Electronic Supplementary Material (ESI) for ChemComm.

First Ever Observation of the Intermediate of Phosphonium Salt & Ylide Hydrolysis: *P*-Hydroxytetraorganophosphorane

Supporting Information

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1. Additional Discussion on Hydrolysis of Cyclic Phosphonium Salts

The results of Westheimer on the hydrolysis of (cyclic) phosphates and phosphonates indicated that in the trigonal bipyramidal (TBP) phosphorane intermediates in these reactions, the leaving group is obliged to depart from an apical site.[1,2] This and other work[3,4,5,6,7,8,9] also strongly demonstrates that (i) electronegative elements preferentially occupy apical positions in TBP phosphoranes, and that (ii) in phosphoranes in which the phosphorus atom is in a cycle of five or fewer members, one of the ring atoms bound to phosphorus preferentially occupies an apical position. This arrangement in small ring cyclic phosphoranes avoids the ring strain resulting from the ring spanning two equatorial sites. In instances where there is a choice between two elements (i.e. where phosphorus is directly bound to two different elements), the most electronegative element occupies the apical site. The assumption that the leaving group is obliged to leave from an apical position in all phosphoranes (based on Westheimer's results)[1] is yet to be contradicted by experimental[3,4,5,6,7] or computational results.[10]

Thus, in the TBP intermediates proposed to be involved in the hydrolysis reactions of cyclic phosphonium salts we should expect that one apical site is occupied by a ring carbon, and the other by the hydroxide oxygen. Then, only two options are available: the hydroxyphosphorane may undergo decomposition to phosphine oxide either (i) by cleavage of the apical P-C ring bond (which in some cases means *P*-alkyl is cleaved in preference to *P*-aryl) without undergoing pseudorotation, or (ii) by cleavage of an exocyclic P-C bond, which must necessarily be accompanied by pseudorotation process(es) to place the leaving group in an apical position in the transition state for the decomposition.[10] Hence, if the putative TBP phosphoranes are involved as intermediates in these reactions, then in the hydrolysis of a *P*-chiral phosphonium salt, the occurrence of ligand permutation by pseudorotation may reveal itself in the racemisation or retention of the stereochemistry of phosphorus (i.e. if a result other than inversion of stereochemistry is obtained). An alternative explanation for ligand permutation would be difficult to construct in the face of the evidence at hand for pseudorotation in TBP entities.

Indeed, it has been observed that alkaline hydrolysis of each of the diastereomeric cyclic phosphonium salts **13a**, **13b**,[11] **14a** & **14b**[12] (see Chart S1) leads to formation of cyclic phosphine oxides (i.e. with loss of the *P*-benzyl group) in which the stereochemistry at phosphorus is retained. Cyclic *P*-phenyl salts **11** & **12** also undergo hydrolysis to give cyclic phosphine oxides, with loss of the phenyl group.[13] In these examples, the process of placing the exocyclic leaving group (benzyl or phenyl) in an apical site in the TBP transition state requires either that the ring spans two equatorial sites or that hydroxide occupies an equatorial site. Elimination of the exocyclic leaving group leaves the small ring intact, and thus the transition state is subject to the incipient ring strain brought about by the transition of the geometry about phosphorus from TBP to tetrahedral. We expect that these two factors cause the activation energy for phosphorane decomposition to be substantially higher than in acyclic cases. Only one set of pseudorotations leads to a *relatively* low energy transition state, and this set of pseudorotations happens to result in retention of the configuration at phosphorus. An example of a pathway involving pseudorotation that leads to retention of configuration at phosphorus is shown in Scheme S1.[11]

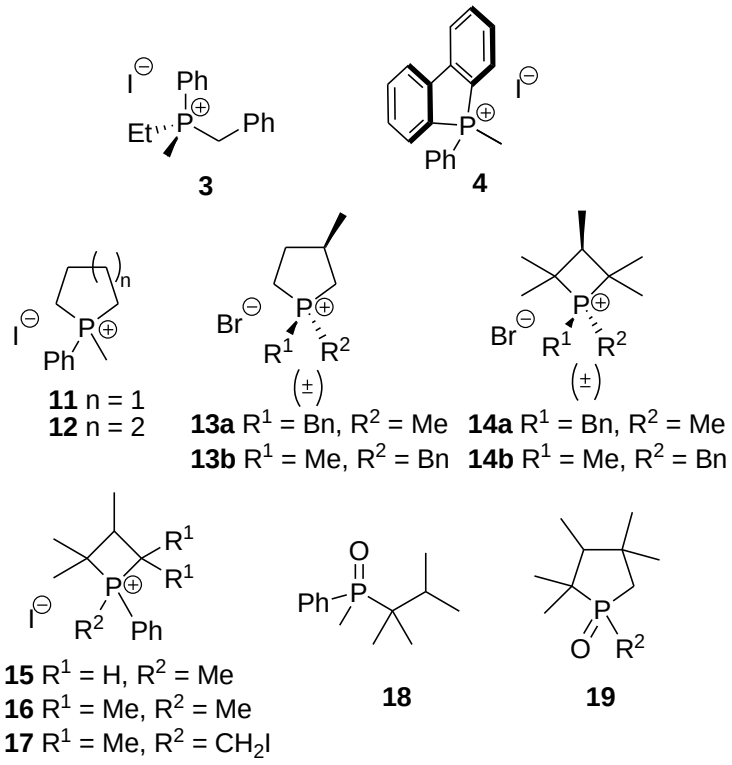
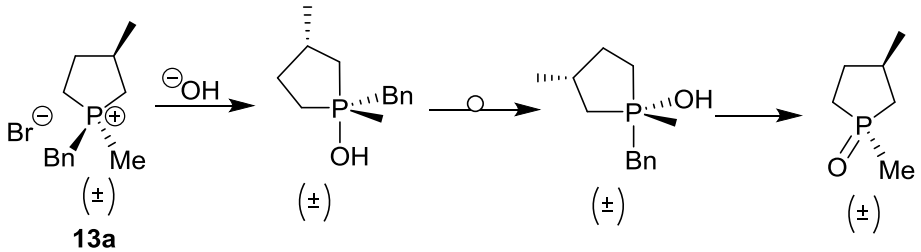


Chart S1. Phosphonium salts & phosphine oxides.

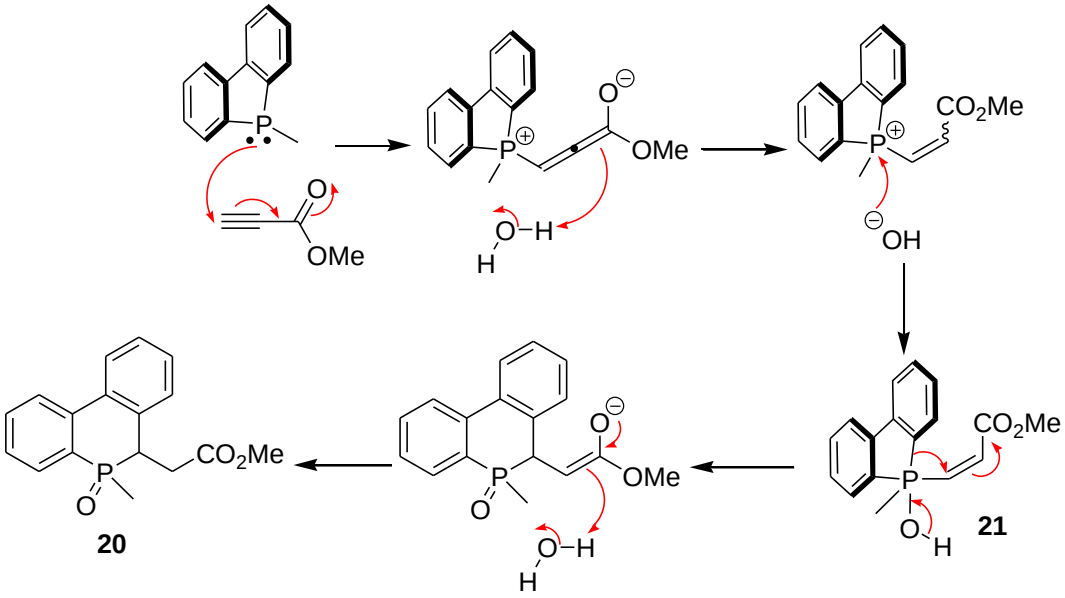
P-phenyl phosphetanium salts **15**, **16** and **17** are close analogues of **13** and **14**. **15** undergoes alkaline hydrolysis with ring opening to give open-chain phosphine oxide **18**,[14] while **16** & **17** give rearrangement products that appear to result from initial ring opening (e.g. **19** from **17**).[14,15] Hydrolysis reactions of phospholium[16] and dibenzophospholium salts[17,18] (e.g. **4**)[17] are also reported to exhibit ring opening (or ring expansion via ring opening, *cf.* Scheme S2 and the associated discussion below)[18] to the exclusion of all other possibilities. For **15**, **16** and **17**, the potential contribution to the activation energy from ring strain energies is even higher than for **13** & **14**, and furthermore, phenyl is a poorer leaving group than benzyl. The only available option energetically thus seems to be for the ring to open i.e. the release of ring strain can make a saturated alkyl group a more effective leaving group than sp^2-hybridised phenyl.



Scheme S1. Pathway for hydrolysis of a chiral phosphonium salt through a TBP hydroxyphosphorane with retention of configuration. The second phosphorane may not be metastable entity, and in fact is likely to be a transition state.[10]

Formation of 9,10-dihydro-9-phosphaphenanthrene 9-Oxide **20** by the reaction of *P*-methyldibenzophosphole with methyl prop-2-ynoate and water[19] presumably occurs through initial formation of a phosphonium salt intermediate, subsequent formation of hydroxyphosphorane (**21**) and finally ring expansion (rearangement) from this

intermediate (see Scheme S2). In this instance, ring opening appears to occur in preference to elimination of an alkenyl group, which should have a leaving group ability to similar to that of phenyl.



Scheme S2. Formation of phosphine oxide **20**.

That ring opening occurs in preference to elimination of a phenyl group in **15**, **16** and **17**, and in particular that the stereochemistry at phosphorus is retained in the hydrolysis of **13** & **14** strongly supports the existence of TBP *P*-hydroxytetraorganophosphorane.

2. Additional Discussion on Differences between Phosphonium Salt & Ylide Hydrolysis

Certain differences between phosphonium salt and ylide hydrolysis have been observed. Hydrolysis of enantiopure phosphonium salt **3** is stereospecific,[20] while that of the enantiopure chiral ylide derived from **3** gives racemic ethylmethylphenylphosphine oxide.[21] Ylide hydrolysis is generally faster than salt hydrolysis.[22] This has been ascribed to the low polarity of the medium in which the ylide must necessarily be prepared compared to the relatively high polarity of the aqueous organic media in which phosphonium salt hydrolysis is usually conducted.[22] Finally, we have reported one specific case where different products were obtained from hydrolysis of a salt and its derived ylide.[23]

3. Experimental

3.1 General Experimental

All chemicals were used without further purification except THF (Aldrich) and THF-*d8* (Apollo Scientific). THF was processed through an Innovative Technology Inc. Pure Solv-400-3-MD solvent purification (Grubbs still) system and stored in Strauss flasks under a nitrogen atmosphere. THF-*d8* was obtained in an ampule, and

contained *ca*. 100 ppm water by Karl Fischer titration. It was dried (< 10 ppm water) over activated 4 Å molecular sieves (Aldrich). The phosphonium salt precursors used to make the ylides – *P*-ethyltriphenylphosphonium bromide, *P*-ethyl-*P*-phenyl-5*H*-dibenzophospholium bromide, and *P*-benzyl-*P*-phenyl-5*H*-dibenzophospholium bromide were synthesised as in reference 8. These phosphonium salts were dried in a vacuum dessicator over P_2O_5 and, together with KHMDS (Aldrich) were stored in an MBraun glove box under an atmosphere of argon. *n*-BuLi was obtained from Acros Organics.

NMR chemical shifts are reported in parts per million (ppm), and coupling constants (*J*) are reported in hertz (Hz). ^{1}H and ^{13}C NMR chemical shifts measured relative to tetramethylsilane. ^{31}P NMR chemical shifts were measured relative to an external orthophosphoric acid standard. NMR spectra were obtained on Varian 300, 400 and 500 MHz instruments. Low temperature NMR was carried out on a 500 MHz instrument equipped for cooling to low temperatures (< -20 °C), the purchase of which was funded by Science Foundation Ireland (SFI) Infrastructural Award [12/RI/2341(2)]. High resolution mass spectra were obtained on a LCT electrospray ionisation mass spectrometer. Samples were dissolved in methanol.

All reactions described here were carried out under an atmosphere of nitrogen. The inert atmosphere was established inside a reaction flask by the standard Schlenk pump and fill technique,[24] using a nitrogen/vacuum manifold that allowed each of five silicone rubber tubes to each be open either to vacuum or to the nitrogen supply by means of a three-way tap (third position is closed to both vacuum and nitrogen). The reaction flask was typically flame dried and attached to the Schlenk manifold by one of the silicone rubber tubes, and evacuated by application of a vacuum pump (Edwards RV5 rotary vane pump) while hot. The flask was allowed to cool under vacuum and then filled with nitrogen. It was then evacuated and re-filled a further two times. This technique was also applied to establish a nitrogen atmosphere in the tubing connected to a sealed Schlenk flask that already contained an inert atmosphere (nitrogen or argon gas). The flask could be opened to the nitrogen supply after the connecting tubing had been evacuated and re-filled three times. When not in use, the the open end of each length of silicone rubber tubing was fitted with a syringe barrel with an attached needle. The needle was inserted through a rubber septum into a conical flask containing dry KOH pellets, and the tip was embedded in amongst the pellets. In this manner the tubing was kept free of ambient moisture by the hygroscopic KOH. The small amount of water gathered on the inside of these tubes (if left untreated) causes substantial ylide hydrolysis even if th ylide is just left stirring attached to the manifold under a flow of nitrogen for a time.

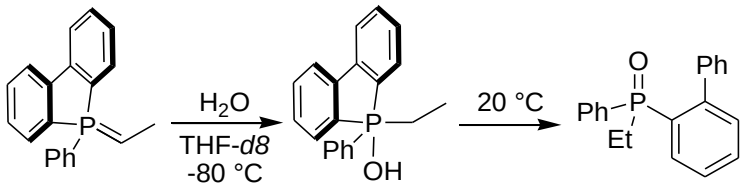
3.2. General Procedure for Ylide Hydrolysis

All glassware used for inert atmosphere operations was flame-dried and cooled under vacuum. Phosphonium salt (1 equivalent) and KHMDS (1.0 equivalent) were added to a flask in a glove box under an atmosphere of dry argon. THF-*d8* (0.8 - 2 ml) was added, and the resulting ylide solution was stirred for 15 minutes. Stirring was then ceased, and the KBr precipitate was allowed to settle. The (brightly coloured) supernatant solution was carefully withdrawn by syringe, and added to an NMR tube, which was then placed in a long Schlenk flask. The Schlenk flask was then sealed with a greased stopper,

removed from the glove box and attached to a nitrogen supply through a nitrogen/vacuum manifold by the pump & fill technique. Standard Schlenk techniques could then be applied when using the long Schlenk flask without the occurrence of oxidation or hydrolysis. We found that diffusion of adventitious oxygen or water down into the NMR tube was extremely slow due to the narrow diameter of the tube and the fact that the solution in the NMR tube was not being stirred. Dry THF (20 ml) was added to the Schlenk flask (*outside* the NMR tube, for the purpose of effectively cooling the contents of the NMR tube). The Schlenk flask was then cooled to -80 °C using a mixture of dry ice & acetone in a deep Dewar flask. After approximately 10 minutes in the cold bath, H_2O (2.0 equivalents) was added to the cold solution of ylide. The Schlenk flask was gently shaken (in the cold bath) and fitted with a rubber septum under a strong flow of nitrogen. The Schlenk flask was closed, detached from the nitrogen/vacuum manifold and brought to the NMR spectrometer in the -80 °C bath. The NMR tube was removed from the Schlenk flask, and immersed immediately in the cold bath while the septum was wrapped first with PTFE tape and then with Parafilm. The NMR tube was then removed from the cold bath, shaken briefly, and placed in the 500 MHz NMR spectrometer at -70 °C. ^{31}P & ^{1}H NMR spectra were recorded as quickly as possible in an attempt to observe signals arising from transient intermediates. Where an intermediate could be observed, further spectra were then recorded at -70 °C (see below).

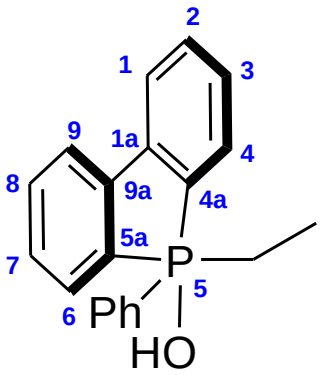
3.3. Ylide Hydrolysis Reactions

Synthesis & characterisation of *P*-hydroxyphosphorane 8 (from ylide 7 + H_2O)



The reaction was carried out as described in the general procedure using *P*-ethyl-*P*-phenyl-5*H*-dibenzophospholium bromide (10 mg, 0.03 mmol) and KHMDS (6 mg, 0.03 mmol) to make ylide **7** in in THF (0.8 ml). A 1.5 mol L^{-1} solution of H_2O in THF-*d8* (0.06 ml, 0.09 mmol) was added at -80 °C. **8** was observed at -70 °C and characterised at this temperature by NMR: $^{31}P\{^1H\}$ (3 second relaxation delay), ^1H (5 second relaxation delay), $^{13}C\{^1H\}$, gCOSY, gHSQC, ^1H-^{13}C HMBC, and ^1H-^{31}P HMBC.

$^{31}P\{^1H\}$ NMR (202 MHz, -70 °C, THF-*d8*) δ_P -11.6 (0.35 P, s, ylide), -80.6 (1.0 P, s, phosphorane).



^1H NMR (500 MHz, -70 °C, THF-*d8*) – for numbering of dibenzophosphole ring positions, see below.
Phosphorane 8: δ_H 8.28 – 8.21 (1 H, m, H-6), 8.06-8.00 (1 H, m, H-9), 7.79-7.73 (1.7 H, m, overlaps with signal of ylide, H-4), 7.63 (1 H, app t, *J* 7.3, H-8), 7.43-7.25 (5.5 H, overlaps with signal of ylide, H-7 & phenyl H), 7.19 (3 H, s, phenyl H), 7.11 (1 H, app t, *J* 7.3, H-3), 6.98 (1 H, app t, *J* 7.1, H-2), 6.74 (1 H, app d, *J* 7.2, H-1), 5.11 (1 H, s, PO*H*), 2.68 (1 H, m, PCH_2), 2.32 (1 H, m, PCH_2), 0.91 (3 H, dt, *J* 22.9, 7.6). The spectrum also contains a signal at δ_H 3.03 (4 H, s, H_2O). The underlined signals contain indeterminate contributions from the ylide. The signal at δ_H 7.43-7.25 is shown by the gCOSY spectrum to contain 2H from the DBP unit of the ylide (= 0.7 H). In total, the two signals contain 2.45 H (= 7 protons) from the ylide and 6 H from the phosphorane (1 H from DBP unit, 5 H from phenyl). The total integration over the two signals is 8.5 H.

Ylide 7: δ_H 8.13 (0.7 H = 2 H of ylide, app d, *J* 7.7), 7.79-7.73 (1.7 H, contains 0.7 H of ylide, overlaps with signal of phosphorane), 7.52 (0.7 H = 2 H of ylide, app t, *J* 7.5). 2.45 H contained in the signals at δ_H 7.43-7.25 and 7.19.

$^{13}C\{^1H\}$ NMR (126 MHz, -70 °C, THF-*d8*)
Phosphorane 8: δ_C 159.3 (d, *J* = 2.1, C-1a), 145.6 (d, *J* = 18.3, C-9a), 143.8 (d, *J* 143.3, Ph *ipso* C), 140.3 (d, *J* = 10.4, C-6), 136.9 (d, *J* = 13.6, C-4a), 135.5 (d, *J* = 149.8, C-5a), 132.6 (s, C-8), 129.1 (d, *J* = 5.0, C-1), 128.2 (d, *J* = 2.6, C-2), 126.7 (s, C-3), 120.4 (d, *J* = 12.2, C-9), 118.6 (s, C-4), 29.0 (d, *J* = 119.0, P*C*H_2), 8.3 (d, *J* = 5.4, *C*H_3).
Ylide 7: δ_C 143.7 (d, *J* = 2.6), 142.2 (d, *J* = 2.5), 130.4 (d, *J* = 21.9), 129.2 (s), 128.7 (d, *J* = 7.6), 121.6 (s).
Signals at δ_C 129.3 (s), 127.7 (s), 127.6 (s), 127.4 (d, *J* = 14.3), 127.1 (d, *J* = 13.5, likely to be phosphorane C-7) could not be unambiguously assigned (to ylide or phosphorane).

After acquisition of this NMR data, the sample of **8** was stored in a freezer (-19 °C) for 5 days. After this time, the sample was removed from the freezer and ^{31}P & ^{1}H NMR spectra were recorded immediately at 25 °C. The broad signal at δ_P -81 indicated the continued presence of **8**. The decomposition of **8** is clearly very slow at -19 °C. The sample was then maintained at 25 °C for 20 hours, after which time ^{31}P & ^{1}H NMR spectra indicated only the presence of phosphine oxides. ^{13}C{^{1}H}, gCOSY, gHSQC and ^{1}H-^{13}C HMBC were also recorded for the sample. The major product (constituting 81% of the sample) was shown to be (Biphenyl-2-yl)ethylphenylphosphine oxide (**10**) by comparison of these spectra with the identical spectra of a sample of **10** synthesised by independent means (see synthesis below). Characteristic signals of **10** are given here (*cf.* full characterisation of this compound below):

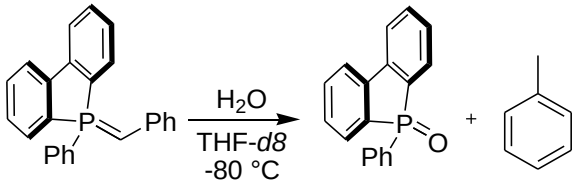
^{31}P NMR (121 MHz, THF-*d8*) δ_P 32.15 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 8.01 (1.3 H, m, overlaps with another signal), 7.54 (1 H, app t, *J* 7.5), 7.17 (2 H, t, *J* 7.6), 7.05 (2 H, m), 1.98 – 1.86 (1 H, m, one of diastereotopic P*CH*$_2$), 1.86 – 1.76 (1 H, m, one of diastereotopic P*CH*$_2$), 0.98 (3 H, dt, *J* 17.6, 7.6, *CH*$_3$); **^{13}C NMR** δ_C (126 MHz, $CDCl_3$) 21.7 (d, *J* 73.3, P*C*H$_2$), 5.6 (d, *J* 4.8, *CH*$_3$).

The sample of the product also contained small quantities of the following:

- *P*-ethyl-*5H*-dibenzophosphole oxide[25] (EtDBPO; 4% of sample) δ_P (THF-*d8*) 41.2 (lit.[25] δ_P 46.11 ($CDCl_3$)).
- *P*-phenyl-*5H*-dibenzophosphole oxide (7% of sample) δ_P (THF-*d8*) 29.5 (lit. δ_P (dioxane-*d8*) 30.0;[26] δ_P ($CDCl_3$) 33.5[27]).
- *P*-phenyl-*5H*-dibenzophosphole (PhDBP; 8% of sample) δ_P (THF-*d8*) -9.7 (lit.[26] δ_P (dioxane-*d8*) -10.0).

The *P*-phenyl-*5H*-dibenzophosphole oxide, we presume, is formed by oxidation of ylide **7**, since similarly small quantities of this compound are also produced in Wittig reactions of this ylide).[8] Thus with the ylide oxidation product removed, the hydrolysis product ratio **10** : EtDBPO : PhDBP is 87 : 4 : 9, and the ratio of the phosphine oxides arising from hydroxyphosphorane **8** (i.e. **10** : EtDBPO) is 95:5 in favour of ring-opened product **10**.

Reaction of *P*-benzylidene-*P*-phenyl-5*H*-dibenzophosphole 6 with H_2O



The reaction was carried out as described in the general procedure using *P*-benzyl-*P*-phenyl-5*H*-dibenzophospholium bromide (13 mg, 0.03 mmol) and KHMDS (6 mg, 0.03 mmol) to make ylide **6** in in THF (). A 1.5 mol L^{-1} solution of H_2O in THF-*d8* (0.02 ml, 0.03 mmol) was added at -80 °C. The initially observed ^{31}P NMR spectrum contained ylide (67%) and *P*-phenyl-*5H*-dibenzophosphole oxide (33%). Later spectra showed increased conversion of the ylide to the phosphine oxide. *P*-phenyl-*5H*-dibenzophosphole oxide was the only phosphine oxide detected. No signals were observed in the high field region of the ^{31}P NMR spectra. The doublet of the benzylidene

proton of the ylide could be assigned based on the phase-sensitive ^{1}H-^{13}C gHSQC (primary CH) and the ^{1}H-^{31}P HMBC of the reaction mixture.

$^{31}P\{^{1}H\}$ NMR (202 MHz, -70 °C, THF-*d8*) δ_P 5.9 (ylide **6**, DBP=CHPh), 29.5 (PhDBPO; lit. δ_P (dioxane-*d8*) 30.0;[26] δ_P ($CDCl_3$) 33.5[27]).).

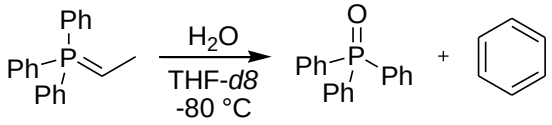
^{1}H NMR (500 MHz, -70 °C, THF-*d8*) δ_H 2.47 (d, *J* 19.6, PhDBP=C*H*Ph), 2.32 (s, PhCH_3).

The reaction described above, carried out in an NMR tube, did not result in complete hydrolysis of the ylide. Thus, we considered that the reactants in the NMR tube might not be mixing efficiently (especially at -70 °C) since, upon addition, the H_2O solution in THF-*d8* could be seen to form a separate layer above the maroon ylide solution. To investigate if poor mixing resulted in incomplete hydrolysis and/or non-formation of an observable phosphorane, the reaction was also carried out by a somewhat modified procedure, described below.

Phosphonium salt (21 mg, 0.05 mmol) and KHMDS (10 mg, 0.05 mmol) were added to a Schlenk flask in a glove box under an atmosphere of dry argon. THF-*d8* (1.0 ml) was added, immediately giving a deep orange solution of ylide. The flask was stoppered using a second tap with a Quickfit joint, and the two taps were closed. The Schlenk flask was then removed from the glove box and attached to a nitrogen supply through a nitrogen/vacuum manifold by the pump & fill technique. The second tap was fitted with a rubber septum, and the space between the septum and the glass key was flushed with nitrogen gas for 20 minutes. The ylide solution was stirred at 20 °C for 15 minutes. The flask was the placed in a cold bath (-80 °C) and stirred for 5 minutes. The key of the second tap was then opened (in this manner the entry of oxygen – and atmospheric water! - into the reaction flask can be almost completely prevented), and a 2.0 mol L^{-1} solution of H_2O in THF-*d8* (0.03 ml, 0.06 mmol) was added to the cold solution of ylide, causing almost immediate dissipation of the maroon colour of the ylide. The reaction mixture was stirred for 5 minutes at -80 °C, and then stirring was then ceased, and the KBr precipitate was allowed to settle.

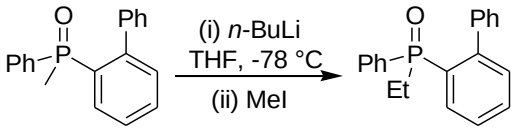
Dry THF (20 ml) was added to a long Schlenk flask (flame-dried, cooled under vacuum and attached to the nitrogen supply) containing an NMR tube (*outside* the NMR tube). This Schlenk flask was then cooled to -80 °C using a mixture of dry ice & acetone in a deep Dewar flask. The supernatant solution in the first Schlenk flask was carefully transferred by cannula to the NMR tube in the long Schlenk flask (taking care to bring across as little salt as possible). The cannula was cooled in advance of the transfer by rubbing the outside of it with some cotton wool soaked with liquid nitrogen. The long Schlenk flask was closed, detached from the nitrogen/vacuum manifold and brought to the NMR spectrometer in the -80 °C bath. The NMR tube was removed from the Schlenk flask, and immersed immediately in the cold bath while the septum was wrapped first with PTFE tape and then with Parafilm. The NMR tube was then removed from the cold bath, shaken briefly, and placed in the 500 MHz NMR spectrometer at -70 °C. ^{31}P & ^{1}H NMR spectra were recorded as quickly as possible. No high field signals were observed in the $^{31}P\{^{1}H\}$ at -70 °C. No signal for the ylide was observed; only *P*-phenyl-*5H*-dibenzophosphole oxide could be detected, δ_P (THF-*d8*) 29.5 (lit. δ_P (dioxane-*d8*) 30.0;[26] δ_P ($CDCl_3$) 33.5[27]).

Reaction of *P*-ethylidenetriphenylphosphorane 5 with H_2O



The reaction was carried out as described in the general procedure using *P*-(ethyl)triphenylphosphonium bromide (22 mg, 0.06 mmol) and KHMDS (12 mg, 0.06 mmol) to make ylide **5** in THF-*d8* (1.6 ml). 0.8 ml of this solution was transferred to an NMR tube, which was placed in a long NMR Schlenk, and a 1.5 mol L^{-1} solution of H_2O in THF-*d8* (0.02 ml, 0.03 mmol) was added at -80 °C. No high field signals were observed in the $^{31}P\{^1H\}$ at -70 °C. Neither was any signal for the ylide observed (δ_P (THF-*d8*, 25 °C) 19.5, from a separate experiment); only triphenylphosphine oxide could be detected, δ_P (THF-*d8*) 29.7 (lit. δ_P (THF-*d8*) 24.7,[28] δ_P ($CDCl_3$) 29.1[29]).

3.4. Syntheis of (Biphenyl-2-yl)ethylphenylphosphine oxide (10)



9 **10**

(Biphenyl-2-yl)methylphenylphosphine oxide **9**[30] (1.275 g, 4.36 mmol) was added to a Schlenk flask (flame-dried & cooled under vacuum) under an atmosphere of nitrogen. THF (20 ml) was added, giving a clear solution. This was cooled to -80 °C, and a 1.6 mol L^{-1} of *n*-BuLi (3.0 ml, 4.8 mmol) was added dropwise while the reaction mixture was stirred, giving a yellow solution. The solution of phosphinoxy carbanion was maintained at temperatures between -65 °C and -80 °C for 1 hour. Methyl iodide (0.28 ml, *ca.* 0.64 g, *ca*. 4.5 mmol) was then added dropwise at -80 °C. The reaction mixture was stirred at this temperature for 20 minutes, then allowed to warm to room temperature (20 °C). After 1 hour, the reaction was cooled to -30 °C and 1 mol L^{-1} aqueous HCl solution (10 ml) was added to quench the reaction. The mixture was extracted with Et_2O (20 ml) and the phases separated. The aqueous phase was extracted twice more with Et_2O (20 ml each time). The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. NMR of the crude product indicated that it contained *ca.* 5% starting material (**9**). This was removed by column chromatography on silica using 85:15 cyclohexane/ethyl acetate. **9** elutes fractionally faster than **10**, and appeared only in the first fractions, mixed with **10**. Later fractions contained **10** exclusively. The yield of product was 0.87 g (65%)

$^{31}P\{^1H\}$ NMR δ_P (162 MHz, $CDCl_3$) 35.41 (s).

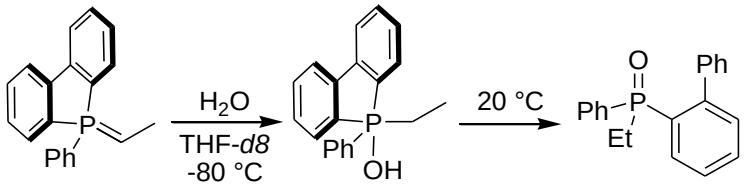
^1H NMR δ_H (500 MHz, $CDCl_3$) 8.01 (1 H, ddd, *J* 12.4, 7.7, 1.2), 7.54 (1 H, tt, *J* 7.5, 1.4), 7.50 – 7.45 (1 H, m), 7.42– 7.22 (m, contains C*H*Cl_3 signal), 7.17 (2 H, app t, *J* 7.6), 7.08 – 7.03 (2 H, m), 1.98 – 1.87 (1 H, m, one of diastereotopic PCH_2), 1.86 – 1.73 (1 H, m, one of diastereotopic PCH_2), 0.98 (3 H, dt, *J* 17.6, 7.6, CH_3).

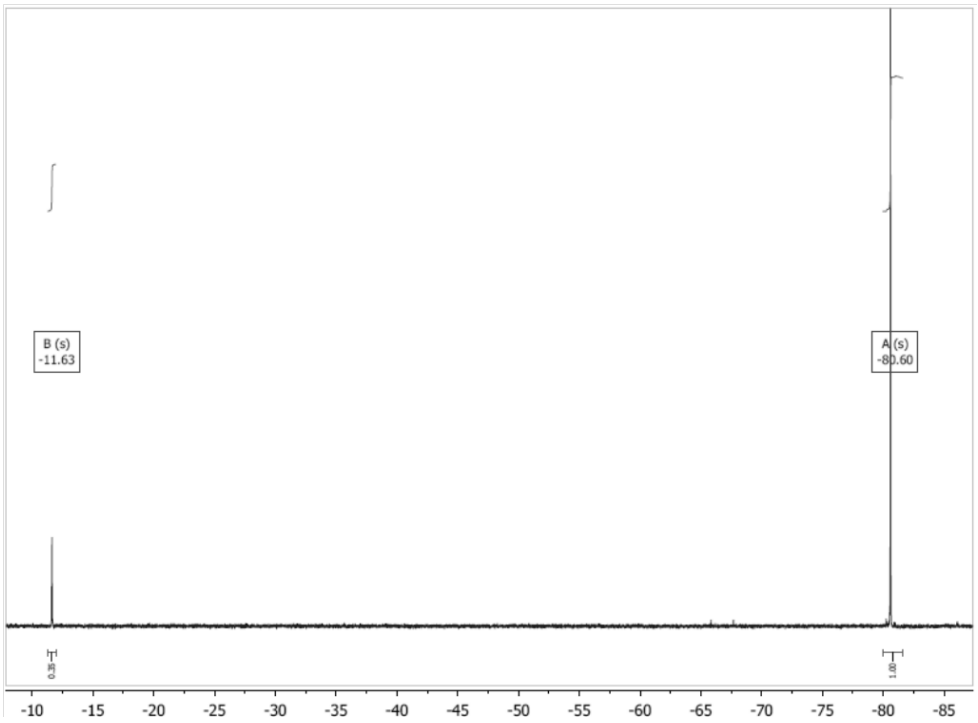
$^{13}C\{^{1}H\}$ NMR δ_C (101 MHz, $CDCl_3$) 146.0 (d, *J* 8.8), 140.7 (d, *J* 3.5), 133.7 (d, *J* 98.8, biphenyl P-C), 132.9 (d, *J* 9.0), 131.9 (app s, 4° C, 2nd half of doublet is likely to be obscured by another signal), 131.4 (d, *J* 12.1), 131.4 (s), 131.0 (d, *J* 2.7), 130.7 (d, *J* 9.4), 129.6 (s), 128.1 (d, *J* 11.7), 127.5 (s), 127.5 (s), 127.0 (d, *J* 11.1), 21.7 (d, *J* 73.4, P*C*H_2), 5.6 (d, *J* 4.8, *C*H_3).

HRMS (ESI+): Calc. for $[M]^+ = C_{20}H_{20}O_2P$ 307.1252; found 307.1259 (2.3 ppm).

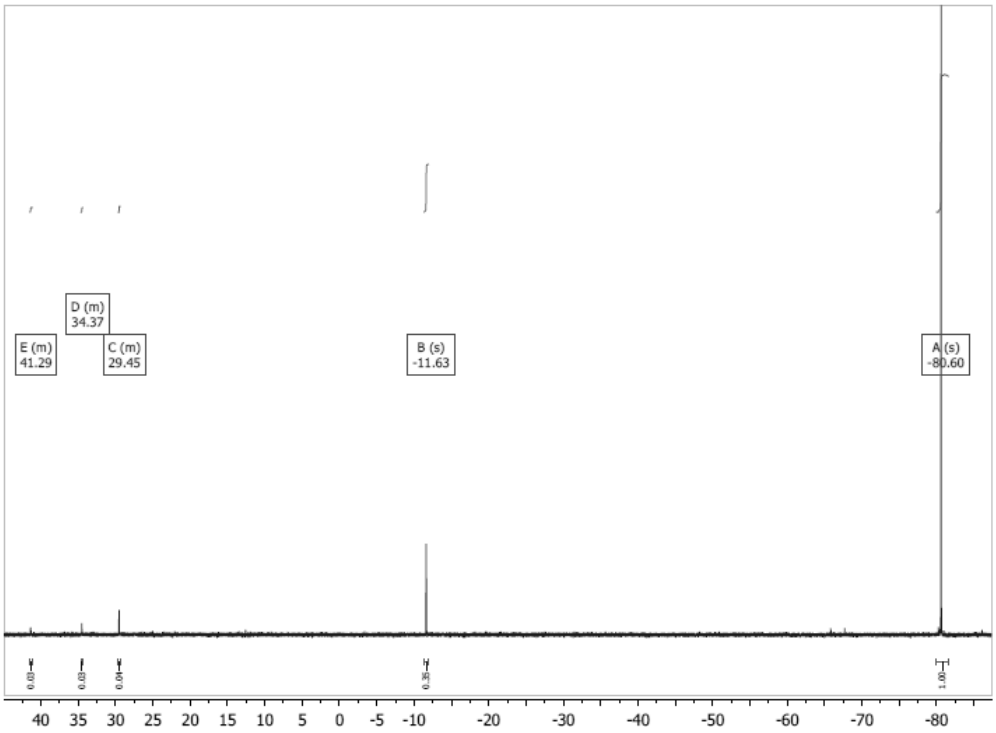
4. NMR Spectra

Synthesis & characterisation of *P*-hydroxyphosphorane 8 (from ylide 7 + H_2O)

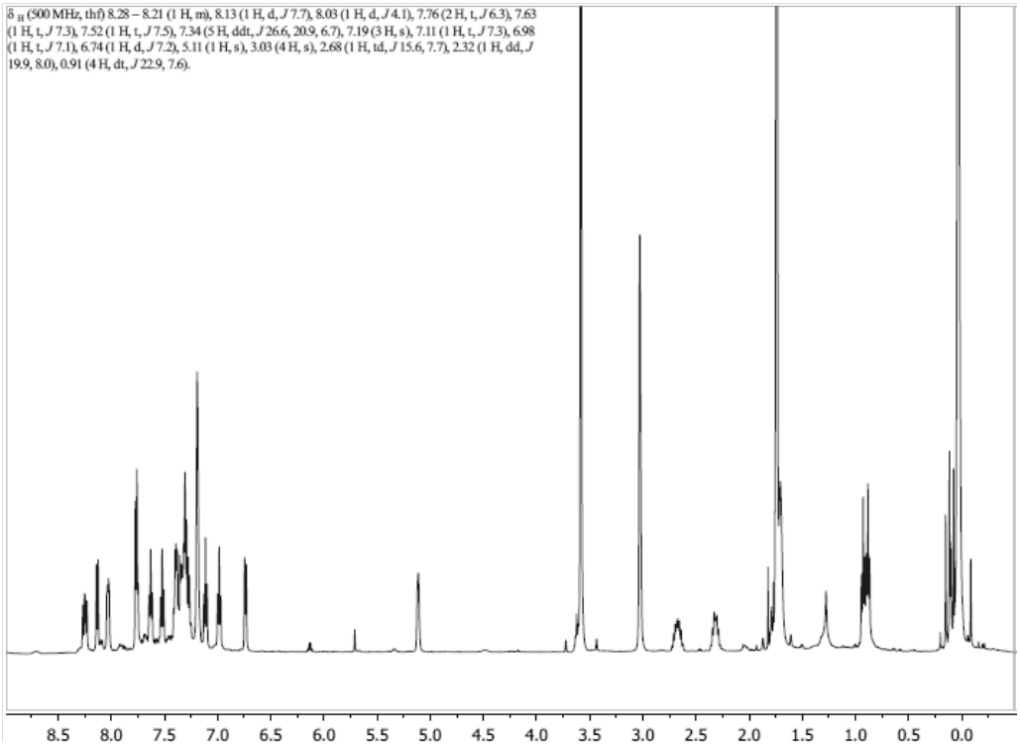




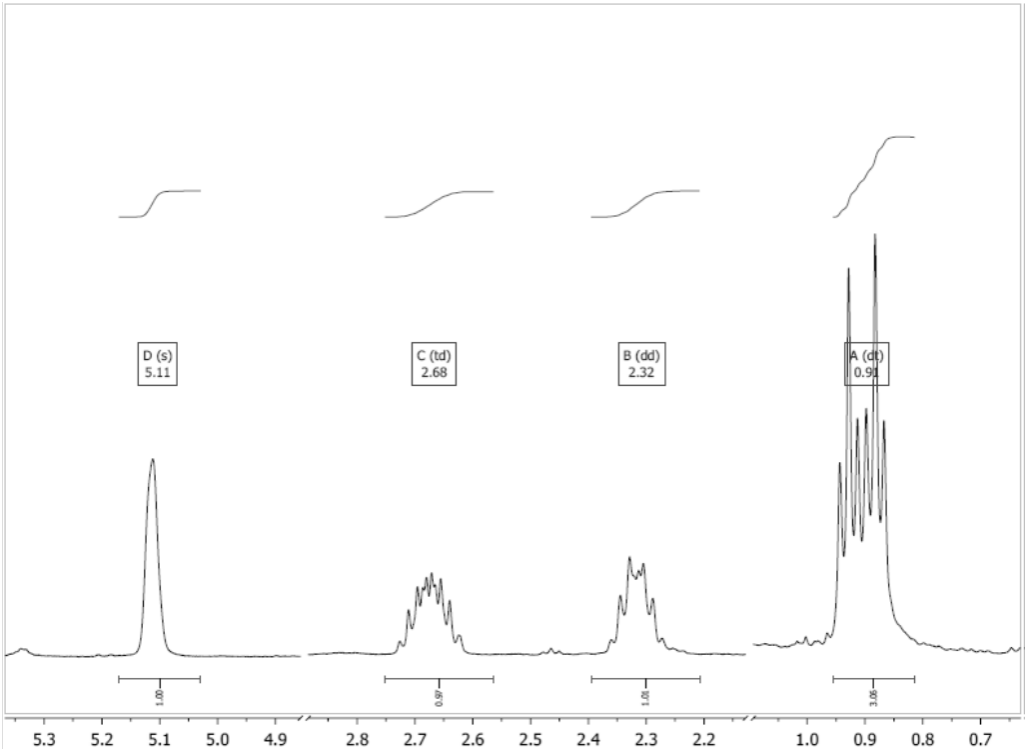
$^{31}P\ \{^{1}H\}$ of phosphorane **8** & ylide **7**, THF-*d8*, -70 °C



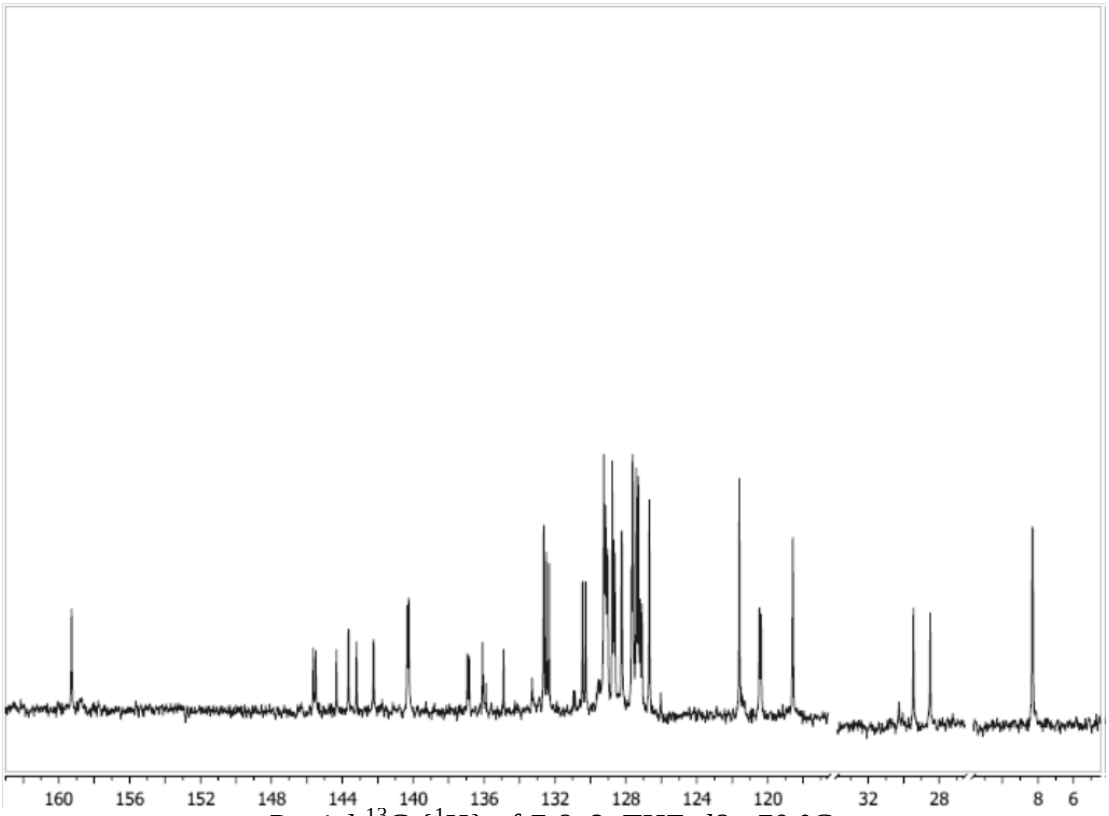
P {^{1}H} of **7** & **8**, THF-*d8*, -70 °C full spectrum



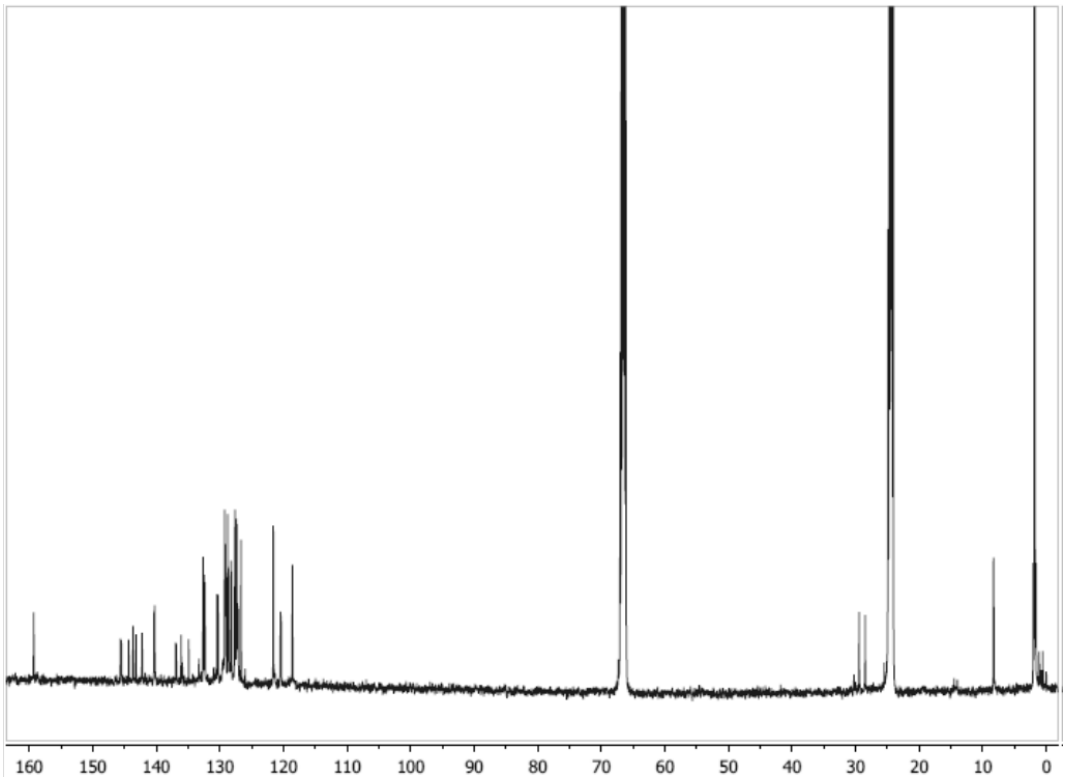
^{1}H NMR of **7** & **8**, THF-*d8*, -70 °C full spectrum



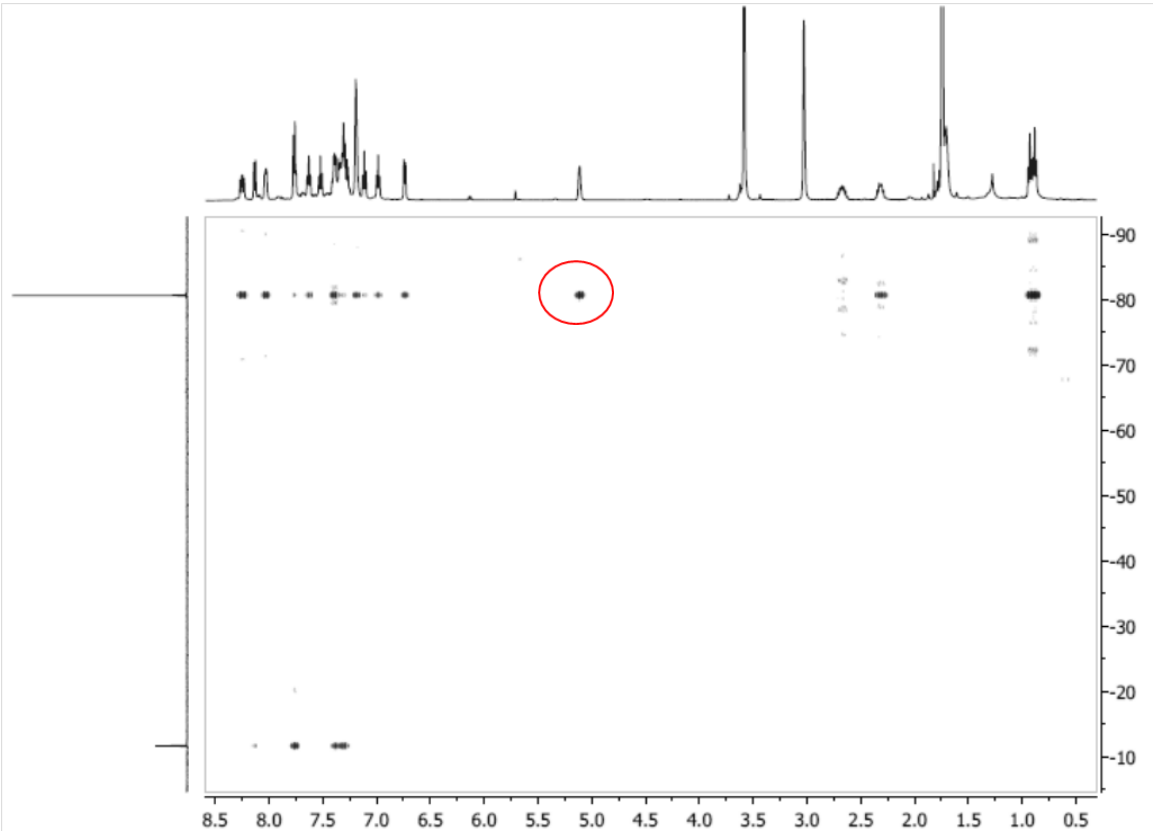
Partial ^{1}H NMR of **7** & **8**, THF-*d8*, -70 °C



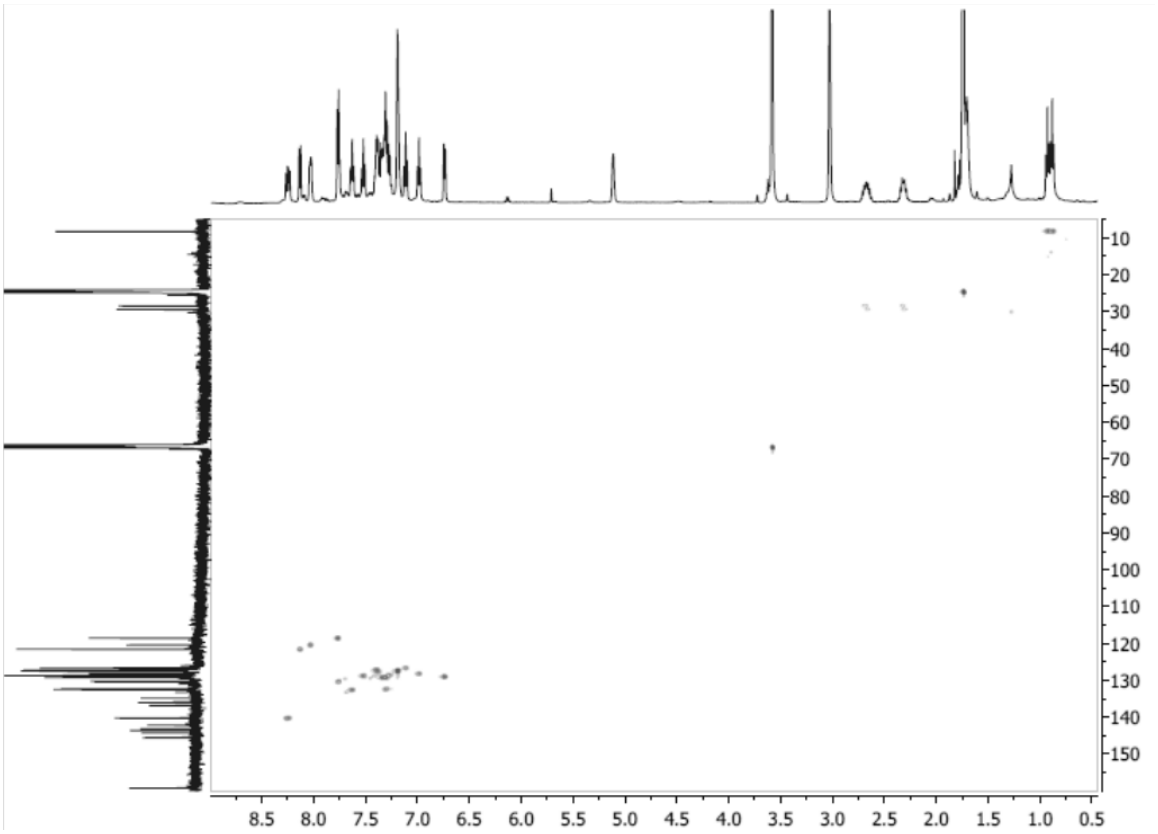
Partial ^{13}C {^{1}H} of **7** & **8**, THF-*d8*, -70 °C



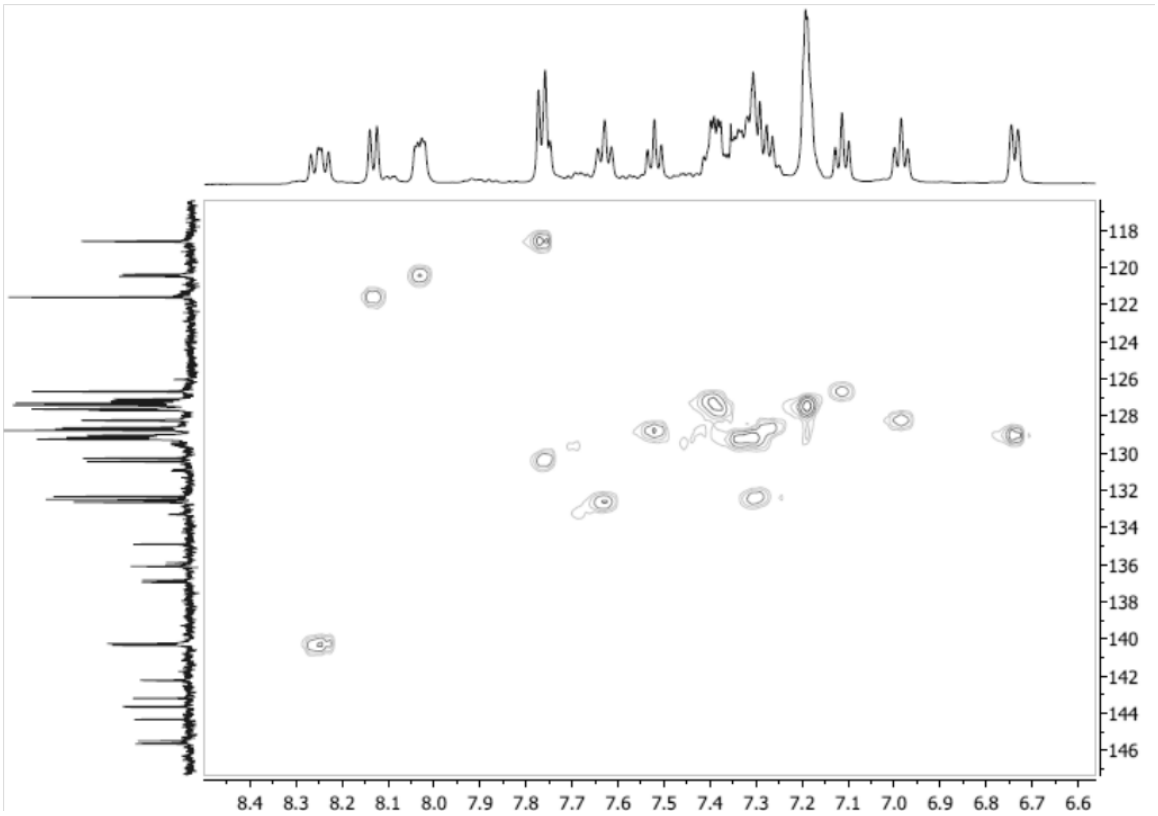
^{13}C {^{1}H} of **7** & **8**, THF-*d8*, -70 °C full spectrum



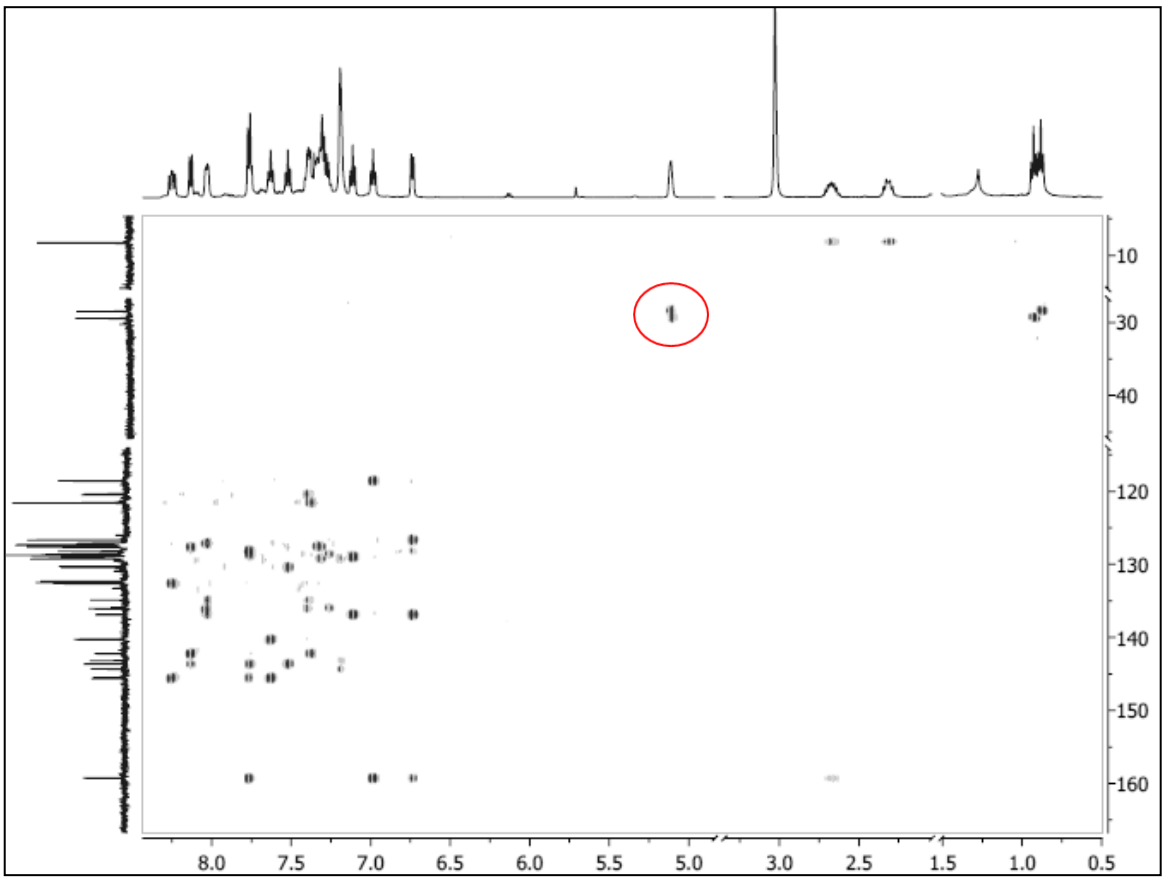
^{1}H-^{31}P HMBC of **7** & **8**,. The signal indicating coupling in **8** between P and O*H* is circled in red.



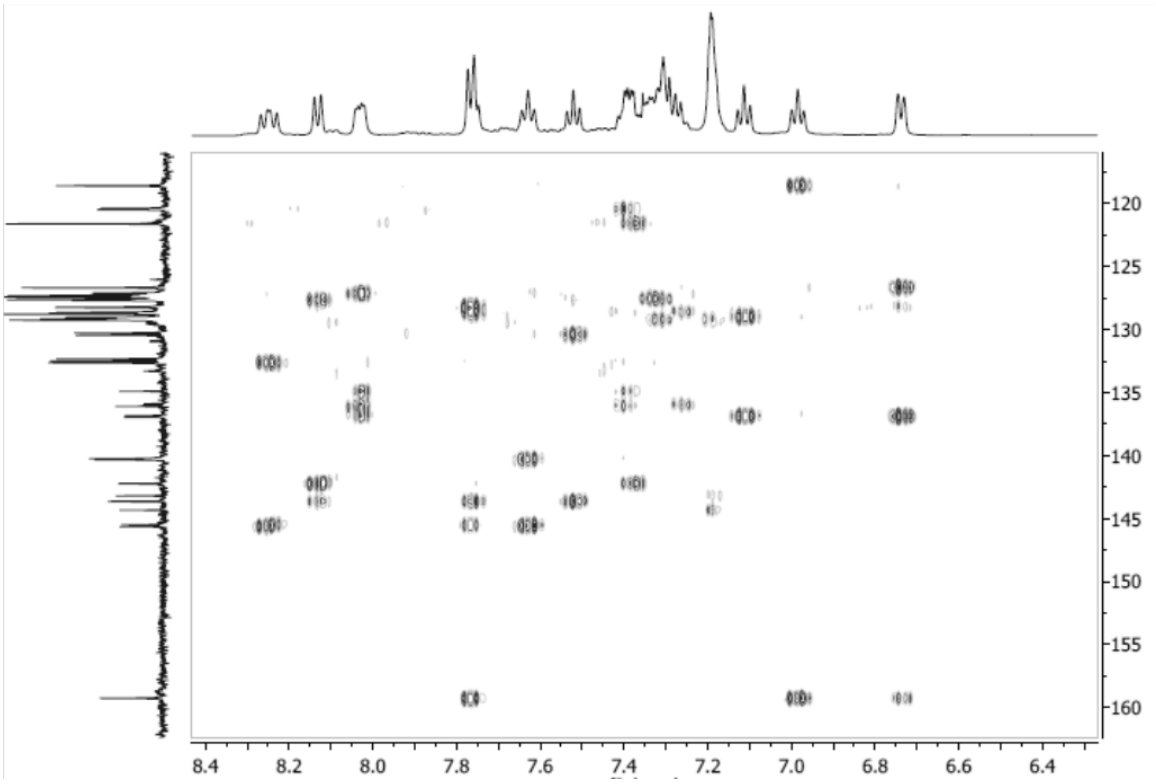
^{1}H-^{13}C gHSQC of **7** & **8**, full spectrum



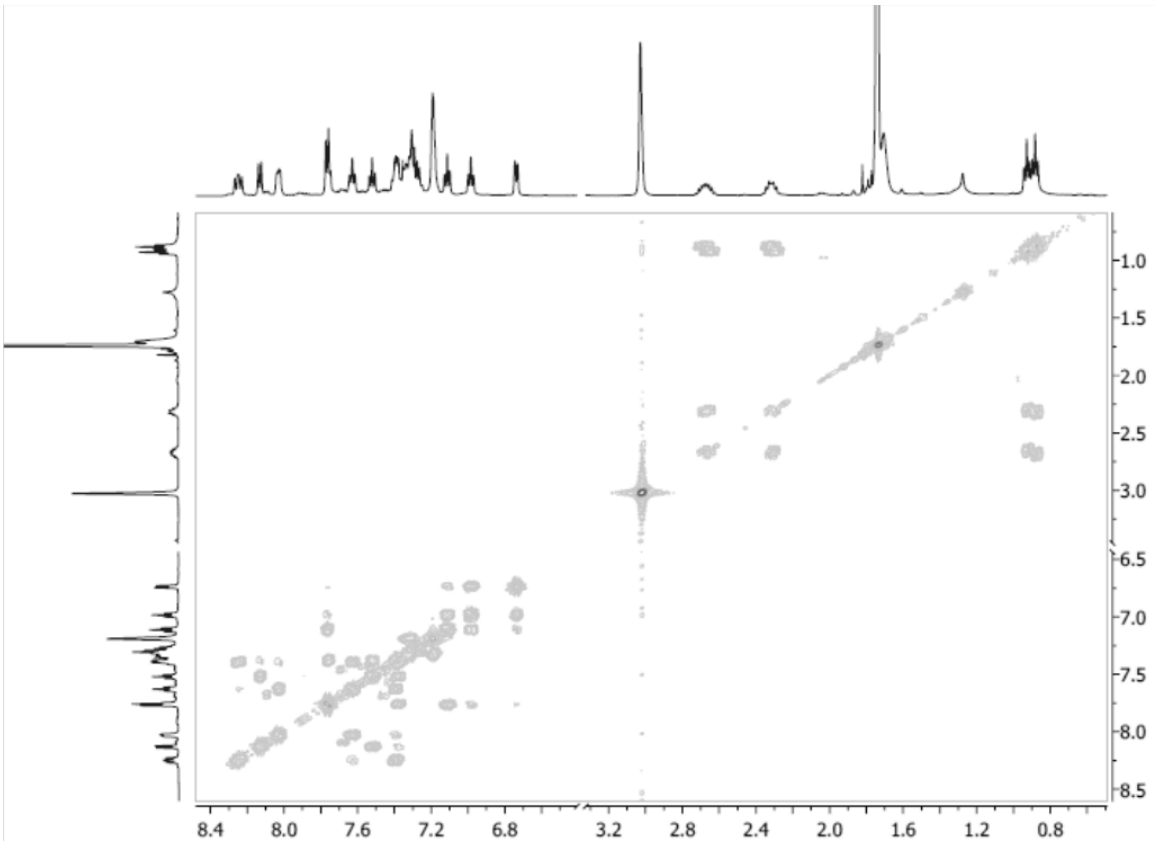
^{1}H-^{13}C gHSQC (aromatic region) of **7** & **8**



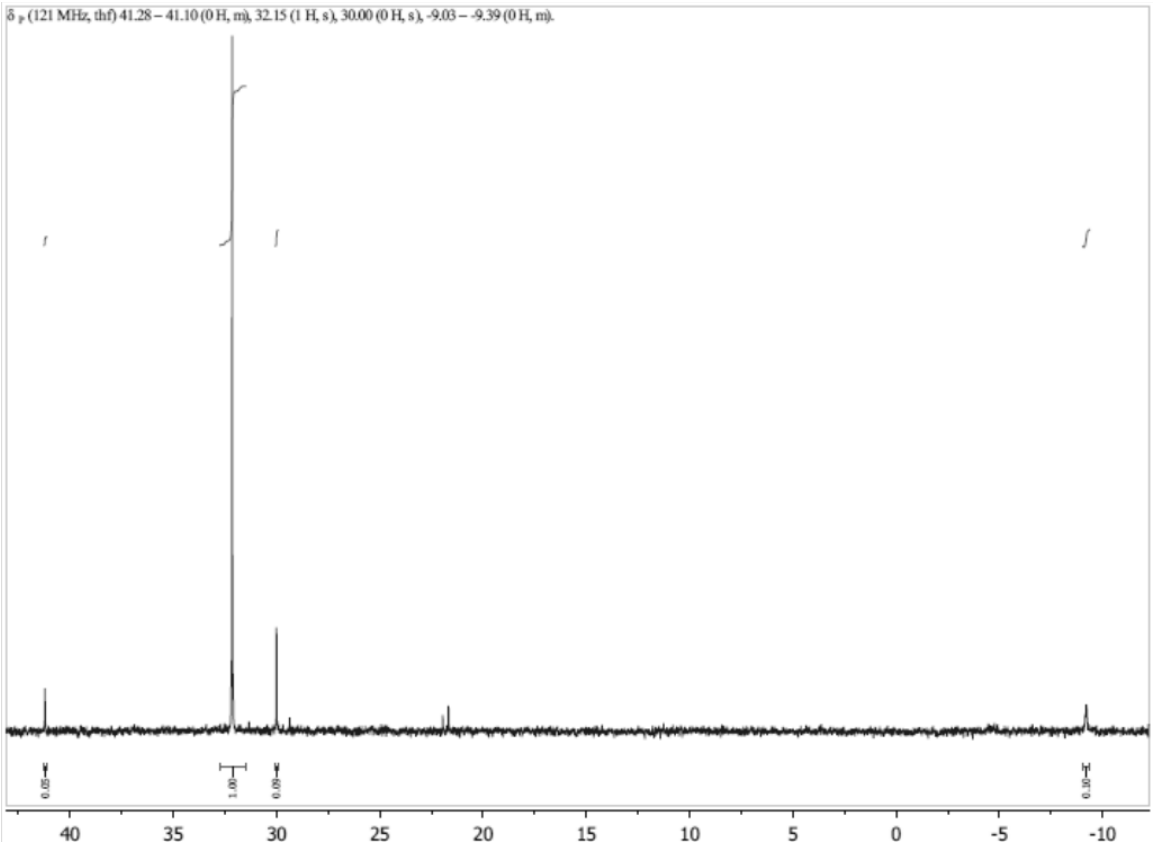
^{1}H-^{13}C gHSQC of **7** & **8**, full spectrum.
The signal indicating coupling between P*C*H$_2$ and PO*H* is circled in red.



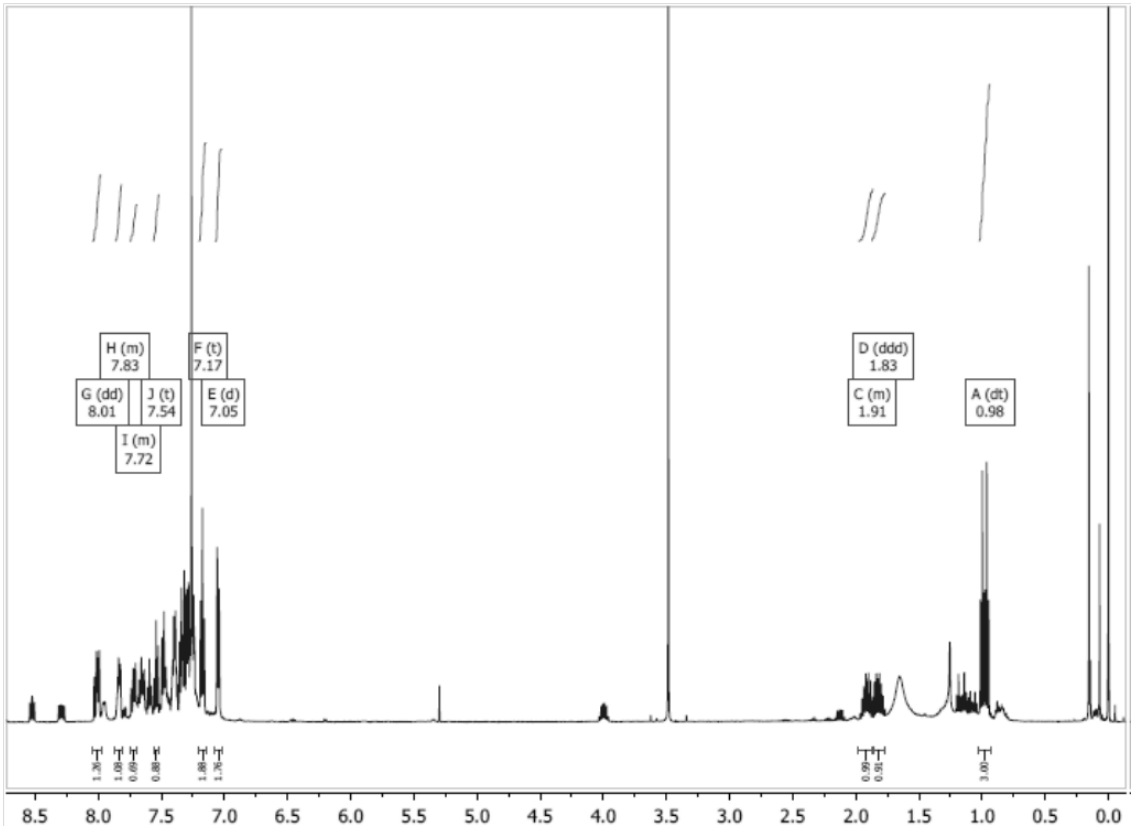
^{1}H-^{13}C gHSQC of **7** & **8** (aromatic region)



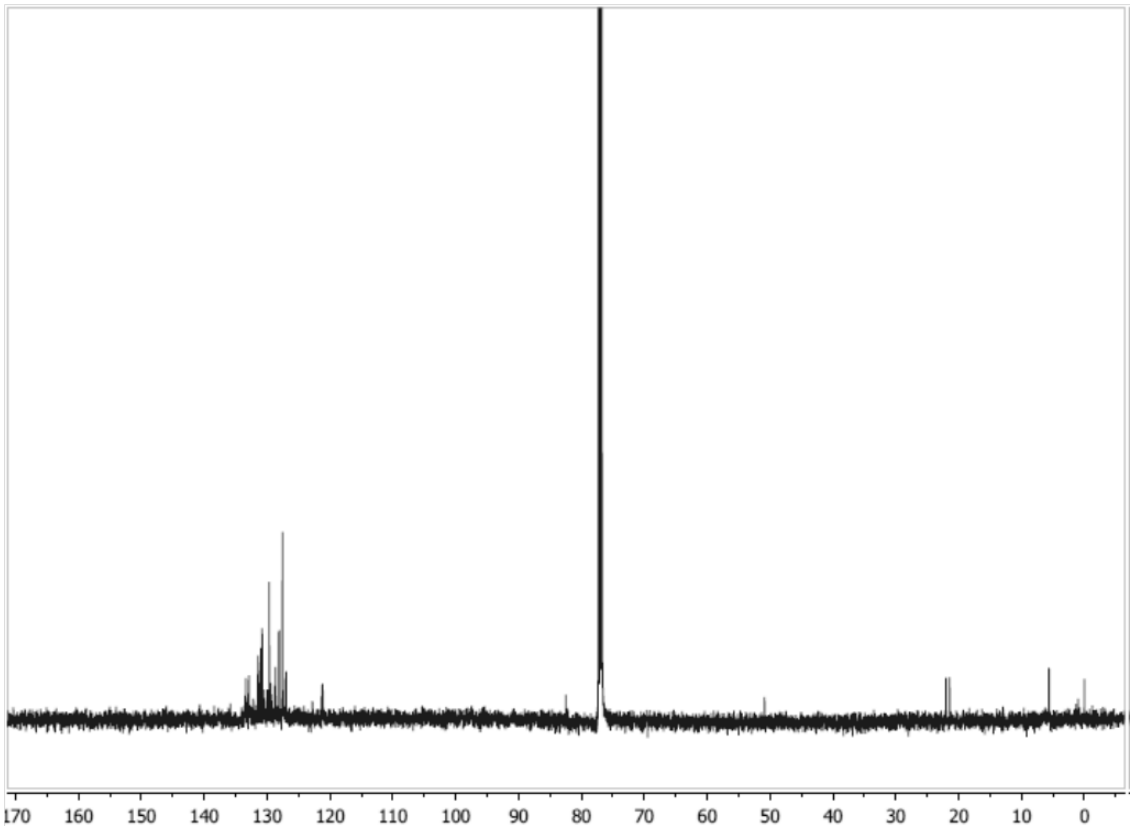
Partial gCOSY of **7** & **8**



$^{31}P\{^{1}H\}$ NMR (THF-*d8*) of crude product of hydroxyphosphorane decomposition.

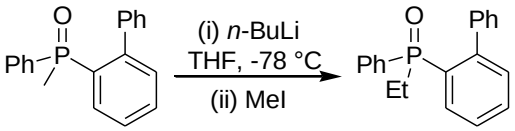


^{1}H NMR of crude product of hydroxyphosphorane decomposition.

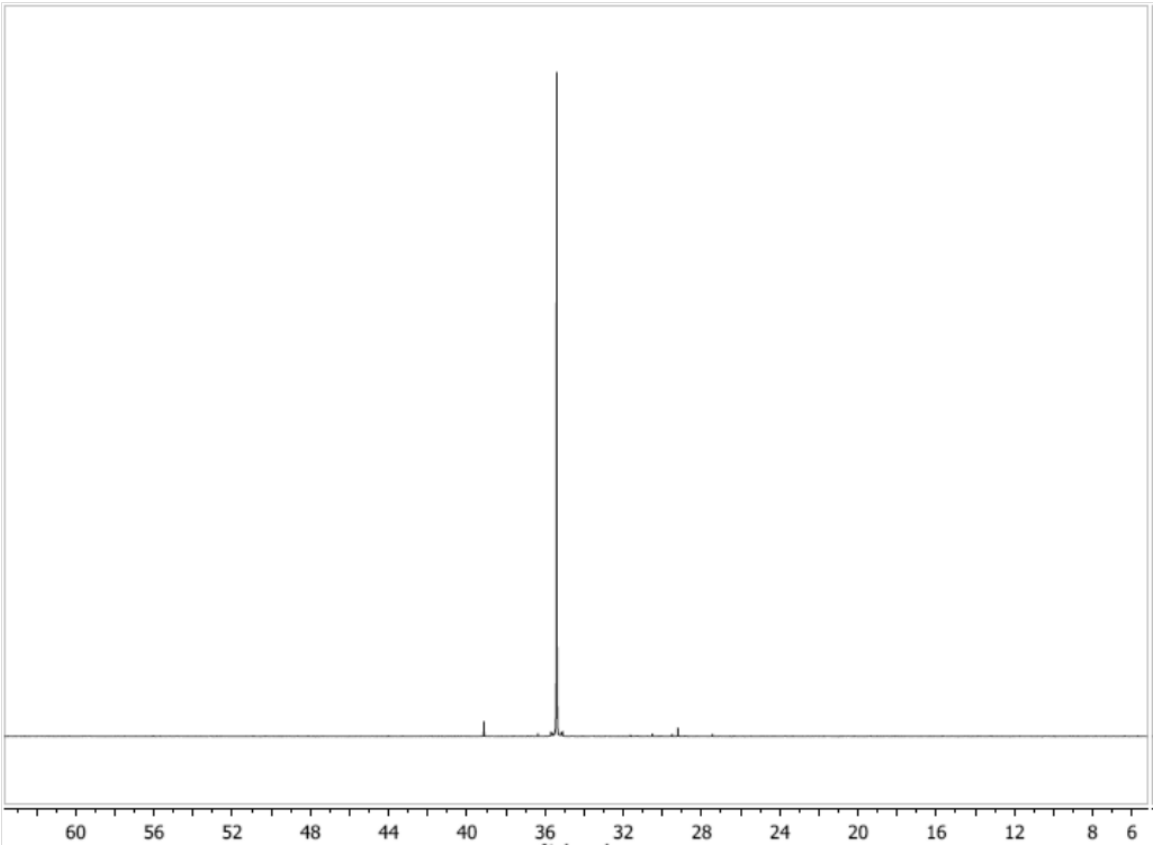


$^{13}C\{^{1}H\}$ NMR of crude product of hydroxyphosphorane decomposition.

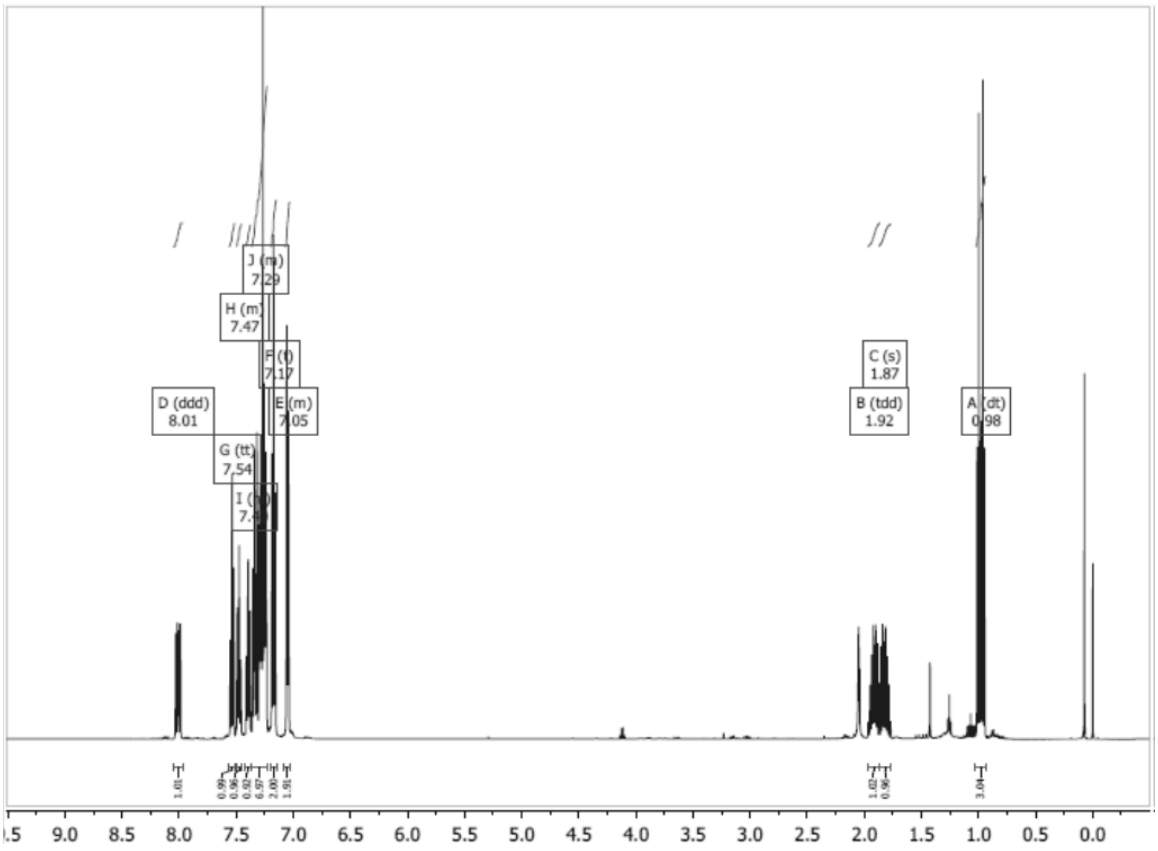
(Biphenyl-2-yl)ethylphenylphosphine oxide (10)



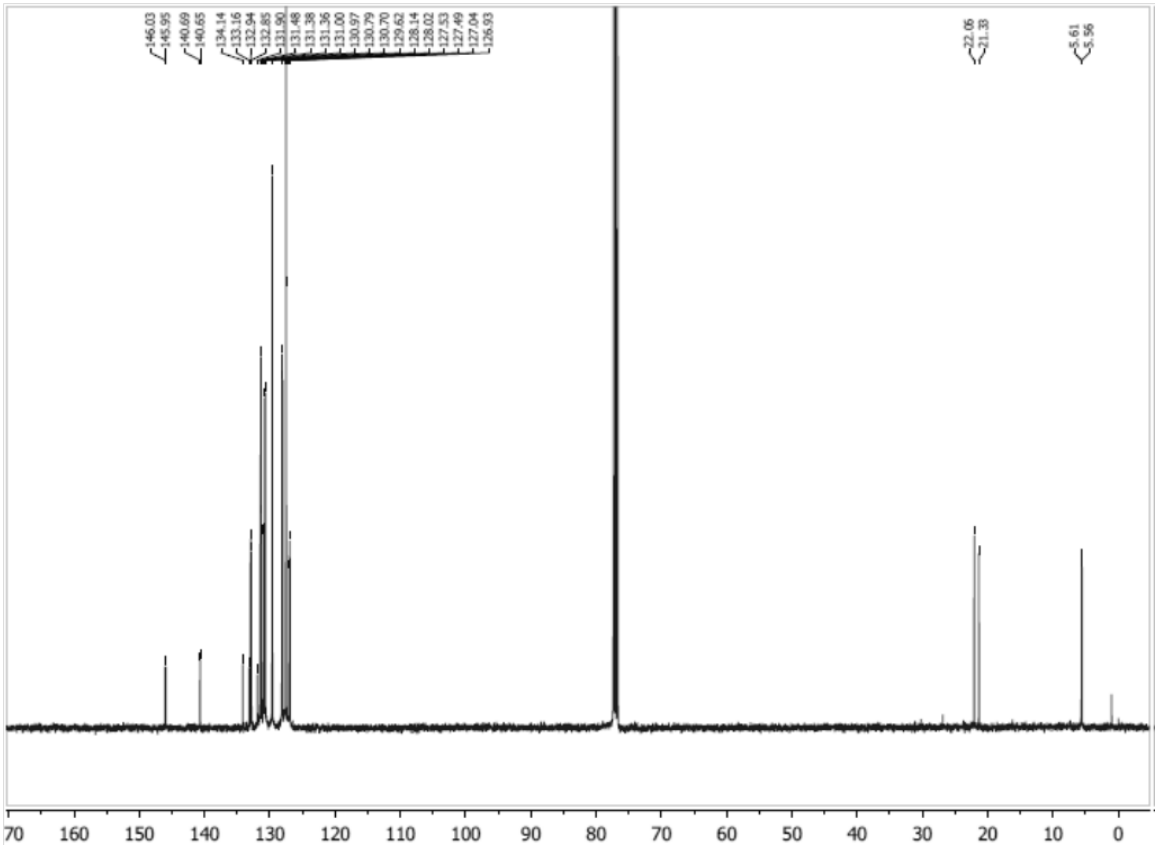
9 **10**



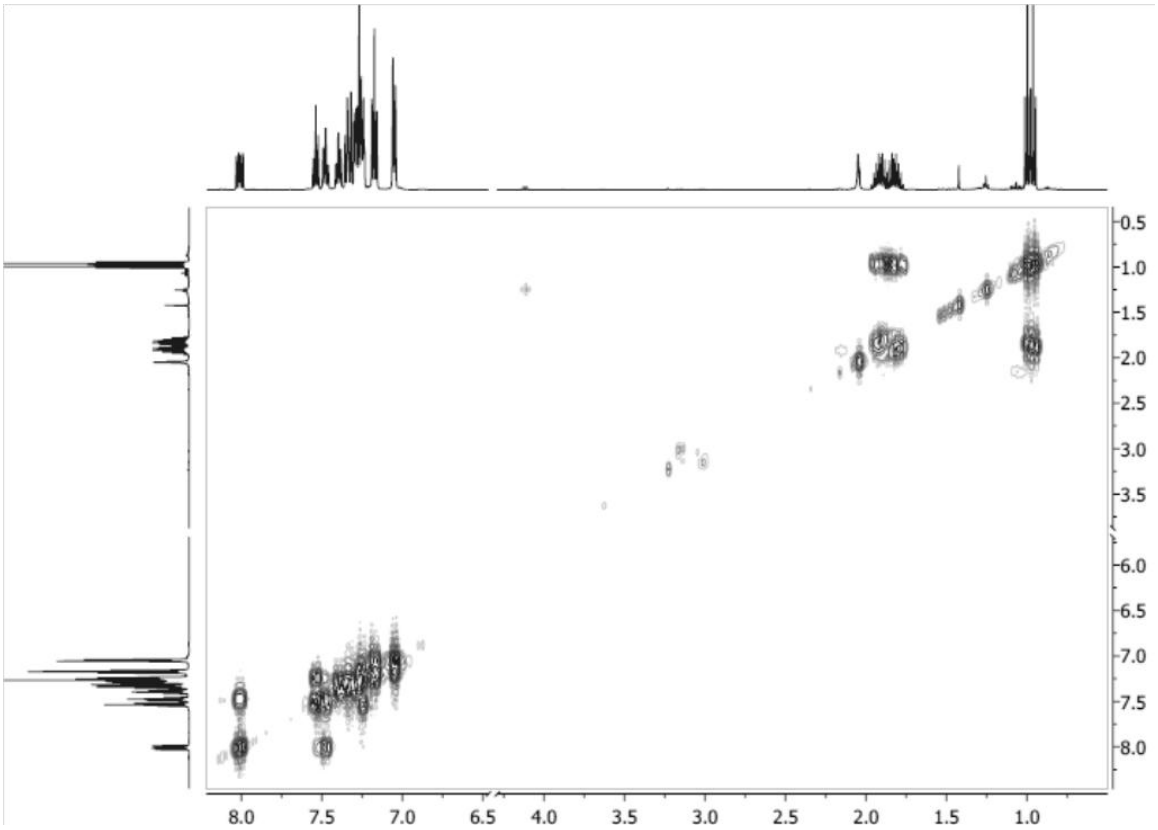
$^{31}P\{^{1}H\}$ NMR of **10**



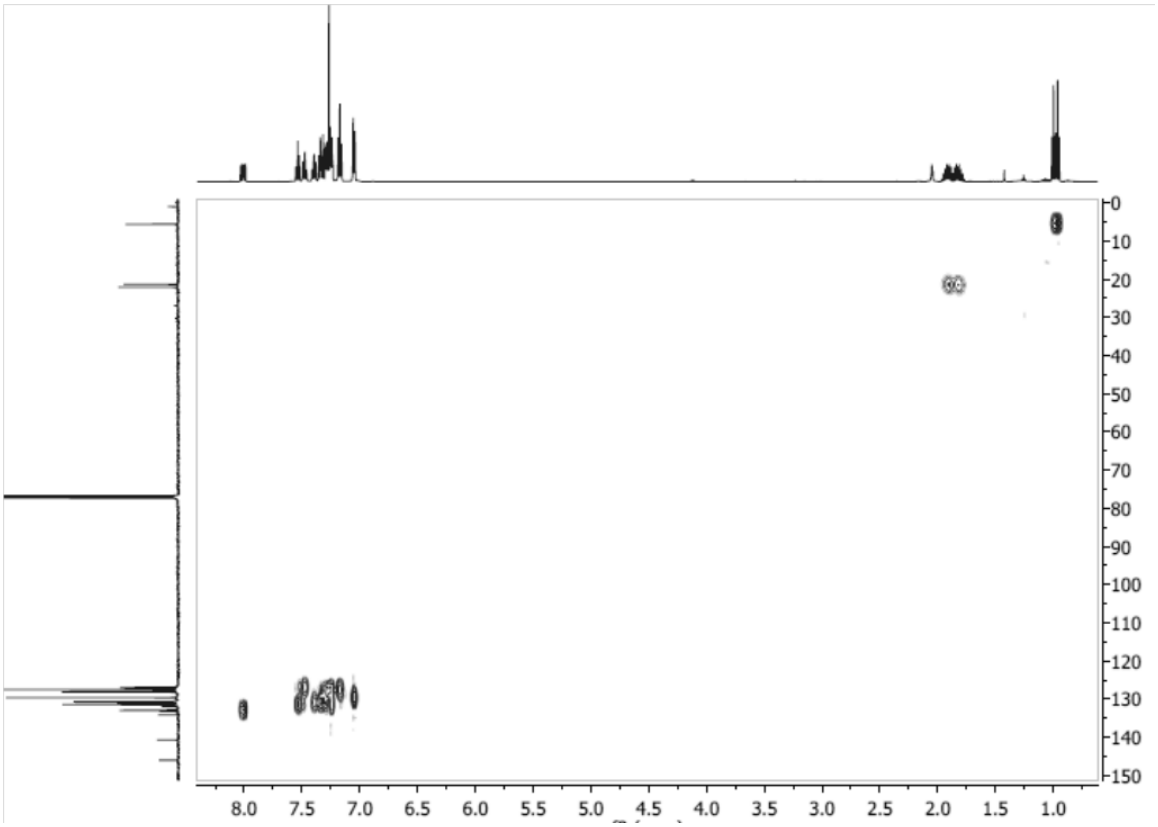
^{1}H NMR of **10**



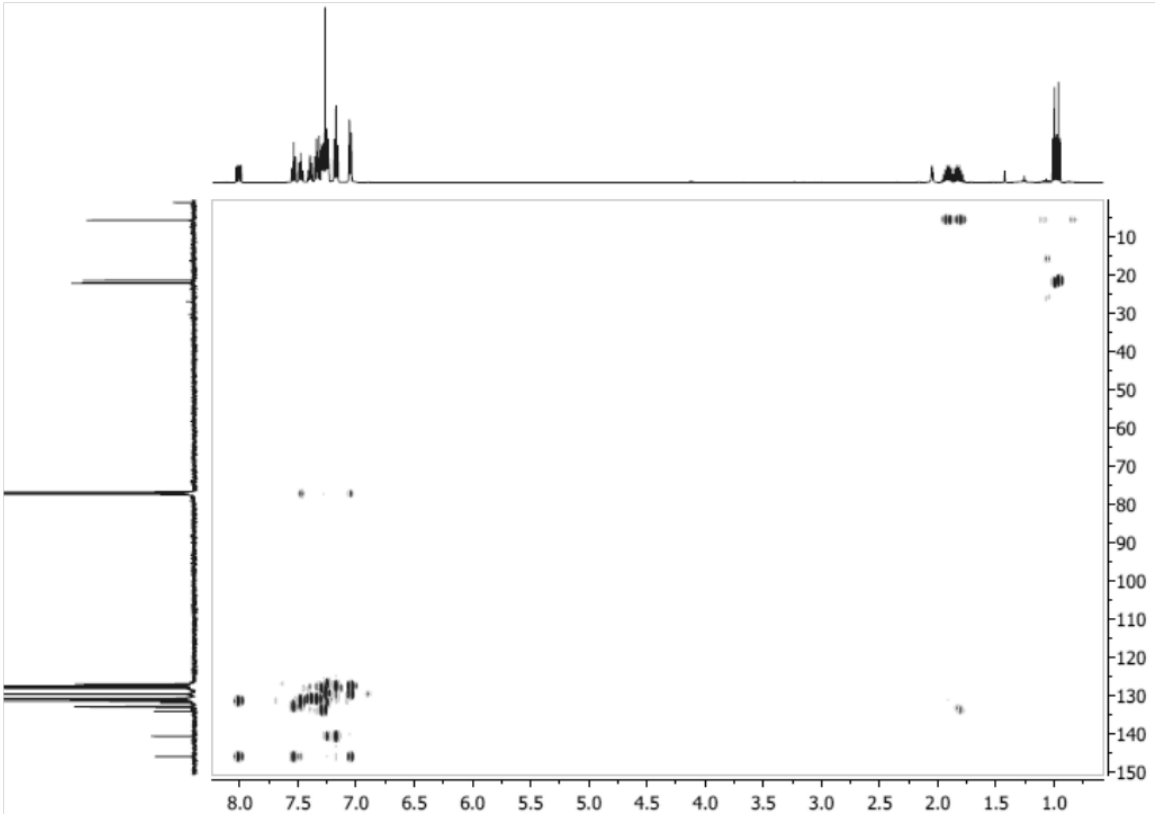
^{13}C{^{1}H} NMR of **10**



gCOSY of **10**

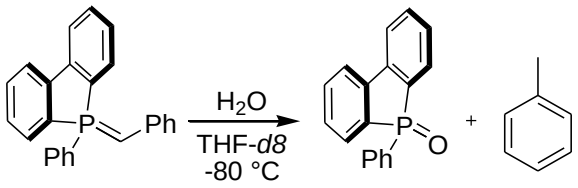


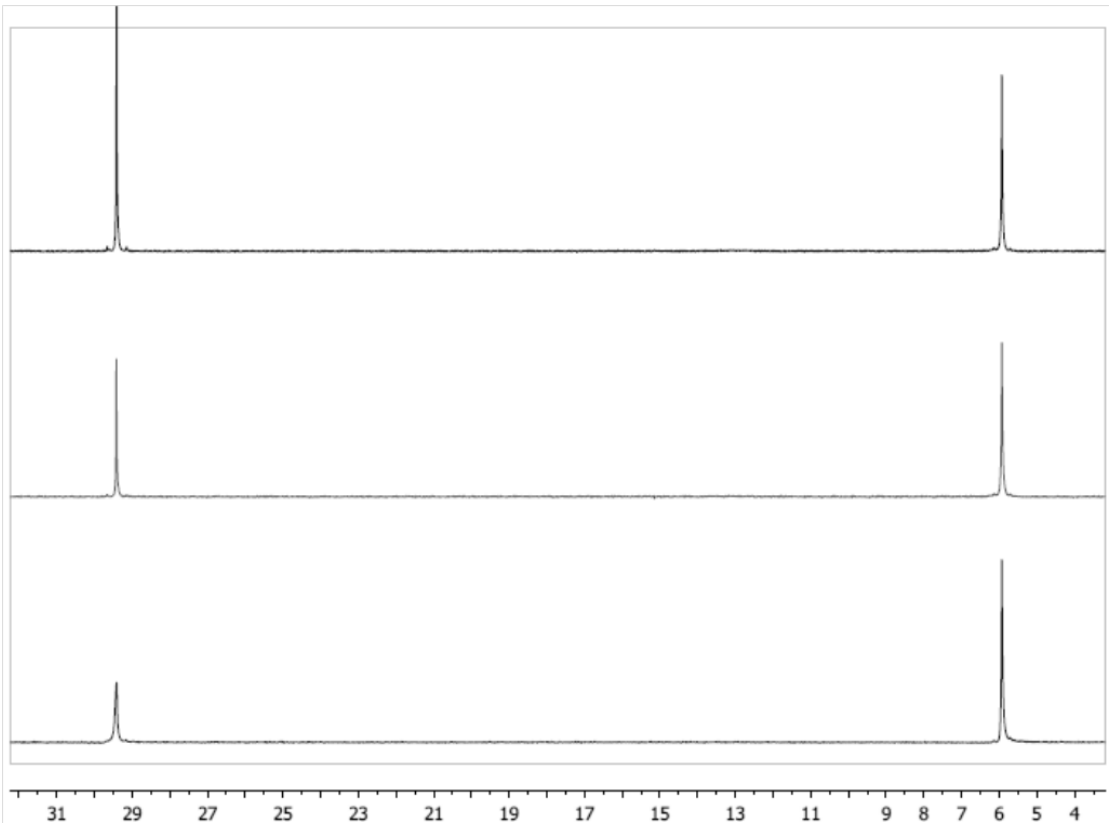
gHSQC of **10**



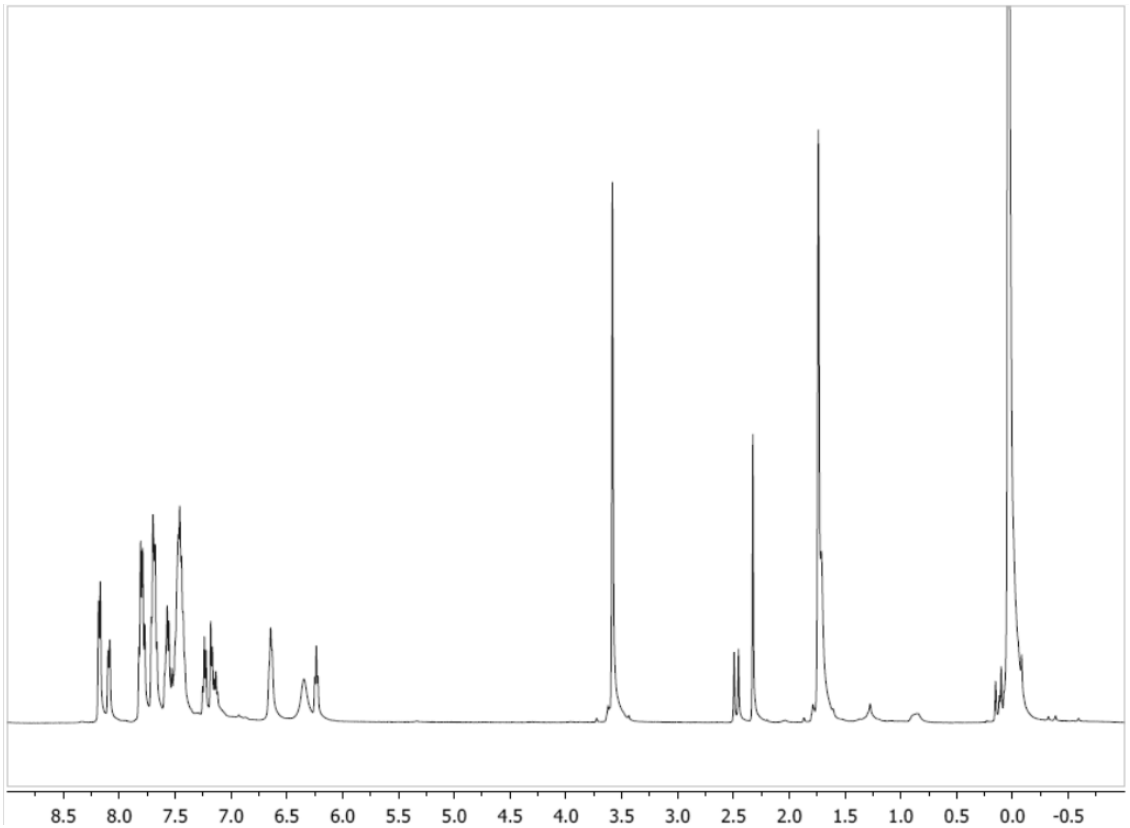
^{1}H-^{13}C gHMBC of **10**

Reaction of *P*-benzylidene-*P*-phenyl-5*H*-dibenzophosphole 6 with H_2O

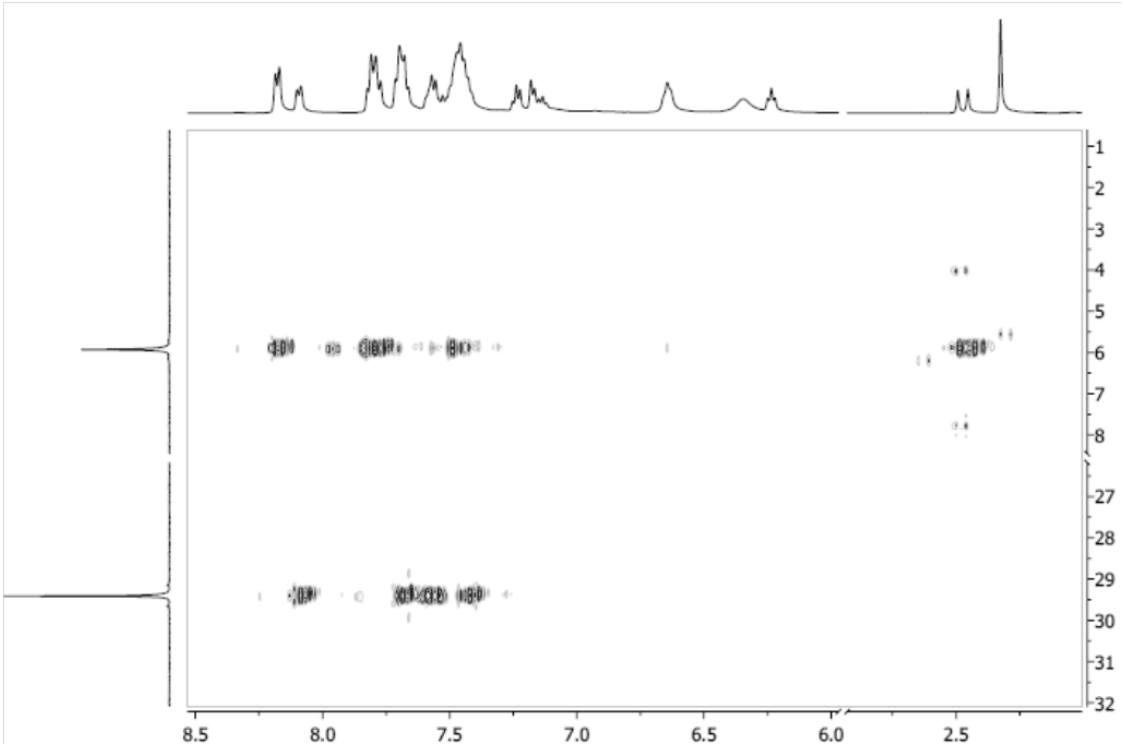




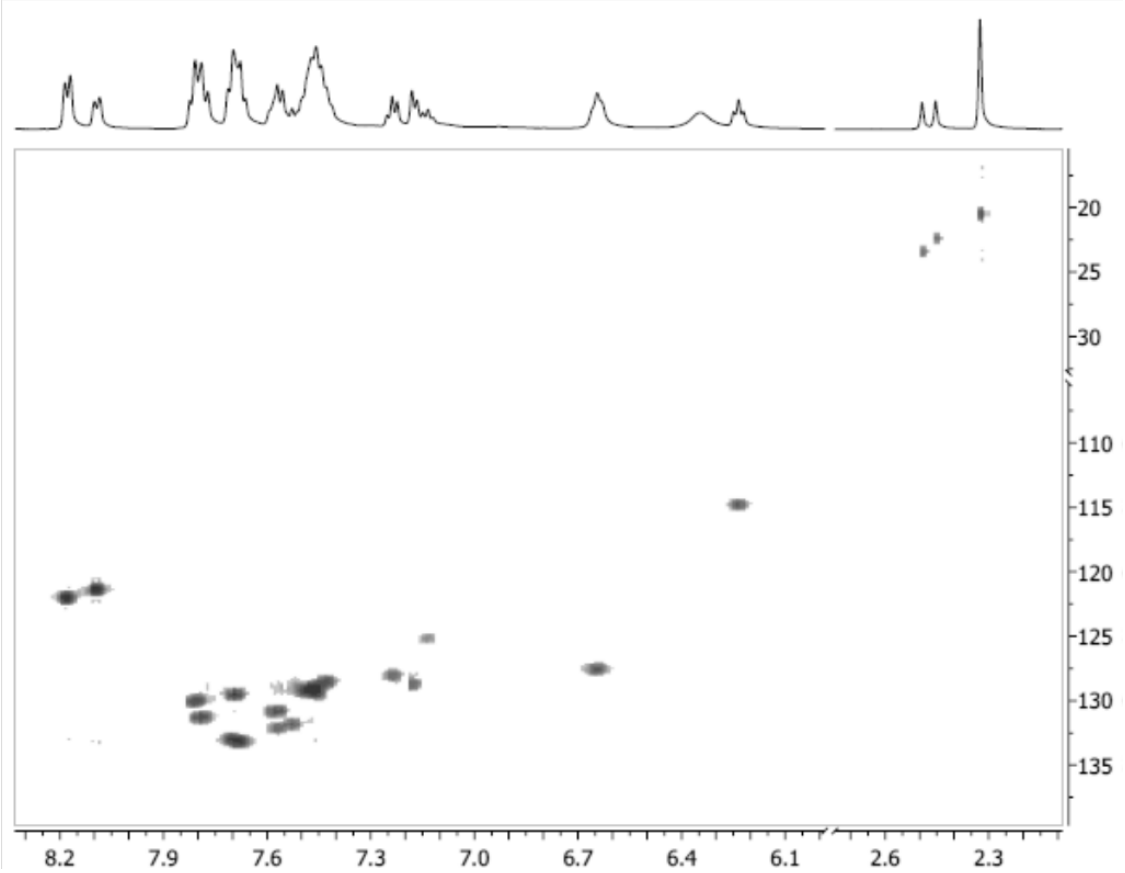
Stacked ^{31}P NMR spectra (first spectrum at bottom, 2nd & 3rd spectra recorded later) showing ylide **6** and phosphine oxide.



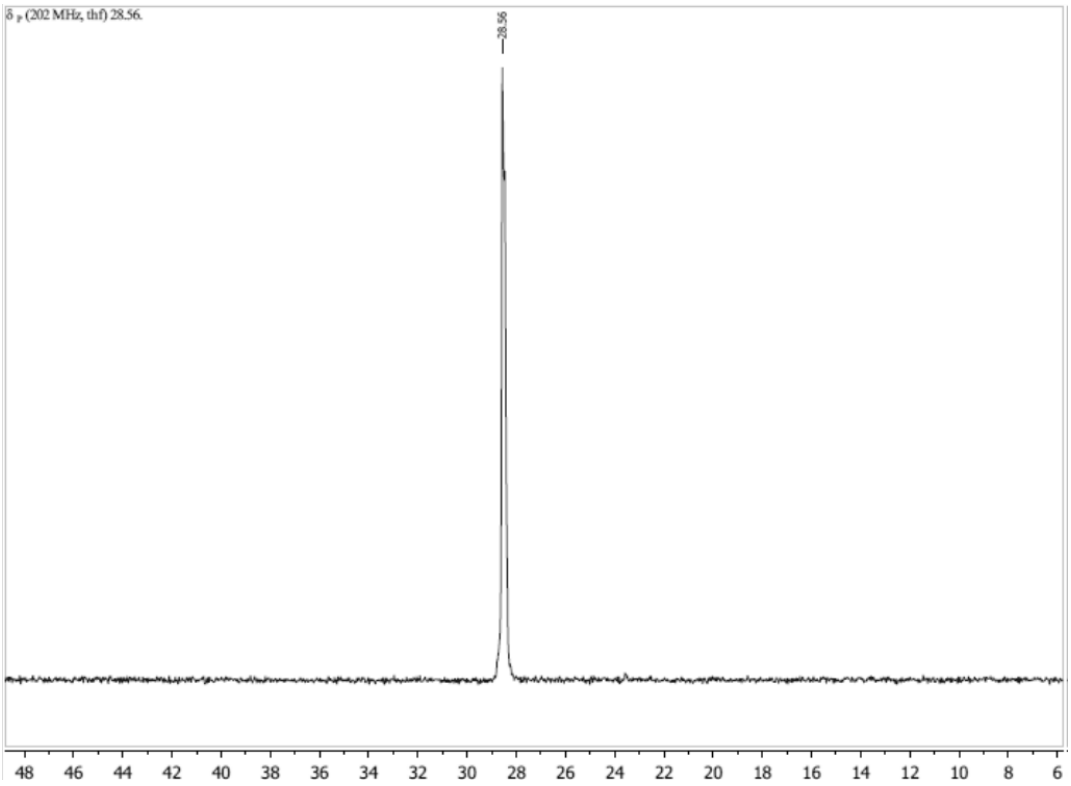
^{1}H NMR of the reaction mixture containing ylide **6** and phosphine oxide.



^{1}H-^{31}P HMBC showing the benzylidene C*H* is attached to the phosphorus whose signal appears at 5.9 ppm.

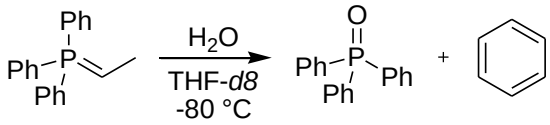


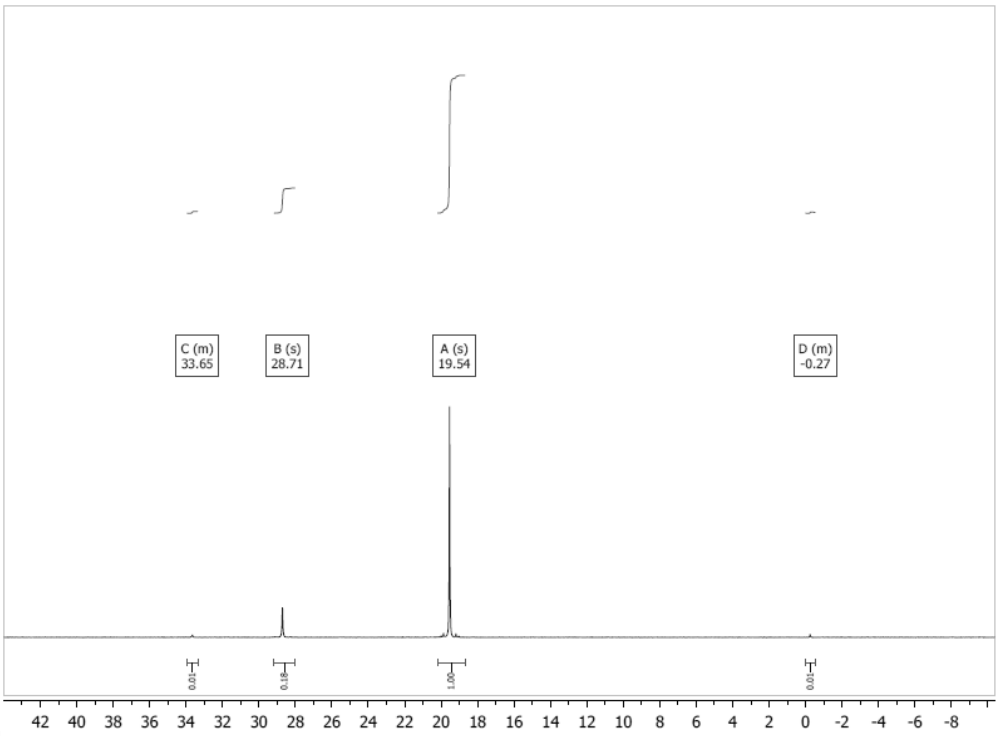
Partial HSQC of mixture of ylide **6** and phosphine oxide.



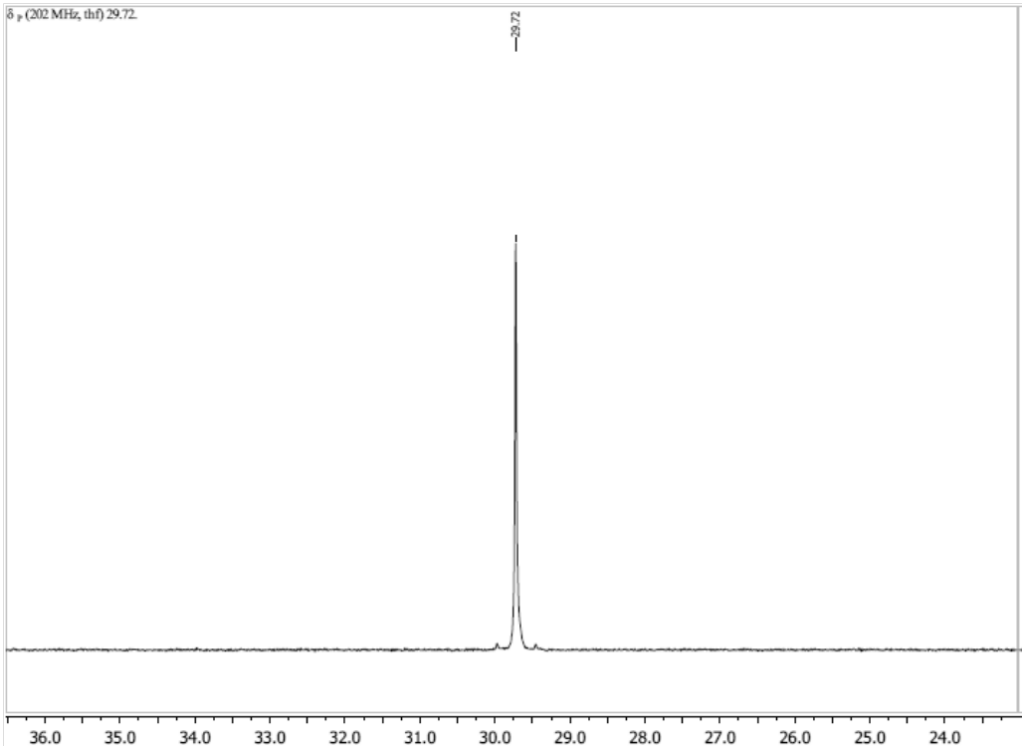
^{31}P NMR of *P*-phenyldibenzophosphole oxide product of reaction done by second procedure described above (reaction in Schlenk flask followed by cannula transfer to NMR tube).

Reaction of *P*-ethylidenetriphenylphosphorane 5 with H_2O





^{31}P NMR of ylide **5** (ethylidenetriphenylphosphorane) in THF-*d8*. Also contains oxidation product (Ph_3P) and small amounts of Ph_3P and $EtPh_2P$ (hydrolysis product).



^{31}P NMR of Ph_3PO product of hydrolysis of **5**.

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2 No exceptions to this assumption have yet been reported.

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