Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Data for:

Boron diamide derivatives containing N-N and N-P molecular fragments

Christopher Major, Shi-Ming Chen, and Douglas W. Stephan

Contents

General Considerations

All reactions and work-up procedures were performed under an inert atmosphere of dry, oxygen-free N_2, using standard Schlenk techniques or a glovebox (Innovative Technology, equipped with a -25 °C freezer) unless otherwise specified. CH_2Cl_2, *n*-pentane, *n*-hexane, Et_2O, and toluene (Sigma-Aldrich) were dried using a Grubbs-type Innovative Technologies solvent purification system, degassed, and stored over activated 3 or 4 Å molecular sieves. Deuterated solvents (C_6D_6, $CDCl_3$) were purchased from Cambridge Isotope Laboratories, Inc. or Sigma-Aldrich, and stored over activated 4Å molecular sieves prior to use, unless otherwise specified. All other reagents were purchased from Sigma-Aldrich. $(HCN(Dipp))_2BBr$ **1,**[1] $(H_2CN(Dipp))_2BBr$ **2,**[2] $(CN(Dipp))_2BNH_2$ **5**, $(HCN(Dipp))_2BNH(SiMe_3)$ **13**, and $(HCN(Dipp))_2BNK(SiMe_3)$ **14** were generated according to literature procedures.[3]Routine NMR spectra were obtained on a Varian MercuryPlus 300 MHz, Bruker Avance III 400 MHz, Agilent DD2 500 MHz, or Agilent DD2 600 MHz spectrometer and spectra were referenced to residual solvent of $CDCl_3$ (^1H = 7.26; ^{13}C = 77.2), C_6D_6 (^1H = 7.16 ppm; ^{13}C = 128.06 ppm), C_6D_5Br (^1H most downfield shift = 7.30 ppm) or externally (^{11}B, $BF_3{\cdot}OEt_2$; ^{19}F, $CFCl_3$; ^{31}P, 85% H_3PO_4). ^{13}C spectra were primarily obtained on a 500 MHz Agilent DD2 NMR Spectrometer, equipped with a cryogenically cooled probe. Chemical shifts (δ) are reported in ppm and coupling constants are listed in Hz. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI), JEOL AccuTOF Plus 4G (DART) and Bruker Autoflex Speed (MALDI).

Preparation of $Br_3B{\cdot}PPh_3$

^1H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 6H), 7.69 – 7.62 (m, 3H), 7.57 – 7.47 (m, 6H). ^{11}B NMR (128 MHz, $CDCl_3$) δ -14.7 (d, $^1J_{P\text{-}B}$ = 146 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.9 (q, $^1J_{P\text{-}B}$ = 146 Hz).

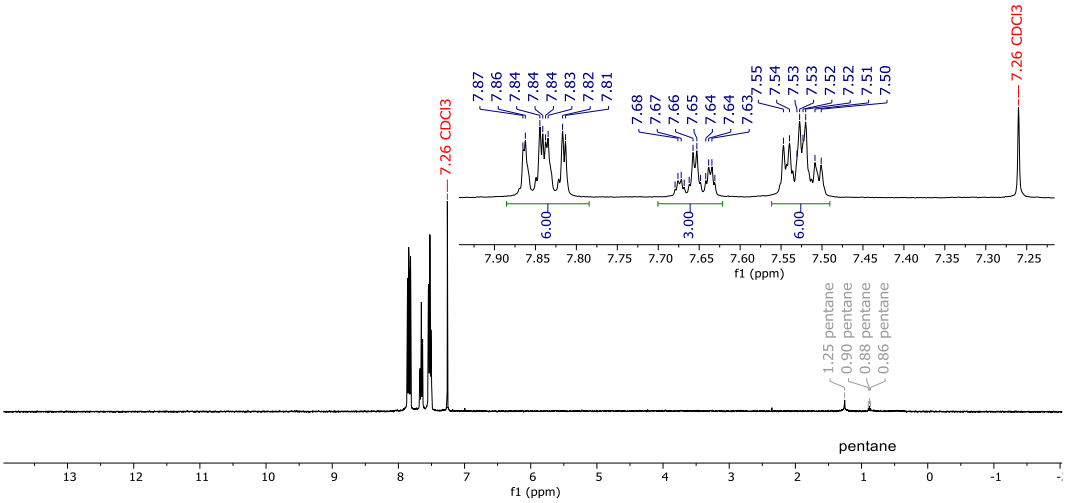


Figure S1. ^{1}H NMR spectrum of $Br_3B{\cdot}PPh_3$ in $CDCl_3$ at 298 K.

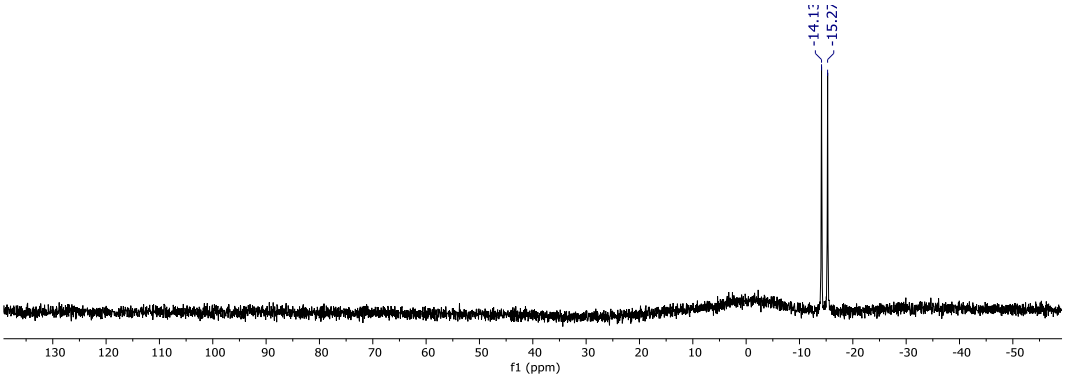


Figure S2. ^{11}B NMR spectrum of $Br_3B{\cdot}PPh_3$ in $CDCl_3$ at 298 K.

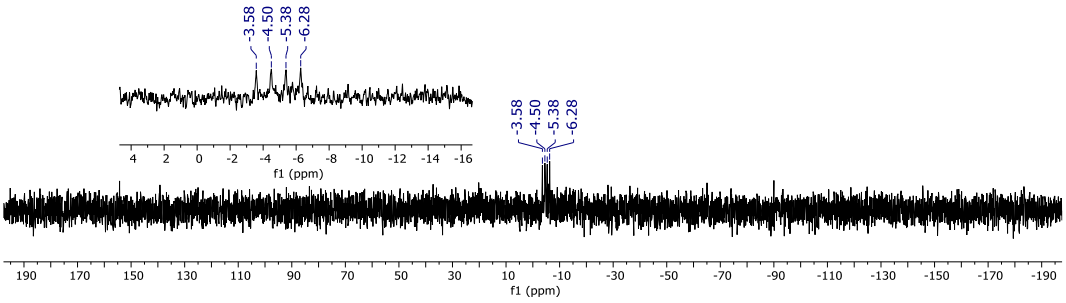


Figure 1. ^{31}P NMR spectrum of $Br_3B{\cdot}PPh_3$ in $CDCl_3$ at 298 K.

Synthesis of $(HCN(Dipp))_2BBr$ 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 1H), 7.26 – 7.20 (m, 2H), 6.31 (s, 1H), 2.97 (hept, $^3J_{H\text{-}H}$ = 7 Hz, 2H), 1.22 (d, $^3J_{H\text{-}H}$ = 7 Hz, 24H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 20.3.

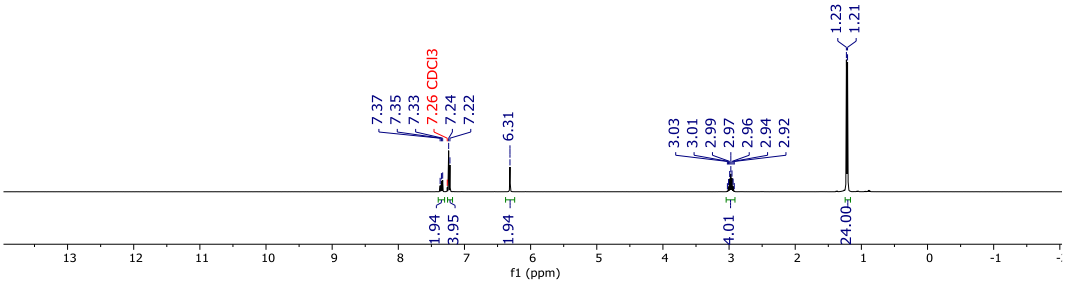


Figure S4. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 298 K.

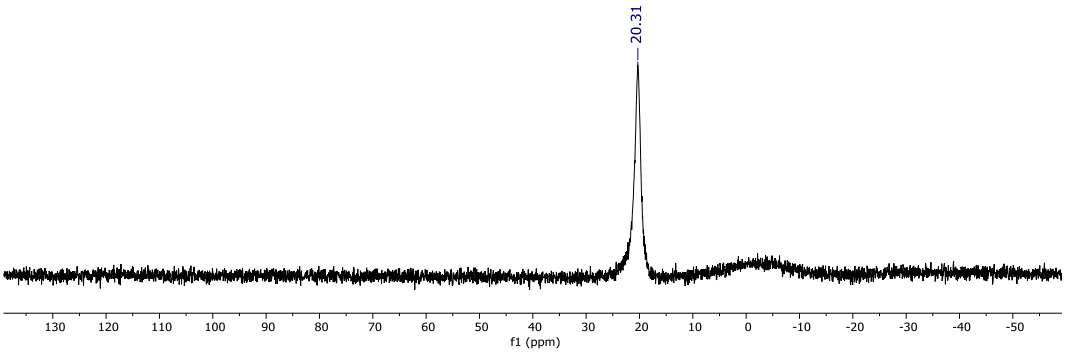


Figure S5. ^{11}B NMR spectrum of **1** in $CDCl_3$ at 298 K.

Synthesis of $(HCN(Dipp))_2BOSO_2CF_3$ 3

^{1}H NMR (400 MHz, C_6D_6) δ 7.24 – 7.17 (m, 2H), 7.13 – 7.08 (m, 4H), 6.01 (s, 2H), 3.16 (hept, $^3J_{H\text{-}H}$ = 7 Hz, 4H), 1.33 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H), 1.16 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.26 – 7.20 (m, 4H), 6.20 (s, 2H), 2.98 (hept, $^3J_{H\text{-}H}$ = 7 Hz, 4H), 1.25 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H), 1.21 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 19.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 18.9. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 146.3, 134.8, 128.4, 123.7, 118.4, 28.7, 25.3, 23.3. ^{19}F NMR (376 MHz, C_6D_6) δ -76.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.4. *HRMS* (TOF, DART+) m/z 537.25672 (high res., calc. for protonated molecular ion, $[C_{27}H_{37}BN_2O_3F_3S]^+$: 537.25646).

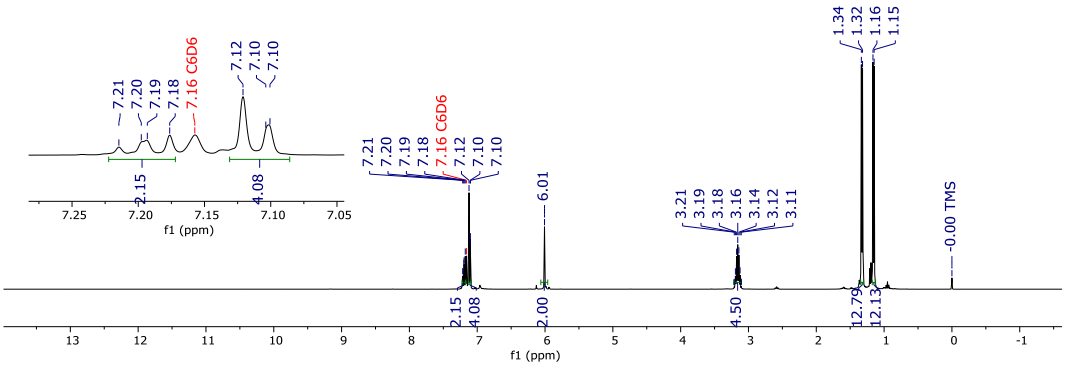


Figure S5. ^{1}H NMR spectrum of **3** in C_6D_6 at 298 K.

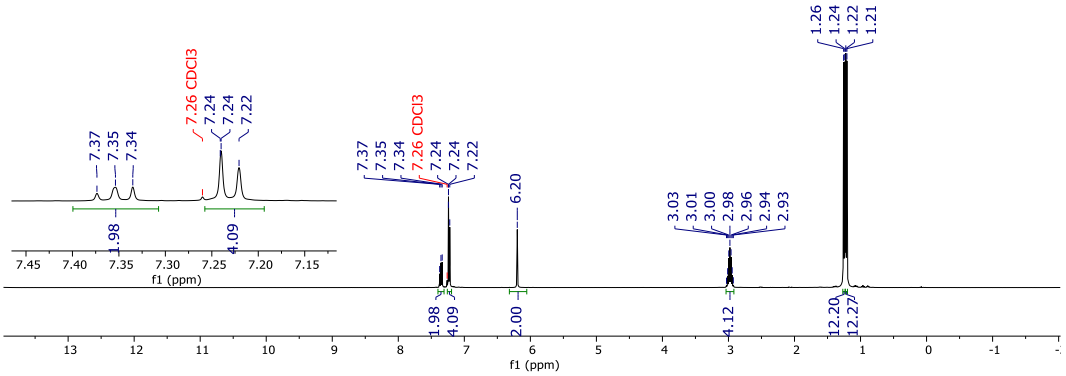


Figure S6. ^{1}H NMR spectrum of **3** in $CDCl_3$ at 298 K.

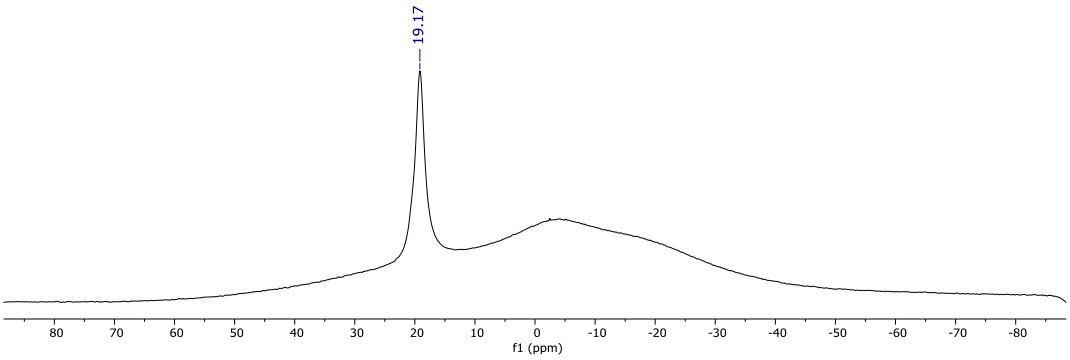


Figure S7. ^{11}B NMR spectrum of **3** in C_6D_6 at 298 K.

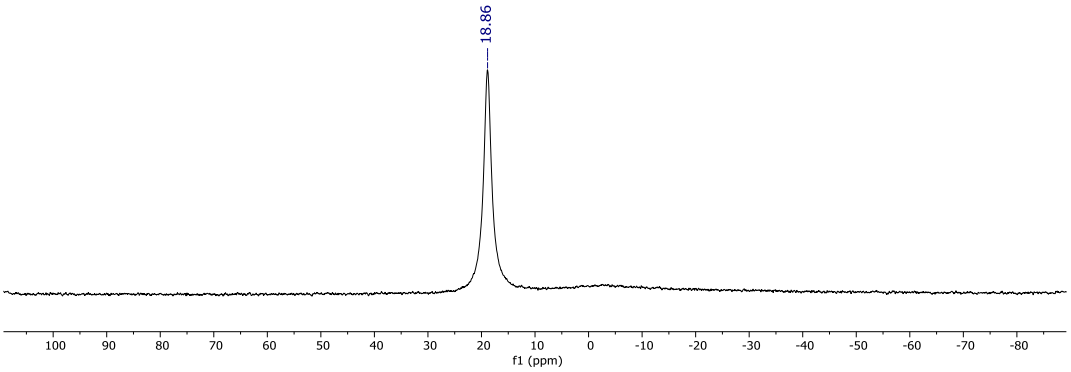


Figure S8. ^{11}B NMR spectrum of **3** in $CDCl_3$ at 298 K.

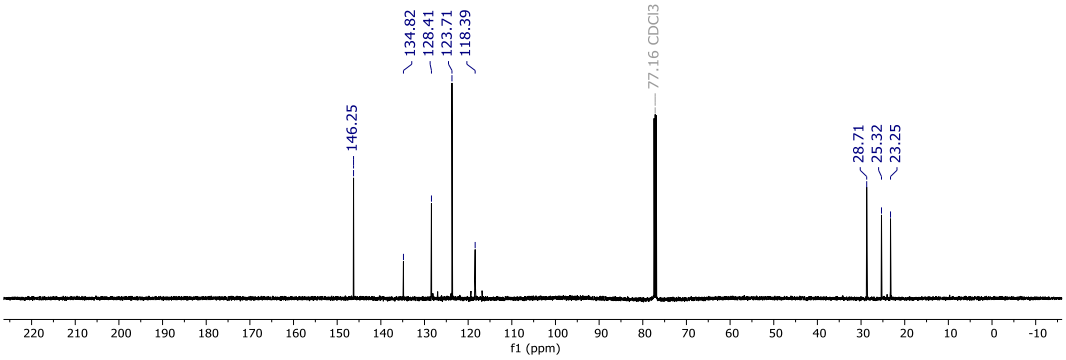


Figure S9. $^{13}C\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ at 298 K.

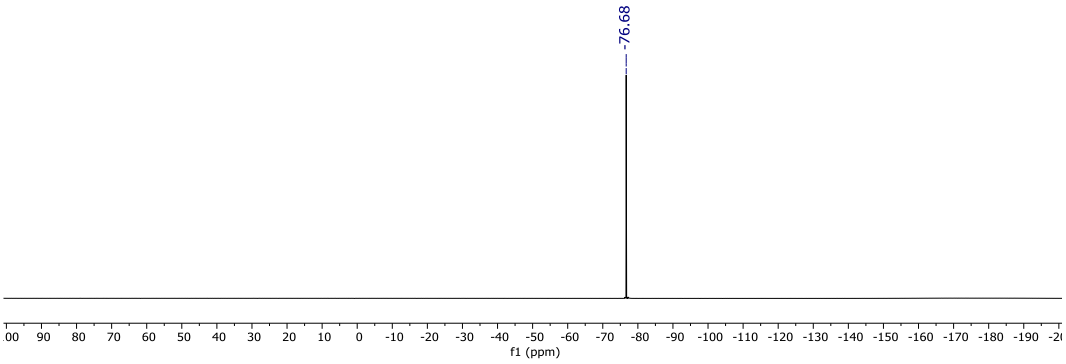


Figure S10. ^{19}F NMR spectrum of **3** in C_6D_6 at 298 K.

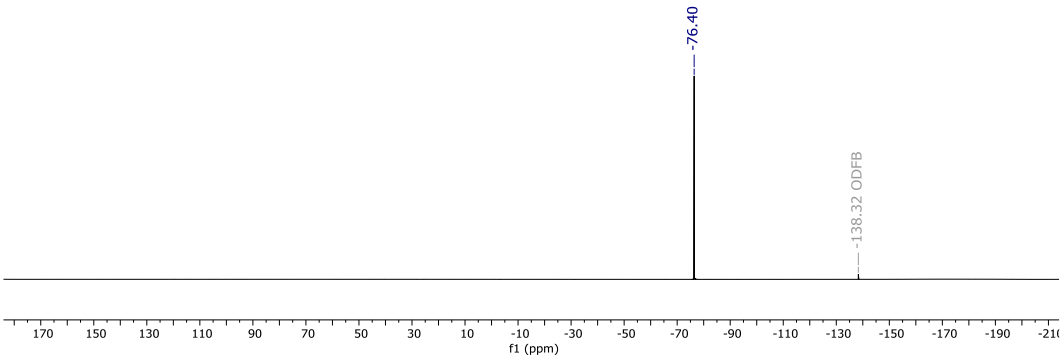
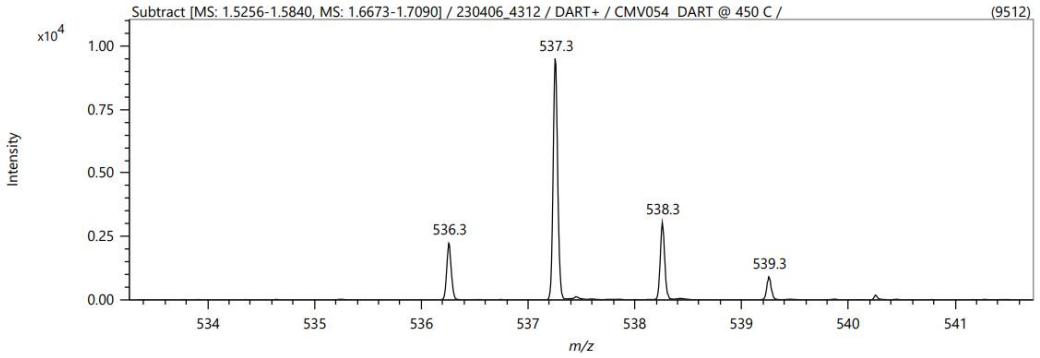


Figure S11. ^{19}F NMR spectrum of **3** in $CDCl_3$ at 298 K.

DART IONIZATION **AccuTOF 4G**

Spectrum



Elemental Composition

Parameters		Elements Set 1:							
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	S	F
Electron:	Odd/Even	Min	0	0	0	0	1	1	3
Charge:	+1	Max	100	200	20	10	1	1	3
DBE:	-1.5 - 100.0								

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
537.25672	9512.00	C27 H37 B N2 O3 F3 S	537.25646	0.27	0.50	9.5
		C25 H35 B N5 O2 F3 S	537.25511	1.61	3.00	10.0
		C30 H35 B N3 F3 S	537.25914	-2.41	-4.49	14.0
		C16 H37 B N8 O6 F3 S	537.25964	-2.92	-5.43	1.5
		C24 H39 B N O6 F3 S	537.25378	2.95	5.49	5.0
		C23 H33 B N8 O F3 S	537.25377	2.95	5.50	10.5

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Figure S12. HR-MS (TOF DART+) data for **3**.

Synthesis of $(H_2CN(Dipp))_2BOSO_2CF_3$ 4

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.16 (m, 4H), 3.73 (s, 4H), 3.37 (hept, $^{3}J_{H\text{-}H}$ = 7 Hz, 4H), 1.31 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H), 1.28 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.8. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.4, 135.7, 127.7, 124.0, 117.7 (q, $^{1}J_{C\text{-}F}$ = 318 Hz, 1C), 77.4, 76.9, 51.2, 28.7, 25.7, 23.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.7. *HRMS* (TOF, DART+) m/z 539.27243 (high res., calc. for protonated molecular ion, $[C_{27}H_{39}BN_2O_3F_3S]^{+}$: 539.27211)

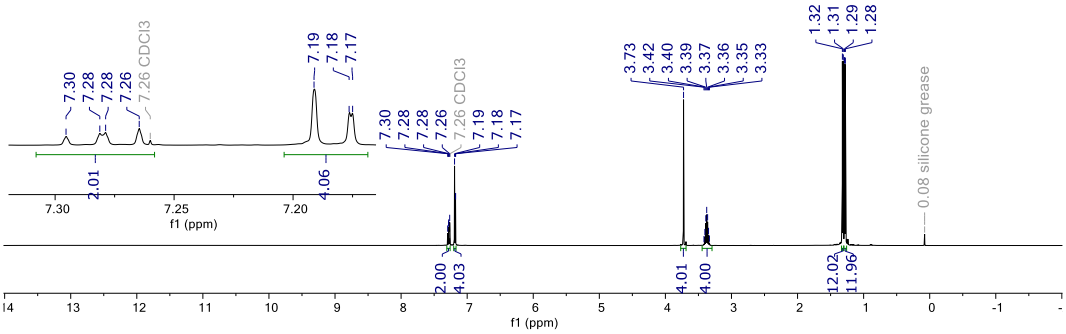


Figure S13. ^{1}H NMR spectrum of **4** in $CDCl_3$ at 298 K.

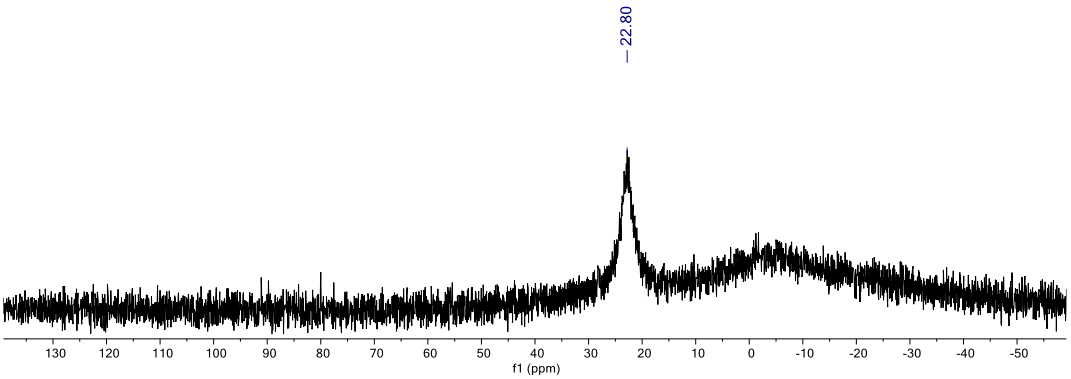


Figure S14. ^{11}B NMR spectrum of **4** in $CDCl_3$ at 298 K.

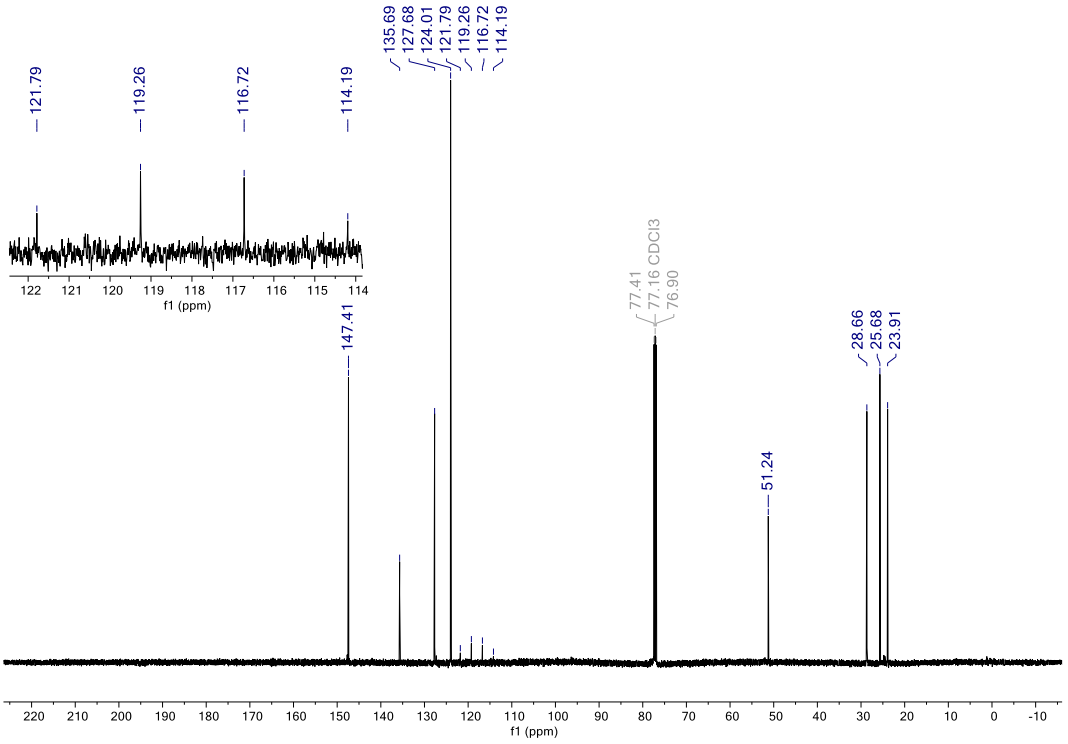


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ at 298 K.

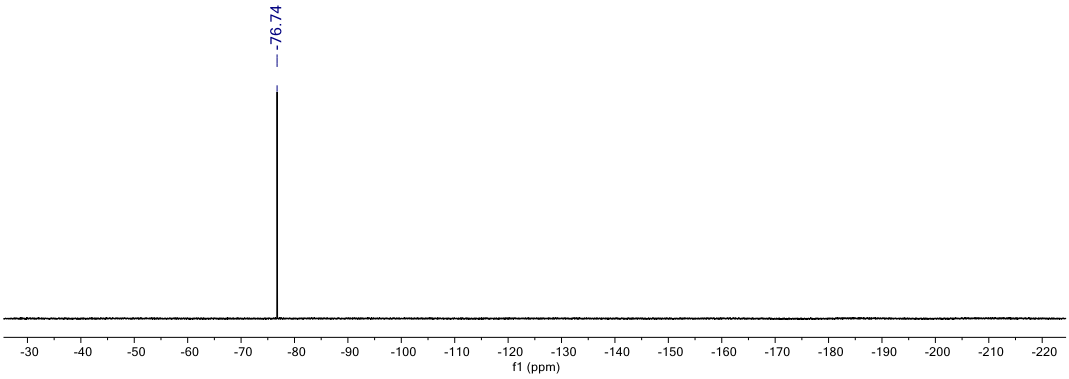
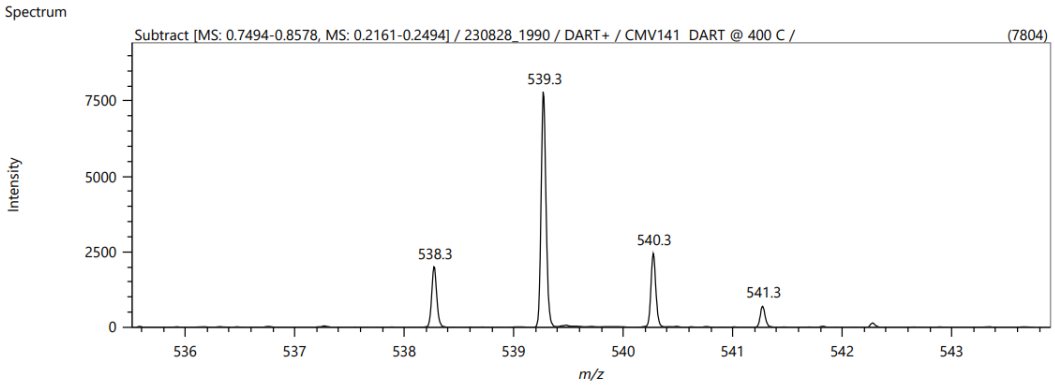


Figure S16. ^{19}F NMR spectrum of **4** in $CDCl_3$ at 298 K.



Elemental Composition

Parameters		Elements Set 1:							
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	F	S
Electron:	Even	Min	0	0	0	0	1	3	1
Charge:	+1	Max	100	200	20	10	1	3	1
DBE:	-1.5 - 100.0								

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
539.27243	7803.84	C27 H39 B N2 O3 F3 S	539.27211	0.33	0.60	8.5
		C16 H39 B N8 O6 F3 S	539.27529	-2.86	-5.31	0.5
		C23 H35 B N8 O F3 S	539.26942	3.01	5.58	9.5
		C32 H39 B O F3 S	539.27613	-3.70	-6.85	12.5
		C22 H39 B N4 O5 F3 S	539.26808	4.35	8.06	4.5
		C20 H43 B N2 O8 F3 S	539.27798	-5.55	-10.29	-0.5

Figure S17. HR-MS (TOF, DART+) for **4**.

Synthesis of $(H_2CN(Dipp))_2BNH_2$ 6

^{1}H NMR (400 MHz, C_6D_6) δ 7.27 – 7.18 (m, 2H), 7.20 – 7.13 (m, 4H), 3.56 (hept, $^{3}J_{H\text{-}H}$ = 7 Hz, 4H), 3.44 (s, 4H), 1.31 (d, J = 7 Hz, 12H), 1.31 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H), 1.05 (s, 2H). ^{11}B NMR (128 MHz, C_6D_6) δ 25.4. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 148.8, 143.8, 140.0, 127.0, 52.0, 28.6, 25.1, 24.7. HRMS (TOF, DART+) m/z 406.33901 (high res., calc. for protonated molecular ion, $[C_{26}H_{41}BN_3]^+$: 406.33881)

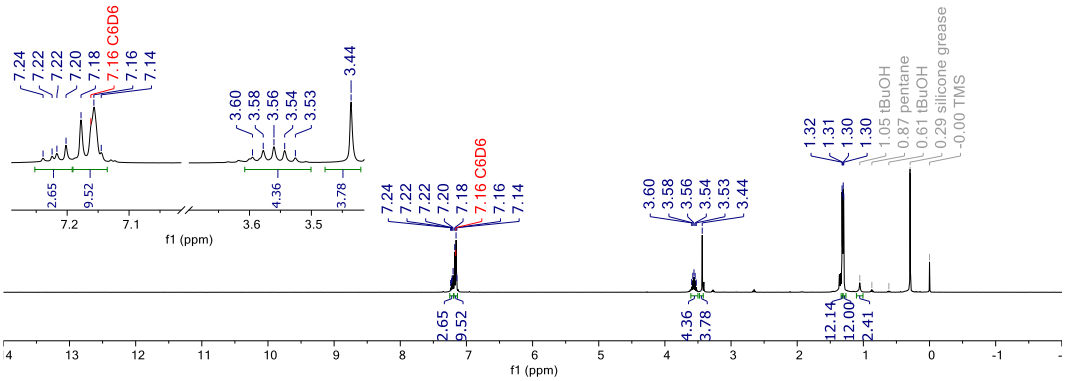


Figure S18. ^{1}H NMR spectrum of **6** in C_6D_6 at 298 K.

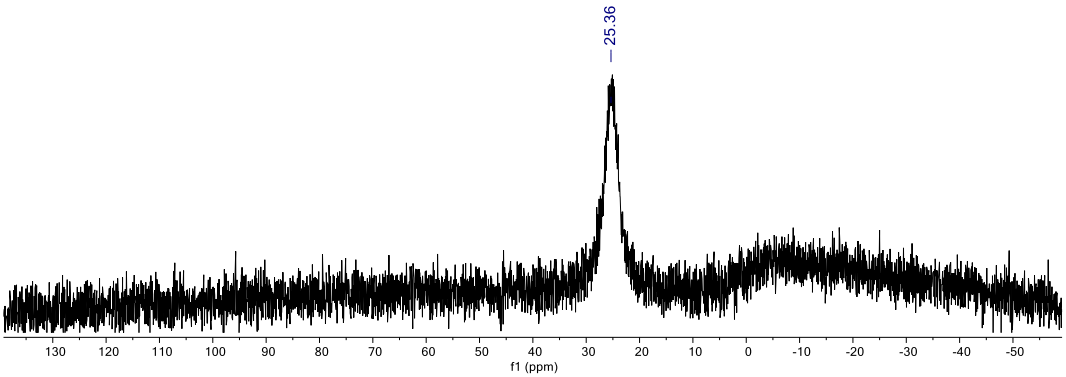


Figure S19. ^{11}B NMR spectrum of **6** in C_6D_6 at 298 K.

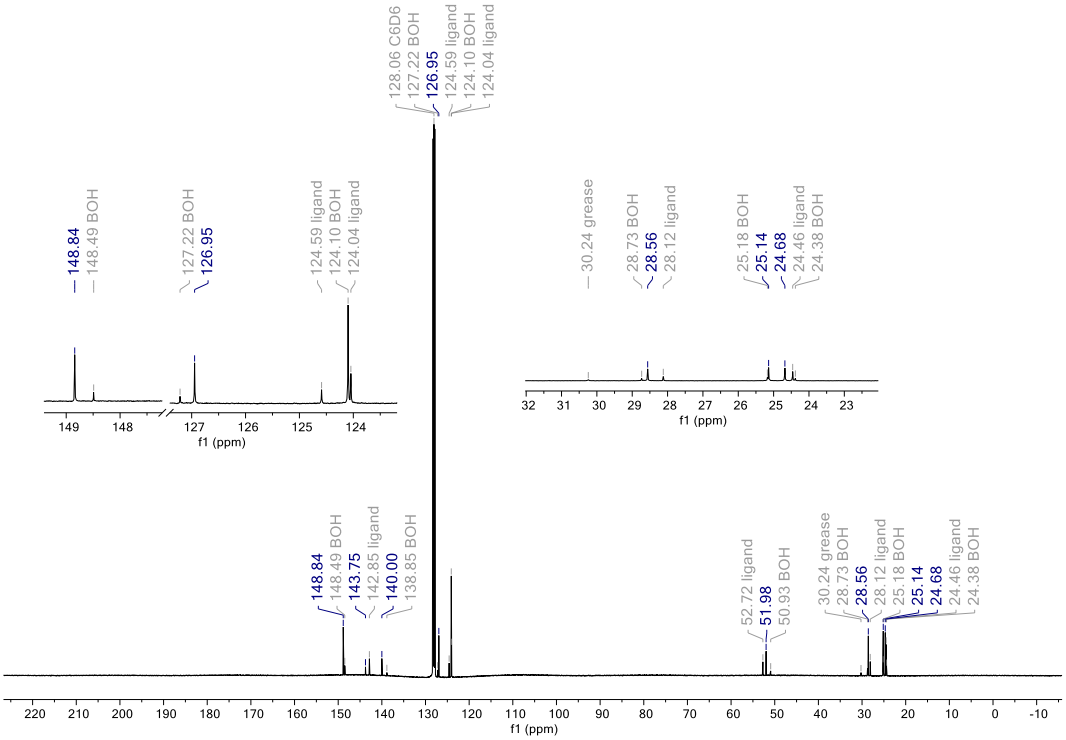
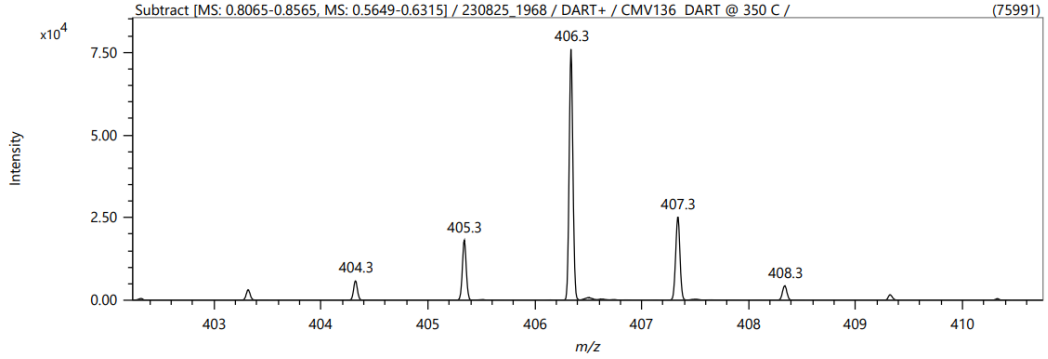


Figure S20. $^{13}C\{^1H\}$ NMR spectrum of **6** in C_6D_6 at 298 K.

DART IONIZATION **AccuTOF 4G**

Spectrum

Subtract [MS: 0.8065-0.8565, MS: 0.5649-0.6315] / 230825_1968 / DART+ / CMV136 DART @ 350 C / (75991)



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	S	B
Electron:	Even	Min	0	0	0	0	0	0
Charge:	+1	Max	100	200	10	10	0	1
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
406.33901	75990.64	C26 H41 B N3	406.33881	0.20	0.50	8.5
		C19 H44 N5 O4	406.33878	0.23	0.55	0.5
		C20 H40 N9	406.34012	-1.11	-2.74	5.5
		C15 H41 B N9 O3	406.34199	-2.99	-7.35	0.5
		C24 H44 N3 O2	406.34280	-3.80	-9.35	4.5
		C21 H41 B N5 O2	406.33478	4.22	10.40	4.5

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Figure S21. HR-MS data (TOF, DART+) for **6**.

Synthesis of $[(HCN(Dipp))_2B(NHNH_3)][O_3SCF_3]$ 7

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 3H), 7.34 – 7.27 (m, 3H), 7.23 – 7.12 (m, 4H), 5.99 (s, 2H), 4.47 (s, 1H), 3.00 (hept, $^{3}J_{H\text{-}H}$ = 7 Hz, 4H), 1.18 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H), 1.13 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 20.7. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.0, 135.4, 128.8, 124.4, 118.1, 28.5, 24.6, 23.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4.

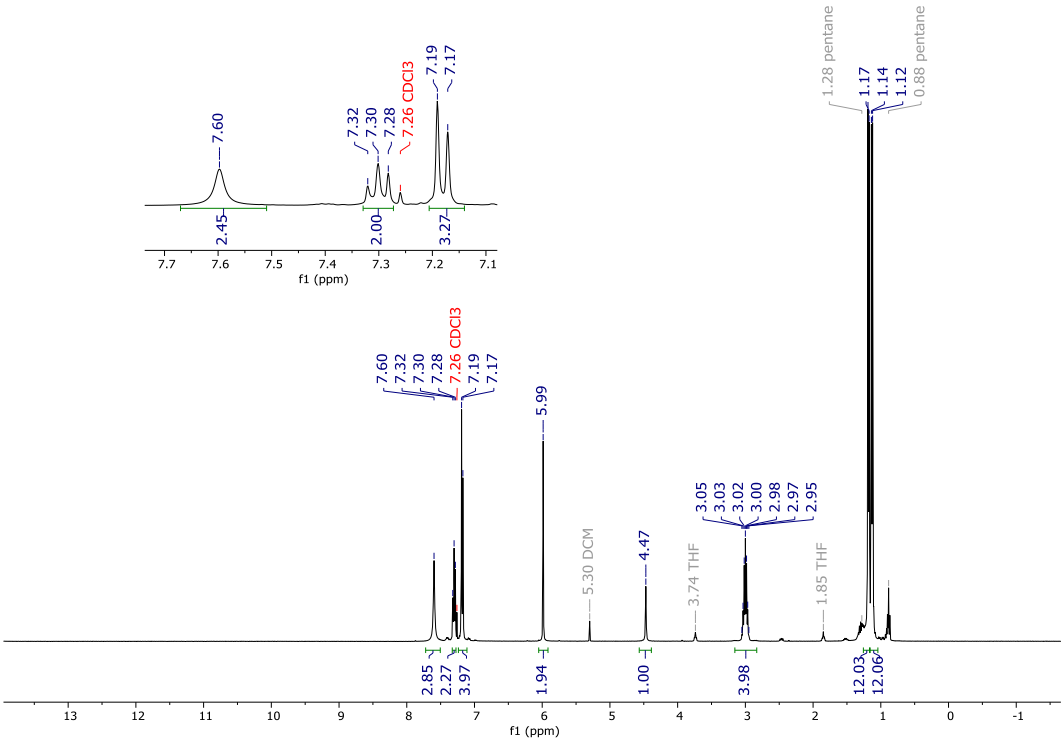


Figure S22. ^{1}H NMR spectrum of **7** in $CDCl_3$ at 298 K.

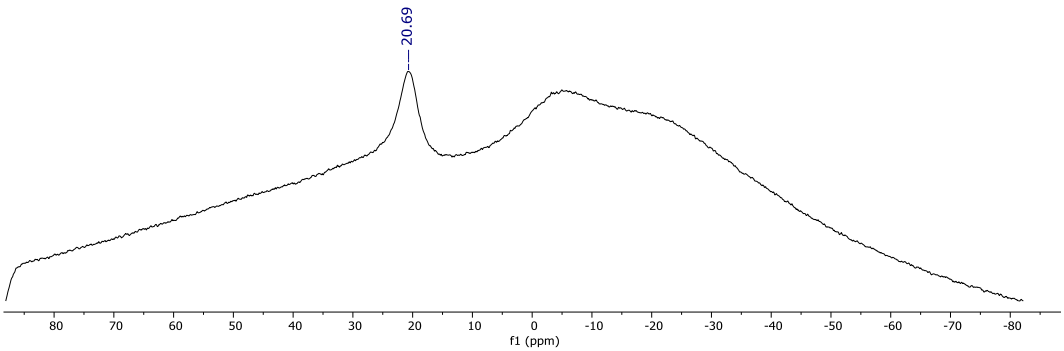


Figure S23. ^{11}B NMR spectrum of **7** in $CDCl_3$ at 298 K.

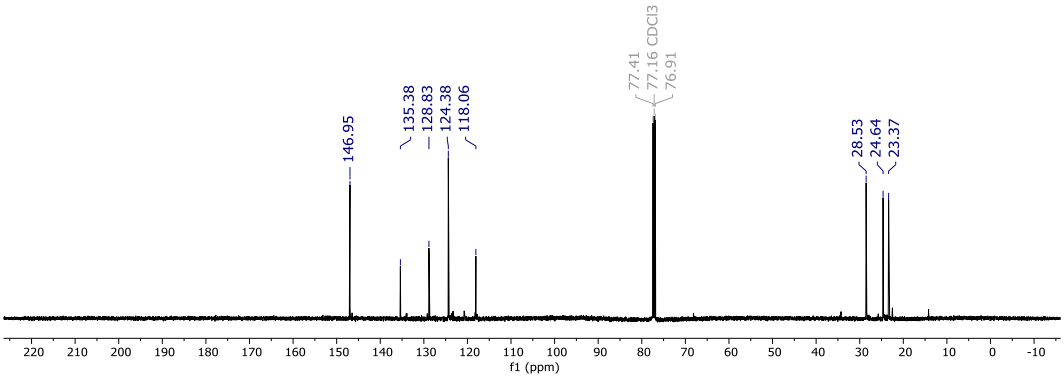


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$ at 298 K.

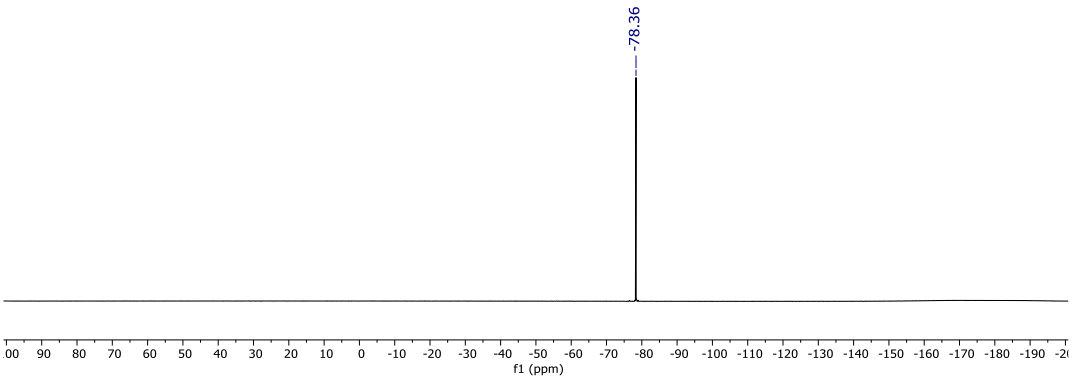


Figure S25. ^{19}F NMR spectrum of **7** in $CDCl_3$ at 298 K.

Synthesis of $[(H_2CN(Dipp))_2B(NHNH_3)][O_3SCF_3]$ 8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 3H), 7.29 – 7.22 (m, 3H), 7.20 – 7.13 (m, 4H), 4.22 (s, 1H), 3.60 (s, 4H), 3.33 (hept, $^{3}J_{H\text{-}H}$ = 7 Hz, 4H), 1.27 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H), 1.17 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 12H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 23.3. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.3, 136.5, 128.2, 124.7, 52.3, 28.4, 25.0, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4.

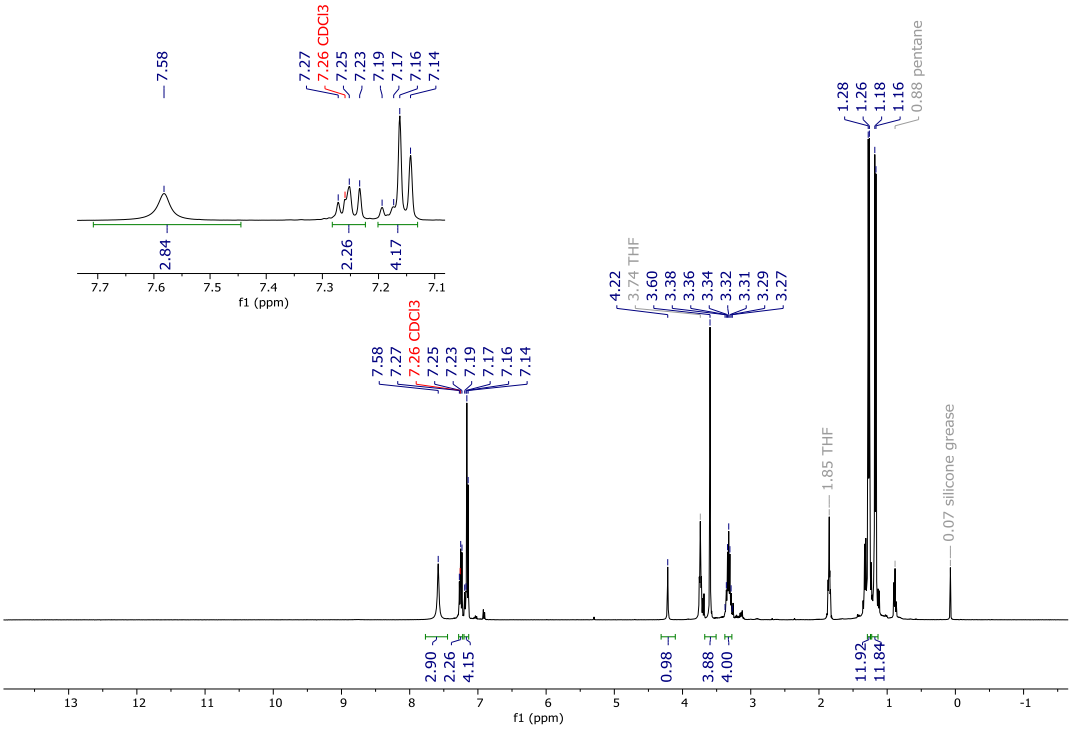


Figure S25. ^{1}H NMR spectrum of **8** in $CDCl_3$ at 298 K.

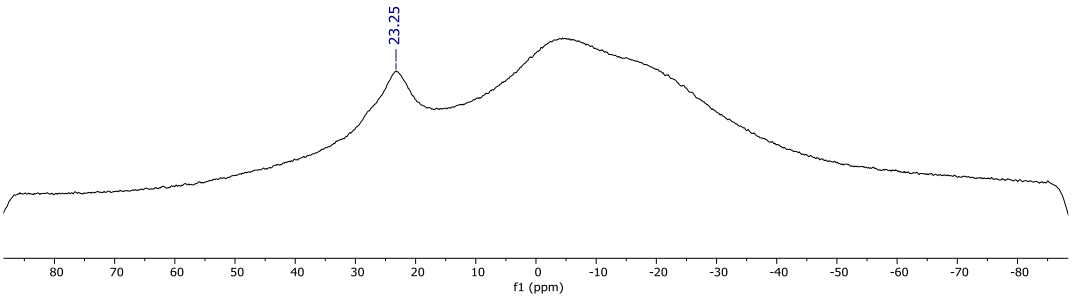


Figure S26. ^{11}B NMR spectrum of **8** in $CDCl_3$ at 298 K.

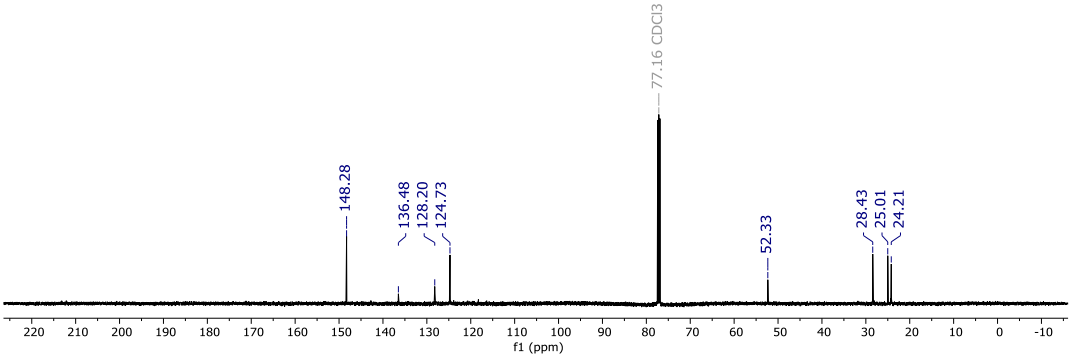


Figure S27. ^{13}C{^{1}H} NMR spectrum of **8** in $CDCl_3$ at 298 K.

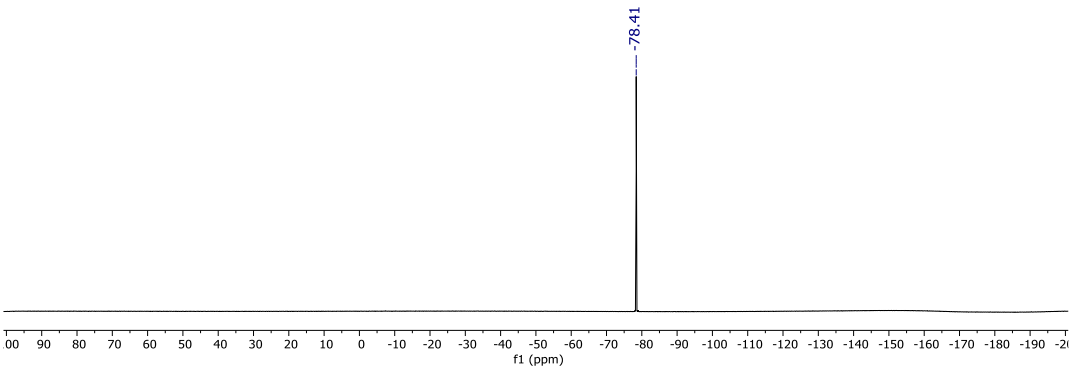


Figure S28. ^{19}F NMR spectrum of **8** in $CDCl_3$ at 298 K.

Synthesis of $(HCN(Dipp))_2B(NHNH_2)$ 9

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.20 – 7.16 (m, 4H), 5.93 (s, 2H), 3.39 (s, 1H), 3.22 (hept, $^{3}J_{H\text{-}H}$ = 7 Hz, 4H), 2.56 (s, 2H), 1.23 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 24H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.0. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 147.0, 138.5, 127.2, 123.4, 117.3, 28.4, 24.4, 23.9. *HRMS* (TOF, DART+) m/z 419.33430 (high res., calc. for protonated molecular ion, $[C_{26}H_{40}BN_4]^{+}$: 419.33405)

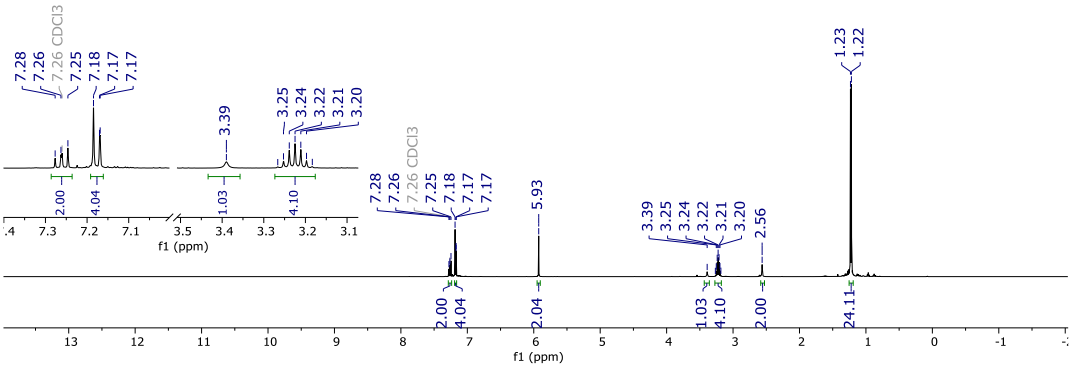


Figure S29. ^{1}H NMR spectrum of **9** in $CDCl_3$ at 298 K.

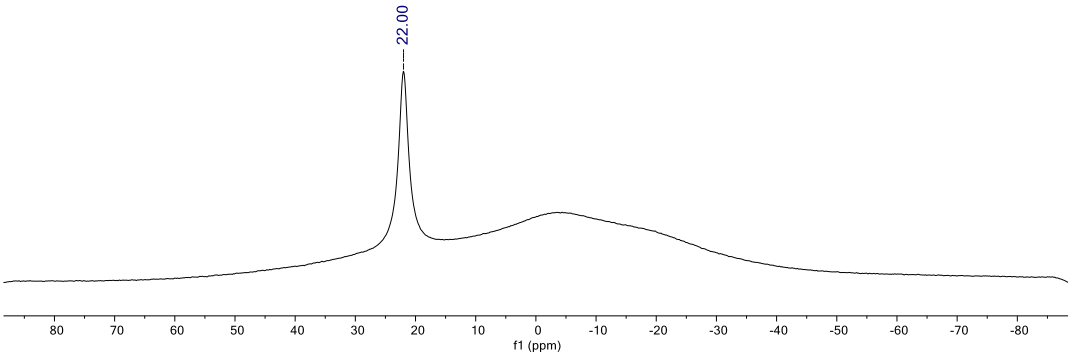


Figure S30. ^{11}B NMR spectrum of **9** in $CDCl_3$ at 298 K.

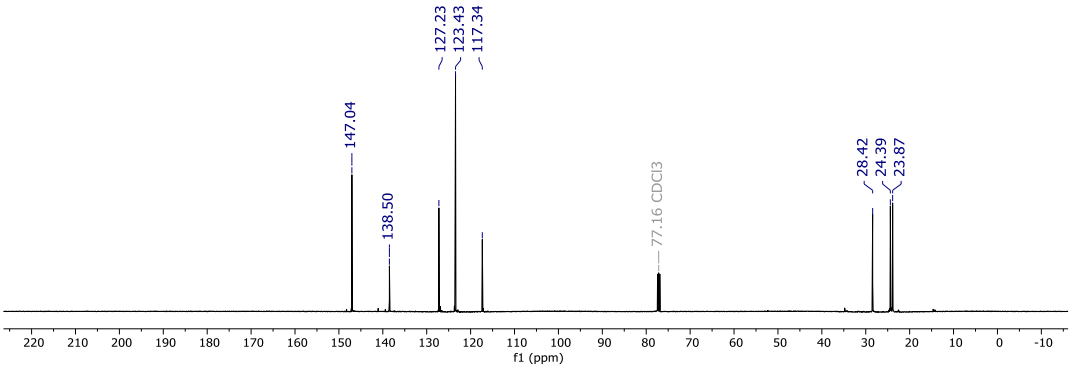
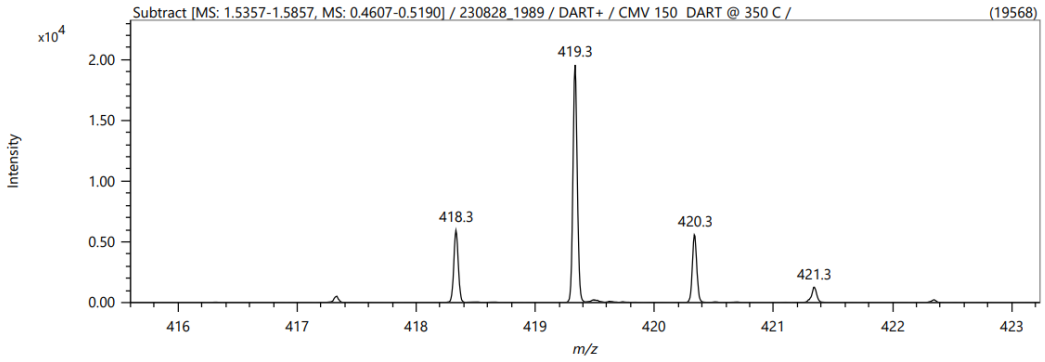


Figure S31. $^{13}C\{^1H\}$ NMR spectrum of **9** in $CDCl_3$ at 298 K.

DART IONIZATION **AccuTOF 4G**

Spectrum



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
419.33430	19567.92	C26 H40 B N4	419.33405	0.25	0.59	9.5
		C25 H44 B O4	419.33272	1.59	3.78	4.5
		C15 H40 B N10 O3	419.33724	-2.94	-7.01	1.5
		C21 H40 B N6 O2	419.33003	4.27	10.19	5.5
		C20 H44 B N2 O6	419.32869	5.61	13.38	0.5
		C19 H44 B N4 O5	419.33993	-5.62	-13.41	0.5

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AIMS Mass Spectrometry Laboratory, University of Toronto **2023-08-28**

Figure S32. HR-MS (TOF DART+) data for **10**.

Synthesis of $(H_2CN(Dipp))_2B(NHNH_2)$ 10:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 2H), 7.17 – 7.12 (m, 4H), 3.54 (s, 4H), 3.50 (hept, $^3J_{H\text{-}H}$ = 7 Hz, 4H), 3.17 (s, 1H), 2.46 (s, 2H), 1.31 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H), 1.26 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 24.6. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 148.3, 139.9, 126.6, 123.8, 52.3, 28.3, 24.8, 24.6. *HRMS* (TOF, DART+) m/z 421.34915 (high res., calc. for protonated molecular ion, $[C_{26}H_{42}BN_4]^+$: 421.34970).

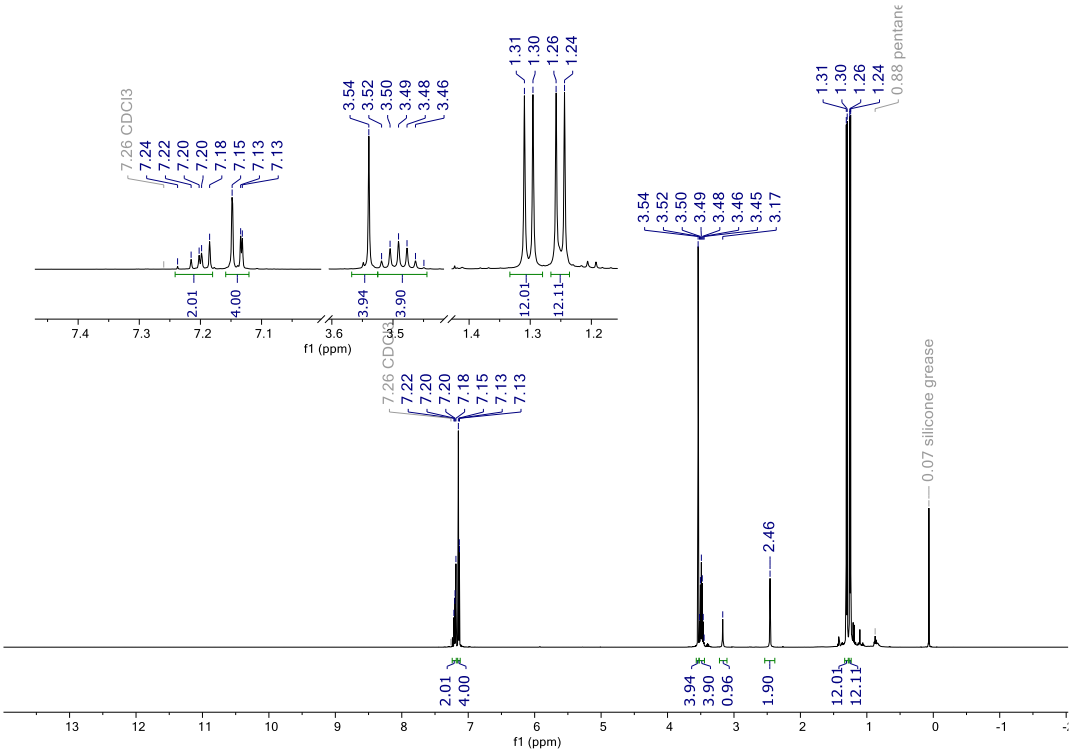


Figure S33. ^{1}H NMR spectrum of **10** in $CDCl_3$ at 298 K.

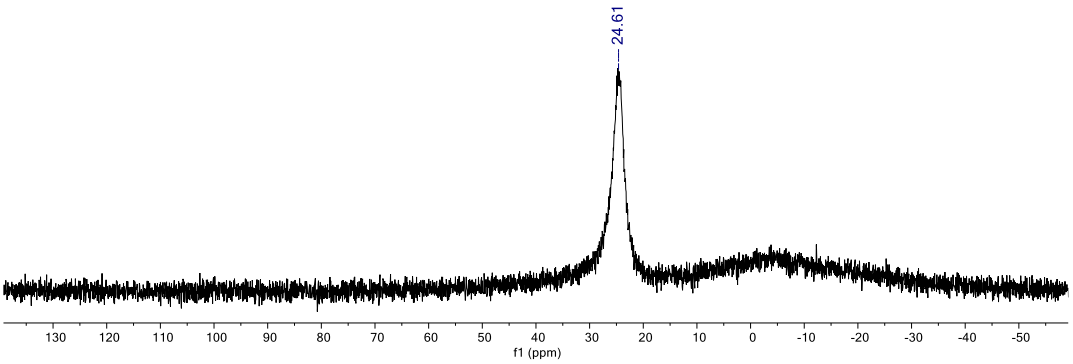


Figure S34. ^{11}B NMR spectrum of **10** in $CDCl_3$ at 298 K.

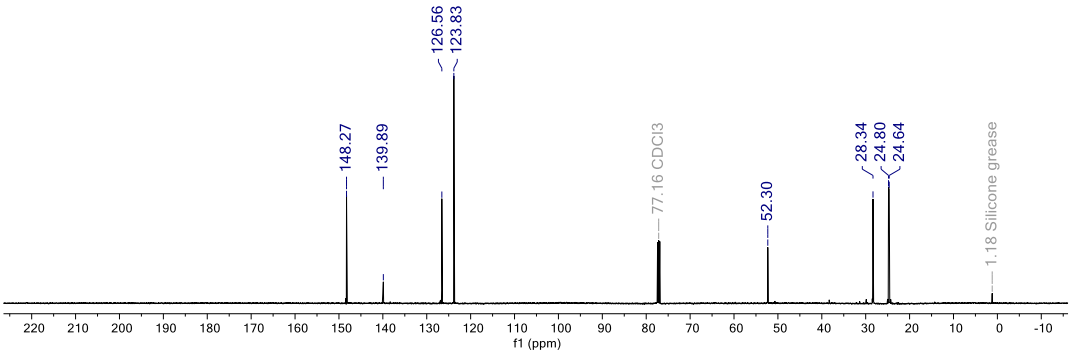
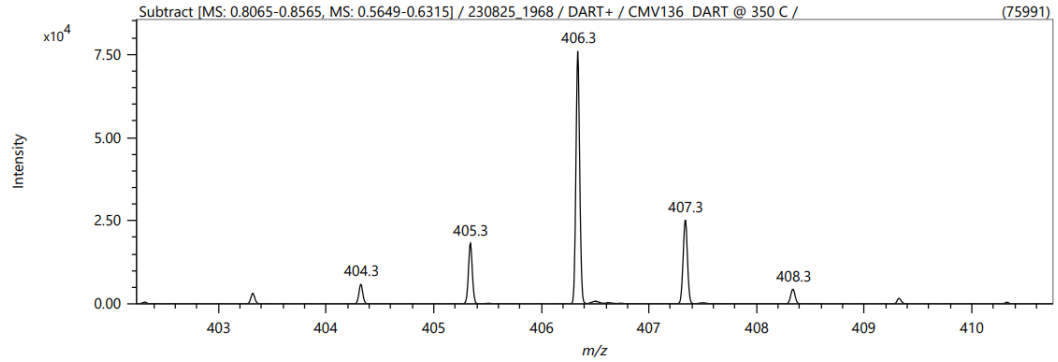


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$ at 298 K.

DART IONIZATION **AccuTOF 4G**

Spectrum

Subtract [MS: 0.8065-0.8565, MS: 0.5649-0.6315] / 230825_1968 / DART+ / CMV136 DART @ 350 C / (75991)



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	S	B
Electron:	Even	Min	0	0	0	0	0	0
Charge:	+1	Max	100	200	10	10	0	1
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
406.33901	75990.64	C26 H41 B N3	406.33881	0.20	0.50	8.5
		C19 H44 N5 O4	406.33878	0.23	0.55	0.5
		C20 H40 N9	406.34012	-1.11	-2.74	5.5
		C15 H41 B N9 O3	406.34199	-2.99	-7.35	0.5
		C24 H44 N3 O2	406.34280	-3.80	-9.35	4.5
		C21 H41 B N5 O2	406.33478	4.22	10.40	4.5

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AIMS Mass Spectrometry Laboratory, University of Toronto **2023-08-25**

Figure S36. HR-MS (TOF DART+) data for **10**.

Synthesis of $(H_2CN(Dipp))_2B(N_3)$ 11

^{1}H NMR (400 MHz, Toluene-d_8) δ 7.18 – 7.10 (m, 2H), 7.08 – 7.03 (m, 4H), 3.46 (hept, $^3J_{H-H}$ = 7.0 Hz, 4H), 3.41 (s, 4H), 1.33 (d, $^3J_{H-H}$ = 7 Hz, 12H), 1.27 (d, $^3J_{H-H}$ = 7 Hz, 12H). ^{11}B NMR (128 MHz, Toluene-d_8) δ 24.4. ^{13}C{^{1}H} NMR (101 MHz, Toluene-d_8) δ 147.8, 124.0, 52.0, 28.8, 24.8, 24.5, 1.4.

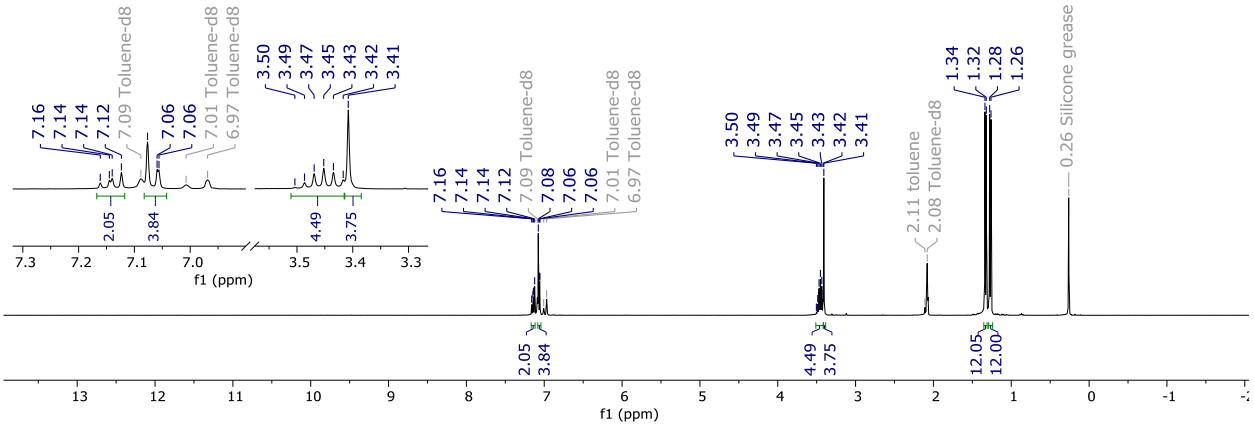


Figure S37. ^{1}H NMR spectrum of **11** in toluene-d_8 at 298 K.

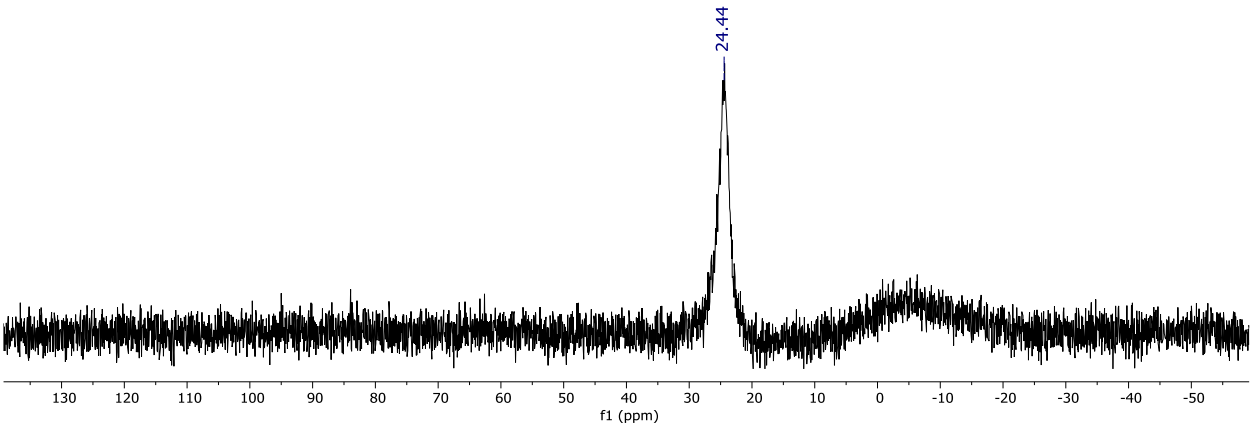


Figure S38. ^{1}H NMR spectrum of **11** in toluene-d_8 at 298 K.

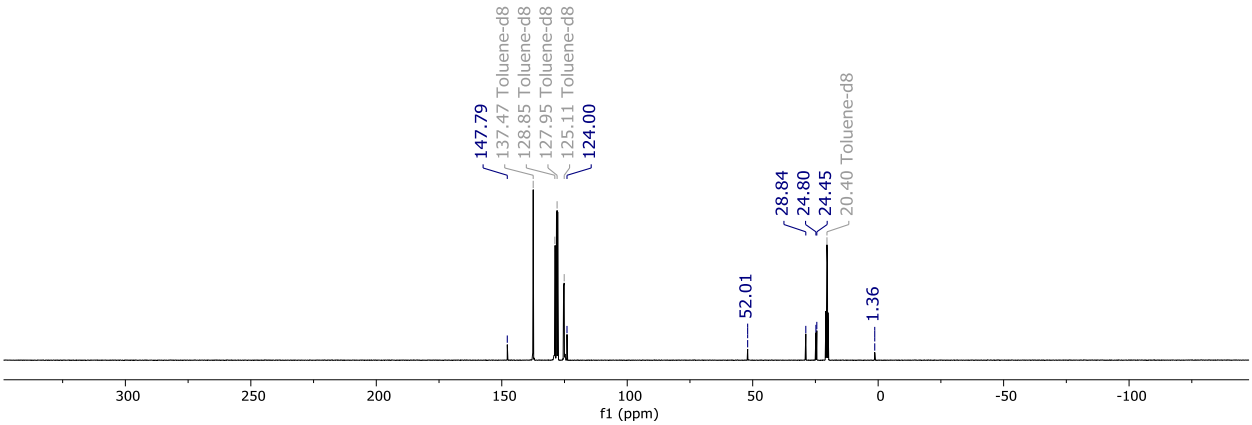


Figure S39. ^{1}H NMR spectrum of **11** in toluene-d_8 at 298 K.

Synthesis of $(HCN(Dipp))_2B(NHPCl_2)$ 12.

^{1}H NMR (400 MHz, Benzene-d_6) δ 7.24 – 7.17 (m, 2H), 7.15 – 7.09 (m, 4H), 5.92 (s, 2H), 4.29 (d, $^{2}J_{P\text{-}H}$ = 11 Hz, 1H), 3.20 (hept, $^{3}J_{H\text{-}H}$ = 7 Hz, 5H), 1.30 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 13H), 1.18 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 13H). ^{11}B NMR (128 MHz, C_6D_6) δ 21.1. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 147.0, 146.9, 146.5, 137.0, 137.0, 128.7, 124.3, 118.2, 28.8, 24.7, 23.9. ^{31}P NMR (162 MHz, C_6D_6) δ 164.2.

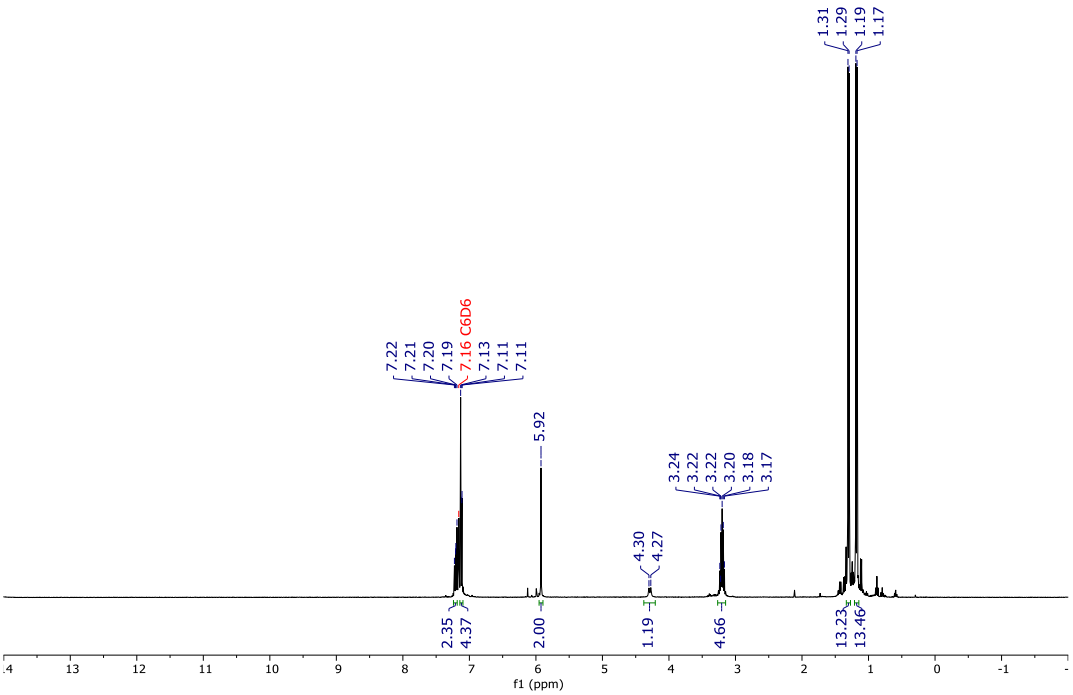


Figure S40. ^{1}H NMR spectrum of **12** in C_6D_6 at 298 K.

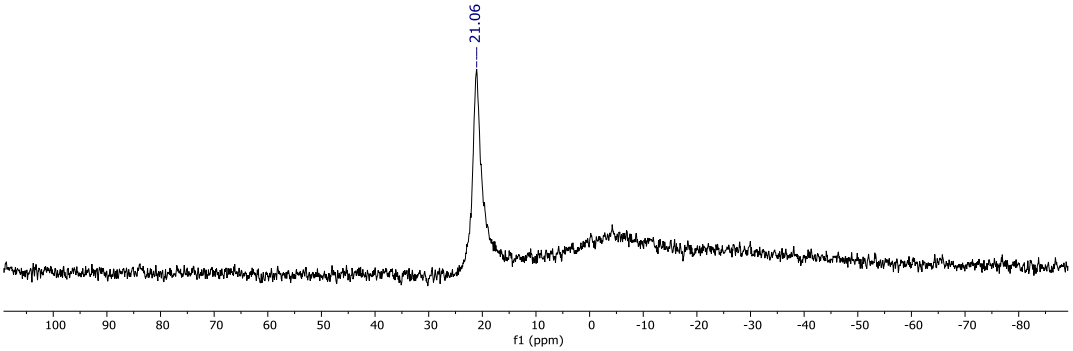


Figure S41. ^{11}B NMR spectrum of **12** in C_6D_6 at 298 K.

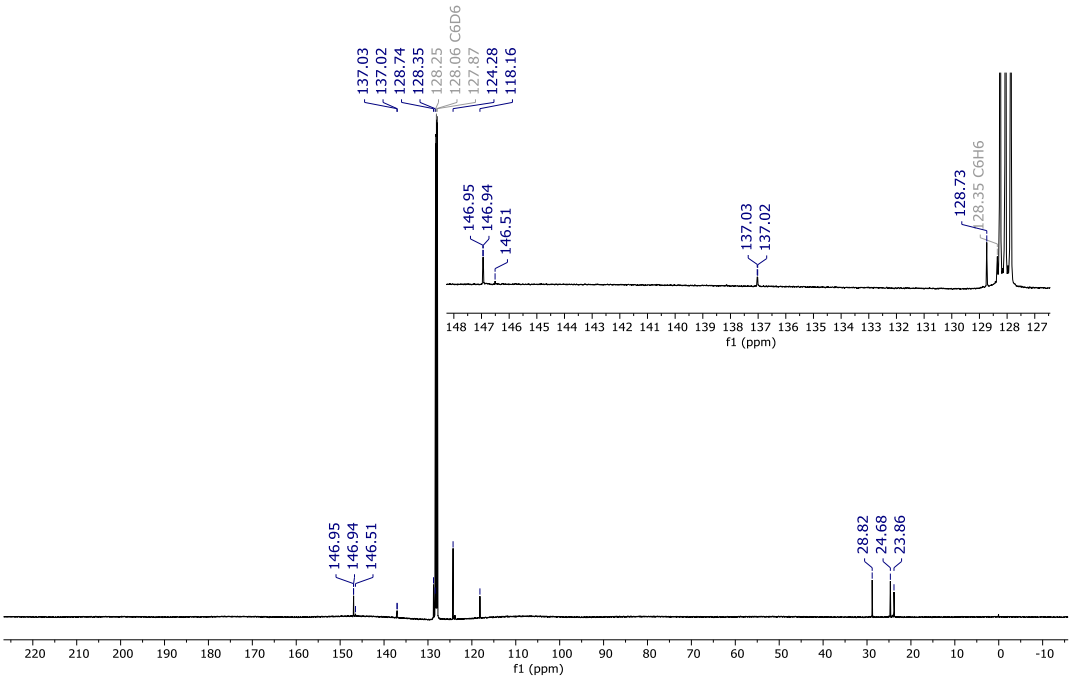


Figure S42. $^{13}C\{^1H\}$ NMR spectrum of **12** in C_6D_6 at 298 K.

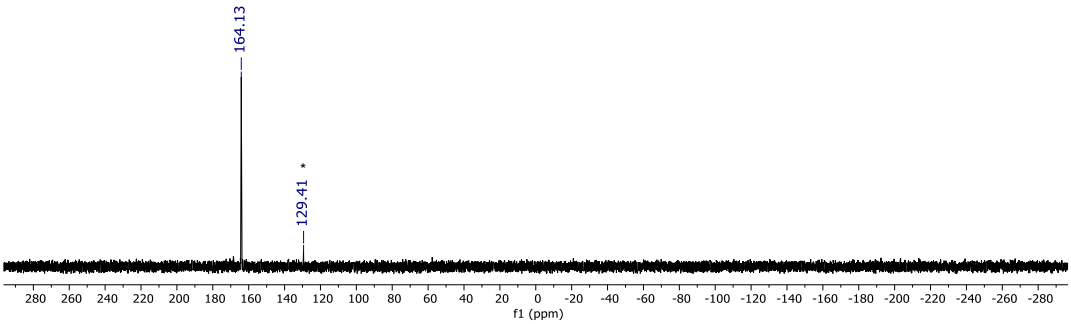


Figure S43. ^{31}P NMR spectrum of **12** in C_6D_6 at 298 K.

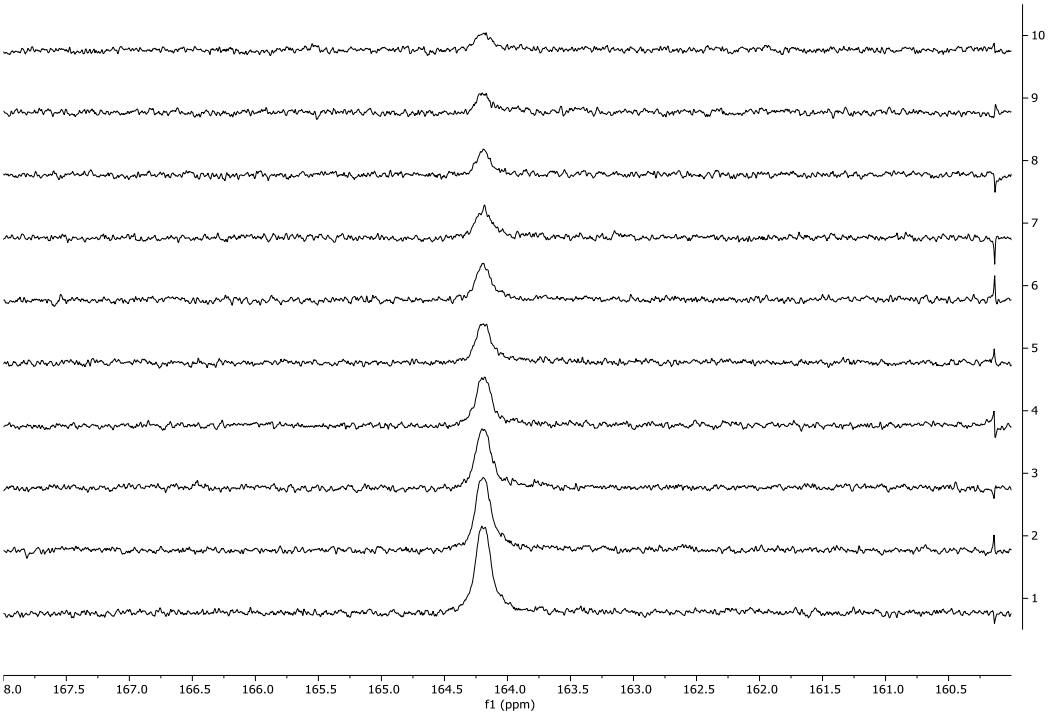


Figure S44. Raw ^{31}P NMR DOSY spectrum of **12** in C_6D_6 at 298 K.

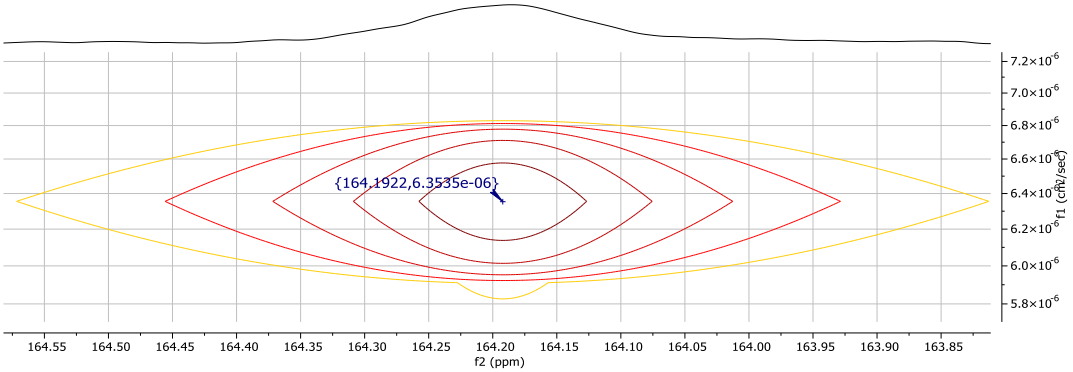


Figure S45. Processed ^{31}P NMR DOSY spectrum of **12** in C_6D_6 at 298 K.

Synthesis of (HCN(Dipp))$_2$B(N(SiMe$_3$)PCl$_2$) 15.

^{1}H NMR (500 MHz, C_6D_6) δ 7.25 – 7.19 (m, 2H), 7.15 – 7.09 (m, 4H), 6.10 (s, 2H), 3.36 (br, 2H), 3.14 (br, 2H), 1.40 (br, 6H), 1.31 (br, 6H), 1.12 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H), 0.19 (s, 9H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.6. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 147.1, 145.9, 137.67, 124.2, 119.9, 29.7, 28.4, 26.5, 23.1, 22.6, 3.0, 3.0. ^{31}P NMR (162 MHz, C_6D_6) δ 175.7. *HRMS* (TOF, DART+) m/z 576.26719 (calc. for protonated molecular ion, $[C_{29}H_{46}BN_3SiPCl_2]^+$: 576.26632) *MS* (TOF, DART+) m/z 540.3 (calc. for Cl^- loss, $[C_{29}H_{45}BN_3SiPCl]^+$: 540.29). *MS* (TOF, DART+) m/z 404.3 (calc. for hydrolysis and protonation *i.e.* –N(PCl$_2$)(SiMe$_3$) to –NH$_3^+$, $[C_{26}H_{39}BN_3]^+$: 404.32).

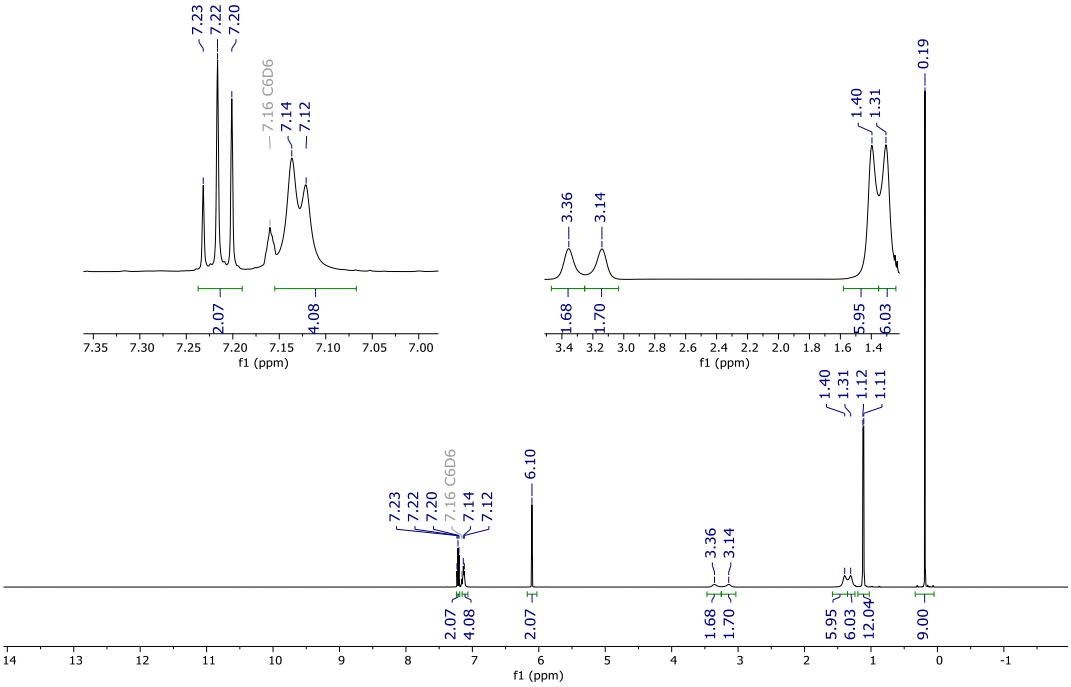


Figure S46. ^{1}H NMR spectrum of **15** in C_6D_6 at 298 K.

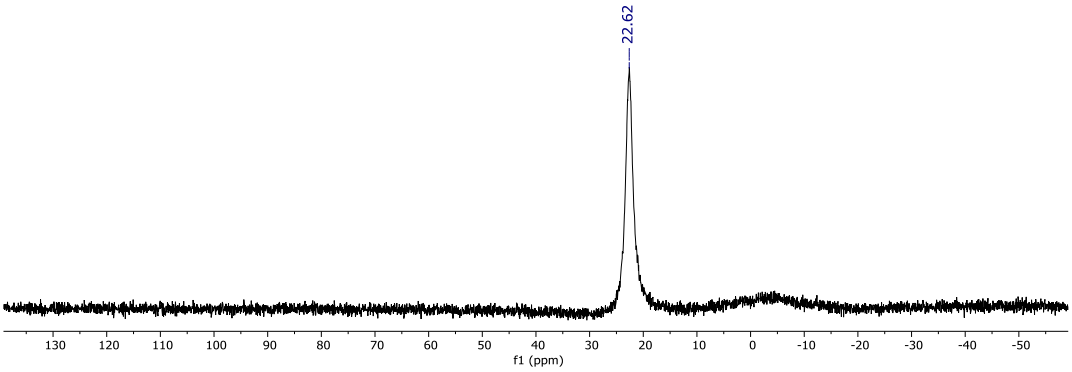


Figure S47. ^{11}B NMR spectrum of **15** in C_6D_6 at 298 K.

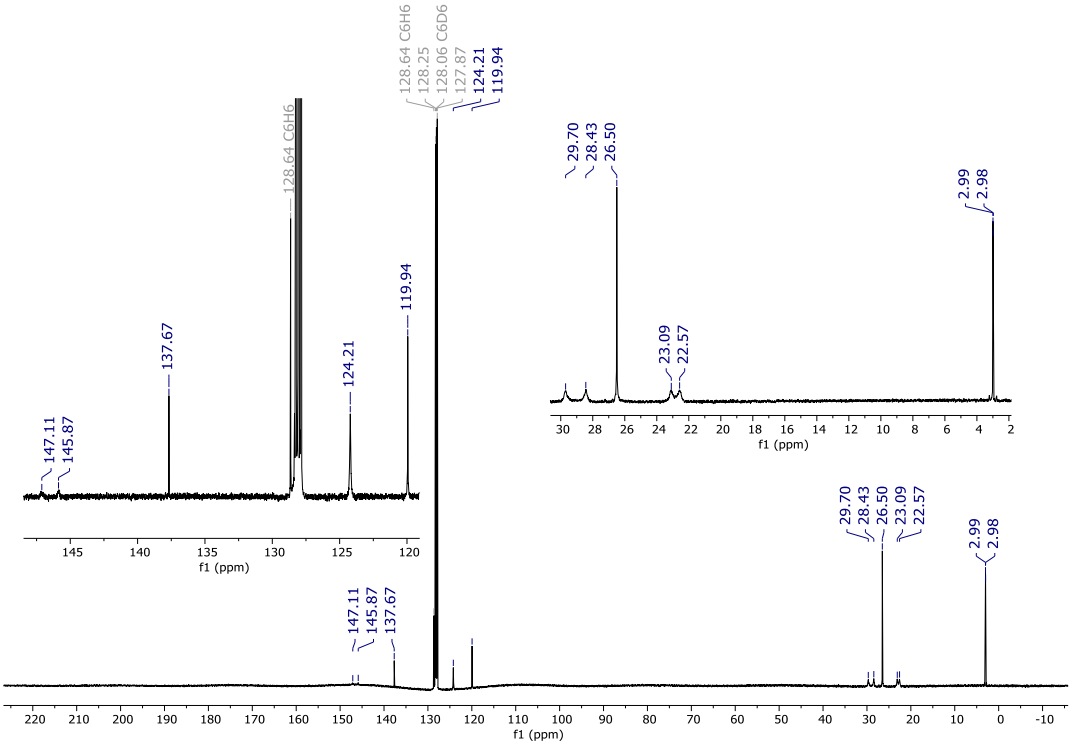


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of **15** in C_6D_6 at 298 K.

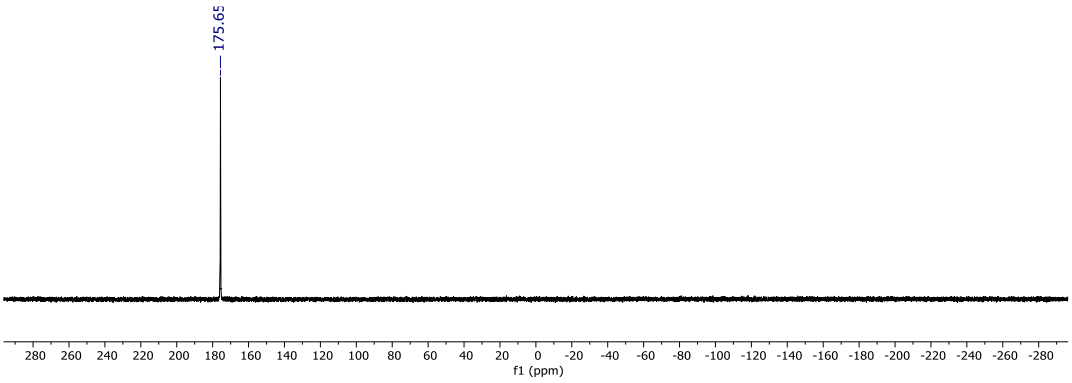


Figure S49. ^{31}P NMR spectrum of **15** in C_6D_6 at 298 K.

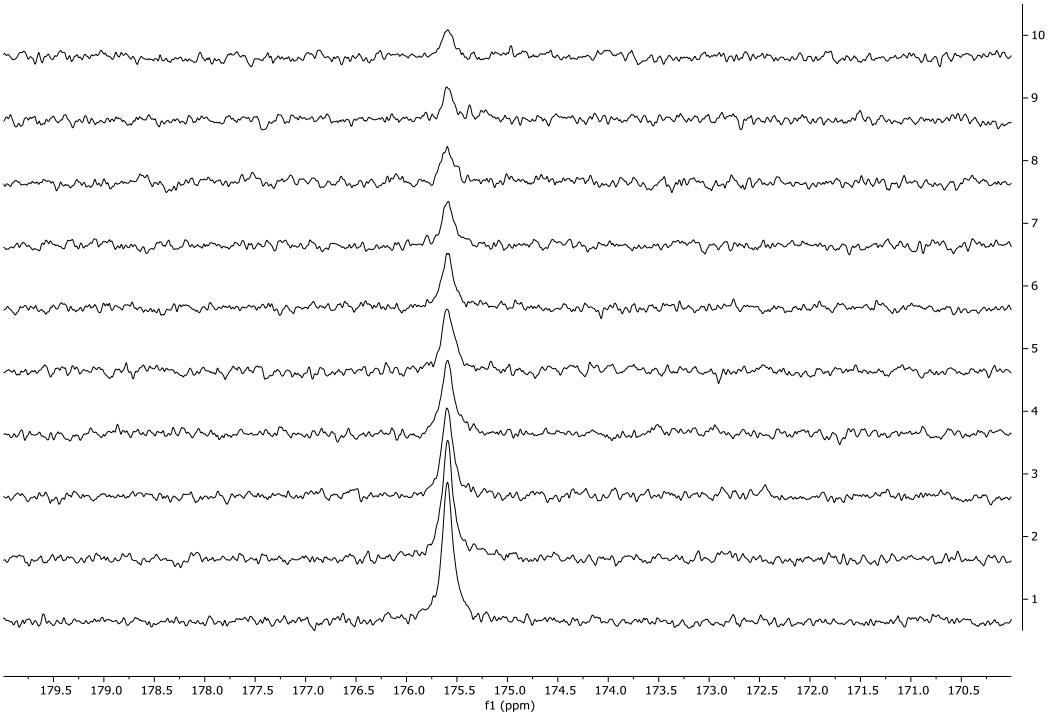


Figure S50. Raw ^{31}P NMR DOSY spectrum of **15** in C_6D_6 at 298 K.

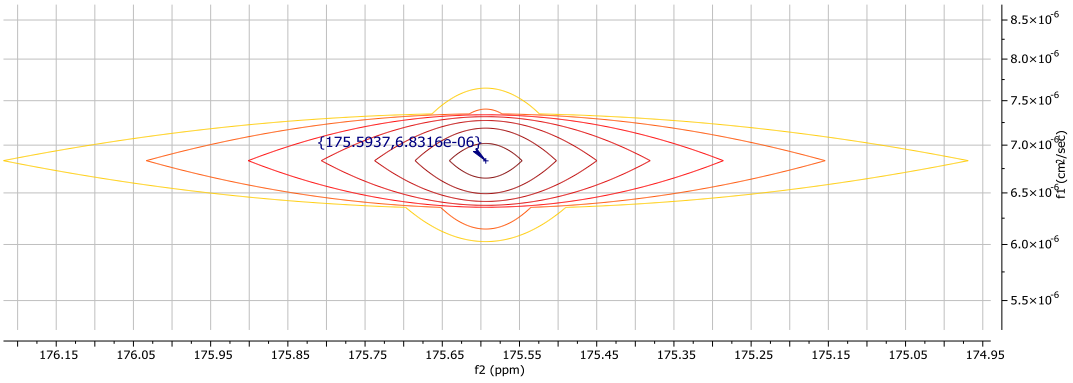
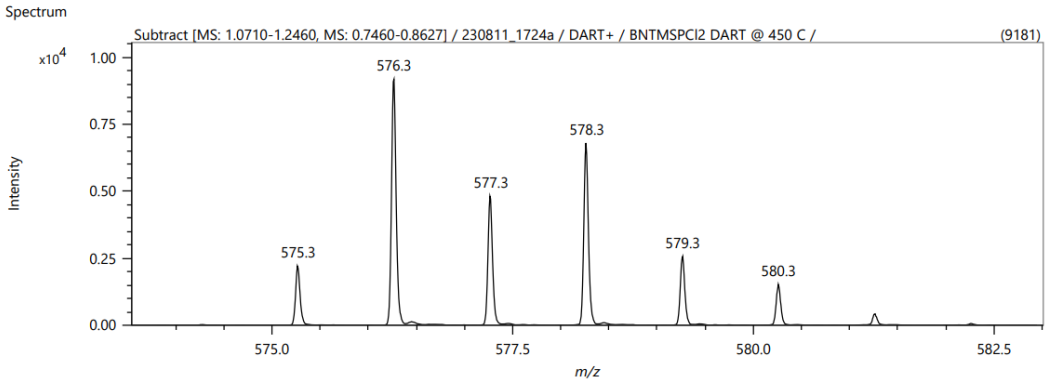


Figure S51. Processed ^{31}P NMR DOSY spectrum of **15** in C_6D_6 at 298 K.

DART IONIZATION **AccuTOF 4G**



Elemental Composition

Parameters		Elements Set 1:							
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	Cl	Si	B	P
Electron:	Even	Min	0	0	0	0	2	0	1	0
Charge:	+1	Max	100	200	10	10	2	1	1	1
DBE:	-1.5 - 100.0									

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
576.26719	9180.68	C28 H41 B N5 O3 Cl2	576.26740	-0.21	-0.37	10.5
		C19 H45 B N7 O6 Si Cl2	576.26652	0.67	1.16	1.5
		C22 H42 B N9 O2 P Cl2	576.26637	0.82	1.42	6.5
		C29 H46 B N3 Si P Cl2	576.26632	0.87	1.50	9.5
		C27 H45 B N O7 Cl2	576.26607	1.12	1.95	5.5
		C26 H46 B N3 O4 P Cl2	576.26906	-1.87	-3.24	5.5

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AIMS Mass Spectrometry Laboratory, University of Toronto **2023-08-11**

Figure S52. HR-MS (TOF DART+) data for **15**.

Synthesis of $(HCN(Dipp))_2B(N(SiMe_3)PCl(O_3SCF_3))$ 16 ^{1}H NMR (400 MHz, C_6D_6) δ 7.35 – 7.26 (m, 1H), 7.21 – 7.17 (m, 2H), 7.11 – 7.04 (m, 1H), 6.05 (s, 2H), 3.28 (br, m, 2H), 3.07 (br, m, 1H), 2.96 (br, m, 1H), 1.47 (d, $^3J_{H\text{-}H}$ = 7 Hz, 3H), 1.38 (d, $^3J_{H\text{-}H}$ = 7 Hz, 3H), 1.32 (d, $^3J_{H\text{-}H}$ = 7 Hz, 3H), 1.21 (d, $^3J_{H\text{-}H}$ = 7 Hz, 3H), 1.17 – 0.99 (br, m, 12H), 0.07 (s, 9H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.1. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 147.0, 146.9, 146.5, 137.0, 137.0, 128.7, 124.3, 118.2, 28.8, 24.7, 23.9, 0.0. ^{19}F NMR (377 MHz, C_6D_6) δ -75.7. ^{31}P NMR (162 MHz, C_6D_6) δ 181.1.

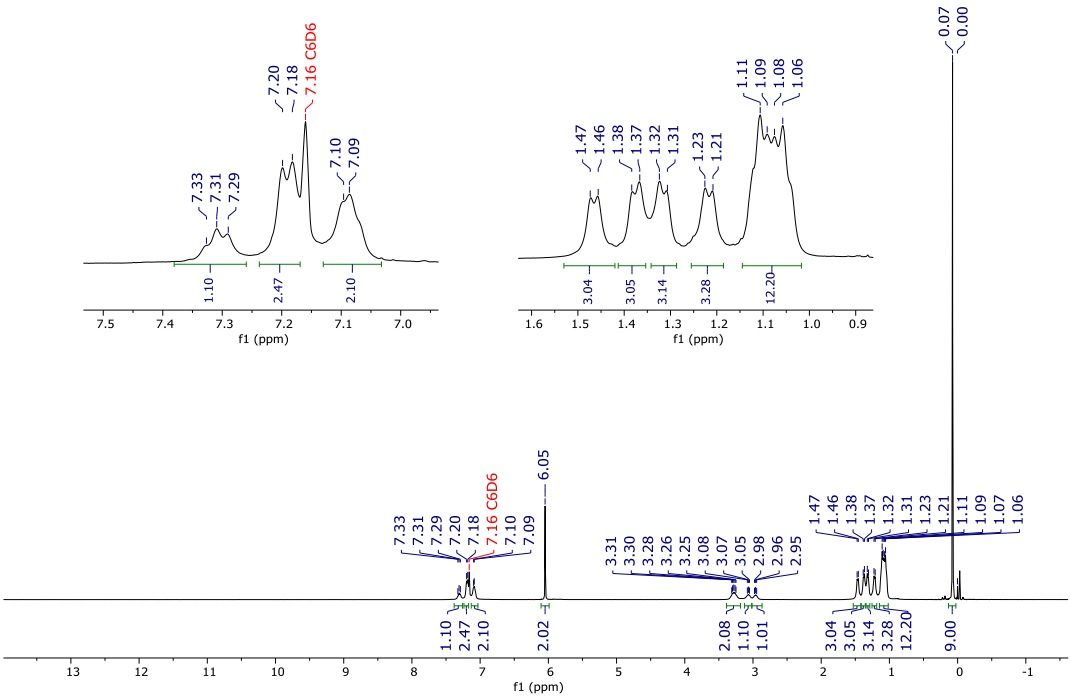

Figure S53. ^{1}H NMR spectrum of **16** in C_6D_6 at 298 K.

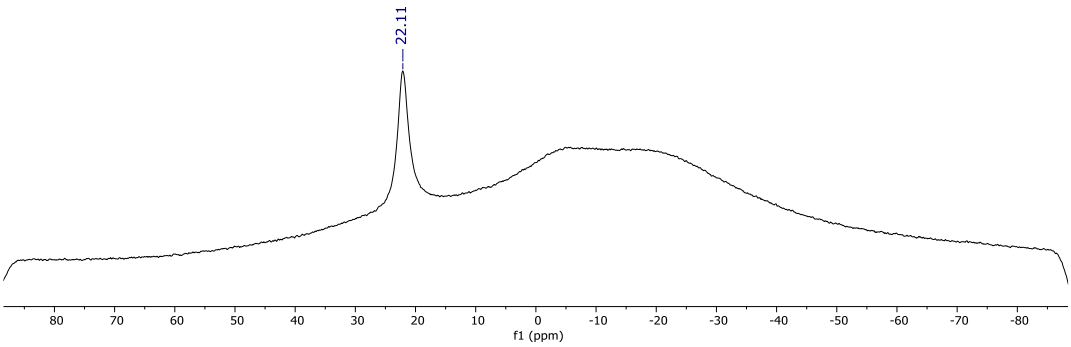

Figure S54. ^{11}B NMR spectrum of **16** in C_6D_6 at 298 K.

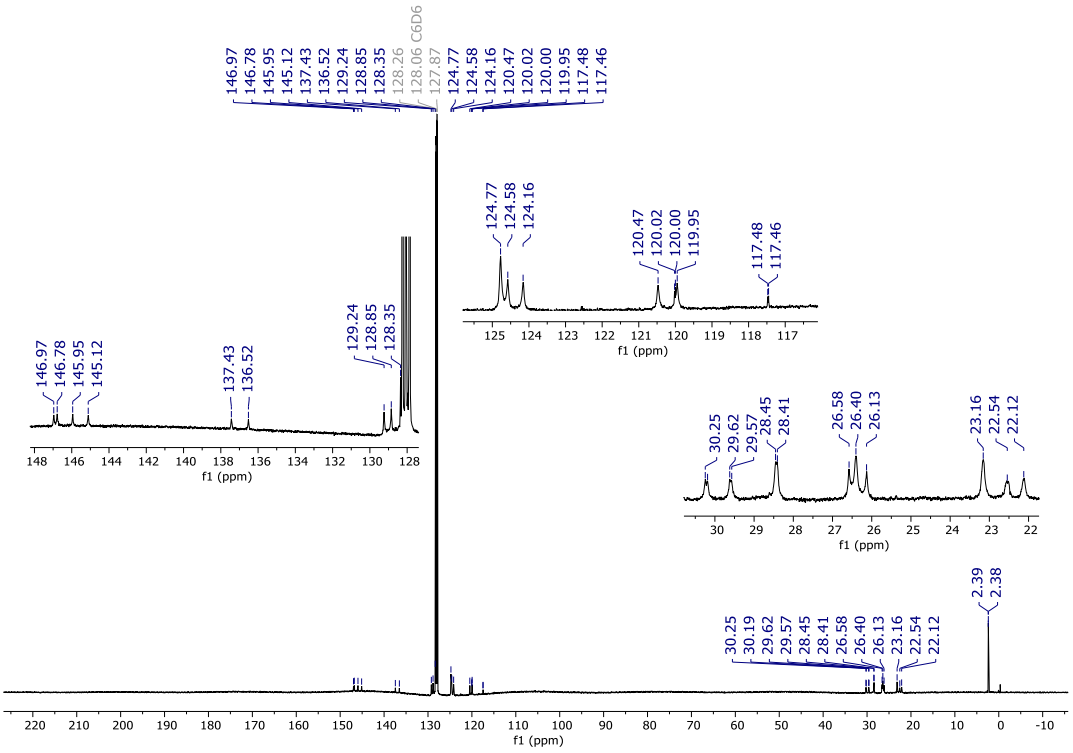

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of **16** in C_6D_6 at 298 K.

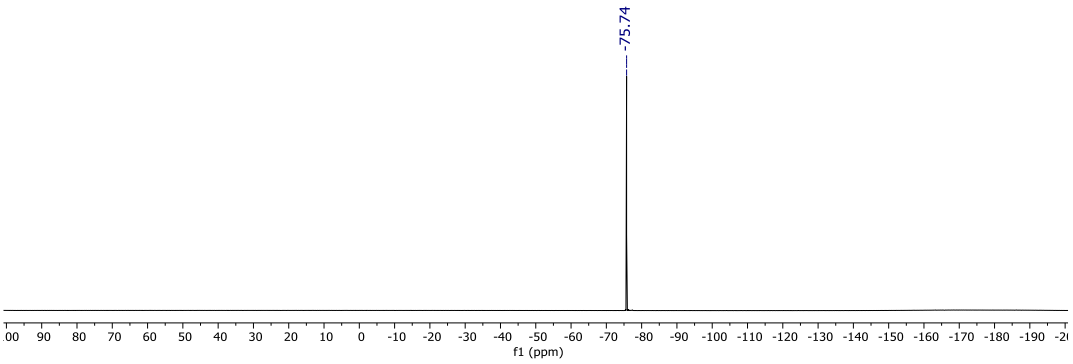

Figure S56. ^{19}F NMR spectrum of **16** in C_6D_6 at 298 K.

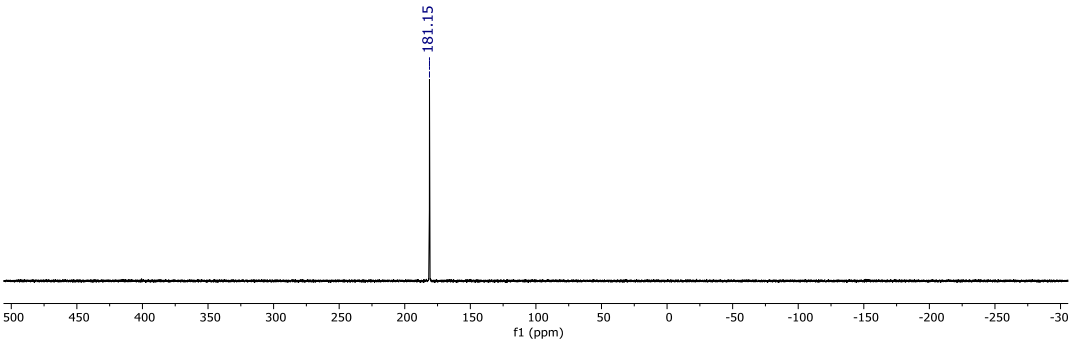

Figure S57. ^{31}P NMR spectrum of **16** in C_6D_6 at 298 K.

Synthesis of $[(HCN(Dipp))_2BNPCl]_2$ 17

^{1}H NMR (300 MHz, C_6D_6) δ 7.22 – 7.18 (m, 4H), 7.10 – 7.03 (m, 8H), 5.91 (s, 4H), 3.15 (hept, $^{3}J_{H\text{-}H}$ = 7 Hz, 8H), 1.27 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 24H), 1.14 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 24H). ^{11}B NMR (128 MHz, C_6D_6) δ 20.1. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 146.8, 137.7, 128.5, 123.9, 119.3, 29.0, 25.8, 23.2. ^{31}P NMR (121 MHz, C_6D_6) δ 228.3.

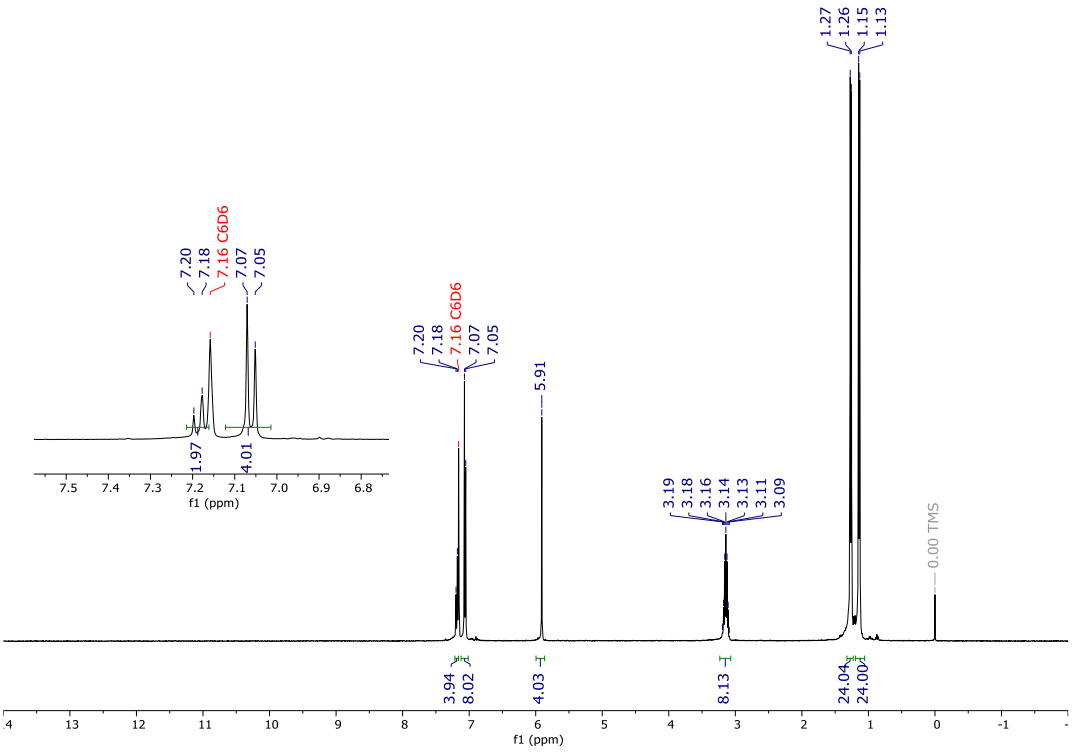

Figure S58. ^{1}H NMR spectrum of **17** in C_6D_6 at 298 K.

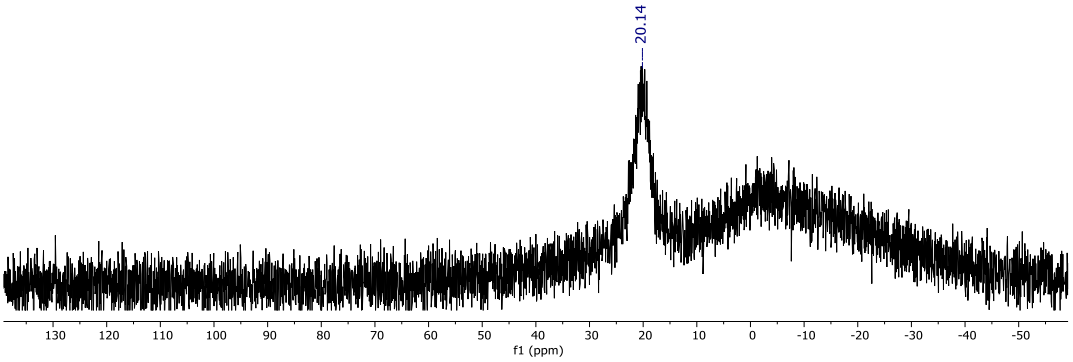

Figure S59. ^{11}B NMR spectrum of **17** in C_6D_6 at 298 K.

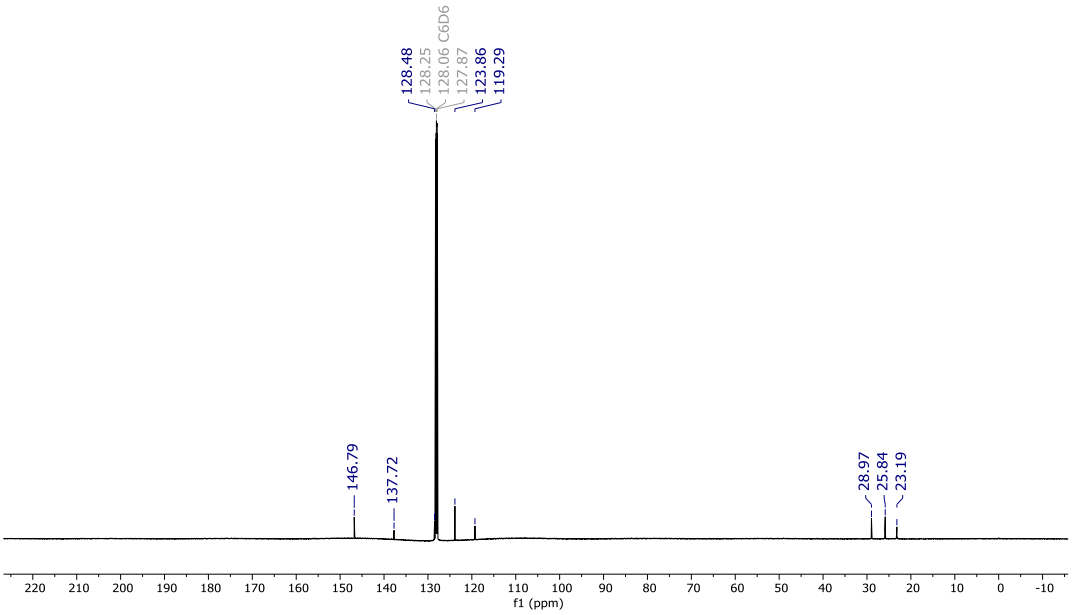

Figure S60. $^{13}C\{^1H\}$ NMR spectrum of **17** in C_6D_6 at 298 K.

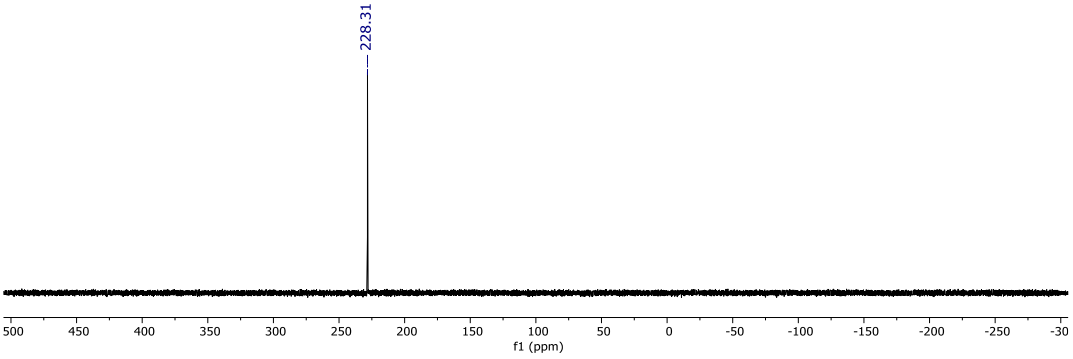

Figure S61. ^{31}P NMR spectrum of **17** in C_6D_6 at 298 K.

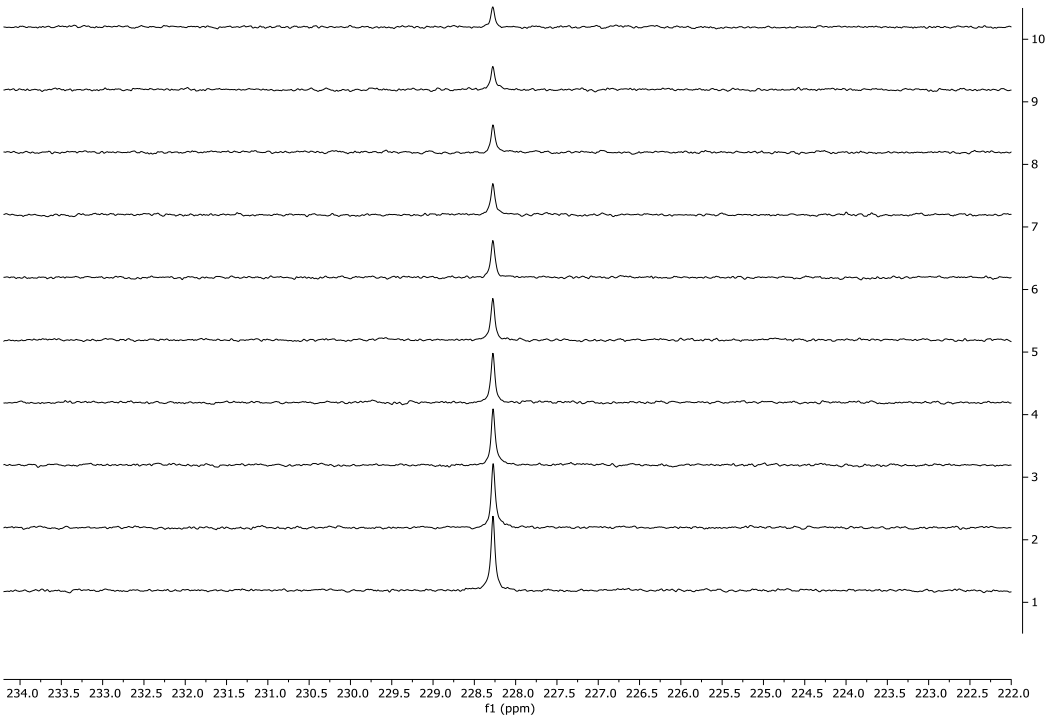

Figure S62. Raw ^{31}P NMR DOSY spectrum of **17** in C_6D_6 at 298 K.

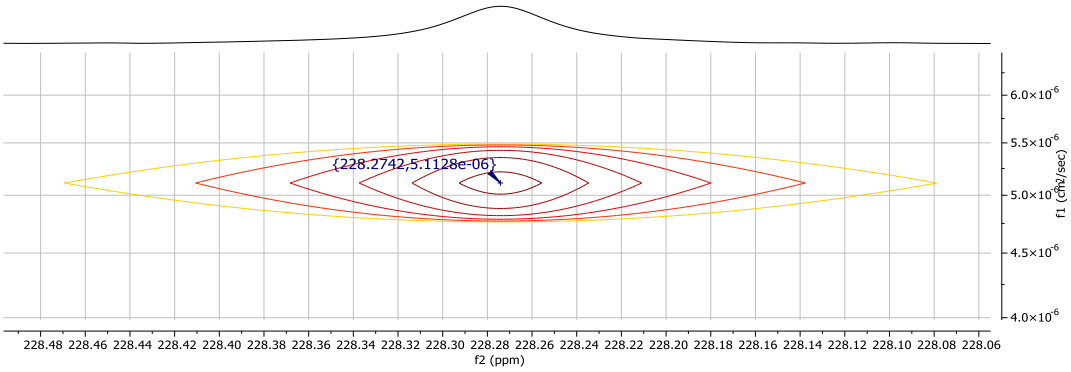

Figure S63. Processed ^{31}P NMR DOSY spectrum of **17** in C_6D_6 at 298 K.

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2. D. Herrmannsdörfer, M. Kaaz, O. Puntigam, J. Bender, M. Nieger and D. Gudat, *Eur. J. Inorg. Chem.*, 2015, **2015**, 4819-4828.
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