

## Supplementary Materials for

### Synthesis and N-C Bond Cleavage Reactions for Cyclic Phosphazanium Dications

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# NMR spectra for (C<sub>6</sub>H<sub>4</sub>)(PPh<sub>2</sub>F<sub>2</sub>)<sub>2</sub> (1)

Figure S1. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 1.

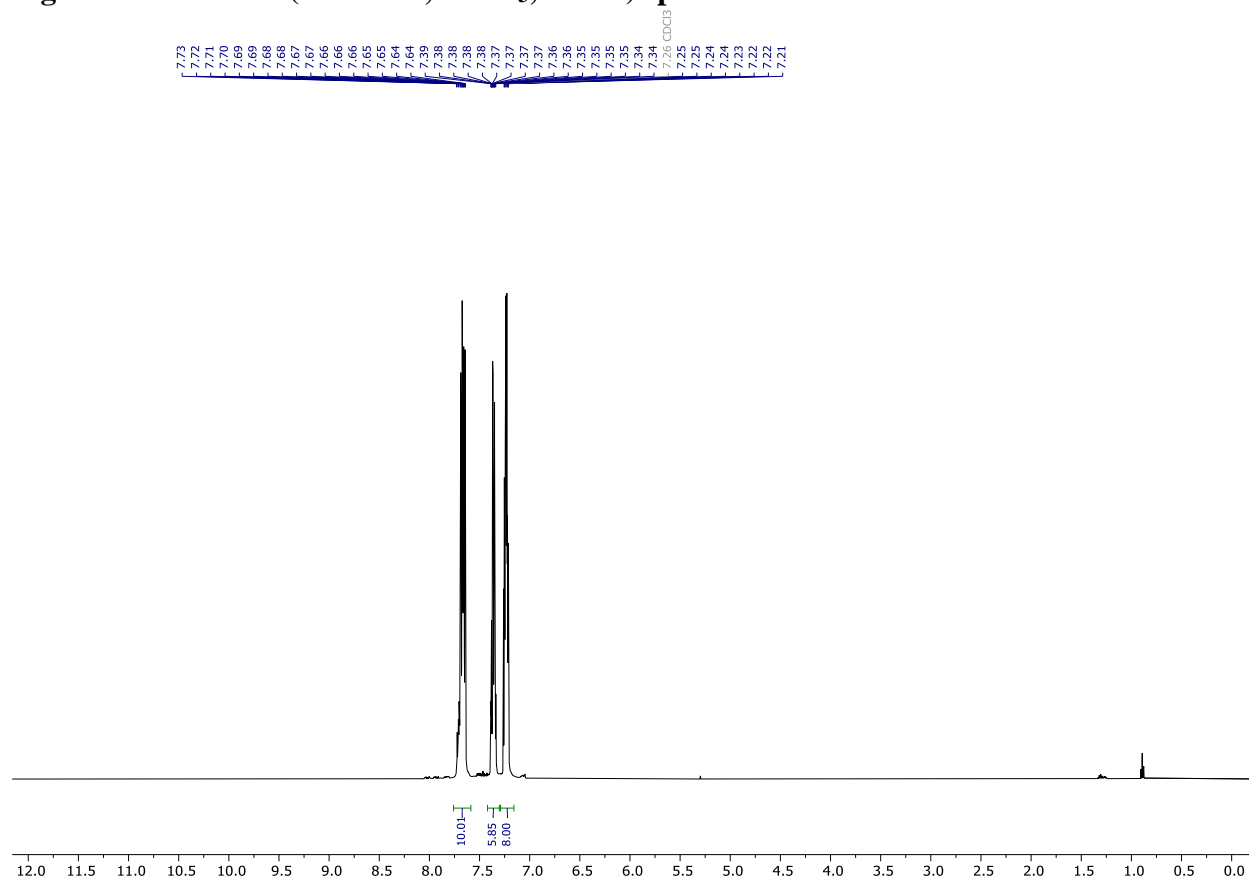


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K) spectrum of **1**.

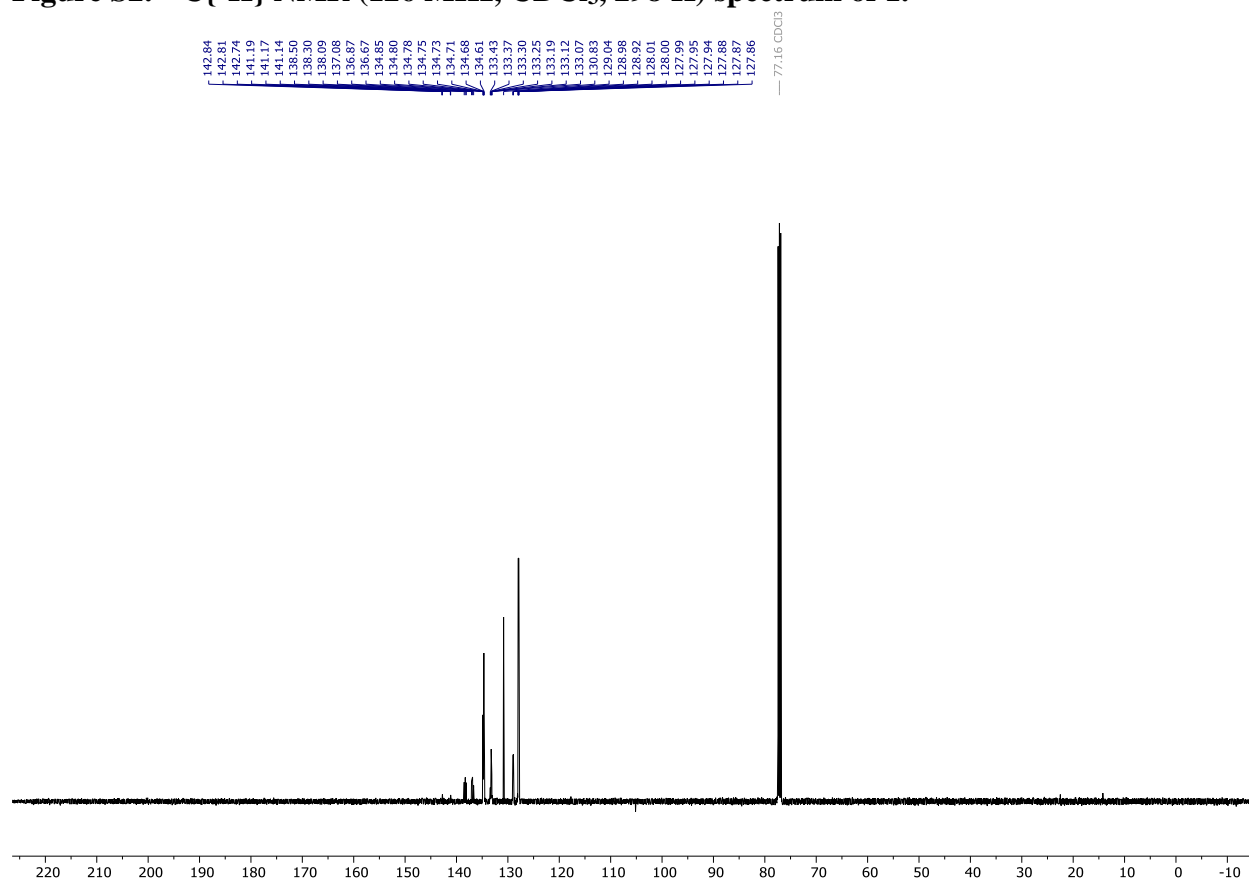


Figure S3.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ , 298K) spectrum of 1.

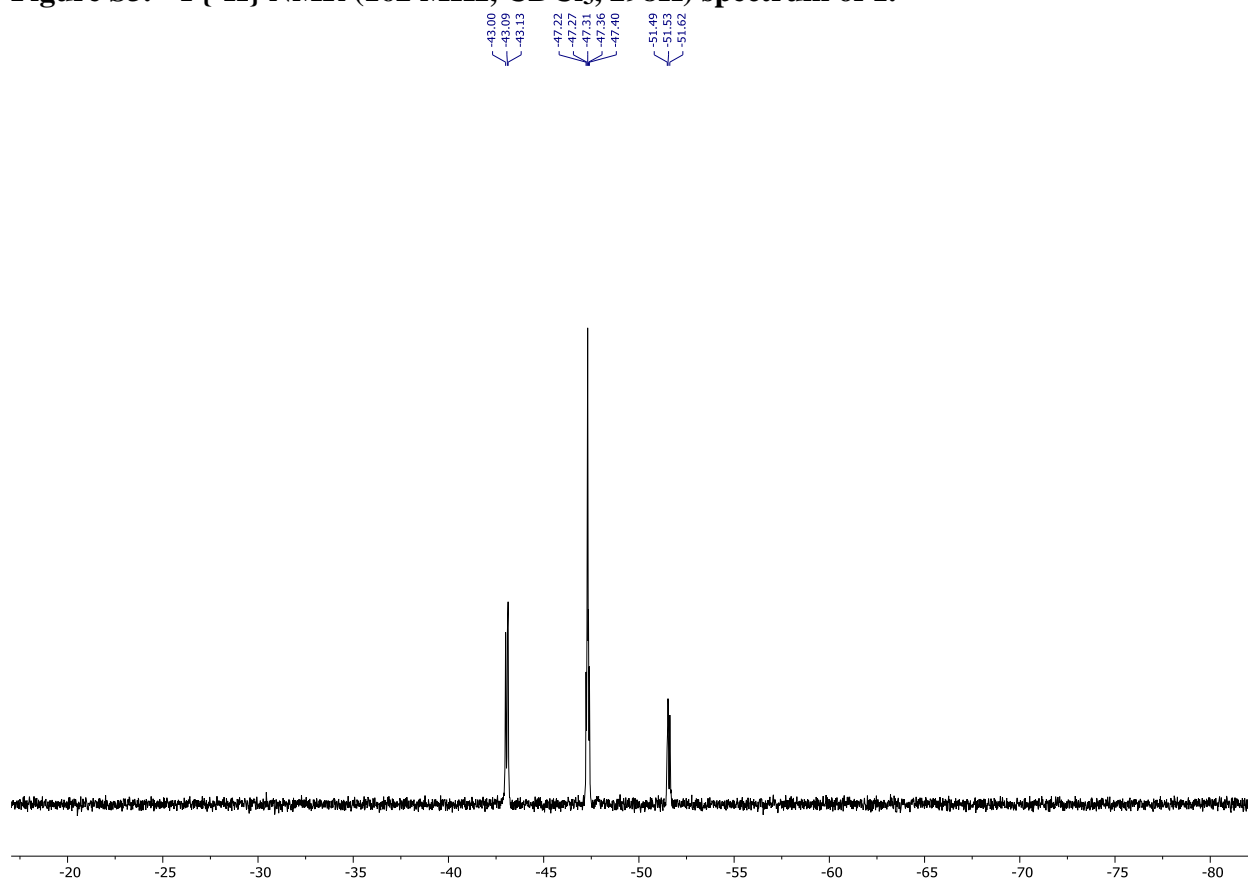
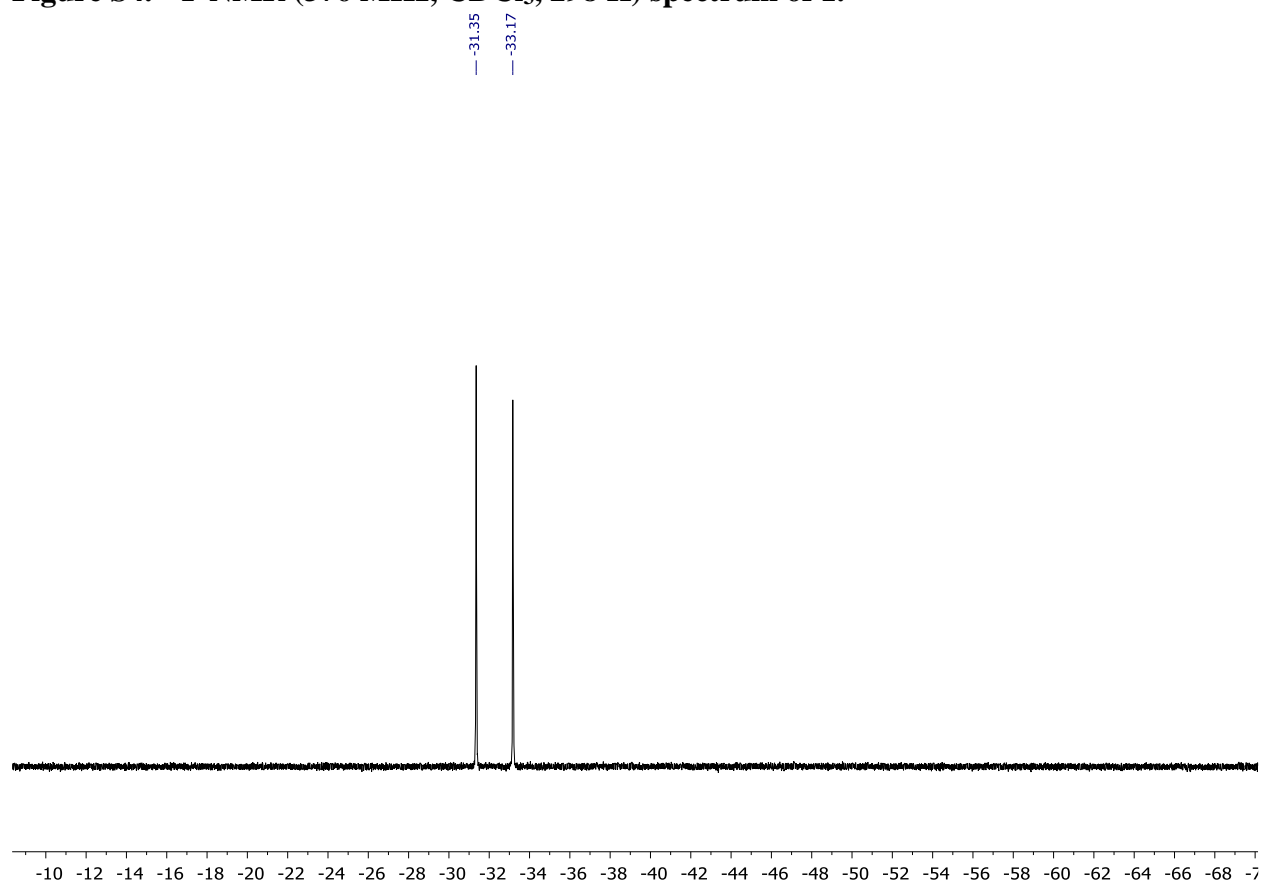


Figure S4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 298 K) spectrum of **1**.



# NMR spectra for $[(C_6H_4)(PPh_2F)_2][B(C_6F_5)_4]_2$ (2)

Figure S5.  $^1H$  NMR (500 MHz,  $CD_2Cl_2$ , 298 K) spectrum of 2.

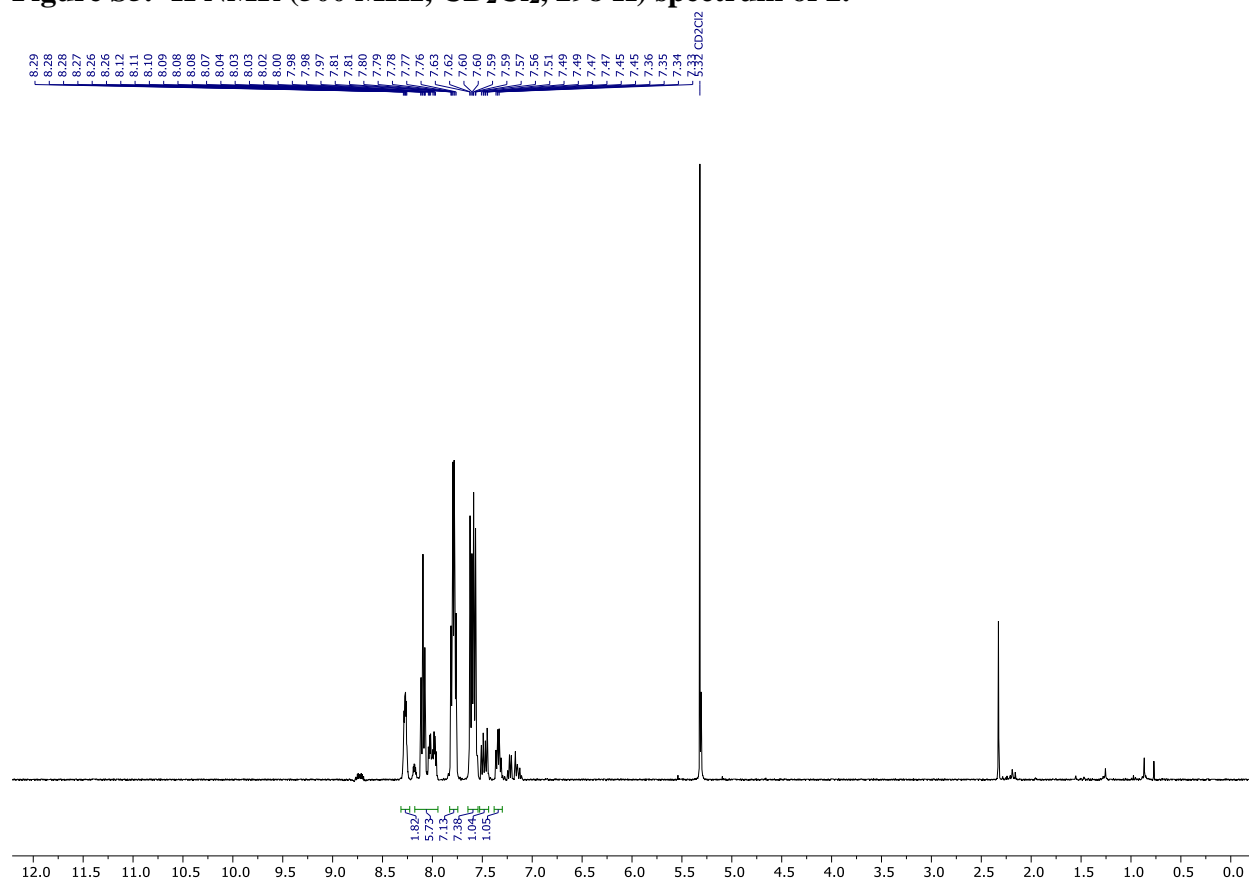


Figure S6.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **2**.

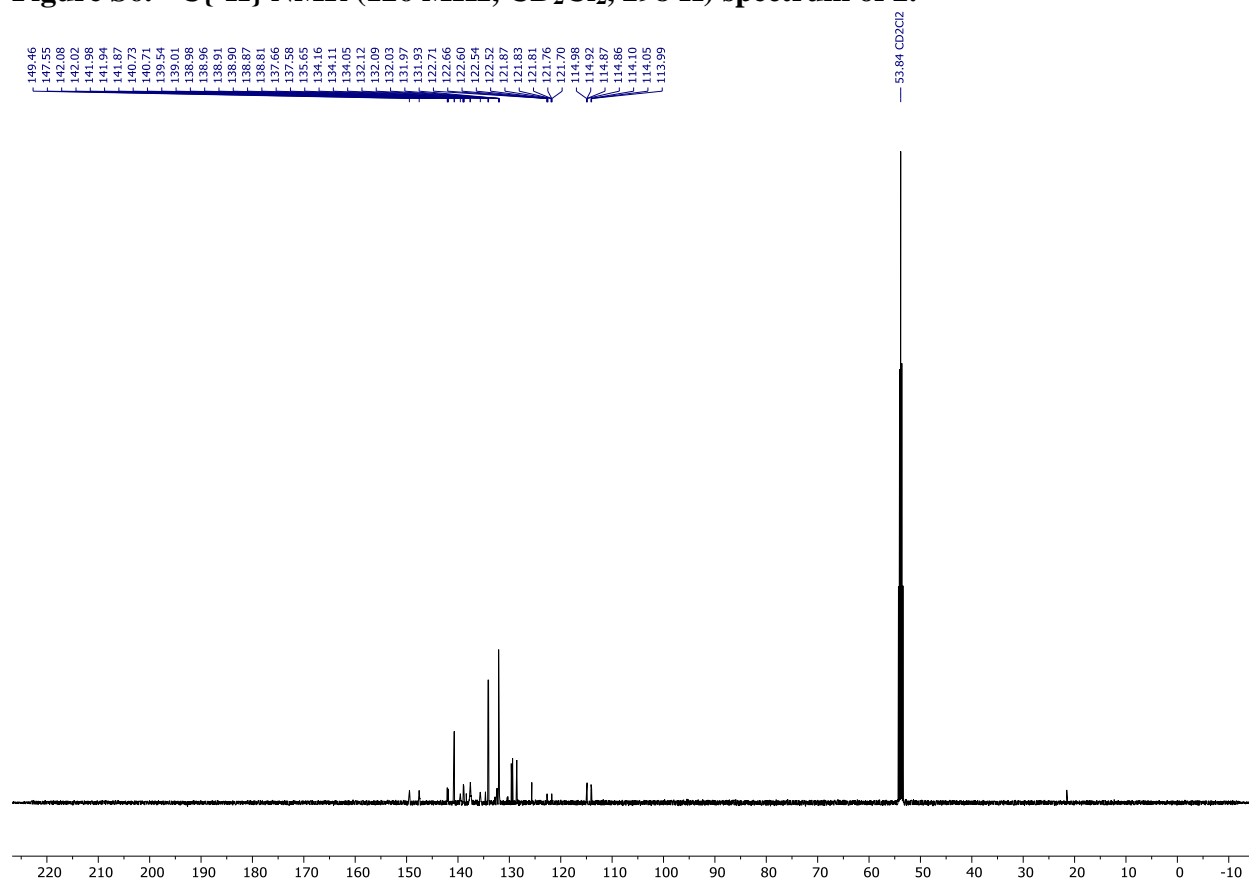




Figure S7.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of 2.

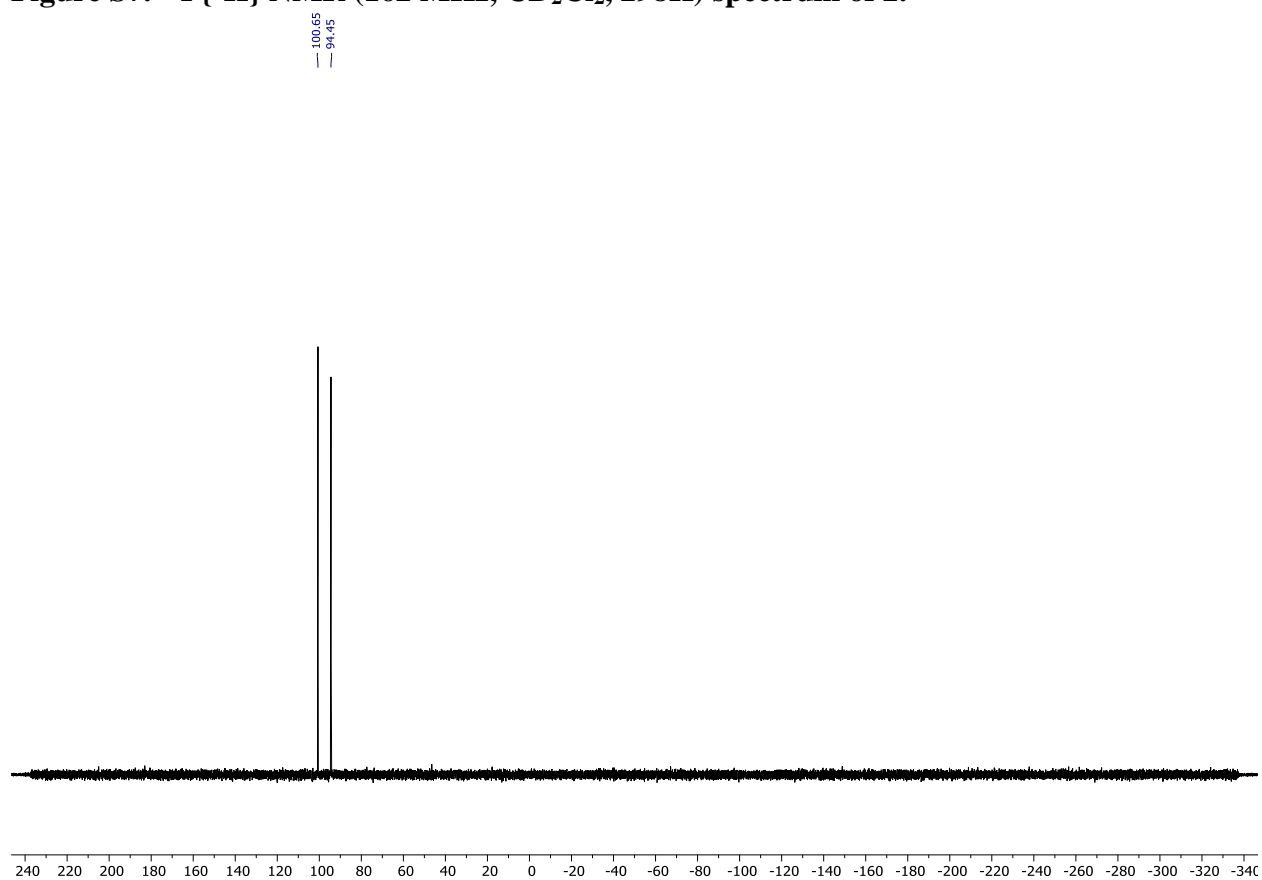


Figure S8.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **2**.

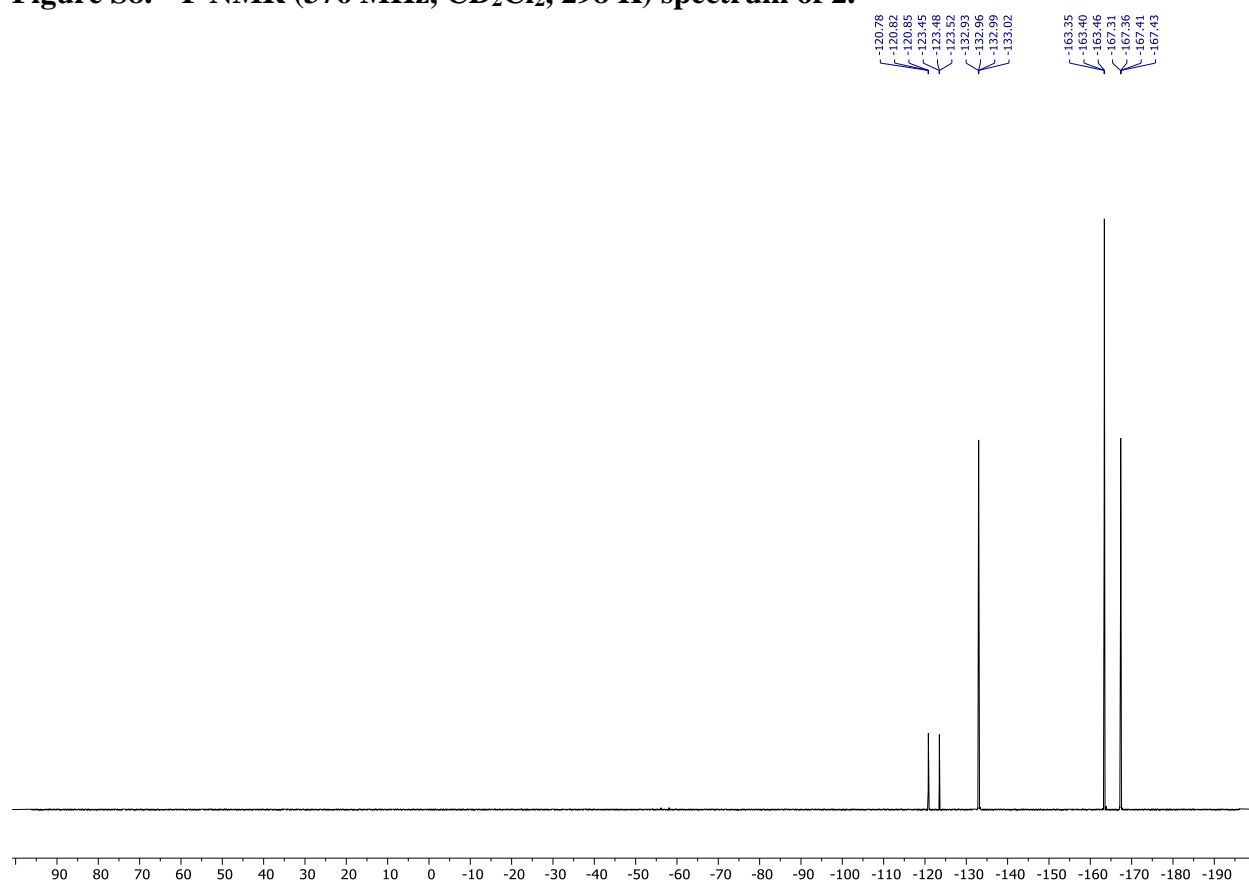
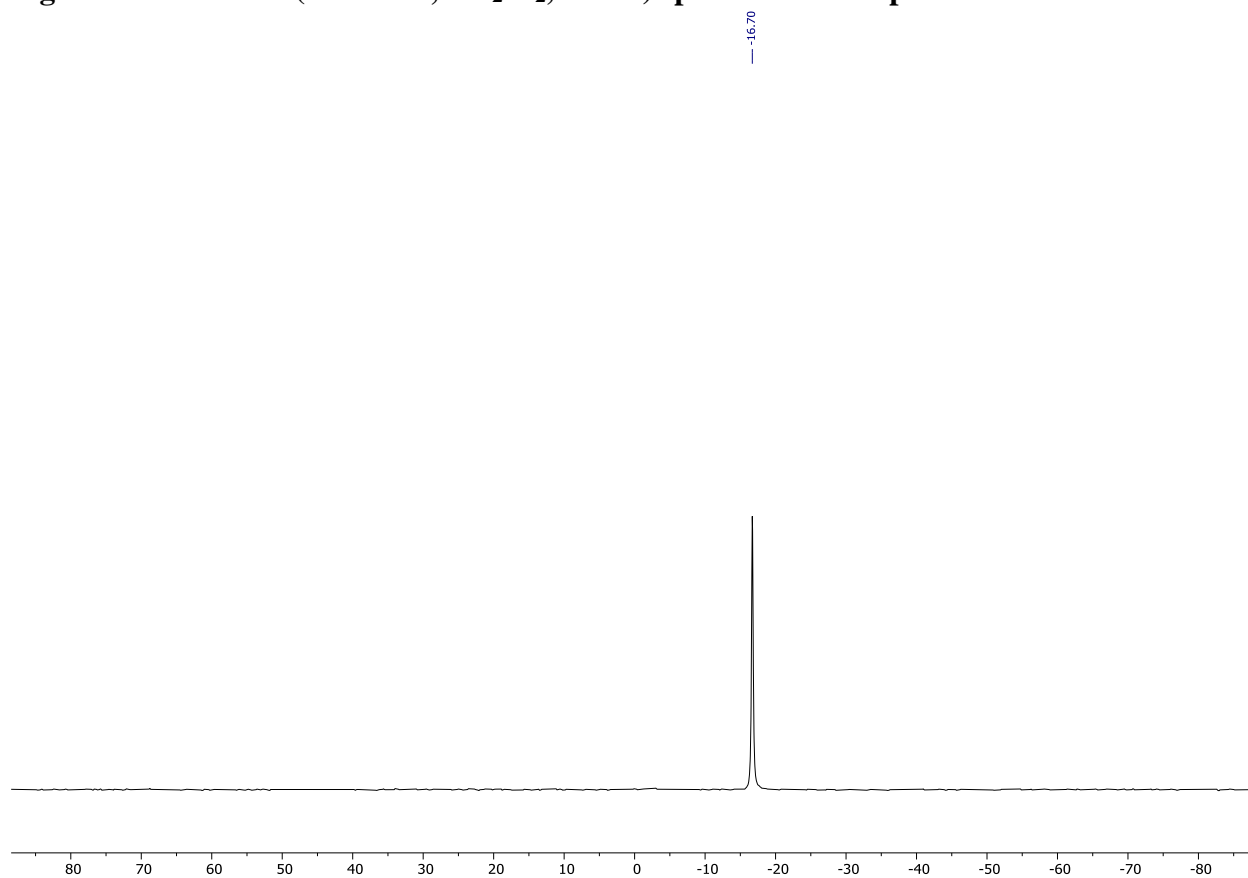


Figure S9.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound 2.



# NMR spectra for $[(C_6H_4)(PPh_2Cl)_2][Cl]_2$ (**3**)

Figure S20.  $^1H$  NMR (500 MHz,  $CD_2Cl_2$ , 298 K) spectrum of **3**.

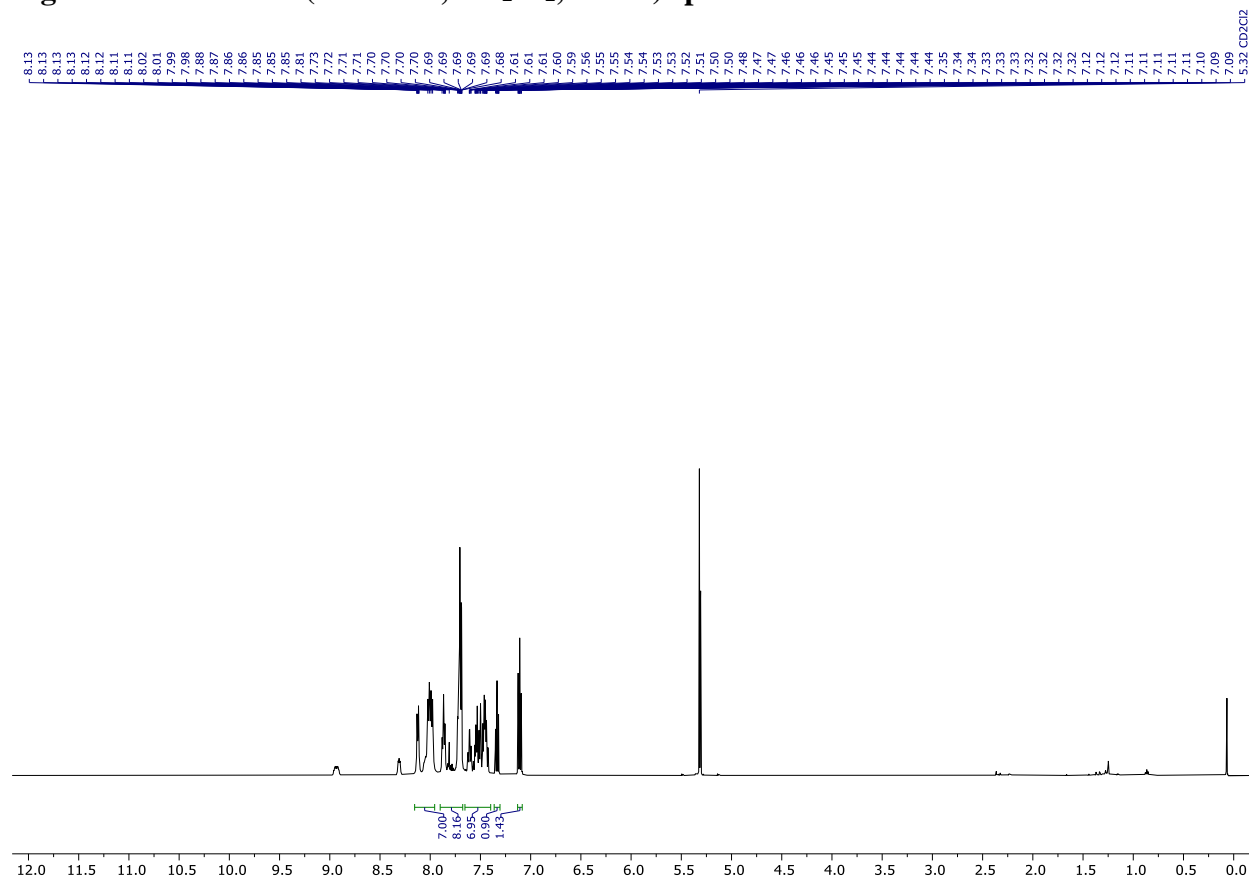


Figure S11.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **3**.

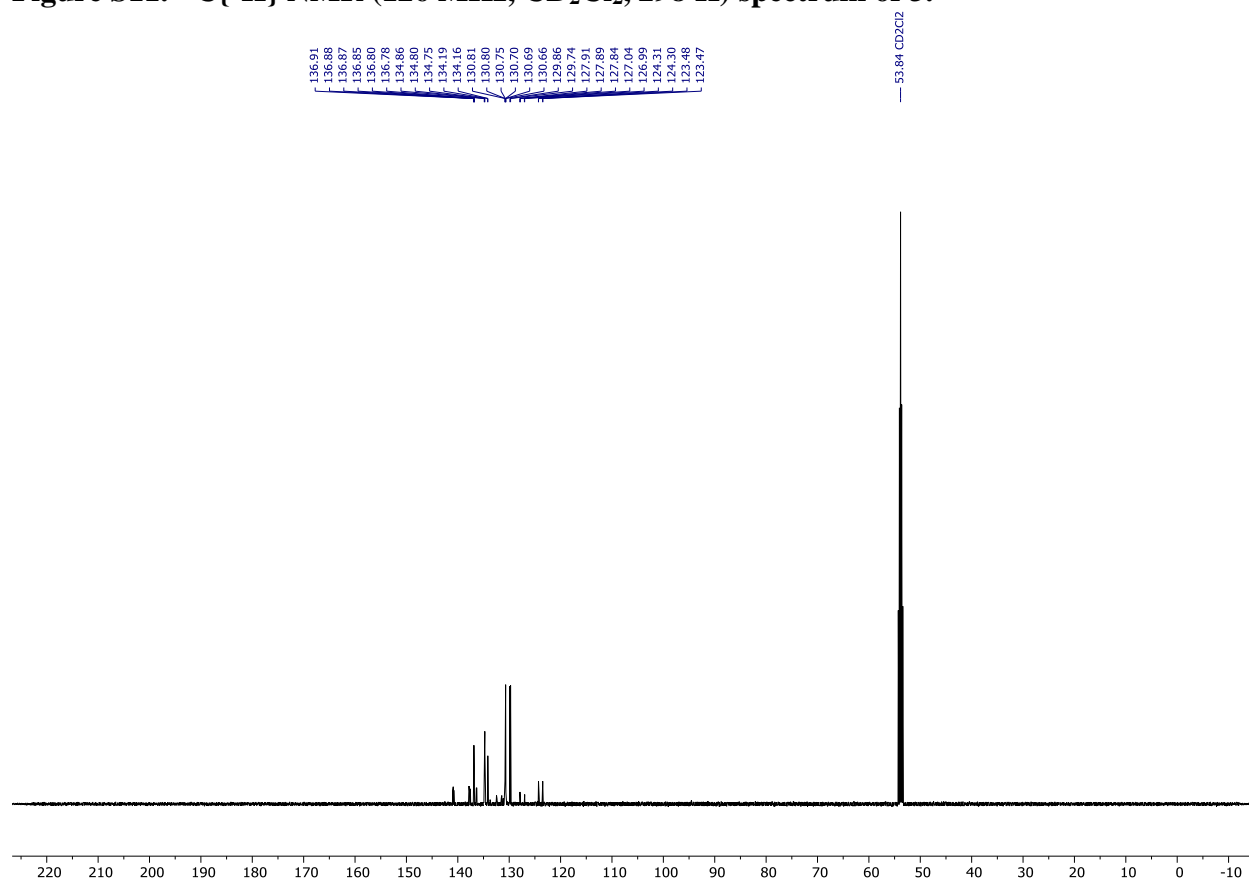
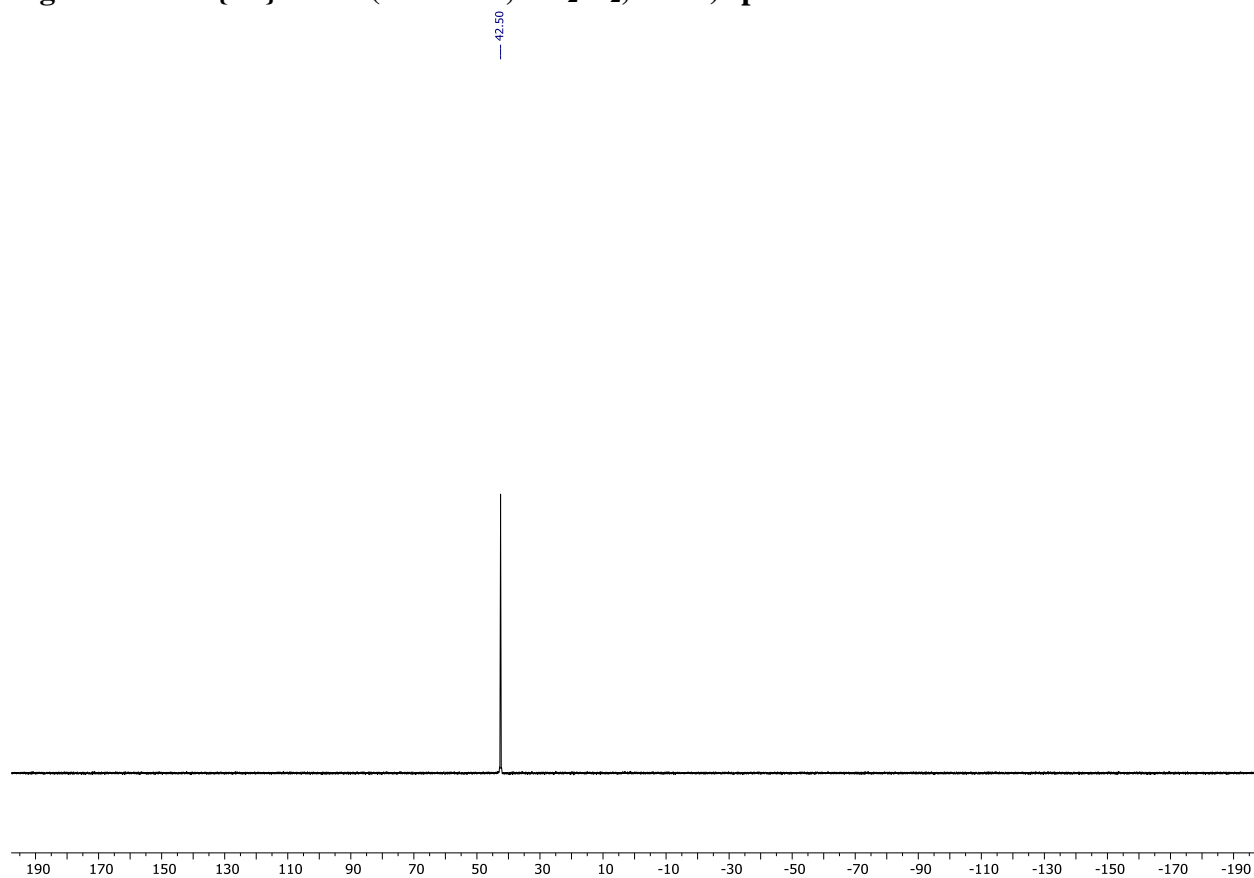


Figure S12.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of 3.



**NMR spectra for  $[(C_6H_4)(PPh_2Cl)_2]_2[BF_{4-n}Cl_n]$  (**3'**)**

**Figure S13.  $^{31}P\{^1H\}$  NMR (162 MHz,  $CH_2Cl_2$ , 298K) spectrum of **3'**.**

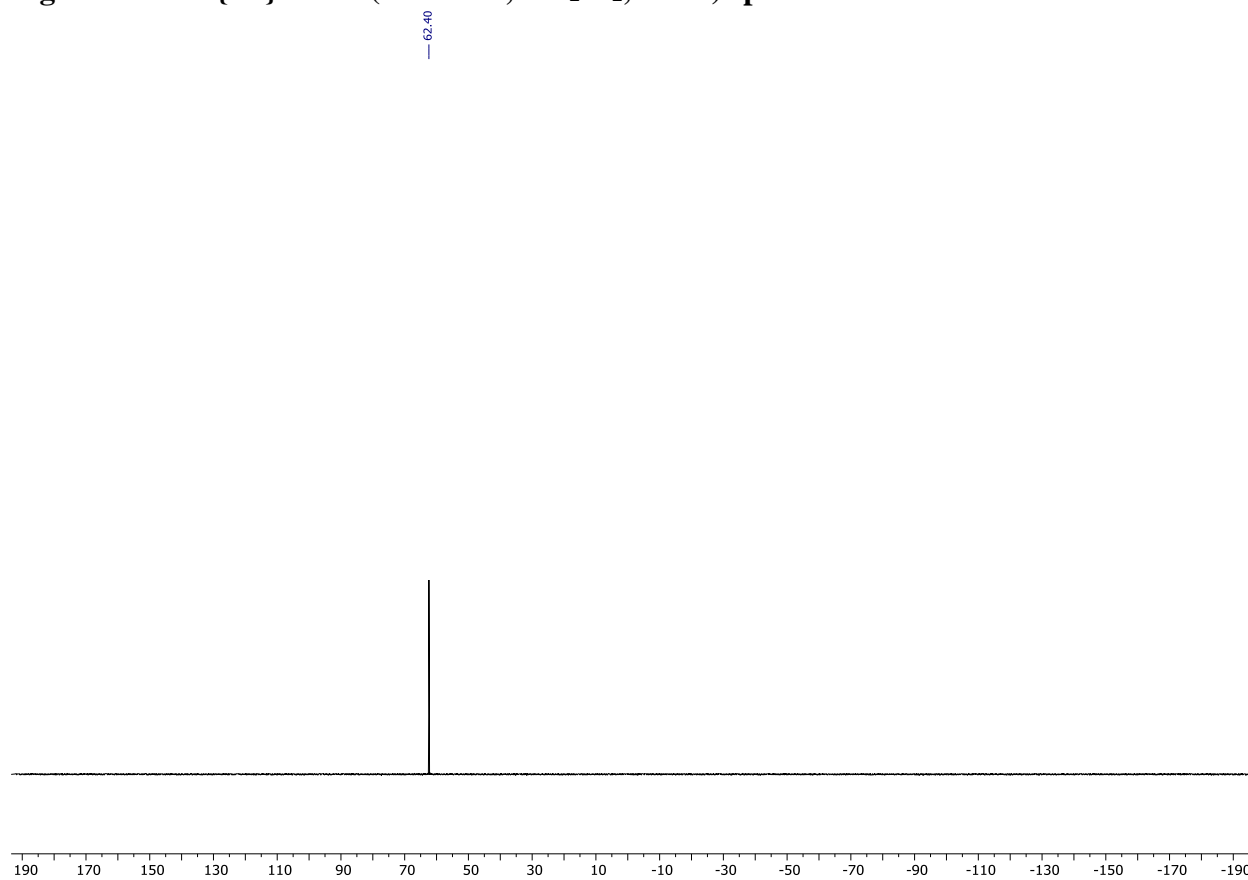
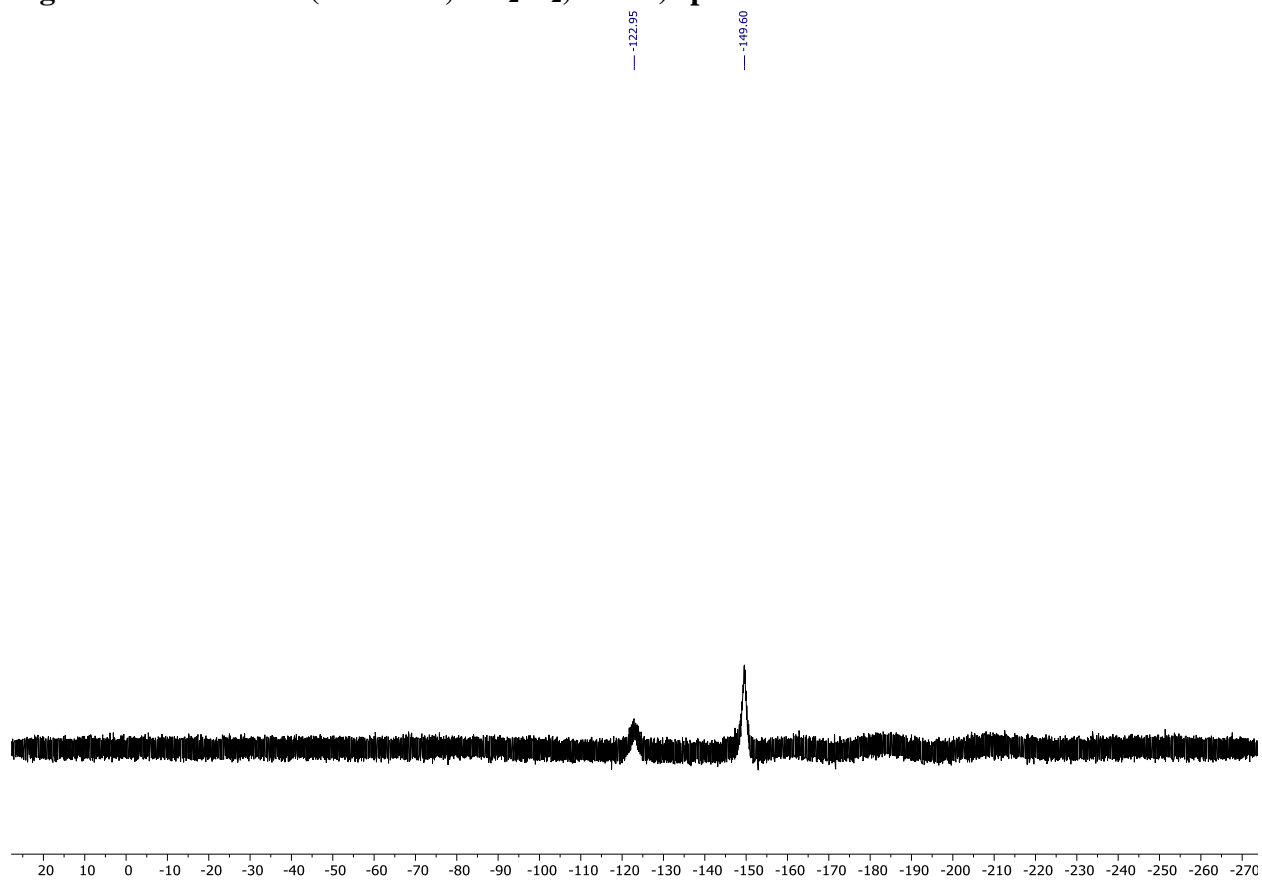


Figure S14.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CH}_2\text{Cl}_2$ , 298 K) spectrum of 3'.





**NMR spectra for  $[(C_6H_4)(PPh_2)_2(\mu-NMe)][B(C_6F_5)_4]_2$  (**4**)**

**Figure S35.  $^1H$  NMR (500 MHz,  $CD_2Cl_2$ , 298 K) spectrum of **4**.**

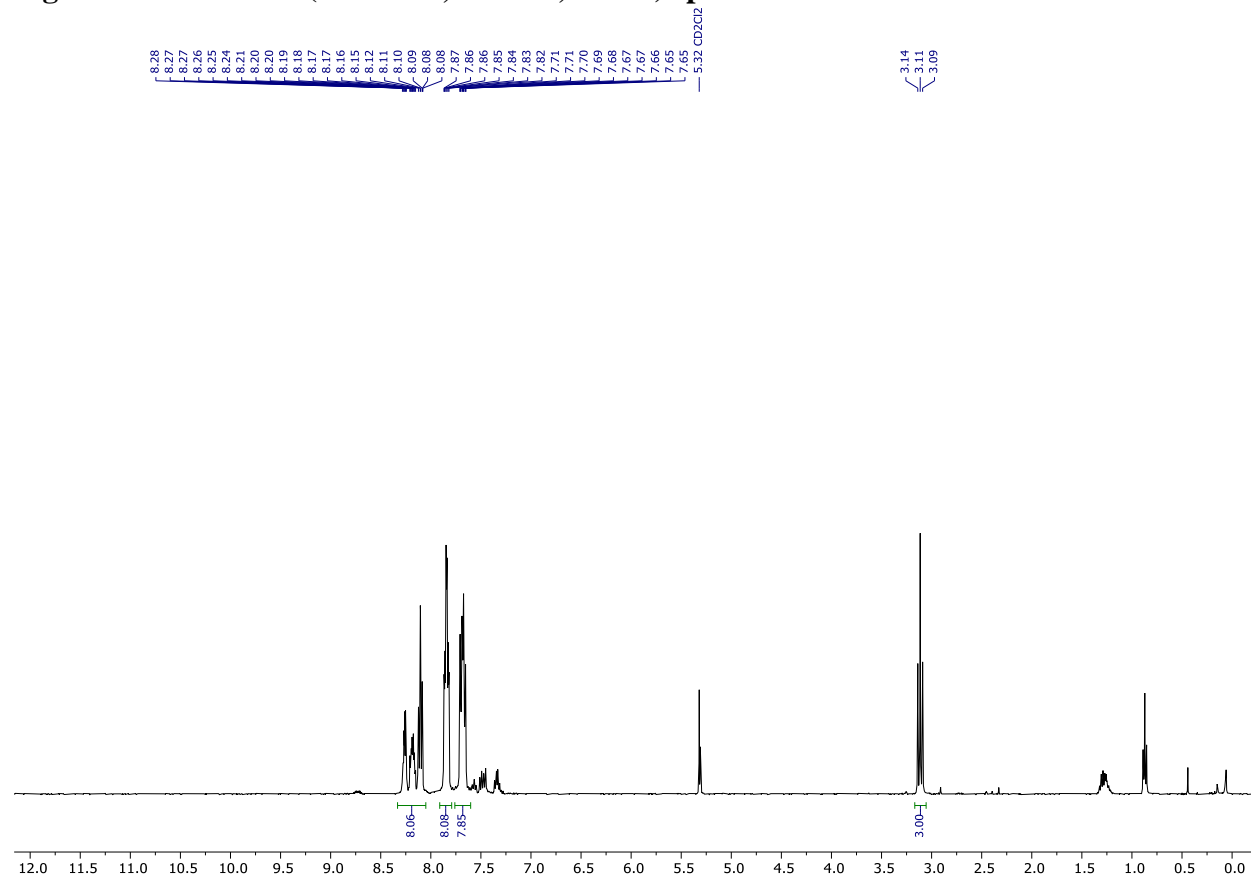


Figure S16.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **4**.

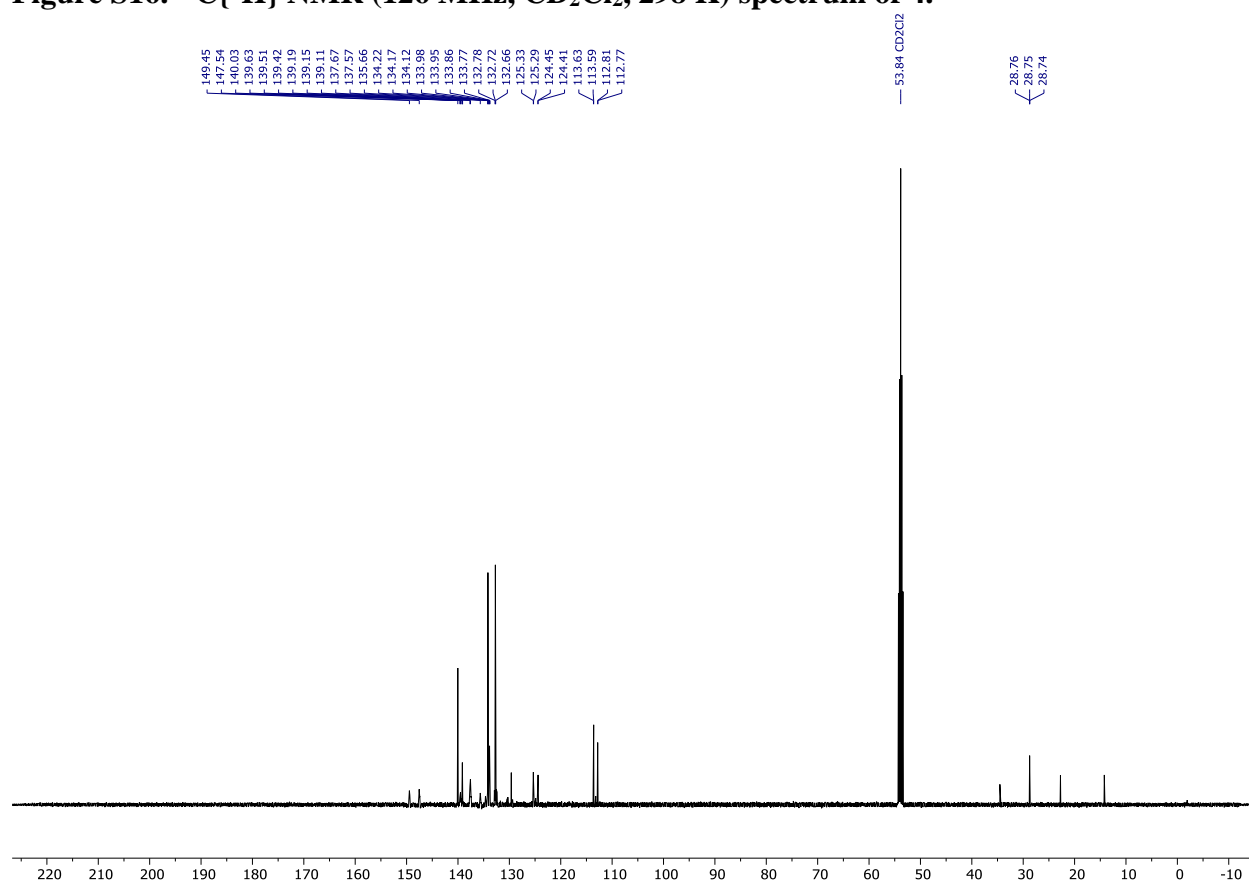


Figure S17.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of 4.

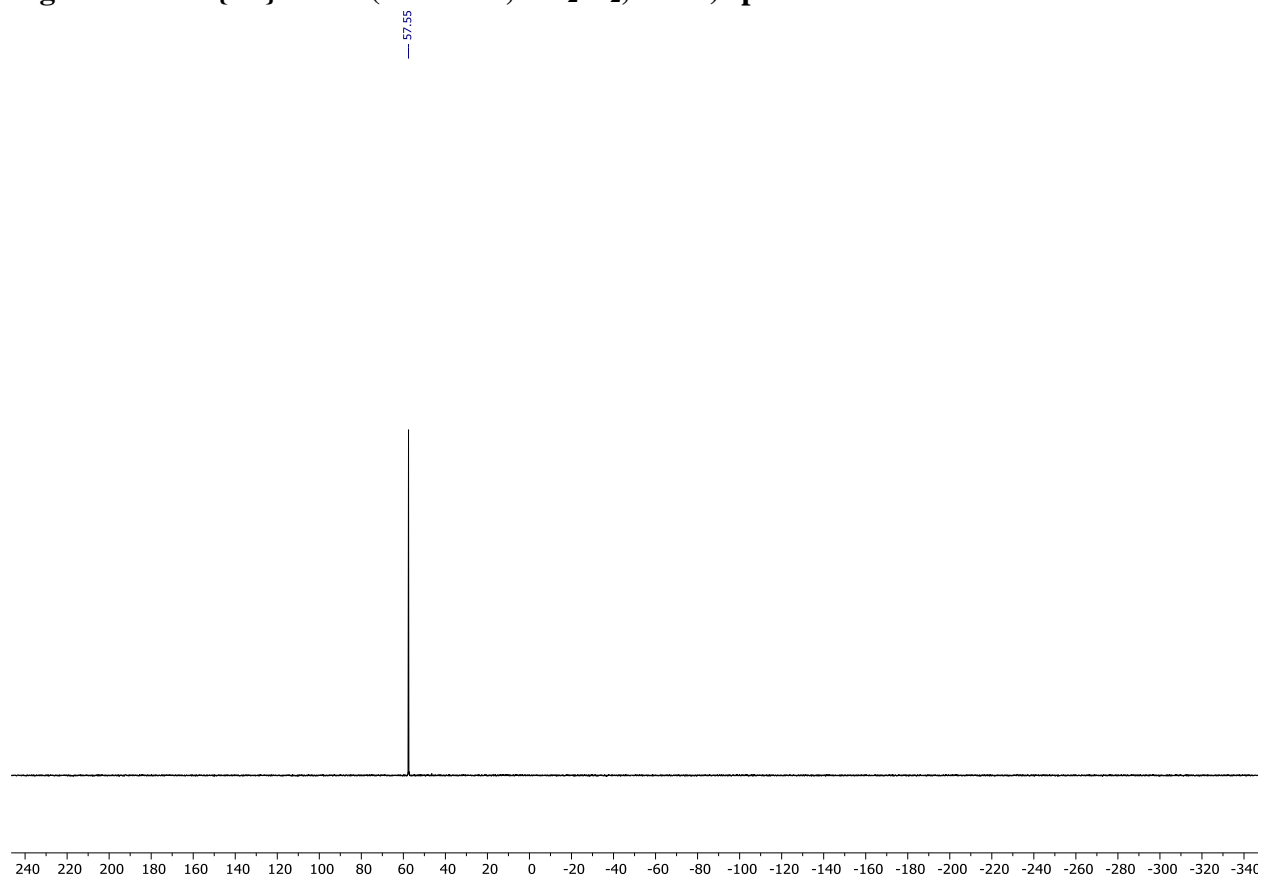


Figure S18.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of 4.

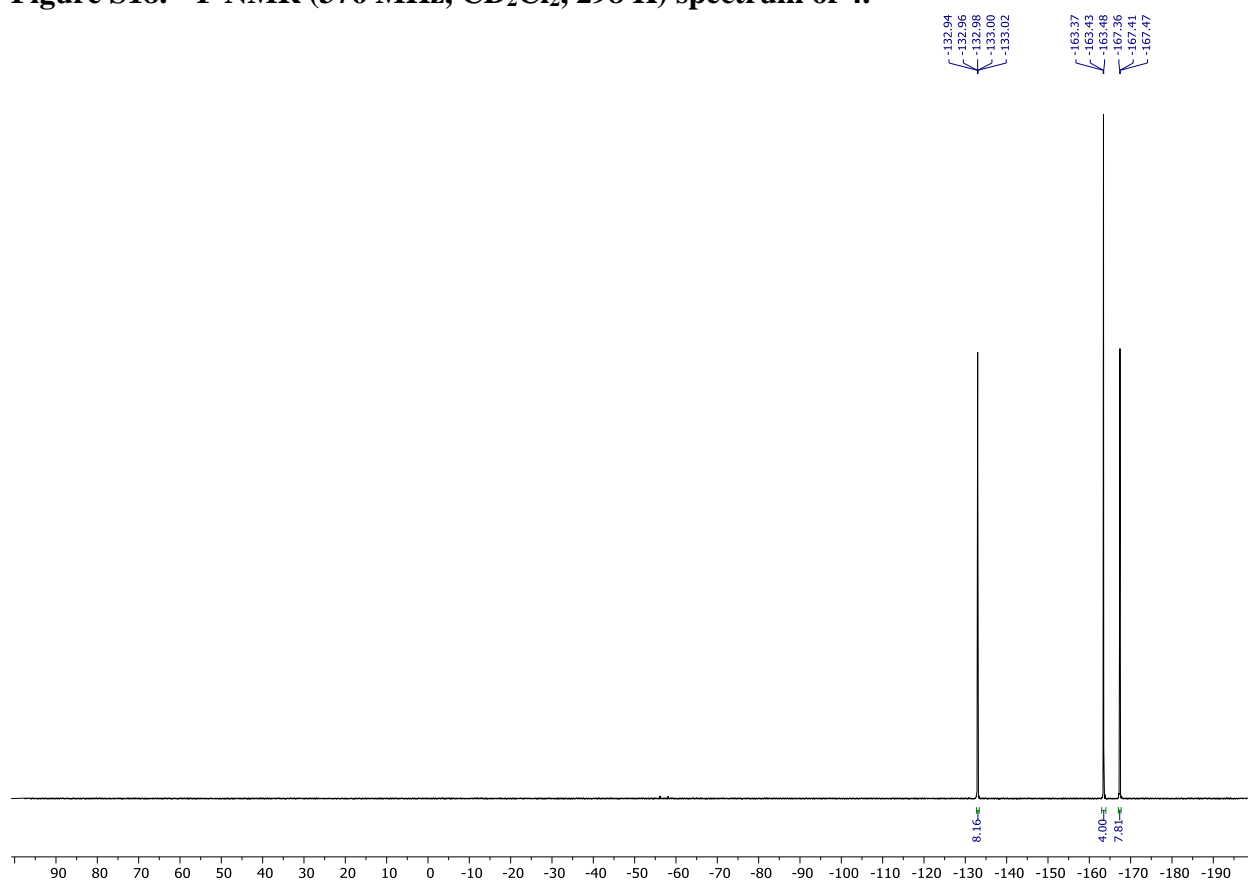
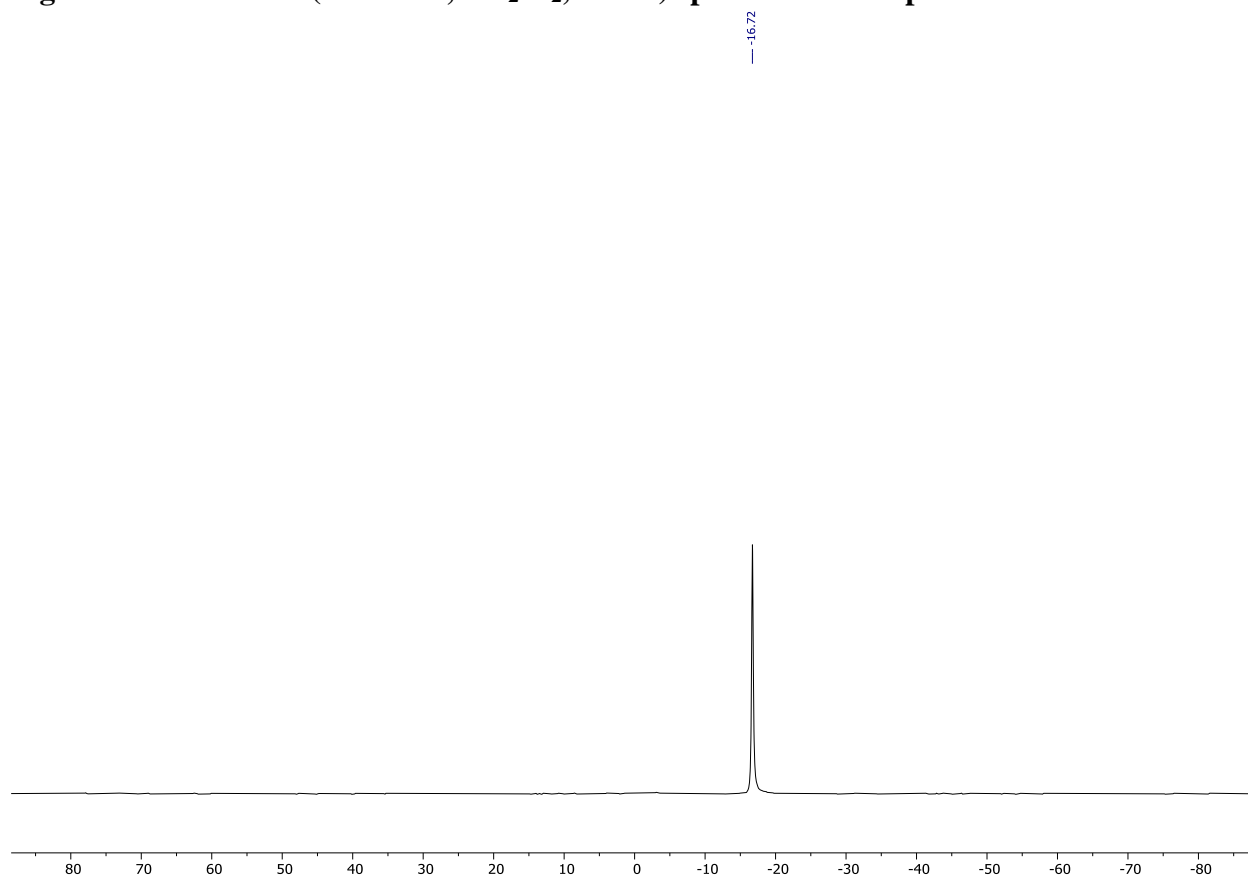


Figure S19.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound 4.



# NMR spectra for $[(C_6H_4)(PPh_2NMe_2)_2][Cl]_2$ (5)

Figure S20.  $^1H$  NMR (500 MHz,  $CD_2Cl_2$ , 298 K) spectrum of 5.

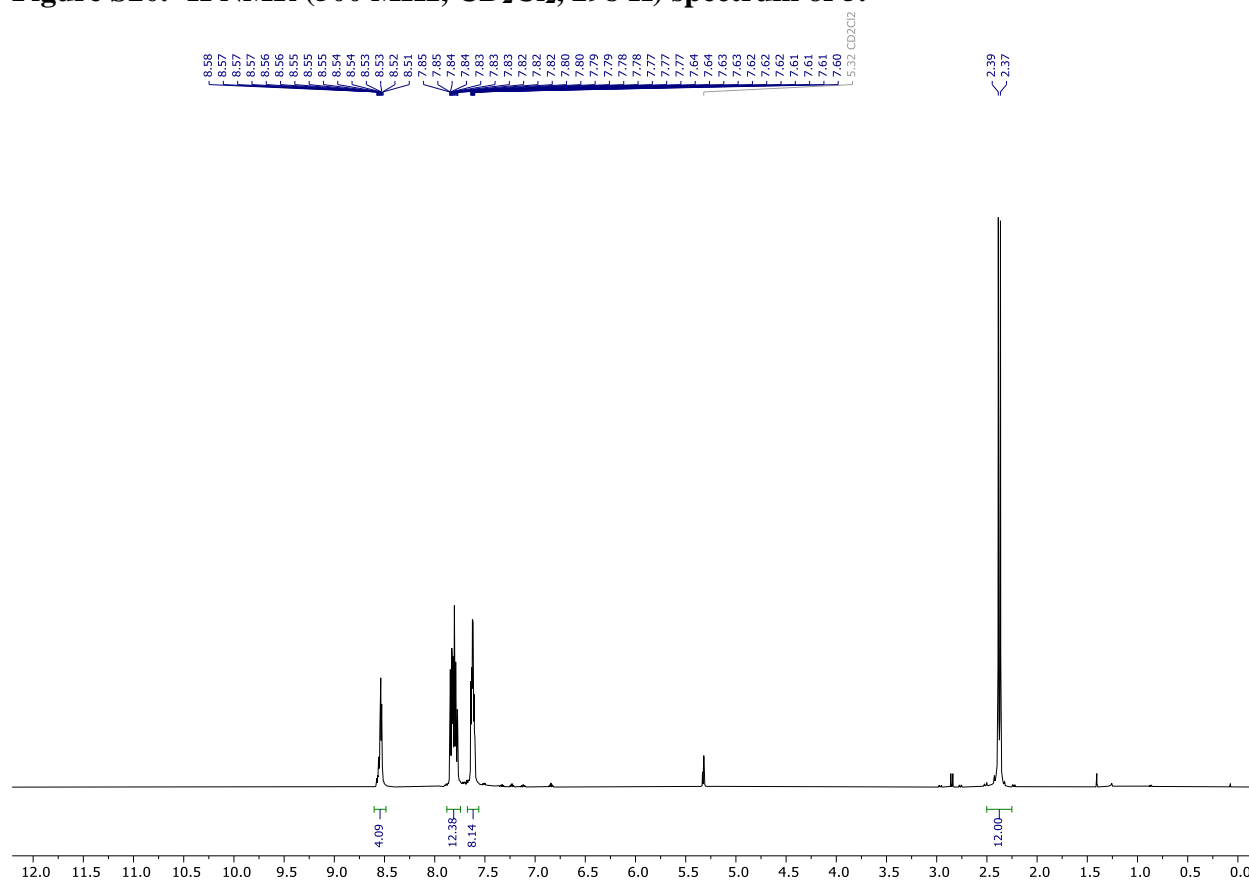


Figure S21.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of 5.

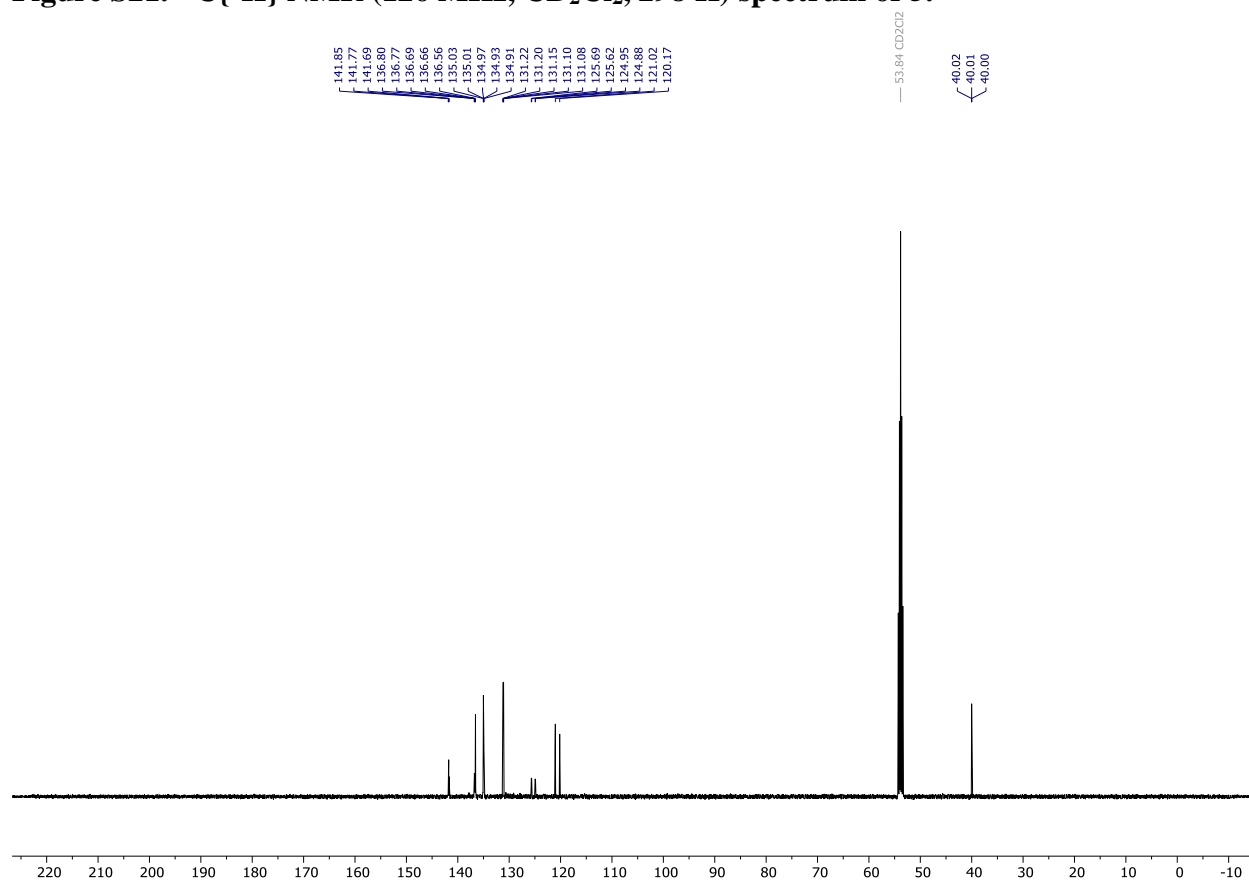
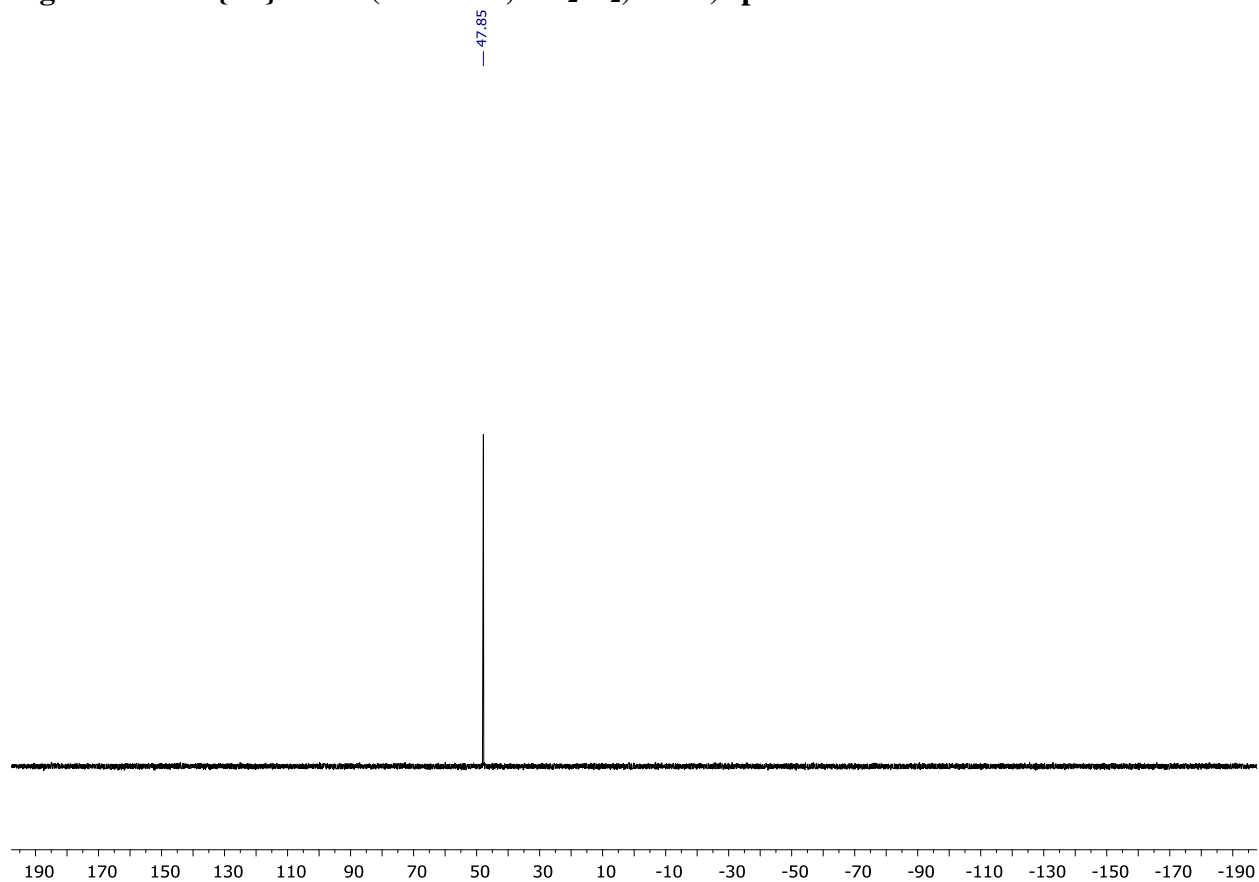


Figure S22.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of 5.





# NMR spectra for $[(C_6H_4)(PPh_2)_2(\mu-N)[Cl]]$ (**6**)

Figure S23.  $^1H$  NMR (500 MHz,  $CD_2Cl_2$ , 298 K) spectrum of **6**.

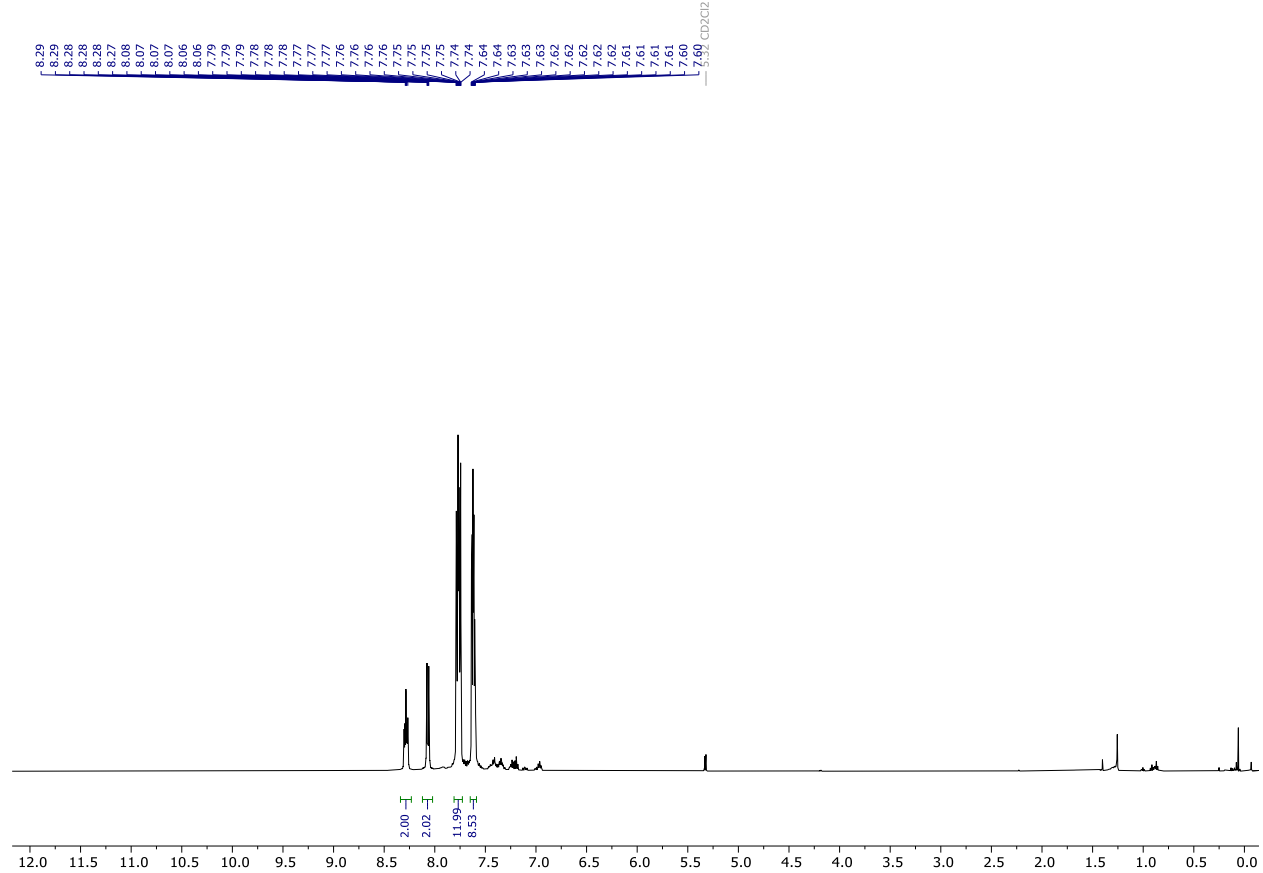


Figure S24.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **6**.

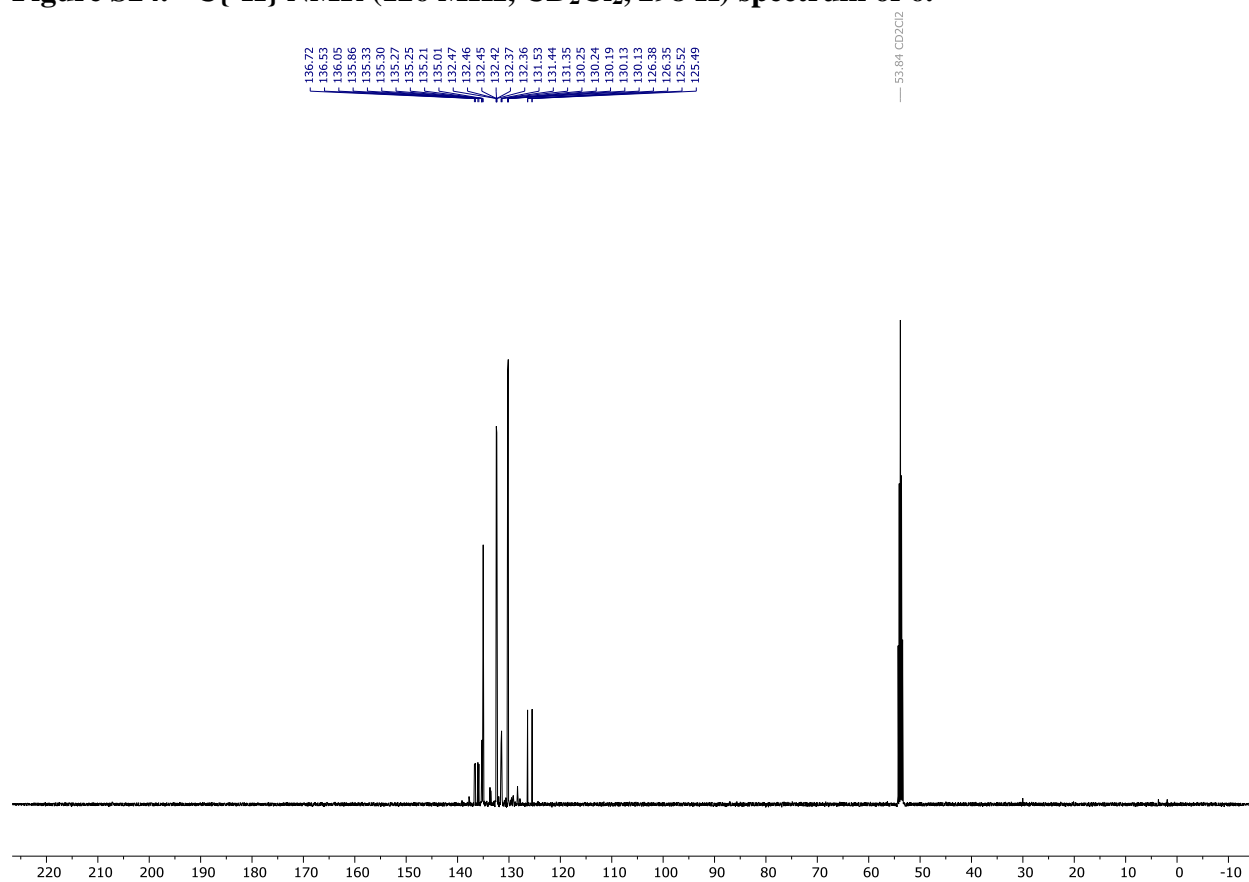
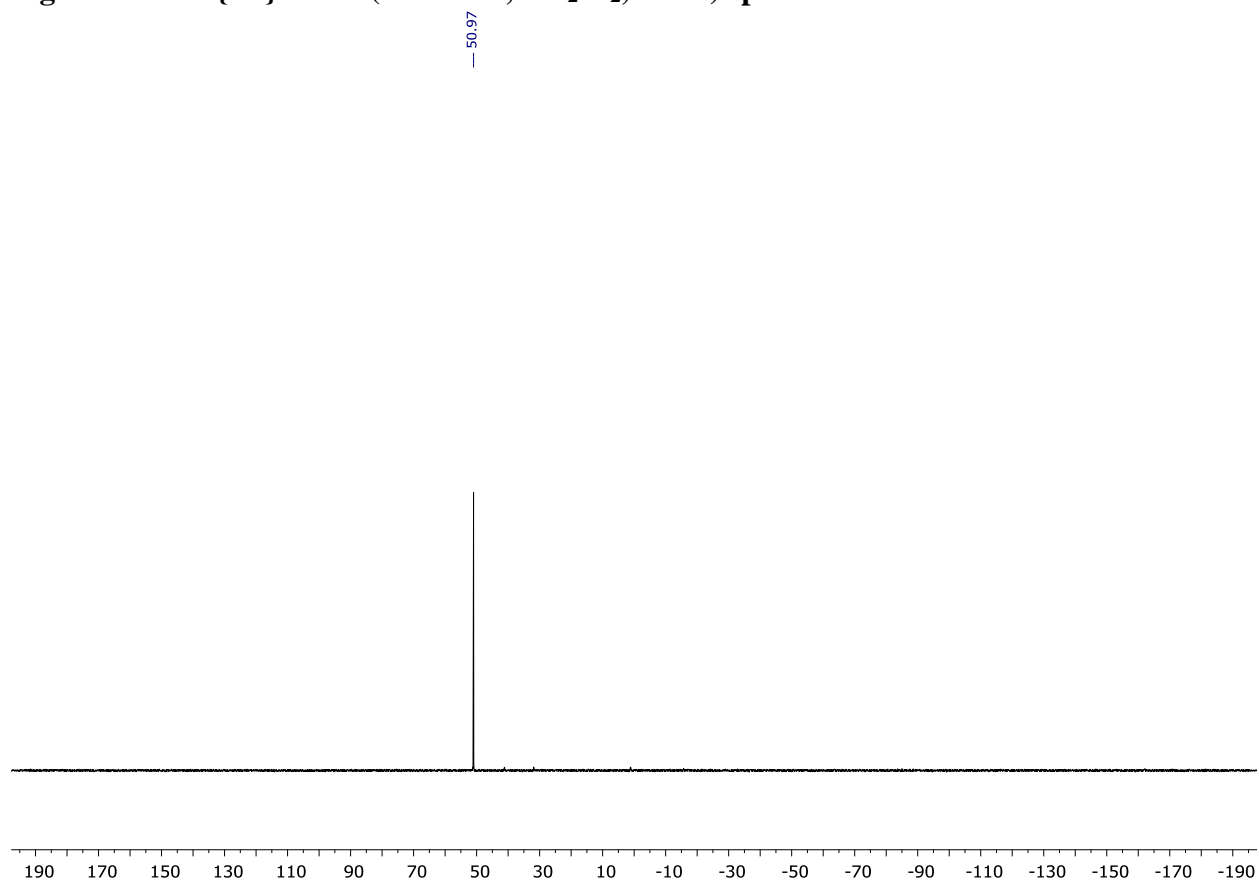


Figure S25.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of **6**.



## NMR spectra for the reaction of Compound 3 with $(\text{Me}_3\text{Si})_2\text{NMe}$

Figure S26. A)  $^1\text{H}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2$  of crude reaction mixture (A) and reaction mixture after exposure to high vacuum (B).

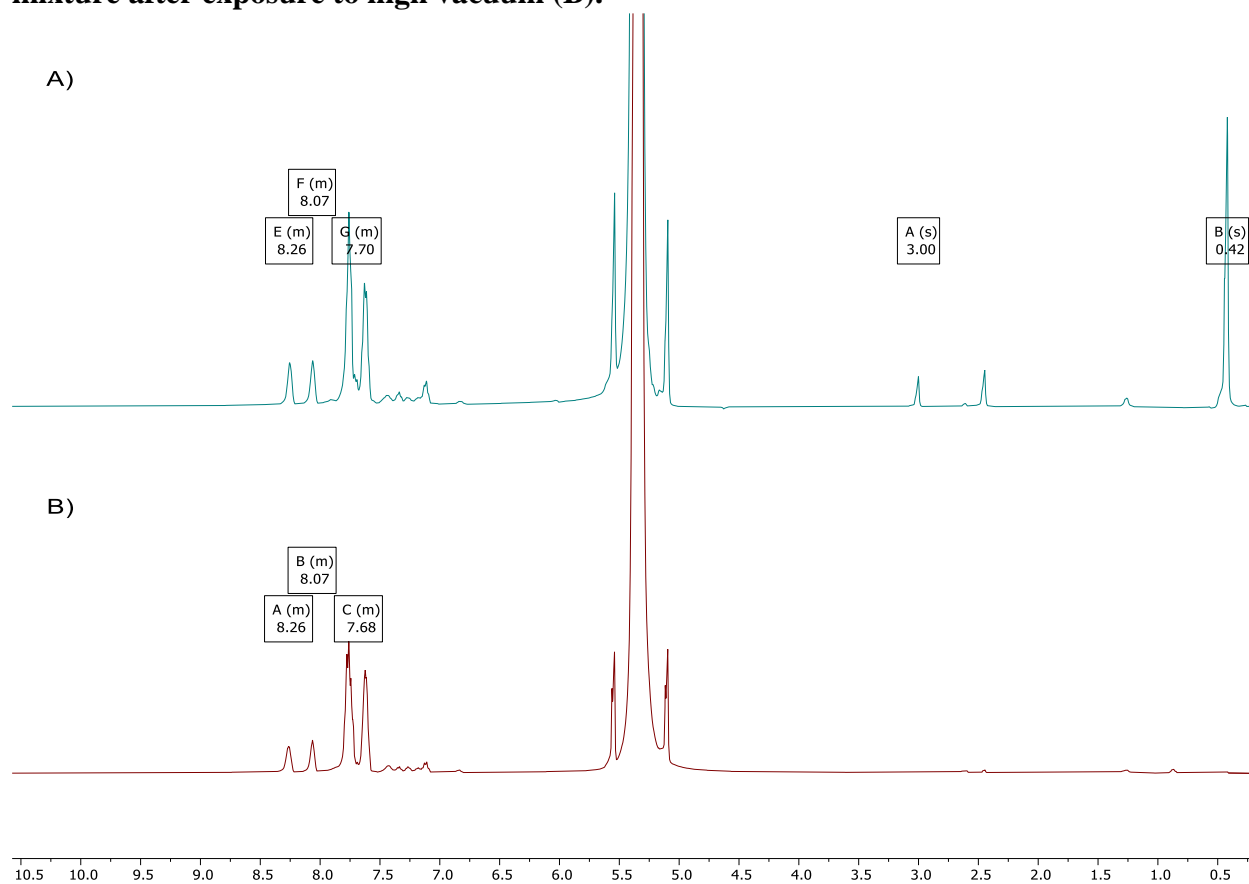
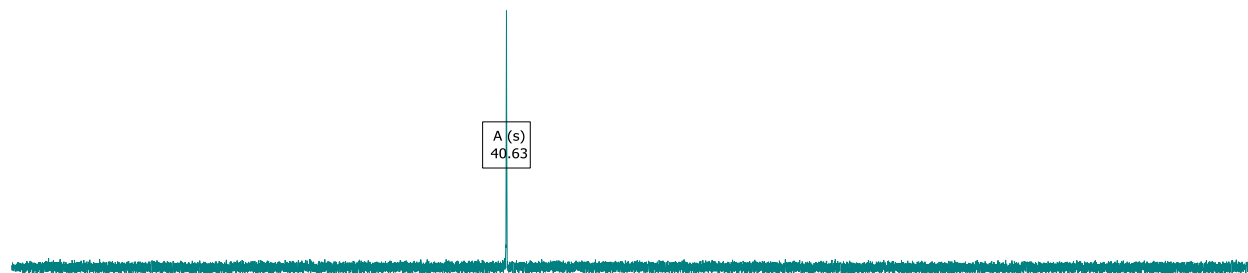
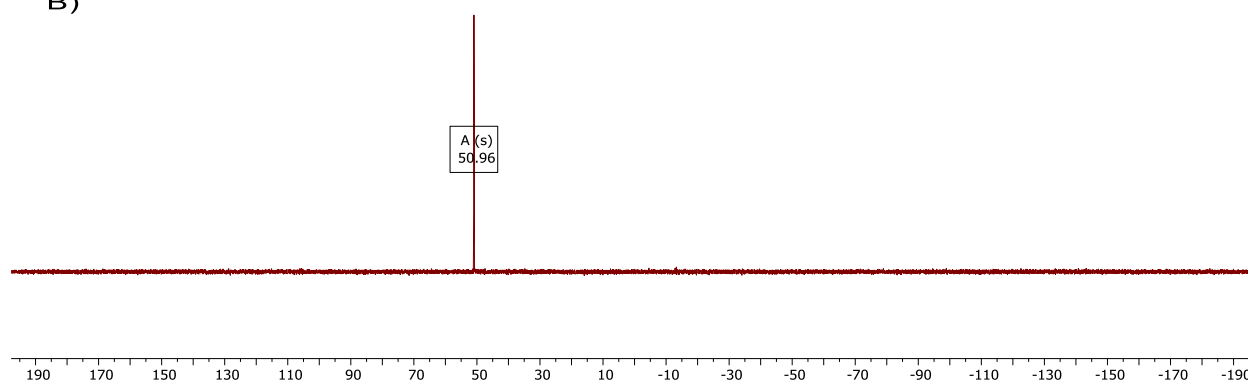


Figure S27.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2$  of 3 (A) and reaction mixture indicating formation of 6 (B).

A)



B)



## NMR spectra for the reaction of Compound 4 with [nBu<sub>4</sub>N][Cl]

Figure S28. A) <sup>1</sup>H NMR spectrum in CH<sub>2</sub>Cl<sub>2</sub> of crude reaction mixture (A) and reaction mixture after exposure to high vacuum (B).

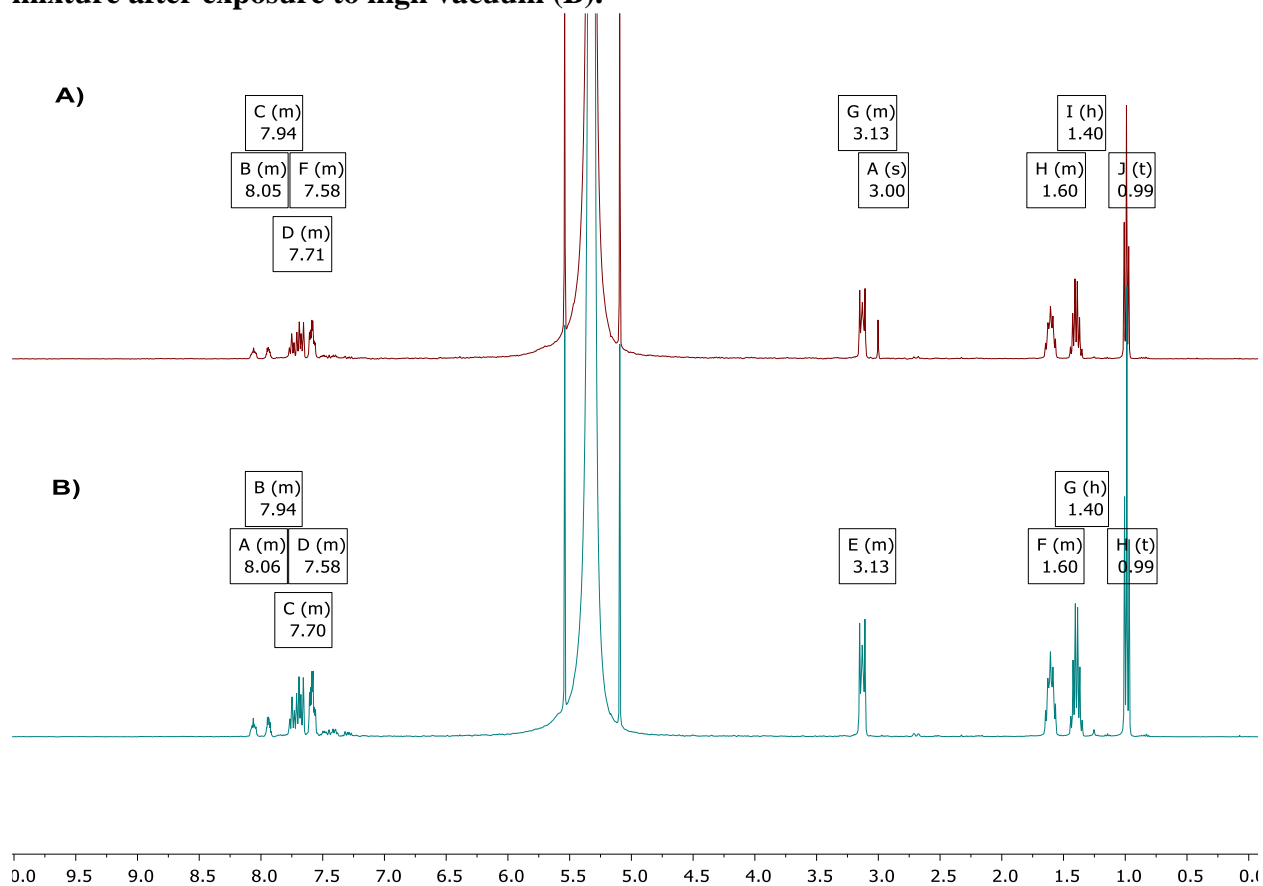
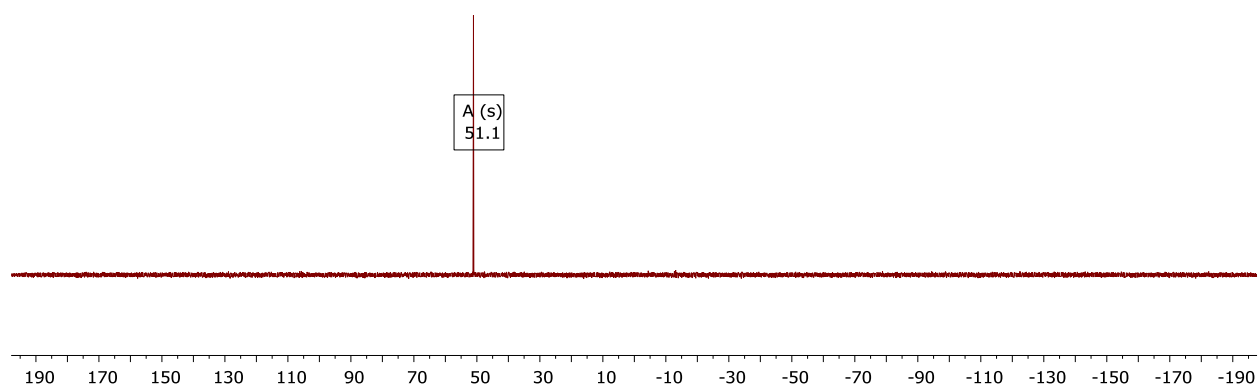


Figure S29.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2$  of **4** (A) and reaction mixture indicating formation of **6'** (B).

A)



B)



# NMR spectra for $[(\text{CH}_2\text{PPh}_2)_2\text{NMe}][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (**8**)

Figure S30.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **8**.

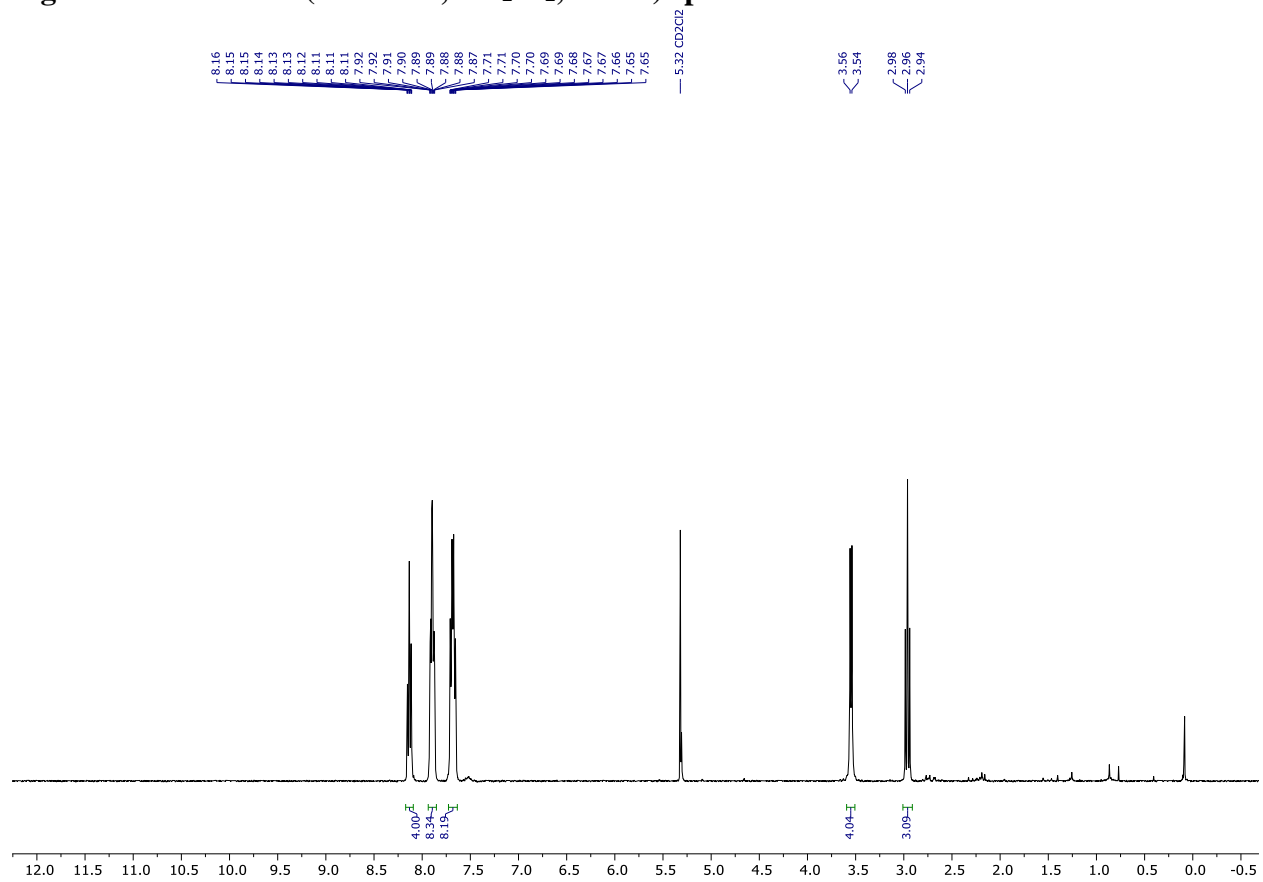




Figure S31.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **8**.

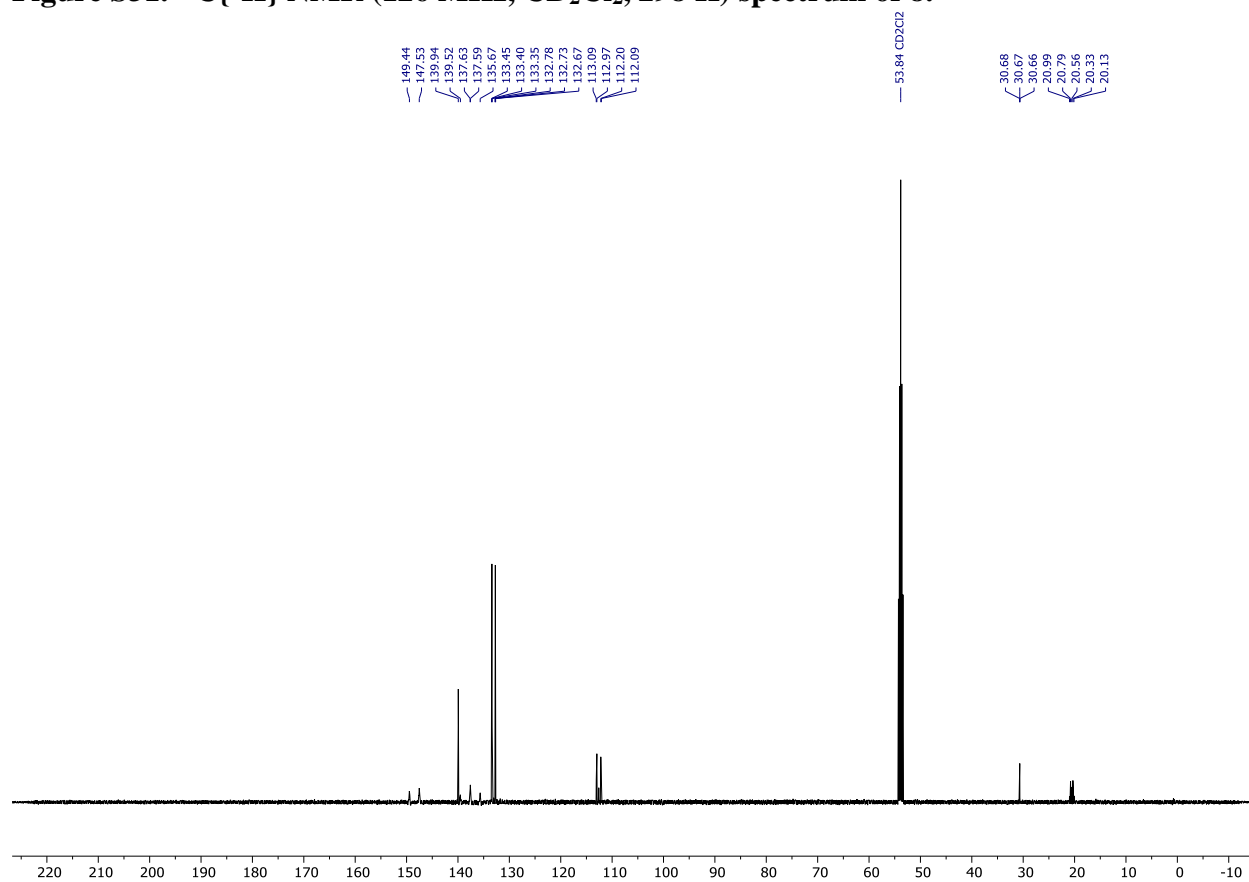


Figure S32.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of **8**.

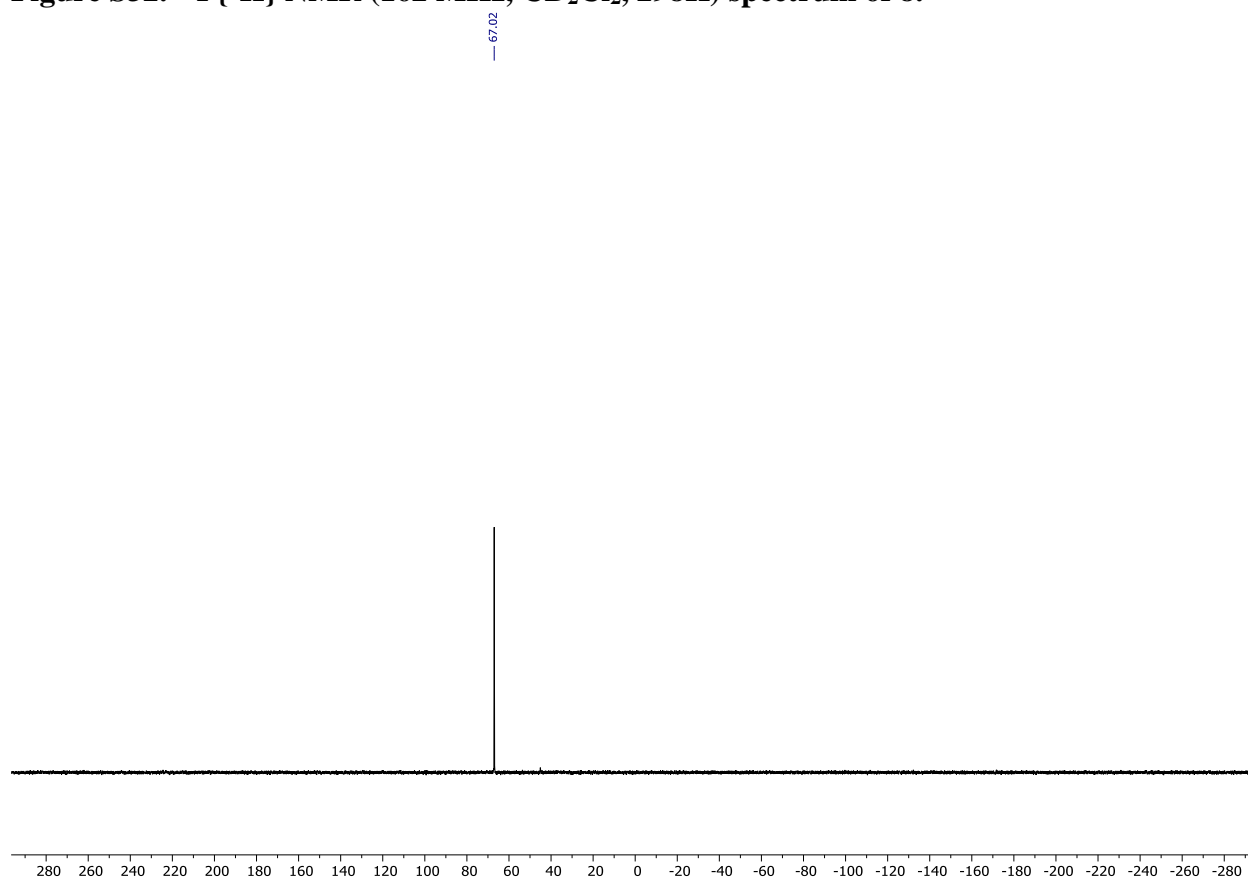


Figure S33.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **8**.

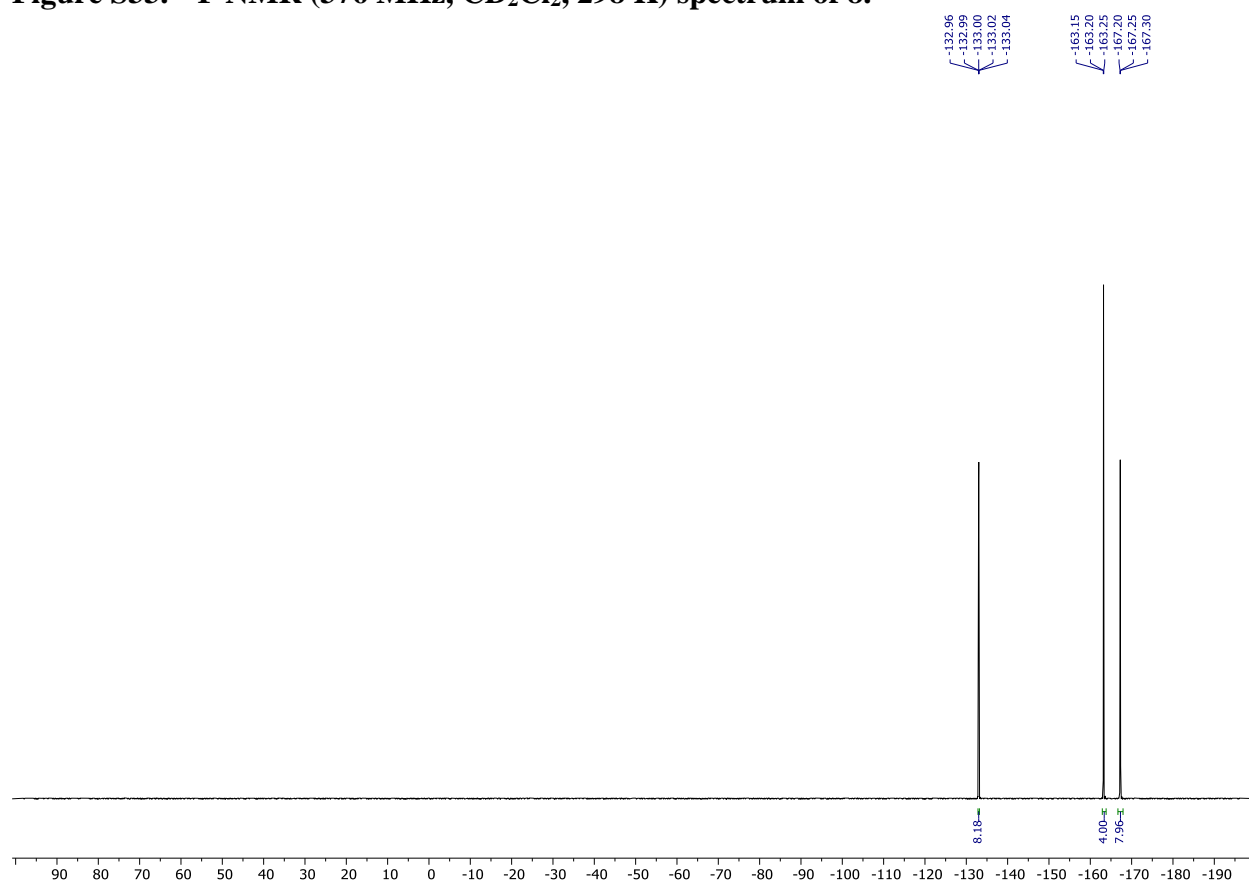
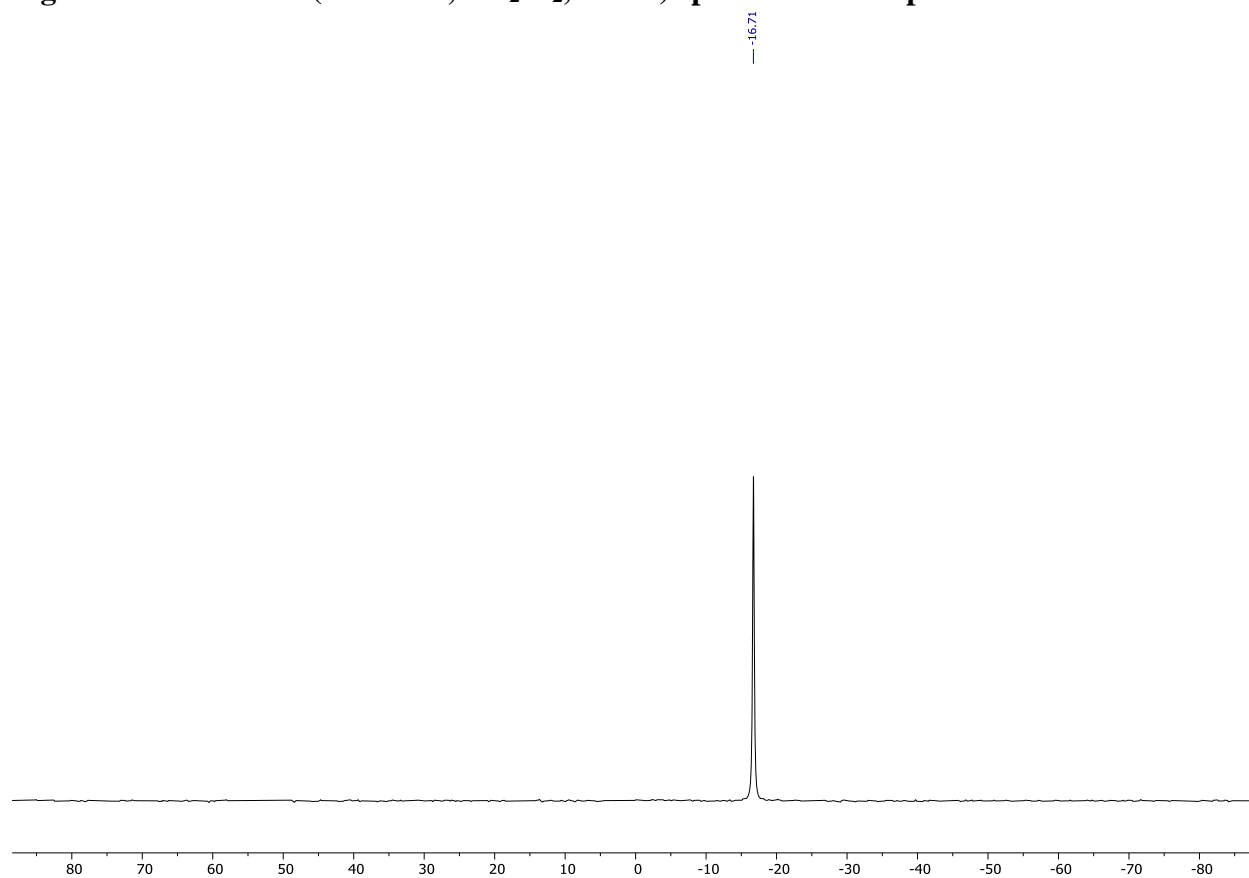


Figure S34.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound 8.



NMR spectra for  $[(\text{CH}_2\text{PPh}_2)_2\text{NCH}_2\text{CHCH}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$  (**9**)

Figure S35.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **9**.

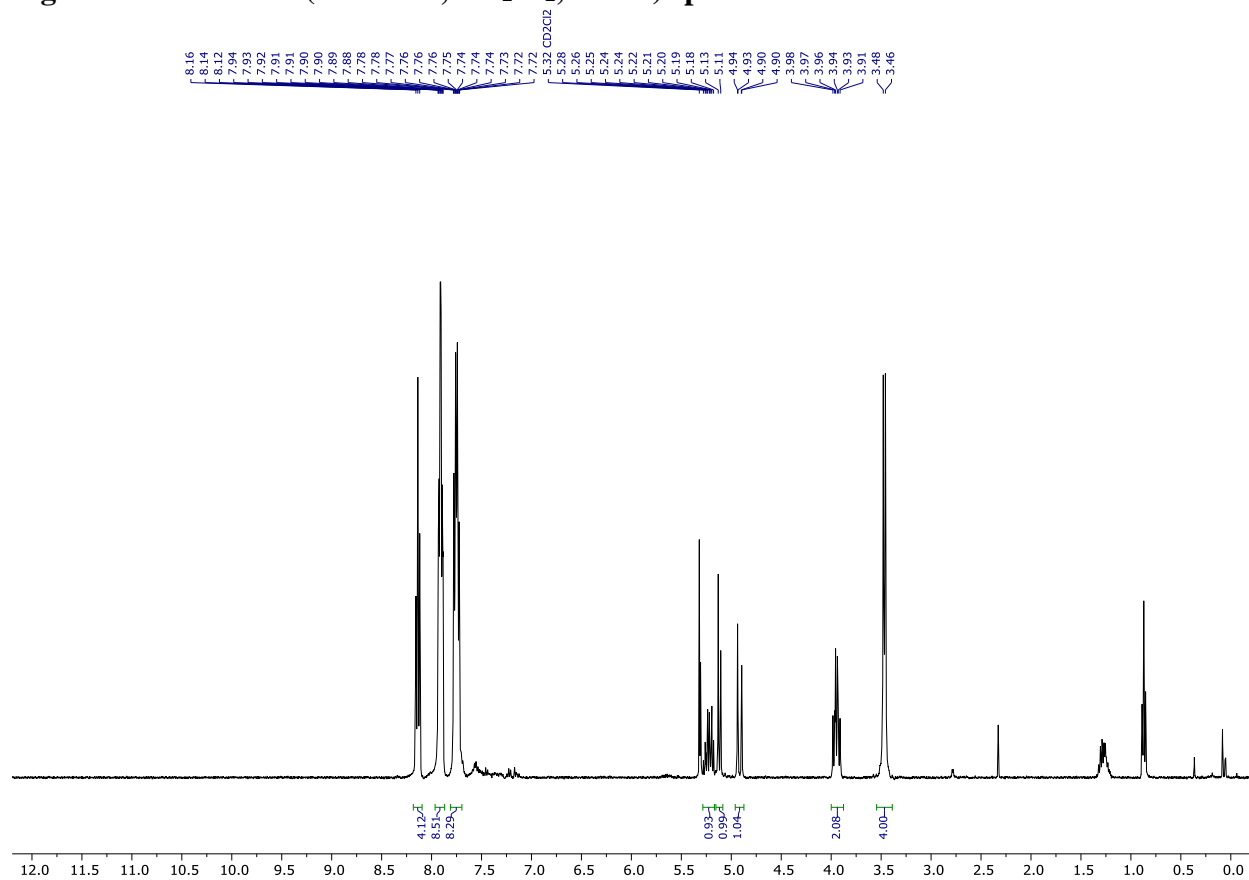


Figure S36.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **9**.

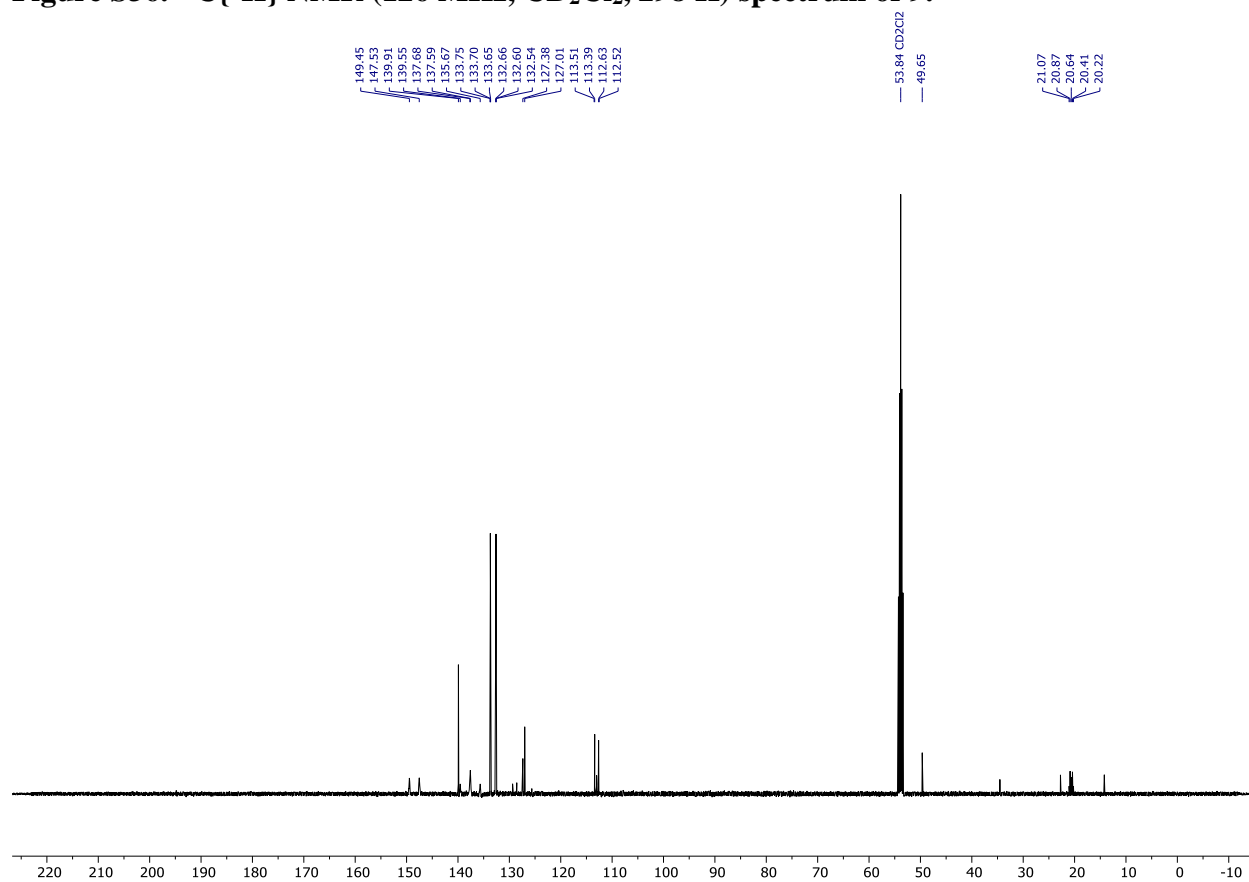


Figure S37.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of **9**.

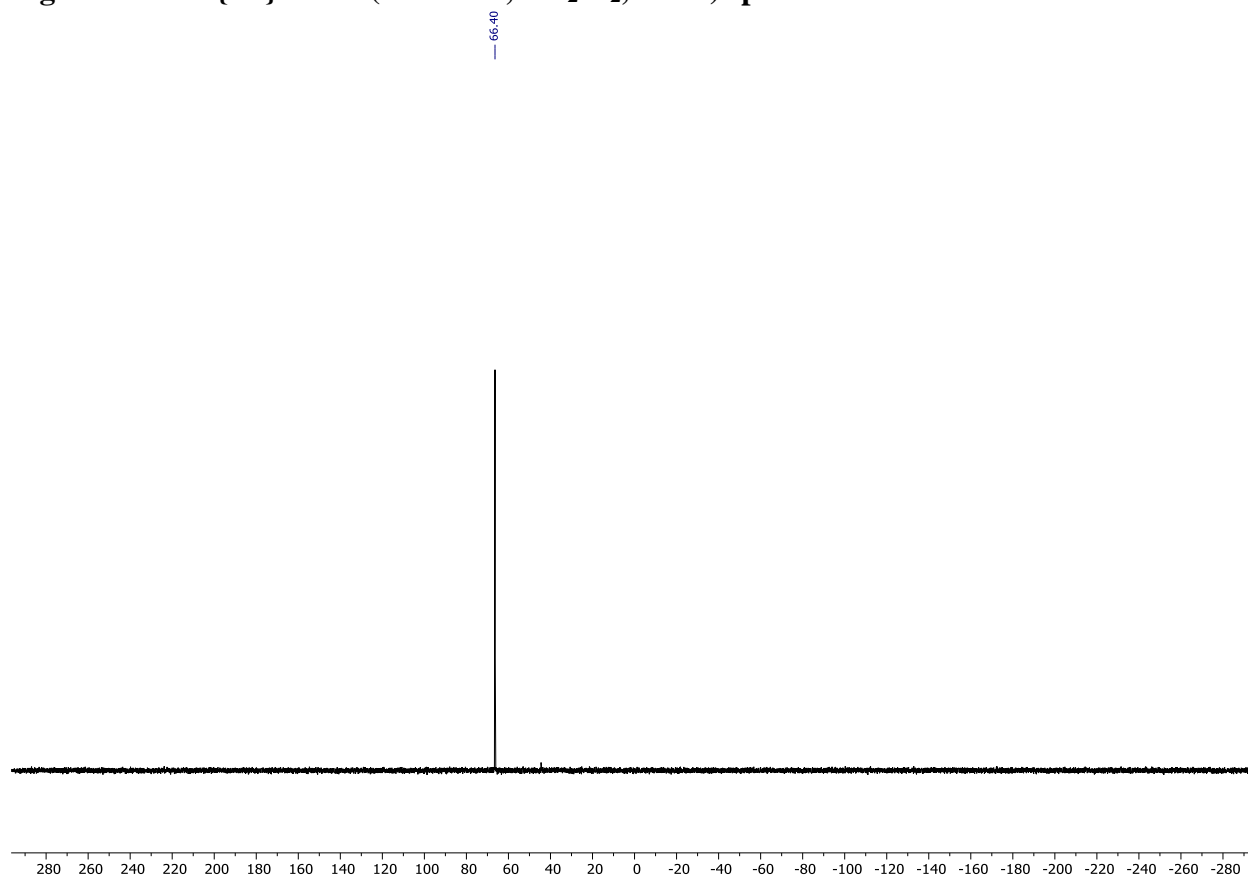


Figure S38.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of 9.

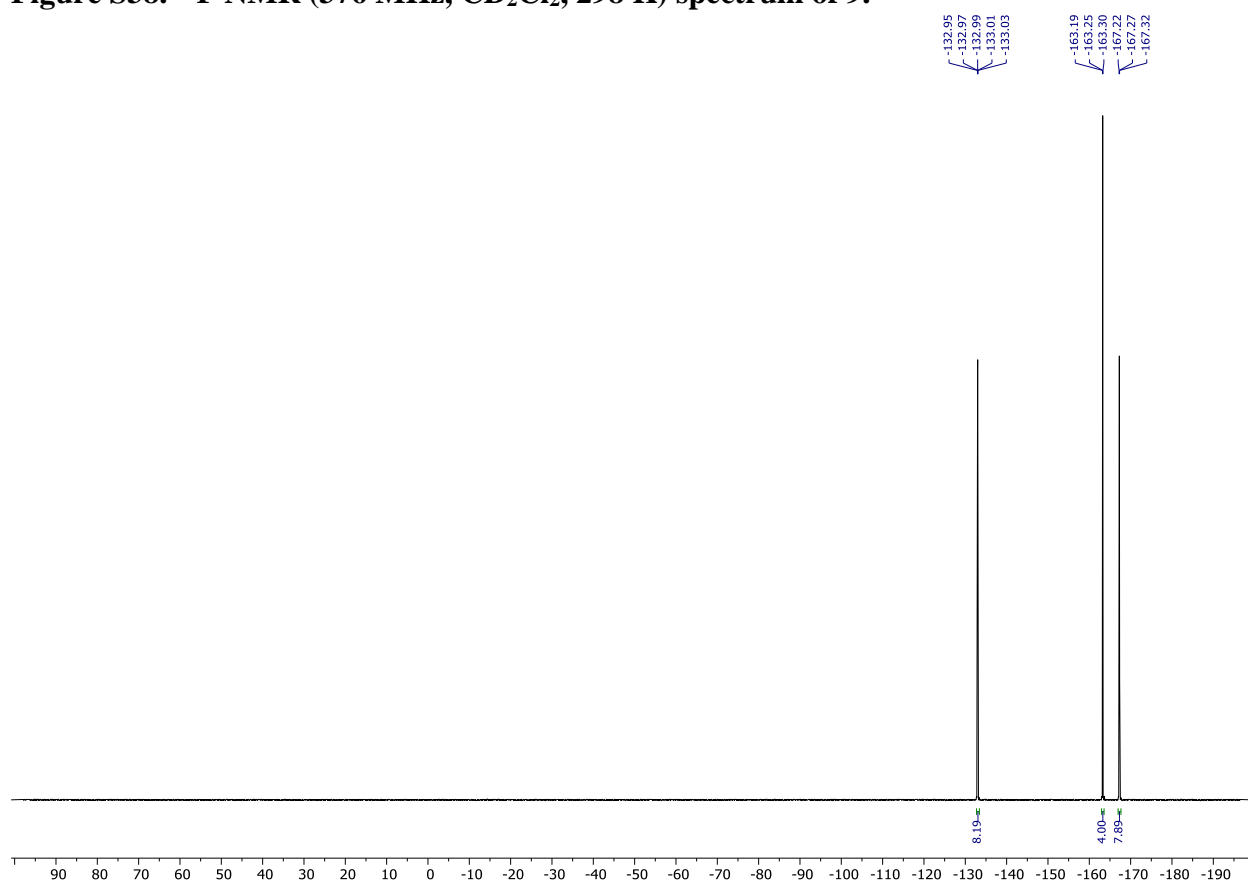
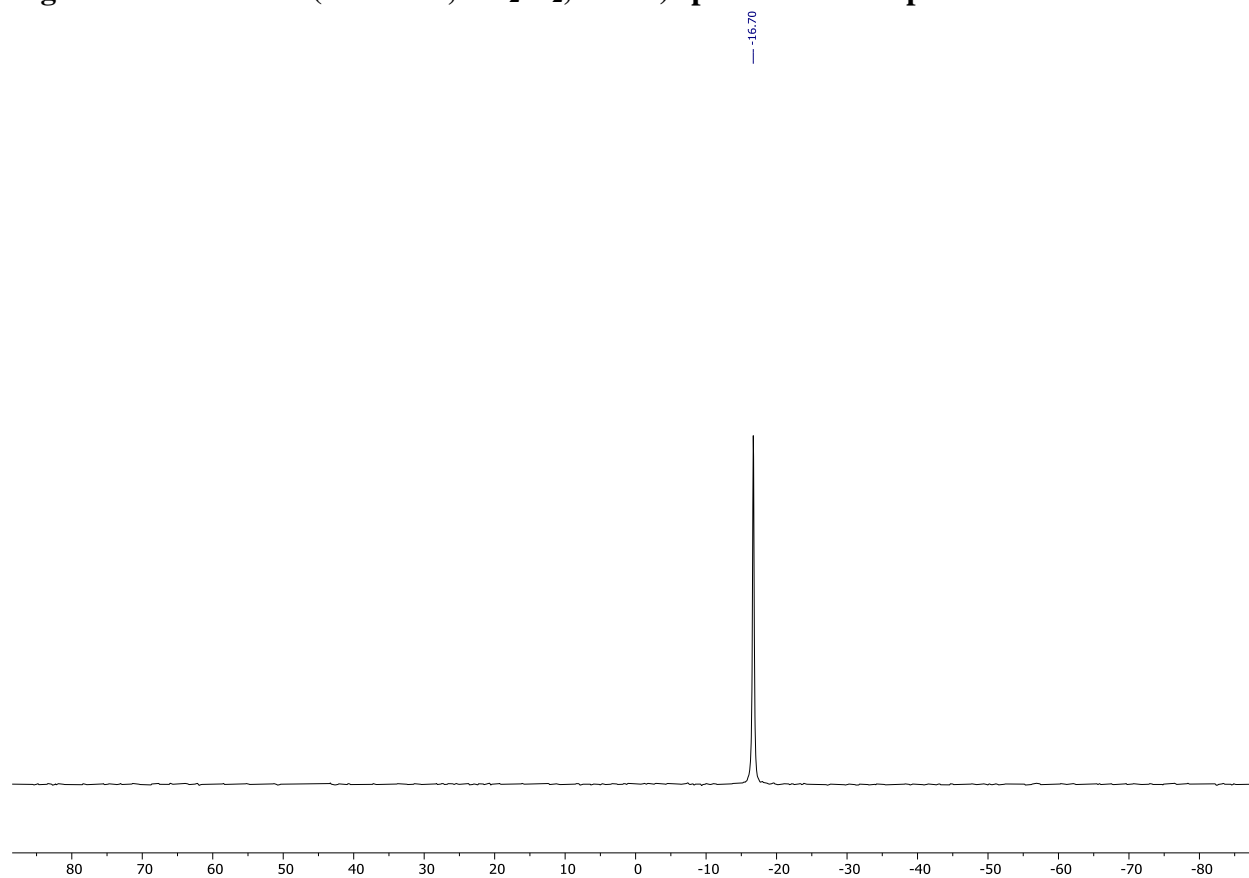




Figure S39.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound 9.



# NMR spectra for $[(\text{CH}_2\text{PPh}_2)_2\text{NCH}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (**10**)

Figure S40.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of **10**.

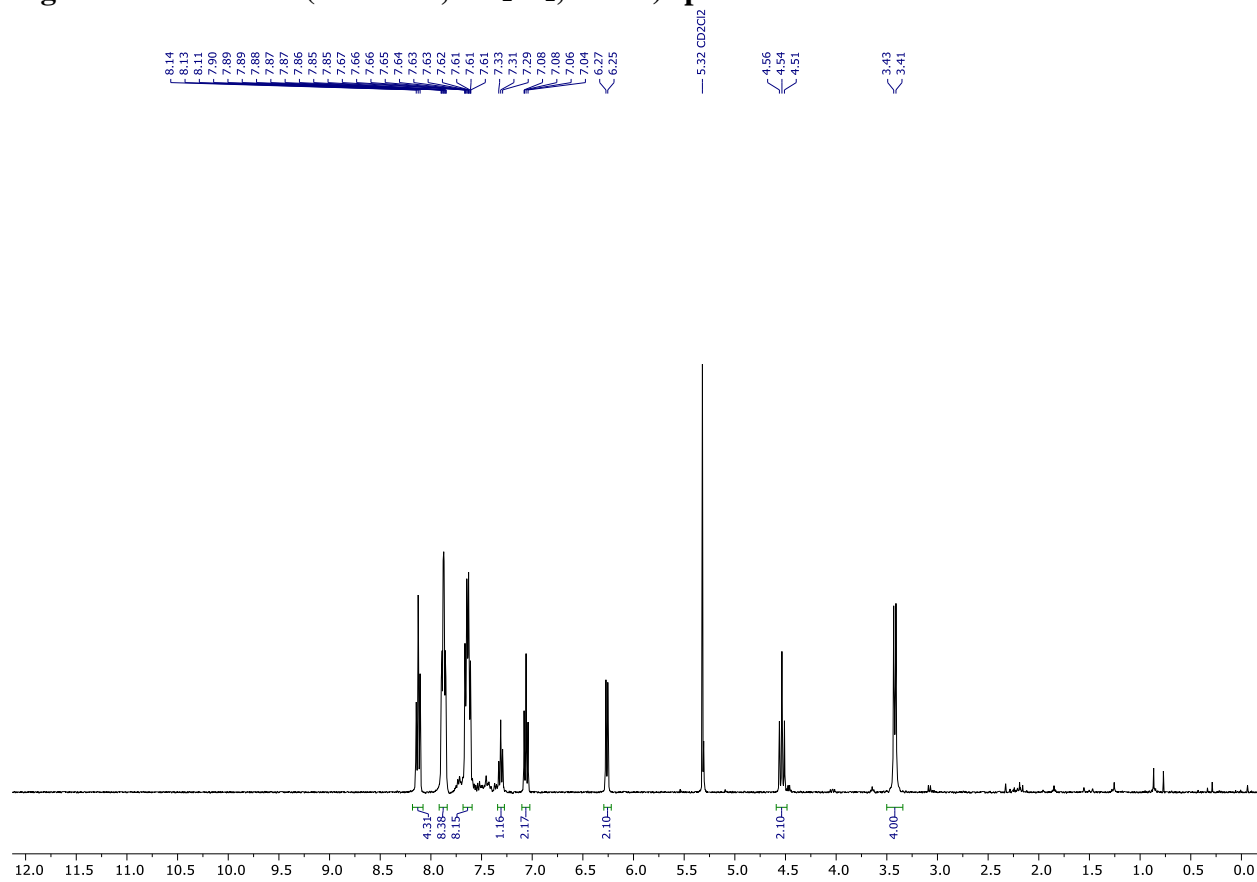


Figure S41.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of 10.

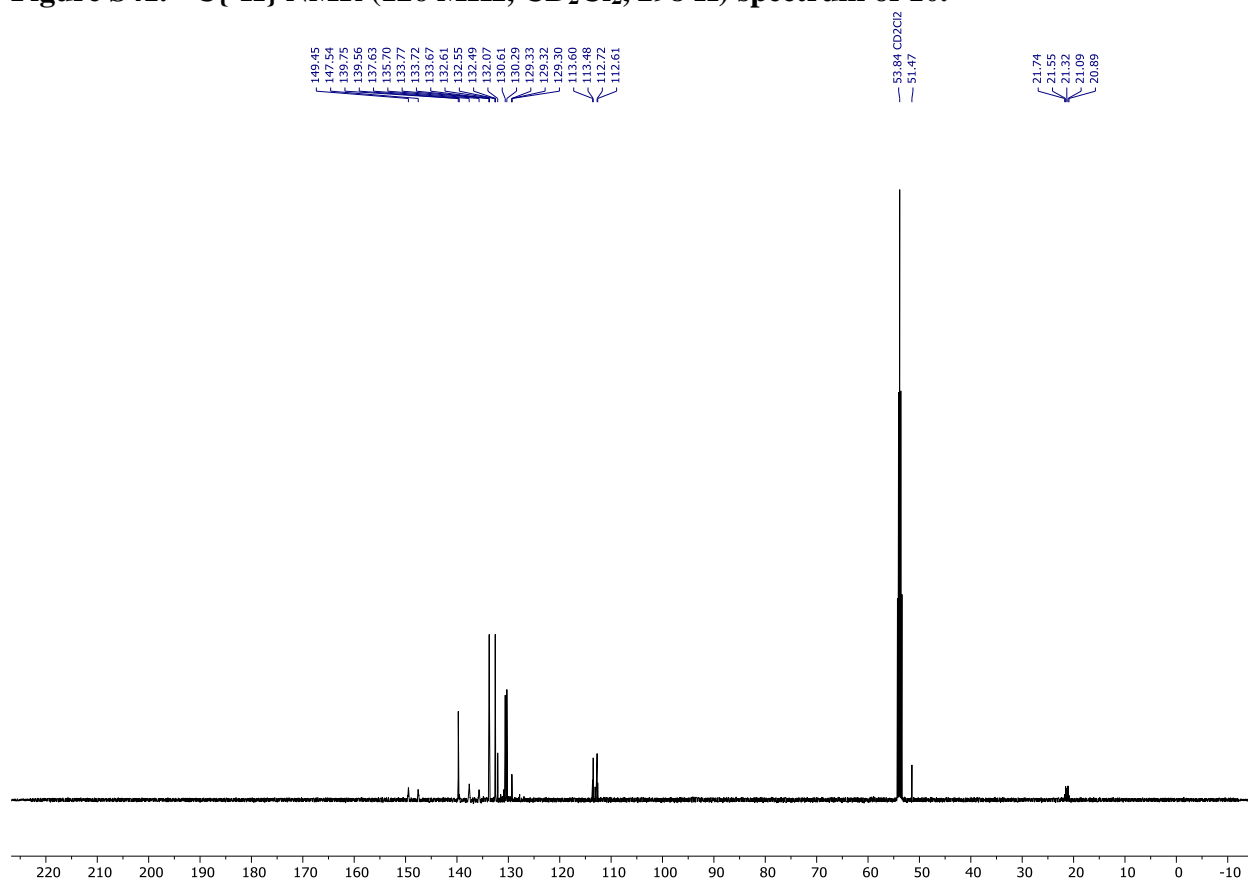


Figure S42.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K) spectrum of 10.

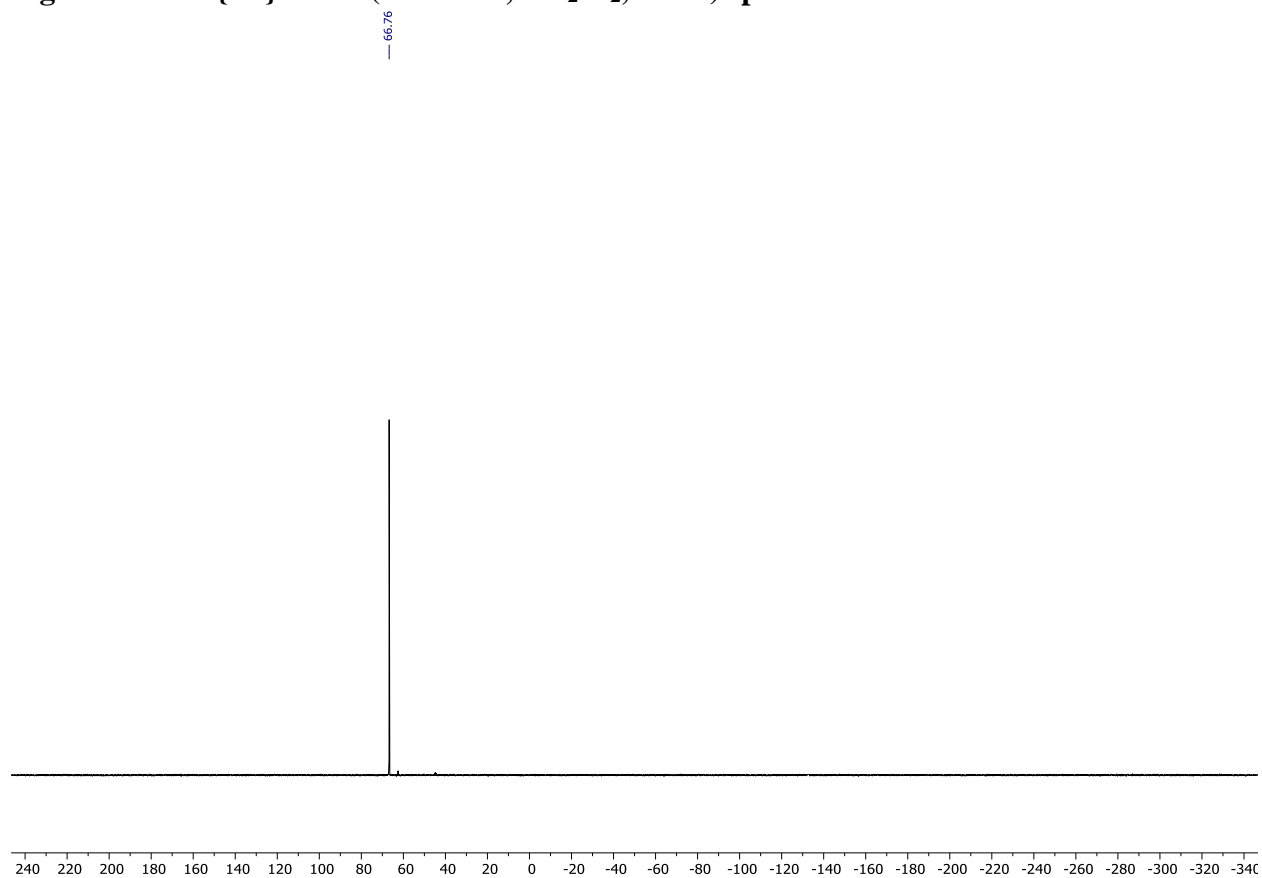


Figure S43.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of 10.

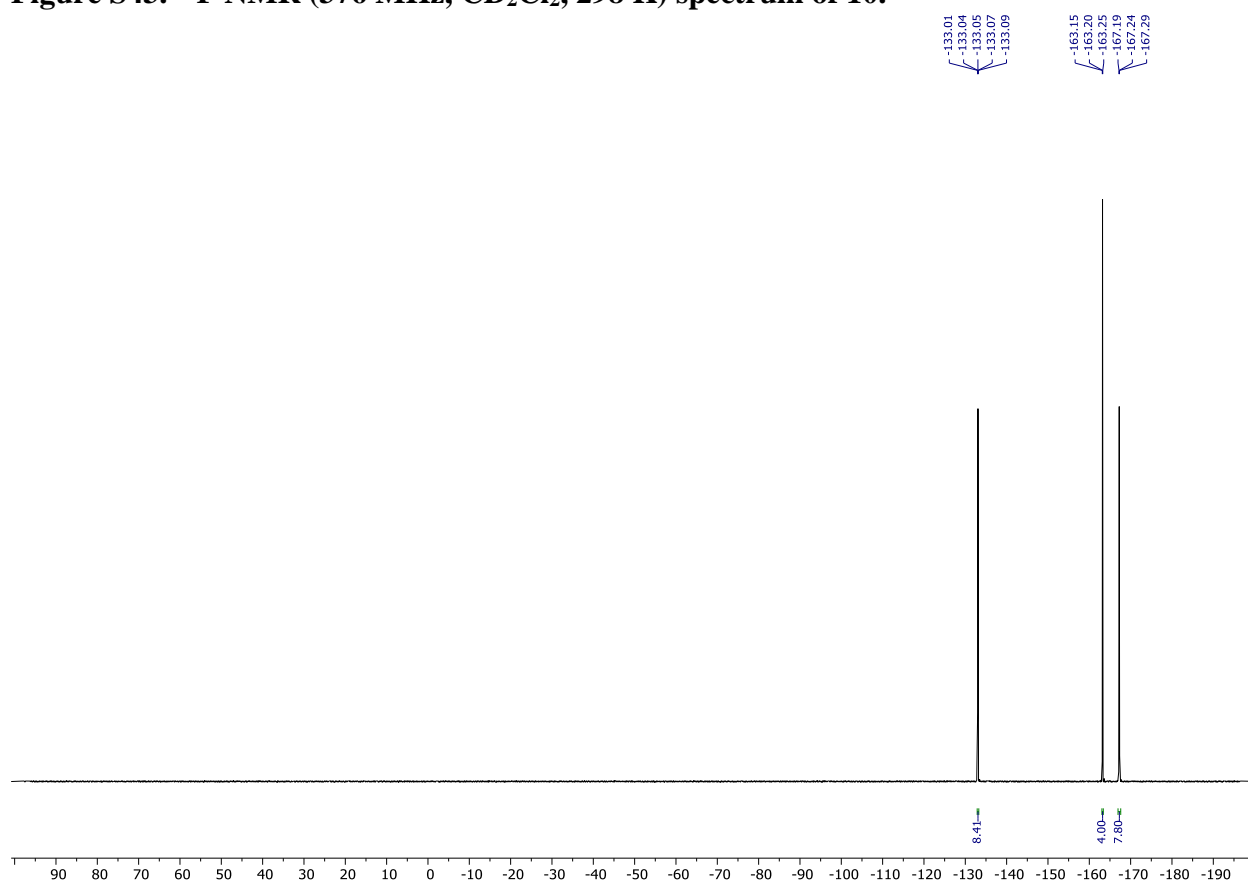
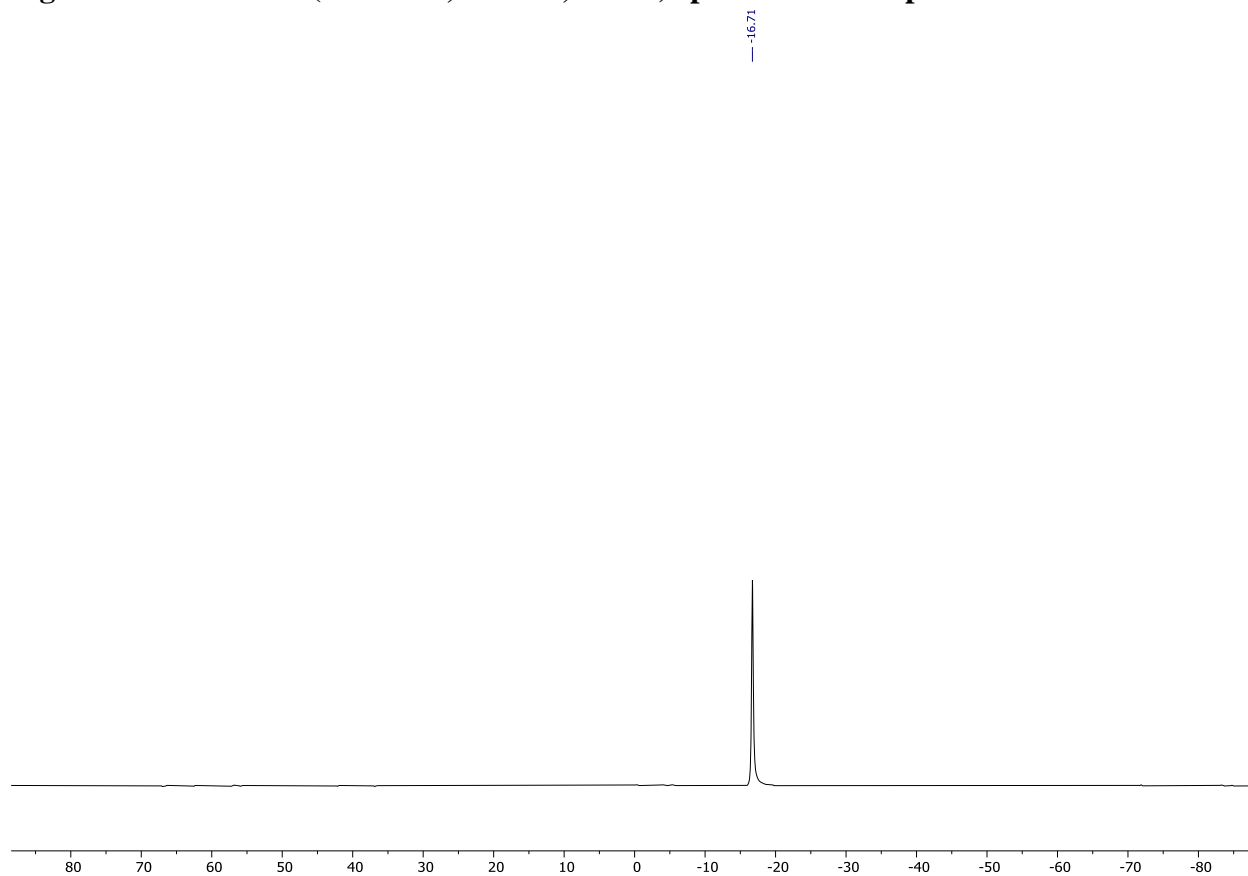
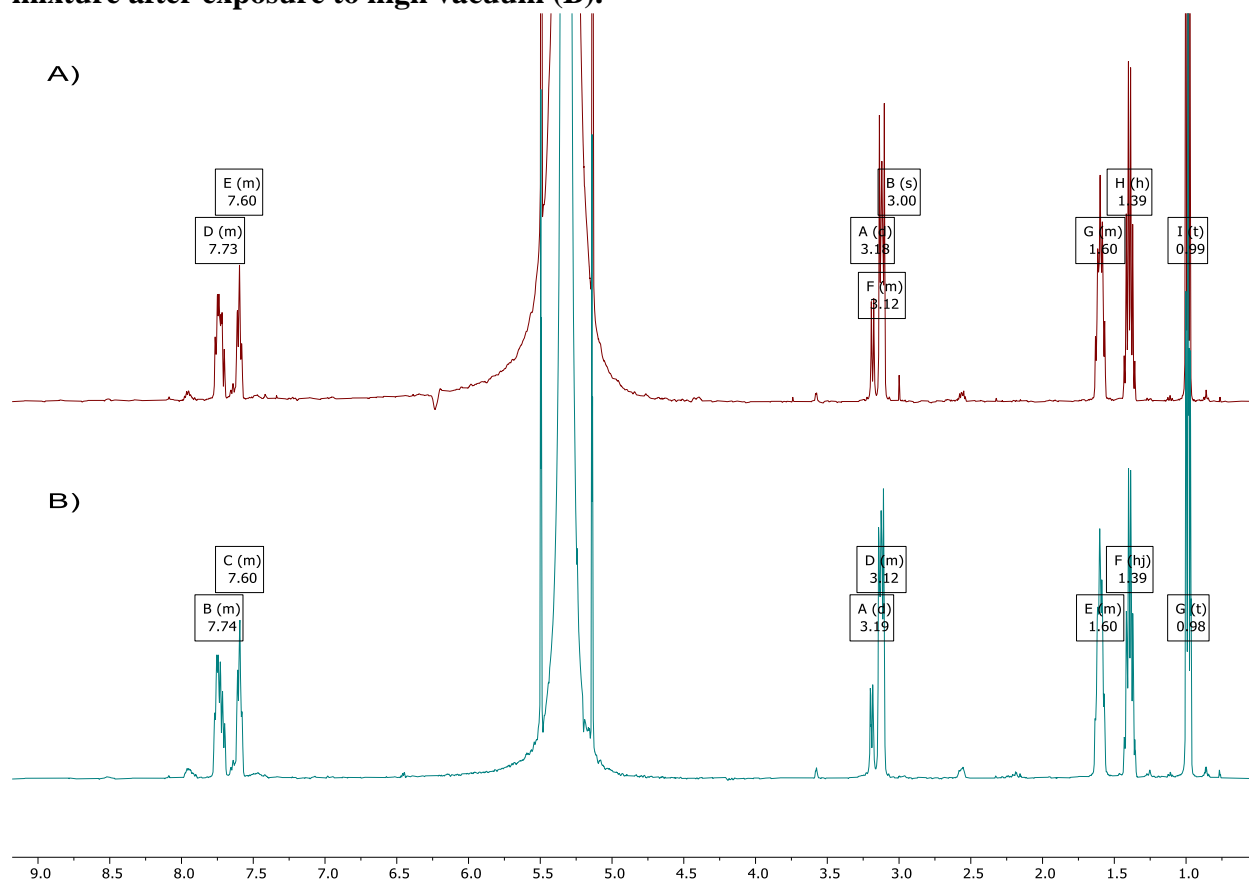


Figure S44.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound 10.



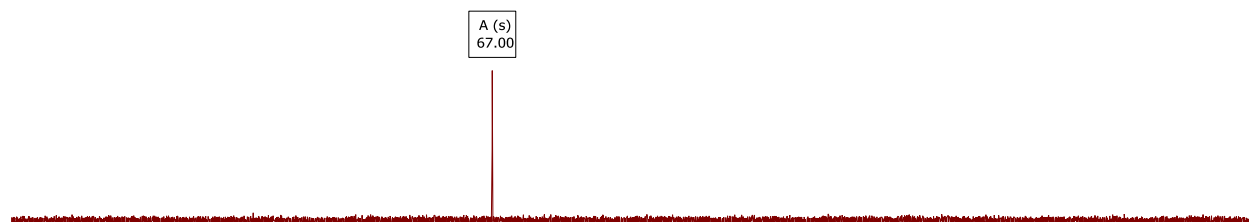
## NMR spectra for the reaction of 8 with [nBu<sub>4</sub>N][Cl]

Figure S45. A) <sup>1</sup>H NMR spectrum in CH<sub>2</sub>Cl<sub>2</sub> of crude reaction mixture (A) and reaction mixture after exposure to high vacuum (B).

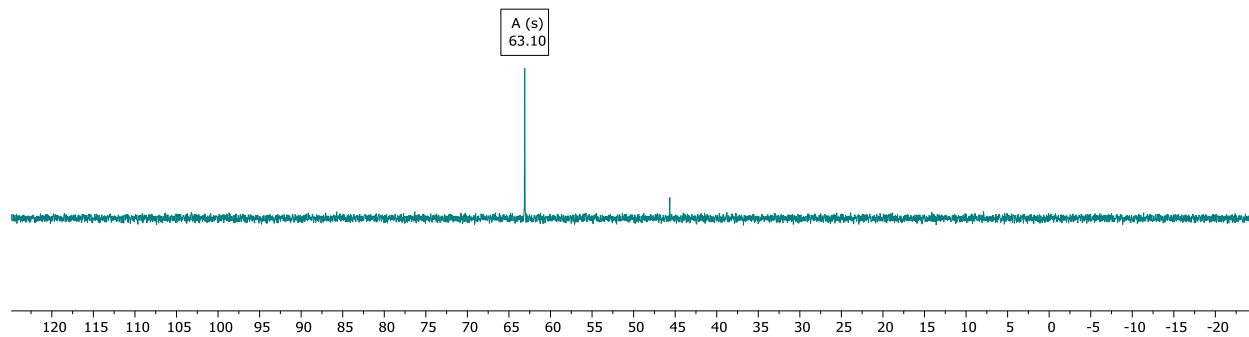


**Figure S46.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2$  of 8 (A) and reaction mixture indicating formation of 11 (B).**

A)



B)





## NMR spectra for the reaction of 9 with [nBu<sub>4</sub>N][Cl]

Figure S47. A) <sup>1</sup>H NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> of crude reaction mixture (A) and reaction mixture spiked with C<sub>3</sub>H<sub>5</sub>Cl (B).

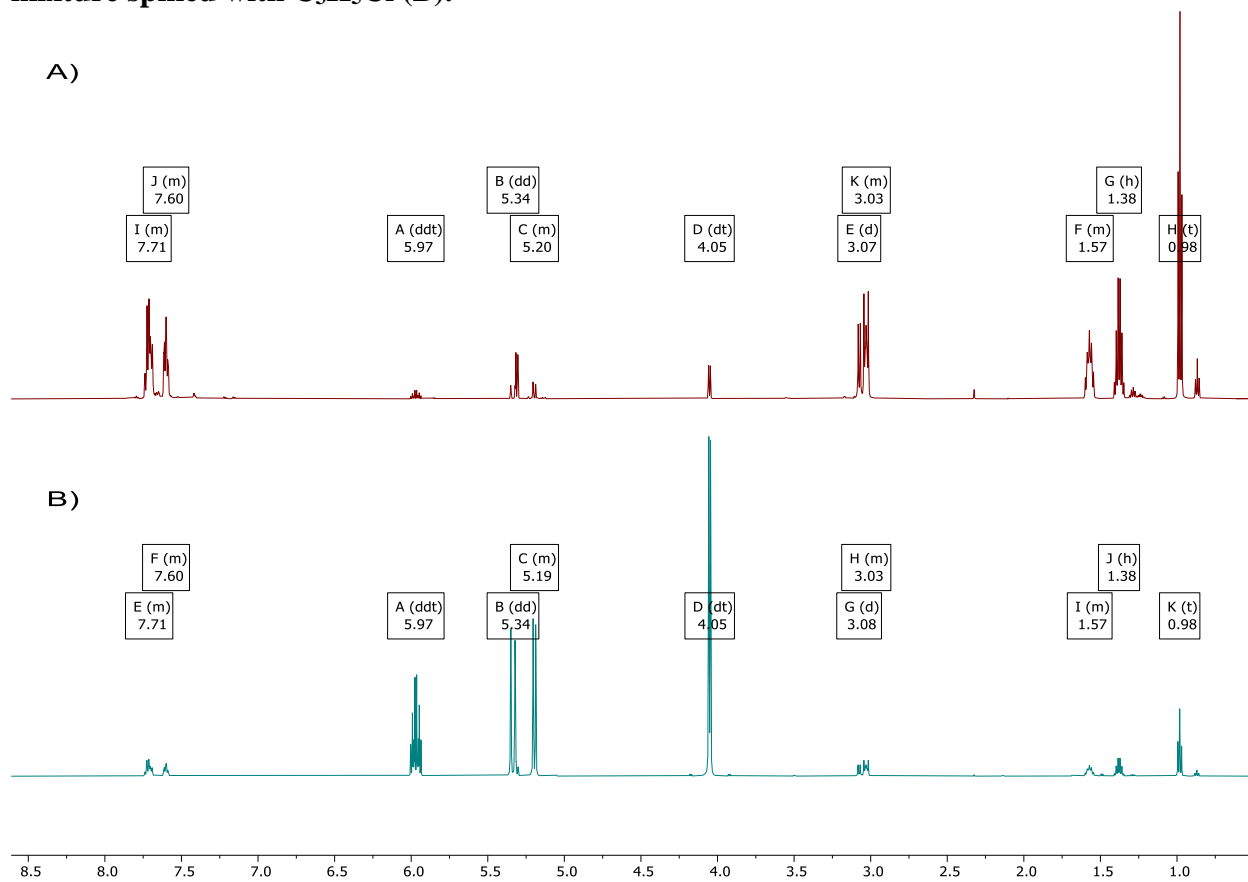
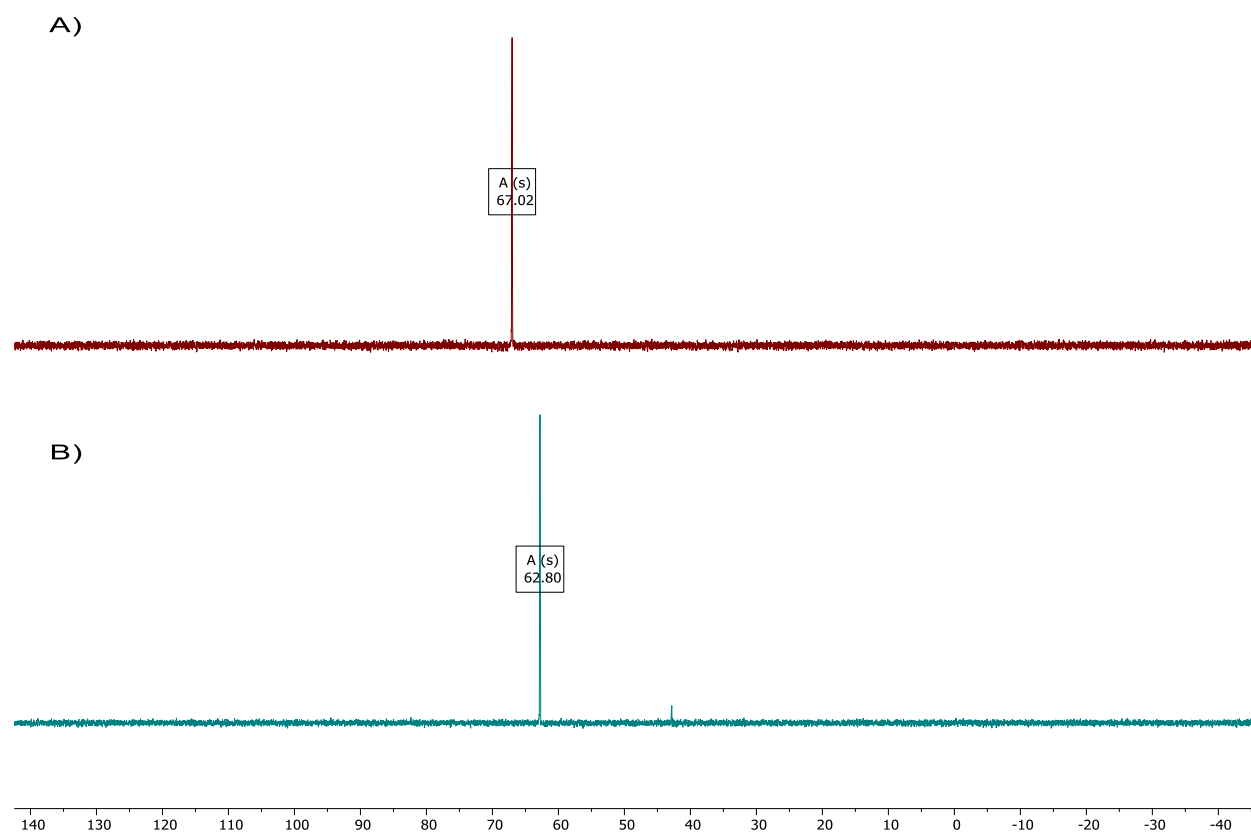


Figure S48.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2$  of **9** (A) and reaction mixture indicating formation of **11** (B).



## NMR spectra for the reaction of 10 with [nBu<sub>4</sub>N][Cl]

Figure S49. A) <sup>1</sup>H NMR spectrum in CH<sub>2</sub>Cl<sub>2</sub> of crude reaction mixture (A) and reaction mixture spiked with BnCl (B).

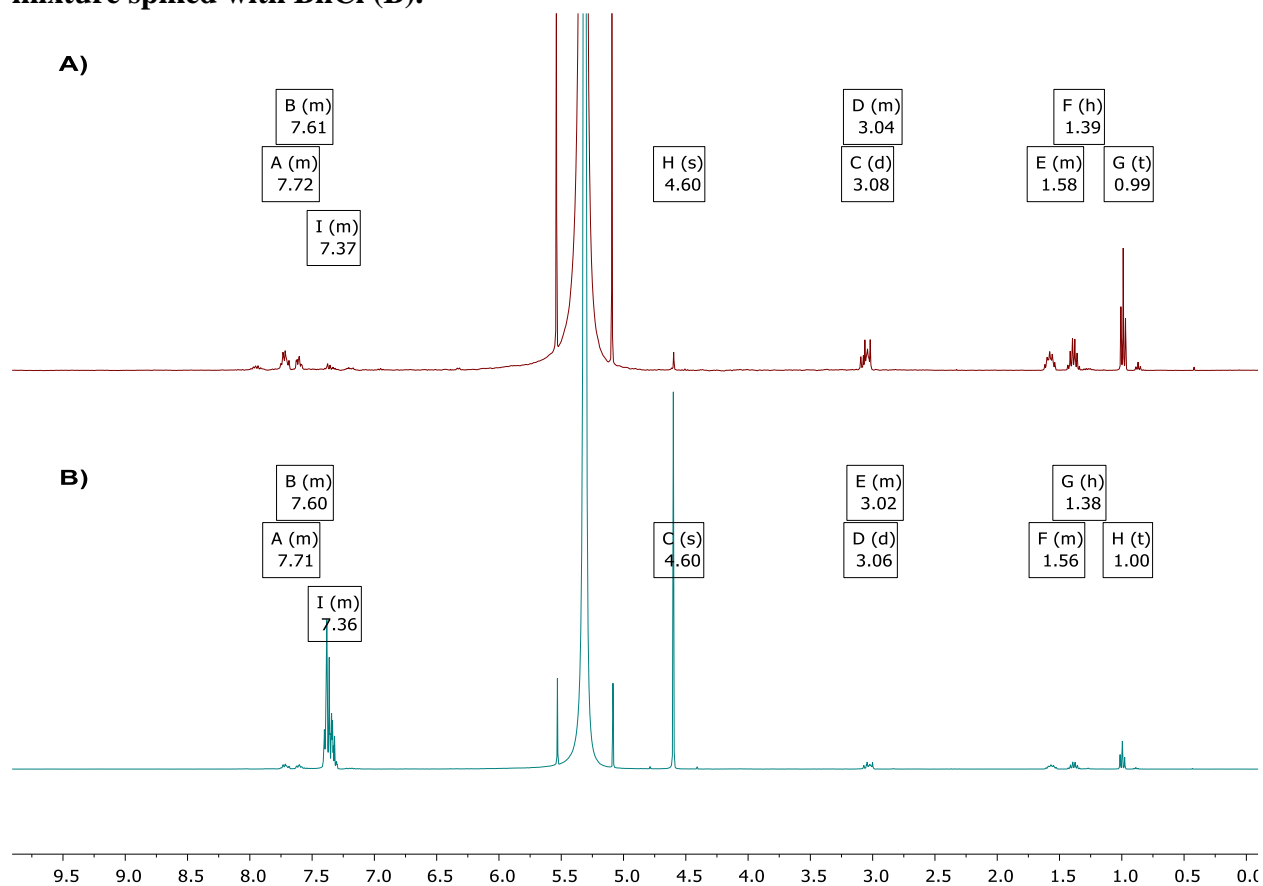


Figure S50.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2$  of 10 (A) and reaction mixture indicating formation of 11 (B).

A)



B)

