Supplementary Materials for

Synthesis and N-C Bond Cleavage Reactions for Cyclic Phosphazenium Dications

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NMR spectra for $(C_6H_4)(PPh_2F_2)_2$ (1)

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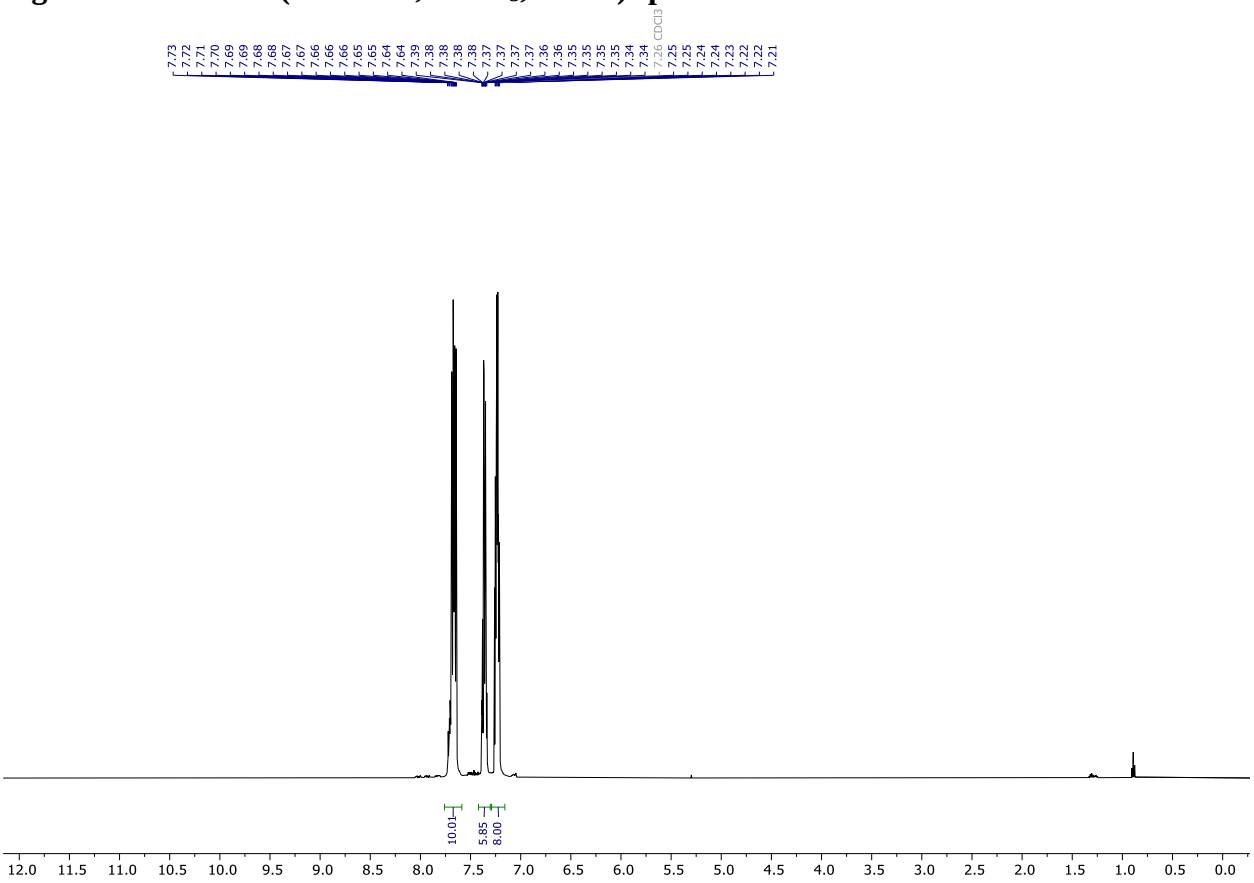


Figure S2. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of 1.

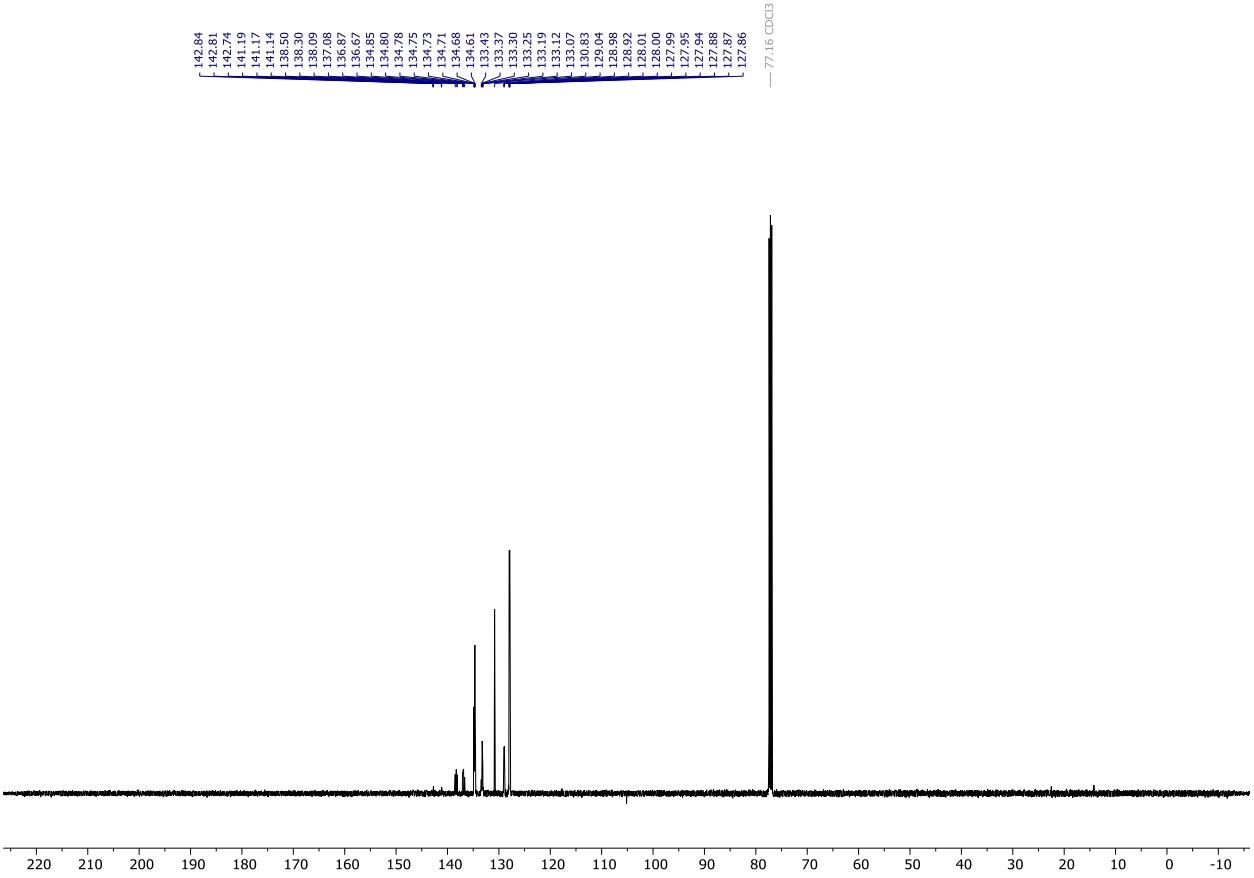


Figure S3. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298K) spectrum of 1.

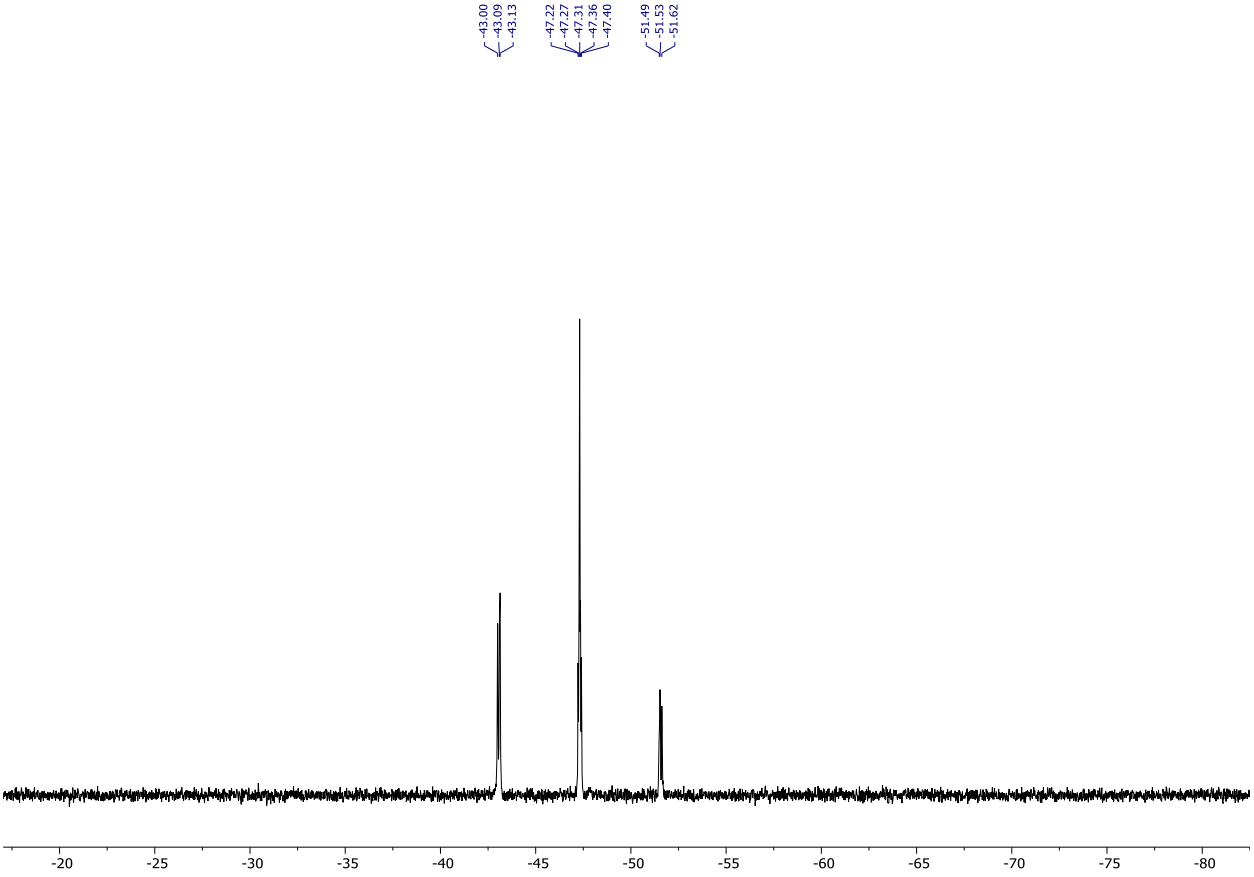
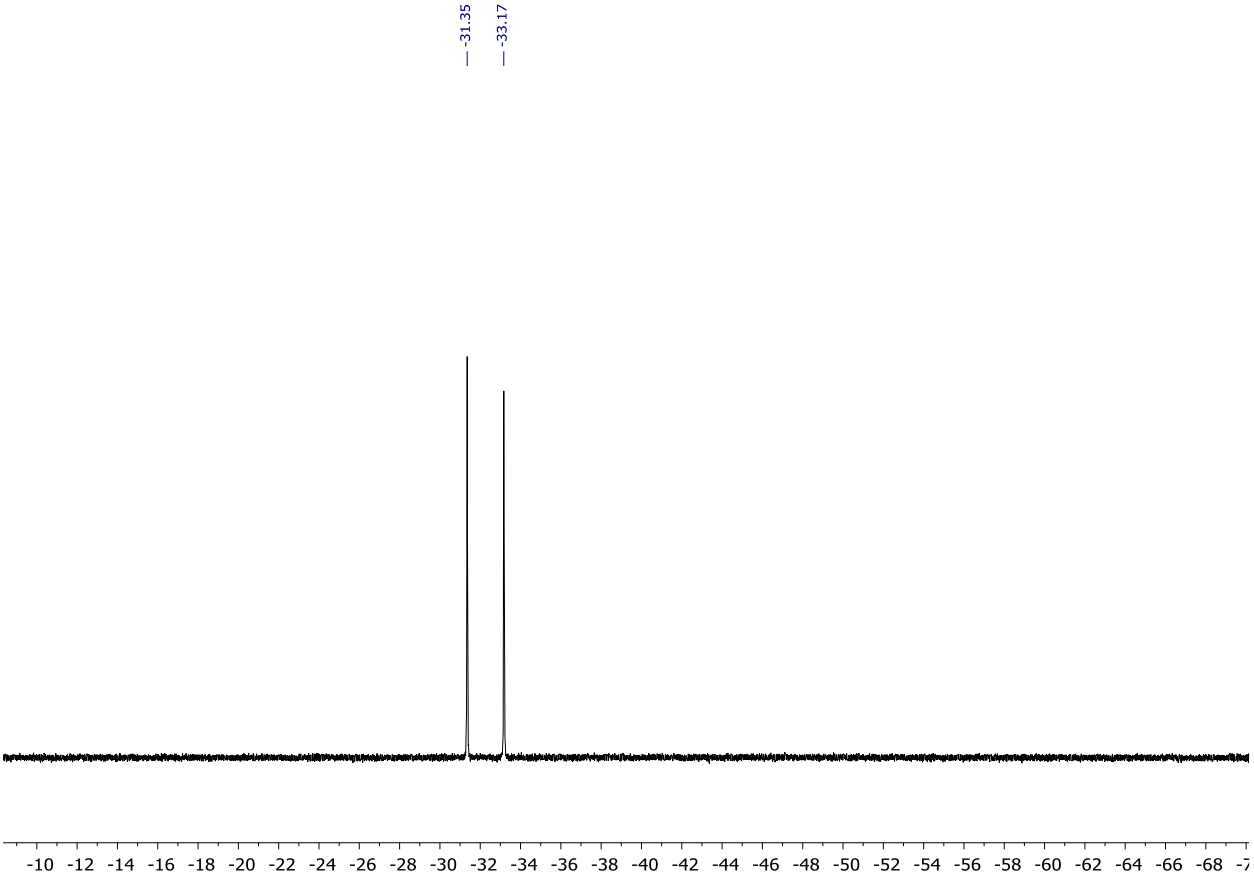


Figure S4. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of 1.



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

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

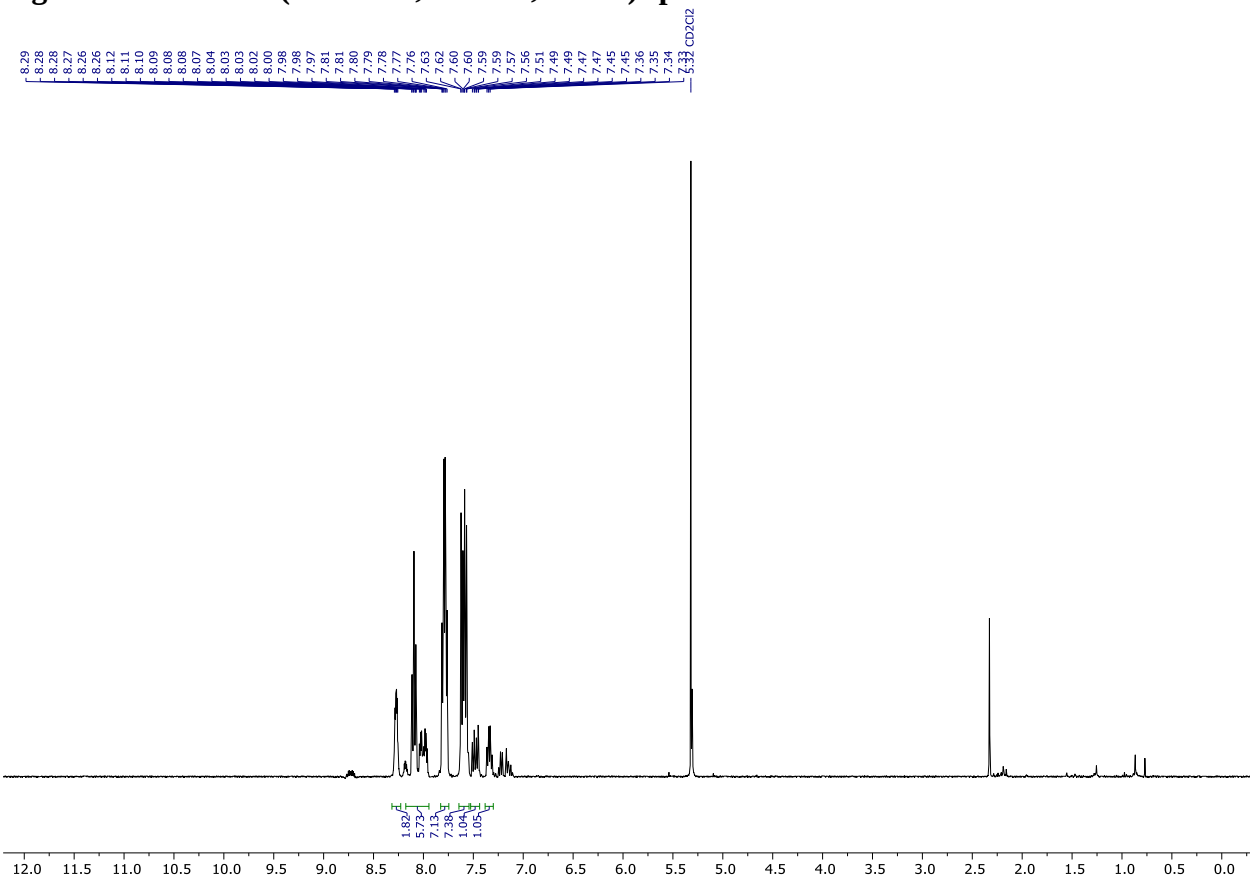


Figure S6. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 2.

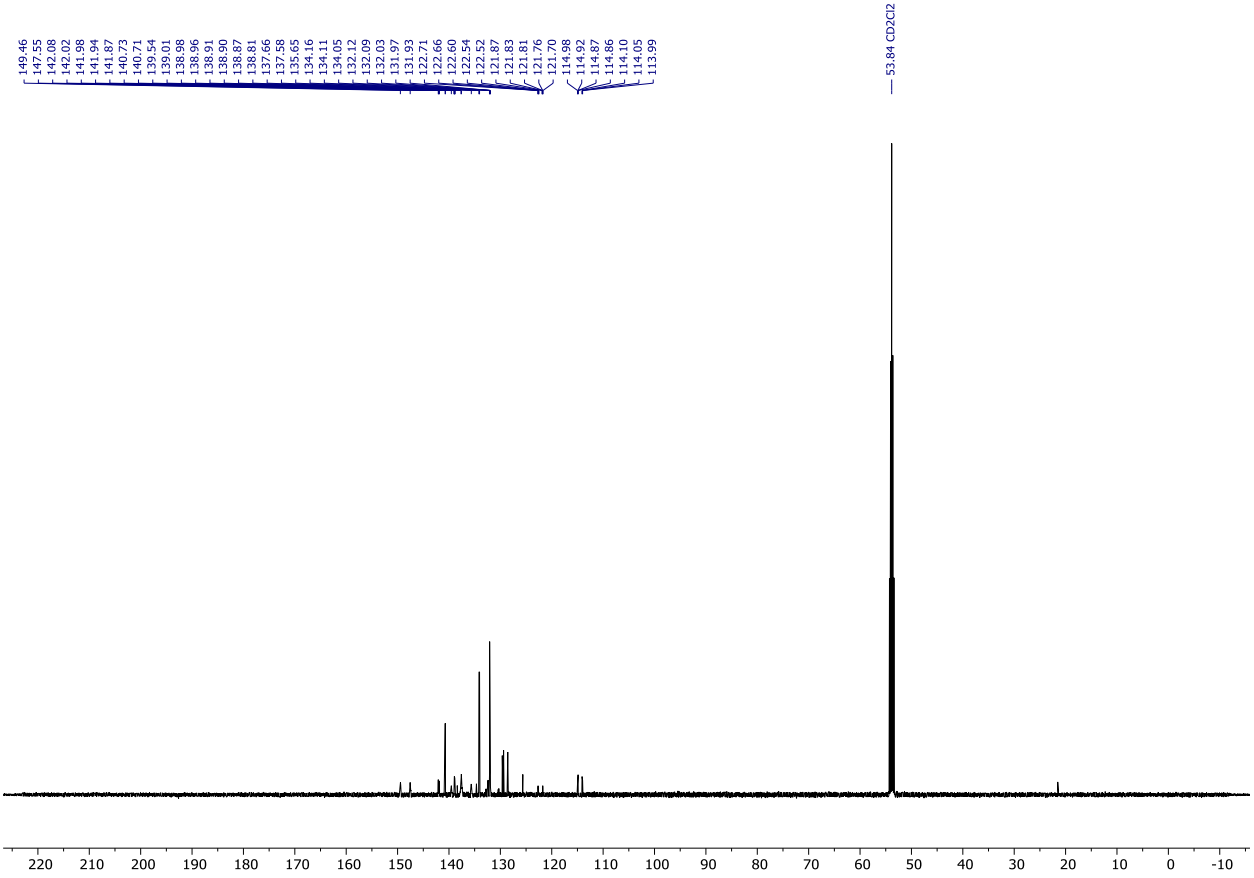


Figure S7. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 2.

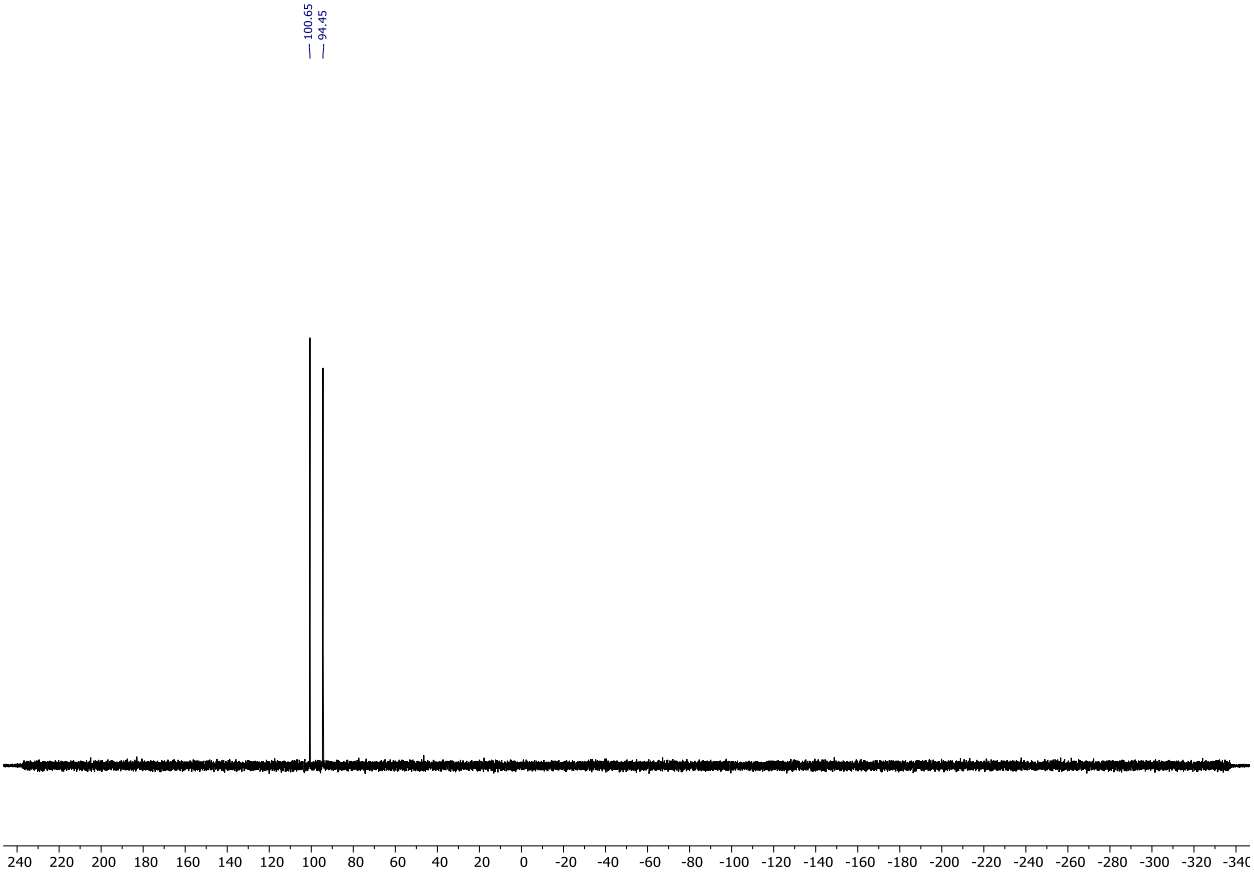


Figure S8. ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K) spectrum of 2.

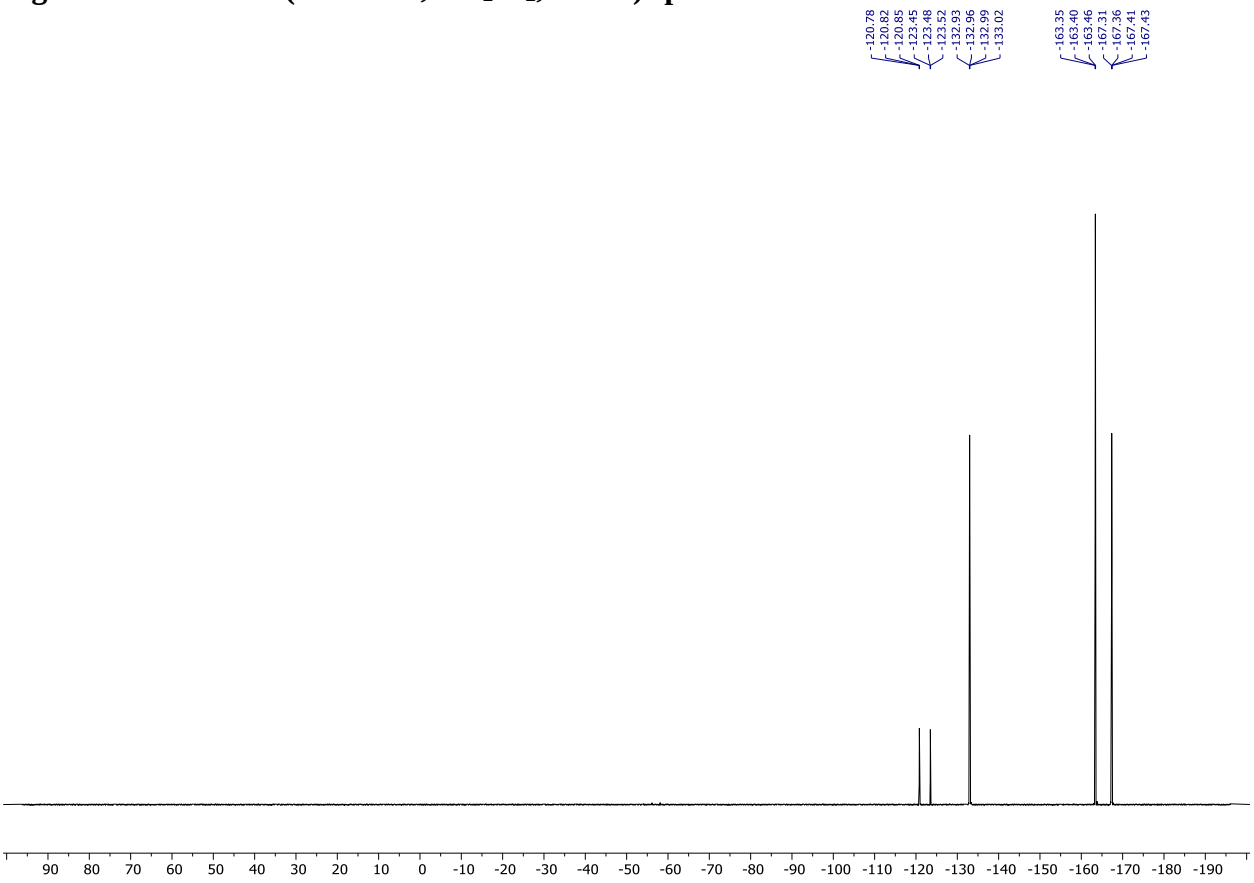
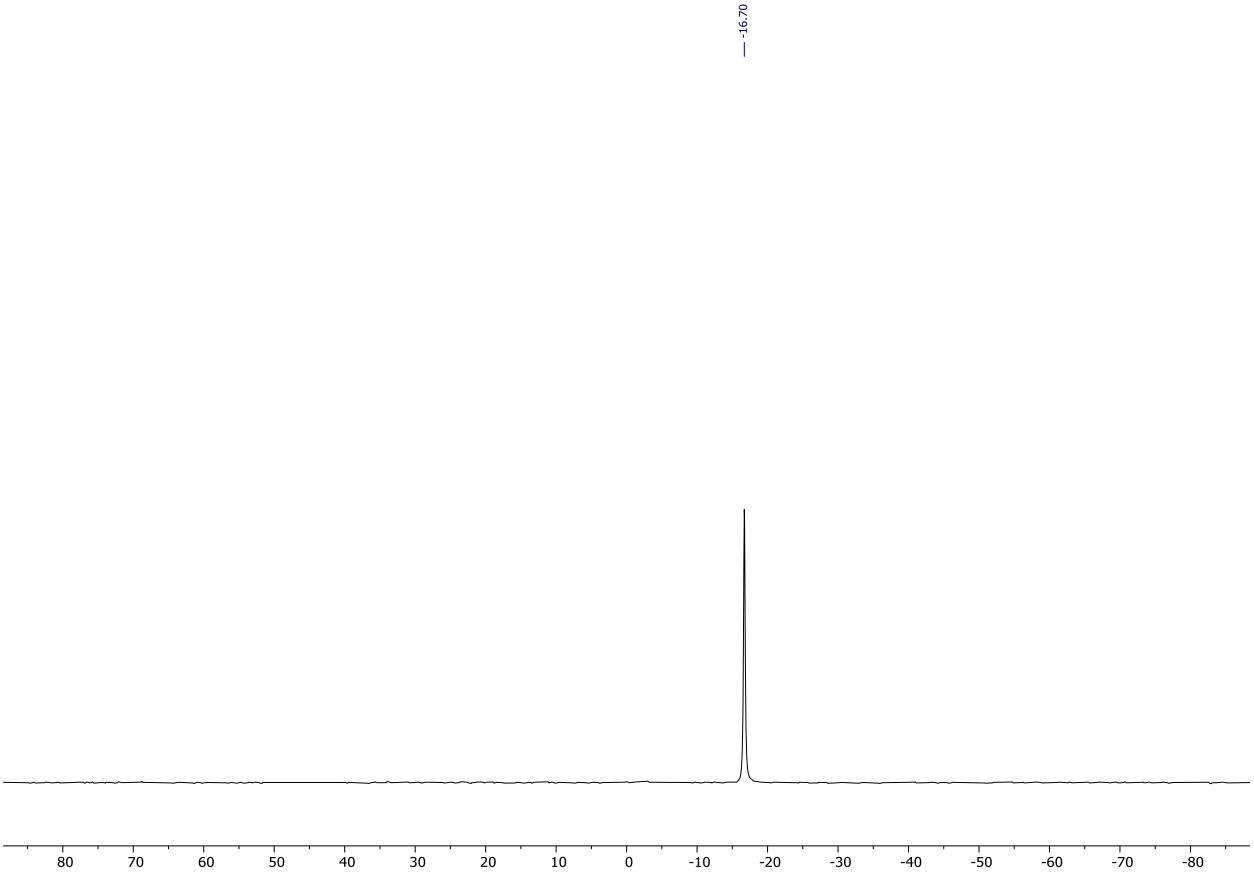


Figure S9. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of compound 2.



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

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

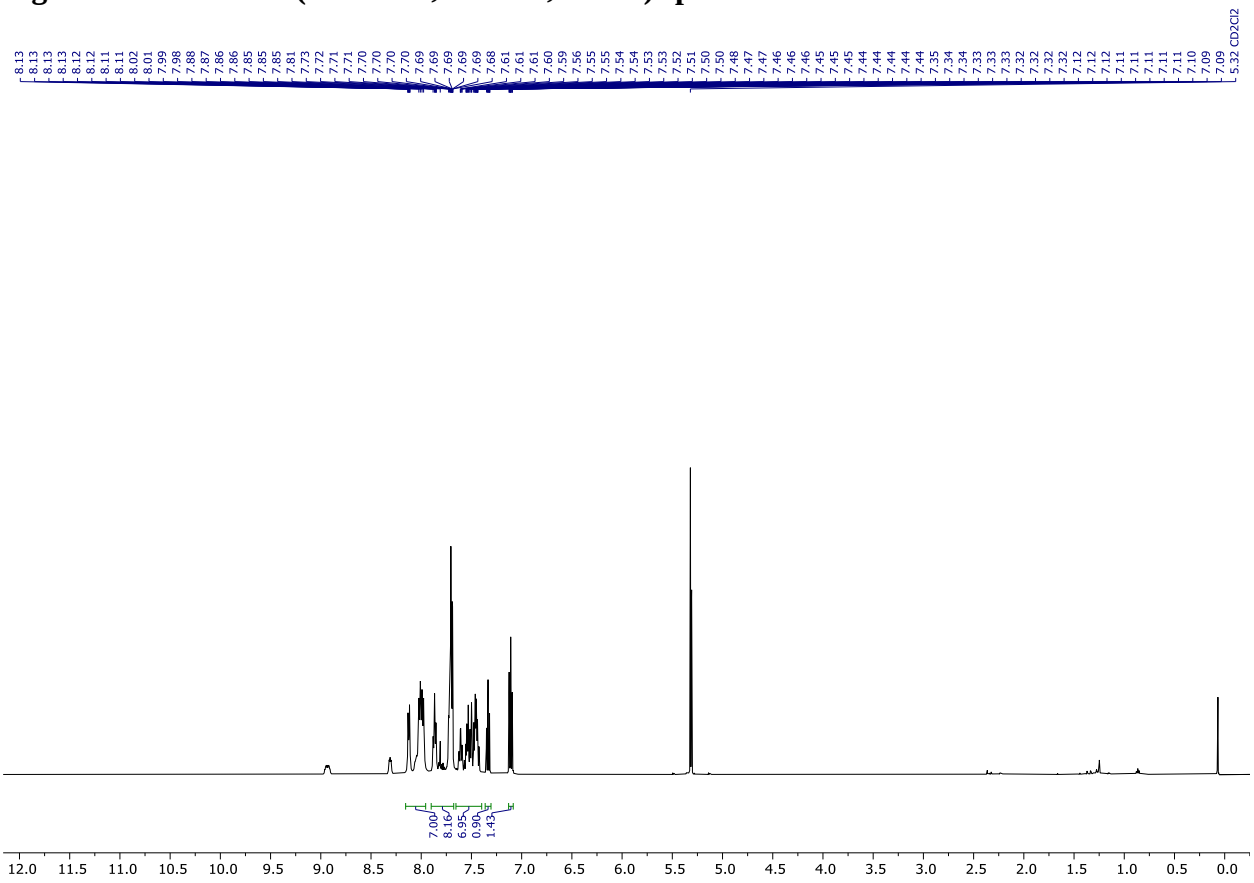


Figure S11. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 3.

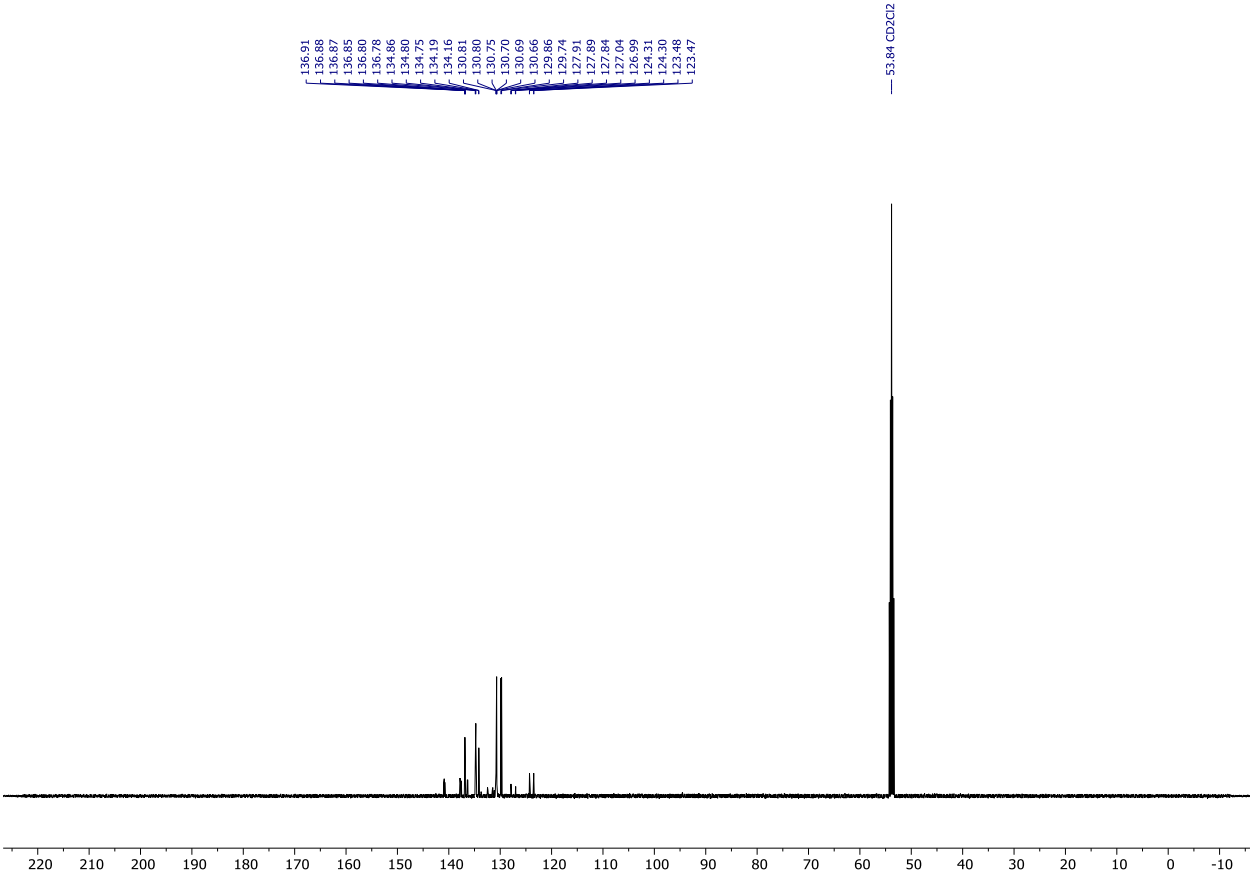
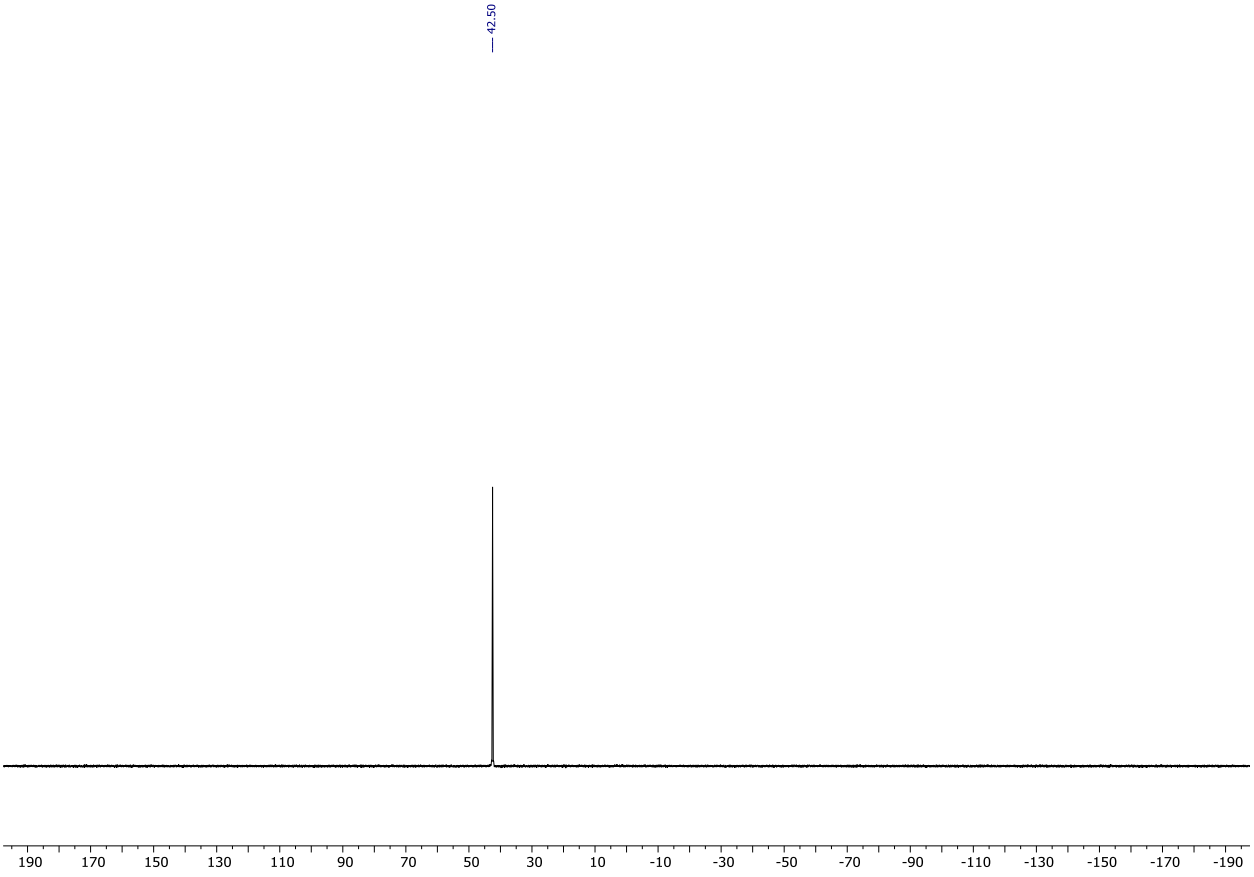


Figure S12. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 3.



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'.

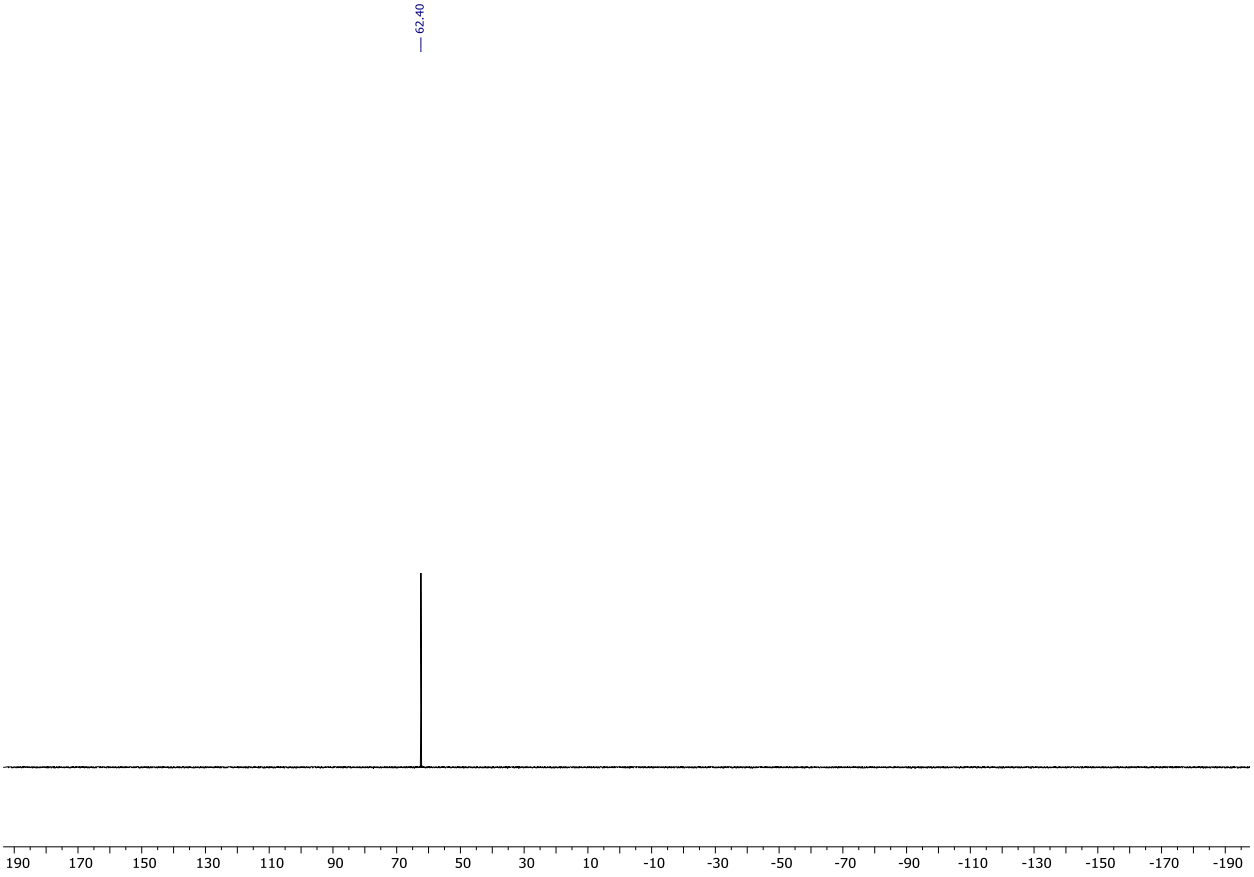
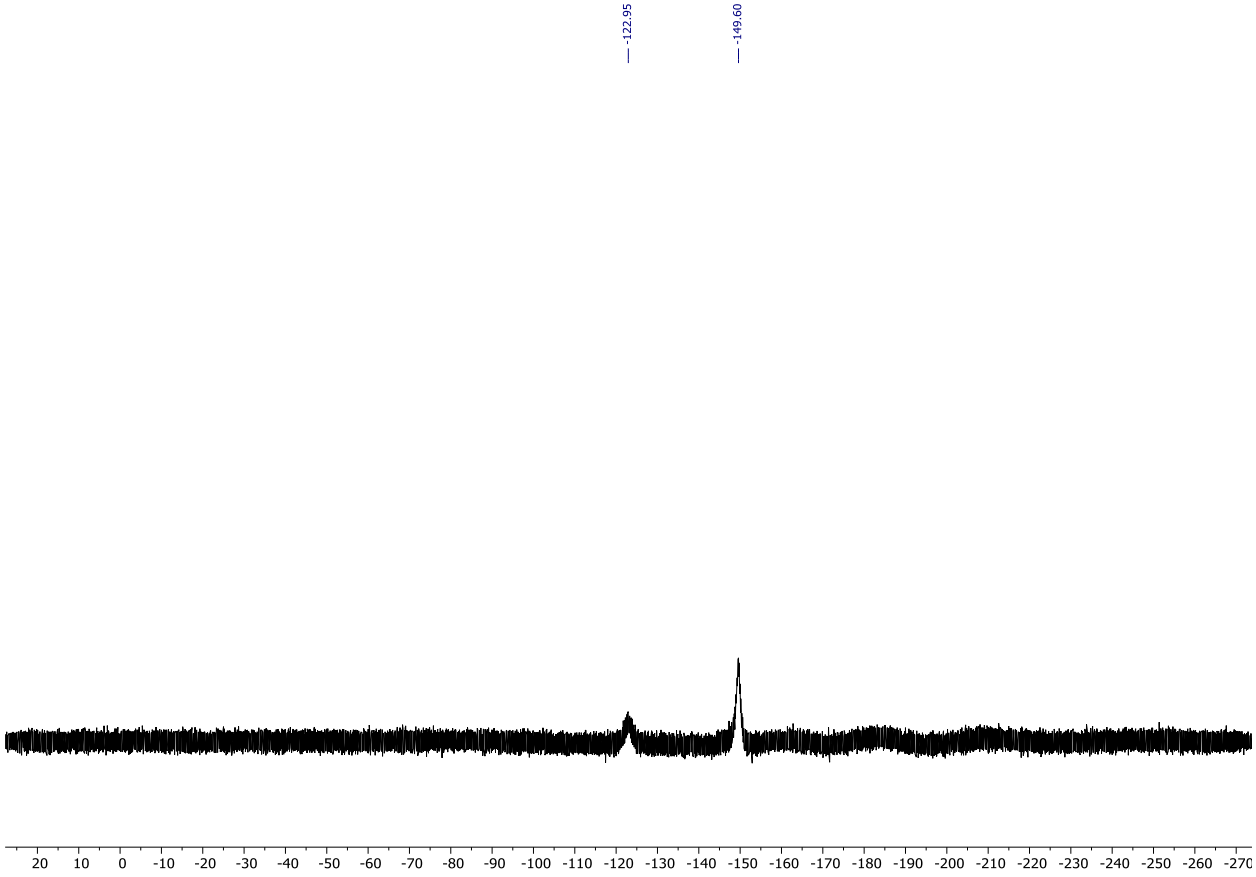


Figure S14. ^{19}F NMR (376 MHz, CH_2Cl_2, 298 K) spectrum of 3'.



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

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

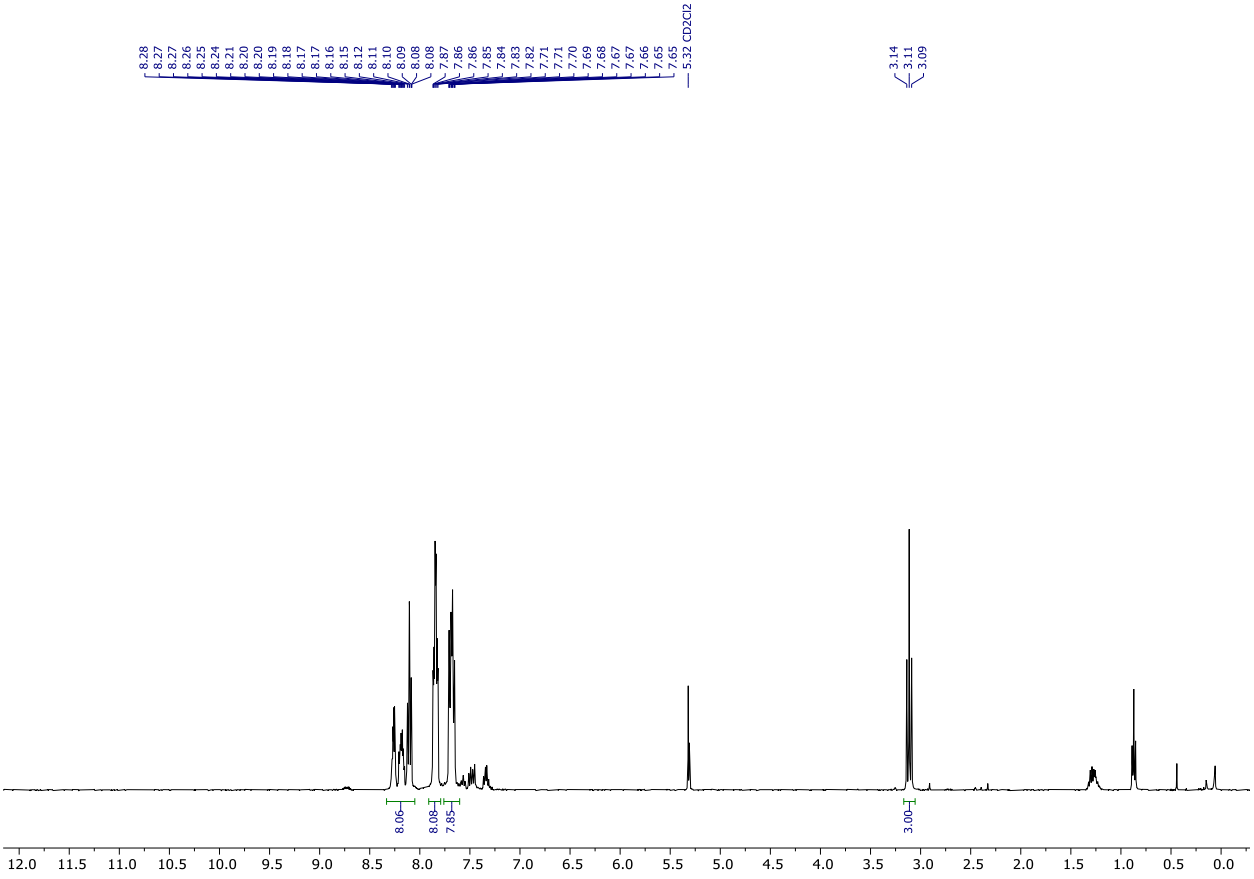


Figure S16. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 4.

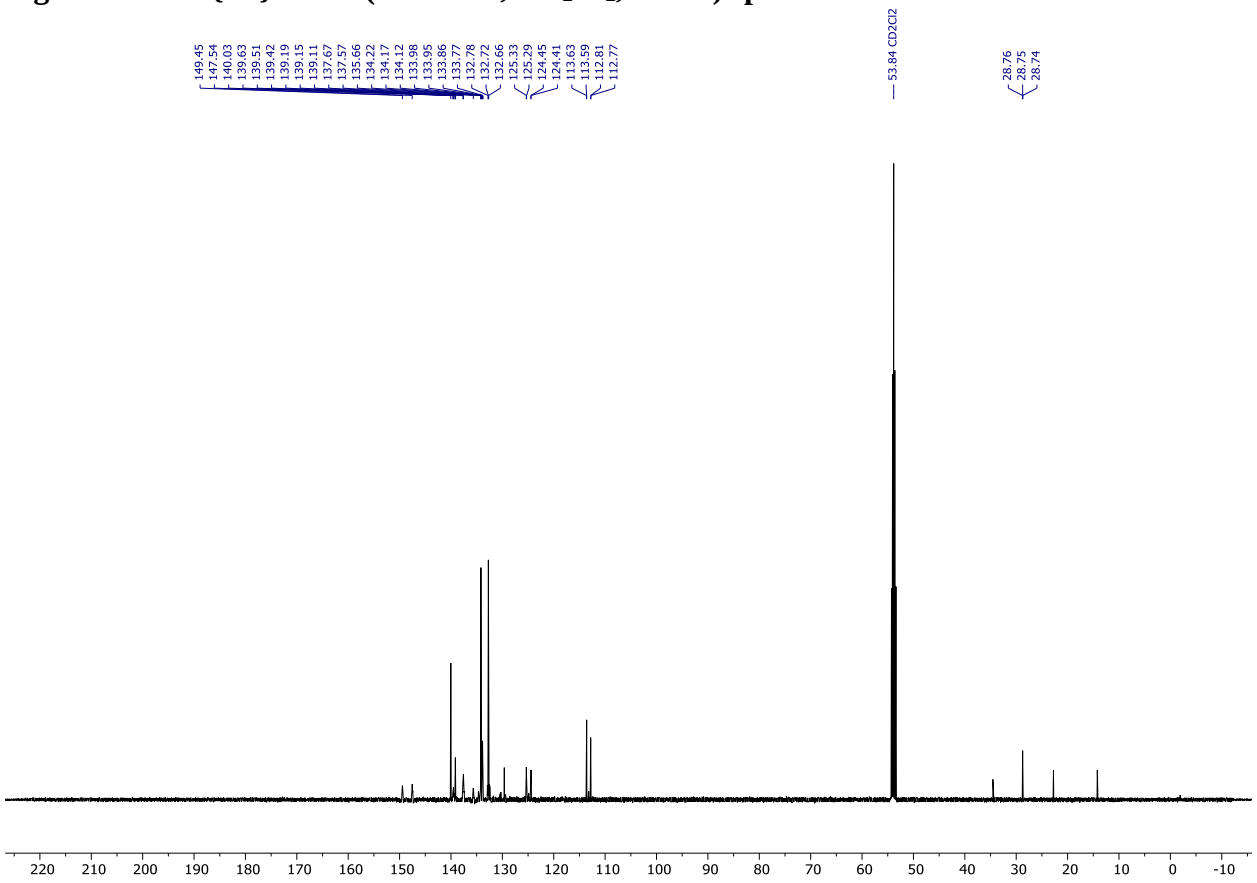


Figure S17. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 4.

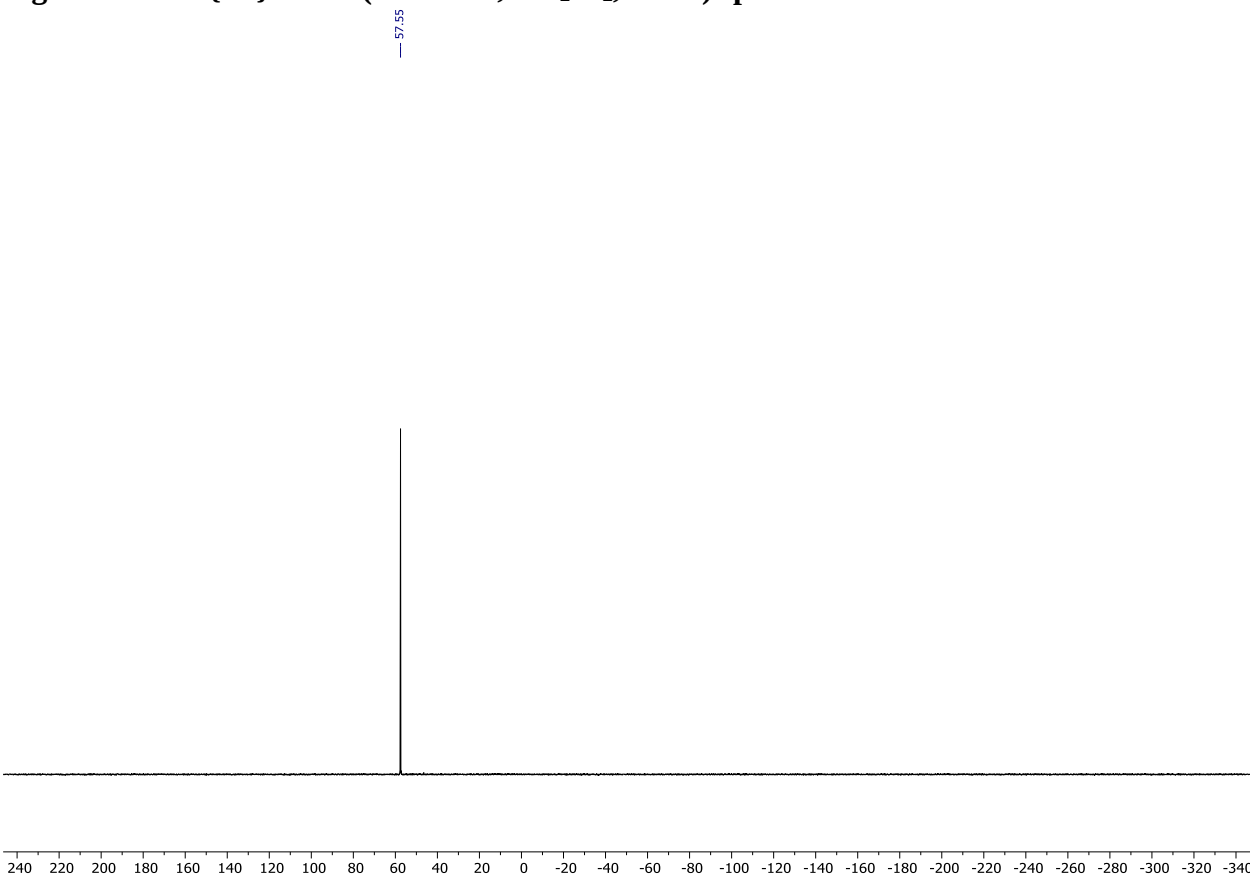


Figure S18. ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K) spectrum of 4.

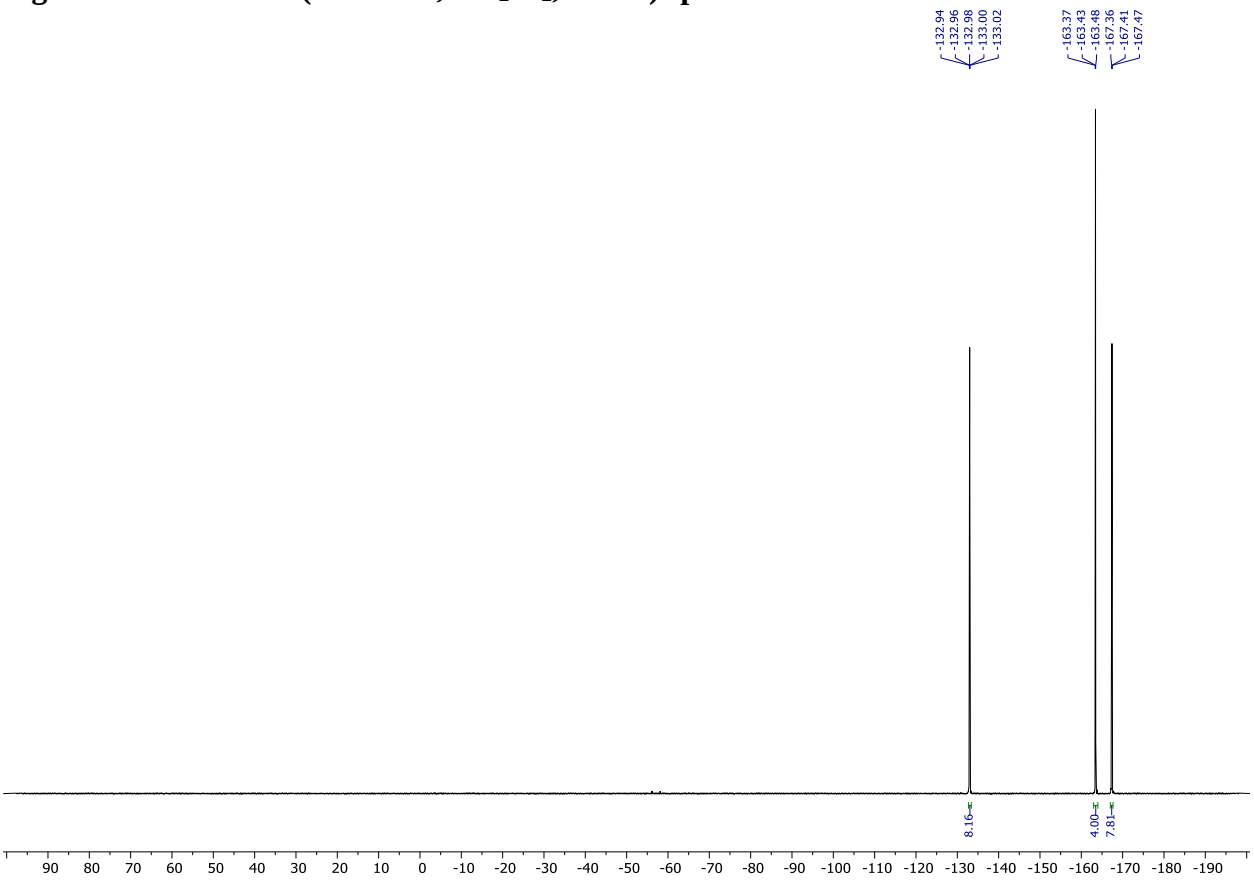
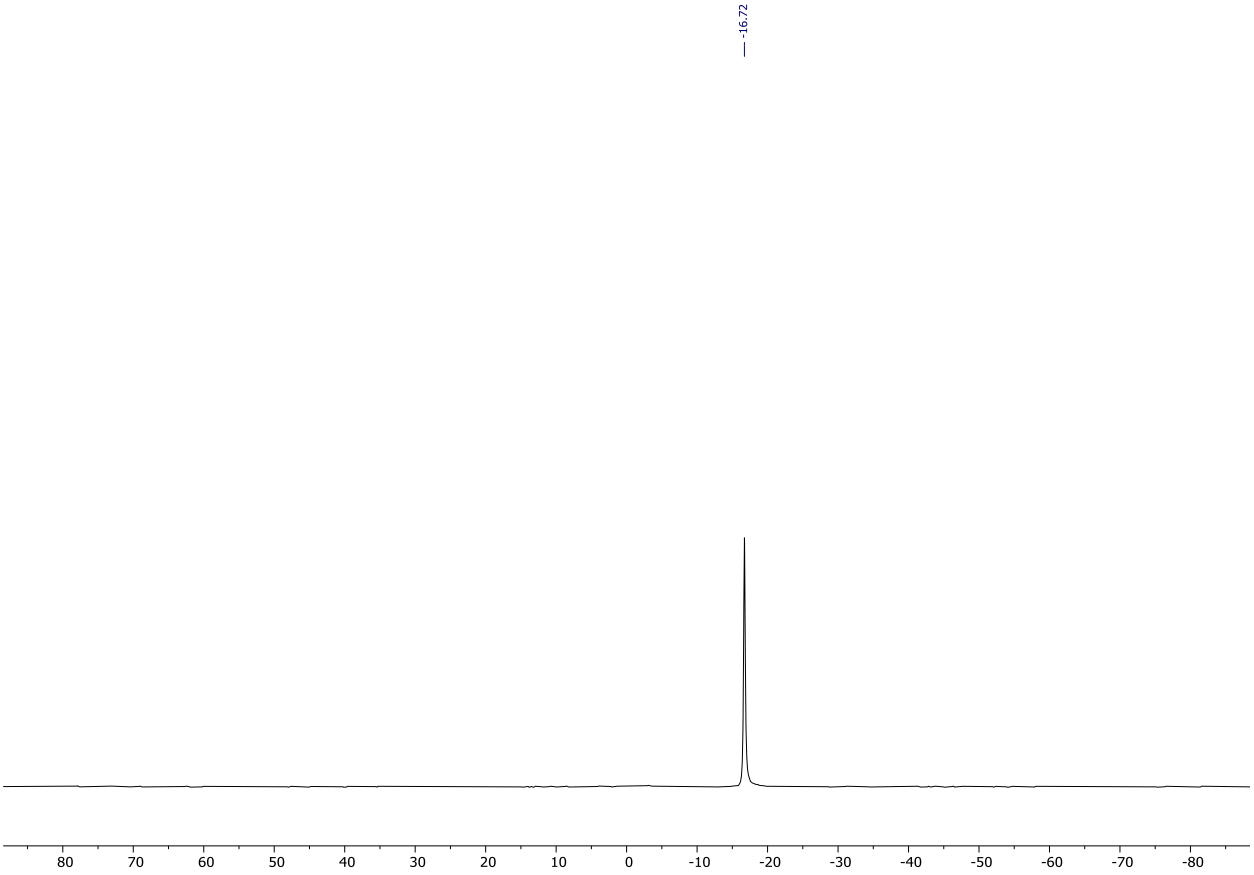


Figure S19. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of compound 4.



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

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

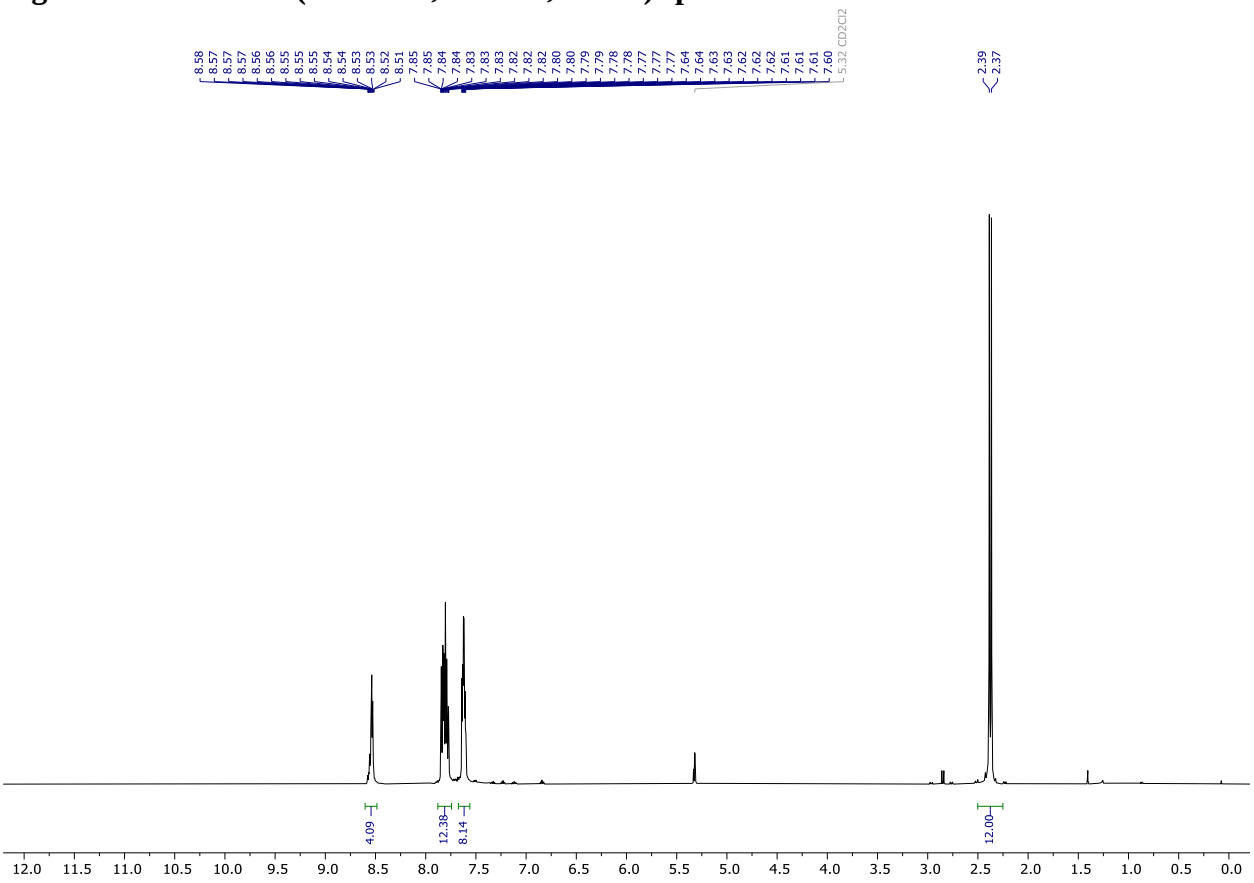


Figure S21. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 5.

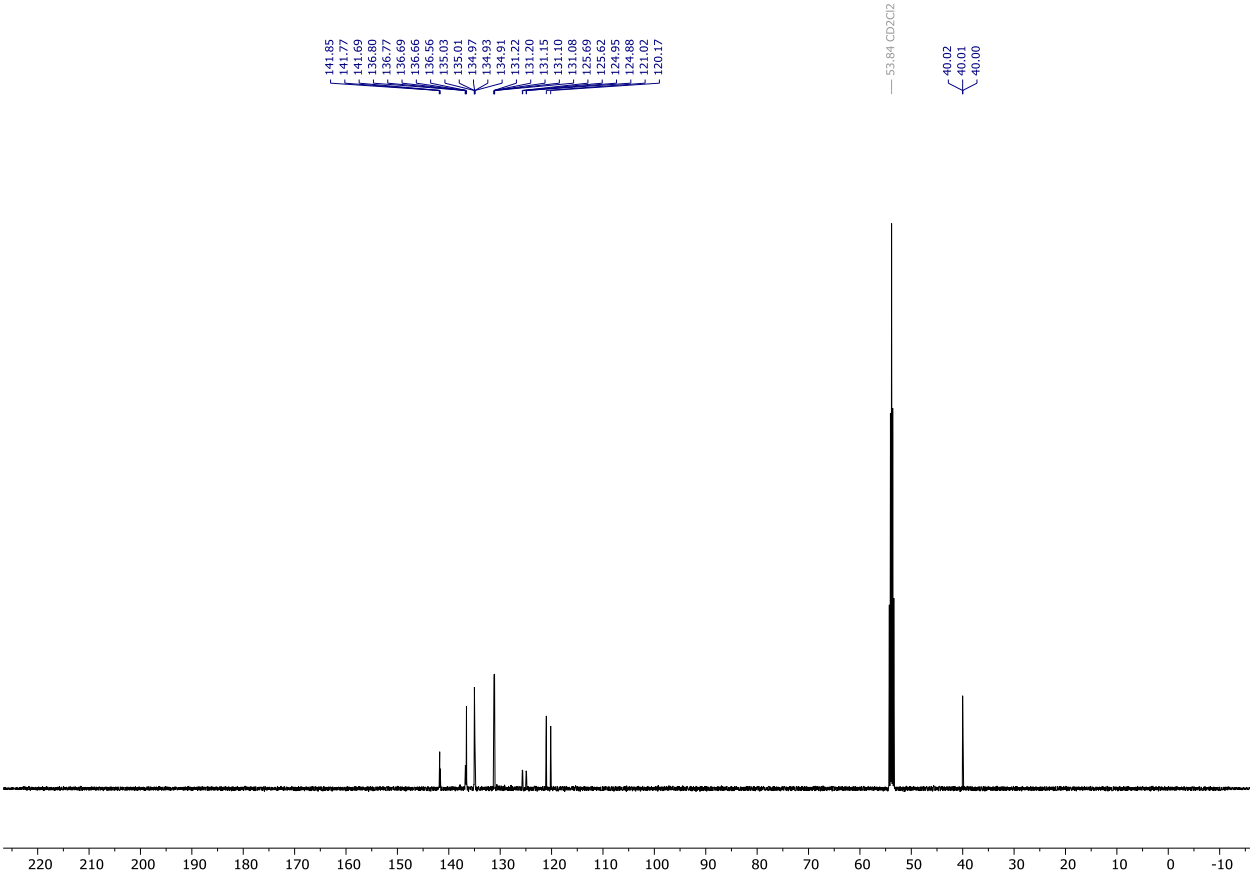
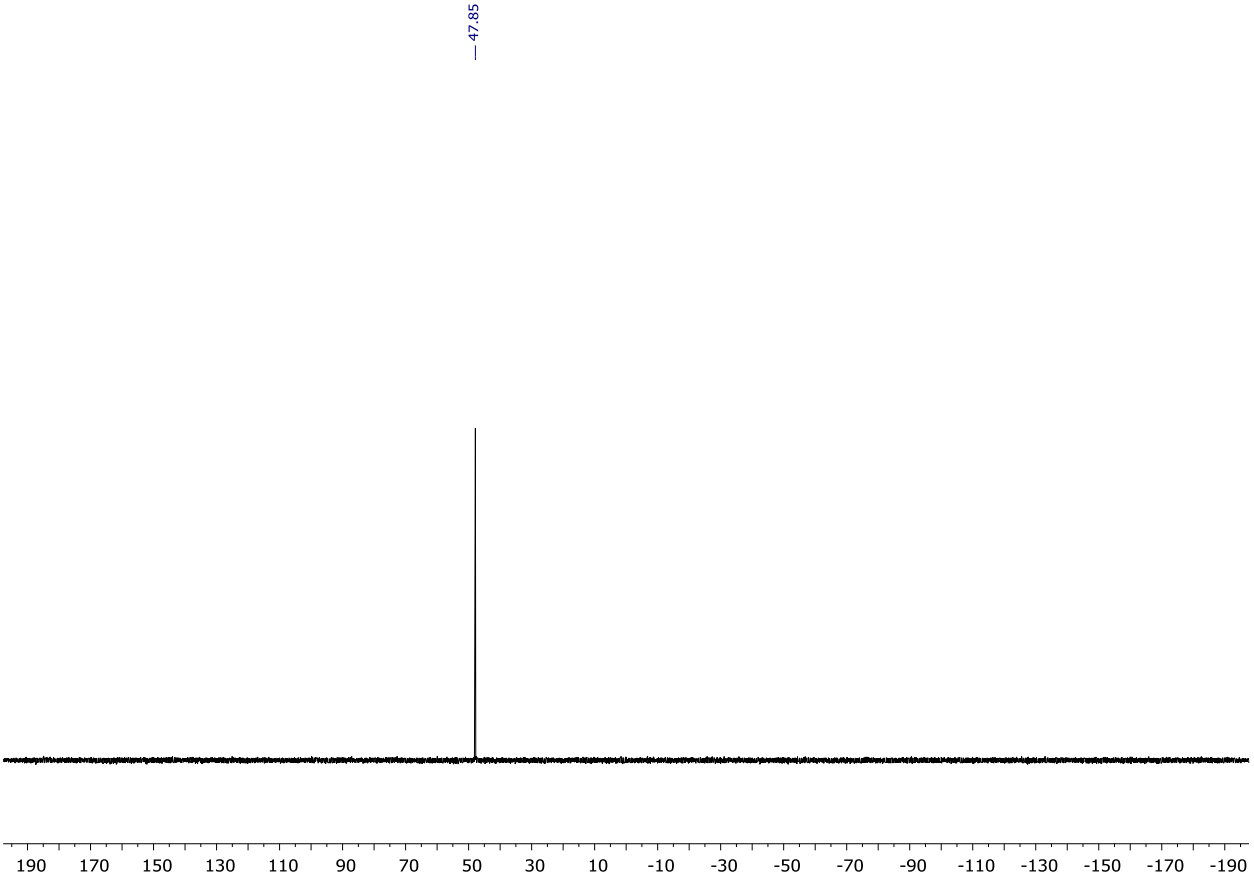


Figure S22. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 5.



NMR spectra for $[(C_6H_4)(PPh_2)_2(\mu\text{-}N)][Cl]$ (6)

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

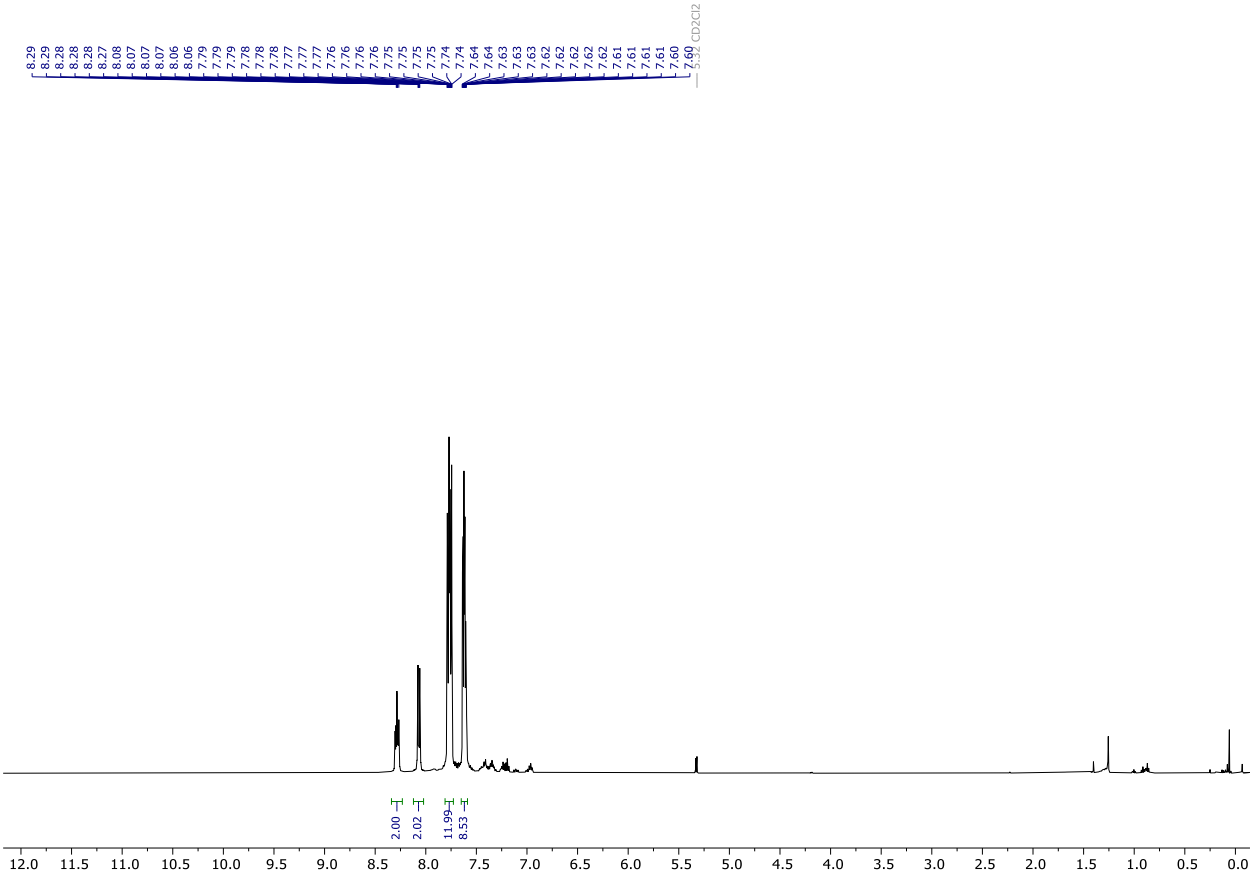


Figure S24. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 6.

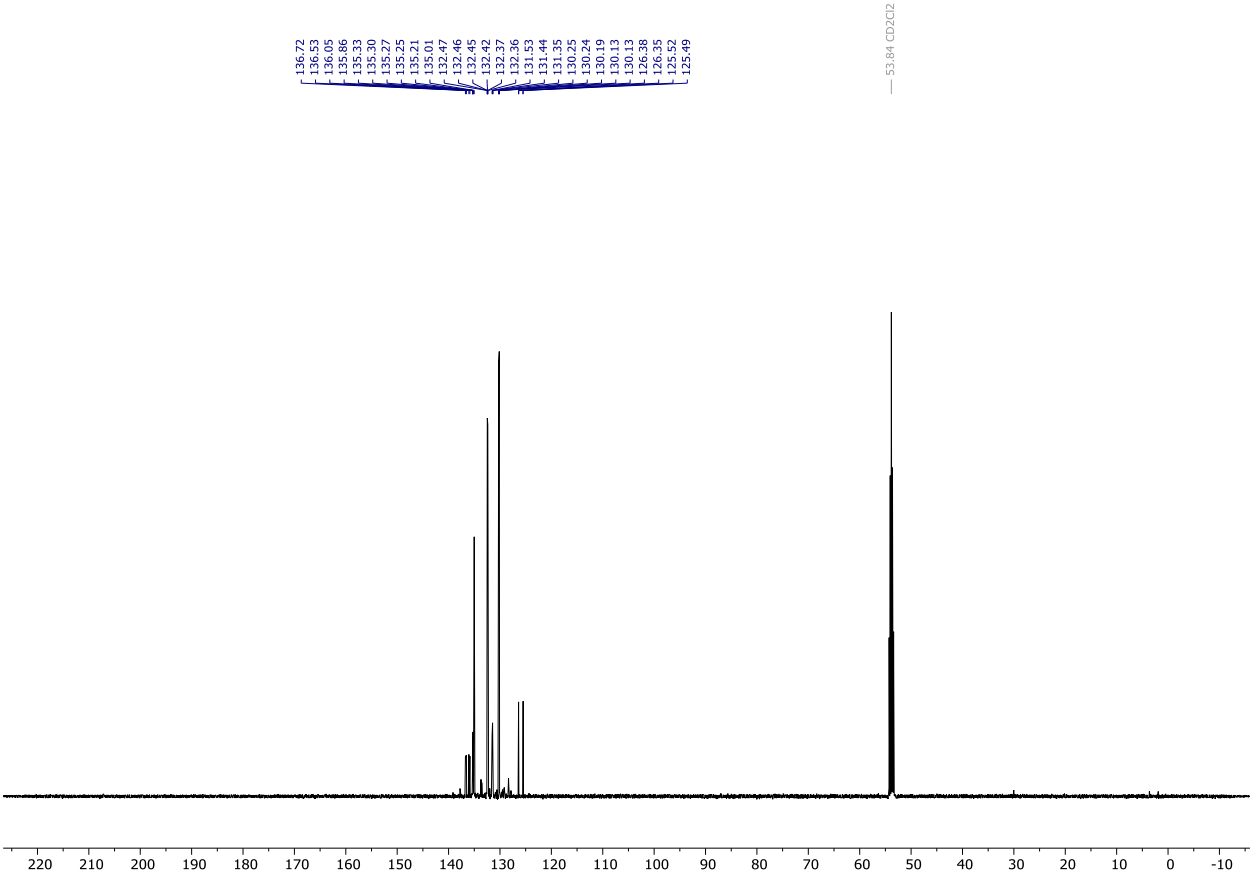
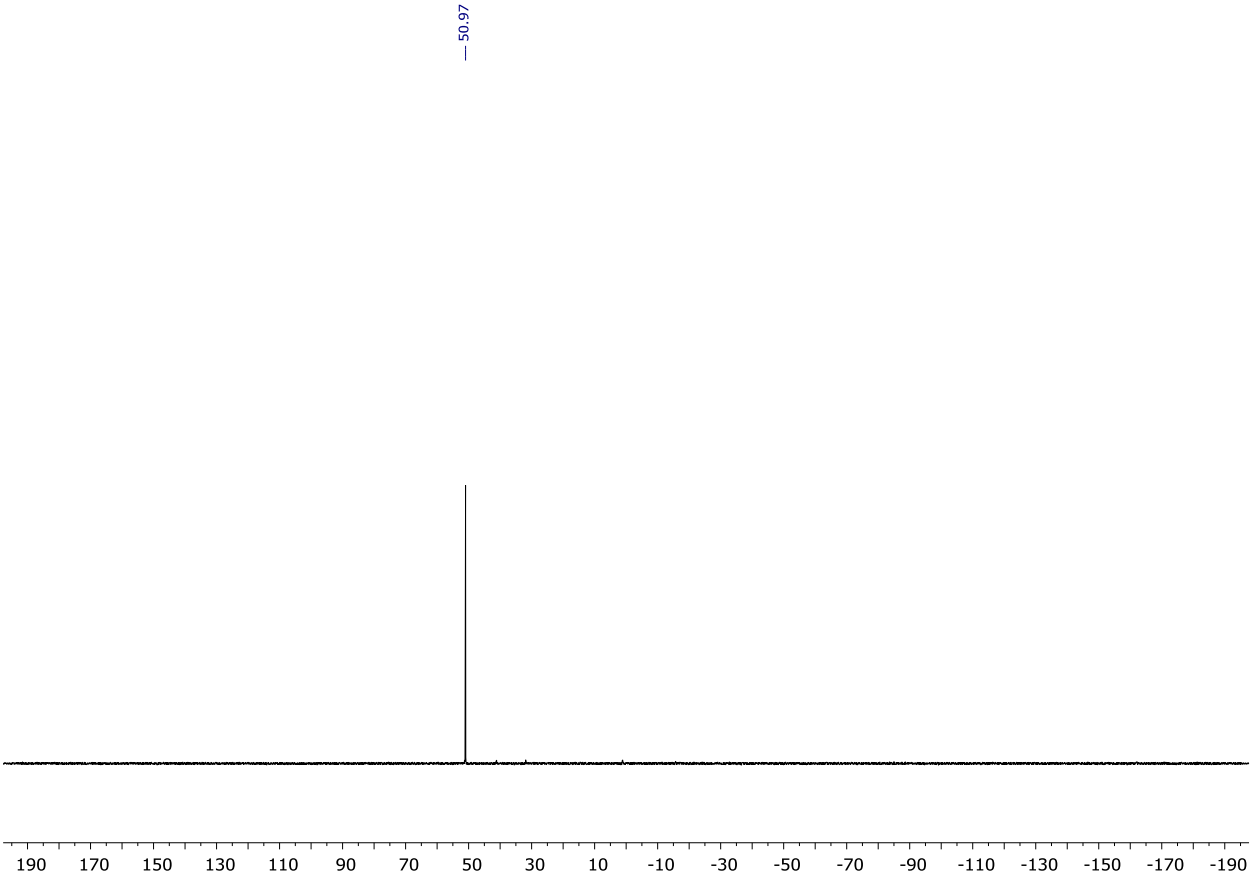


Figure S25. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 6.



NMR spectra for the reaction of Compound 3 with $(Me_3Si)_2NMe$

Figure S26. A) ^{1}H NMR spectrum in CH_2Cl_2 of crude reaction mixture (A) and reaction mixture after exposure to high vacuum (B).

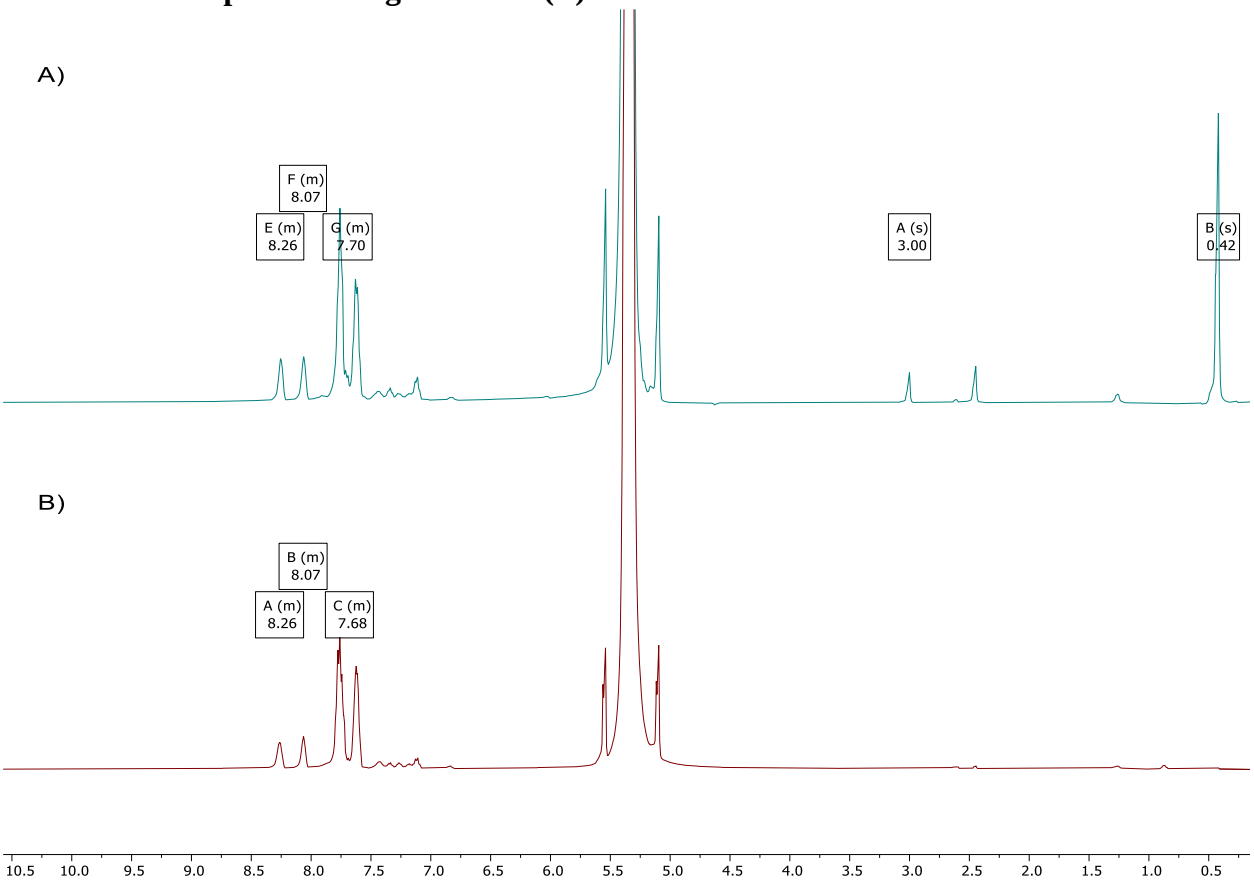
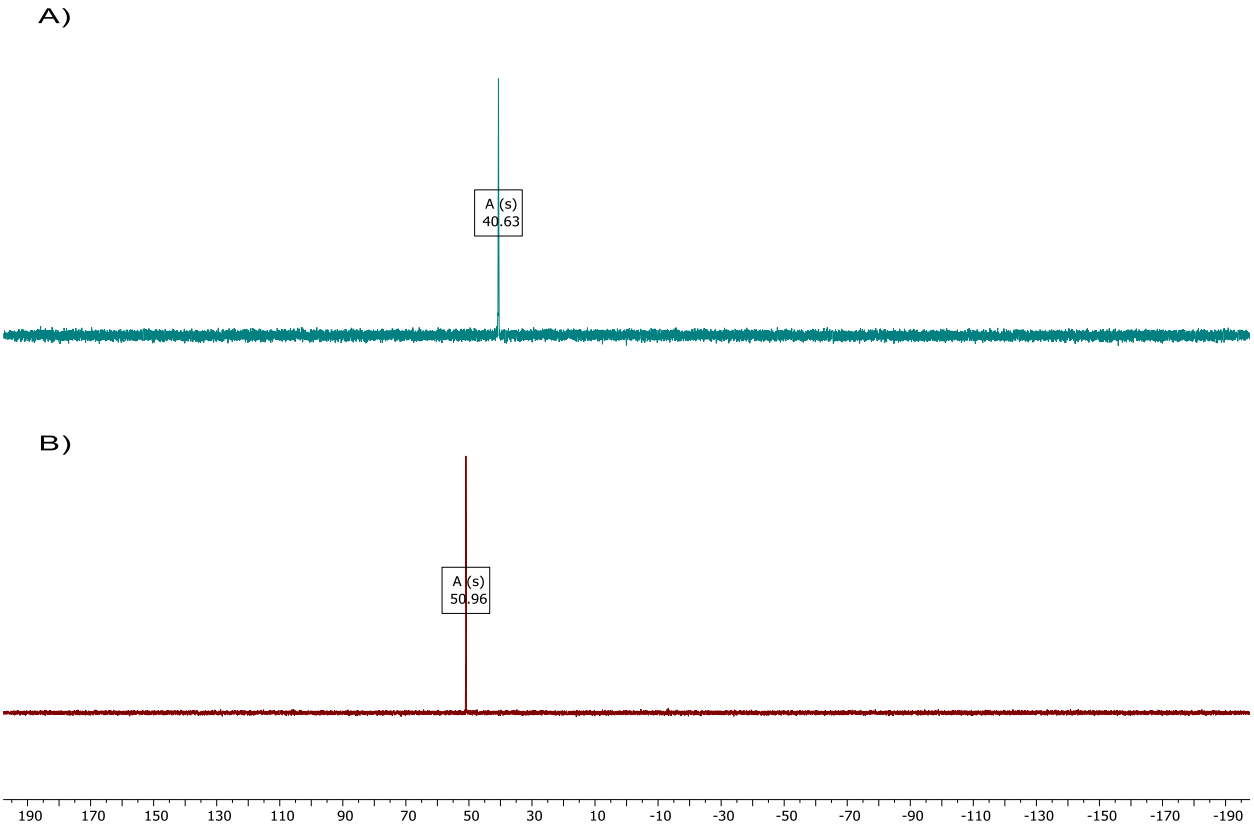


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum in CH_2Cl_2 of 3 (A) and reaction mixture indicating formation of 6 (B).



NMR spectra for the reaction of Compound 4 with [nBu$_4$N][Cl]

Figure S28. A) ^{1}H NMR spectrum in CH_2Cl_2 of crude reaction mixture (A) and reaction mixture after exposure to high vacuum (B).

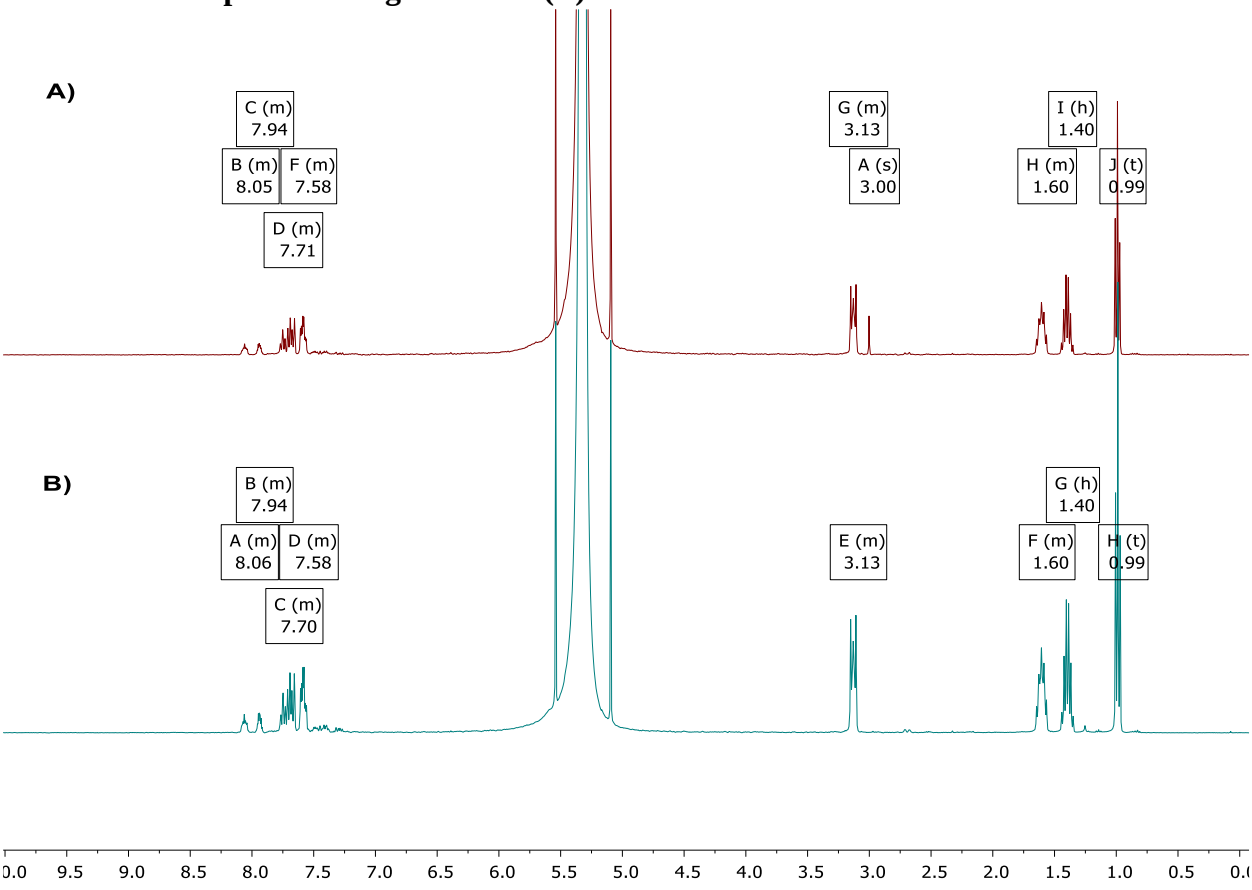
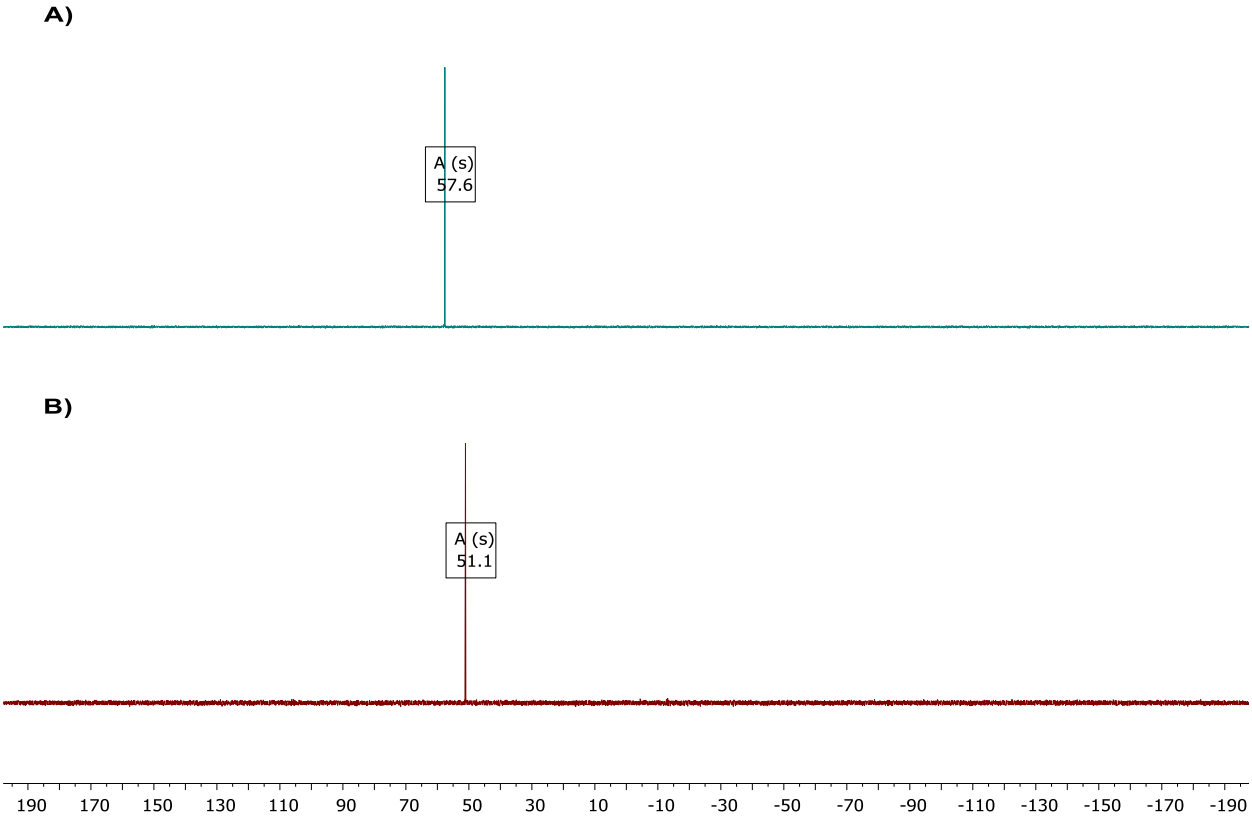


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum in CH_2Cl_2 of 4 (A) and reaction mixture indicating formation of 6' (B).



NMR spectra for $[(CH_2PPh_2)_2NMe][B(C_6F_5)_4]_2$ (8)

Figure S30. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of 8.

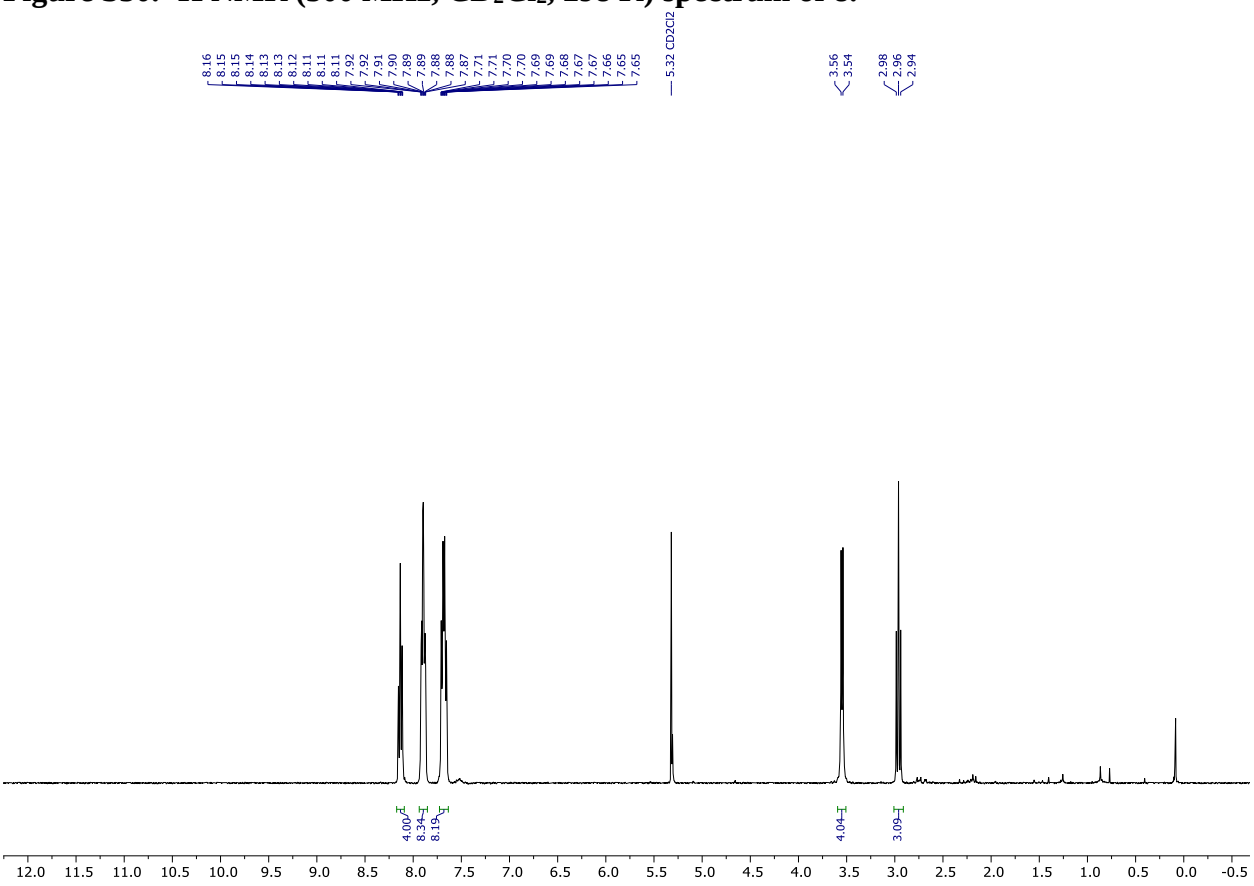


Figure S31. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 8.

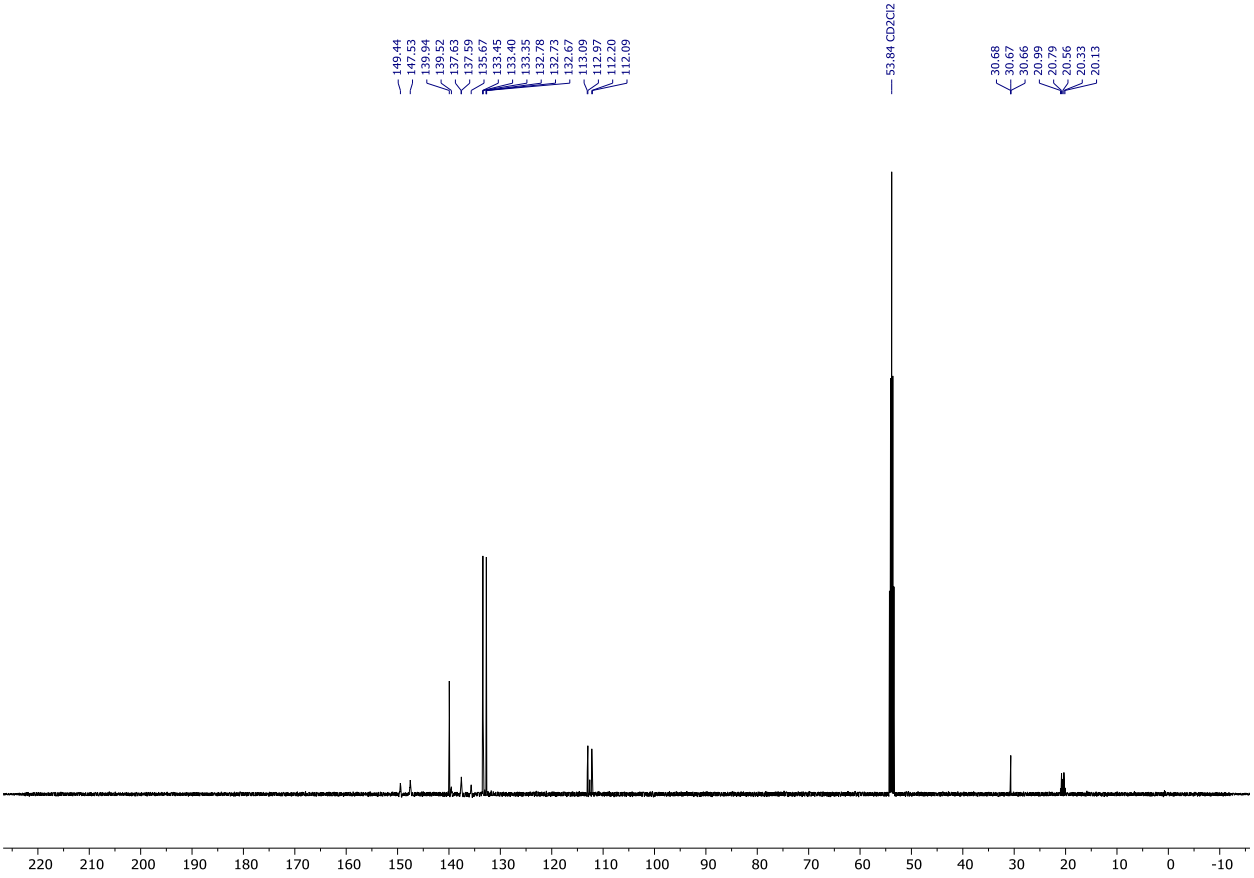


Figure S32. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 8.

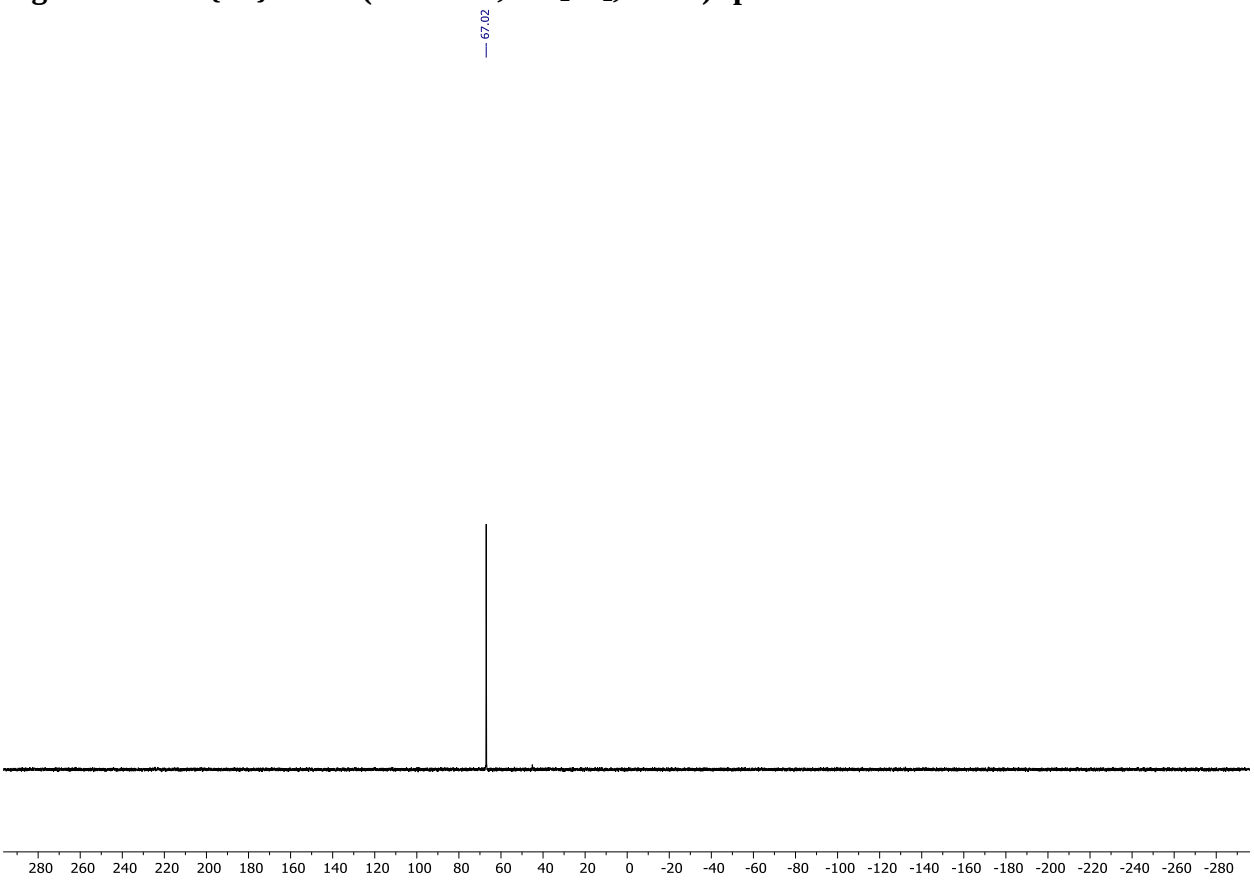


Figure S33. ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K) spectrum of 8.

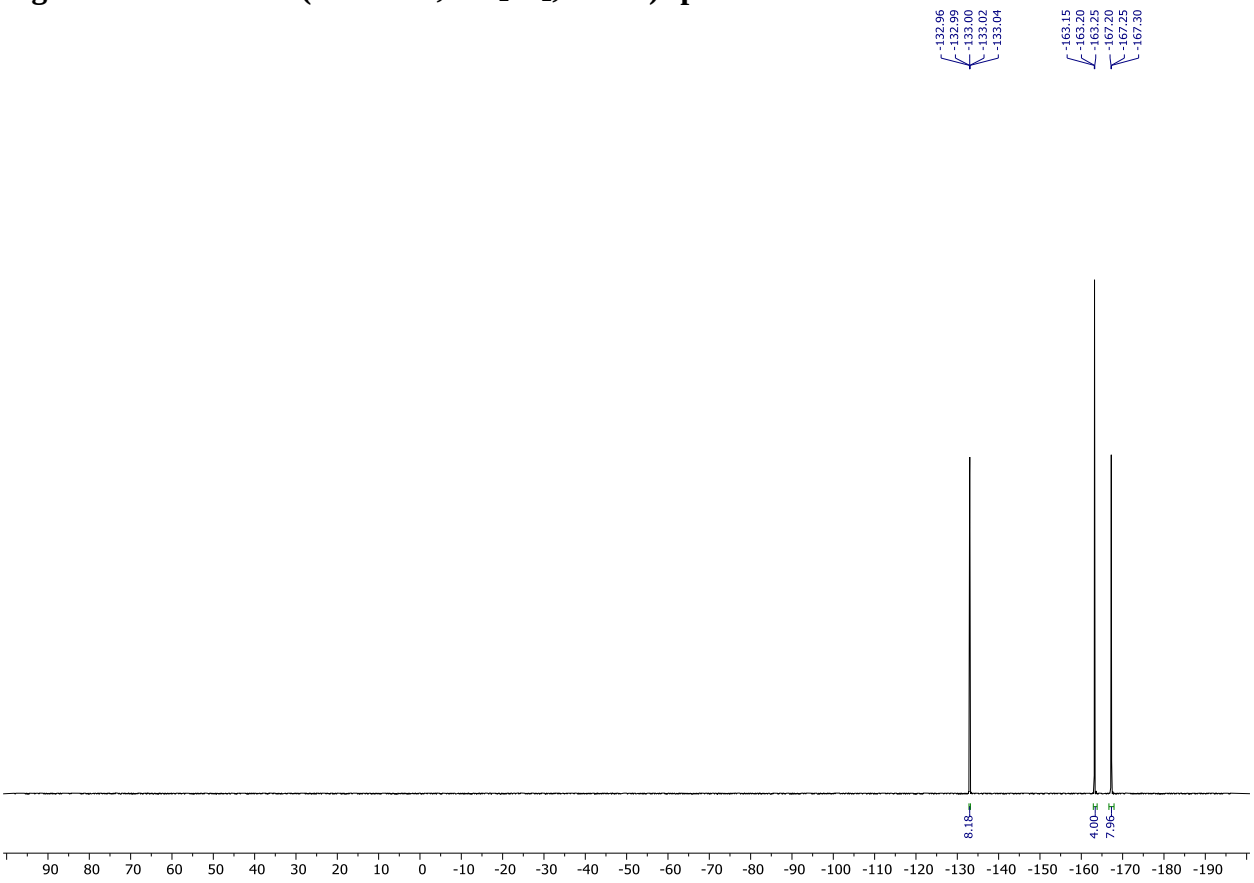
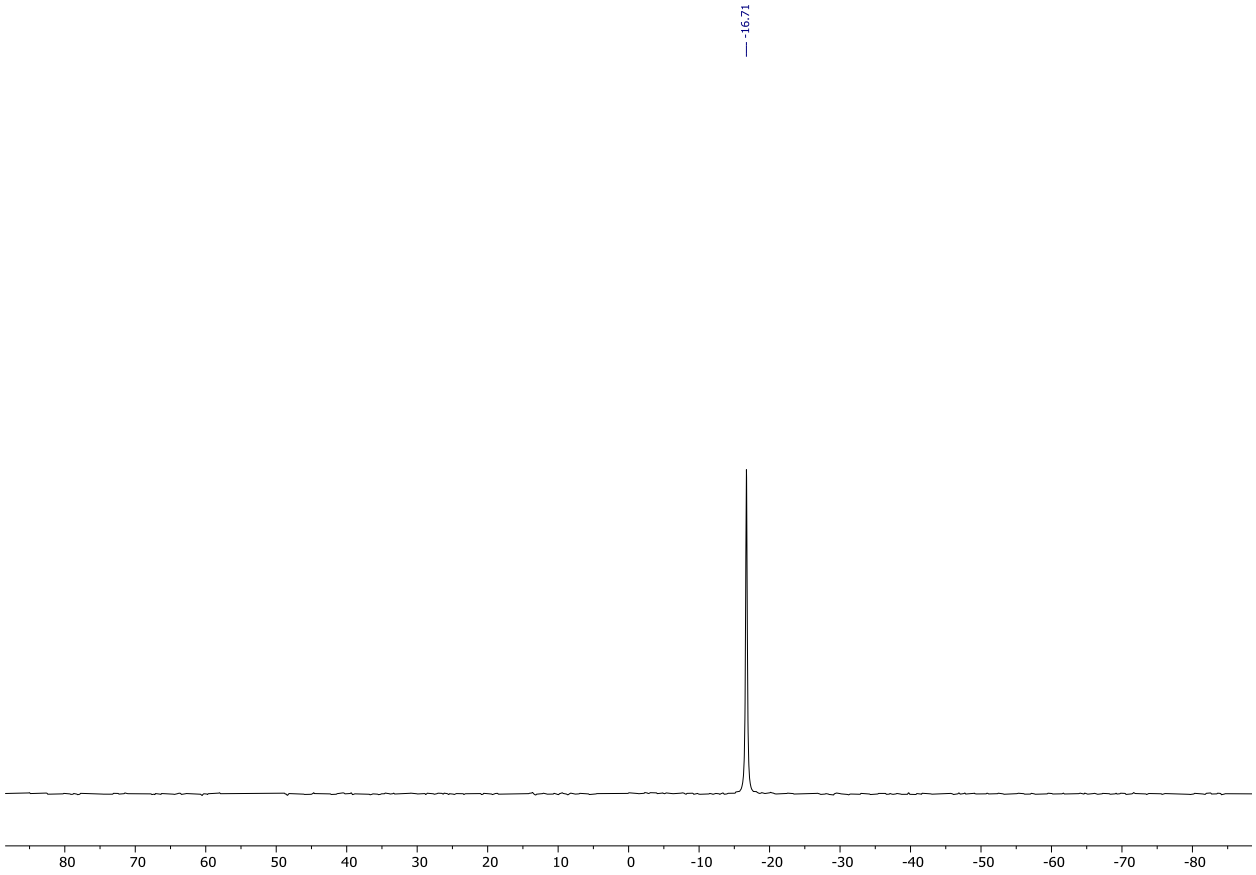


Figure S34. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of compound 8.



NMR spectra for $[(CH_2PPh_2)_2NCH_2CHCH_2][B(C_6F_5)_4]_2$ (9)

Figure S35. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of 9.

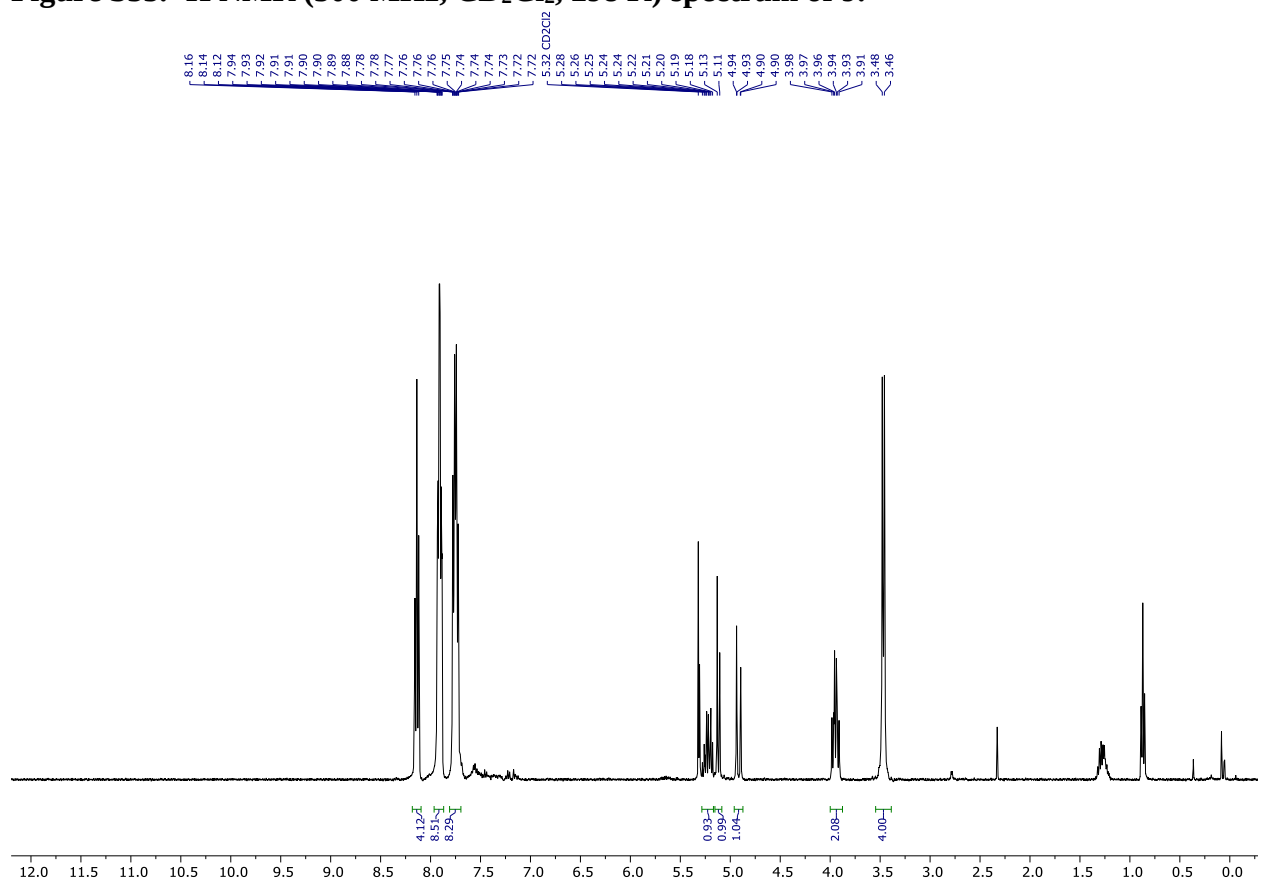


Figure S36. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 9.

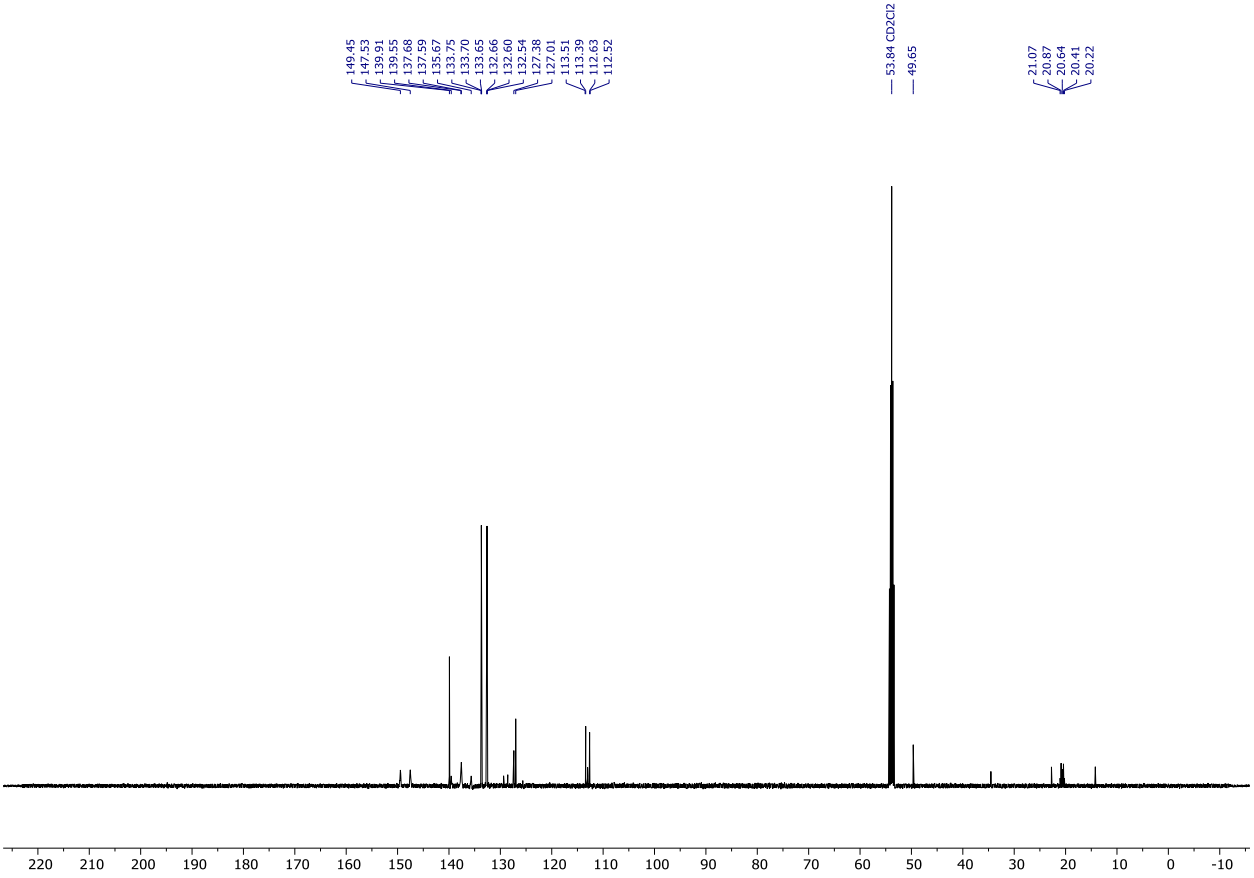


Figure S37. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 9.

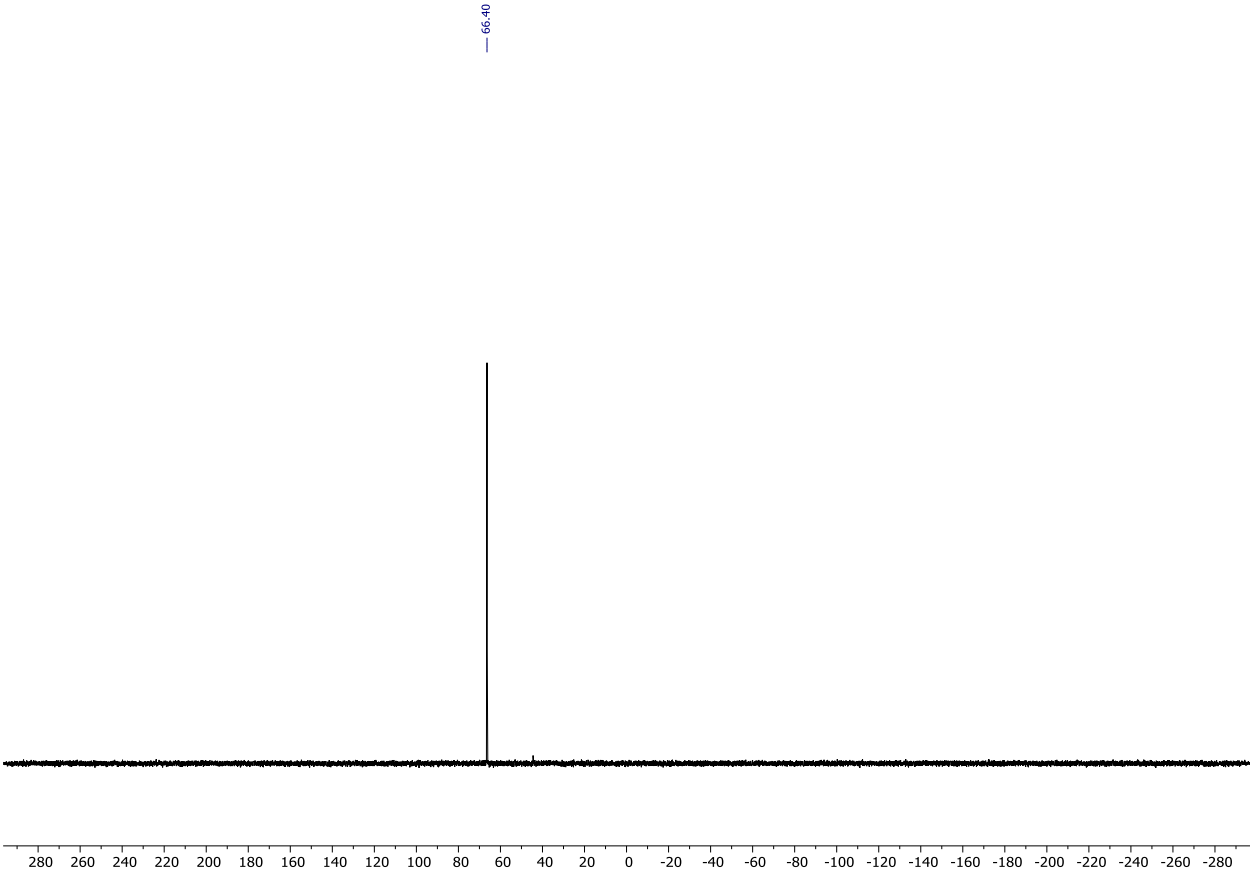


Figure S38. ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K) spectrum of 9.

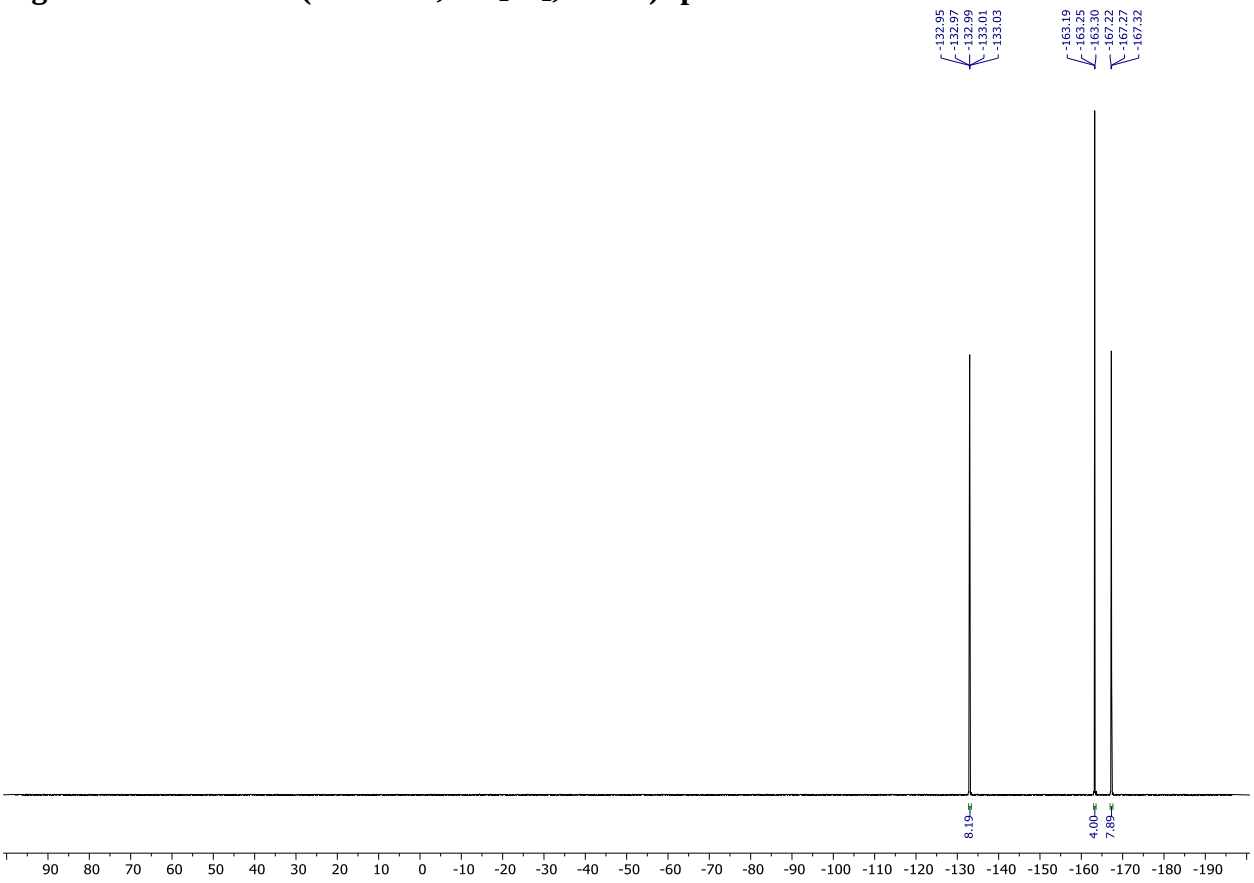
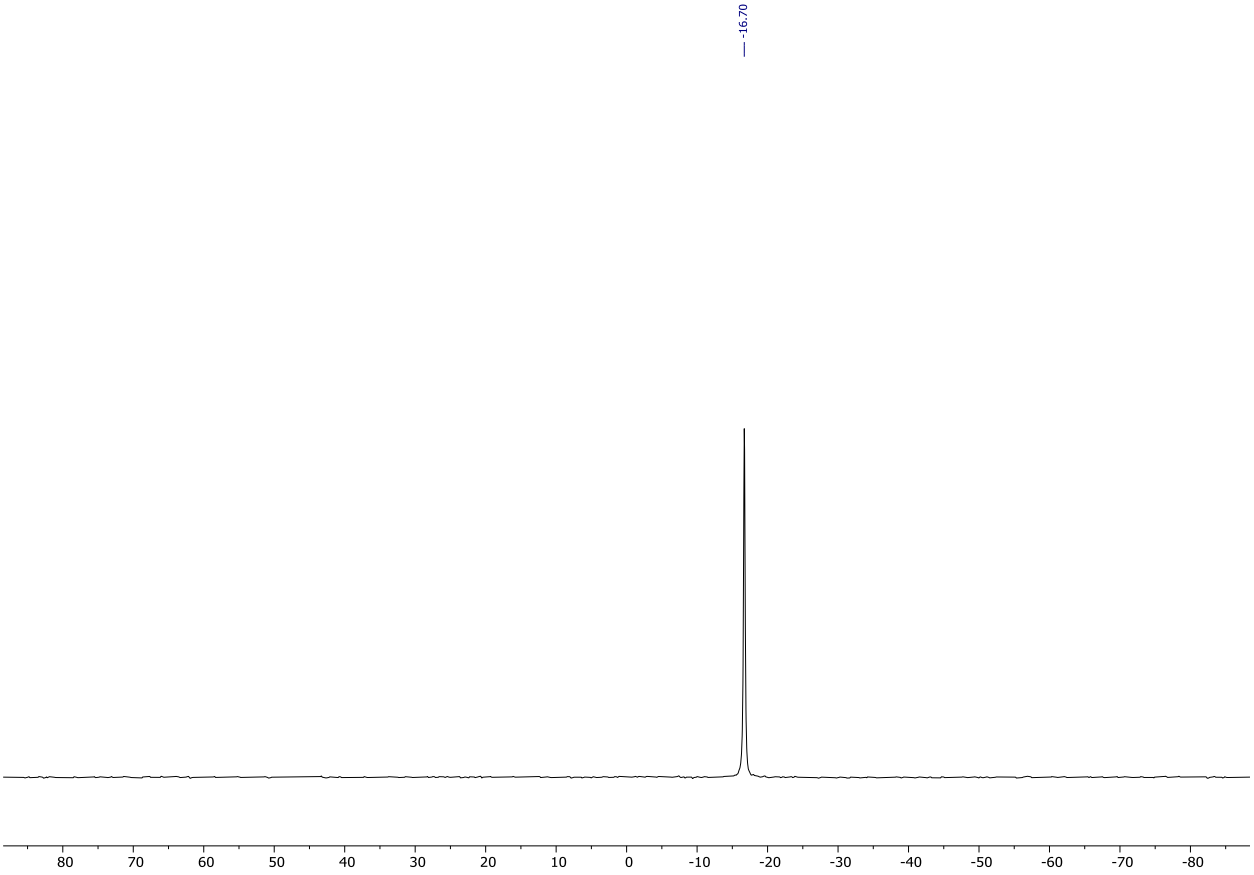


Figure S39. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of compound 9.



NMR spectra for $[(CH_2PPh_2)_2NCH_2Ph][B(C_6F_5)_4]_2$ (10)

Figure S40. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of 10.

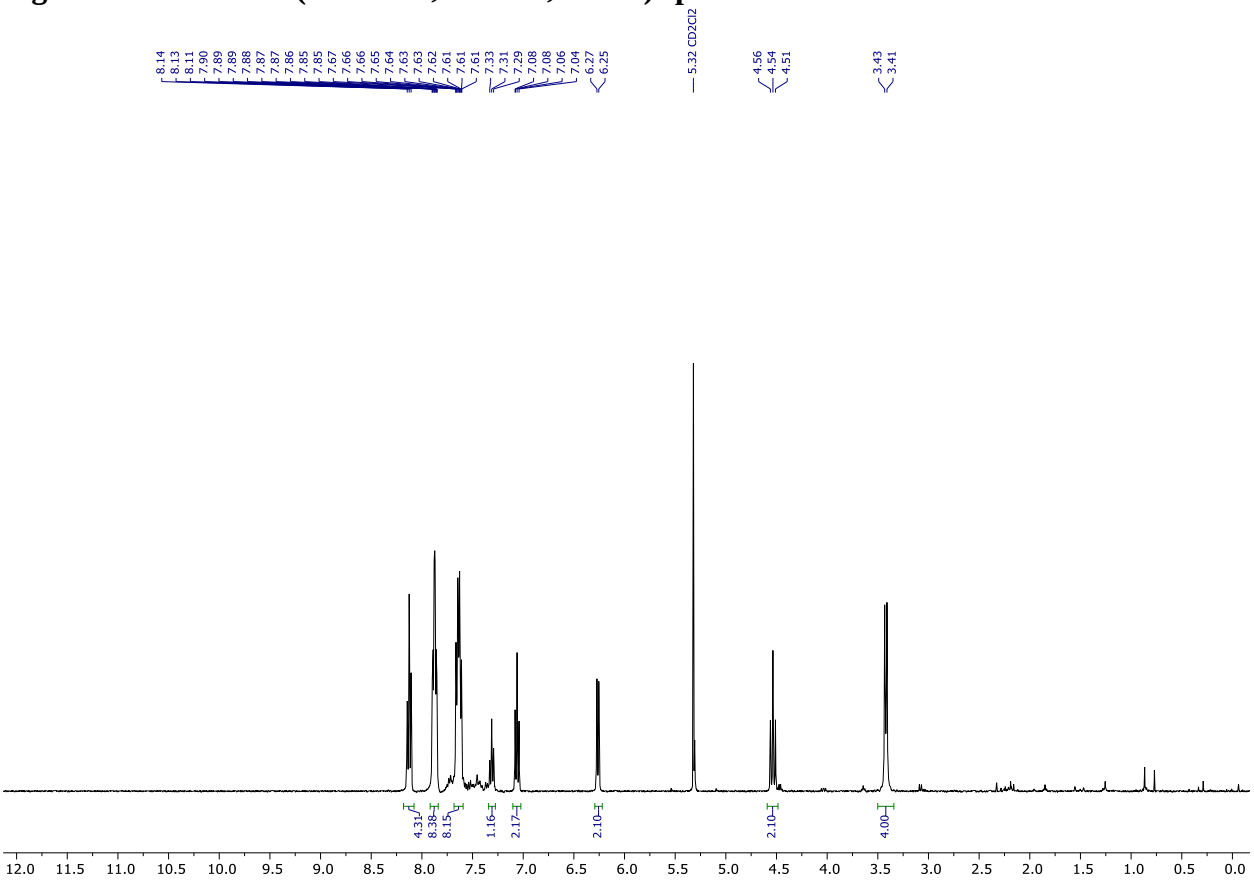


Figure S41. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of 10.

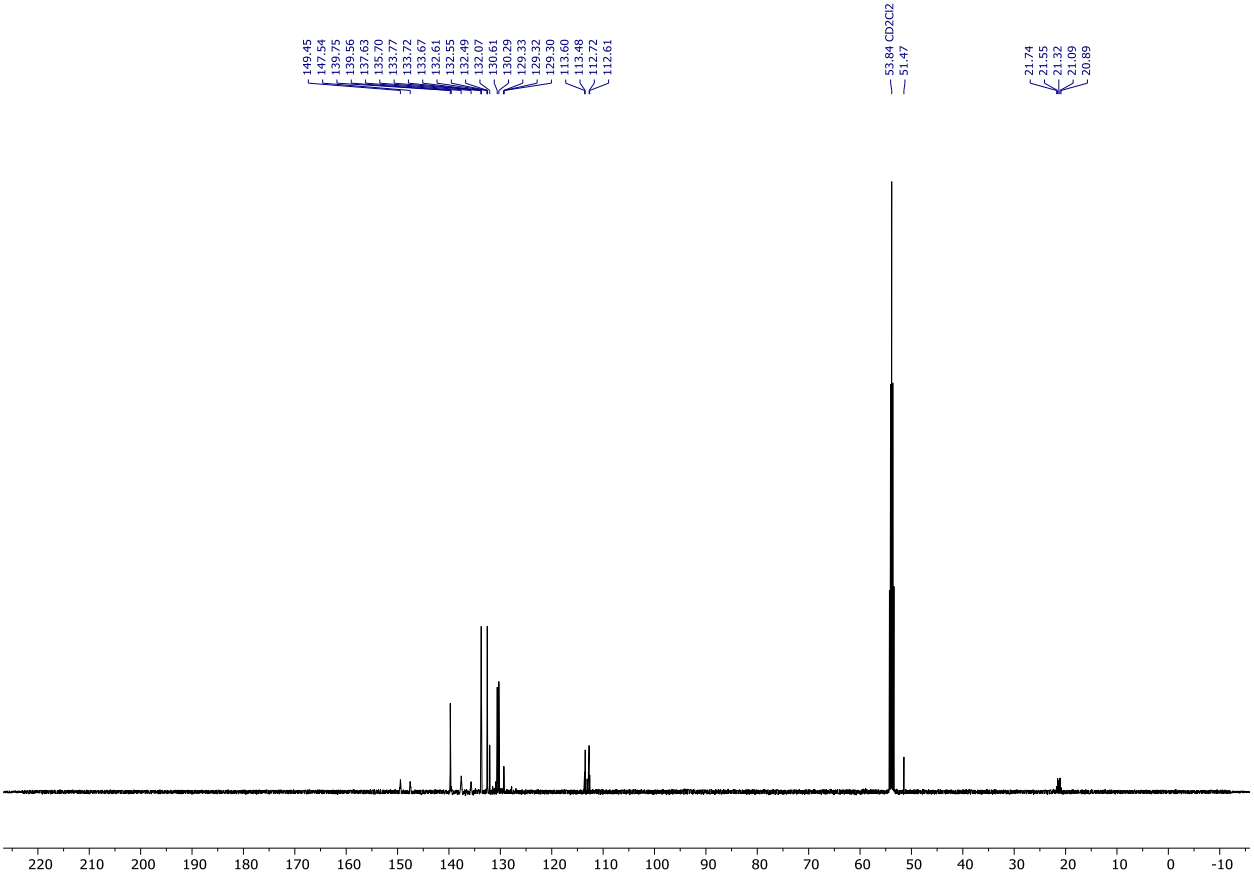


Figure S42. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298K) spectrum of 10.

Figure S43. ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K) spectrum of 10.

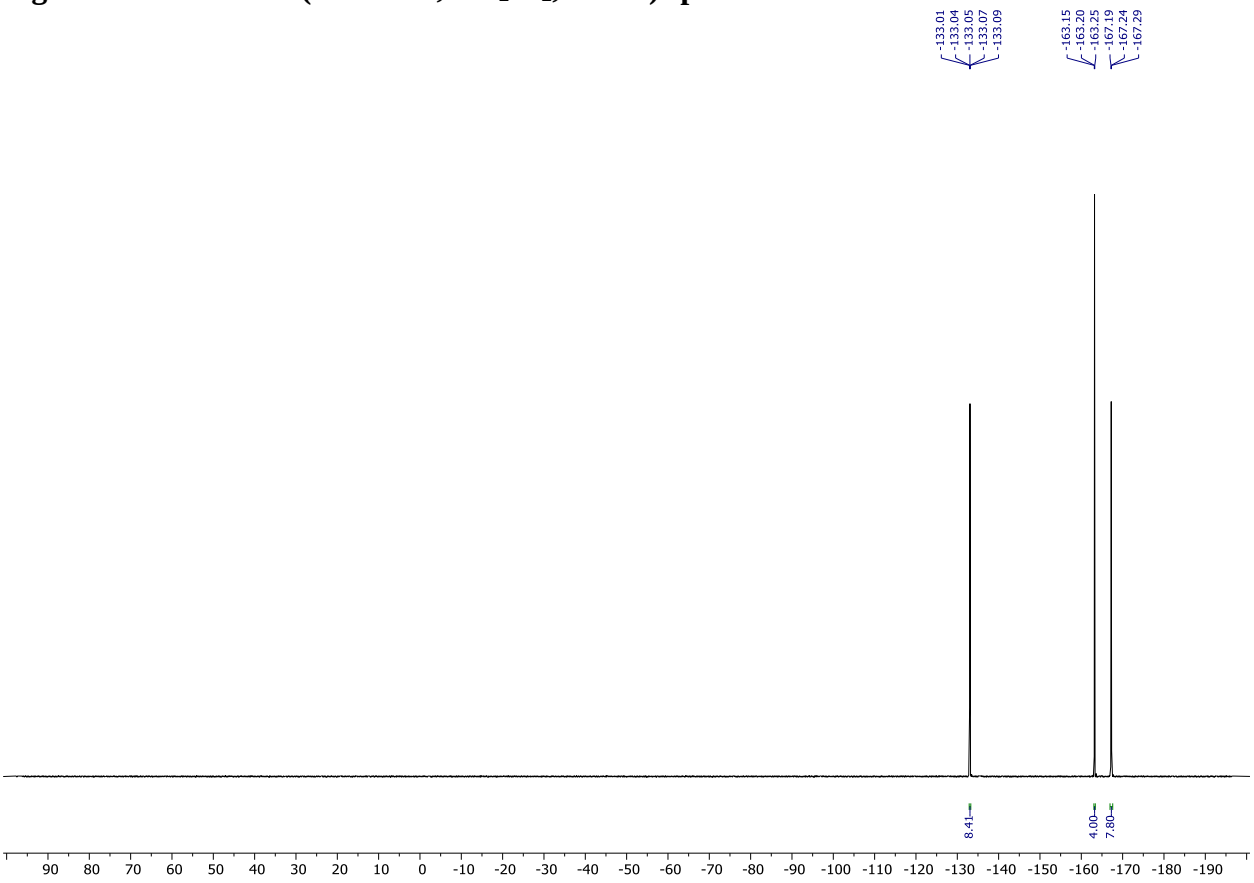
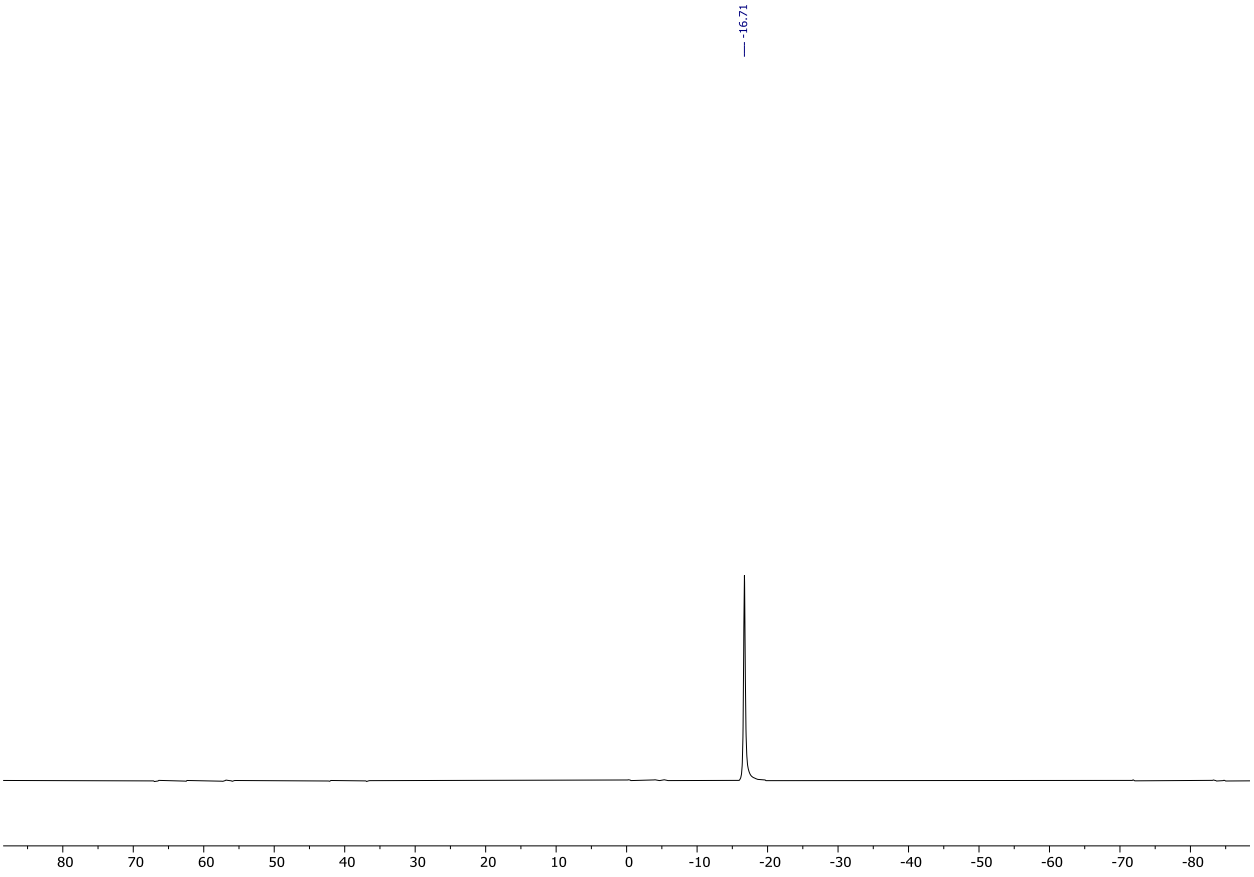


Figure S44. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of compound 10.



NMR spectra for the reaction of 8 with [nBu$_4$N][Cl]

Figure S45. A) ^{1}H NMR spectrum in CH_2Cl_2 of crude reaction mixture (A) and reaction mixture after exposure to high vacuum (B).

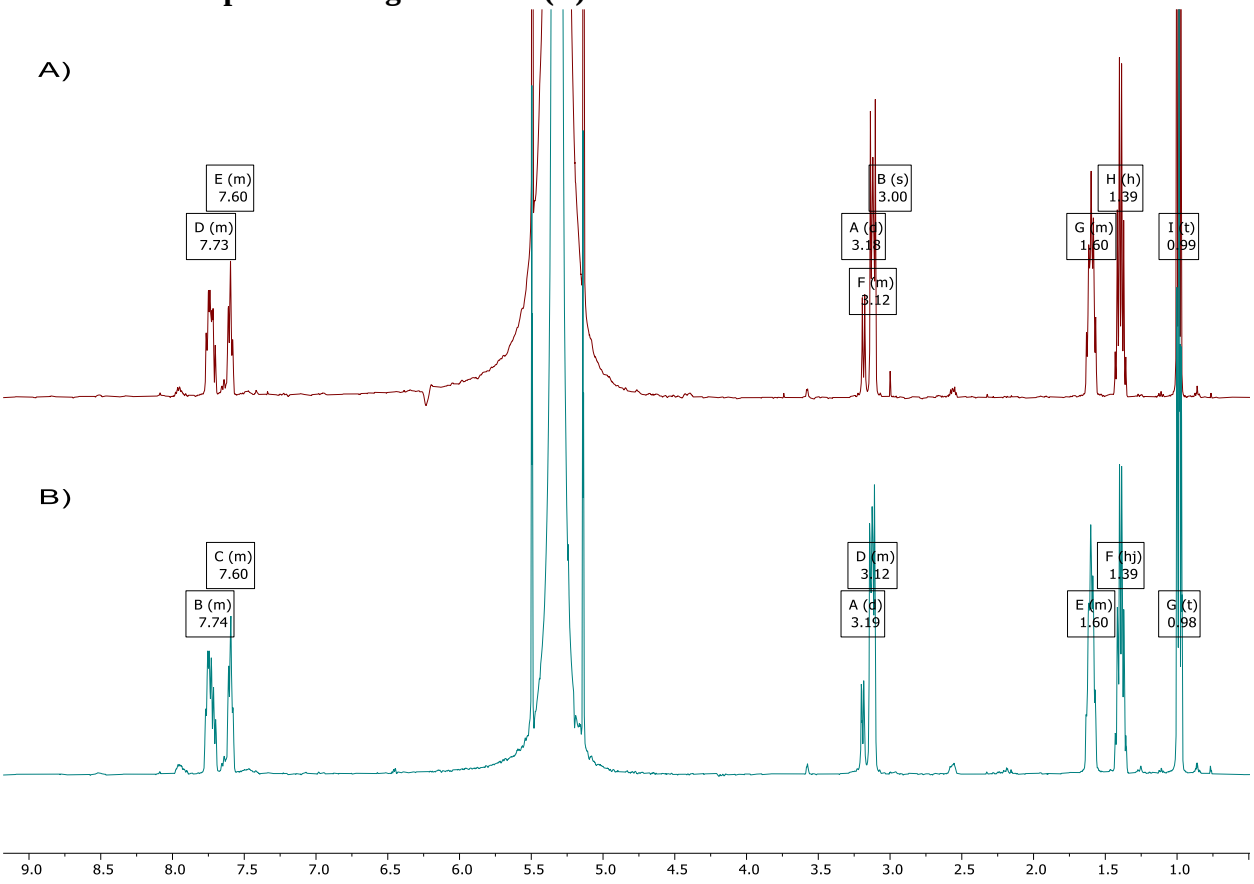
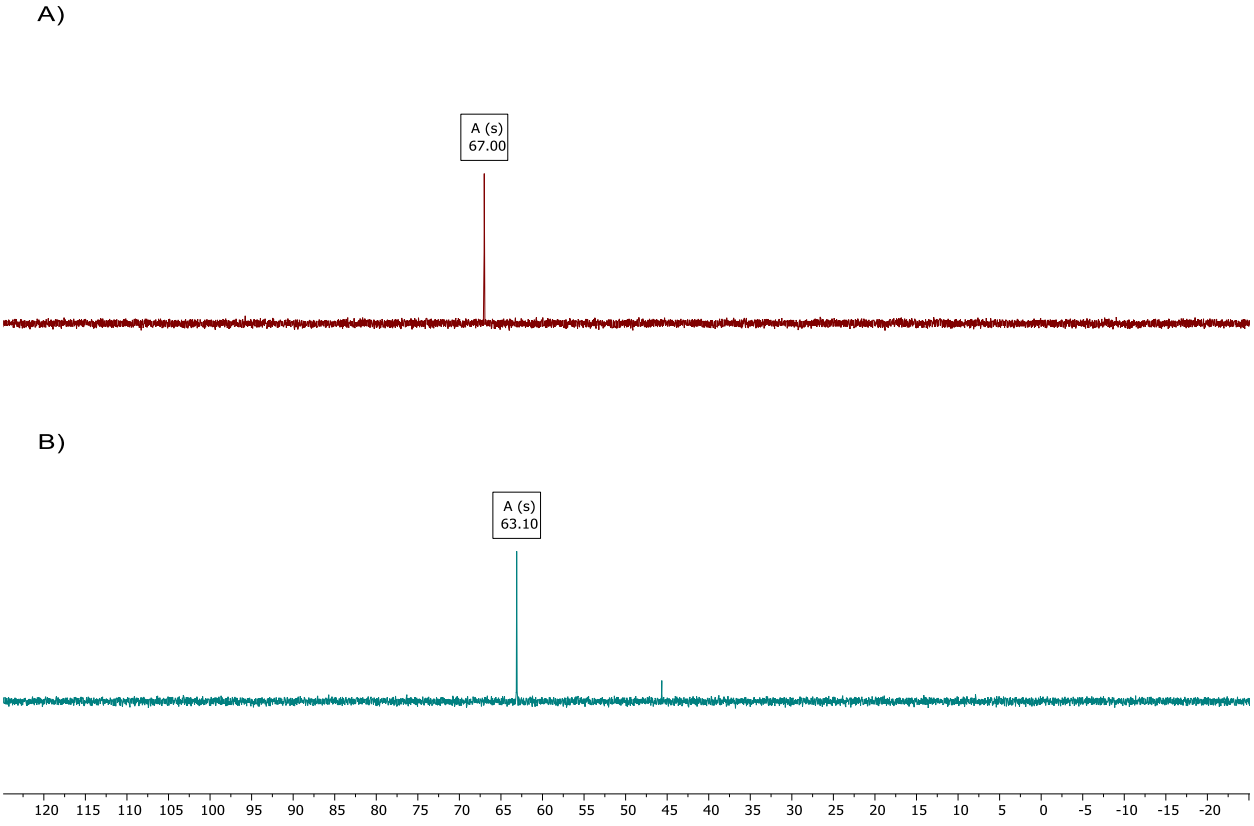


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum in CH_2Cl_2 of 8 (A) and reaction mixture indicating formation of 11 (B).



NMR spectra for the reaction of 9 with [nBu_4N][Cl]

Figure S47. A) ^{1}H NMR spectrum in CD_2Cl_2 of crude reaction mixture (A) and reaction mixture spiked with C_3H_5Cl (B).

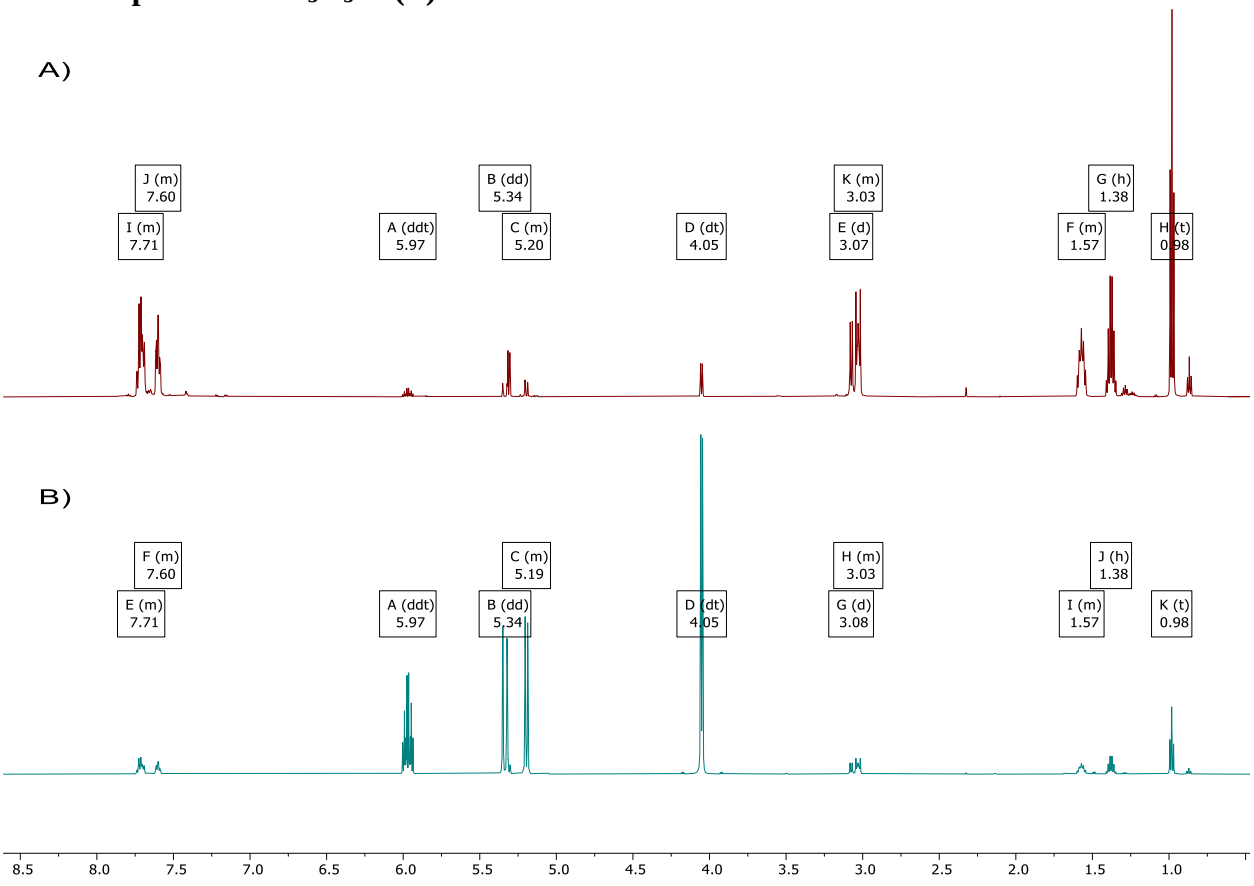
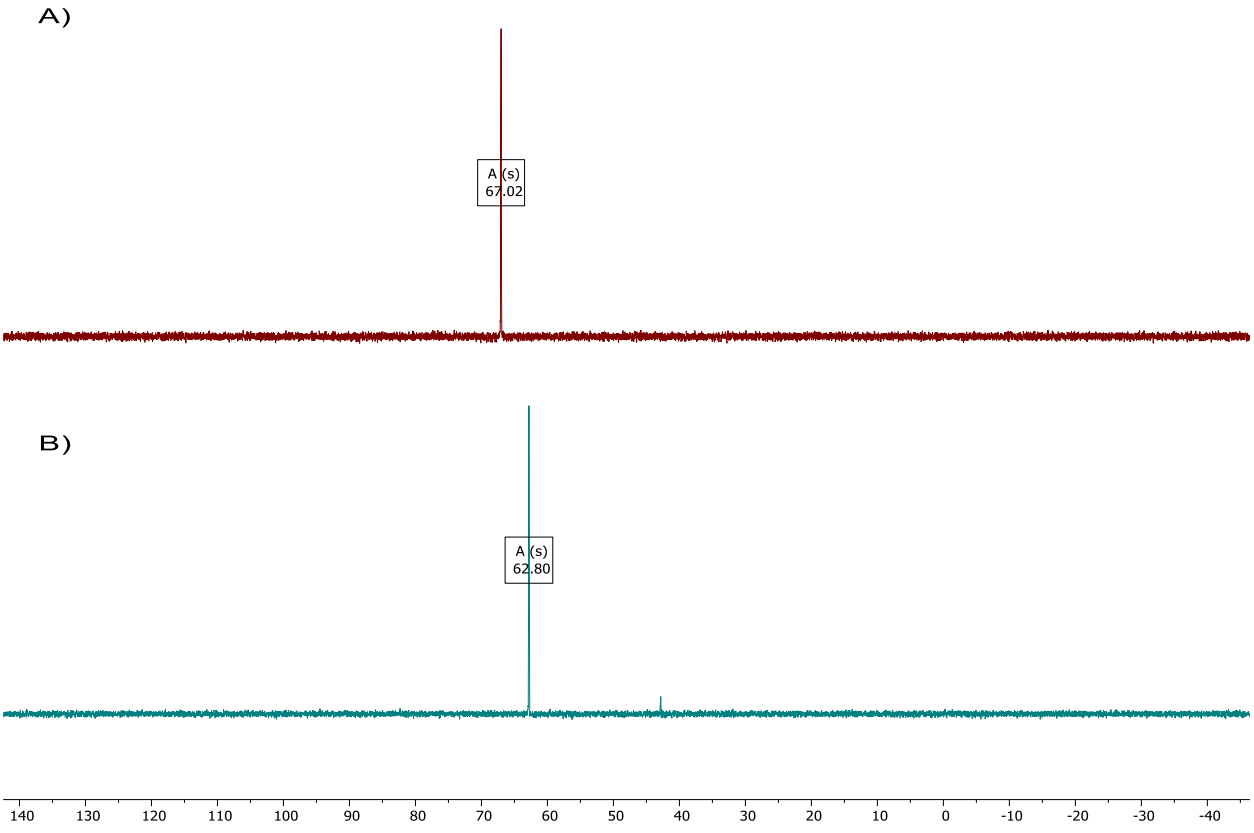


Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum in CH_2Cl_2 of 9 (A) and reaction mixture indicating formation of 11 (B).



NMR spectra for the reaction of 10 with [nBu$_4$N][Cl]

Figure S49. A) ^{1}H NMR spectrum in CH_2Cl_2 of of crude reaction mixture (A) and reaction mixture spiked with BnCl (B).

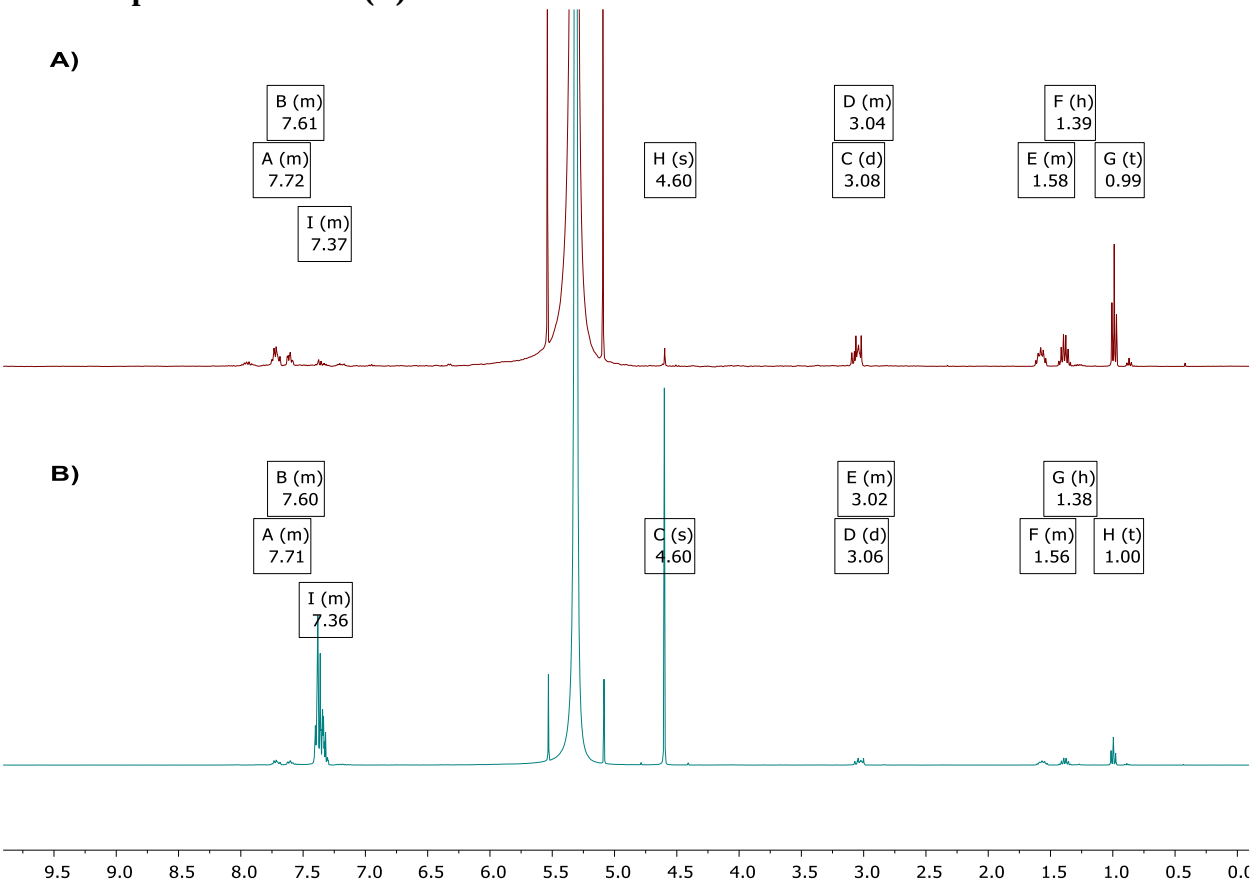


Figure S50. $^{31}P\{^{1}H\}$ NMR spectrum in CH_2Cl_2 of 10 (A) and reaction mixture indicating formation of 11 (B).