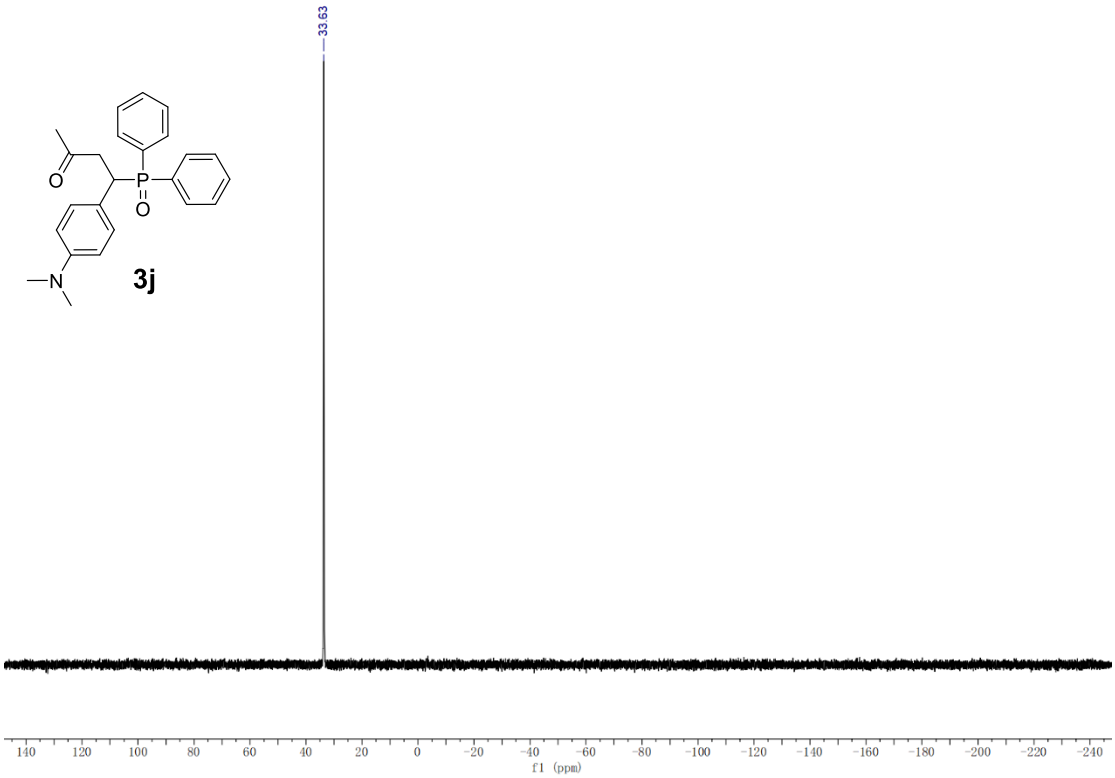


Figure S3.31 ^{31}P NMR spectrum of **3j** (162 MHz, $CDCl_3$).

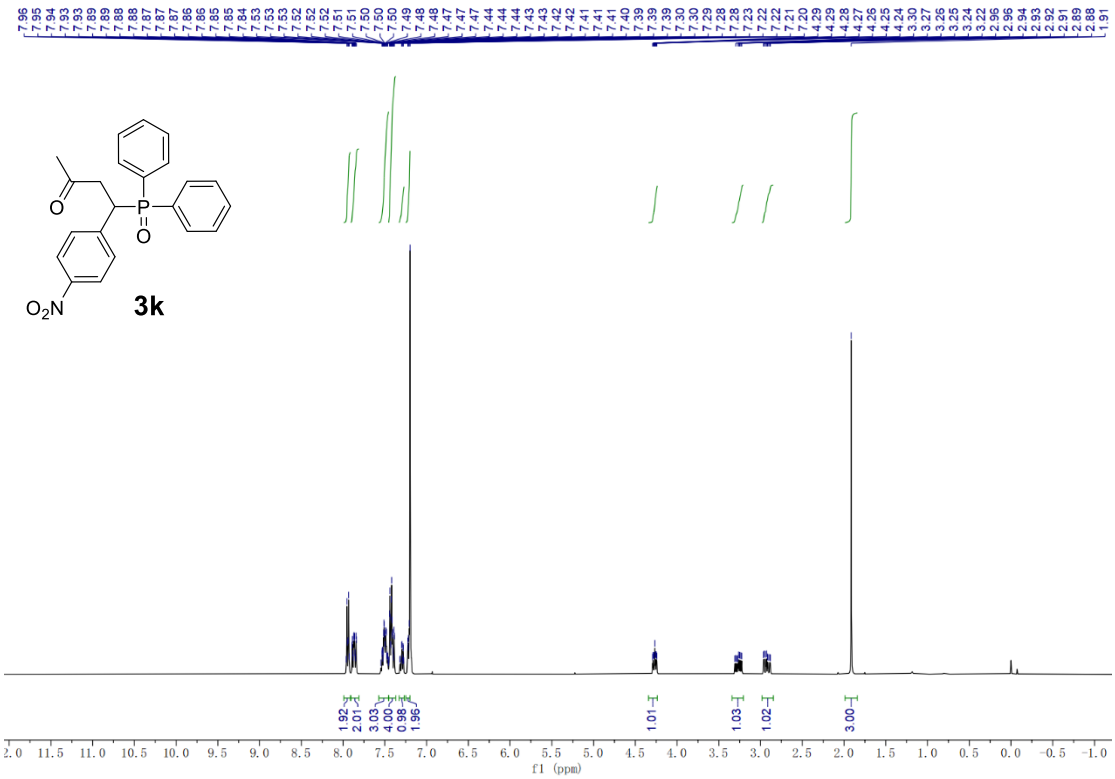


Figure S3.32 ^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$).

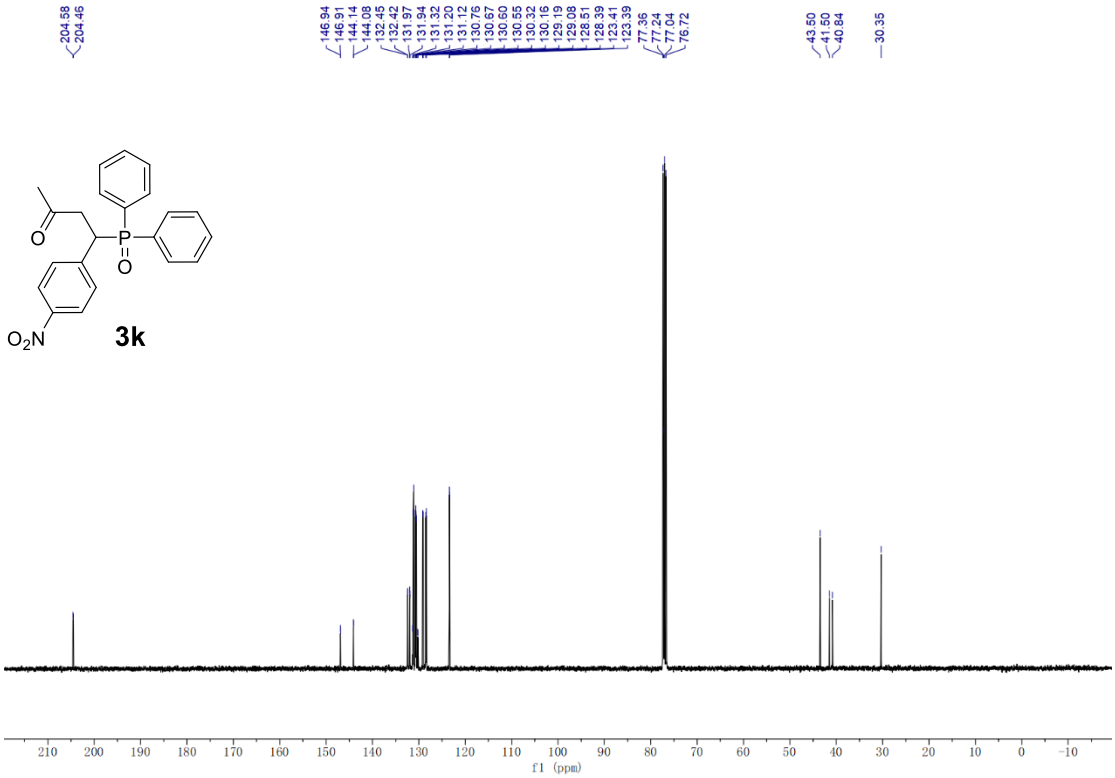


Figure S3.33 ^{13}C NMR spectrum of **3k** (101 MHz, $CDCl_3$).

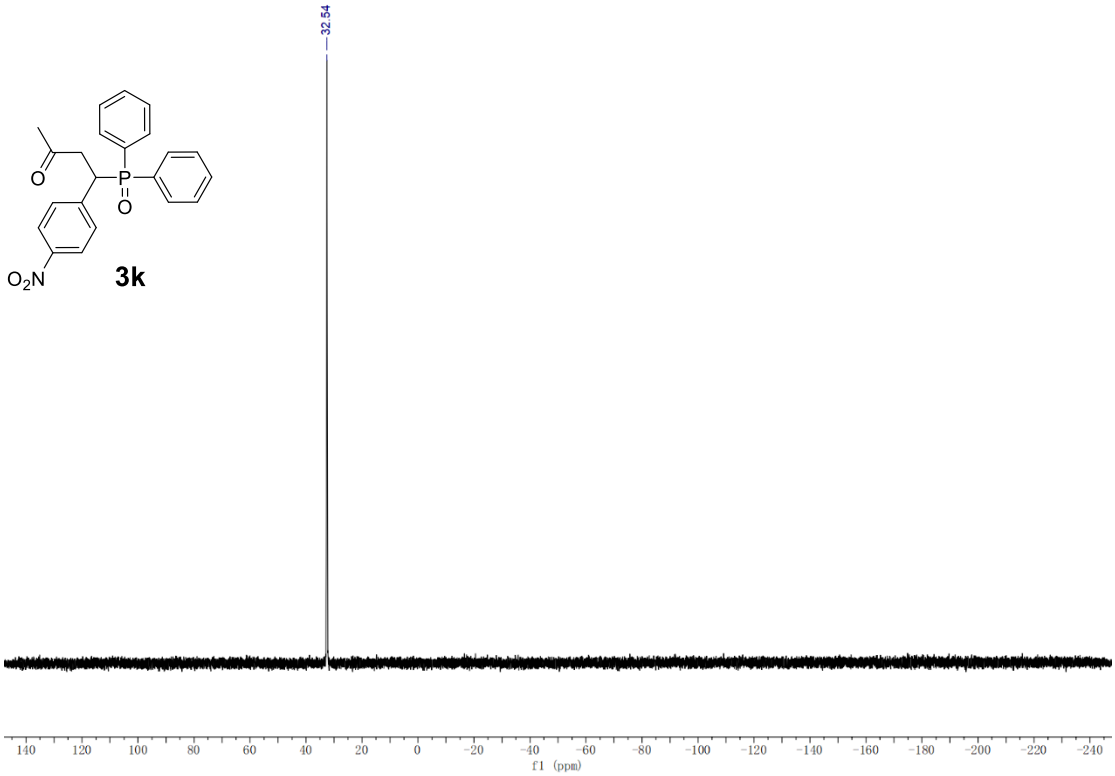


Figure S3.34 ^{31}P NMR spectrum of **3k** (162 MHz, $CDCl_3$).

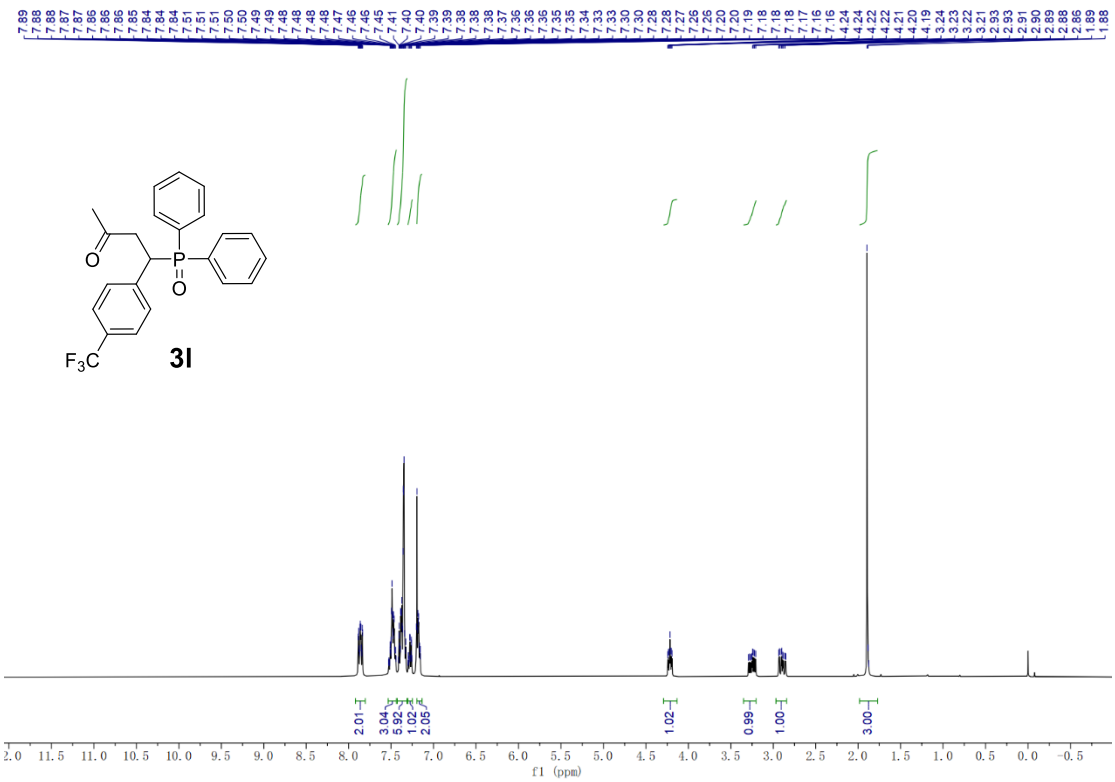


Figure S3.35 ^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$).

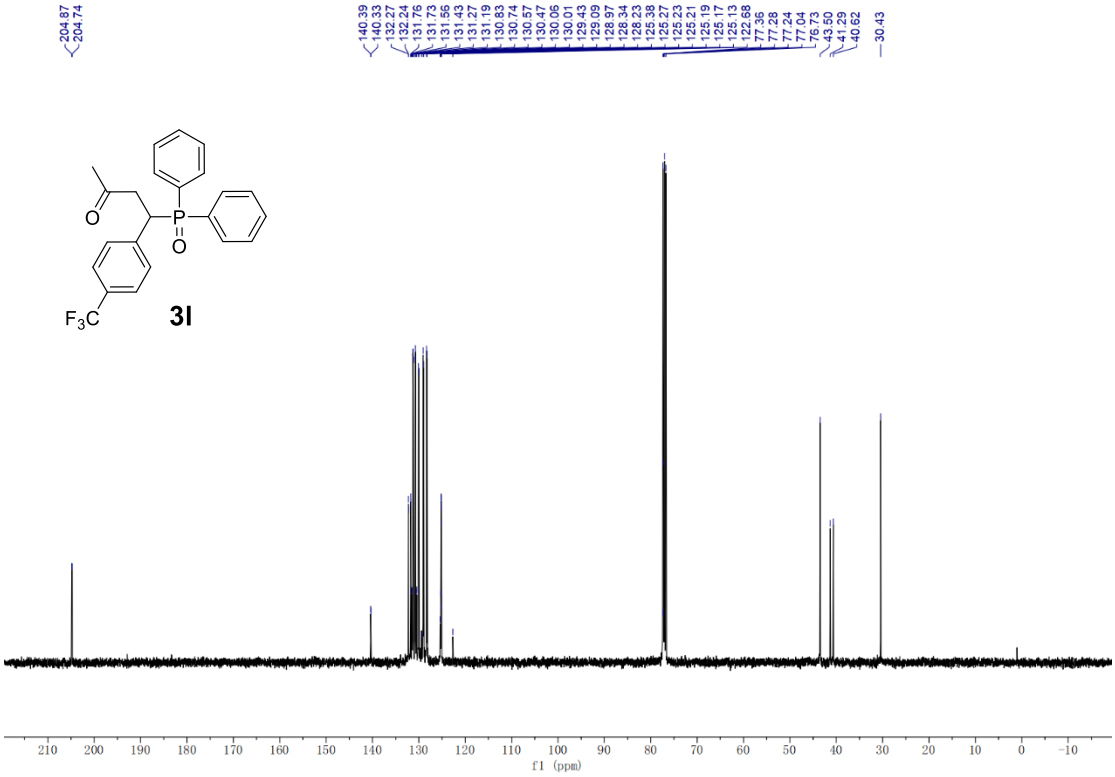


Figure S3.36 ^{13}C NMR spectrum of **3l** (101 MHz, $CDCl_3$).

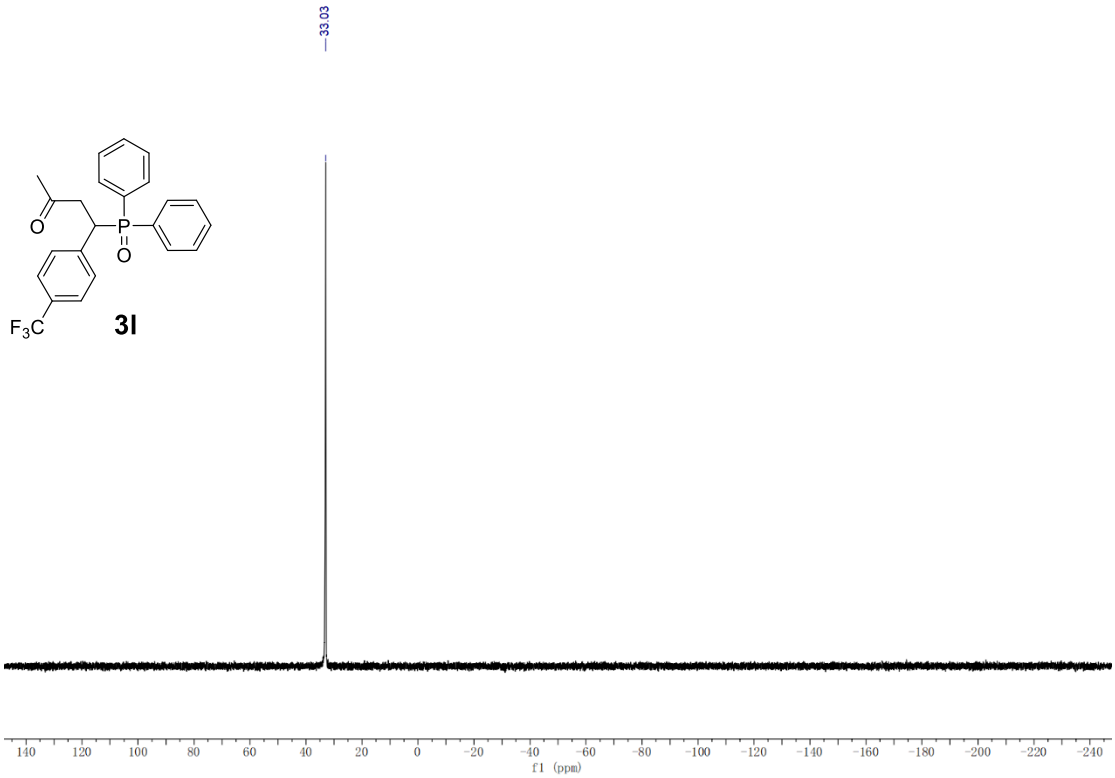


Figure S3.37 ^{31}P NMR spectrum of **3l** (162 MHz, $CDCl_3$).

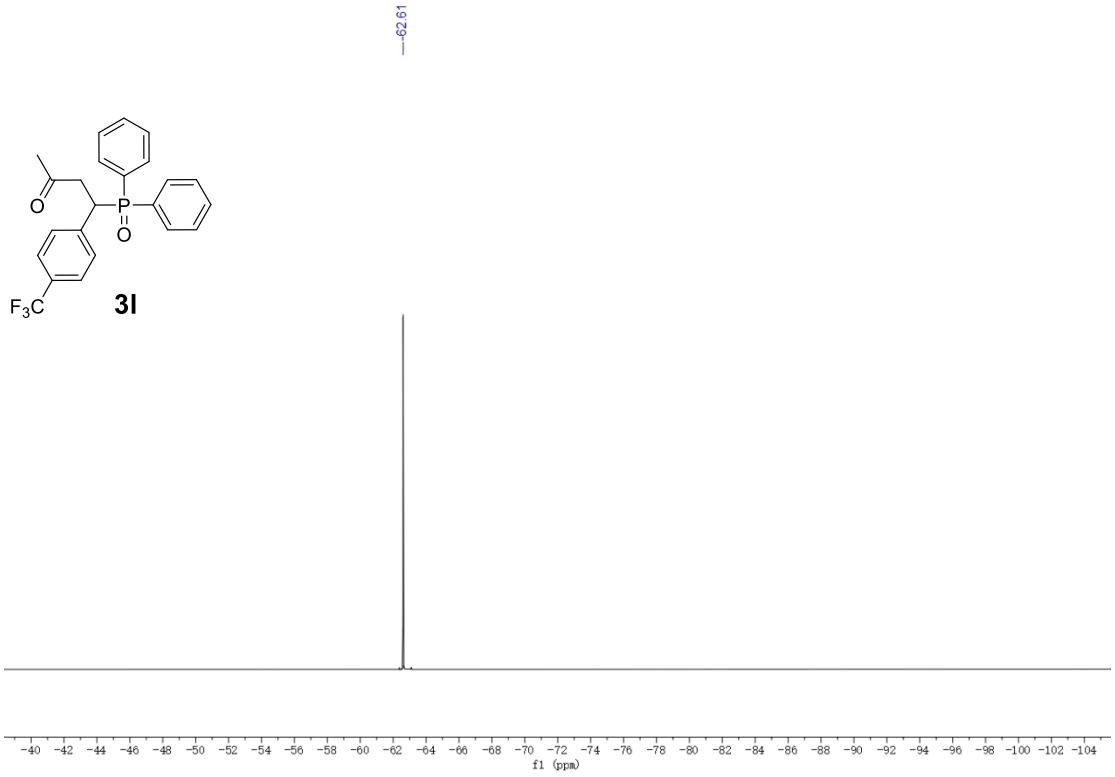


Figure S3.38 ^{19}F NMR spectrum of **3l** (376 MHz, $CDCl_3$).

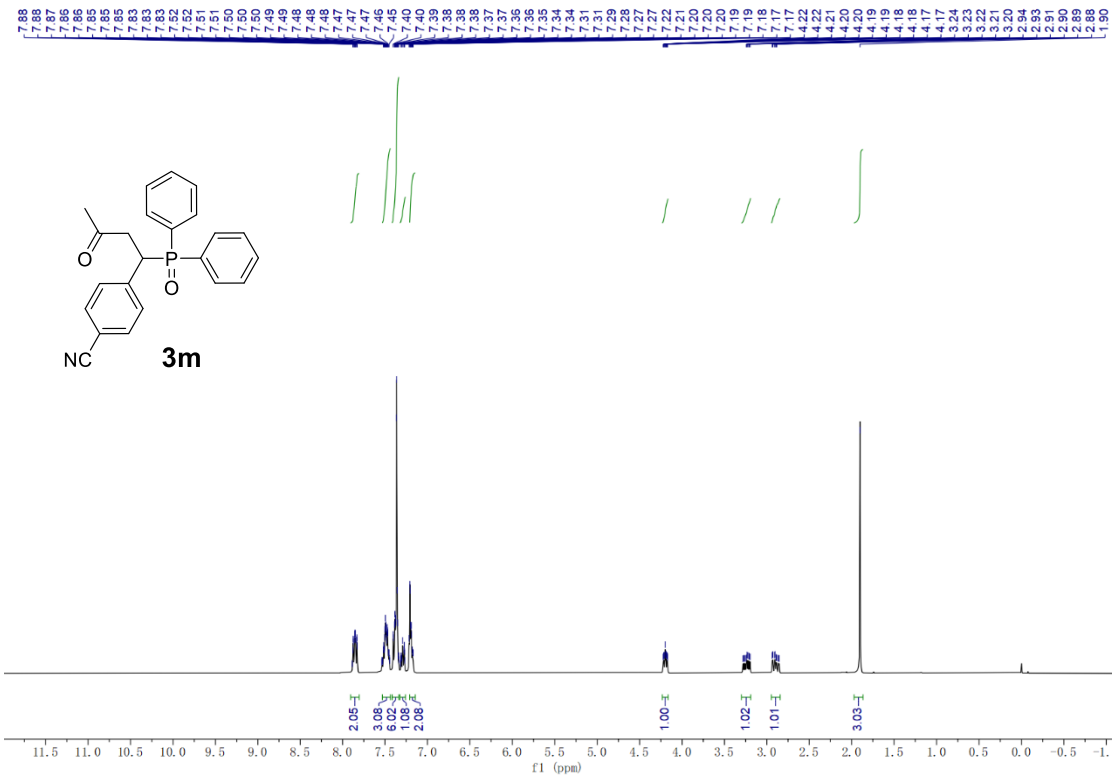


Figure S3.39 ^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$).

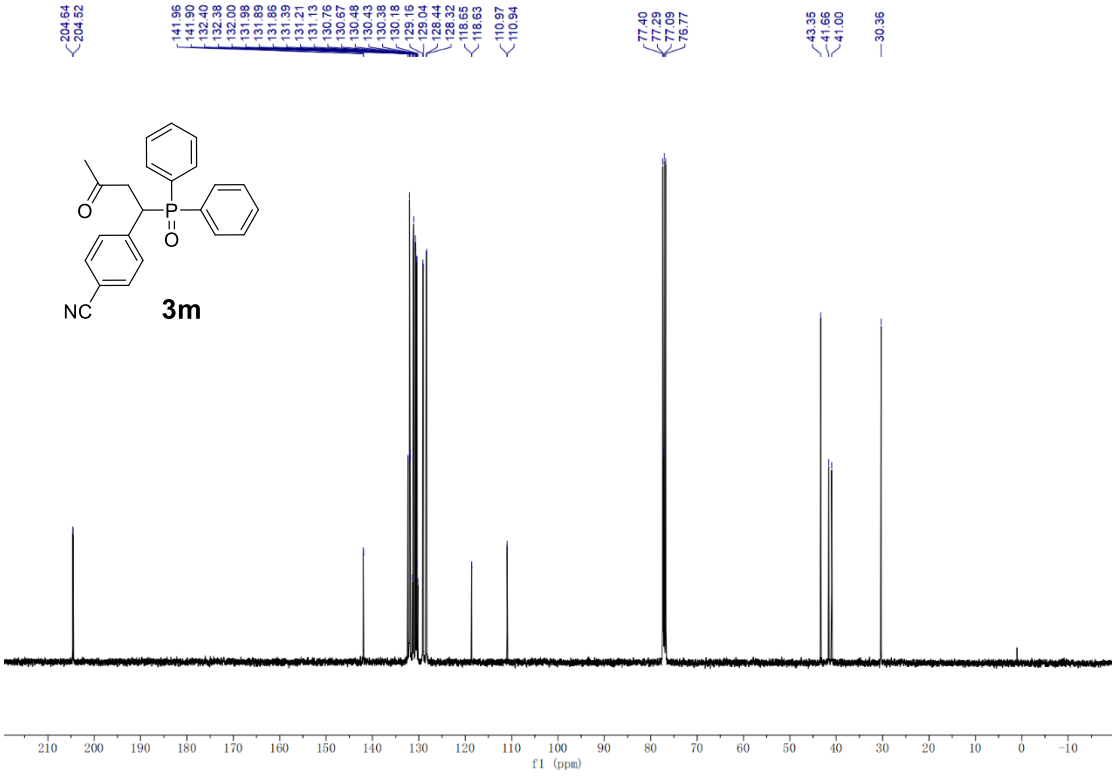


Figure S3.40 ^{13}C NMR spectrum of **3m** (101 MHz, $CDCl_3$).

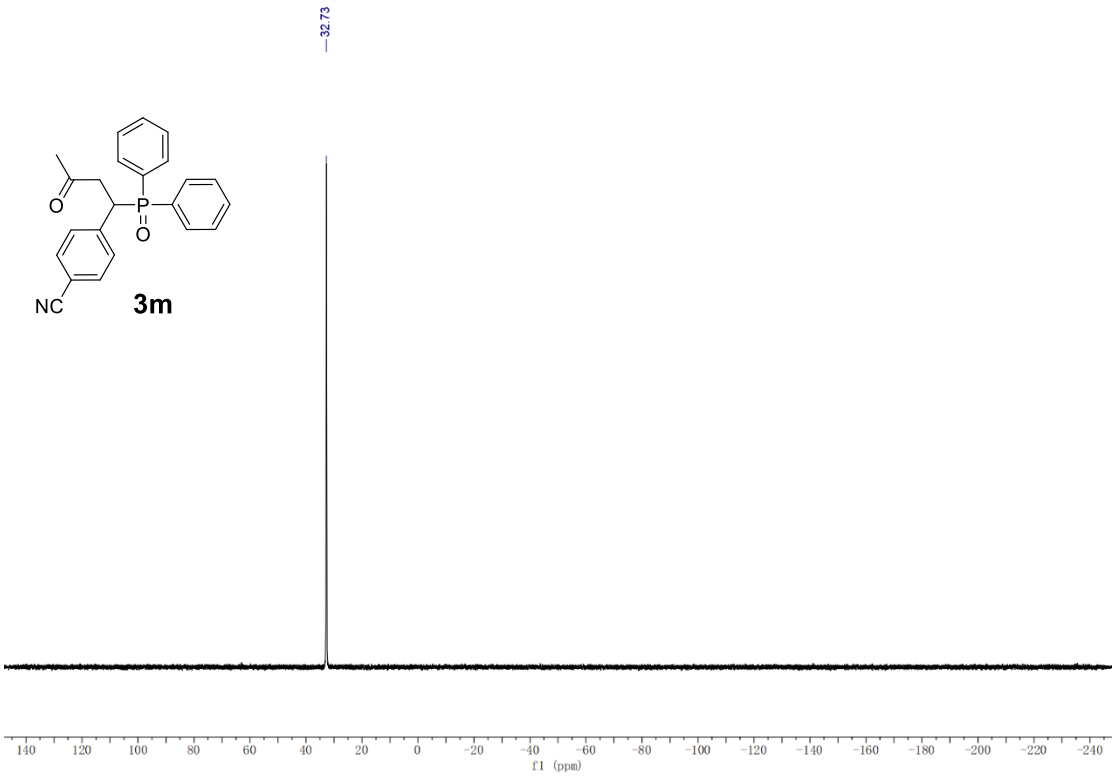


Figure S3.41 ^{31}P NMR spectrum of **3m** (162 MHz, $CDCl_3$).

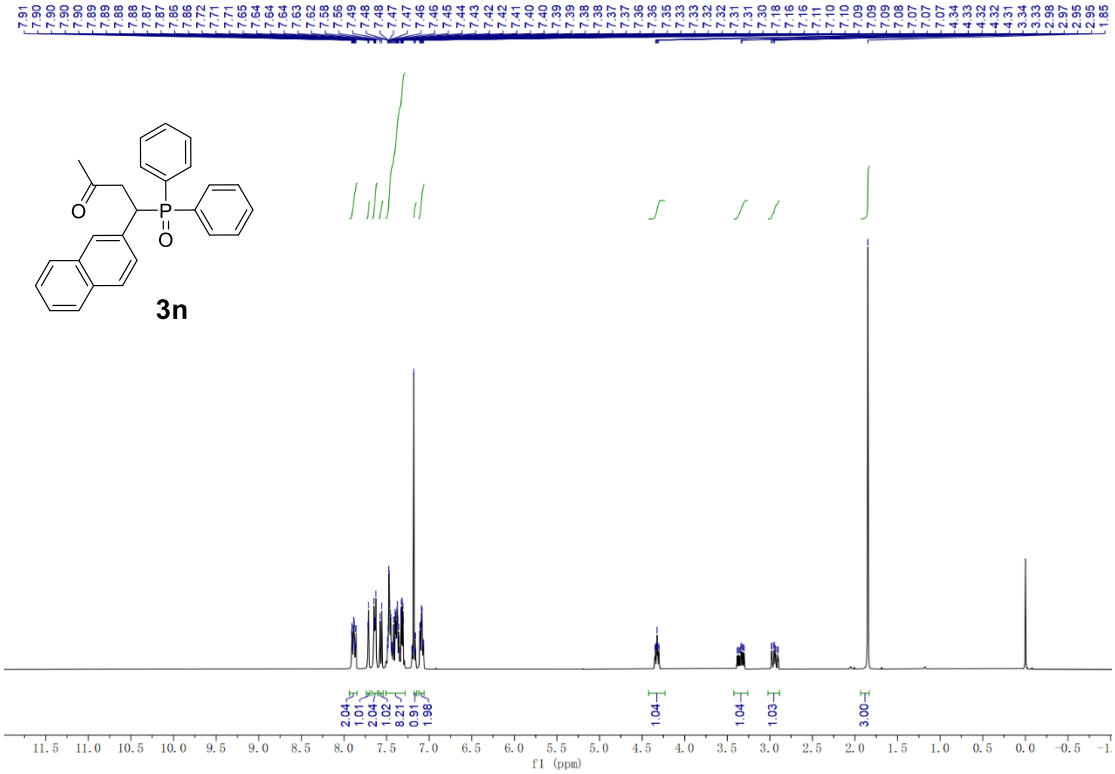


Figure S3.42 ^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$).

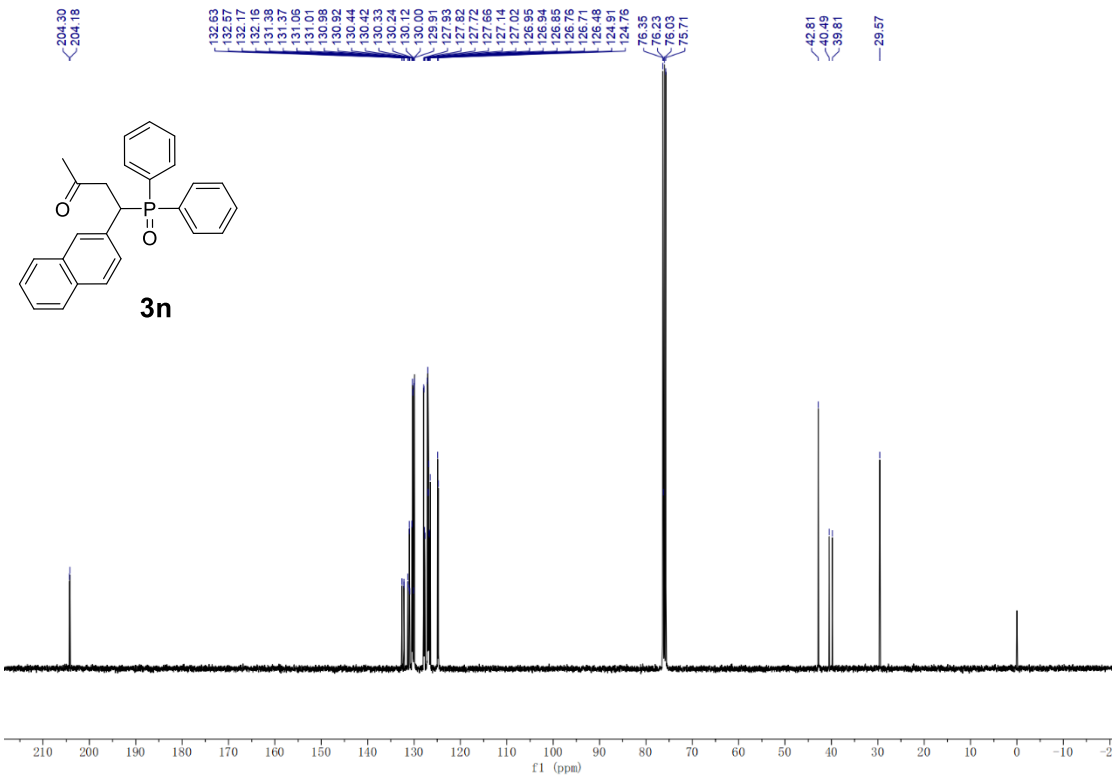


Figure S3.43 ^{13}C NMR spectrum of **3n** (101 MHz, $CDCl_3$).

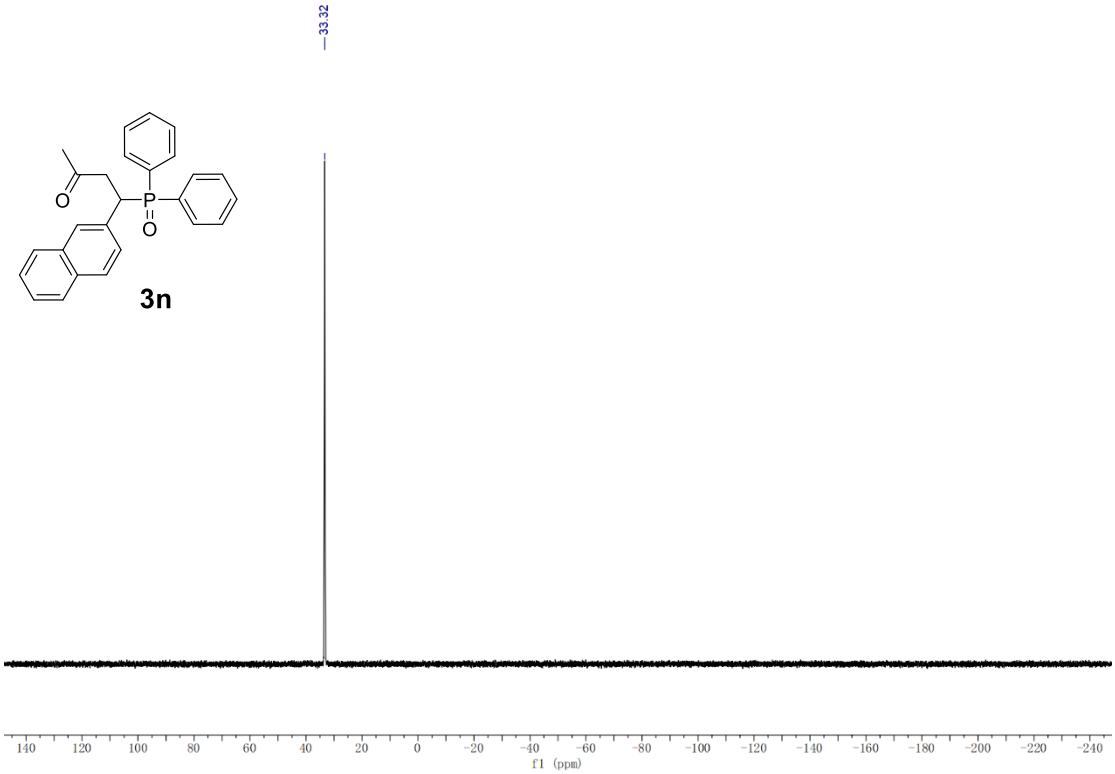


Figure S3.44 ^{31}P NMR spectrum of **3n** (162 MHz, $CDCl_3$).

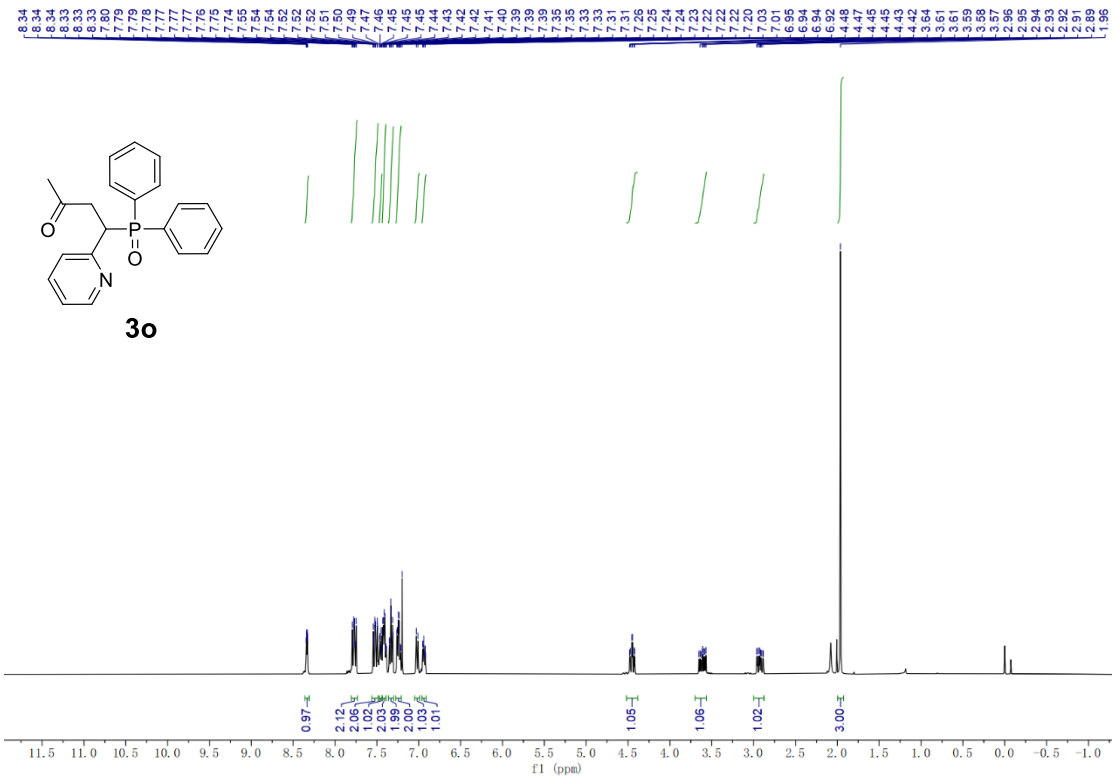


Figure S3.45 ^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$).

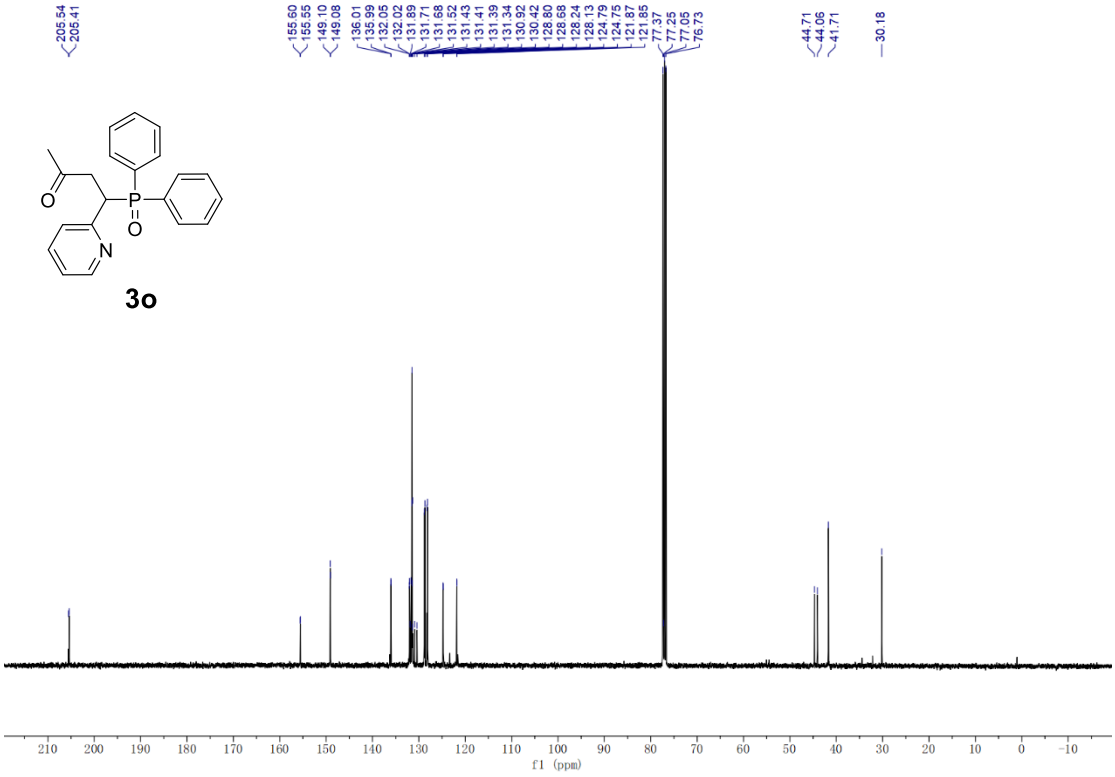


Figure S3.46 ^{13}C NMR spectrum of **3o** (101 MHz, $CDCl_3$).

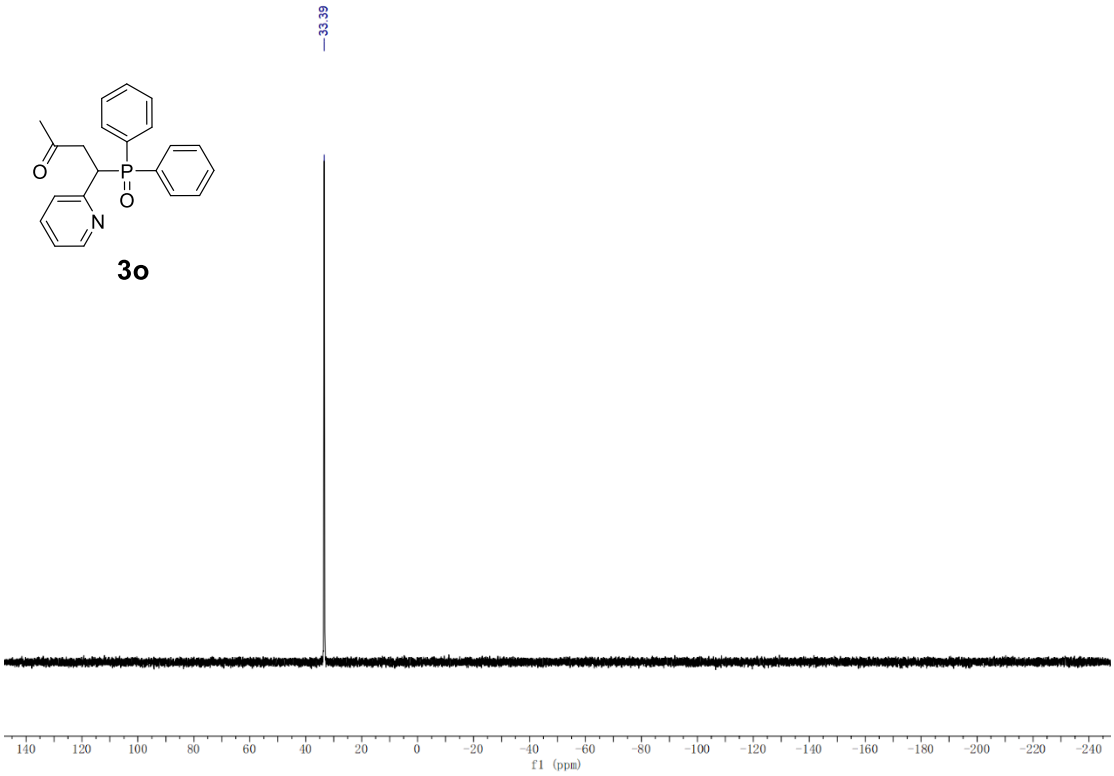


Figure S3.47 ^{31}P NMR spectrum of **3o** (162 MHz, $CDCl_3$).

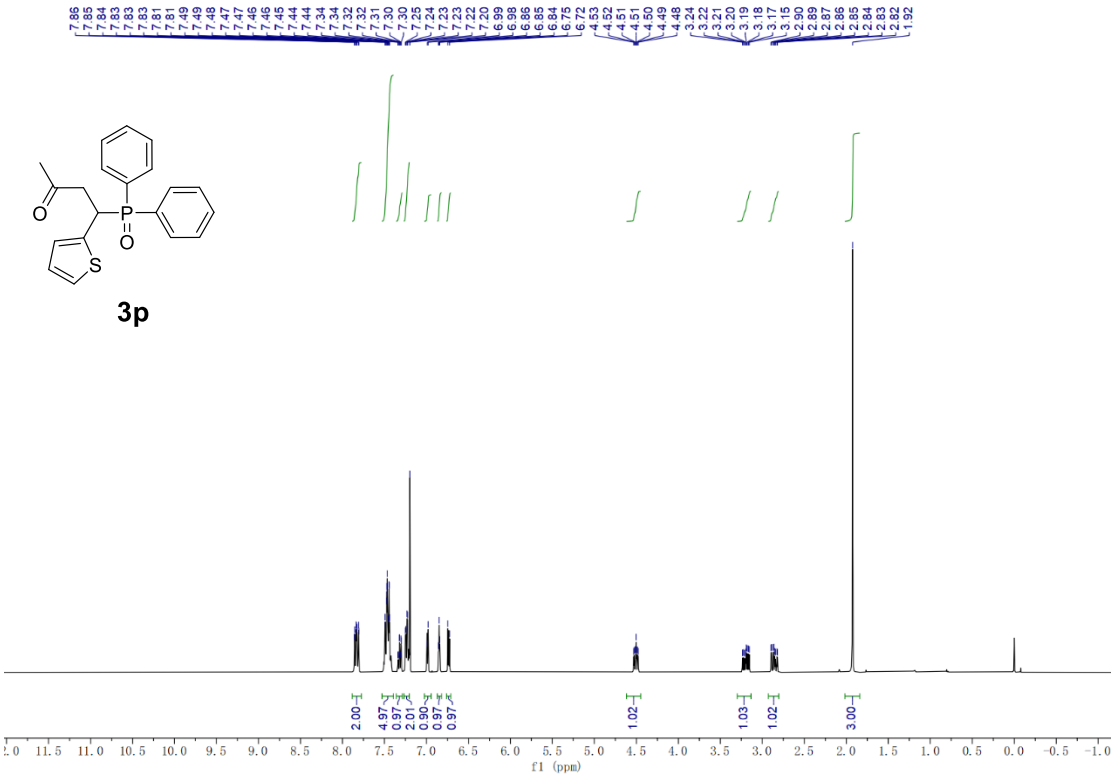


Figure S3.48 ^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$).

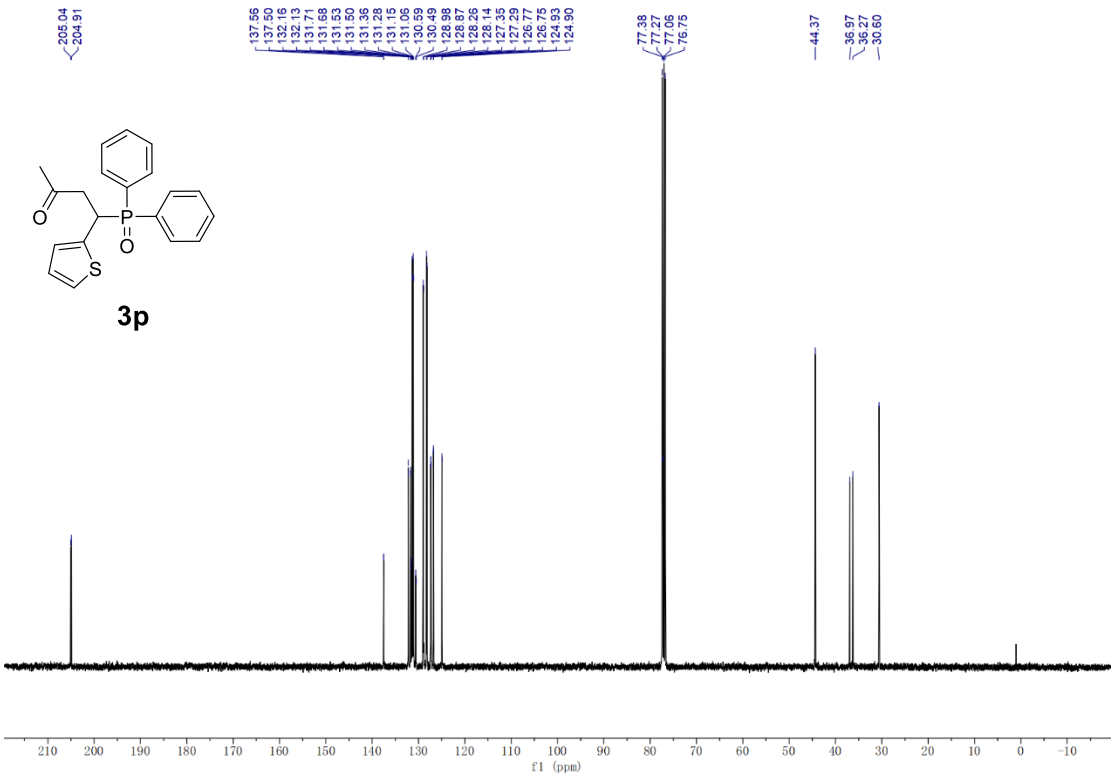


Figure S3.49 ^{13}C NMR spectrum of **3p** (101 MHz, $CDCl_3$).

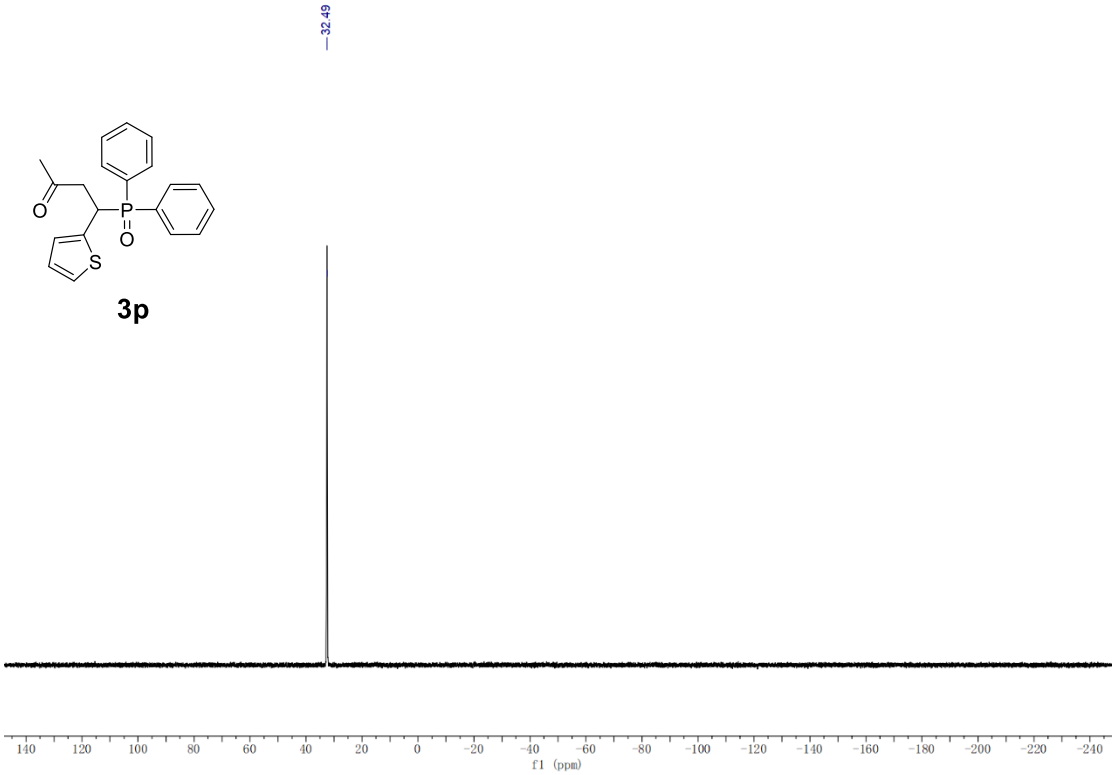


Figure S3.50 ^{31}P NMR spectrum of **3p** (162 MHz, $CDCl_3$).

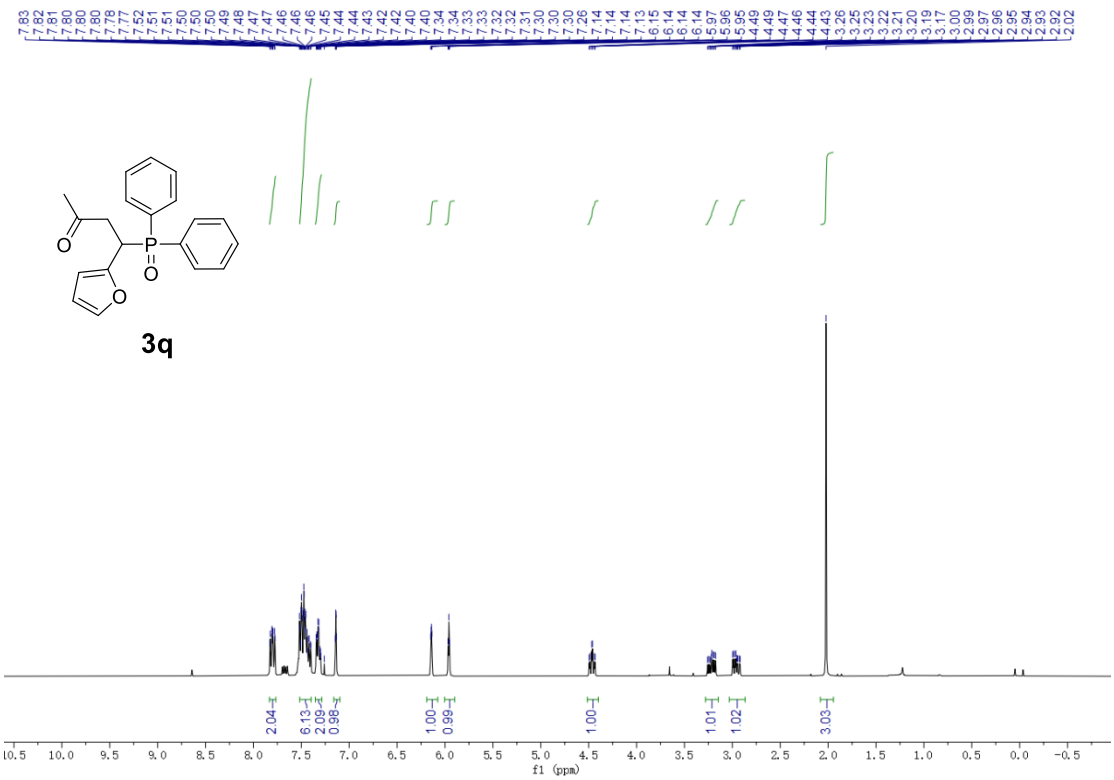


Figure S3.51 ^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$).

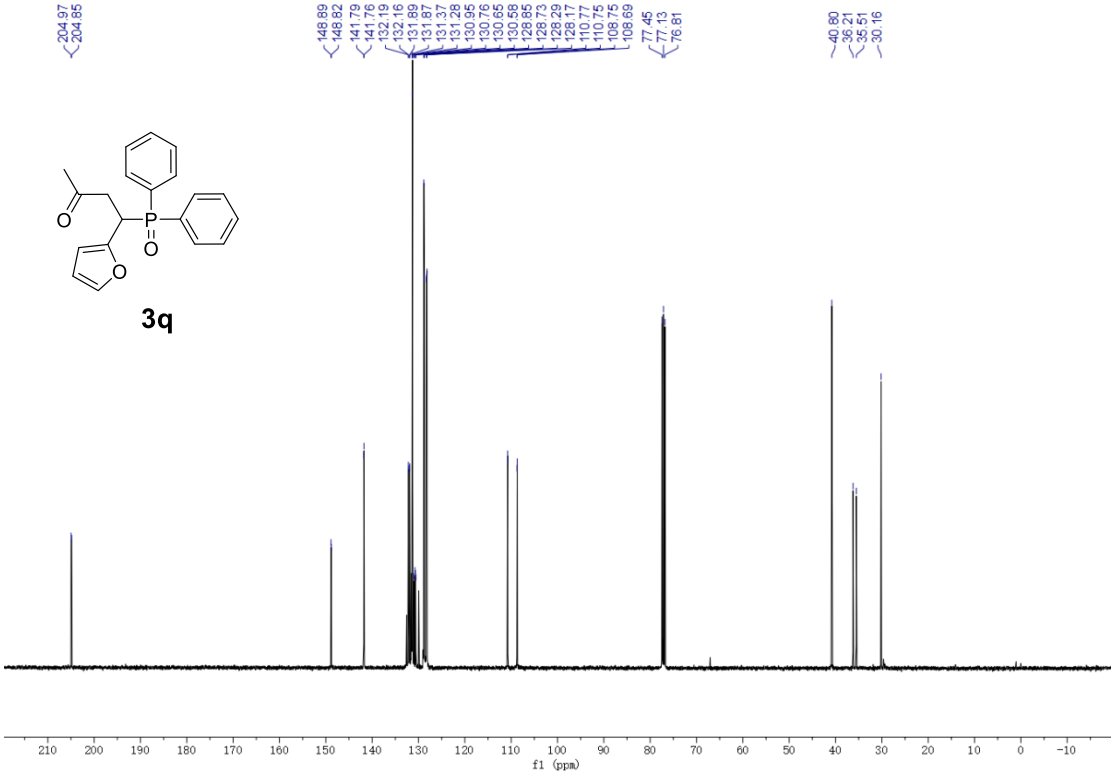


Figure S3.52 ^{13}C NMR spectrum of **3q** (101 MHz, $CDCl_3$).

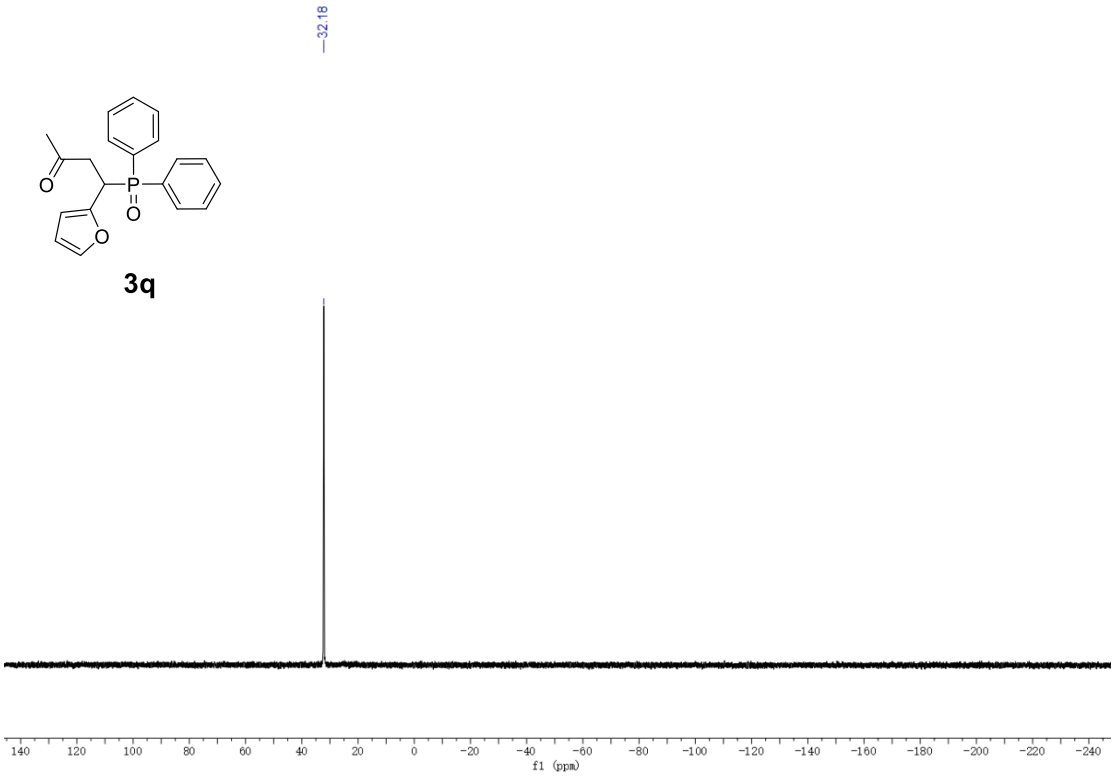


Figure S3.53 ^{31}P NMR spectrum of **3q** (162 MHz, $CDCl_3$).

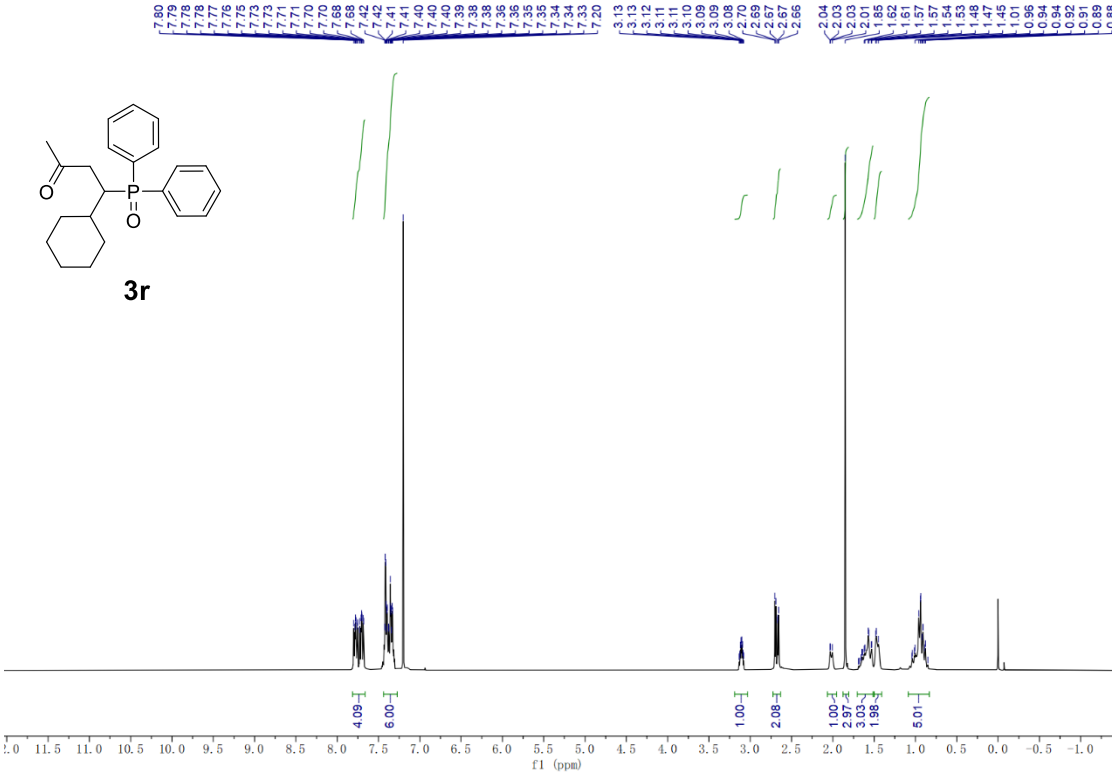


Figure S3.54 ^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$).

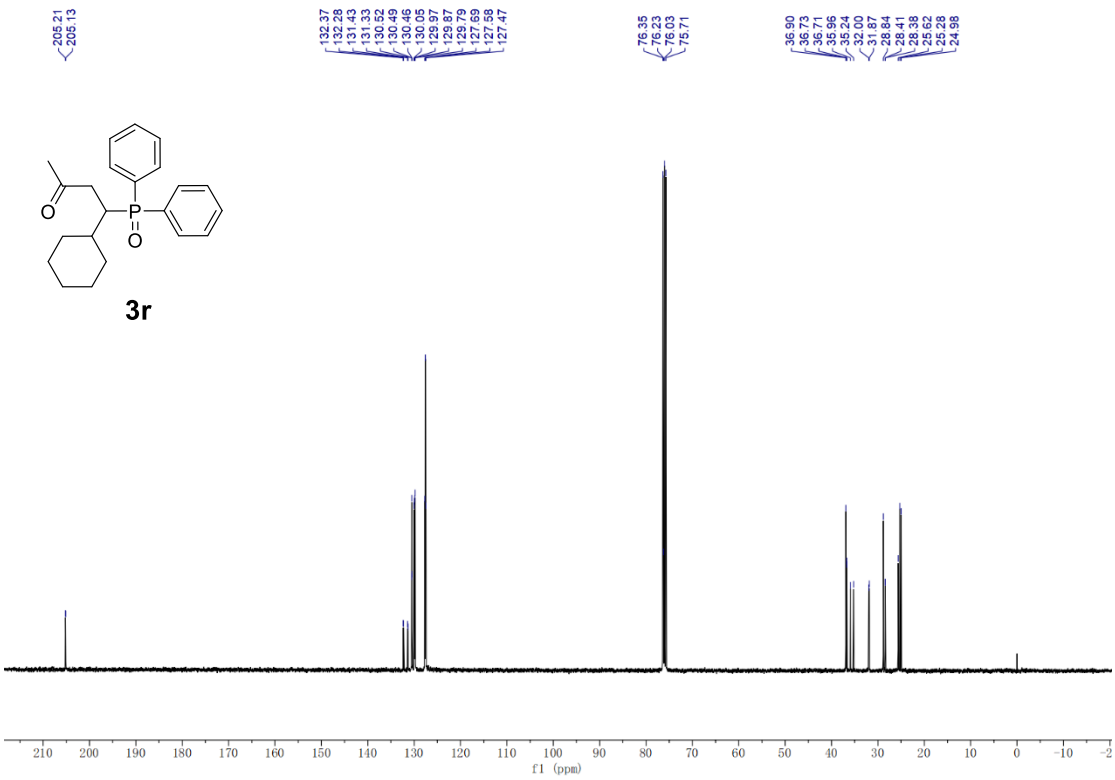


Figure S3.55 ^{13}C NMR spectrum of **3r** (101 MHz, $CDCl_3$).

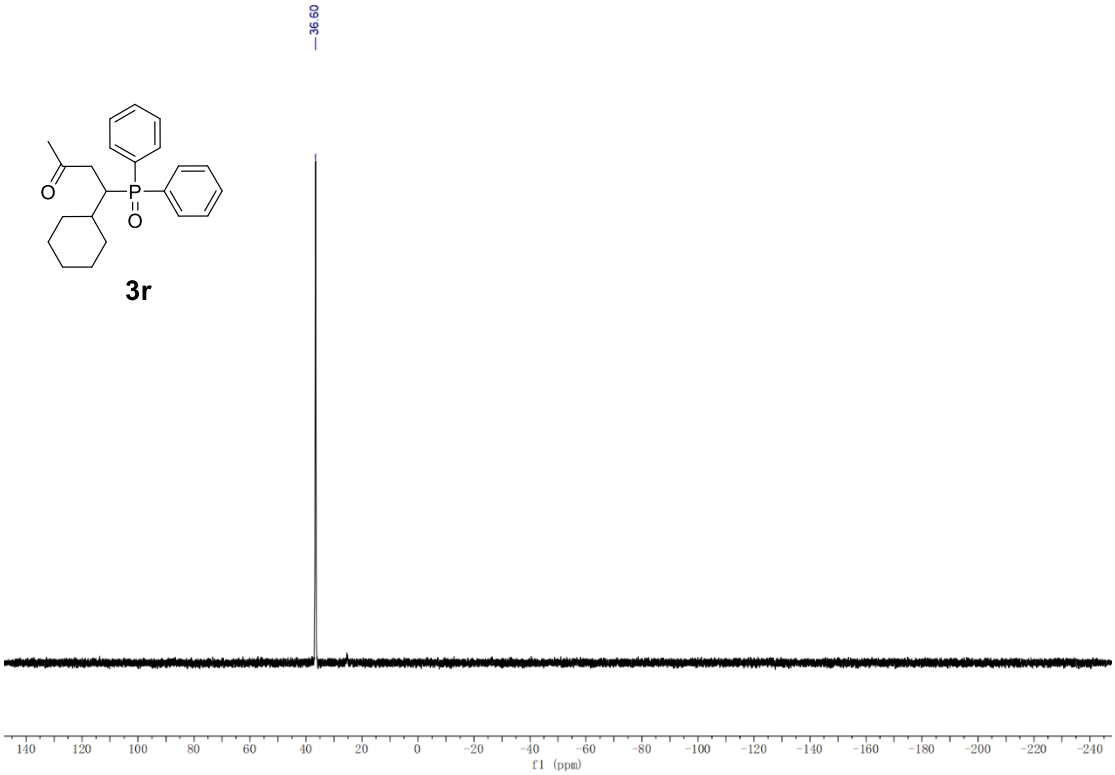


Figure S3.56 ^{31}P NMR spectrum of **3r** (162 MHz, $CDCl_3$).

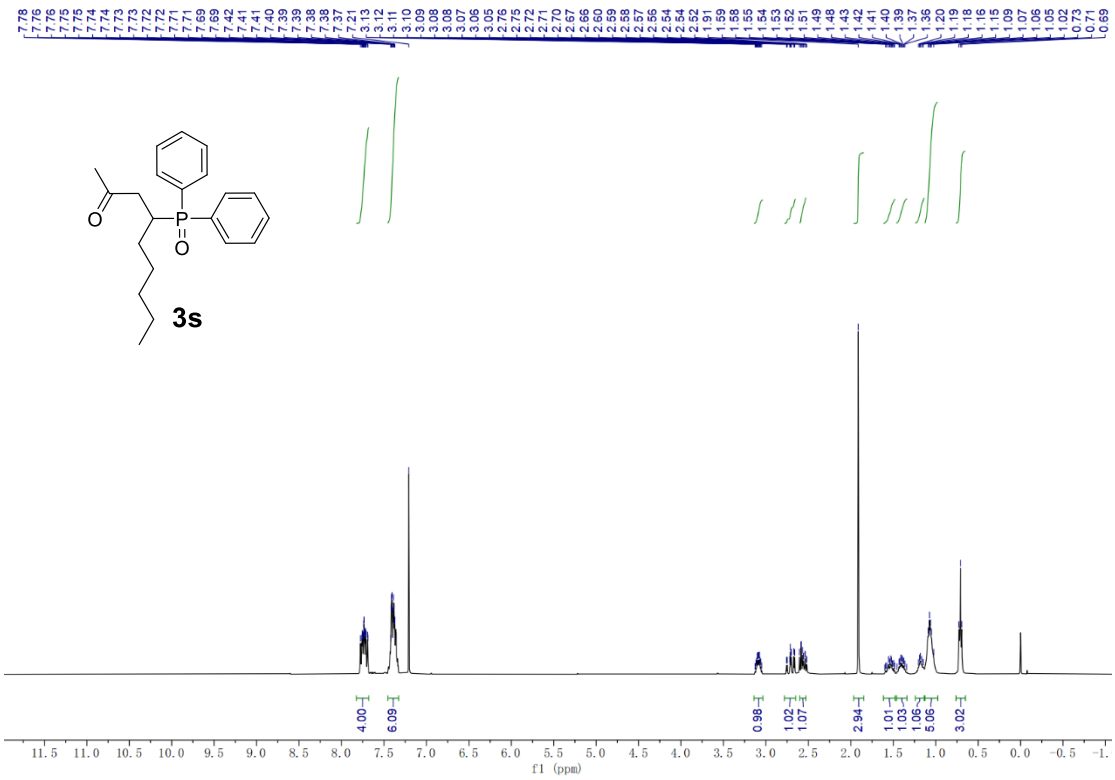


Figure S3.57 ^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$).

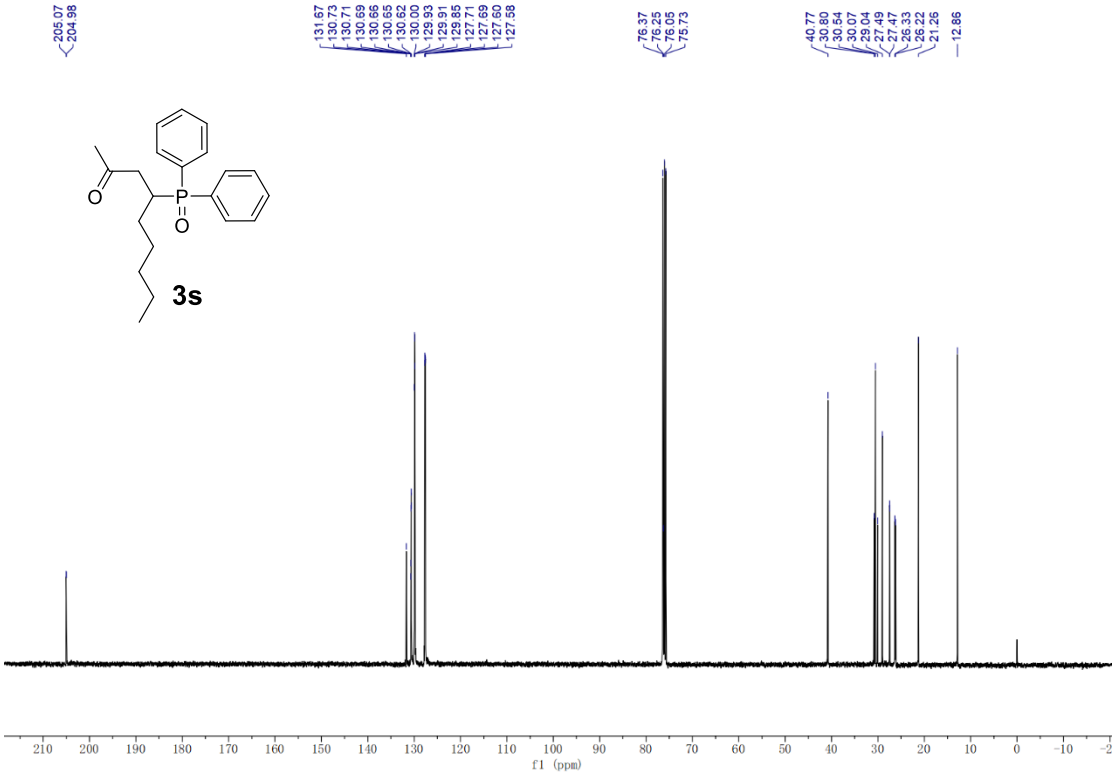


Figure S3.58 ^{13}C NMR spectrum of **3s** (101 MHz, $CDCl_3$).

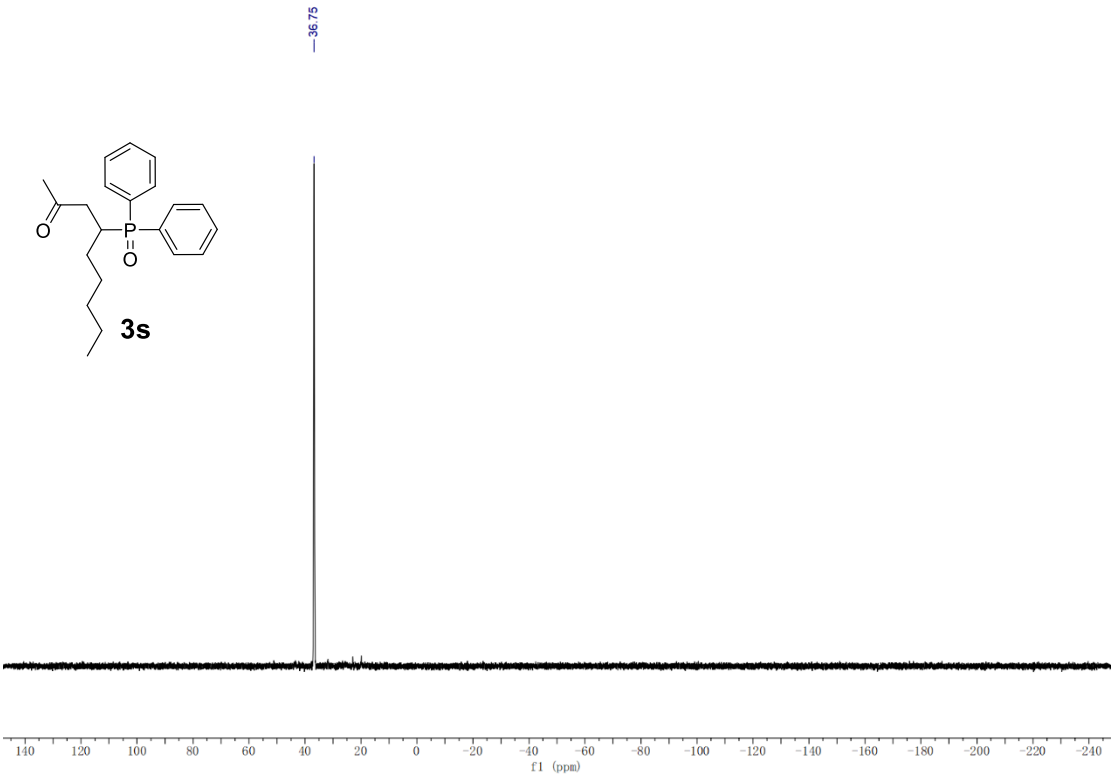


Figure S3.59 ^{31}P NMR spectrum of **3s** (162 MHz, $CDCl_3$).

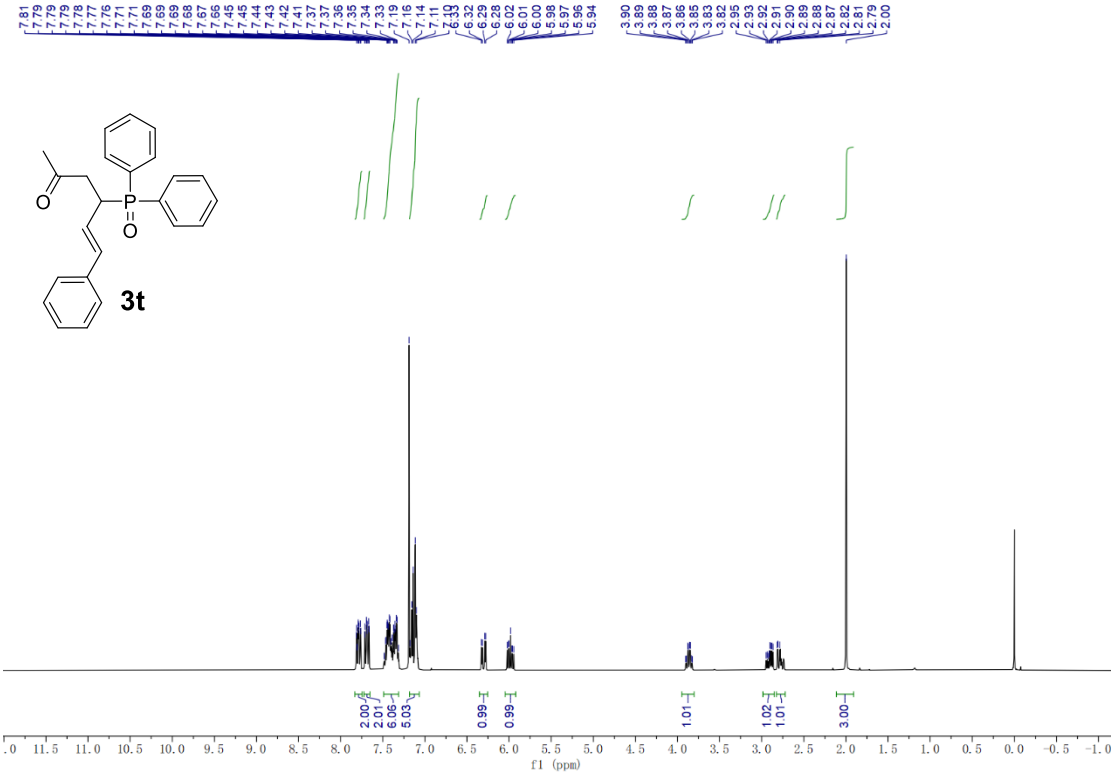


Figure S3.60 ^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$).

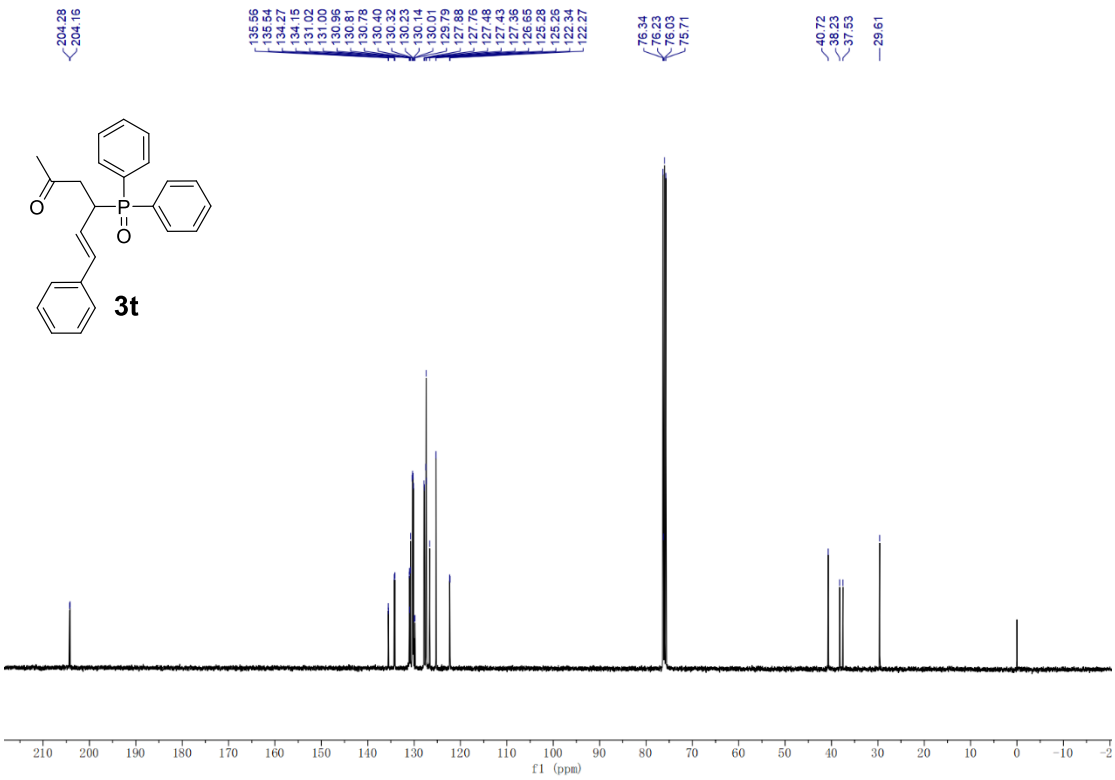


Figure S3.61 ^{13}C NMR spectrum of **3t** (101 MHz, $CDCl_3$).

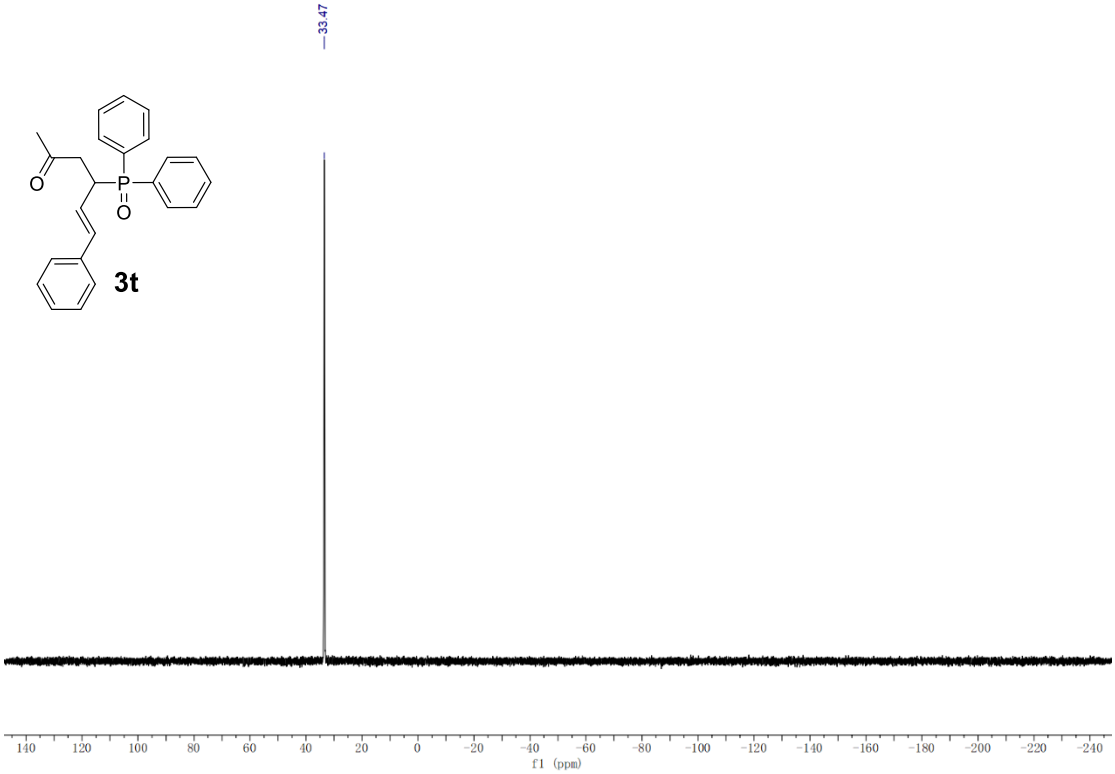


Figure S3.62 ^{31}P NMR spectrum of **3t** (162 MHz, $CDCl_3$).

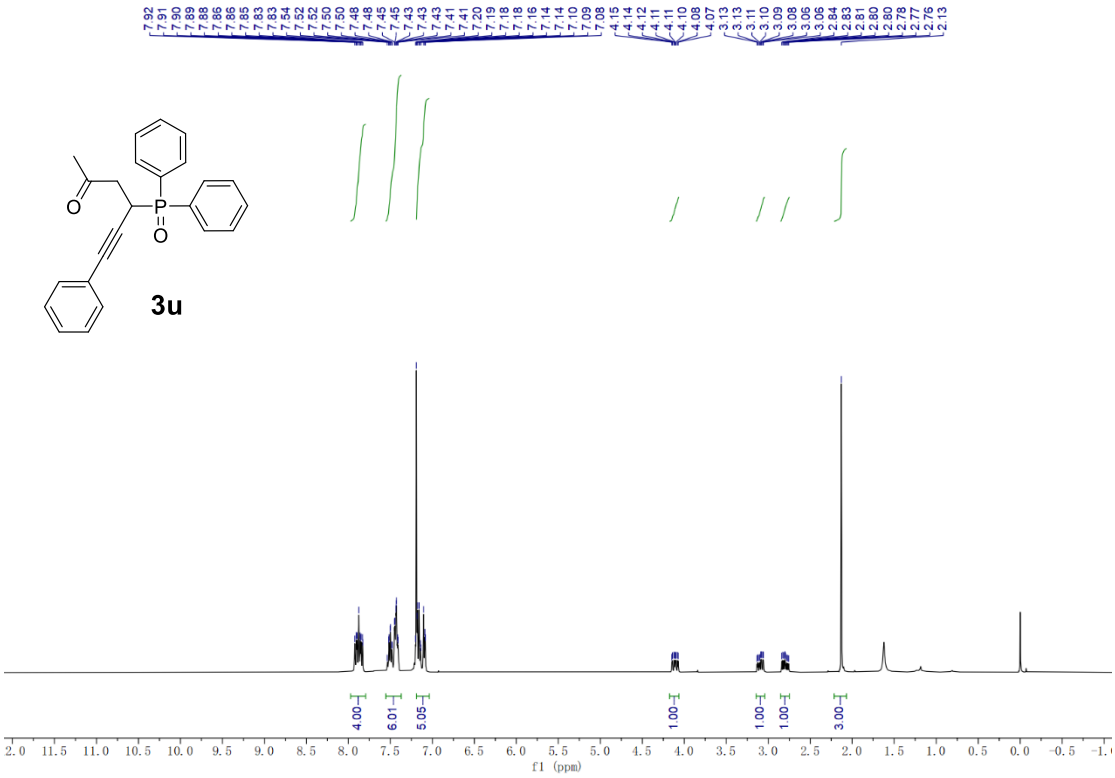


Figure S3.63 ^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$).

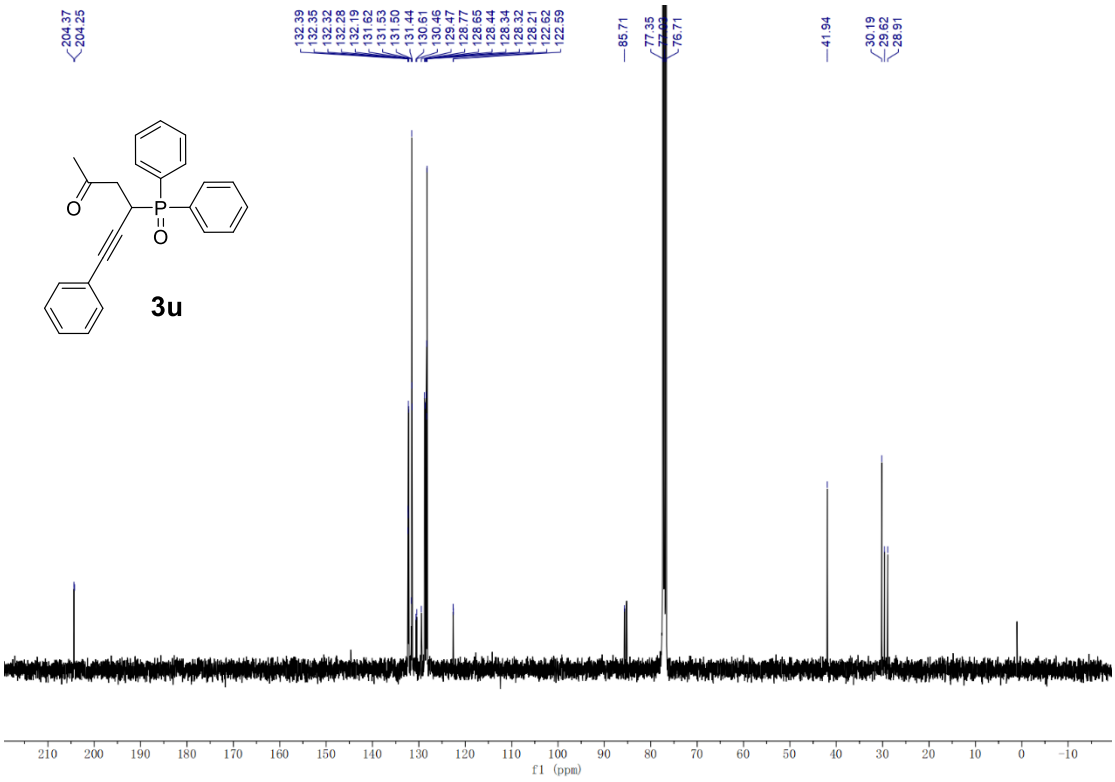


Figure S3.64 ^{13}C NMR spectrum of **3u** (101 MHz, $CDCl_3$).

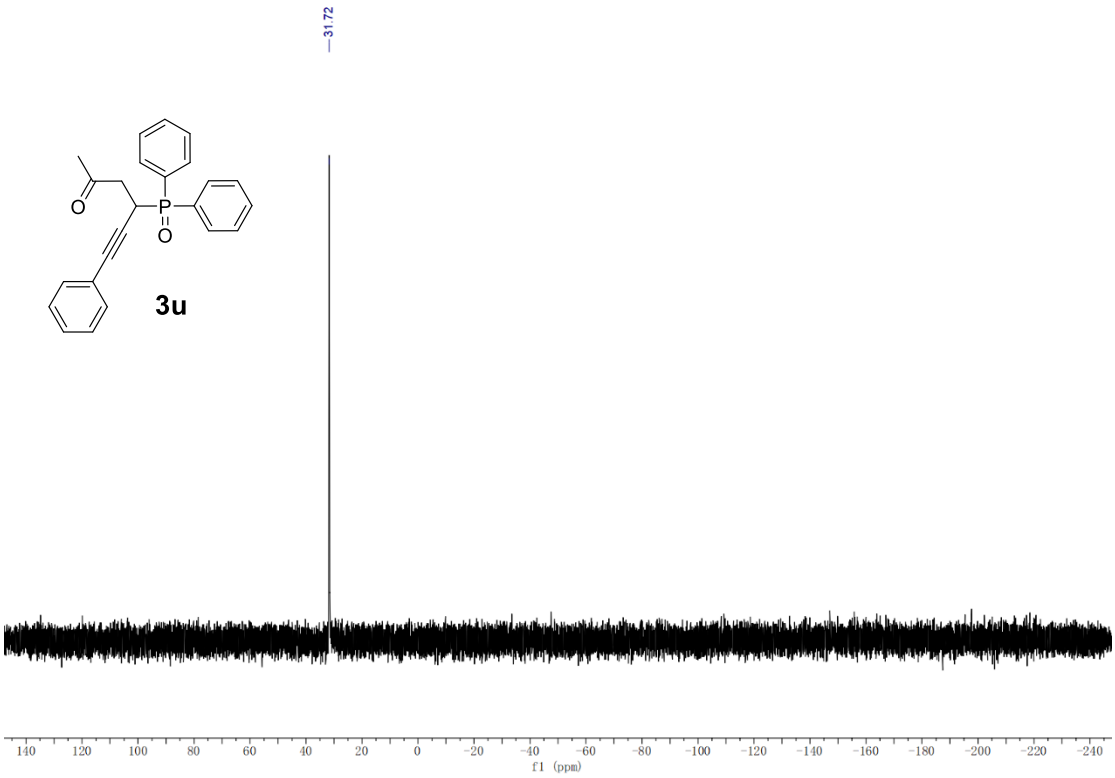


Figure S3.65 ^{31}P NMR spectrum of **3u** (162 MHz, $CDCl_3$).

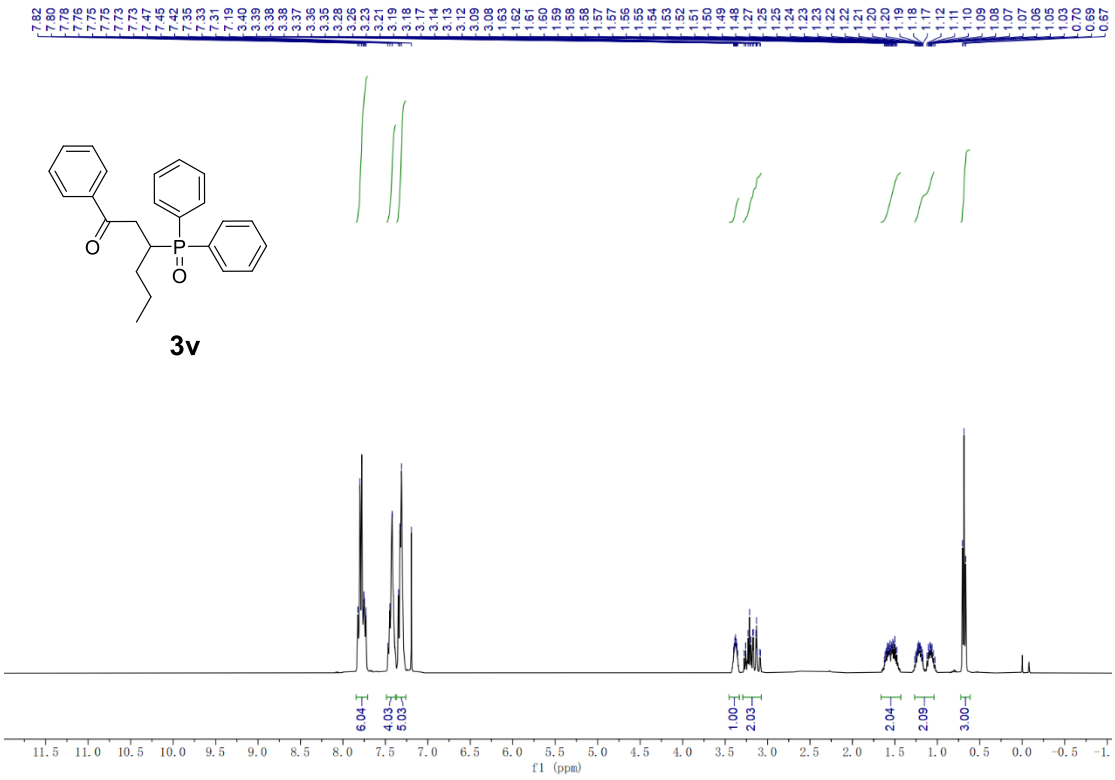


Figure S3.66 ^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$).

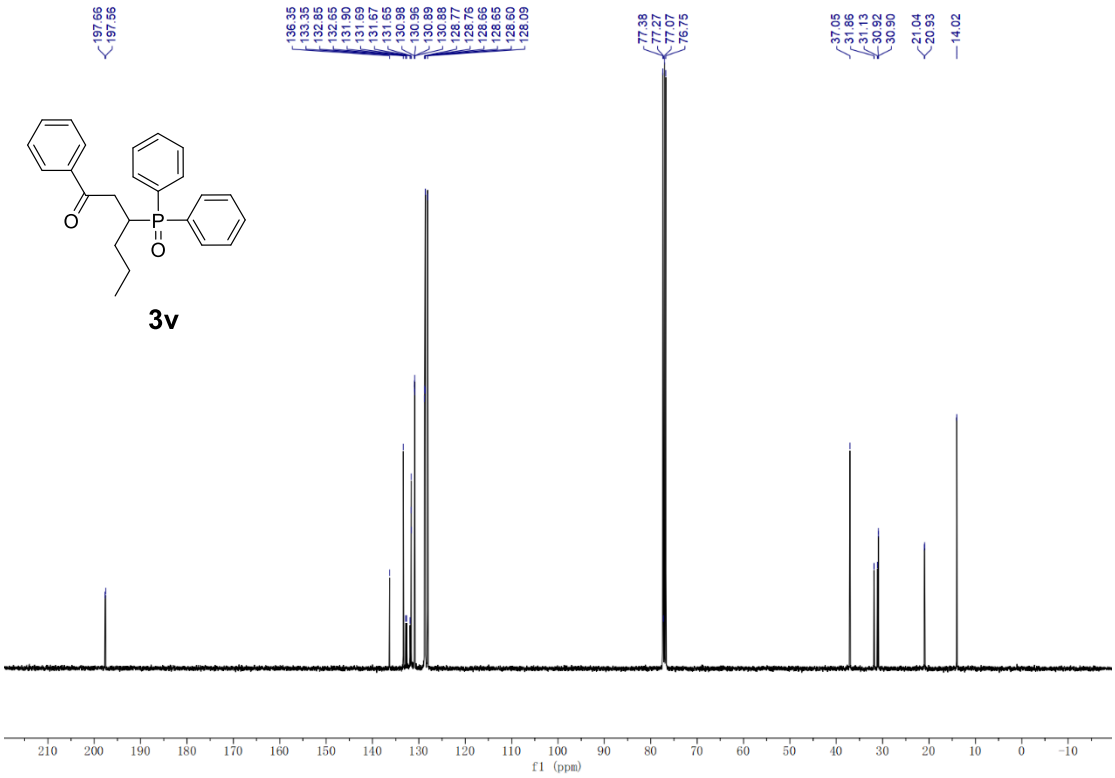


Figure S3.67 ^{13}C NMR spectrum of **3v** (101 MHz, $CDCl_3$).

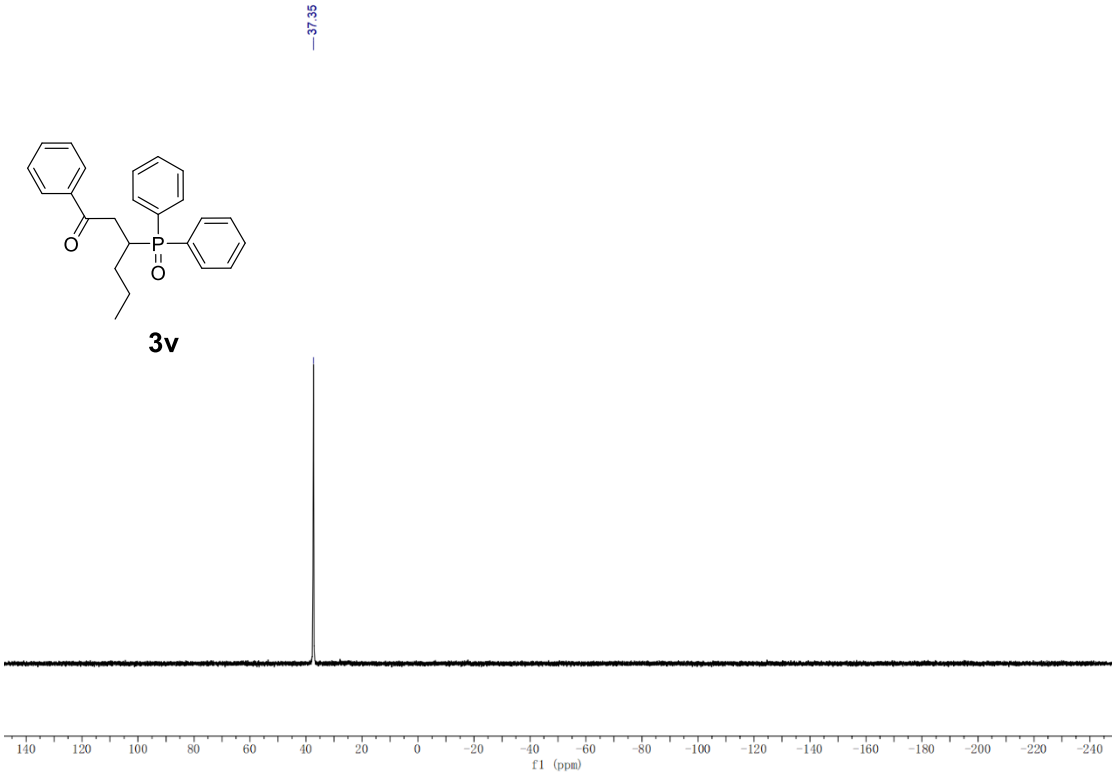


Figure S3.68 ^{31}P NMR spectrum of **3v** (162 MHz, $CDCl_3$).

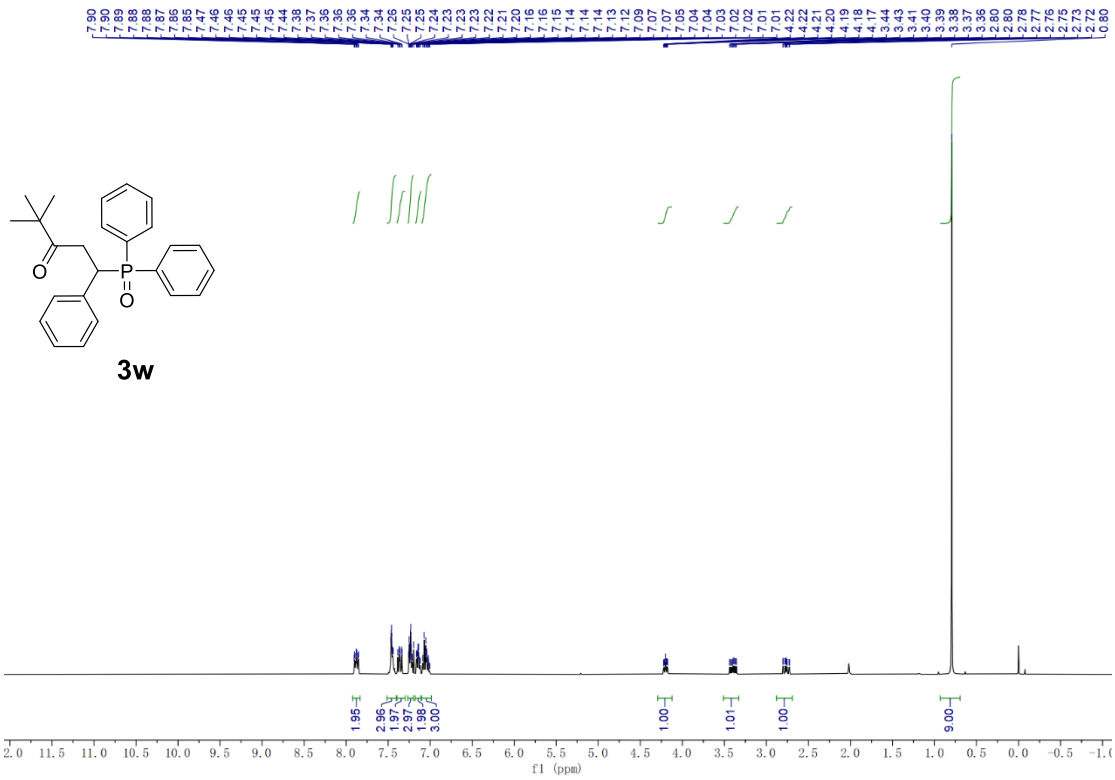


Figure S3.69 ^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$).

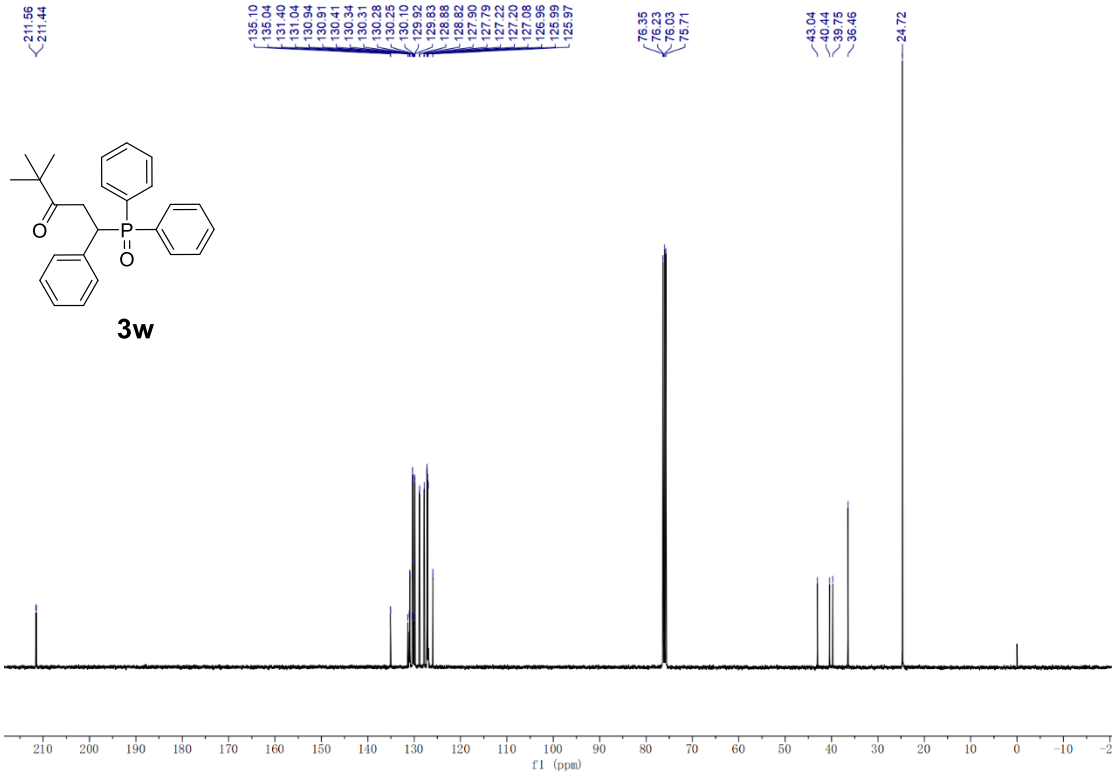


Figure S3.70 ^{13}C NMR spectrum of **3w** (101 MHz, $CDCl_3$).

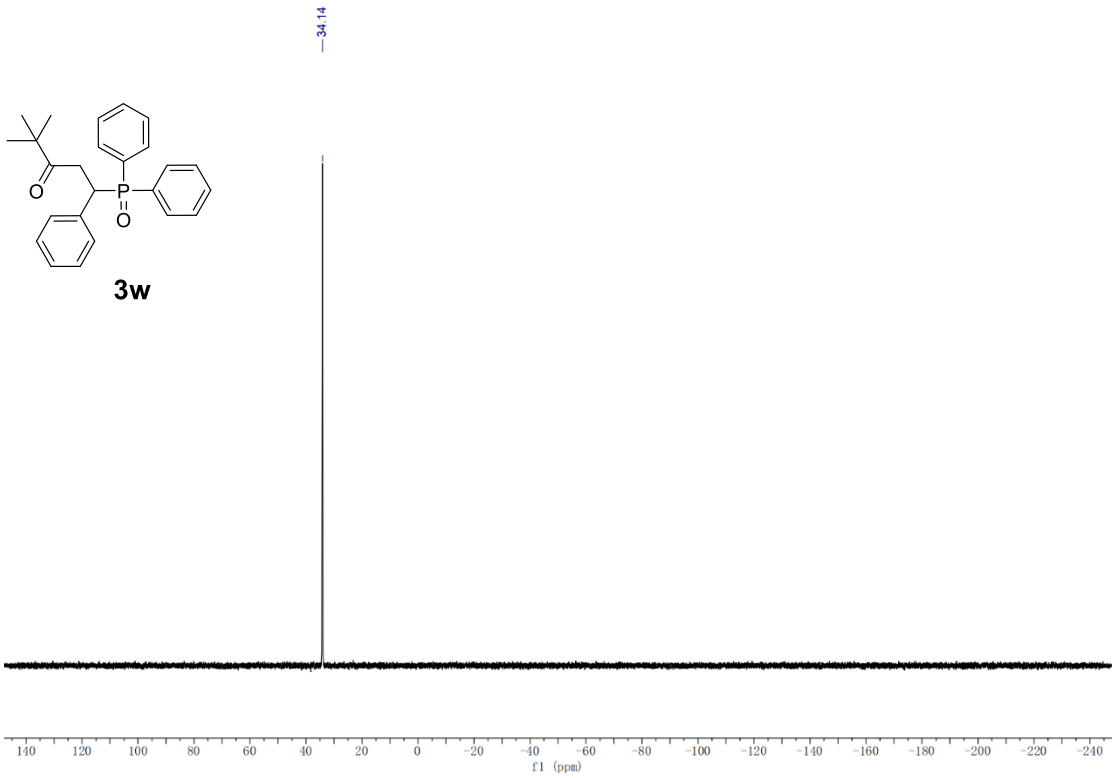


Figure S3.71 ^{31}P NMR spectrum of **3w** (162 MHz, $CDCl_3$).

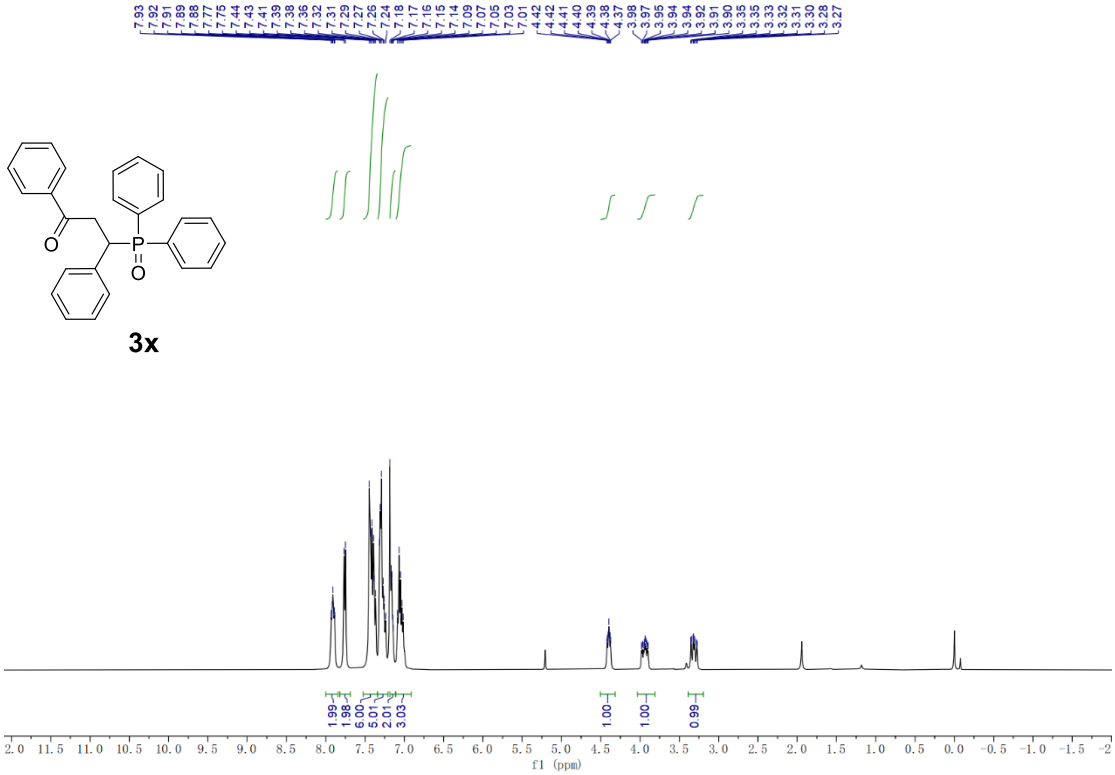


Figure S3.72 ^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$).

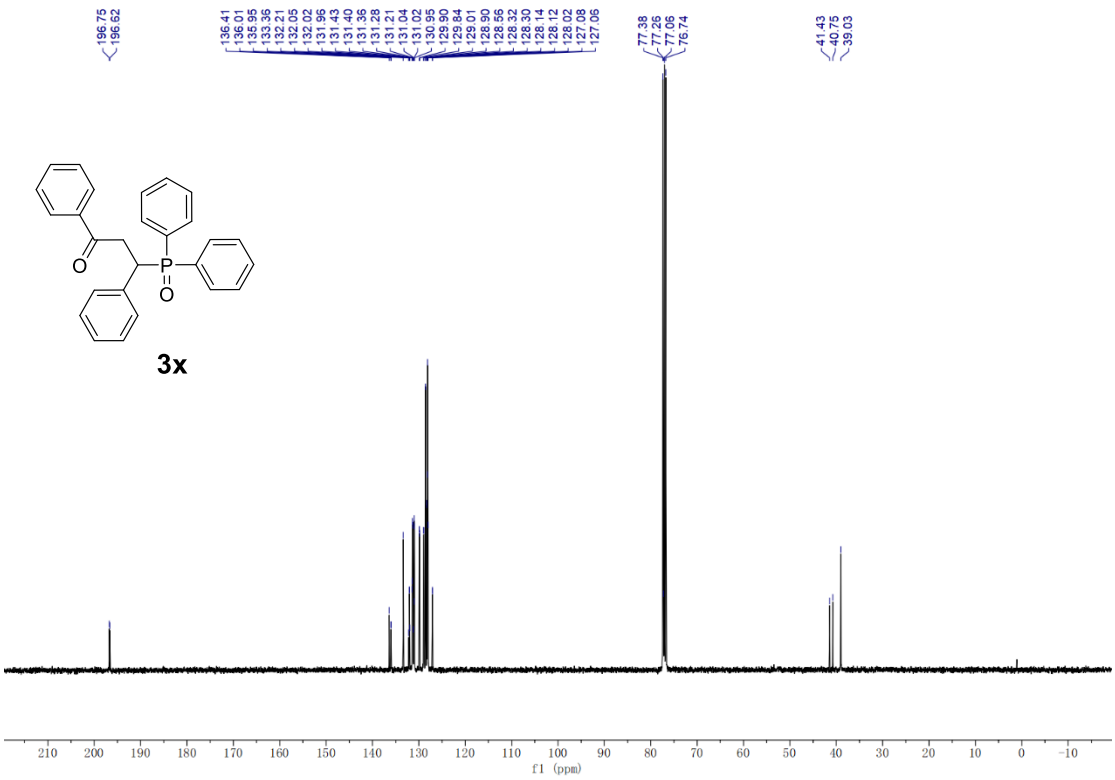


Figure S3.73 ^{13}C NMR spectrum of **3x** (101 MHz, $CDCl_3$).

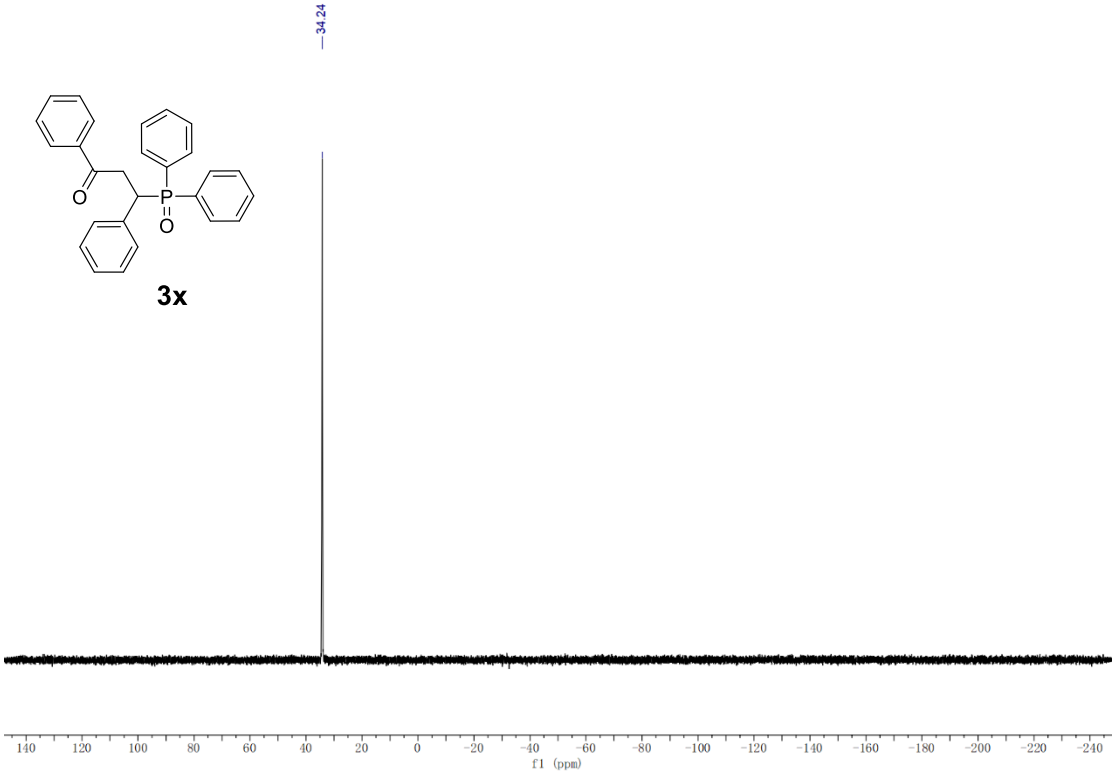


Figure S3.74 ^{31}P NMR spectrum of **3x** (162 MHz, $CDCl_3$).

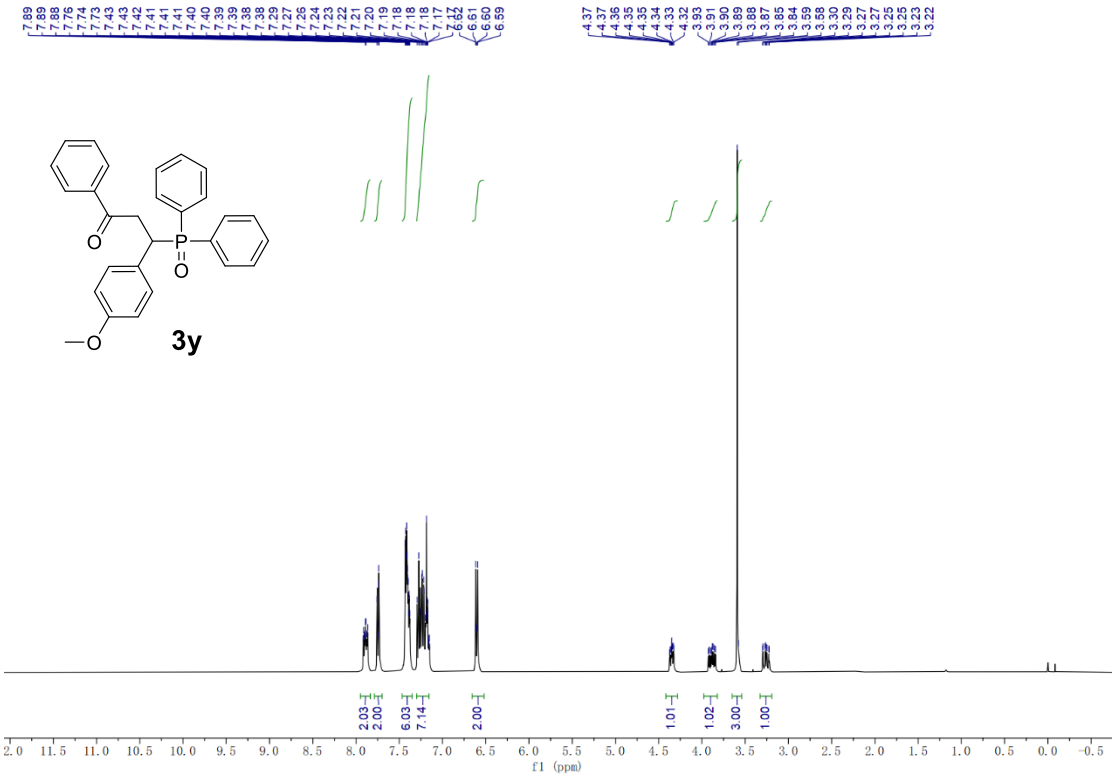


Figure S3.75 ^{1}H NMR spectrum of **3y** (400 MHz, $CDCl_3$).

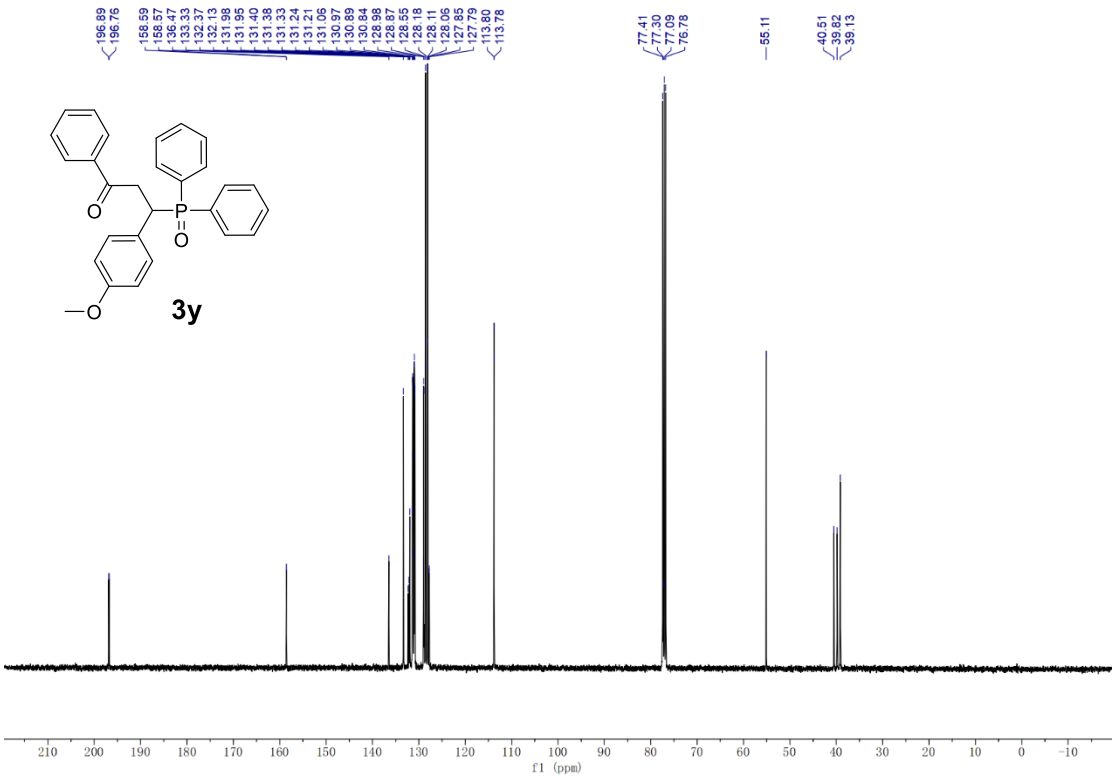


Figure S3.76 ^{13}C NMR spectrum of **3y** (101 MHz, $CDCl_3$).

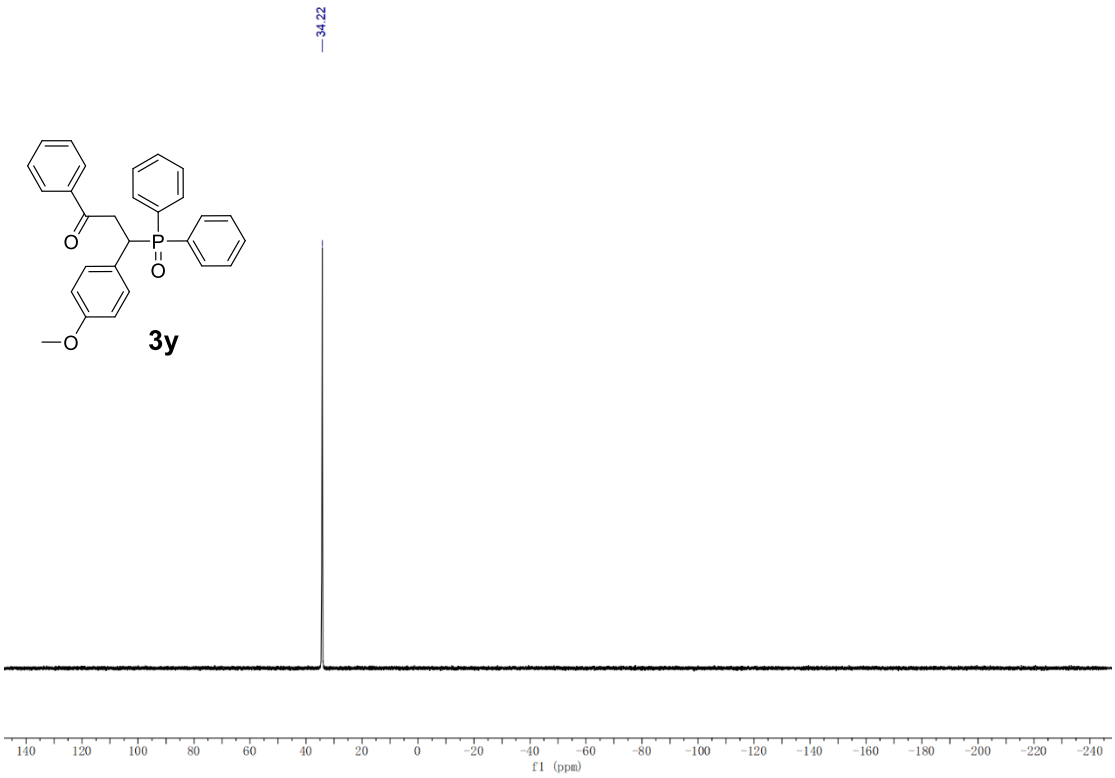


Figure S3.77 ^{31}P NMR spectrum of **3y** (162 MHz, $CDCl_3$).

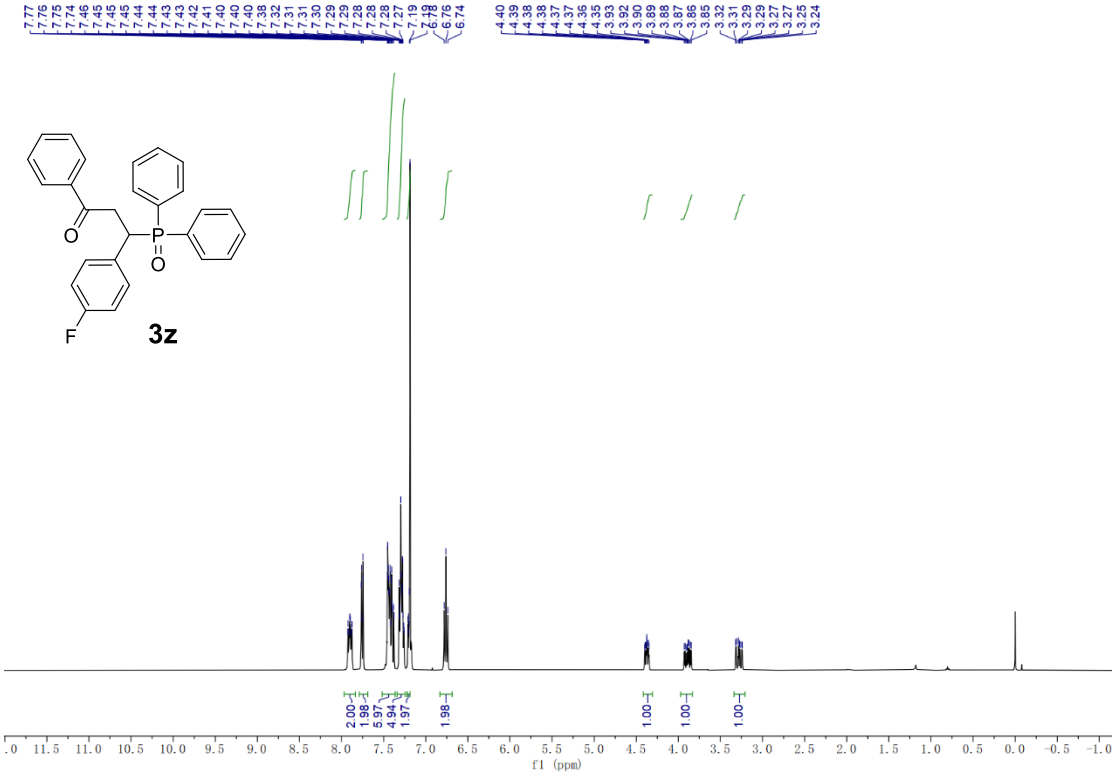


Figure S3.78 ^{1}H NMR spectrum of **3z** (400 MHz, $CDCl_3$).

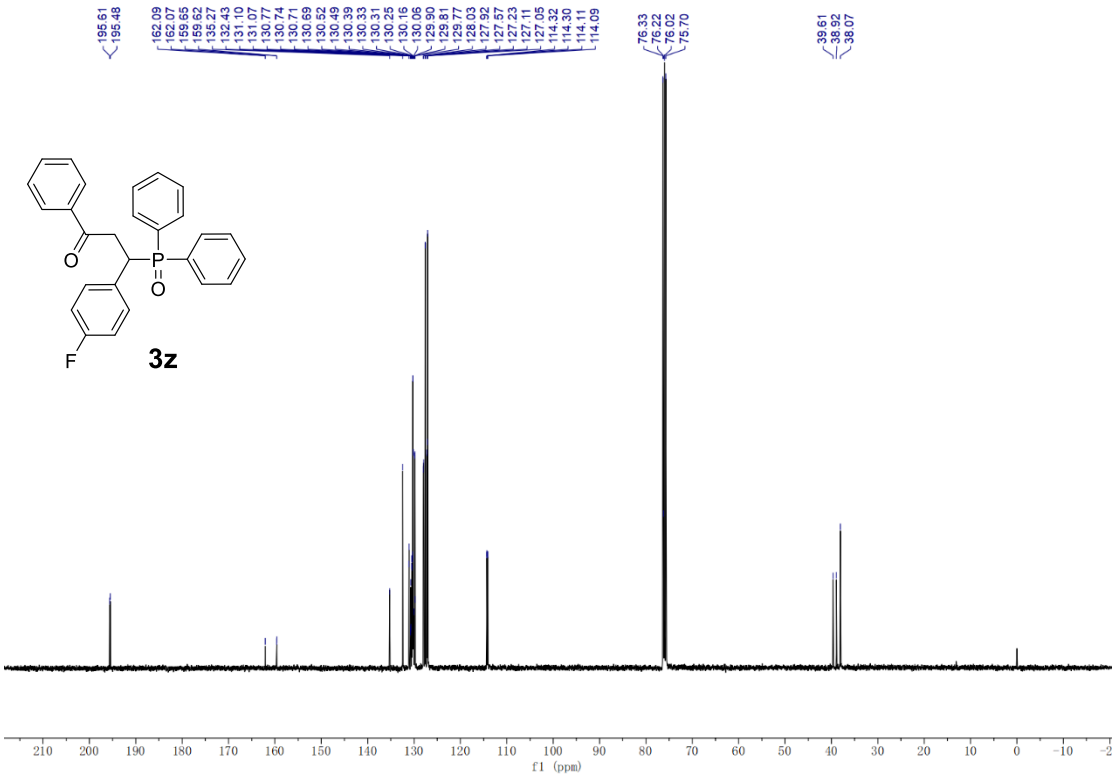


Figure S3.79 ^{13}C NMR spectrum of **3z** (101 MHz, $CDCl_3$).

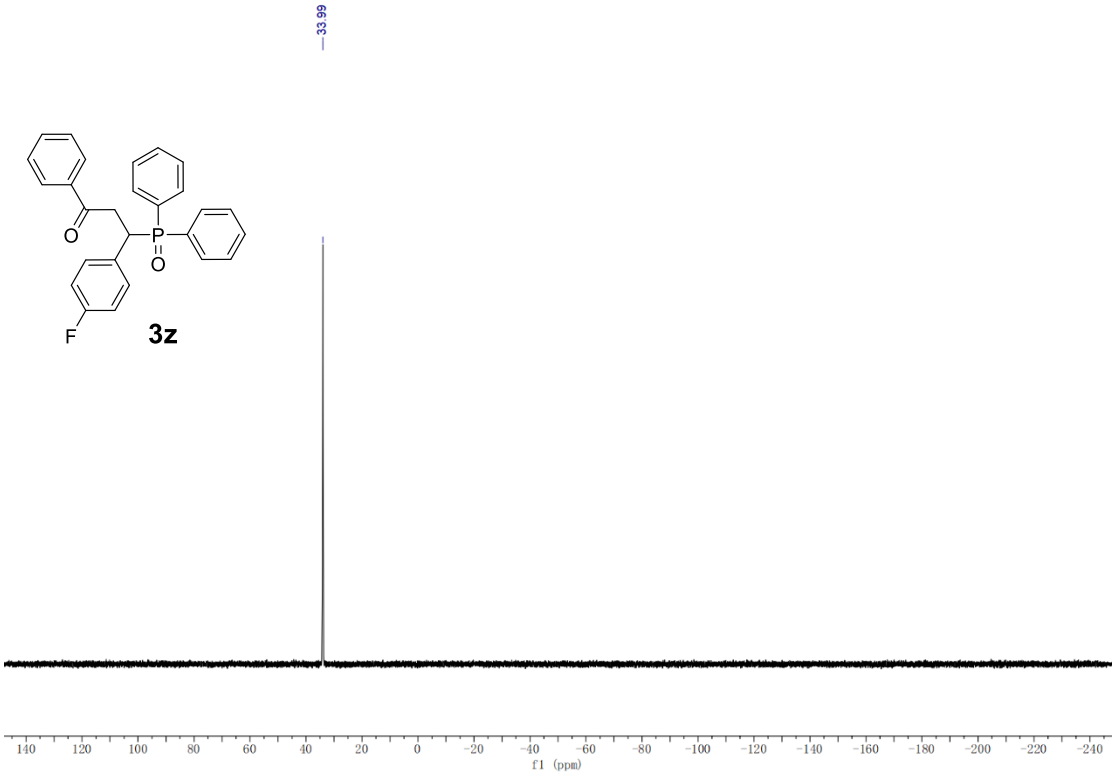


Figure S3.80 ^{31}P NMR spectrum of **3z** (162 MHz, $CDCl_3$).

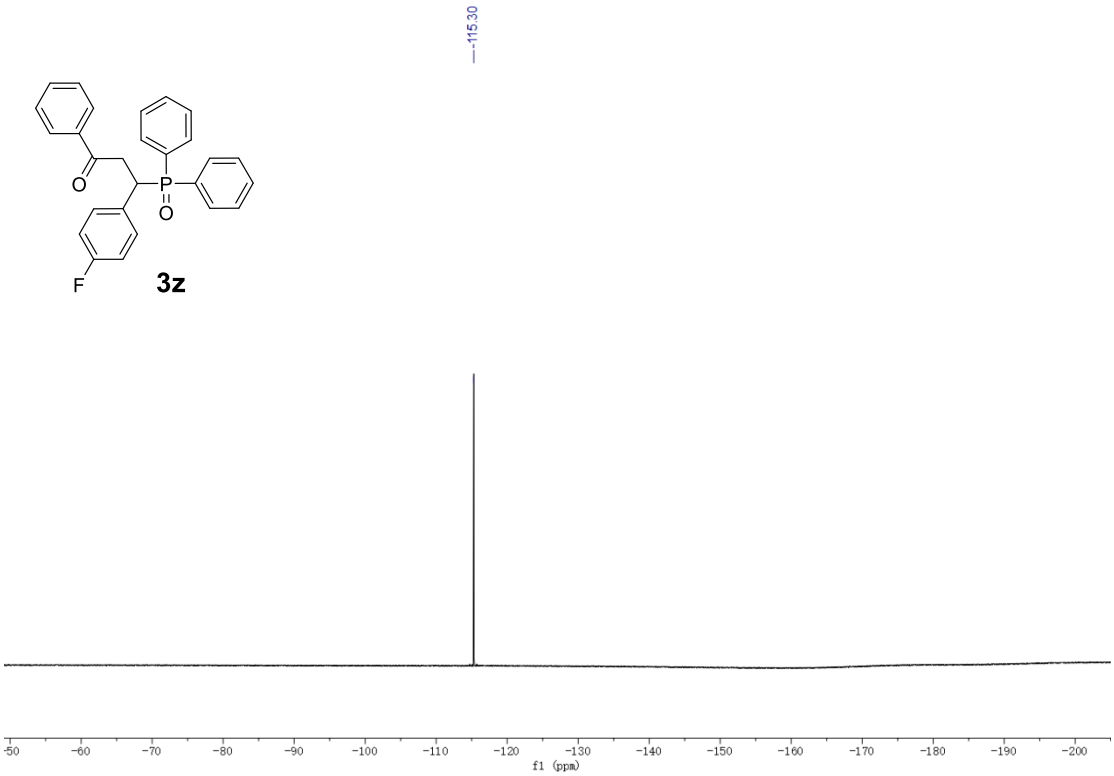


Figure S3.81 ^{19}F NMR spectrum of **3z** (376 MHz, $CDCl_3$).

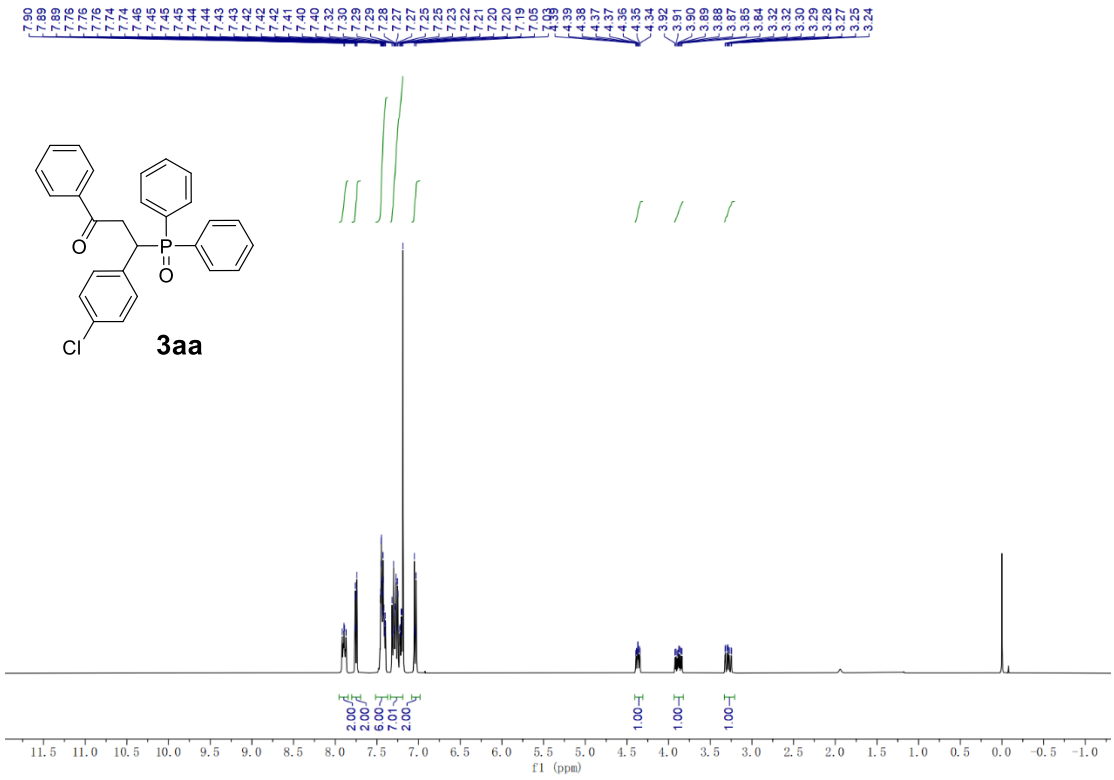


Figure S3.82 ^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$).

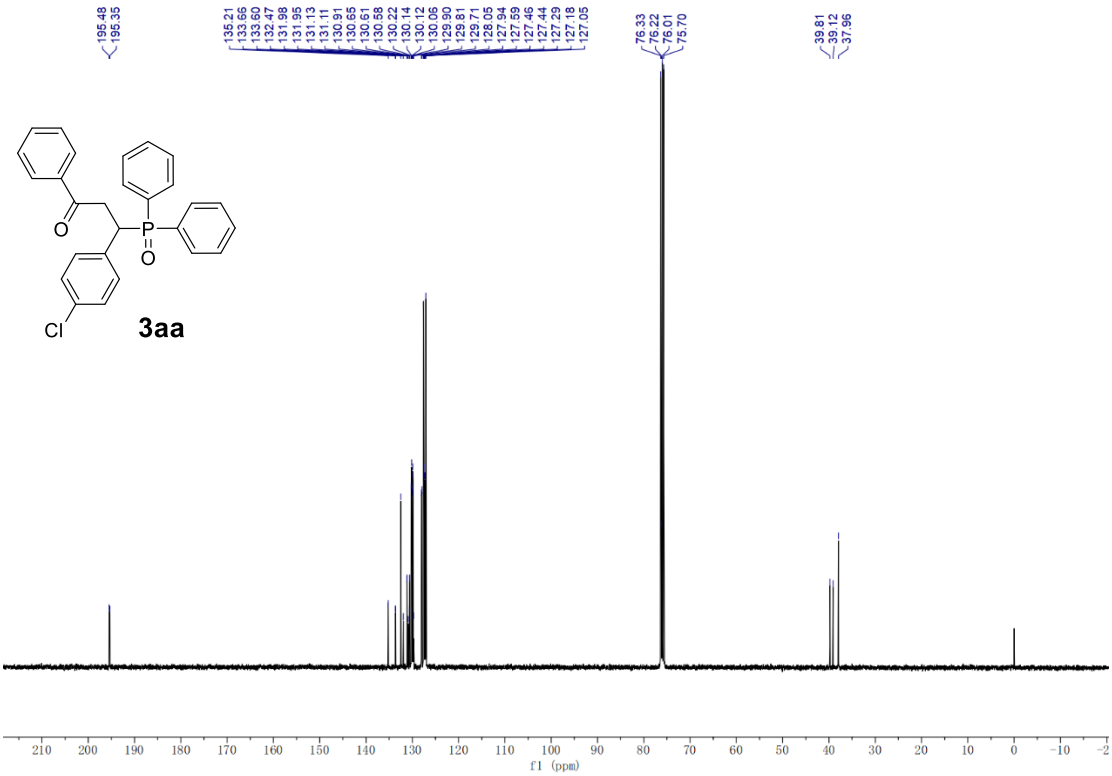


Figure S3.83 ^{13}C NMR spectrum of **3aa** (101 MHz, $CDCl_3$).

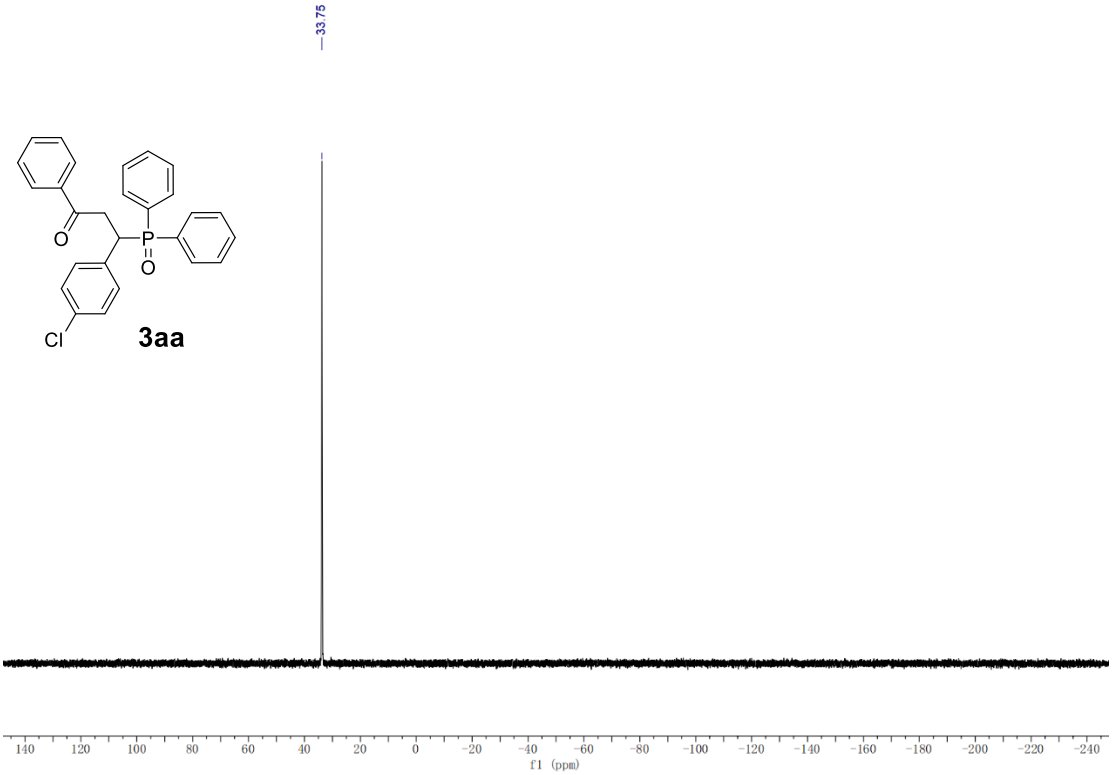


Figure S3.84 ^{31}P NMR spectrum of **3aa** (162 MHz, $CDCl_3$).

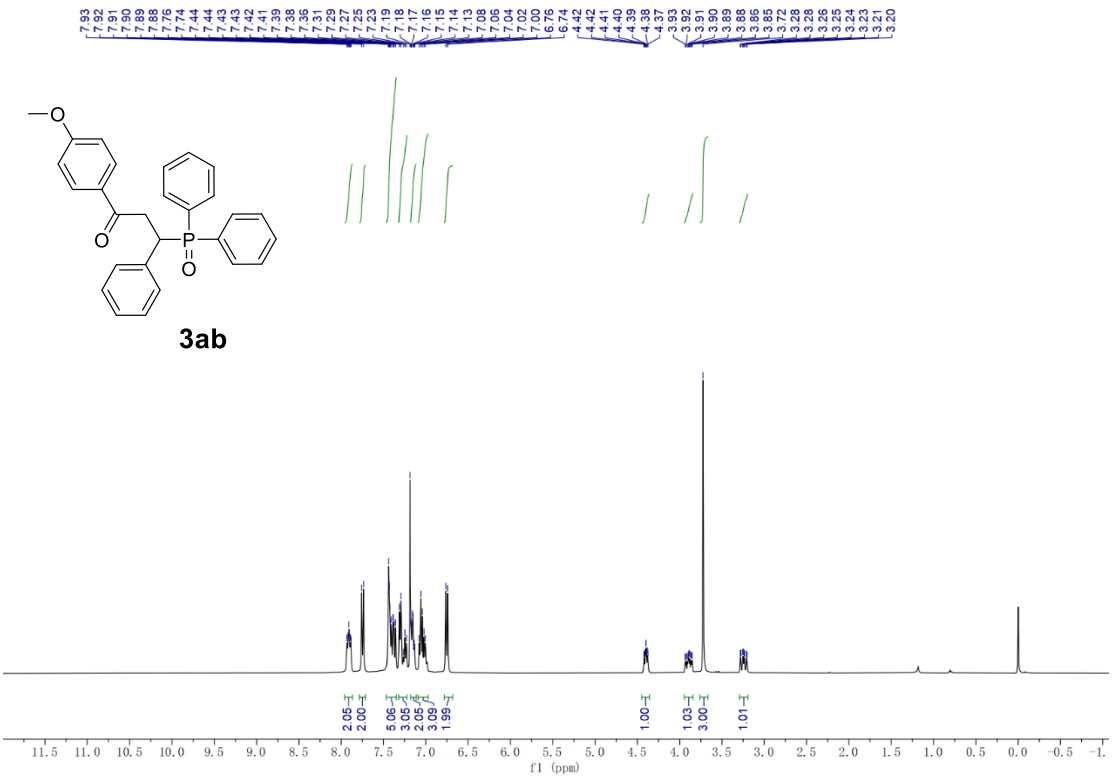


Figure S3.85 ^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$).

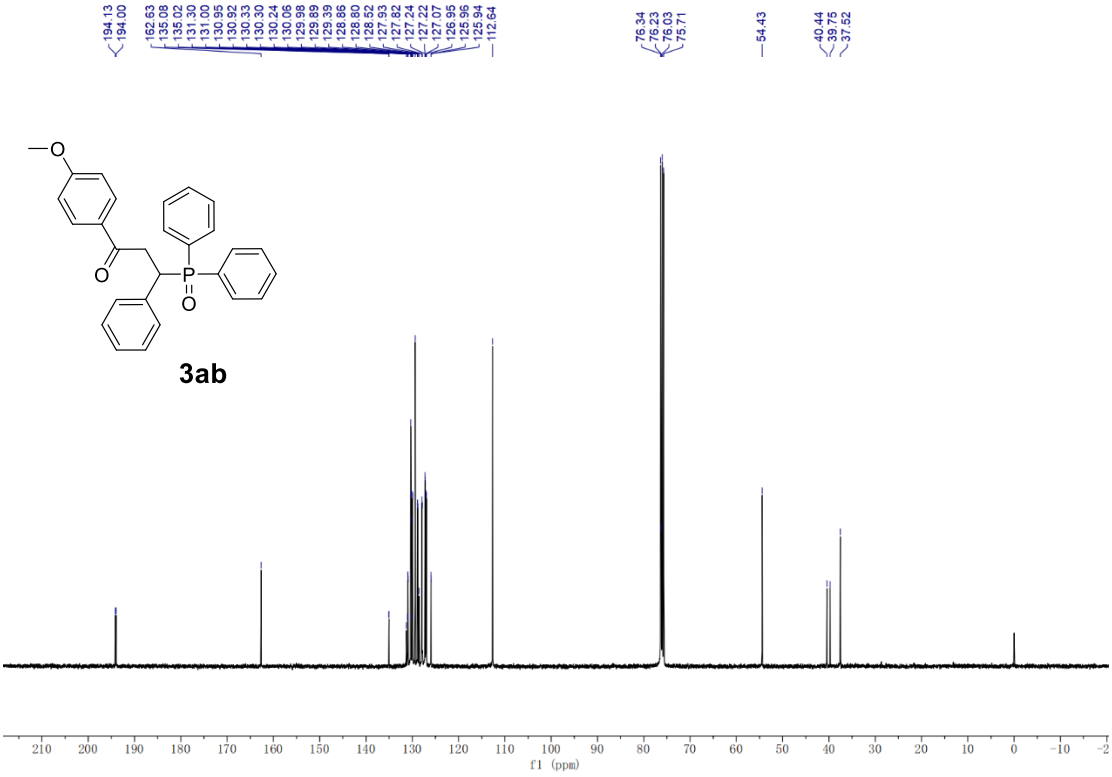


Figure S3.86 ^{13}C NMR spectrum of **3ab** (101 MHz, $CDCl_3$).

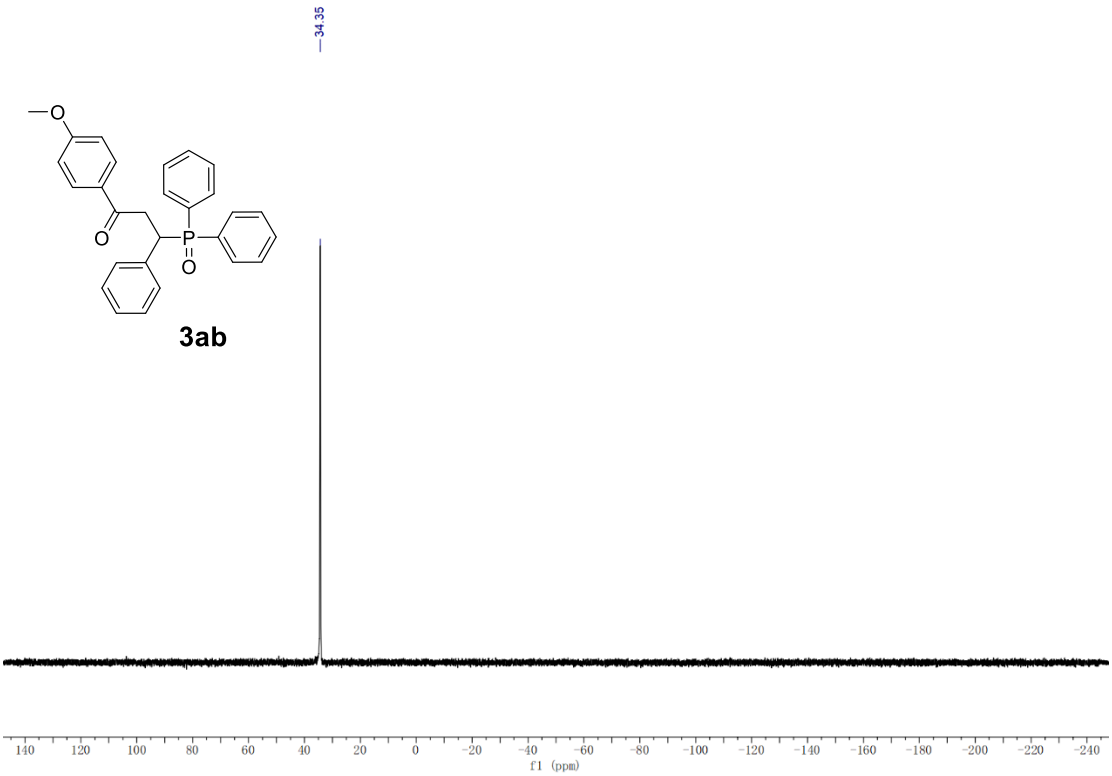


Figure S3.87 ^{31}P NMR spectrum of **3ab** (162 MHz, $CDCl_3$).

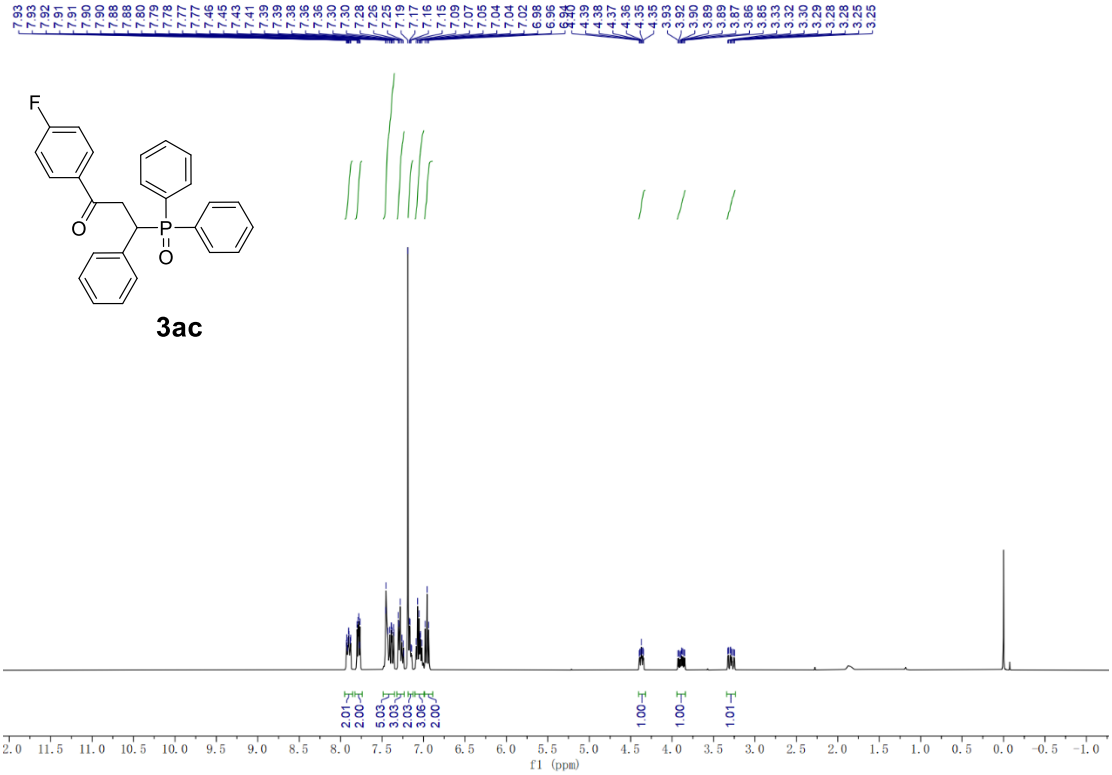


Figure S3.88 ^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$).

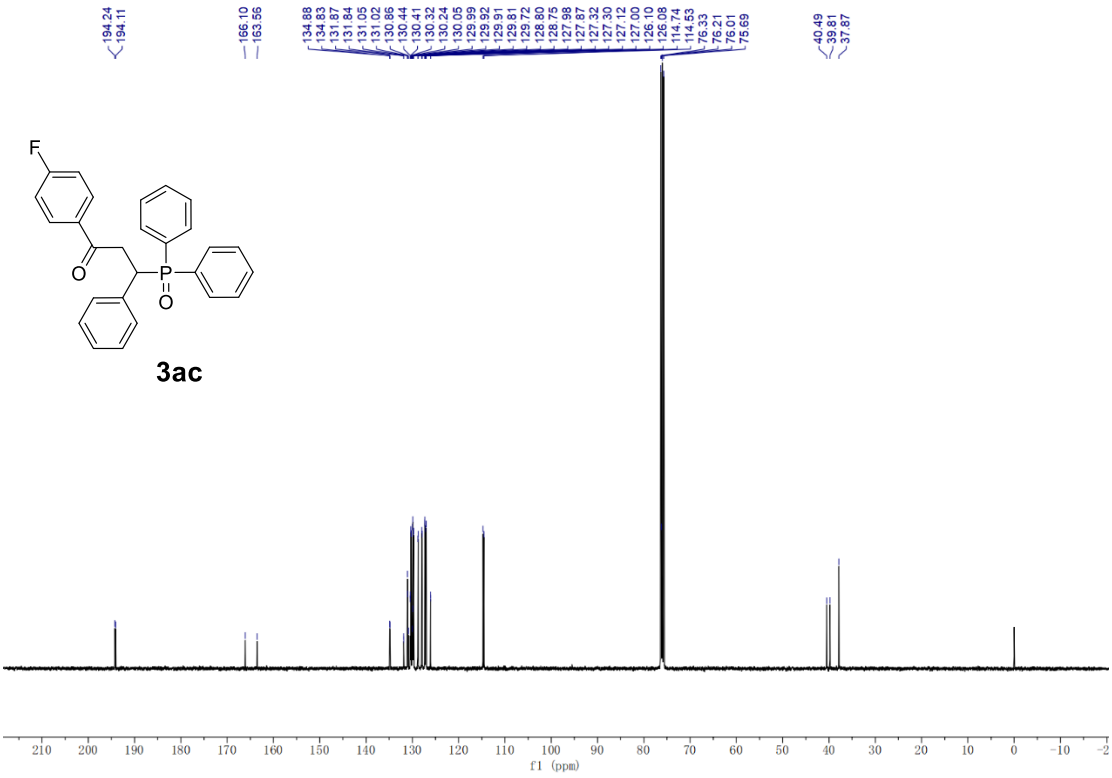


Figure S3.89 ^{13}C NMR spectrum of **3ac** (101 MHz, $CDCl_3$).

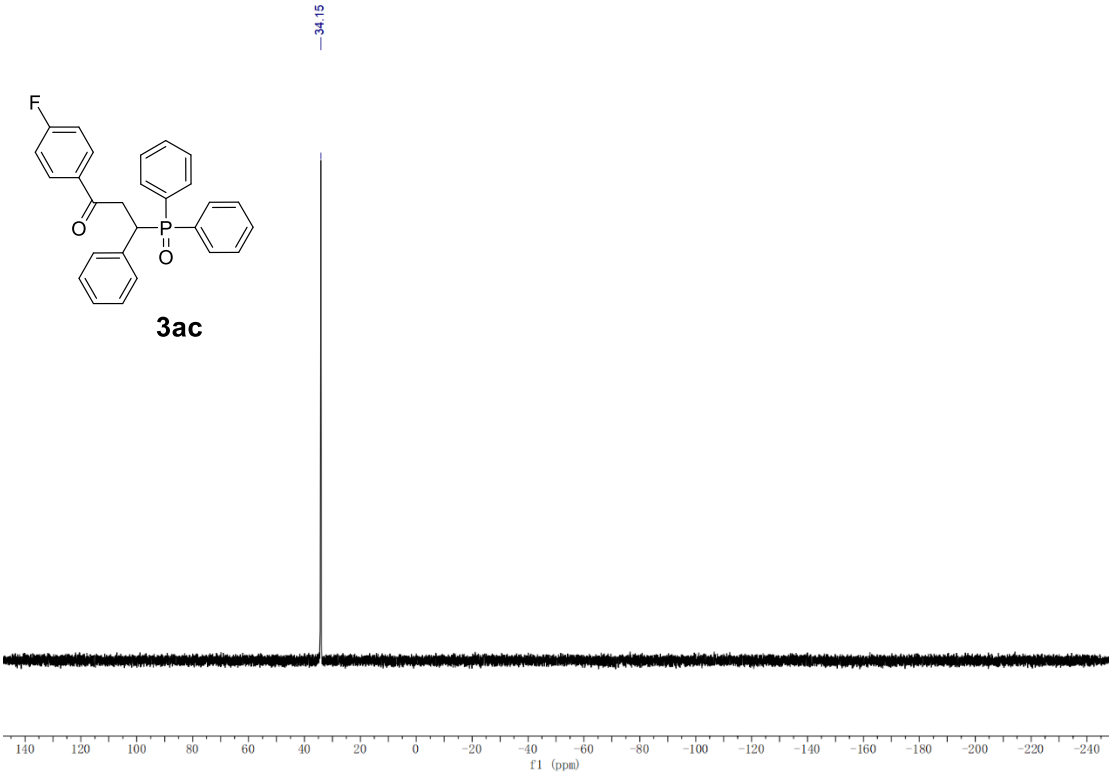


Figure S3.90 ^{31}P NMR spectrum of **3ac** (162 MHz, $CDCl_3$).

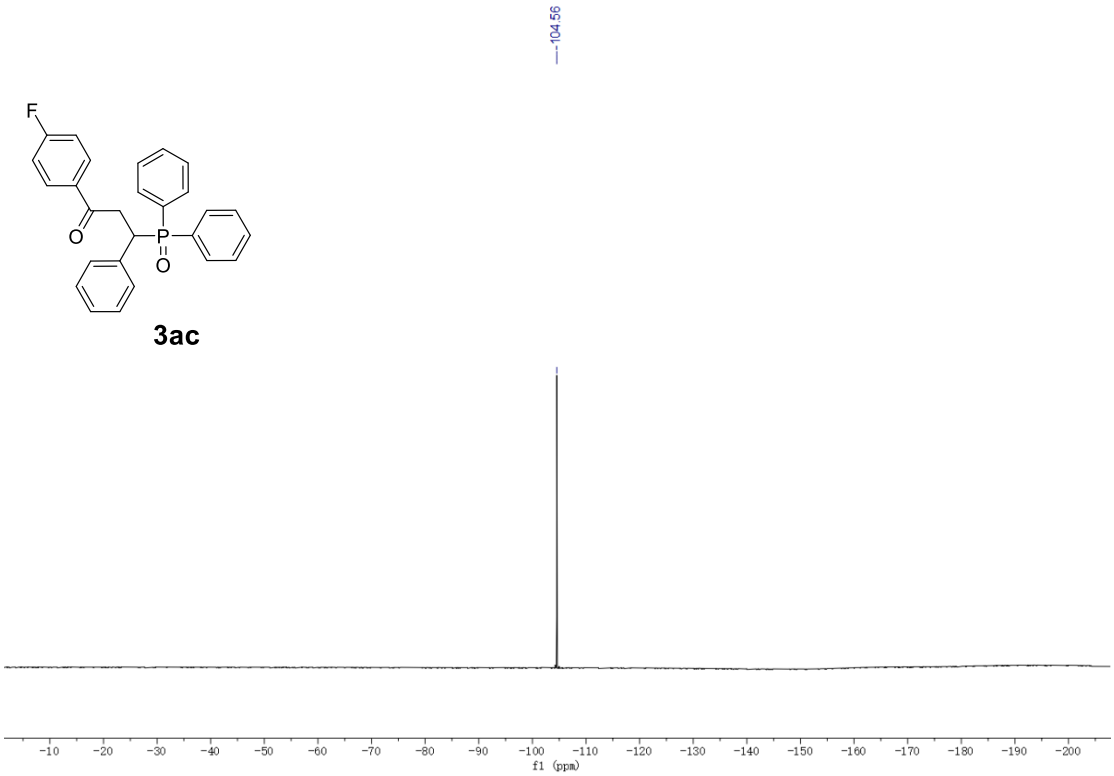


Figure S3.91 ^{19}F NMR spectrum of **3ac** (376 MHz, $CDCl_3$).

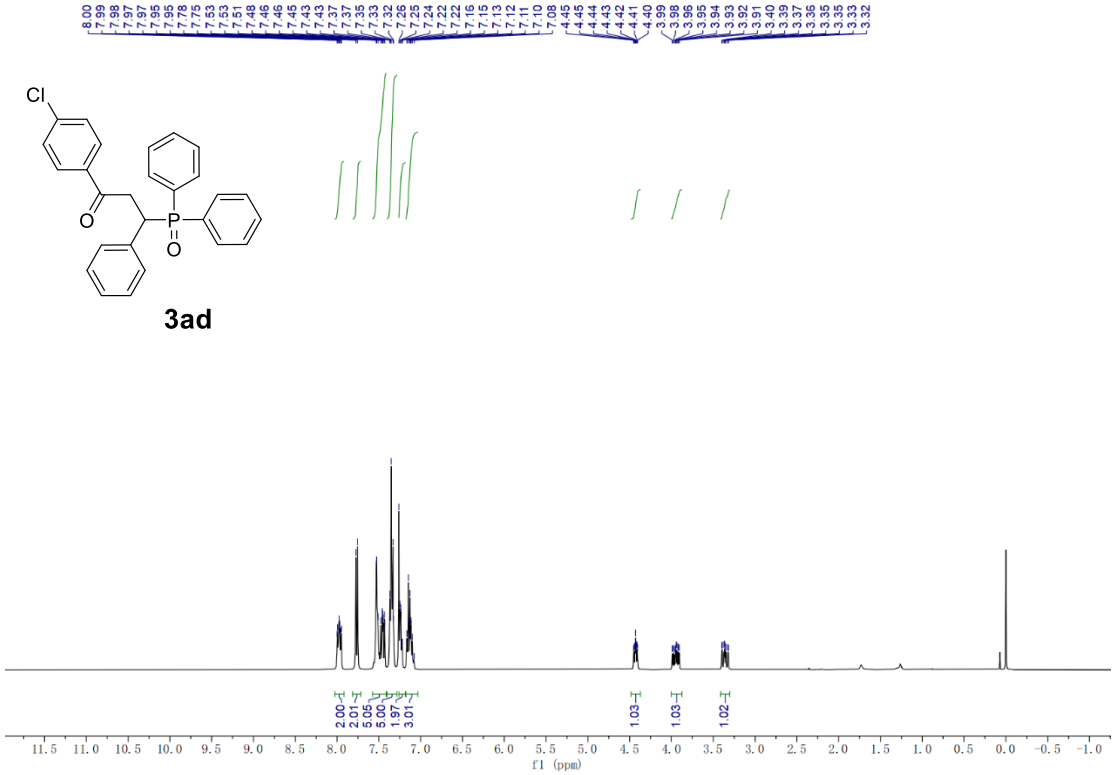


Figure S3.92 ^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$).

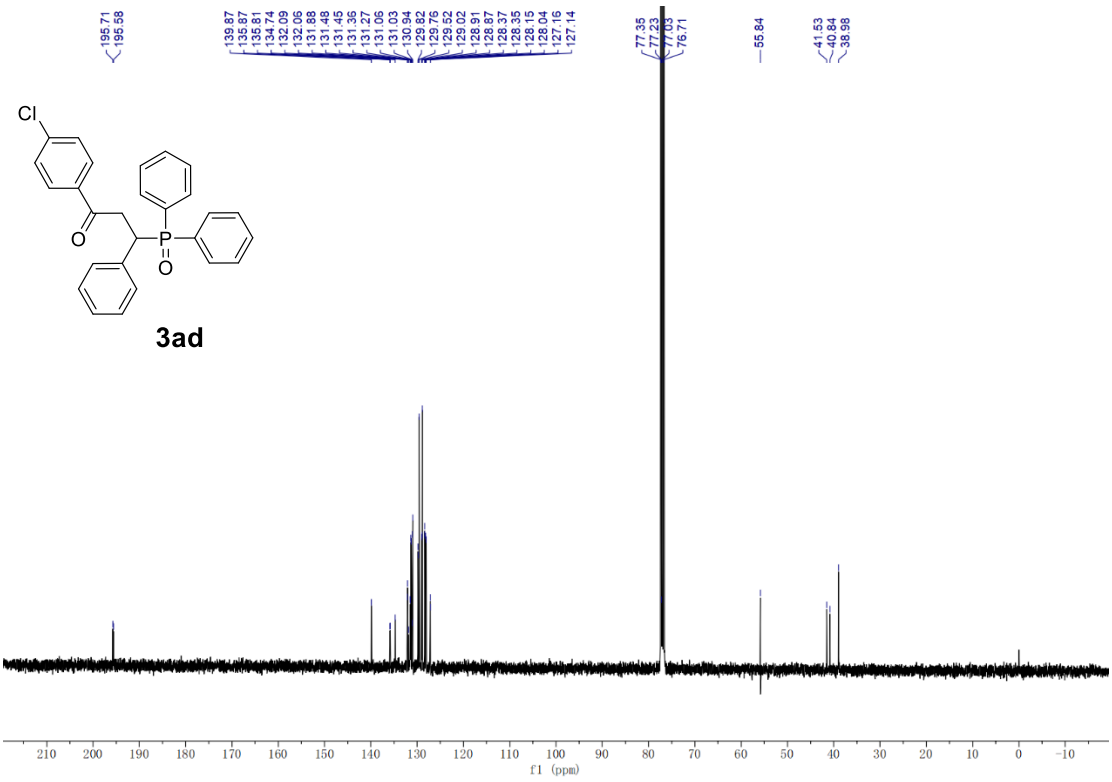


Figure S3.93 ^{13}C NMR spectrum of **3ad** (101 MHz, $CDCl_3$).

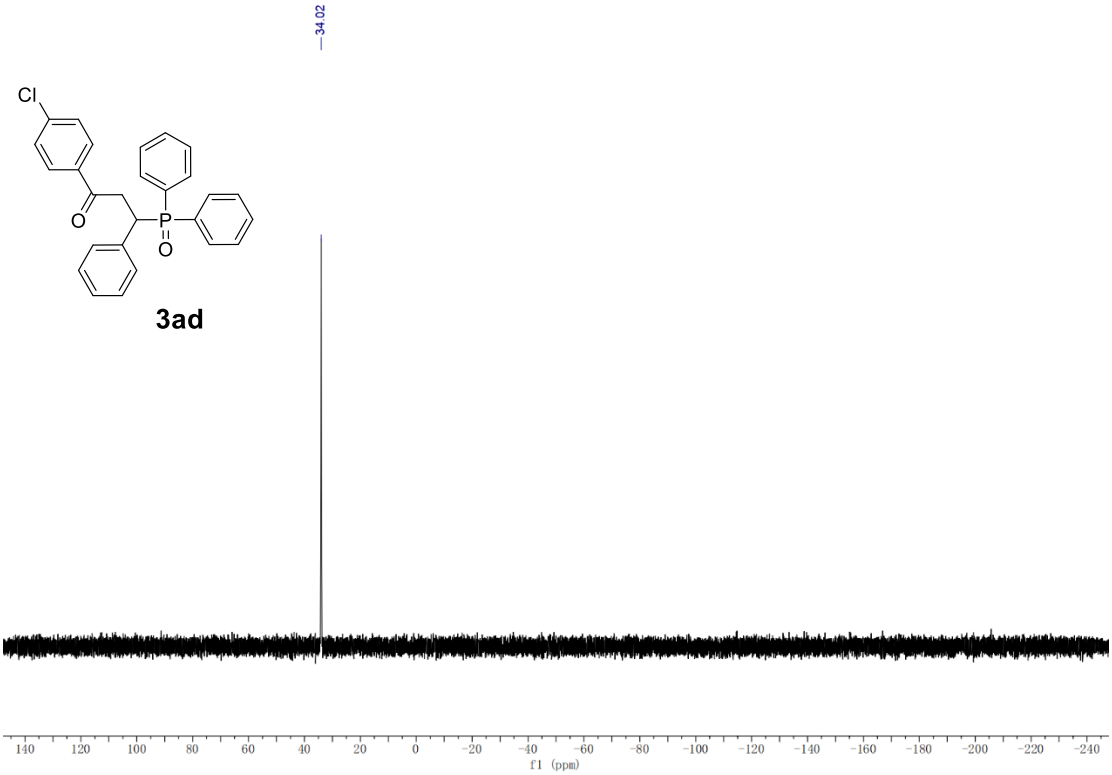


Figure S3.94 ^{31}P NMR spectrum of **3ad** (162 MHz, $CDCl_3$).

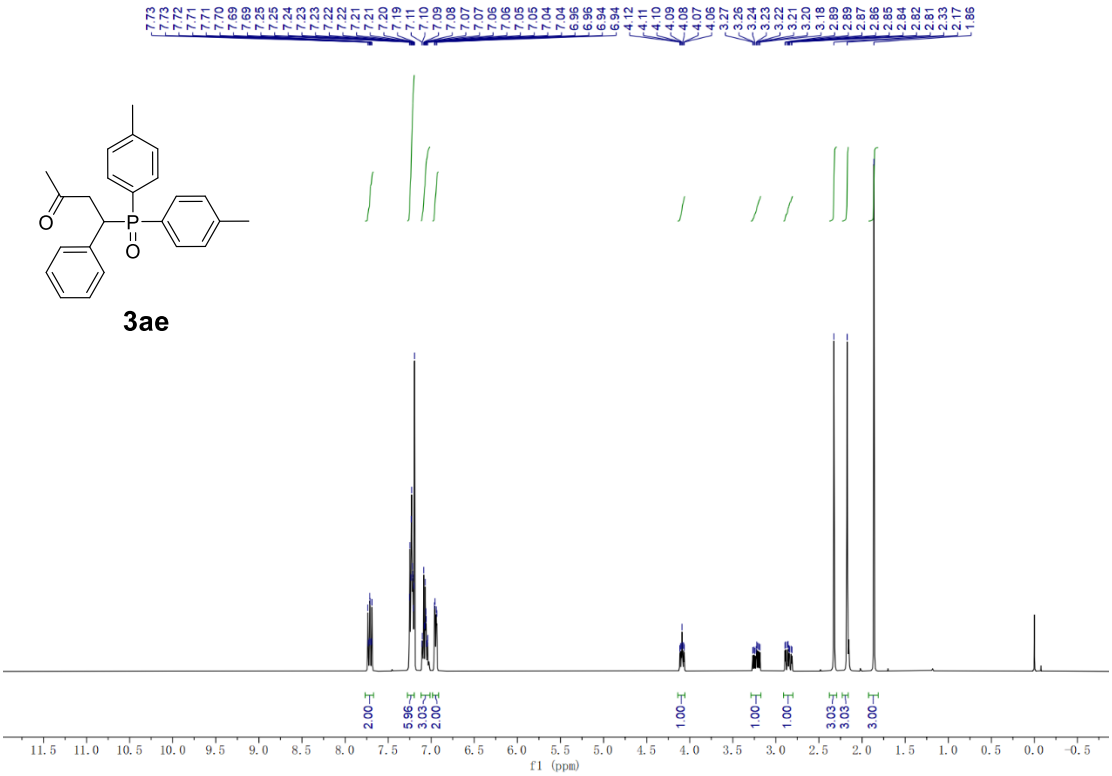


Figure S3.95 ^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$).

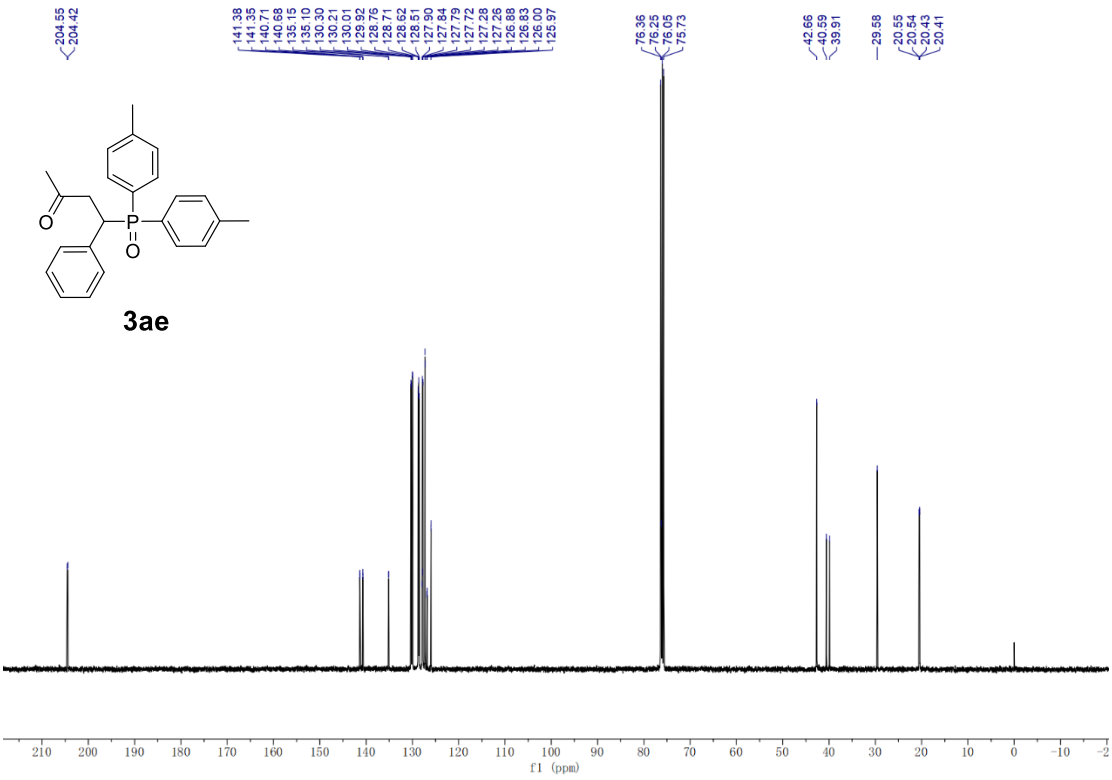


Figure S3.96 ^{13}C NMR spectrum of **3ae** (101 MHz, $CDCl_3$).

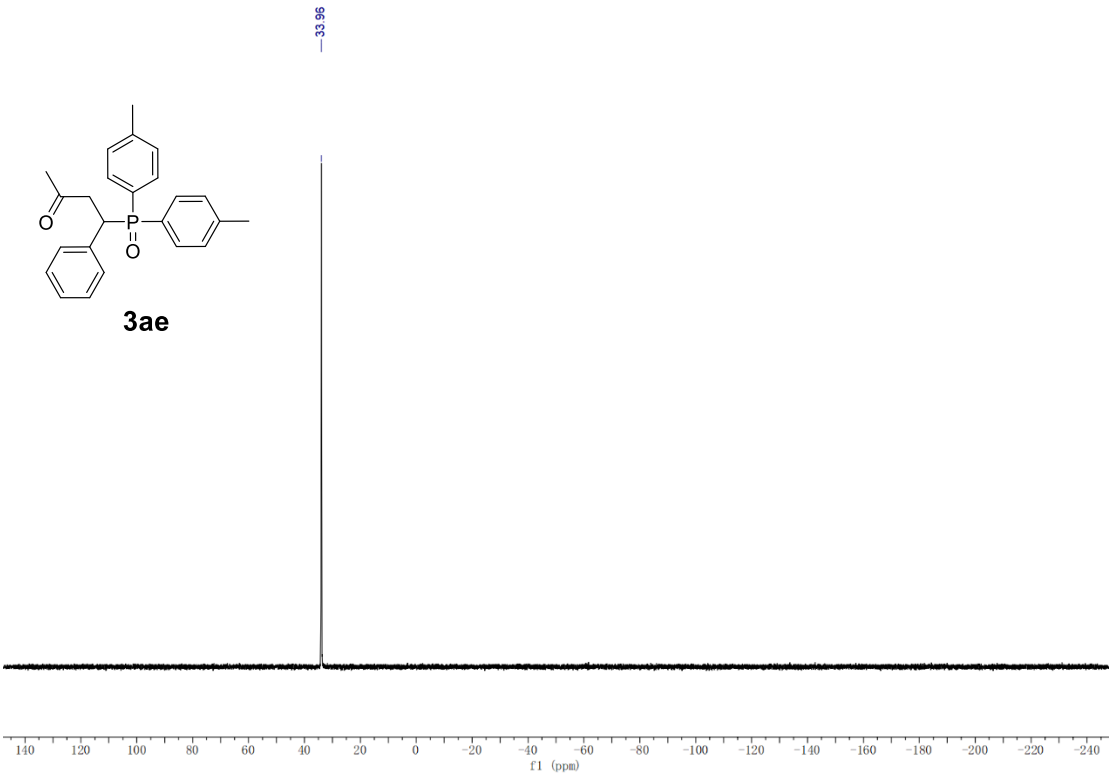


Figure S3.97 ^{31}P NMR spectrum of **3ae** (162 MHz, $CDCl_3$).

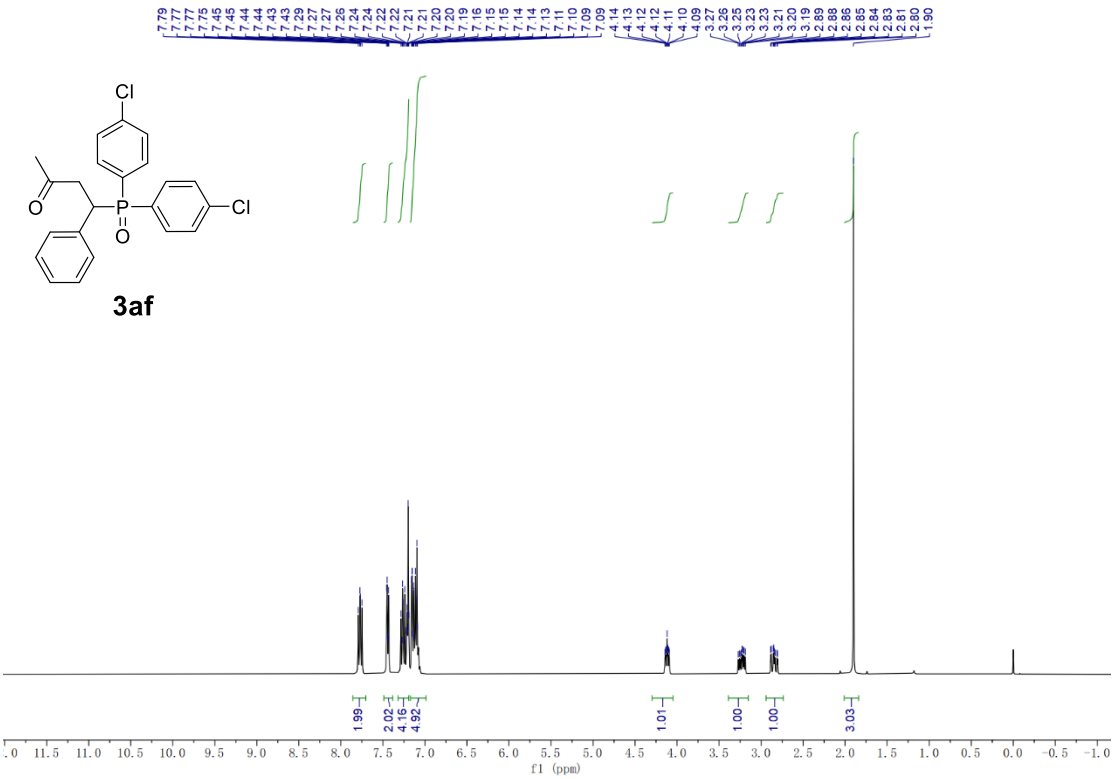


Figure S3.98 ^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$).

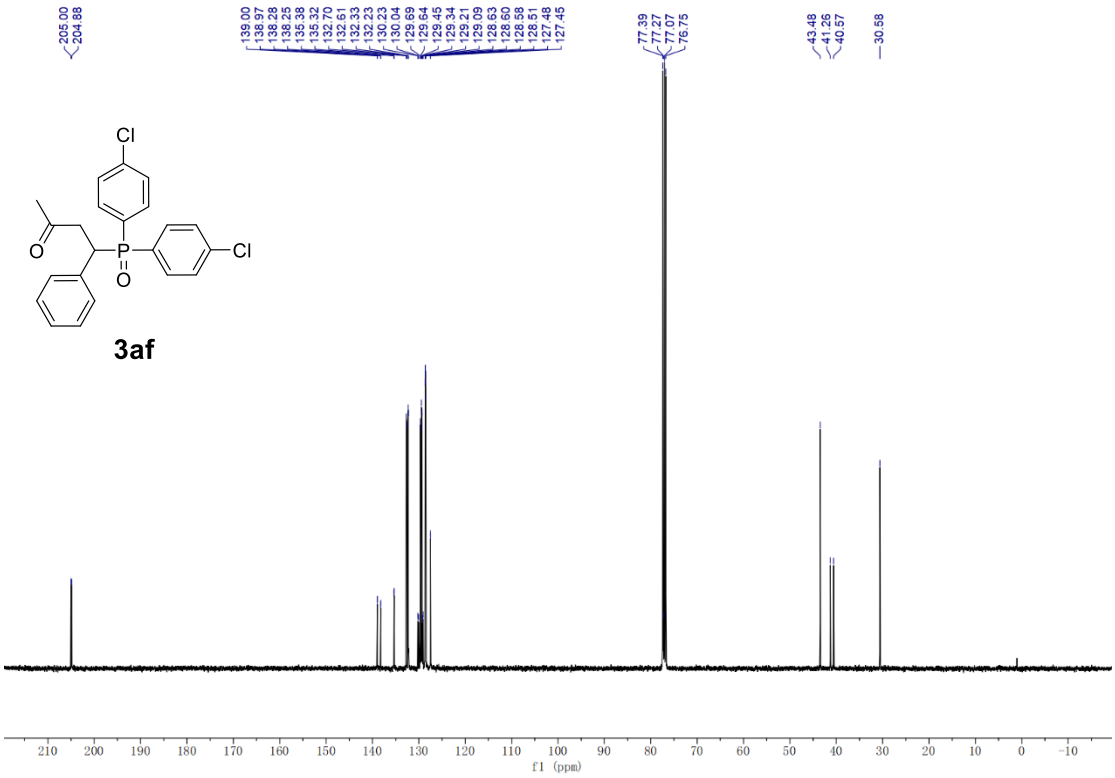


Figure S3.99 ^{13}C NMR spectrum of **3af** (101 MHz, $CDCl_3$).

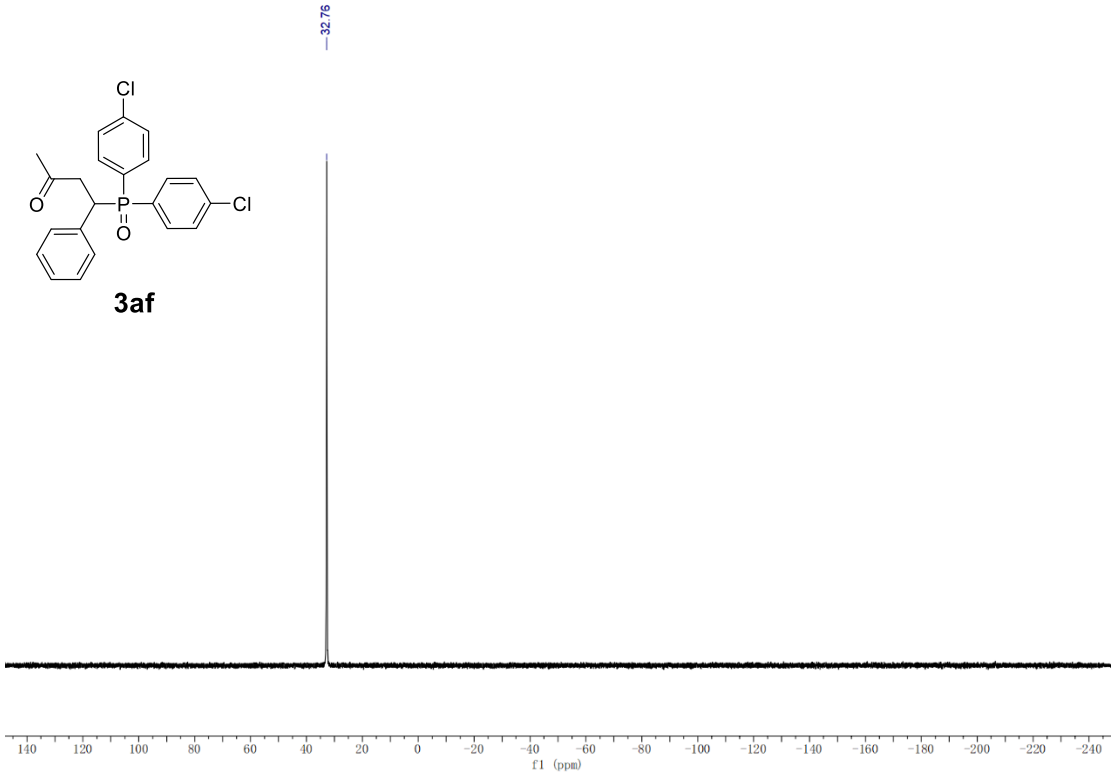


Figure S3.100 ^{31}P NMR spectrum of **3af** (162 MHz, $CDCl_3$).

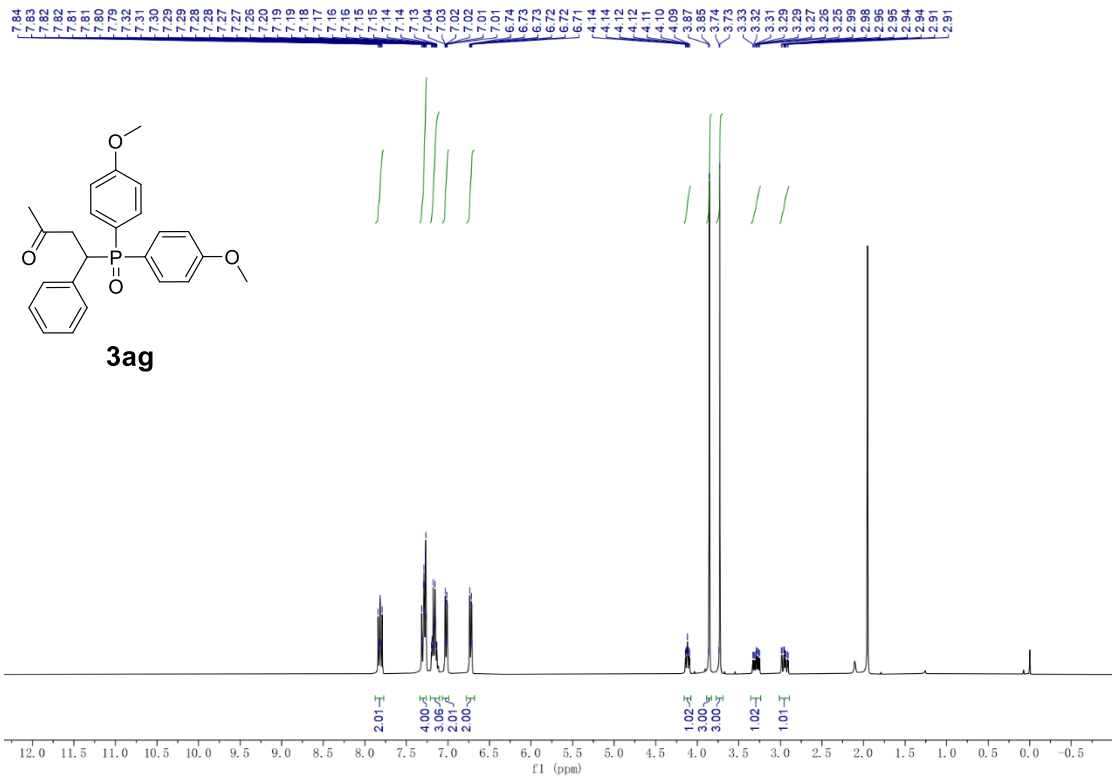


Figure S3.101 ^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$).

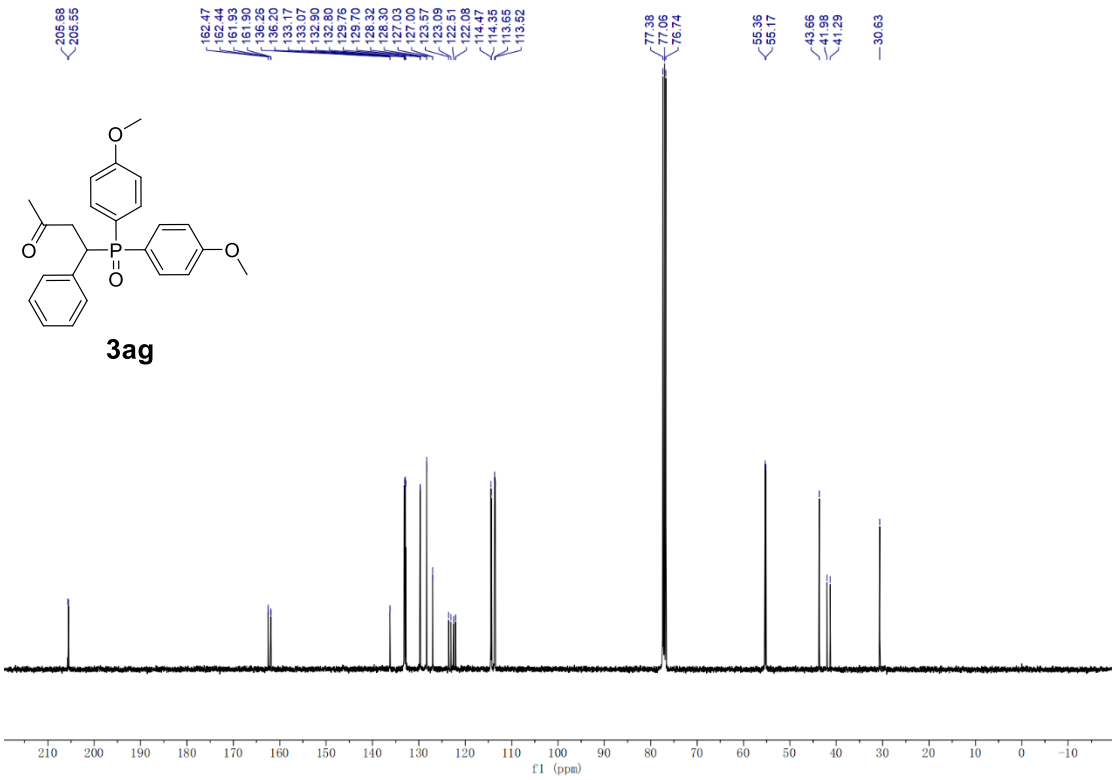


Figure S3.102 ^{13}C NMR spectrum of **3ag** (101 MHz, $CDCl_3$).

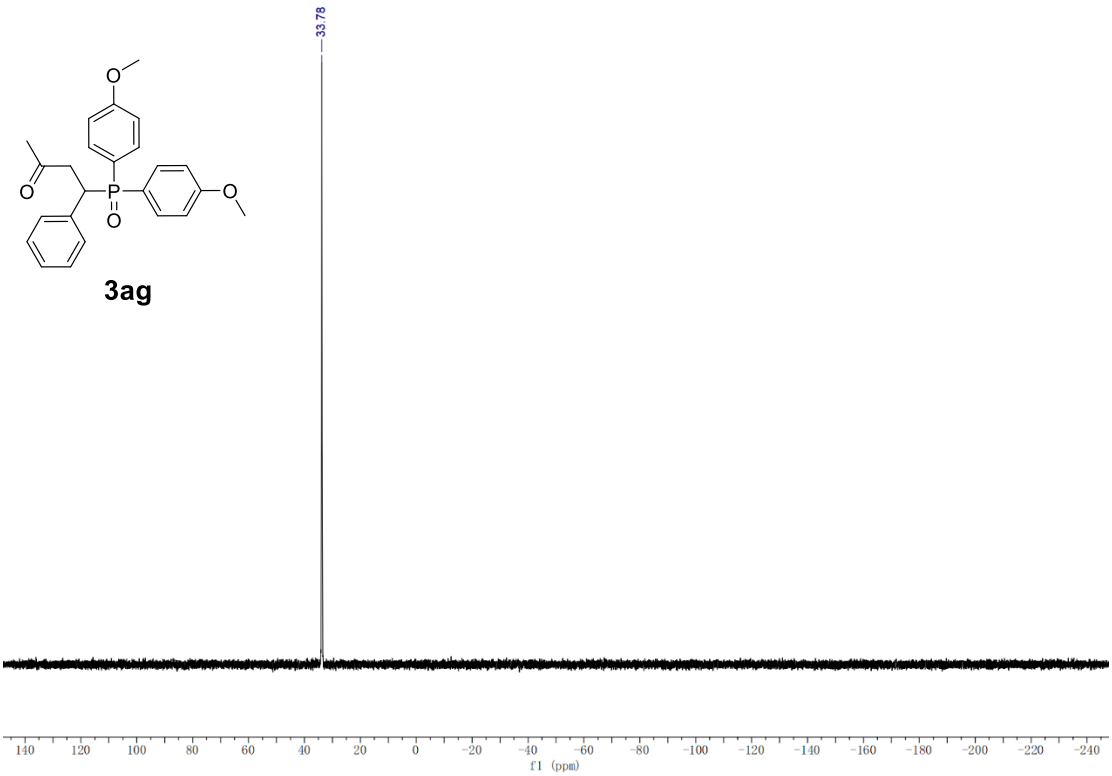


Figure S3.103 ^{31}P NMR spectrum of **3ag** (162 MHz, $CDCl_3$).

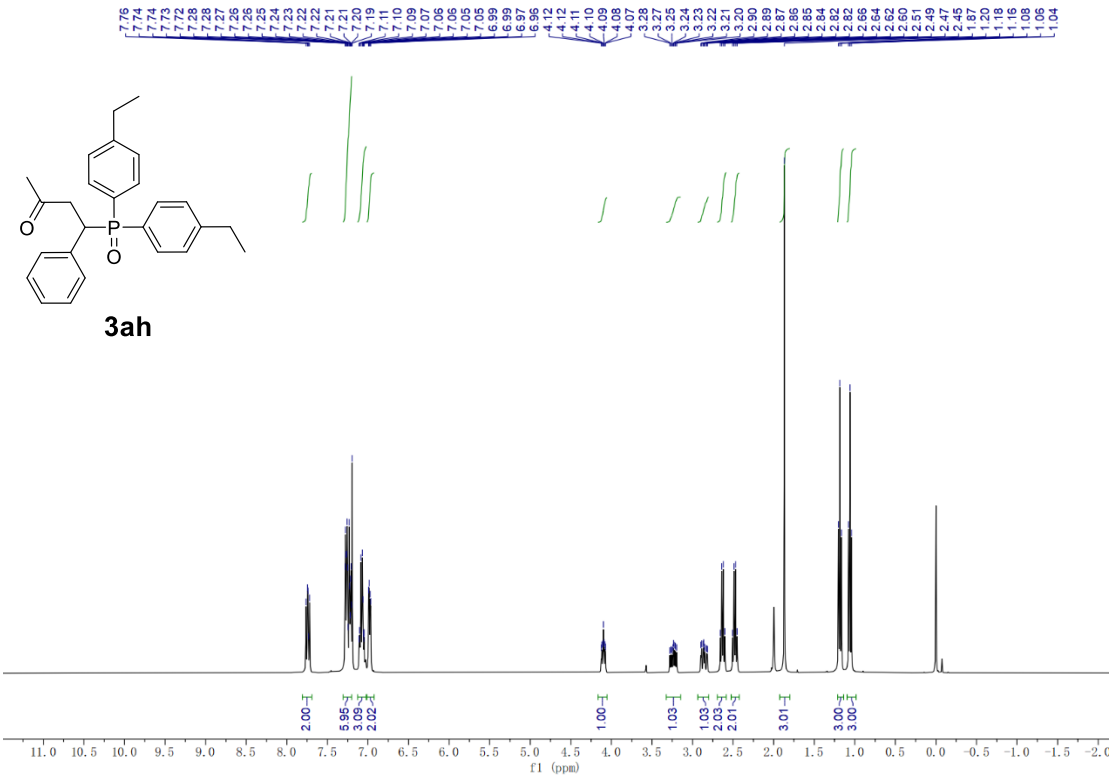


Figure S3.104 ^{1}H NMR spectrum of **3ah** (400 MHz, $CDCl_3$).

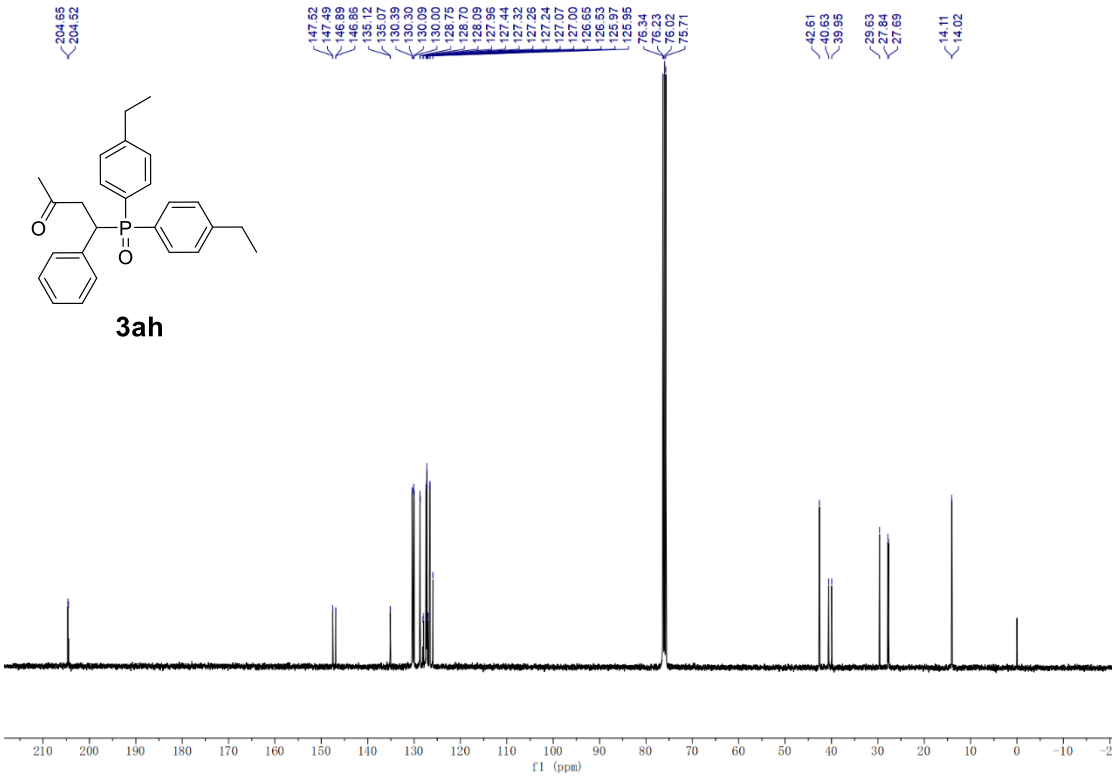


Figure S3.105 ^{13}C NMR spectrum of **3ah** (101 MHz, $CDCl_3$).

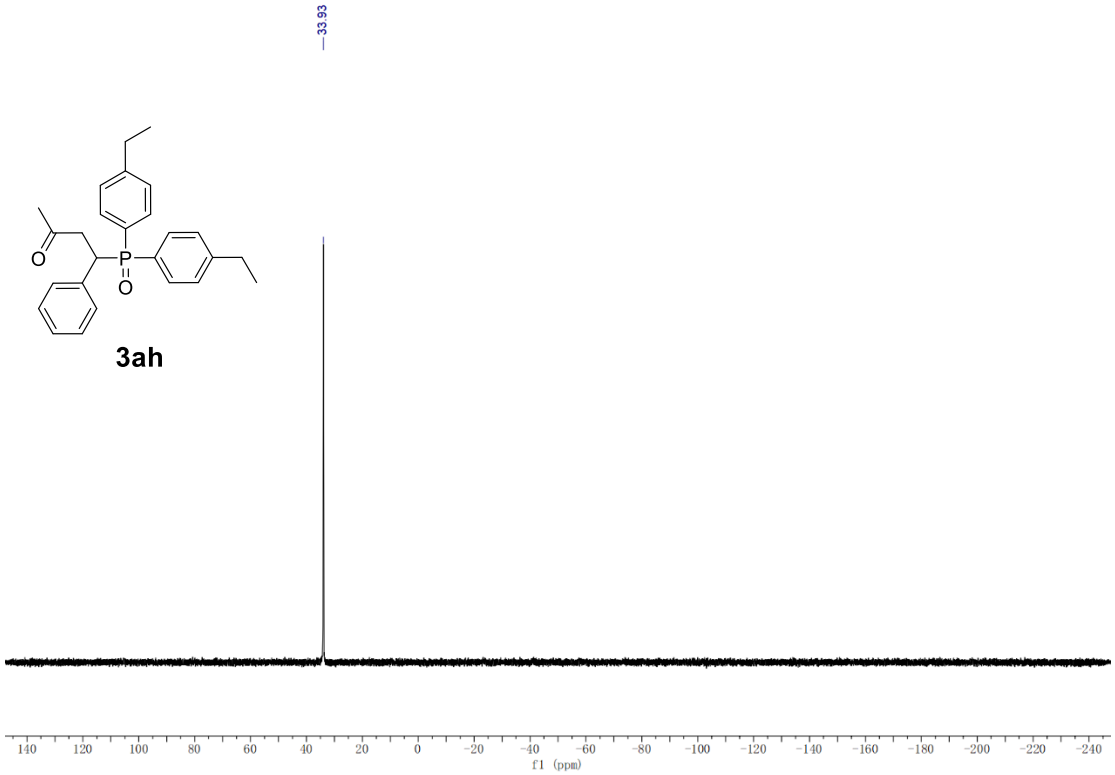


Figure S3.106 ^{31}P NMR spectrum of **3ah** (162 MHz, $CDCl_3$).

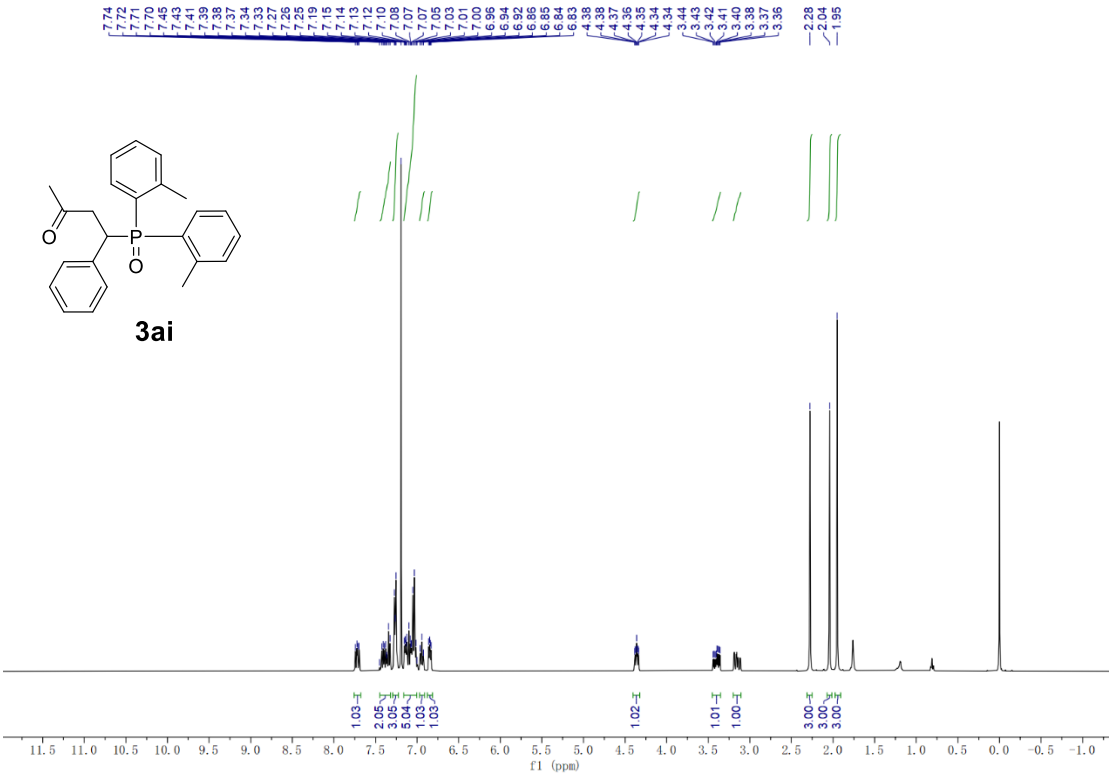


Figure S3.107 ^{1}H NMR spectrum of **3ai** (400 MHz, $CDCl_3$).

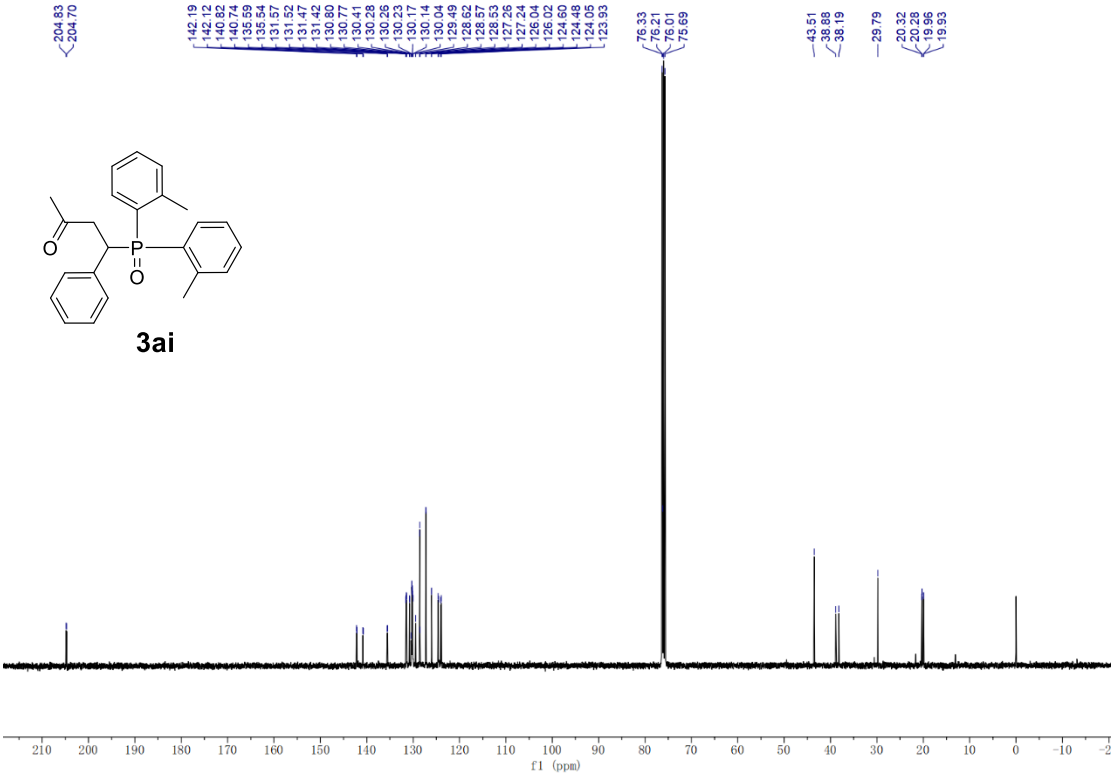


Figure S3.108 ^{13}C NMR spectrum of **3ai** (101 MHz, $CDCl_3$).

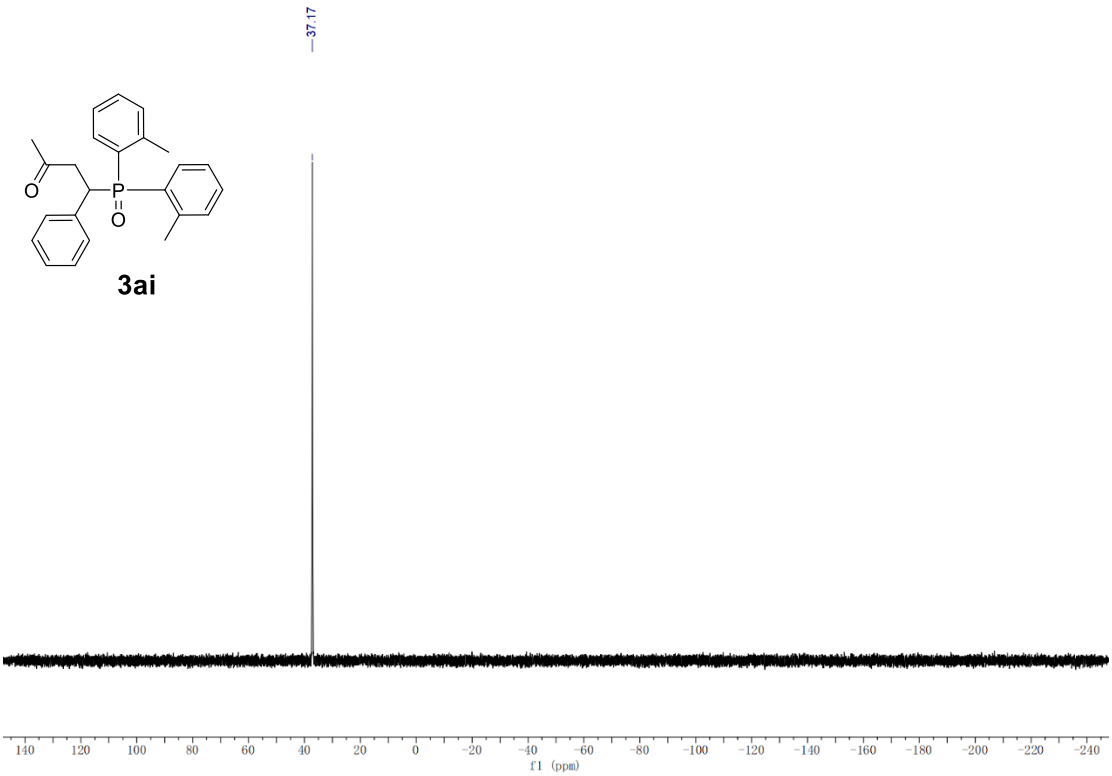


Figure S3.109 ^{31}P NMR spectrum of **3ai** (162 MHz, $CDCl_3$).

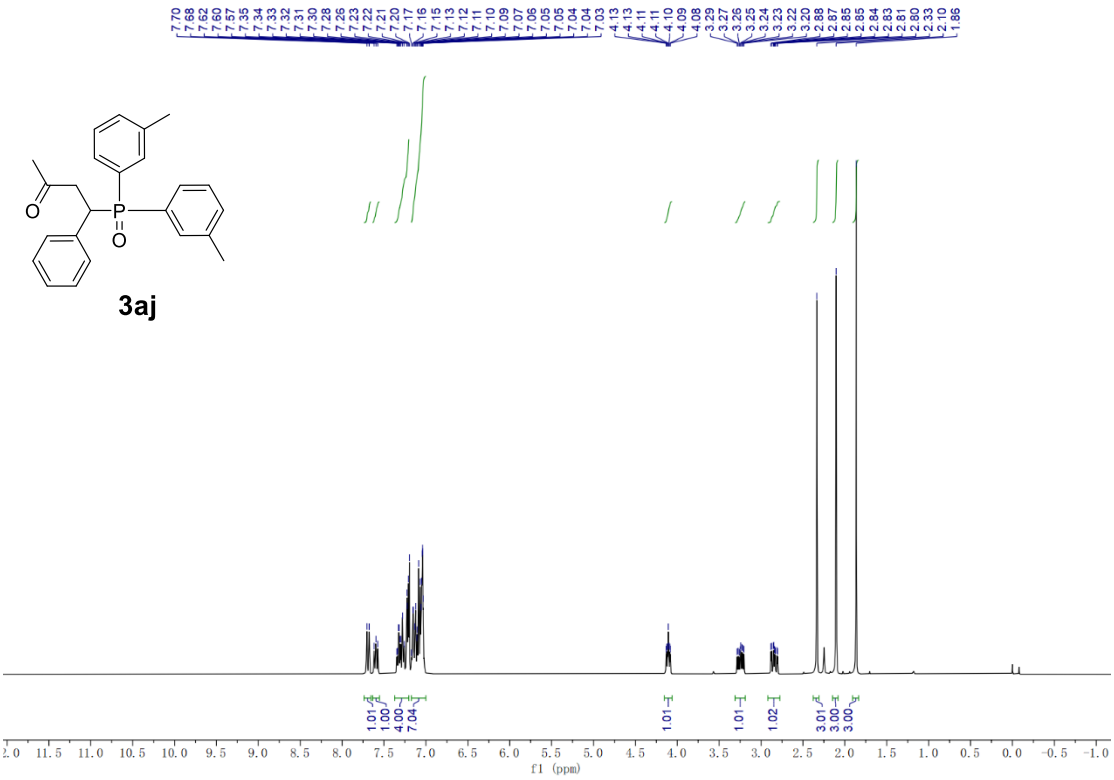


Figure S3.110 ^{1}H NMR spectrum of **3aj** (400 MHz, $CDCl_3$).

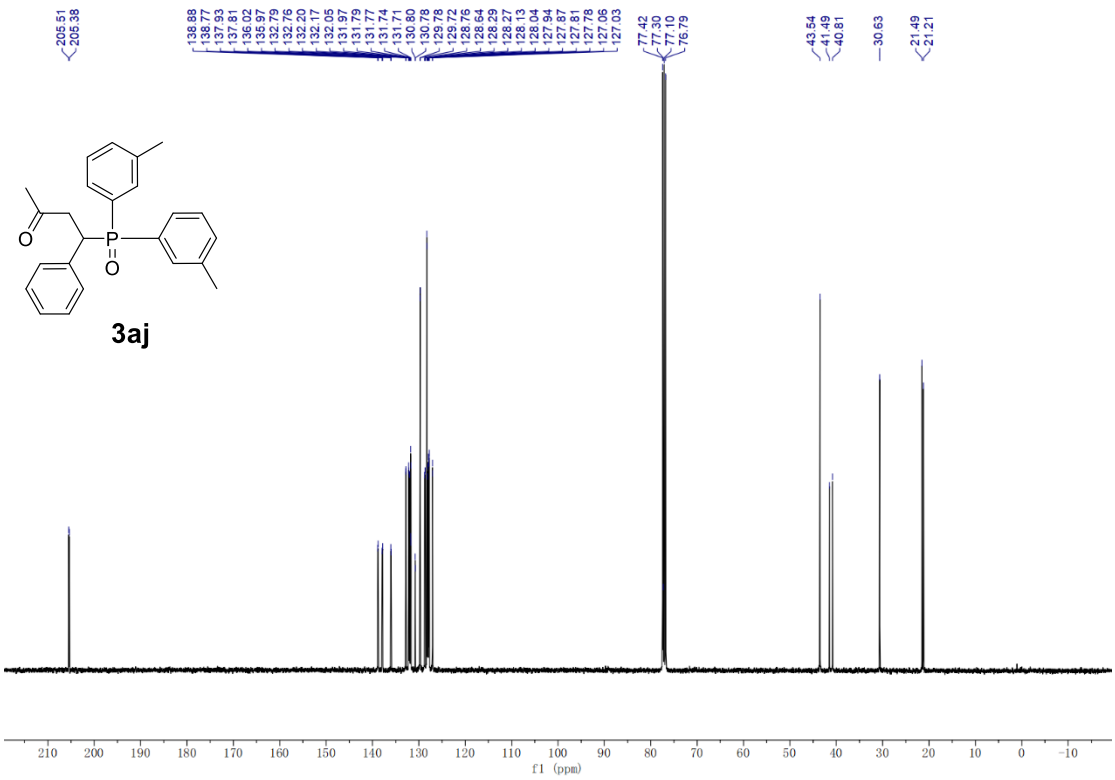


Figure S3.111 ^{13}C NMR spectrum of **3aj** (101 MHz, $CDCl_3$).

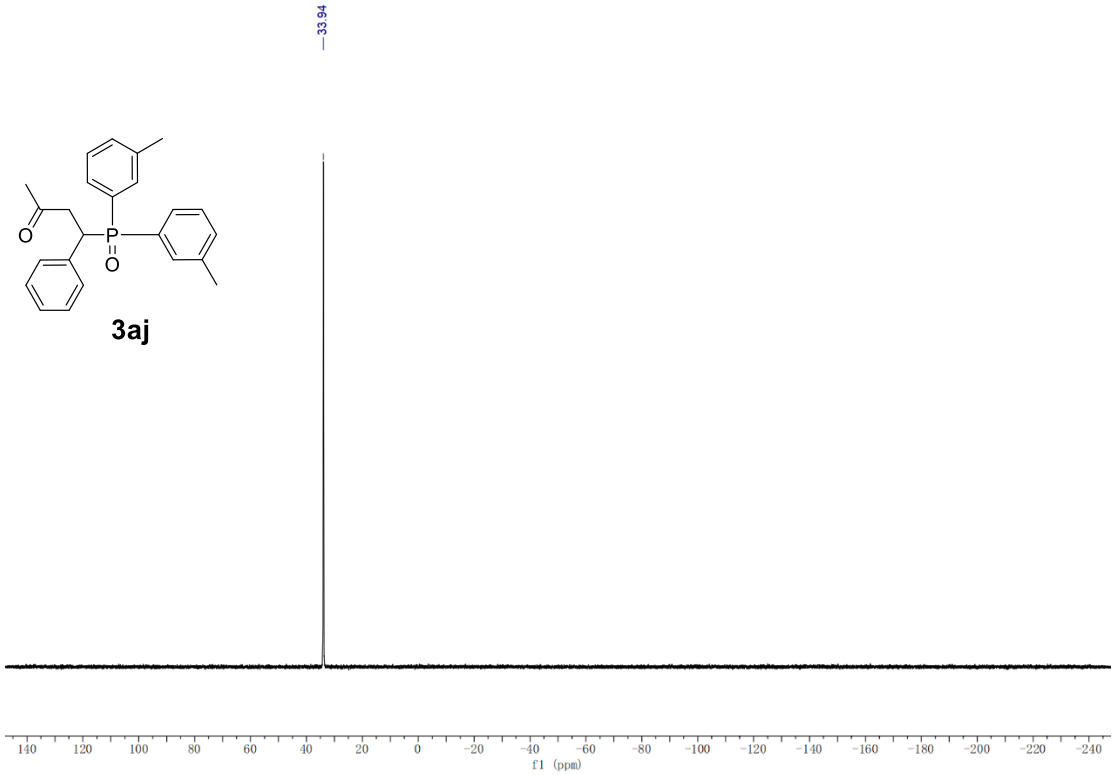


Figure S3.112 ^{31}P NMR spectrum of **3aj** (162 MHz, $CDCl_3$).

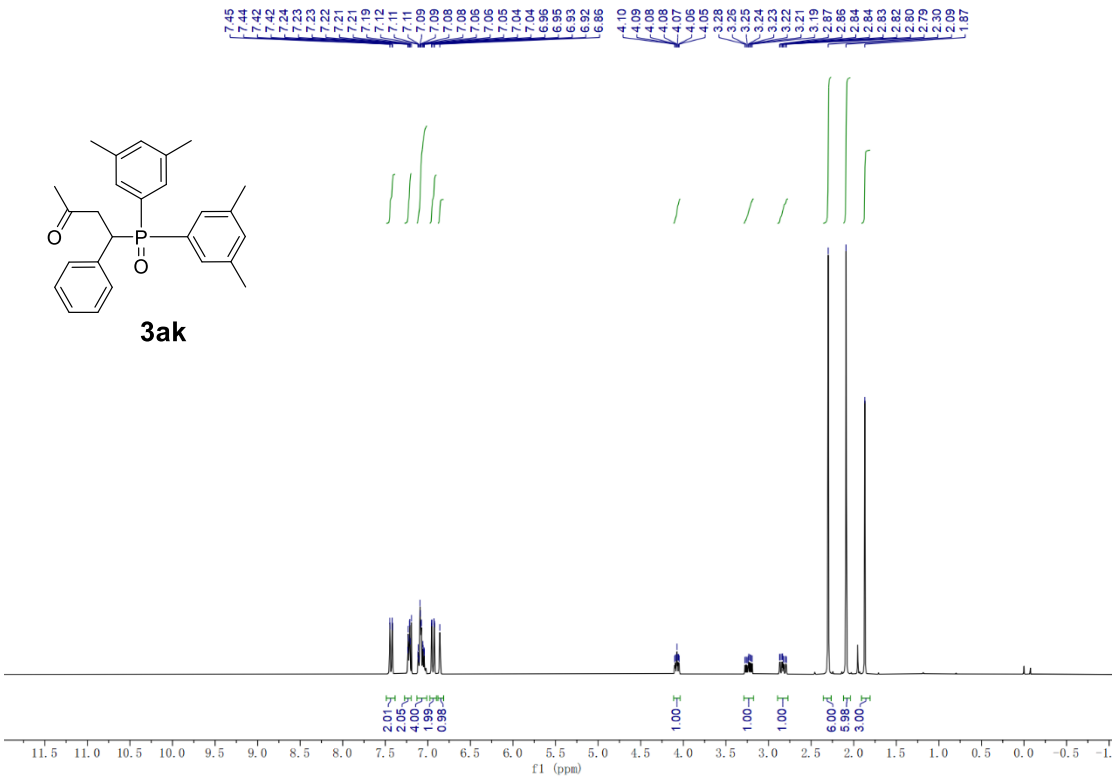


Figure S3.113 ^{1}H NMR spectrum of **3ak** (400 MHz, $CDCl_3$).

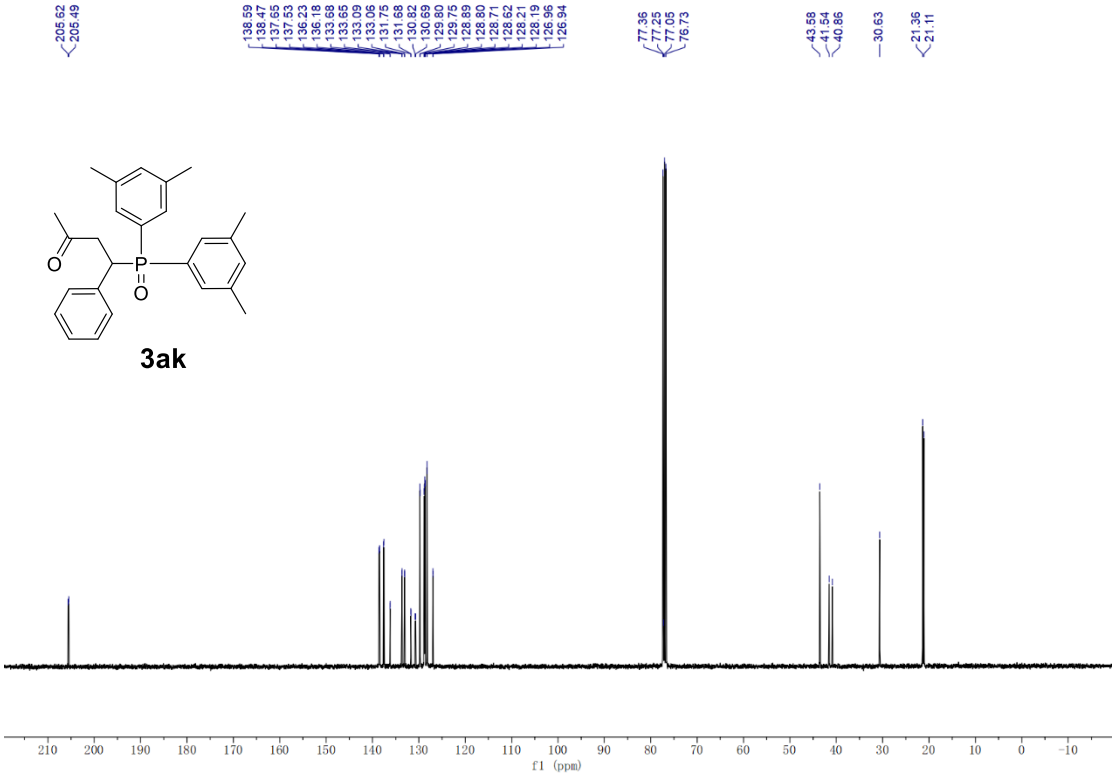


Figure S3.114 ^{13}C NMR spectrum of **3ak** (101 MHz, $CDCl_3$).

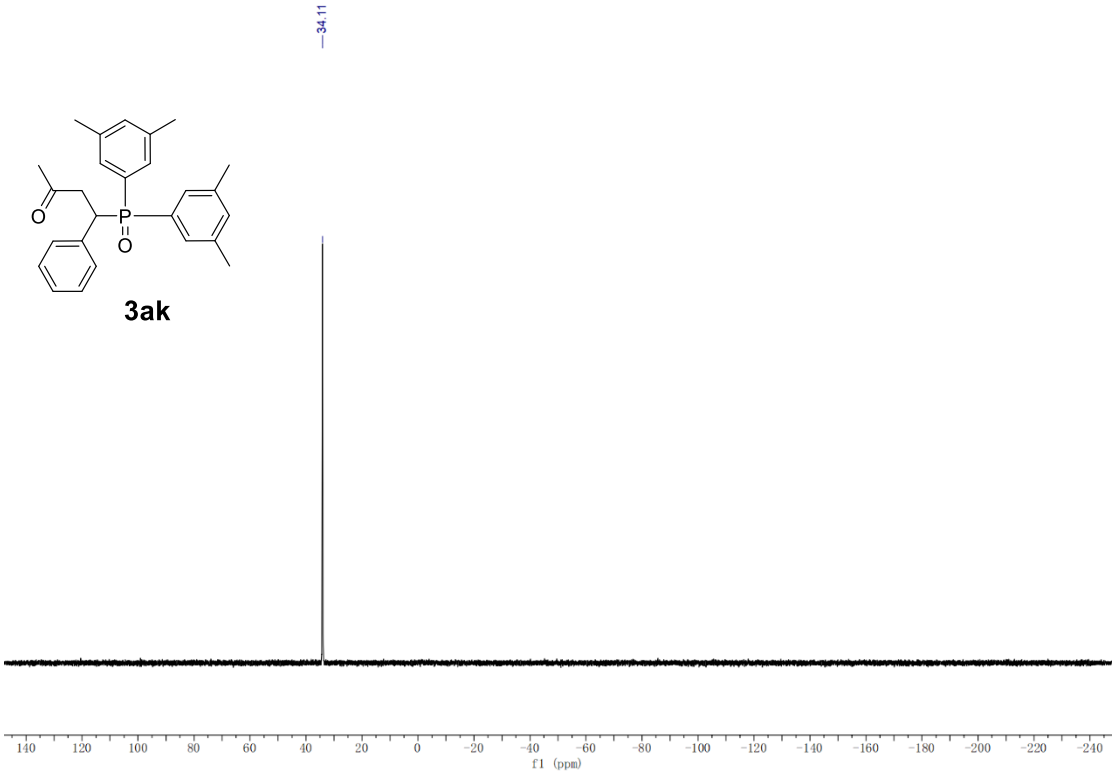


Figure S3.115 ^{31}P NMR spectrum of **3ak** (162 MHz, $CDCl_3$).

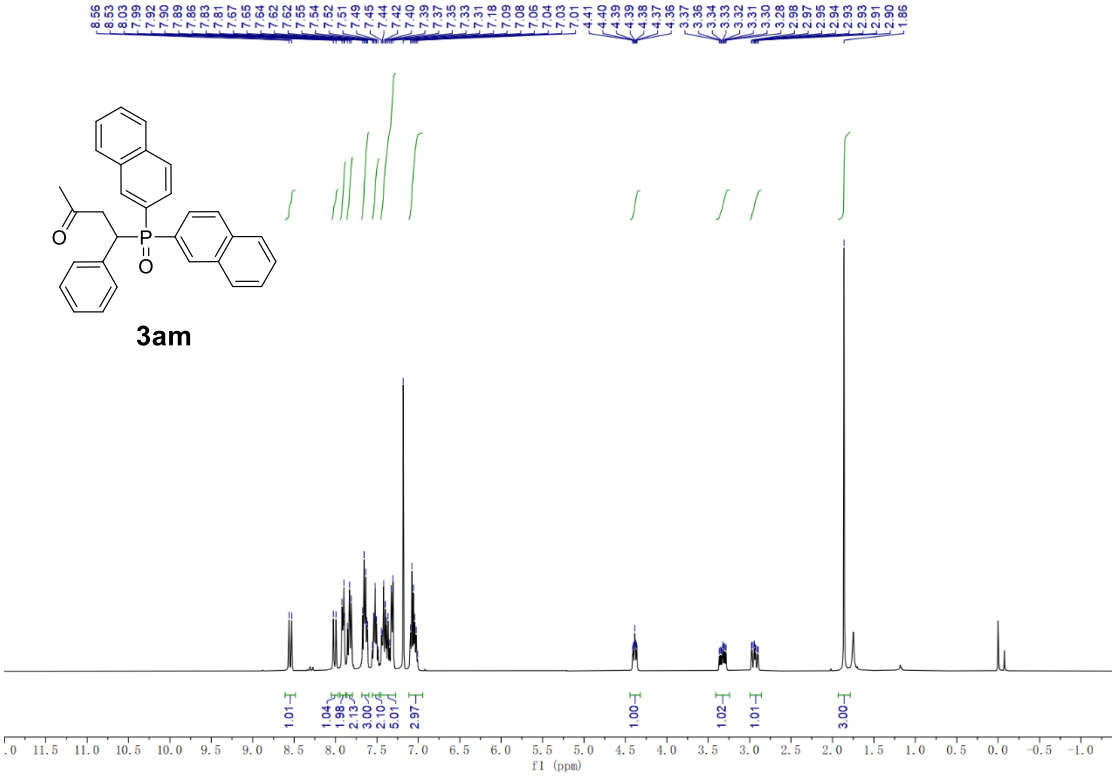


Figure S3.116 ^{1}H NMR spectrum of **3am** (400 MHz, $CDCl_3$).

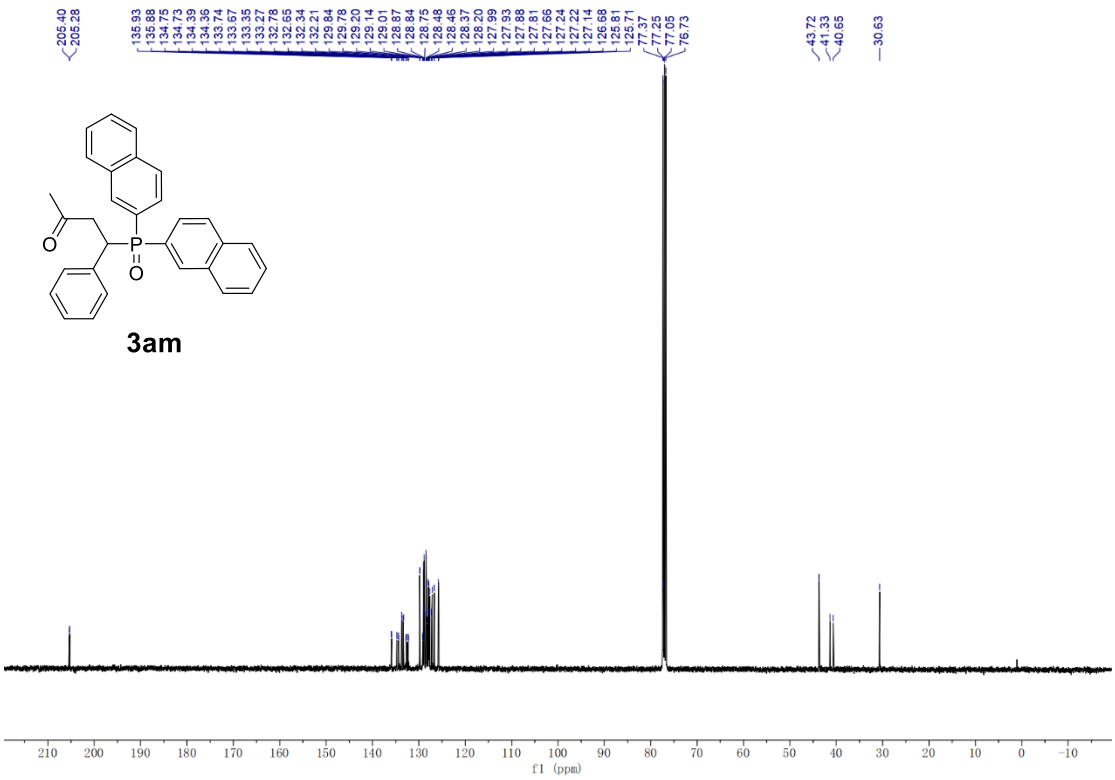


Figure S3.117 ^{13}C NMR spectrum of **3am** (101 MHz, $CDCl_3$).

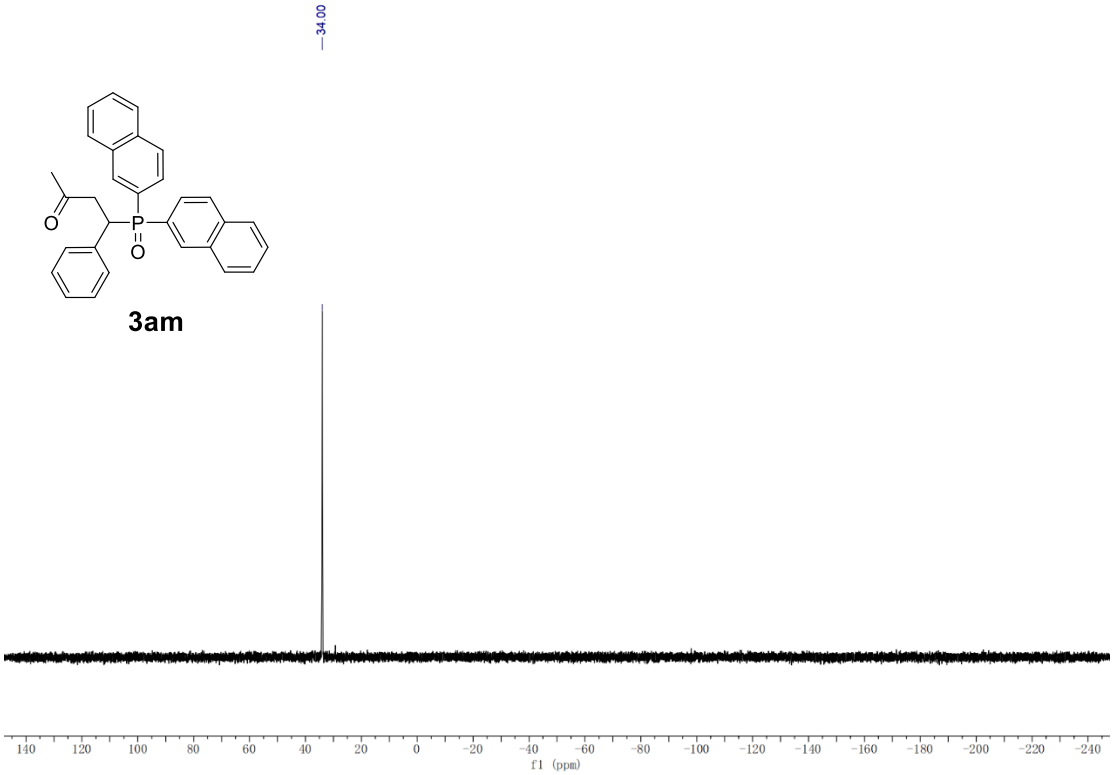
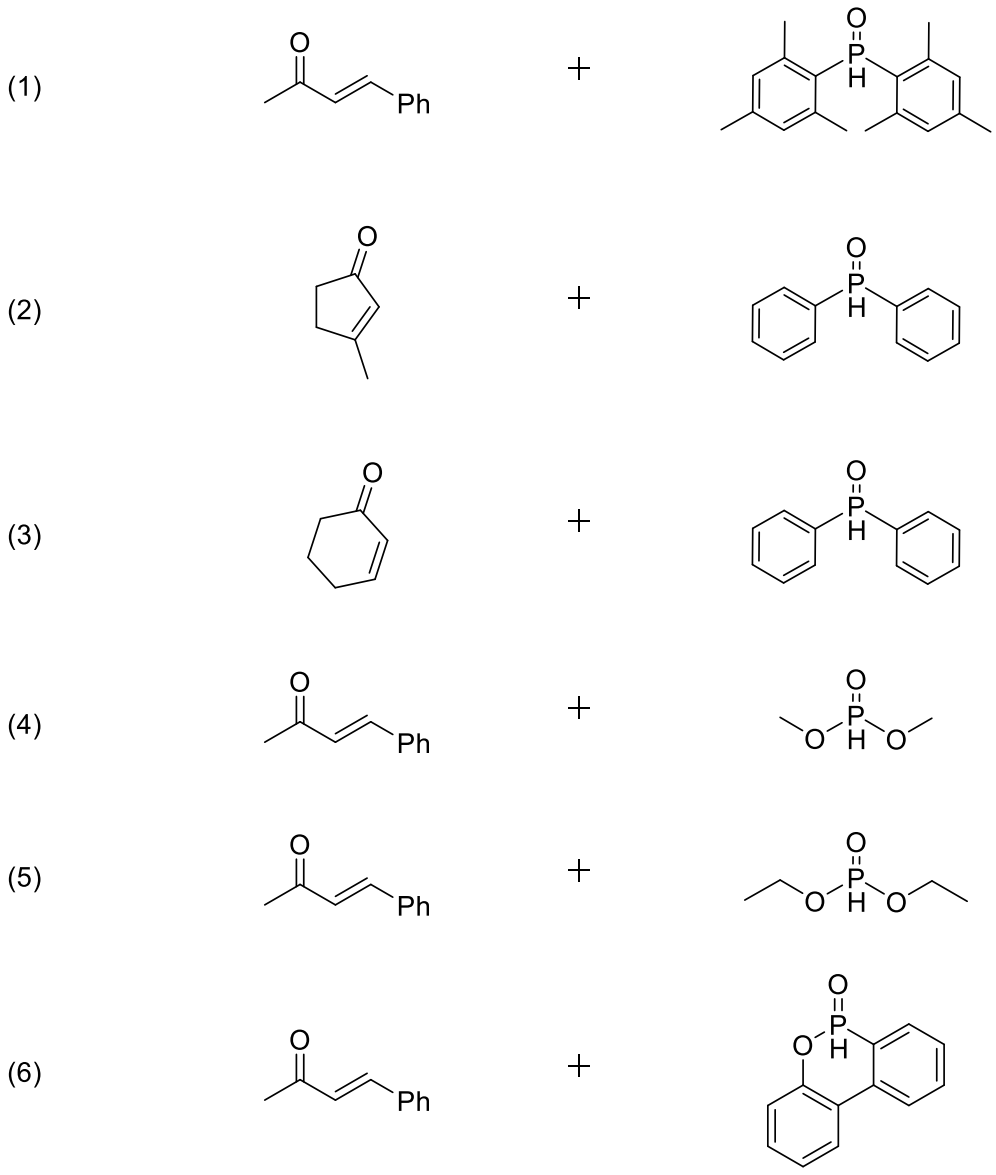


Figure S3.118 ^{31}P NMR spectrum of **3am** (162 MHz, $CDCl_3$).

4. Substrate Scope Limitations and Observed Challenges

During the exploration of the substrate scope, we also encountered several limitations, as illustrated in **Scheme S4.1**. For instance, reactions (1) and (2) resulted in low yields, likely due to severe steric hindrance associated with the substituents. Reactions (3) through (6) led to the formation of multiple side products, and no clear chemoselectivity was observed under the standard conditions. These examples underline the steric and electronic sensitivity of the current catalytic system.

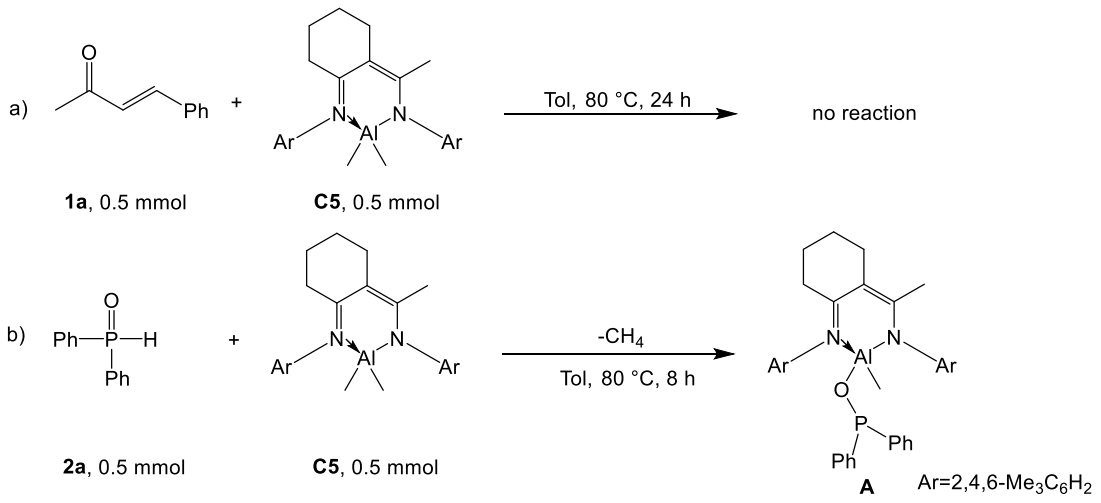


Scheme S4.1 Representative Cases Highlighting Substrate Limitations

5. Control experiments for the mechanistic investigation

Initially, we reacted compound **1a** (0.5 mmol) with an equal amount of catalyst **C5** in toluene at 80 °C for 24 h under nitrogen atmosphere. Under vacuum, the solution after the reaction was drained to obtain a yellow solid, and the solid obtained was tested by NMR. The results indicated that the ^{1}H NMR spectral analysis of the reaction between **1a** and **C5** showed no significant changes compared to the original data (**Scheme S5.1** a).

C5 (0.2 mmol) was reacted with 1.0 equivalent of diphenylphosphine oxide in deuterated chloroform ($CDCl_3$) at 60 °C under a nitrogen atmosphere for 24 hours. After completion of the reaction, the mixture was subjected to ^{1}H NMR analysis. As shown in **Figure S5.1** b, a new signal appeared at –0.95 ppm in the ^{1}H NMR spectrum, whereas the corresponding resonance for the starting material **C5** was observed at –1.23 ppm. The newly emerged signal at –0.95 ppm is tentatively attributed to the Al–Me proton in intermediate **A**. In addition, a distinct new peak was detected at 0.13 ppm, which is consistent with the chemical shift of methane. This observation supports the mechanistic proposal that the formation of intermediate **A** from **C5** and diphenylphosphine oxide is accompanied by the release of one equivalent of methane.



Scheme S5.1 Control experiments

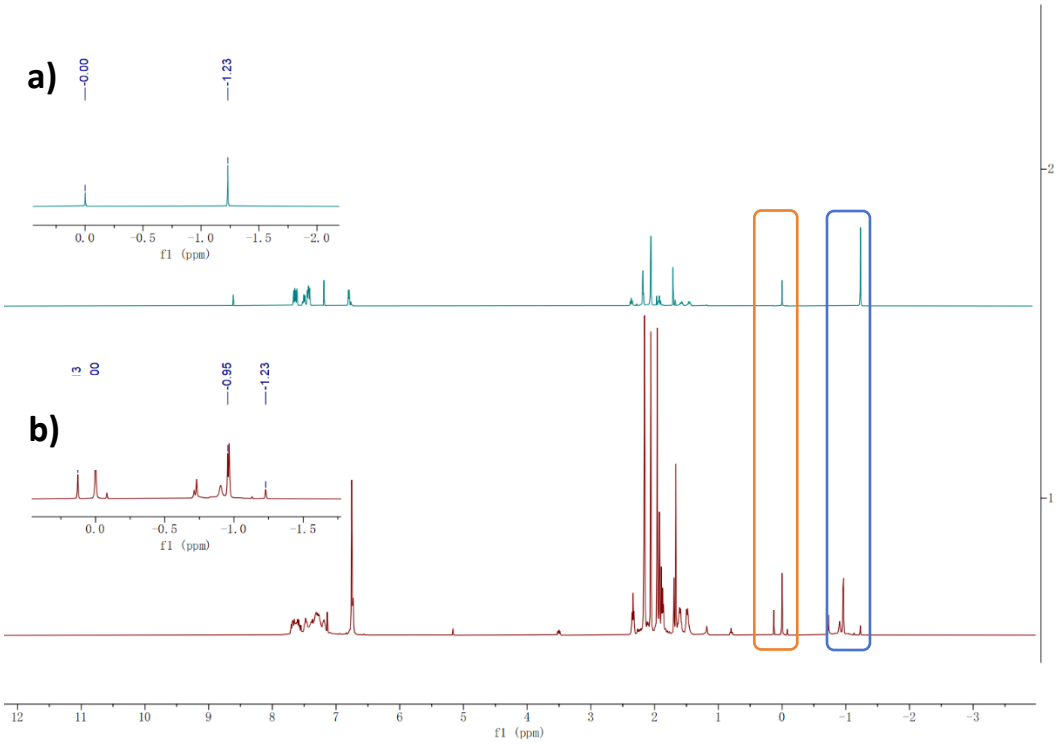


Figure S5.1 ^{1}H NMR spectrum of a mixture of **C5** and diphenylphosphine oxide: a) before reaction of **C5** with diphenylphosphine oxide; b) after reaction of **C5** with diphenylphosphine oxide.

Finally, we conducted a ^{31}P NMR test, which revealed a distinct single peak at 23.01 ppm (**Figure S5.2**). This result is consistent with similar observations reported in the literature[6] for Al-O-P, which is typically found around 24.26 ppm.

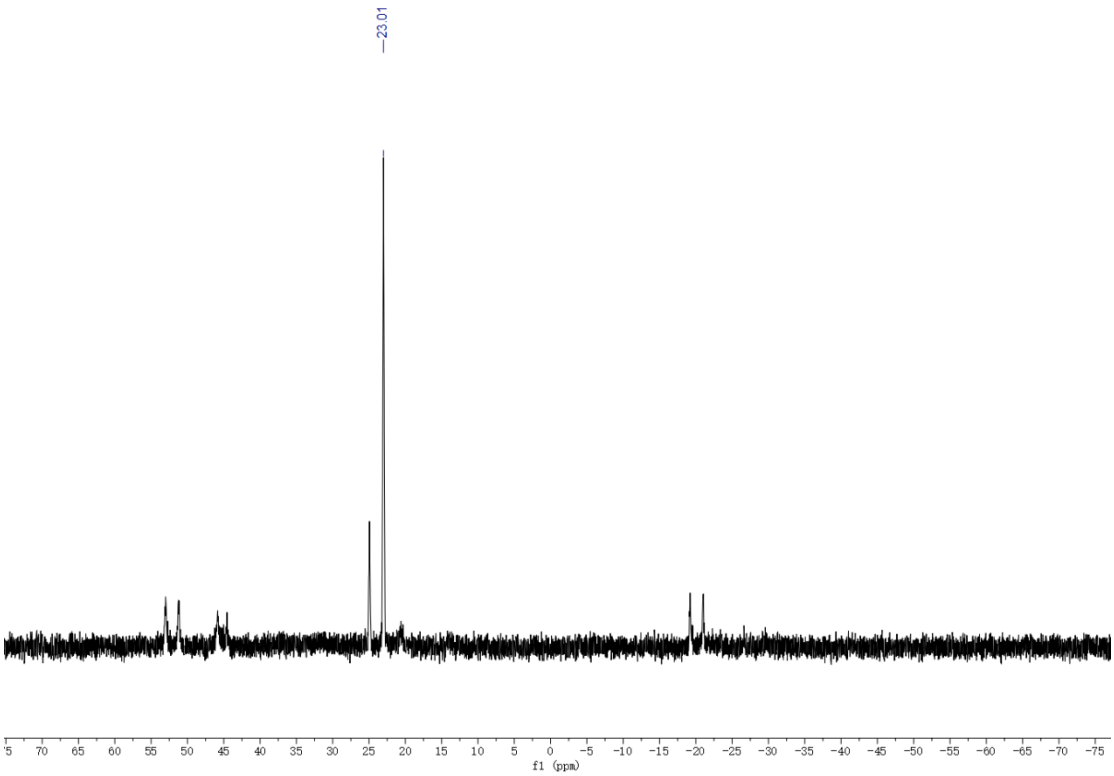


Figure S5.2 ^{31}P NMR spectrum of a mixture after reaction of **C5** with diphenylphosphine oxide

In addition, we performed liquid-phase mass spectrometric (LC-MS) analysis on the reaction mixture obtained from the treatment of **C5** with diphenylphosphine oxide (**2a**). Although partial decomposition occurred during the measurement, a molecular ion corresponding to the proposed structure of intermediate A was still clearly observed. The data are as follows:

MS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{39}H_{46}AlN_2OPH^+$: 617.3241; found: 617.3233.

This result complements the NMR data presented in the main text and strongly supports the in situ formation of intermediate A in the reaction system.

6. References

1. J. D. Nobbs, D. W. P. Tay, Y. H. Yeap, Y. L. Tiong, S. Ye, S. Aitipamula, C. Wang, C. B. Cheong and M. van Meurs, *Dalton Trans.*, 2023, **52**, 17954-17965.
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3. G. M. Sheldrick, *Acta Cryst. C*., 2015, **71**, 3-8.
4. G. M. Sheldrick, *Acta Crystallogr. A Found. Adv.*, 2008, **64**, 112-122.
5. G. M. Sheldrick, *Acta Crystallogr. A Found. Adv.*, 2015, **71**, 3-8.

6. P. Hao, Z. Yang, X. Ma, X. Wang, Z. Liu, H. W. Roesky, K. Sun, J. Li and M. Zhong, *Dalton Trans.*, 2012, **41**, 13520-13524.