Electronic Supporting Information

Experimental and Computational Exploration of the Dynamic Behavior of (PNP)BF_2, a Boron Compound Supported By an Amido/Bis(Phosphine) Pincer Ligand

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General considerations. Unless otherwise noted, all manipulations and reactions were performed under argon, using standard glove box and Schlenk line techniques. Diethyl ether, toluene, pentane, and C_6D_6 were dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. CD_2Cl_2 was dried over CaH_2, vacuum transferred and stored over molecular sieves in an Ar-filled glove box. ^{Me}(PNP)H (**4**) was prepared according to literature procedure.[1] All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 300 (^{1}H NMR, 299.951 MHz; ^{13}C NMR, 75.426 MHz; ^{31}P NMR, 121.422 MHz; ^{19}F NMR, 282.211 MHz), Varian NMRS 500 (^{1}H NMR, 499.682 MHz; ^{13}C NMR, 125.660 MHz; ^{31}P NMR, 202.265 MHz; ^{19}F NMR, 470.111 MHz) and Varian iNova 400 (^{11}B NMR, 128.191 MHz). Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR, the residual solvent peak was used to reference the spectra. ^{31}P NMR spectra were referenced using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced using CF_3CO_2H at δ -78.5 ppm. ^{11}B NMR spectra were referenced using Et_2OBF_3 at δ 0 ppm. Temperatures reported for ^{11}B{1H} NMR spectra are based on readings from the Varian iNova 400 temperature controller. Temperatures reported for ^{31}P{^{1}H}, ^{19}F and ^{1}H NMR spectra were evaluated using a methanol standard. Crystallographic data were collected on a Bruker-Nonius Kappa Apex II CCD instrument. Elemental analysis was performed by Complete Analysis Laboratories Inc., Parsippany, NJ, USA.

Irradiation of 6. A concentrated solution of **6** was prepared in C_6D_6 in a J. Young NMR tube. The tube was placed in a UV box and radiated at 350 nm overnight. When exposed to the UV light, blue luminescence was observed. The radiated solution was bright orange in color and precipitation was observed after 16 h. NMR spectra displayed evidence of significant decomposition.

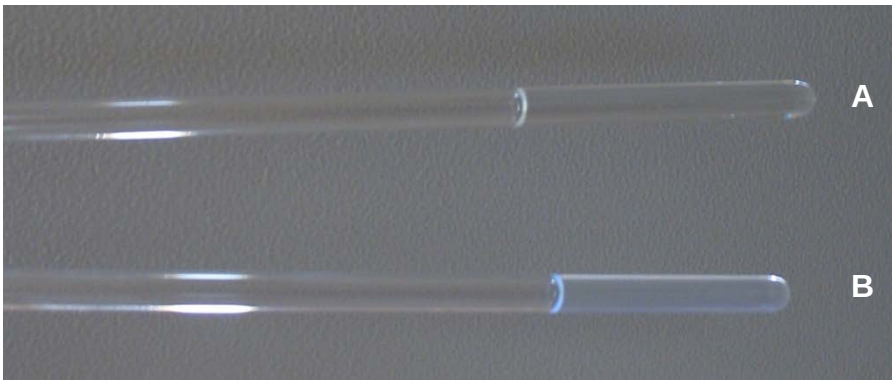

Figure S1. Comparison of luminescence observed for toluene solution of **6,** (B), against toluene control, (A), under ambient light.

Figure S2. C_6D_6 solution of **6** in UV box, 350 nm.

Room Temperature $^{11}B\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra

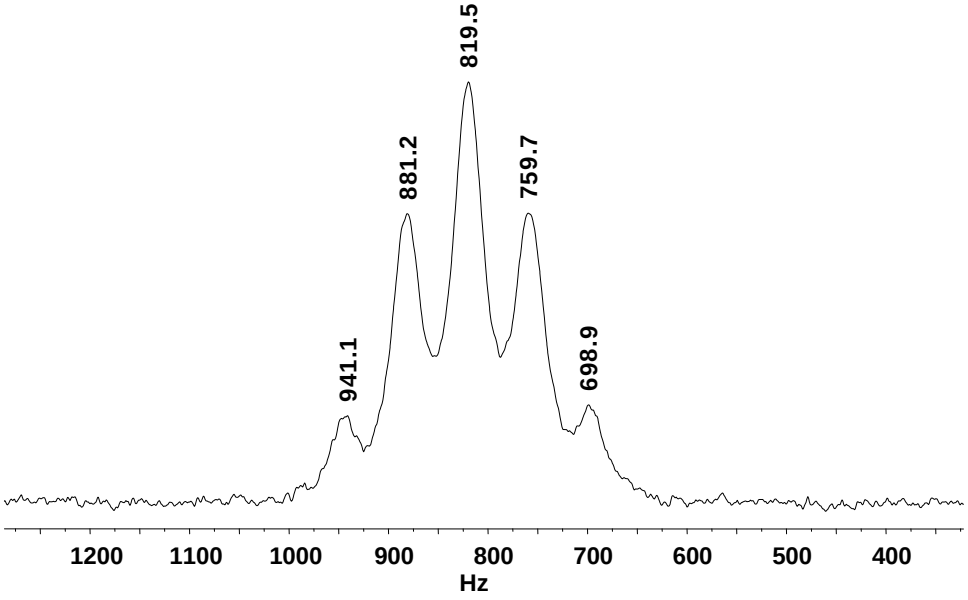

Figure S3. $^{11}B\{^1H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C measured on a 400 MHz Varian iNova (^{11}B NMR frequency of 128.191 MHz).

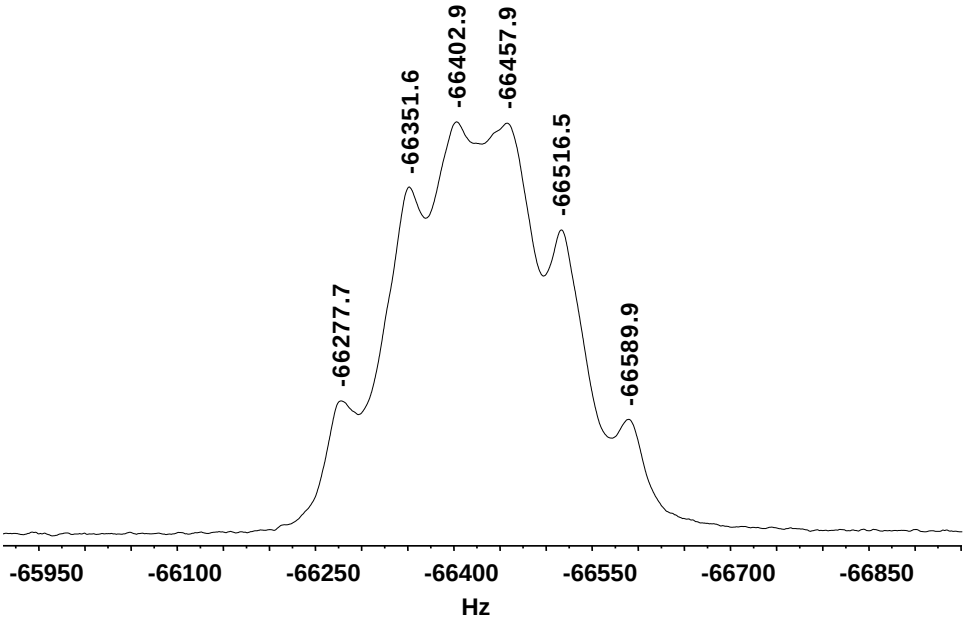

Figure S4. ^{19}F NMR spectrum of **6** in CD_2Cl_2 at 23°C measured on a 500 MHz Varian NMRS (^{19}F NMR frequency of 470.111 MHz).

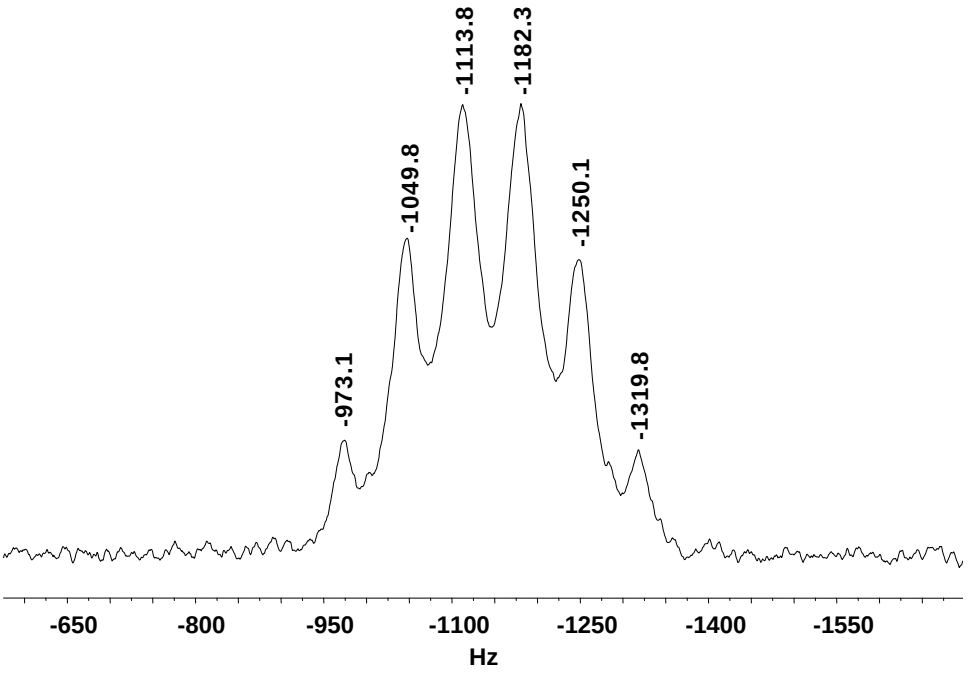

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C measured on a 500 MHz Varian NMRS (^{31}P NMR frequency of 202.265 MHz).

Determination of heteronuclear coupling constants, $J_{P\text{-}B}$ and $J_{P\text{-}F}$, in 23°C $^{31}P\{^{1}H\}$ NMR spectrum using WinDNMR

Using the WinDNMR[2] simulation program, coupling constants for $^{31}P\{^{1}H\}$ were determined to be, $J_{P\text{-}B}$ = 68 ± 4 Hz and $J_{P\text{-}F}$ = 72 Hz ± 4 Hz. As shown below, three parameters were independently adjusted. The line width (Wa) was adjusted between 35-45 Hz. J_{AX} and J_{BX} were used to mimic the coupling to ^{11}B and J_{CX} was used to mimic the coupling to ^{19}F.

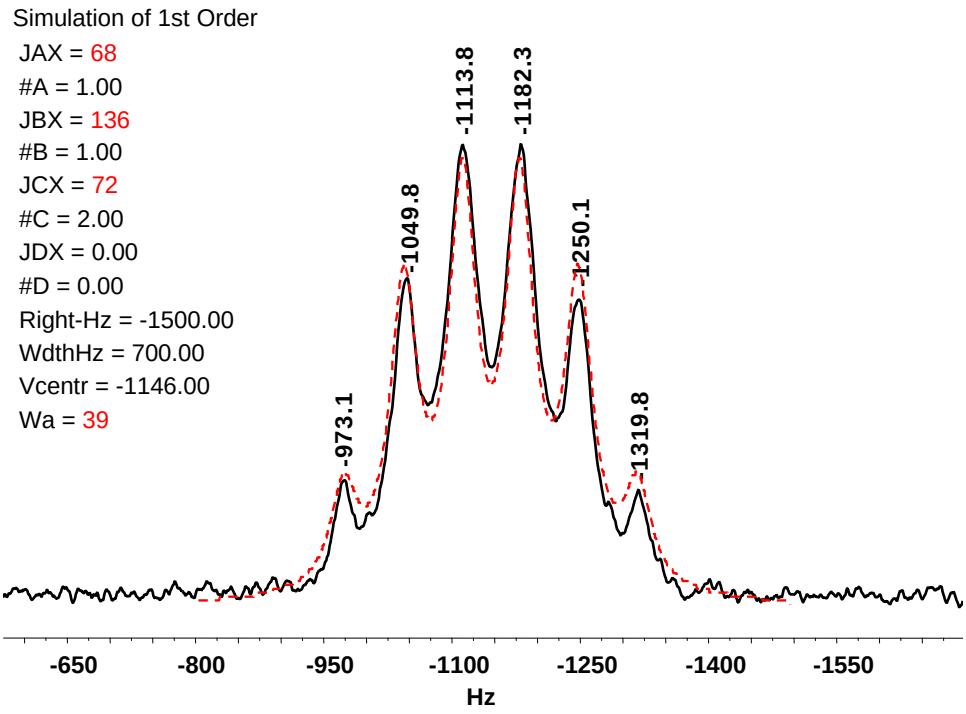

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectrum using ^{31}P NMR frequency of 202.265 MHz and $J_{P\text{-}B}$ = 68 Hz, $J_{P\text{-}F}$ = 72 Hz, Wa = 39 Hz.

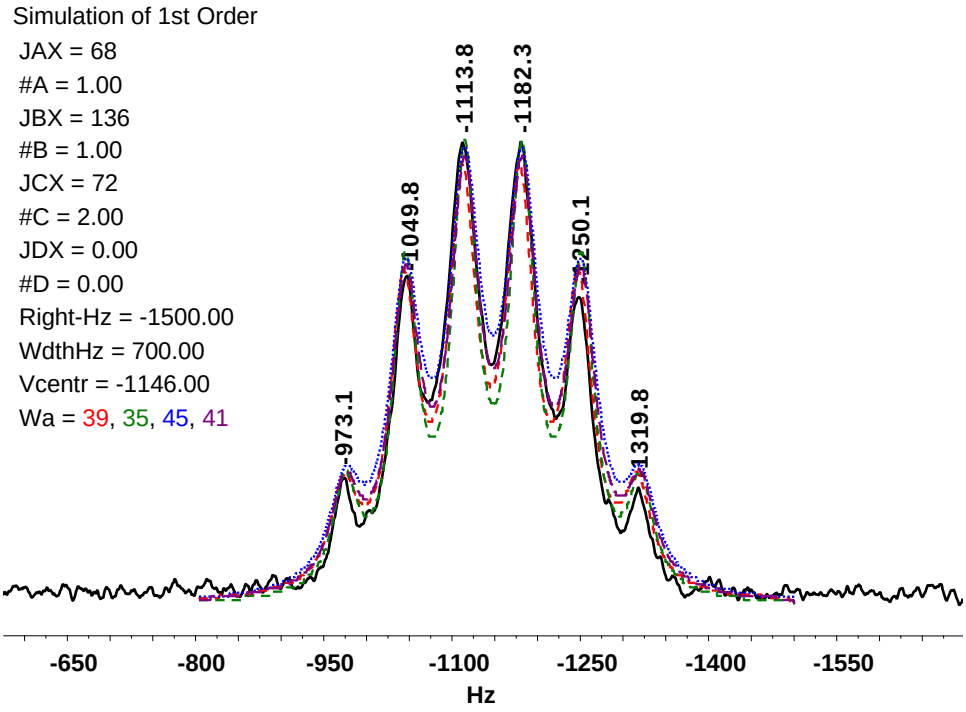

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{31}P NMR frequency of 202.265 MHz and $J_{P\text{-}B}$ = 68 Hz, $J_{P\text{-}F}$ = 72 Hz, Wa = 39-41 Hz.

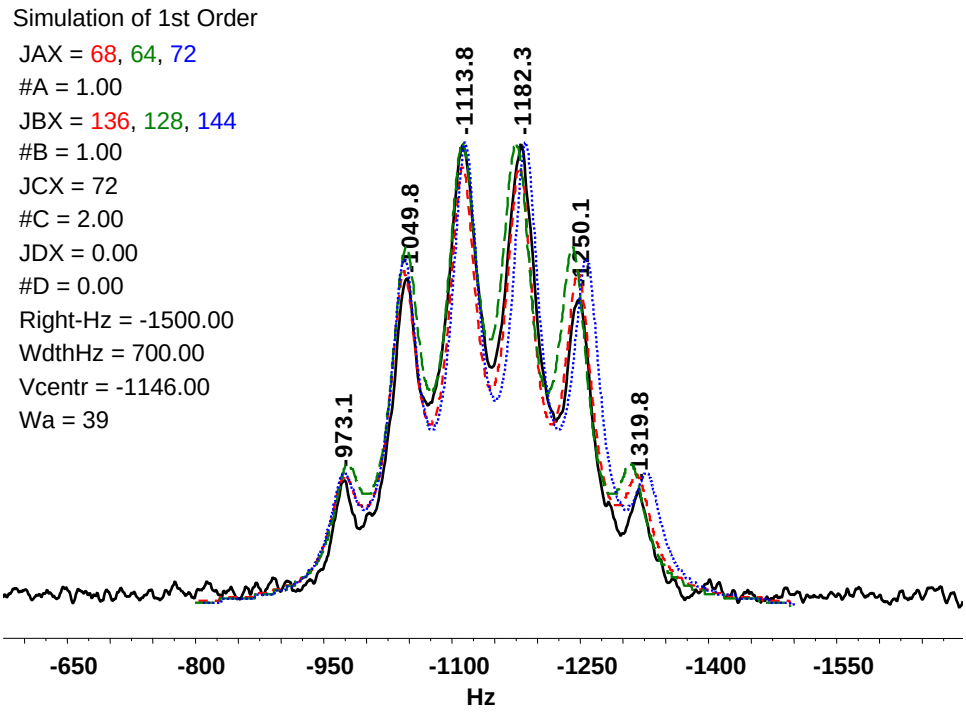

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{31}P NMR frequency of 202.265 MHz and $J_{P\text{-}B}$ = 64-72 Hz, $J_{P\text{-}F}$ = 72 Hz, Wa = 39 Hz.

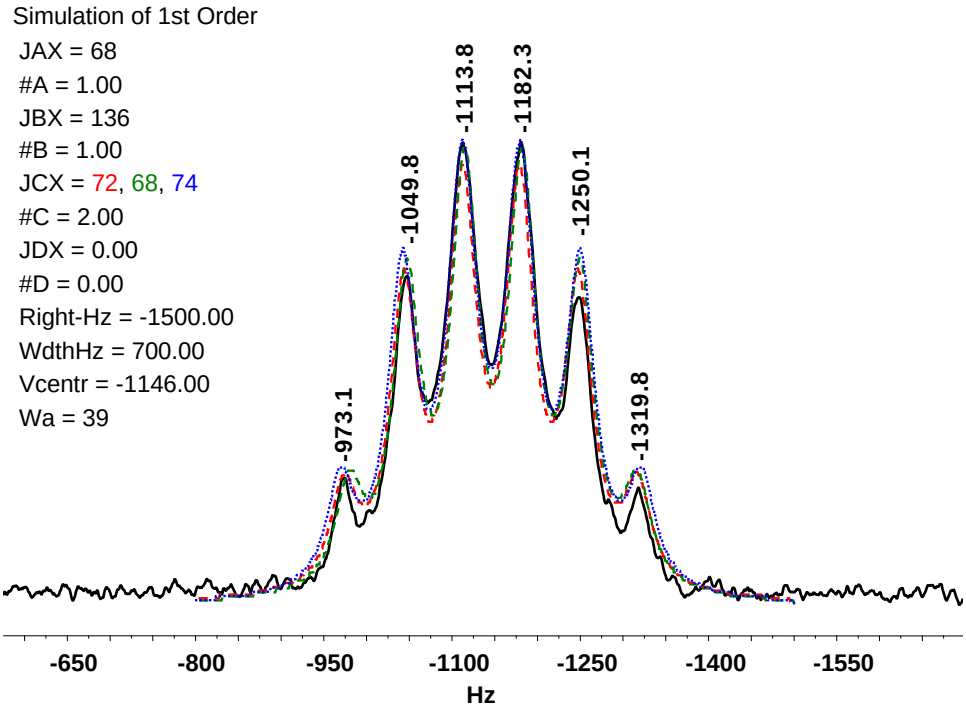

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{31}P NMR frequency of 202.265 MHz and $J_{P\text{-}B}$ = 68 Hz, $J_{P\text{-}F}$ = 68-74 Hz, Wa = 39 Hz.

Determination of heteronuclear coupling constants, J_{F-B} and J_{P-F}, in 23°C ^{19}F NMR spectrum using WinDNMR

Using the WinDNMR simulation program, coupling constants for ^{19}F were determined to be approximately, J_{F-B} = 55 ± 5 Hz and J_{P-F} = 75 ± 5 Hz. As shown below, three parameters were independently adjusted. The line width (Wa) was adjusted between 35-45 Hz. J_{AX} and J_{BX} were used to mimic the coupling to ^{11}B and J_{CX} was used to mimic the coupling to ^{31}P.

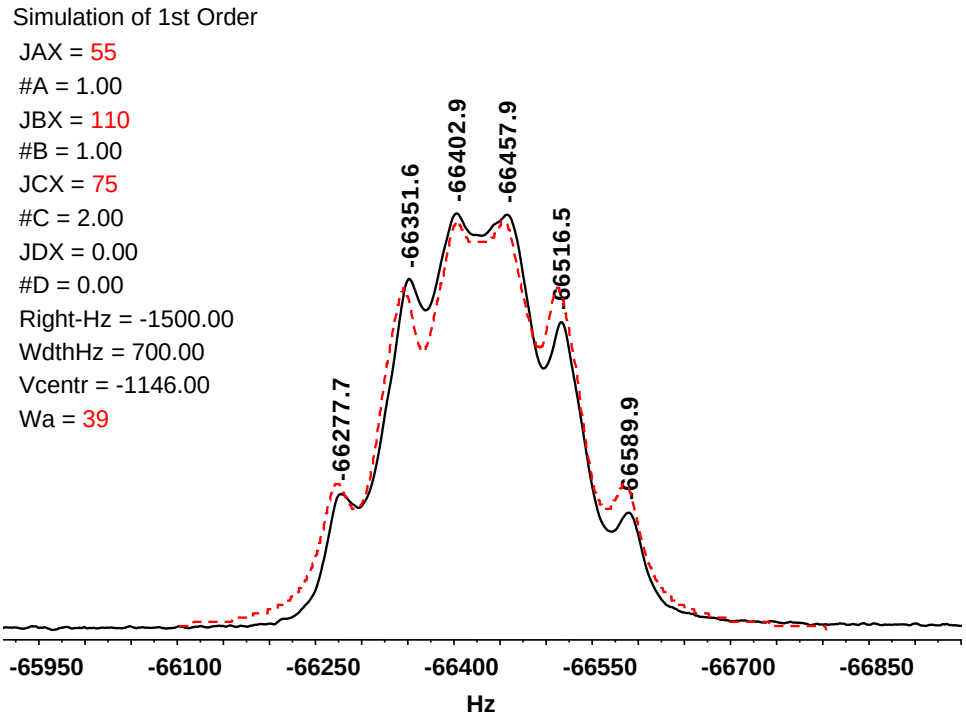

Figure S10. ^{19}F NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectrum using ^{19}F NMR frequency of 470.111 MHz and J_{F-B} = 55 Hz, J_{P-F} = 75 Hz, Wa = 39 Hz.

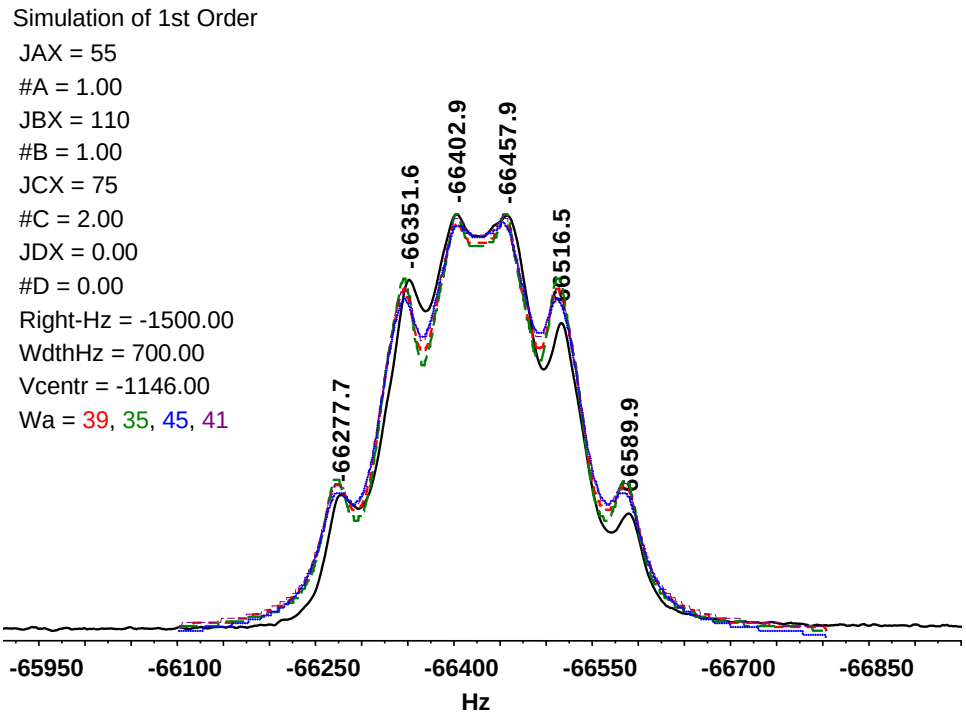

Figure S11. ^{19}F NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{19}F NMR frequency of 470.111 MHz and $J_{F\text{-}B}$ = 55 Hz, $J_{P\text{-}F}$ = 75 Hz, Wa = 35-45 Hz.

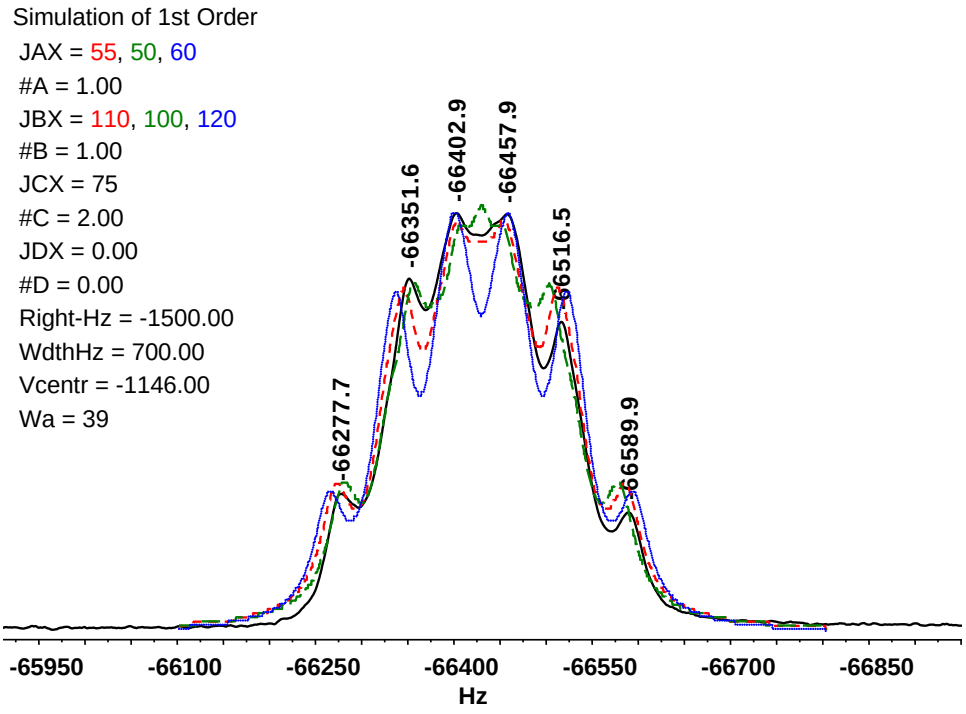

Figure S12. ^{19}F NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{19}F NMR frequency of 470.111 MHz and $J_{F\text{-}B}$ = 50-60 Hz, $J_{P\text{-}F}$ = 75 Hz, Wa = 39 Hz.

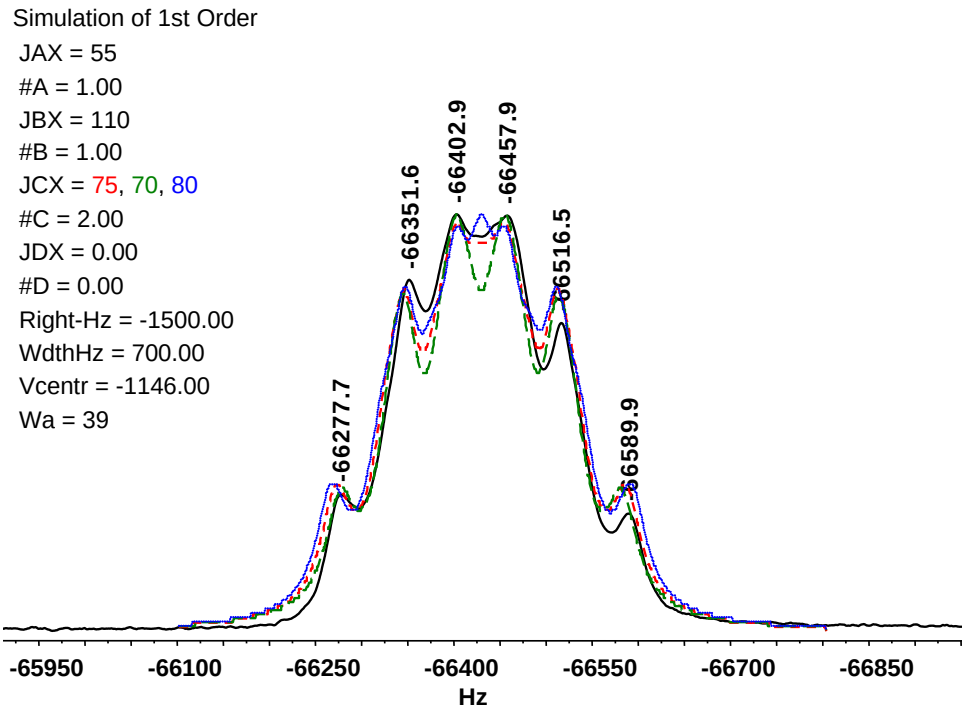

Figure S13. ^{19}F NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{19}F NMR frequency of 470.111 MHz and $J_{F\text{-}B}$ = 55 Hz, $J_{P\text{-}F}$ = 70-80 Hz, Wa = 39 Hz.

Determination of heteronuclear coupling constants, $J_{F\text{-}B}$ and $J_{P\text{-}B}$, in 23°C ^{11}B{^{1}H} NMR spectrum using WinDNMR

Using the WinDNMR simulation program, coupling constants for ^{11}B were determined to be approximately, $J_{F\text{-}B}$ = 57 ± 2 Hz and $J_{P\text{-}B}$ = 69 ± 2 Hz with the line width (Wa) = 30 Hz. J_{AX} and J_{BX} were used to mimic the coupling to ^{19}F and ^{31}P, respectively.

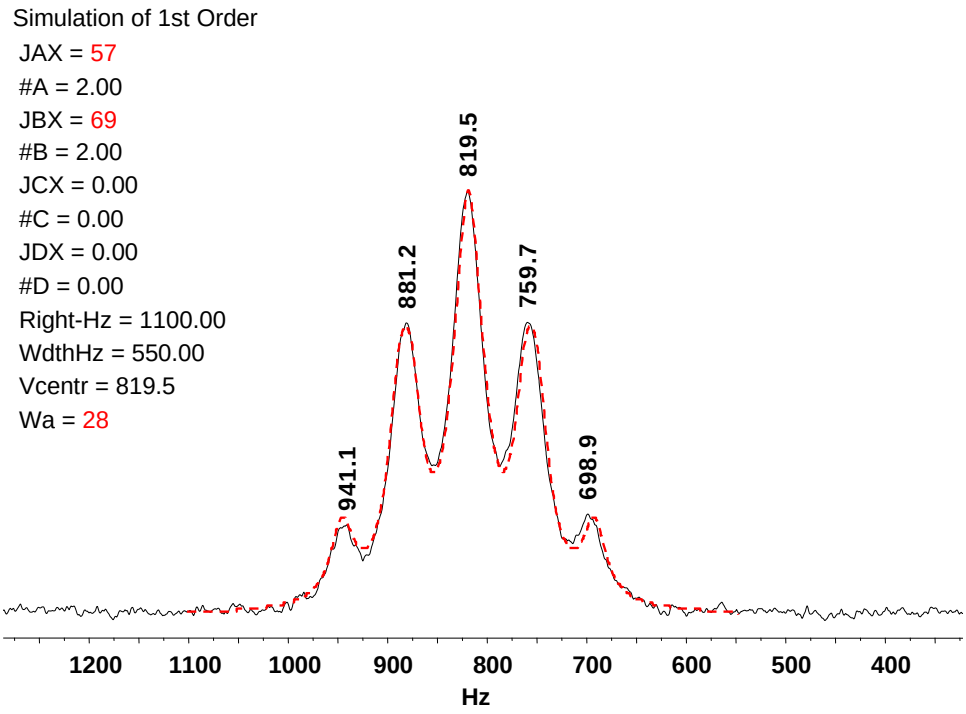

Figure S14. $^{11}B\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectrum using ^{11}B NMR frequency of 128.191 MHz and $J_{F\text{-}B}$ = 57 Hz, $J_{P\text{-}B}$ = 69 Hz, Wa = 28 Hz.

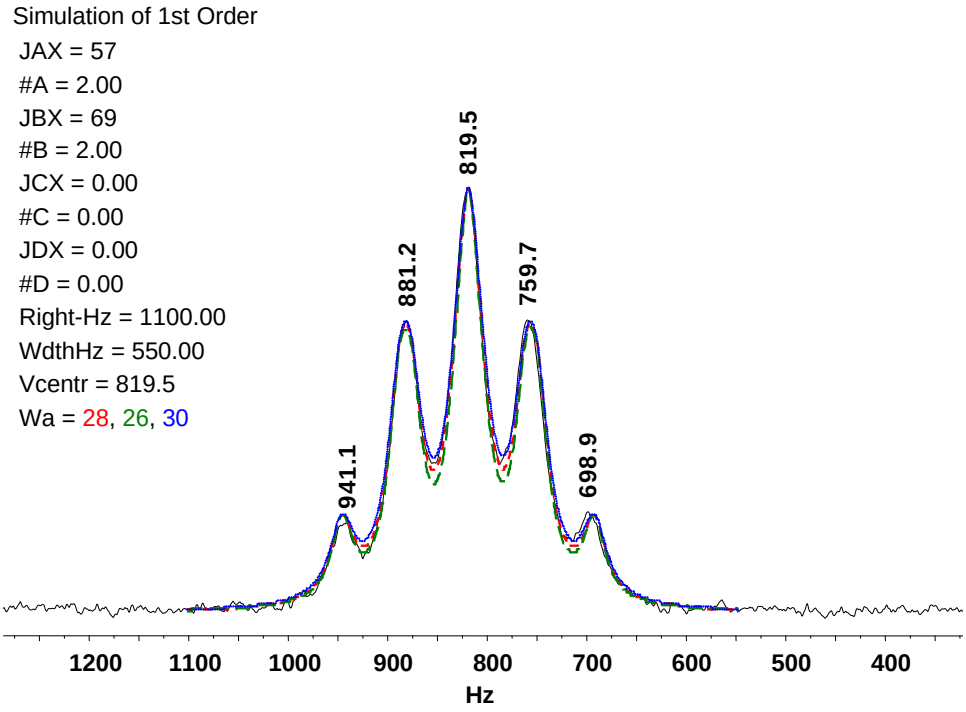

Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{11}B NMR frequency of 128.191 MHz and $J_{F\text{-}B}$ = 57 Hz, $J_{P\text{-}B}$ = 69 Hz, Wa = 26-30 Hz.

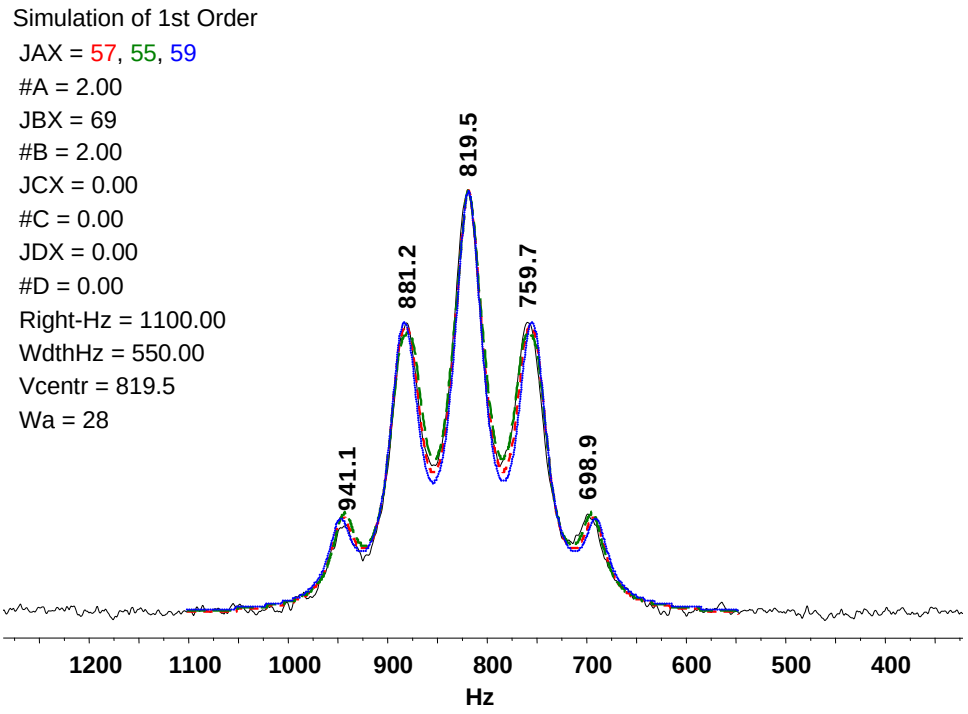

Figure S16. $^{11}B\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{11}B NMR frequency of 128.191 MHz and $J_{F\text{-}B}$ = 55-59 Hz, $J_{P\text{-}B}$ = 69 Hz, Wa = 28 Hz.

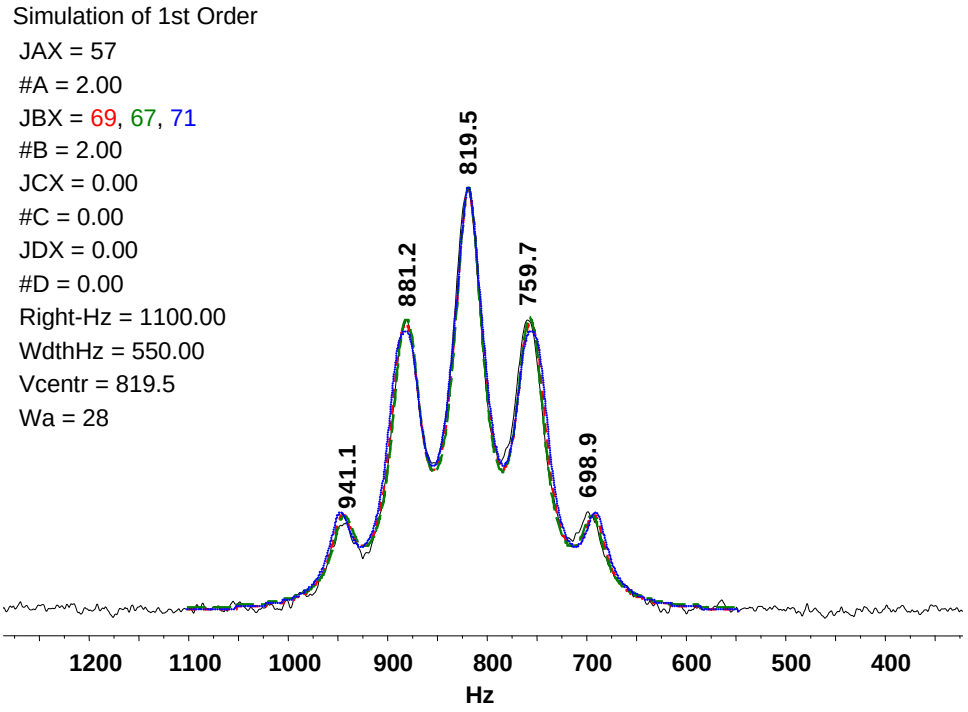

Figure S17. $^{11}B\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 23°C with overlay of simulated spectra using ^{11}B NMR frequency of 128.191 MHz and $J_{F\text{-}B}$ = 57 Hz, $J_{P\text{-}B}$ = 67-71 Hz, Wa = 28 Hz.

Exchange rate analysis of 6 from ^{1}H and ^{19}F low temperature NMR studies

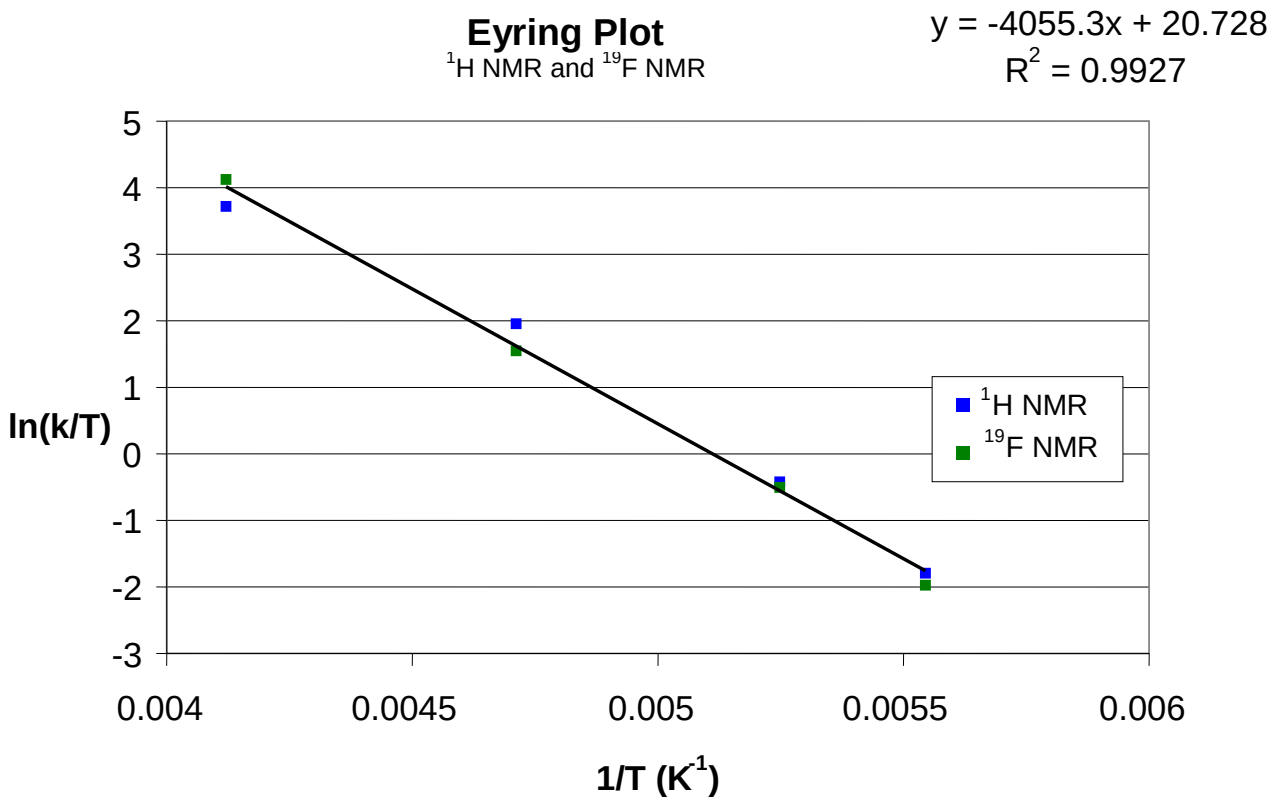

Figure S18. Eyring plot for exchange rate analysis from low temperature ^{1}H NMR and ^{19}F NMR studies of **6.**

$$\ln\left(\frac{k}{T}\right) = \left(\frac{-\Delta H^{\ddagger}}{T}\right)\left(\frac{1}{T}\right) + \ln\left(\frac{k_b}{h}\right) + \left(\frac{\Delta S^{\ddagger}}{R}\right)$$

k_b = 1.380 x 10^{-23} J•K^{-1}
h = 6.626 x 10^{-34} J•s
R = 8.3145 J•$K^{-1}$$mol^{-1}$

T (°C)	T (K)	Rate (s^{-1})	ln(k/T)	1/T (K^{-1})
-30.5	243	10000	3.72	0.0041
-60.9	212	1500	1.96	0.0047
-82.6	191	125	-0.42	0.0052
-92.8	180	30	-1.79	0.0055

Table S1. Exchange rates found for -31°C thru -93°C from low temperature ^{1}H NMR studies of **6** and corresponding Eyring plot parameters.

T (°C)	T (K)	Rate (s^{-1})	ln(k/T)	1/T (K^{-1})
-30.5	243	15000	4.12	0.0041
-60.9	212	1000	1.55	0.0047
-82.6	191	115	-0.50	0.0052
-92.8	180	25	-1.98	0.0055

Table S2. Exchange rates found for -31°C thru -93°C from low temperature ^{19}F NMR studies of **6** and corresponding Eyring plot parameters.

The approximate rates of fluxionality were determined from low temperature ^{1}H NMR (Table S1) and ^{19}F NMR studies (Table S2). An Eyring plot (Figure S18) was used to obtain the enthalpy and entropy of activation, $\Delta H^{\ddagger}$ = 8.1(3) kcal/mol and $\Delta S^{\ddagger}$ = -6.0(15) cal/mol·K, respectively. From these values, $\Delta G^{\ddagger}$ at 298 K was calculated to be 9.9(5) kcal/mol. The rates of exchange were determined through comparison of experimental data to simulated line shapes using gNMR software[3] with an estimated 10% error based on the sensitivity of the fits to changes in the rates of exchange. An estimated error of 1 K was taken for the temperature of the NMR probe calibrated with a methanol temperature standard. Errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined using the error propagation formulas presented by Girolami et al.[4]

Comparison of experimental ^{1}H NMR and ^{19}F NMR spectral data to simulated line shapes using gNMR software

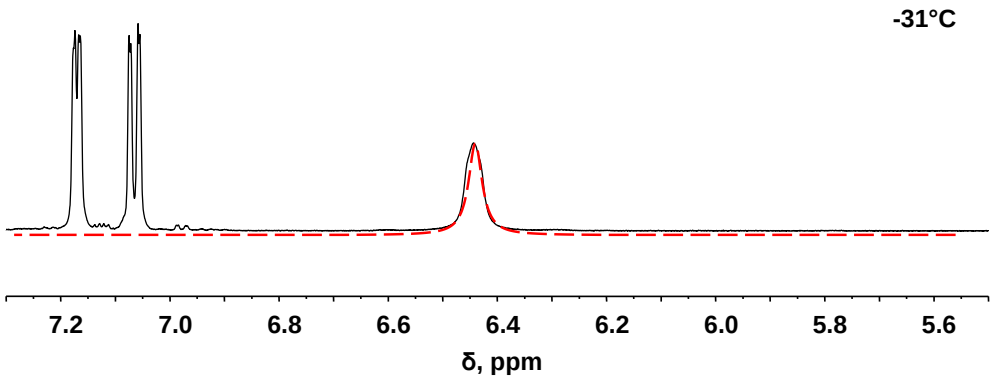

Figure S19. ^{1}H NMR (500 MHz) spectrum of **6** at -31°C with simulated ^{1}H NMR spectrum, shown in red, with k = 10,000 Hz.

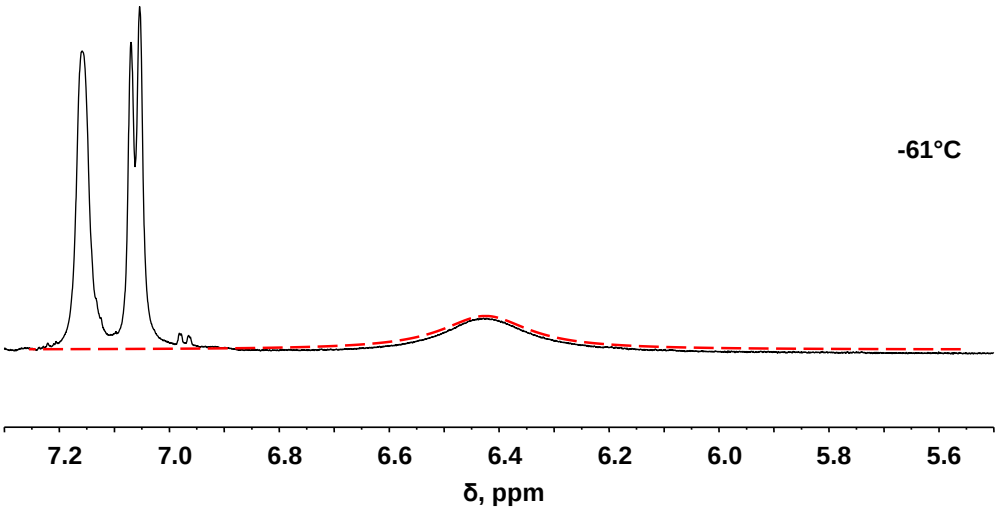

Figure S20. ^{1}H NMR (500 MHz) spectrum of **6** at -61°C with simulated ^{1}H NMR spectrum, shown in red, with k = 1500 Hz.

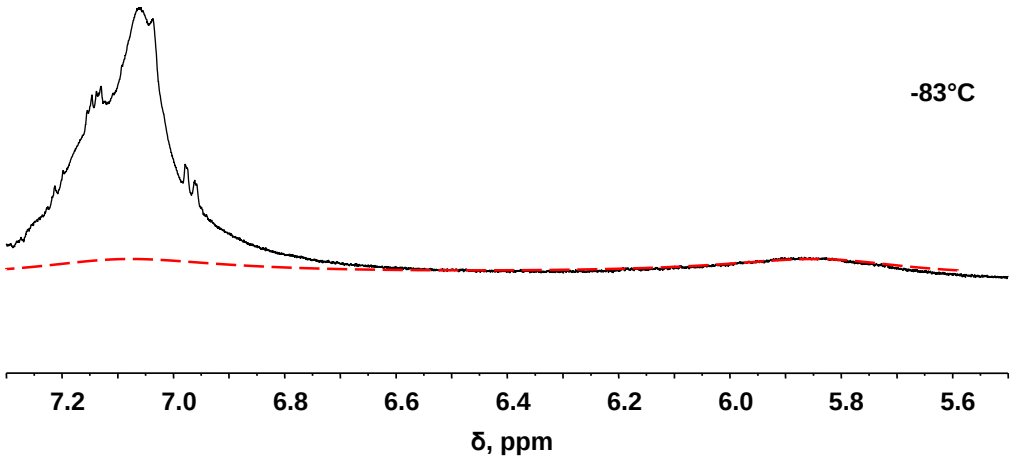

Figure S21. ^{1}H NMR (500 MHz) spectrum of **6** at -83°C with simulated ^{1}H NMR spectrum, shown in red, with k = 125 Hz.

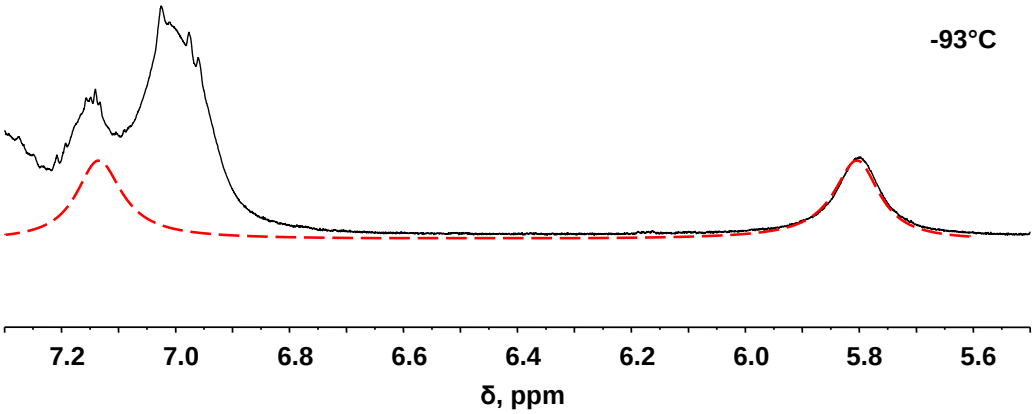

Figure S22. ^{1}H NMR (500 MHz) spectrum of **6** at -93°C with simulated ^{1}H NMR spectrum, shown in red, with k = 30 Hz.

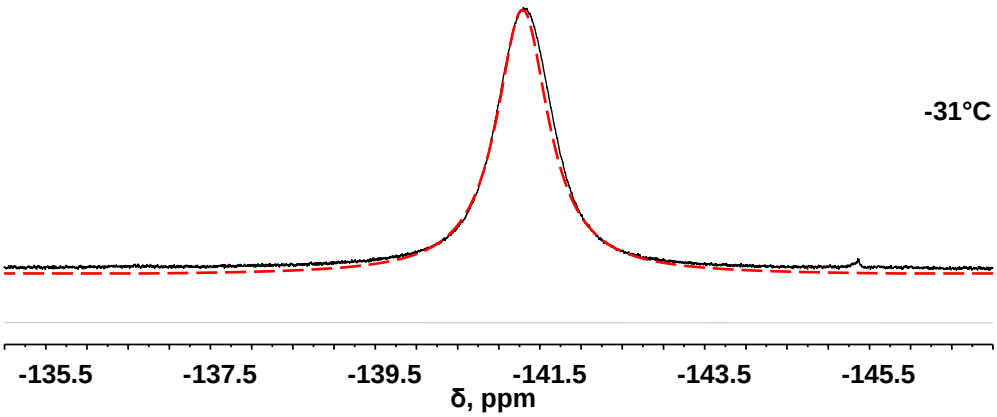

Figure S23. ^{19}F NMR (470.111 MHz) spectrum of **6** at -31°C with simulated ^{19}F NMR spectrum, shown in red, with k = 15,000 Hz.

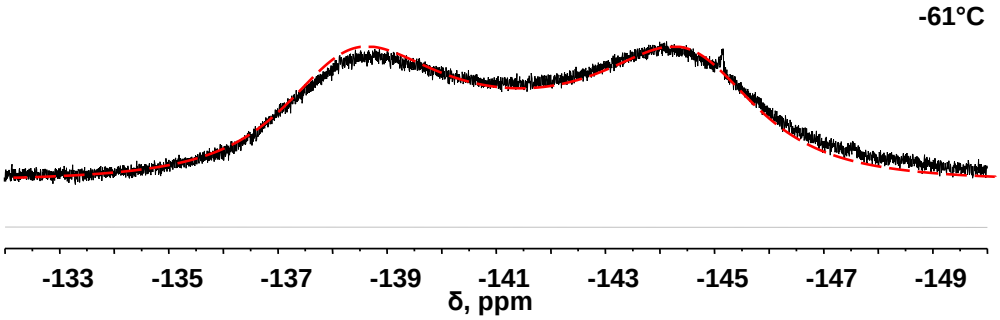

Figure S24. ^{19}F NMR (470.111 MHz) spectrum of **6** at -61°C with simulated ^{19}F NMR spectrum, shown in red, with k = 1000 Hz.

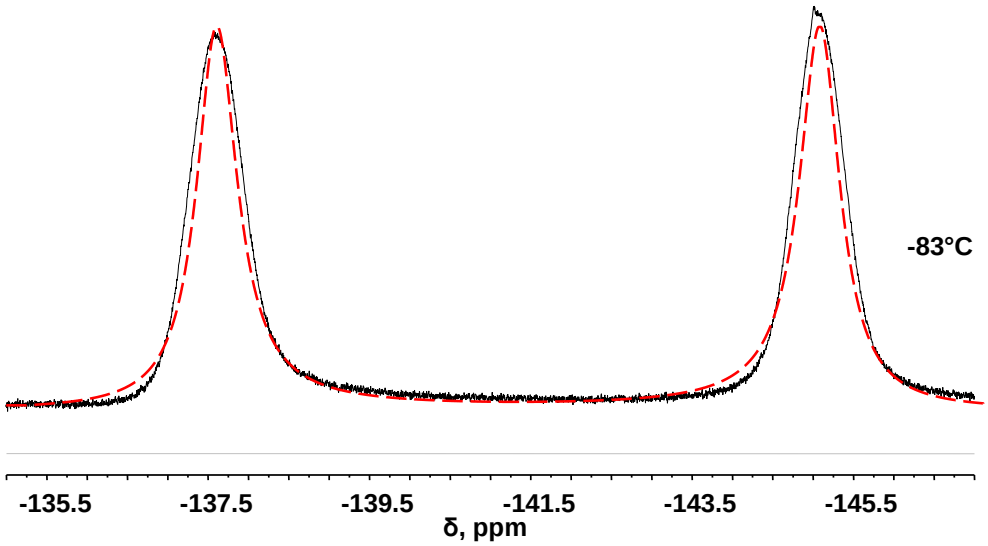

Figure S25. ^{19}F NMR (470.111 MHz) spectrum of **6** at -83°C with simulated ^{19}F NMR spectrum, shown in red, with k = 115 Hz.

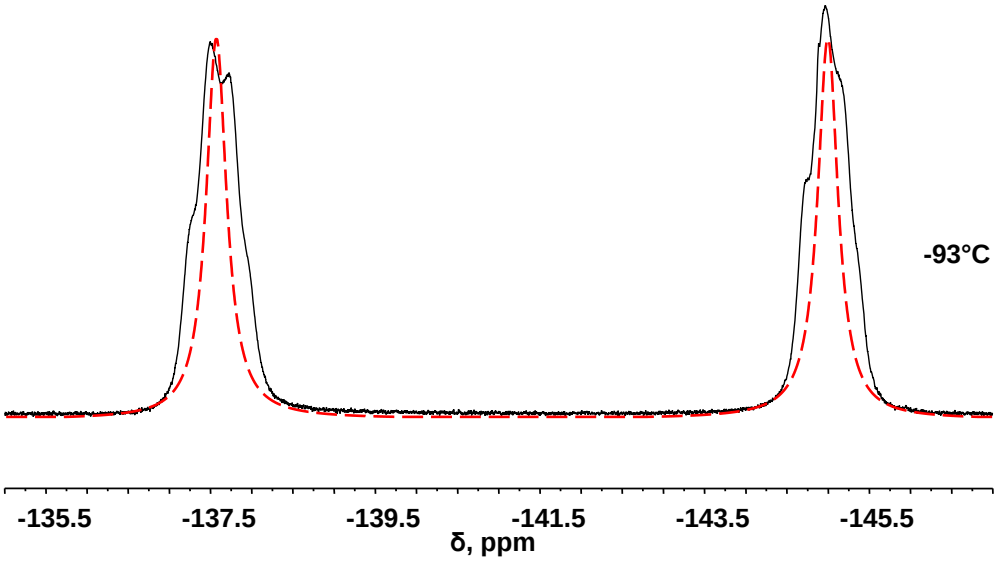

Figure S26. ^{19}F NMR (470.111 MHz) spectrum of **6** at -93°C with simulated ^{19}F NMR spectrum, shown in red, with k = 25 Hz.

Data on the structures computed by DFT methods

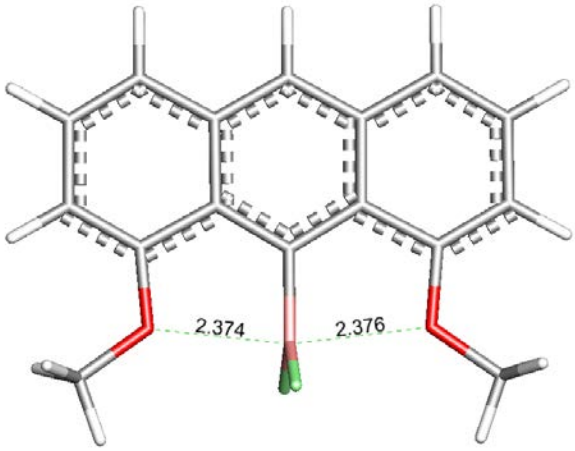

Figure S27. Calculated structure of **3**.

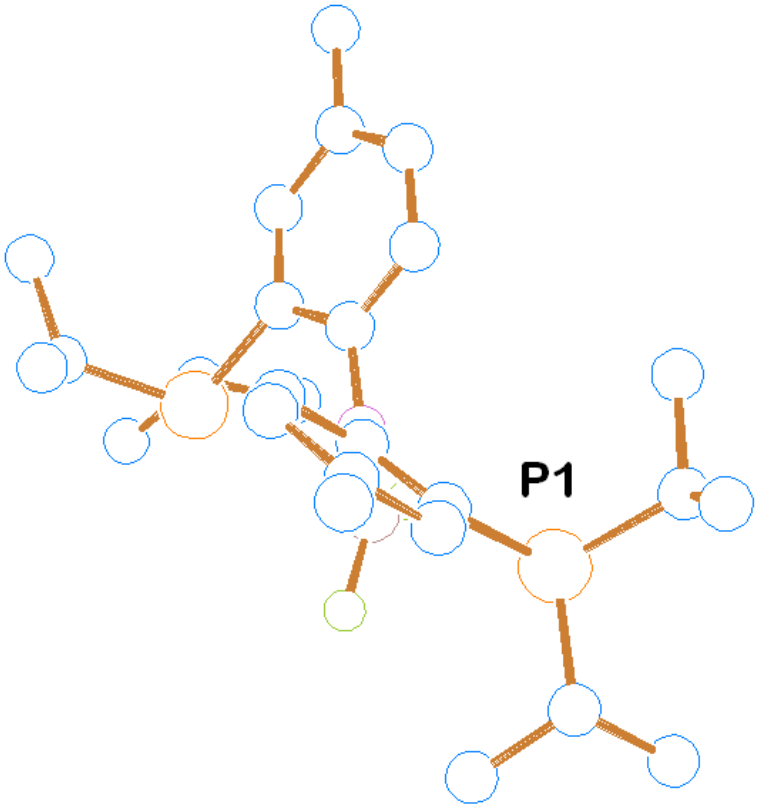

Figure S28. View along the approximate direction of the lone pair of P in 6-sym demonstrating that the apparent directionality of the lone pair on P is not aligned with the boron atom.

Table S3. Calculated relative electronic energies, enthalpies, and free energies (kcal/mol) in gas phase for the BF_2(PNP*) complexes.

	ΔE	ΔH	ΔG
6-asym	0.00	0.00	0.00
6-asymTS	6.56	5.85	7.23
6-sym	4.48	4.73	4.85
8-asym	0.00	0.00	0.00
8-asymTS	5.32	4.69	6.50
8-sym	0.77	1.11	0.35
9-asym	0.00	0.00	0.00
9-sym	17.81	17.74	16.78
10-asym	0.00	0.00	0.00
10-symTS	7.71	7.17	7.44
11-asym	0.00	0.00	0.00
11-symTS	8.05	7.32	7.81
12-asym	0.00	0.00	0.00
12-asymTS	9.07	8.37	8.71
13-asym	0.00	0.00	0.00
13-symTS	8.43	7.75	8.06

Table S4. Calculated bond distance data (in Å) for BF_2(PNP*) complexes.

	B-N (Å)	B-F (Å)	B-P (Å)
6-asym	1.529	1.399	2.072
		1.404	3.958
6-sym	1.429	1.341	3.064
6-asymTS	1.475	1.354	2.461
		1.364	3.224
8-asym	1.527	1.392	2.070
		1.402	3.820
8-sym	1.413	1.343	3.207
8-asymTS	1.482	1.361	2.334
		1.375	3.311
9-asym	1.521	1.379	2.094
		1.406	3.445
9-sym	1.465	1.345	2.769
			2.770
10-asym	1.556	1.390	2.054
		1.397	3.128
10-symTS	1.475	1.345	2.765
			2.766
11-asym	1.567	1.389	2.050
		1.391	3.116
11-symTS	1.493	1.343	2.738
			2.746
12-asym	1.572	1.385	2.043
		1.393	3.123
12-asymTS	1.493	1.340	2.692
		1.345	2.785
13-asym	1.530	1.392	2.045
		1.400	3.247
13-symTS	1.464	1.345	2.788

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