Supporting Information

Keggin structure heteropolyacids-catalyzed phosphinylation of secondary propargyl alcohols with phosphine oxides to *γ*-ketophosphine oxides

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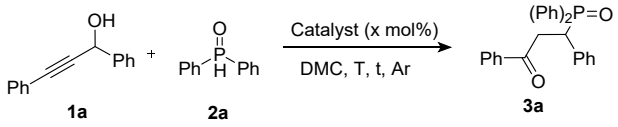
1. Optimization of Reaction Conditions

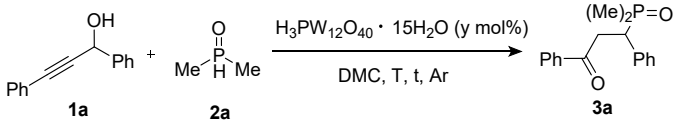
Table S1. Optimization of the reaction conditions.[a]



Entry	Cat. (mol%)	T (°C)	Yield (%)[b]
1	4.5	120	72
2	0.9	120	52
3	2.7	120	62
4	9	120	64
5	4.5	rt	NR[c]
6	4.5	40	trace
7	4.5	60	20
8	4.5	80	59
9	4.5	100	60
10	4.5	140	69

[a] Reaction condition: **1a** (0.6 mmol), **2a** (0.3 mmol) and $H_3PW_{12}O_{40}{\cdot}15H_2O$ (4.5 mol%) dissolved in DMC (2 mL) were stirred at T °C for 18 h under argon. [b] Isolated yield. [c] NR: No reaction.

Table S2. Investigation of the activity between 1,3-diphenylprop-2-yn-1-ol and dimethylphosphine oxide.[a]



Entry	Cat. (mol%)	T (°C)	t (h)	Yield (%)
1	4.5	120	12	NR[b]
2	9	120	12	NR[b]
3	4.5	120	14	NR[b]
4	4.5	120	16	NR[b]
5	4.5	140	12	NR[b]

[a] Reaction condition: **1a** (0.6 mmol), **2a** (0.3 mmol) and $H_3PW_{12}O_{40}{\cdot}15H_2O$ (y mol%) dissolved in DMC (2 mL) were stirred at T °C for certain time under argon. [b] NR: No reaction.

2. Testing the Content of Water in Catalysts

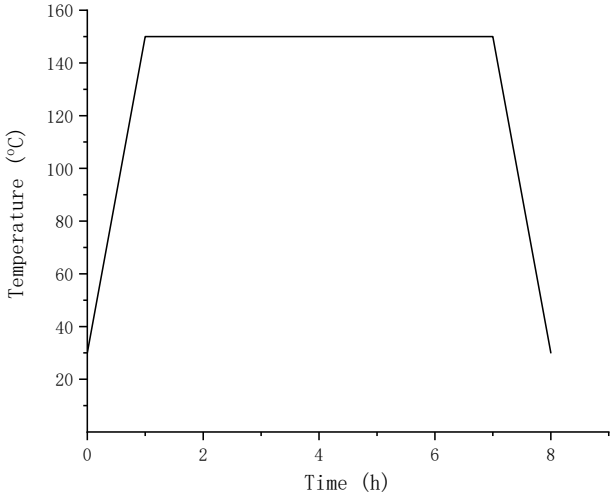


Figure S1. The procedure for losing the water molecules in muffle furnace (Initial temperature: 30 °C, from 30 to 150 °C at 5 °C/min, holding for 6 h, then cooling from 150 to 30 °C at 5 °C/min).

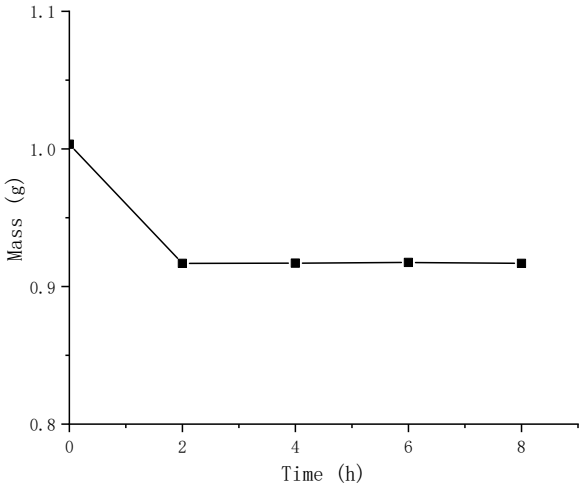


Figure S2. Weight change of phosphotungstic acid at 150 °C for different hours (Initial weight of phosphotungstic acid: 1.0034 g, at 150 °C holding for 2 h, terminal weight: 0.9168 g; t = 4 h, terminal weight: 0.9170 g; t = 6 h, terminal weight: 0.9175 g; t = 8 h, terminal weight: 0.9168 g; According to the data, the number of water molecules in $H_3PW_{12}O_{40}$ is about 15 through calculation).

Initial weight of phosphomolybdic acid: 1.0101 g, at 150 °C holding for 2 h, terminal weight: 0.9065 g; According to the data, the number of water molecules in $H_3P_4Mo_{12}O_{40}$ is about 11 through calculation.

3. The HRMS of 3a with ^{18}O Isotopic Labelling

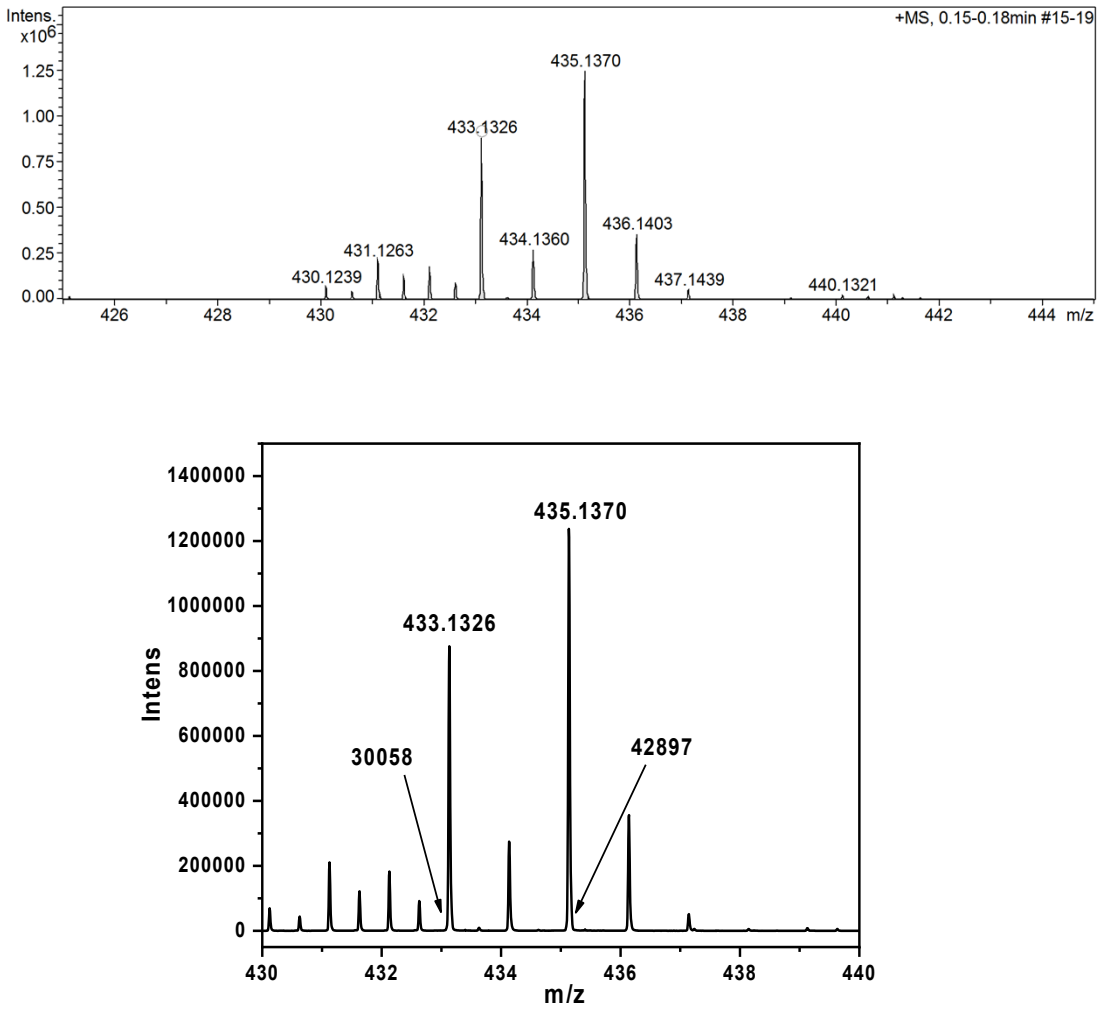


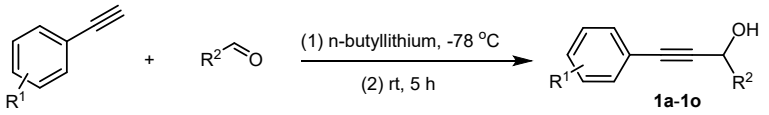
Figure S3. The HRMS of **3a** with ^{18}O isotopic labelling detected in the reaction of Scheme **6b**.

4. Experimental Details

General Information

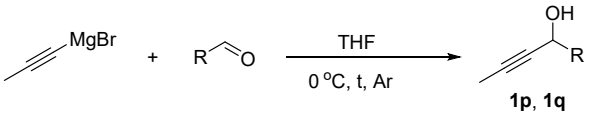
All chemical reagents and catalysts etc. were purchased from Makclin Biochemical Co., Ltd. and used without further purification. Analytical thin-layer chromatography (TLC) plates produced from Qingdao Hailang were bought. Aluminum oxide (200-300) from Sinopharm Chemical Reagent Co., Ltd. was used for column chromatography, and the eluent was a mixture of ethyl acetate and dichloromethane. Unless noted, a Schlenk tube purchased from the Synthware Glass company was the main reacton vessel. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR were recorded on a Bruker AVANCE III 400 MHz spectrometer in $CDCl_3$. $CDCl_3$ residual signals were used as an internal standard. Chemical shift values (δ) are reported in ppm and coupling constants (*J* values) are reported in Hertz (Hz). A Bruker micrOTOF-QII mass spectrometer with an ESI source was used to give High-resolution mass spectra (HRMS).

General Procedure for the Synthesis of Propargyl Alcohols



1a-1o

To a stirring solution of alkyne (2.5 mmol) in THF (10 mL) was added dropwise *n*-butyllithium (2.5 mmol in THF) at -78 °C. Then, aldehyde (5 mmol) was added dropwise with stirring at room temperature after 5 h and determined by TLC. After the reaction was completed, the mixture was quenched with saturated ammonium chloride (10 mL), and extracted with ethyl acetate (3×15 mL). The combined organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate to obtain the pure product propargyl alcohols, **1a**,[S1] **1b**,[S2] **1c**,[S3] **1d**,[S4] **1e**-**1g**,[S5] **1h**,[S6] **1i**-**1l**,[S7] **1m**-**1n**,[S8] **1o**.[S9]



1p, **1q**

To a stirring solution of 1-propynylmagnesium bromide (2.5 mmol) in THF (10 mL) was added dropwise aldehyde (2.5 mmol) dissolved in THF at 0 °C. Then, the mixture was stirred and warmed to room temperature over certain hours, and determined by TLC. After the reaction was completed, the mixture was quenched with saturated ammonium chloride (10 mL), and extracted with ether (3×15 mL). The combined organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate to obtain the pure product propargyl alcohols **1p**,[S10] and **1q**.[S11]

General Procedure for the Synthesis of *γ*-Ketophosphine Oxides

Propargyl alcohol 1 (125.1 mg, 0.6 mmol) and 2 (60.6 mg, 0.3 mmol) dissolved in DMC (2 mL) were added a certain amount of catalyst and H_2O (140 μL) under argon. The above system was stirred for several hours at a definite temperature and monitored by TLC. After the reaction was over, the mixture was extracted with dichloromethane and concentrated under a vacuum. The crude product was purified by aluminum oxide (200−300 mesh) with dichloromethane/ethyl acetate as eluent.

5. Characterization Data of the Products

3-(Diphenylphosphoryl)-1,3-diphenylpropan-1-one (**3a**):[S12] 85% yield, 105 mg; white solid, melting points: 246.1 °C-246.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.95 (m, 2H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.42 (m, 6H), 7.41 – 7.29 (m, 5H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.13 (dt, *J* = 13.8, 7.2 Hz, 3H), 4.47 (t, *J* = 8.6 Hz, 1H), 4.03 (ddd, *J* = 18.0, 10.4, 4.2 Hz, 1H), 3.39 (dd, *J* = 18.2, 11.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7 (d, $J_{C\text{-}P}$=13.1 Hz), 136.4, 136.0 (d, $J_{C\text{-}P}$=6.1 Hz), 133.3, 132.0 (d, $J_{C\text{-}P}$=3.0 Hz), 131.4 (d, $J_{C\text{-}P}$=4.1 Hz), 131.3 (d, $J_{C\text{-}P}$=4.1 Hz), 131.0 (d, $J_{C\text{-}P}$=9.1 Hz), 129.8 (d, $J_{C\text{-}P}$=6.1 Hz), 129.0, 128.9, 128.5, 128.3 (d, $J_{C\text{-}P}$=2.0 Hz), 128.1 (d, $J_{C\text{-}P}$=2.0 Hz), 128.0, 127.1 (d, $J_{C\text{-}P}$=2.0 Hz), 41.1 (d, $J_{C\text{-}P}$=68.0 Hz), 39.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.57.

3-(Diphenylphosphoryl)-1-phenyl-3-(2-tolyl)propan-1-one (**3b**):[S12] 54% yield, 71 mg; white solid, melting points: 205.3 °C-205.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (ddd, *J* = 10.0, 6.2, 2.1 Hz, 2H), 7.87 – 7.75 (m, 3H), 7.57 (tt, *J* = 4.3, 2.7 Hz, 3H), 7.50 – 7.44 (m, 1H), 7.40 – 7.30 (m, 3H), 7.25 – 7.13 (m, 5H), 7.08 – 7.02 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 4.67 (ddd, *J* = 10.0, 7.2, 2.4 Hz, 1H), 4.07 (ddd, *J* = 18.2, 10.2, 4.4 Hz, 1H), 3.41 (ddd, *J* = 18.2, 11.1, 2.4 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (d, $J_{C\text{-}P}$=14.1 Hz), 137.4 (d, $J_{C\text{-}P}$=6.1 Hz), 136.4, 134.4 (d, $J_{C\text{-}P}$=5.1 Hz), 133.3, 132.4, 132.2 (d, $J_{C\text{-}P}$=3.1 Hz), 131.7 (d, $J_{C\text{-}P}$=8.1 Hz), 131.5 (d, $J_{C\text{-}P}$=2.1 Hz), 131.45, 131.0 (d, $J_{C\text{-}P}$=9.1 Hz), 130.05, 129.0 (d, $J_{C\text{-}P}$=11.0 Hz), 128.8, 128.5, 128.1, 127.8 (d, $J_{C\text{-}P}$=12.1 Hz), 127.1 (d, $J_{C\text{-}P}$=3.0 Hz), 126.2 (d, $J_{C\text{-}P}$=2.0 Hz), 39.9, 36.1 (d, $J_{C\text{-}P}$=68.7 Hz), 19.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.95.

3-(Diphenylphosphoryl)-1-phenyl-3-(3-tolyl)propan-1-one (**3c**):[S12] 65% yield, 83 mg; white solid, melting points: 231.2 °C-231.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (tt, *J* = 7.9, 2.3 Hz, 2H), 7.90 – 7.78 (m, 2H), 7.54 – 7.42 (m, 6H), 7.40 – 7.30 (m, 3H), 7.27 – 7.23 (m, 2H), 7.20 – 7.12 (m, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 4.44 (ddd, *J* = 10.0, 7.1, 2.5 Hz, 1H), 3.99 (ddd, *J* = 18.1, 10.2, 4.4 Hz, 1H), 3.39 (ddd, *J* = 18.1, 11.4, 2.6 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8 (d, $J_{C\text{-}P}$=13.1 Hz), 136.8 (d, $J_{C\text{-}P}$=3.0 Hz), 136.5, 133.5, 132.8 (d, $J_{C\text{-}P}$=6.1 Hz), 132.1 (d, $J_{C\text{-}P}$=2.0 Hz), 131.5 (d, $J_{C\text{-}P}$=3.0 Hz), 131.4 (d, $J_{C\text{-}P}$=9.1 Hz), 131.2 (d, $J_{C\text{-}P}$=9.1 Hz), 129.8 (d, $J_{C\text{-}P}$=6.1 Hz), 129.2 (d, $J_{C\text{-}P}$=2.0 Hz), 129.1, 129.0, 128.7, 128.3 (d, $J_{C\text{-}P}$=3.0 Hz), 128.2, 40.6 (d, $J_{C\text{-}P}$=70.0 Hz), 39.2, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.43.

3-(Diphenylphosphoryl)-3-(4-ethylphenyl)-1-phenylpropan-1-one (**3d**):[S13] 65% yield, 83 mg; white solid, melting points: 210.9 °C-211.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.86 – 7.81 (m, 2H), 7.55 – 7.42 (m, 6H), 7.40 – 7.30 (m, 3H), 7.30 – 7.21 (m, 4H), 6.97 (d, *J* = 7.9 Hz, 2H), 4.46 (ddd, *J* = 9.7, 6.9, 2.4 Hz, 1H), 4.05 – 3.95 (m, 1H), 3.37 (ddd, *J* = 18.2, 11.3, 2.4 Hz, 1H), 2.56 – 2.45 (m, 2H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (d, $J_{C\text{-}P}$=13.1 Hz), 143.0 (d, $J_{C\text{-}P}$=3.0 Hz), 136.5, 133.4, 131.44, 131.35, 131.14, 131.05, 129.8 (d, $J_{C\text{-}P}$=6.1 Hz), 129.0 (d, $J_{C\text{-}P}$=9.1 Hz), 128.6, 128.2 (d, $J_{C\text{-}P}$=3.0 Hz), 128.0, 127.9 (d, $J_{C\text{-}P}$=2.0 Hz), 41.0 (d, $J_{C\text{-}P}$=69.7 Hz), 39.1, 28.4, 15.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.43.

3-(Diphenylphosphoryl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3e**):[S12] 44% yield, 63 mg; white solid, melting points: 245.2 °C-245.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.93 (m, 2H), 7.88 – 7.78 (m, 2H), 7.51 (dddd, *J* = 15.0, 11.3, 5.9, 1.5 Hz, 8H), 7.38 (ddd, *J* = 14.8, 7.8, 2.4 Hz, 5H), 7.31 – 7.27 (m, 1H), 7.25 (s, 1H), 4.52 (dd, *J* = 6.7, 3.8 Hz, 1H), 4.01 (ddd, *J* = 18.3, 10.5, 4.3 Hz, 1H), 3.41 (ddd, *J* = 18.3, 10.9, 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3 (d, $J_{C\text{-}P}$=13.1 Hz), 136.1, 133.6, 132.3 (d, $J_{C\text{-}P}$=3.0 Hz), 131.7 (d, $J_{C\text{-}P}$=3.0 Hz), 131.2 (d, $J_{C\text{-}P}$=9.1 Hz), 130.8 (d, $J_{C\text{-}P}$=9.1 Hz), 130.2 (d, $J_{C\text{-}P}$=6.1 Hz), 129.1 (d, $J_{C\text{-}P}$=11.1 Hz), 128.7, 128.3 (d, $J_{C\text{-}P}$=12.1 Hz), 128.1, 41.1 (d, $J_{C\text{-}P}$=68.7 Hz), 39.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.73.

3-(Diphenylphosphoryl)-3-(4-fluorophenyl)-1-phenylpropan-1-one (**3f**):[S12] 75% yield, 96 mg; white solid, melting points: 228.5 °C-229.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (ddt, *J* = 9.5, 5.8, 2.1 Hz, 2H), 7.87 – 7.81 (m, 2H), 7.58 – 7.44 (m, 6H), 7.41 – 7.33 (m, 5H), 7.31 – 7.23 (m, 2H), 6.88 – 6.80 (m, 2H), 4.45 (ddd, *J* = 10.6, 6.8, 2.4 Hz, 1H), 3.98 (ddd, *J* = 18.2, 10.6, 4.2 Hz, 1H), 3.35 (ddd, *J* = 18.1, 10.8, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7 (d, $J_{C\text{-}P}$=13.1 Hz), 163.20 (dd, $J_{C\text{-}P}$=249.5 Hz , $J_{C\text{-}P}$=3.0 Hz), 133.6, 132.2 (d, $J_{C\text{-}P}$=3.0 Hz), 131.8, 131.7 (d, $J_{C\text{-}P}$=3.0 Hz), 131.5, 131.4 (d, $J_{C\text{-}P}$=2.0 Hz), 131.4, 131.3, 131.0, 130.9, 129.2 (d, $J_{C\text{-}P}$=12.1 Hz), 128.7, 128.3 (d, $J_{C\text{-}P}$=12.1 Hz), 128.2, 115.5 (d, $J_{C\text{-}P}$=2.0 Hz), 115.3 (d, $J_{C\text{-}P}$=2.0 Hz), 40.4 (d, $J_{C\text{-}P}$=69.7 Hz), 39.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.12.

3-(4-Chlorophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (**3g**):[S12] 69% yield, 92 mg, white solid, melting points: 256.5 °C-256.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.86 – 7.80 (m, 2H), 7.57 – 7.45 (m, 6H), 7.42 – 7.25 (m, 7H), 7.15 – 7.10 (m, 2H), 4.44 (ddd, *J* = 10.6, 6.8, 2.4 Hz, 1H), 3.97 (ddd, *J* = 18.2, 10.6, 4.2 Hz, 1H), 3.36 (ddd, *J* = 18.2, 10.8, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6 (d, $J_{C\text{-}P}$=13.1 Hz), 136.3, 134.7 (d, $J_{C\text{-}P}$=6.1 Hz), 133.7, 133.1 (d, $J_{C\text{-}P}$=2.0 Hz), 132.3 (d, $J_{C\text{-}P}$=3.0 Hz), 132.0, 131.8 (d, $J_{C\text{-}P}$=3.0 Hz), 131.4, 131.3 (d, $J_{C\text{-}P}$=2.0 Hz), 131.2, 131.0 (d, $J_{C\text{-}P}$=9.1 Hz), 130.8, 129.1 (d, $J_{C\text{-}P}$=11.1 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$=2.0 Hz), 128.4 (d, $J_{C\text{-}P}$=12.1 Hz), 128.2, 40.6 (d, $J_{C\text{-}P}$=69.7 Hz), 39.1; ^{31}P NMR (162 MHz, $CDCl_{3)}$ δ 33.82.

3-(4-Bromophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (**3h**):[S12] 63% yield, 92 mg, white solid, melting points: 257.3 °C-258.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.86 – 7.80 (m, 2H), 7.57 – 7.45 (m, 6H), 7.42 – 7.25 (m, 7H), 7.15 – 7.10 (m, 2H), 4.44 (ddd, *J* = 10.6, 6.8, 2.4 Hz, 1H), 3.97 (ddd, *J* = 18.2, 10.6, 4.2 Hz, 1H), 3.36 (ddd, *J* = 18.2, 10.8, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5 (d, $J_{C\text{-}P}$=13.1 Hz), 136.3, 135.3 (d, $J_{C\text{-}P}$=5.5 Hz), 133.6, 132.3 (d, $J_{C\text{-}P}$=2.0 Hz), 131.8 (d, $J_{C\text{-}P}$=3.0 Hz), 131.6, 131.5 (d, $J_{C\text{-}P}$=3.0 Hz), 131.3 (d, $J_{C\text{-}P}$=8.1 Hz), 131.0, 130.9, 129.2 (d, $J_{C\text{-}P}$=11.2 Hz), 128.7, 128.4 (d, $J_{C\text{-}P}$=12.1 Hz), 128.2, 40.6 (d, $J_{C\text{-}P}$=68.7 Hz), 39.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.68.

3-(Diphenylphosphoryl)-1-(4-ethylphenyl)-3-phenylpropan-1-one (**3i**):[S13] 86% yield, 113 mg, white solid, melting points: 198.2 °C-198.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.86 – 7.81 (m, 2H), 7.56 – 7.42 (m, 6H), 7.40 – 7.31 (m, 3H), 7.30 – 7.21 (m, 4H), 6.97 (d, *J* = 7.9 Hz, 2H), 4.46 (ddd, *J* = 9.7, 6.9, 2.4 Hz, 1H), 4.00 (ddd, *J* = 18.1, 10.3, 4.3 Hz, 1H), 3.37 (ddd, *J* = 18.2, 11.3, 2.4 Hz, 1H), 2.55 – 2.46 (m, 2H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7 (d, $J_{C\text{-}P}$=13.1 Hz), 143.0 (d, $J_{C\text{-}P}$=3.0 Hz), 136.4, 133.3, 132.9 (d, $J_{C\text{-}P}$=6.1 Hz), 132.3, 131.94 (d, $J_{C\text{-}P}$=2.0 Hz), 131.3 (d, $J_{C\text{-}P}$=8.1 Hz), 131.0 (d, $J_{C\text{-}P}$=11.1 Hz), 129.7 (d, $J_{C\text{-}P}$=6.0 Hz), 128.9, 128.8, 128.5, 128.1 (d, $J_{C\text{-}P}$=3.0 Hz), 128.0, 127.8(d, $J_{C\text{-}P}$=2.0 Hz), 40.9 (d, $J_{C\text{-}P}$=69.7 Hz), 39.0, 28.4, 15.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.43.

3-(Diphenylphosphoryl)-1-(4-fluorophenyl)-3-phenylpropan-1-one (**3j**):[S12] 82% yield, 105 mg, white solid, melting points: 225.1 °C-225.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 10.2, 6.3, 2.3 Hz, 2H), 7.92 – 7.82 (m, 2H), 7.56 – 7.41 (m, 5H), 7.40 – 7.30 (m, 3H), 7.28 – 7.20 (m, 2H), 7.13 (dt, *J* = 13.3, 6.5 Hz, 3H), 7.03 (t, *J* = 8.5 Hz, 2H), 4.45 (ddd, *J* = 9.9, 6.9, 2.5 Hz, 1H), 3.98 (ddd, *J* = 18.0, 10.3, 4.6 Hz, 1H), 3.36 (ddd, *J* = 18.0, 11.1, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3(d, $J_{C\text{-}P}$=14.1 Hz), 167.2 (d, $J_{C\text{-}F}$=256.5 Hz), 135.9 (d, $J_{C\text{-}P}$=6.0 Hz), 132.9 (d, $J_{C\text{-}P}$=3.0 Hz), 132.2 (d, $J_{C\text{-}P}$=3.0 Hz), 131.9, 131.6 (d, $J_{C\text{-}P}$=3.0 Hz), 131.4, 131.3, 131.1, 131.0, 130.9, 130.8, 129.9 (d, $J_{C\text{-}P}$=5.1 Hz), 129.1 (d, $J_{C\text{-}P}$=11.1 Hz), 128.4 (d, $J_{C\text{-}P}$=2.0 Hz), 128.2 (d, $J_{C\text{-}P}$=9.1 Hz), 127.2 (d, $J_{C\text{-}P}$=3.0 Hz), 115.8 (d, $J_{C\text{-}F}$=22.2 Hz), 41.2 (d, $J_{C\text{-}P}$=69.7 Hz), 39.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.22.

1-(4-Chlorophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (**3k**):[S12] 69% yield, 92 mg, white solid, melting points: 238.2 °C-239.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.79 – 7.74 (m, 2H), 7.52 (td, *J* = 4.3, 3.7, 2.1 Hz, 3H), 7.45 (ddd, *J* = 11.3, 7.5, 1.4 Hz, 2H), 7.35 (ddd, *J* = 11.7, 7.1, 2.5 Hz, 5H), 7.28 – 7.21 (m, 2H), 7.18 – 7.06 (m, 3H), 4.44 (ddd, *J* = 9.9, 6.9, 2.6 Hz, 1H), 3.96 (ddd, *J* = 18.1,

10.3, 4.7 Hz, 1H), 3.36 (ddd, *J* = 18.1, 11.0, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7(d, J_{C-P}=13.1 Hz), 140.0, 135.9 (d, J_{C-P}=5.0 Hz), 134.8, 132.2 (d, J_{C-P}=2.0 Hz), 131.6 (d, J_{C-P}=3.0 Hz), 131.4 (d, J_{C-P}=8.1 Hz), 131.1 (d, J_{C-P}=9.1 Hz), 129.9 (d, J_{C-P}=6.1 Hz), 129.6, 129.1, 129.0 (d, J_{C-P}=5.1 Hz), 128.5 (d, J_{C-P}=2.0 Hz), 128.3, 128.1, 127.3 (d, J_{C-P}=2.0 Hz), 41.6 (d, J_{C-P}=69.7 Hz), 39.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.15.

1-(4-Bromophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (**3l**):[S12] 67% yield, 98 mg, white solid, melting points: 227.1 °C-227.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.72 – 7.66 (m, 2H), 7.52 (ddd, *J* = 8.5, 4.9, 1.8 Hz, 5H), 7.45 (ddd, *J* = 11.3, 5.3, 3.2 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.27 – 7.22 (m, 2H), 7.13 (dt, *J* = 12.8, 6.8 Hz, 3H), 4.43 (ddd, *J* = 9.9, 6.9, 2.6 Hz, 1H), 3.96 (ddd, *J* = 18.0, 10.3, 4.6 Hz, 1H), 3.41 – 3.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9 (d, J_{C-P}=14.1 Hz), 135.9 (d, J_{C-P}=5.1 Hz), 135.2, 133.5 , 132.1 (d, J_{C-P}=12.1 Hz), 132.0, 131.6 (d, J_{C-P}=3.0 Hz), 131.4 (d, J_{C-P}=8.1 Hz), 131.1 (d, J_{C-P}=9.1 Hz), 129.9 (d, J_{C-P}=5.1 Hz), 129.7, 129.1 (d, J_{C-P}=11.1 Hz), 128.7 (d, J_{C-P}=7.1 Hz), 128.5 (d, J_{C-P}=2.0 Hz), 128.3, 128.2, 127.3 (d, J_{C-P}=3.0 Hz), 41.2 (d, J_{C-P}=68.7 Hz), 39.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.16.

3-(Diphenylphosphoryl)-1,3-bis(4-ethylphenyl)propan-1-one (**3m**): 44% yield, 61 mg, white solid, melting points: 200.7 °C-201.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.81 – 7.74 (m, 2H), 7.55 – 7.42 (m, 5H), 7.37 – 7.31 (m, 1H), 7.30 – 7.21 (m, 4H), 7.21 – 7.17 (m, 2H), 7.01 – 6.94 (m, 2H), 4.46 (ddd, *J* = 10.5, 6.9, 2.4 Hz, 1H), 3.99 (ddd, *J* = 18.1, 10.4, 4.2 Hz, 1H), 3.33 (ddd, *J* = 18.1, 11.3, 2.4 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.54 – 2.46 (m, 2H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5 (d, J_{C-P}=13.1 Hz), 150.5, 143.0 (d, J_{C-P}=3.0 Hz), 134.3, 133.1 (d, J_{C-P}=6.1 Hz), 132.5, 132.2, 132.0 (d, J_{C-P}=3.0 Hz), 131.4 (d, J_{C-P}=12.1 Hz), 131.1 (d, J_{C-P}=8.1 Hz), 129.9 (d, J_{C-P}=5.1 Hz), 129.0 (d, J_{C-P}=9.1 Hz), 128.5, 128.2 (d, J_{C-P}=4.0 Hz), 128.1, 127.9 (d, J_{C-P}=2.0 Hz), 40.6 (d, J_{C-P}=168.7 Hz), 39.0, 29.0, 28.5, 15.5, 15.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.57; HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{31}H_{31}O_2PNa^+$ 489.1954, found 489.1958.

1,3-Bis(4-chlorophenyl)-3-(diphenylphosphoryl)propan-1-one (**3n**): 47% yield, 67 mg, white solid, melting points: 243.9 °C-244.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dtt, *J* = 10.7, 4.8, 2.0 Hz, 2H), 7.87 – 7.80 (m, 1H), 7.71 – 7.64 (m, 1H), 7.56 – 7.42 (m, 7H), 7.35 (dddd, *J* = 13.6, 8.0, 4.7, 1.6 Hz, 4H), 7.26 – 7.20 (m, 2H), 7.13 (q, *J* = 6.1, 5.5 Hz, 3H), 4.45 (dddd, *J* = 17.3, 10.0, 6.9, 2.6 Hz, 1H), 3.97 (dddd, *J* = 28.4, 18.0, 10.3, 4.7 Hz, 1H), 3.46 – 3.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5 (d, J_{C-P}=14.1 Hz), 140.2, 134.6 (d, J_{C-P}=2.0 Hz), 134.5, 133.2 (d, J_{C-P}=3.0 Hz), 132.3 (d, J_{C-P}=3.0 Hz), 131.8 (d, J_{C-P}=3.0 Hz), 131.6, 131.3 (d, J_{C-P}=8.1 Hz), 131.2 (d, J_{C-P}=6.1 Hz), 131.0 (d, J_{C-P}=3.0 Hz), 130.7 (d, J_{C-P}=14.1 Hz), 129.6, 129.2 (d, J_{C-P}=11.1 Hz), 129.0, 128.7 (d, J_{C-P}=2.0 Hz), 128.5, 128.4, 40.6 (d, J_{C-P}=68.7 Hz), 39.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.78; HRMS (ESI) Calcd. for $C_{27}H_{21}Cl_2O_2P$ $[M+Na]^+$ 501.0548, found 501.0543.

3-(diphenylphosphoryl)-4,4-dimethyl-1-phenylpentan-1-one (3o): 69% yield, 80 mg, white solid, melting points: 203.9 °C-204.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 2H), 7.78 – 7.69 (m, 4H), 7.50 – 7.44 (m, 4H), 7.38 – 7.31 (m, 2H), 7.24 – 7.12 (m, 3H), 3.59 (dt, J = 6.9, 4.8 Hz, 1H), 3.41 – 3.14 (m, 2H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8 (d, J_{C-P}=7.1 Hz), 136.1, 133.1, 131.2 (d, J_{C-P}=2.0 Hz), 131.0 (d, J_{C-P}=2.0 Hz), 130.8, 130.7, 128.5 (d, J_{C-P}=11.1 Hz), 128.37 , 128.3 (d, J_{C-P}=11.1 Hz), 127.8, 40.8 (d, J_{C-P}=71.7 Hz), 35.7 (dd, J_{C-P}=9.1 Hz, J_{C-P}=2.0 Hz), 29.8 (d, J_{C-P}=6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.06. HRMS (ESI) Calcd. for $C_{25}H_{27}O_2P$ $[M+H]^+$ 391.1821, found 391.1822.

4-(diphenylphosphoryl)-4-phenylbutan-2-one (3p): 23% yield, 24 mg, white solid, melting points: 173.7 °C-174.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (ddt, *J* = 10.8, 6.4, 1.7 Hz, 2H), 7.59 – 7.49 (m, 3H), 7.44 (ddd, *J* = 11.3, 8.3, 1.4 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.23 (ddd, *J* = 8.5, 6.8, 3.0 Hz, 2H), 7.19 – 7.08 (m, 3H), 4.22 (ddd, *J* = 10.2, 7.3, 3.0 Hz, 1H), 3.32 (ddd, *J* = 17.9, 10.1, 5.4 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 205.33 (d, J_{C-P}=13.0 Hz), 132.0 (d, J_{C-P}=3.0 Hz), 131.4 (d, J_{C-P}=3.0 Hz), 131.4, 131.3, 131.0 (d, J_{C-P}=9.0 Hz), 129.7 (d, J_{C-P}=6.0 Hz), 128.9 (d, J_{C-P}=11.0

Hz), 128.3 (d, $J_{C\text{-}P}$=2.0 Hz), 128.06 (d, $J_{C\text{-}P}$=12.0 Hz), 127.1 (d, $J_{C\text{-}P}$=2.0 Hz), 43.6, 41.1 (d, $J_{C\text{-}P}$=69.0 Hz), 30.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.68. HRMS (ESI) Calcd. for $C_{22}H_{23}O_2P$ $[M+H]^+$ 351.1508, found 351.1516.

3-(Di-3-tolylphosphoryl)-1,3-diphenylpropan-1-one (**3r**): 64% yield, 84 mg, white solid, melting points: 165.5°C-166.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 3H), 7.77 – 7.69 (m, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.42 – 7.31 (m, 6H), 7.27 – 7.21 (m, 2H), 7.20 – 7.07 (m, 5H), 4.44 (ddd, *J* = 9.8, 6.8, 2.5 Hz, 1H), 4.01 (ddd, *J* = 18.1, 10.4, 4.5 Hz, 1H), 3.40 (dd, *J* = 11.0, 2.5 Hz, 1H), 2.39 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7(d, $J_{C\text{-}P}$=13.1 Hz), 139.0 (d, $J_{C\text{-}P}$=11.1 Hz), 137.9 (d, $J_{C\text{-}P}$=11.1 Hz), 136.4, 136.1 (d, $J_{C\text{-}P}$=5.1 Hz), 133.4, 132.8 (d, $J_{C\text{-}P}$=3.0 Hz), 132.2 (d, $J_{C\text{-}P}$=3.0 Hz), 132.0 (d, $J_{C\text{-}P}$=8.1 Hz), 131.8 (d, $J_{C\text{-}P}$=8.1 Hz), 129.9 (d, $J_{C\text{-}P}$=5.1 Hz), 128.8 (d, $J_{C\text{-}P}$=12.1 Hz), 128.6, 128.3 (d, $J_{C\text{-}P}$=2.0 Hz), 128.1, 127.9 (d, $J_{C\text{-}P}$=2.0 Hz), 127.0 (d, $J_{C\text{-}P}$=3.0 Hz), 41.1 (d, $J_{C\text{-}P}$=68.7 Hz), 39.0, 21.5, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.78; HRMS (ESI) Calcd. for $C_{29}H_{21}O_2PH$ $[M+H]^+$ 439.1821, found 439.1824.

3-(Bis(4-ethylphenyl)phosphoryl)-1,3-diphenylpropan-1-one (**3s**): 88% yield, 123 mg, white solid, melting points: 215.3°C- 215.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 4H), 7.51 – 7.46 (m, 1H), 7.42 – 7.28 (m, 8H), 7.19 – 7.07 (m, 3H), 7.04 (dd, *J* = 8.1, 2.8 Hz, 2H), 4.42 (ddd, *J* = 9.9, 7.1, 2.4 Hz, 1H), 4.00 (ddd, *J* = 18.1, 10.4, 4.2 Hz, 1H), 3.37 (ddd, *J* = 18.1, 11.1, 2.4 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H), 1.28 – 1.24 (m, 2H), 0.91 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (d, $J_{C\text{-}P}$=13.1 Hz), 142.5 (d, $J_{C\text{-}P}$=3.0 Hz), 141.8 (d, $J_{C\text{-}P}$=2.0 Hz), 136.5, 136.3 (d, $J_{C\text{-}P}$=5.1 Hz), 133.4, 131.4 (d, $J_{C\text{-}P}$=8.1 Hz), 131.1 (d, $J_{C\text{-}P}$=9.1 Hz), 130.0 (d, $J_{C\text{-}P}$=5.1 Hz), 129.8, 129.7, 129.0, 128.9, 128.6, 128.4 (d, $J_{C\text{-}P}$=2.0 Hz), 128.2, 127.1(d, $J_{C\text{-}P}$=2.0 Hz), 41.3 (d, $J_{C\text{-}P}$=9.1 Hz), 39.3, 31.7, 22.8, 21.7 (dd, $J_{C\text{-}P}$=1.0 Hz, 8.1 Hz), 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.70; HRMS (ESI) Calcd. for $C_{31}H_{31}O_2PH$ $[M+H]^+$ 467.2134, found 467.2125.

3-(Bis(4-methoxyphenyl)phosphoryl)-1,3-diphenylpropan-1-one (**3t**):[S13] 66% yield, 93 mg, white solid, melting points: 165.1 °C-165.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 4H), 7.53 – 7.47 (m, 1H), 7.41 – 7.28 (m, 6H), 7.19 – 7.10 (m, 3H), 7.03 – 6.99 (m, 2H), 6.77 – 6.72 (m, 2H), 4.37 (s, 1H), 3.99 (ddd, *J* = 18.2, 10.3, 4.4 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.40 (ddd, *J* = 18.1, 11.3, 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 (d, $J_{C\text{-}P}$=13.1 Hz), 162.6 (d, $J_{C\text{-}P}$=2.0 Hz), 162.0 (d, $J_{C\text{-}P}$=3.0 Hz), 136.5, 136.4 (d, $J_{C\text{-}P}$=5.1 Hz), 133.4, 133.3 (d, $J_{C\text{-}P}$=9.1 Hz), 133.0 (d, $J_{C\text{-}P}$=11.1 Hz), 130.0 (d, $J_{C\text{-}P}$=6.7 Hz), 128.6, 128.4 (d, $J_{C\text{-}P}$=2.0 Hz), 128.2, 127.1 (d, $J_{C\text{-}P}$=2.0 Hz), 123.8, 123.0, 122.7, 122.0, 114.6 (d, $J_{C\text{-}P}$=12.1 Hz), 113.7 (d, $J_{C\text{-}P}$=12.1 Hz), 55.4 (d, $J_{C\text{-}P}$=13.1 Hz), 42.0, 41.3, 39.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.84.

3-(Bis(4-fluorophenyl)phosphoryl)-1,3-diphenylpropan-1-one (**3u**):[S13] 65% yield, 87 mg, white solid, melting points: 204.5 °C-205.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.87 – 7.82 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.34 (m, 6H), 7.26 – 7.10 (m, 5H), 6.94 (td, *J* = 8.7, 2.2 Hz, 2H), 4.44 (ddd, *J* = 9.7, 6.8, 2.6 Hz, 1H), 3.98 (ddd, *J* = 18.2, 9.9, 4.9 Hz, 1H), 3.39 (ddd, *J* = 18.2, 11.9, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5(d, $J_{C\text{-}P}$=13.1 Hz), 165.0 (d, $J_{C\text{-}F}$=254.5 Hz, $J_{C\text{-}P}$=50.5 Hz), 136.3, 135.8 (d, $J_{C\text{-}P}$=6.1 Hz), 134.0, 133.9, 133.8, 133.6, 133.5 (d, $J_{C\text{-}P}$=1.0 Hz), 133.4, 129.9 (d, $J_{C\text{-}P}$=5.1 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$=2.0 Hz), 128.2, 127.4 (d, $J_{C\text{-}P}$=2.0 Hz), 116.8, 116.6, 116.6, 116.4, 115.9, 115.7, 115.6, 115.5, 41.4 (d, $J_{C\text{-}P}$=70.7 Hz), 39.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.45.

3-Butyl(phenyl)phosphoryl)-1,3-diphenylpropan-1-one (**3v**): 34% yield, 40 mg, white solid, melting points: 198.6 °C-199.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 4H), 7.56 – 7.46 (m, 6H), 7.35 (td, *J* = 7.9, 6.5 Hz, 4H), 7.28 (q, *J* = 1.5 Hz, 1H), 4.01 – 3.83 (m, 2H), 3.19 (ddd, *J* = 17.7, 10.5, 2.2 Hz, 1H), 1.66 (dddd, *J* = 11.9, 9.9, 6.2, 3.5 Hz, 2H), 1.37 – 1.23 (m, 2H), 1.19 – 1.14 (m, 2H), 0.71 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9(d, $J_{C\text{-}P}$=13.1 Hz), 136.5, 133.4, 132.0, 131.1 (d, $J_{C\text{-}P}$=9.1 Hz), 129.6 (d, $J_{C\text{-}P}$=6.1 Hz), 129.0 (d, $J_{C\text{-}P}$=2.0 Hz), 128.9, 128.7, 128.2, 127.6, 42.2 (d, $J_{C\text{-}P}$=66.7 Hz), 38.72, 28.3 (d, $J_{C\text{-}P}$=70.7 Hz), 24.1 (d, $J_{C\text{-}P}$=15.2 Hz), 23.4(d, $J_{C\text{-}P}$=4.0 Hz), 13.61. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{25}H_{27}O_2PNa^+$ 413.1641, found 413.1637.

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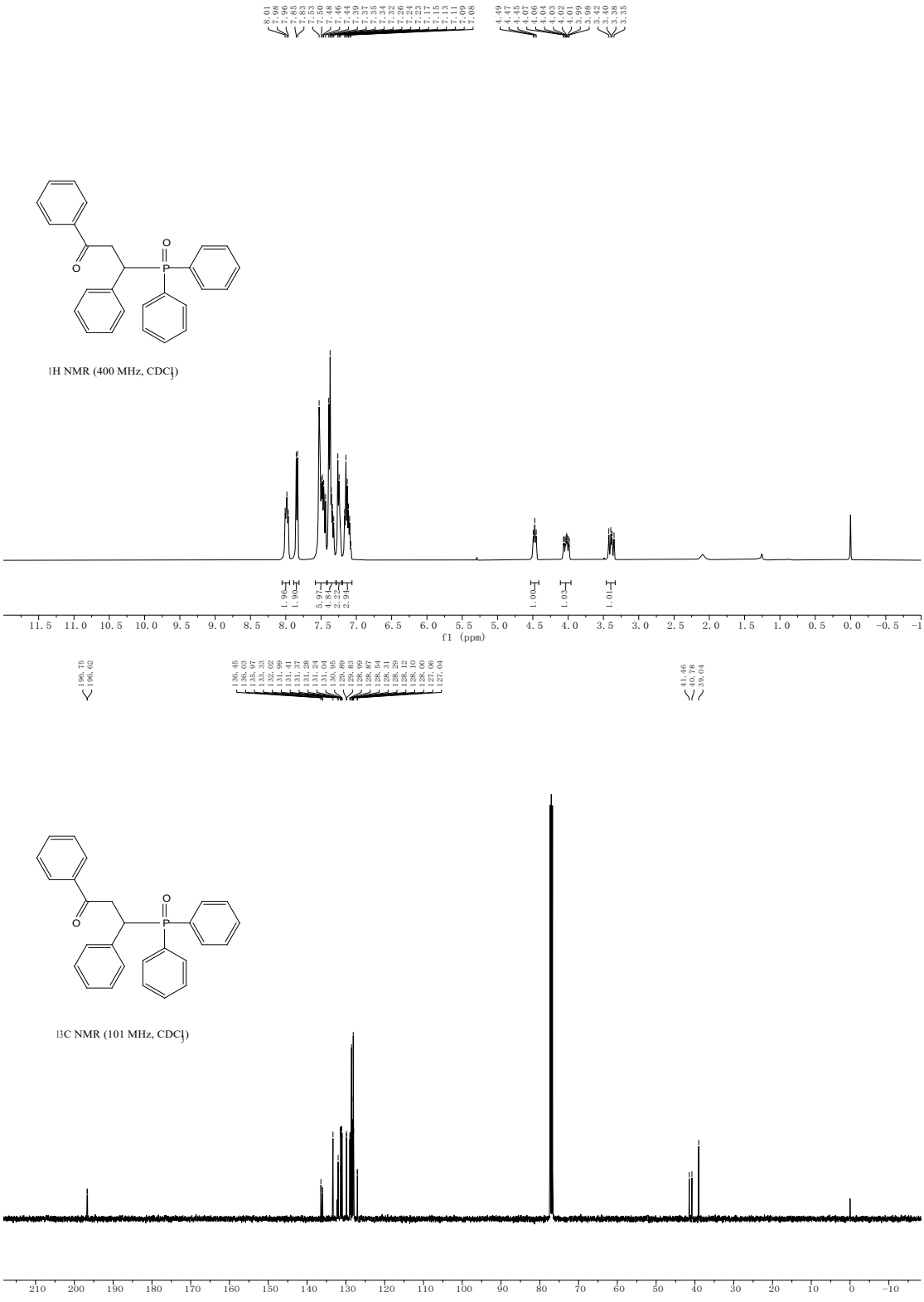
6. The NMR Spectra of the Products



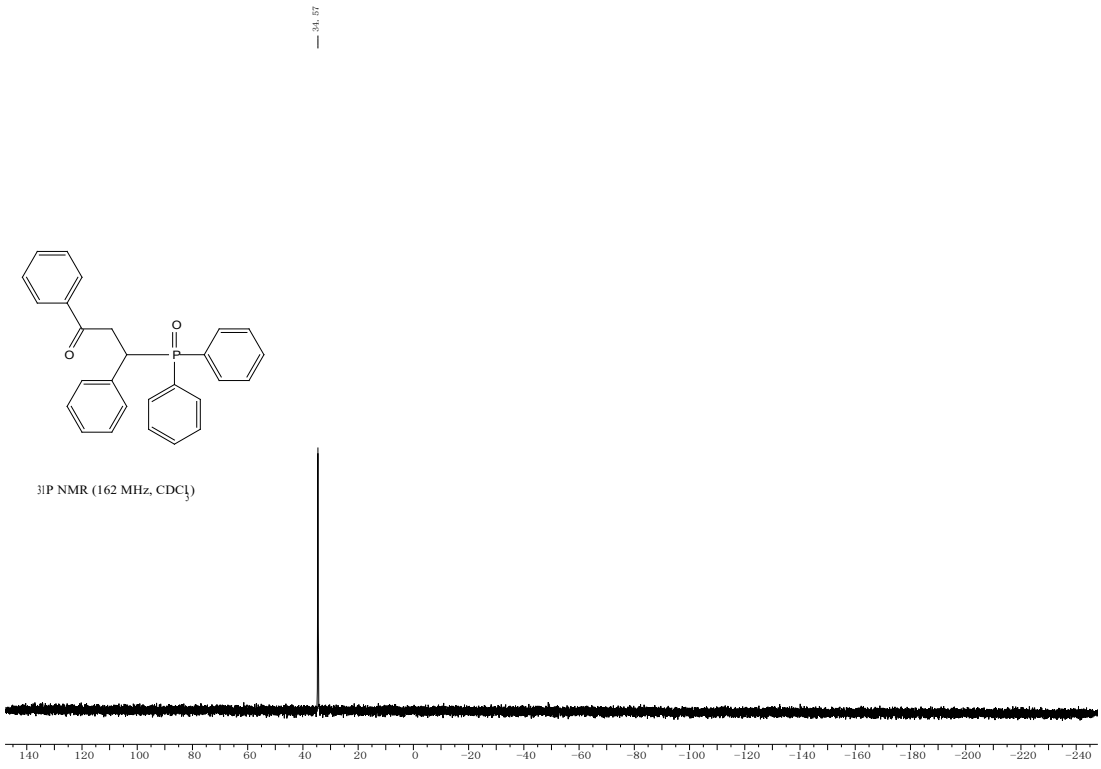
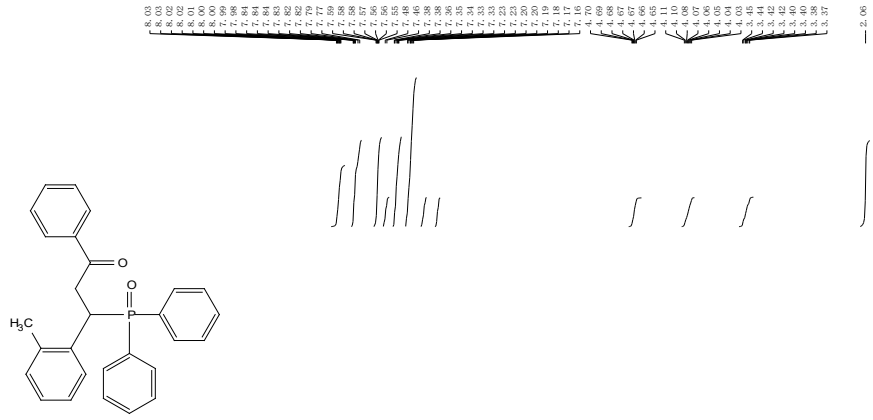
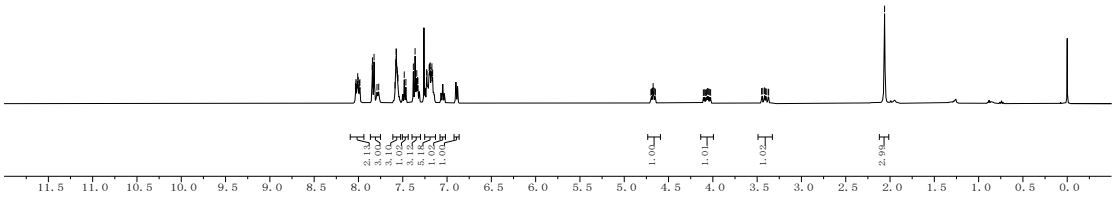
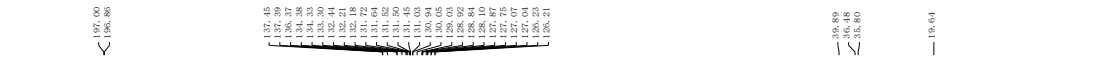


Figure S4. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3a**.

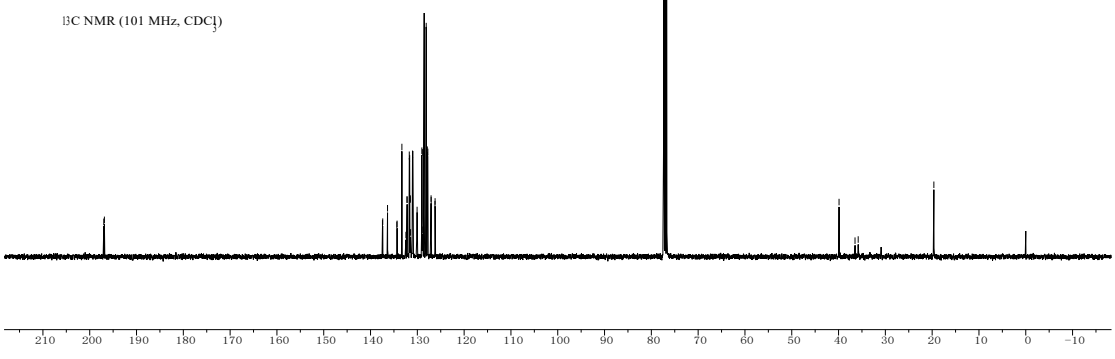


^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (101 MHz, $CDCl_3$)



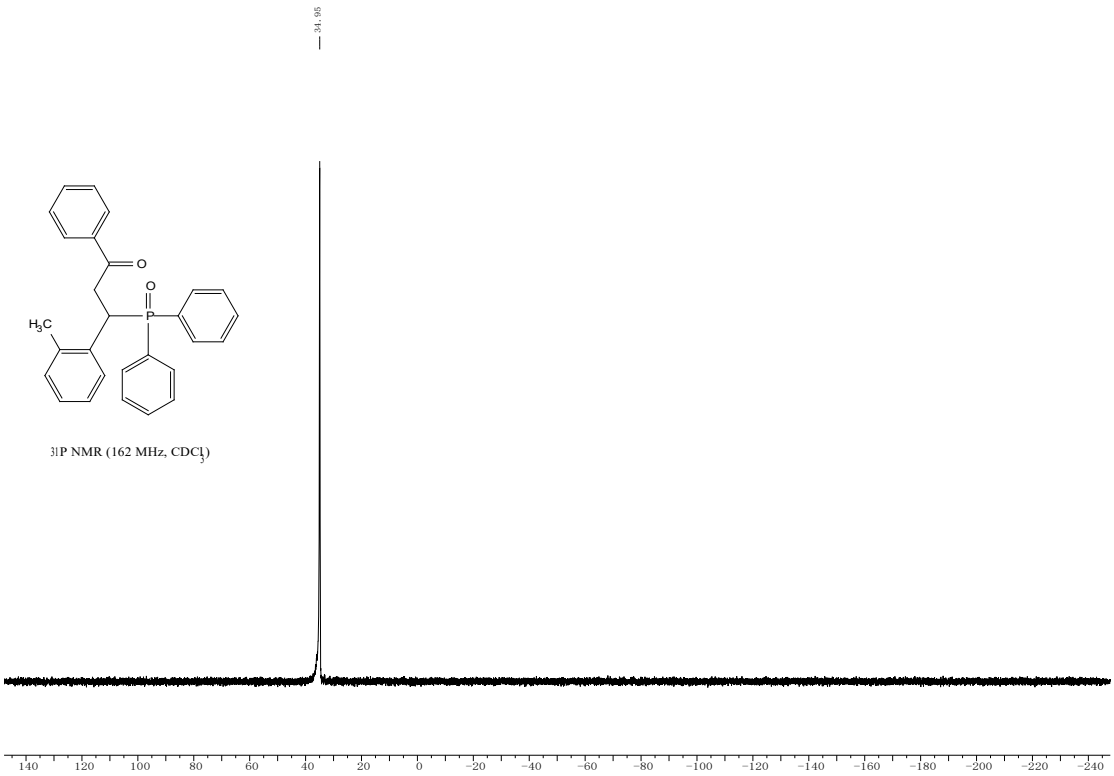
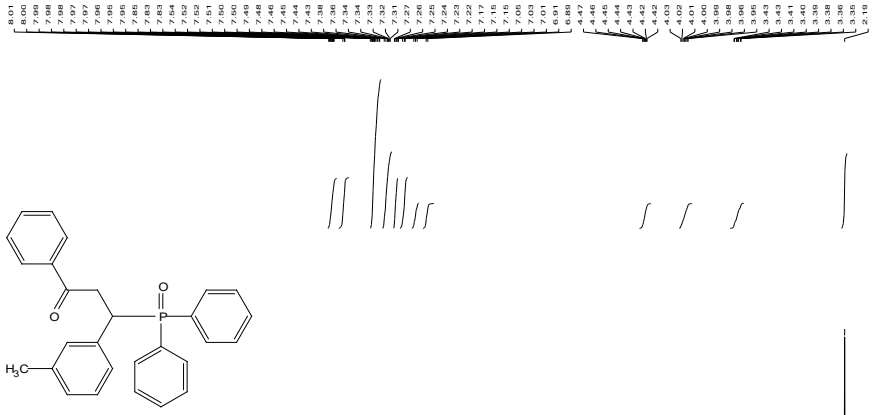
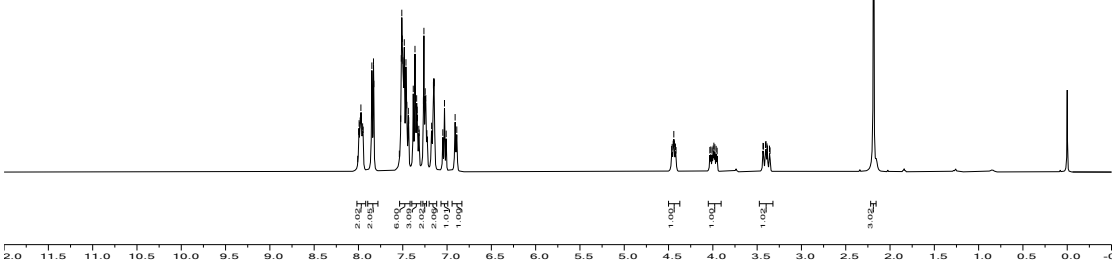
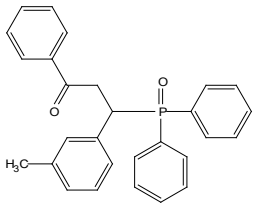


Figure S5. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3b**.

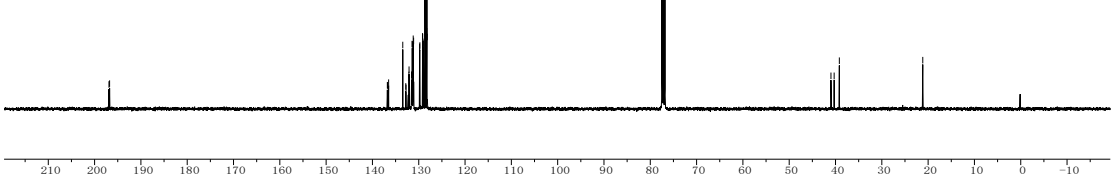


1H NMR (400 MHz, $CDCl_3$)





13C NMR (101 MHz, $CDCl_3$)



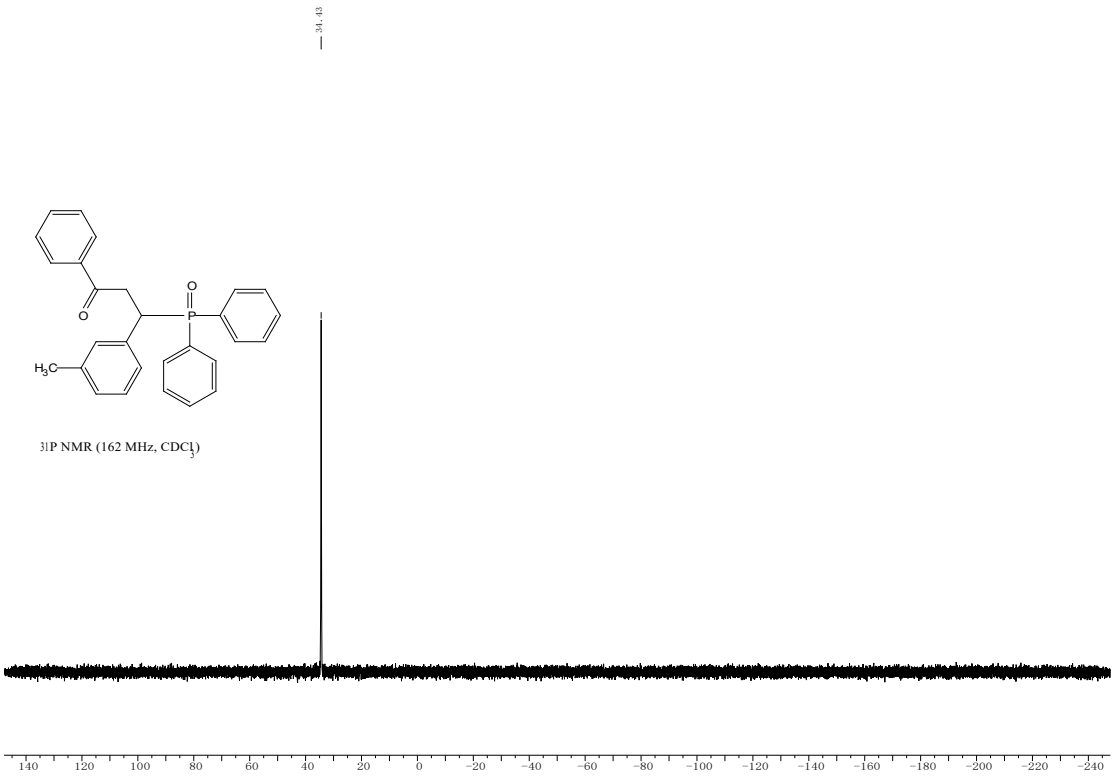
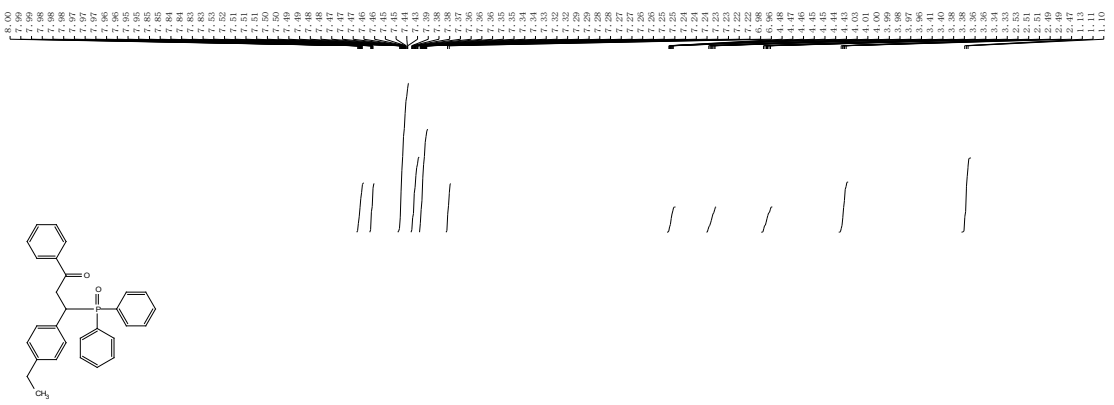
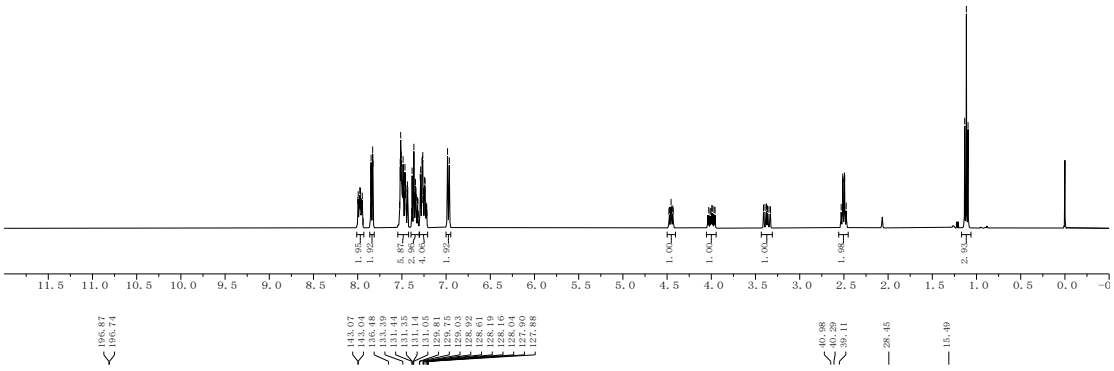
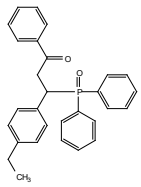


Figure S6. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3c**.



1H NMR (400 MHz, $CDCl_3$)





13C NMR (101 MHz, $CDCl_3$)

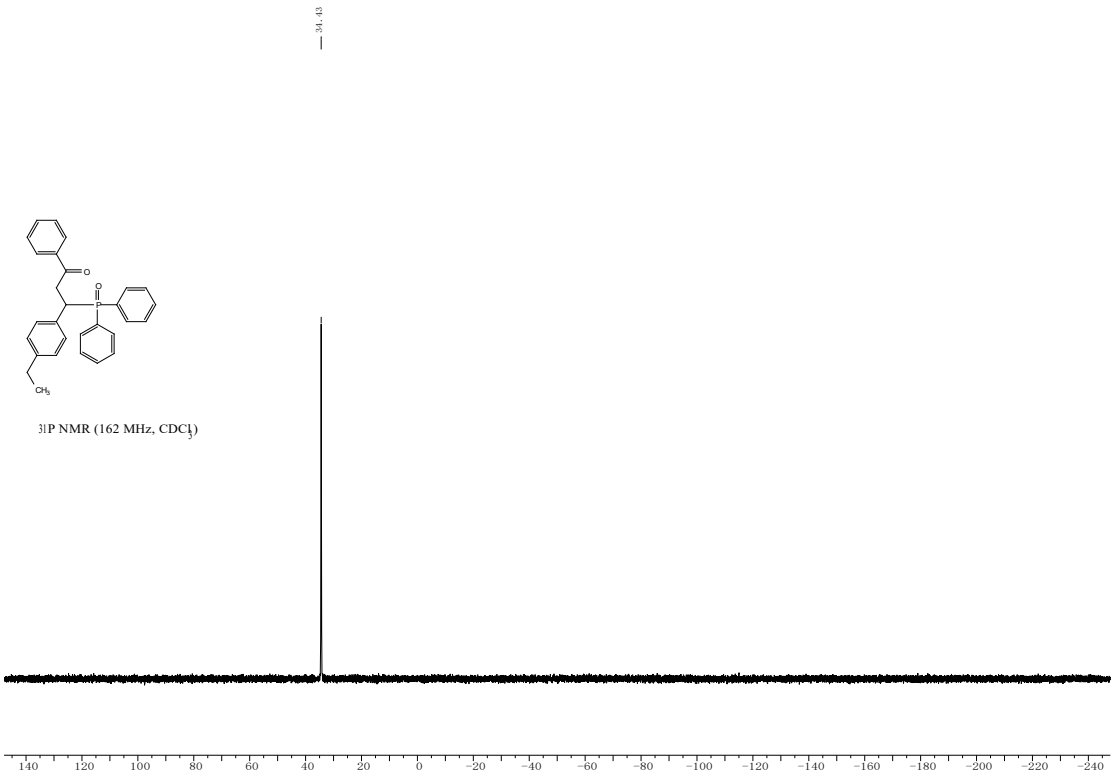
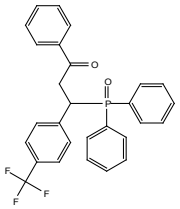
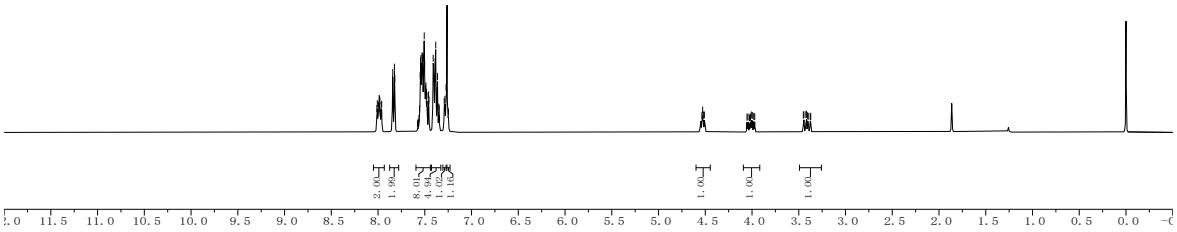
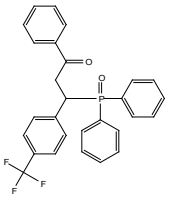


Figure S7. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3d**.



1H NMR (400 MHz, $CDCl_3$)





13C NMR (101 MHz, $CDCl_3$)

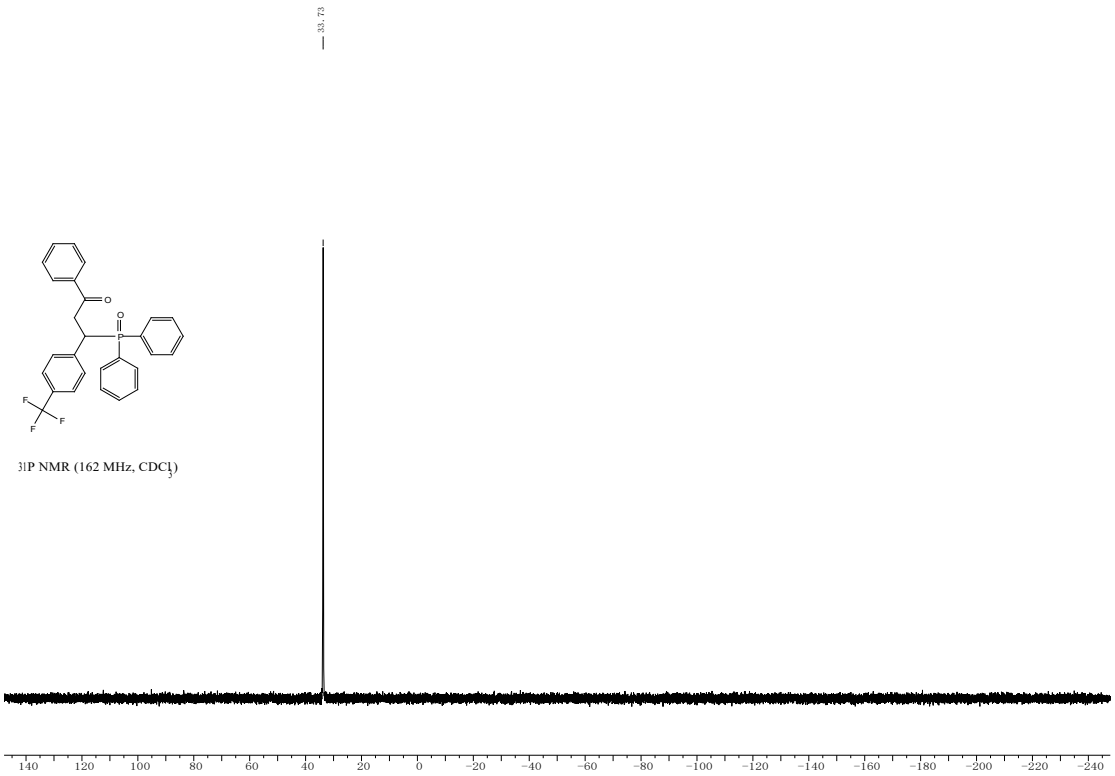
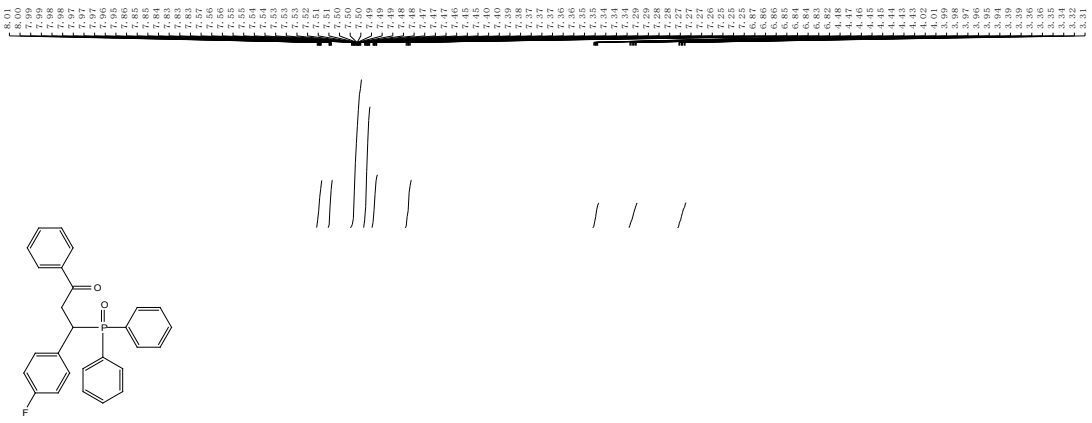
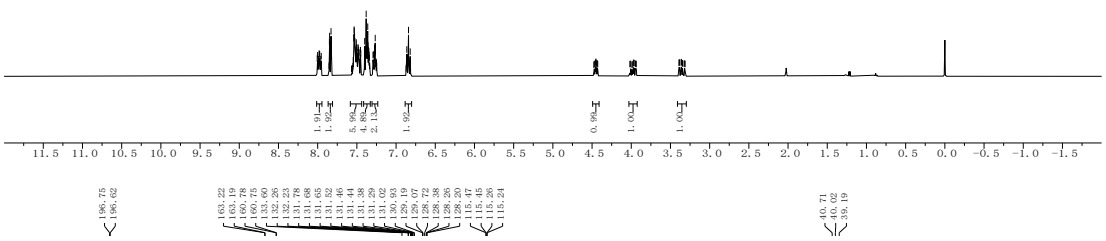
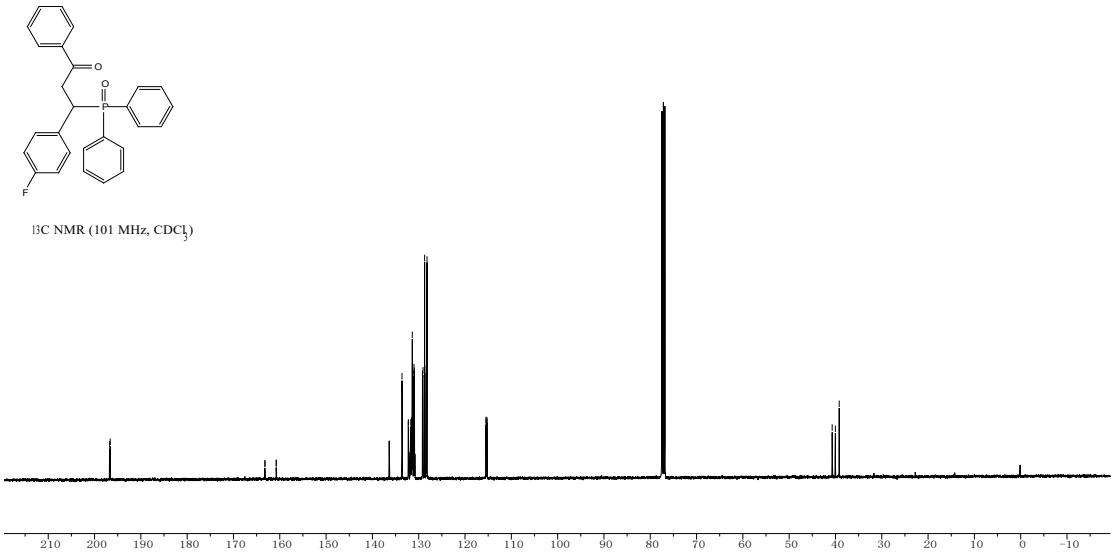


Figure S8. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3e**.



^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (101 MHz, $CDCl_3$)

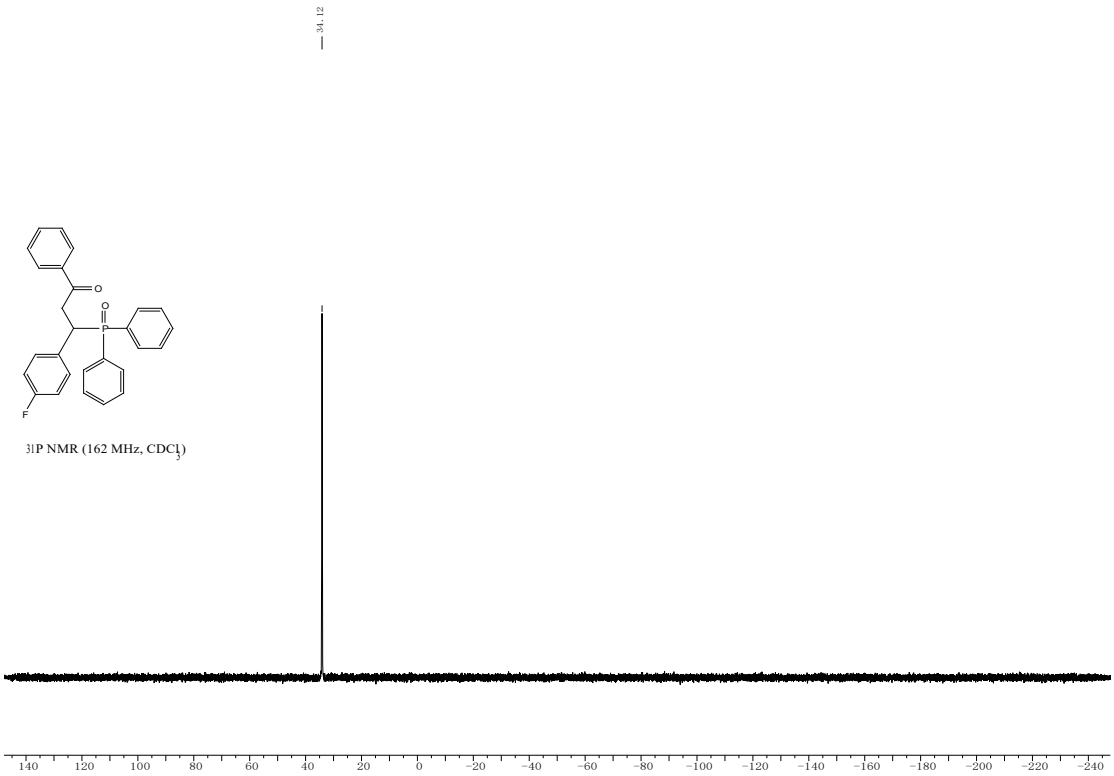
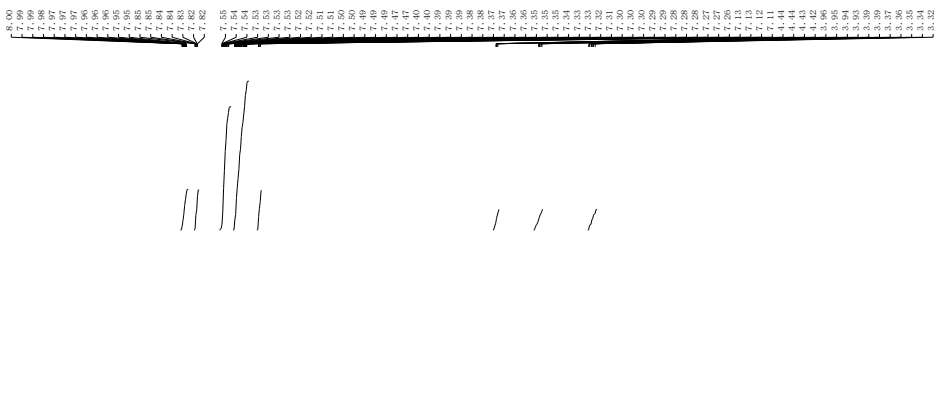
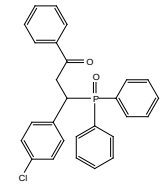
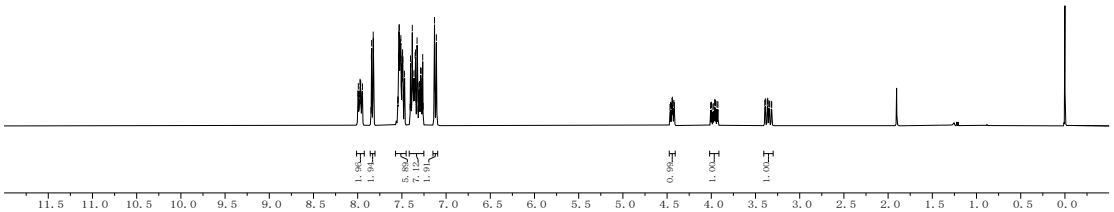


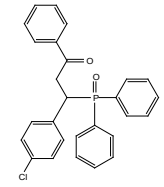
Figure S9. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3f**.



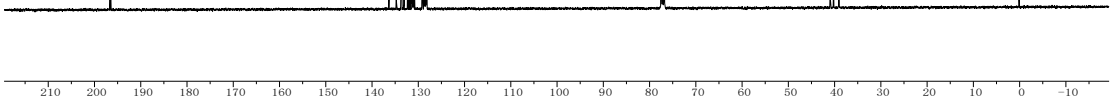


1H NMR (400 MHz, $CDCl_3$)





13C NMR (101 MHz, $CDCl_3$)



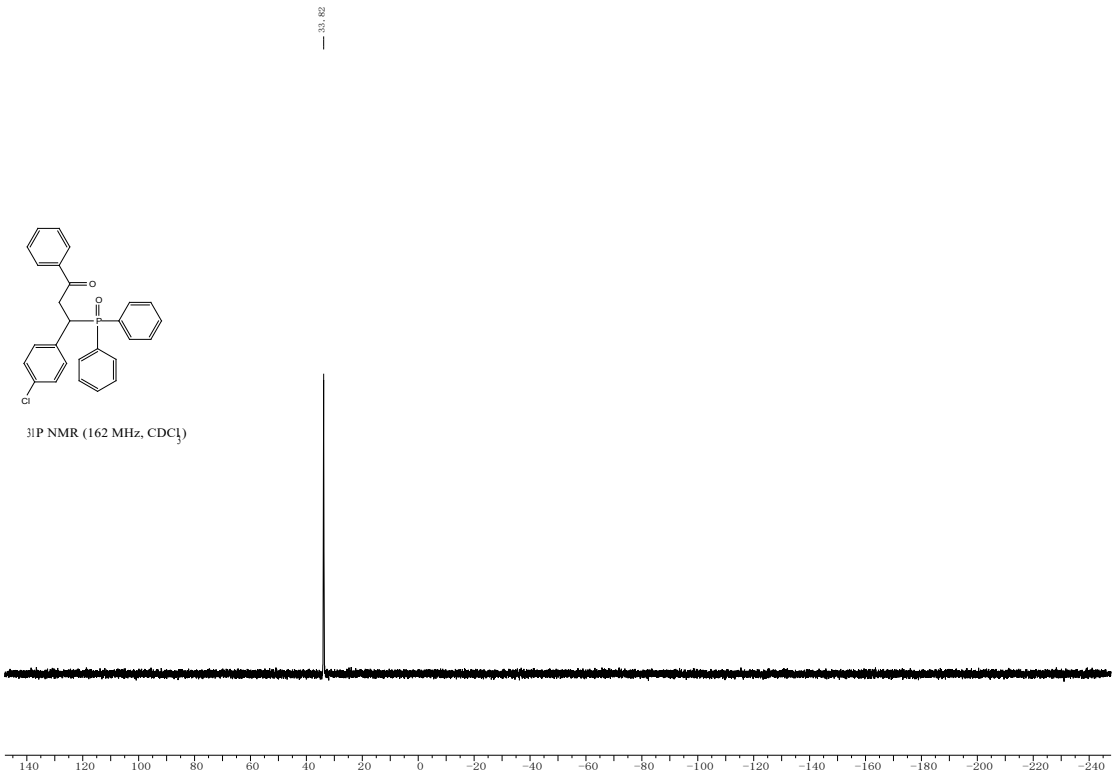
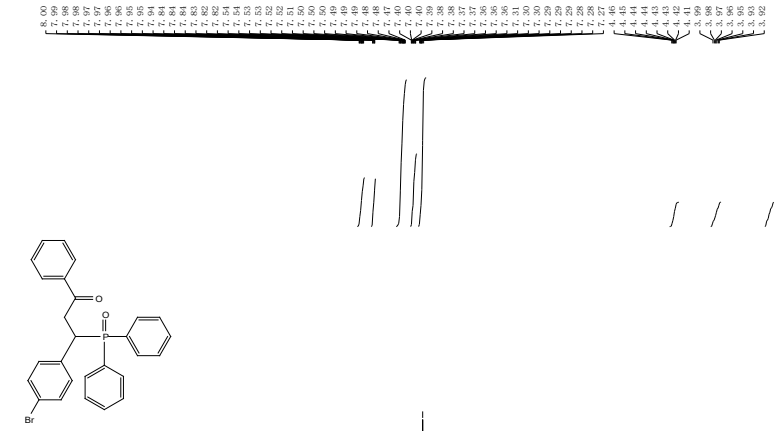


Figure S10. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3g**.



1H NMR (400 MHz, $CDCl_3$)

13C NMR (101 MHz, $CDCl_3$)

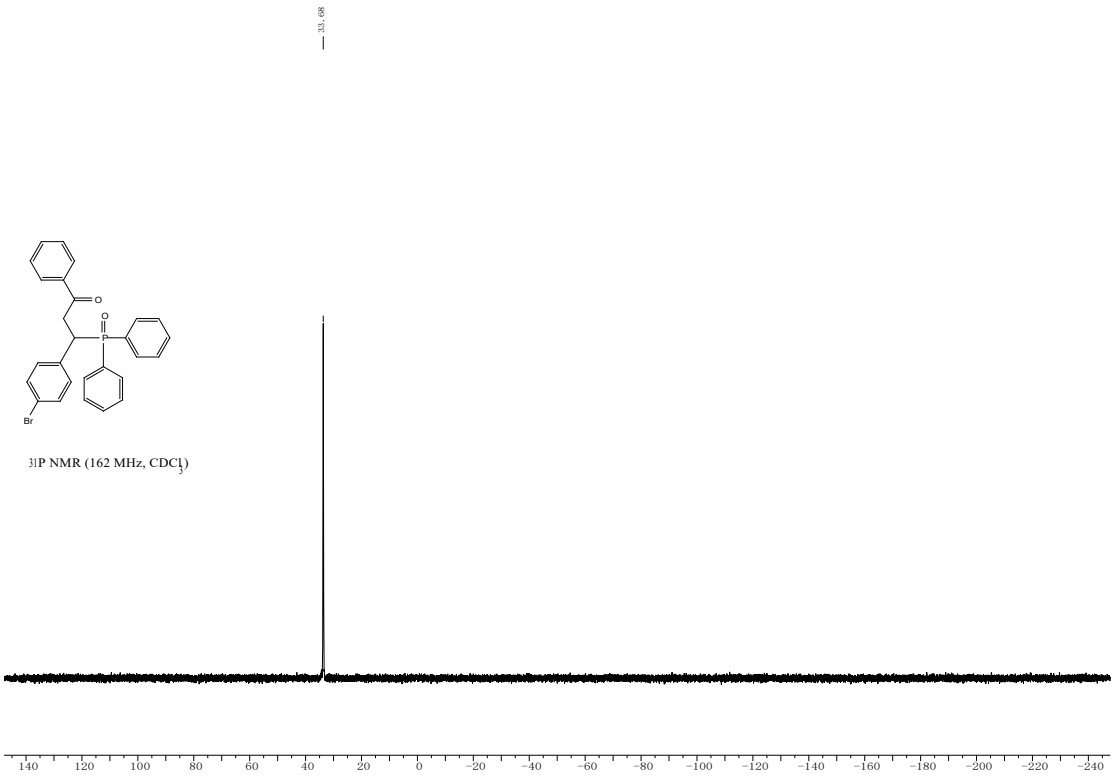
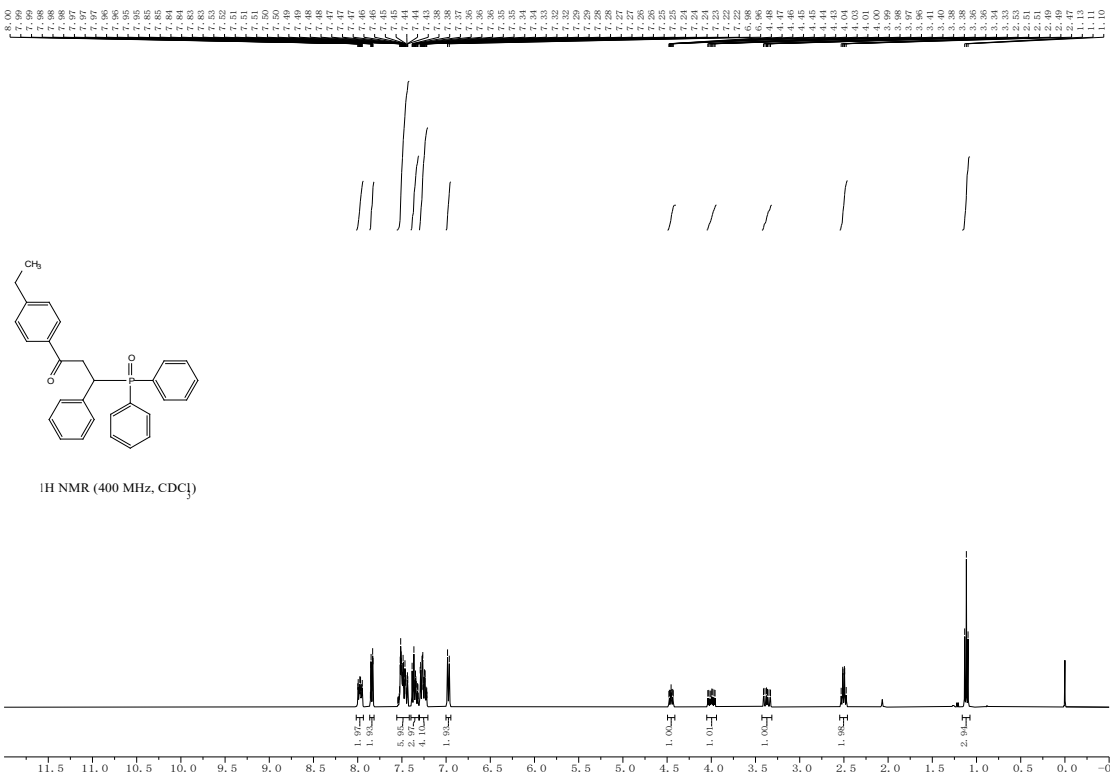


Figure S11. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3h**.



^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$)

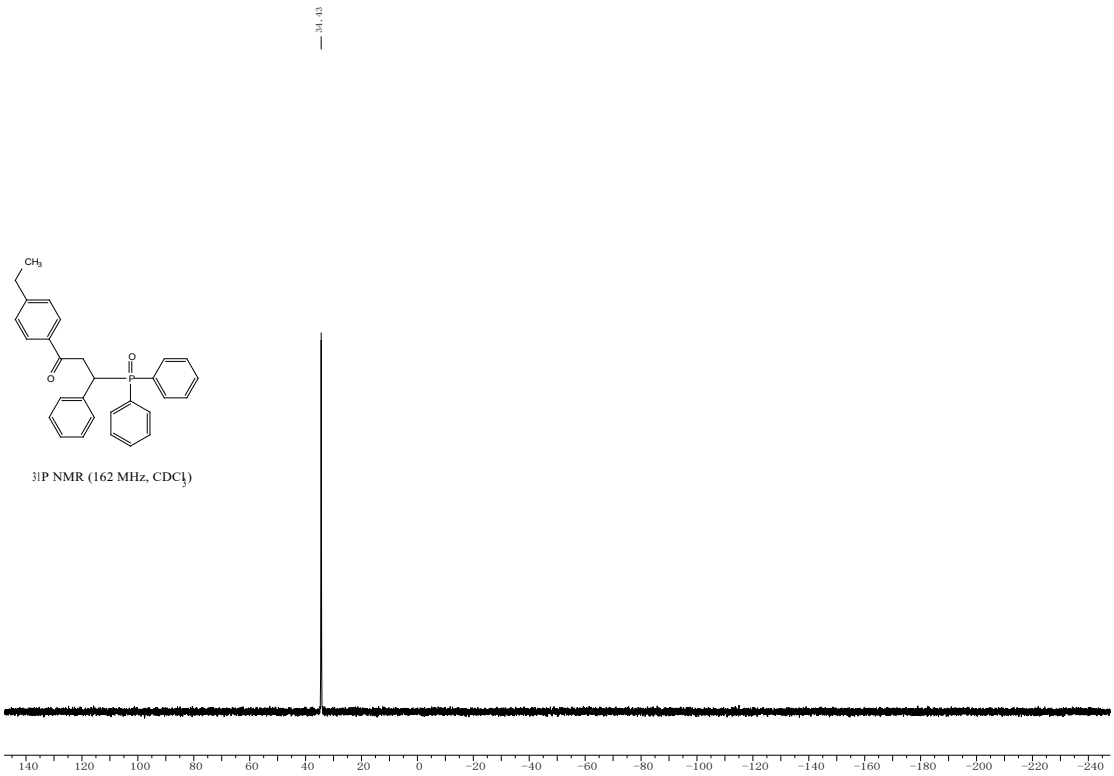
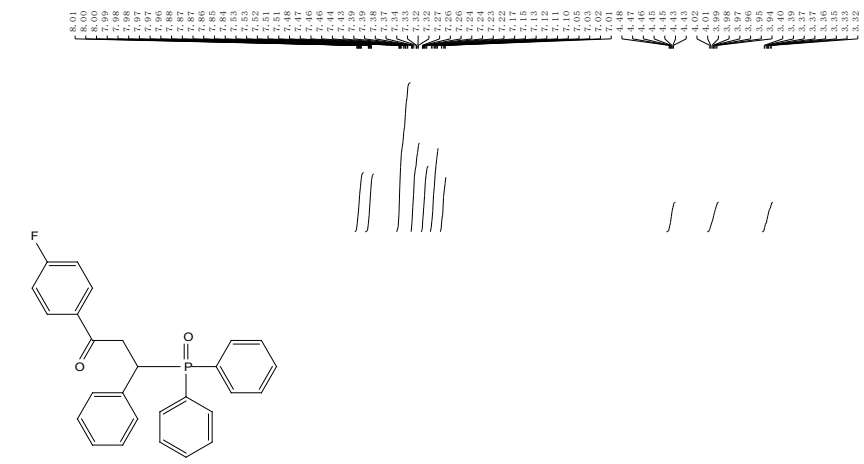
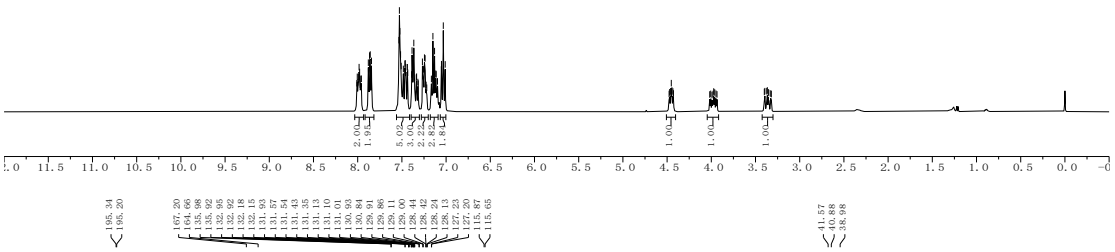
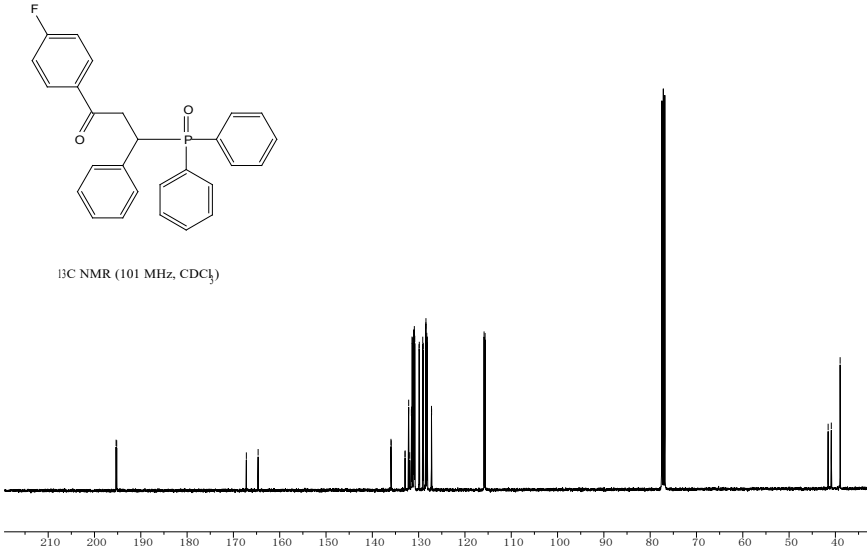


Figure S12. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3i**.



^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (101 MHz, $CDCl_3$)

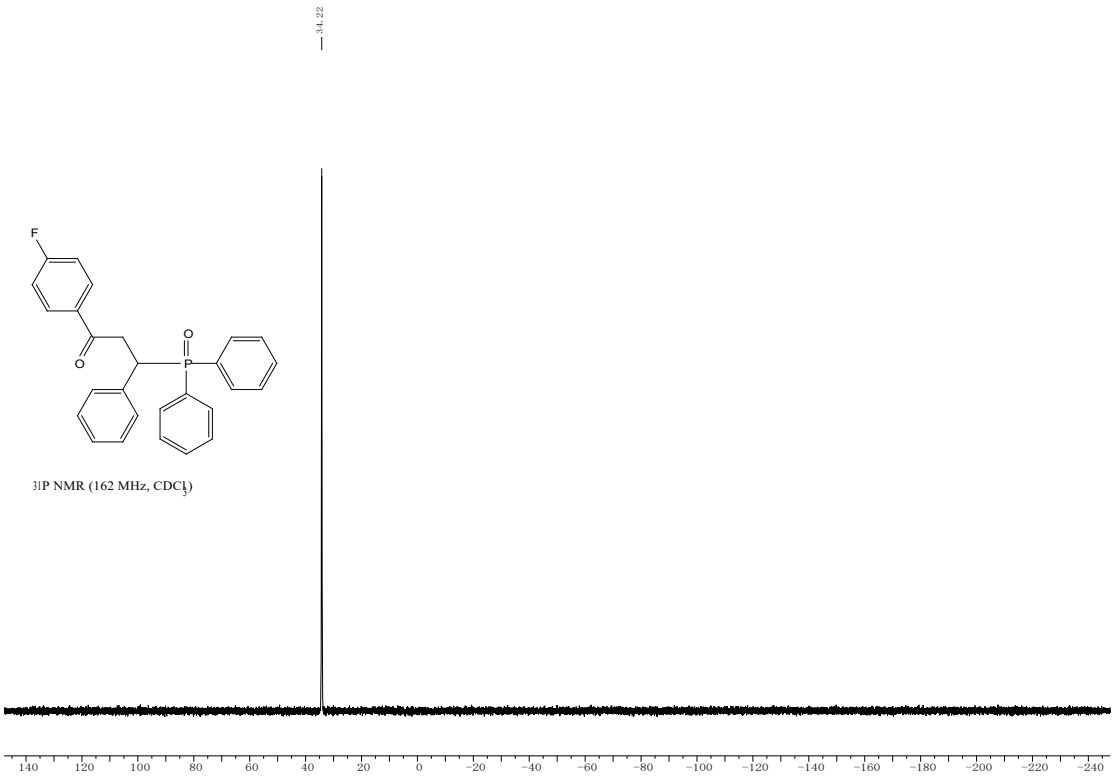
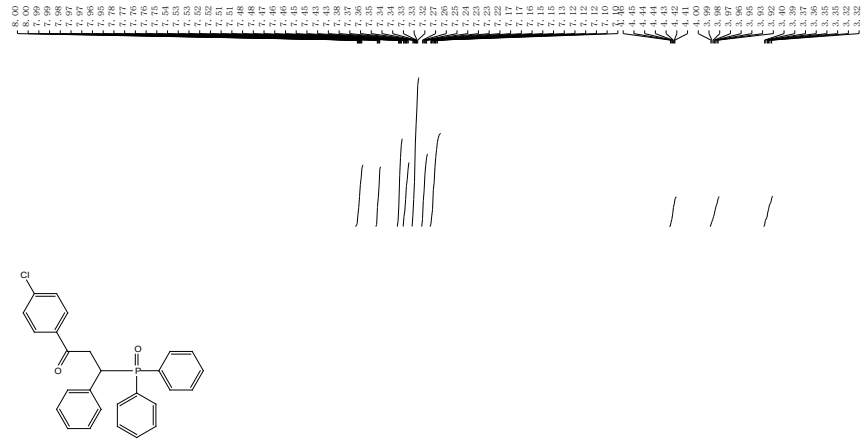
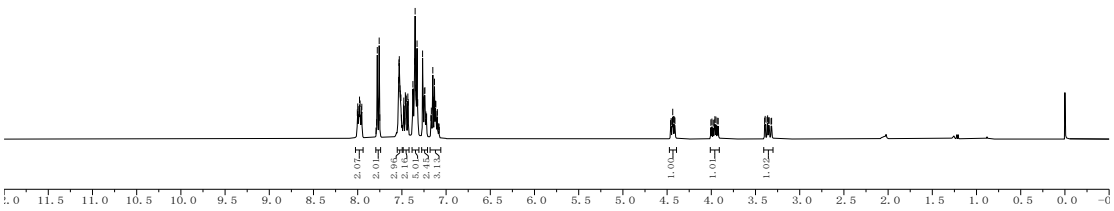


Figure S13. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3j**.



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

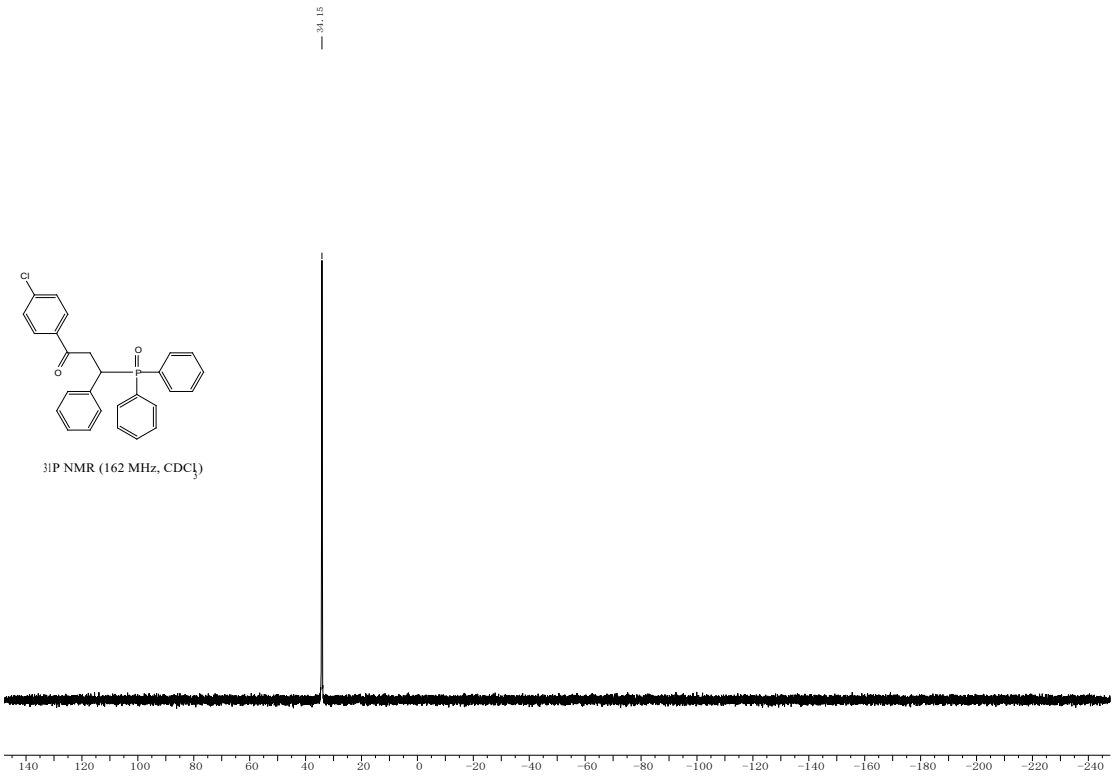
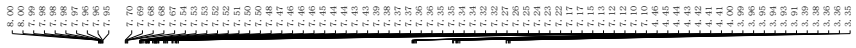
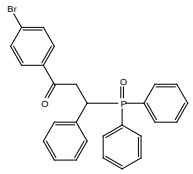
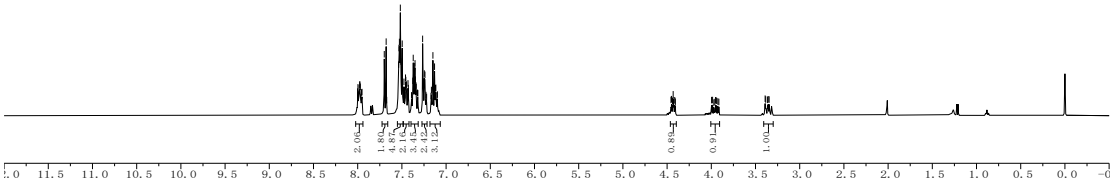


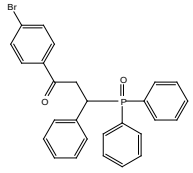
Figure S14. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3k**.



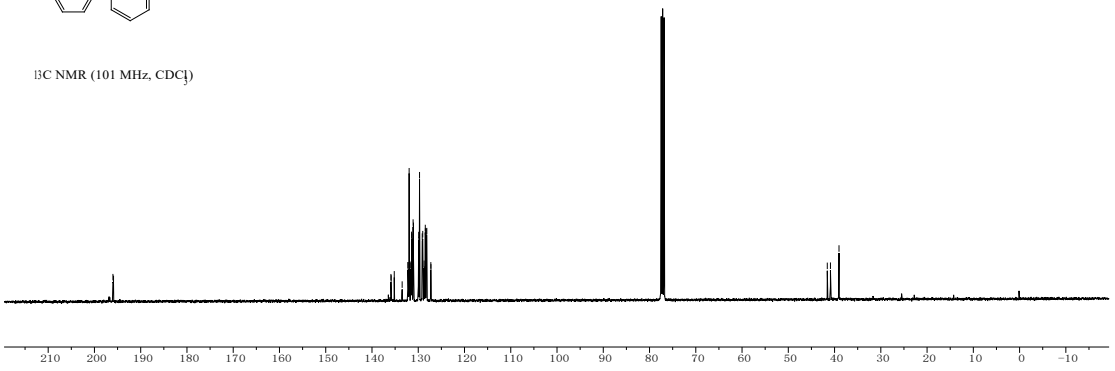


^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (101 MHz, $CDCl_3$)



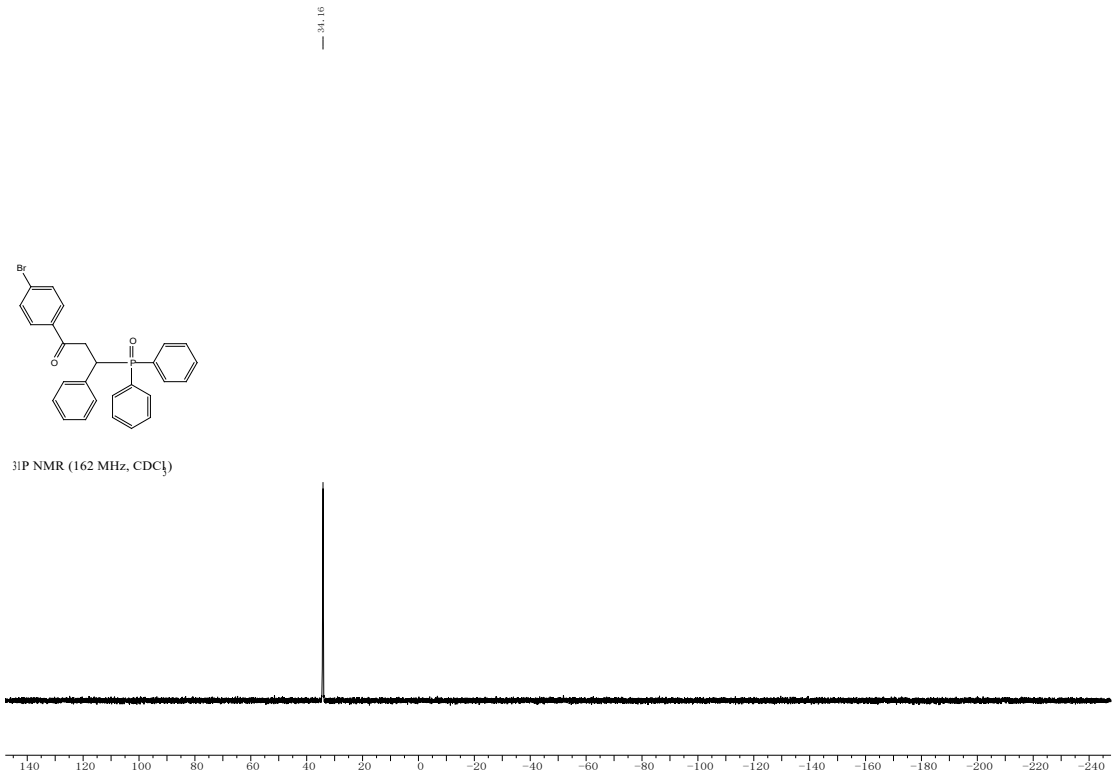
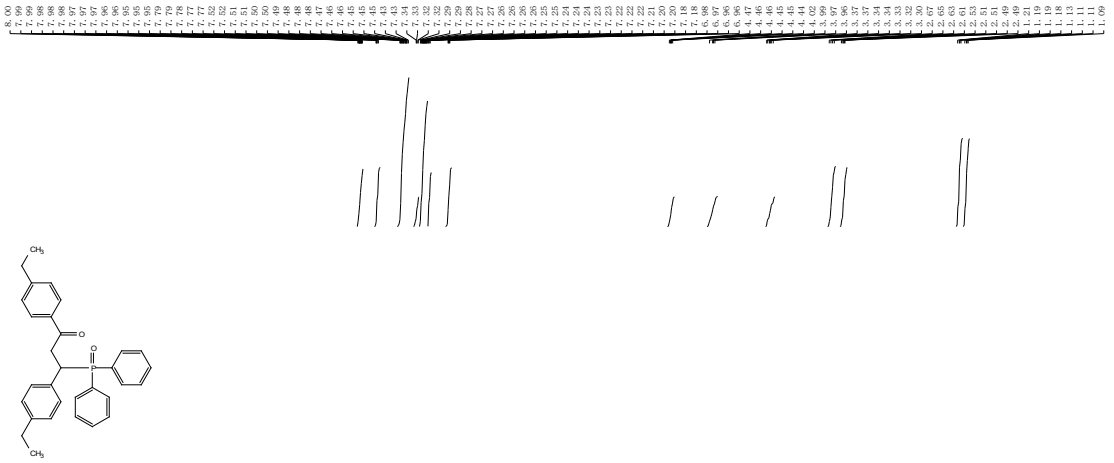
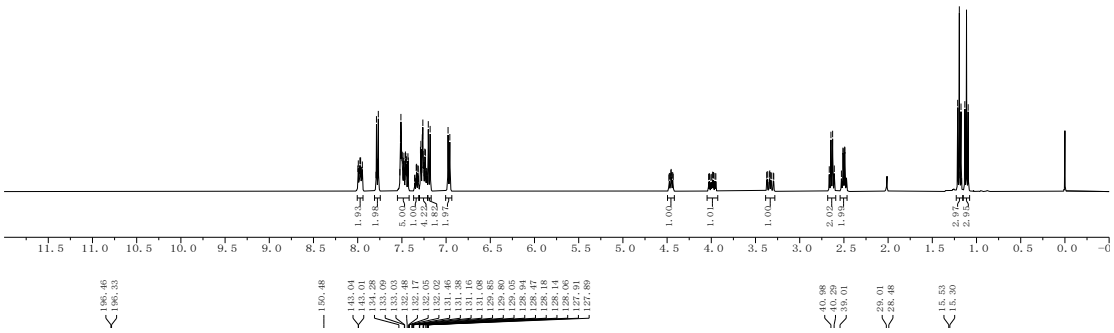
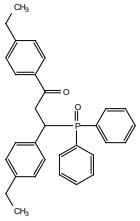


Figure S15. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3l**.

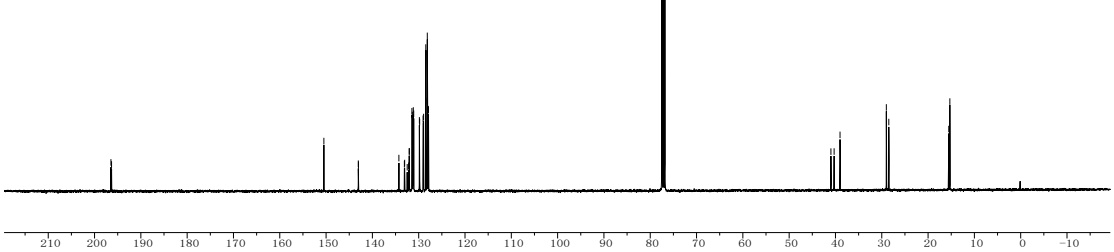


^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (101 MHz, $CDCl_3$)



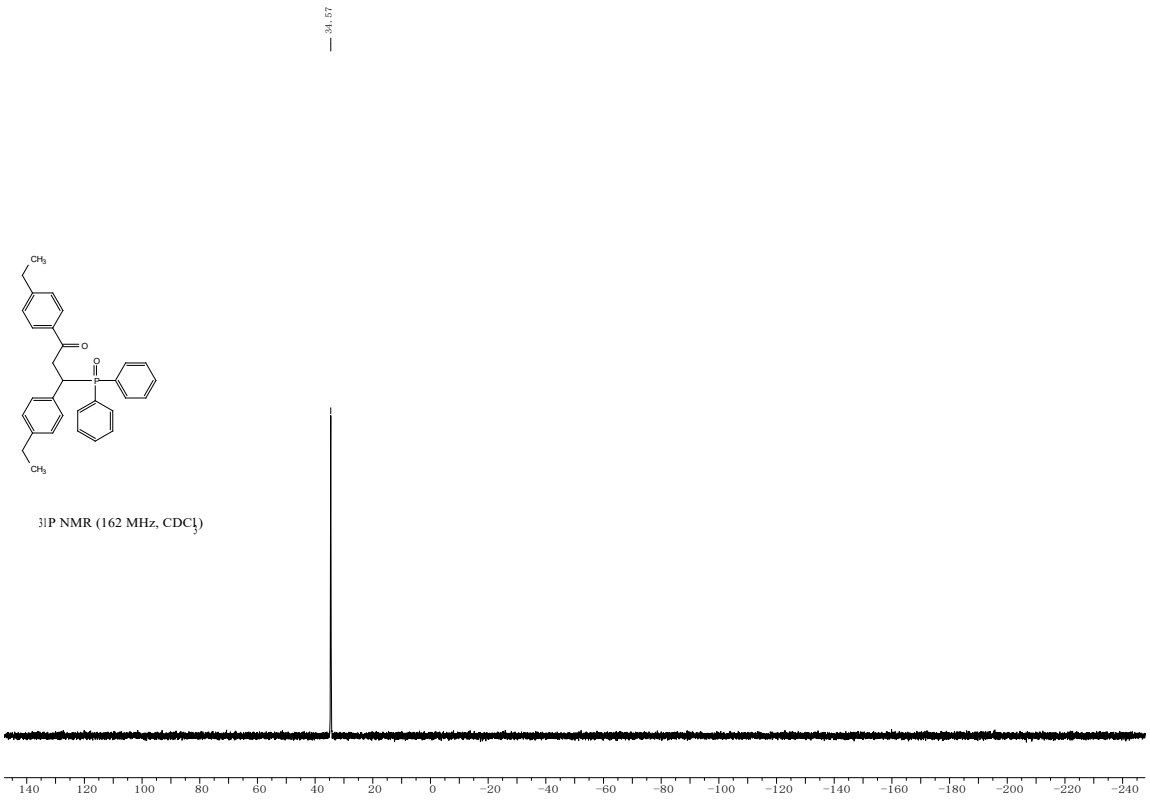
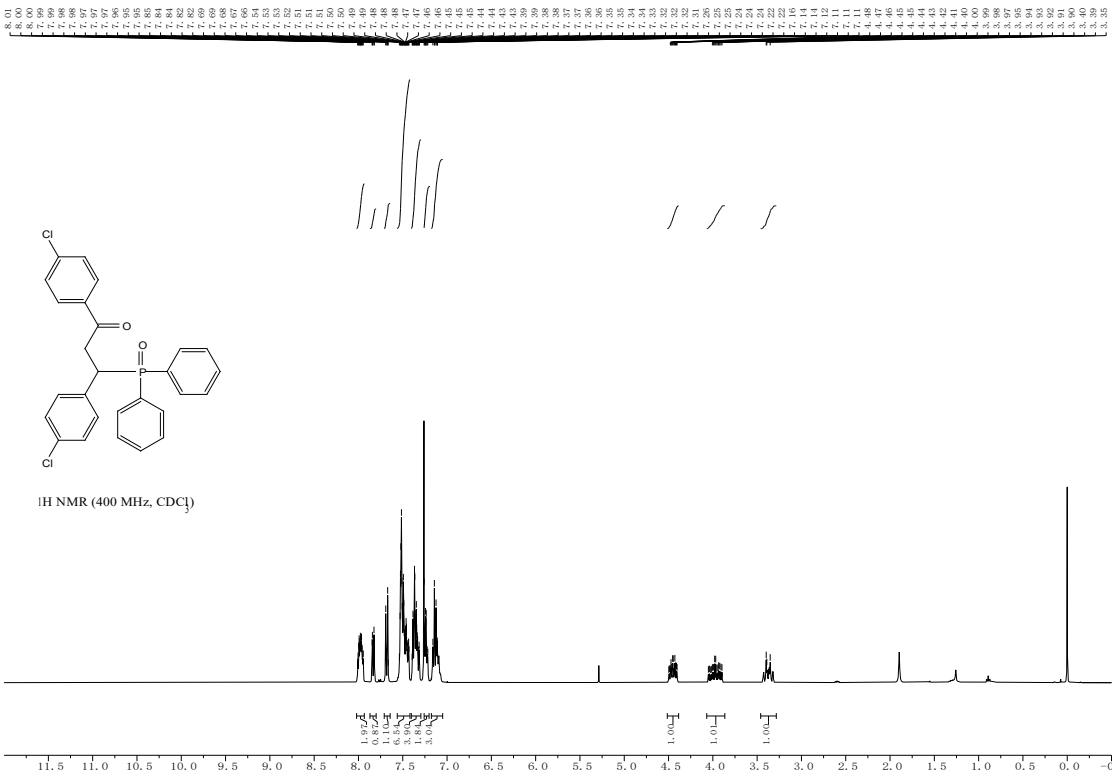
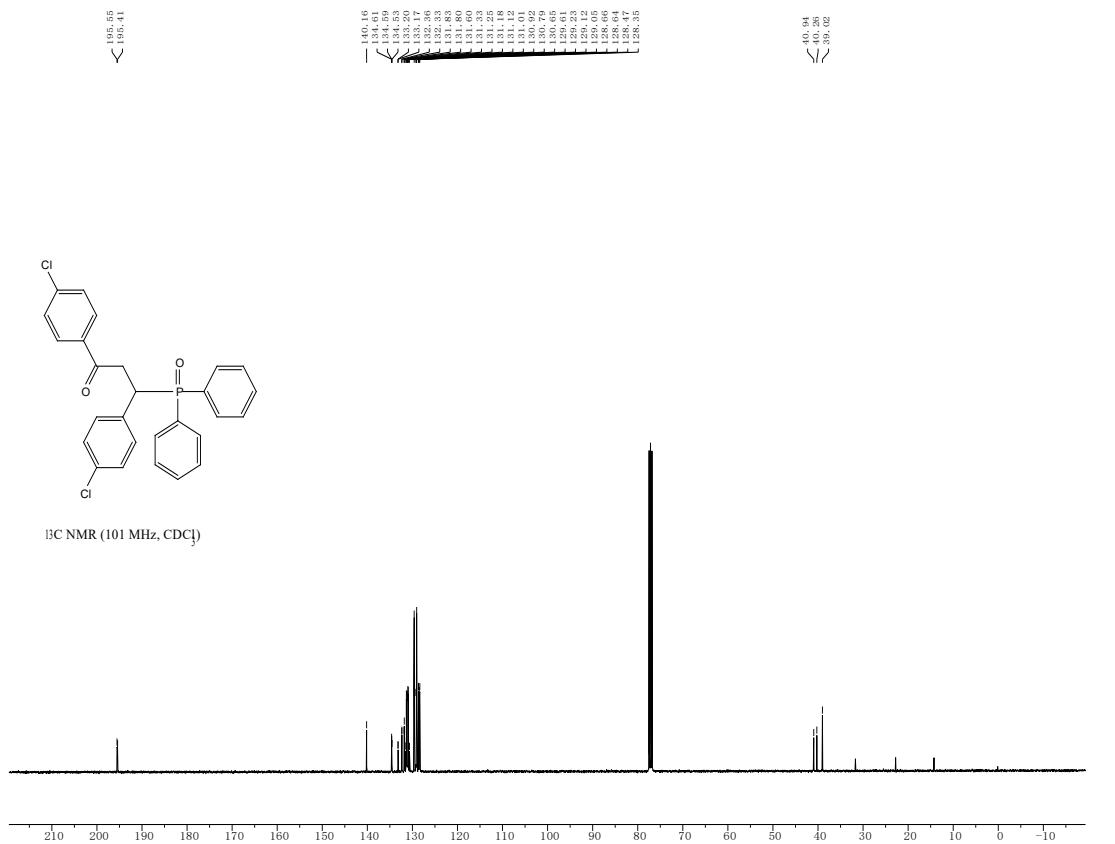


Figure S16. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3m**.


Cl
O
O
P
Cl
1H NMR (400 MHz, CDCl3)


Cl
O
O
P
Cl
13C NMR (101 MHz, CDCl3)

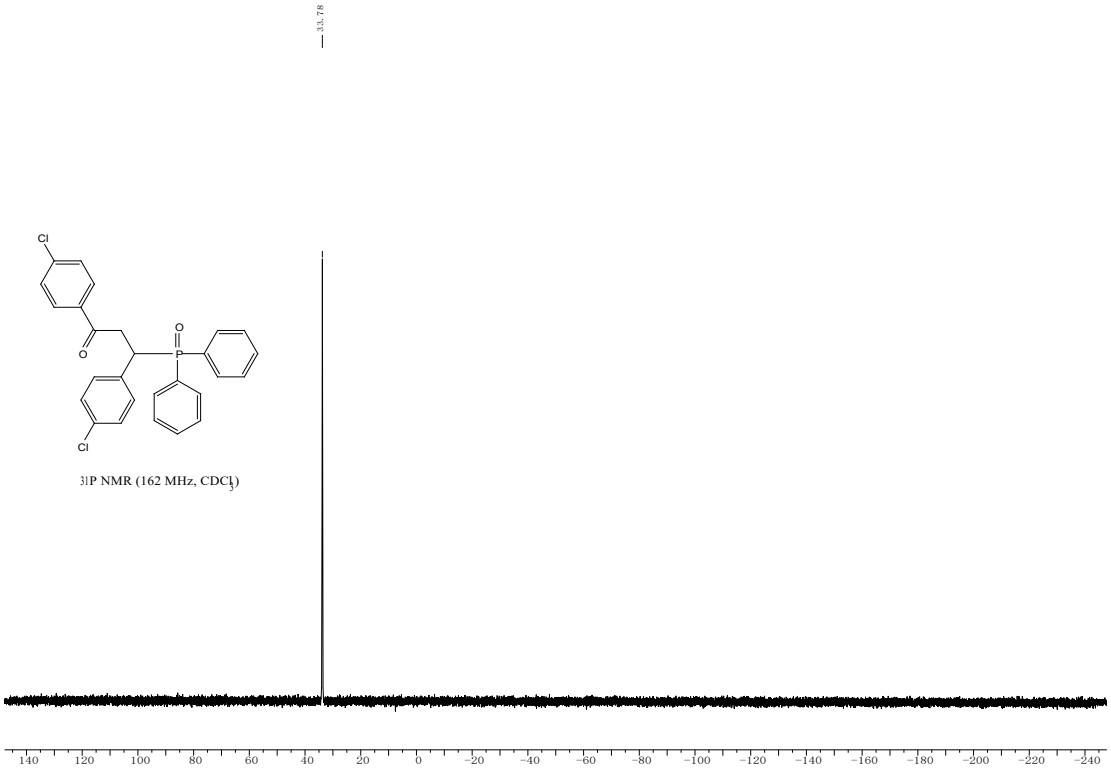
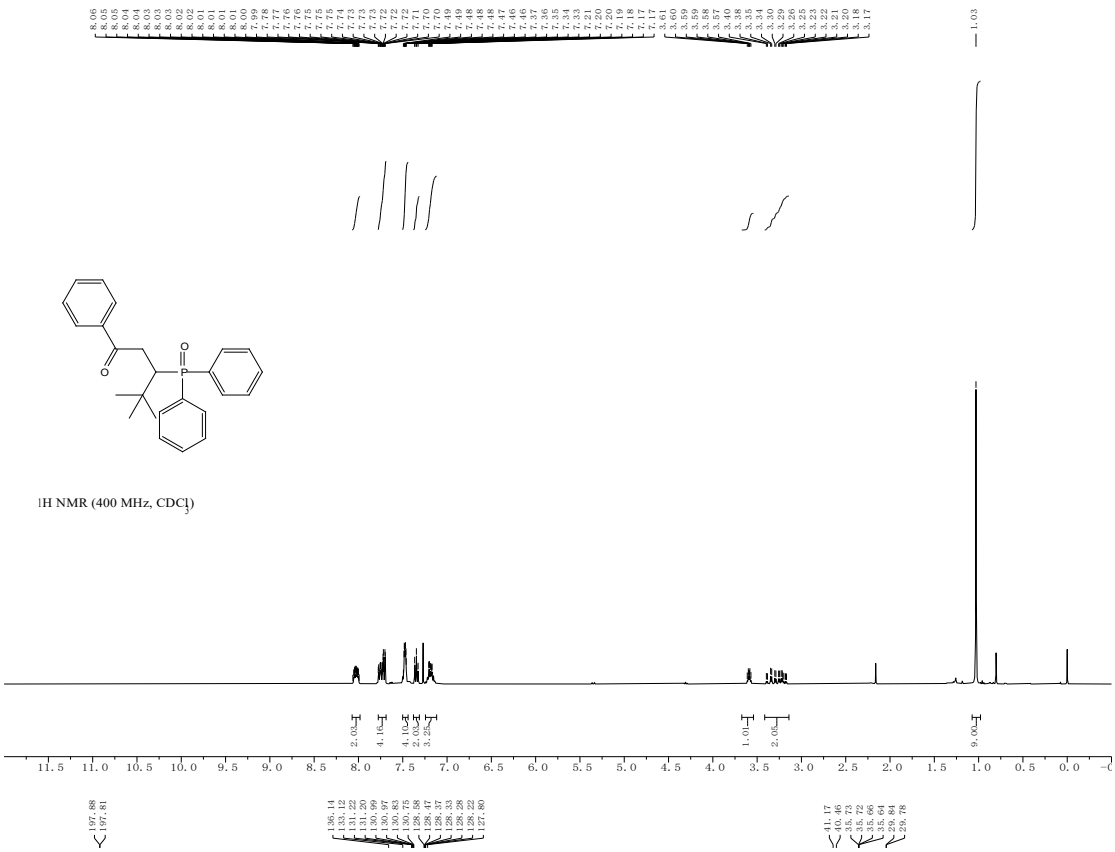
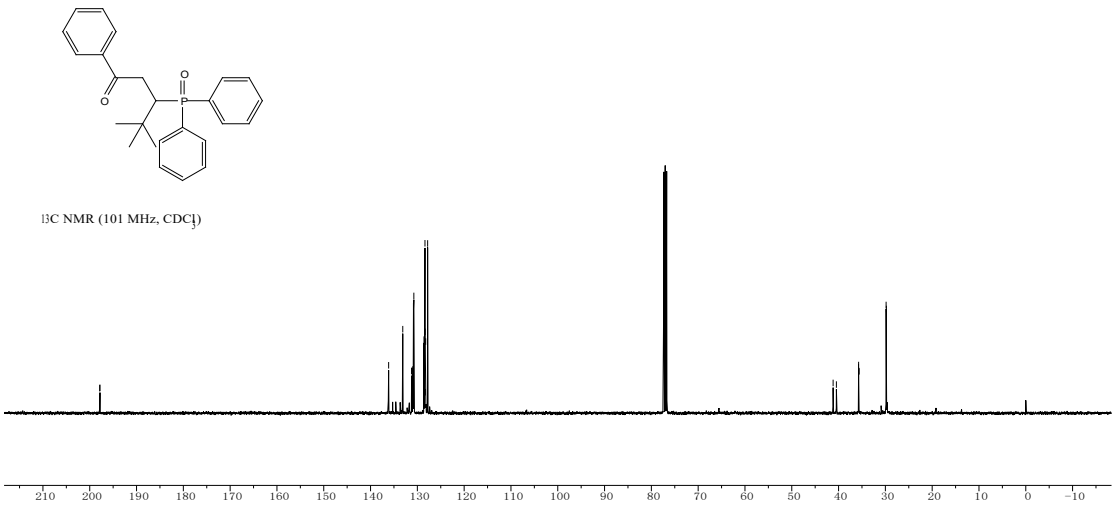


Figure S17. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3n**.



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

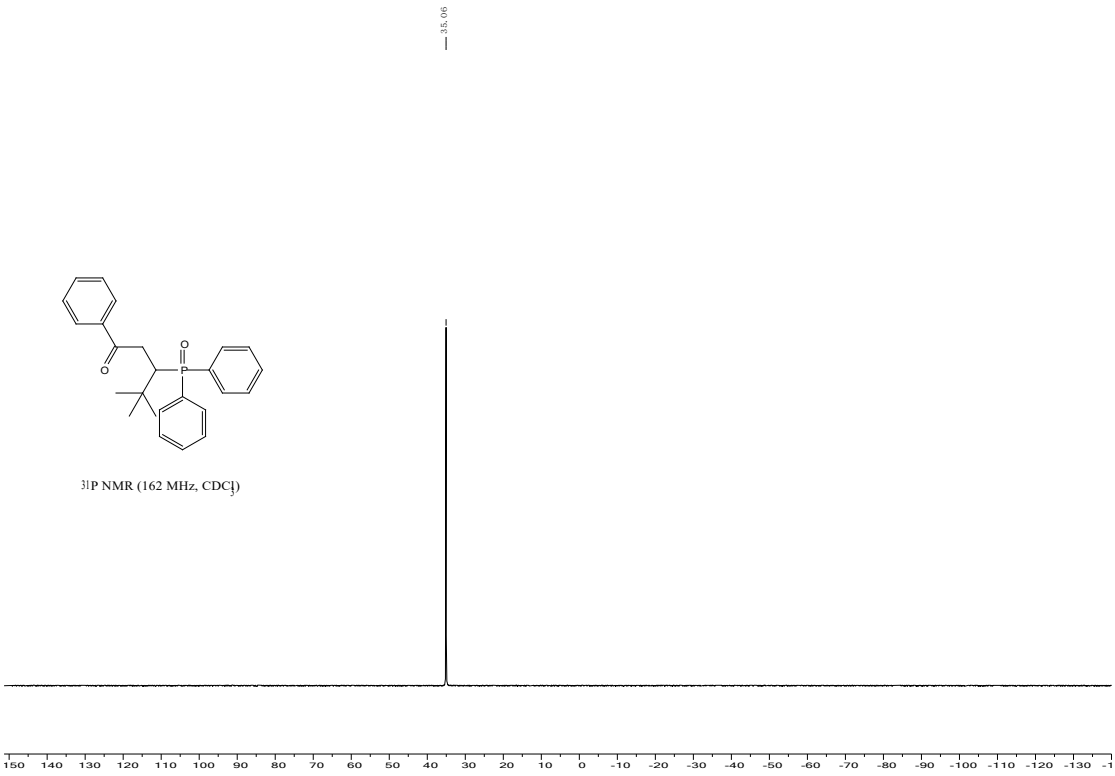
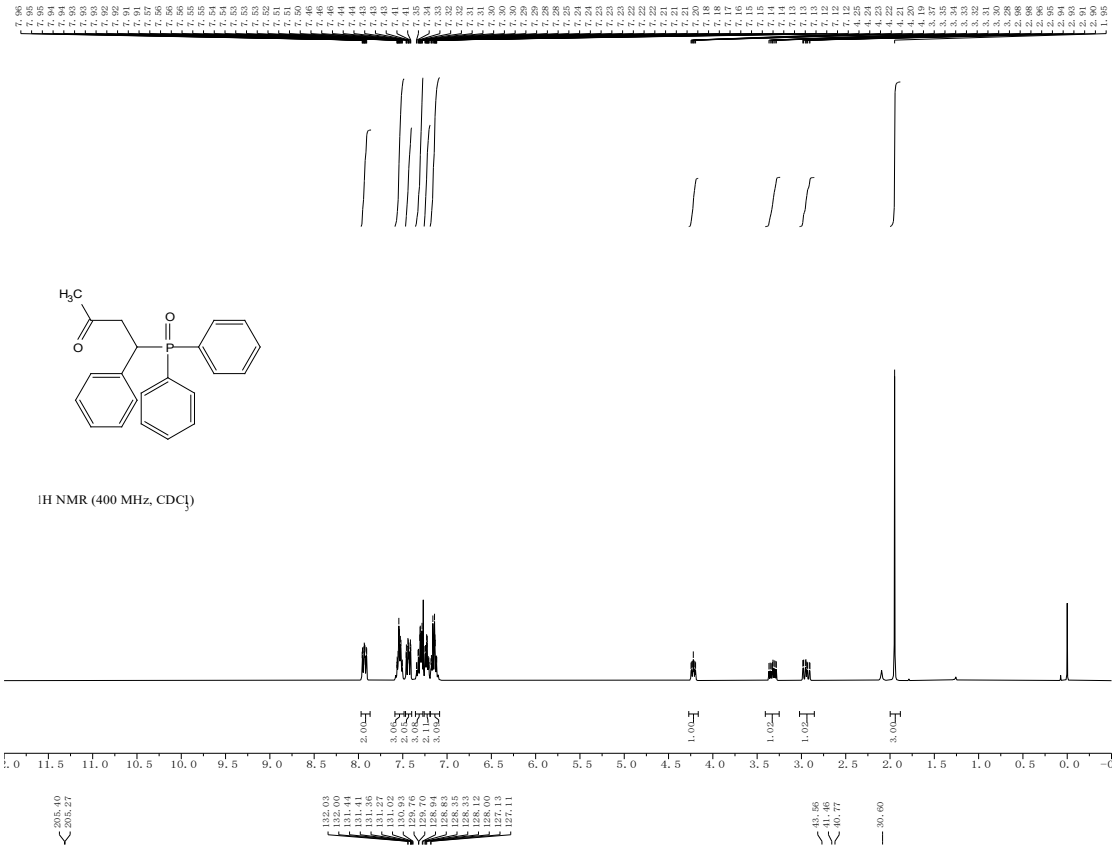
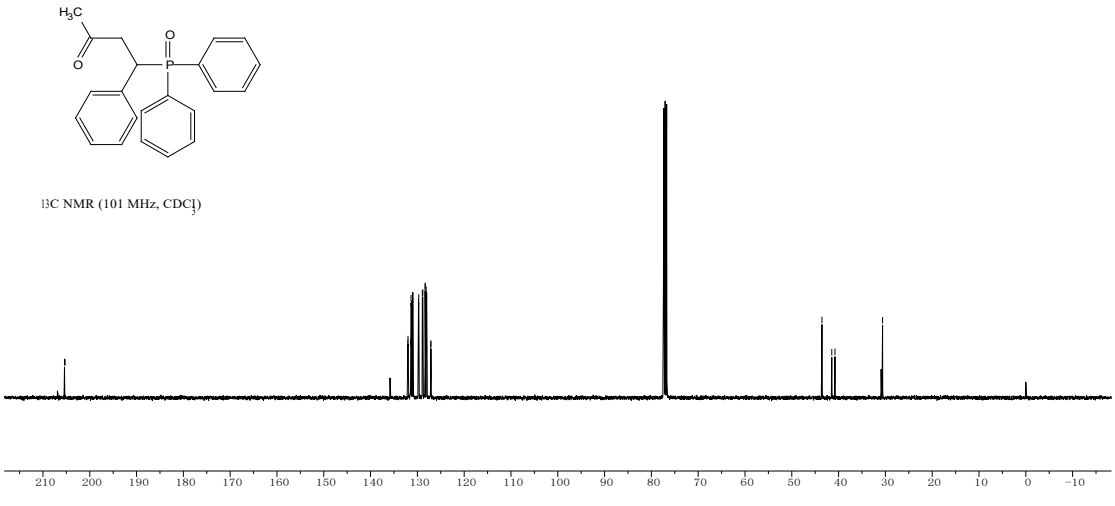


Figure S18. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3o**.


H3C
O
O
P
1H NMR (400 MHz, CDCl3)


H3C
O
O
P
13C NMR (101 MHz, CDCl3)

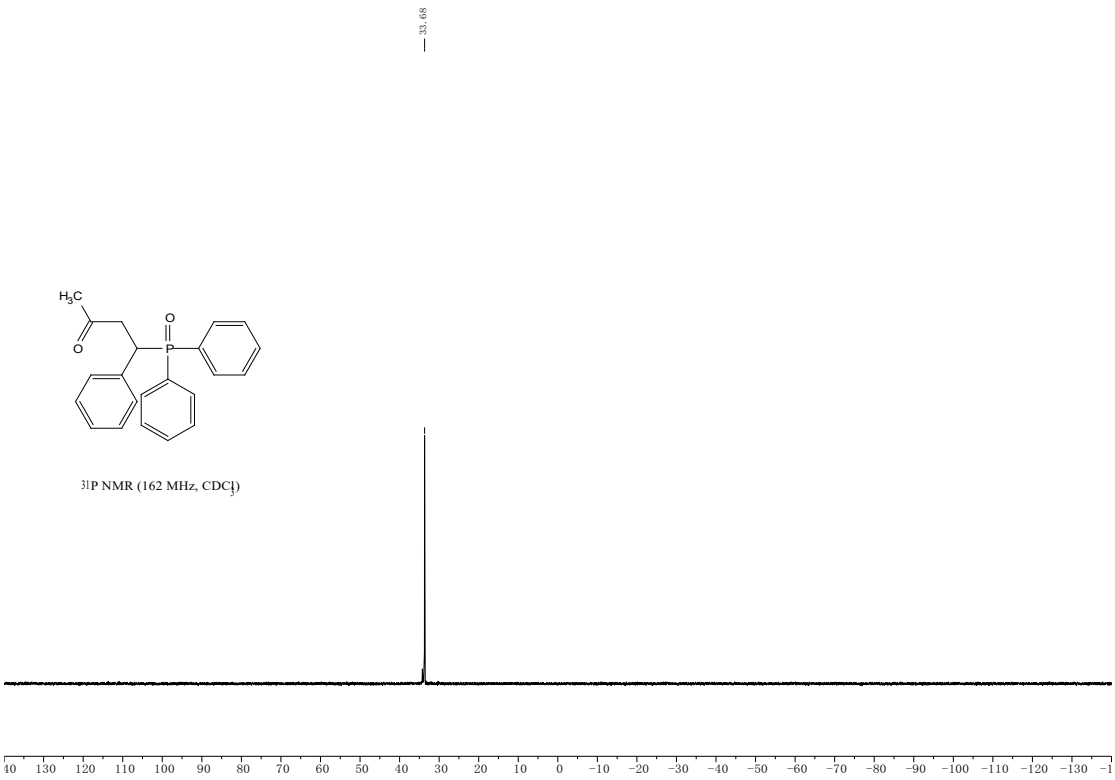
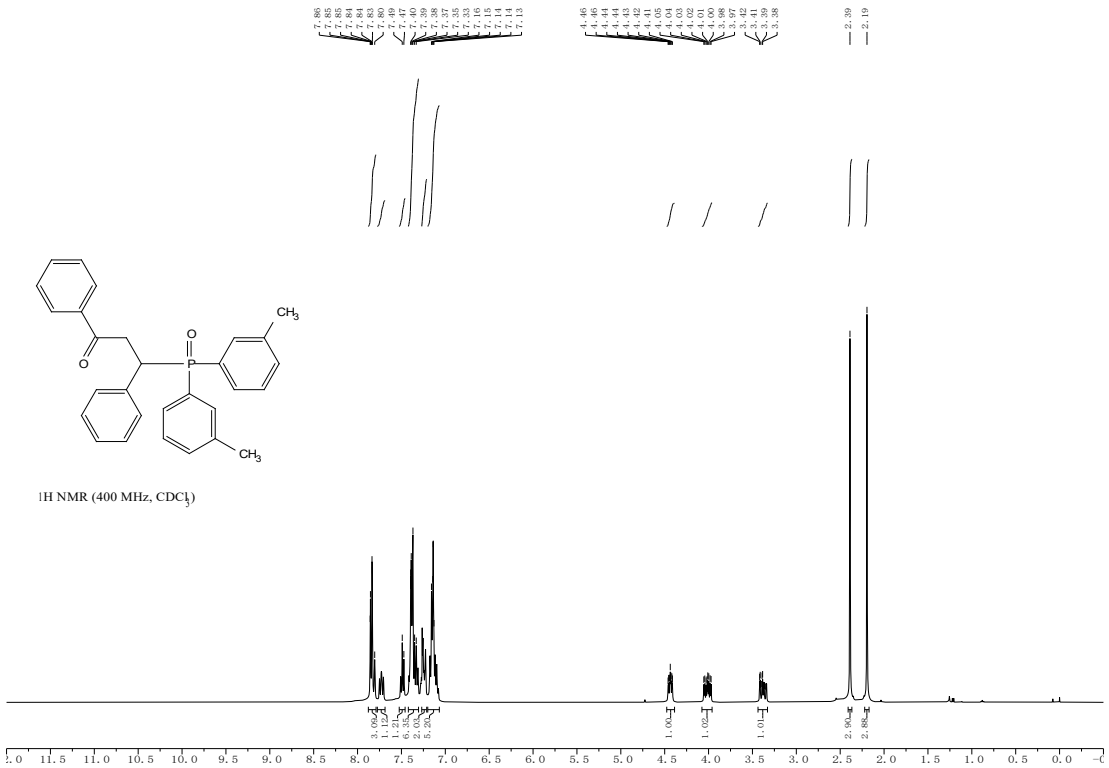
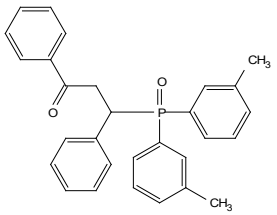


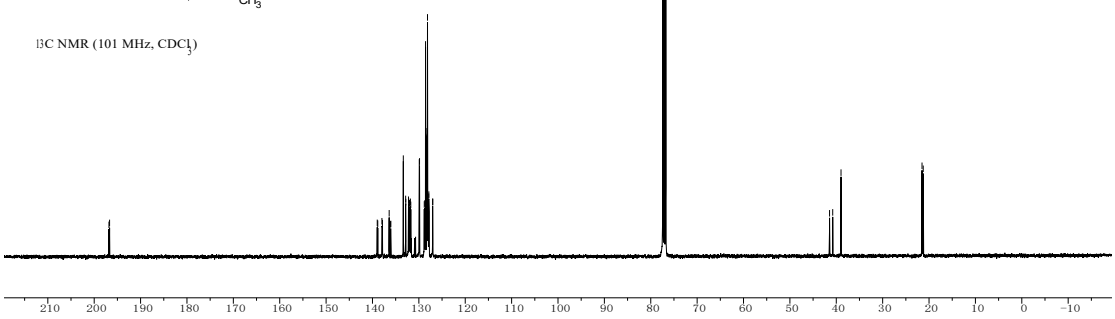
Figure S19. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3p**.



1H NMR (400 MHz, $CDCl_3$)



13C NMR (101 MHz, $CDCl_3$)



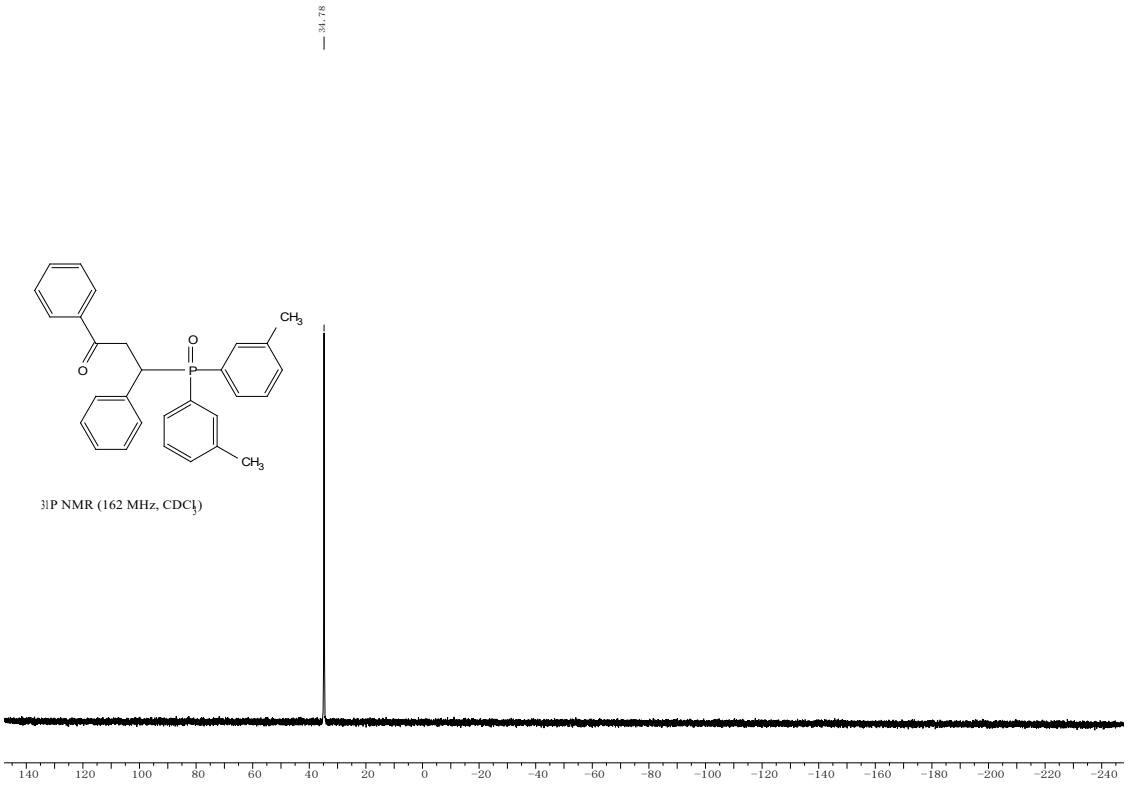
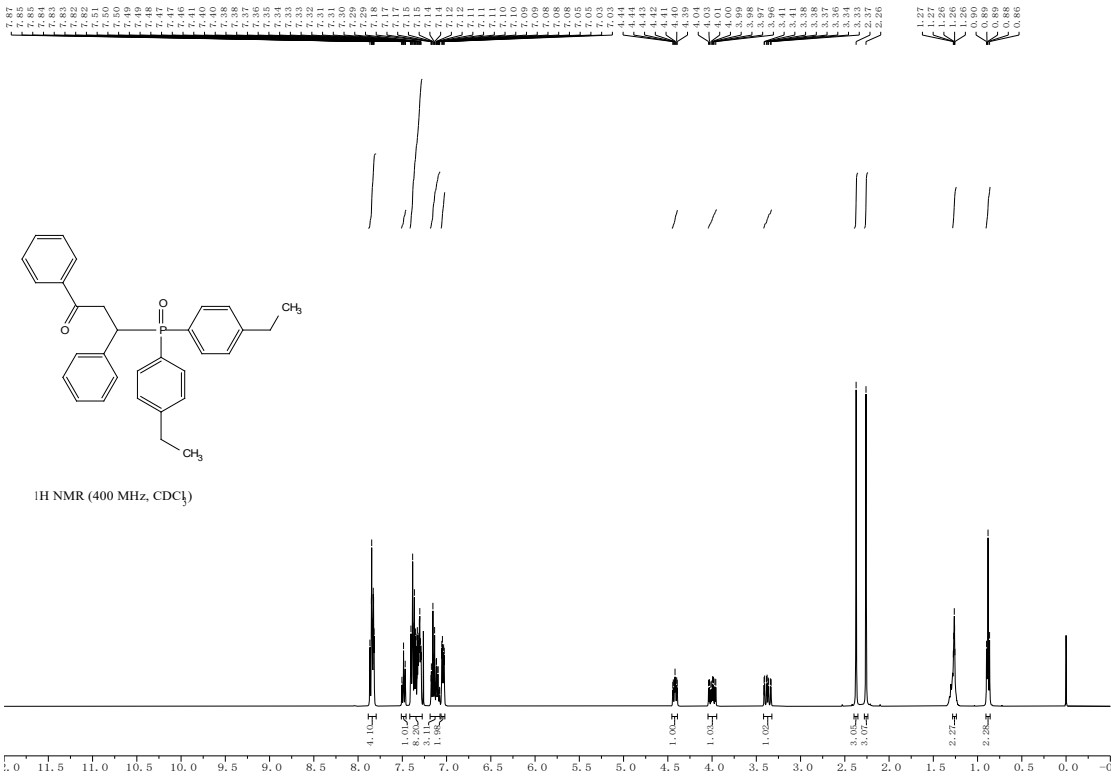
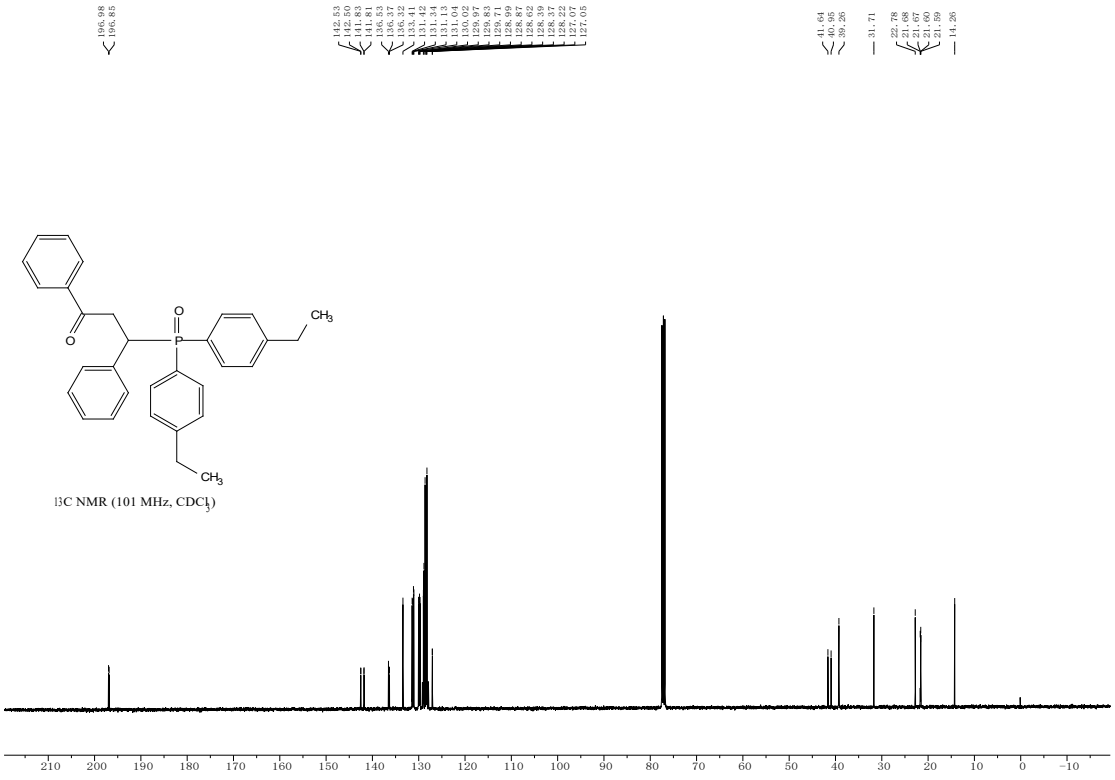


Figure S20. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3r**.



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

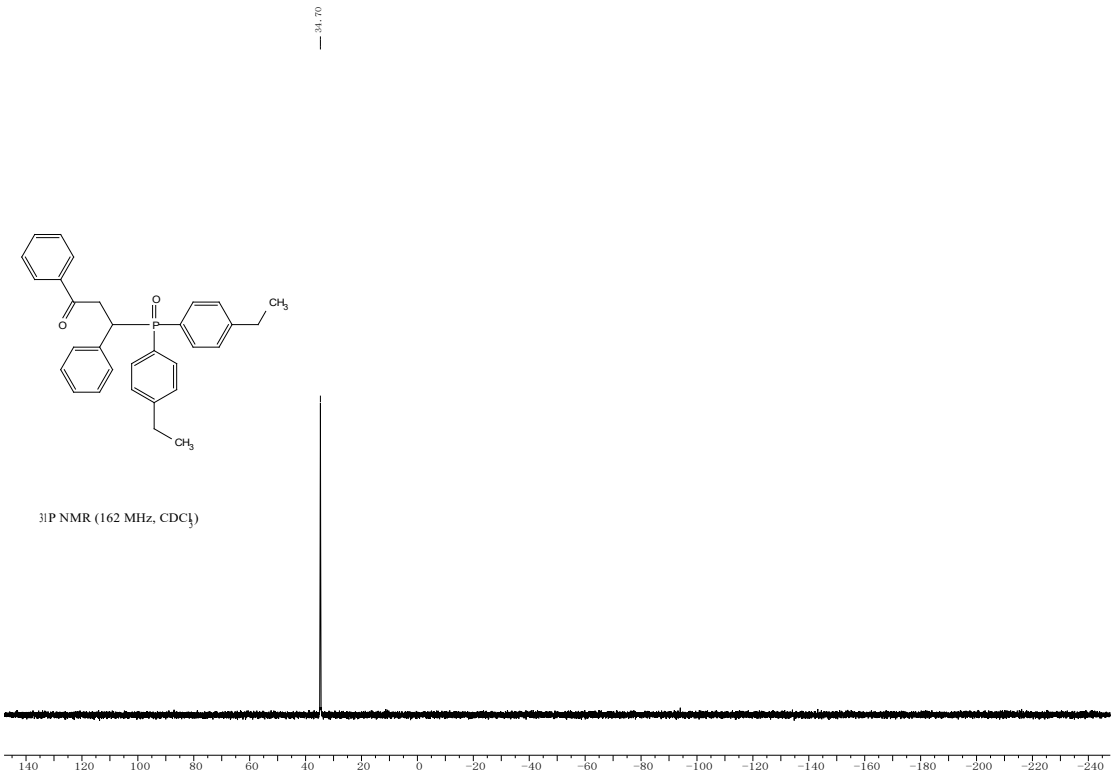
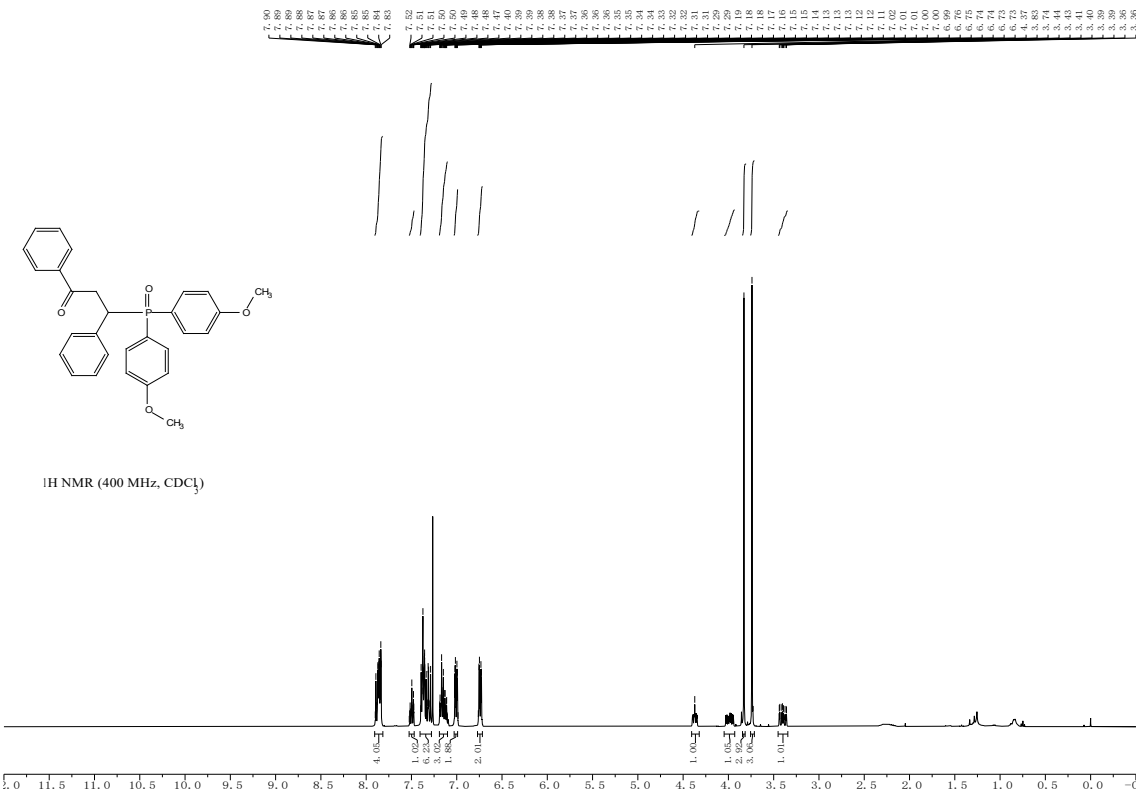
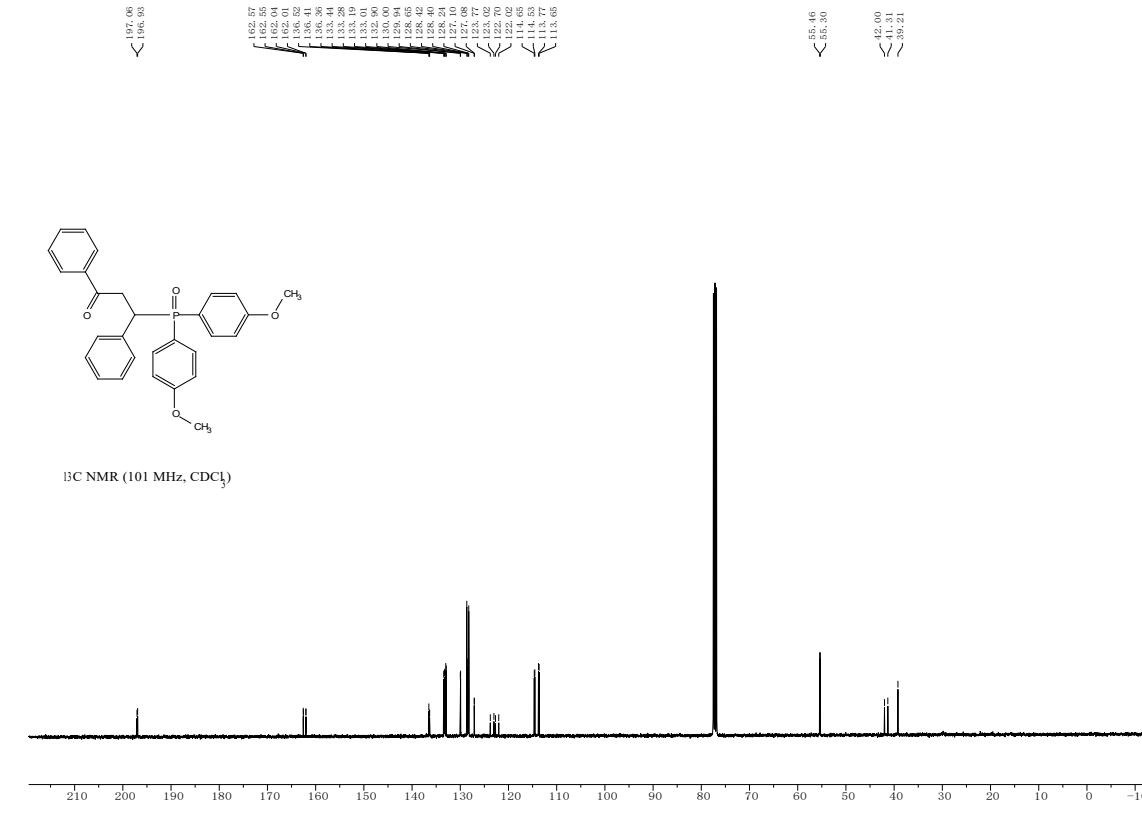


Figure S21. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3s**.



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

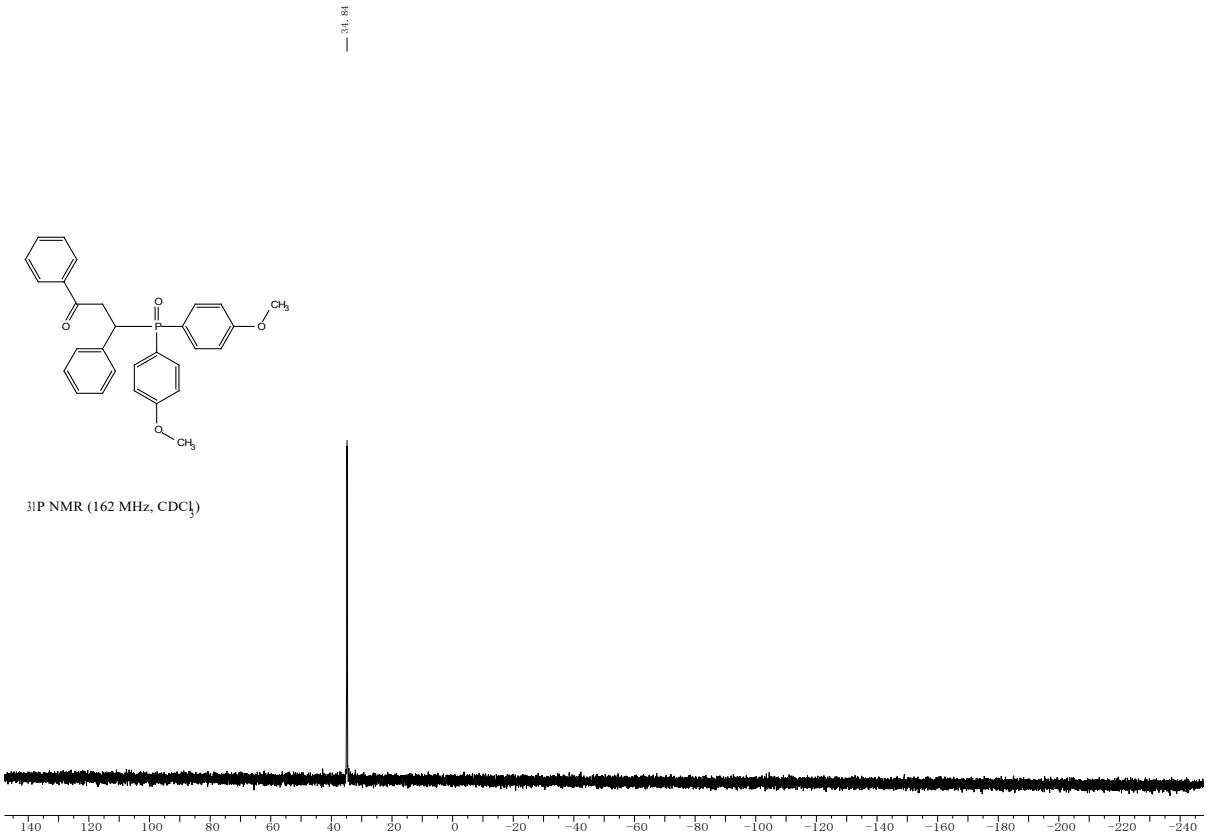
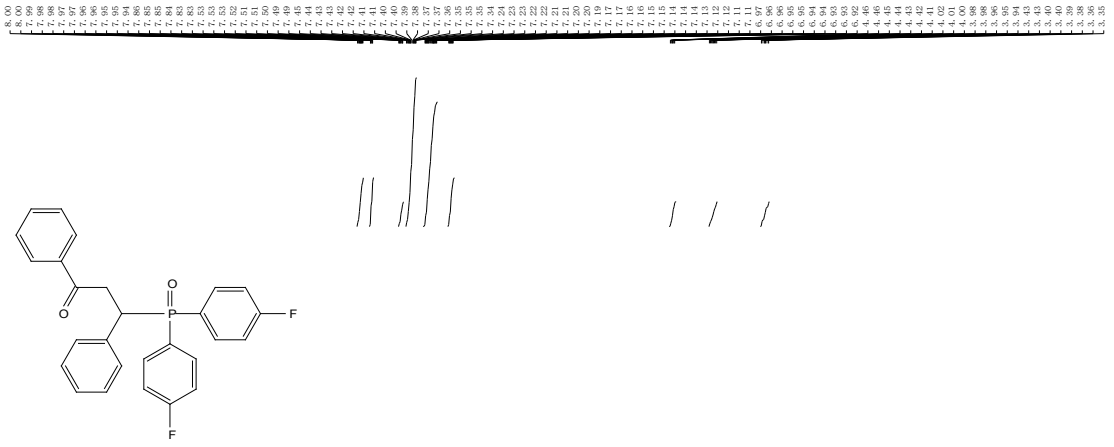
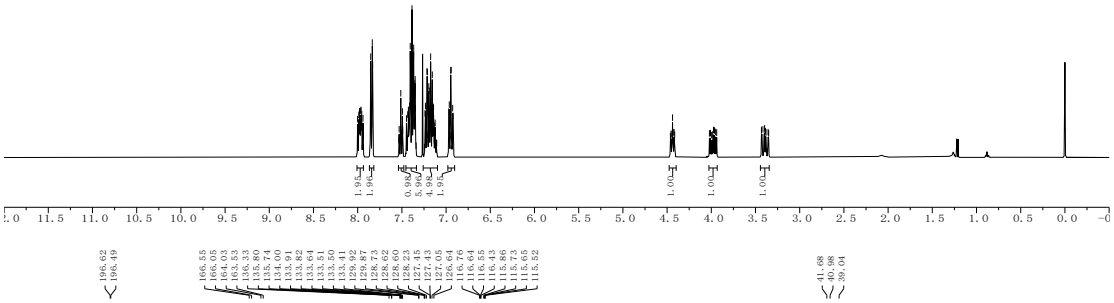
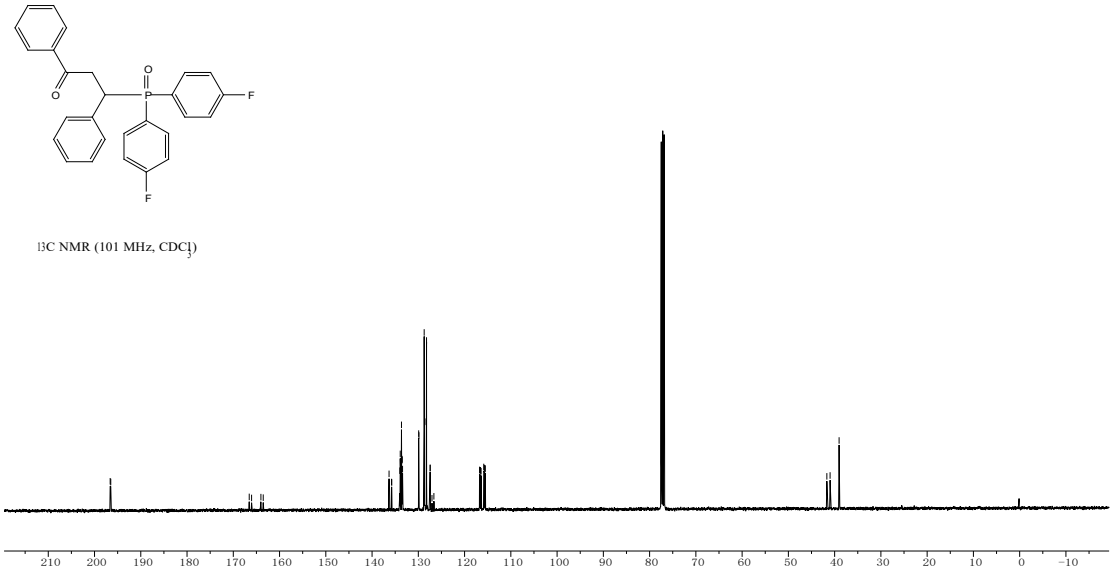


Figure S22. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of **3t**.



^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (101 MHz, $CDCl_3$)

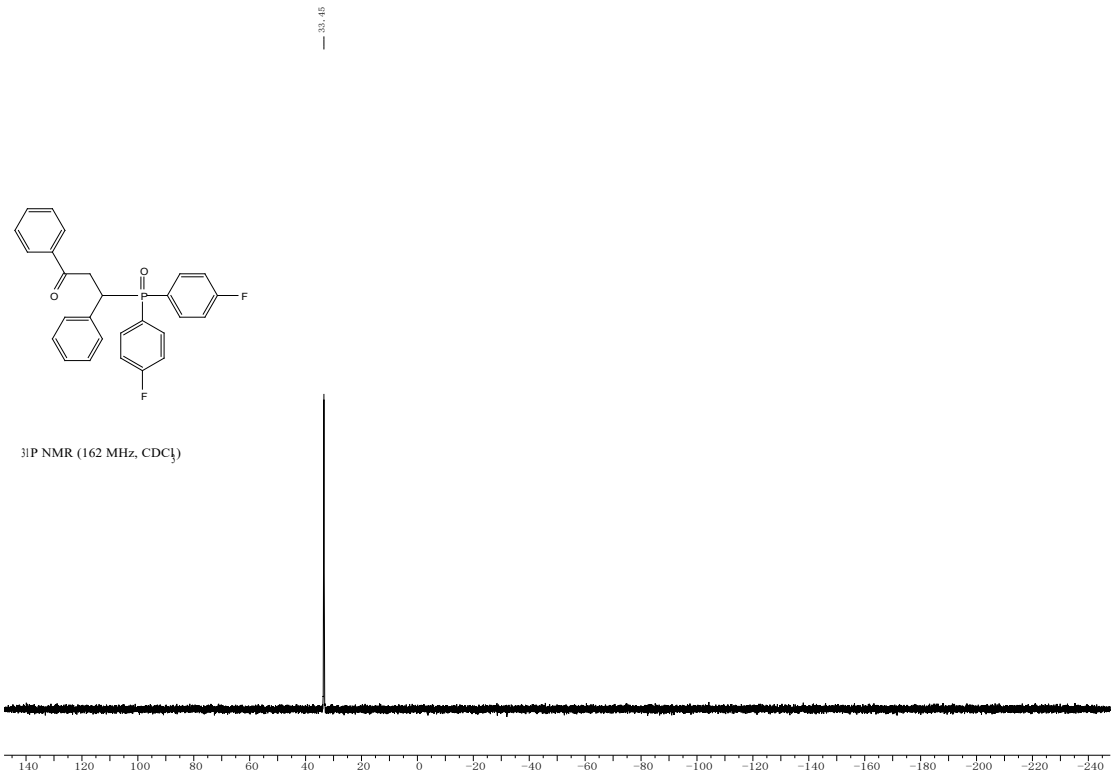
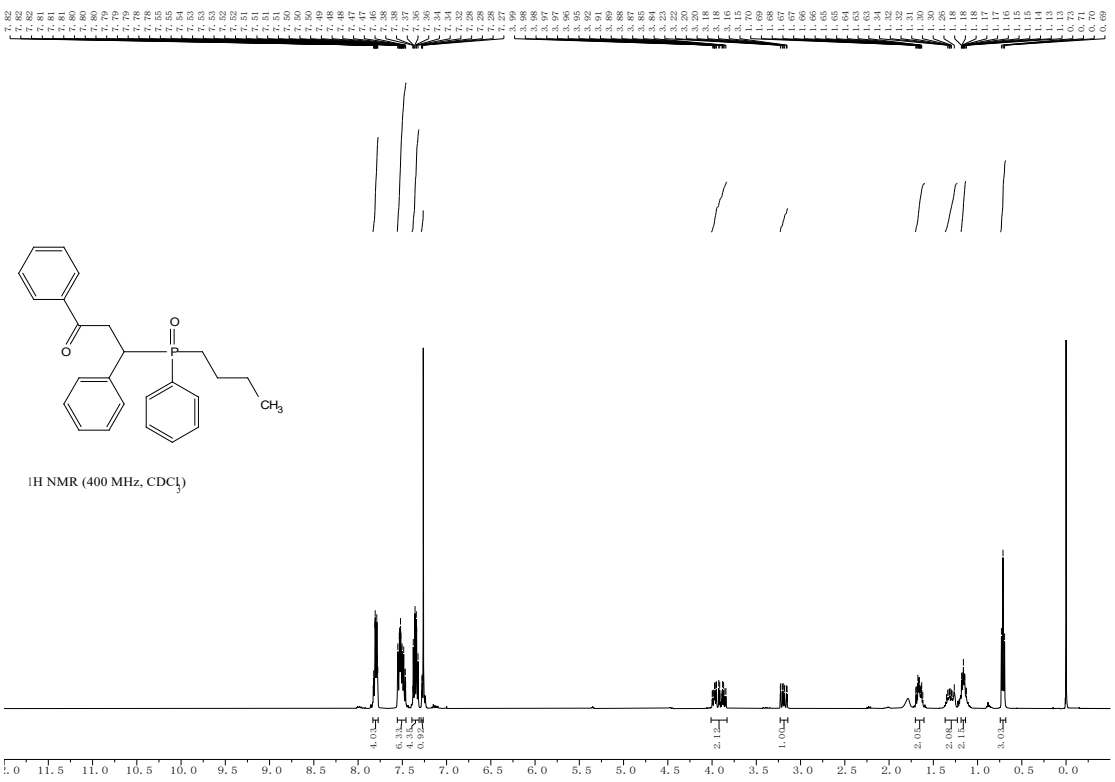
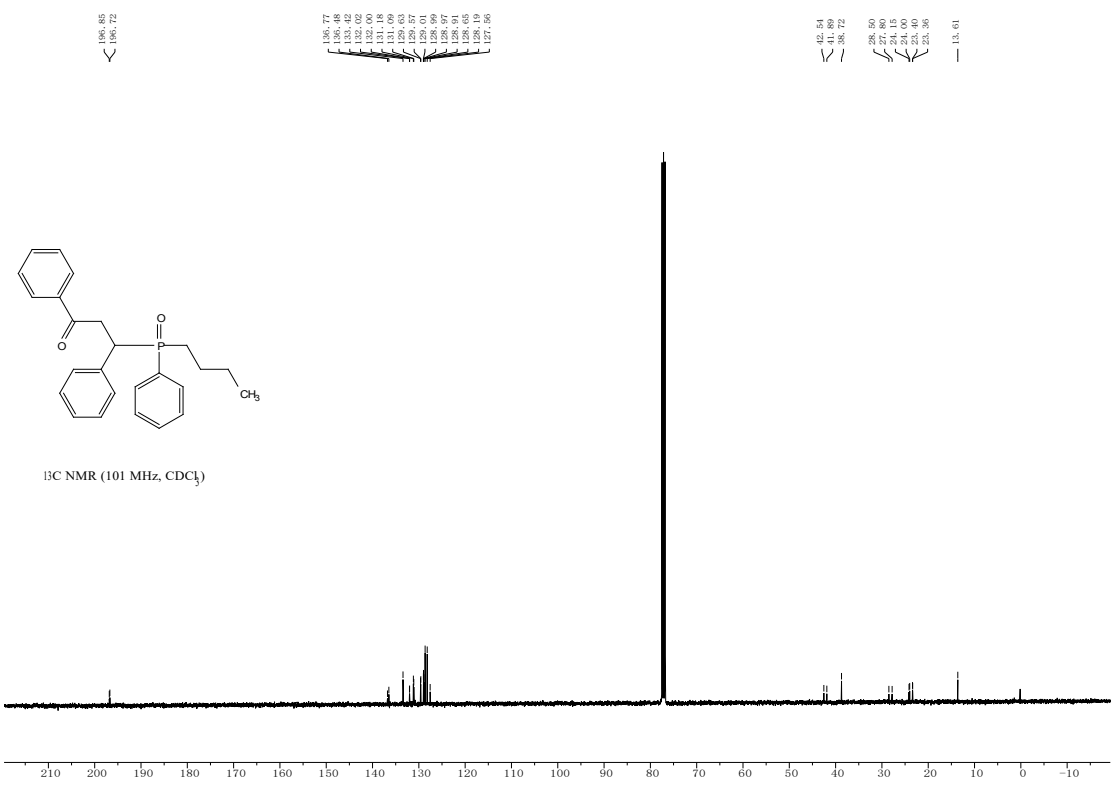


Figure S23. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra of **3u**.



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

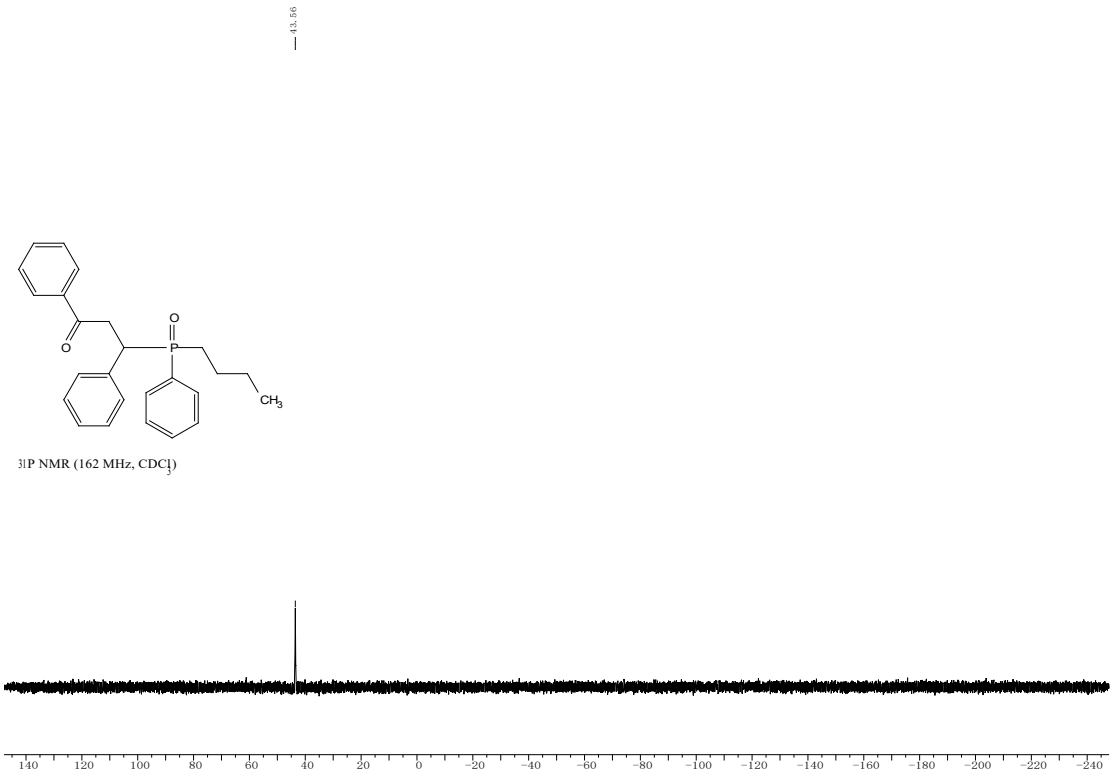


Figure S24. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra of **3v**.