# Electronic Supporting Information

# Highly Efficient and Well-Defined Phosphinous Acid-Ligated Pd(II) Precatalysts for Hirao Cross-Coupling Reaction

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## 1. The general experimental methods:

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-flushed glovebox. Unless otherwise specified, all manipulations were performed in air. Solvents were purified by a solvent purification system to remove water and oxygen. All reagents were directly used as received unless otherwise stated.

Routine $^{1}H$ NMR spectra were recorded on a Brucker-AV-400 (400 MHz) spectrometer. The chemical shifts were reported in ppm relative to the internal standards TMS (δ 0.00 ppm) and $CHCl_3$ (δ 7.26 ppm). $^{31}P$ and $^{13}C\{H\}$ NMR spectra were recorded at 162.0 and 100.6 MHz, respectively. The chemical shifts for the former and the latter are reported in ppm relative to external standards $H_3PO_4$ (δ 0.0 ppm) and $CHCl_3$ (δ 77.0 ppm), respectively. Elemental analyses were carried out on an Elementar Vario EL cube analyzer.

The crystals were mounted on a diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). Intensity data were collected with ω scans. Data collection and reduction were performed with the CrysAlisPro software,[1] and the absorptions were corrected by using the SCALE3 ABSPACK multiscan method.[2] The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by structure solution, performed by direct methods with the SHELXTL package.[3] All non-hydrogen atoms were located from successive Fourier maps and hydrogen atoms were refined by using a riding model. Anisotropic thermal parameters were used for all

non-hydrogen atoms, and fixed isotropic parameters were used for hydrogen atoms.[4]

A Thermo Scientific LTQ XL linear ion trap mass spectrometer performed the analysis in this study. The samples were diluted and pumped using a Thermo Scientific Surveyor MS pump delivering 8 μL /min to electrospray ionization (ESI) source. Each spectrum was acquired 60 scans in negative mode. The potential of ESI was applied by -4.1kV, combining with the tube lens in -40 V. The temperature of the ion transfer tube was varied from 350 °C to 200 °C, depending on the analytes and experimental purpose. To avoid samples reacting with oxygen or water vapor in the ionization region, the ESI source housing was purged with nitrogen by a home-built line system.

## 2. Crystallographic data table for Precatalyst 1a, 1c, 4c

| | Precatalyst 1a | 1c | 4c |
|---|---|---|---|
| Formula | $C_{38}H_{46}Cl_2OP_2Pd$ | $C_{40}H_{62}C_{l4}O_2P_2Pd_2$ | $C_{26}H_{23}OP$ |
| Fw | 757.99 | 991.43 | 382.41 |
| T, K | 150(2) | 150(2) | 150(2) |
| Crystal system | triclinic | Monoclinic | Triclinic |
| Space group | P -1 | $P2_1/c$ | P-1 |
| *a*, Å | 9.6484(5) | 11.7915(4) | 9.3661(5) |
| *b*, Å | 10.6341(6) | 16.4016(5) | 9.7124(5) |
| *c*, Å | 18.3612(10) | 12.2069(4) | 11.4886(5) |
| *a* ° | 97.385(2) | 90° | 77.950(2) |
| $\beta$ ° | 94.546(2) | 105.1584(12) | 88.0780(19) |
| $\gamma$ ° | 110.352(2)° | 90° | 79.4227(18) |
| *V*, Å$^3$ | 1736.00(16) | 2278.67(13) | 1004.68(9) |
| Z | 2 | 2 | 2 |
| $\rho_{calc}$, Mg/m$^3$ | 1.450 | 1.445 | 1.264 |
| μ(MoKα), mm$^{-1}$ | 0.810 | 1.125 | 0.150 |
| Reflections collected | 36109 | 41419 | 21500 |
| No. of parameters | 401 | 230 | 272 |
| Indep. reflns ($R_{int}$) | 9733 (0.0360) | 5394 (0.0392) | 4787 (0.0306) |
| Final R indices $R_1$[a],$wR_2$[a] | 0.0234, 0.0639 | 0.0245, 0.0629 | 0.0628, 0.1662 |
| GoF [b] | 0.994 | 1.032 | 1.046 |

[a] $R_1 = [|F_0| - |F_c|]/ |F_0|]$, $wR_2 = [w(F_0^2 - F_c^2)^2/ w(F_0^2)^2]^{1/2}$, w= 0.10.

[b] GoF = $[\Sigma w(F_0^2-F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

## 3. Bond dissociation free energies (BDFE) of P-donor ligands

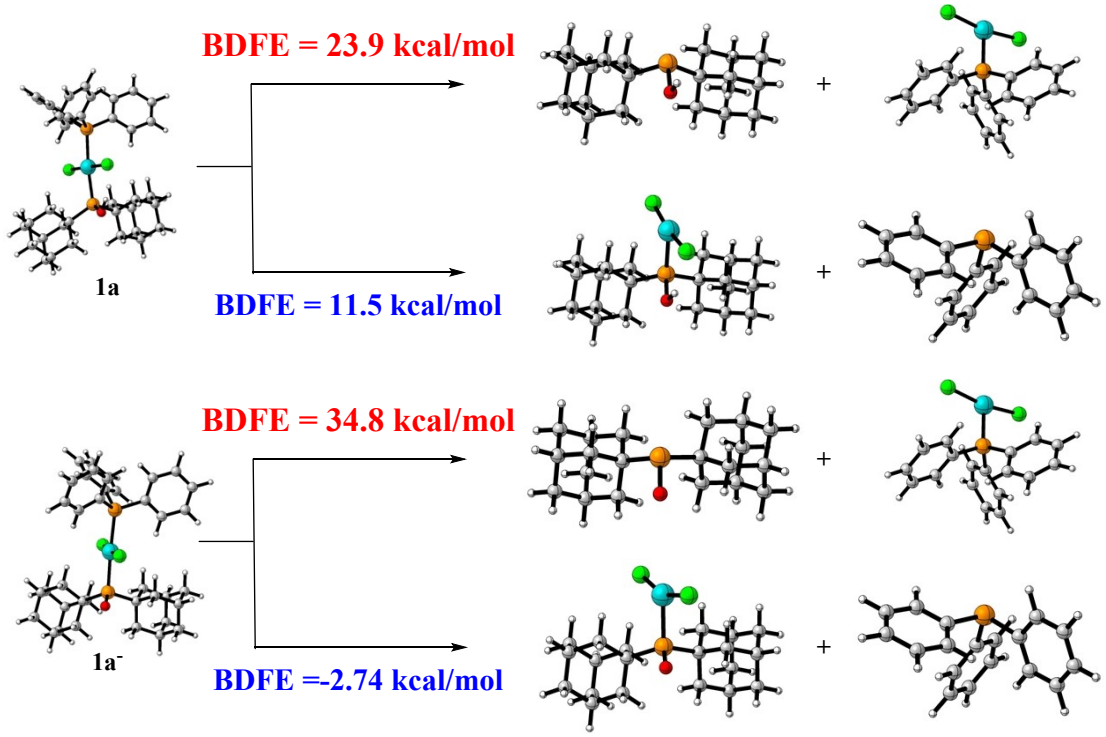
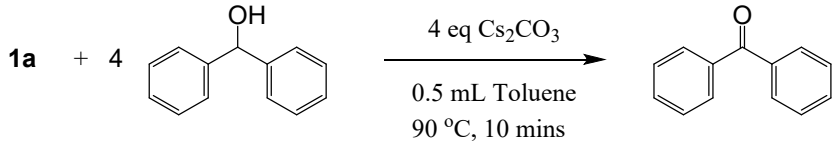



**Figure S1.** DFT-calculated bond dissociation free energy (BDFE in kcal/mol) in EtOH for dissociation of $PPh_3$, di(1-adamantyl)phosphinous acid ($Ad_2P$-OH), and deprotonated di(1-adamantyl)phosphinous acid ($Ad_2P$-$O^-$) in (a) **1a** and (b) deprotonated **1a**$^-$. (Gas-phase optimization: G09-ωB97X-D/6-31+G(d) for non-metals and SDD for Pd. The BDFEs were considered with the solvation effects of EtOH by using IEFPCM model based on the gas-phase optimized geometries.)

## 4. Experiment for the reduction of precatalyst 1a

**Table S1.** The reaction between precatalyst **1** and Diphenylmethanol




| Entry | [Pd] | Reducing agent | Base | Solvent | Yield |
|---|---|---|---|---|---|
| **1** | **1a** | Diphenylmethanol | $Cs_2CO_3$ | Toluene | 72% |

Precatalyst **1a** (0.0757 g, 0.1 mmol), 4.0 eq. of diphenylmethanol (0.0736 g, 0.4 mmole), and 4.0 eq. of $Cs_2CO_3$ (0.0652 g, 0.2 mmol) were put into a 4-mL glass vail. After the via was sealed with a septum screw cap, the vial was capped, vacuumed and back-filled with $N_2$ for three times. Subsequently, toluene (0.5 mL) was injected into the tube. The reaction was carried out at 90 °C for 10 minutes. Product was isolated by column chromatography (EA/hexanes = 8/1).

## 5. Kinetic data for 1a-1c catalysed Hirao coupling

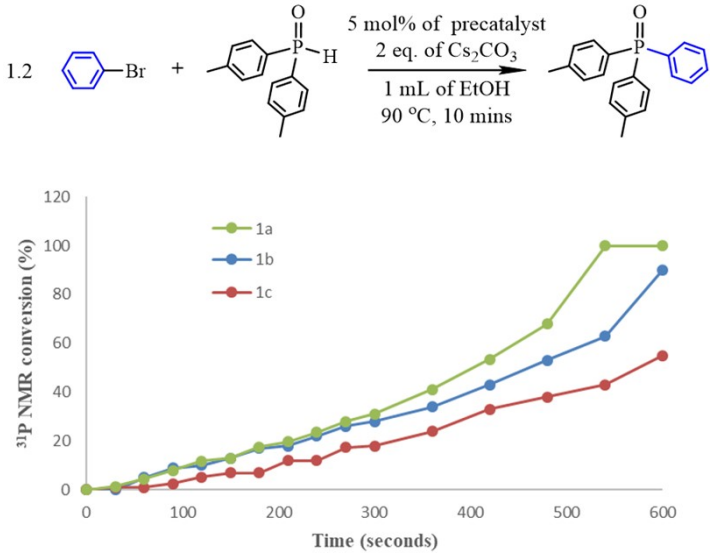



**Figure S2.** Kinetic data of the precatalyst **1a**, **1b**, and **1c**-catalysed Hirao coupling of phenyl bromide and di-*p*-tolylphosphine oxide **2a**

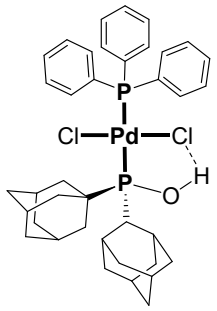
**Table S2.** Kinetic data of the precatalyst **1a**, **1b**, and **1c**-catalysed Hirao coupling of phenyl bromide and di-*p*-tolylphosphine oxide. $^{31}$P NMR conversions were reported.

| **Time** (seconds) | **1a** (conversion %) | **1b** (conversion %) | **1c** (conversion %) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 30 | 1 | 0 | 1 |
| 60 | 4 | 5 | 1 |
| 90 | 8 | 9 | 3 |
| 120 | 12 | 10 | 5 |
| 150 | 13 | 13 | 7 |
| 180 | 18 | 17 | 7 |
| 210 | 20 | 18 | 12 |
| 240 | 24 | 22 | 12 |
| 270 | 28 | 26 | 17 |
| 300 | 31 | 28 | 18 |
| 360 | 41 | 34 | 24 |
| 420 | 54 | 43 | 33 |
| 480 | 68 | 53 | 38 |
| 540 | 100 | 63 | 43 |
| 600 | 100 | 90 | 55 |

**Experimental procedure for kinetic study**

The precatalyst (0.01 mmol), $Cs_2CO_3$ (130.3 mg, 0.4 mmol), and di-*p*-tolylphosphine oxide (46.1 mg, 0.2 mmol) were weighed and added into a Schlenk tube with a magnetic stir bar. The tube was purged with nitrogen gas three times and then continuously flushed with nitrogen. After preheating ethanol (1ml) and bromobenzene (25.1 μL, 0.24 mmol) at 90°C, they were injected into the Schlenk tube to initiate the catalytic reaction. At the beginning of the reaction (t = 0), 25μL of the reaction mixture was taken out of the Schlenk tube using a gas-tight syringe. After each sampling, the syringe was rinsed with cold ethanol, and subsequent samples were taken every 30 seconds in the first five minutes. Thereafter, the samples were taken every 60 seconds until the end of the reaction at the tenth minute. The samples were transferred into an NMR tube and the solution was evaporated in vacuo. The $^{31}P$ NMR analysis (in $CDCl_3$) was performed to estimate the conversion.

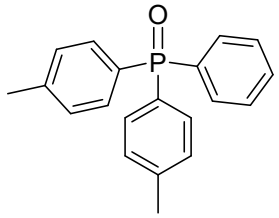
## 6. Spectroscopic data for complexes and catalytic products




**Precatalyst 1a (yellow crystal)**

**Reagents: 1c** (0.099 g, 0.1 mmol), $PPh_3$ (0.052 g, 0.2 mmol).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.62 (m, 6H), 7.45 – 7.38 (m, 9H), 6.51 (dd, J = 7.1, 3.6 Hz, 1H), 2.35 (s, 12H), 2.03 (s, 6H), 1.76 (q, J = 12.1 Hz, 12H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** 28.4 (d, $^1J_{C-P}$ = 10.1 Hz), 36.7, 38.7, 45.1 (dd, $^1J_{C-P}$ = 12.0 Hz, $^3J_{C-P}$ = 6.0 Hz,), 128.2 (d, J = 10.1 Hz,), 129.8 (d, $^1J_{C-P}$ = 40.0 Hz,), 130.5, 134.9 (d, J = 10.1 Hz); **$^{31}$P NMR (162 MHz, $CDCl_3$) δ** 115.6 (d, J = 511.6 Hz), 18.3 (d, J = 511.8 Hz); **Anal. Calcd** for C38H46Cl2OP2Pd: C, 60.21; H, 6.12. Found: C, 60.35; H,6.09; **MS (ESI-) calcd** for C20H30Cl2OPPd (m/z [M-(C18H15P + H)]-) 494.75, found 495.17. **IR** ν(PO-H): 3180 $cm^{-1}$.

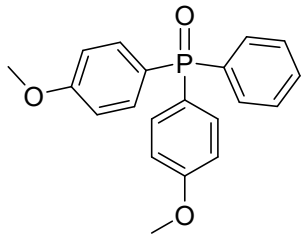


**phenyldi-p-tolylphosphine oxide (2a, 3a)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and bromobenzene (25.1 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=6/4). The isolated yield was 95%. The characterization data is consistent with the data previously reported in the literature.[5]

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.62 (m, 2H), 7.58 – 7.49 (m, 5H), 7.47 – 7.41 (m, 2H), 7.28 – 7.24 (m, 4H), 2.39 (s, 6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 142.3 (d, J = 2.5 Hz), 133.0 (d, J = 104.1 Hz), 132.0 (d, J = 10.3 Hz), 132.0 (d, J = 9.7 Hz), 131.7 (d, J = 2.5 Hz), 129.2 (d, J = 12.5 Hz), 128.4 (d, J = 12.0 Hz), 21.5; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.4.

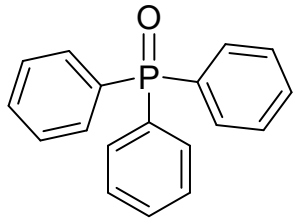


**bis(4-methoxyphenyl)(phenyl)phosphine oxide (slight yellow oil) (2b)**

**Reagents:** Bis(4-methoxyphenyl)phosphine oxide (52.45 mg, 0.20 mmol) and bromobenzene (25.1 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 87%. The characterization data is consistent with the data previously reported in the literature.[5]

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.64 (ddd, J = 12.0, 8.2, 1.3 Hz, 2H), 7.59 – 7.52 (m, 4H), 7.50 (dd, J = 7.4, 1.5 Hz, 1H), 7.46 – 7.40 (m, 2H), 6.97 – 6.92 (m, 4H), 3.82 (6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 162.4 (d, J = 2.6 Hz), 133.9 (d, J = 11.3 Hz), 132.8 , 132.0 (d, J = 10.0 Hz), 131.6 (d, J = 2.3 Hz), 128.4 (d, J = 12.1 Hz), 123.9 (d, J = 110.7 Hz), 114.0 (d, J = 13.2 Hz), 55.3; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.1.

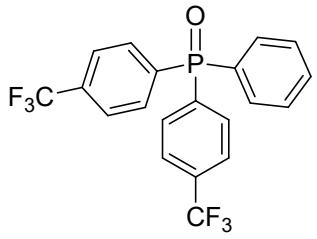


**triphenylphosphine oxide (colorless oil) (2c)**

**Reagents:** Diphenylphosphine oxide (40.44 mg, 0.20 mmol) and bromobenzene (25.1 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=6/4). The isolated yield was 80%. The characterization data is consistent with the data previously reported in the literature.[5]

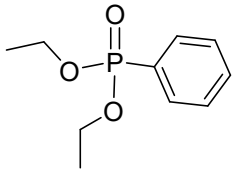
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.63 (m, 6H), 7.54 (m, 3H), 7.46 (m, 6H). **$^{13}$C NMR (101 MHz, CDCl3)** δ 132.1 (d, J = 10.1 Hz), δ 132.9 (d, J = 9.2 Hz),131.8, 128.5 (d, J = 12.4 Hz). **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.1.



**phenylbis(4-(trifluoromethyl)phenyl)phosphine oxide (2d)**

**Reagents:** Bis(4-(trifluoromethyl)phenyl)phosphine oxide (67.64 mg, 0.20 mmol) and bromobenzene (25.1 μL, 0.24 mmol).

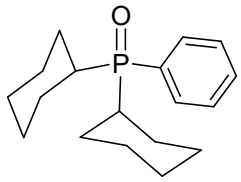
**$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 26.9 (s). The $^{31}$P NMR chemical shift is the same as the reported data of product **3p** in the literature.[6]



**diethyl phenylphosphonate (2e)**

**Reagents:** Diethyl phosphonate (67.64 mg, 0.20 mmol) and bromobenzene (25.1 μL, 0.24 mmol).

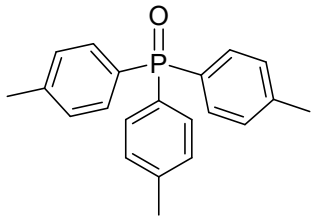
**$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 18.8 (s). The $^{31}$P NMR chemical shift is the same as the reported data of product **3t** in the literature.[7]



**dicyclohexyl(phenyl)phosphine oxide (2f)**

**Reagents:** SPO-Cy (58.08 mg, 0.20 mmol) and bromobenzene (25.1 μL, 0.24 mmol).

**$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 45.0 (s). The $^{31}$P NMR chemical shift is the same as the reported data of product **16-oxide** in the literature.[8]

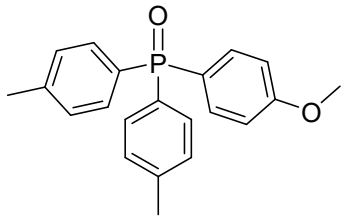


**tri-p-tolylphosphine oxide (white solid) (3b)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 1-bromo-4-methylbenzene (29.6 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 79%. The characterization data is in consistent with the data previously reported in the literature.[9]

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.54 (dd, J = 11.8, 8.1 Hz, 6H), 7.26 – 7.22 (m, 6H), 2.39 (s, 9H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 142.1 (d, J = 2.5 Hz), 132.0 (d, J = 10.2 Hz), 129.6 (d, J = 106.5 Hz), 129.1 (d, J = 12.5 Hz), 21.5; **$^{31}$P NMR (162 MHz, CDCl3)** δ 29.3.



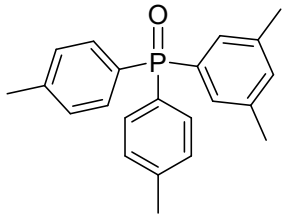
**(4-methoxyphenyl)di-p-tolylphosphine oxide (yellow oil) (3c)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 1-bromo-4-methoxybenzene (30.9 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 79%.

The characterization data is consistent with the previously reported data in the literature.[10]

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.55 (m, 6H), 7.25 (m, 4H), 6.95 (m, 2H), 3.84 (3H), 2.39 (6H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 162.4 (d, *J* = 3.0 Hz), 142.2 , 133.9 (d, *J* = 11.3 Hz), 132.1 (d, *J* = 10.3 Hz), 130.3 , 129.1 (d, *J* = 12.6 Hz), 124.1 (d, *J* = 110.4 Hz), 114.0 (d, *J* = 13.1 Hz), 55.3 , 33.2 (d, *J* = 700.2 Hz), 21.6 ; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.5 .

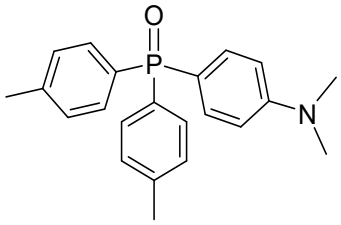


**(3,5-dimethylphenyl)di-p-tolylphosphine oxide (yellow oil) (3d)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 1-bromo-3,5-dimethylbenzene (32.6 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 79%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.55 (dd, J = 11.8, 7.6 Hz, 4H), 7.31 – 7.22 (m, 6H), 7.14 (1H), 2.39 (6H), 2.30 (6H); **$^{13}$C NMR** δ 142.1 (d, J = 2.6 Hz), 138.0 (d, J = 12.7 Hz), 133.5 (d, J = 2.6 Hz), 133.0 , 132.0 (d, J = 10.3 Hz), 130.1 , 129.5 (d, J = 9.8 Hz), 129.1 (d, J = 12.6 Hz), 21.5 , 21.2; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.7 . **MS (ESI+) calcd for** $C_{22}H_{23}OP$ (m/z $[M + H)]^+$) 334.40, found 335.25.

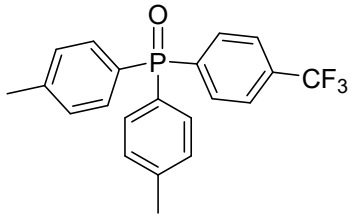


**(4-(dimethylamino)phenyl)di-p-tolylphosphine oxide (yellow solid) (3e)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 4-bromo-N,N-dimethylaniline (36.3 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 88%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.51 (m, 4H), 7.49 – 7.41 (m, 2H), 7.23 (dd, J = 7.9, 2.4 Hz, 4H), 6.71 – 6.64 (m, 2H), 2.99 (6H), 2.38 (6H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 152.3 , 141.8 (d, *J* = 2.6 Hz), 133.4 (d, *J* = 11.3 Hz), 132.0 (d, *J* = 10.2 Hz), 130.4 (d, *J* = 107.1 Hz), 129.0 (d, *J* = 12.4 Hz), 117.8 , 116.6 , 111.2 (d, *J* = 13.0 Hz), 39.9 , 21.5; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.9 . **MS (ESI+) calcd for** C22H24NOP (m/z [M + H)]$^{+}$) 349.41, found 350.17.

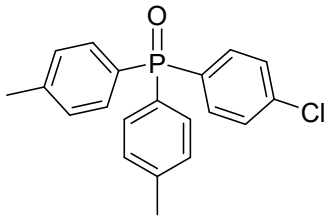



**di-p-tolyl(4-(trifluoromethyl)phenyl)phosphine oxide (pale yellow oil) (3f)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 1-bromo-4-(trifluoromethyl)benzene (33.0 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 77%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.85 – 7.77 (m, 2H), 7.70 (dd, J = 8.3, 2.0 Hz, 2H), 7.58 – 7.50 (m, 4H), 7.32 – 7.25 (m, 4H), 2.41 (6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 142.8 (d, J = 2.7 Hz), 137.7 (d, J = 100.6 Hz), 132.5 (d, J = 10.0 Hz), 132.0 (d, J = 10.3 Hz), 129.4 (d, J = 12.7 Hz), 128.7 (d, J = 20.3 Hz), 128.4 (d, J = 107.9 Hz), 125.4 – 125.0 (m), 21.6; **$^{31}$P NMR (162 MHz, $CDCl_3$) δ** 28.3. **MS (ESI+) calcd for** C21H18F3OP (m/z $[M + H]^+$) 374.34, found 375.25.

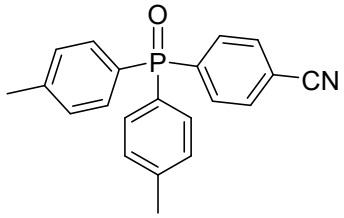



**(4-chlorophenyl)di-p-tolylphosphine oxide (colorless solid) (3g)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and bromochlorobenzene (23.6 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 92%.

**$^{1}$H NMR (400 MHz, CDCl3)** δ 7.62 – 7.56 (m, 2H), 7.56 – 7.49 (m, 4H), 7.45 – 7.40 (m, 2H), 7.27 (ddd, J = 6.4, 2.7, 2.3 Hz, 4H), 2.40 (6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 142.6 (d, J = 2.5 Hz), 138.3 , 133.4 (d, J = 10.7 Hz), 132.0 (d, J = 10.3 Hz), 129.3 (d, J = 12.6 Hz), 128.7 (d, J = 12.6 Hz), 21.6 ; **$^{31}$P NMR (162 MHz, CDCl3)** δ 28.6 . **MS (ESI+) calcd for** C20H18ClOP (m/z $[M + H)]^{+}$) 340.79, found 341.17.

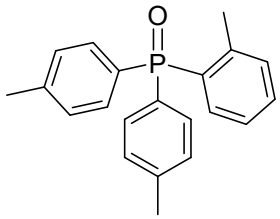



**4-(di-p-tolylphosphoryl)benzonitrile (pale yellow solid) (3h,3s)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 4-bromobenzenecarbonitrile (23.6 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 70%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.78 (ddt, J = 17.2, 12.5, 8.1 Hz, 4H), 7.59 – 7.49 (m, 4H), 7.31 (dd, J = 11.6, 8.5 Hz, 4H), 2.43 (d, J = 14.6 Hz, 6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ143.1 (d, J = 2.6 Hz), 139.0 (d, J = 98.9 Hz), 132.5 (d, J = 9.8 Hz), 132.0 (d, J = 10.3 Hz), 131.9 (d, J = 11.8 Hz), 129.5 (d, J = 12.8 Hz), 128.0 (d, J = 108.1 Hz), 117.9, 115.4 (d, J = 3.0 Hz), 21.6; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.3. **MS (ESI+) calcd for** $C_{21}H_{18}NOP$ (m/z $[M + H]^+$) 331.35, found 332.25.



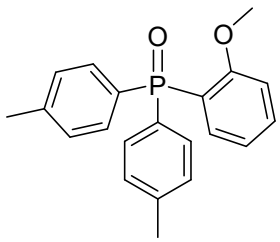
**o-tolyldi-p-tolylphosphine oxide (bright yellow oil) (3i)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 2-methylphenyl bromide (29.1 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 88%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.57 – 7.49 (m, 4H), 7.42 – 7.37 (m, 1H), 7.30 – 7.23 (m, 5H), 7.11 (dq, J = 7.7, 3.4 Hz, 1H), 7.03 (ddd, J = 13.9, 7.7, 1.5 Hz, 1H), 2.45 (d, J = 1.2 Hz, 3H), 2.40 (6H); **$^{13}$C NMR** δ 143.2 (d, J = 8.1 Hz), 142.1 (d, J = 2.8 Hz), 133.4 (d, J = 12.9 Hz), 131.9 (d, J = 9.8 Hz), 131.8 (d, J = 14.7 Hz), 131.4 (d, J = 142.2 Hz), 129.6 (d, J = 104.4 Hz), 129.2 (d, J = 12.4 Hz), 128.5 (d, J = 12.1 Hz), 125.0 (d, J = 13.0 Hz), 21.6 (d, J = 4.7 Hz), 21.5; **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 32.0 .

**MS (ESI+) calcd for** C21H21OP (m/z $[M + H]^+$) 320.37, found 321.25.

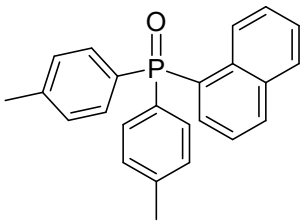


**2-methoxyphenyl)di-p-tolylphosphine oxide (yellow oil) (3j)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 2-bromoanisole (29.9 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 82%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.74 (ddd, *J* = 13.4, 7.6, 1.7 Hz, 1H), 7.58 (dd, *J* = 12.3, 8.1 Hz, 4H), 7.54 – 7.48 (m, 1H), 7.25 – 7.19 (m, 4H), 7.09 – 7.02 (m, 1H), 6.90 (dd, *J* = 8.2, 5.2 Hz, 1H), 3.57 (3H), 2.38 (6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 160.9, 141.7 (d, J = 2.7 Hz), 134.9 (d, J = 7.2 Hz), 134.0, 131.8 (d, J = 10.7 Hz), 130.1 (d, J = 109.4 Hz), 128.8 (d, J = 12.9 Hz), 120.8 (d, J = 11.6 Hz), 120.7 (d, J = 103.4 Hz), 111.3 (d, J = 6.5 Hz), 55.2 , 21.6 ; **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 27.5 . **MS (ESI+) calcd for** C21H21O2P (m/z $[M + H)]^+$) 336.37, found 337.25.

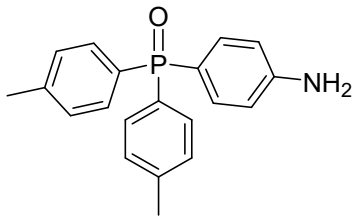


**naphthalen-1-yldi-p-tolylphosphine oxide (pale yellow oil) (3k)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 1-Bromonaphthalene (33.6 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 80%. The characterization data is in agreement with the data previously reported in the literature.[11]

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.59 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.45 (dddd, J = 16.8, 8.3, 6.9, 1.3 Hz, 2H), 7.39 – 7.28 (m, 2H), 7.26 (ddd, J = 6.3, 4.7, 1.4 Hz, 4H), 2.38 (d, J = 10.0 Hz, 6H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 142.2 (d, J = 2.6 Hz), 133.9, 133.8 (d, J = 3.6 Hz), 133.6 (d, J = 11.8 Hz), 133.1 (d, J = 2.6 Hz), 132.0 (d, J = 10.2 Hz), 129.6 (d, J = 107.1 Hz), 129.4 (d, J = 102.0 Hz), 129.3 (d, J = 12.6 Hz), 128.7, 127.7 (d, J = 5.8 Hz), 126.8 (d, J = 83.3 Hz), 124.1 (d, J = 14.2 Hz), 21.6; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 32.6.

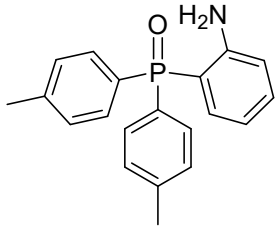



**(4-aminophenyl)di-p-tolylphosphine oxide (brown solid) (3l)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 4-bromoaniline (22.9 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=6/4). The isolated yield was 74%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.48 (m, 4H), 7.39 – 7.31 (m, 2H), 7.25 – 7.19 (m, 4H), 6.66 – 6.60 (m, 2H), 4.11 (q, J = 7.1 Hz, 1H), 2.37 (s, 6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 149.8, 141.9, 133.7 (d, J = 11.1 Hz), 132.0 (d, J = 10.2 Hz), 130.2 (d, J = 106.6 Hz), 129.0 (d, J = 12.4 Hz), 120.2 (d, J = 113.7 Hz), 114.2 (d, J = 13.2 Hz), 21.5; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 29.7. **MS (ESI+) calcd for** C20H20NOP (m/z $[M + H]^+$) 321.36, found 322.25.

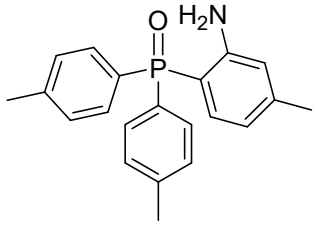



**(2-aminophenyl)di-p-tolylphosphine oxide (brown solid) (3m)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 2-bromoaniline (26.2 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=6/4). The isolated yield was 72%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.52 (dd, J = 11.9, 8.1 Hz, 4H), 7.26 (dd, J = 8.0, 2.3 Hz, 4H), 7.06 (d, J = 8.3 Hz, 1H), 6.62 – 6.54 (m, 2H), 5.12 (s, 2H), 2.40 (s, 6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 152.3 (d, J = 4.3 Hz), 142.3 (d, J = 2.5 Hz), 133.3, 133.1 (d, J = 4.9 Hz), 132.0 (d, J = 10.4 Hz), 129.2 (d, J = 12.6 Hz), 129.2 (d, J = 106.8 Hz), 116.5 (dd, J = 21.9, 10.4 Hz), 112.9 , 111.8, 21.6; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 35.5. **MS (ESI+) calcd for** C20H20NOP (m/z $[M + H)]^+$) 321.36, found 322.17.

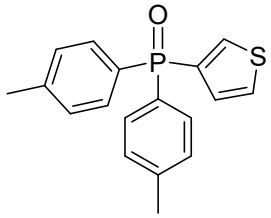



**(2-amino-4-methylphenyl)di-p-tolylphosphine oxide (brown solid) (3n)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 2-bromo-5-methylaniline (30.3 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=6/4). The isolated yield was 73%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.75 – 7.63 (m, 1H), 7.52 (dd, J = 11.9, 8.1 Hz, 4H), 7.26 (dd, J = 8.0, 2.3 Hz, 5H), 7.06 (d, J = 8.3 Hz, 1H), 6.62 – 6.54 (m, 2H), 2.40 (6H), 2.10 (3H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 150.0 (d, J = 4.2 Hz), 142.2 (d, J = 2.3 Hz), 134.0 (d, J = 1.8 Hz), 132.9 (d, J = 11.2 Hz), 132.0 (d, J = 10.4 Hz), 129.3 (d, J = 106.5 Hz), 129.2 (d, J = 12.6 Hz), 125.5 (d, J = 12.7 Hz), 116.9 (d, J = 8.9 Hz), 113.3 (d, J = 105.6 Hz), 21.6, 20.4; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 35.3. **MS (ESI+) calcd for** C21H22NOP (m/z $[M + H)]^+$) 335.39, found 336.25.

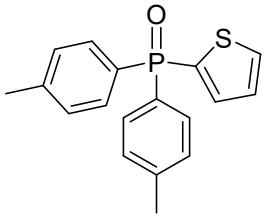



**thiophen-3-yldi-p-tolylphosphine oxide (pale yellow oil) (3o)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 3-Bromothiophene (22.6 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 81%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.70 (ddd, J = 7.5, 2.8, 1.2 Hz, 1H), 7.60 – 7.53 (m, 4H), 7.44 (ddd, J = 4.9, 2.8, 2.0 Hz, 1H), 7.28 – 7.22 (m, 5H), 2.39 (6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 142.4 (d, J = 2.6 Hz), 135.08 (d, J = 14.4 Hz), 134.6 (d, J = 108.1 Hz), 131.7 (d, J = 10.6 Hz), 129.7 (d, J = 110.3 Hz), 129.5 (d, J = 14.8 Hz), 129.2 (d, J = 12.7 Hz), 127.4 (d, J = 15.0 Hz), 21.5; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 22.8. **MS (ESI+) calcd for** C18H17OPS (m/z $[M + H)]^+$) 312.37, found 313.17.

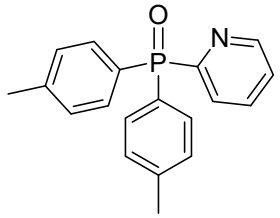



**thiophen-2-yldi-p-tolylphosphine oxide (pale yellow oil) (3p)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 2-Bromothiophene (23.0 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 49%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.63 (m, 1H), 7.62 – 7.50 (m, 4H), 7.49 – 7.41 (m, 1H), 7.33 – 7.27 (m, 3H), 7.25 (ddd, J = 7.8, 2.4, 0.6 Hz, 1H), 2.40 (6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 143.0 (d, J = 2.7 Hz), 132.0 (d, J = 9.7 Hz), 131.9, 130.7 (d, J = 11.8 Hz), 129.6 (d, J = 13.2 Hz), 129.1 (d, J = 12.5 Hz), 128.5 (d, J = 12.1 Hz), 128.3 (d, J = 103.8 Hz),21.6; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 21.7. **MS (ESI+) calcd for** C18H17OPS (m/z $[M + H)]^+$) 312.37, found 313.25.

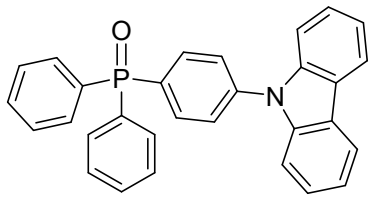



**pyridin-2-yldi-p-tolylphosphine oxide (pale yellow oil) (3q)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 2-Bromopyridine (23.2 μL, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 52%. The characterization data is in agreement with the data previously reported in the literature.[12]

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.75 (ddd, J = 4.7, 1.5, 1.0 Hz, 1H), 8.28 (ddt, J = 7.8, 5.8, 1.1 Hz, 1H), 7.82 (tdd, J = 7.7, 3.8, 1.7 Hz, 1H), 7.78 – 7.71 (m, 4H), 7.54 (dd, J = 11.8, 8.1 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.26 – 7.23 (m, 4H), 2.37 (6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 156.8 (d, J = 131.8 Hz), 150.0 (d, J = 19.1 Hz), 142.3 (d, J = 2.6 Hz), 136.0 (d, J = 9.1 Hz), 132.1 (d, J = 9.9 Hz), 129.0, 129.0 (d, J = 12.3 Hz), 128.9 (d, J = 106.7 Hz), 128.2 (d, J = 19.8 Hz), 125.0 (d, J = 2.8 Hz), 21.5; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 21.7.

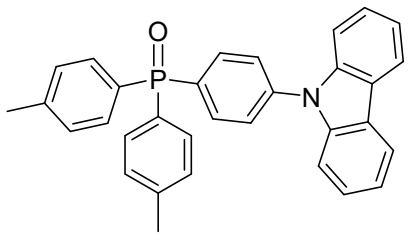



**(4-(9H-carbazol-9-yl)phenyl)diphenylphosphine oxide(white foam) (4a)**

**Reagents:** SPO-Ph (40.44 mg, 0.20 mmol) and N-(4-bromophenyl)carbazole (77.33 mg, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 79%. The characterization data is in agreement with the data previously reported in the literature.[13]

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.17 (dd, J = 13.1, 7.6 Hz, 2H), 8.02 – 7.89 (m, 2H), 7.89 – 7.69 (m, 6H), 7.53 (dtd, J = 20.5, 14.5, 7.3 Hz, 10H), 7.39 – 7.26 (m, 2H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 141.2 (d, J = 2.9 Hz), 140.1, 133.7 (d, J = 10.6 Hz), 132.1 (d, J = 2.6 Hz), 132.1 (d, J = 106.1Hz), 132.0 (d, J = 9.9 Hz), 131.2 (d, J = 104.6 Hz), 128.6 (d, J = 12.2 Hz), 128.4, 126.4 (d, J = 12.5 Hz), 126.1, 123.7, 120.4 (d, J = 15.0 Hz), 109.6; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 28.6**.**

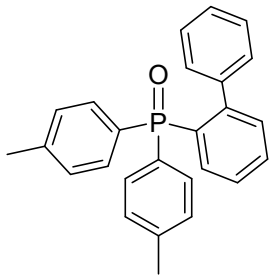



**(4-(9H-carbazol-9-yl)phenyl)di-p-tolylphosphine oxide (white foam) (4b)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and N-(4-bromophenyl)carbazole (77.33 mg, 0.24 mmol).

**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 86%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, J = 7.7 Hz, 2H), 7.97 – 7.89 (m, 2H), 7.74 – 7.69 (m, 5H), 7.50 (d, J = 8.2 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.36 (dd, J = 8.2, 2.6 Hz, 5H), 7.34 – 7.27 (m, 2H), 2.46 (s, 6H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 141.0, 140.2, 133.7 (d, J = 10.5 Hz), 132.1 (d, J = 10.3 Hz), 131.9 (d, J = 104.4 Hz), 129.6, 129.3 (d, J = 12.6 Hz), 128.5, 128.4, 126.4 (d, J = 12.5 Hz), 126.1, 123.7 120.4 (d, J = 10.4 Hz), 109.6, 21.6; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 28.3. **MS (ESI+) calcd for** $C_{32}H_{26}NOP$ (m/z $[M + H)]^+$) 471.54, found 472.33.



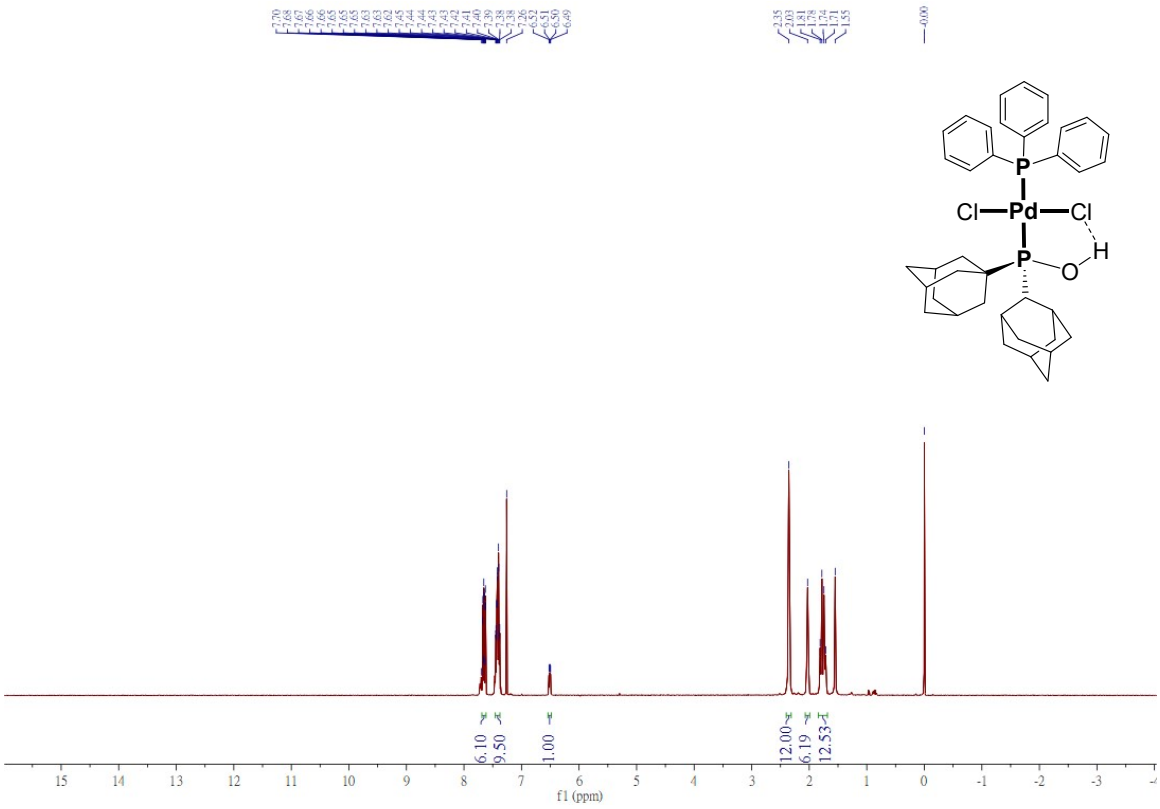
**[1,1'-biphenyl]-2-yldi-p-tolylphosphine oxide (colorless crystal) (4c)**

**Reagents:** *Di-p-tolylphosphine oxide* (46.05 mg, 0.20 mmol) and 2-Bromo-biphenyl (55.94 mg, 0.24 mmol).

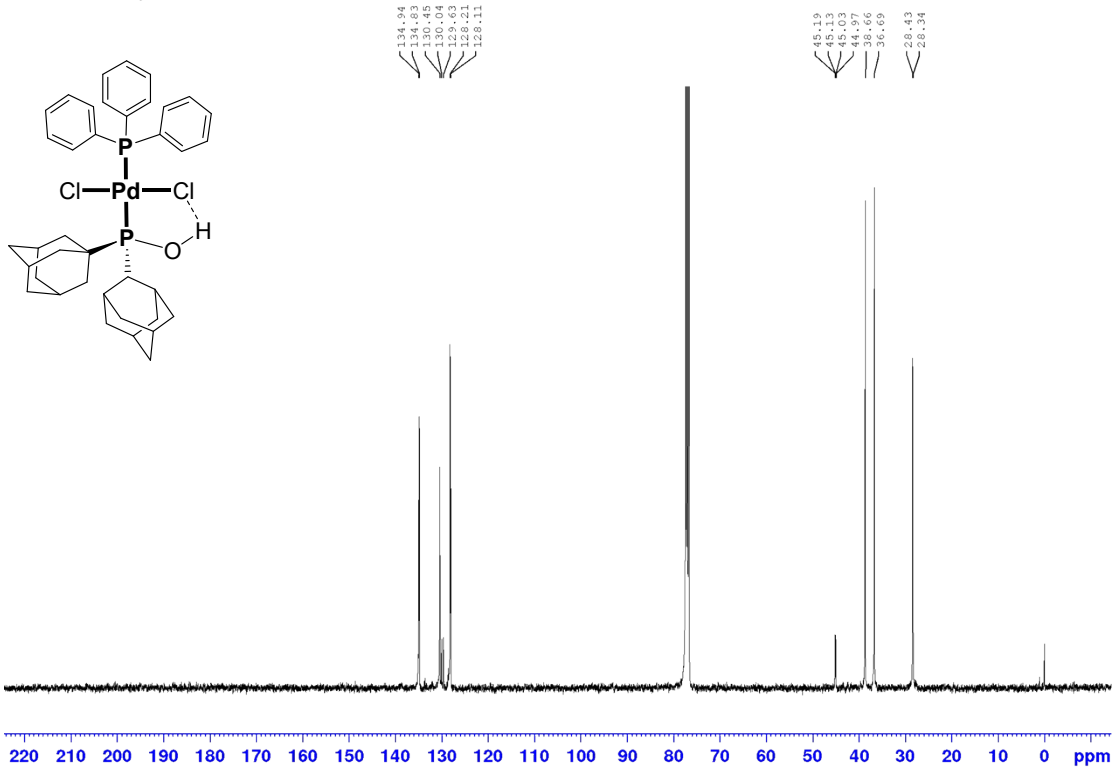
**Isolations:** The crude product was purified by chromatography on silica gel (hexanes/EtOAc=7/3). The isolated yield was 87%.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.54 (ddd, J = 8.9, 3.0, 1.5 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.35 – 7.29 (m, 2H), 7.20 – 7.16 (m, 2H), 7.13 – 7.08 (m, 4H), 7.08 – 7.05 (m, 1H), 7.05 – 7.01 (m, 1H), 2.33 (5H); **$^{13}$C NMR (101 MHz, CDCl3)** δ 147.6 (d, J = 8.4 Hz), 141.4 (d, J = 2.8 Hz), 140.5 (d, J = 3.9 Hz), 134.0 (d, J = 12.0 Hz), 132.6, 131.9 (d, J = 9.8 Hz), 131.6 (d, J = 9.7 Hz), 130.1, 130.0 (d, J = 107.0 Hz),128.8 (d, J = 12.5 Hz), 127.0 (d, J = 6.8 Hz), 126.4 (d, J = 12.3 Hz), 21.5; **$^{31}$P NMR (162 MHz, $CDCl_3$)** δ 28.7. **MS (ESI+) calcd for** C26H23OP (m/z $[M + H]^+$) 382.44, found 383.33.

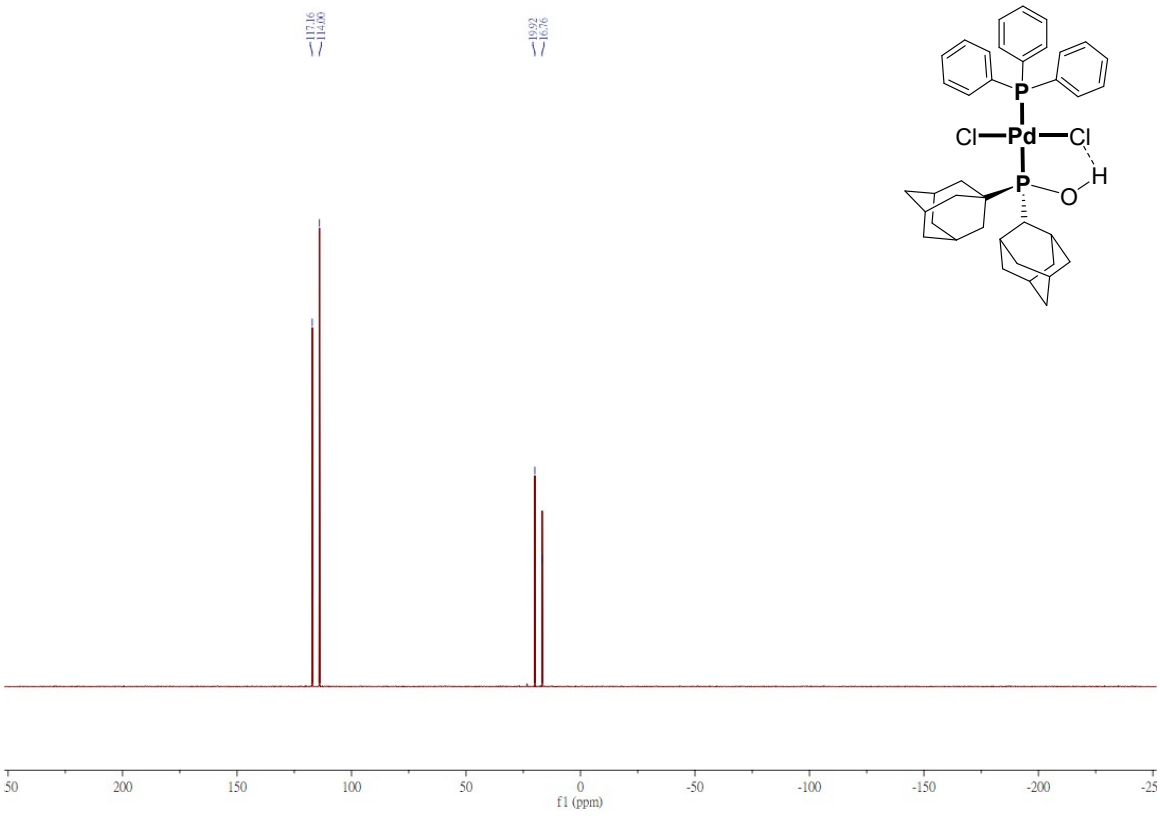
## Precatalyst 1a: $^{1}$H NMR



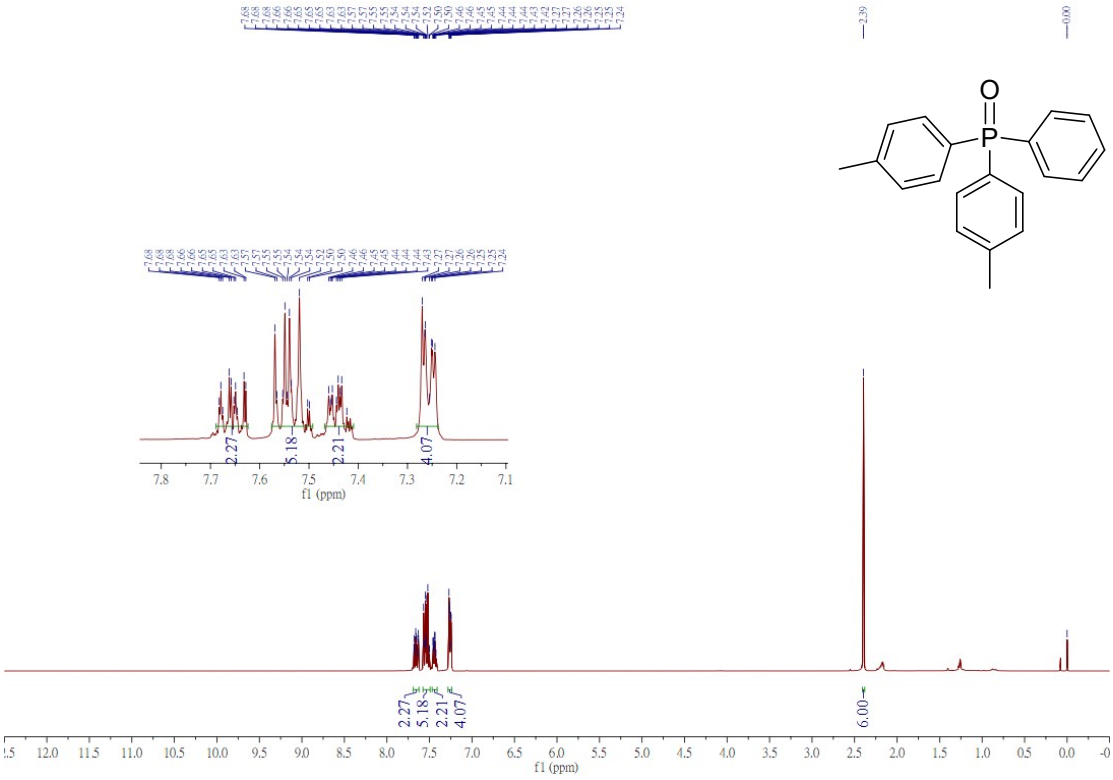

## Precatalyst 1a: $^{13}$C NMR



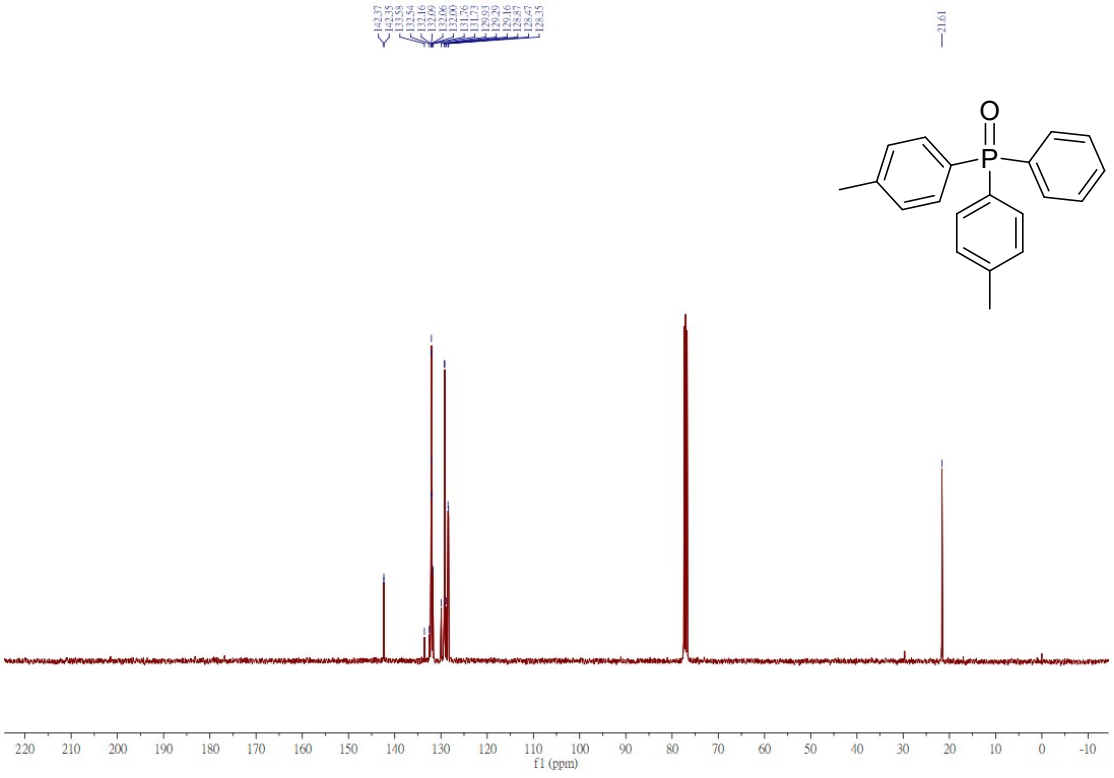
## Precatalyst 1a: $^{31}$P NMR



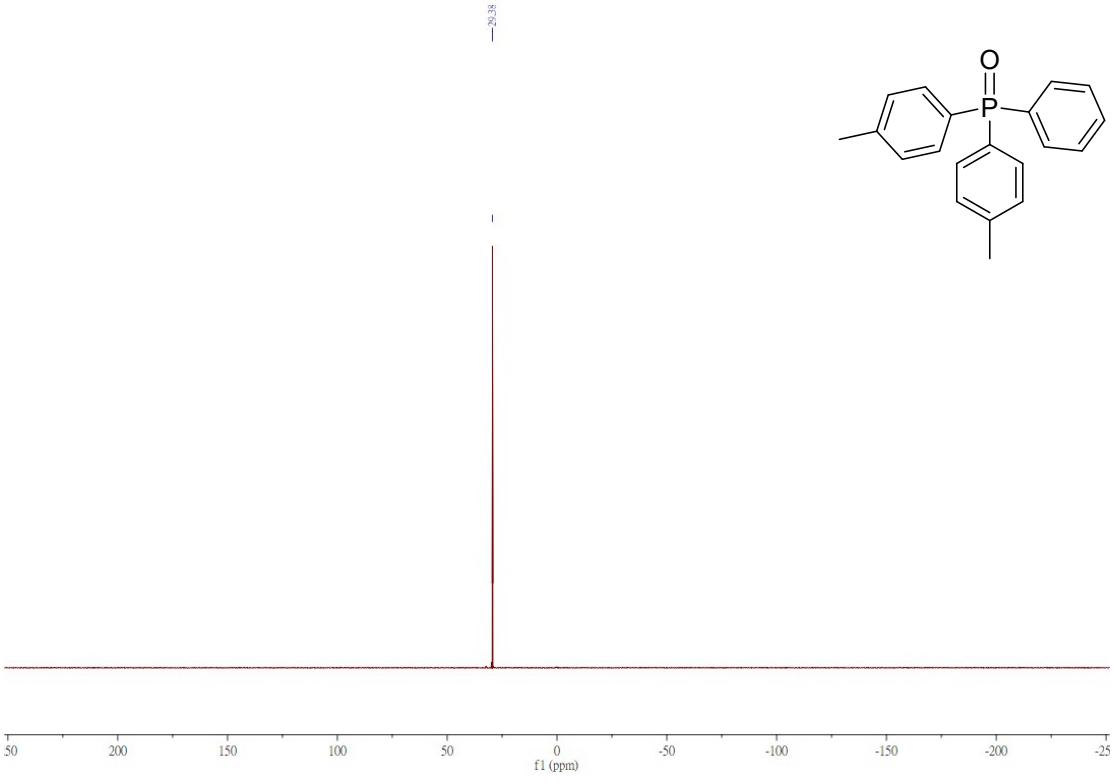

## phenyldi-p-tolylphosphine oxide (2a,3a): $^{1}$H NMR



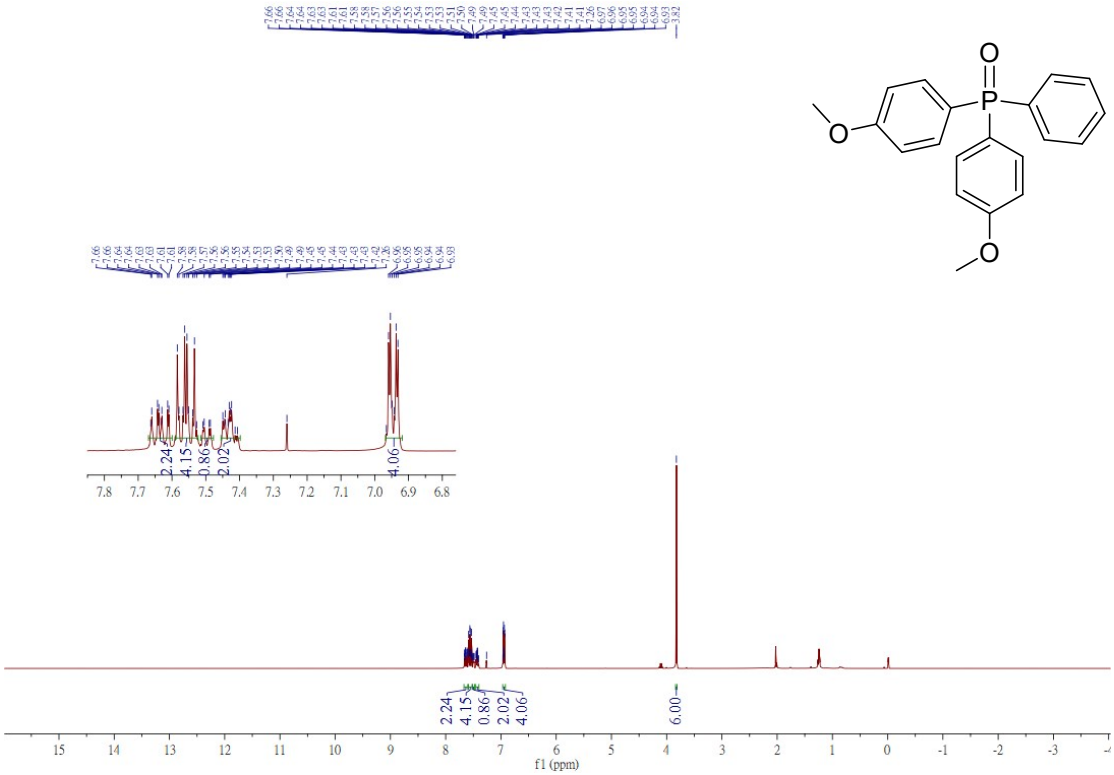
## phenyldi-p-tolylphosphine oxide (2a,3a): $^{13}C$ NMR



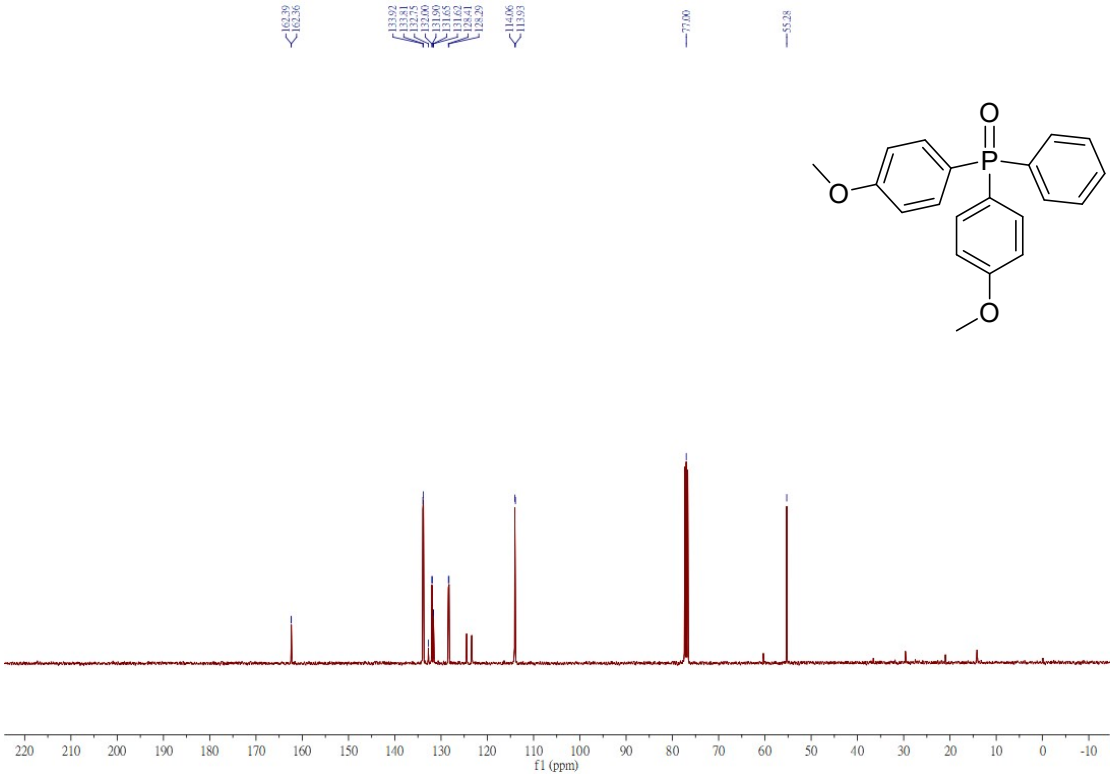

## phenyldi-p-tolylphosphine oxide (2a,3a): $^{31}P$ NMR



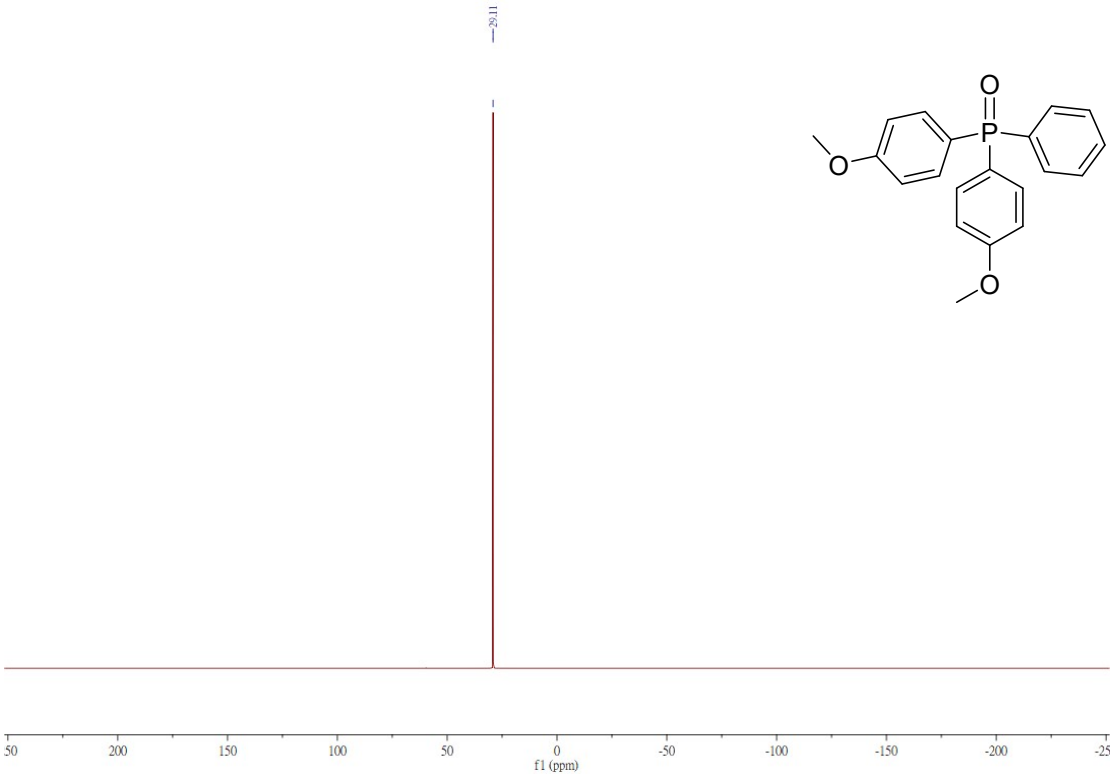
## bis(4-methoxyphenyl)(phenyl)phosphine oxide(2b): $^{1}$H NMR



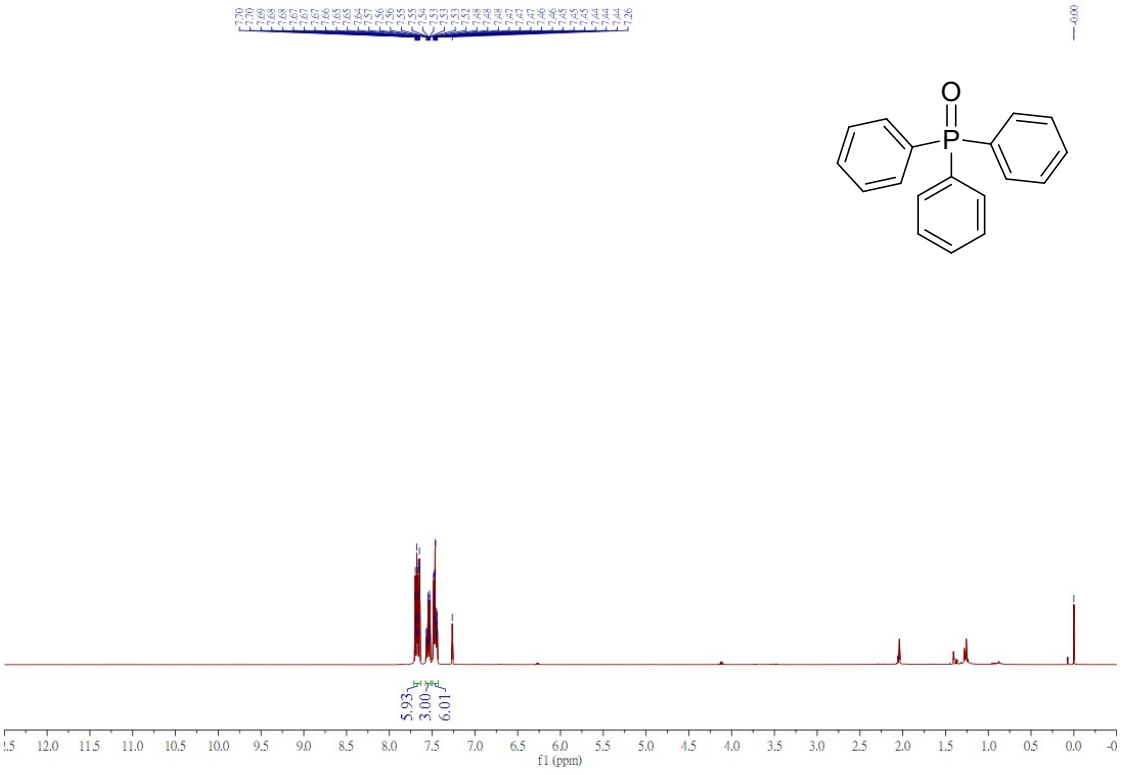

## bis(4-methoxyphenyl)(phenyl)phosphine oxide(2b): $^{13}$C NMR



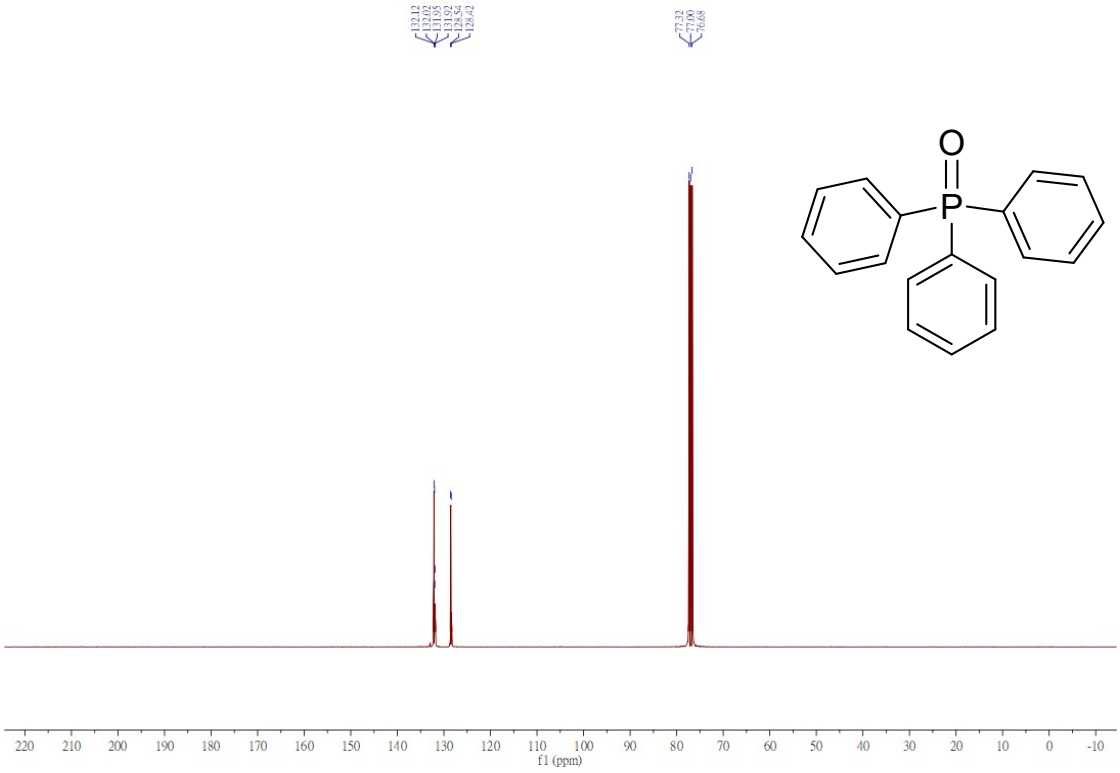
## bis(4-methoxyphenyl)(phenyl)phosphine oxide(2b): $^{31}$P NMR



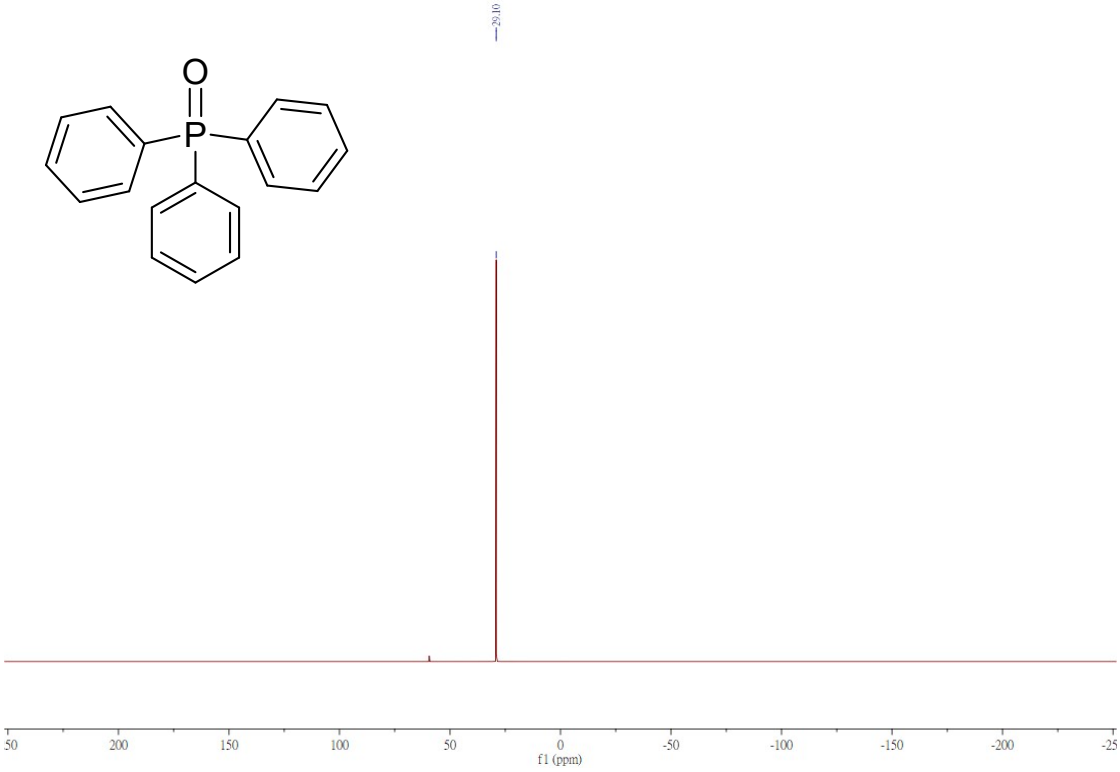

## triphenylphosphine oxide (2c): $^{1}$H NMR



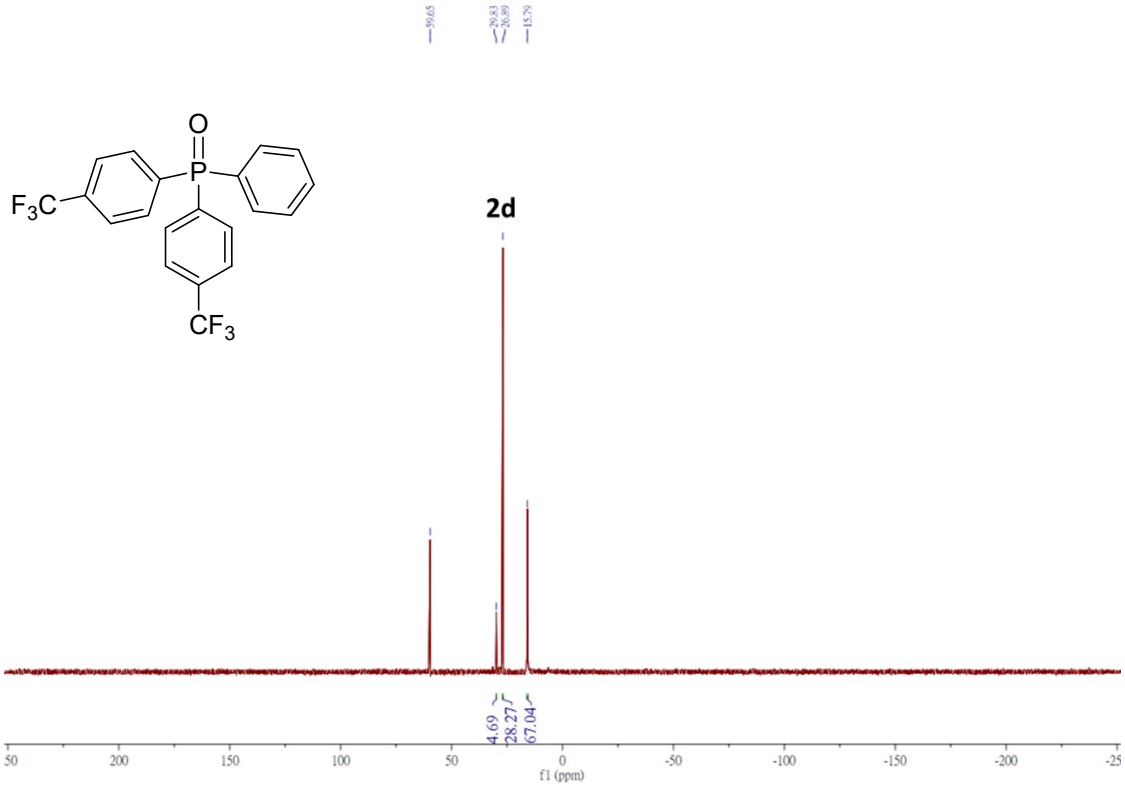
**triphenylphosphine oxide (2c): $^{13}$C NMR**



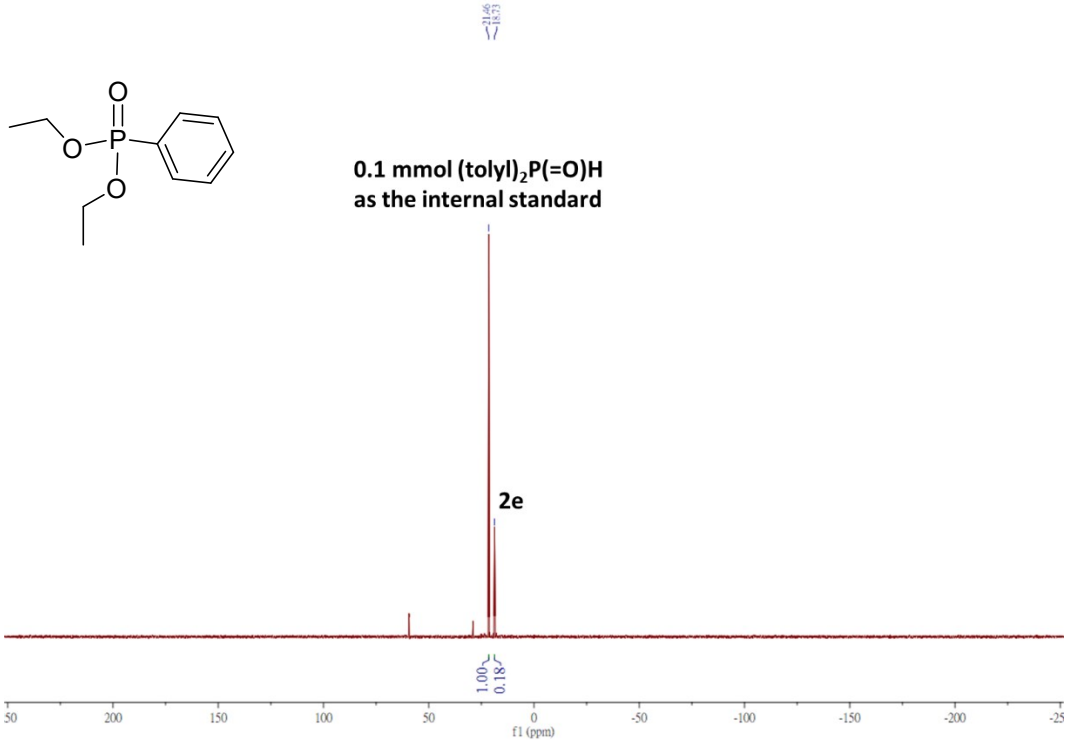

**triphenylphosphine oxide (2c): $^{31}$P NMR**



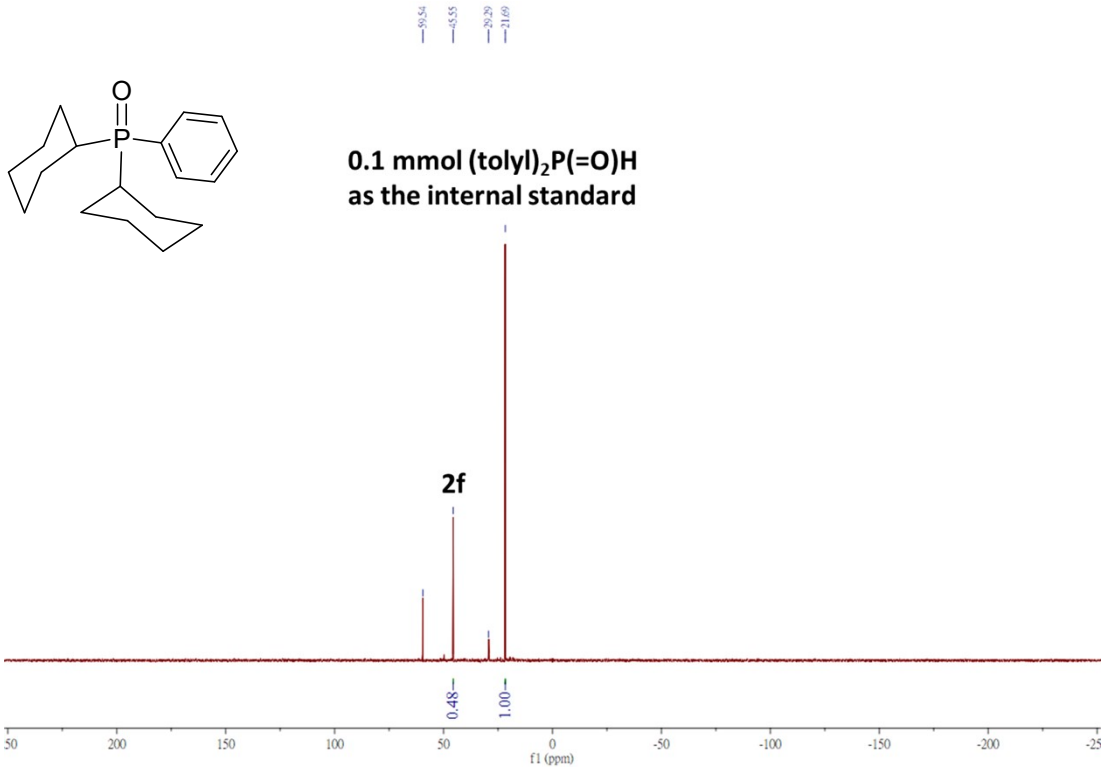
## phenylbis(4-(trifluoromethyl)phenyl)phosphine oxide (2d)



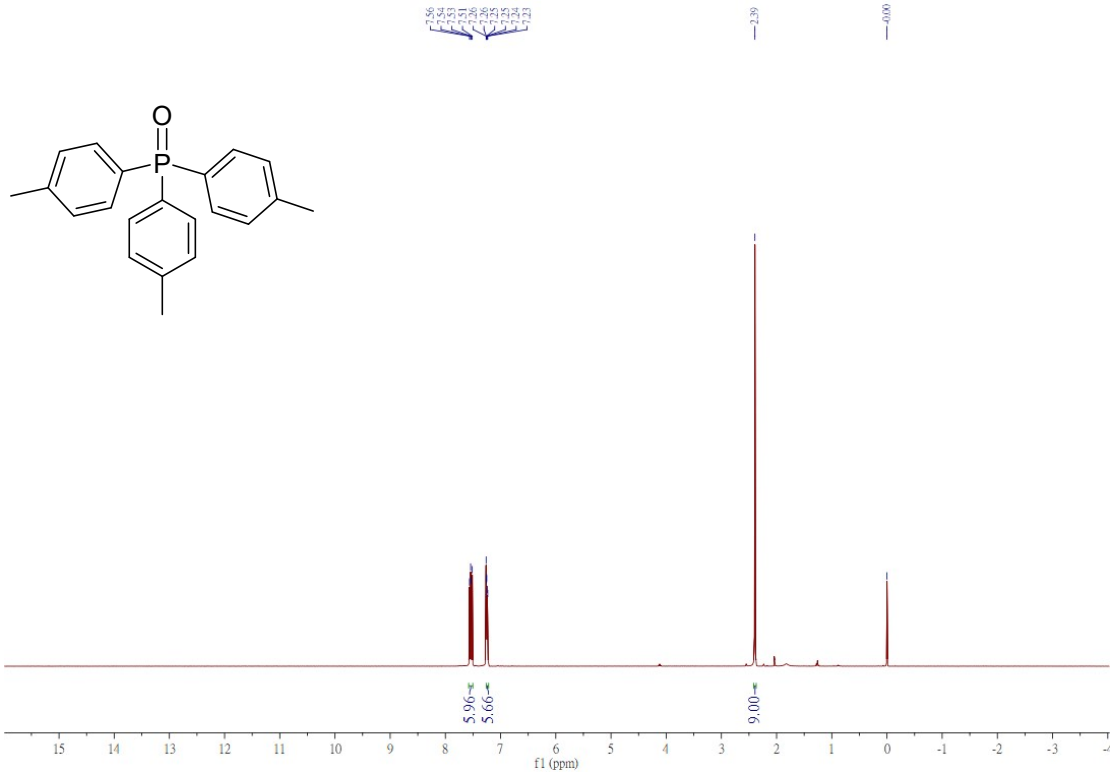

## diethyl phenylphosphonate (2e)



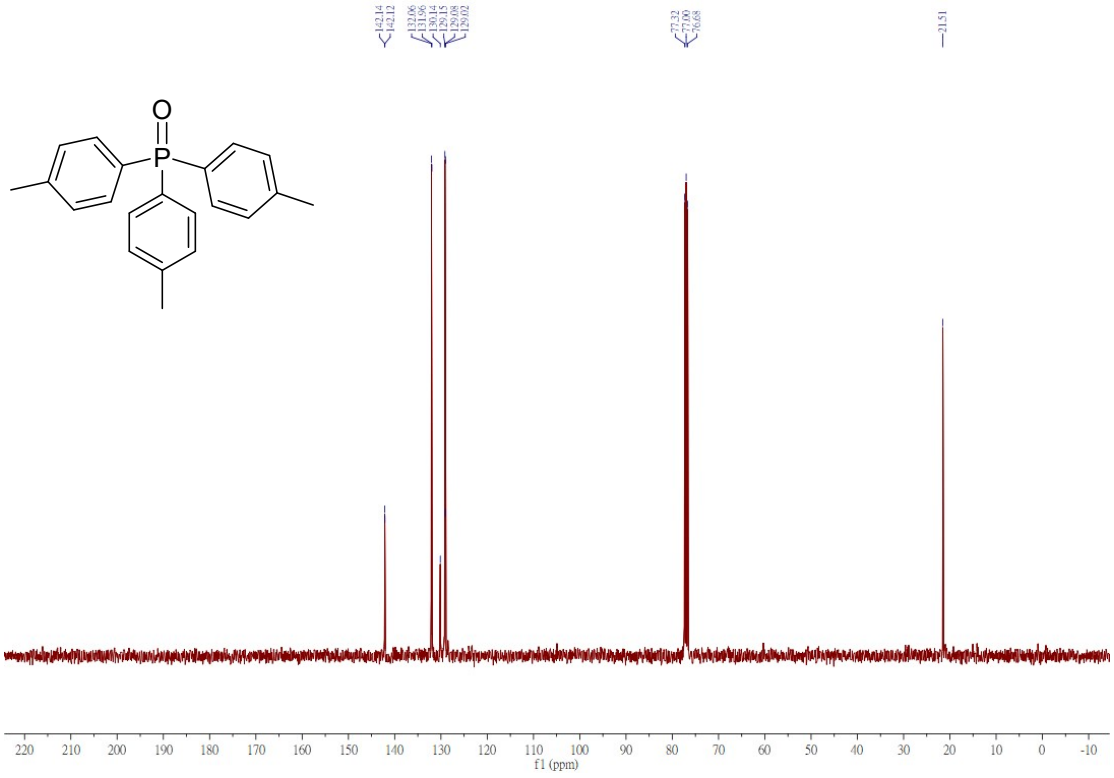
## dicyclohexyl(phenyl)phosphine oxide (2f)



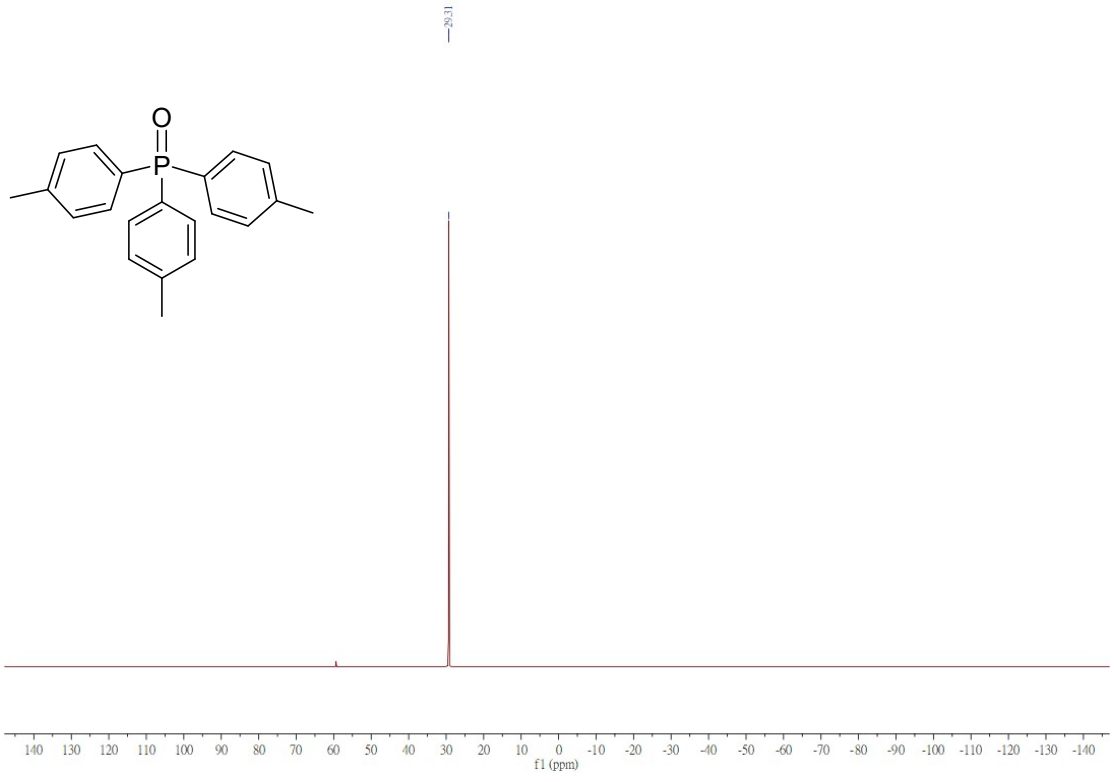

## tri-p-tolylphosphine oxide (3b): $^{1}$H NMR



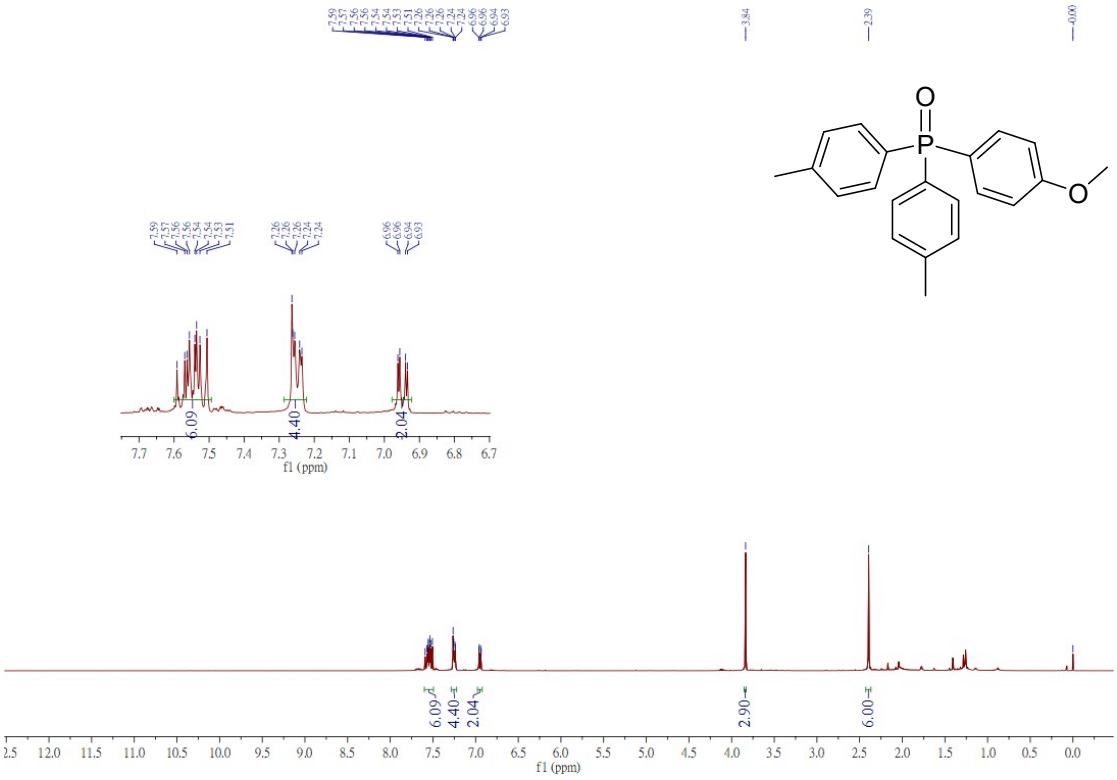
## tri-p-tolylphosphine oxide (3b): $^{13}$C NMR



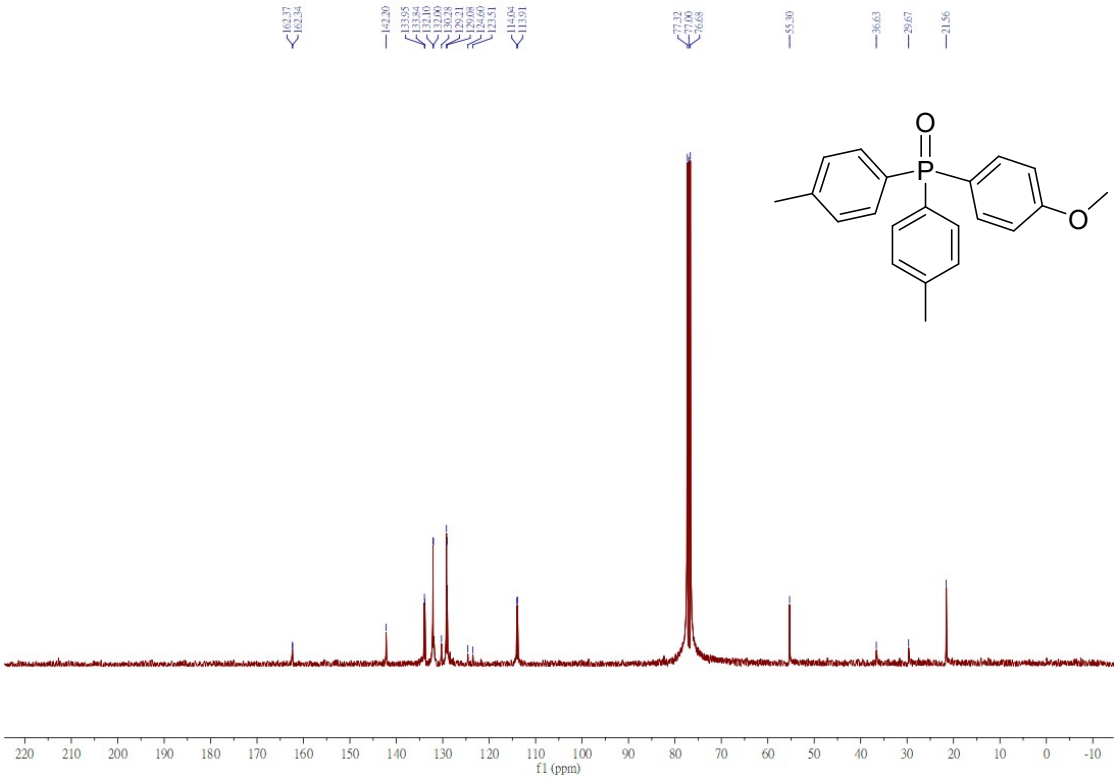

## tri-p-tolylphosphine oxide (3b): $^{31}$P NMR



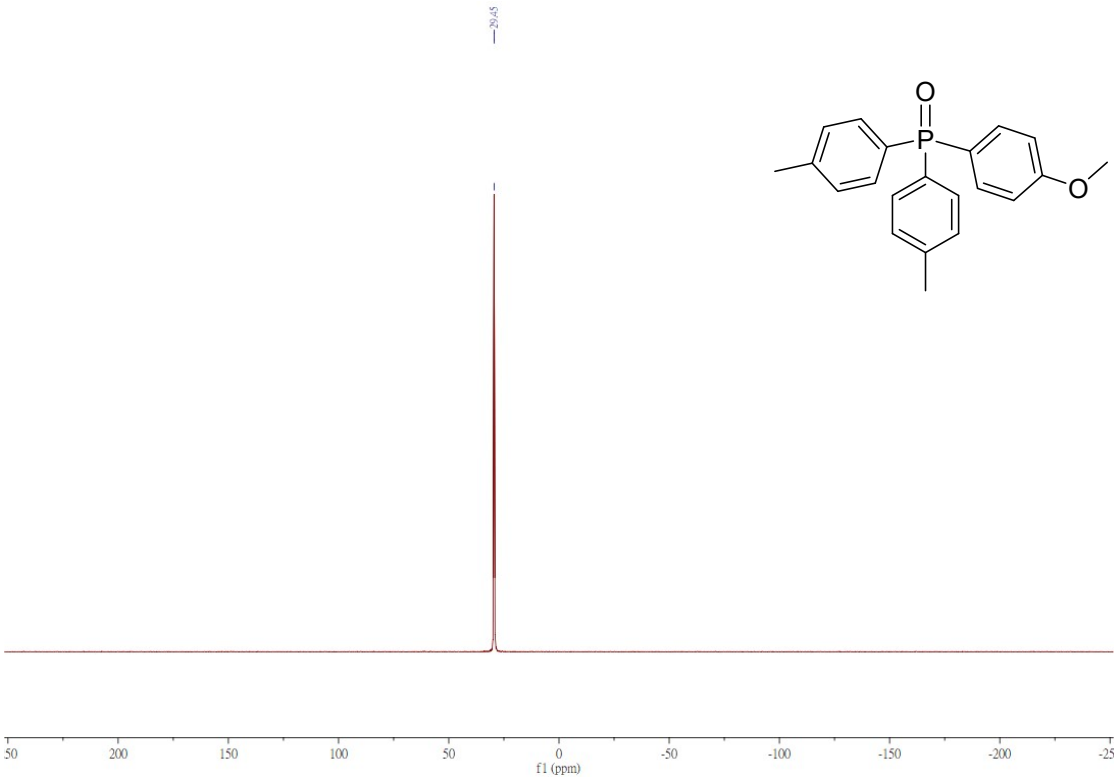
## (4-methoxyphenyl)di-p-tolylphosphine oxide (3c): $^{1}$H NMR



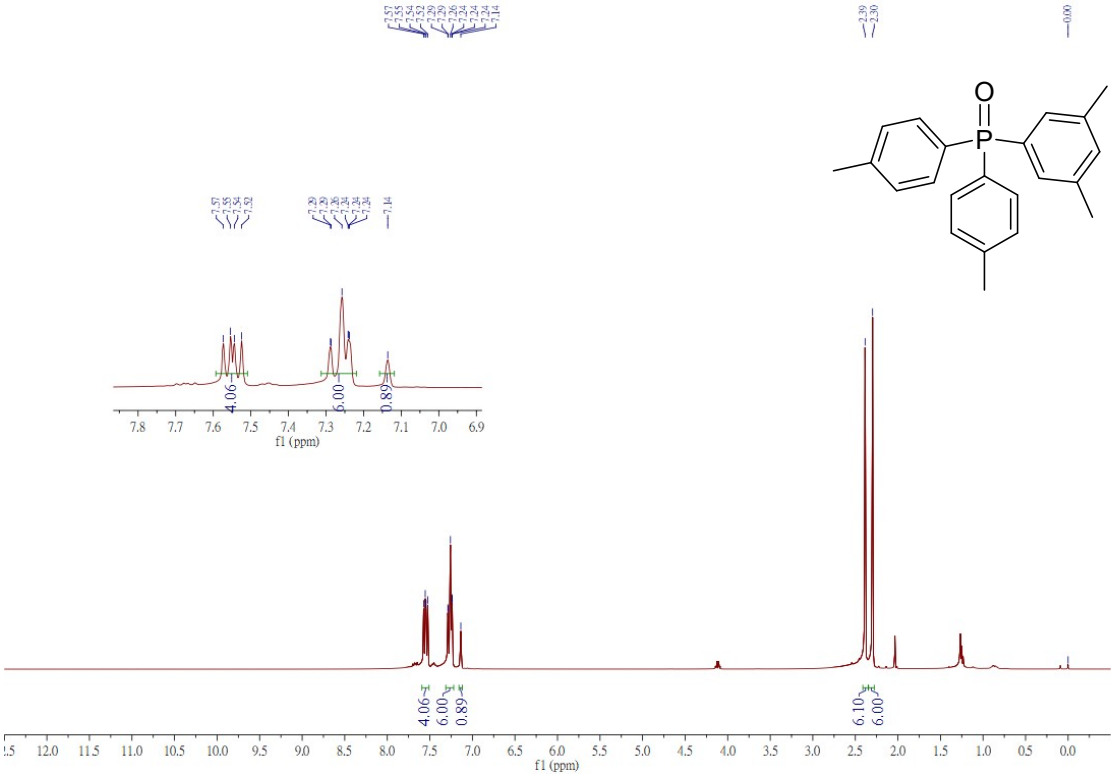

## (4-methoxyphenyl)di-p-tolylphosphine oxide (3c): $^{13}$C NMR



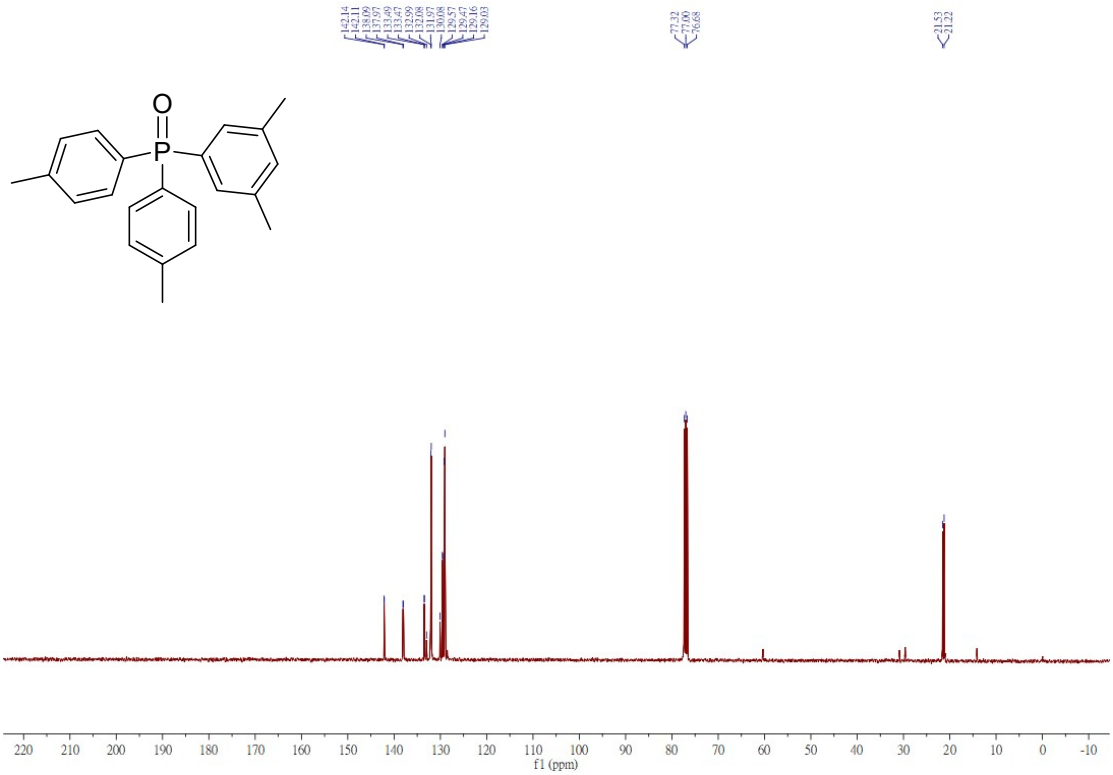
## (4-methoxyphenyl)di-p-tolylphosphine oxide (3c): $^{31}$P NMR



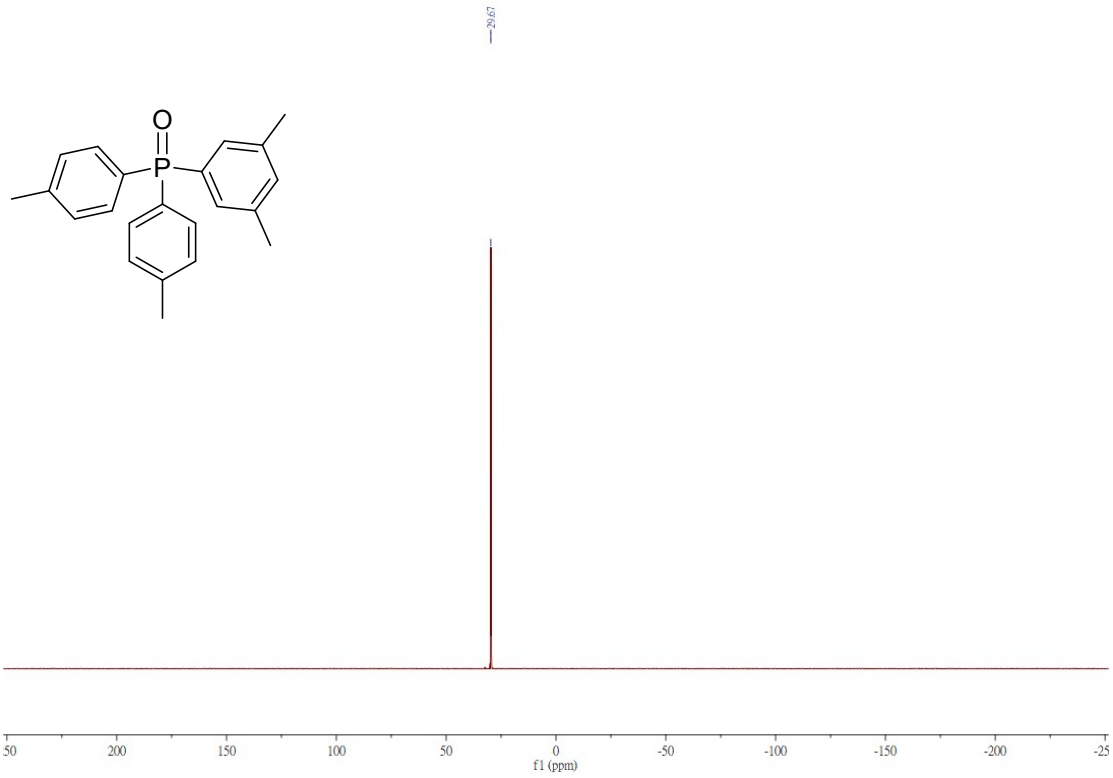

## (3,5-dimethylphenyl)di-p-tolylphosphine oxide (3d): $^{1}$H NMR



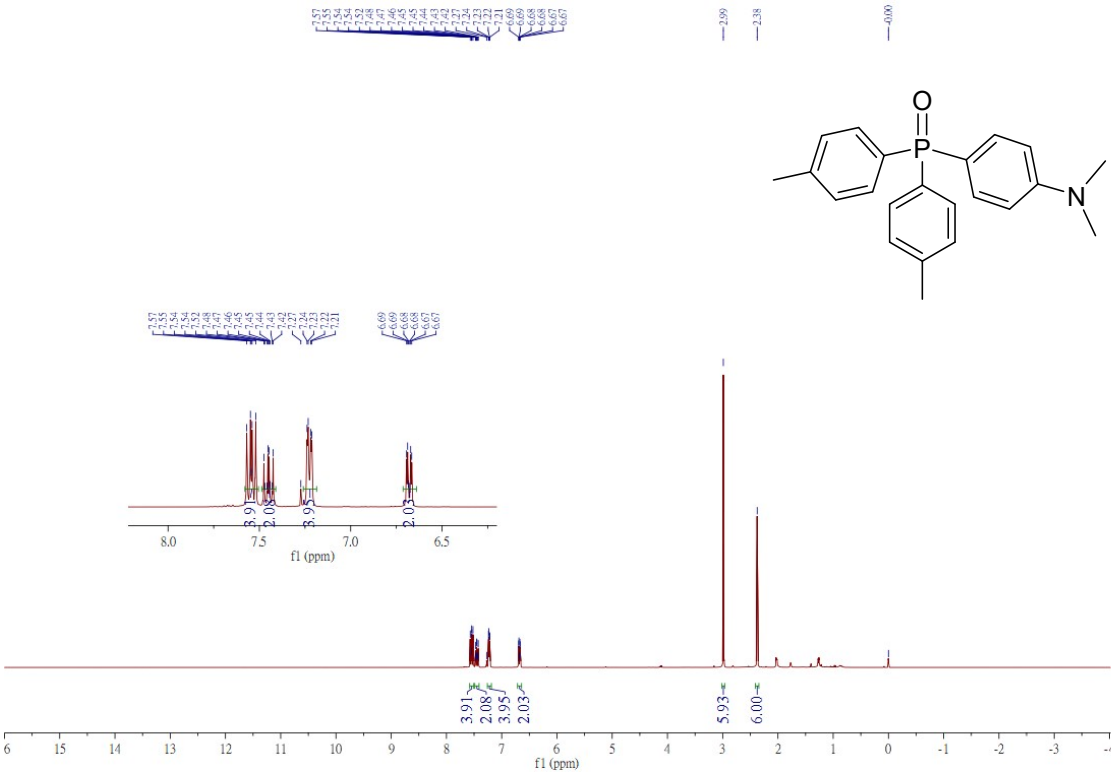
## (3,5-dimethylphenyl)di-p-tolylphosphine oxide (3d): $^{13}$C NMR



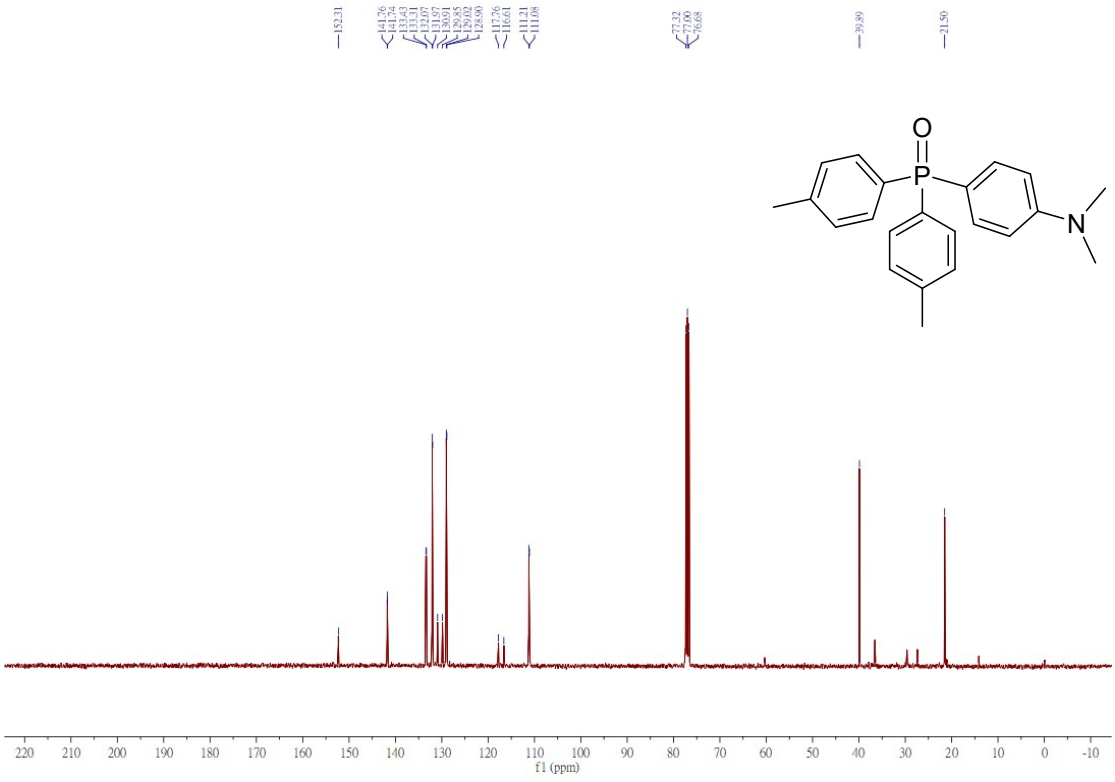

## (3,5-dimethylphenyl)di-p-tolylphosphine oxide (3d): $^{31}$P NMR



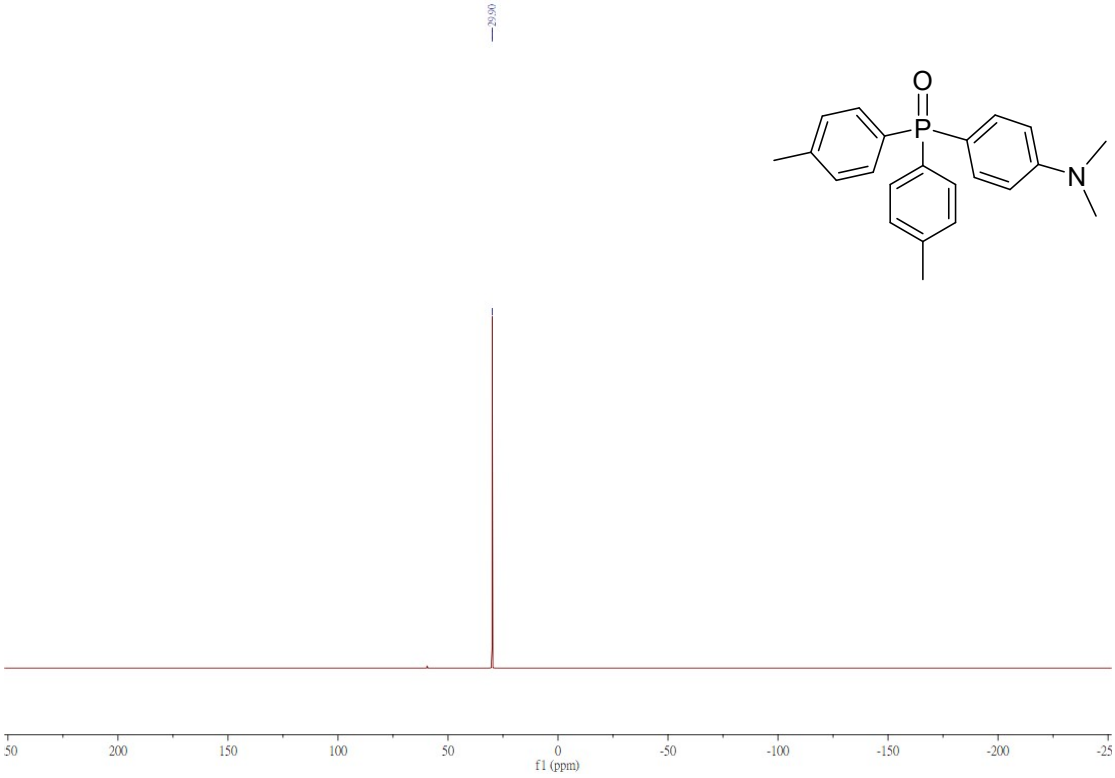
## (4-(dimethylamino)phenyl)di-p-tolylphosphine oxide (3e): $^{1}$H NMR



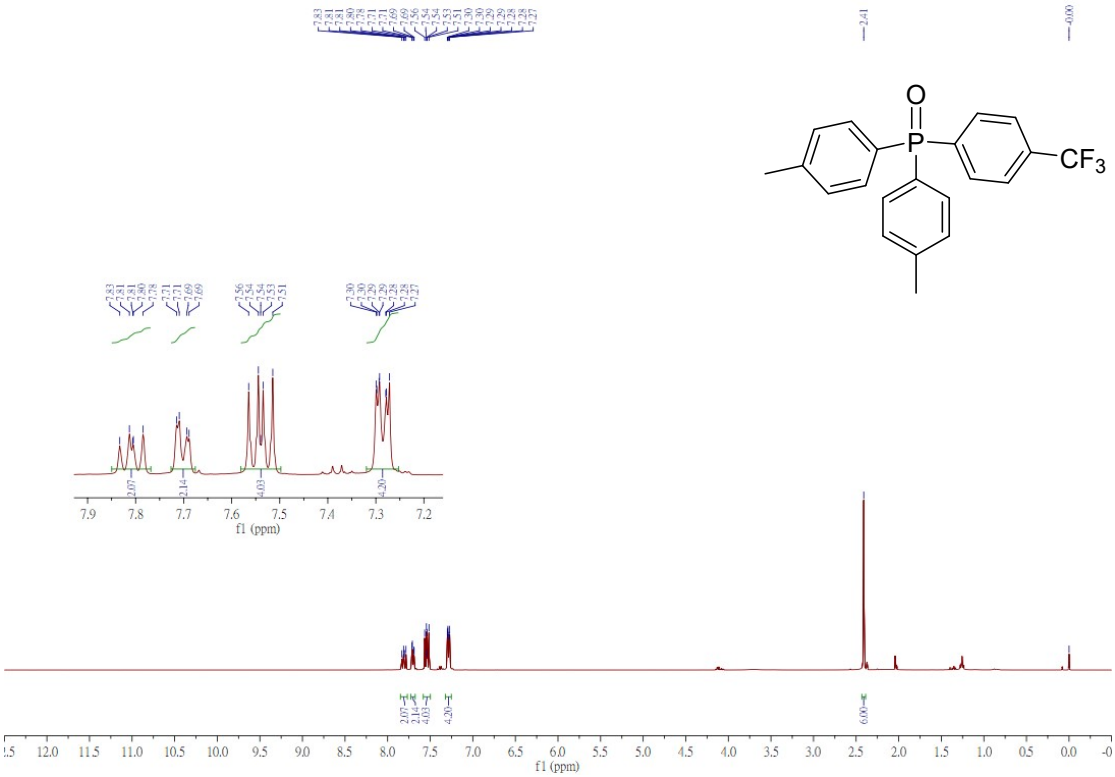

## (4-(dimethylamino)phenyl)di-p-tolylphosphine oxide (3e): $^{13}$C NMR



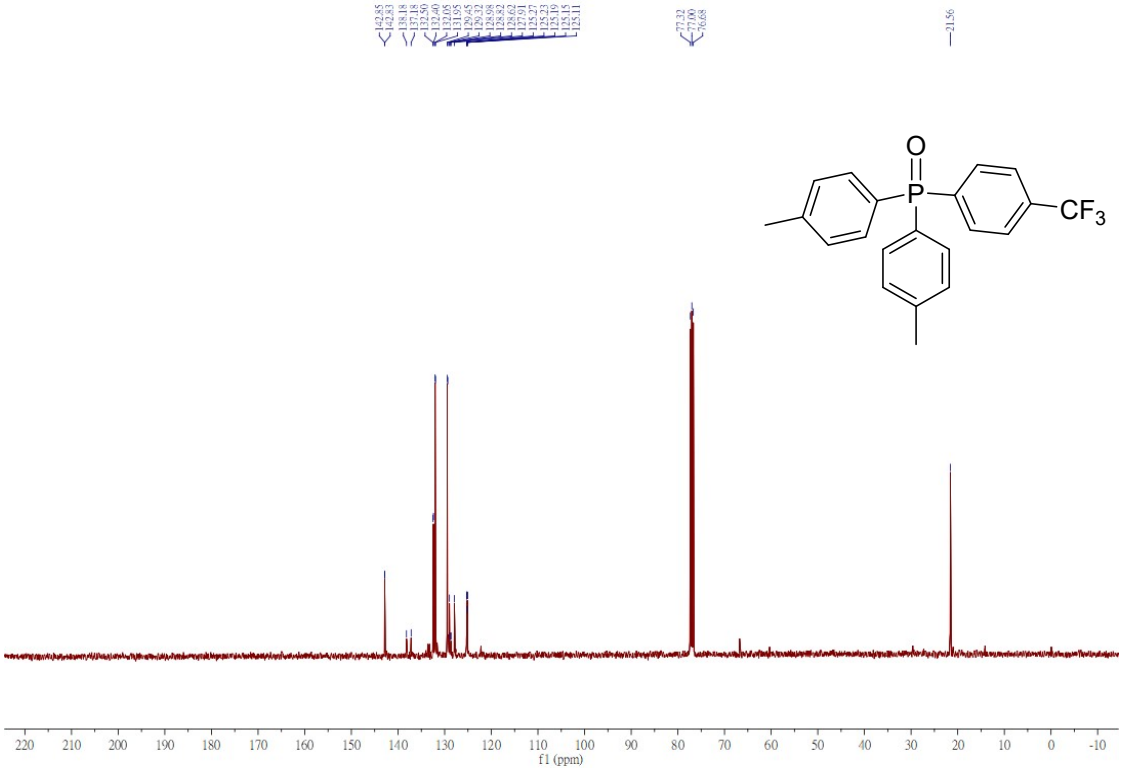
## (4-(dimethylamino)phenyl)di-p-tolylphosphine oxide (3e): $^{31}$P NMR



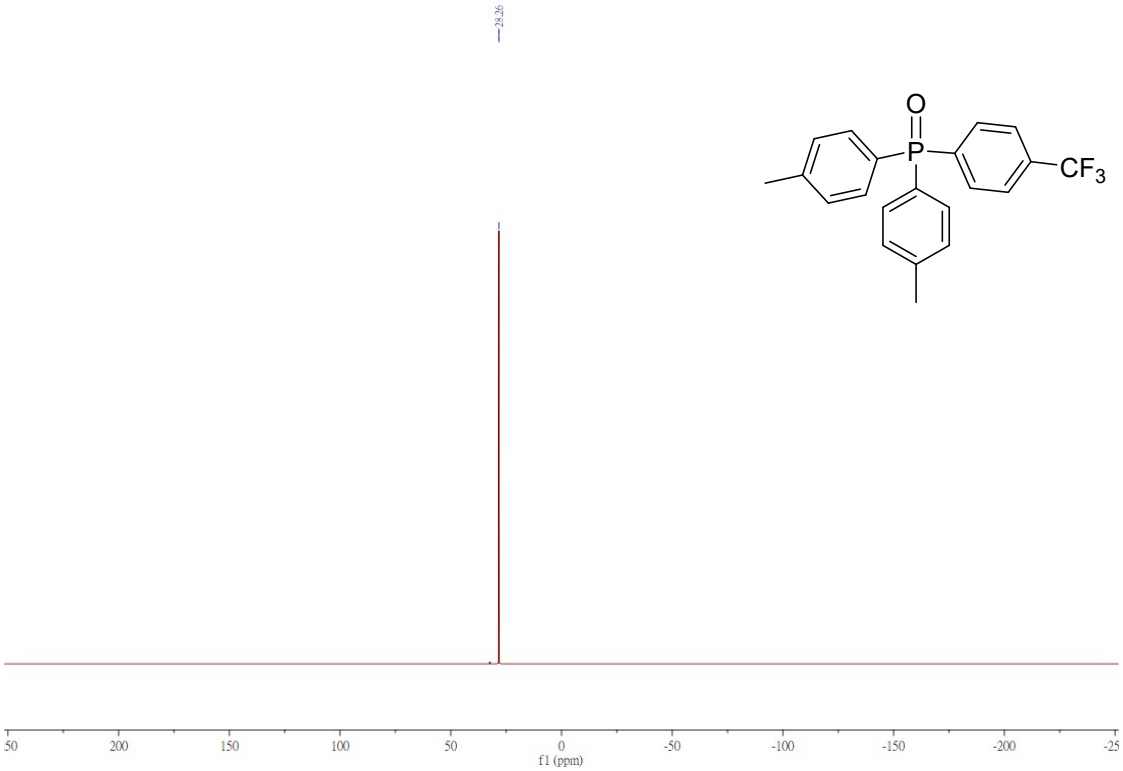

## di-p-tolyl(4-(trifluoromethyl)phenyl)phosphine oxide (3f): $^{1}$H NMR



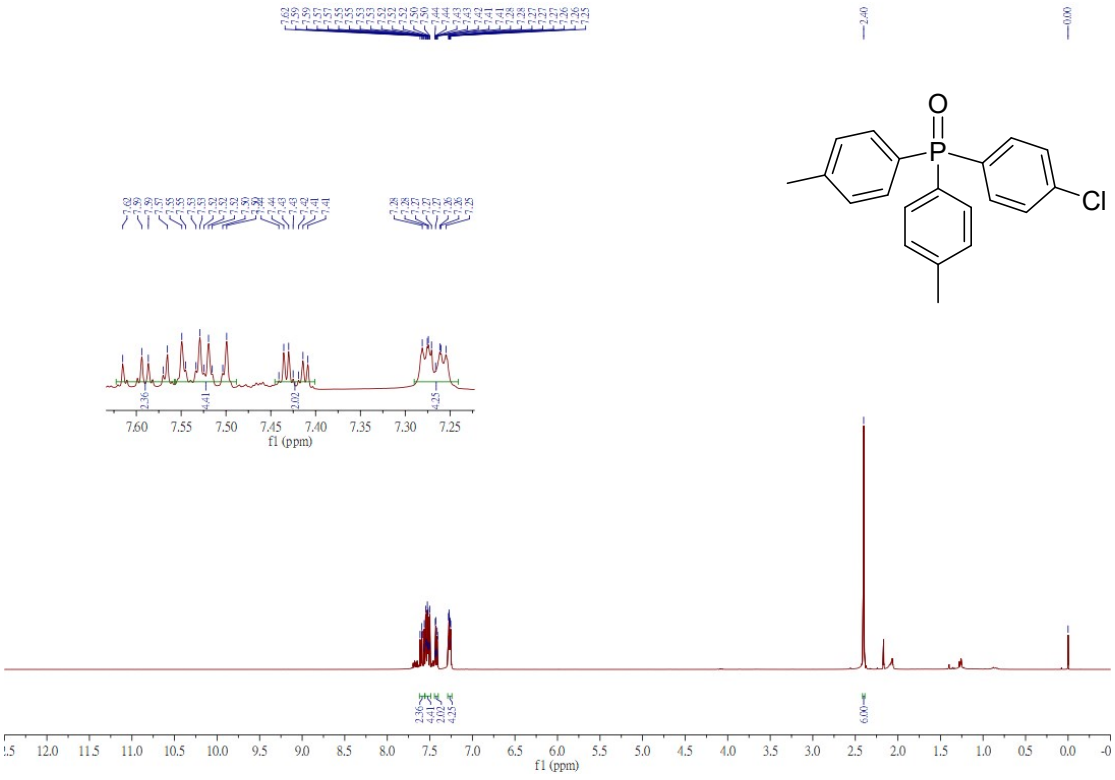
## di-p-tolyl(4-(trifluoromethyl)phenyl)phosphine oxide (3f): $^{13}C$ NMR



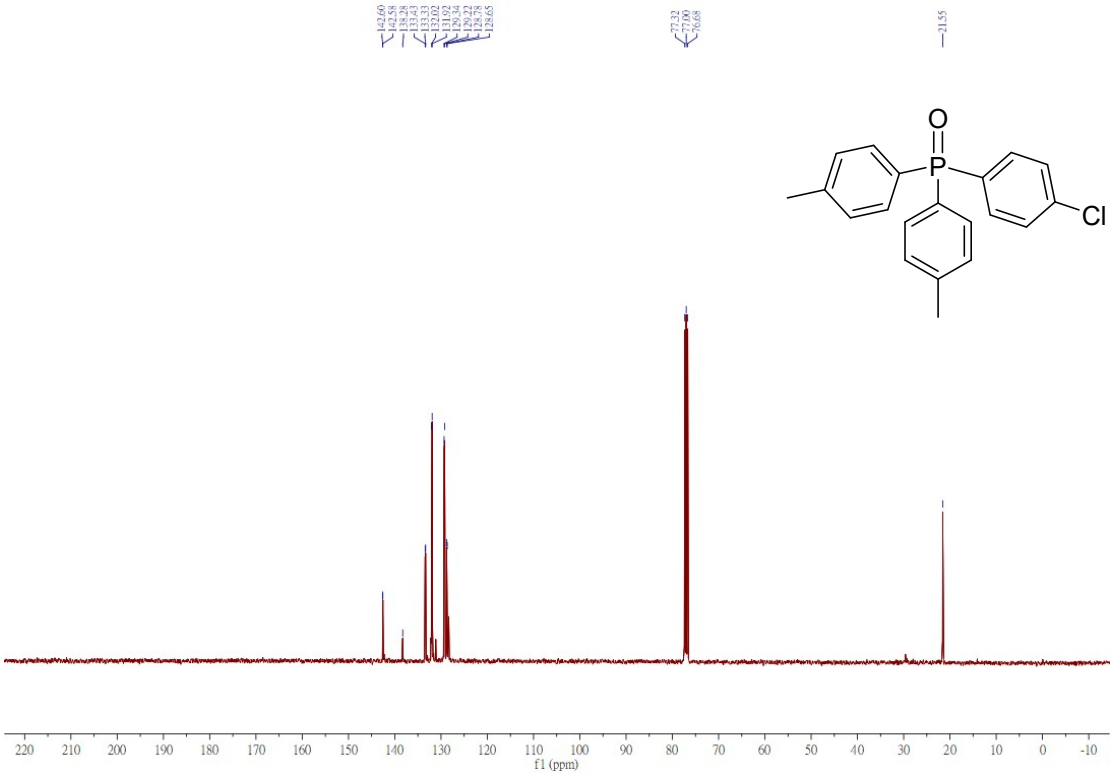

## di-p-tolyl(4-(trifluoromethyl)phenyl)phosphine oxide (3f): $^{31}P$ NMR



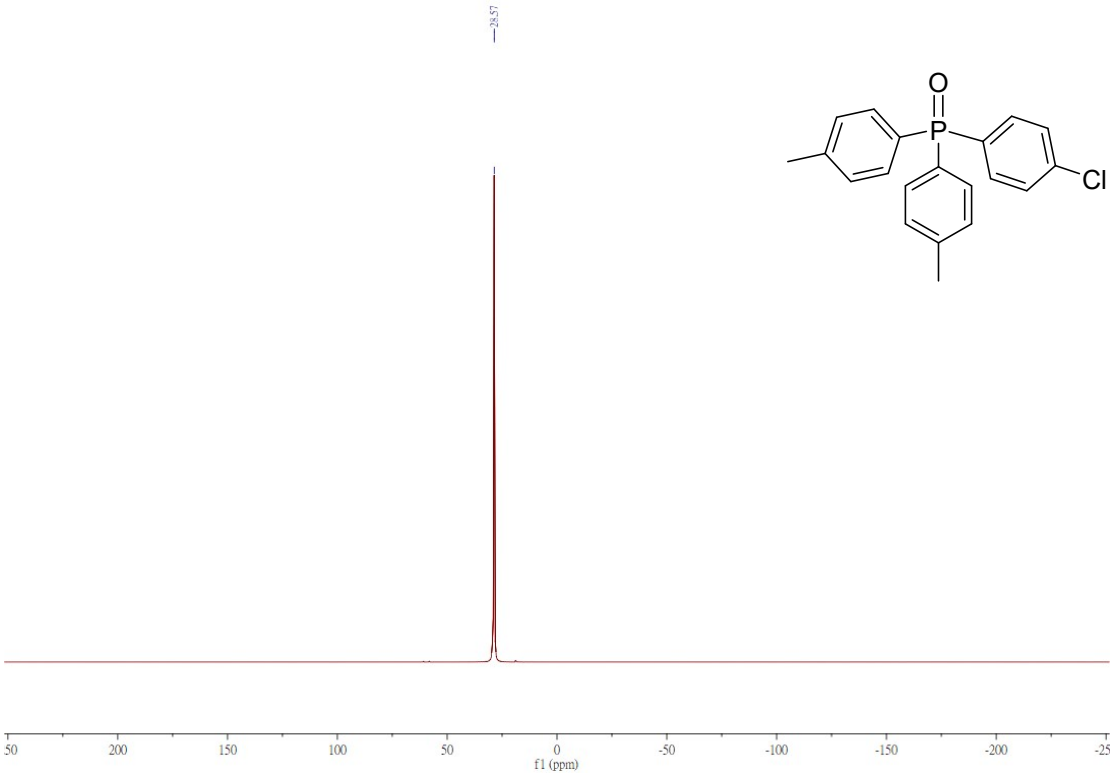
## (4-chlorophenyl)di-p-tolylphosphine oxide (3g): $^{1}$H NMR



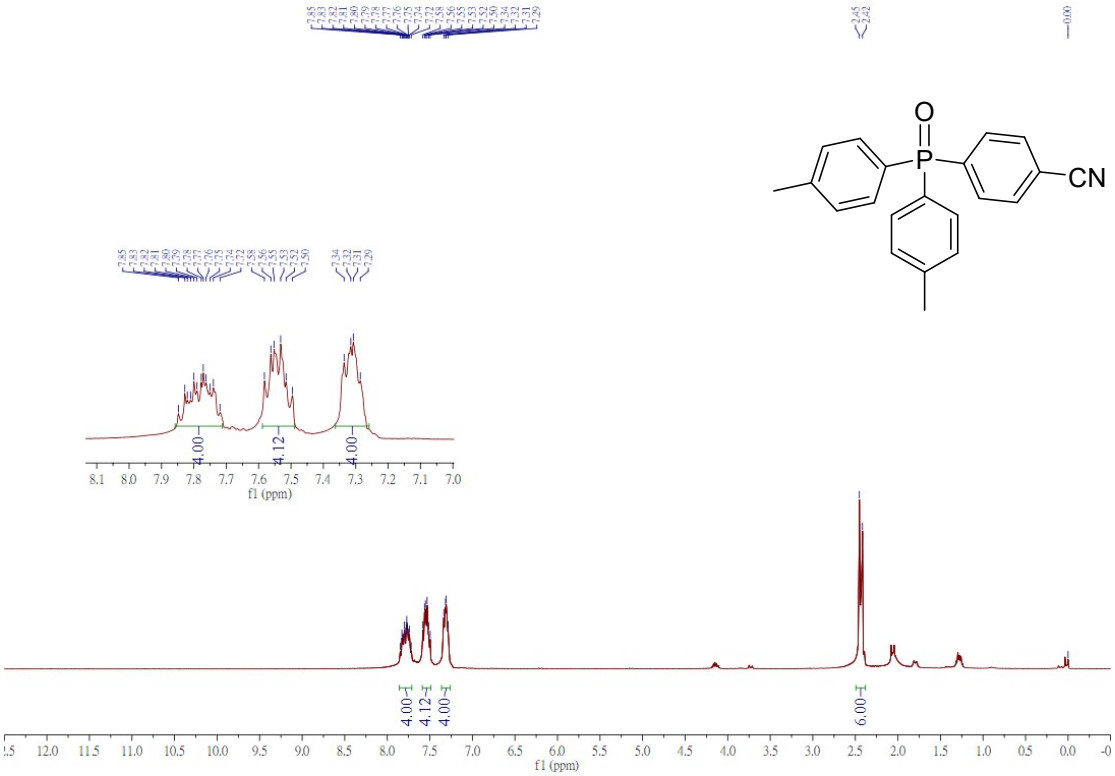

## (4-chlorophenyl)di-p-tolylphosphine oxide (3g): $^{13}$C NMR



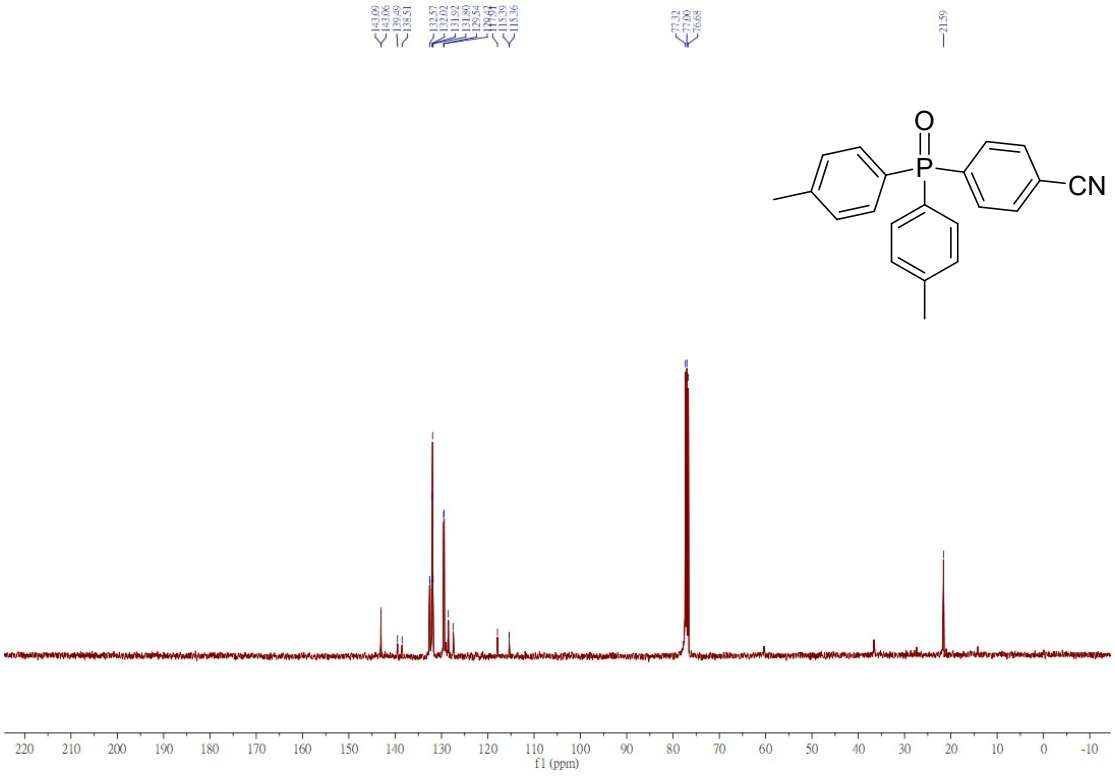
## (4-chlorophenyl)di-p-tolylphosphine oxide (3g): $^{31}$P NMR



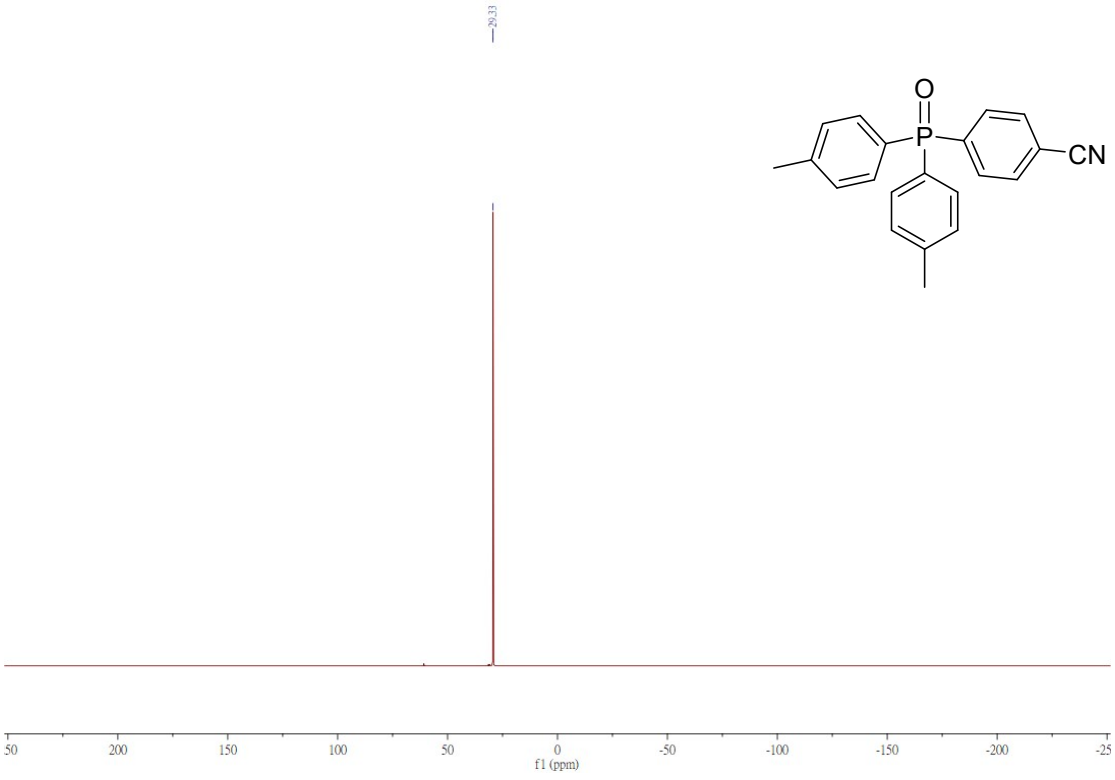

## 4-(di-p-tolylphosphoryl)benzonitrile (3h): $^{1}$H NMR



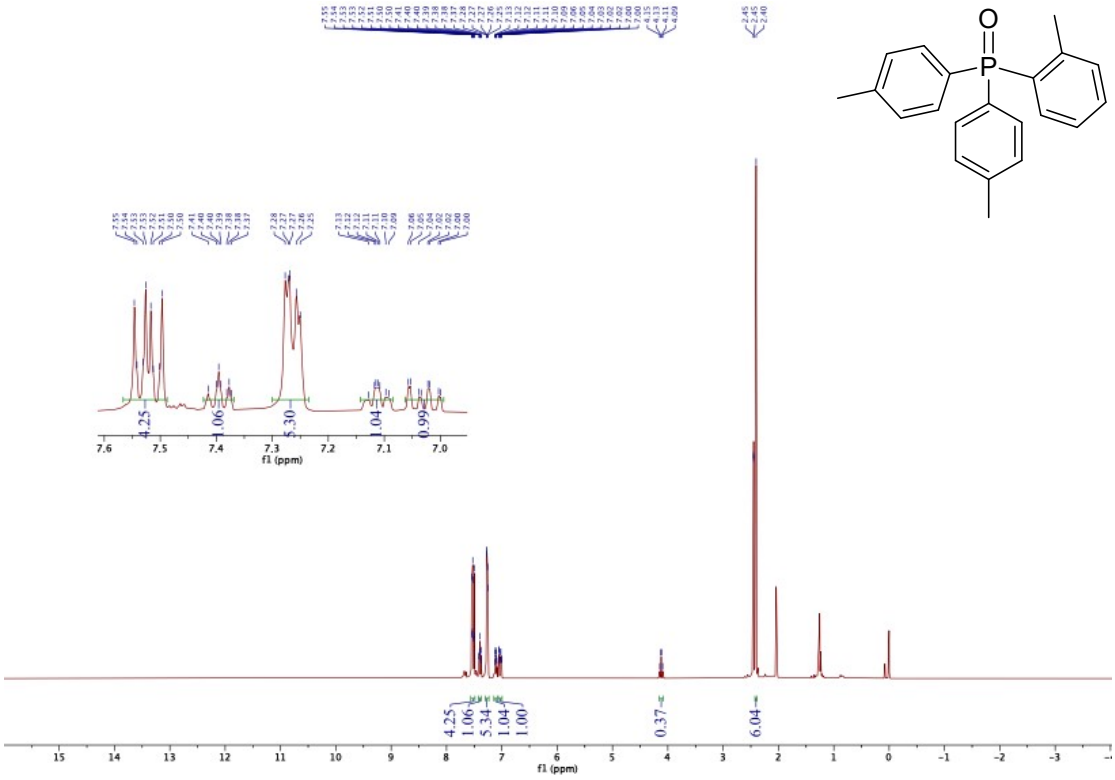
## 4-(di-p-tolylphosphoryl)benzonitrile (3h): $^{13}$C NMR



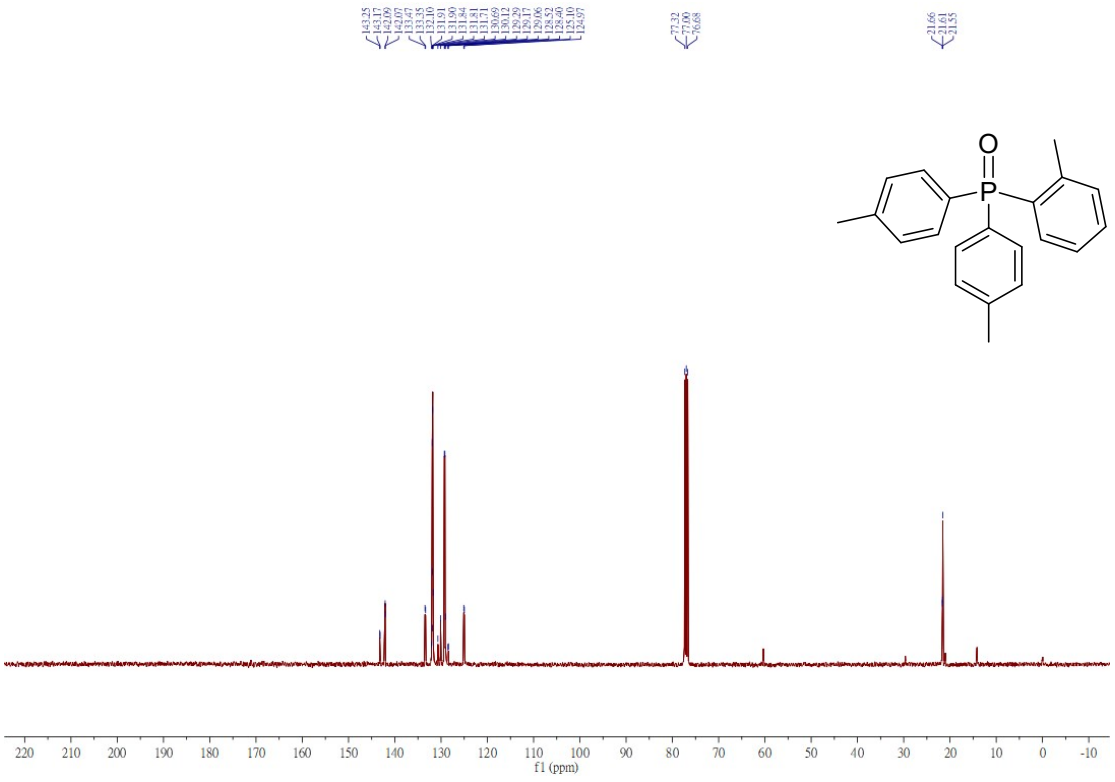

## 4-(di-p-tolylphosphoryl)benzonitrile (3h): $^{31}$P NMR



## o-tolyldi-p-tolylphosphine oxide (3i): $^{1}$H NMR

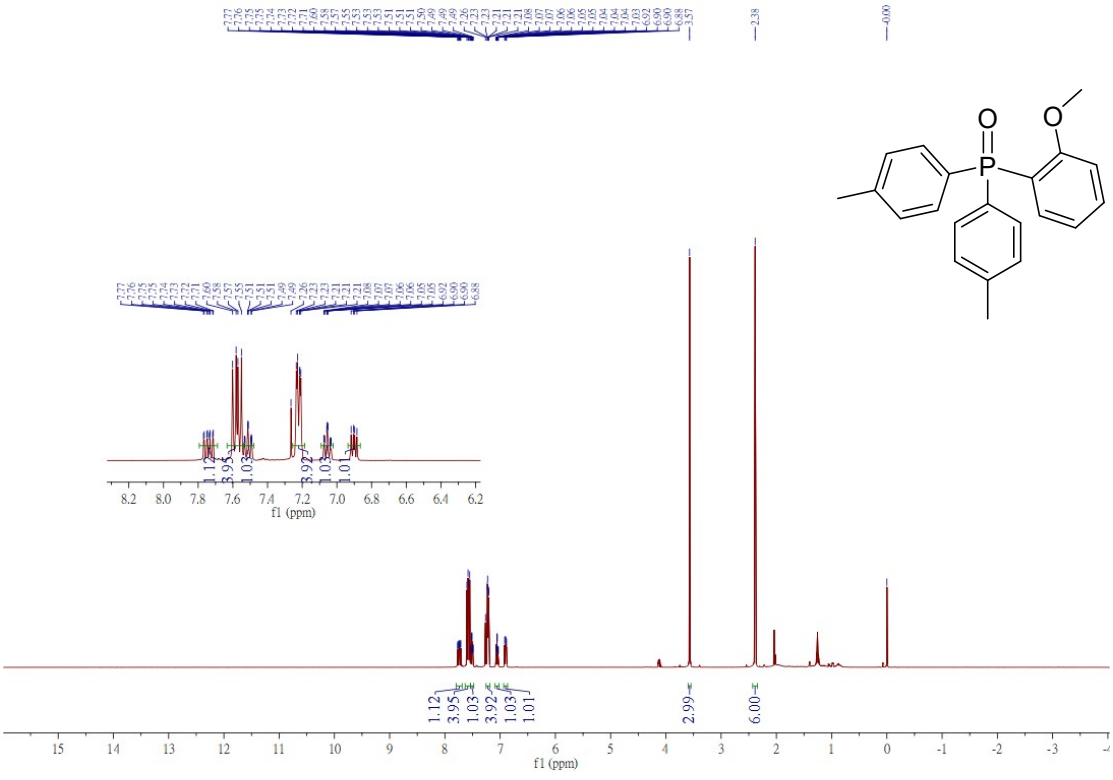



## o-tolyldi-p-tolylphosphine oxide (3i): $^{13}$C NMR

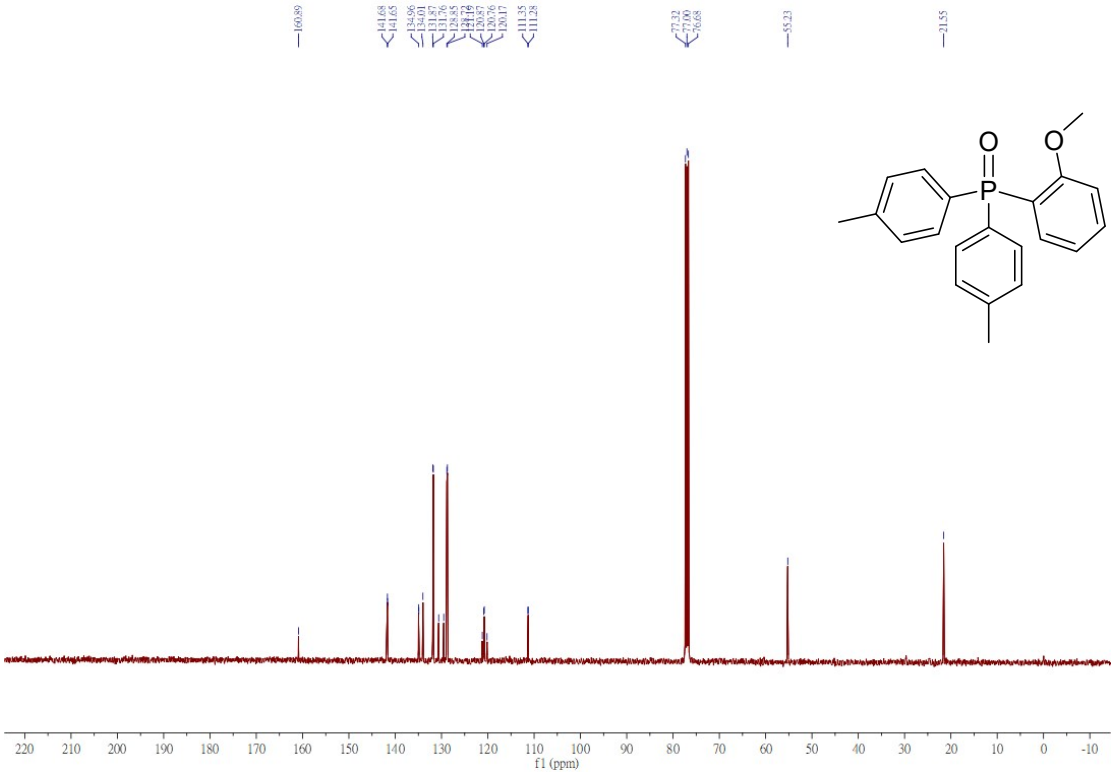


## o-tolyldi-p-tolylphosphine oxide (3i): $^{31}$P NMR

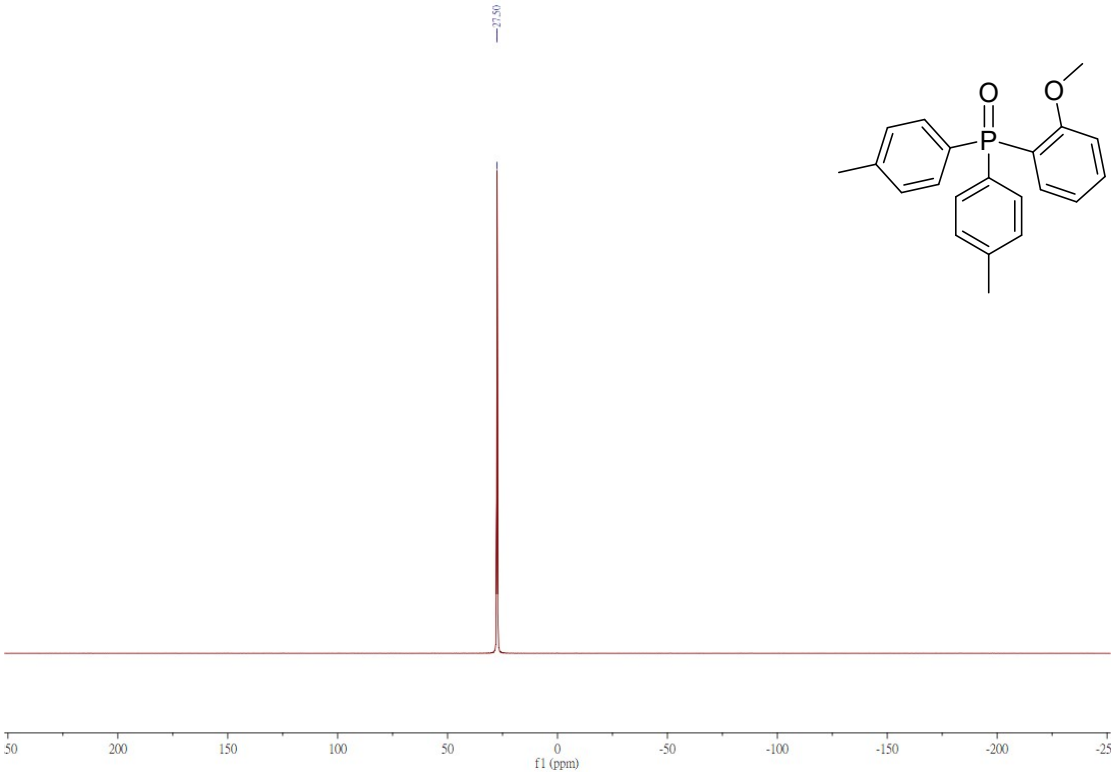

## (2-methoxyphenyl)di-p-tolylphosphine oxide (3j): $^{1}$H NMR



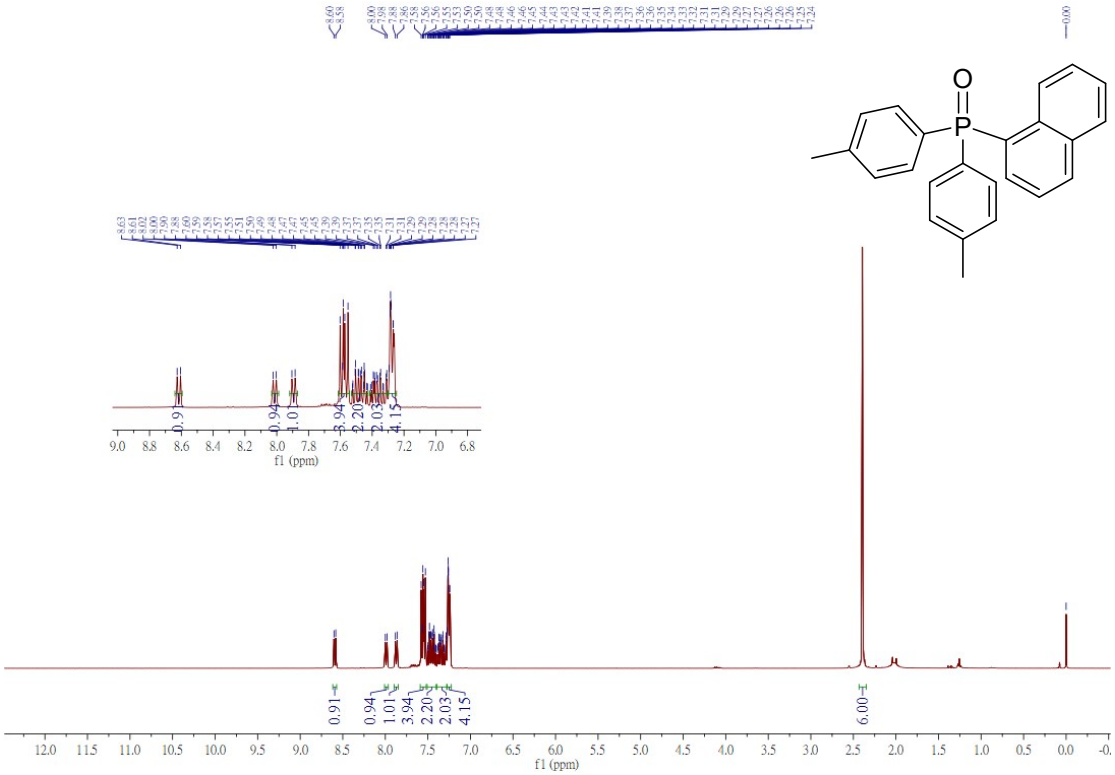
## (2-methoxyphenyl)di-p-tolylphosphine oxide (3j): $^{13}C$ NMR



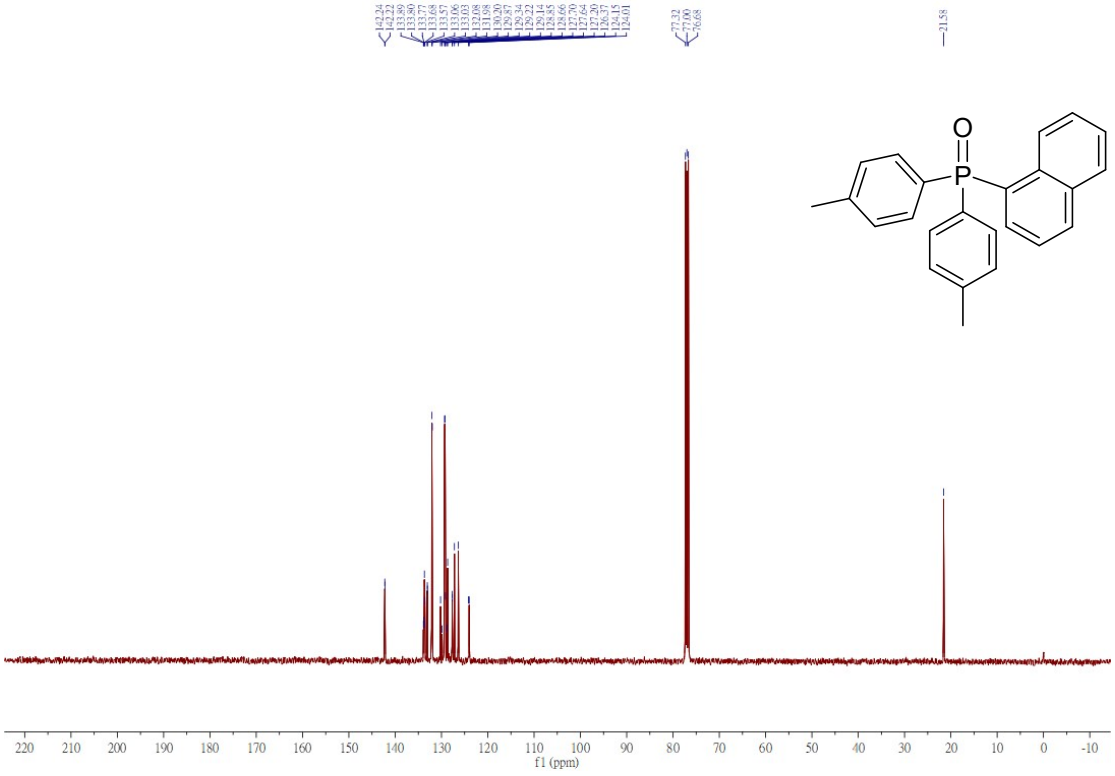

## (2-methoxyphenyl)di-p-tolylphosphine oxide (3j): $^{31}P$ NMR



## naphthalen-1-yldi-p-tolylphosphine oxide (3k): $^{1}$H NMR

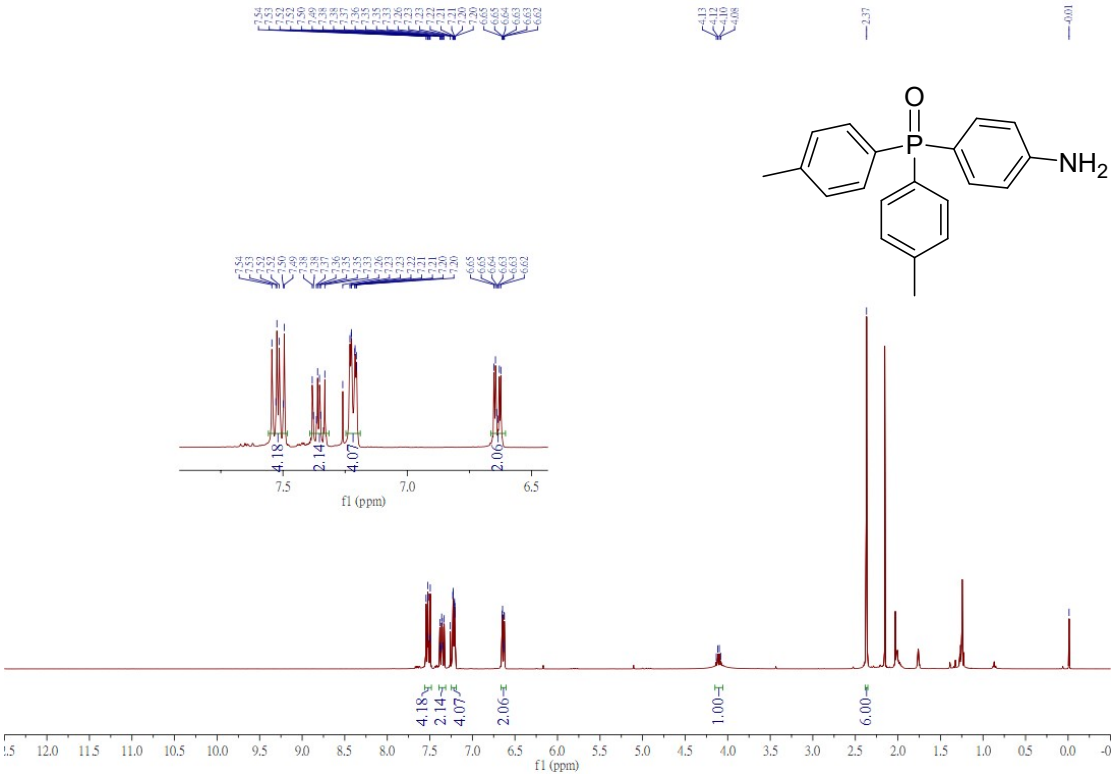



## naphthalen-1-yldi-p-tolylphosphine oxide (3k): $^{13}$C NMR

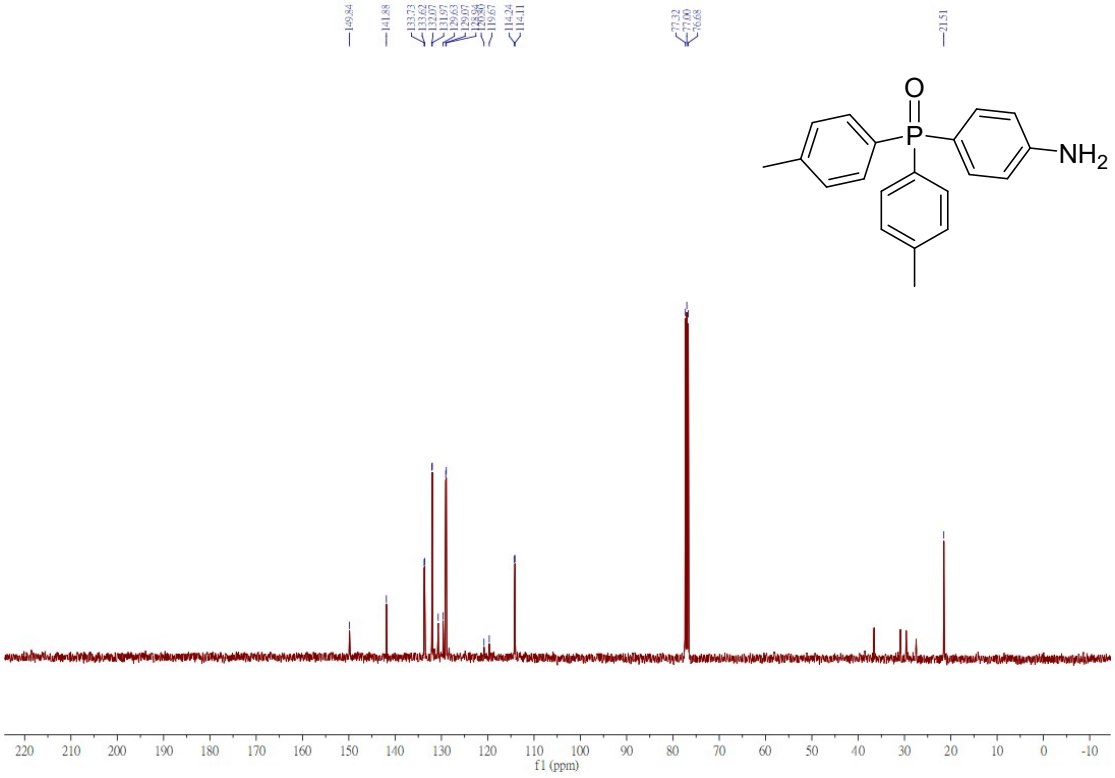


## naphthal en-1-yldi-p-tolylphosphine oxide (3k): $^{31}$P NMR

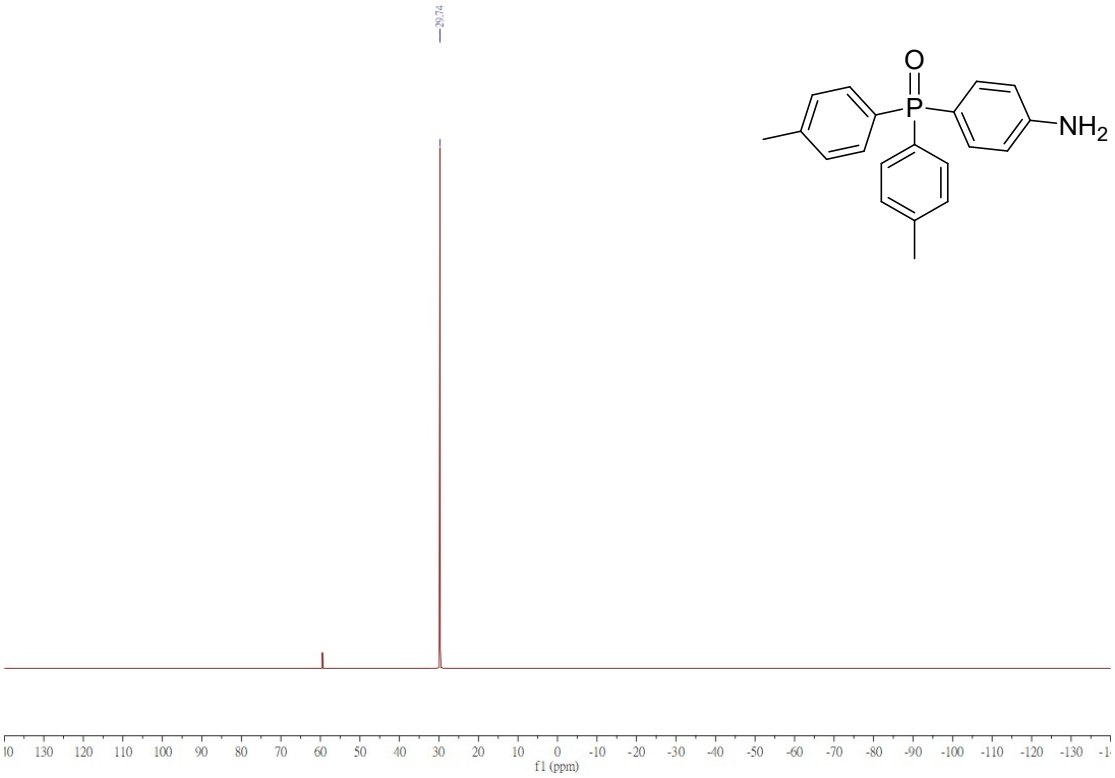

## (4-aminophenyl)di-p-tolylphosphine oxide (3l): $^{1}$H NMR



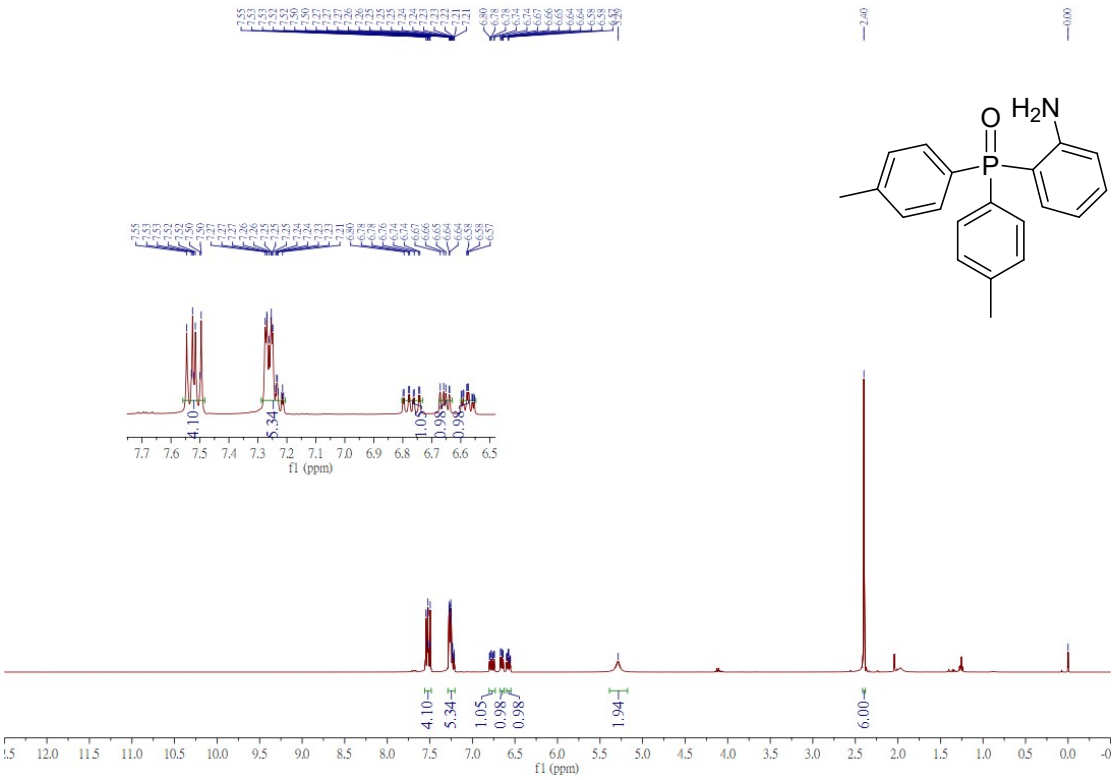
## (4-aminophenyl)di-p-tolylphosphine oxide (3l): $^{13}$C NMR



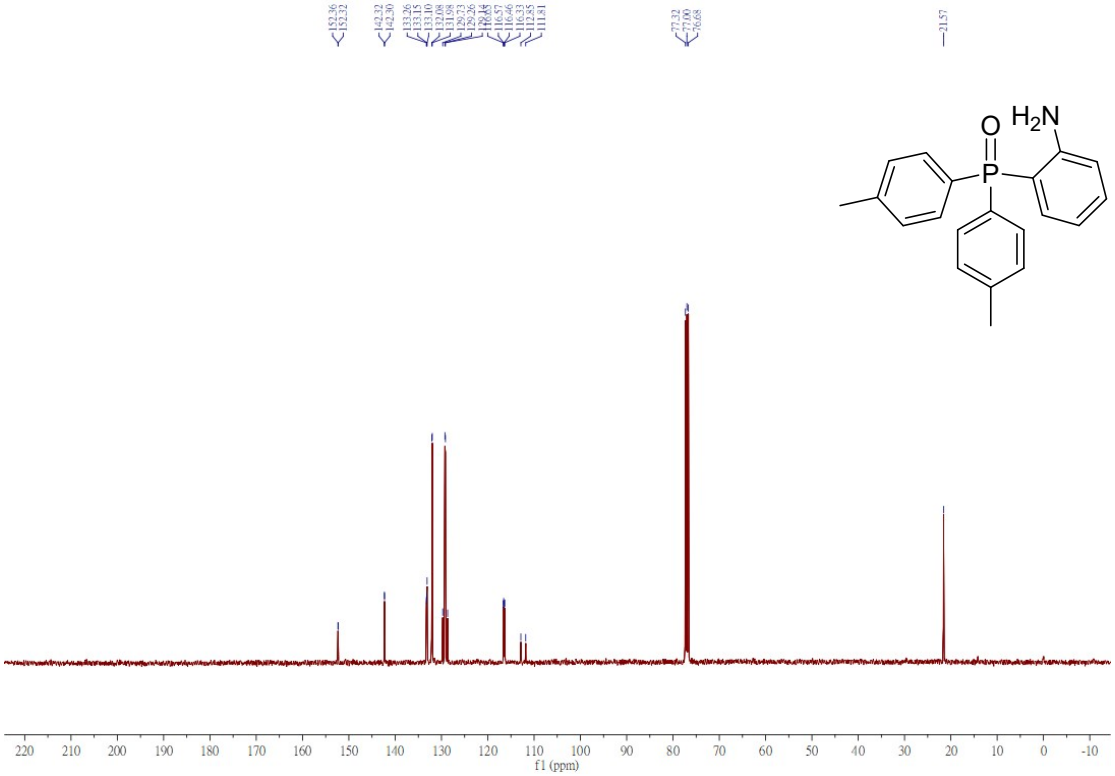

## (4-aminophenyl)di-p-tolylphosphine oxide (3l): $^{31}$P NMR



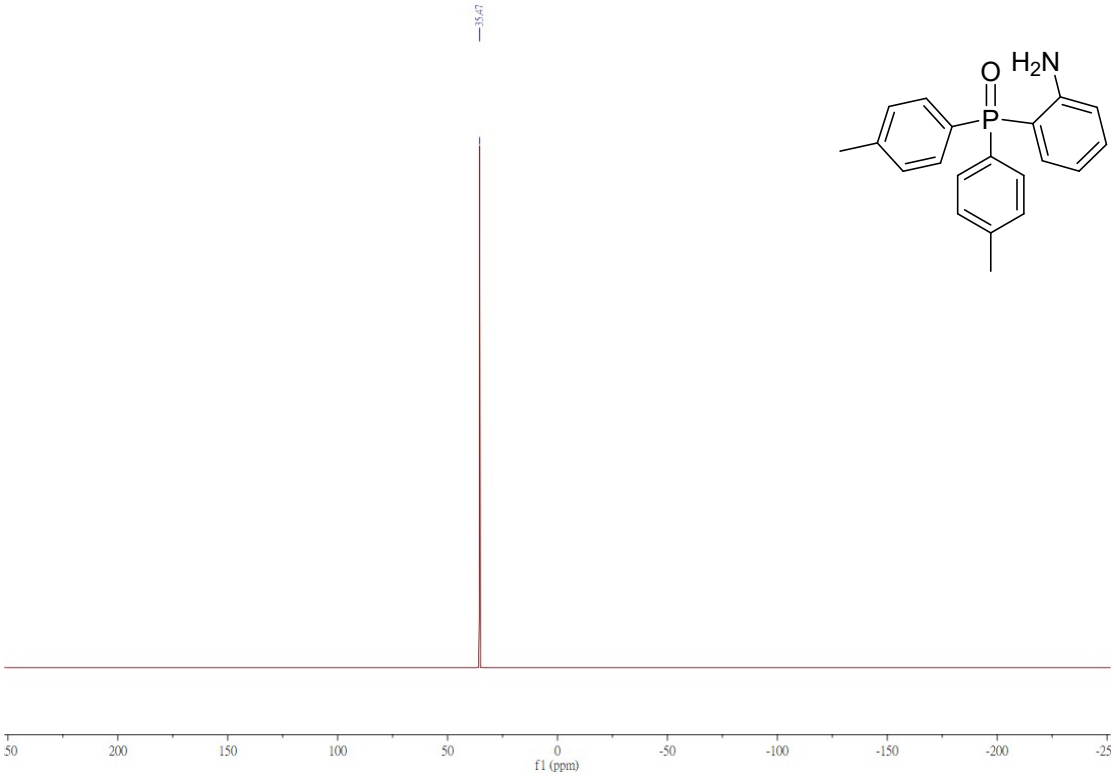
## (2-aminophenyl)di-p-tolylphosphine oxide (3m): $^{1}$H NMR



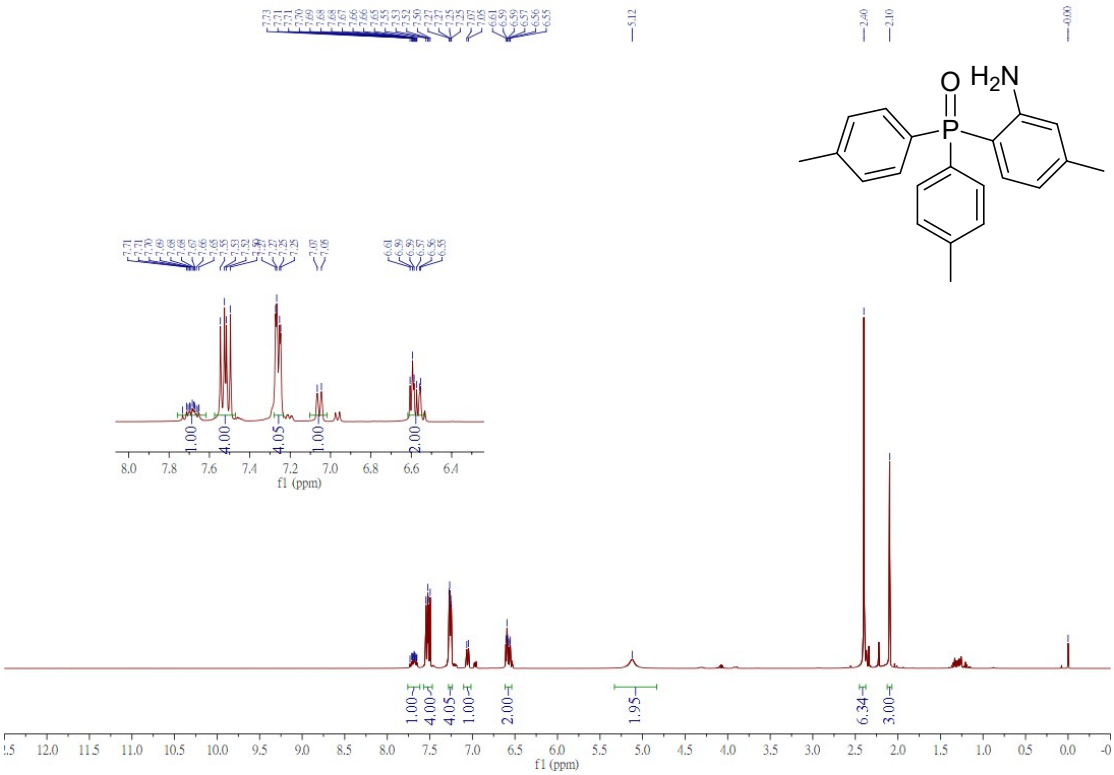

## (2-aminophenyl)di-p-tolylphosphine oxide (3m): $^{13}$C NMR



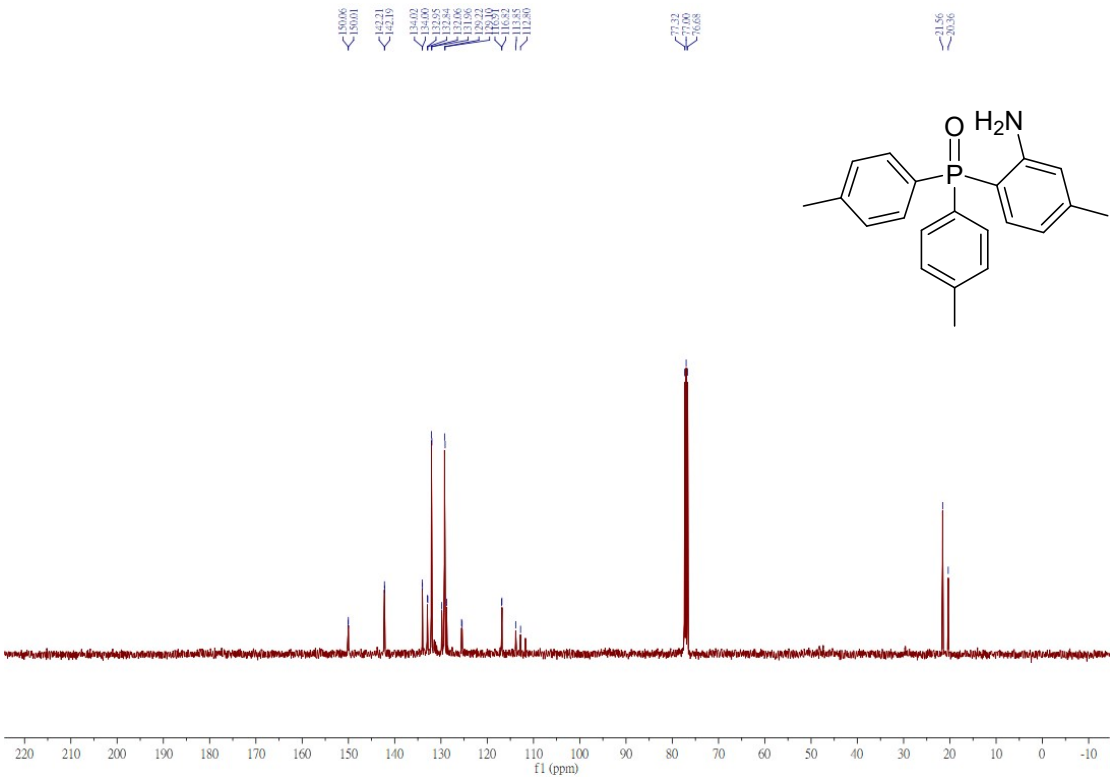
## (2-aminophenyl)di-p-tolylphosphine oxide (3m): $^{31}$P NMR



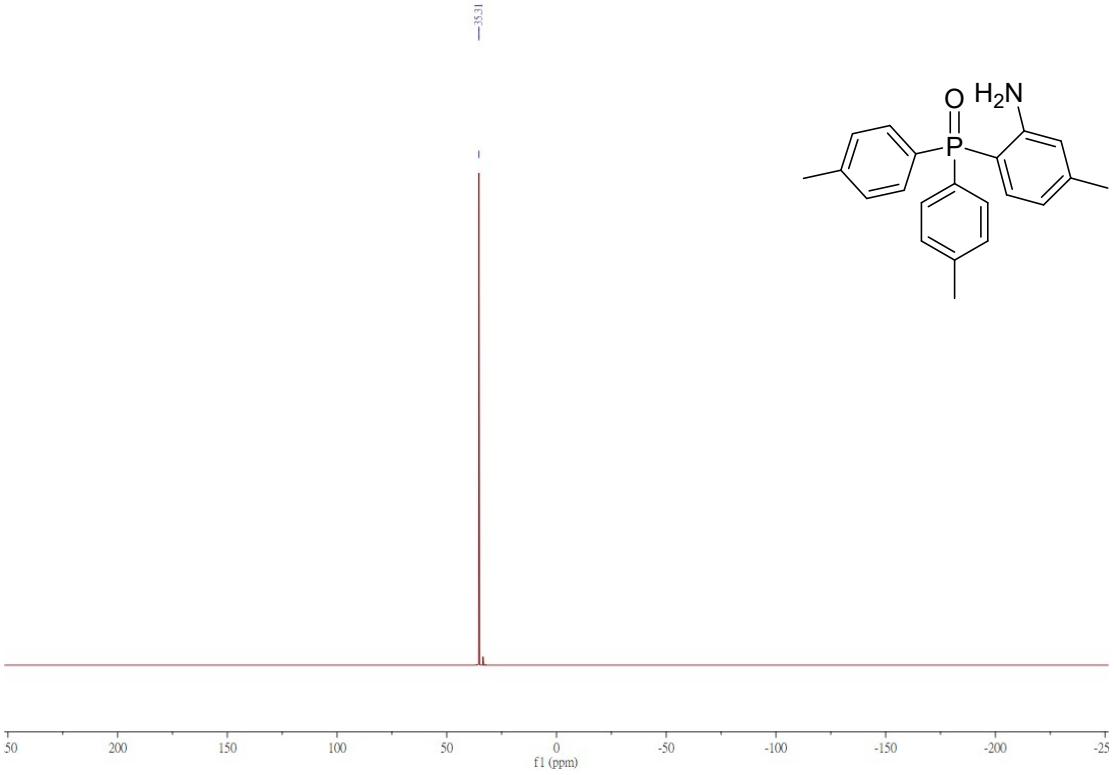

## (2-amino-4-methylphenyl)di-p-tolylphosphine oxide (3n): $^{1}$H NMR



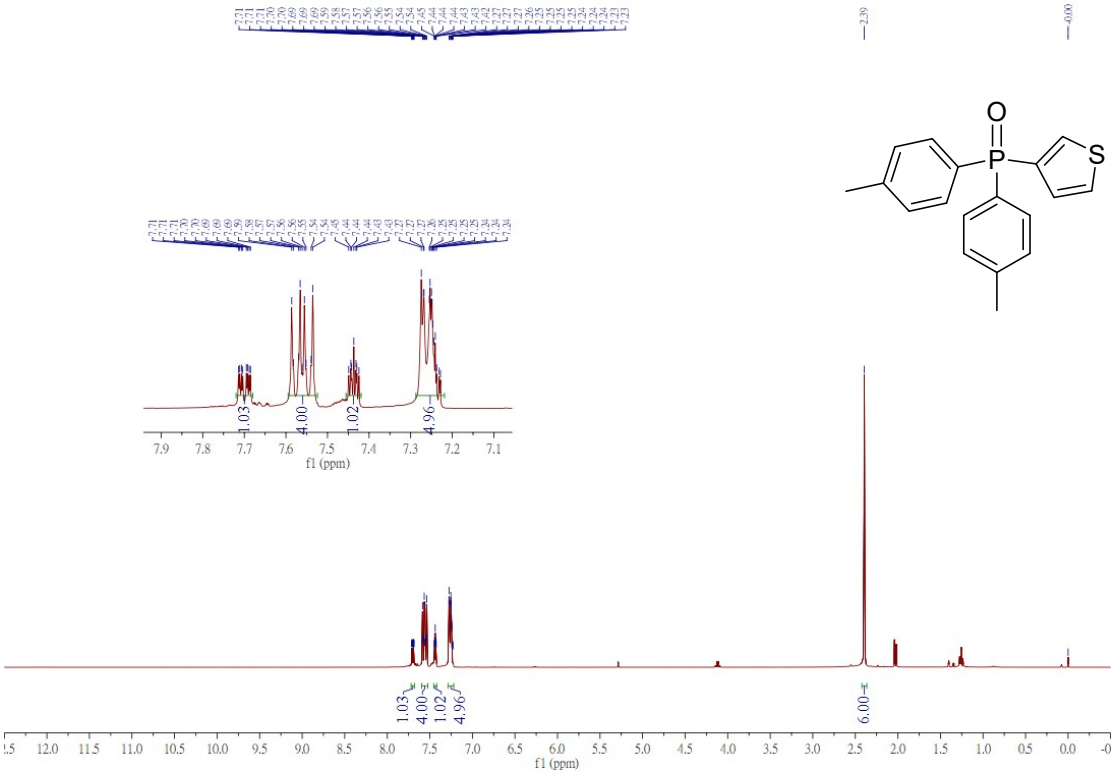
## (2-amino-4-methylphenyl)di-p-tolylphosphine oxide (3n): $^{13}C$ NMR



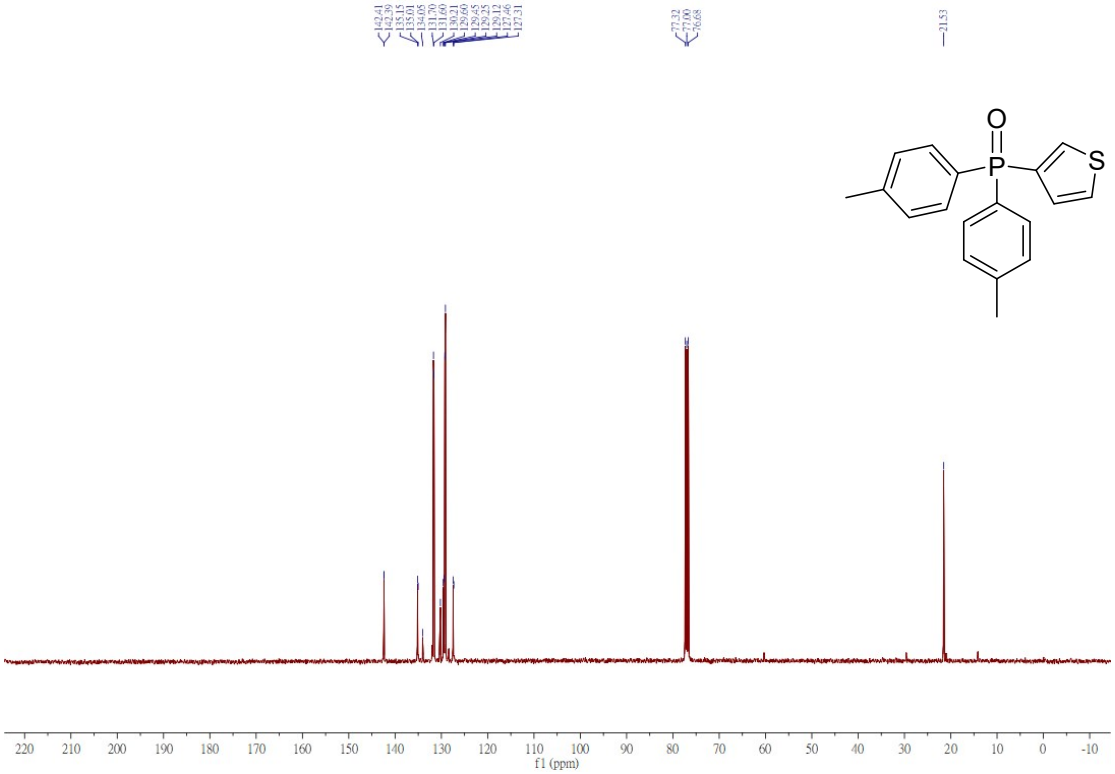

## (2-amino-4-methylphenyl)di-p-tolylphosphine oxide (3n): $^{31}P$ NMR



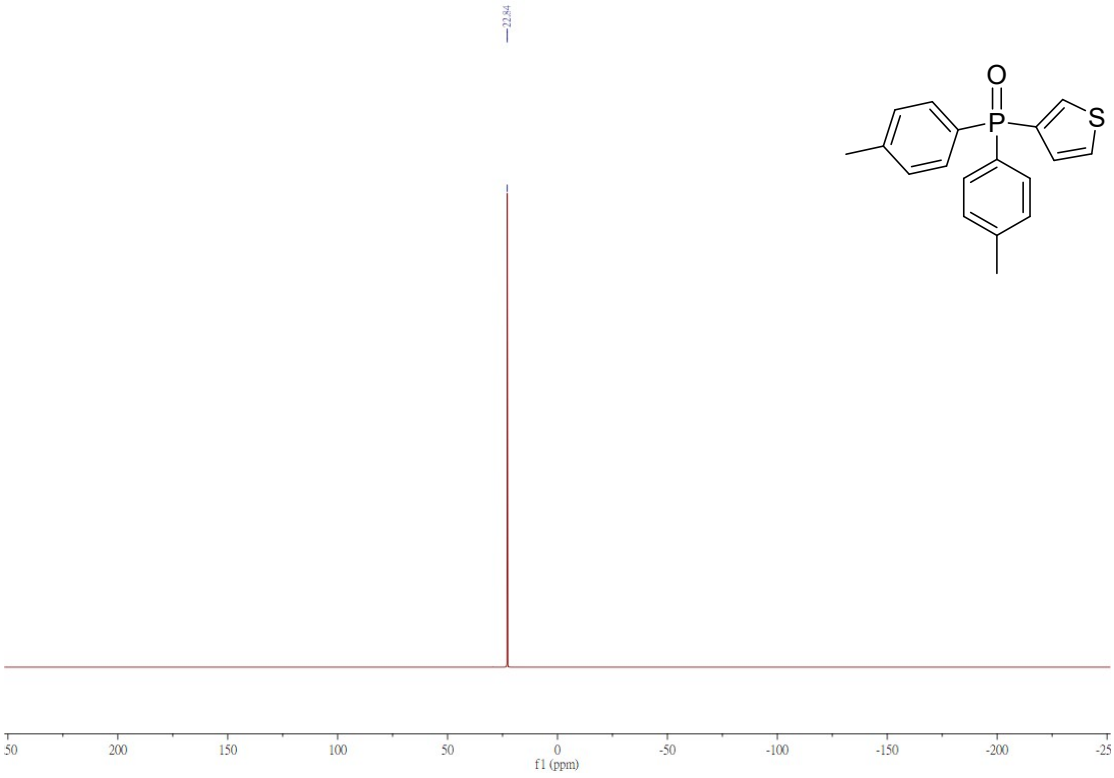
## thiophen-3-yldi-p-tolylphosphine oxide (3o): $^{1}$H NMR



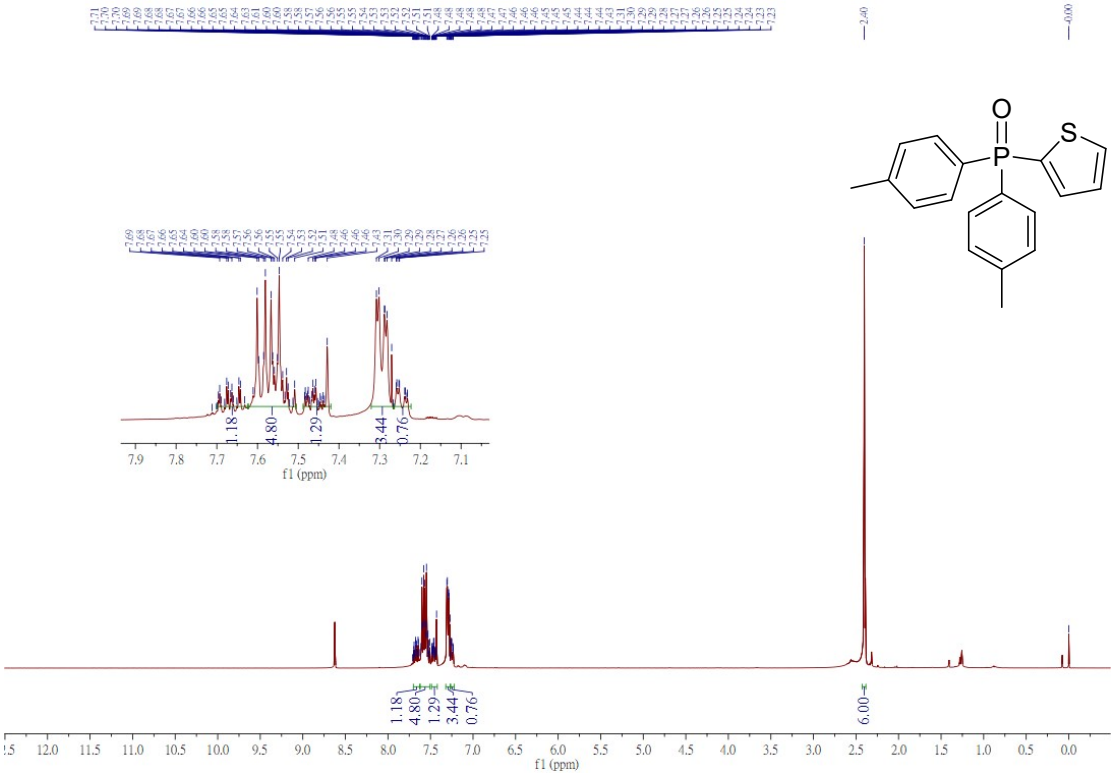

## thiophen-3-yldi-p-tolylphosphine oxide (3o): $^{13}$C NMR



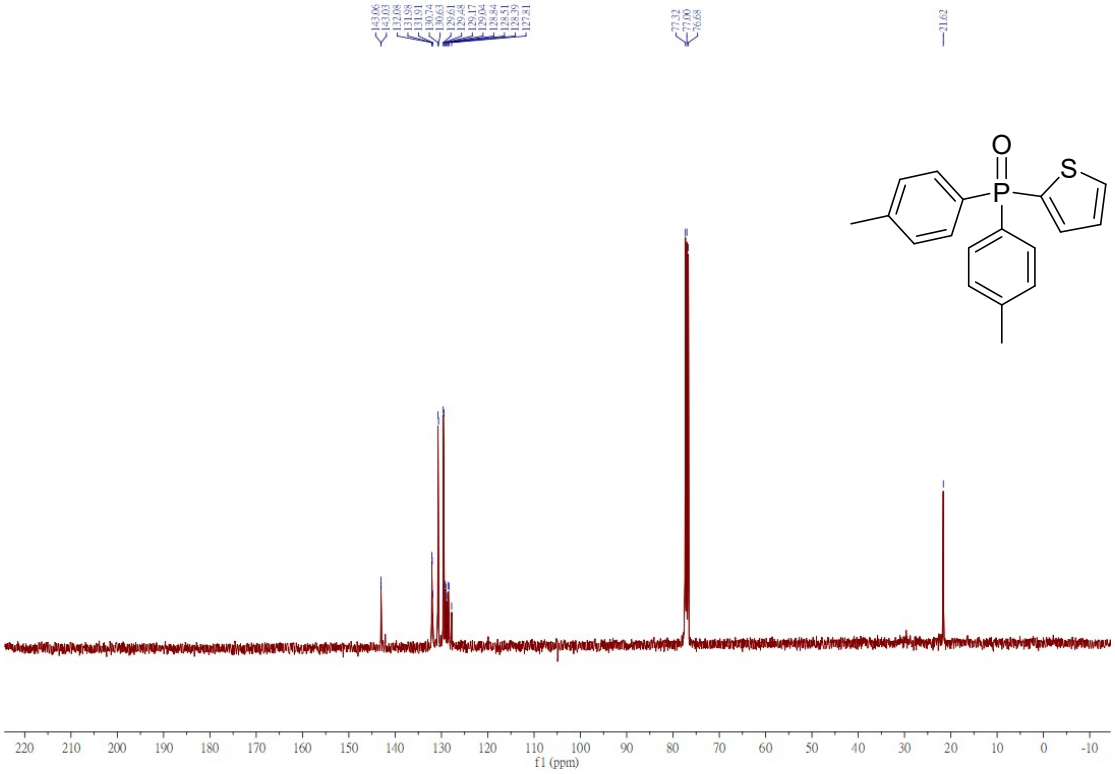
## thiophen-3-yldi-p-tolylphosphine oxide (3o): $^{31}P$ NMR



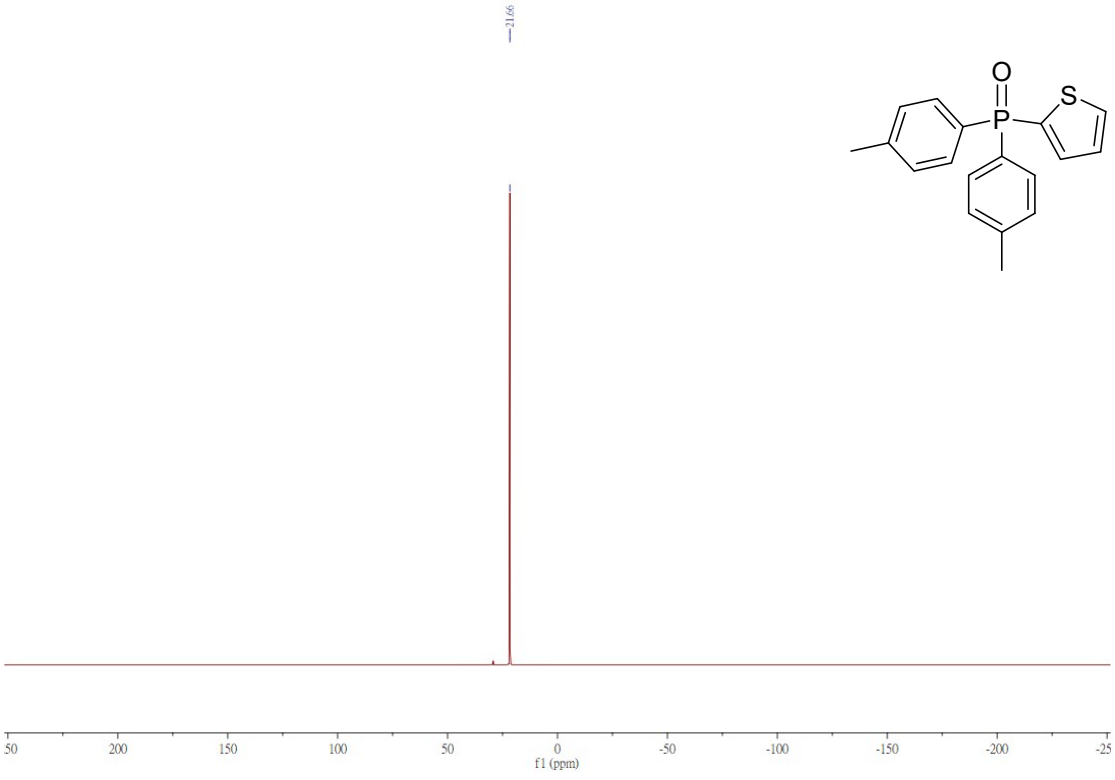

## thiophen-2-yldi-p-tolylphosphine oxide (3p): $^{1}H$ NMR



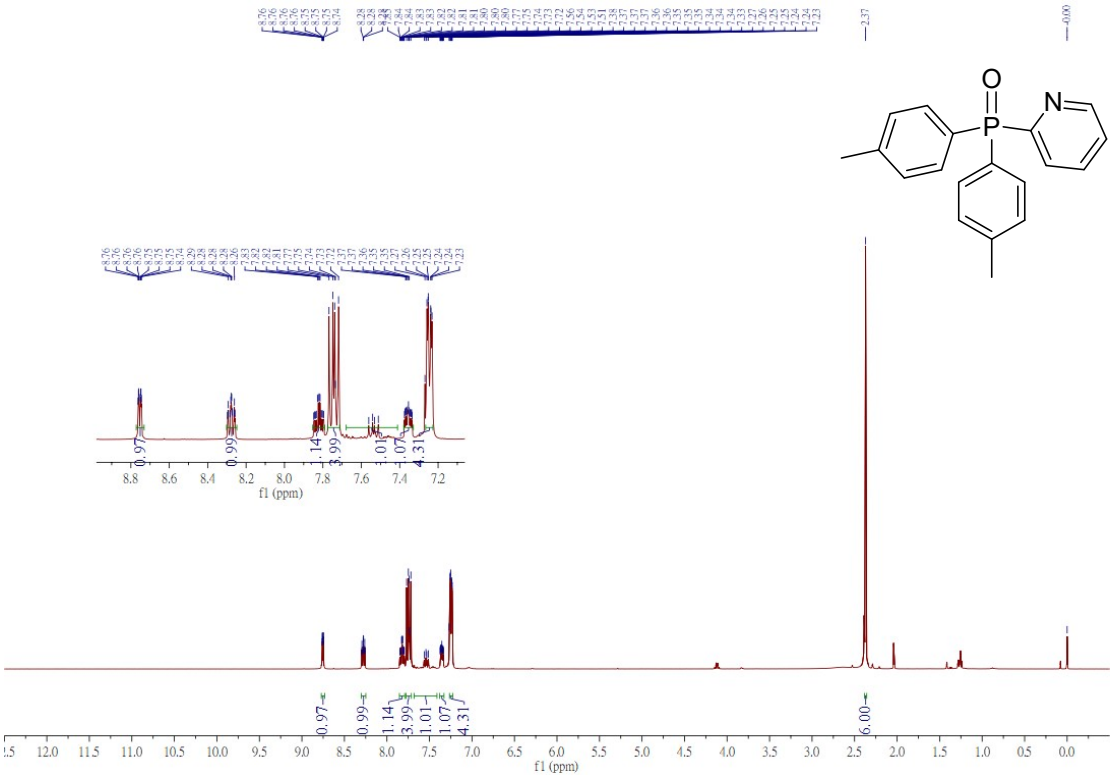
## thiophen-2-yldi-p-tolylphosphine oxide (3p): $^{13}C$ NMR



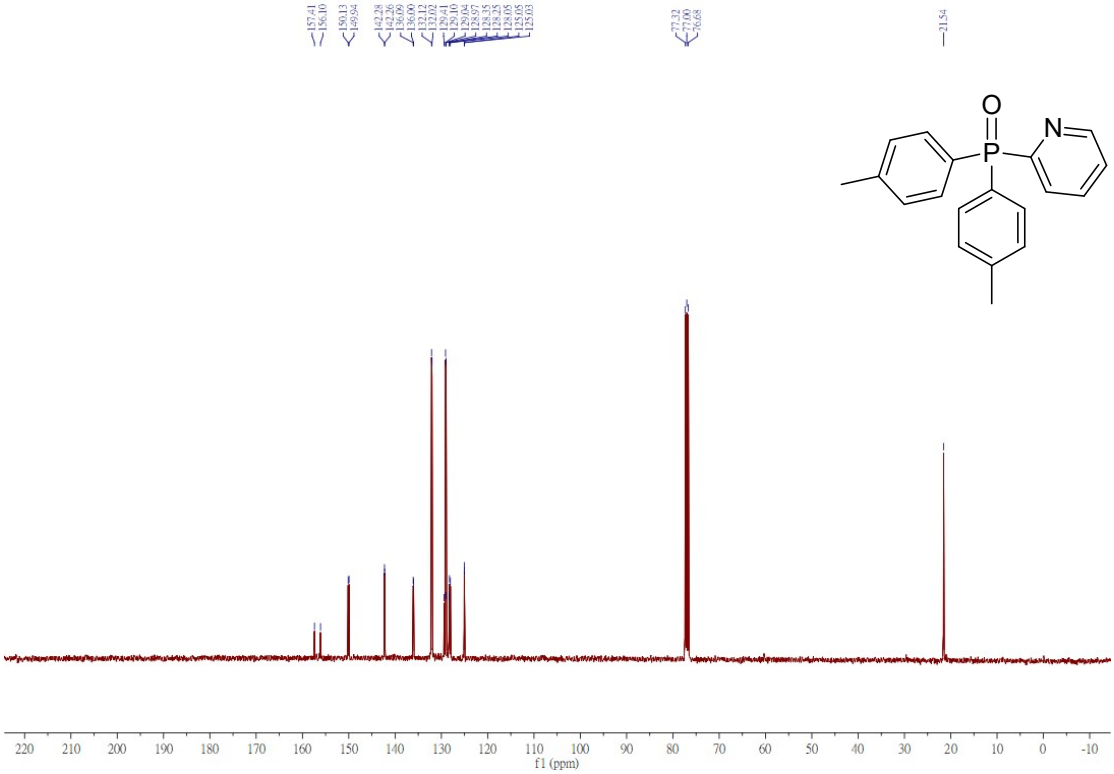

## thiophen-2-yldi-p-tolylphosphine oxide (3p): $^{31}P$ NMR



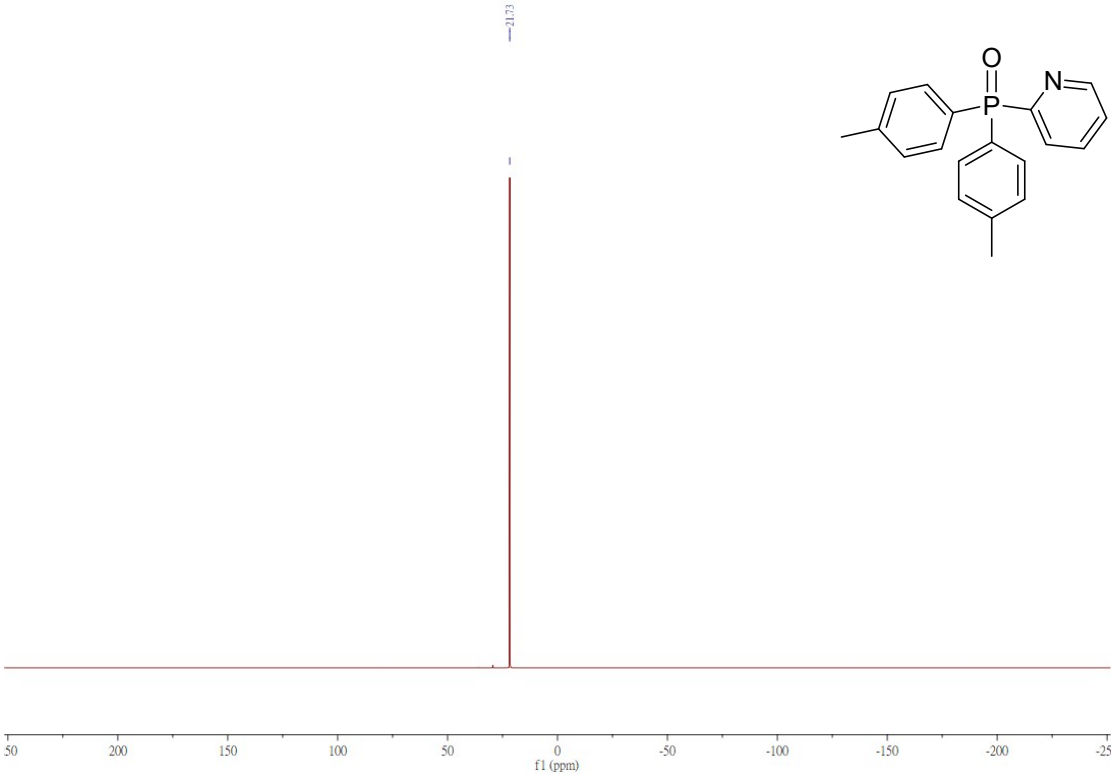
## pyridin-2-yldi-p-tolylphosphine oxide (3q): $^{1}$H NMR



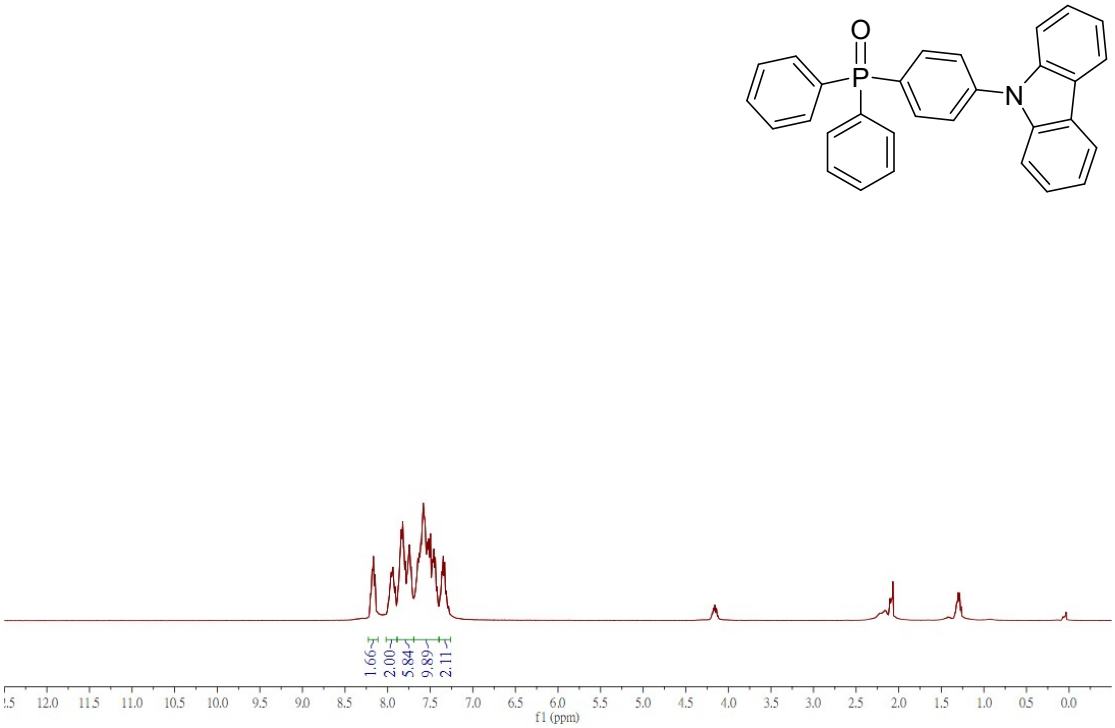

## pyridin-2-yldi-p-tolylphosphine oxide (3q): $^{13}$C NMR



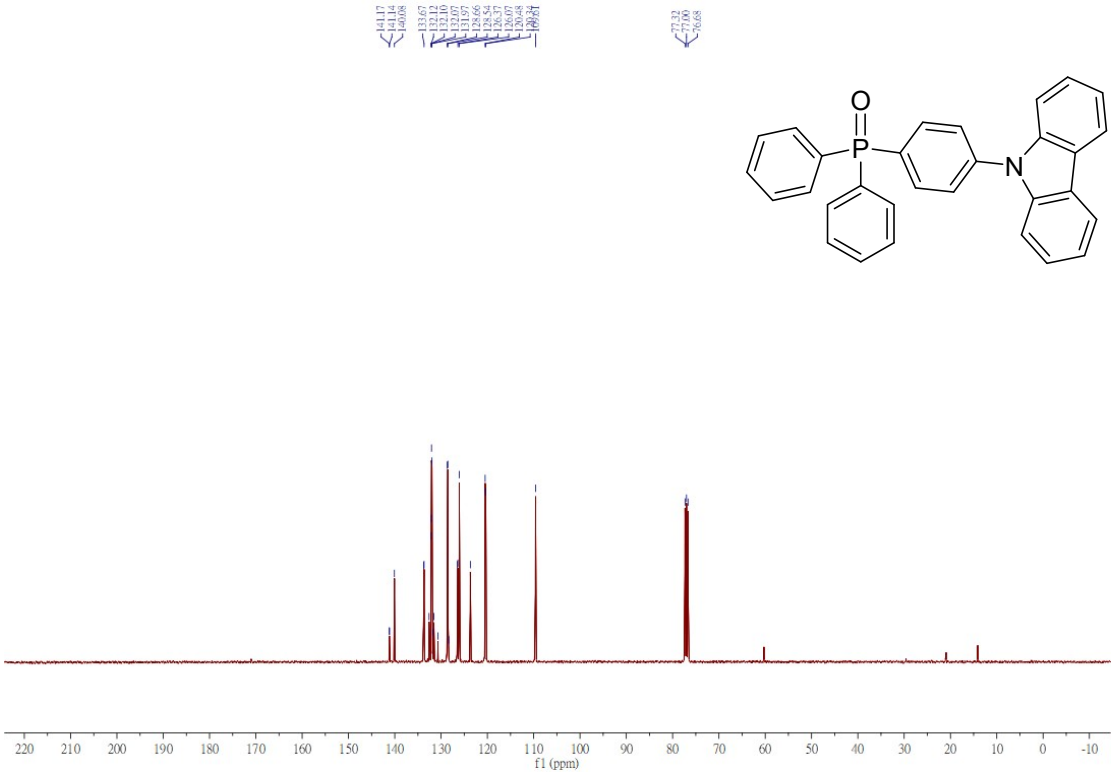
**pyridin-2-yldi-p-tolylphosphine oxide (3q): $^{31}$P NMR**



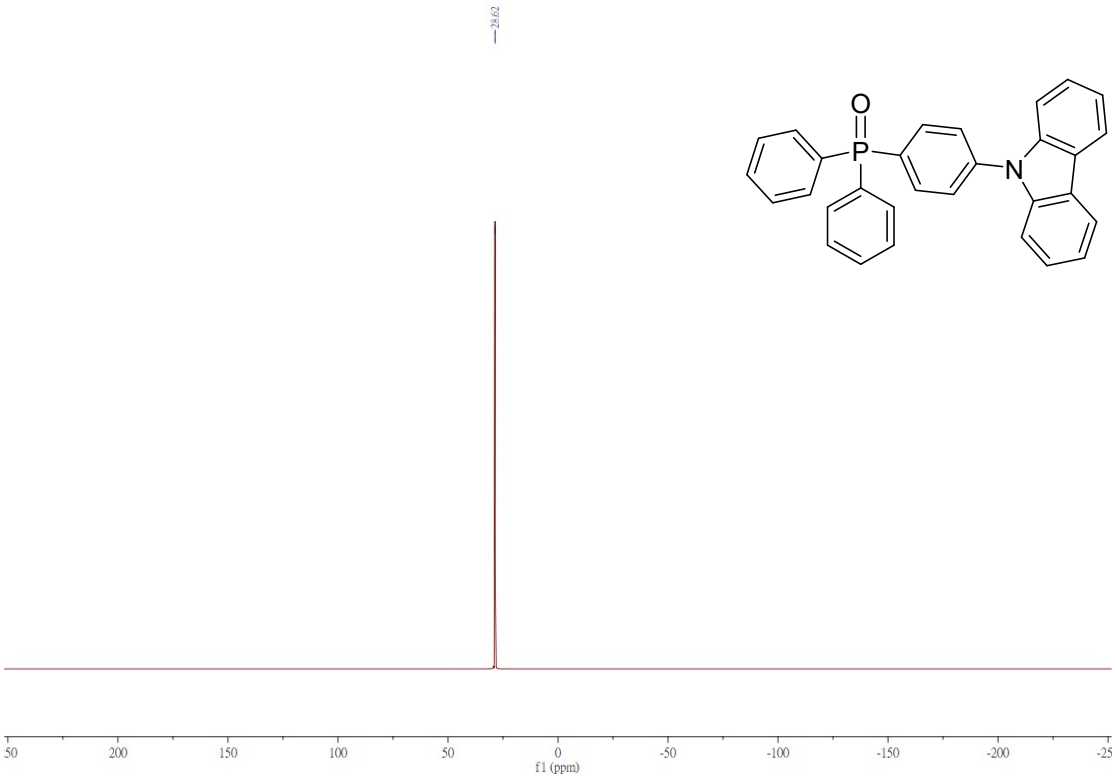

**(4-(9H-carbazol-9-yl)phenyl)diphenylphosphine oxide (4a): $^{1}$H NMR**



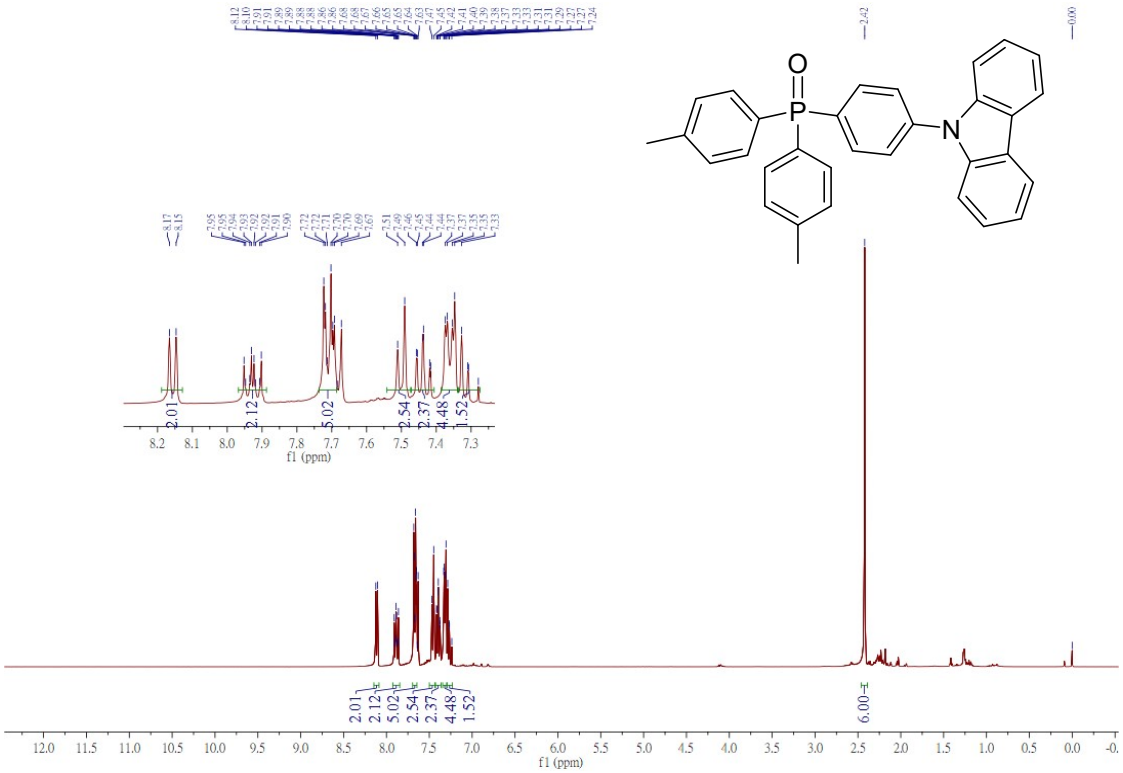
## (4-(9H-carbazol-9-yl)phenyl)diphenylphosphine oxide (4a): $^{13}$C NMR



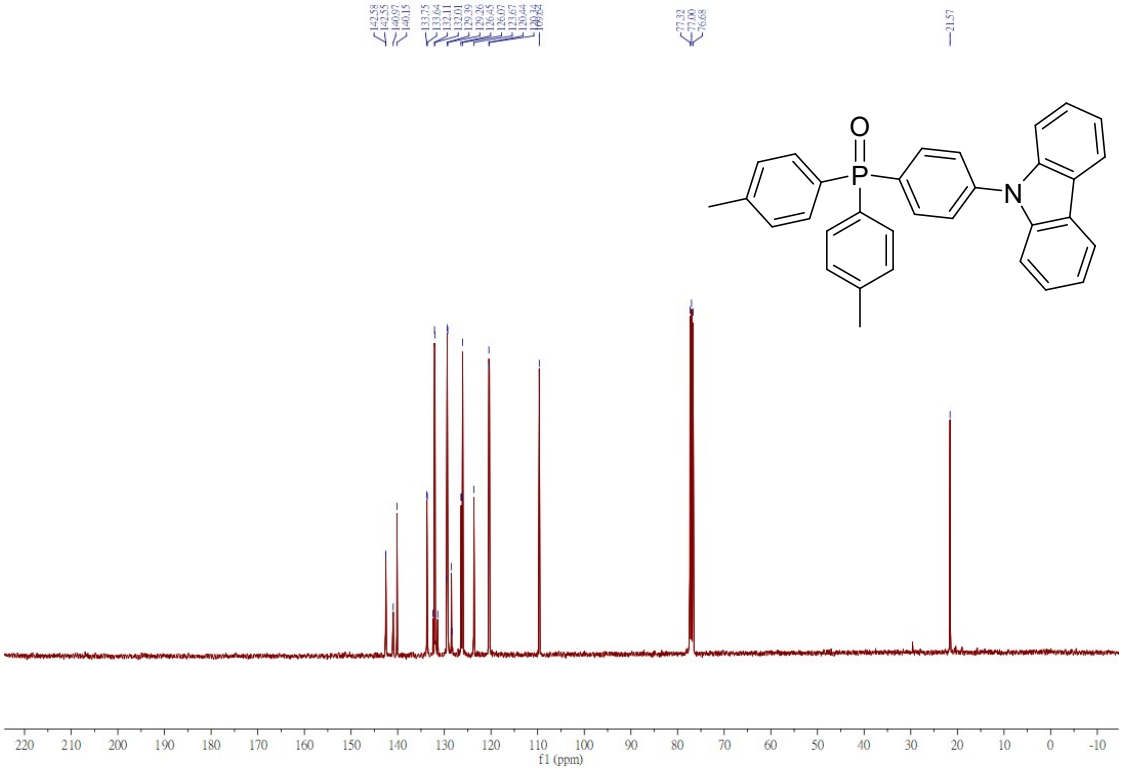

## (4-(9H-carbazol-9-yl)phenyl)diphenylphosphine oxide (4a): $^{31}$P NMR



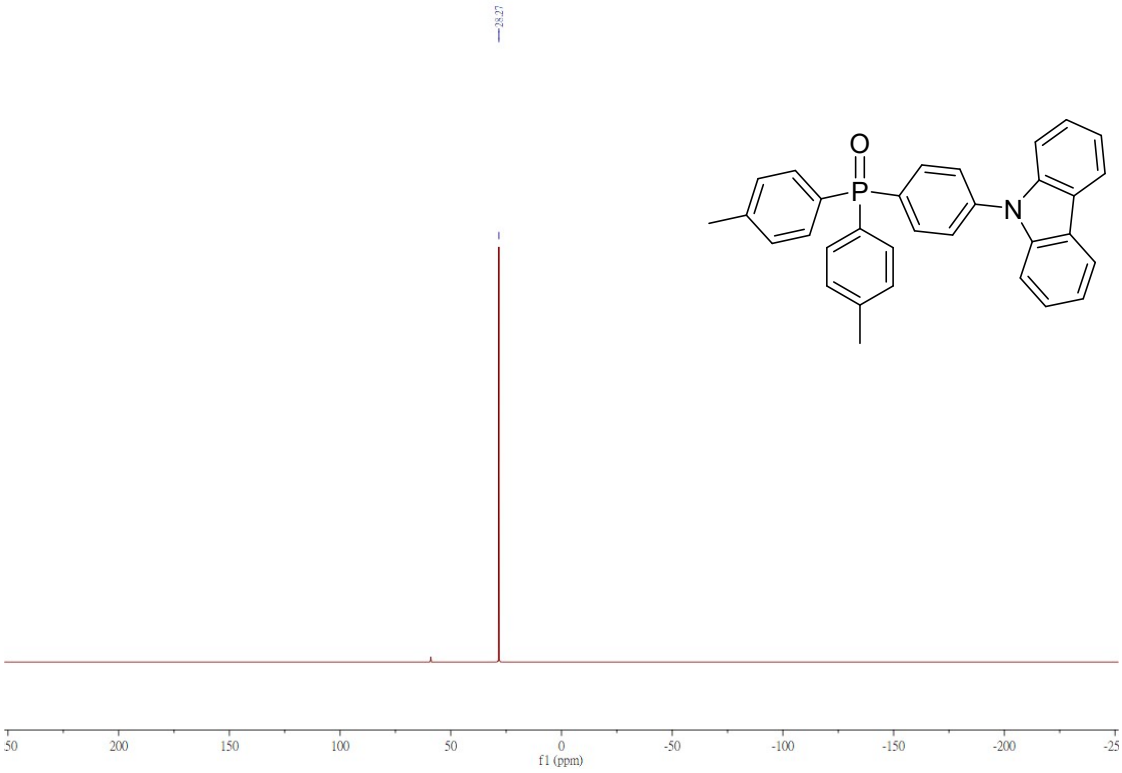
## (4-(9H-carbazol-9-yl)phenyl)di-p-tolylphosphine oxide (4b): $^{1}$H NMR



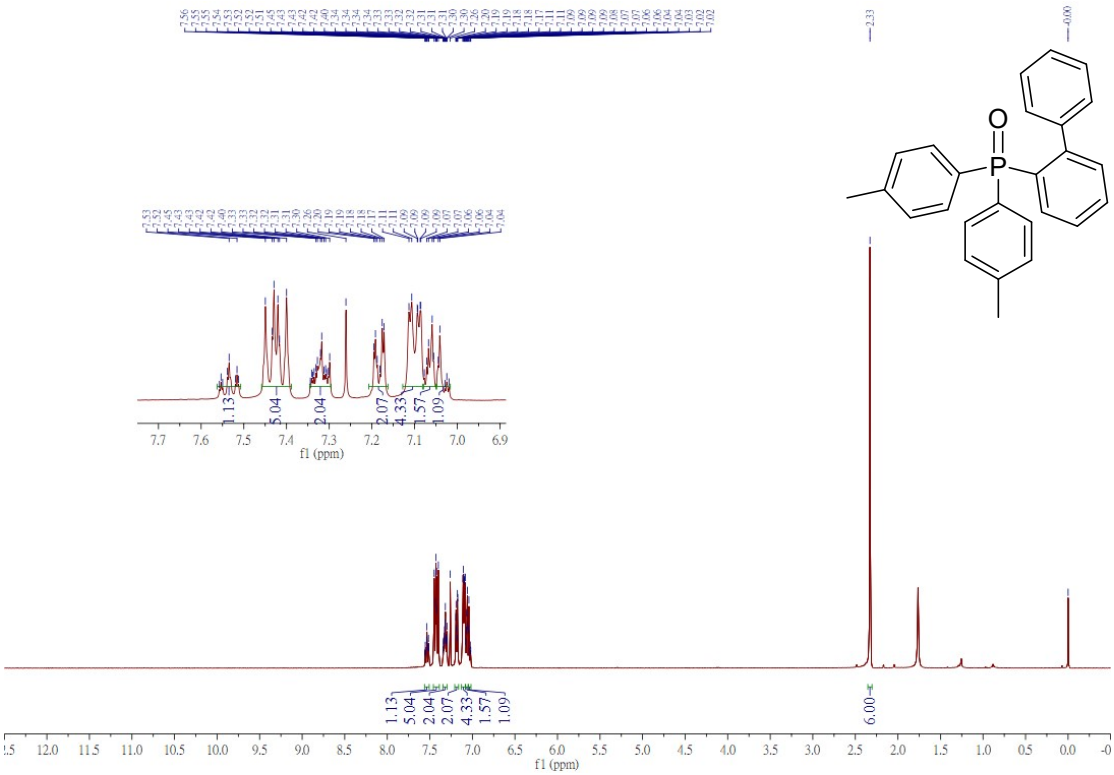

## (4-(9H-carbazol-9-yl)phenyl)di-p-tolylphosphine oxide (4b): $^{13}$C NMR



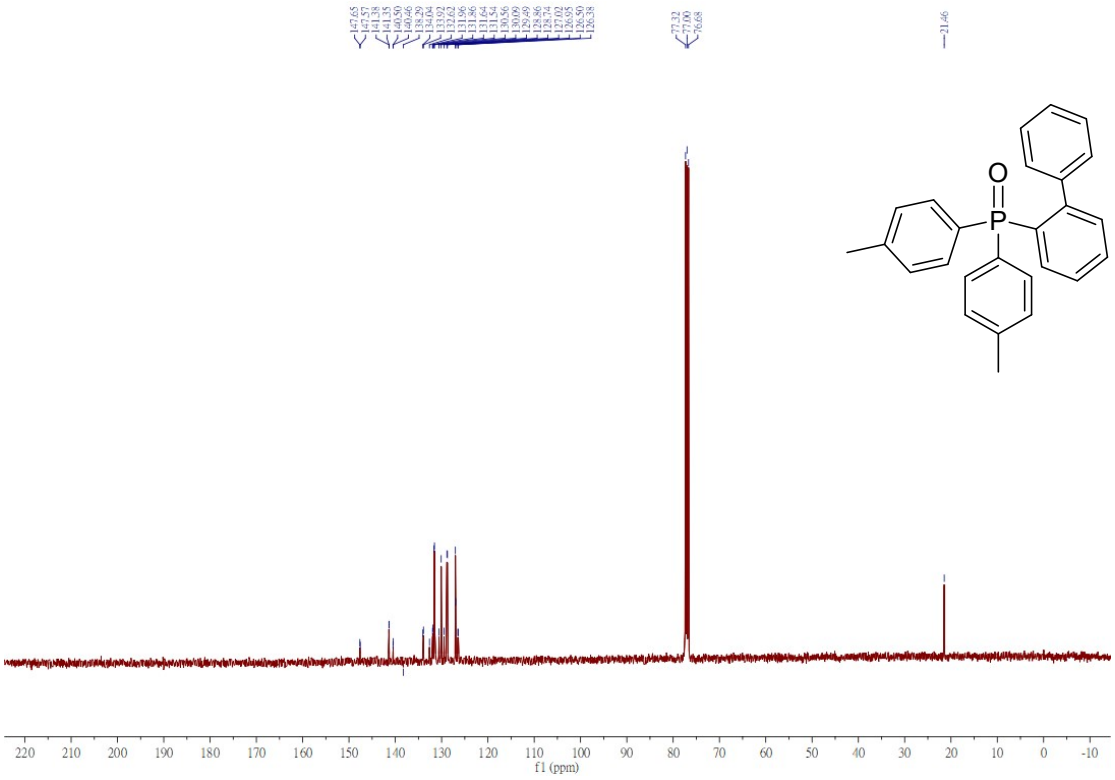
## (4-(9H-carbazol-9-yl)phenyl)di-p-tolylphosphine oxide (4b): $^{31}$P NMR



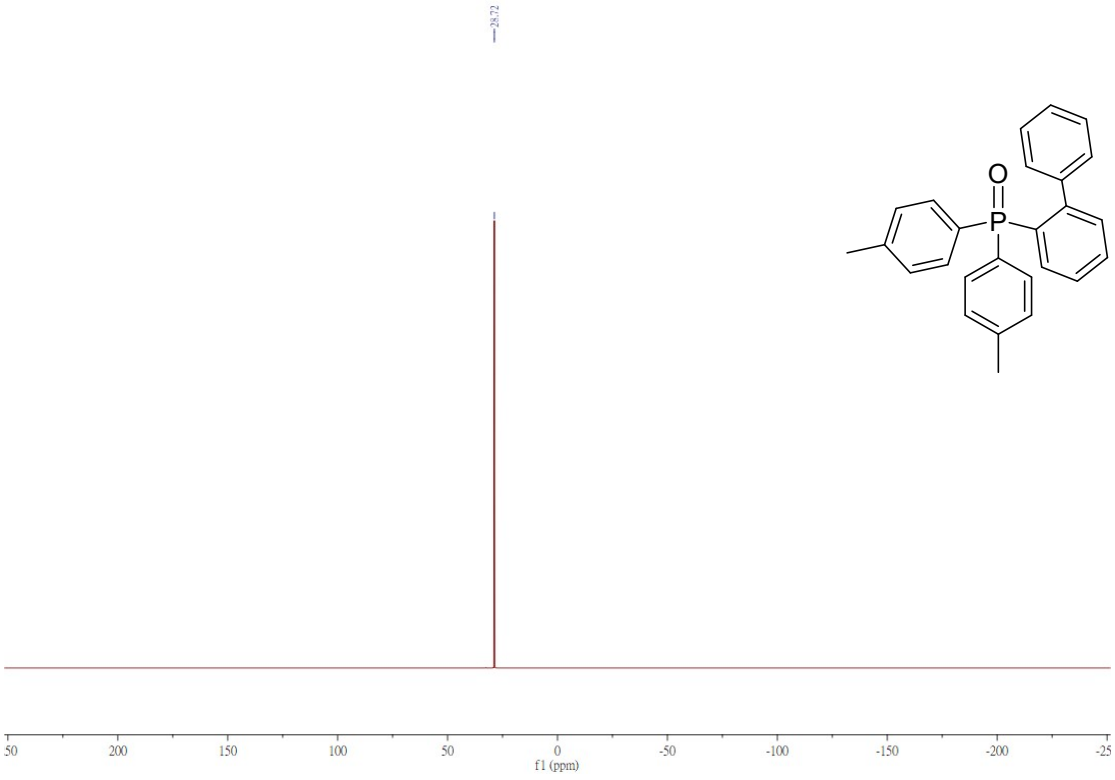

## [1,1'-biphenyl]-2-yldi-p-tolylphosphine oxide (4c): $^{1}$H NMR



## [1,1'-biphenyl]-2-yldi-p-tolylphosphine oxide (4c): $^{13}$C NMR




## [1,1'-biphenyl]-2-yldi-p-tolylphosphine oxide (4c): $^{31}$P NMR

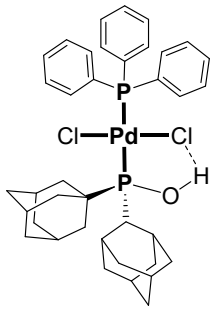


## 7. Computational Methods

All geometry optimizations and vibrational frequency calculations were performed with the Gaussian 09 package.[14] The ωB97X-D functional[15] was used in conjunction with MWB28 ECP and valence basis set for Pd[16] and 6-31+G(d) basis set for the other atoms. The optimized structures were confirmed to be local minima by frequency calculations (no imaginary frequency). The transition states were characterized to have only one imaginary frequency following the reaction path. The intrinsic reaction coordinate (IRC) calculations were performed to ensure the transition state connecting the expected reactant and product complex.[17] With the gas-phase optimized structures, polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM)[18] was employed to account for the solvation effect of EtOH. When calculating the bond dissociation free energies in EtOH, an energy correction of 1.89 kcal/mol was added to the solvation free energies of solutes to deal with the change of standard state of a solute from gas phase to solution (1 atm to 1 M).[19] The CYLview20 was also used to visualize the optimized structures.[20]

## 8. The wB97X-D-optimized Cartesian coordinates:

**1a (trans): HF= -3281.7283384 a.u./$N_{imag}$ =0**

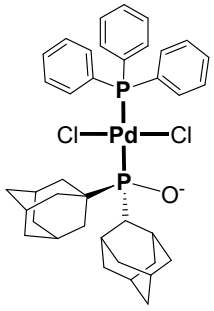



| Atom | x | y | z |
|---|---|---|---|
| Pd | -0.35557 | 0.212619 | -0.30835 |
| Cl | 0.053771 | 0.787647 | 1.910924 |
| Cl | -0.74932 | -0.29804 | -2.58014 |
| P | 1.955226 | 0.015603 | -0.71877 |
| P | -2.71136 | 0.173398 | 0.056184 |
| O | 2.240789 | -0.00676 | -2.3299 |
| H | 1.389259 | -0.12755 | -2.80153 |
| C | 3.059237 | 1.429213 | -0.20928 |
| C | 2.222181 | 2.719599 | -0.41388 |
| H | 1.894007 | 2.785595 | -1.46039 |
| H | 1.324379 | 2.682614 | 0.212768 |
| C | 3.05624 | 3.956037 | -0.04492 |
| H | 2.441982 | 4.852748 | -0.19349 |
| C | 3.477896 | 3.855359 | 1.429475 |
| H | 4.050899 | 4.746751 | 1.719613 |
| H | 2.588515 | 3.814523 | 2.071754 |
| C | 4.331237 | 2.593366 | 1.631808 |
| H | 4.630934 | 2.515977 | 2.684255 |
| C | 5.578884 | 2.663758 | 0.738848 |
| H | 6.18976 | 3.536108 | 1.008792 |
| H | 6.202493 | 1.772067 | 0.892405 |
| C | 5.145412 | 2.757837 | -0.73203 |
| H | 6.031663 | 2.793773 | -1.37831 |
| C | 4.31553 | 1.518479 | -1.11283 |
| H | 4.933357 | 0.620536 | -1.00493 |
| H | 4.016984 | 1.578294 | -2.16369 |
| C | 3.508769 | 1.345102 | 1.265918 |
| H | 4.130547 | 0.454708 | 1.418252 |

| | | | |
|---|---|---|---|
| H | 2.639888 | 1.259768 | 1.924657 |
| C | 4.302906 | 4.025597 | -0.93799 |
| H | 4.895814 | 4.916953 | -0.69073 |
| H | 4.008156 | 4.115046 | -1.99237 |
| C | 2.545412 | -1.66644 | -0.16739 |
| C | 2.260497 | -1.92333 | 1.329518 |
| H | 2.810532 | -1.21718 | 1.960108 |
| H | 1.197671 | -1.76637 | 1.541452 |
| C | 2.659703 | -3.3632 | 1.696623 |
| H | 2.463375 | -3.51765 | 2.764611 |
| C | 4.153517 | -3.57987 | 1.408364 |
| H | 4.758532 | -2.89052 | 2.013426 |
| H | 4.448021 | -4.59992 | 1.690368 |
| C | 4.426024 | -3.34878 | -0.08673 |
| H | 5.493383 | -3.49423 | -0.29513 |
| C | 3.596008 | -4.33708 | -0.919 |
| H | 3.884483 | -5.36903 | -0.67715 |
| H | 3.793 | -4.18756 | -1.98911 |
| C | 2.104346 | -4.12126 | -0.62392 |
| H | 1.502876 | -4.8131 | -1.22687 |
| C | 1.715291 | -2.68344 | -0.99557 |
| H | 0.645604 | -2.53055 | -0.80457 |
| H | 1.877206 | -2.52062 | -2.06719 |
| C | 4.043663 | -1.9038 | -0.45653 |
| H | 4.658933 | -1.21549 | 0.134271 |
| H | 4.256752 | -1.71353 | -1.51581 |
| C | 1.828955 | -4.35488 | 0.868691 |
| H | 2.084187 | -5.3873 | 1.144219 |
| H | 0.759783 | -4.21666 | 1.079275 |
| C | -3.36141 | 0.949794 | 1.578932 |
| C | -3.05546 | 0.368392 | 2.816341 |
| H | -2.45047 | -0.53201 | 2.859392 |
| C | -3.52425 | 0.937741 | 3.994429 |
| H | -3.28181 | 0.476025 | 4.947083 |
| C | -4.29158 | 2.101971 | 3.953343 |
| H | -4.65377 | 2.548726 | 4.875008 |
| C | -4.59052 | 2.69014 | 2.727825 |
| H | -5.18758 | 3.596765 | 2.687079 |

| | | | |
|---|---|---|---|
| C | -4.13008 | 2.115867 | 1.543322 |
| H | -4.38049 | 2.580005 | 0.594399 |
| C | -3.65309 | 0.976858 | -1.2867 |
| C | -3.13026 | 2.148702 | -1.84375 |
| H | -2.16486 | 2.522366 | -1.51117 |
| C | -3.83121 | 2.827764 | -2.83516 |
| H | -3.4151 | 3.734408 | -3.26446 |
| C | -5.05255 | 2.331821 | -3.2897 |
| H | -5.59421 | 2.854546 | -4.07305 |
| C | -5.57088 | 1.157827 | -2.74745 |
| H | -6.51599 | 0.760879 | -3.107 |
| C | -4.87547 | 0.482217 | -1.74639 |
| H | -5.28557 | -0.43523 | -1.33434 |
| C | -3.33964 | -1.54578 | 0.152178 |
| C | -4.50277 | -1.85962 | 0.867031 |
| H | -5.04503 | -1.08073 | 1.395508 |
| C | -4.96799 | -3.17105 | 0.91333 |
| H | -5.87066 | -3.40171 | 1.472002 |
| C | -4.27678 | -4.18282 | 0.248316 |
| H | -4.63849 | -5.20645 | 0.289987 |
| C | -3.12152 | -3.87717 | -0.46762 |
| H | -2.57865 | -4.65961 | -0.99022 |
| C | -2.65354 | -2.56608 | -0.51621 |
| H | -1.76068 | -2.334 | -1.08814 |

**1a$^-$ (trans): HF= -3281.1828762 a.u./$N_{imag}$ =0**



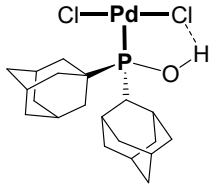

| Atom | x | y | z |
|---|---|---|---|
| Pd | 0.268235 | -0.11898 | -0.35419 |
| Cl | -0.11292 | -0.79138 | 1.891481 |
| Cl | 0.799711 | 0.604302 | -2.54085 |
| P | -2.01926 | 0.011205 | -0.92303 |

| | | | |
|---|---|---|---|
| P | 2.693026 | -0.11899 | 0.033513 |
| O | -2.34534 | 0.049342 | -2.40526 |
| C | -3.00198 | -1.46709 | -0.24119 |
| C | -2.10637 | -2.7156 | -0.43976 |
| H | -1.79377 | -2.77315 | -1.49156 |
| H | -1.20065 | -2.62199 | 0.167859 |
| C | -2.85865 | -3.99434 | -0.04139 |
| H | -2.19562 | -4.85896 | -0.18287 |
| C | -3.26679 | -3.89529 | 1.437265 |
| H | -3.78141 | -4.81594 | 1.752381 |
| H | -2.37134 | -3.78498 | 2.062739 |
| C | -4.19064 | -2.68237 | 1.631671 |
| H | -4.48265 | -2.60949 | 2.688531 |
| C | -5.44318 | -2.84629 | 0.757769 |
| H | -5.99578 | -3.75314 | 1.047863 |
| H | -6.11931 | -1.99185 | 0.906648 |
| C | -5.02156 | -2.9308 | -0.71767 |
| H | -5.91401 | -3.02982 | -1.35166 |
| C | -4.26476 | -1.65251 | -1.12019 |
| H | -4.93285 | -0.78902 | -1.01548 |
| H | -3.97073 | -1.69168 | -2.1735 |
| C | -3.44858 | -1.39318 | 1.232543 |
| H | -4.12836 | -0.54355 | 1.37584 |
| H | -2.58603 | -1.24055 | 1.885059 |
| C | -4.11202 | -4.15295 | -0.91435 |
| H | -4.65046 | -5.0749 | -0.64584 |
| H | -3.82445 | -4.23856 | -1.97139 |
| C | -2.61394 | 1.649629 | -0.19386 |
| C | -2.31699 | 1.872312 | 1.300864 |
| H | -2.81443 | 1.118468 | 1.919212 |
| H | -1.24378 | 1.760526 | 1.489068 |
| C | -2.7823 | 3.275436 | 1.73116 |
| H | -2.57491 | 3.406513 | 2.801957 |
| C | -4.29156 | 3.425092 | 1.477978 |
| H | -4.84533 | 2.678137 | 2.064849 |
| H | -4.63545 | 4.417405 | 1.807297 |
| C | -4.58155 | 3.233853 | -0.01976 |
| H | -5.66067 | 3.335008 | -0.20255 |

| | | | |
|---|---|---|---|
| C | -3.82004 | 4.295428 | -0.82754 |
| H | -4.15721 | 5.303313 | -0.54102 |
| H | -4.02976 | 4.171459 | -1.89876 |
| C | -2.31307 | 4.143042 | -0.57072 |
| H | -1.76148 | 4.890807 | -1.15696 |
| C | -1.85916 | 2.739163 | -0.99822 |
| H | -0.77962 | 2.632563 | -0.83234 |
| H | -2.02452 | 2.584143 | -2.07014 |
| C | -4.12664 | 1.828002 | -0.44828 |
| H | -4.6994 | 1.086423 | 0.122303 |
| H | -4.33831 | 1.658567 | -1.51116 |
| C | -2.02475 | 4.341738 | 0.925283 |
| H | -2.33175 | 5.349713 | 1.244069 |
| H | -0.94577 | 4.253189 | 1.112398 |
| C | 3.359668 | -0.9322 | 1.541656 |
| C | 3.024007 | -0.38896 | 2.789114 |
| H | 2.397489 | 0.496246 | 2.839827 |
| C | 3.476265 | -0.97948 | 3.963495 |
| H | 3.203415 | -0.54474 | 4.921261 |
| C | 4.256753 | -2.13494 | 3.913112 |
| H | 4.603149 | -2.60148 | 4.831937 |
| C | 4.580624 | -2.69197 | 2.679294 |
| H | 5.181981 | -3.59622 | 2.627767 |
| C | 4.136739 | -2.09258 | 1.499717 |
| H | 4.402644 | -2.53718 | 0.545256 |
| C | 3.653466 | -0.93964 | -1.29828 |
| C | 3.038354 | -1.99438 | -1.97983 |
| H | 2.000964 | -2.2376 | -1.76651 |
| C | 3.736994 | -2.70874 | -2.94979 |
| H | 3.244502 | -3.52154 | -3.47645 |
| C | 5.052364 | -2.36652 | -3.25883 |
| H | 5.594121 | -2.91735 | -4.02378 |
| C | 5.665586 | -1.30441 | -2.59595 |
| H | 6.687218 | -1.02419 | -2.84019 |
| C | 4.969092 | -0.59593 | -1.61869 |
| H | 5.45308 | 0.233978 | -1.11117 |
| C | 3.436915 | 1.562116 | 0.16484 |
| C | 4.614982 | 1.809986 | 0.881338 |

| | | | |
|---|---|---|---|
| H | 5.119476 | 0.995273 | 1.394003 |
| C | 5.142954 | 3.096827 | 0.956245 |
| H | 6.058358 | 3.271751 | 1.516048 |
| C | 4.496712 | 4.154859 | 0.318061 |
| H | 4.905914 | 5.16023 | 0.380525 |
| C | 3.323164 | 3.917247 | -0.39423 |
| H | 2.810628 | 4.735587 | -0.89289 |
| C | 2.793514 | 2.630274 | -0.47134 |
| H | 1.88692 | 2.445195 | -1.04091 |

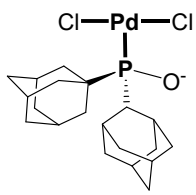
**$PdCl_2$-PA-Ad: HF= -2245.5949312 a.u./$N_{imag}$ =0**




| Atom | x | y | z |
|---|---|---|---|
| Pd | -0.2428 | 2.316958 | 0.279085 |
| Cl | 0.531586 | 1.825147 | 2.389805 |
| Cl | -1.14806 | 3.295041 | -1.56021 |
| P | -0.0157 | 0.30244 | -0.62246 |
| O | -0.07715 | 0.438871 | -2.24733 |
| H | -0.0002 | -0.41367 | -2.6994 |
| C | 1.653432 | -0.49493 | -0.31335 |
| C | 2.719669 | 0.631493 | -0.34136 |
| H | 2.675548 | 1.163122 | -1.30106 |
| H | 2.510663 | 1.359599 | 0.448257 |
| C | 4.120215 | 0.034567 | -0.12565 |
| H | 4.8515 | 0.850909 | -0.14433 |
| C | 4.162934 | -0.6697 | 1.239194 |
| H | 5.166551 | -1.07558 | 1.422899 |
| H | 3.947668 | 0.049171 | 2.039582 |
| C | 3.127435 | -1.804 | 1.259945 |
| H | 3.149414 | -2.30668 | 2.234061 |
| C | 3.435555 | -2.8145 | 0.145607 |
| H | 4.425392 | -3.26318 | 0.300859 |
| H | 2.703277 | -3.63368 | 0.165687 |
| C | 3.393963 | -2.09976 | -1.21255 |
| H | 3.598608 | -2.81695 | -2.01696 |

| | | | |
|---|---|---|---|
| C | 1.99493 | -1.49801 | -1.44741 |
| H | 1.257266 | -2.30746 | -1.49772 |
| H | 2.00707 | -0.98528 | -2.41724 |
| C | 1.717809 | -1.22644 | 1.045085 |
| H | 0.994305 | -2.04931 | 1.069866 |
| H | 1.465916 | -0.53558 | 1.855015 |
| C | 4.43824 | -0.97451 | -1.23794 |
| H | 5.442607 | -1.39372 | -1.09337 |
| H | 4.433664 | -0.47535 | -2.21614 |
| C | -1.49308 | -0.74647 | -0.18421 |
| C | -1.7247 | -0.79753 | 1.34342 |
| H | -0.8674 | -1.24139 | 1.85853 |
| H | -1.83262 | 0.218352 | 1.738248 |
| C | -2.99219 | -1.61455 | 1.647734 |
| H | -3.12981 | -1.6475 | 2.73474 |
| C | -2.83322 | -3.04169 | 1.101514 |
| H | -1.97596 | -3.53626 | 1.578735 |
| H | -3.72357 | -3.63824 | 1.33965 |
| C | -2.63216 | -2.98844 | -0.42097 |
| H | -2.50837 | -4.00414 | -0.81646 |
| C | -3.84082 | -2.313 | -1.08394 |
| H | -4.75055 | -2.89474 | -0.88598 |
| H | -3.7073 | -2.2833 | -2.17399 |
| C | -3.99289 | -0.88833 | -0.53093 |
| H | -4.84751 | -0.3949 | -1.00843 |
| C | -2.72688 | -0.07516 | -0.84536 |
| H | -2.83844 | 0.949891 | -0.47336 |
| H | -2.58734 | 0.001547 | -1.9295 |
| C | -1.35605 | -2.186 | -0.73484 |
| H | -0.4974 | -2.69394 | -0.28281 |
| H | -1.19839 | -2.17529 | -1.82338 |
| C | -4.20617 | -0.94354 | 0.989046 |
| H | -5.12105 | -1.50459 | 1.221767 |
| H | -4.33807 | 0.070287 | 1.388527 |

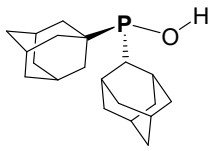
**$PdCl_2$-PA-Ad$^-$: HF= -2245.0970507 a.u./$N_{imag}$ =0**



| Atom | x | y | z |
|---|---|---|---|
| Pd | -0.28487 | 2.247336 | 0.23985 |
| Cl | 0.646389 | 1.894125 | 2.367152 |
| Cl | -1.45588 | 3.321181 | -1.44833 |
| P | -0.01866 | 0.269732 | -0.8141 |
| O | -0.05756 | 0.318229 | -2.32125 |
| C | 1.660925 | -0.46914 | -0.34923 |
| C | 2.703223 | 0.674737 | -0.4278 |
| H | 2.640407 | 1.157441 | -1.4118 |
| H | 2.475444 | 1.434667 | 0.326158 |
| C | 4.119874 | 0.128273 | -0.19107 |
| H | 4.834687 | 0.960331 | -0.24275 |
| C | 4.182585 | -0.51896 | 1.201538 |
| H | 5.198335 | -0.89202 | 1.401908 |
| H | 3.944399 | 0.227697 | 1.969841 |
| C | 3.17416 | -1.67625 | 1.27071 |
| H | 3.21565 | -2.14065 | 2.265217 |
| C | 3.514676 | -2.72103 | 0.19697 |
| H | 4.519498 | -3.13448 | 0.370719 |
| H | 2.804457 | -3.55894 | 0.251718 |
| C | 3.443902 | -2.06421 | -1.19046 |
| H | 3.671747 | -2.80998 | -1.96471 |
| C | 2.027852 | -1.51412 | -1.43498 |
| H | 1.313336 | -2.3451 | -1.4274 |
| H | 1.959113 | -1.0484 | -2.42299 |
| C | 1.749909 | -1.14084 | 1.033706 |
| H | 1.048064 | -1.98207 | 1.092128 |
| H | 1.480962 | -0.4275 | 1.817725 |
| C | 4.461987 | -0.91661 | -1.26291 |
| H | 5.48049 | -1.30359 | -1.10795 |
| H | 4.434617 | -0.45439 | -2.25912 |
| C | -1.47109 | -0.76522 | -0.20846 |
| C | -1.69428 | -0.74105 | 1.316496 |
| H | -0.82228 | -1.13359 | 1.849468 |
| H | -1.82285 | 0.291532 | 1.659403 |
| C | -2.93937 | -1.56981 | 1.678967 |

| | | | |
|---|---|---|---|
| H | -3.07441 | -1.54756 | 2.768478 |
| C | -2.75407 | -3.02197 | 1.210547 |
| H | -1.87981 | -3.46773 | 1.706314 |
| H | -3.63031 | -3.62569 | 1.490533 |
| C | -2.5611 | -3.04748 | -0.31432 |
| H | -2.41925 | -4.0836 | -0.65198 |
| C | -3.79497 | -2.44256 | -0.99963 |
| H | -4.69012 | -3.0349 | -0.75684 |
| H | -3.66901 | -2.4719 | -2.09067 |
| C | -3.97238 | -0.99074 | -0.53063 |
| H | -4.84582 | -0.54636 | -1.02575 |
| C | -2.72479 | -0.17258 | -0.89902 |
| H | -2.85776 | 0.872747 | -0.59682 |
| H | -2.57515 | -0.16303 | -1.98439 |
| C | -1.31033 | -2.22889 | -0.68075 |
| H | -0.43864 | -2.6937 | -0.20526 |
| H | -1.14407 | -2.25009 | -1.76516 |
| C | -4.17448 | -0.96665 | 0.99256 |
| H | -5.07654 | -1.53487 | 1.266141 |
| H | -4.32278 | 0.066724 | 1.332853 |

**PA-Ad: HF= -1197.215157 a.u./$N_{imag}$ =0**

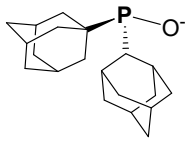



| Atom | x | y | z |
|---|---|---|---|
| P | 0.000657 | 1.386537 | -0.65303 |
| O | -0.04612 | 2.484783 | 0.629561 |
| H | 0.098242 | 3.377429 | 0.29844 |
| C | -1.54585 | 0.417287 | -0.20519 |
| C | -2.70576 | 1.268992 | -0.7889 |
| H | -2.70633 | 2.259788 | -0.31499 |
| H | -2.547 | 1.425635 | -1.86432 |
| C | -4.06166 | 0.584311 | -0.56072 |
| H | -4.85584 | 1.211885 | -0.98451 |
| C | -4.05535 | -0.78489 | -1.2571 |
| H | -5.0233 | -1.28563 | -1.11894 |

| | | | |
|---|---|---|---|
| H | -3.90905 | -0.65654 | -2.33826 |
| C | -2.92839 | -1.6488 | -0.67113 |
| H | -2.91811 | -2.62787 | -1.16653 |
| C | -3.15666 | -1.83464 | 0.837632 |
| H | -4.11067 | -2.35065 | 1.012195 |
| H | -2.36514 | -2.4674 | 1.262578 |
| C | -3.16322 | -0.46169 | 1.529404 |
| H | -3.31999 | -0.59444 | 2.607387 |
| C | -1.80777 | 0.233315 | 1.305631 |
| H | -1.01968 | -0.36881 | 1.766349 |
| H | -1.79552 | 1.20915 | 1.803069 |
| C | -1.56868 | -0.96294 | -0.89621 |
| H | -0.77903 | -1.60575 | -0.48914 |
| H | -1.37615 | -0.8553 | -1.9736 |
| C | -4.29374 | 0.397712 | 0.945598 |
| H | -5.26554 | -0.08363 | 1.121738 |
| H | -4.32063 | 1.374923 | 1.446145 |
| C | 1.541967 | 0.406673 | -0.20642 |
| C | 1.882317 | -0.53858 | -1.38373 |
| H | 1.109667 | -1.30769 | -1.49916 |
| H | 1.908512 | 0.029452 | -2.32394 |
| C | 3.24209 | -1.21972 | -1.14765 |
| H | 3.453273 | -1.89521 | -1.9862 |
| C | 3.195281 | -2.02248 | 0.162704 |
| H | 2.423981 | -2.80253 | 0.099663 |
| H | 4.15541 | -2.53057 | 0.326076 |
| C | 2.891996 | -1.07586 | 1.335476 |
| H | 2.852953 | -1.64811 | 2.271154 |
| C | 3.991076 | -0.0077 | 1.429148 |
| H | 4.964139 | -0.4824 | 1.615173 |
| H | 3.791511 | 0.665364 | 2.273854 |
| C | 4.034397 | 0.791895 | 0.118333 |
| H | 4.808614 | 1.56689 | 0.182633 |
| C | 2.671654 | 1.464671 | -0.10734 |
| H | 2.702885 | 2.063987 | -1.02941 |
| H | 2.457615 | 2.150984 | 0.7205 |
| C | 1.525829 | -0.40465 | 1.102926 |
| H | 0.757738 | -1.18509 | 1.055197 |

| | | | |
|---|---|---|---|
| H | 1.274772 | 0.252277 | 1.945499 |
| C | 4.342606 | -0.15293 | -1.05284 |
| H | 5.320567 | -0.63125 | -0.90582 |
| H | 4.398367 | 0.414922 | -1.99157 |

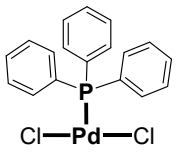
**PA-Ad$^-$: HF= -1196.6443373 a.u./$N_{imag}$ =0**




| Atom | x | y | z |
|---|---|---|---|
| P | 0.000138 | -1.54907 | -0.55938 |
| O | 0.02064 | -2.5678 | 0.618744 |
| C | 1.543085 | -0.43767 | -0.20056 |
| C | 2.713733 | -1.27284 | -0.77689 |
| H | 2.71541 | -2.26055 | -0.29695 |
| H | 2.546041 | -1.44188 | -1.85033 |
| C | 4.067825 | -0.57909 | -0.56559 |
| H | 4.872513 | -1.1987 | -0.98825 |
| C | 4.046582 | 0.786773 | -1.26956 |
| H | 5.011663 | 1.301249 | -1.13899 |
| H | 3.895071 | 0.646955 | -2.34958 |
| C | 2.909067 | 1.64109 | -0.68839 |
| H | 2.893207 | 2.620977 | -1.18852 |
| C | 3.146879 | 1.838642 | 0.818866 |
| H | 4.098223 | 2.368439 | 0.98462 |
| H | 2.347989 | 2.464179 | 1.243014 |
| C | 3.16815 | 0.470095 | 1.523081 |
| H | 3.335969 | 0.617104 | 2.600352 |
| C | 1.818065 | -0.23668 | 1.300861 |
| H | 1.02767 | 0.366127 | 1.761051 |
| H | 1.790263 | -1.21541 | 1.795347 |
| C | 1.556495 | 0.931809 | -0.89937 |
| H | 0.76088 | 1.5741 | -0.49929 |
| H | 1.35813 | 0.809 | -1.97542 |
| C | 4.307531 | -0.37781 | 0.938385 |
| H | 5.277916 | 0.115425 | 1.108233 |
| H | 4.342498 | -1.35316 | 1.442984 |

| | | | |
|---|---|---|---|
| C | -1.54177 | -0.43423 | -0.20532 |
| C | -1.87861 | 0.485277 | -1.39439 |
| H | -1.09887 | 1.245498 | -1.53248 |
| H | -1.90431 | -0.10785 | -2.32021 |
| C | -3.23223 | 1.189662 | -1.17924 |
| H | -3.44626 | 1.849448 | -2.03332 |
| C | -3.17724 | 2.025534 | 0.111523 |
| H | -2.39565 | 2.7947 | 0.025986 |
| H | -4.13393 | 2.549356 | 0.264115 |
| C | -2.87692 | 1.107275 | 1.308835 |
| H | -2.83305 | 1.708202 | 2.229641 |
| C | -3.99081 | 0.057349 | 1.433163 |
| H | -4.96006 | 0.549449 | 1.61181 |
| H | -3.79147 | -0.5973 | 2.292887 |
| C | -4.04402 | -0.77875 | 0.144939 |
| H | -4.83327 | -1.53989 | 0.233076 |
| C | -2.68688 | -1.46516 | -0.06939 |
| H | -2.72466 | -2.08788 | -0.97647 |
| H | -2.45334 | -2.14162 | 0.761332 |
| C | -1.52154 | 0.410146 | 1.080336 |
| H | -0.74556 | 1.184132 | 1.01607 |
| H | -1.26946 | -0.23523 | 1.932685 |
| C | -4.34741 | 0.140517 | -1.04907 |
| H | -5.32178 | 0.636396 | -0.91439 |
| H | -4.40882 | -0.45442 | -1.97154 |

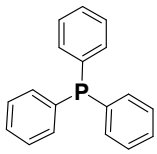
**$PdCl_2$-$PPh_3$: HF= -2084.4365547 a.u./$N_{imag}$ =0**




| Atom | x | y | z |
|---|---|---|---|
| Pd | 0.663144 | -1.99324 | -0.17831 |
| Cl | -1.34048 | -3.06605 | -0.01361 |
| Cl | 2.864152 | -1.37341 | -0.35482 |
| P | -0.04847 | 0.11021 | 0.001166 |
| C | -1.77392 | 0.304007 | 0.549908 |
| C | -2.80445 | -0.13971 | -0.28879 |

| | | | |
|---|---|---|---|
| H | -2.57101 | -0.63343 | -1.22712 |
| C | -4.12966 | 0.040754 | 0.083336 |
| H | -4.92253 | -0.30783 | -0.57122 |
| C | -4.43831 | 0.653743 | 1.298955 |
| H | -5.47606 | 0.78959 | 1.589522 |
| C | -3.41723 | 1.086165 | 2.13911 |
| H | -3.65123 | 1.561393 | 3.087018 |
| C | -2.08389 | 0.914654 | 1.767136 |
| H | -1.29601 | 1.264066 | 2.426774 |
| C | 0.948515 | 1.03152 | 1.212007 |
| C | 1.361675 | 0.387849 | 2.382975 |
| H | 1.155058 | -0.66945 | 2.526251 |
| C | 2.056433 | 1.096411 | 3.356986 |
| H | 2.379846 | 0.590971 | 4.261761 |
| C | 2.350003 | 2.445757 | 3.162355 |
| H | 2.900377 | 2.995846 | 3.920156 |
| C | 1.949675 | 3.084936 | 1.991507 |
| H | 2.186278 | 4.13264 | 1.831702 |
| C | 1.248121 | 2.381448 | 1.014552 |
| H | 0.946377 | 2.885835 | 0.10155 |
| C | 0.035453 | 1.015181 | -1.58022 |
| C | -0.87088 | 2.055006 | -1.83189 |
| H | -1.64662 | 2.297081 | -1.11196 |
| C | -0.78298 | 2.786626 | -3.0123 |
| H | -1.49138 | 3.588035 | -3.20017 |
| C | 0.204051 | 2.48583 | -3.94927 |
| H | 0.266483 | 3.052129 | -4.8741 |
| C | 1.107447 | 1.454972 | -3.70069 |
| H | 1.877281 | 1.214814 | -4.42758 |
| C | 1.027192 | 0.718613 | -2.52141 |
| H | 1.739614 | -0.07771 | -2.33004 |

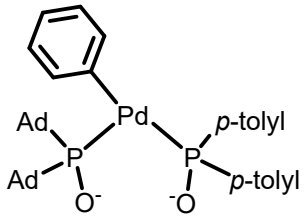
**$PPh_3$: HF= -1036.0653135 a.u./$N_{imag}$ =0**



| Atom | x | y | z |
|---|---|---|---|
| P | 0.000946 | -0.00979 | -1.25993 |
| C | 1.433383 | -0.82823 | -0.43835 |
| C | 1.337049 | -1.62816 | 0.70495 |
| H | 0.368737 | -1.80463 | 1.164609 |
| C | 2.476692 | -2.20406 | 1.263904 |
| H | 2.38416 | -2.82492 | 2.150871 |
| C | 3.727679 | -1.98226 | 0.69287 |
| H | 4.614566 | -2.43122 | 1.131585 |
| C | 3.834841 | -1.18848 | -0.44837 |
| H | 4.805544 | -1.01628 | -0.90475 |
| C | 2.694164 | -0.62606 | -1.01422 |
| H | 2.783562 | -0.02 | -1.91345 |
| C | -0.00188 | 1.642606 | -0.44193 |
| C | -0.88581 | 2.600567 | -0.95568 |
| H | -1.5219 | 2.345578 | -1.80099 |
| C | -0.96573 | 3.870625 | -0.39294 |
| H | -1.66385 | 4.598874 | -0.79646 |
| C | -0.1428 | 4.210809 | 0.680082 |
| H | -0.1939 | 5.20624 | 1.112468 |
| C | 0.750316 | 3.271638 | 1.188975 |
| H | 1.39962 | 3.531762 | 2.020435 |
| C | 0.818232 | 1.993952 | 0.634536 |
| H | 1.516562 | 1.269531 | 1.044435 |
| C | -1.42941 | -0.82818 | -0.43269 |
| C | -1.93298 | -1.99182 | -1.02754 |
| H | -1.48929 | -2.35992 | -1.95019 |
| C | -2.99842 | -2.68212 | -0.45485 |
| H | -3.377 | -3.58253 | -0.93008 |
| C | -3.58582 | -2.20894 | 0.717132 |
| H | -4.42329 | -2.74054 | 1.160611 |
| C | -3.10112 | -1.04503 | 1.310877 |
| H | -3.55765 | -0.66623 | 2.221173 |

| | | | |
|---|---|---|---|
| C | -2.02855 | -0.36063 | 0.741898 |
| H | -1.65909 | 0.543772 | 1.216849 |

**Intermediate b: HF= -2514.5567357 a.u./$N_{imag}$ =0**

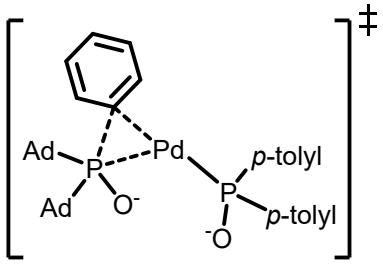



| Atom | x | y | z |
|---|---|---|---|
| Pd | -0.612580 | 0.770942 | 0.460015 |
| P | -0.486536 | -1.469050 | 0.921090 |
| P | 0.890767 | 1.292544 | -1.272107 |
| O | -0.933278 | -1.960707 | 2.289968 |
| O | 0.891715 | 0.801202 | -2.717521 |
| C | 1.309152 | -2.052744 | 0.755147 |
| C | 2.150584 | -1.072236 | 1.606317 |
| H | 2.055422 | -0.064966 | 1.195946 |
| H | 1.750969 | -1.046222 | 2.628838 |
| C | 3.630295 | -1.480925 | 1.623360 |
| H | 4.196011 | -0.749692 | 2.217133 |
| C | 4.169275 | -1.500306 | 0.184855 |
| H | 4.095702 | -0.499301 | -0.257349 |
| H | 5.233730 | -1.780360 | 0.183981 |
| C | 3.361061 | -2.507651 | -0.647866 |
| H | 3.741550 | -2.522326 | -1.677740 |
| C | 3.489256 | -3.906896 | -0.024123 |
| H | 2.927003 | -4.637733 | -0.623410 |
| H | 4.541887 | -4.227863 | -0.023259 |
| C | 2.943363 | -3.876704 | 1.413027 |
| H | 3.020942 | -4.878667 | 1.858264 |
| C | 1.461931 | -3.454511 | 1.396003 |
| H | 1.052069 | -3.431905 | 2.411317 |
| H | 0.887866 | -4.202243 | 0.838807 |
| C | 1.877443 | -2.097192 | -0.674665 |
| H | 1.768549 | -1.131186 | -1.175862 |
| H | 1.323310 | -2.824214 | -1.281327 |
| C | 3.762931 | -2.878668 | 2.245216 |

| | | | |
|---|---|---|---|
| H | 4.819311 | -3.186301 | 2.273676 |
| H | 3.397056 | -2.865907 | 3.281422 |
| C | -1.596177 | -2.251558 | -0.388670 |
| C | -1.436369 | -1.619929 | -1.785908 |
| H | -1.618645 | -0.540108 | -1.727514 |
| H | -0.415485 | -1.727925 | -2.166088 |
| C | -2.434590 | -2.250616 | -2.771344 |
| H | -2.290954 | -1.793992 | -3.759136 |
| C | -2.193315 | -3.766135 | -2.861457 |
| H | -2.888650 | -4.219359 | -3.584029 |
| H | -1.174105 | -3.961276 | -3.224133 |
| C | -2.386870 | -4.399419 | -1.473885 |
| H | -2.206249 | -5.482077 | -1.532927 |
| C | -3.819124 | -4.139112 | -0.985184 |
| H | -4.543184 | -4.596861 | -1.676193 |
| H | -3.969155 | -4.602078 | 0.000153 |
| C | -4.053336 | -2.623766 | -0.892656 |
| H | -5.071715 | -2.428344 | -0.530426 |
| C | -3.048018 | -2.007539 | 0.092700 |
| H | -3.230375 | -0.930689 | 0.184862 |
| H | -3.178337 | -2.433371 | 1.094414 |
| C | -1.378950 | -3.777097 | -0.490837 |
| H | -1.483130 | -4.232876 | 0.502440 |
| H | -0.367028 | -3.996595 | -0.850300 |
| C | -3.868149 | -1.992349 | -2.281753 |
| H | -4.054101 | -0.911110 | -2.227420 |
| H | -4.595146 | -2.415350 | -2.991882 |
| C | -0.123032 | 2.846467 | -1.137476 |
| C | -0.139394 | 3.661333 | 0.004593 |
| H | 0.605492 | 3.528342 | 0.784590 |
| C | -1.095984 | 4.665010 | 0.155243 |
| H | -1.097497 | 5.269308 | 1.060038 |
| C | -2.069244 | 4.880488 | -0.818965 |
| C | -2.045743 | 4.077154 | -1.967266 |
| H | -2.793061 | 4.234966 | -2.743447 |
| C | -1.099604 | 3.071943 | -2.121315 |
| H | -1.095375 | 2.438459 | -3.005381 |
| C | -3.150016 | 5.912710 | -0.614909 |

| | | | |
|---|---|---|---|
| H | -3.561313 | 6.257223 | -1.570142 |
| H | -3.976323 | 5.491966 | -0.027911 |
| H | -2.772844 | 6.785634 | -0.070687 |
| C | 2.600500 | 1.852353 | -0.859055 |
| C | 3.560280 | 1.835321 | -1.872878 |
| H | 3.244180 | 1.557873 | -2.875755 |
| C | 4.891783 | 2.141894 | -1.597757 |
| H | 5.625496 | 2.116538 | -2.402151 |
| C | 5.304355 | 2.466057 | -0.302817 |
| C | 4.340049 | 2.484889 | 0.710283 |
| H | 4.636928 | 2.724849 | 1.730056 |
| C | 3.011014 | 2.175339 | 0.437940 |
| H | 2.294015 | 2.152322 | 1.256346 |
| C | 6.755049 | 2.743460 | 0.008548 |
| H | 7.249439 | 1.846441 | 0.403052 |
| H | 7.302577 | 3.055415 | -0.887564 |
| H | 6.858716 | 3.533125 | 0.761387 |
| C | -2.237610 | 1.034348 | 1.674564 |
| C | -3.173378 | 1.951302 | 1.160541 |
| C | -2.464467 | 0.550652 | 2.970489 |
| C | -4.273863 | 2.379917 | 1.907107 |
| H | -3.049776 | 2.351306 | 0.153318 |
| C | -3.555505 | 0.982548 | 3.728160 |
| H | -1.796255 | -0.209715 | 3.368202 |
| C | -4.466607 | 1.899564 | 3.201954 |
| H | -4.981542 | 3.085970 | 1.474099 |
| H | -3.702383 | 0.589140 | 4.733087 |
| H | -5.321728 | 2.227673 | 3.790034 |

**TS(Ad): HF= -2514.52397409 a.u./$N_{imag}$ =1**



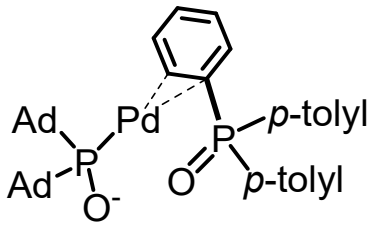

| Atom | x | y | z |
|---|---|---|---|
| Pd | -0.233147 | -0.725764 | 0.780149 |

| | | | |
|---|---|---|---|
| P | 2.172264 | 0.128845 | 0.869476 |
| P | -1.816438 | -0.465314 | -0.946487 |
| O | 3.291004 | 0.360532 | 1.875493 |
| O | -1.412484 | -0.446397 | -2.428720 |
| C | 1.584053 | 1.900915 | 0.435265 |
| C | 0.606380 | 2.350111 | 1.550054 |
| H | -0.283062 | 1.703947 | 1.544062 |
| H | 1.093141 | 2.241824 | 2.528769 |
| C | 0.180041 | 3.813577 | 1.350491 |
| H | -0.520696 | 4.089060 | 2.150435 |
| C | -0.509890 | 3.961836 | -0.012130 |
| H | -1.406439 | 3.336467 | -0.049141 |
| H | -0.832325 | 5.003418 | -0.161731 |
| C | 0.464605 | 3.547222 | -1.123222 |
| H | -0.032963 | 3.636897 | -2.097320 |
| C | 1.705620 | 4.451866 | -1.077546 |
| H | 2.405829 | 4.173781 | -1.878702 |
| H | 1.418433 | 5.500703 | -1.245819 |
| C | 2.390886 | 4.302281 | 0.290351 |
| H | 3.287554 | 4.937002 | 0.326985 |
| C | 2.817291 | 2.837659 | 0.499188 |
| H | 3.317710 | 2.712701 | 1.464283 |
| H | 3.546971 | 2.568928 | -0.271213 |
| C | 0.887615 | 2.079934 | -0.927765 |
| H | 0.013436 | 1.431653 | -1.003881 |
| H | 1.553335 | 1.794258 | -1.749115 |
| C | 1.417851 | 4.720570 | 1.402391 |
| H | 1.122478 | 5.772728 | 1.274016 |
| H | 1.910678 | 4.635548 | 2.381341 |
| C | 2.915800 | -0.766698 | -0.616643 |
| C | 1.875733 | -1.324628 | -1.605085 |
| H | 1.196415 | -2.015842 | -1.090360 |
| H | 1.230606 | -0.536076 | -2.006668 |
| C | 2.579342 | -2.063083 | -2.754786 |
| H | 1.814321 | -2.445483 | -3.440968 |
| C | 3.507718 | -1.092361 | -3.500866 |
| H | 3.993037 | -1.602159 | -4.346563 |
| H | 2.919496 | -0.262014 | -3.914428 |

| | | | |
|---|---|---|---|
| C | 4.571464 | -0.554842 | -2.530301 |
| H | 5.229158 | 0.152068 | -3.055016 |
| C | 5.401188 | -1.721664 | -1.978030 |
| H | 5.907420 | -2.250036 | -2.799679 |
| H | 6.180639 | -1.343148 | -1.302034 |
| C | 4.470245 | -2.679238 | -1.221532 |
| H | 5.055134 | -3.510180 | -0.803518 |
| C | 3.786247 | -1.926148 | -0.067593 |
| H | 3.178473 | -2.629013 | 0.506800 |
| H | 4.531081 | -1.520300 | 0.626445 |
| C | 3.878445 | 0.184266 | -1.371566 |
| H | 4.627471 | 0.578116 | -0.672944 |
| H | 3.334479 | 1.036780 | -1.787355 |
| C | 3.406856 | -3.227357 | -2.187687 |
| H | 2.746843 | -3.930468 | -1.660479 |
| H | 3.890604 | -3.785328 | -3.003477 |
| C | -3.182371 | -1.714102 | -0.757652 |
| C | -3.560259 | -2.219316 | 0.487049 |
| H | -3.028463 | -1.894568 | 1.381445 |
| C | -4.598208 | -3.143791 | 0.600499 |
| H | -4.878042 | -3.521083 | 1.583311 |
| C | -5.275800 | -3.602988 | -0.531821 |
| C | -4.883280 | -3.107455 | -1.780404 |
| H | -5.394569 | -3.456438 | -2.677369 |
| C | -3.851999 | -2.178319 | -1.892707 |
| H | -3.540396 | -1.800904 | -2.864511 |
| C | -6.374302 | -4.633706 | -0.420740 |
| H | -6.006300 | -5.635651 | -0.677721 |
| H | -6.775362 | -4.680858 | 0.597906 |
| H | -7.204649 | -4.406635 | -1.099751 |
| C | -2.846116 | 1.061076 | -0.668627 |
| C | -3.112339 | 1.905200 | -1.746149 |
| H | -2.739686 | 1.616253 | -2.726870 |
| C | -3.819738 | 3.094208 | -1.562763 |
| H | -4.008443 | 3.745175 | -2.415834 |
| C | -4.277790 | 3.472075 | -0.298842 |
| C | -4.014063 | 2.619075 | 0.779966 |
| H | -4.357193 | 2.894545 | 1.776600 |

| | | | |
|---|---|---|---|
| C | -3.302305 | 1.437456 | 0.597823 |
| H | -3.079997 | 0.804379 | 1.456326 |
| C | -4.992476 | 4.784907 | -0.086544 |
| H | -5.442877 | 5.148865 | -1.016823 |
| H | -5.788972 | 4.691409 | 0.660946 |
| H | -4.297948 | 5.557662 | 0.268599 |
| C | 1.165560 | -1.267784 | 2.176073 |
| C | 1.186202 | -2.666351 | 2.020968 |
| C | 1.100032 | -0.750376 | 3.483141 |
| C | 1.121679 | -3.514213 | 3.129789 |
| H | 1.234250 | -3.106560 | 1.029756 |
| C | 1.033991 | -1.594452 | 4.584882 |
| H | 1.118497 | 0.323394 | 3.634636 |
| C | 1.048554 | -2.980979 | 4.412387 |
| H | 1.126367 | -4.591830 | 2.983135 |
| H | 0.974722 | -1.170911 | 5.584850 |
| H | 1.004248 | -3.639308 | 5.276859 |

**PC(Ad): HF= -2514.55472018 a.u./$N_{imag}$ =0**



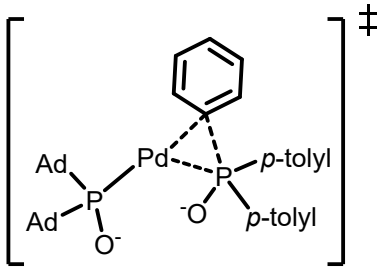

| Atom | x | y | z |
|---|---|---|---|
| Pd | -1.111151 | -1.410945 | -0.792171 |
| P | 1.752486 | -0.198900 | 0.357419 |
| P | -3.099936 | -0.129897 | -1.000063 |
| O | 1.014989 | -0.200211 | 1.672828 |
| O | -3.692196 | 0.425750 | -2.303127 |
| C | 1.666938 | 1.492153 | -0.463289 |
| C | 0.367088 | 1.591360 | -1.297543 |
| H | 0.379990 | 0.880354 | -2.129543 |
| H | -0.488931 | 1.320562 | -0.677173 |
| C | 0.171430 | 3.010275 | -1.847945 |
| H | -0.762523 | 3.024392 | -2.421259 |
| C | 1.358466 | 3.372230 | -2.751519 |
| H | 1.412706 | 2.674798 | -3.599301 |

| | | | |
|---|---|---|---|
| H | 1.230362 | 4.381549 | -3.168896 |
| C | 2.654901 | 3.305789 | -1.929986 |
| H | 3.514603 | 3.553086 | -2.568305 |
| C | 2.575071 | 4.302234 | -0.762273 |
| H | 3.507815 | 4.274292 | -0.179372 |
| H | 2.465110 | 5.325159 | -1.150363 |
| C | 1.379705 | 3.941893 | 0.133418 |
| H | 1.322539 | 4.644696 | 0.975718 |
| C | 1.565657 | 2.522772 | 0.693258 |
| H | 0.722187 | 2.255859 | 1.336287 |
| H | 2.466817 | 2.491127 | 1.318725 |
| C | 2.852695 | 1.881727 | -1.374652 |
| H | 2.946116 | 1.179751 | -2.213031 |
| H | 3.799228 | 1.853419 | -0.823577 |
| C | 0.082039 | 4.006273 | -0.684605 |
| H | -0.073970 | 5.025679 | -1.068012 |
| H | -0.778054 | 3.758784 | -0.052319 |
| C | 3.524455 | -0.728455 | 0.702850 |
| C | 4.404820 | -1.017121 | -0.532454 |
| H | 3.935982 | -1.792017 | -1.150064 |
| H | 4.511726 | -0.127689 | -1.161053 |
| C | 5.802707 | -1.490457 | -0.091716 |
| H | 6.413335 | -1.670181 | -0.986587 |
| C | 6.466977 | -0.410787 | 0.777856 |
| H | 7.477765 | -0.730761 | 1.069782 |
| H | 6.574980 | 0.520467 | 0.203569 |
| C | 5.609579 | -0.158751 | 2.028815 |
| H | 6.080784 | 0.614962 | 2.649667 |
| C | 5.477879 | -1.459723 | 2.833584 |
| H | 6.469216 | -1.803572 | 3.163400 |
| H | 4.876431 | -1.282804 | 3.735475 |
| C | 4.809037 | -2.529287 | 1.957797 |
| H | 4.695413 | -3.458618 | 2.531416 |
| C | 3.417750 | -2.044187 | 1.519907 |
| H | 2.942023 | -2.821120 | 0.909086 |
| H | 2.776264 | -1.879087 | 2.392642 |
| C | 4.215369 | 0.327117 | 1.598711 |
| H | 3.589604 | 0.522390 | 2.478327 |

| | | | |
|---|---|---|---|
| H | 4.325246 | 1.276947 | 1.063052 |
| C | 5.675388 | -2.790270 | 0.716305 |
| H | 5.217257 | -3.573005 | 0.096593 |
| H | 6.670883 | -3.150068 | 1.015102 |
| C | -4.494636 | -0.976126 | -0.093181 |
| C | -5.779712 | -0.934756 | -0.631078 |
| H | -5.925095 | -0.404442 | -1.570238 |
| C | -6.846415 | -1.560526 | 0.018358 |
| H | -7.843384 | -1.516559 | -0.419752 |
| C | -6.657125 | -2.242183 | 1.221609 |
| C | -5.362927 | -2.286129 | 1.756570 |
| H | -5.188808 | -2.815387 | 2.693367 |
| C | -4.299420 | -1.669631 | 1.105827 |
| H | -3.297073 | -1.729628 | 1.529231 |
| C | -7.802448 | -2.929535 | 1.927326 |
| H | -7.661355 | -4.017848 | 1.953031 |
| H | -7.893951 | -2.588667 | 2.966278 |
| H | -8.755682 | -2.729962 | 1.424873 |
| C | -2.951746 | 1.319094 | 0.174610 |
| C | -3.606047 | 2.513847 | -0.132945 |
| H | -4.189667 | 2.557757 | -1.050613 |
| C | -3.500198 | 3.622909 | 0.705786 |
| H | -4.015648 | 4.547350 | 0.445331 |
| C | -2.728725 | 3.573171 | 1.871201 |
| C | -2.067661 | 2.378194 | 2.171664 |
| H | -1.440785 | 2.316512 | 3.060574 |
| C | -2.170641 | 1.270281 | 1.332837 |
| H | -1.594333 | 0.374059 | 1.560875 |
| C | -2.556611 | 4.794205 | 2.742760 |
| H | -1.686773 | 5.385271 | 2.424738 |
| H | -3.434324 | 5.449078 | 2.692634 |
| H | -2.398869 | 4.517935 | 3.791661 |
| C | 1.125599 | -1.483389 | -0.786151 |
| C | 1.565093 | -1.573110 | -2.139735 |
| C | 0.538184 | -2.645942 | -0.195328 |
| C | 1.439561 | -2.744072 | -2.860452 |
| H | 2.025352 | -0.709429 | -2.610834 |
| C | 0.394386 | -3.826984 | -0.970262 |

| | | | |
|---|---|---|---|
| H | 0.398586 | -2.687103 | 0.883508 |
| C | 0.845189 | -3.879912 | -2.276629 |
| H | 1.783335 | -2.780209 | -3.890945 |
| H | -0.059111 | -4.700933 | -0.510336 |
| H | 0.729119 | -4.791186 | -2.857285 |

**TS(Tolyl): HF= -2514.52597138 a.u./$N_{imag}$ =1**

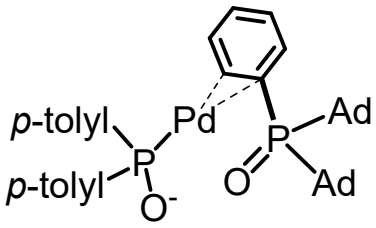



| Atom | x | y | z |
|---|---|---|---|
| Pd | 0.607903 | -0.835746 | -1.127741 |
| P | -1.394430 | 0.466827 | -1.436141 |
| P | 2.225651 | -1.777538 | 0.443503 |
| O | -1.769236 | 0.652048 | -2.920422 |
| O | 2.774320 | -3.165811 | 0.713416 |
| C | -1.139539 | 2.221561 | -0.740563 |
| C | -0.084424 | 2.837087 | -1.692970 |
| H | 0.816599 | 2.204181 | -1.692420 |
| H | -0.475131 | 2.819588 | -2.716913 |
| C | 0.280232 | 4.267862 | -1.271659 |
| H | 1.029601 | 4.673316 | -1.966072 |
| C | 0.852723 | 4.252917 | 0.154021 |
| H | 1.767178 | 3.644112 | 0.181094 |
| H | 1.130060 | 5.271031 | 0.467995 |
| C | -0.192408 | 3.666072 | 1.114685 |
| H | 0.215201 | 3.645855 | 2.135681 |
| C | -1.458362 | 4.539566 | 1.079986 |
| H | -2.207842 | 4.137967 | 1.777302 |
| H | -1.222909 | 5.563141 | 1.409376 |
| C | -2.031139 | 4.560185 | -0.348152 |
| H | -2.937435 | 5.182191 | -0.370568 |
| C | -2.387598 | 3.122432 | -0.772630 |
| H | -2.821007 | 3.112159 | -1.781348 |
| H | -3.151295 | 2.738997 | -0.084206 |

| | | | |
|---|---|---|---|
| C | -0.550424 | 2.234064 | 0.680733 |
| H | 0.339765 | 1.596941 | 0.700777 |
| H | -1.249323 | 1.802430 | 1.405084 |
| C | -0.982140 | 5.143478 | -1.306931 |
| H | -0.738563 | 6.177868 | -1.019031 |
| H | -1.385362 | 5.173975 | -2.328502 |
| C | -2.940158 | -0.285117 | -0.623114 |
| C | -3.034477 | -0.103785 | 0.899574 |
| H | -2.118765 | -0.471879 | 1.377278 |
| H | -3.129504 | 0.959289 | 1.153704 |
| C | -4.263695 | -0.843461 | 1.459578 |
| H | -4.311766 | -0.690422 | 2.547369 |
| C | -5.535727 | -0.281384 | 0.802273 |
| H | -6.426580 | -0.780940 | 1.213233 |
| H | -5.631361 | 0.790862 | 1.027697 |
| C | -5.462939 | -0.489538 | -0.720894 |
| H | -6.371604 | -0.085058 | -1.189602 |
| C | -5.353102 | -1.991347 | -1.025179 |
| H | -6.240215 | -2.523505 | -0.647848 |
| H | -5.313754 | -2.148935 | -2.111910 |
| C | -4.080760 | -2.547978 | -0.368609 |
| H | -3.986628 | -3.620059 | -0.592139 |
| C | -2.850649 | -1.804156 | -0.913005 |
| H | -1.938276 | -2.207508 | -0.451873 |
| H | -2.758888 | -1.962349 | -1.995972 |
| C | -4.231053 | 0.243894 | -1.280625 |
| H | -4.154289 | 0.118454 | -2.366735 |
| H | -4.343449 | 1.318570 | -1.098916 |
| C | -4.159617 | -2.344454 | 1.152569 |
| H | -3.262783 | -2.758904 | 1.628508 |
| H | -5.031033 | -2.876653 | 1.565104 |
| C | 3.389522 | -0.461182 | 0.955407 |
| C | 4.515082 | -0.845986 | 1.682460 |
| H | 4.669350 | -1.902538 | 1.886807 |
| C | 5.422211 | 0.111353 | 2.136408 |
| H | 6.295447 | -0.205376 | 2.703940 |
| C | 5.227311 | 1.469252 | 1.876164 |
| C | 4.096605 | 1.847146 | 1.142395 |

| | | | |
|---|---|---|---|
| H | 3.923028 | 2.899944 | 0.925937 |
| C | 3.192504 | 0.895977 | 0.683576 |
| H | 2.322940 | 1.204305 | 0.105274 |
| C | 6.212537 | 2.509550 | 2.350957 |
| H | 6.774496 | 2.932516 | 1.508992 |
| H | 5.701864 | 3.339669 | 2.852539 |
| H | 6.935795 | 2.082884 | 3.053907 |
| C | 0.856320 | -1.613373 | 1.684781 |
| C | 0.639496 | -0.500342 | 2.497886 |
| H | 1.246680 | 0.391271 | 2.380833 |
| C | -0.356623 | -0.515040 | 3.472842 |
| H | -0.516970 | 0.374118 | 4.080093 |
| C | -1.157581 | -1.639849 | 3.671278 |
| C | -0.919527 | -2.761780 | 2.870023 |
| H | -1.521203 | -3.658004 | 3.012087 |
| C | 0.066398 | -2.751545 | 1.892728 |
| H | 0.247242 | -3.638970 | 1.293349 |
| C | -2.248803 | -1.660542 | 4.712112 |
| H | -3.176341 | -2.074003 | 4.298669 |
| H | -1.966731 | -2.280350 | 5.573163 |
| H | -2.465935 | -0.652657 | 5.081483 |
| C | 2.433720 | -1.757545 | -1.551921 |
| C | 2.219260 | -3.008640 | -2.160610 |
| C | 3.216845 | -0.806036 | -2.226745 |
| C | 2.735968 | -3.280604 | -3.422154 |
| H | 1.665560 | -3.770753 | -1.621997 |
| C | 3.744360 | -1.087223 | -3.486798 |
| H | 3.424841 | 0.154445 | -1.767549 |
| C | 3.500155 | -2.319781 | -4.086810 |
| H | 2.547345 | -4.244814 | -3.887393 |
| H | 4.338860 | -0.336449 | -4.001233 |
| H | 3.907519 | -2.535142 | -5.071763 |

**PC(Tolyl): HF= -2514.55512237 a.u./$N_{imag}$ =0**

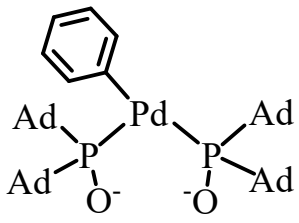



| Atom | x | y | z |
|---|---|---|---|
| Pd | 0.469139 | -0.651372 | -1.537212 |
| P | -1.444471 | 0.790352 | -1.551189 |
| P | 2.492579 | -2.137768 | 0.738045 |
| O | -2.121209 | 1.176262 | -2.881412 |
| O | 3.201130 | -3.375053 | 1.221933 |
| C | -1.050647 | 2.441934 | -0.682057 |
| C | -0.218771 | 3.214254 | -1.734315 |
| H | 0.657434 | 2.609156 | -2.013965 |
| H | -0.818200 | 3.337009 | -2.643736 |
| C | 0.235593 | 4.577209 | -1.191728 |
| H | 0.822565 | 5.100177 | -1.960193 |
| C | 1.098176 | 4.370750 | 0.063601 |
| H | 1.992209 | 3.783261 | -0.189213 |
| H | 1.443953 | 5.339355 | 0.456521 |
| C | 0.274948 | 3.628023 | 1.126358 |
| H | 0.890325 | 3.468696 | 2.024566 |
| C | -0.962170 | 4.466911 | 1.488673 |
| H | -1.547989 | 3.952209 | 2.264479 |
| H | -0.655165 | 5.439070 | 1.903844 |
| C | -1.826462 | 4.673775 | 0.232284 |
| H | -2.713755 | 5.269021 | 0.491730 |
| C | -2.271220 | 3.300280 | -0.307447 |
| H | -2.924599 | 3.417274 | -1.181990 |
| H | -2.854708 | 2.797699 | 0.474868 |
| C | -0.178416 | 2.268576 | 0.569926 |
| H | 0.692045 | 1.652867 | 0.316918 |
| H | -0.723729 | 1.725149 | 1.346992 |
| C | -1.002112 | 5.414725 | -0.831720 |
| H | -0.699011 | 6.403933 | -0.454943 |
| H | -1.613090 | 5.579337 | -1.729958 |
| C | -2.786432 | -0.130682 | -0.555635 |
| C | -2.458452 | -0.305353 | 0.936499 |

| | | | |
|---|---|---|---|
| H | -1.454096 | -0.735209 | 1.050585 |
| H | -2.452078 | 0.670073 | 1.441831 |
| C | -3.507185 | -1.198718 | 1.621562 |
| H | -3.254951 | -1.309285 | 2.685092 |
| C | -4.892075 | -0.543218 | 1.484100 |
| H | -5.653495 | -1.153189 | 1.994387 |
| H | -4.886797 | 0.443455 | 1.970840 |
| C | -5.245860 | -0.390361 | -0.006192 |
| H | -6.233850 | 0.082947 | -0.101282 |
| C | -5.277476 | -1.781409 | -0.656595 |
| H | -6.042611 | -2.409901 | -0.174385 |
| H | -5.547803 | -1.691587 | -1.717809 |
| C | -3.890868 | -2.429365 | -0.526558 |
| H | -3.895908 | -3.417044 | -1.009495 |
| C | -2.843526 | -1.537237 | -1.206129 |
| H | -1.856537 | -2.011977 | -1.137552 |
| H | -3.068192 | -1.427747 | -2.275263 |
| C | -4.188837 | 0.492595 | -0.698669 |
| H | -4.415498 | 0.618233 | -1.764415 |
| H | -4.220414 | 1.491012 | -0.249737 |
| C | -3.527590 | -2.583323 | 0.958568 |
| H | -2.538102 | -3.052654 | 1.055237 |
| H | -4.253867 | -3.236488 | 1.466933 |
| C | 3.658676 | -0.755916 | 0.482999 |
| C | 4.944670 | -0.931298 | 0.997764 |
| H | 5.194596 | -1.873291 | 1.478889 |
| C | 5.892311 | 0.086045 | 0.890547 |
| H | 6.889596 | -0.067046 | 1.298364 |
| C | 5.581597 | 1.295546 | 0.266205 |
| C | 4.292469 | 1.460881 | -0.253743 |
| H | 4.026171 | 2.391099 | -0.752057 |
| C | 3.342179 | 0.452988 | -0.148708 |
| H | 2.347126 | 0.593745 | -0.578426 |
| C | 6.602337 | 2.399288 | 0.137482 |
| H | 6.860613 | 2.573951 | -0.913963 |
| H | 6.214979 | 3.342840 | 0.538922 |
| H | 7.525139 | 2.155760 | 0.674260 |
| C | 1.284535 | -1.564883 | 1.982793 |

| | | | |
|---|---|---|---|
| C | 1.175189 | -0.234977 | 2.392827 |
| H | 1.817531 | 0.525746 | 1.962711 |
| C | 0.236862 | 0.137271 | 3.348456 |
| H | 0.159761 | 1.183932 | 3.636766 |
| C | -0.630051 | -0.799979 | 3.912957 |
| C | -0.496541 | -2.135625 | 3.526308 |
| H | -1.151120 | -2.888702 | 3.960129 |
| C | 0.456594 | -2.517287 | 2.586653 |
| H | 0.569373 | -3.567820 | 2.333655 |
| C | -1.695473 | -0.362261 | 4.885421 |
| H | -2.207334 | -1.220266 | 5.333402 |
| H | -1.272783 | 0.244977 | 5.694420 |
| H | -2.451510 | 0.247710 | 4.375233 |
| C | 1.595953 | -2.415181 | -0.825704 |
| C | 0.621391 | -3.461950 | -0.822017 |
| C | 2.116072 | -1.995341 | -2.084491 |
| C | 0.210658 | -4.064175 | -1.991790 |
| H | 0.212417 | -3.803735 | 0.123656 |
| C | 1.649217 | -2.611175 | -3.277241 |
| H | 3.002951 | -1.368701 | -2.137381 |
| C | 0.722149 | -3.633184 | -3.232620 |
| H | -0.529599 | -4.858812 | -1.955001 |
| H | 2.051896 | -2.274817 | -4.228505 |
| H | 0.376266 | -4.095659 | -4.152940 |

**Intermediate b': HF= -2752.84555076 a.u./$N_{imag}$ =0**



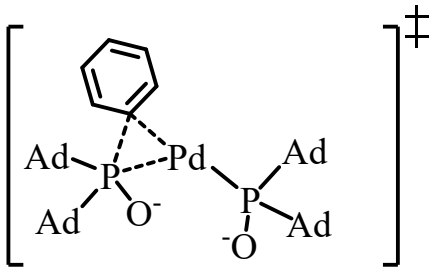

| Atom | x | y | z |
|---|---|---|---|
| Pd | -0.002519 | -0.064440 | 1.041283 |
| P | 2.209398 | 0.443869 | 0.652136 |
| O | 3.175078 | 0.654564 | 1.804625 |
| C | 2.235731 | 2.071347 | -0.309166 |
| C | 1.817001 | 3.132577 | 0.740607 |
| H | 0.793319 | 2.920293 | 1.080237 |

| | | | |
|---|---|---|---|
| H | 2.472472 | 3.056312 | 1.615790 |
| C | 1.883830 | 4.545804 | 0.143098 |
| H | 1.582059 | 5.273769 | 0.908862 |
| C | 0.938258 | 4.638570 | -1.063510 |
| H | -0.094852 | 4.453678 | -0.742570 |
| H | 0.969901 | 5.650927 | -1.494393 |
| C | 1.357817 | 3.601009 | -2.116407 |
| H | 0.674204 | 3.645606 | -2.974004 |
| C | 2.793663 | 3.901923 | -2.574864 |
| H | 3.097980 | 3.181937 | -3.347744 |
| H | 2.850493 | 4.905159 | -3.023648 |
| C | 3.742649 | 3.808107 | -1.368239 |
| H | 4.773638 | 4.010344 | -1.691061 |
| C | 3.674828 | 2.389168 | -0.773696 |
| H | 4.370883 | 2.287566 | 0.067713 |
| H | 3.981440 | 1.674220 | -1.548118 |
| C | 1.294728 | 2.185284 | -1.517341 |
| H | 0.273953 | 1.952515 | -1.223594 |
| H | 1.543526 | 1.456481 | -2.292735 |
| C | 3.323903 | 4.837081 | -0.307000 |
| H | 3.394487 | 5.854707 | -0.719633 |
| H | 4.003771 | 4.784891 | 0.554755 |
| C | 2.871933 | -1.010718 | -0.356168 |
| C | 2.414021 | -1.048387 | -1.825489 |
| H | 1.321198 | -1.012134 | -1.904347 |
| H | 2.794169 | -0.165649 | -2.353918 |
| C | 2.978823 | -2.301296 | -2.522518 |
| H | 2.632049 | -2.313411 | -3.564113 |
| C | 4.515468 | -2.249653 | -2.484945 |
| H | 4.937407 | -3.121157 | -3.007711 |
| H | 4.873756 | -1.351822 | -3.008722 |
| C | 4.991472 | -2.227228 | -1.022484 |
| H | 6.088990 | -2.179446 | -0.992600 |
| C | 4.512236 | -3.499258 | -0.306981 |
| H | 4.933194 | -4.391898 | -0.793707 |
| H | 4.862809 | -3.497081 | 0.734260 |
| C | 2.977615 | -3.548400 | -0.345039 |
| H | 2.620934 | -4.447585 | 0.176008 |

| | | | |
|---|---|---|---|
| C | 2.407471 | -2.304882 | 0.354840 |
| H | 1.311512 | -2.350428 | 0.357730 |
| H | 2.723338 | -2.278442 | 1.405866 |
| C | 4.418939 | -0.988745 | -0.310899 |
| H | 4.748974 | -0.950193 | 0.732602 |
| H | 4.804939 | -0.086195 | -0.796674 |
| C | 2.505879 | -3.576441 | -1.807423 |
| H | 1.413688 | -3.652108 | -1.853298 |
| H | 2.912033 | -4.463470 | -2.316668 |
| C | 0.619057 | -0.375514 | 2.930443 |
| C | 0.519228 | -1.679311 | 3.440066 |
| C | 0.855652 | 0.659769 | 3.847924 |
| C | 0.619353 | -1.938434 | 4.810265 |
| H | 0.366359 | -2.519160 | 2.762979 |
| C | 0.941327 | 0.411106 | 5.216090 |
| H | 0.999473 | 1.673893 | 3.483993 |
| C | 0.823623 | -0.891555 | 5.705851 |
| H | 0.542271 | -2.961816 | 5.173822 |
| H | 1.117372 | 1.235847 | 5.904475 |
| H | 0.902939 | -1.087489 | 6.773054 |
| P | -1.499485 | -0.047318 | -0.919386 |
| O | -1.145106 | 0.197984 | -2.395317 |
| C | -2.883688 | 1.184687 | -0.492683 |
| C | -2.175417 | 2.551697 | -0.327715 |
| H | -1.406565 | 2.480406 | 0.453911 |
| H | -1.661188 | 2.798832 | -1.264768 |
| C | -3.170715 | 3.666294 | 0.021914 |
| H | -2.626193 | 4.613524 | 0.140012 |
| C | -3.886690 | 3.314142 | 1.334437 |
| H | -3.155393 | 3.237603 | 2.150869 |
| H | -4.598430 | 4.107974 | 1.606134 |
| C | -4.624920 | 1.977517 | 1.166127 |
| H | -5.142458 | 1.721381 | 2.100853 |
| C | -5.649712 | 2.098519 | 0.024798 |
| H | -6.191466 | 1.148802 | -0.092712 |
| H | -6.395805 | 2.869650 | 0.268693 |
| C | -4.926632 | 2.454792 | -1.286134 |
| H | -5.661649 | 2.537740 | -2.099054 |

| | | | |
|---|---|---|---|
| C | -3.913784 | 1.345824 | -1.629014 |
| H | -3.381070 | 1.572377 | -2.560405 |
| H | -4.458652 | 0.411856 | -1.797564 |
| C | -3.617919 | 0.865019 | 0.822202 |
| H | -2.895057 | 0.747675 | 1.645031 |
| H | -4.162196 | -0.083061 | 0.735007 |
| C | -4.199093 | 3.796175 | -1.111270 |
| H | -4.921277 | 4.594499 | -0.882450 |
| H | -3.691446 | 4.071868 | -2.045829 |
| C | -2.223909 | -1.809182 | -0.806618 |
| C | -2.283791 | -2.324815 | 0.647287 |
| H | -1.301770 | -2.194972 | 1.128122 |
| H | -3.004030 | -1.752864 | 1.243374 |
| C | -2.663504 | -3.815435 | 0.687119 |
| H | -2.708277 | -4.148196 | 1.732868 |
| C | -4.036630 | -4.007728 | 0.021644 |
| H | -4.331052 | -5.067128 | 0.061052 |
| H | -4.800873 | -3.438130 | 0.569861 |
| C | -3.973174 | -3.529464 | -1.438978 |
| H | -4.956418 | -3.662871 | -1.911783 |
| C | -2.920697 | -4.352828 | -2.196712 |
| H | -3.198943 | -5.417547 | -2.193449 |
| H | -2.875682 | -4.029577 | -3.245845 |
| C | -1.550270 | -4.155949 | -1.531591 |
| H | -0.788617 | -4.729954 | -2.077619 |
| C | -1.184666 | -2.666339 | -1.564976 |
| H | -0.203034 | -2.518730 | -1.101124 |
| H | -1.100781 | -2.305441 | -2.596571 |
| C | -3.595297 | -2.035442 | -1.468284 |
| H | -3.570781 | -1.666790 | -2.502255 |
| H | -4.373831 | -1.473222 | -0.937688 |
| C | -1.608200 | -4.633866 | -0.072712 |
| H | -0.623831 | -4.506857 | 0.400020 |
| H | -1.855277 | -5.705157 | -0.029454 |

**TS(Ad'): HF= -2752.81867798 a.u./$N_{imag}$ =1**



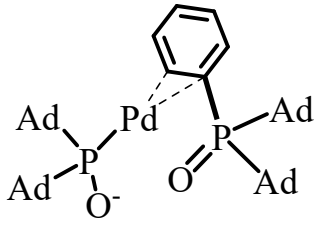

| Atom | x | y | z |
|---|---|---|---|
| Pd | 0.066135 | -0.073836 | 0.939432 |
| P | 2.635398 | -0.019338 | 0.802116 |
| O | 3.851236 | -0.063125 | 1.717204 |
| C | 2.601089 | 1.789945 | 0.191944 |
| C | 1.998046 | 2.648072 | 1.331604 |
| H | 0.957658 | 2.341682 | 1.512684 |
| H | 2.564102 | 2.474235 | 2.256255 |
| C | 2.046879 | 4.144343 | 0.977909 |
| H | 1.600804 | 4.718069 | 1.801834 |
| C | 1.256297 | 4.394373 | -0.313586 |
| H | 0.205648 | 4.132304 | -0.165109 |
| H | 1.291840 | 5.462637 | -0.575649 |
| C | 1.856179 | 3.554949 | -1.451866 |
| H | 1.278959 | 3.716915 | -2.371468 |
| C | 3.316806 | 3.982893 | -1.667120 |
| H | 3.762816 | 3.402292 | -2.487320 |
| H | 3.363091 | 5.043494 | -1.956529 |
| C | 4.111571 | 3.750275 | -0.371312 |
| H | 5.159692 | 4.044050 | -0.522982 |
| C | 4.066755 | 2.257664 | -0.001760 |
| H | 4.629732 | 2.066114 | 0.917146 |
| H | 4.555142 | 1.687444 | -0.796151 |
| C | 1.801902 | 2.056716 | -1.097159 |
| H | 0.765538 | 1.726835 | -0.979124 |
| H | 2.210121 | 1.482448 | -1.936230 |
| C | 3.504310 | 4.578897 | 0.769202 |
| H | 3.548368 | 5.651818 | 0.529307 |
| H | 4.082686 | 4.424821 | 1.690929 |
| C | 2.941109 | -1.240676 | -0.609177 |
| C | 1.689705 | -1.544699 | -1.445719 |
| H | 0.903847 | -1.932002 | -0.793347 |

| | | | |
|---|---|---|---|
| H | 1.265221 | -0.642947 | -1.899574 |
| C | 2.002726 | -2.585025 | -2.529940 |
| H | 1.086472 | -2.773763 | -3.102378 |
| C | 3.098913 | -2.044337 | -3.460148 |
| H | 3.316980 | -2.769304 | -4.258550 |
| H | 2.751294 | -1.121185 | -3.943325 |
| C | 4.369300 | -1.767131 | -2.640227 |
| H | 5.153505 | -1.364095 | -3.296206 |
| C | 4.856116 | -3.070589 | -1.992425 |
| H | 5.088708 | -3.815335 | -2.768150 |
| H | 5.779931 | -2.888134 | -1.425717 |
| C | 3.762096 | -3.599755 | -1.054599 |
| H | 4.106342 | -4.523486 | -0.569375 |
| C | 3.468888 | -2.550127 | 0.030799 |
| H | 2.740660 | -2.958060 | 0.735482 |
| H | 4.371638 | -2.329384 | 0.611619 |
| C | 4.058813 | -0.725605 | -1.548677 |
| H | 4.963691 | -0.510058 | -0.966507 |
| H | 3.750173 | 0.201238 | -2.041294 |
| C | 2.486169 | -3.883332 | -1.865363 |
| H | 1.699726 | -4.276386 | -1.205309 |
| H | 2.685925 | -4.652466 | -2.626466 |
| C | 1.344069 | -0.855253 | 2.326016 |
| C | 0.978238 | -2.214841 | 2.362545 |
| C | 1.524593 | -0.190856 | 3.552433 |
| C | 0.769478 | -2.872609 | 3.575030 |
| H | 0.823933 | -2.763034 | 1.438396 |
| C | 1.311377 | -0.846007 | 4.760692 |
| H | 1.844558 | 0.845300 | 3.558717 |
| C | 0.935424 | -2.190342 | 4.777453 |
| H | 0.469348 | -3.918156 | 3.574216 |
| H | 1.441986 | -0.305626 | 5.695508 |
| H | 0.775031 | -2.701779 | 5.723627 |
| P | -1.672308 | 0.032021 | -0.713398 |
| O | -1.277360 | 0.033010 | -2.205747 |
| C | -2.856080 | 1.510664 | -0.509656 |
| C | -1.920033 | 2.736149 | -0.404023 |
| H | -1.258234 | 2.604199 | 0.462785 |

| | | | |
|---|---|---|---|
| H | -1.278764 | 2.773391 | -1.294825 |
| C | -2.708814 | 4.045777 | -0.268216 |
| H | -2.009143 | 4.890273 | -0.194228 |
| C | -3.573779 | 3.980661 | 0.999369 |
| H | -2.931180 | 3.871801 | 1.884343 |
| H | -4.143989 | 4.913957 | 1.122142 |
| C | -4.532114 | 2.784653 | 0.896880 |
| H | -5.155308 | 2.732695 | 1.800921 |
| C | -5.431809 | 2.958894 | -0.339349 |
| H | -6.132530 | 2.114543 | -0.412653 |
| H | -6.035147 | 3.874226 | -0.241057 |
| C | -4.562247 | 3.028089 | -1.607093 |
| H | -5.208330 | 3.149843 | -2.488098 |
| C | -3.753321 | 1.724934 | -1.745569 |
| H | -3.121880 | 1.744116 | -2.641598 |
| H | -4.449284 | 0.889352 | -1.871546 |
| C | -3.729700 | 1.477413 | 0.755788 |
| H | -3.098909 | 1.318834 | 1.643303 |
| H | -4.438209 | 0.641734 | 0.709490 |
| C | -3.608157 | 4.226869 | -1.499915 |
| H | -4.179561 | 5.164455 | -1.420776 |
| H | -2.990162 | 4.295176 | -2.405774 |
| C | -2.689138 | -1.563324 | -0.422457 |
| C | -2.954665 | -1.852901 | 1.070139 |
| H | -2.006826 | -1.828178 | 1.626746 |
| H | -3.596170 | -1.083102 | 1.512918 |
| C | -3.627631 | -3.227087 | 1.247111 |
| H | -3.817216 | -3.401227 | 2.315435 |
| C | -4.958345 | -3.251973 | 0.475766 |
| H | -5.459551 | -4.221821 | 0.616017 |
| H | -5.633318 | -2.477973 | 0.869134 |
| C | -4.692802 | -3.002978 | -1.018781 |
| H | -5.645056 | -3.014319 | -1.568117 |
| C | -3.770320 | -4.103394 | -1.562976 |
| H | -4.251767 | -5.088100 | -1.461461 |
| H | -3.582780 | -3.939087 | -2.633139 |
| C | -2.443213 | -4.075258 | -0.791055 |
| H | -1.769727 | -4.849714 | -1.184572 |

| | | | |
|---|---|---|---|
| C | -1.783316 | -2.699333 | -0.956770 |
| H | -0.839526 | -2.691345 | -0.397654 |
| H | -1.534953 | -2.503419 | -2.006732 |
| C | -4.023438 | -1.626285 | -1.189054 |
| H | -3.845601 | -1.412453 | -2.251355 |
| H | -4.714258 | -0.862108 | -0.812548 |
| C | -2.707711 | -4.329798 | 0.701199 |
| H | -1.757839 | -4.329535 | 1.254462 |
| H | -3.170793 | -5.317870 | 0.845869 |

**PC(Ad'): HF= -2752.85236064 a.u./$N_{imag}$ =0**



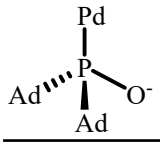

| Atom | x | y | z |
|---|---|---|---|
| Pd | -0.118753 | 0.057747 | 1.171078 |
| P | 3.150201 | -0.051281 | 0.869055 |
| O | 4.501381 | -0.066075 | 1.552814 |
| C | 2.905193 | 1.671525 | 0.124827 |
| C | 2.444049 | 2.645933 | 1.238149 |
| H | 1.462399 | 2.339223 | 1.620601 |
| H | 3.155319 | 2.614583 | 2.073128 |
| C | 2.357736 | 4.088025 | 0.712557 |
| H | 2.023325 | 4.738928 | 1.531722 |
| C | 1.349491 | 4.148210 | -0.441298 |
| H | 0.358073 | 3.852134 | -0.083926 |
| H | 1.266979 | 5.177420 | -0.821399 |
| C | 1.809069 | 3.206705 | -1.563165 |
| H | 1.083707 | 3.229300 | -2.386102 |
| C | 3.190945 | 3.655418 | -2.065476 |
| H | 3.524391 | 2.999458 | -2.882204 |
| H | 3.136487 | 4.676758 | -2.470709 |
| C | 4.197813 | 3.601125 | -0.904176 |
| H | 5.190625 | 3.908833 | -1.260579 |
| C | 4.294508 | 2.164188 | -0.361702 |
| H | 5.009476 | 2.111455 | 0.466329 |

| | | | |
|---|---|---|---|
| H | 4.682903 | 1.513918 | -1.151090 |
| C | 1.903968 | 1.761542 | -1.045326 |
| H | 0.913377 | 1.398061 | -0.743358 |
| H | 2.225884 | 1.125774 | -1.875970 |
| C | 3.737344 | 4.542631 | 0.217155 |
| H | 3.685548 | 5.578146 | -0.150493 |
| H | 4.462002 | 4.524277 | 1.043392 |
| C | 3.111299 | -1.387807 | -0.453409 |
| C | 1.770333 | -1.626065 | -1.185051 |
| H | 0.966211 | -1.857229 | -0.489237 |
| H | 1.421178 | -0.734974 | -1.710149 |
| C | 1.906348 | -2.782838 | -2.186513 |
| H | 0.933162 | -2.924334 | -2.671203 |
| C | 2.968404 | -2.433455 | -3.238549 |
| H | 3.058065 | -3.243078 | -3.978025 |
| H | 2.666857 | -1.527616 | -3.781619 |
| C | 4.317404 | -2.208789 | -2.537789 |
| H | 5.080989 | -1.935363 | -3.279064 |
| C | 4.736159 | -3.497046 | -1.815785 |
| H | 4.840362 | -4.318230 | -2.540267 |
| H | 5.713887 | -3.359748 | -1.333155 |
| C | 3.676721 | -3.846841 | -0.761002 |
| H | 3.974333 | -4.759591 | -0.227010 |
| C | 3.573035 | -2.694748 | 0.250731 |
| H | 2.879985 | -2.976882 | 1.049159 |
| H | 4.543698 | -2.519249 | 0.729013 |
| C | 4.182780 | -1.056049 | -1.525839 |
| H | 5.147835 | -0.858824 | -1.042125 |
| H | 3.896399 | -0.153888 | -2.076750 |
| C | 2.317262 | -4.064064 | -1.445694 |
| H | 1.554105 | -4.320773 | -0.697190 |
| H | 2.379283 | -4.908562 | -2.148060 |
| C | 1.832158 | -0.398020 | 2.126830 |
| C | 0.961193 | -1.540509 | 2.134908 |
| C | 2.000131 | 0.279581 | 3.377112 |
| C | 0.318031 | -1.939927 | 3.340572 |
| H | 0.990066 | -2.278898 | 1.343908 |
| C | 1.345045 | -0.112384 | 4.523833 |

| | | | |
|---|---|---|---|
| H | 2.708600 | 1.097504 | 3.438764 |
| C | 0.490015 | -1.234760 | 4.508632 |
| H | -0.311316 | -2.826286 | 3.316838 |
| H | 1.510752 | 0.434053 | 5.448781 |
| H | -0.015927 | -1.548543 | 5.418381 |
| P | -1.771107 | 0.004456 | -0.521777 |
| O | -1.211123 | -0.054489 | -1.962095 |
| C | -2.949564 | 1.496242 | -0.519873 |
| C | -2.001996 | 2.711125 | -0.380165 |
| H | -1.434803 | 2.616693 | 0.557563 |
| H | -1.272447 | 2.688808 | -1.200875 |
| C | -2.773625 | 4.036995 | -0.391155 |
| H | -2.066835 | 4.872544 | -0.286925 |
| C | -3.765428 | 4.047556 | 0.782626 |
| H | -3.218944 | 3.973287 | 1.733233 |
| H | -4.326533 | 4.994249 | 0.800878 |
| C | -4.733593 | 2.862569 | 0.640930 |
| H | -5.446778 | 2.867972 | 1.477522 |
| C | -5.498513 | 2.989130 | -0.688360 |
| H | -6.206341 | 2.153965 | -0.792425 |
| H | -6.088626 | 3.918284 | -0.697473 |
| C | -4.502689 | 2.979327 | -1.861750 |
| H | -5.052675 | 3.066173 | -2.809665 |
| C | -3.711586 | 1.657990 | -1.850014 |
| H | -2.992432 | 1.618257 | -2.676692 |
| H | -4.408968 | 0.826851 | -2.000545 |
| C | -3.948361 | 1.537090 | 0.647776 |
| H | -3.414669 | 1.411351 | 1.601400 |
| H | -4.663760 | 0.708946 | 0.565659 |
| C | -3.539510 | 4.167290 | -1.716355 |
| H | -4.096930 | 5.116232 | -1.743366 |
| H | -2.831226 | 4.179251 | -2.556291 |
| C | -2.801344 | -1.582607 | -0.288631 |
| C | -3.229903 | -1.815627 | 1.173768 |
| H | -2.350372 | -1.741490 | 1.827571 |
| H | -3.929182 | -1.038677 | 1.504336 |
| C | -3.899875 | -3.193452 | 1.330026 |
| H | -4.206940 | -3.331377 | 2.376432 |

| | | | |
|---|---|---|---|
| C | -5.135544 | -3.271038 | 0.416759 |
| H | -5.636230 | -4.243857 | 0.537314 |
| H | -5.860464 | -2.494998 | 0.702394 |
| C | -4.707550 | -3.072470 | -1.047421 |
| H | -5.591948 | -3.121881 | -1.698706 |
| C | -3.715182 | -4.176715 | -1.441466 |
| H | -4.193018 | -5.164747 | -1.356315 |
| H | -3.410539 | -4.049399 | -2.489509 |
| C | -2.482474 | -4.099288 | -0.528030 |
| H | -1.761831 | -4.878880 | -0.813157 |
| C | -1.824888 | -2.720574 | -0.676194 |
| H | -0.942340 | -2.667699 | -0.024552 |
| H | -1.473965 | -2.560164 | -1.702463 |
| C | -4.040514 | -1.691859 | -1.195781 |
| H | -3.748728 | -1.513750 | -2.239321 |
| H | -4.775829 | -0.923231 | -0.925632 |
| C | -2.910741 | -4.300691 | 0.933979 |
| H | -2.028119 | -4.265125 | 1.588422 |
| H | -3.374693 | -5.290260 | 1.065144 |

**Pd-POAd$_2$: HF= -1324.5957471 a.u./N$_{imag}$ =0**

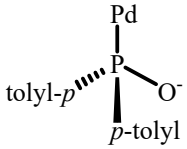



| Atom | x | y | z |
|---|---|---|---|
| Pd | 0.042430 | 2.720128 | -0.280275 |
| P | -0.004542 | 0.721801 | 0.784858 |
| O | -0.006252 | 0.640388 | 2.320534 |
| C | 1.539910 | -0.261922 | 0.227059 |
| C | 2.696936 | 0.399643 | 1.015412 |
| H | 2.729097 | 1.470822 | 0.768065 |
| H | 2.482774 | 0.329543 | 2.088269 |
| C | 4.044310 | -0.260443 | 0.686752 |
| H | 4.842070 | 0.233835 | 1.259707 |
| C | 4.330128 | -0.125035 | -0.816967 |
| H | 4.390857 | 0.937654 | -1.089896 |
| H | 5.299412 | -0.585166 | -1.066300 |
| C | 3.201390 | -0.801946 | -1.609520 |

| | | | |
|---|---|---|---|
| H | 3.398163 | -0.704305 | -2.687082 |
| C | 3.141425 | -2.292055 | -1.231622 |
| H | 2.348589 | -2.791940 | -1.807207 |
| H | 4.091041 | -2.788045 | -1.486556 |
| C | 2.858656 | -2.428557 | 0.274009 |
| H | 2.808695 | -3.493763 | 0.543645 |
| C | 1.510143 | -1.756691 | 0.597114 |
| H | 1.269678 | -1.865929 | 1.662940 |
| H | 0.726514 | -2.273533 | 0.028367 |
| C | 1.857019 | -0.129658 | -1.274608 |
| H | 1.879632 | 0.935761 | -1.543980 |
| H | 1.067425 | -0.586396 | -1.882982 |
| C | 3.985933 | -1.748770 | 1.065405 |
| H | 4.948828 | -2.238144 | 0.849735 |
| H | 3.799888 | -1.851480 | 2.143595 |
| C | -1.566192 | -0.244068 | 0.252641 |
| C | -1.562116 | -0.714484 | -1.210904 |
| H | -1.353089 | 0.139005 | -1.872402 |
| H | -0.765451 | -1.452153 | -1.371343 |
| C | -2.907926 | -1.368439 | -1.576161 |
| H | -2.879642 | -1.701535 | -2.623964 |
| C | -3.145552 | -2.579986 | -0.657788 |
| H | -4.091160 | -3.077687 | -0.924021 |
| H | -2.340369 | -3.316328 | -0.796304 |
| C | -3.182906 | -2.116272 | 0.809026 |
| H | -3.347648 | -2.984844 | 1.463303 |
| C | -4.329873 | -1.111156 | 0.990487 |
| H | -5.294569 | -1.584884 | 0.748738 |
| H | -4.377720 | -0.785346 | 2.038827 |
| C | -4.085362 | 0.100821 | 0.078709 |
| H | -4.892300 | 0.835142 | 0.215013 |
| C | -2.739713 | 0.750012 | 0.435481 |
| H | -2.564488 | 1.631561 | -0.196562 |
| H | -2.750639 | 1.105293 | 1.474484 |
| C | -1.841405 | -1.452005 | 1.172281 |
| H | -1.837414 | -1.111167 | 2.214190 |
| H | -1.045005 | -2.198251 | 1.084479 |
| C | -4.050059 | -0.358285 | -1.387573 |

| | | | |
|---|---|---|---|
| H | -3.894130 | 0.508384 | -2.045123 |
| H | -5.011144 | -0.816327 | -1.669520 |

**Pd-POTolyl$_2$: HF= -1086.30000241 a.u./N$_{imag}$ =0**




| Atom | x | y | z |
|---|---|---|---|
| Pd | 0.026116 | -2.745571 | -0.423693 |
| P | 0.004096 | -0.895314 | 0.849411 |
| O | 0.009515 | -0.912715 | 2.381443 |
| C | 1.381677 | 0.264336 | 0.343210 |
| C | 2.033050 | 1.008171 | 1.326943 |
| H | 1.723858 | 0.870634 | 2.361095 |
| C | 3.055212 | 1.898607 | 0.991792 |
| H | 3.551164 | 2.468843 | 1.777319 |
| C | 3.453692 | 2.071321 | -0.335110 |
| C | 2.801349 | 1.319086 | -1.320199 |
| H | 3.098678 | 1.431340 | -2.363043 |
| C | 1.790018 | 0.424239 | -0.984178 |
| H | 1.312332 | -0.175295 | -1.758364 |
| C | 4.572524 | 3.017079 | -0.704408 |
| H | 5.474482 | 2.470041 | -1.009269 |
| H | 4.287576 | 3.666949 | -1.541151 |
| H | 4.845236 | 3.659227 | 0.140879 |
| C | -1.396212 | 0.239504 | 0.348561 |
| C | -1.864268 | 0.333958 | -0.962247 |
| H | -1.427993 | -0.310537 | -1.724835 |
| C | -2.890311 | 1.217370 | -1.296764 |
| H | -3.237436 | 1.274030 | -2.328312 |
| C | -3.491759 | 2.021335 | -0.324426 |
| C | -3.035898 | 1.909157 | 0.993533 |
| H | -3.499181 | 2.516065 | 1.771920 |
| C | -2.003906 | 1.033601 | 1.325036 |
| H | -1.654012 | 0.939960 | 2.351083 |
| C | -4.596969 | 2.988556 | -0.679184 |
| H | -4.245286 | 4.027971 | -0.638836 |

| | | | |
|---|---|---|---|
| H | -4.975374 | 2.806836 | -1.691680 |
| H | -5.442116 | 2.903696 | 0.015001 |

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