Synthesis of α-aminophosphorus derivatives using a deep eutectic solvent (DES) in a dual role

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Electronic Supporting Information

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1. Experimental Section

1a. General Information

All the reactions were performed in an open atmosphere by using oven-dried glassware. Diphenyl phosphine oxide and diethyl phosphite were taken from the glove box because of their hygroscopic nature. ^{1}H (600 MHz and 400 MHz), ^{31}P (243 MHz), and ^{13}C (100 MHz and 150 MHz) NMR spectra were recorded by using Bruker advance III-400 and Bruker advance III-600 spectrometer. Mass spectroscopy data of phosphine oxides and amino phosphonates were collected on ESI-HRMS mass spectrometer. The NMR solvent $CDCl_3$ and all other reagents were purchased from Sigma Aldrich and were used without additional purification.

1b. General procedure for synthesis of DES

DES was synthesized according to the procedure reported in the literature.[1] In a dry 50 mL round bottom flask, Choline chloride (ChCl) (0.028 mol, 4.0 g) and urea (0.057 mol, 3.4 g) were added in a 1:2 ratio and then heated at 60 °C for 30 min. A colorless liquid was formed. The liquid eutectic mixture is used as such for catalytic experiments without any purification. The DES is characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

1c. General procedure for Kabachnik–Fields condensation reaction.

Preparation of α-aminophosphine oxide derivatives (1a-1z)

In a 25 mL dry Schlenk tube, the corresponding aromatic aldehyde (0.495 mmol), aromatic amine (0.495 mmol), diphenyl phosphine oxide (0.495 mmol, 100 mg), and DES (0.096 mmol, 25 mg, 20 mol%) were mixed. The colorless reaction mixture was heated at 60 °C for one hour in an oil bath. The reaction progress was monitored by TLC. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature, and diluted with water (10 mL) followed by ethyl acetate (4 x 5 mL). The combined ethyl acetate extracts were washed with saturated aq. sodium bicarbonate solution (2 x 5 mL) and dried over anhydrous sodium sulfate. The combined ethyl acetate extracts were concentrated *in vacuo* and the resulting product was directly charged on a small silica gel column and eluted with a mixture of hexane: ethyl acetate (EtOAc) (3:2) to afford the pure α-aminophosphorous derivative in each case. Each derivative is characterized by ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR spectroscopy, and Mass spectrometry.

Preparation of α-aminophosphonate derivatives (2a-2q)

In a 25 mL dry Schlenk tube, the corresponding aromatic aldehyde (0.724 mmol), aromatic amine (0.724 mmol), diethyl phosphite (0.724 mmol, 100 mg), and DES (0.138 mmol, 36 mg, 20 mol%) were mixed. The colorless reaction mixture was heated at 60 °C for one hour in an oil bath. The reaction progress was monitored by TLC. After completion of the reaction, the corresponding products were isolated and characterized by following the similar procedure mentioned above.

1d. Recyclability Test

The reusability test was performed on the multicomponent model reaction between benzaldehyde, aniline, and diethylphosphite in DES in 1:1:1:0.2 molar ratio under optimized conditions (at 60 °C temperature for one hour). After completion of the reaction, DES was recovered from water phase by evaporation at 85 °C under reduced pressure. The remainder of the viscous DES was further dried at 70 °C for 3 h under reduced pressure to remove any traces of water and then subjected to the next run with the same reactants without further addition of DES in the cycle.

No of cycle	Amount of DES taken (mg)	Amount of DES recovered (mg)	% of DES recovered
Fresh	36.0	32.4	90
1st cycle	32.4	27.9	86
2nd cycle	27.9	23.6	85
3rd cycle	23.6	19.0	80
4th cycle	19.0	14.2	75

1e. Gram scale Kabachnik–Fields condensation reaction.

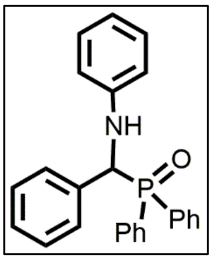
In a 50 mL dry Schlenk tube, the aromatic aldehyde, benzaldehyde (0.0049 mol, 0.52 g), aniline (0.0049 mol, 0.46 g), diphenylphosphine oxide (0.0049 mol, 1.0 g), and DES (0.1 mmol, 0.25 g, 20 mol%) were mixed. The colorless reaction mixture was heated at 60 °C for one hour in an oil bath. The reaction progress was monitored by TLC. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature, diluted with water (40 mL) followed by ethyl acetate (5 x 10 mL). The combined ethyl acetate extracts were washed with saturated aq. sodium bicarbonate solution (2 x 10 mL) and dried over anhydrous sodium sulfate. The combined ethyl acetate extracts were concentrated *in vacuo* and the resulting product was directly charged on a small silica gel column and eluted with a mixture of hexane:

EtOAc (3:2) to afford the pure product of diphenyl(phenyl(phenylamino)methyl)phosphine oxide (**1a**) with the yield of 89 % (1.7 g). The product is characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

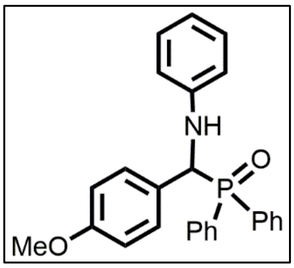
Characterization data of DES:

^{1}H NMR (600 MHz, D_2O, 25 ºC): δ_H 5.94 (s, 1H), 4.79 (s, 8H), 4.15 - 4.10 (m, 2H), 3.63 - 3.58 (m, 2H), 3.28 (s, 9H) ppm. ^{13}C{^{1}H} NMR (150 MHz, D_2O, 25 ºC): δ_C 162.42, 67.56, 55.79, 54.04 ppm.

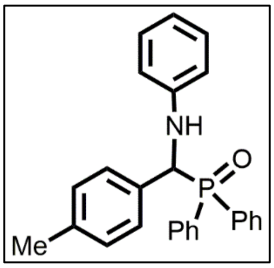
Characterization data of α-aminophosphine oxides (1a-1z):



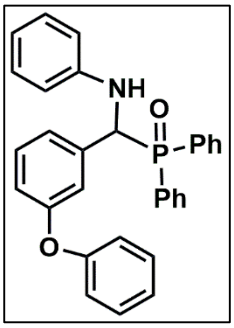
Diphenyl(phenyl(phenylamino)methyl)phosphine oxide (**1a**).[2] Yield: 171 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.85 - 7.88 (m, 2H, Ar*H*), 7.55 - 7.57 (m, 1H, Ar*H*), 7.52 - 7.48 (m, 2H, Ar*H*), 7.44 - 7.35 (m, 3H, Ar*H*), 7.30 - 7.24 (m, 2H, Ar*H*), 7.16 - 7.06 (m, 7H, Ar*H*), 6.66 - 6.68 (m, 1H, Ar*H*), 6.58 - 6.62 (m, 2H, Ar*H*), 5.18 - 5.22 (m, 2H, C*H* and N*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 146.1, 135.1, 132.4, 132.1, 131.8, 131.7, 129.3, 129.0, 129.0, 128.5, 128.5, 128.3, 128.2, 127.8, 118.5, 114.0, 57.8, 57.1 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.3 ppm.



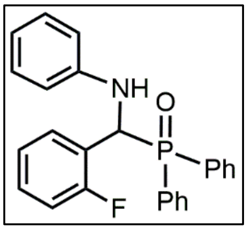
((4-methoxyphenyl)(phenylamino)methyl)diphenylphosphine oxide (**1b**). Yield: 188 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.93 - 7.79 (m, 2H, Ar*H*), 7.60 - 7.24 (m, 8H, Ar*H*), 7.13 - 7.04 (m, 4H, Ar*H*), 6.80 - 6.47 (m, 5H, Ar*H*), 5.20 - 5.09 (m, 2H, C*H* and N*H*), 3.70 (s, 3H, OC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 159.2, 146.2, 146.1, 132.4, 132.1, 131.8, 131.8, 131.7, 131.7, 131.3, 130.8, 130.4, 129.8, 129.6, 129.5, 129.3, 129.0, 128.9, 128.4, 128.3, 126.8, 118.5, 114.1, 113.8, 113.8, 57.1, 56.3, 55.3, 29.8 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.4 ppm. HRMS (ESI) m/z: [(M+H)$^{+}$] calcd for $C_{26}H_{24}PNO_2$ 414.1514, found 414.1589.



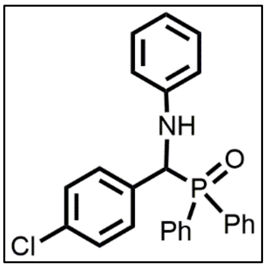
Diphenyl((phenylamino)(*p*-tolyl)methyl)phosphine oxide (**1c**). Yield: 179 mg, 91%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.89 - 7.83 (m, 2H, Ar*H*), 7.57 - 7.54 (m, 1H, Ar*H*), 7.50 - 7.41 (m, 5H, Ar*H*), 7.27 - 7.29 (m, 2H, Ar*H*), 7.10 - 7.02 (m, 4H, Ar*H*), 6.93 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.67 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.60 (d, *J* = 7.7 Hz, 2H, Ar*H*), 5.20 - 5.13 (m, 2H, C*H* and N*H*), 2.22 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 146.3, 146.2, 137.4, 132.4, 132.4, 132.0, 131.9, 131.8, 131.7, 130.7, 130.0, 129.3, 129.0, 129.0, 128.9, 128.8, 128.4, 128.3, 128.3, 128.2, 118.4, 114.0, 57.4, 56.9 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.1 ppm. HRMS (ESI) m/z: [(M+H)$^{+}$] calcd for $C_{26}H_{24}PNO$ 398.1614, found 398.1623.



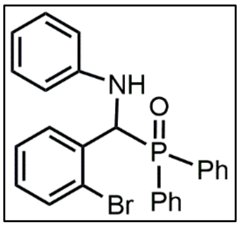
((3-phenoxyphenyl)(phenylamino)methyl)diphenylphosphine oxide (**1d**). Yield: 212 mg, 90%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.89 - 7.84 (m, 2H, Ar*H*), 7.57 - 7.53 (m, 1H, Ar*H*), 7.43 - 7.49 (m, 5H, Ar*H*), 7.36 - 7.24 (m, 4H, Ar*H*), 7.15 - 7.03 (m, 5H, Ar*H*), 6.81 - 6.77 (m, 2H, Ar*H*), 6.75 - 6.67 (m, 3H, Ar*H*), 6.62 - 6.59 (m, 2H, Ar*H*), 5.25 - 5.15 (m, 2H, C*H* and N*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 157.0, 156.7, 146.0, 145.9, 137.4, 132.4, 132.1, 131.7, 131.7, 131.6, 131.6, 131.1, 130.4, 129.7, 129.7, 129.7, 129.2, 128.9, 128.8, 128.3, 128.2, 123.4, 123.4, 123.1, 119.2, 119.2, 118.5, 114.0, 57.4, 56.9 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.1 ppm. HRMS (ESI) m/z: [(M+H)$^{+}$] calcd for $C_{31}H_{26}PNO_2$ 476.1667, found 476.174.



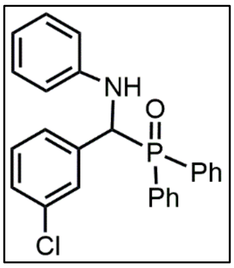
((2-fluorophenyl)(phenylamino)methyl)diphenylphosphine oxide (**1e**). Yield: 181 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.91 - 7.83 (m, 2H, Ar*H*), 7.60 - 7.37 (m, 6H, Ar*H*), 7.34 - 7.24 (m, 2H, Ar*H*), 7.15 - 7.07 (m, 4H, Ar*H*), 6.82 (t, *J* = 8.6 Hz, 2H, Ar*H*), 6.69 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.61 - 6.55 (m, 2H, Ar*H*), 5.21 - 5.13 (m, 2H, C*H* and N*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 146.0, 132.6, 132.3, 131.8, 131.8, 131.7, 131.7, 130.0, 129.4, 129.1, 128.9, 128.5, 128.3, 118.7, 115.4, 115.2, 114.0, 57.1, 56.4 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.2 ppm. ^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$, 25 ºC): δ_F -126.8 ppm. HRMS (ESI) m/z: [(M+H)$^{+}$] calcd for $C_{25}H_{21}PFNO$ 402.1318, found 402.1394.



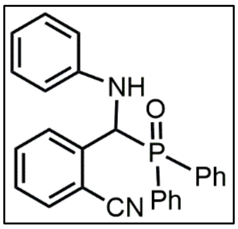
((4-chlorophenyl)(phenylamino)methyl)diphenylphosphine oxide (**1f**). Yield: 192 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.92 - 7.80 (m, 2H, Ar*H*), 7.65 - 7.25 (m, 8H, Ar*H*), 7.22 - 6.94 (m, 6H, Ar*H*), 6.78 - 6.50 (m, 3H, Ar*H*), 5.23 - 5.15 (m, 2H, C*H* and N*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 145.9, 145.8, 133.8, 133.6, 133.6, 132.6, 132.6, 132.4, 132.3, 131.8, 131.7, 131.7, 131.6, 130.0, 129.7, 129.7, 129.4, 129.1, 128.9, 128.5, 128.5, 128.4, 118.8, 114.0, 57.3, 56.5 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.1 ppm. HRMS (ESI) m/z: [(M+H) $^{+}$] calcd for $C_{25}H_{21}PClNO$ 418.1023, found 418.1098.



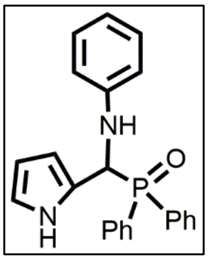
((2-bromophenyl)(phenylamino)methyl)diphenylphosphine oxide (**1g**). Yield: 206 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 8.03 - 7.92 (m, 2H, Ar*H*), 7.74 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.61 - 7.48 (m, 3H, Ar*H*), 7.38 - 7.32 (m, 1H, Ar*H*), 7.29 - 7.24 (m, 3H, Ar*H*), 7.21 - 7.13 (m, 3H, Ar*H*), 7.10 - 7.03 (m, 2H, Ar*H*), 7.02 - 6.96 (m, 1H, Ar*H*), 6.66 - 6.58 (m, 3H, Ar*H*), 5.80 - 5.65 (m, 2H, C*H* and N*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 145.9, 145.7, 135.2, 132.6, 132.6, 132.2, 132.1, 132.0, 131.7, 131.6, 130.1, 130.0, 129.5, 129.5, 129.4, 129.1, 129.0, 128.1, 127.9, 127.8, 125.1, 125.1, 118.4, 113.8, 55.4, 54.7 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.6 ppm. HRMS (ESI) m/z: [(M+Na) $^{+}$] calcd for $C_{25}H_{21}PBrNO$ 486.0409, found 486.0393.



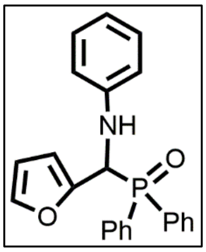
((3-chlorophenyl)(phenylamino)methyl)diphenylphosphine oxide (**1h**). Yield: 188 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.91 - 7.82 (m, 2H, Ar*H*), 7.61 - 7.54 (m, 1H, Ar*H*), 7.53 - 7.37 (m, 5H, Ar*H*), 7.33 - 7.28 (m, 2H, Ar*H*), 7.15 - 6.99 (m, 6H, Ar*H*), 6.70 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.61 - 6.56 (m, 2H, Ar*H*), 5.23 - 5.14 (m, 2H, C*H* and N*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 145.9, 137.6, 134.2, 132.7, 132.4, 131.8, 131.8, 131.7, 131.7, 130.1, 129.6, 129.4, 129.1, 129.0, 128.6, 128.5, 128.5, 128.4, 128.0, 126.5, 126.5, 118.8, 114.0, 57.4, 56.9 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.2 ppm. HRMS (ESI) m/z: [(M+H) $^{+}$] calcd for $C_{25}H_{21}PClNO$ 418.1017, found 418.1093.



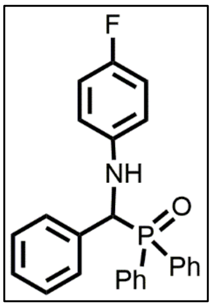
2-((diphenylphosphoryl)(phenylamino)methyl)benzonitrile (**1i**). Yield: 178 mg, 88%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.92 - 7.81 (m, 2H, Ar*H*), 7.60 - 7.55 (m, 1H, Ar*H*), 7.54 - 7.35 (m, 7H, Ar*H*), 7.33 - 7.22 (m, 4H, Ar*H*), 7.11 - 7.06 (m, 2H, Ar*H*), 6.70 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.60 - 6.52 (m, 2H, Ar*H*), 5.38 - 5.24 (m, 2H, C*H* and N*H*) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 145.6, 145.5, 141.4, 132.7, 132.5, 131.9, 131.6, 131.6, 131.6, 131.5, 130.4, 130.0, 129.8, 129.4, 129.3, 129.1, 129.1, 129.0, 128.6, 128.5, 119.0, 118.7, 113.9, 111.4, 57.7, 57.3 ppm. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 32.7 ppm. HRMS (ESI) m/z: [(M+H) $^{+}$] calcd for $C_{26}H_{21}PN_2O$ 409.136, found 409.1433.



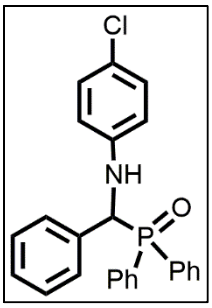
Diphenyl((phenylamino)(1H-pyrrol-2-yl)methyl)phosphine oxide (**1j**). Yield: 166 mg, 90%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 10.44 (s, 1H, Pyrrole-N*H*), 7.90 - 7.82 (m, 2H, Ar*H*), 7.62 - 7.24 (m, 8H, Ar*H*), 7.10 (t, *J* = 7.9 Hz, 2H, Ar*H*), 6.75 - 6.68 (m, 3H, Ar*H*), 6.56 (d, *J* = 1.4 Hz, 1H, Ar*H*), 5.92 (dd, *J* = 5.6, 2.7 Hz, 1H, C*H*), 5.69 (s, 2H, Ar*H*), 5.46 (t, *J* = 10.6 Hz, 1H, N*H*) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 159.1, 152.7, 140.3, 132.3, 132.0, 131.8, 131.8, 131.7, 130.8, 129.6, 129.5, 128.8, 128.8, 128.3, 128.2, 127.0, 115.4, 114.8, 113.7, 113.7, 57.9, 57.4, 55.7, 55.2 ppm. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 34.1 ppm. HRMS (ESI) m/z: [(M+Na) $^{+}$] calcd for $C_{23}H_{21}PN_2O$ 395.1258, found 395.1256.



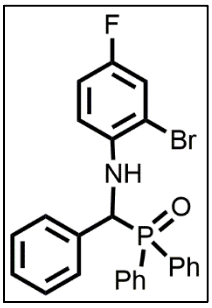
(Furan-2-yl(phenylamino)methyl)diphenylphosphine oxide (**1k**). Yield: 162 mg, 88%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.92 - 7.81 (m, 2H, Ar*H*), 7.64 - 7.53 (m, 3H, Ar*H*), 7.51 - 7.45 (m, 3H, Ar*H*), 7.38 (m, 2H, Ar*H*), 7.20 - 7.06 (m, 3H, Ar*H*), 6.75 - 6.64 (m, 3H, Ar*H*), 6.26 (t, *J* = 3.1 Hz, 1H, Ar*H*), 6.20 - 6.18 (m, 1H, Ar*H*), 5.36 (dd, *J* = 12.0, 9.9 Hz, 1H, C*H*), 4.96 - 4.93 (m, 1H, N*H*) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 149.1, 146.1, 142.3, 132.5, 132.3, 131.7, 131.7, 131.6, 131.6, 129.4, 128.9, 128.9, 128.4, 128.4, 119.1, 114.2, 110.9, 109.7, 52.5, 52.0 ppm. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 30.9 ppm. HRMS (ESI) m/z: [(M+H) $^{+}$] calcd for $C_{23}H_{20}PNO_2$ 374.1216, found 374.1292.



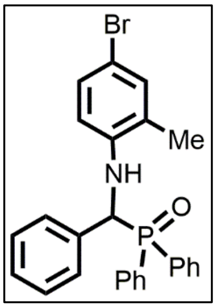
(((4-fluorophenyl)amino)(phenyl)methyl)diphenylphosphine oxide (**1l**). Yield: 173 mg, 87%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.96 - 7.82 (m, 2H, Ar*H*), 7.59 - 7.56 (m, 1H, Ar*H*), 7.51 - 7.48 (m, 2H, Ar*H*), 7.45 - 7.34 (m, 3H, Ar*H*), 7.32 - 7.24 (m, 2H, Ar*H*), 7.15 - 7.10 (m, 5H, Ar*H*), 6.78 (t, *J* = 8.7 Hz, 2H, Ar*H*), 6.55 - 6.47 (m, 2H, Ar*H*), 5.15 - 5.09 (m, 2H, C*H* and N*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 157.1, 155.6, 142.5, 134.9, 132.5, 132.2, 131.8, 131.7, 131.1, 130.5, 130.4, 129.7, 129.0, 128.9, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 115.9, 115.7, 115.0, 114.9, 58.4, 57.9 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.2 ppm. ^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$, 25 ºC): δ_F -126.8 ppm. HRMS (ESI) m/z: [(M+H)$^{+}$] calcd for $C_{25}H_{21}PFNO$ 402.1331, found 402.1342.



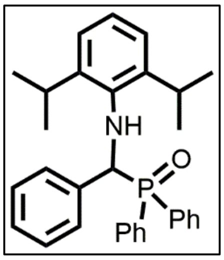
(((4-chlorophenyl)amino)(phenyl)methyl)diphenylphosphine oxide (**1m**). Yield: 184 mg, 89%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.87 - 7.83 (m, 2H, Ar*H*), 7.60 - 7.55 (m, 1H, Ar*H*), 7.54 - 7.47 (m, 2H, Ar*H*), 7.44 - 7.33 (m, 3H, Ar*H*), 7.32 - 7.23 (m, 3H, Ar*H*), 7.23 - 7.04 (m, 4H, Ar*H*), 7.06 - 6.97 (m, 2H, Ar*H*), 6.53 - 6.48 (m, 2H, Ar*H*), 5.27 (t, *J* = 8.6 Hz, 1H, N*H*), 5.11 (dd, *J* = 11.2, 8.9 Hz, 1H, C*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 132.6, 132.2, 131.8, 131.7, 131.7, 129.2, 129.1, 129.0, 128.4, 128.3, 128.3, 123.2, 115.2, 57.9, 57.4 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.3 ppm. HRMS (ESI) m/z: [(M+Na)$^{+}$] calcd for $C_{25}H_{21}PClNO$ 440.101, found 440.0906.



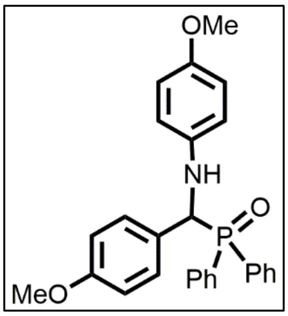
(((2-bromo-4-fluorophenyl)amino)(phenyl)methyl)diphenylphosphine oxide (**1n**). Yield: 209 mg, 88%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.81 - 7.77 (m, 2H, Ar*H*), 7.61 - 7.55 (m, 3H, Ar*H*), 7.50 - 7.45 (m, 3H, Ar*H*), 7.36 - 7.33 (m, 2H, Ar*H*), 7.19 - 7.11 (m, 6H, Ar*H*), 6.77 - 6.71 (m, 1H, Ar*H*), 6.46 - 6.43 (m, 1H, Ar*H*), 5.38 (t, *J* = 8.6 Hz, 1H, N*H*), 5.18 (dd, *J* = 13.4, 8.8 Hz, 1H, C*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 156.1, 154.5, 134.3, 132.6, 132.6, 132.3, 132.1, 132.0, 131.9, 131.8, 128.9, 128.8, 128.5, 128.4, 128.3, 128.3, 128.1, 119.8, 119.7, 115.1, 115.0, 113.3, 113.2, 110.3, 110.2, 58.7, 58.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 31.7 ppm. ^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$, 25 ºC): δ_F -125.2 ppm. HRMS (ESI) m/z: [(M+Na)$^{+}$] calcd for $C_{25}H_{20}PBrFNO$ 502.0306, found 502.0288.



(((4-bromo-2-methylphenyl)amino)(phenyl)methyl)diphenylphosphine oxide (**1o**). Yield: 212 mg, 90%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.92 - 7.78 (m, 2H, Ar*H*), 7.58 - 7.55 (m, 1H, Ar*H*), 7.53 - 7.35 (m, 5H, Ar*H*), 7.31 - 7.26 (m, 2H, Ar*H*), 7.24 - 7.06 (m, 6H, Ar*H*), 7.04 - 7.00 (m, 1H, Ar*H*), 6.35 (d, *J* = 8.7 Hz, 1H, Ar*H*), 5.22 - 5.15 (m, 1H, Ar*H*), 5.20 - 5.00 (m, 2H, C*H* and N*H*), 2.08 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 143.3, 143.3, 134.7, 132.8, 132.5, 132.5, 132.2, 132.2, 131.7, 131.7, 131.7, 131.7, 130.9, 130.2, 129.6, 129.0, 128.9, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 127.9, 127.9, 125.5, 113.0, 110.0, 57.8, 57.4, 17.3 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.0 ppm. HRMS (ESI) m/z: [(M+Na)$^{+}$] calcd for $C_{26}H_{23}PBrNO$ 498.0558, found 498.0558.

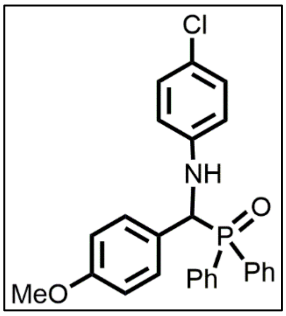


(((2,6-diisopropylphenyl)amino)(phenyl)methyl)diphenylphosphine oxide (**1p**). Yield: 204 mg, 88%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.87 - 7.80 (m, 2H, Ar*H*), 7.50 - 7.45 (m, 3H, Ar*H*), 7.44 - 7.37 (m, 2H, Ar*H*), 7.35 - 7.31 (m, 1H, Ar*H*), 7.28 - 7.22 (m, 4H, Ar*H*), 7.14 - 7.04 (m, 3H, Ar*H*), 6.96 - 6.79 (m, 3H, Ar*H*), 4.73 - 4.55 (m, 2H, C*H* and N*H*), 2.82 - 2.71 (m, 2H, i-propyl C*H*), 0.99 (d, *J* = 6.8 Hz, 6H, i-propyl C*H*$_3$), 0.75 (d, *J* = 6.7 Hz, 6H, i-propyl C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 141.7, 140.8, 140.8, 136.8, 132.5, 131.8, 131.8, 131.8, 131.6, 131.5, 131.5, 131.5, 131.2, 131.1, 131.0, 129.1, 129.0, 128.2, 128.2, 127.6, 123.4, 123.4, 64.0, 63.4, 27.4, 24.0, 24.0 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 32.4 ppm. HRMS (ESI) m/z: [(M)$^{+}$] calcd for $C_{31}H_{35}PNO$ 468.2424, found 468.2420.

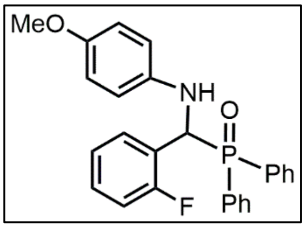


((4-methoxyphenyl)((4-methoxyphenyl)amino)methyl)diphenylphosphine oxide (**1q**). Yield: 195 mg, 89%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.89 - 7.83 (m, 2H, Ar*H*), 7.55 - 7.40 (m, 6H, Ar*H*), 7.32 - 7.25 (m, 2H, Ar*H*), 7.07 - 7.03 (m, 2H, Ar*H*), 6.71 - 6.60 (m, 4H, Ar*H*), 6.55 - 6.52 (m, 2H, Ar*H*), 5.10 - 4.86 (m, 2H, C*H* and N*H*), 3.69 (s, 3H, OC*H*$_3$), 3.66 (s, 3H, OC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 159.1, 152.7, 140.3, 132.3, 132.0, 131.8, 131.8, 131.7, 130.8, 129.6, 129.5, 128.8, 128.8, 128.3, 128.2, 127.0, 115.4, 114.8, 113.7, 113.7, 57.9, 57.4, 55.7, 55.2 ppm.

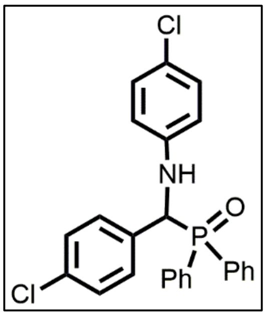
$^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.4 ppm. HRMS (ESI) m/z: [$(M+Na)^+$] calcd for $C_{27}H_{26}PNO_3$ 466.1615, found 466.1611.



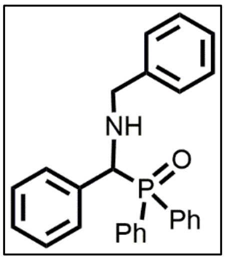
(((4-chlorophenyl)amino)(4-methoxyphenyl)methyl)diphenylphosphine oxide (**1r**). Yield: 200 mg, 90%. ^1H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.89 - 7.82 (m, 2H, Ar*H*), 7.58 - 7.38 (m, 6H, Ar*H*), 7.33 - 7.26 (m, 2H, Ar*H*), 7.14 - 6.89 (m, 4H, Ar*H*), 6.68 - 6.65 (m, 2H, Ar*H*), 6.53 - 6.49 (m, 2H, Ar*H*), 5.26 (t, *J* = 8.5 Hz, 1H, N*H*), 5.08 (dd, *J* = 10.8, 9.0 Hz, 1H, C*H*), 3.70 (s, 3H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 159.3, 144.9, 144.9, 132.5, 132.2, 131.8, 131.7, 131.6, 130.9, 130.8, 129.6, 129.5, 129.1, 129.1, 129.0, 128.9, 128.3, 128.3, 126.5, 123.1, 115.2, 113.9, 113.8, 57.1, 56.6, 55.3 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.4 ppm. HRMS (ESI) m/z: [$(M+H)^+$] calcd for $C_{26}H_{23}PClNO_2$ 448.1179, found 448.1252.



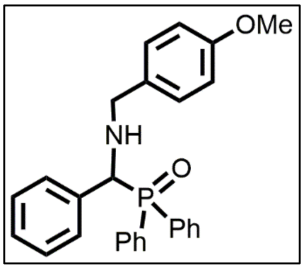
((2-fluorophenyl)((4-methoxyphenyl)amino)methyl) diphenylphosphine oxide (**1s**). Yield: 186 mg, 87%. ^1H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.98 - 7.89 (m, 2H, Ar*H*), 7.63 - 7.36 (m, 7H, Ar*H*), 7.26 - 7.23 (m, 2H, Ar*H*), 7.09 - 7.03 (m, 2H, Ar*H*), 6.70 - 6.50 (m, 5H, Ar*H*), 5.61 (t, *J* = 10.6 Hz, 1H, N*H*), 5.04 (dd, *J* = 10.7, 8.9 Hz, 1H, C*H*), 3.66 (s, 3H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 152.8, 139.9, 139.8, 132.4, 132.1, 131.7, 131.6, 131.5, 131.4, 130.7, 130.3, 129.6, 129.5, 129.4, 129.4, 129.0, 128.9, 128.1, 128.0, 124.7, 123.4, 123.3, 115.0, 114.9, 114.6, 114.5, 55.7, 49.9, 49.3 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.0 ppm. $^{19}F\{^1H\}$ NMR (565 MHz, $CDCl_3$, 25 ºC): δ_F -118.6 ppm. HRMS (ESI) m/z: [$(M+H)^+$] calcd for $C_{26}H_{23}PFNO_2$ 432.1414, found 432.1490.



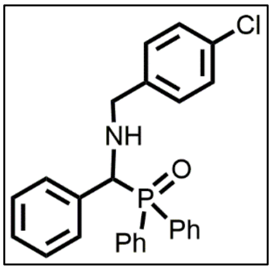
((4-chlorophenyl)((4-chlorophenyl)amino)methyl)diphenylphosphine oxide(**1t**). Yield: 192 mg, 86%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.87 - 7.82 (m, 2H, Ar*H*), 7.62 - 7.57 (m, 1H, Ar*H*), 7.52 - 7.49 (m, 2H, Ar*H*), 7.47 - 7.45 (m, 1H, Ar*H*), 7.41 - 7.37 (m, 2H, Ar*H*), 7.34 - 7.25 (m, 2H, Ar*H*), 7.10 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.07 - 6.99 (m, 4H, Ar*H*), 6.50 - 6.47 (m, 2H, Ar*H*), 5.22 (t, *J* = 8.6 Hz, 1H, N*H*), 5.09 (dd, *J* = 11.2, 8.8 Hz, 1H, C*H*). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 132.7, 132.5, 131.7, 131.7, 131.6, 129.7, 129.7, 129.3, 129.1, 129.1, 128.6, 128.5, 128.4, 123.5, 115.1, 57.4 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 32.9 ppm. HRMS (ESI) m/z: [(M+H) $^{+}$] calcd for $C_{25}H_{20}PCl_2NO$ 452.0618, found 452.0697.



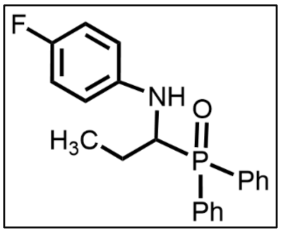
((Benzylamino)(phenyl)methyl)diphenylphosphine oxide (**1u**).[3] Yield: 179 mg, 91%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.80 - 7.75 (m, 2H, Ar*H*), 7.55 - 7.51 (m, 1H, Ar*H*), 7.46 - 7.40 (m, 4H, Ar*H*), 7.35 - 7.31 (m, 1H, Ar*H*), 7.28 - 7.16 (m, 10H, Ar*H*), 7.12 - 7.09 (m, 2H, Ar*H*), 4.37 (d, *J* = 10.6 Hz, 1H, N*H*), 3.82 (d, *J* = 13.3 Hz, 1H, CH_2), 3.49 (d, *J* = 13.4 Hz, 1H, CH_2), 2.57 (s, 1H, C*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 139.0, 135.1, 132.0, 132.0, 131.9, 131.8, 131.5, 131.5, 131.5, 129.1, 129.1, 128.7, 128.4, 128.3, 128.3, 128.3, 128.0, 128.0, 127.8, 127.8, 127.2, 61.3, 60.8, 51.0, 50.9 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 31.6 ppm.



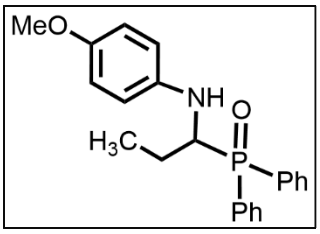
(((4-methoxybenzyl)amino)(phenyl)methyl)diphenylphosphine oxide (**1v**). Yield: 194 mg, 92%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.82 - 7.74 (m, 2H, Ar*H*), 7.57 - 7.51 (m, 1H, Ar*H*), 7.48 - 7.39 (m, 4H, Ar*H*), 7.35 - 7.30 (m, 1H, Ar*H*), 7.29 - 7.14 (m, 7H, Ar*H*), 7.04 - 7.01 (m, 2H, Ar*H*), 6.83 - 7.79 (m, 2H, Ar*H*), 4.36 (d, *J* = 10.6 Hz, 1H, N*H*), 3.82 - 3.72 (m, 4H, OCH_3 and CH_2), 3.43 (d, *J* = 13.1 Hz, 1H, CH_2), 2.56 (s, 1H, C*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 158.8, 135.1, 132.0, 132.0, 131.8, 131.8, 131.8, 131.5, 131.5, 131.0, 129.9, 129.2, 129.1, 128.4, 128.3, 128.3, 128.0, 128.0, 127.8, 127.7, 113.6, 61.1, 60.5, 55.3, 50.3, 50.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 31.7 ppm. HRMS (ESI) m/z: [(M+H) $^{+}$] calcd for $C_{27}H_{26}PNO_2$ 428.1674, found 428.1747.



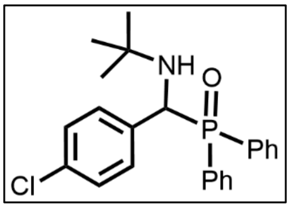
(((4-chlorobenzyl)amino)(phenyl)methyl)diphenylphosphine oxide (**1w**). Yield: 192 mg, 90%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ_H 7.73 - 7.67 (m, 2H, Ar*H*), 7.46 - 7.22 (m, 6H, Ar*H*), 7.18 - 7.05 (m, 9H, Ar*H*), 6.92 (d, *J* = 7.8 Hz, 2H, Ar*H*), 4.21 (d, *J* = 10.2 Hz, 1H, N*H*), 3.69 (d, *J* = 13.6 Hz, 1H, CH_2), 3.36 (d, *J* = 13.6 Hz, 1H, CH_2), 2.54 (s, 1H, C*H*) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 137.6, 135.0, 132.8, 131.9, 131.9, 131.6, 131.6, 131.5, 131.4, 130.0, 129.1, 129.1, 128.4, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 61.3, 60.7, 50.2, 50.1 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 31.7 ppm. HRMS (ESI) m/z: [(M+H) $^+$] calcd for $C_{26}H_{23}PClNO$ 432.1179, found 432.1251.



(1-((4-fluorophenyl)amino)propyl)diphenylphosphine oxide (**1x**). Yield: 143 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.86 - 7.79 (m, 2H, Ar*H*), 7.73 - 7.67 (m, 2H, Ar*H*), 7.52 - 7.41 (m, 6H, Ar*H*), 6.89 - 6.81 (m, 2H, Ar*H*), 6.60 - 6.53 (m, 2H, Ar*H*), 5.17 (brs, 1H, N*H*), 4.61 – 4.51 (m, 1H, C*H*), 1.86 - 1.73 (m, 2H, C$H_2$$CH_3$), 0.60 (t, *J* = 7.5 Hz, 3H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 157.3, 155.0, 142.8, 131.8, 131.7, 131.4, 131.3, 128.8, 128.7, 128.3, 128.2, 115.7, 115.5, 114.9, 114.8, 61.2, 60.4, 21.1, 13.5 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.6 ppm. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 ºC): δ_F -127.1 ppm. HRMS (ESI) m/z: [(M+H) $^+$] calcd for $C_{21}H_{21}PFNO$ 353.1335, found 354.1410.

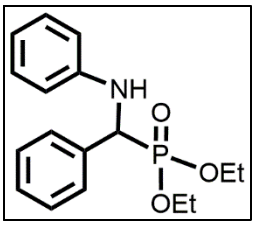


(1-((4-methoxyphenyl)amino)propyl)diphenylphosphine oxide (**1y**).[4] Yield: 144 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.88 - 7.79 (m, 2H, Ar*H*), 7.76 - 7.67 (m, 2H, Ar*H*), 7.51 - 7.40 (m, 6H, Ar*H*), 6.78 - 6.71 (m, 2H, Ar*H*), 6.63 - 6.56 (m, 2H, Ar*H*), 5.15 (brs, 1H, N*H*), 4.61 - 4.54 (m, 1H, C*H*), 3.72 (s, 3H, OCH_3), 1.84 - 1.73 (m, 2H, C$H_2$$CH_3$), 0.59 (t, *J* = 7.5 Hz, 3H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 152.5, 140.7, 140.5, 134.2, 134.1, 131.8, 131.7, 131.5, 131.4, 128.7, 128.6, 128.2, 128.1, 115.2, 114.7, 61.4, 60.6, 55.7, 21.0, 13.6 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.6 ppm.

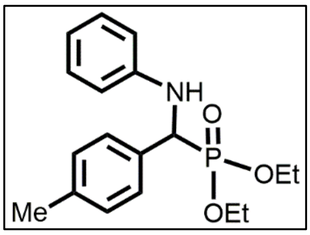


((Tert-butylamino)(4-chlorophenyl)methyl)diphenylphosphine oxide (**1z**). Yield: 167 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.96 - 7.86 (m, 2H, Ar*H*), 7.65 - 7.52 (m, 3H, Ar*H*), 7.51 - 7.28 (m, 5H, Ar*H*), 7.15 – 7.08 (m, 4H, Ar*H*), 4.54 (d, *J* = 13.5 Hz, 1H, C*H*), 0.87 (s, 9H, ^{t}Bu-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 137.9, 133.2, 132.3, 132.2, 132.0, 131.9, 131.8, 130.1, 130.1, 128.5, 128.3, 128.3, 128.2, 128.1, 58.5, 57.7, 52.6, 30.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 31.1 ppm. HRMS (ESI) m/z: [(M+Na) $^{+}$] calcd for $C_{23}H_{25}ClPNO$ 397.1338, found 420.1230.

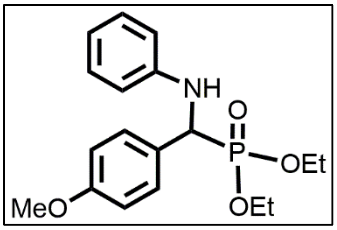
Characterisation data of α-amino phosphonate derivatives:



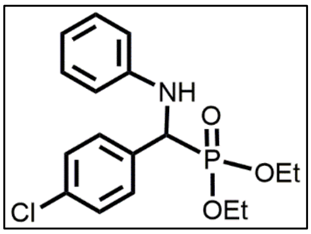
Diethyl(phenyl(phenylamino)methyl)phosphonate (**2a**).[5] Yield: 201 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.49 - 7.45 (m, 2H, Ar*H*), 7.35 - 7.21 (m, 3H, Ar*H*), 7.11 - 7.06 (m, 2H, Ar*H*), 6.67 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.59 (d, *J* = 7.8 Hz, 2H, Ar*H*), 4.91 - 4.72 (m, 2H, C*H* and N*H*), 4.19 - 4.03 (m, 2H, OEt-CH_2), 3.98 - 3.87 (m, 1H, OEt-CH_2), 3.69 - 3.63 (m, 1H, OEt-CH_2), 1.27 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.10 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 146.4, 146.3, 136.0, 135.9, 129.2, 128.6, 128.6, 128.0, 127.9, 127.9, 118.4, 113.9, 63.3, 63.3, 63.3, 63.3, 56.8, 55.3, 16.5, 16.4, 16.2, 16.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.7 ppm.



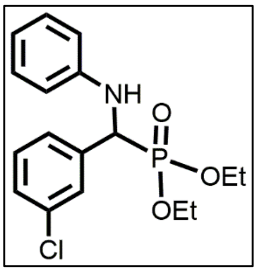
Diethyl((phenylamino)(p-tolyl)methyl)phosphonate (**2b**).[5] Yield: 215 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.43 - 7.33 (m, 2H, Ar*H*), 7.28 - 6.99 (m, 4H, Ar*H*), 6.84 - 6.53 (m, 3H, Ar*H*), 4.95 - 4.70 (m, 2H, C*H* and N*H*), 4.18 - 4.11 (m, 2H, OEt-CH_2), 3.98 - 3.95 (m, 1H, OEt-CH_2), 3.74 - 3.68 (m, 1H, OEt-CH_2), 2.31 (s, 3H, CH_3), 1.29 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.14 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 146.4, 146.3, 137.5, 137.5, 132.7, 129.3, 129.2, 129.1, 127.7, 127.7, 118.2, 113.8, 63.2, 63.2, 63.1, 63.1, 56.4, 54.9, 21.1, 16.4, 16.4, 16.2, 16.1 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.9 ppm.



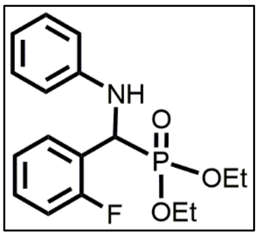
Diethyl((4-methoxyphenyl)(phenylamino)methyl)phosphonate (**2c**).[6] Yield: 227 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.42 - 7.38 (m, 2H, Ar*H*), 7.09 (t, *J* = 7.8 Hz, 2H, Ar*H*), 6.86 (d, *J* = 8.6 Hz, 2H, Ar*H*), 6.73 - 6.57 (m, 3H, Ar*H*), 4.94 - 4.68 (m, 2H, C*H* and N*H*), 4.24 - 4.04 (m, 2H, OEt-CH_2), 3.99 - 3.90 (m, 1H, OEt-CH_2), 3.76 - 3.66 (m, 4H, OEt-CH_2 and OCH_3), 1.27 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.13 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, v): δ_C 159.2, 159.2, 146.4, 146.3, 129.0, 128.9, 128.9, 127.6, 127.6, 118.2, 114.0, 113.9, 113.8, 63.2, 63.1, 63.1, 63.1, 56.0, 55.1, 54.5, 16.4, 16.3, 16.2, 16.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 23.0 ppm.



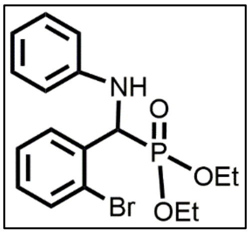
Diethyl((4-chlorophenyl)(phenylamino)methyl)phosphonate (2d).[7] Yield: 220 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.43 - 7.39 (m, 2H, Ar*H*), 7.32 - 7.28 (m, 2H, Ar*H*), 7.13 - 7.08 (m, 2H, Ar*H*), 6.71 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.58 - 6.54 (m, 2H, Ar*H*), 4.81 - 4.68 (m, 2H, C*H* and N*H*), 4.20 - 4.04 (m, 2H, OEt-CH_2), 4.02 - 3.95 (m, 1H, OEt-CH_2), 3.81- 3.74 (m, 1H, OEt-CH_2), 1.29 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.15 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 146.2, 146.1, 134.7, 133.8, 129.4, 129.3, 129.2, 128.9, 128.9, 118.8, 114.0, 63.6, 63.5, 63.4, 56.4, 54.9, 16.6, 16.5, 16.4, 16.3 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.0 ppm.



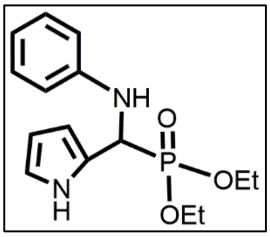
Diethyl((3-chlorophenyl)(phenylamino)methyl)phosphonate (**2e**).[8] Yield: 218 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.47 (d, *J* = 1.8 Hz, 1H, Ar*H*), 7.39 - 7.35 (m, 1H, Ar*H*), 7.30 - 7.20 (m, 2H, Ar*H*), 7.14 - 7.09 (m, 2H, Ar*H*), 6.71 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.59 - 6.55 (m, 2H, Ar*H*), 4.88 - 4.68 (m, 2H, C*H* and N*H*), 4.19 - 4.06 (m, 2H, OEt-CH_2), 4.02 - 3.93 (m, 1H, OEt-CH_2), 3.80 - 3.74 (m, 1H, OEt-CH_2), 1.28 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.15 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 157.1, 155.6, 146.2, 146.0, 138.4, 138.4, 134.6, 134.6, 129.9, 129.9, 129.3, 128.2, 128.2, 128.0, 128.0, 126.1, 126.0, 118.7, 113.8, 63.6, 63.5, 63.4, 56.5, 55.0, 16.5, 16.4, 16.3, 16.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 21.9 ppm.



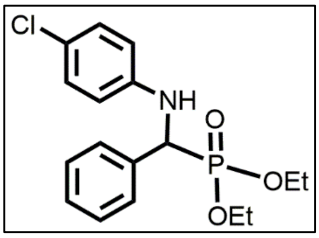
Diethyl((2-fluorophenyl)(phenylamino)methyl)phosphonate (**2f**).[9] Yield : 207 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.54 - 7.48 (m, 1H, Ar*H*), 7.29 - 7.00 (m, 5H, Ar*H*), 6.76 - 6.56 (m, 3H, Ar*H*), 5.20 - 4.85 (m, 2H, C*H* and N*H*) 4.28 - 4.15 (m, 2H, OEt-C*H*$_2$), 4.03 - 3.87 (m, 1H, OEt-C*H*$_2$), 3.76 - 3.70 (m, 1H, OEt-C*H*$_2$), 1.32 (t, *J* = 7.1 Hz, 3H, OEt-C*H*$_3$), 1.09 (t, *J* = 7.1 Hz, 3H, OEt-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 162.1, 159.7, 146.0, 145.8, 129.7, 129.6, 129.4, 129.0, 128.9, 128.9, 124.7, 124.7, 118.8, 115.4, 115.2, 113.7, 63.6, 63.6, 63.5, 63.5, 49.0, 47.5, 16.6, 16.5, 16.2, 16.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.0 ppm. ^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$, 25 ºC): δ_F -118.4 ppm.



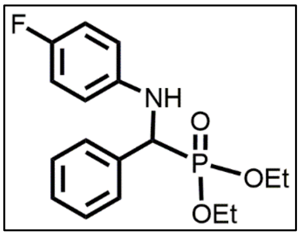
Diethyl((2-bromophenyl)(phenylamino)methyl)phosphonate (**2g**).[10] Yield: 242 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.64 - 7.51 (m, 2H, Ar*H*), 7.28 - 7.10 (m, 4H, Ar*H*), 6.74 - 6.55 (m, 3H, Ar*H*), 5.35 (t, *J* = 9.2 Hz, 1H, N*H*), 5.02 (dd, *J* = 24.6, 8.6 Hz, 1H, C*H*), 4.26 - 4.18 (m, 2H, OEt-C*H*$_2$), 3.87 - 3.92 (m, 1H, OEt-C*H*$_2$), 3.59 - 3.63 (m, 1H, OEt-C*H*$_2$), 1.34 (t, *J* = 7.1 Hz 3H, OEt-C*H*$_3$), 1.06 (t, *J* = 7.1 Hz, 3H, OEt-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 145.9, 145.7, 135.8, 132.9, 132.9, 129.5, 129.5, 129.4, 129.3, 129.2, 128.1, 128.1, 124.9, 124.8, 118.6, 113.7, 63.7, 63.6, 63.5, 55.1, 53.6, 16.6, 16.5, 16.2, 16.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.1 ppm.



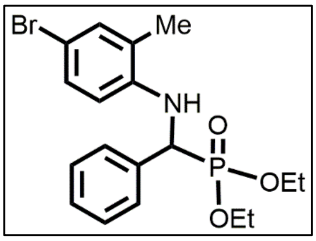
Diethyl((phenylamino)(1H-pyrrol-2-yl)methyl)phosphonate (**2h**). Yield: 187 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 9.71 (s, 1H, pyrrole-N*H*), 7.18 - 7.11 (m, 2H, Ar*H*), 6.76 - 6.66 (m, 4H, Ar*H*), 6.28 - 6.07 (m, 2H, Ar*H*), 5.05 - 4.89 (m, 2H, C*H* and N*H*), 4.23 - 4.07 (m, 2H, OEt-C*H*$_2$), 4.00 - 3.94 (m, 1H, OEt-C*H*$_2$), 3.76 - 3.70 (m, 1H, OEt-C*H*$_2$), 1.29 (t, *J* = 7.1 Hz, 3H, OEt-C*H*$_3$), 1.19 (t, *J* = 7.1 Hz, 3H, OEt-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 146.9, 146.8, 129.2, 125.3, 125.2, 118.7, 118.6, 114.2, 114.2, 108.4, 108.3, 63.6, 63.6, 63.5, 50.7, 49.6, 16.6, 16.5, 16.4, 16.4 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.1 ppm. HRMS (ESI) m/z: [$(M+Na)^+$] calcd for $C_{15}H_{21}PN_2O_3$ 331.1170, found 331.1165.



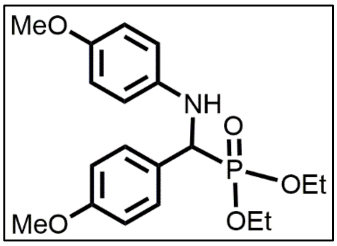
Diethyl(((4-chlorophenyl)amino)(phenyl)methyl)phosphonate (**2i**).[11] Yield: 226 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.47 - 7.43 (m, 2H, Ar*H*), 7.34 - 7.21 (m, 3H, Ar*H*), 7.07 - 6.95 (m, 2H, Ar*H*), 6.58 - 6.48 (m, 2H, Ar*H*), 5.12 (t, *J* = 8.6 Hz, 1H, N*H*), 4.72 (dd, *J* = 24.2, 7.9 Hz, 1H, C*H*), 4.23 - 4.02 (m, 2H, OEt-CH_2), 3.94 - 3.88 (m, 1H, OEt-CH_2), 3.72 - 3.59 (m, 1H, OEt-CH_2), 1.27 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.09 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 145.1, 144.9, 135.5, 135.5, 128.9, 128.6, 128.6, 128.0, 128.0, 127.8, 127.8, 122.8, 114.9, 63.4, 63.3, 63.3, 63.2, 56.8, 55.3, 16.4, 16.4, 16.2, 16.1 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.4 ppm.



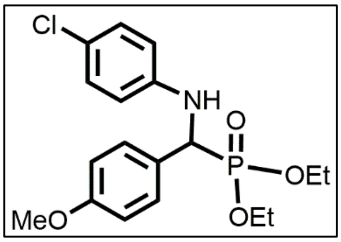
Diethyl(((4-fluorophenyl)amino)(phenyl)methyl)phosphonate (**2j**).[12] Yield: 210 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.46 - 7.43 (m, 2H, Ar*H*), 7.38 - 7.25 (m, 3H, Ar*H*), 6.83 - 6.77 (m, 2H, Ar*H*), 6.54 - 6.49 (m, 2H, Ar*H*), 4.82 - 4.60 (m, 2H, C*H* and N*H*), 4.20 - 4.03 (m, 2H, OEt-CH_2), 3.98 - 3.87 (m, 1H, OEt-CH_2), 3.70 - 3.63 (m, 1H, OEt-CH_2), 1.29 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.11 (t, *J* = 7.0 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 157.2, 155.6, 142.7, 142.6, 135.8, 128.8, 128.8, 128.2, 128.2, 128.0, 127.9, 115.8, 115.7, 115.0, 114.9, 63.5, 63.5, 63.4, 63.4, 57.3, 56.3, 16.6, 16.5, 16.3, 16.3 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.6 ppm. ^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$, 25 ºC): δ_F -126.8 ppm.



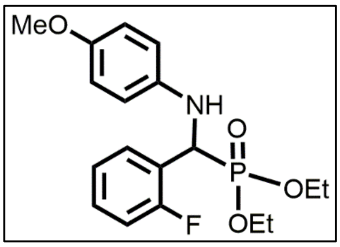
Diethyl(((4-bromo-2-methylphenyl)amino)(phenyl)methyl)phosphonate (**2k**).[13] Yield: 254 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.43 - 7.40 (m, 2H, Ar*H*), 7.35 - 7.26 (m, 3H, Ar*H*), 7.16 (d, *J* = 1.9 Hz, 1H, Ar*H*), 7.04 - 7.00 (m, 1H, Ar*H*), 6.24 (d, *J* = 8.6 Hz, 1H, Ar*H*), 4.87 - 4.54 (m, 2H, C*H* and N*H*), 4.22 - 3.84 (m, 3H, OEt-CH_2), 3.77 - 3.62 (m, 1H, OEt-CH_2), 2.25 (s, 3H, CH_3), 1.28 (t, *J* = 7.1Hz, 3H, OEt-CH_3), 1.12 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 ºC): δ_C 143.5, 143.4, 135.5, 135.5, 132.8, 129.6, 128.8, 128.8, 128.2, 128.2, 127.8, 127.7, 125.3, 113.0, 110.0, 63.6, 63.5, 63.5, 63.4, 56.7, 55.7, 17.5, 16.6, 16.5, 16.3, 16.3 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.5 ppm.



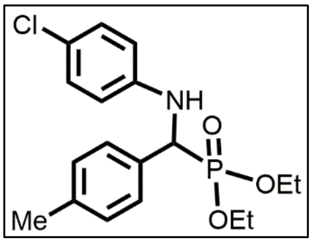
Diethyl((4-methoxyphenyl)((4-methoxyphenyl)amino)methyl)phosphonate (**2l**).[7] Yield: 241 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.43 - 7.24 (m, 2H, Ar*H*), 6.85 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.70 - 6.66 (m, 2H, Ar*H*), 6.56 - 6.52 (m, 2H, Ar*H*), 4.65 - 4.50 (m, 2H, C*H* and N*H*), 4.14 - 4.07 (m, 2H, OEt-CH_2), 3.97 - 3.92 (m, 1H, OEt-CH_2), 3.78 - 3.65 (m, 7H, OCH_3 and OEt-CH_2), 1.28 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.13 (t, *J* = 7.0 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 159.3, 159.3, 152.7, 140.5, 140.4, 129.1, 129.0, 127.8, 115.3, 114.8, 114.1, 114.1, 63.3, 63.3, 63.2, 57.1, 55.7, 55.6, 55.3, 16.6, 16.5, 16.4, 16.3 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 23.1 ppm.



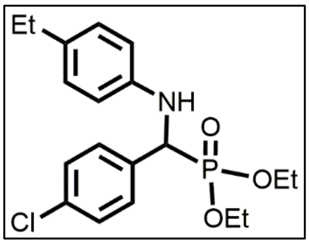
Diethyl(((4-chlorophenyl)amino)(4-methoxyphenyl)methyl)phosphonate (**2m**).[11] Yield: 247 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.40 - 7.34 (m, 2H, Ar*H*), 7.04 - 7.00 (m, 2H, Ar*H*), 6.87 - 6.83 (m, 2H, Ar*H*), 6.54 - 6.50 (m, 2H, Ar*H*), 5.02 - 4.62 (m, 2H, C*H* and N*H*), 4.17 - 4.04 (m, 2H, OEt-CH_2), 3.91 - 3.95 (m, 1H, OEt-CH_2), 3.75 (s, 3H, OCH_3), 3.66 - 3.70 (m, 1H, OEt-CH_2), 1.28 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.13 (t, *J* = 7.0 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 159.4, 159.4, 145.1, 144.9, 129.0, 128.9, 127.2, 127.2, 122.8, 115.0, 114.1, 114.1, 63.4, 63.3, 63.2, 63.2, 56.2, 55.2, 54.6, 16.5, 16.4, 16.3, 16.2 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.6 ppm.



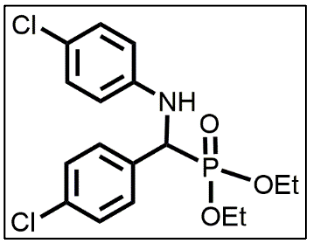
Diethyl((2-fluorophenyl)((4-methoxyphenyl)amino)methyl)phosphonate (**2n**).[14] Yield: 231 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.55 - 7.50 (m, 1H, Ar*H*), 7.28 - 7.17 (m, 1H, Ar*H*), 7.13 - 6.98 (m, 2H, Ar*H*), 6.70 - 6.55 (m, 4H, Ar*H*), 5.17 - 4.85 (m, 2H, C*H* and N*H*), 4.26 - 4.15 (m, 2H, OEt-CH_2), 3.97 - 3.90 (m, 1H, OEt-CH_2), 3.78 - 3.70 (m, 1H, OEt-CH_2), 3.66 (s, 3H, *OCH3*), 1.31 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.08 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 162.1, 162.1, 159.7, 159.6, 152.8, 139.9, 139.8, 129.6, 129.5, 129.5, 129.4, 128.9, 128.9, 128.8, 124.6, 124.6, 124.6, 123.8, 123.7, 115.3, 115.3, 115.1, 115.1, 115.0, 114.8, 63.6, 63.5, 63.3, 63.3, 55.6, 49.8, 48.2, 16.5, 16.4, 16.2, 16.1 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.2 ppm. $^{19}F\{^1H\}$ NMR (565 MHz, $CDCl_3$, 25 ºC): δ_F -118.6 ppm.



Diethyl(((4-chlorophenyl)amino)(p-tolyl)methyl)phosphonate (**2o**).[15] Yield: 237 mg, 89%. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.33 - 7.26 (m, 2H, Ar*H*), 7.13 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.05 - 7.01 (m, 2H, Ar*H*), 6.52 - 6.49 (m, 2H, Ar*H*), 4.82 (t, *J* = 8.4 Hz, 1H, N*H*), 4.66 (dd, *J* = 23.8, 7.8 Hz, 1H, C*H*), 4.16 - 4.07 (m, 2H, OEt-CH_2), 3.97 - 3.89 (m, 1H, OEt-CH_2), 3.72 - 3.64 (m, 1H, OEt-CH_2), 2.31 (s, 3H, CH_3), 1.29 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.12 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 145.1, 145.0, 138.0, 132.4, 129.5, 129.5, 129.1, 127.8, 127.8, 123.1, 115.1, 63.5, 63.5, 63.4, 63.3, 56.7, 55.2, 21.3, 16.6, 16.5, 16.4, 16.3 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.5 ppm.



Diethyl((4-chlorophenyl)((4-ethylphenyl)amino)methyl)phosphonate (**2p**). Yield: 241 mg, 87%. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.45 - 7.38 (m, 2H, Ar*H*), 7.29 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.93 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.50 (d, *J* = 8.5 Hz, 2H, Ar*H*), 4.78 - 4.68 (m, 2H, C*H* and N*H*), 4.20 - 4.05 (m, 2H, OEt-CH_2), 4.01 - 3.94 (m, 1H, OEt-CH_2), 3.86 - 3.69 (m, 1H, OEt-CH_2), 2.48 (q, *J* = 7.6 Hz, 2H, Et-CH_2), 1.27 (t, *J* = 7.1 Hz, 3H, Et-CH_3), 1.17 - 1.10 (m, 6H, OEt-CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 144.0, 143.8, 134.8, 134.8, 134.4, 133.6, 133.5, 129.2, 129.1, 128.7, 128.7, 128.5, 113.9, 63.4, 63.3, 63.2, 63.2, 56.5, 55.0, 27.8, 16.4, 16.3, 16.2, 16.2, 15.7 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 22.2 ppm. HRMS (ESI) m/z: [(M+Na)$^+$] calcd for $C_{19}H_{25}PClNO_3$ 404.1135, found 404.1131.



Diethyl ((4-chlorophenyl)((4-chlorophenyl)amino)methyl) phosphonate (**2q**).[16] Yield: 244 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 7.32 - 7.29 (m, 2H, Ar*H*), 7.25 - 7.14 (m, 2H, Ar*H*), 7.02 - 6.89 (m, 2H, Ar*H*), 6.47 - 6.36 (m, 2H, Ar*H*), 4.92 (t, *J* = 8.6 Hz, 1H, N*H*), 4.60 (dd, *J* = 24.4, 7.6 Hz, 1H, C*H*), 4.10 - 3.97 (m, 2H, OEt-CH_2), 3.95 - 3.83 (m, 1H, OEt-CH_2), 3.77 - 3.60 (m, 1H, OEt-CH_2), 1.20 (t, *J* = 7.1 Hz, 3H, OEt-CH_3), 1.07 (t, *J* = 7.1 Hz, 3H, OEt-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ_C 144.8, 144.7, 134.2, 134.2, 133.9, 133.9, 129.2, 129.1, 129.1, 128.9, 128.9, 123.3, 115.0, 63.5, 63.5, 63.5, 63.5, 56.4, 54.9, 16.5, 16.4, 16.3, 16.3 ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 21.7 ppm.

NMR spectra of α- amino phosphine oxide:

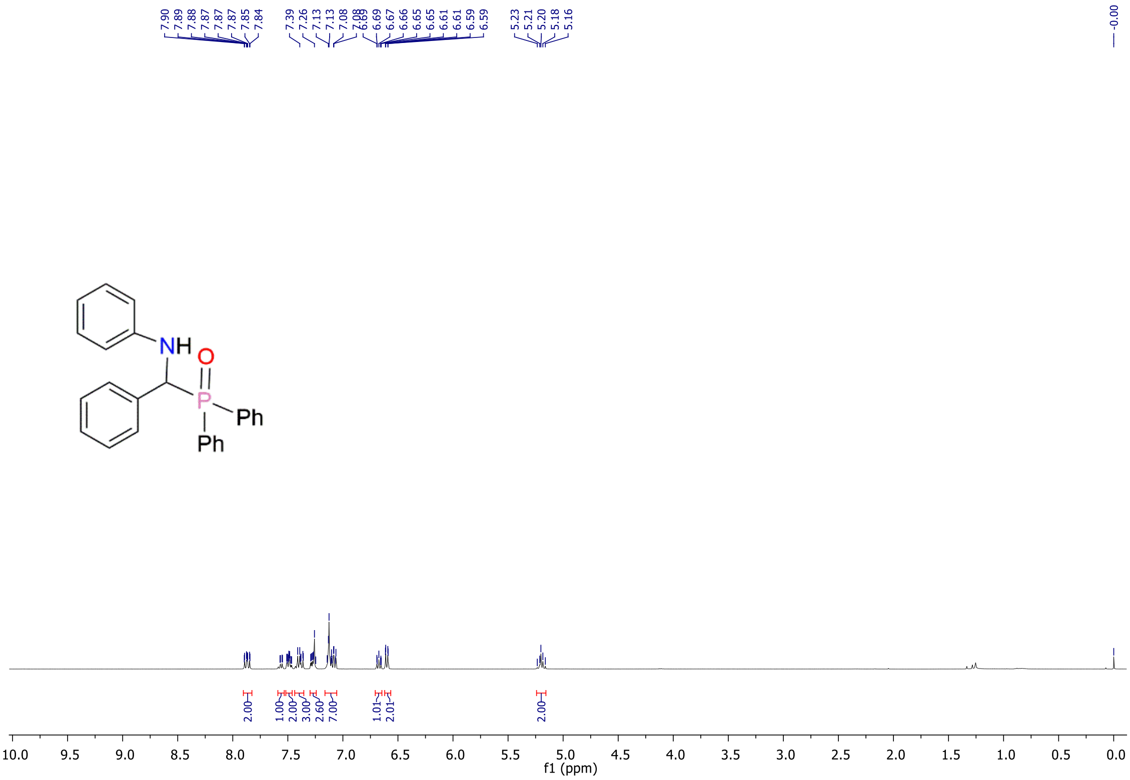


Fig S1. ^{1}H NMR spectra of **1a** ($CDCl_3$, 400MHz).

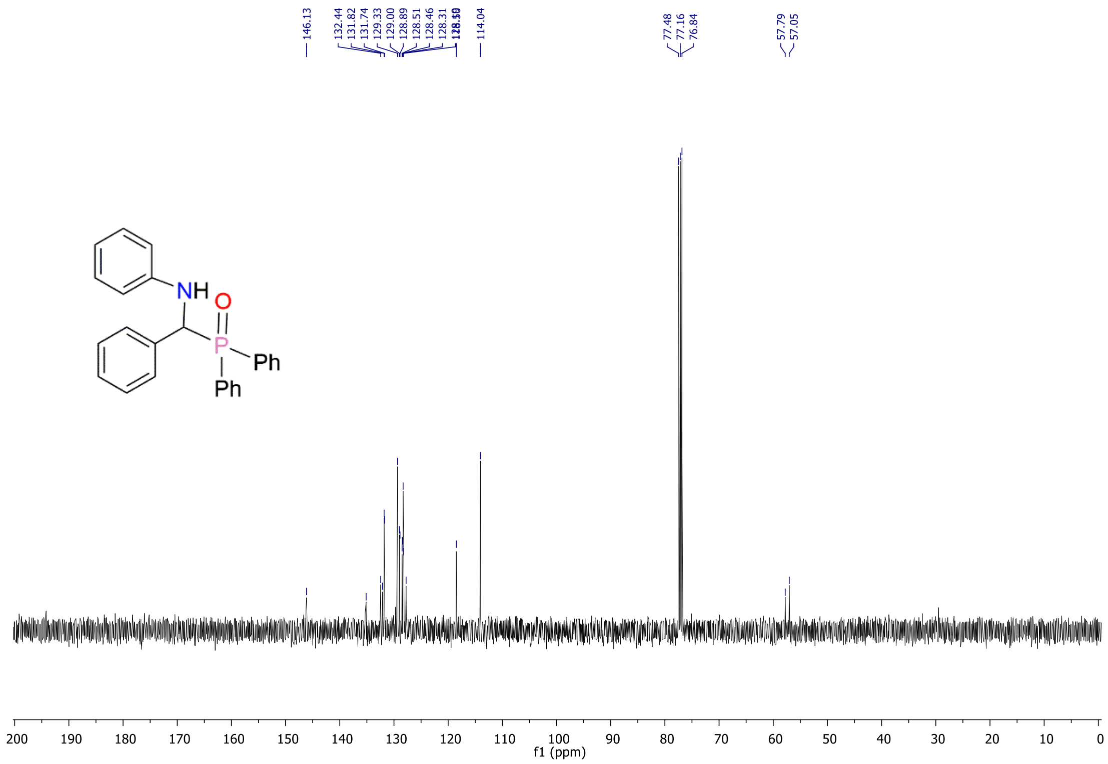


Fig S2. $^{13}C\{^1H\}$ NMR spectra of **1a** ($CDCl_3$, 100 MHz).

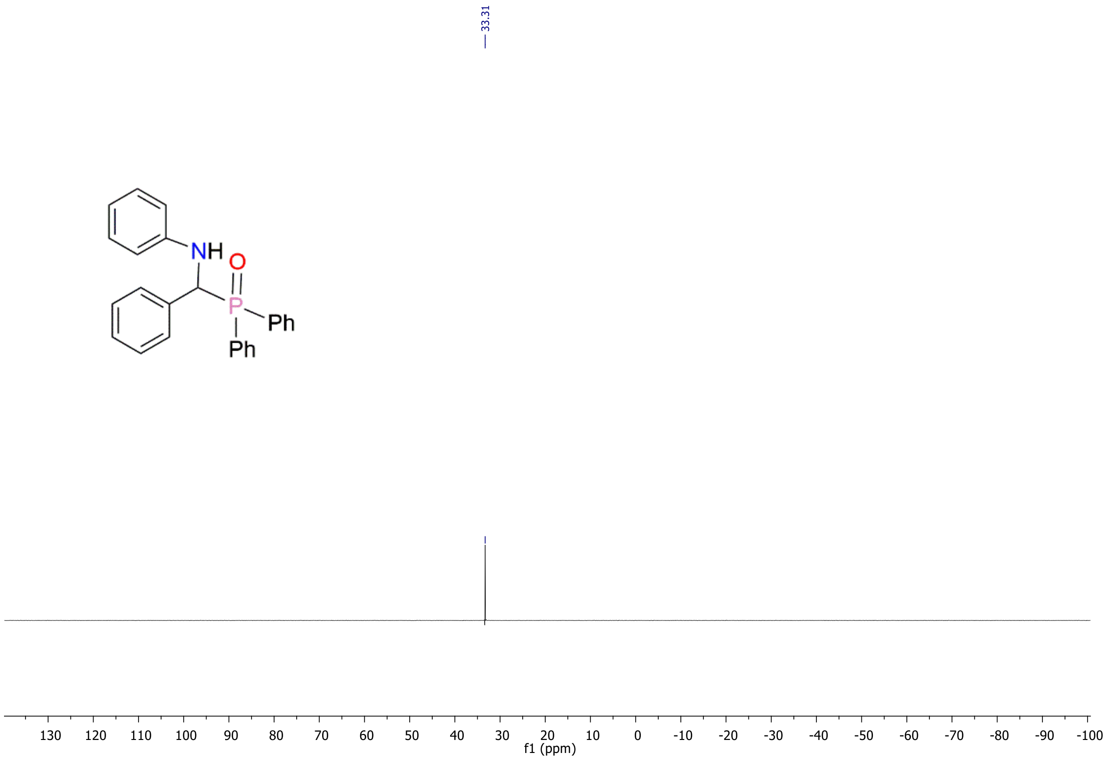


Fig S3. $^{31}P\{^{1}H\}$ NMR spectra of **1a** ($CDCl_3$, 243 MHz).

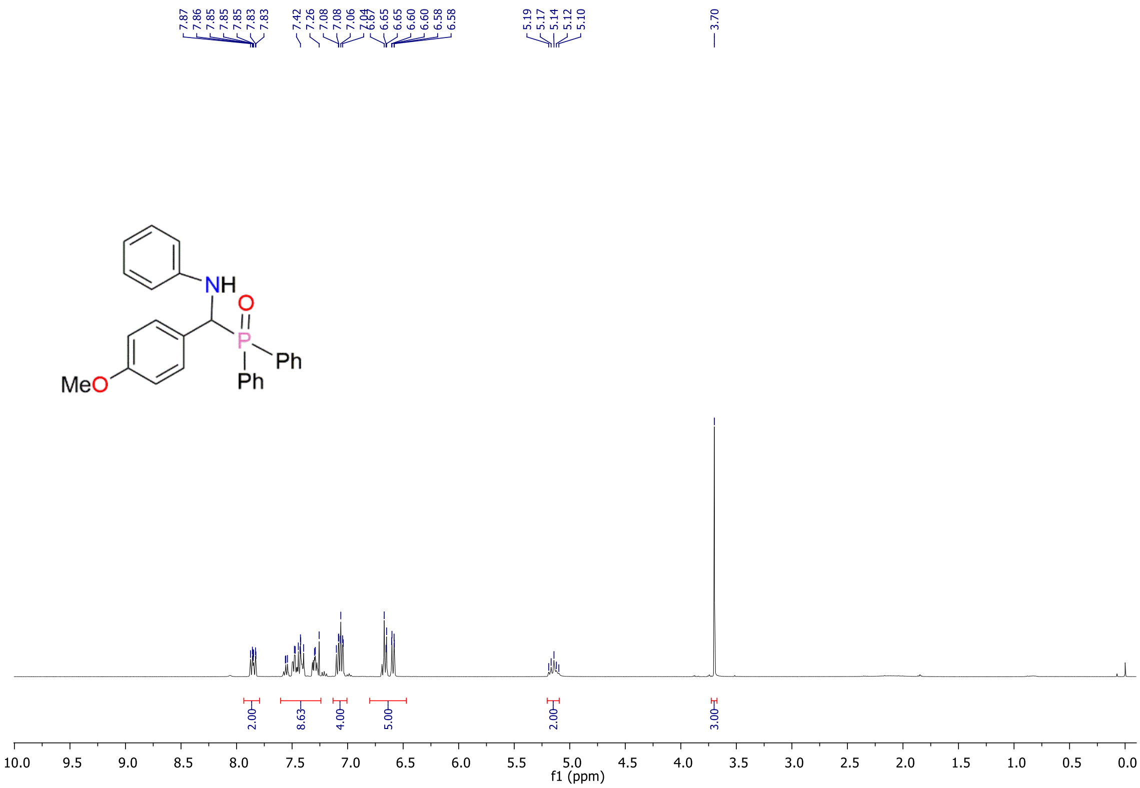


Fig S4. ^{1}H NMR spectra of **1b** ($CDCl_3$, 400 MHz).

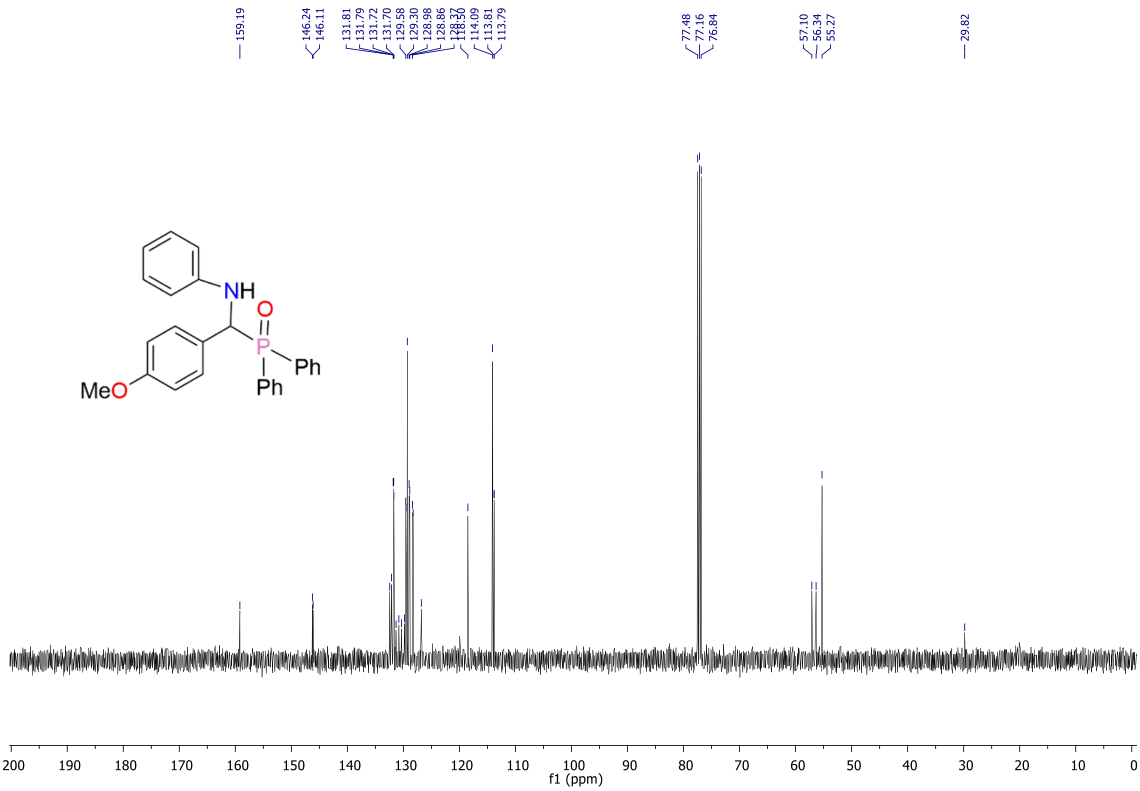


Fig S5. $^{13}C\{^1H\}$ NMR spectra of **1b** ($CDCl_3$, 100 MHz).

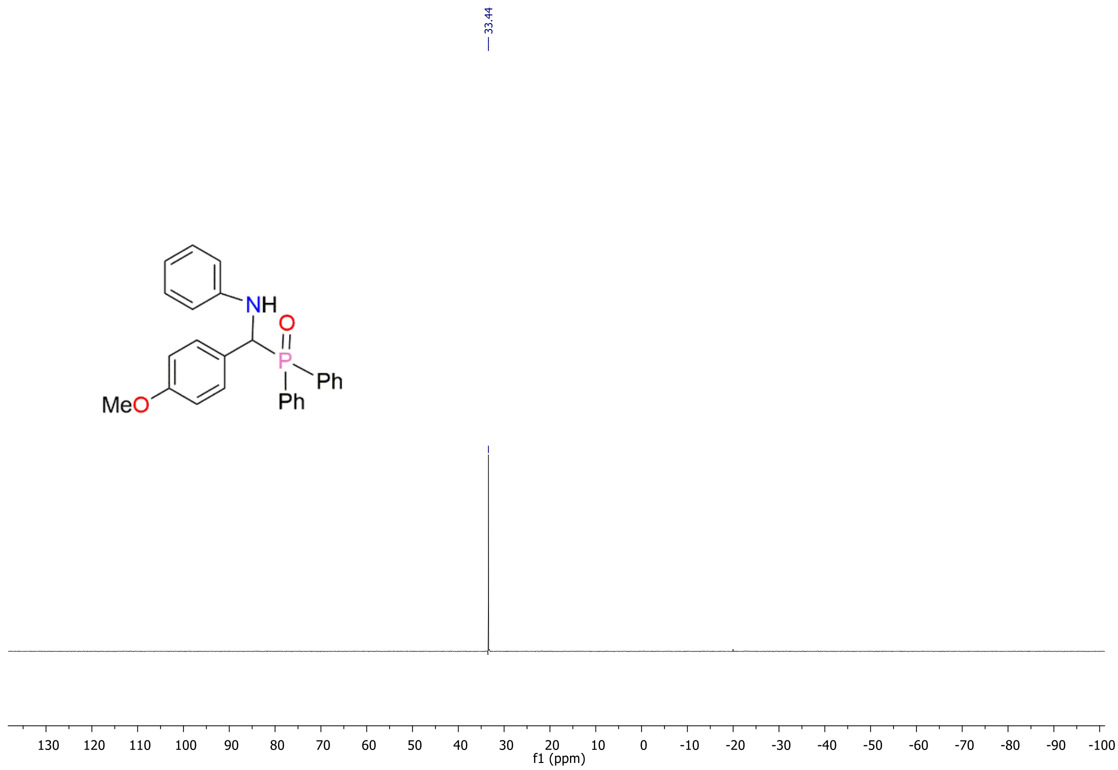


Fig S6. $^{31}P\{^1H\}$ NMR spectra of **1b** ($CDCl_3$, 243 MHz).

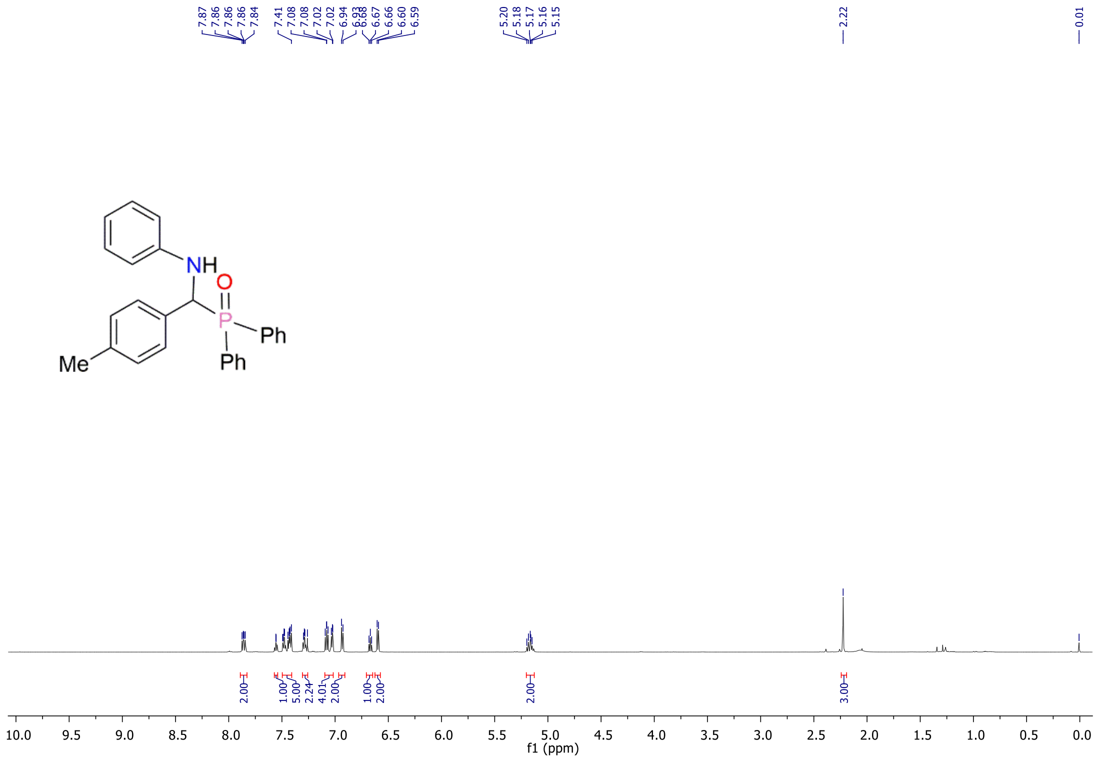


Fig S7. ^{1}H NMR spectra of **1c** ($CDCl_3$, 600 MHz).

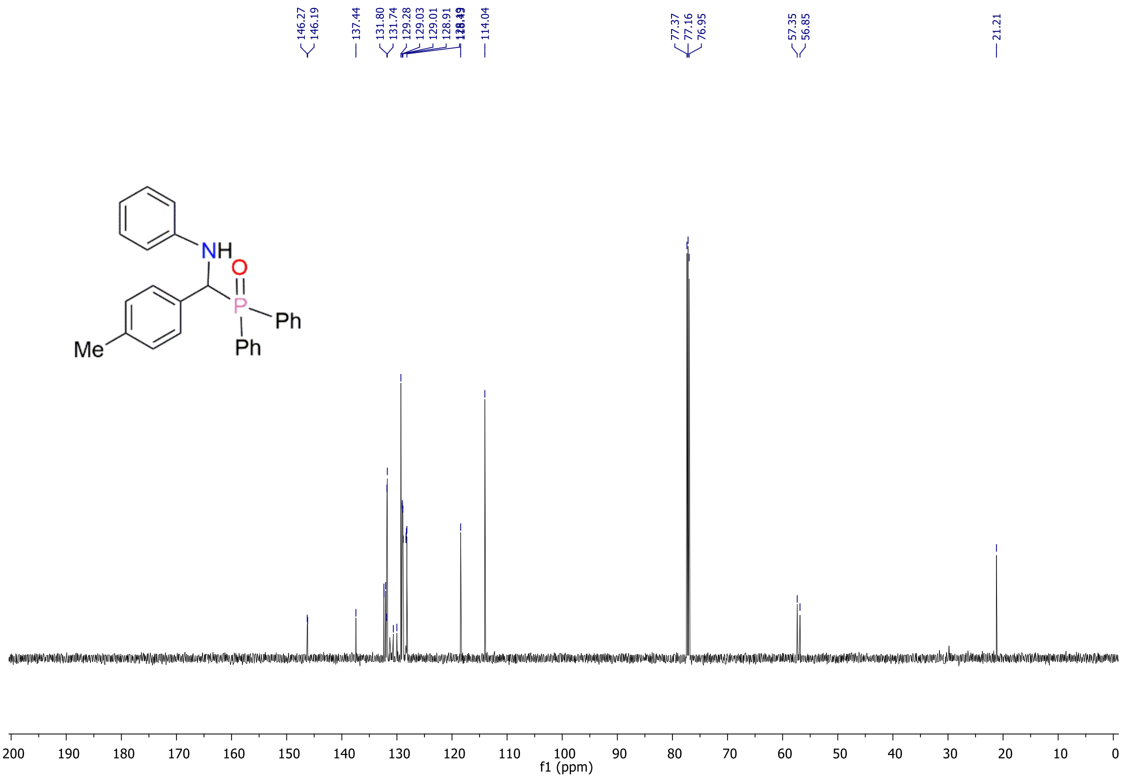


Fig S8. $^{13}C\{^{1}H\}$ NMR spectra of **1c** ($CDCl_3$, 150 MHz).

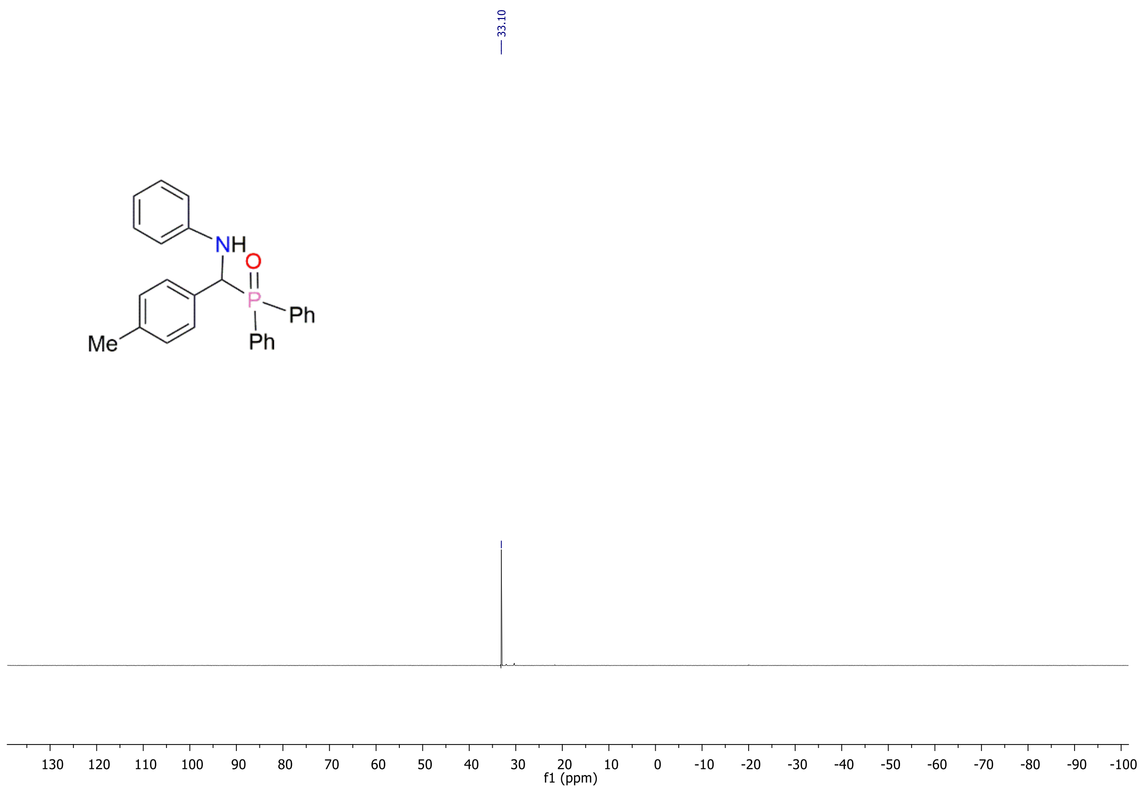


Fig S9. $^{31}P\{^1H\}$ NMR spectra of **1c** ($CDCl_3$, 243 MHz).

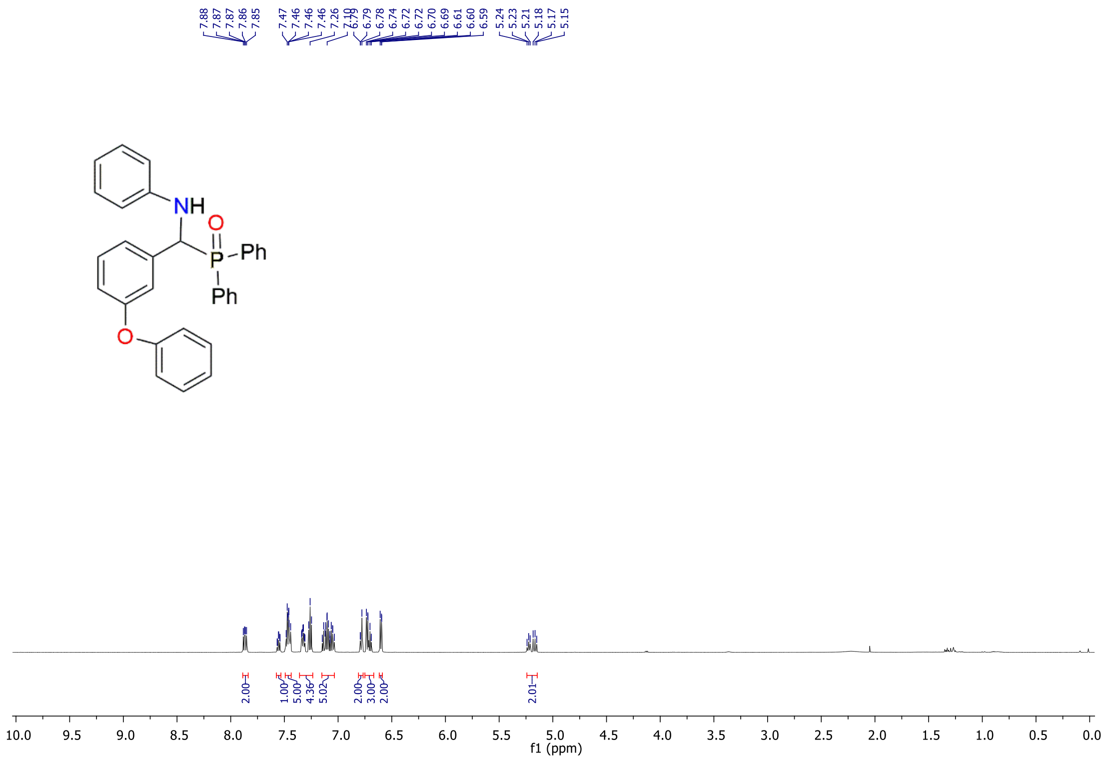


Fig S10. ^1H NMR spectra of **1d** ($CDCl_3$, 600 MHz).

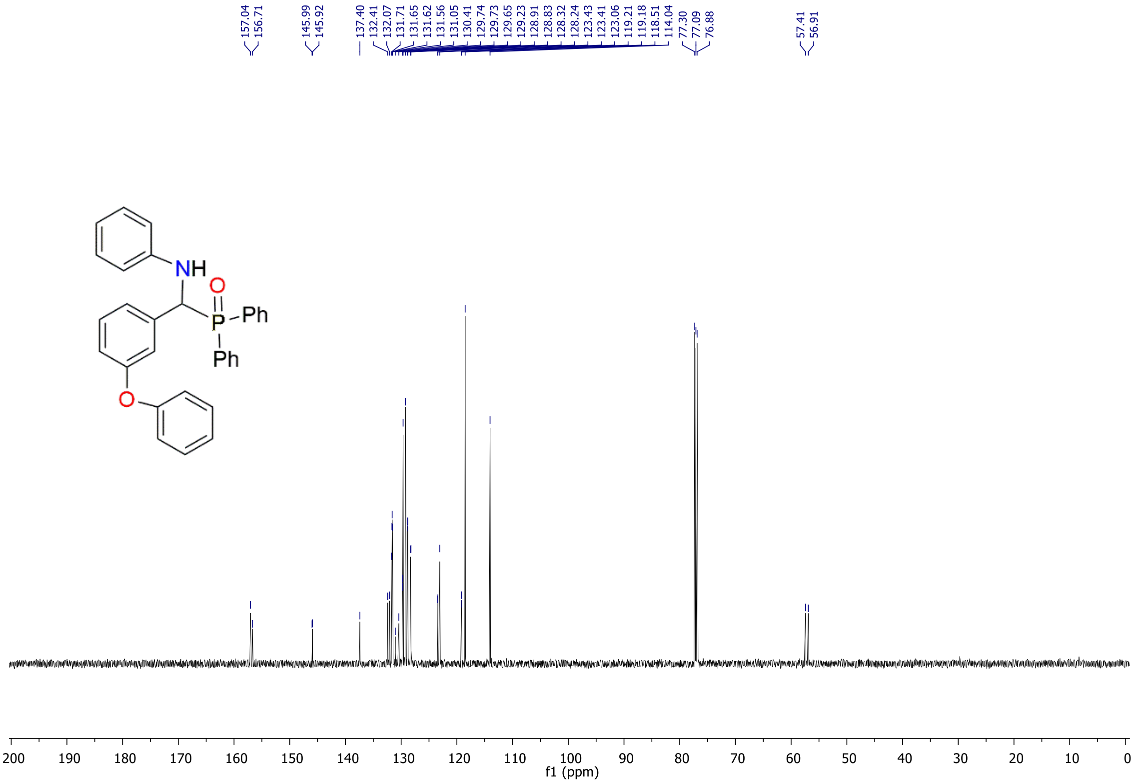


Fig S11. $^{13}C\{^{1}H\}$ NMR spectra of **1d** ($CDCl_3$, 150 MHz).

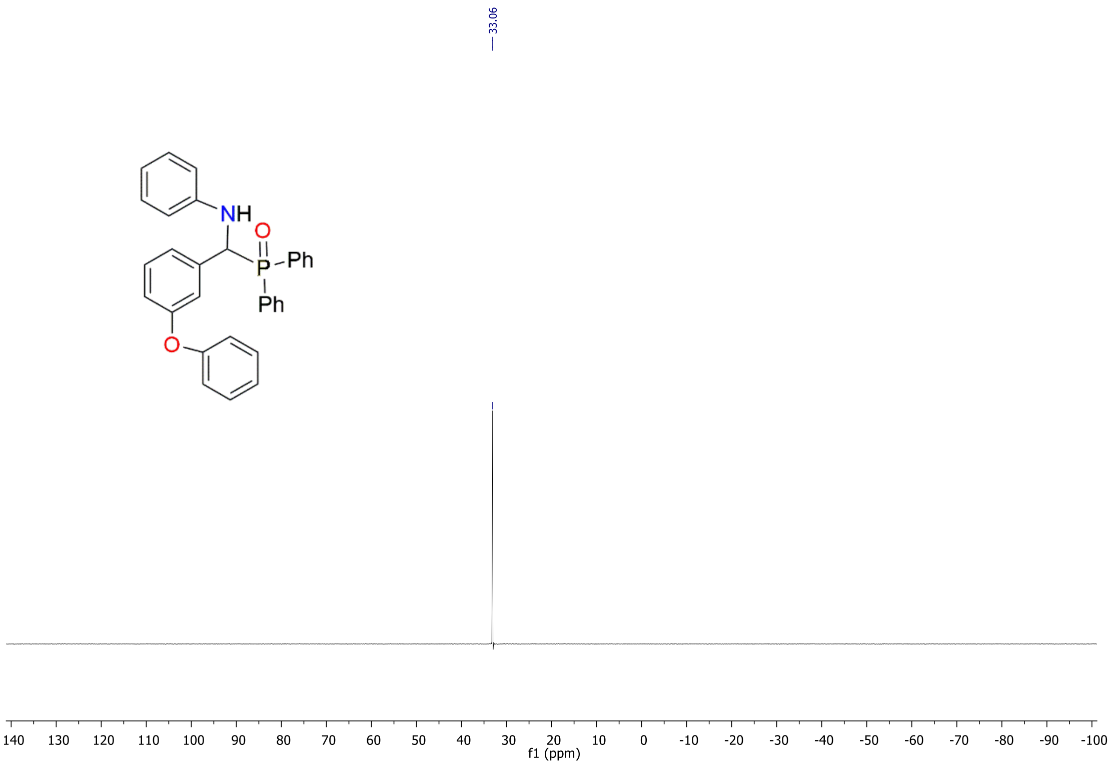


Fig S12. $^{31}P\{^{1}H\}$ NMR spectra of **1d** ($CDCl_3$, 243 MHz).

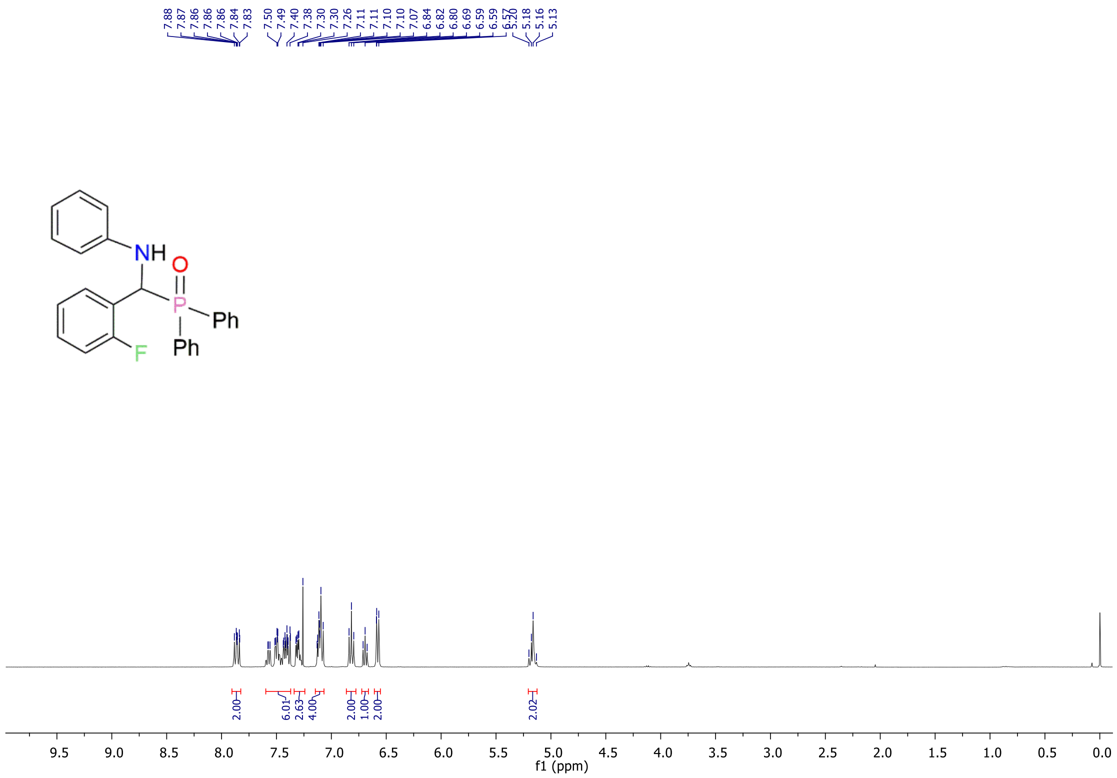


Fig S13. ^{1}H NMR spectra of **1e** ($CDCl_3$, 400 MHz).

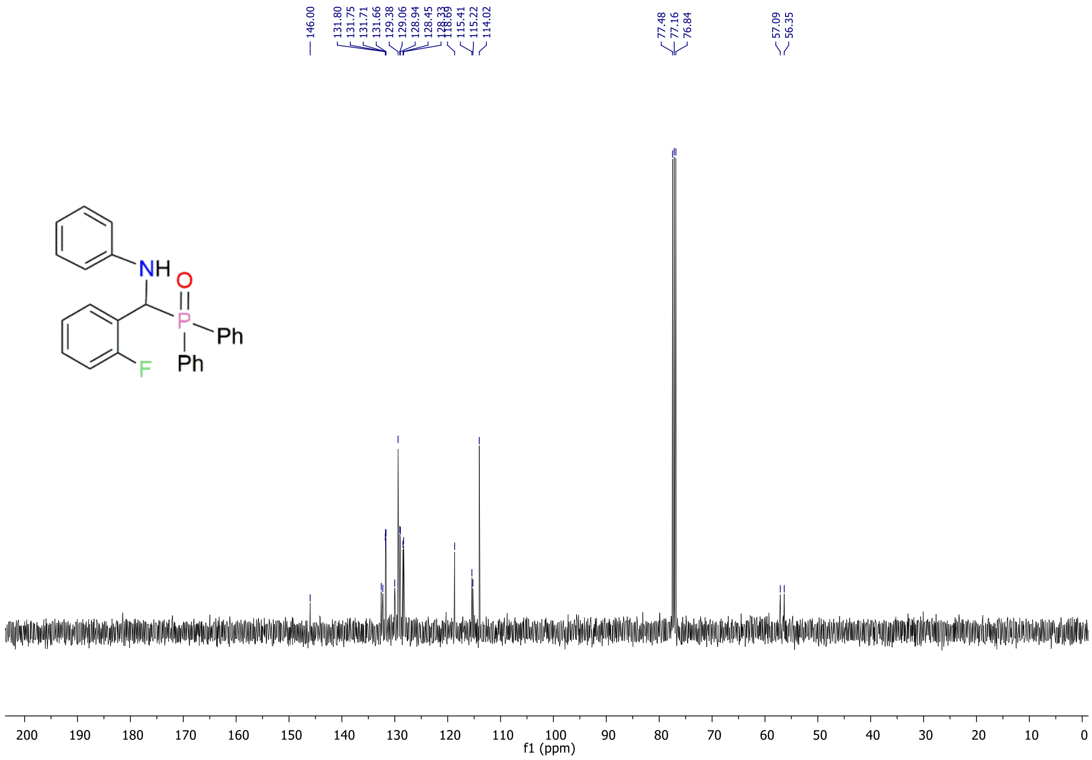


Fig S14. ^{13}C{^{1}H} NMR spectra of **1e** ($CDCl_3$, 100MHz).

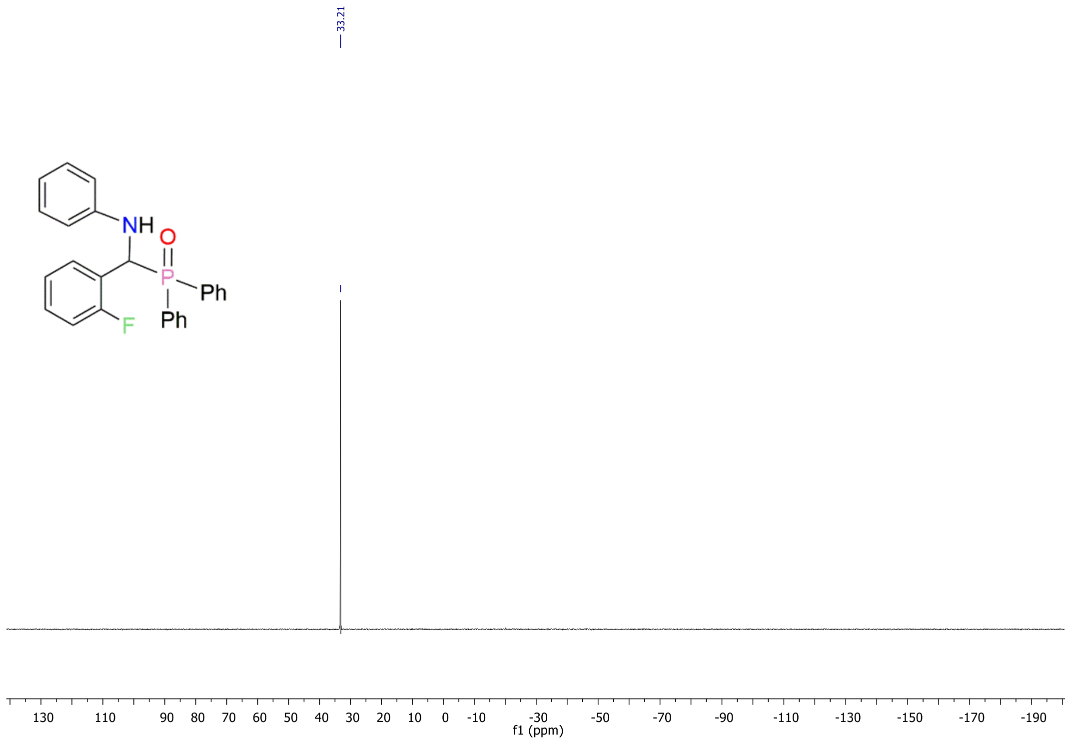


Fig S15. $^{31}P\{^{1}H\}$ NMR spectra of **1e** ($CDCl_3$, 243 MHz).

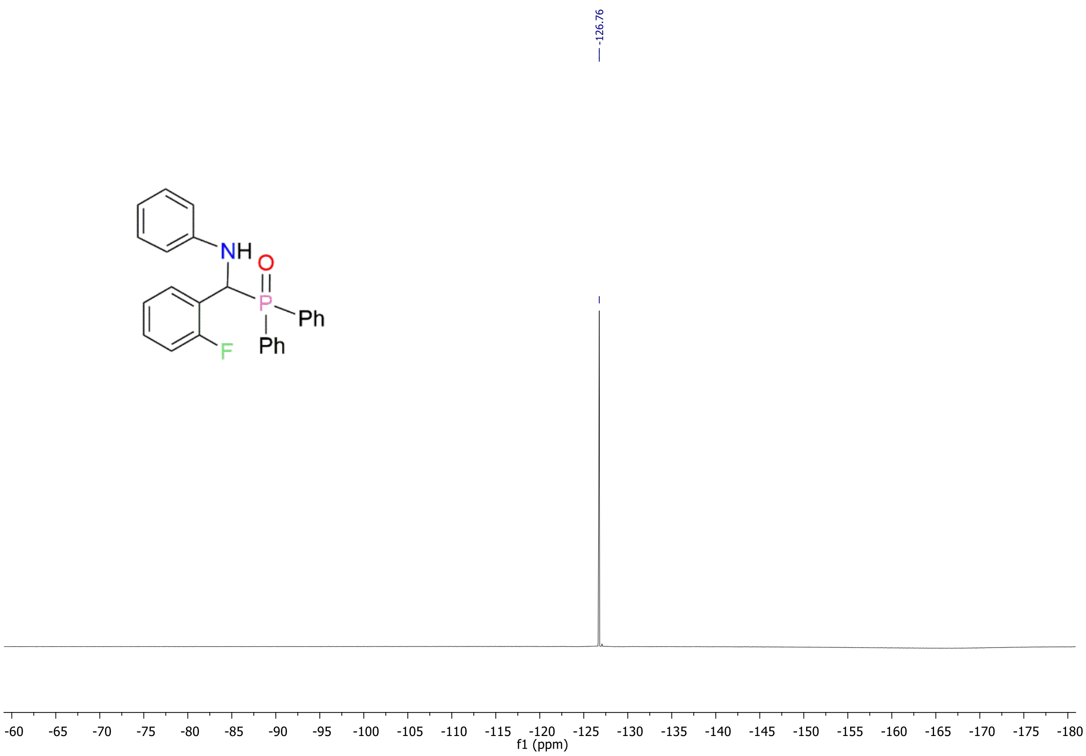


Fig S16. $^{19}F\{^{1}H\}$ NMR spectra of **1e** ($CDCl_3$, 565 MHz).

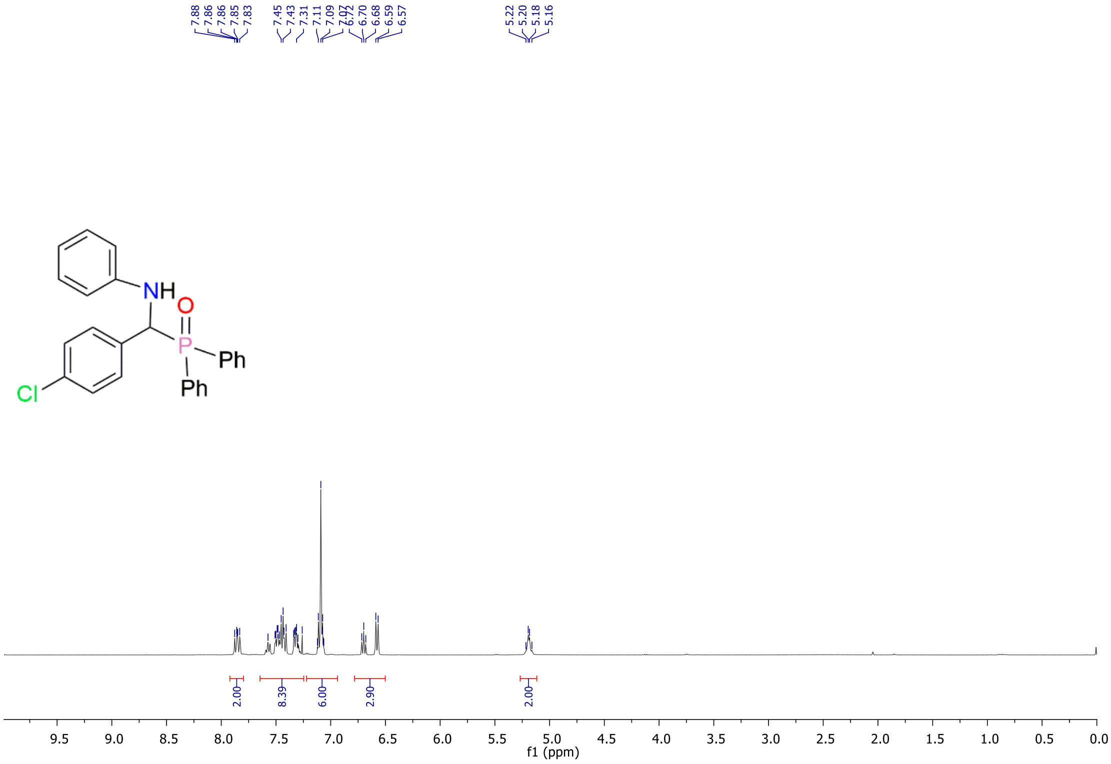


Fig S17. ^{1}H NMR spectra of **1f** ($CDCl_3$, 400MHz).

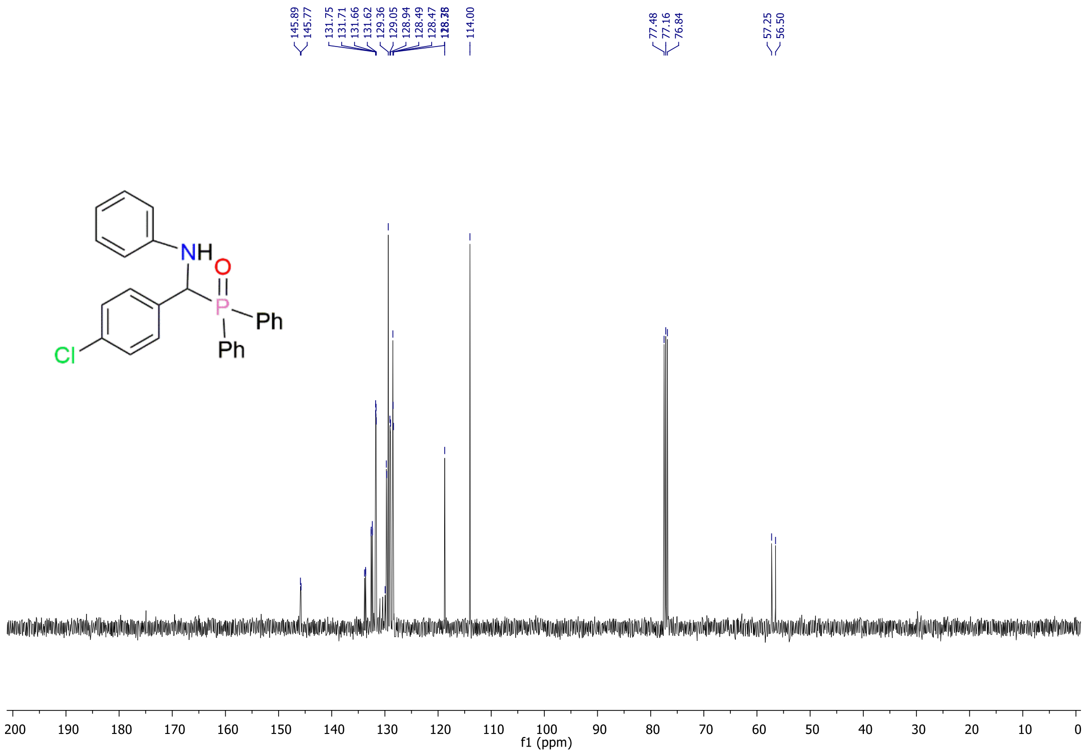


Fig S18. $^{13}C\{^{1}H\}$ NMR spectra of **1f** ($CDCl_3$, 100 MHz).

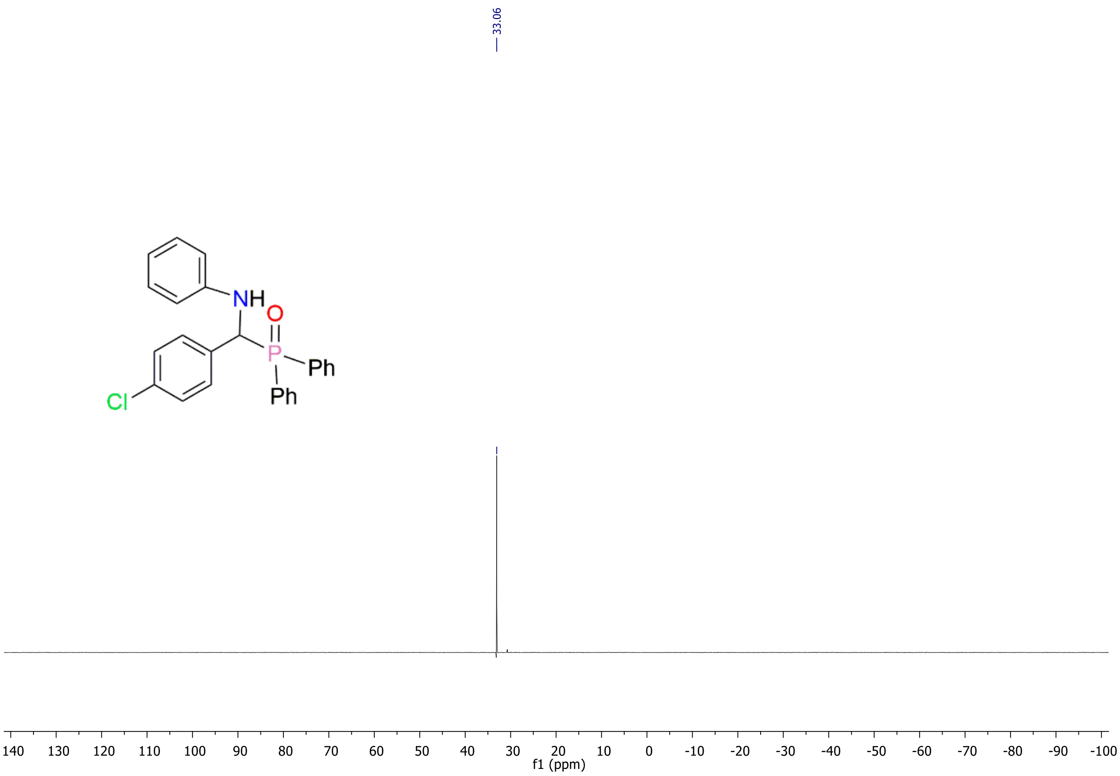


Fig S19. $^{31}P\{^{1}H\}$ NMR spectra of **1f** ($CDCl_3$, 243 MHz).

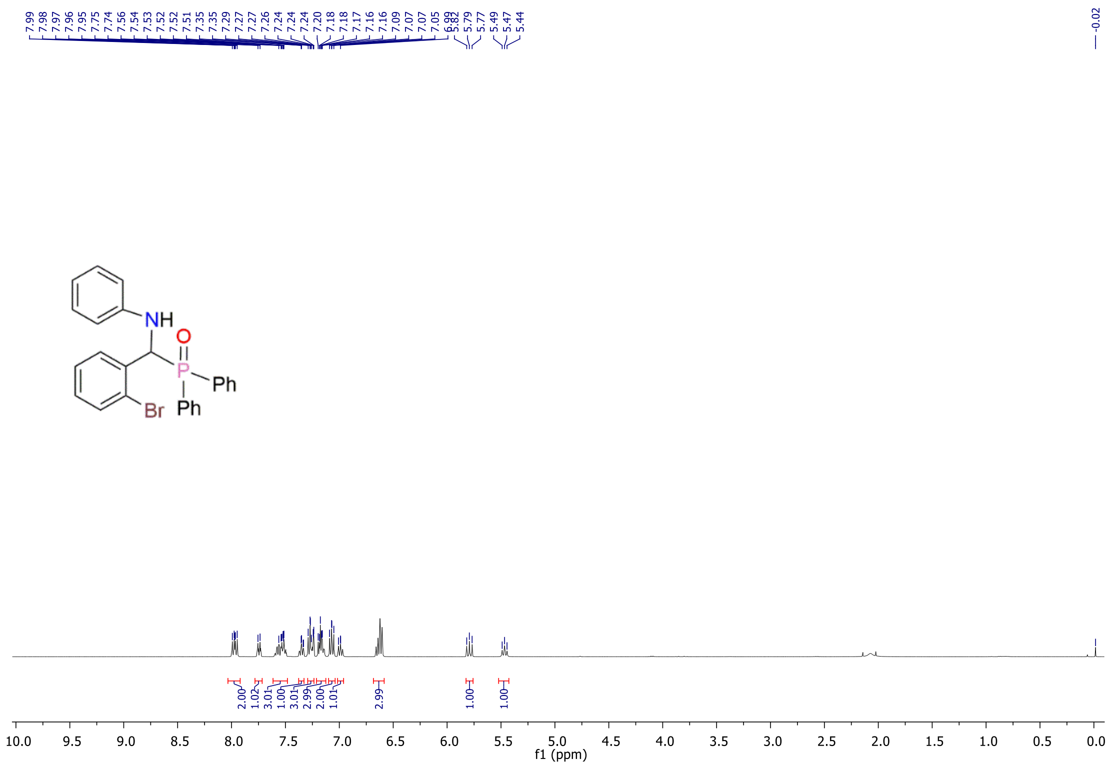


Fig S20. ^{1}H NMR spectra of **1g** ($CDCl_3$, 400 MHz).

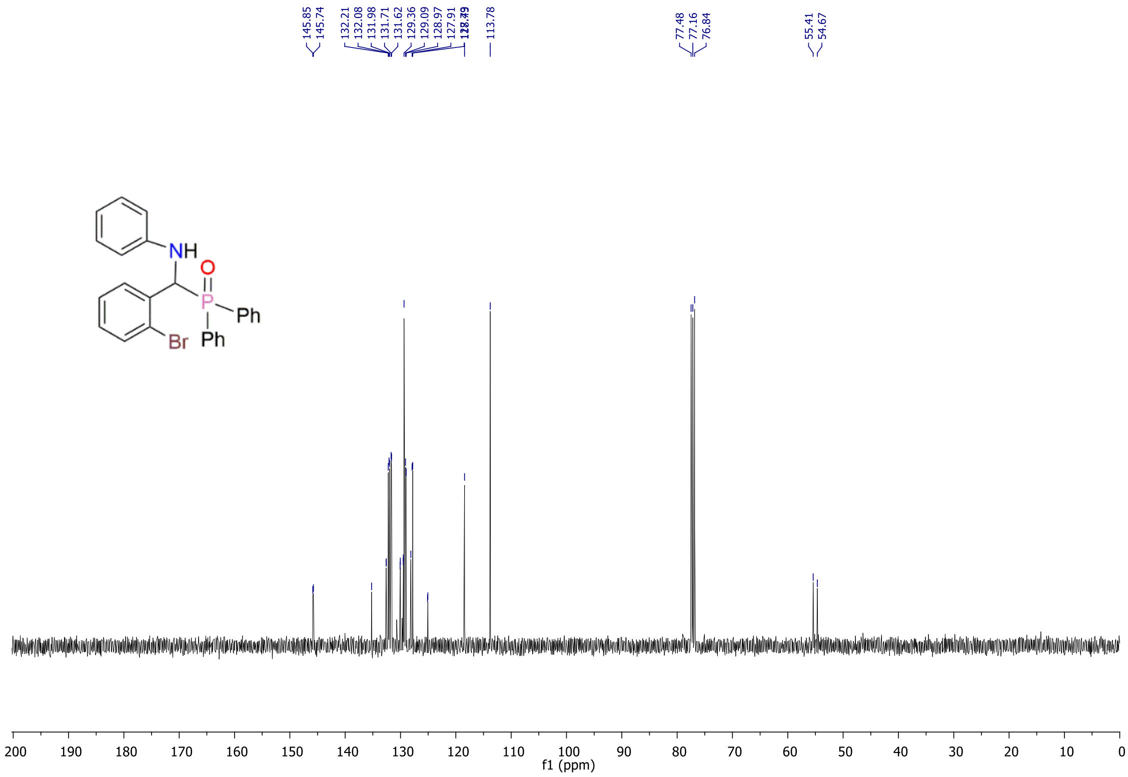


Fig S21. $^{13}C\{^{1}H\}$ NMR spectra of **1g** ($CDCl_3$, 100MHz).

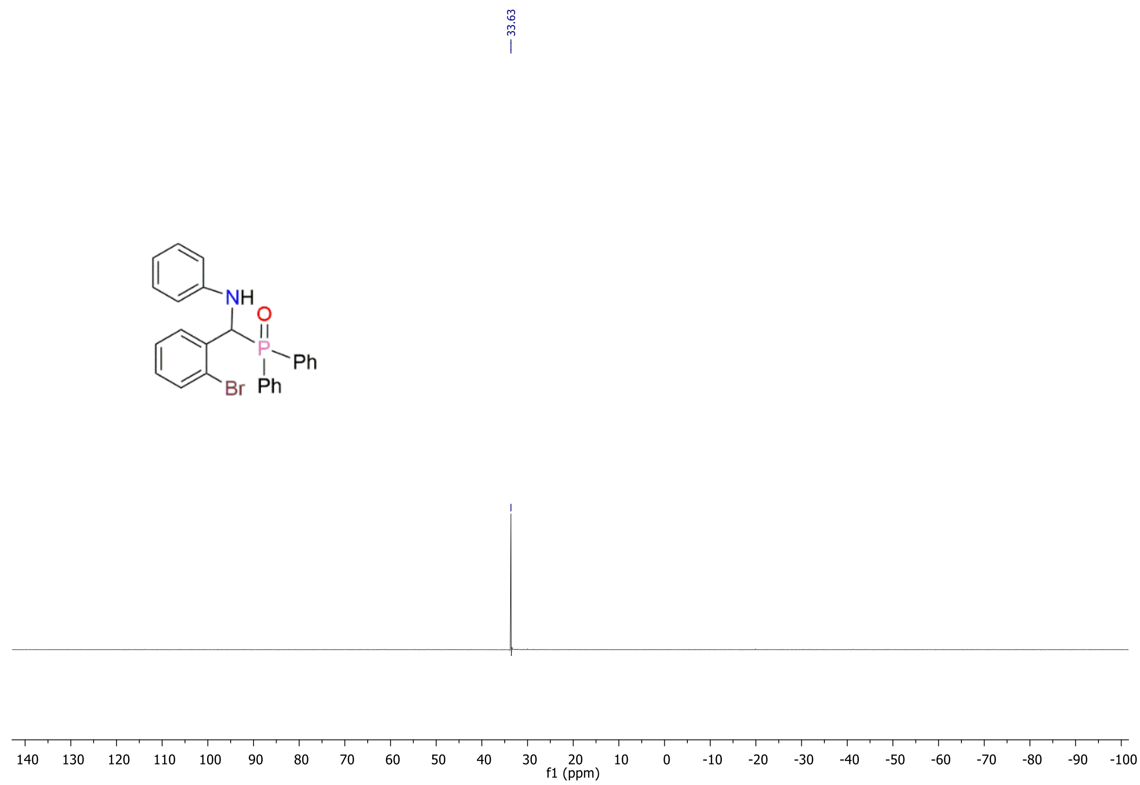


Fig S22. $^{31}P\{^{1}H\}$ NMR spectra of **1g** ($CDCl_3$, 243 MHz).

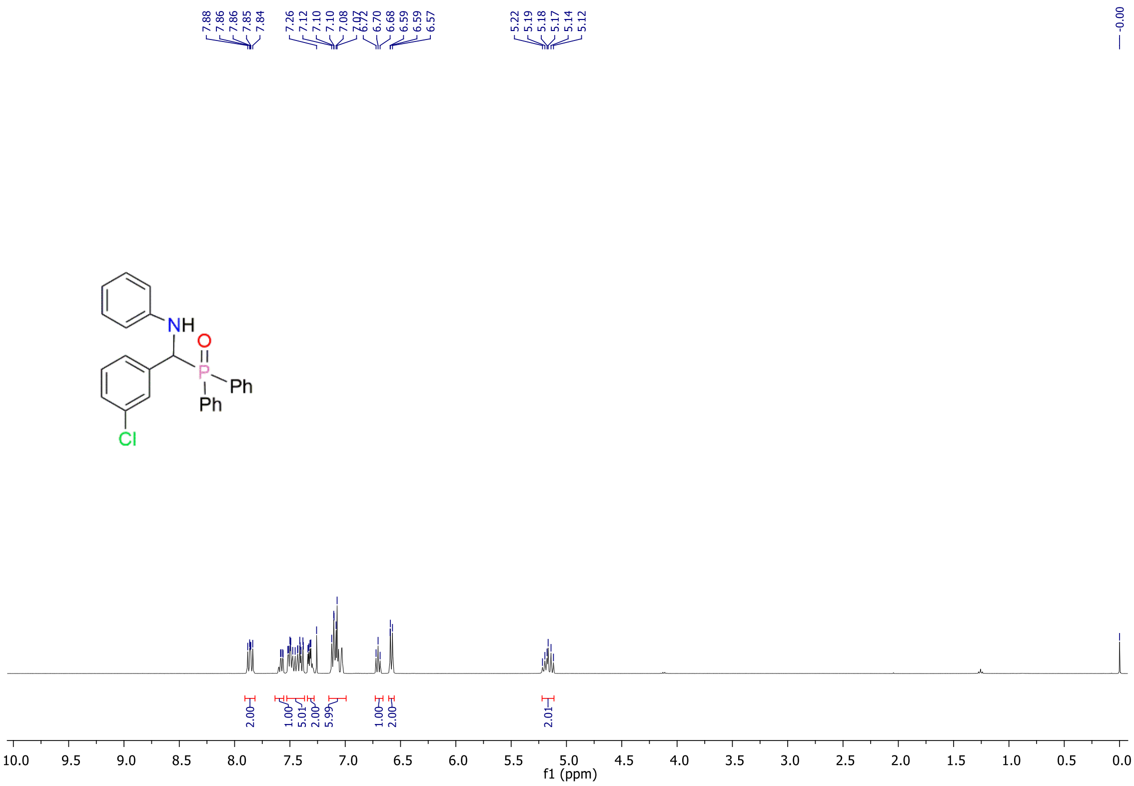


Fig S23. ^{1}H NMR spectra of **1h** ($CDCl_3$, 400 MHz).

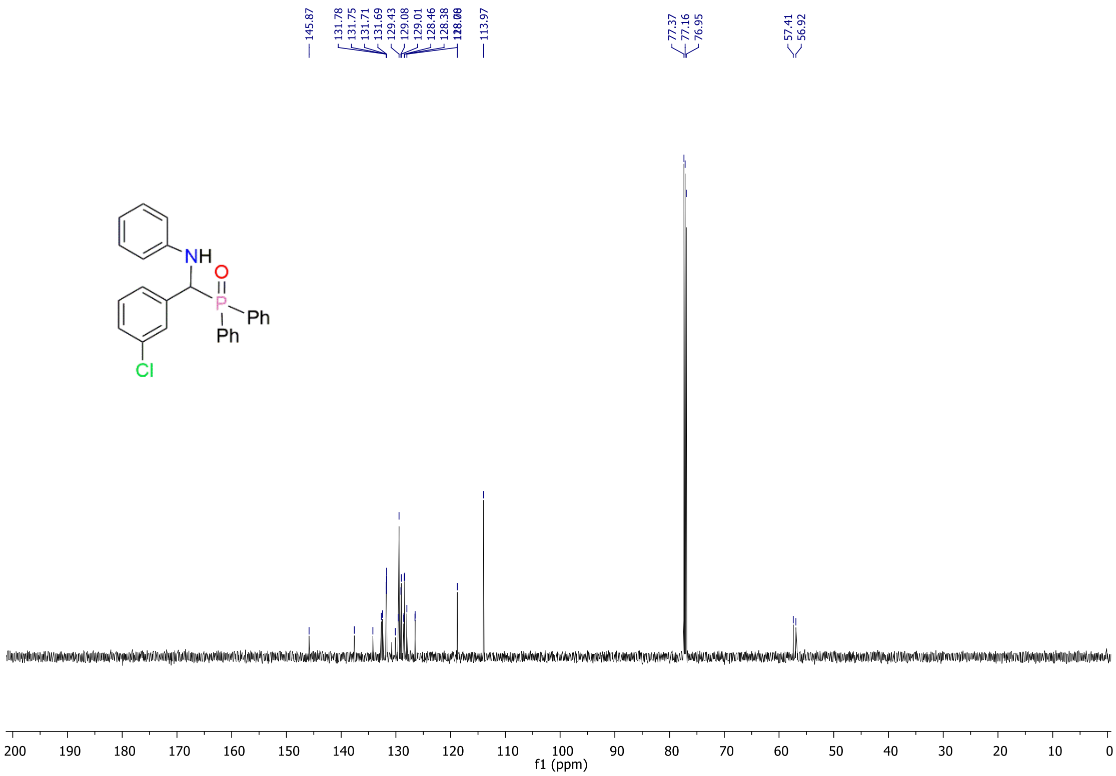


Fig S24. $^{13}C\{^{1}H\}$ NMR spectra of **1h** ($CDCl_3$, 150 MHz).

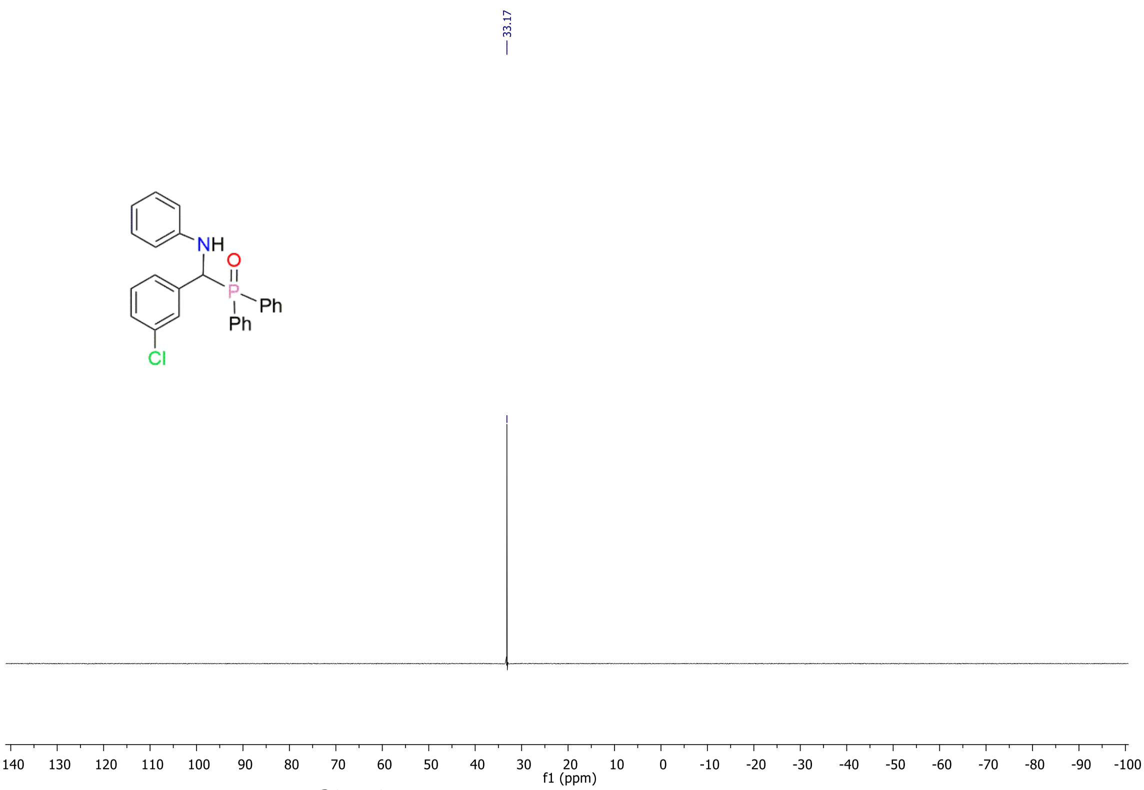


Fig S25. $^{31}P\{^1H\}$ NMR spectra of **1h** ($CDCl_3$, 243 MHz).

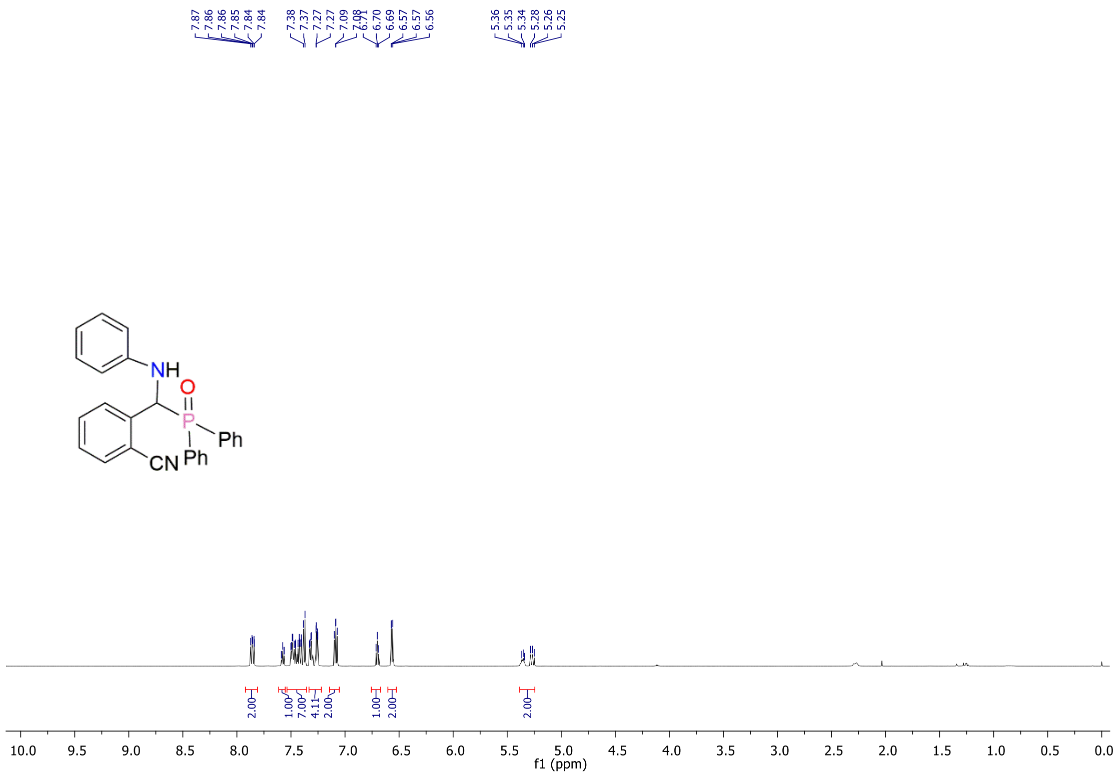


Fig S26. ^1H NMR spectra of **1i** ($CDCl_3$, 600MHz).

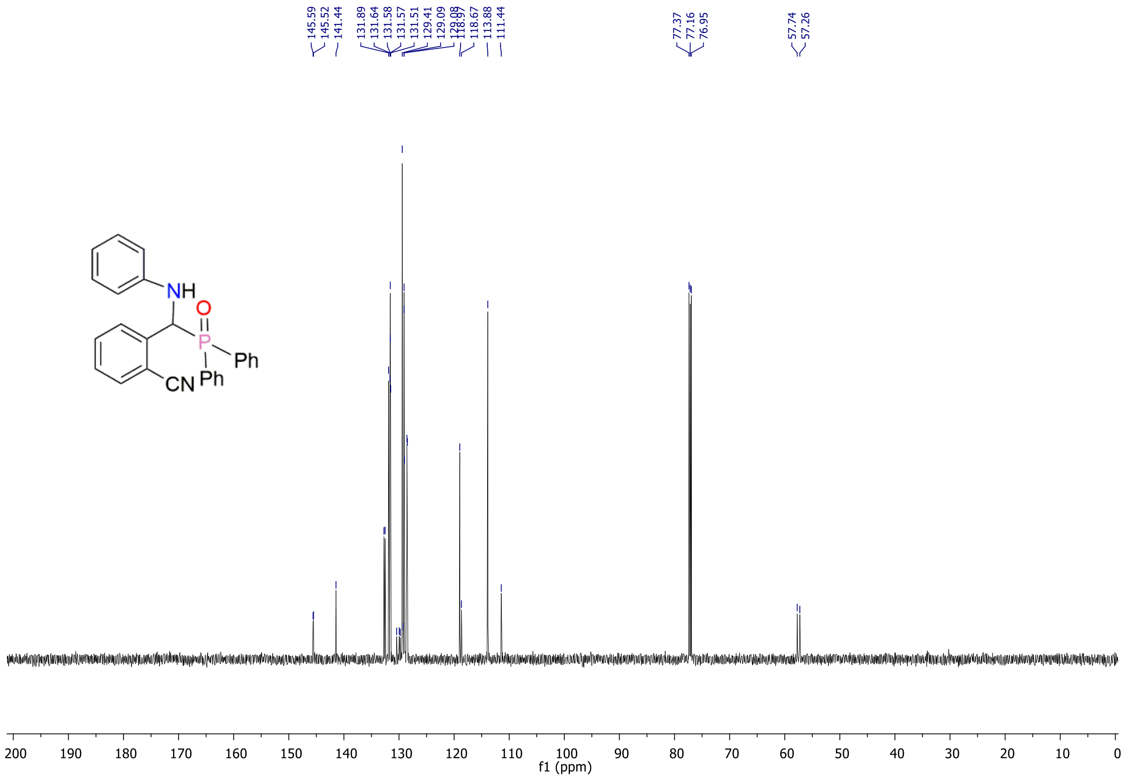


Fig S27. $^{13}C\{^{1}H\}$ NMR spectra of **1i** ($CDCl_3$, 150 MHz).

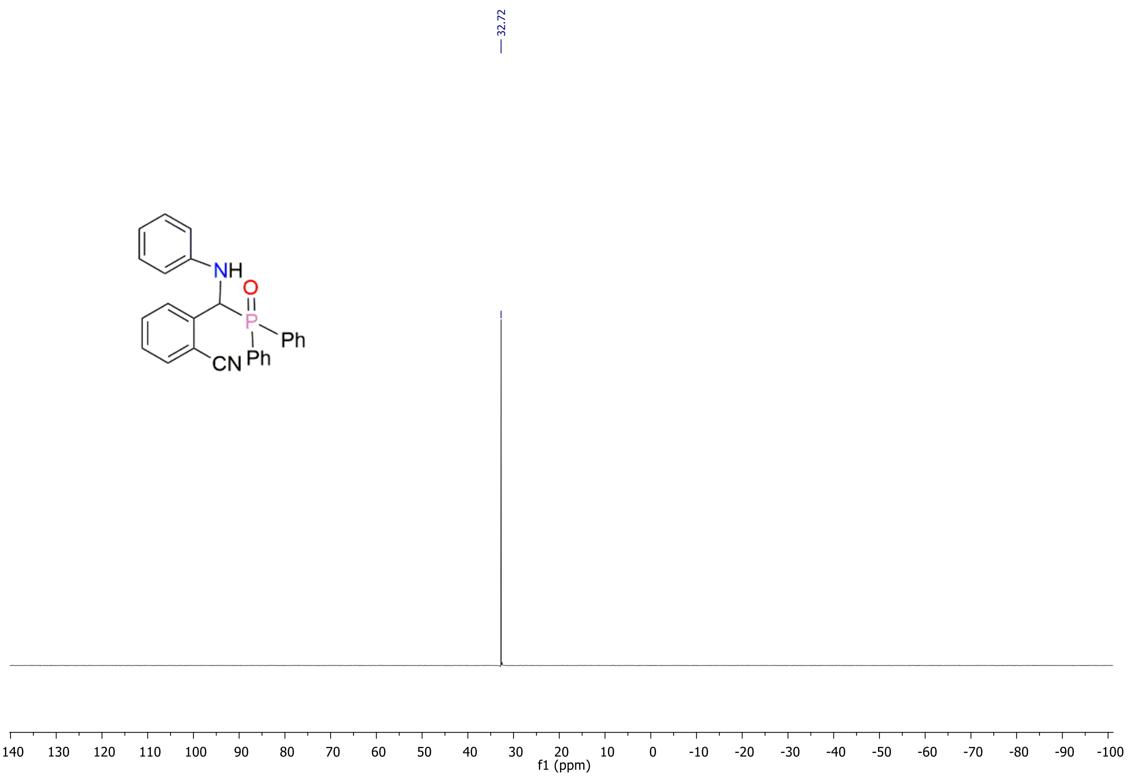


Fig S28. $^{31}P\{^{1}H\}$ NMR spectra of **1i** ($CDCl_3$, 243 MHz).

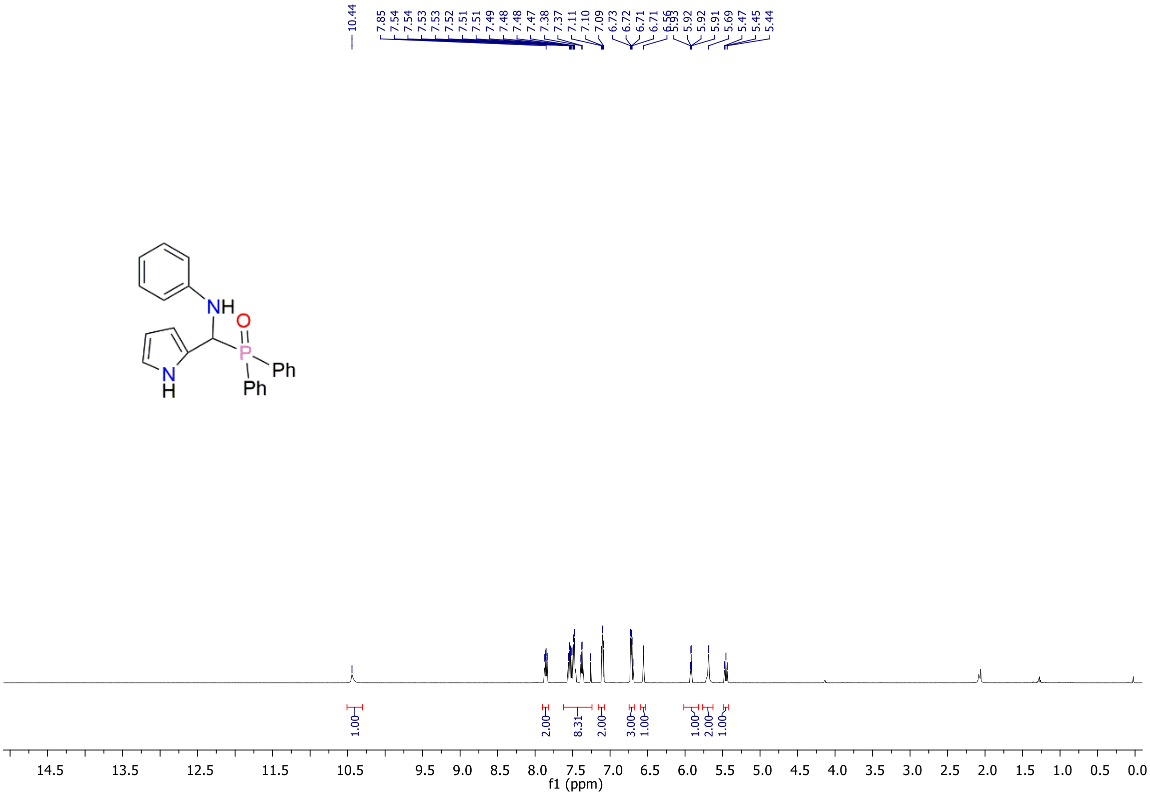


Fig S29. ^{1}H NMR spectra of **1j** ($CDCl_3$, 600 MHz).

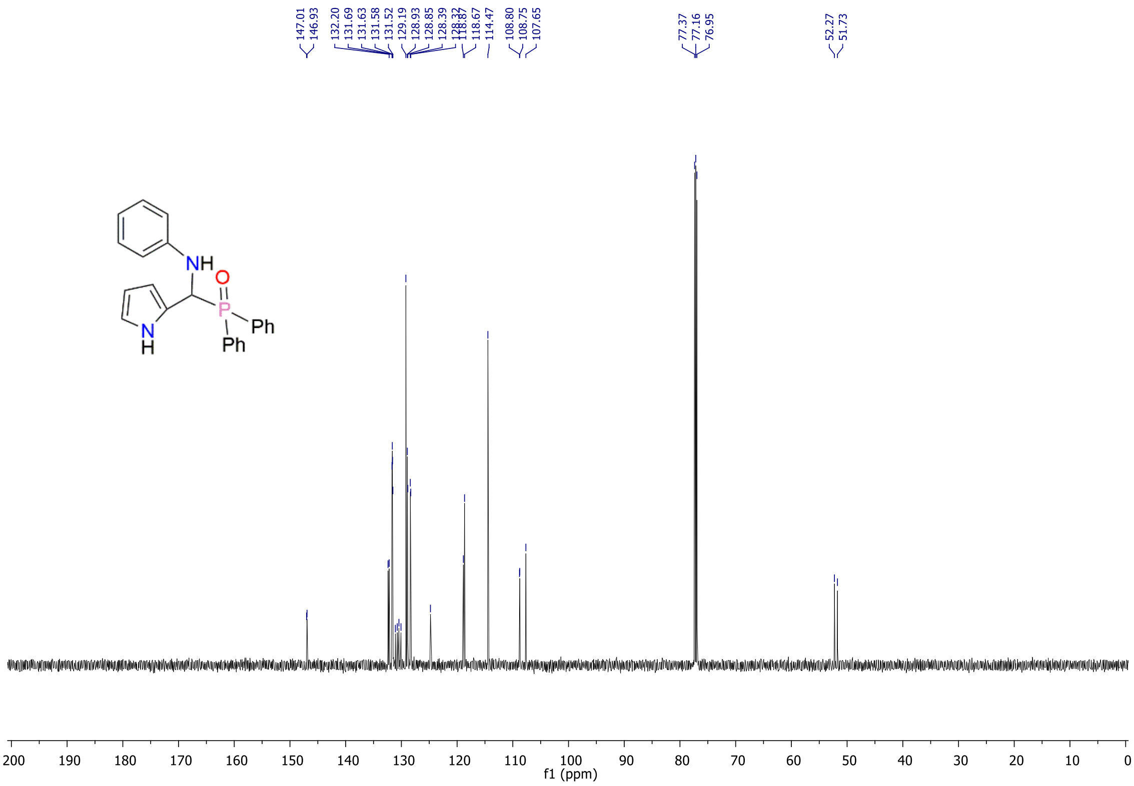


Fig S30. $^{13}C\{^{1}H\}$ NMR spectra of **1j** ($CDCl_3$, 150 MHz).

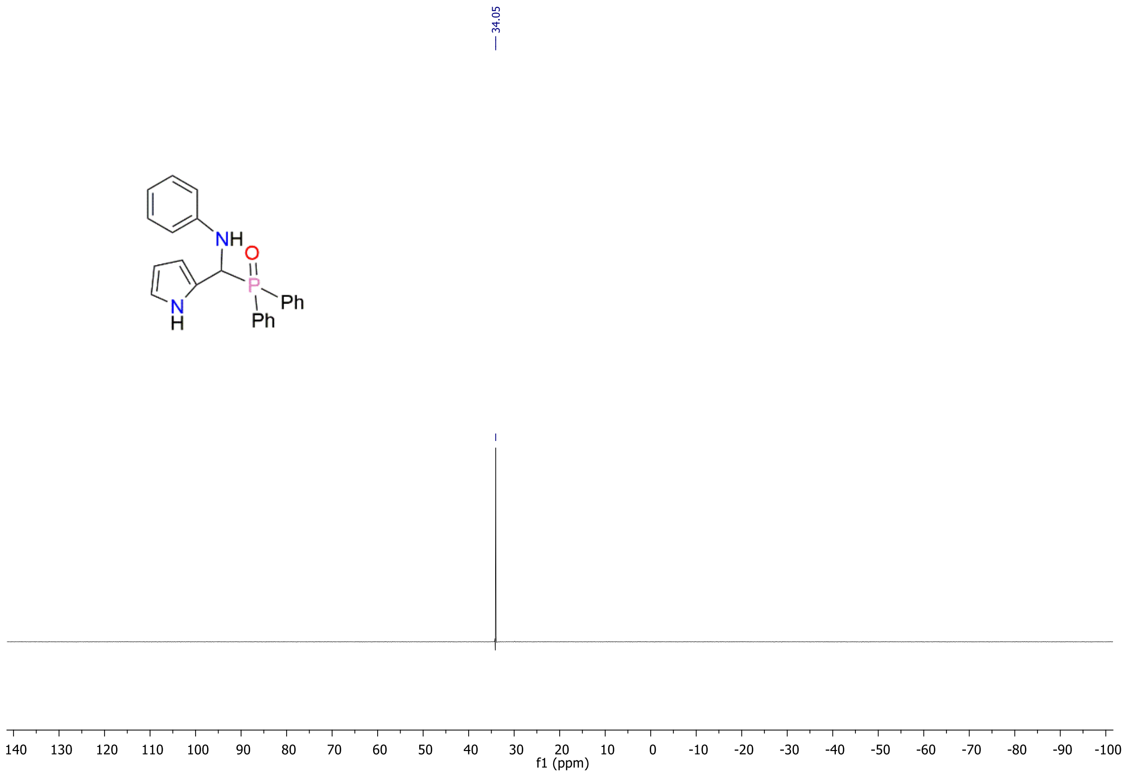


Fig S31. $^{31}P\{^{1}H\}$ NMR spectra of **1j** ($CDCl_3$, 243 MHz).

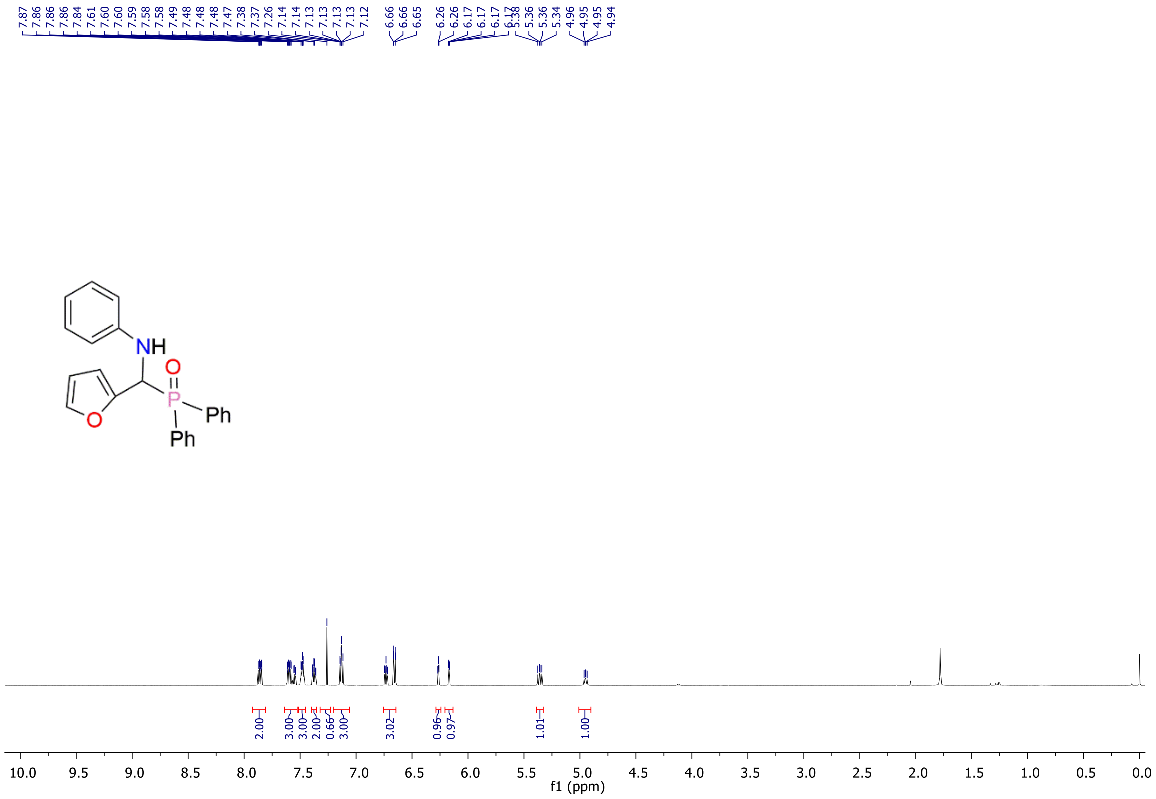


Fig S32. ^{1}H NMR spectra of **1k** ($CDCl_3$, 600 MHz).

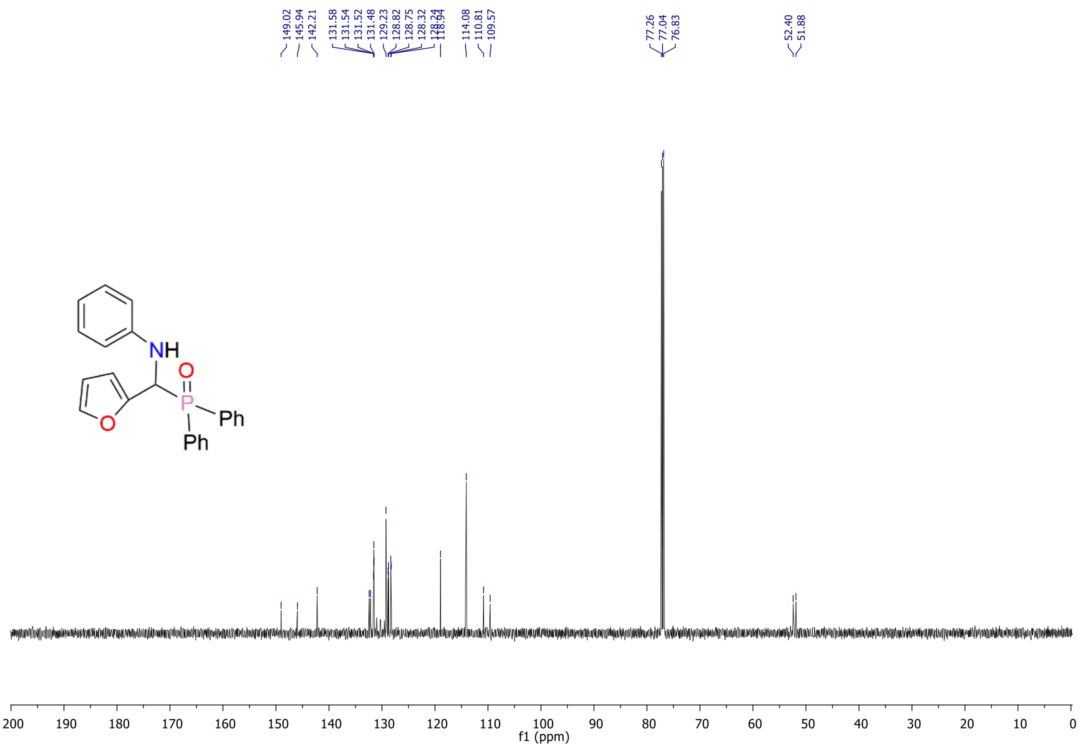


Fig S33. $^{13}C\{^{1}H\}$ NMR spectra of **1k** ($CDCl_3$, 150 MHz).

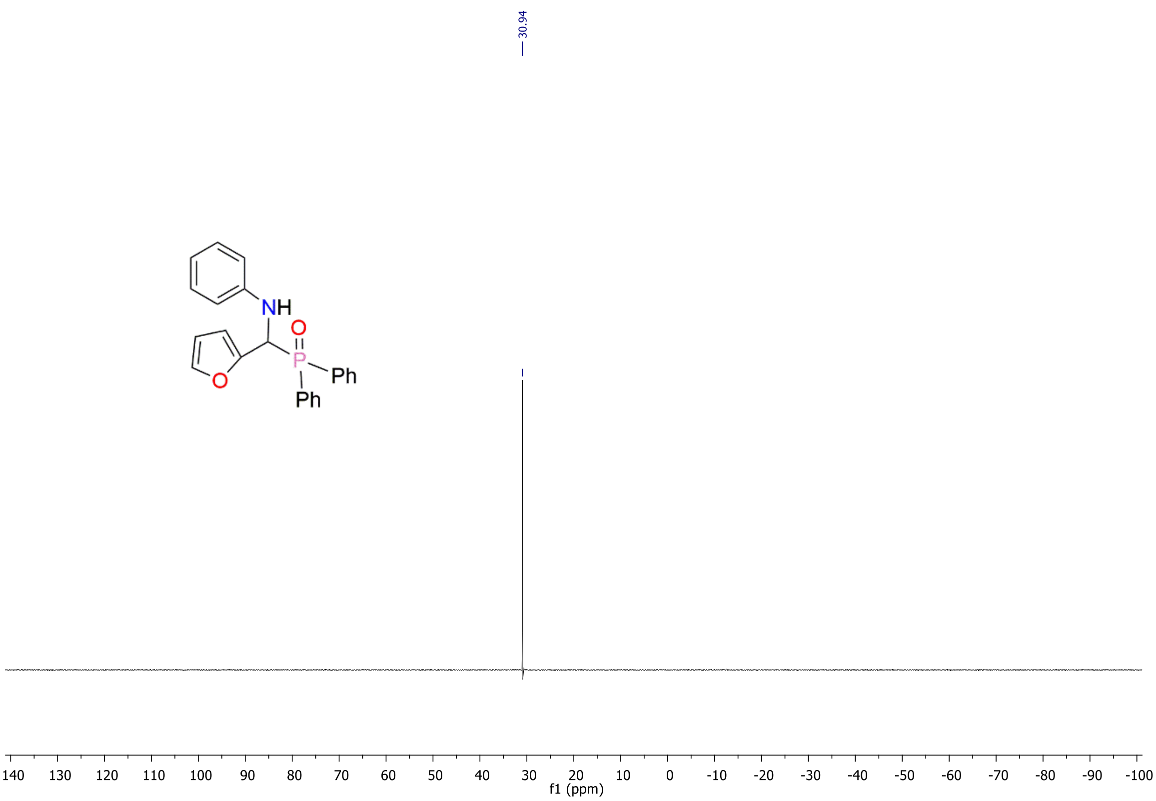


Fig S34. $^{31}P\{^{1}H\}$ NMR spectra of **1k** ($CDCl_3$, 243 MHz)

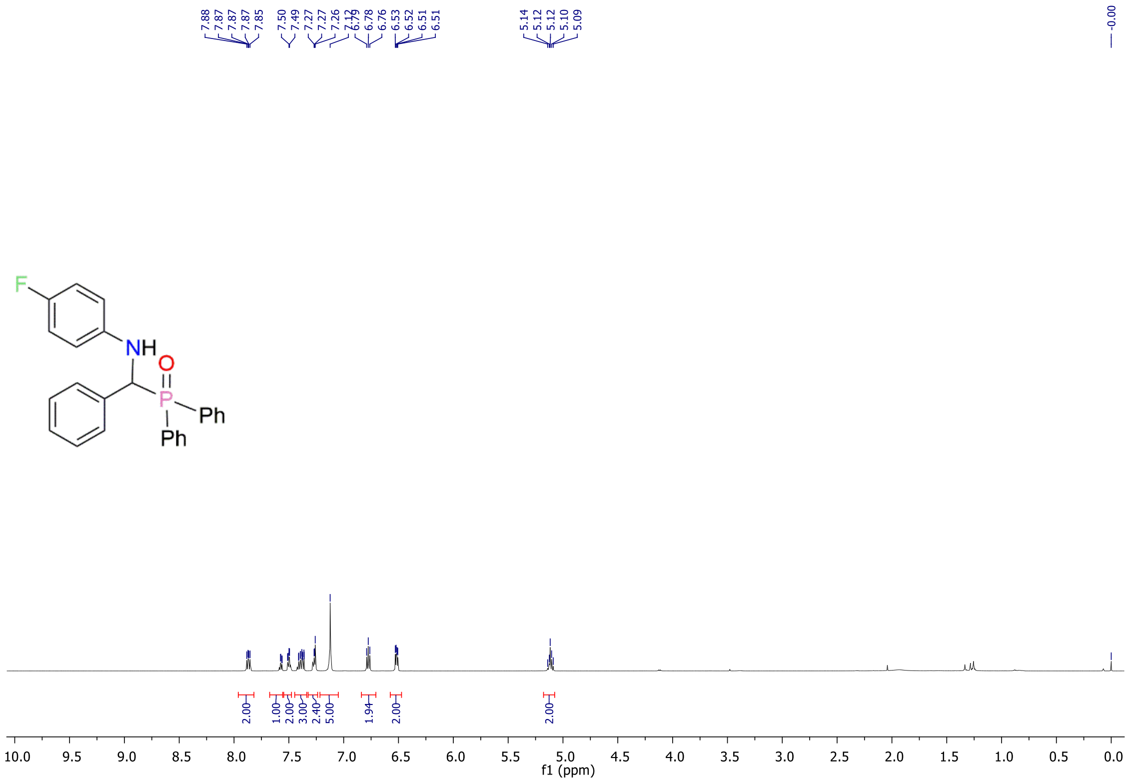


Fig S35. ^{1}H NMR spectra of **1l** ($CDCl_3$, 600 MHz).

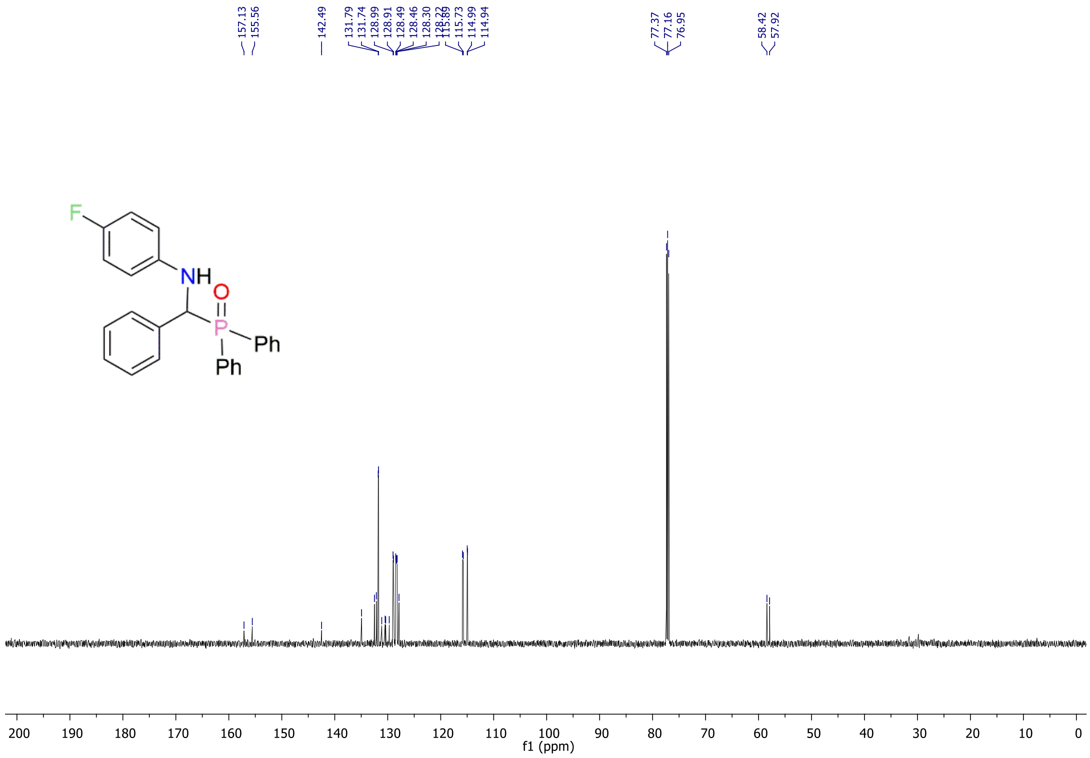


Fig S36. $^{13}C\{^{1}H\}$ NMR spectra of **1l** ($CDCl_3$, 150 MHz).

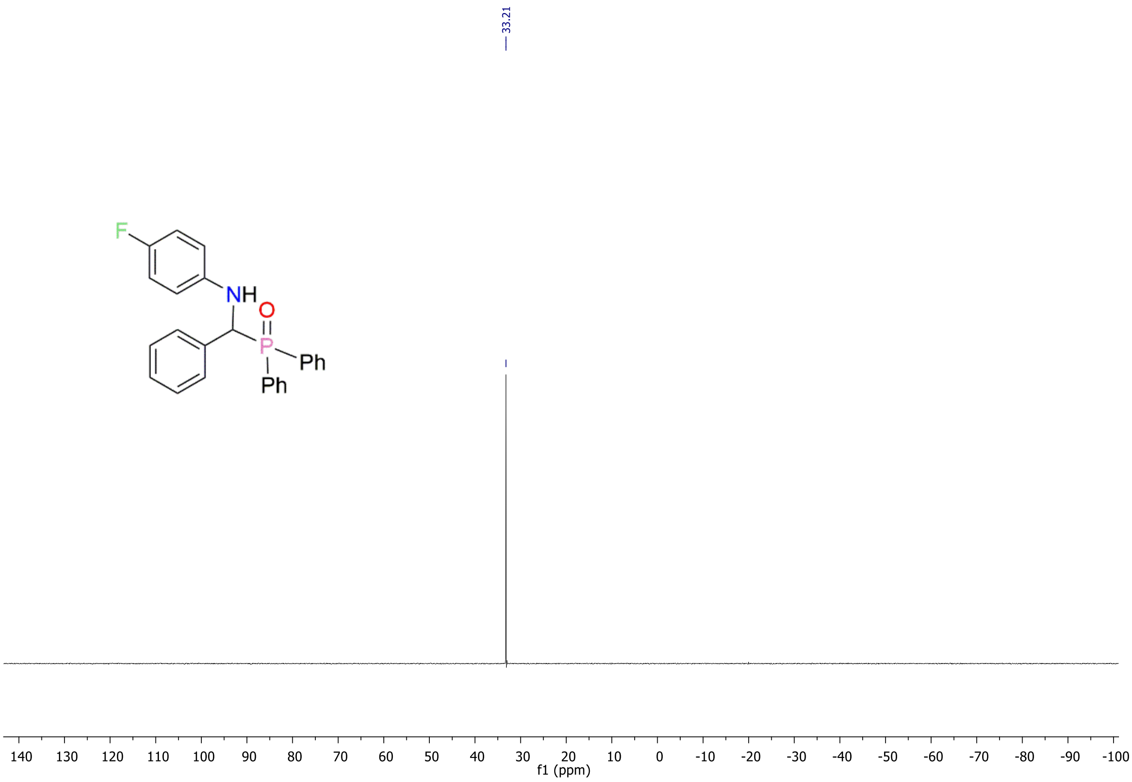


Fig S37. $^{31}P\{^1H\}$ NMR spectra of **1l** ($CDCl_3$, 243 MHz).

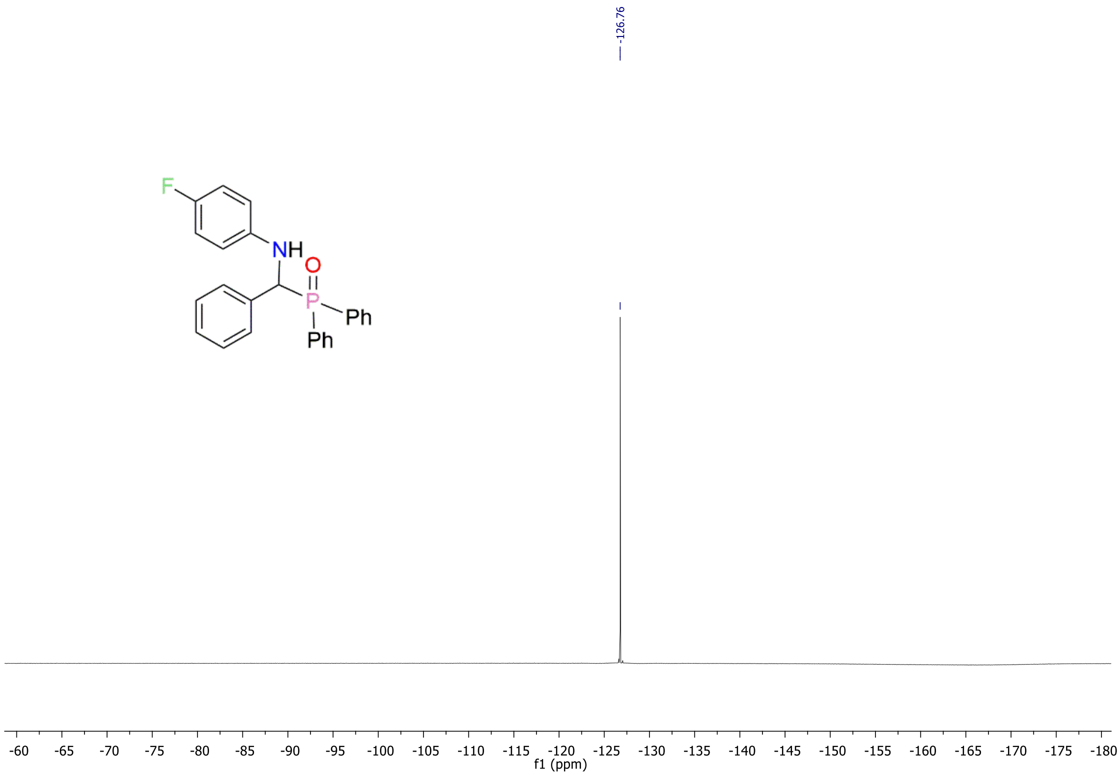


Fig S38. $^{19}F\{^1H\}$ NMR spectra of **1l** ($CDCl_3$, 565 MHz).

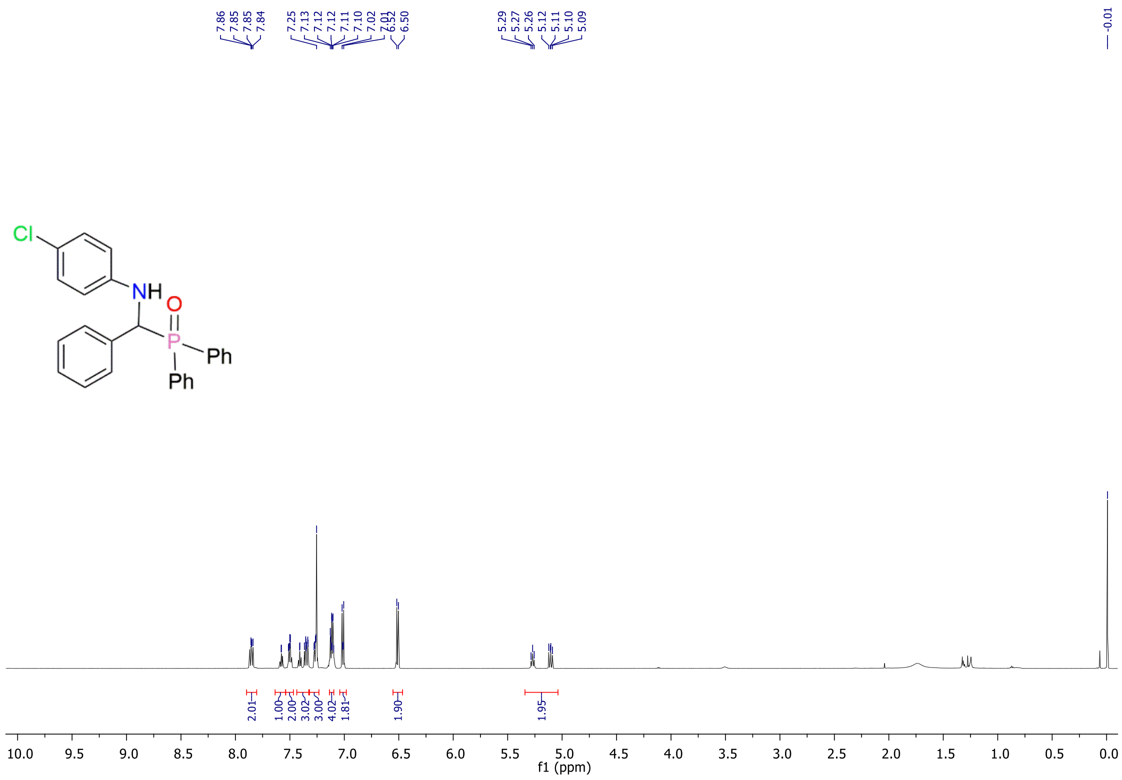


Fig S39. ^{1}H NMR spectra of **1m** ($CDCl_3$, 600 MHz).

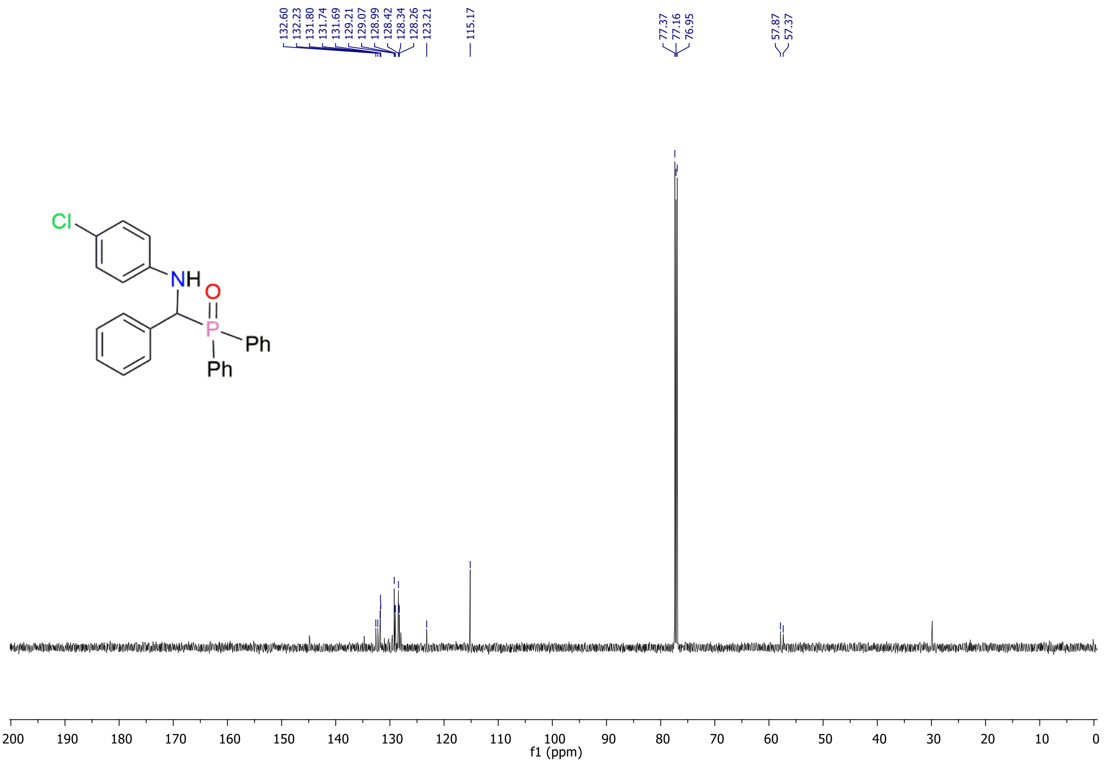


Fig S40. $^{13}C\{^{1}H\}$ NMR spectra of **1m** ($CDCl_3$, 150 MHz).

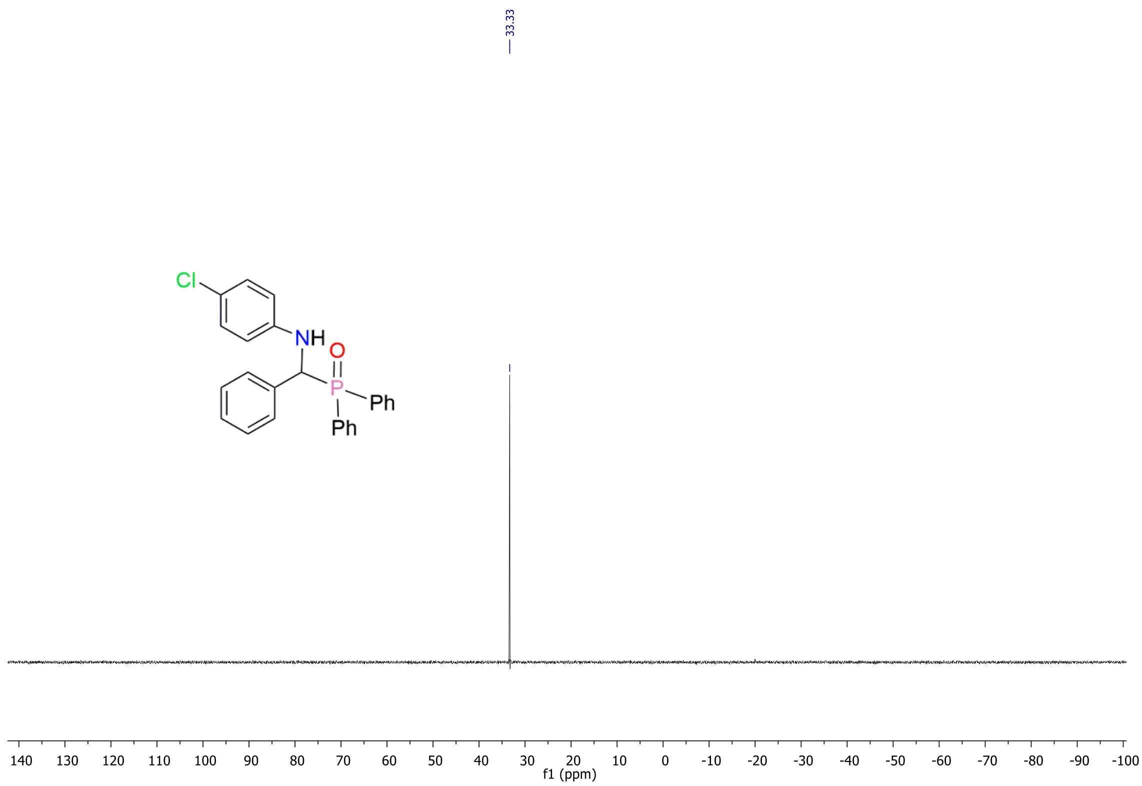


Fig S41. $^{31}P\{^{1}H\}$ NMR spectra of **1m** ($CDCl_3$, 243 MHz).

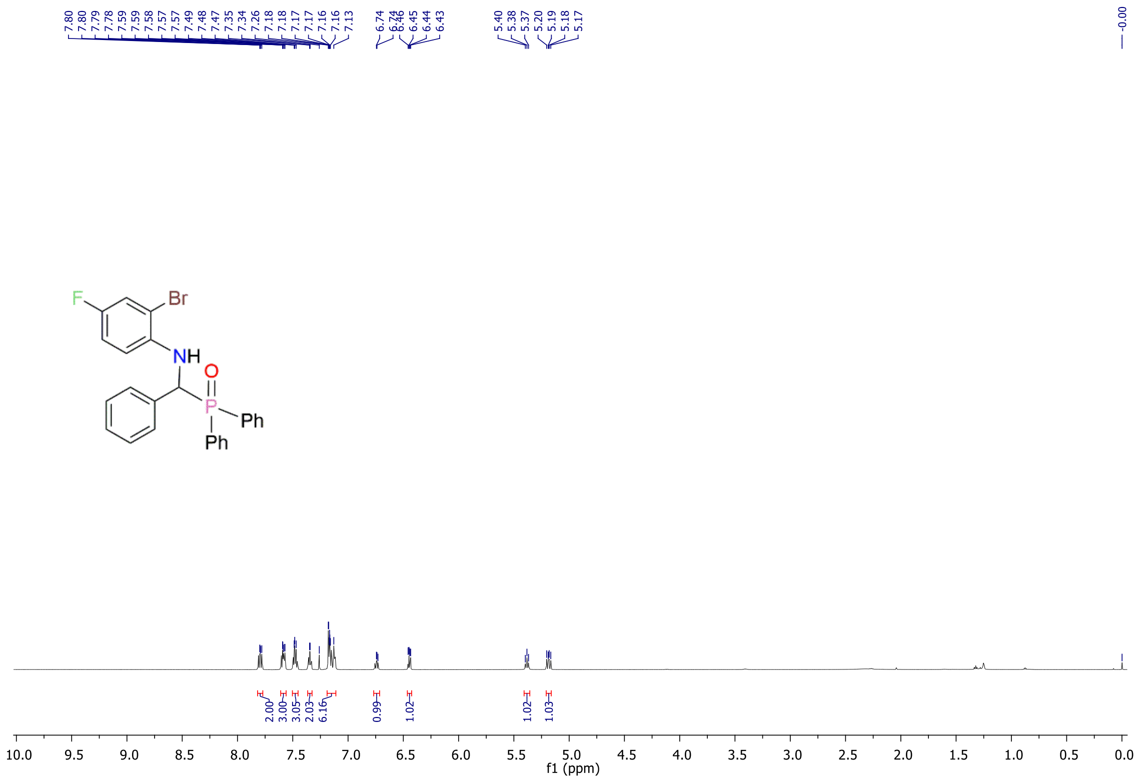


Fig S42. ^{1}H NMR spectra of **1n** ($CDCl_3$, 600 MHz).

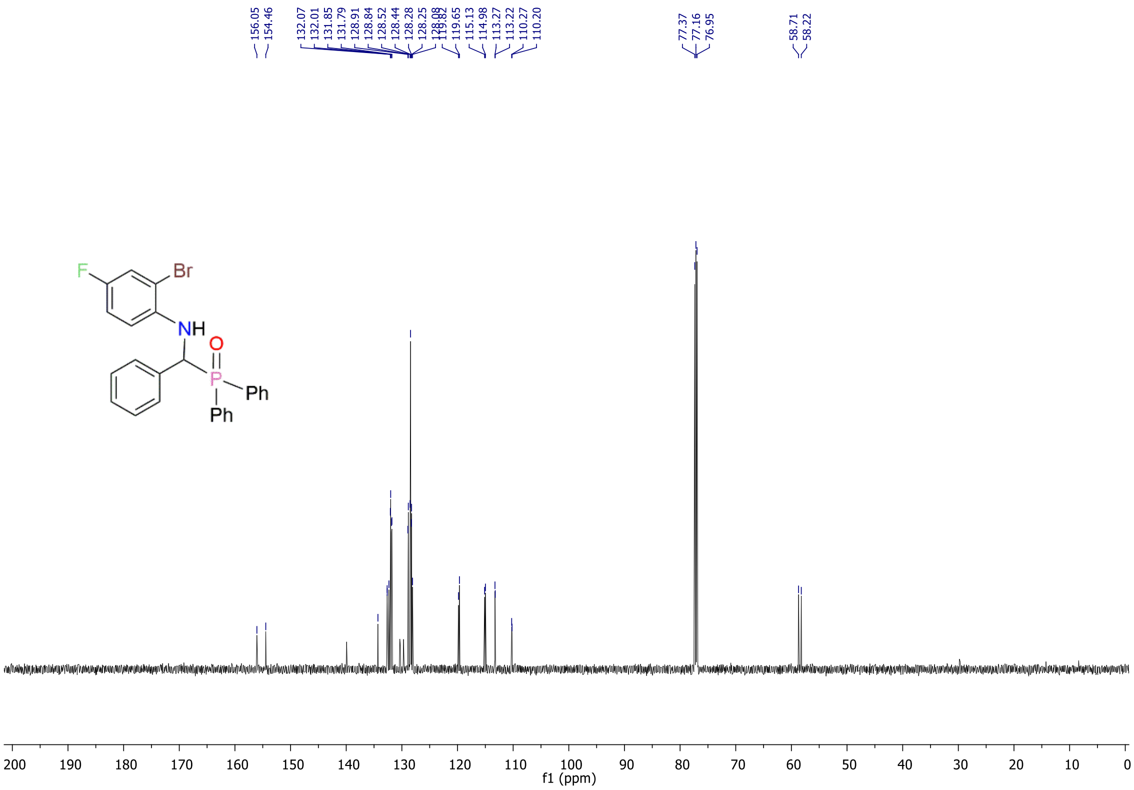


Fig S43. $^{13}C\{^{1}H\}$ NMR spectra of **1n** ($CDCl_3$, 150 MHz).

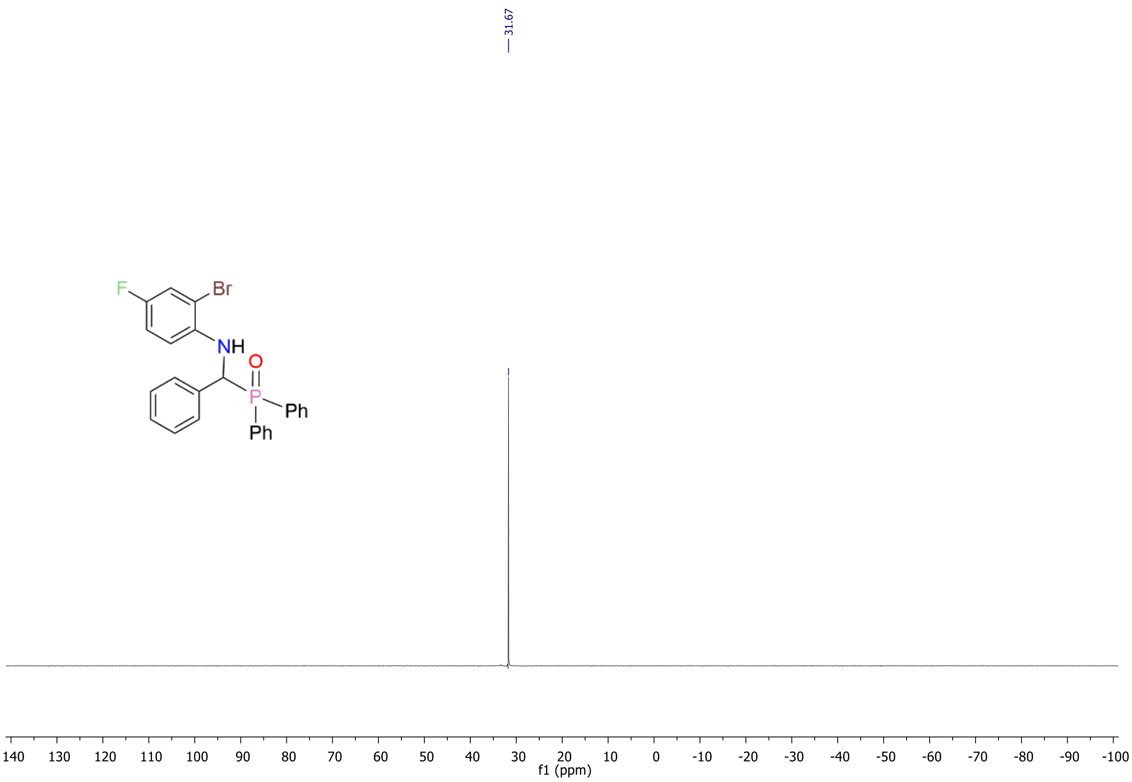


Fig S44. $^{31}P\{^{1}H\}$ NMR spectra of **1n** ($CDCl_3$, 243 MHz).

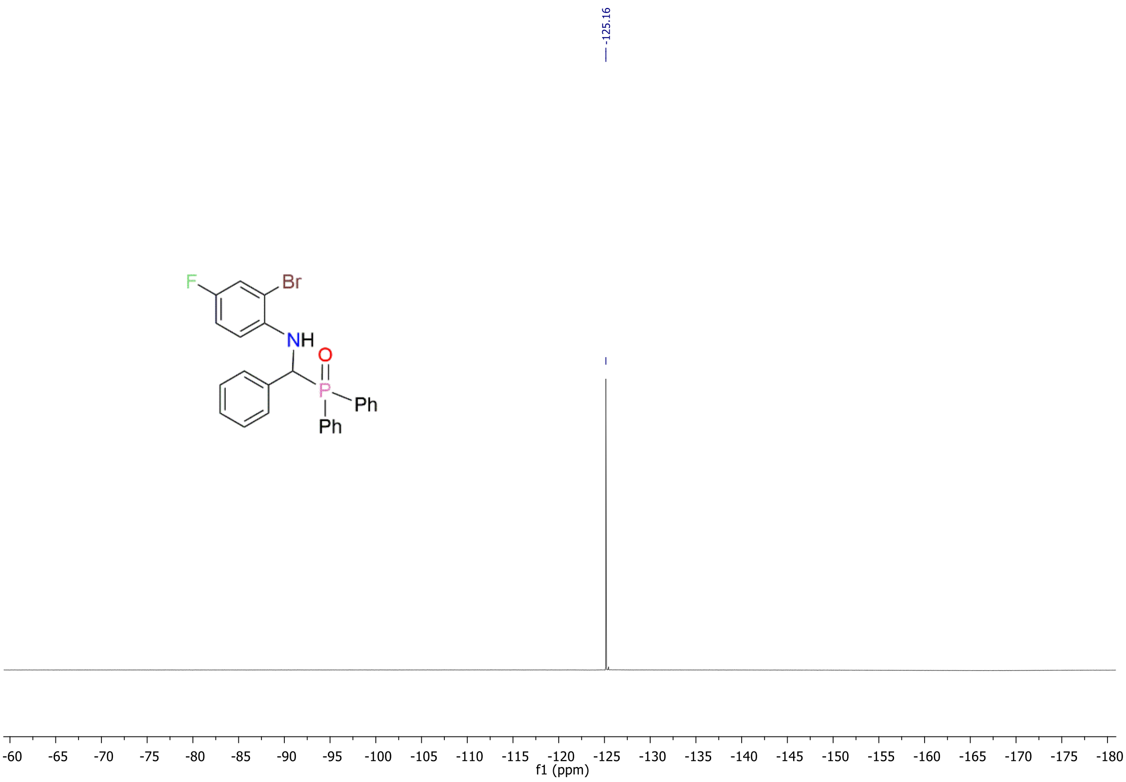


Fig S45. $^{19}F\{^{1}H\}$ NMR spectra of **1n** ($CDCl_3$, 565 MHz).

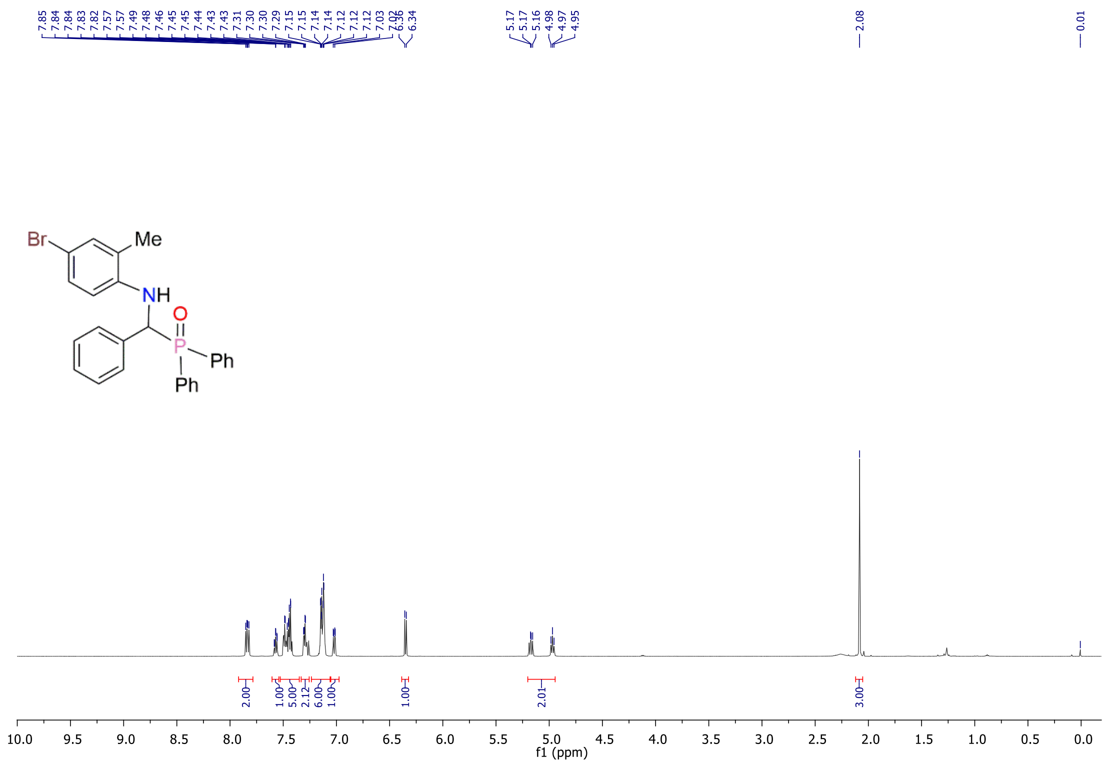


Fig S46. ^{1}H NMR spectra of **1o** ($CDCl_3$, 600 MHz).

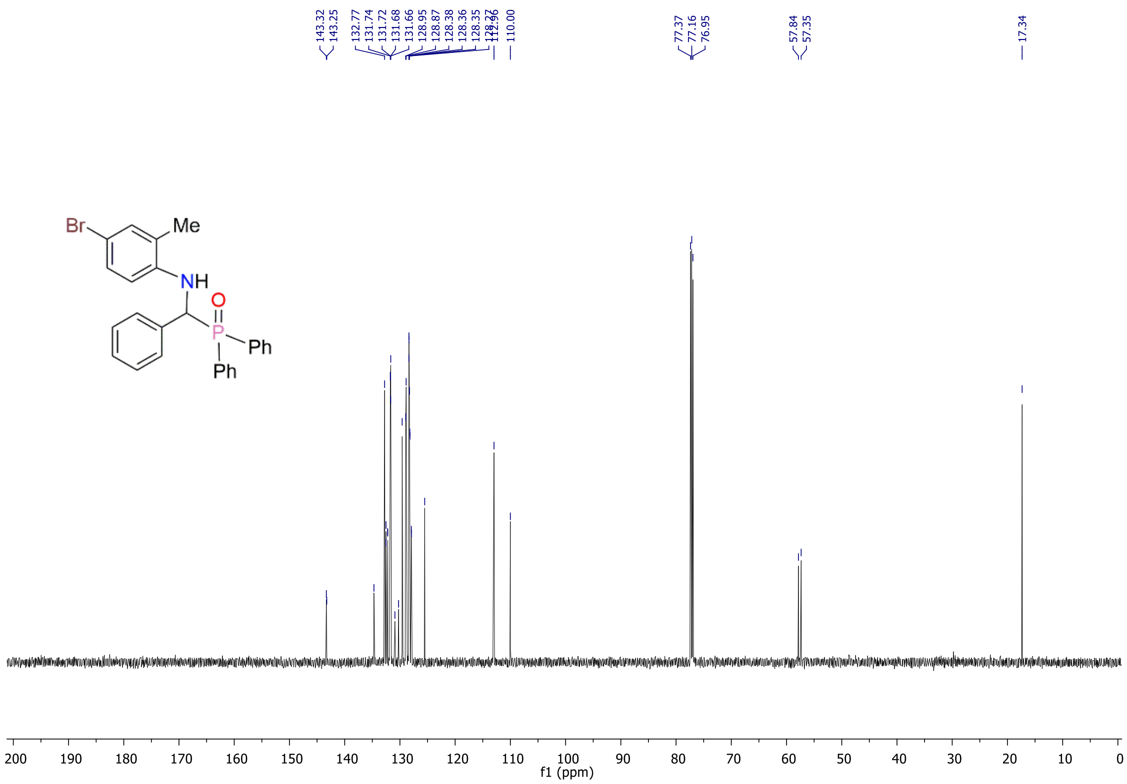


Fig S47. $^{13}C\{^{1}H\}$ NMR spectra of **1o** ($CDCl_3$, 150 MHz).

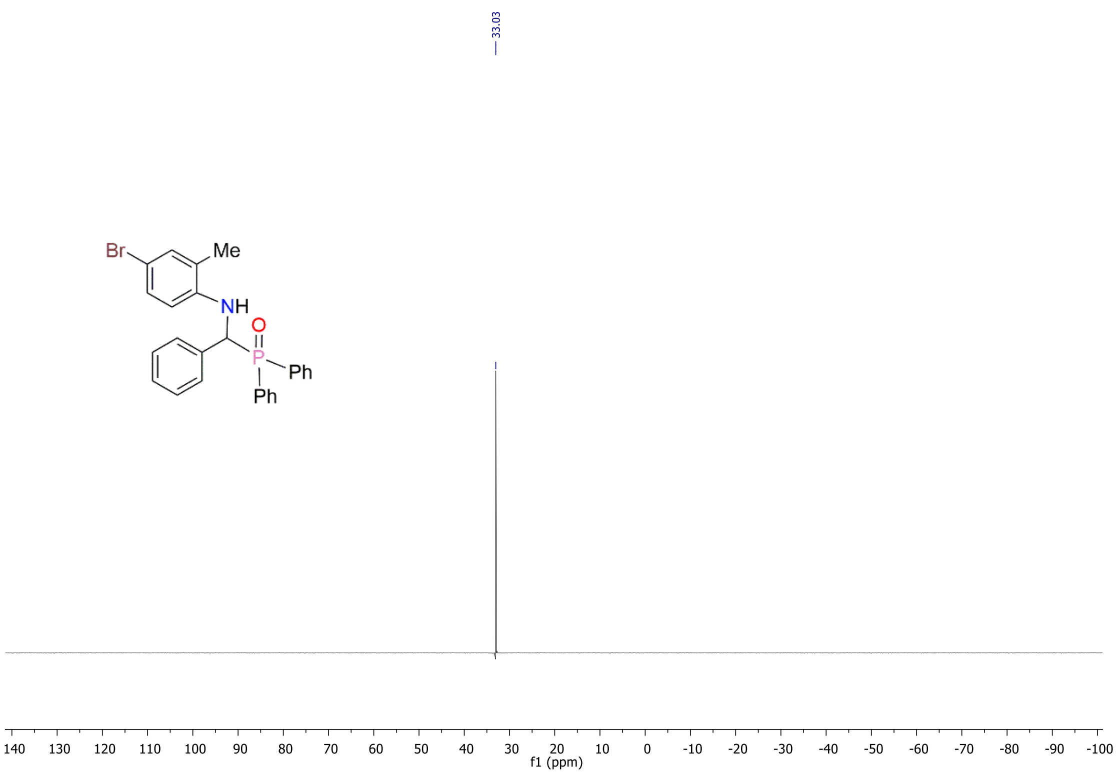


Fig S48. $^{31}P\{^{1}H\}$ NMR spectra of **1o** ($CDCl_3$, 243 MHz).

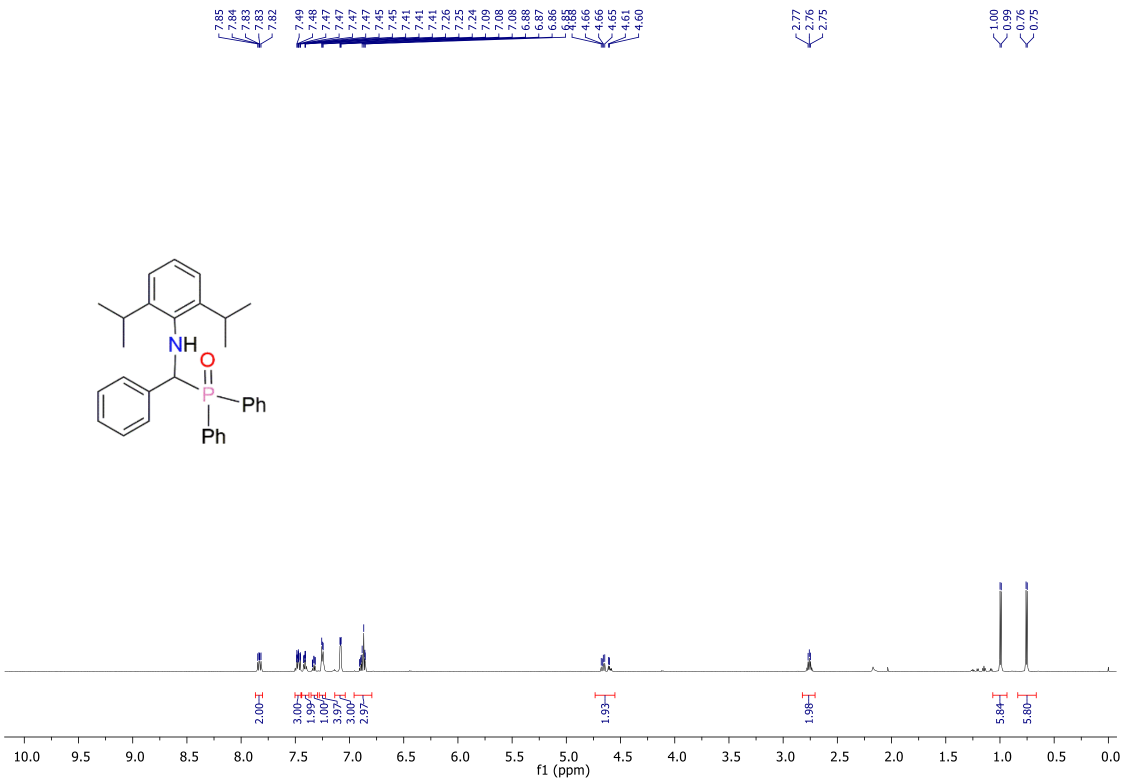


Fig S49. ^{1}H NMR spectra of **1p** ($CDCl_3$, 600 MHz).

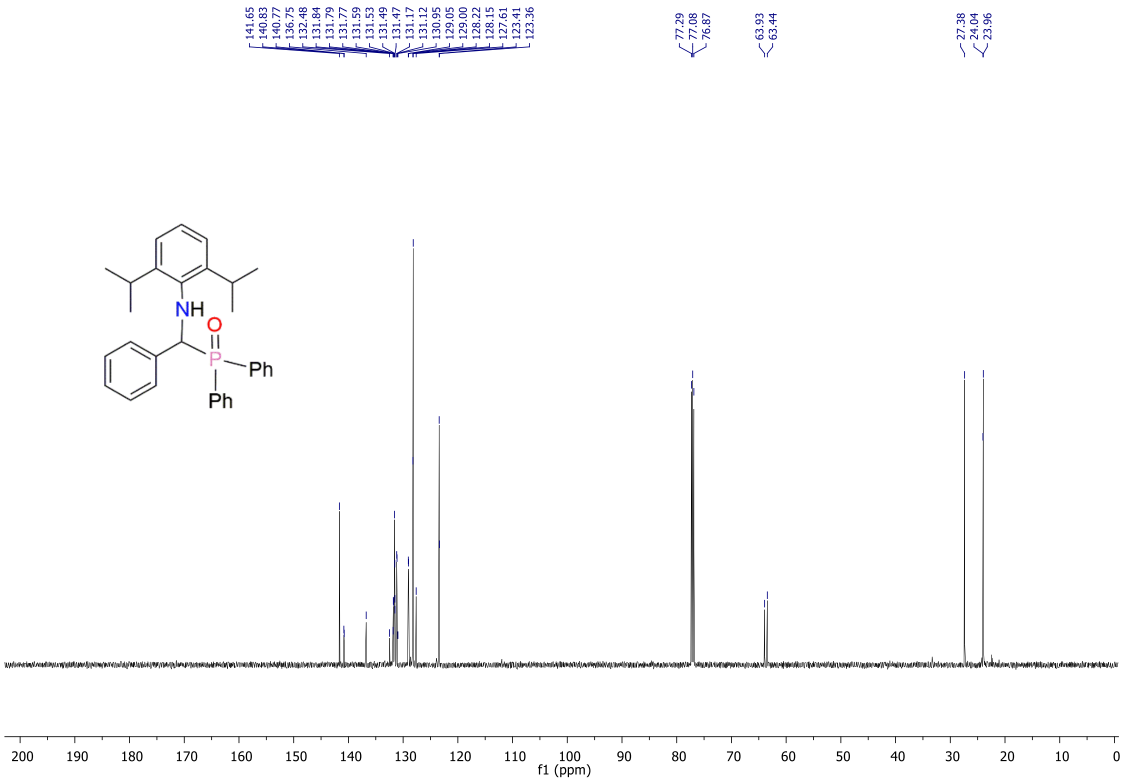


Fig S50. $^{13}C\{^{1}H\}$ NMR spectra of **1p** ($CDCl_3$, 150 MHz).

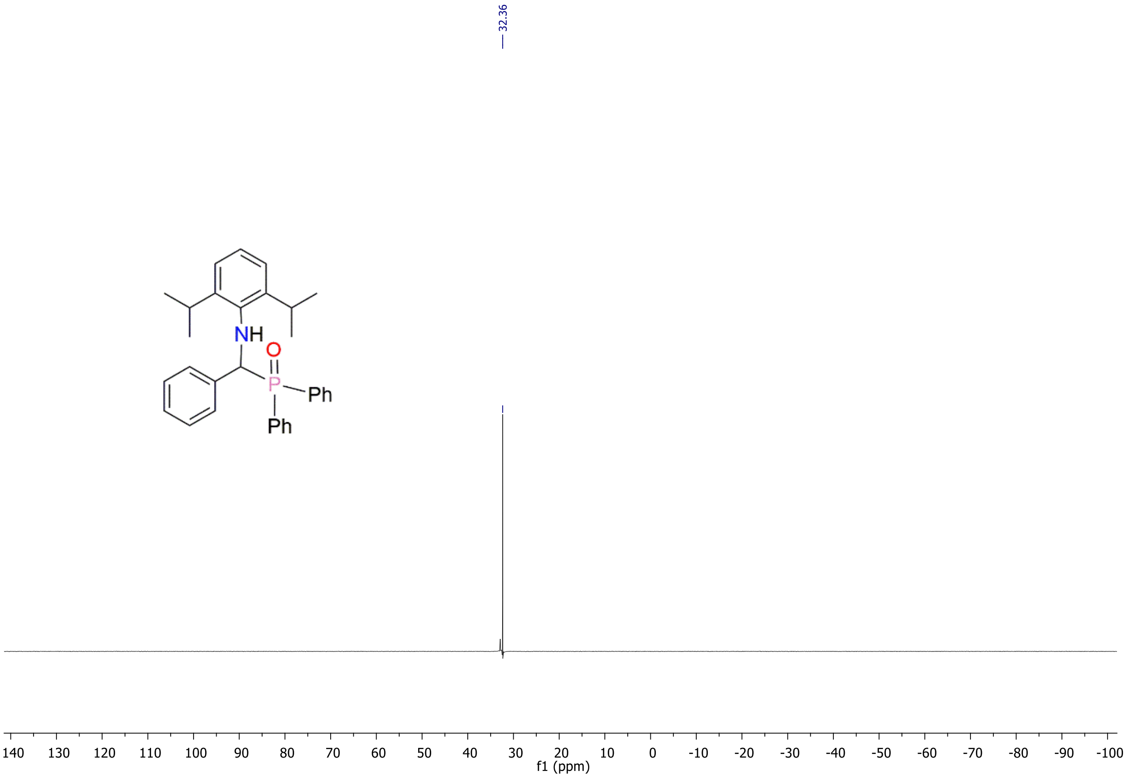


Fig S51. $^{31}P\{^{1}H\}$ NMR spectra of **1p** ($CDCl_3$, 243 MHz).

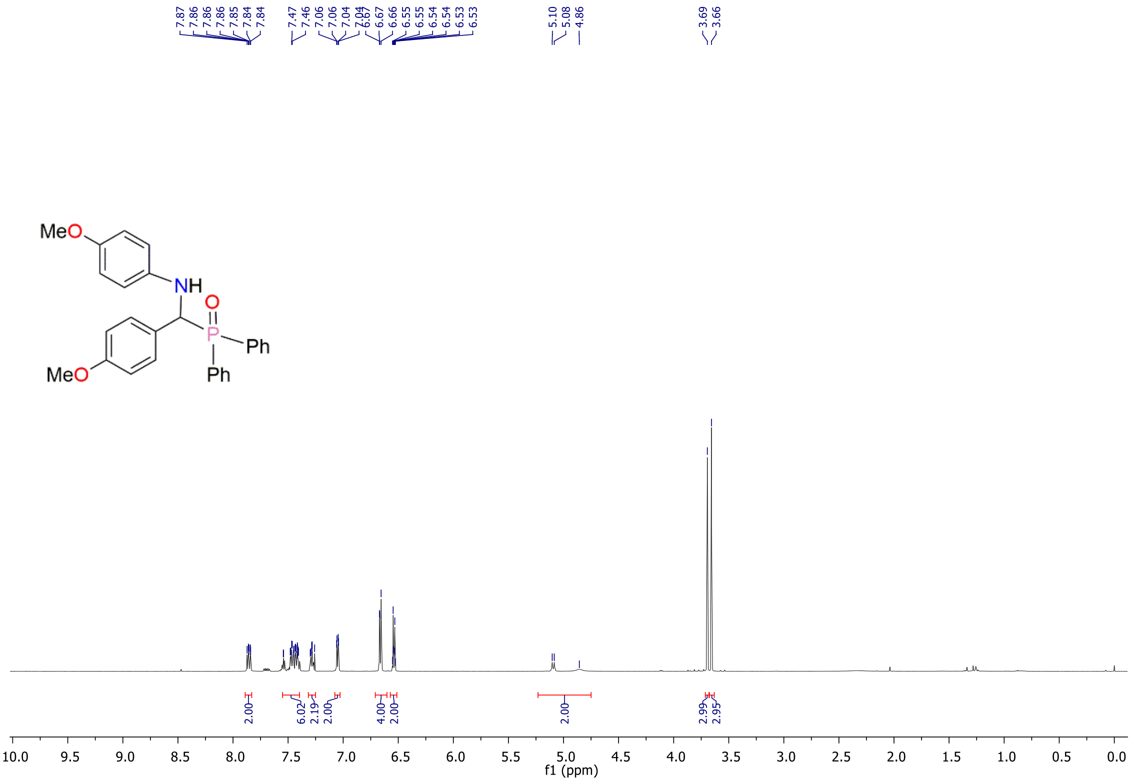


Fig S52. ^{1}H NMR spectra of **1q** ($CDCl_3$, 600 MHz).

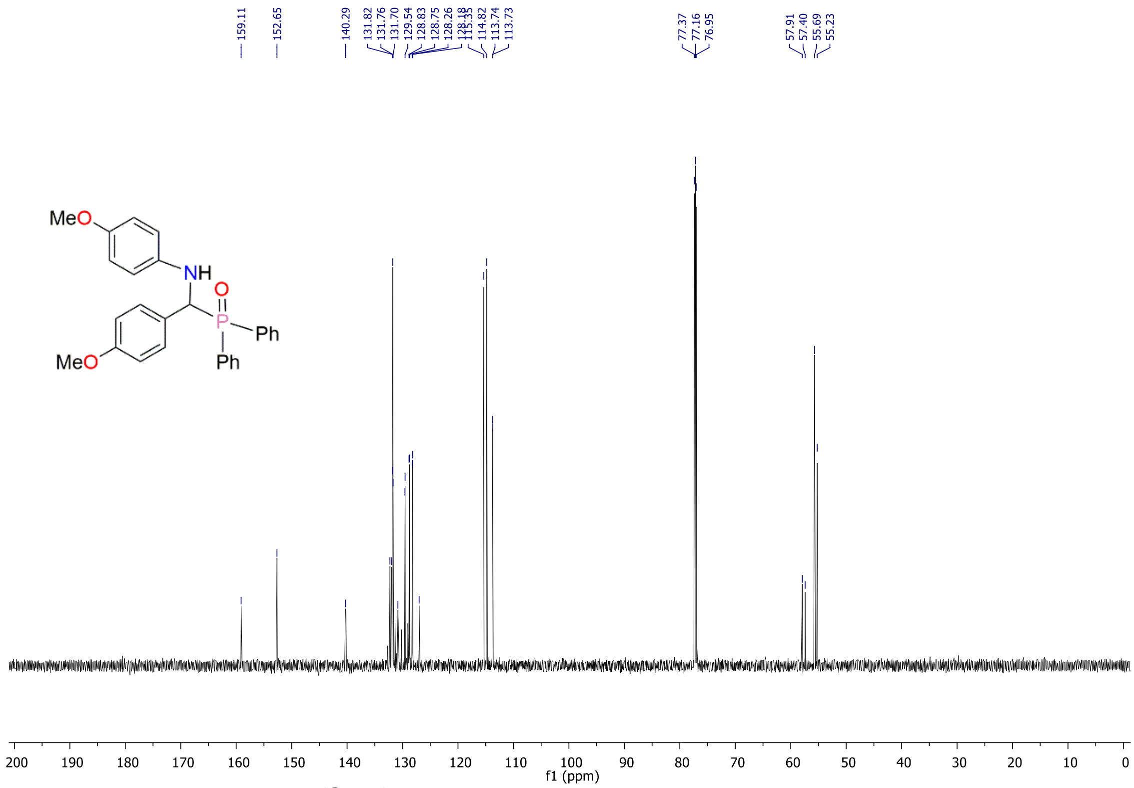


Fig S53. $^{13}C\{^1H\}$ NMR spectra of **1q** ($CDCl_3$, 150 MHz).

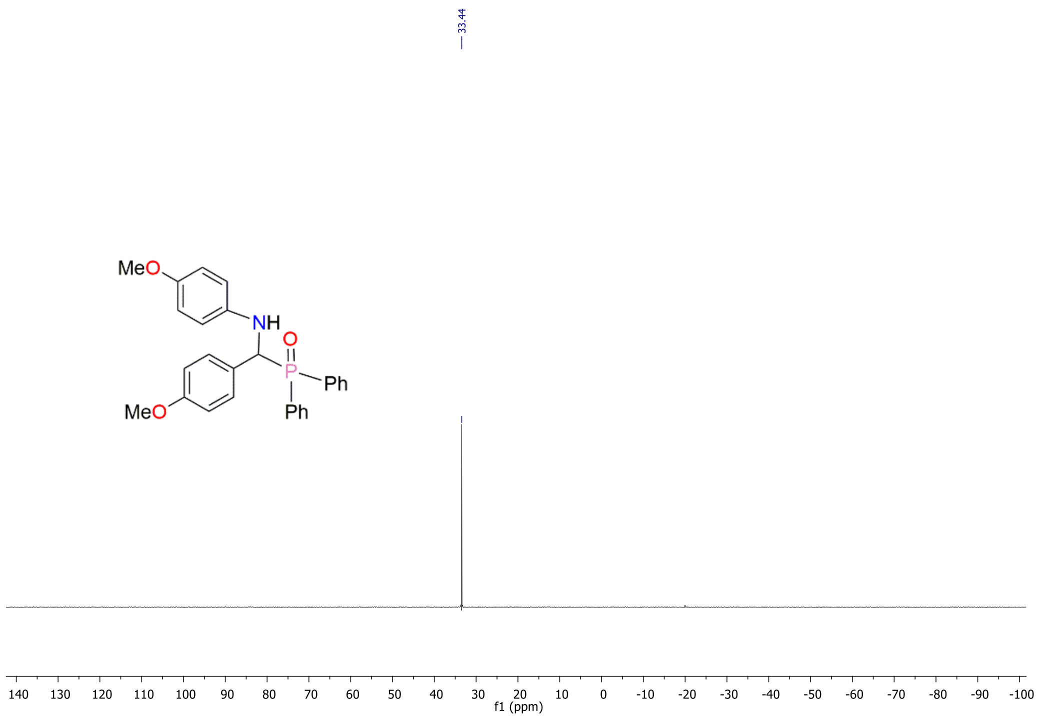


Fig S54. $^{31}P\{^1H\}$ NMR spectra of **1q** ($CDCl_3$, 243 MHz).

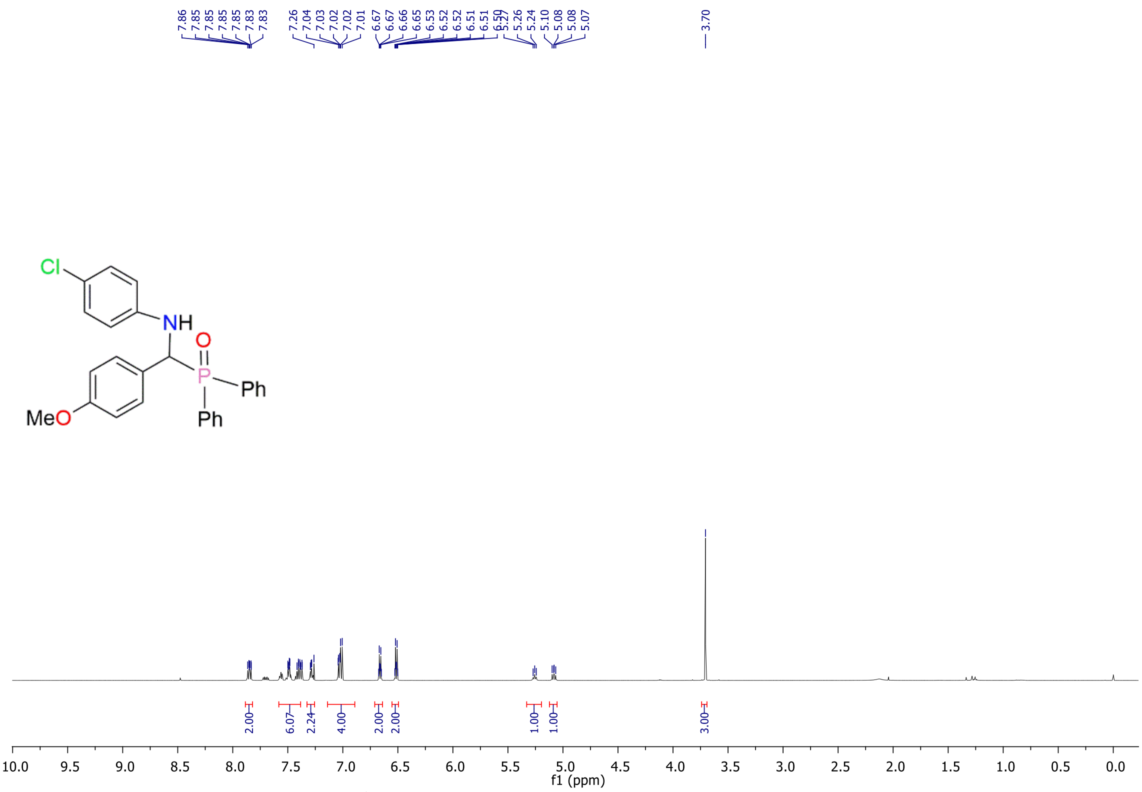


Fig S55. ^{1}H NMR spectra of **1r** ($CDCl_3$, 600 MHz).

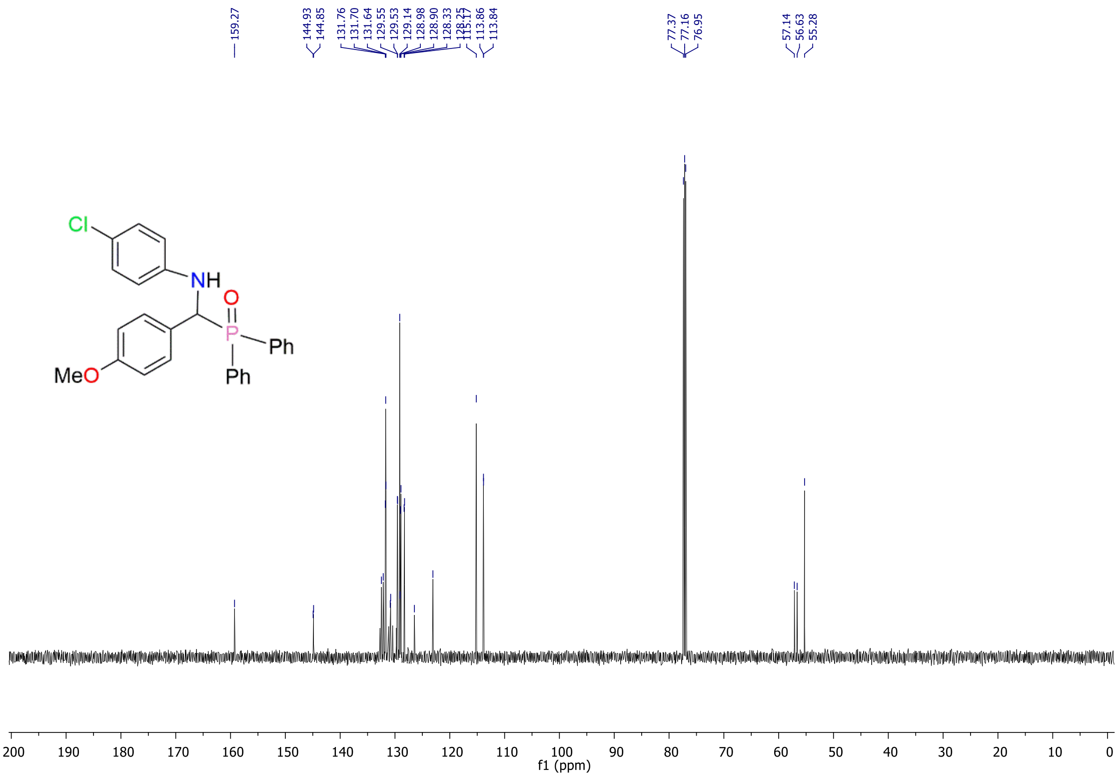


Fig S56. ^{13}C{^{1}H} NMR spectra of **1r** ($CDCl_3$, 150 MHz).

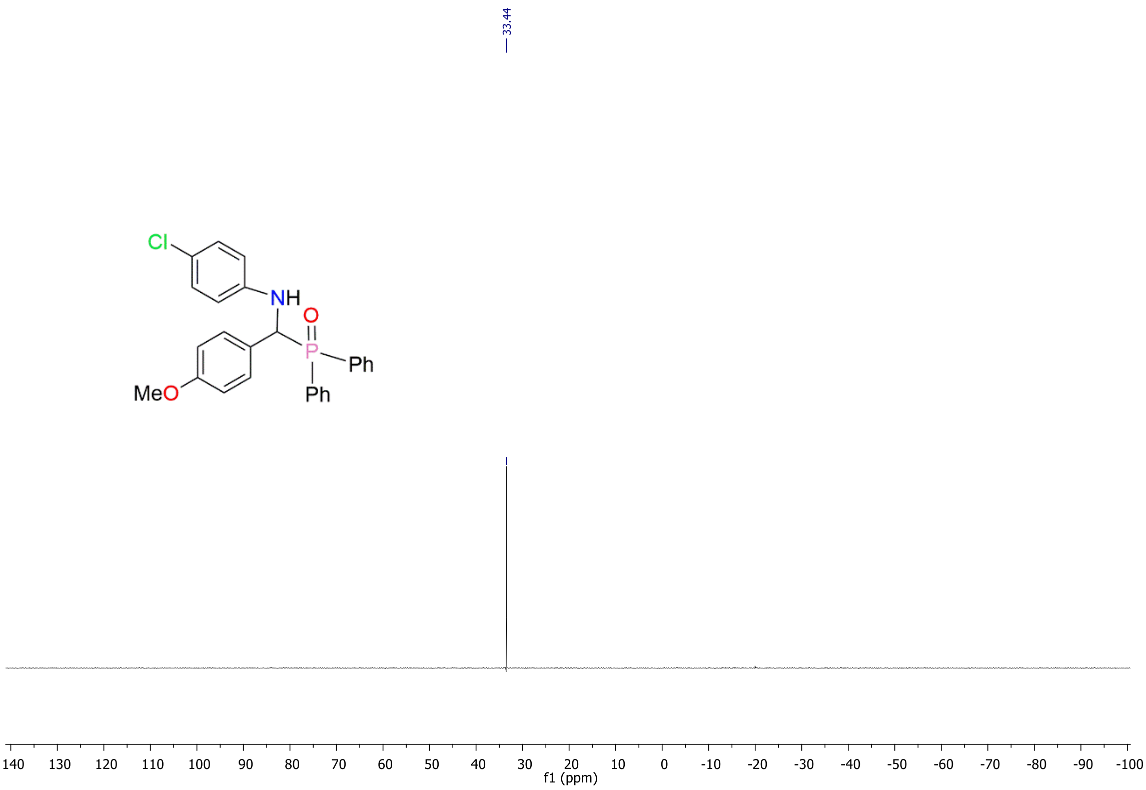


Fig S57. $^{31}P\{^{1}H\}$ NMR spectra of **1r** ($CDCl_3$, 243 MHz).

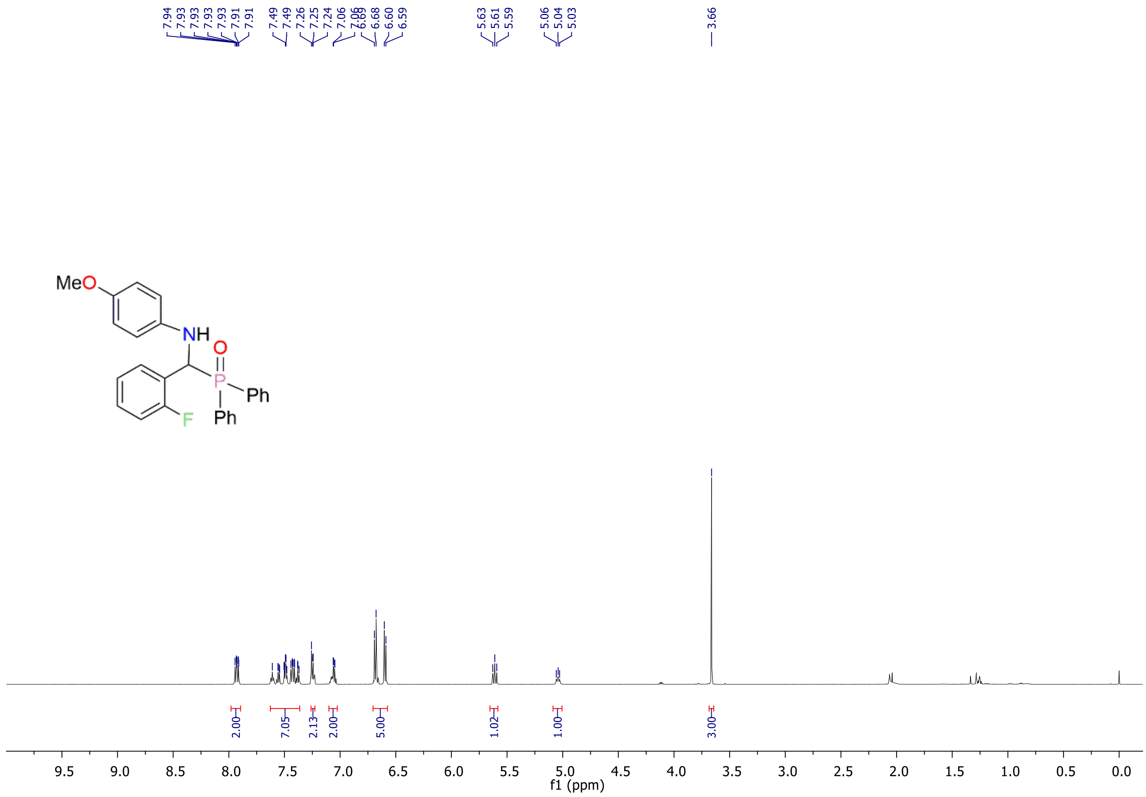


Fig S58. ^{1}H NMR spectra of **1s** ($CDCl_3$, 600 MHz).

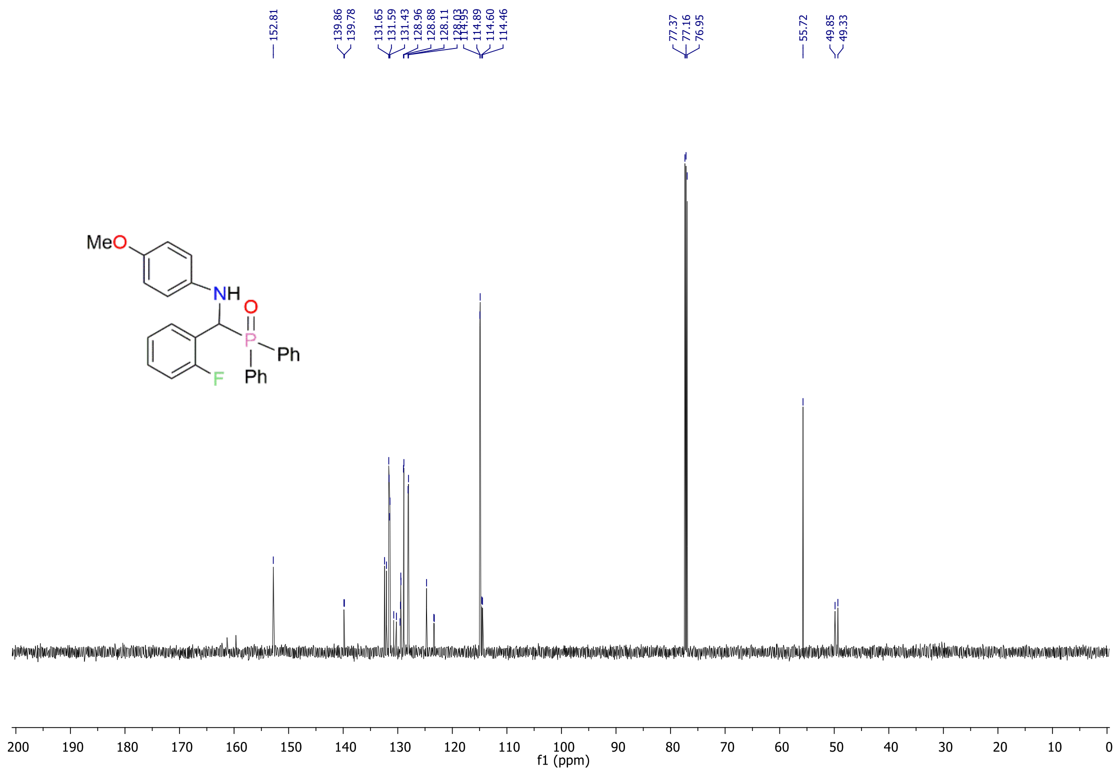


Fig S59. $^{13}C\{^{1}H\}$ NMR spectra of **1s** ($CDCl_3$, 150 MHz).

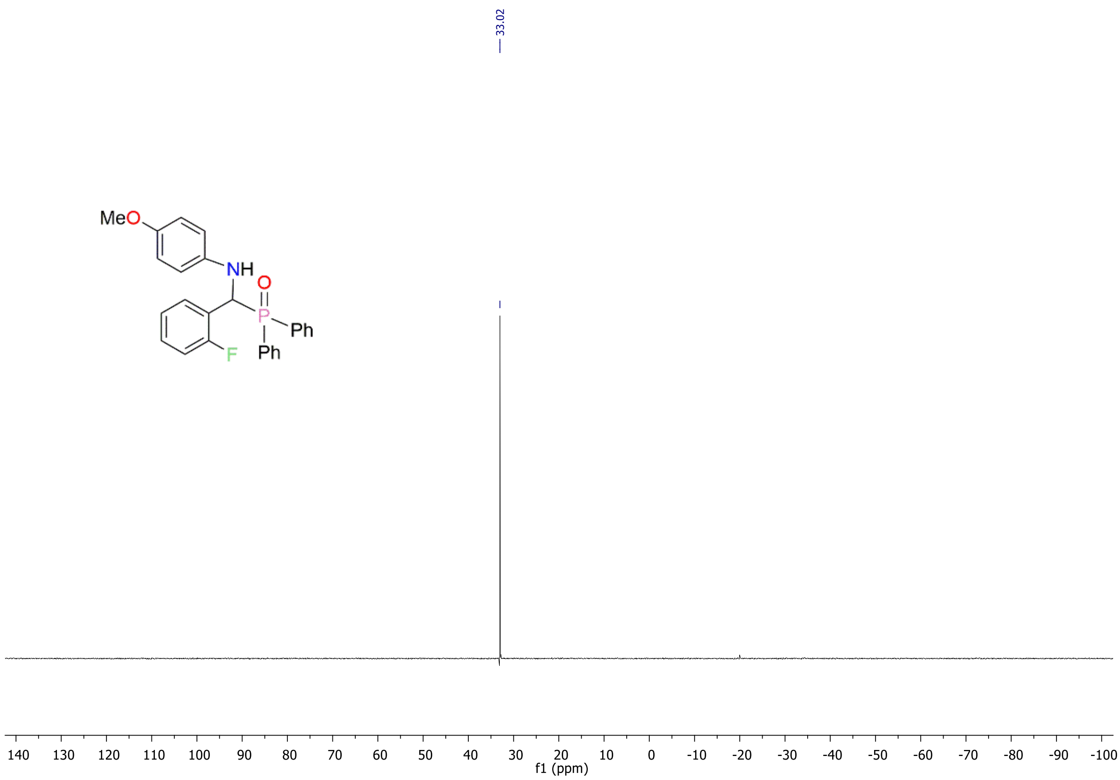


Fig S60. $^{31}P\{^{1}H\}$ NMR spectra of **1s** ($CDCl_3$, 243 MHz).

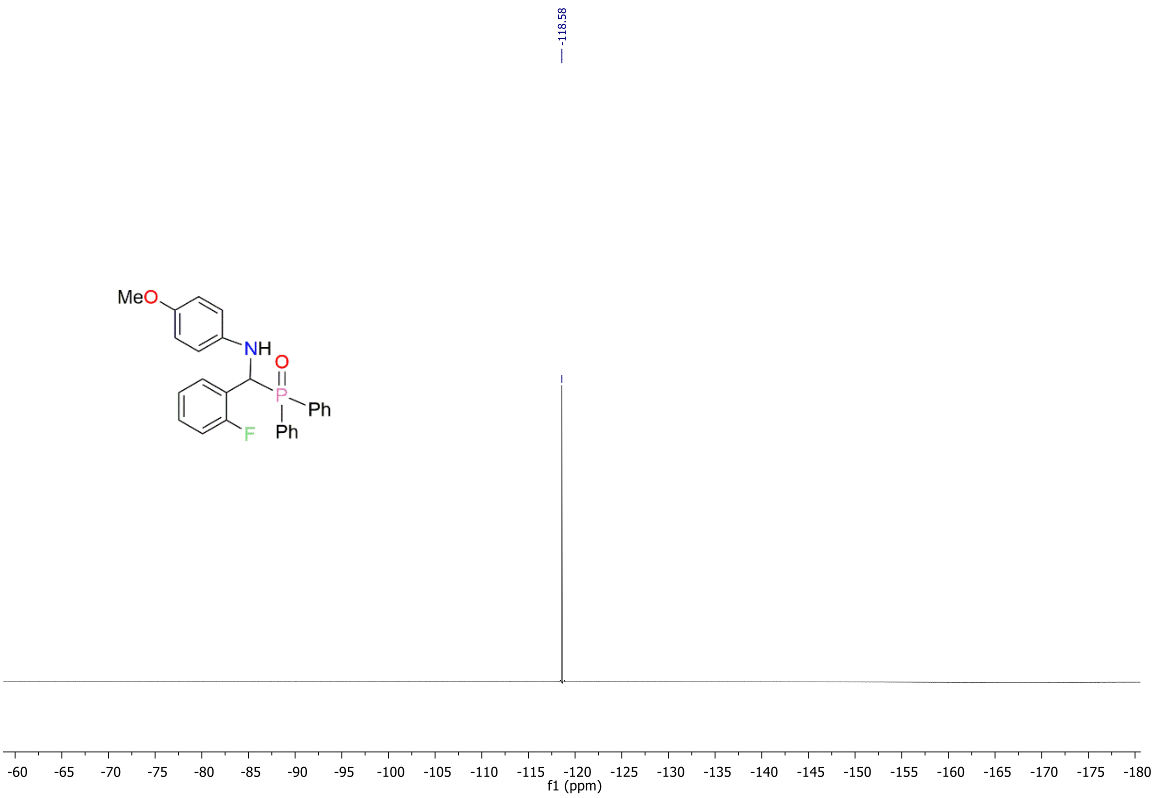


Fig S61. $^{19}F\{^{1}H\}$ NMR spectra of **1s** ($CDCl_3$, 565 MHz).

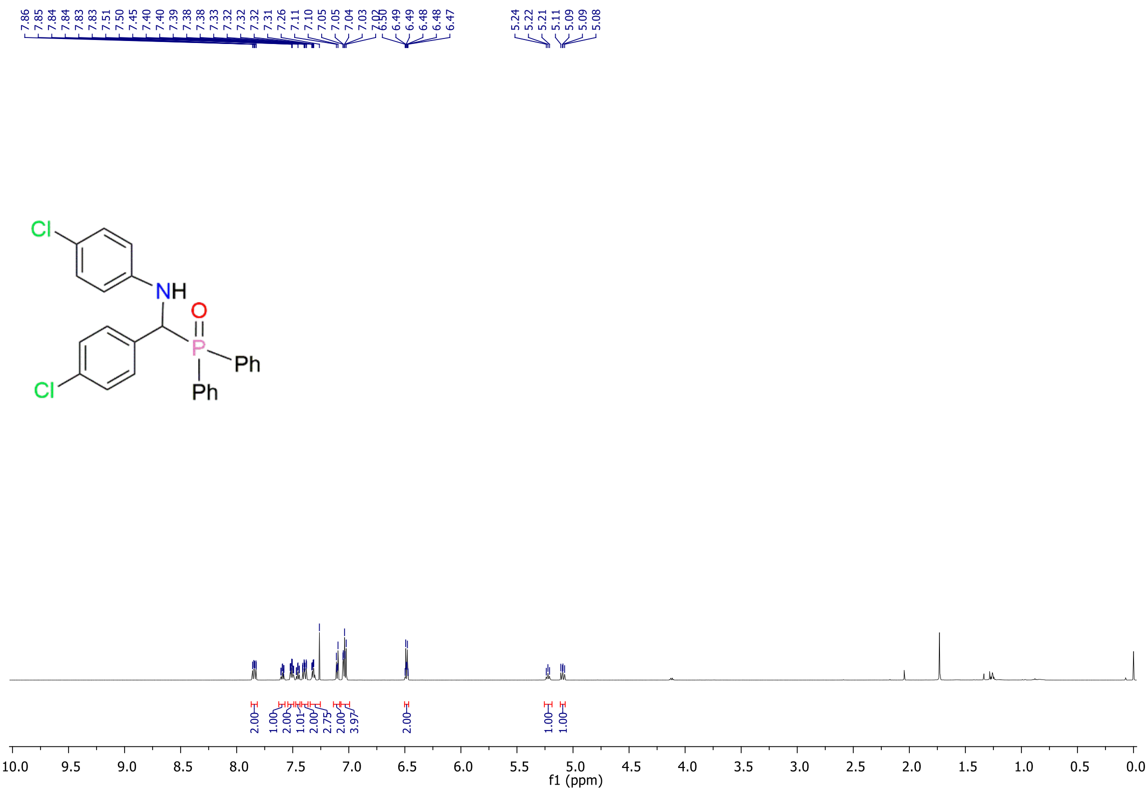


Fig S62. ^{1}H NMR spectra of **1t** ($CDCl_3$, 600 MHz).

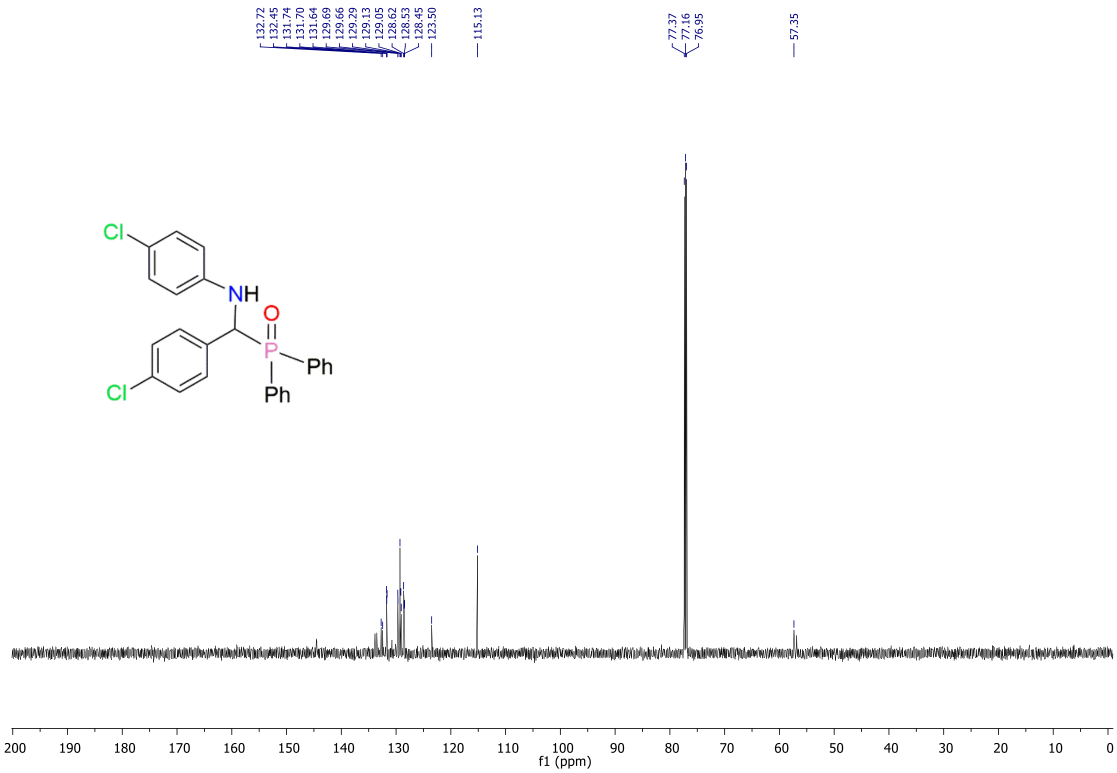


Fig S63. $^{13}C\{^{1}H\}$ NMR spectra of **1t** ($CDCl_3$, 150 MHz).

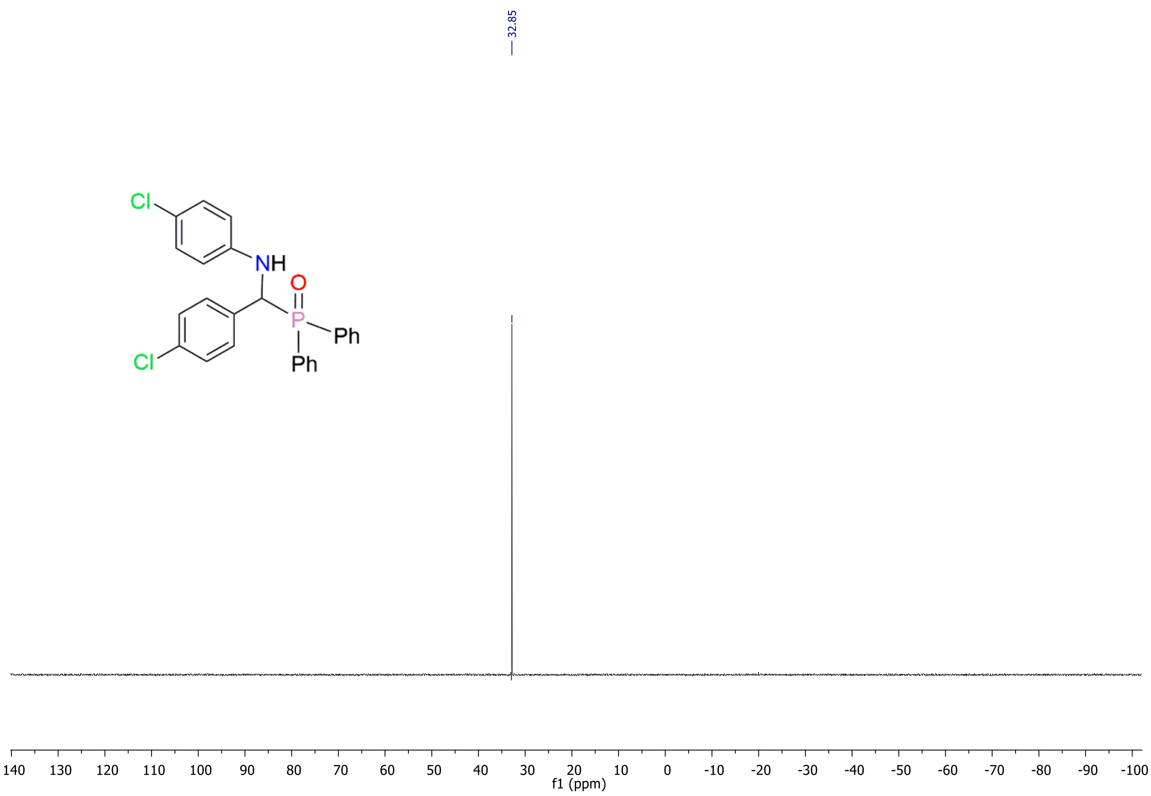


Fig S64. $^{31}P\{^{1}H\}$ NMR spectra of **1t** ($CDCl_3$, 243 MHz).

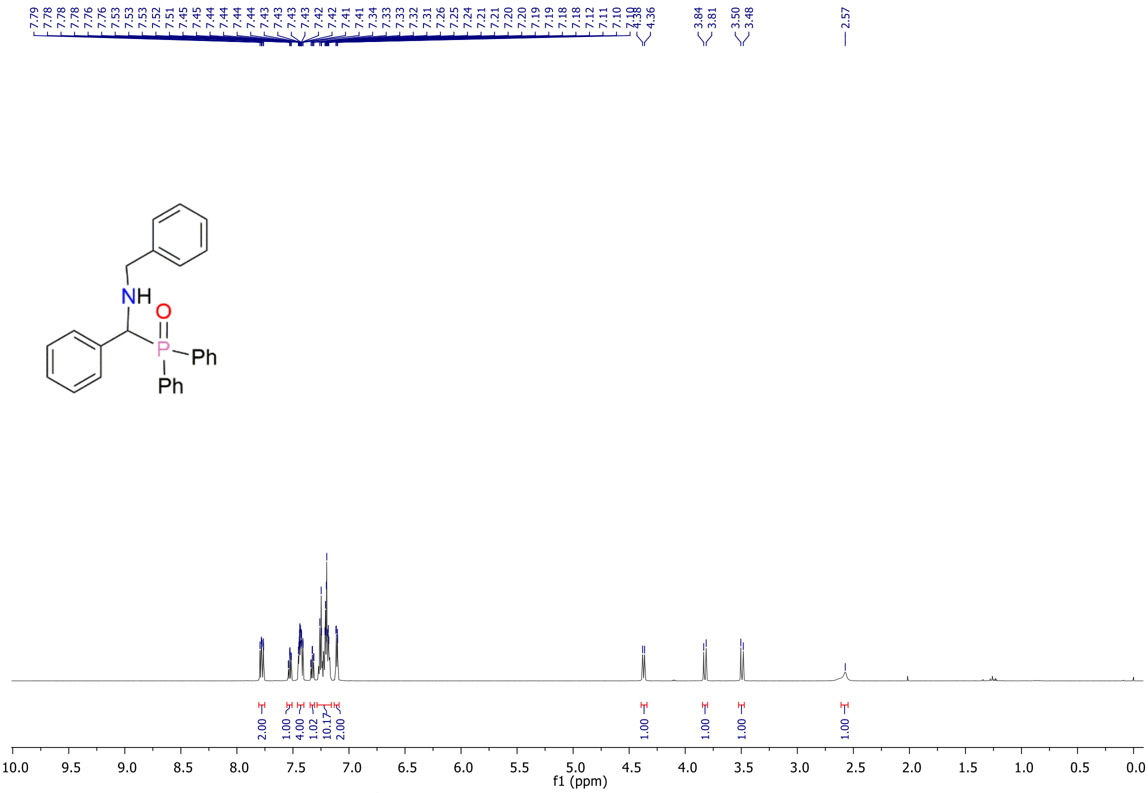


Fig S65. ^{1}H NMR spectra of **1u** ($CDCl_3$, 600 MHz).

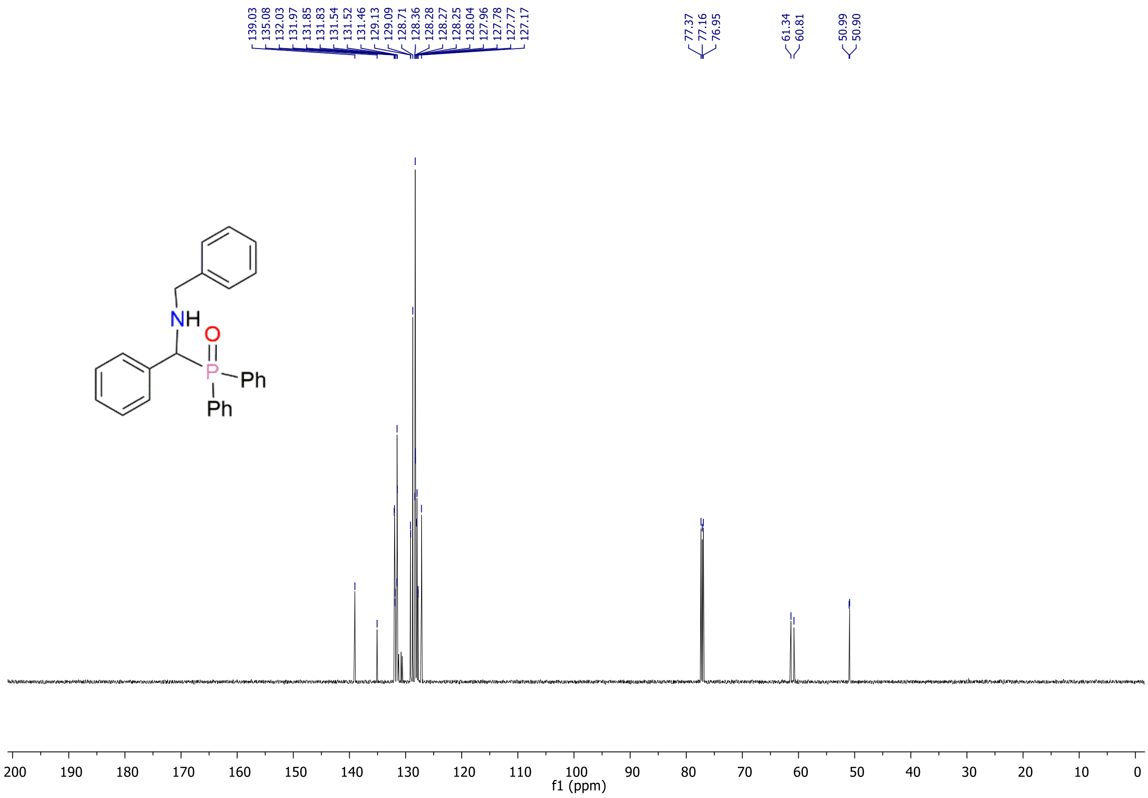


Fig S66. $^{13}C\{^{1}H\}$ NMR spectra of **1u** ($CDCl_3$, 150 MHz).

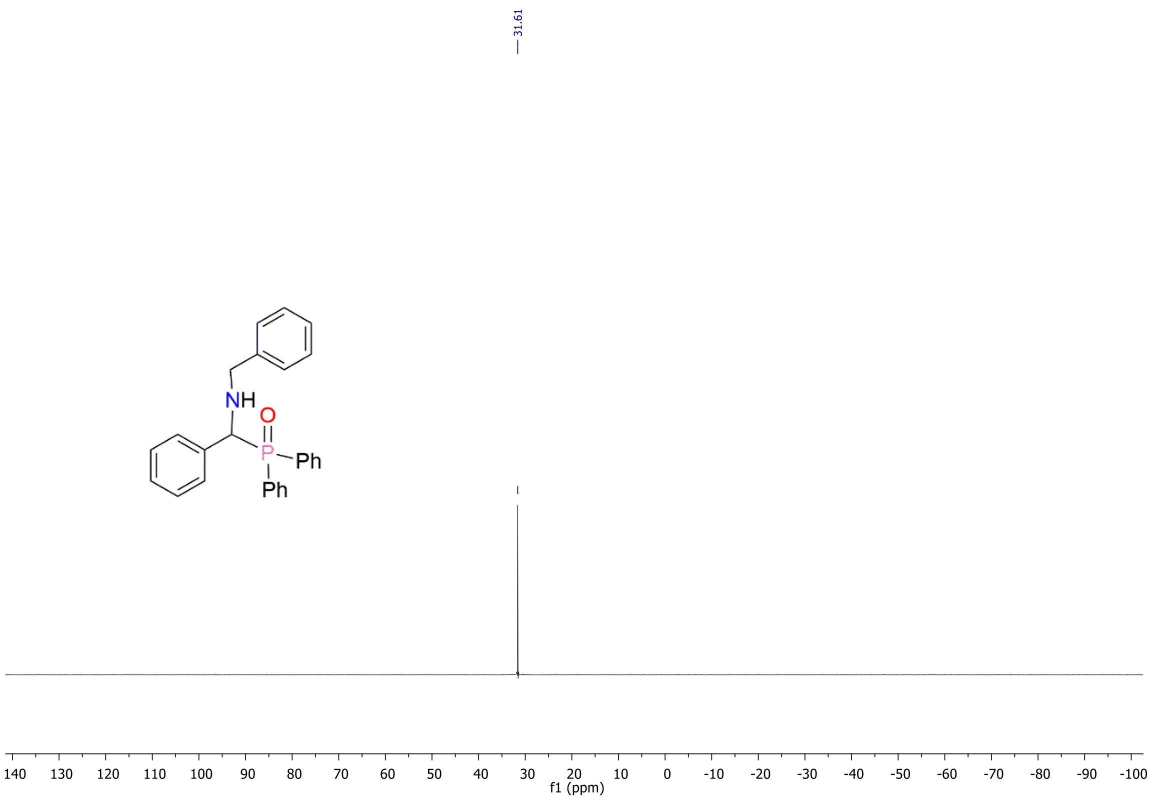


Fig S67. $^{31}P\{^{1}H\}$ NMR spectra of **1u** ($CDCl_3$, 243 MHz).

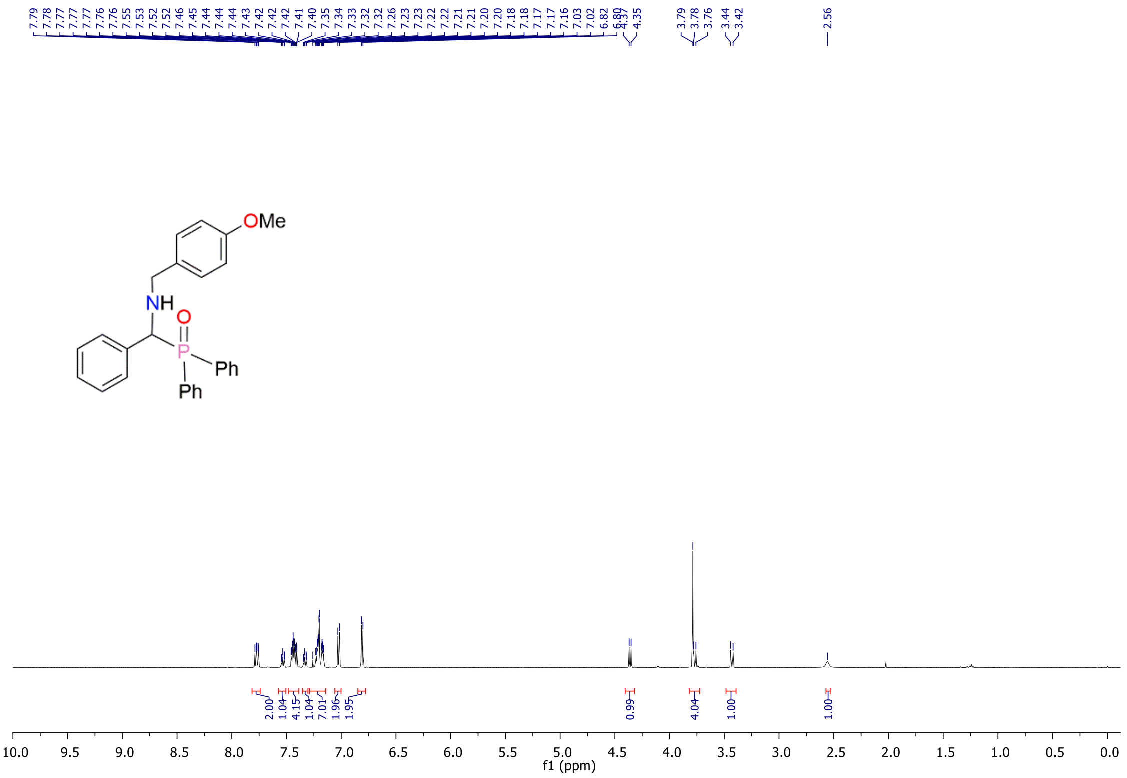


Fig S68. ^{1}H NMR spectra of **1v** ($CDCl_3$, 600 MHz).

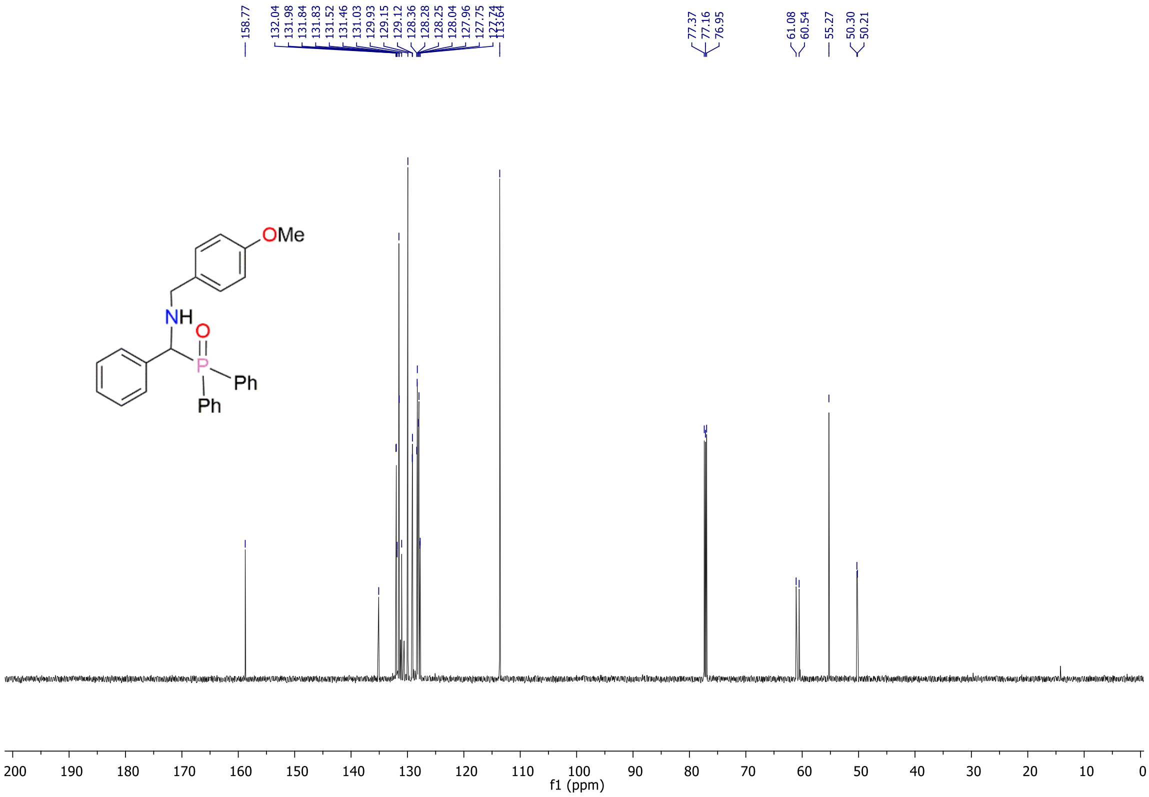


Fig S69. $^{13}C\{^{1}H\}$ NMR spectra of **1v** ($CDCl_3$, 150 MHz).

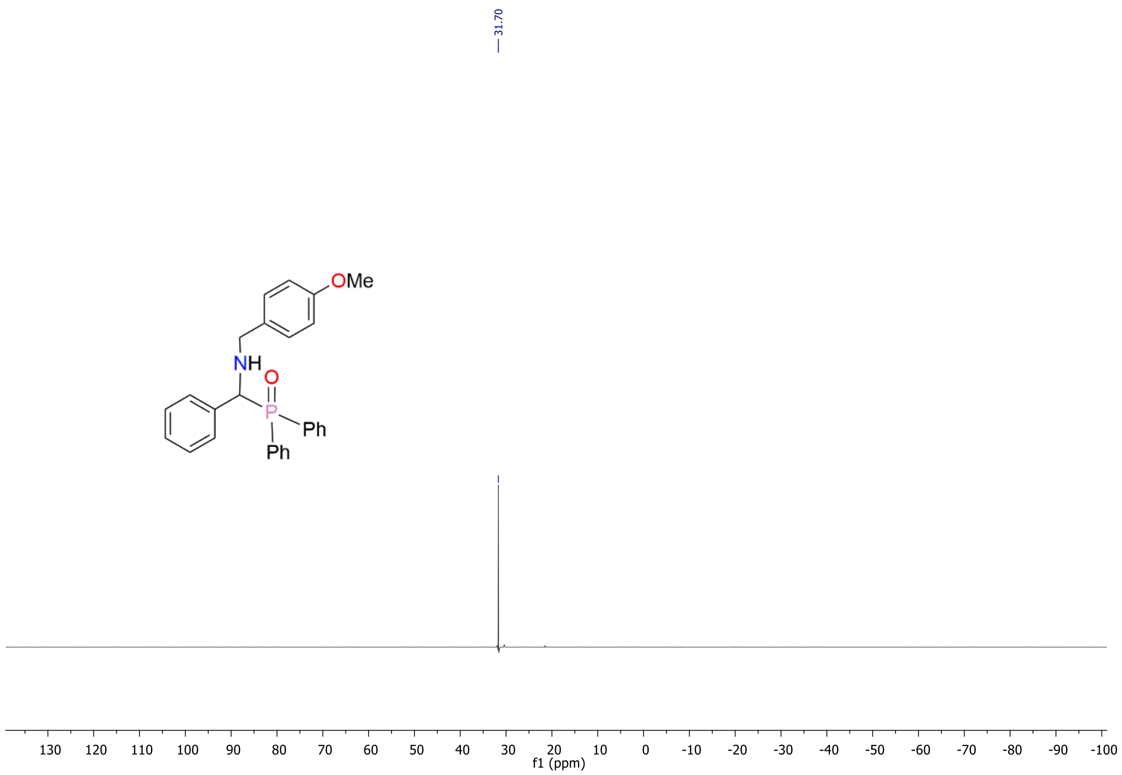


Fig S70. $^{31}P\{^{1}H\}$ NMR spectra of **1v** ($CDCl_3$, 243 MHz).

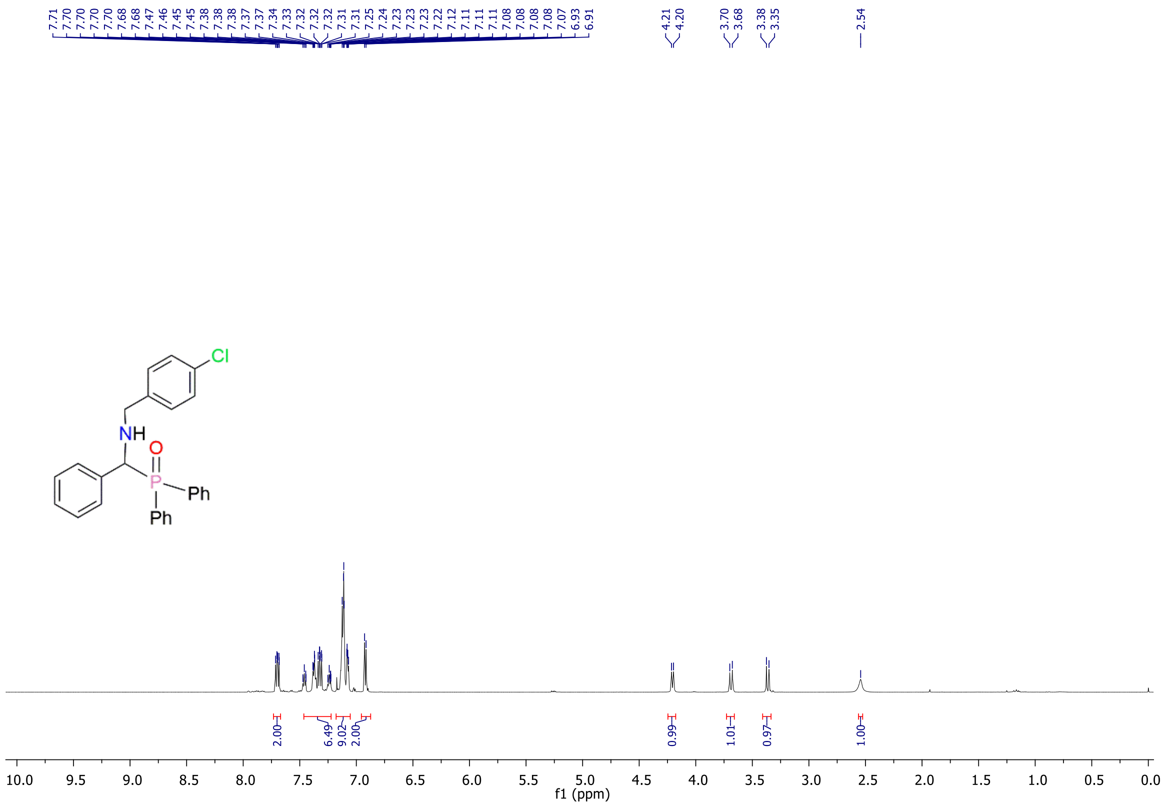


Fig S71. ^{1}H NMR spectra of **1w** ($CDCl_3$, 600 MHz).

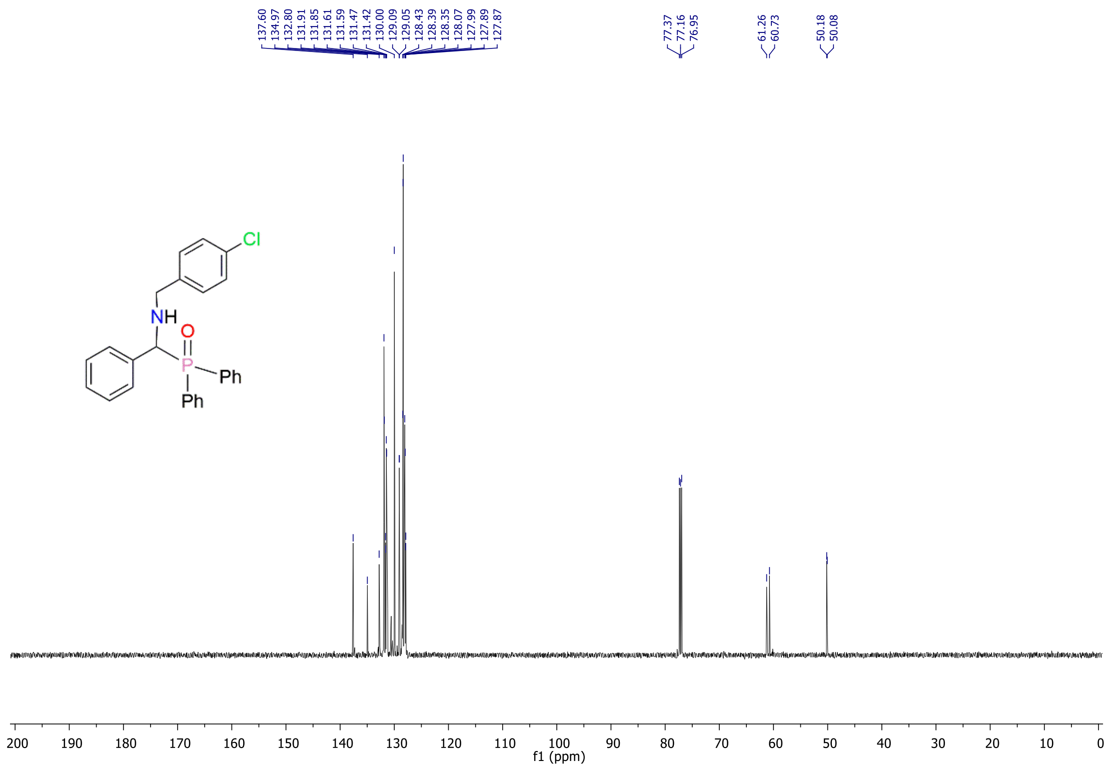


Fig S72. $^{13}C\{^{1}H\}$ NMR spectra of **1w** ($CDCl_3$, 150 MHz).

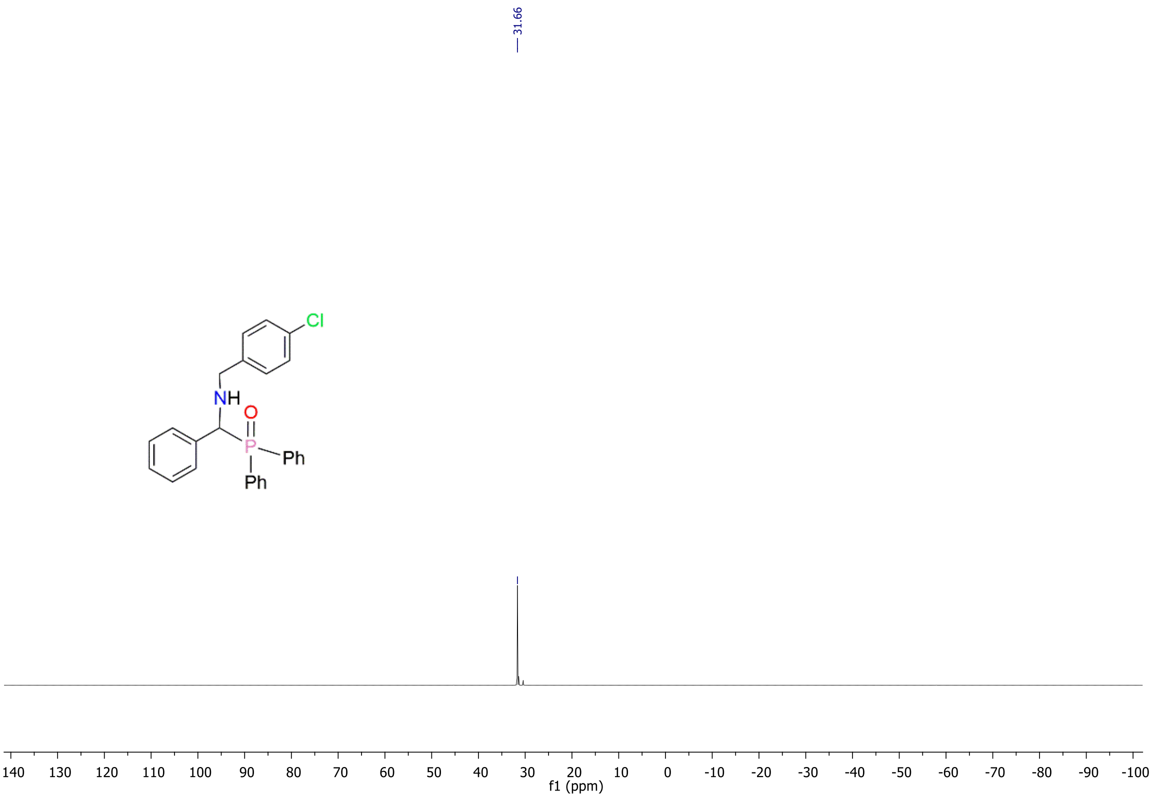


Fig S73. $^{31}P\{^1H\}$ NMR spectra of **1w** ($CDCl_3$, 243 MHz).

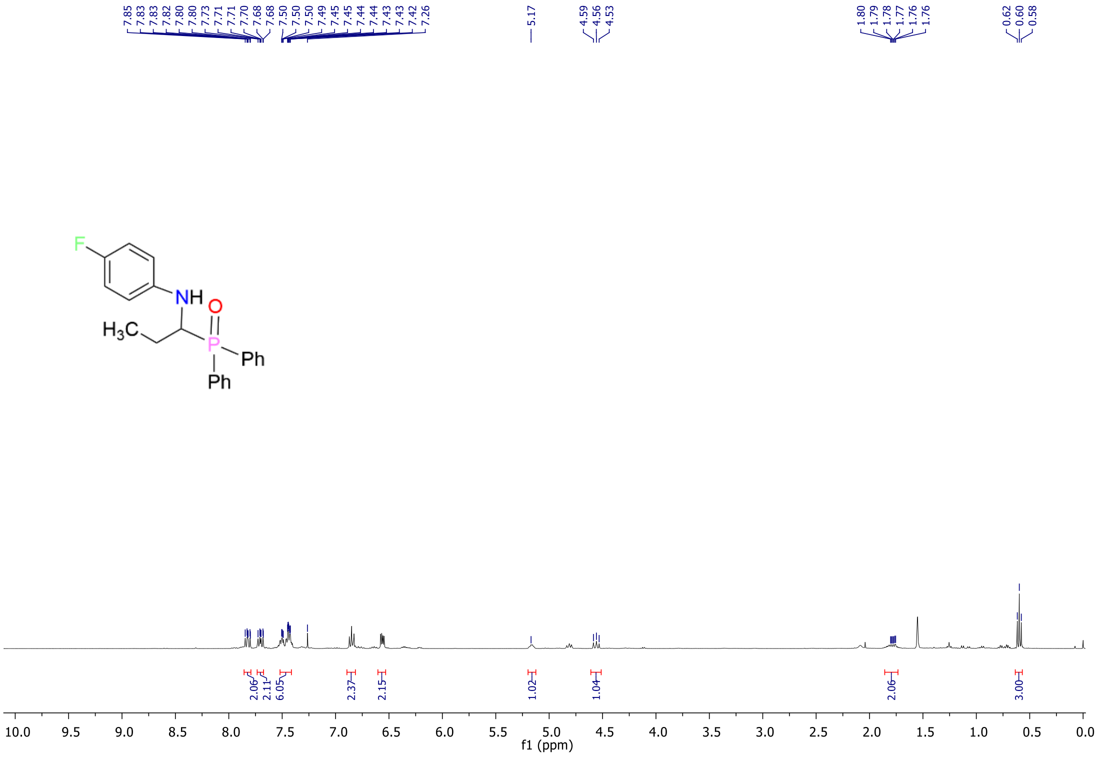


Fig S74. ^1H NMR spectra of **1x** ($CDCl_3$, 400 MHz).

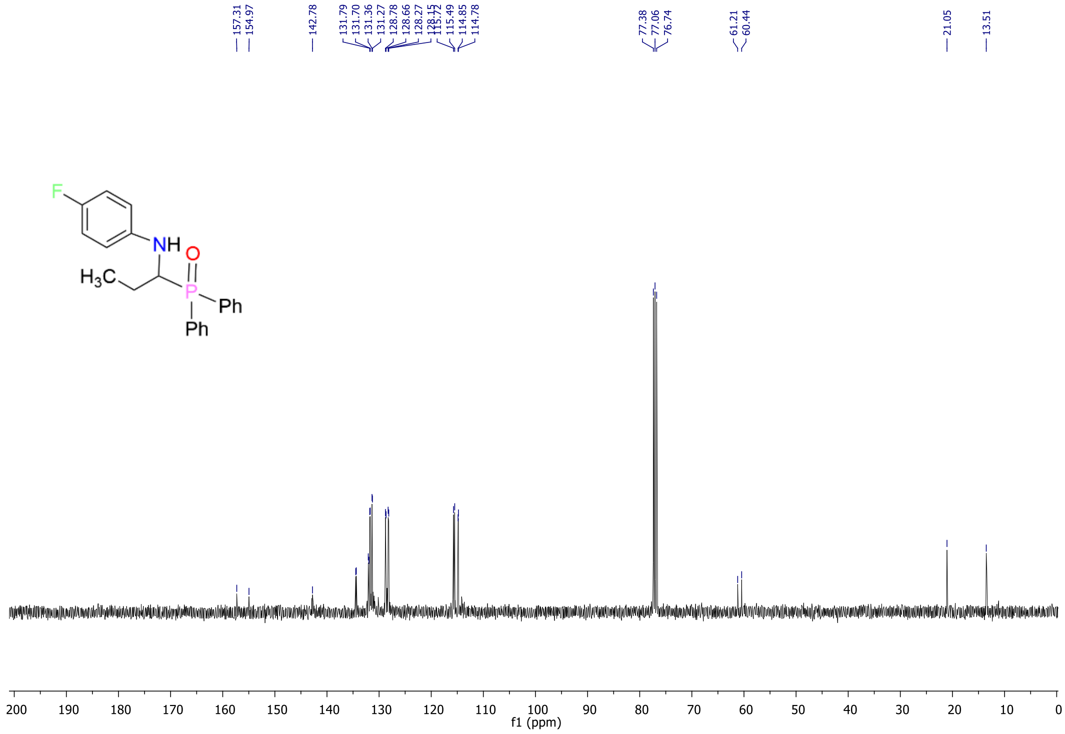


Fig S75. $^{13}C\{^{1}H\}$ NMR spectra of **1x** ($CDCl_3$, 100 MHz).

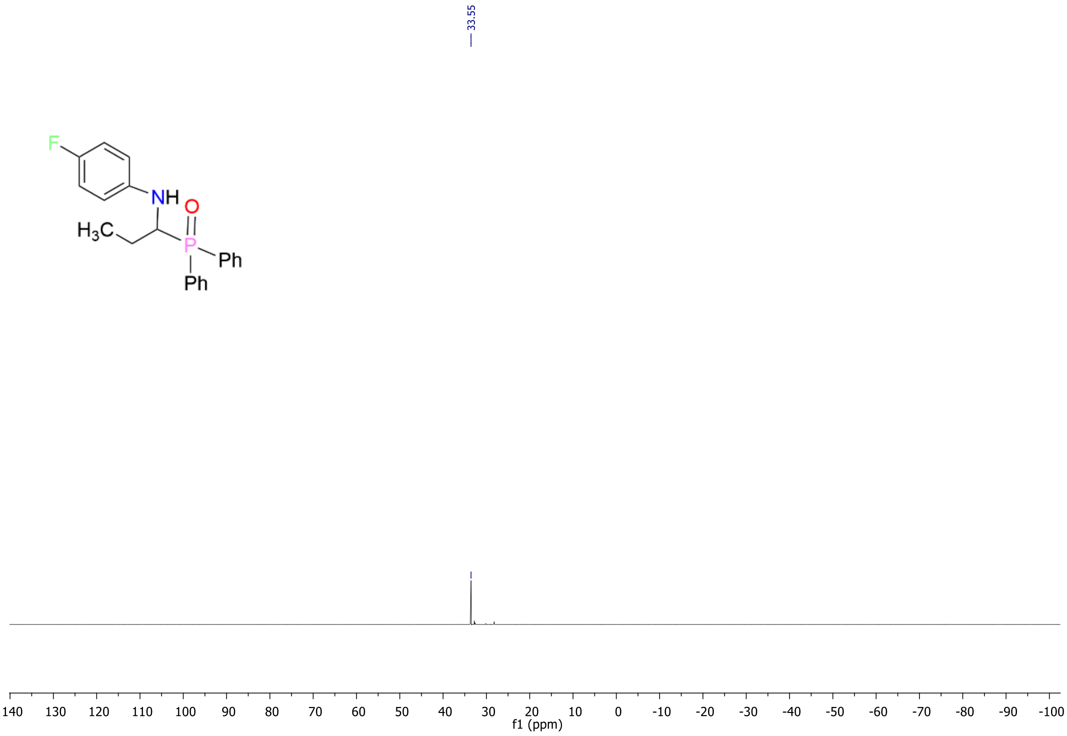


Fig S76. $^{31}P\{^{1}H\}$ NMR spectra of **1x** ($CDCl_3$, 243 MHz).

Fig S77. ^{19}F{^{1}H} NMR spectra of **1x** ($CDCl_3$, 376 MHz).

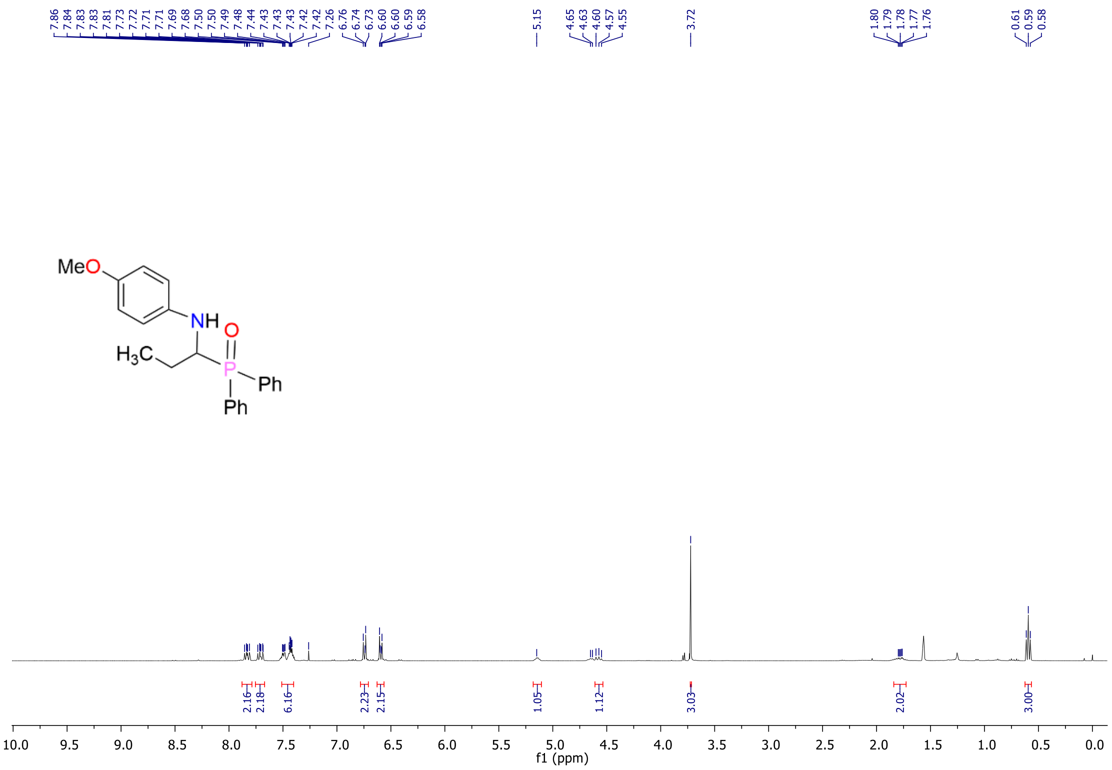


Fig S78. ^{1}H NMR spectra of **1y** ($CDCl_3$, 400 MHz).

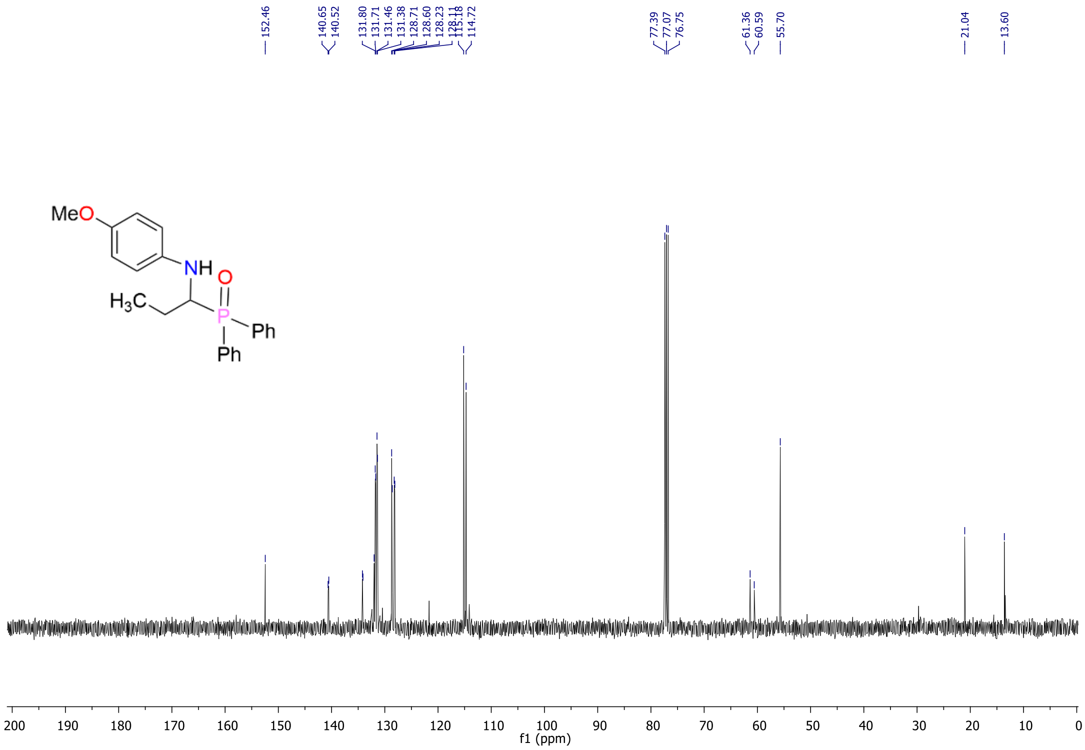


Fig S79. $^{13}C\{^1H\}$ NMR spectra of **1y** ($CDCl_3$, 100 MHz).

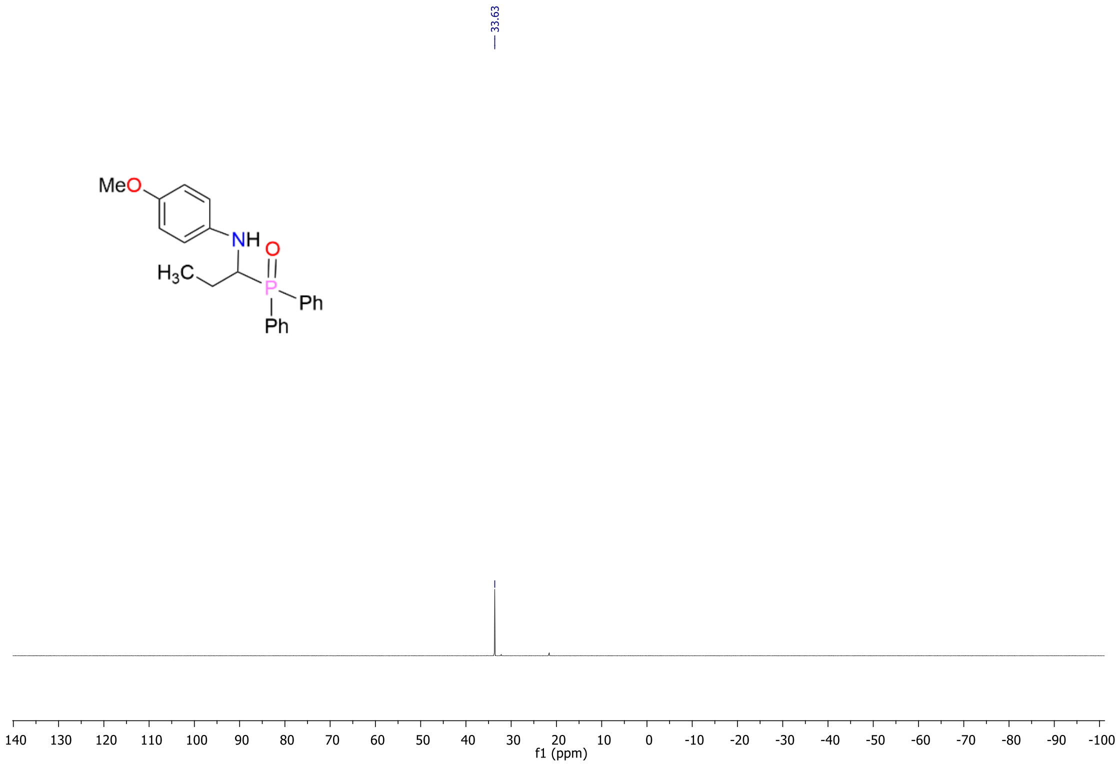


Fig S80. $^{31}P\{^1H\}$ NMR spectra of **1y** ($CDCl_3$, 243 MHz).

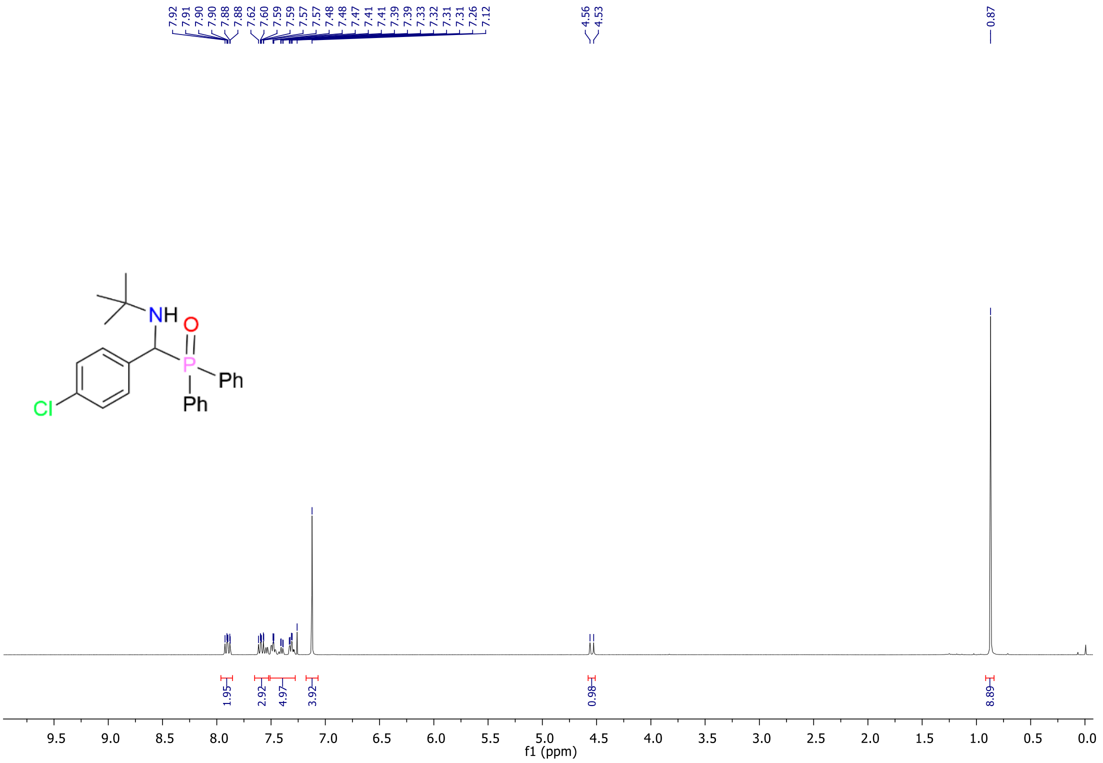


Fig S81. ^{1}H NMR spectra of **1z** ($CDCl_3$, 400 MHz).

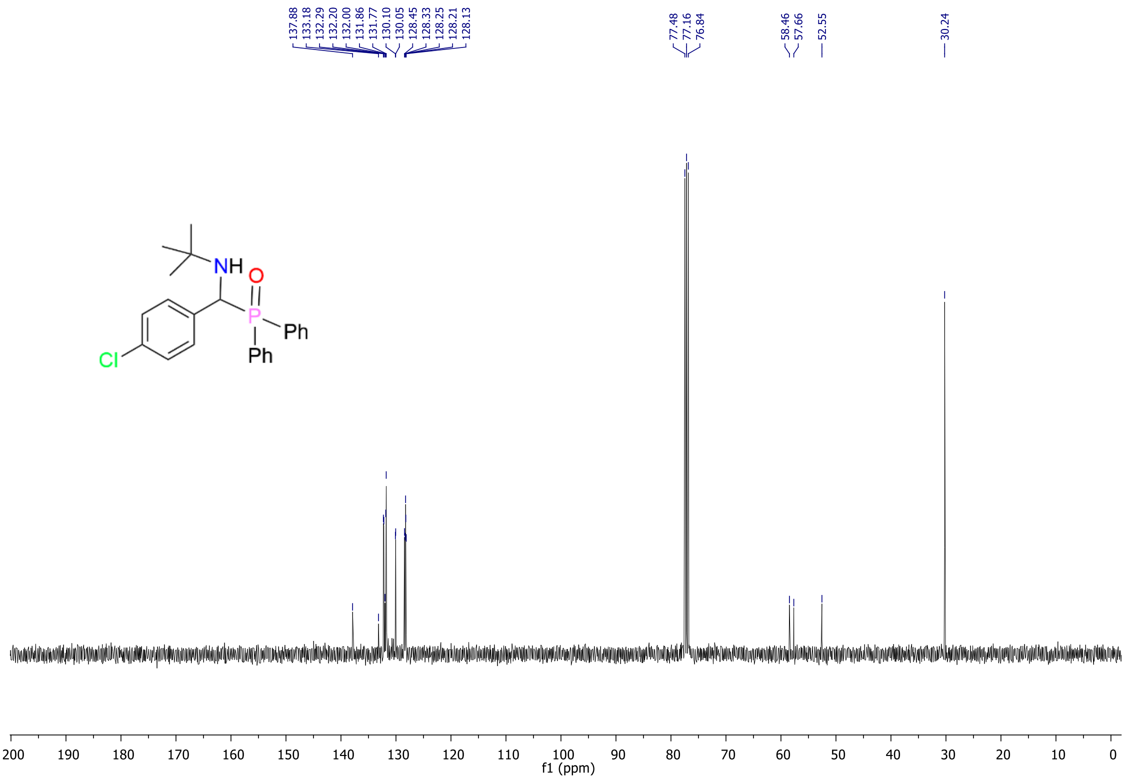


Fig S82. $^{13}C\{^{1}H\}$ NMR spectra of **1z** ($CDCl_3$, 100 MHz).

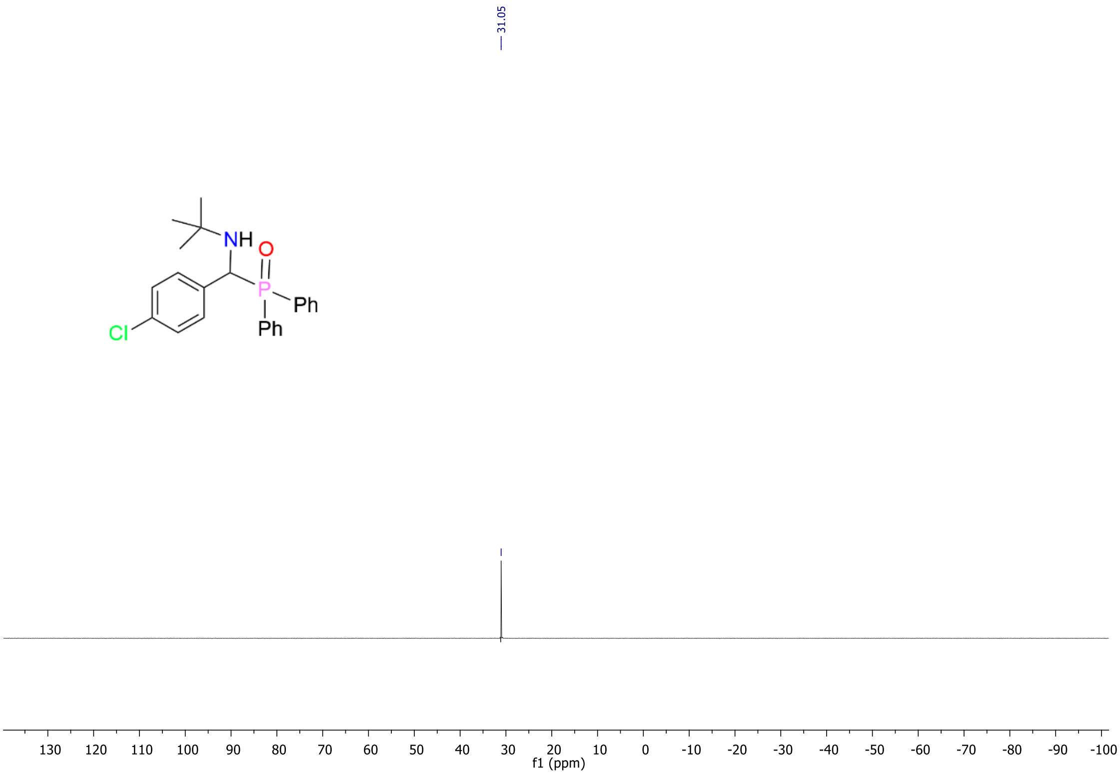


Fig S83. $^{31}P\{^{1}H\}$ NMR spectra of **1z** ($CDCl_3$, 243 MHz).

NMR spectra of α-amino phosphonate derivatives (2a-2q):

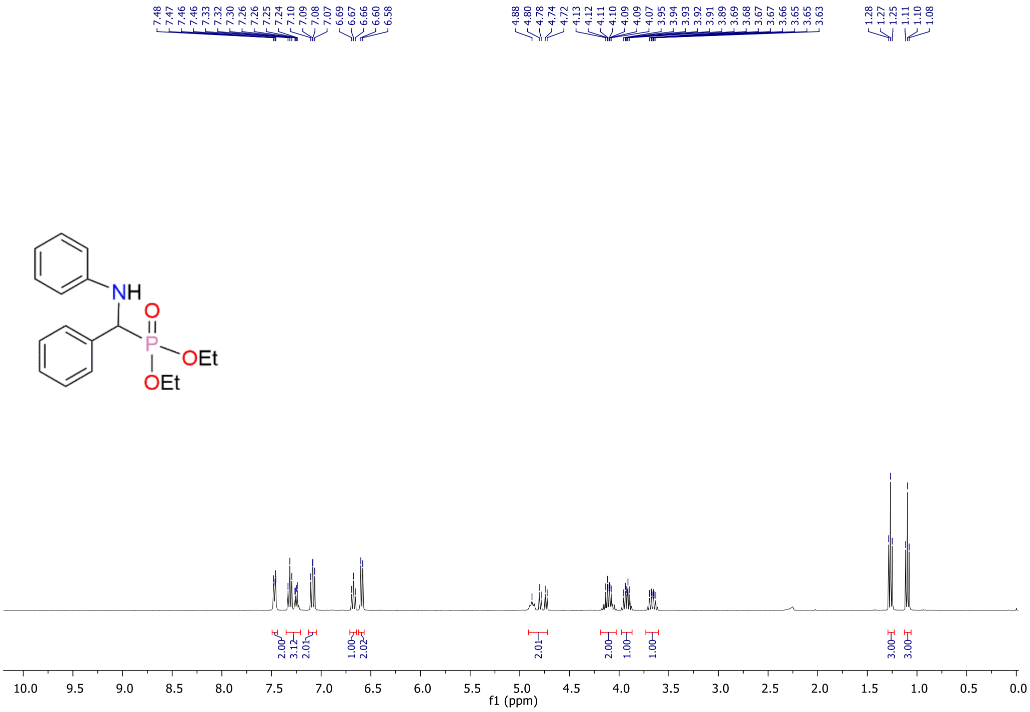


Fig S84. ^{1}H NMR spectra of **2a** ($CDCl_3$, 400 MHz).

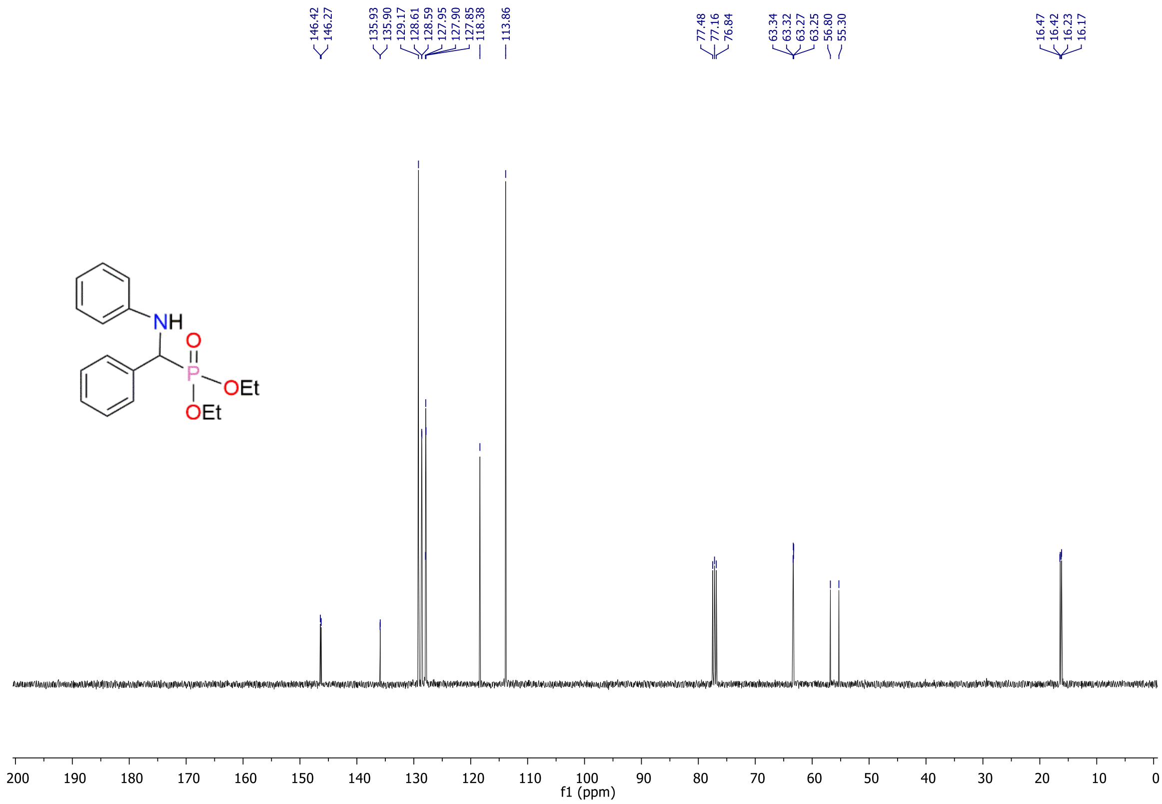


Fig S85. $^{13}C\{^{1}H\}$ NMR spectra of **2a** ($CDCl_3$, 100 MHz).

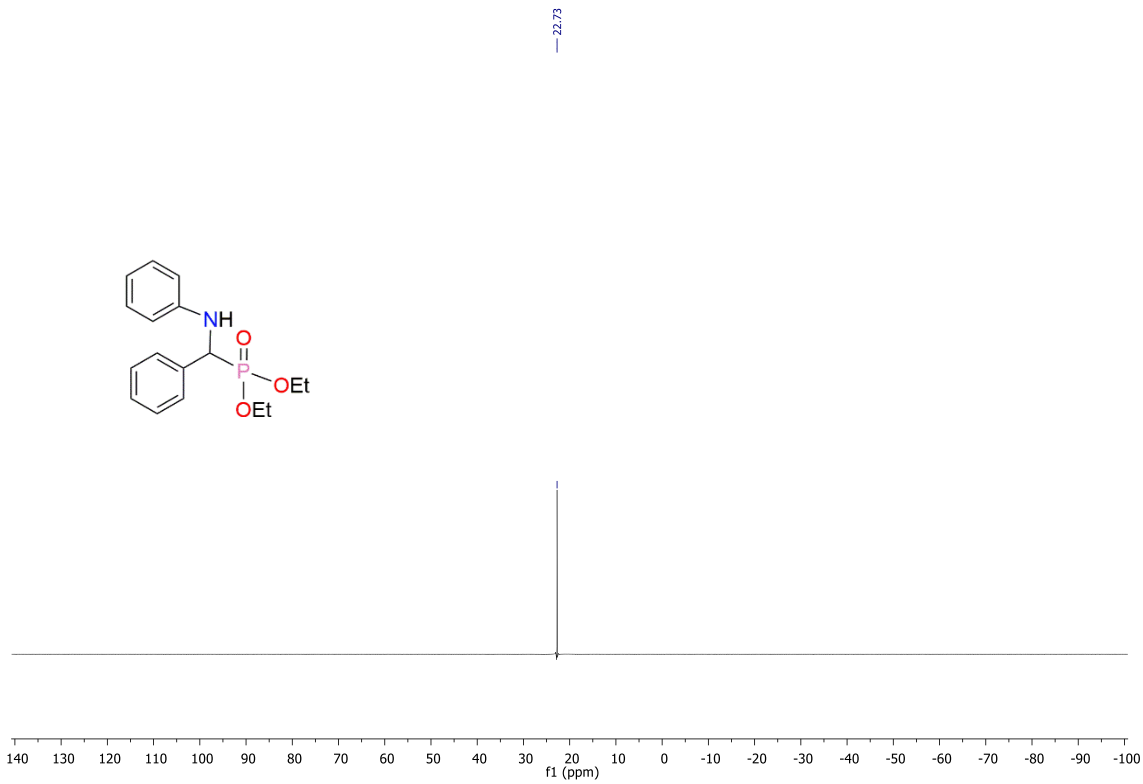


Fig S86. $^{31}P\{^{1}H\}$ NMR spectra of **2a** ($CDCl_3$, 243 MHz).

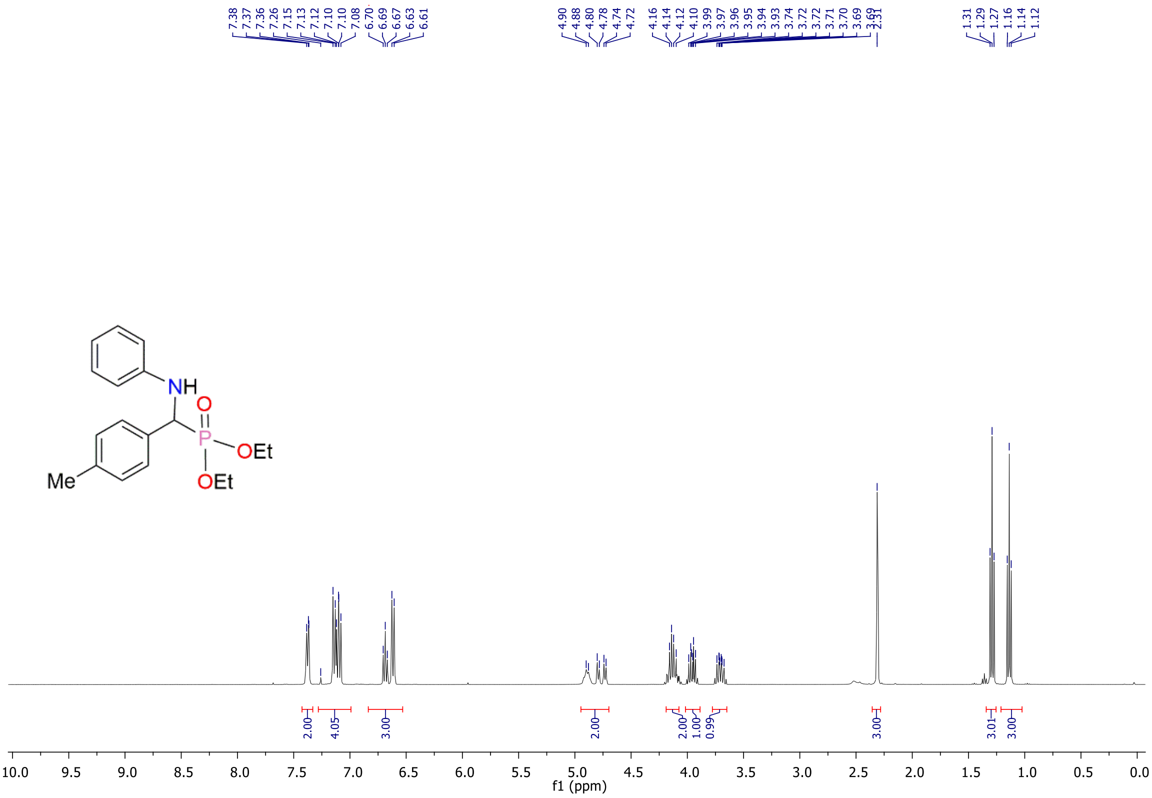


Fig S87. ^{1}H NMR spectra of **2b** ($CDCl_3$, 400 MHz).

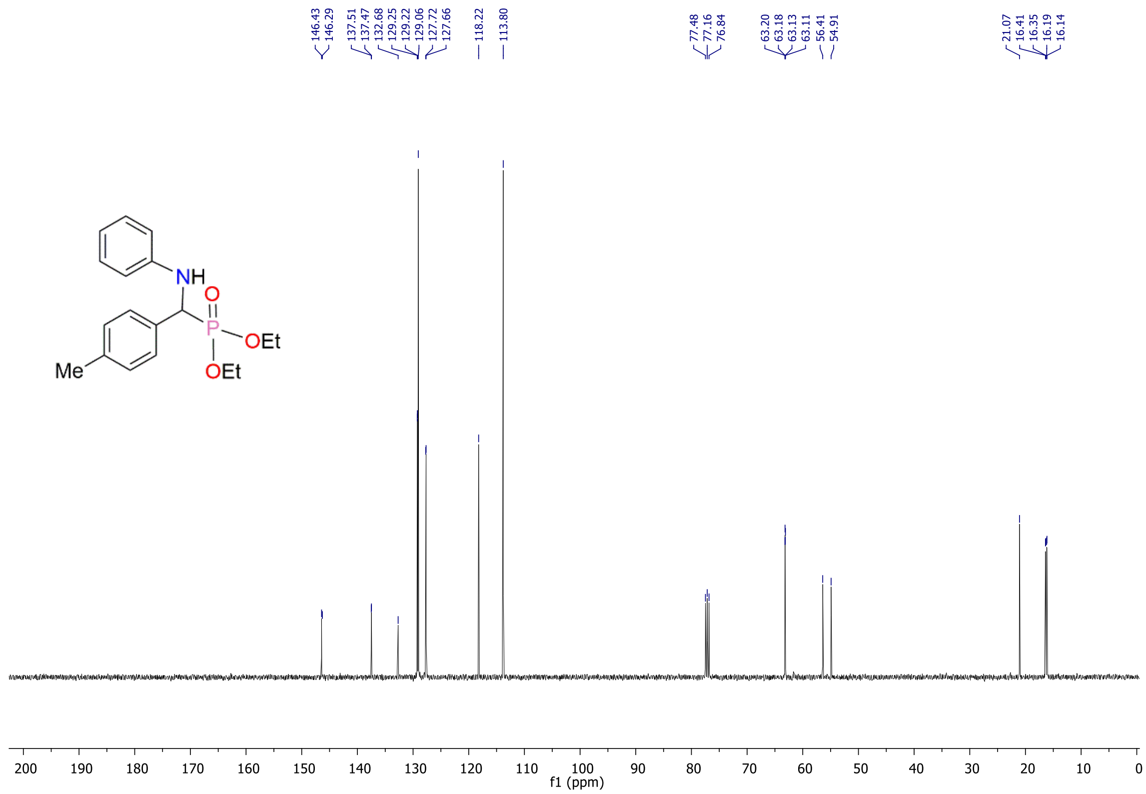


Fig S88. $^{13}C\{^{1}H\}$ NMR spectra of **2b** ($CDCl_3$, 100 MHz).

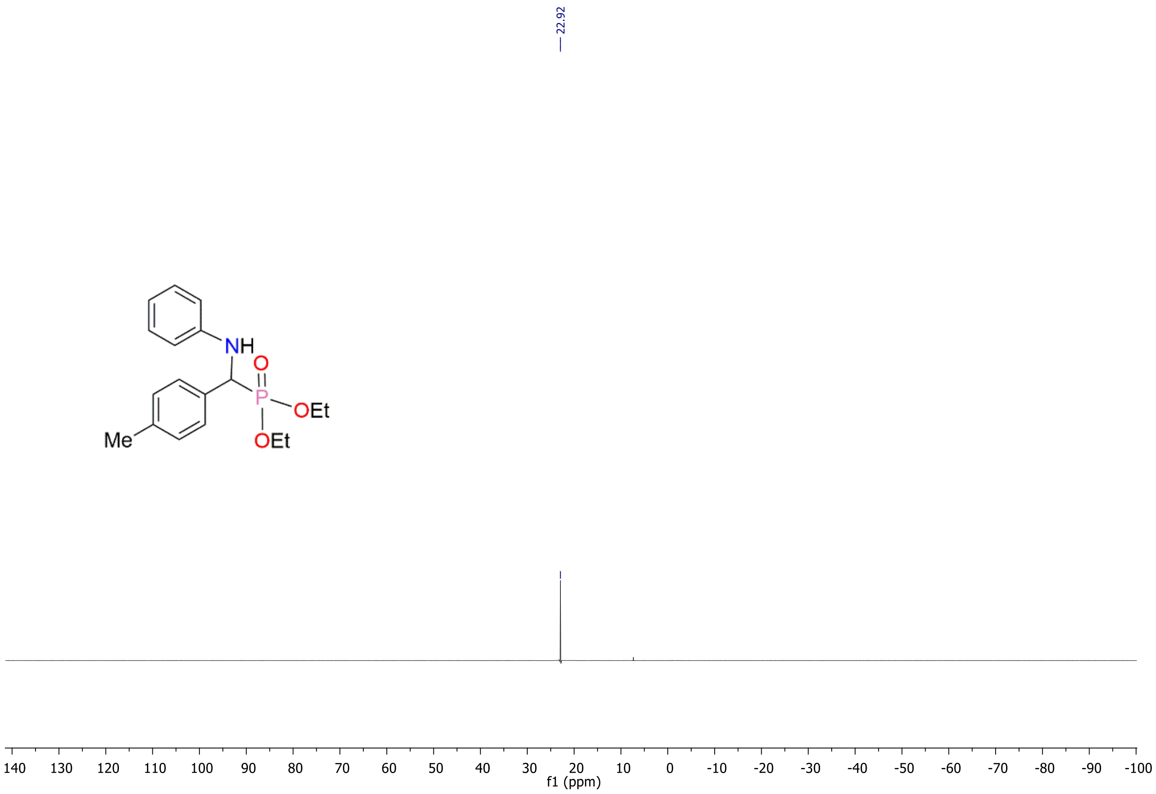


Fig S89. $^{31}P\{^{1}H\}$ NMR spectra of **2b** ($CDCl_3$, 243 MHz).

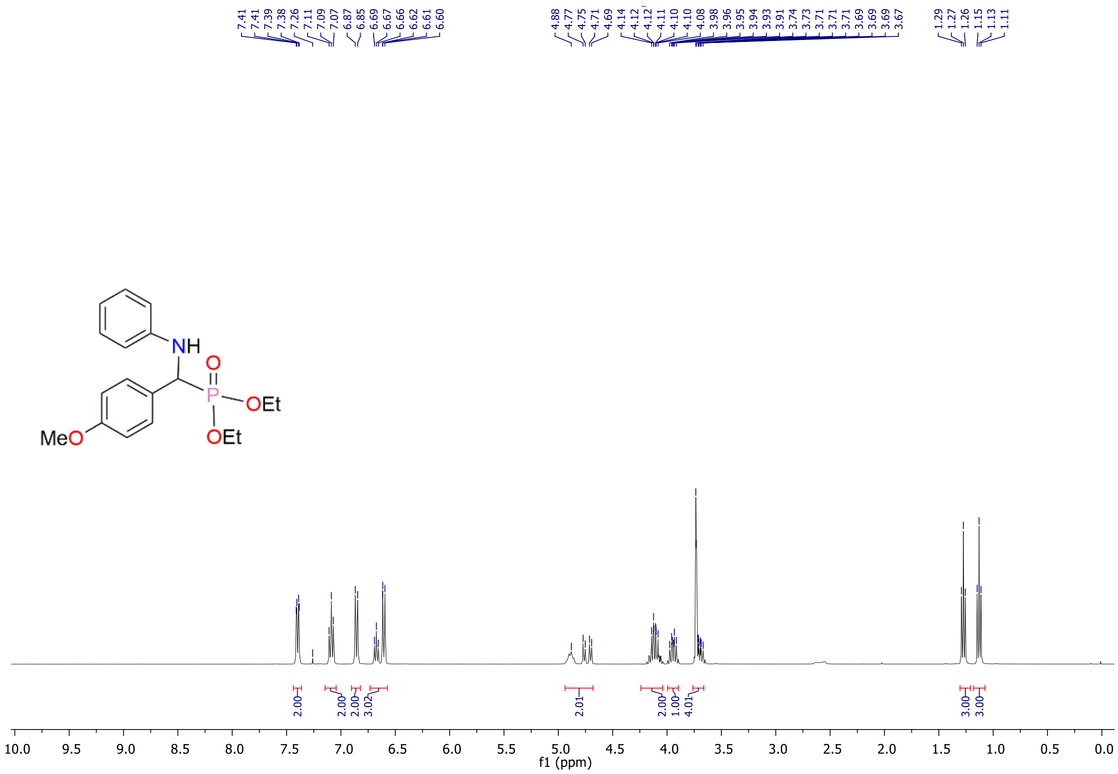


Fig S90. ^{1}H NMR spectra of **2c** ($CDCl_3$, 400 MHz).

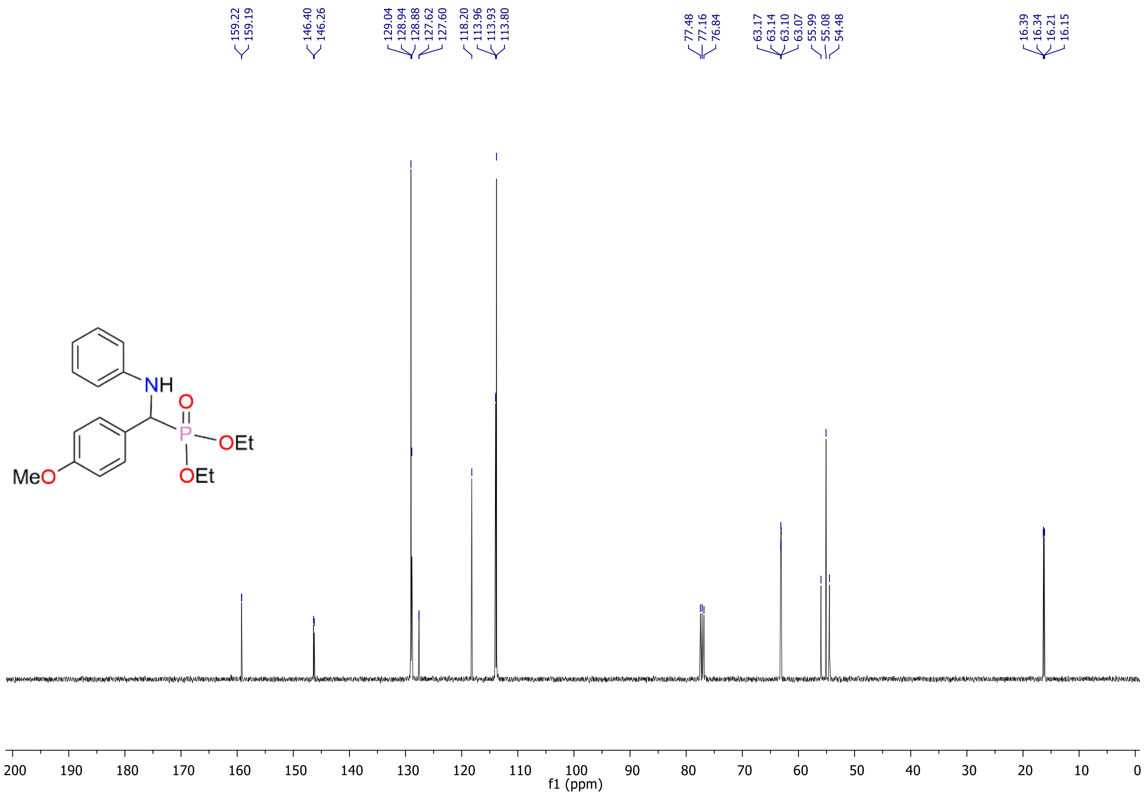


Fig S91. $^{13}C\{^{1}H\}$ NMR spectra of **2c** ($CDCl_3$, 100 MHz).

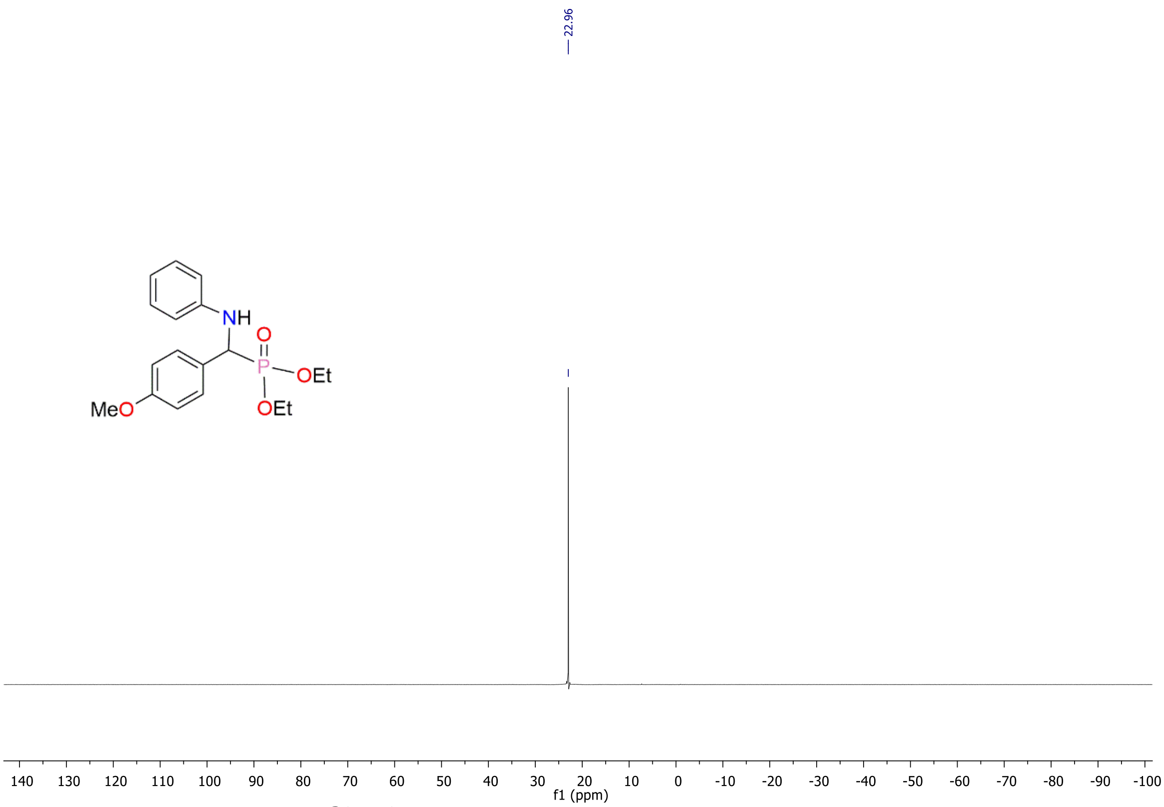


Fig S92. $^{31}P\{^{1}H\}$ NMR spectra of **2c** ($CDCl_3$, 243 MHz).

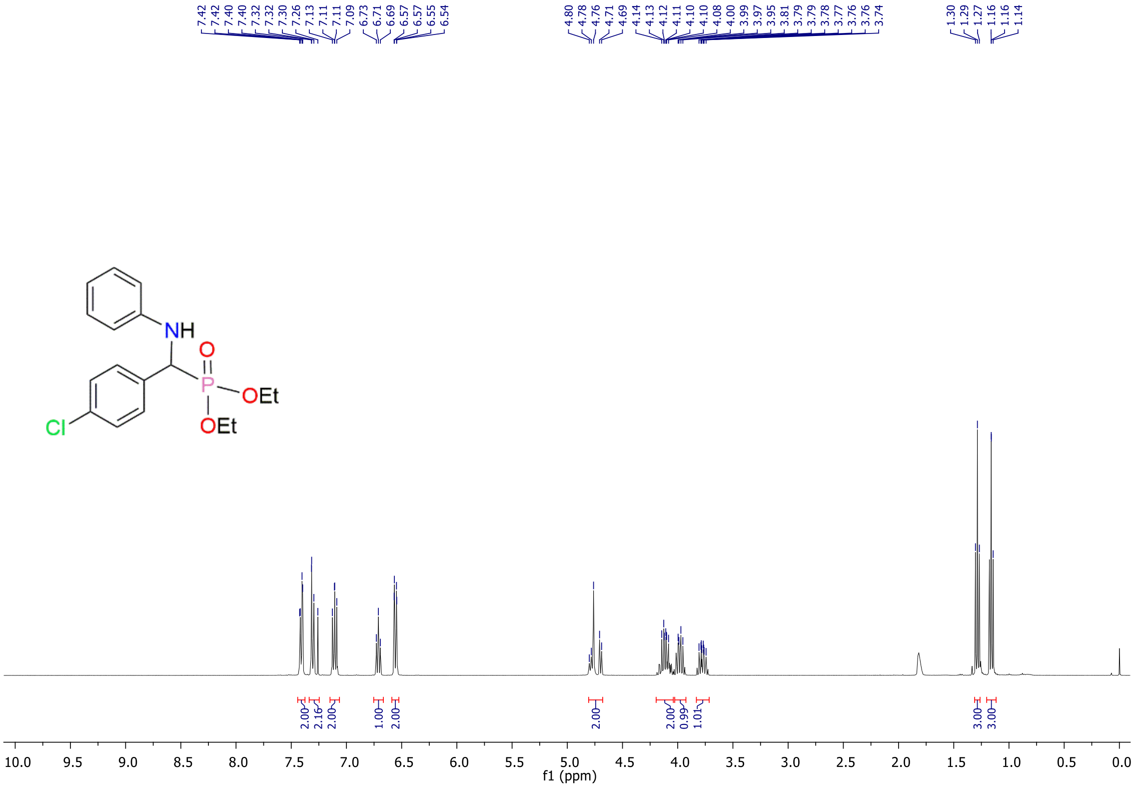


Fig S93. ^{1}H NMR spectra of **2d** ($CDCl_3$, 400 MHz).

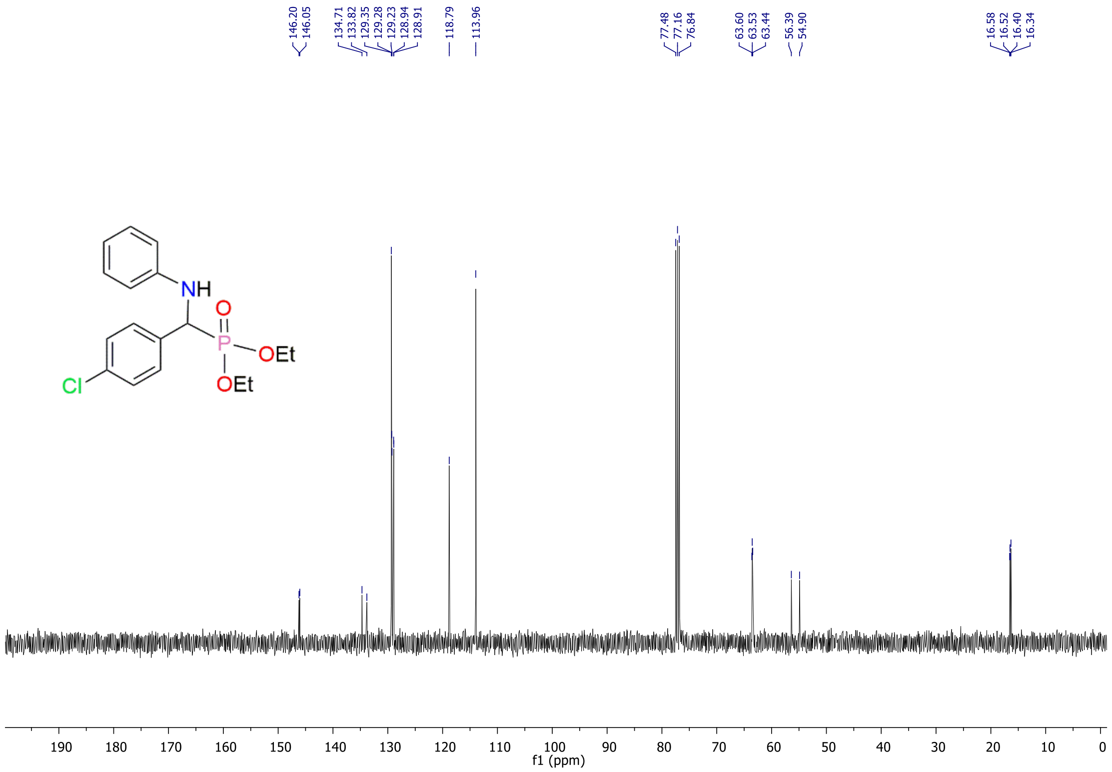


Fig S94. $^{13}C\{^{1}H\}$ NMR spectra of **2d** ($CDCl_3$, 100 MHz).

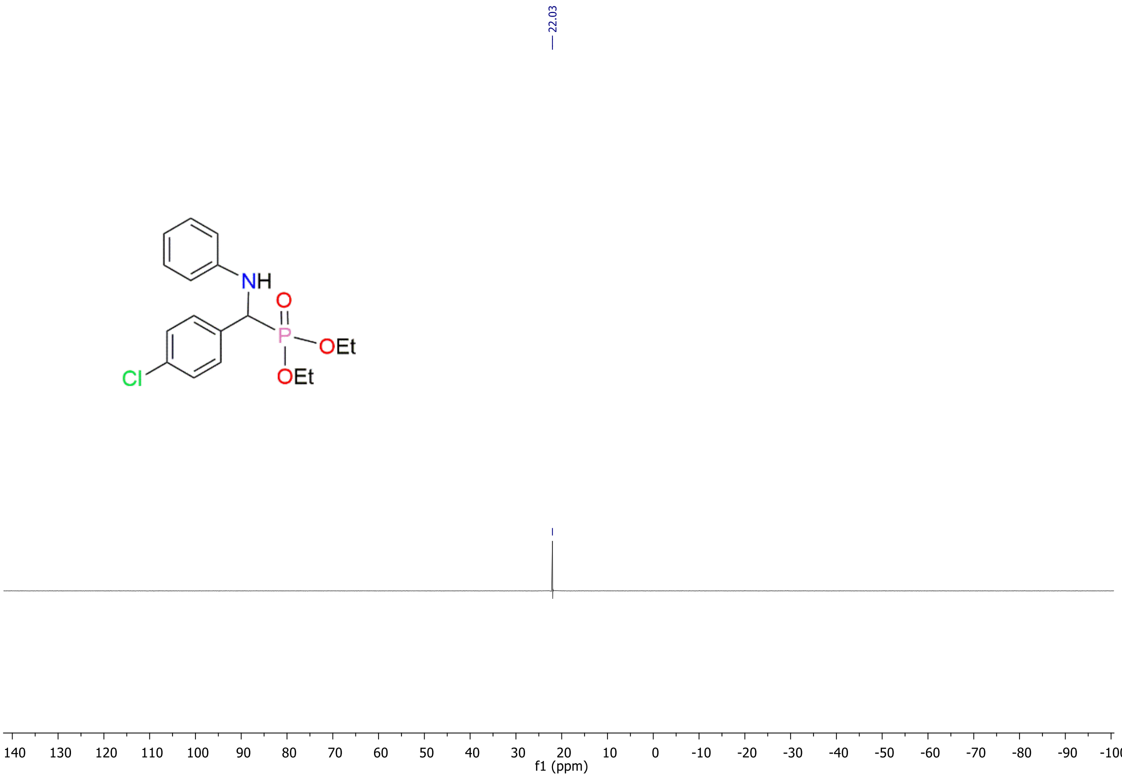


Fig S95. $^{31}P\{^{1}H\}$ NMR spectra of **2d** ($CDCl_3$, 243 MHz).

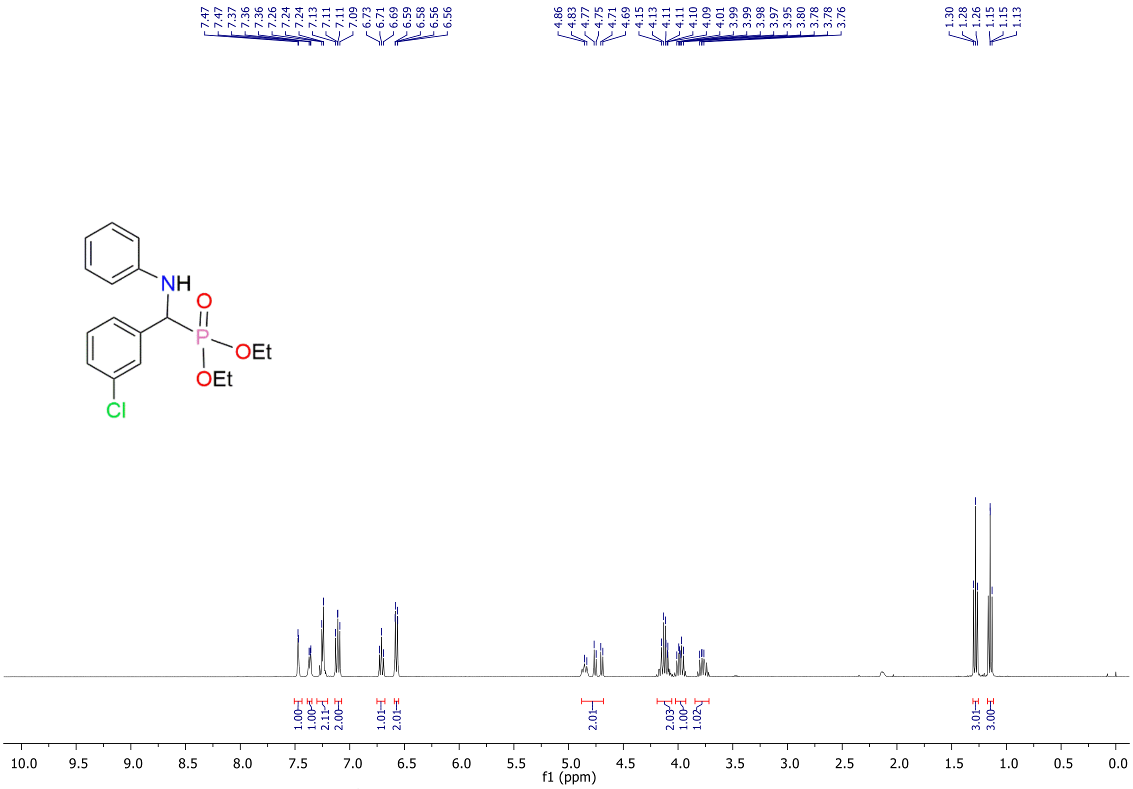


Fig S96. ^{1}H NMR spectra of **2e** ($CDCl_3$, 400 MHz).

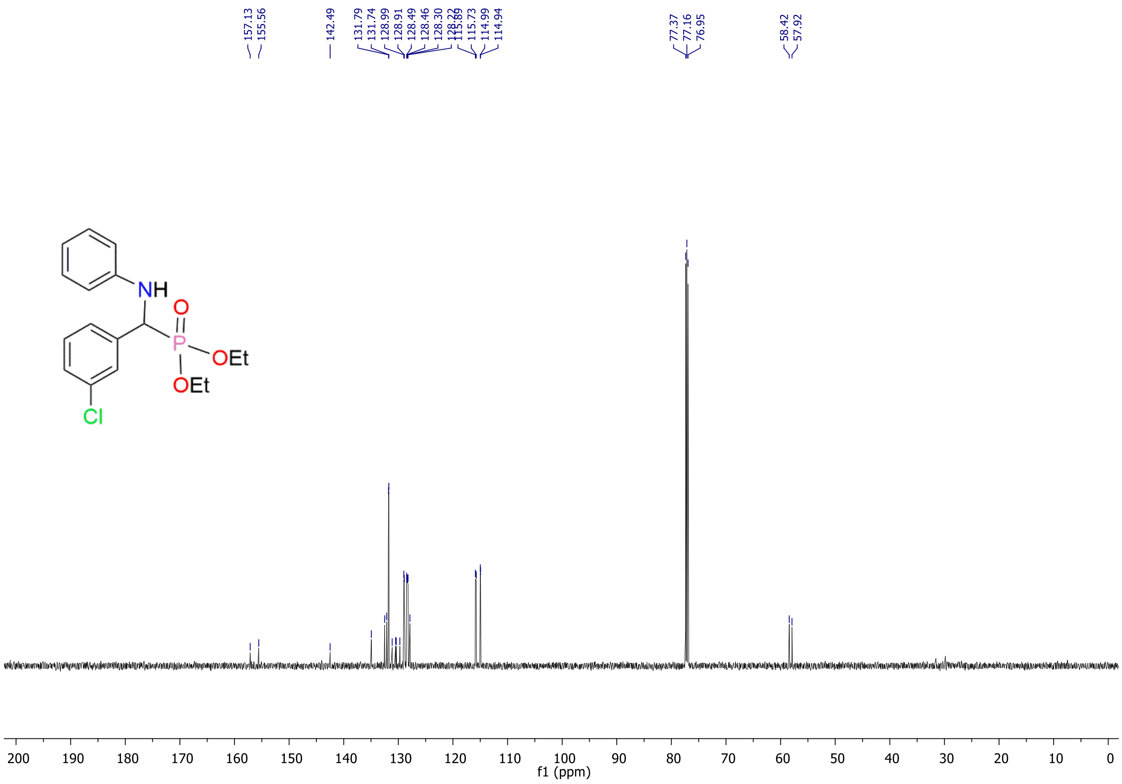


Fig S97. $^{13}C\{^1H\}$ NMR spectra of **2e** ($CDCl_3$, 100 MHz).

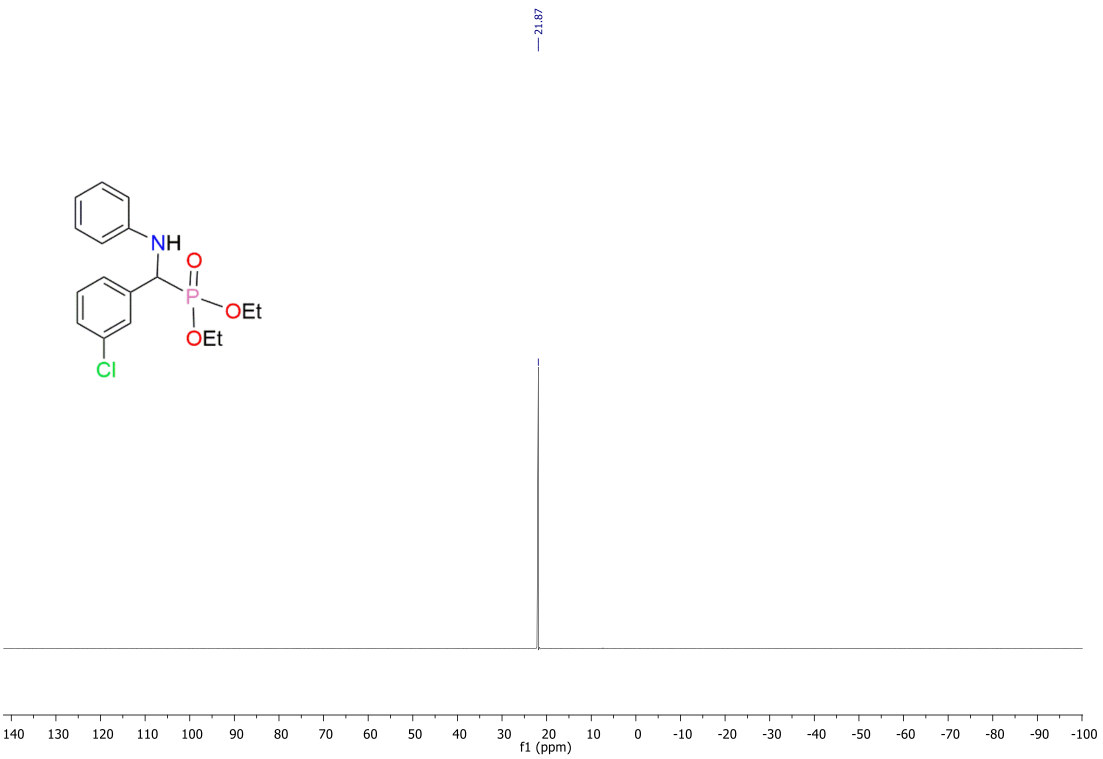


Fig S98. $^{31}P\{^1H\}$ NMR spectra of **2e** ($CDCl_3$, 243 MHz).

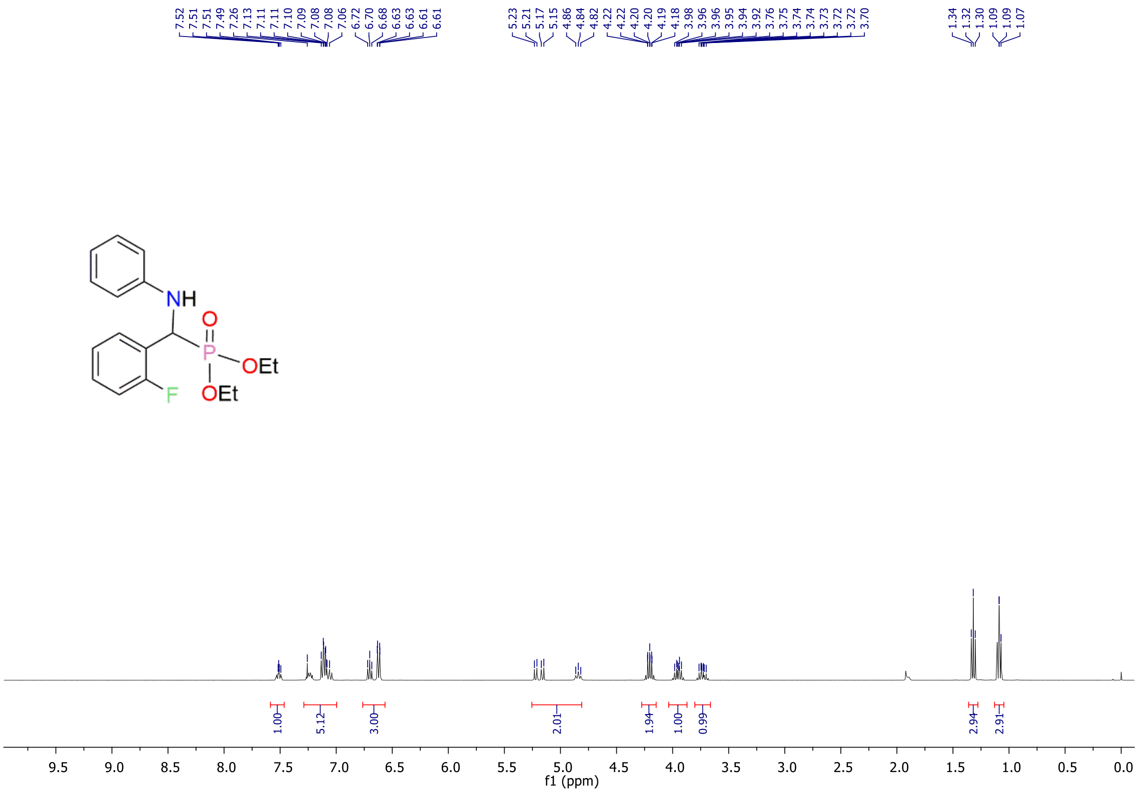


Fig S99. ^{1}H NMR spectra of **2f** ($CDCl_3$, 400 MHz).

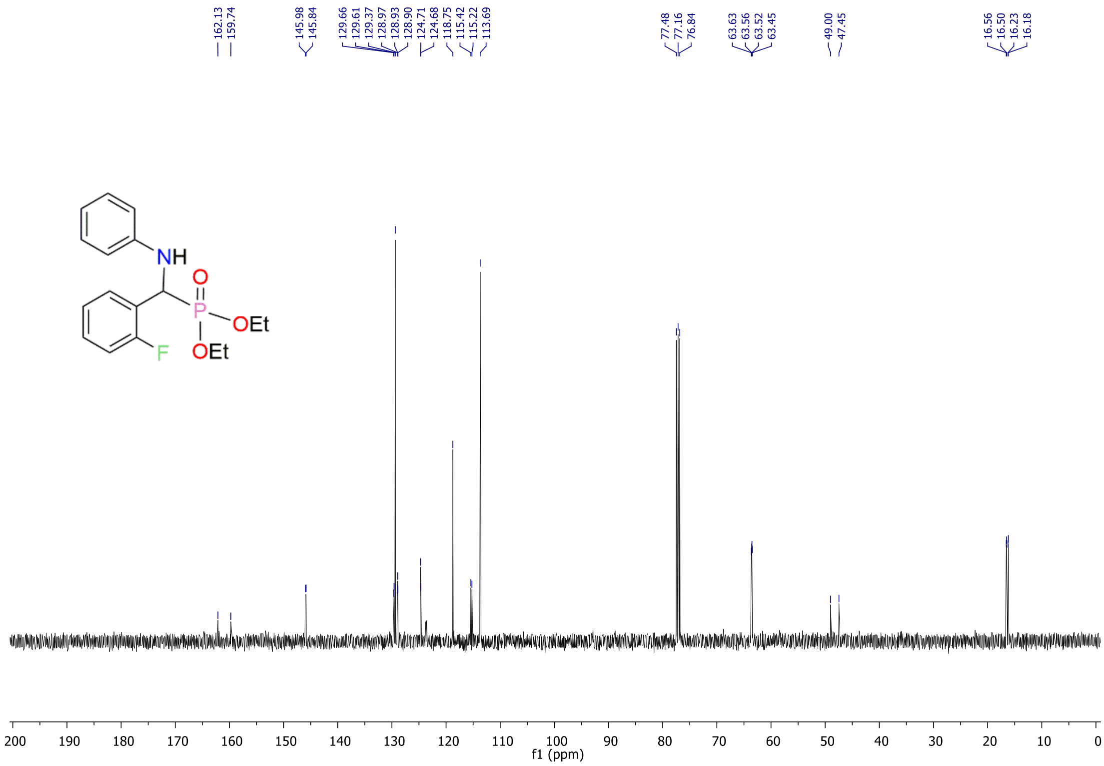


Fig S100. ^{13}C{^{1}H} NMR spectra of **2f** ($CDCl_3$, 100 MHz).

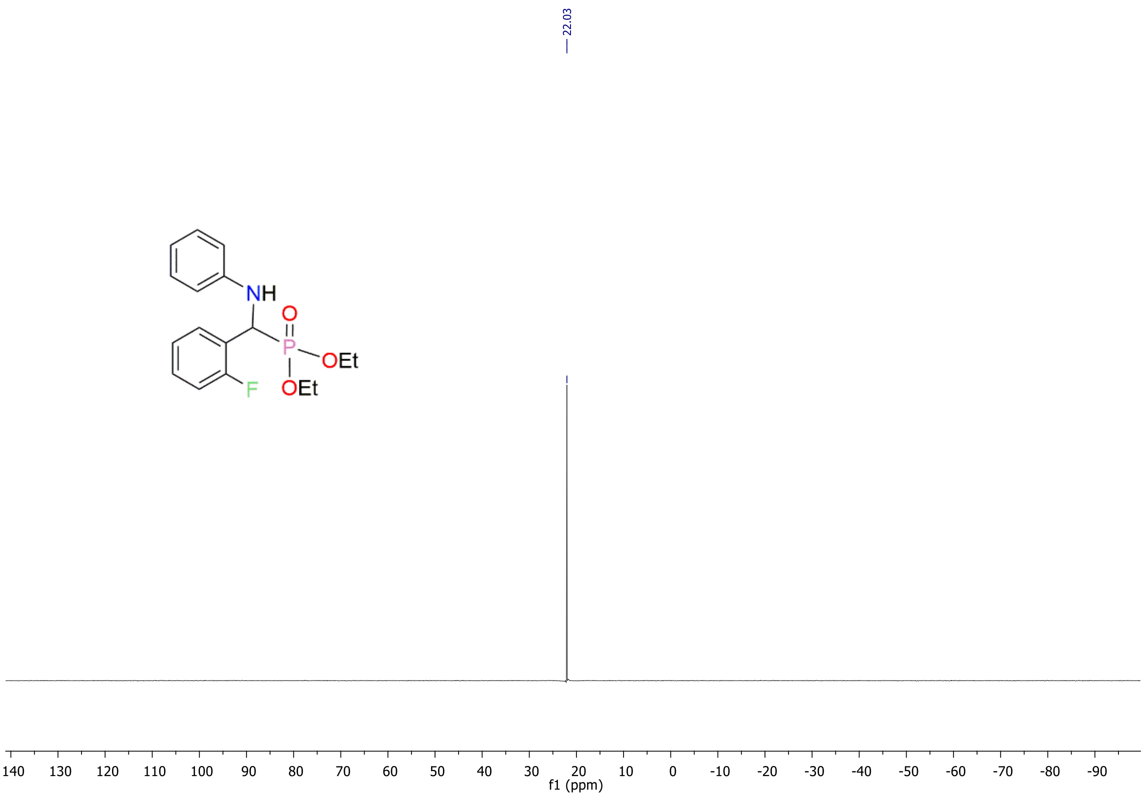


Fig S101. $^{31}P\{^{1}H\}$ NMR spectra of **2f** ($CDCl_3$, 243 MHz).

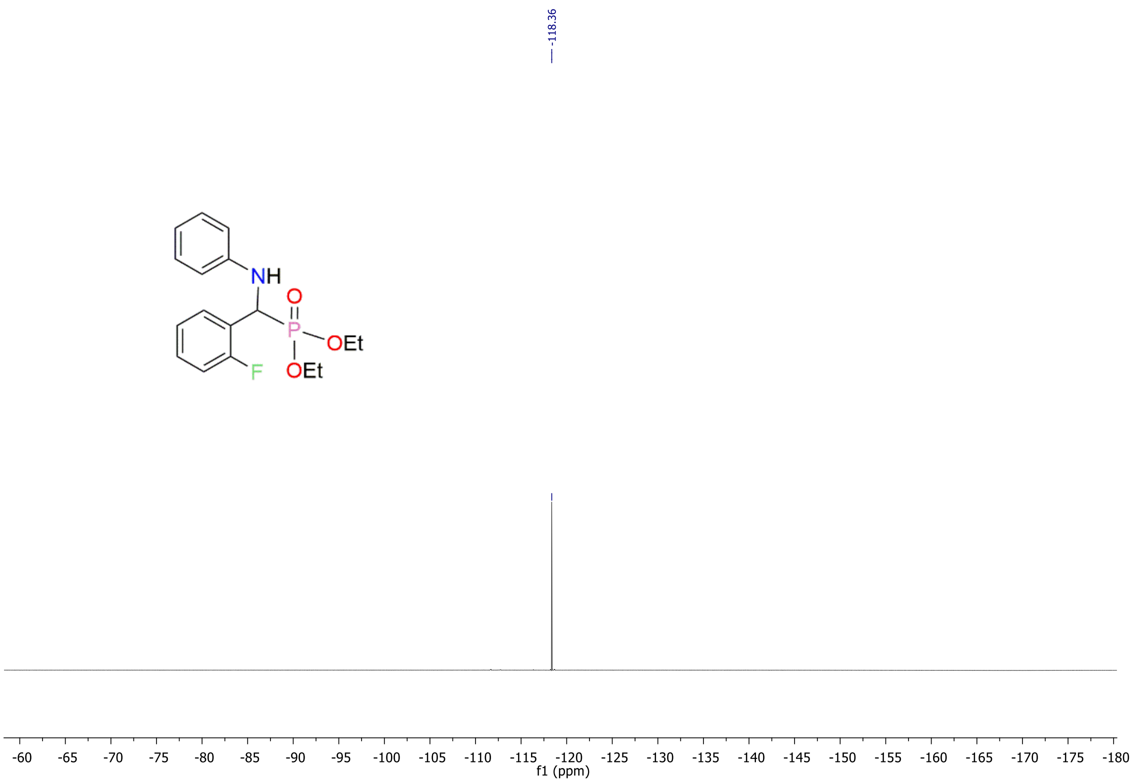


Fig S102. $^{19}F\{^{1}H\}$ NMR spectra of **2f** ($CDCl_3$, 565 MHz).

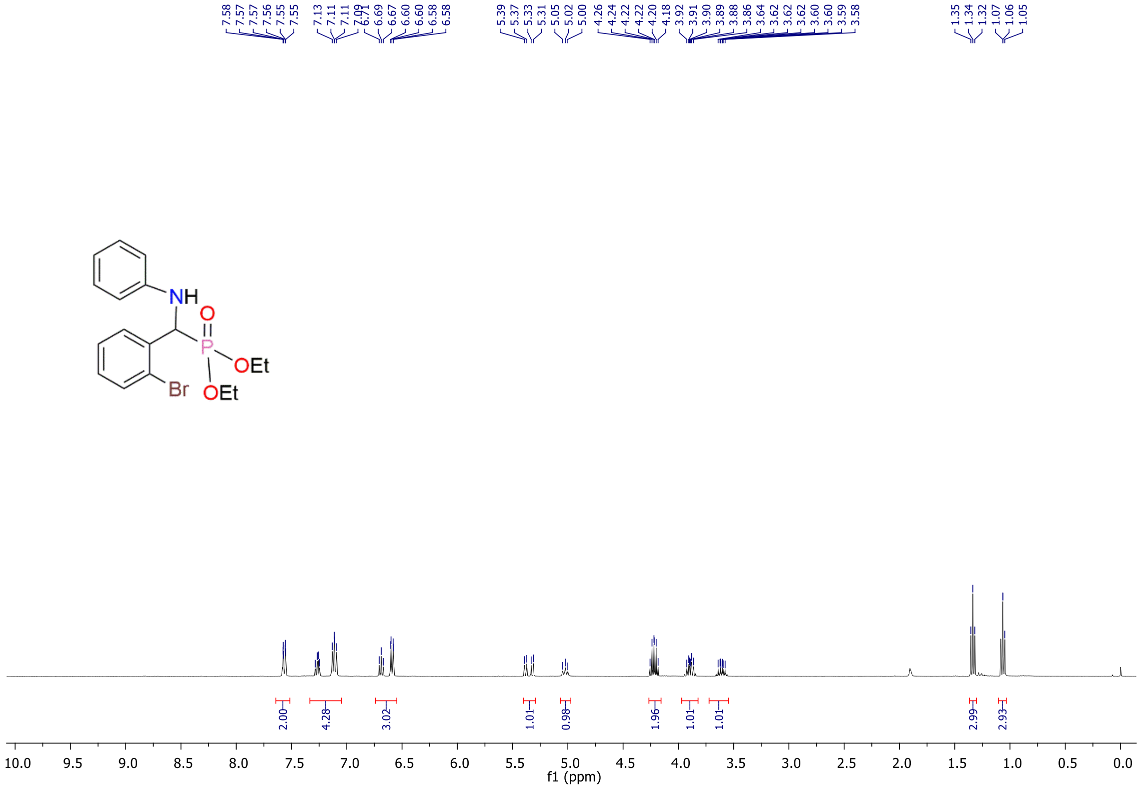


Fig S103. ^{1}H NMR spectra of **2g** ($CDCl_3$, 400 MHz).

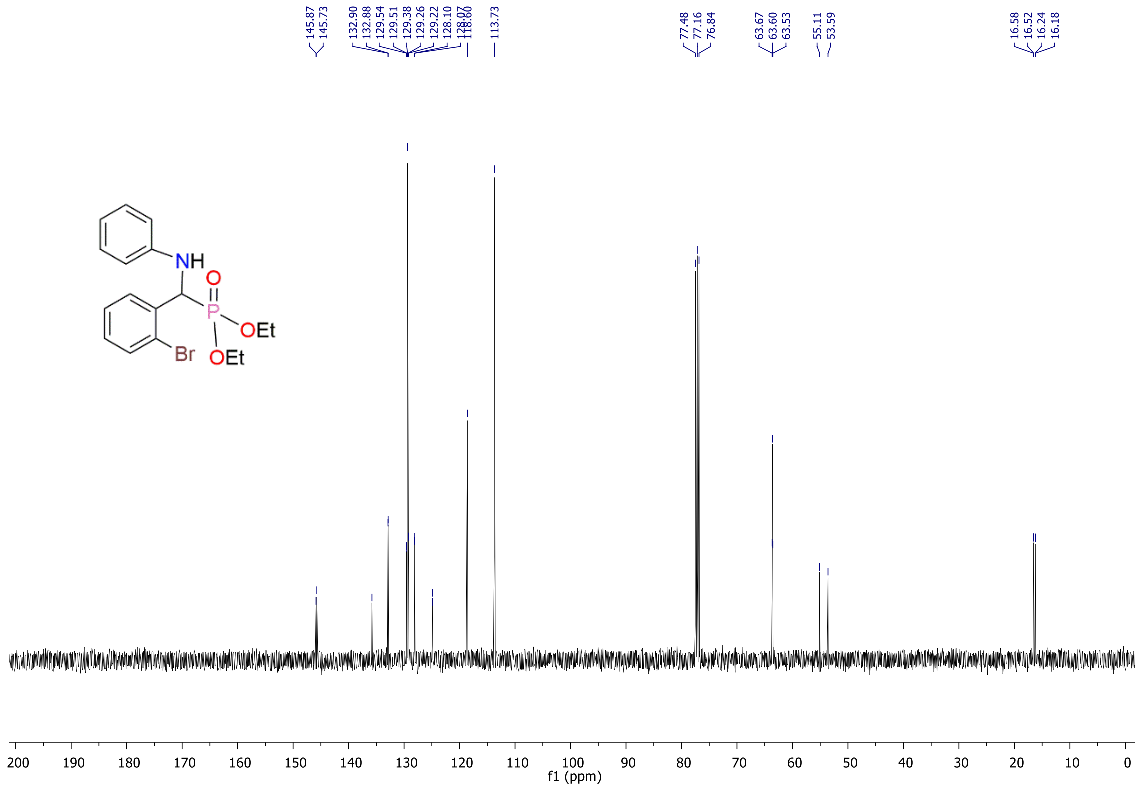


Fig S104. $^{13}C\{^{1}H\}$ NMR spectra of **2g** ($CDCl_3$, 100 MHz).

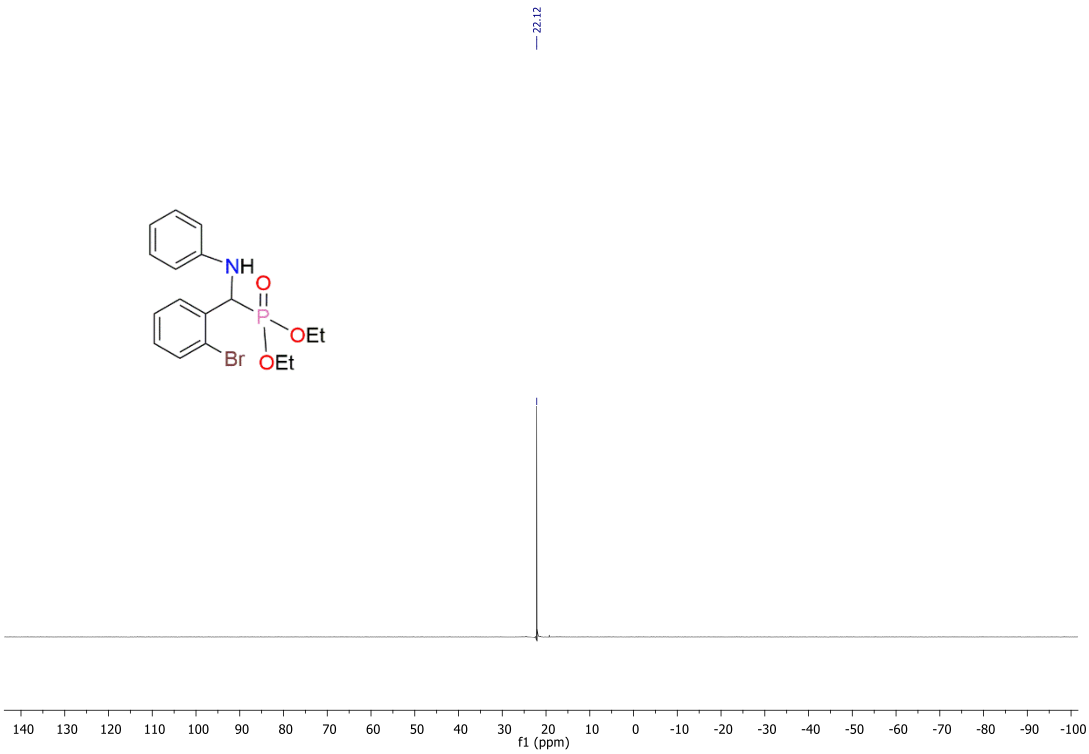


Fig S105. $^{31}P\{^{1}H\}$ NMR spectra of **2g** ($CDCl_3$, 243 MHz).

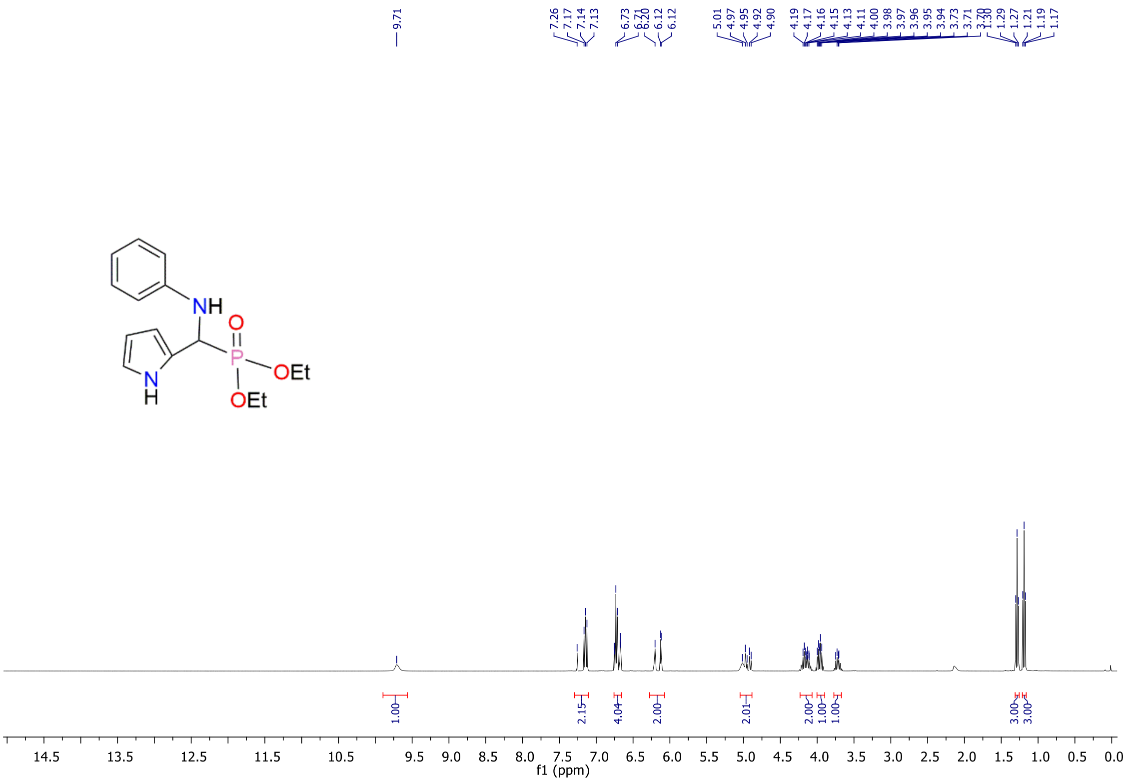


Fig S106. ^{1}H NMR spectra of **2h** ($CDCl_3$, 400 MHz).

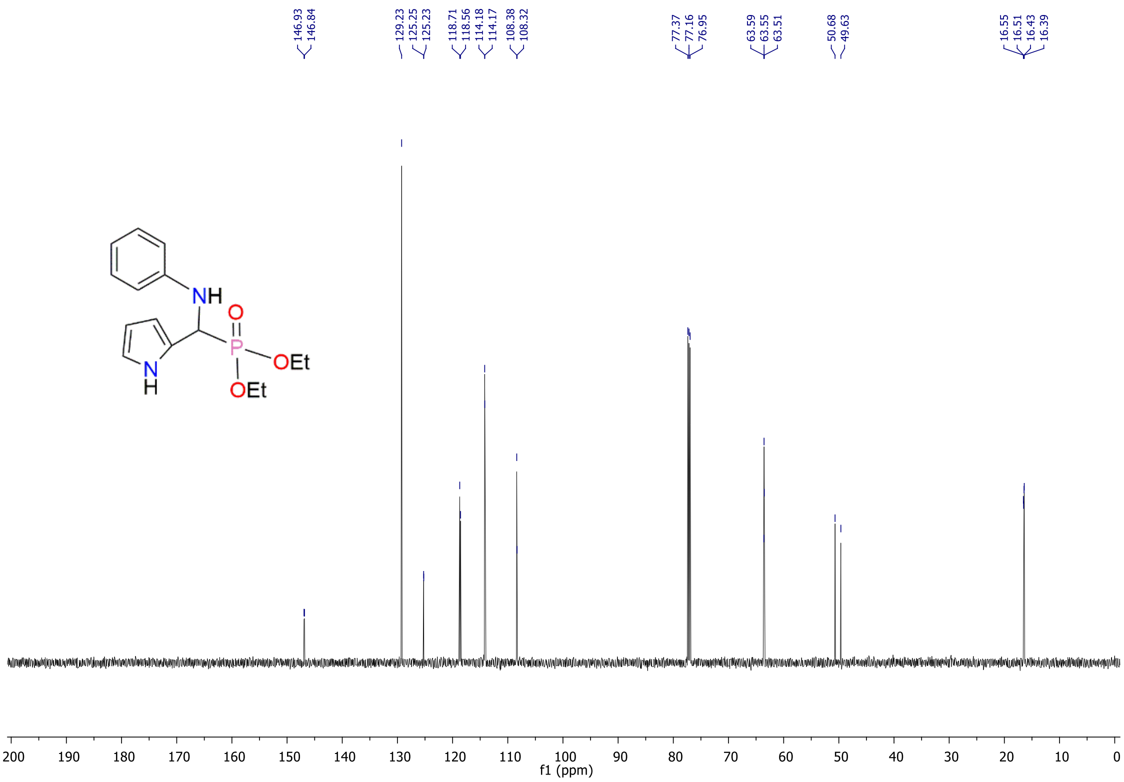


Fig S107. $^{13}C\{^1H\}$ NMR spectra of **2h** ($CDCl_3$, 100 MHz).

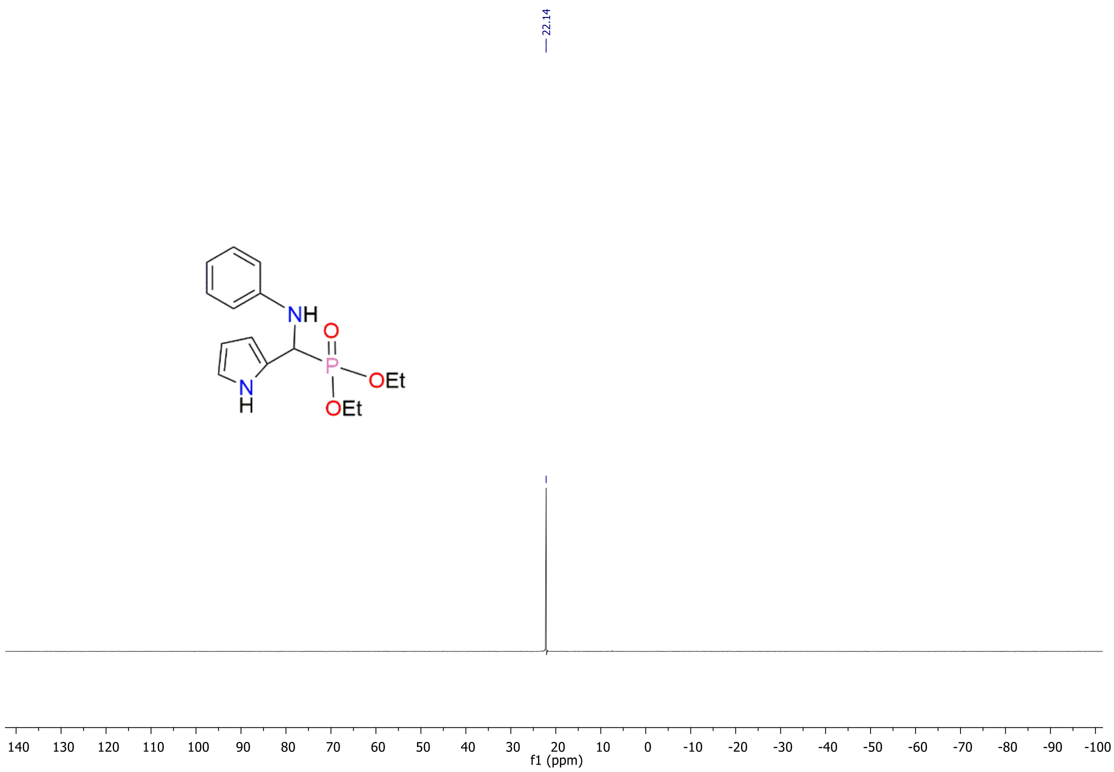


Fig S108. $^{31}P\{^1H\}$ NMR spectra of **2h** ($CDCl_3$, 243 MHz).

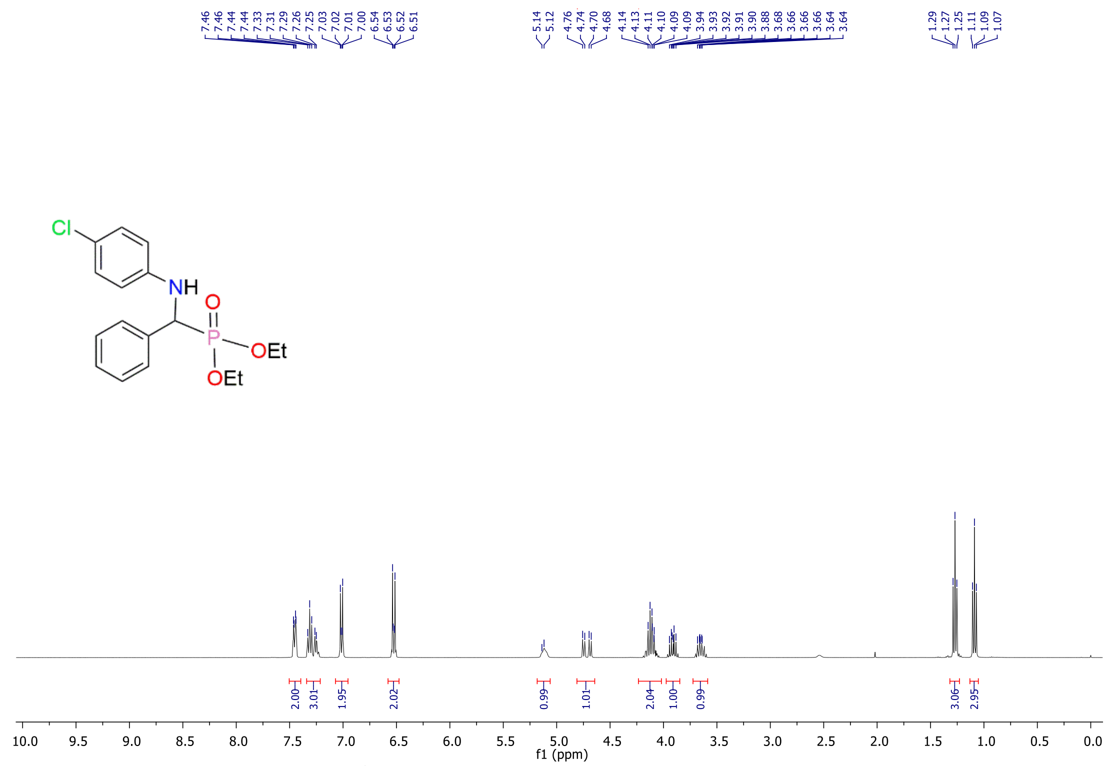


Fig S109. ^{1}H NMR spectra of **2i** ($CDCl_3$, 400 MHz).

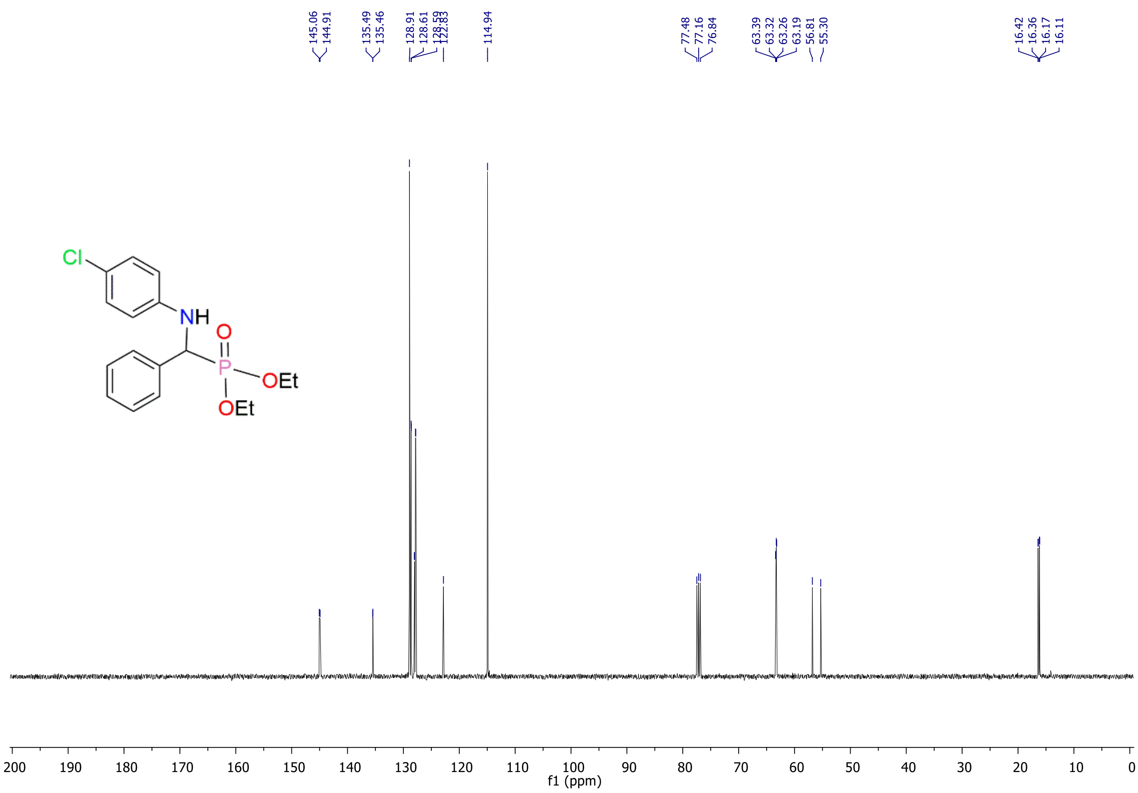


Fig S110. $^{13}C\{^{1}H\}$ NMR spectra of **2i** ($CDCl_3$, 100 MHz).

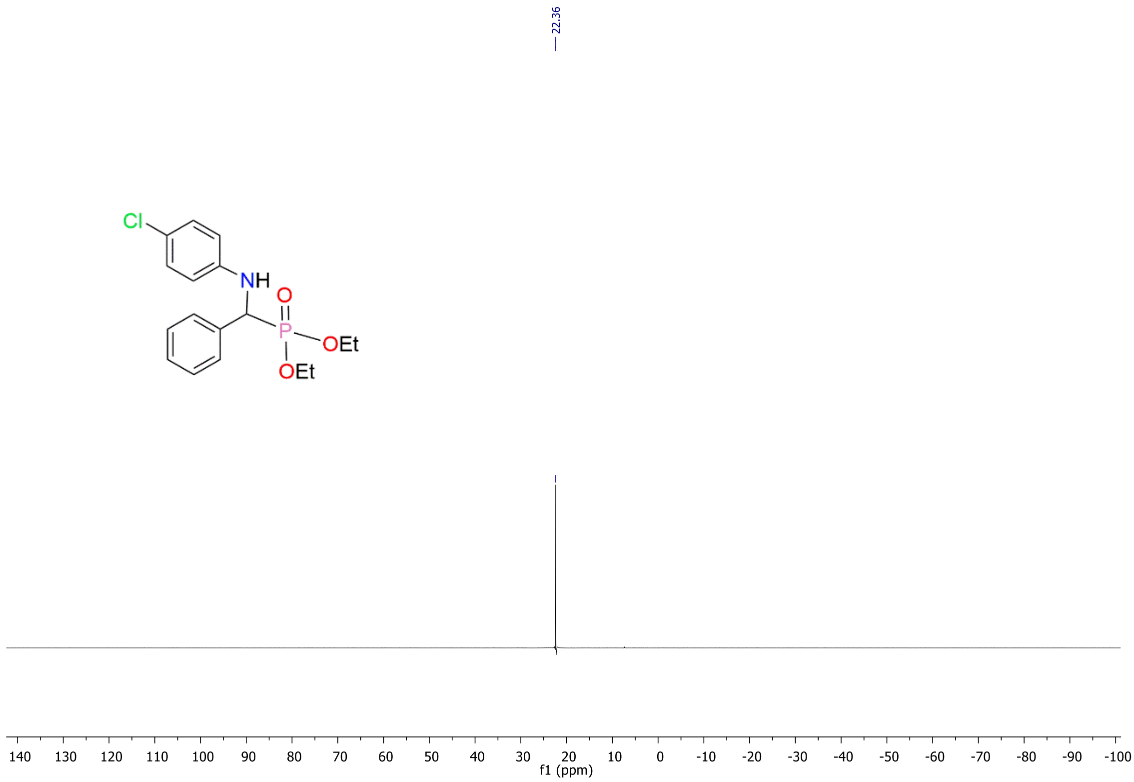


Fig S111. $^{31}P\{^{1}H\}$ NMR spectra of **2i** ($CDCl_3$, 243 MHz).

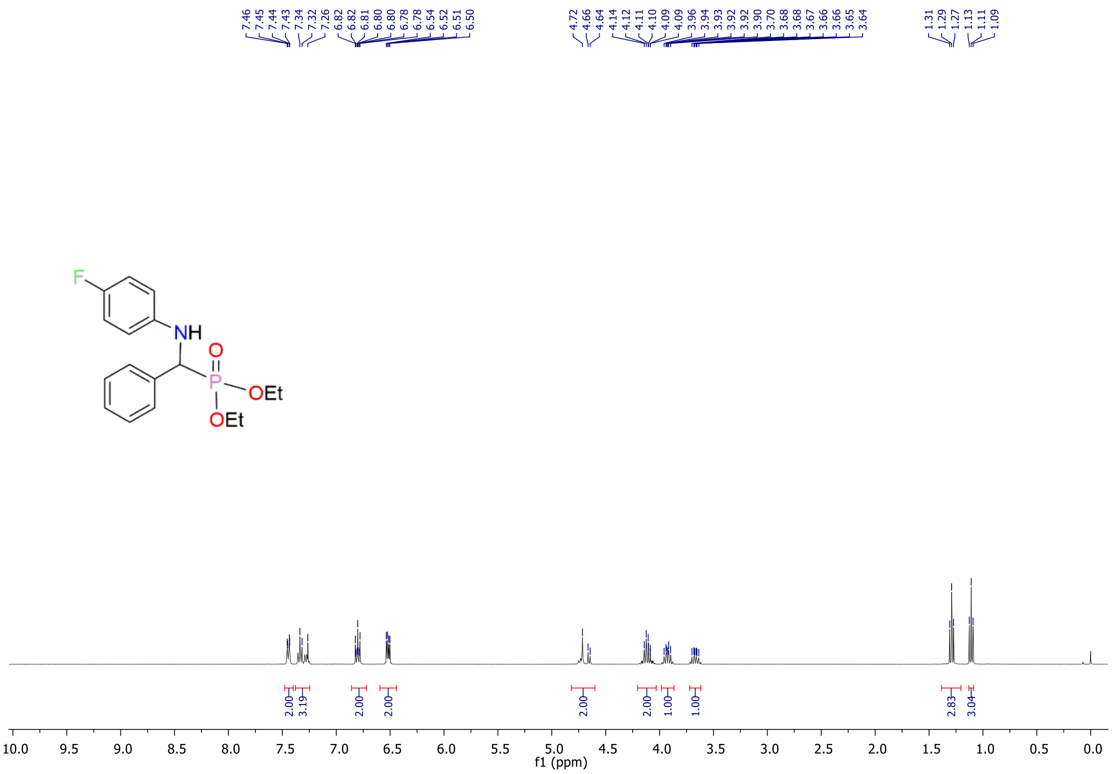


Fig S112. ^{1}H NMR spectra of **2j** ($CDCl_3$, 400 MHz).

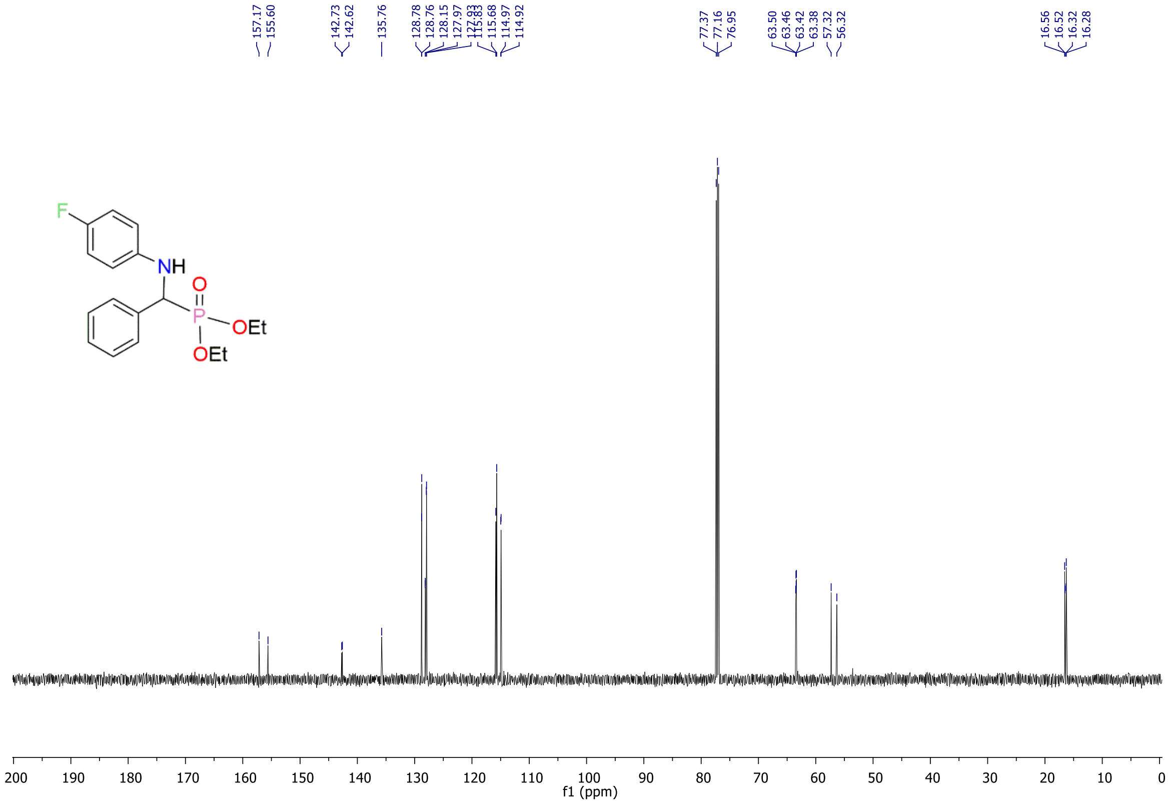


Fig S113. $^{13}C\{^{1}H\}$ NMR spectra of **2j** ($CDCl_3$, 150 MHz).

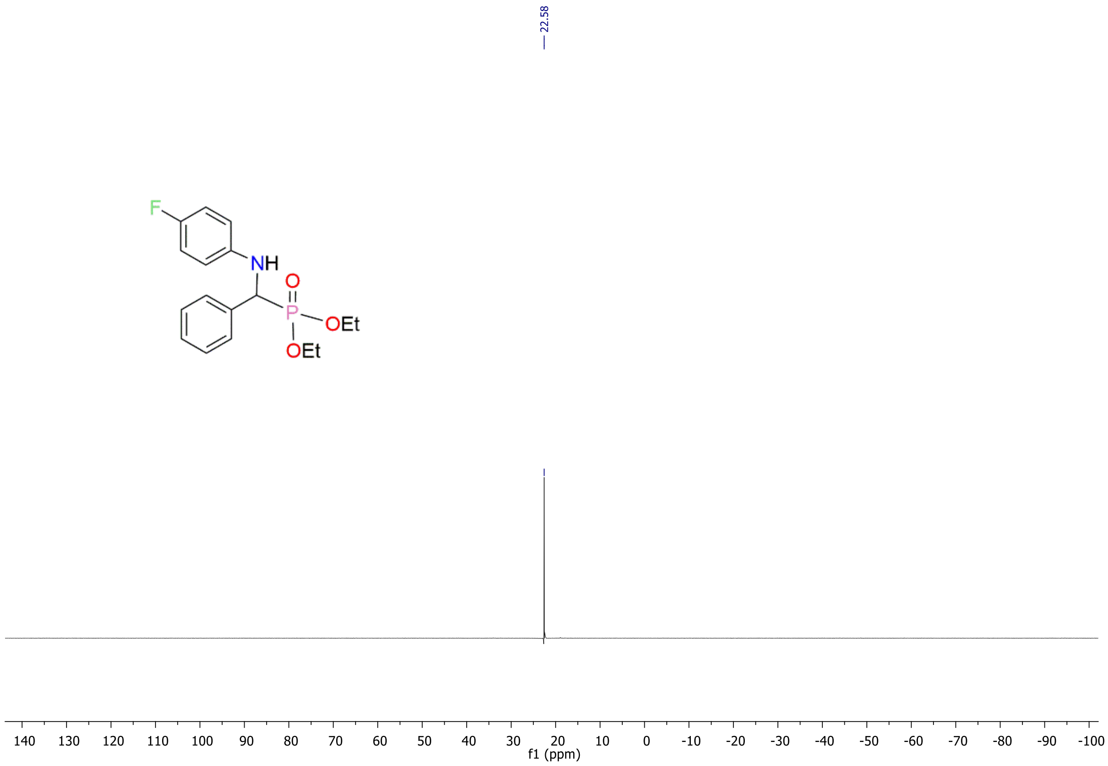


Fig S114. $^{31}P\{^{1}H\}$ NMR spectra of **2j** ($CDCl_3$, 243 MHz).

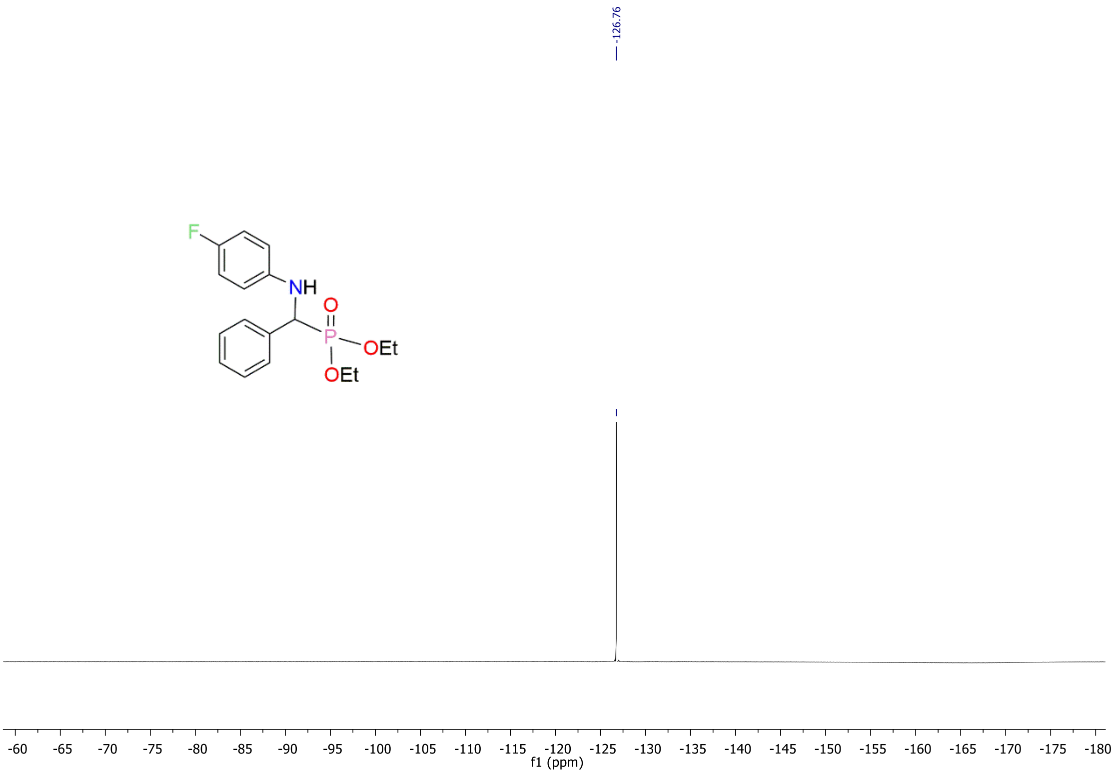


Fig S115. $^{19}F\{^{1}H\}$ NMR spectra of **2j** ($CDCl_3$, 565 MHz).

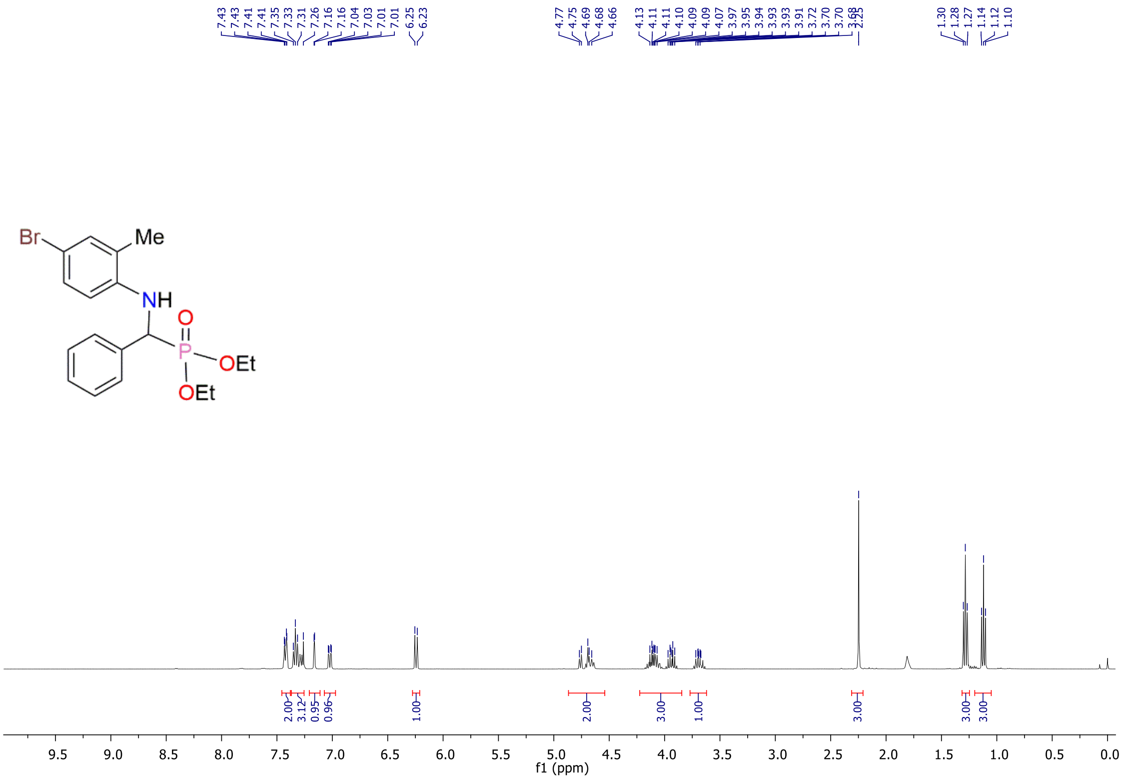


Fig S116. ^{1}H NMR spectra of **2k** ($CDCl_3$, 400 MHz).

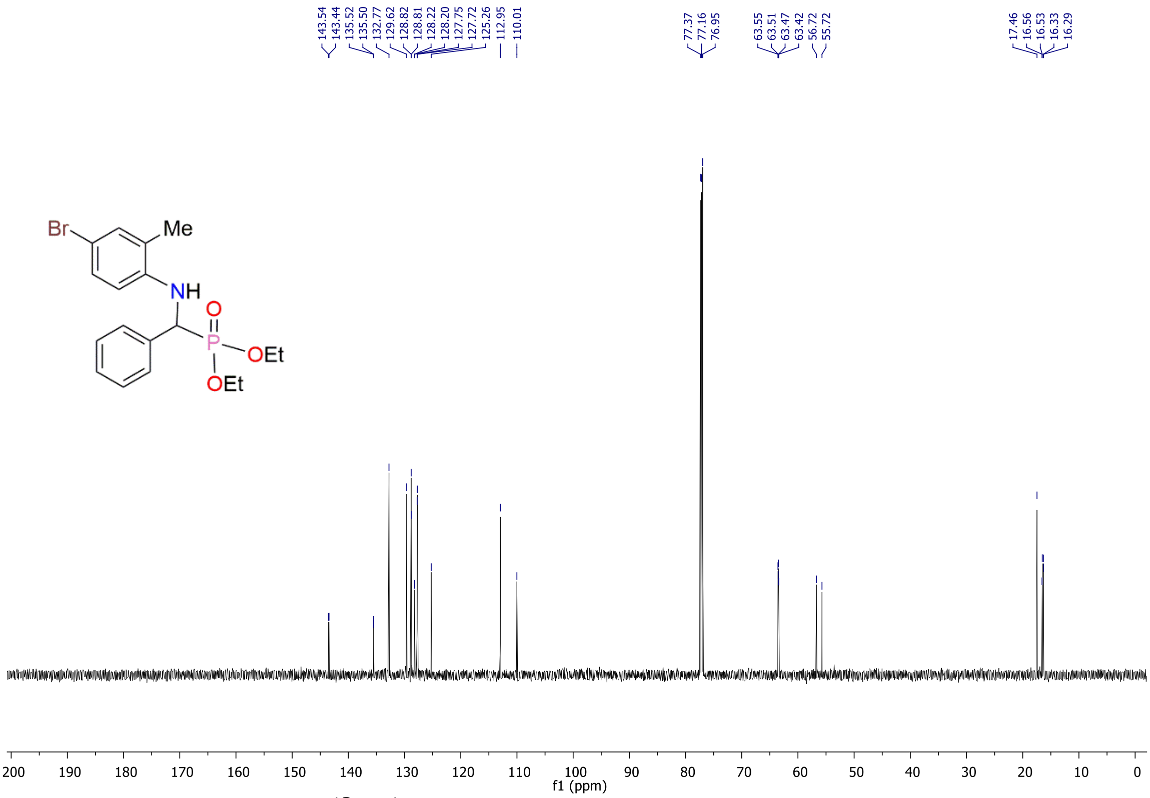


Fig S117. $^{13}C\{^1H\}$ NMR spectra of **2k** ($CDCl_3$, 150 MHz).

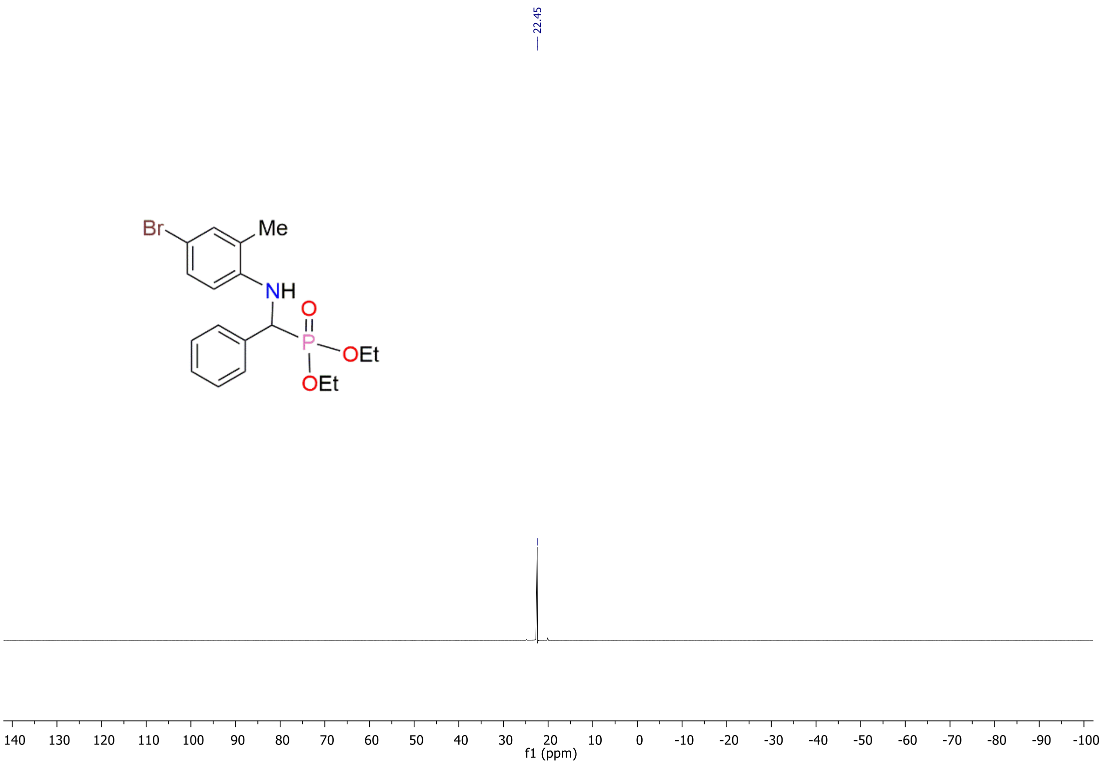


Fig S118. $^{31}P\{^1H\}$ NMR spectra of **2k** ($CDCl_3$, 243 MHz).

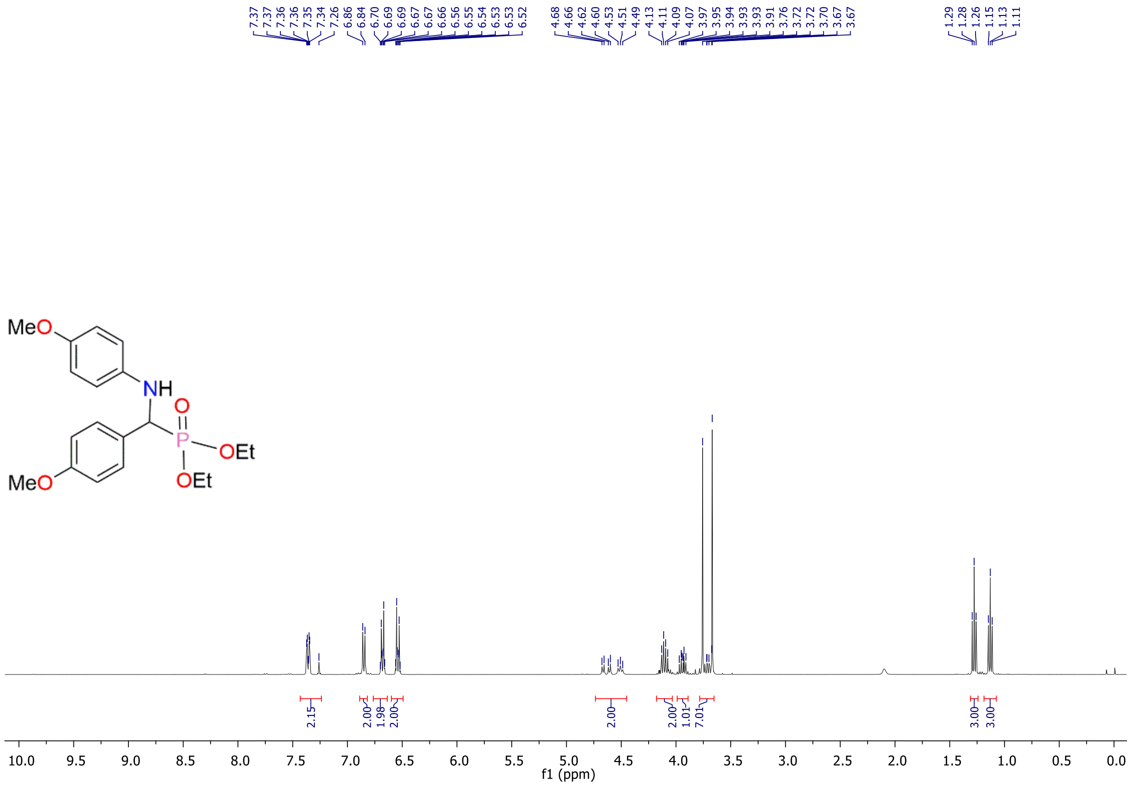


Fig S119. ^{1}H NMR spectra of **2l** ($CDCl_3$, 400 MHz).

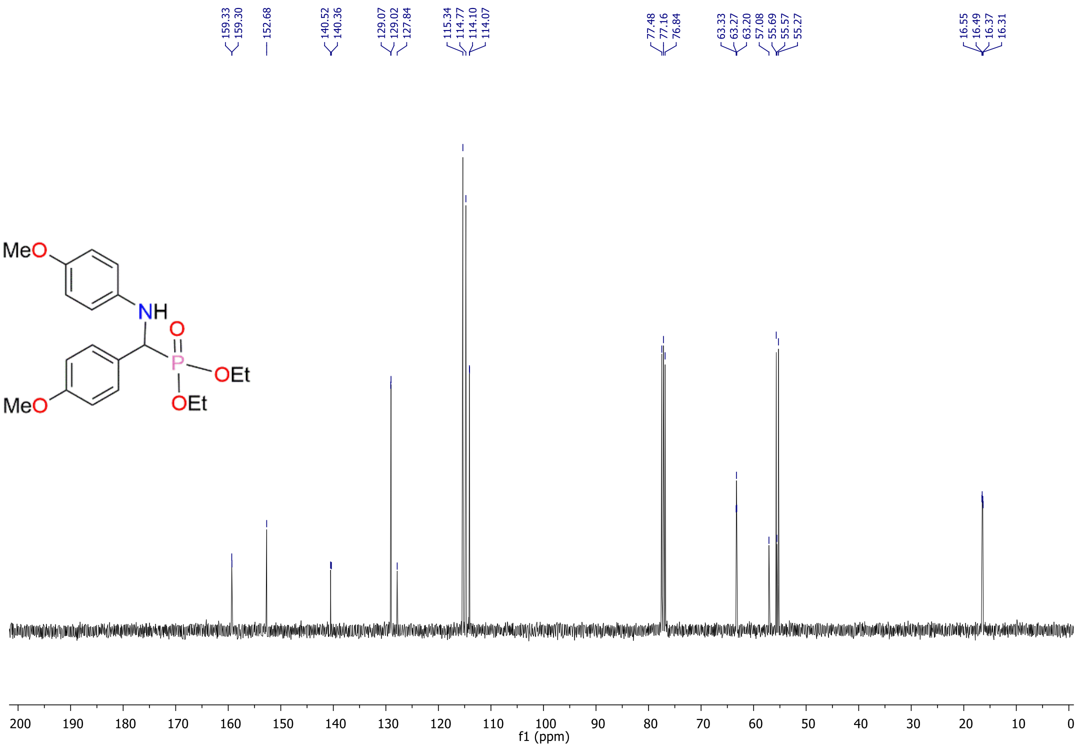


Fig S120. $^{13}C\{^{1}H\}$ NMR spectra of **2l** ($CDCl_3$, 100 MHz).

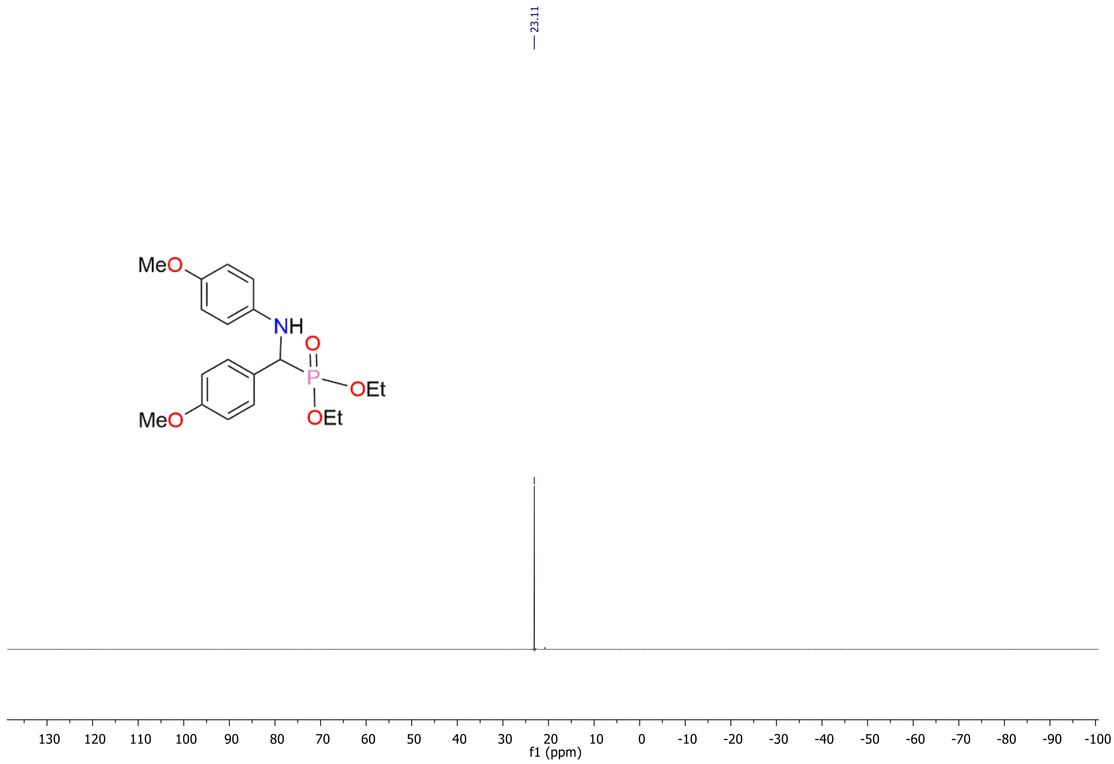


Fig S121. $^{31}P\{^{1}H\}$ NMR spectra of **2l** ($CDCl_3$, 243 MHz)

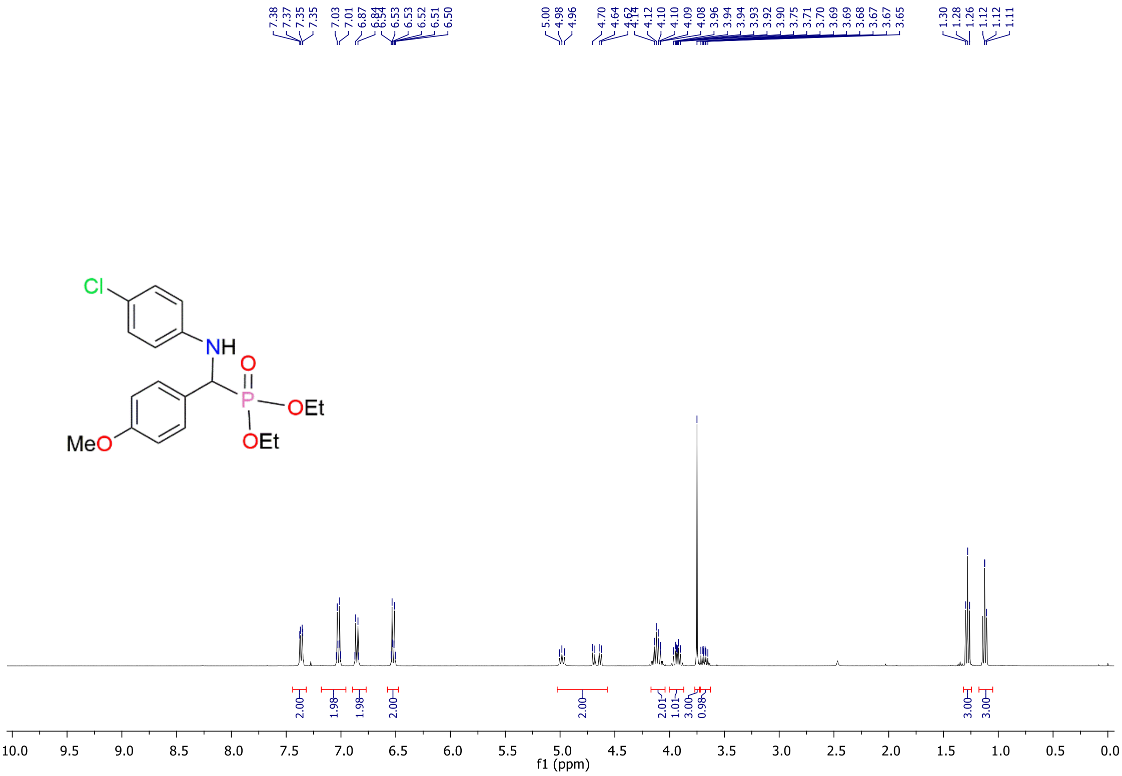


Fig S122. ^{1}H NMR spectra of **2m** ($CDCl_3$, 400 MHz).

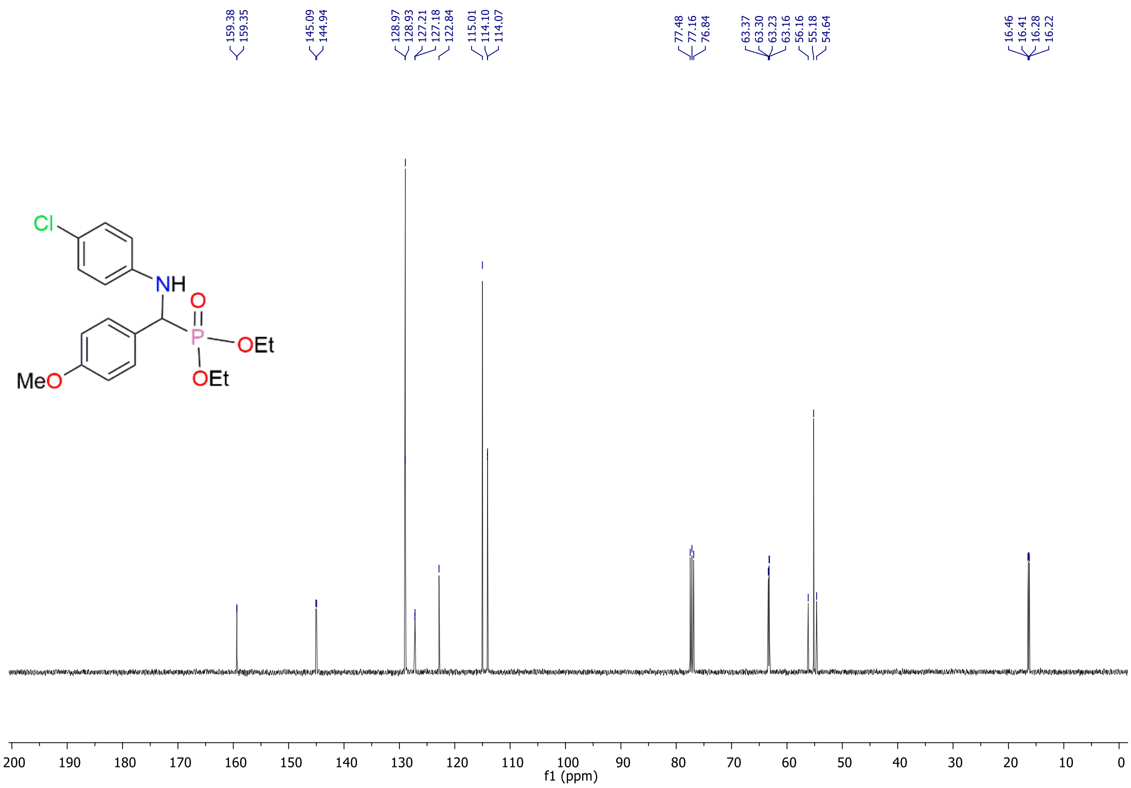


Fig S123. $^{13}C\{^1H\}$ NMR spectra of **2m** ($CDCl_3$, 100 MHz).

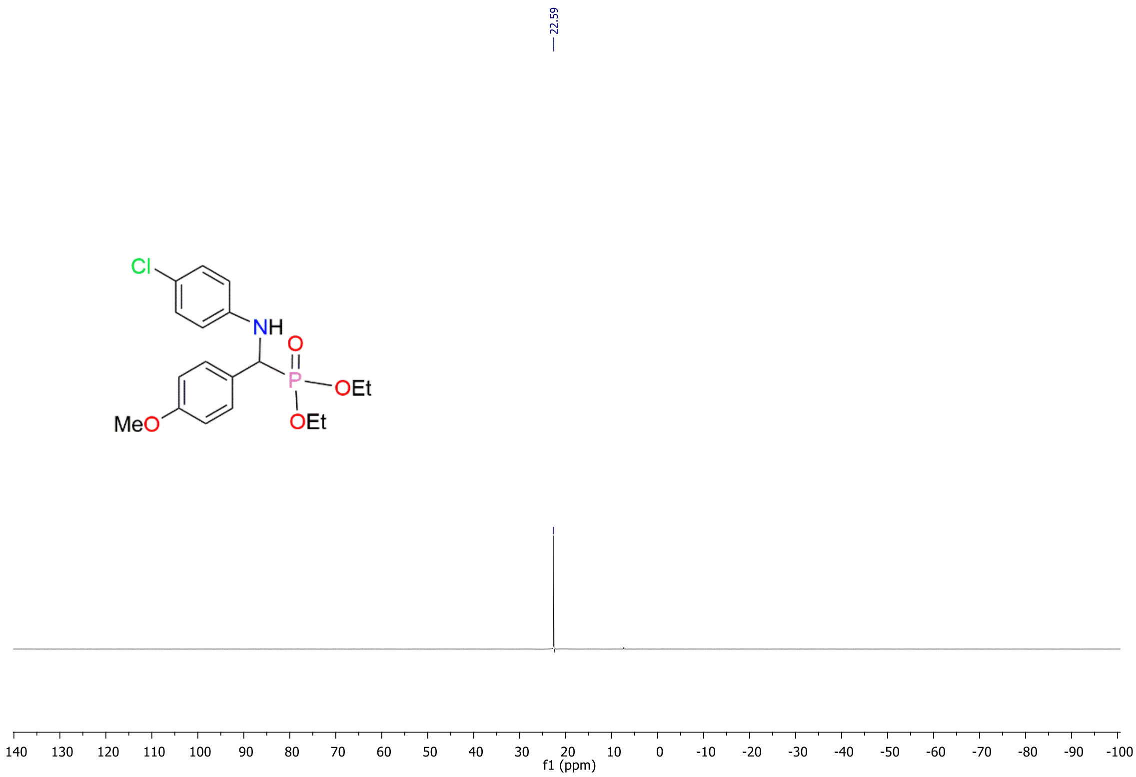


Fig S124. $^{31}P\{^1H\}$ NMR spectra of **2m** ($CDCl_3$, 243 MHz).

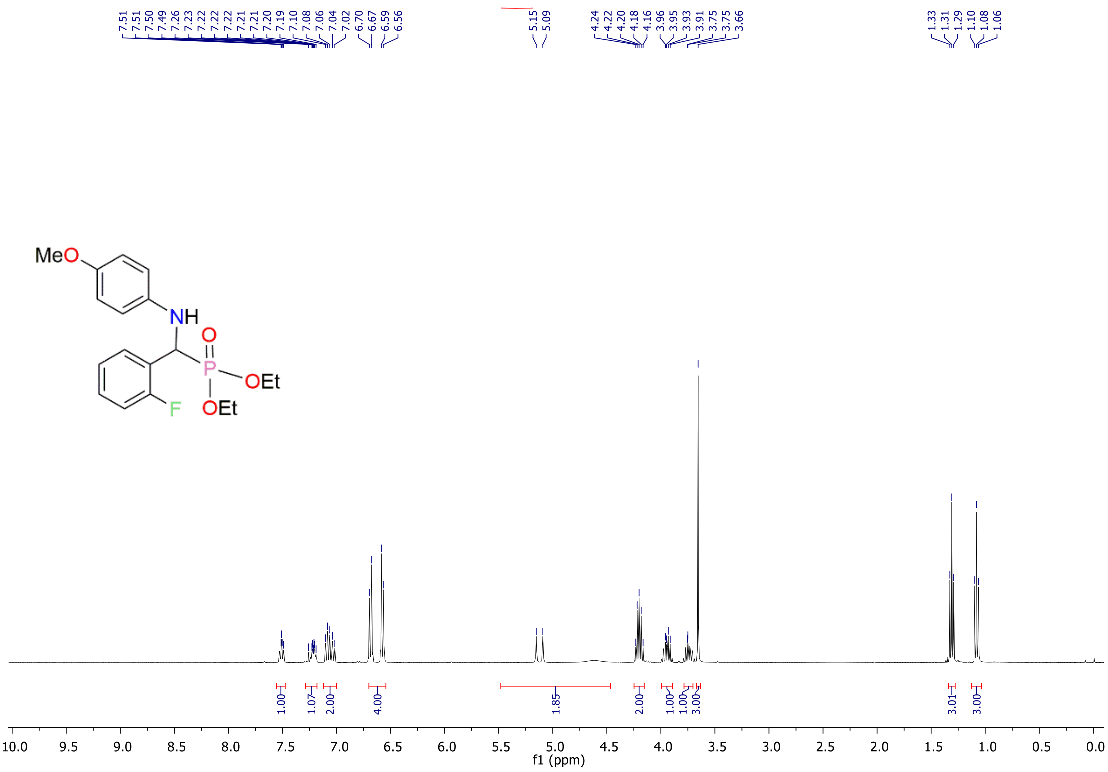


Fig S125. ^{1}H NMR spectra of **2n** ($CDCl_3$, 400 MHz).

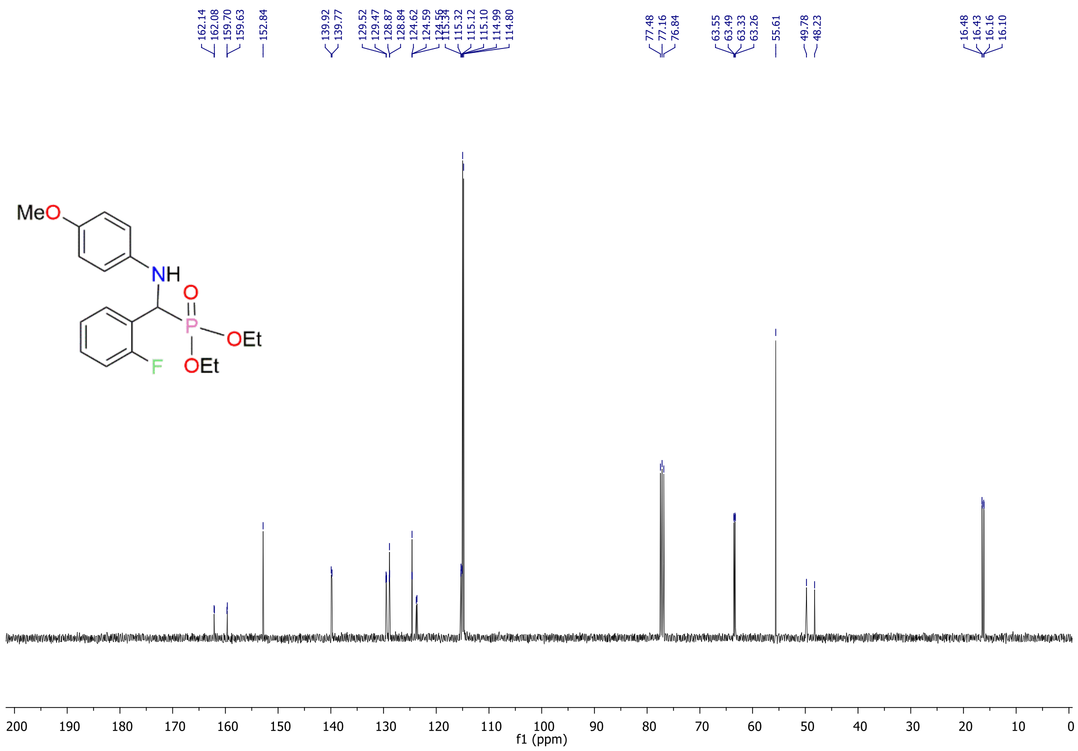


Fig S126. ^{13}C{^{1}H} NMR spectra of **2n** ($CDCl_3$, 100 MHz).

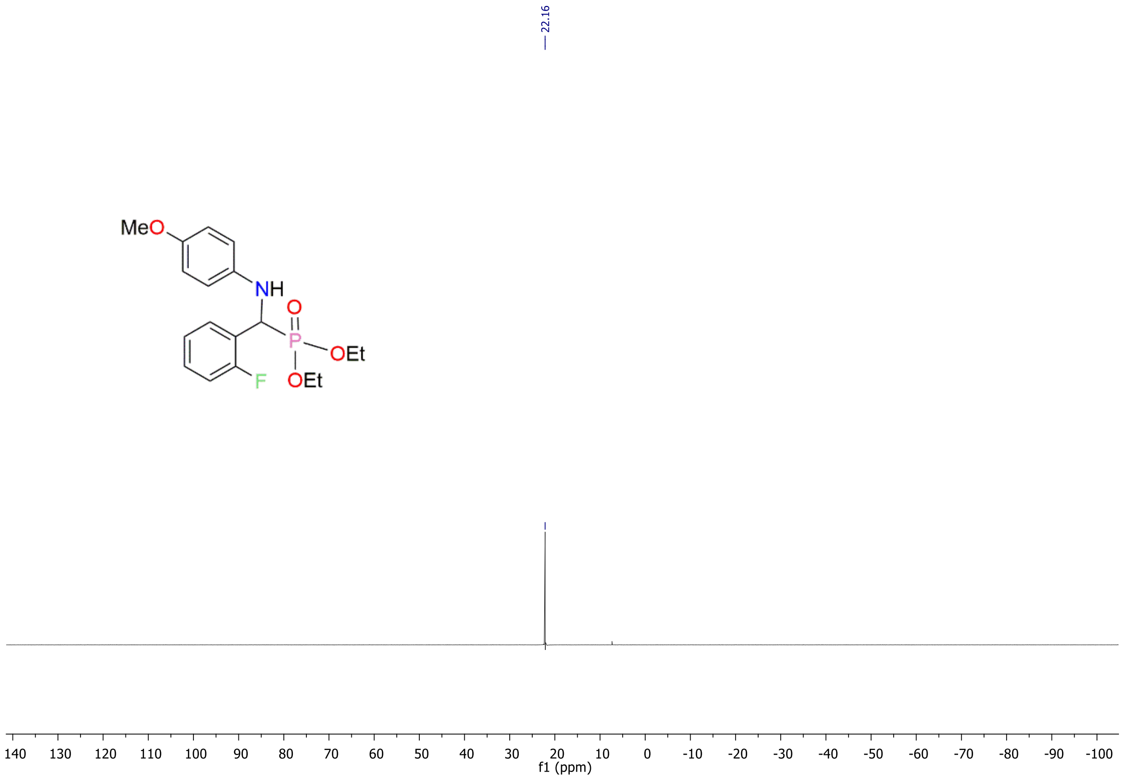


Fig S127. $^{31}P\{^{1}H\}$ NMR spectra of **2n** ($CDCl_3$, 243 MHz).

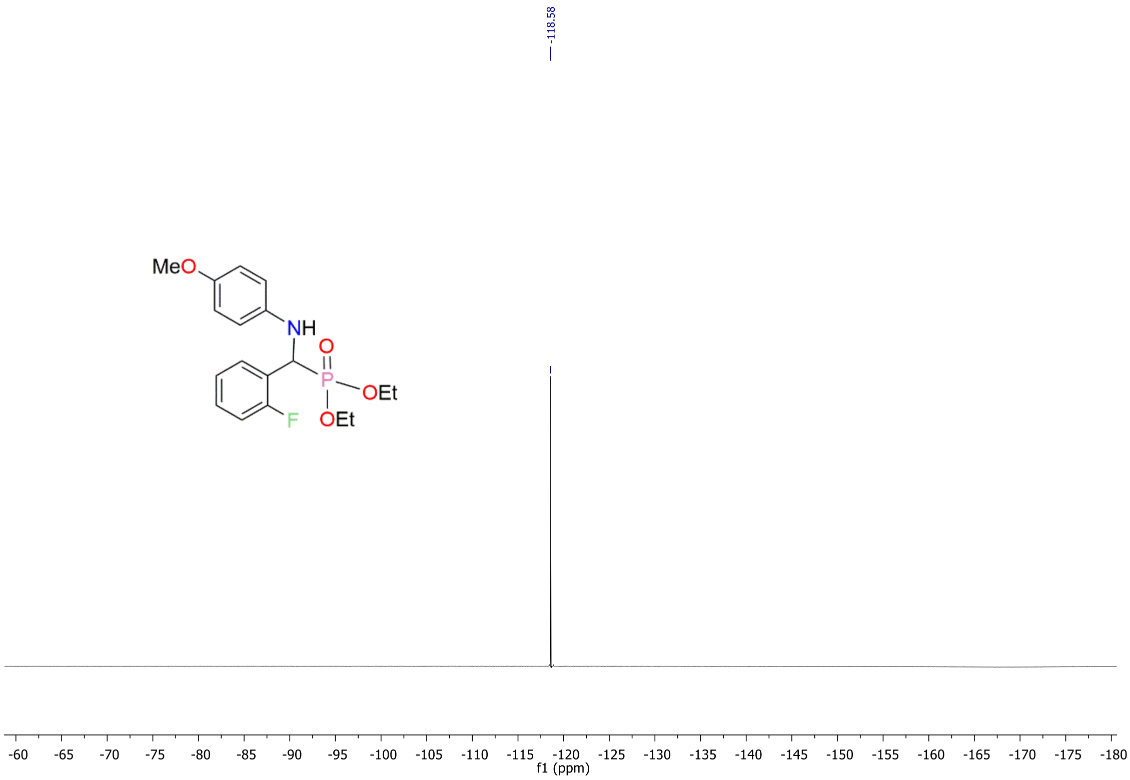


Fig S128. $^{19}F\{^{1}H\}$ NMR spectra of **2n** ($CDCl_3$, 565 MHz).

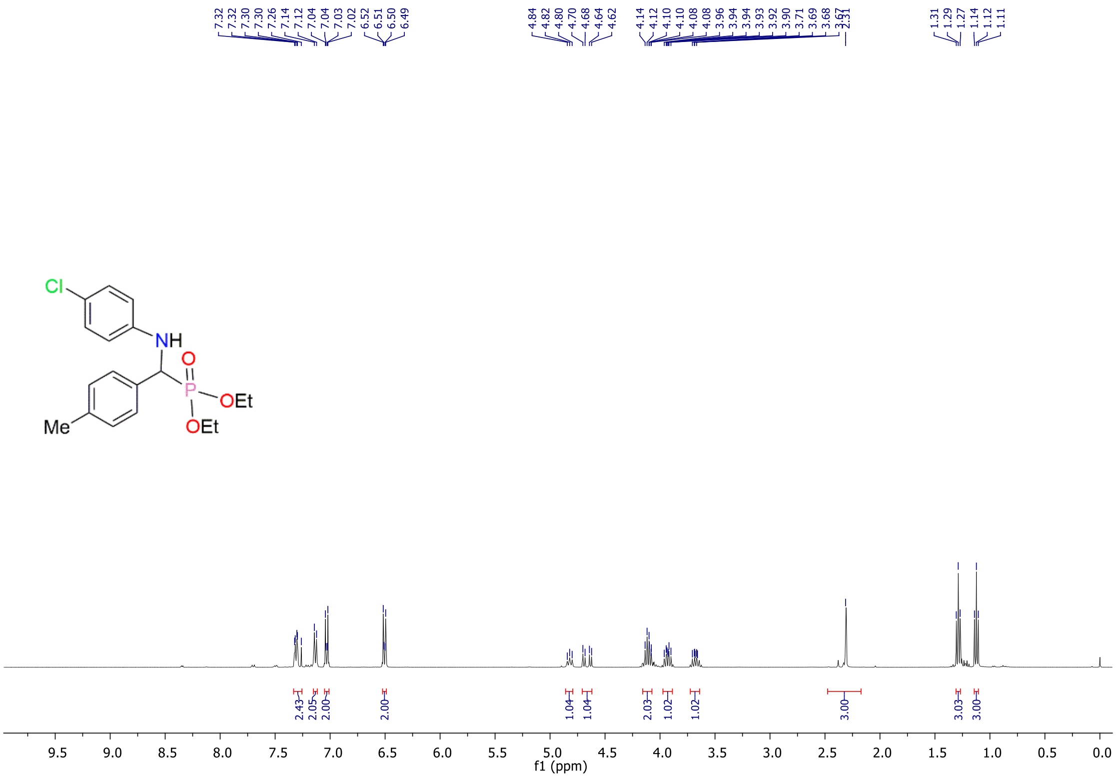


Fig S129. ^{1}H NMR spectra of **2o** ($CDCl_3$, 400 MHz).

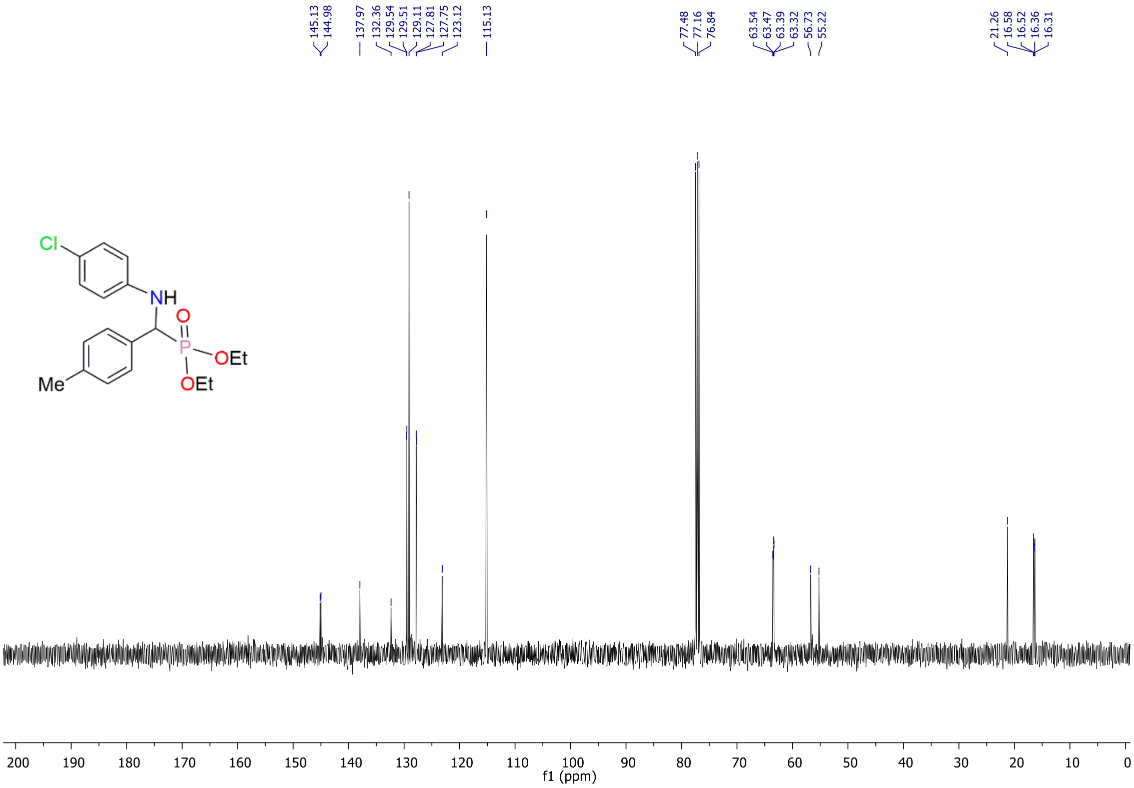


Fig S130. $^{13}C\{^{1}H\}$ NMR spectra of **2o** ($CDCl_3$, 100 MHz).

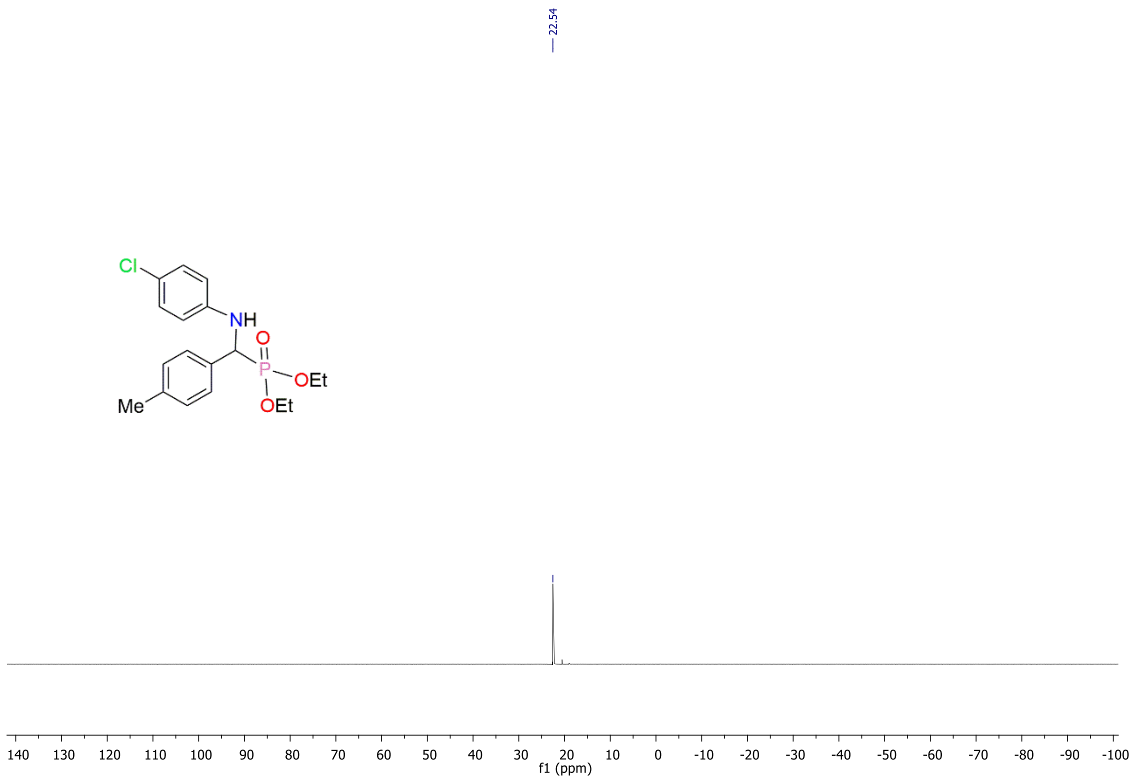


Fig S131. $^{31}P\{^1H\}$ NMR spectra of **2o** ($CDCl_3$, 243 MHz).

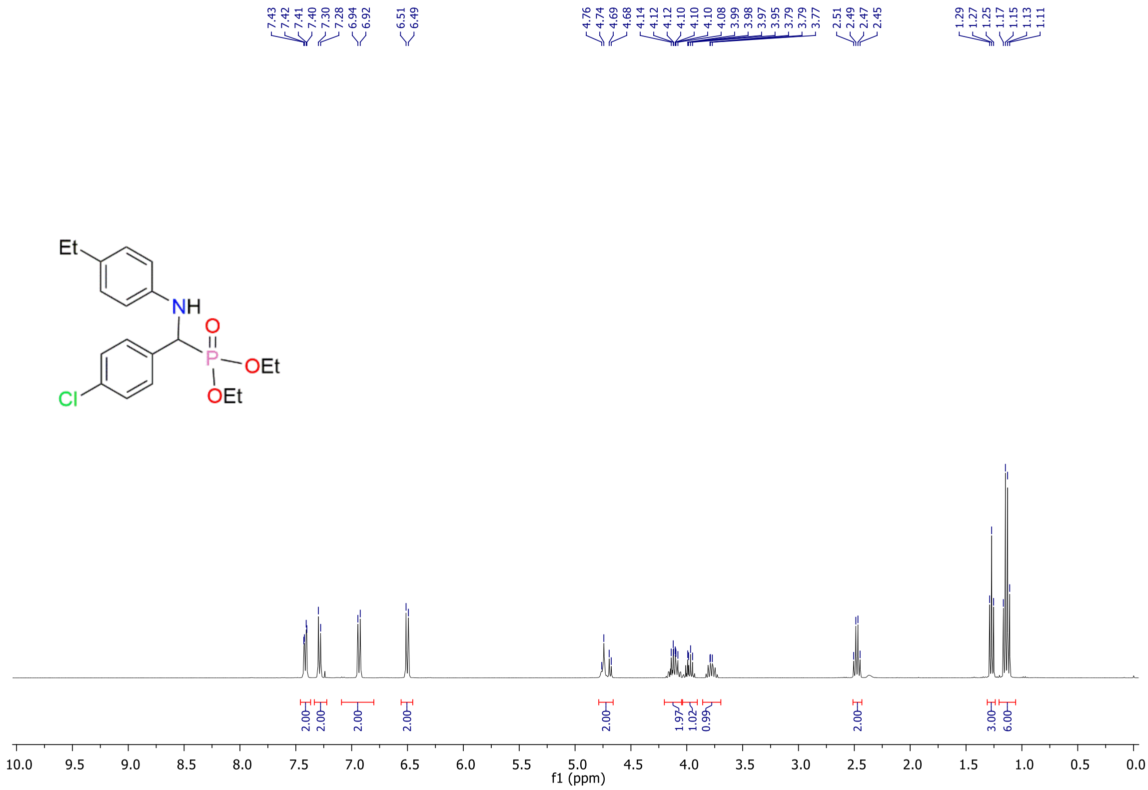


Fig S132. ^1H NMR spectra of **2p** ($CDCl_3$, 400 MHz).

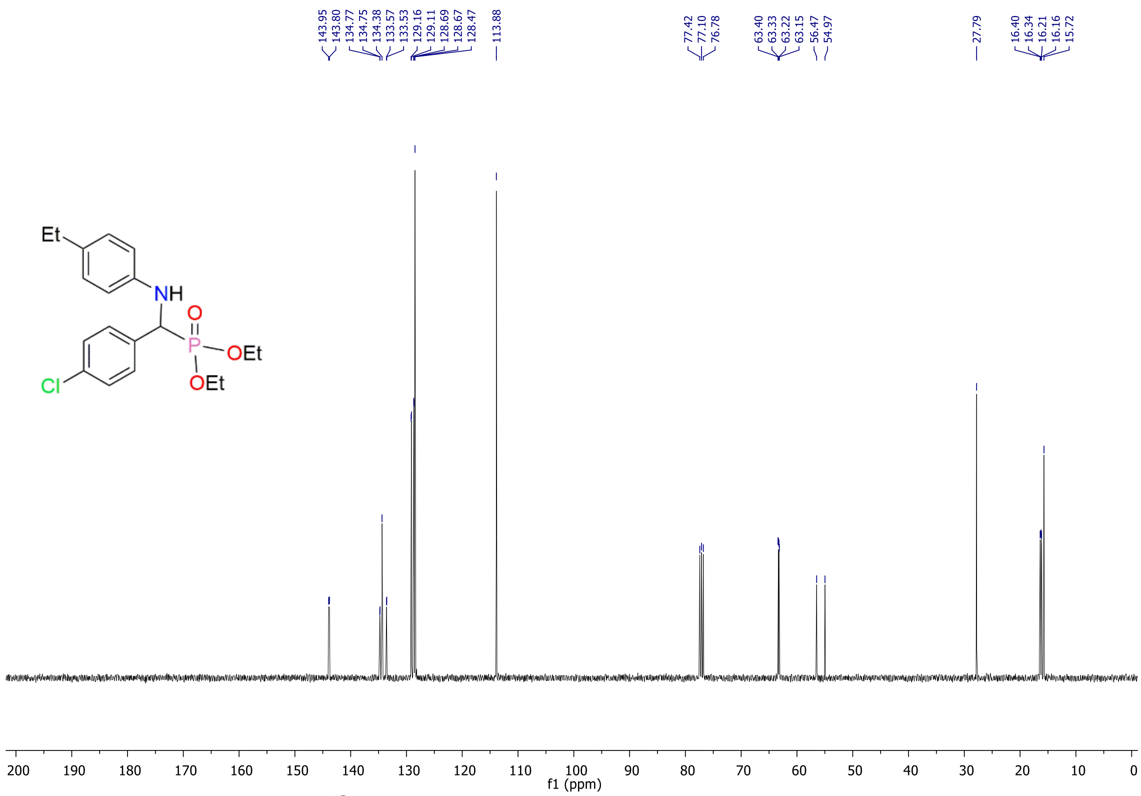


Fig S133. $^{13}C\{^{1}H\}$ NMR spectra of **2p** ($CDCl_3$, 100 MHz).

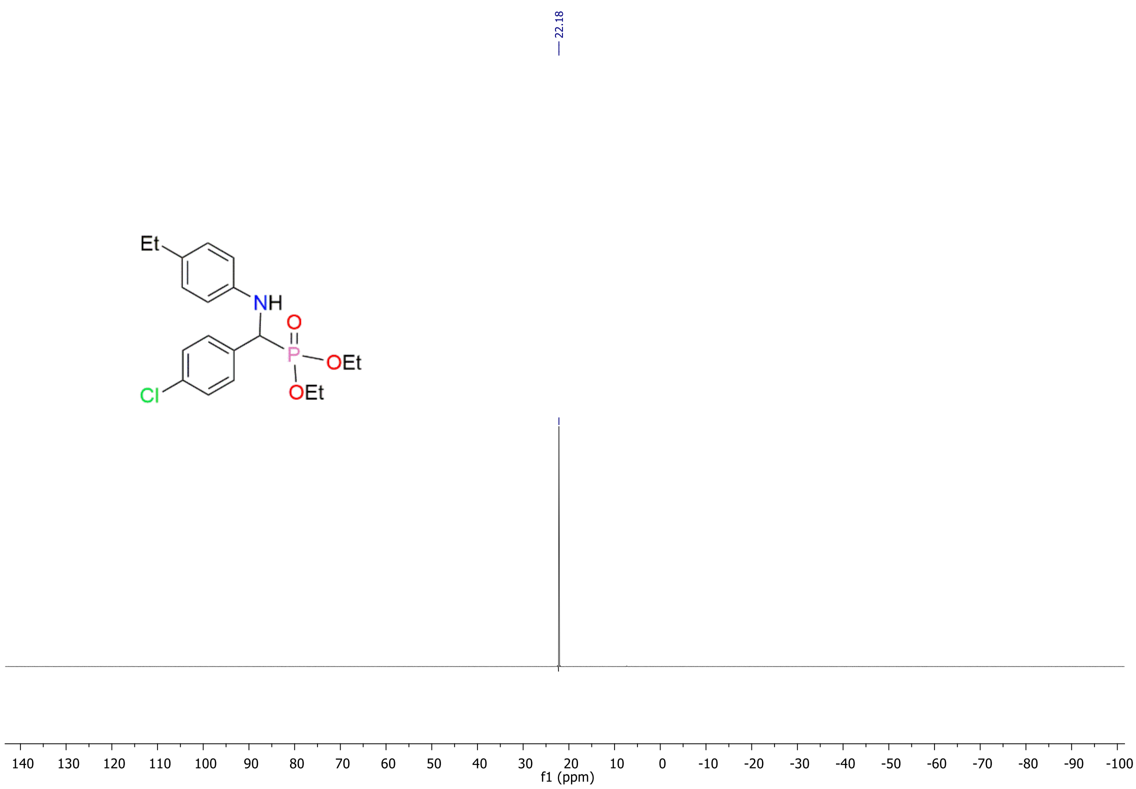


Fig S134. $^{31}P\{^{1}H\}$ NMR spectra of **2p** ($CDCl_3$, 243 MHz).

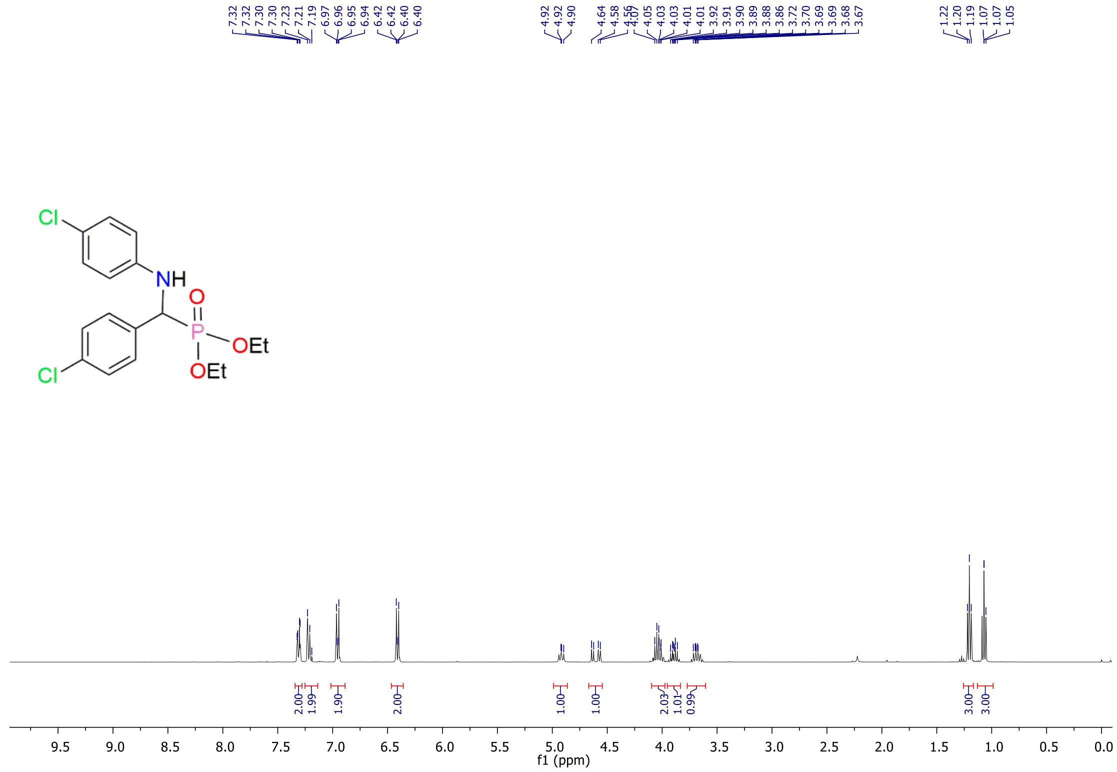


Fig S135. ^{1}H NMR spectra of **2q** ($CDCl_3$, 400 MHz).

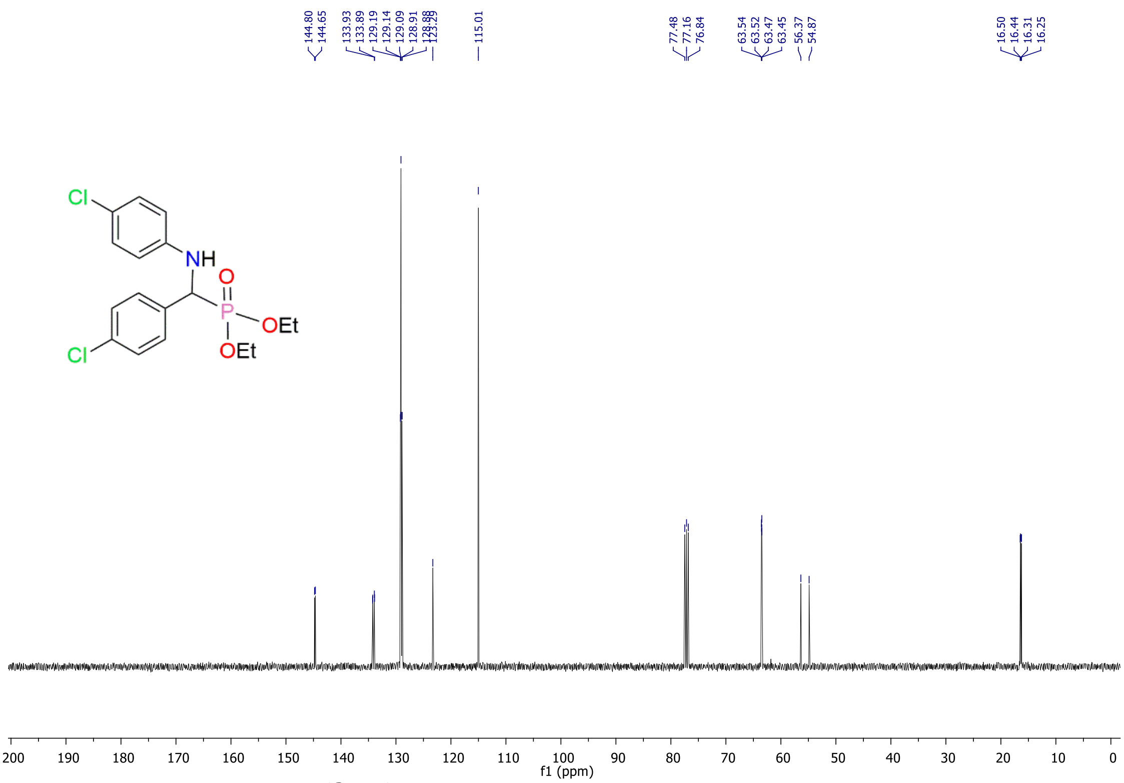


Fig S136. $^{13}C\{^{1}H\}$ NMR spectra of **2q** ($CDCl_3$, 100 MHz).

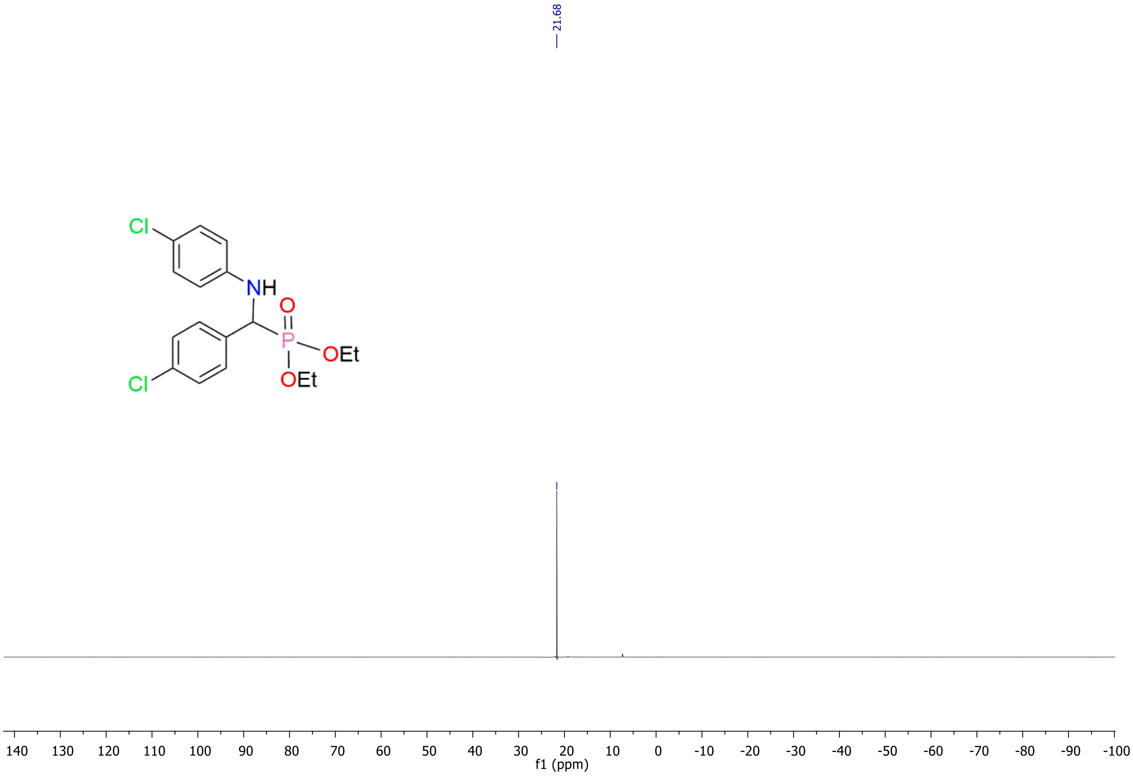


Fig S137. $^{31}P\{^{1}H\}$ NMR spectra of **2q** ($CDCl_3$, 243 MHz).

NMR spectra of DES:

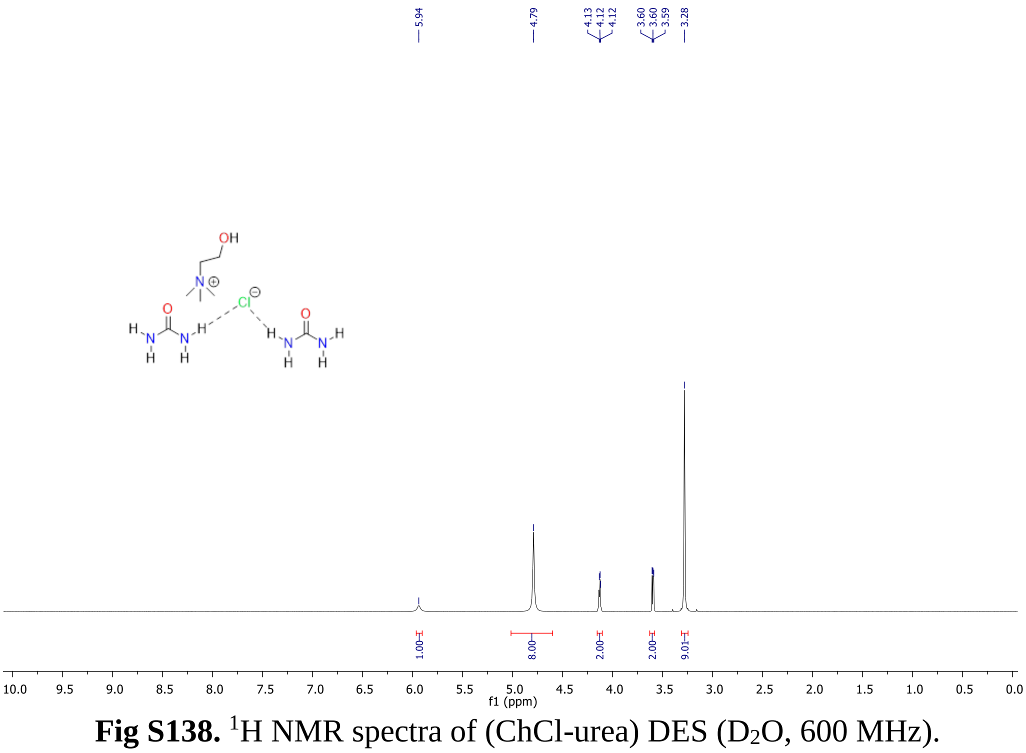


Fig S138. ^{1}H NMR spectra of (ChCl-urea) DES (D_2O, 600 MHz).

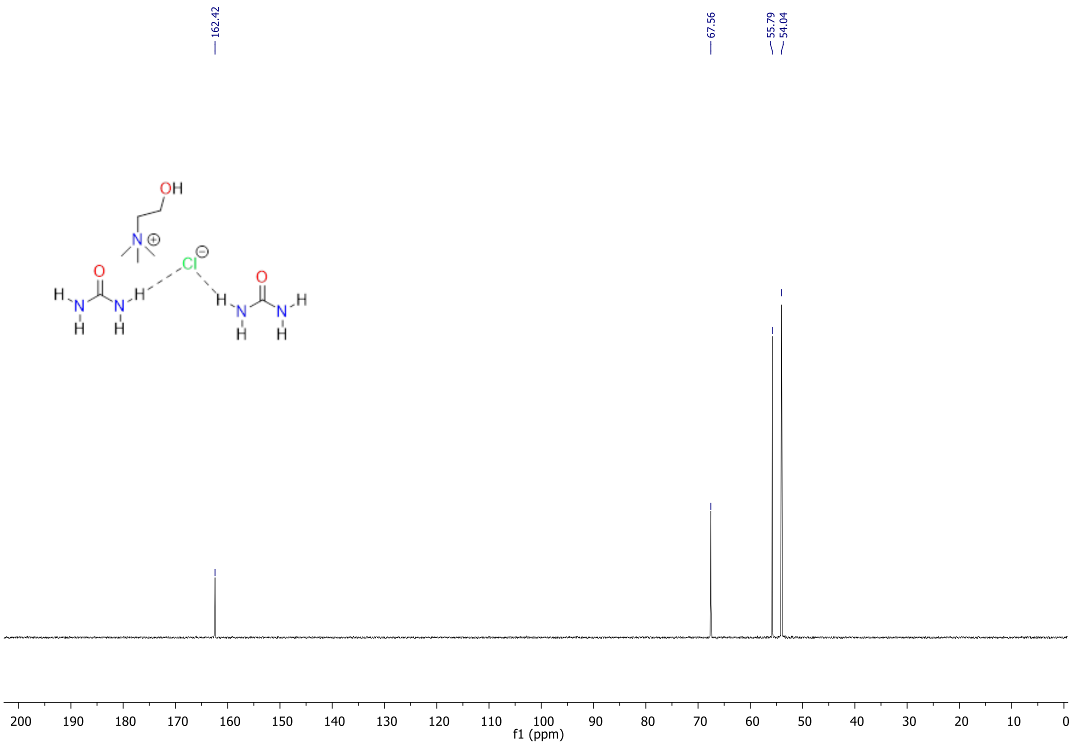


Fig S139. $^{13}C\{^1H\}$ NMR spectra of (ChCl-urea) DES (D_2O, 150 MHz).

Characterisation data of 6(phenyl(phenylamino)methyl)dibenzo[d,f][1,3,2]dioxaphos-phepine 6-oxide:[17]

^1H NMR (400 MHz, DMSO-d_6, 25 ºC): δ_H 9.17 (s, 1H, N*H*), 7.16 - 7.07 (m, 10H, Ar*H*), 6.90 - 6.86 (m, 4H, Ar*H*), 6.84 - 6.79 (m, 4H, Ar*H*), 4.03 (d, J = 7.1 Hz, 1H, C*H*) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 ºC): δ_C 154.43, 131.48, 128.00, 125.86, 118.75, 115.68 ppm. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, 25 ºC): δ_P 33.3 ppm.

NMR spectra of 6-(phenyl(phenylamino)methyl)dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide:

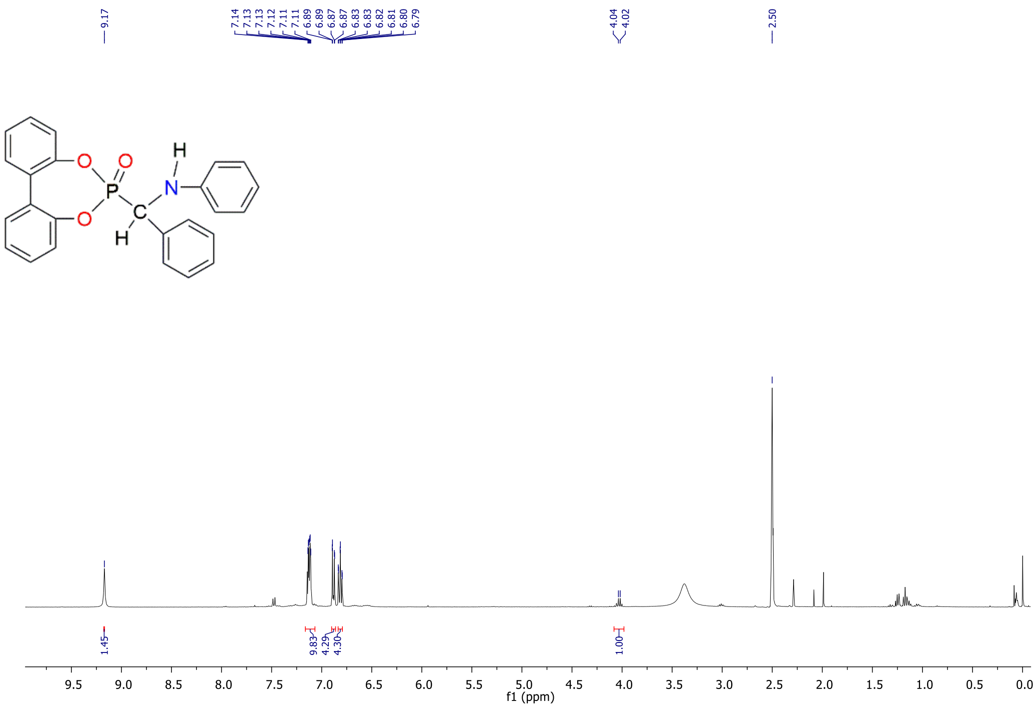


Fig S140. ^{1}H NMR spectra (DMSO-d_6, 400 MHz).

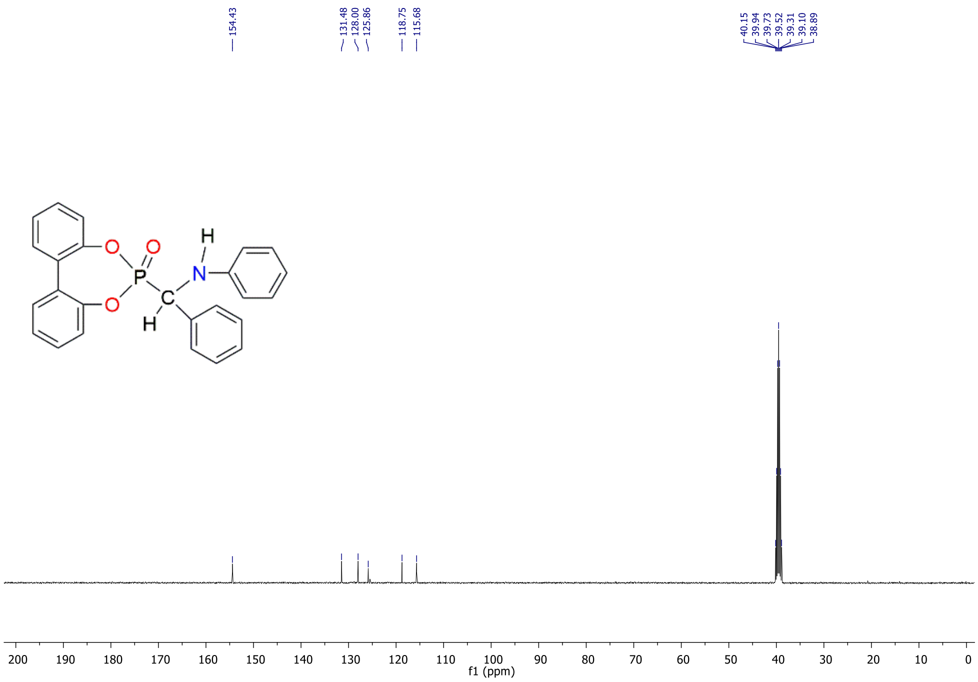


Fig S141. $^{13}C\{^{1}H\}$ NMR spectra (DMSO-d_6, 100 MHz).

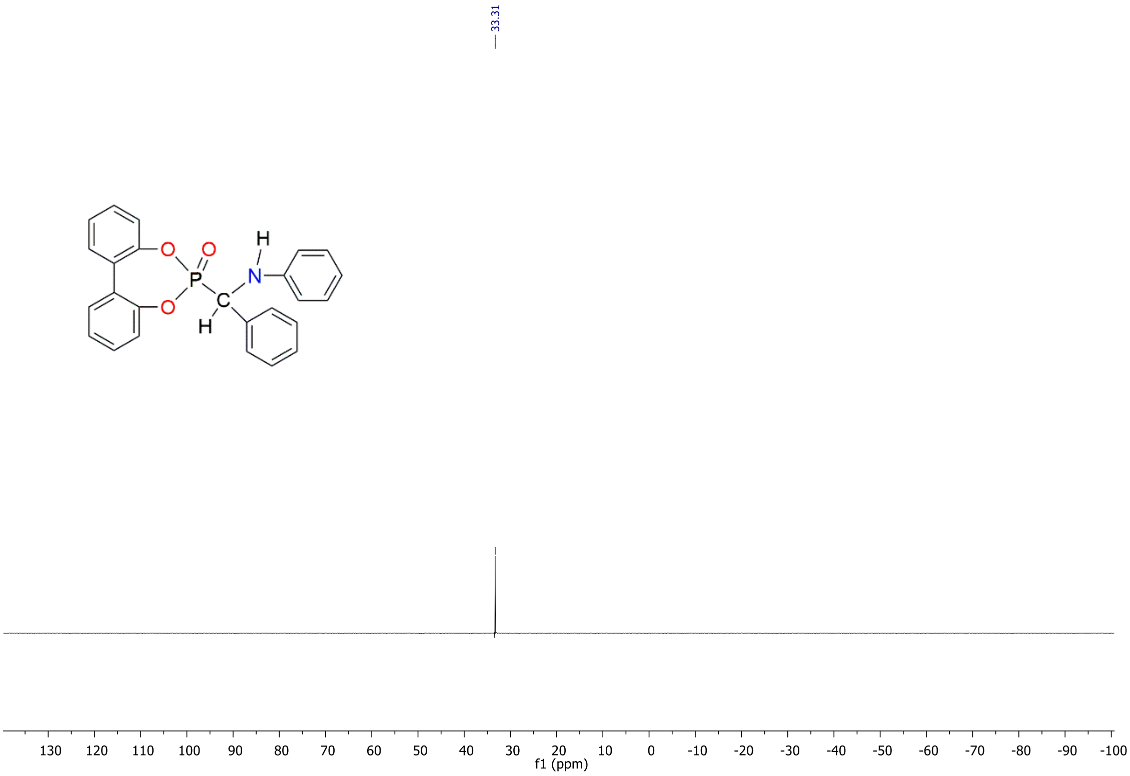


Fig S142. $^{31}P\{^{1}H\}$ NMR spectra (DMSO-d_6, 243 MHz).

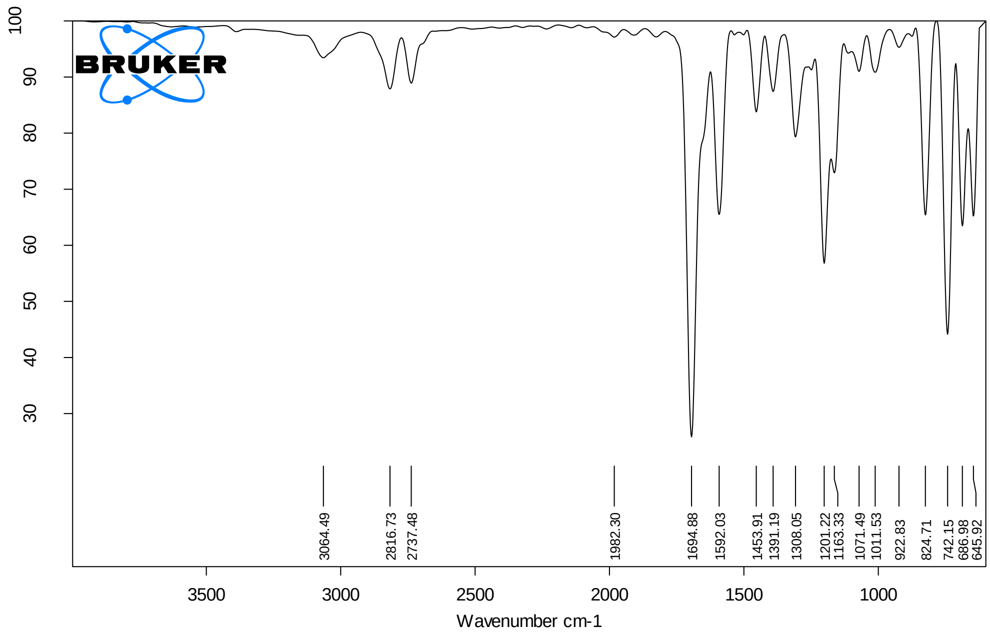


Fig S143. FT-IR spectra of benzaldehyde with **C-O** stretching at 1695 cm^{-1}.

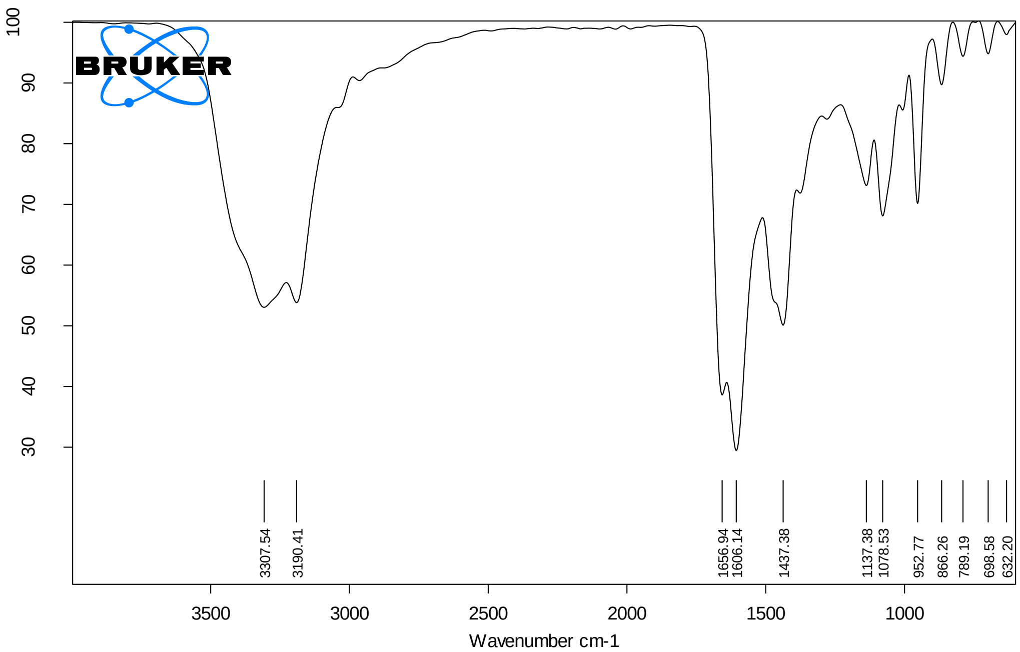


Fig S144. FT-IR spectra of benzaldehyde in DES (ChCl-Urea) with **C-O** stretching at 1656 cm^{-1}.

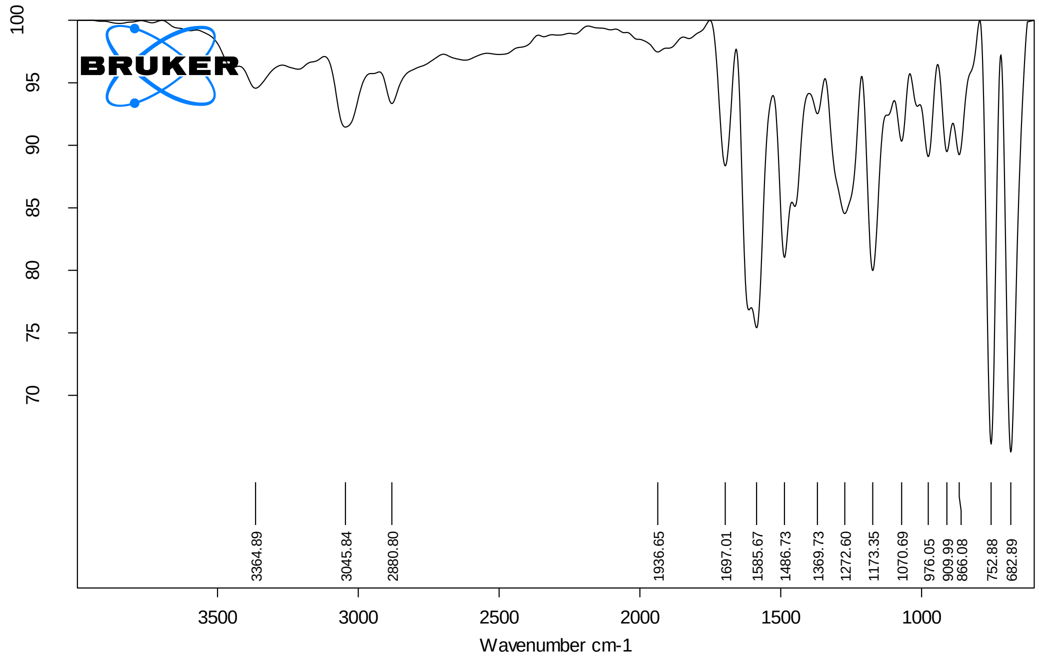


Fig S145. FT-IR spectra of imine with **C-N** stretching at 1697 cm^{-1}.

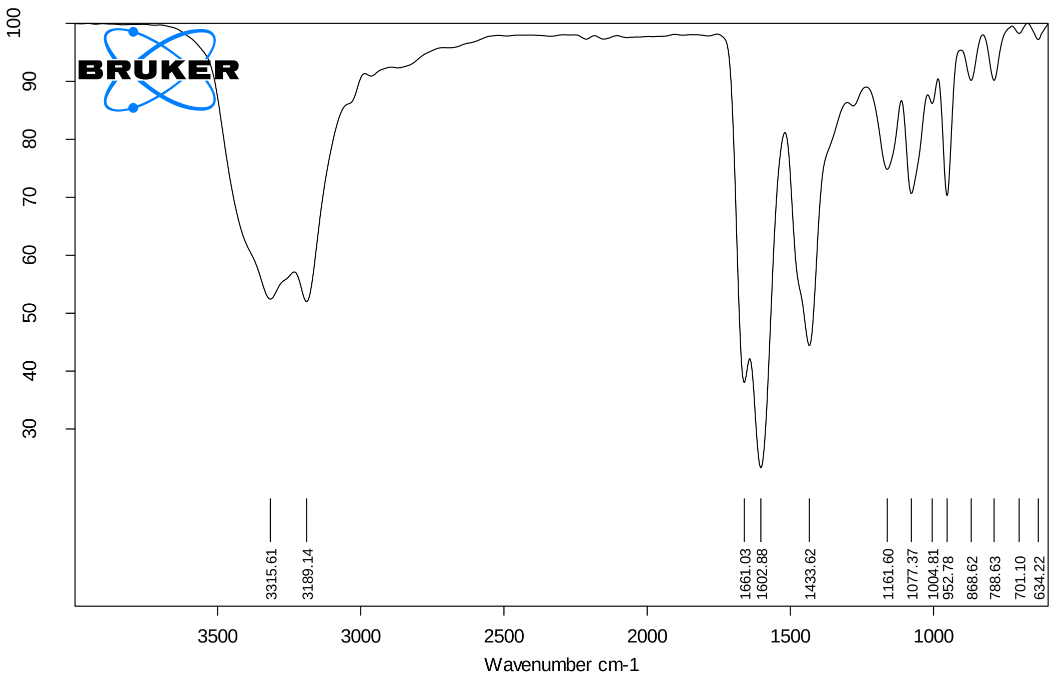


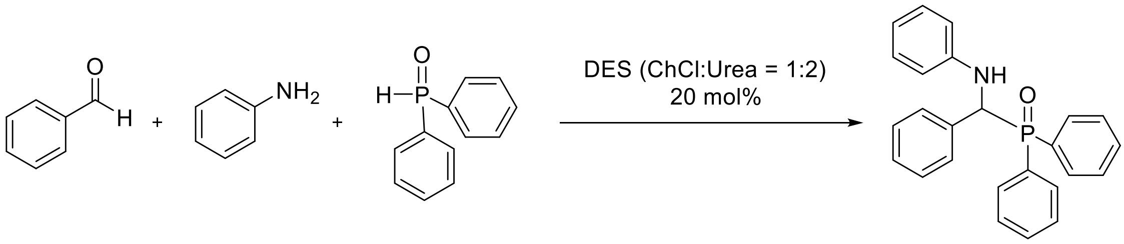
Fig S146. FT-IR spectra of imine in DES (ChCl-Urea) with **C-N** stretching at 1661 cm^{-1}.

Green chemistry metrics calculations for hydrophosphorylation reaction:

Here we have calculated different parameters of green chemistry metric.[18,19] The parameters are as follows:

1) E-factor or environmental factor
2) Atom economy (AE)
3) Atom efficiency
4) Carbon efficiency
5) Product mass intensity (PMI)
6) Reaction mass efficiency (RME)

Calculations of green chemistry metrics for the synthesis of phosphine oxide derivatives:



MW: 106.124 g/mol 93.13 g/mol 202.19 g/mol 383.43 g/mol

Amount: 0.4945 mmol 0.4945 mmol 0.4945 mmol

	Name	**Chemical formula**	**Molecular weight**	**millimole**	**mg**
Reactant 1	Benzaldehyde	C_7H_6O	106.12	0.4945	52.5
Reactant 2	Aniline	C_6H_7N	93.13	0.4945	46
Reactant 3	Diphenylphosphine oxide	$C_{12}H_{11}OP$	202.19	0.4945	100
Solvent	DES (ChCl: Urea = 1:2)	-	-	0.099	-
Product	Diphenyl(phenyl(p-henylamino)-methyl)phosphine oxide	$C_{25}H_{22}NOP$	383.43	-	171

Yield of product = 90%.

E - factor or environmental factor: It measures the mass of generated waste per unit mass of the product. Ideal value of E - factor is zero.

$$\textbf{E factor} = \frac{\text{Total mass of the waste}}{\text{Mass of the product}}$$

Where total mass of waste = total mass of raw materials − the total mass of product

$$\text{E} - \text{factor} = \frac{\{(106.12 \times 0.4945) + (93.13 \times 0.4945) + (202.19 \times 0.4945) - 171\}\ \text{mg}}{171\ \text{mg}}$$

$$\mathbf{E - factor = 0.16}$$

Atom economy (AE): It is a calculation of how many atoms of the reactants present in the final product. The ideal value of AE factor is 100%.

$$\text{Atom economy} = \frac{\text{MW of product}}{\Sigma\ (\text{MW of reactants})} \times 100$$

$$= \frac{383.43}{(106.12\ + 93.13 + 202.19)} \times 100$$

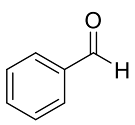
$$= 92.5\%$$

$$\textbf{Atom efficiency} = \frac{\%\ \text{yield of product}\ \times \%\ \text{atom economy}}{100}$$

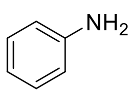
$$= \frac{90\%\ \times 92.5\%}{100}$$

$$\textbf{Atom efficiency} = \mathbf{83.3}\%$$

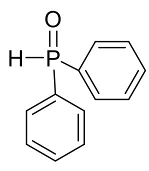
$$\textbf{Carbon efficiency} = \frac{\text{No of carbon atoms in product}}{\Sigma\ (\text{No of carbon atoms in reactants})} \times 100$$



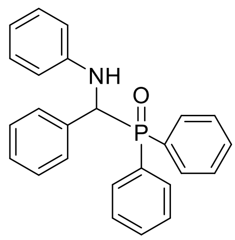
Chemical formula: C_7H_6O



Chemical formula: C_6H_7N



Chemical formula: $C_{12}H_{11}OP$



Chemical formula: $C_{25}H_{22}NOP$

$$\text{Carbon efficiency (CE)} = \frac{25}{(7 + 6 + 12)} \times 100$$

$$\textbf{Carbon efficiency (CE)} = \mathbf{100}\%$$

Product mass intensity (PMI): PMI is defined as the total mass of the input materials (reactants) including solvent in a chemical reaction divided by the mass of product.

$$\text{PMI} = \frac{\Sigma\ (\text{Mass of reactants including solvent})}{\text{Mass of the product}}$$

$$\text{PMI} = \frac{(106.12\ \times 0.4945) + (93.13\ \times 0.4945) + (202.19\ \times 0.4945)}{171}$$

= 1.16

Ideal value of PMI = **E – factor + 1**

Here **PMI = 0.16 + 1 = 1.16**.

Reaction mass efficiency (RME): RME is a mass-based metric which is defined as the mass of product divided by the total mass of stoichiometric reactants. The value of RME varies from 0- 100%. It is the measure of percentage of the mass of reactants in the final product. The more RME values greener will be the reaction.

$$\text{RME} = \frac{\text{Mass of product}}{\Sigma\ (\text{mass of reactants})} \times 100$$

$$= \frac{171}{(106.12\ \times 0.4945) + (93.13\ \times 0.4945) + (202.19\ \times 0.4945)} \times 100$$

$$\mathbf{RME = 86.13\%}$$

Summary of green metric parameters:

E- factor	0.16
Atom economy (AE)	92.5 %
Atom efficiency	83.3%
Carbon efficiency	100%
PMI	1.16
RME	86.13%

References:

1. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70-71.
2. Q. Huang, L. Zhua, D. Yib, X. Zhaoc and W. Wei, *Chin Chem Lett*, 2020, **31**, 373-376.
3. Y. Gao, Z. Huang, R. Zhuang, J. Xu, P. Zhang, G. Tang and Y. Zhao, *Org. Lett.*, 2013, **15**(16), 4214-4217.
4. L. L. Mao, C. C. Li, Q. Yang, M. X. Cheng and S. D. Yang, *Chem. Commun.*, 2017, **53**, 4473.
5. S. Das, P. Rawal, J. Bhattacharjee, A. Devadkar, K. Pal, P. Gupta and T. K. Panda, *Inorg. Chem. Front.*, 2021, **8**, 1142.
6. Y. Q. Yu and D. Z. Xu, *Synthesis*, 2015, **47**(13), 1869-1876.
7. M. H. Sarvari, *Tetrahedron*, 2008, **64**(23), 5459-5466.
8. C. K. Khatri, V. B. Satalkar and G. U. Chaturbhuj, *Tetrahedron Lett.*, 2017, **58**(7), 694-698.
9. A. B. Amol, O. Jeongsu, K. T. Jong and J. T. Yeon, *Monatsh. Chem.*, 2014, **145**(2), 329-336.
10. A. Mozhgan, G. Maryam and N. Mohammad, *Inorg. Nano-Met. Chem.*, 2017, **47**(4), 591-596.
11. N. K. Gupta, C. Verma, R. Salghi, H. Lgaz, A. K. Mukherjee and M. A. Quraishi, *New J. Chem.*, 2017, **41**(21), 13114-13129.
12. J. Wu, W. Sun, H. G. Xia and X. Sun, *Org. Biomol. Chem.*, 2006, **4**(9), 1663-1666.
13. X. Jia, X. Liu, Y. Yuan, P. Li, W. Hou and K. He, *Chem Asian J*, 2018, **13**(15), 1911-1914.
14. S. Rasal, S. Jain and N. G. Shimpi, *Synth Commun*, 2018, **48**(18), 2420-2434.
15. E. Hossein, M. Mahdi, H. Maede and E. Majid, *Phosphorus Sulfur Silicon Relat Elem*, 2015, **190**(10), 1606-1620.
16. F. Cecilia, S. Irena, L. Stipe, H. Ivan, M. Katia, D. Francesco, R. C. Pier, P. Andrea, S. Oleksii, B. Dario, P. L. Jean, V. David and C. Evelina, *ACS Sustain. Chem. Eng.*, 2020, **8**(51), 18889-18902.
17. M. Kasthuraiah, K. A. Kumar, C. S. Reddy and C. D. Reddy, *Heteroat. Chem.*, 2007, **18**, 2-8.
18. V. P. Charpe, A. A. Hande, A. Sagadevan and K. C. Hwang, *Green Chem.*, 2018, **20**, 4859.
19. S. Mathavan, K. Kannan and R. B. R. D. Yamajala, *Org. Biomol. Chem.*, 2019, **17**, 9620.