

Supporting Information for:

## Room-Temperature Reduction of Sulfur Hexafluoride with Metal Phosphides

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**General Considerations** All reagents and solvents were dispensed in a 2001 issue IT Glovebox (H<sub>2</sub>O levels vary between 2-6 ppm) unless otherwise stated. All reactions were conducted at ambient temperature unless otherwise stated. <sup>1</sup>H, <sup>31</sup>P, <sup>19</sup>F, <sup>11</sup>B and <sup>13</sup>C NMR data were collected at 300K on either a Bruker AV-300 or AV-500 spectrometer, and heteronuclei were referenced to external standards. Benzene *d*-6 was added to samples to enable autosampler use/automated locking on the Bruker instruments. <sup>1</sup>H NMR spectra are referenced to residual non-deuterated NMR solvent from the sample (C<sub>6</sub>D<sub>5</sub>H = 7.16 ppm). <sup>13</sup>C NMR spectra are referenced to as follows (C<sub>6</sub>D<sub>6</sub> = 128.06 ppm). Sulfur hexafluoride was dispensed from a “Pretext” 12 inch “party balloon” latex balloon, purchased from Amazon. The balloon was taped with electrical tape to a cut 6 mL syringe equipped with a Luer lock

## Solvents

**Dichloromethane** was purchased in drum, ACS grade from Fisher, and used as received.

**Tetrahydrofuran** was purchased as anhydrous >99% ACS grade from Sigma Aldrich and stored over 3Å molecular sieves under nitrogen.

**Toluene** was purchased in a drum, ACS grade from Fisher and was passed through a double column purification system (activated alumina and activated Q-5) from MBraun Inc. and stored over 3Å molecular sieves under nitrogen.

**Ether** was purchased as anhydrous >99% ACS grade from Sigma Aldrich and stored over 3Å molecular sieves under nitrogen.

## Reagents

**Borane dimethyl sulfide** was purchased from Sigma Aldrich and used as received.

***n*-butyllithium** and ***tert*-butyllithium** were purchased from Sigma Aldrich and used as received.

**Di-*tert*-butylphosphine, diphenyl(trimethylsilyl)phosphine and triphenyl phosphine** were purchased from Sigma Aldrich and used as received.

**Diphenylphosphine, dicyclohexylphosphine and 1,3,5,7-Tetramethyl-2,4,6-trioxaphosphaadamantane** (35 wt % in xylenes) were obtained from Cytec/Solvay and diluted to 0.5 M solutions in THF before use.

**Potassium diphenylphosphide solution** (0.5M in THF) was purchased from Sigma Aldrich and used as received.

**Potassium hydride** was obtained as a suspension in mineral oil from Sigma Aldrich, and was washed with pentane inside a glovebox, then stored as the solid in a sample vial.

**Sulfur Hexafluoride** was purchased from Air-Liquide in an F-Cylinder as “Chemically Pure, 7, grade, CGA-590.”

**Sulfur Powder** was purchased from Sigma Adrich as 99.98% trace metal basis.

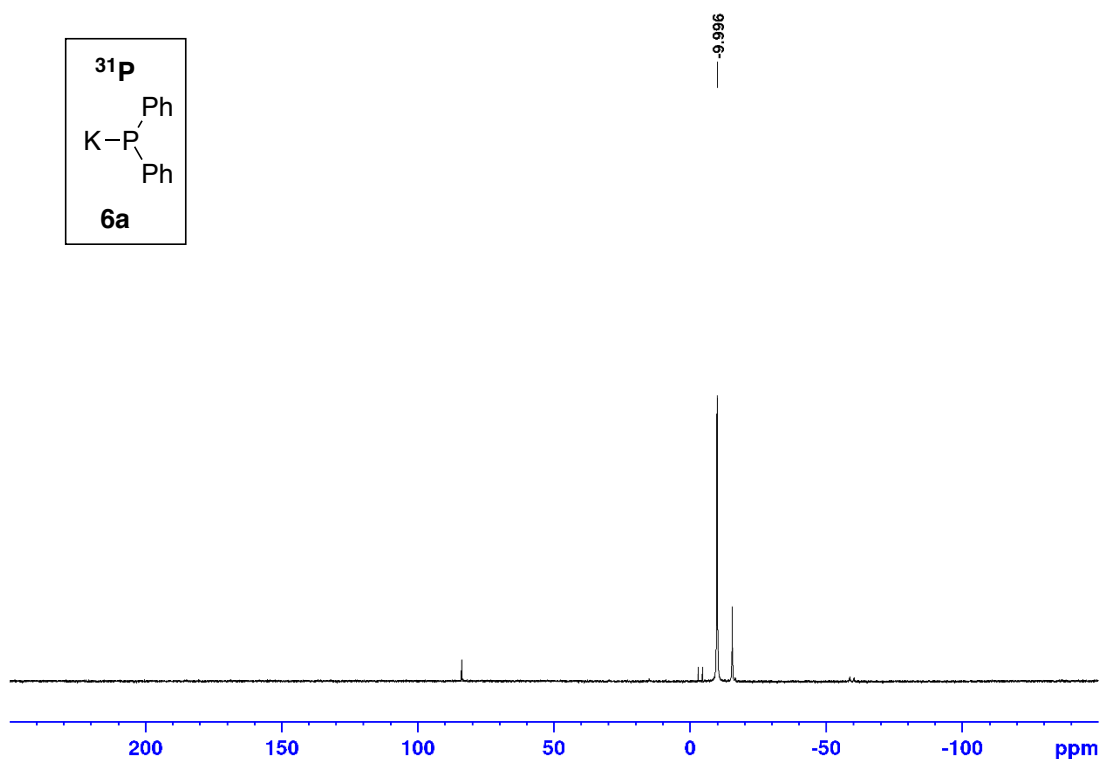
## Synthetic Procedures:

### Reaction of potassium diphenylphosphide and SF<sub>6</sub> gas:

Potassium diphenylphosphide (0.2 mL, 0.1 mmol, 0.5M in THF) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.55 mL THF and 0.05 mL benzene-*d*<sub>6</sub>). The solution was then transferred to an NMR tube and the sample was capped with a septum. An SF<sub>6</sub> gas filled balloon equipped with a needle was used to bubble SF<sub>6</sub> through the solution for 15s. The solution went from an orange to clear/yellow colour during this period in which the needle and septum were removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy. The dominant product was **7a**, but small amounts of other products were observed. Their analysis is described later.

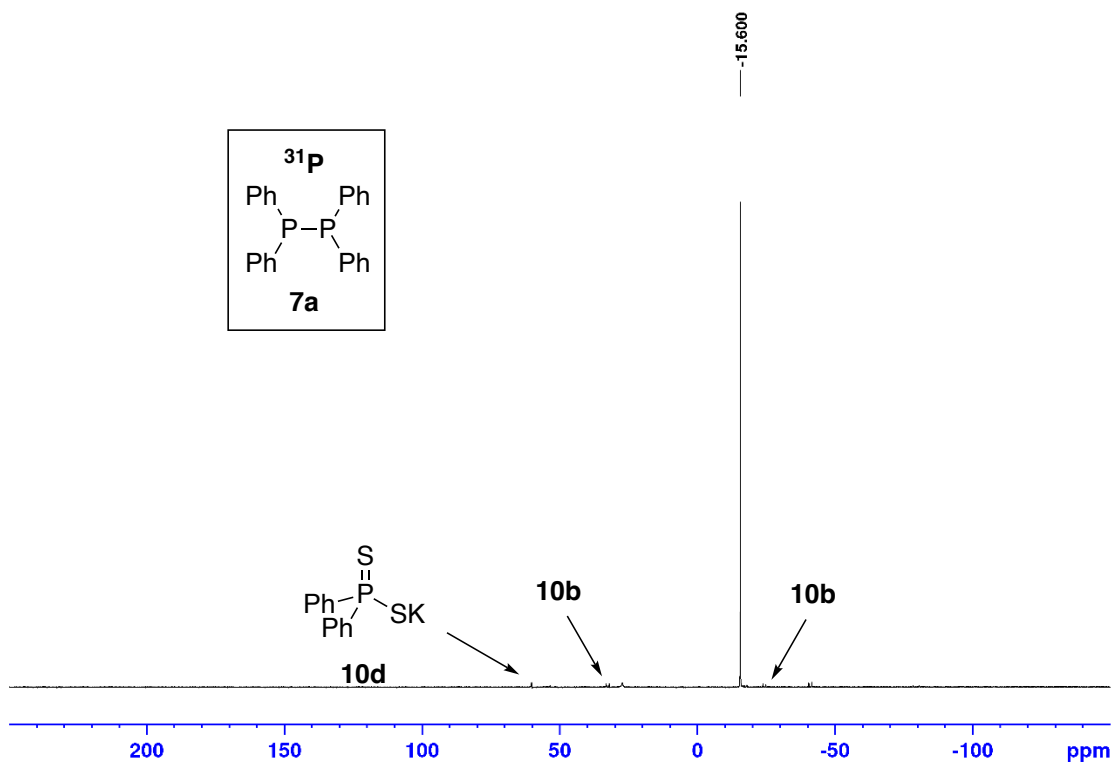
### Initial <sup>31</sup>P NMR Spectrum of KPPH<sub>2</sub> solution:

<sup>31</sup>P (202 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ -10.0 (s).



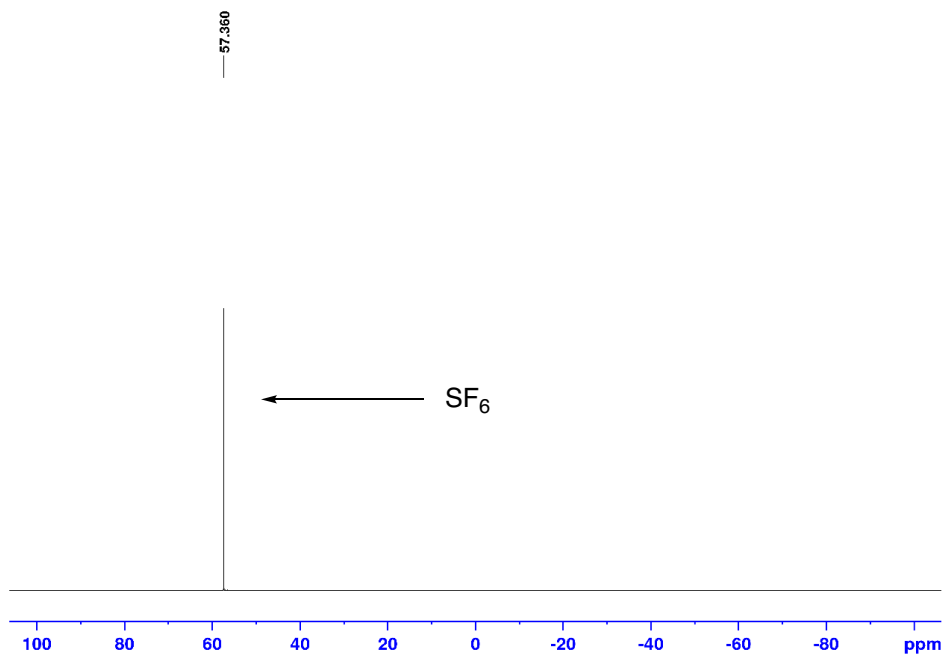
**$^{31}\text{P}$  NMR Spectrum after  $\text{SF}_6$  addition:**

$^{31}\text{P}$  (202 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -15.6 (s).

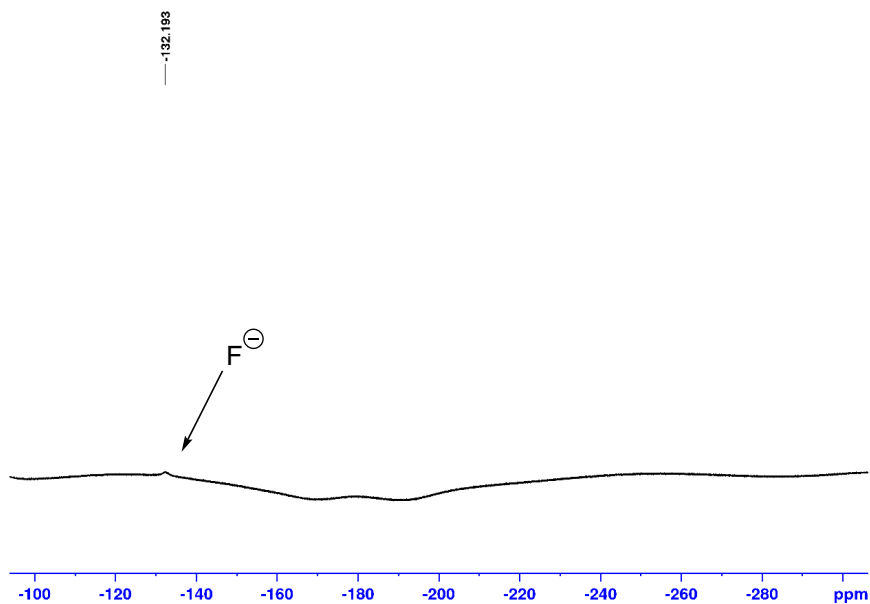


$^{19}\text{F}$  (470 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  57.4 (s) ( $\text{SF}_6$ )

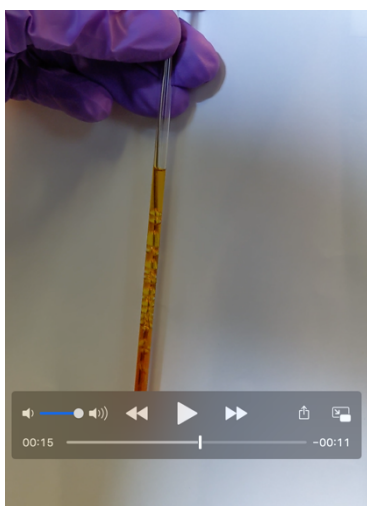
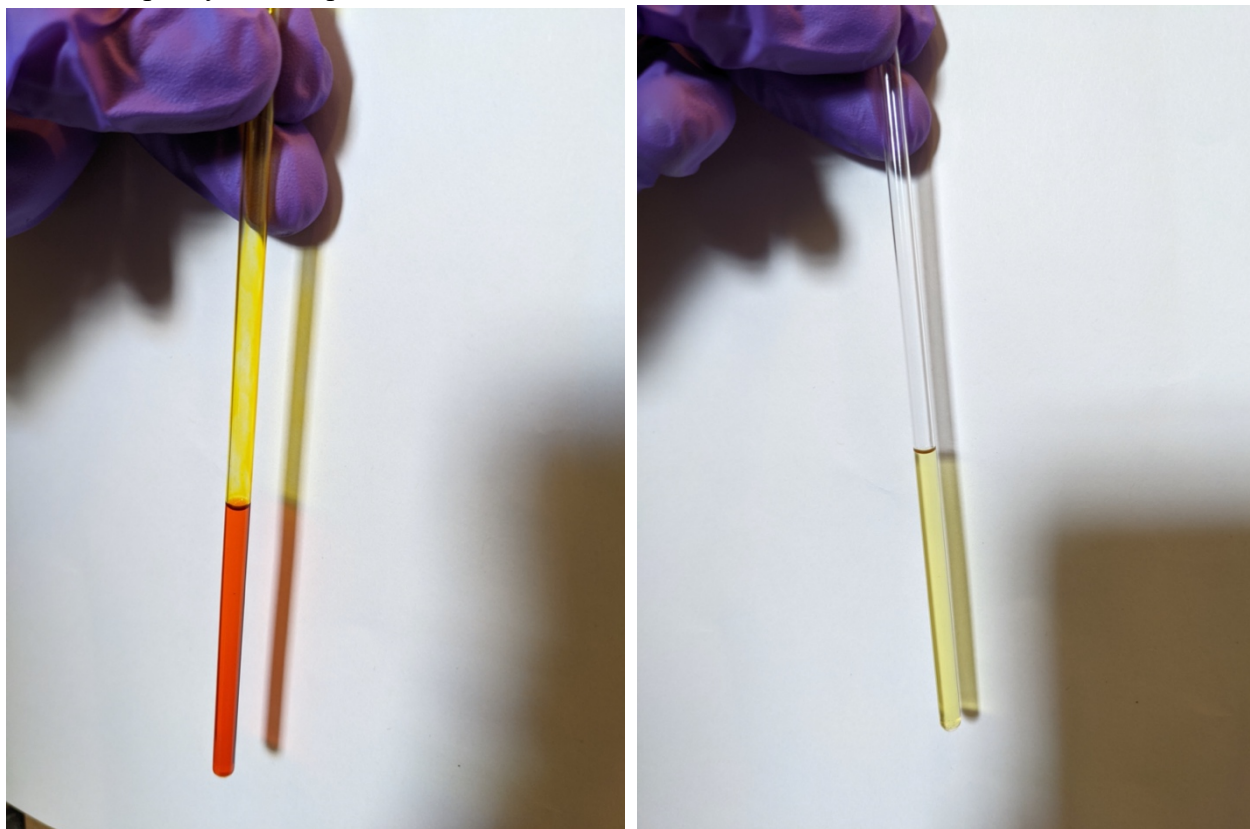
$^{19}\text{F}$  spectrum of reaction after  $\text{SF}_6$  addition- 0 center point



-200 center point  $^{19}\text{F}$  spectrum (470 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -132 (br, s).



**Figure S1:**  $KPPh_2$  solution before  $SF_6$  addition (left), and after  $SF_6$  addition (right). The images are described as follows: The tube on the right contains a bright orange liquid, the tube on the right contains a pale yellow liquid.

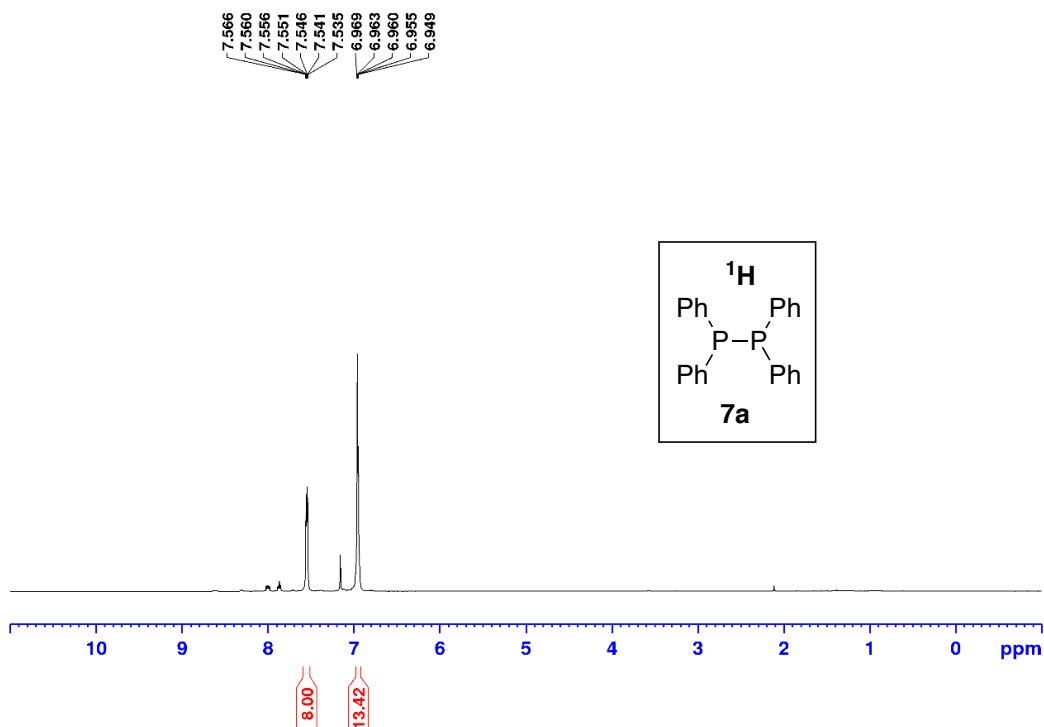


A video of the experiment is separately available (the image provided at left is a thumbnail, not a link). A short description of the video is provided here: An NMR tube containing a bright orange liquid and equipped with a rubber septum is held in a nitrile gloved hand. A needle connected to a  $SF_6$  balloon is inserted into the NMR tube below the liquid level. It should be noted the orange film on the sides of the NMR tube above the liquid immediately becomes colourless as the needle is introduced, due to reaction with the  $SF_6$ . A second, smaller needle is inserted, providing an outlet. Bubbles are observed, and within 5 seconds the colour of the liquid turns from bright orange to a dull yellow.

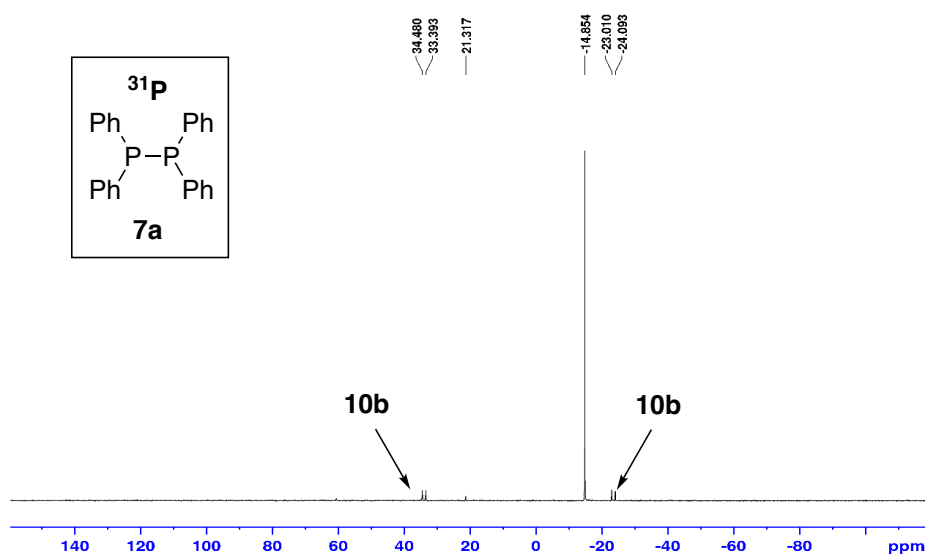
### Scale up and isolation of tetraphenyldiphosphine:

Reaction of potassium diphenylphosphide and SF<sub>6</sub> gas: Potassium diphenylphosphide (2 mL, 1 mmol, 0.5M in THF) was dispensed into a 10 mL round bottom flask equipped with a septum. The solution was diluted with additional solvent (2 mL THF). An SF<sub>6</sub> gas filled balloon equipped with a needle was used to bubble SF<sub>6</sub> through the solution until all orange color dissipated and then the bubbling was continued for an additional 15s. The solution was then analyzed using NMR spectroscopy to confirm reaction completion. Volatiles were then removed in vacuo and ether was added (10 mL). The slurry was filtered over a fine porous frit and then washed with additional ether (2 x 5mL). The ether was then removed in vacuo and the solid taken up in toluene (3 mL). The solution was filtered through a 0.3 micron HPLC syringe filter and the toluene was then removed in vacuo. The crude solid obtained (177 mg) was then characterized without further purification. Minor amounts of **10b** and **10c** were noted in the spectrum.

<sup>1</sup>H (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.55 (8H, m), 6.96 (12H, m).



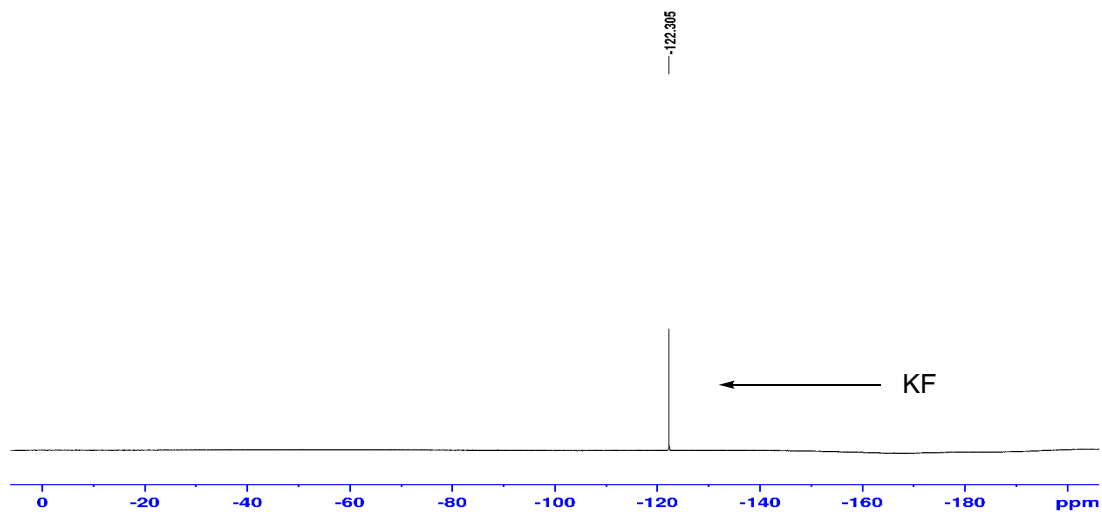
$^{31}\text{P}$  (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -14.8 (s).



#### NMR analysis of the crude solution in $\text{D}_2\text{O}$ :

A portion of the solid remaining from filtration was taken up in  $\text{D}_2\text{O}$ , and a fluorine NMR spectrum was acquired. Analysis of the NMR spectrum indicated the presence of potassium fluoride by a strong, sharp peak in the appropriate region.

$^{19}\text{F}$  (470 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  -122 (s).

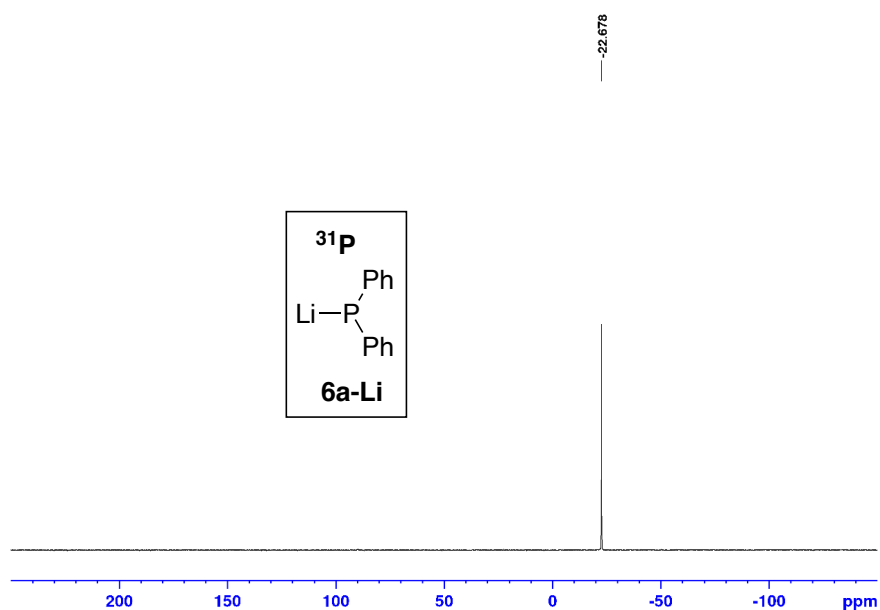




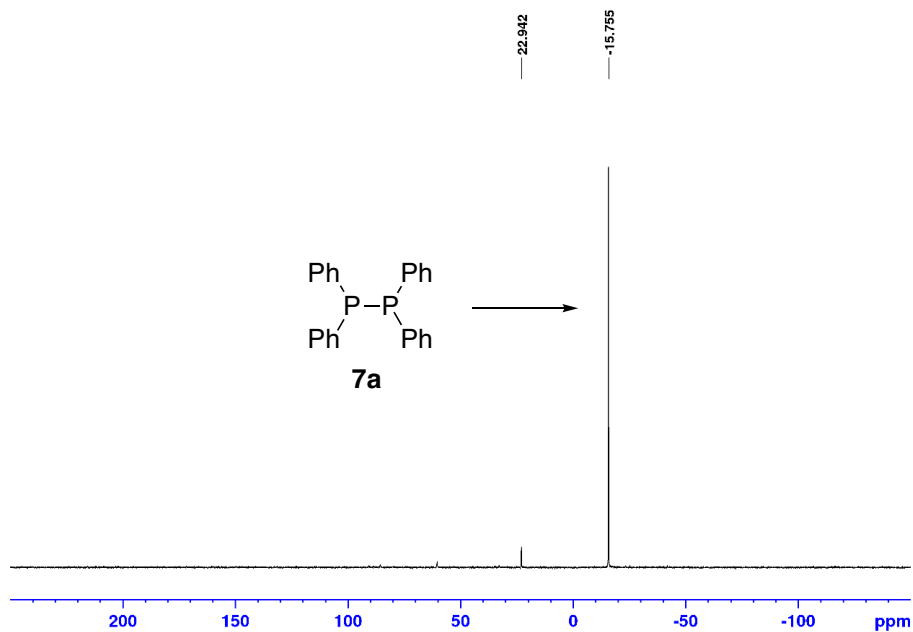
### Reaction of lithium diphenylphosphide and SF<sub>6</sub> gas:

Diphenylphosphine (0.2 mL, 0.1 mmol, 0.5 M in THF) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.55 mL THF and 0.05 mL benzene-*d*<sub>6</sub>). *n*-butyllithium (0.04 mL, 0.1 mmol, 2.5M) was then added and the solution turned orange. The solution was then transferred to an NMR tube and the sample was capped with a septum. An SF<sub>6</sub> gas filled balloon equipped with a needle was used to bubble SF<sub>6</sub> through the solution for 15s. The solution went from orange to clear/yellow colour during this period in which the needle and septum were removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy.

Spectrum of LiPPh<sub>2</sub> before SF<sub>6</sub> addition: <sup>31</sup>P (121 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ -22.7 (s).



Spectrum after SF<sub>6</sub> addition: <sup>31</sup>P (121 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ -15.7 (s).



### Aqueous Sulfide test:

To determine the presence of potassium sulfide, reaction of with lead (II) acetate was initially tested, but inconclusive. An expected black precipitate did not form, however a white precipitate did form. Exposure of lead (II) acetate to solutions of KF also resulted in white precipitates, so presumably the presence of fluoride interferes with this test. Qualitatively a rotten egg smell was observed when cleaning glassware used to conduct the reactions with phosphides and SF<sub>6</sub>.

A qualitative test with *N,N*-dimethyl-phenylenediamine **9** and iron (III) chloride was successful in detecting aqueous sulfide.<sup>1</sup> Residual phosphine appeared to interfere with the test reaction, by slowing formation of the blue colour, possibly through reduction of the methylene blue that was formed, so removal of the phosphine by extraction with dichloromethane was conducted as described. The test solutions were prepared as follows:

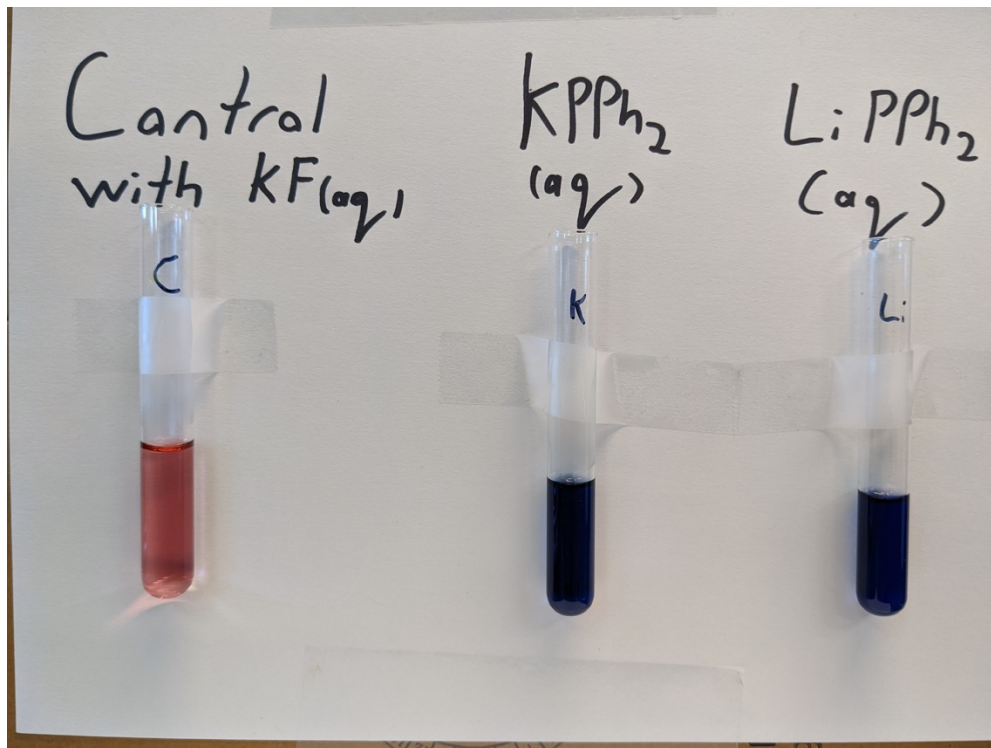
*N,N*-dimethyl-phenylenediamine (20 mg) was dissolved in 10 mL of 6M HCl.

FeCl<sub>3</sub> (30 mg) was dissolved in 10 mL of 6M HCl.

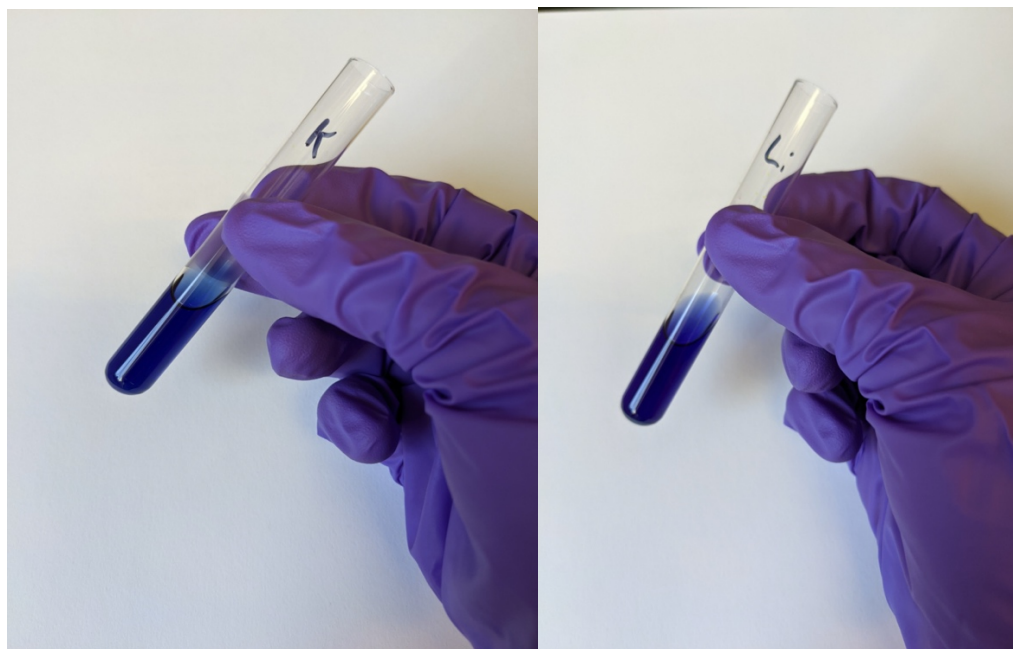
Scale up of LiPPh<sub>2</sub> and KPPh<sub>2</sub> for testing for sulfides:

Diphenylphosphine (0.5 mL, 0.25 mmol, 0.5 M THF) was dispensed into a 1 dram vial. This solution was further diluted with THF (0.5 mL). A base was then added either as *n*-butyllithium (0.1 mL, 0.25 mmol, 2.5M) or potassium hydride (10 mg, 0.25 mmol). The solution was then stirred at room temperature for 30 min and then analyzed using NMR spectroscopy to show the presence of the phosphides. Sulfur hexafluoride was then added as per the previous procedures, then the solutions were again analyzed using NMR spectroscopy. The sample was then transferred to a flask and the volatiles removed *in vacuo*. Deionized water was then added (approx. 5-7 mL) followed by DCM (5 mL) and the mixture shaken. The aqueous layer was then removed and filtered through a 0.3 micron HPLC syringe filter to remove small amounts of insoluble materials. An aliquot of this solution was then added to a standard culture tube and diluted. A solution of *N,N*-dimethyl-*p*-phenylenediamine (approx. 0.3-0.5 mL) was added, followed by the solution of acidic iron trichloride (approx.. 0.3-0.5 mL). The mixture was left for approximately 1h in which time the pink color became a deep blue. A control was conducted with KF (25 mg) in water (4 mL) under the same conditions which remained pink.

**Figure S2:** Sulfide test reactions. Control (KF) solution on left, reaction with residue from  $KPPh_2$  reaction in middle, reaction with residue from  $LiPPh_2$  reaction on right. Description of images: three vials taped to a labelled card, the vial on the left is half-filled with a pink liquid, and the two other vials are half-filled with dark blue liquid.

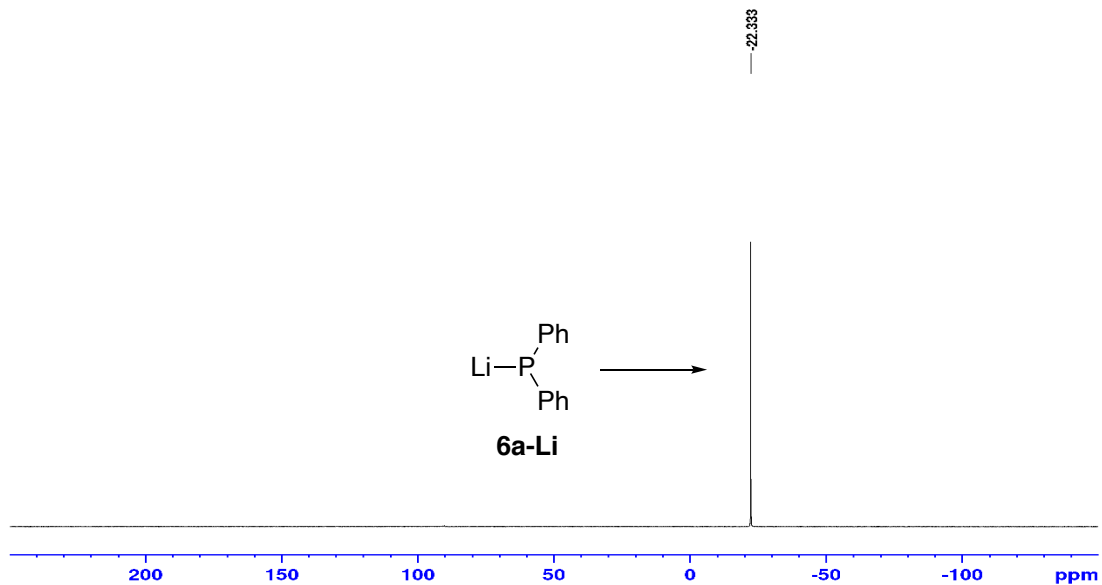


**Figure S3:** Individual test reactions. Description: vials half-filled with blue liquid are held in a gloved hand.

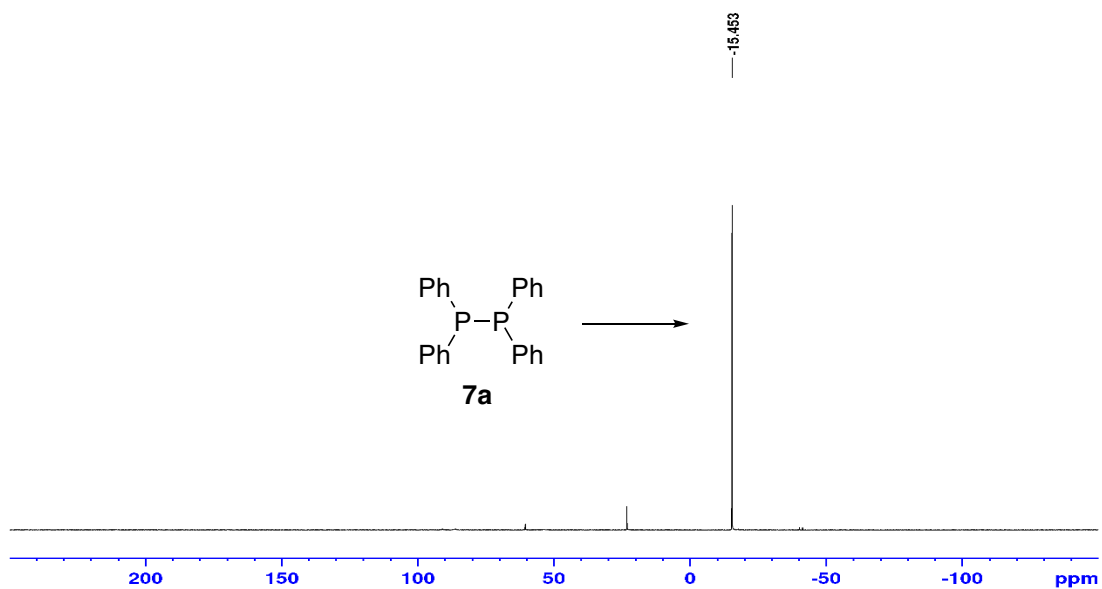


**NMR spectra for samples used in sulfide test:**

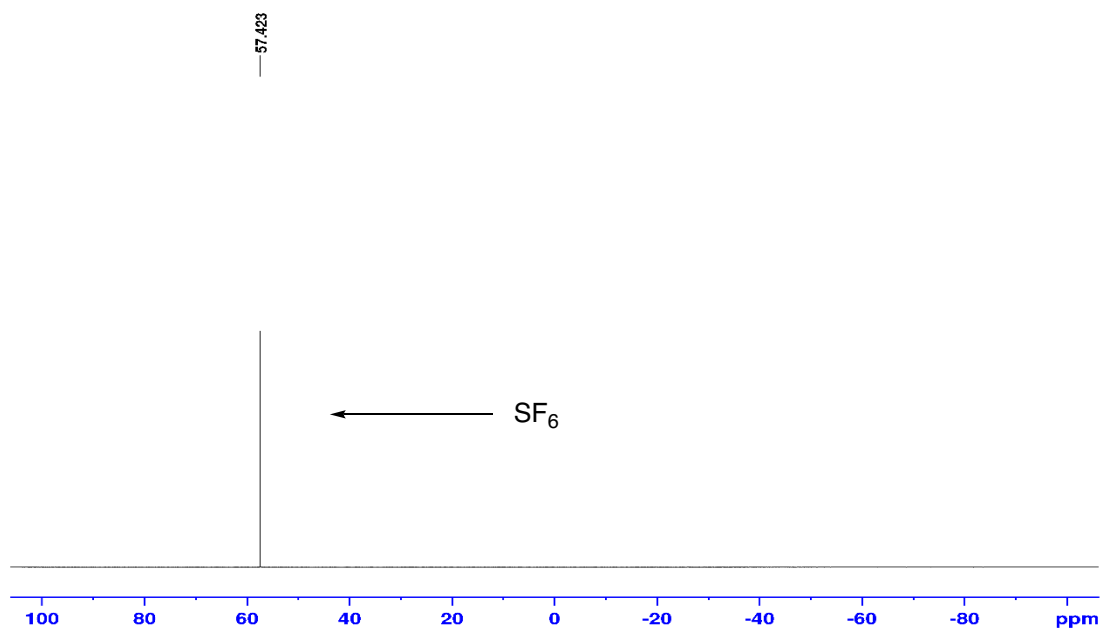
**Spectrum of lithium diphenylphosphide in THF:  $^{31}\text{P}$  (202 MHz, THF, no lock):  $\delta$  -22.3 (s).**



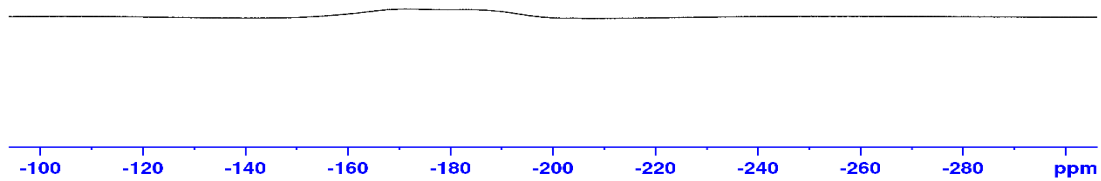
**Spectrum of lithium diphenylphosphide after  $\text{SF}_6$  addition:  $^{31}\text{P}$  (202 MHz, THF, no lock):  $\delta$  -15.4 (s).**



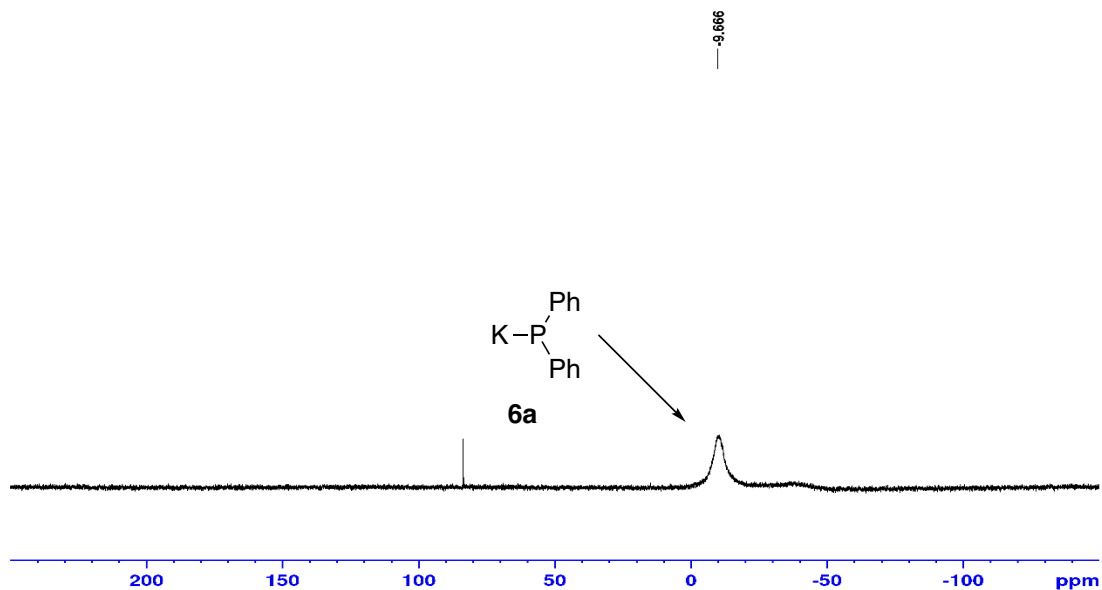
$^{19}\text{F}$  (470 MHz, THF, no lock):  $\delta$  57.4 (s)  $\text{SF}_6$ .



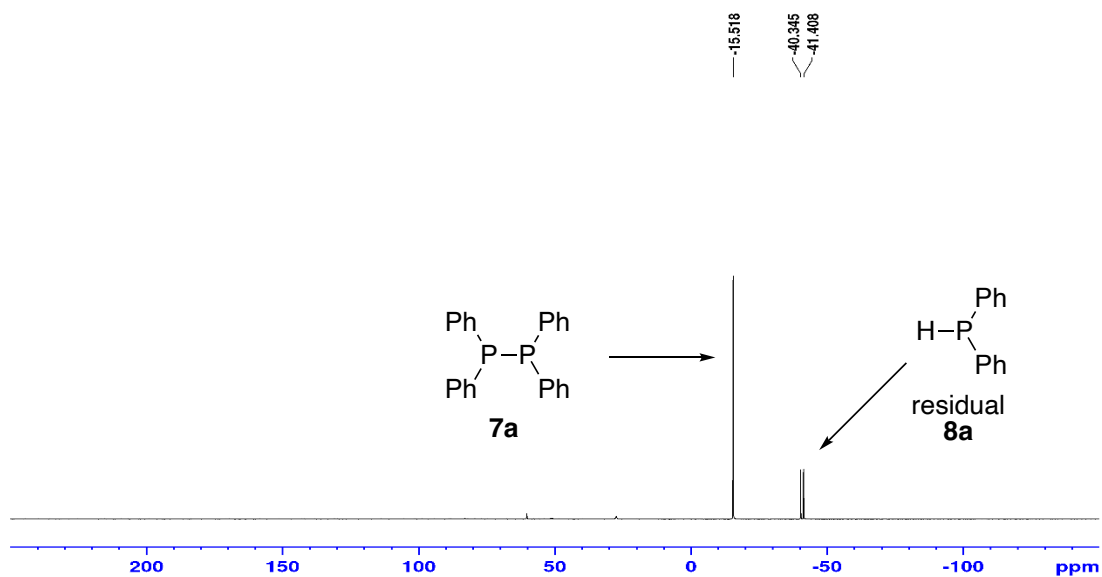
$^{19}\text{F}$  (470 MHz, THF, no lock): sharp peak due to fluoride ions not observed.



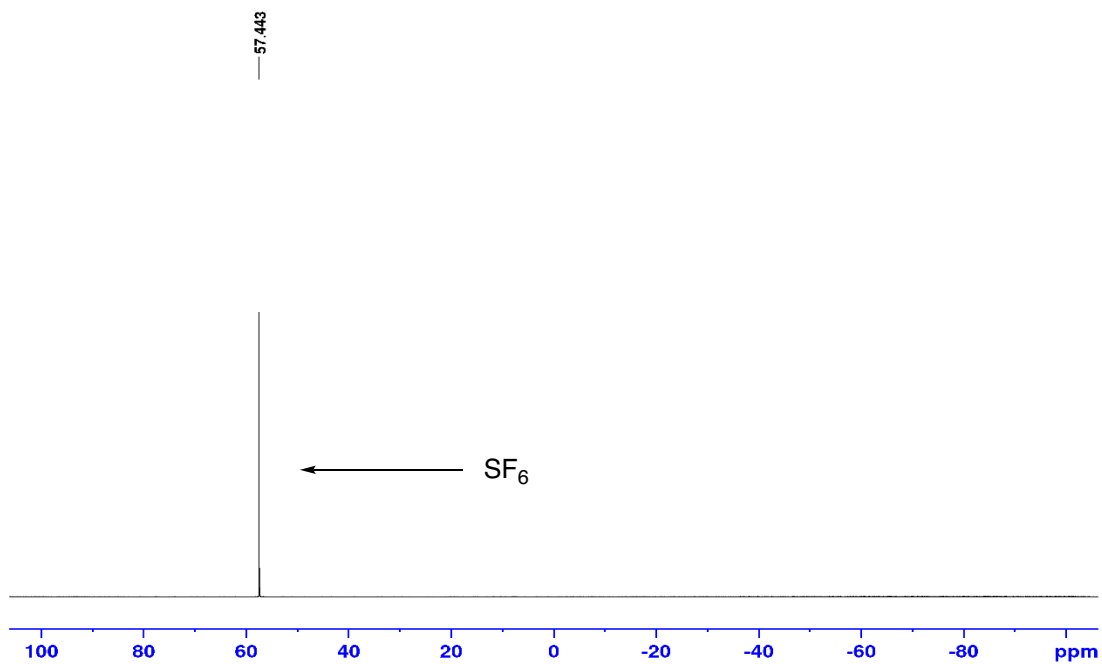
Spectrum of potassium diphenylphosphide prepared from KH and HPPh<sub>2</sub> in THF: <sup>31</sup>P (202 MHz, THF, no lock): δ -9.7 (s).



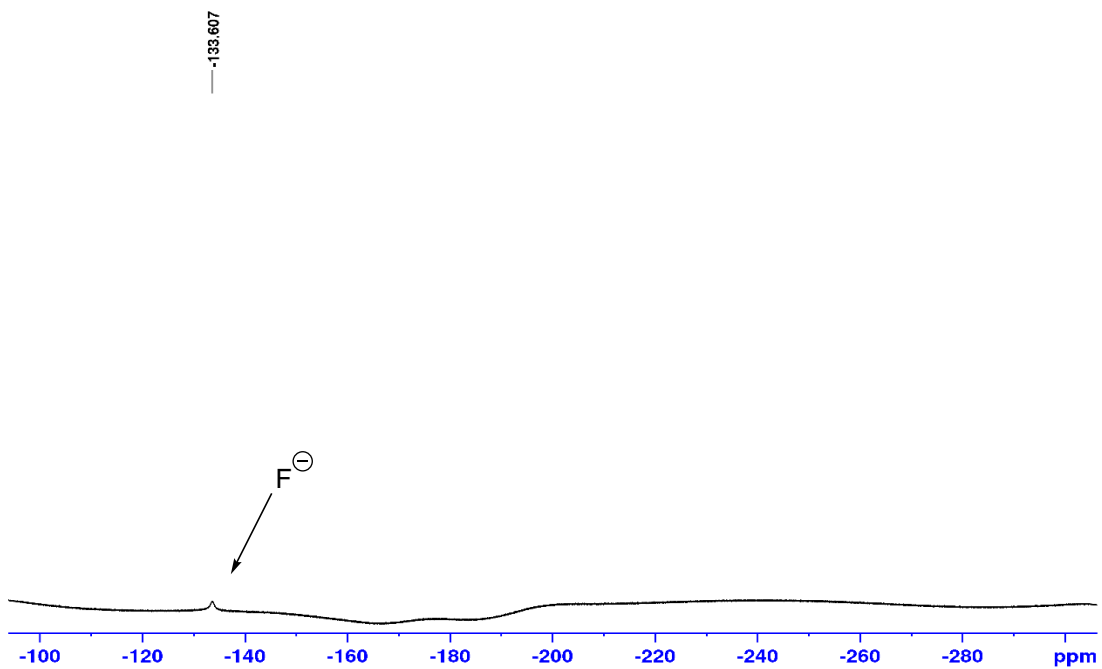
Spectrum of potassium diphenylphosphide after SF<sub>6</sub> addition: <sup>31</sup>P (202 MHz, THF, no lock): δ -9.9 (s).



$^{19}\text{F}$  (470 MHz, THF, no lock):  $\delta$  57.4 (s)  $\text{SF}_6$ .



$^{19}\text{F}$  (470 MHz, THF, no lock):  $\delta$  -133.





## Detection of Sulfur Containing Products

Potassium diphenylphosphide (12 mL, 6 mmol, 0.5M in THF) was dispensed into a 100 mL Schlenk flask equipped with a septum. The solution was diluted with additional THF (24 mL THF). The flask was then chilled in icewater. A SF<sub>6</sub> gas filled balloon equipped with a needle was placed through the septum, and used to bubble SF<sub>6</sub> through the solution until the orange color dissipated to a light brown and then the bubbling was continued for an additional 15s. Volatiles were then removed in vacuo, and the flask was taken into the glovebox. The flask contained 1.6 grams of solids after the concentration, which is consistent with the mass of 6 mmol of KPPH<sub>2</sub> (1.345 g) and 1 mmol reacted SF<sub>6</sub> (146 mg), (1.492 g mass gain would be expected on a 6.000 mmol scale). Filtration on this scale proved to be impossible in a variety of solvents (diethyl ether, dichloromethane, chloroform, or toluene), with rapid clogging of the frit, even when using a filter aid such as celite.

**Figure S4.** Appearance of mixture before SF<sub>6</sub> addition (left), after SF<sub>6</sub> addition, and during concentration (centre), and after concentration (right).

Image descriptions: A Schlenk flask half-filled with a bright orange solution is on left. In the centre is a Schlenk flask containing a cloudy light brown mixture, equipped with a rubber vacuum hose. On the right is a Schlenk flask containing a beige powder, also equipped with a rubber vacuum hose.

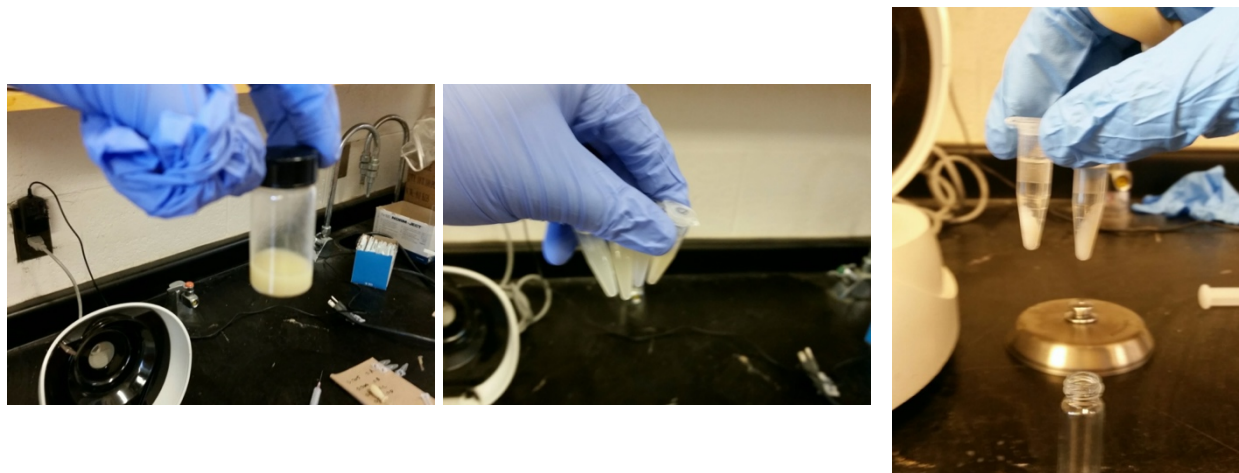


A portion of the solid (350 mg) was removed from the glovebox, and 4 mL acetone was added. Elemental sulfur has low solubility in ethanol and acetone, but only acetone was suitable to dissolve the majority of the phosphorus containing material, with ethanol being unable to dissolve the diphosphine. We found acetone reacted with the diphosphine to give a complex mixture of products. The mixture was sonicated for 1 minute to make a pale yellow suspension. The suspension was divided and balanced across 4 Eppendorf microcentrifuge tubes and centrifuged at 5000 rpm in an Eppendorf microcentrifuge for 10 minutes. The solvent was carefully removed,

and fresh acetone was added, followed by additional centrifuging, then solvent removal. The solids were then dried in vacuo.

**Figure S5.** Appearance of suspension after sonication (left image), before centrifuging (centre image), and after centrifuging (right image).

Image description. In the left image, a gloved hand is holding a vial containing a yellow/beige suspension. In the centre image, a gloved hand is holding four mini-centrifuge tubes containing the yellow/beige suspension. In the right image an off-white suspension has settled from a clear colourless supernatant.



The solids obtained after the initial centrifuging were suspended in acetonitrile, and 100 mg triphenylphosphine were added. After 12 hours,  $^{31}\text{P}$  NMR showed no formation of triphenylphosphine sulfide. Separately, 350 mg of solid from the initial reaction mixture was suspended in acetonitrile, and 100 mg of triphenylphosphine were added. In this case,  $^{31}\text{P}$  NMR showed no formation of triphenylphosphine sulfide.

Separately triphenylphosphine and an authentic sample of sulfur were mixed in acetonitrile. After 12 hours,  $^{31}\text{P}$  NMR showed formation of triphenylphosphine sulfide **10b** (43.0 ppm)

## Analysis of soluble sulfur-containing compounds

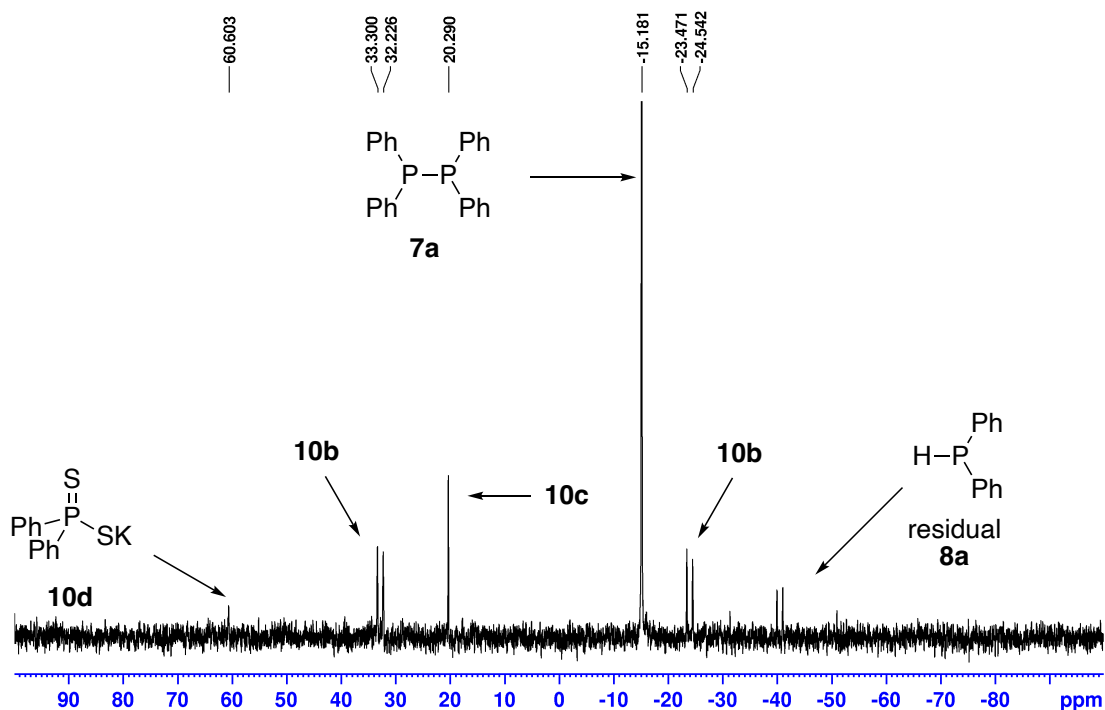
The phosphorus containing components of the reaction  $\text{KPPh}_2$  (**6a**) and product **7a** could react with  $\text{S}(0)$  that is formed in the reaction, and such products were observed in the  $^{31}\text{P}$  spectra of the reactions. Varying amounts were observed in different runs, and it is likely the rate of addition of the  $\text{SF}_6$  plays a role here. Rapid consumption of  $\text{KPPh}_2$  (**6a**) might minimize reaction between **6a** and elemental sulfur products, whereas if the addition of  $\text{SF}_6$  was slower, then elemental sulfur could form while  $\text{KPPh}_2$  was still present.

Compounds **10b** and **10c** are known compounds, however spectra were not reported in THF. Analysis of the residue of the above reaction in  $\text{CDCl}_3$  showed signals matching literature values for the proposed compounds. The  $^{31}\text{P}$  spectra in THF are also shown for comparison. Separation of these minor reaction components was not attempted.

**Spectrum of crude reaction mixture in THF:**  $^{31}\text{P}$  (202 MHz, THF, no lock):  $\delta$

**10b** 32.9 (d,  $J=229$  Hz), -24.0 (d,  $J=229$  Hz).

**10c** s, 20.29 ppm

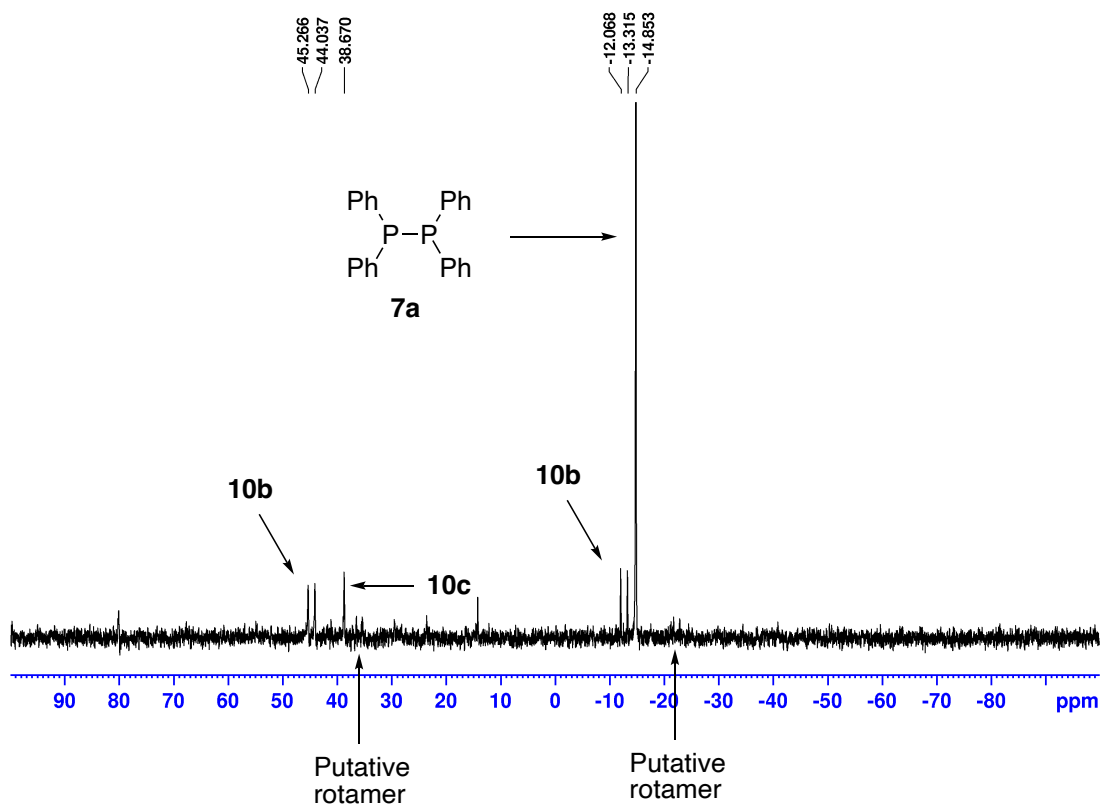


**Spectrum of crude reaction mixture in CDCl<sub>3</sub>: <sup>31</sup>P (202 MHz): δ**

**10b** 44.6 (d, *J*= 252 Hz), -12.7 (d, *J*= 252 Hz) ppm

**10c** 38.7 ppm

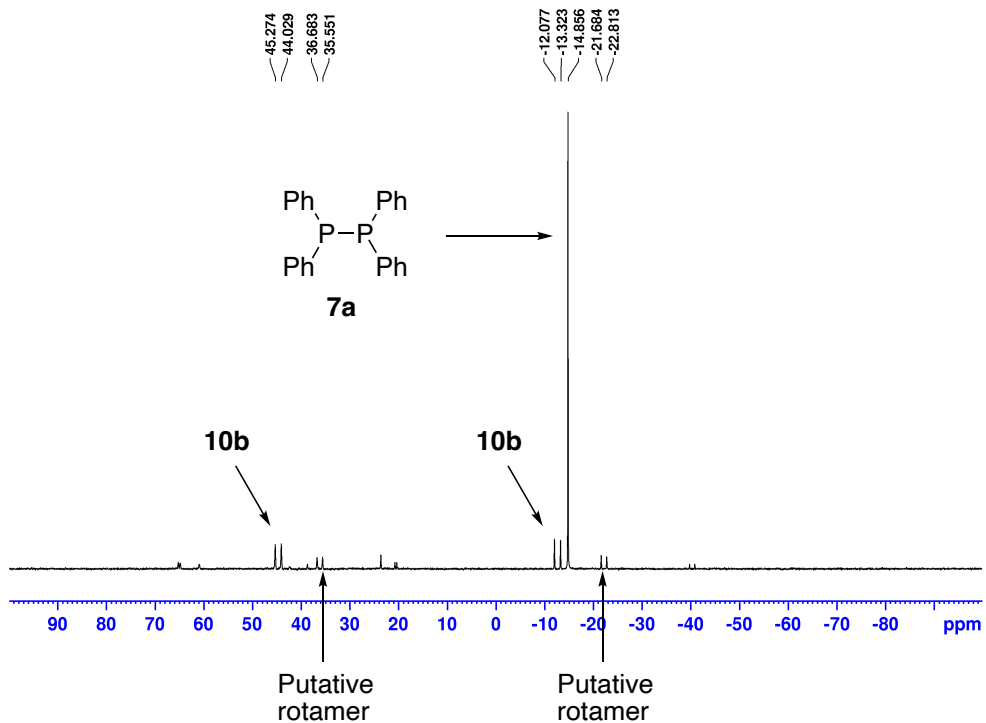
Literature values for **10b** in CDCl<sub>3</sub>: <sup>31</sup>P δ 45.4 (d, *J*= 253 Hz), -12.2 (d, *J*= 252 Hz).<sup>2</sup> It should be noted this reference also shows a minor rotamer for **10b**, where the lone pair on P is trans to the P=S bond, and appears at <sup>31</sup>P δ 37.5 (d, *J*= 230 Hz), -21.5 (d, *J*= 230 Hz). This is visible in the baseline of this spectrum, and more closely resembles the shifts of the compound in THF (a more polar solvent). Literature value for **10c** = 39.3 ppm.<sup>3</sup>



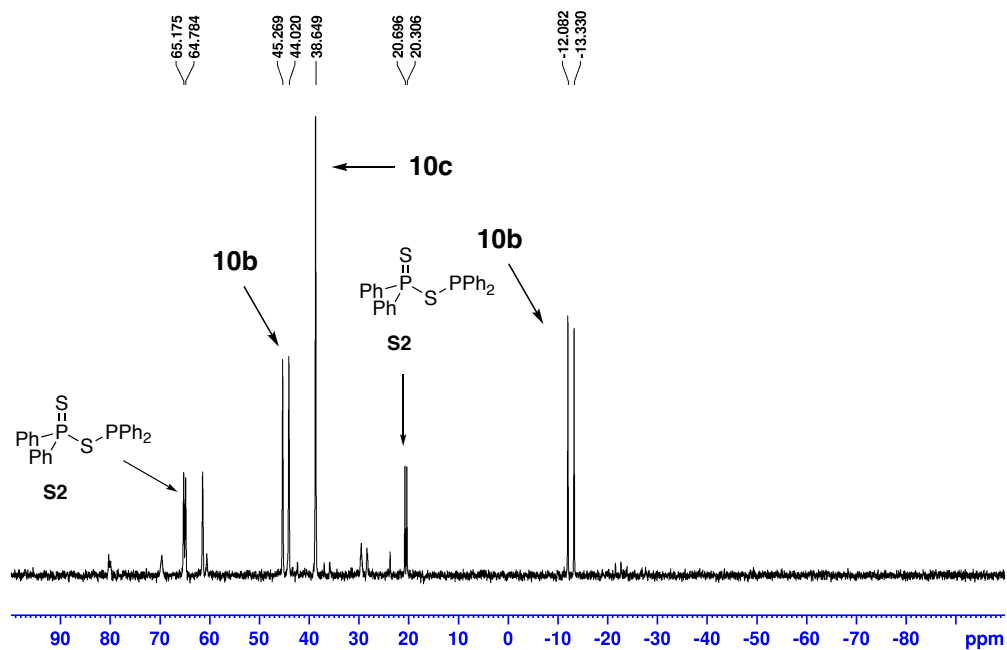
### Reaction of S<sub>8</sub> and compound **7a**

We determined compound **7a** independently reacts with sulfur in THF. In one reaction, 100 mg **7a** (0.27 mmol) was dissolved in THF, and 2 mg S<sub>8</sub> (0.06 mmol S, 0.23 equiv) were added. After 5 minutes, solvent was removed and the residue taken up in CDCl<sub>3</sub>. Analysis by <sup>31</sup>P NMR spectroscopy showed unreacted **7a**, and the formation of both rotamers of **10b**. Separately, 100 mg of **7a** (0.27 mmol) was dissolved in THF, and 10 mg S<sub>8</sub> (0.312 mmol S, 1.15 equiv) were added. The solvent was removed after 15 minutes, and the residue taken up in CDCl<sub>3</sub>. Analysis by <sup>31</sup>P NMR spectroscopy showed consumption of **7a**, and formation of **10b**, **10c**, and non-symmetrical product, **S2**, which agreed with literature values for a tautomeric isomer of **10c**.<sup>3</sup>

Spectrum of crude reaction mixture with minimal S<sub>8</sub> in CDCl<sub>3</sub>: <sup>31</sup>P (202 MHz):



Spectrum of crude reaction mixture with excess S<sub>8</sub> in CDCl<sub>3</sub>: <sup>31</sup>P (202 MHz): δ

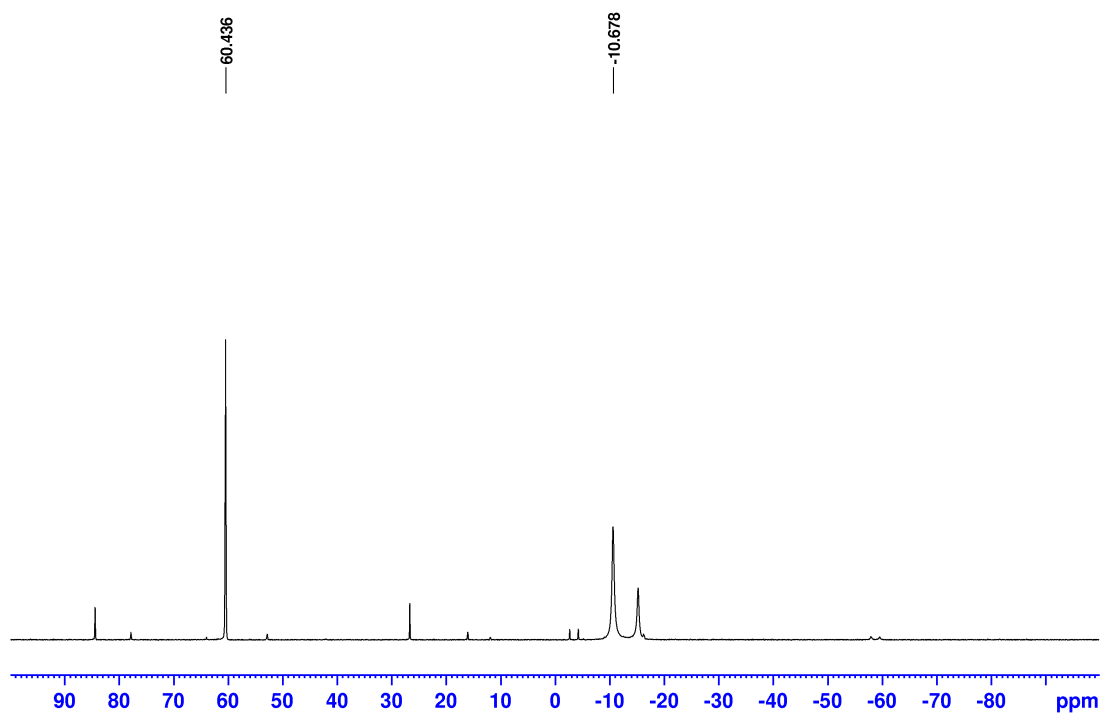


## Reaction of S<sub>8</sub> and KPPh<sub>2</sub>

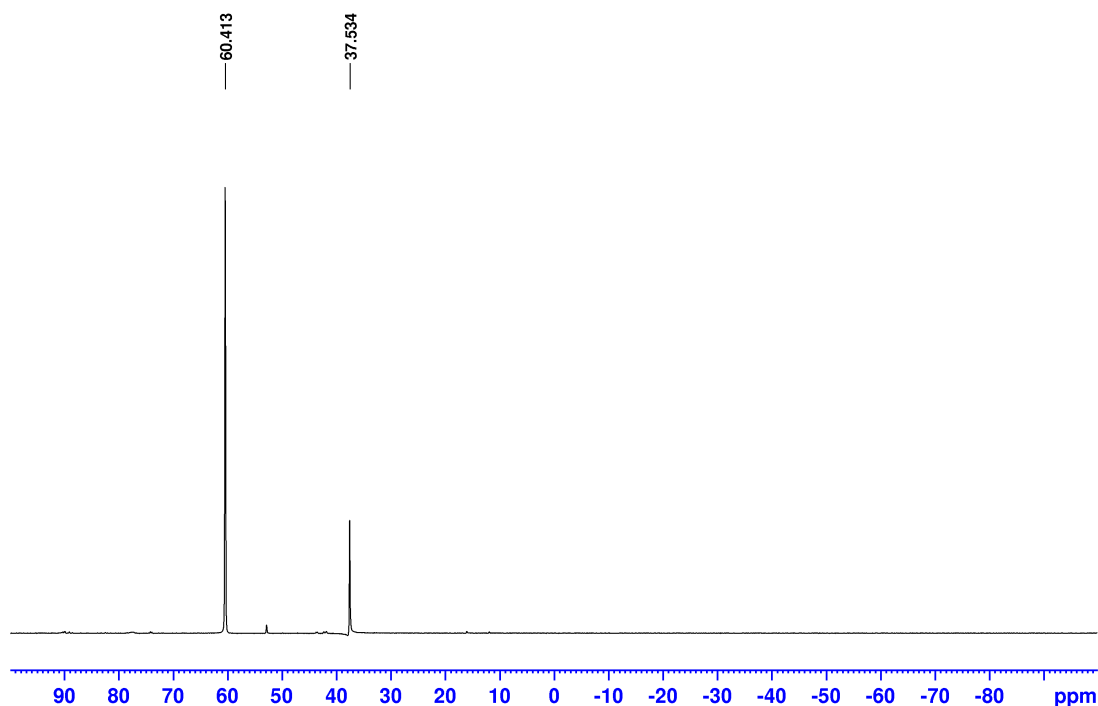
A signal distinct from **10b** and **10c** was noted in the reactions between phosphide **6a** and SF<sub>6</sub>. This signal could be reproduced by adding S<sub>8</sub> to KPPh<sub>2</sub> in THF.

KPPh<sub>2</sub> in THF (1 mL, 0.5 mmol) was added to 1/8 of an equivalent of S<sub>8</sub> (16 mg). The orange colour of the KPPh<sub>2</sub> persisted. <sup>31</sup>P NMR spectroscopy showed a mixture of compound **10e** and unreacted KPPh<sub>2</sub>. The reaction was repeated with 1/4 of an equivalent of S<sub>8</sub> (32 mg) which resulted in discharge of the orange colour of KPPh<sub>2</sub>. The peak at 60 ppm was also observed in reactions with KPPh<sub>2</sub> and SF<sub>6</sub>, implying that sulfur that is formed can also react with phosphides during the reaction.

**Spectrum of potassium diphenylphosphide and 1/8 equivalent S<sub>8</sub> in THF: <sup>31</sup>P (202 MHz, THF, no lock): δ 60.4 (s).**



**Spectrum of potassium diphenylphosphide and 1/4 equivalent S<sub>8</sub> in THF: <sup>31</sup>P (202 MHz, THF, no lock): δ 60.4 (s).**



### Scale up of S1 (Diphenylphosphinodithioic acid)

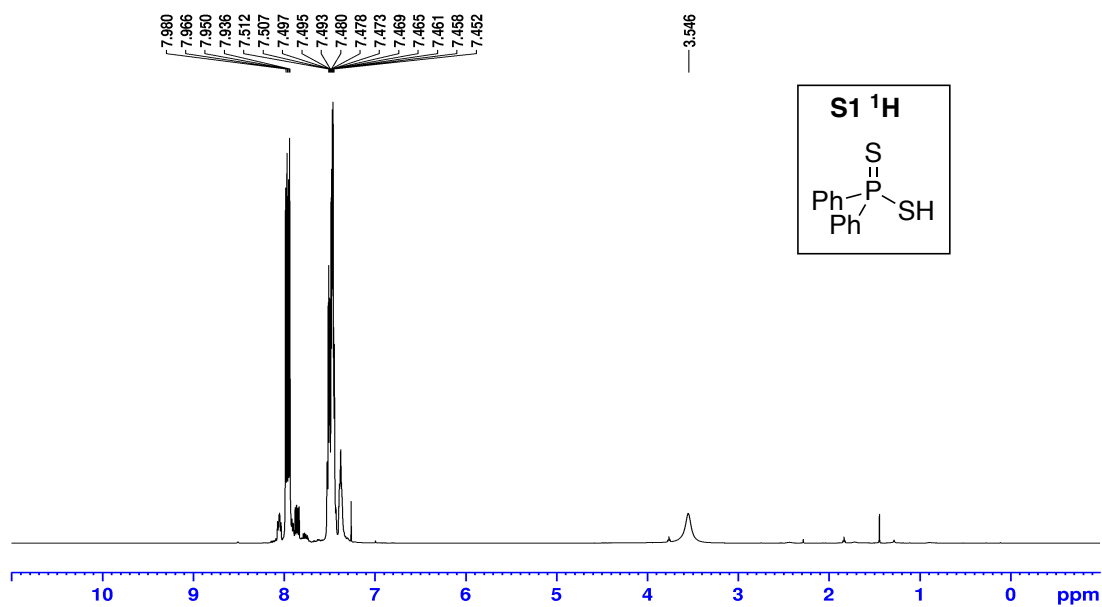
Reaction of Ph<sub>2</sub>PLi with sulfur has been reported, to presumably gave Ph<sub>2</sub>P(S)SLi, but this was not isolated, and was used as a reactive intermediate.<sup>3</sup> The spectrum of compound **10e** as the potassium salt has not been reported in THF. We found **10e** was insoluble in CDCl<sub>3</sub>. The identity of **10e** was confirmed by protonation of **10e** with dilute hydrochloric acid to form diphenylphosphinodithioic acid **S1**, and NMR spectra of this compound were in agreement with literature values for **S1** in CDCl<sub>3</sub>.<sup>4</sup> In a 1 dram vial, 3.0 mL of KPPH<sub>2</sub> **6a** (0.5 M, 1.5 mmol) was added to 100 mg S<sub>8</sub> (3.12 mmol S). The mixture was pipetted in and out of the vial, until the orange colour faded (within 1 minute). The vial warmed during this procedure. The contents of the vial were removed from the glovebox, diluted with CH<sub>2</sub>Cl<sub>2</sub>, and made acidic with 2M aqueous HCl. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give the diphenylphosphinodithioic acid (**S1**) as an oil that set to a solid. While impure, spectral data were in agreement with reported literature values in CDCl<sub>3</sub> for <sup>1</sup>H (the exchangeable proton was slightly different), <sup>13</sup>C, and <sup>31</sup>P spectra.<sup>4</sup>

<sup>1</sup>H δ 7.95 (dd, *J*= 15.1, 6.8 Hz, 4H), 7.54–7.42 (m, 6H), 3.55 (br. S, 1H)

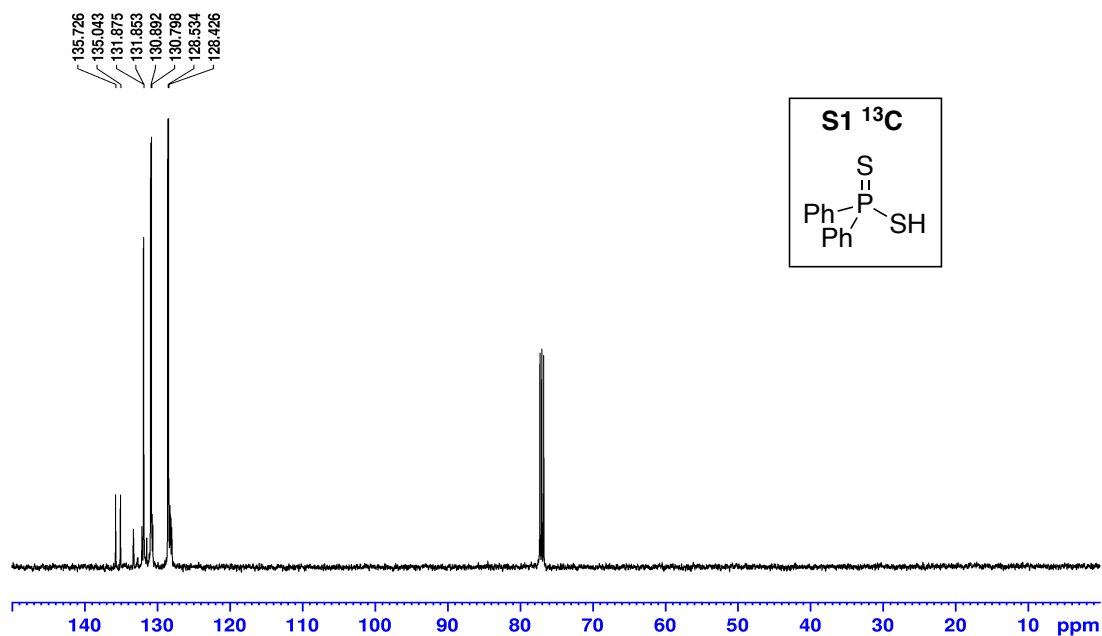
<sup>13</sup>C δ 135.4 (d, *J*= 85.8 Hz), 131.9 (d, *J*= 2.8 Hz), 130.8 (d, *J*=12.1 Hz), 128.5 (d, *J*= 13.2 Hz)

<sup>31</sup>P δ 55.9 ppm

Spectrum of isolated S1 in CDCl<sub>3</sub>: <sup>1</sup>H (500 MHz): δ

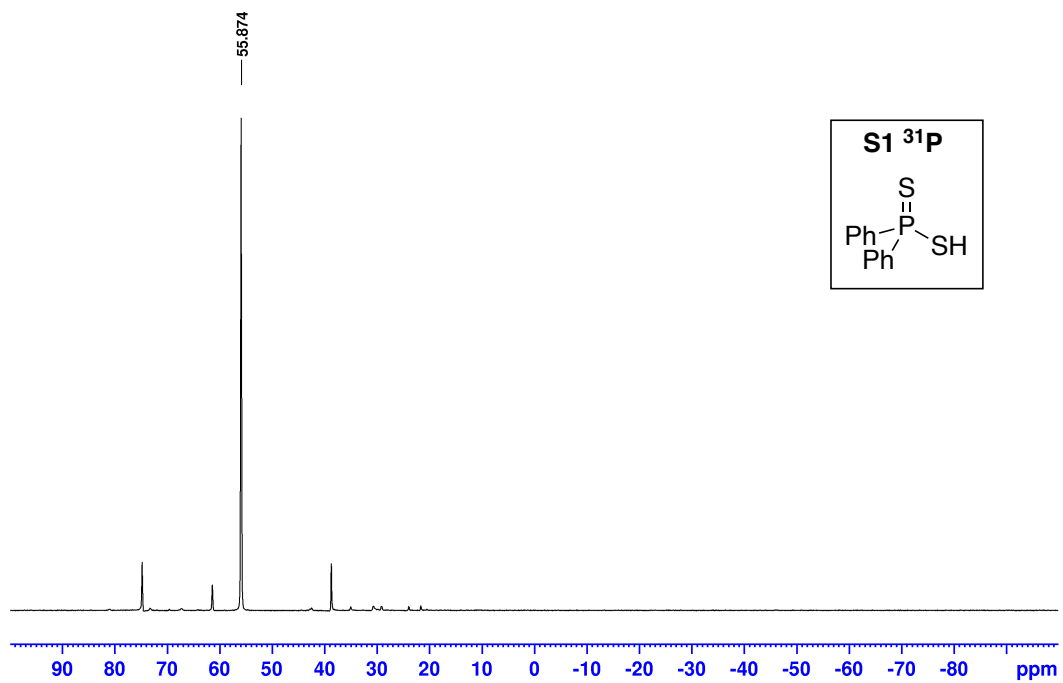


Spectrum of isolated S1 in CDCl<sub>3</sub>: <sup>13</sup>C (101 MHz):



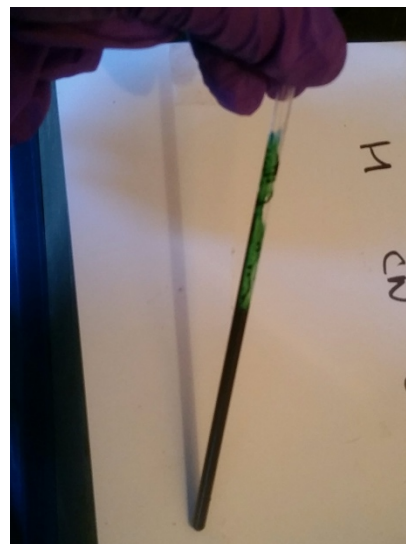


Spectrum of isolated S1 in CDCl<sub>3</sub>: <sup>31</sup>P (202 MHz)



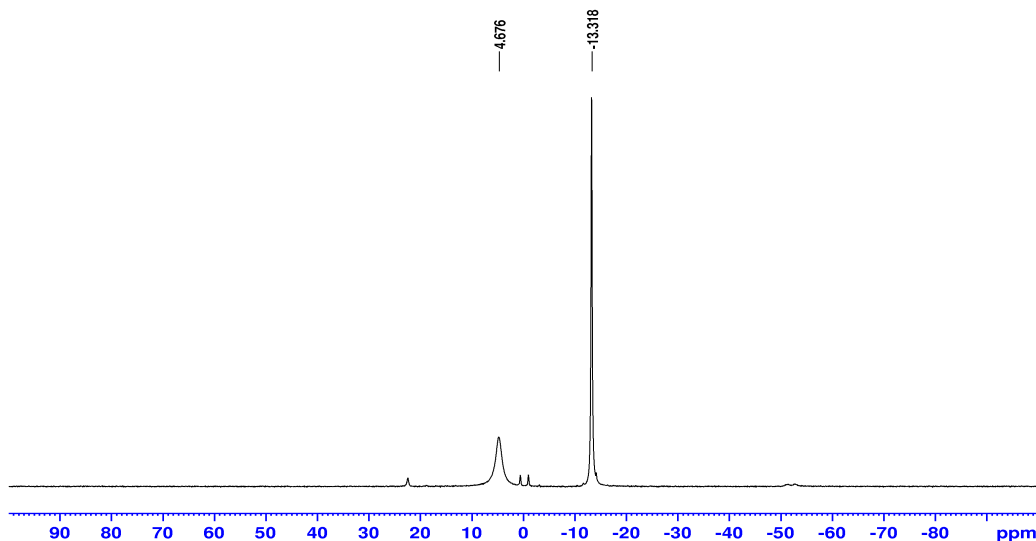
## Reaction between potassium diphenylphosphide and benzophenone

A 1.0 mL portion of 0.5 M THF solution of potassium diphenylphosphide was added to 91 mg (0.5 mmol, 1 equivalent) of solid benzophenone. Immediate formation of a deep blue/green colour characteristic of ketyl radical was noted. Attempted analysis of the mixture by  $^{31}\text{P}$  NMR spectroscopy showed featureless peaks, with the positive one being broad. Phosphide shifts are rather variable depending on metal coordination, so we cannot draw any conclusions about species present, or why there are two peaks. Bubbling  $\text{SF}_6$  through this mixture resulted in immediate discharge of the blue-green colour. Further analysis by  $^{31}\text{P}$  NMR spectroscopy showed a sharp peak corresponding to tetraphenyldiphosphine **7a**. These results imply that potassium diphenylphosphide is capable of single electron transfer to an acceptor such as benzophenone. Since it is also known that ketyl radicals are sufficiently reducing to react with  $\text{SF}_6$ <sup>5</sup> this shows that single electron transfer mechanisms cannot be ruled out.

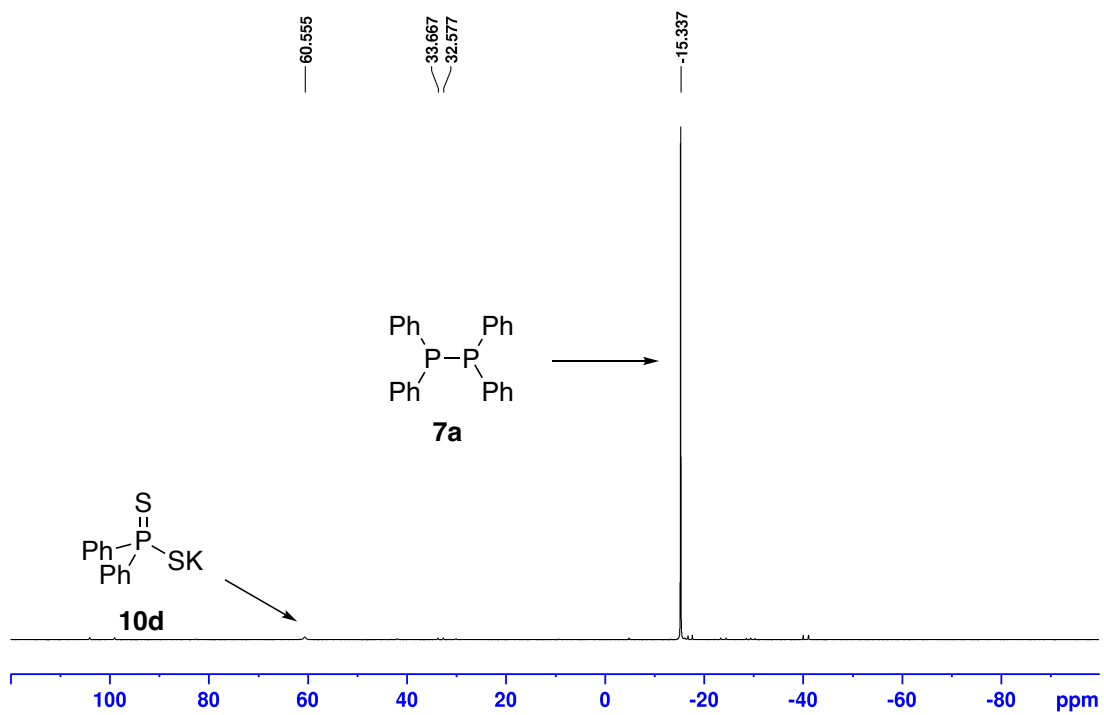


**Figure S6** Appearance of a mixture of  $\text{KPPh}_2$  and benzophenone 1 minute after mixing. Description of image: An NMR tube containing a deep blue-green mixture that is opaque is held in a gloved hand. Some of the mixture coats the upper wall of the tube, allowing the blue-green colour to be more clearly seen.

**Spectrum of potassium diphenyl phosphide and benzophenone  $^{31}\text{P}$  (202 MHz, THF, no lock):**  
 $\delta$  -4.6, -13.3 (s).



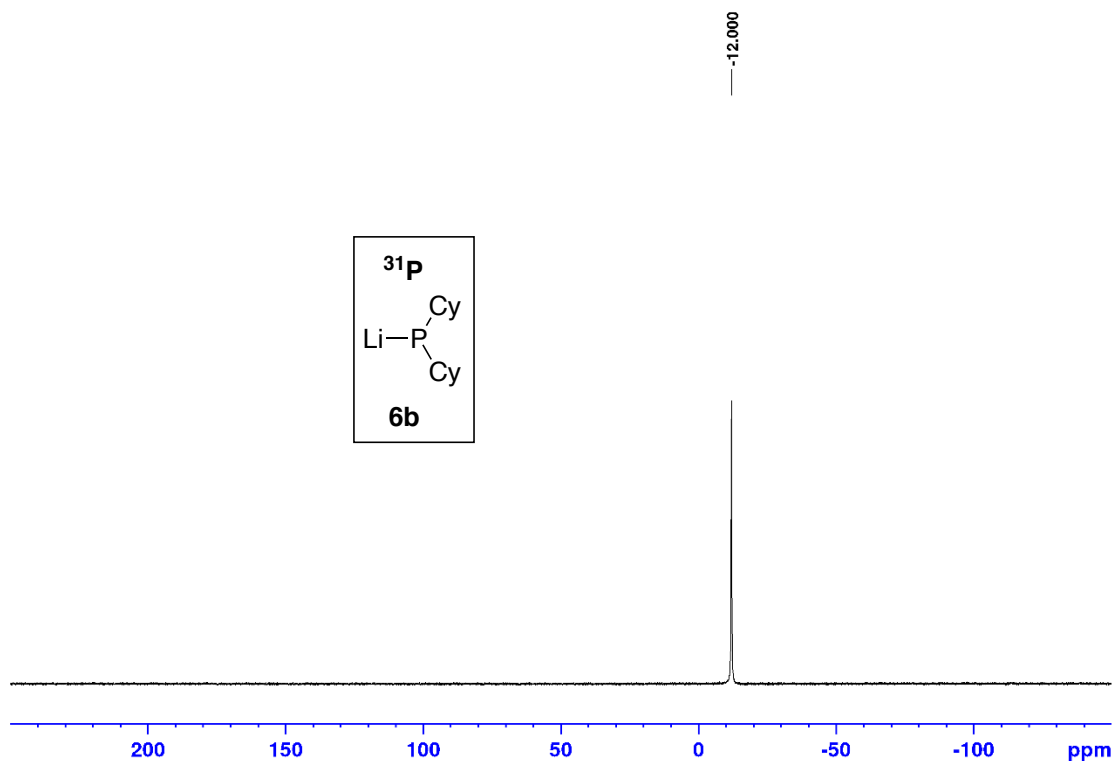
Spectrum of potassium diphenyl phosphide and benzophenone after SF<sub>6</sub> addition <sup>31</sup>P (202 MHz, THF, no lock): δ -9.9 (s).



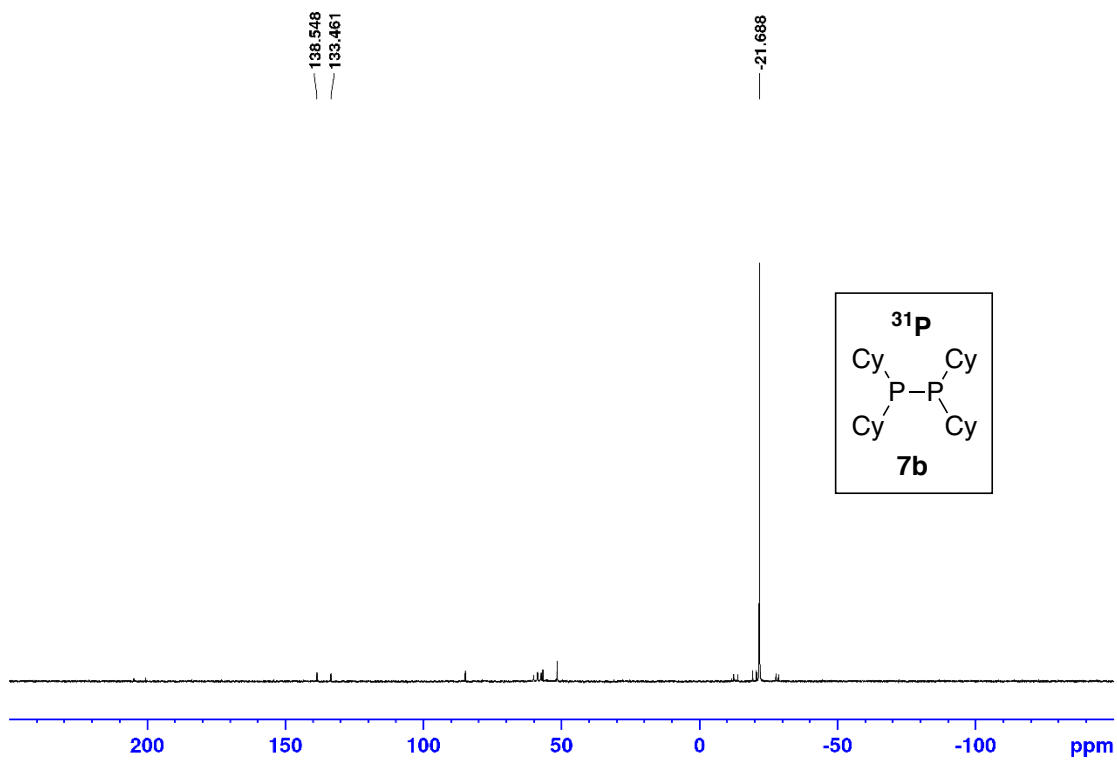
### Reaction of lithium dicyclohexylphosphide and SF<sub>6</sub> gas:

Dicyclohexylphosphine (0.2 mL, 0.1 mmol, 0.5M in THF) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.55 mL THF and 0.05 mL benzene-*d*<sub>6</sub>). N-butyllithium (0.04 mL, 0.1 mmol, 2.5M) was then added and the solution turned orange. The solution was then transferred to an NMR tube and the sample was capped with a septum. An SF<sub>6</sub> gas filled balloon equipped with a needle was then inserted into the solution and bubbled through for 15s. The solution went from orange to clear/yellow colour during this period in which the needle and septum were removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy.

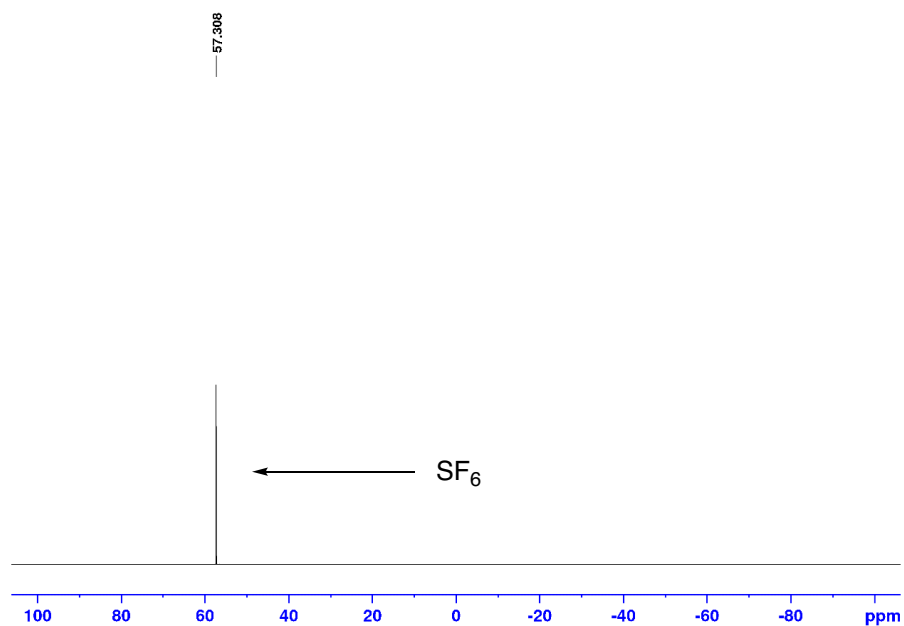
Spectrum of LiPCy<sub>2</sub> before SF<sub>6</sub> addition: <sup>31</sup>P (202 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ -12 (s).



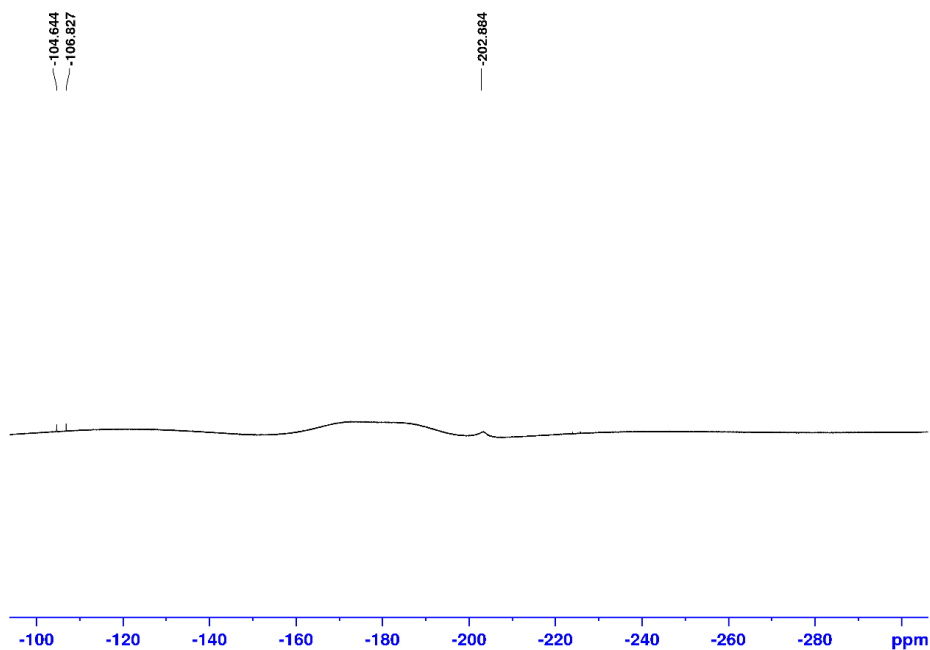
Spectrum after SF<sub>6</sub> addition: <sup>31</sup>P (202 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ -21.7 (s).



**$^{19}\text{F}$  spectrum after  $\text{SF}_6$  addition 0 center point (470 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  57.3 (s). ( $\text{SF}_6$ .)**



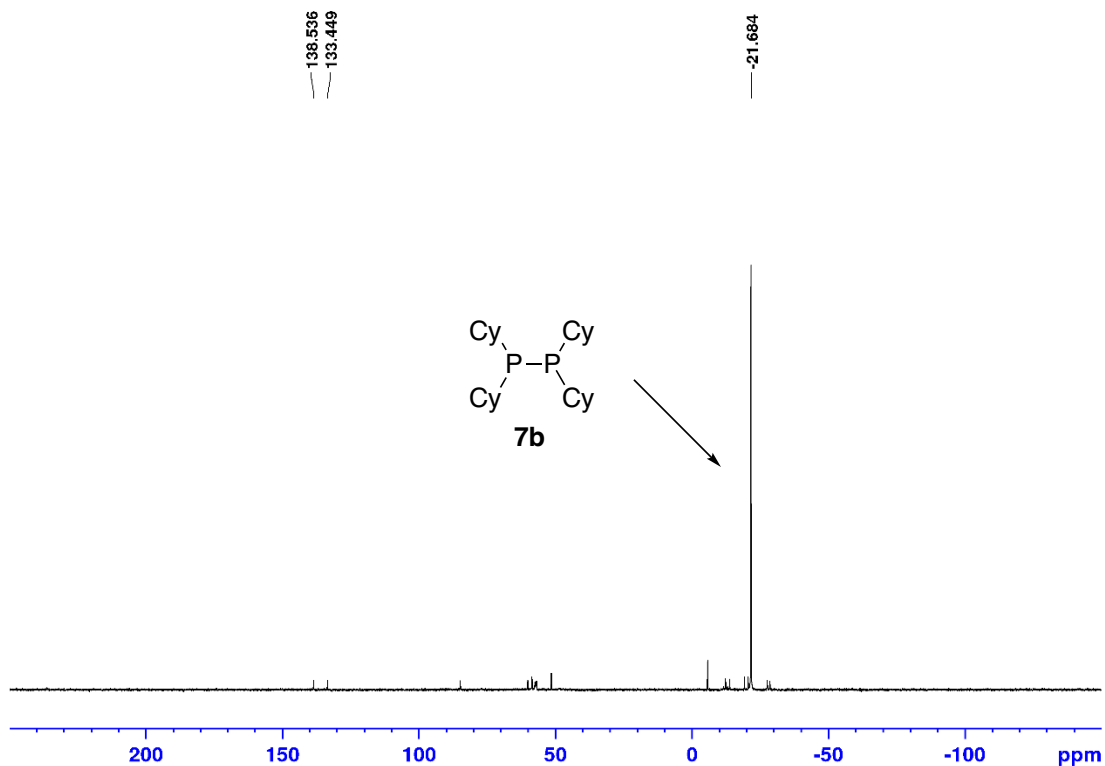
**-200 center point  $^{19}\text{F}$  (470 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -106 (d,  $^1J_{\text{P,F}} = 1027$  Hz), -202 (s).**

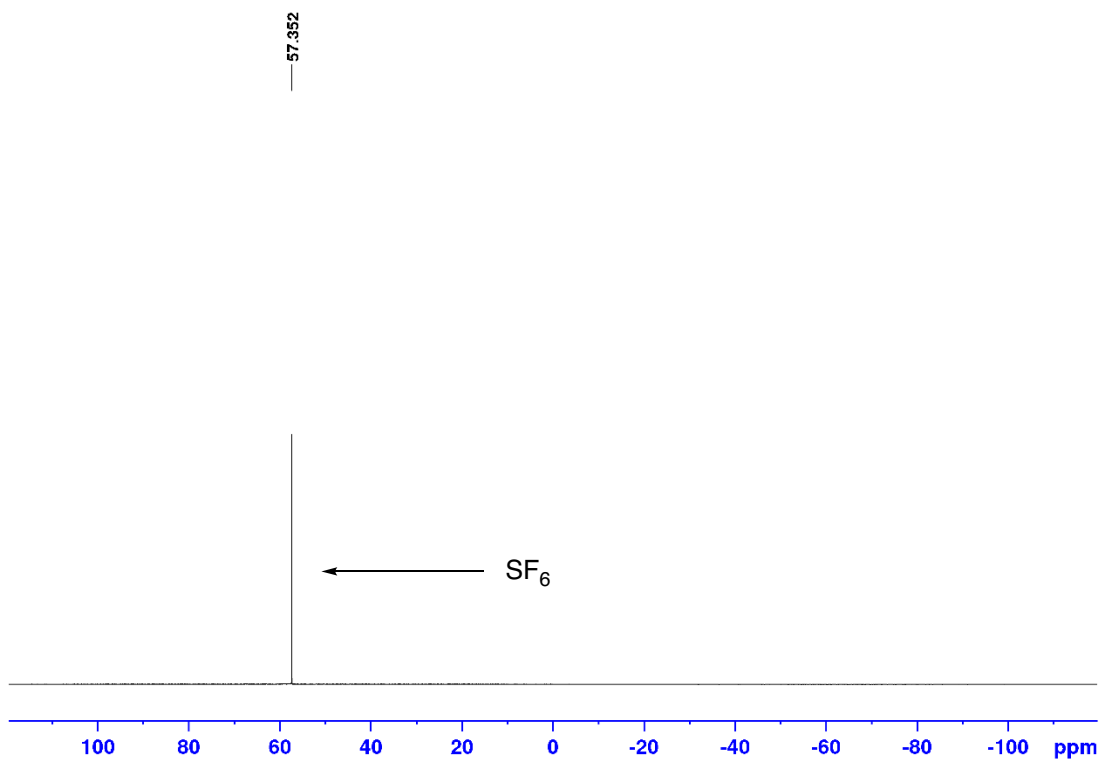


The reaction was repeated at  $-15\text{ }^{\circ}\text{C}$ , but  $^{31}\text{P}$  NMR did not show any significant change in purity.

Dicyclohexylphosphine (0.2 mL, 0.1 mmol, 0.5M in THF) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.55 mL THF and 0.05 mL benzene- $d_6$ ). N-butyllithium (0.04 mL, 0.1 mmol, 2.5M) was then added and the solution turned orange. The solution was then transferred to an NMR tube and the sample was capped with a septum. The sample was cooled to  $-15\text{ }^{\circ}\text{C}$  in an ice/acetone bath. An  $\text{SF}_6$  gas filled balloon equipped with a needle was then inserted into the solution and bubbled through for 15s. The solution went from orange to clear/yellow colour during this period in which the needle and septum were removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy.

$^{31}\text{P}$  (202 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -21.7 (s).





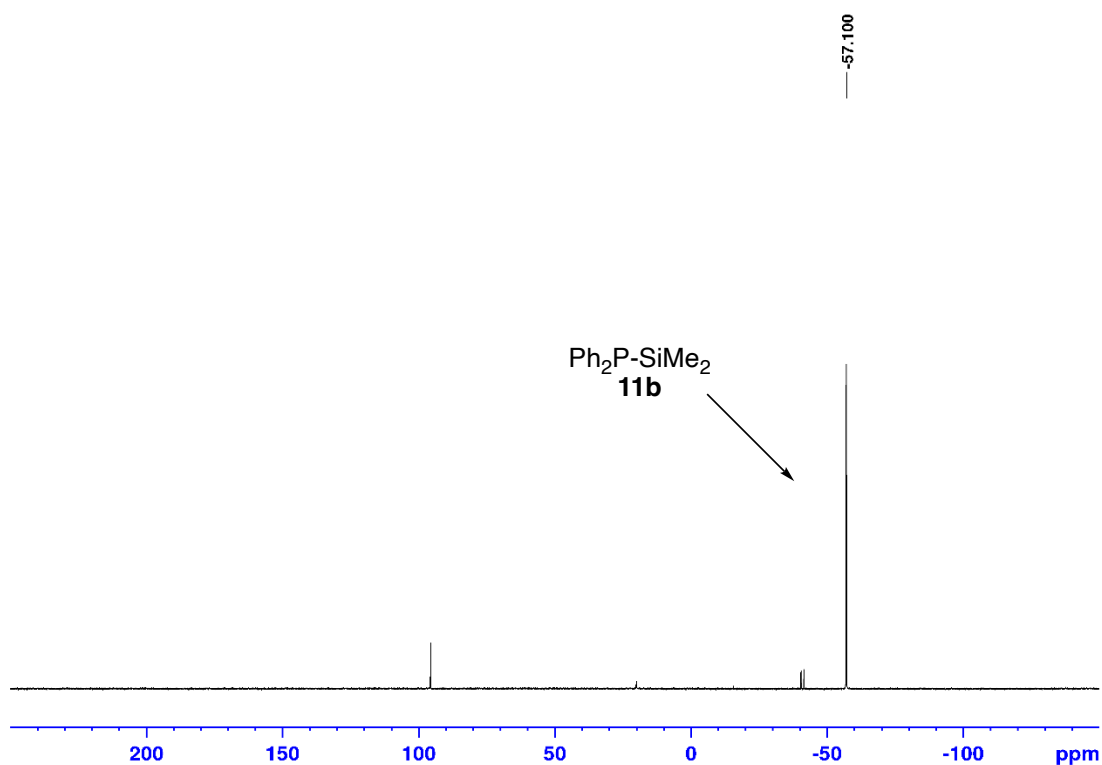


### Reaction of (trimethylsilyl)diphenylphosphine:

(Trimethylsilyl)diphenylphosphine (25.8 mg, 0.1 mmol) was weighed into a 1-dram vial. The solution was diluted with additional solvent (0.75 mL THF and 0.05 mL benzene-*d*<sub>6</sub>). The solution was then transferred to an NMR tube and analyzed. The sample was capped with a septum and an SF<sub>6</sub> gas filled balloon equipped with a needle was then inserted into the solution and bubbled through for 15s. The septum was removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy.

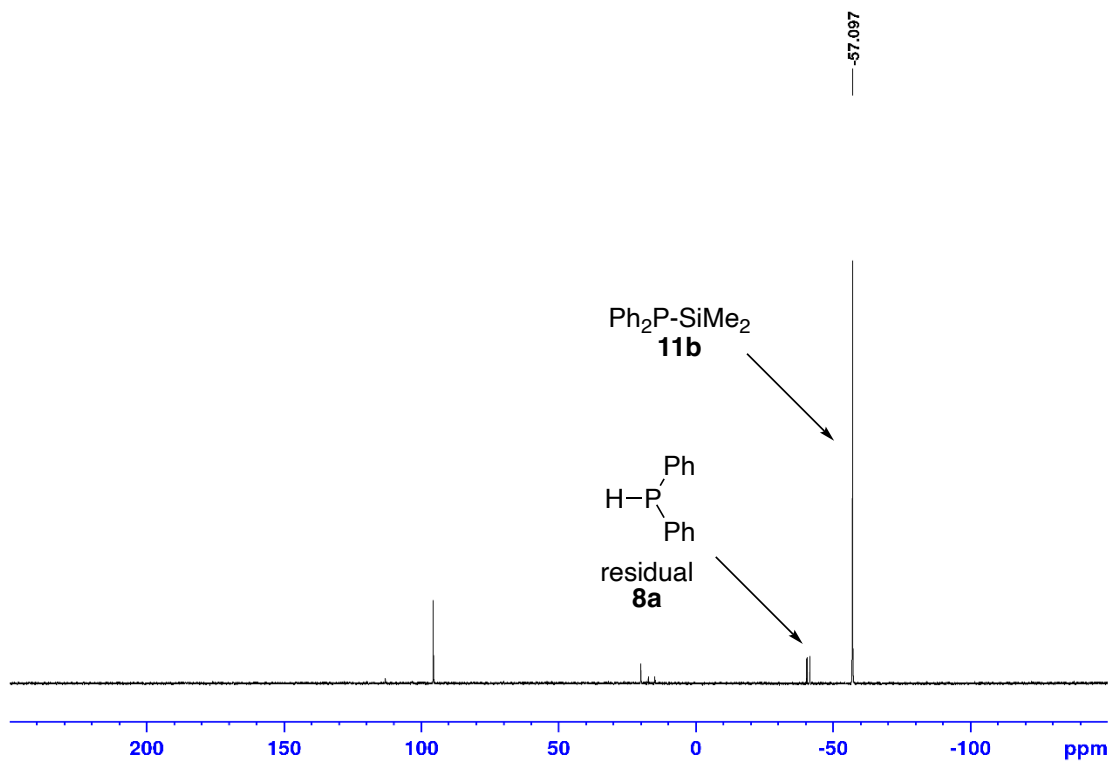
<sup>31</sup>P NMR spectrum of **11b** in THF before addition of SF<sub>6</sub>.

<sup>31</sup>P (202 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ -57.1 (s).



$^{31}\text{P}$  NMR spectrum of **11b** in THF after addition of  $\text{SF}_6$ .

$^{31}\text{P}$  (202 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -57.1 (s).

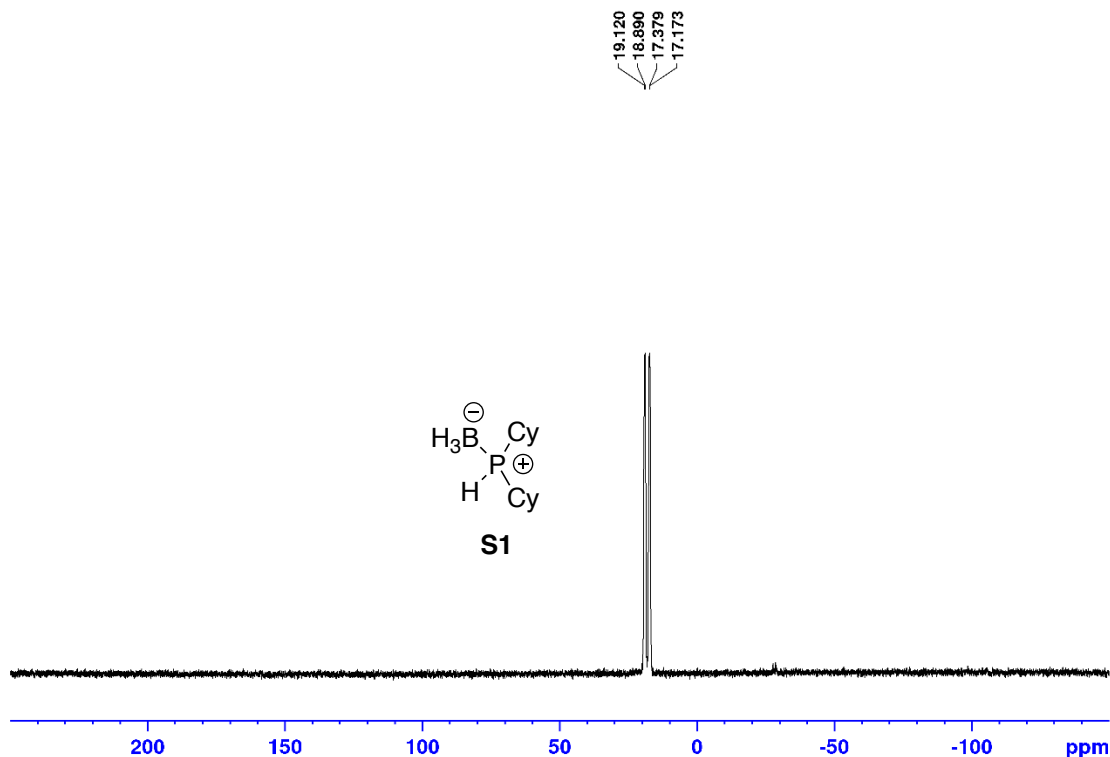


### Reaction of lithium dicyclohexylphosphide borane adduct **11a** and SF<sub>6</sub> gas:

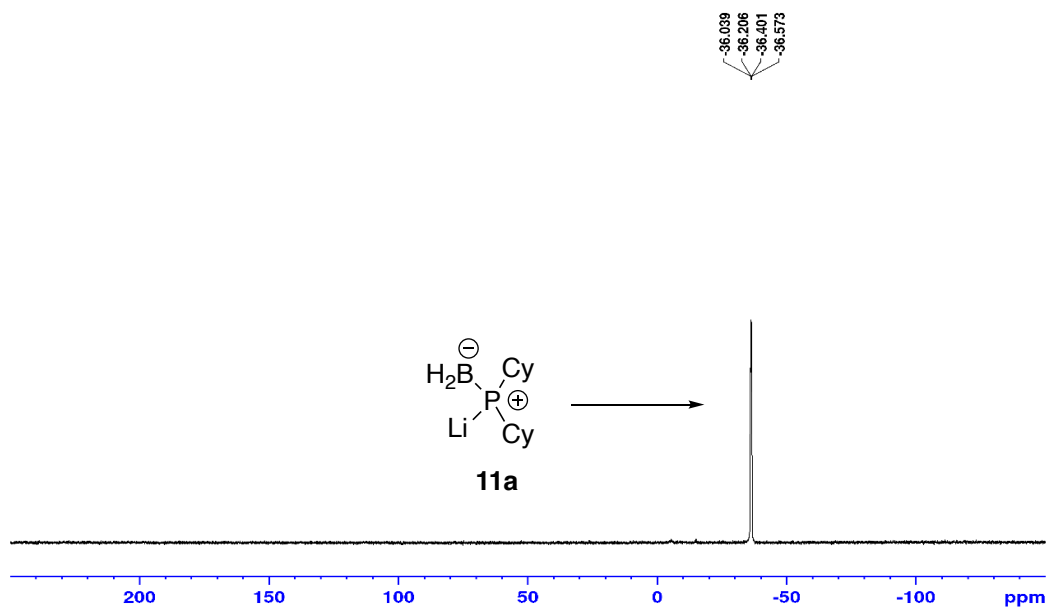
Dicyclohexylphosphine (0.2 mL, 0.1 mmol, 0.5M in THF) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.55 mL THF and 0.05 mL benzene-*d*<sub>6</sub>). Borane dimethylsulfide (0.1 mL, 0.1 mmol, 1M toluene) was added to the vial, solution was then transferred to a NMR tube and an NMR spectrum was acquired. *N*-butyllithium (0.04 mL, 0.1 mmol, 2.5M) was then added and the solution turned a yellow colour. The sample cap was then replaced with a septum. An SF<sub>6</sub> gas filled balloon equipped with a needle was then inserted into the solution and bubbled through for 15s. The solution went from orange to clear/yellow colour during this period in which the needle and septum were removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy.

<sup>31</sup>P NMR spectrum of mixture of HPCy<sub>2</sub> and BH<sub>3</sub> in THF.

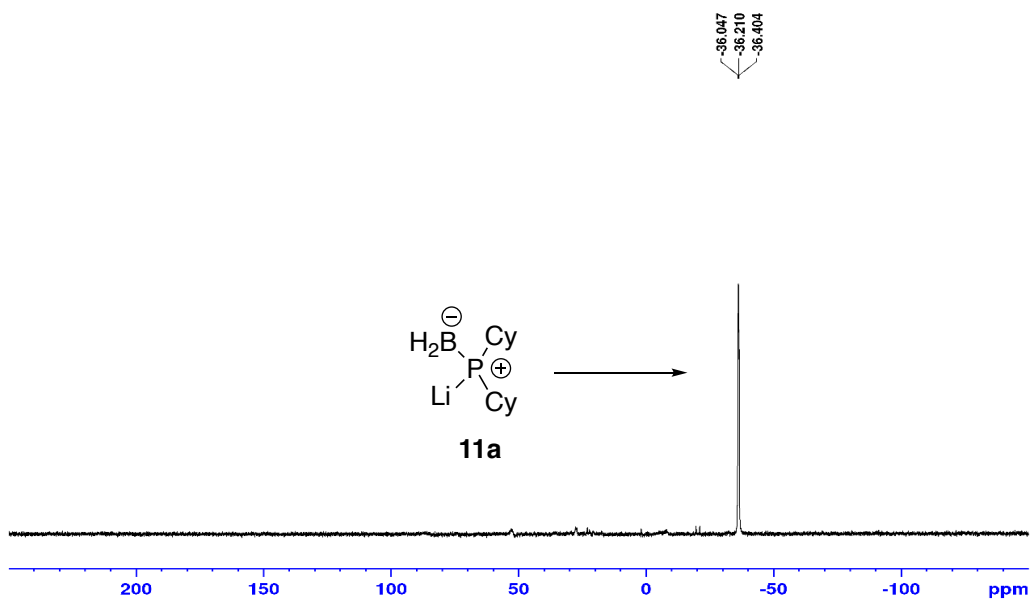
<sup>31</sup>P (202 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ 18 (d, <sup>1</sup>J<sub>P,H</sub> = 350 Hz).



$^{31}\text{P}$  NMR spectrum of nBuLi deprotonation of HPCy<sub>2</sub> and BH<sub>3</sub> adduct.  $^{31}\text{P}$  (202 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)):  $\delta$  -36 (m).



$^{31}\text{P}$  NMR spectrum after addition of SF<sub>6</sub>.  $^{31}\text{P}$  (202 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)):  $\delta$  -36 (m).

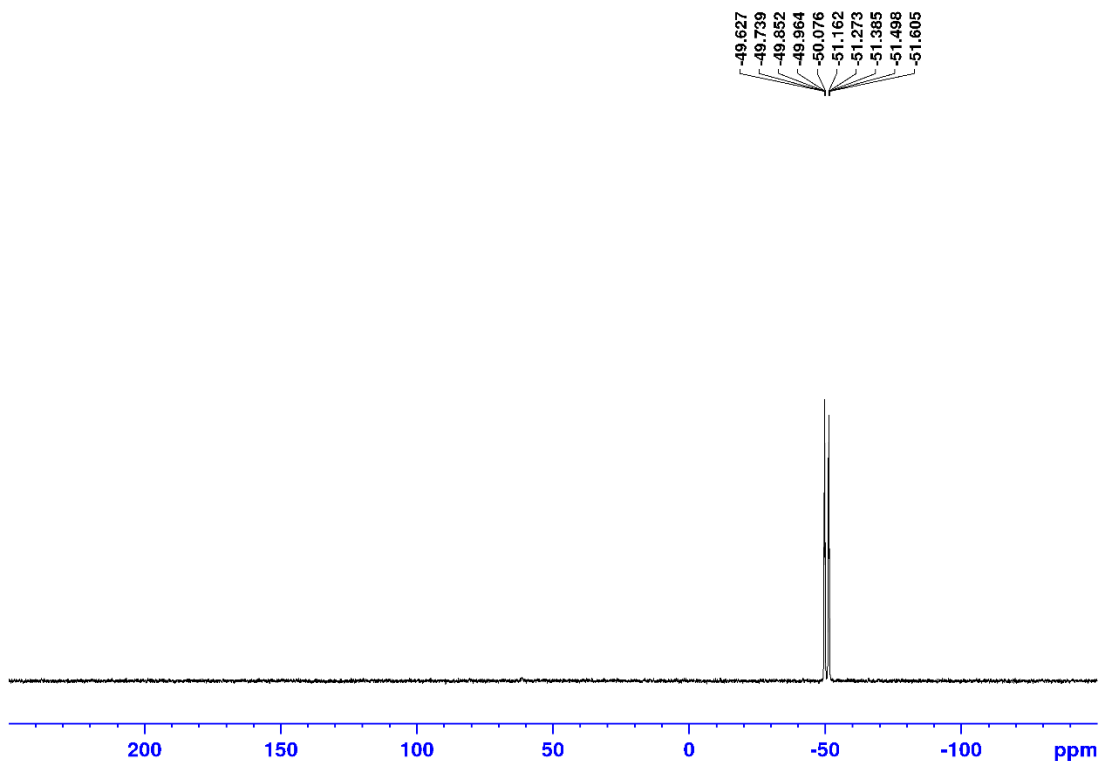


### Cage Phos deprotonation attempt 1:

Cage Phos (67 mg, 0.1 mmol, ~32% w/w in xylene) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.75 mL THF and 0.05 mL benzene- $d_6$ ). *n*-butyllithium (0.04 mL, 0.1 mmol, 2.5M) was then added and the solution turned orange. The solution was then transferred to an NMR tube and the sample was capped with a septum. The sample was analyzed and found no change in the  $^{31}\text{P}$  NMR spectrum. An  $\text{SF}_6$  gas filled balloon equipped with a needle was then inserted into the solution and bubbled through for 15s. The solution went from an orange to clear/yellow colour during this period in which the needle and septum were removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy, however no formation of soluble, NMR active, new phosphorus containing products were observed.

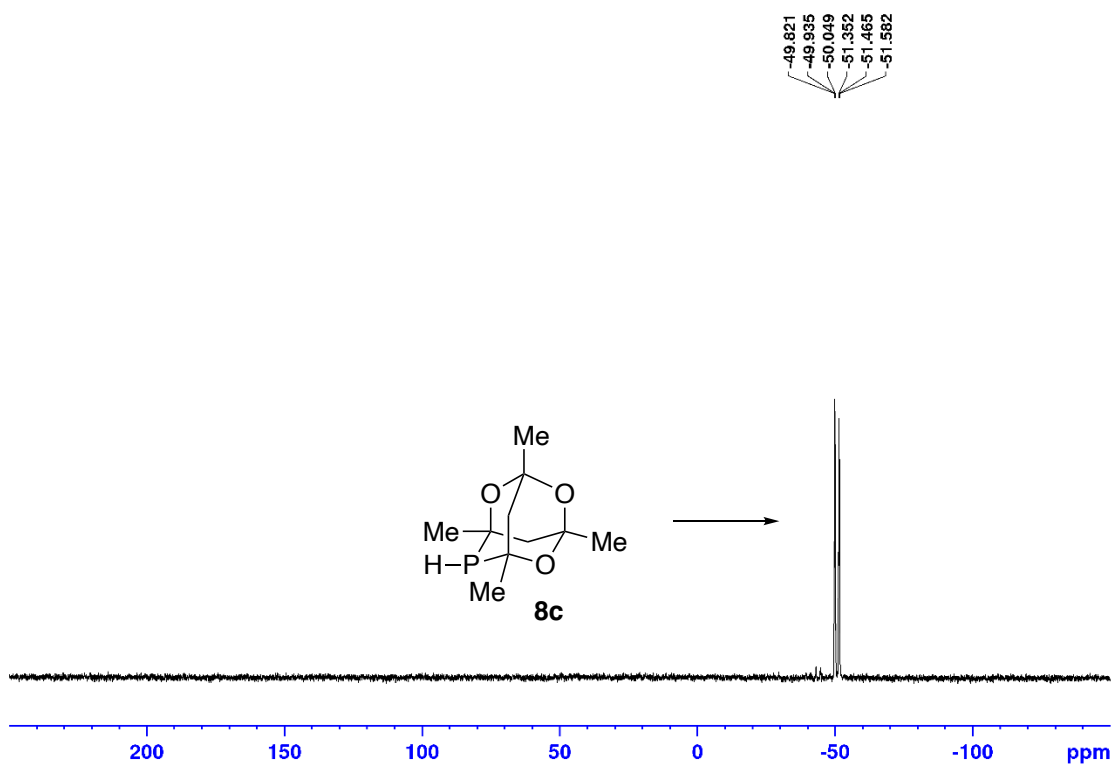
$^{31}\text{P}$  NMR spectrum of **8c** before addition of *n*-BuLi:

$^{31}\text{P}$  (121 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -50.6 (d,  $^1J_{\text{P,H}} = 187$  Hz).



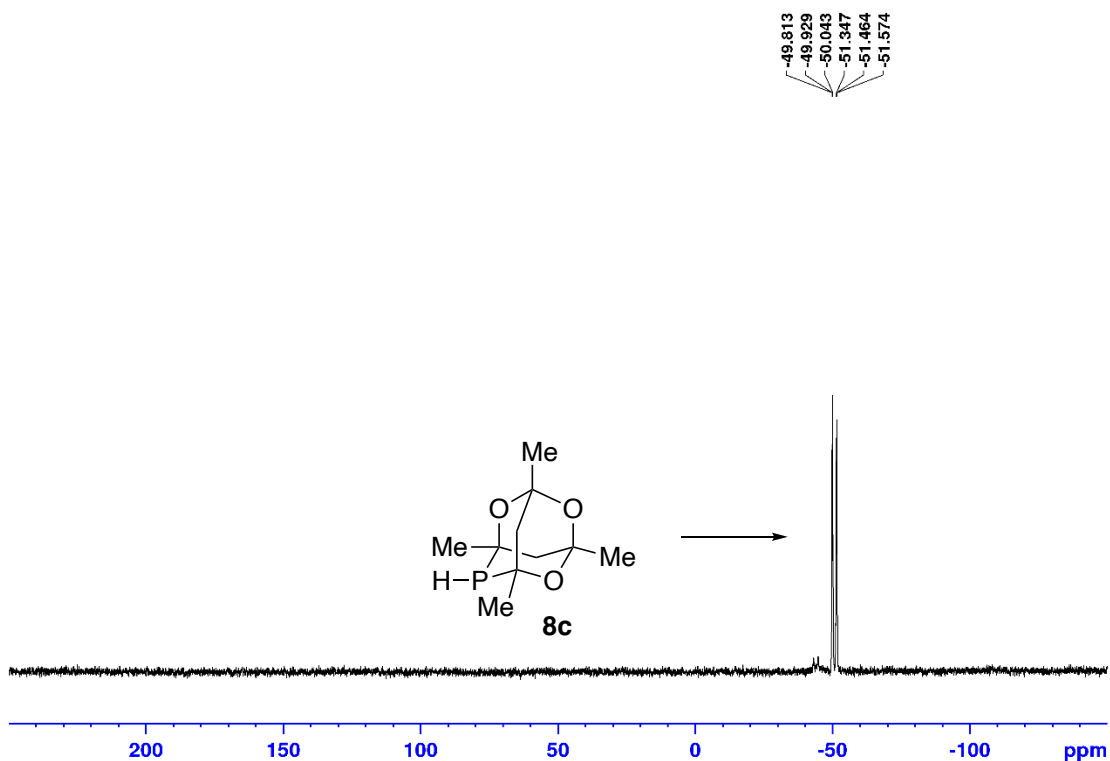
$^{31}\text{P}$  NMR spectrum of **8c** after addition of *n*-BuLi:

$^{31}\text{P}$  (121 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -50.6 (d,  $^1J_{\text{P,H}} = 187$  Hz).



$^{31}\text{P}$  NMR spectrum of **8c** and *n*-BuLi, after addition of SF<sub>6</sub>:

$^{31}\text{P}$  (121 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)):  $\delta$  -50.6 (d,  $^1J_{\text{P,H}} = 187$  Hz).

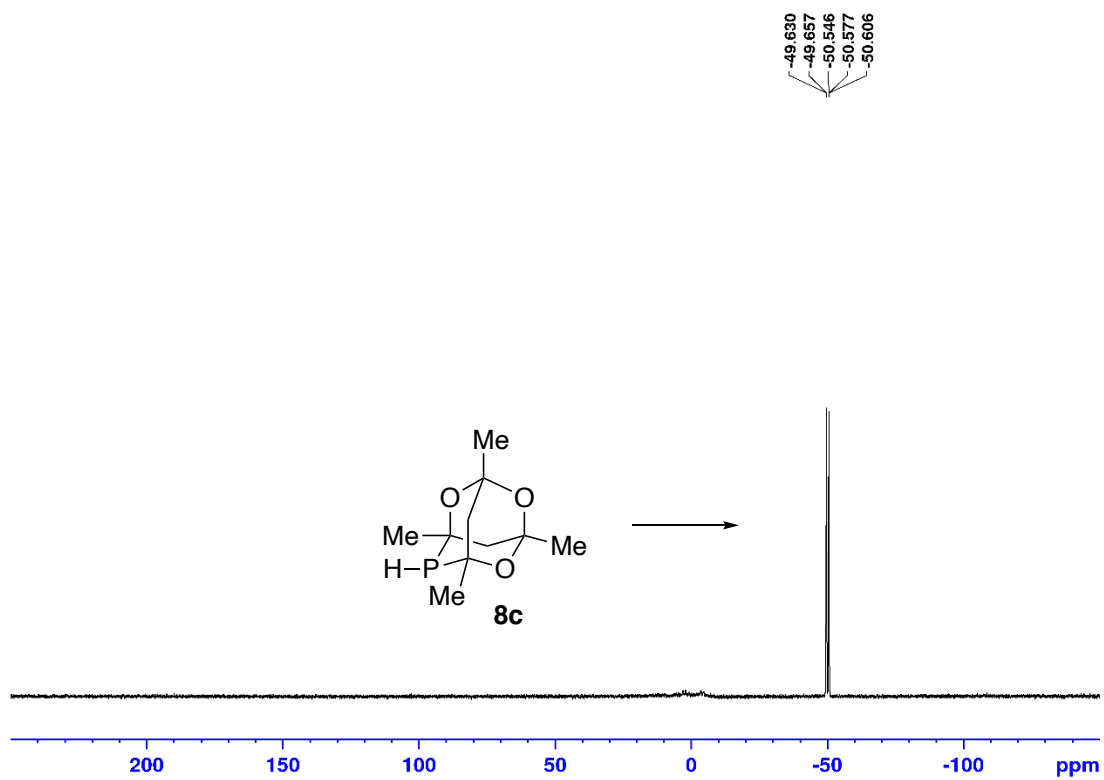


### Cage Phos deprotonation attempt 2:

Cage Phos (67 mg, 0.1 mmol, ~32% w/w in xylene) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.75 mL THF and 0.05 mL benzene-*d*<sub>6</sub>) The solution was then cooled to -35 °C. *Tert*-butyllithium (0.06 mL, 0.1 mmol, 1.7 M) was then added and the solution turned orange. The solution was stirred for an hour and then analyzed by NMR analysis and found no change in the spectrum.

$^{31}\text{P}$  NMR spectrum of **8c** after addition of *tert*-BuLi:

$^{31}\text{P}$  (202 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -50.5 (d,  $^1J_{\text{P,H}} = 187$  Hz).



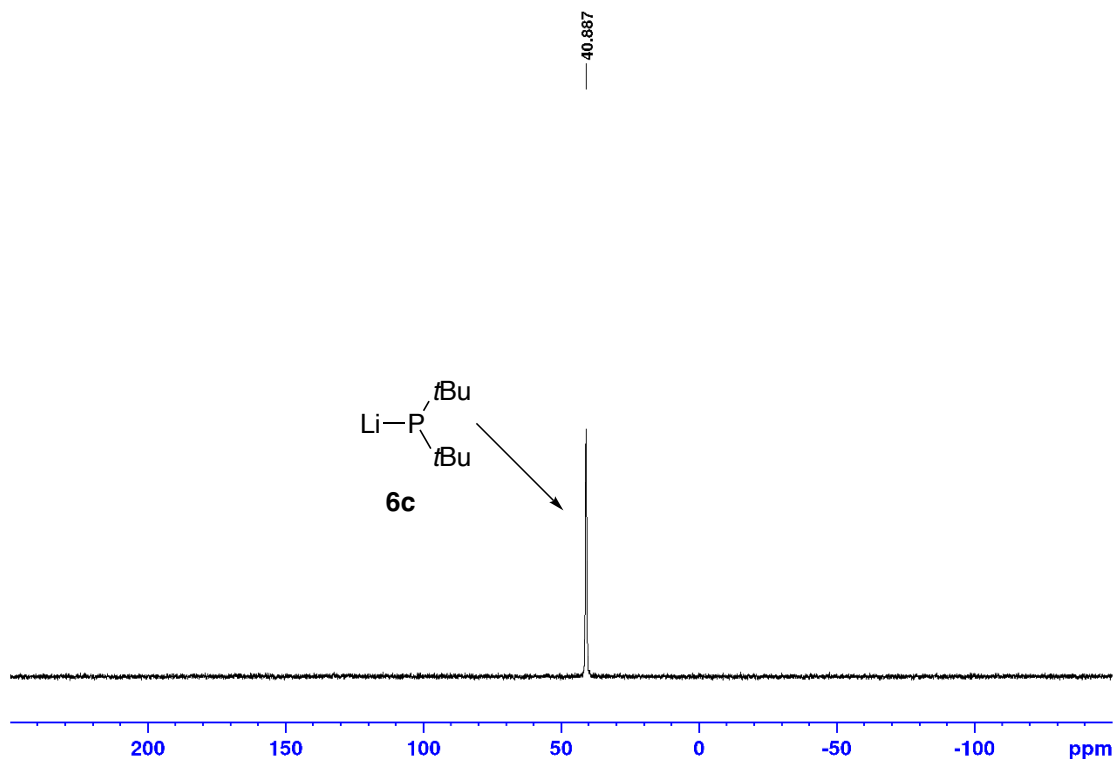


### Reaction of lithium ditertbutylphosphide and SF<sub>6</sub> gas:

Ditertbutylphosphine (0.2 mL, 0.1 mmol, 0.5M in THF) was dispensed into a 1-dram vial. The solution was diluted with additional solvent (0.55 mL THF and 0.05 mL benzene-*d*<sub>6</sub>). *n*-butyllithium (0.04 mL, 0.1 mmol, 2.5M) was then added and the solution turned orange. The solution was then transferred to an NMR tube and the sample was capped with a septum. An SF<sub>6</sub> gas filled balloon equipped with a needle was then inserted into the solution and bubbled through for 15s. The solution went from orange to clear/yellow colour during this period in which the needle and septum were removed and replaced with a standard NMR cap. The solution was then analyzed using NMR spectroscopy. Mass spectrometry identified the presence of dimer **7c**, but fragments corresponding to the other components observed by NMR were not observed by mass spectrometry.

<sup>31</sup>P NMR spectrum of **6c** formed from mixing **8d** and *n*-BuLi in THF:

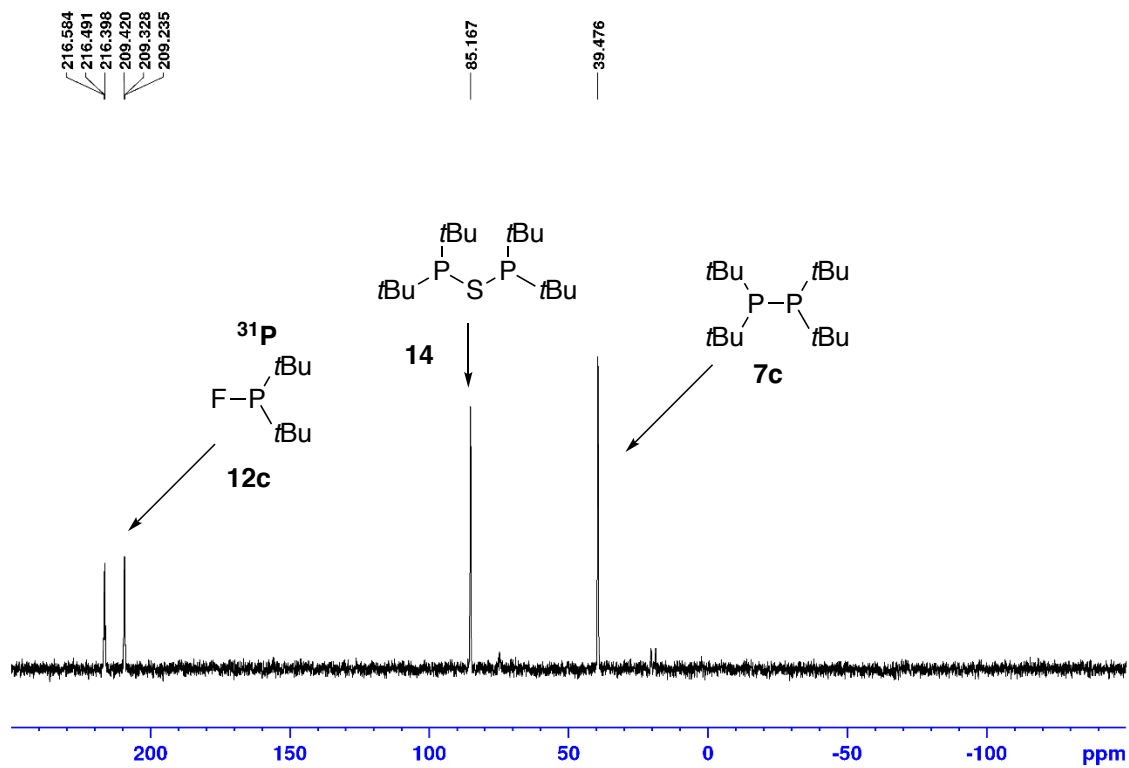
<sup>31</sup>P (121 MHz, THF, C<sub>6</sub>D<sub>6</sub> (lock)): δ 40.8 (s).



$^{31}\text{P}$  NMR spectrum of addition of  $\text{SF}_6$  to **6c** in THF:

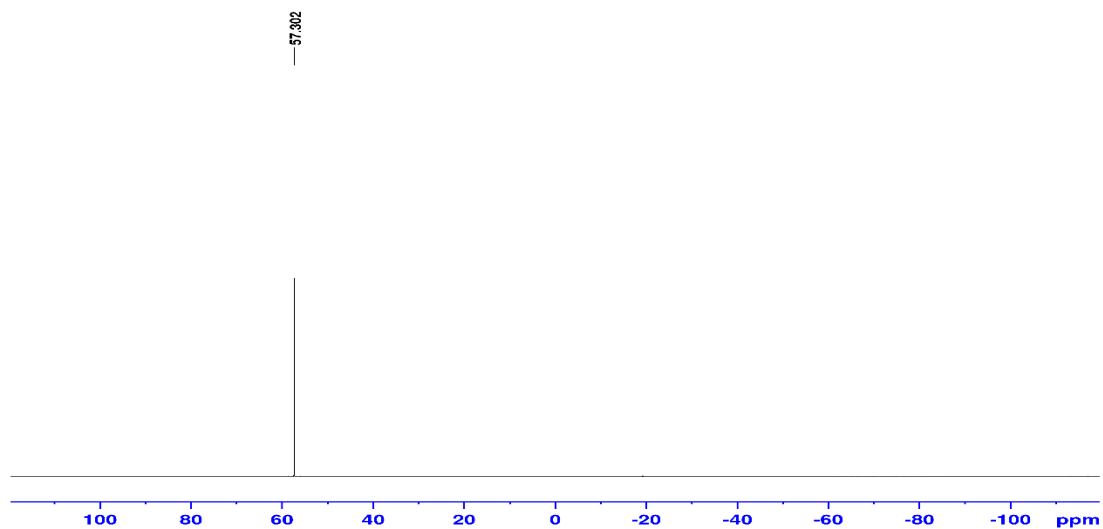
**HRMS (ESI):** calc'd for  $\text{C}_{16}\text{H}_{37}\text{P}_2$  [ $\text{M} + \text{H}^+$ ] 291.2365; Found: 291.2363.

$^{31}\text{P}$  (121 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  212 (d,  $^1J_{\text{P,F}} = 870$  Hz), 85.2 (s), 39.5 (s).



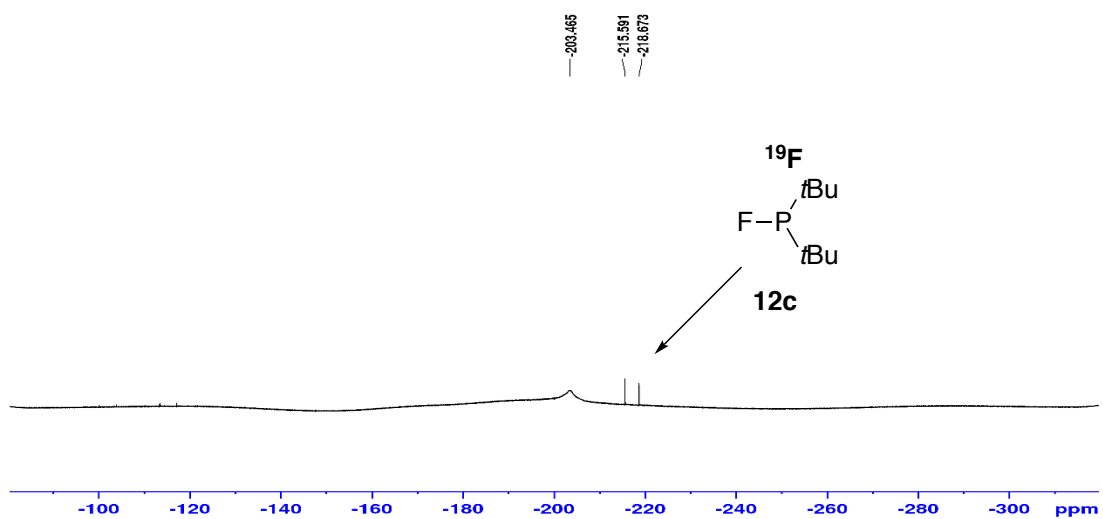
$^{19}\text{F}$  NMR spectrum of addition of  $\text{SF}_6$  to **6c** in THF:

$^{19}\text{F}$  (282 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  57.3 (s).  $\text{SF}_6$ .



**-200 center point**

$^{19}\text{F}$  (282 MHz, THF,  $\text{C}_6\text{D}_6$  (lock)):  $\delta$  -203 (s), -217 (d,  $^1J_{\text{P,F}} = 870$  Hz).



## References:

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- <sup>1</sup> J. D. Cline, *Limnol. Oceanogr.*, 1969, **14**, 454.
- <sup>2</sup> M. Gruber, P. G. Jones, R. Schmutzler, *Chem. Ber.*, 1990, **123**, 1313.
- <sup>3</sup> Y. Sato, M. Nishimura, S.-i. Kawaguchi, A. Nomoto, A. Ogawa, *Chem. Eur. J.*, 2019, **25**, 6797.
- <sup>4</sup> J. Wagner, M. Ciesielski, C. A. Fleckenstein, H. Denecke, F. Garlich, A. Ball, M. Doering, *Org. Process Res. Dev.*, 2013, **17**, 47.
- <sup>5</sup> S. Kim, Y. Khomutnyk, A. Bannykh, P. Nagorny, *Org. Lett.*, 2021, **23**, 190.