Supporting information for:

Synthesis of Bis(NHC) Based CNC-Pincer Rare-Earth Metal Amido Complexes and Their Application for the Hydrophosphination of Heterocumulenes

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I. ^{1}H NMR and ^{13}C NMR data of 9a-9o

^{i}PrN=C(PPh$_2$)(NH^{i}Pr) (9a): White solid, yield (618 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (s, 10H, C_6H_5), 4.04 – 3.89 (m, 2H, CH(CH$_3$)$_2$), 3.40 (d, ^{3}J = 6.5 Hz, 1H, NH), 0.93– 0.88 (m, 12H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8 (d, $^{1}J_{P\text{-}C}$ = 30.8 Hz), 133.8 (d, $^{1}J_{P\text{-}C}$ = 13.2 Hz), 133.1 (d, $^{2}J_{P\text{-}C}$ = 19.5 Hz), 128.3, 127.9 (d, $^{3}J_{P\text{-}C}$ = 6.9 Hz), 50.9 (d, $^{3}J_{P\text{-}C}$ = 35.9 Hz), 41.6, 23.8, 21.4. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ -17.11 ppm. HRMS (ESI): *m/z*: calcd 313.1828 for $C_{19}H_{26}N_2P$ [M+H]$^+$, found: 313.1831. Anal. Calcd for $C_{19}H_{25}N_2P$: C, 73.05; H, 8.07; N, 8.97. Found: C, 73.34; H, 8.29; N, 8.63. IR (KBr pellets, cm^{-1}): *v* 3416 (s), 2958 (s), 2862 (s), 1593 (s),1476 (s), 1433 (s), 1371 (m), 1344 (m), 1306 (m), 1221 (m), 1173 (s), 1090 (m), 1028 (m), 997 (m), 974 (m), 920 (w), 837 (w), 800 (w), 754 (m), 744 (s), 721 (m), 697 (s).

***Cy*N=C(PPh$_2$)(NH*Cy*) (9b):** White solid, yield (777 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 – 7.25 (m, 10H, C_6H_5), 3.78 – 3.69 (m, 1H, CH), 3.61 – 3.50 (m, 2H, CH), 1.74 – 0.78 (m, 20H, Cy). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.7 (d, $^{1}J_{P\text{-}C}$ = 30.7 Hz), 134.0 (d, $^{2}J_{P\text{-}C}$ = 13.3 Hz), 133.1 (d, $^{2}J_{P\text{-}C}$ = 19.5 Hz), 128.3, 127.9 (d, $^{3}J_{P\text{-}C}$ = 6.9 Hz), 59.2 (d, $^{3}J_{P\text{-}C}$ = 34.3 Hz), 47.5, 34.1, 31.2, 25.1, 24.9, 24.1, 23.1. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ -16.60 ppm; HRMS (ESI): *m/z*: calcd 393.2454 for $C_{25}H_{34}N_2P$ [M+H]$^+$; found: 393.2458. Anal. Calcd for $C_{25}H_{33}N_2P$: C, 76.50; H, 8.47; N, 7.14. Found: C, 76.85; H, 8.44; N, 6.87. IR (KBr pellets, cm^{-1}): *v* 3422 (s), 2928 (s), 2849 (s), 1584 (s), 1481 (s), 1447 (s), 1435 (s), 1367 (m), 1309 (m), 1252 (m), 1219 (m), 1190 (w), 1101 (m), 1026 (m), 997 (m), 974 (m), 916 (w), 848 (w), 894 (w), 752 (s), 741 (s), 696 (s).

^{i}PrN=C[P(C$_6$H$_4$-CH$_3$-4)$_2$](NH^{i}Pr) (9c): White solid, yield (674 mg, 99%).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.13 (m, 4H, C_6H_5), 7.09 (d, J = 7.7 Hz, 4H, C_6H_5), 3.94 (m, 2H, CH(CH$_3$)$_2$), 2.28 (s, 6H, CH_3), 0.90 (t, J = 6.7 Hz, 12H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7 (d, $^{1}J_{P\text{-}C}$ = 29.9 Hz), 139.6, 134.4 (d, $^{1}J_{P\text{-}C}$ = 19.7 Hz), 131.72 (d, $^{2}J_{P\text{-}C}$ = 11.2 Hz), 130.0 (d, $^{2}J_{P\text{-}C}$ = 7.0 Hz), 52.0 (d, $^{3}J_{P\text{-}C}$ = 35.3 Hz), 42.8 (d, $^{3}J_{P\text{-}C}$ =

11.2 Hz), 25.2, 22.8, 21.8. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ -18.89 ppm; HRMS (ESI): *m/z*: calcd 341.2141 for $C_{21}H_{30}N_2P$ $[M+H]^+$; found: 341.2141. Anal. Calcd for $C_{21}H_{29}N_2P$: C, 74.09; H, 8.59; N, 8.23. Found: C, 74.32; H, 8.73; N, 7.86. IR (KBr pellets, cm^{-1}): *v* 3408 (s), 2965 (s), 2864 (s), 1595 (s),1495 (s), 1449 (s), 1396 (m), 1373 (m), 1308 (m), 1227 (m), 1171 (s), 1119 (s), 1088 (s), 1040 (m), 1018 (m), 976 (m), 922 (w), 837 (w), 804 (m), 723 (m), 712 (s).

***Cy*N=C[P(C_6H_4-CH_3-4)$_2$](NH*Cy*) (9d):** White solid, yield (824 mg, 98%) ^1H NMR (300 MHz, $CDCl_3$): δ 7.30 (t, J = 7.7 Hz, 4H, C_6H_4), 7.18 (d, J = 7.5 Hz, 4H, C_6H_4), 3.89 – 3.74 (m, 1H, C*H*), 3.72 – 3.50 (m, 1H, C*H*), 2.37 (s, 6H, CH_3), 1.83 – 0.89 (m, 20H, Cy). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.6 (d, $^1J_{P\text{-}C}$ = 30.5 Hz), 139.5, 134.3 (d, $^1J_{P\text{-}C}$ = 19.7 Hz), 131.9 (d, $^2J_{P\text{-}C}$ = 12.1 Hz), 129.9 (d, $^3J_{P\text{-}C}$ = 7.0 Hz), 60.3 (d, $^3J_{P\text{-}C}$ = 33.6 Hz), 48.9, 35.4, 32.6, 26.4, 26.3, 25.5, 24.5, 21.7. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ -18.23 ppm; HRMS (ESI): *m/z*: calcd 421.2767 for $C_{27}H_{38}N_2P$ $[M+H]^+$; found: 421.2767. Anal. Calcd for $C_{27}H_{37}N_2P$: C, 77.11; H, 8.87; N, 6.66. Found: C, 77.40; H, 9.09; N, 6.46. IR (KBr pellets, cm^{-1}): *v* 3404 (s), 2940 (s), 2868 (s), 1601 (s),1495 (s), 1396 (m), 1381 (m), 1308 (m), 1204 (m), 1184 (s), 1153 (s), 1088 (s), 1040 (m), 991 (w), 976 (s), 920 (w), 843 (w), 806 (m), 752 (m), 711 (s).

S=C(PPh_2)(NH*Ph*) (9e): yellow solid, yield (642 mg, 100%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.72 (bs, 1H, N-*H*), 7.63 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, C_6H_5), 7.59 – 7.56 (m, 4H, C_6H_5), 7.46 (s, 6H), 7.35 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.8 Hz, 1H, C_6H_5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.2 (d, $^1J_{P\text{-}C}$ = 39.6 Hz), 139.2, 134.8 (d, $^2J_{P\text{-}C}$ = 20.6 Hz), 130.8, 129.8 (d, $^3J_{P\text{-}C}$ = 7.1 Hz), 129.4, 127.5, 122.8. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 19.64 ppm; HRMS (ESI): *m/z*: calcd 322.0814 for $C_{19}H_{17}NPS$ $[M+H]^+$; found: 322.0815. Anal. Calcd for $C_{19}H_{16}NPS$: C, 71.01; H, 5.02; N, 4.36; S, 9.98. Found: C, 71.38; H, 5.22; N, 4.17; S, 10.15. IR (KBr pellets, cm^{-1}): *v* 3300 (s), 2958 (s), 2872 (m), 2280 (w), 1985 (w), 1886 (w), 1825 (w), 1665 (w), 1595 (s), 1516 (m), 1485 (s), 1431 (s), 1381 (s), 1204 (m), 1155 (w), 1080 (m), 1024 (m), 997 (m), 974 (m), 924 (w), 905 (m), 852 (w), 797 (m), 721 (s), 692 (s).

S=C(PPh_2)(NH*C_6H_4-F-4*) (9f): yellow solid, yield (678 mg, 100%).^1H NMR (300 MHz, $CDCl_3$): δ 8.67 (s, 1H, N*H*), 7.61 – 7.55 (m, 6H, C_6H_5), 7.54 – 7.47 (m, 6H,

C_6H_5), 7.04 (t, $^3J_{F–H} = ^3J_{H–H}$ = 8.4 Hz, 2H, C_6H_5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.7 (d, $^1J_{P-C}$ = 39.8 Hz), 161.13 (d, $^1J_{F-C}$ = 247.6 Hz), 135.3 (br), 134.9, 134.8, 134.7, 130.8, 129.8 (d, $^3J_{P-C}$ = 7.4 Hz), 125.1 (d, $^3J_{F-C}$ = 8.1 Hz), 116.2 (d, $^2J_{F-C}$ = 22.7 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 19.58 ppm; HRMS (ESI): *m/z*: calcd 340.0720 for $C_{19}H_{16}NPSF$ $[M+H]^+$; found: 340.0726. Anal. Calcd for $C_{19}H_{15}NPSF$: C, 67.24; H, 4.46; N, 4.13; S, 9.45. Found: C, 66.91; H, 4.86; N, 4.56; S, 9.21. IR (KBr pellets, cm^{-1}): *v* 3310 (s), 2925 (m), 1881 (w), 1822 (w), 1639 (w), 1609 (m), 1524 (m), 1497 (s), 1433 (s), 1371 (s), 1223 (m), 1157 (w), 1099 (m), 1080 (m), 1024 (m), 997 (m), 984 (m), 925(w), 916 (m), 837 (s), 746 (m), 729 (s), 692 (s).

S=C(PPh$_2$)(NH*C_6H_4-Br-4*) (9g): yellow solid, yield (798 mg, 100%).^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (s, 1H, NH), 7.58 – 7.43 (m, 14H, C_6H_5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.7 (d, $^1J_{P-C}$ = 40.2 Hz), 138.3, 134.8 (d, $^2J_{P-C}$ = 20.5 Hz), 130.9, 129.8 (d, $^3J_{P-C}$ = 7.4 Hz), 124.4, 120.2; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 20.62 ppm; HRMS (ESI): *m/z*: calcd 399.9920 for $C_{19}H_{16}NPS^{79}Br$ $[M+H]^+$; found: 399.9926; calcd 401.9899 for $C_{19}H_{16}NPS^{81}Br$ $[M+H]^+$; found: 401.9905. Anal. Calcd for $C_{19}H_{15}NPSBr$: C, 57.01; H, 3.78; N, 3.50; S, 8.01. Found: C, 56.64; H, 3.40; N, 3.81; S, 7.78. IR (KBr pellets, cm^{-1}): *v* 3310 (s), 3055 (m), 1965 (w),1888 (w), 1591 (m), 1584 (m), 1514 (m), 1483 (s), 1433 (s), 1396 (w), 1279 (s), 1177 (w), 1113 (m), 1084 (m), 1024 (m), 999 (m), 982 (m), 918 (m), 825 (s), 746 (s), 727 (s), 696 (s).

S=C(PPh$_2$)(NH*C_6H_4-CH_3-4*) (9h): yellow solid, yield (630 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (s, 1H, N*H*), 7.58 – 7.55 (m, 4H, C_6H_5), 7.49 (d, *J* = 8.4 Hz, 2H, C_6H_5), 7.46 – 7.45 (m, 6H, C_6H_5), 7.15 (d, *J* = 8.3 Hz, 2H, C_6H_5), 2.32 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.7 (d, $^1J_{P-C}$ = 39.1 Hz), 137.11 (d, $^1J_{P-C}$ = 89.6 Hz), 135.0 (d, $^2J_{P-C}$ = 15.4 Hz), 134.8 (d, $^1J_{P-C}$ = 20.6 Hz), 130.7, 129.9, 129.71 (d, $^3J_{P-C}$ = 7.3 Hz), 122.9, 21.6. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 18.90 ppm; HRMS (ESI): *m/z*: calcd 336.0970 for $C_{20}H_{19}NPS$ $[M+H]^+$; found: 336.0972. Anal. Calcd for $C_{20}H_{18}NPS$: C, 71.62; H, 5.41; N, 4.18; S, 9.56. Found: C, 71.99; H, 5.75; N, 3.83; S, 9.72. IR (KBr pellets, cm^{-1}): *v* 3302 (s), 2916 (m), 1961 (w),1892 (w), 1595 (m), 1584 (m), 1518 (m), 1474 (s), 1433 (s), 1381 (w), 1290 (m), 1179 (w), 1121 (m), 1084 (m), 1026 (m), 997 (m), 980 (m), 924 (m), 827 (s), 744 (s), 723 (s), 696 (s).

S=C(PPh$_2$)(NH*C_6H_4-OCH_3-4*) (9i): yellow solid, yield (604 mg, 86%).^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (s, 1H, N*H*), 7.60 – 7.51 (m, 6H, C_6H_5), 7.46 – 7.45 (m, 6H, C_6H_5), 6.87 (d, *J* = 9.0 Hz, 2H, C_6H_5), 3.79 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.4 (d, $^{1}J_{P\text{-}C}$ = 39.2 Hz), 158.6, 135.1 (d, $^{2}J_{P\text{-}C}$ = 15.7 Hz), 134.8 (d, $^{1}J_{P\text{-}C}$ = 20.5 Hz), 132.4, 130.7, 129.7 (d, $^{3}J_{P\text{-}C}$ = 7.3 Hz), 124.7, 114.4, 55.9. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 18.39 ppm; HRMS (ESI): *m/z*: calcd 352.0925 for $C_{20}H_{19}NOPS$ $[M+H]^+$; found: 352.0927. Anal. Calcd for $C_{20}H_{18}NOPS$: C, 68.36; H, 5.16; N, 3.99; S, 9.12. Found: C, 67.98; H, 5.54; N, 4.21; S, 8.85. IR (KBr pellets, cm^{-1}): *v* 3302 (s), 2951 (m), 2932 (m), 1964 (w),1902 (w), 1595 (s), 1568 (m), 1506 (m), 1474 (s), 1433 (s), 1375 (m), 1301 (m), 1157 (w), 1113 (m), 1084 (m), 1031 (m), 999 (m), 981 (m), 924 (m), 833 (s), 731 (s), 696 (s).

S=C[P(C_6H_4-CH_3-4)$_2$](NH*Ph*) (9j): Yellow solid, yield (691 mg, 99%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (bs, 1H, N-*H*), 7.66 – 7.26 (m, 13H, Ar-*H*), 2.40 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.3 (d, $^{1}J_{P\text{-}C}$ = 39.7 Hz), 141.0, 139.3, 134.9 (d, $^{2}J_{P\text{-}C}$ = 20.8 Hz), 131.7 (d, $^{2}J_{P\text{-}C}$ = 14.4 Hz), 130.6 (d, $^{3}J_{P\text{-}C}$ = 7.5 Hz), 129.4, 127.4, 122.9, 21.9. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 18.80 ppm; HRMS (ESI): *m/z*: calcd 350.1127 for $C_{21}H_{21}NPS$ $[M+H]^+$; found: 350.1128. Anal. Calcd for $C_{21}H_{20}NPS$: C, 72.18; H, 5.77; N, 4.01; S, 9.18. Found: C, 72.44; H, 6.02; N, 3.68; S, 8.93. IR (KBr pellets, cm^{-1}): *v* 3308 (s), 2916 (m), 2859 (m), 1936 (m), 1906 (w), 1659 (m), 1593 (s), 1510 (m), 1491 (s), 1437 (s), 1395 (m), 1350 (m), 1287 (s), 1120 (s), 1117 (m), 1024 (m), 1086 (s), 1018 (m), 984 (m), 901 (m), 847 (w), 812 (s), 800 (s), 758 (s), 719 (s), 708 (s).

S=C[P(C_6H_4-CH_3-4)$_2$](NH*C_6H_4-F-4*) (9k): Yellow solid, yield (727 mg, 99%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (bs, 1H, N-*H*), 7.62 – 7.02 (m, 12H, Ar-*H*), 2.39 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.8 (d, $^{1}J_{P\text{-}C}$ = 39.8 Hz), 161.1 (d, $^{1}J_{F\text{-}C}$ = 247.5 Hz), 141.0, 135.27, 134.8 (d, $^{2}J_{P\text{-}C}$ = 20.9 Hz), 131.5 (d, $^{2}J_{P\text{-}C}$ = 14.1 Hz), 130.5 (d, $^{3}J_{P\text{-}C}$ = 7.7 Hz), 125.1 (d, $^{3}J_{F\text{-}C}$ = 7.9 Hz), 116.1 (d, $^{2}J_{F\text{-}C}$ = 22.7 Hz), 21.9. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 18.76 ppm; HRMS (ESI): *m/z*: calcd 368.1033 for $C_{21}H_{20}NPSF$ $[M+H]^+$; found: 368.1037. Anal. Calcd for $C_{21}H_{19}NPSF$: C, 68.65; H, 5.21; N, 3.81; S, 8.73. Found: C, 68.31; H, 5.47; N, 3.50; S, 8.66. IR (KBr pellets, cm^{-1}): ν 3310 (s), 2918 (m), 2860 (m), 1879 (w), 1827 (w), 1593 (s), 1522 (s), 1495 (s), 1443 (s), 1395 (m), 1395 (m), 1348 (m), 1287 (m), 1221(m), 1194 (m), 1157 (s), 1119 (w), 1094 (m), 1038 (m), 1018 (m), 988 (m), 924(w), 833 (s), 816 (m), 800 (s), 748 (s), 733 (s), 710 (s).

S=C[P(C_6H_4-CH_3-4)$_2$](NH*C_6H_4-Br-4*) (9l): Yellow solid, yield (820 mg, 96%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (bs, 1H, N-*H*), 7.57 – 7.25 (m, 12H, Ar-*H*), 2.40 (s, 6H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.9 (d, $^1J_{P\text{-}C}$ = 39.9 Hz), 141.1, 138.3, 134.9 (d, $^2J_{P\text{-}C}$ = 20.9 Hz), 132.3, 131.5 (d, $^2J_{P\text{-}C}$ = 13.9 Hz), 130.6 (d, $^3J_{P\text{-}C}$ = 7.6 Hz), 124.4, 120.1, 21.9. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 19.85 ppm; HRMS (ESI): *m/z*: calcd 428.0232 for $C_{21}H_{20}NPS^{79}Br$ [M+H]$^+$; found: 428.0234; calcd 430.0212 for $C_{21}H_{20}NPS^{81}Br$ [M+H]$^+$; found: 430.0213. Anal. Calcd for $C_{21}H_{19}NPSBr$: C, 58.89; H, 4.47; N, 3.27; S, 7.49. Found: C, 59.16; H, 4.23; N, 3.42; S, 7.54. IR (KBr pellets, cm^{-1}): ν 3308 (s), 2916 (m), 2860 (m), 1892 (w), 1589 (s), 1518 (s), 1483 (s), 1396 (m), 1356 (s), 1304 (s), 1277 (m), 1198 (m), 1186 (s), 1115 (w), 1094 (m), 1084 (m), 1038 (m), 1007 (s), 984 (m), 939(w), 853 (s), 839 (s), 819 (s), 802 (s), 729 (s), 710 (s).

S=C[P(C_6H_4-CH_3-4)$_2$](NH*C_6H_4-CH_3-4*) (9m): Yellow solid, yield (654 mg, 90%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (s, 1H, N-*H*), 7.52 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.48 (t, *J* = 7.5 Hz, 4H, Ar-*H*), 7.28 (d, *J* = 7.1 Hz, 4H, Ar-*H*), 7.18 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 2.41 (s, 6H, C*H*$_3$), 2.35 (s, 3H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.7 (d, $^1J_{P\text{-}C}$ = 39.2 Hz), 140.9, 137.1 (d, $^2J_{P\text{-}C}$ = 61.9 Hz), 137.4, 136.9, 134.8 (d, $^2J_{P\text{-}C}$ = 20.7 Hz), 131.8 (d, $^3J_{P\text{-}C}$ = 14.1 Hz), 130.5 (d, $^3J_{P\text{-}C}$ = 7.7 Hz), 129.9, 123.0, 21.9, 21.6. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 18.05 ppm; HRMS (ESI): *m/z*: calcd 364.1283 for $C_{22}H_{23}NPS$ [M+H]$^+$; found: 364.1286. Anal. Calcd for $C_{22}H_{22}NPS$: C, 72.70; H, 6.10 N, 3.85; S, 8.82. Found: C, 72.88; H, 6.47; N, 3.52; S, 9.12. IR (KBr pellets, cm^{-1}): ν 3306 (s), 2860 (m), 1896 (m), 1595 (s), 1518 (s), 1506 (s), 1445 (m), 1395 (m), 1368 (s), 1341 (s), 1288 (m), 1213 (m), 1196 (s), 1120 (m), 1105 (w), 1084 (m), 1036 (m), 1016 (m), 980 (s), 939 (w), 851 (s), 841 (s), 812 (s), 802 (s), 730 (m), 710 (m).

S=C[P(C_6H_4-CH_3-4)$_2$](NH*C_6H_4-OCH_3-4*) (9n): Yellow solid, yield (614 mg, 81%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71 (s, 1H, N-*H*), 7.56 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.49 (t, J = 7.5 Hz, 4H, Ar-H), 7.28 (d, J = 7.6 Hz, 4H, Ar-H), 6.90 (d, J = 8.3 Hz, 2H, Ar-H), 3.82 (s, 3H, OCH_3), 2.41 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.5 (d, $^1J_{P\text{-}C}$ = 38.9 Hz), 158.5, 140.9, 134.8 (d, $^2J_{P\text{-}C}$ = 20.8 Hz), 132.5, 131.8 (d, $^2J_{P\text{-}C}$ = 14.5 Hz), 130.5 (d, $^3J_{P\text{-}C}$ = 7.6 Hz), 124.8, 114.4, 55.9, 21.9. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 17.55 ppm; HRMS (ESI): m/z: calcd 380.1233 for $C_{22}H_{23}NOPS$ $[M+H]^+$; found: 380.1235. Anal. Calcd for $C_{22}H_{22}NOPS$: C, 69.64; H, 5.84, N, 3.69; S, 8.45. Found: C, 69.39; H, 6.02; N, 3.47; S, 8.26. IR (KBr pellets, cm^{-1}): v 3304 (s), 2830 (m), 1927 (m), 1902 (m), 1595 (s), 1526 (s), 1503 (s), 1435 (m), 1375 (m), 1346(s), 1302 (s), 1248 (m), 1206 (m), 1179 (s), 1111 (m), 1086 (m), 1032 (m), 1018 (m), 984 (s), 924 (w), 856 (m), 831 (s), 814 (s), 800 (s), 733 (m), 706 (m).

O=C(PPh$_2$)(NH*Cy*) (9o): White solid, yield (604 mg, 97%) ^{1}H NMR (300 MHz, C_6D_6): δ 7.74 – 7.72 (m, 4H, C_6H_5), 7.16 (m, 6H, C_6H_5), 5.78 (bd, $^3J_{H-H}$= 4.4 Hz, 1H, NH), 4.06-4.03 (m, 1H, CH), 1.74 – 1.71 (m, 2H, CH_2), 1.35-1.24 (m, 3H, CH_2), 1.17-1.10 (m, 2H, CH_2), 0.93-0.81 (m, 3H, CH_2). ^{13}C NMR (75 MHz, C_6D_6): δ 174.7 (d, $^1J_{P\text{-}C}$ = 12.5 Hz), 135.1 (d, $^1J_{P\text{-}C}$ = 11.8 Hz), 135.0, 134.4 (d, $^2J_{P\text{-}C}$ = 19.0 Hz), 129.3, 128.8 (d, $^3J_{P\text{-}C}$ = 7.1 Hz), 48.5, 32.6, 25.3, 24.5. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ -3.66 ppm; HRMS (ESI): m/z: calcd 312.1512 for $C_{19}H_{23}NOP$ $[M+H]^+$; found: 312.1514. Anal. Calcd for $C_{19}H_{22}NOP$: C, 73.29; H, 7.12, N, 4.50; S, 9.95. Found: C, 73.45; H, 7.36; N, 4.31; S, 9.74. IR (KBr pellets, cm^{-1}): v 3254 (s), 2930 (m), 1977 (m), 1952 (m), 1625 (s), 1506 (s), 1453 (m), 1375 (m), 1347(s), 1308 (s), 1258 (m), 1216 (m), 1189 (s), 1161 (m), 1096 (m), 1023 (m), 1018 (m), 884 (s), 841 (s), 814 (s), 800 (s), 733 (m), 706 (m).

II. Crystallographic data of complexes 1-6, 8 and compound 7 and 10a.

Table S1. Summary of crystal and refinement data for complexes 1-3.

Crystal data	**1**	**2**	**3**
Empirical formula	$C_{34}H_{58}N_7Si_4Y$	$C_{34}H_{58}N_7Si_4Eu$	$C_{34}H_{58}N_7Si_4Er$

cryst system, space group	Monoclinic, *P2(1)/c*	Triclinic, *P*(-1)	Monoclinic, *P2(1)/c*
a (Å)	11.8957(14)	11.9169(8)	11.8985(11)
b (Å)	29.649(3)	29.663(2)	29.713(3)
c (Å)	12.2559(14)	12.2490(8)	12.2534(11)
α (deg)	90	90	90
β(deg)	105.336(2)	105.2560(10)	104.9590(10)
γ(deg)	90	90	90
T (K)	293(2)	293(2)	293(2)
V ($Å^3$)	4168.7(8)	4177.3(5)	4185.2(7)
Z	4	4	4
wavelength (Å)	0.71073	0.71073	0.71073
Dcalcd ($g\ cm^{-3}$)	1.221	1.318	1.340
μ (mm^{-1})	1.545	1.647	2.151
F (000)	1624	1720	1740
θ range	1.37 to 27.60	1.37 to 27.42	1.77 to 27.67
R_1/wR_2[I>2ó(I)]	0.0511, 0.0975	0.0424, 0.0750	0.0633, 0.1830
R_1/wR_2(all data)	0.1052, 0.1134	0.0798, 0.0853	0.0805, 0.1935

Table S2. Summary of crystal and refinement data for complexes 4-6 and 8.

Crystal data	**4**	**5**	**6**	**8**

Empirical formula	$C_{38}H_{66}N_7Si_4Y$	$C_{38}H_{66}N_7Si_4Er$	$C_{38}H_{66}N_7Si_4Yb$	$C_{32}H_{48}N_6Si_2IYb$
cryst system, space group	Triclinic, *P*(-1)	Triclinic, *P*(-1)	Triclinic, *P*(-1)	Monoclinic, *C*2/c
a (Å)	10.9565(18)	10.9610(6)	10.929(4)	28.4314(15)
b (Å)	12.319(3)	12.3125(7)	12.244(4)	11.3802(6)
c (Å)	17.945(3)	17.9218(10)	17.881(6)	22.8123(12)
α (deg)	77.695(2)	77.7490(10)	77.729(4)	90
β(deg)	74.583(2)	74.6450(10)	74.611(4)	90.9180(10)
γ(deg)	80.281(2)	80.2260(10)	80.560(5)	90
T (K)	293(2)	293(2)	293(2)	293(2)
V ($Å^3$)	2265.1(8)	2262.6(2)	2239.5(13)	7380.1(7)
Z	2	2	2	8
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Dcalcd (g cm^{-3})	1.200	1.322	1.344	1.571
μ (mm^{-1})	1.425	1.994	2.229	3.465
F (000)	872	934	938	3464
θ range	1.70 to 27.62	1.70 to 27.79	1.71 to 25.00	1.43 to 27.58
R_1/wR_2[I>2ó(I)]	0.0631, 0.1547	0.0347, 0.0797	0.0742, 0.1959	0.0615, 0.1944
R_1/wR_2 (all data)	0.1158, 0.1786	0.0488, 0.0851	0.0930, 0.2140	0.0802, 0.2134

Table S3. Summary of crystal and refinement data for fused-heterocyclic

compound 7 and 10a.

Crystal data	**7**	**10a**
Empirical formula	$C_{22}H_{23}N_5$	$C_{21}H_{12}F_3N_3O_3$
cryst system, space group	Triclinic, *P*(-1)	Monoclinic, *C*2/c
a (Å)	10.2958(16)	17.763(2)
b (Å)	11.9008(18	16.761(2)
c (Å)	17.378(3)	8.1510(10)
α (deg)	91.658(2)	90
β(deg)	100.274(2)	93.210(2)
γ(deg)	113.611(2)	90
T (K)	293(2)	293(2)
V ($Å^3$)	1907.8(5)	2422.8(5)
Z	4	4
wavelength (Å)	0.71073	0.71073
Dcalcd (g cm^{-3})	1.244	1.128
μ (mm^{-1})	0.077	0.092
F (000)	760	840
θ range	1.88 to 27.60	1.67 to 27.70
R_1/wR_2[I>2ó(I)]	0.0604, 0.1705	0.0479, 0.1185
R_1/wR_2(all data)	0.0954, 0.1931	0.0912, 0.1305

III. Copies of ^{1}H NMR, ^{13}C NMR Spectra of complexes (1, 4) and compound 7.

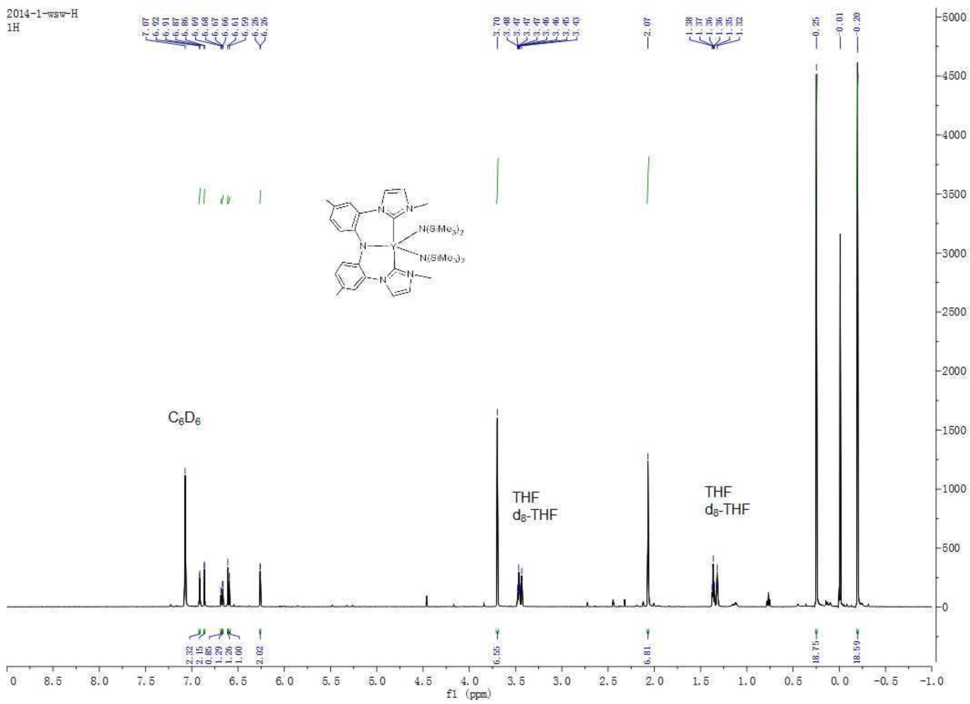

Figure S1. ^{1}H NMR spectrum (500 MHz, C_6D_6/d_8-THF: V/V = 3:1, 298 K) of [$\mathbf{L^2}$Y{N(SiMe$_3$)$_2$}$_2$] (**1**).

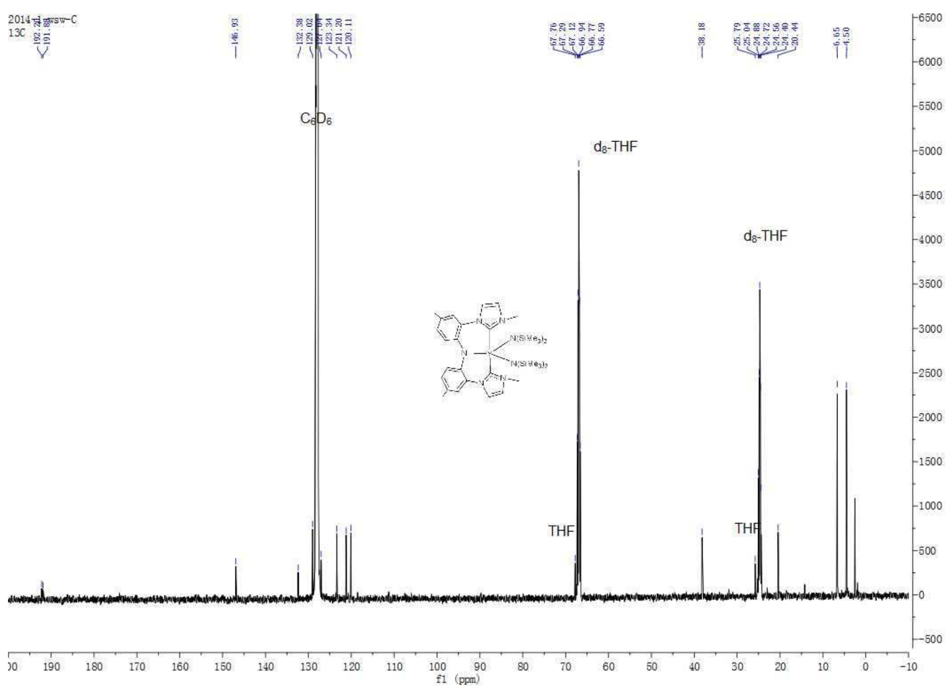

Figure S2. ^{13}C NMR spectrum (125 MHz, C_6D_6/d_8-THF: V/V = 3:1, 298 K) of [$\mathbf{L^2}$Y{N(SiMe$_3$)$_2$}$_2$] (**1**).

Because complex **1** could ligate to THF, there are some coordinating THF residual peacks at 1.32 ppm, 3.43 ppm in the ^{1}H NMR spectrum and 25.8 ppm, 67.8 ppm in the ^{13}C NMR spectrum.

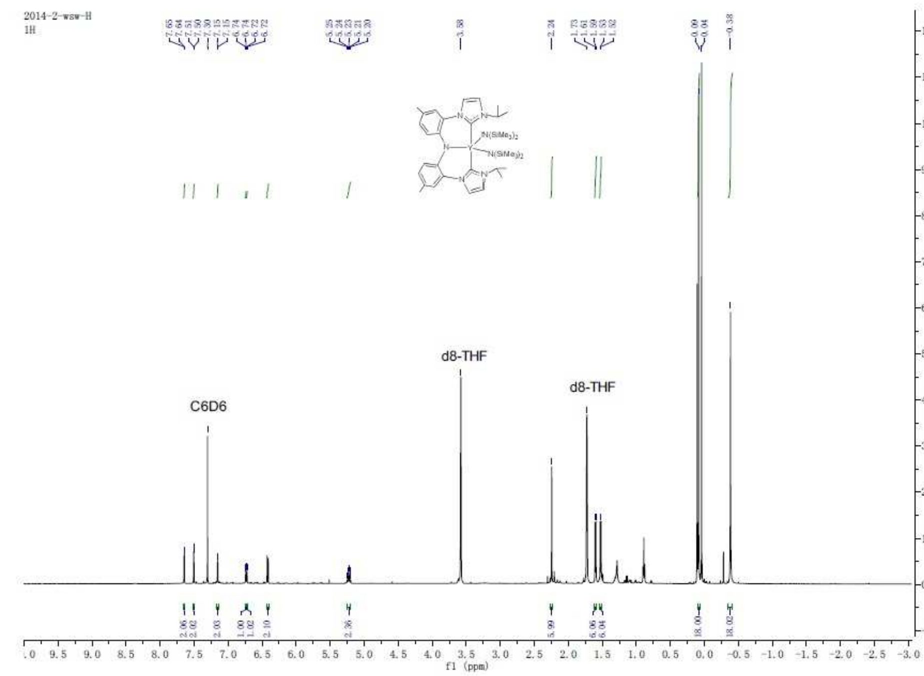

Figure S3. ^{1}H NMR spectrum (500 MHz, C_6D_6/d_8-THF: V/V = 1:5, 298 K) of $[\mathbf{L^3}Y\{[N(SiMe_3)_2]_2\}_2]$ (**4**).

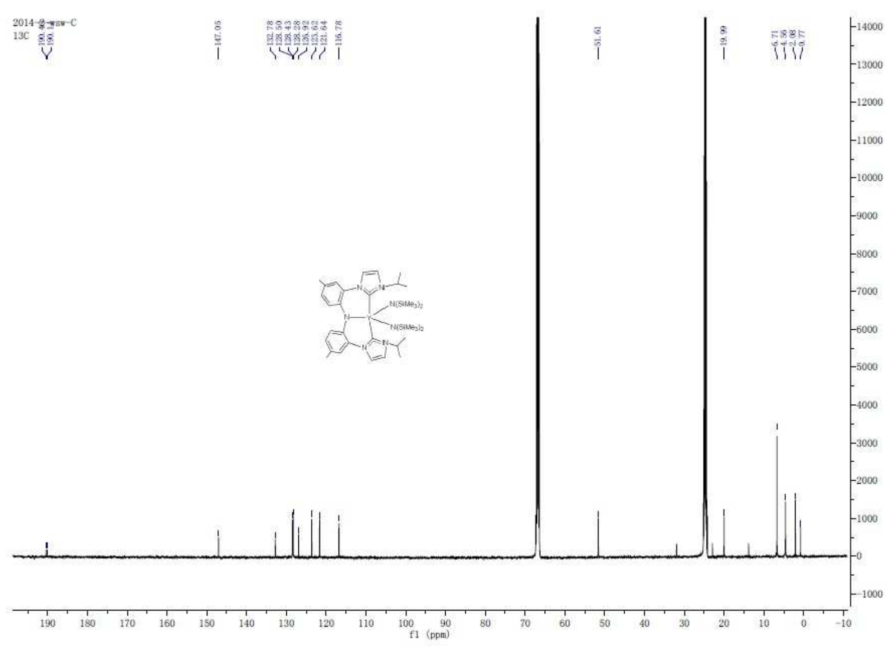

Figure S4. ^{13}C NMR spectrum (125 MHz, C_6D_6/d_8-THF: V/V = 1:5, 298 K) of $[\mathbf{L^3}Y\{[N(SiMe_3)_2]_2\}_2]$ (**4**).

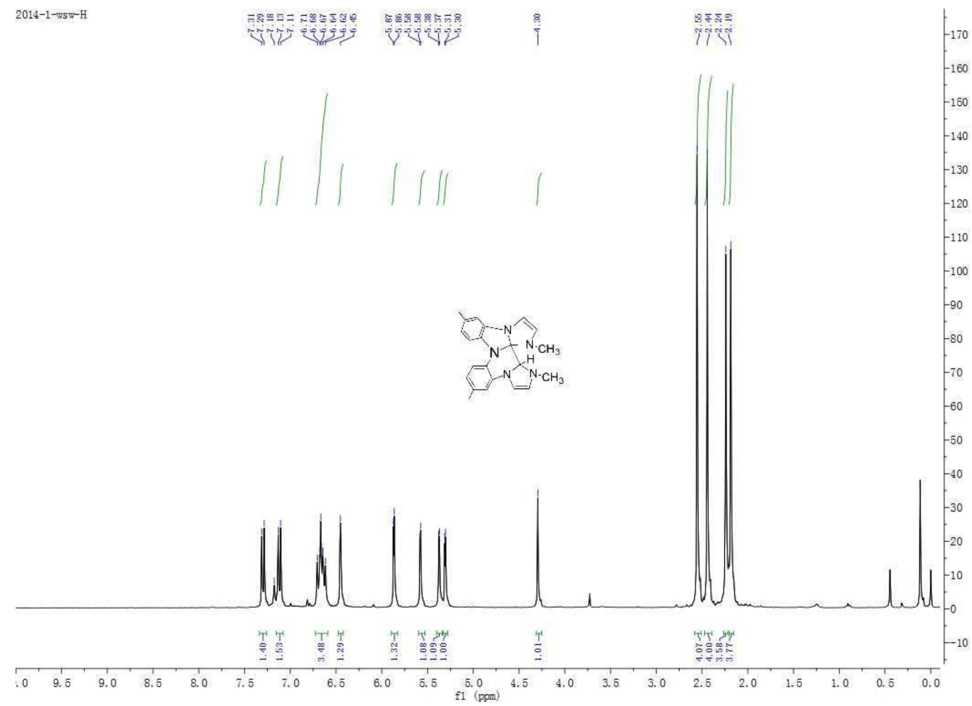

Figure S5. ^{1}H NMR spectrum (300 MHz, C_6D_6, 298 K) of fused-heterocyclic compound **7**.

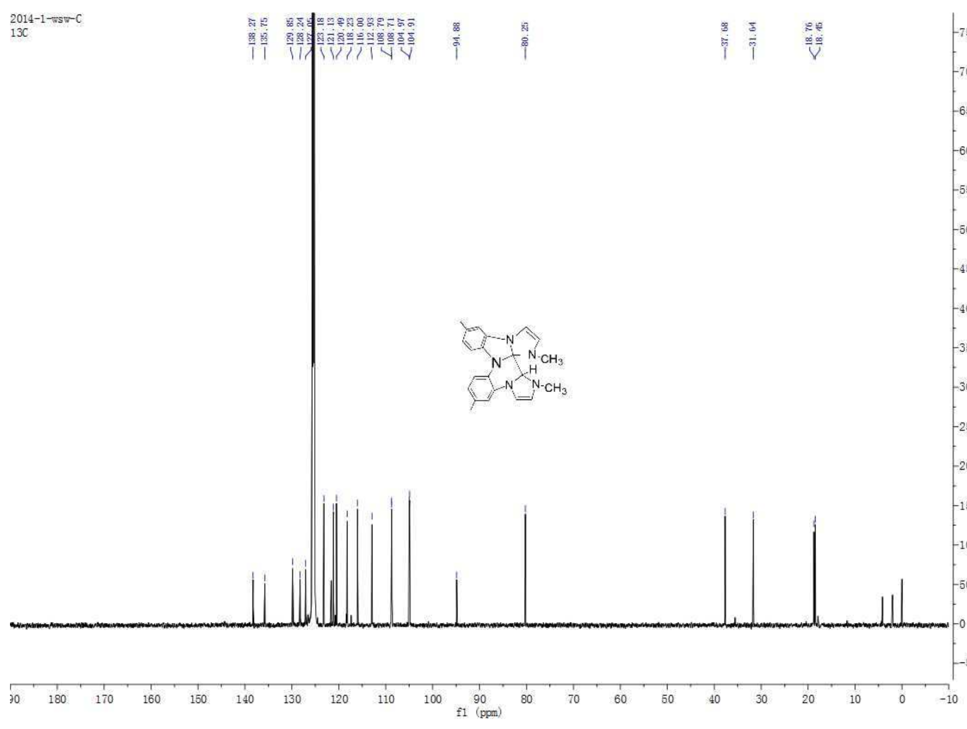

Figure S6. ^{13}C NMR spectrum (125 MHz, C_6D_6, 298 K) of fused-heterocyclic compound **7**.

IV. Copies of ^{1}H NMR, ^{13}C NMR Spectra and of 9a-9o

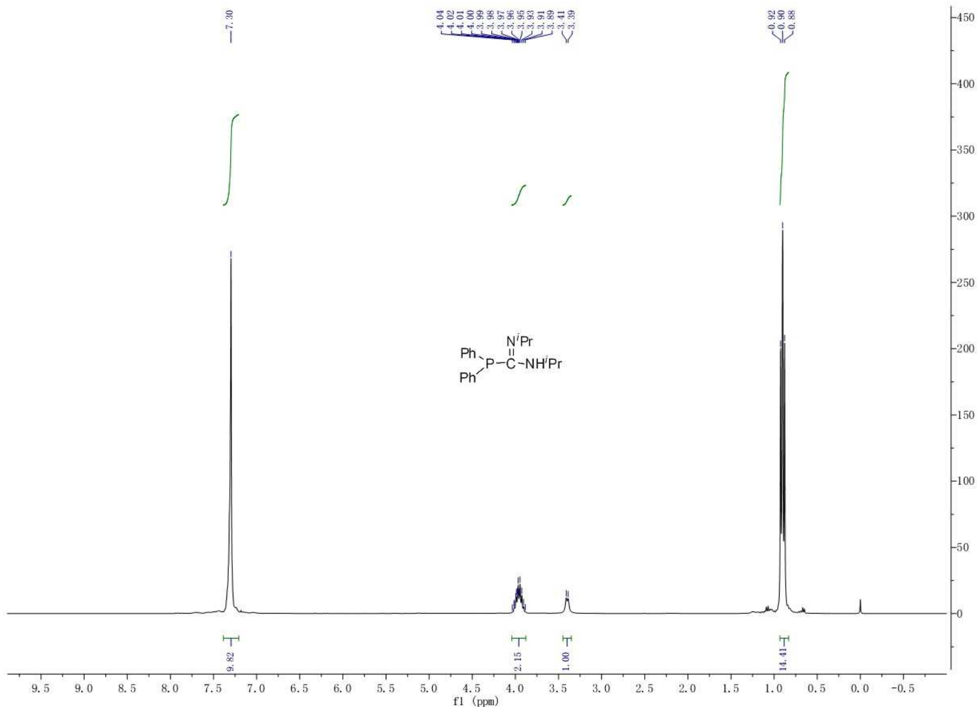

Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9a**.

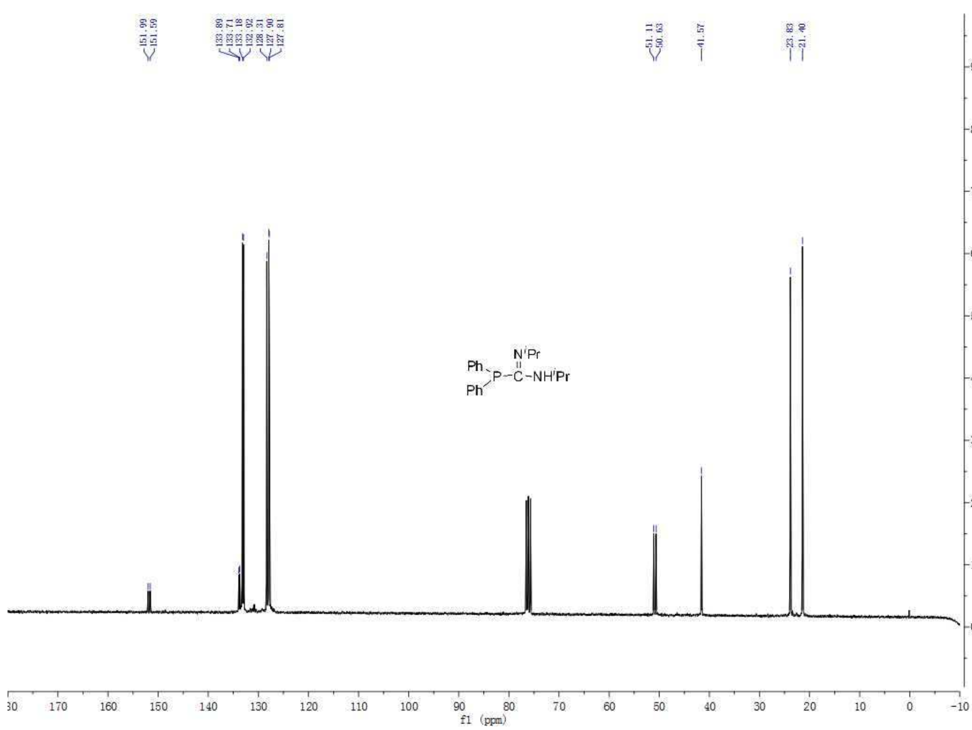

Figure S8. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **9a**.

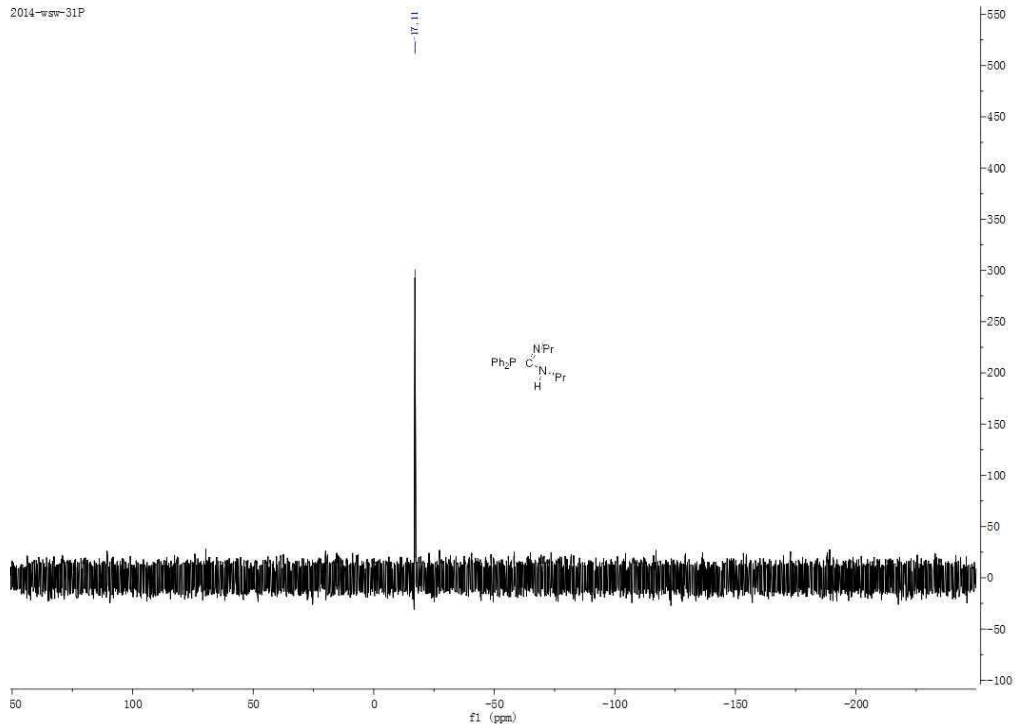

Figure S9. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9a**.

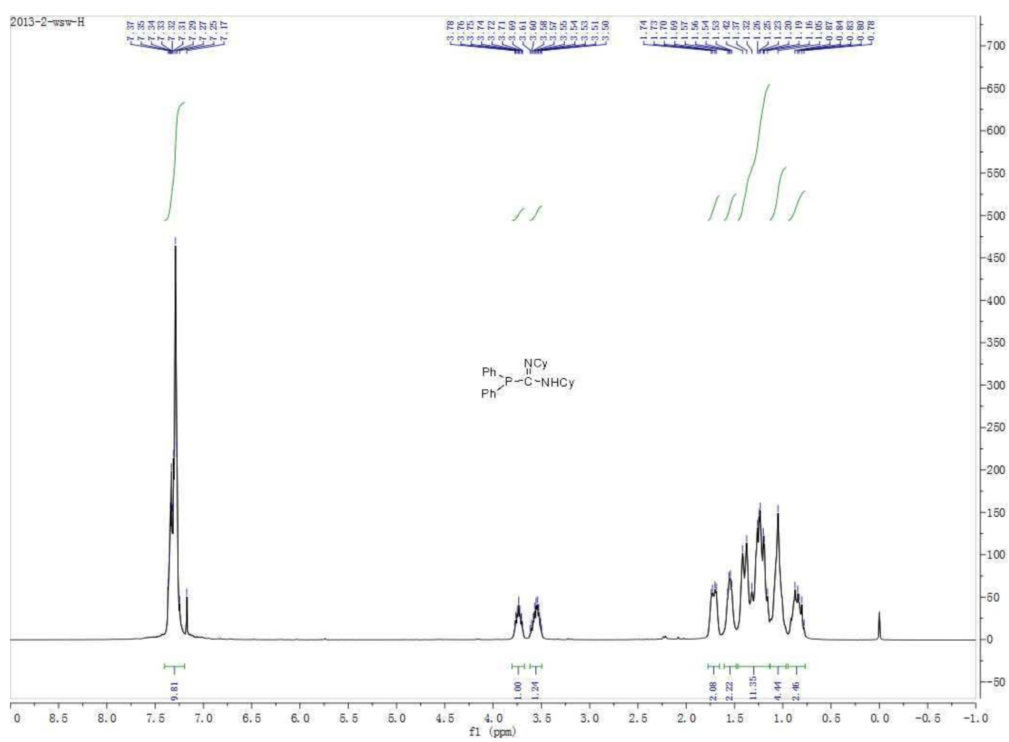

Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9b**.

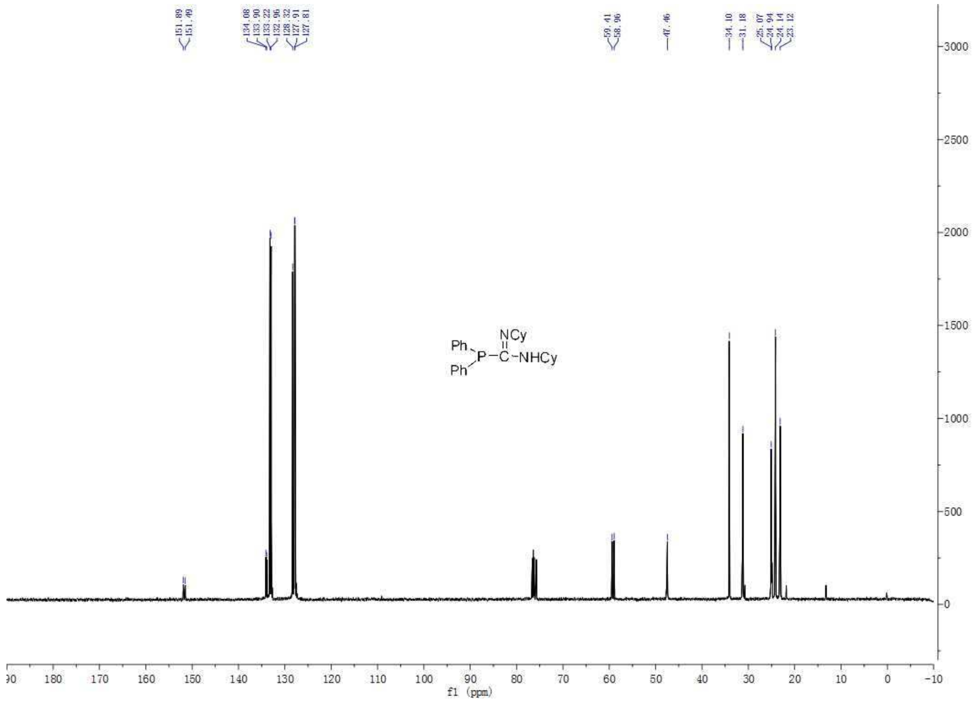

Figure S11. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **9b**.

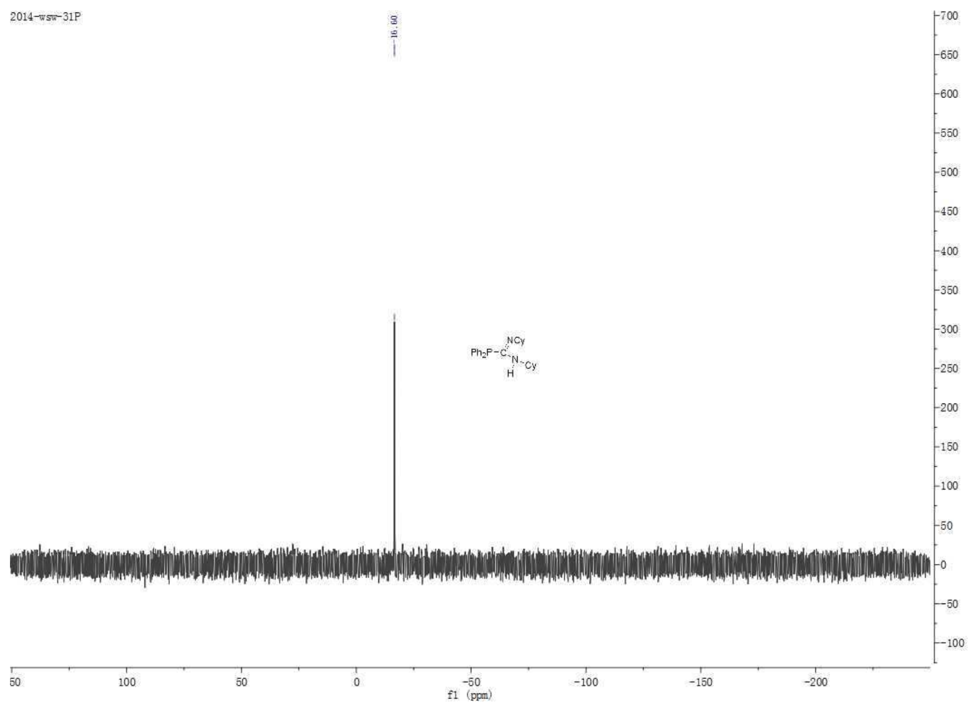

Figure S12. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9b**.

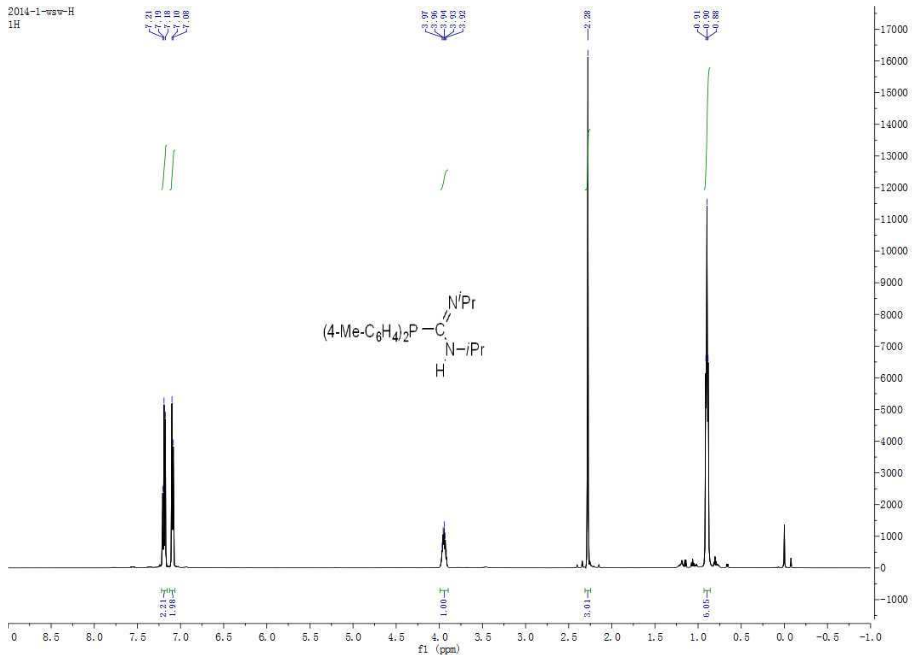

Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **9c**.

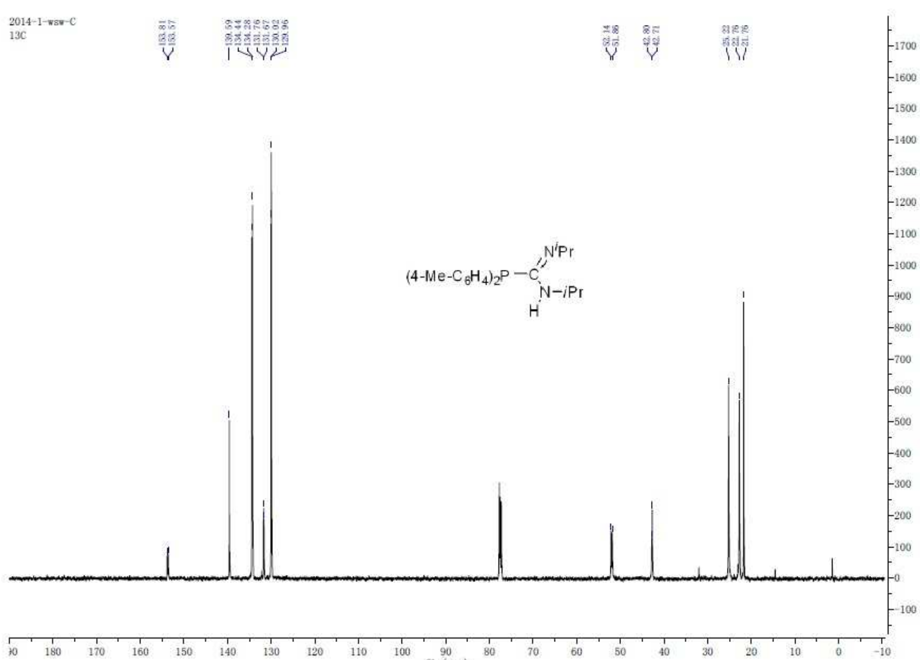

Figure S14. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9c**.

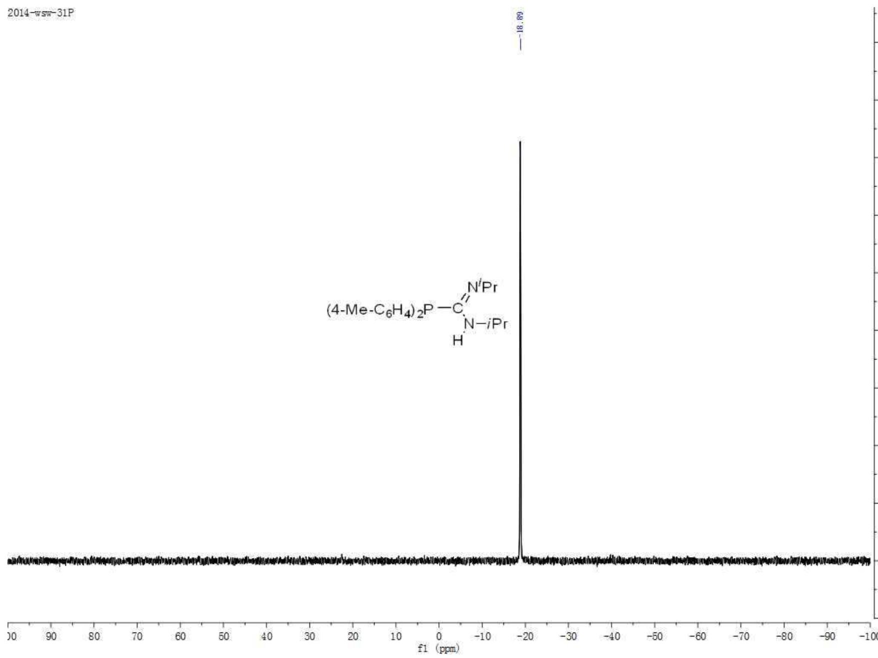

Figure S15. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9c**.

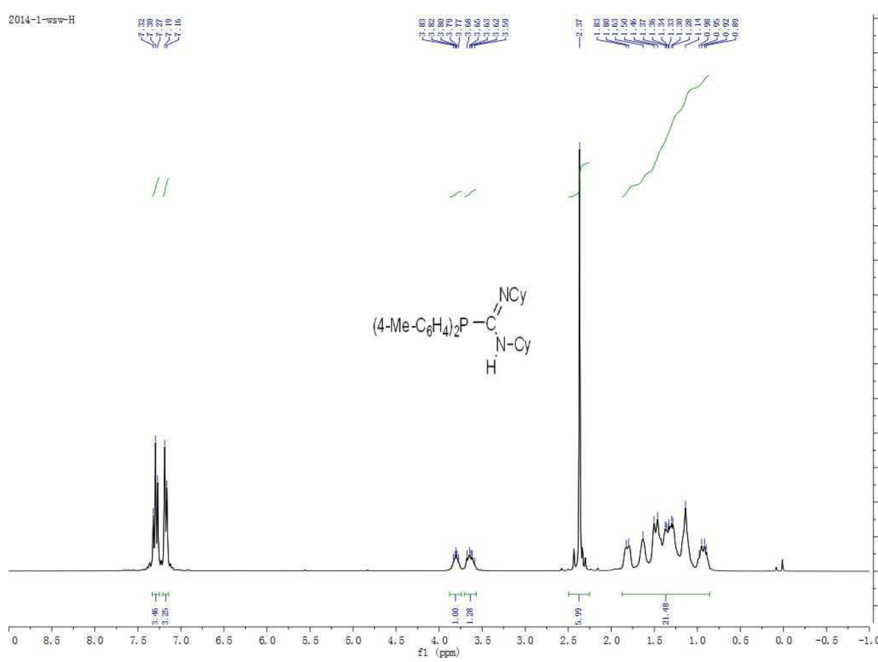

Figure S16. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9d**.

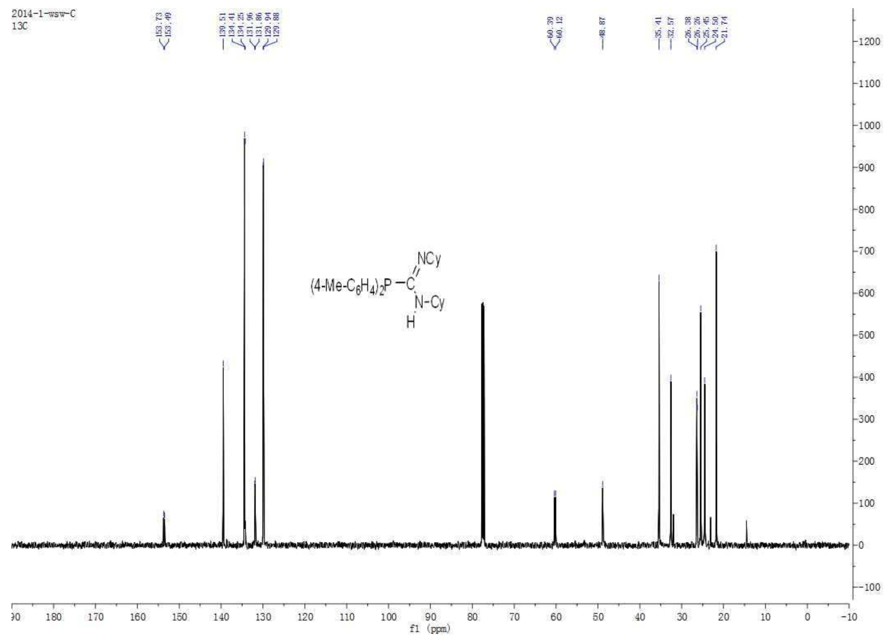

Figure S17. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9d**.

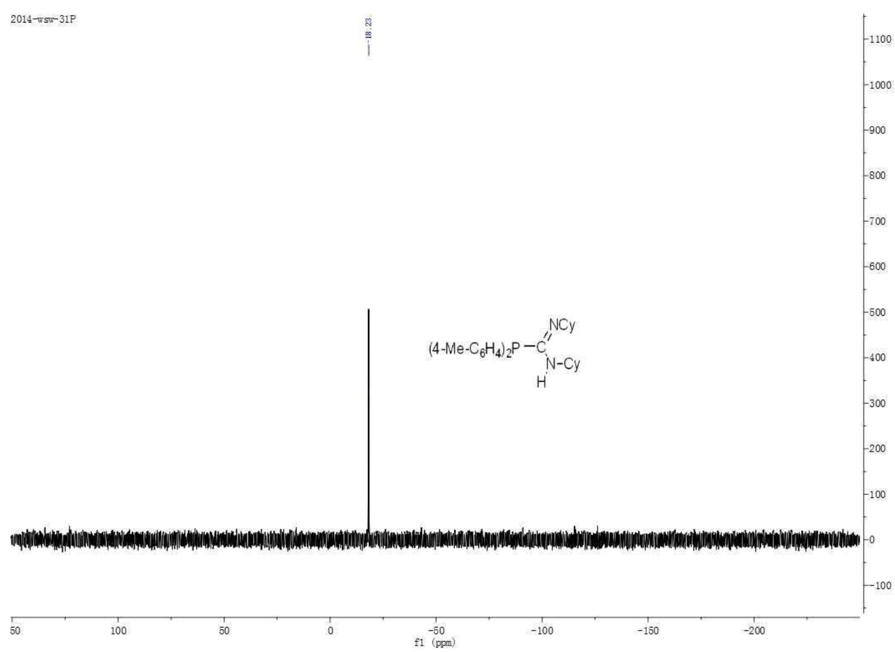

Figure S18. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9d**.

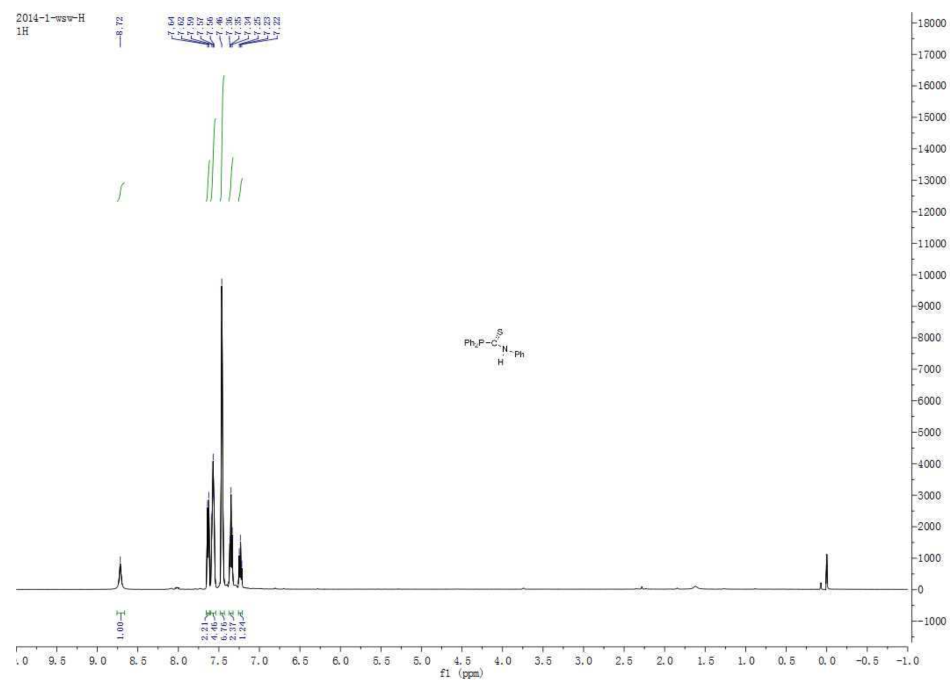

Figure S19. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **9e**.

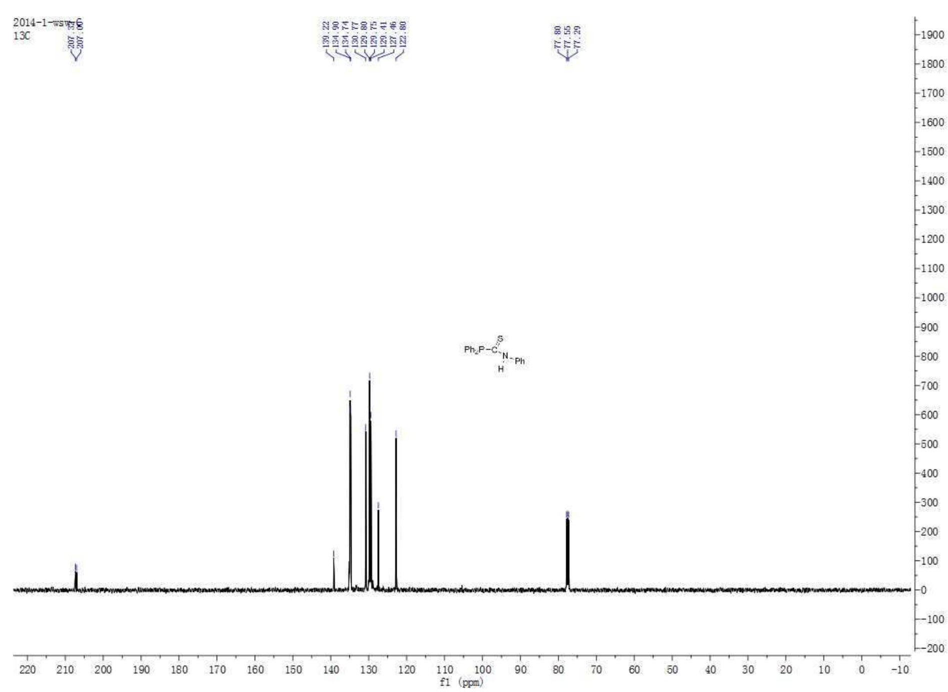

Figure S20. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9e**.

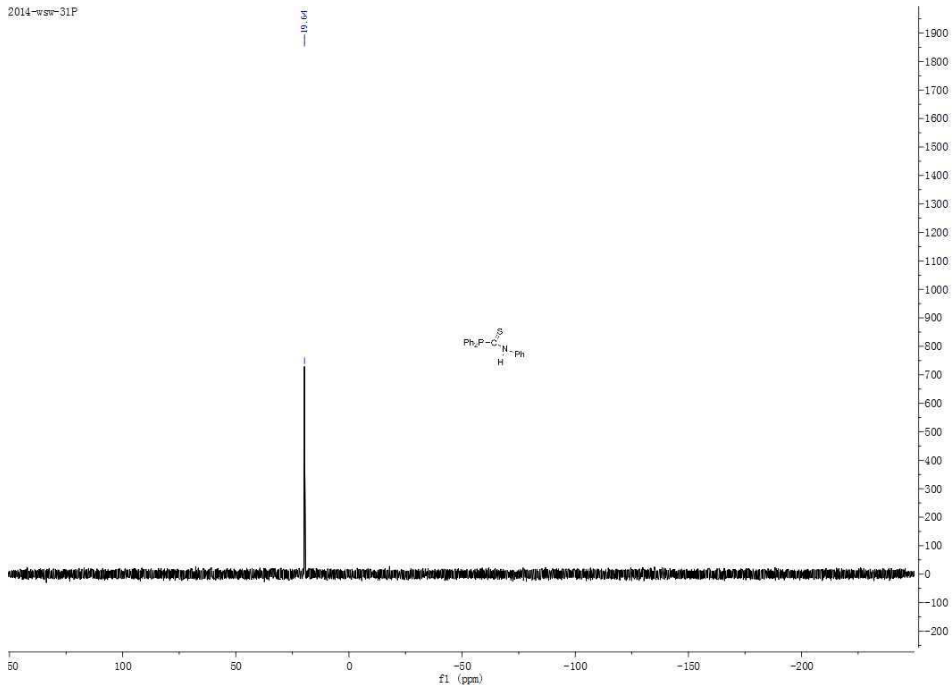

Figure S21. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9e**.

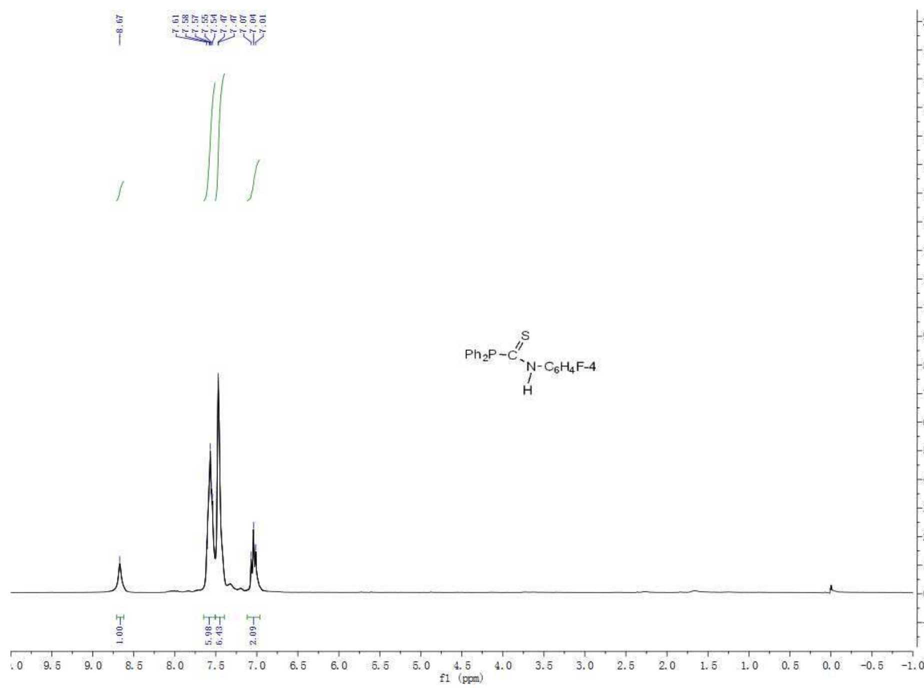

Figure S22. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9f**.

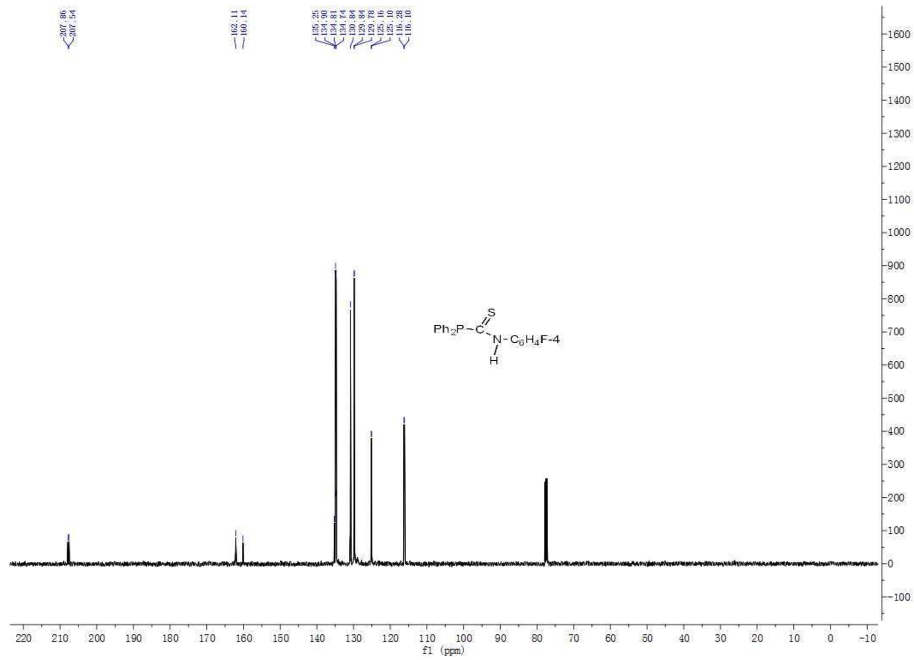

Figure S23. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9f**.

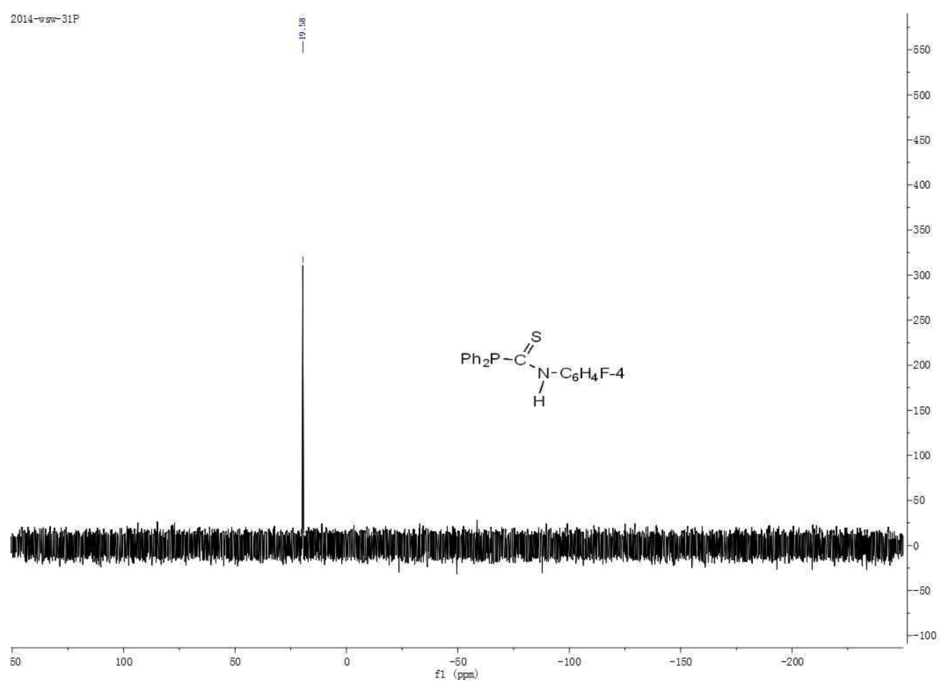

Figure S24. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9f**.

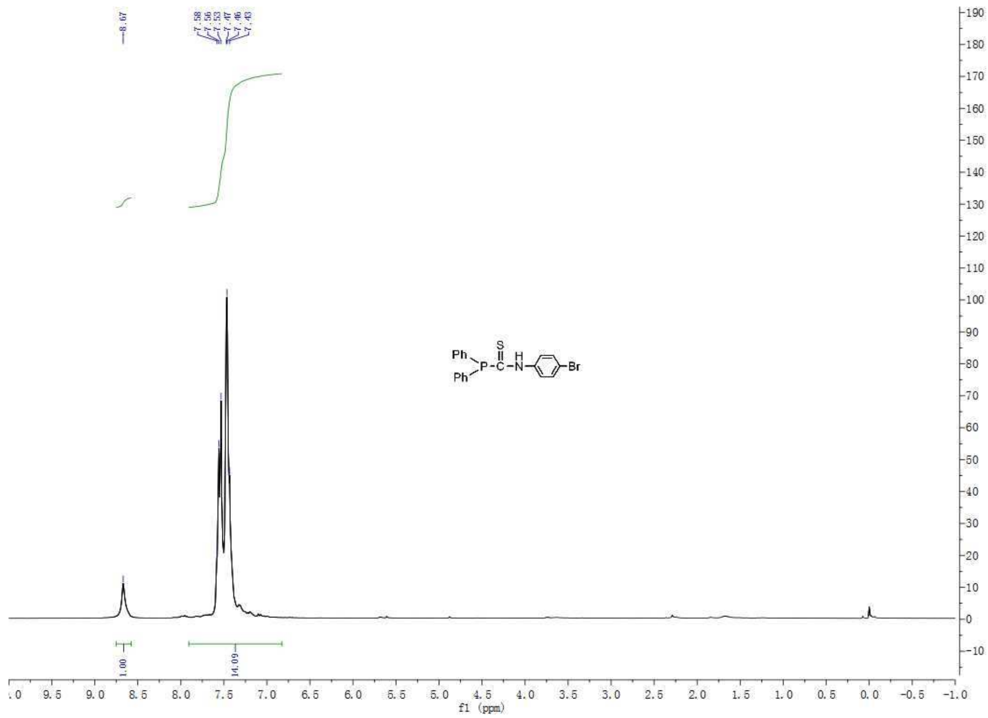

Figure S25. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9g**.

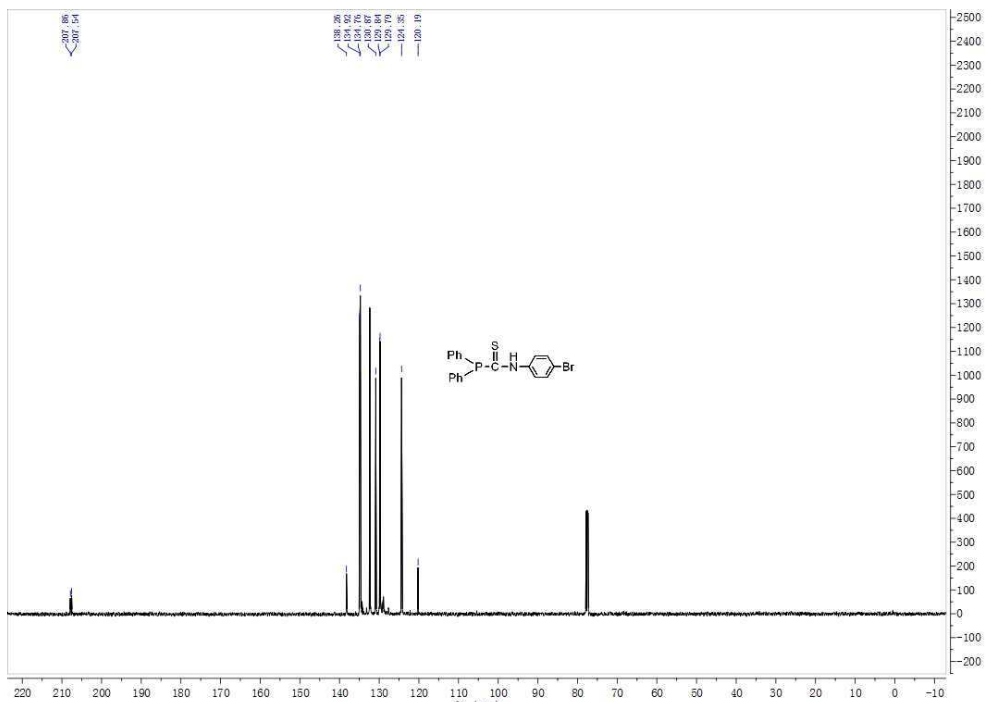

Figure S26. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9g**.

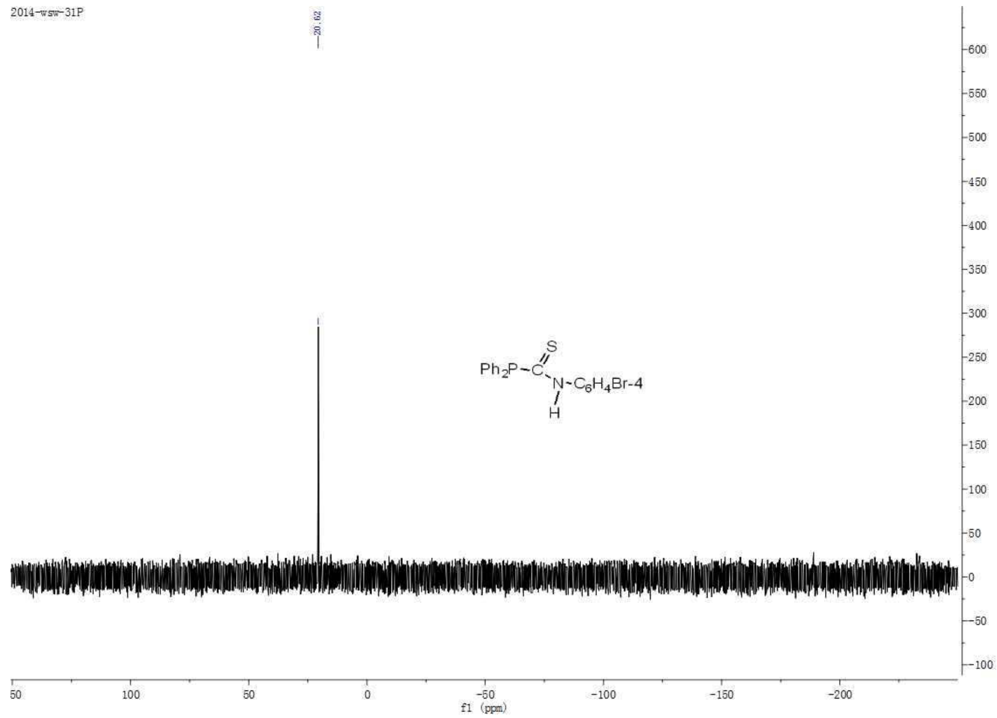

Figure S27. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9g**.

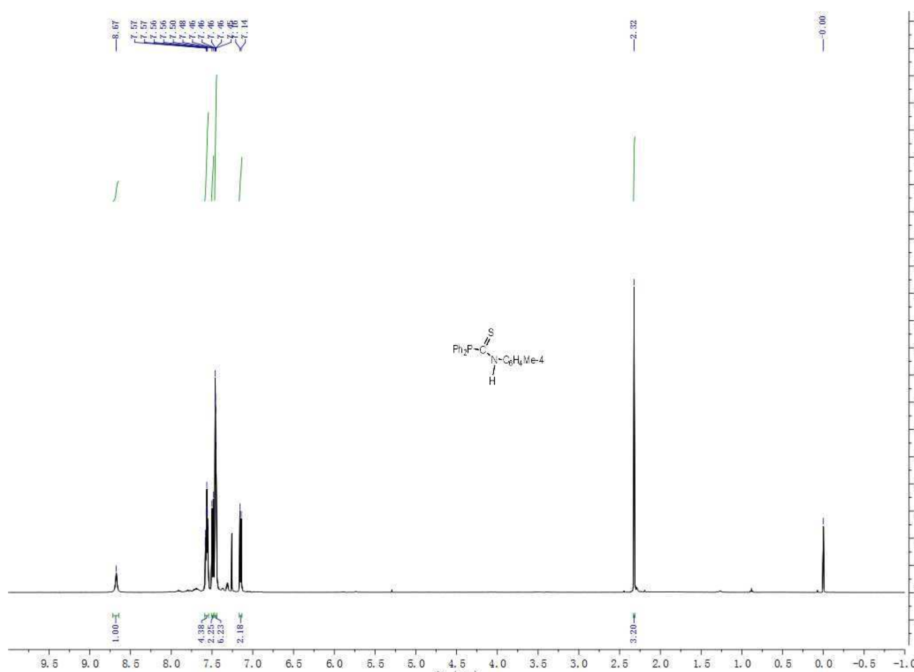

Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **9h**.

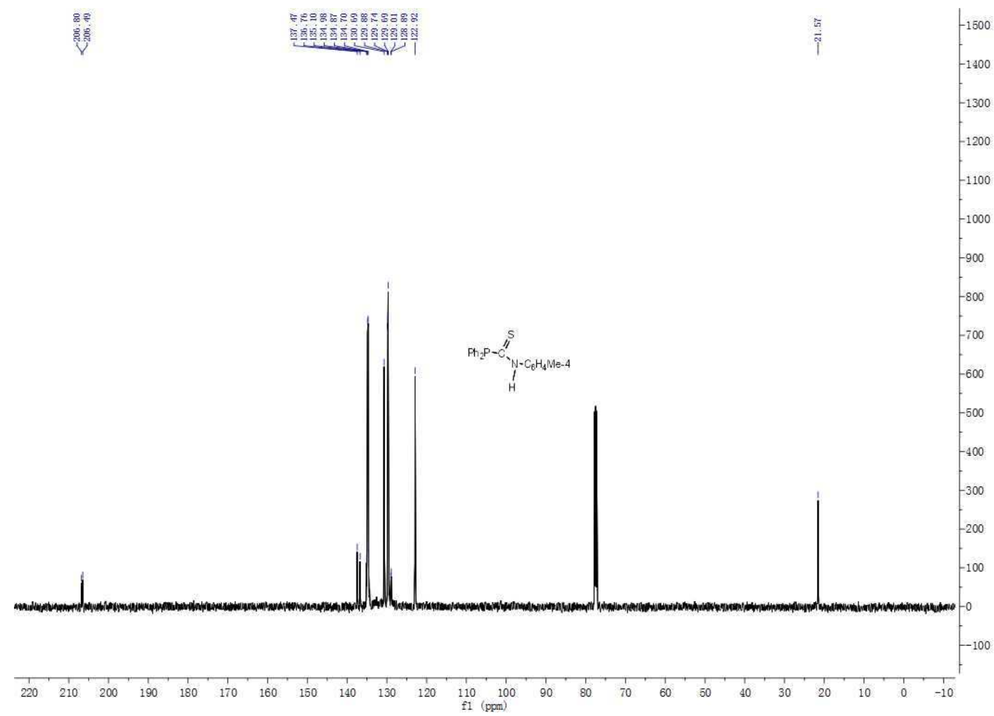

Figure S29. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9h**.

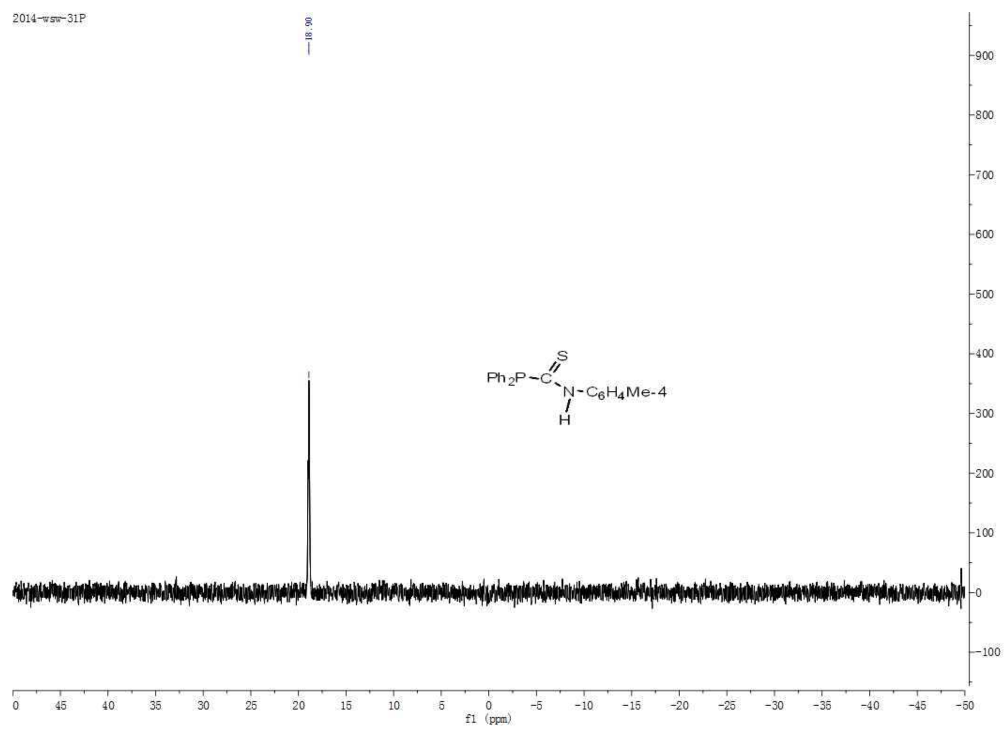

Figure S30. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9h**.

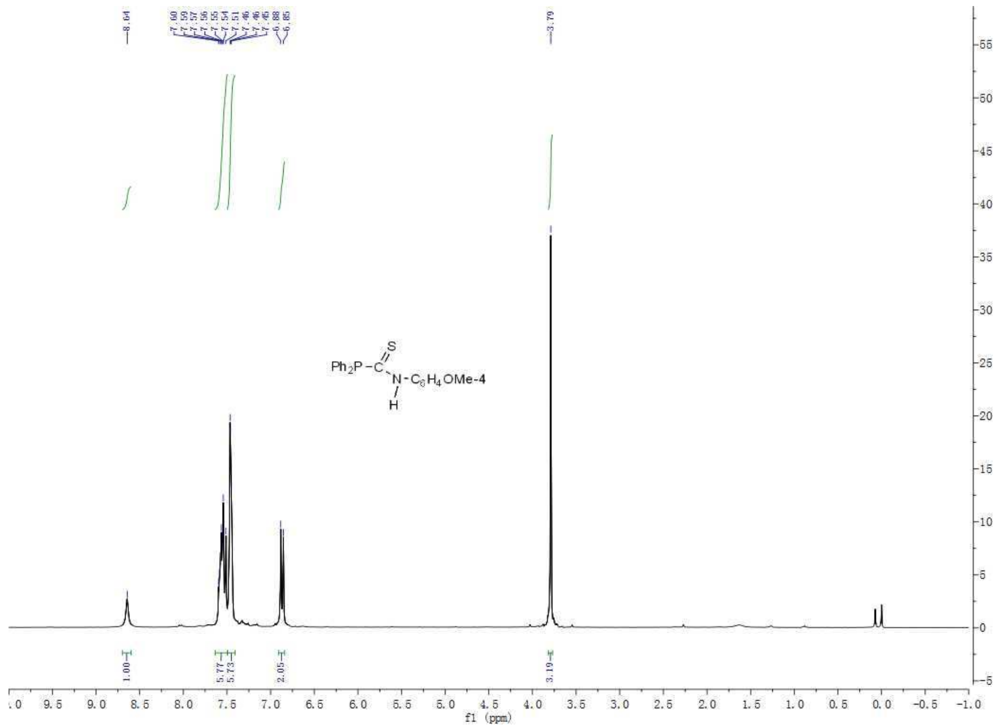

Figure S31. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9i**.

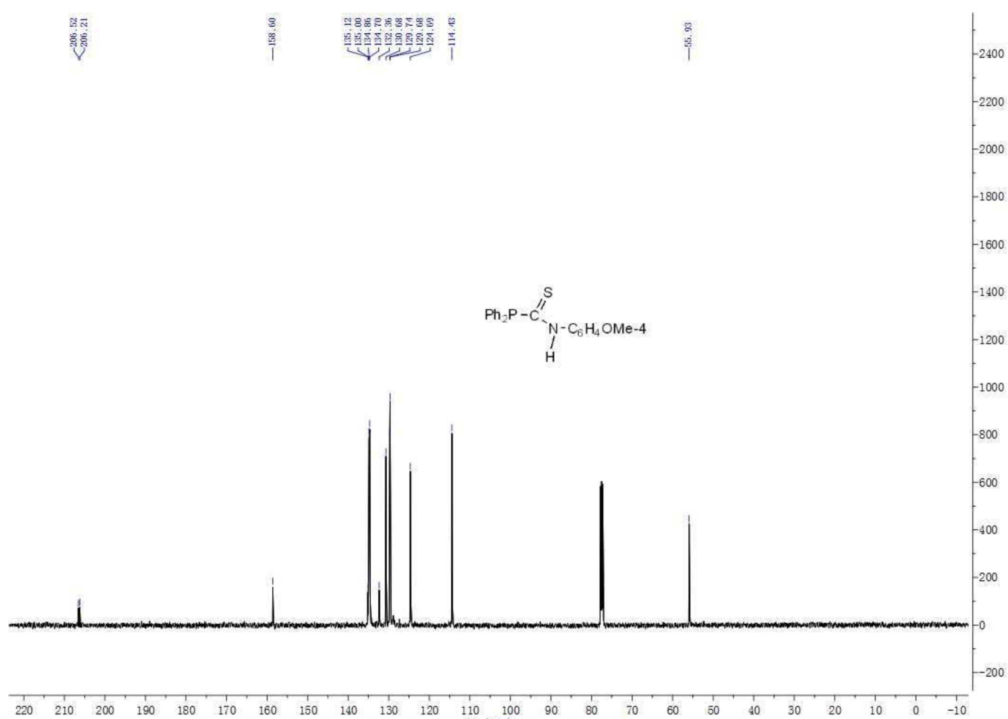

Figure S32. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9i**.

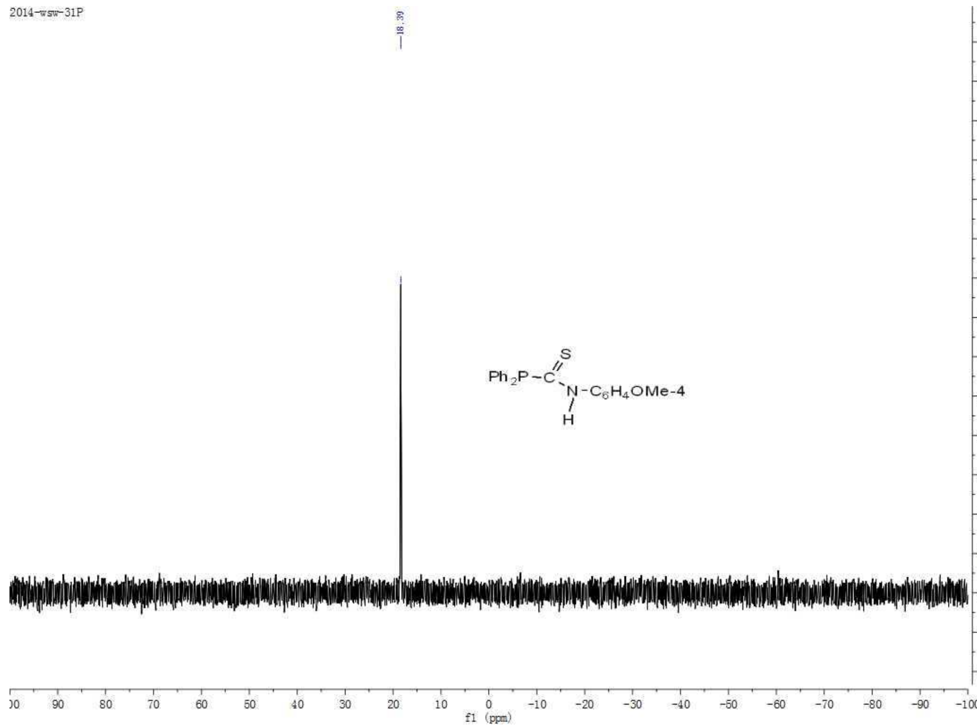

Figure S33. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9i**.

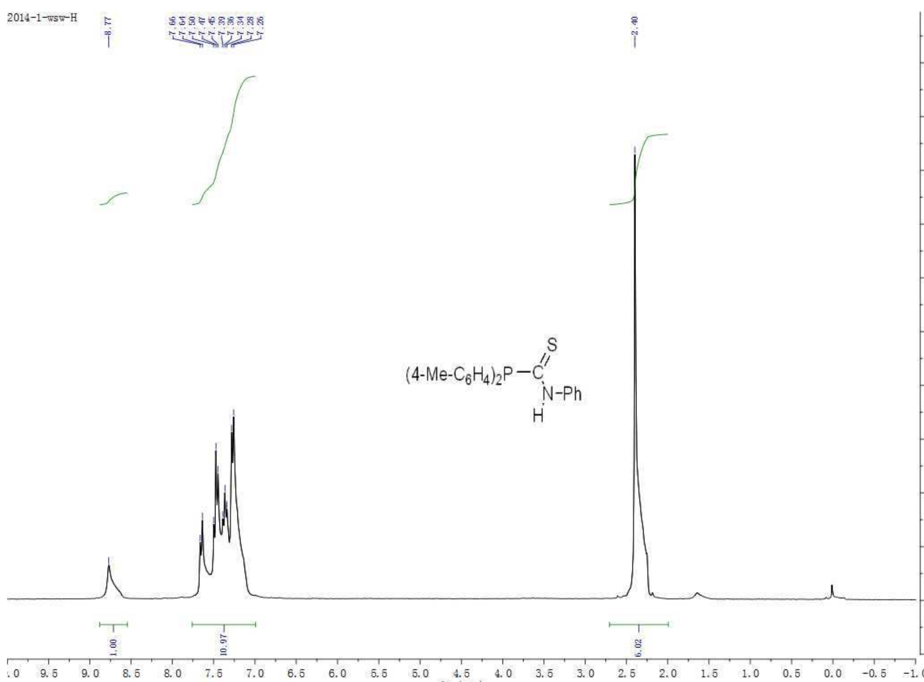

Figure S34. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9j**.

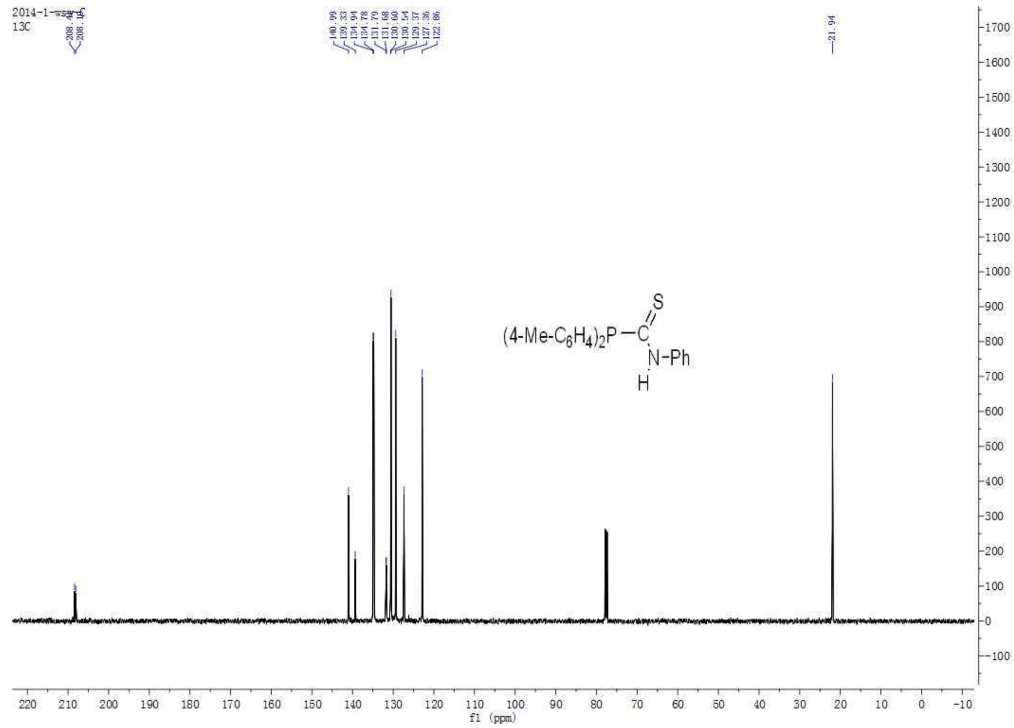

Figure S35. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9j**.

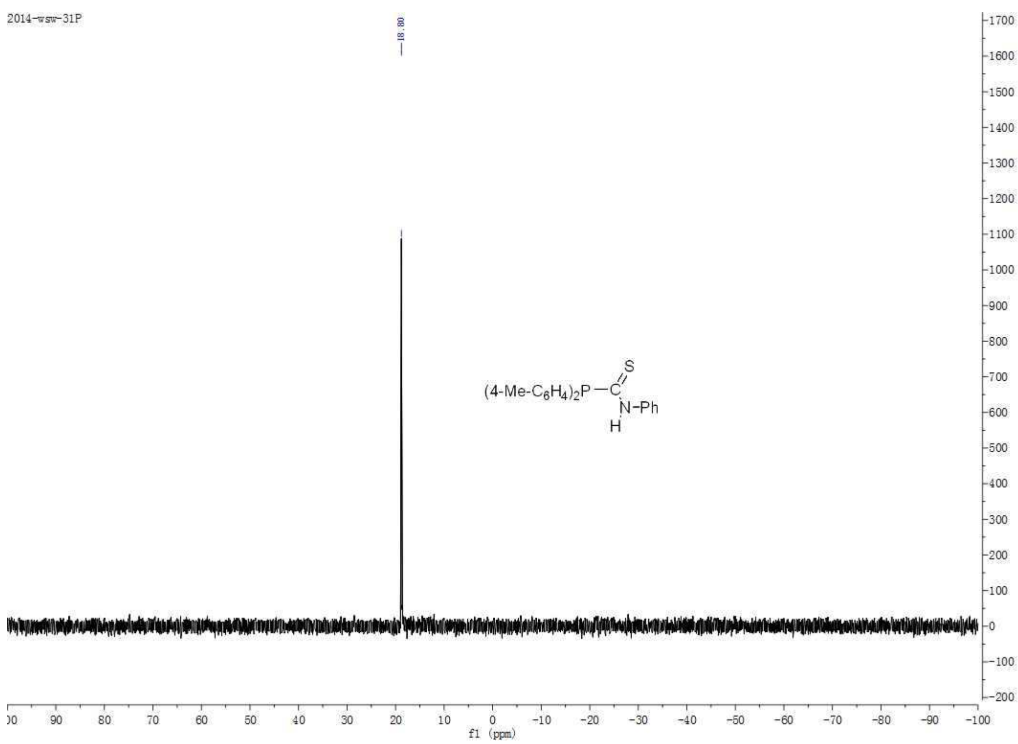

Figure S36. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9j**.

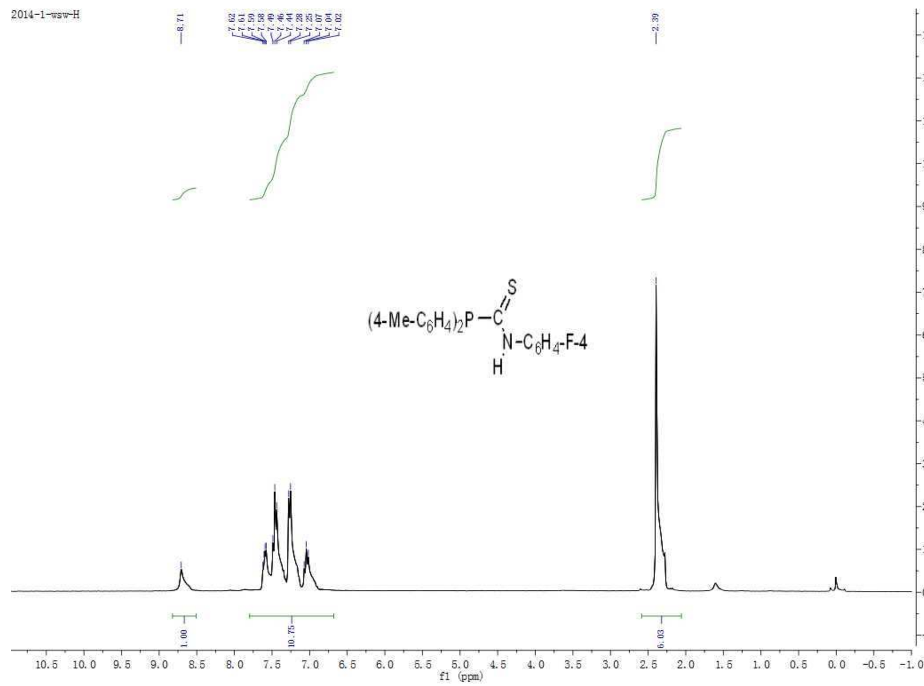

Figure S37. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9k**.

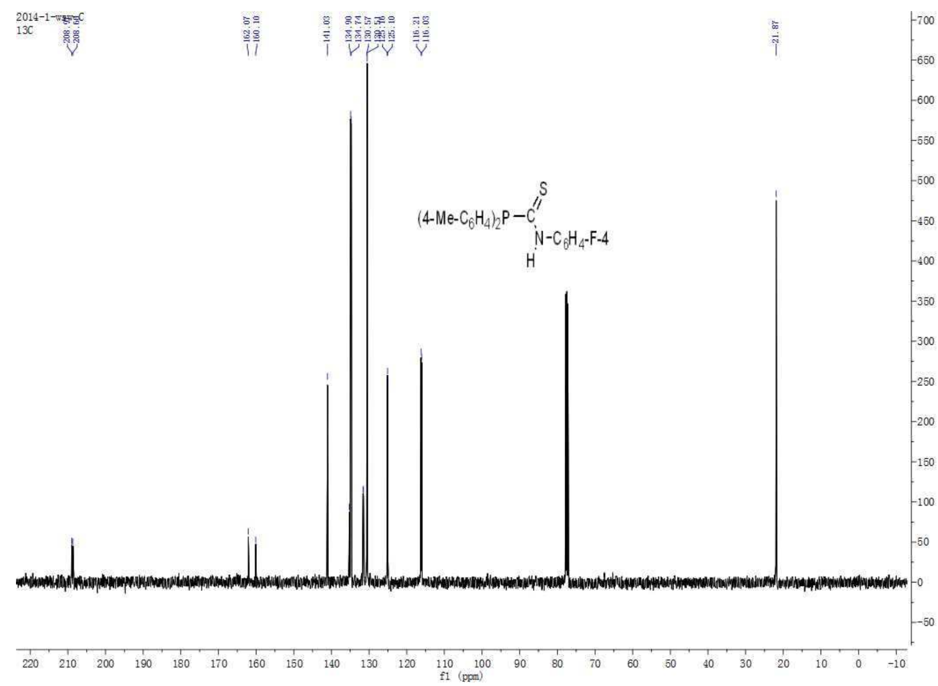

Figure S38. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9k**.

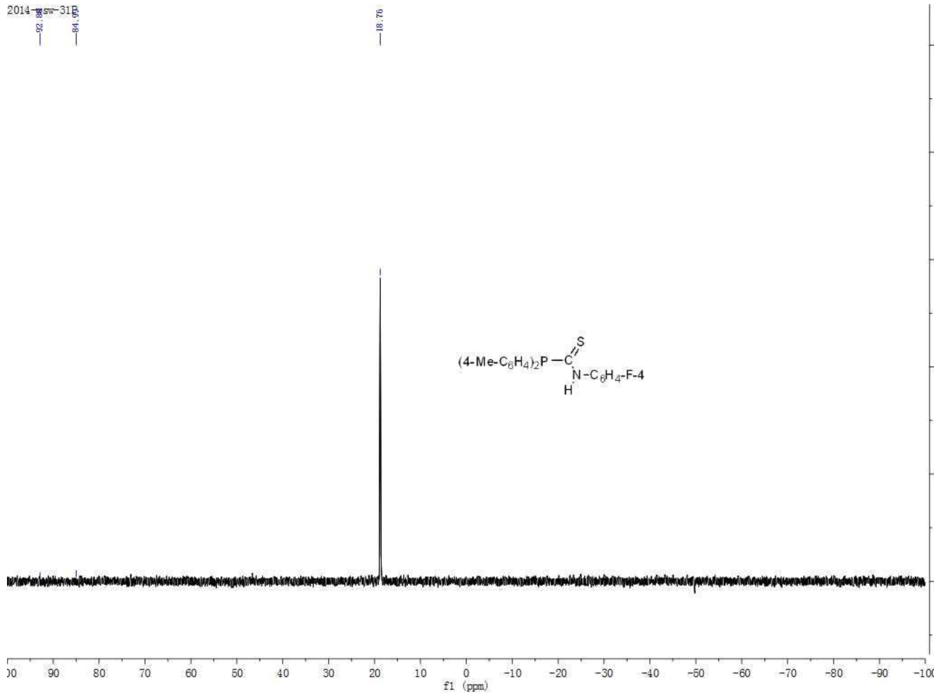

Figure S39. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9k**.

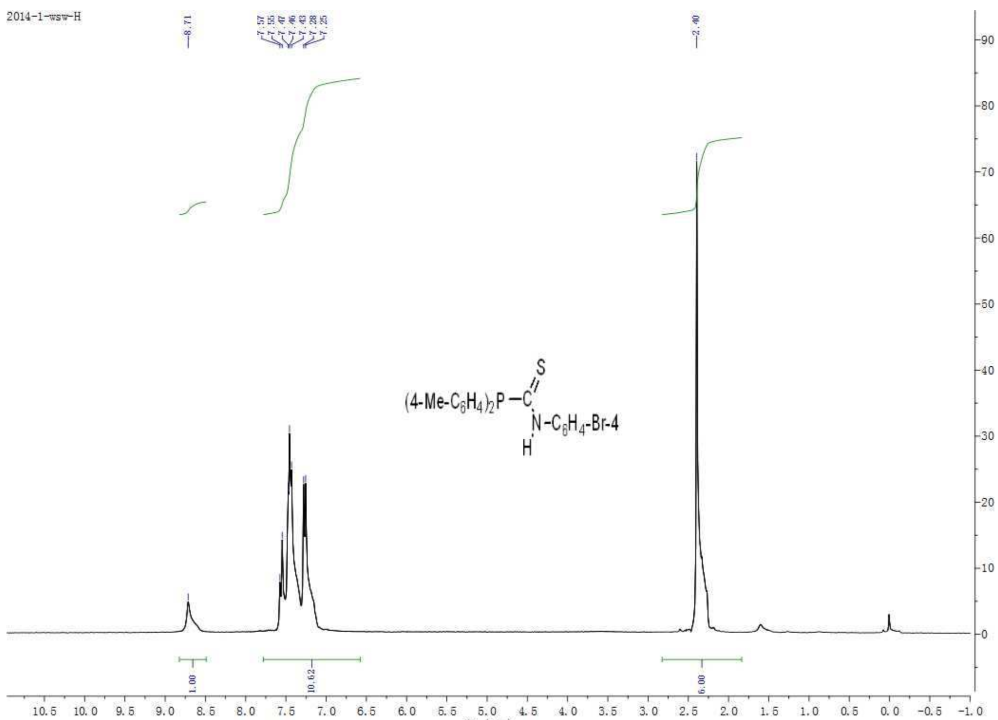

Figure S40. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9l**.

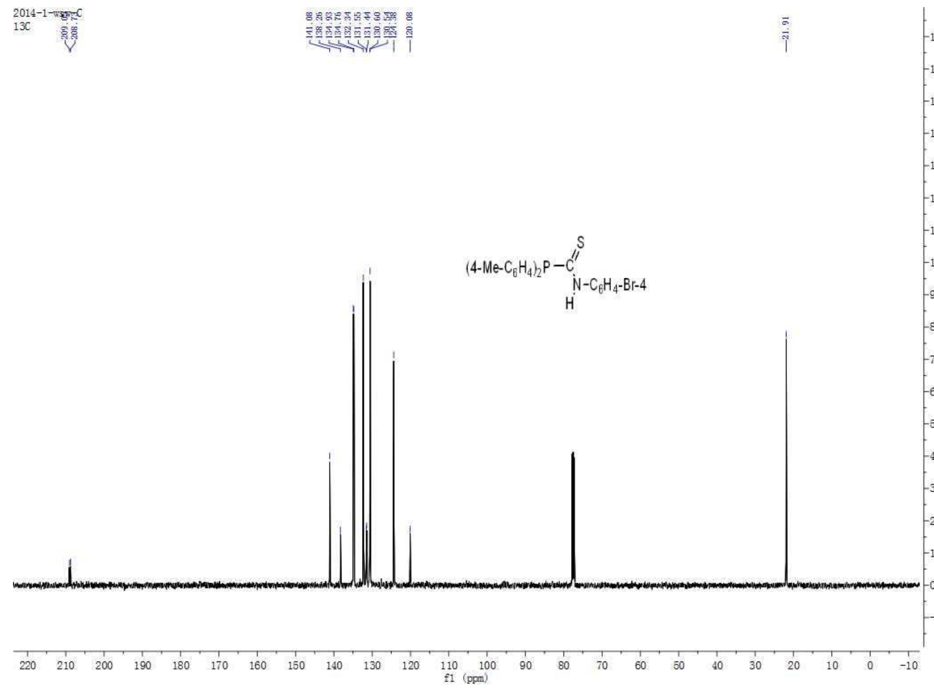

Figure S41. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9l**.

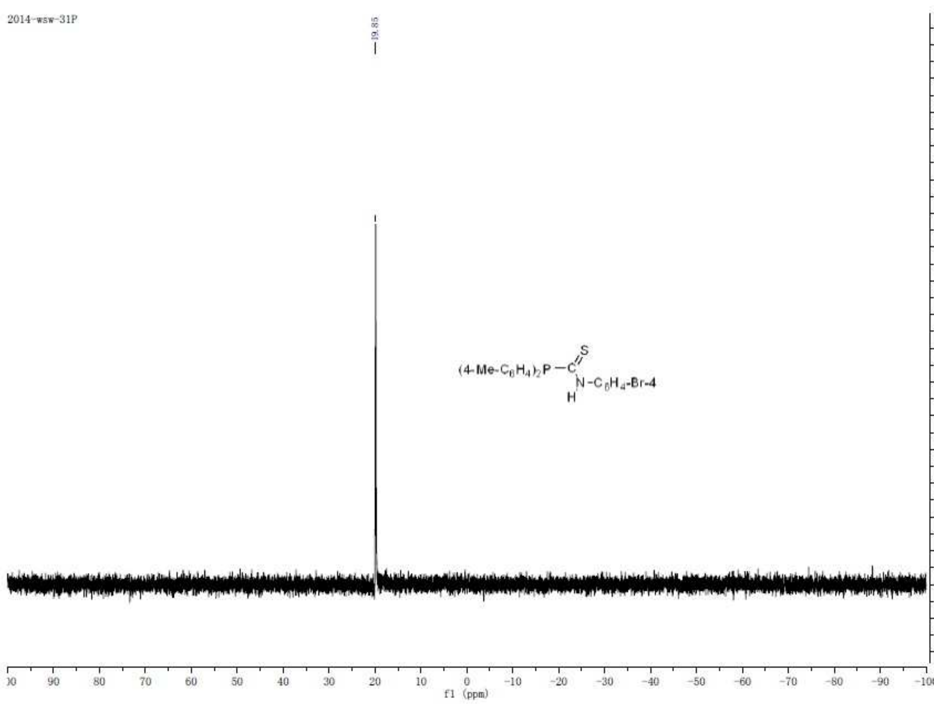

Figure S42. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9l**.

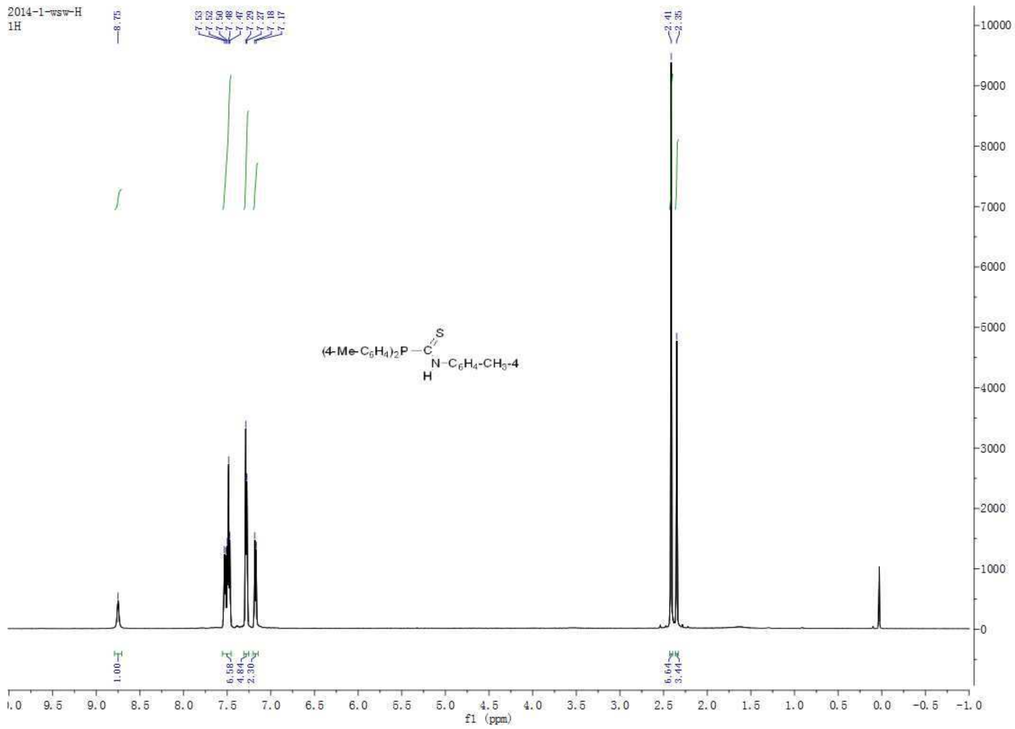

Figure S43. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **9m**.

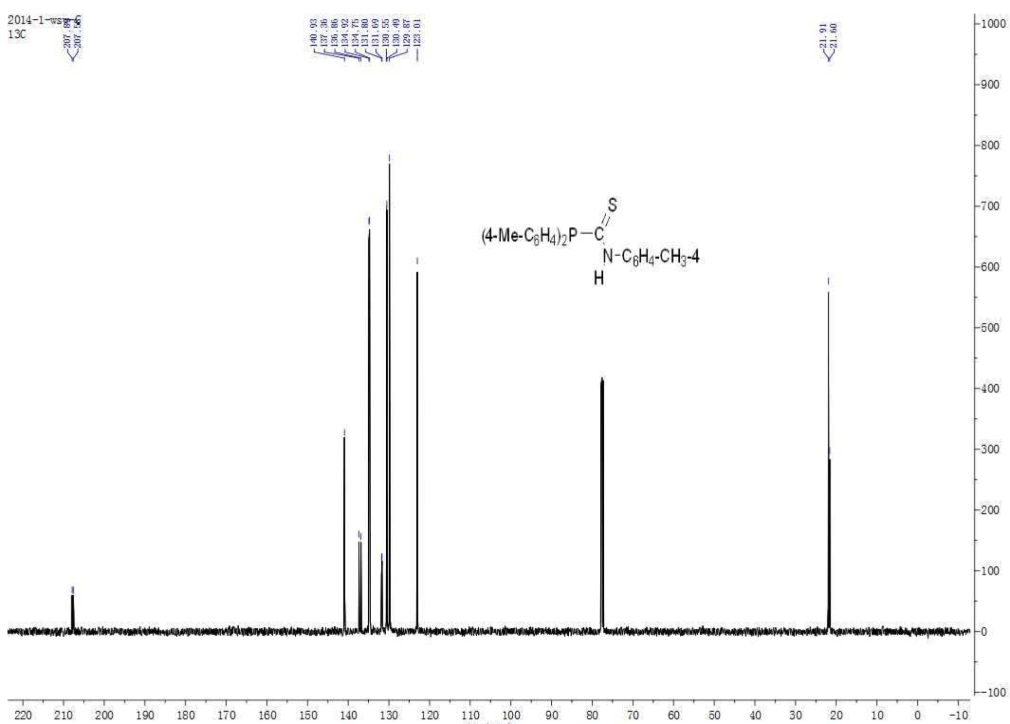

Figure S44. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9m**.

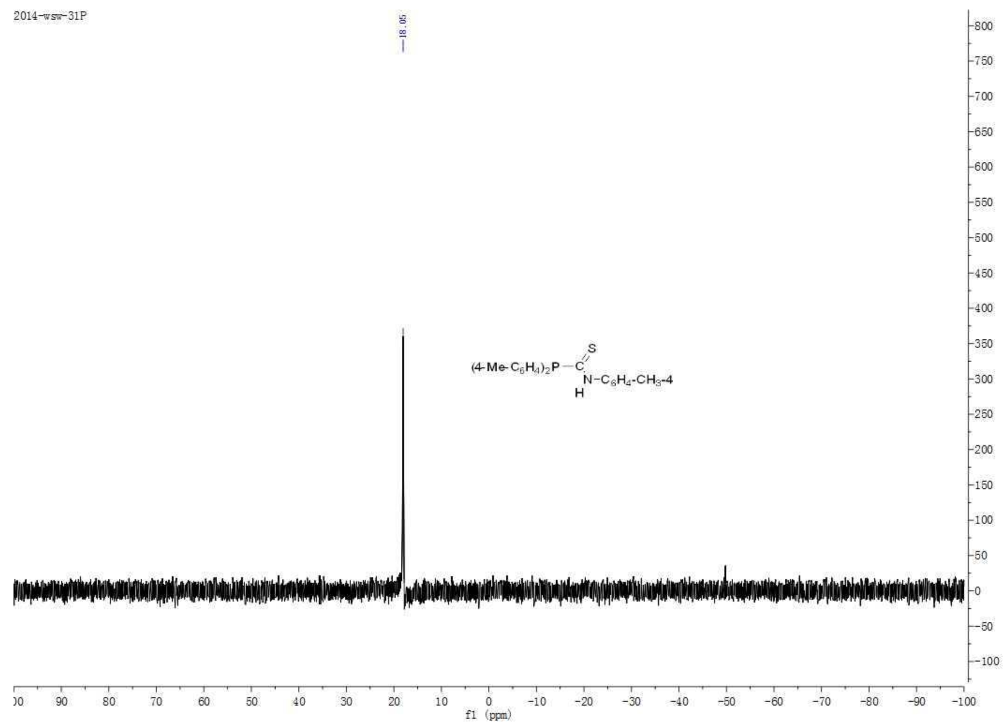

Figure S45. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9m**.

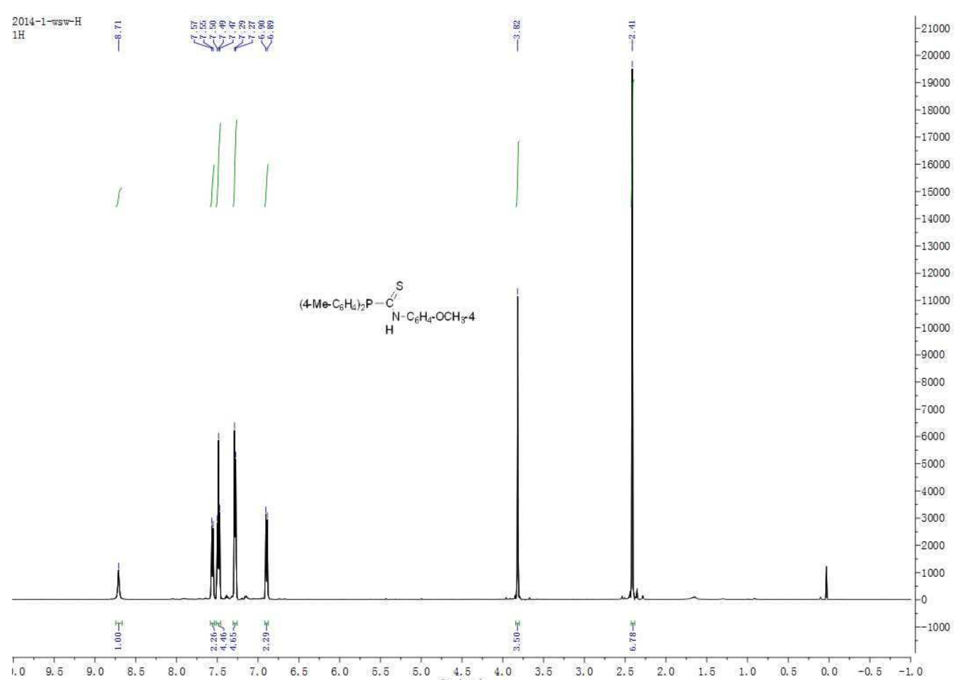

Figure S46. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **9n**.

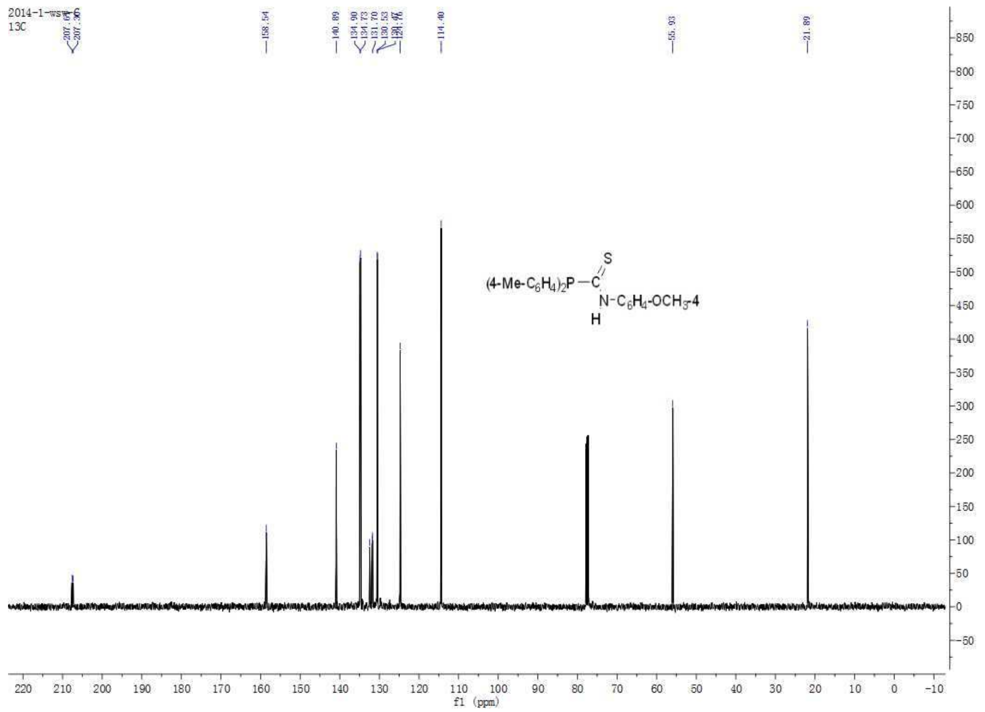

Figure S47. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9n**.

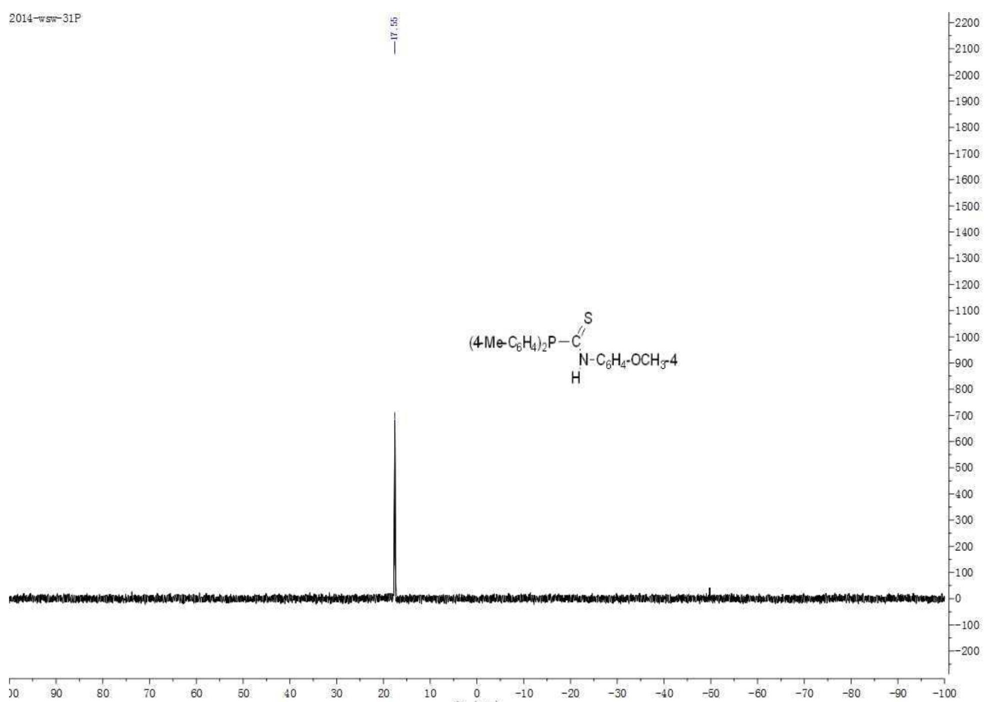

Figure S48. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9n**.

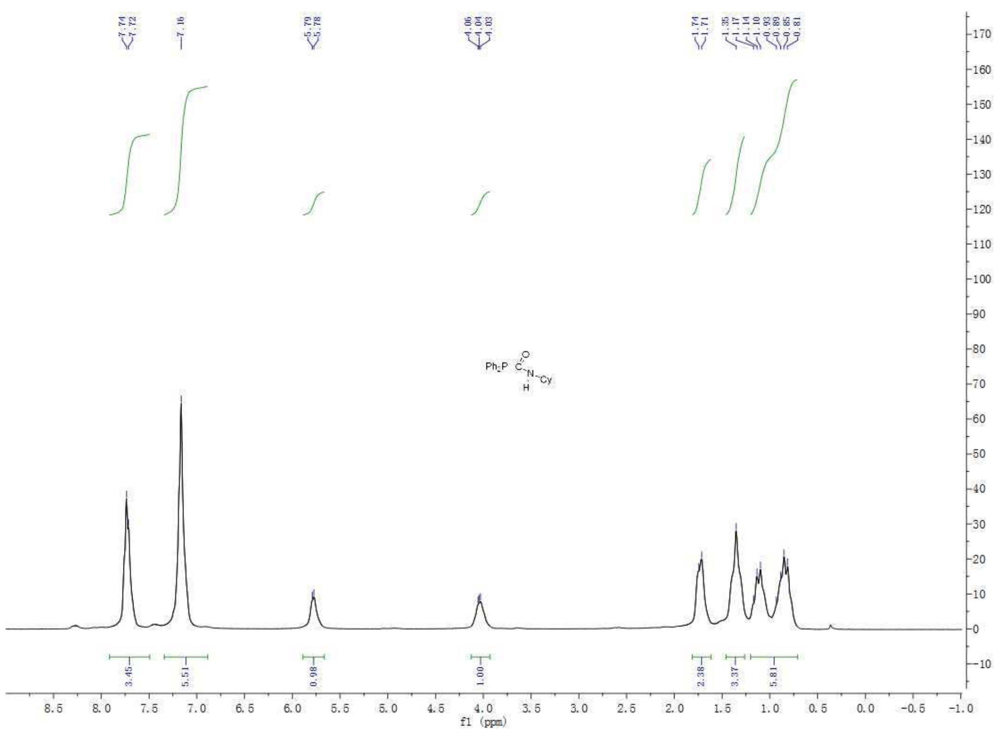

Figure S49. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **9o**.

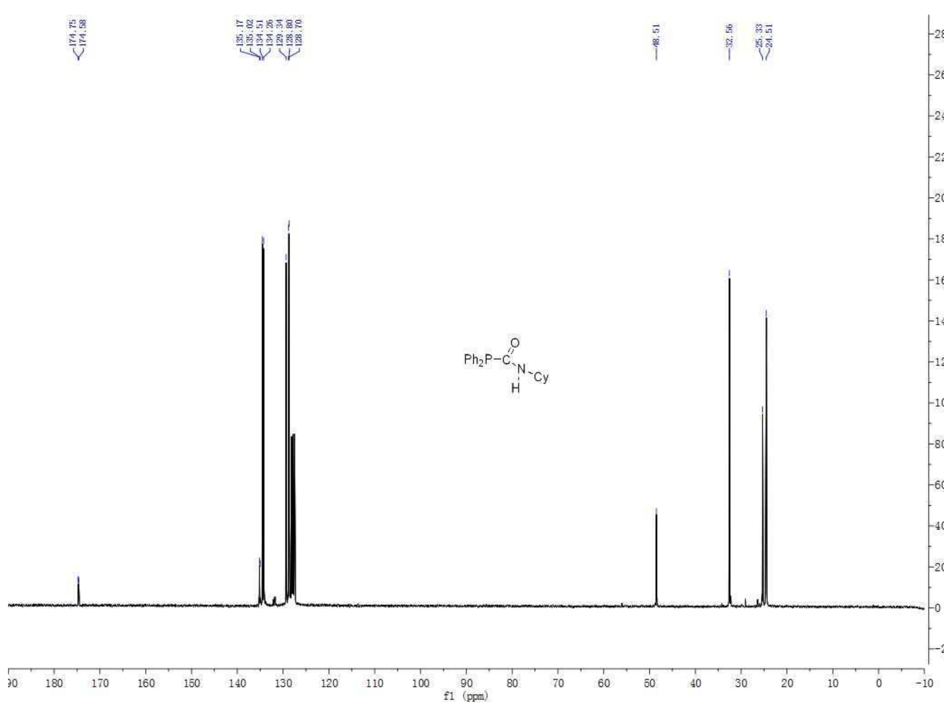

Figure S50. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **9o**.

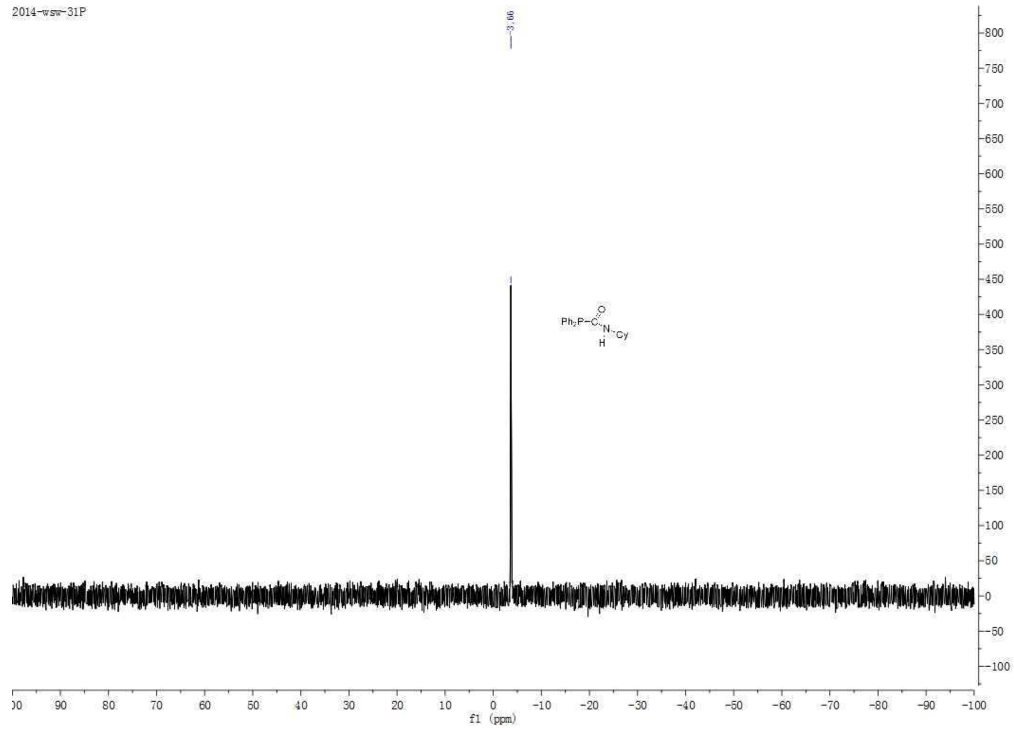

Figure S51. ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 298 K) of **9o**.