Supporting Information

for

Ni-catalyzed construction of C–P bond from electron-deficient phenols via the in situ aryl C–O activation by PyBroP

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Contents

1. General Information

All reactions were carried out under N_2 atmosphere. The solvents were dried over Zeolite or distilled according to the standard method. Anhydrous $NiCl_2$ and ligands were purchased from *J*&K Chemical Ltd and Alfa Aesar, respectively. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ or in DMSO-D_6 using tetramethylsilane (TMS) as the internal standard. 85% H_3PO_4 was used as external standard for ^{31}P NMR. All shifts were given in ppm. All coupling constants (*J* values) were reported in Hertz (Hz). High resolution mass was measured by using IonSpec 7.0T MALDI-FTICRMs. Column chromatography was performed on silica gel 200-300 mesh.

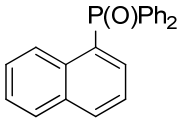
2. Experimental Procedures

General procedure for the cross-coupling of phenols with H-phosphine oxide (or H-phosphite) through in situ phenol activation mediated by PyBroP.

Phenol (0.5 mmol), PyBroP (1.1 equiv), and anhydrous K_2CO_3 (2.0 mmol) were charged in an oven-dried Schlenk tube equipped with a magnetic bar. The tube was then evacuated (3 × 5 min) under vacuum and backfilled with N_2. Dried MeCN (3 mL) were injected *via* syringe. The reaction mixture was stirred at 100 ºC for 3 h until phenol had disappeared as monitored by TLC. The reaction vessel was cooled down and recharged with $NiCl_2$(dppp) (0.05 mmol, 10 mol%) and diphenylphosphine oxide (0.75 mmol). The reaction mixture was then stirred at 100–120 ºC for additional hours. After cooling down, the reaction mixture was poured into water (30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. The crude material was purified by flash chromatography on silica gel using a mixture of hexane and acetone as eluents to give the desired cross-coupled products.

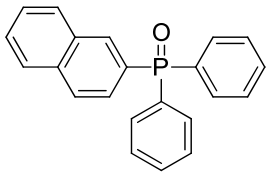
3. Spectral Data.

1-Naphthalenyldiphenylphosphine oxide (3a)[1]



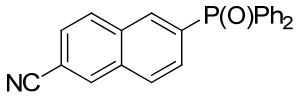
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.59 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.72–7.66 (m, 4H), 7.58–7.52 (m, 2H), 7.52–7.41 (m, 6H), 7.41–7.36 (m, 1H), 7.34–7.28 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.89 (d, *J* = 7.5 Hz), 133.73 (d, *J* = 10.5 Hz), 133.24, 133.19, 132.49, 132.06 (d, *J* = 9.0 Hz), 131.85, 129.27, 128.73, 128.56 (d, *J* = 12.0 Hz), 127.60 (d, *J* = 4.5 Hz), 127.32, 126.47, 124.11 (d, *J* = 15.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 32.12.

Naphthalen-2-yldiphenylphosphine oxide (3b)[2]



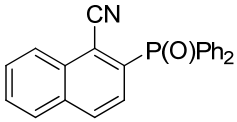
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 13.8 Hz, 1H), 7.92–7.87 (m, 3H), 7.74–7.70 (m, 4H), 7.66–7.53 (m, 5H), 7.49–7.46 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 134.54, 133.83 (d, *J* = 9.0 Hz), 132.73, 132.25 (d, *J* = 13.5 Hz), 131.96 (d, *J* = 9.0 Hz), 131.85, 129.43 (d, *J* = 103.5 Hz), 128.77, 128.39 (d, *J* = 12.0 Hz), 128.20, 128.11, 127.66, 126.81, 126.66 (d, *J* = 10.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 28.96.

6-(diphenylphosphoryl)-2-naphthonitrile (3c)



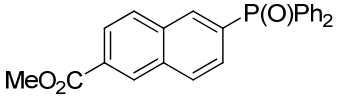
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 13.4 Hz, 1H), 8.27 (s, 1H), 8.00–7.94 (m, 2H), 7.79–7.74 (m, 1H), 7.74–7.67 (m, 5H), 7.61–7.56 (m, 2H), 7.52-7.47 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 134.07, 133.80, 133.69 (d, *J* = 9.1 Hz), 133.54 (d, *J* = 12.1 Hz), 133.40, 132.26, 132.02 (d, *J* = 10.6 Hz), 131.8 (d, *J* = 105.7 Hz), 130.18, 128.66 (d, *J* = 12.1 Hz), 128.65, 128.58, 127.40, 118.54, 111.63. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 28.02. HRMS: $[M+H]^+$ *m/z* calcd for $C_{23}H_{17}NOP$: 354.1048, found: 354.1014.

2-(diphenylphosphoryl)-1-naphthonitrile (3d)



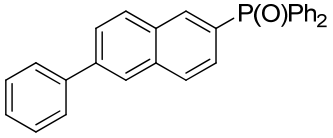
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.35 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 8.02–7.96 (m, 2H), 7.86–7.79 (m, 4H), 7.77–7.70 (m, 2H), 7.64–7.59 (m, 2H), 7.55–7.50 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 136.63 (d, *J* = 93.6 Hz), 134.00, 133.22 (d, *J* = 9.1 Hz), 132.57, 132.47, 132.28 (d, *J* = 10.6 Hz), 130.87 (d, *J* = 107.2 Hz), 129.43, 129.28, 128.71 (d, *J* = 12.1 Hz), 128.59, 128.11 (d, *J* = 7.6 Hz), 125.9, 115.38 (d, *J* = 6.0 Hz), 114.02 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 27.14. HRMS: $[M+H]^+$ *m/z* calcd for $C_{23}H_{17}NOP$: 354.1048, found: 354.1019.

Methyl 6-(diphenylphosphoryl)-2-naphthoate (3e)



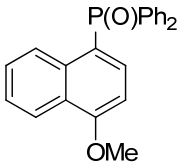
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.63 (s, 1H), 8.33 (d, *J* = 13.6 Hz, 1H), 8.13 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.01 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.75–7.68 (m, 5H), 7.60–7.55 (m, 2H), 7.52–7.46 (m, 4H), 3.99 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 166.74, 134.40 (d, *J* = 13.5 Hz), 133.80, 133.62 (d, *J* = 9.0 Hz), 132.81, 132.17 (d, *J* = 103.5 Hz), 132.15, 132.08, 130.71, 129.63, 129.54, 129.22, 128.63 (d, *J* = 12.0 Hz), 127.65 (d, *J* =10.5 Hz), 126.32, 52.41. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 28.56. HRMS: $[M+H]^+$ *m/z* calcd for $C_{24}H_{20}O_3P$: 387.1150, found: 387.1179.

Diphenyl(6-phenylnaphthalen-2-yl)phosphine oxide (3f)



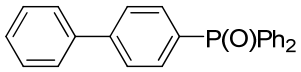
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.31 (d, *J* = 13.7 Hz, 1H), 8.07 (s, 1H), 7.98–7.93 (m, 2H), 7.83–7.80 (m, 1H), 7.76–7.69 (m, 6H), 7.69–7.64 (m, 1H), 7.59–7.54 (m, 2H), 7.53–7.45 (m, 6H), 7.43–7.39 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 140.75, 140.17, 134.78, 133.50 (d, *J* = 9.1 Hz), 132.77, 132.08, 131.92 (d, *J* = 10.6 Hz), 131.79, 131.34 (d, *J* = 13.6 Hz), 129.44 (d, *J* = 104.2 Hz), 129.24, 128.74, 128.35 (d, *J* = 12.1 Hz), 127.63, 127.22, 127.10 (d, *J* = 10.6 Hz), 126.49, 125.37. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 28.82. HRMS: $[M+H]^+$ *m/z* calcd for $C_{28}H_{22}OP$: 405.1408, found: 405.1392.

(4-methoxynaphthalen-1-yl)diphenylphosphine oxide (3g)



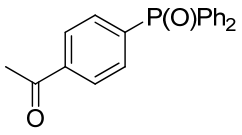
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.49 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 7.72–7.65 (m, 4H), 7.57–7.50 (m, 2H), 7.50–7.41 (m, 6H), 7.25–7.21 (m, 1H), 6.73–6.69 (m, 1H), 4.02 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.10, 135.20 (d, *J* = 13.6 Hz), 134.81 (d, *J* = 9.1 Hz), 133.23 (d, *J* = 105.7 Hz), 132.04 (d, *J* = 9.1 Hz), 131.62, 128.42 (d, *J* = 12.1 Hz), 127.70, 127.30 (d, *J* = 4.5 Hz), 126.05 (d, *J* = 10.6 Hz), 125.74, 122.46, 120.06 (d, *J* = 108.7 Hz), 102.13 (d, *J* = 15.1 Hz), 55.59. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 31.84. HRMS: $[M+H]^+$ *m/z* calcd for $C_{23}H_{20}O_2P$: 359.1201, found: 359.1209.

(4-Biphenylyl)diphenylphosphine oxide (3h) [1,3]



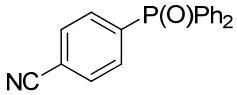
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.77–7.66 (m, 8H), 7.62–7.58 (m, 2H), 7.58–7.53 (m, 2H), 7.51–7.44 (m, 6H), 7.41–7.37 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.69, 139.83, 132.82, 132.56 (d, *J* = 10.6 Hz), 132.09, 132.02, 131.93, 130.99 (d, *J* = 104.2 Hz), 128.90, 128.49 (d, *J* = 12.1 Hz), 127.50 (d, *J* = 105.0 Hz), 127.09. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 29.02.

(4-Acetylphenyl)diphenylphosphine oxide (3i) [1, 3]



^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.05–7.99 (m, 2H), 7.83–7.77 (m, 2H), 7.70–7.63 (m, 4H), 7.60–7.55 (m, 2H), 7.52–7.45 (m, 4H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.38, 139.37, 137.61 (d, *J* = 100.0 Hz), 132.29 (d, *J* = 11.0 Hz), 132.17, 131.89 (d, *J* = 9.0 Hz), 131.13, 128.56 (d, *J* = 12.0 Hz), 127.92 (d, *J* = 12.0 Hz), 26.69. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 27.97.

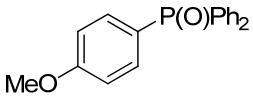
(4-Cyanophenyl)diphenylphosphane oxide (3j) [4]



^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83–7.78 (m, 2H), 7.77–7.73 (m, 2H), 7.68–7.63 (m, 4H), 7.62–7.57 (m, 2H), 7.53–7.48 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 138.17 (d, *J* = 96.0

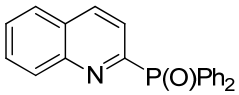
Hz), 132.42, 132.36, 131.84, 131.79, 131.73, 130.9 (d, J = 105.0 Hz), 128.63 (d, J = 12.0 Hz), 116.53 (d, J = 334.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 27.57.

(4-Methoxyphenyl)diphenylphosphine oxide (3k) [1, 4]



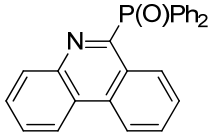
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72–7.63 (m, 4H), 7.63–7.51 (m, 4H), 7.51–7.43 (m, 4H), 7.01–6.95 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.49, 133.95 (d, J = 10.5 Hz), 132.92 (d, J = 103.5 Hz), 132.04 (d, J = 10.5 Hz), 131.77, 128.42 (d, J = 12.0 Hz), 123.50 (d, J = 109.5 Hz), 114.08 (d, J = 13.5 Hz), 55.31. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 28.89.

Diphenyl(quinolin-2-yl)phosphine oxide (3l)



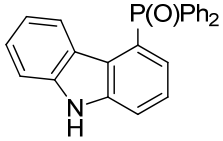
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.38–8.30 (m, 2H), 8.17 (d, J = 8.5 Hz, 1H), 8.03–7.96 (m, 4H), 7.87 (d, J = 8.1, 1H), 7.78–7.73 (m, 1H), 7.64–7.60 (m, 1H), 7.54–7.48 (m, 2H), 7.48–7.42 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.12 (d, J = 131.4 Hz), 148.10 (d, J = 22.7 Hz), 136.08 (d, J = 9.1 Hz), 132.83, 132.19, 132.13, 131.74, 130.29, 129.97, 128.23 (d, J = 12.1 Hz), 128.10, 127.83, 123.32 (d, J = 22.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 20.18. HRMS: $[M+H]^+$ *m/z* calcd for $C_{21}H_{17}NOP$: 330.1048, found: 330.1034.

Phenanthridin-6-yldiphenylphosphine oxide (3m)



^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.52 (d, J = 8.3 Hz, 1H), 8.67 (d, J = 8.3 Hz, 1H), 8.63–8.59 (m, 1H), 8.09–8.04 (m, 1H), 7.98–7.90 (m, 4H), 7.89–7.83 (m, 1H), 7.76–7.67 (m, 3H), 7.55–7.49 (m, 2H), 7.48–7.42 (m, 4H). ^{13}C NMR (150 MHz, DMSO) δ = 156.65 (d, J = 126.84 Hz), 142.97 (d, J = 22.7 Hz), 132.77 (d, J = 102.7 Hz), 132.19 (d, J = 7.6 Hz), 131.87, 131.68, 131.62, 130.41, 129.35 (d, J = 3.0 Hz), 128.45 (d, J = 12.1 Hz), 127.93, 127.55, 126.91, 126.76, 123.77, 123.05, 122.88. ^{31}P NMR (162 MHz, DMSO) δ = 25.41. HRMS: $[M+H]^+$ *m/z* calcd for $C_{25}H_{19}NOP$: 380.1204, found: 380.1187.

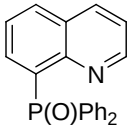
(9H-carbazol-4-yl)diphenylphosphine oxide (3n)



^{1}H NMR (600 MHz, DMSO) δ = 11.69 (s, 1H), 8.51 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.63–7.55 (m, 6H), 7.55–7.49 (m, 4H), 7.49–7.45 (m, 1H), 7.45–7.39 (m, 1H), 7.32 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.76 (dd, J = 14.8, 7.2 Hz, 1H). ^{13}C NMR (150 MHz, DMSO) δ = 140.09 (d, J = 12.1 Hz), 140.00, 132.75 (d, J = 102.7 Hz), 131.86, 131.56 (d, J =

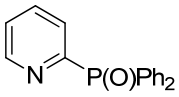
9.1Hz), 128.65 (d, *J* = 12.1 Hz), 125.98, 125.38 (d, *J* = 102.7 Hz), 125.35, 124.35 (d, *J* = 4.5Hz), 124.34 (d, *J* = 30.2 Hz), 123.15 (d, *J* = 9.1 Hz), 120.87, 118.23, 115.49, 110.74. ^{31}P NMR (162 MHz, DMSO) δ = 29.50. HRMS: $[M+H]^+$ *m/z* calcd for $C_{24}H_{19}NOP$: 368.1204, found: 368.1203.

Diphenyl(quinolin-8-yl)phosphine oxide (3o) [5]



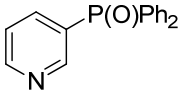
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.80–8.73 (m, 1H), 8.37 (dd, *J* = 14.1, 7.1 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.88–7.80 (m, 4H), 7.71–7.65(m, 1H), 7.51–7.46 (m, 2H), 7.44–7.37 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 149.81, 148.00 (d, *J* = 4.5 Hz), 137.30 (d, *J* = 7.6 Hz), 136.1, 133.62 (d, *J* = 108.7 Hz), 132.80, 132.18 (d, *J* = 10.6 Hz), 131.24, 131.23 (d, *J* = 101.2 Hz), 128.24 (d, *J* = 6.0 Hz), 127.91 (d, *J* = 12.1 Hz), 126.96 (d, *J* = 13.6 Hz), 121.47. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 28.84.

2-Pyridyldiphenylphosphine Oxide (3p) [6]



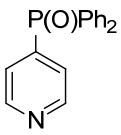
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.80–8.76 (m, 1H), 8.34–8.29 (m, 1H), 7.92–7.83 (m, 5H), 7.54–7.49 (m, 2H), 7.47–7.42 (m, 4H), 7.41–7.36 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 156.37 (d, *J* = 130.5 Hz), 150.08 (d, *J* = 19.5 Hz), 136.11 (d, *J* = 9.0 Hz), 132.50, 132.05 (d, *J* = 9.0 Hz), 131.82, 128.32, 128.24, 125.20. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 20.60.

3-Pyridyldiphenylphosphine Oxide (3q)



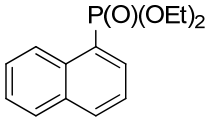
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.80 (m, 2H), 8.11–8.05 (m, 1H), 7.72–7.65 (m, 4H), 7.62–7.57 (m, 2H), 7.54–7.48 (m, 4H), 7.48–7.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.53, 152.41, 139.73 (d, *J* = 7.0 Hz), 132.36, 131.94 (d, *J* = 10.0 Hz), 131.00, 129.64, 128.73 (d, *J* = 13.0 Hz), 123.45 (d, *J* = 9.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 26.09. HRMS: $[M+H]^+$ *m/z* calcd for $C_{17}H_{15}NOP$: 280.0891, found: 280.0875.

Diphenyl(pyridin-4-yl)phosphine oxide (3r)



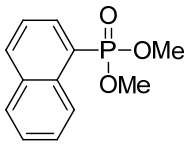
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.80–8.73 (m, 2H), 7.70–7.64 (m, 4H), 7.64–7.58 (m, 4H), 7.54–7.48 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 149.82 (d, *J* = 9.1 Hz), 142.06 (d, *J* = 96.6 Hz), 132.44, 131.88 (d, *J* = 9.1 Hz), 130.84 (d, *J* = 105.7 Hz), 128.70 (d, *J* = 12.1 Hz), 125.66 (d, *J* = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 26.65. HRMS: $[M+H]^+$ *m/z* calcd for $C_{17}H_{15}NOP$: 280.0891, found: 280.0886.

Diethyl naphthalen-1-ylphosphonate (5a) [7-12]



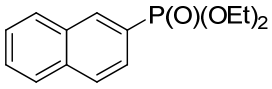
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.53 (d, *J* = 8.5 Hz, 1H), 8.25 (ddd, *J* = 16.3, 7.0, 1.0 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.64–7.58 (m, 1H), 7.58–7.50 (m, 2H), 4.15 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 134.47 (d, *J* = 9.1 Hz), 133.48 (d, *J* = 3.0 Hz), 133.47 (d, *J* = 12.0 Hz), 132.57 (d, *J* = 10.6 Hz), 128.62, 127.26, 126.53 (d, *J* = 19.6 Hz), 126.21, 124.53 (d, *J* = 182.7 Hz), 124.38 (d, *J* = 16.6 Hz), 62.01 (d, *J* = 6.0 Hz), 16.19 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 18.88.

Dimethyl naphthalen-1-ylphosphonate (5b)



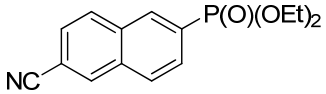
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.47 (d, *J* = 8.4 Hz, 1H), 8.24 (dd, *J* = 7.2, 16.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 6.6 Hz, 1H), 7.57–7.53 (m, 2H), 3.80 (d, *J* = 12.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 134.87 (d, *J* = 9.0 Hz), 133.85 (d, *J* = 1.5 Hz), 133.53 (d, *J* = 12.0 Hz), 132.61 (d, *J* = 10.5 Hz), 128.76, 127.61, 126.40, 126.37, 124.47 (d, *J* = 16.5 Hz), 123.15 (d, *J* = 183.0 Hz), 52.6 (d, *J* = 5.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 22.04.

Diethyl naphthalen-2-ylphosphonate (5c) [7, 8, 10, 11, 12]



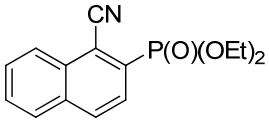
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.44 (d, *J* = 15.5 Hz, 1H), 7.96–7.90 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.79–7.74 (m, 1H), 7.54–7.62 (m, 2H), 4.15 (m, 4H), 1.34 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 134.79, 133.81 (d, *J* = 10.6 Hz), 132.15 (d, *J* = 16.6 Hz), 128.70, 128.17 (d, *J* = 13.6 Hz), 128.04, 127.60, 126.67, 126.24 (d, *J* = 10.6 Hz), 125.26 (d, *J* = 188.8 Hz), 61.97 (d, *J* = 4.5 Hz), 16.15 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 18.80.

Diethyl (6-cyanonaphthalen-2-yl)phosphonate (5d)



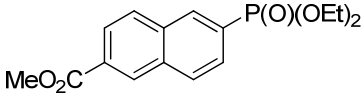
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.47 (d, *J* = 15.3 Hz, 1H), 8.28 (s, 1H), 8.05–8.01 (m, 1H), 8.01–7.97 (m, 1H), 7.93–7.87 (m, 1H), 7.72–7.69 (m, 1H), 4.18 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.77, 133.60, 133.53, 133.40, 130.11, 130.00, 128.69 (d, *J* = 15.1 Hz), 128.23 (d, *J* = 9.1 Hz), 127.28, 118.52, 111.61, 62.40 (d, *J* = 6.0 Hz), 16.27 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 16.77. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{15}H_{16}NO_3PNa$: 312.0765, found: 312.0762.

Diethyl (1-cyanonaphthalen-2-yl)phosphonate (5e)



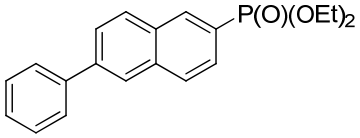
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.43 (d, *J* = 8.4 Hz, 1H), 8.19–8.09 (m, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.80–7.75 (m, 1H), 7.75–7.70 (m, 1H), 4.30 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 134.18, 132.85, 132.76, 132.40 (d, *J* = 13.6 Hz), 132.07 (d, *J* = 185.7 Hz), 129.24 (d, *J* = 15.1 Hz), 128.49, 128.18 (d, *J* = 7.6 Hz), 125.96, 115.56 (d, *J* = 7.6 Hz), 113.46 (d, *J* = 4.5 Hz), 63.22 (d, *J* = 6.0 Hz), 16.13 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 12.84. HRMS: $[M+Na]^+$ *m/z* calcd for $C_{15}H_{16}NO_3PNa$: 312.0765, found: 312.0749.

Methyl 6-(diethoxyphosphoryl)-2-naphthoate (5f)



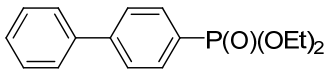
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.64 (s, 1H), 8.46 (d, *J* = 15.4 Hz, 1H), 8.16–8.11 (m, 1H), 8.06–8.01 (m, 1H), 8.01–7.96 (m, 1H), 7.86–7.80 (m, 1H), 4.17 (m, 4H), 4.00 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 166.55, 134.19 (d, *J* = 18.1 Hz), 133.92, 133.39 (d, *J* = 9.1 Hz), 130.53, 129.53 (d, *J* = 15.1 Hz), 129.38, 129.02, 128.09 (d, *J* = 187.2 Hz), 127.12 (d, *J* = 10.6 Hz), 126.08, 62.19 (d, *J* = 4.5 Hz), 52.23, 16.21 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 17.65. HRMS: $[M+H]^+$ *m/z* calcd for $C_{16}H_{20}O_5P$: 323.1048, found: 323.1046.

Diethyl (6-phenylnaphthalen-2-yl)phosphonate (5g)



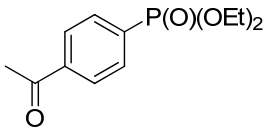
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.46 (d, *J* = 15.4 Hz, 1H), 8.07 (s, 1H), 8.03–7.99 (m, 1H), 7.99–7.95(m, 1H), 7.85–7.81 (m, 1H), 7.81–7.76 (m, 1H), 7.74–7.71 (m, 2H), 7.53–7.48 (m, 2H), 7.44–7.39 (m, 1H), 4.17 (m, 4H), 1.35 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 140.92, 140.41, 135.23, 133.71 (d, *J* = 10.6 Hz), 131.43 (d, *J* = 16.6 Hz), 129.37, 128.89, 128.53 (d, *J* = 15.1 Hz), 127.77, 127.40, 126.86 (d, *J* = 10.6 Hz), 126.56, 125.53, 125.36 (d, *J* = 187.2 Hz), 62.12 (d, *J* = 4.5 Hz), 16.30 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 18.81. HRMS: $[M+H]^+$ *m/z* calcd for $C_{20}H_{22}O_3P$: 341.1306, found: 341.1316.

Diethyl biphenyl-4-ylphosphonate (5h) [7, 11, 12]



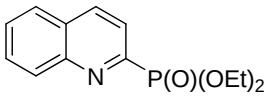
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (dd, *J* = 13.0, 8.1 Hz, 2H), 7.69 (dd, *J* = 8.1, 3.8 Hz, 2H), 7.63–7.59 (m, 2H), 7.49–7.44 (m, 2H), 7.42–7.38 (m, 1H), 4.15 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 145.10, 139.86, 132.20 (d, *J* = 10.6 Hz), 128.84, 128.06, 127.16, 127.01, 126.81 (d, *J* = 190.3 Hz), 62.06 (d, *J* = 4.5 Hz), 16.26 (d, *J* = 7.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 18.71.

Diethyl 4-acetylphenylphosphonate (5i) [7, 9, 11, 12]



^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.05–8.01 (m, 2H), 7.95–7.89 (m, 2H), 4.15 (m, 4H), 2.64 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.41, 139.79, 133.34 (d, *J* = 187.2 Hz), 132.01 (d, *J* = 9.1 Hz), 127.98 (d, *J* = 15.1 Hz), 62.38 (d, *J* = 6.0 Hz), 26.73, 16.26 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 16.58.

Diethyl quinolin-2-ylphosphonate (5j)



^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.30–8.26 (m, 2H), 8.03–7.99 (m, 1H), 7.89-7.85 (m, 1H), 7.81–7.76 (m, 1H), 7.66–7.62 (m, 1H), 4.32 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 152.57 (d, *J* = 225.0 Hz), 148.04 (d, *J* = 27.2 Hz), 136.00 (d, *J* = 12.1 Hz), 130.23, 129.98, 128.38 (d, *J* = 3.0 Hz), 128.16, 127.54, 123.13 (d, *J* = 27.2 Hz), 63.99 (d, *J* = 6.0 Hz), 16.20 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 10.19. HRMS: $[M+H]^+$ *m/z* calcd for $C_{13}H_{17}NO_3P$: 266.0946, found: 266.0948.

References

1. X.-H. Zhang, H.-Z. Liu, X.-M. Hu, et al. *Org. Lett*. **2011**, *13*, 3478–3481.
2. M. Sun, H.-Y. Zhang, Q. Han, K. Yang, S.-D. Yang, *Chem. Eur. J*. **2011**, *17*, 9566–9570.
3. L.-J. Xu, *J*. Mo, C. Baillie, J.-L Xiao, *J. Organometallic. Chem.* **2003**, *687*, 301–312.
4. S. E. Vaillard, C. Mück-Lichtenfeld, S. Grimme, A. Studer, *Angew. Chem. Int. Ed.* **2007**, *46*, 6533–6536.
5. W. Sun, Q.-S. Zhang, L. Qin, et al, *Eur. J. Inorg. Chem*. **2010**, *25*, 4009–4017.
6. G. R. Newkome, D. C. Hager, *J. Org. Chem*. **1978**, *43*, 947–949.
7. R.-Q. Zhang, J. Xu, Z.-S. Cai, et al. *Org. Lett*. **2011**, *13*, 2110–2113.
8. M. Kalek, M. Jezowska, J. Stawinskia, *Adv. Synth. Catal*. **2009**, *351*, 3207–3216.
9. M. Andaloussi, J. Lindh, J. Sävmarker, et al. *Chem. Eur. J*. **2009**, *15*, 13069–13074.
10. M. Kalek, A. Ziadi, *J*. Stawinski. *Org. Lett*. **2008**, *10*, 4637–4640.
11. G.-Q. Yang, C.-R. Shen, L. Zhang, W.-B. Zhang, *Tetrahedron Lett.* **2011**, *52*, 5032–5035.
12. Y. Luo, J. Wu, *Organometallics* **2009**, *28*, 6823–6826.

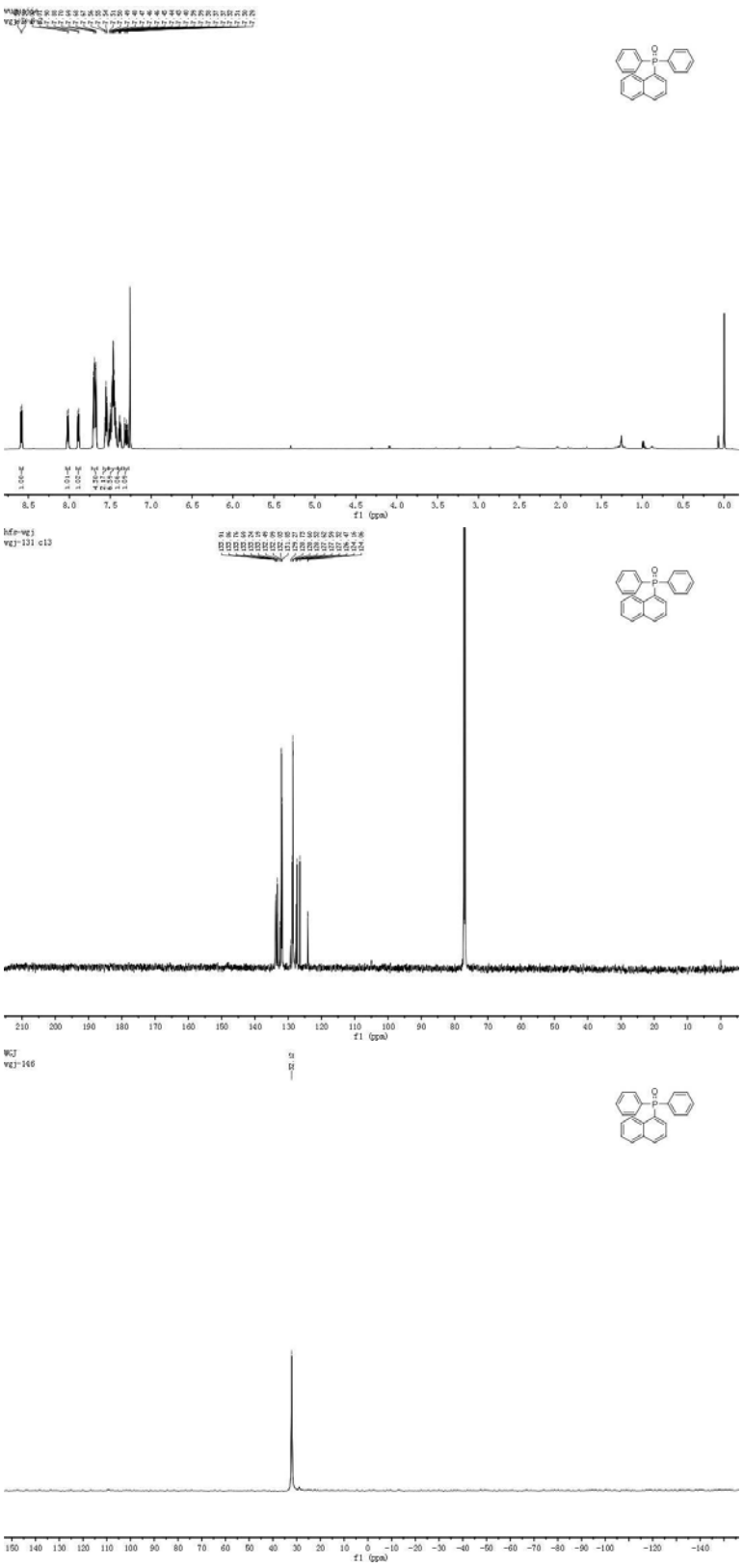


Figure S1. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3a**

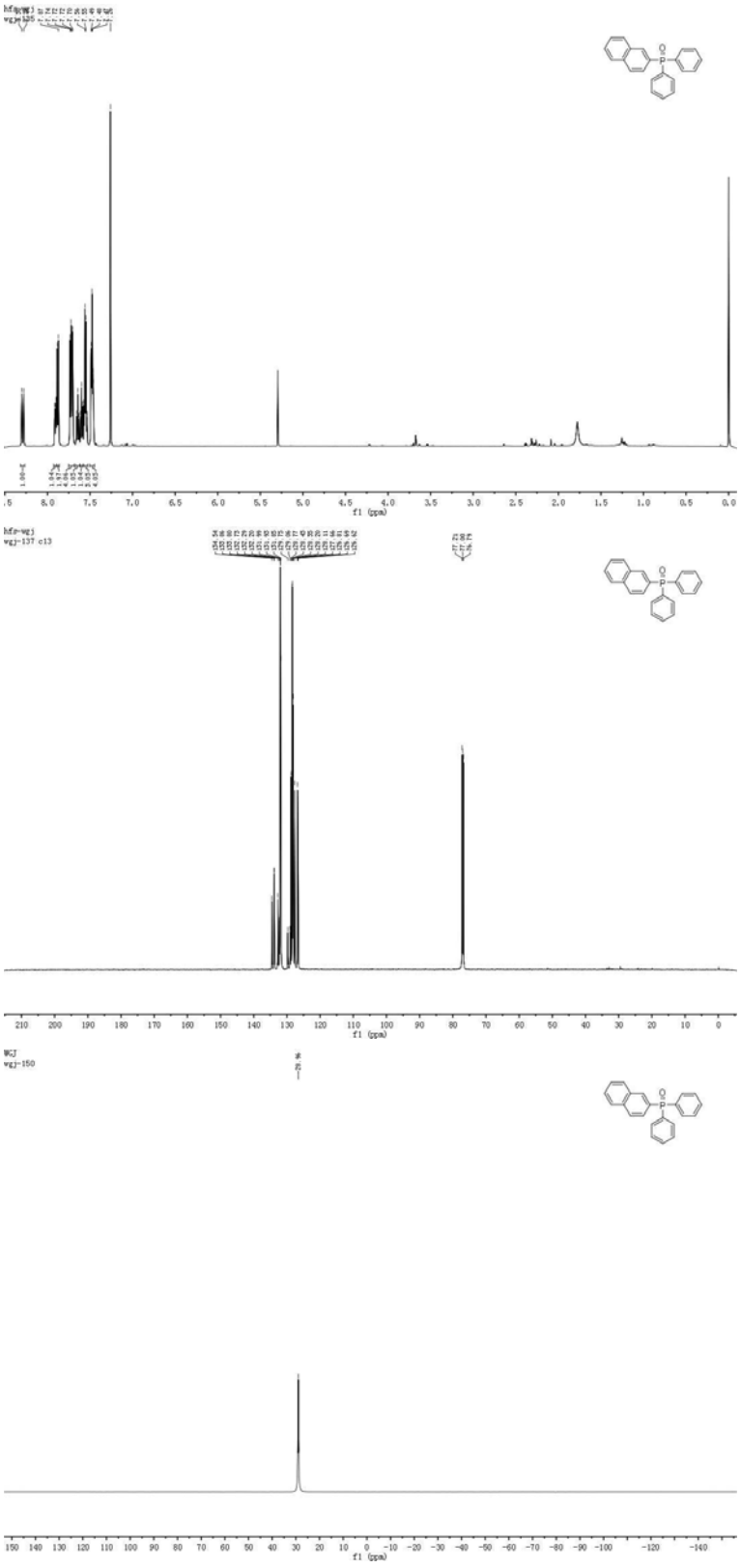


Figure S2. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3b**

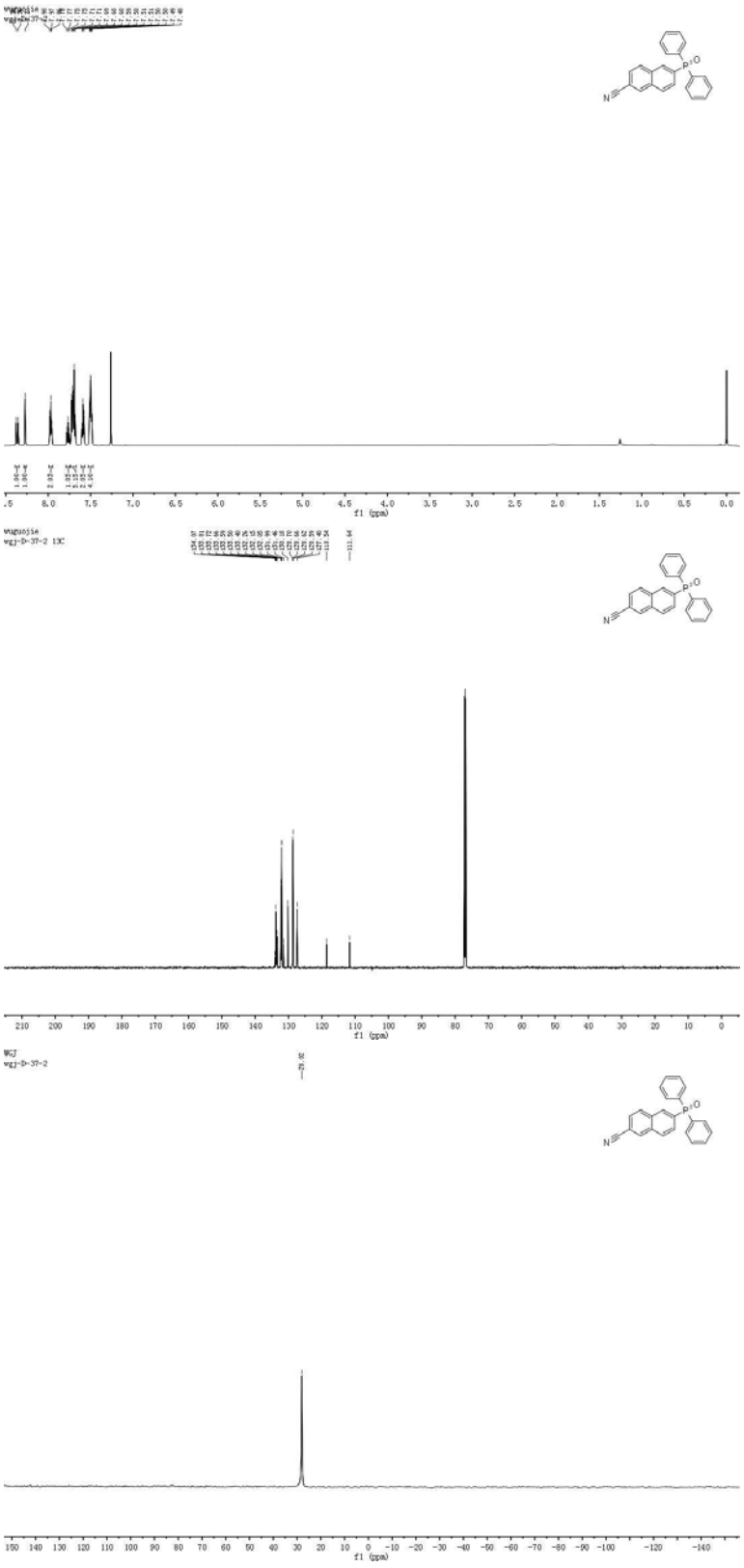


Figure S3. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3c**

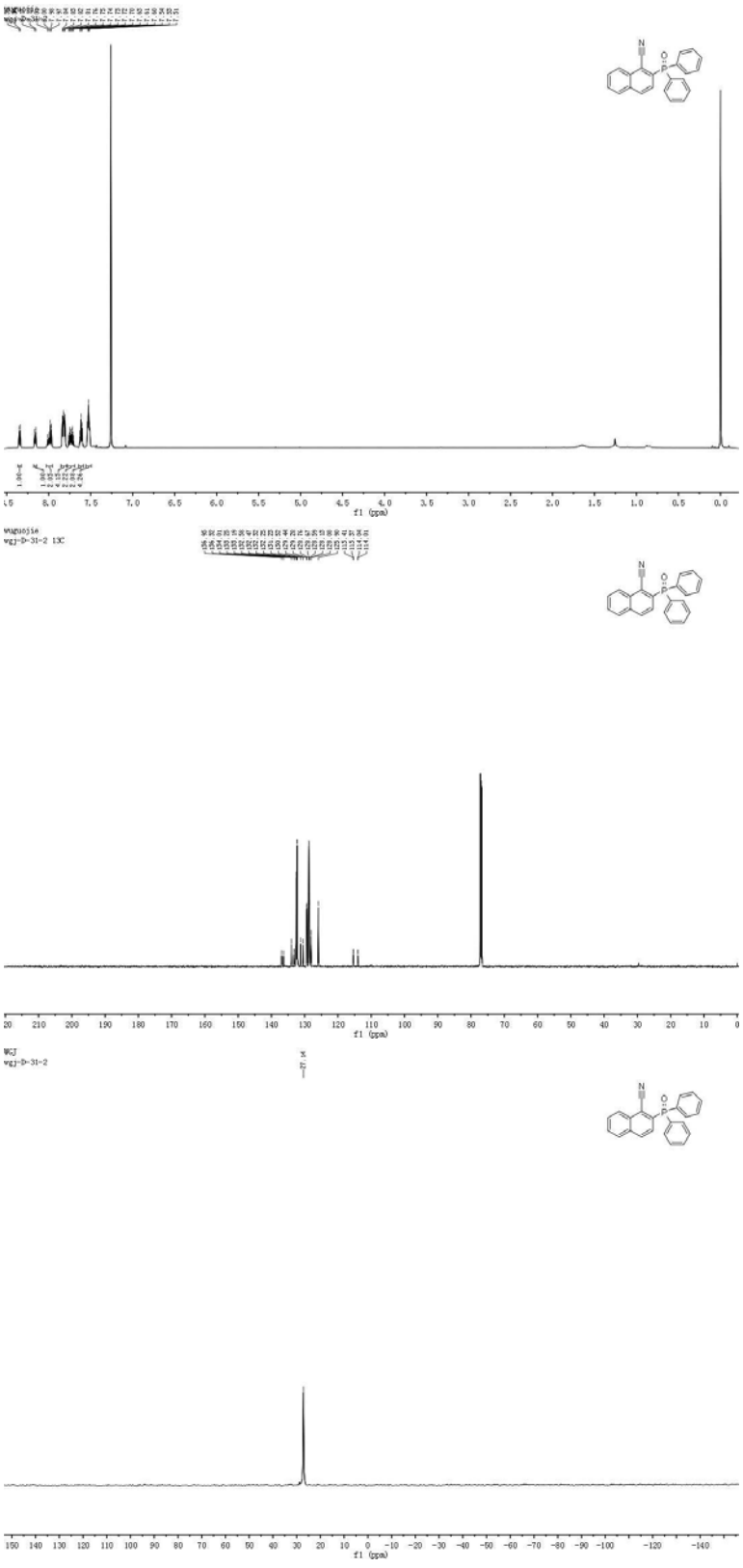


Figure S4. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3d**

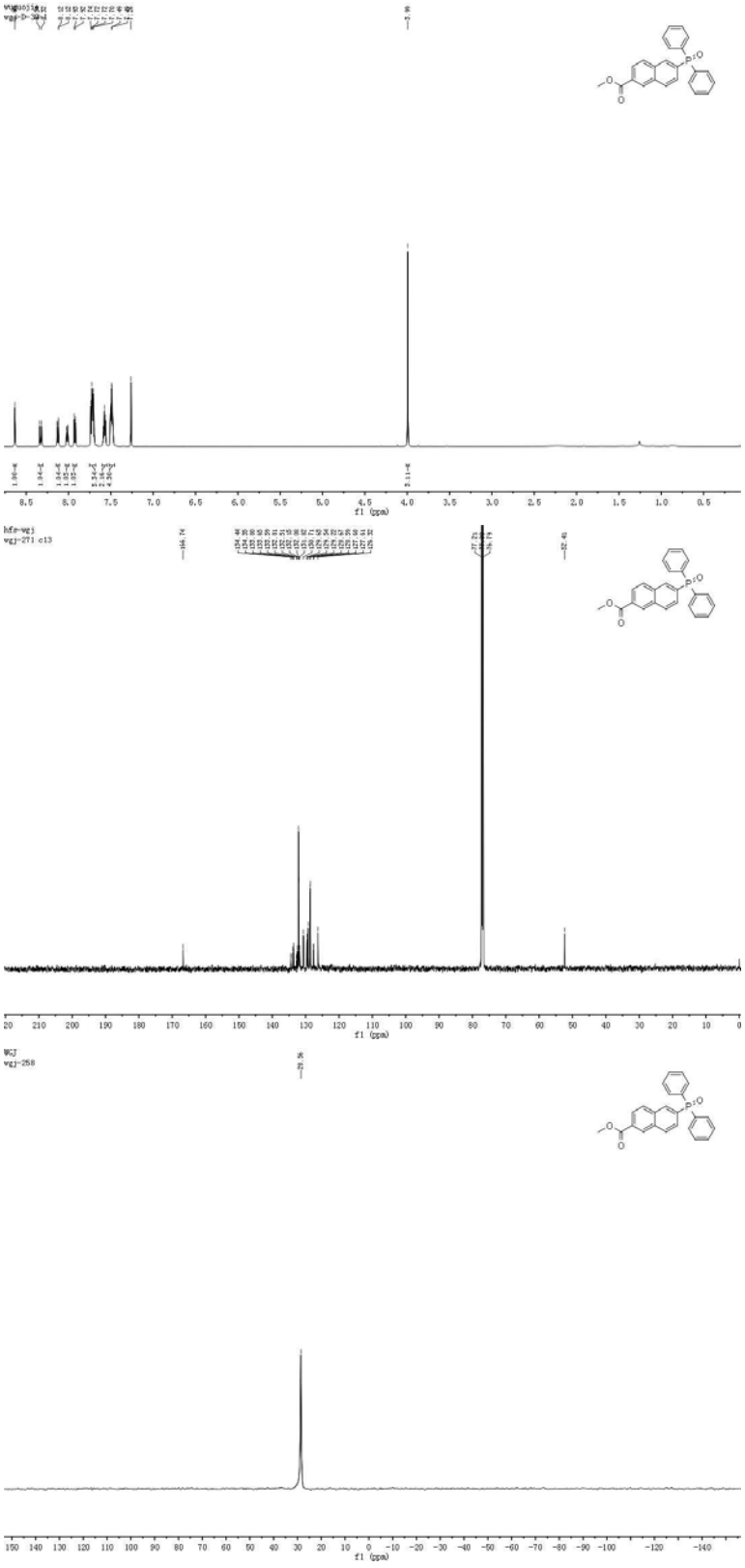


Figure S5. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3e**

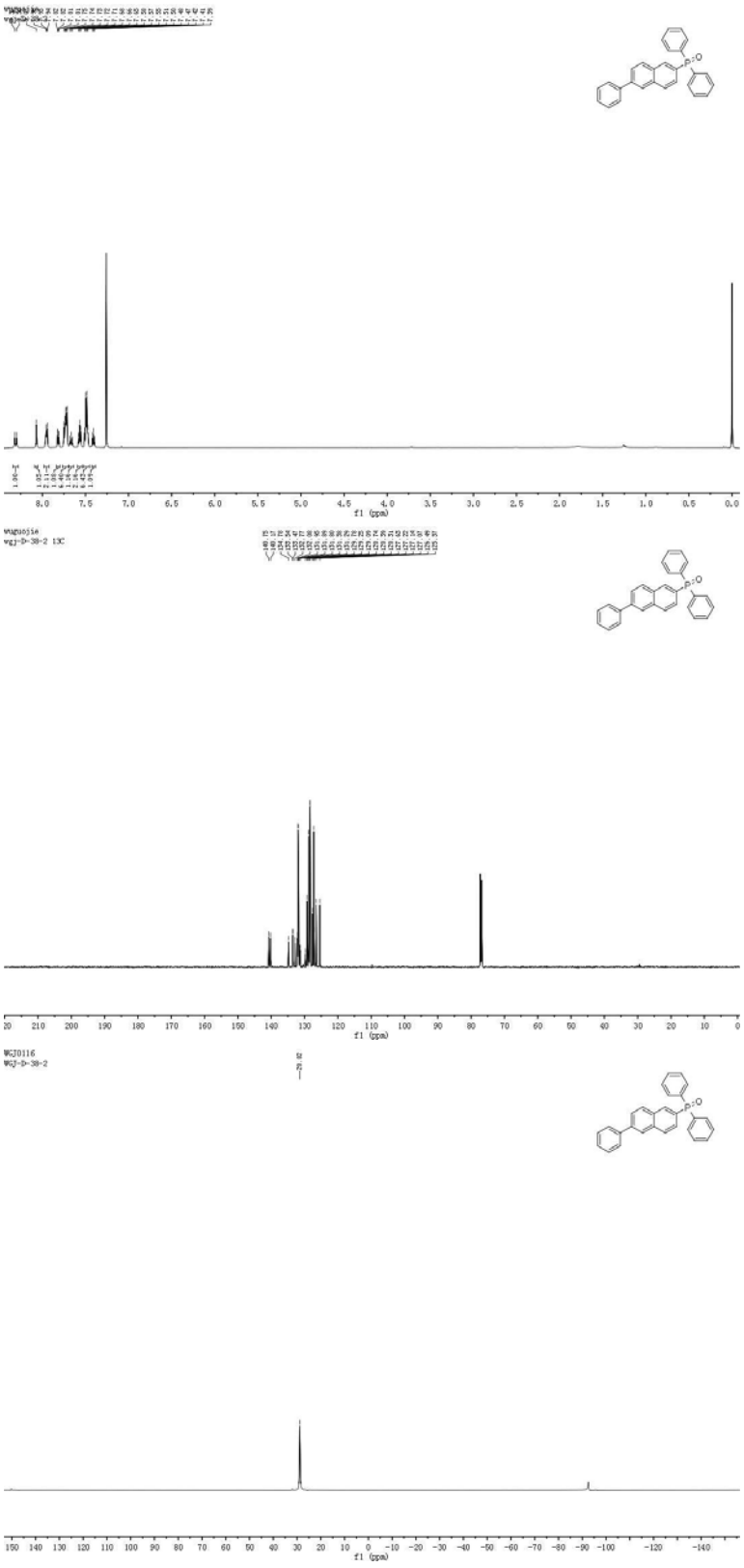


Figure S6. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3f**

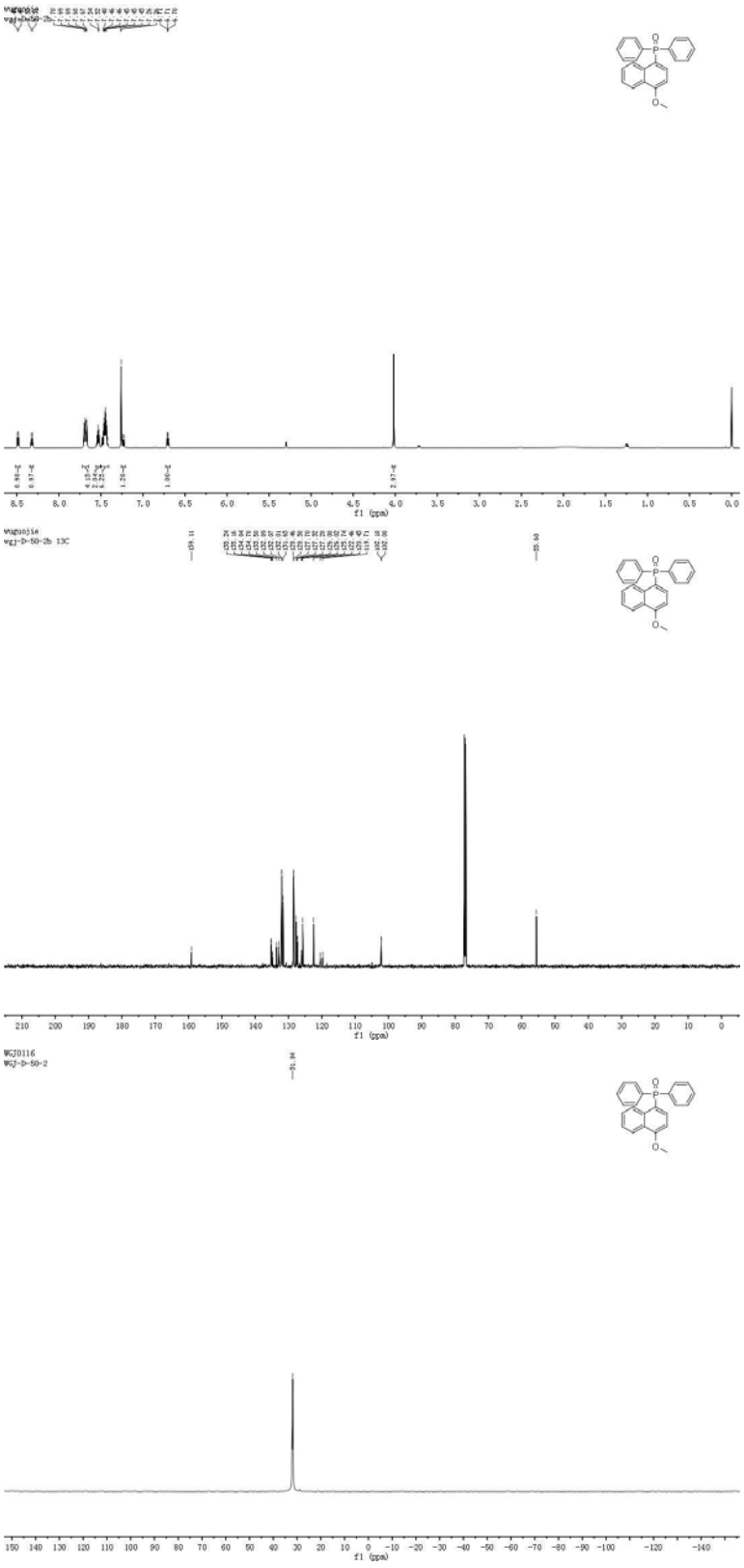


Figure S7. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3g**

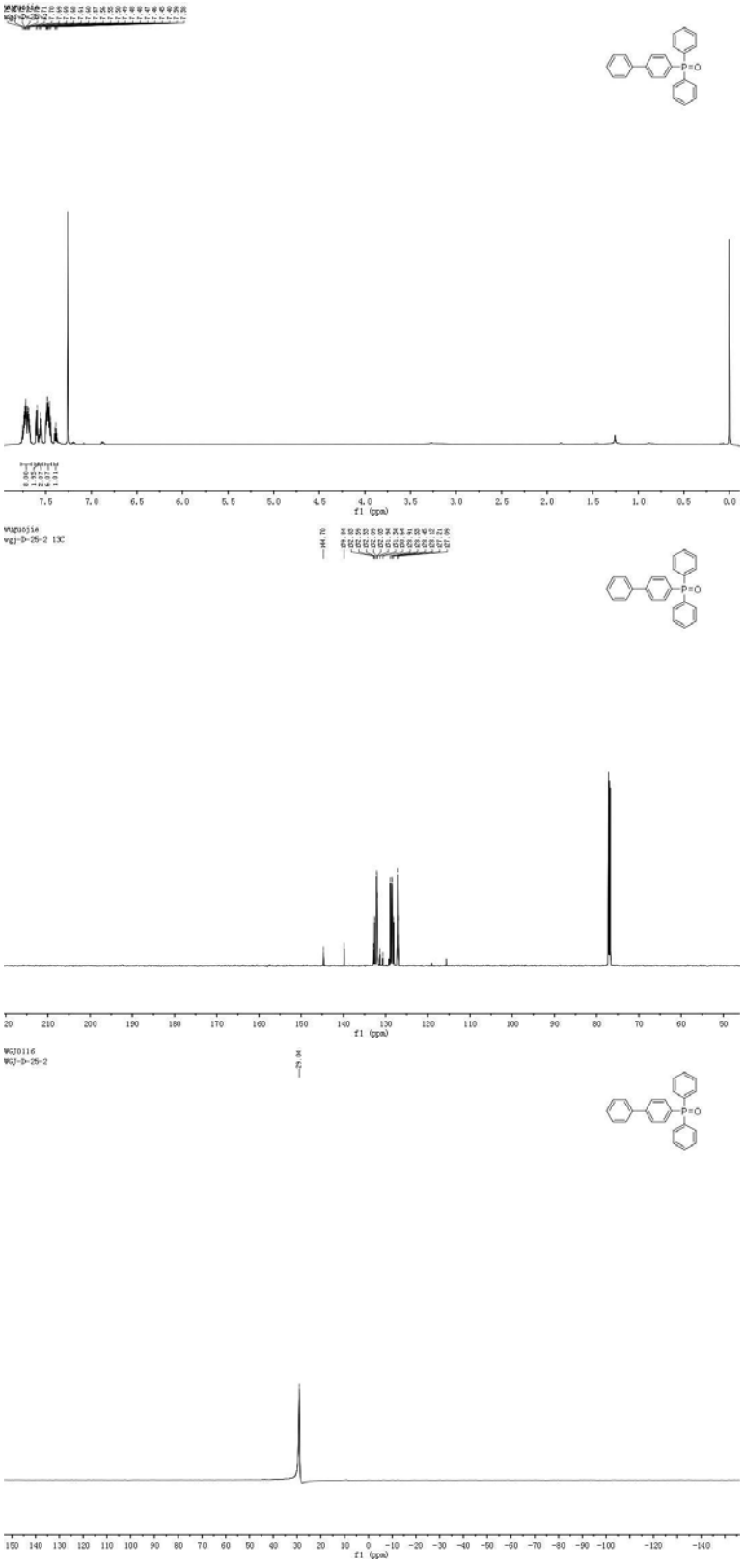


Figure S8. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3h**

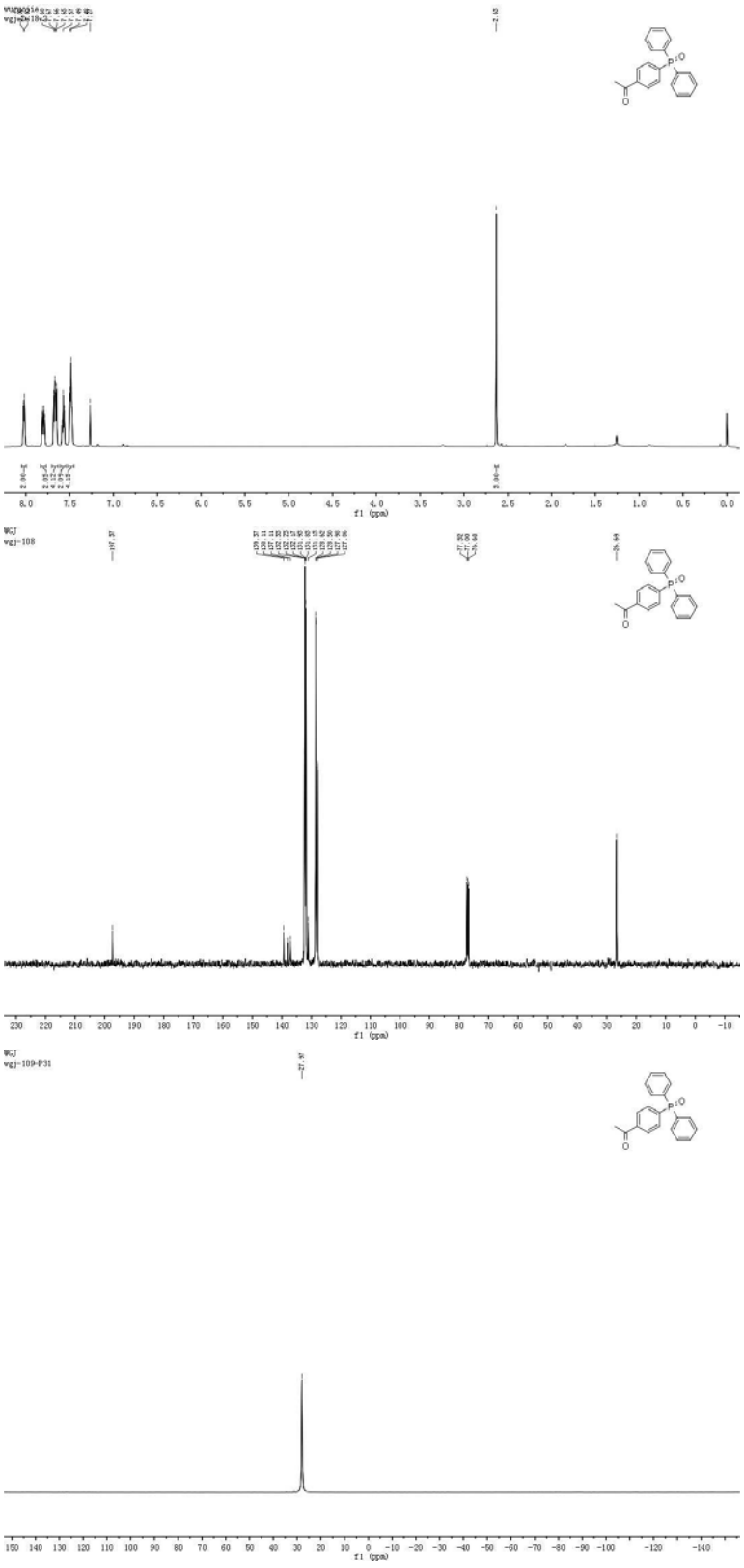


Figure S9. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3i**

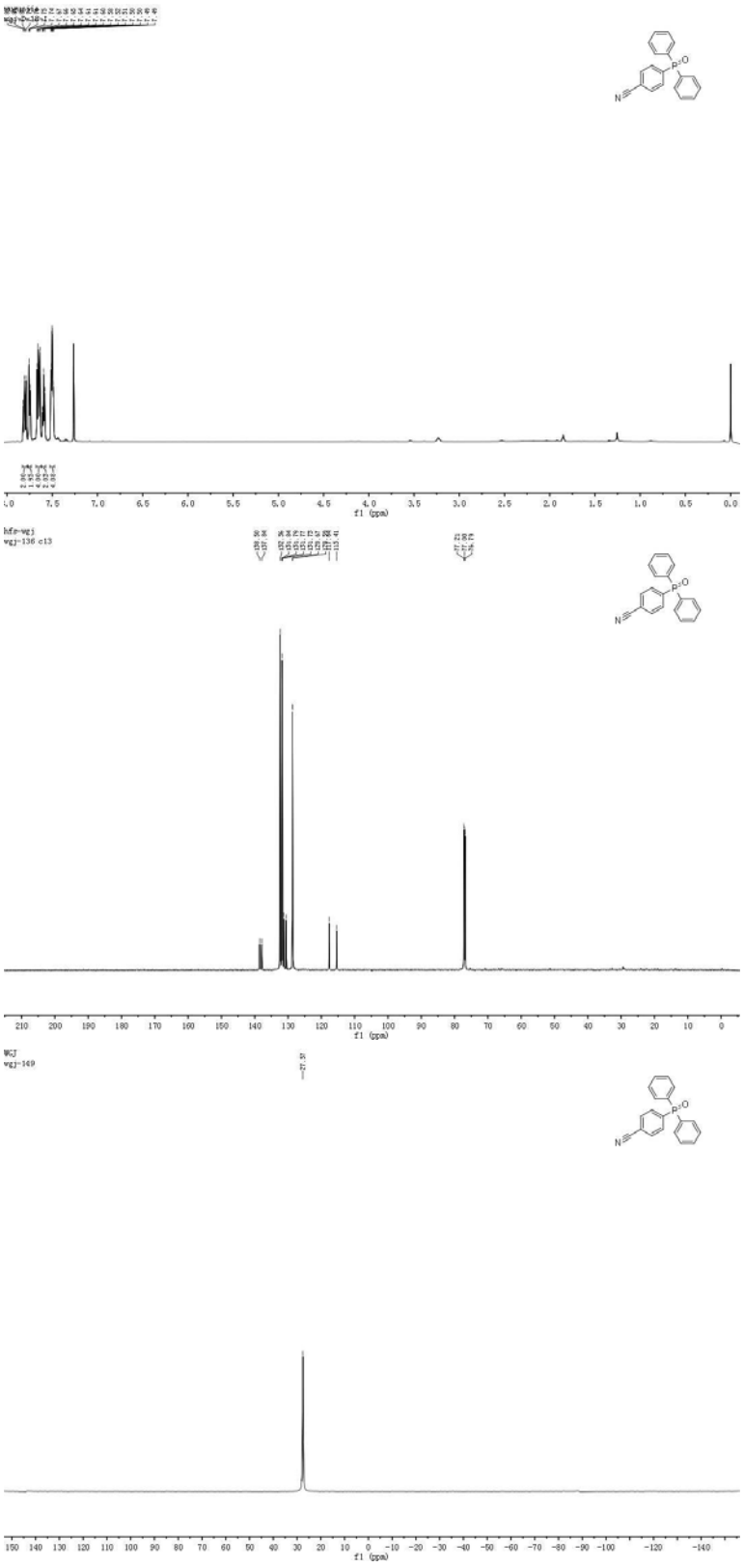


Figure S10. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3j**

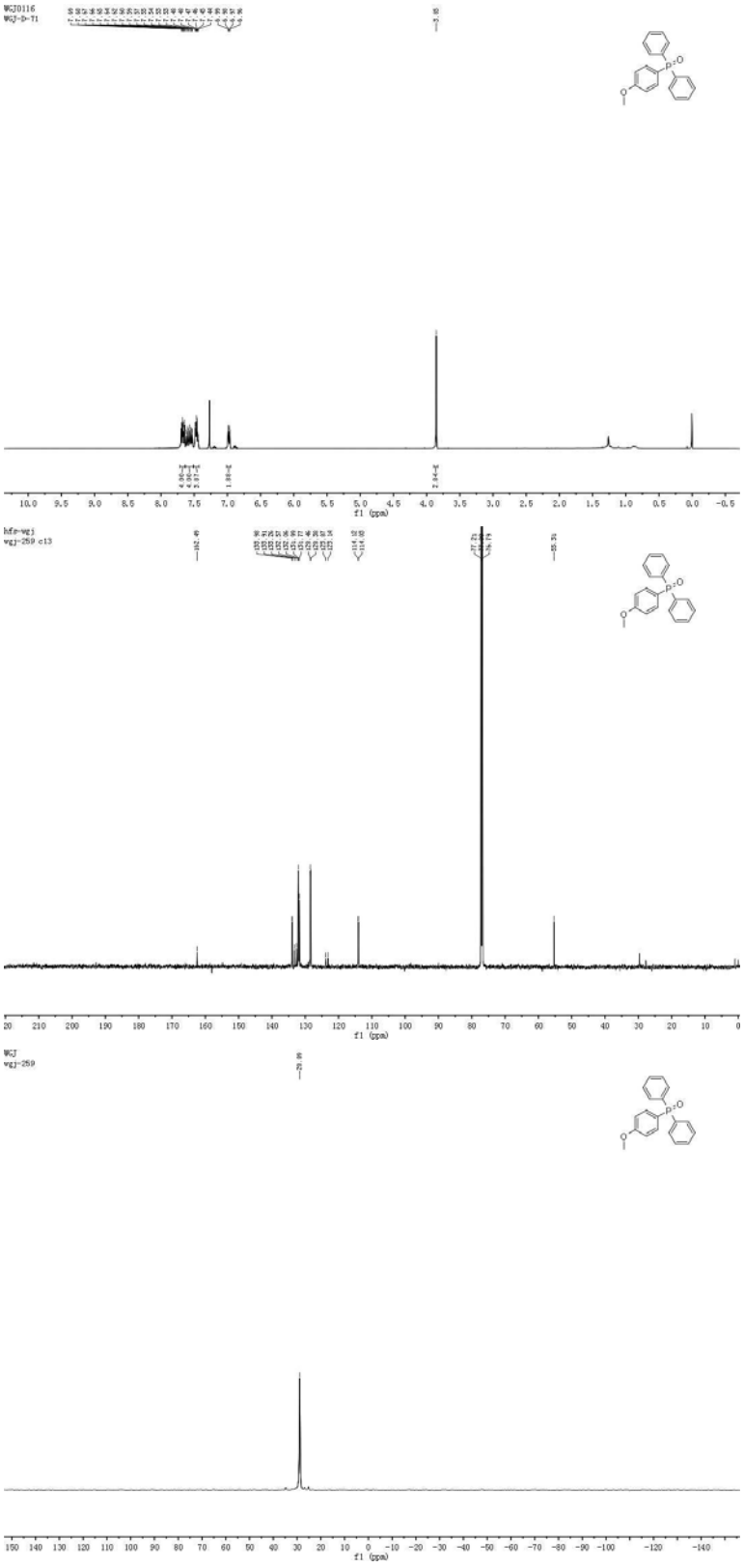


Figure S11. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3k**

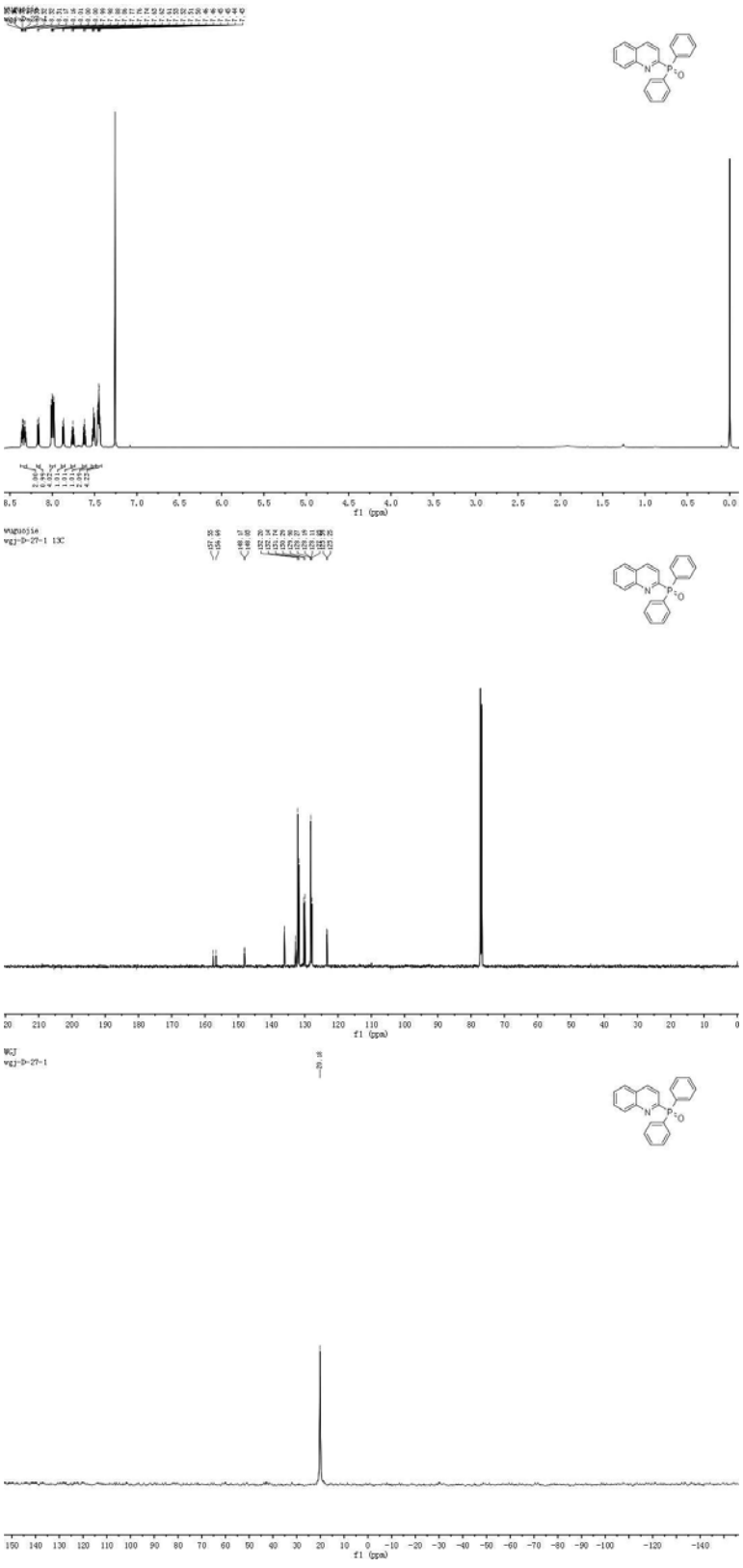


Figure S12. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3l**

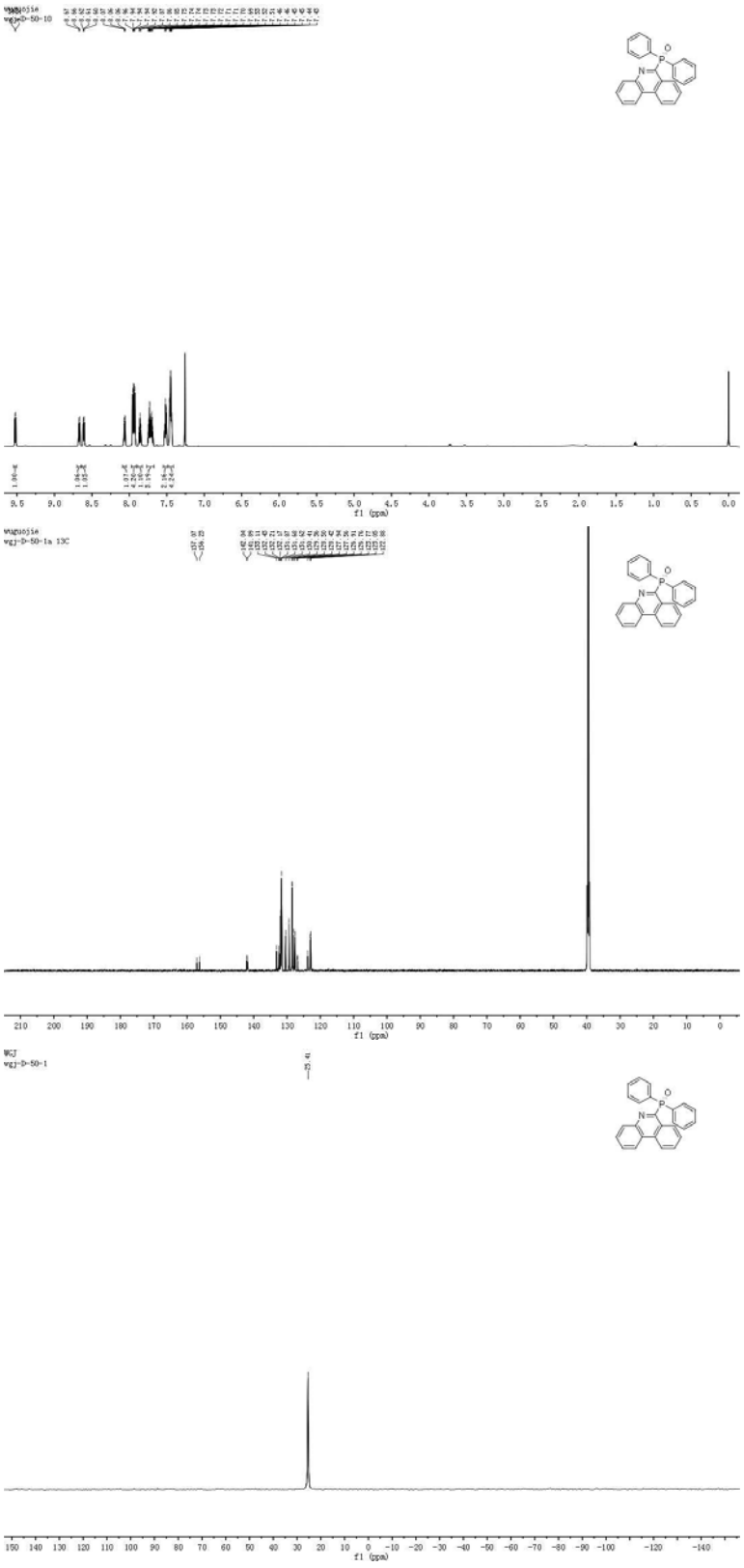


Figure S13. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3m**

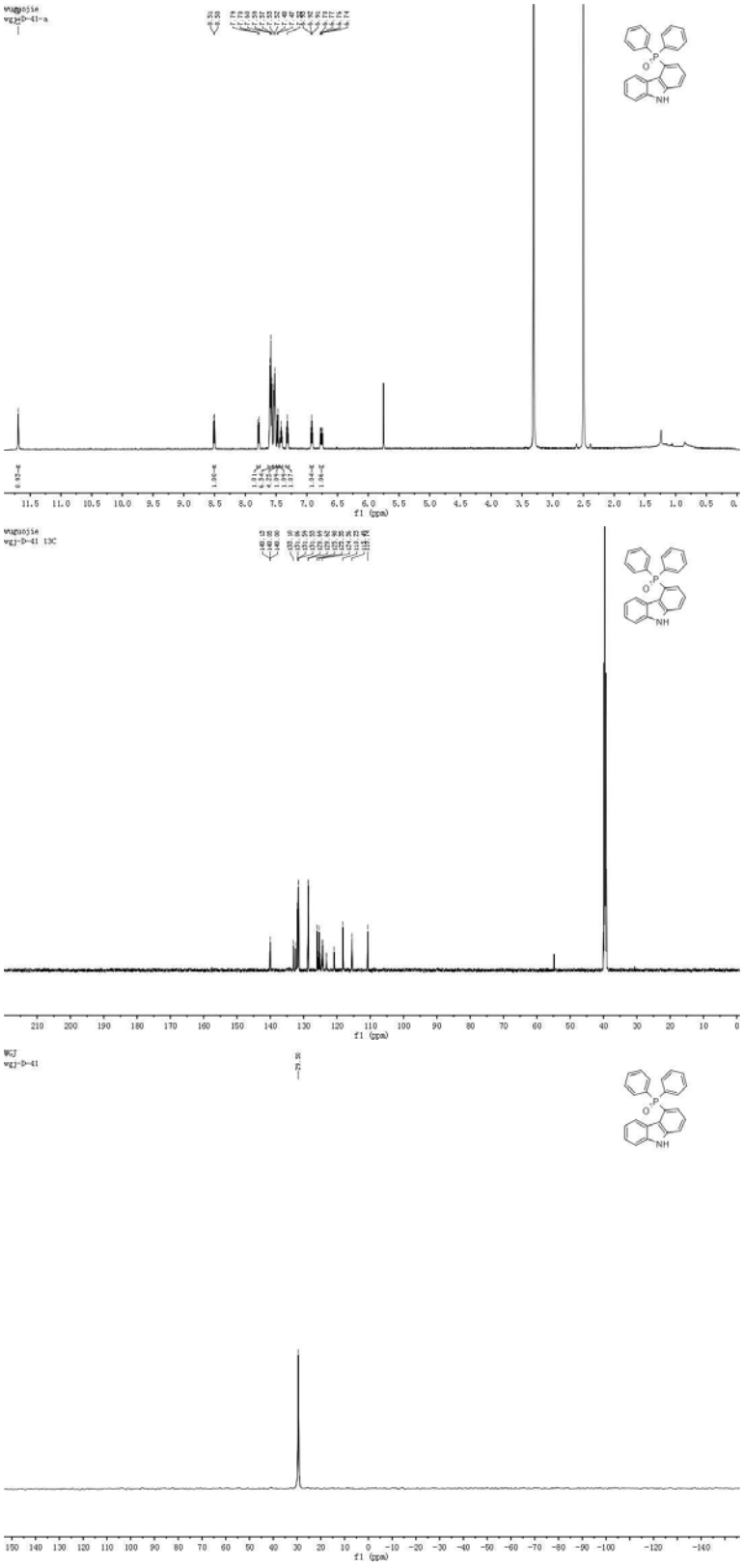


Figure S14. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3n**

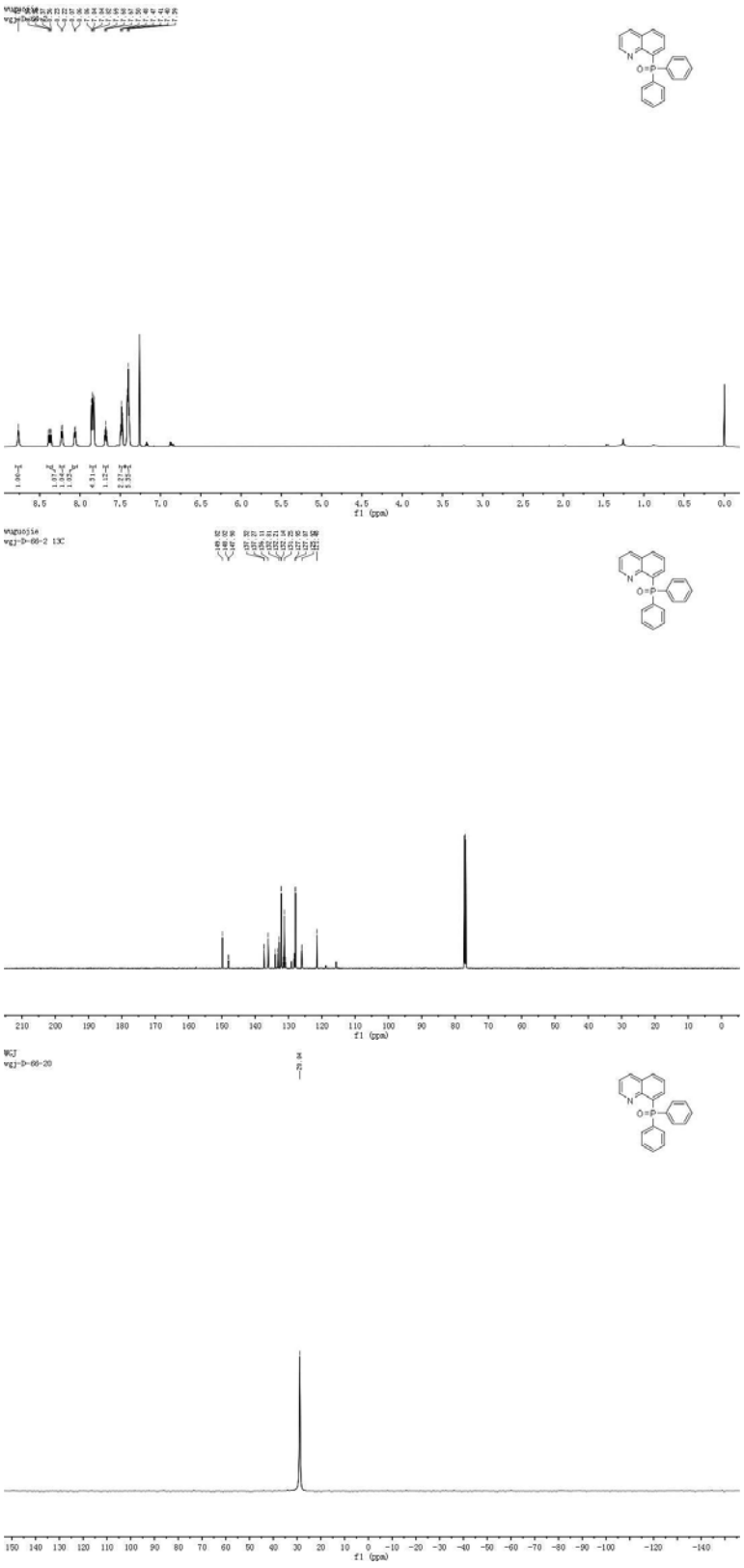


Figure S15. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3o**

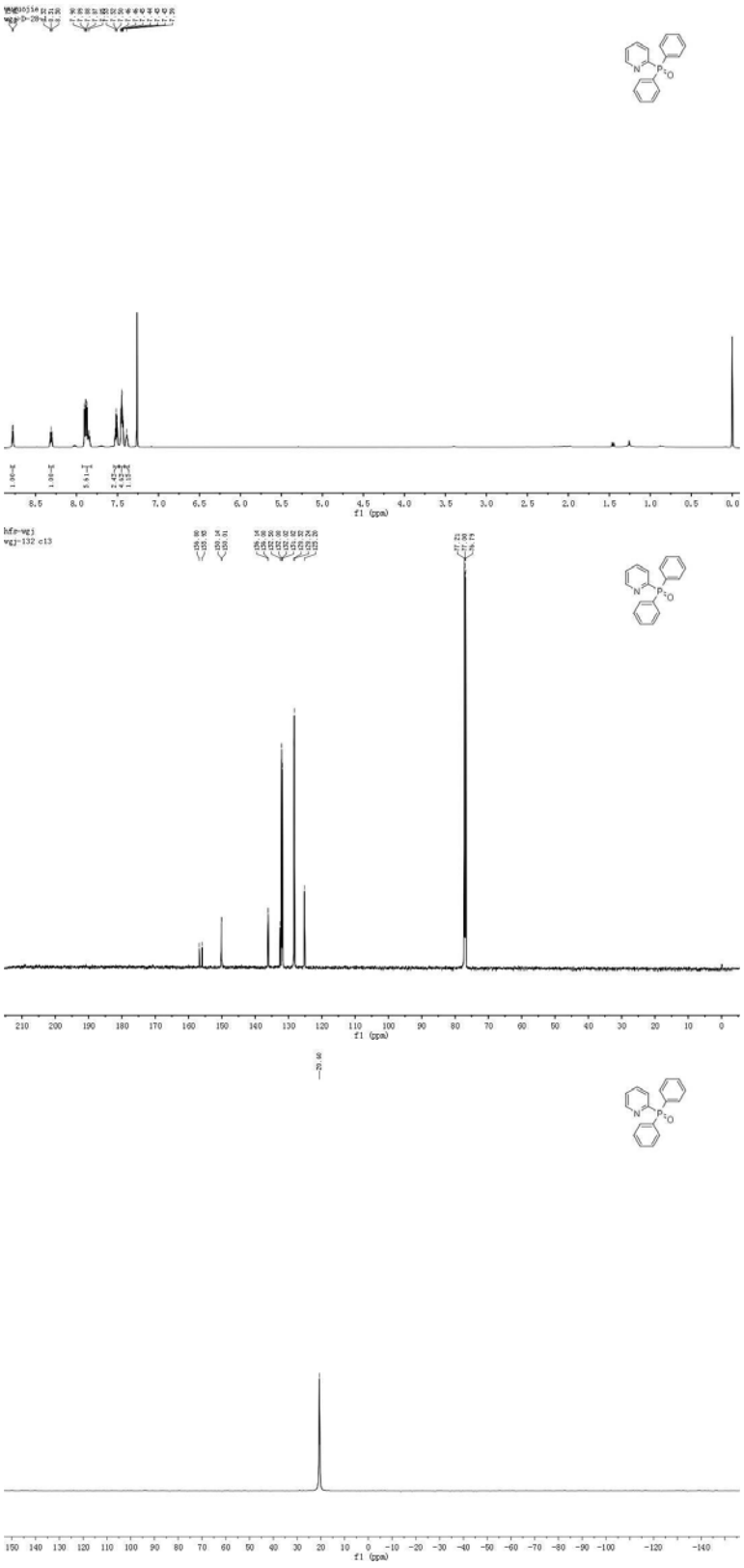


Figure S16. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3p**

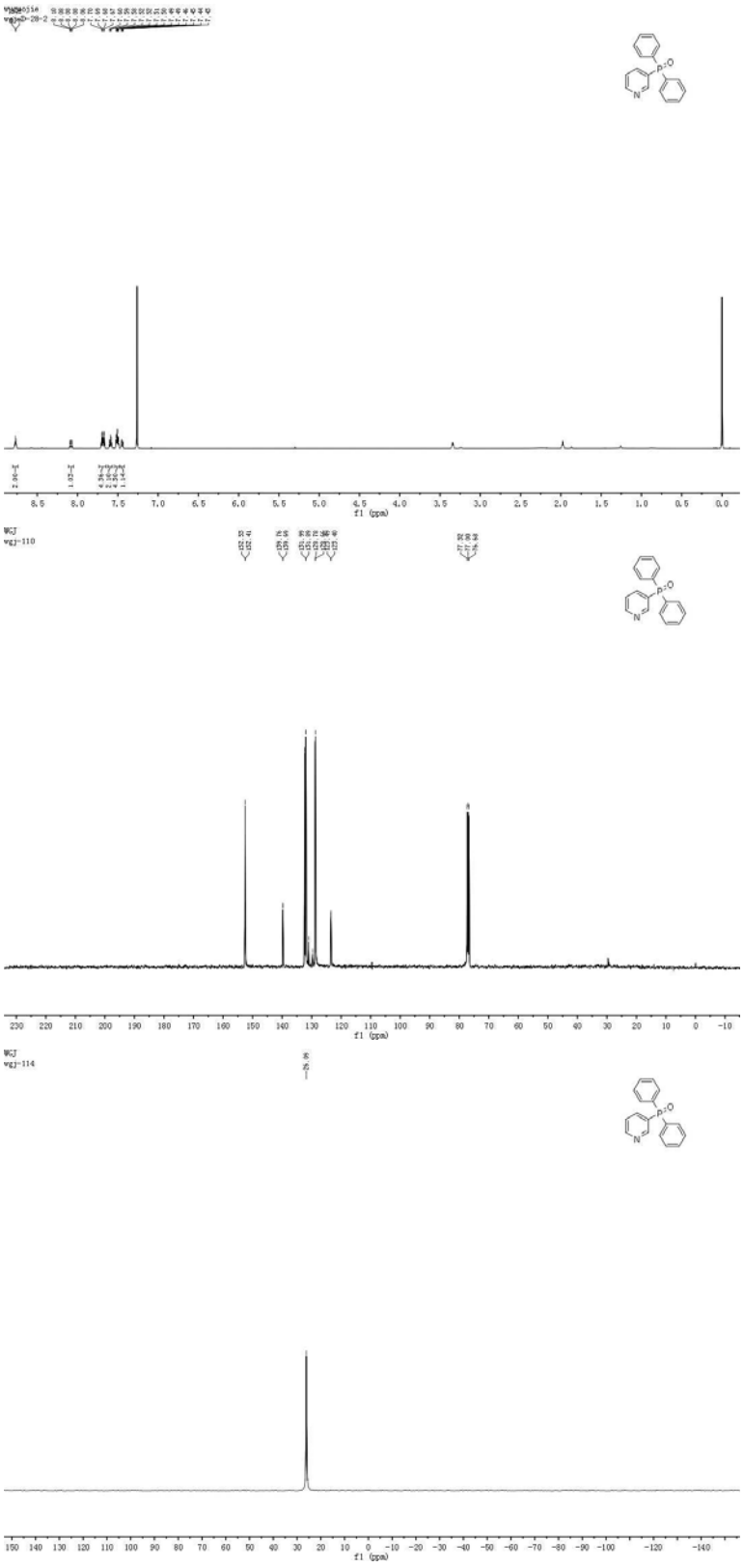


Figure S17. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3q**

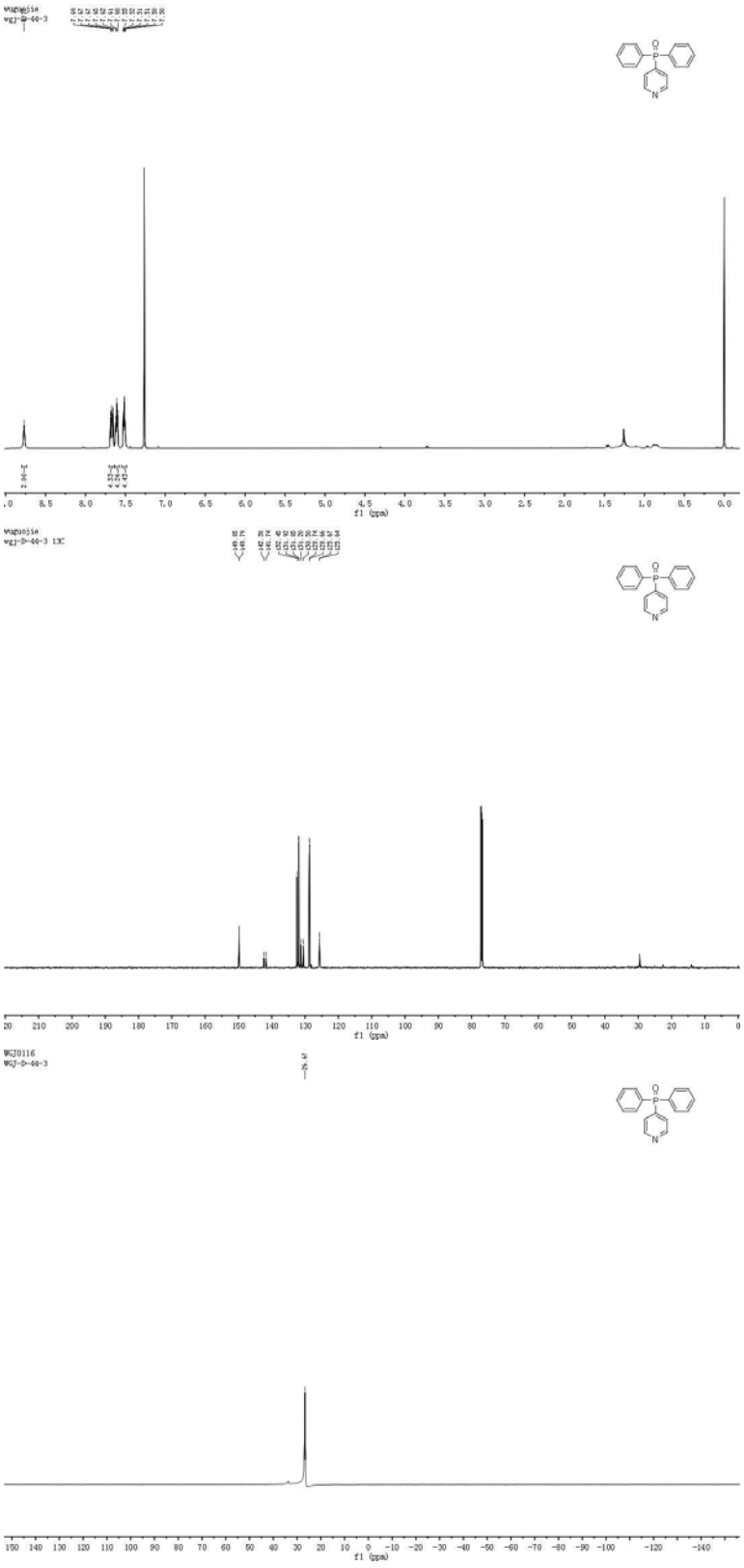


Figure S18. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **3r**

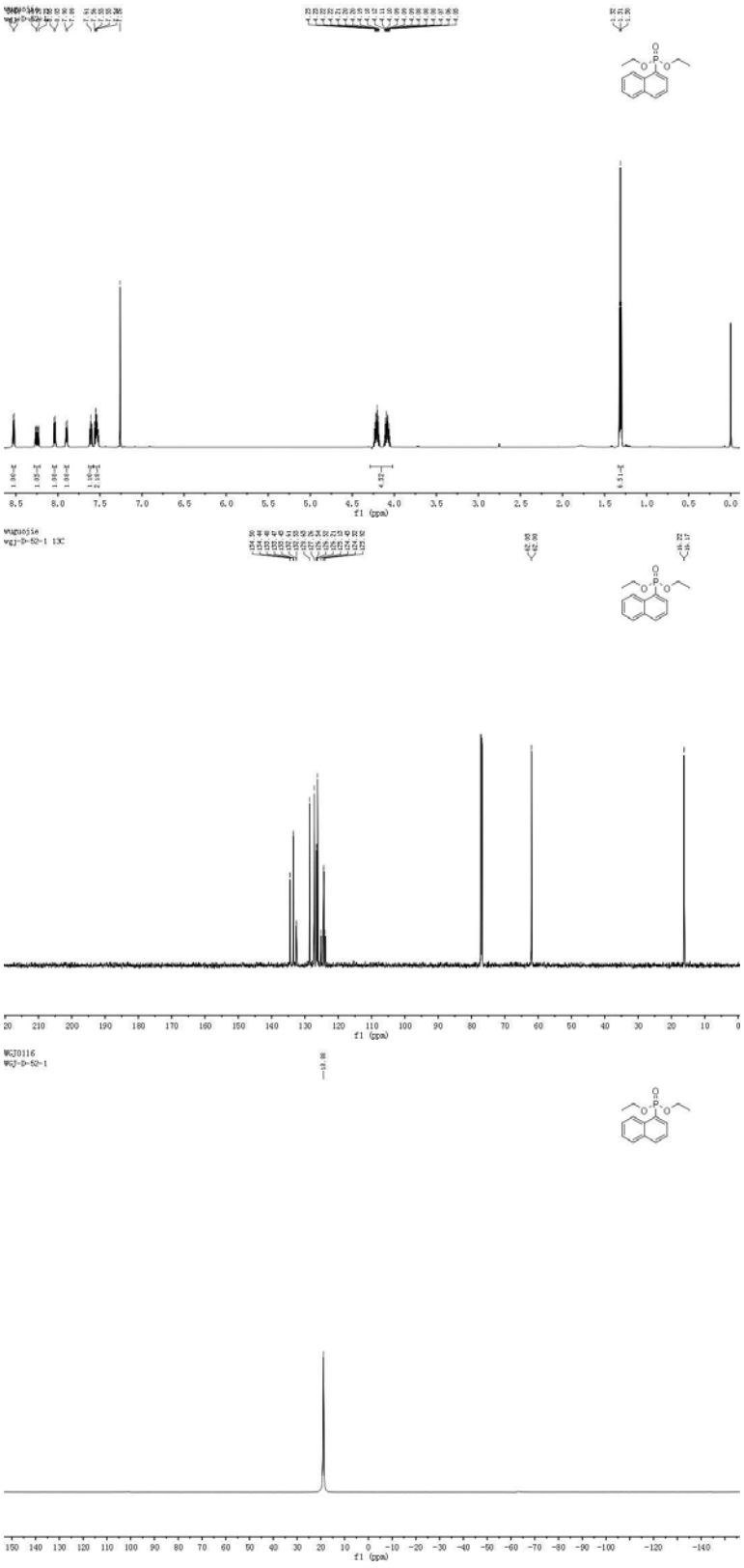


Figure S19. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5a**

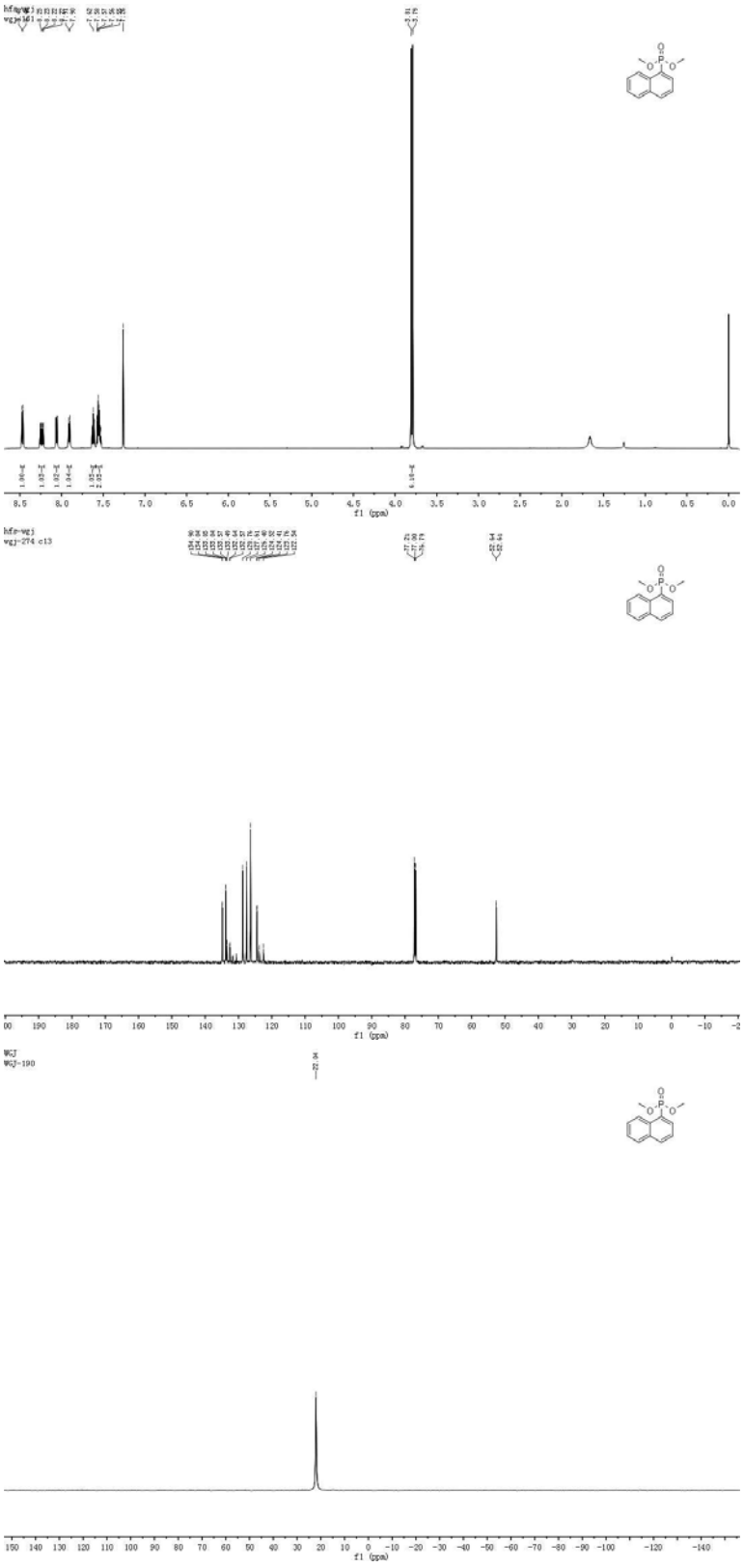


Figure S20. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5b**

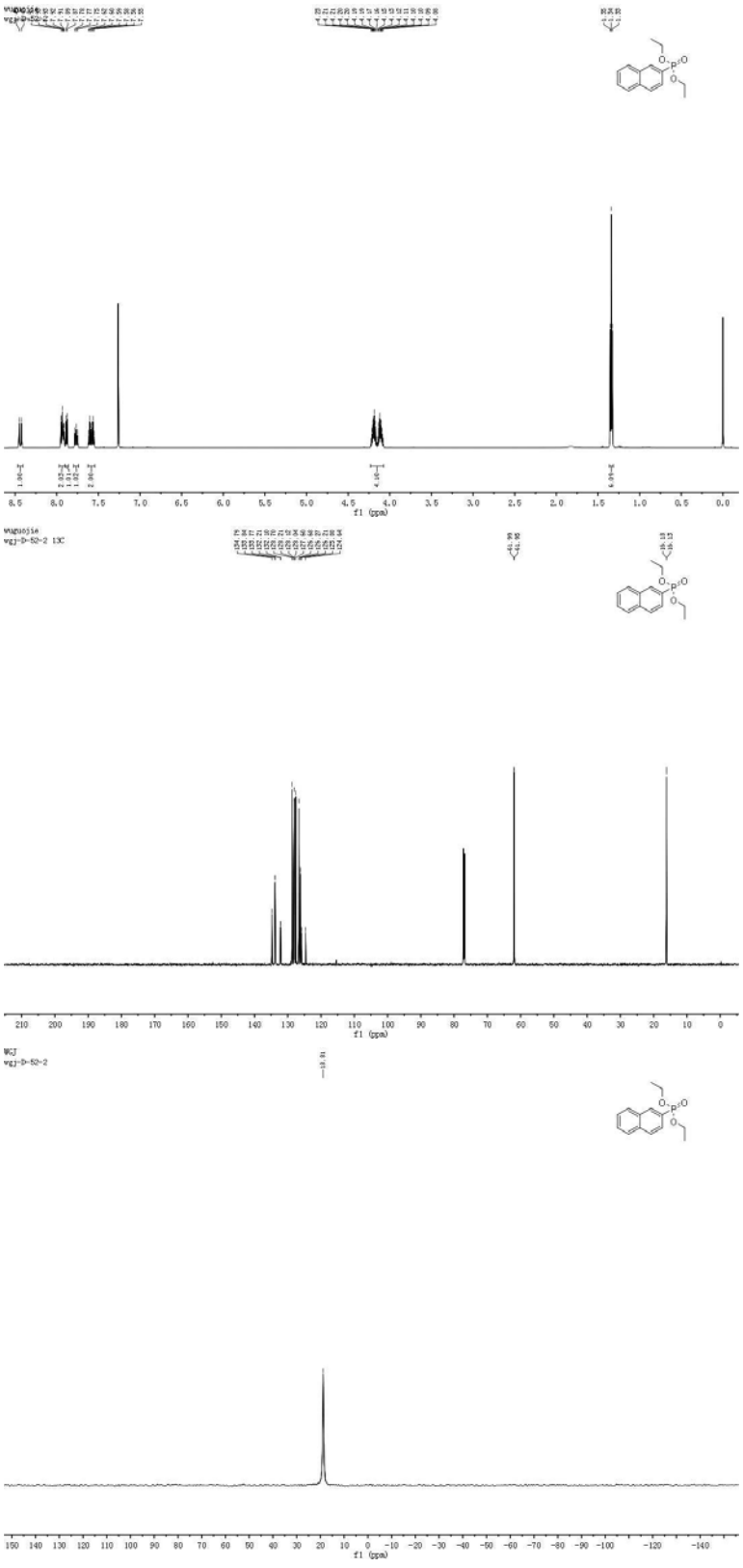


Figure S21. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5c**

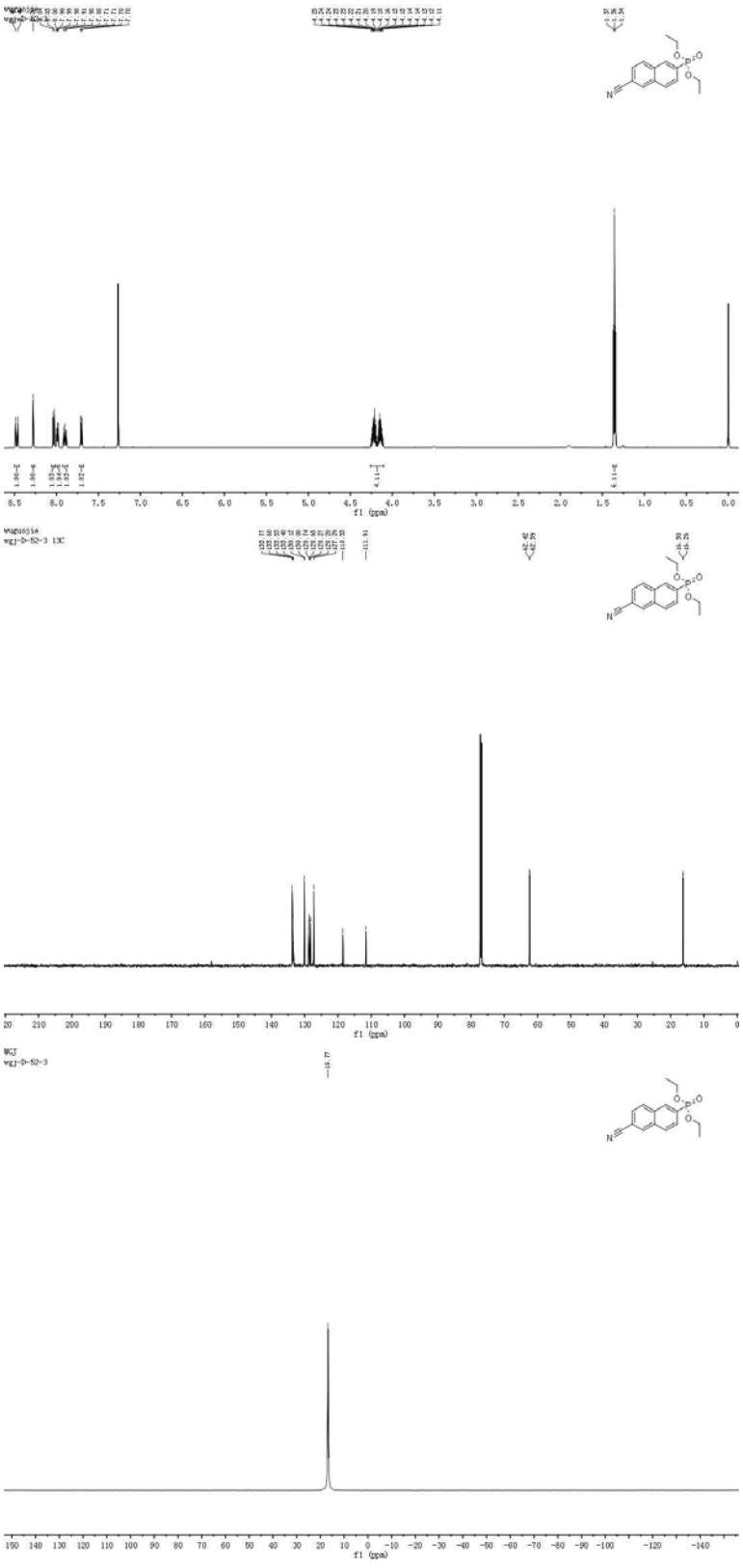


Figure S22. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5d**

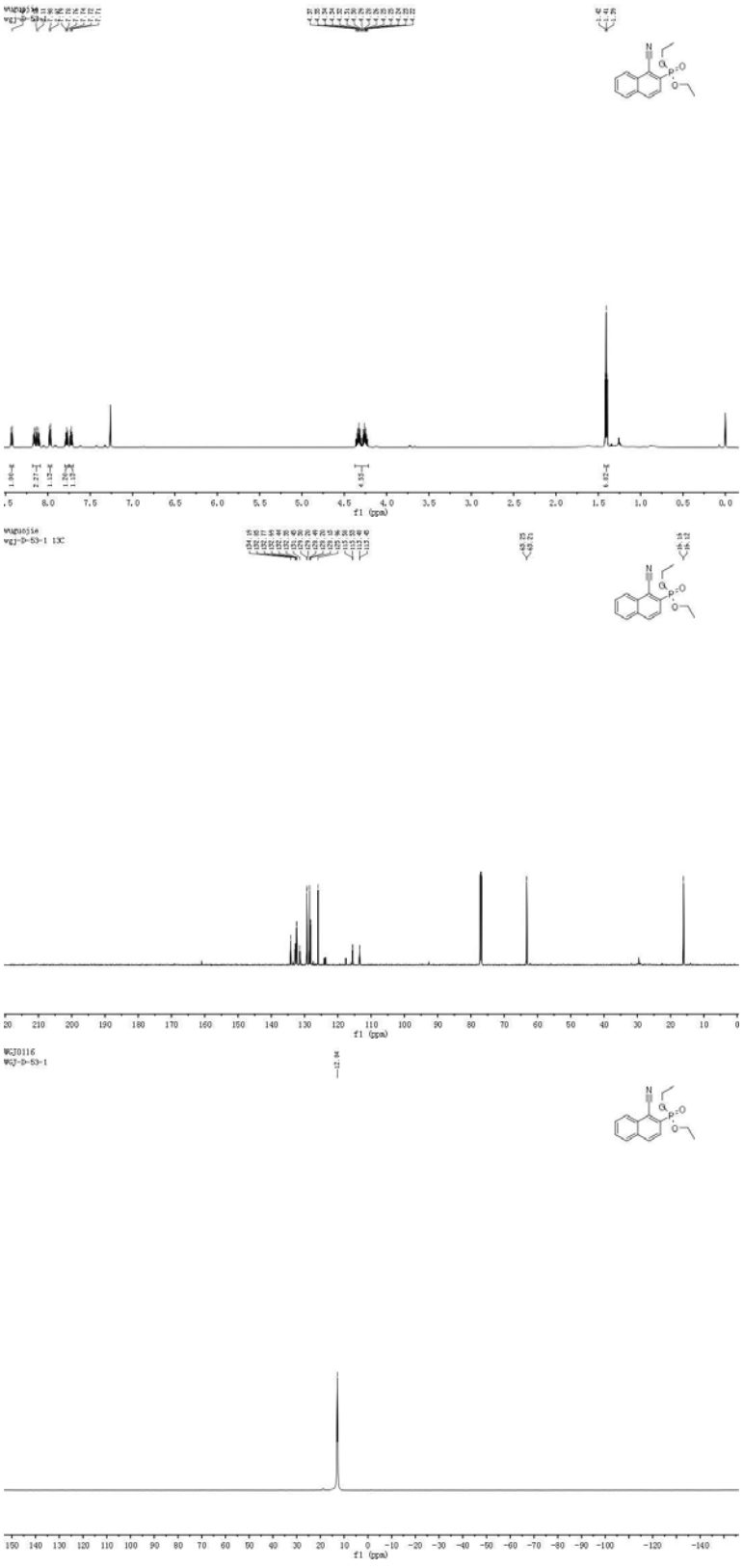


Figure S23. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5e**

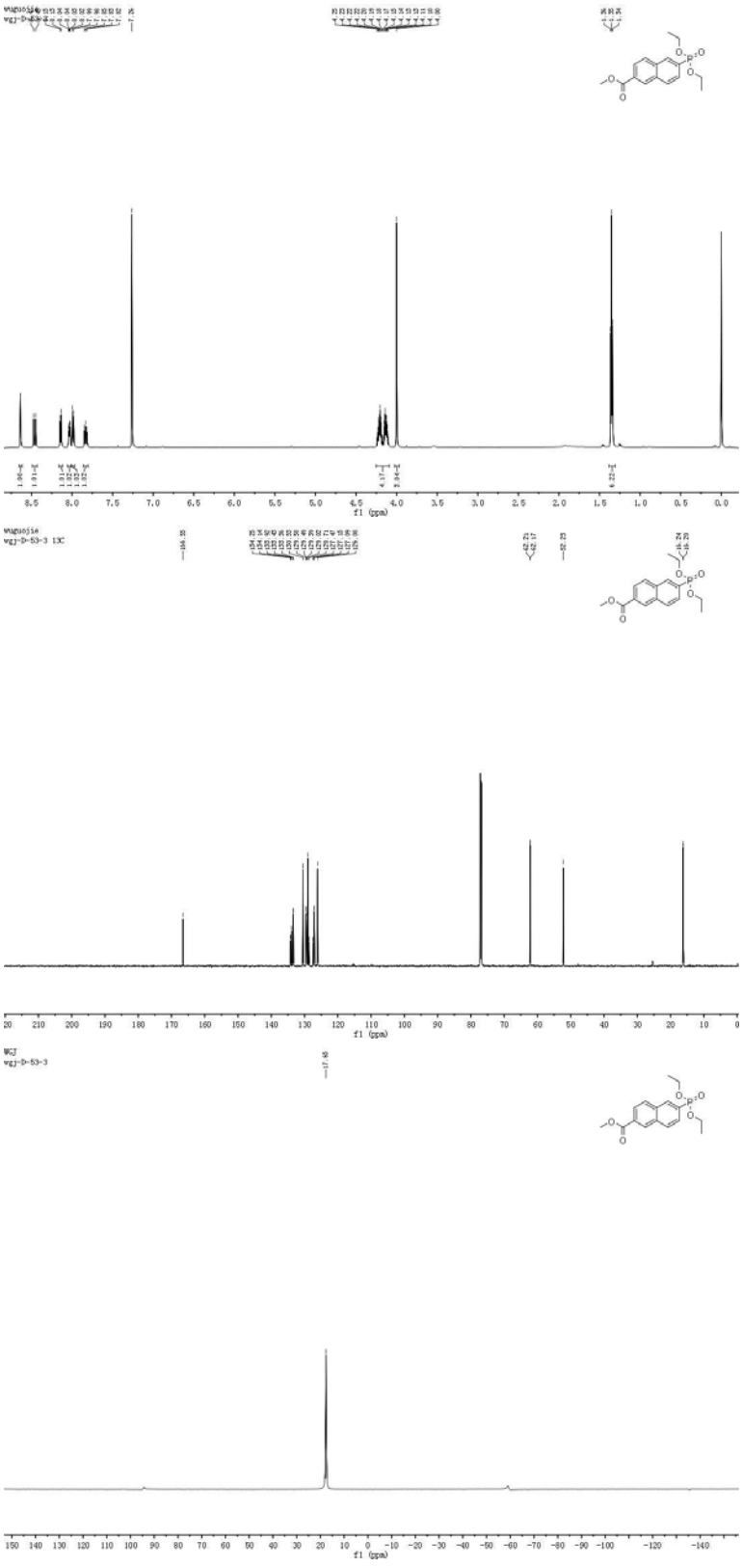


Figure S24. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5f**

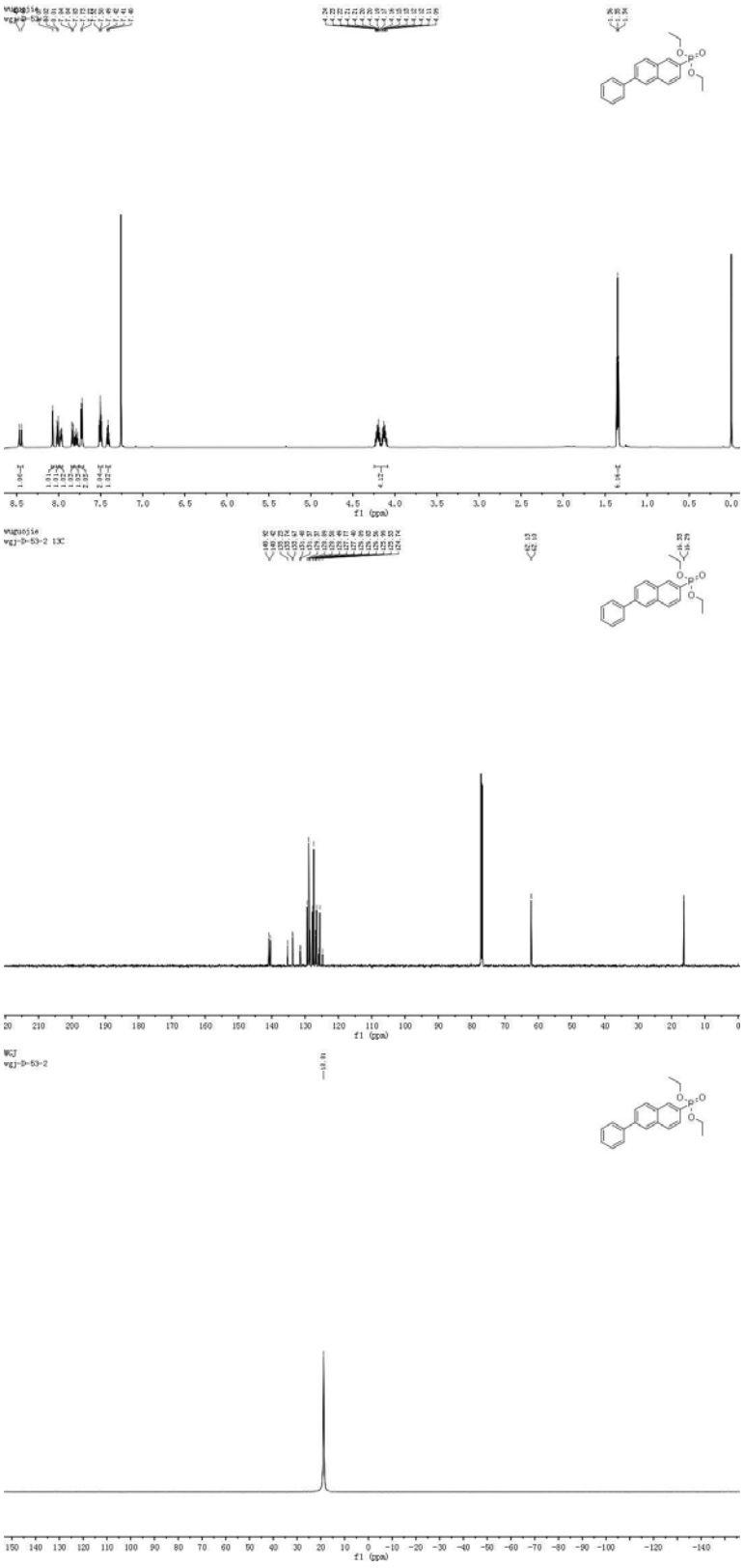


Figure S25. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5g**

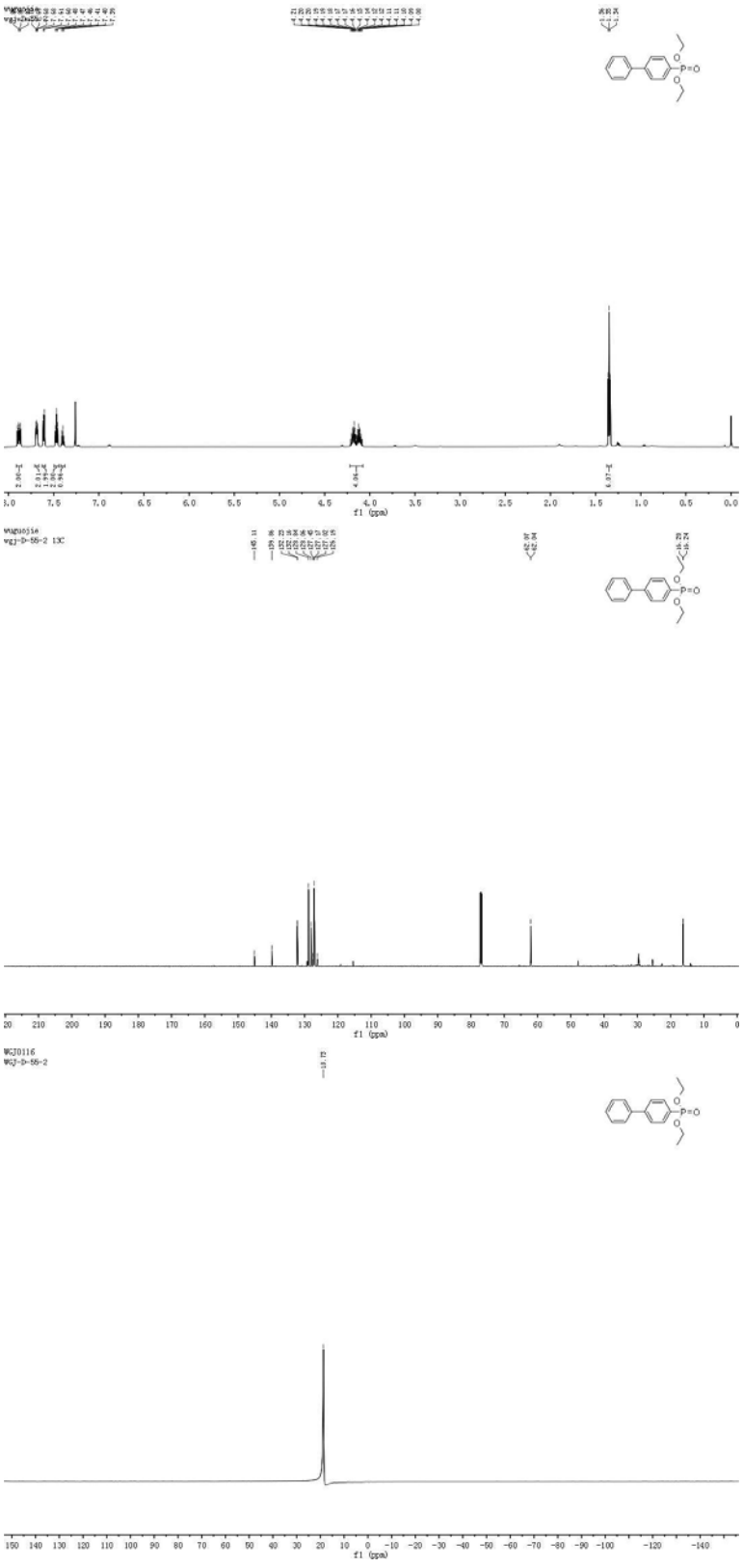


Figure S26. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5h**

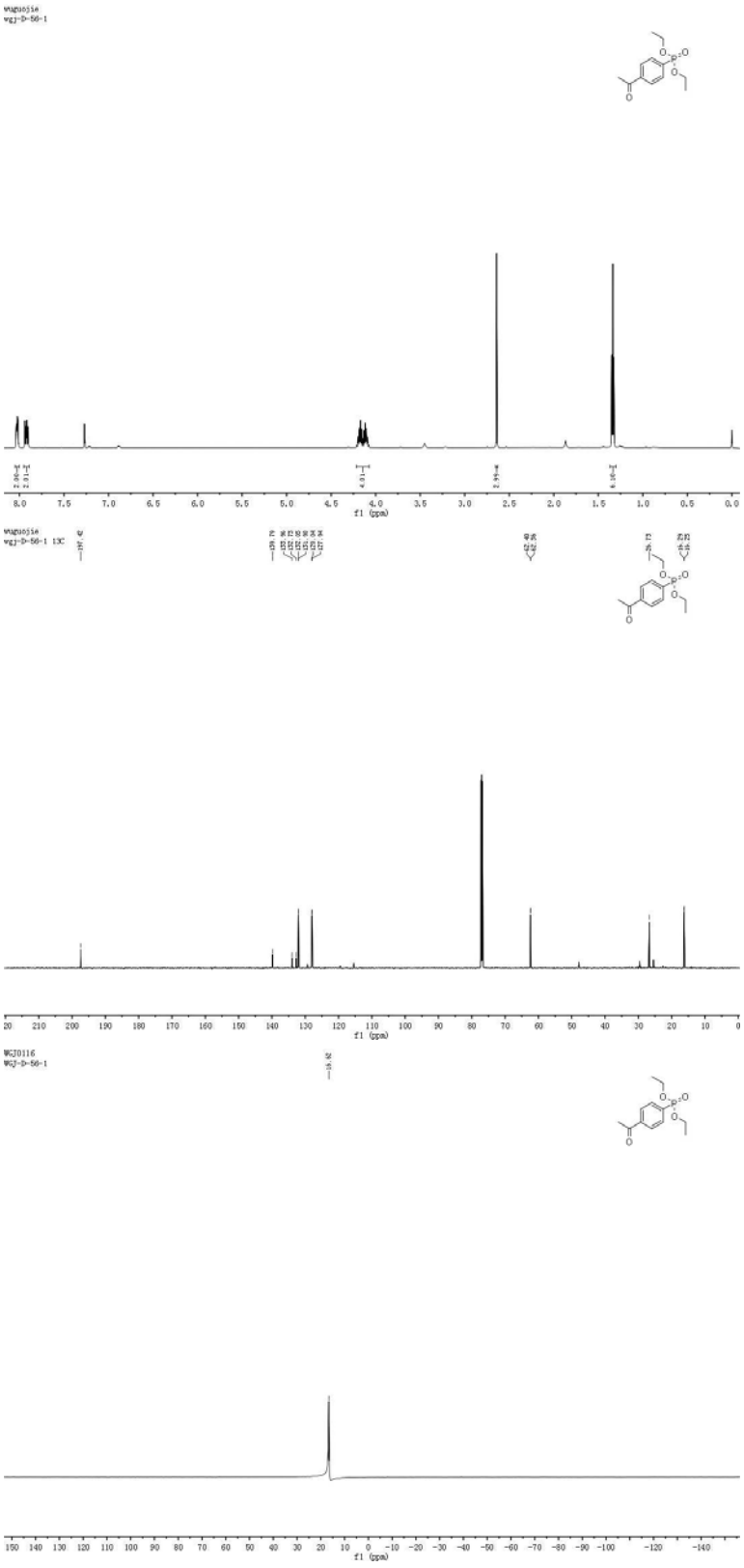


Figure S27. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5i**

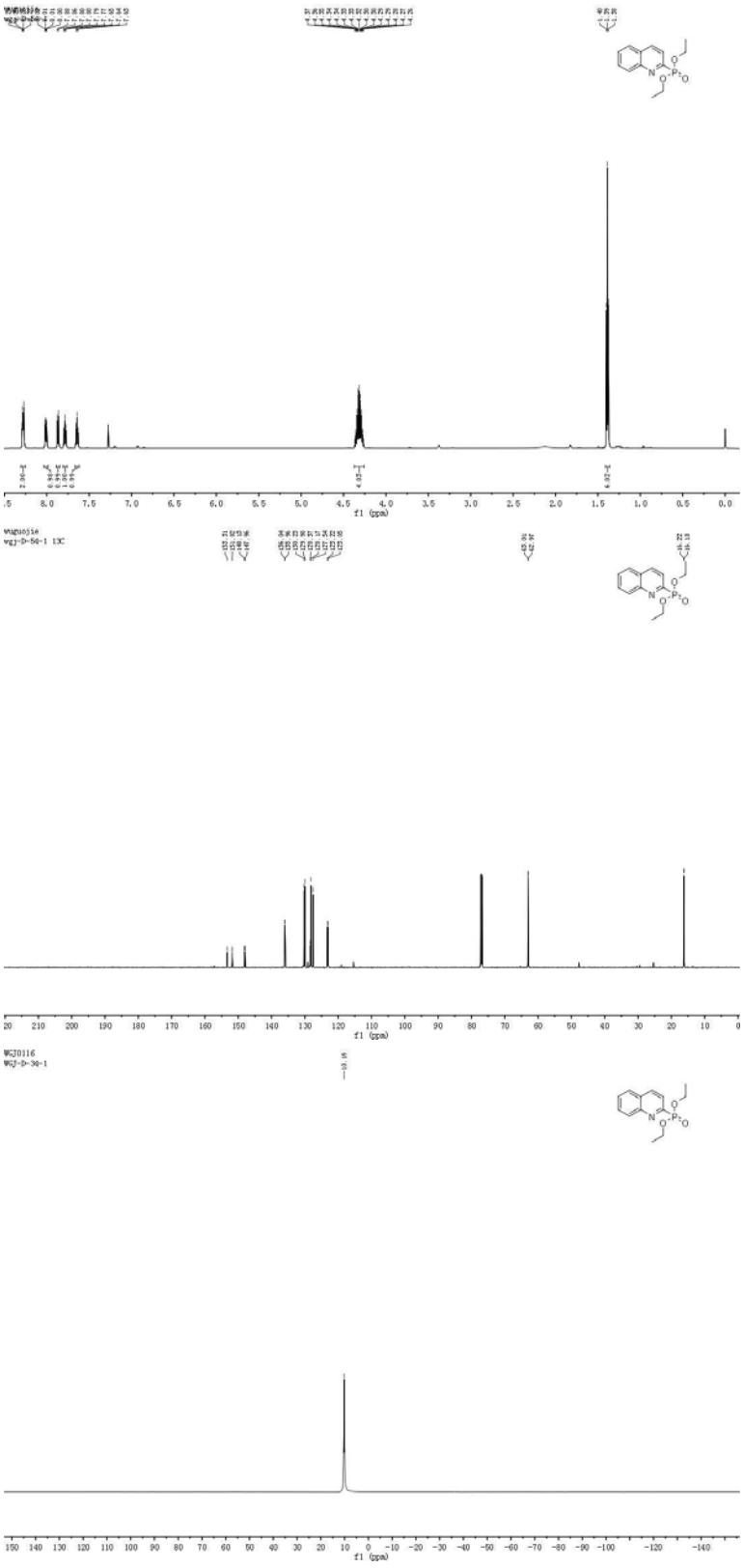


Figure S28. ^{1}H-, ^{13}C-, and ^{31}P NMR of compound **5j**