A Catalyst-Free Synthesis of Phosphinic Amides using *O*-Benzoylhydroxylamines

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Supporting Information

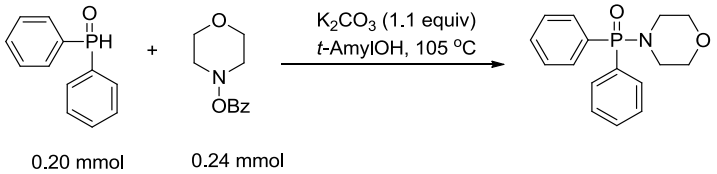
General Information

The reactions were carried out in Schlenk tubes fitted with glass stoppersunder under open air atmosphere. Flash column chromatography was performed using 40-63 μm silica gel as the stationary phase. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AC-400 FT spectrometer using solvent residue as an internal reference (7.26 and 77.00 ppm for $CDCl_3$, respectively). High resolution mass spectral analysis (HRMS) was performed on Water XEVO G2 Q-TOF (Waters Corporation).

EPR experiments

EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.062 GHz. Typical spectrometer parameters are shown as follows, scan range: 10 mT; center field set: 324 mT; time constant: 0.1s; scan time: 60 s; modulation amplitude: 0.3 mT; modulation frequency: 100 kHz; microwave power: 10 mW.

The interaction between diphenylphosphine oxide, *N*-benzoyloxylmorpholine, and K_2CO_3 was investigated by electron paramagnetic resonance (EPR) (X band, 9.1GHz, RT): diphenylphosphine oxide (0.20 mmol), *N*-benzoyloxylmorpholine (1.2 equiv), K_2CO_3 (1.1 equiv) and *t*-AmylOH (2 ml) were added sequentially in a schlenk tube under open air atmosphere. The reaction was stirred at 105 ^{o}C for 20 min, then put the reaction system into liquid nitrogen. Afterwards, 60 μL of the melting mixture was quickly taken out into a small tube and analyzed by EPR.



0.20 mmol 0.24 mmol

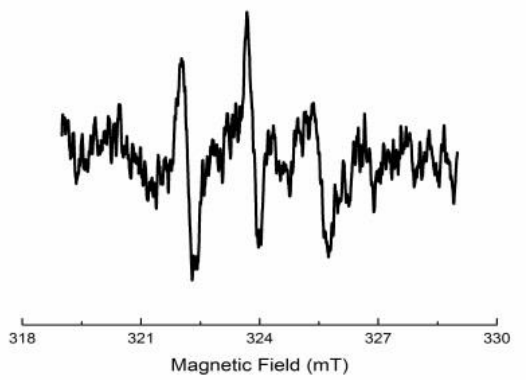
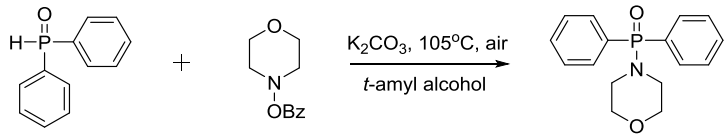


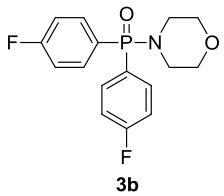
Figure S1 The EPR spectra

Typical Procedures for the preparation of 3a:



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

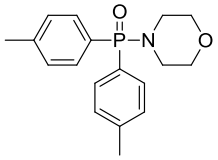
N-benzoyloxylmorpholine **2a** (50 mg, 0.24 mmol, 1.2 equiv) was added to a solution of **1a** (40 mg, 0.20 mmol, 1.0 equiv) and potassium carbonate (30 mg, 0.22 mmol, 1.1 equiv) in *t*-amyl alcohol (2.0 mL) at room temperature. The mixture was stirred at 105 ℃ for 8 h under air atmosphere before being diluted with water (15 mL) and extracted with dichloromethane (3×10 mL). The combined organic layer was washed with brine (15 mL), dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (ethyl acetate, then hexane/dichloromethane 40/1) to afford **3a** (49 mg, 85%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.78 (m, 4 H), 7.58-7.38 (m, 6 H), 3.70 (t, *J* = 4.6 Hz, 4 H), 3.6-2.99 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.4 (d, *J* = 9.1 Hz), 131.9 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 128.3 Hz), 128.7 (d, *J* = 12.3 Hz), 67.2 (d, *J* = 6.7 Hz), 44.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.08; HRMS (ESI) calcd. for $C_{16}H_{19}NO_2P$ $[M + H]^+$: 288.1153, found 288.1154.



3b

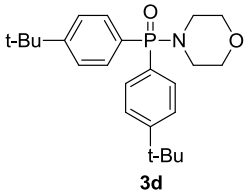
3b (52 mg, 81%, reaction time: 6 h) (R_f 0.4, EA) was prepared following the typical procedure in 0.20 mmol scale as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.70 (m, 4 H), 7.26-7.03 (m, 4 H), 3.69 (t, *J* = 4.6 Hz, 4 H), 3.15-2.96 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2 (dd, *J* = 252.5 ($C_{C,F}$), 3.3 Hz), 134.8 (dd, *J* = 10.4, 8.8 Hz), 126.7 (dd, *J* = 132.7, 3.4 ($C_{C,F}$) Hz), 116.2 (dd, *J* = 21.2, 13.6 Hz), 67.2 (d, *J* = 6.6 Hz), 45.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -106.43; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.26; HRMS (ESI) calcd. for

$C_{16}H_{17}F_2NO_2P$ $[M + H]^+$: 324.0965, found 324.0966.



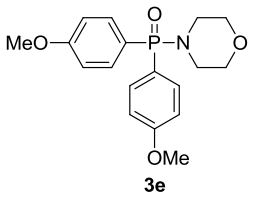
3c

3c (49 mg, 78%, reaction time: 10 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.65 (m, 4 H), 7.32-7.18 (m, 4 H), 3.68 (t, *J* = 4.4 Hz, 4 H), 3.19-2.91 (m, 4 H), 2.35 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 9.4 Hz), 129.4 (d, *J* = 12.8 Hz), 127.7 (d, *J* = 130.8 Hz), 67.2 (d, *J* = 6.8 Hz), 44.9, 21.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.58; HRMS (ESI) calcd. for $C_{18}H_{23}NO_2P$ $[M + H]^+$: 316.1466, found 316.1463.



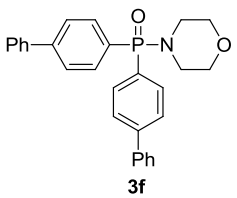
3d

3d (61 mg, 88%, reaction time: 8 h) (R_f 0.4, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.72 (m, 4 H), 7.50-7.41 (m, 4 H), 3.69 (t, *J* = 4.4 Hz, 4 H), 3.19-2.95 (m, 4 H), 1.29 (s, 18 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 9.4 Hz), 127.8 (d, *J* = 130.6 Hz), 125.60 (d, *J* = 12.5 Hz), 67.25 (d, *J* = 6.9 Hz), 44.89, 34.90, 31.05; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.25; HRMS (ESI) calcd. for $C_{24}H_{35}NO_2P$ $[M + H]^+$: 400.2405, found 400.2404.



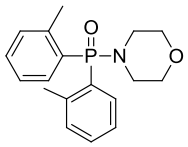
3e

3e (61 mg, 88%, reaction time: 10 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.69 (m, 4 H), 7.00-6.91 (m, 4 H), 3.83 (s, 6 H), 3.69 (t, *J* = 4.4 Hz, 4 H), 3.11-2.99 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 134.1 (d, *J* = 10.4 Hz), 122.4 (d, *J* = 135.2 Hz), 114.2 (d, *J* = 13.3 Hz), 67.3 (d, *J* = 6.9 Hz), 55.3, 44.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.27; HRMS (ESI) calcd. for $C_{18}H_{23}NO_4P$ $[M + H]^+$: 348.1365, found 348.1368.



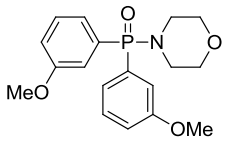
3f

3f (74 mg, 84%, reaction time: 12 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 11.2, 8.0 Hz, 4 H), 7.70 (dd, *J* = 8.4, 3.2 Hz, 4 H), 7.66-7.55 (m, 4 H), 7.54-7.41 (m, 4 H), 7.41-7.33 (m, 2 H), 3.76 (t, *J* = 4.6 Hz, 4 H), 3.25-3.06 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.8 (d, *J* = 2.8 Hz), 139.8, 132.87 (d, *J* = 9.4 Hz), 129.3 (d, *J* = 130.4 Hz), 128.9, 128.1, 127.5, 127.4, 67.2 (d, *J* = 6.6 Hz), 45.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.11; HRMS (ESI) calcd. for $C_{28}H_{27}NO_2P$ $[M + H]^+$: 440.1779, found 440.1783.



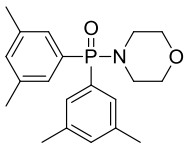
3g

3g (37 mg, 59%, reaction time: 15 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.36 (m, 4 H), 7.31-7.16 (m, 4 H), 3.71 (t, *J* = 4.4 Hz, 4 H), 3.26-3.09 (m, 4 H), 2.53 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.0 (d, *J* = 9.1 Hz), 132.7 (d, *J* = 11.5 Hz), 132.05, 131.90 (t, *J* = 3.2 Hz), 130.0 (d, *J* = 122.1 Hz), 125.39 (d, *J* = 12.9 Hz), 67.36 (d, *J* = 5.3 Hz), 44.96, 21.58 (d, *J* = 3.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.60; HRMS (ESI) calcd. for $C_{18}H_{23}NO_2P$ $[M + H]^+$: 316.1466, found 316.1465.



3h

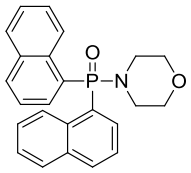
3h (47 mg, 68%, reaction time: 12 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.32 (m, 6 H), 7.09-6.98 (m, 2 H), 3.83 (s, 6 H), 3.70 (t, *J* = 4.4 Hz, 4 H), 3.15-3.01 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7 (d, *J* = 15.6 Hz), 132.2 (d, *J* = 127.8 Hz), 129.9 (d, *J* = 14.6 Hz), 124.3 (d, *J* = 8.7 Hz), 118.1 (d, *J* = 2.7 Hz), 117.3 (d, *J* = 10.3 Hz), 67.2 (d, *J* = 6.7 Hz), 55.4, 45.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.16; HRMS (ESI) calcd. for $C_{18}H_{23}NO_4P$ $[M + H]^+$: 348.1365, found 348.1370.



3i

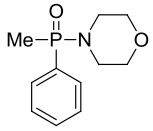
3i (57 mg, 83%, reaction time: 12 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (bd, *J* = 11.6 Hz, 4 H), 7.11 (bs, 2 H), 3.70 (t, *J* = 4.6 Hz, 4 H), 3.14-2.96 (m, 4 H), 2.33 (s, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.3 (d, *J* = 12.9 Hz), 133.6 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 127.0

Hz), 129.9 (d, *J* = 9.0 Hz), 67.25 (d, *J* = 6.5 Hz), 45.01, 21.27; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.02; HRMS (ESI) calcd. for $C_{20}H_{27}NO_2P$ $[M + H]^+$: 344.1779, found 344.1786.



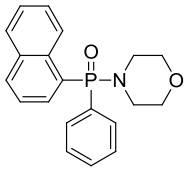
3j

3j (58 mg, 75%, reaction time: 12 h) (R_f 0.4, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.01-8.79 (m, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.92-7.82 (m, 2 H), 7.71-7.47 (m, 6 H), 7.47-7.34 (m, 2 H), 3,67 (t, *J* = 4.4 Hz, 4 H), 3.37-3.20 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.9 (dd, *J* = 9.7, 6.9 Hz), 133.3 (d, *J* = 2.9 Hz), 133.1 (d, *J* = 11.4 Hz), 128.7 (d, *J* = 1.0 Hz), 128.7, 127.7, 127.6 (d, *J* = 4.6 Hz), 127.5, 127.0 (d, *J* = 85.4 Hz), 124.4 (d, *J* = 14.9 Hz), 67.3 (d, *J* = 4.9 Hz), 45.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.65; HRMS (ESI) calcd. for $C_{24}H_{23}NO_2P$ $[M + H]^+$: 388.1466, found 388.1469.



3k

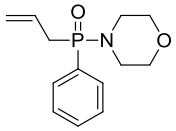
3k (29 mg, 64%, reaction time: 9 h) (R_f 0.2, EA) was prepared following the typical procedure in 0.20 mmol scale as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.71 (m, 2 H), 7.64-7.35 (m, 3 H), 3.75-3.58 (m, 4 H), 3.15-2.93 (m, 4 H), 1.71 (d, *J* = 13.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.1 (d, *J* = 123.5 Hz), 132.0 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 9.5 Hz), 128.7 (d, *J* = 12.3 Hz), 67.1 (d, *J* = 7.0 Hz), 44.2, 13.8 (d, *J* = 92.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.43; HRMS (ESI) calcd. for $C_{11}H_{17}NO_2P$ $[M + H]^+$: 226.0997, found 226.1000.



3l

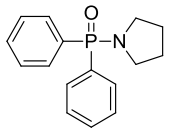
3l (49 mg, 72%, reaction time: 10 h) (R_f 0.4, EA) was prepared following the typical procedure in 0.20 mmol scale as wihte solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.4 Hz, 1 H), 7.98 (d, *J* = 8.1 Hz, 1 H), 7.93-7.73 (m, 4 H), 7.64-7.34 (m, 6 H), 3.69 (t, *J* = 4.5 Hz, 4H), 3.26-3.05 (m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 133.83 (d, *J* = 13.8 Hz), 133.78 133.6 (t, *J* = 11.3 Hz), 133.3 (d, *J* = 3.0 Hz), 132.3, 132.2 (d, *J* = 3.7 Hz), 131.9 (d, *J* = 3.7 Hz), 129.3 (d, *J* = 272.0 Hz), 128.8 (d, *J* = 1.7 Hz), 128.6 (d, *J* = 16.7 Hz), 126.9 (d, *J* = 95.1 Hz),

126.8 (d, *J* = 5.6 Hz), 126.3, 124.4 (d, *J* = 19.3 Hz), 67.2 (d, *J* = 5.9 Hz), 45.0; **^{31}P NMR** (121 MHz, $CDCl_3$) δ 32.40; HRMS (ESI) calcd. for $C_{20}H_{21}NO_2P$ $[M + H]^+$: 338.1310, found 338.1309.



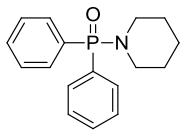
3m

3m (45 mg, 90%, reaction time: 9 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.67 (m, 2 H), 7.61-7.41 (m, 3 H), 6.95-6.70 (m, 0.1 H), 5.98-5.84 (m, 0.2 H), 5.84-5.67 (m, 0.9 H), 5.24-5.01 (m, 1.8 H), 3.67 (t, *J* = 4.6 Hz, 4 H), 3.18-2.99 (m, 4 H), 2.95-2.83 (m, 1.7 H), 1.94-1.88 (m, 0.3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.0 (d, *J* = 2.7 Hz), 131.8 (dd, *J* = 9.2, 4.7 Hz), 131.1 (d, *J* = 121.4 Hz), 128.6 (dd, *J* = 12.2, 4.8 Hz), 127.7 (d, *J* = 8.6 Hz), 120.24 (d, *J* = 12.4 Hz), 67.07 (d, *J* = 6.6 Hz), 44.43 (d, *J* = 4.5 Hz), 33.7 (d, *J* = 87.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.41; HRMS (ESI) calcd. for $C_{13}H_{19}NO_2P$ $[M + H]^+$: 252.1153, found 252.1154.



3n

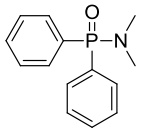
3n (44 mg, 82%, reaction time: 8 h) (R_f 0.4, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06-7.87 (m, 2 H), 7.87-7.73 (m, 2 H), 7.58-7.37 (m, 6 H), 3.87 (td, *J* = 8.4, 3.6 Hz, 1 H), 3.09-2.96 (m, 1 H), 2.96-2.83 (m, 1 H), 2.17 (bs, 1 H), 2.08-1.87 (m, 2 H), 1.87-1.62 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.0, 131.8 (d, *J* = 8.6 Hz), 131.5 (d, *J* = 112.6 Hz), 131.7 (dd, *J* = 12.0, 2.7 Hz), 131.1 (d, *J* = 8.7 Hz), 128.5 (dd, *J* = 11.2, 4.2 Hz), 56.9 (d, *J* = 84.4 Hz), 48.3 (d, *J* = 8.6 Hz), 26.6, 26.4 (d, *J* = 6.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.43; HRMS (ESI) calcd. for $C_{16}H_{19}NOP$ $[M + H]^+$: 272.1204, found 272.1208.



3o

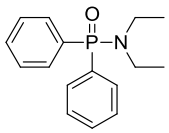
3o (52 mg, 91%, reaction time: 8 h) (R_f 0.4, EA) was prepared following the typical procedure in 0.20 mmol scale as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.79 (m, 4 H), 7.54-7.35 (m, 6 H), 3.00 (dd, *J* = 10.8, 6.4 Hz, 4 H), 1.72-1.45 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.2 (d, *J* = 10.0 Hz), 132.0 (d, *J* = 128.5 Hz), 131.5 (d, *J* = 2.7 Hz), 128.5 (d, *J* = 12.3 Hz), 45.7, 26.2 (d, *J* = 6.8 Hz), 24.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.98;

HRMS (ESI) calcd. for $C_{17}H_{21}NOP$ $[M + H]^+$: 286.1361, found 286.1357.



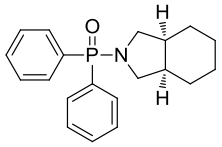
3p

3p (45 mg, 91%, reaction time: 9 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.76 (m, 4 H), 7.55-7.36 (m, 6 H), 2.66 (s, 3 H), 2.63 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.3 (d, *J* = 9.2 Hz), 131.8 (d, *J* = 128.4 Hz) 131.7 (d, *J* = 2.7 Hz), 128.5 (d, *J* = 12.3 Hz), 37.1 (d, *J* = 2.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.27; HRMS (ESI) calcd. for $C_{14}H_{17}NOP$ $[M + H]^+$: 246.1048, found 246.1044.

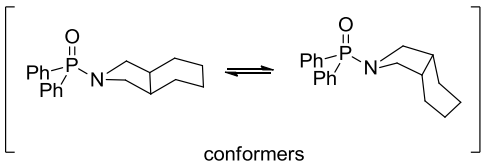


3q

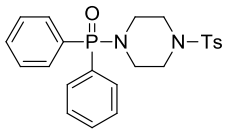
3q (37 mg, 67%, reaction time: 10 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.80 (m, 4 H), 7.60-7.37 (m, 6 H), 3.61-3.47 (m, 1 H), 2.89-2.72 (m, 1 H), 2.58-2.40 (m, 1 H), 1.85 (bs, 1 H), 1.31 (dd, *J* = 15.6, 6.8 Hz, 3 H), 1.01 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.8 (d, *J* = 183.7 Hz), 131.68 (dd, *J* = 40.6, 8.4 Hz), 131.67 (t, *J* = 2.5 Hz), 128.4 (dd, *J* = 15.6, 11.1 Hz), 52.6 (d, *J* = 83.6 Hz), 42.3 (d, *J* = 11.7 Hz), 15.3, 14.2 (d, *J* = 1.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.11; HRMS (ESI) calcd. for $C_{16}H_{21}NOP$ $[M + H]^+$: 274.1361, found 274.1361.



3s

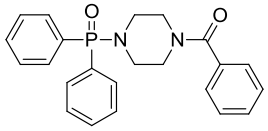


3s (56 mg, 86%, reaction time: 12 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as white solid. **Conformers were observed by NMR analysis. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11-7.92 (m, 2 H), 7.92-7.75 (m, 2 H), 7.62-7.34 (m, 6 H), 4.20 (t, *J* = 8.8 Hz, 0.1 H), 3.80 (dd, *J* = 6.8, 4.4 Hz, 0.9 H), 3.22-3.12 (m, 0.1 H),2.89-2.68 (m,1.9 H), 2.56-2.34 (m, 1 H), 2.15 (s, 1 H), 2.08-1.92 (m, 1 H), 1.69-1.11 (m, 8 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.1 (d, *J* = 92.8 Hz), 131.9, 131.7 (dd, *J* = 99.4, 8.4 Hz), 131.6 (dd, *J* = 12.4, 2.6 Hz), 130.9, 128.4 (dd, *J* = 11.0, 8.8 Hz), 59.9, 59.0, 51.5 (d, *J* = 4.7 Hz), 39.0 (d, *J* = 3.3 Hz), 27.3 (d, *J* = 5.3 Hz), 26.0, 23.4, 22.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.63; HRMS (ESI) calcd. for $C_{20}H_{25}NOP$ $[M + H]^+$: 326.1674, found 326.1677.



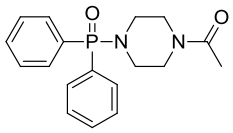
3t

3t (42 mg, 48%, reaction time: 12 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.70 (m, 4H), 7.65-7.4 (m, 7H), 7.28 (d, *J* = 8.0 Hz, 3H), 3.81-3.68 (m, 1 H), 3.64 (d, *J* = 12.0 Hz, 2 H), 3.51 (bs, 1 H), 3.09 (d, *J* = 13.2 Hz, 1 H), 2.99-2.85 (m, 1 H), 2.52-2.35 (m, 4 H), 2.32-2.18 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.9, 132.5 (dd, *J* = 21.8, 2.7 Hz), 132.3, 131.4 (d, *J* = 11.1 Hz), 131.2 (d, *J* = 9.1 Hz), 129.0 (d, *J* = 10.6 Hz), 128.8 (d, *J* = 11.7 Hz), 128.7 (d, *J* = 209.5 Hz), 53.8 (d, *J* = 80.4 Hz), 46.4, 45.6 (dd, *J* = 34.5, 6.3 Hz), 29.7, 21.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.88; HRMS (ESI) calcd. for $C_{23}H_{26}N_2O_3PS$ $[M + H]^+$: 441.1402, found 441.1401.



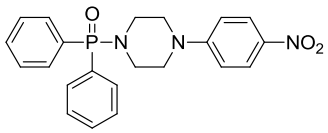
3u

3u (64 mg, 82%, reaction time: 8 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.76 (m, 4 H), 7.60-7.41 (m, 6 H), 7.41-7.28 (m, 5 H), 3.61 (bd, *J* = 12.8 Hz, 4 H), 3.08 (bs, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 135.4, 132.2 (d, *J* = 9.2 Hz), 132.1 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 128.1 Hz), 129.8, 128.7 (d, *J* = 12.4 Hz), 128.5, 126.9, 45.0 (m); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.66; HRMS (ESI) calcd. for $C_{23}H_{24}N_2O_2P$ $[M + H]^+$: 391.1575, found 391.1576.



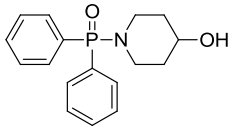
3v

3v (49 mg, 74%, reaction time: 10 h) (R_f 0.3, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.77 (m, 4 H), 7.58-7.40 (m, 6 H), 3.68-3.56 (m, 2 H), 3.53-3.39 (m, 2 H), 3.16-3.06 (m, 2 H), 3.06-2.97 (m, 2 H),2.06 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.1, 132.2 (d, *J* = 9.2 Hz), 132.1 (d, *J* = 2.7 Hz), 130.8 (d, *J* = 170.8 Hz), 128.8 (d, *J* = 12.5 Hz), 46.9 (d, *J* = 6.3 Hz), 44.9 (d, *J* = 5.9 Hz), 41.9 (d, *J* = 6.1 Hz), 21.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.70; HRMS (ESI) calcd. for $C_{18}H_{22}N_2O_2P$ $[M + H]^+$: 329.1419, found 329.1414.



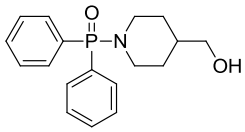
3w

3w (52 mg, 64%, reaction time: 10 h) (R_f 0.2, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18-8.07 (m, 2 H), 7.97-7.84 (m, 4 H), 7.62-7.44 (m, 6 H), 6.87-6.75 (m, 2 H), 3.47-3.38 (m, 4 H), 3.31-3.20 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 139.0, 132.3 (d, *J* = 9.2 Hz), 132.2 (d, *J* = 2.7 Hz), 130.8 (d, *J* = 128.3 Hz), 128.8 (d, *J* = 12.5 Hz), 125.9, 113.10, 47.8 (d, *J* = 6.5 Hz), 44.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.53; HRMS (ESI) calcd. for $C_{22}H_{23}N_3O_3P$ $[M + H]^+$: 408.1477, found 408.1477.



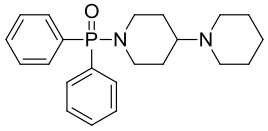
3x

3x (40 mg, 67%, reaction time: 8 h) (R_f 0.1, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.75 (m, 4 H), 7.58-7.35 (m, 6 H), 3.93-3.72 (m, 1 H), 3.42-3.18 (m, 2 H), 2.96-2.74 (m, 2 H), 2.54 (bs, 1 H), 1.97-1.79 (m, 2 H), 1.66-1.46 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.2 (d, *J* = 9.2 Hz), 131.8 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 128.5 Hz), 128.6 (d, *J* = 12.4 Hz), 67.7, 42.8, 34.9 (d, *J* = 6.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.52; HRMS (ESI) calcd. for $C_{17}H_{21}NO_2P$ $[M + H]^+$: 302.1310, found 302.1310.



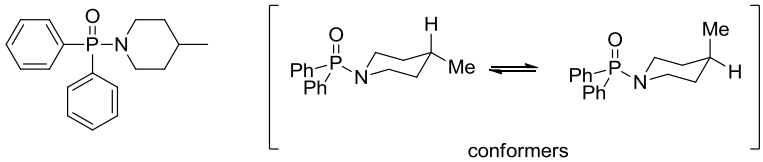
3y

3y (56 mg, 89%, reaction time: 10 h) (R_f 0.2, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.67 (m, 4 H), 7.57-7.34 (m, 6 H), 3.50 (d, *J* = 5.6 Hz, 2 H), 3.37-3.20 (m, 2 H), 2.91 (bs, 1 H), 2.84-2.68 (m, 2 H), 1.76-1.57 (m, 2 H), 1.37-1.15 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.2 (d, *J* = 9.2 Hz), 131.7 (d, *J* = 2.7 Hz), 130.9, 128.5 (d, *J* = 12.3 Hz), 67.3, 44.9, 38.7, 29.2 (d, *J* = 6.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.50; HRMS (ESI) calcd. for $C_{18}H_{23}NO_2P$ $[M + H]^+$: 316.1466, found 316.1468.



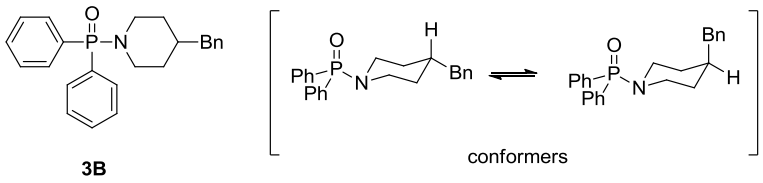
3z

3z (39 mg, 53%, reaction time: 8 h) (R_f 0.5, dichloromethane/methanol 20/1 + 2% triethylamine) was prepared following the typical procedure in 0.20 mmol scale as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-7.74 (m, 4 H), 7.58-7.32 (m, 6 H), 3.40-3.24 (m, 2 H), 2.83-2.66 (m, 2 H), 2.48 (t, *J* = 5.0 Hz, 4 H), 2.42-2.26 (m, 1 H), 1.77 (bd, *J* = 12.0 Hz, 2 H), 1.65-1.45 (m, 6 H), 1.45-1.31 (m, 2 H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 132.1 (d, *J* = 9.0 Hz), 131.7 (d, *J* = 128.6 Hz), 131.6 (d, *J* = 2.7 Hz), 128.46 (d, *J* = 12.3 Hz), 62.4, 50.1, 44.7, 28.7 (d, *J* = 7.3 Hz), 26.2, 24.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.92; HRMS (ESI) calcd. for $C_{22}H_{30}N_2OP$ $[M + H]^+$: 369.2096, found 369.2091.



3A

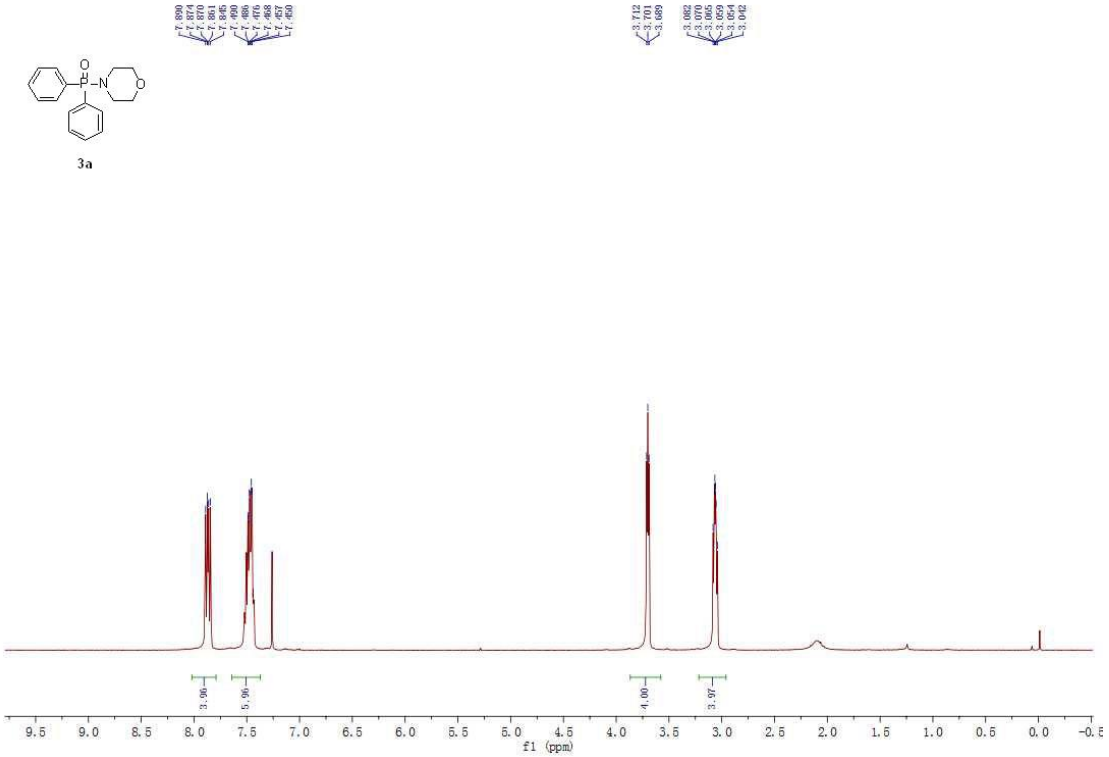
3A (40 mg, 67%, reaction time: 10 h) (R_f 0.2, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **Conformers were observed by NMR analysis.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.72 (m, 4 H), 7.60-7.37 (m, 6 H), 3.77-3.67 (m, 0.7 H), 3.49-3.40 (m, 0.3 H), 3.17-3.09 (m, 0.3 H), 3.07-2.96 (m, 0.7 H), 2.88-2.77 (m, 0.7 H), 2.60 (td, *J* = 12.4, 2.4 Hz, 0.3 H), 2.25-2.09 (m, 1 H), 1.90-1.79 (m, 1 H), 1.79-1.41 (m, 3 H), 1.34-1.23 (m, 1 H), 0.99 (d, *J* = 6.8 Hz, 2 H), 0.87 (d, *J* = 6.4 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.9 (d, *J* = 3.2 Hz), 131.80 (d, *J* = 91.8 Hz), 131.79 (d, *J* = 1.8 Hz), 131.7 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 8.5 Hz), 131.4 (d, *J* = 8.8 Hz), 131.2 (d, *J* = 8.5 Hz), 128.6 (d, *J* = 2.4 Hz), 128.5 (d, *J* = 1.7 Hz), 128.4, 56.8, 56.0, 51.5, 50.7, 47.5 (d, *J* = 14.3 Hz), 41.9 (d, *J* = 10.0 Hz), 34.9, 33.5, 32.4, 31.6 (d, *J* = 12.5 Hz), 31.5, 25.8 (d, *J* = 8.5 Hz), 22.5, 18.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.73, 31.19; HRMS (ESI) calcd. for $C_{18}H_{23}NOP$ $[M + H]^+$: 300.1517, found 300.1515.



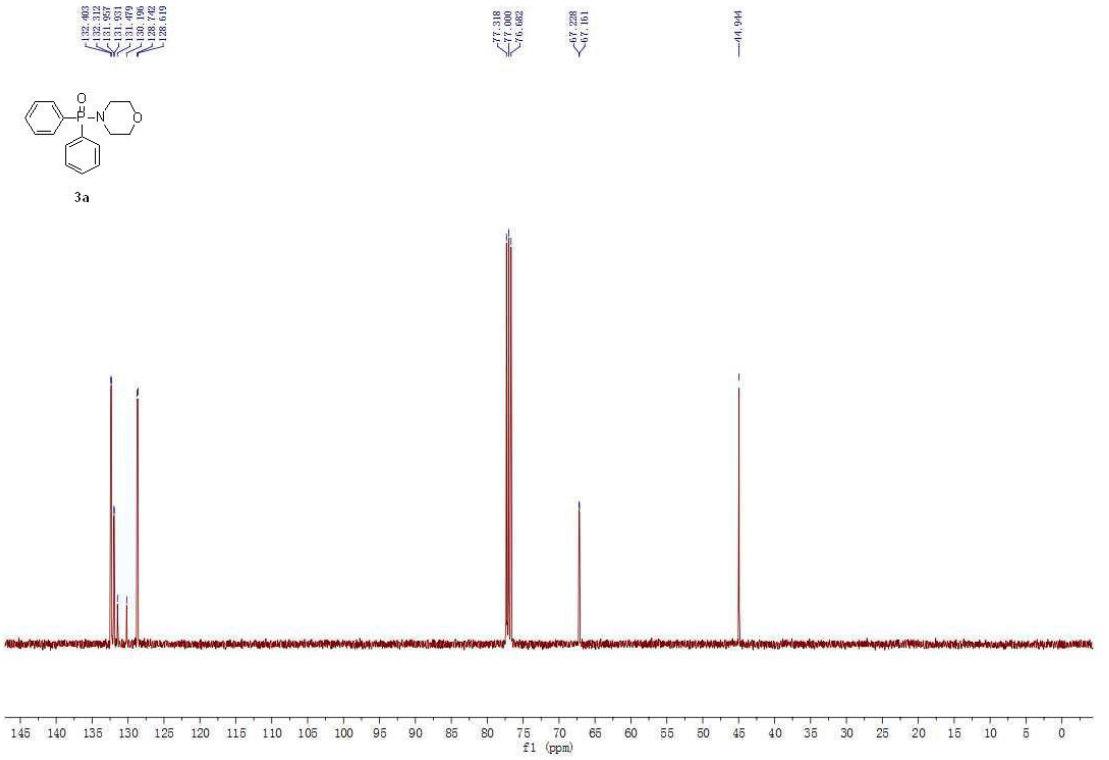
3B

3B (41 mg, 55%, reaction time: 7 h) (R_f 0.2, EA) was prepared following the typical procedure in 0.20 mmol scale as yellow oil. **Conformers were observed by NMR analysis.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05-7.83 (m, 2 H), 7.83-7.65 (m, 2 H), 7.59-7.45 (m, 4 H), 7.45-7.35 (m, 1 H), 7.33-7.00 (m, 6 H), 3.78-3.70 (m, 0.7 H), 3.48-3.40 (m, 0.3 H), 3.16-3.04 (m, 1 H), 2.97-2.84 (m, 1 H), 2.76-2.59 (m, 1 H), 2.58-2.47 (m, 1 H), 2.44-2.26 (m, 1 H), 1.87-1.74 (m, 2 H), 1.74-1.61 (m, 1 H), 1.61-1.48 (m, 1 H), 1.44-1.25 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.4, 131.9 (d, *J* = 2.6 Hz), 131.7 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 8.5 Hz), 131.2 (d, *J* = 8.7 Hz), 129.0 128.59 (dd, *J* = 12.3, 11.4 Hz), 128.58 (d, *J* = 89.2 Hz), 128.2, 51.9, 51.1, 42.2 (d, *J* = 9.4 Hz), 39.2, 33.2 (d, *J* = 8.1 Hz), 30.4, 29.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.88, 31.36; HRMS (ESI) calcd. for $C_{24}H_{27}NOP$ $[M + H]^+$: 376.1830, found 376.1832.

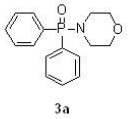
^{1}H NMR of **3a**



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

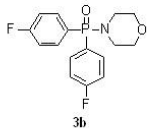


^{31}P NMR of **3a**



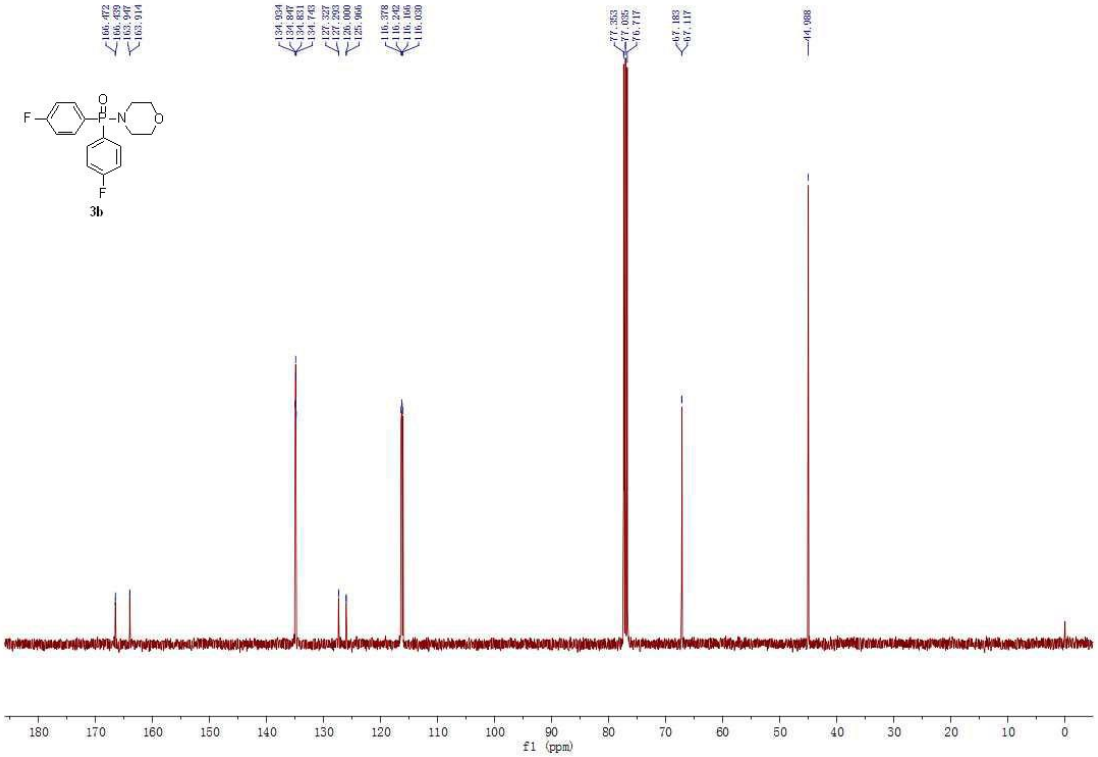
3a

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

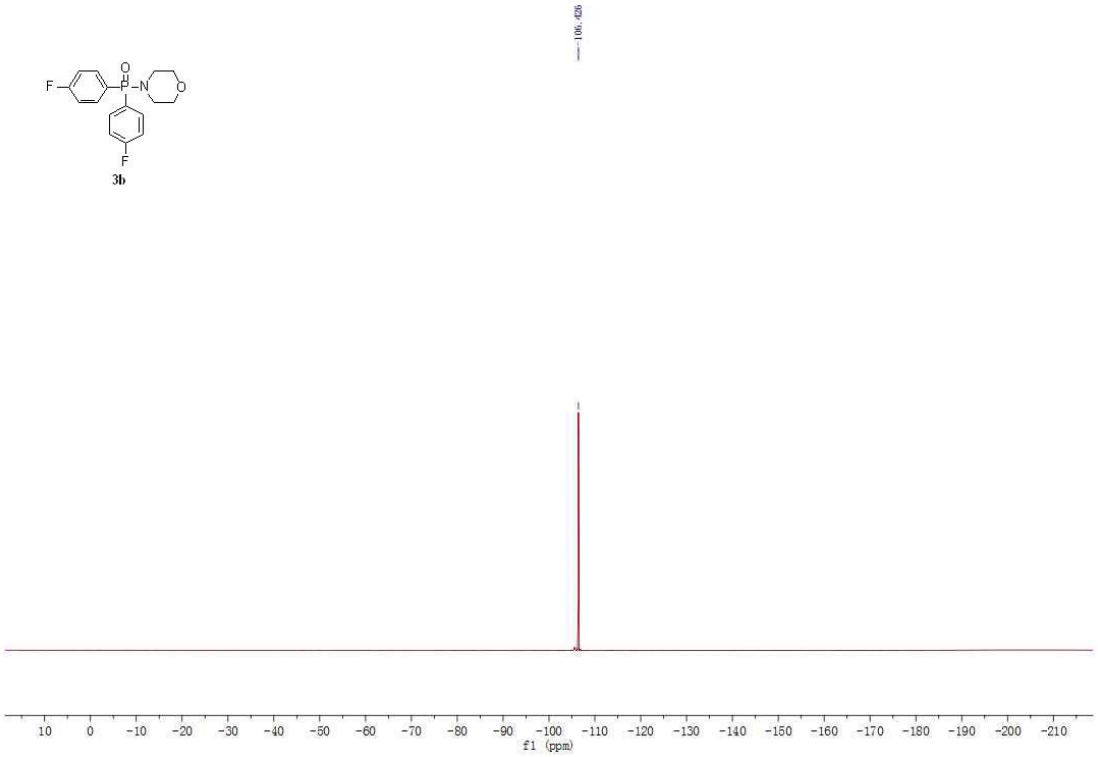


3b

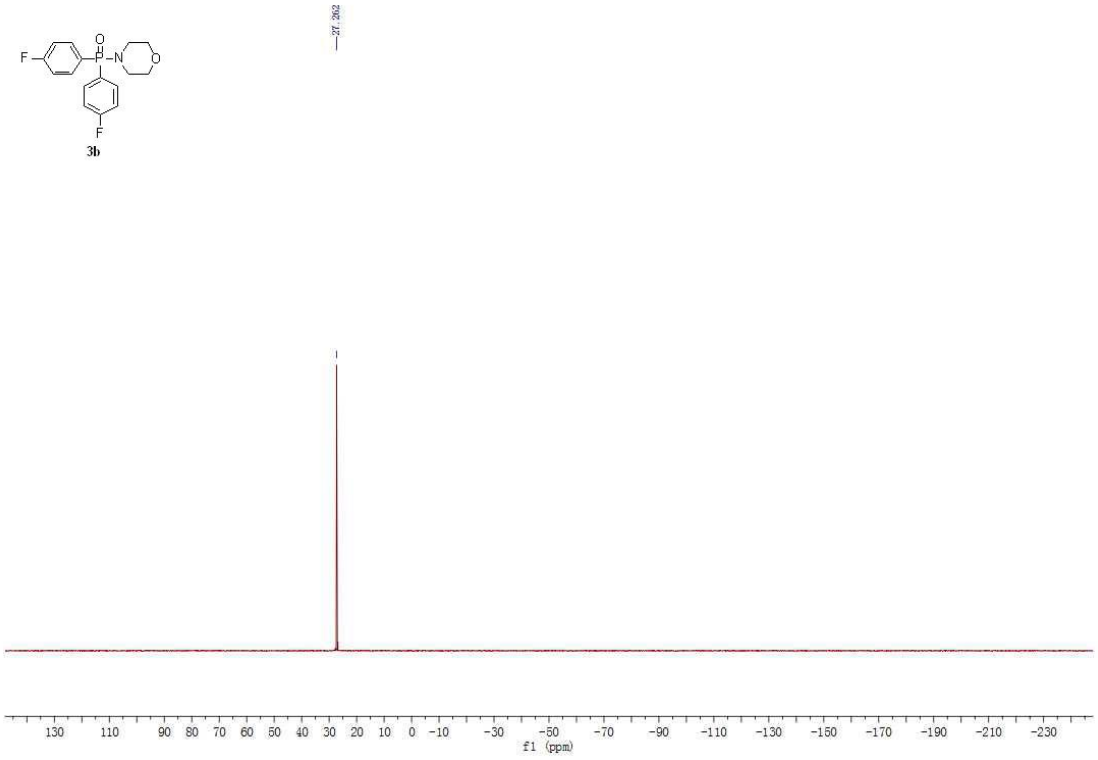
^{13}C NMR of **3b**



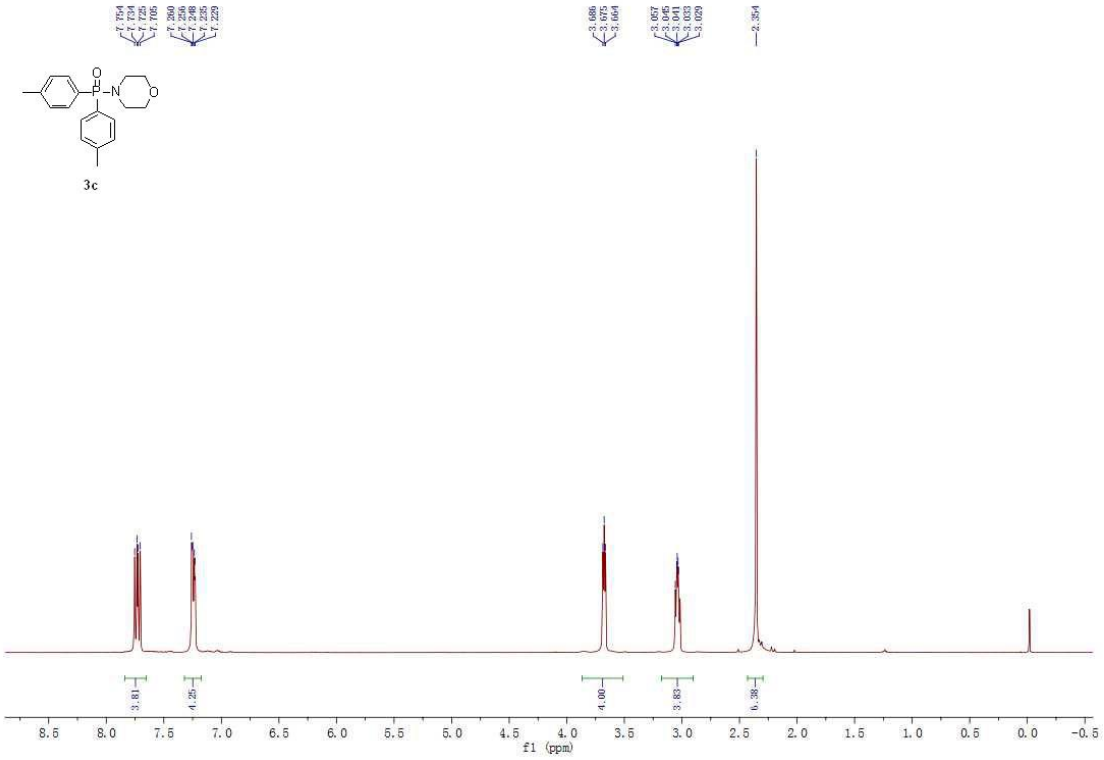
^{19}F NMR of **3b**



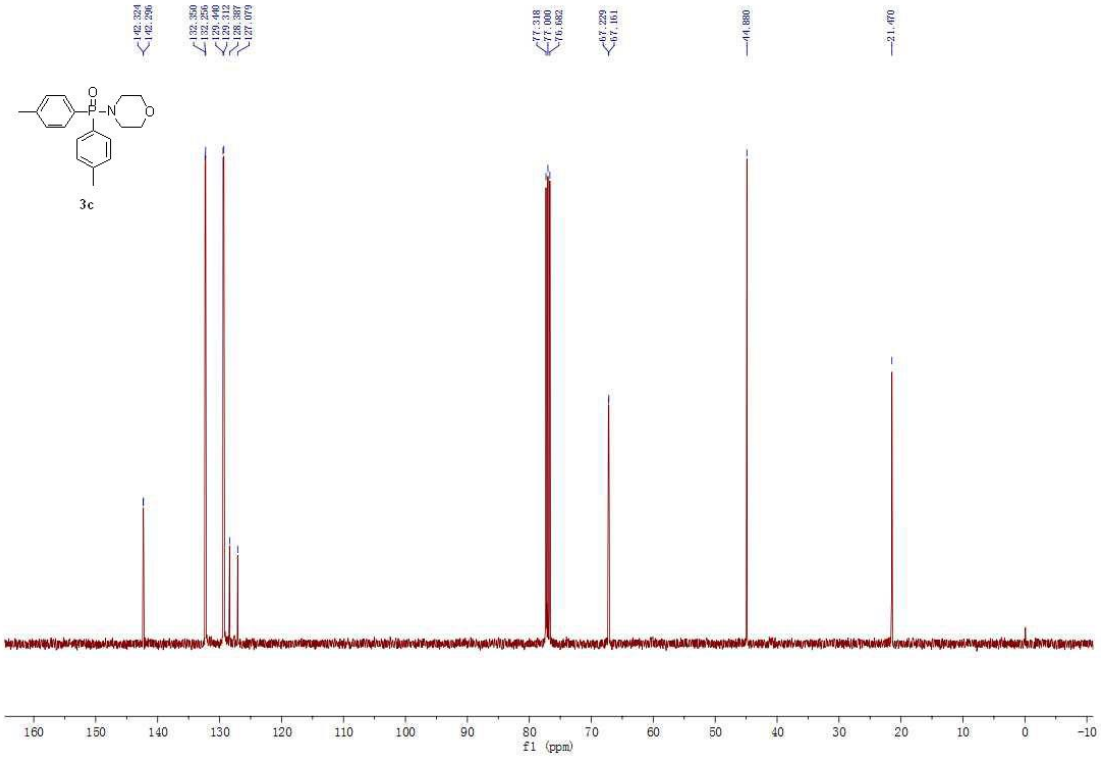
^{31}P NMR of **3b**



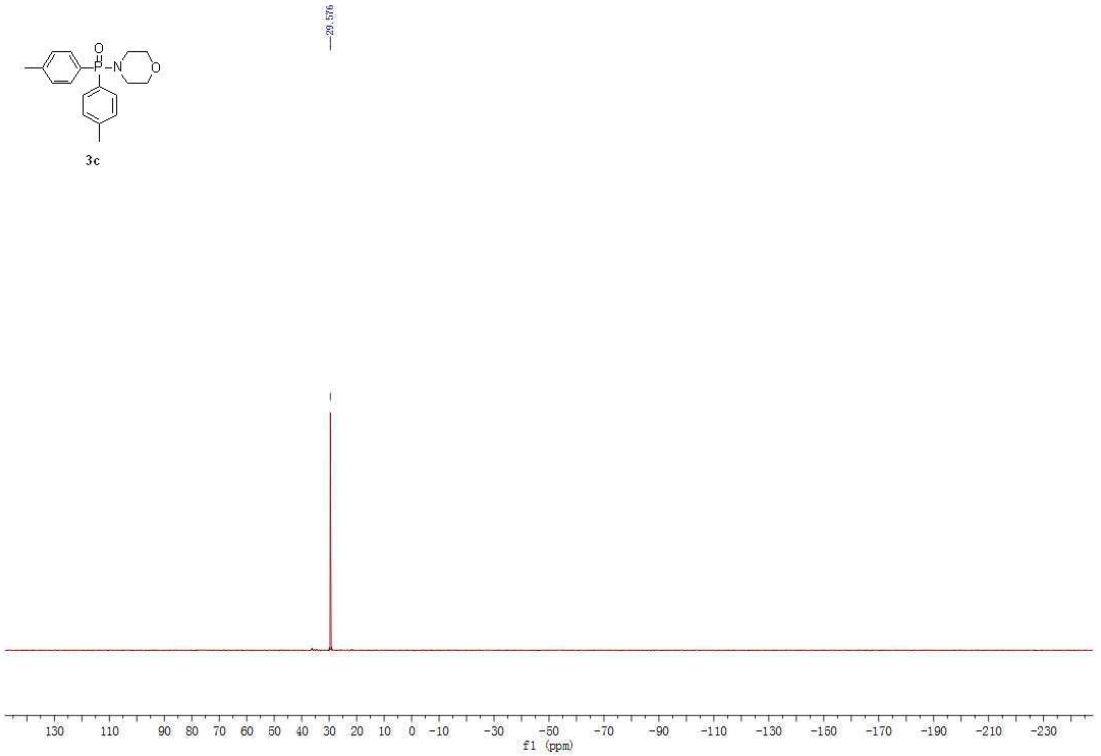
^{1}H NMR of **3c**



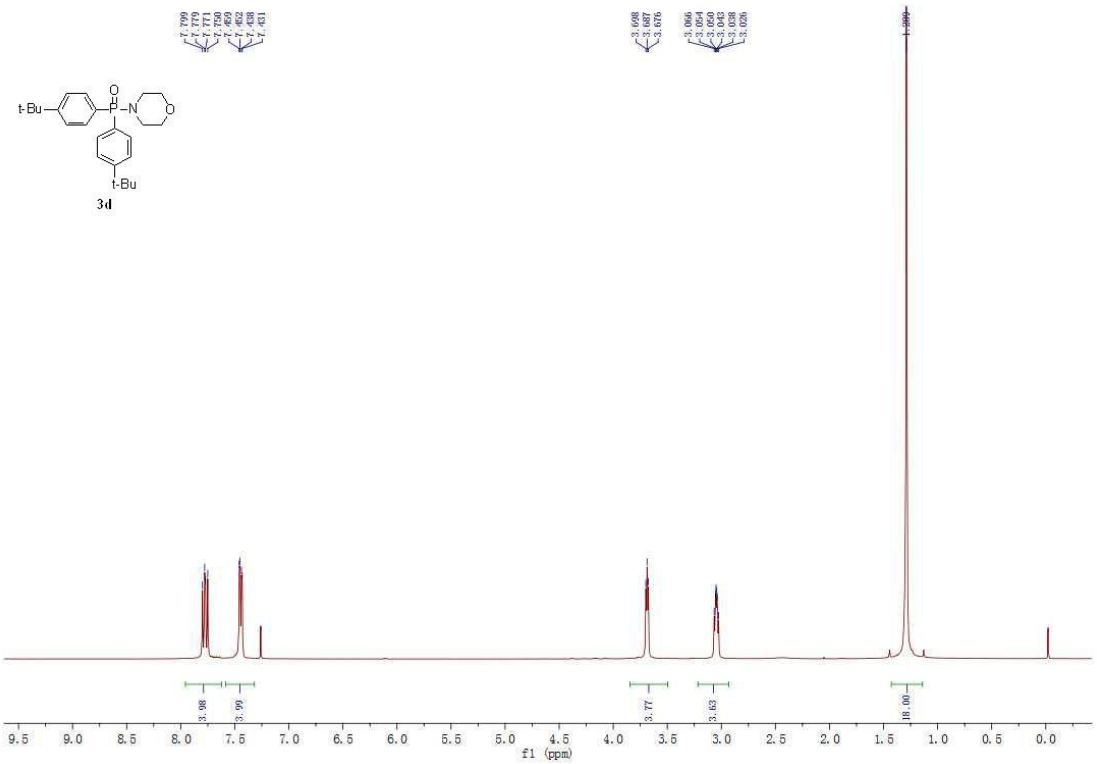
^{13}C NMR of **3c**



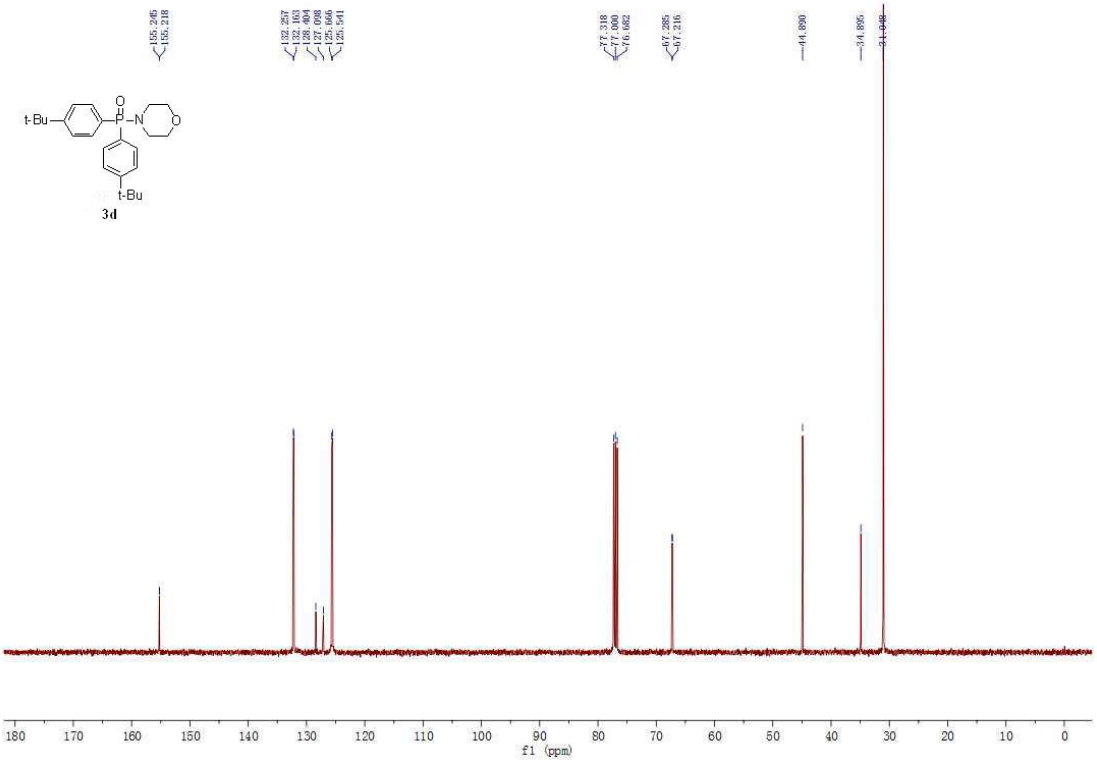
^{31}P NMR of **3c**



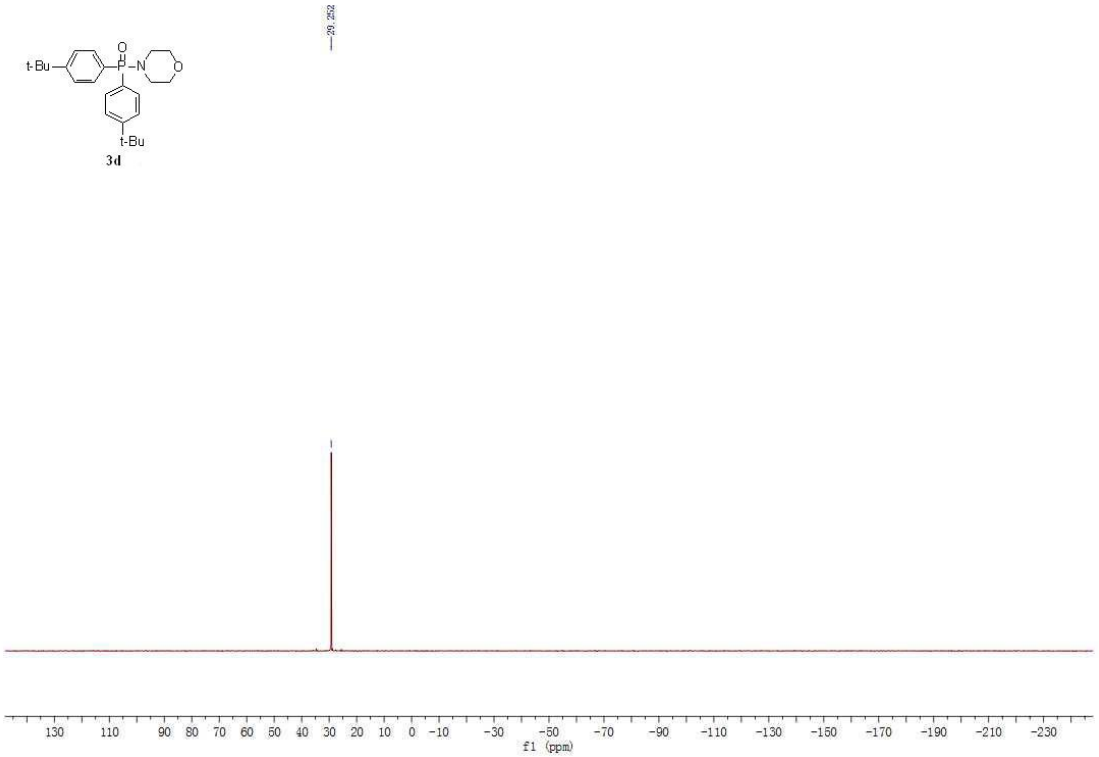
^{1}H NMR of **3d**



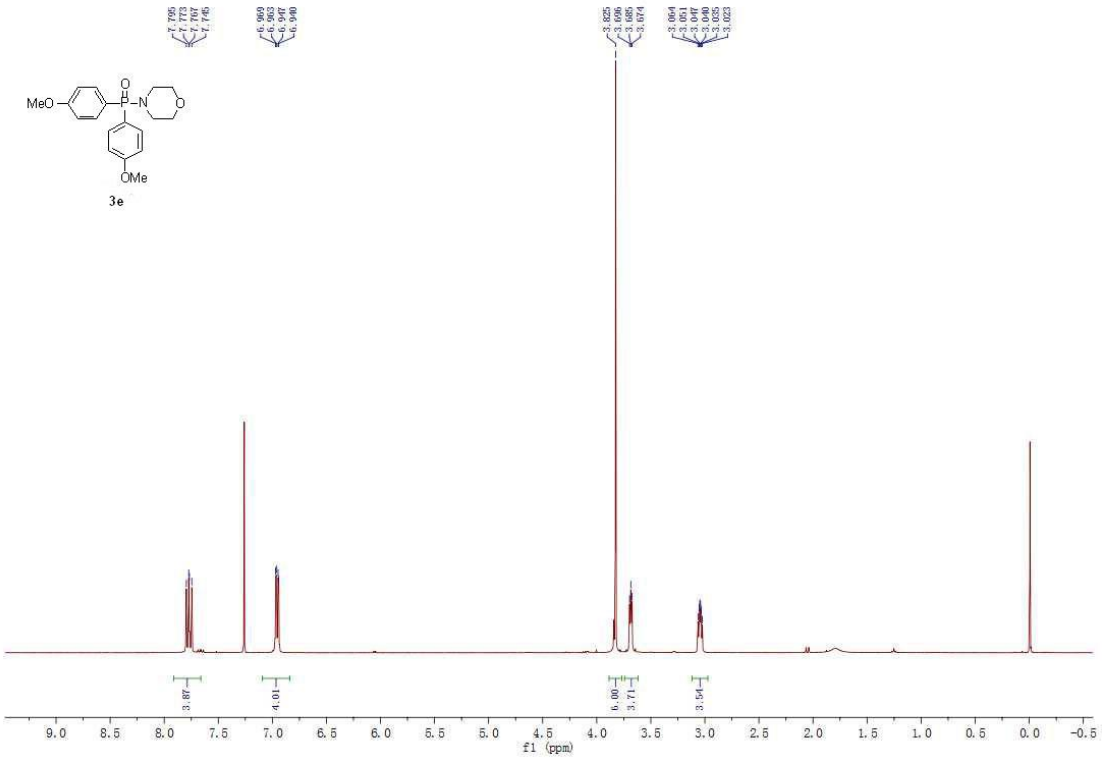
^{13}C NMR of **3d**



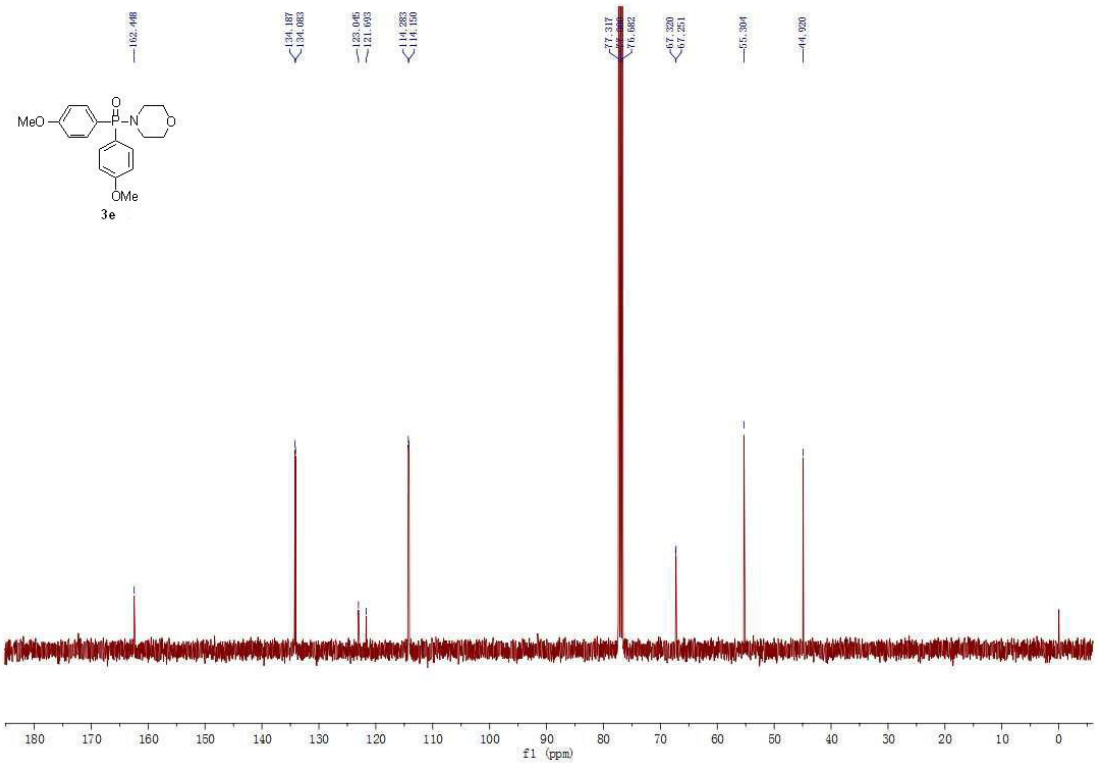
^{31}P NMR of **3d**



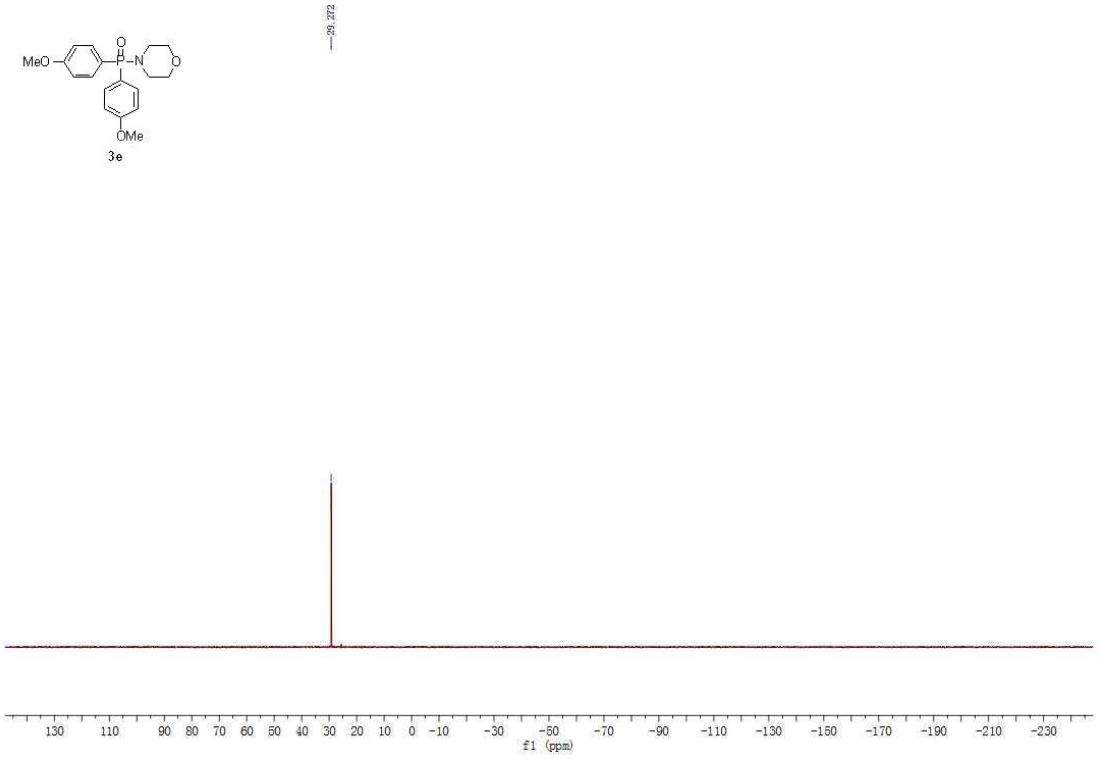
^{1}H NMR of **3e**



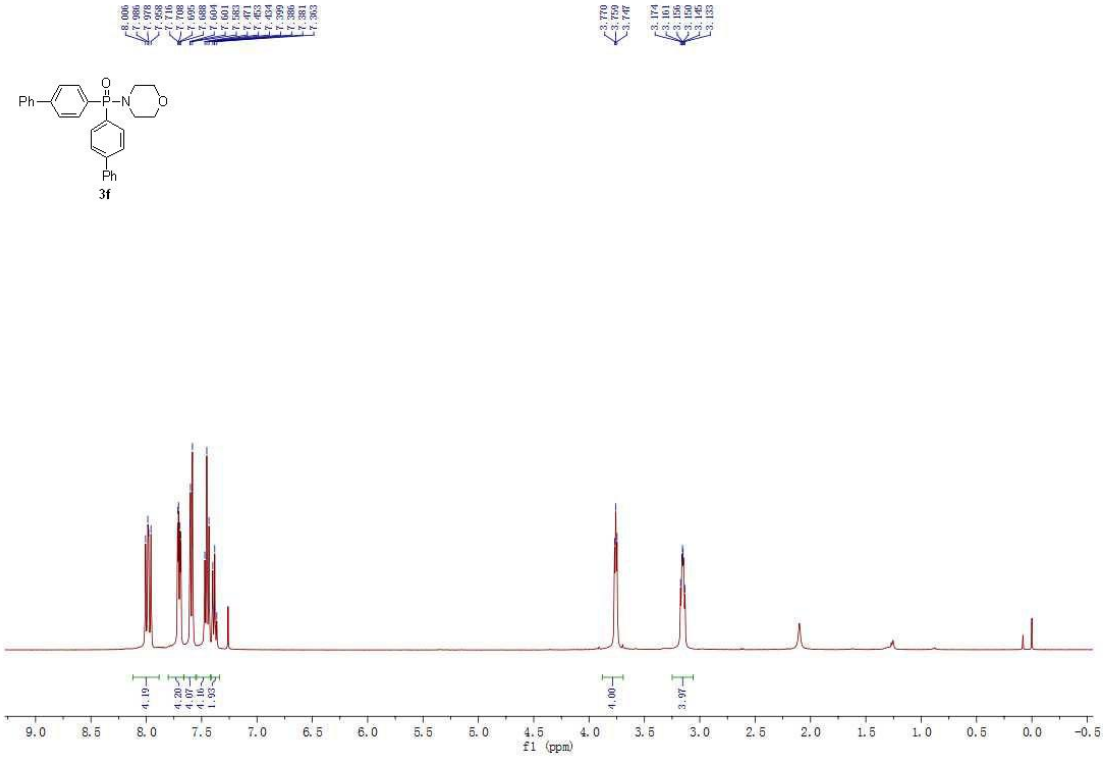
^{13}C NMR of **3e**



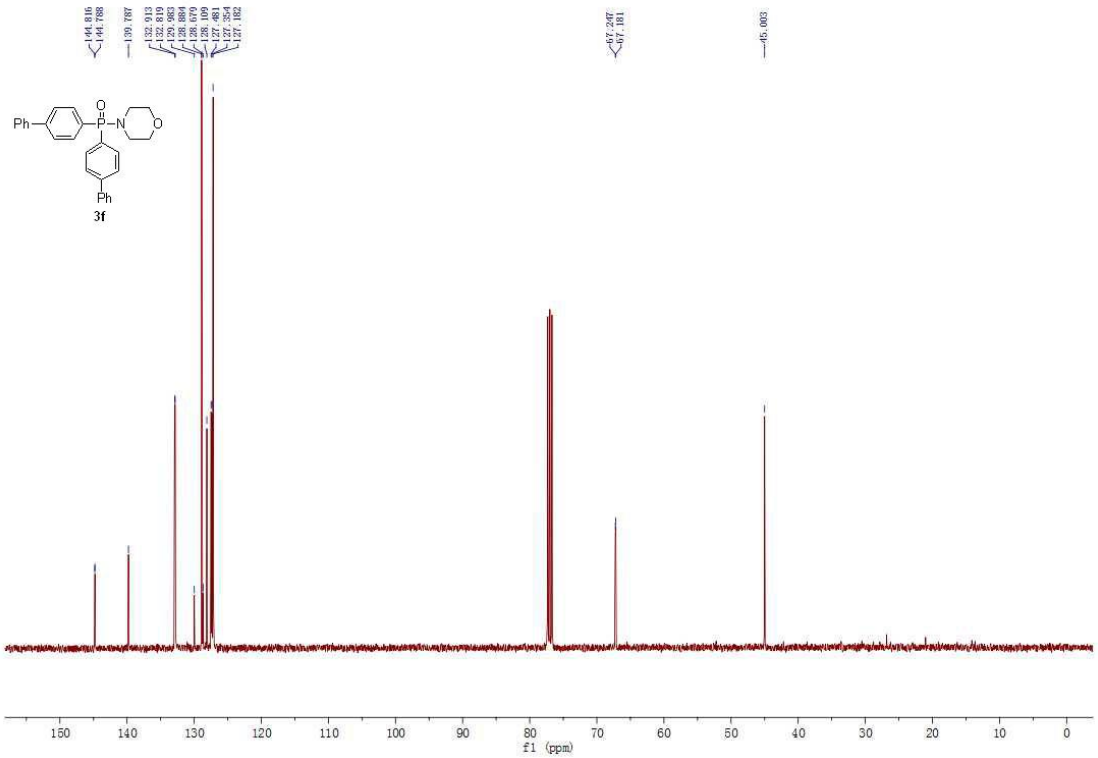
^{31}P NMR of **3e**



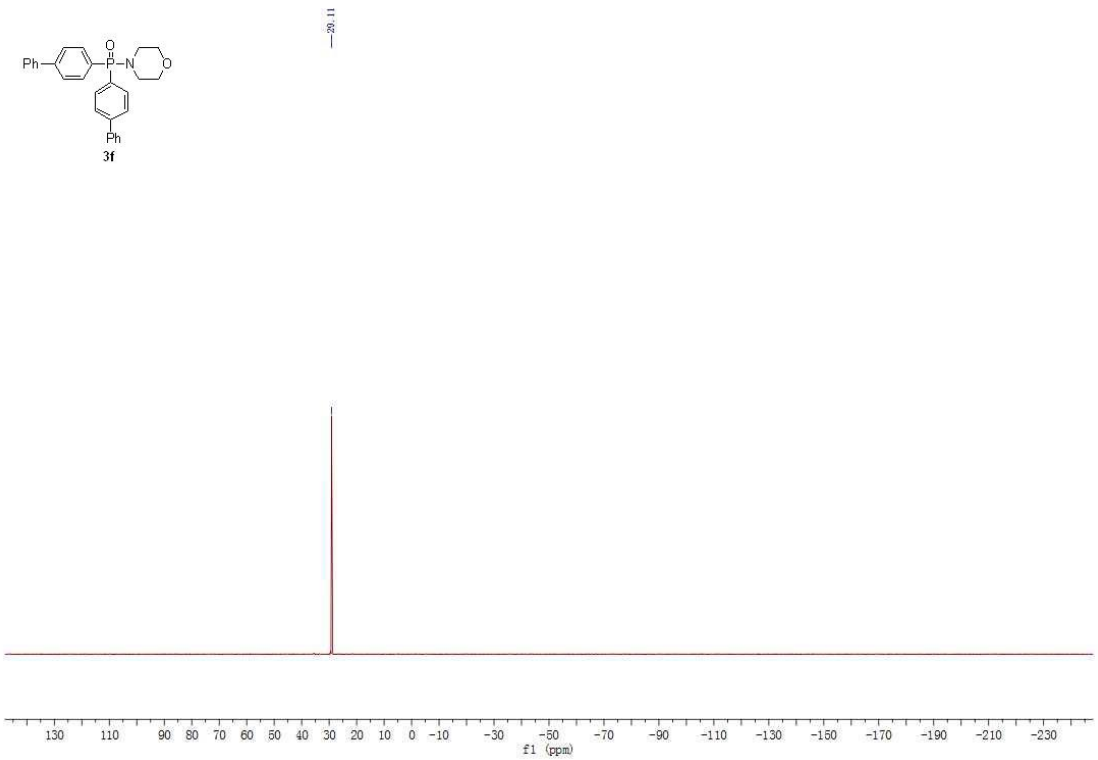
^{1}H NMR of **3f**



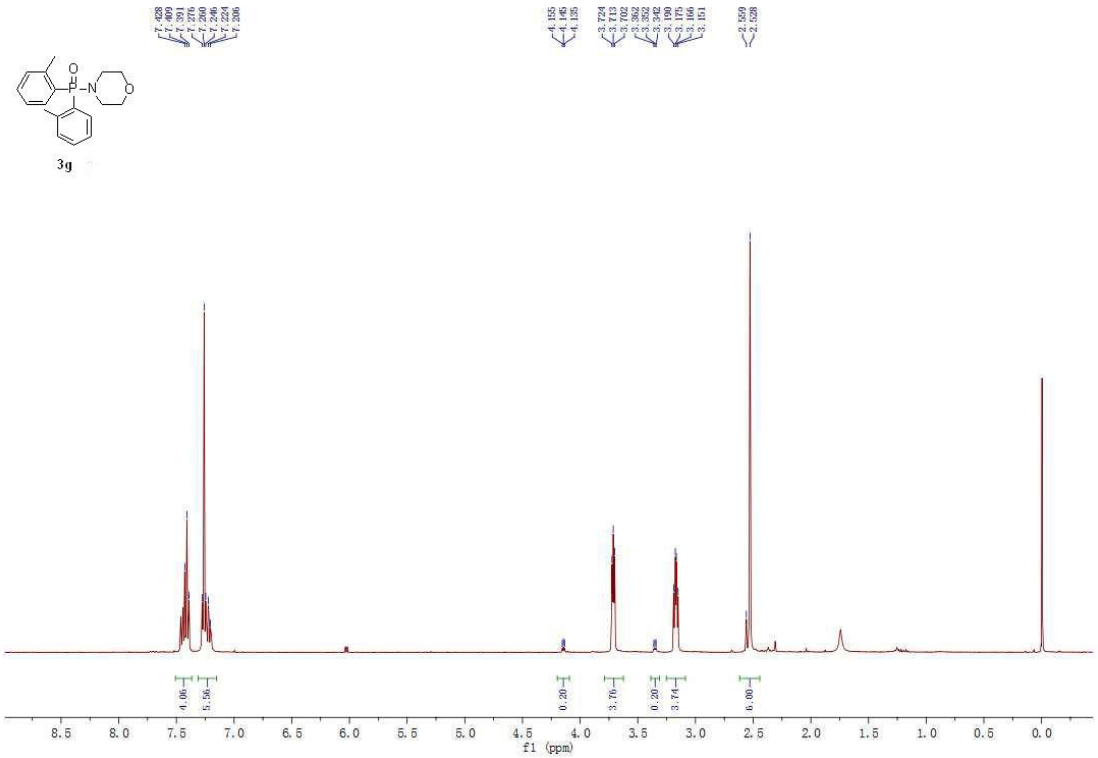
^{13}C NMR of **3f**



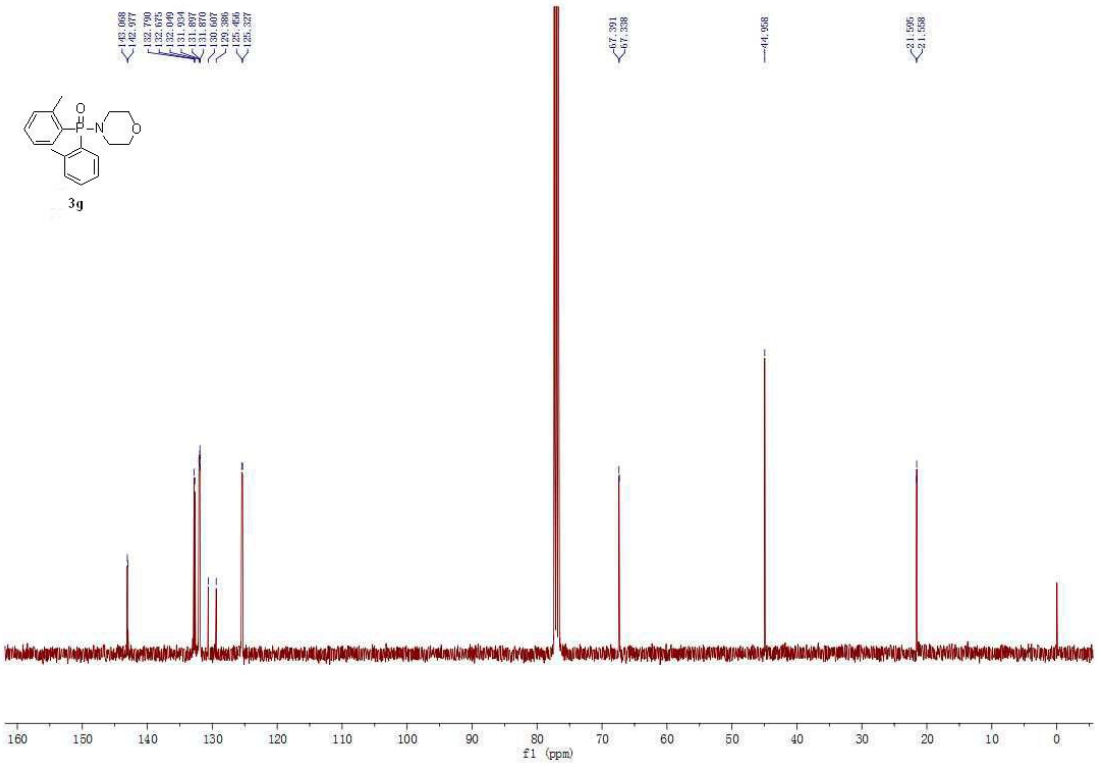
^{31}P NMR of **3f**



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



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



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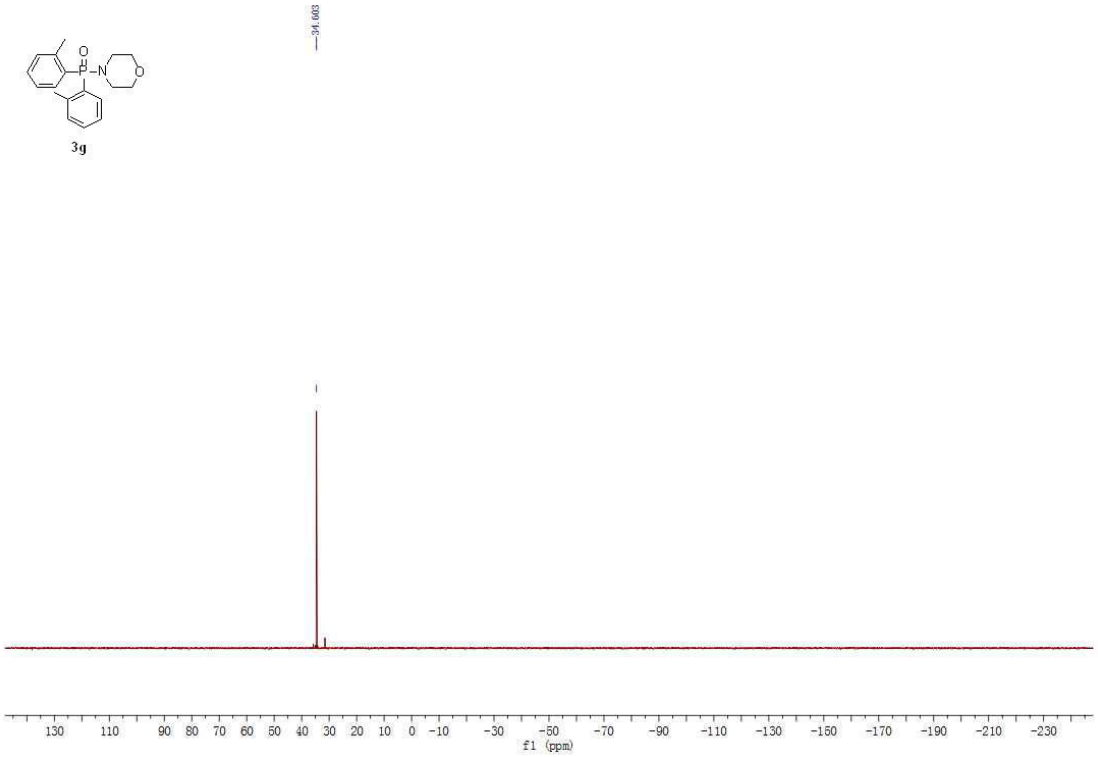
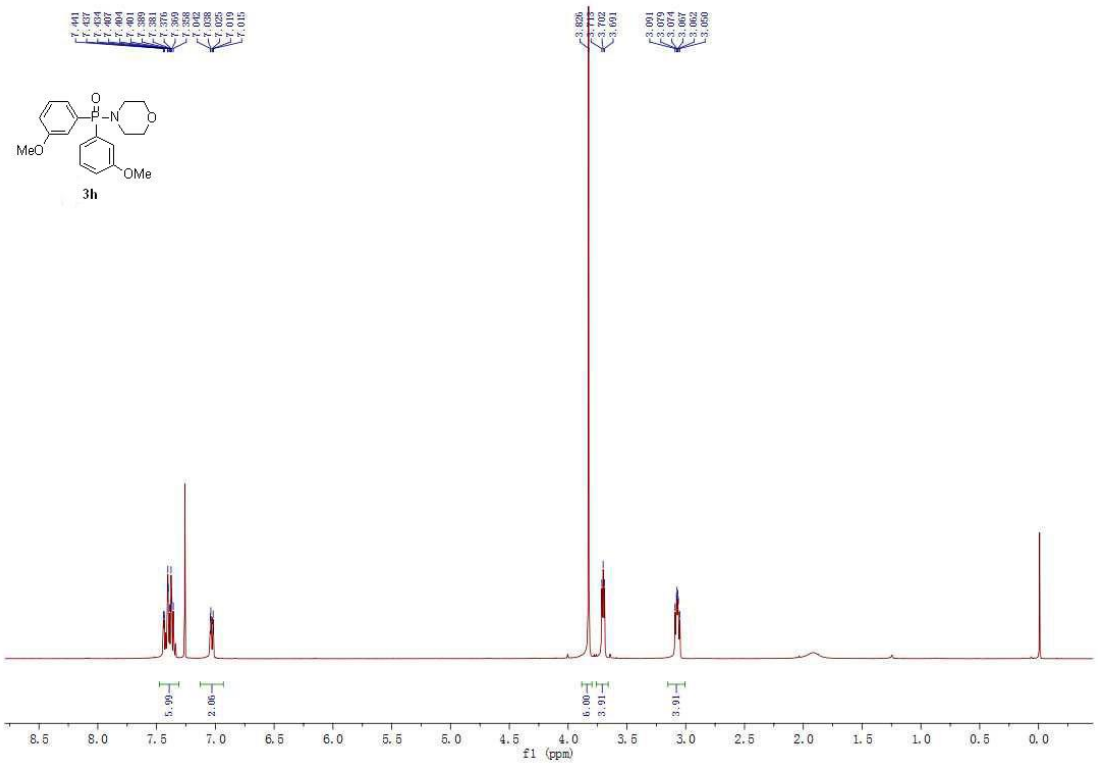
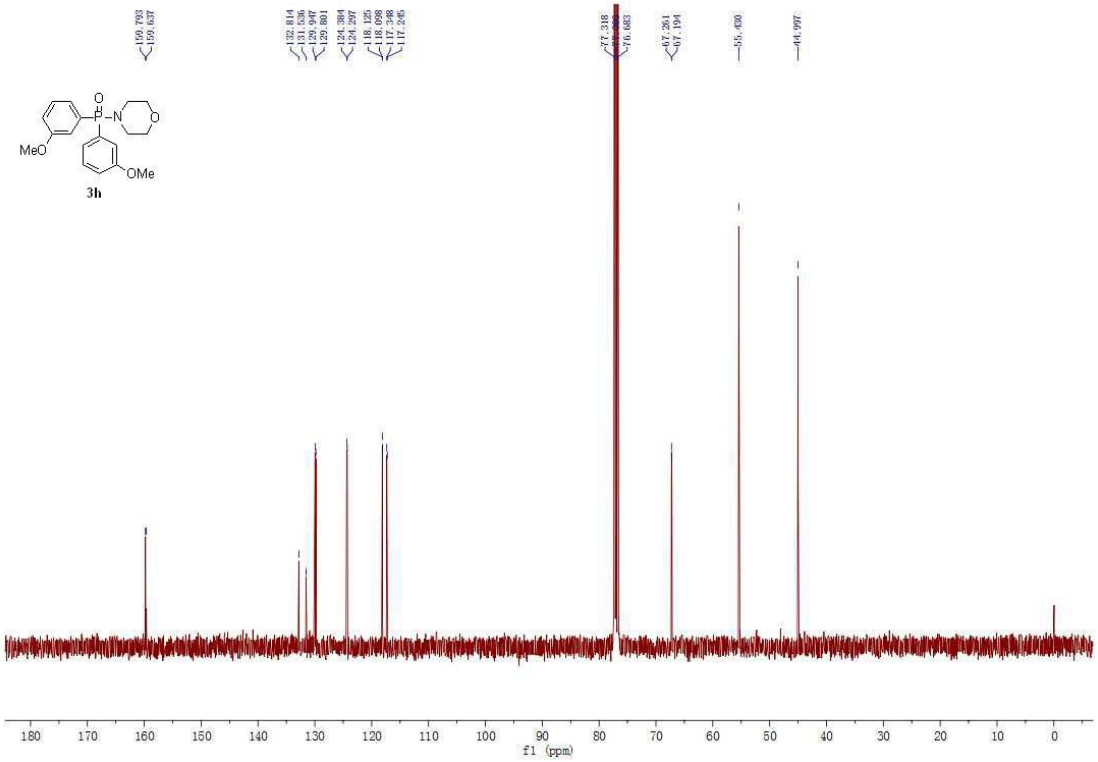


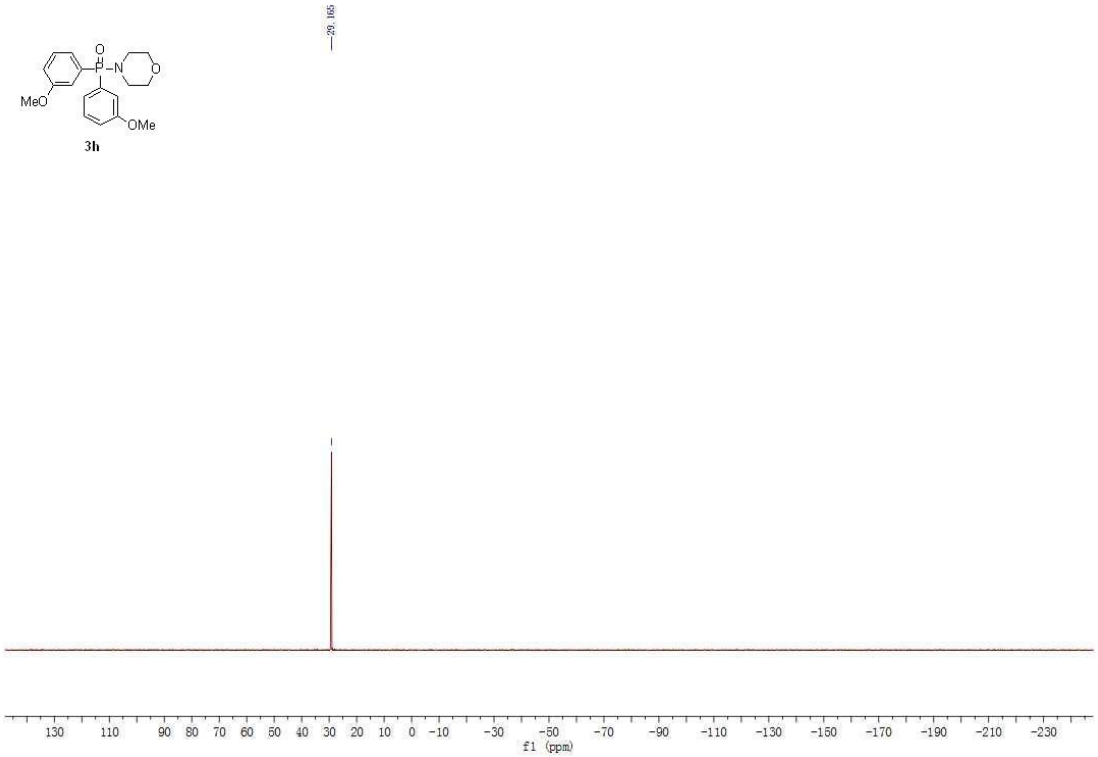
^{1}H NMR of **3h**



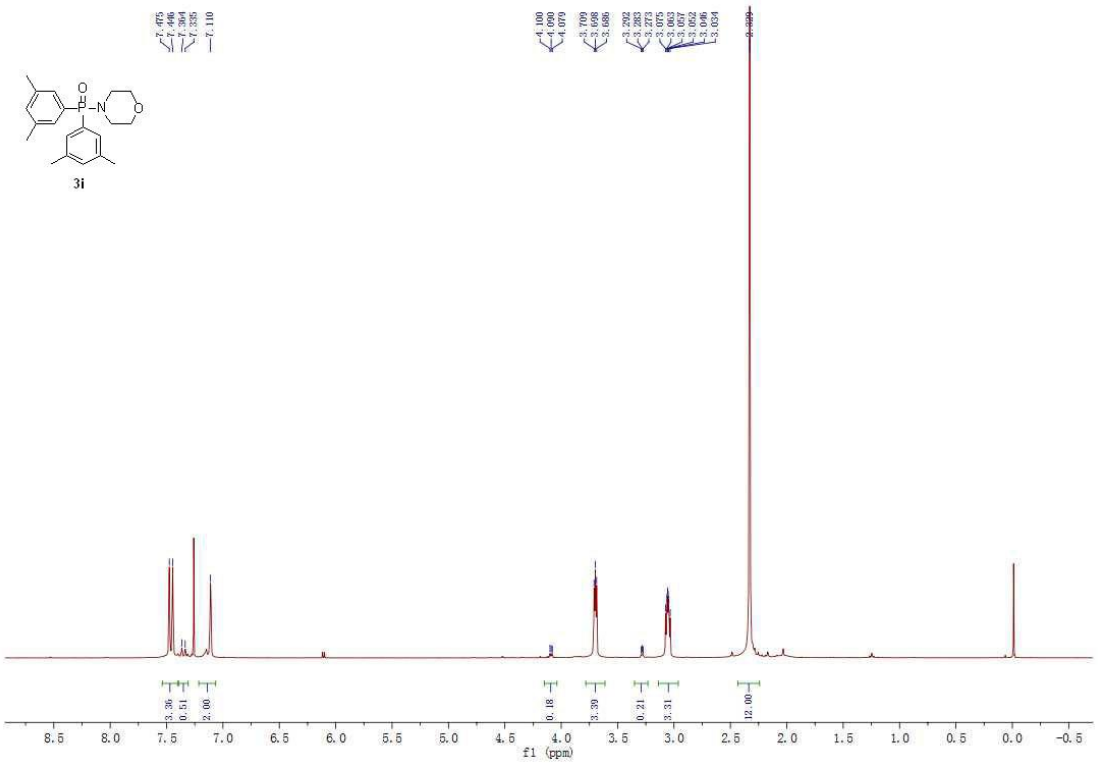
^{13}C NMR of **3h**



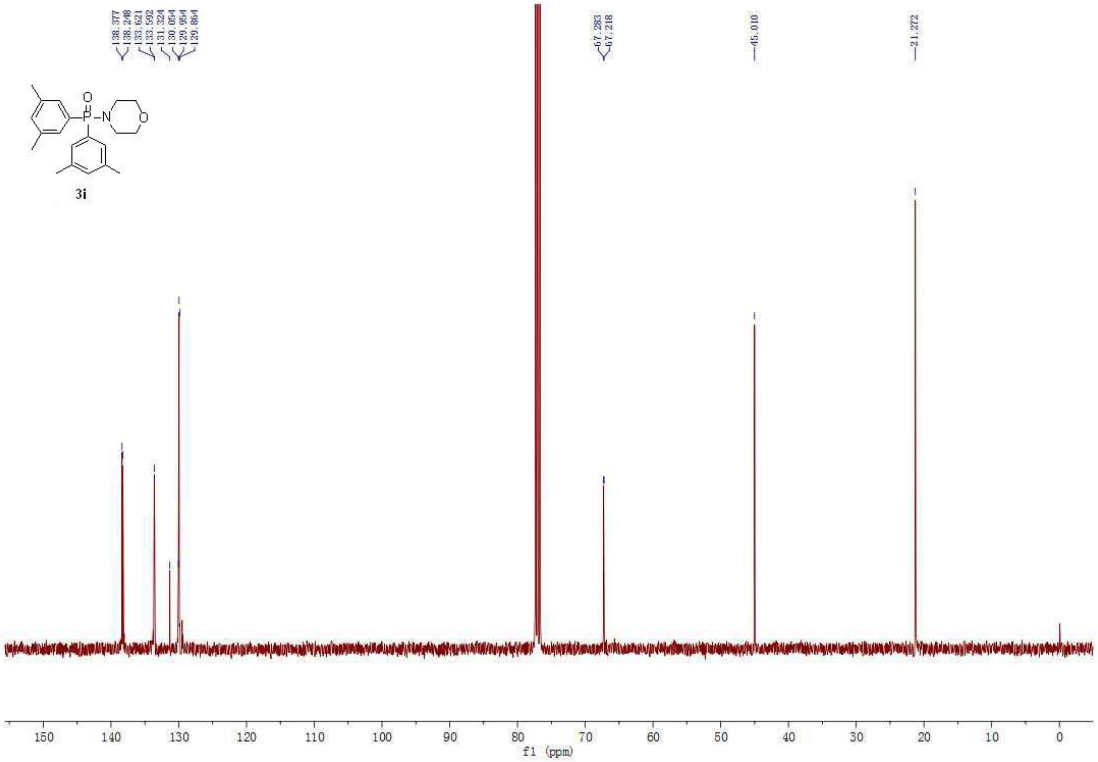
^{31}P NMR of **3h**



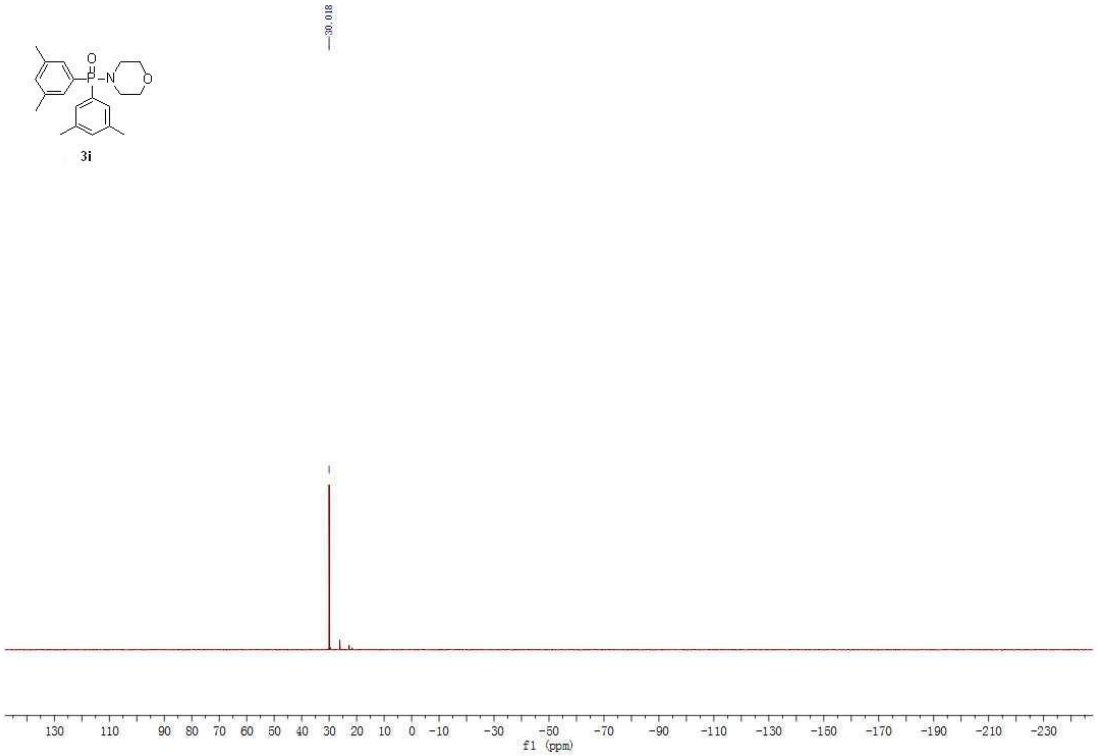
^{1}H NMR of **3i**



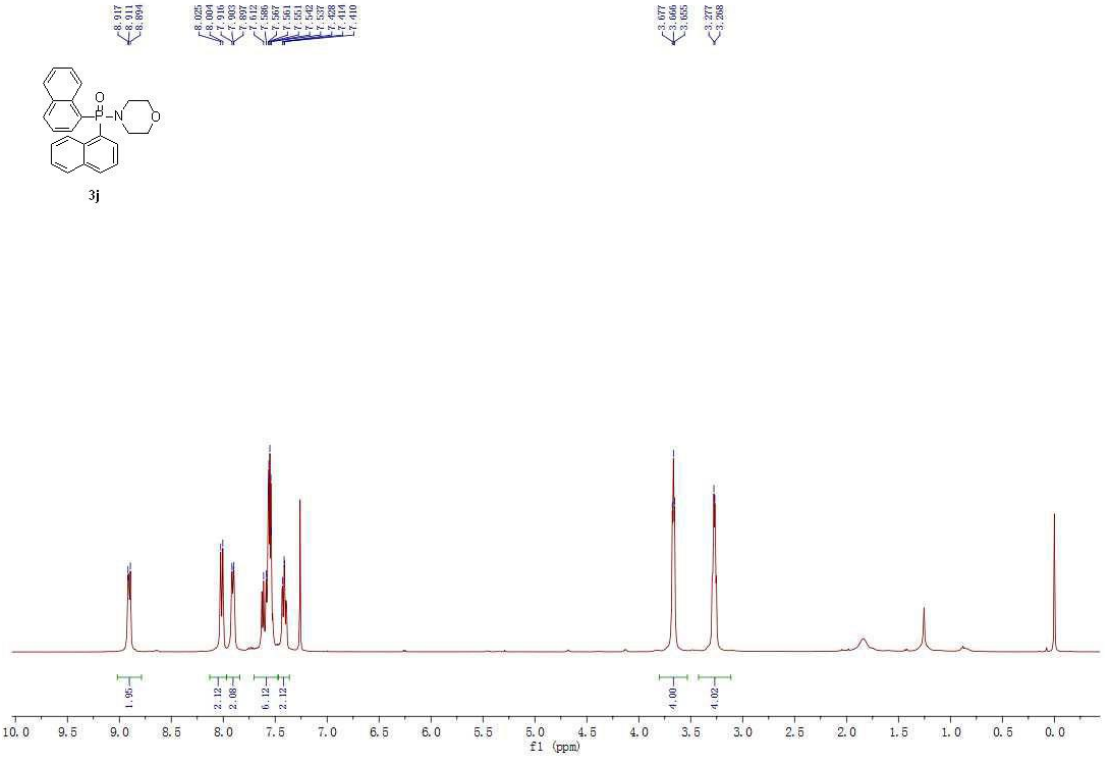
^{13}C NMR of **3i**



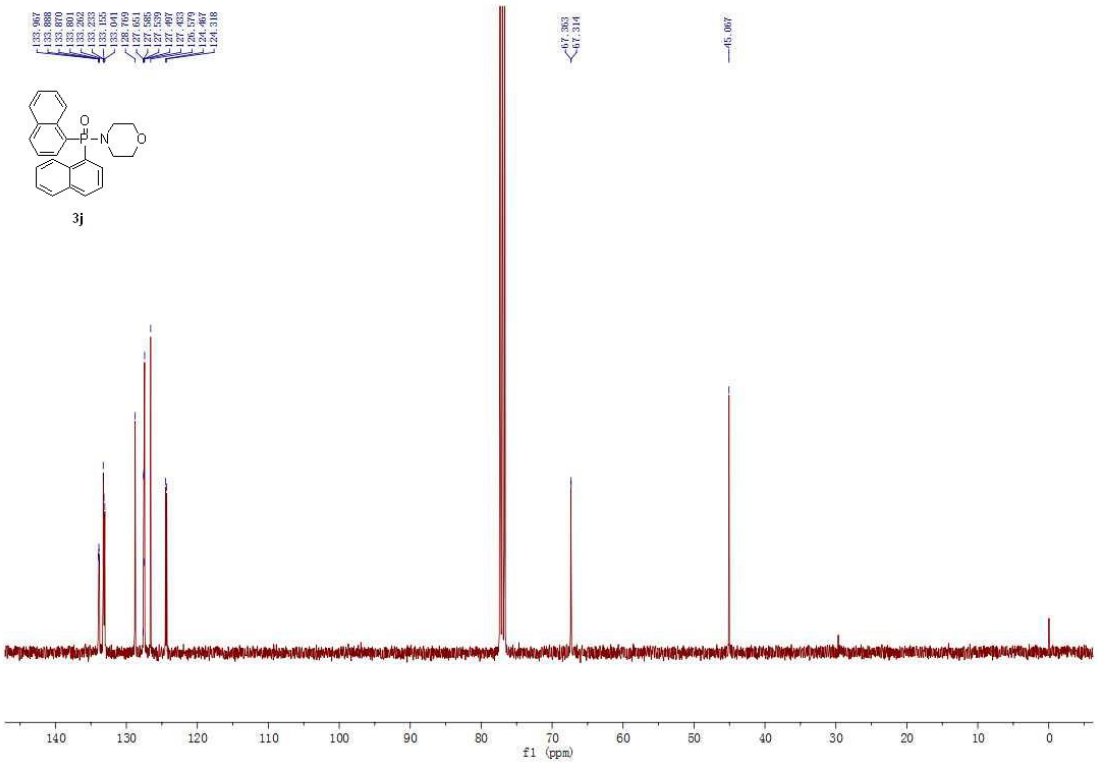
^{31}P NMR of **3i**



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



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



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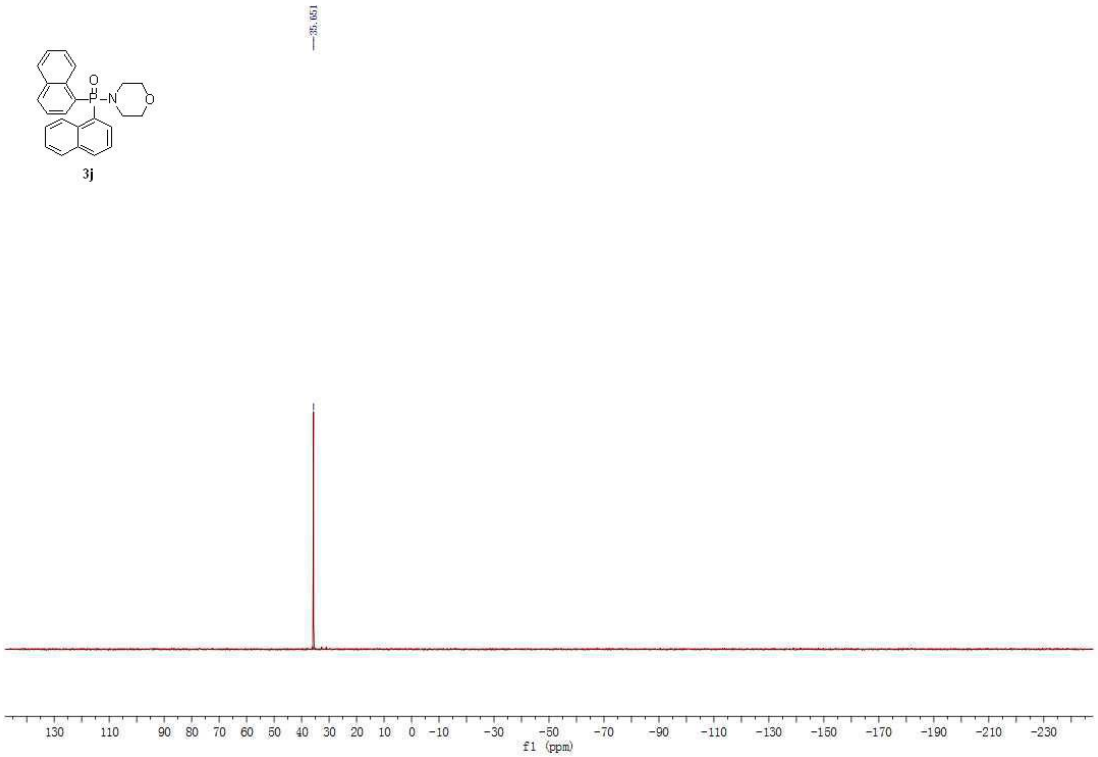

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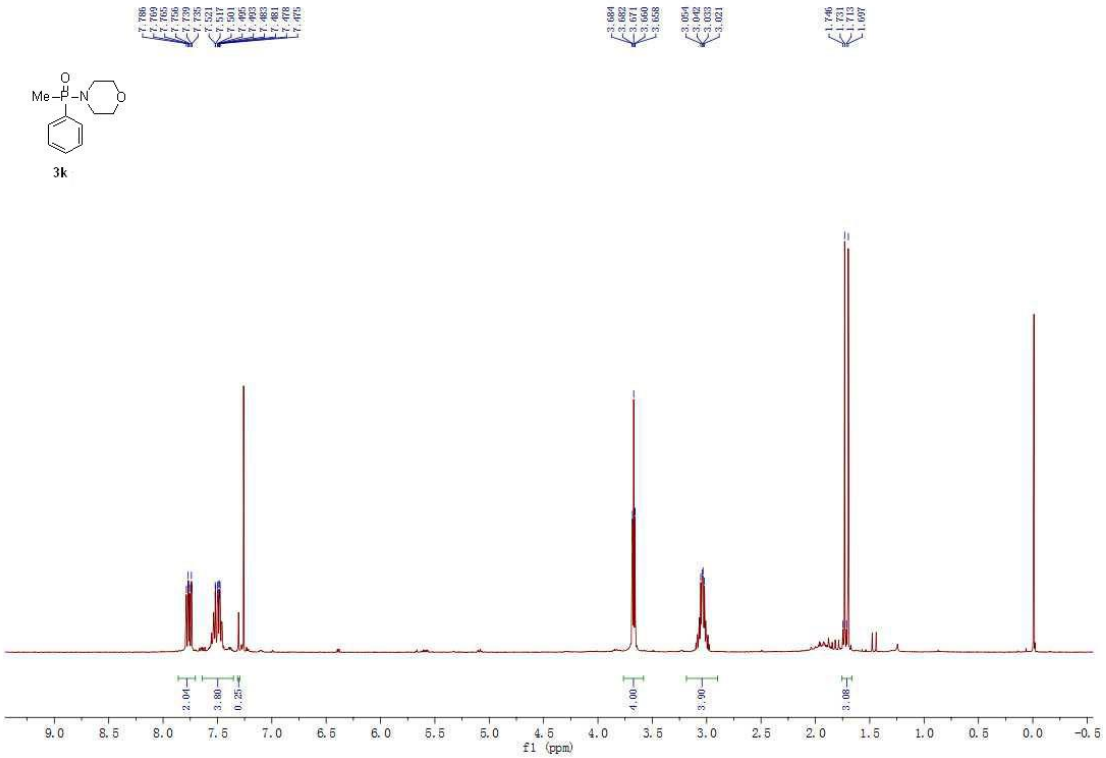
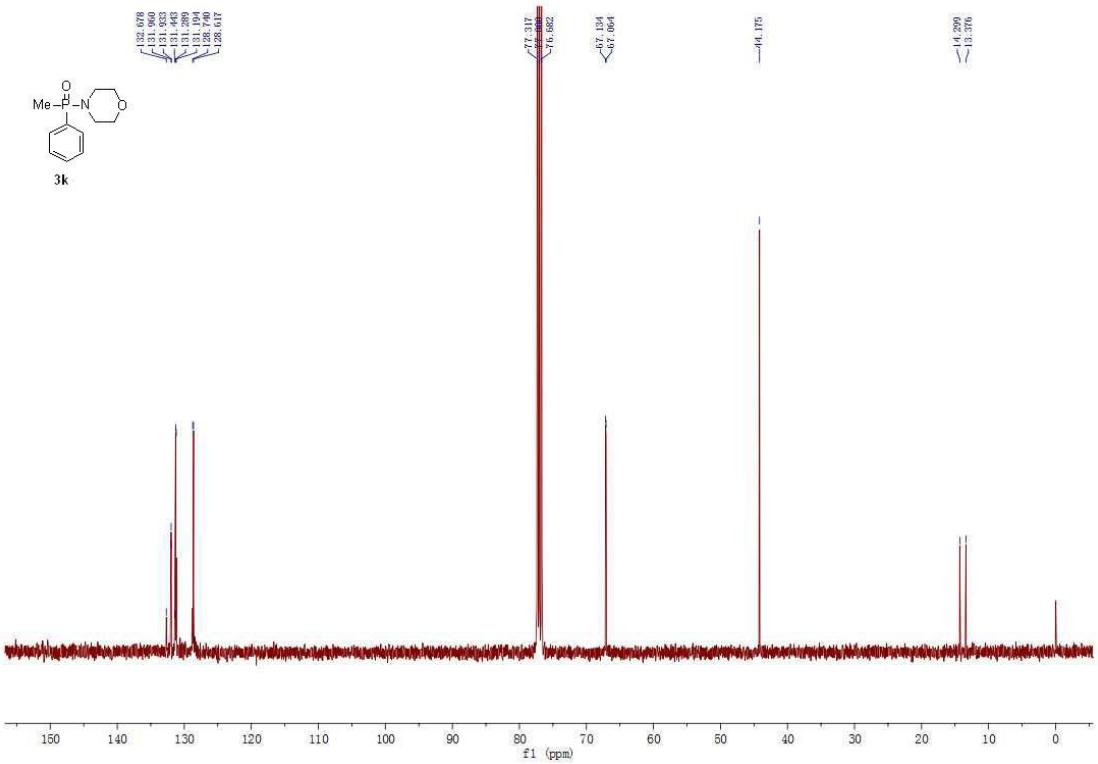


^{13}C NMR of **3k**



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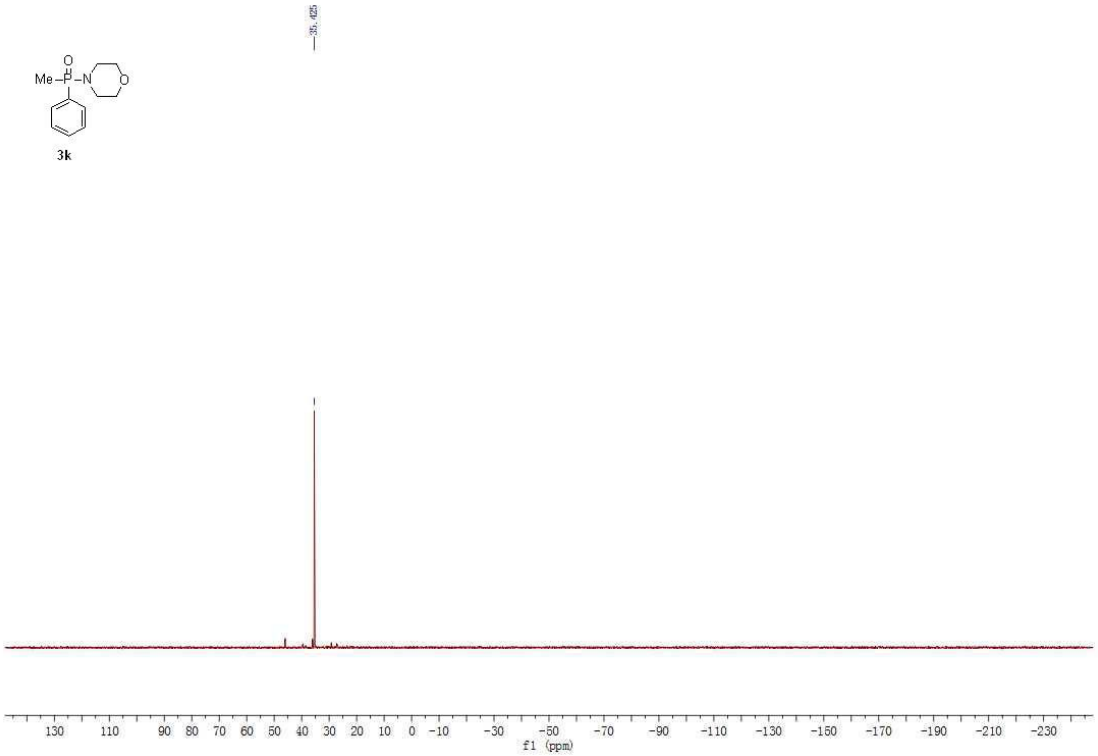
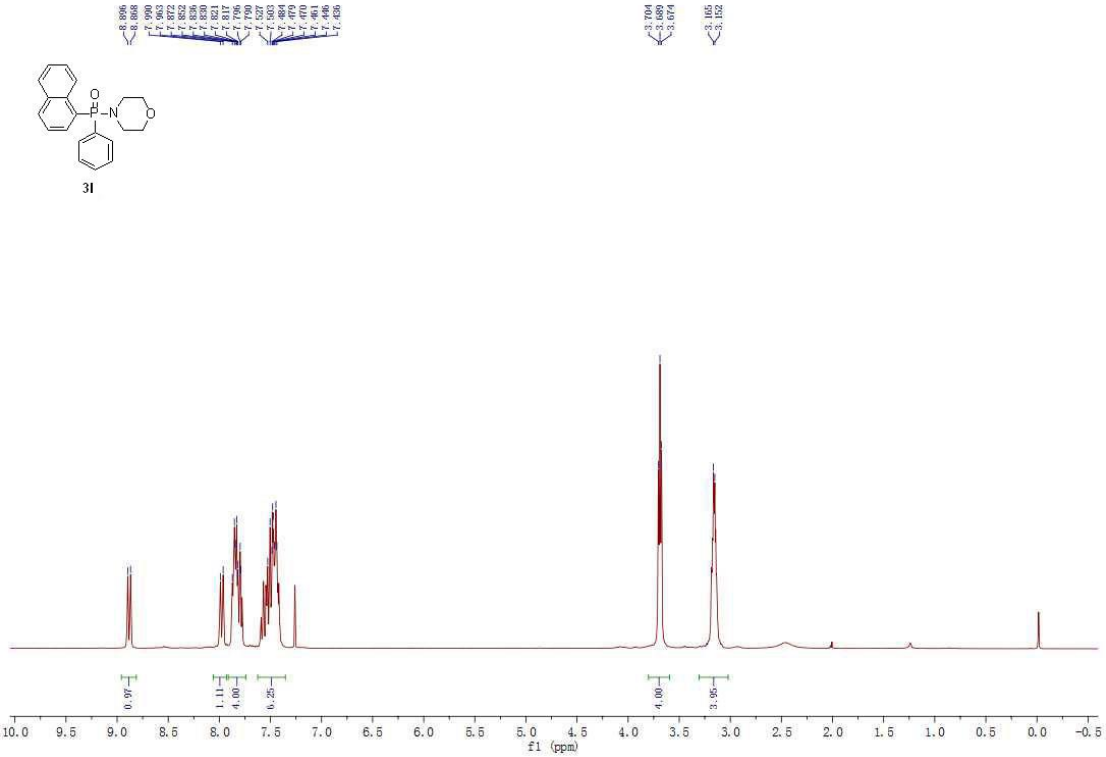
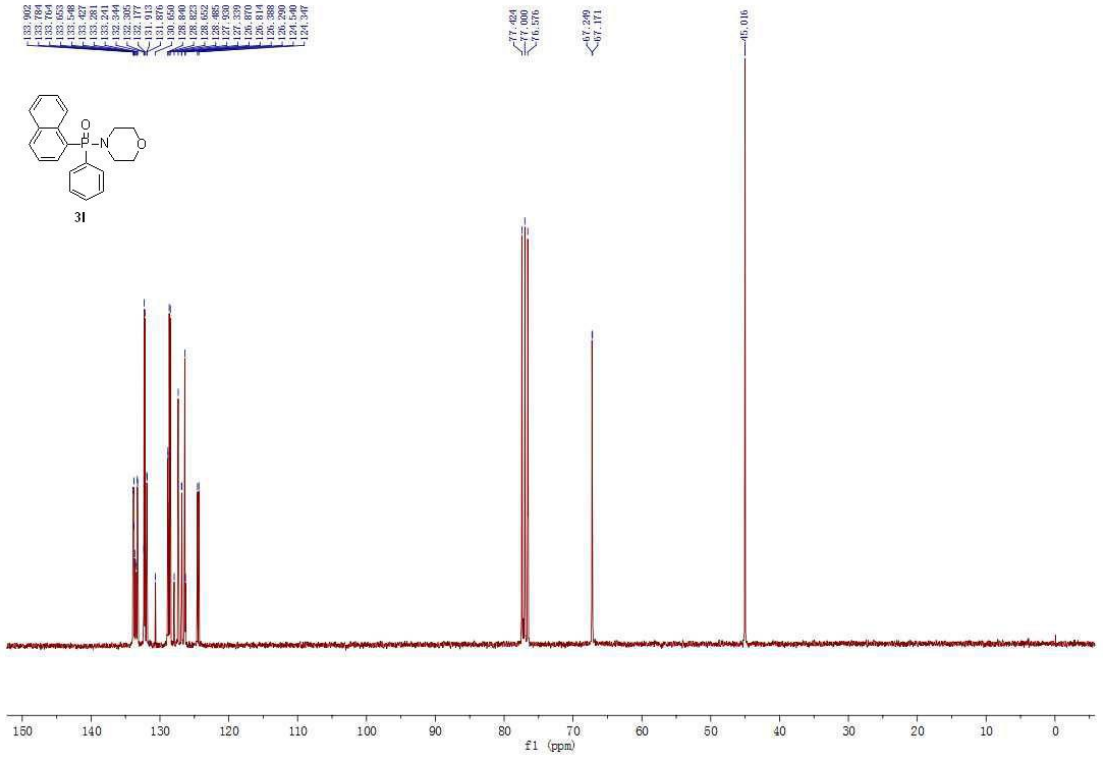


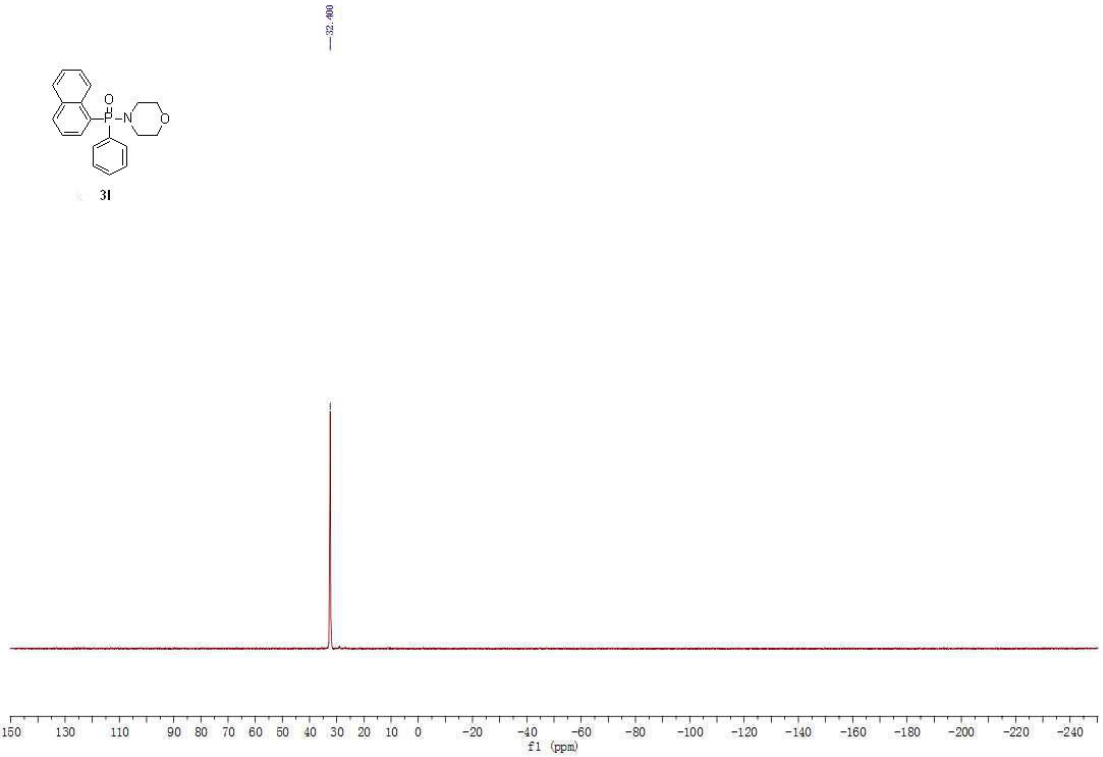
^{1}H NMR of **3l**



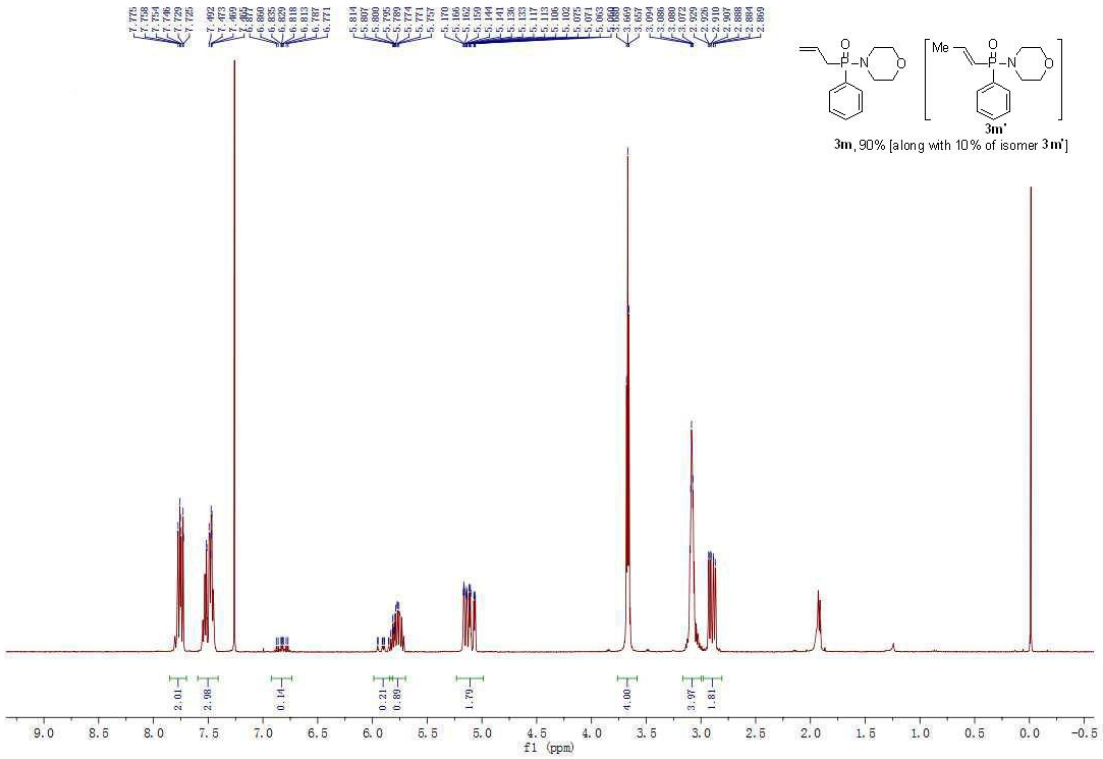
^{13}C NMR of **3l**



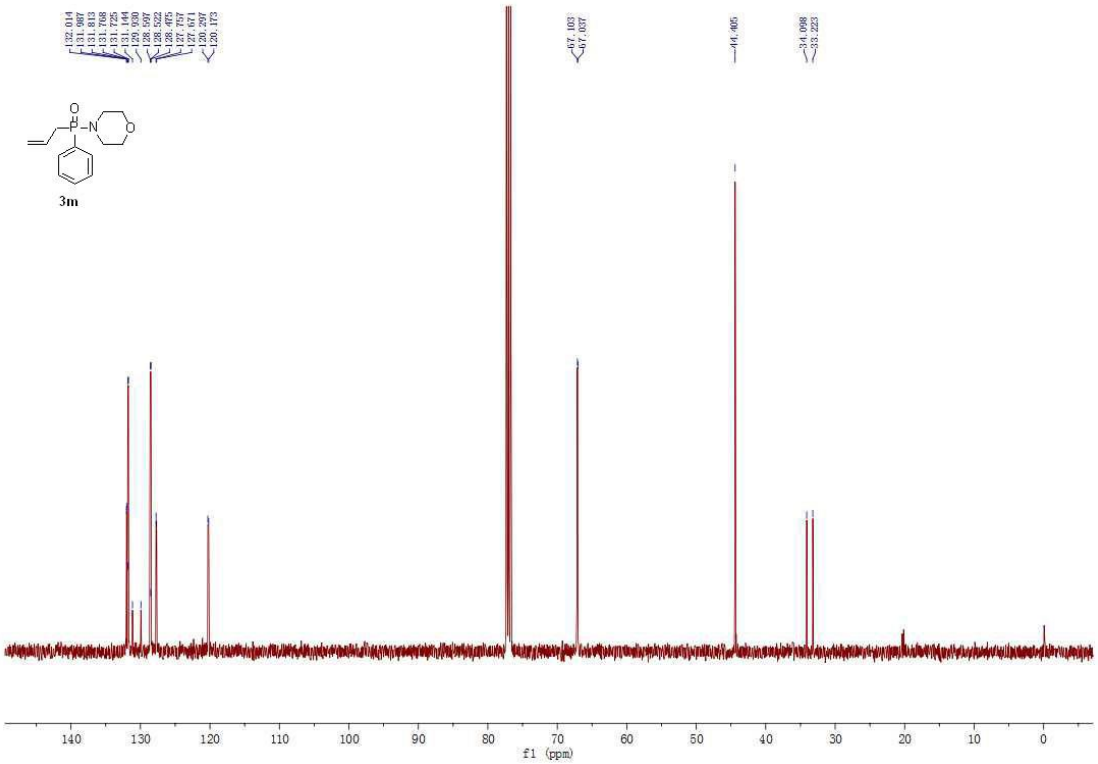
^{31}P NMR of **3l**



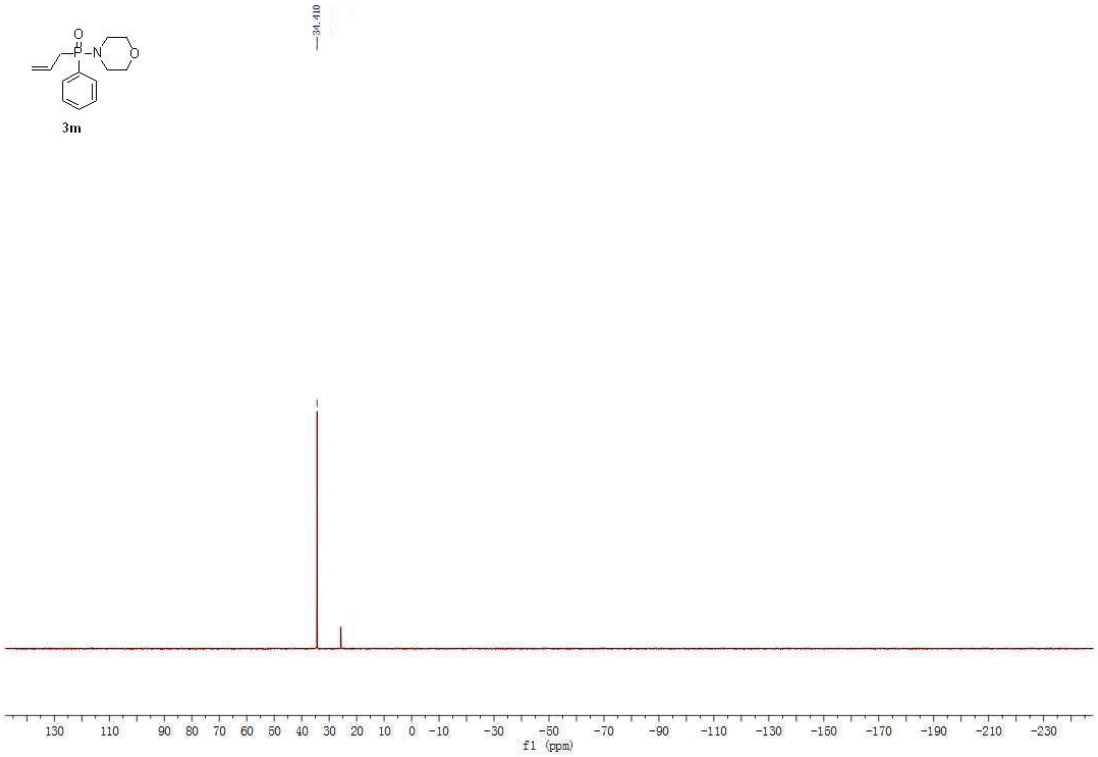
^{1}H NMR of **3m**



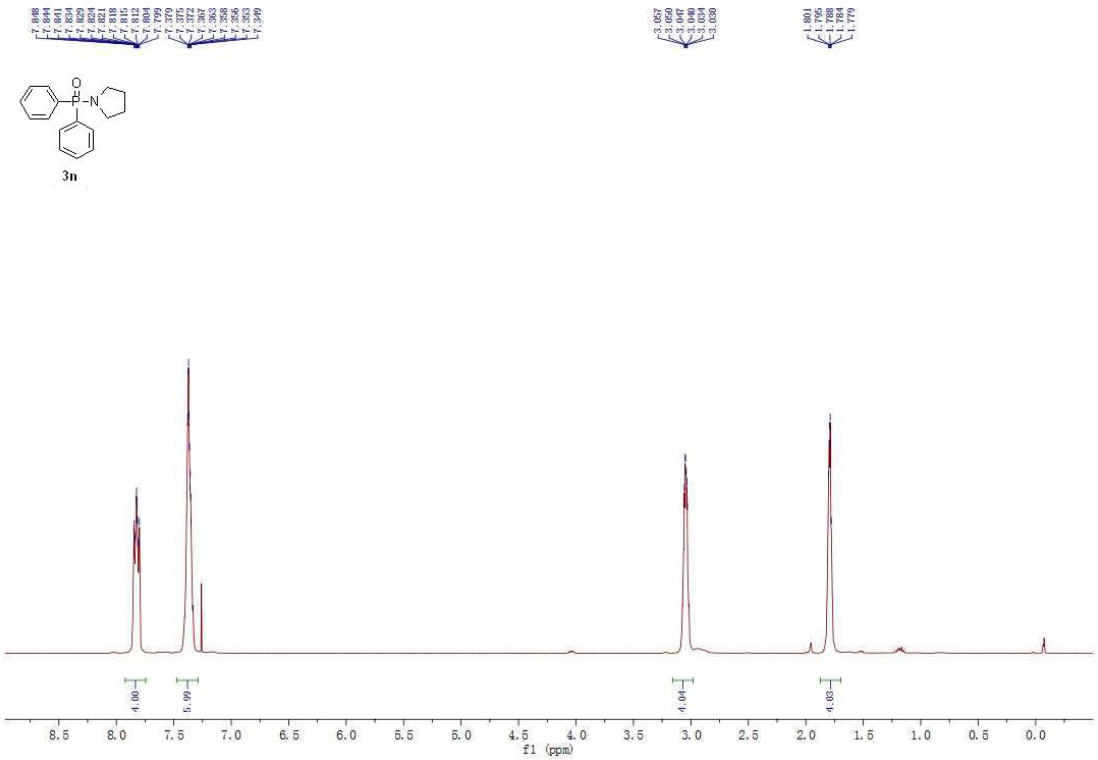
^{13}C NMR of **3m**



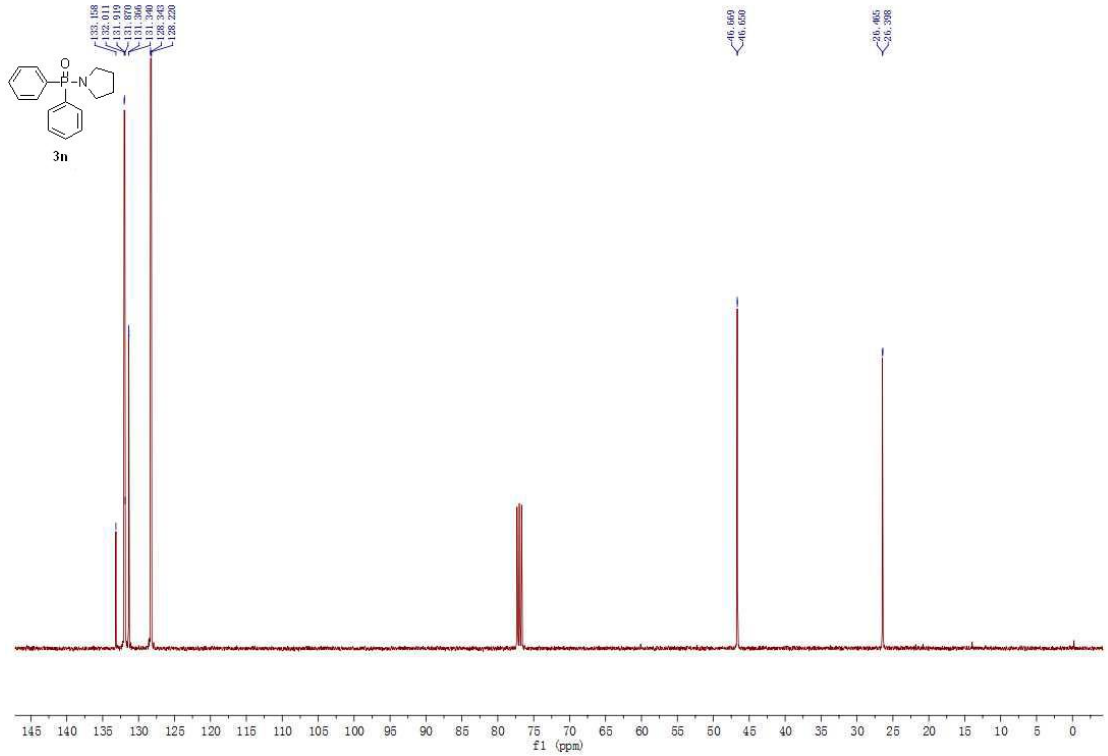
^{31}P NMR of **3m**



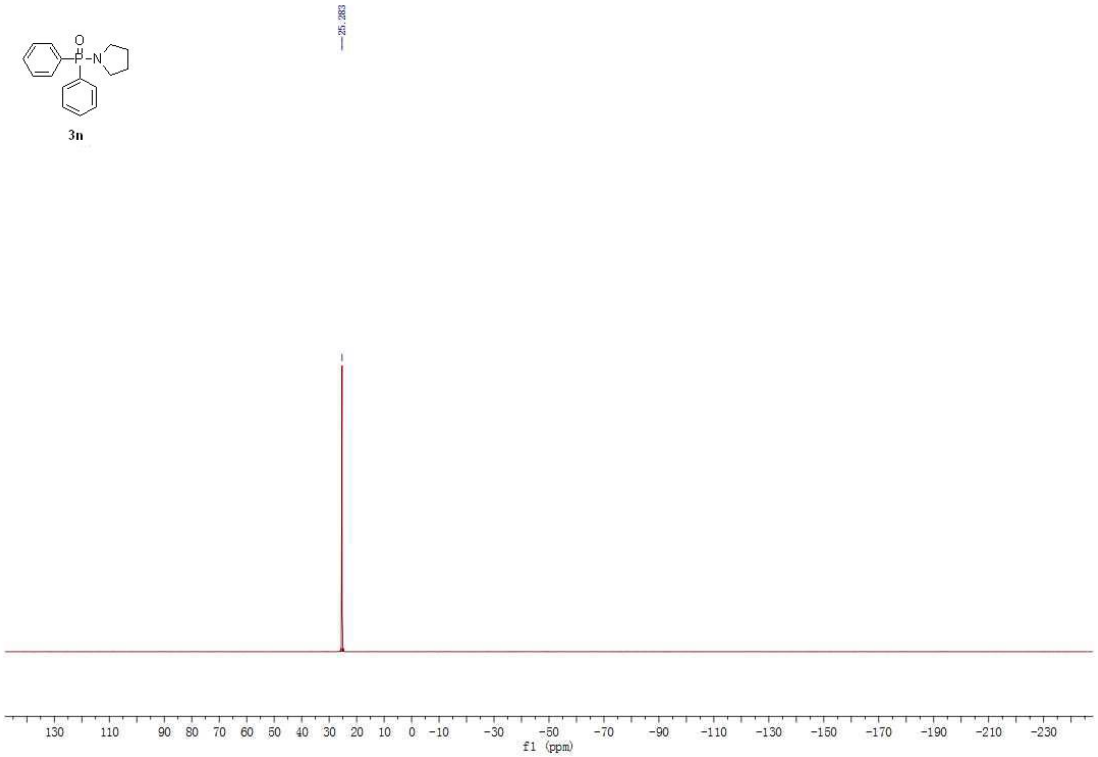
^{1}H NMR of **3n**



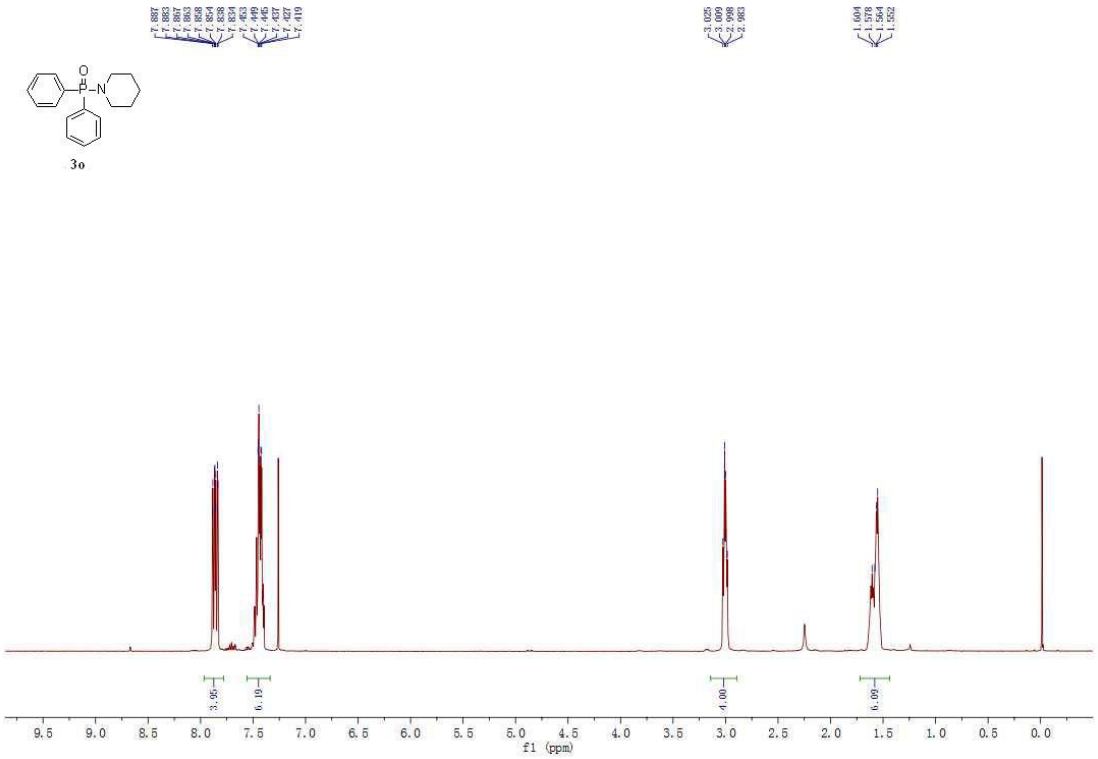
^{13}C NMR of **3n**



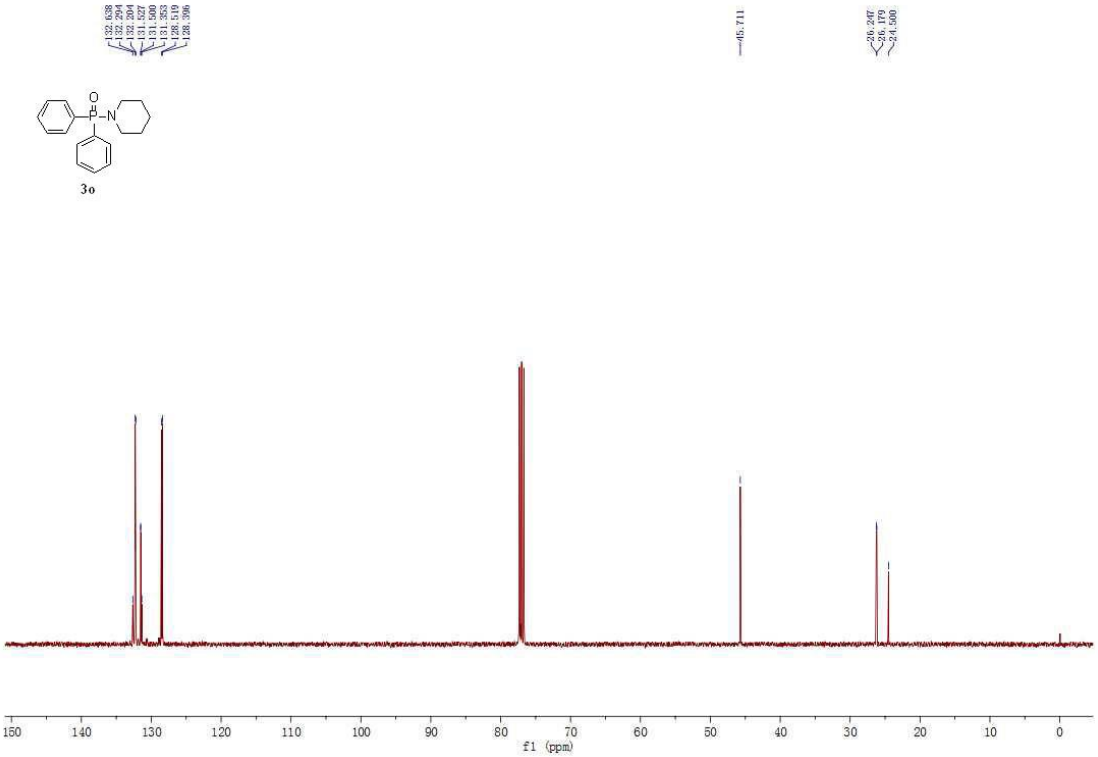
^{31}P NMR of **3n**



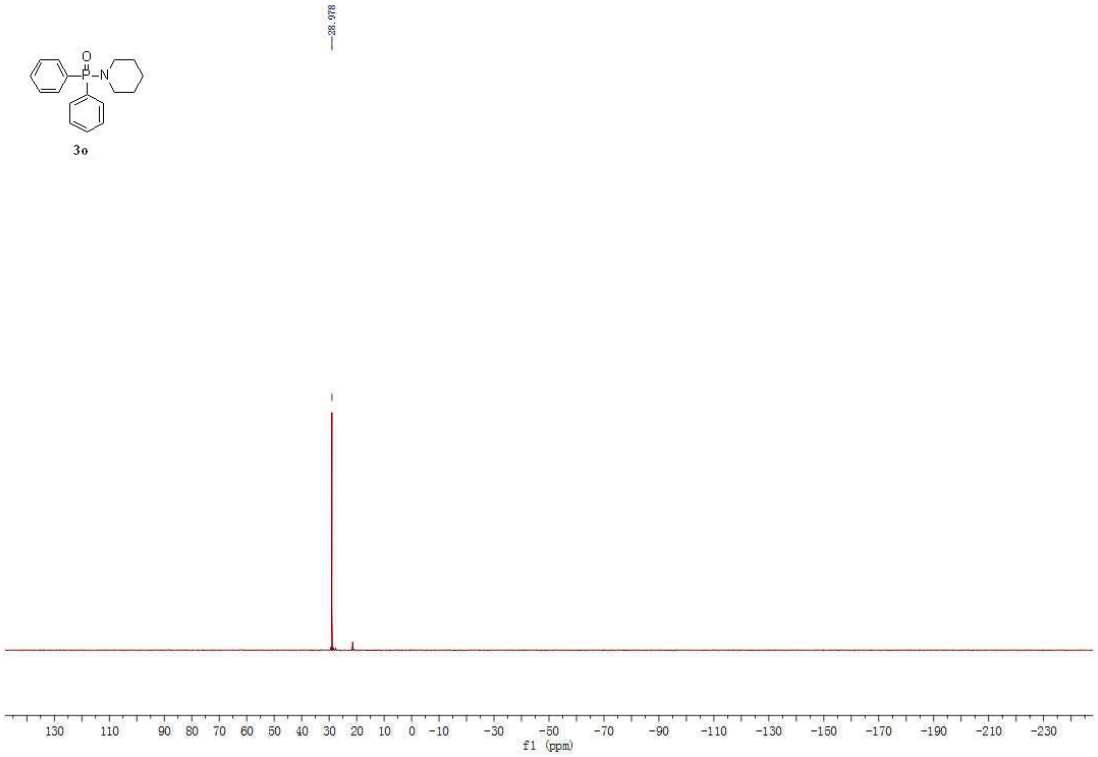
^{1}H NMR of **3o**



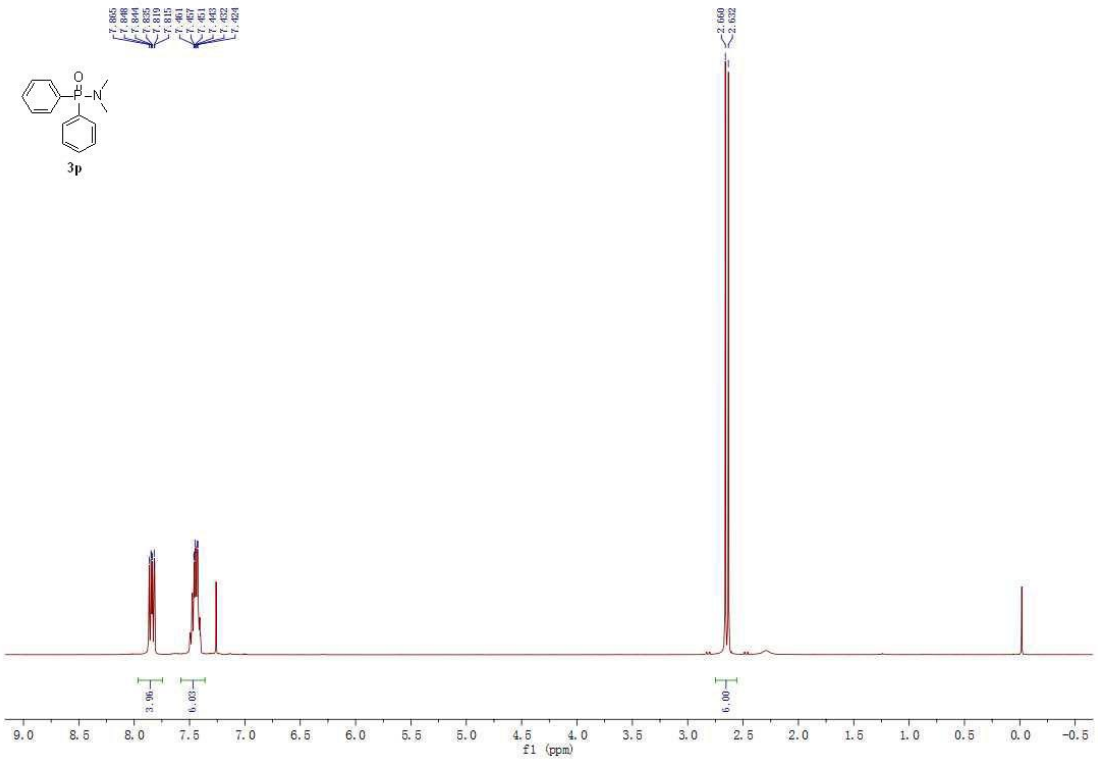
^{13}C NMR of **3o**



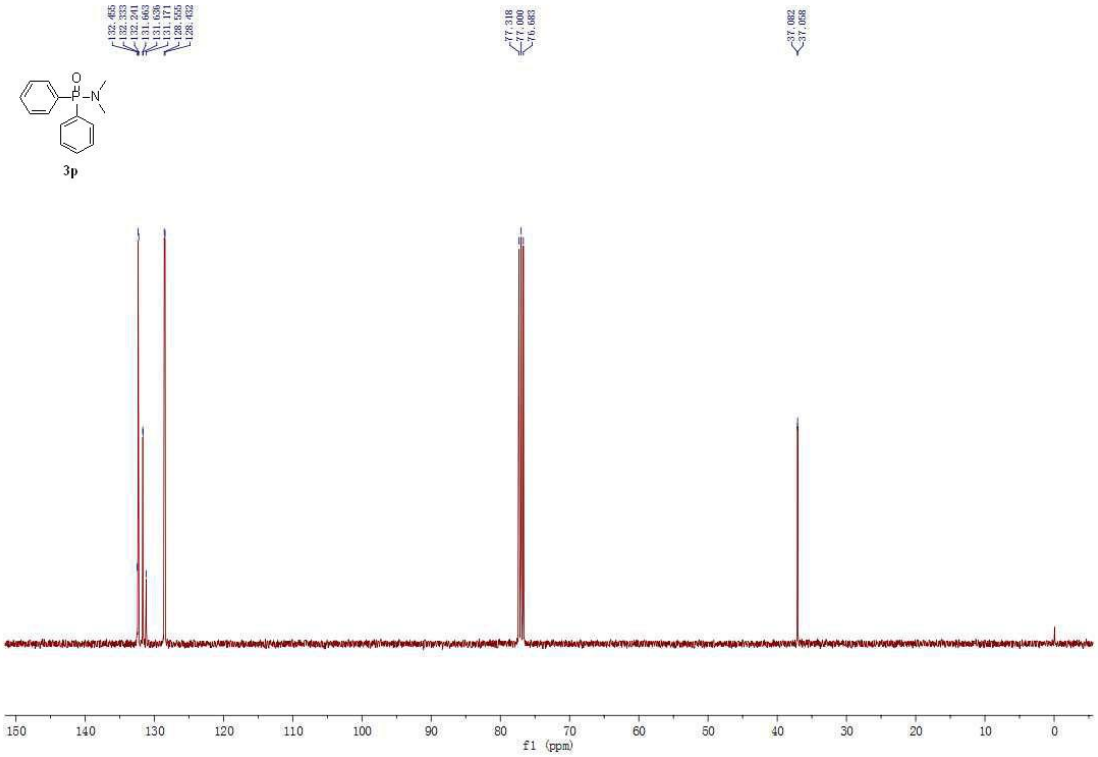
^{31}P NMR of **3o**



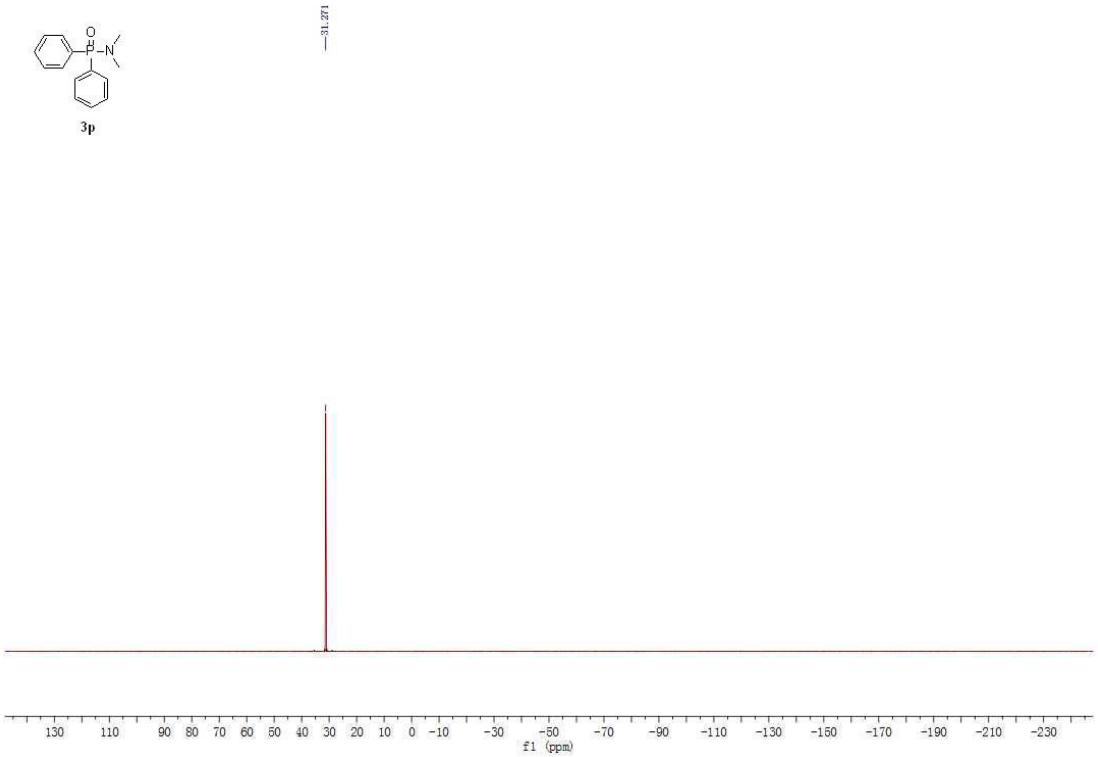
^{1}H NMR of **3p**



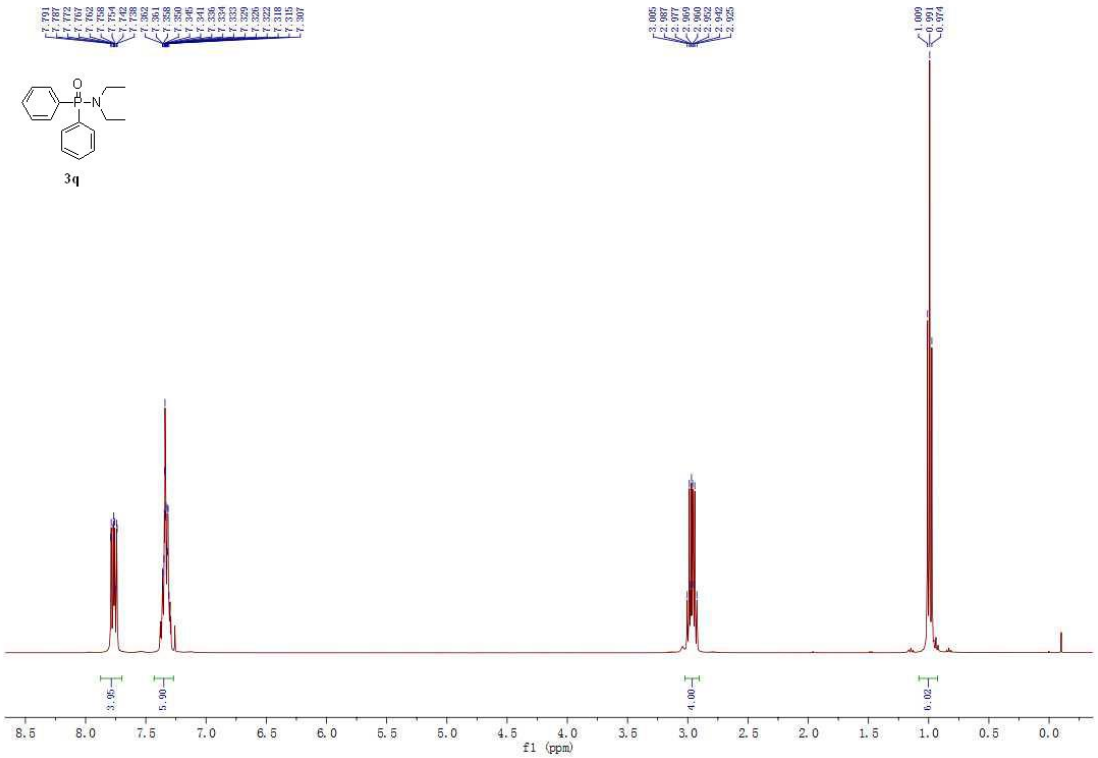
^{13}C NMR of **3p**



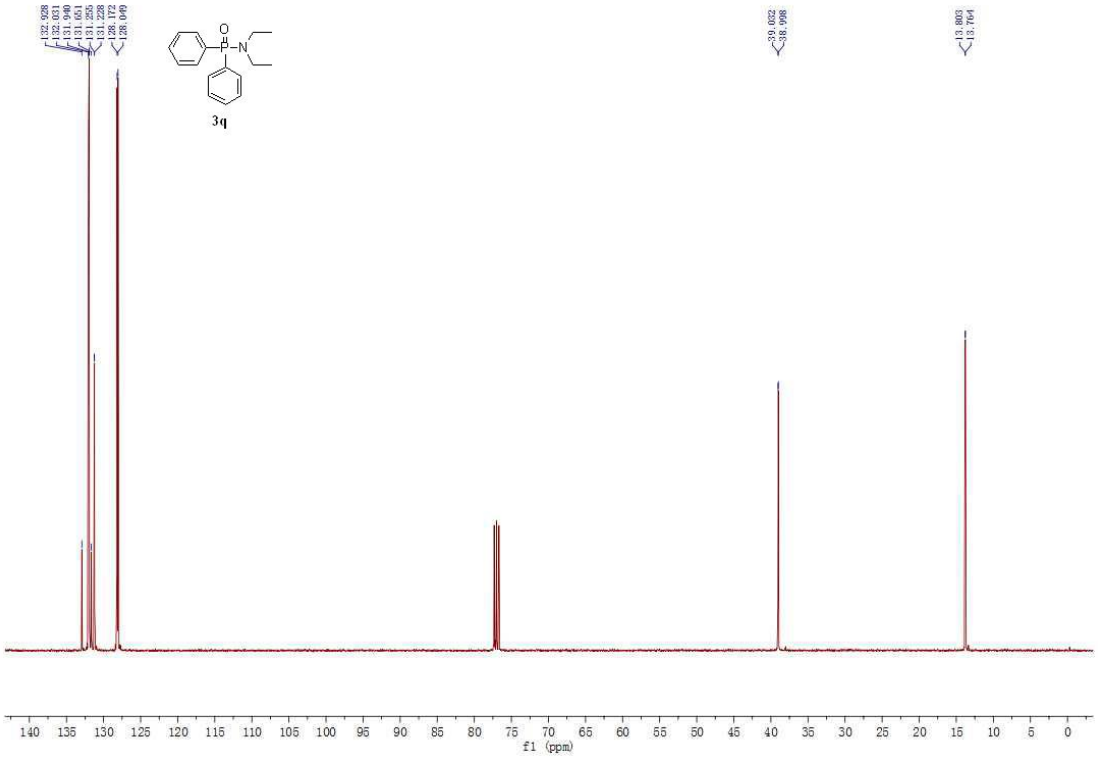
^{31}P NMR of **3p**



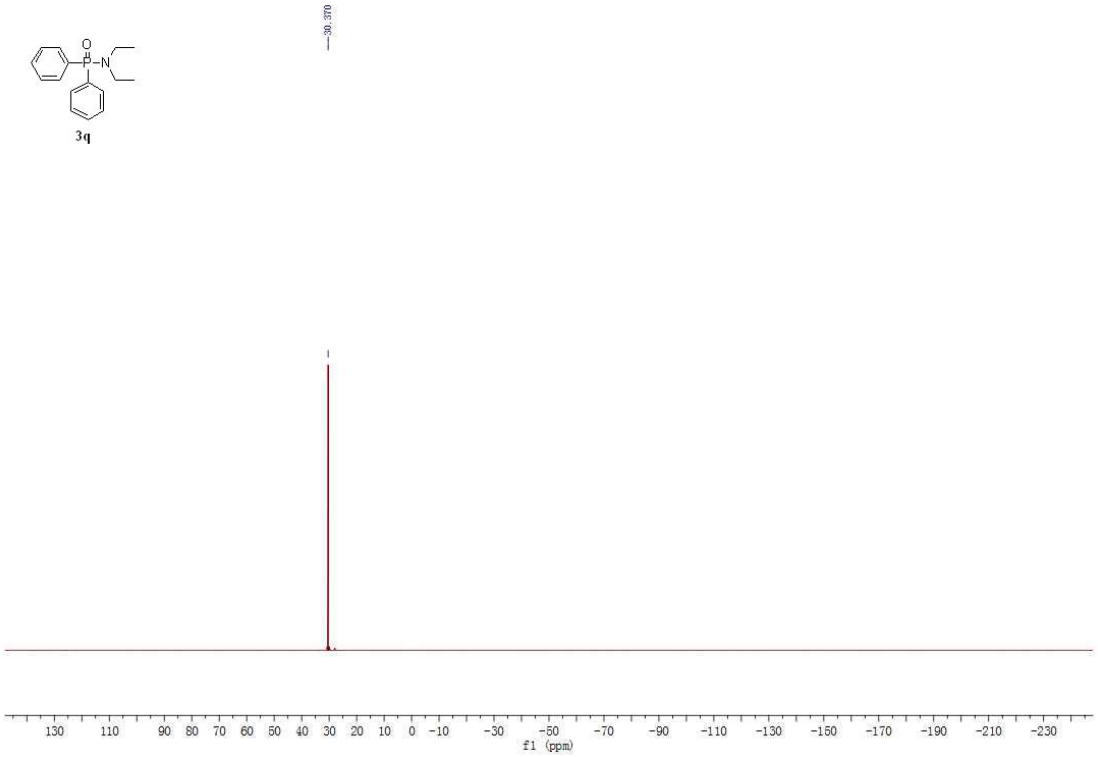
^{1}H NMR of **3q**



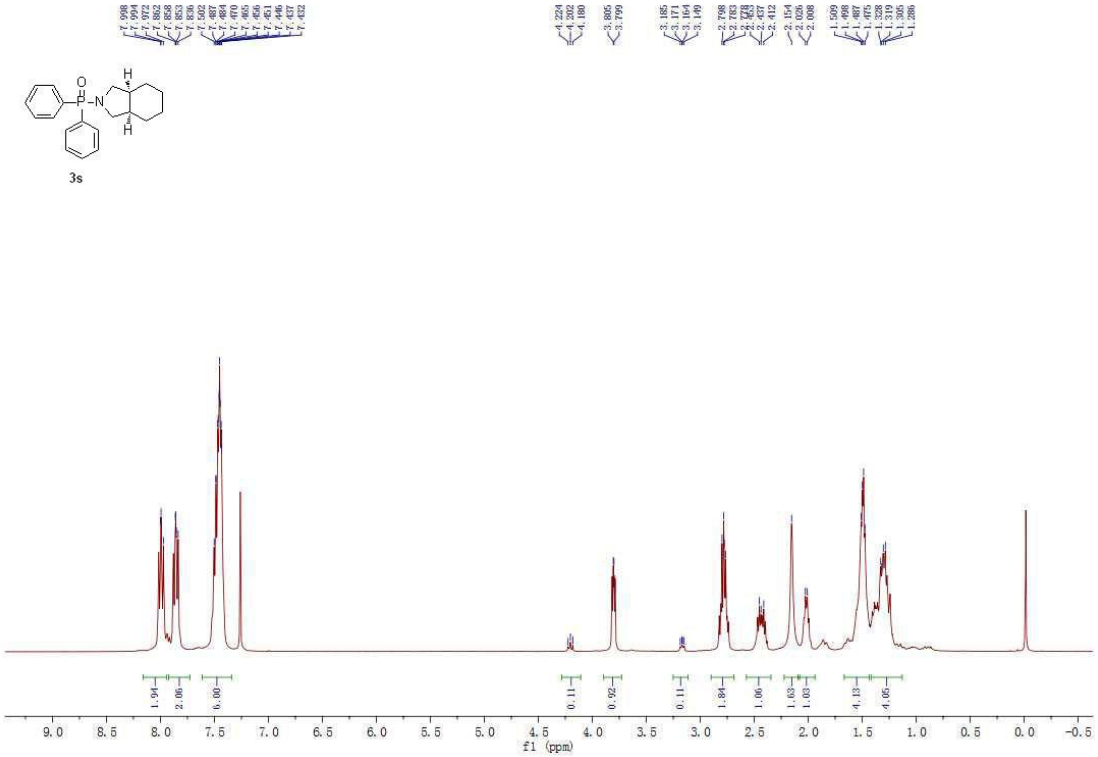
^{13}C NMR of **3q**



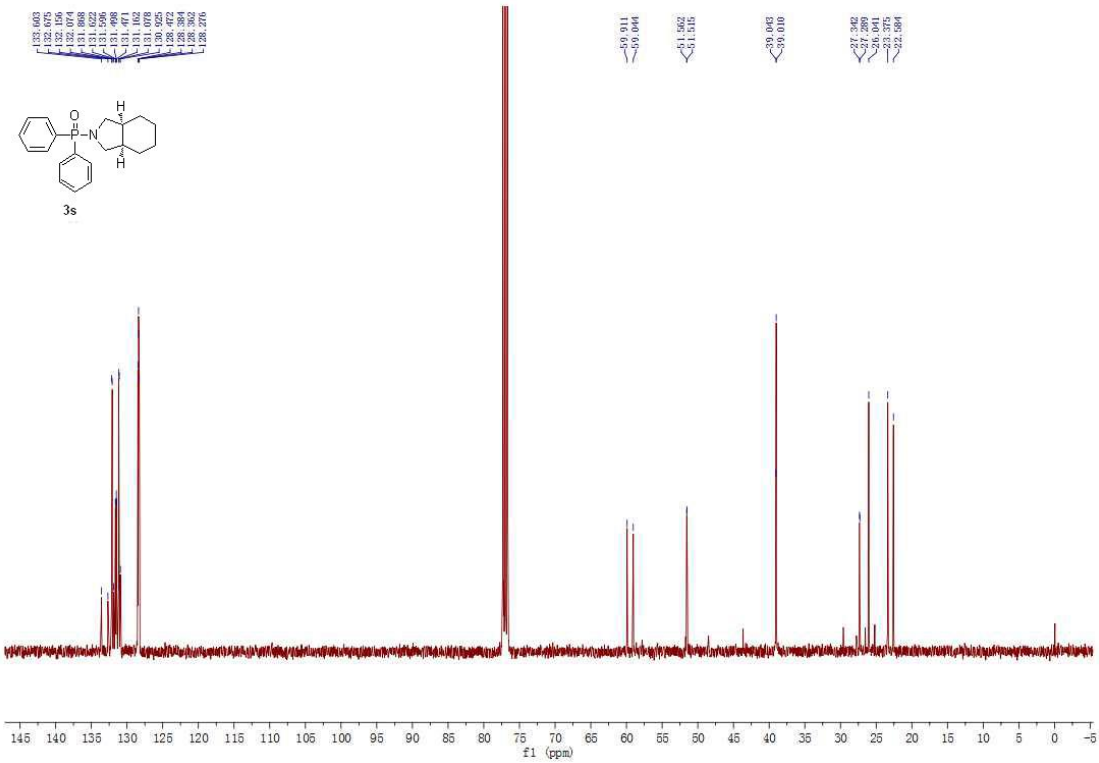
^{31}P NMR of **3q**



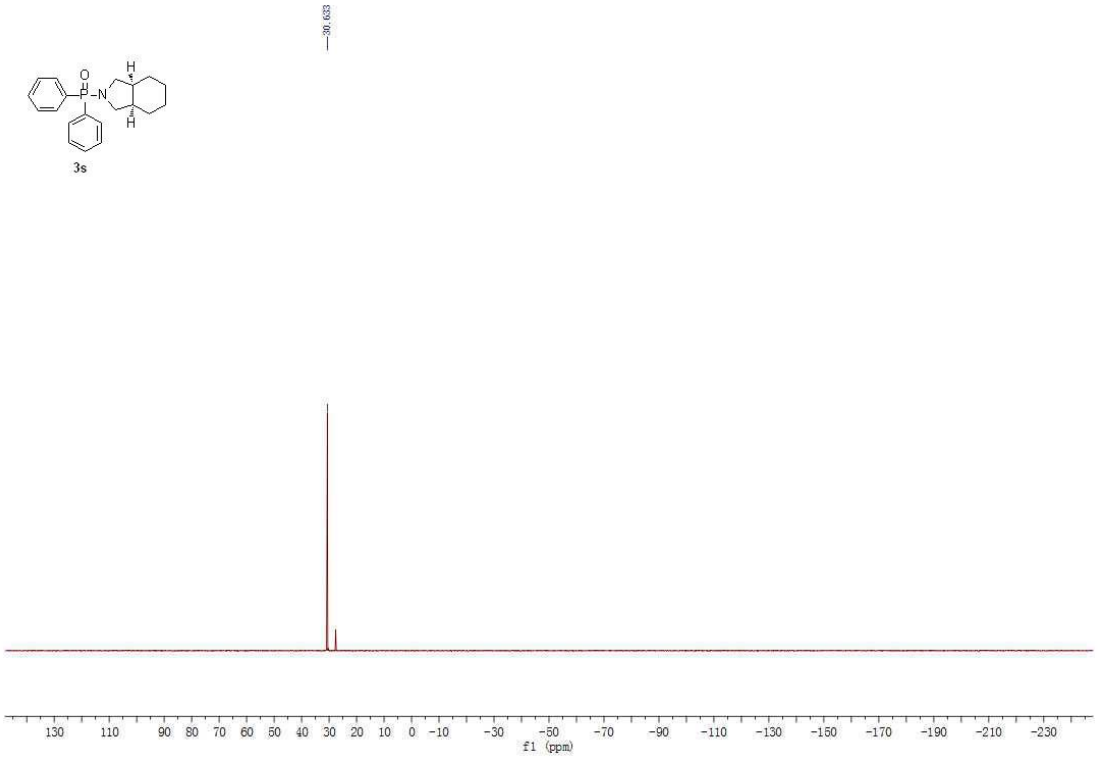
^{1}H NMR of **3s**



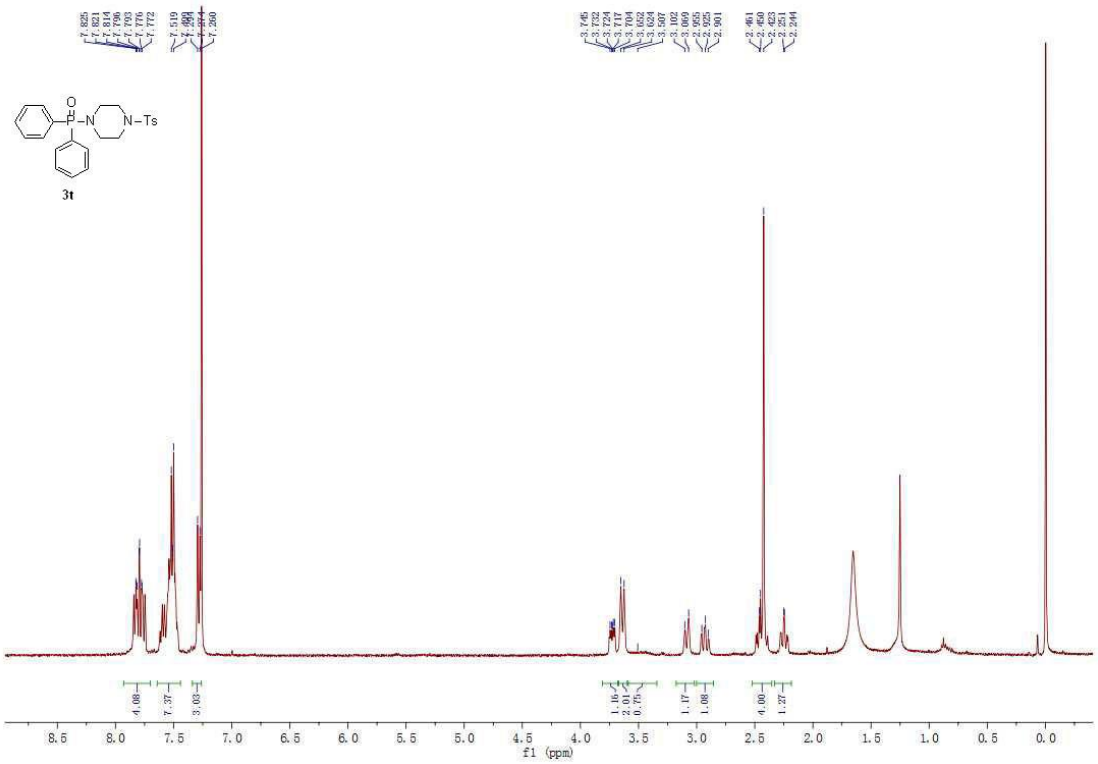
^{13}C NMR of **3s**



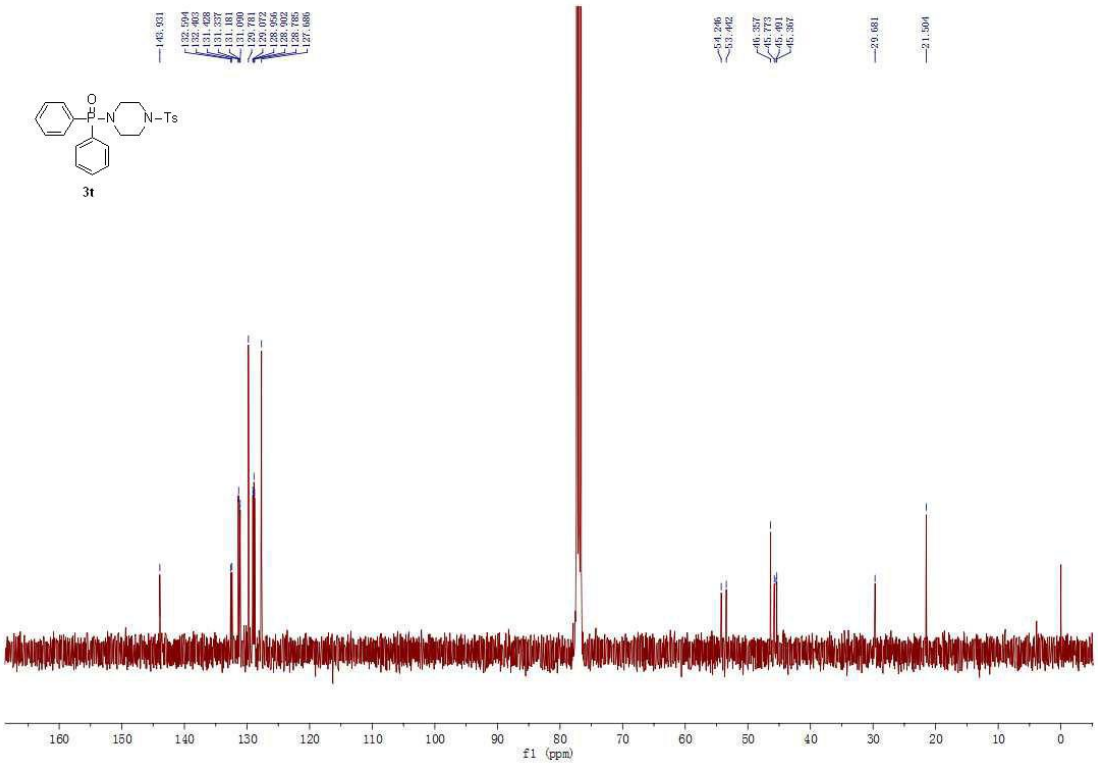
^{31}P NMR of **3s**



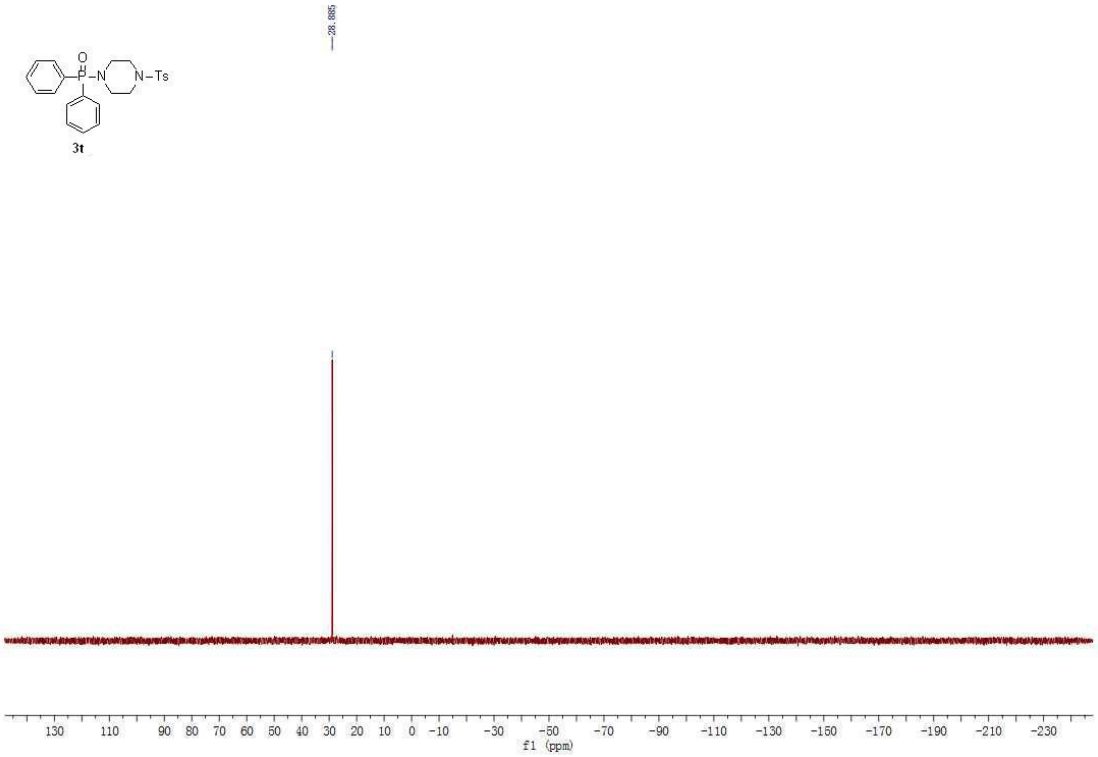
^{1}H NMR of **3t**



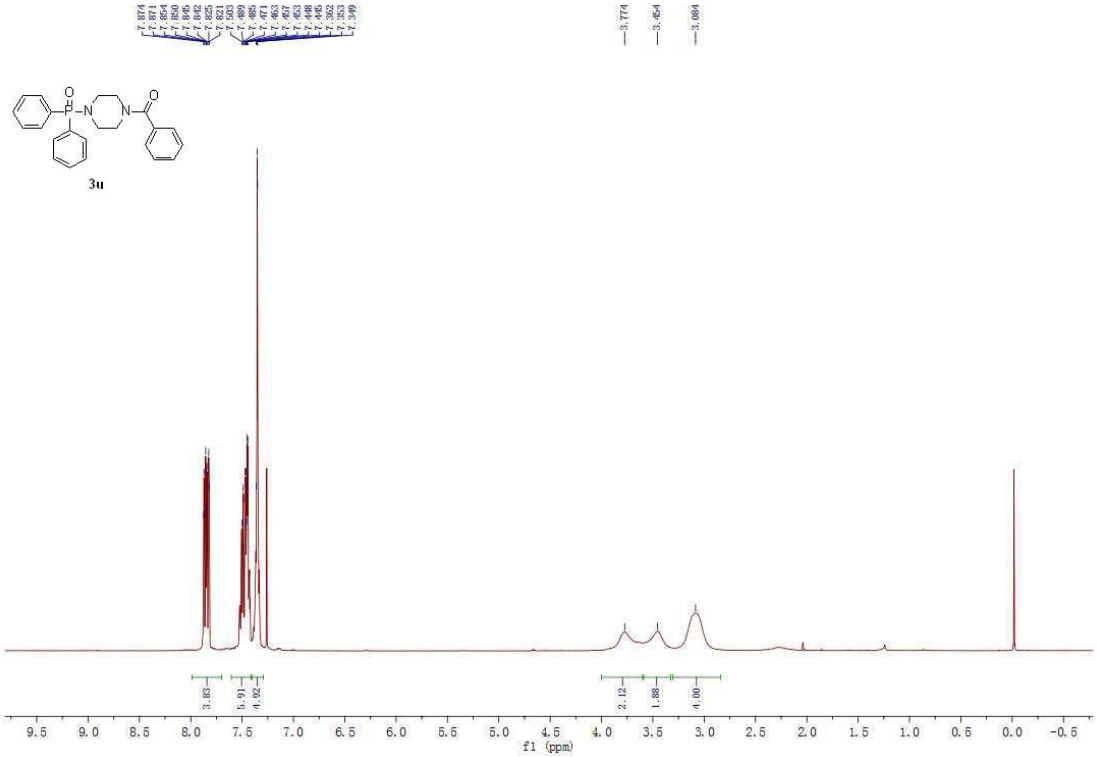
^{13}C NMR of **3t**



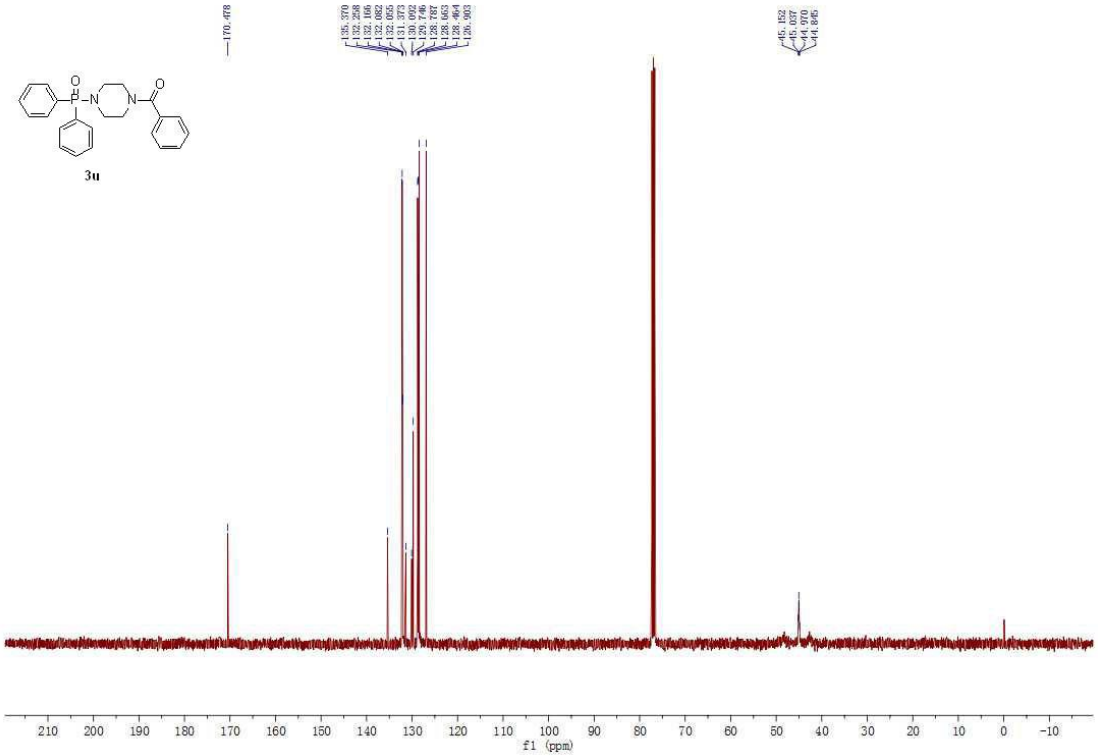
^{31}P NMR of **3t**



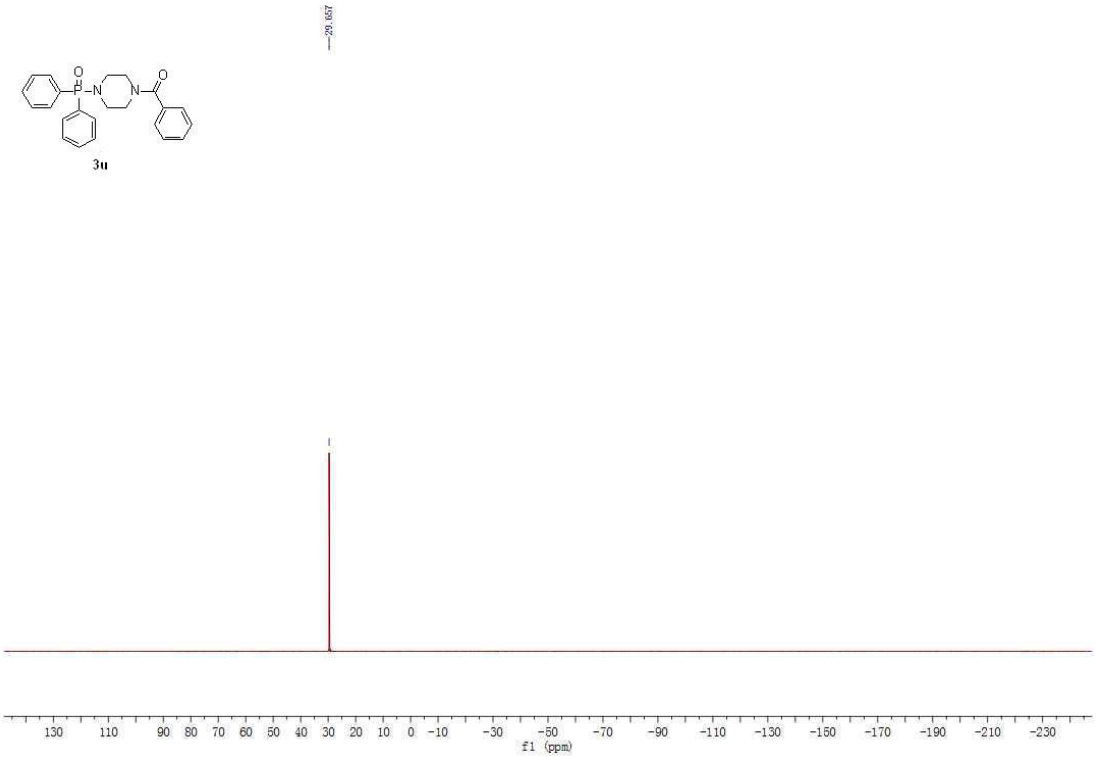
^{1}H NMR of **3u**



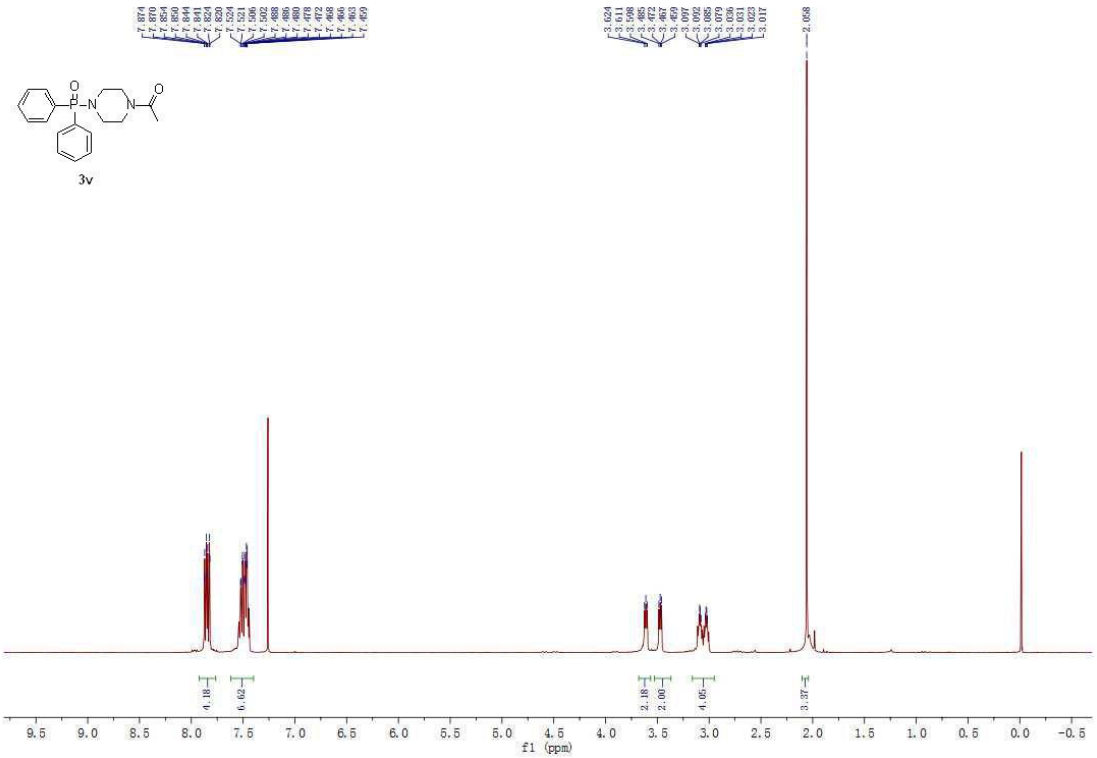
^{13}C NMR of **3u**



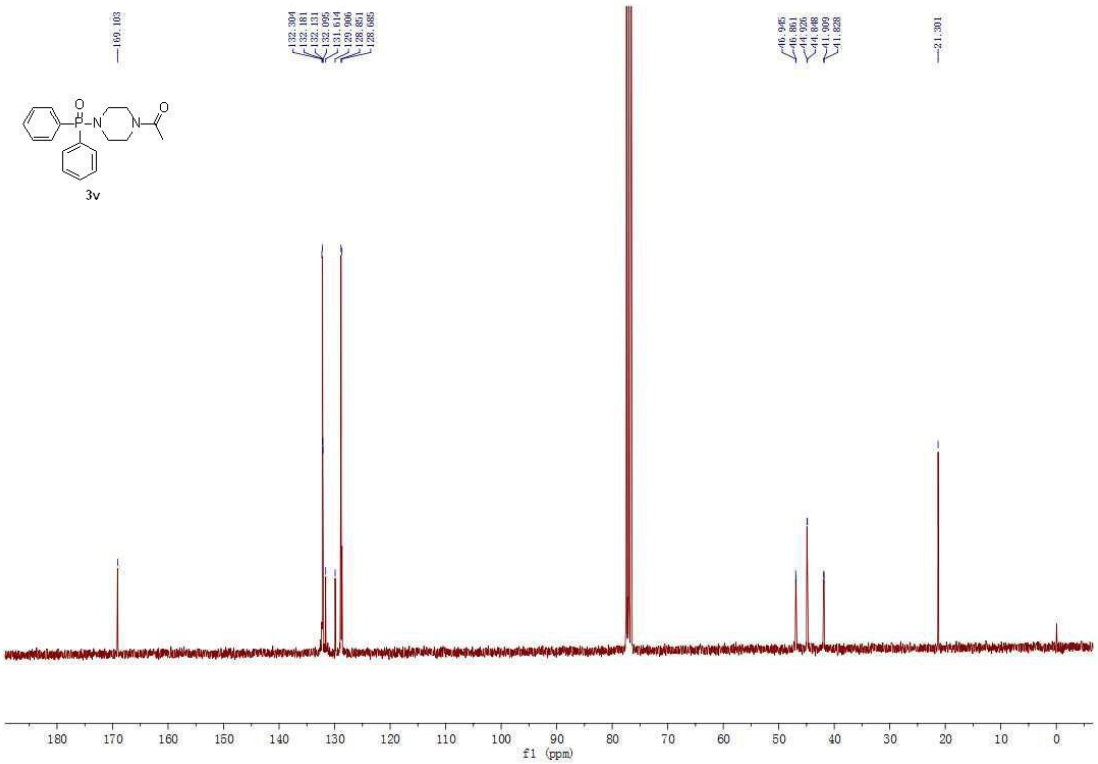
^{31}P NMR of **3u**



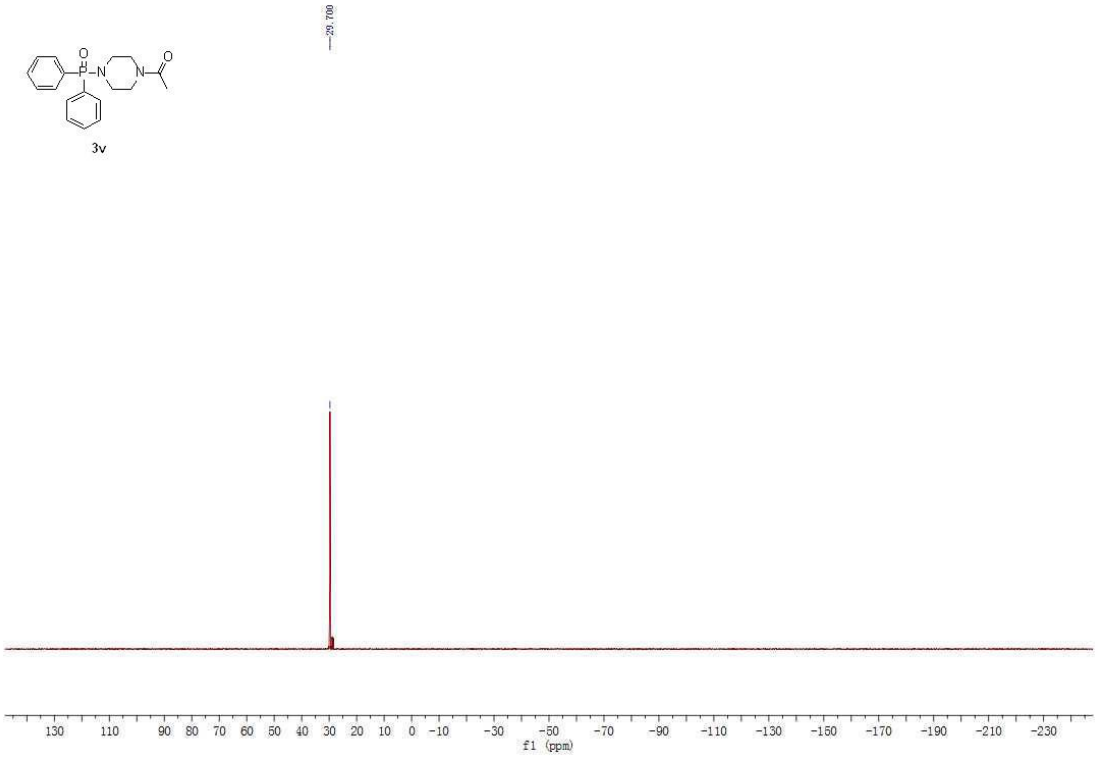
^{1}H NMR of **3v**



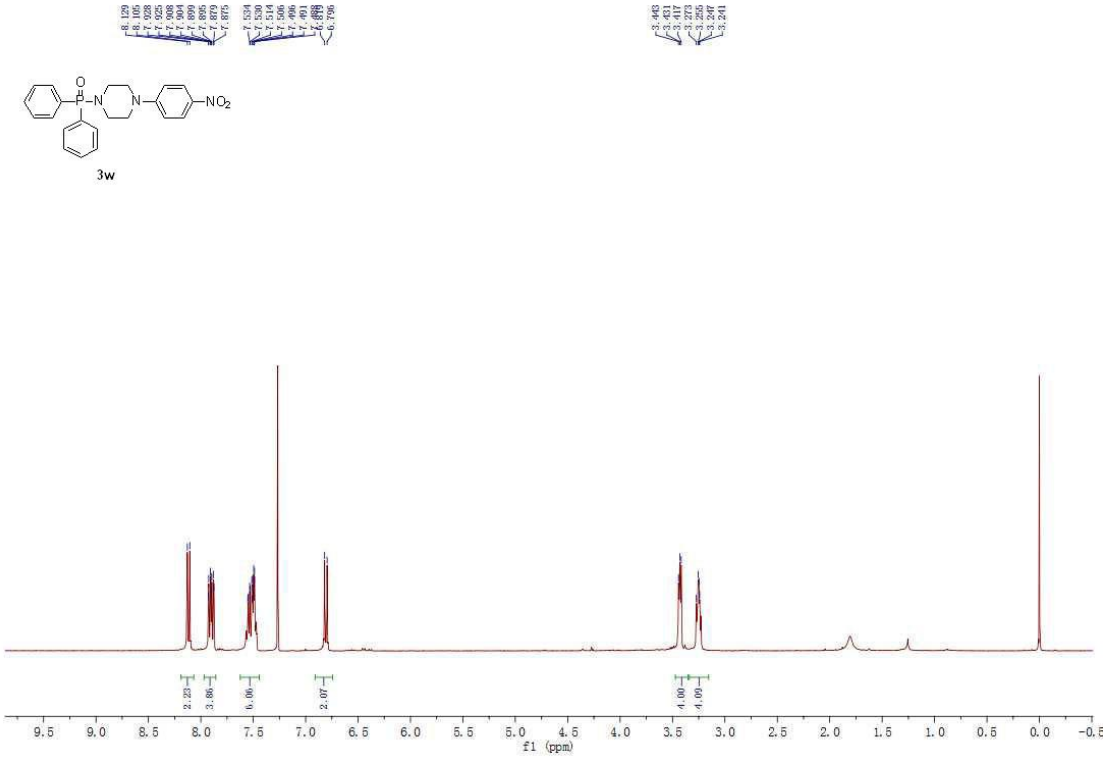
^{13}C NMR of **3v**



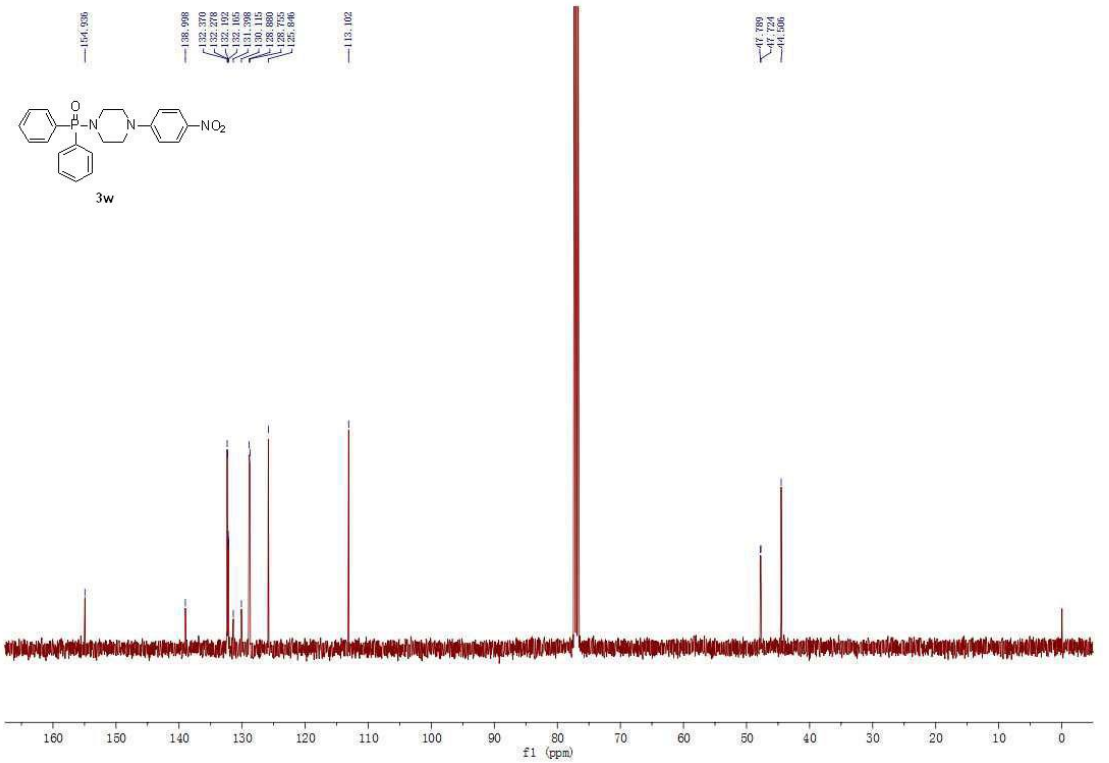
^{31}P NMR of **3v**



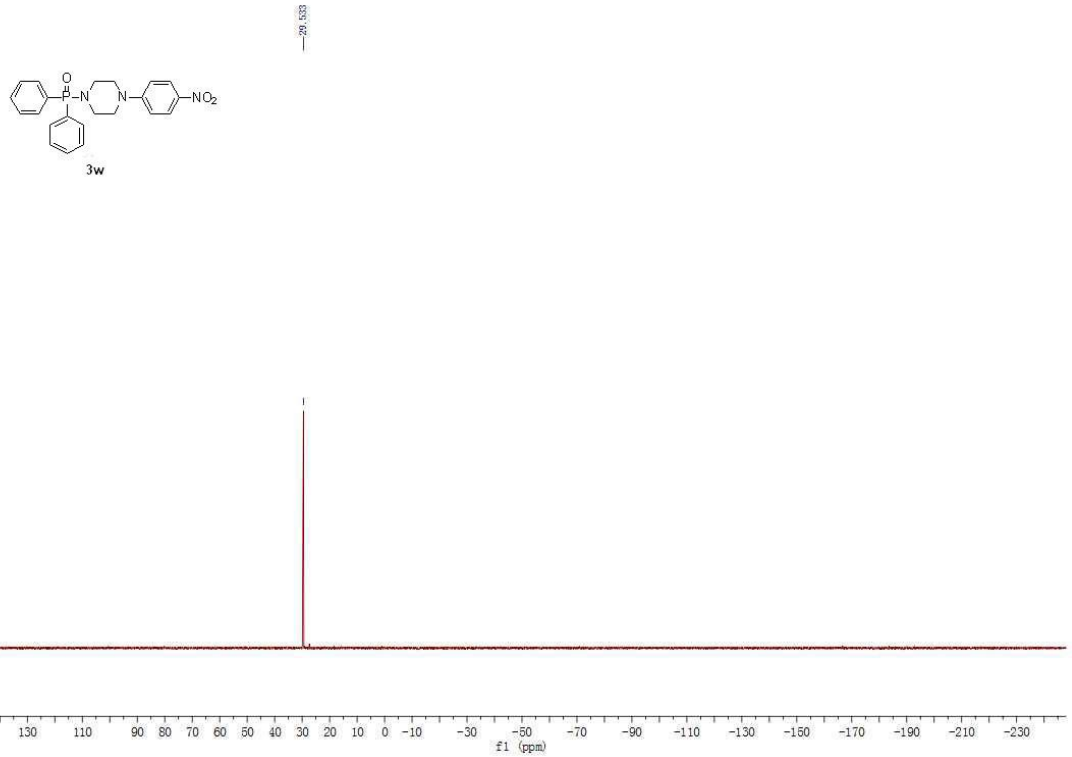
^{1}H NMR of **3w**



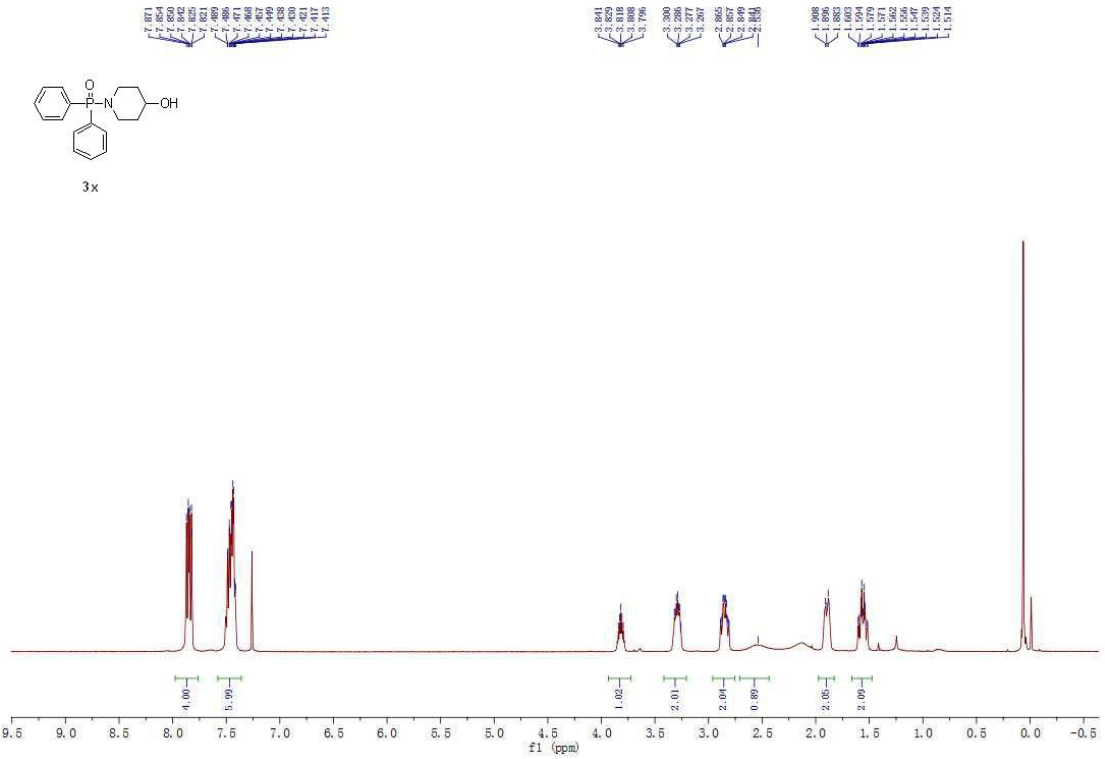
^{13}C NMR of **3w**



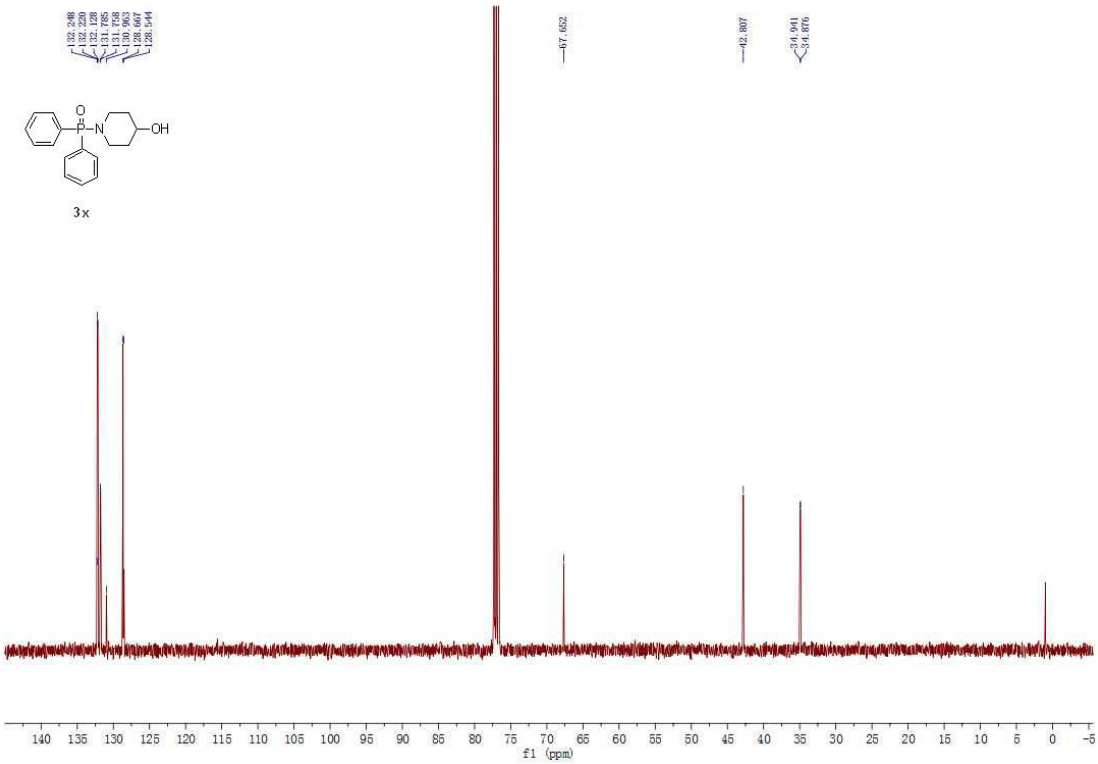
^{31}P NMR of **3w**



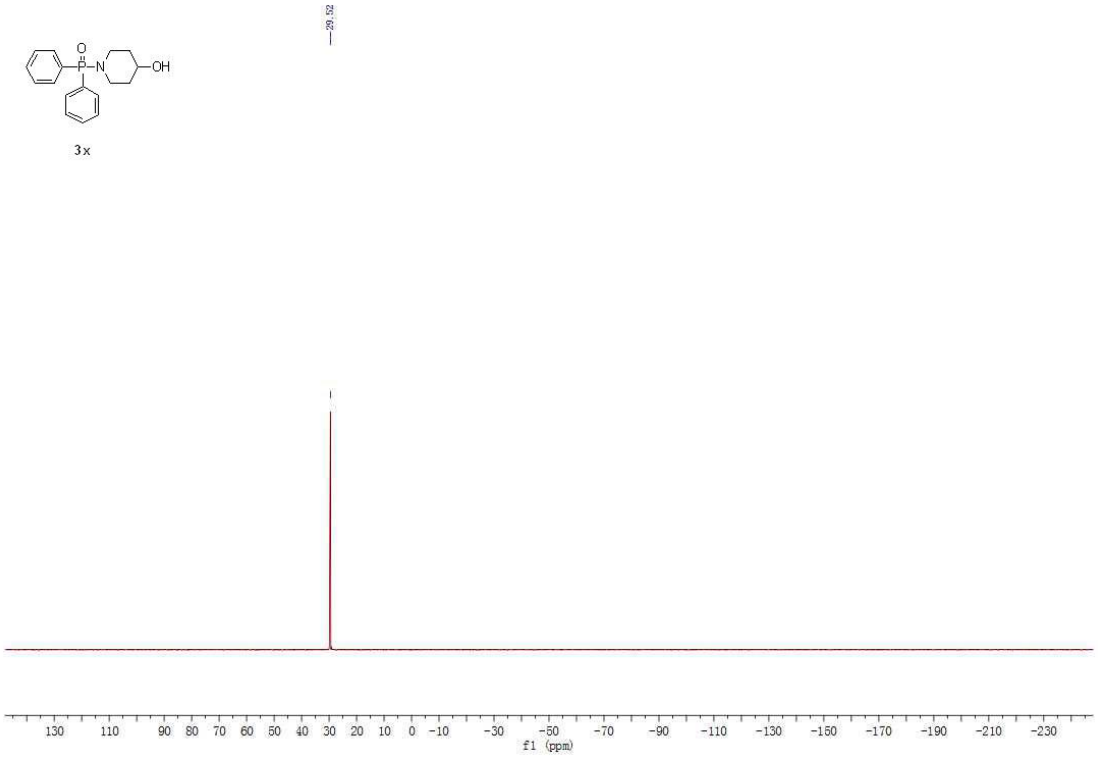
^{1}H NMR of **3x**



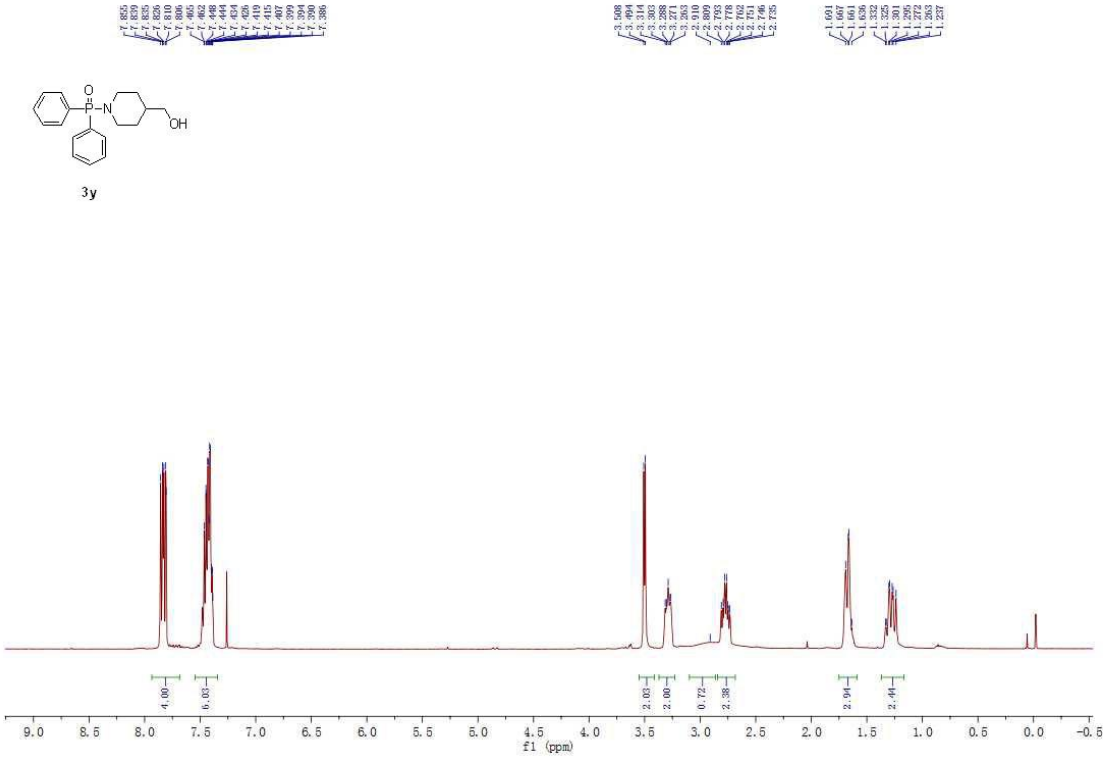
^{13}C NMR of **3x**



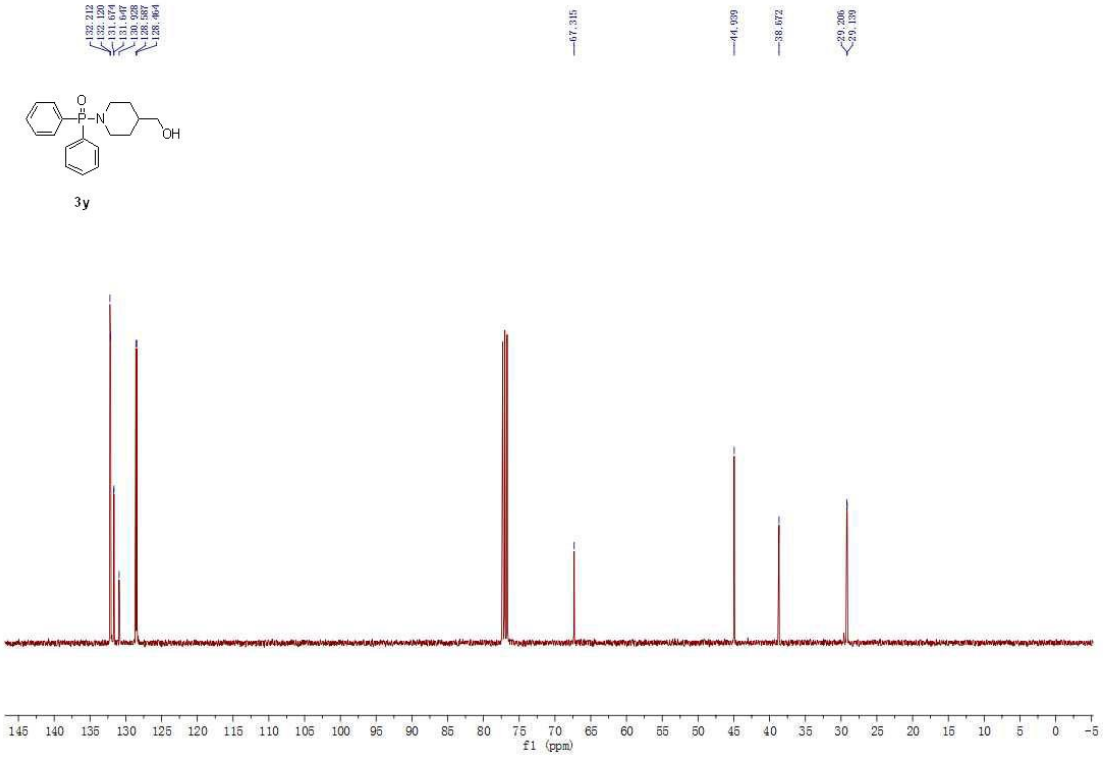
^{31}P NMR of **3x**



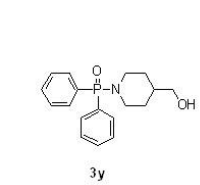
^{1}H NMR of **3y**



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

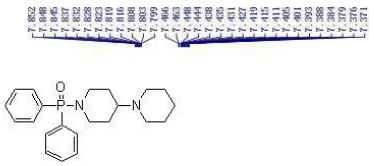


^{31}P NMR of **3y**



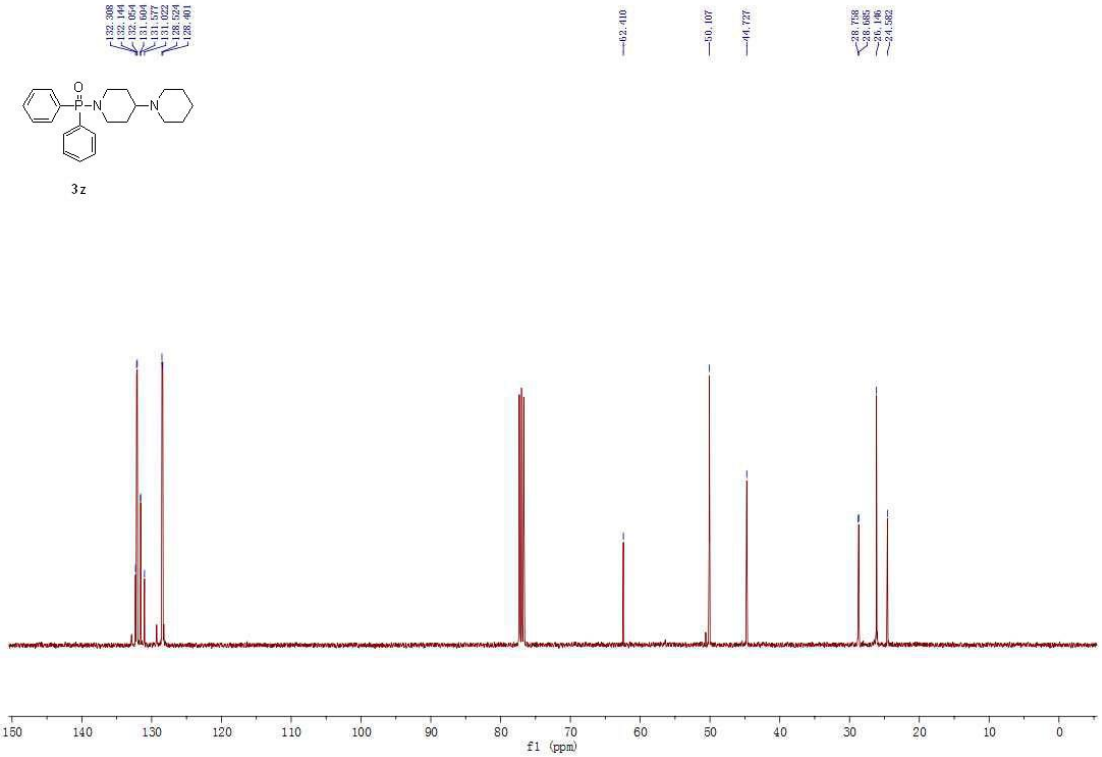
3y

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

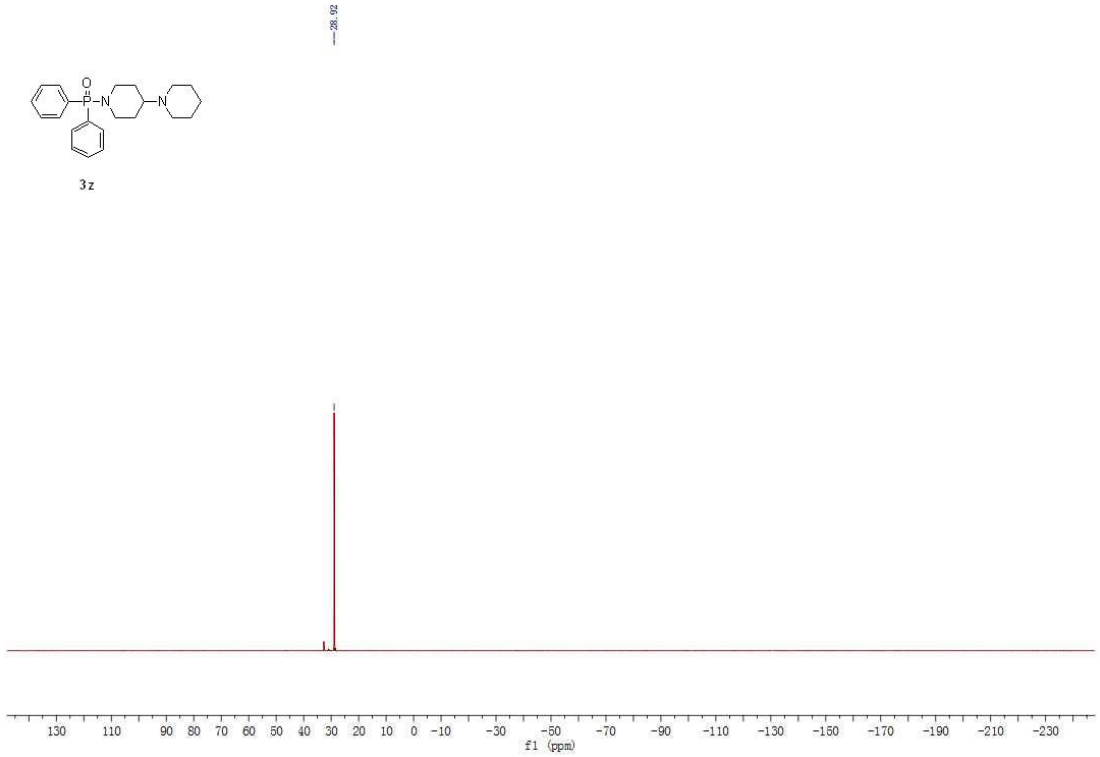


3z

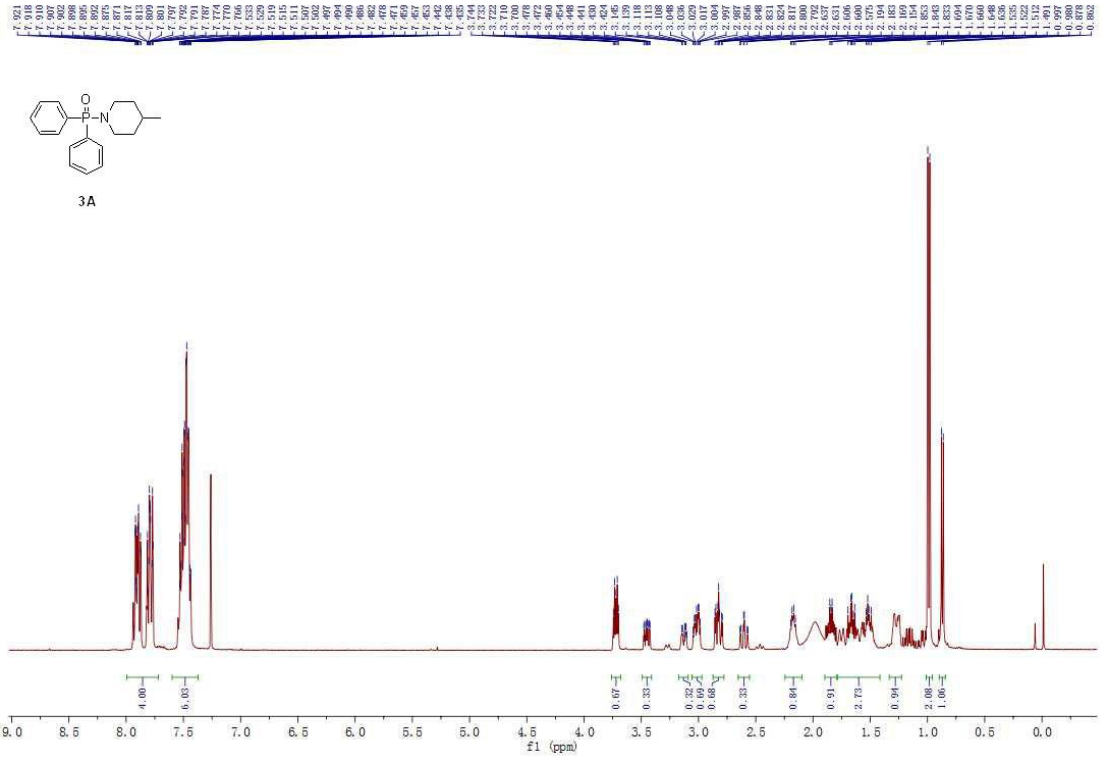
^{13}C NMR of **3z**



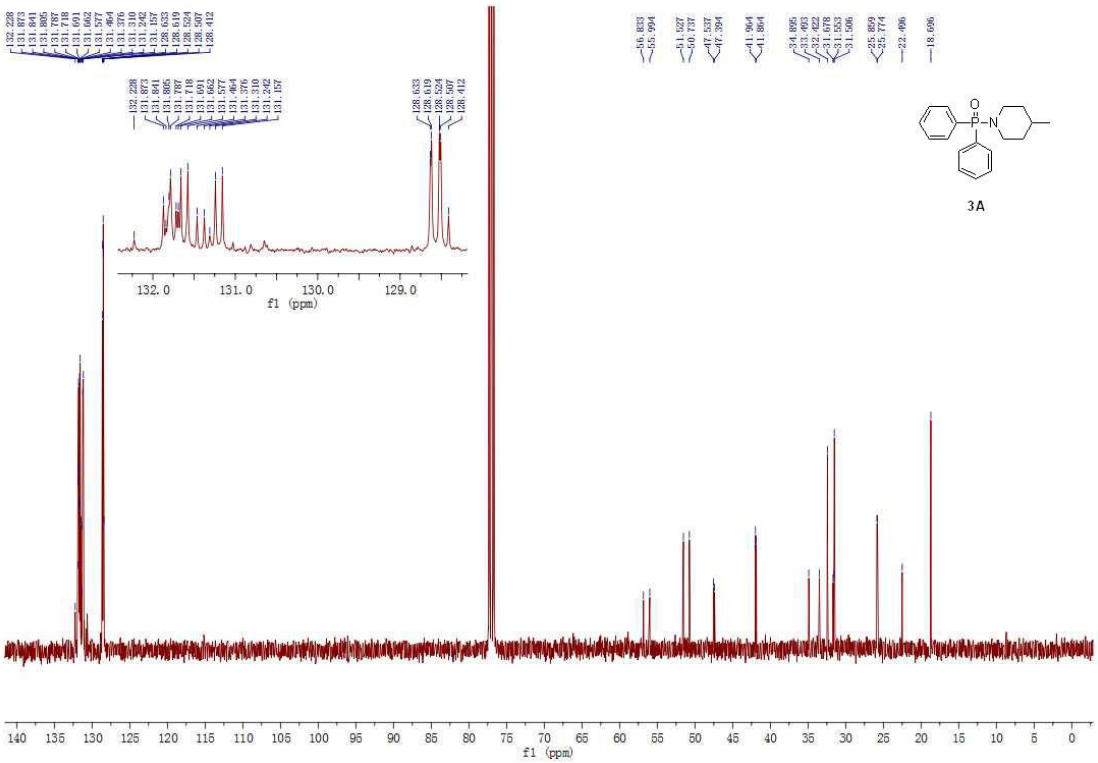
^{31}P NMR of **3z**



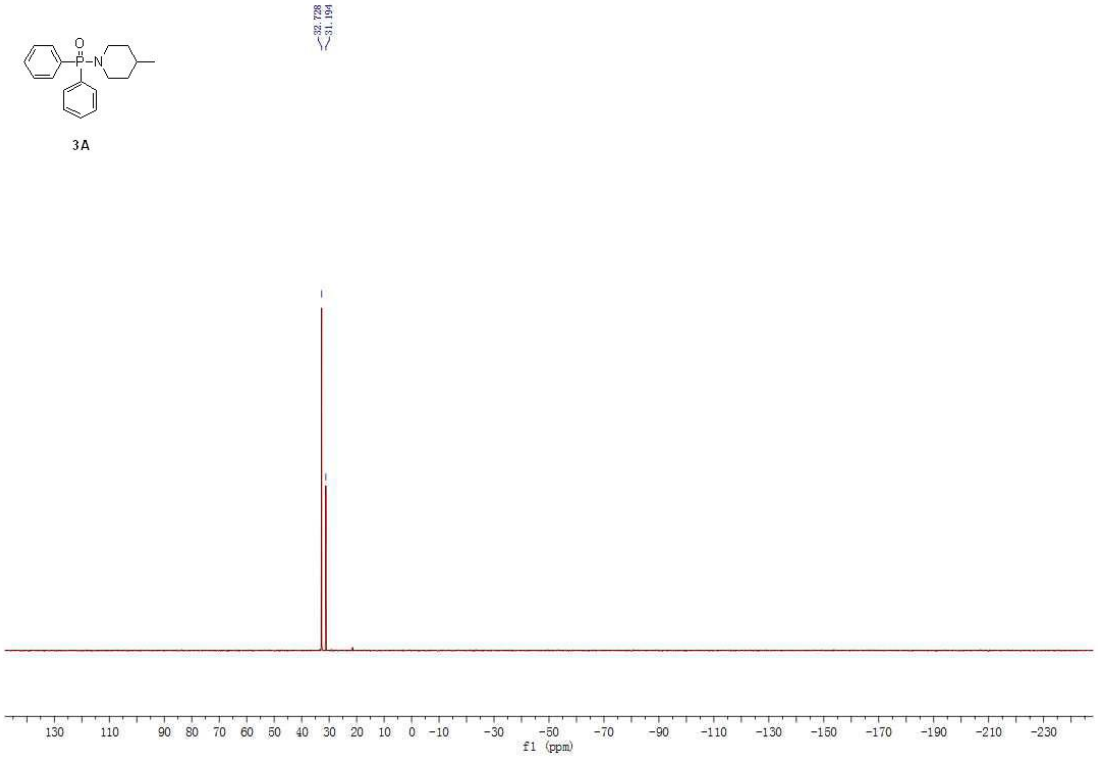
^{1}H NMR of **3A**



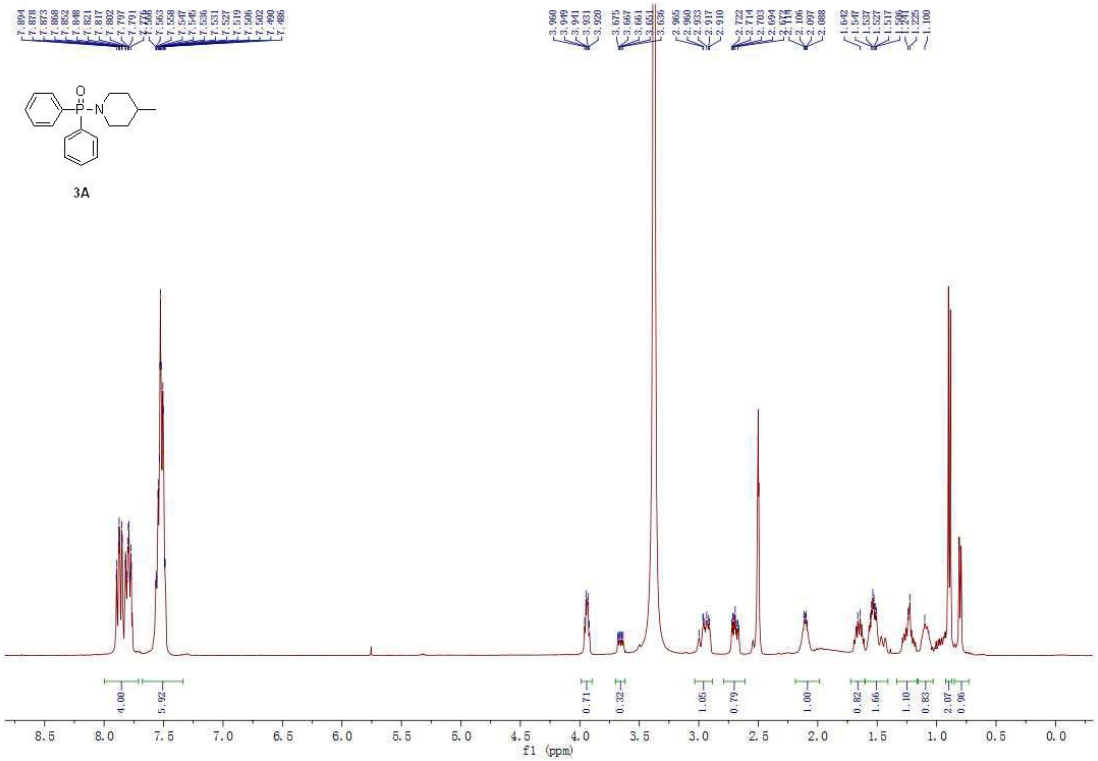
^{13}C NMR of **3A**



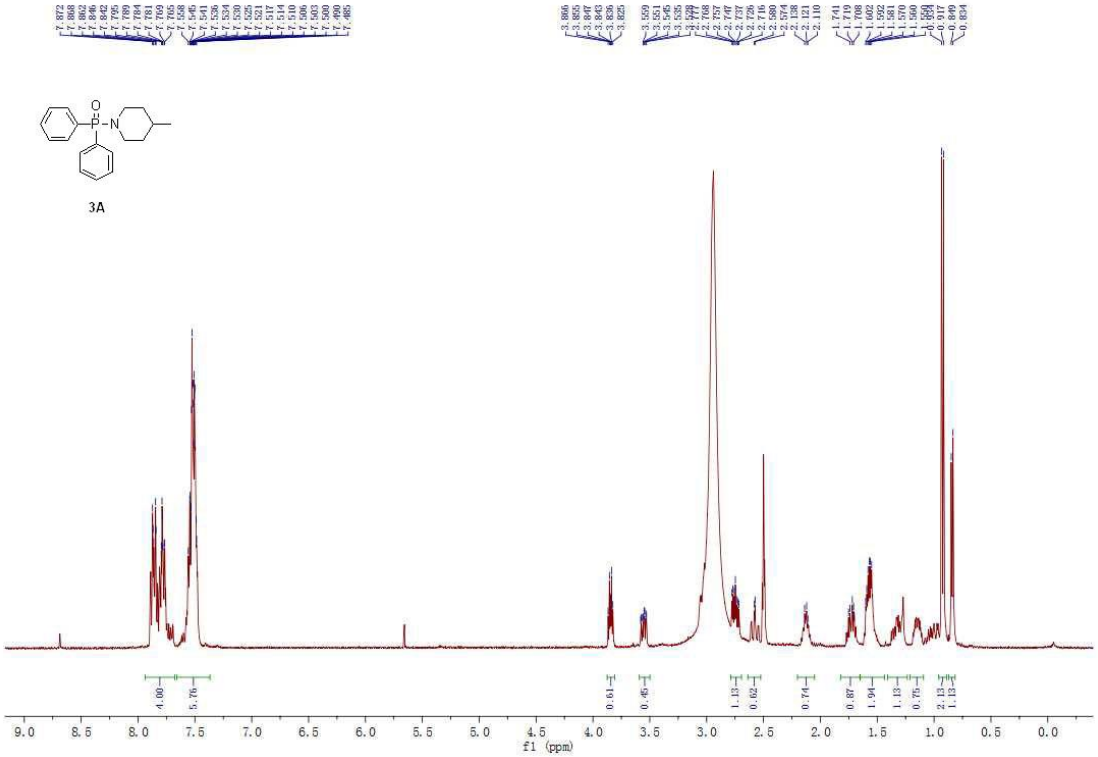
^{31}P NMR of **3A**



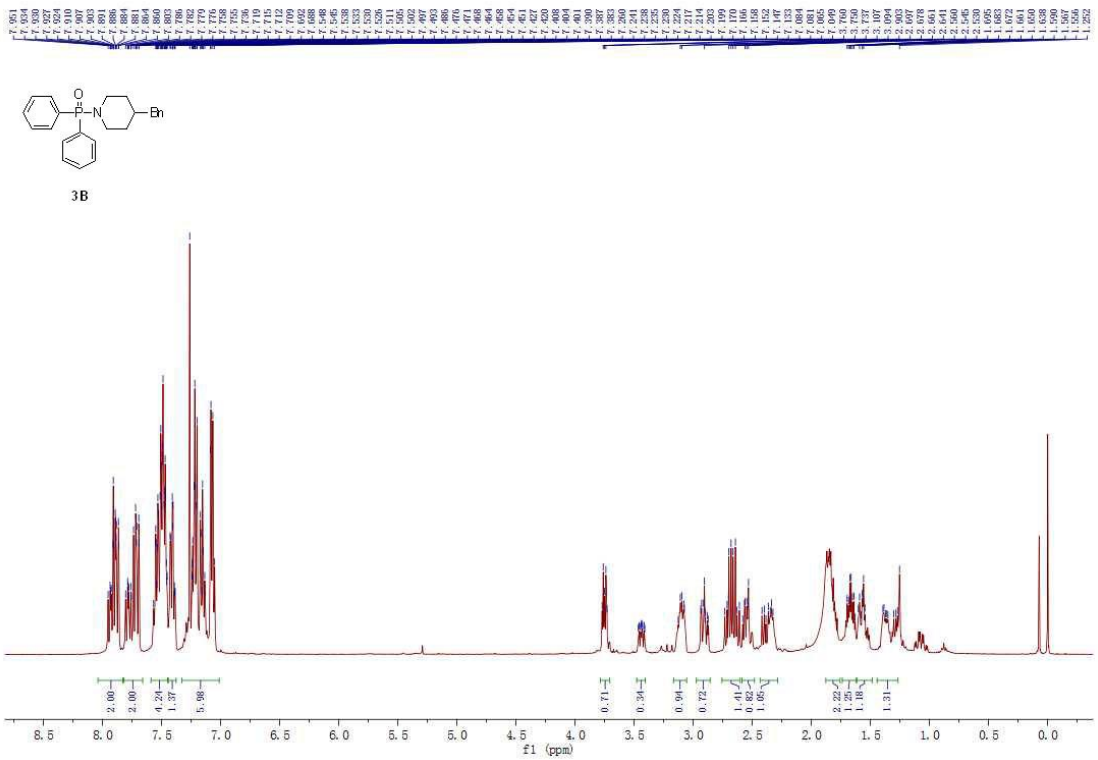
^{1}H NMR of **3A** (d_6-DMSO)



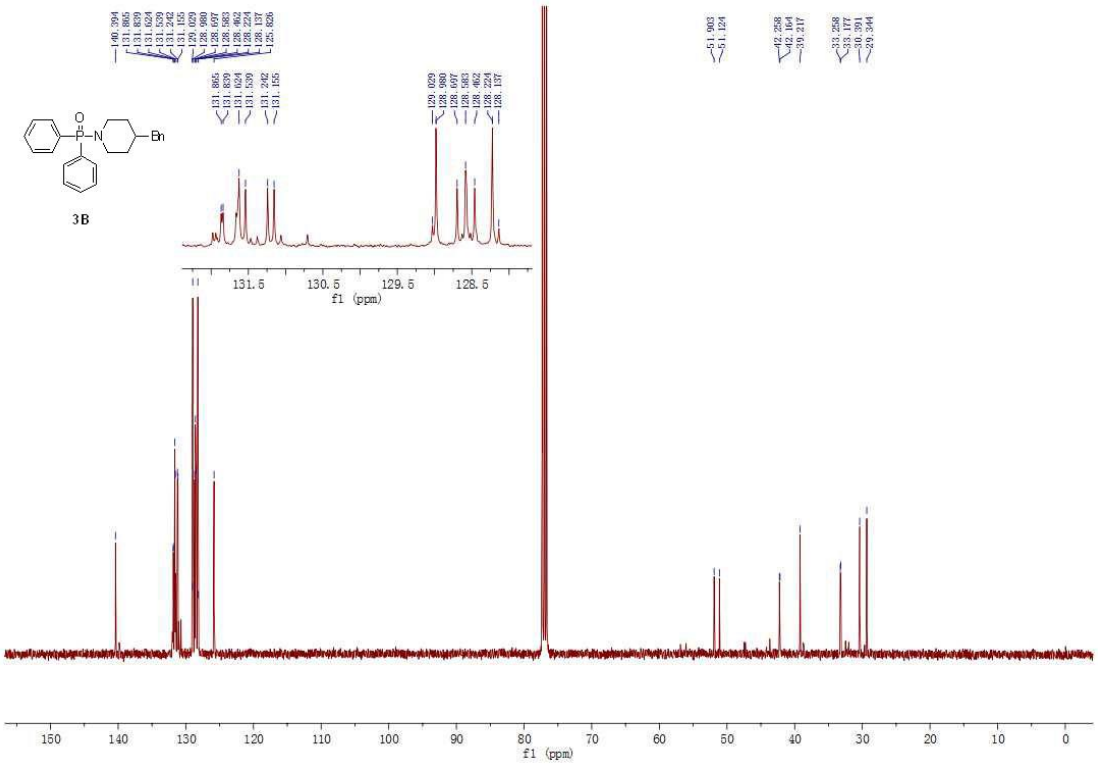
^{1}H NMR of **3A** (d_6-DMSO at 100^{o}C)



^{1}H NMR of **3B**



^{13}C NMR of **3B**



^{31}P NMR of **3B**