Supporting Information

Flow Electrosynthesis of Phosphinamides and Phosphoramidates through P–N Coupling

Table of contents

1. Experimental

1.1. General experimental

All solvents are used after drying and reagents were used as received without purification.

Thin-layer chromatography (TLC)

Thin-layer chromatography (TLC) was performed on pre-coated aluminium sheets of Merck silica gel 60 F254 (0.20 mm) and visualised by UV radiation (254 nm).

Column chromatography

Automated column chromatography was performed on a Biotage® Isolera Four using Biotage® cartridges SNAP Ultra 25 g.

NMR spectra

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured on Bruker DPX 400 or 500 apparatus and were referenced to the residual proton solvent peak (^{1}H NMR: $CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm) and solvent ^{13}C signal ($CDCl_3$: δ = 77.2 ppm). Chemical shifts δ were reported in ppm, multiplicity of the signals was declared as followed: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, hep = septet, dd = doublet of doublets, m = multiplet, b = broad; and coupling constants (J) in Hertz.

IR spectra

IR spectra were recorded on a Shimadzu FTIR Affinity-1S apparatus. Wavenumbers are quoted in cm^{-1}.

Mass spectrometry

Mass spectrometric measurements were performed by R. Jenkins, R. Hick, T. Williams and S. Waller at Cardiff University on a Water LCR Premier XEtof. Ions were generated by Electron Ionisation (EI) and Electron Spray (ES). The molecular ion peaks values quoted for either molecular ion $[M]^+$, molecular ion plus hydrogen $[M+H]^+$ or molecular ion plus sodium $[M+Na]^+$.

Melting points

Melting points were measured using a Gallenkamp variable heater with samples in open capillary tubes.

Electrochemical flow reactor

The electrochemical reactions were carried out in a galvanostatic mode using a Vapourtec Ion Electrochemical flow reactor.

Cyclic voltammogram

The cyclic voltammogram studies were performed using an Orygalys OGF500 Potentiostat/Galvanostat with OGFPWR power supply

1.2. Ion electrochemical reactor

The undivided Ion electrochemical reactor developed by Vapourtec Ltd was used to carry out the oxidative coupling of phosphine oxides and amines. The body of the microreactor consists of two stainless steel parts (e, f), each part can accommodate a (50 mm × 50 mm) electrode (a, b), the two electrodes are separated by a 500 µm thickness fluorinated ethylene propylene (FEP) spacer (c) and then on top of electrodes stainless steel spacer (d) is used followed by a clamp is used to assemble the reactor (h) (Figure S1)

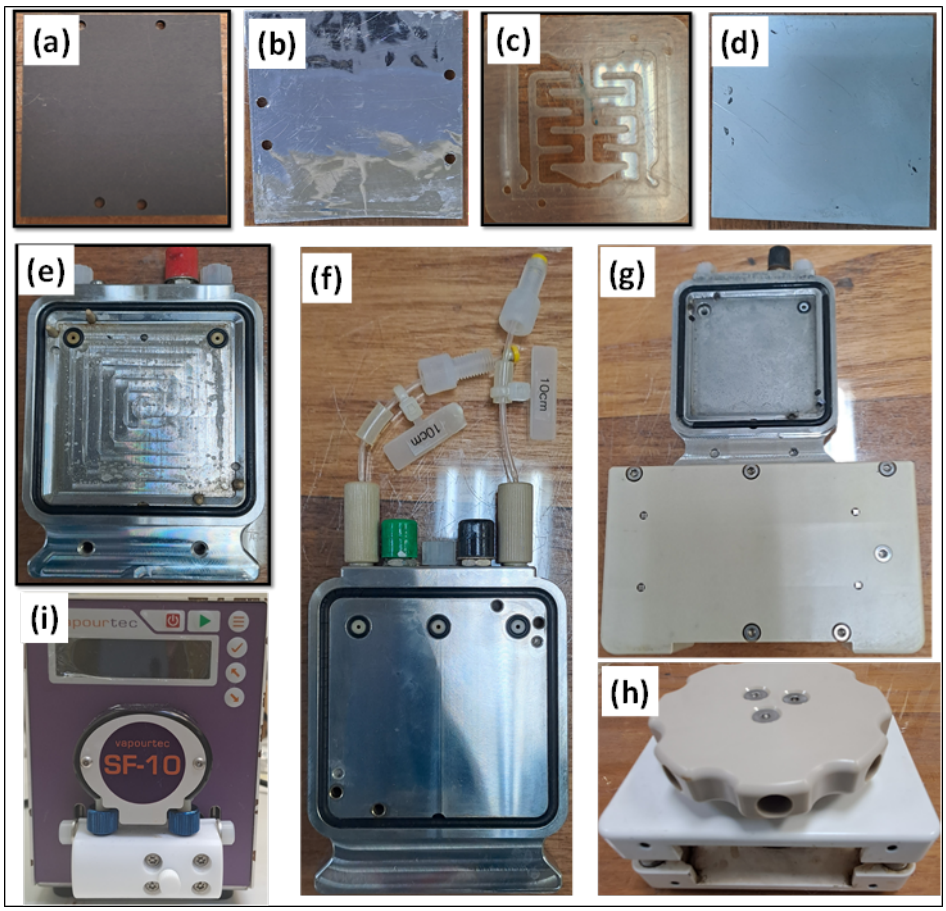


Figure S1: Vapourtec Ion electrochemical reactor, (a) graphite electrode (50 × 50 mm), (b) platinum electrode (50 × 50 mm), (c) spacer (0.5 mm thickness), (d) stainless stain separator, (e, f) body of the reactor containing plug for anode, cathode, inlet and outlet, (g) body of reactor for temperature required reactions, (h) clamp to assemble the reactor, (i) peristaltic pump for large scale reaction.

2. Batch electrochemical procedure

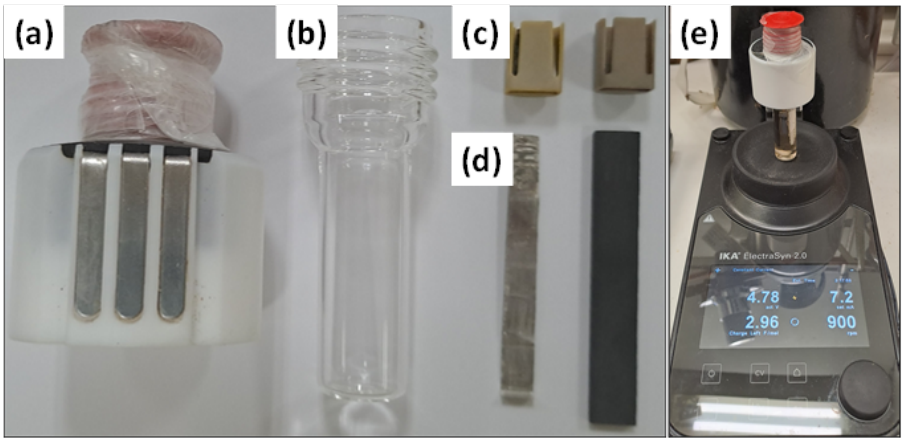
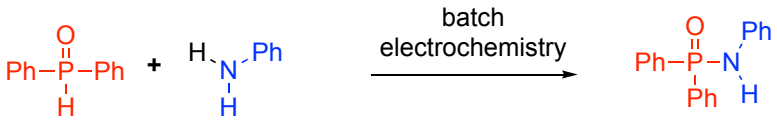


Figure S2. Batch electrochemical reaction set-up: (a) Electrasyn cap, (b) electrochemical cell (5 mL), (c) electrodes holder, (d) electrodes (cathode (Pt), anode (Gr)), (e) Electrasyn reaction set-up.

3. Optimisation of batch electrochemical parameters



4 **5a** **6a**

Scheme S1. Flow electrochemical reaction.

Table S1. Optimisation of batch reaction conditions.

Conditions[a]	**6a** Yield (%)[b]
Optimisation of electrode	
Pt as the cathode and GC as the anode	10
Pt as the cathode and Gr as the anode	13
Optimisation of current	
30 mA	10
20 mA	23
15 mA	34
10 mA	36
Optimisation of solvent	
CH_3CN:H_2O as solvent	7
MeOH as solvent	Trace
EtOH as solvent	No product

a. Standard reaction conditions: Undivided batch electrochemical cell, Pt cathode and glassy carbon (Gr) as anode, **4** (30 mg, 0.15 mmol) and **5a** (14 mg, 0.15 mmol) in MeCN (5 mL), KI 20 mol% (5 mg, 0.15 mmol) as electrolyte, and constant current: 10 mA, charge: 3.5 F/mol, 900 rpm. b. Yield determined by ^{1}H NMR spectroscopy using dodecane as internal standard.

4. Optimisation of flow electrochemical parameters at constant current (galvanostatic reaction)

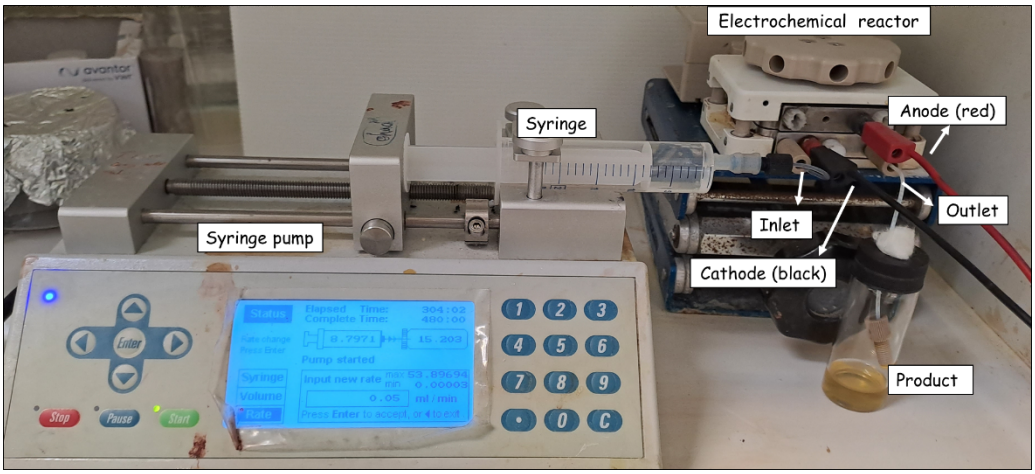
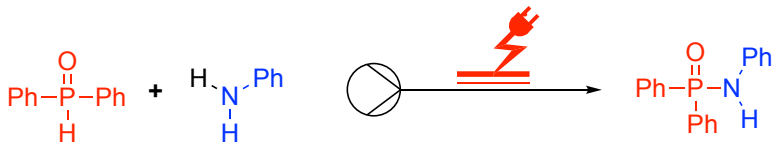


Figure S3. Flow rection setup

a. Standard reaction conditions: Undivided flow cell, Pt cathode and graphite (Gr) as anode, interelectrode distance: 0.5 mm, **4** (0.03 M) and **5a** (0.03 M) in MeCN (10 mL), KI 30 mol% (0.009 M) as electrolyte, and flow rate: 0.05 mL min^{-1}, constant current: 7 mA, charge: 3 F/mol, retention time: 12 min. b. Yield determined by ^{1}H NMR spectroscopy using dodecane as internal standard.

Table S2. Deviation from the standard conditions at constant current (galvanostatic reaction).

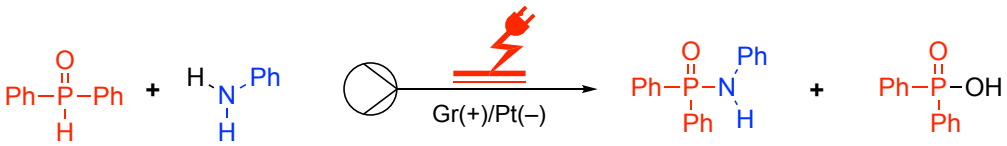


4 **5a** **6a**

Optimisation	Conditions	Retention time	**6a** Yield (%)
	No deviation		76
	without electricity *RT, no inert atm		No reaction
Electrode	Pt (platinum) as the anode		43
	GC (glassy carbon) as the anode		67
	Gr (graphite) as the anode		71
	GC as the cathode		39
	Gr as the cathode		33
	SS (stainless steel) as the cathode		55
	Cu (copper) as the cathode		56
F/mol	2.5 F/mol, 20 mol% KI, 6 mA		43
	3.5 F/mol, 20 mol% KI, 8.4 mA		40
Flow rate	0.025 mL/min, 20 mol% KI, 3 mA	24 min	53
	0.08 mL/min, 20 mol% KI, 11.6 mA	7.5 min	35
	0.1 mL/min, 20 mol% KI, 14 mA	6 min	29
Electrolyte	KI (30 mol%)		71
	tetrabutylammonium bromide		20, complex reaction mixture
	tetramethylammonium chloride		traces, complex reaction mixture
	tetramethylammonium iodide		23, complex reaction mixture
	ammonium iodide		31, complex reaction mixture, deep dark coloured solution
	tetramethylammonium iodide		insoluble

mol% of KI	without KI	10
	10 mol% KI	43
	30 mol% KI	76
	35 mol% KI	65
	40 mol% KI	52
Solvent	$CH_3CN:H_2O$ as solvent	19
	MeOH as solvent	traces
	EtOH as solvent	0
Concentration	0.225 mmol **4**, 0.225 mmol **5a**, 0.0225 M	26
	0.1 mmol **4**, 0.1 mmol **5a**, 0.02 M	28
Temperature	30 °C	55
	40 °C	14, degradation of starting material, black precipitate observed
	50 °C	traces, degradation of starting material, black precipitate observed

Table S3. Optimisation at constant voltage (potentiostatic) under flow conditions.

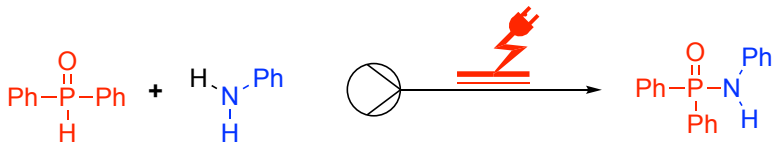


4 **5a** **6a** **22**

Conditions		**6a** Yield (%)	**22** Yield (%)	**4** Yield (%)
Optimisation of voltage				
Voltage (V)	Current (mA)			
0.73	1	5	6	87
1	1	8	trace	85
1.5	1	15	trace	82
2	2	59	-	36
2.25	4	70	5	12
2.5	6	64	17	-
2.75	8	62	3	25
3	10	63	2	24

a. Standard reaction conditions: Undivided flow cell, platinum (Pt) cathode and graphite (Gr) as anode, interelectrode distance: 0.5 mm, **4** (0.03 M) and **5a** (0.03 M) in MeCN (10 mL), KI 30 mol% (0.009 M) as electrolyte, and flow rate: 0.05 mL min^{-1}, retention time: 12 min. b. Yield determined by ^{31}P NMR spectroscopy using triphenylphosphine as an internal standard.

Table S4. Optimisation at constant voltage (potentiostatic) in batch conditions.

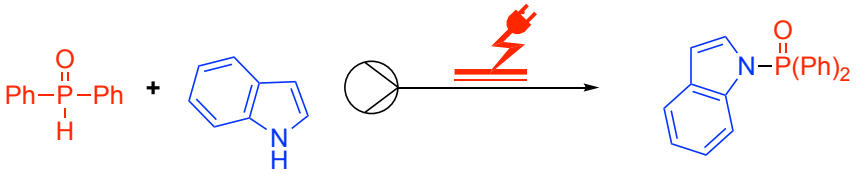


4 **5a** **6a**

Voltage (V)	Time (h)	**6a** Yield (%)
0.73	1	no product, starting material recovered
0.73	3	
0.73	5	
0.73	12	
0.73	24	
1	3	no product, starting material recovered
1	12	
1.5	3	no product, starting material recovered
1.5	12	
2	3	trace
2.5	3	25
2.5	5	27
2.5	12	31
3	3	29

a. Reaction conditions: Undivided electrasyn cell (5 ml), platinum (Pt) as cathode and graphite (Gr) as anode, **4** (30 mg, 0.15 mmol) and **5a** (14 mg, 0.15 mmol) in MeCN (5 mL), KI 30 mol% (8 mg) as electrolyte, rpm 700 b. Yield determined by ^{31}P NMR spectroscopy using triphenylphosphine as an internal standard.

Table S5. Optimisation of flow parameters for indole substrate at constant current (Galvanostatic reaction).

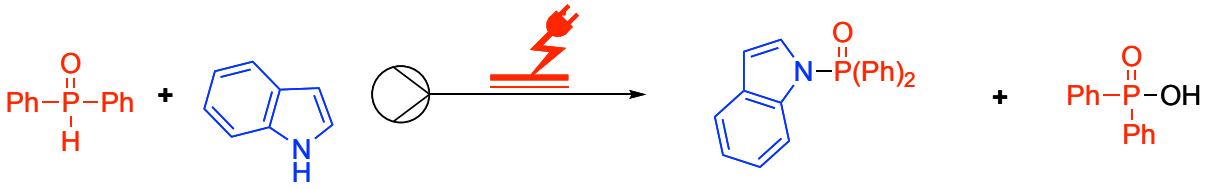


4 **7f**

Optimisation	Conditions				**7f** Yield (%)
	No deviation				79
Flow rate	Flow rate (mL/min)	Current (mA)	Reaction time (min)		
	0.025	3.6	24		30
	0.03	4.3	20		45
	0.05	7.2	12		35
	0.1	14.4	6		13
F/mol	F/mol	Flow rate (mL/min)	Current (mA)	Reaction time	
	1	0.04	2	15	traces
	1.5		3		35
	2		4		40
	2.5		5		64
	3.5		7		53
mmol of Indole	0.15				79
	0.30				53
	0.45				45

a. Standard reaction conditions: Undivided flow cell, Pt cathode and graphite (Gr) as anode, interelectrode distance: 0.5 mm, **4** (0.03 M) and indole (0.03 M) in MeCN (10 mL), KI 30 mol% (0.009 M) as electrolyte, and flow rate: 0.04 mL min^{-1}, charge: 3 F/mol, reaction time: 15 min. b. Yield determined by ^{31}P NMR spectroscopy using triphenylphosphine as an internal standard.

Table S6. Optimisation of flow parameters for indole substrate at constant voltage (potentiostatic reaction).

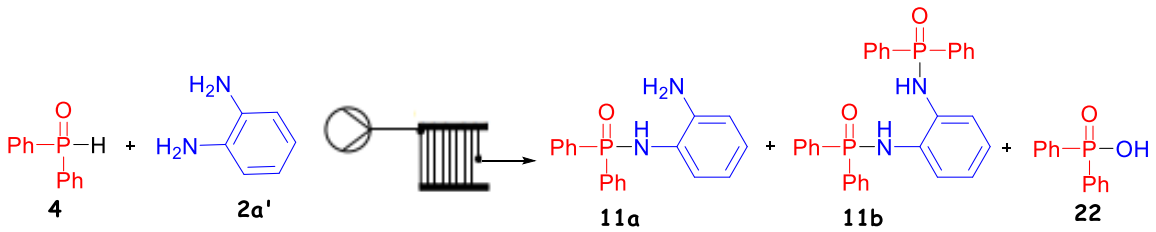


4 **7f** **22**

Constant cell voltage (V)	Flow rate (mL/min)	Current (mA)	**7f** Yield (%)	**22** Yield (%)	**4** Yield (%)
2.2	0.04	4	42	trace	-
2.3	0.04	5	52	-	-
2.4	0.04	6	58	-	-
3	0.04	7	69	-	11
3.5	0.04	8	60	-	7
4	0.04	9	51	-	-

a. Standard reaction conditions: Undivided flow cell, Pt cathode and graphite (Gr) as anode, interelectrode distance: 0.5 mm, **4** (0.03 M) and indole (0.03 M) in MeCN (10 mL), KI 30 mol% (0.009 M) as electrolyte, and flow rate: 0.04 mL min^{-1}, Retention time: 15 min. b. Yield determined by ^{31}P NMR spectroscopy using triphenylphosphine as an internal standard.

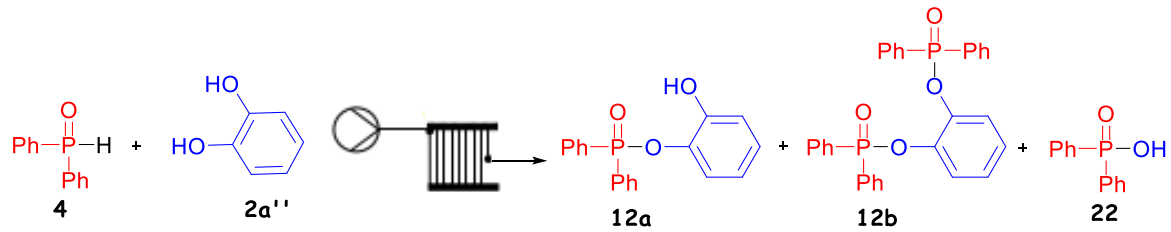
Table S7. Optimisation of flow parameters for 1,2-diaminobenzene.



Optimization	Conditions		Yield (%) **11a**	Yield (%) **11b**	Yield (%) **22**
Concentration	**4** (0.04 M), **2a'** (0.03 M)		22	15	14
	4 (0.05 M), **2a'** (0.03 M)		17	trace	63
	4 (0.06 M), **2a'** (0.03 M)		10	trace	75
	4 (0.03 M), **2a'** (0.04 M)		36	19	-
	4 (0.03 M), **2a'** (0.05 M)		23	50	-
	4 (0.03 M), **2a'** (0.06 M)		36	56	-
F/mol	4 F/mol, 30 mol% KI, 19.2 mA		18	21	trace
	5 F/mol, 30 mol% KI, 24 mA		decomposition		
	6 F/mol, 30 mol% KI, 28.9 mA		decomposition		
Flow rate		Reaction time			
	0.045 mL/min, 30 mol% KI, 13 mA, 3 F/mol	13.3 min	22	22	21
	0.04mL/min, 30 mol% KI, 11 mA, 3 F/mol	15 min	47	19	14
	0.03 mL/min, 30 mol% KI, 9 mA, 3 F/mol	20 min	49	20	12
	0.02 mL/min, 30 mol% KI, 6 mA, 3 F/mol	Passivation of electrode surface led to blocking			

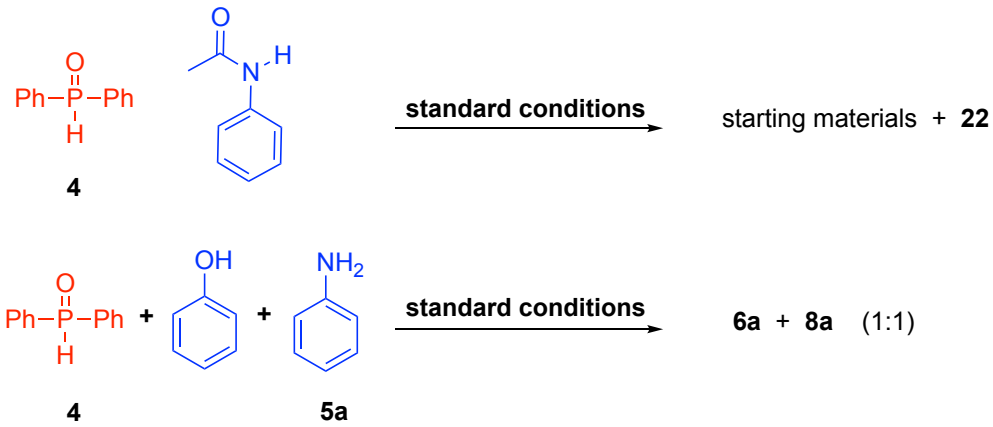
a. Standard reaction conditions: Undivided flow cell, platinum (Pt) cathode and graphite (Gr) as anode, interelectrode distance: 0.5 mm, **4** (0.03 M) and **2a'** (0.06 M) in MeCN (10 mL), KI 30 mol% (0.009 M) as electrolyte, and flow rate: 0.05 mL min^{-1}, retention time: 12 min. b. Yield determined by ^{1}H NMR using triphenylphosphine as internal standard.

Table S8. Optimisation of flow parameters for catechol.



Optimization	Conditions	Yield (%) **12a**	Yield (%) **12b**	Yield (%) **22**
Concentration	**4** (0.04 M), **2a''** (0.03 M)	20	-	74
	4 (0.05 M), **2a''** (0.03 M)	42	-	51
	4 (0.06 M), **2a''** (0.03 M)	23	trace	6 (passivation of electrode surface resulted in increase of voltage)
	4 (0.03 M), **2a''** (0.04 M)	41	trace	15 (passivation of electrode surface)
	4 (0.03 M), **2a''** (0.05 M)	trace	-	65 (passivation of electrode surface)
F/mol	4 F/mol, 30 mol% KI, 19.2 mA	decomposition and increase in voltage		
	5 F/mol, 30 mol% KI, 24 mA	decomposition and increase in voltage		
	6 F/mol, 30 mol% KI, 28.9 mA	decomposition and increase in voltage		
Flow rate		Reaction time		
	0.045 mL/min, 30 mol% KI, 13 mA, 3 F/mol	13.3 min	8	-	46
	0.04mL/min, 30 mol% KI, 11 mA, 3 F/mol	15 min	26	-	24
	0.035 mL/min, 30 mol% KI, 10 mA, 3 F/mol	17 min	18	trace	72
	0.03 mL/min, 30 mol% KI, 9 mA, 3 F/mol	20 min	Passivation of electrode surface led to blocking		

5. Control experiments for chemoselectivity



6. Mechanistic experiments

(i) Cyclic Voltammetry (CV)

All CVs were taken in MeCN, using a GC carbon disk (immersed surface area: 0.03 cm^2), Pt wire counter electrode, 0.01 M $Ag/AgNO_3$ reference at a scan rate of n = 100 mV s^{-1}, electrolyte $^nBu_4NClO_4$ (0.1 M), **4** (0.03 M), **5a** (0.03 M), KI (0.009 M).

(ii) Randles-Sevcik equation

The Randles-Sevcik equation[3] is a fundamental equation in electrochemistry that describes the relationship between the current (I) and the scan rate (v) in cyclic voltammetry experiments for a reversible redox reaction occurring at an electrode. It is expressed as:

$I_p = nFAD^{1/2} v^{1/2}C$

Where,

- I_P is the peak current,
- n is the number of electrons transferred in the redox reaction,
- F is the Faraday constant (96,485 C/mol),
- A is the electrode area,
- D is the diffusion coefficient of the electroactive species,
- v is the scan rate, and
- C is the concentration of the electroactive species.

The Randles-Sevcik equation describes the relationship between the peak current and the square root of the scan rate in cyclic voltammetry experiments and is used to analyse the electrochemical behaviour of redox-active species at an electrode surface.

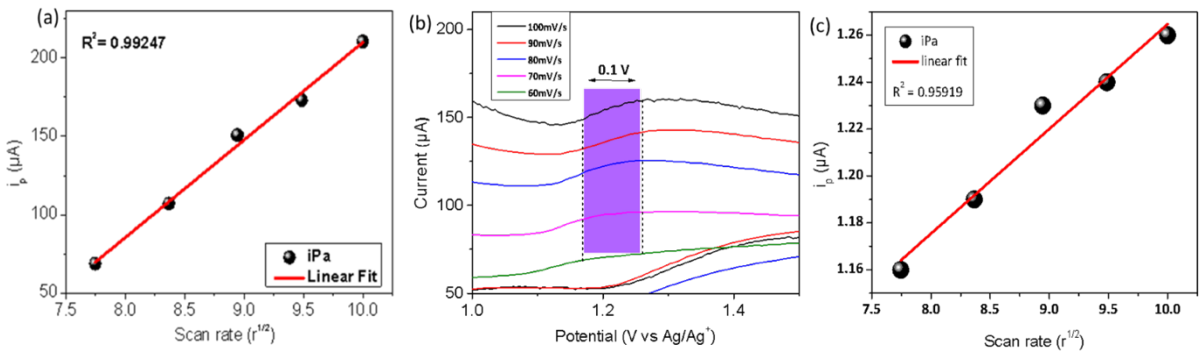


Figure S4. (a) Linear fit of peak current v/s square root of scan rate (diffusion control process) corresponding to 1st oxidation peak of graph (c), (b) CV at different scan rate of second oxidation peak illustrating the variation in peak current and shift in potential (c) linear fit of peak current v/s square root of scan rate (diffusion control process).

(iii) Dunn equation- defined by the linear relationship between log (peak current) v/s log (scan rate) and slope comes near 0.5, it demonstrates a diffusion controlled process.

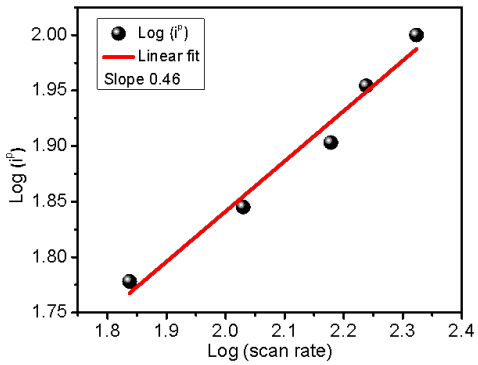
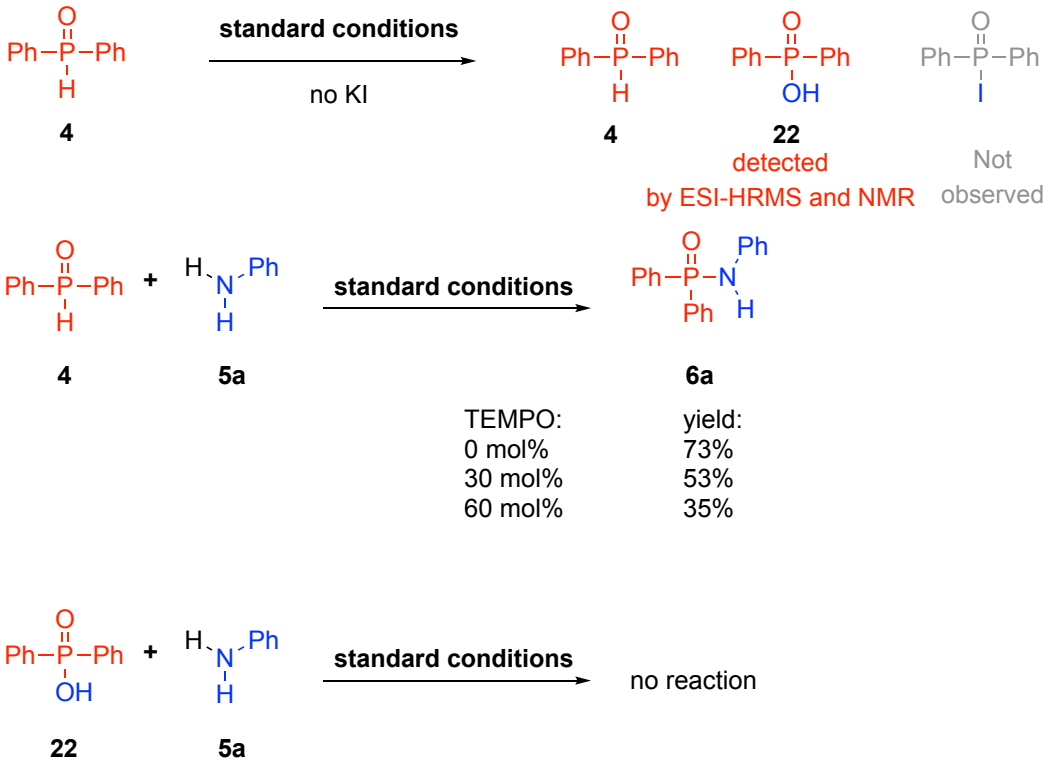


Figure S5. Dunn method, log (peak current) v/s log (scan rate)

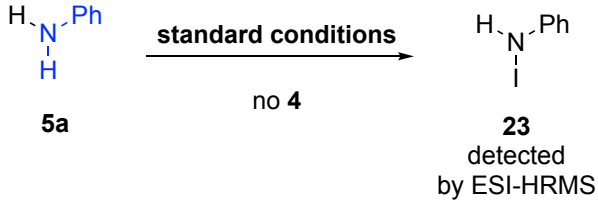
7. Control experiments

(a) Control experiments



(b) Mass spectra

(i) Reaction of aniline **5a** in the presence of KI without **4** using standard conditions.



5a **23** detected by ESI-HRMS

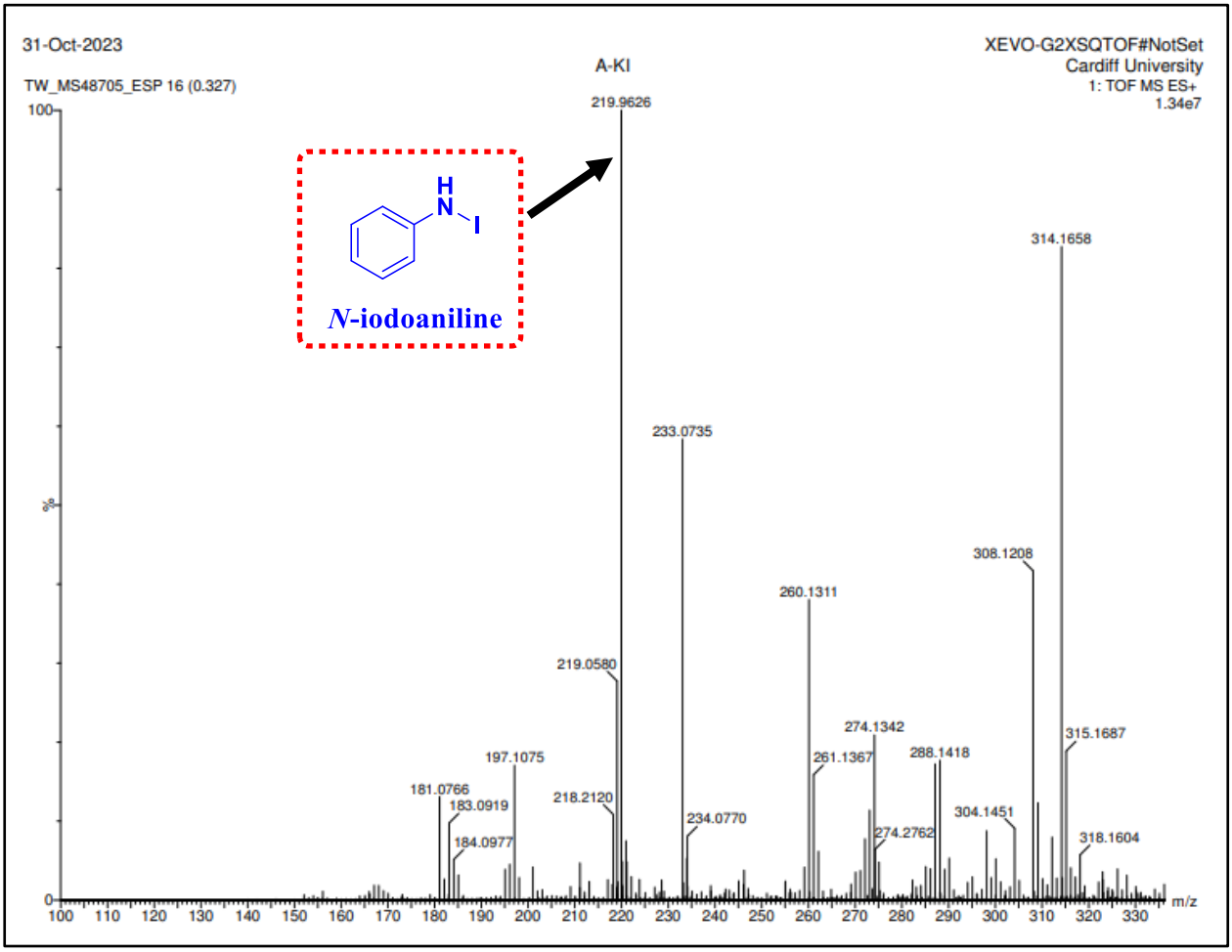
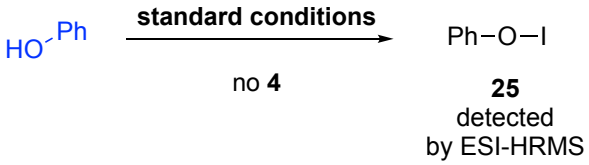


Figure S6. Mass spectrum of *N*-iodoaniline **23** formed as an intermediate.

(ii) Reaction of phenol in presence of KI without **1a** using standard conditions.



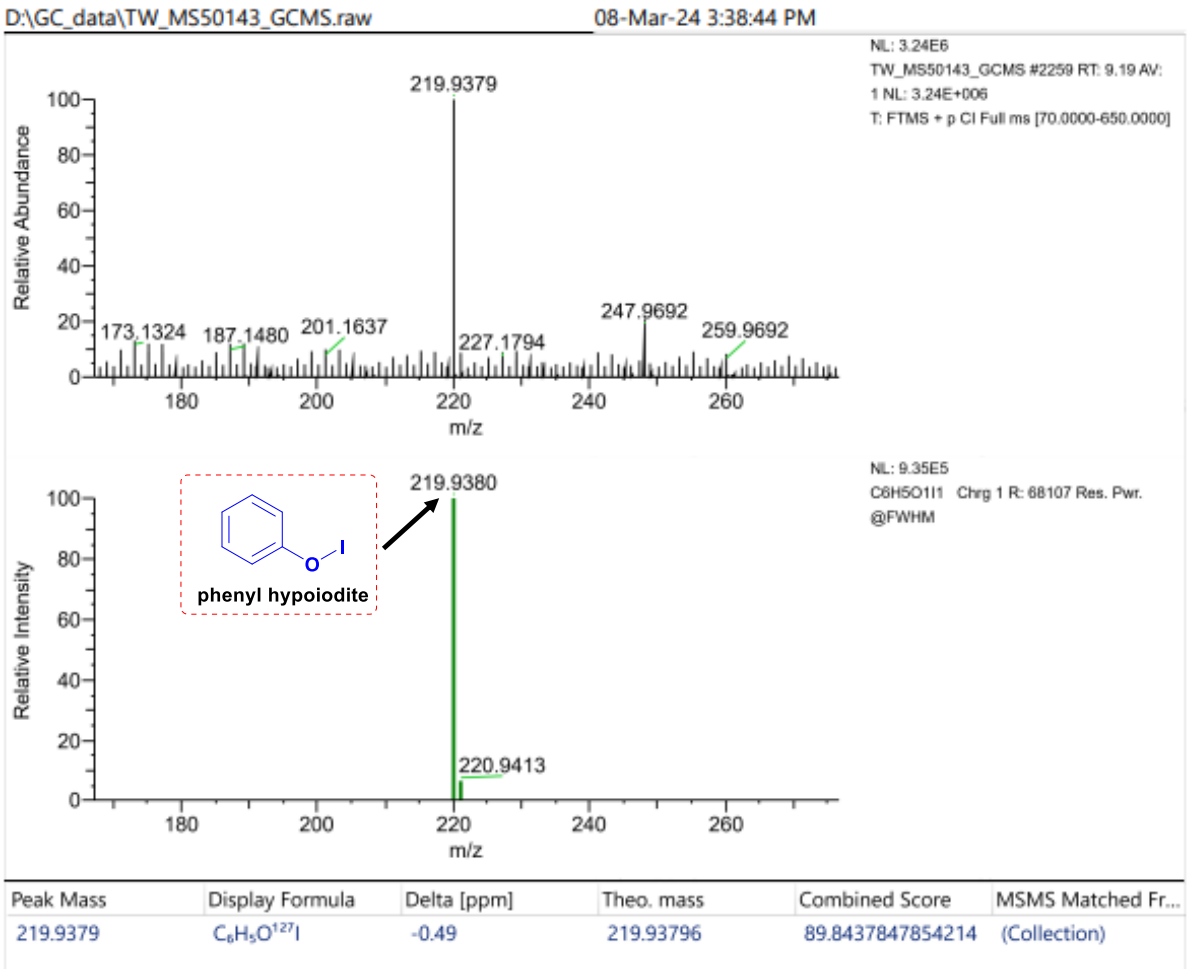
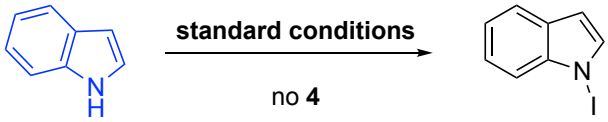
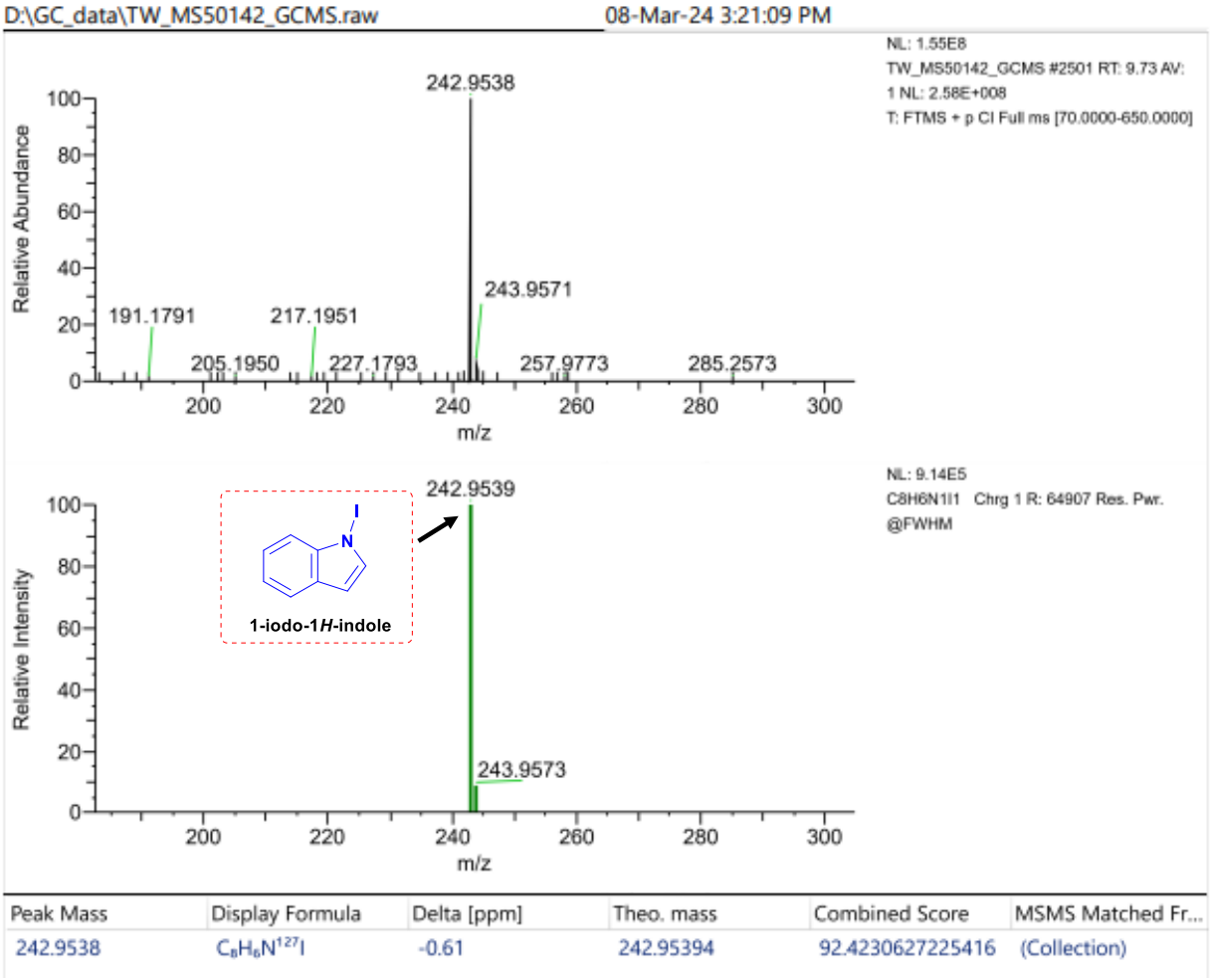


Figure S7. Mass spectrum of phenyl hypoiodite **25** formed as an intermediate.

Reaction of indole in presence of KI without **1a** using standard conditions.



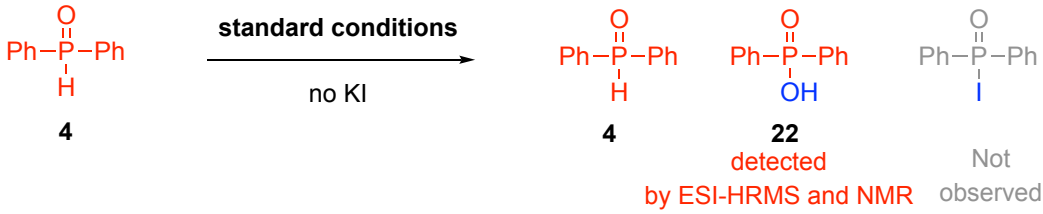
24
detected
by ESI-HRMS



Peak Mass	Display Formula	Delta [ppm]	Theo. mass	Combined Score	MSMS Matched Fr...
242.9538	$C_8H_6N^{127}I$	-0.61	242.95394	92.4230627225416	(Collection)

Figure S8. Mass spectrum of 1-iodo-1*H*-indole **24** formed as an intermediate.

Reaction of **4** in presence of KI without **5a** using standard conditions.



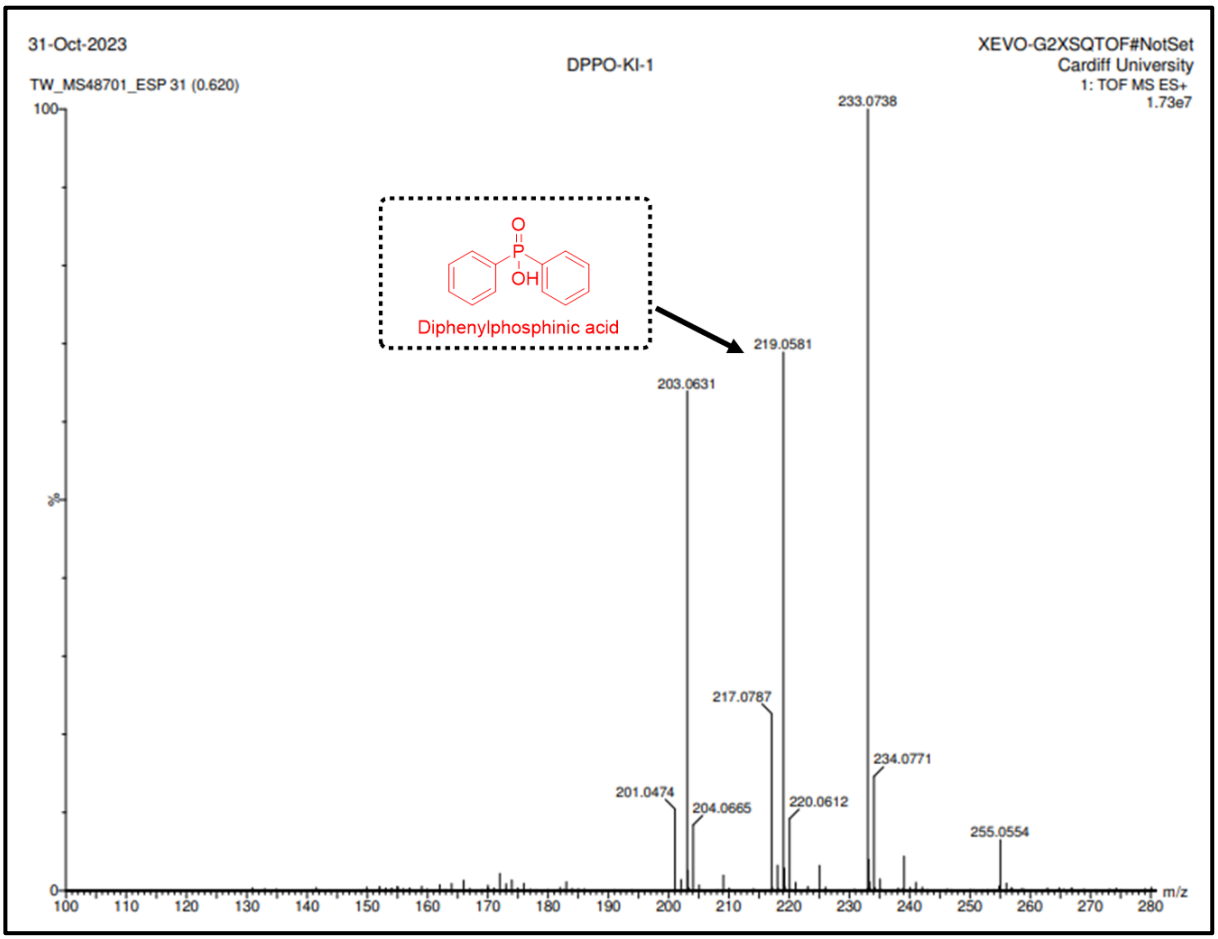


Figure S9. Mass spectrum of diphenylphosphinic acid **22**.

(c) Evidence for evolution of hydrogen gas at the cathode

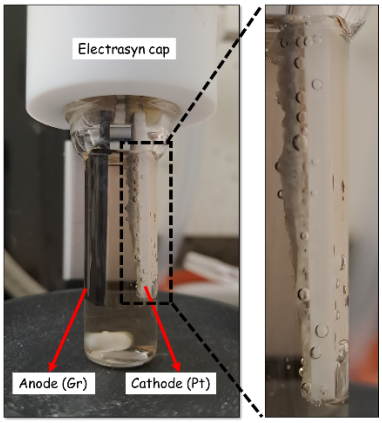
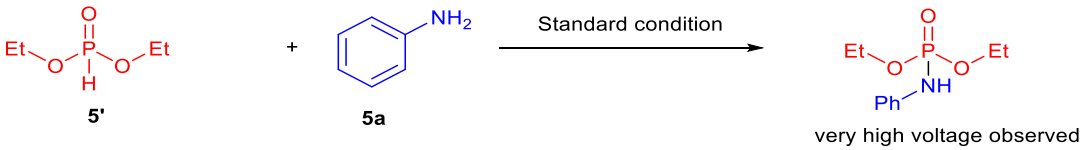


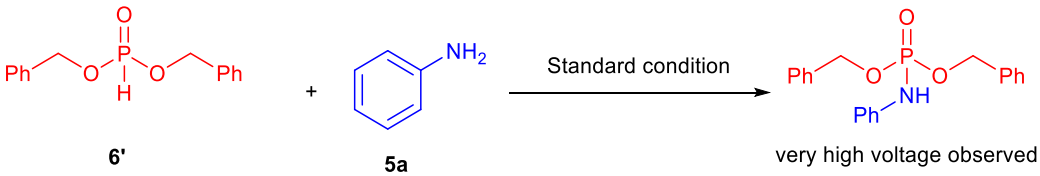
Figure S10. Formation of bubbles at cathode (Pt) indicating the evolution of H_2 as product during the batch electrolysis of **4** and **5a** under batch conditions.

a. Batch electrochemical conditions: undivided Electrasyn setup, cell (5 mL), platinum (Pt) cathode and graphite (Gr) as anode, **4** (0.03 M) and **5a** (0.03 M) in MeCN (5 mL), KI (30 mol%), current: 7 mA, time: 90 min.

Unsuccessful experiments:



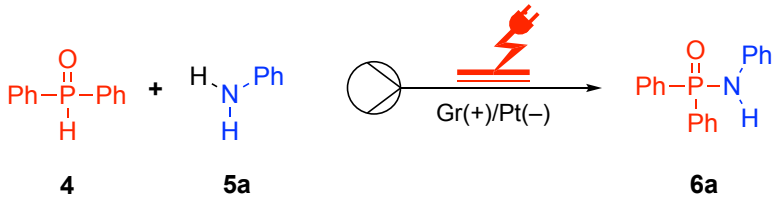
Observation: Voltage increased after 30 min of the reaction, which is due to the passivation of the surface of electrode, resulted in a blockage of the outlet. This passivation seems to be due to a fragmentation of the graphite electrode surface. This observation implies that the electrode material is not suitable for substrate **5'**.



Observation: Voltage increased up to 32 V after 45 min of the reaction, which is due to the passivation of the surface of electrode, resulting in a blockage of the outlet. This passivation seems to be due to a fragmentation of the graphite electrode surface. This observation implies that the electrode material is not suitable for substrate **6'**.

8. Scale-up of the reaction

(a) Reaction set-up for gram-scale synthesis



4 **5a** **6a**

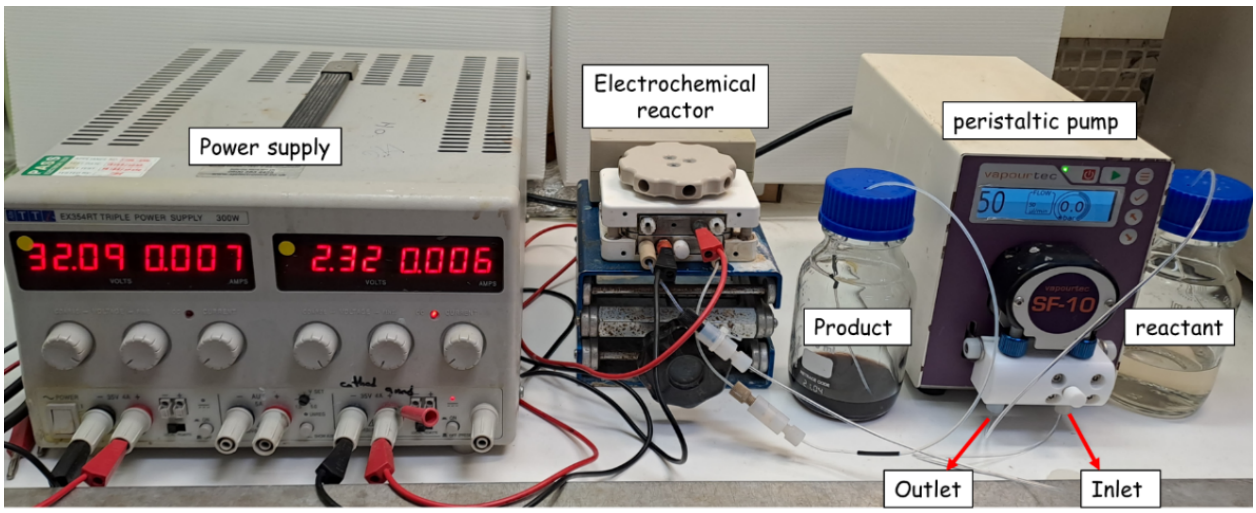
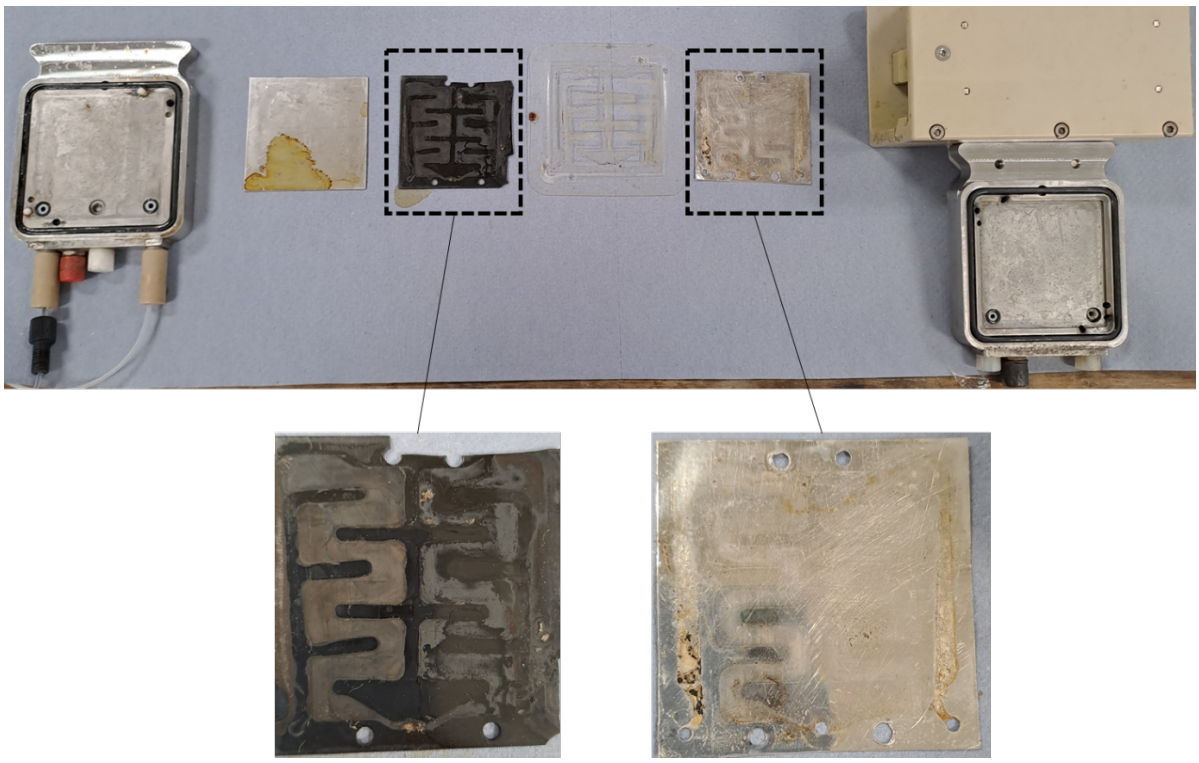


Figure S11. Reaction setup for scale-up

(b) Galvanostatic reaction (at constant current)

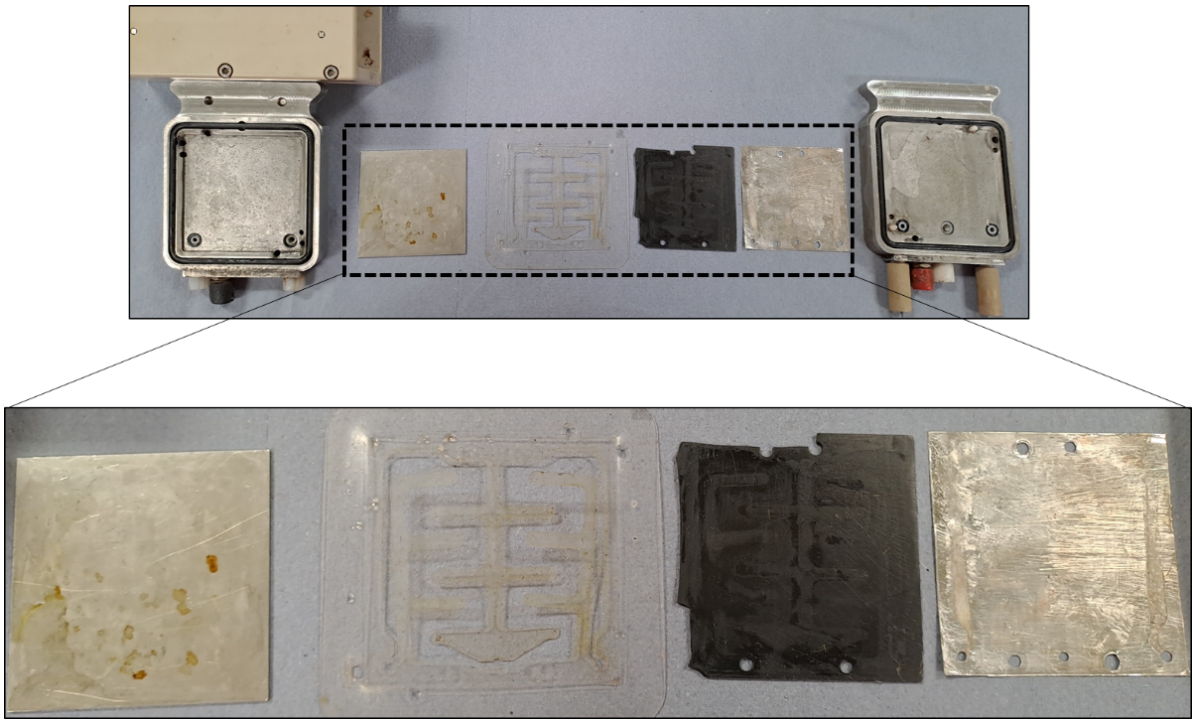
The electrolysis was performed in an undivided cell using a Vapourtec Ion Electrochemical Flow Reactor (reactor volume = 0.6 mL, spacer 0.5 mm) using a Graphite (Gr) electrode as the anode and a platinum (Pt) electrode as the cathode (active surface area: 2 × 12 cm^2). A solution of diphenylphosphine oxide **4** (1 g, 4.95 mmol) and aniline **5a** (452 µL, 4.95 mmol) in acetonitrile (165 mL) with KI (30 mol%, 1.48 mmol, 246 mg) was stirred for 15 min at room temp. to prepare a homogenous reaction mixture. The reactor was assembled and connected to the syringe pump with a flow rate of 0.05 mL/min and the current was set at 7.2 mA. Then, the solution was pumped into a PTFE coil (1 mm internal diameter) to the inlet of the electrochemical reactor through peristaltic pump. The product was collected into a reagent bottle as shown in the figure below after 18 min for 55 hr 7 min. The collected product was purified by flash column chromatography (solvent system: cyclohexane/ethyl acetate 30:70, v/v) to get the pure product with an isolated yield of 899 mg of **6a** (62%). Also the reaction yield was monitored via ^{31}P NMR throughout the reaction at different time intervals.



(i) Figure S12. Electrodes after electrolysis at constant current.

(c) Potentiostatic reaction (at constant voltage)

The electrolysis was performed in an undivided cell using a Vapourtec Ion Electrochemical Flow Reactor (reactor volume = 0.6 mL, spacer 0.5 mm) using a Graphite (Gr) electrode as the anode and a platinum (Pt) electrode as the cathode (active surface area: 2 × 12 cm^2). A solution of diphenyl-phosphine oxide **4** (1 g, 4.95 mmol) and aniline **5a** (452 µL, 4.95 mmol) in acetonitrile (165 mL) with KI (30 mol%, 1.48 mmol, 246 mg) was stirred for 15 min at room temp. to prepare a homogenous reaction mixture. The reactor was assembled and connected to the syringe pump with a flow rate of 0.05 mL/min and the voltage was set at 2.25 V. Then, the solution was pumped into a PTFE coil (1 mm internal diameter) to the inlet of the electrochemical reactor through peristaltic pump. The product was collected into a reagent bottle as shown in the figure below after 18 min for 55 h and 7 min. The collected product was purified by flash column chromatography (solvent system: cyclohexane/ethyl acetate 30:70, v/v) to get the pure product **6a** with an isolated yield of 924 mg (64%). The reaction yield was monitored via ^{31}P NMR throughout the reaction at different time interval using triphenylphosphine as internal standard.



(ii) Figure S13. Electrodes after electrolysis at constant cell voltage (potentiostatic reaction): no passivation observed on the electrodes surface.

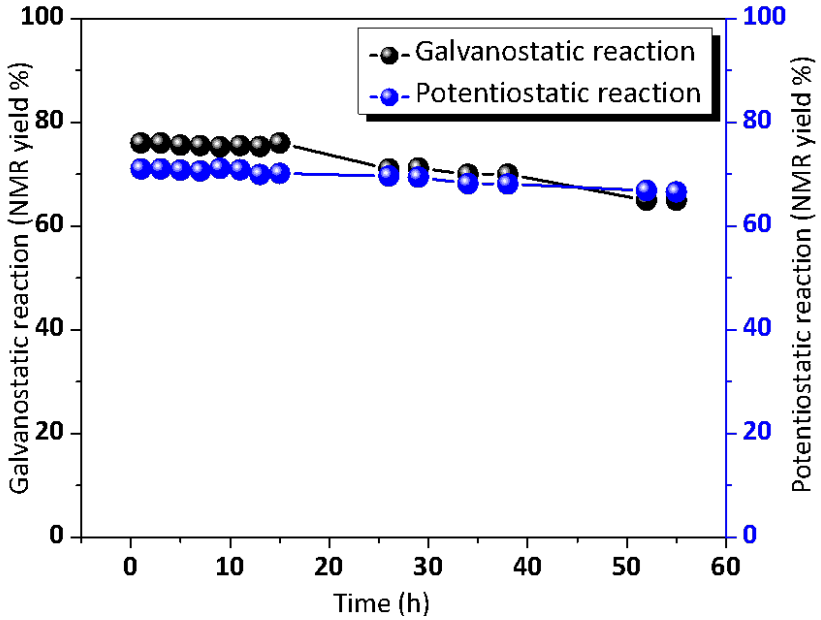


Figure S14. NMR yield at different time intervals for gram scale synthesis using triphenylphosphine as an internal standard.

9. Computational study

ORCA/5.0.0 was used to fully optimise all the structures reported in this paper at the B3LYP level of density functional theory (DFT). The def2-SVP basis set was used for all atoms. Frequency calculations were carried out at the same level of theory as those for the structural optimisation.

9.1. Optimisation and determination of molecular orbitals

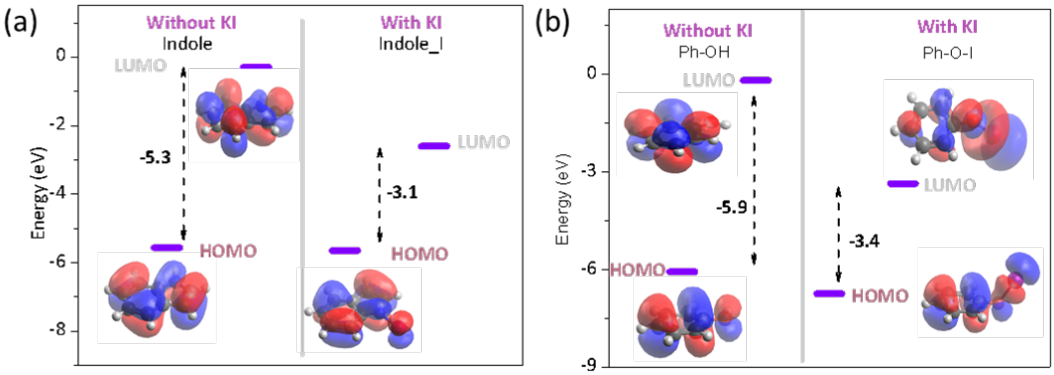


Figure S15. HOMO-LUMO energy gap of (a) indole and (b) phenol substrate with and without KI.

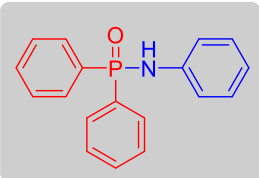
10. General flow electrochemical procedure

10.1. General procedure for electrochemical phosphinamide synthesis (GP1):

The electrolysis was performed in an undivided cell using a Vapourtec Ion Electrochemical Flow Reactor (reactor volume = 0.6 mL, spacer 0.5 mm) using a Graphite (Gr) electrode as the anode and a platinum (Pt) electrode as the cathode (active surface area: 2 × 12 cm^2). A solution of diphenylphosphine oxide **4** (60 mg, 0.30 mmol) and amine (0.30 mmol) in acetonitrile (10 mL) with KI (30 mol%, 15 mg) was placed in volumetric flask stirred at room temp. to prepare a homogenous reaction mixture and filled in a syringe. The reactor was assembled and connected to the syringe pump with a flow rate of 0.05 mL/min and the current was set at 7.2 mA. Then, the solution was pumped into a PTFE coil (1 mm internal diameter) to the inlet of the electrochemical reactor. The product was collected into a glass vial after 18 min for 200 min (10 mL) and purified by flash column chromatography (solvent system: petroleum ether/ethyl acetate 30:70, v/v) to get the pure product.

10.2. Synthesis and spectral characterisation of phosphinamides:

Synthesis of *N*,*P*,*P*-triphenylphosphinic amide (**6a**)[1,8]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), aniline (28 µL, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6a**. The compound **6a** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 64 mg, 0.22 mmol, 73%. Crystals were grown from a saturated solution of **6a** in CH_3CN at room temperature.

m.p.: 229–231 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.87 (m, 4H), 7.55–7.51 (m, 2H), 7.48–7.44 (m, 4H), 7.11 (m, 2H), 6.96 (m, 2H), 6.89 (m, 1H), 5.23 (d, J = 9.4 Hz, 1H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.7, 132.8 (d, J = 2.9 Hz), 132.4 (d, J = 10.0 Hz), 131.8, 129.7, 129.2 (d, J = 13.0 Hz), 122.3, 118.9 (d, J = 6.6 Hz) ppm

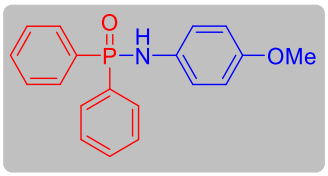
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.4 (s) ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{15}NOP$ $[M-H]^+$ 292.0891, found: 292.0891

IR (neat): 598, 691, 727, 1186, 1217, 1489, 1740, 2886, 3019, 3075 cm^{-1}

NMR spectroscopic data matches the literature data.[8]

Synthesis of *N*-(4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6b**)[2,8]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 4-methoxy aniline (37 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6b**. The compound **6b** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a dark brown solid. Yield: 80 mg, 0.25 mmol, 83%.

m.p.: 141–142 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 4H), 7.54–7.50 (m, 2H), 7.47–7.43 (m, 4H), 6.98–6.95 (m, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 5.12 (d, *J* = 8.8 Hz, 1H), 3.70 (s, 3H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.5, 133.6 (d, J = 1.4 Hz), 132.9, 132.6 (d, J = 2.9 Hz), 132.5 (d, J = 9.9 Hz), 129.1 (d, J = 12.9 Hz), 121.1 (d, J = 6.2 Hz), 115.1, 55.8 (d, J = 4.0 Hz) ppm

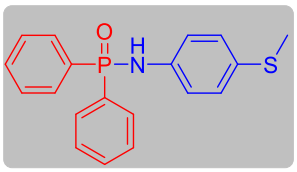
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.6 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{19}NO_2P$ $[M+H]^+$ 324.1153, found: 324.1156

IR (neat): 582, 692, 734, 767, 935, 1118, 1226, 1400, 1508, 1587, 2835, 2905, 3095 cm^{-1}

NMR spectroscopic data matches the literature data.[2,8]

Synthesis of *N*-(4-(methylthio) phenyl)-*P*,*P*-diphenylphosphinic amide (**6c**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (30 mg, 0.15 mmol), 4-(methylthio)aniline (19 µL, 0.15 mmol) and KI (30 mol%, 8 mg) in CH_3CN (5 mL) to afford **6c**. The compound **6c** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70) as the solvent system. The product was obtained as a colourless solid. Yield: 40 mg, 0.12 mmol, 80%.

m.p.: 200–202 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92–7.84 (m, 4H), 7.56–7.52 (m, 2H), 7.47 (m, 4H), 7.13–7.05 (m, 2H), 6.98–6.92 (m, 2H), 5.24 (d, *J* = 6.2 Hz, 1H), 2.39 (s, 3H) ppm

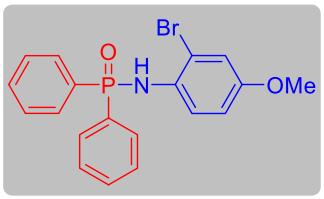
^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.3, 132.4 (d, J = 2.8 Hz), 132.0 (d, J = 10.1 Hz), 130.6, 129.2, 128.9 (d, J = 13.0 Hz), 119.2 (d, J = 6.4 Hz), 29.7, 17.2 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.6 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{19}NOPS$ $[M+H]^+$ 340.0925, found: 340.0923

IR (neat): 509, 551, 691, 727, 937, 1107, 1177, 1273, 1437, 1493, 1599, 2849, 2918, 3019, 3096 cm^{-1}

Synthesis of *N*-(2-bromo-4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6d**)[6]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2-bromo-4-methoxyaniline (40 µL, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6d**. The compound **6d** was purified by flash column chromatography using petroleum ether and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 89 mg, 0.225 mmol, 75%.

m.p.: 137–139 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92–7.87 (m, 4H), 7.54–7.50 (m, 2H), 7.46 (m, 4H), 7.33–7.31 (m, 1H), 7.06 (dd, *J* = 2.8, 0.7 Hz, 1H), 6.62 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.56 (d, *J* = 10.1 Hz, 1H), 3.69 (s, 3H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.0, 132.2, 132.1, 131.8 (d, J = 10.0 Hz), 131.7, 131.1, 128.8 (d, J = 13.0 Hz), 120.5, 117.8, 114.1, 55.6 ppm

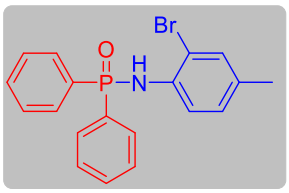
^{31}P NMR (202 MHz, $CDCl_3$): δ = 19.0 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{18}BrNO_2P$ $[M+H]^+$ 402.0291, found: 402.0291

IR (neat): 579, 645, 755, 783, 953, 1121, 1493, 1591, 2835, 3047 cm^{-1}

NMR spectroscopic data matches the literature data.[6]

Synthesis of *N*-(2-bromo-4-methylphenyl)-*P*,*P*-diphenylphosphinic amide (**6e**)[6]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2-bromo-4-methylaniline (110 µL, 0.90 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6e**. The compound **6e** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a brown solid. Yield: 90 mg, 0.235 mmol, 78%.

m.p.: 160–162 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (m, 4H), 7.47–7.43 (m, 2H), 7.38 (m, 4H), 7.22 (s, 1H), 7.16 (d, J = 8.3 Hz, 1H), 6.76 (dd, J = 8.2, 1.5 Hz, 1H), 5.68 (d, J = 10.3 Hz, 1H), 2.11 (s, 3H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.8, 132.9, 132.7, 132.4 (d, J = 2.8 Hz), 131.9 (d, J = 10.1 Hz), 131.1, 129.2, 128.9 (d, J = 13.0 Hz), 119.3 (d, J = 3.7 Hz), 113.2 (d, J = 9.0 Hz), 20.3 ppm

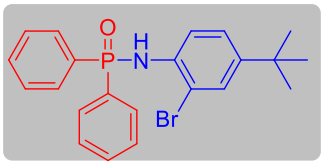
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.9 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{18}BrNOP$ $[M+H]^+$ 386.0309, found: 386.0309

IR (neat): 692, 783, 997, 1071, 1246, 1591, 1688, 2799, 3049 cm^{-1}

NMR spectroscopic data matches the literature data.[6]

Synthesis of *N*-(2-bromo-4-(tert-butyl)phenyl)-*P*,*P*-diphenylphosphinic amide (**6f**)[7]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2-Bromo-4-(*tert*-butyl)aniline (103 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6f**. The compound **6f** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 104 mg, 0.244 mmol, 82%.

m.p.: 151–153 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93–7.88 (m, 4H), 7.56–7.52 (m, 2H), 7.48 (m, 4H), 7.23 (d, J = 8.5 Hz, 1H), 7.07–7.03 (m, 1H), 5.77 (d, J = 10.1 Hz, 1H), 1.22 (s, 9H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.3, 135.7, 132.4 (d, J = 2.8 Hz), 131.8 (d, J = 10.1 Hz), 131.3, 129.3, 128.9 (d, J = 13.1 Hz), 125.6, 118.7 (d, J = 3.8 Hz), 113.1 (d, J = 8.9 Hz), 34.2, 31.2 ppm

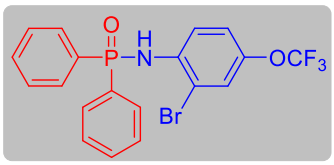
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.9 ppm

HRMS (ESI) m/z: calcd for $C_{22}H_{23}BrNOP$ $[M+H]^+$ 428.0771, found: 428.0771

IR (neat): 571, 940, 1241, 1435, 3055 cm^{-1}

NMR spectroscopic data matches the literature data.[7]

Synthesis of *N*-(2-bromo-4-(trifluoromethoxy) phenyl)-*P*,*P*-diphenylphosphinic amide (**6g**)[6]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (30 mg, 0.15 mmol), 2-bromo-4-(trifluoromethoxy)aniline (114 mg, 0.45 mmol) and KI (30 mol%, 8 mg) in CH_3CN (5 mL) to afford **6g**. The compound **6g** was purified by flash column chromatography using petroleum ether and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 28 mg, 0.062 mmol, 40%.

m.p: 155–158 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (m, 4H), 7.59–7.56 (m, 2H), 7.50 (m, 4H), 7.40 (d, J = 2.7 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 6.95 (dd, J = 8.9, 2.7 Hz, 1H), 5.84 (d, J = 9.9 Hz, 1H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.3, 137.7, 132.7 (d, J = 2.9 Hz), 131.8 (d, J = 10.2 Hz), 130.6, 129.9 (d, J = 13.1 Hz), 125.5, 121.5, 119.3 (d, J = 3.8 Hz), 112.8 (d, J = 8.8 Hz), 29.7 ppm

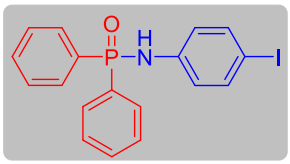
^{31}P NMR (202 MHz, $CDCl_3$): δ = 19.6 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{15}BrF_3NO_2P$ $[M+H]^+$ 455.9910, found: 455.9910

IR (neat): 579, 655, 937, 1072, 1246, 1437, 1585, 1687 2836, 3055 cm^{-1}

NMR spectroscopic data matches the literature data.[6]

Synthesis of *N*-(4-iodophenyl)-*P*,*P*-diphenylphosphinic amide (**6h**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (30 mg, 0.15 mmol), 4-iodoaniline (98 mg, 0.45 mmol) and KI (30 mol%, 8 mg) in CH_3CN (5 mL) to afford **6h**. The compound **6h** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 30 mg, 0.072 mmol, 48%. m.p.: 228–230 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89–7.84 (m, 4H), 7.55 (m, 2H), 7.50–7.46 (m, 4H), 7.44–7.41 (m, 2H), 6.78–6.75 (m, 2H), 5.26 (d, J = 9.5 Hz, 1H) ppm

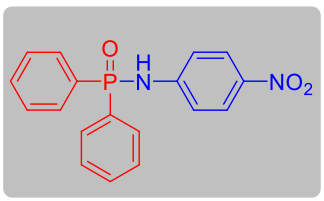
^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.5, 138.5, 132.9, 132.7 (d, J = 10.0 Hz), 132.3, 129.4 (d, J = 13.0 Hz), 120.9 (d, J = 6.5 Hz), 84.9 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 19.0 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{16}INOP$ $[M+H]^+$ 419.9902, found: 419.9902

IR (neat): 579, 937, 1246, 1585, 2800, 3055 cm^{-1}

Synthesis of *N*-(4-nitrophenyl)-*P,P*-diphenylphosphinic amide (**6i**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 4-nitroaniline (62 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6i**. The desired compound **6i** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The desired product obtained as a semi yellow solid. Yield: 37 mg, 0.11 mmol, 37%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 – 8.01 (m, 1H), 7.89 –7.83 (m, 2H), 7.62 –7.56 (m, 1H), 7.50 (m, 2H), 7.07 –7.03 (m, 1H), 5.92 (d, *J* = 9.9 Hz, 1H) ppm

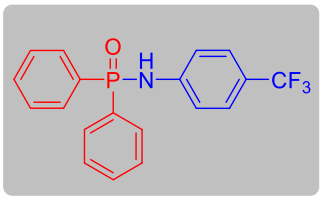
^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4, 142.5, 133.4 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 10.3 Hz), 130.4, 129.6 (d, *J* = 13.3 Hz), 126, 118 (d, *J* = 6.6 Hz) ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 19.6 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{16}N_2O_3P$ $[M+H]^+$ 339.0899, found: 39.0907

IR (neat): 727, 904, 1124, 1170, 1358, 1423, 1537, 3080 cm^{-1}

Synthesis of *P,P*-diphenyl-*N*-(4-(trifluoromethyl)phenyl)phosphinic amide (**6j**)[20]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 4-(trifluoromethyl)aniline (72 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6j**. The desired compound **6j** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The desired product obtained as a light brown solid. Yield: 47 mg, 0.13 mmol, 43%.

m.p.: 160-162 ^{0}C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.85 (m, 4H), 7.59–7.53 (m, 2H), 7.48 (m, 4H), 7.23–7.20 (m, 2H), 7.18– 7.12 (m, 2H), 5.53 (d, *J* = 9.3 Hz, 1H) ppm

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.5, 133 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 10.1 Hz), 131.1, 130.3, 129.4 (d, *J* = 13.0 Hz), 121.8 (d, *J* = 6.0 Hz), 118.9 (d, *J* = 3.9 Hz) ppm

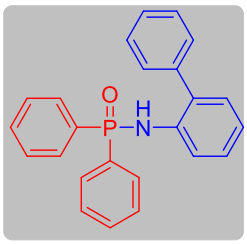
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.9 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{16}NOF_3P$ $[M+H]^+$ 362.0922, found: 362.0923

IR (neat): 518, 725, 1128, 1170, 1421, 1595, 1743, 2879, 3080 cm^{-1}

NMR spectroscopic data matches the literature data.[20]

Synthesis of *N*-([1,1'-biphenyl]-2-yl)-*P,P*-diphenylphosphinic amide (**6k**)[8]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), [1,1'-biphenyl]-2-amine (48 µL, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6k**. The compound **6k** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a light pink solid. Yield: 93 mg, 0.255 mmol, 85%.

m.p.: 149–151 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.55 (m, 5H), 7.29–7.27 (m, 4H), 7.22 (m, 2H), 7.21–7.17 (m, 4H), 7.08 (d, J = 8.2 Hz, 1H), 6.99 (dt, J = 7.5, 1.2 Hz, 1H), 6.89 (td, J = 7.9, 1.6 Hz, 1H), 6.79–6.75 (m, 1H), 5.33 (d, J = 9.9 Hz, 1H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.6, 137.4, 132.6, 132.2 (d, J = 2.8 Hz), 131.7 (d, J = 10.0 Hz), 131.6, 131.1 (d, *J* = 8.1 Hz), 130.3, 129.2 (d, J = 6.7 Hz), 128.9 (d, J = 13.0 Hz), 128.6, 127.9, 121.9, 118.4 (d, J = 4.2 Hz) ppm

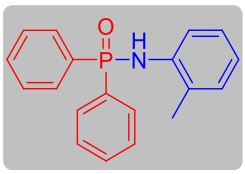
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.0 ppm

HRMS (ESI) m/z: calcd for $C_{24}H_{21}NOP$ $[M+H]^+$ 370.1359, found: 370.1361

IR (neat): 607, 719, 770, 1011, 1182, 1209, 1275, 1300, 1445, 1503, 1736, 2925, 3057, 3366 cm^{-1}

NMR spectroscopic data matches the literature data.[8]

Synthesis of *P*,*P*-diphenyl-*N*-(*o*-tolyl) phosphinic amide (**6l**)[8]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), o-toluidine (48 µL, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6l**. The compound **6l** was purified by flash column chromatography using petroleum ether and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 66 mg, 0.214 mmol, 71%.

m.p.: 154–156 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (m, 4H), 7.53 (m, 2H), 7.46 (m, 4H), 7.20 (dd, J = 8.6, 3.2 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.94 (m, 1H), 6.84 (t, J = 5.0 Hz, 1H), 5.05 – 5.01 (d, 1H), 2.28 (s, 3H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.8, 132.8, 132.4 (d, J = 2.9 Hz), 132.0 (d, J = 9.9 Hz), 130.6, 129.0 (d, J = 13.0 Hz), 127.2, 125.6 (d, J = 8.1 Hz), 122.2, 119.0 (d, J = 4.2 Hz), 18.0 ppm

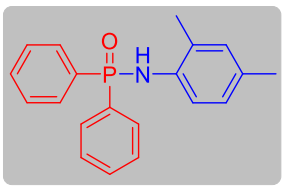
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.5 ppm

HRMS (ESI) m/z calcd for $C_{19}H_{19}NOP$ $[M+H]^+$ 308.1203, found: 308.1204

IR (neat): 770, 816, 932, 951, 1121, 1159, 1275, 1288, 1379, 1579, 1734, 2890, 2980, 3366 cm^{-1}

NMR spectroscopic data matches the literature data.[8]

Synthesis of *N*-(2, 4-dimethylphenyl)-*P*,*P*-diphenylphosphinic amide (**6m**)[2]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2,4-dimethylaniline (56 µL, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6m**. The compound **6m** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 70 mg, 0.22 mmol, 74%.

m.p.: 160–162 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 4H), 7.53–7.49 (m, 2H), 7.47–7.43 (m, 4H), 7.10 (d, J = 8.1 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.74 (d, J = 8.3, 1H), 4.93 (d, J = 8.7 Hz, 1H), 2.25 (s, 3H), 2.19 (s, 3H) ppm

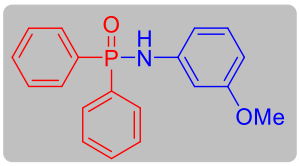
^{13}C NMR (126 MHz, $CDCl_3$): δ = 136.3, 133, 132.7, 132.3, 132.0 (d, J = 4.5 Hz), 131.6, 129.2 (d, J = 12.9 Hz), 127.9, 126.3, 119.7 (d, J = 4.1 Hz), 20.9, 18.2 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.6 ppm

HRMS (ESI) m/z: calcd for $C_{20}H_{21}NOP$ $[M+H]^+$ 322.1361, found: 322.1358

NMR spectroscopic data matches the literature data.[2]

Synthesis of *N*-(3-methoxyphenyl)-*P,P*-diphenylphosphinic amide (**6n**)[9]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 3-methoxy aniline (56 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6n**. The compound **6n** was purified by flash column chromatography using petroleum ether and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 74 mg, 0.23 mmol, 76%.

m.p.: 212–213 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (m, 4H), 7.54 (m, 2H), 7.47 (m, 4H), 7.04 (t, J = 8.2 Hz, 2H), 6.58–6.53 (m, 1H), 6.46 (d, J = 10.0 Hz, 1H), 5.24 (d, J = 9.1 Hz, 1H), 3.65 (s, 3H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.1, 148.1, 139.8, 130.5, 110, 108.3, 107, 104.3, 101.5, 99.3, 55.5 ppm

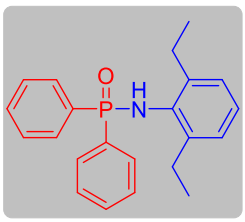
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.2 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{18}NO_2P$ $[M+H]^+$ 324.1140, found: 324.1141

IR (neat): 519, 947, 1293, 1560, 2963, 3095 cm^{-1}

NMR spectroscopic data matches the literature data.[9]

Synthesis of *N*-(2, 6-diethylphenyl)-*P,P*-diphenylphosphinic amide (**6o**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2,6-diethylaniline (67 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6o**. The compound **6o** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 71 mg, 0.204 mmol, 68%.

m.p.: 161–163 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.73 (m, 4H), 7.52–7.47 (m, 2H), 7.40 (m, 4H), 7.09–7.04 (m, 1H), 7.00 (d, J = 7.5 Hz, 2H), 4.52 (s, 1H), 2.71 (q, J = 7.5 Hz, 4H), 1.10 (t, J = 7.5 Hz, 6H) ppm

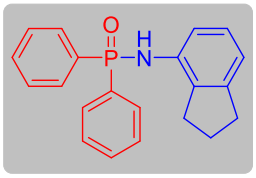
^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.7 (d, J = 3.3 Hz), 134.3 (d, J = 4.3 Hz), 132.8, 131.9 (d, J = 2.7 Hz), 131.8 (d, J = 9.6 Hz), 128.9 (d, J = 12.9 Hz), 128.4 (d, J = 12.7 Hz), 126.4, 25.2, 14.5 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 21.4 ppm

HRMS (ESI) m/z calcd for $C_{22}H_{25}NOP$ $[M+H]^+$ 350.1674, found: 350.1673

IR (neat): 420, 592, 746, 800, 916, 1122, 1186, 1257, 1327, 1435, 3161 cm^{-1}

Synthesis of *N*-(2, 3-dihydro-1*H*-inden-4-yl)-*P*,*P*-diphenylphosphinic amide (**6p**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2,3-dihydro-1*H*-inden-4-amine (60 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6p**. The compound **6p** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 75 mg, 0.225 mmol, 75%.

m.p.: 172–174 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 4H), 7.55–7.51 (m, 2H), 7.46 (m, 4H), 6.91–6.86 (m, 2H), 6.80 (m, 1H), 4.98 (d, J = 9.0 Hz, 1H), 2.93 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H), 2.11 (q, J = 7.5 Hz, 2H) ppm

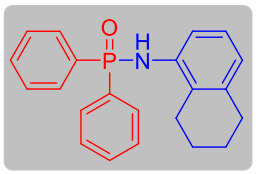
^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.5, 136.5, 132.4 (d, J = 2.9 Hz), 132.2 (d, J = 2.9 Hz), 131.9 (d, J = 10.0 Hz), 131.7 (d, J = 16.2 Hz), 128.9 (d, J = 13.0 Hz), 127.4, 118.1, 115.7 (d, J = 4.1 Hz), 33.4, 29.8, 24.6 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.4 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{21}NOP$ $[M-H]^+$ 334.1361, found: 334.1361

IR (neat): 403, 422, 492, 596, 619, 716, 810, 951, 1022, 1067, 1279, 1310, 1327, 1485, 1589, 2206, 3630, cm^{-1}

Synthesis of *P*,*P*-diphenyl-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl) phosphinic amide (**6q**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 5,6,7,8-tetrahydronaphthalen-1-amine (66 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **6q**. The compound **6q** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 86 mg, 0.25 mmol, 85%.

m.p.: 185–187 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (m, 4H), 7.62 (m, 2H), 7.42 (m, 4H), 7.02 (d, J = 8.0 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 5.01 (d, J = 9.0 Hz, 1H), 2.74 (t, J = 6.3 Hz, 2H), 2.56 (t, J = 6.5 Hz, 2H), 1.88 (m, 2H), 1.76 (m, 2H) ppm

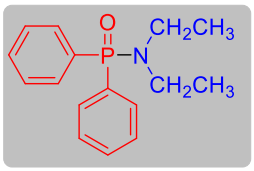
^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.4 (d, J = 12.3 Hz), 132.9, 132.3 (d, J = 2.8 Hz), 132.0 (d, J = 10.0 Hz), 131.9, 129 (d, J = 12.9 Hz), 126.0, 124.7 (d, J = 7.9 Hz), 123.2, 116.2 (d, J = 4.3 Hz), 30.1, 24.6, 23.2, 22.7 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.5 ppm

HRMS (ESI) m/z: calcd for $C_{22}H_{23}NOP$ $[M+H]^+$ 348.1517, found: 348.1516

IR (neat): 519, 692, 717, 727, 748, 770, 849, 878, 934, 978, 1036, 1107, 1125, 1186, 1198, 1439, 1464, 1491, 1584, 2818, 2924, 3059 cm^{-1}

Synthesis of *N*,*N*-diethyl-*P*,*P*-diphenylphosphinic amide (**7a**)[10]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), diethylamine (23 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **7a**. The compound **7a** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a yellow semi-solid. Yield: 65 mg, 0.24 mmol, 80%.

m.p.: 123–125 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.77 (m, 4H), 7.44–7.40 (m, 2H), 7.39–7.35 (m, 4H), 2.99 (dt, J = 10.8, 7.1 Hz, 4H), 1.03 (t, J = 7.1 Hz, 6H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 132.4 (d, J = 2.9 Hz), 131.8 (d, J = 10.1 Hz), 130.5, 128.7 (d, J = 13.2 Hz), 51.7 (d, J = 6.0 Hz), 29.8 ppm

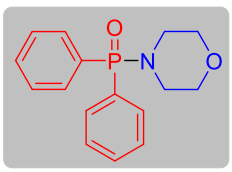
^{31}P NMR (202 MHz, $CDCl_3$): δ = 33.4 ppm

HRMS (ESI) m/z: calcd for $C_{16}H_{21}NOP$ $[M+H]^+$ 274.1361, found: 274.1362

IR (neat): 591, 690, 727, 1186, 1217, 1347, 2886, 3019, 3072 cm^{-1}

NMR spectroscopic data matches the literature data.[10]

Synthesis of morpholinodiphenylphosphine oxide (**7b**)[11]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), morpholine (26 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **7b**. The compound **7b** was purified by flash column chromatography using cyclohexane and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a yellow thick liquid. Yield: 71 mg, 0.25 mmol, 82%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (m, 4H), 7.51–7.43 (m, 6H), 3.70 (m, 4H), 3.04 (m, 4H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 132.3 (d, J = 9.2 Hz), 132.0 (d, J = 2.8 Hz), 131.4, 128.7 (d, J = 12.5 Hz), 67.2 (d, J = 6.5 Hz), 45.0 ppm

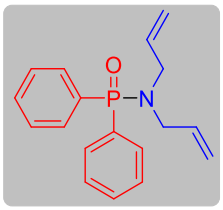
^{31}P NMR (202 MHz, $CDCl_3$): δ = 29.2 ppm

HRMS (ESI) m/z: calcd for $C_{16}H_{19}NO_2P$ $[M+H]^+$ 288.1153, found: 288.1151

IR (neat): 591, 690, 694, 727, 1024, 1186, 1202, 1357, 2886, 3045 cm^{-1}

NMR spectroscopic data matches the literature data.[11]

Synthesis of *N*,*N*-diallyl-*P*,*P*-diphenylphosphinic amide (**7c**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), diallylamine (29 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **7c**. The compound **7c** was purified by flash column chromatography using cyclohexane and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 71 mg, 0.24 mmol, 79%.

m.p.: 158–160 °C

^{1}H NMR (500 MHz, $CDCl_3$): 7.92–7.82 (m, 4H), 7.50–7.40 (m, 6H), 5.82–5.72 (m, 2H), 5.18–5.06 (m, 4H), 3.56 (m, 4H) ppm

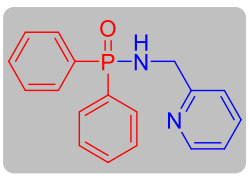
^{13}C NMR (126 MHz, $CDCl_3$): δ = 134.6, 132.5, 131.9, 131.6, 128.6, 118.6, 47.9 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 30.7 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{21}NOP$ $[M-H]^+$ 298.1361, found: 298.1361

IR (neat): 598, 691, 727, 1186, 1217, 1489, 1740, 2886, 3019, 3075 cm^{-1}

Synthesis of *P*,*P*-diphenyl-*N*-(pyridin-2-ylmethyl) phosphinic amide (**7d**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), pyridin-2-ylmethanamine (49 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **7d**. The compound **7d** was purified by flash column chromatography using cyclohexane and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 74 mg, 0.243 mmol, 81%.

m.p.: 193–195 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 7.68–7.62 (m, 4H), 7.52 (d, J = 9.0 Hz, 1H), 7.32–7.28 (m, 2H), 7.24–7.21 (m, 4H), 7.15 (m, 1H), 7.06 (d, J = 8.1 Hz, 1H), 4.00 (s, 2H) ppm

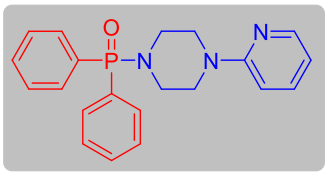
^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.4, 148.9, 138.6, 136.9, 131.3 (d, J = 9.6 Hz), 130.2 (d, J = 2.8 Hz), 127.9 (d, J = 12.3 Hz), 122.9, 122.2, 48.9 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 21.4 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{18}N_2OP$ $[M+H]^+$ 309.1157, found: 309.1162

IR (neat): 519, 692, 727, 748, 770, 849, 878, 978, 1036, 1125, 1186, 1439, 1464, 1584, 2818, 3059 cm^{-1}

Synthesis of diphenyl (4-(pyridin-2-yl) piperazin-1-yl)phosphine oxide (**7e**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 1-(pyridin-2-yl)piperazine (49 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **7e**.The compound **7e** was purified by flash column chromatography using cyclohexane and ethyl acetate (20:80, v/v) as the solvent system. The product obtained as a colourless liquid. Yield: 92 mg, 0.252 mmol, 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21–8.16 (m, 1H), 7.89 (m, 4H), 7.57–7.44 (m, 7H), 6.69–6.60 (m, 2H), 3.59–3.50 (m, 4H), 3.22–3.18 (m, 4H) ppm

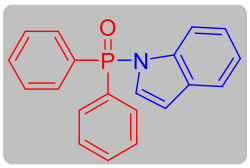
^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.0, 148.4, 138.0, 132.8 (d, J = 9.2 Hz), 132.4 (d, J = 2.8 Hz), 132.3, 131.0, 129.2 (d, J = 12.4 Hz), 114.3, 107.8, 92.0, 46.4 (d, J = 7.1 Hz), 45.1 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.3 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{23}N_3OP$ $[M+H]^+$ 364.1579, found: 364.1592

IR (neat): 422, 538, 646, 721, 964, 1244, 1437, 1593, 1973, 2260, 2521 cm^{-1}

Synthesis of (1*H*-indol-1-yl)diphenylphosphine oxide (**7f**)[12]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 1*H*-indole (35 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **7f**. The compound **7f** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a pink solid. Yield: 69 mg, 0.22 mmol, 74%.

m.p.: 194–196 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.66 (m, 4H), 7.6 –7.60 (m, 3H), 7.58–7.56 (m, 1H), 7.50 (m, 4H), 7.19–7.16 (m, 1H), 7.13–7.10 (m, 1H), 6.82 (t, J = 3.3 Hz, 1H), 6.62 (m, 1H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.5 (d, J = 3.3 Hz), 132.1 (d, J = 2.9 Hz), 131.1 (d, J = 10.7 Hz), 130.4 (d, J = 6.5 Hz), 128.5, 127.9 (d, J = 13.5 Hz), 127.7 (d, J = 5.9 Hz), 122.4, 120.0, 121.1, 113.7, 106.2 (d, J = 6.7 Hz) ppm

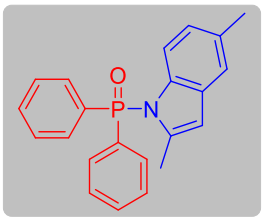
^{31}P NMR (202 MHz, $CDCl_3$): δ = 25 ppm

HRMS (ESI) m/z calcd for $C_{20}H_{17}NOP$ $[M+H]^+$ 318.1048, found: 318.1048

IR (neat): 519, 692, 748, 878, 978, 1036, 1107, 1186, 1198, 1439, 1491, 1584, 2924, 3059 cm^{-1}

NMR spectroscopic data matches the literature data.[12]

Synthesis of (2,5-dimethyl-1*H*-indol-1-yl)diphenylphosphine oxide (**7g**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2,5-dimethyl-1*H*-indole (65 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **7g**. The compound **7g** was purified by flash column chromatography using cyclohexane and ethyl acetate (60:40, v/v) as the solvent system. The product obtained as a light brown semi solid. Yield: 72 mg, 0.21 mmol, 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.58 (m, 6H), 7.51–7.45 (m, 4H), 7.15 (m, 1H), 6.72 (dd, J = 8.6, 1.8 Hz, 1H), 6.37 (d, J = 8.6 Hz, 1H), 5.32 (s, 1H), 2.38 (s, 3H), 2.37 (s, 3H) ppm

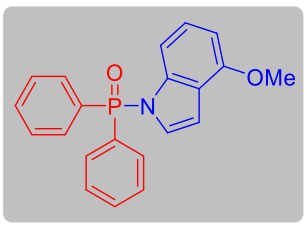
^{13}C NMR (101 MHz, $CDCl_3$): δ = δ 133.3 (d, J = 2.9 Hz), 132.2, 132, 129.1 (d, J = 13.5 Hz), 124.9, 121, 117.2, 116.4, 113.9, 111.8, 107.8, 21.1, 17.4 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.7 ppm

HRMS (ESI) m/z: calcd for $C_{22}H_{21}NOP$ $[M+H]^+$ 346.1283, found: 346.1283

IR (neat): 422, 536, 646, 771, 902, 1149, 1504, 1934, 1956, 1994, 2027, 2255, 2517, 3730 cm^{-1}

Synthesis of (4-methoxy-1*H*-indol-1-yl)diphenylphosphine oxide (**7h**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (90 mg, 0.45 mmol), 4-methylindole (90 mg, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **7h**. The compound **7h** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as a greenish liquid. Yield: 87 mg, 0.25 mmol, 56%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63–7.57 (m, 4H), 7.54 (m, 2H), 7.44–7.39 (m, 4H), 7.12 (m, 1H), 6.97 (ddd, J = 8.4, 7.9, 0.4 Hz, 1H), 6.68–6.63 (m, 2H), 6.53 (dd, J = 7.9, 0.6 Hz, 1H), 3.86 (s, 3H) ppm

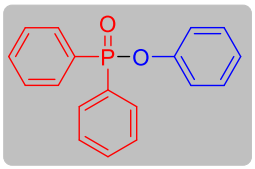
^{13}C NMR (126 MHz, $CDCl_3$): δ = 153.6 (d, J = 1.2 Hz), 140.3 (d, J = 3.7 Hz), 133.5 (d, J = 2.9 Hz), 132.5 (d, J = 10.7 Hz), 130.8, 129.8, 129.3 (d, J = 13.5 Hz), 127.7 (d, J = 5.9 Hz), 124.7, 122.3 (d, J = 6.9 Hz), 108.2 (d, J = 1.2 Hz), 104.7 (d, J = 7.0 Hz), 102.5, 55.7 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.5 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{19}NO_2P$ $[M+H]^+$ 348.1153, found: 348.1165

IR (neat): 422, 484, 571, 648, 694, 723, 904, 1144, 1539, 2019, 2255, 2513, 3750 cm^{-1}

Synthesis of phenyl diphenylphosphinate (**8a**)[13]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), phenol (28 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **8a**. The compound **8a** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 75 mg, 0.25 mmol, 85%.

m.p.: 138–140 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (m, 4H), 7.55–7.52 (m, 2H), 7.46 (m, 4H), 7.24–7.18 (m, 4H), 7.10 –7.05 (m, 1H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.9 (d, J = 8.2 Hz), 132.4 (d, J = 2.8 Hz), 131.8 (d, J = 10.4 Hz), 130.5, 129.6, 128.6 (d, J = 13.5 Hz), 124.6, 120.7 (d, J = 4.8 Hz) ppm

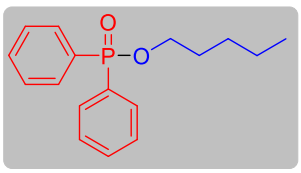
^{31}P NMR (202 MHz, $CDCl_3$): δ = 30.3 ppm

HRMS (ESI) m/z calcd for $C_{18}H_{16}O_2P$ $[M+H]^+$ 295.0888, found: 295.0885

IR (neat): 513, 532, 582, 685, 695, 701, 746, 901, 1128, 1167, 1115, 1166, 1439, 1489 cm^{-1}

NMR spectroscopic data matches the literature data.[13]

Synthesis of pentyl diphenylphosphinate (**8b**)[14]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), pentan-1-ol (27 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **8b**. The compound **8b** was purified by flash column chromatography using cyclohexane ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 65 mg, 0.225 mmol, 75%.

m.p.: 166–167 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.77 (m, 4H), 7.49 (m, 2H), 7.45–7.40 (m, 4H), 4.01 (q, J = 6.7 Hz, 2H), 1.41 (q, J = 6.7 Hz, 2H), 1.39–1.26 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 132.6, 132.4 (d, J = 2.8 Hz), 131.9 (d, J = 10.0 Hz), 131.5, 128.8 (d, J = 13.1 Hz), 65.4 (d, J = 6.1 Hz), 30.6 (d, J = 6.6 Hz), 28.1, 22.5, 14.3 ppm

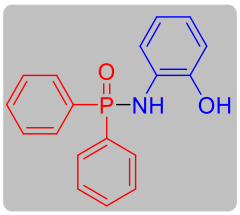
^{31}P NMR (202 MHz, $CDCl_3$): δ = 31.1 ppm

HRMS (ESI) m/z calcd for $C_{17}H_{22}O_2P$ $[M+H]^+$ 289.1302, found: 289.1302

IR (neat): 592, 600, 646, 729, 995, 1150, 1435, 3267, 3366 cm^{-1}

NMR spectroscopic data matches the literature data.[14]

Synthesis of *N*-(2-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**9a**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2-aminophenol (33 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **9a**. The compound **9a** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 58 mg, 0.19 mmol, 62%.

m.p.: 210–212 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.90 (s, 1H), 7.94–7.86 (m, 4H), 7.55 (m, 2H), 7.48 (m, 4H), 7.02 (m, 1H), 6.97–6.88 (m, 2H), 6.71 (m, 1H), 5.06 (d, *J* = 9.8 Hz, 1H) ppm

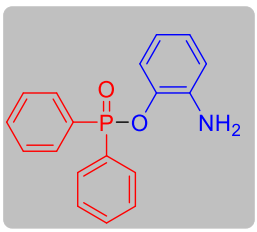
^{13}C NMR (126 MHz, $CDCl_3$): δ = 133.0 (d, J = 2.6 Hz), 132.4 (d, J = 10.3 Hz), 131.5 (d, J = 1.5 Hz), 130.5, 129.3, 129.2, 126.6, 124.6, 120.8, 118.6 (d, J = 4.7 Hz) ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 25.6 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{17}NO_2P$ $[M+H]^+$ 310.0997, found: 310.0995

IR (neat): 554, 1040, 1101, 1246, 1281, 1304, 1402, 1510, 3370 cm^{-1}

Synthesis of 2-aminophenyl diphenylphosphinate (**9b**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 2-aminophenol (33 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **9b**. The compound **9b** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 24 mg, 0.075 mmol, 25%.

m.p.: 224–225 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.87 (m, 4H), 7.58–7.53 (m, 2H), 7.47 (m, 4H), 6.95–6.89 (m, 1H), 6.90–6.86 (m, 1H), 6.75–6.72 (m, 1H), 6.51 (m, 1H), 4.11 (s, 2H) ppm

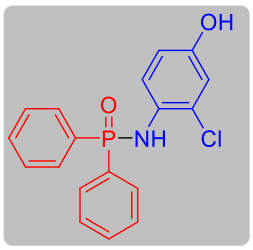
^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.4 (d, J = 14.6 Hz), 132.4 (d, J = 2.9 Hz), 131.6 (d, J = 10.4 Hz), 131, 129.6, 128.5 (d, J = 13.4 Hz), 125.3 (d, J = 1.0 Hz), 121 (d, J = 3.7 Hz), 118.4 (d, J = 1.1 Hz), 116.8 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 32.6 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{17}NO_2P$ $[M+H]^+$ 310.0991, found: 310.0992

IR (neat): 585, 1107, 1285, 1304, 1402, 1612, 3370 cm^{-1}

Synthesis of *N*-(2-chloro-4-hydroxyphenyl)-*P,P*-diphenylphosphinic amide (**10a**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 4-amino-3-chlorophenol (64 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **10a**. The compound **10a** was purified by flash column chromatography using cyclohexane and ethyl acetate (40:60, v/v) as the solvent system. The product obtained as a dark brown solid. Yield: 39 mg, 0.114 mmol, 38%.

m.p.: 198–200 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93–7.86 (m, 4H), 7.57–7.52 (m, 2H), 7.51–7.46 (m, 4H), 7.09 (d, J = 11.0 Hz, 1H), 6.86 (d, J = 3.3 Hz, 1H), 6.46 (d, J = 8.8 Hz, 1H), 5.50 (d, J = 9.8 Hz, 1H), 4.11 (s, 1H) ppm

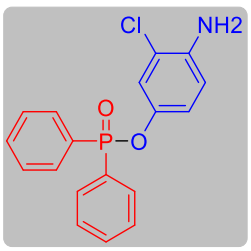
^{13}C NMR (101 MHz, $CDCl_3$): δ = 153, 148.3, 133 (d, J = 2.9 Hz), 132.3 (d, J = 10.3 Hz), 131, 129.5, 129.4, 119.6 (d, J = 16.1 Hz), 117.4, 115.9 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.7 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{16}NO_2PCl$ $[M+H]^+$ 344.0602, found: 344.0604

IR (neat): 529, 691, 754, 818, 943, 1042, 1236, 1441, 1501, 3103 cm^{-1}

Synthesis of *N*-(2-chloro-4-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**10b**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 4-amino-3-chlorophenol (64 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **10b**. The compound **10b** was purified by flash column chromatography using cyclohexane and ethyl acetate (40:60, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 48 mg, 0.14 mmol, 47%.

m.p.: 190–192 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88–7.83 (m, 4H), 7.54 (m, 2H), 7.46 (m, 4H), 7.11 (dd, J = 2.7, 1.3 Hz, 1H), 6.92 (ddd, J = 8.8, 2.7, 1.3 Hz, 1H), 6.59 (d, J = 8.8 Hz, 1H), 4.04–3.74 (s, 2H) ppm

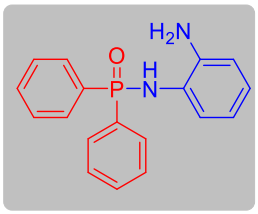
^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.8 (d, J = 8.4 Hz), 140.5, 133.0 (d, J = 2.9 Hz), 132.2 (d, J = 10.3 Hz), 130.5, 129 0 (d, J = 13.4 Hz), 122.2 (d, J = 4.7 Hz), 120.7 (d, J = 4.3 Hz), 119.6, 116.4 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 31.2 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{16}NO_2PCl$ $[M+H]^+$ 344.0607, found: 344.0607

IR (neat): 529, 579, 691, 721, 739, 754, 818, 853, 943, 1042, 1123, 1157, 1236, 1279, 1344, 1383, 1441, 1462, 1501, 3103 cm^{-1}

Synthesis of *N*-(2-aminophenyl)-*P,P*-diphenylphosphinic amide (**11a**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (90 mg, 0.45 mmol), benzene-1,2-diamine (48 mg, 0.45 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **11**. The compound **11** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as a brown solid. Yield: 104 mg, 0.346 mmol, 77%.

m.p.: 163–165 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = δ 7.96–7.83 (m, 4H), 7.52–7.37 (m, 6H), 7.07–6.98 (m, 1H), 6.86–6.81 (m, 1H), 6.73–6.66 (m, 1H), 6.56–6.52 (m, 1H), 5.20 (m, 1H), 3.52 (s, 2H) ppm

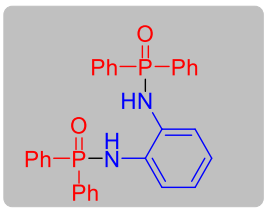
^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.1 (d, J = 5.6 Hz), 132.6–132.4 (m), 131.7 (d, J = 9.8 Hz), 131.5, 129.1 (d, J = 12.9 Hz), 129.0, 128.5 (d, J = 12.2 Hz), 127.1 (d, J = 2.2 Hz), 125.8, 124.7, 120.0, 117.9 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.8 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{18}N_2OP$ $[M+H]^+$ 309.1157, found: 309.1168

IR (neat): 482, 538, 646, 721, 903, 964, 1123, 1244, 1434, 1593, 1973, 2033, 2261, 2521 cm^{-1}

Synthesis of *N,N'*-(1,2-phenylene)bis(*P,P*-diphenylphosphinic amide) (**11b**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), 1, 2-diaminobenzene (65 mg, 0.6 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **11b**. The desired compound **11b** was purified by flash column chromatography using CH_2Cl_2 and MeOH (100:1, v/v) as the solvent system. The desired product obtained as brown wax. Yield: 75 mg, 0.15 mmol, 50%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.79 (m, 8H), 7.44–7.41 (m, 4H), 7.36–7.32 (m, 8H), 7.10 (s, 2H), 6.95–6.95 (m, 2H), 6.60–6.56 (m, 2H) ppm

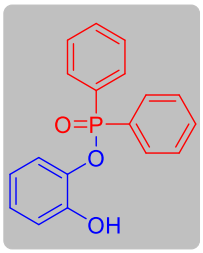
^{13}C NMR (126 MHz, $CDCl_3$): δ = 133.3 (d, *J* = 6.6 Hz), 132.5 (d, *J* = 10.2), 132.4 (d, *J* = 10.0 Hz), 131.5, 129 (d, *J* = 12.9 Hz), 125.1, 124.9 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.0 ppm

HRMS (ESI) m/z: calcd for $C_{30}H_{27}N_2O_2P_2$: 509.1548, found: 509.1548

IR (neat): 3460, 2970, 2341, 2185, 2023, 2024, 1737, 1369, 1219, 1064, 702, 530 cm^{-1}

Synthesis of 2-hydroxyphenyl diphenylphosphinate (**12**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (90 mg, 0.45 mmol), pyrocatechol (50 mg, 0.45 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **12**. The compound **12** was purified by flash column chromatography using CH_2Cl_2 and MeOH (99:1, v/v) as the solvent system. The product obtained as a yellow liquid. Yield: 49 mg, 0.158 mmol, 35%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (s, 1H), 7.86–7.78 (m, 4H), 7.54–7.49 (m, 2H), 7.45–7.40 (m, 4H), 6.98–6.89 (m, 2H), 6.77 (m, 1H), 6.65–6.58 (m, 1H) ppm

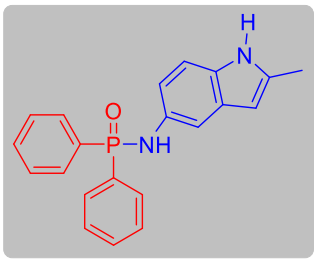
^{13}C NMR (126 MHz, $CDCl_3$): δ 148.4 (d, J = 3.1 Hz), 139.4 (d, J = 9.5 Hz), 133.5 (d, J = 2.9 Hz), 132.3 (d, J = 10.7 Hz), 129.2 (d, J = 13.6 Hz), 128.5, 126.8 (d, J = 1.4 Hz), 122.8 (d, J = 4.5 Hz), 120.8, 120.1 (d, J = 1.3 Hz) ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 39.0 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{16}O_3P$ $[M+H]^+$ 311.0837, found: 311.0847

IR (neat): 538, 652, 725, 903, 1204, 1377, 1495, 1738, 2257 cm^{-1}

Synthesis of *N*-(2-methyl-1*H*-indol-5-yl)-*P*,*P*-diphenylphosphinic amide (**13**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (90 mg, 0.45 mmol), 2-methyl-1H-indol-5-amine (87 mg, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN:EtOH (3:2 v/v, 15 mL) to afford **13**. The compound **13** was purified by flash column chromatography using cyclohexane and ethyl acetate (60:40, v/v) as the solvent system. The product obtained as a reddish solid. Yield: 104 mg, 0.30 mmol, 67%.

m.p.: 153–155 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.88 (m, 4H), 7.82 (s, 1H), 7.49 (m, 2H), 7.42 (m, 4H), 7.20 (d, *J* = 2.1 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.88–6.84 (m, 1H), 6.03 (s, 1H), 5.16 (d, *J* = 9.3 Hz, 1H), 2.37 (s, 3H) ppm

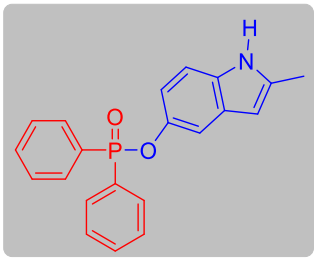
^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.8, 133.4, 132.6 (d, J = 1.7 Hz), 132.5 (d, J = 9.8 Hz), 132.3 (d, J = 2.7 Hz), 130.0, 129.1 (dd, J = 12.9, 3.6 Hz), 115.8, 115 (d, J = 6.4 Hz), 111.3, 110.8 (d, J = 6.3 Hz), 100.2, 27.3 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.7 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{20}N_2OP$ $[M+H]^+$ 347.1313, found: 347.1323

IR (neat): 409, 727, 904, 1975, 2031, 2174, 2498 cm^{-1}

Synthesis of 2-methyl-1*H*-indol-5-yl diphenylphosphinate (**14**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (90 mg, 0.45 mmol), 2-methyl-1*H*-indol-5-ol (88 mg, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **14**. The compound **14** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as a light brown solid. Yield: 95 mg, 0.27 mmol, 61%.

m.p.: 160–162 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.93–7.87 (m, 4H), 7.51–7.45 (m, 2H), 7.44–7.38 (m, 4H), 7.24 (d, J = 0.9 Hz, 1H), 6.98 (d, J = 8.7 Hz, 1H), 6.89–6.86 (m, 1H), 6.03 (d, J = 1.1 Hz, 1H), 2.31 (s, 3H) ppm

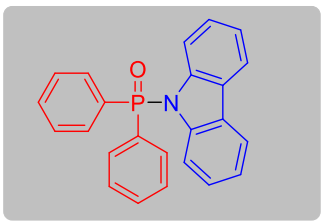
^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.4 (d, J = 8.5 Hz), 136.9, 133.4, 132.4 (d, J = 2.9 Hz), 132.1, 132.01 (d, J = 10.3 Hz), 130.8, 129.5, 128.6 (d, J = 13.3 Hz), 114.3 (d, J = 4.4 Hz), 110.9 (t, J = 2.4 Hz), 100.5, 13.8 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.9 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{19}NO_2P$ $[M+H]^+$ 348.1153, found: 348.1159

IR (neat): 420, 729, 903, 1917, 2019, 2525 cm^{-1}

Synthesis of (9*H*-carbazol-9-yl)diphenylphosphine oxide (**15**)[21]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), carbazole (75 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **15**. The desired compound **15** was purified by flash column chromatography using cyclohexane and ethyl acetate (40:60, v/v) as the solvent system. The desired product obtained as a off white solid. Yield: 59 mg, 0.16 mmol, 53%.

m.p.: 143–145 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–8.01 (m, 2H), 7.78–7.71 (m, 4H), 7.62 (m, 2H), 7.52–7.46 (m, 4H), 7.32 –7.26 (m, 4H), 7.19 (m, 2H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.0 (d, *J* = 3.6 Hz), 133.6 (d, *J* = 2.8 Hz), 132.5 (d, *J* = 10.9 Hz), 131.7, 130.7, 129.5 (d, *J* = 13.5 Hz), 126.7, 122.3, 120.3, 115.4 ppm

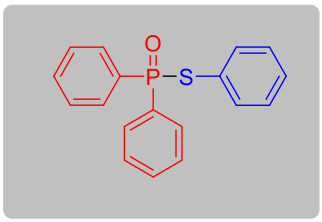
^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.3 ppm

HRMS (ESI) m/z: calcd for $C_{24}H_{19}NOP$ $[M+H]^+$ 368.1204, found: 368.1205

IR (neat): 650, 725, 904, 1456, 1508, 1543, 1560, 2249, 2376, 2985 cm^{-1}

NMR spectroscopic data matches the literature data.[21]

Synthesis of *S*-phenyl diphenylphosphinothioate (**16**)[22]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), thiophenol (61 µL, 0.60 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **16**. The desired compound **16** was purified by flash column chromatography using cyclohexane and ethyl acetate (40:60, v/v) as the solvent system. The desired product obtained as an off white solid. Yield: 40 mg, 0.13 mmol, 44%.

m.p.: 87–89 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.81 (m, 4H), 7.52–7.48 (m, 2H), 7.44 (m, 6H), 7.26–7.22 (m, 1H), 7.21–7.16 (m, 2H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.5 (d, *J* = 3.9 Hz), 132.9, 132.4 (d, *J* = 3.1 Hz), 132.1, 131.7 (d, *J* = 10.3 Hz), 129.2 (d, *J* = 1.8 Hz), 129.1 (d, *J* = 2.2 Hz), 128.6 (d, *J* = 13.1 Hz), 126.2 (d, *J* = 5.2 Hz) ppm

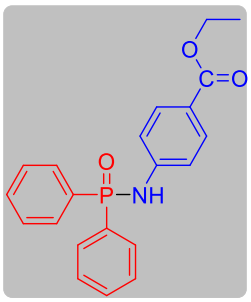
^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.6 ppm

HRMS (ESI) m/z: calcd for $C_{18}H_{16}OPS$ $[M+H]^+$ 311.0659, found: 311.0658

IR (neat): 526, 653, 700, 904, 1114, 1195, 1440, 1546, 2256, 2978 cm^{-1}

NMR spectroscopic data matches the literature data.[22]

Synthesis of ethyl 4-((diphenylphosphoryl)amino) benzoate (**17**)[2]



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), ethyl 4-aminobenzoate (74 mg, 0.45 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **17**. The compound **17** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 74 mg, 0.204 mmol, 68%.

m.p.: 253–254 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90–7.82 (m, 6H), 7.57–7.54 (m, 2H), 7.48 (m, 4H), 7.02–6.97 (d, 2H), 5.53 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H) ppm

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.6, 145.2, 133 (d, J = 2.8 Hz), 132.3 (d, J = 10.1 Hz), 131.6, 131.2, 129.4 (d, J = 13.0 Hz), 124.2, 118.0 (d, J = 6.6 Hz), 61.1, 14.7 ppm

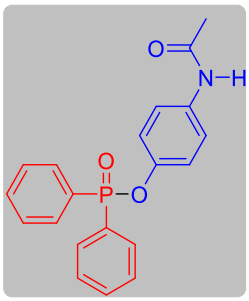
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.7 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{21}NOP$ $[M+H]^+$ 366.1201, found: 366.1201

IR (neat): 598, 625, 796, 833, 968, 1169, 1240, 1371, 1449, 1508, 1609, 1616, 2347, 3327 cm^{-1}

NMR spectroscopic data matches the literature data.[2]

Synthesis of 4-acetamidophenyl diphenylphosphinate (**18**)



Synthesised in accordance with General Procedure 1 using diphenylphosphine oxide (60 mg, 0.30 mmol), N-(4-hydroxyphenyl)acetamide (45 mg, 0.30 mmol) and KI (30 mol%, 15 mg) in CH_3CN (10 mL) to afford **18**. The compound **18** was purified by flash column chromatography using petroleum ether and ethyl acetate (30:70, v/v) as the solvent system. The product was obtained as a colourless solid. Yield: 77 mg, 0.219 mmol, 73%.

m.p.: 202–204 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (s, 1H), 7.80 (m, 4H), 7.48 (m, 2H), 7.42–7.38 (m, 4H), 7.29–7.25 (m, 2H), 6.99–6.96 (m, 2H), 2.04 (s, 3H) ppm

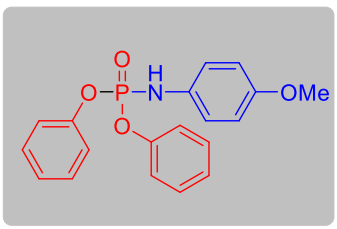
^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.7, 146.8 (d, J = 8.4 Hz), 135.1, 132.8 (d, J = 2.9 Hz), 131.9 (d, J = 10.5 Hz), 130.3, 128.8 (d, J = 13.5 Hz), 121.5, 121.3 (d, J = 4.6 Hz), 24.5 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 31.0 ppm

HRMS (ESI) m/z: calcd for $C_{20}H_{19}NO_3P$ $[M-H]^+$ 352.1103, found: 352.1102

IR (neat): 523, 689, 729, 1107, 1437, 1589, 2880, 2957, 3061, 3630 cm^{-1}

Synthesis of diphenyl (4-methoxyphenyl) phosphoramidate (**19a**)



Synthesised in accordance with General Procedure 1 using diphenyl phosphonate (86 µL, 0.45 mmol), 4-methoxyaniline (74 mg, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **19a**. The compound **19a** was purified by flash column chromatography using cyclohexane and ethyl acetate (10:90) as the solvent system. The product obtained as a colourless solid. Yield: 123 mg, 0.35 mmol, 78 %.

m.p.: 141–142 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 4H), 7.29–7.26 (m, 4H), 7.24–7.19 (m, 2H), 7.14–7.09 (m, 2H), 7.05 (d, J = 10.9 Hz, 1H), 6.91–6.87 (m, 2H), 3.85 (s, 3H) ppm

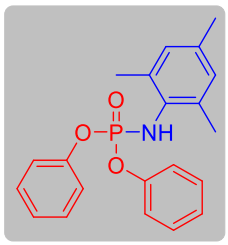
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.3 (d, J = 0.4 Hz), 150.4, 150.4, 132.0, 129.7 (d, J = 1.1 Hz), 125.2 (d, J = 1.3 Hz), 120.4 (d, J = 4.9 Hz), 120.1 (d, J = 7.3 Hz), 114.6, 55.5 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = –6.1 ppm

HRMS (ESI) m/z: calcd for $C_{19}H_{19}NO_4P$ $[M+H]^+$ 356.1052, found: 356.1059

IR (neat): 492, 567, 687, 754, 833, 984, 1034, 1180, 1242, 1263, 1396, 1508, 1543, 1585, 3179 cm^{-1}

Synthesis of diphenyl mesitylphosphoramidate (**19b**)



Synthesised in accordance with General Procedure 1 using diphenyl phosphonate (86 µL, 0.45 mmol), 2,4,6-trimethylaniline (85 µL, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **19b**. The compound **19b** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as an off white solid. Yield: 117 mg, 0.32 mmol, 71%.

m.p.: 129–131 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 4H), 7.19–7.12 (m, 6H), 6.86 (s, 2H), 4.60 (d, J = 8.9 Hz, 1H), 2.28 (s, 6H), 2.26 (s, 3H) ppm

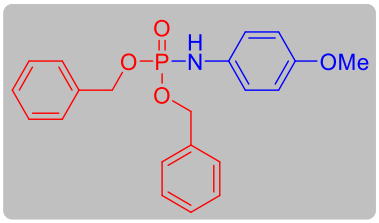
^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.5 (d, J = 7.5 Hz), 136.7, 136.6 (d, J = 1.4 Hz), 131.7 (d, J = 1.8 Hz), 130.1, 129.7 (d, J = 1.9 Hz), 125.4 (d, J = 1.3 Hz), 120.8 (d, J = 4.8 Hz), 21.2, 19.4 (d, J = 1.1 Hz) ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = –5.3 (d, J = 8.9 Hz) ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO_3P$ $[M+H]^+$ 368.1416, found: 368.1421

IR (neat): 446, 499, 540, 729, 906, 1192, 1159, 1541, 1942, 1935, 1960, 2027, 2234, 2517, 3711 cm^{-1}

Synthesis of dibenzyl (4-methoxyphenyl) phosphoramidate (**20a**)



Synthesised in accordance with General Procedure 1 using dibenzyl phosphonate (100 µL, 0.45 mmol), 4-methoxyaniline (74 mg, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **20a**. The compound **20a** was purified by flash column chromatography using cyclohexane and ethyl acetate (10:90, v/v) as the solvent system. The product obtained as a yellow liquid. Yield: 125 mg, 0.33 mmol, 73%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (s, 10H), 6.88–6.84 (m, 2H), 6.70–6.65 (m, 2H), 6.02 (d, J = 9.4 Hz, 1H), 5.07–5.01 (m, 2H), 4.96 (m, 2H), 3.67 (s, 3H) ppm

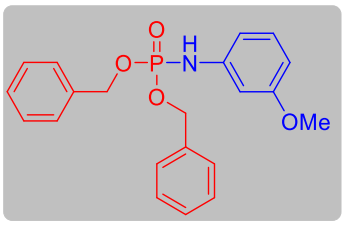
^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.3, 136.2 (d, J =7.9 Hz), 132.8, 128.8, 128.7, 128.3, 119.9 (d, J = 6.9 Hz), 114.9, 68.6 (d, J = 4.7 Hz), 55.9, 27.3 ppm

^{31}P NMR (202 MHz, $CDCl_3$): δ = 3.4 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO_4P$ $[M+H]^+$ 384.1365, found: 384.1375

IR (neat): 446, 650, 725, 997, 1217, 1244, 1377, 1512, 2253 cm^{-1}

Synthesis of dibenzyl (3-methoxyphenyl)phosphoramidate (**20b**)



Synthesised in accordance with General Procedure 1 using dibenzyl phosphonate (100 µL, 0.45 mmol), 3-methylaniline (70 µL, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **20b**. The compound **20b** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as a brown liquid. Yield: 114 mg, 0.30 mmol, 68%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (s, 10H), 7.13–7.08 (m, 1H), 6.60–6.49 (m, 3H), 6.12 (d, J = 9.3 Hz, 1H), 5.14 (dd, J = 11.6, 7.6 Hz, 2H), 5.05 (dd, J = 11.6, 7.5 Hz, 2H), 3.67 (s, 3H) ppm

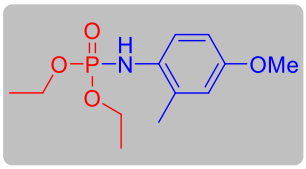
^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.9 (d, J = 6.8 Hz), 141.0, 136.2 (d, J = 7.8 Hz), 130.5, 128.9 (d, J = 6.5 Hz), 128.5, 110.7 (d, J = 7.7 Hz), 108.1, 104.0 (d, J = 7.3 Hz), 68.9 (d, J = 4.8 Hz), 55.6, 27.4 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 2.5 ppm

HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO_4P$ $[M+H]^+$ 384.1365, found: 384.1375

IR (neat): 409, 495, 538, 694, 745, 1001, 1163, 1206, 1605, 1960, 1981, 1995, 2023, 2243, 2513 cm^{-1}

Synthesis of diethyl (4-methoxy-2-methylphenyl) phosphoramidate (**21a**)[6]



Synthesised in accordance with General Procedure 1 using diethyl phosphonate (60 µL, 0.45 mmol), 2-methyl-4-methylaniline (78 µL, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **21a**. The compound **21a** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as a brown solid. Yield: 92 mg, 0.34 mmol, 76%.

m.p.: 130–132 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.3 Hz, 1H), 6.67 (d, J = 8.7 Hz, 2H), 4.79 (d, J = 8.7 Hz, 1H), 4.18–4.00 (m, 4H), 3.74 (s, 3H), 2.22 (s, 3H), 1.29 (m, 6H) ppm

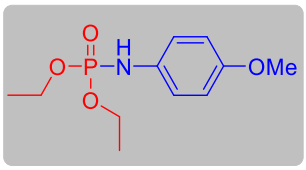
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.5, 131.1, 128.6 (d, J = 10.1 Hz), 120.1 (d, J = 1.6 Hz), 116.7, 112.2, 63.2 (d, J = 5.1 Hz), 55.9, 18.6, 16.5 (d, J = 7.1 Hz) ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 3.03 (q, J = 8.2 Hz) ppm

HRMS (ESI) m/z: calcd for $C_{12}H_{21}NO_4P$ $[M+H]^+$ 274.1208, found: 274.1216

IR (neat): 783, 962, 1022, 1209, 1501, 1558, 1978, 2162, 2517, 3215, 3713 cm^{-1}

Synthesis of diethyl (4-methoxyphenyl)phosphoramidate (**21b**)[15]



Synthesised in accordance with General Procedure 1 using diethyl phosphonate (62 µL, 0.45 mmol), 4-methylaniline (74 mg, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **21b**. The compound **21b** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as reddish brown solid. Yield: 82 mg, 0.32 mmol, 71%.

m.p.: 63–65 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = δ 6.9–6.87 (m, 2H), 6.75–6.68 (m, 2H), 6.35–6.28 (m, 1H), 4.14–3.94 (m, 4H), 3.69 (s, 3H), 1.23 (t, J = 7.0, 0.8 Hz, 6H) ppm

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.1, 133.4, 119.3 (d, J = 7.1 Hz), 115.0, 63.0 (d, J = 4.9 Hz), 55.9, 16.5 (d, J = 7.2 Hz) ppm

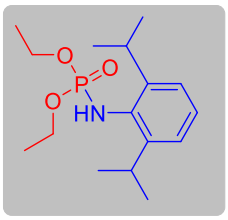
^{31}P NMR (162 MHz, $CDCl_3$): δ = 3.1 (m, 1H) ppm

HRMS (ESI) m/z: calcd for $C_{11}H_{19}NO_4P$ $[M+H]^+$ 260.1052, found: 260.1053

IR (neat): 409, 538, 648, 725, 827, 976, 1026, 1215, 1510 cm^{-1}

NMR spectroscopic data matches the literature data.[15]

Synthesis of diethyl (2,6-diisopropylphenyl)phosphoramidate (**21c**)



Synthesised in accordance with General Procedure 1 using diethyl phosphonate (60 µL, 0.45 mmol), 2,6-diisopropylaniline (114 µL, 0.60 mmol) and KI (30 mol%, 22 mg) in CH_3CN (15 mL) to afford **21c**. The compound **21c** was purified by flash column chromatography using cyclohexane and ethyl acetate (30:70, v/v) as the solvent system. The product obtained as light brown liquid. 90 mg, 0.29mmol, 64%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–6.97 (m, 3H), 4.91 (d, J = 8.4 Hz, 1H), 4.22–4.02 (m, 4H), 3.00–2.80 (m, 2H), 1.32 (t, J = 7.1 Hz, 6H), 1.24 (dd, J = 12.7, 6.9 Hz, 12H) ppm

^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.7, 130.5, 124.7, 124.2, 63.3, 28.1, 24.6, 23.2, 16.6 ppm

^{31}P NMR (162 MHz, $CDCl_3$): δ = 2.9 ppm

IR (neat): 422, 461, 648, 725, 905, 1389, 2254 cm^{-1}

11. Crystal structure determination

Single-crystal X-ray diffraction data were collected on an Agilent SuperNova Dual Atlas diffractometer, equipped with a mirror monochromator and using Mo radiation. An Oxford Cryosystems cooling apparatus was used for temperature regulation. The data were processed using CrysAlisPro[16] and the crystal structures were solved using SHELXT[17] and refined using SHELXL[17]. Non-hydrogen atoms were refined with anisotropic displacement parameters. In the final cycles of refinement, hydrogen atom geometry was idealized, and a riding model was used with U_{iso} set at 1.2 or 1.5 times the value of U_{eq} for the atom to which the hydrogen atoms are bonded. Crystal and structure refinement data are shown in Table S9.

Table S9. Crystal and structure refinement data.

Compound	**6a**	**22**	**8a**	**17**	**9a**
Empirical formula	$C_{18}H_{16}NOP$	$C_{12}H_{11}O_2P$	$C_{18}H_{15}O_2P$	$C_{21}H_{20}NO_3P$	$C_{18}H_{16}NO_2P$
Formula weight	293.29	218.18	294.27	365.35	309.29
Temperature (K)	296(2)	200(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pca2_1$	$P\ 2_1/c$	$P2_1/n$	$P\ 2_1/c$	$P2_1/c$
a (Å)	16.9837(12)	11.4422(6)	9.2605(4)	10.5388(6)	15.6012(12)
b (Å)	9.6048(6)	6.0033(3)	11.3986(5)	19.0742(9)	9.0207(5)
c (Å)	9.6892(7)	15.6542(9)	14.1564(5)	9.8492(5)	11.7490(9)
α (°)	90.	90	90	90	90
b (°)	90	100.064(5)	93.665(3)	107.023(5)	107.452(8)
g (°)	90	90	90	90	90
Volume ($Å^3$)	1580.55(19)	1058.76(10)	1491.25(11)	1893.13(18)	1577.4(2)
Z	4	4	4	4	4
Density (cal) (Mg/m^3)	1.233	1.369	1.311	1.282	1.302
Abs. coeff. (mm^{-1})	0.172	0.234	0.185	0.165	0.180
Crystal size (mm^3)	0.50x0.37x 0.29	0.49x0.27x 0.13	0.70x0.27x 0.10	0.35x0.19x 0.08	0.20x0.05x0.04
Refs collected	7472	8963	13775	10099	14047
Independent refs	3179	2558	3683	4550	3903
R(int)	0.0259	0.0344	0.0301	0.0243	0.0729
Parameters	190	137	190	240	200
Goodness-of-fit on F^2	1.086	1.115	1.069	1.058	1.037
R1 [I>2σ(I)]	0.0454	0.0406	0.0570	0.0460	0.0620
wR2 [I>2σ(I)]	0.0927	0.0914	0.1411	0.1085	0.1278
Absolute structure parameter	0.05(6)	-	-	-	-
Largest diff. peak / hole ($e.Å^{-3}$)	0.190 / -0.261	0.279 / -0.408	1.392 / -0.460	0.303 / -0.364	.279 / -0.448

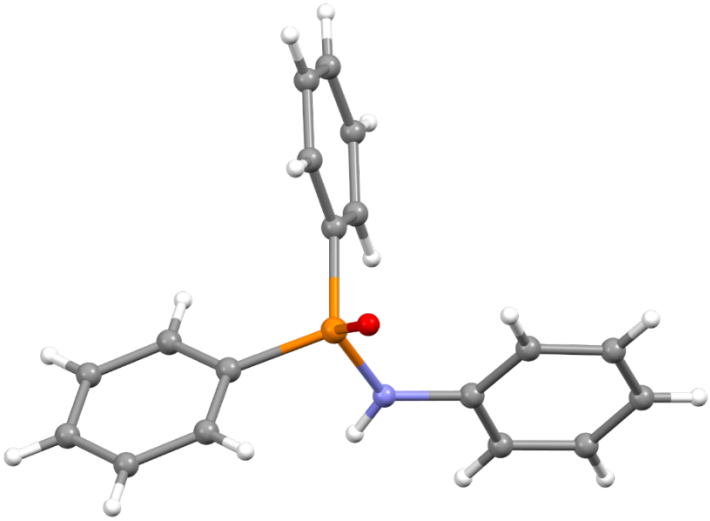


Figure S16: Structure of compound **6a**. The structure has been reported[18] with CSD code VATSOZ, CCDC 2367670.

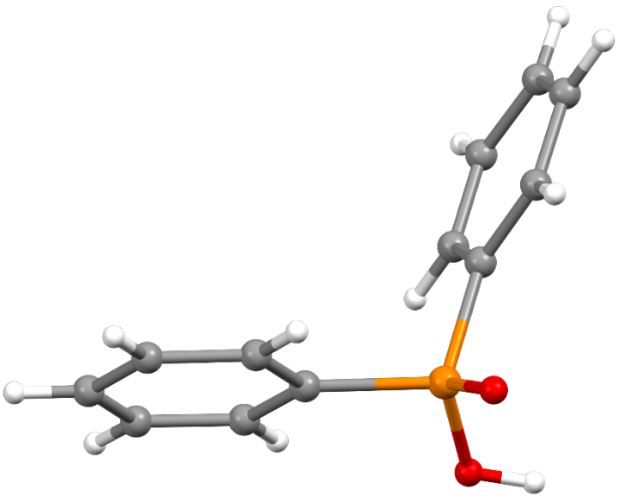


Figure S17: Structure of compound **22**. The structure has been reported[19] with CSD code DPPHIN10, CCDC 2367668.

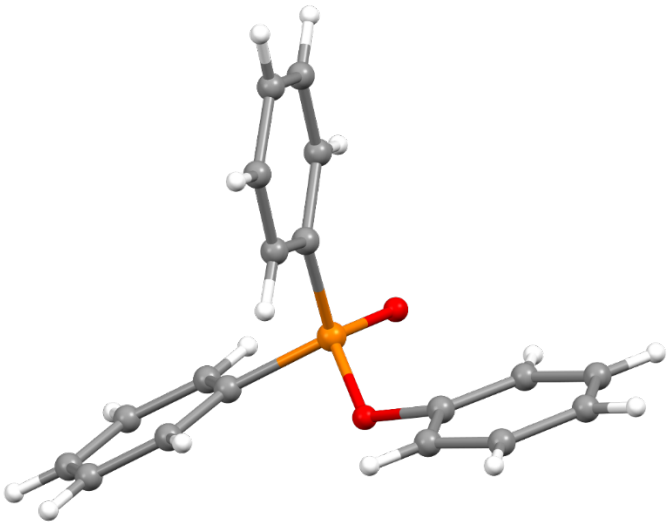


Figure S18: Structure of compound **8a**, CCDC 2367671.

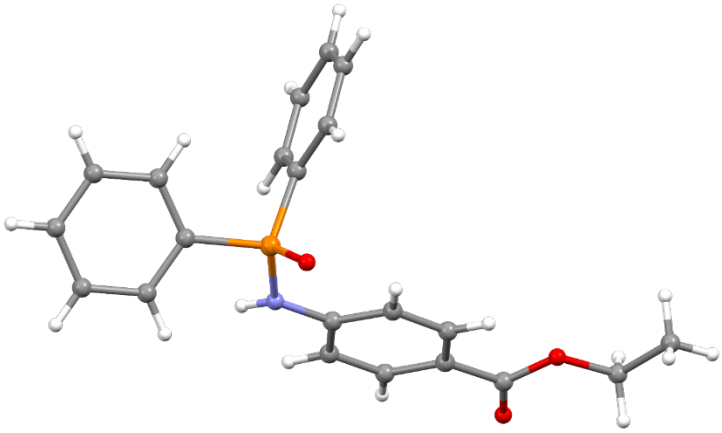
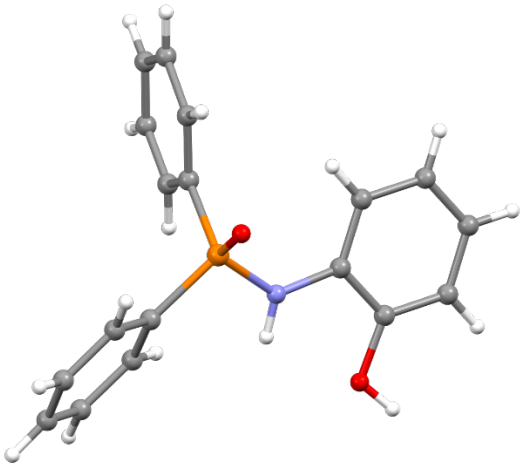


Figure S19: Structure of compound **17**, CCDC 2367667.



Fiure S20: Structure of compound **9a**, CCDC 2367669.

12. NMR Spectra

Figure S21: *N*,*P*,*P*-triphenylphosphinic amide (**6a**)[1]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

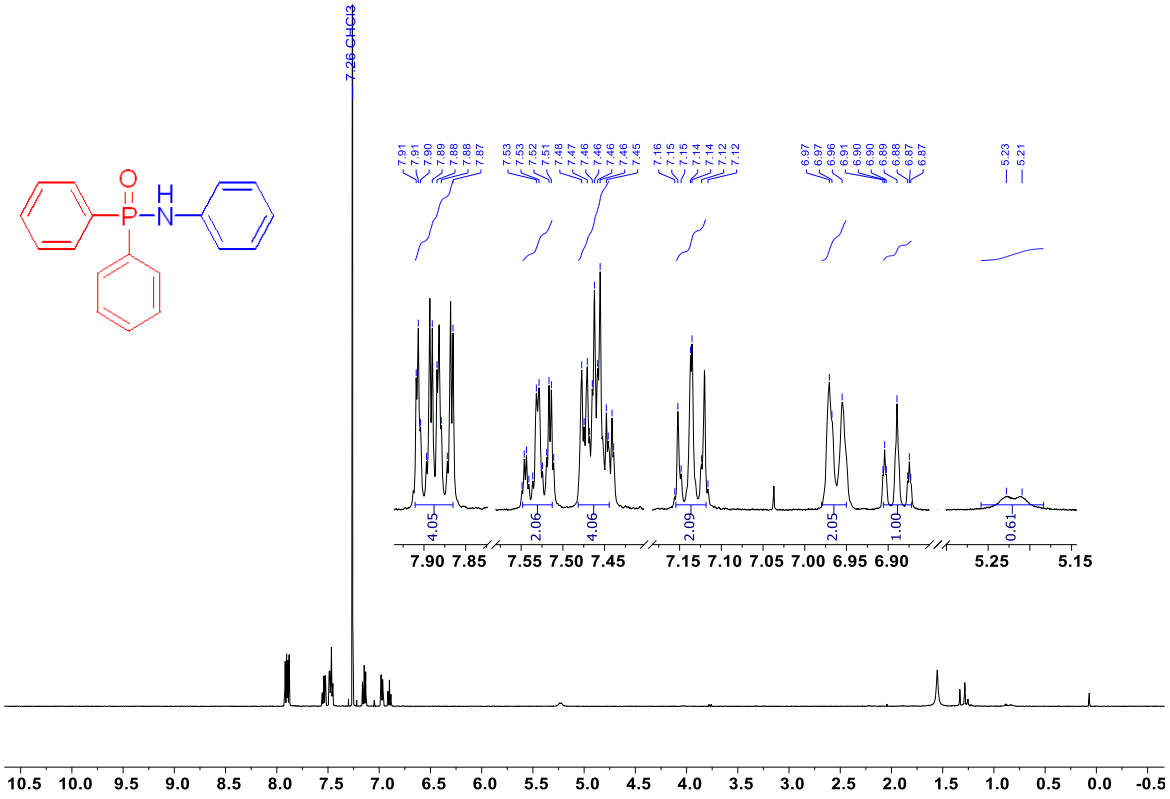


Figure S22: *N*,*P*,*P*-triphenylphosphinic amide (**6a**)[1]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

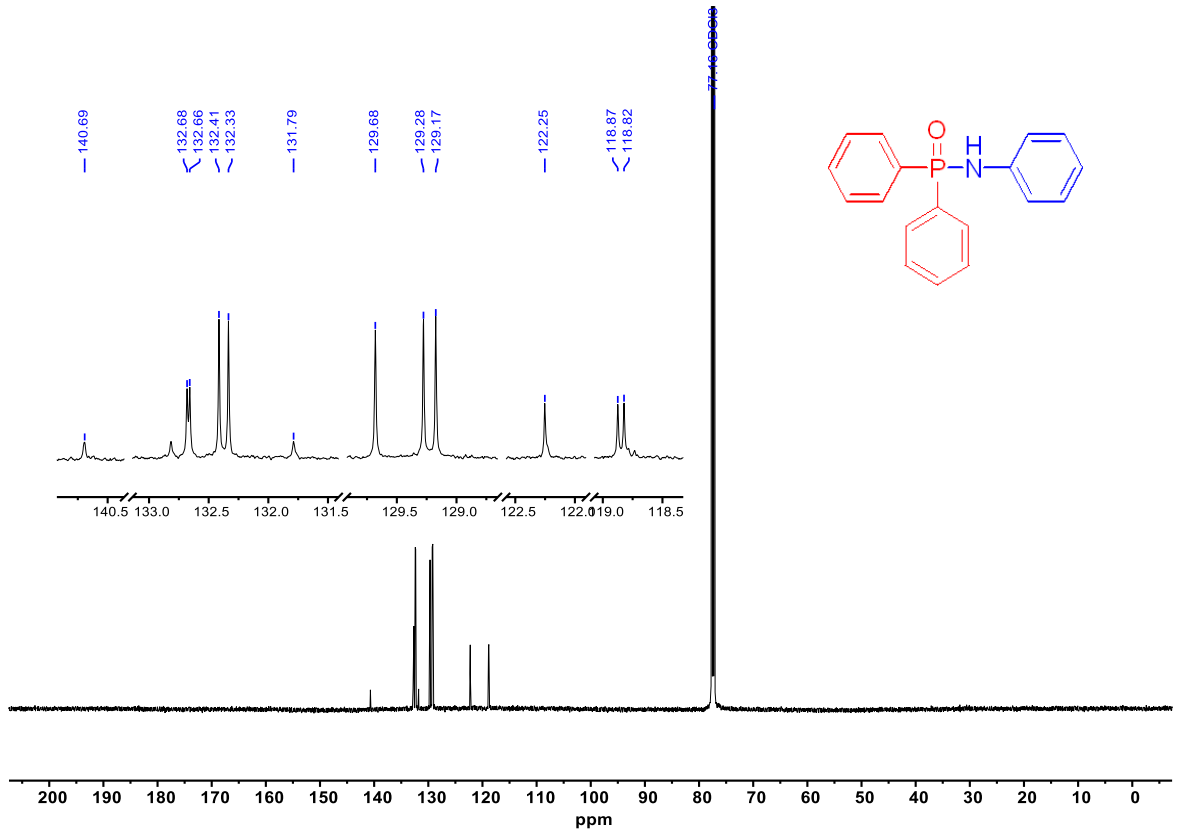


Figure S23: *N*,*P*,*P*-triphenylphosphinic amide (**6a**)[1]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

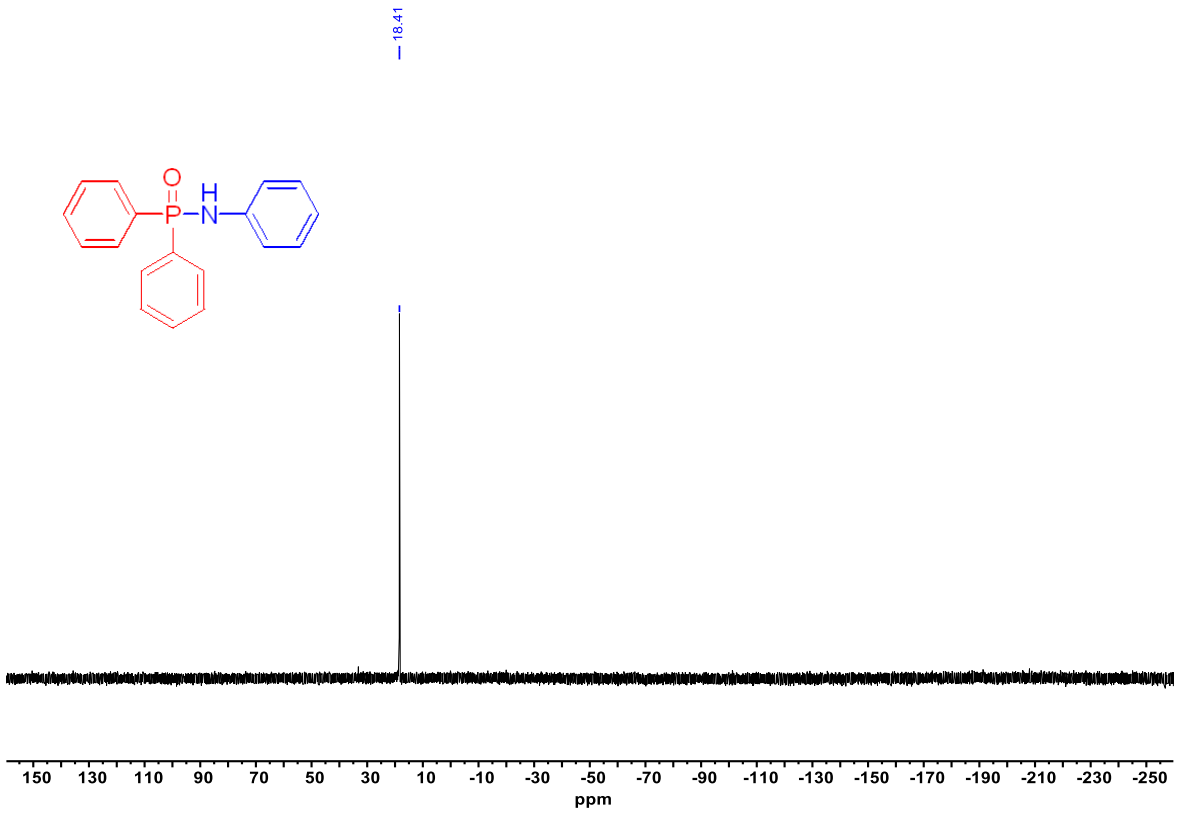


Figure S24: *N*-(4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6b**)[1]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

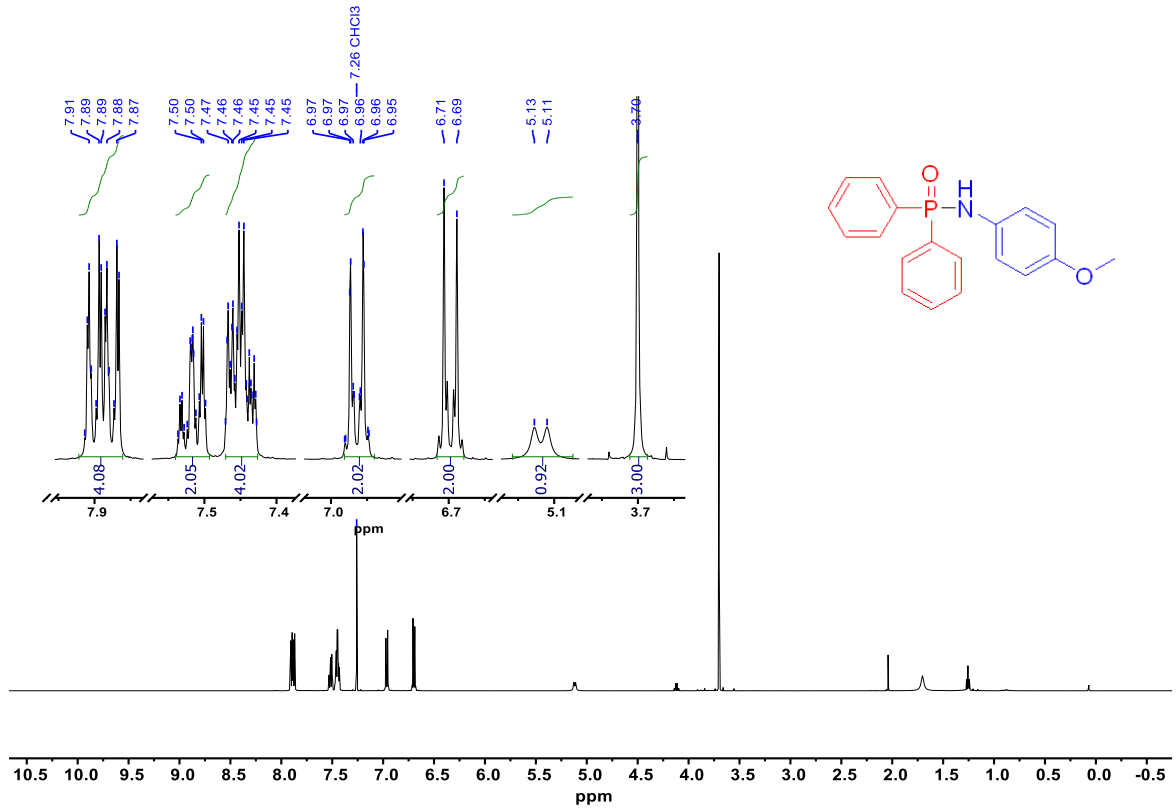


Figure S25: *N*-(4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6b**)[1]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

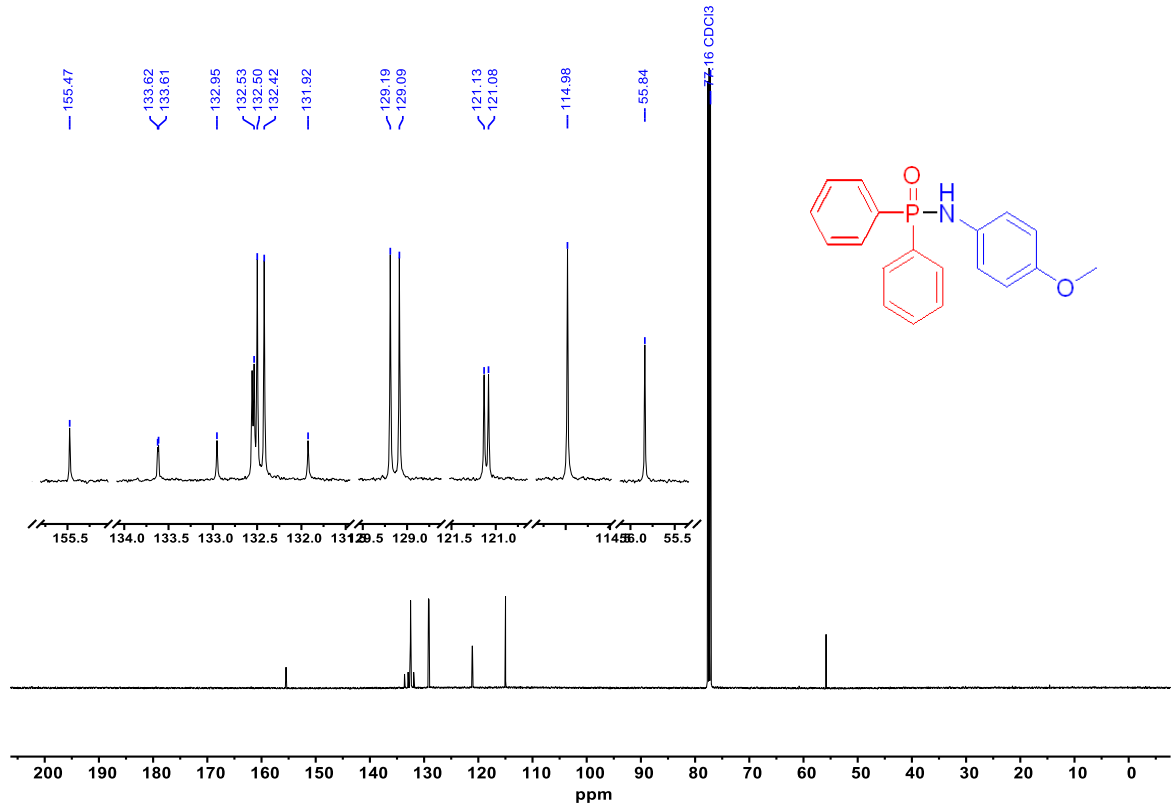


Figure S26: *N*-(4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6b**)[1]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

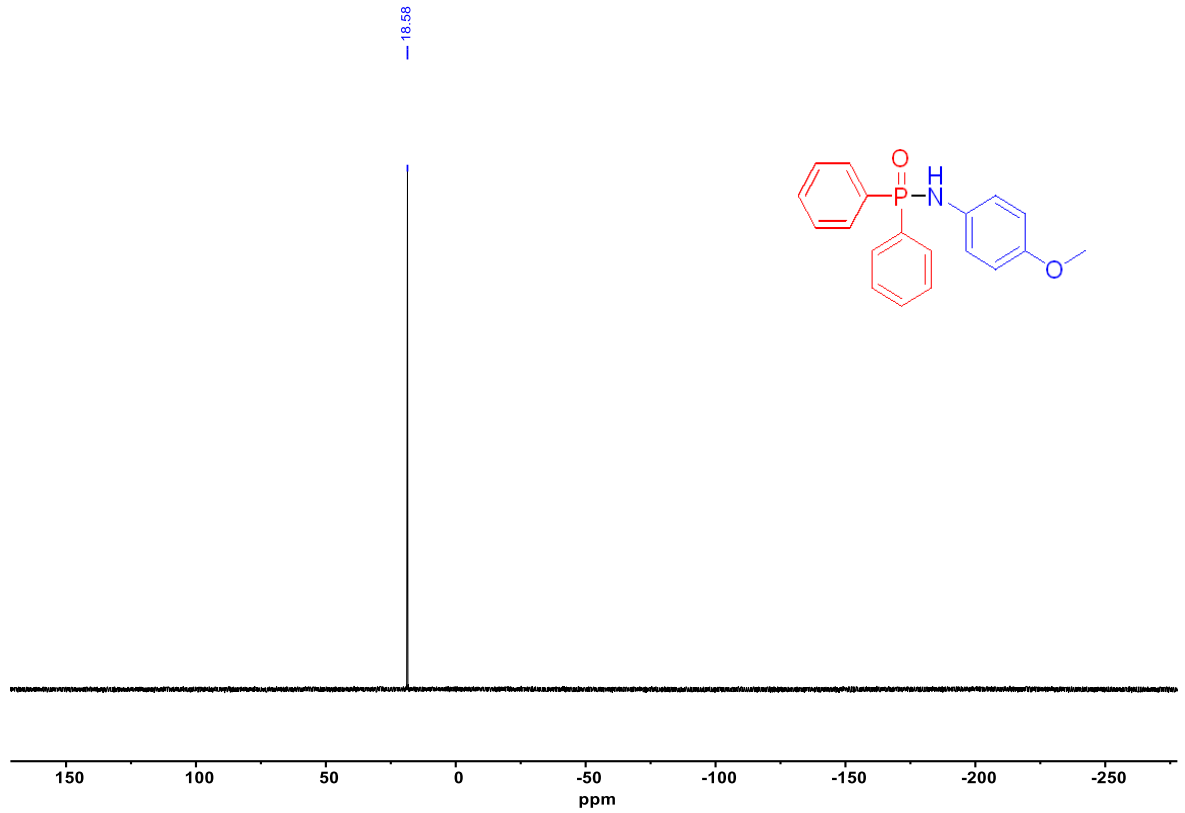


Figure S27: *N*-(4-(methylthio)phenyl)-*P*,*P*-diphenylphosphinic amide (**6c**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

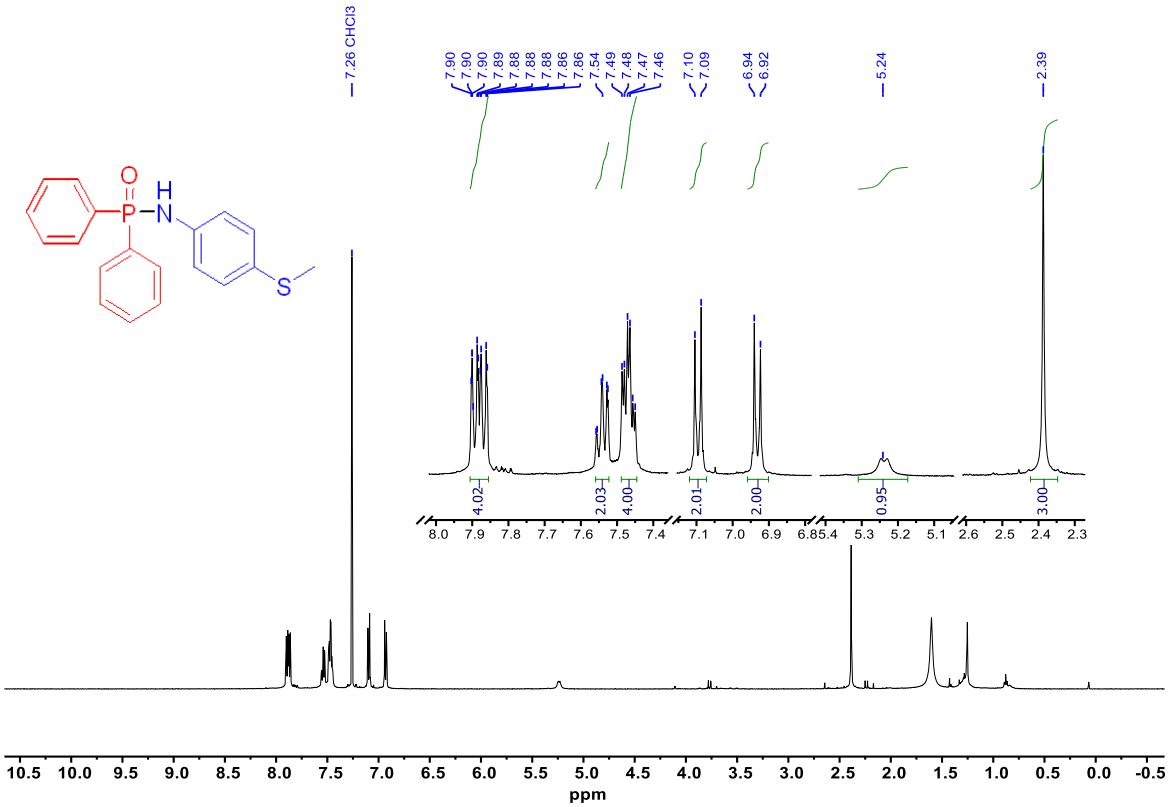


Figure S28: *N*-(4-(methylthio)phenyl)-*P*,*P*-diphenylphosphinic amide (**6c**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

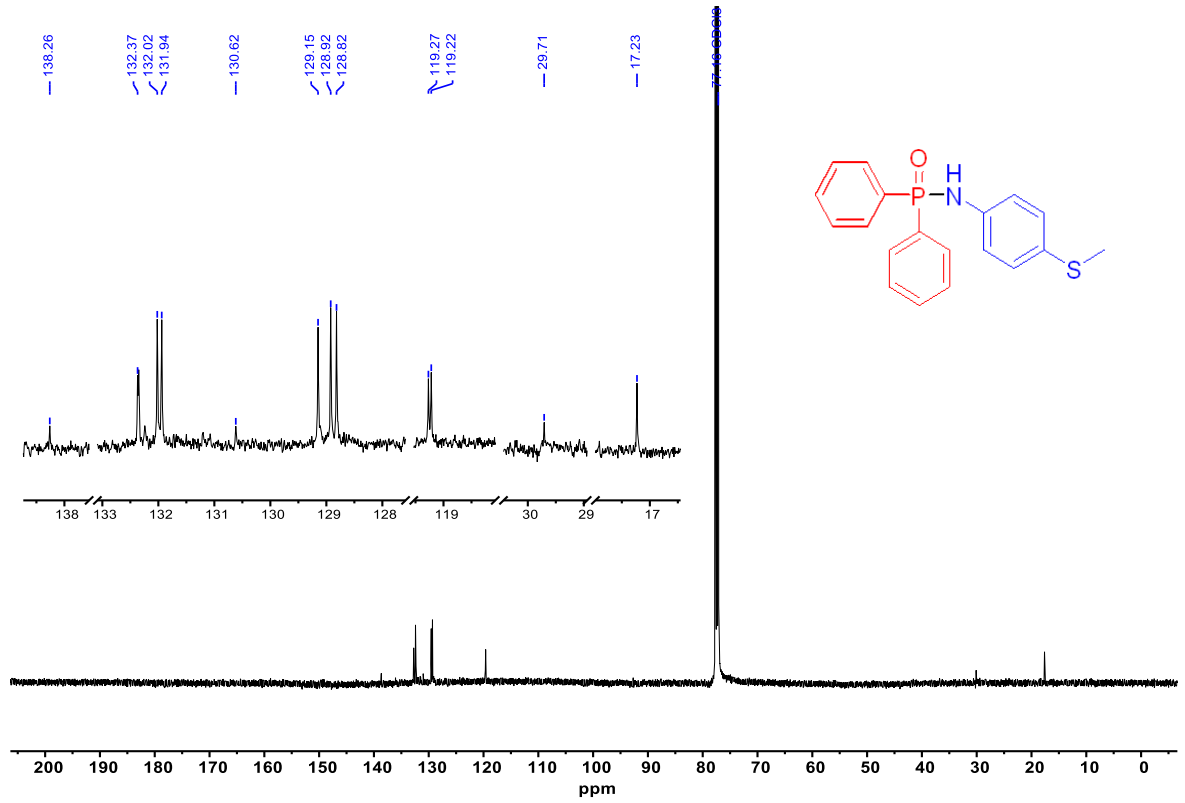


Figure S29: *N*-(4-(methylthio)phenyl)-*P*,*P*-diphenylphosphinic amide (**6c**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

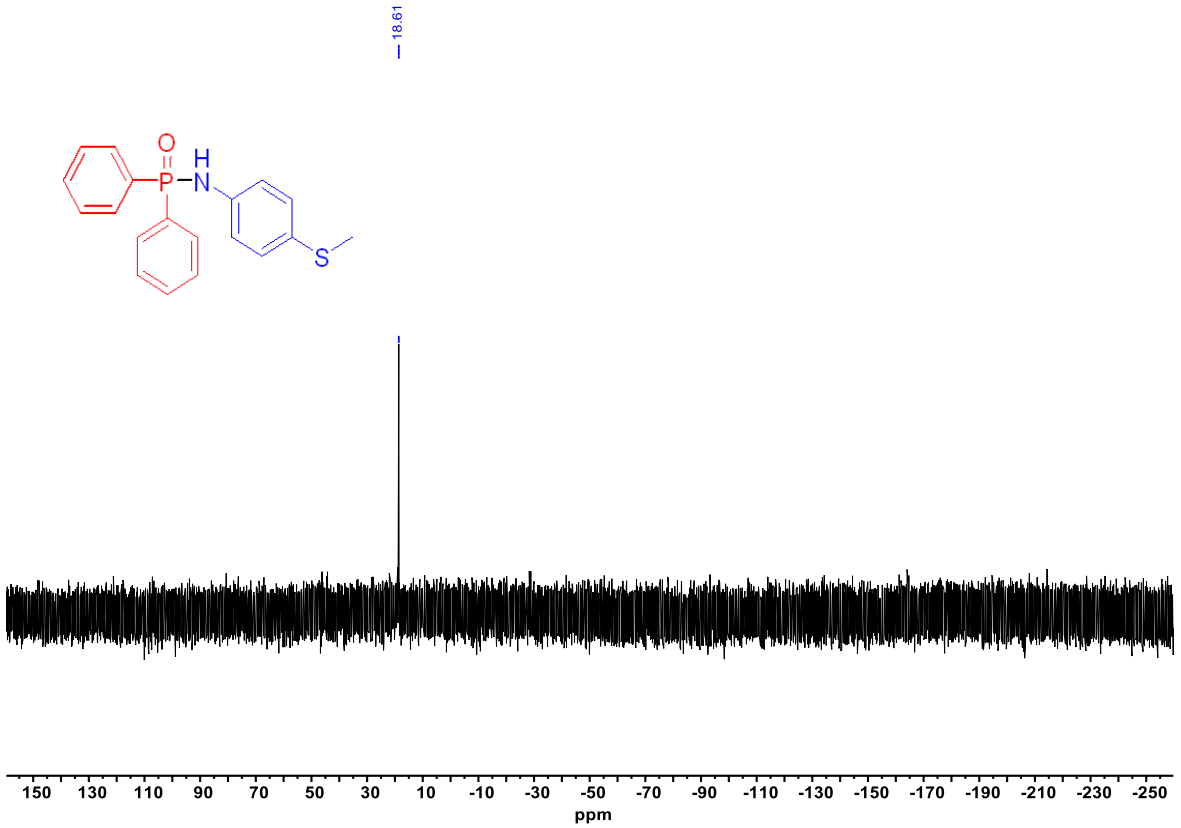


Figure S30: *N*-(2-bromo-4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6d**)[6]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

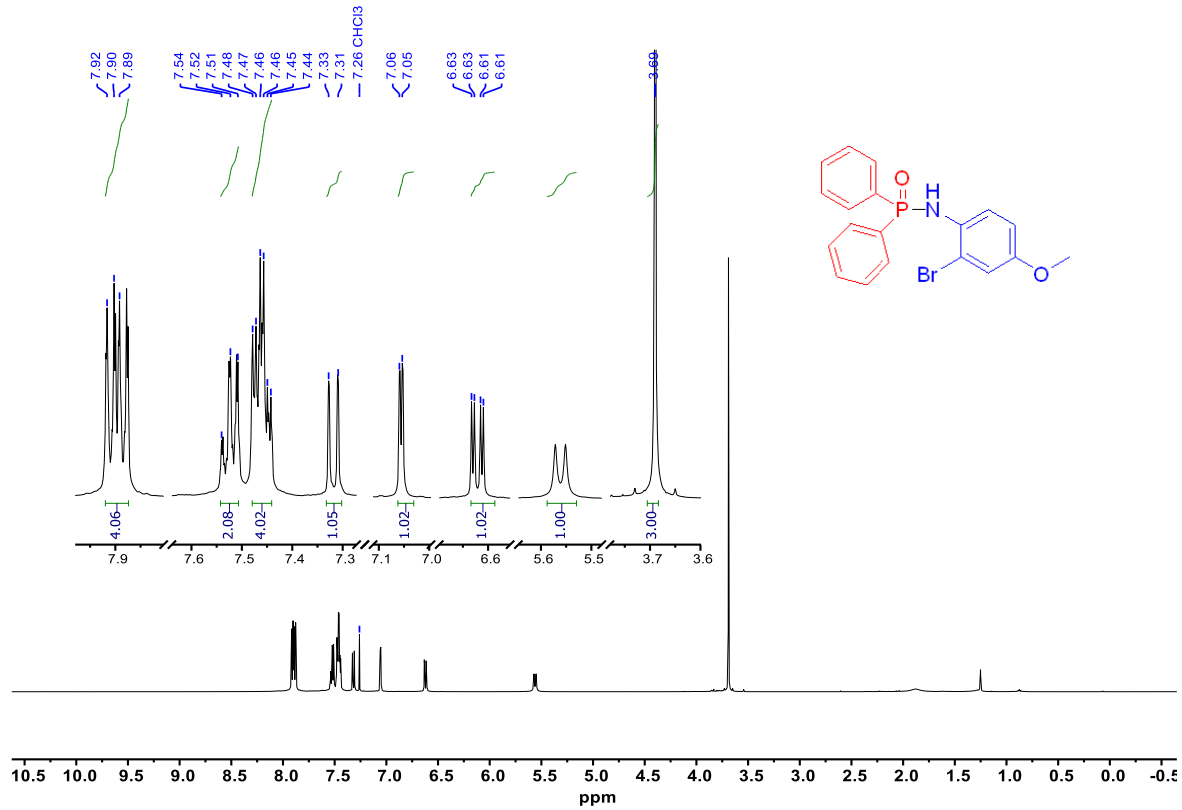


Figure S31: *N*-(2-bromo-4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6d**)[6]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

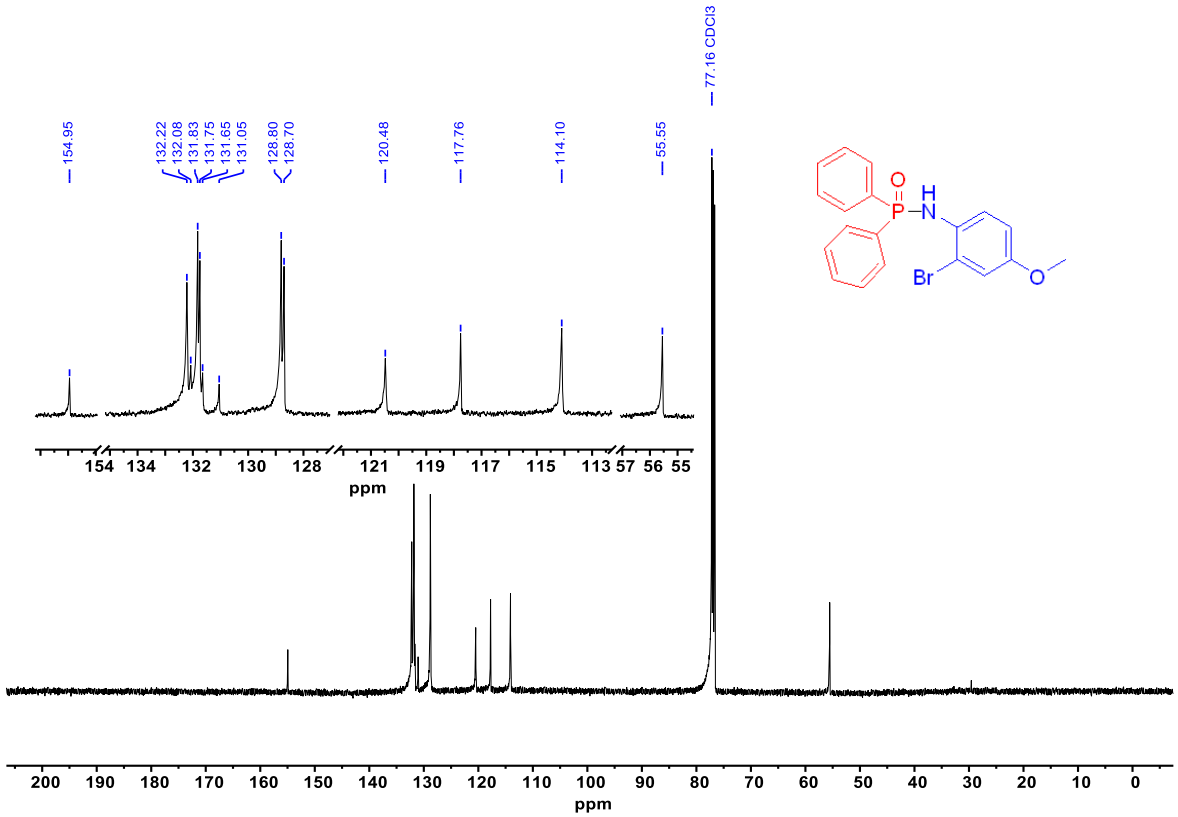


Figure S32: *N*-(2-bromo-4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6d**) [6]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

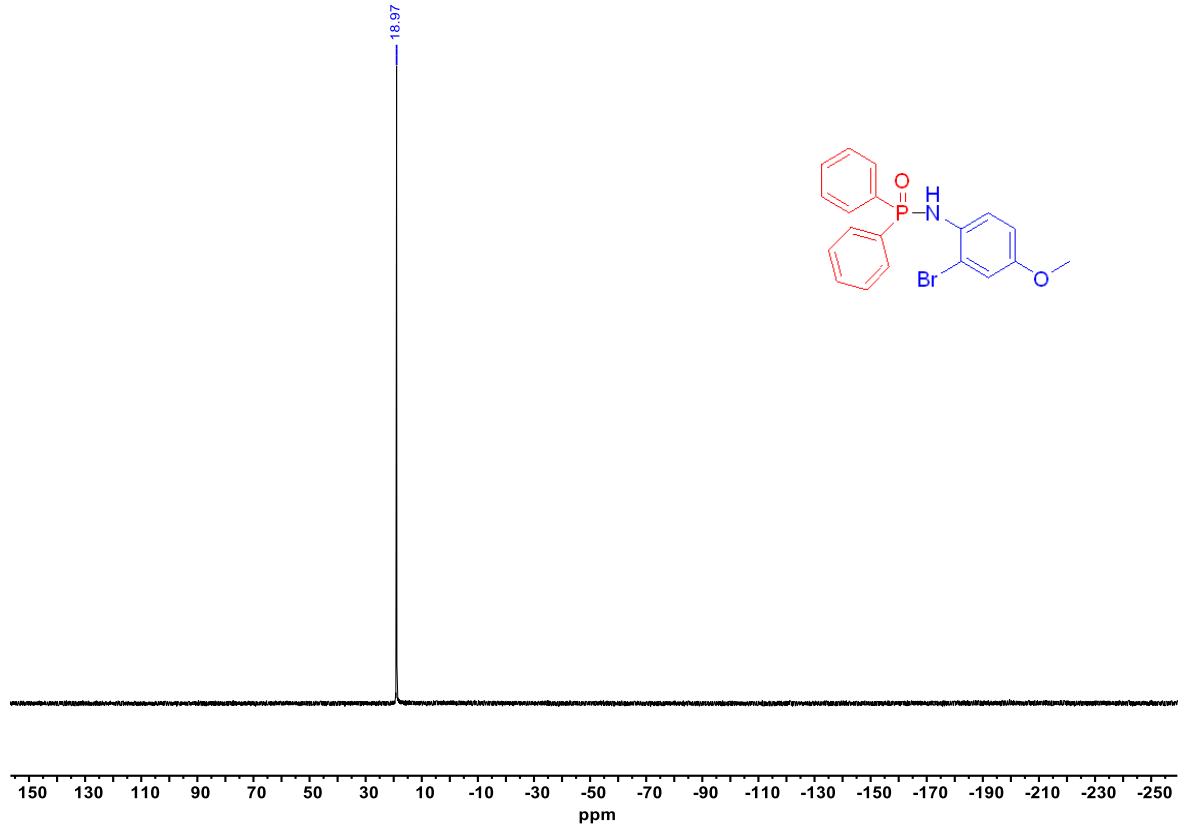


Figure S33: *N*-(2-bromo-4-methylphenyl)-*P*,*P*-diphenylphosphinic amide (**6e**)[6]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

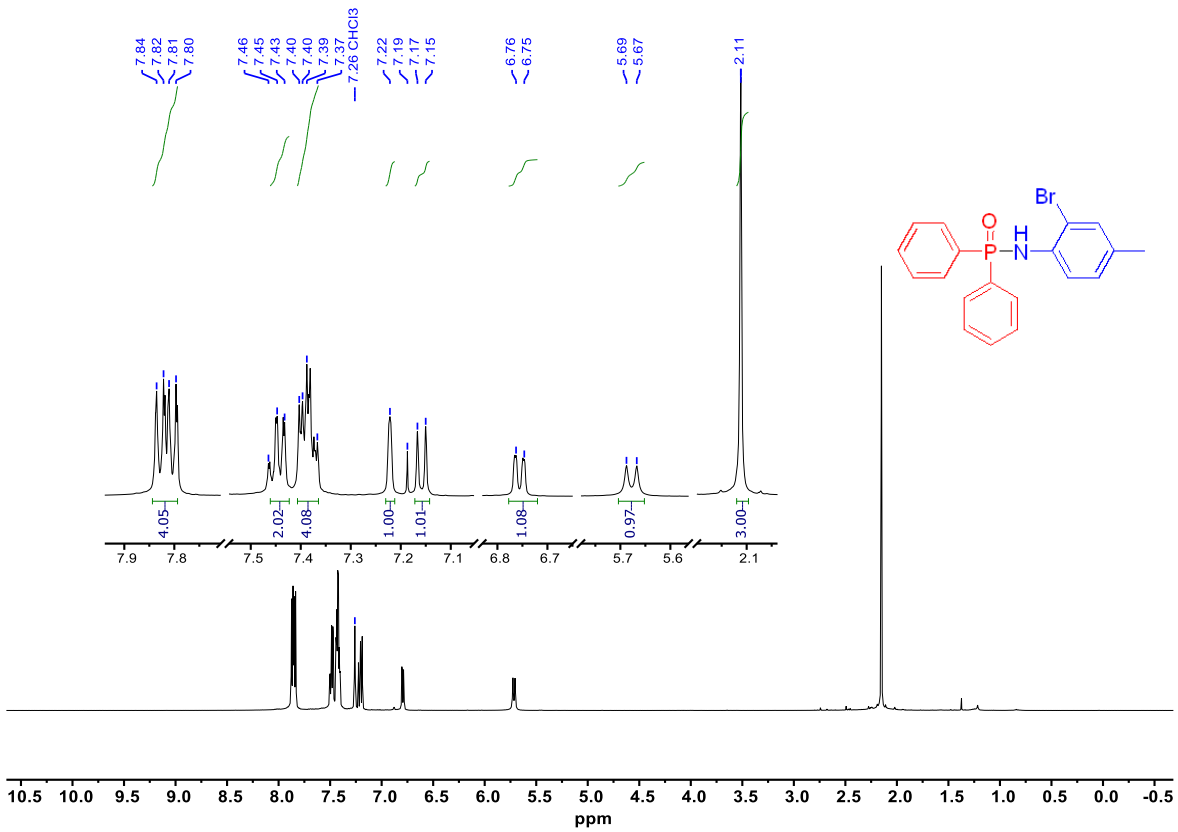


Figure S34: *N*-(2-bromo-4-methylphenyl)-*P*,*P*-diphenylphosphinic amide (**6e**)[6]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

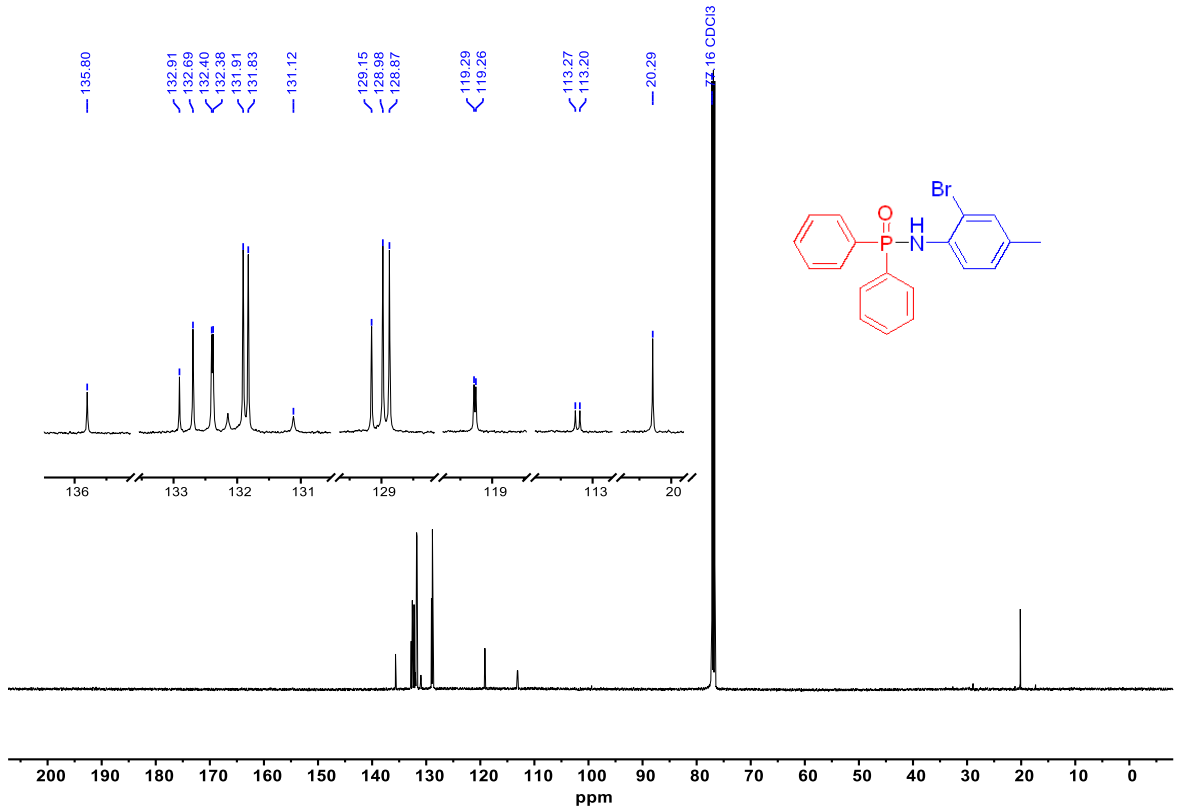


Figure S35: *N*-(2-bromo-4-methylphenyl)-*P*,*P*-diphenylphosphinic amide (**6e**)[6]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

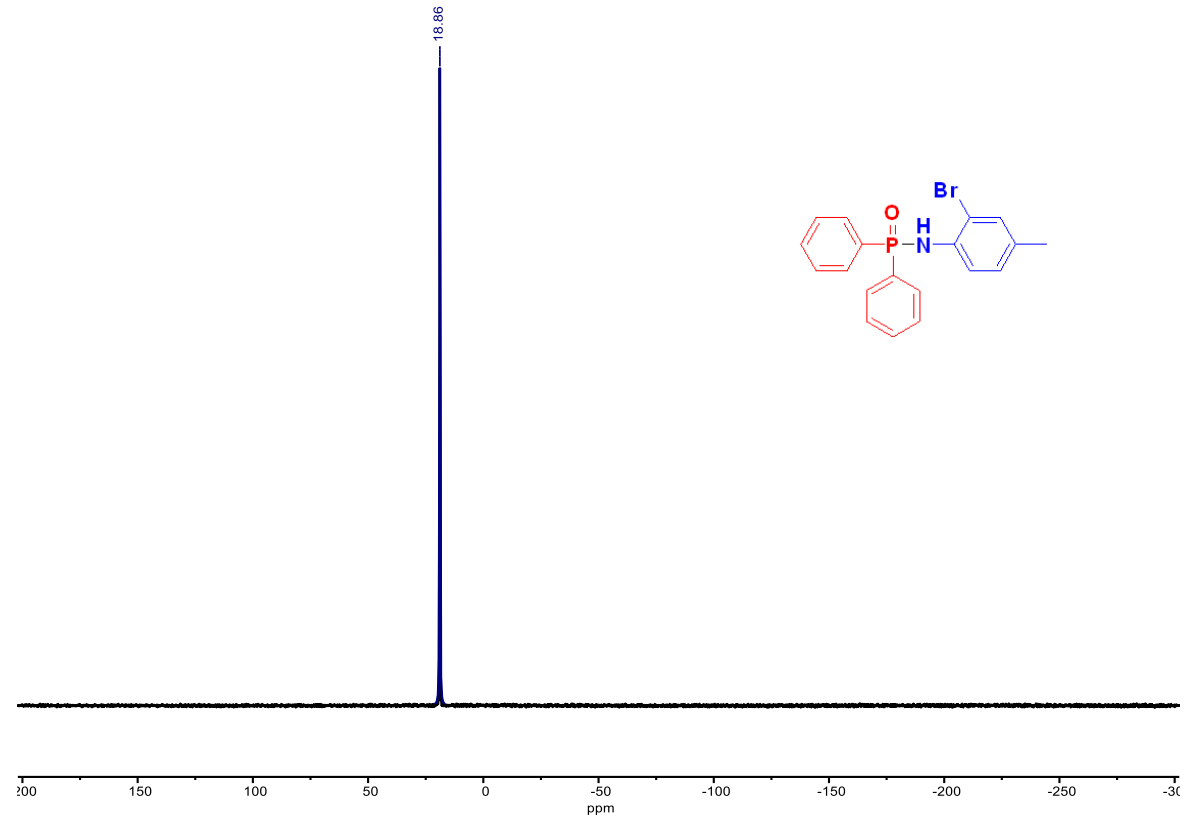


Figure S36: *N*-(2-bromo-4-(tert-butyl)phenyl)-*P*,*P*-diphenylphosphinic amide (**6f**)[7]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

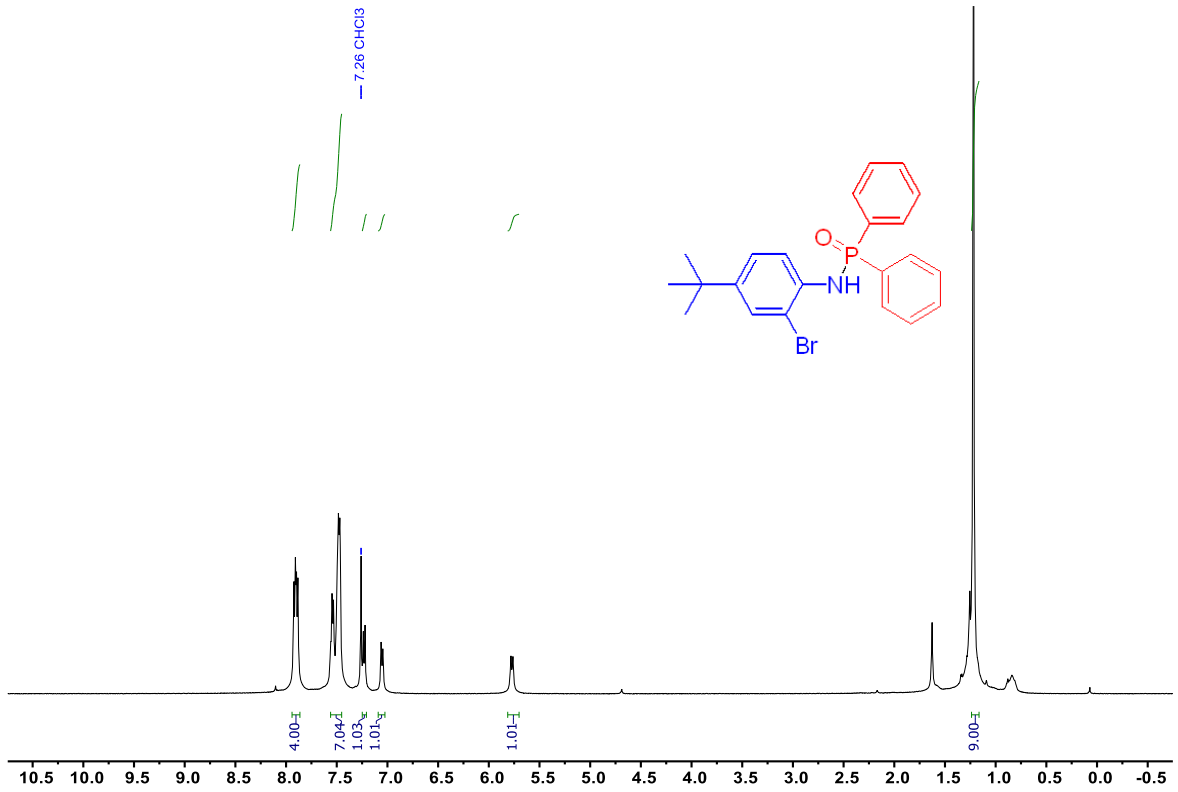


Figure S37: *N*-(2-bromo-4-(tert-butyl)phenyl)-*P*,*P*-diphenylphosphinic amide (**6f**)[7]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

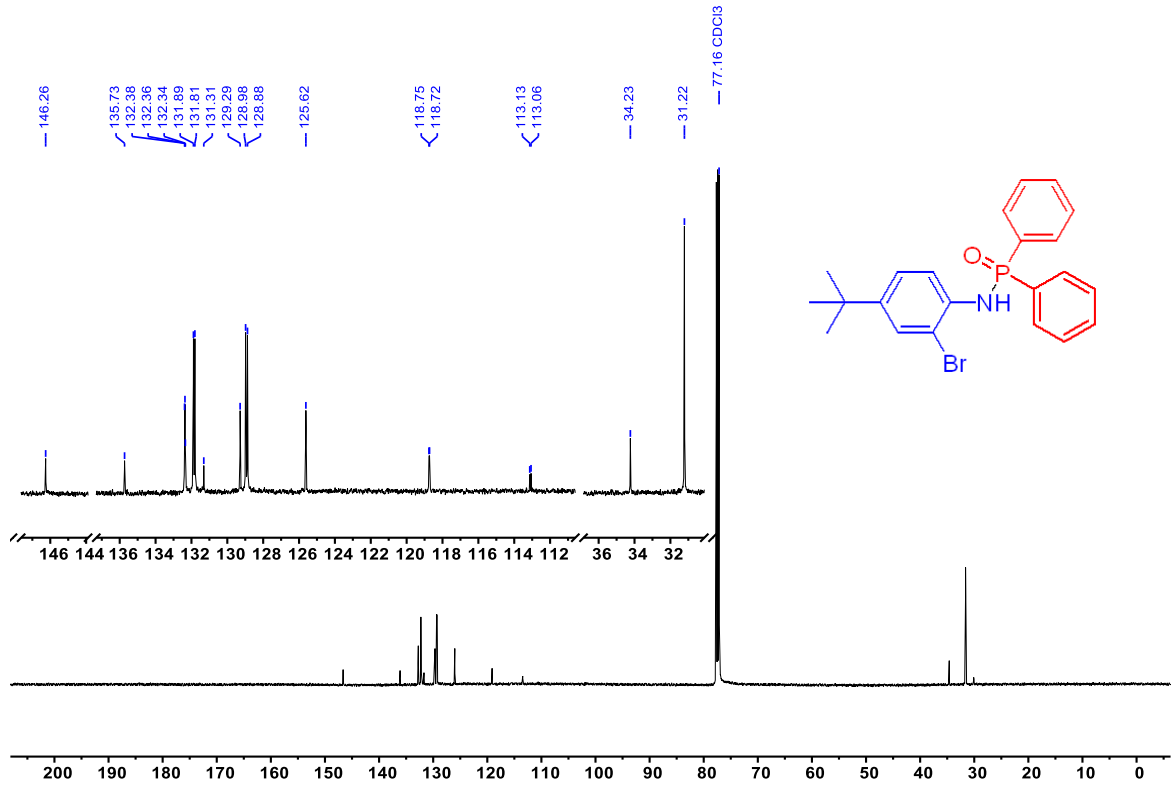


Figure S38: *N*-(2-bromo-4-(tert-butyl)phenyl)-*P*,*P*-diphenylphosphinic amide (**6f**)[7]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

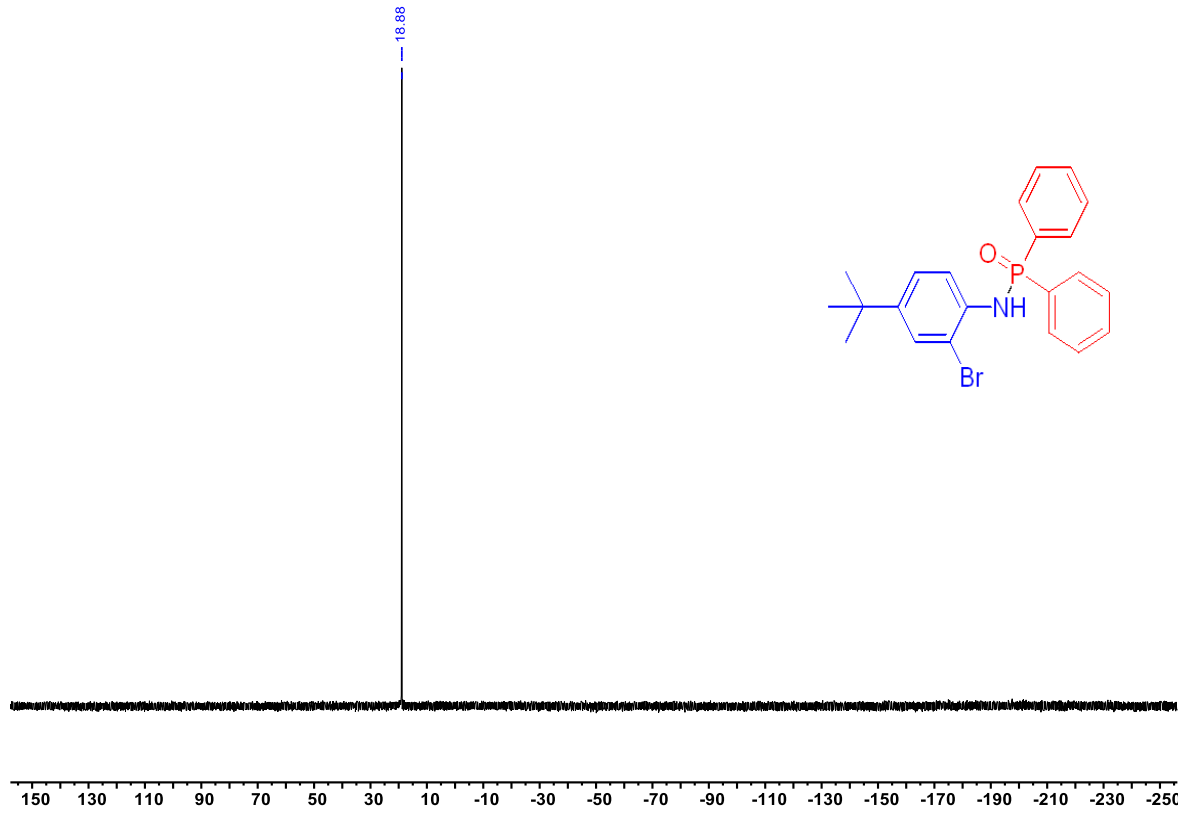


Figure S39: *N*-(2-bromo-4-(trifluoromethoxy)phenyl)-*P*,*P*-diphenylphosphinic amide (**6g**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

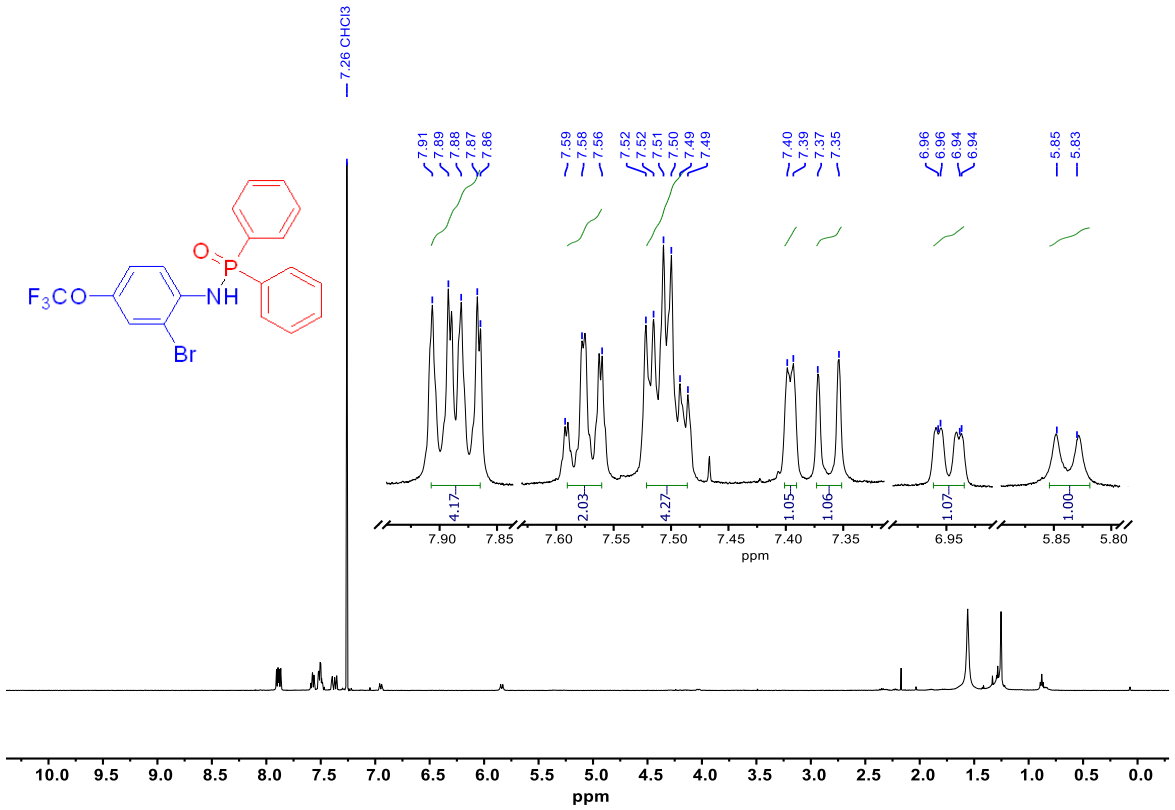


Figure S40: *N*-(2-bromo-4-(trifluoromethoxy)phenyl)-*P*,*P*-diphenylphosphinic amide (**6g**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

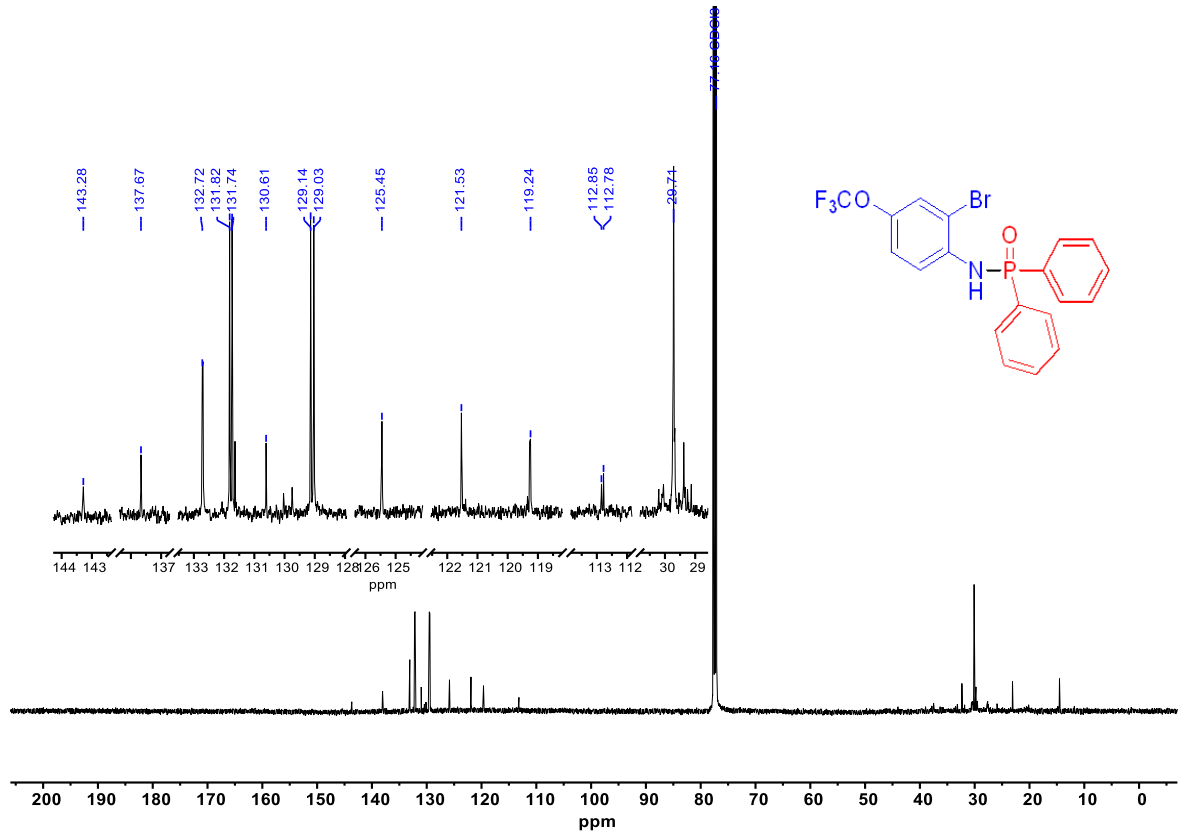


Figure S41: *N*-(2-bromo-4-(trifluoromethoxy)phenyl)-*P*,*P*-diphenylphosphinic amide (**6g**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

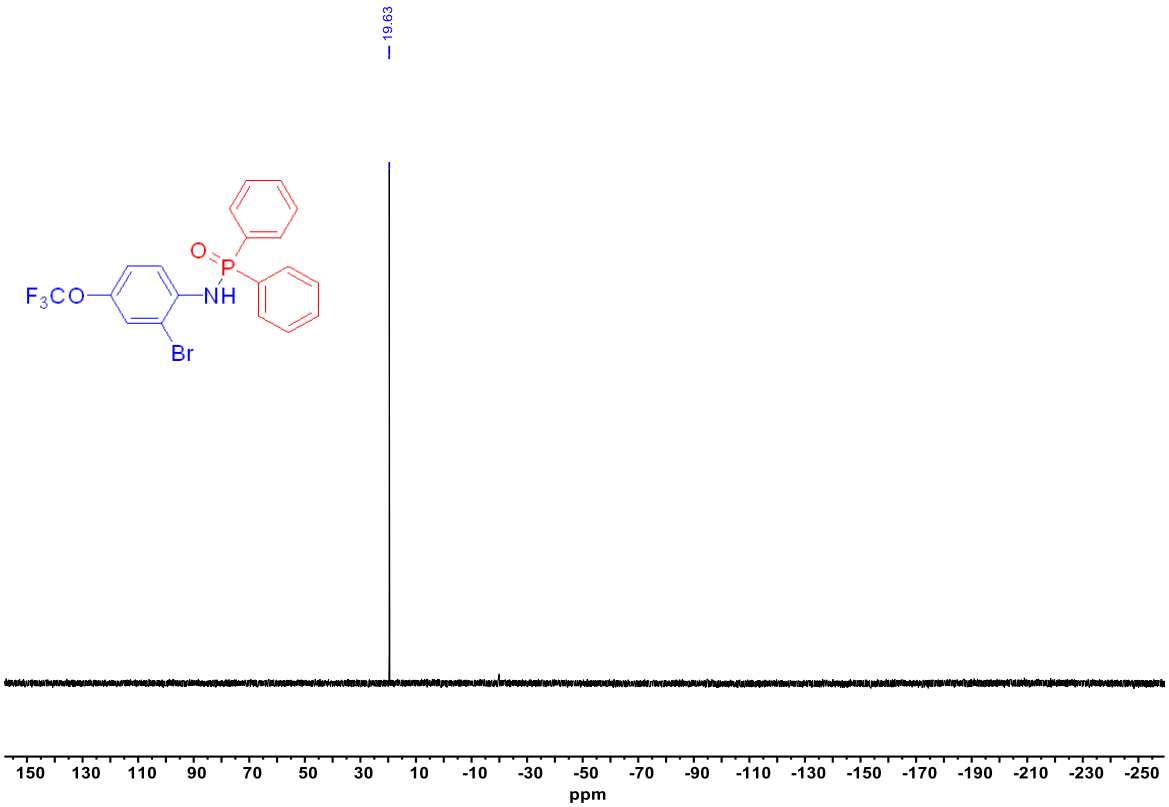


Figure S42: *N*-(4-iodophenyl)-*P*,*P*-diphenylphosphinic amide (**6h**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

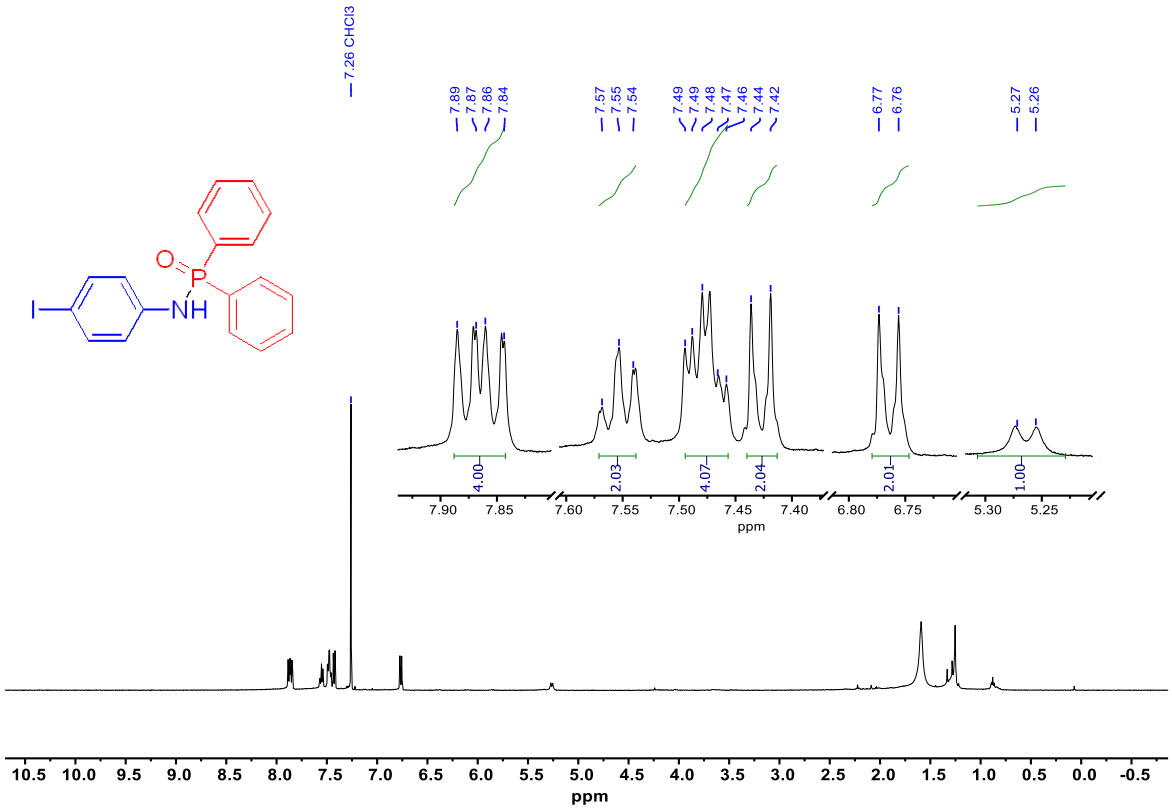


Figure S43: *N*-(4-iodophenyl)-*P*,*P*-diphenylphosphinic amide (**6h**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

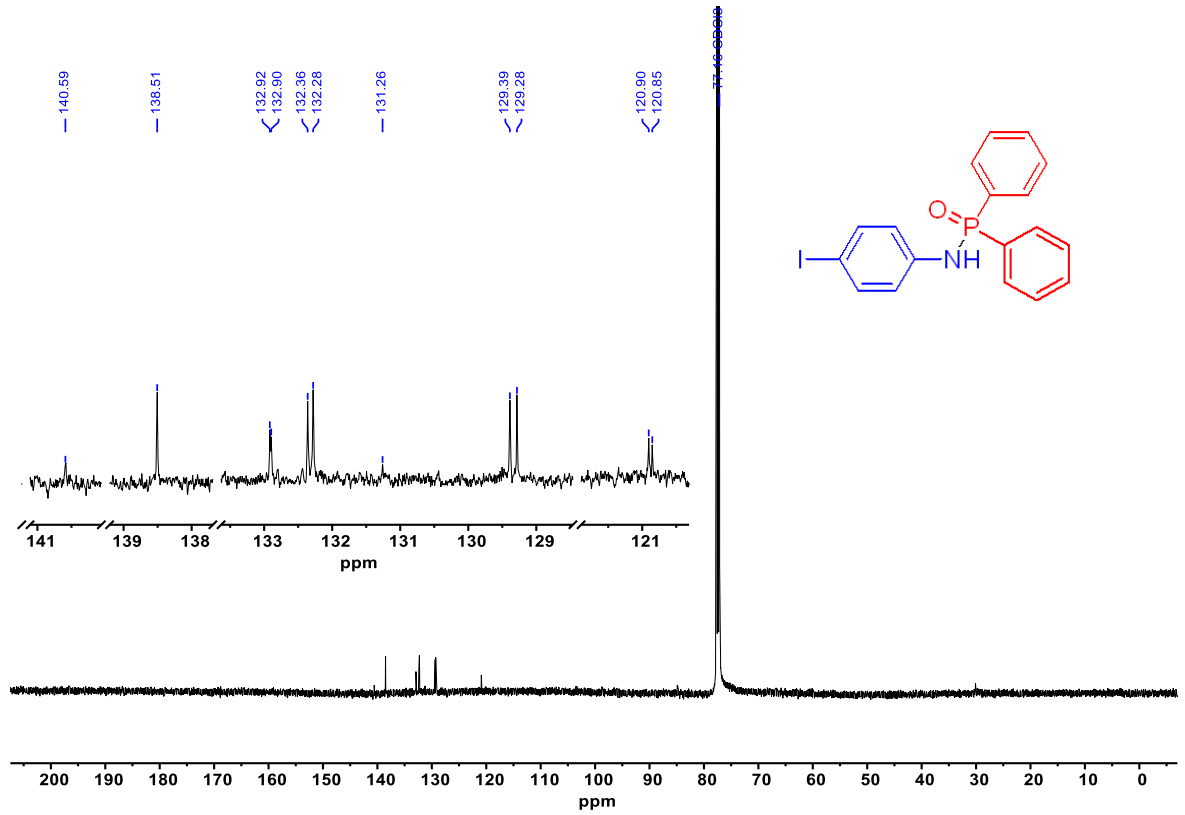


Figure S44: *N*-(4-iodophenyl)-*P*,*P*-diphenylphosphinic amide (**6h**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

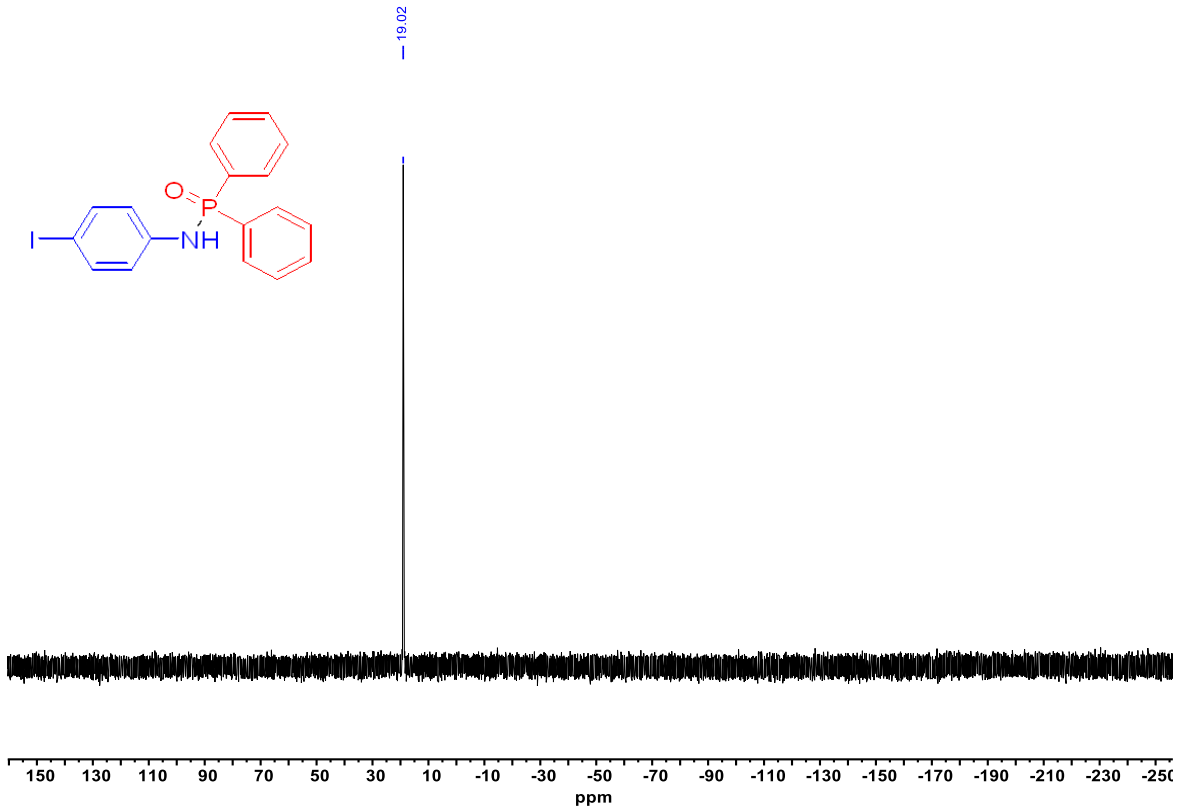


Figure S45: *N*-(4-nitrophenyl)-*P,P*-diphenylphosphinic amide (**6i**)

^{1}H NMR (400 MHz, $CDCl_3$)

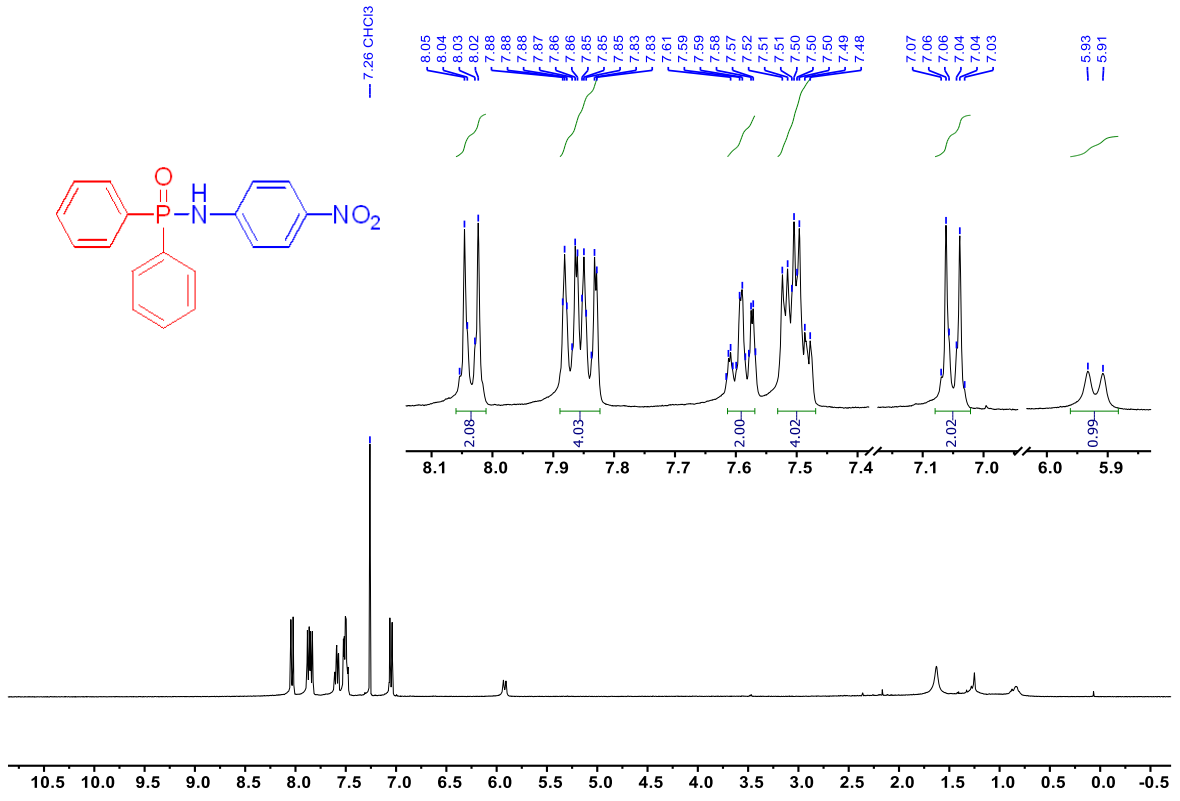


Figure S46: *N*-(4-nitrophenyl)-*P,P*-diphenylphosphinic amide (**6i**)

^{13}C NMR (101 MHz, $CDCl_3$)

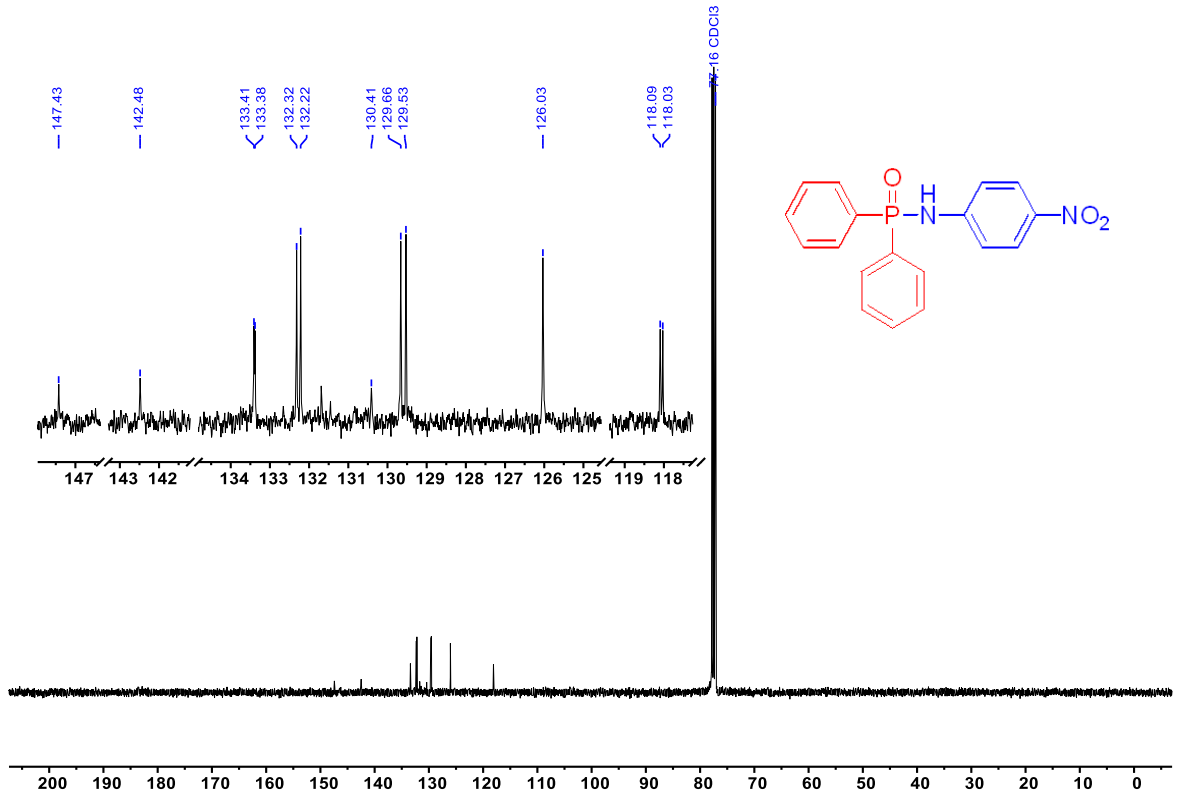


Figure S47: *N*-(4-nitrophenyl)-*P,P*-diphenylphosphinic amide (**6i**)

^{31}P NMR (162 MHz, $CDCl_3$)

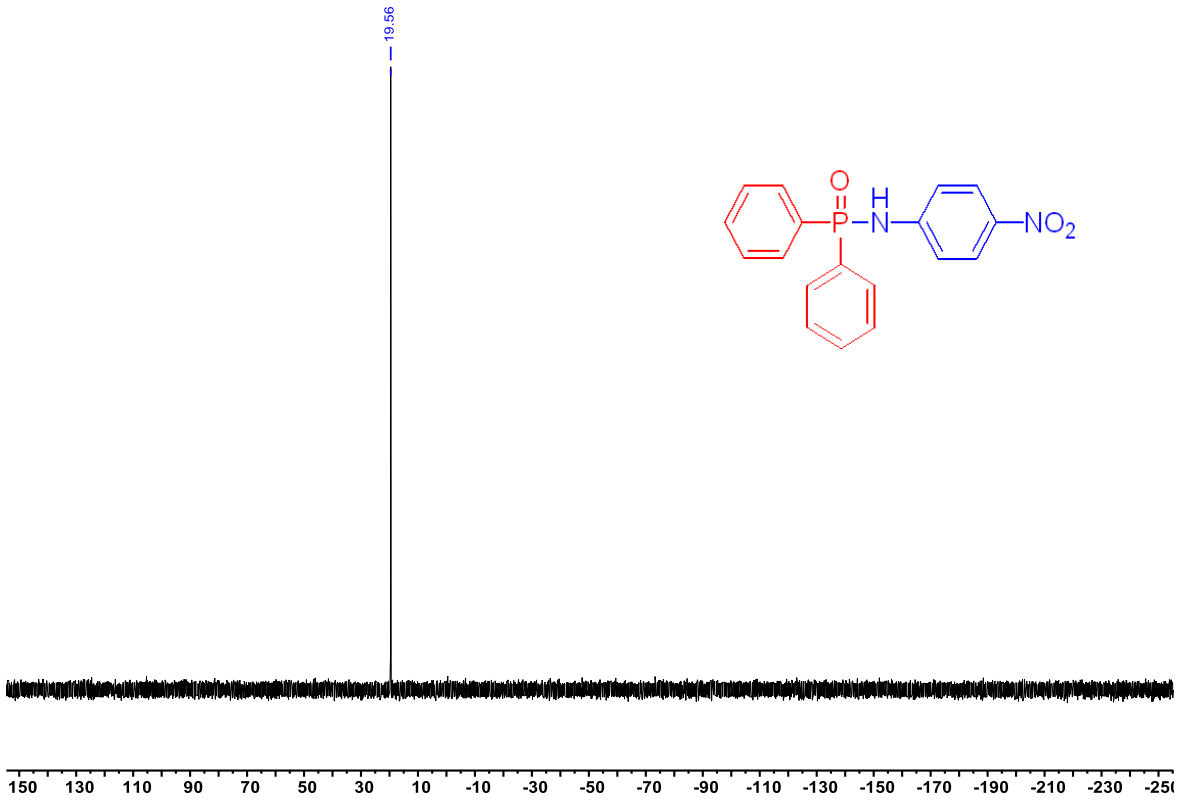


Figure S48: *P,P*-diphenyl-*N*-(4-(trifluoromethyl)phenyl)phosphinic amide (**6j**)

^{1}H NMR (400 MHz, $CDCl_3$)

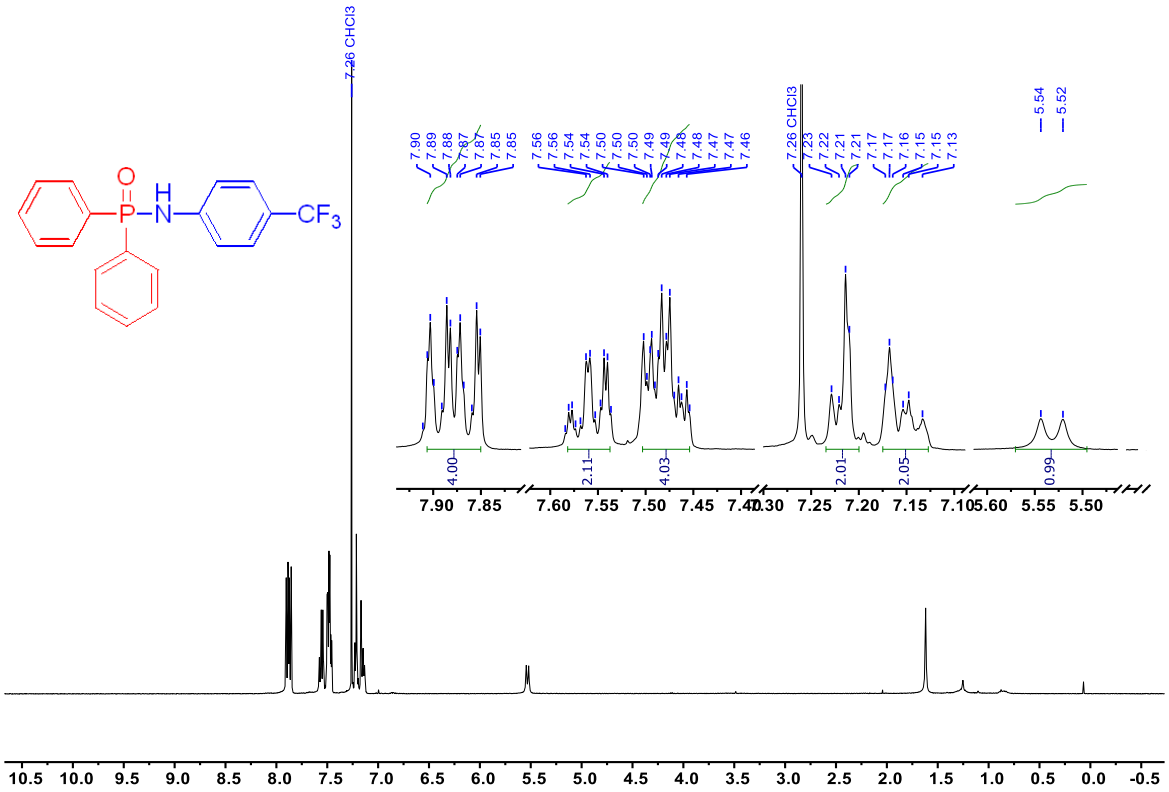


Figure S49: *P,P*-diphenyl-*N*-(4-(trifluoromethyl)phenyl)phosphinic amide (**6j**)

^{13}C NMR (101 MHz, $CDCl_3$)

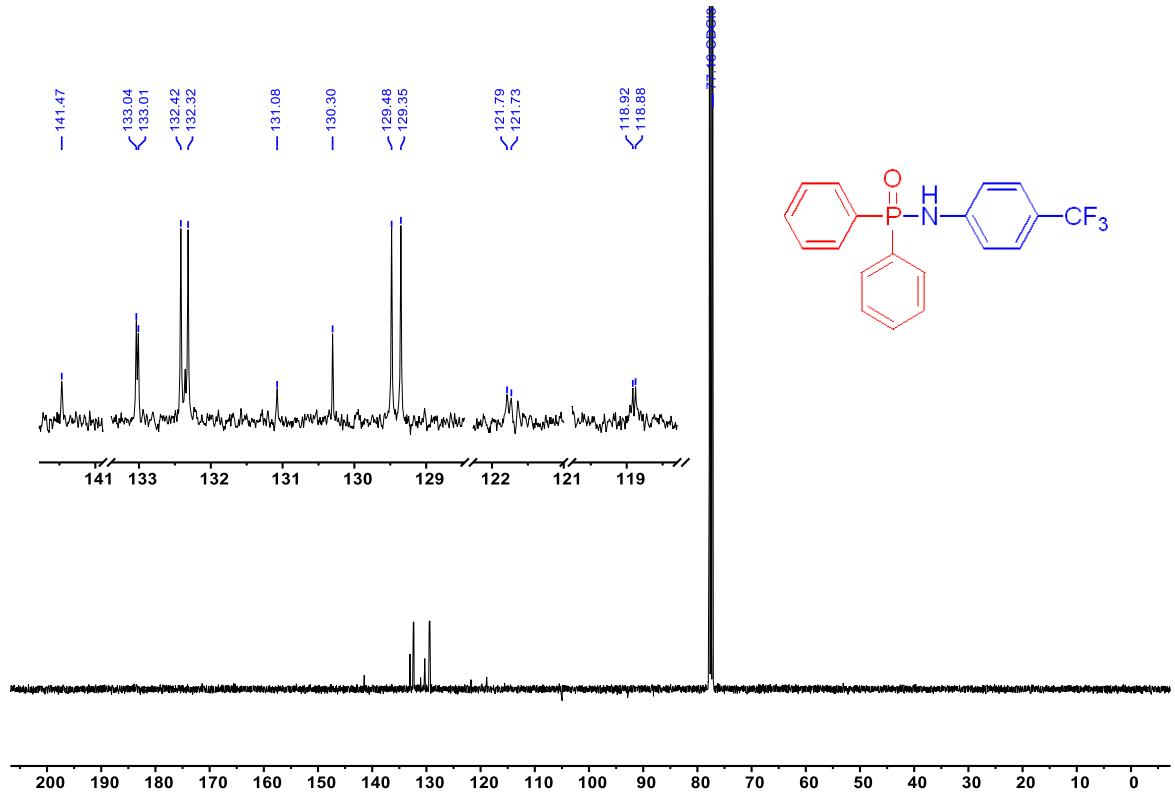


Figure S50: *P,P*-diphenyl-*N*-(4-(trifluoromethyl)phenyl)phosphinic amide (**6j**)

^{31}P NMR (162MHz, $CDCl_3$)

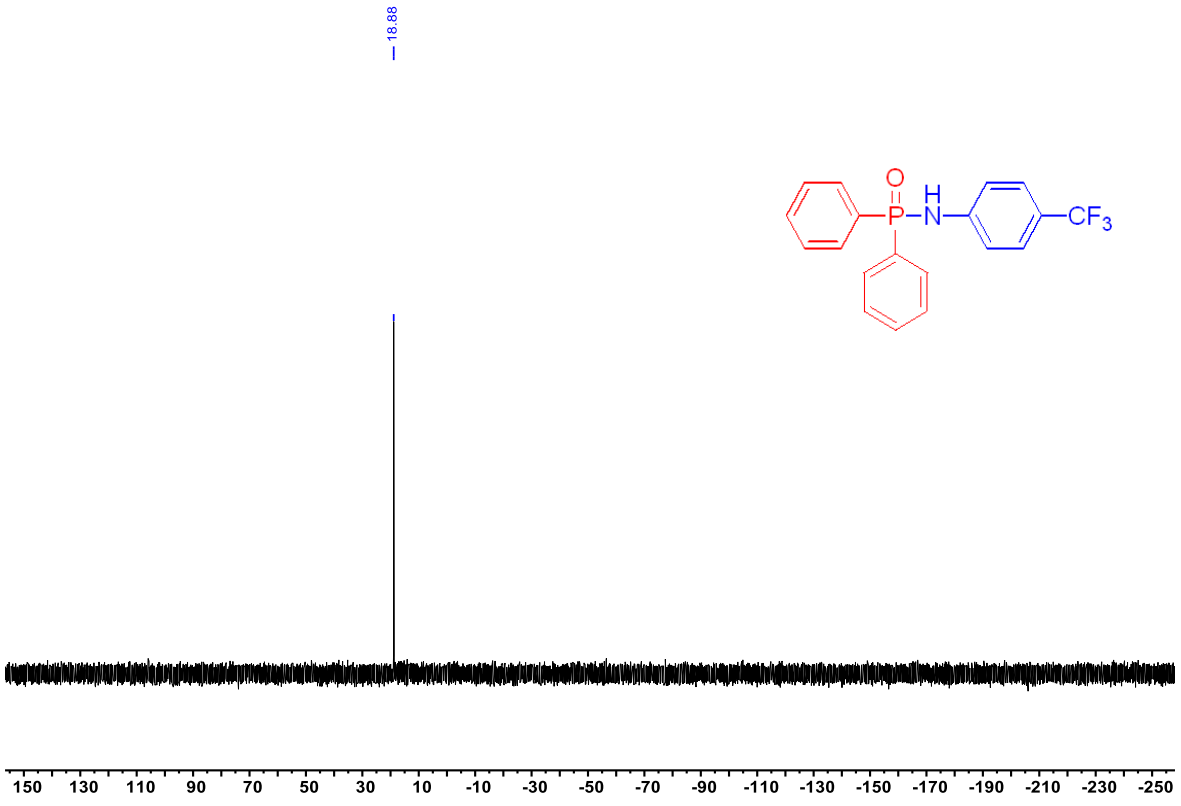


Figure S51: *N*-([1,1'-biphenyl]-2-yl)-*P*,*P*-diphenylphosphinic amide (**6k**)[8]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

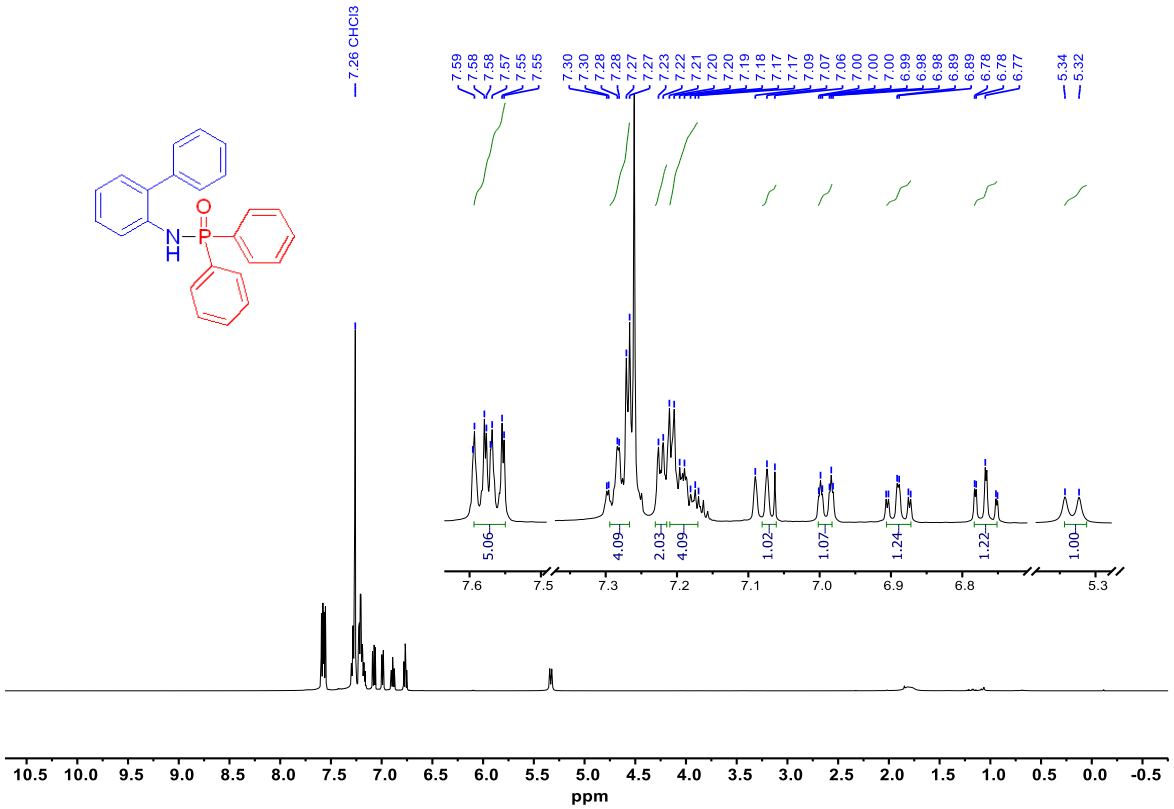


Figure S52: *N*-([1,1'-biphenyl]-2-yl)-*P*,*P*-diphenylphosphinic amide (**6k**)[8]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

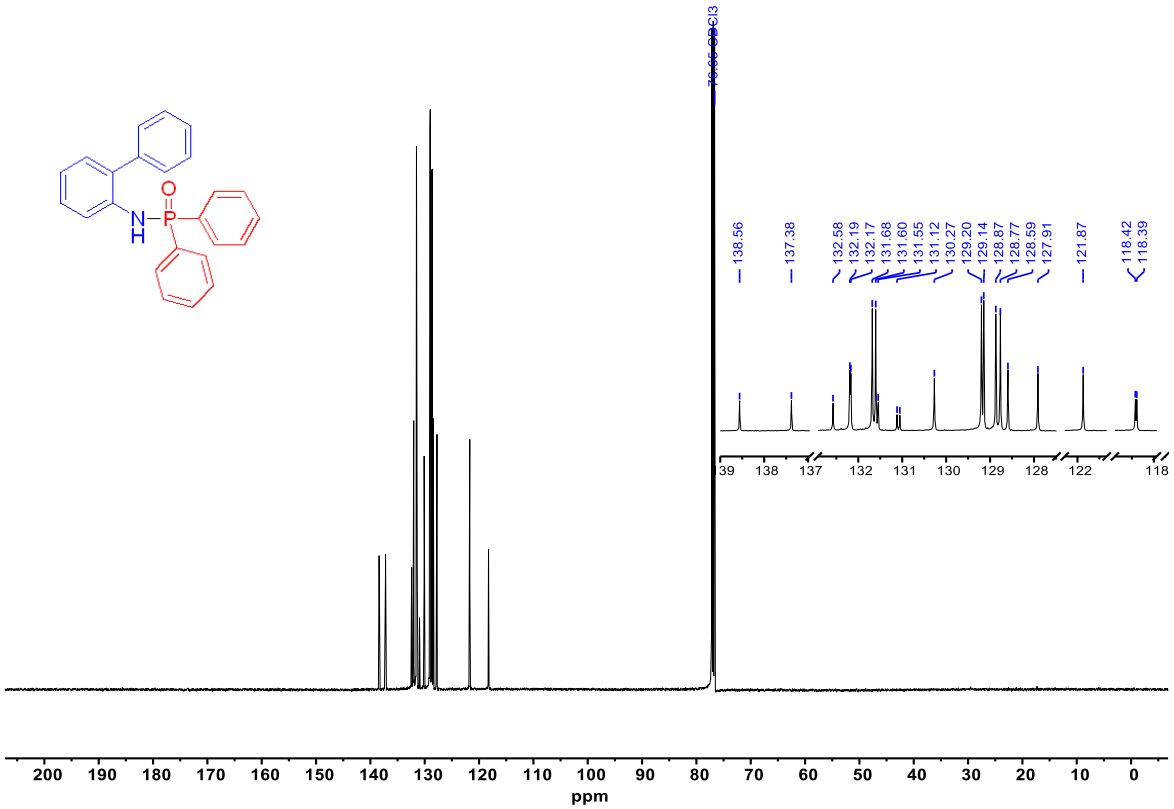


Figure S53: *N*-([1,1'-biphenyl]-2-yl)-*P*,*P*-diphenylphosphinic amide (**6k**)[8]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

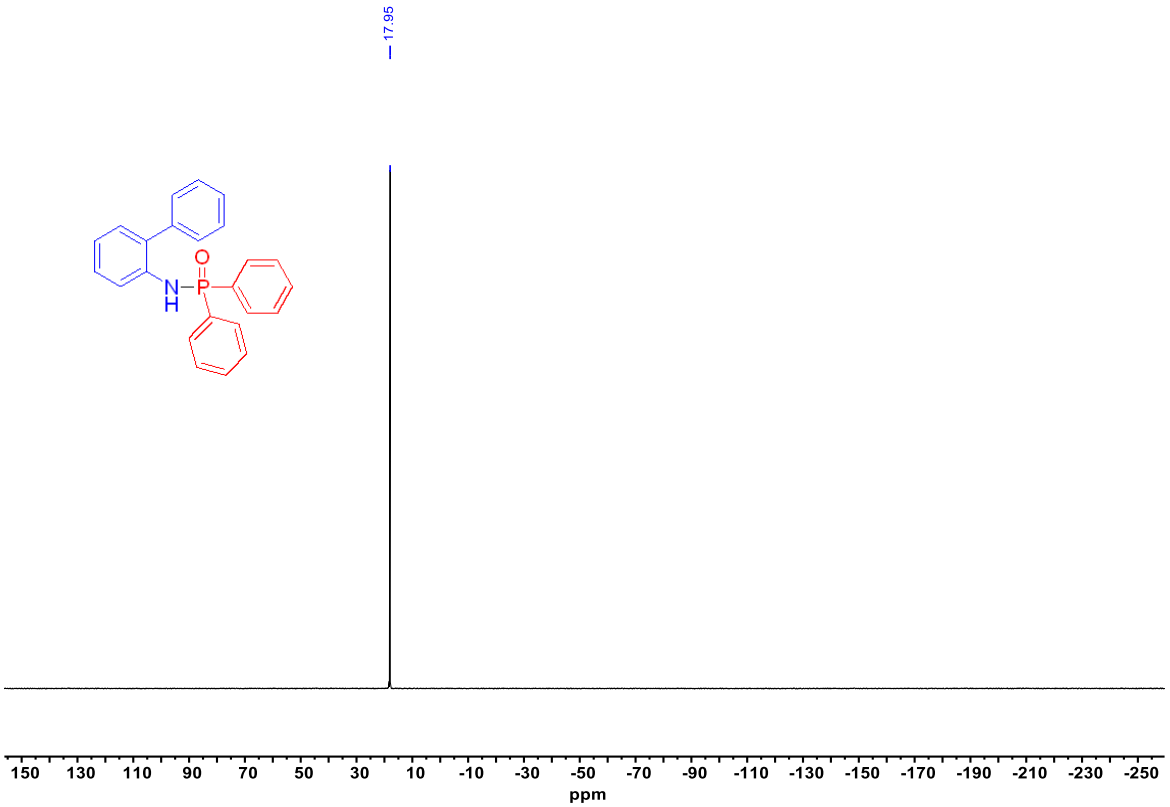


Figure S54: *P*,*P*-diphenyl-*N*-(o-tolyl)phosphinic amide (**6l**)[8]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

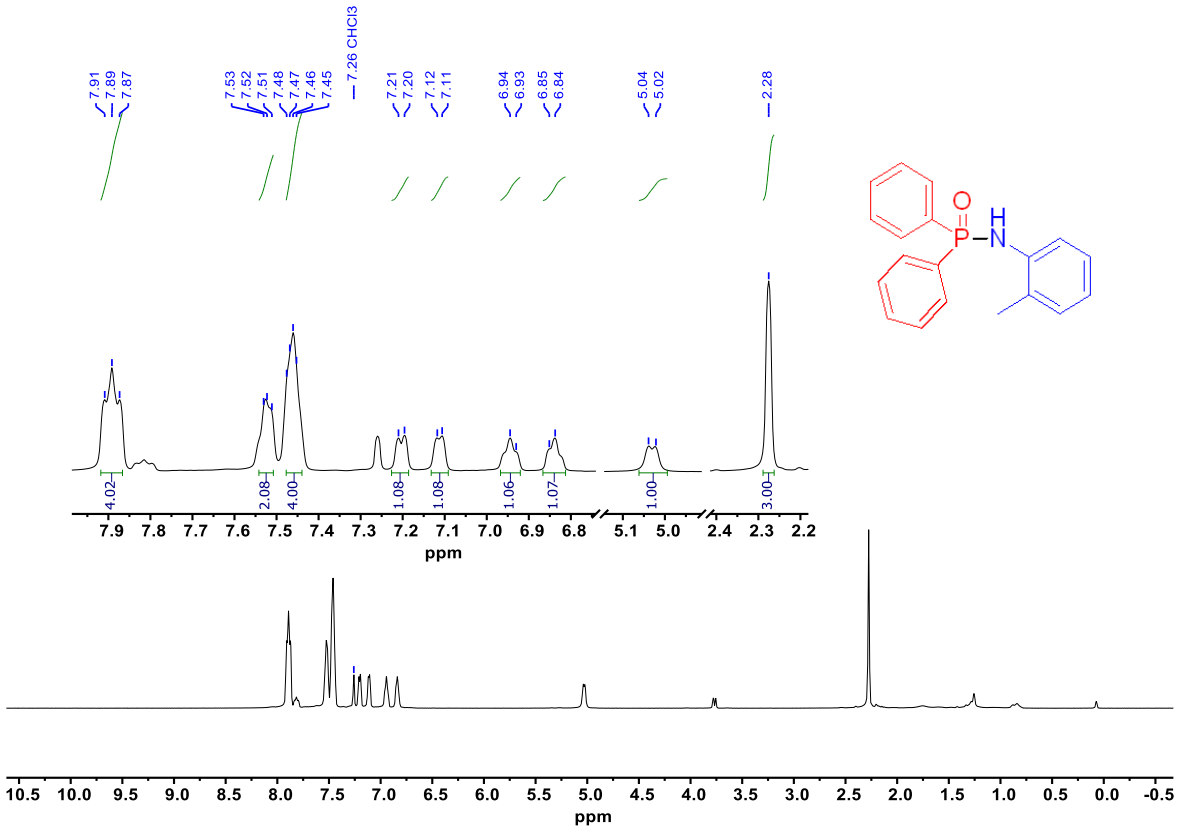


Figure S55: *P*,*P*-diphenyl-*N*-(o-tolyl)phosphinic amide (**6l**)[8]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

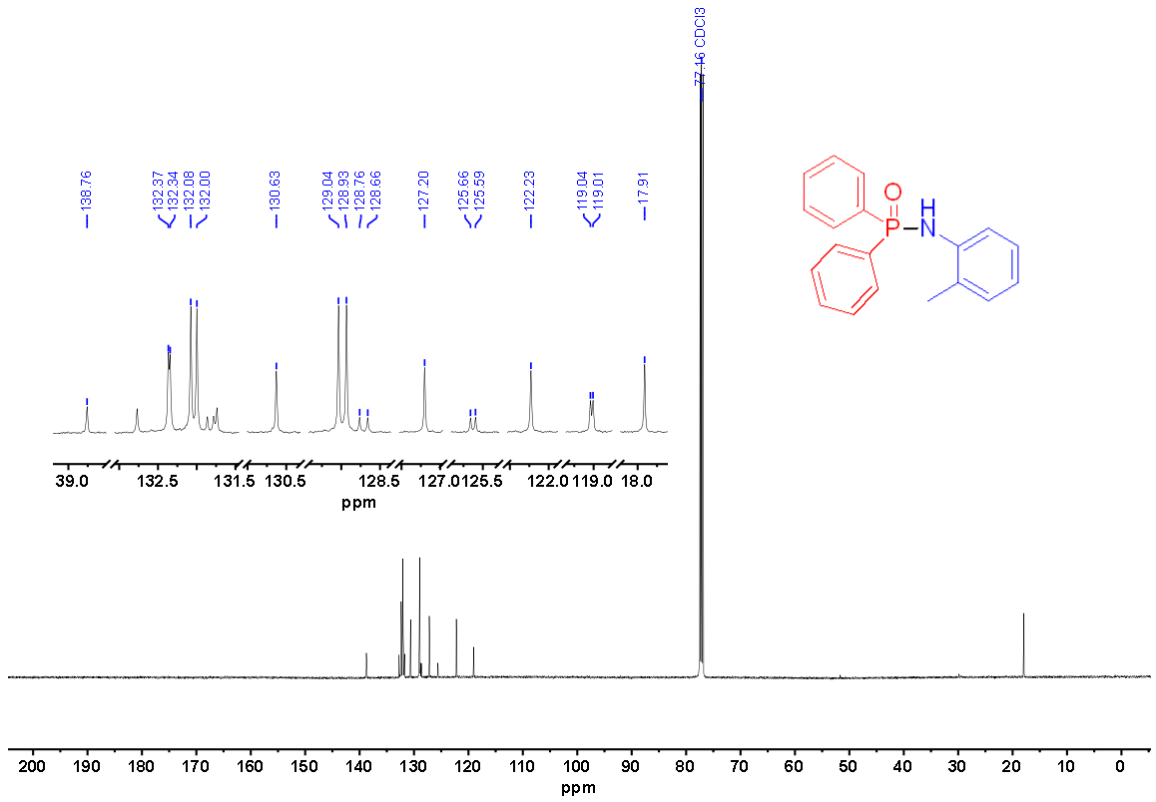


Figure S56: *P*,*P*-diphenyl-*N*-(o-tolyl)phosphinic amide (**6l**)[8]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

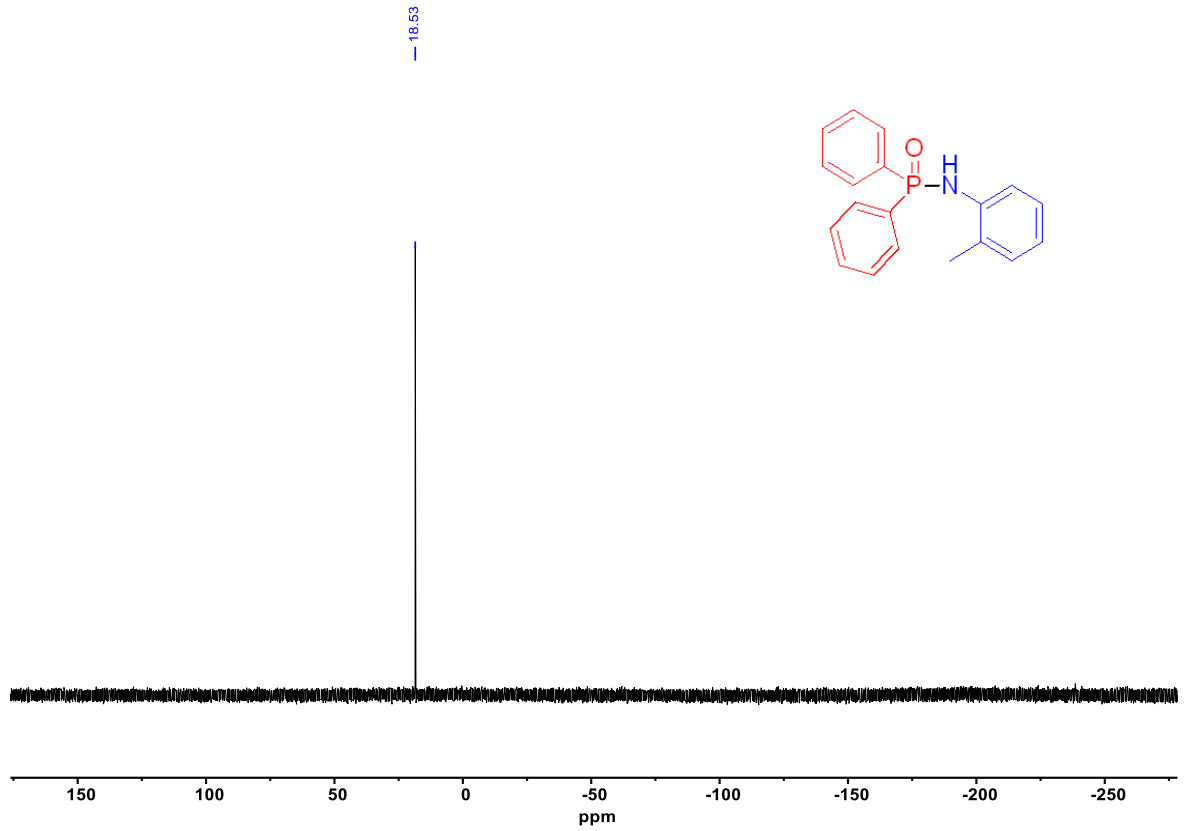


Figure S57: *N*-(2,4-dimethylphenyl)-*P*,*P*-diphenylphosphinic amide (**6m**)[2]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

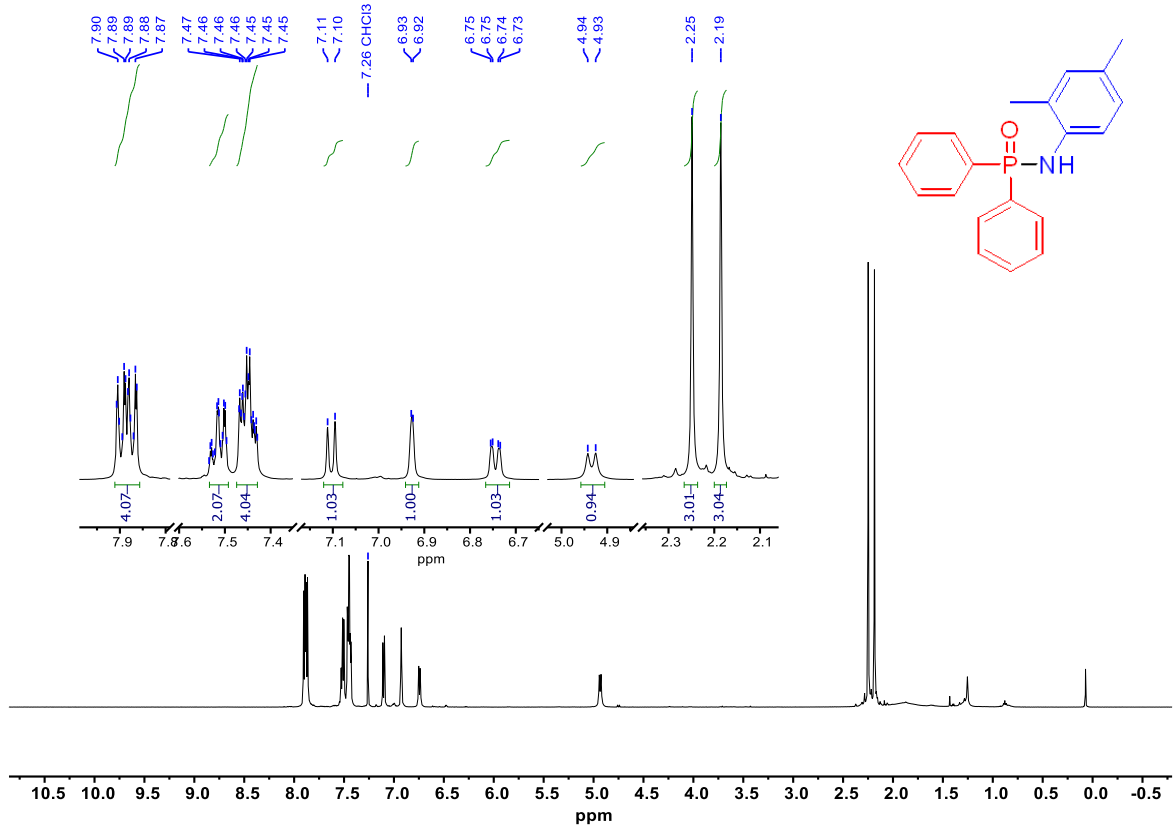


Figure S58: *N*-(2,4-dimethylphenyl)-*P*,*P*-diphenylphosphinic amide (**6m**) [2]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

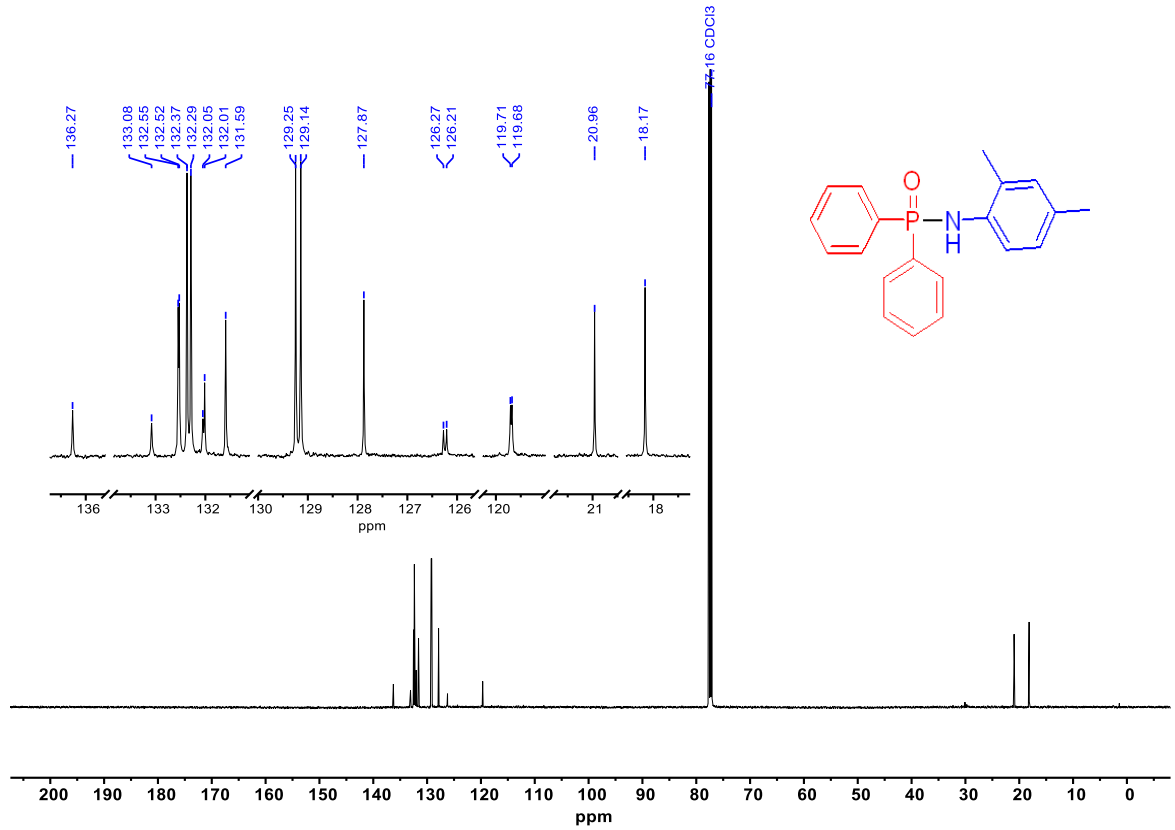


Figure S59: *N*-(2,4-dimethylphenyl)-*P*,*P*-diphenylphosphinic amide (**6m**)[2]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

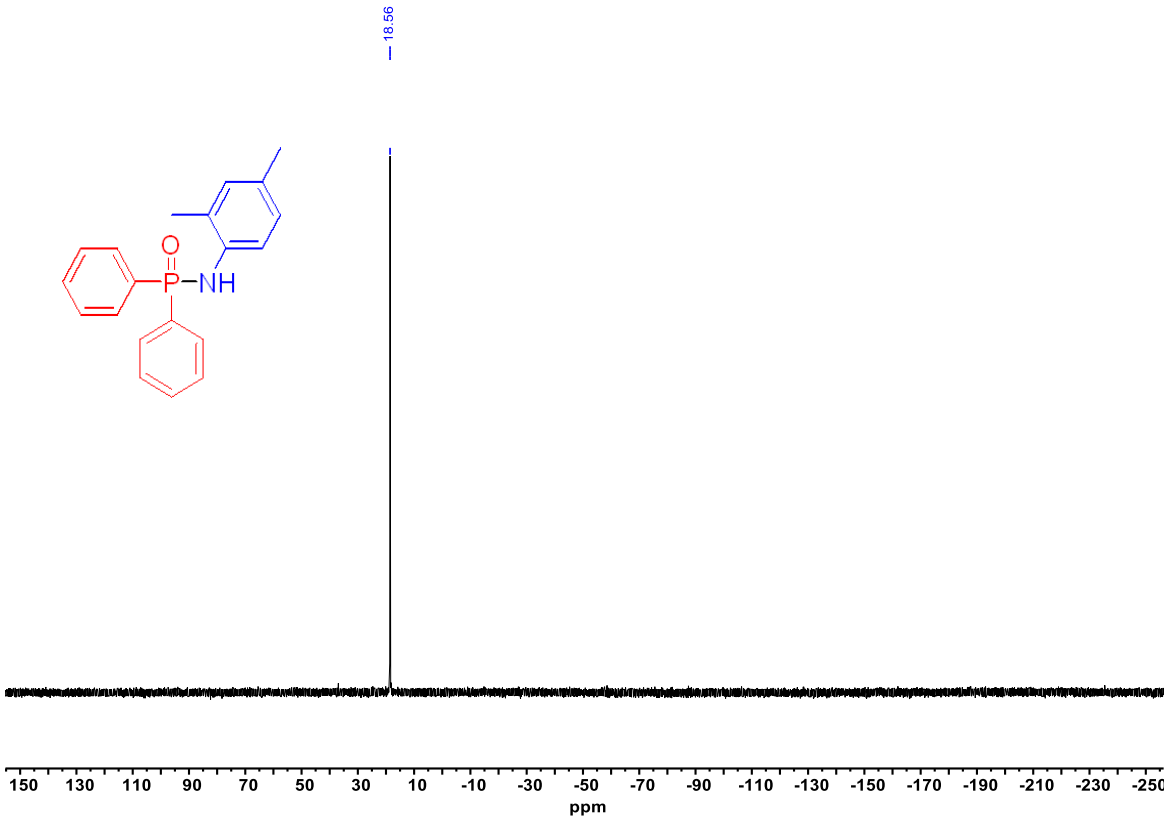


Figure S60: *N*-(3-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6n**)[9]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

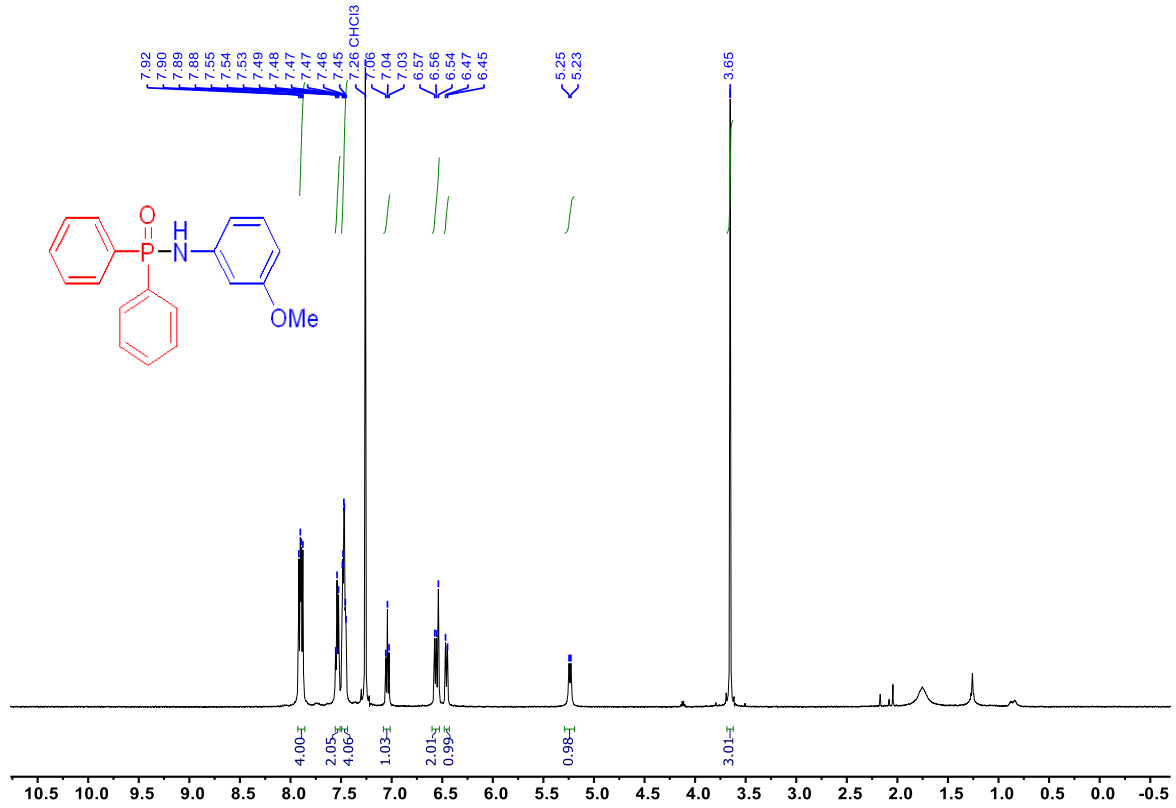


Figure S61: *N*-(3-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6n**)[9]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

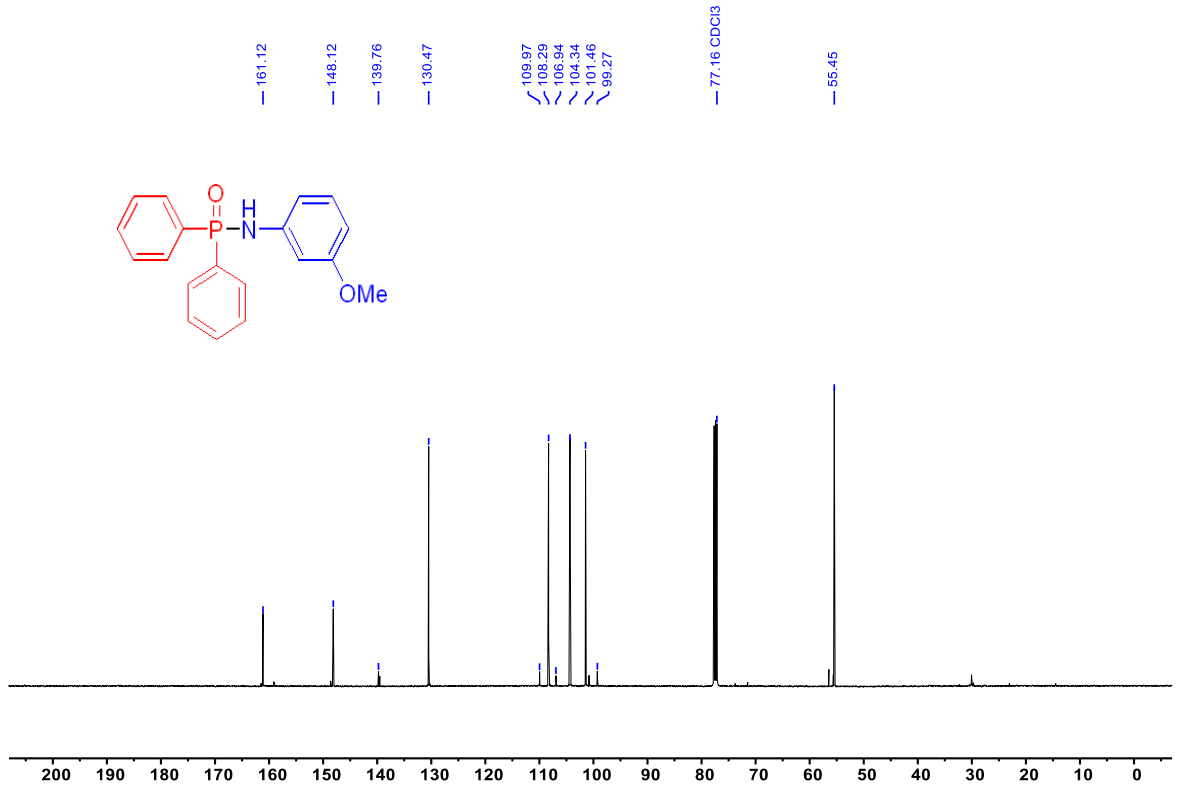


Figure S62: *N*-(3-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (**6n**)[9]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

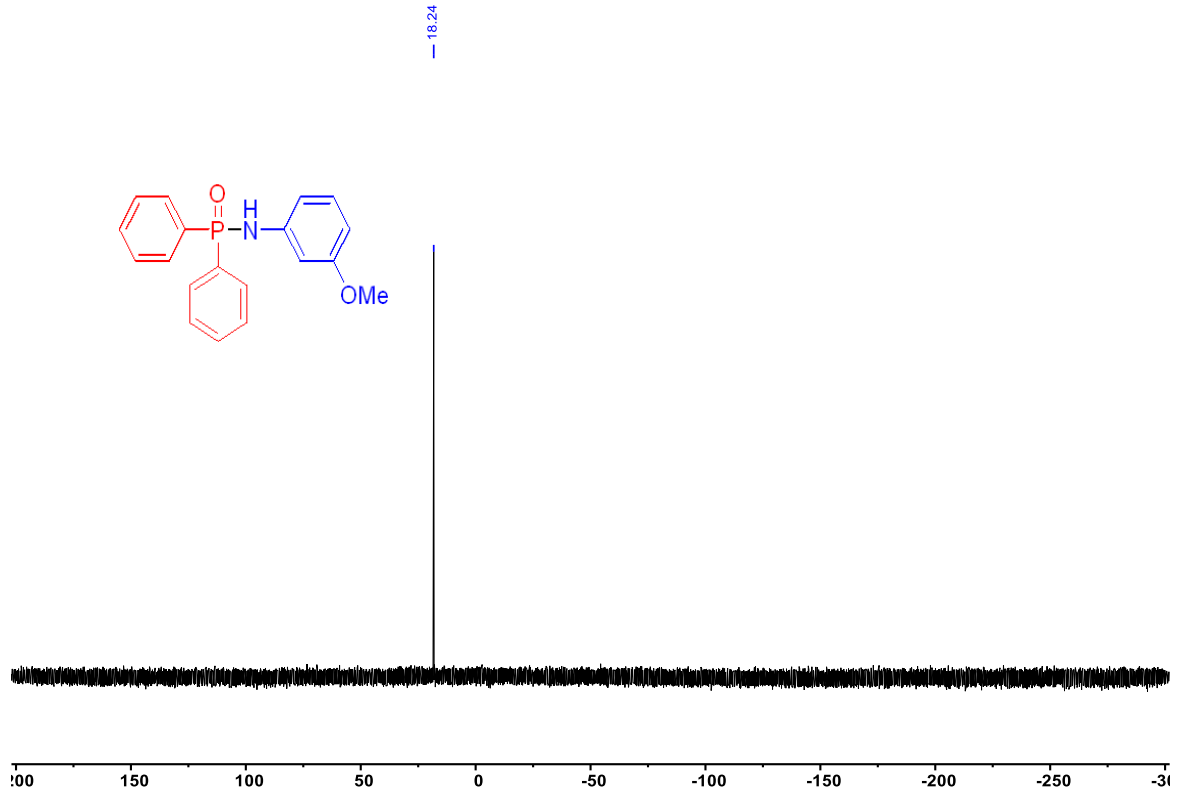


Figure S63: *N*-(2,6-diethylphenyl)-*P*,*P*-diphenylphosphinic amide (**6o**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

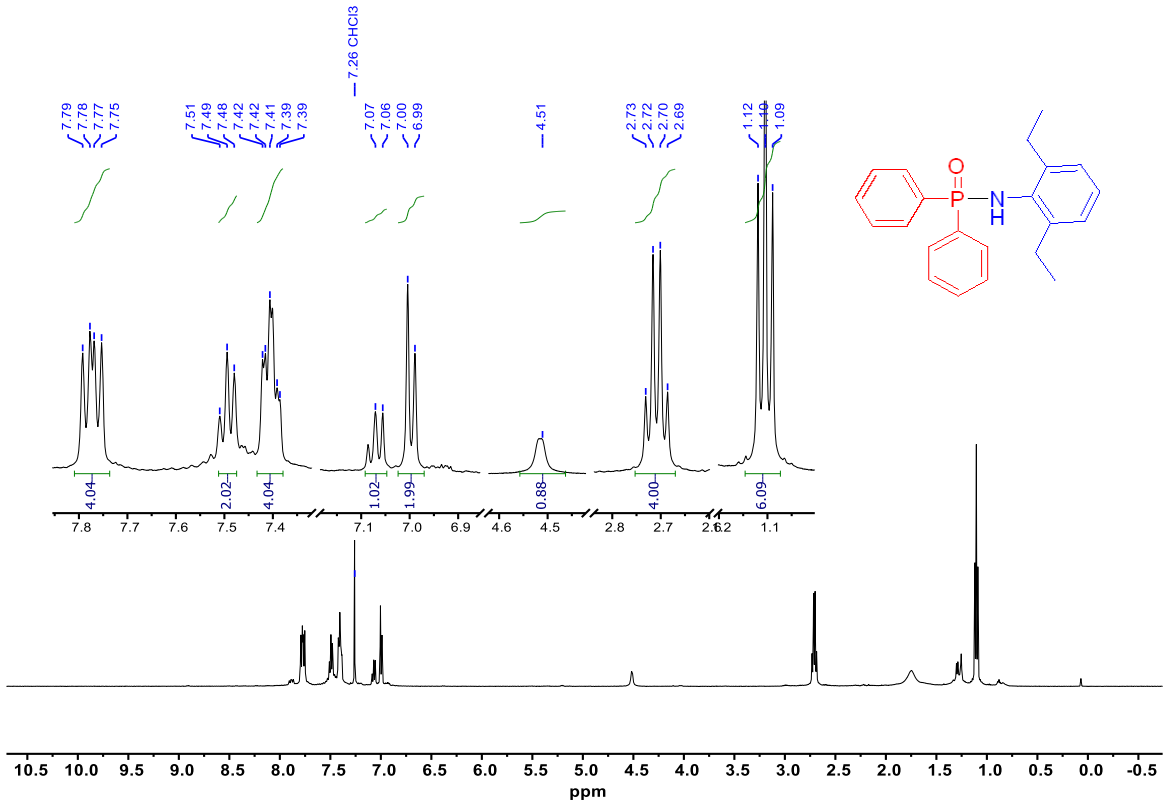


Figure S64: *N*-(2,6-diethylphenyl)-*P*,*P*-diphenylphosphinic amide (**6o**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

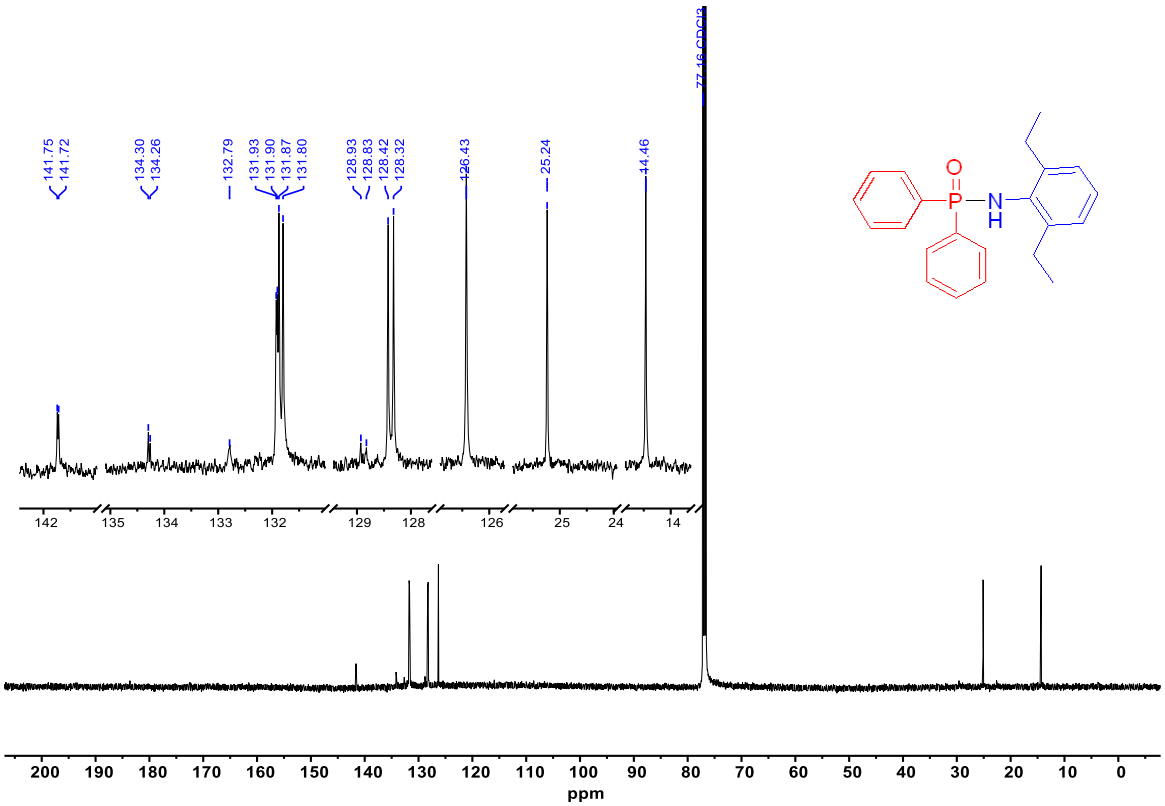


Figure S65: *N*-(2,6-diethylphenyl)-*P*,*P*-diphenylphosphinic amide (**6o**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

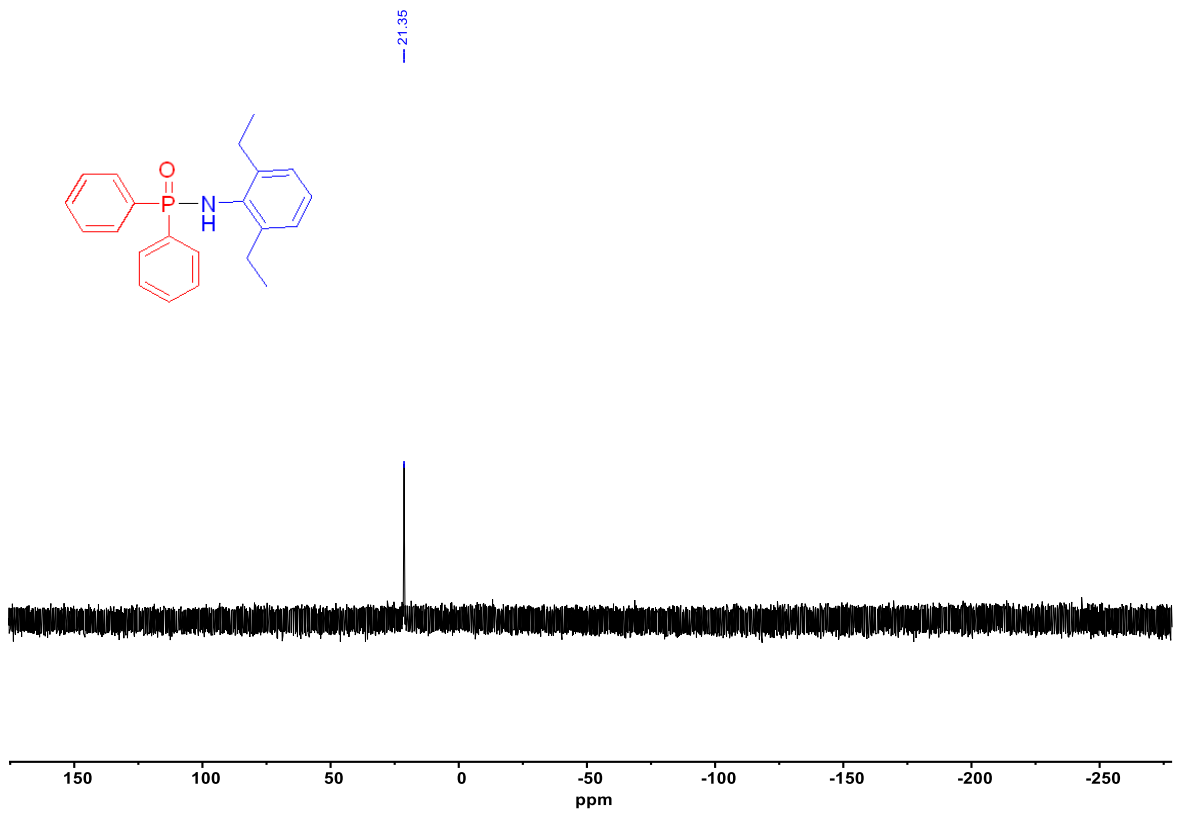


Figure S66: *N*-(2,3-dihydro-1H-inden-4-yl)-*P*,*P* diphenylphosphinic amide (**6p**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

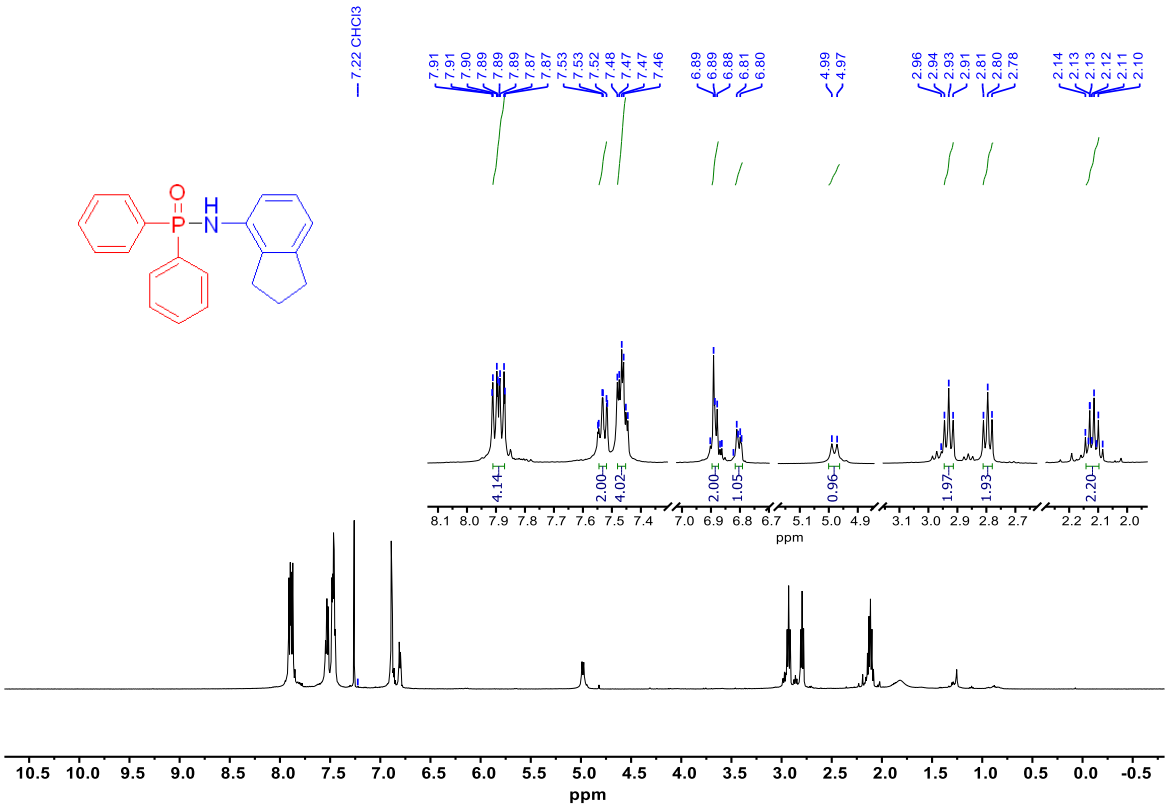


Figure S67: *N*-(2,3-dihydro-1H-inden-4-yl)-*P*,*P* diphenylphosphinic amide (**6p**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

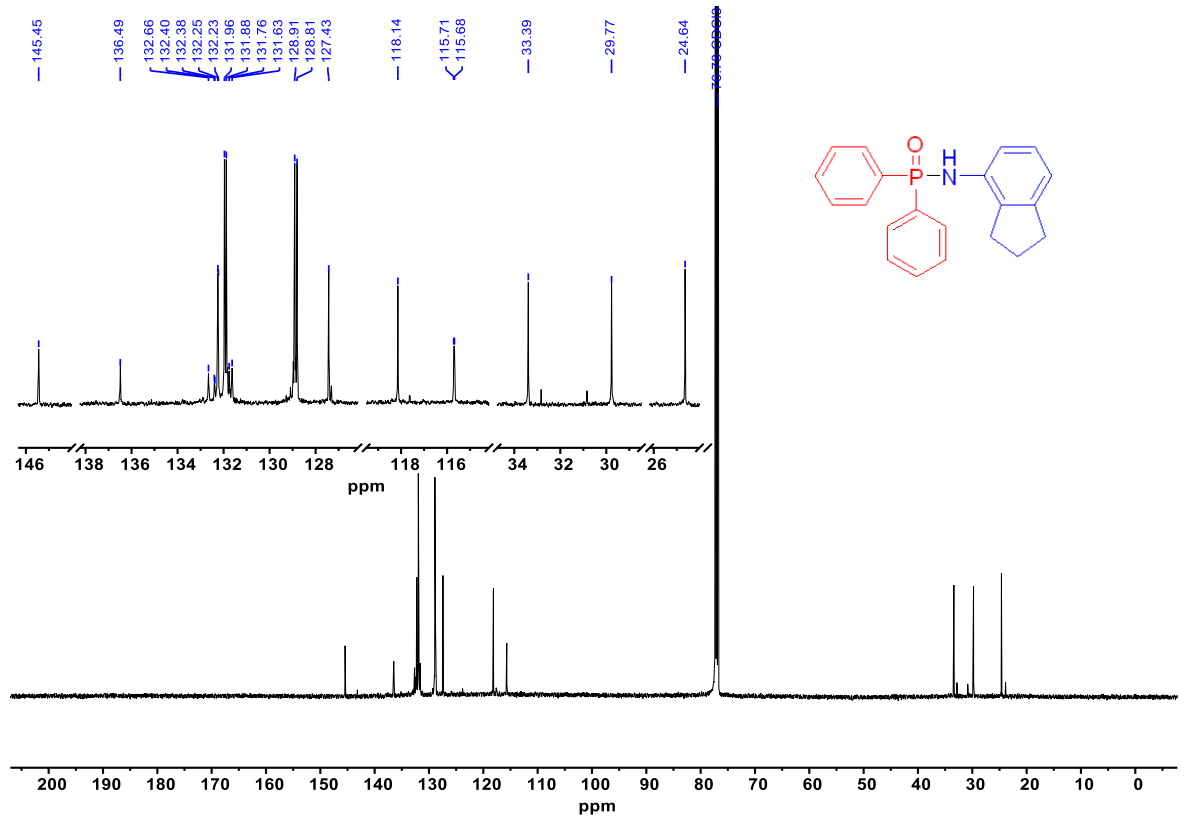


Figure S68: *N*-(2,3-dihydro-1H-inden-4-yl)-*P*,*P* diphenylphosphinic amide (**6p**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

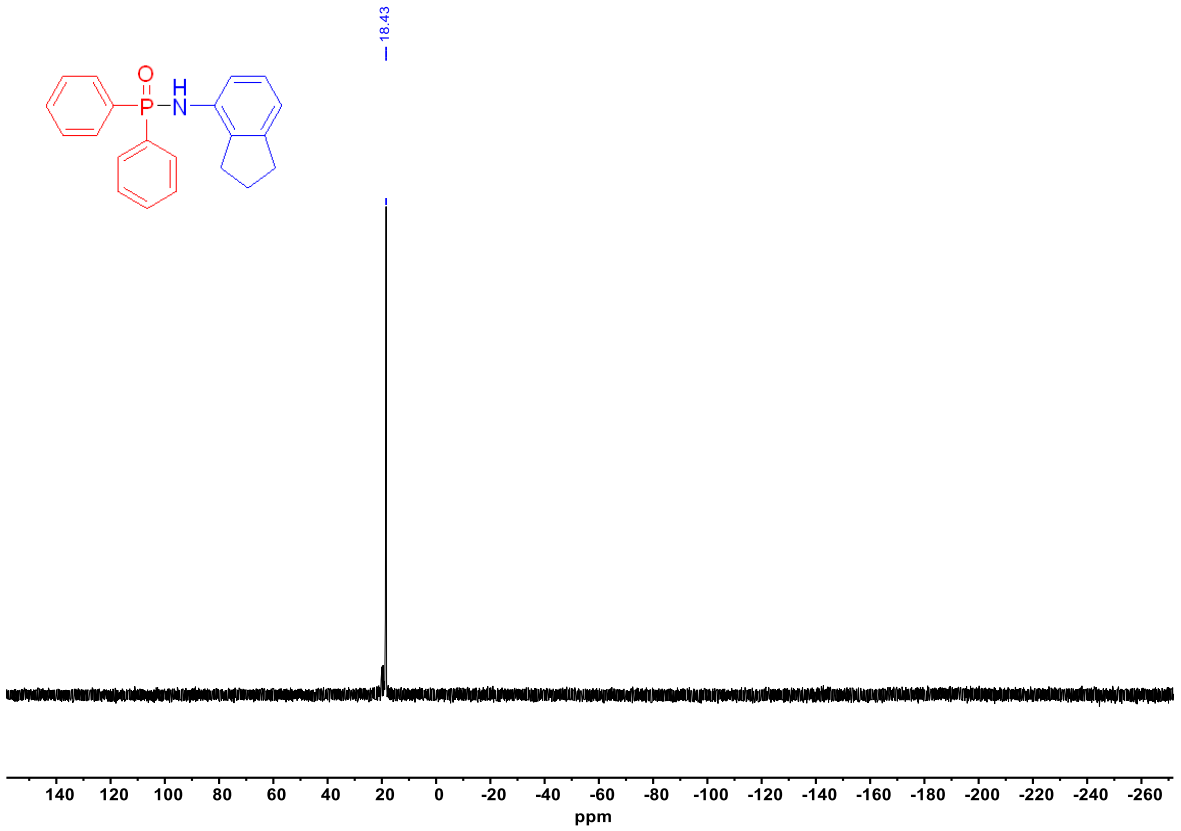


Figure S69: *P*,*P*-diphenyl-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl)phosphinic amide (**6q**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

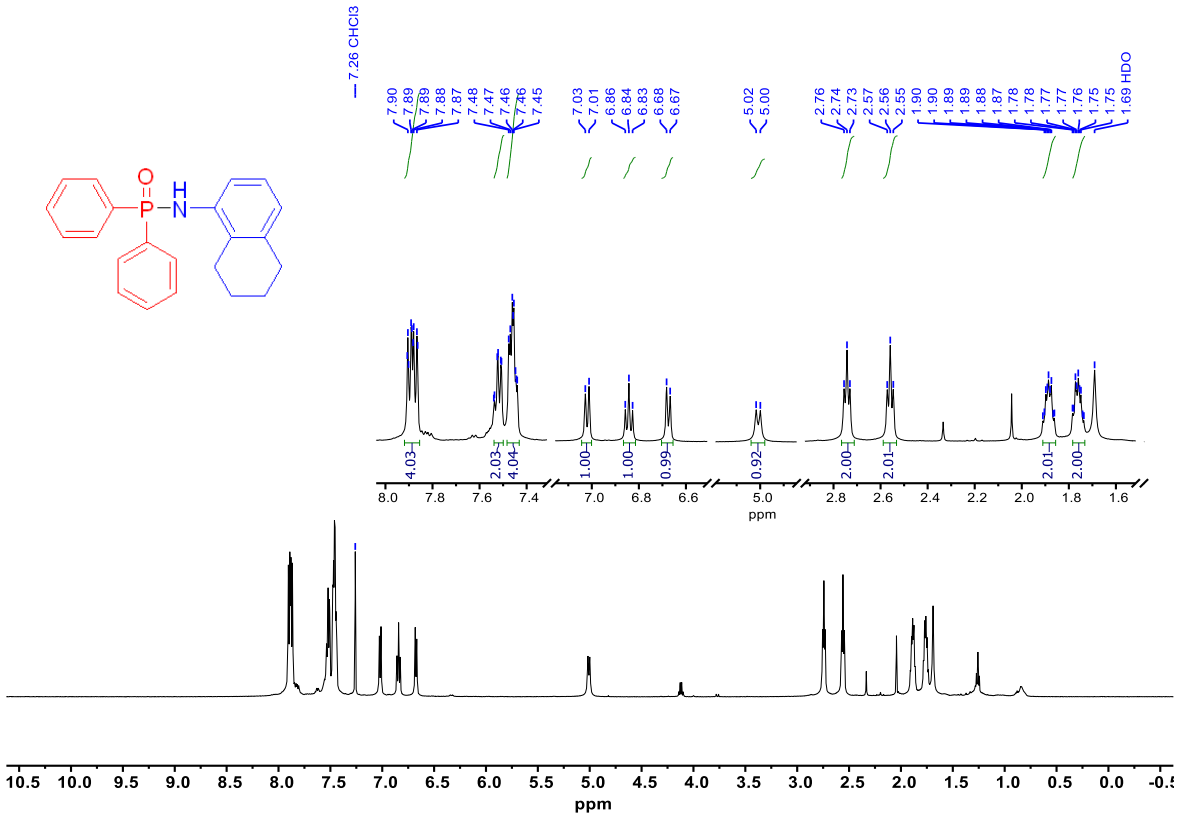


Figure S70: *P*,*P*-diphenyl-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl)phosphinic amide (**6q**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

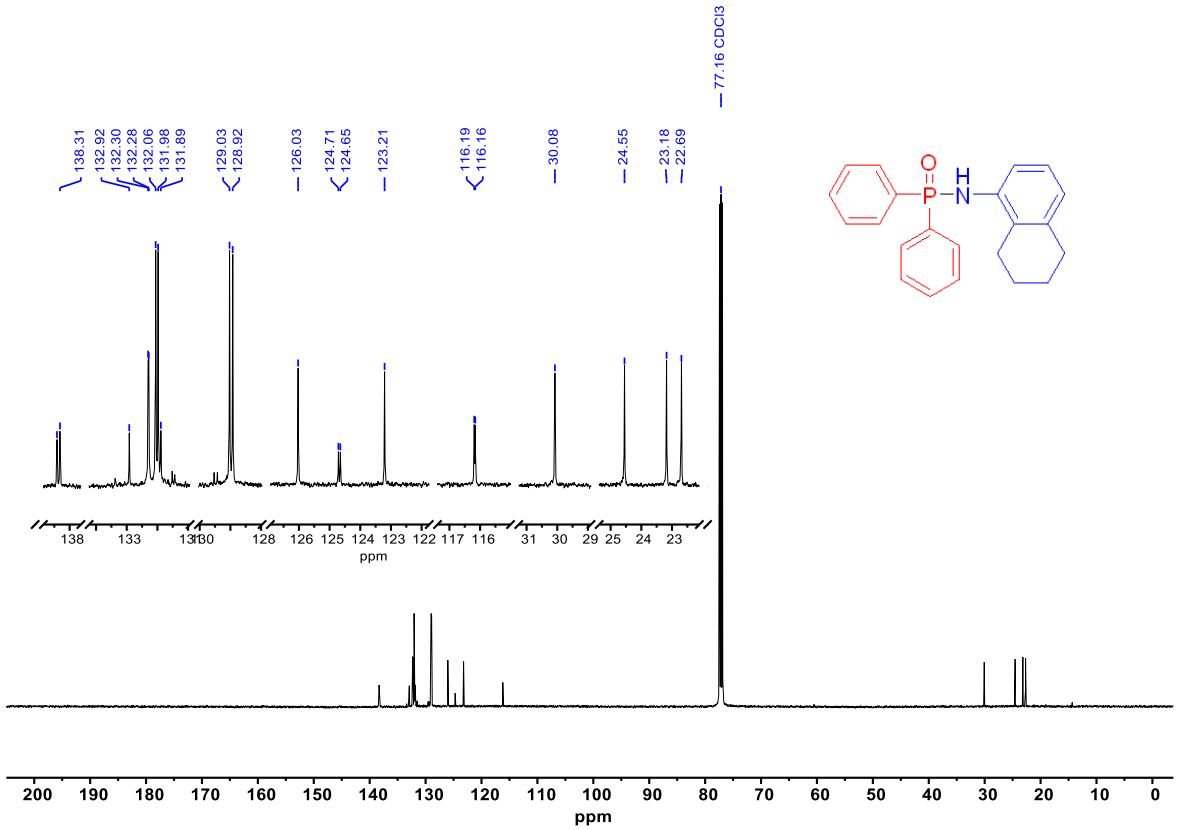


Figure S71: *P*,*P*-diphenyl-*N*-(5,6,7,8-tetrahydronaphthalen-1-yl)phosphinic amide (**6q**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

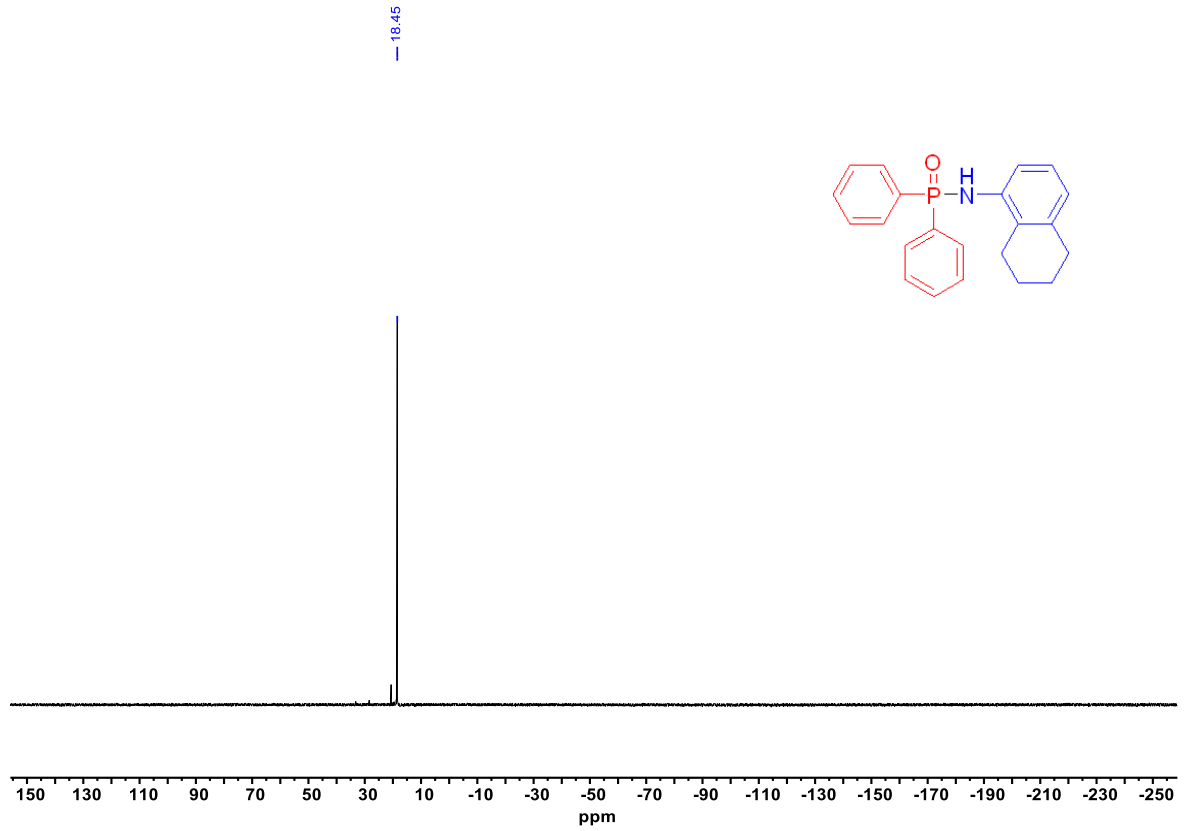


Figure S72: *N*,*N*-diethyl-*P*,*P*-diphenylphosphinic amide (**7a**) [10]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

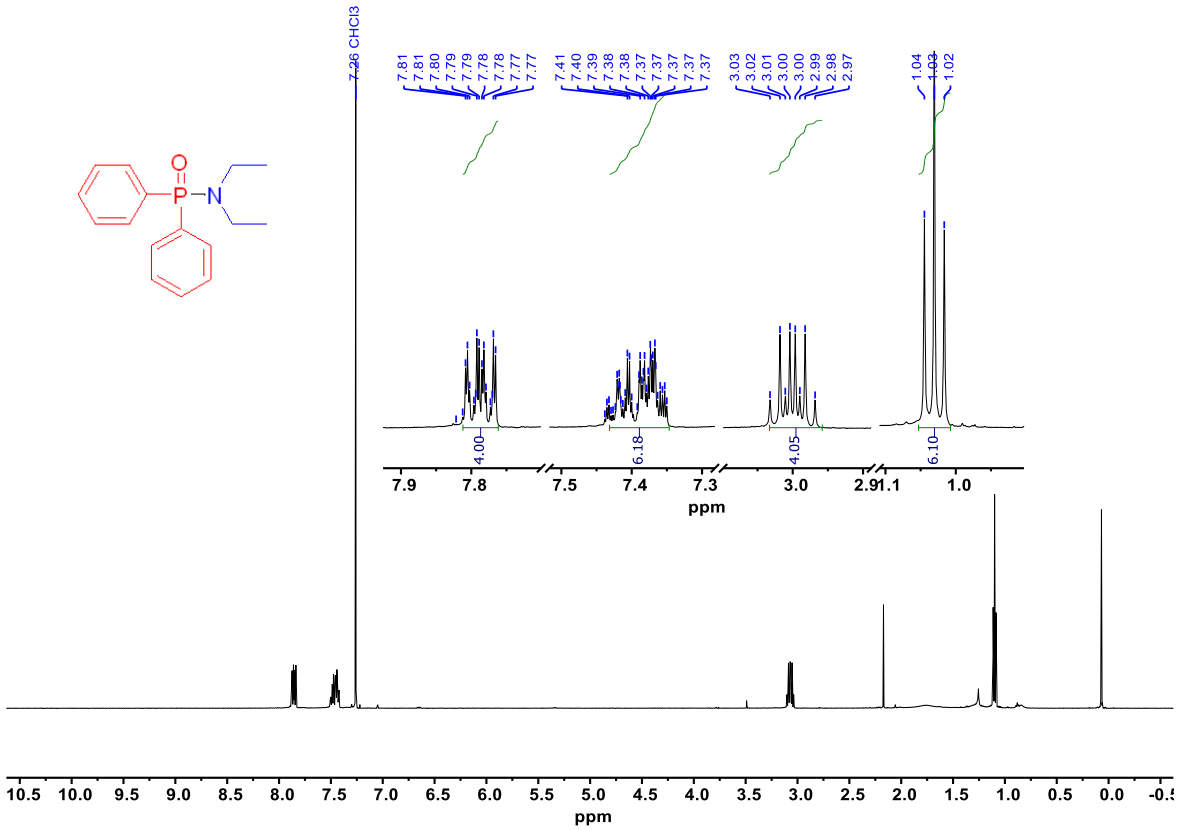


Figure S73: *N*,*N*-diethyl-*P*,*P*-diphenylphosphinic amide (**7a**)[10]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

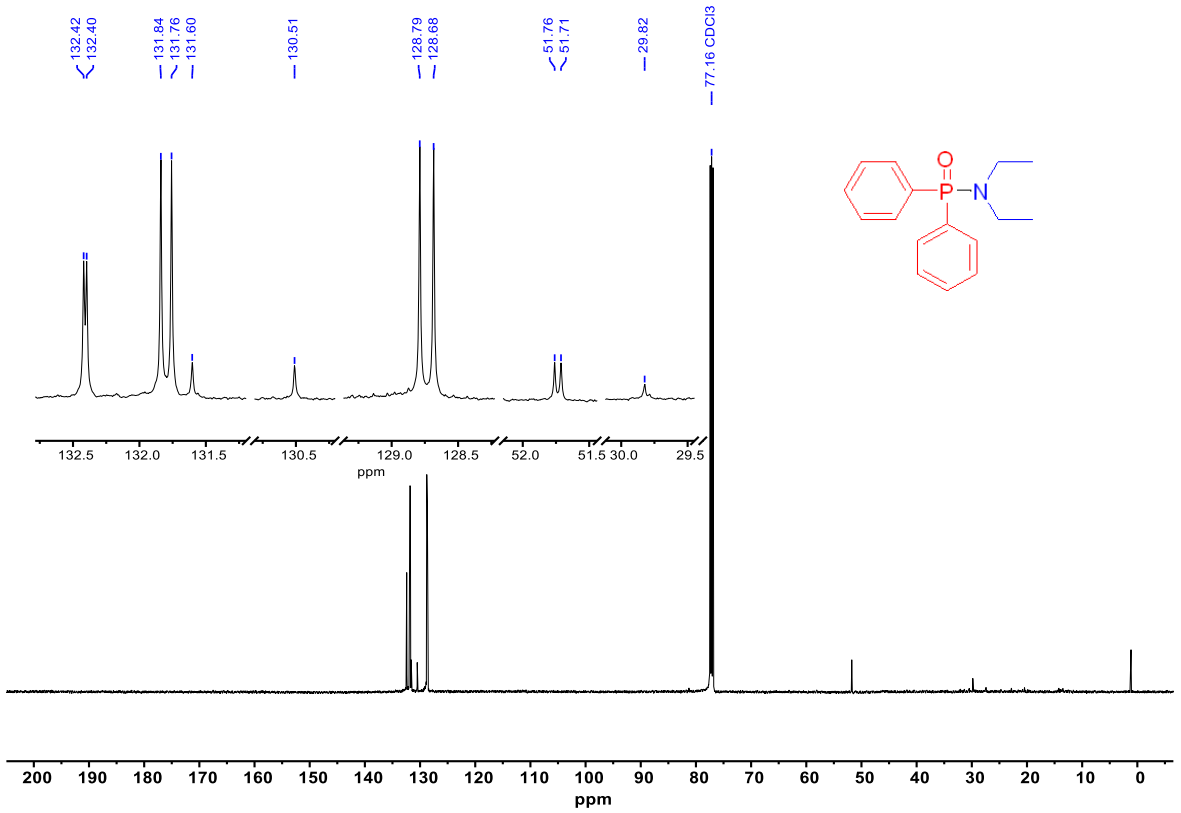


Figure S74: *N*,*N*-diethyl-*P*,*P*-diphenylphosphinic amide (**7a**)[10]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

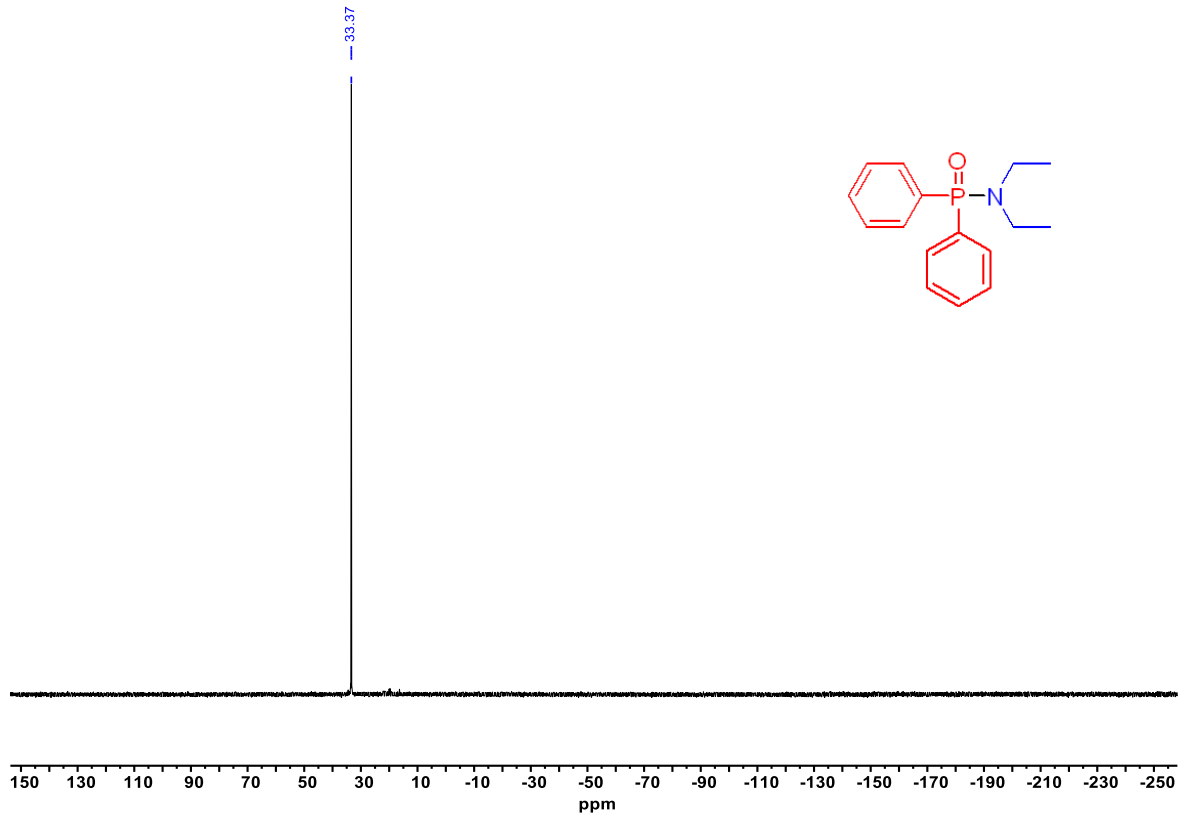


Figure S75: morpholinodiphenylphosphine oxide (**7b**)[10]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

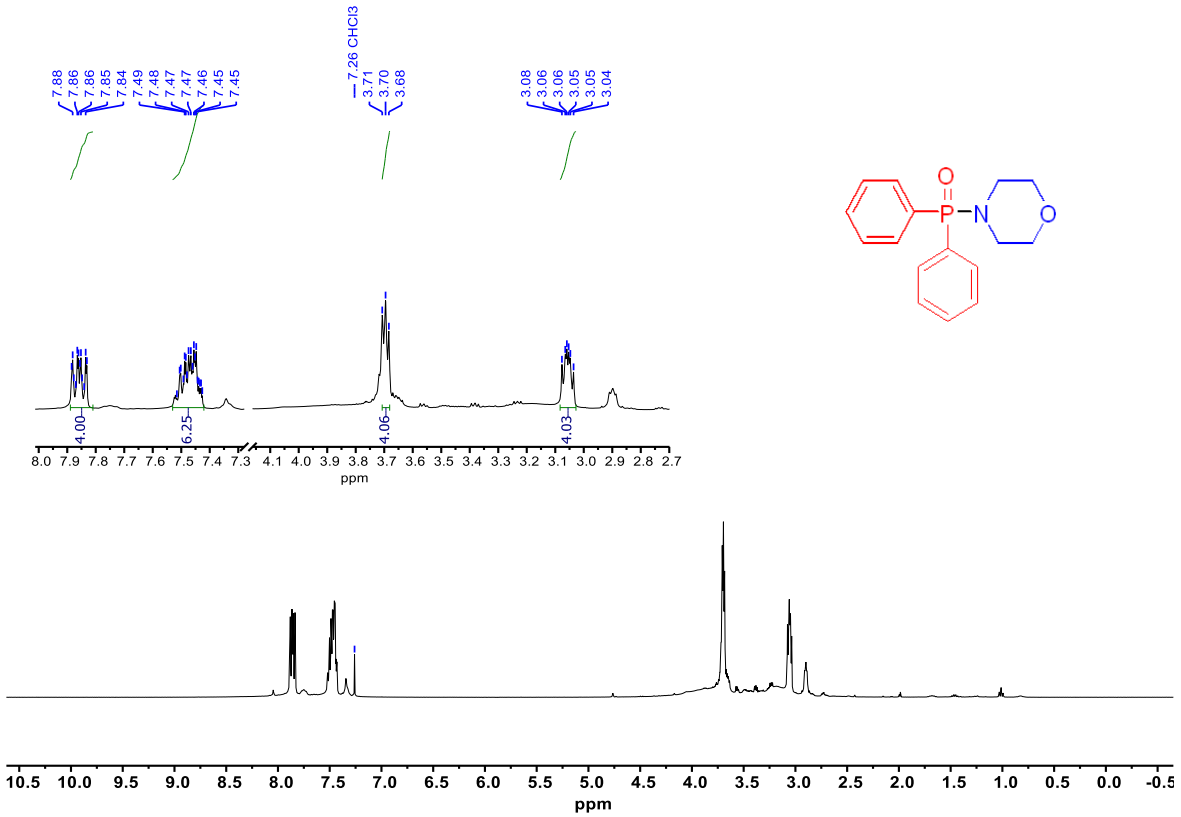


Figure S76: morpholinodiphenylphosphine oxide (**7b**)[10]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

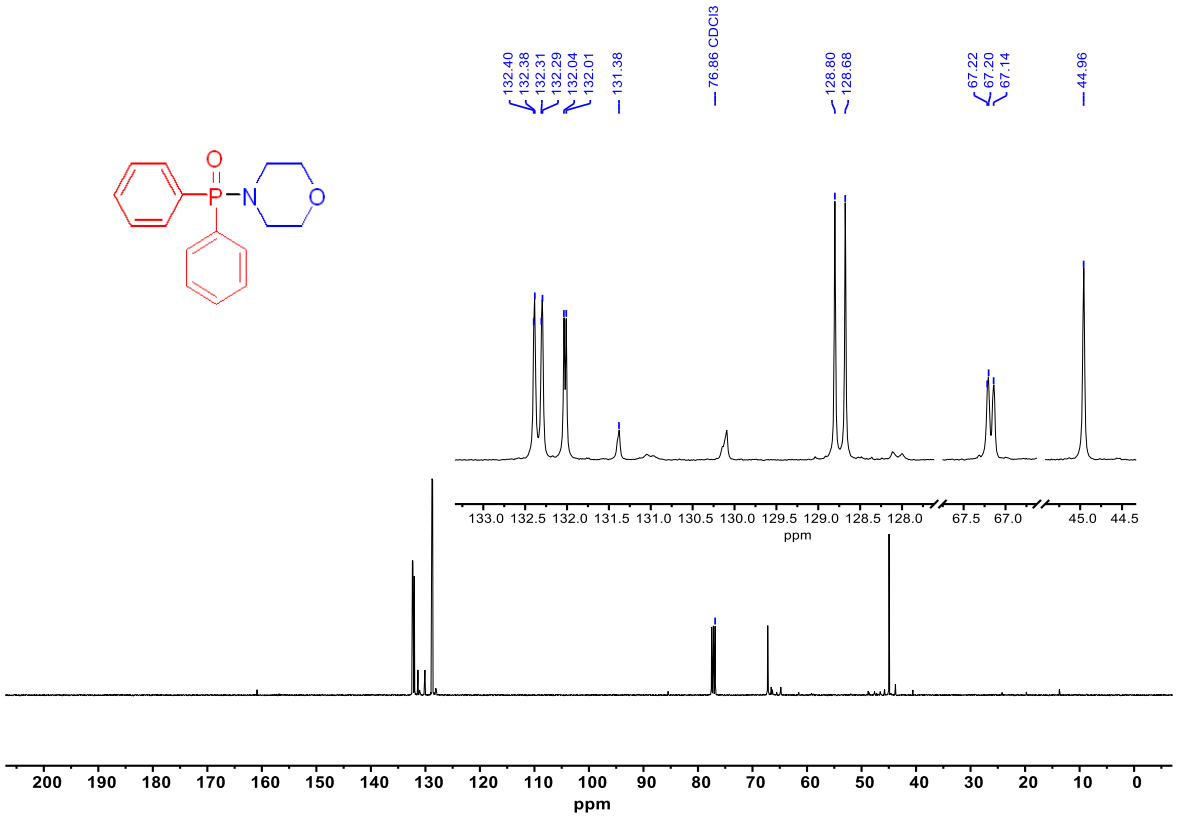


Figure S77: morpholinodiphenylphosphine oxide (**7b**)[10]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

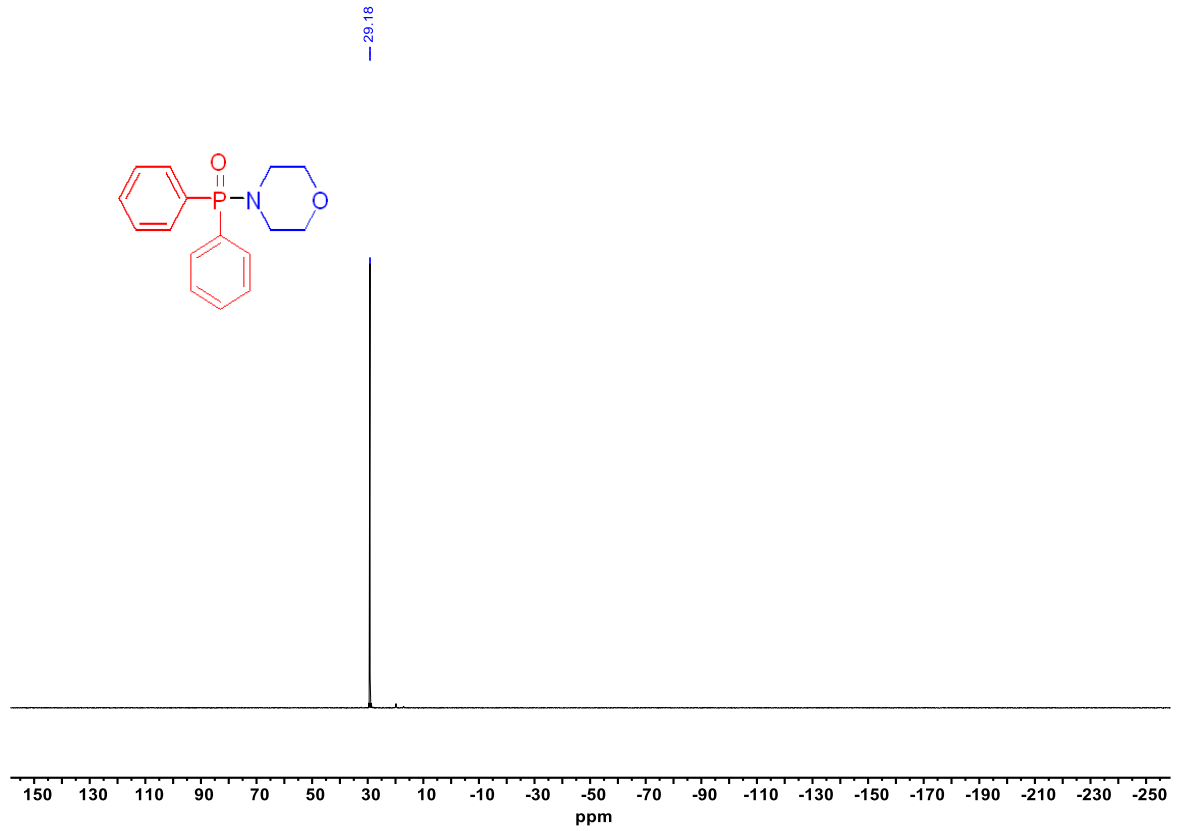


Figure S78: *N*,*N*-diallyl-*P*,*P*-diphenylphosphinic amide (**7c**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

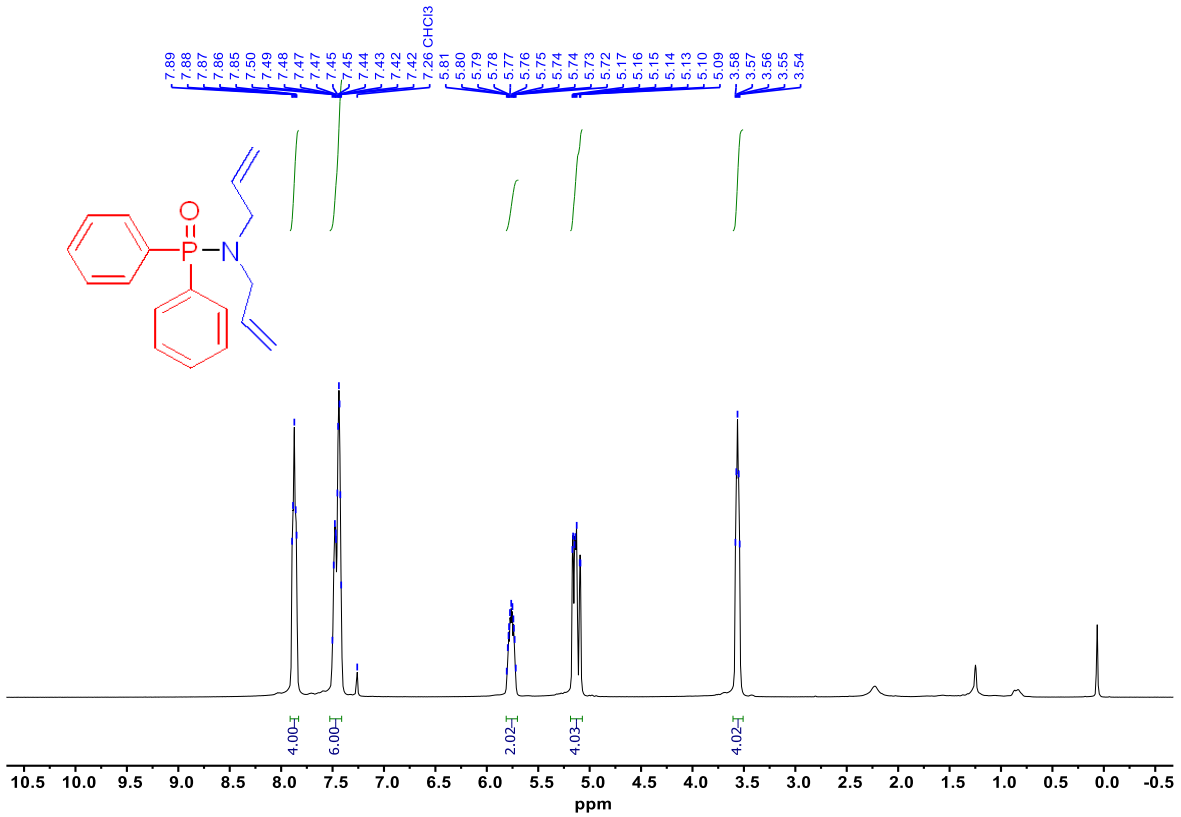


Figure S79: *N*,*N*-diallyl-*P*,*P*-diphenylphosphinic amide (**7c**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

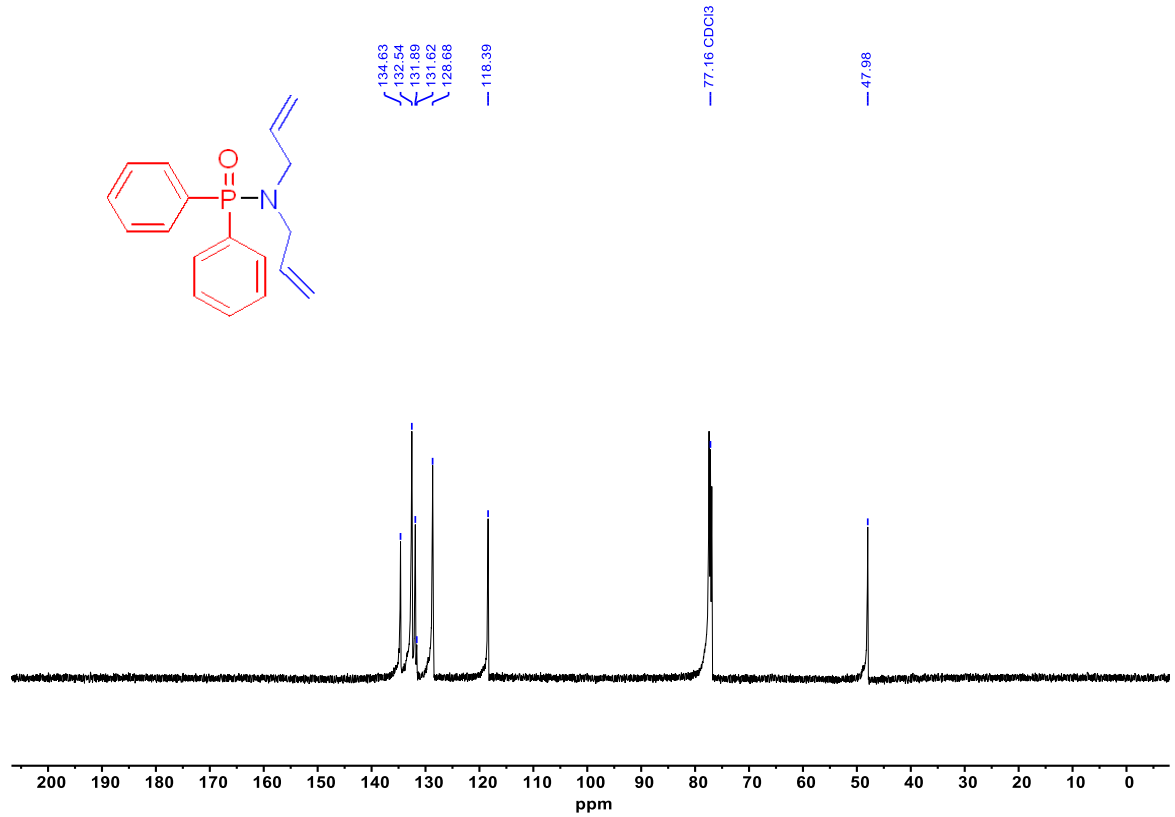


Figure S80: *N*,*N*-diallyl-*P*,*P*-diphenylphosphinic amide (**7c**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

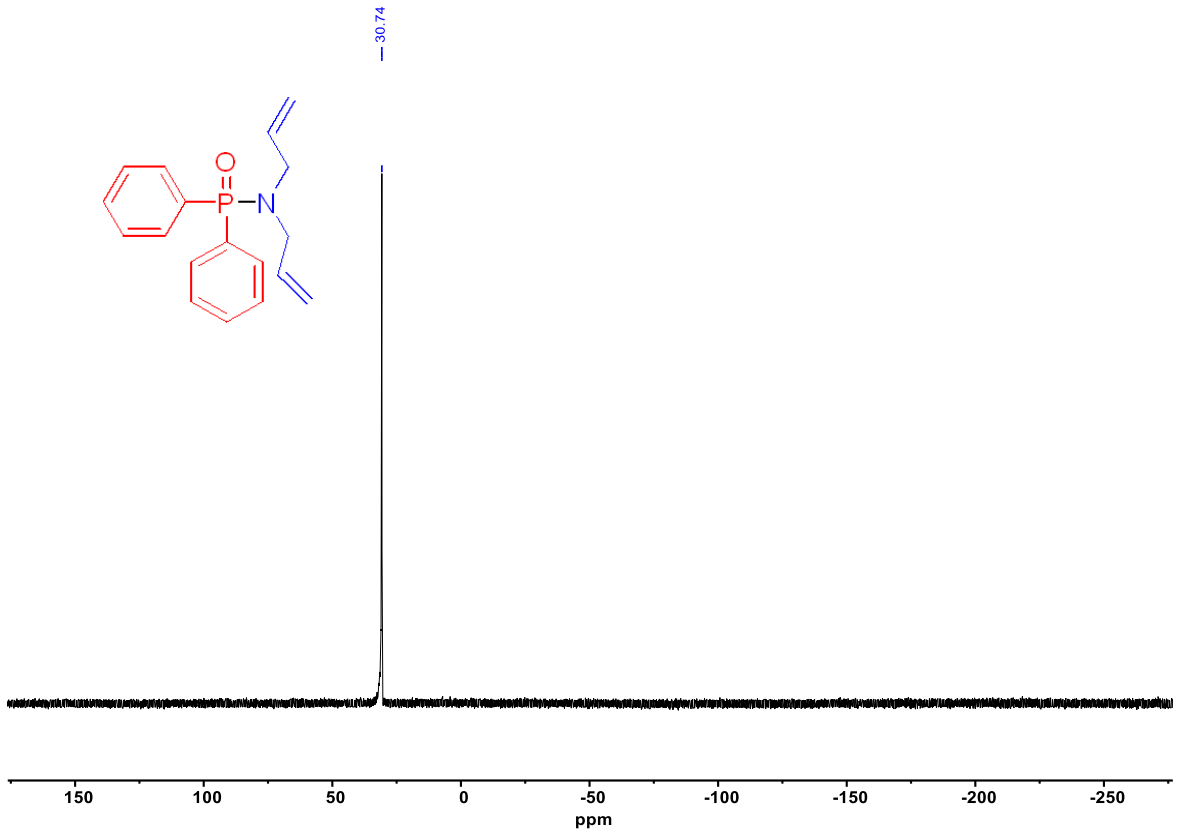


Figure S81: *P*,*P*-diphenyl-*N*-(pyridin-2-ylmethyl)phosphinic amide (**7d**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

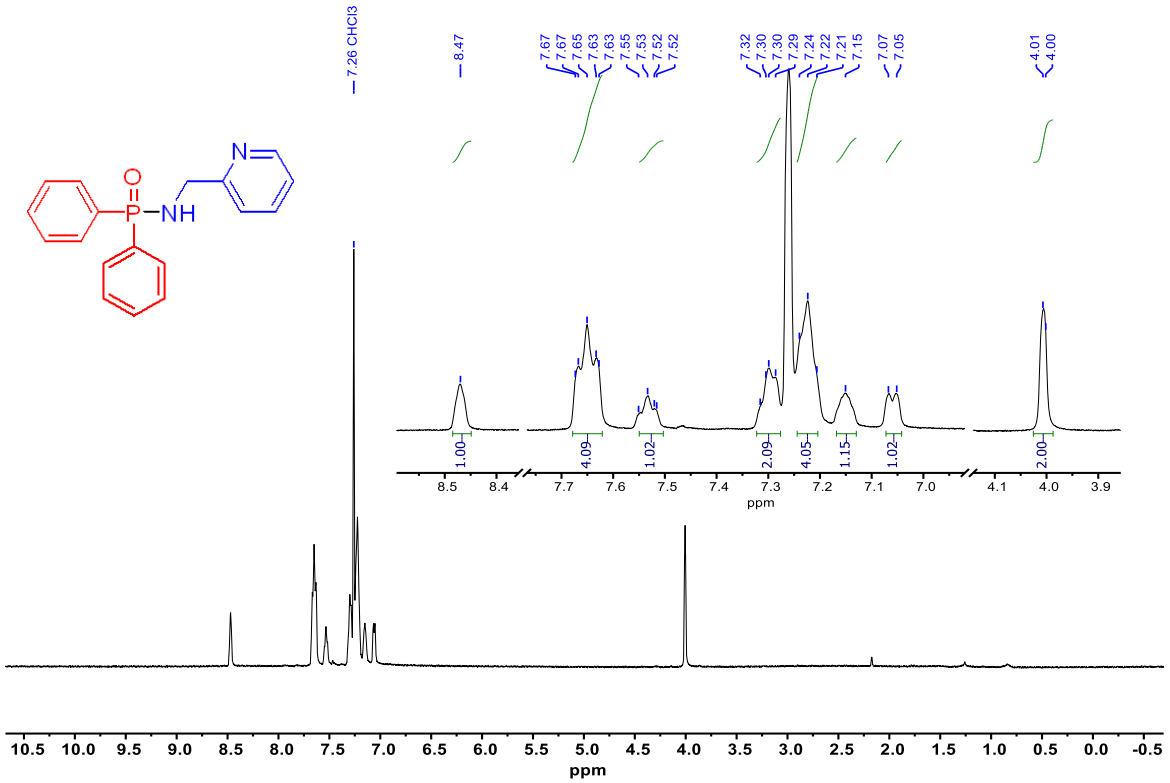


Figure S82: *P*,*P*-diphenyl-*N*-(pyridin-2-ylmethyl)phosphinic amide (**7d**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

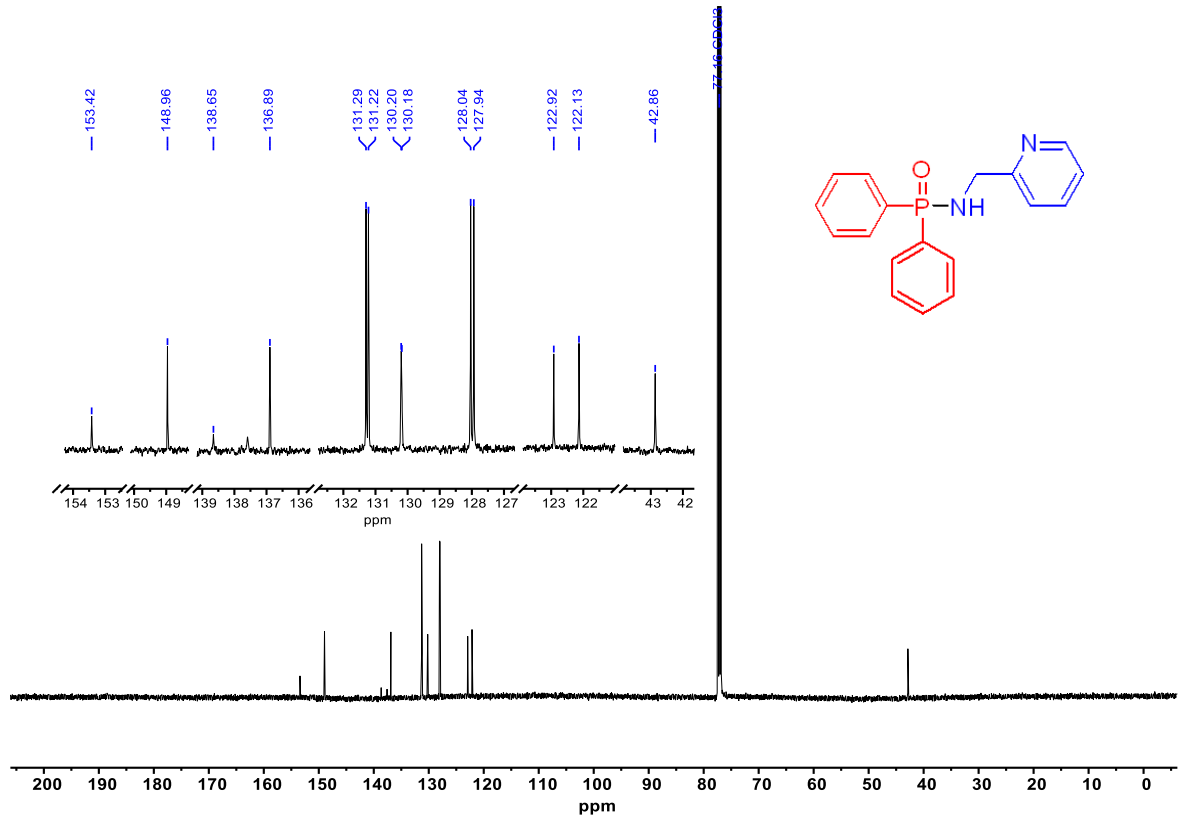


Figure S83: *P*,*P*-diphenyl-*N*-(pyridin-2-ylmethyl)phosphinic amide (**7d**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

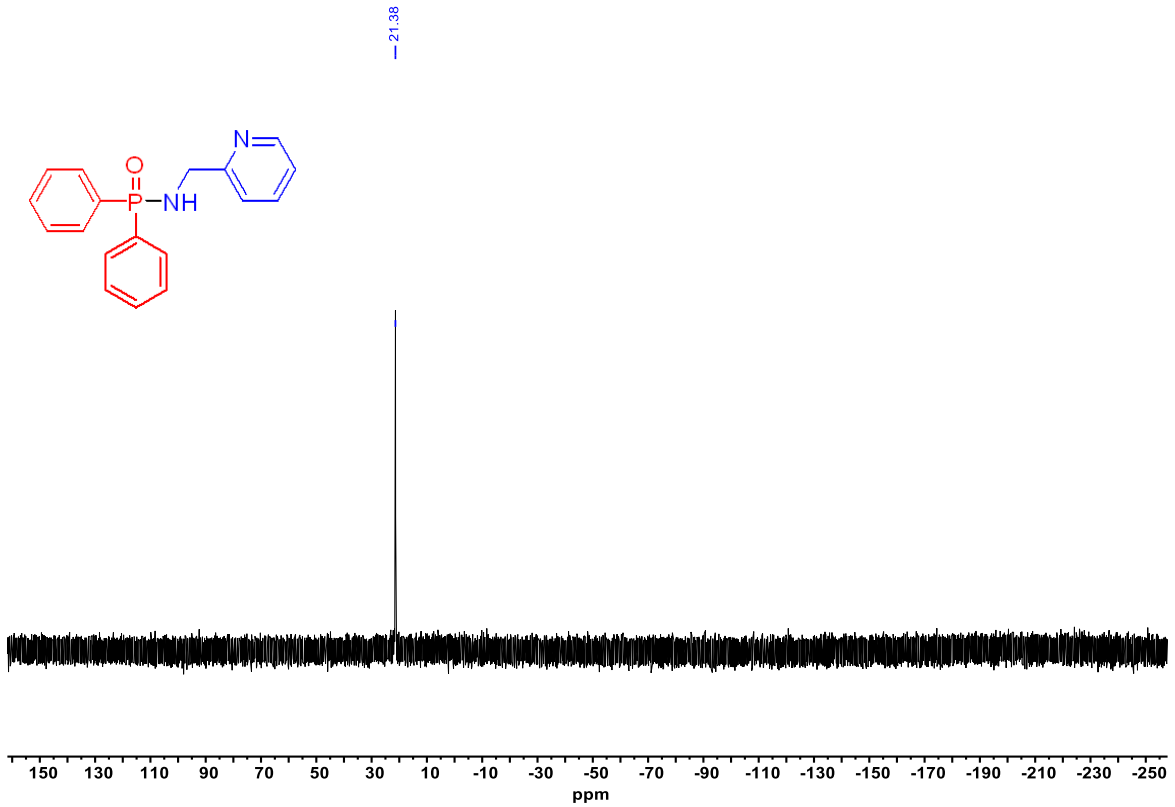


Figure S84: diphenyl(4-(pyridin-2-yl)piperazin-1-yl)phosphine oxide (**7e**)

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

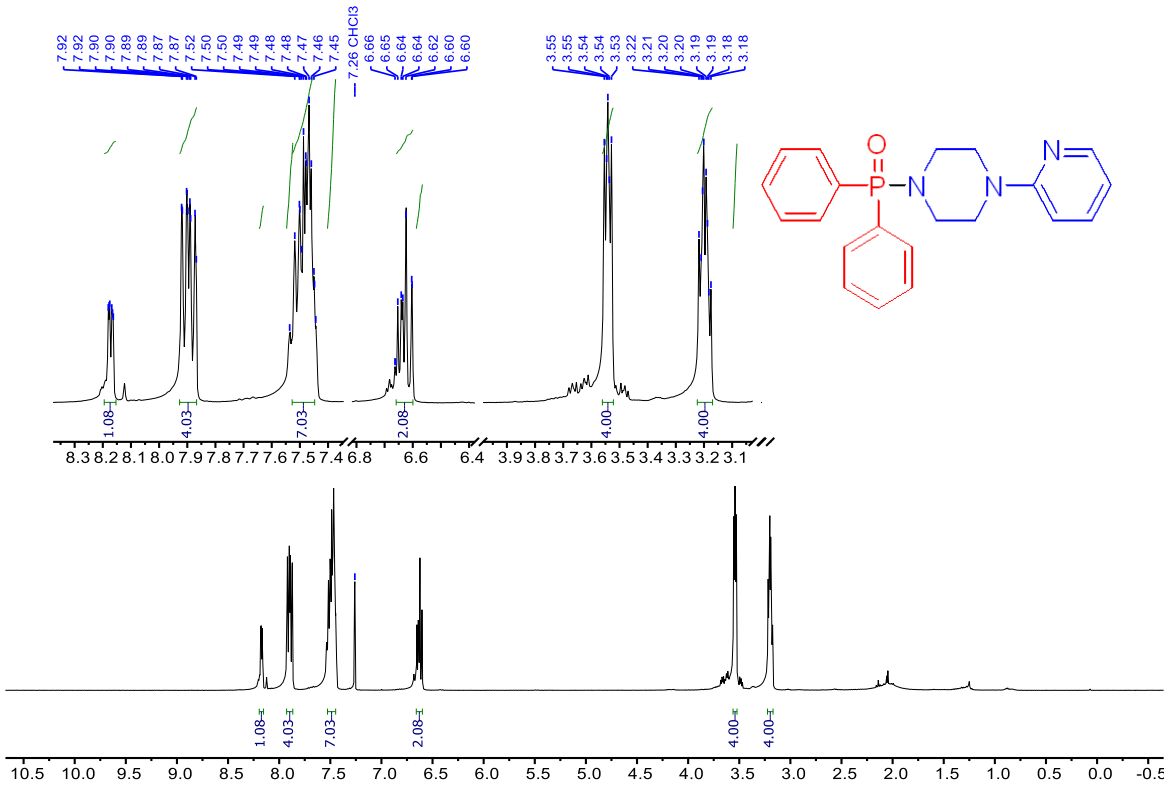


Figure S85: diphenyl(4-(pyridin-2-yl)piperazin-1-yl)phosphine oxide (**7e**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

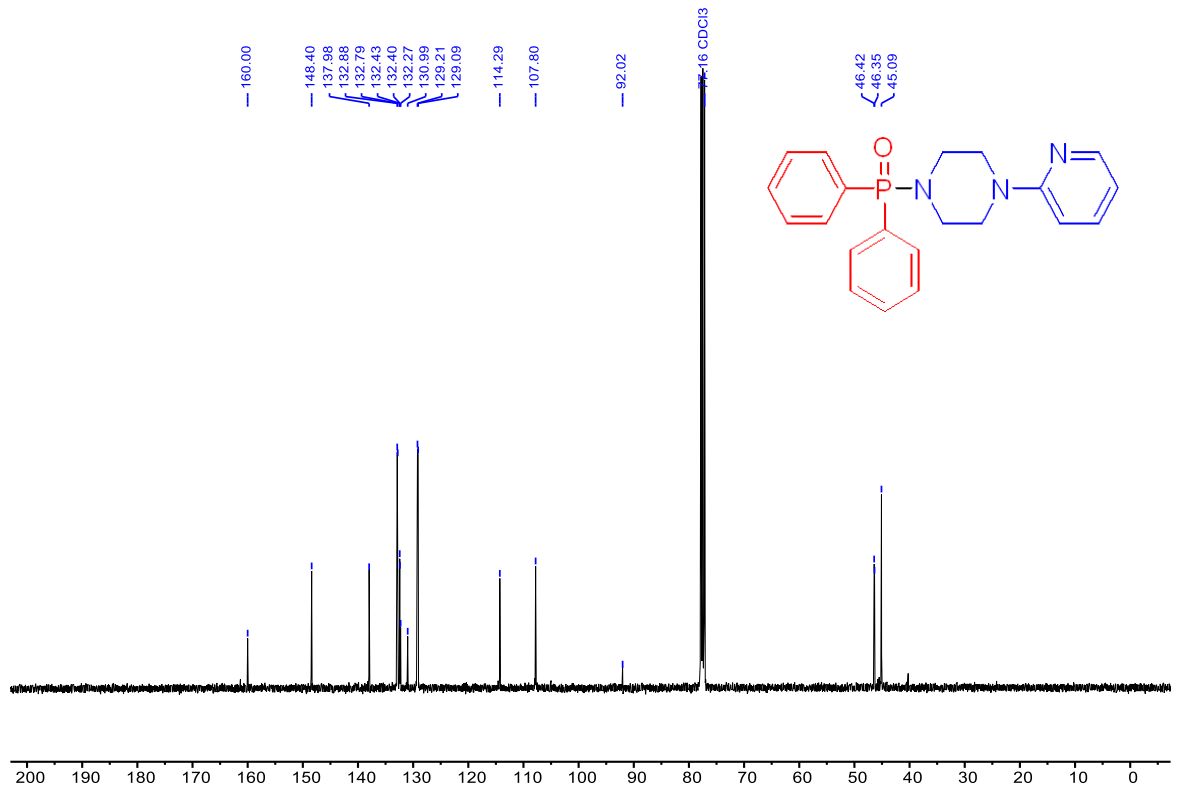


Figure S86: diphenyl(4-(pyridin-2-yl)piperazin-1-yl)phosphine oxide (**7e**)

^{31}P NMR spectrum (126 MHz, $CDCl_3$)

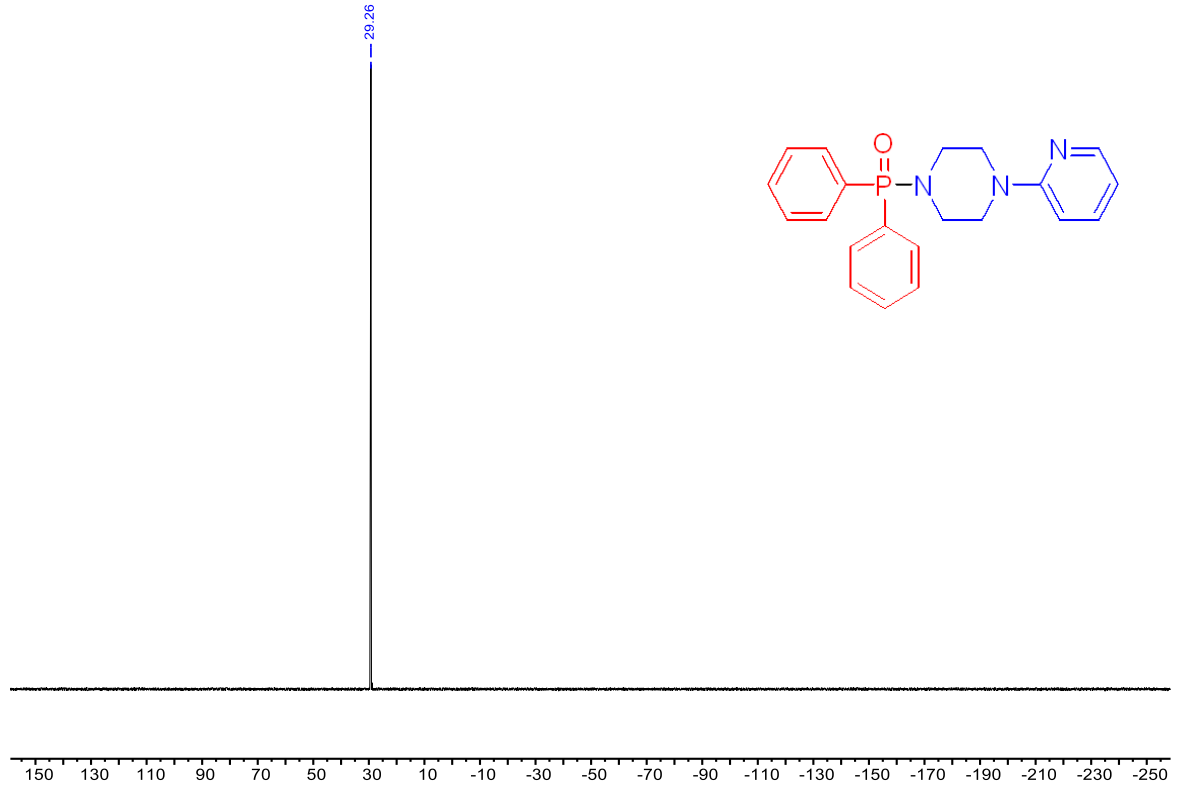


Figure S87: (1*H*-indol-1-yl)diphenylphosphine oxide (**7f**)[11]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

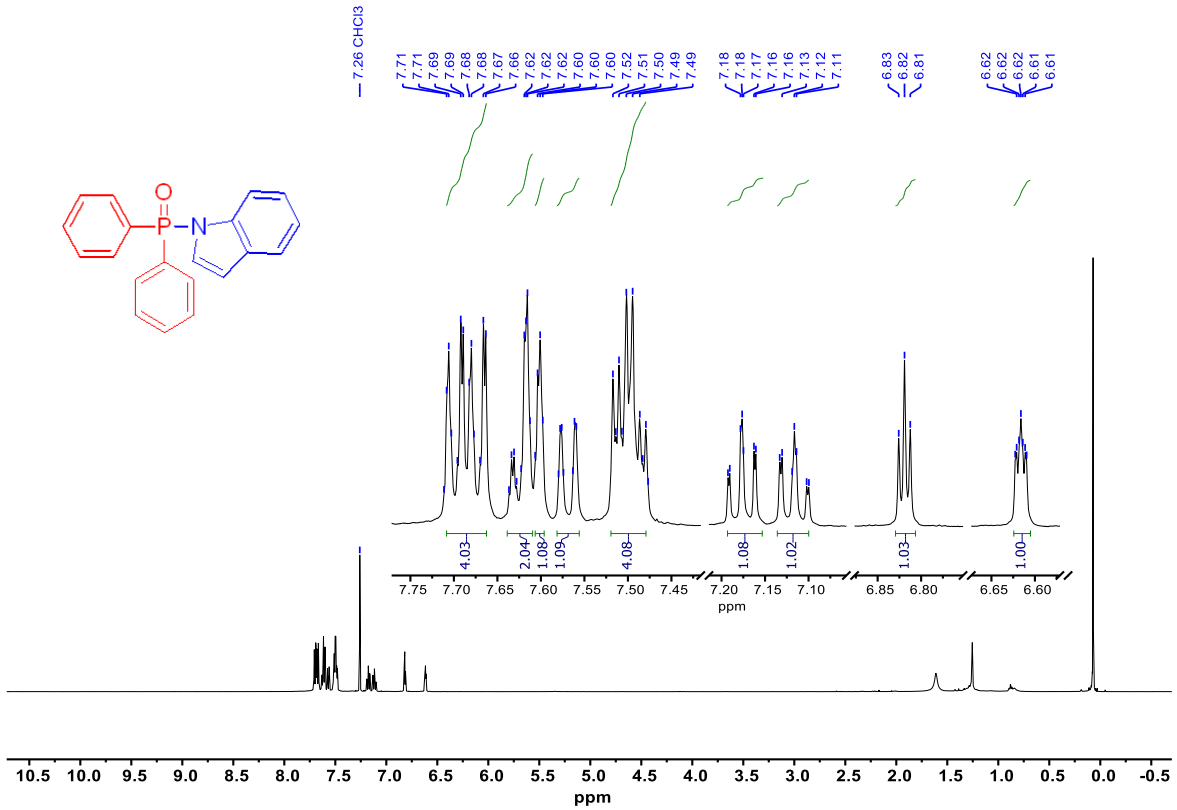


Figure S88: (1*H*-indol-1-yl)diphenylphosphine oxide (**7f**)[11]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

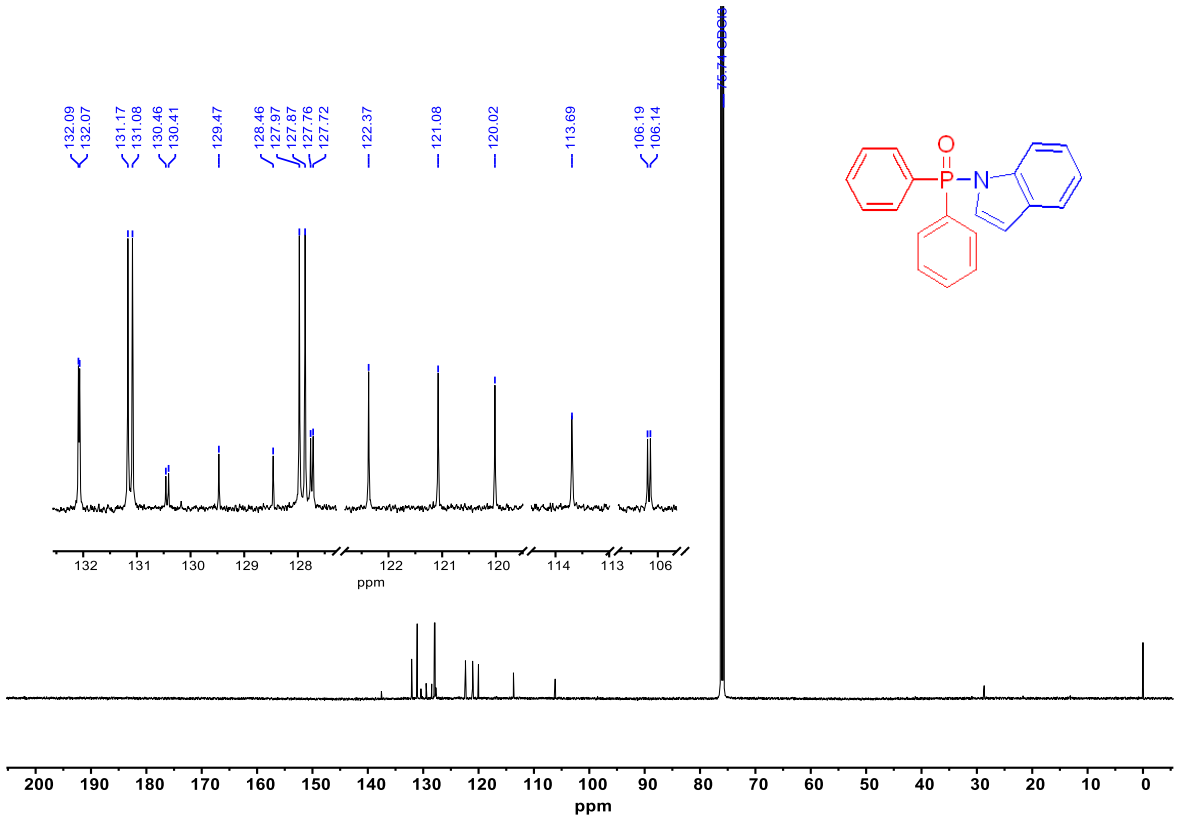


Figure S89: (1*H*-indol-1-yl)diphenylphosphine oxide (**7f**)[11]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

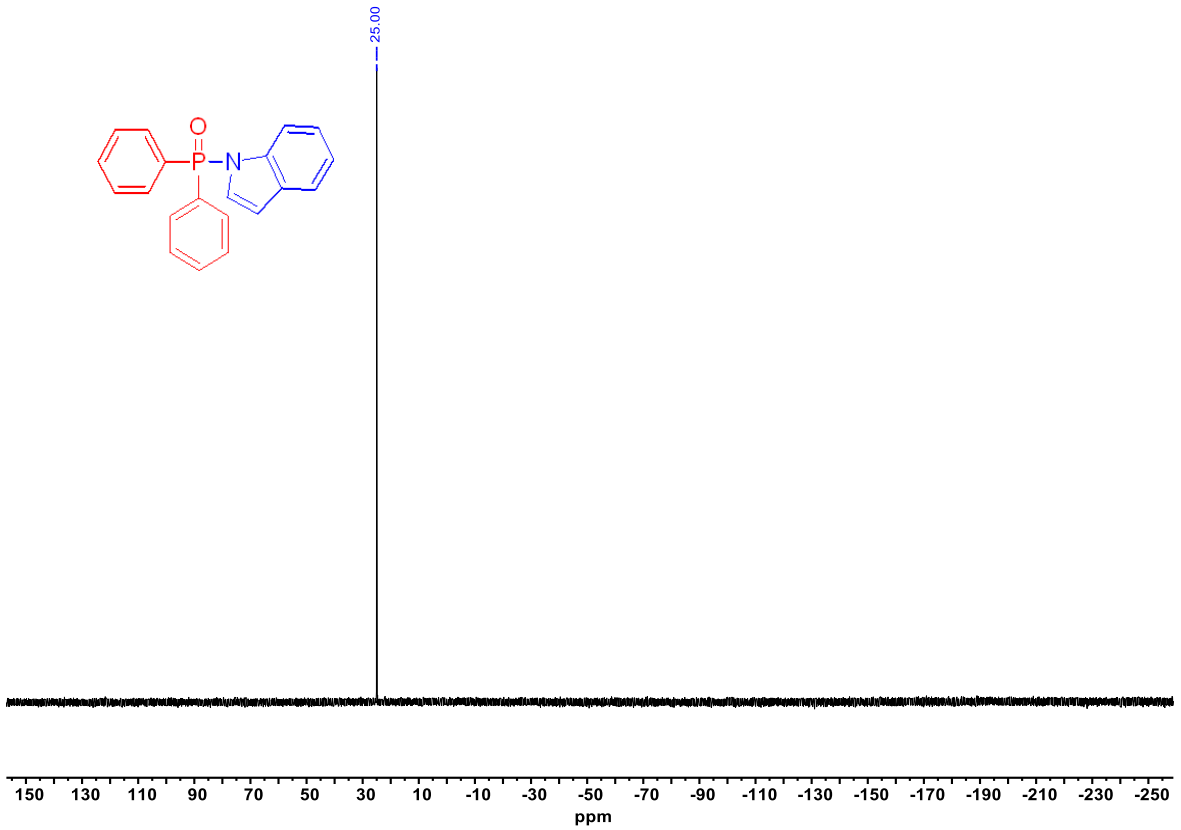


Figure S90: (2,5-dimethyl-1*H*-indol-1-yl)diphenylphosphine oxide (**7g**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

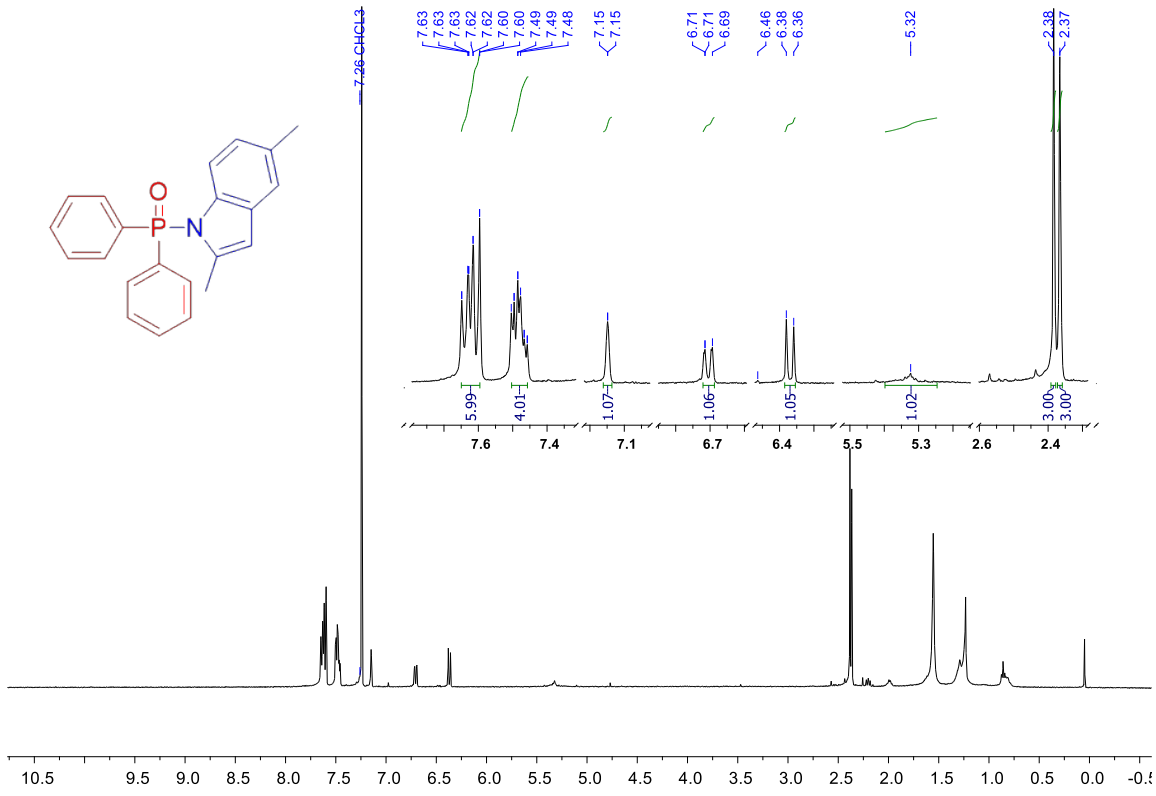


Figure S91: (2,5-dimethyl-1*H*-indol-1-yl)diphenylphosphine oxide (**7g**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

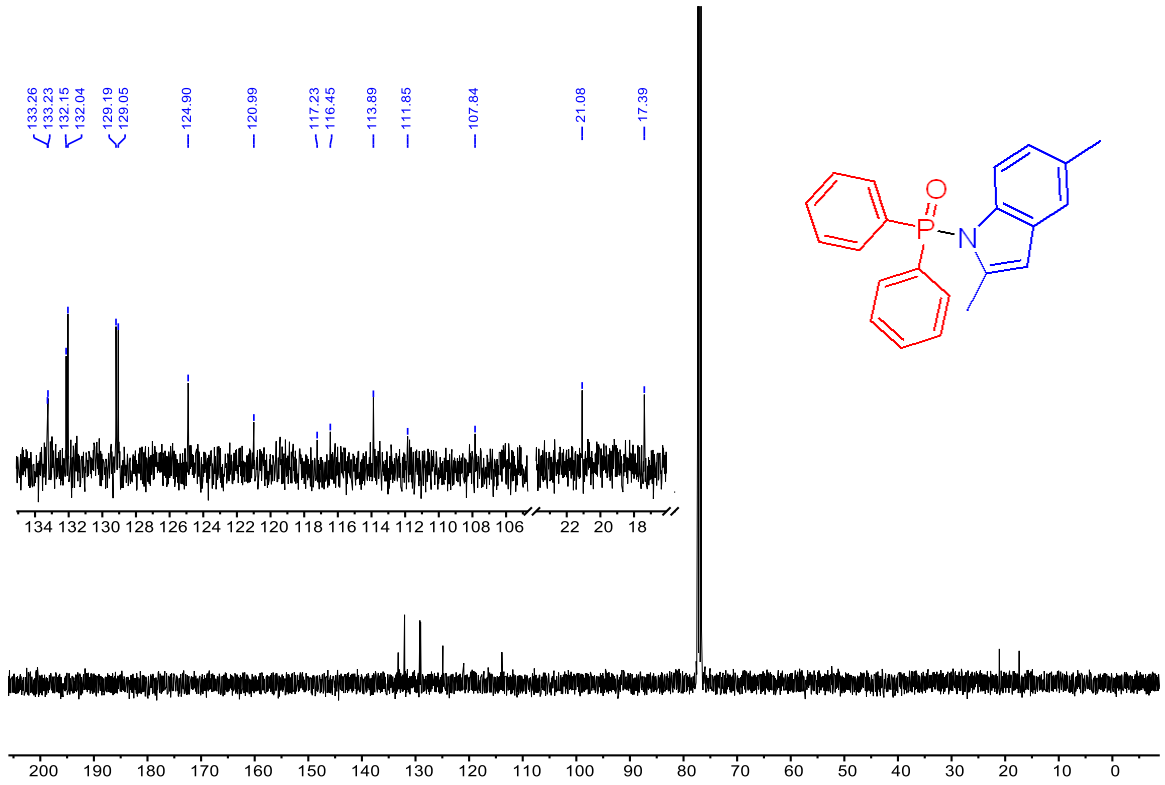


Figure S92: (2,5-dimethyl-1*H*-indol-1-yl)diphenylphosphine oxide (**7g**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

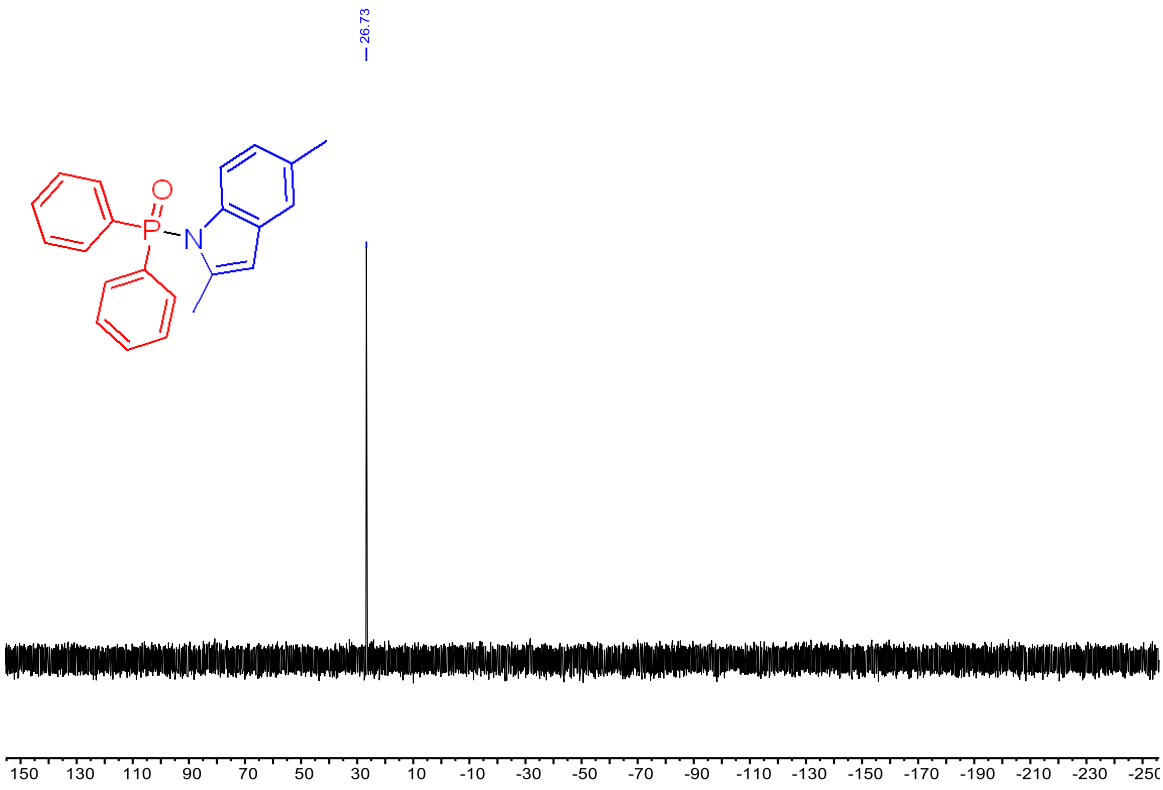


Figure S93: (4-methoxy-1*H*-indol-1-yl)diphenylphosphine oxide (**7h**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

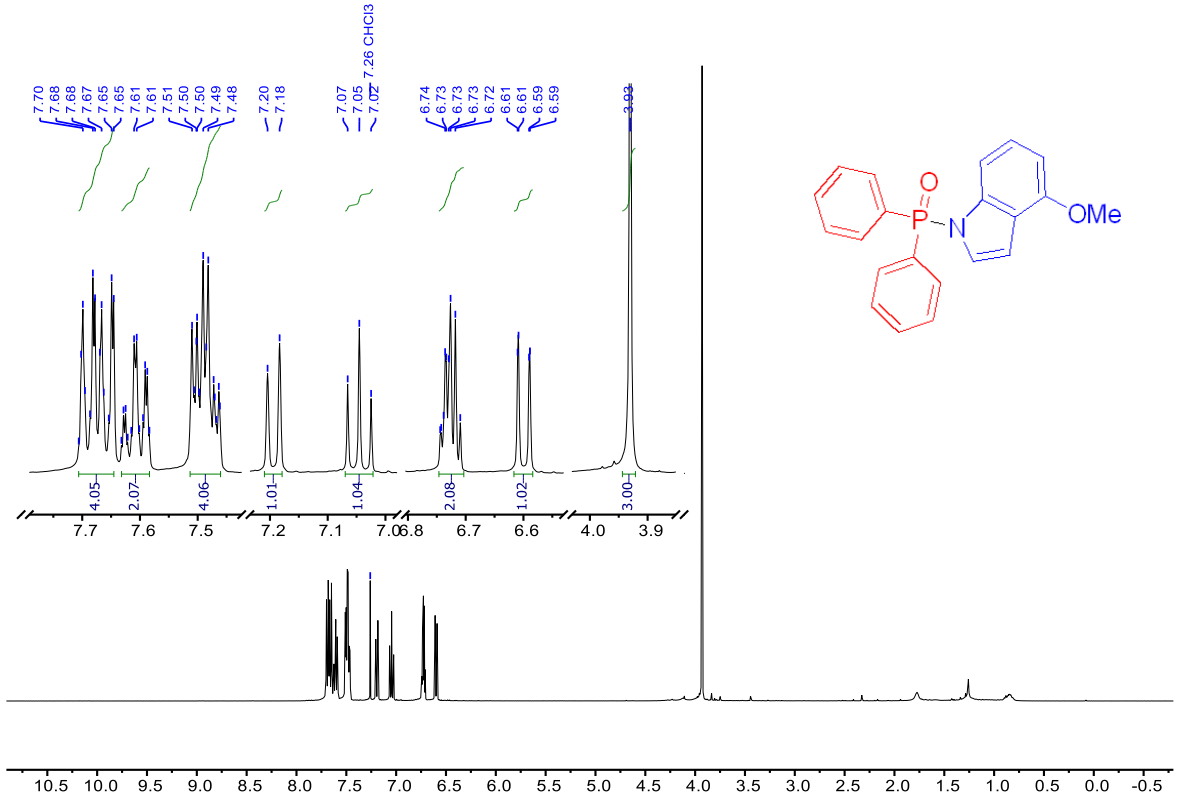


Figure S94: (4-methoxy-1*H*-indol-1-yl)diphenylphosphine oxide (**7h**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

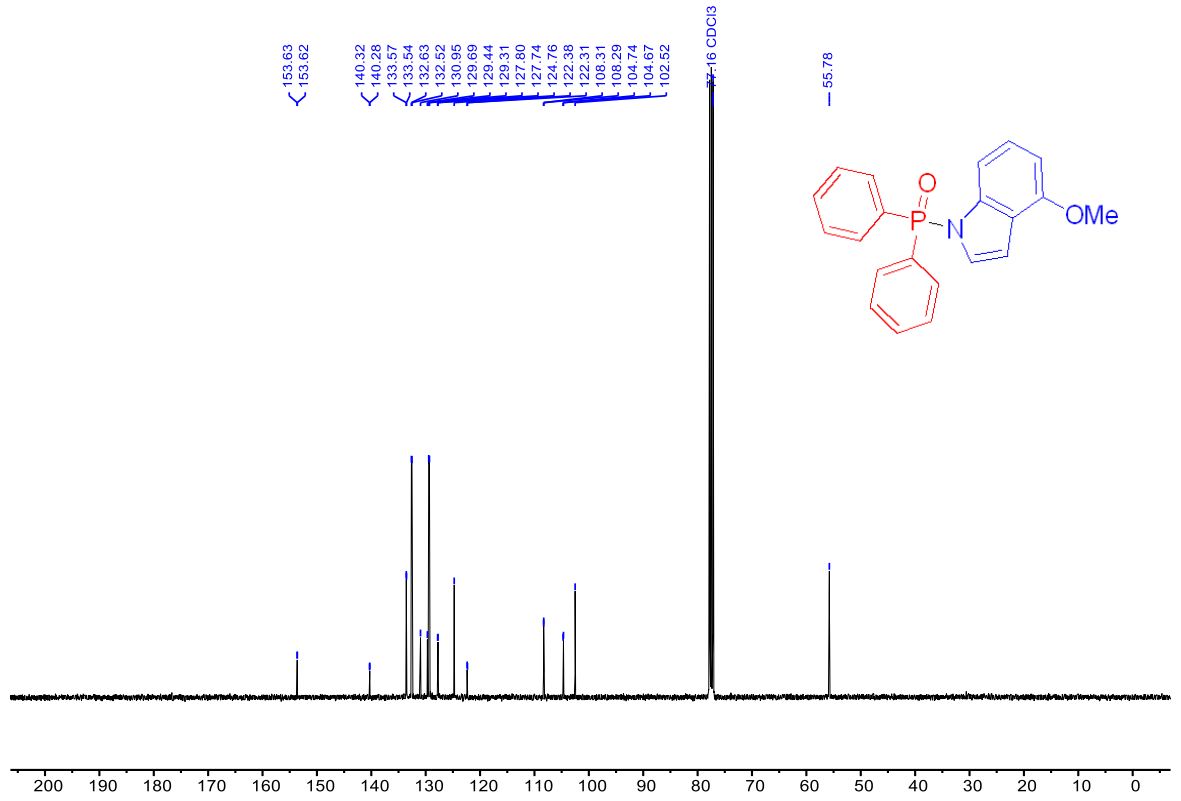


Figure S95: (4-methoxy-1*H*-indol-1-yl)diphenylphosphine oxide (**7h**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

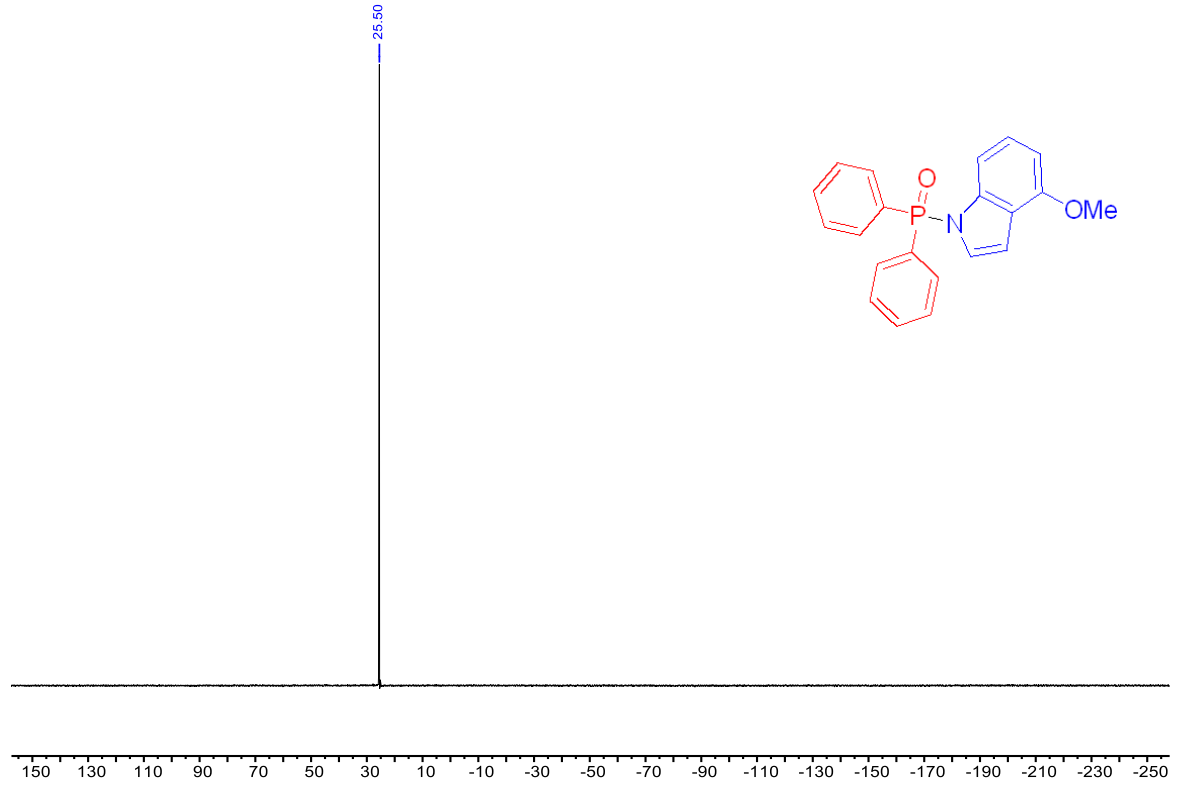


Figure S96: phenyl diphenylphosphinate (**8a**)[12]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

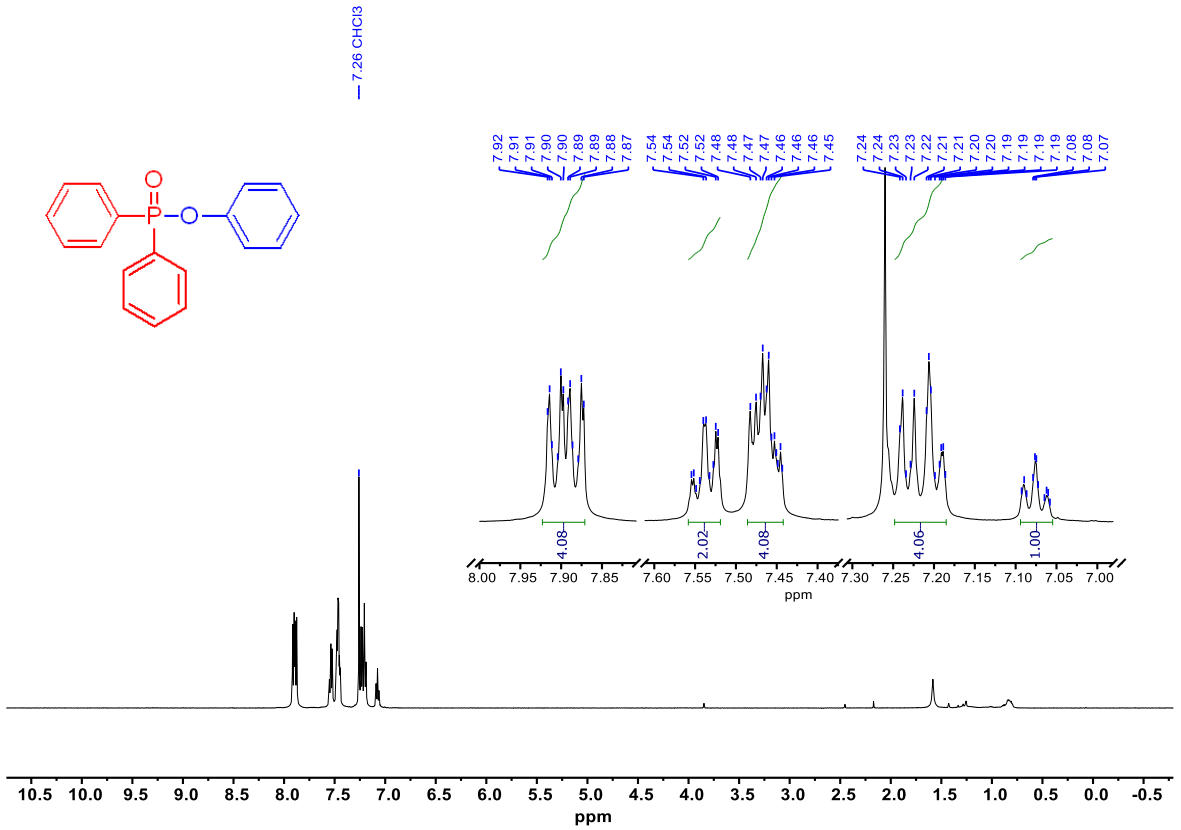


Figure S97: phenyl diphenylphosphinate (**8a**) [12]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

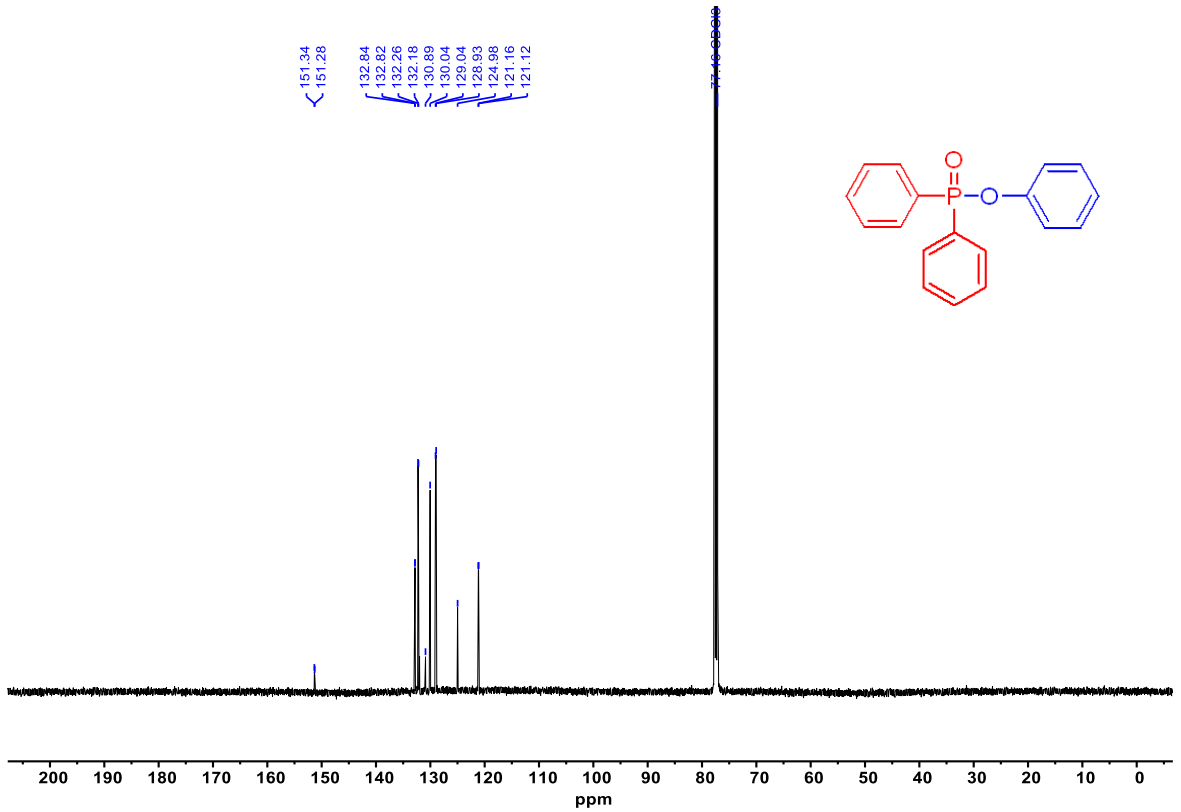


Figure S98: phenyl diphenylphosphinate (**8a**)[12]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

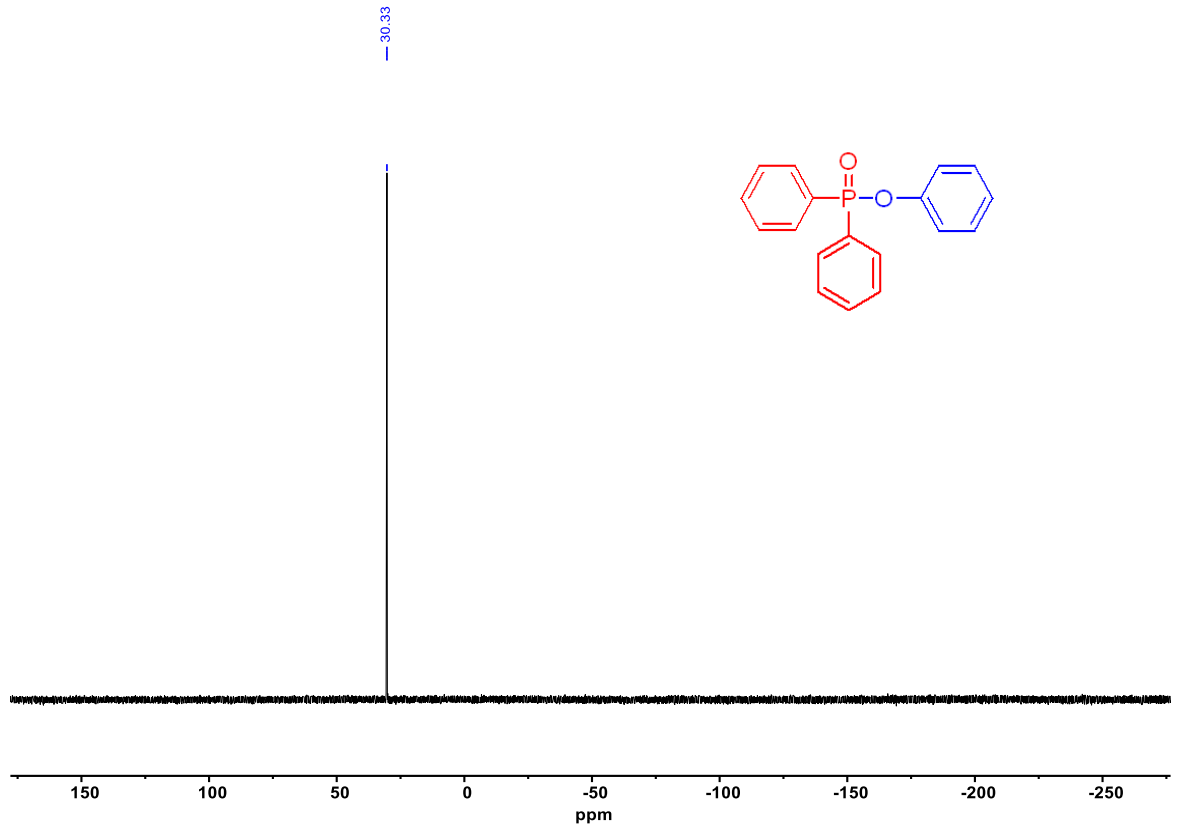


Figure S99: pentyl diphenylphosphinate (**8b**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

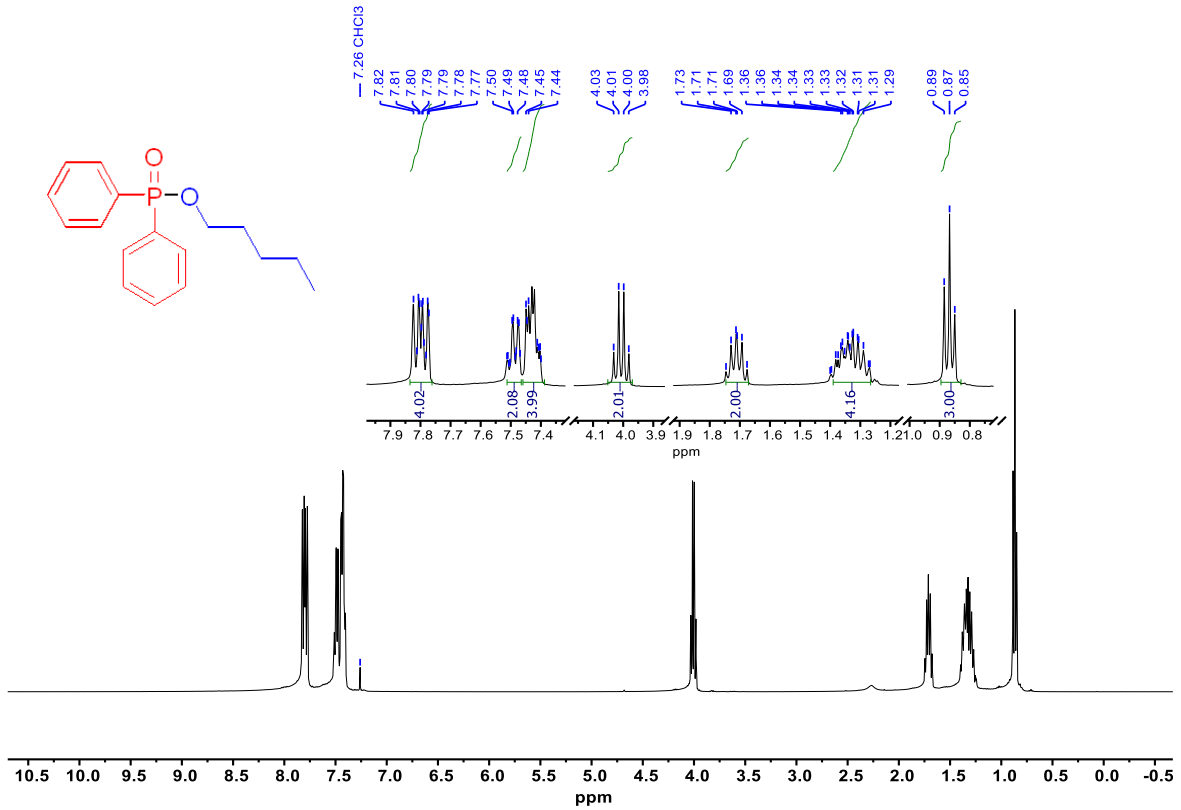


Figure S100: pentyl diphenylphosphinate (**8b**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

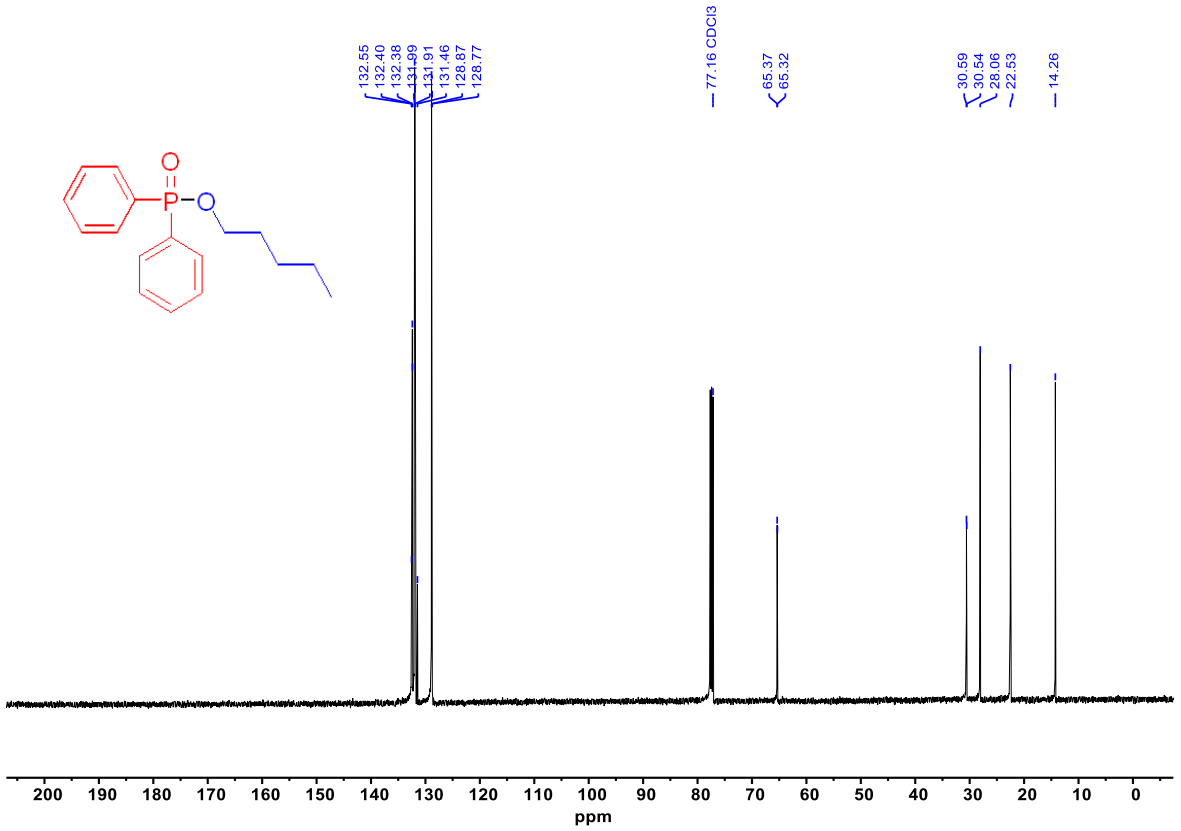


Figure S101: pentyl diphenylphosphinate (**8b**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

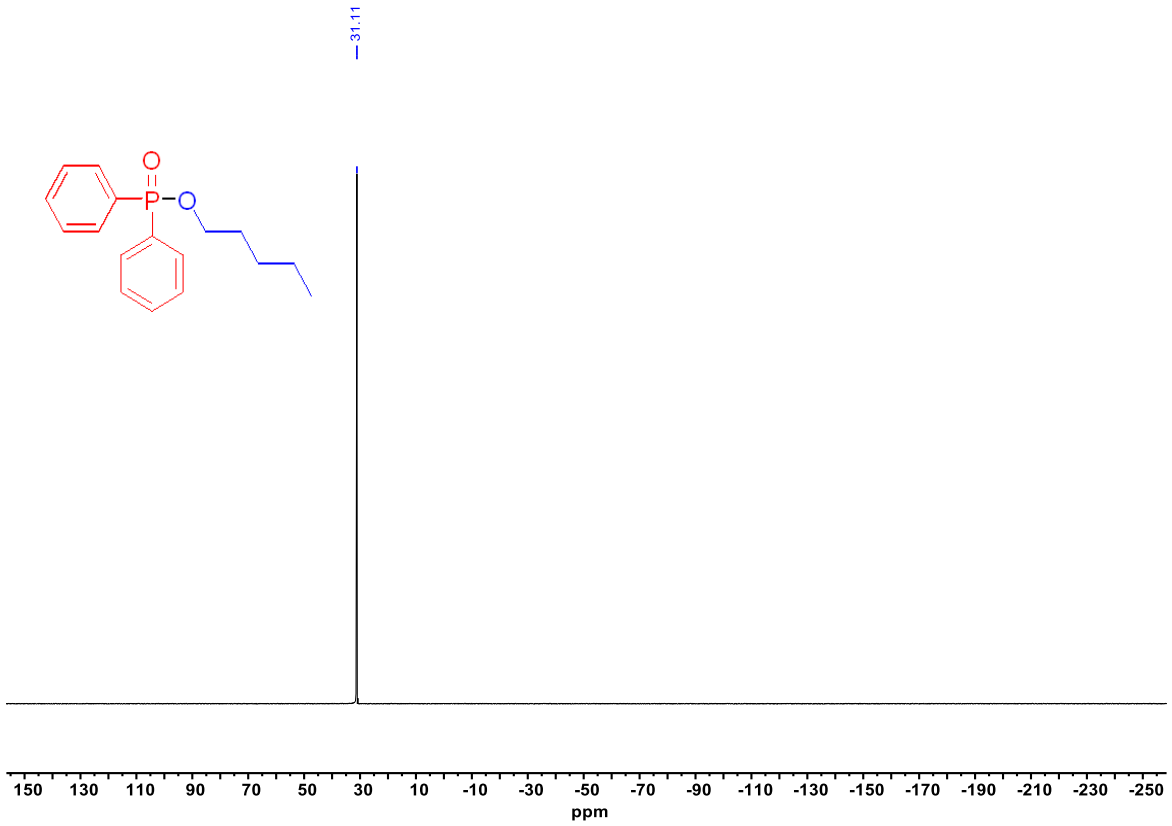


Figure S102: *N*-(2-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**9a**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

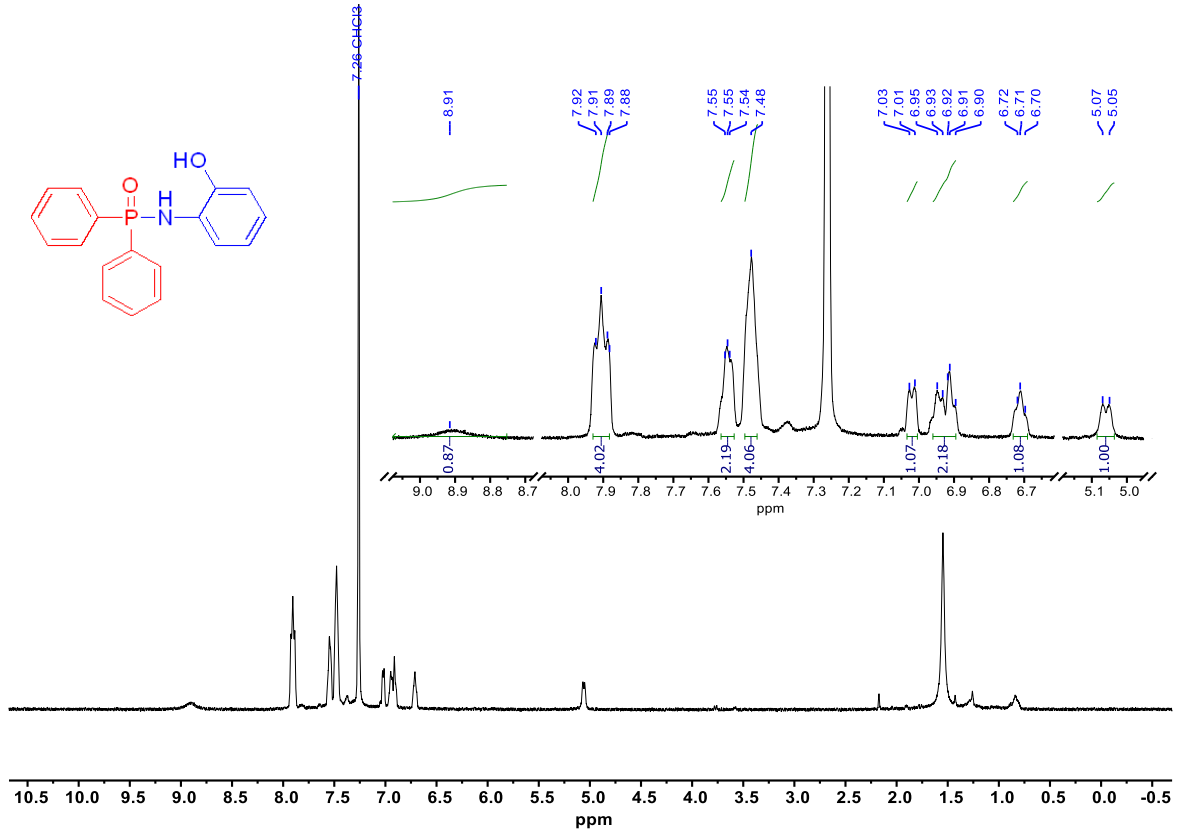


Figure S103: *N*-(2-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**9a**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

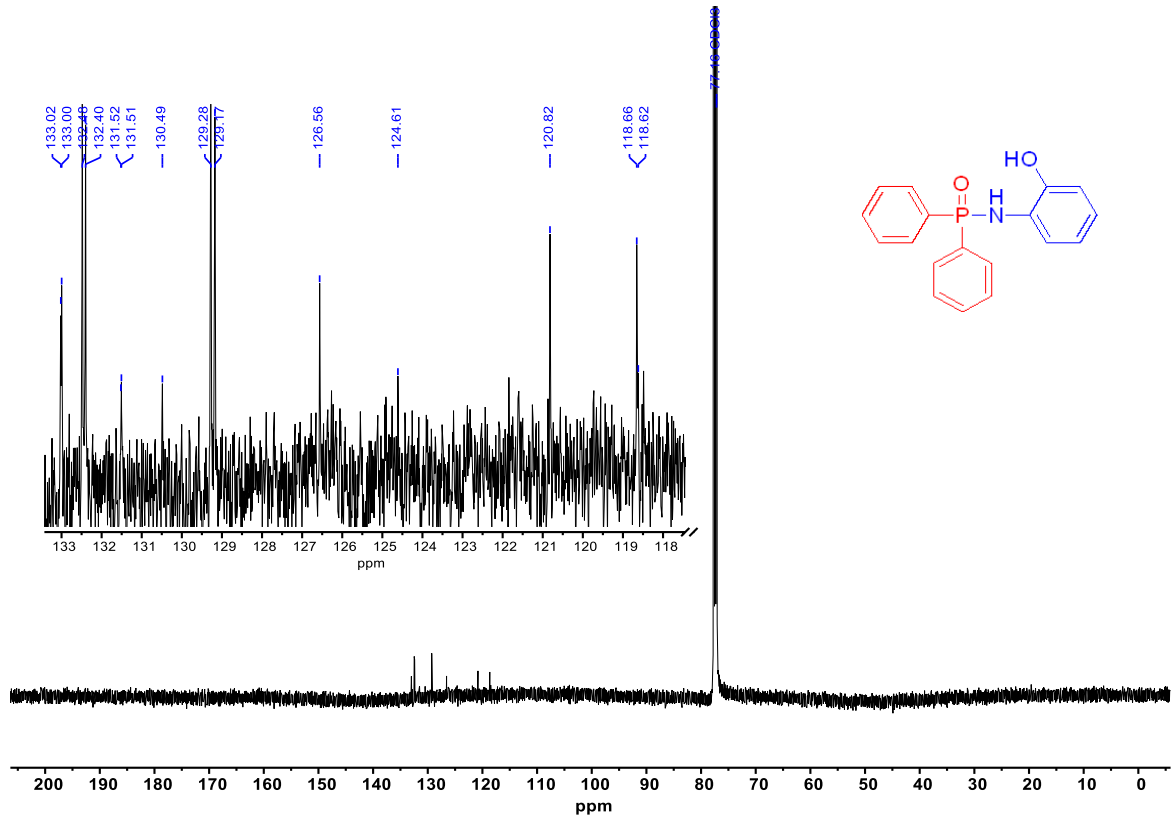


Figure S104: *N*-(2-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**9a**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

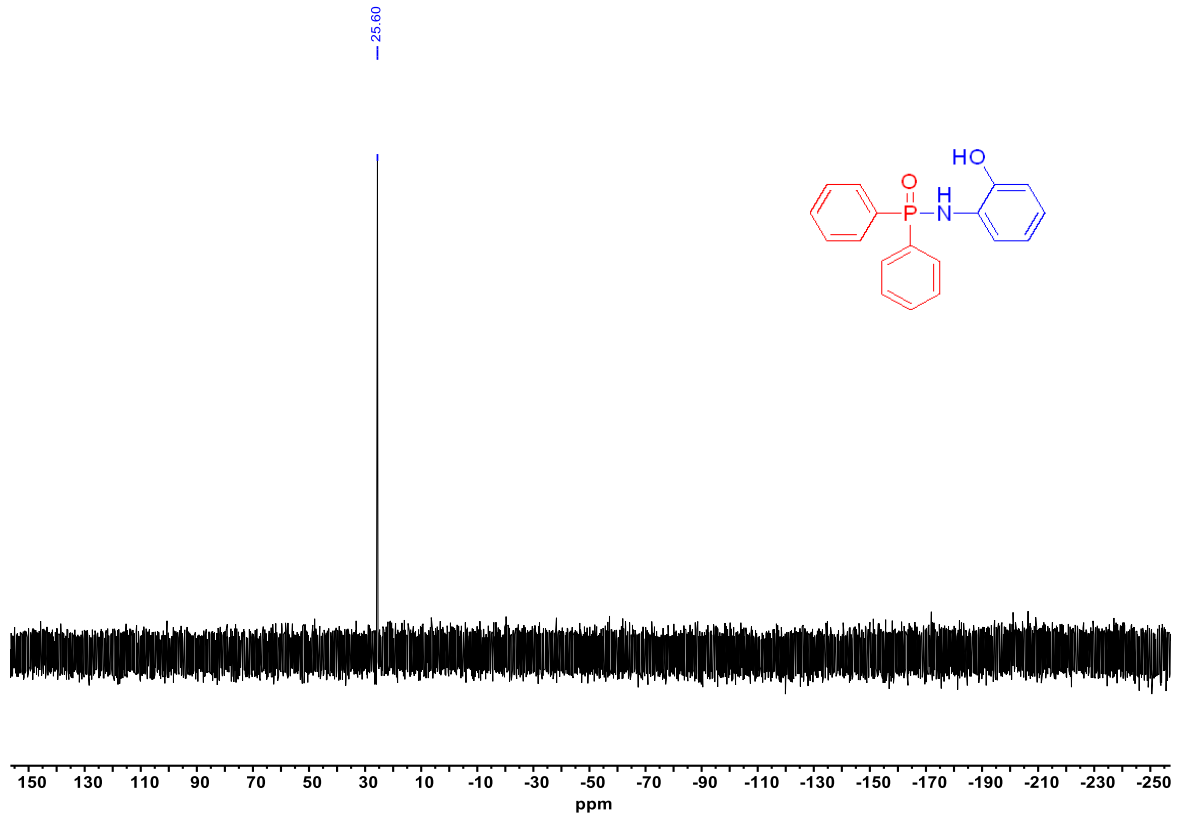


Figure S105: 2-aminophenyl diphenylphosphinate (**9b**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

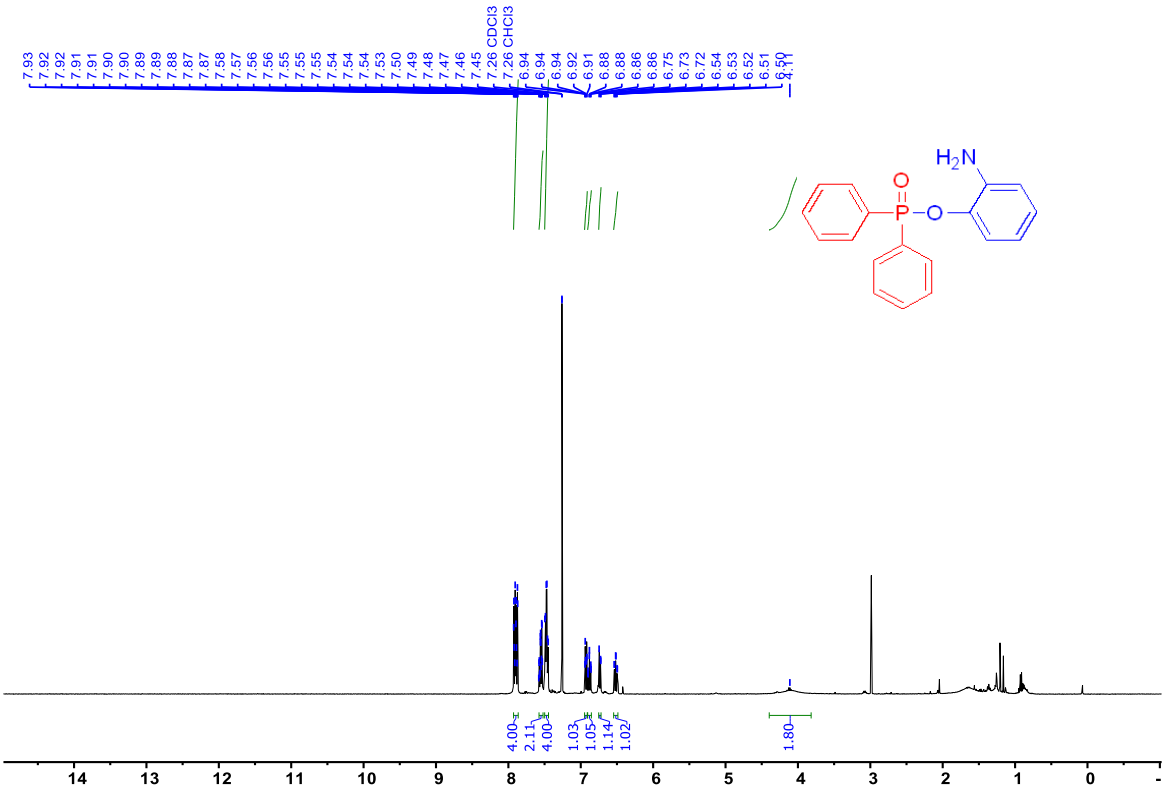


Figure S106: 2-aminophenyl diphenylphosphinate (**9b**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

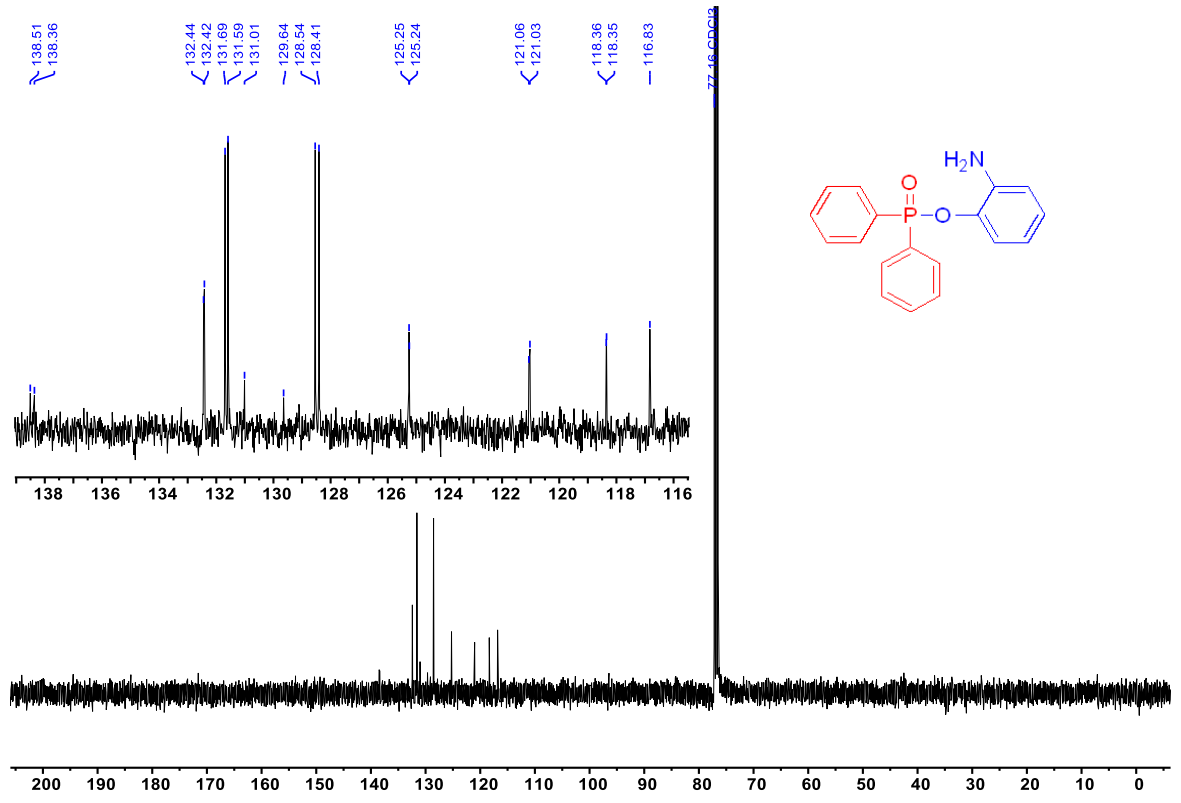


Figure S107: 2-aminophenyl diphenylphosphinate (**9b**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

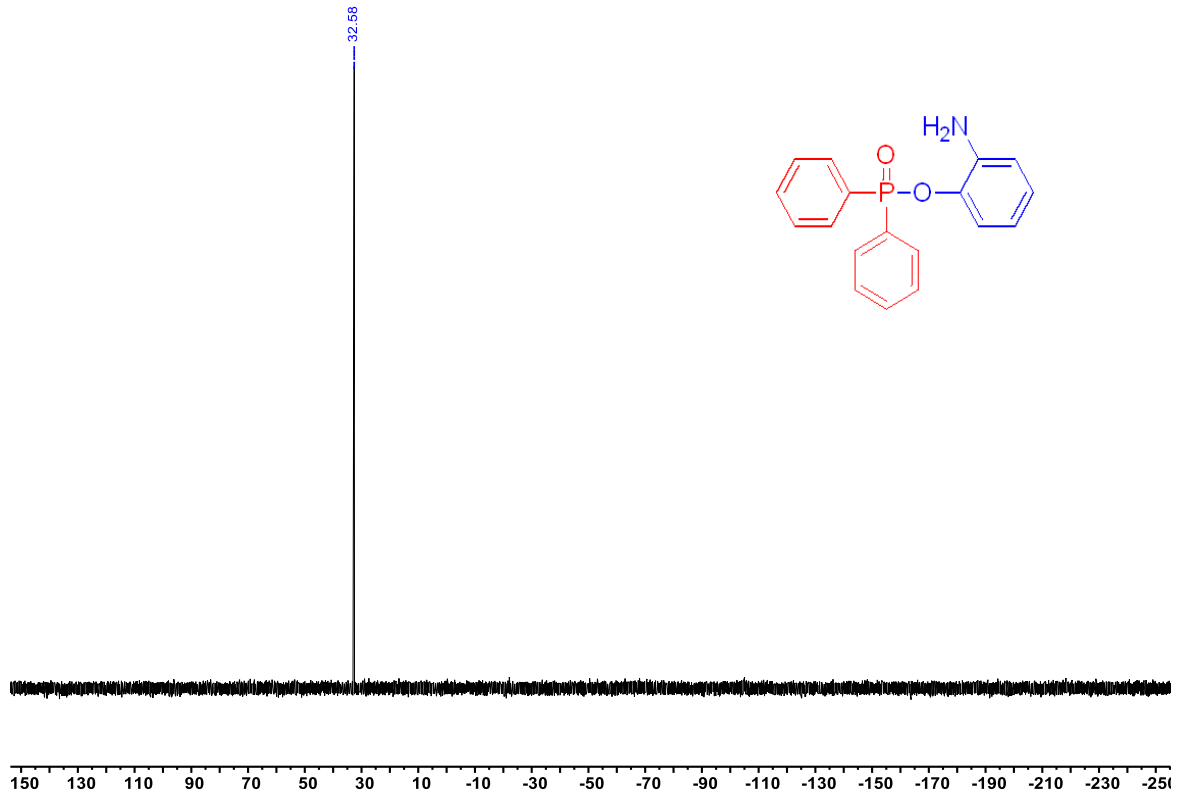


Figure S108: *N*-(2-chloro-4-hydroxyphenyl)-*P,P*-diphenylphosphinic amide (**10a**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

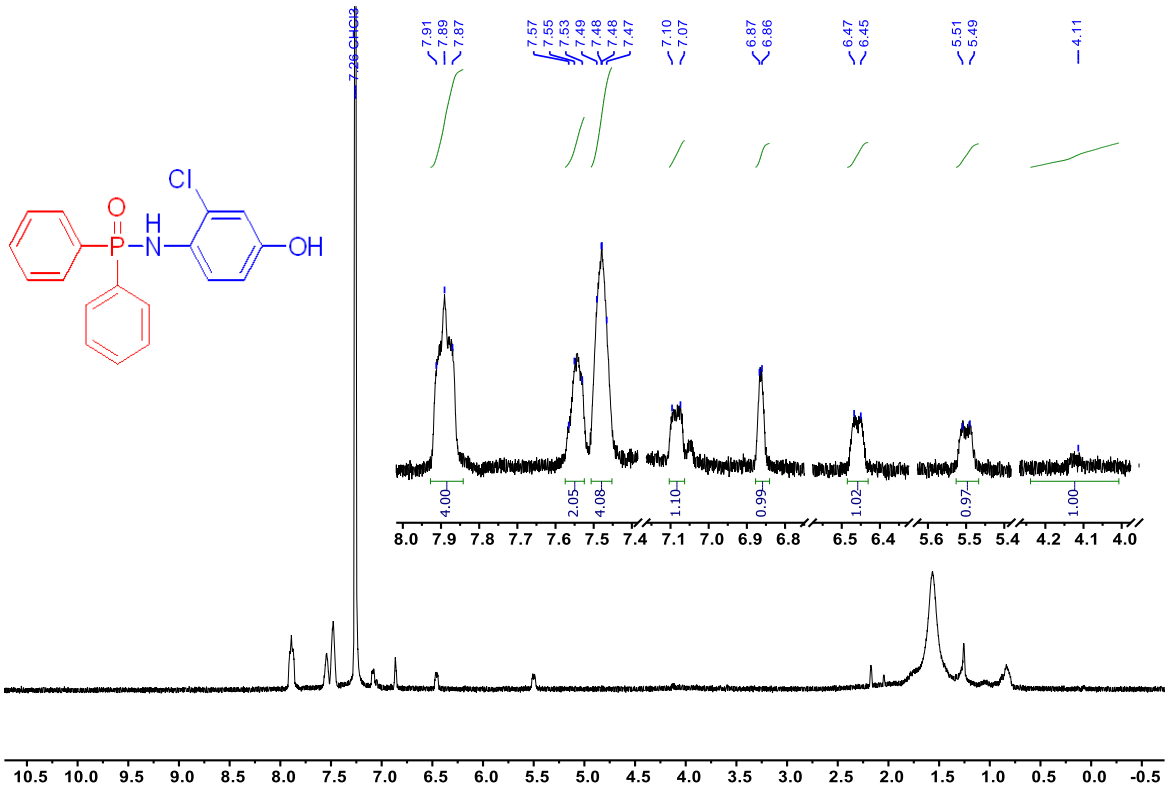


Figure S109: *N*-(2-chloro-4-hydroxyphenyl)-*P,P*-diphenylphosphinic amide (**10a**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

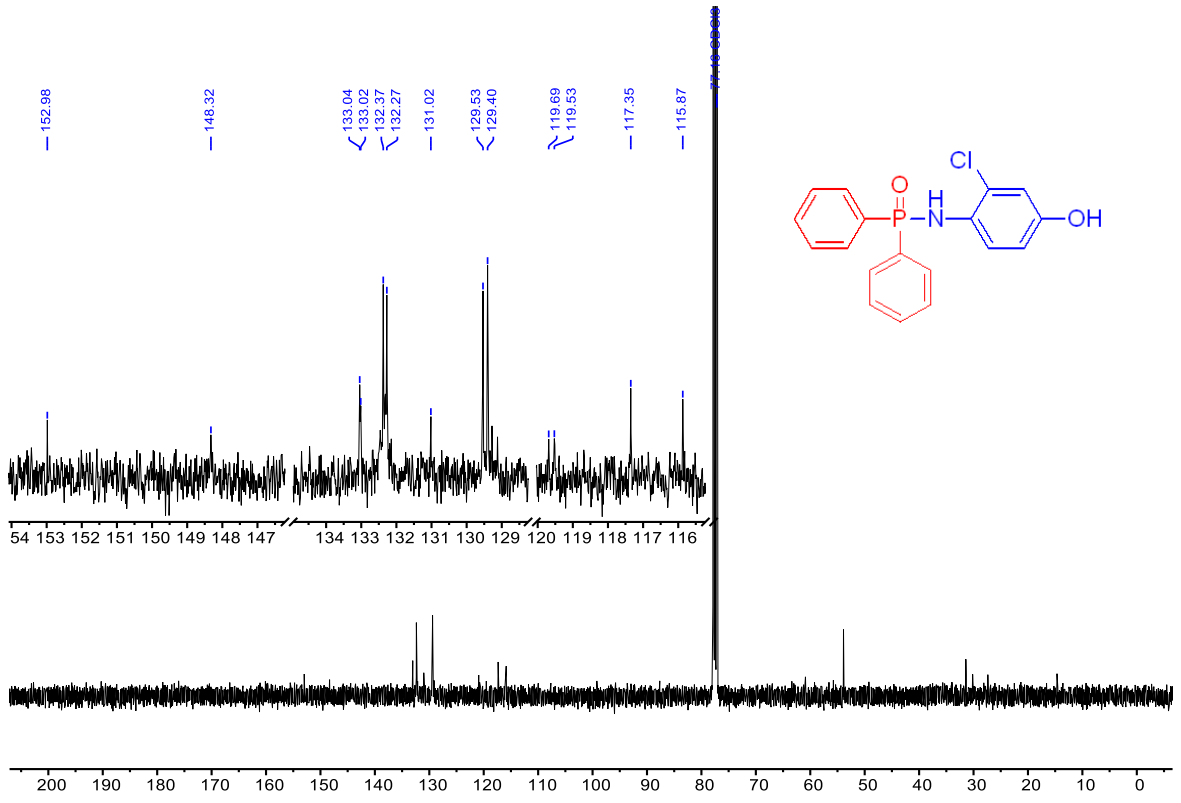


Figure S110: *N*-(2-chloro-4-hydroxyphenyl)-*P,P*-diphenylphosphinic amide (**10a**)

^{31}P NMR spectrum (126 MHz, $CDCl_3$)

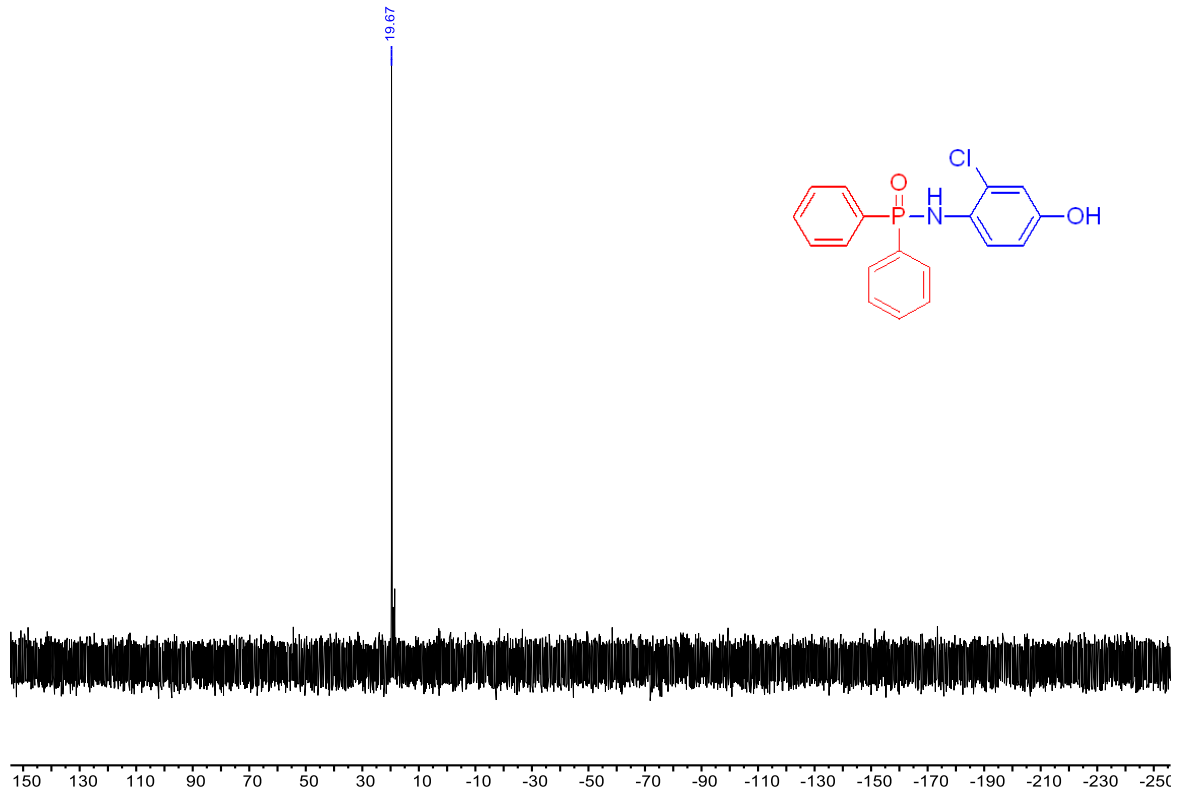


Figure S111: *N*-(2-chloro-4-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**10b**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

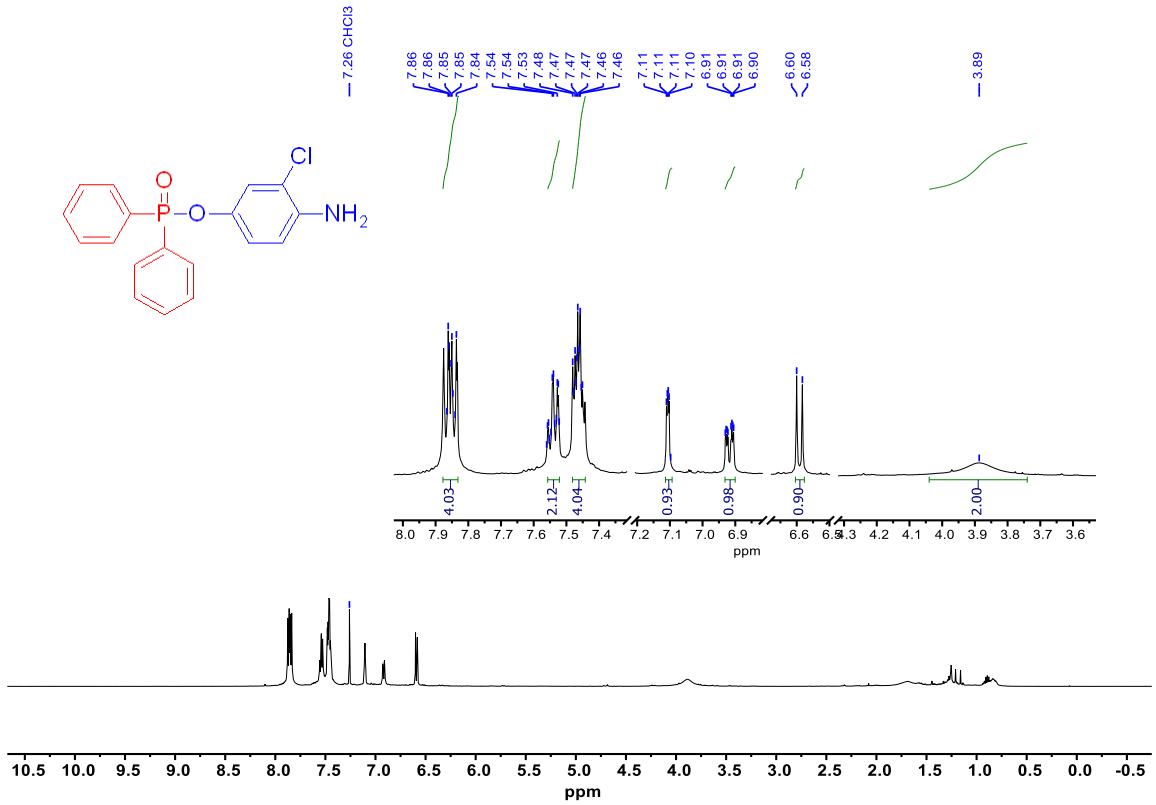


Figure S112: *N*-(2-chloro-4-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**10b**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

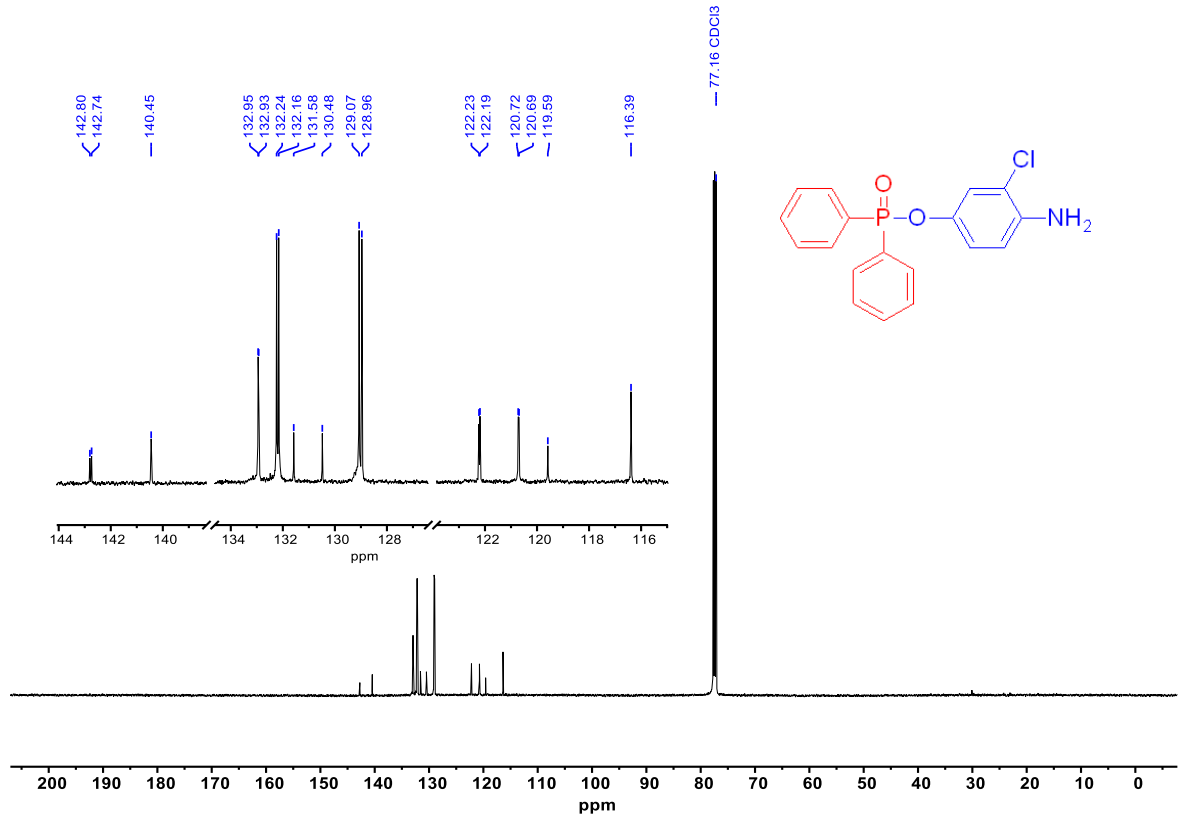


Figure S113: *N*-(2-chloro-4-hydroxyphenyl)-*P*,*P*-diphenylphosphinic amide (**10b**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

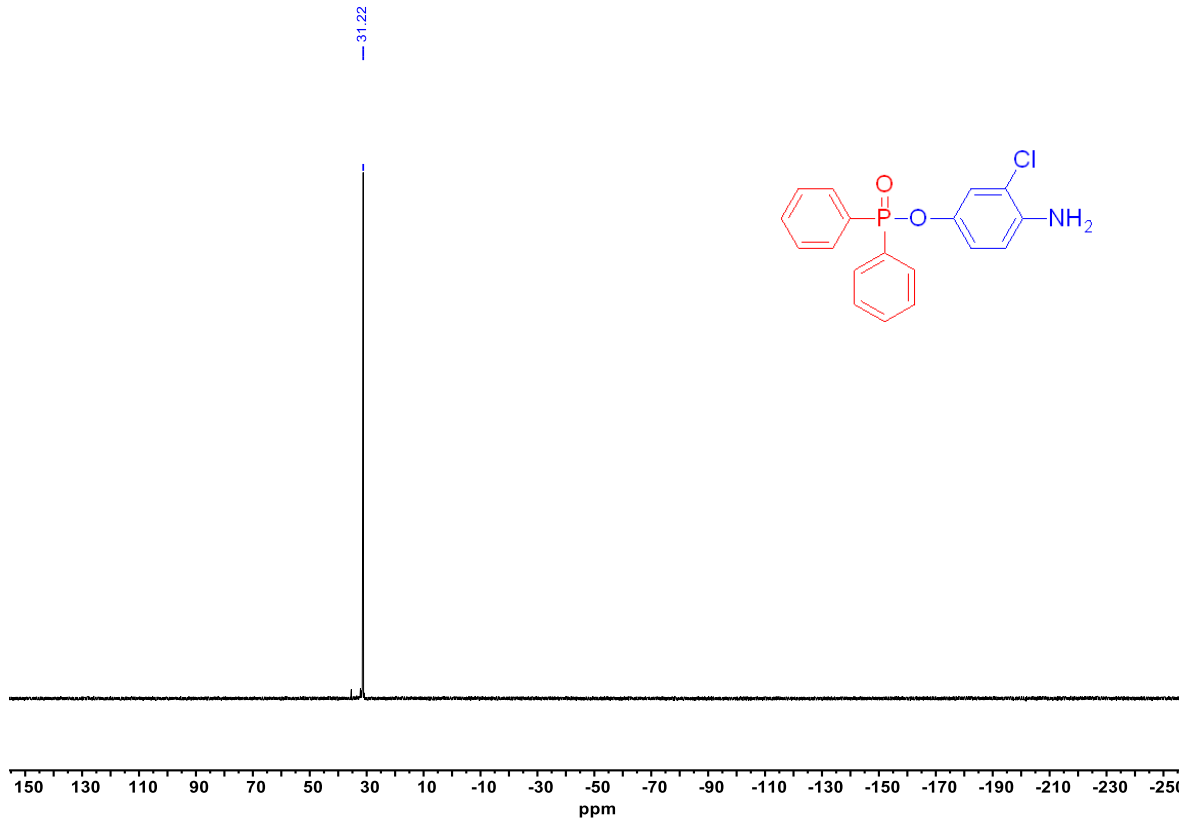


Figure S114: *N*-(2-aminophenyl)-*P,P*-diphenylphosphinic amide (**11a**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

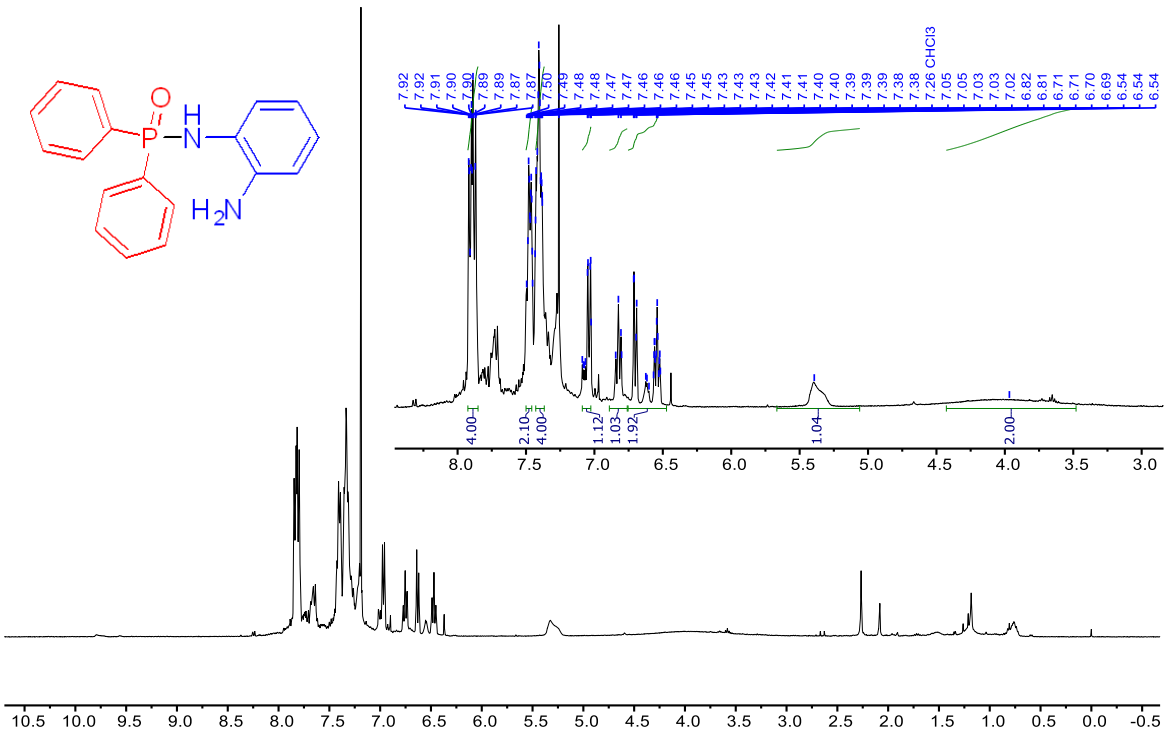


Figure S115: *N*-(2-aminophenyl)-*P,P*-diphenylphosphinic amide (**11a**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

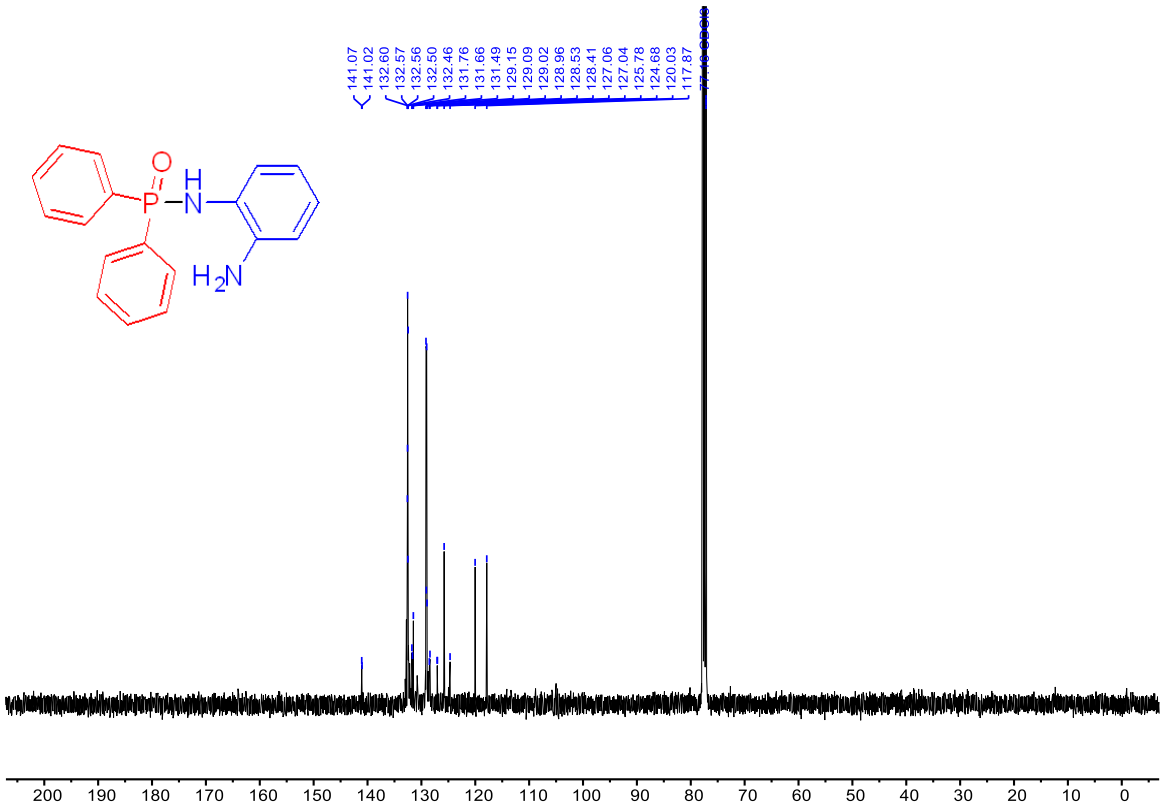


Figure S116: *N*-(2-aminophenyl)-*P,P*-diphenylphosphinic amide (**11a**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

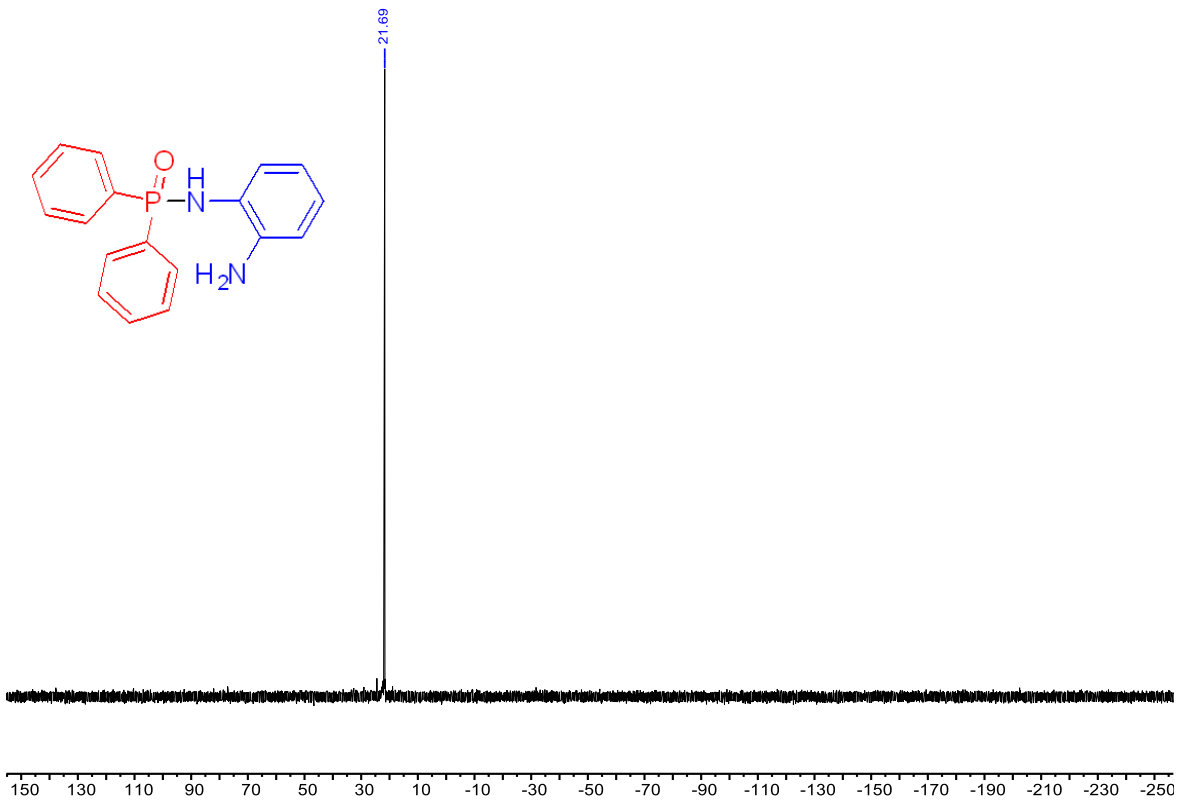


Figure S117: *N,N'*-(1,2-phenylene)bis(*P,P*-diphenylphosphinic amide) (**11b**)

^{1}H NMR (500 MHz, $CDCl_3$)

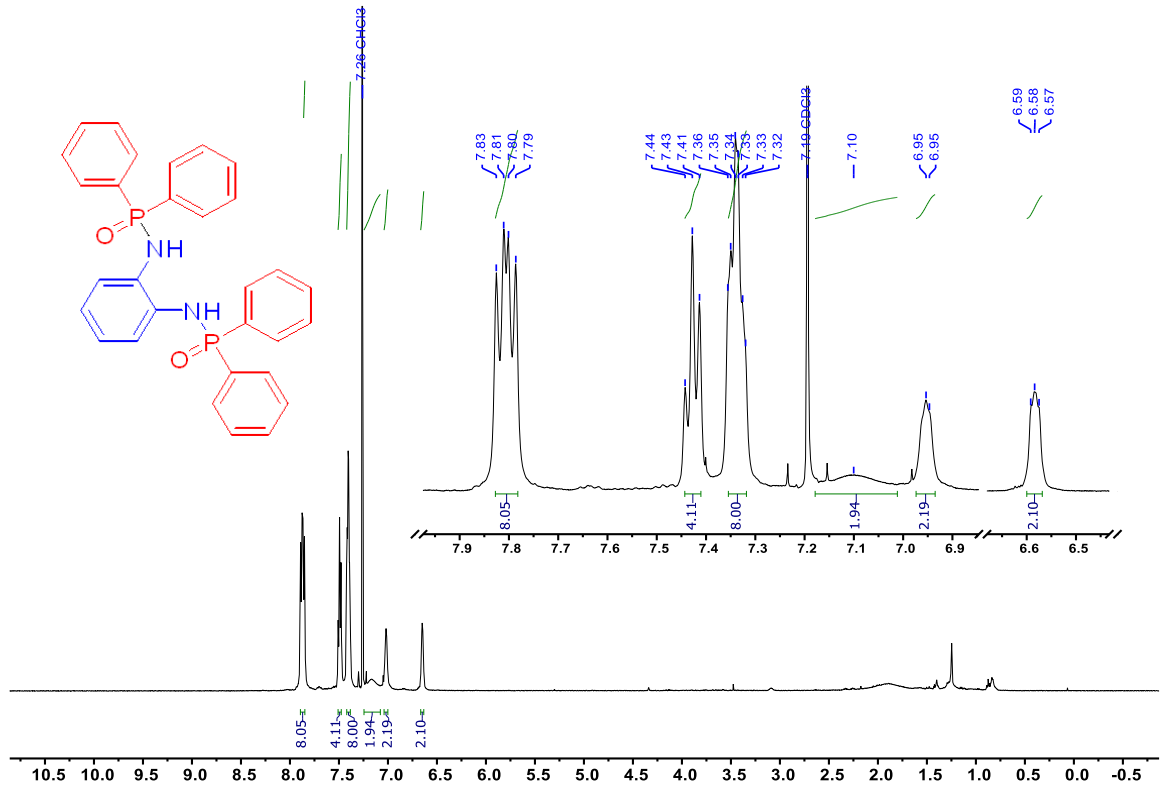


Figure S118: *N,N'*-(1,2-phenylene)bis(*P,P*-diphenylphosphinic amide) (**11b**)

^{13}C NMR (126 MHz, $CDCl_3$)

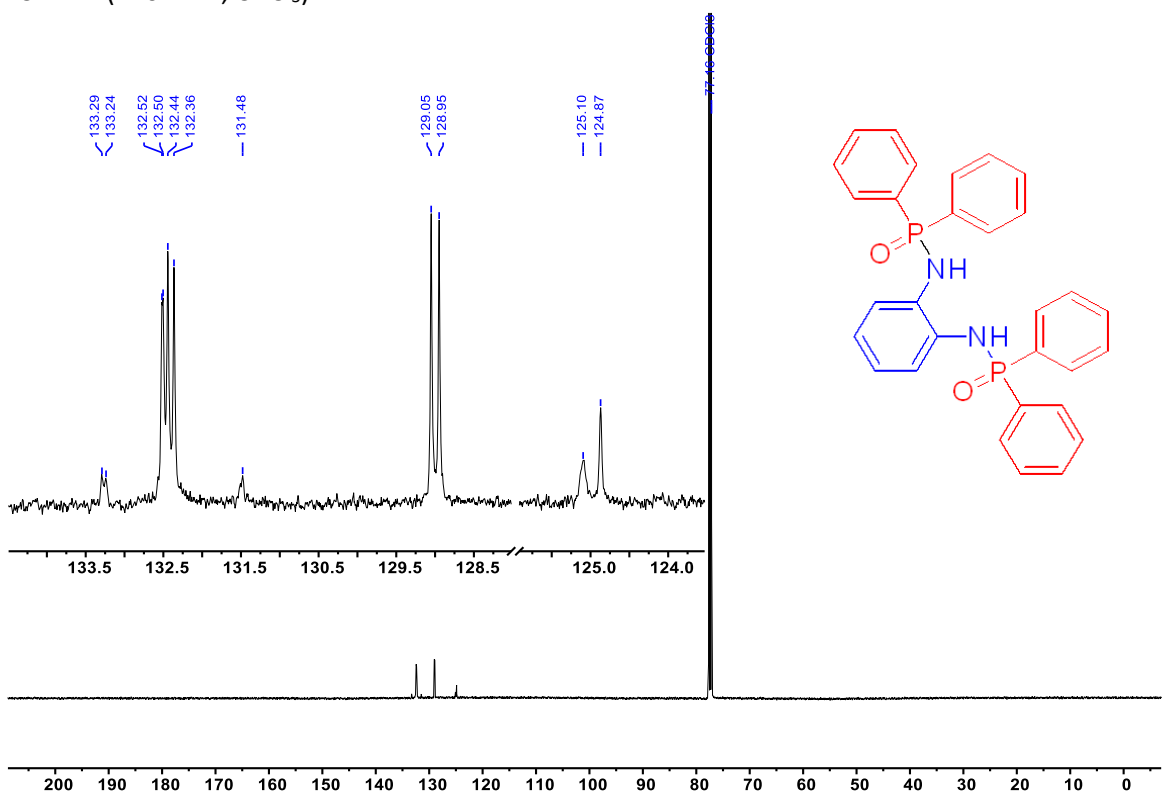


Figure S119: *N,N'*-(1,2-phenylene)bis(*P,P*-diphenylphosphinic amide) (**11b**)

^{31}P NMR (202 MHz, $CDCl_3$)

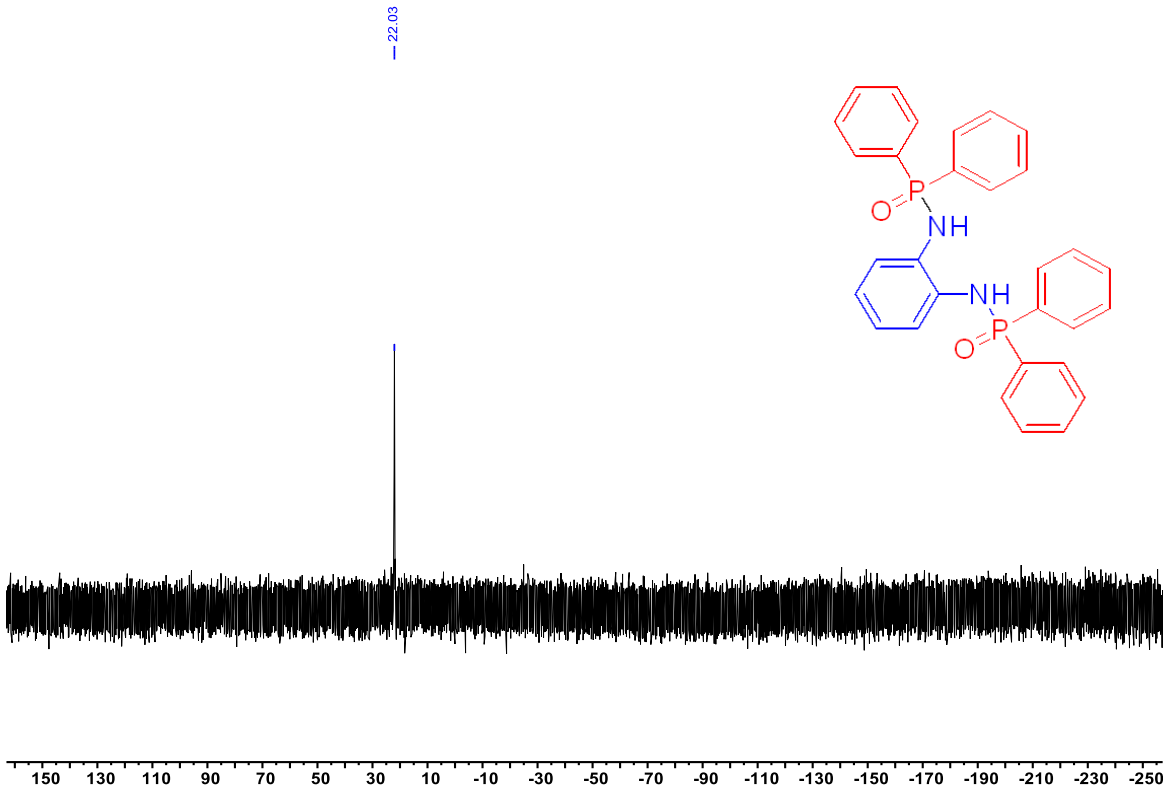


Figure S120: 2-hydroxyphenyl diphenylphosphinate (**12**)

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

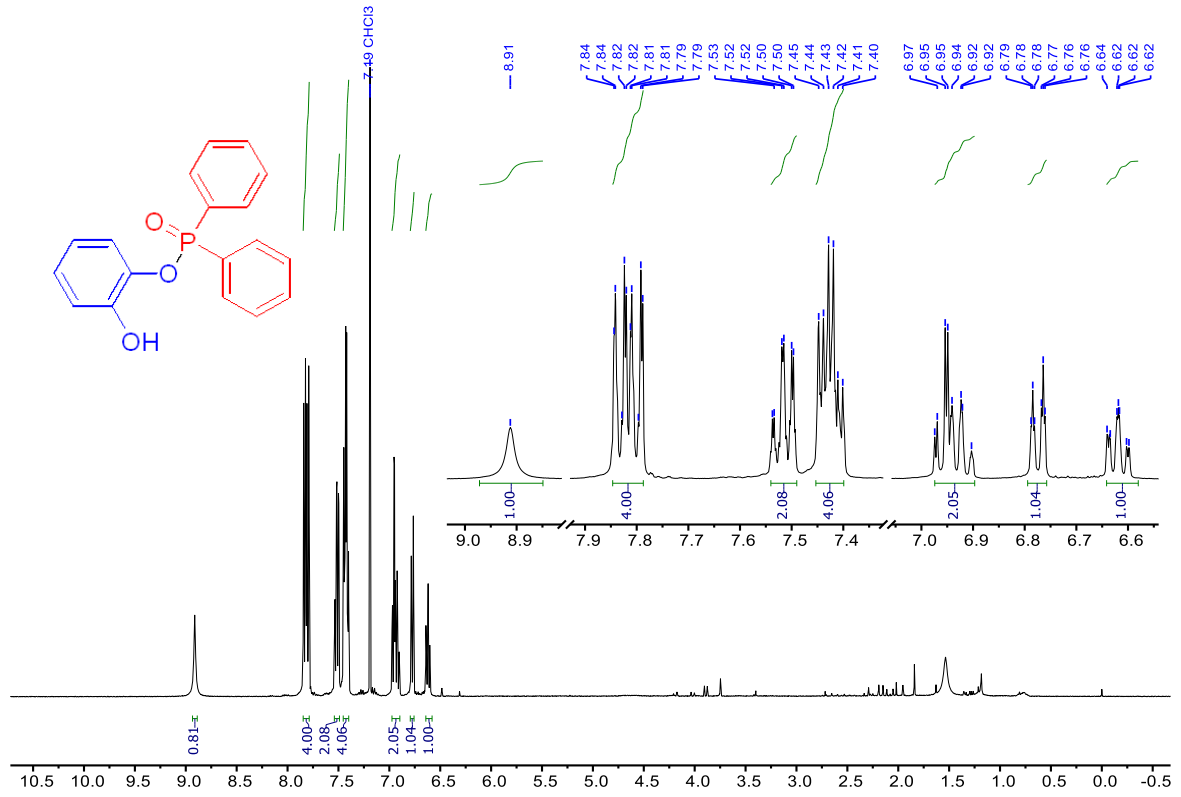


Figure S121: 2-hydroxyphenyl diphenylphosphinate (**12**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

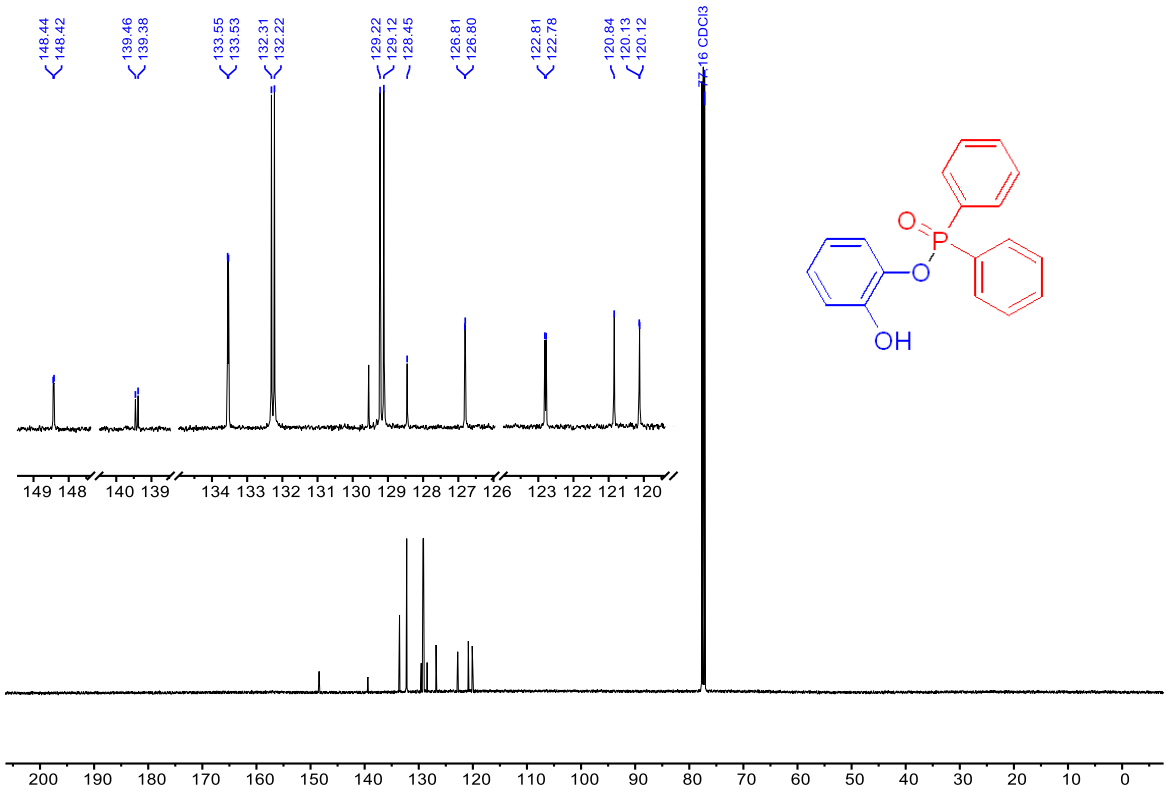


Figure S122: 2-hydroxyphenyl diphenylphosphinate (**12**)

^{31}P NMR spectrum (162 MHz, $CDCl_3$)

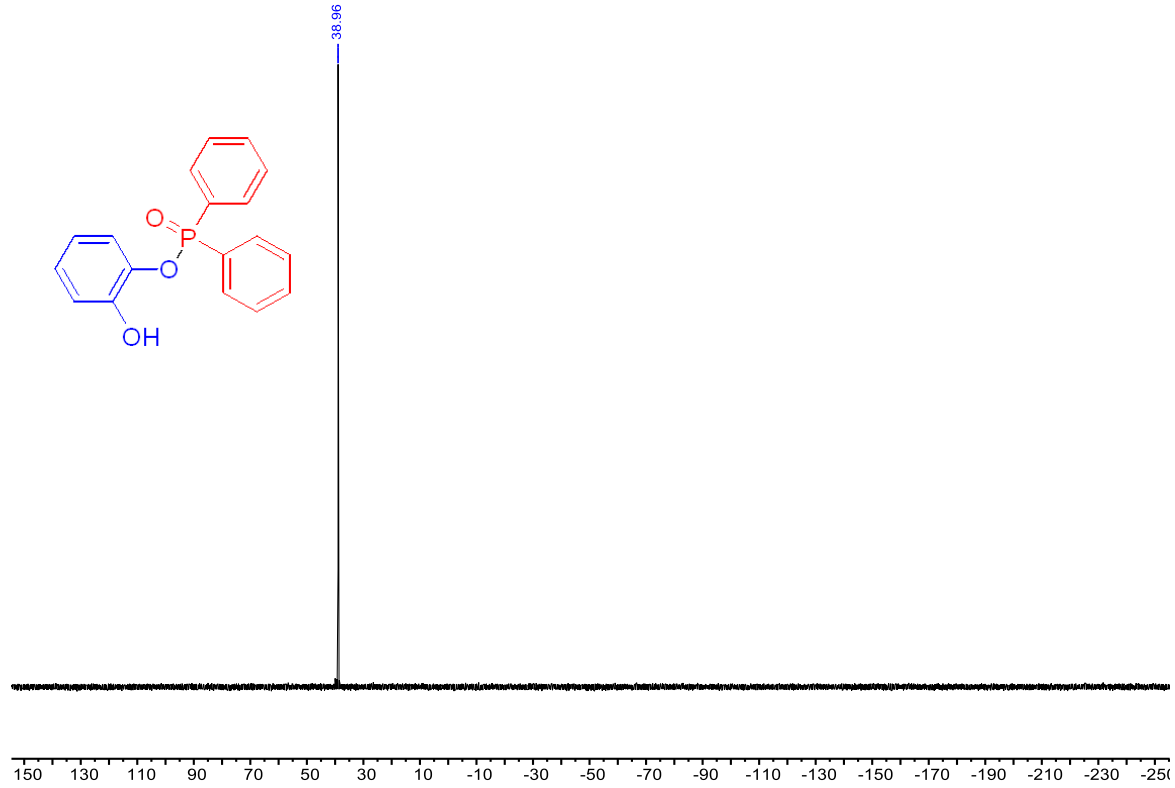


Figure S123: *N*-(2-methyl-1*H*-indol-5-yl)-*P*,*P*-diphenylphosphinic amide (**13**)

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

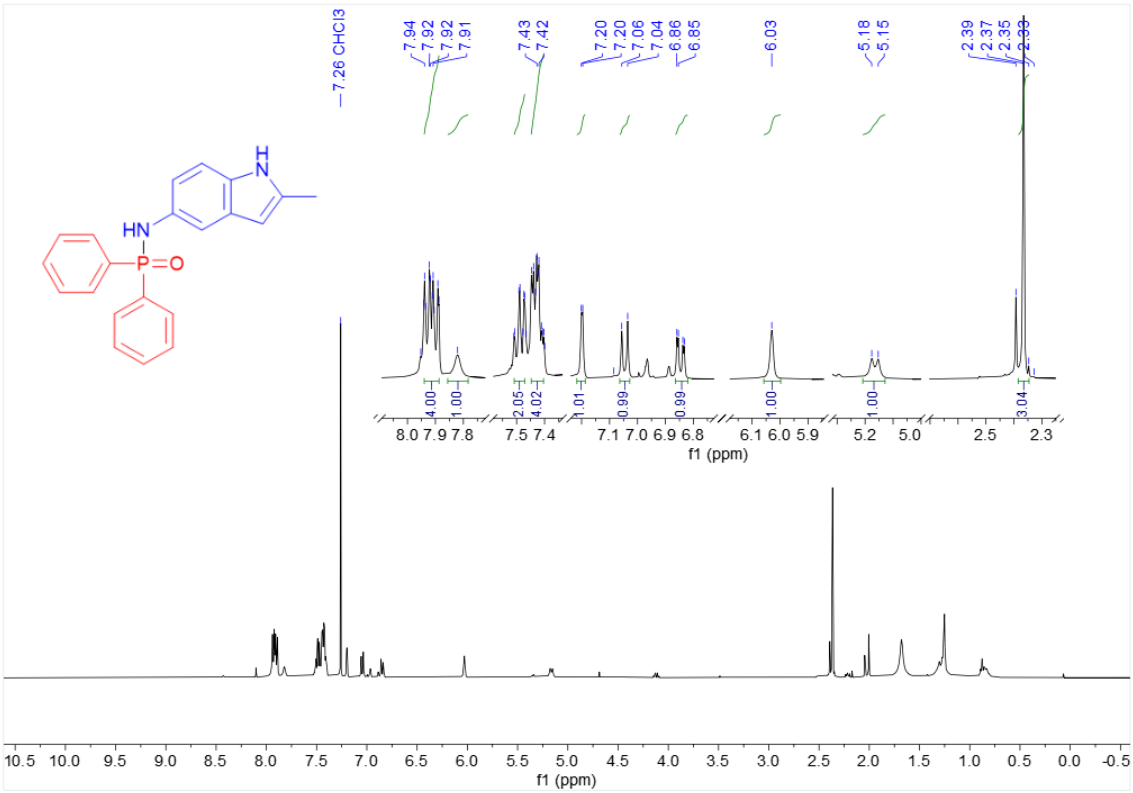


Figure S124: *N*-(2-methyl-1*H*-indol-5-yl)-*P*,*P*-diphenylphosphinic amide (**13**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

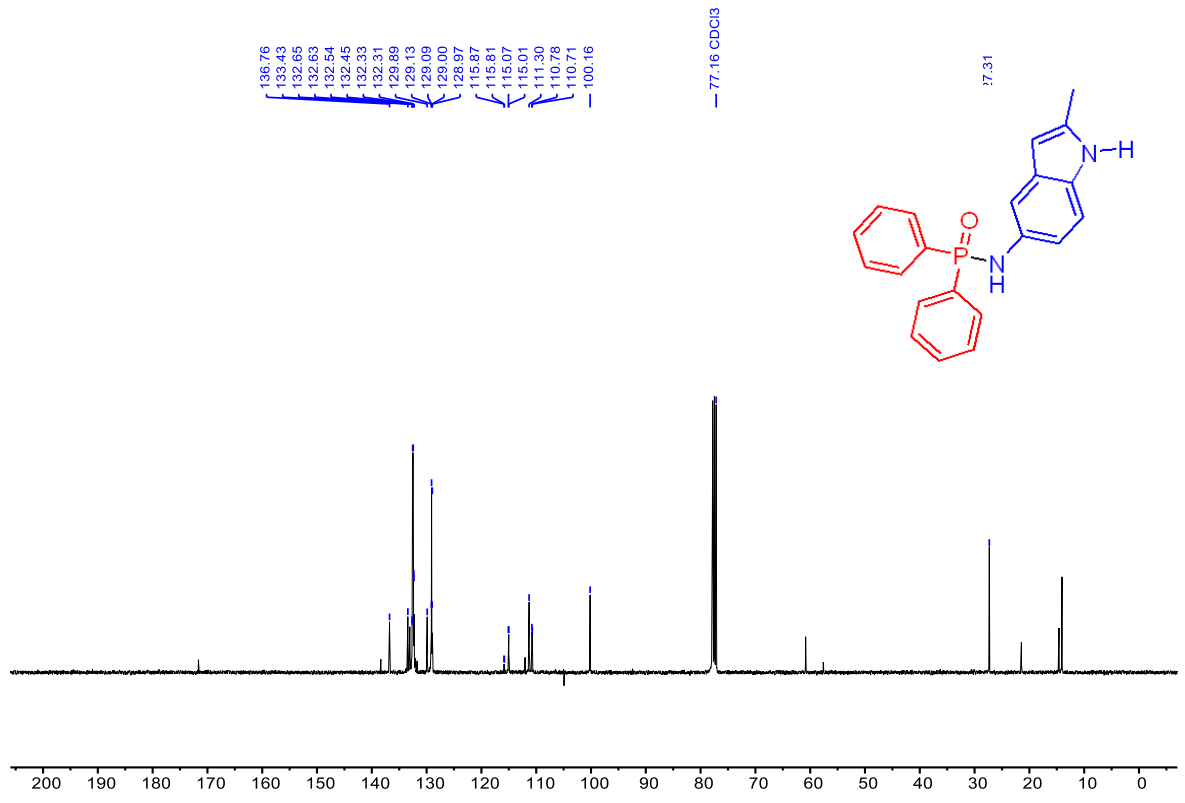


Figure S125: *N*-(2-methyl-1*H*-indol-5-yl)-*P*,*P*-diphenylphosphinic amide (**13**)

^{31}P NMR spectrum (162 MHz, $CDCl_3$)

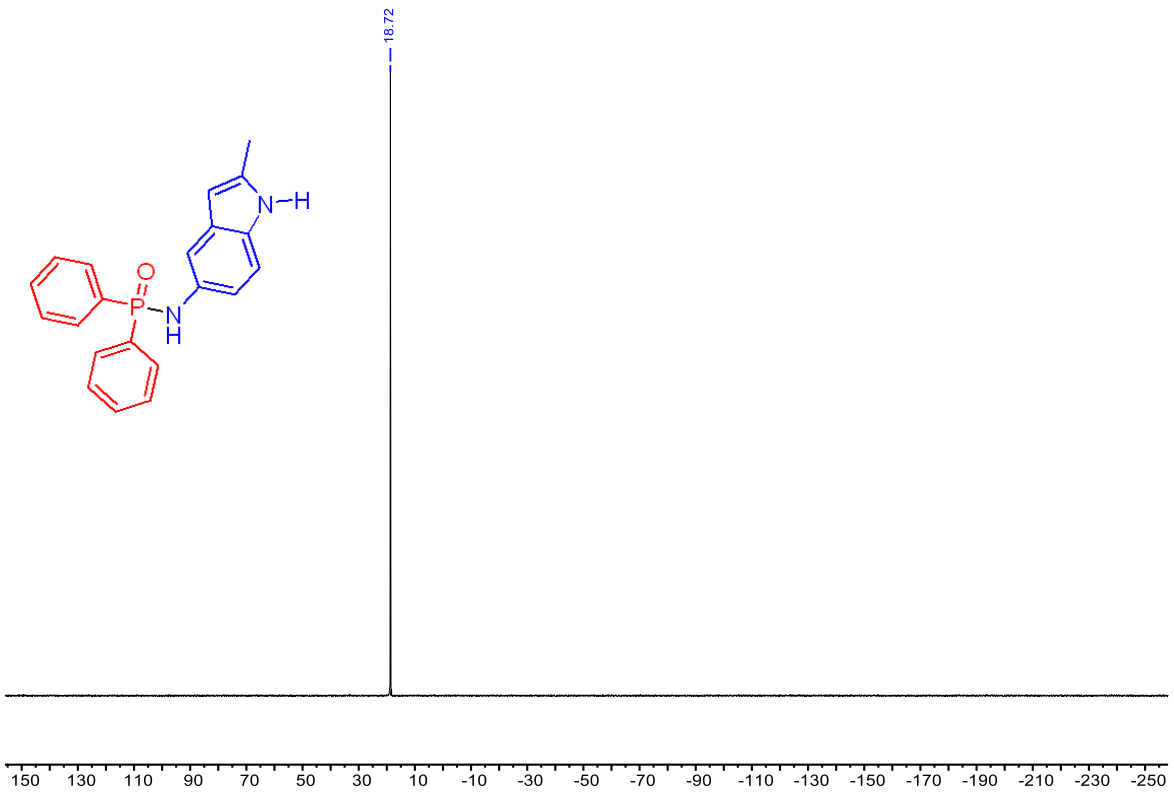


Figure S126: 2-methyl-1*H*-indol-5-yl diphenylphosphinate (**14**)

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

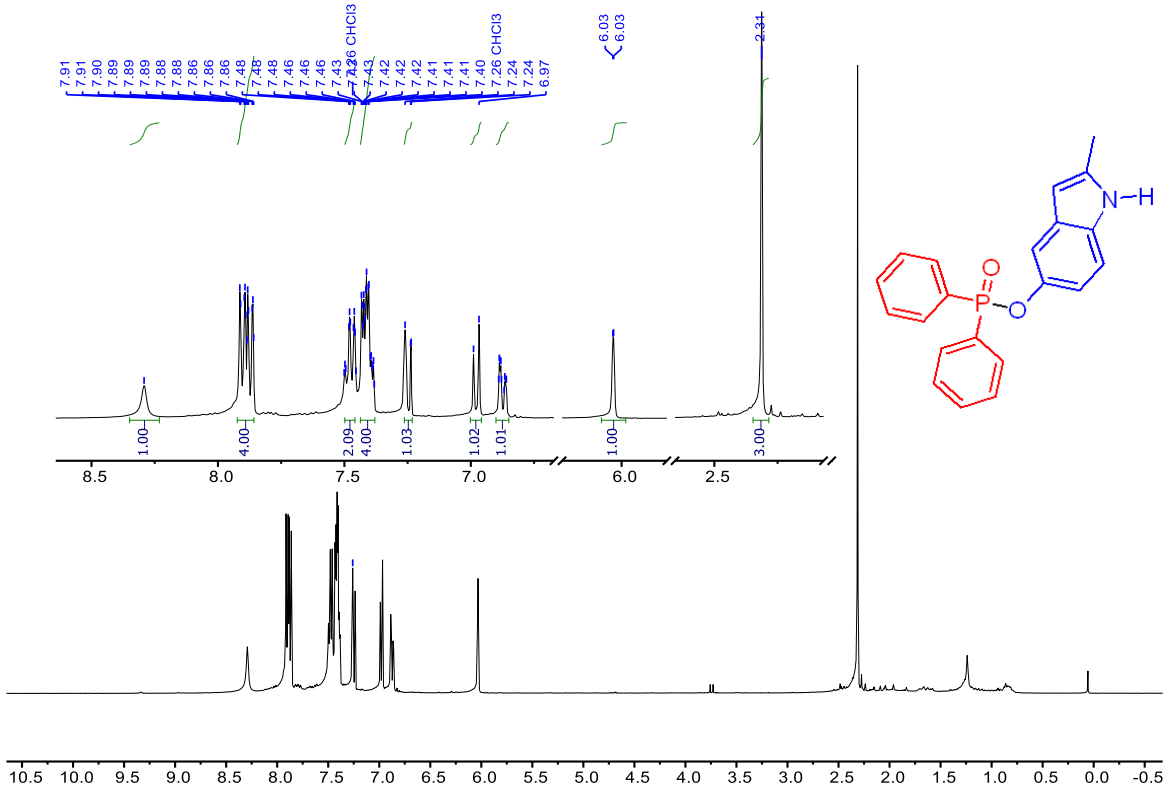


Figure S127: 2-methyl-1*H*-indol-5-yl diphenylphosphinate (**14**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

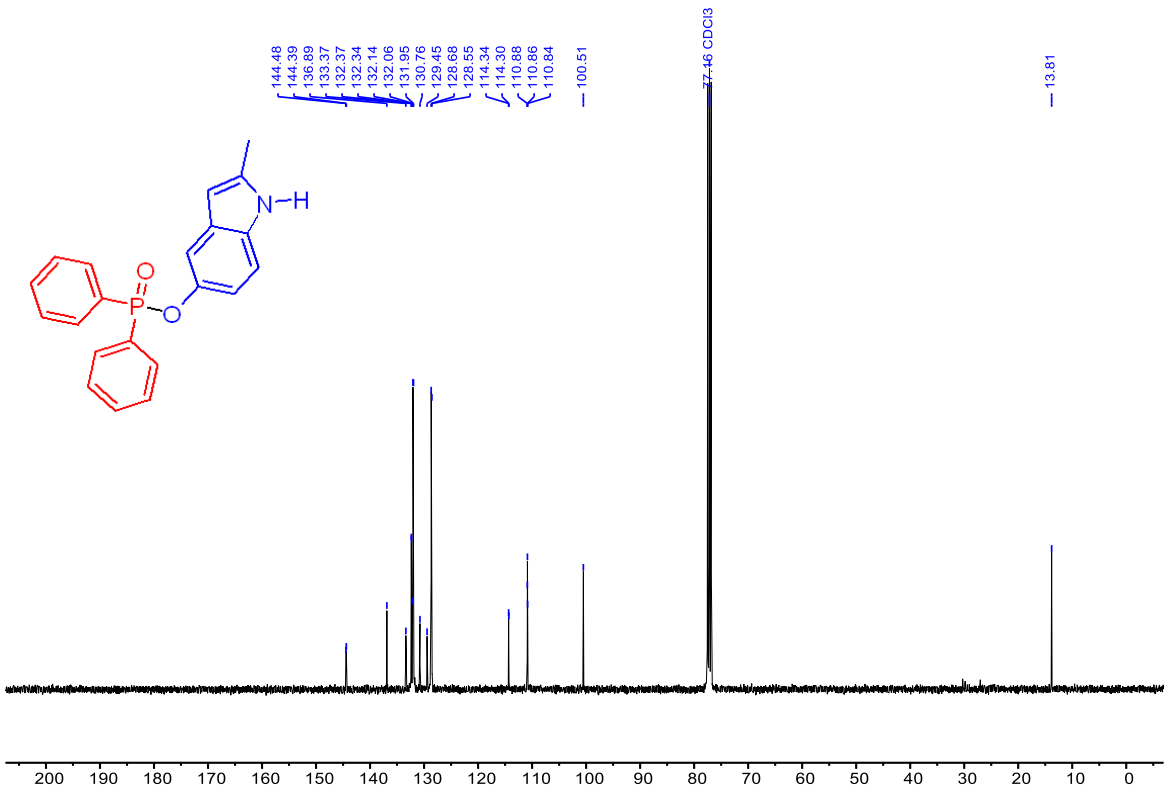


Figure S128: 2-methyl-1*H*-indol-5-yl diphenylphosphinate (**14**)

^{31}P NMR spectrum (162 MHz, $CDCl_3$)

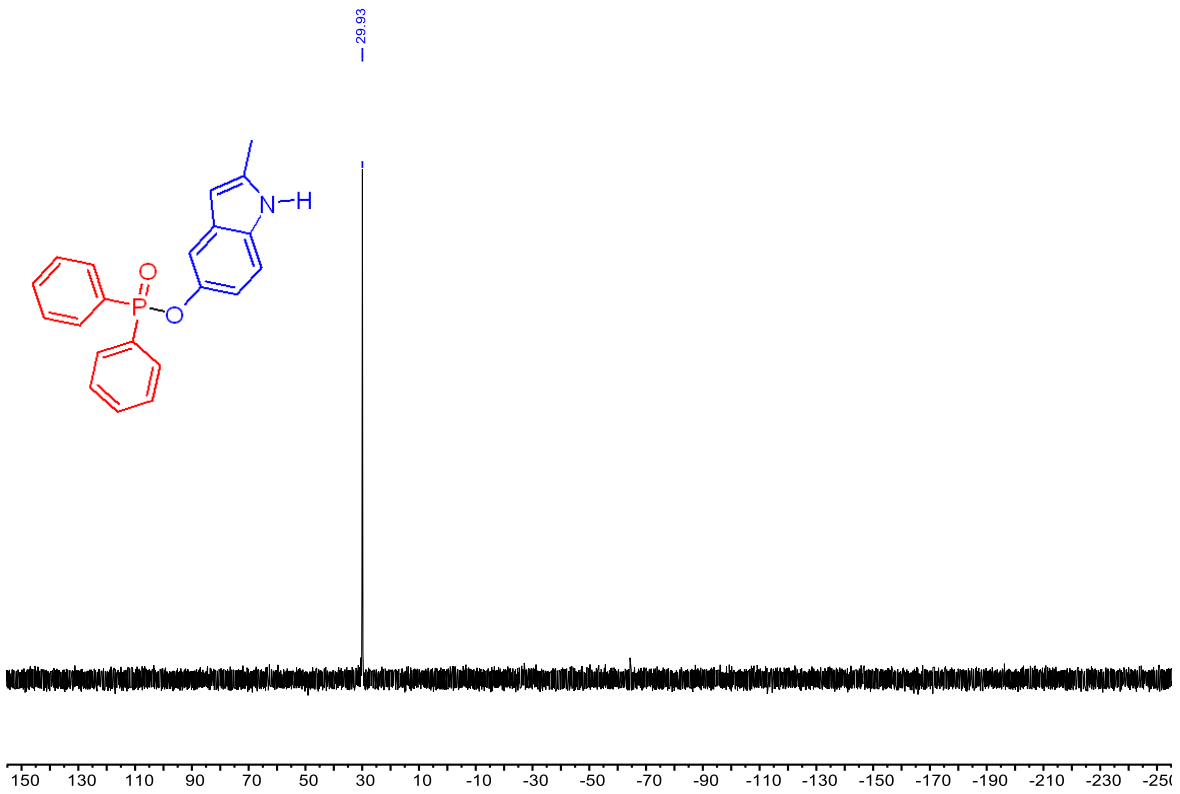


Figure S129: (9*H*-carbazol-9-yl)diphenylphosphine oxide (**15**)

^{1}H NMR (500 MHz, $CDCl_3$)

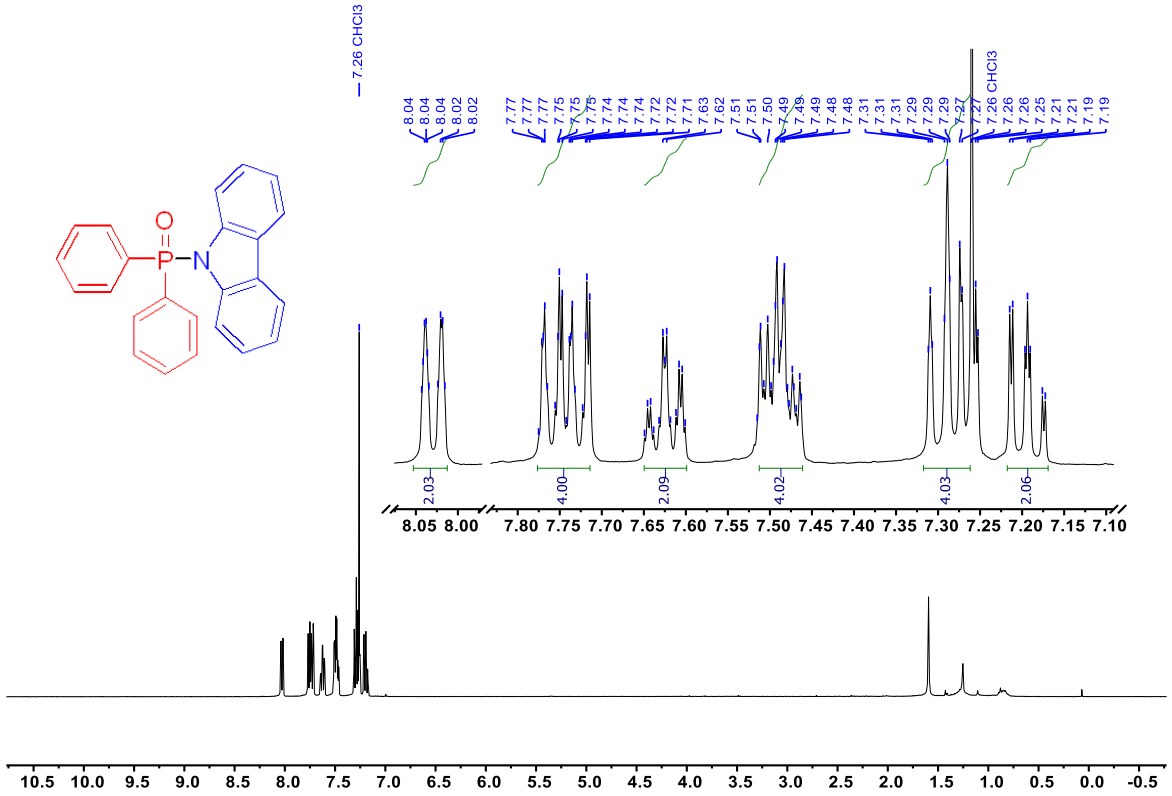


Figure S130: (9*H*-carbazol-9-yl)diphenylphosphine oxide (**15**)

^{13}C NMR (126 MHz, $CDCl_3$)

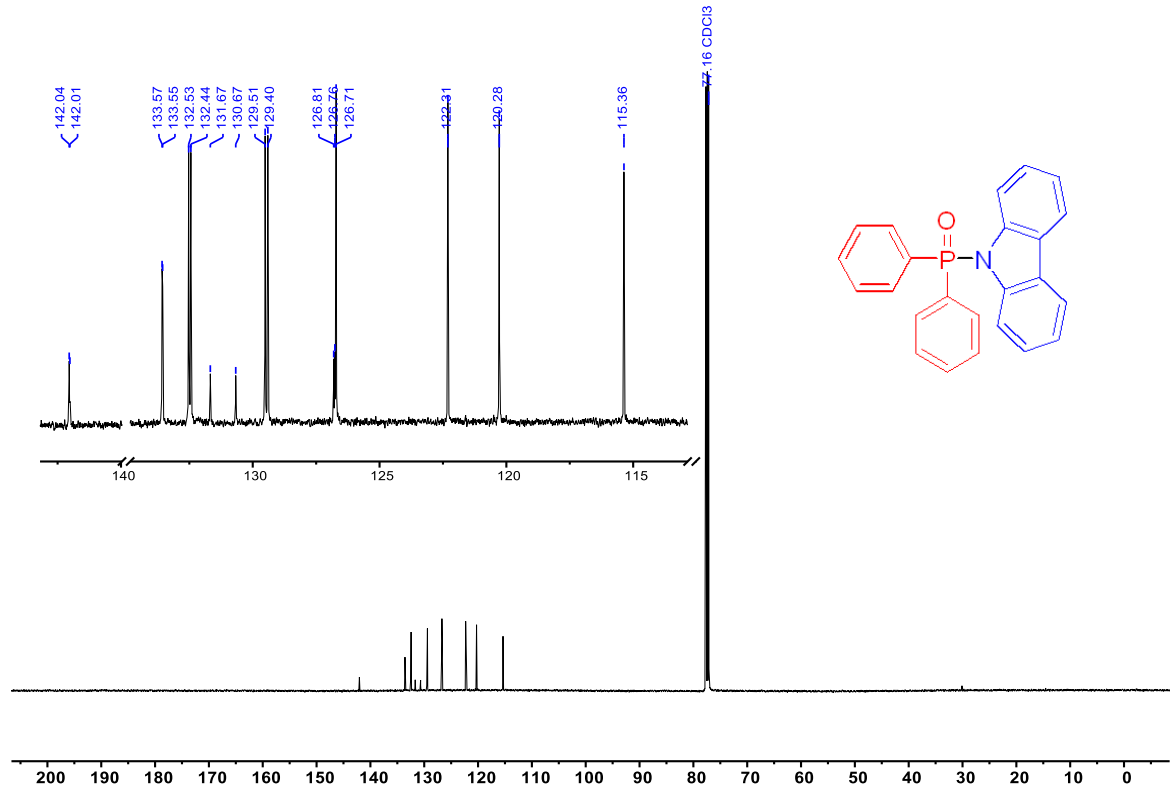


Figure S131: (9*H*-carbazol-9-yl)diphenylphosphine oxide (**15**)

^{31}P NMR (162 MHz, $CDCl_3$)

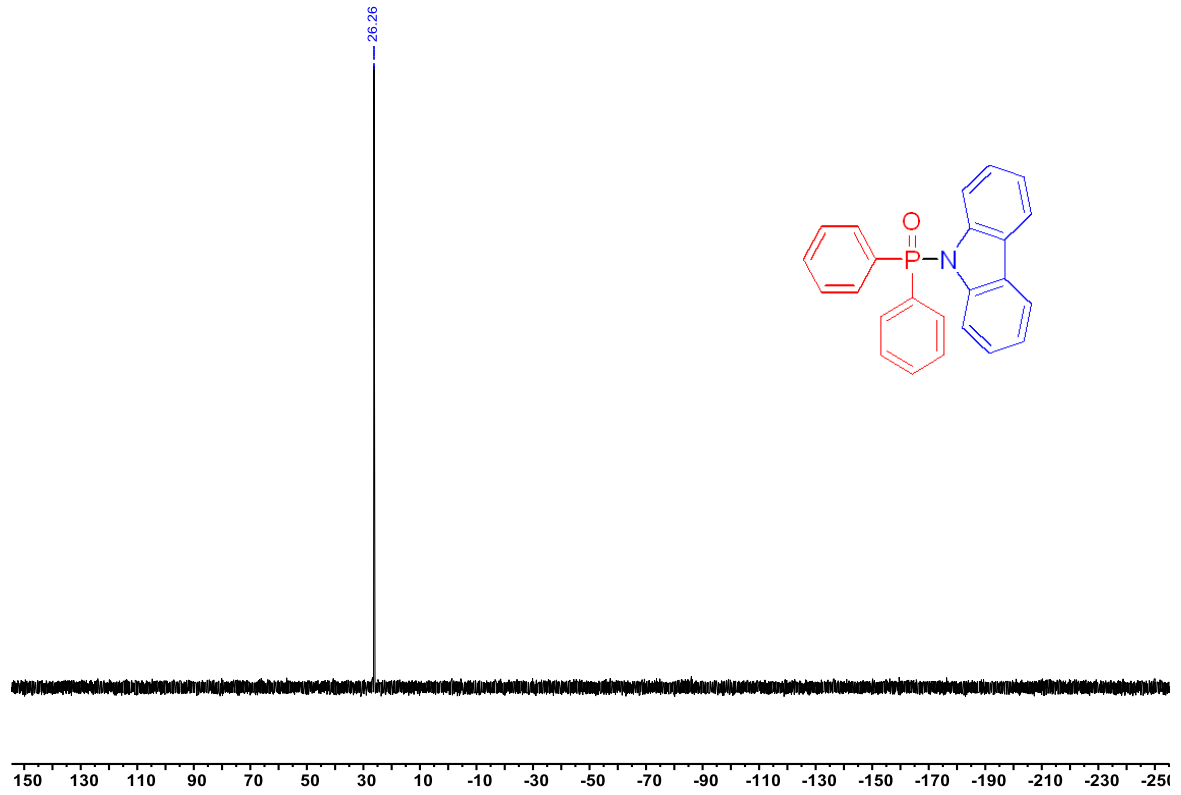


Figure S132: S-phenyl diphenylphosphinothioate (**16**)

^{1}H NMR (500 MHz, $CDCl_3$)

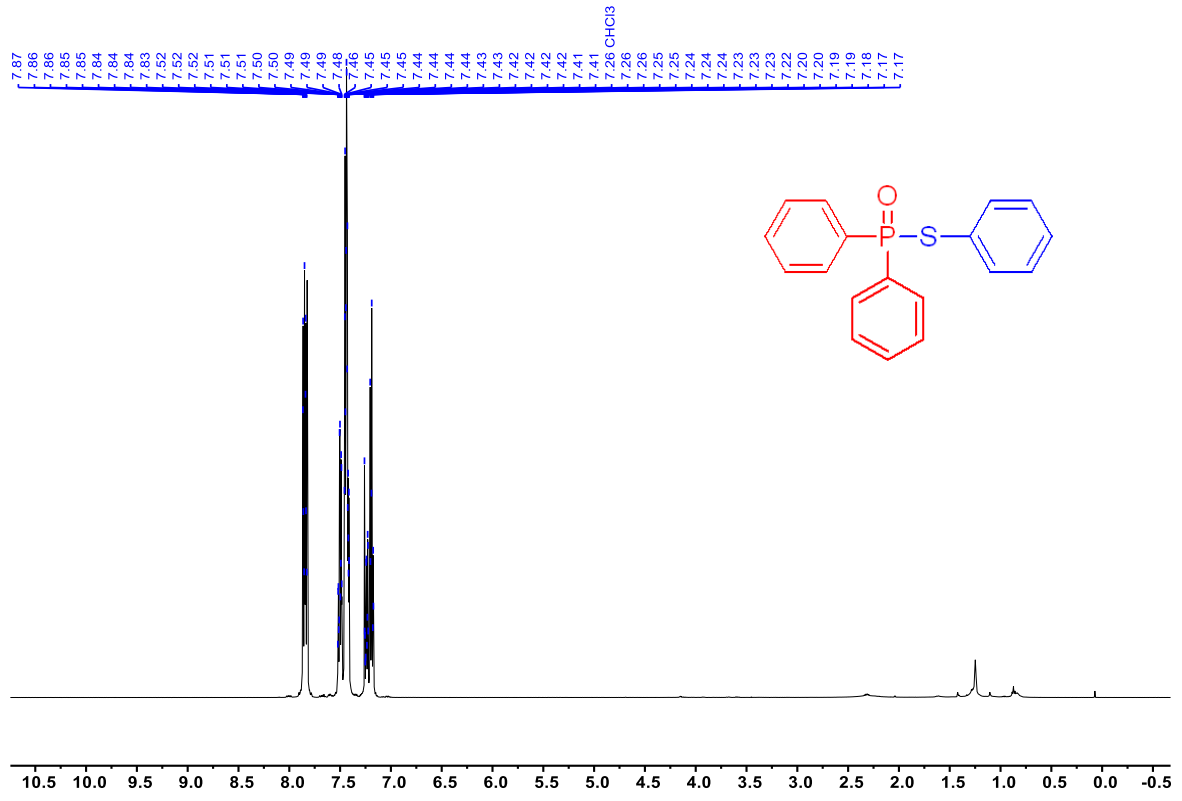


Figure S133: S-phenyl diphenylphosphinothioate (**16**)

^{13}C NMR (126 MHz, $CDCl_3$)

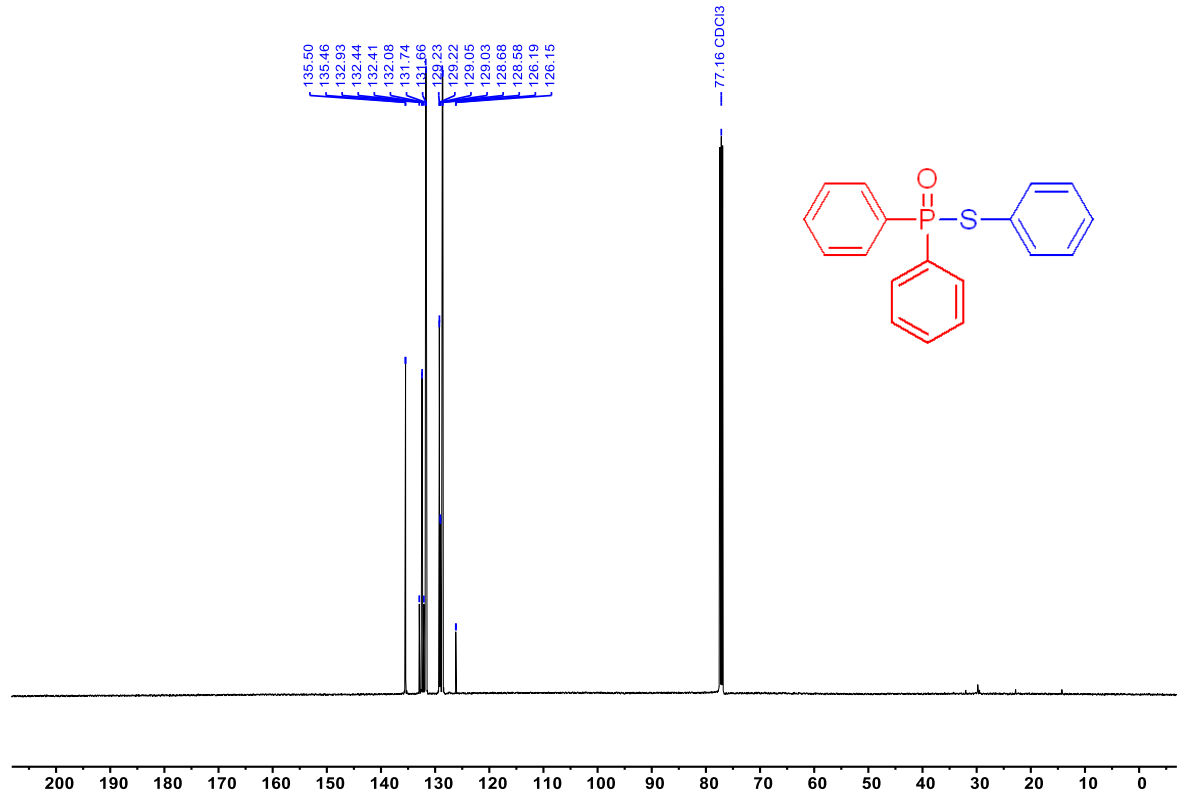


Figure S134: S-phenyl diphenylphosphinothioate (**16**)

^{31}P NMR (202 MHz, $CDCl_3$)

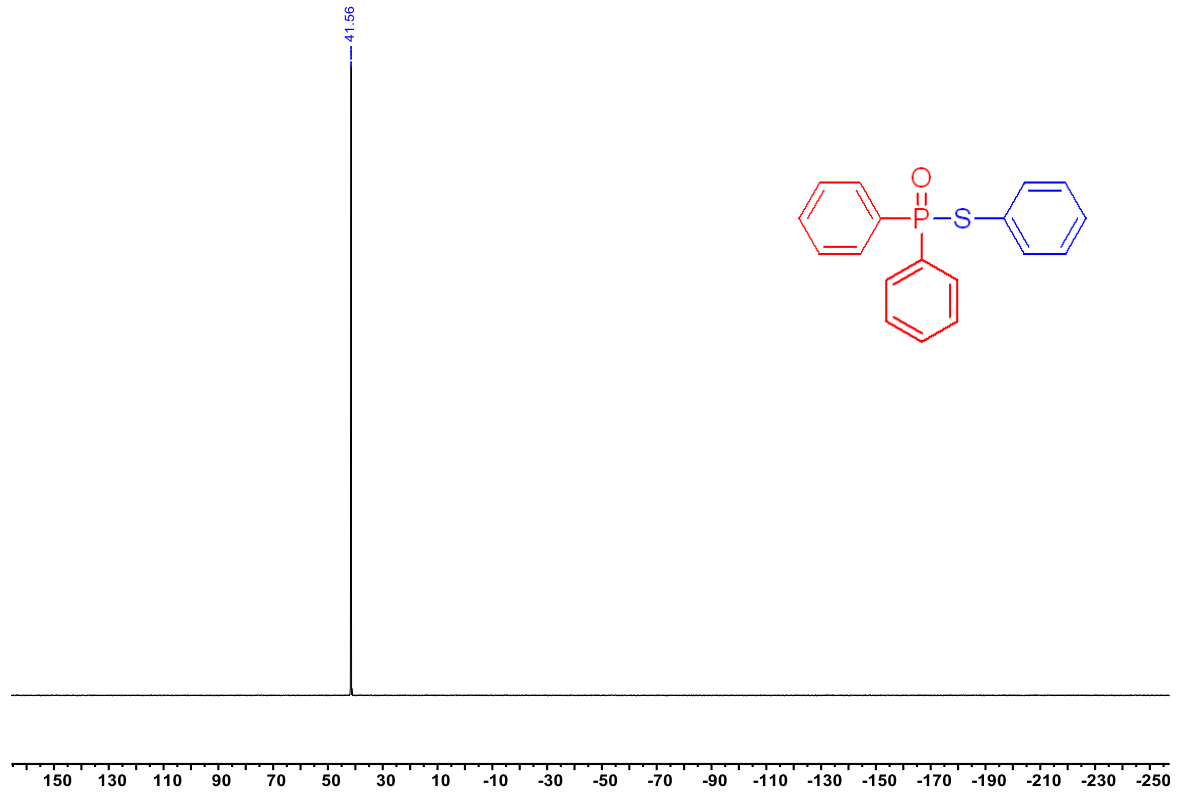


Figure S135: ethyl 4-((diphenylphosphoryl)amino)benzoate (**17**)[2]

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

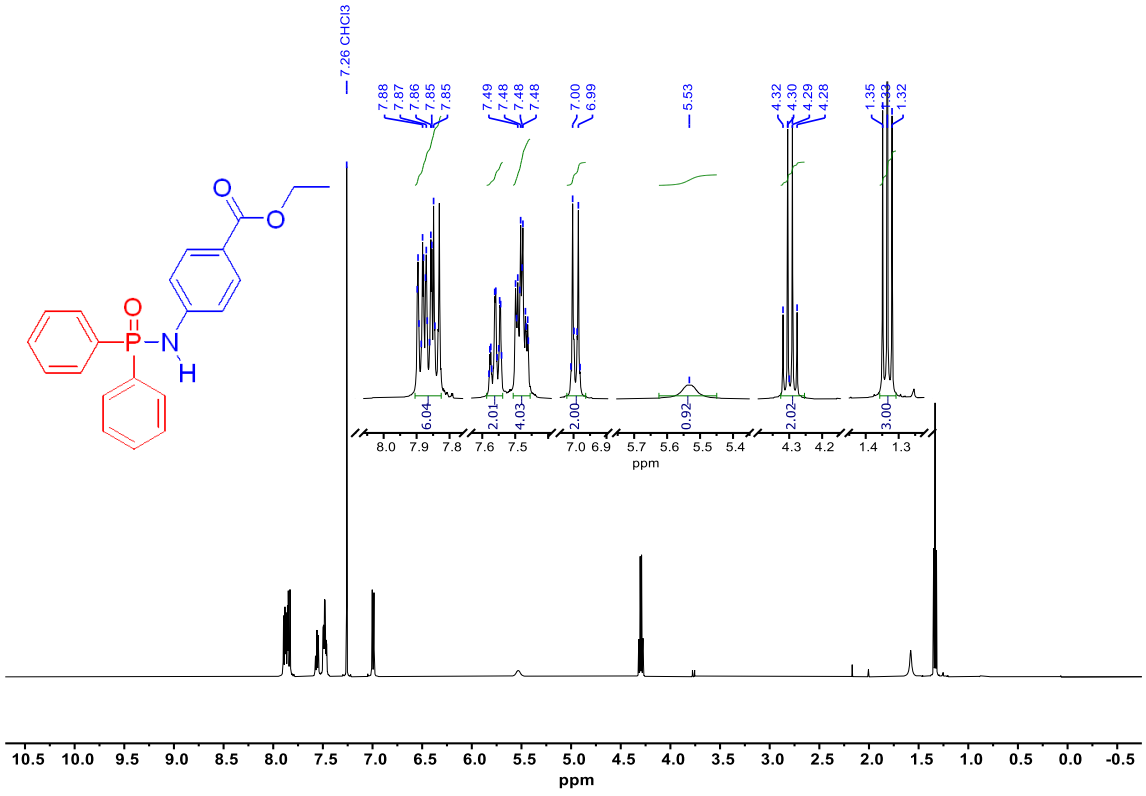


Figure S136: ethyl 4-((diphenylphosphoryl)amino)benzoate (**17**)[2]

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

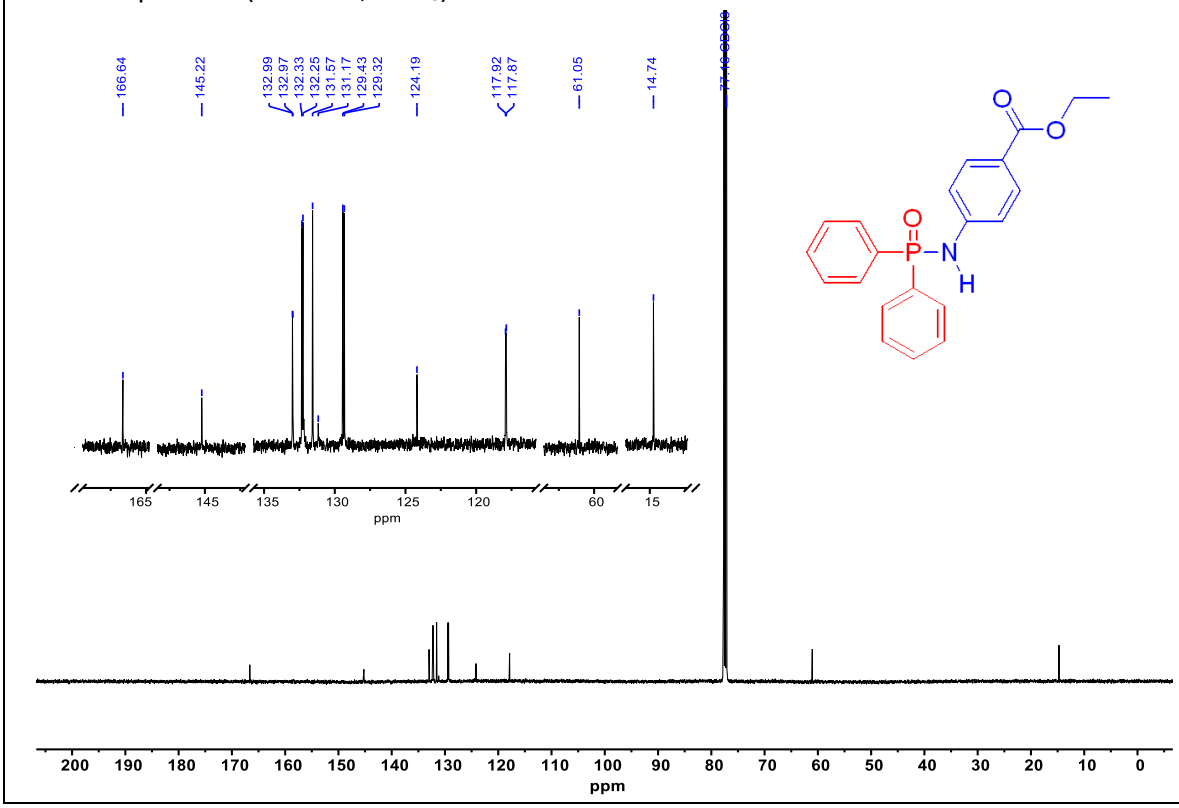


Figure S137: ethyl 4-((diphenylphosphoryl)amino)benzoate (**17**)[2]

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

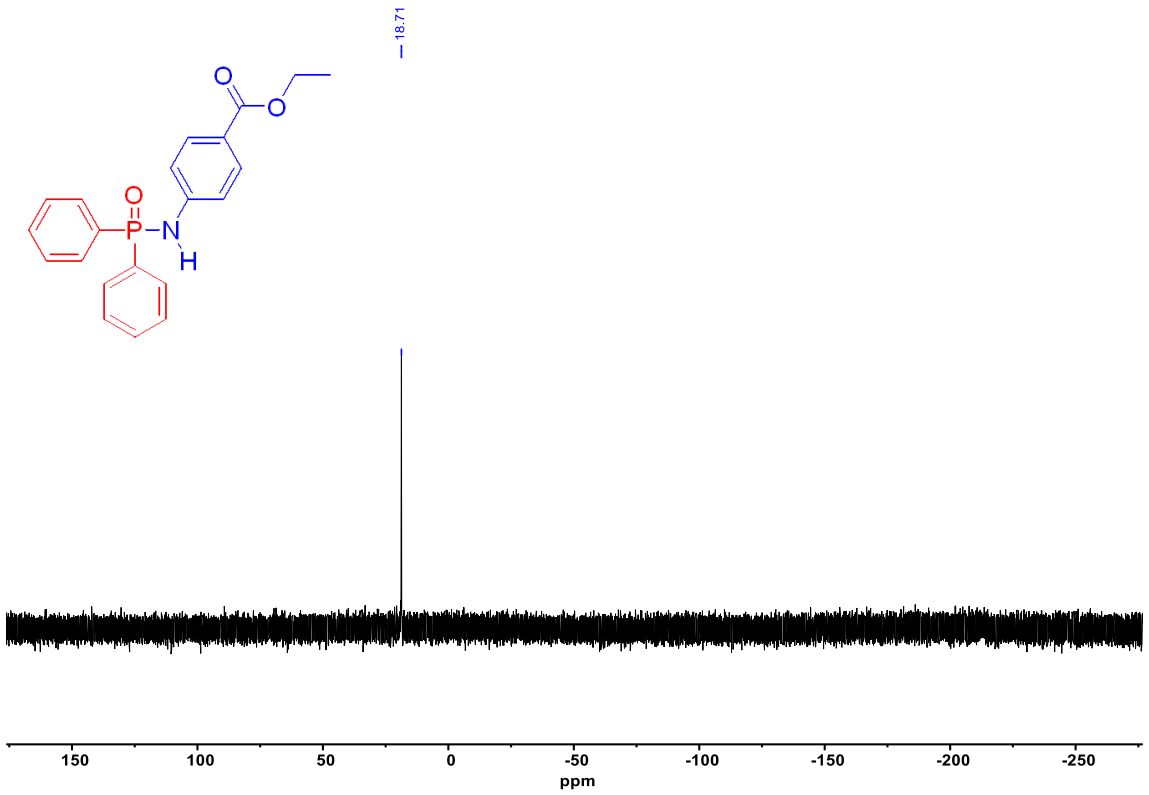


Figure S138: 4-acetamidophenyl diphenylphosphinate (**18**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

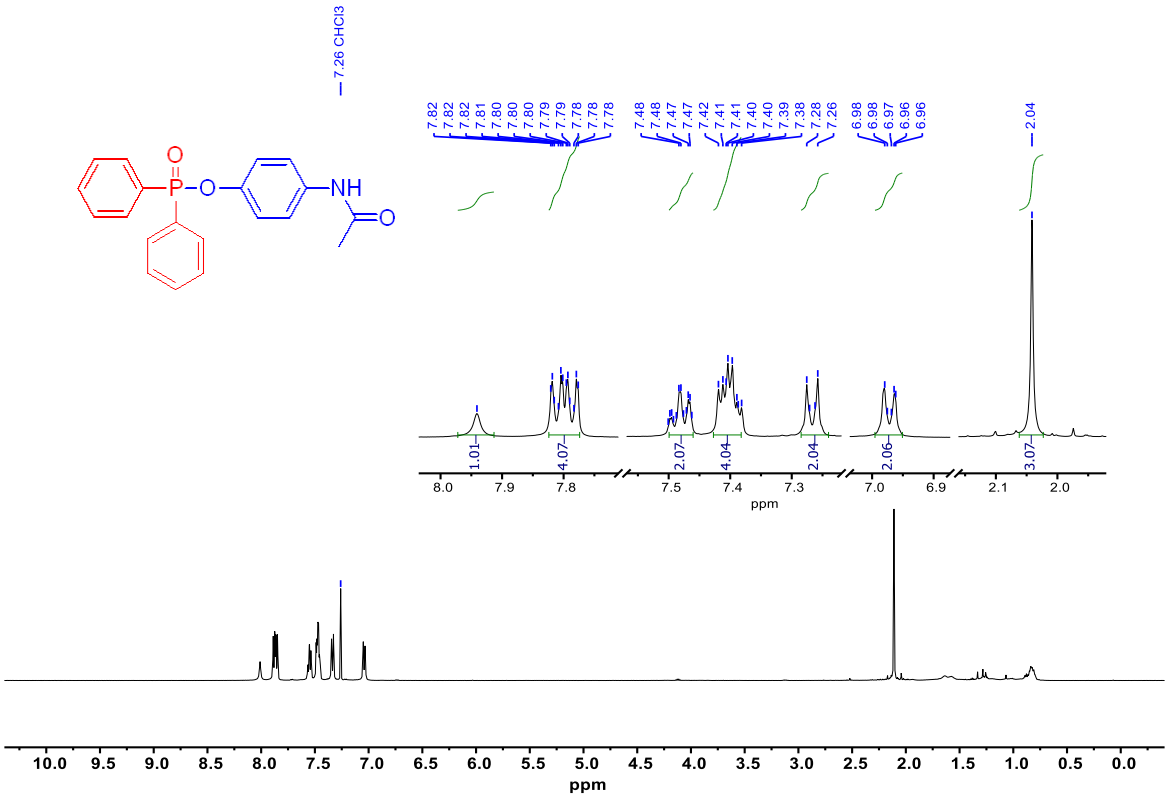


Figure S139: 4-acetamidophenyl diphenylphosphinate (**18**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

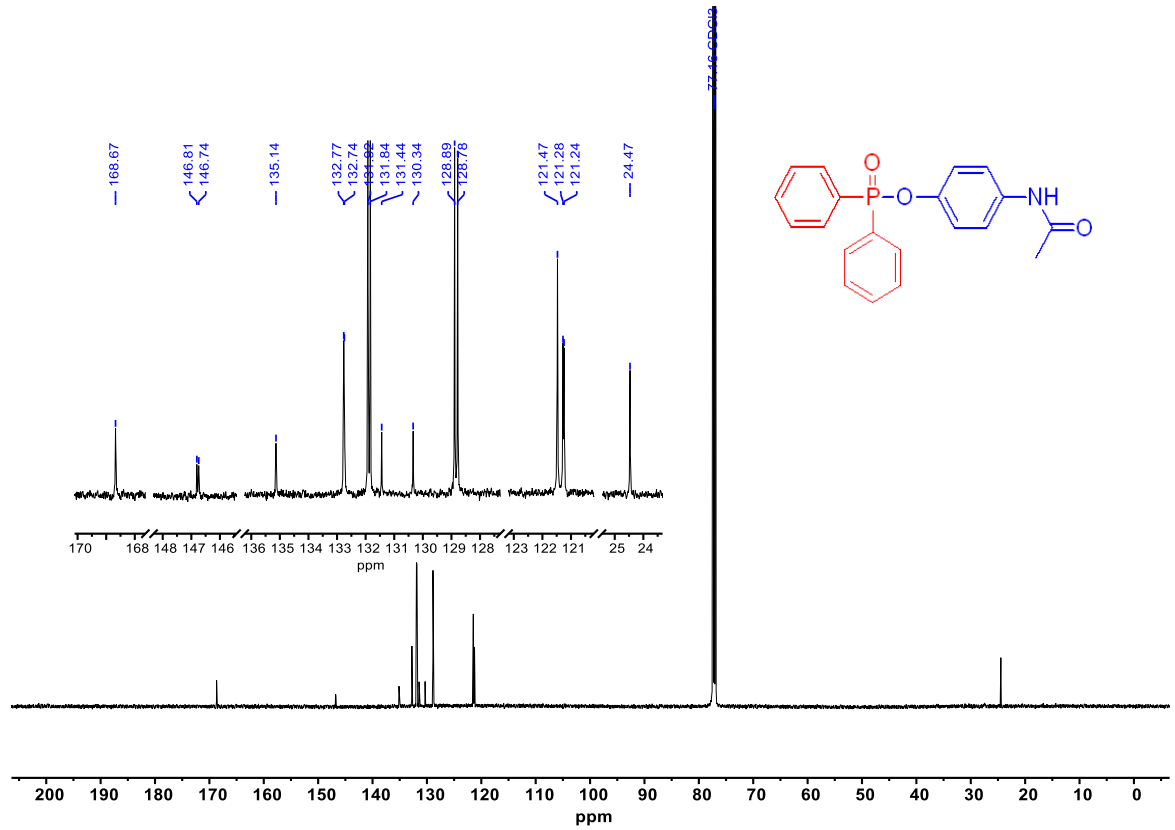


Figure S140: 4-acetamidophenyl diphenylphosphinate (**18**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

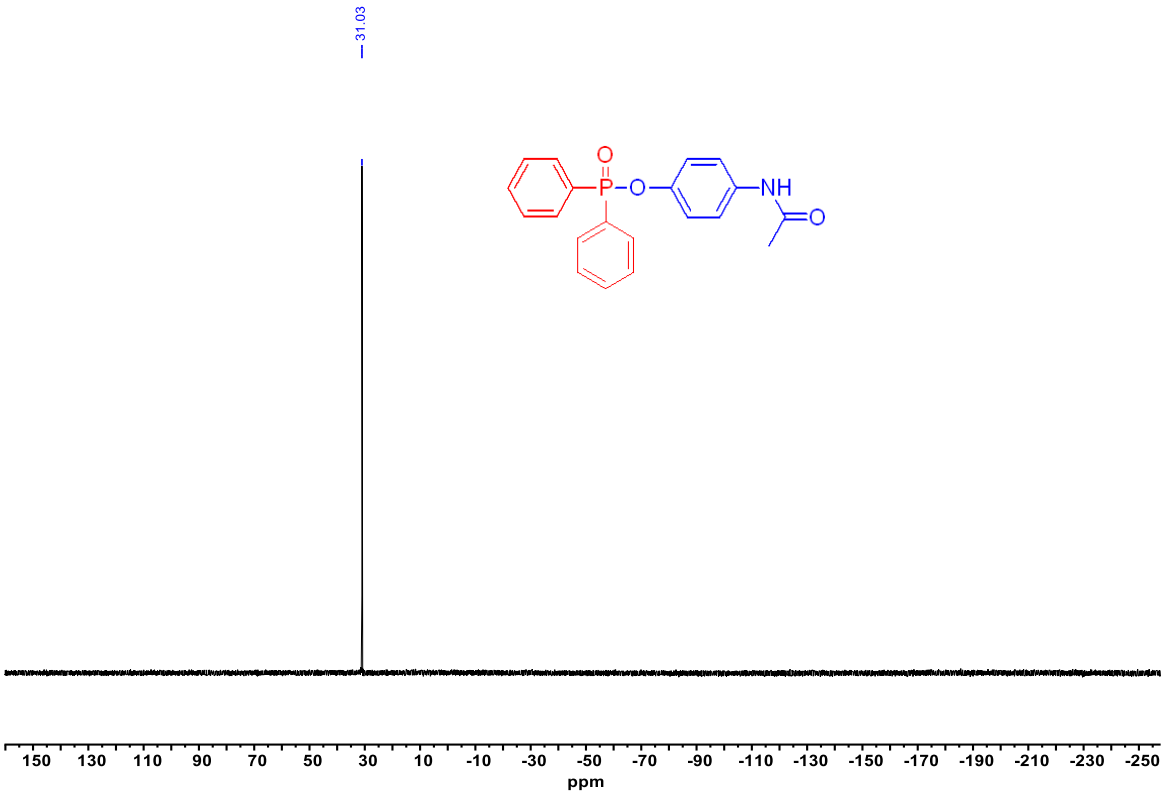


Figure S141: diphenyl (4-methoxyphenyl)phosphoramidate (**19a**)

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

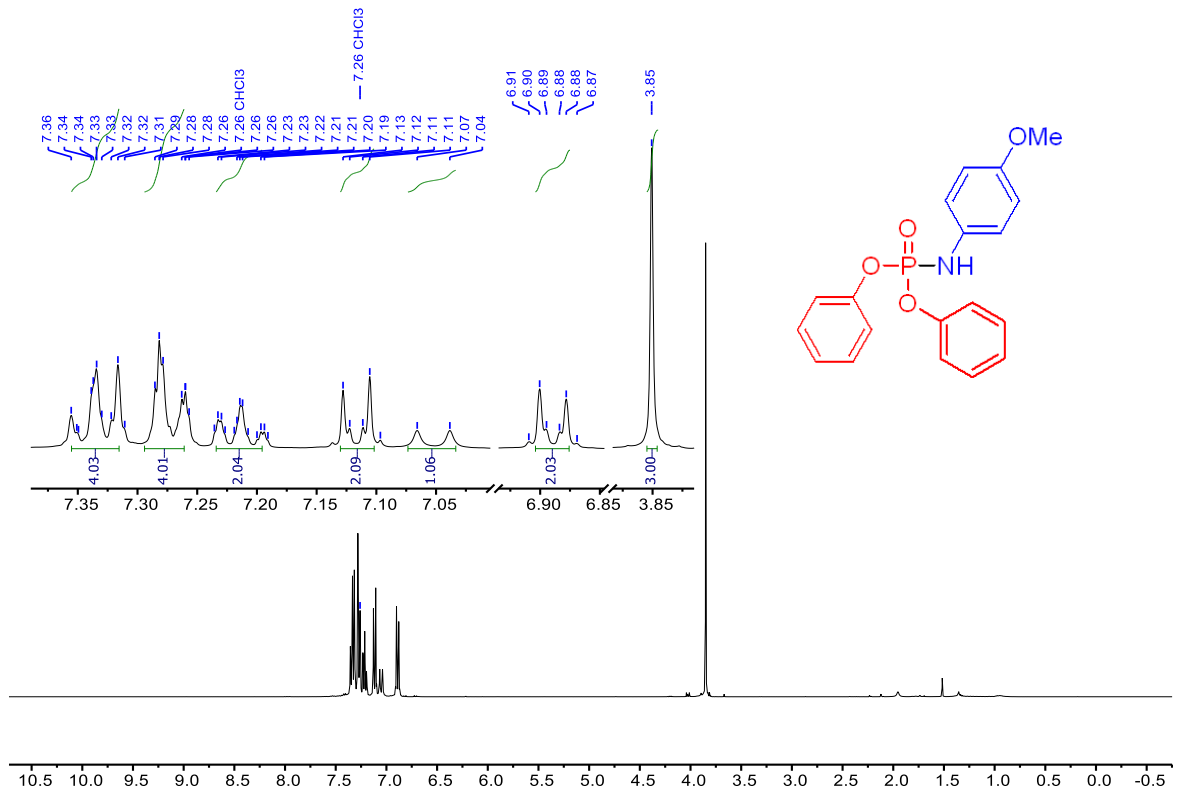


Figure S142: diphenyl (4-methoxyphenyl)phosphoramidate (**19a**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

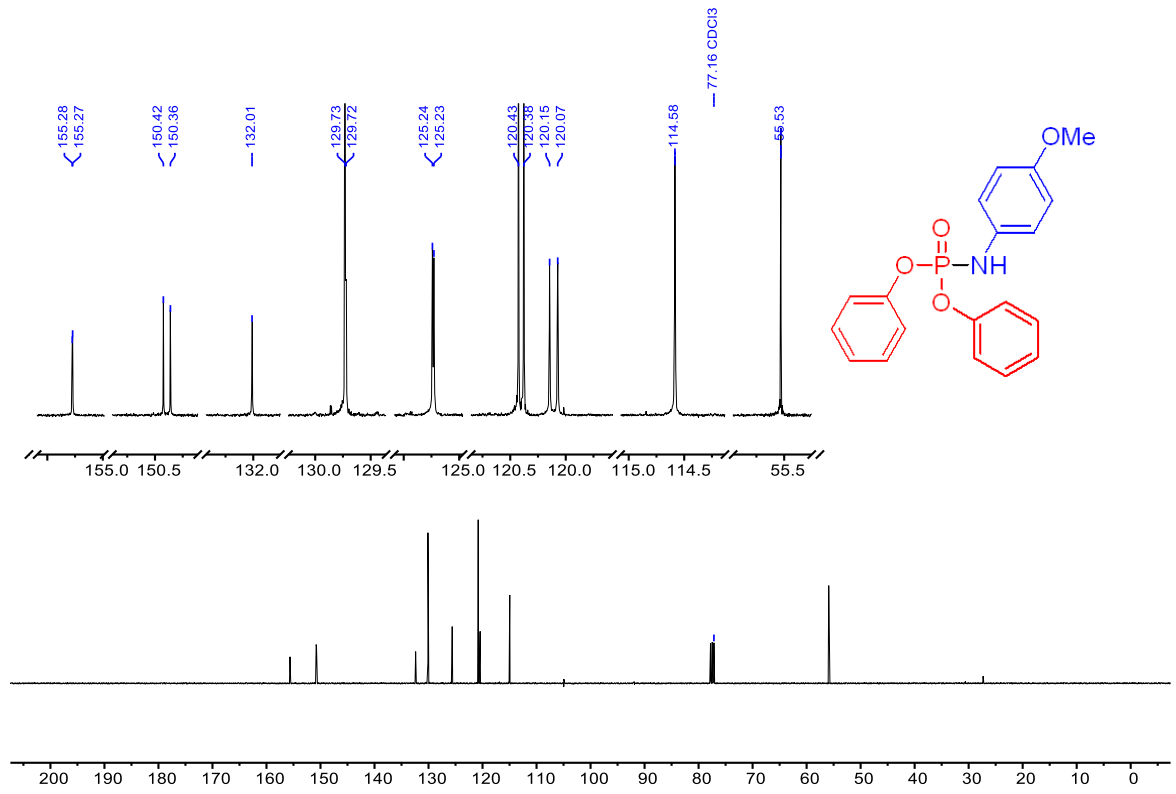


Figure S143: diphenyl (4-methoxyphenyl)phosphoramidate (**19a**)

^{31}P NMR spectrum (162 MHz, $CDCl_3$)

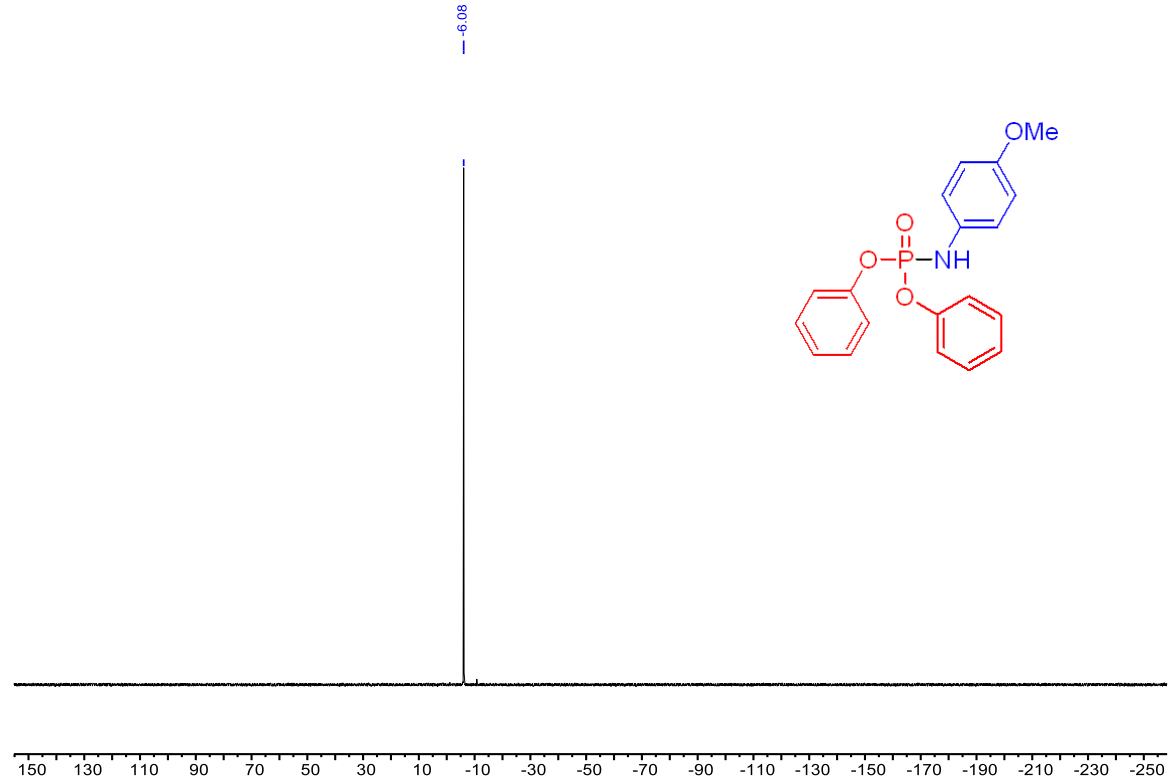


Figure S144: diphenyl mesitylphosphoramidate (**19b**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

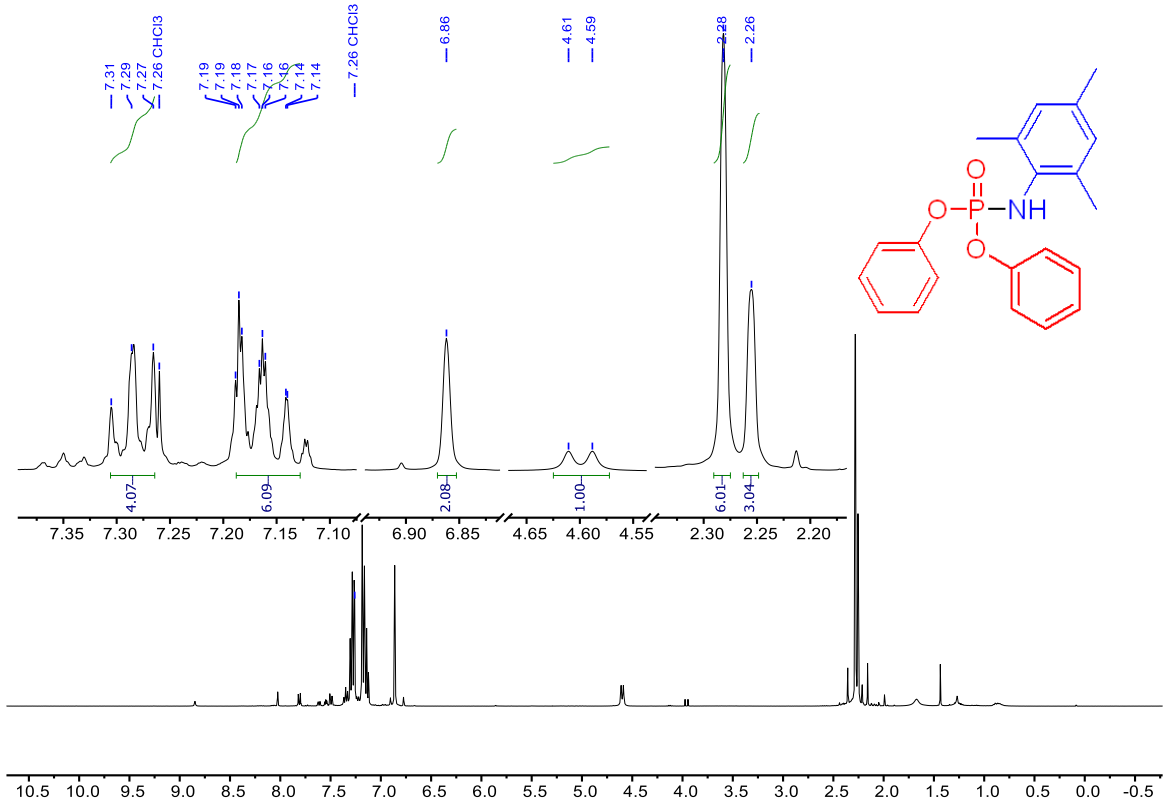


Figure S145: diphenyl mesitylphosphoramidate (**19b**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

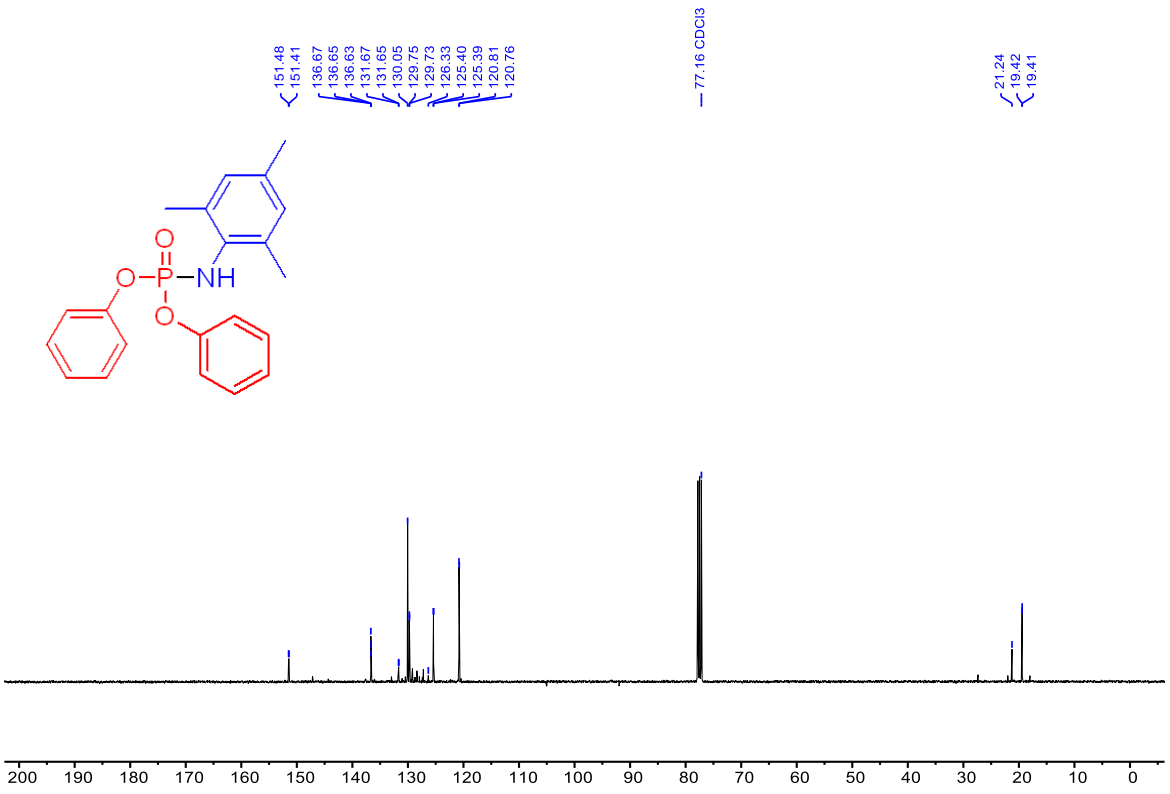


Figure S146: diphenyl mesitylphosphoramidate (**19b**)

^{31}P NMR spectrum (126 MHz, $CDCl_3$)

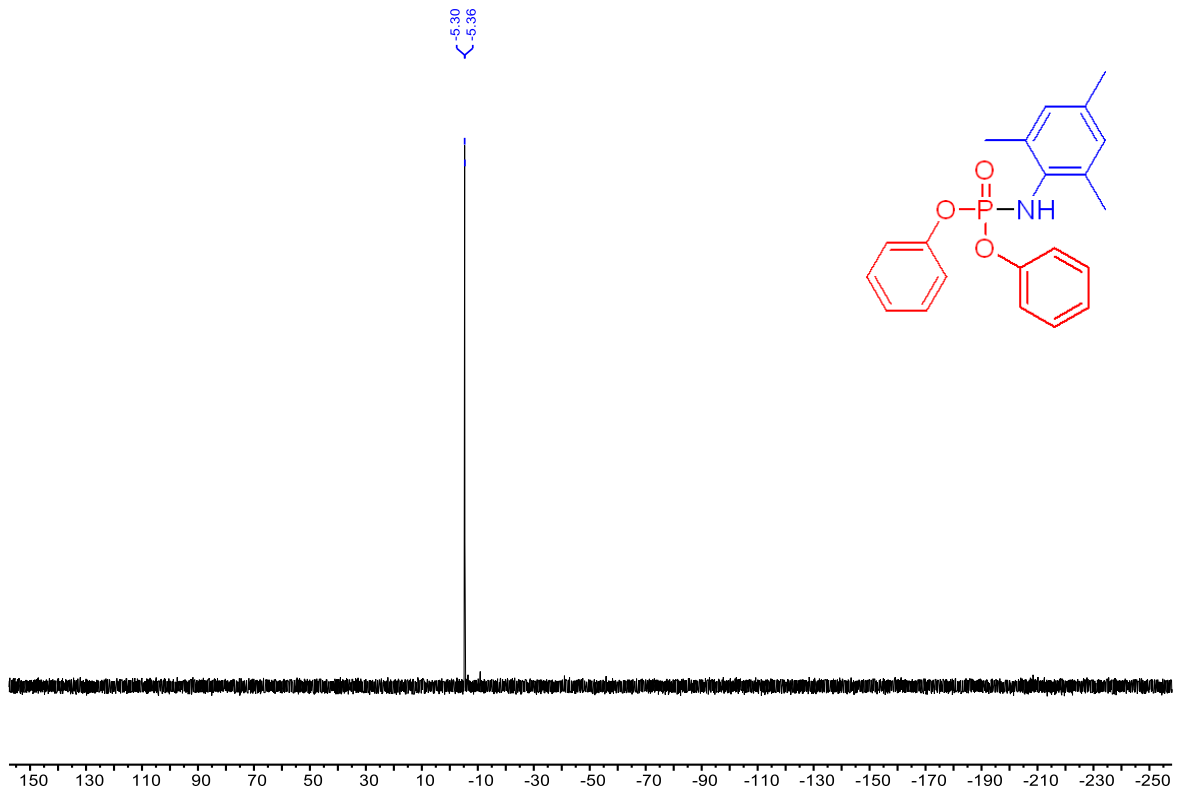


Figure S147: dibenzyl (4-methoxyphenyl)phosphoramidate (**20a**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

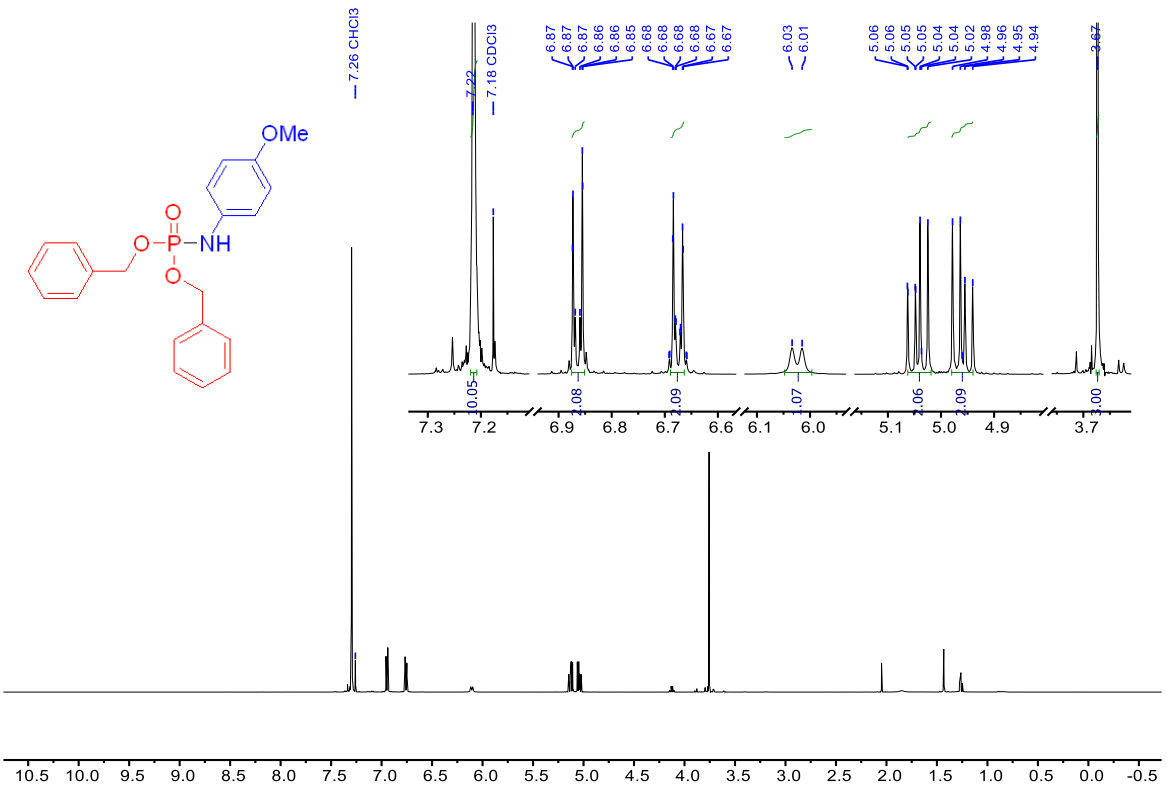


Figure S148: dibenzyl (4-methoxyphenyl)phosphoramidate (**20a**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

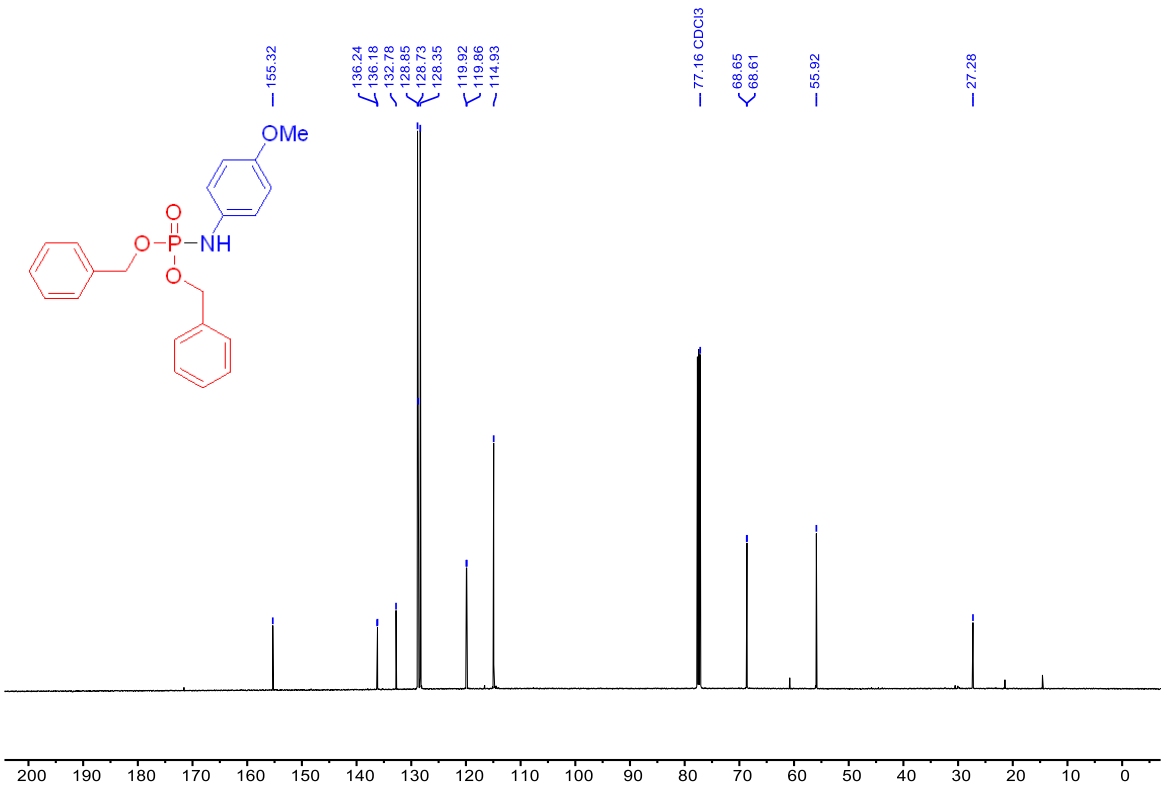


Figure S149: dibenzyl (4-methoxyphenyl)phosphoramidate (**20a**)

^{31}P NMR spectrum (126 MHz, $CDCl_3$)

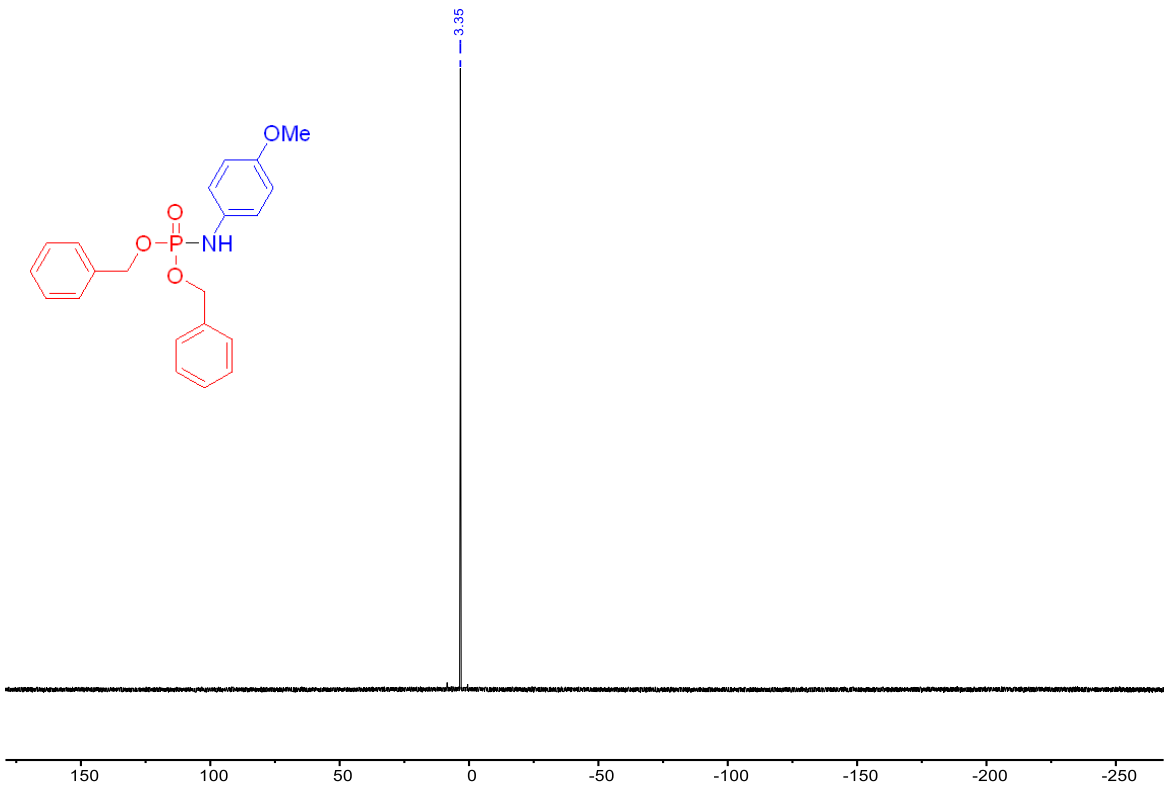


Figure S150: dibenzyl (3-methoxyphenyl)phosphoramidate (**20b**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

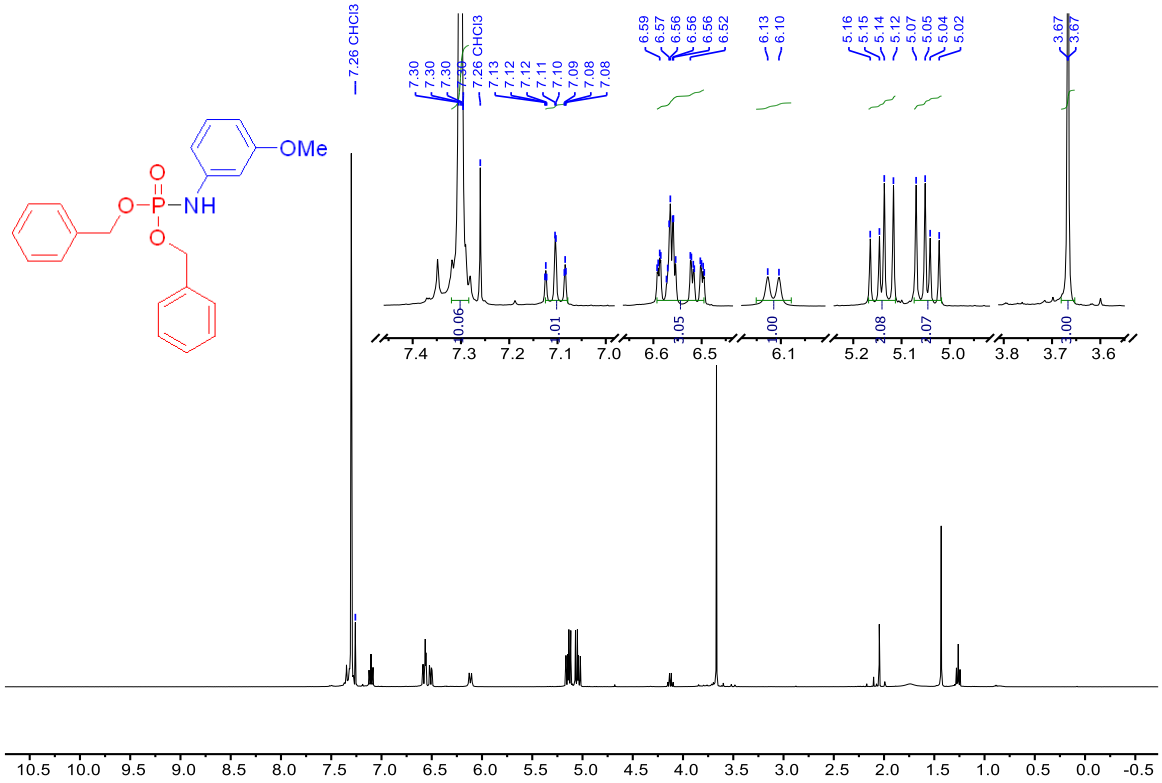


Figure S151: dibenzyl (3-methoxyphenyl)phosphoramidate (**20b**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

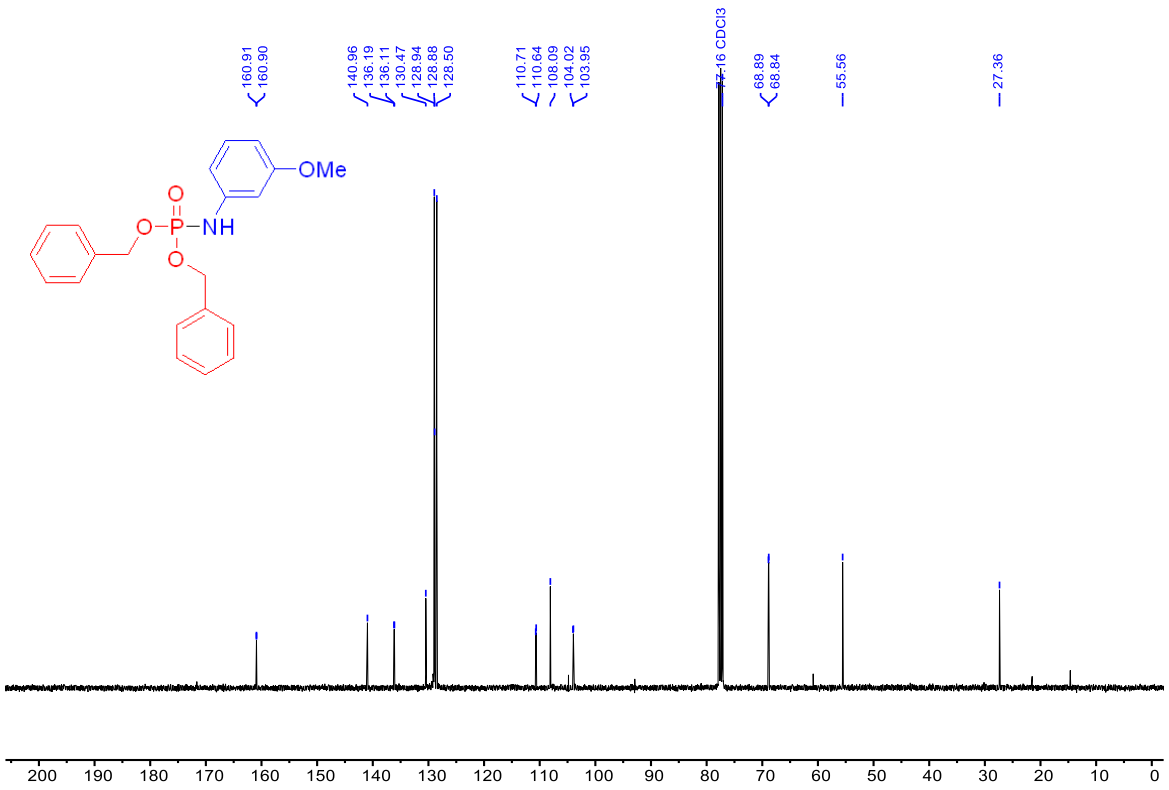


Figure S152: dibenzyl (3-methoxyphenyl)phosphoramidate (**20b**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

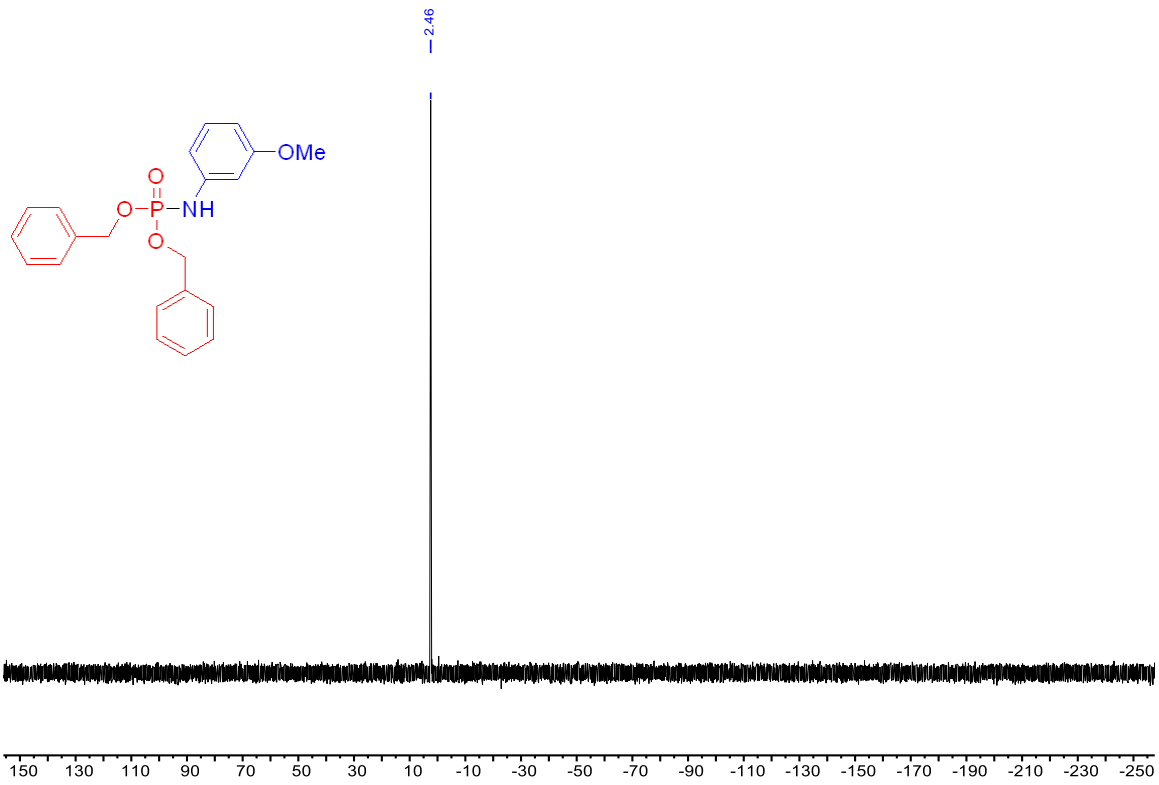


Figure S153: diethyl (4-methoxy-2-methylphenyl)phosphoramidate (**21a**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

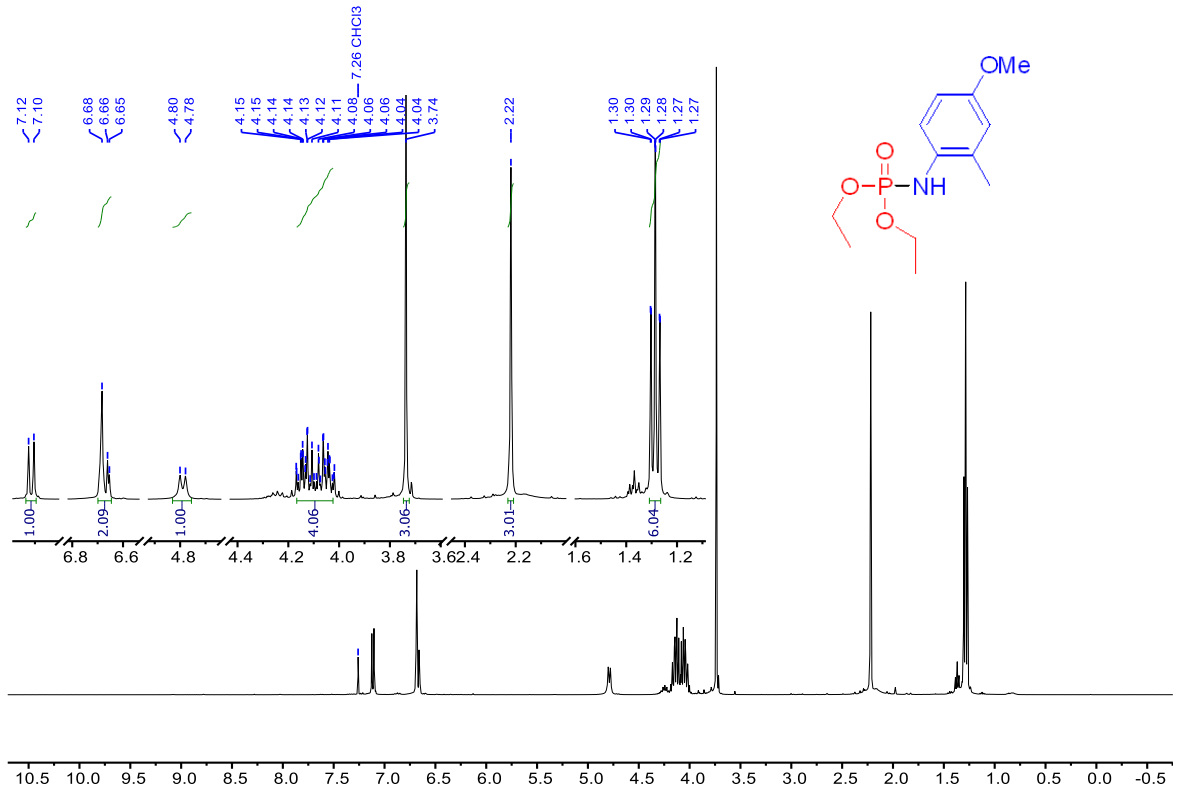


Figure S154: diethyl (4-methoxy-2-methylphenyl)phosphoramidate (**21a**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

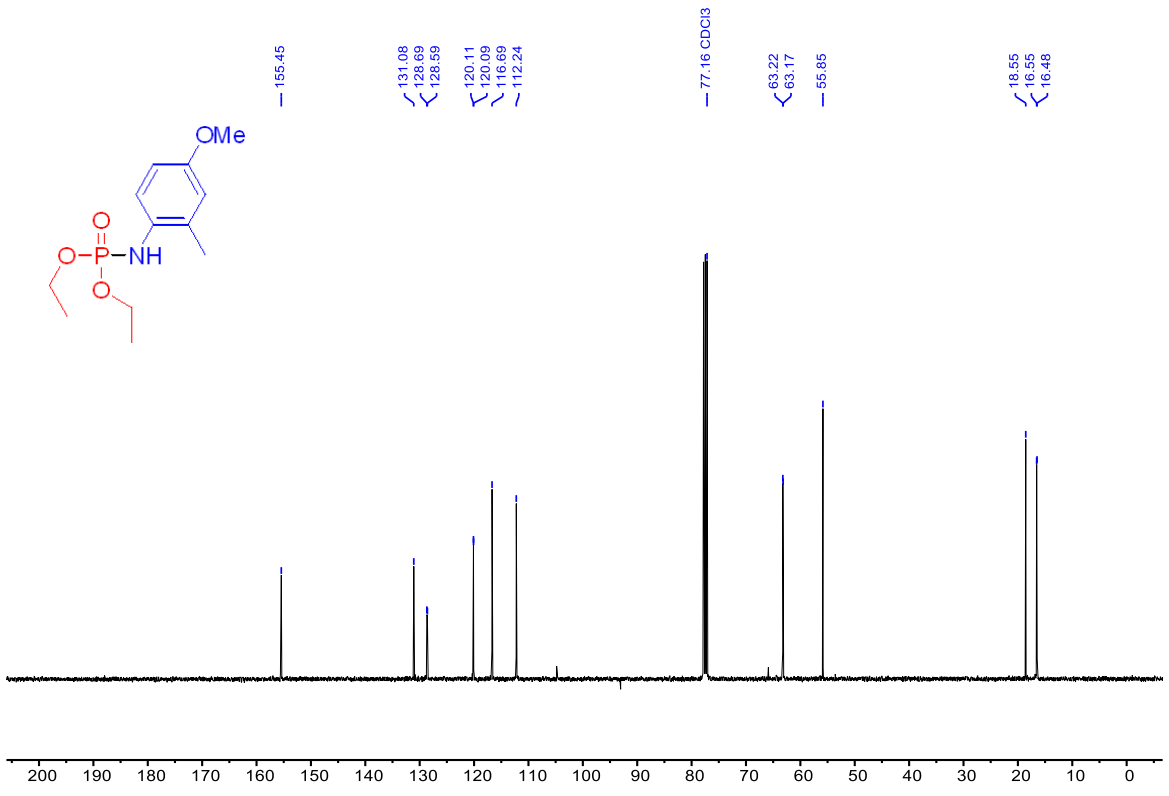


Figure S155: diethyl (4-methoxy-2-methylphenyl)phosphoramidate (**21a**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)

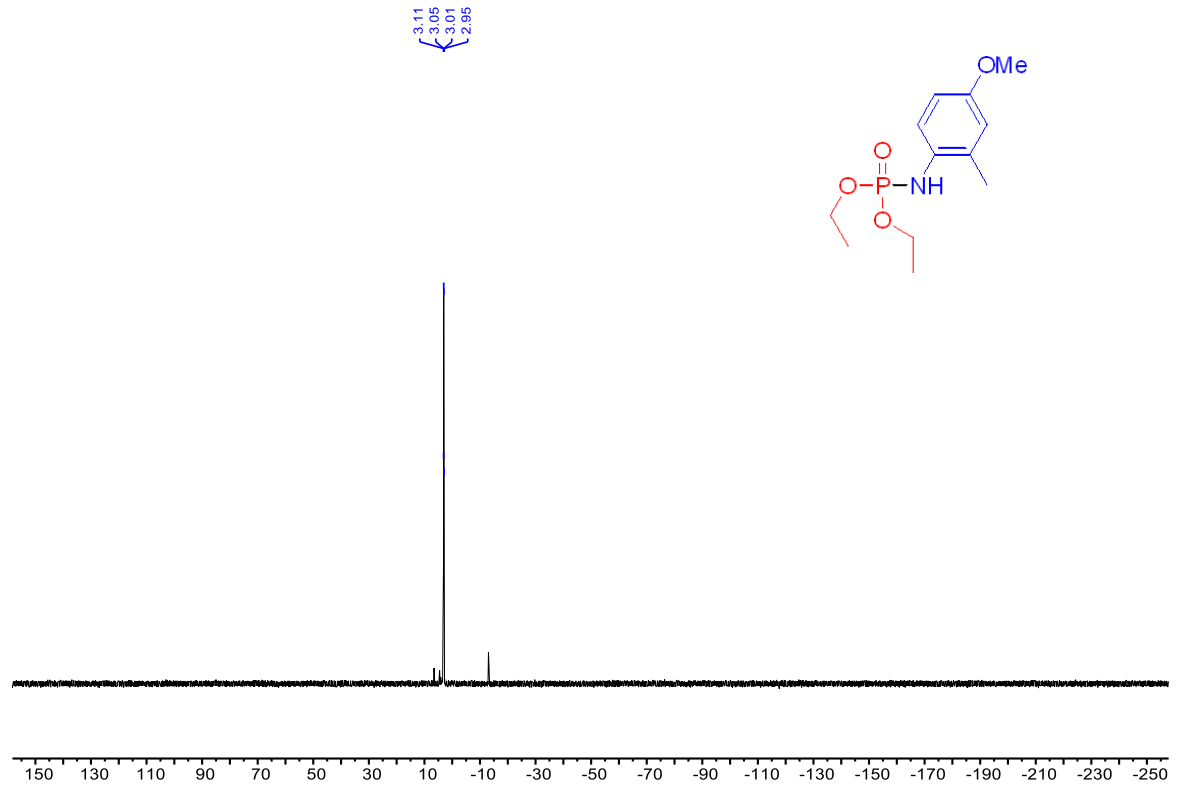


Figure S156: diethyl (4-methoxyphenyl)phosphoramidate (**21b**)

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

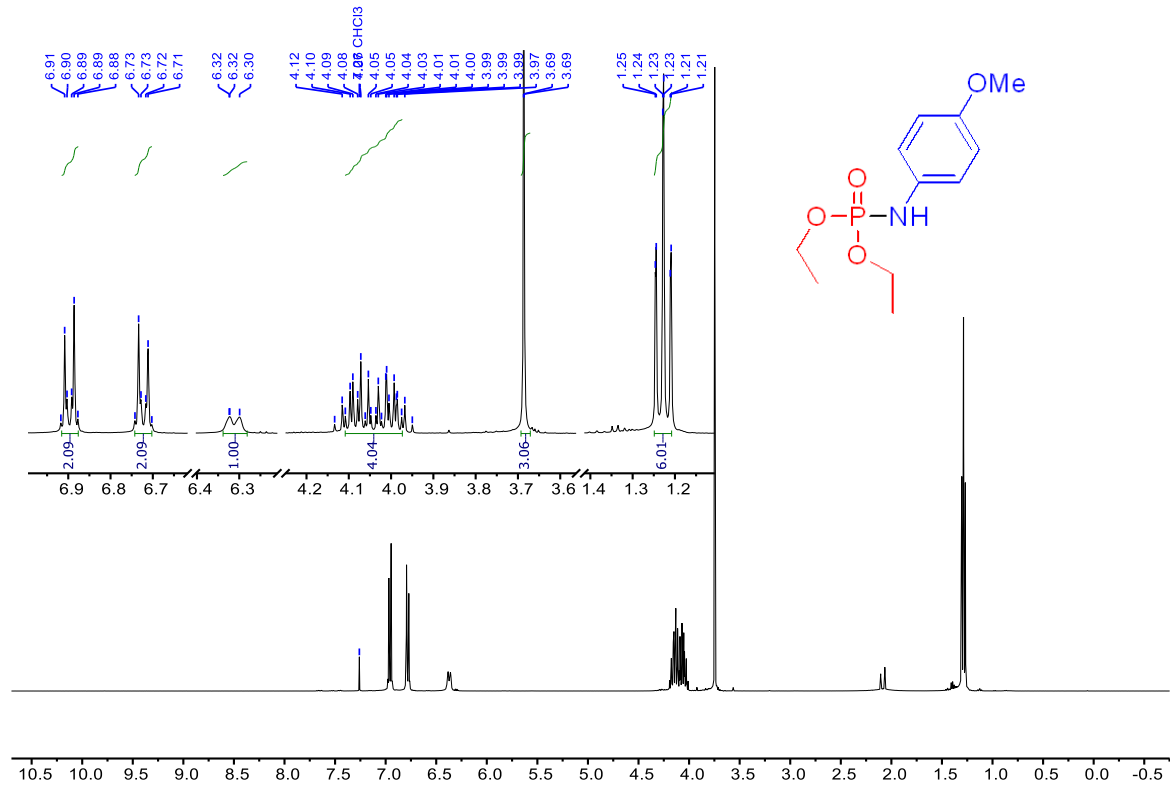


Figure S157: diethyl (4-methoxyphenyl)phosphoramidate (**21b**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

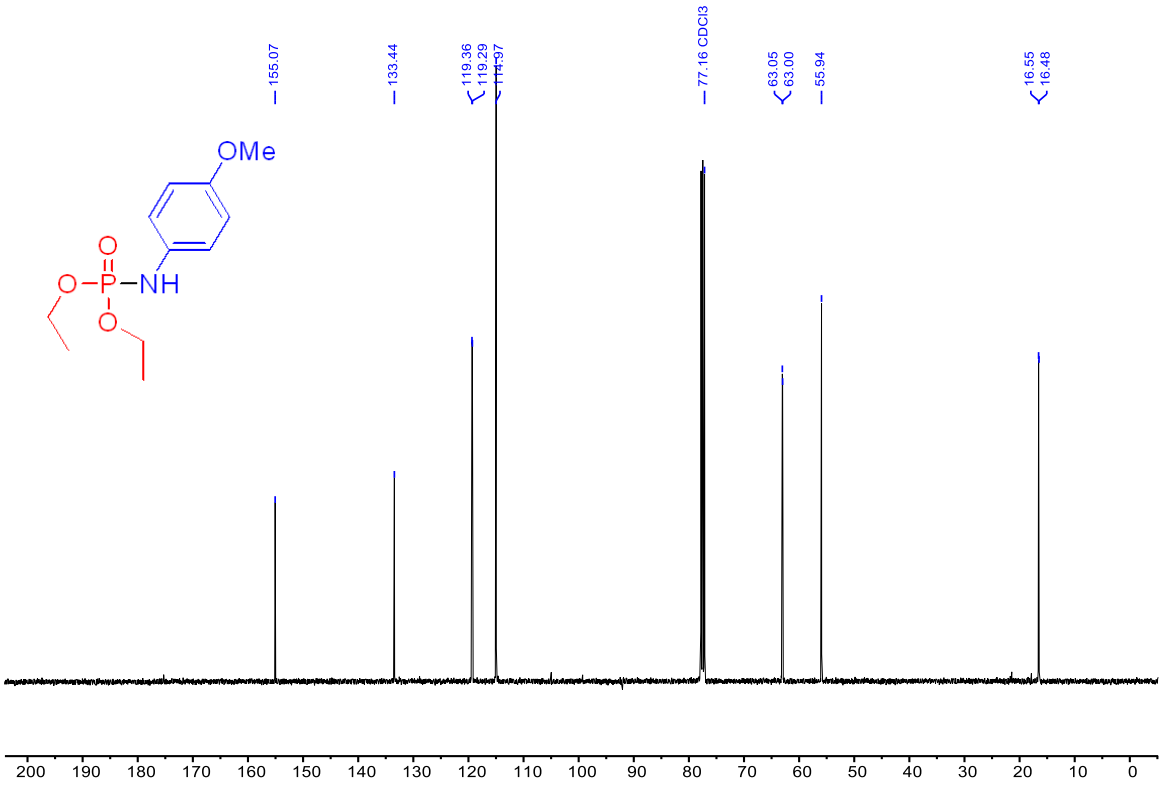


Figure S158: diethyl (4-methoxyphenyl)phosphoramidate (**21b**)

^{31}P NMR spectrum (162 MHz, $CDCl_3$)

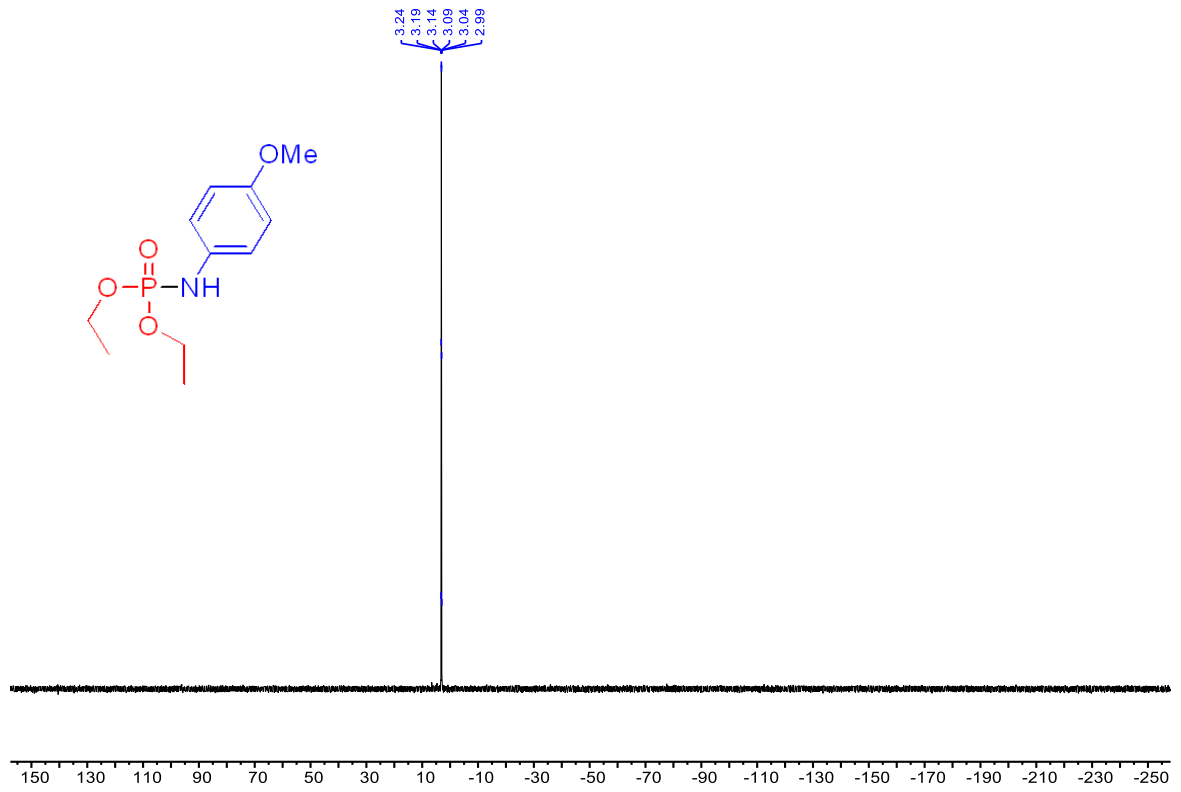


Figure S159: diethyl (2,6-diisopropylphenyl)phosphoramidate (**21c**)

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

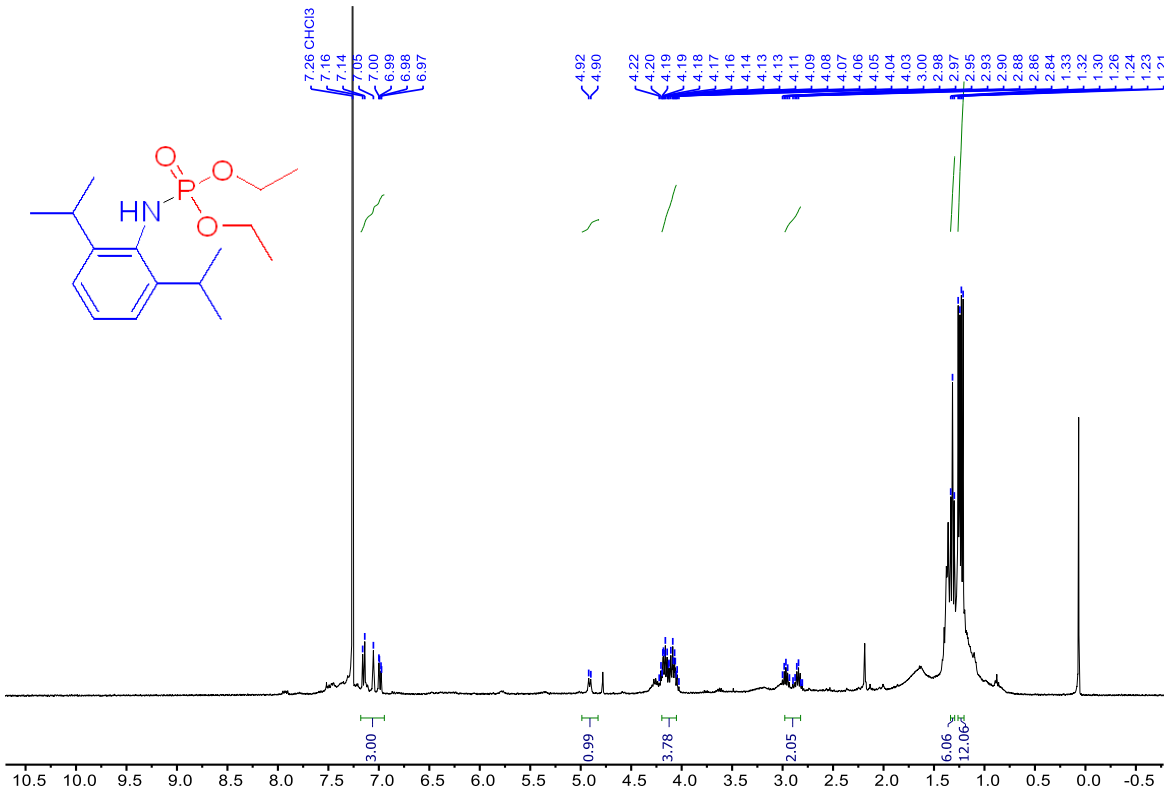


Figure S160: diethyl (2,6-diisopropylphenyl)phosphoramidate (**21c**)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

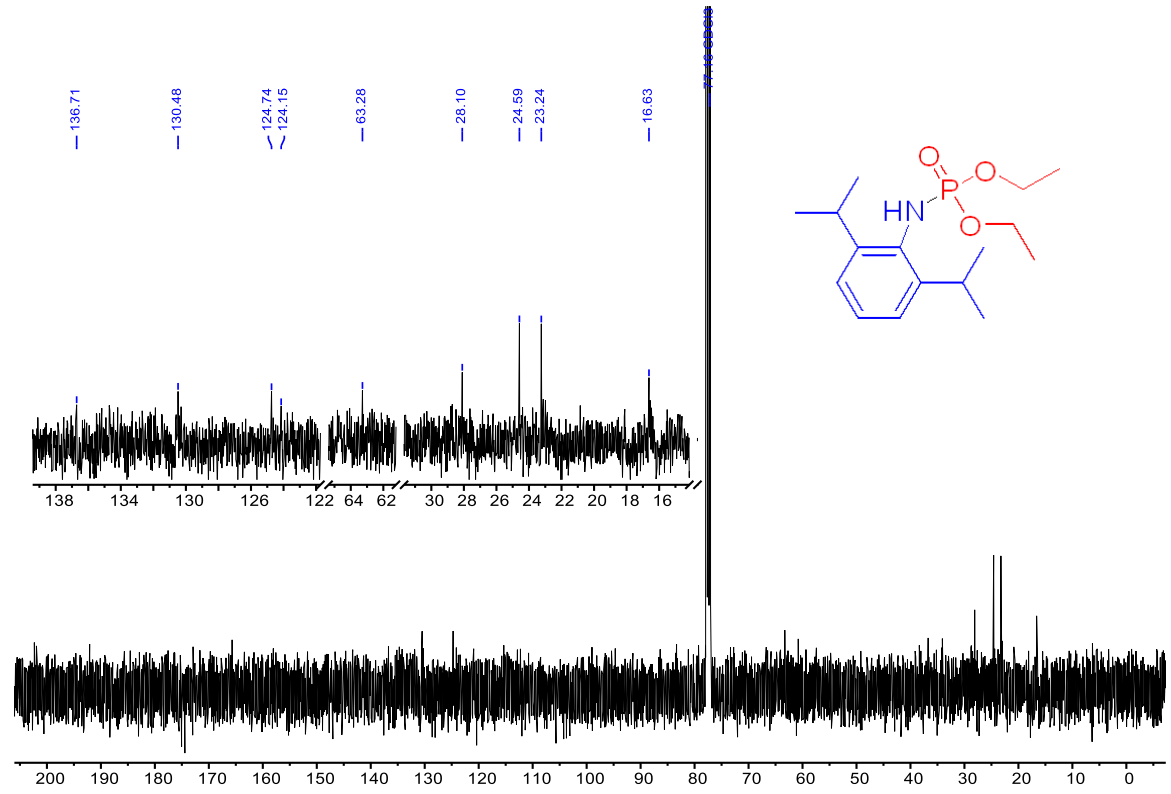


Figure S161: diethyl (2,6-diisopropylphenyl)phosphoramidate (**21c**)

^{31}P NMR spectrum (162 MHz, $CDCl_3$)

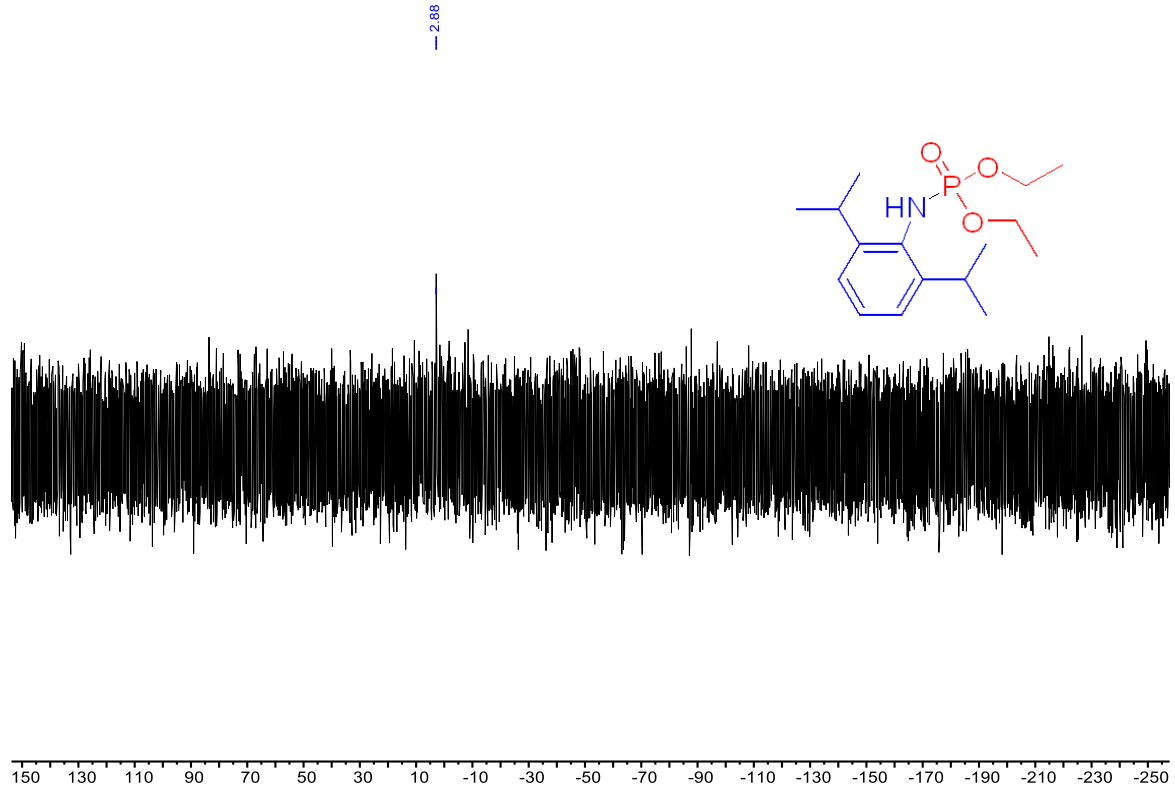


Figure S162: diphenylphosphinic acid (**22**)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

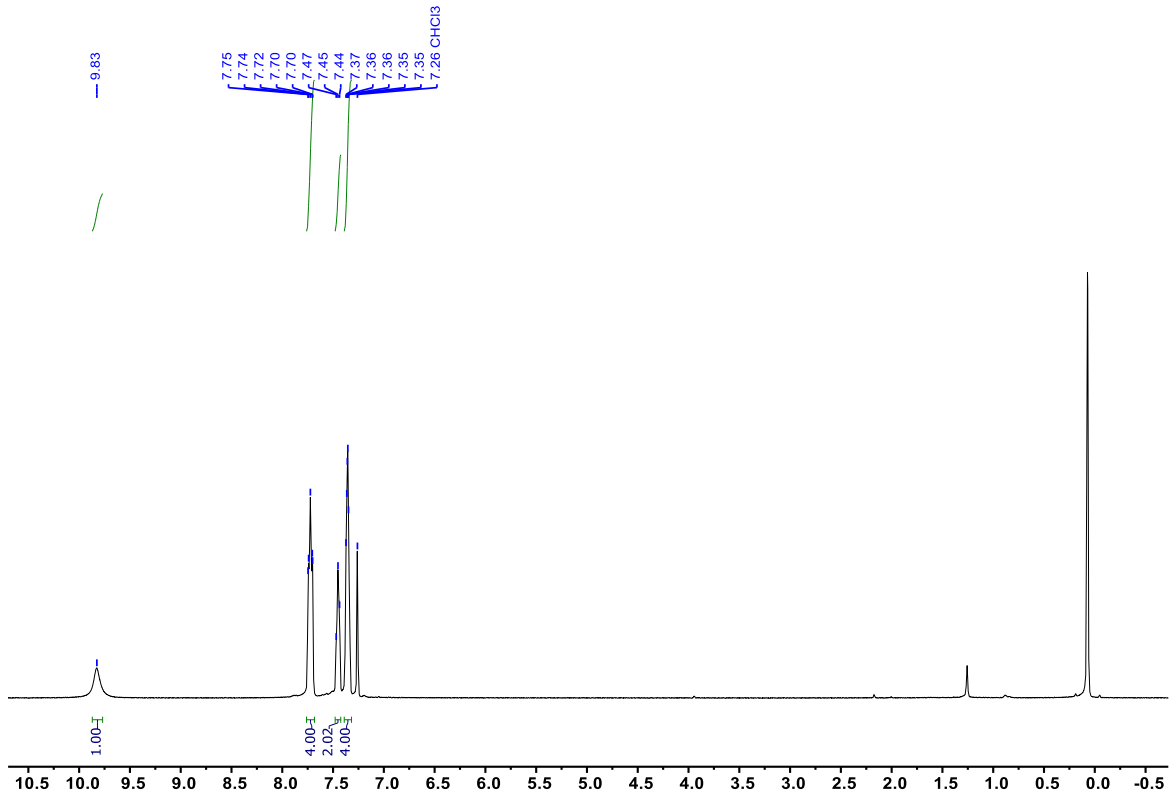


Figure S163: diphenylphosphinic acid (**22**)

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

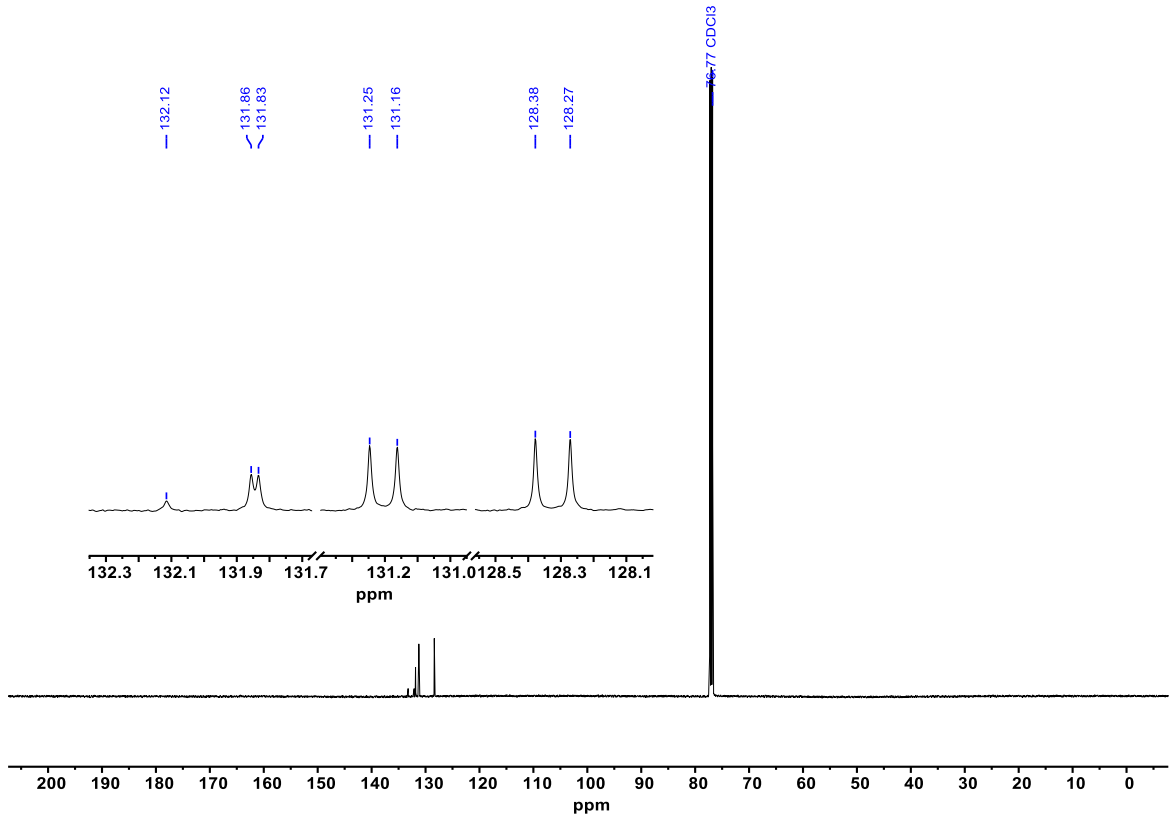
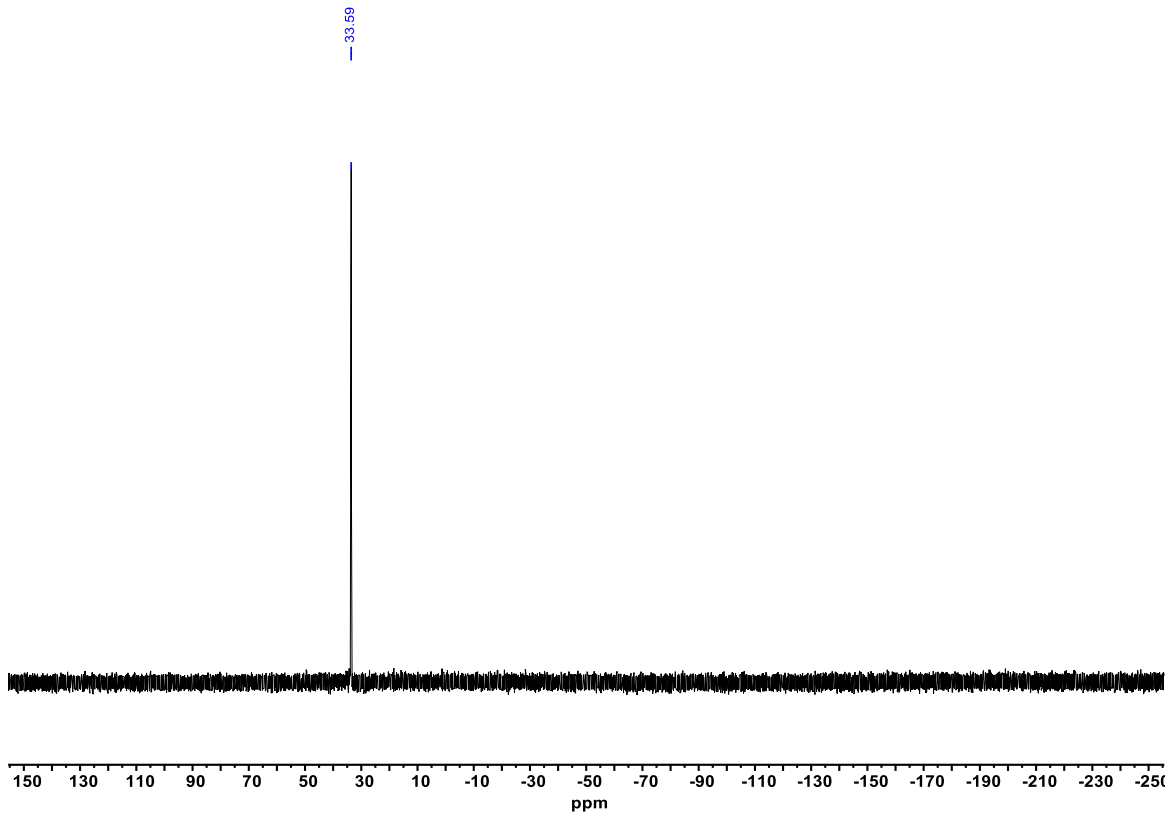


Figure S164: diphenylphosphinic acid (**22**)

^{31}P NMR spectrum (202 MHz, $CDCl_3$)



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