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Room temperature hydrophosphination using a simple iron salen pre-catalyst

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General considerations

Reagents were purchased from Sigma Aldrich or prepared as stated. CH_3CN was dried over CaH_2 (reflux), distilled and then degassed using three freeze-pump-thaw cycles. NMR data was collected at 300, 400 or 500 MHz on Bruker instruments in $CDCl_3$ or CD_3CN at 293 K and referenced to residual protic solvent. Elemental analyses were carried out by Dr S. Boyer at London Metropolitan University. Mass Spectrometry data was collected by the EPSRC NMSF at the University of Swansea.

4-Methoxystyrene, 4-chlorostyrene, 3-methylstyrene and 4-trifluoromethylstyrene were purchased and purified by trap-to-trap distillation then degassed using three freeze-pump-thaw cycles before transferring to the glove box.

Method of synthesis of styrenes

A benzaldehyde derivative (5 mmol) was added to potassium carbonate (1.1 g, 8 mmol) and methyltriphenylphosphonium bromide (2.1 g, 6 mmol) in anhydrous 1,4-dioxane (5 mL) and heated at reflux for 16 h. The reaction mixture was then cooled, filtered and washed with pentane and then concentrated *in vacuo.*

Two methods of isolation can be used:

1. The residue was dissolved in hot pentane, cooled to 0 °C, filtered (to remove triphenylphosphine oxide: sparingly soluble in cold pentane) and washed with cold pentane. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo* to give the styrene derivative.

2. Isolate *via* silica gel column chromatography in 40% EtOAc/pentane (ensuring dioxane is removed prior to isolation).

All styrene derivatives were then vacuum distilled (may require gentle heating) and degassed before transferring to the glove box.

Synthesis of 1

A mixture of salicylaldehyde (2.49 g, 18.3 mmol, 3.5 eq) and ethylenediamine (0.31 g, 5.2 mmol, 1 eq) in dry EtOH (40 mL) was heated at reflux for 2 h. The solution was cooled to 0 °C and filtered, and the resultant yellow solid was washed with cold EtOH. The product was then dried *in vacuo* (1.07g, 77%). Comparable to the commercially available compound (CAS: 94-93-9).

Synthesis of 2a

$Fe(OAc)_2$ (109 mg, 0.6 mmol, 1 eq) was weighed into a flask and dissolved in ethanol (5 mL) leaving a brown solution. To this, a solution of *N*,*N*'-Bis(salicylidene)ethylenediamine (200 mg, 0.7 mmol, 1.2 eq) in ethanol (10 mL) was added forming a red solution. The mixture was then stirred at 80 °C for 2 h. The flask was allowed to cool to RT before filtering off the solid and washing it with ethanol. The dark red solid was dried under vacuum.

Synthesis of 2b

Manipulations carried out under an inert atmosphere (Ar) with rigorous air sensitive handling. $FeCl_2$ (142 mg, 1.12 mmol, 1 eq., 99.9% purity) and *N*,*N*'-Bis(salicylidene)ethylenediamine (300 mg, 1.12 mmol, 1 eq, dried under vacuum) were combined in an ampule. Freshly dried THF (15 mL) was

cannulated onto the mixture which was then stirred at 80 °C for 2 h before cooling to RT. Using a metal cannula with a glass paper frit, the reaction solution was filtered away from the precipitate leaving a straw yellow solid which was then washed with THF (2 x 5 mL). The solid was then dried under vacuum before storing in a glovebox freezer (-30 °C).

Method for the conversion of 2b into 2a

2b (50 mg, 0.155 mmol), stored under an atmosphere of argon, was placed under air, an immediate colour change from yellow to red was observed. The solid was dissolved in MeCN (wet) and filtered using a glass paper cannula to yield **2a** as the analytically pure product (18 mg, 18%). Large quantities of black nanoparticulate material were observed to form and are believed to be the major product in the reaction.

General method for hydrophosphination with 2a

Carried out under an inert argon atmosphere in an M-Braun glove box.

2a (1.8 mg, 1 mol% Fe-centre) was weighed out into a Schlenk tube. CH_3CN (350 µL)[1] was added to this (forming a deep red solution) followed by styrene (1.04 mmol, 1.86 eq) and finally diphenylphosphine (100 µL, 0.57 mmol, 1 eq).[2] After stirring at room temperature for 24 h, the Schlenk tube was placed under vacuum and the excess starting styrene and solvent removed leaving an orange/red oil.[3]

For spectroscopic yields reaction solutions were exposed to air and filtered through a silica gel plug using CH_2Cl_2. This removed the iron residue leaving a colourless oil.[2,4] Solvent was removed by blowing nitrogen over the oil before addition of 45 µL 1,2-dichloroethane as an integration standard. $CDCl_3$ was used as the NMR solvent.[5]

Products were then isolated by column chromatography 1 - 5% EtOAc/pentane. The products oxidised slowly over time (this can be observed in some $^{31}P\{^1H\}$ spectra as a peak at ~20 ppm).

Method for hydrophosphination with radical trap

Carried out as in general method for hydrophosphination. The appropriate quantity of Cumene or TEMPO added to the Schlenk tube after loading the pre-catalyst and CH_3CN. Monitoring of the rate of reaction of styrene (1.04 mmol) and $HPPh_2$ (0.57 mmol) in the presence of cumene (0.57 mmol) was carried out using the 'general method for kinetic studies of hydrophosphination' procedure (below).

Method for hydrophosphination with 2b

Carried out as in general method for hydrophosphination. The appropriate quantity of base added to the Schlenk after loading the pre-catalyst and CH_3CN. Colour change – yellow to colourless upon addition of NEt_3. Addition of diphenylphosphine to NaO^tBu and an orange solution formed which gradually returned to colourless after 30 mins.

Method for hydrophosphination without catalyst

Carried out as in general method for hydrophosphination (without catalyst).

Addition of diphenylphosphine to NaO^tBu solution an orange solution formed which did not go back to colourless until the solution was opened to air.

General method for kinetic studies of hydrophosphination.

2a (1.8 mg, 0.01 eq) was weighed out into a vial. CD_3CN (350 µL) was added to this (forming a deep red solution) followed by diphenylphosphine (100 µL, 0.056 mmol). This solution was syringed into a

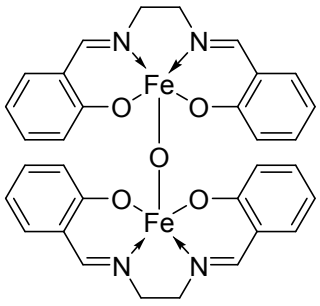
vial containing an integration standard - 1,3,5-trimethoxybenzene (3.4 mg).[6] This solution was then syringed into a J-Young NMR tube and sealed. Styrene derivative was syringed into a separate J-Young NMR tube and sealed. The two J-Young NMR tubes were then attached to a Schlenk line through vacuum transfer apparatus. The samples were degassed using three freeze-pump-thaw cycles. With the CD_3CN containing tube kept frozen, the styrene was allowed to warm to RT and transferred on top of the CD_3CN solution. Once all the styrene was transferred, the sample was removed from liquid N_2 and placed in acetone/solid CO_2 the NMR tube was then refilled with argon and kept frozen. When ready to collect kinetic data the sample was allowed to defrost – the sample was inverted to speed up this process. Once all solid had melted the outside of the tube was wiped down to remove condensation/ ice forming on the outside and placed in the spectrometer.

Table S1: Spectroscopic yields with various solvents using the general conditions for HP with **2a**.

Entry	Solvent	Yield (%)
1	No solvent	98
2	THF	84
3	Toluene	76
4	CH_2Cl_2	98
5	MeCN	89
6	Methanol	92

Products

2a



Dark red solid (143 mg, 72%). IR (solid) ν 3049, 1610, 1597, 851 cm^{-1}; m.p. (decomp.) 296 °C.

Crystal structure obtained, with compound data being comparable to other published methods.[7]

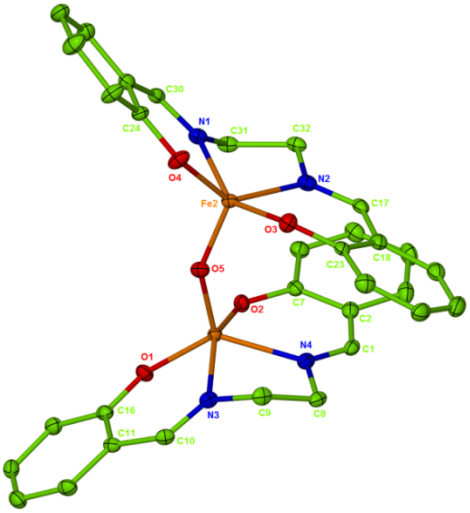


Table S2: Crystal data and structure refinement for **2a**.

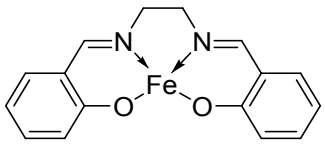
Identification code	k14rlw1
Empirical formula	C32 H28 Fe2 N4 O5
Formula weight	660.28
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.7340(3)Å alpha = 67.142 (1)°
	b = 10.8150(2)Å beta = 85.858 (1)°
	c = 13.7380(4)Å gamma = 73.156 (2)°
Volume	1405.06 (6) $Å^3$
Z	2
Density (calculated)	1.561 Mg/m^3
Absorption coefficient	1.083 mm^{-1}
F(000)	680
Crystal size	0.15 x 0.1 x 0.07 mm
Theta range for data collection	3.71 to 24.99 °.
Index ranges	-12<=h<=12; -12<=k<=12; -16<=l<=16
Reflections collected	20793
Independent reflections	4911 [R(int) = 0.0669]
Reflections observed (>2sigma)	3673
Data Completeness	0.992
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.989 and 0.899
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4911 / 0 / 388
Goodness-of-fit on F^2	1.035

Final R indices [I>2sigma(I)]	R1 = 0.0404 *wR*2 = 0.0837
R indices (all data)	R1 = 0.0672 *wR*2 = 0.0933
Largest diff. peak and hole	0.319 and -0.365 eÅ^{-3}

2a Elemental analysis:

Element	**Expected (%)**	**Found (1)**	**Found (2)**
Carbon	59.66	59.47	59.45
Hydrogen	4.38	4.30	4.26
Nitrogen	8.70	8.61	8.55

2b

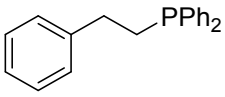


Yellow solid (276 mg, 77%). IR (solid) ν 2966, 1638, 1606 cm^{-1}; m.p. (decomp.) 174 °C. Compound data is comparable to other published data.[8]

2b Elemental Analysis:

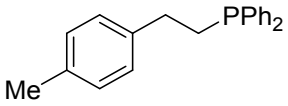
Element	**Expected (%)**	**Found (1)**	**Found (2)**
Carbon	58.21	58.29	58.22
Hydrogen	4.27	4.12	4.16
Nitrogen	8.49	8.11	8.17

3a (Table 1, Entry 1)



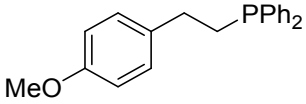
Colourless oil, 147 mg (88%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.47 – 7.15 (m, 14H), 2.73 - 2.67 (m, 2H), 2.39 - 2.33 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 142.7 (d, *J* = 12.7 Hz), 138.6 (d, *J* = 19.2 Hz), 132.8 (d, *J* = 13.2 Hz), 128.9, 128.6 (d, *J* = 6.2 Hz), 128.2, 128.0, 126.1, 32.3 (d, *J* = 3.3 Hz), 30.2 (d, *J* = 7.7 Hz); ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.0; IR (solid) ν 3055, 2936, 1603, 1585, 1481 cm^{-1}; HRMS (EI) 291.1303 (calcd.), 291.1297 (obs.). Unknown impurity present at 20.1 ppm.[9]

3b (Table 1, Entry 2)



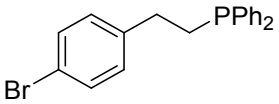
Colourless oil, 136 mg (79%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.58 - 7.55 (m, 4H), 7.43 - 7.41 (m, 6H), 7.17 (s, 4H), 2.83 - 2.75 (m, 2H), 2.48 - 2.40 (m, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 139.6 (d, *J* = 13.4 Hz), 138.5 (d, *J* = 12.7 Hz), 135.6, 132.8 (d, *J* = 18.3 Hz), 129.2, 128.7, 128.6 (d, *J* = 6.5 Hz), 128.1, 31.8 (d, *J* = 17.6 Hz), 30.4 (d, *J* = 12.5 Hz), 21.13; ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.1; IR (solid) ν 3052, 2915, 1590, 1516, 1482, 1437, 801, 862, 738, 693 cm^{-1}; HRMS (EI) $[M + H]^+$ 305.1454 (calcd.), 305.1452 (obs.)

3c (Table 1, Entry 3)



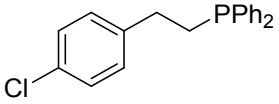
Colourless oil, 163 mg (89%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.63 - 7.60 (m, 4H), 7.46 - 7.43 (m, 6H), 7.23 (d, 2H, *J* = 8.7, 2.1 Hz), 6.99 - 6.92 (dd, 2H, *J* = 8.6, 2.3 Hz), 3.90 (s, 3H), 2.84 - 2.81 (m, 2H), 2.52 - 2.46 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 158.0, 138.7 (d, *J* = 13.0 Hz), 134.6 (d, *J* = 13.3 Hz), 132.8 (d, *J* = 18.3 Hz), 129.1, 128.6, 128.5 (d, *J* = 6.5 Hz), 113.9, 55.3, 31.2 (d, *J* = 17.7 Hz), 30.4 (d, *J* =12.7 Hz); ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.3; IR (solid) ν 3053, 2934, 2904, 2833, 1610, 1584, 1510, 1464, 818, 734, 695, 717 cm^{-1}; HRMS (EI) $[M + H]^+$ 321.1403 (calcd.), 321.1403 (obs.)

3d (Table 1, Entry 4)



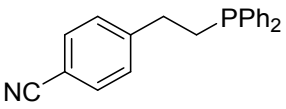
Colourless oil, 136 mg (65%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.54 - 7.33 (m, 12H), 7.09 (d, 2H, *J* = 8.3 Hz), 2.78 - 2.70 (m, 2H), 2.43 - 2.37 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 141.5 (d, *J* = 12.7 Hz), 138.3 (d, *J* = 13.0 Hz), 132.8 (d, *J* = 18.3 Hz), 131.5, 130.1, 128.8, 128.6 (d, *J* = 6.5 Hz), 119.9, 31.7 (d, *J* = 18.0 Hz), 30.1 (d, *J* = 13Hz); ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.4; IR (solid) ν 3052, 2933, 1487, 1433, 842, 799, 736, 693 cm^{-1}; HRMS (EI) $[M + H]^+$ 369.0402 (calcd.), 369.0397 (obs.) Unknown impurity present at 20.1 ppm.[9]

3e (Table 1, Entry 5)



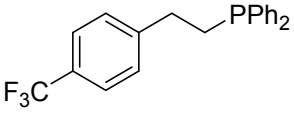
Colourless oil, 136 mg (74%, 114 h). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.50 - 7.47 (m, 4H), 7.38 - 7.31 (m, 6H), 7.25 (dd, 2H, *J* = 8.6, 2.1 Hz), 7.10 (dd, 2H, *J* = 8.6, 2.1 Hz), 2.76 -2.68 (m, 2H), 2.39 - 2.34 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 141.1 (d, *J* 13.0 Hz), 138.4 (d, *J* = 13.0 Hz), 132.9 (d, *J* = 18.6 Hz), 130.9 (d, *J* = 9.3 Hz), 129.7, 128.8, 128.7, 128.6 (d, *J* = 2.8 Hz), 31.7 (d, *J* = 18.0 Hz), 30.3 (d, *J* = 13.3 Hz); ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.2; IR (solid) ν 3064, 2898, 1591, 1492, 1435, 843, 801, 736, 720, 693 cm^{-1}; HRMS (EI) $[M + H]^+$ 325.0907 (calcd.), 325.0903 (obs.)

3f (Table 1, Entry 6)



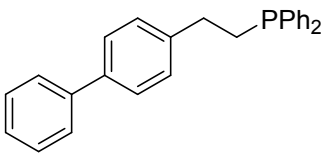
Colourless oil, 77 mg (43%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.56 (d, 2H, *J* = 8.4 Hz), 7.49 - 7.43 (m, 4H), 7.38 - 7.35 (m, 6H), 7.28 (d, 2H, *J* = 8.4 Hz), 2.92 - 2.67 (m, 2H), 2.47 - 2.31 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 148.1 (d, *J* = 12.7 Hz), 137.9 (d, *J* = 12.2 Hz), 132.8 (d, *J* = 18.6 Hz), 132.4, 130.8 (d, *J* = 9.3Hz), 129.1 (d, *J* = 12.1 Hz), 128.7 (d, *J* = 6.8 Hz) 119.1, 110.0, 32.5 (d, *J* = 17.3 Hz), 29.7 (d, *J* = 13.4 Hz); ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.4; IR (solid) ν 3060, 2943, 2905, 2227, 1605, 1506, 1480, 1435, 822, 741, 695 cm^{-1}; HRMS (EI) $[M + H]^+$ 316.1250 (calcd.), 316.1245 (obs.)

3g (Table 1, Entry 7)



Colourless oil, 170 mg (83%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7. 51 - 7.41 (m, 6H), 7.37 - 7.30 (m, 6H), 7.24 (d, 2H, *J* = 8.1 Hz), 2.80 - 2.72 (m, 2H), 2.38 - 2.33 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 146.7 (d, *J* = 12.7 Hz), 138.3 (d, *J* = 12.7 Hz), 132.8 (d, *J* = 18.6 Hz), 128.7, 128.53. 128.45, 128.0 (d, *J* = 10.5 Hz), 126.1, 125.3 (q, *J* = 3.7 Hz), 32.2 (d, *J* = 18.3 Hz), 30.0 (d, *J* = 13.4 Hz); ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.3; IR (solid) ν 3049, 2922, 1590, 1567, 1480, 1434, 1323, 844, 820, 748, 735, 695 cm^{-1}; HRMS (EI) $[M + H]^+$ 359.1171 (calcd.), 359.1166 (obs.) Unknown impurity present at 20.1 ppm.[9]

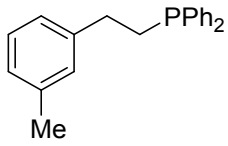
3h (Table 1, Entry 8)



Colourless oil, 122 mg (58% at 60°C). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.70 - 7.33 (m, 19H), 2.90 - 2.85 (m, 2H), 2.55 - 2.50 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ 141.7 (d, *J* = 13.0 Hz), 141.1, 139.0, 138.5 (d, *J* = 12.4 Hz), 132.7 (d, *J* = 18.6 Hz), 128.7, 128.62, 128.56, 128.50 (d, *J* = 6.5 Hz),

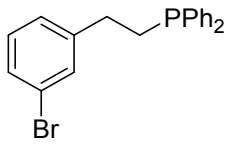
127.2, 127.03, 126.98, 31.9 (d, *J* =17.7 Hz), 30.2 (d, *J* = 12.4 Hz); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -14.9; IR (solid) ν 3050, 2944, 2903, 1586, 1481, 1433, 821, 744, 693 cm^{-1}; HRMS (EI) $[M + H]^+$ 367.1610 (calcd.), 367.1606 (obs.)

3i (Table 1, Entry 9)



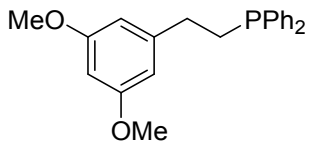
Colourless oil, 164 mg (95%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.63 - 7.60 (m, 4H), 7.46 - 7.42 (m, 6H), 7.29 (dd, 1H, *J* = 8.1, 7.2 Hz), 7.13 - 7.09 (m, 3H), 2.88 - 2.80 (m, 2H), 2.53 - 2.42 (m, 2H), 2.44 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 142.6 (d, *J* = 13.4 Hz), 138.6 (d, *J* =13.0 Hz), 138.0, 134.0 (d, *J* = 16.8 Hz), 132.8 (d, *J* = 18.6 Hz), 129.0, 128.6 (*J* = 8.1 Hz), 128.4 (d, *J* = 5.3 Hz), 126.8, 125.2, 32.2, 30.3, 21.5; $^{31}P\{^{1}H\}$ NMR (121.5 MHz , 298 K, $CDCl_3$) δ -14.8; IR (solid) ν 3052, 2917, 2856, 1608, 1586, 1480, 1433, 1377, 735, 695 cm^{-1}; HRMS (EI) $[M + H]^+$ 305.1454 (calcd.), 305.1454 (obs.) Unknown impurity present at 20.1 ppm.[9]

3j (Table 1, Entry 10)



Colourless oil, 202 mg (96%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.55 - 7.52 (m, 4H), 7.42 - 7.36 (m, 8H), 7.18 - 7.15 (m, 2H), 2.80 - 2.72 (m, 2H), 2.44 - 2.39 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 144.9 (d, *J* = 13.4 Hz), 138.1 (d, *J* = 12.4 Hz), 132.8 (d, *J* =18.6 Hz), 131.2, 130.0, 129.2, 128.8, 128.6 (d, *J* = 6.9 Hz), 126.9, 122.5, 31.9 (d, *J* = 18.3 Hz), 30.0 (d, *J* = 12.8 Hz); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.2; IR (solid) ν 3057, 2943, 2923, 2830, 1583, 1567, 1491, 1475, 1464, 1431, 885, 796, 775, 739, 695 cm^{-1}; HRMS (EI) 369.0402 (calcd.), 369.0406 (obs.) Unknown impurity present at 20.1 ppm.[9]

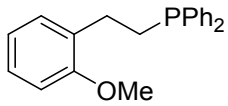
3k (Table 1, Entry 11)



Colourless oil, 178 mg (89%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.54 - 7.42 (m, 4H), 7.41 - 7.39 (m, 6H), 6.41 (d, 2H, *J* = 2.3 Hz), 6.37 (t, 1H, *J* = 2.3 Hz), 3.81 (s, 6H) 2.78 - 2.70 (m, 2H) 2.47 - 2.41 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 160.9, 145.1 (d, *J* = 13.4 Hz), 138.5, 133.0 (d, *J* = 18.6 Hz),

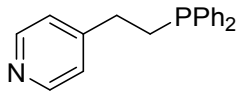
128.8, 128.6 (d, *J* = 6.5 Hz), 106.3, 98.0, 55.3, 32.6 (d, *J* = 18.0 Hz), 30.0 (d, *J* =12.4 Hz); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -14.9; IR (solid) ν 3048, 2920, 2849, 1591, 1567, 1470, 1433, 843, 782 cm^{-1}; HRMS (EI) 351.1508 (calcd.), 351.1505 (obs.)

3l (Table 1, Entry 12)



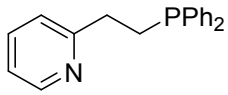
Colourless oil, 113 mg (62%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.64 - 7.59 (m, 2H), 7.47 - 7.42 (m, 6H), 7.32 - 7.23 (m, 2H), 7.01 (app. td, 1H, *J* = 7.4, 1.0 Hz), 6.93 (d, 1H, *J* = 8.1 Hz) 3.88 (s, 3H), 2.94 - 2.86 (m, 2H), 2.52 - 2.47 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 157.3, 138.7 (d, *J* = 12.7 Hz), 132.8 (d, *J* = 18.3 Hz), 131.0 (d, *J* = 13.6 Hz), 129.6, 128.4 (d, *J* = 6.5 Hz), 127.4, 120.4, 110.2, 55.1, 28.4 (d, *J* = 12.1 Hz), 27.2 (d, *J* = 18.3 Hz); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -14.5; IR (solid) ν 3059, 2948, 2922, 2902, 2830, 1600, 1583, 1490, 1464, 1432, 852, 742, 696 cm^{-1}; HRMS (EI) $[M + H]^+$ 321.1403 (calcd.), 321.1404 (obs.)

3m (Table 1, Entry 13)



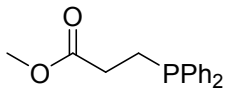
Colourless oil, 125 mg (75%, after 72 h). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 8.46 (dd, 2H, *J* = 4.3, 1.7 Hz), 7.47 - 7.42 (m, 4H), 7.36 - 7.31 (m, 6H), 7.07 (dd, 2H, *J* = 4.3, 1.7 Hz), 2.76 -2.58 (m, 2H), 2.44 - 2.25 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 151.4 (d, *J* = 13.0 Hz), 149.9, 138.1 (d, *J* = 12.7 Hz), 132.8 (d, *J* = 18.6 Hz), 129.0, 128.7 (d, *J* = 6.8 Hz), 123.7, 31.6 (d, *J* = 18.7 Hz), 29.1 (d, *J* = 13.3 Hz); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -15.2; IR (solid) ν 3051, 2928, 1599, 1559, 1480, 1433, 850, 801, 737, 694 cm^{-1}; HRMS (EI) $[M + H]^+$ 292.1250 (calcd.), 292.1246 (obs.) Unknown impurity present at 20.1 ppm.[9]

3n (Table 1, Entry 14)



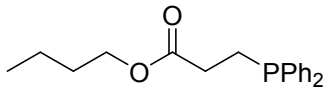
Colourless oil, 143 mg (86%, after 72 h). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 8.56 (d, 1H, *J* = 4.1 Hz), 7.62 - 7.43 (m, 5H), 7.43 - 7.29 (m, 6H), 7.20 - 7.03 (m, 2H), 3.05-2.82 (m, 2H), 2.64 - 2.48 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 161.9 (d, *J* = 13.3 Hz), 149.5, 138.5 (d, *J* = 13.0 Hz), 136.4, 132.9 (d, *J* = 18.6 Hz), 128.7, 128.6 (d, *J* = 6.8 Hz), 122.8, 121.3, 34.7 (d, *J* = 17.7 Hz), 28.1 (d, *J* = 12.4 Hz); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -14.6; IR (solid) ν 3046, 2920, 2949, 1590, 1567, 1470, 1479, 1433, 843, 781, 749, 735, 723, 697, cm^{-1}; HRMS (EI) $[M + H]^+$ 292.1250 (calcd.), 292.1249 (obs.)

3o (Table 1, Entry 15)



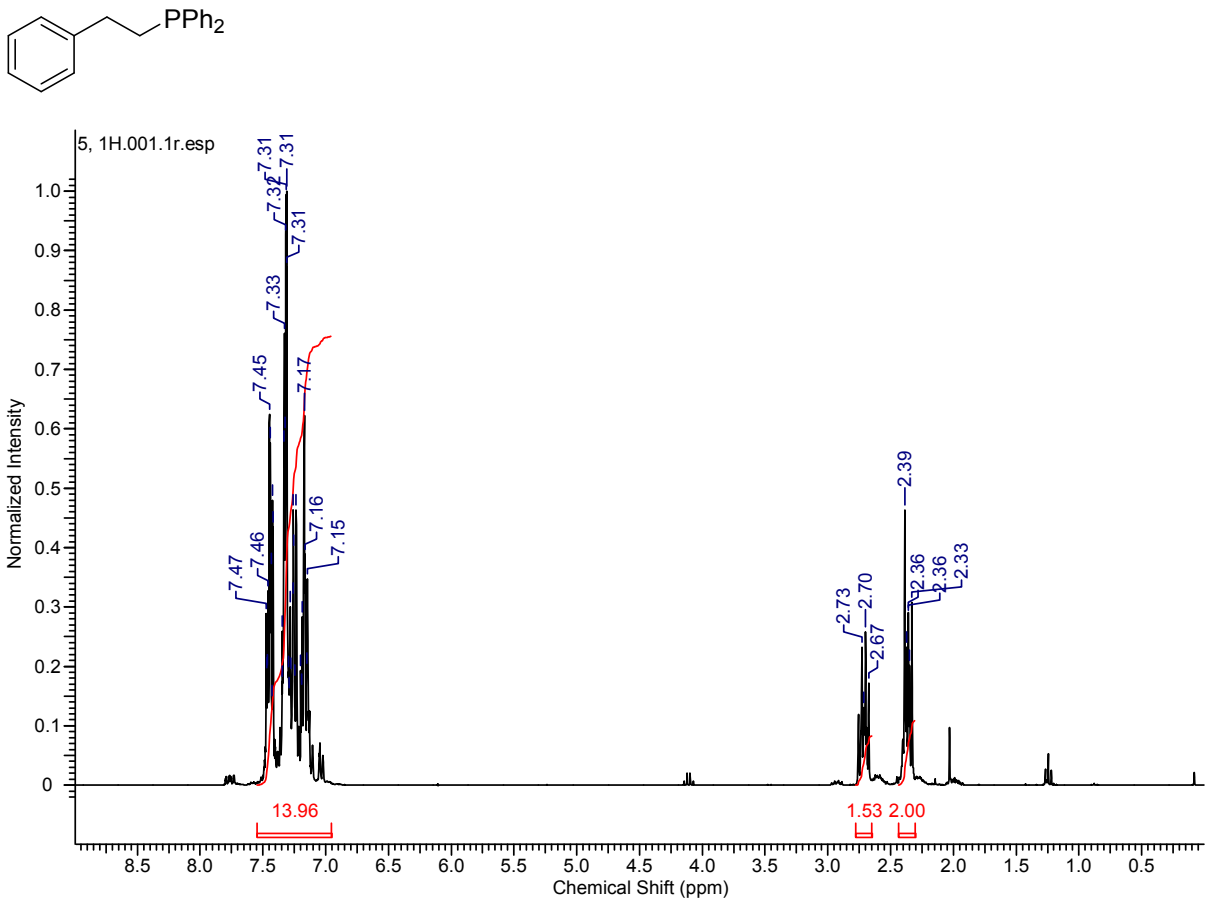
Colourless oil, 120 mg (69%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.50 - 7.47 (m, 4H), 7.37 - 7.35 (m, 6H), 3.66 (s, 3H), 2.45 - 2.42 (m, 4H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 173.5 (d, *J* = 14.9 Hz), 137.7 (d, *J* =12.1 Hz), 132.7 (d, *J* = 18.3 Hz), 128.8, 128.5 (d, *J* = 6.5 Hz), 51.7, 30.5 (d, *J* = 19.3 Hz), 22.9 (d, *J* = 11.5 Hz); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -14.9; IR (solid) ν 3054, 2950, 1735, 1585, 1481, 1433, 1354, 848, 736, 694 cm^{-1}; HRMS (EI) $[M + H]^+$ 273.1039 (calcd.), 273.1040 (obs.)

3p (Table 1, Entry 16)

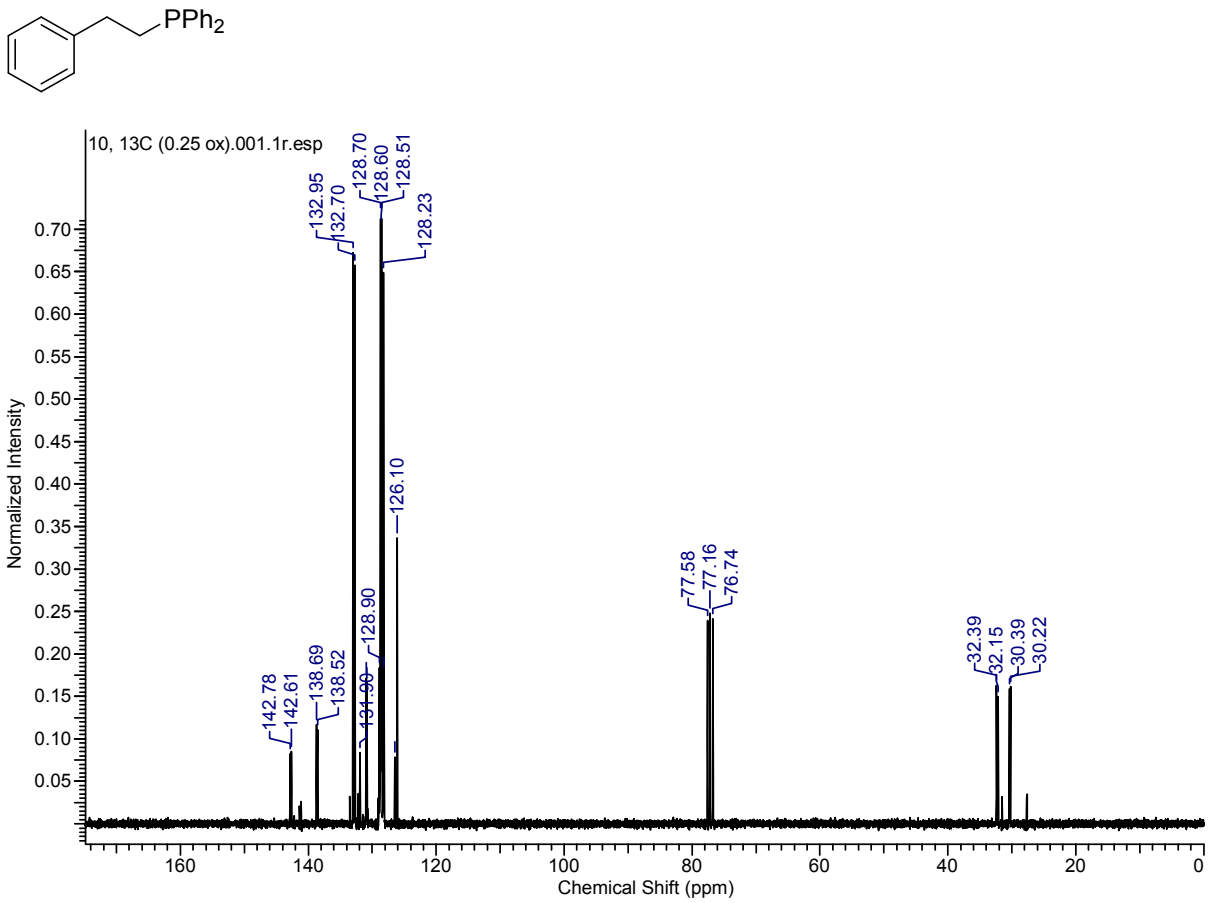


Colourless oil, 142 mg (76%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ 7.49 - 7.46 (m, 4H), 7.37 - 7.35 (m, 6H), 4.08 (t, 2H, *J* = 6.7 Hz), 2.44 - 2.39 (m, 4H), 1.61 (app. tt, 2H, *J* = 15.5, 6.7 Hz), 1.37 (app. tq, 2H, *J* = 15.5, 7.4 Hz), 0.95 (t, 3H, *J* = 7.4 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ 173.3 (d, *J* = 15.2 Hz), 137.8 (d, *J* = 18.6 Hz), 132.8 (d, *J* = 18.6 Hz), 128.9, 128.6 (d, *J* = 6.8 Hz), 64.6, 30.9, 30.7, 23.0 (d, *J* = 11.5 Hz), 19.2, 13.8; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) δ -14.9; IR (solid) ν 3054, 2958, 2872, 1731, 1586, 1481, 1465, 1433, 1348, 737, 696 cm^{-1}; HRMS (EI) 315.1508 (calcd.), 315.1509 (obs.)

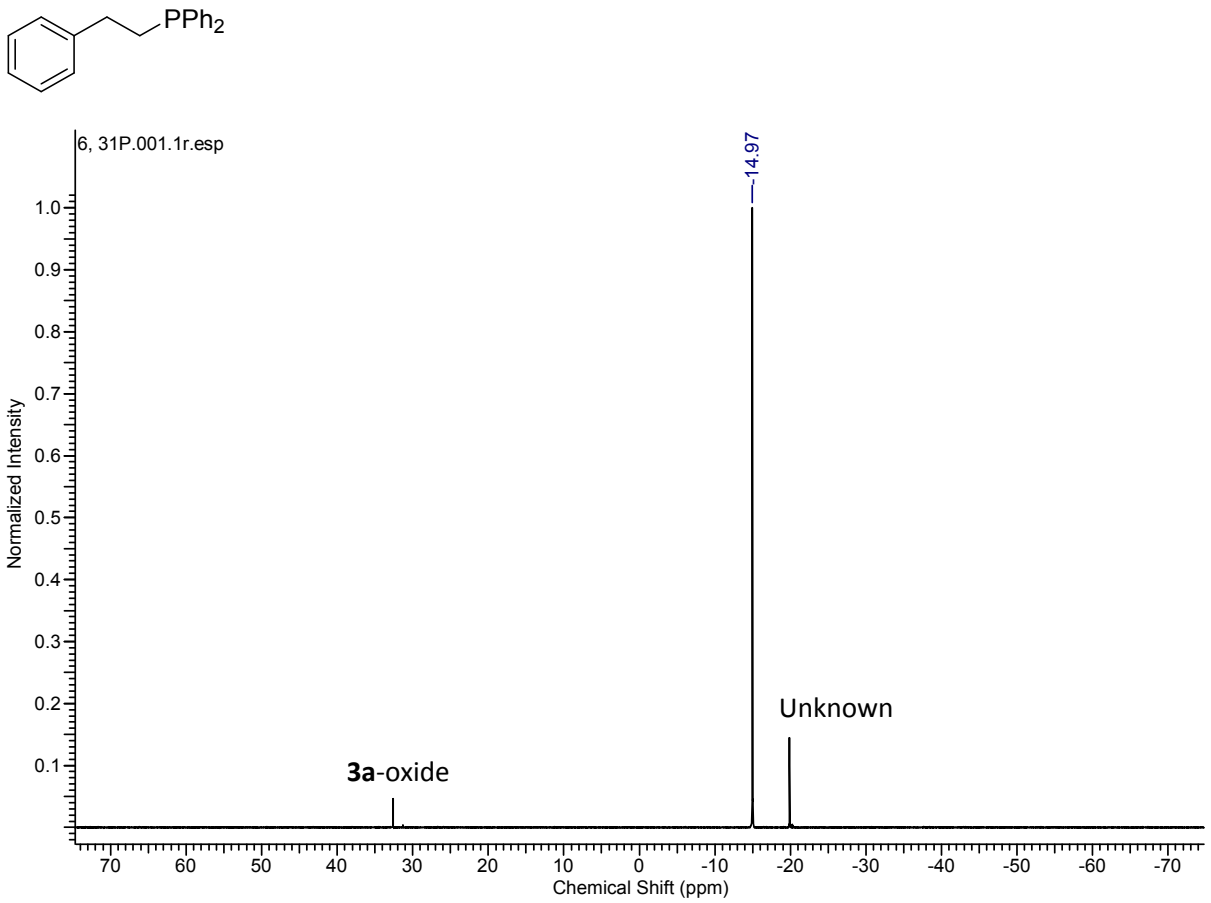
^{1}H NMR, **3a** (Table 1, Entry 1)



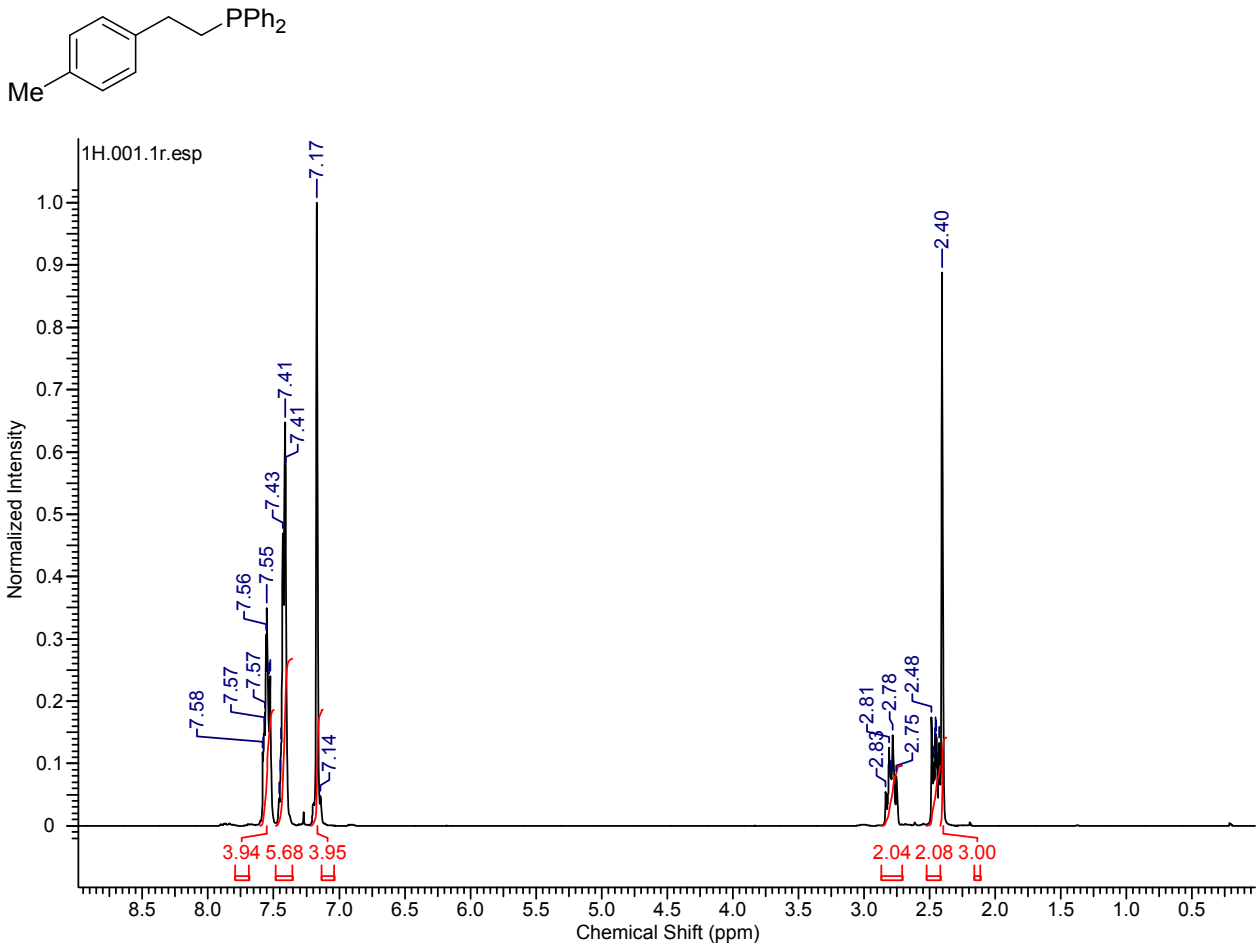
$^{13}C\{^{1}H\}$ NMR, **3a** (Table 1, Entry 1)



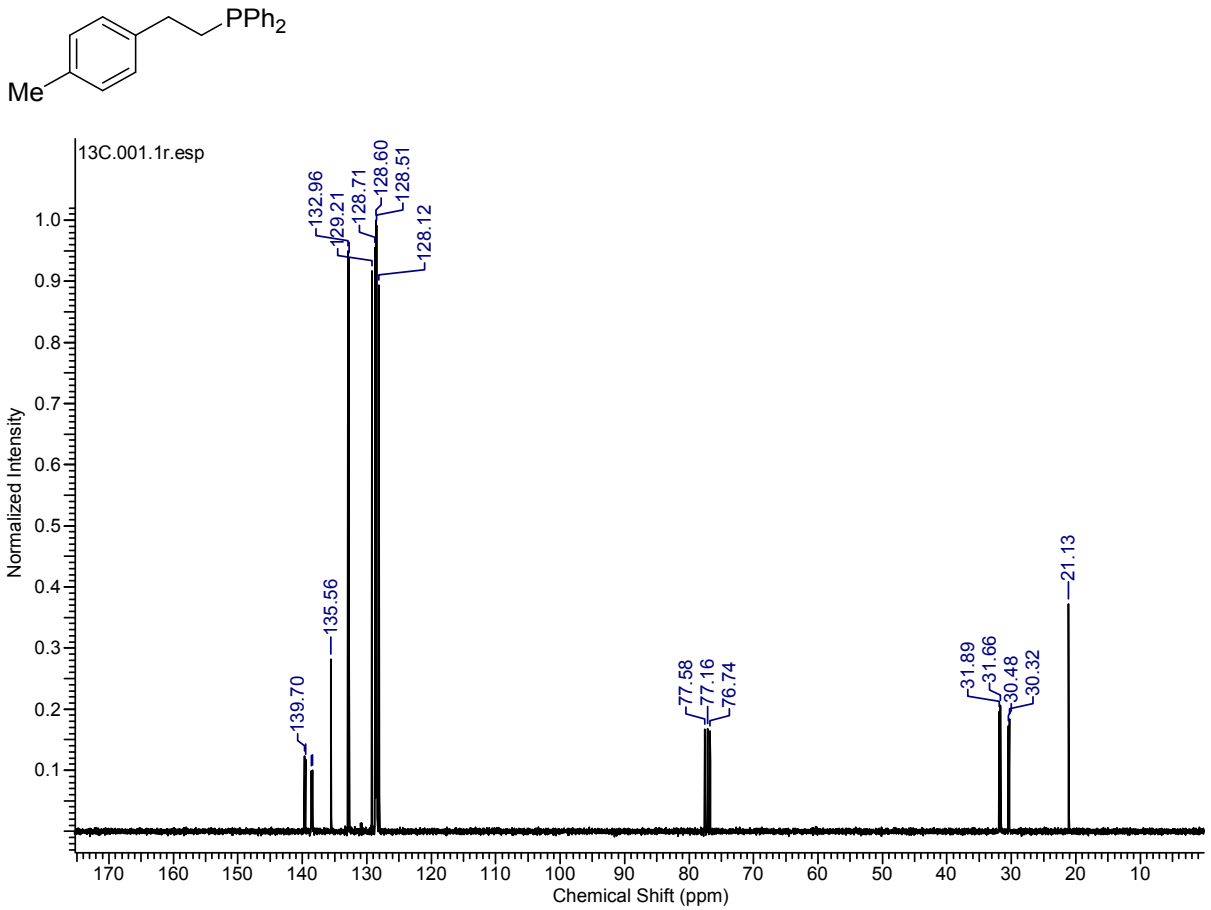
$^{31}P\{^{1}H\}$ NMR, **3a** (Table 1, Entry 1)



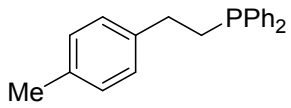
^{1}H NMR, **3b** (Table 1, Entry 2)

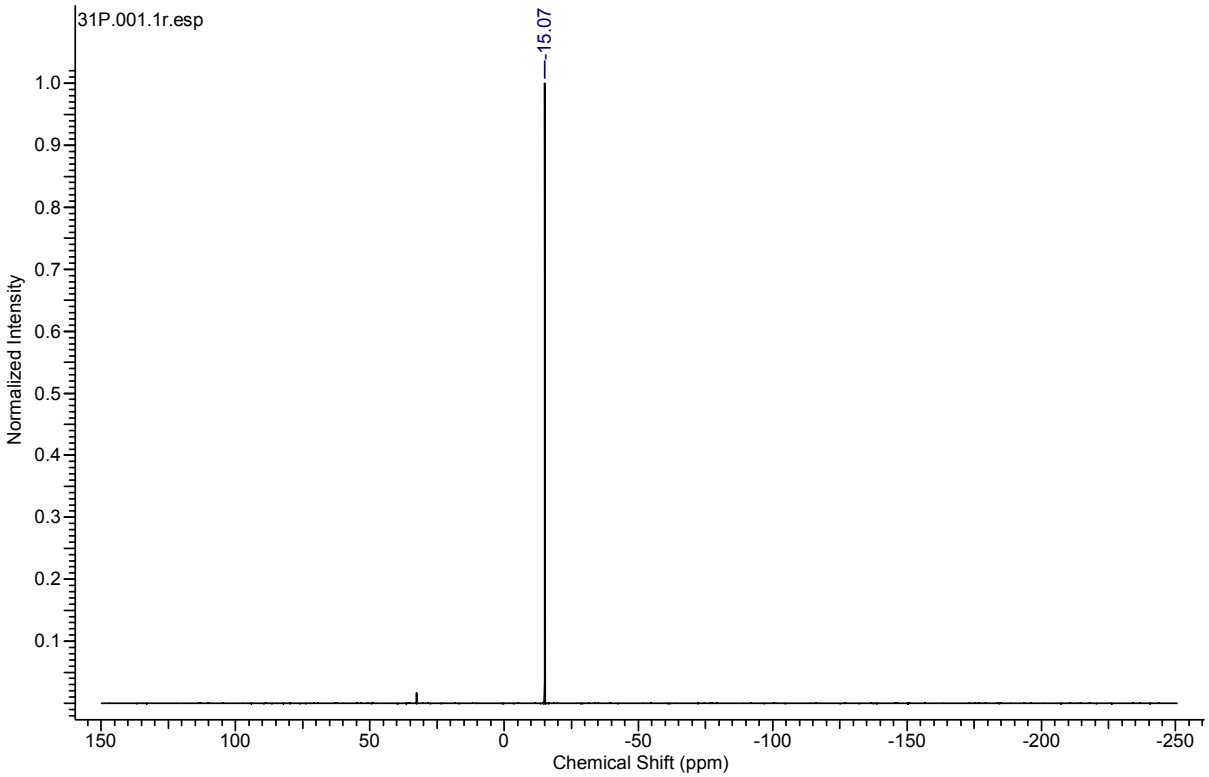


$^{13}C\{^{1}H\}$ NMR, **3b** (Table 1, Entry 2)

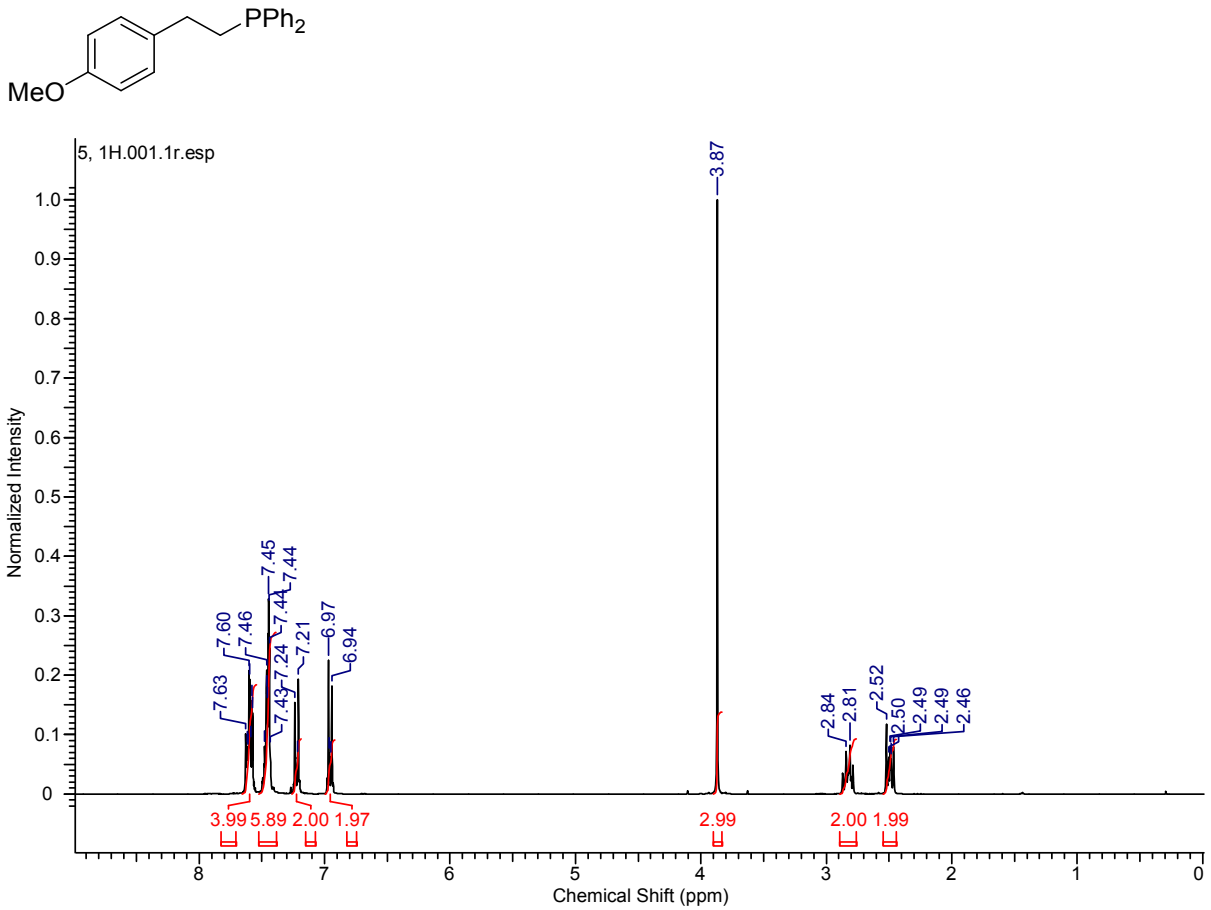


$^{31}P\{^{1}H\}$ NMR, **3b** (Table 1, Entry 2)

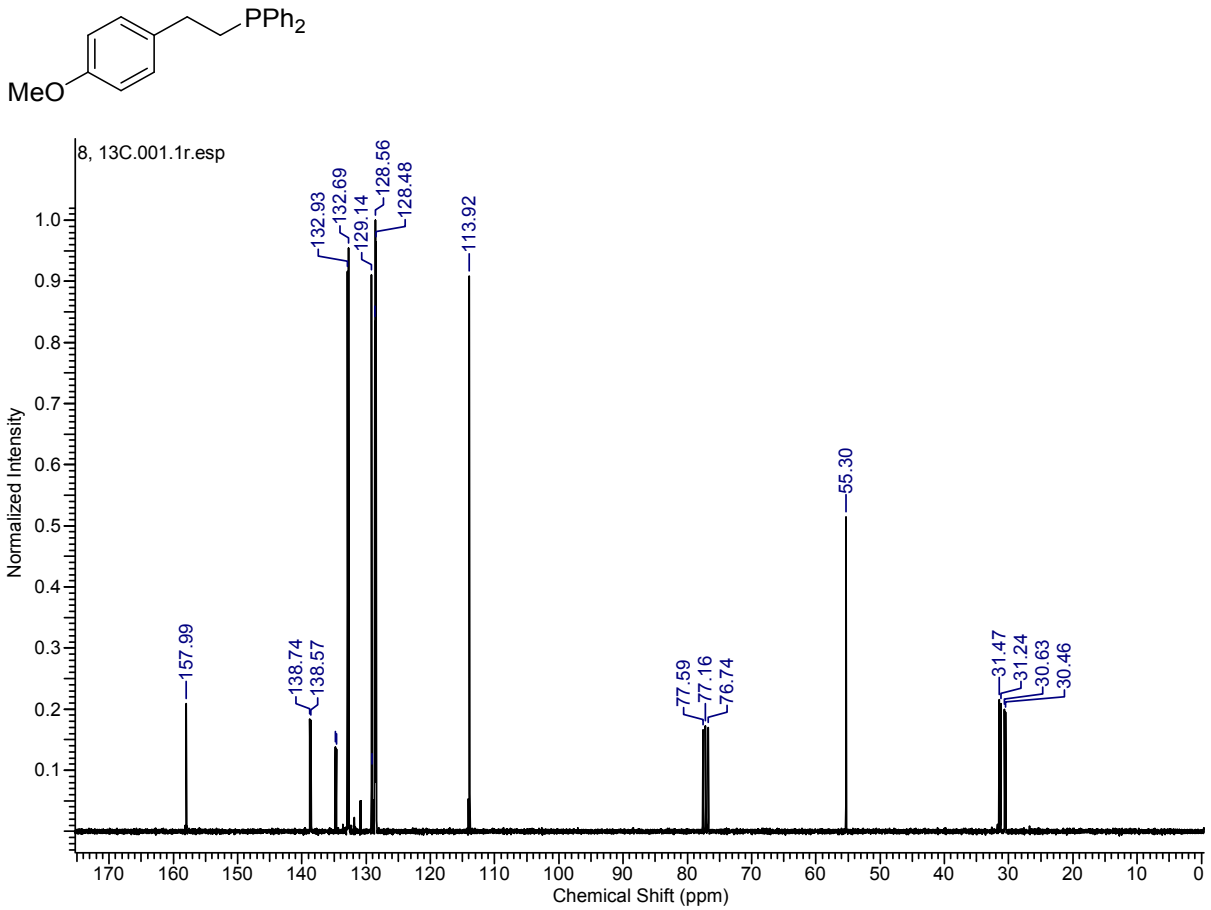




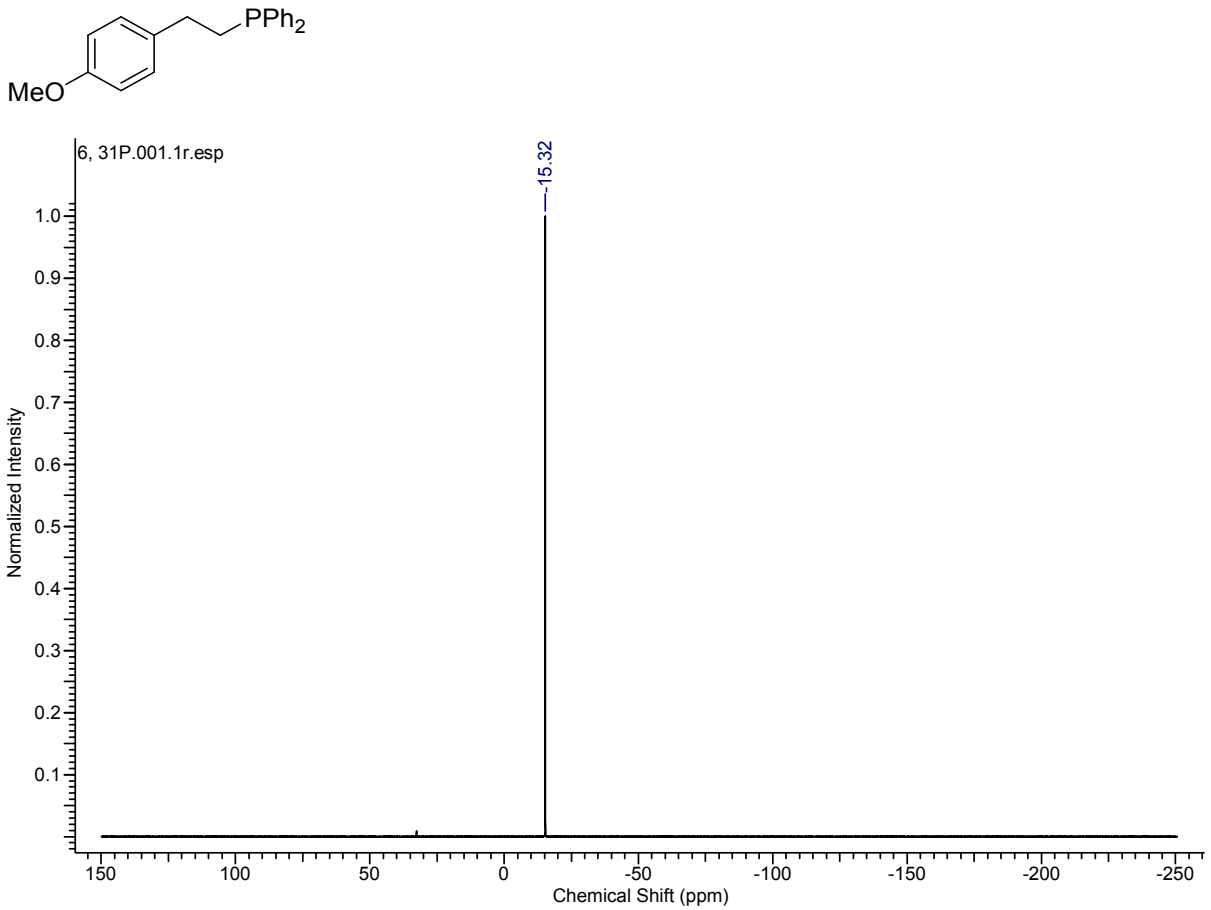
^{1}H NMR, **3c** (Table 1, Entry 3)



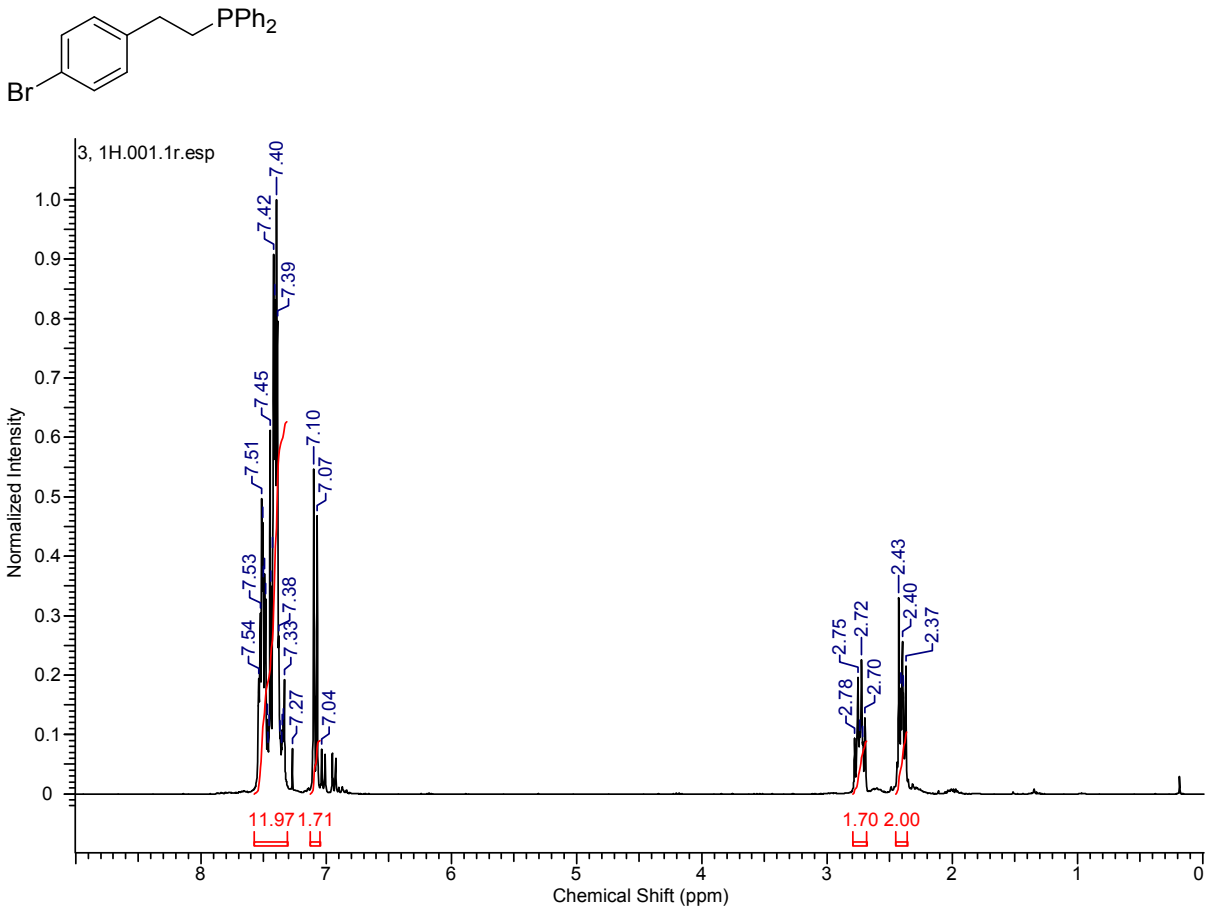
$^{13}C\{^{1}H\}$ NMR, **3c** (Table 1, Entry 3)



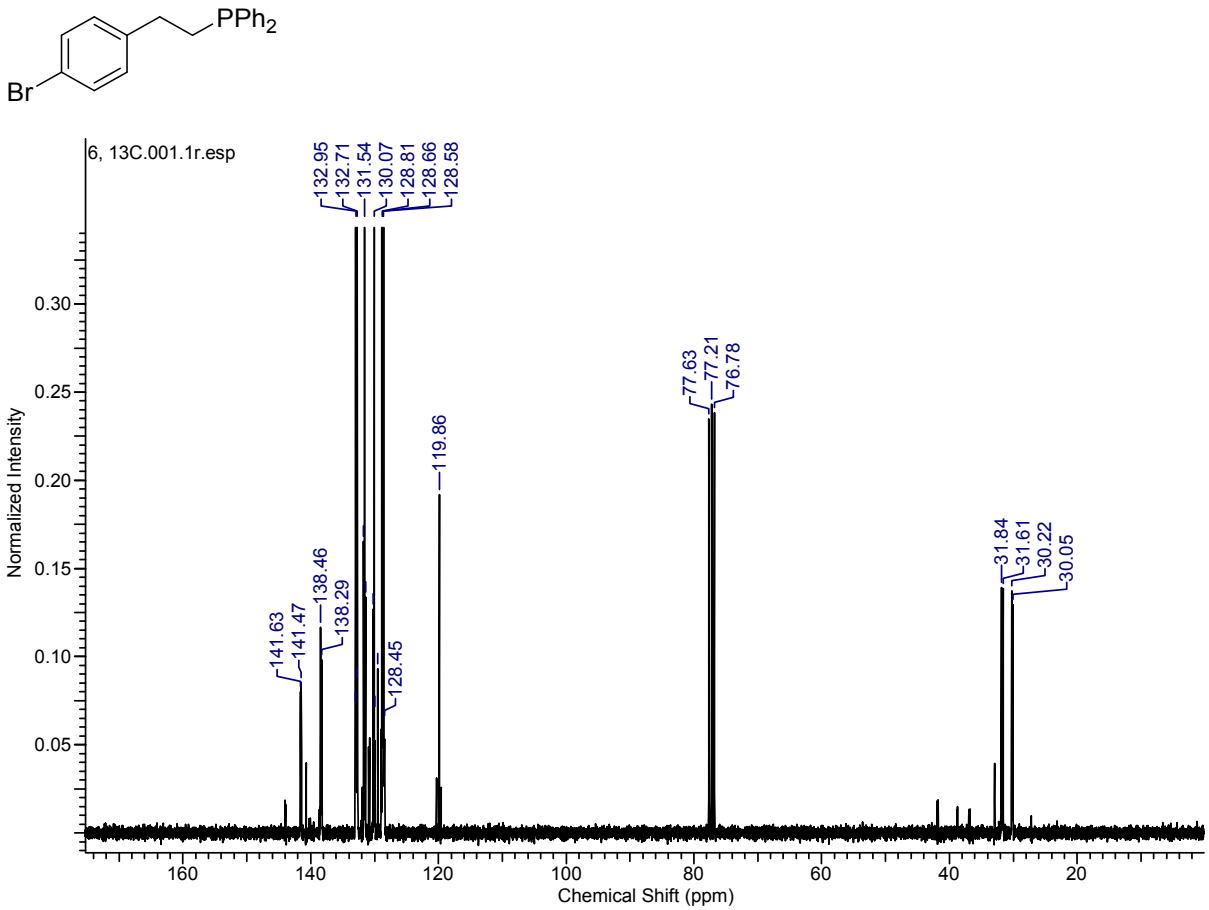
$^{31}P\{^{1}H\}$ NMR, **3c** (Table 1, Entry 3)



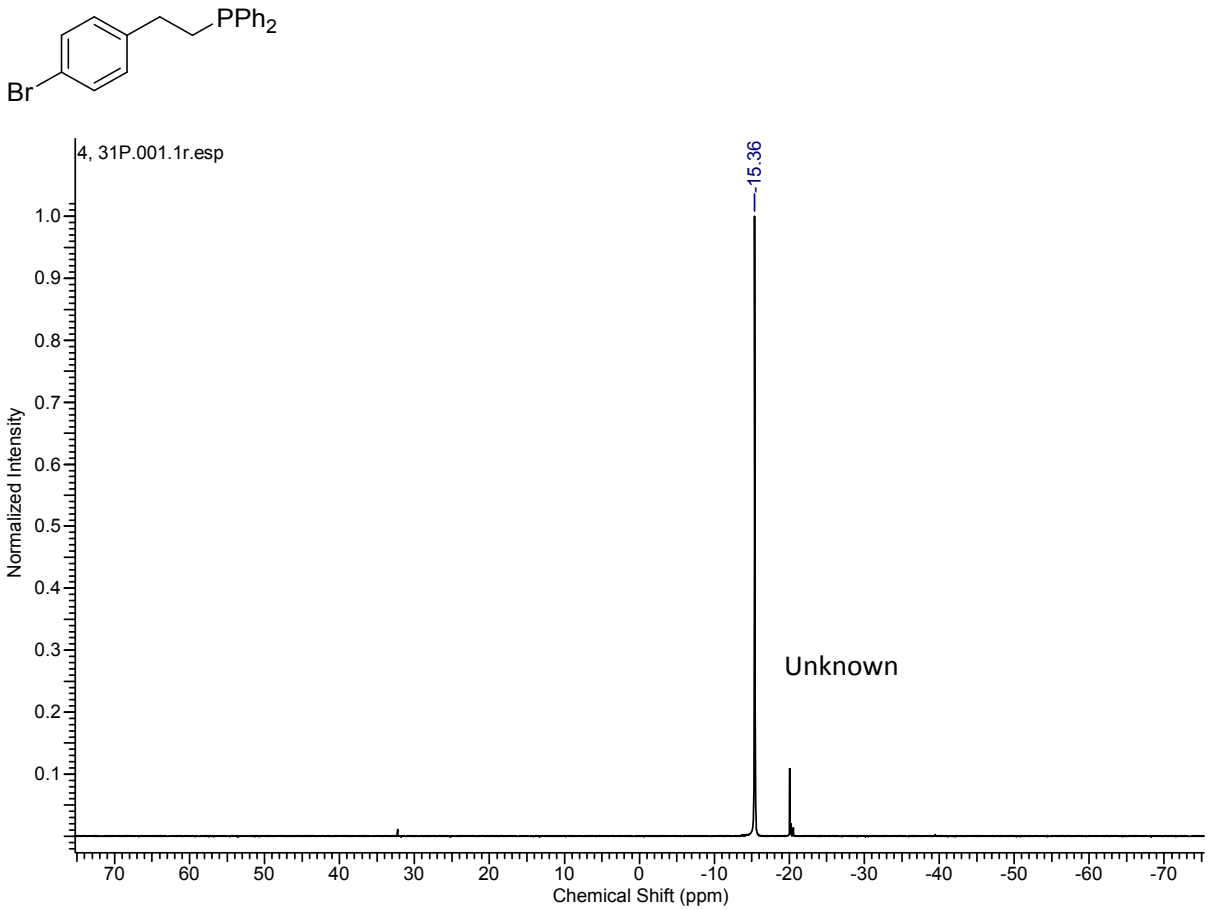
^{1}H NMR, **3d** (Table 1, Entry 4)



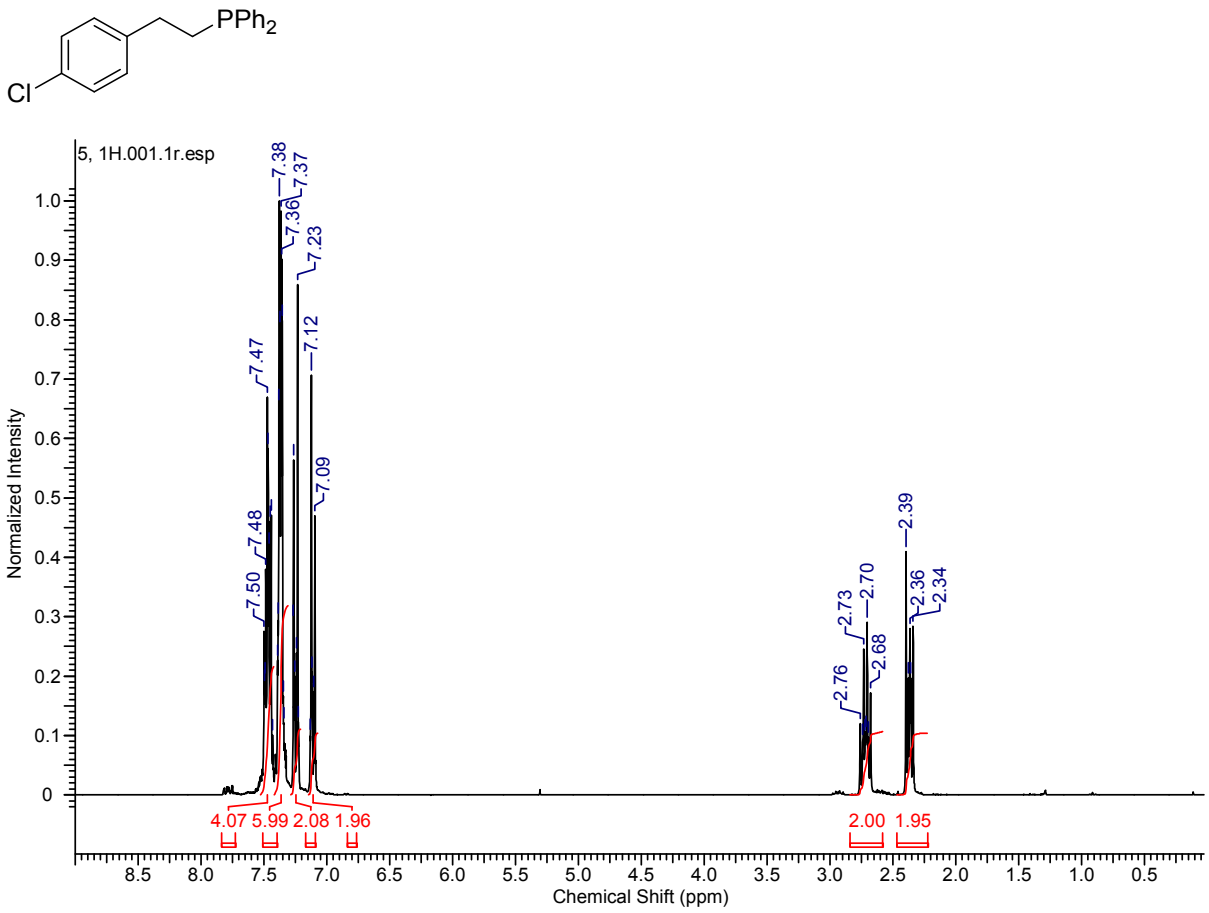
$^{13}C\{^{1}H\}$ NMR, **3d** (Table 1, Entry 4)



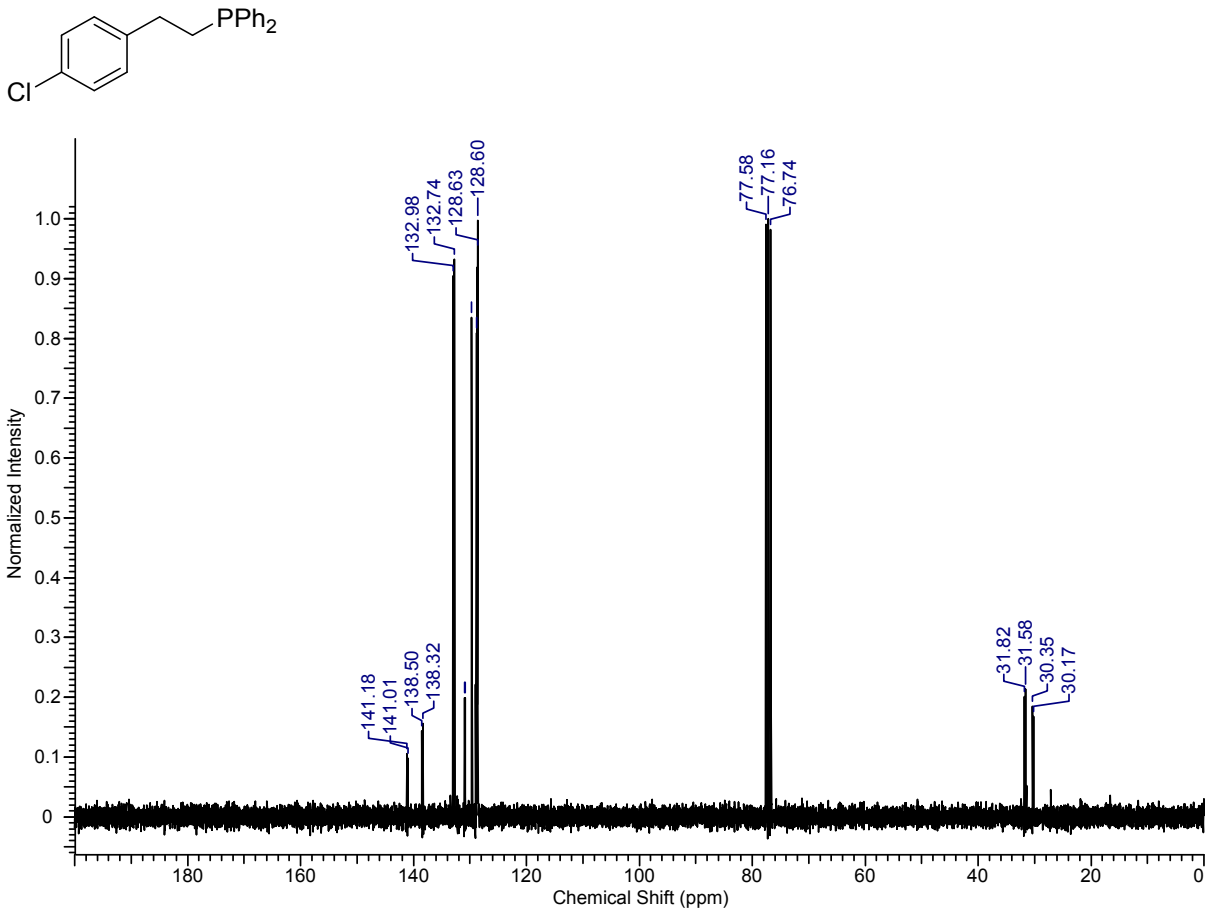
$^{31}P\{^{1}H\}$ NMR, **3d** (Table 1, Entry 4)



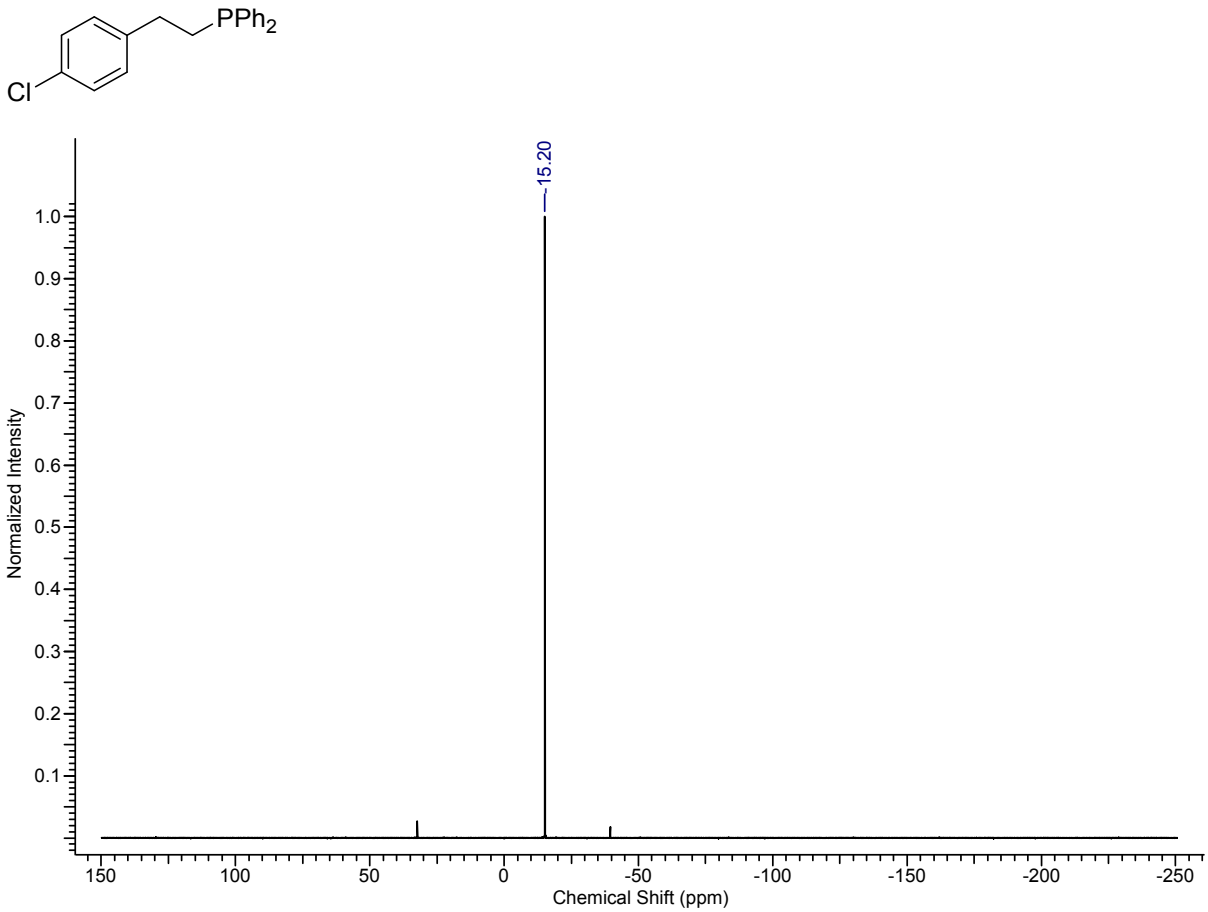
^{1}H NMR, **3e** (Table 1, Entry 5)



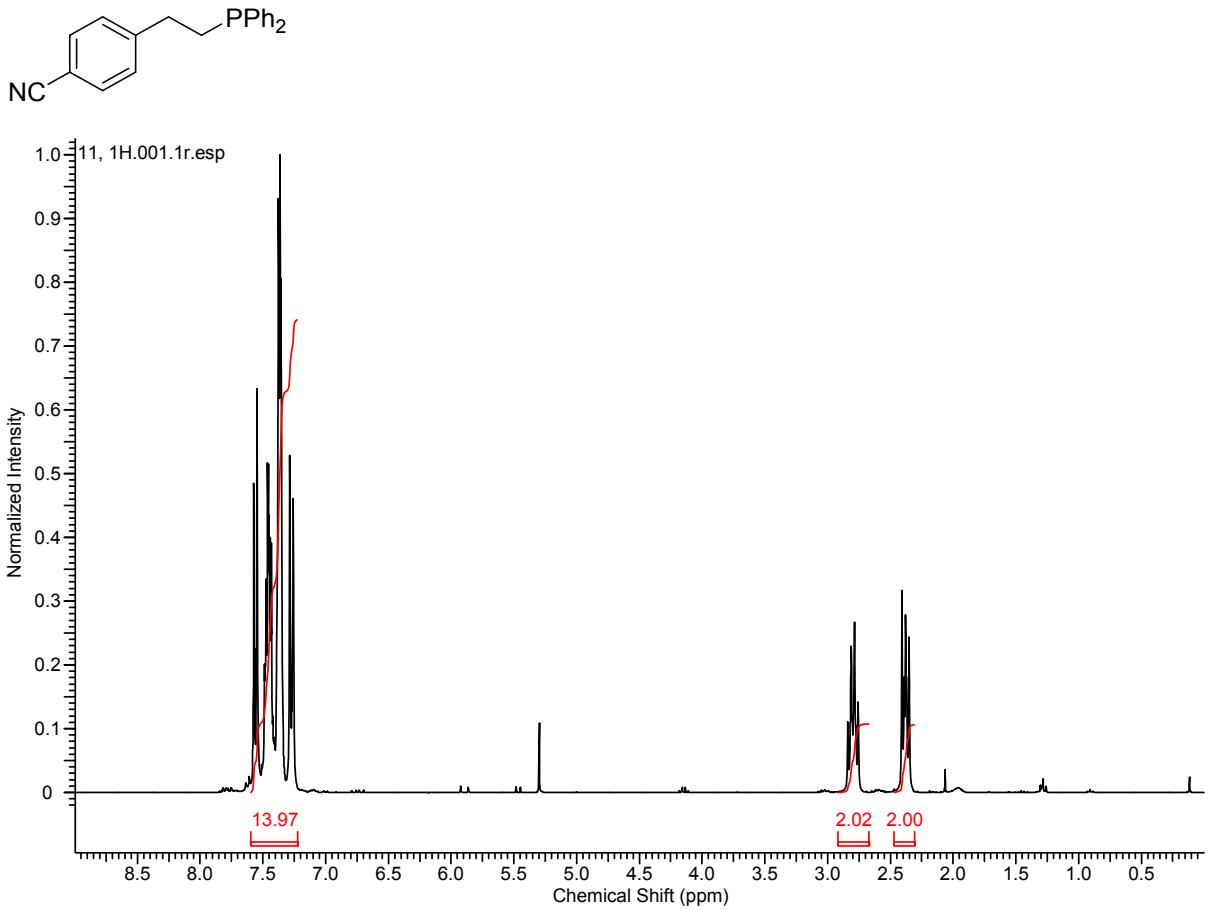
$^{13}C\{^{1}H\}$ NMR, **3e** (Table 1, Entry 5)



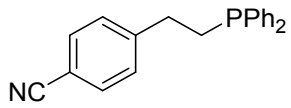
$^{31}P\{^{1}H\}$ NMR, **3e** (Table 1, Entry 5)

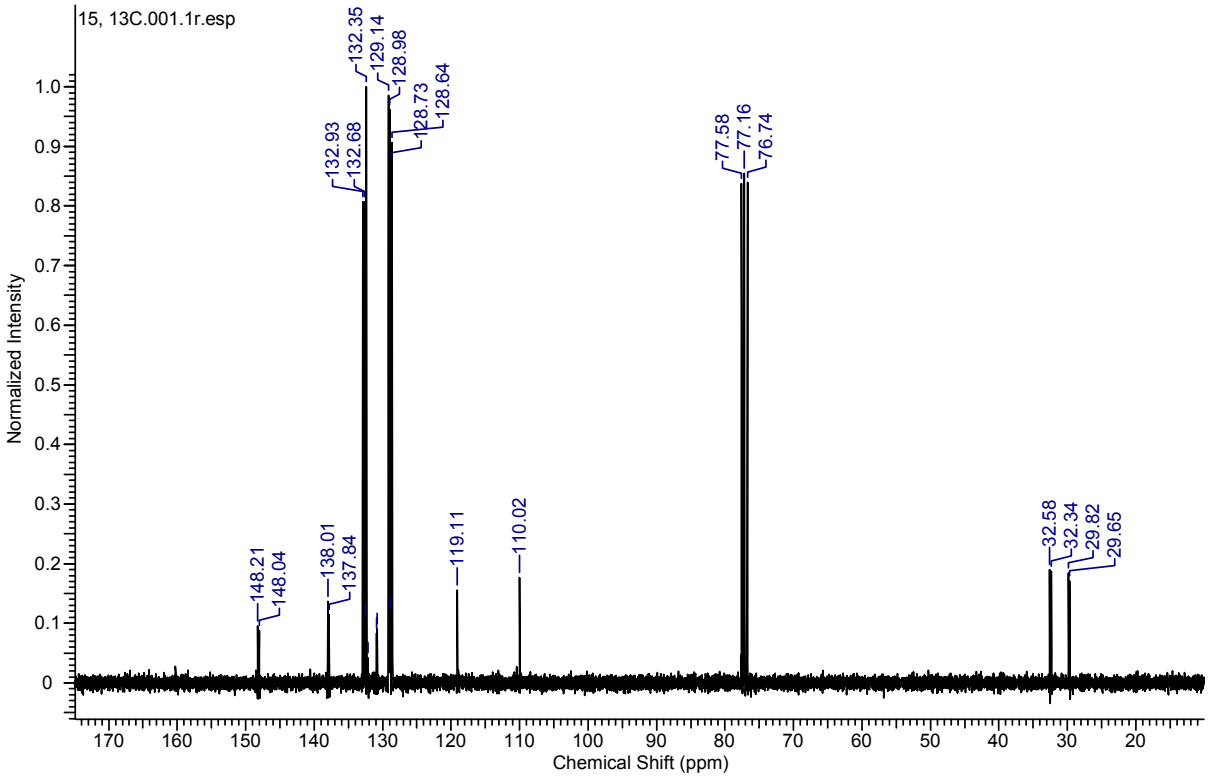


^{1}H NMR, **3f** (Table 1, Entry 6)

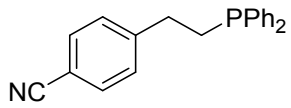


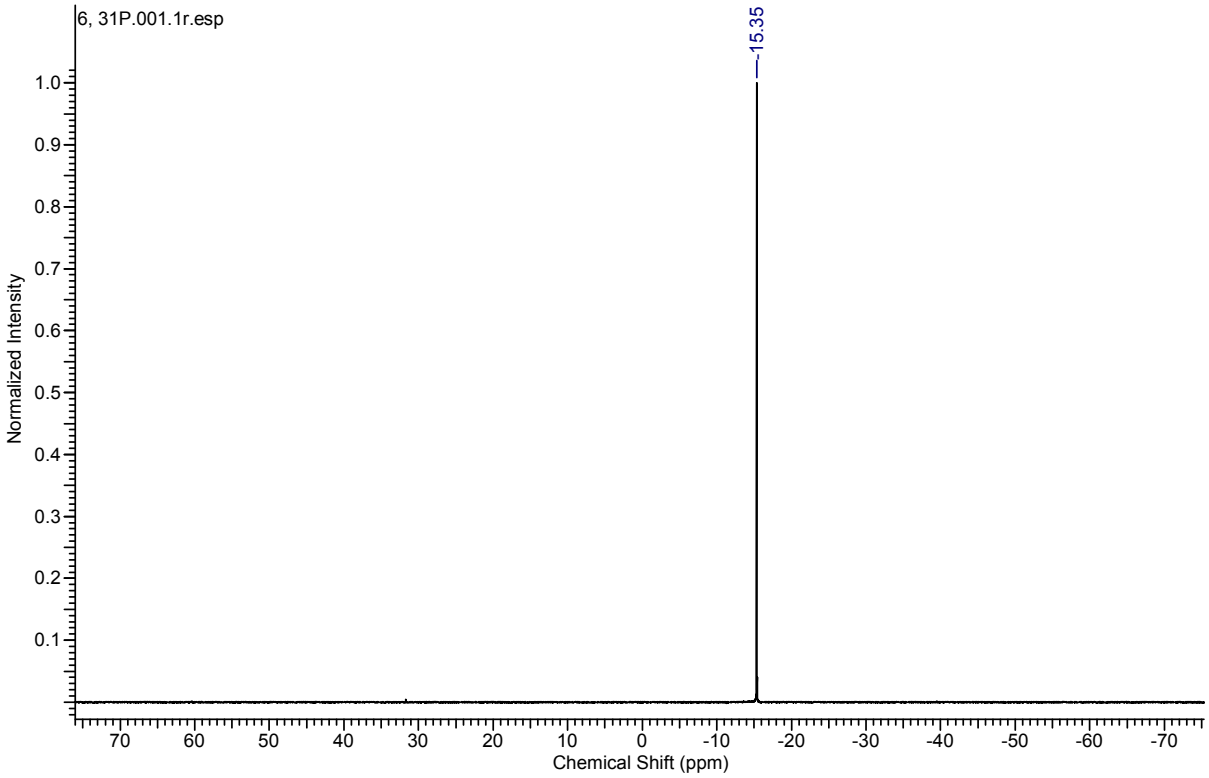
$^{13}C\{^{1}H\}$ NMR, **3f** (Table 1, Entry 6)



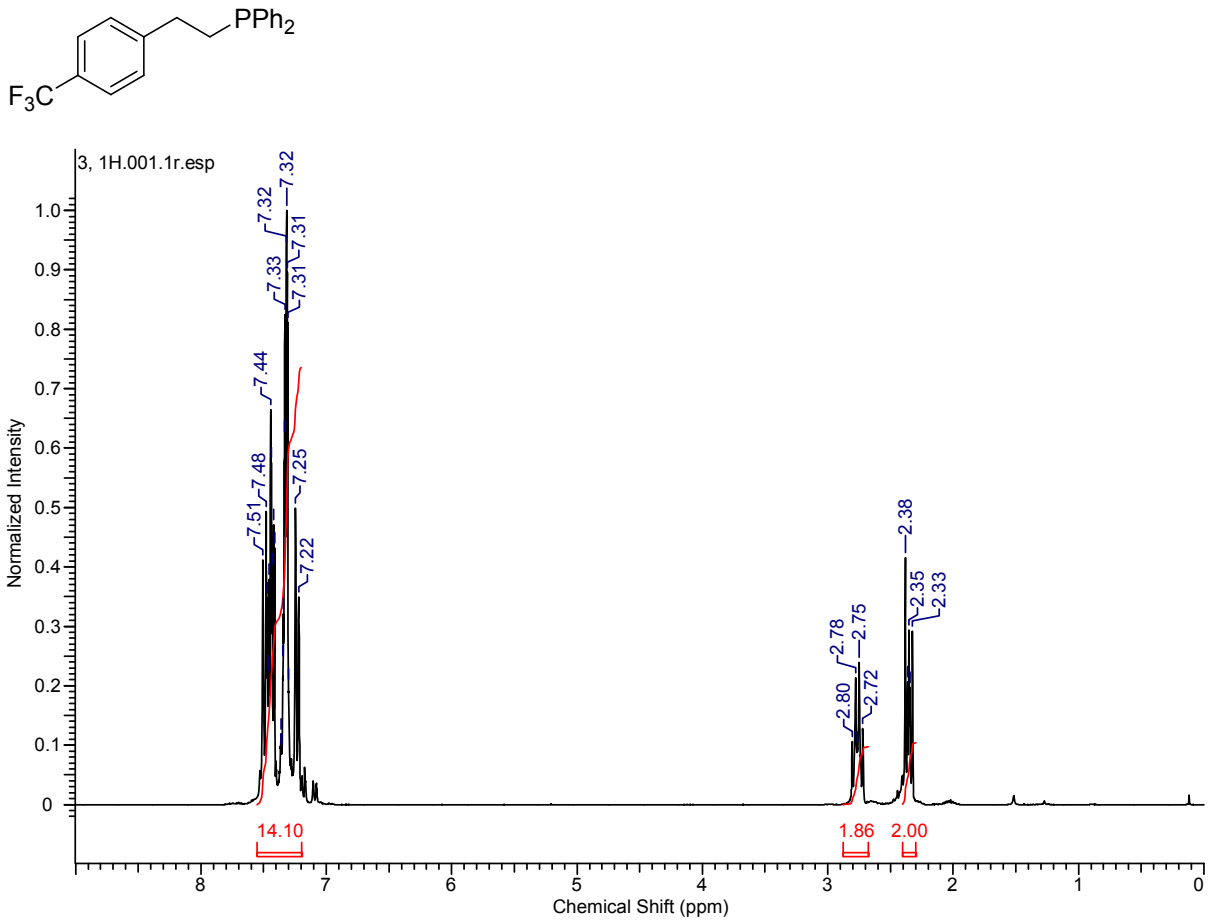


$^{31}P\{^{1}H\}$ NMR, **3f** (Table 1, Entry 6)

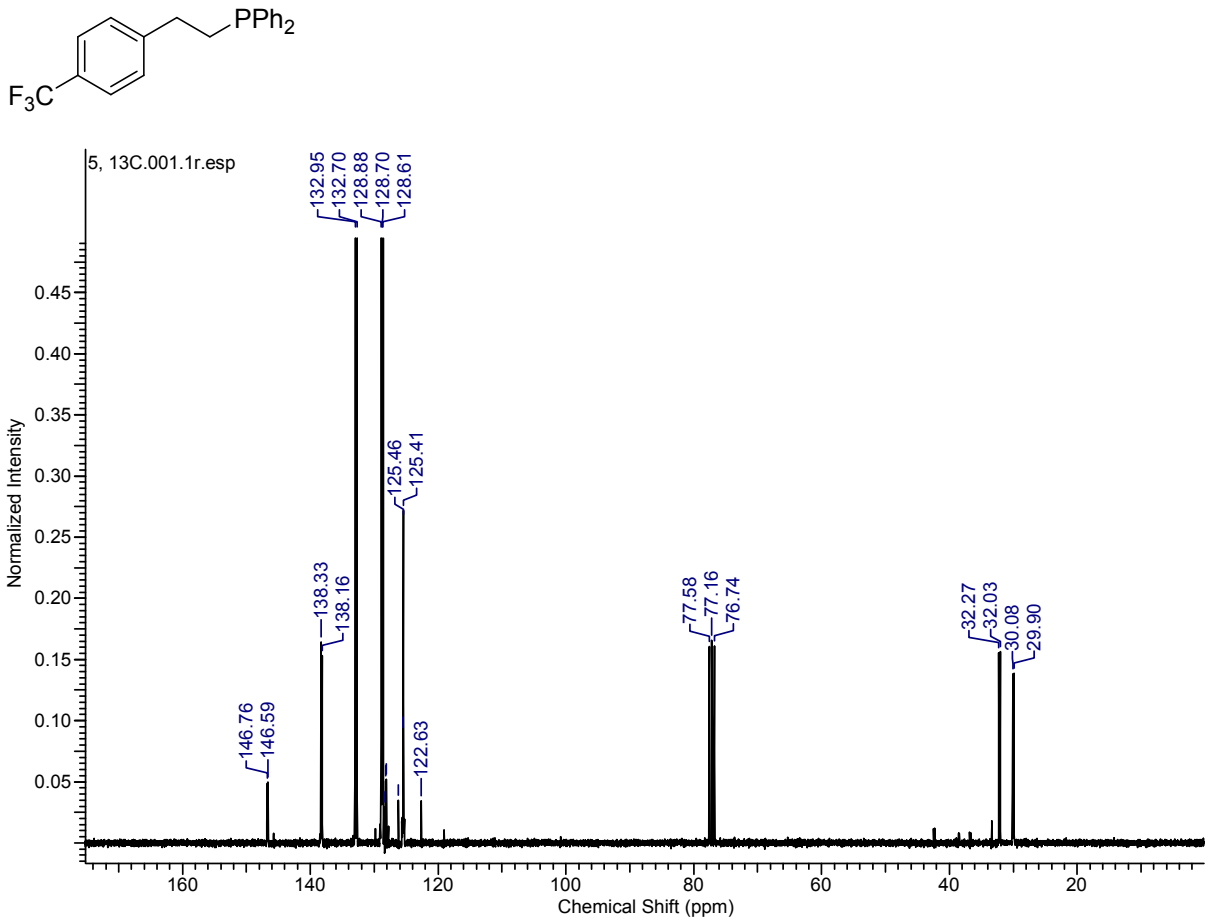




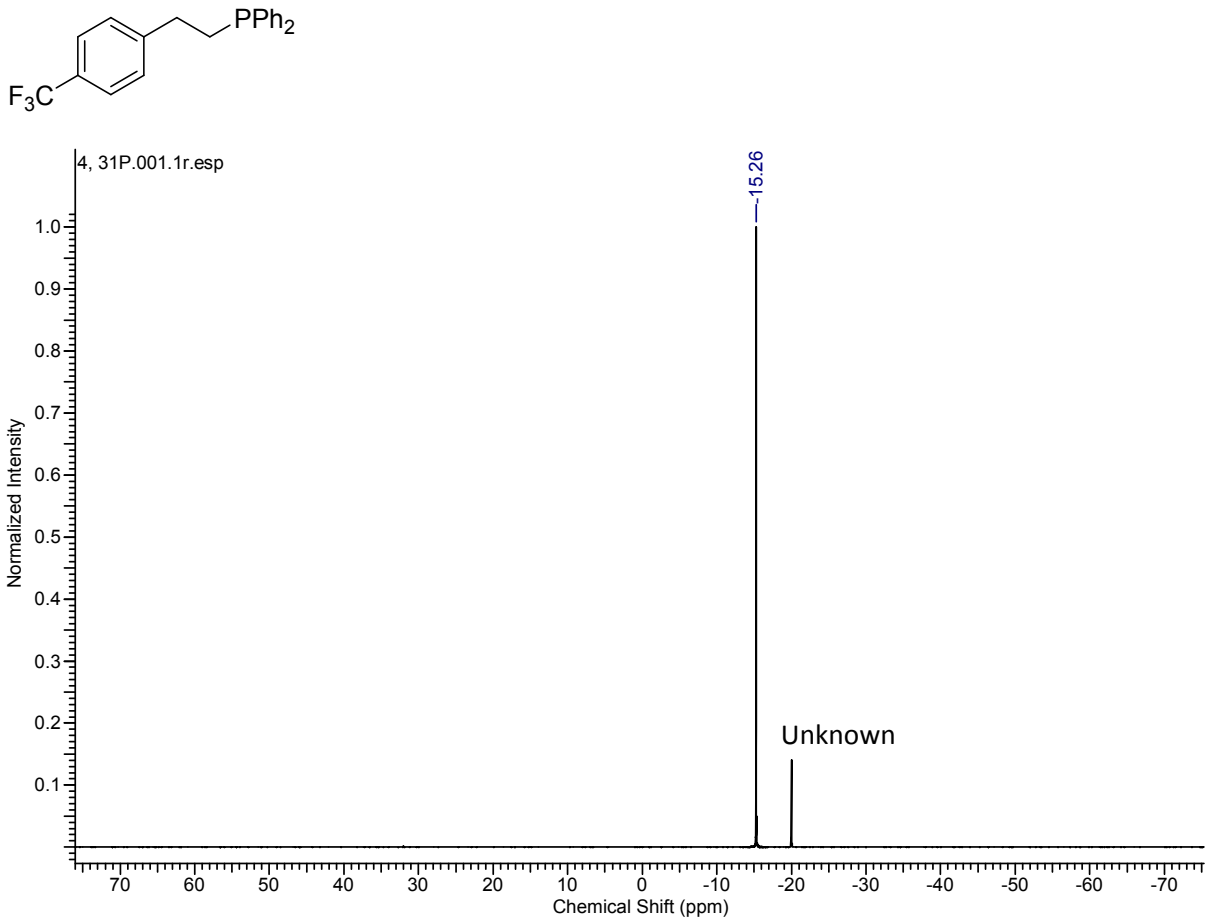
^{1}H NMR, **3g** (Table 1, Entry 7)



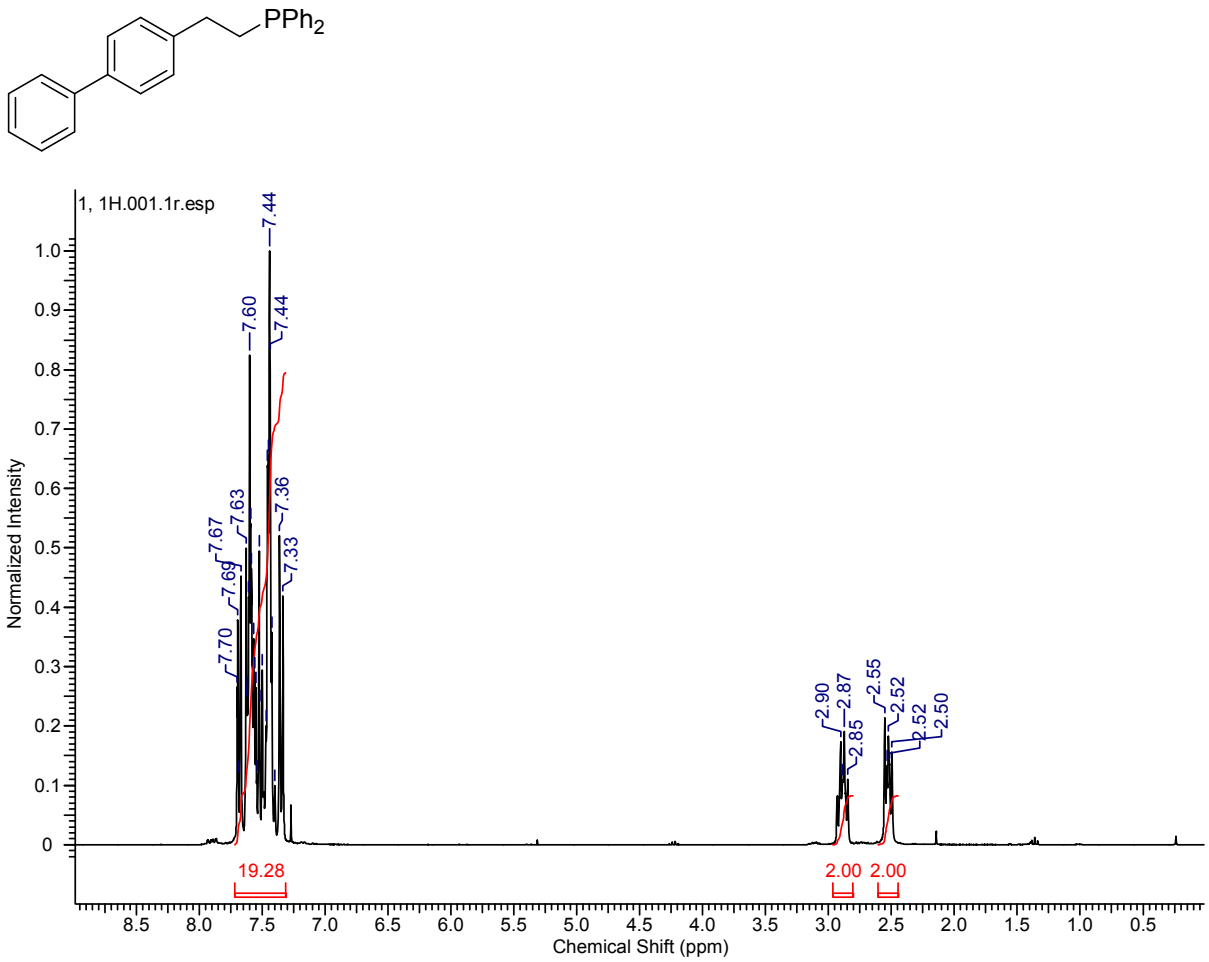
$^{13}C\{^{1}H\}$ NMR, **3g** (Table 1, Entry 7)



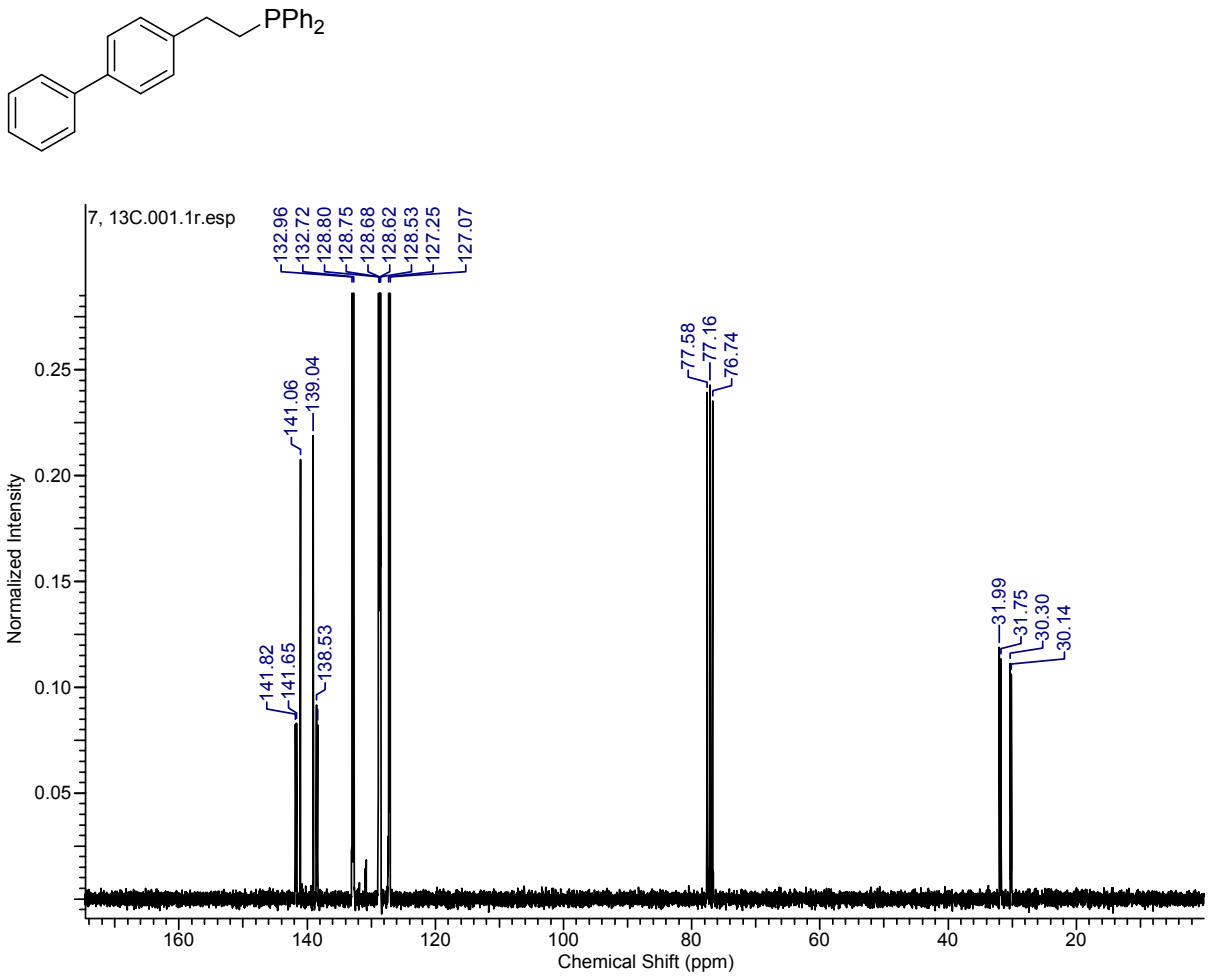
$^{31}P\{^{1}H\}$ NMR, **3g** (Table 1, Entry 7)



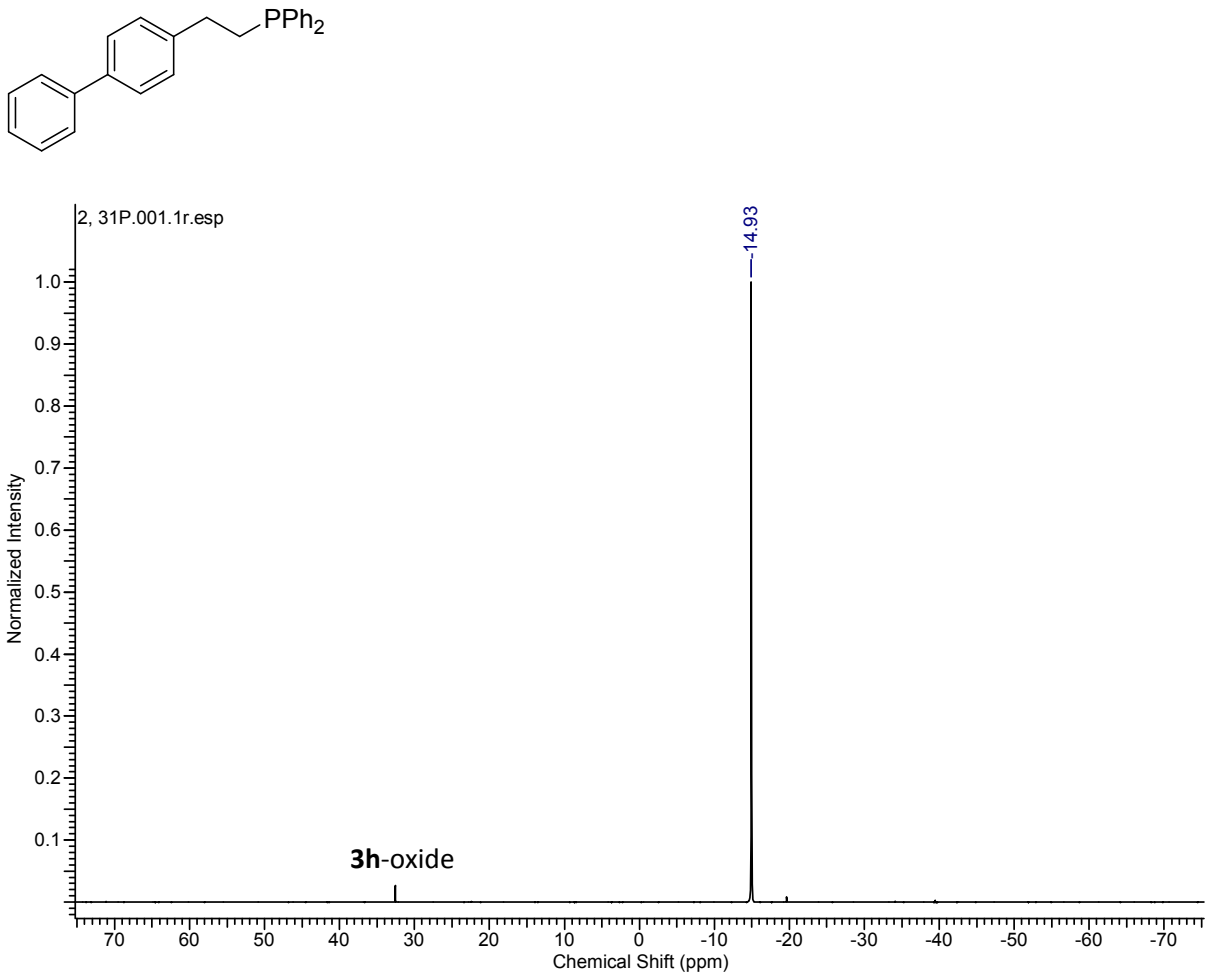
^{1}H NMR, **3h** (Table 1, Entry 8)



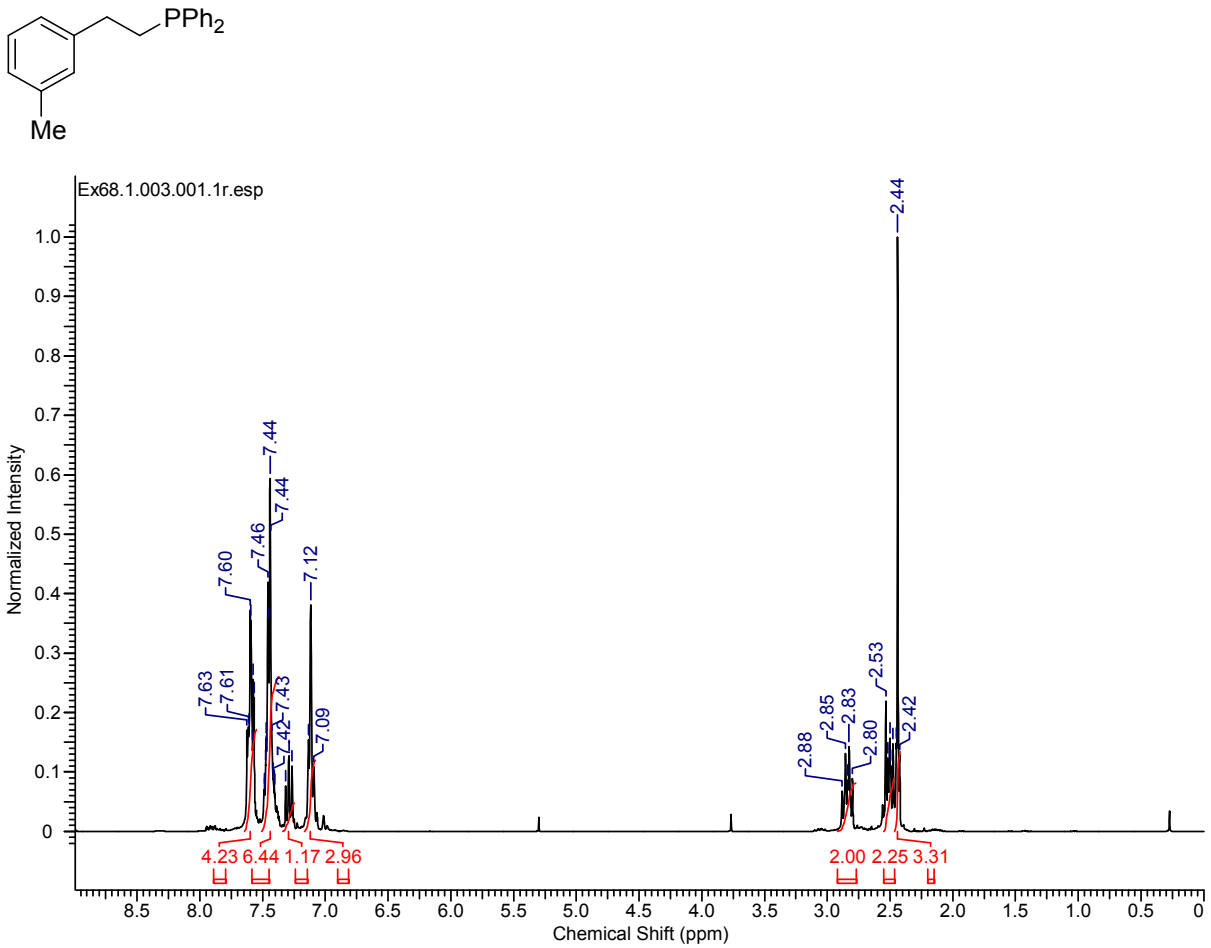
$^{13}C\{^{1}H\}$ NMR, **3h** (Table 1, Entry 8)



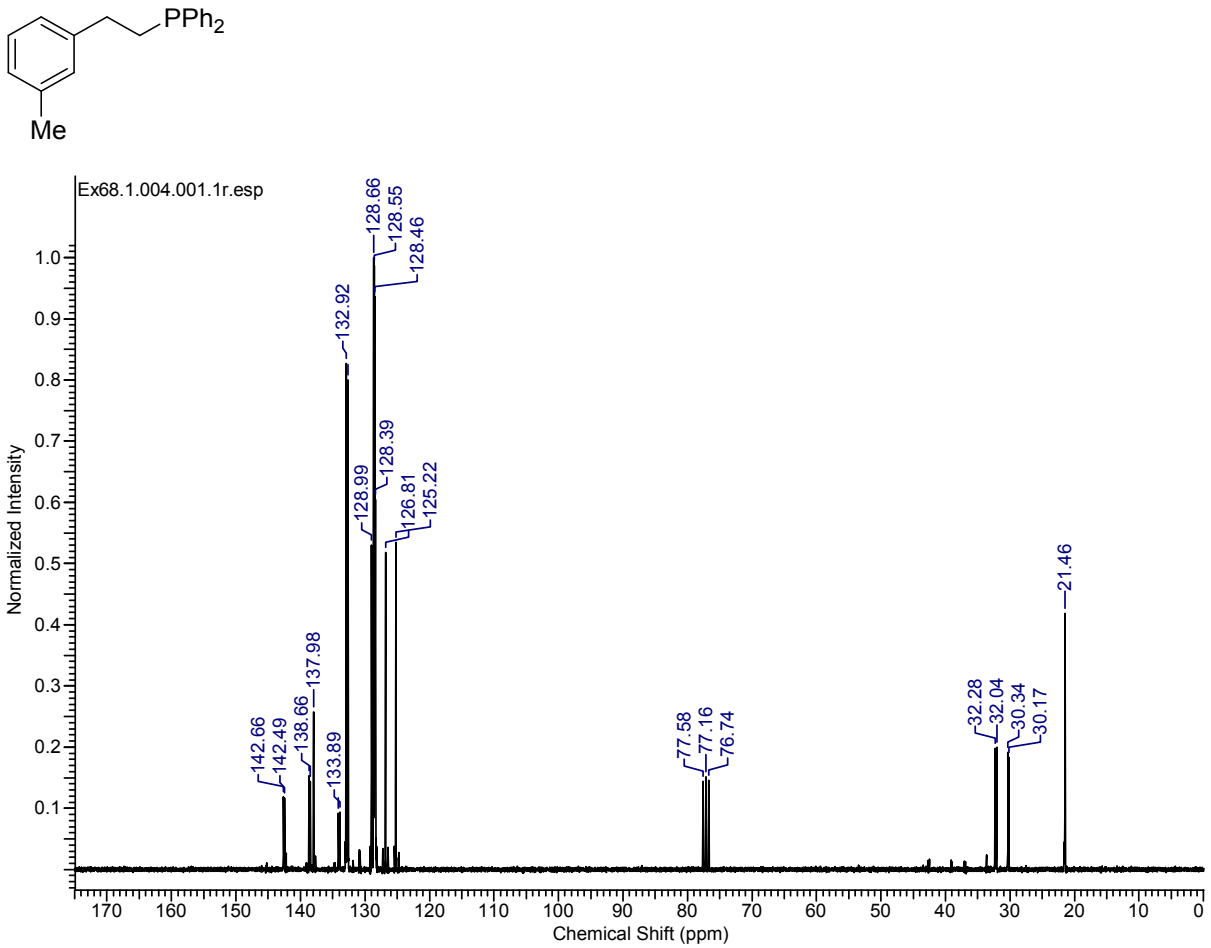
$^{31}P\{^{1}H\}$ NMR, **3h** (Table 1, Entry 8)



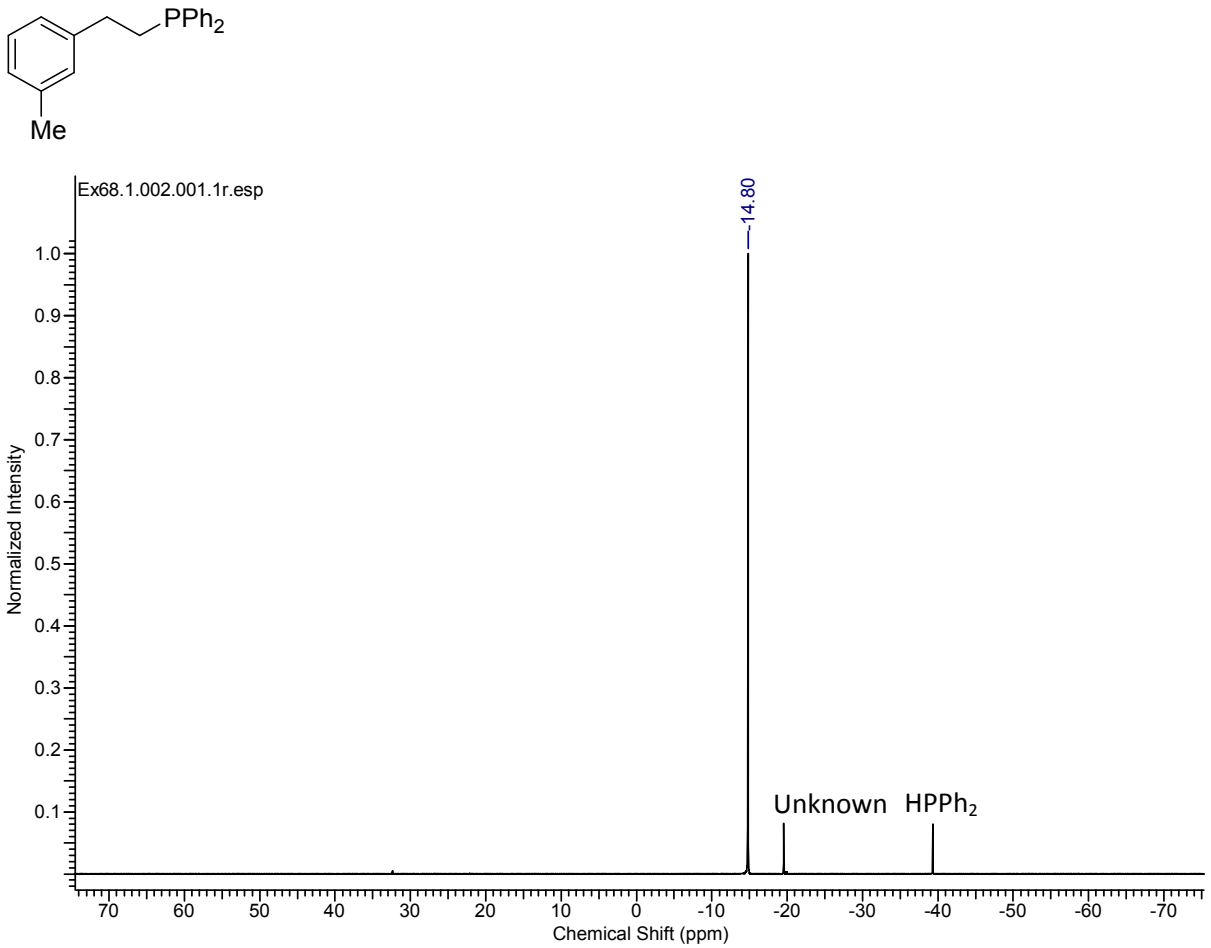
^{1}H NMR, **3i** (Table 1, Entry 9)



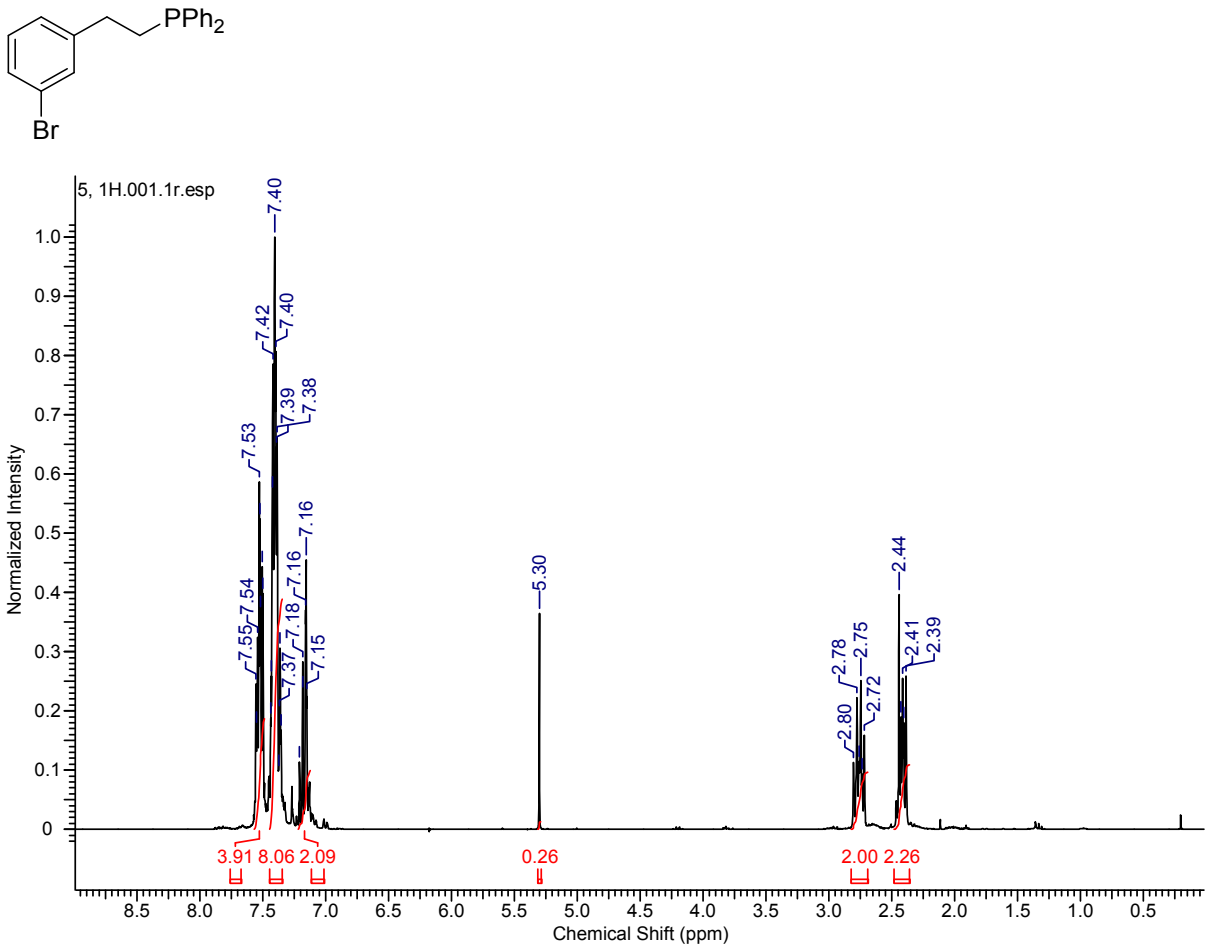
$^{13}C\{^{1}H\}$ NMR, **3i** (Table 1, Entry 9)



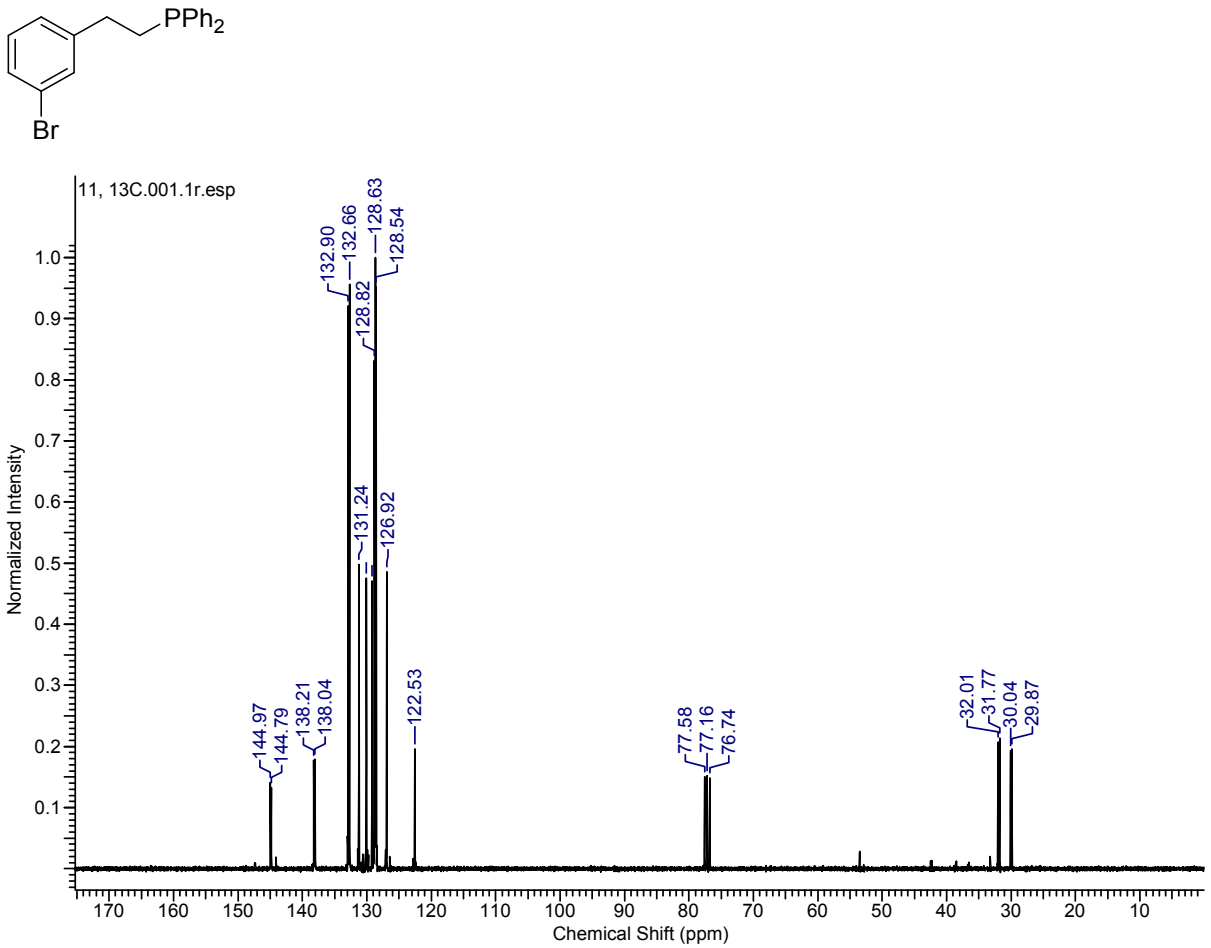
$^{31}P\{^{1}H\}$ NMR, **3i** (Table 1, Entry 9)



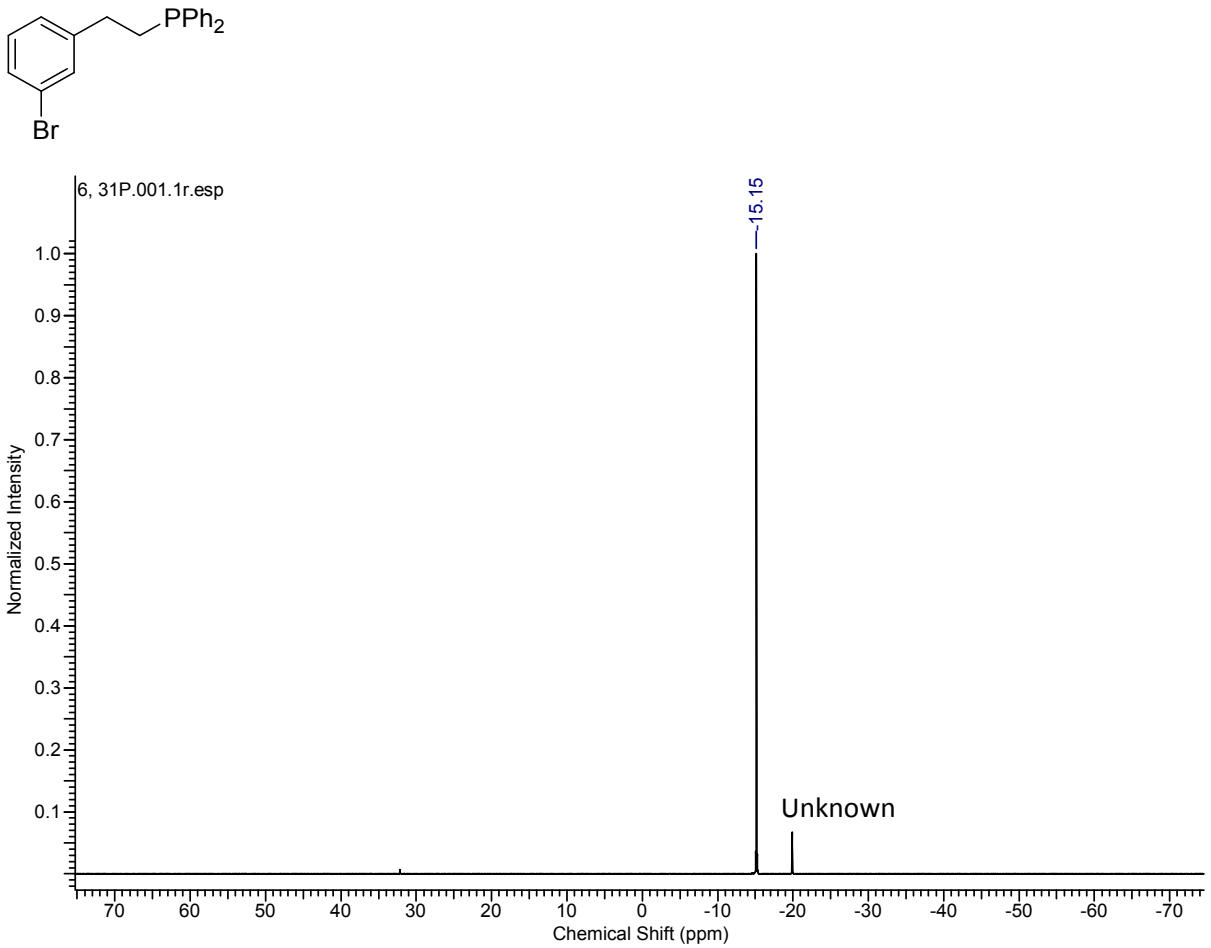
^{1}H NMR, **3j** (Table 1, Entry 10)



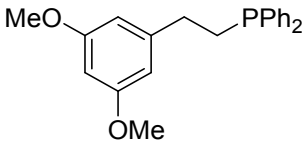
$^{13}C\{^{1}H\}$ NMR, **3j** (Table 1, Entry 10)

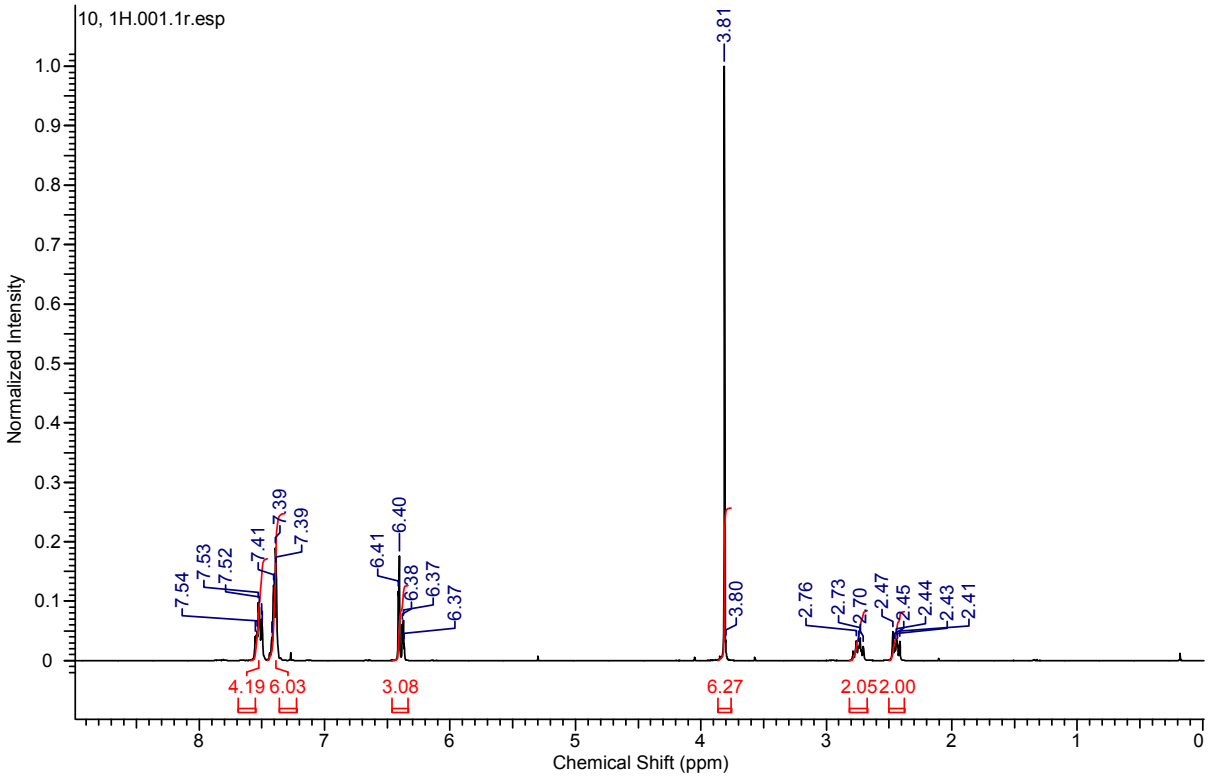


$^{31}P\{^{1}H\}$ NMR, **3j** (Table 1, Entry 10)

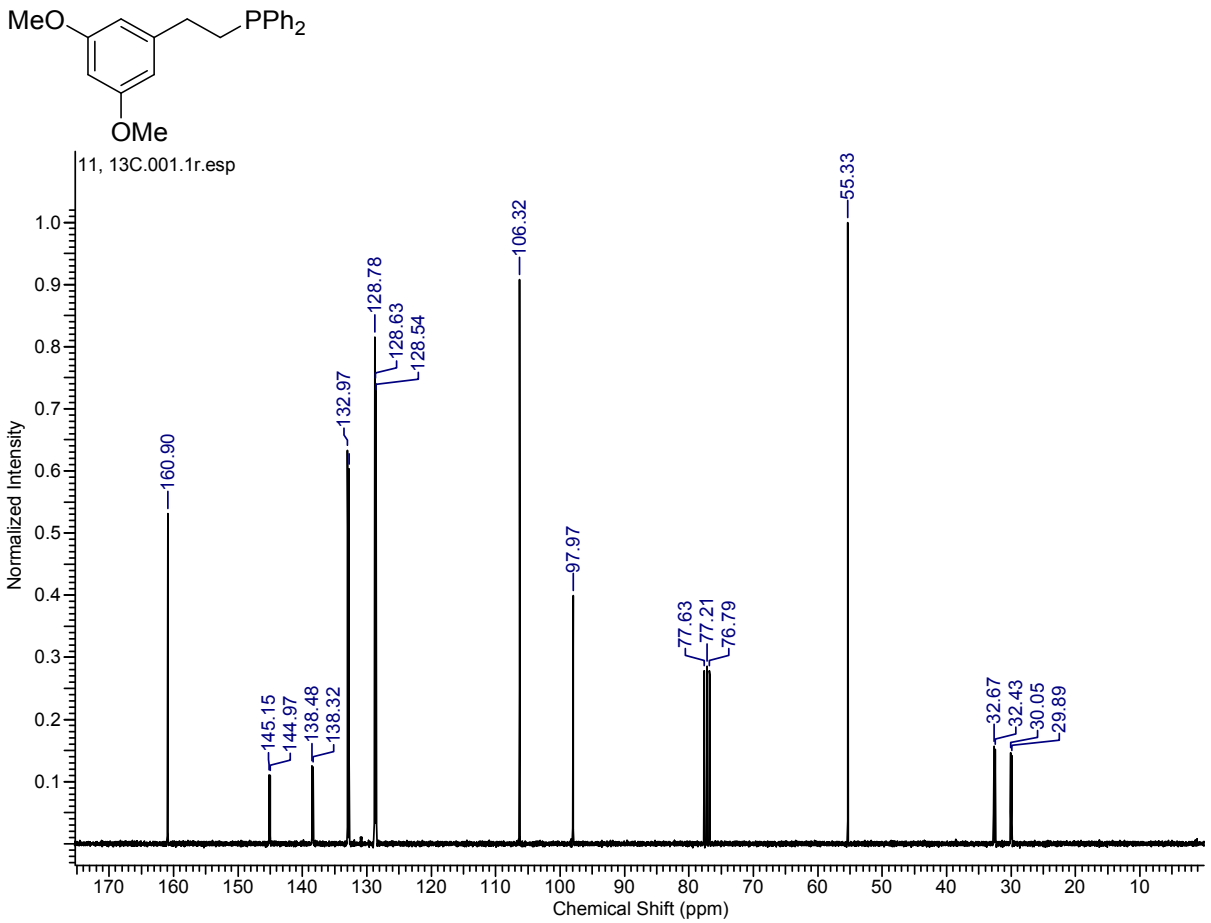


^{1}H NMR, **3k** (Table 1, Entry 11)

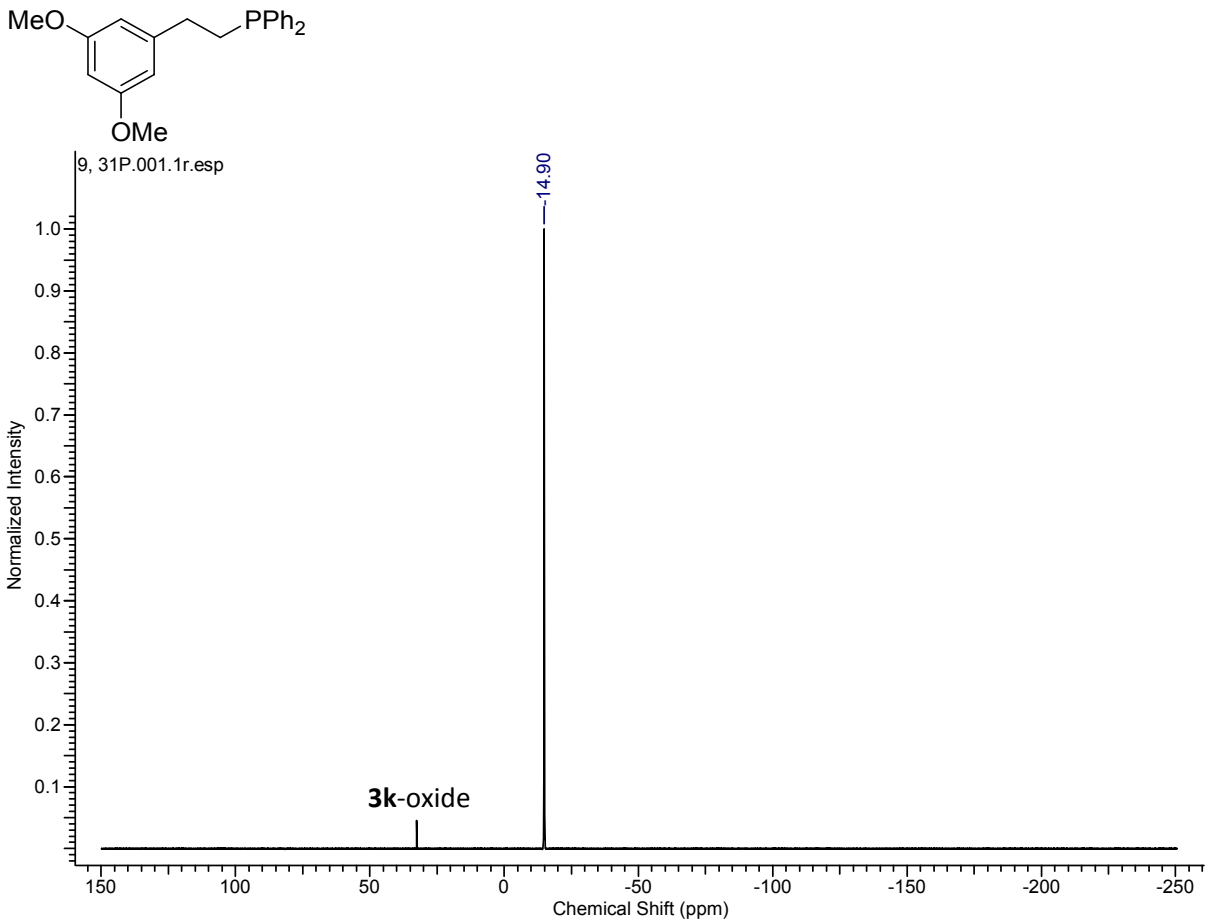




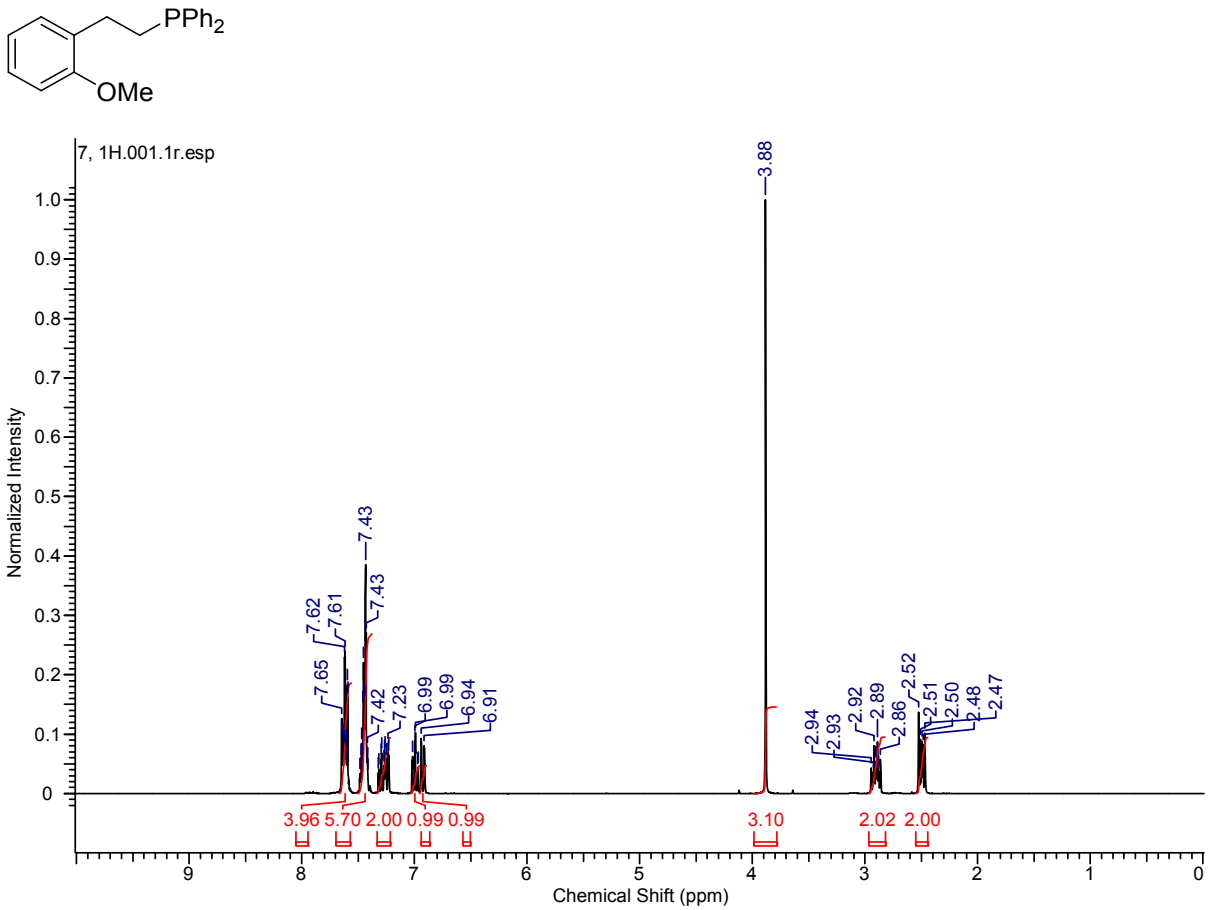
$^{13}C\{^{1}H\}$ NMR, **3k** (Table 1, Entry 11)



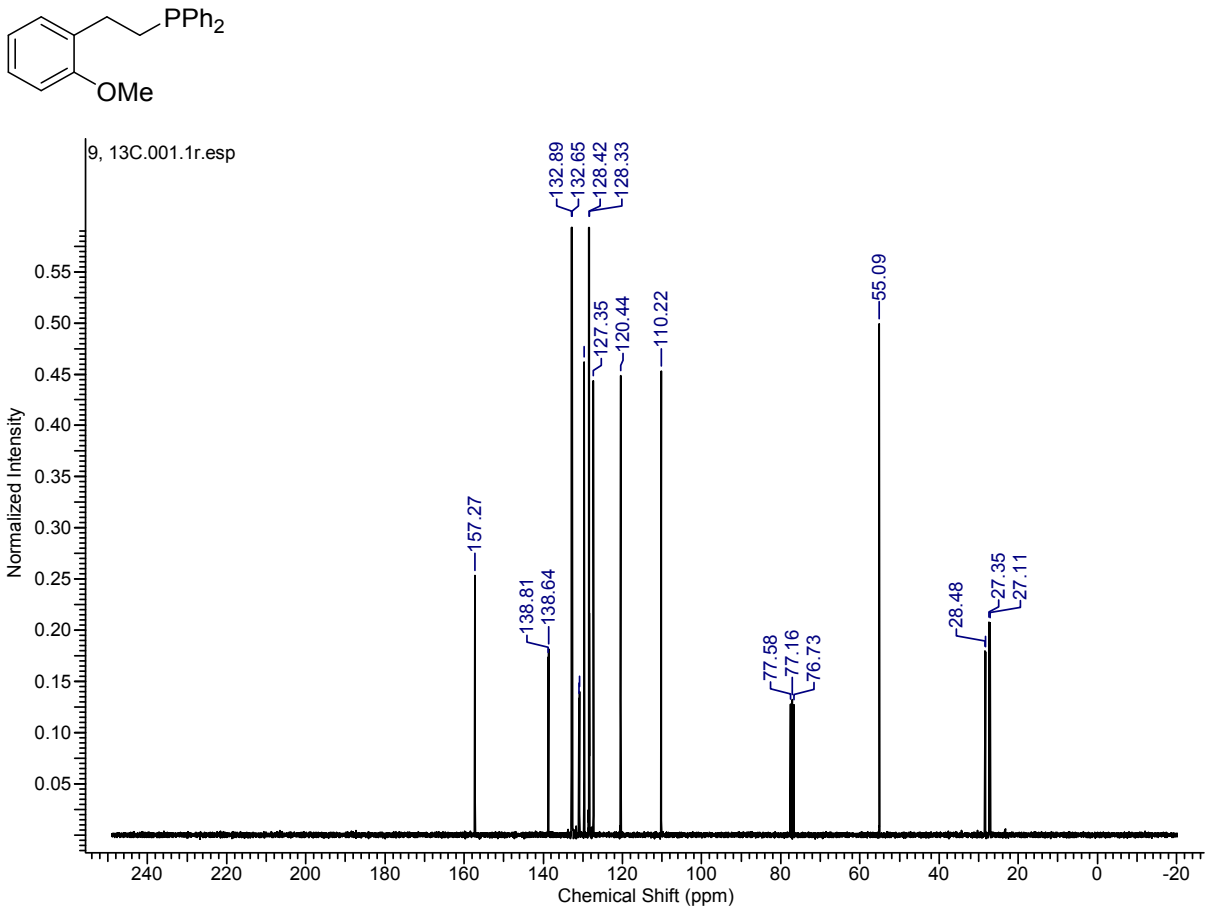
$^{13}C\{^{1}H\}$ NMR, **3k** (Table 1, Entry 11)



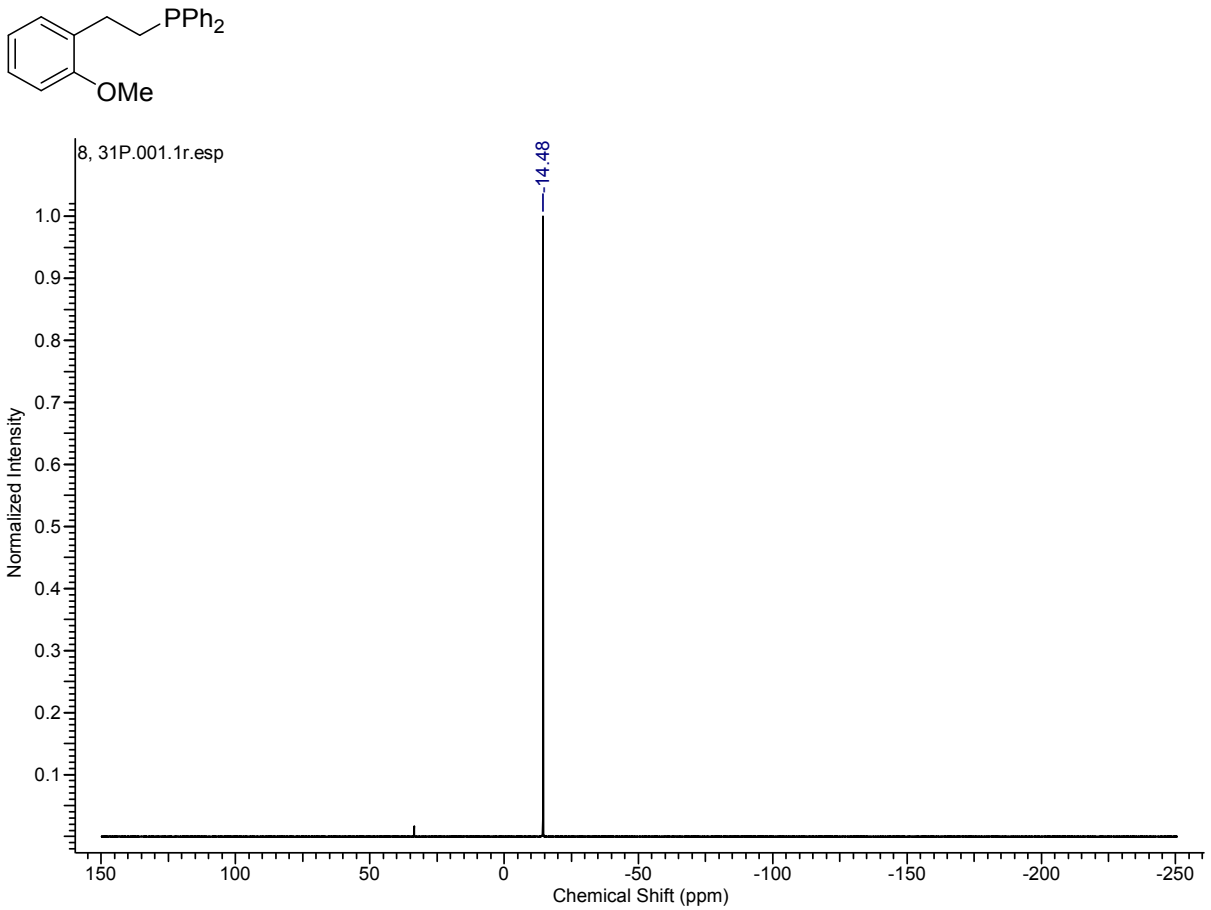
^{1}H NMR, **3l** (Table 1, Entry 12)



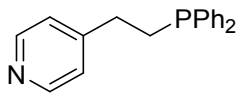
$^{13}C\{^{1}H\}$ NMR, **3l** (Table 1, Entry 12)

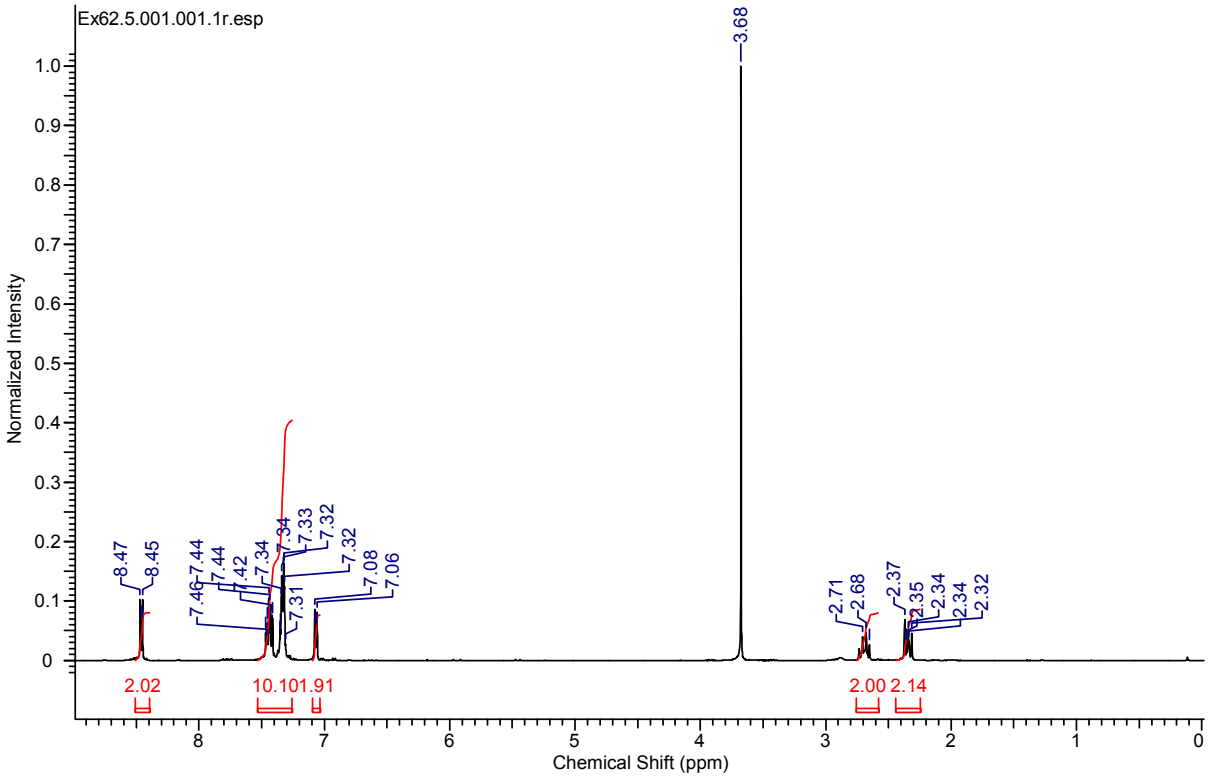


$^{31}P\{^{1}H\}$ NMR, **3l** (Table 1, Entry 12)

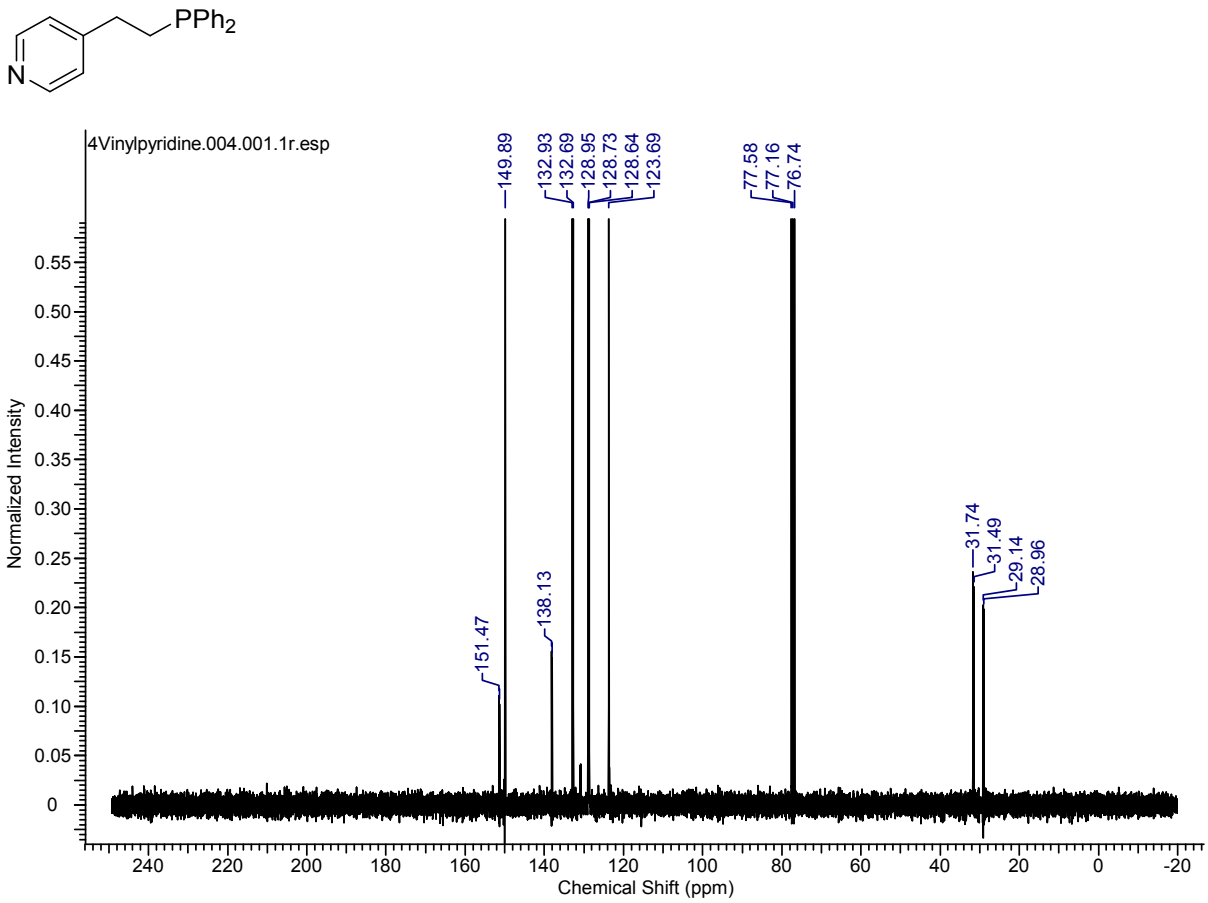


^{1}H NMR, **3m** (Table 1, Entry 13)

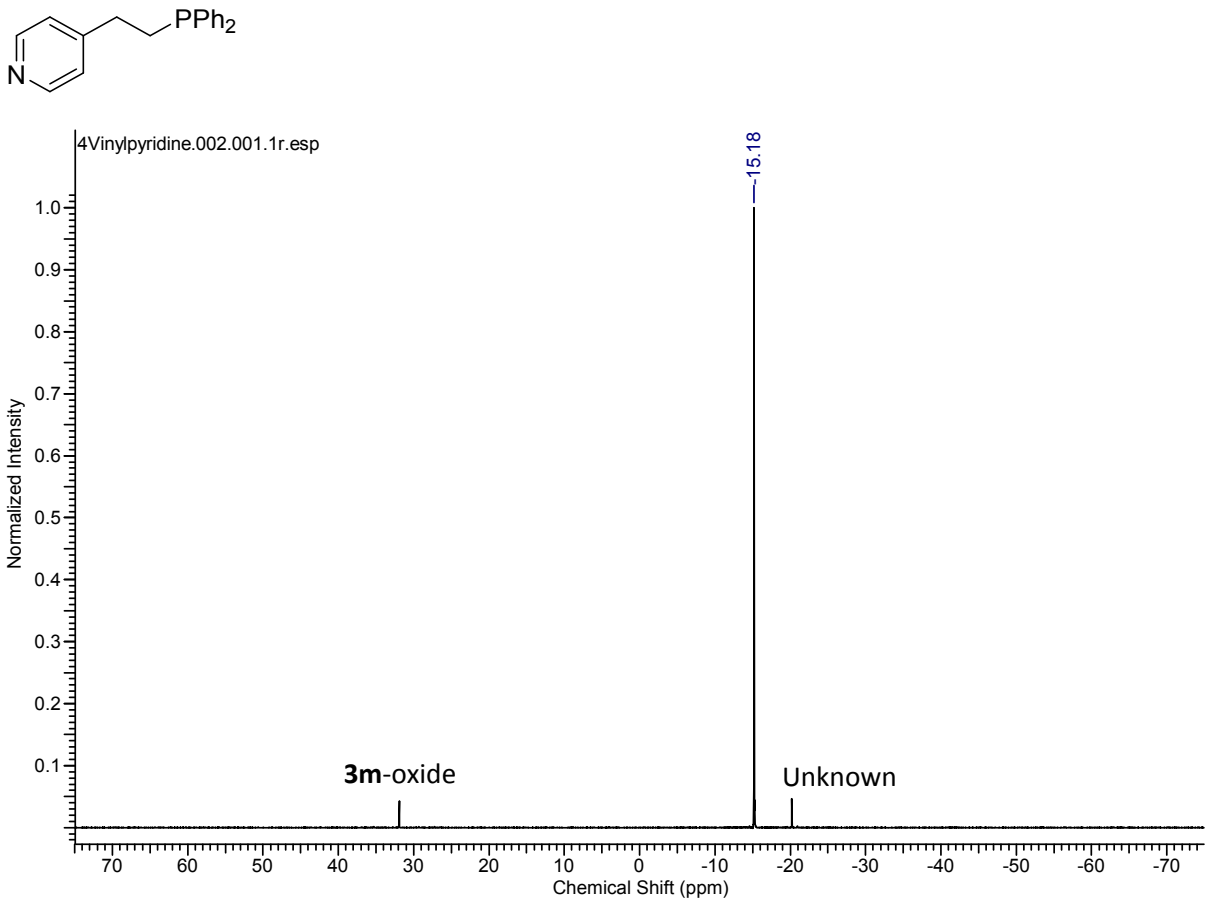




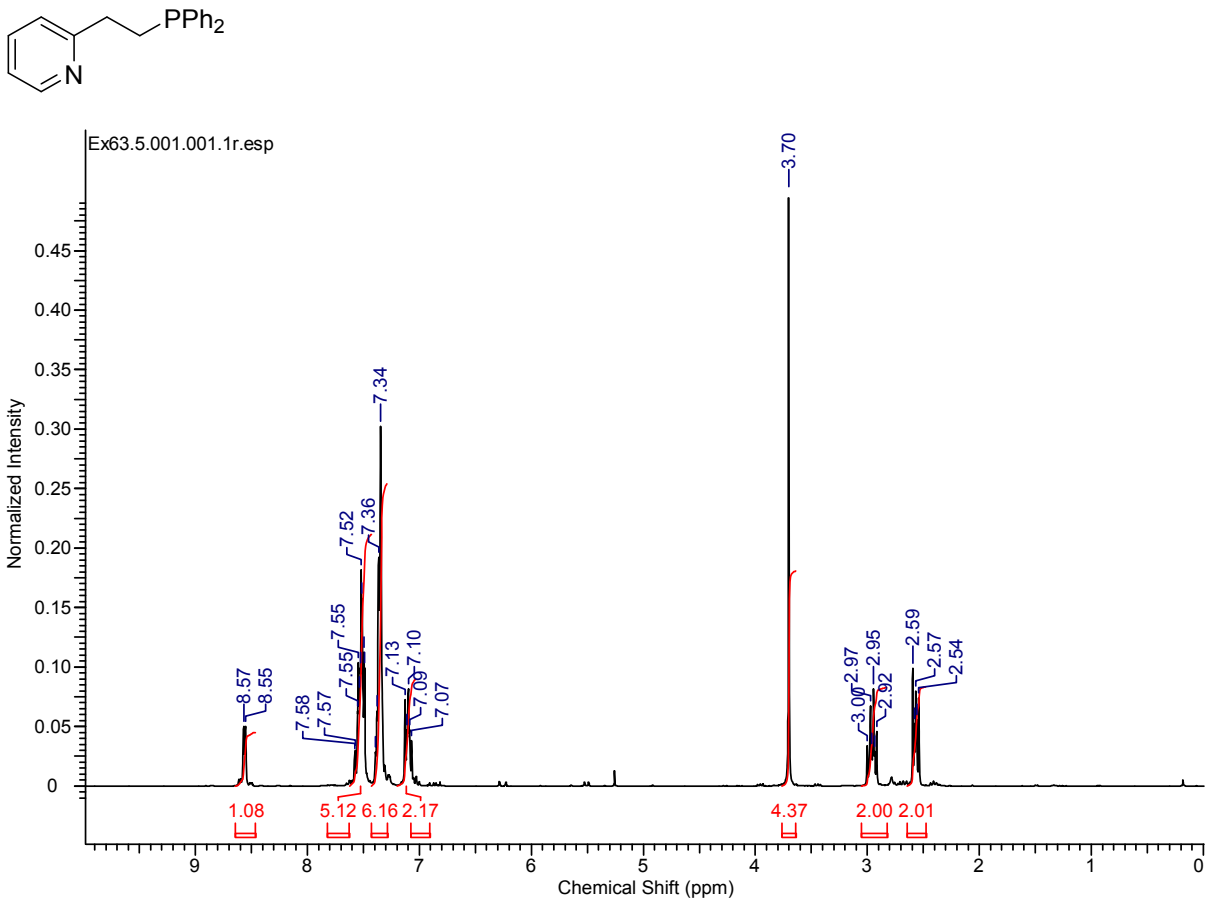
$^{13}C\{^{1}H\}$ NMR, **3m** (Table 1, Entry 13)



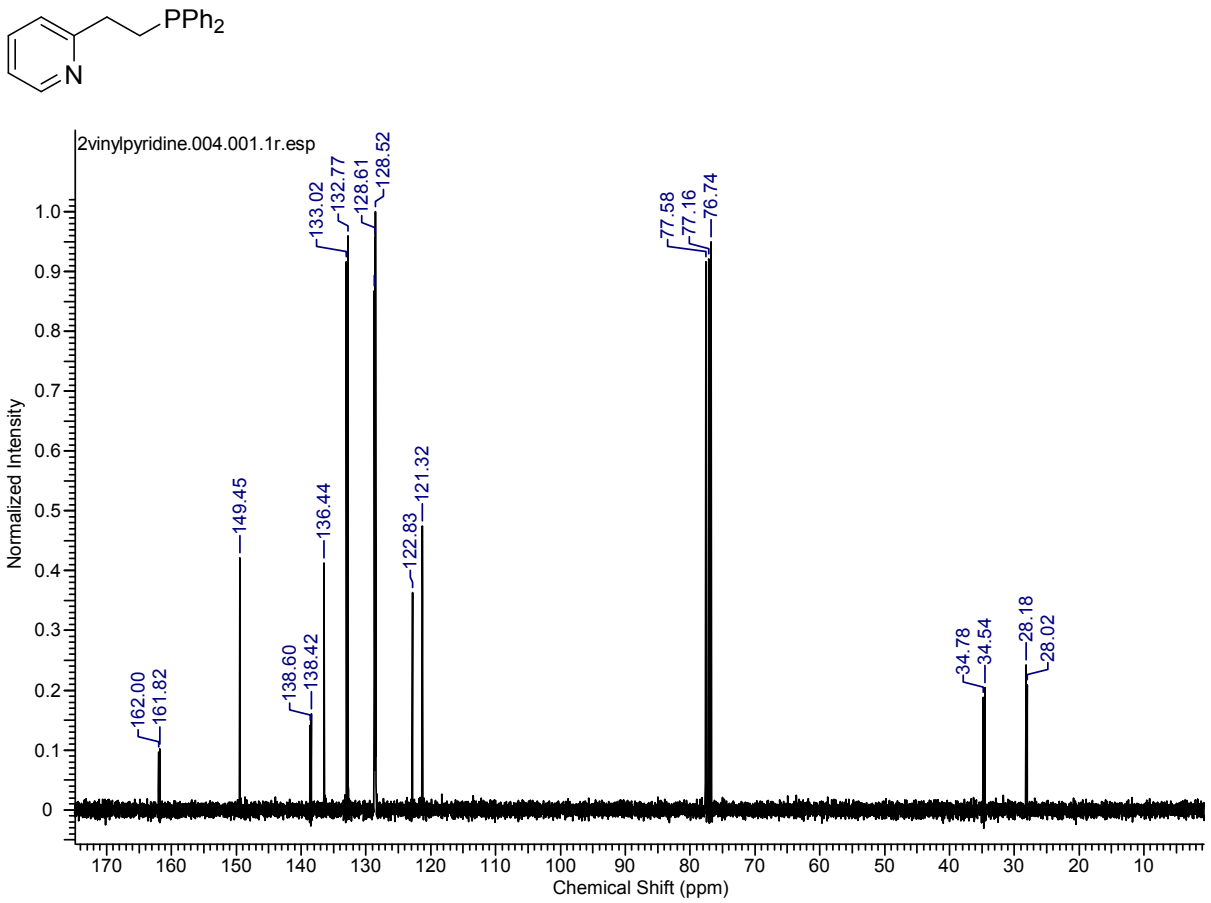
$^{31}P\{^{1}H\}$ NMR, **3m** (Table 1, Entry 13)



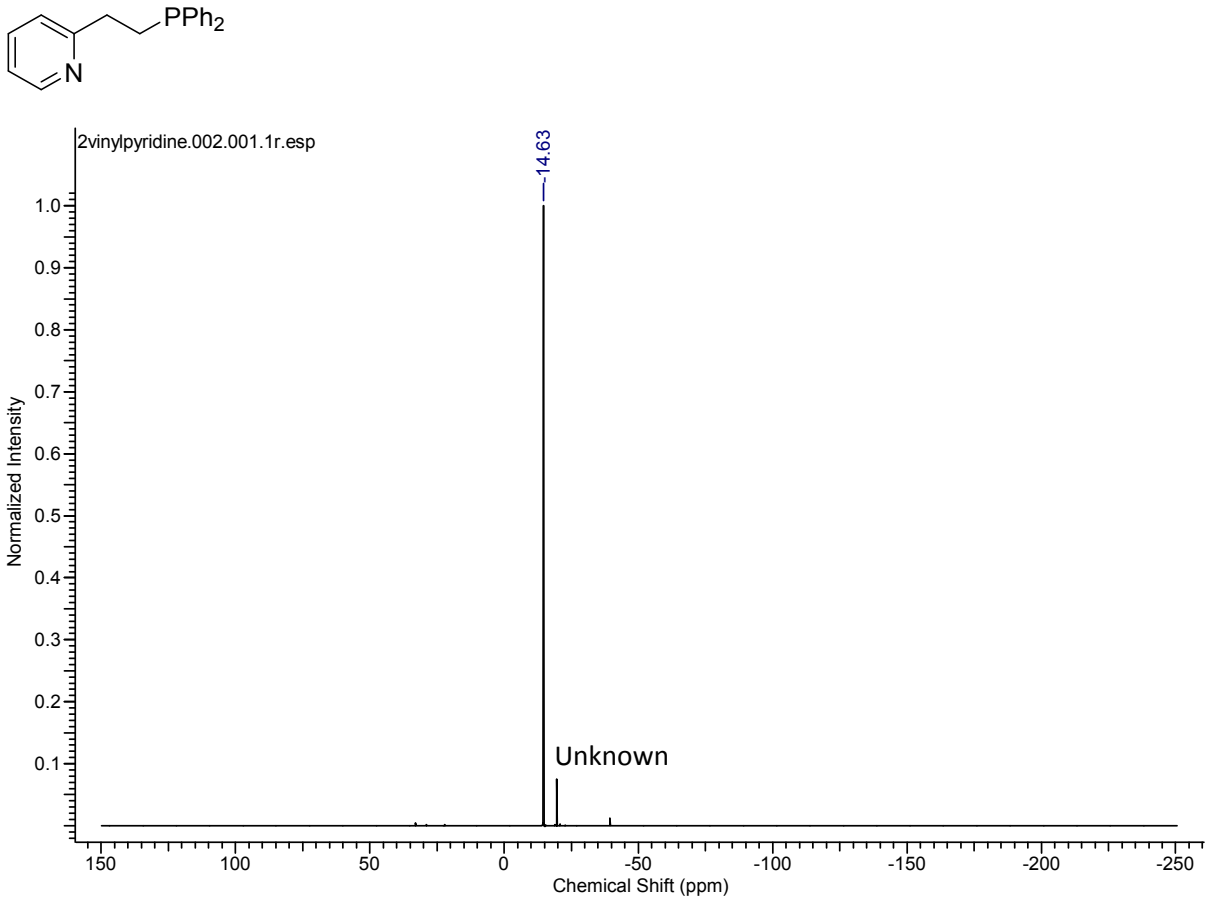
^{1}H NMR, **3n** (Table 1, Entry 14)



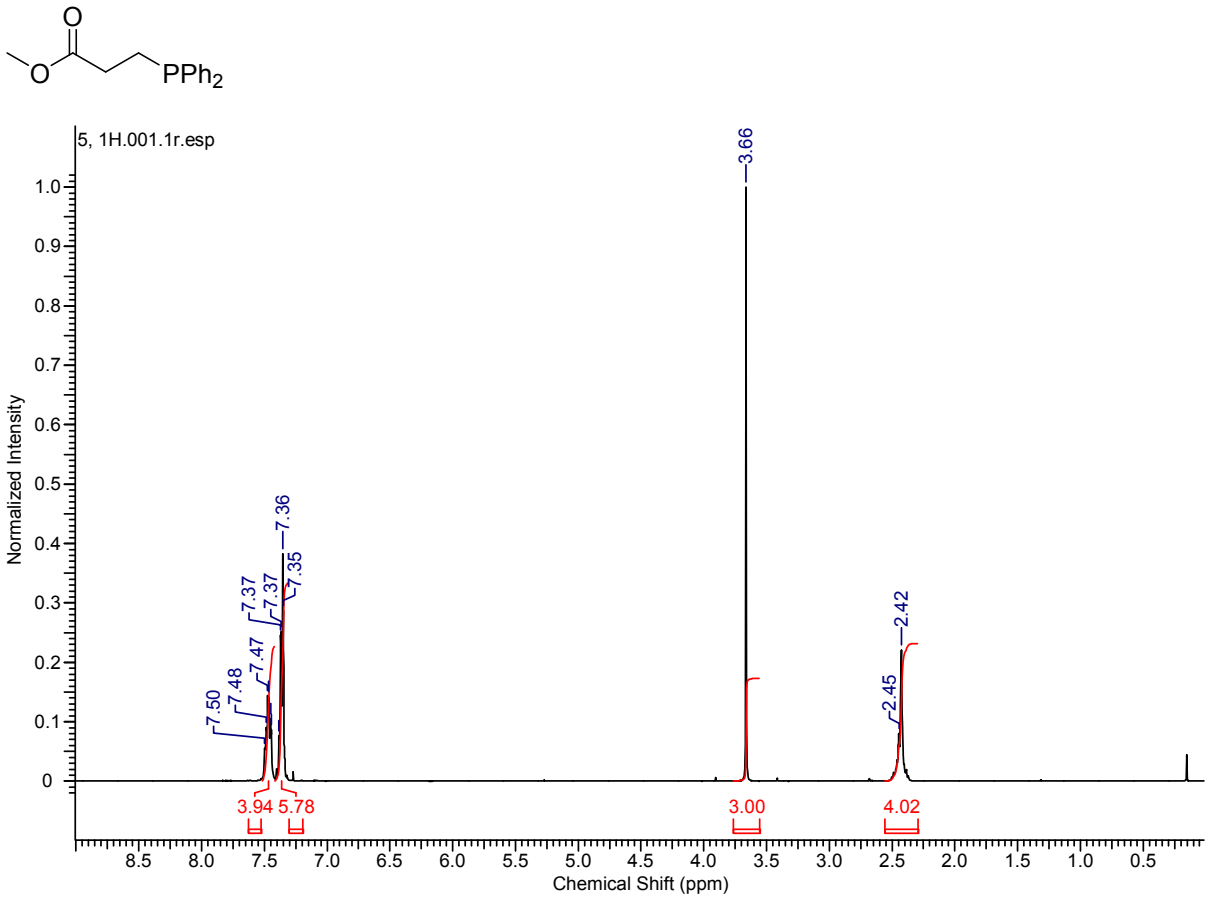
$^{13}C\{^{1}H\}$ NMR, **3n** (Table 1, Entry 14)



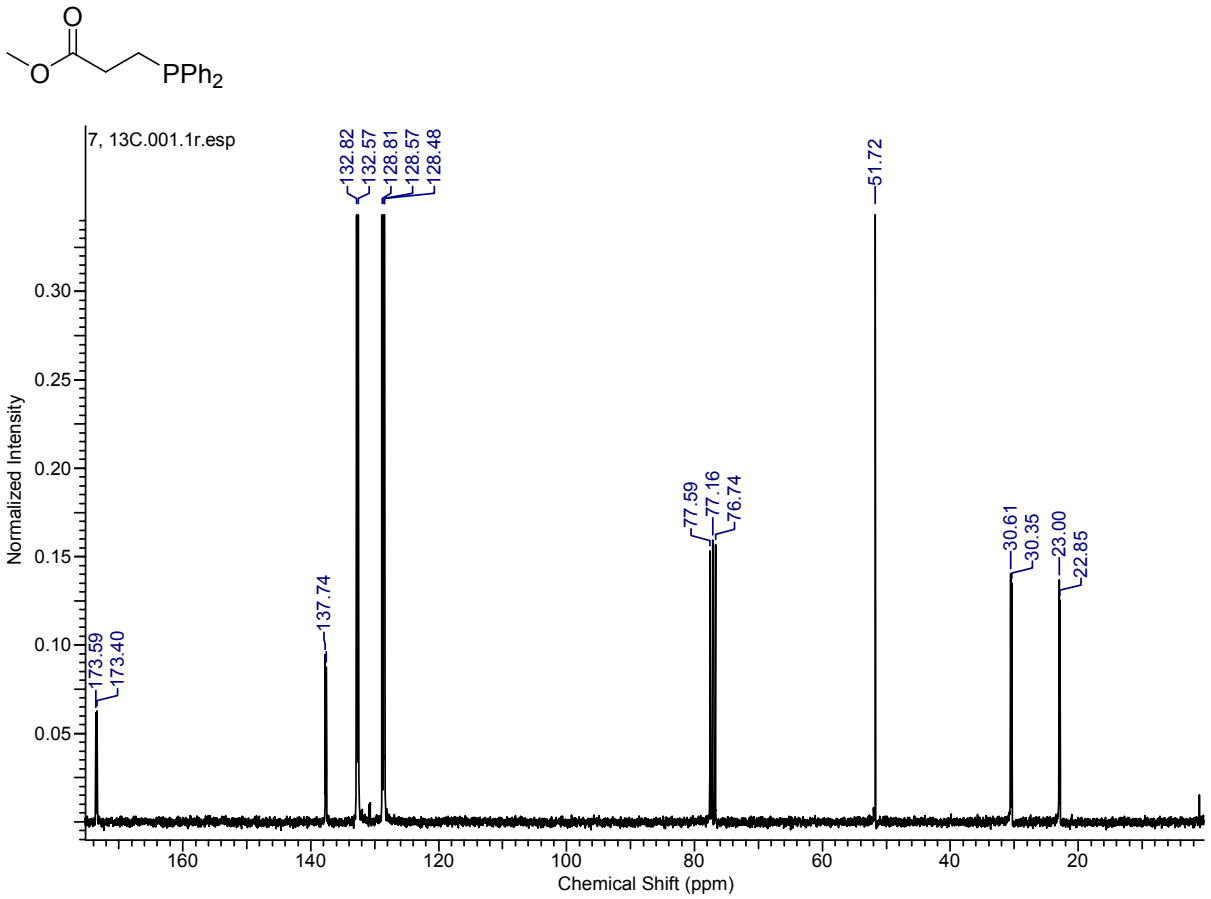
$^{31}P\{^{1}H\}$ NMR, **3n** (Table 1, Entry 14)



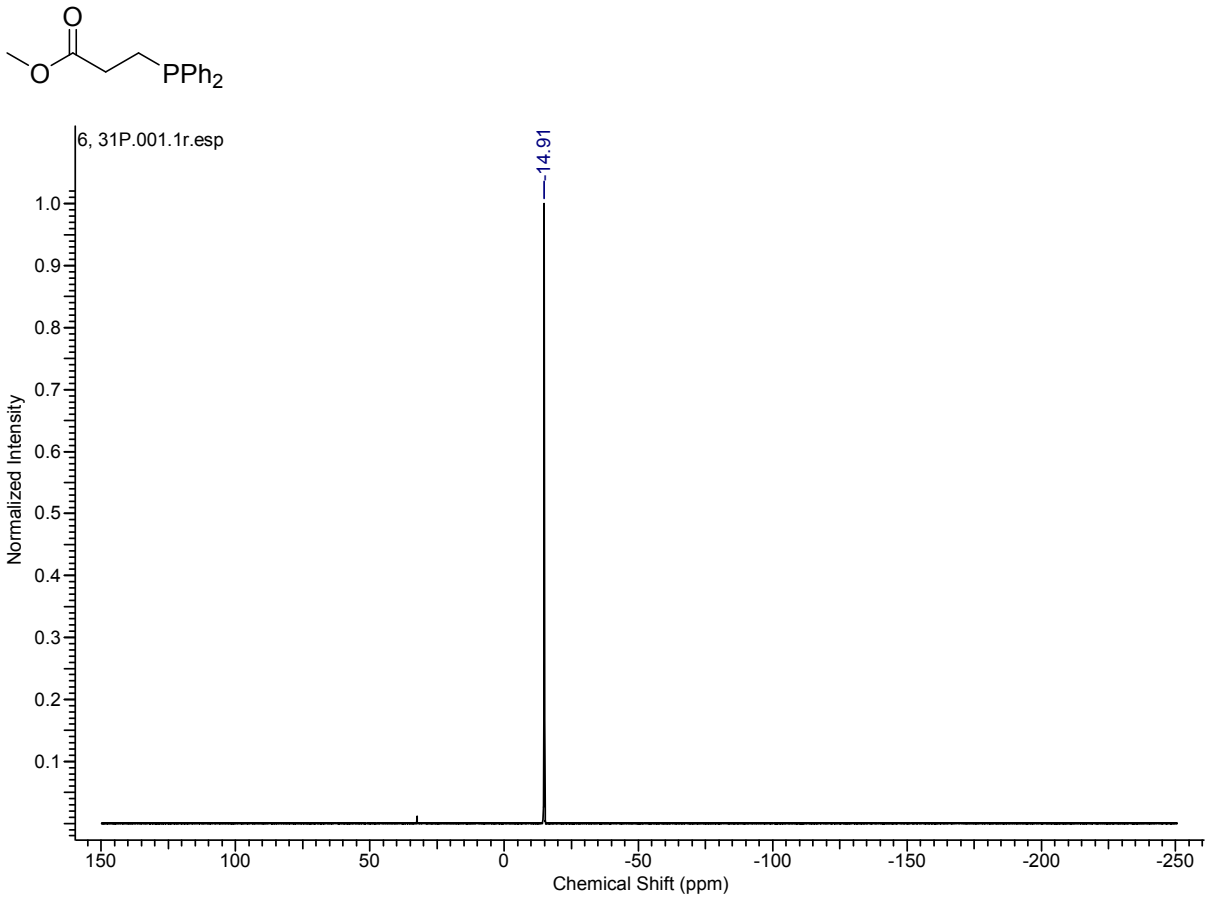
^{1}H NMR, **3o** (Table 1, Entry 15)



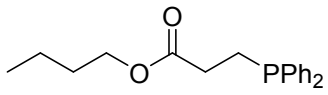
$^{13}C\{^{1}H\}$ NMR, **3o** (Table 1, Entry 15)

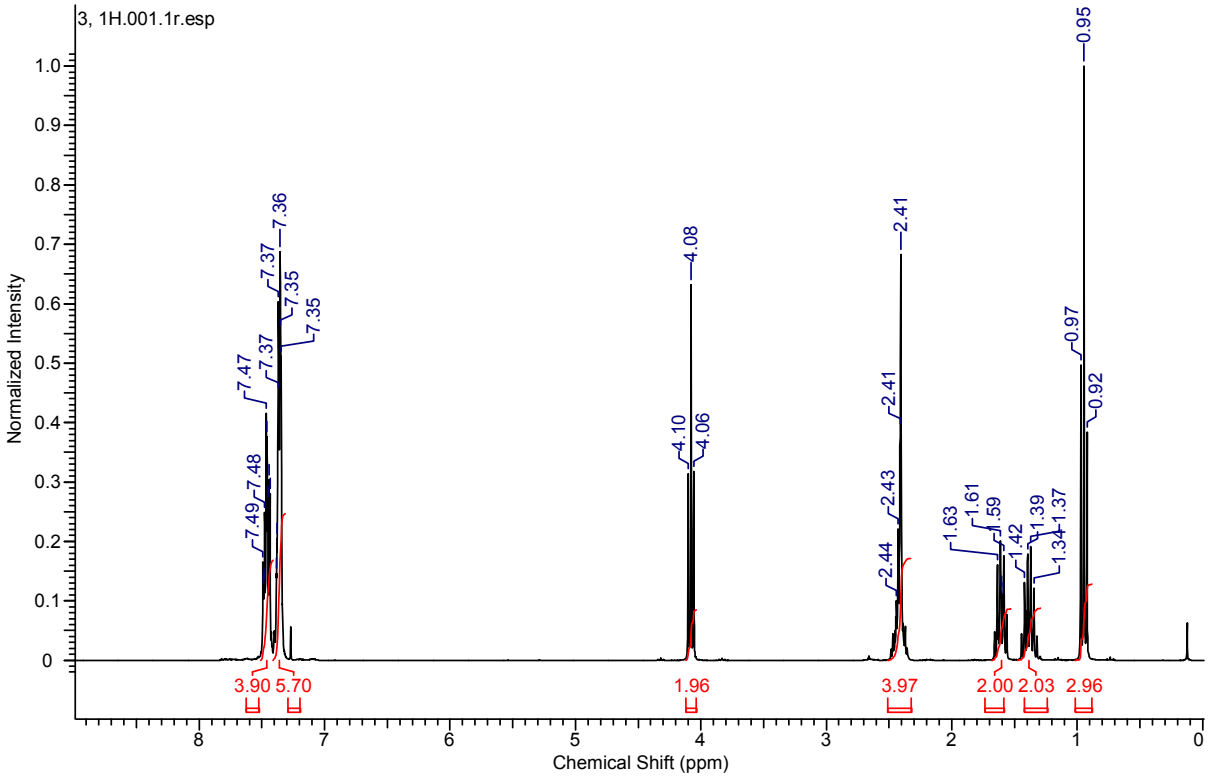


$^{31}P\{^{1}H\}$ NMR, **3o** (Table 1, Entry 15)

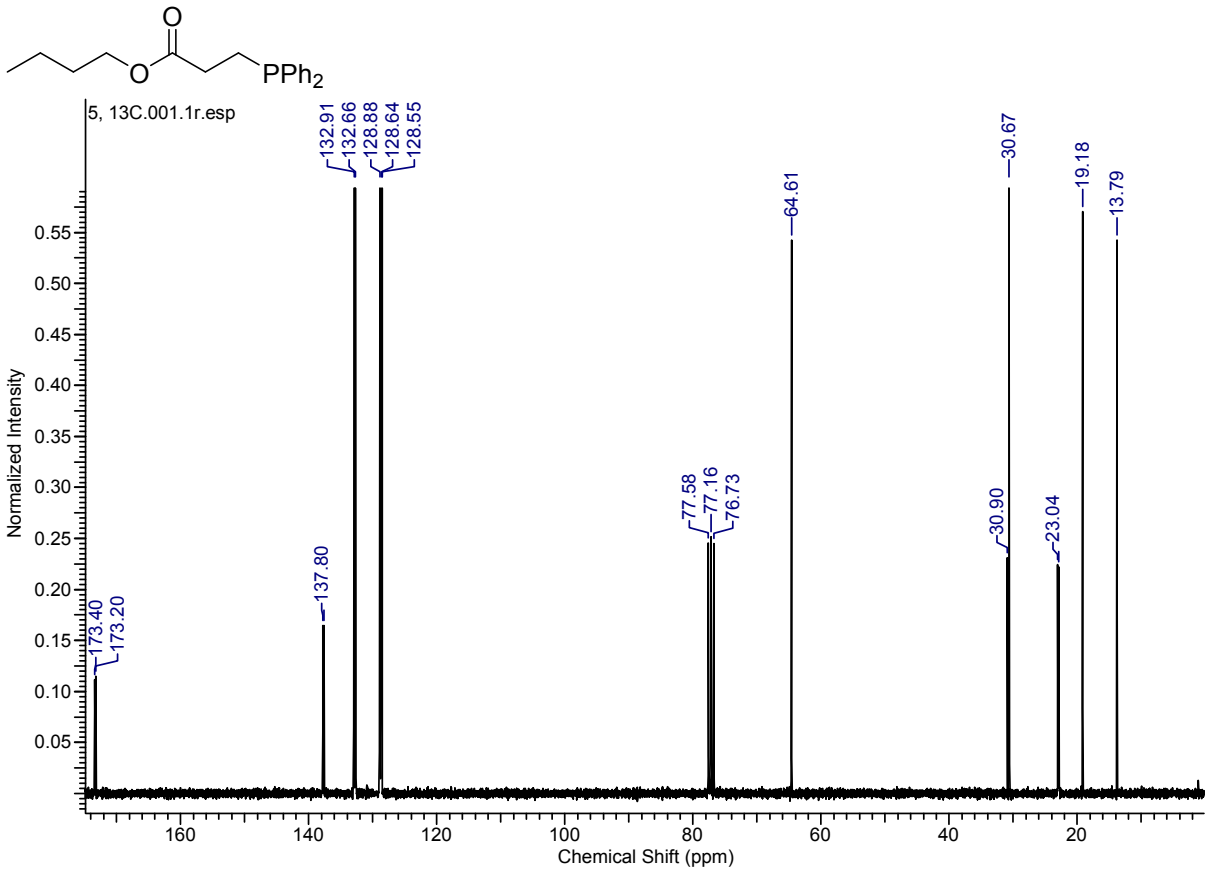


^{1}H NMR, **3p** (Table 1, Entry 16)

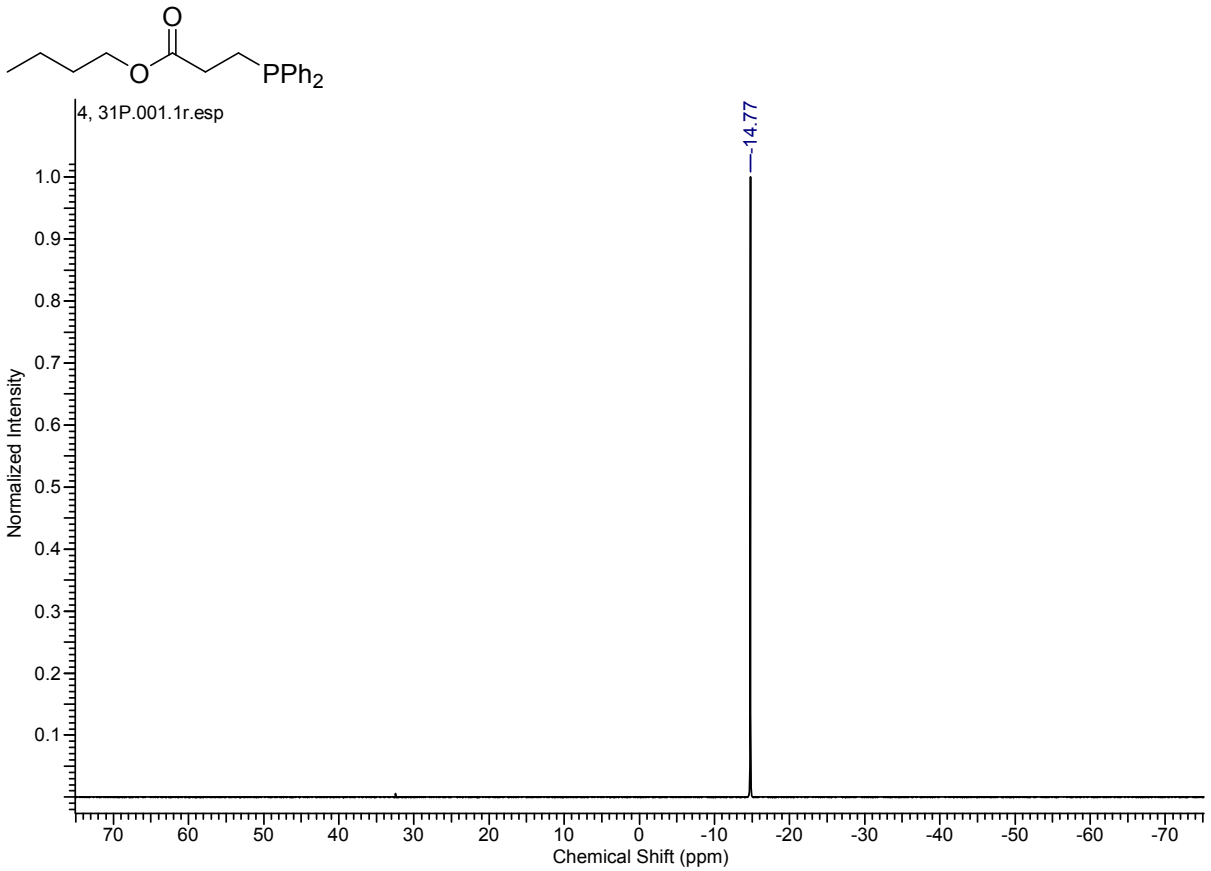




$^{13}C\{^{1}H\}$ NMR, **3p** (Table 1, Entry 16)

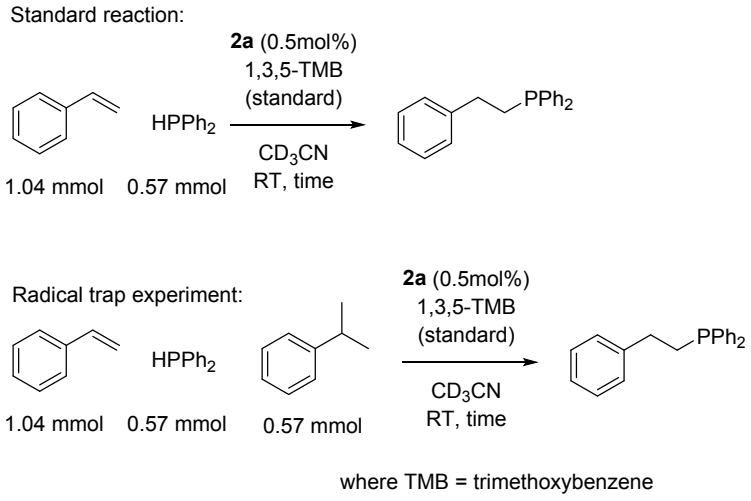


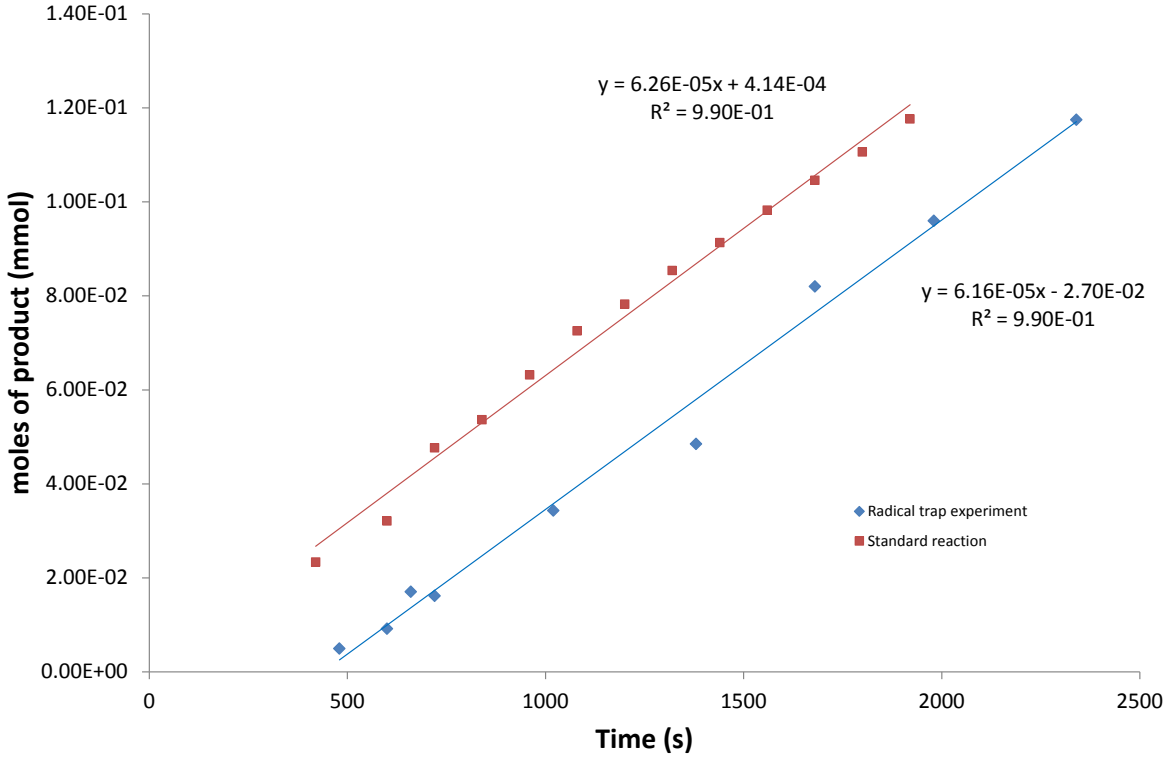
$^{31}P\{^{1}H\}$ NMR, **3p** (Table 1, Entry 16)



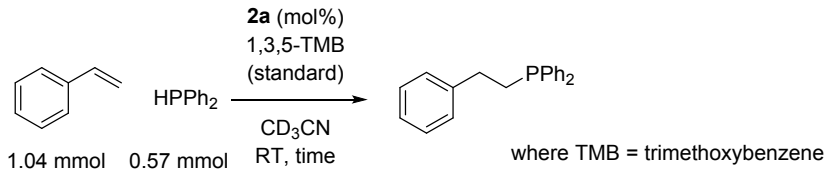
Mechanistic studies

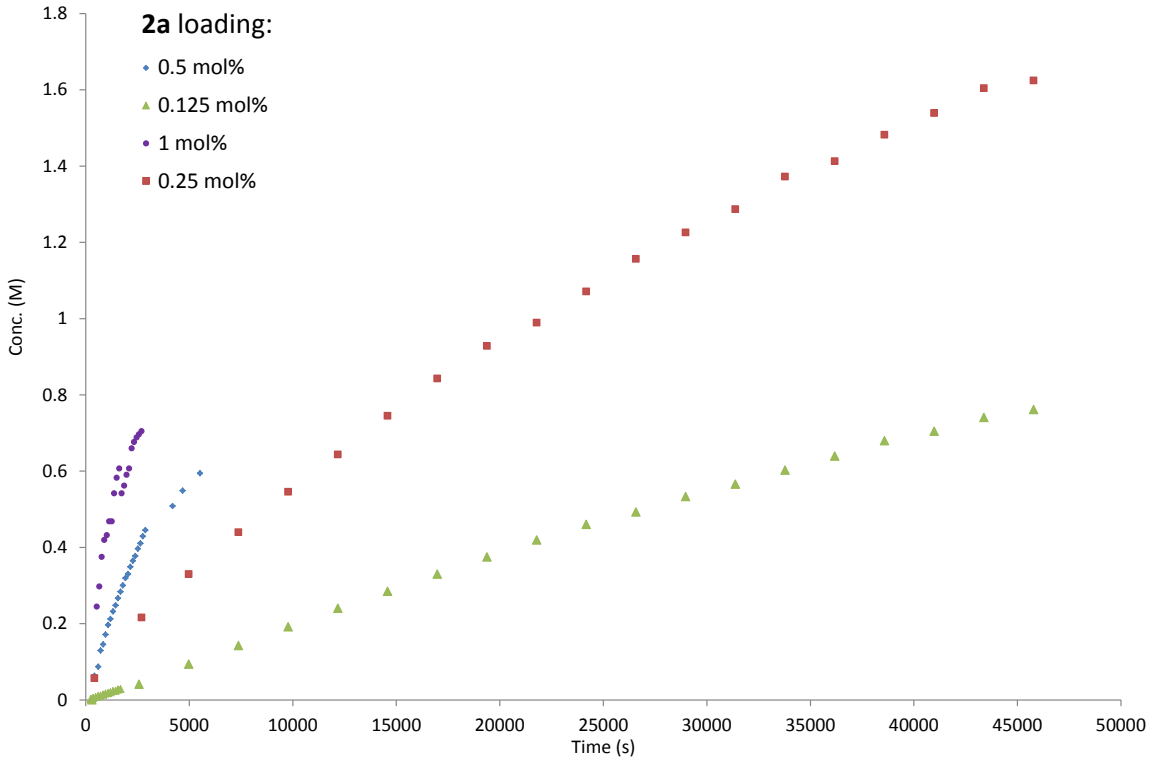
1. Reaction monitoring: comparison of standard reaction vs. radical trap experiment (standard reaction + 0.57 mmol cumene)



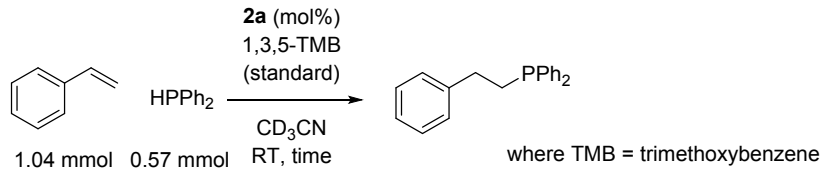


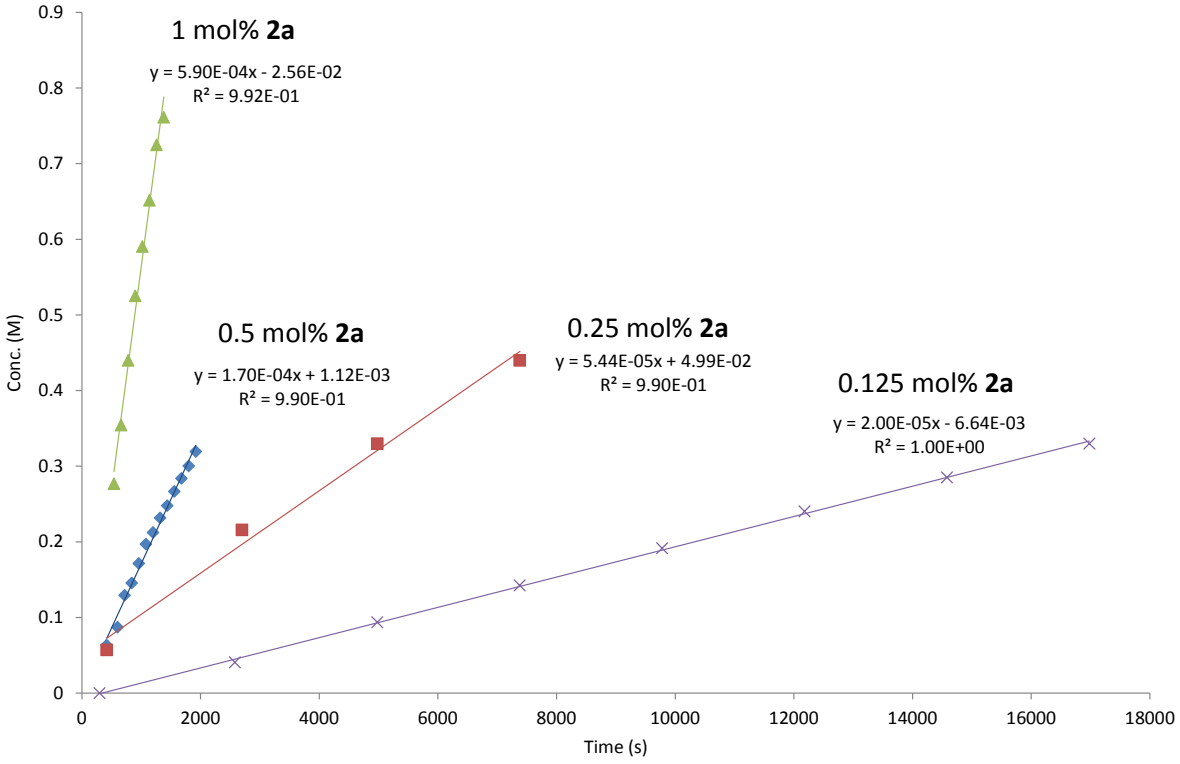
2. Reaction progress at different pre-catalyst loadings:





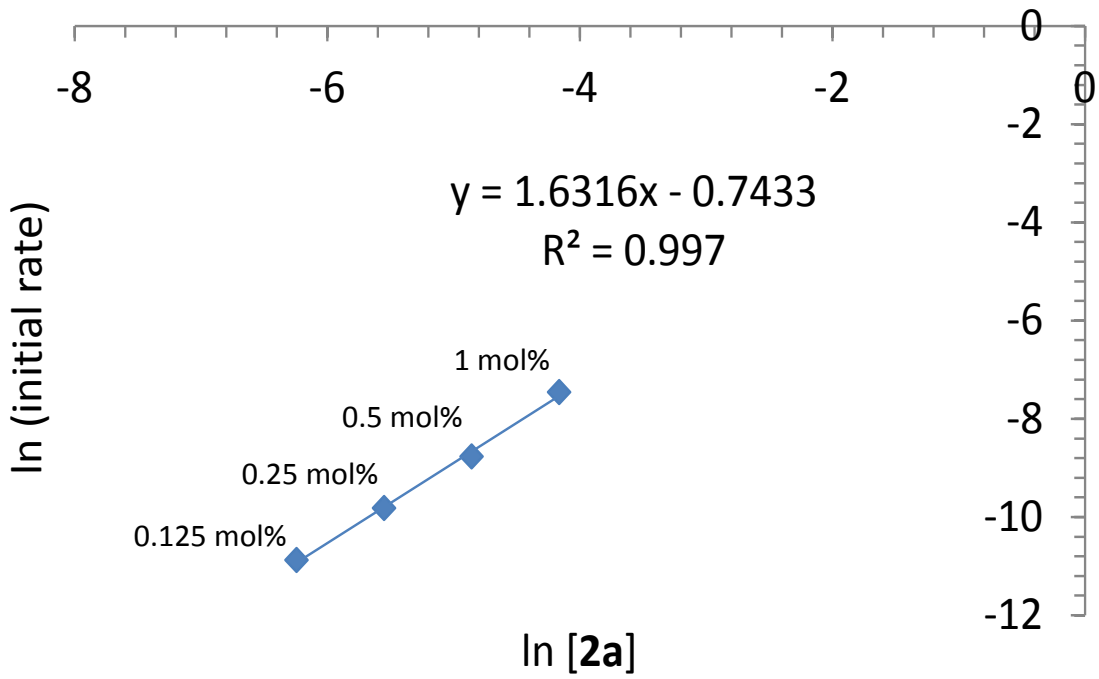
3. Initial rates at various pre-catalyst loadings:



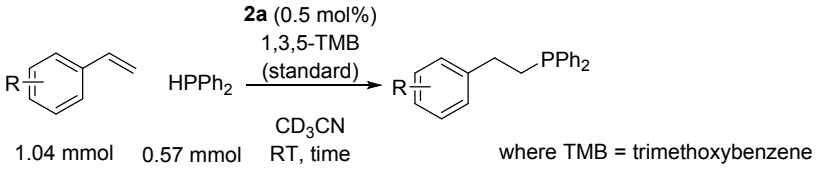


4. Log-log plot to determine order in 2a (using initial rates from page 45)

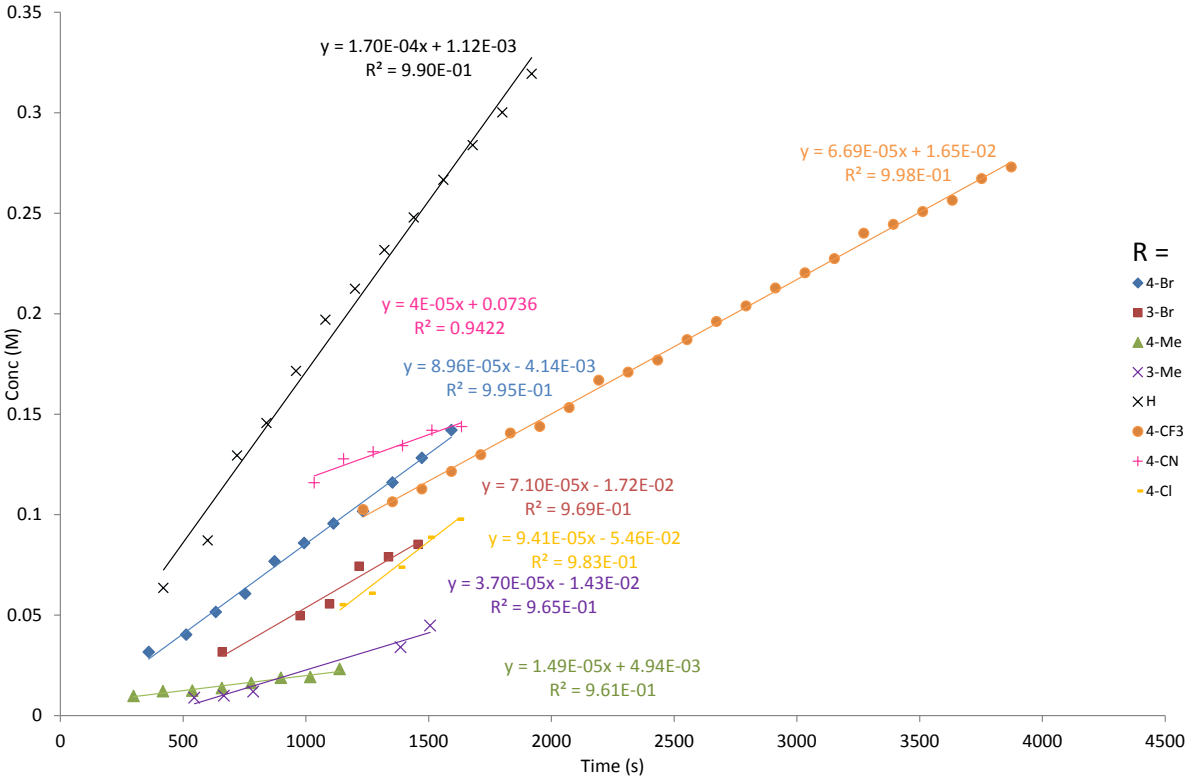
Order in **2a** = 1.6



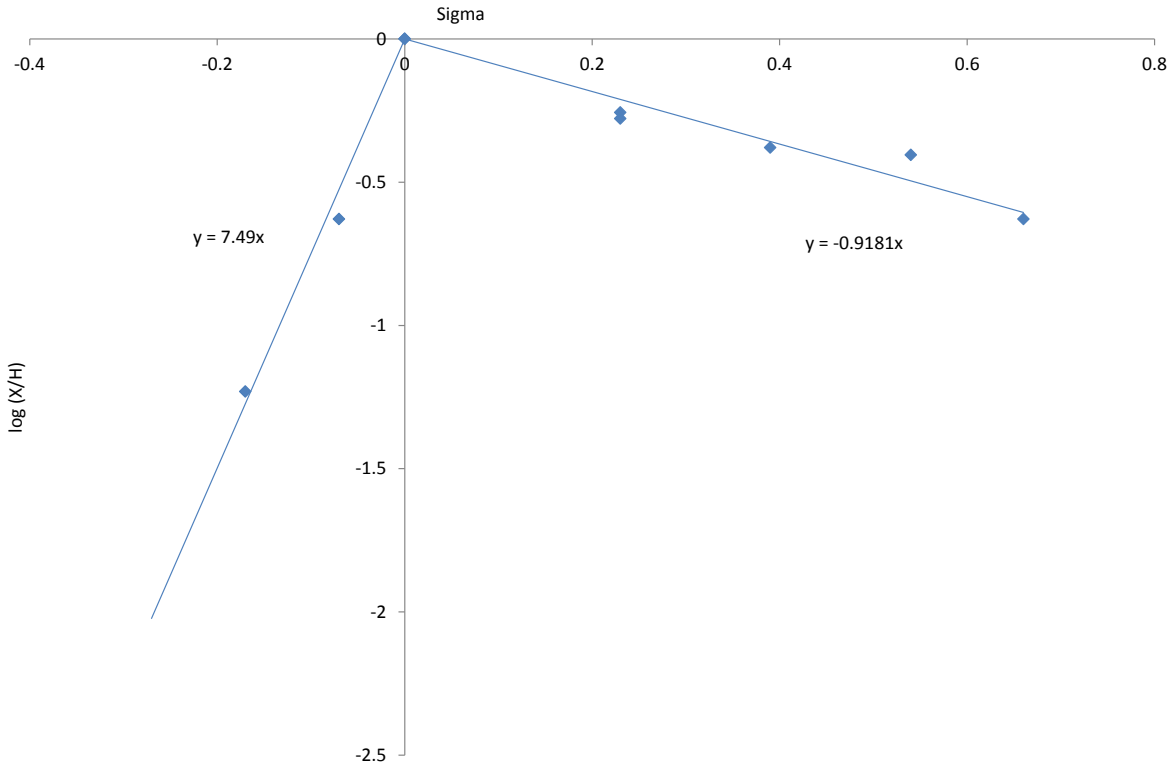
5. Initial rates (styrenes)



N.B. Reaction monitoring carried *in situ* by ^{1}H NMR, earliest data point collected is dependent on the time taken for the instrument to lock and shim.



6. Hammett plot



Notes and references

1) In the case of 4-phenyl-styrene, 750 µL CH_3CN were used to wash the insoluble styrene into an ampule which was then heated at 60 °C for 24 h.
2) Upon addition of diphenylphosphine to 2-vinylpyridine reaction, solution turned aubergine purple.
   In the case of 2-vinylstyrene a lavender-coloured oil remained
3) 4-vinylstyrene and 2-vinylstyrene reacted for 72 h; 4-chlorostyrene reacted for 114 h.
4) In the case of 4-vinylstyrene a yellow oil remained.
5) In the case of 3-methylstyrene, 4-vinylstyrene and 2-vinylstyrene no additional purification was necessary.
6) Non deutero THF (4.1 mg) was used for an integration standard in the case of 4-MeO-, 4-Me- and 3-methylstyrene.
7) a) L.-Z. Li, G.-L. Song, G.-Y. Tang, *Z. Kristallogr.- New Cryst. Struct*. **2012**, *227*, 544; b) S. Koner, S. Iijima, M. Watanabe, M. Sato, *J. Coord. Chem*. **2003**, *56*, 103; c) J. E. Davies, B. M. Gatehouse, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *29*, 1934; d) P. Coggon, A. T. McPhail, F. E. Mabbs, V. N. McLachlan, *J. Chem. Soc. A*, **1971**, 1014; e) L. O. Atovmyan, O. A. D'yachenko, S. V. Soboleva, *Zh. Strukt. Khim. Russ. J. Struct. Chem.* **1970**, *11*, 557; f) F. Calderazzo, C. Floriani, R. Henzi, F. L'Eplattenier, *J. Chem. Soc. A: Inorg., Phys., Theor*. **1969**, 1378−1386; g) M. Gerloch, E. D. McKenzie, A. D. C. Towl, *J. Chem. Soc. A: Inorg., Phys., Theor.* **1969**, 2850−2858.
8) a) P. Roy, K. Dhara, J. Chakraborty, M. Nethaji, P. Banerjee, *Indian J. Chem., Sect.A: Inorg., Bio-*

inorg., Phys., Theor. Anal. Chem. **2007**, *46*, 1947; b) N. Re, R. Crescenzi, C. Floriani, H. Miyasaka, N. Matsumoto, *Inorg. Chem*. **1998**, *37*, 2717−2722.
9) M. F. Cain, R. P. Hughes, D. S. Glueck, J. A. Golen, C. E. Moore, A. L. Rheingold, *Inorg. Chem*. **2010**, *49*, 7650–7662.