Supporting Information

for

Nucleophilic Substitution at a Coordinatively Saturated Five-Membered NHC·Haloborane Centre

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S1. Spectroscopic characterization of `1-8

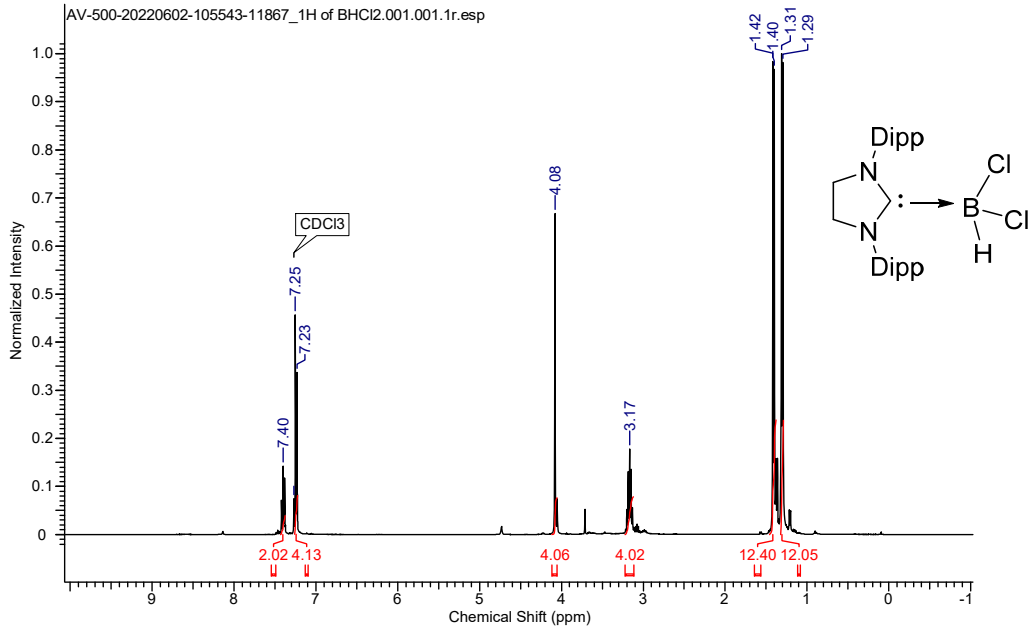


Figure S1.[1]H NMR spectrum of **1**.

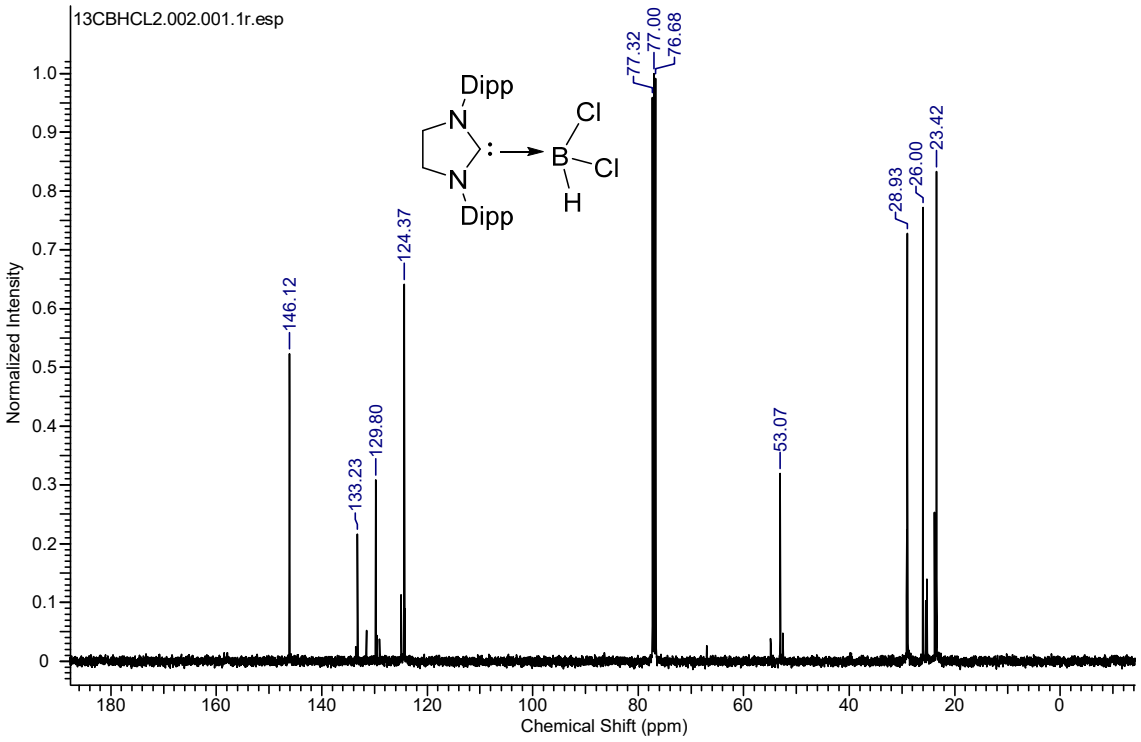


Figure S2.[13]C NMR spectrum of **1**.

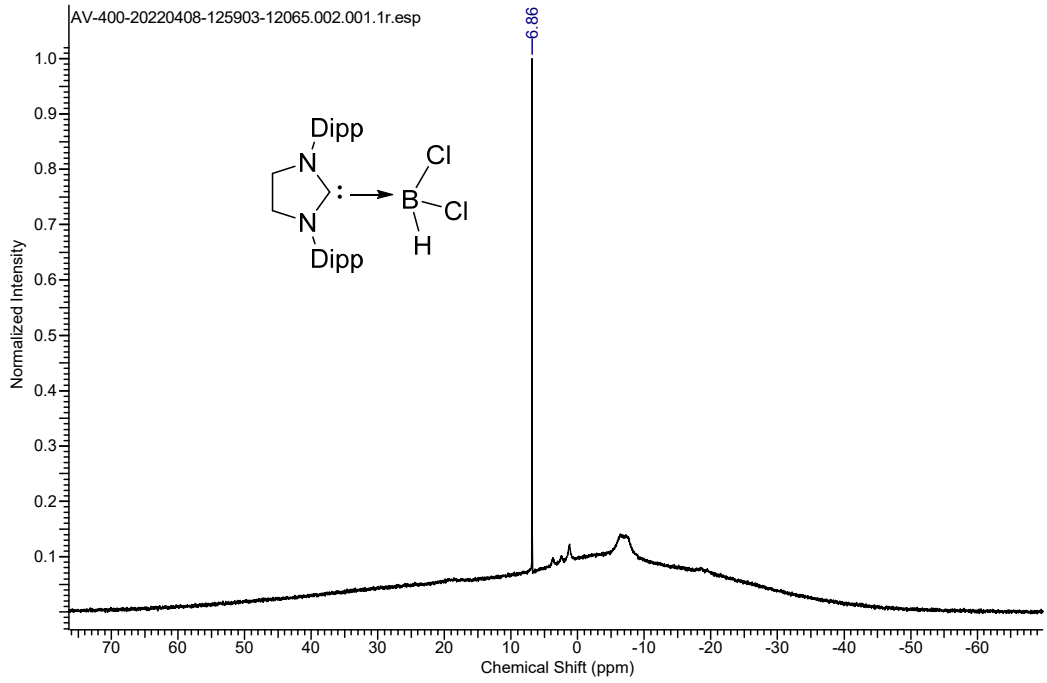


Figure S3.[11]B NMR spectrum of **1**.

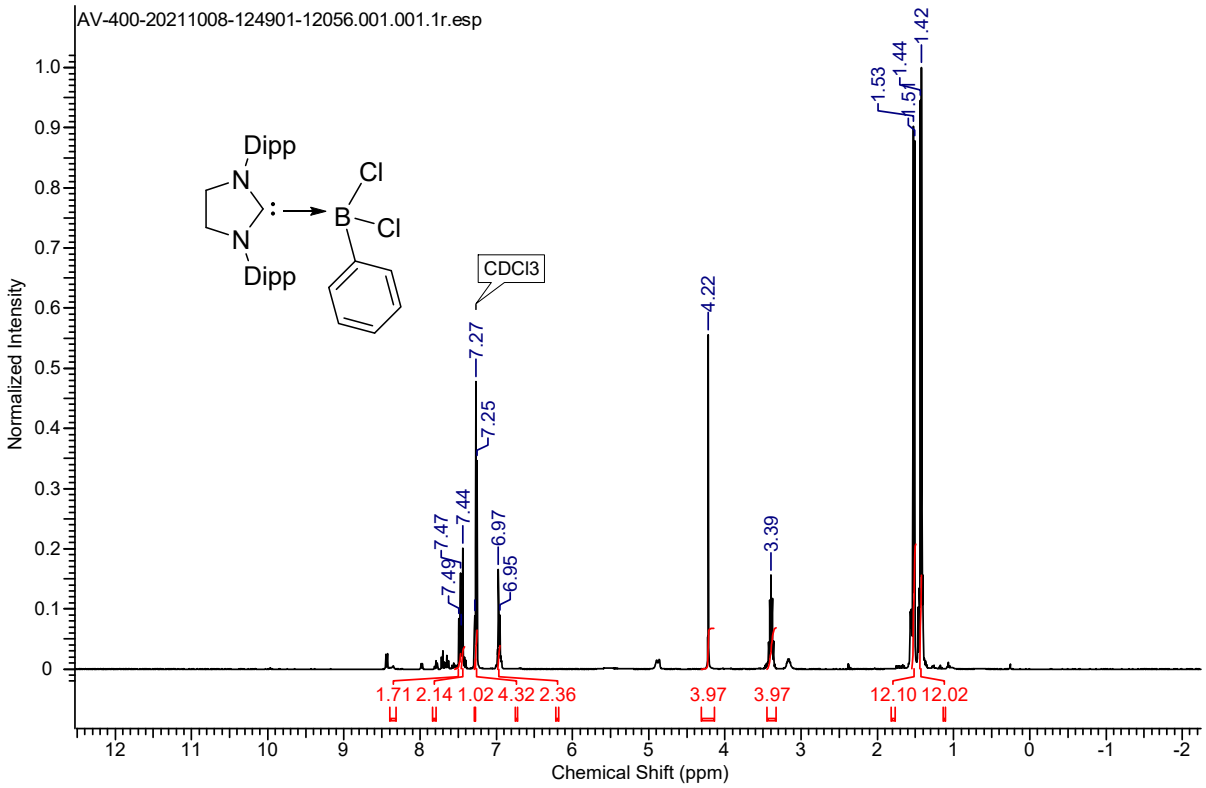


Figure S4.[1]H NMR spectrum of **2**.

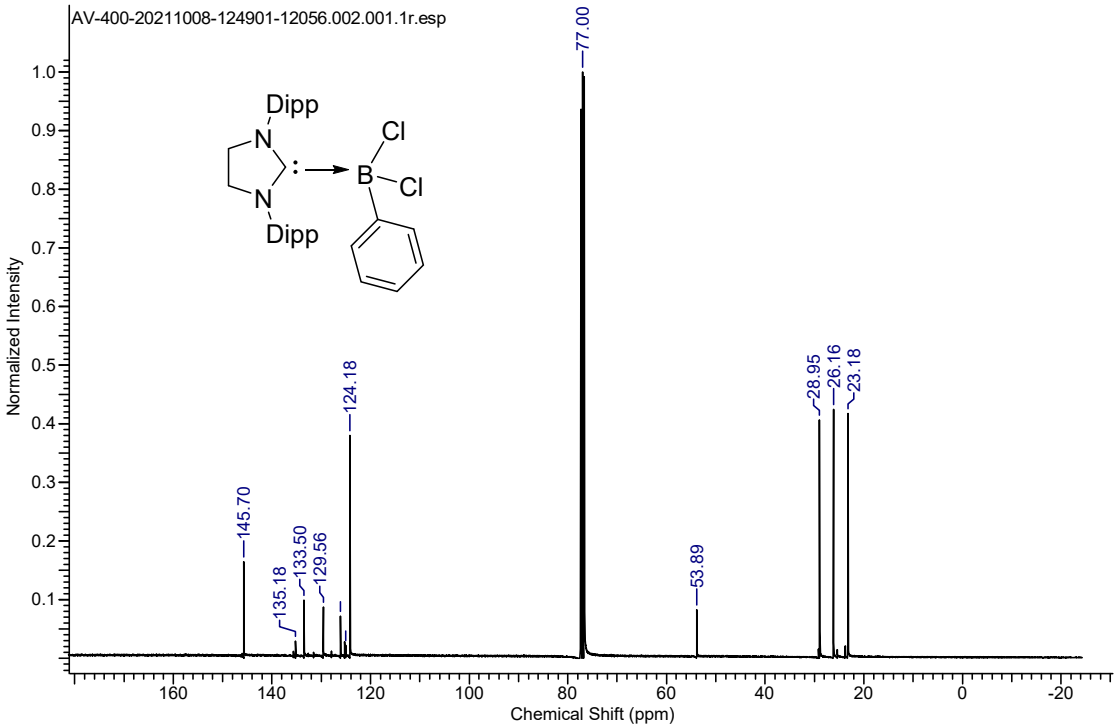


Figure S5.[13]C NMR spectrum of **2**.

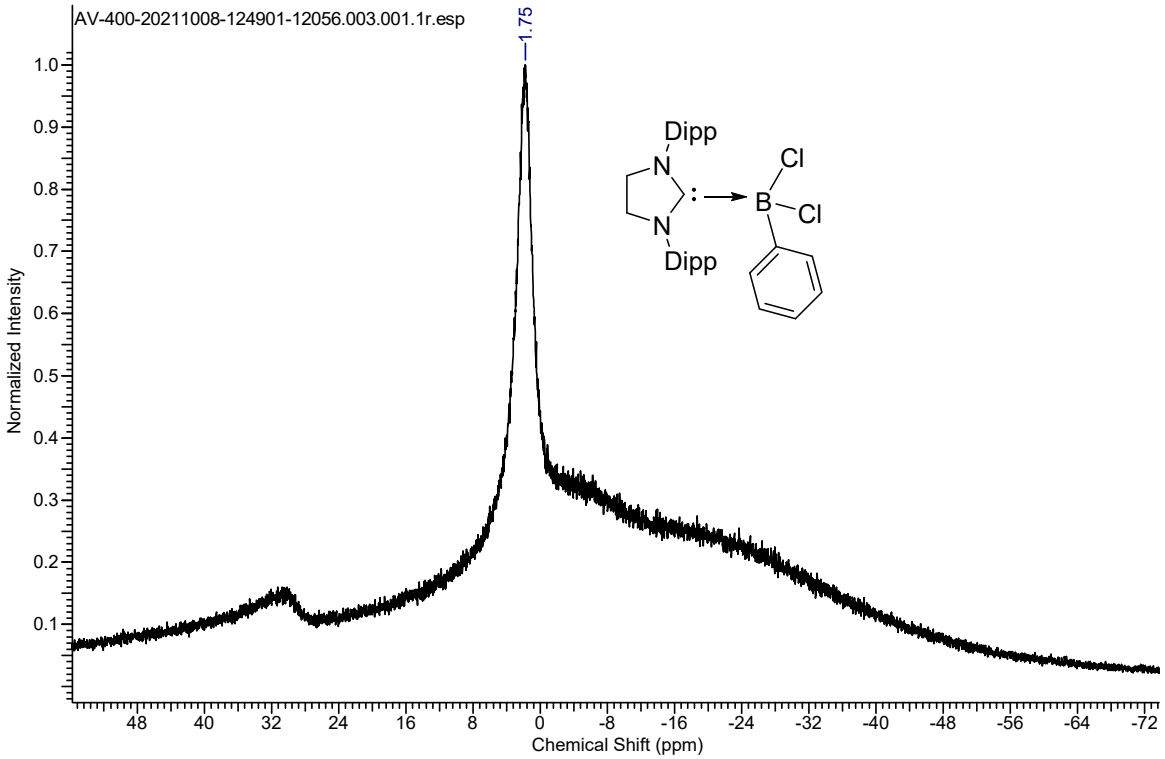


Figure S6.[11]B NMR spectrum of **2**.

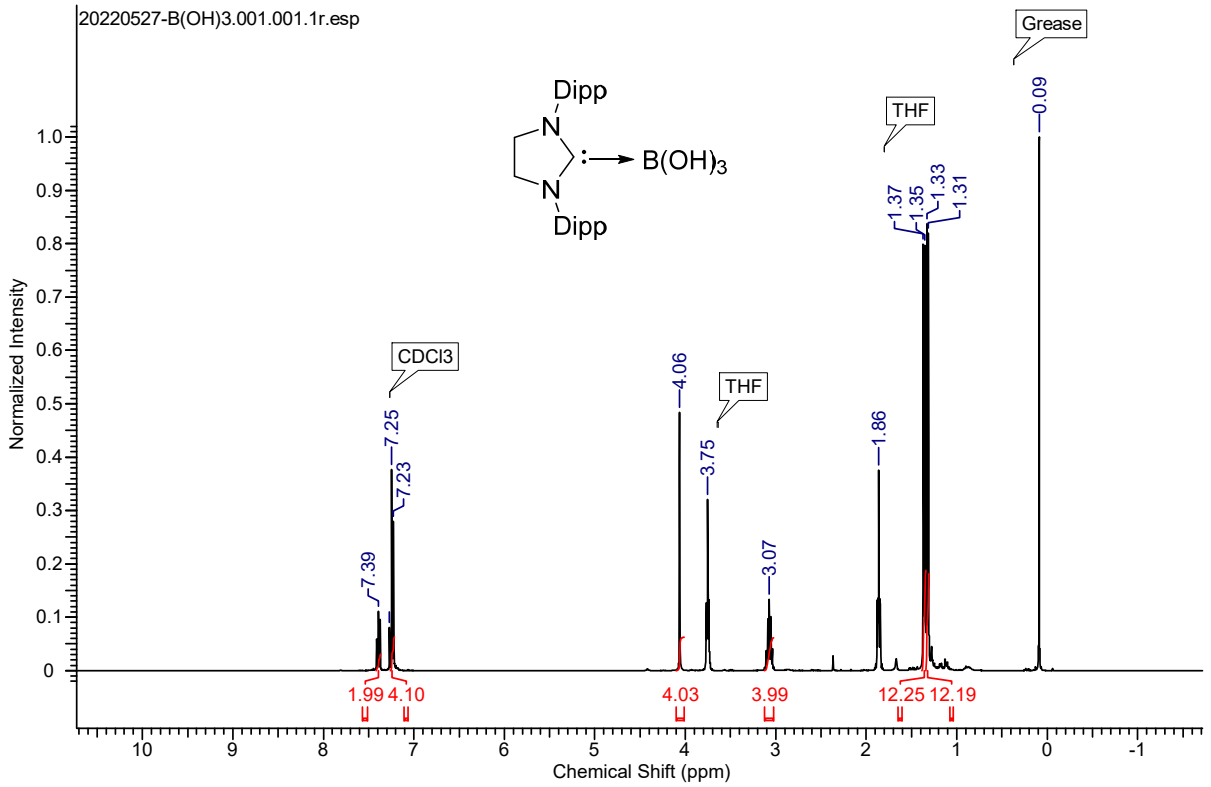


Figure S7.[1]H NMR spectrum of **3**.

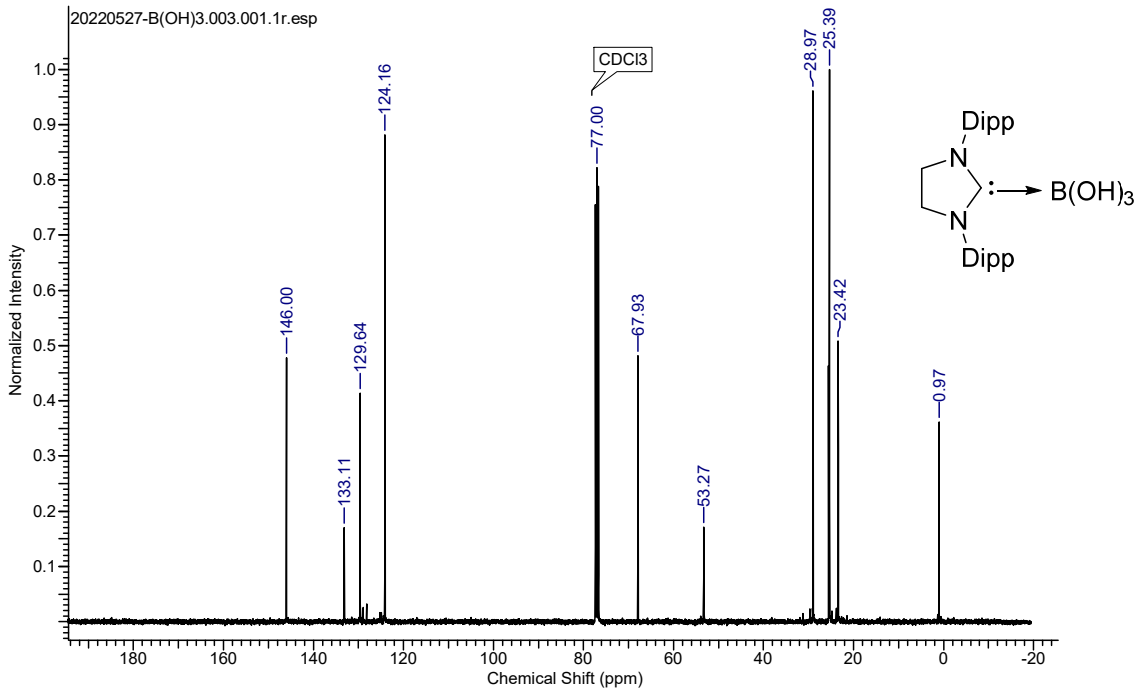


Figure S8.[13]C NMR spectrum of **3**.

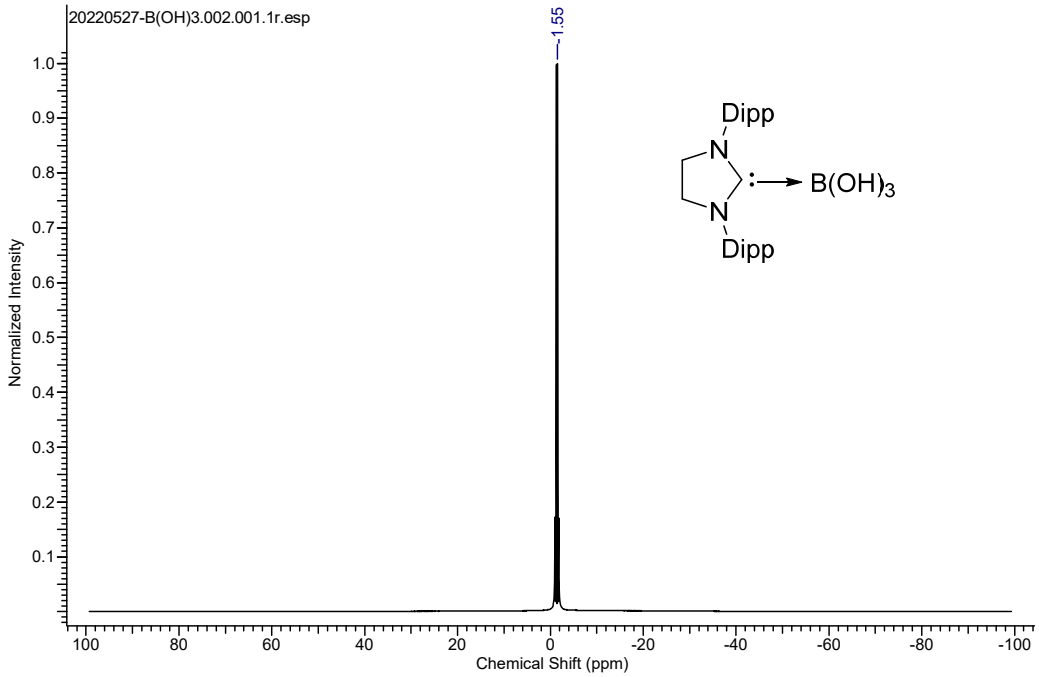


Figure S9.[11]B NMR spectrum of **3**.

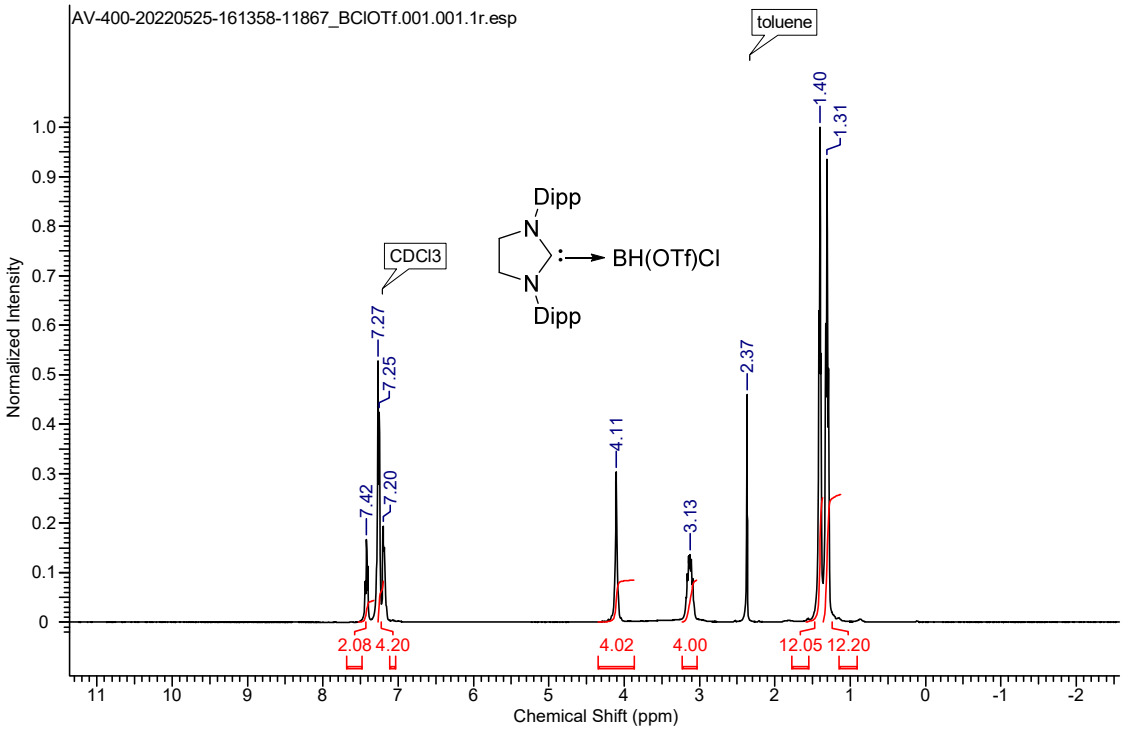


Figure S10.[1]H NMR spectrum of **4**.

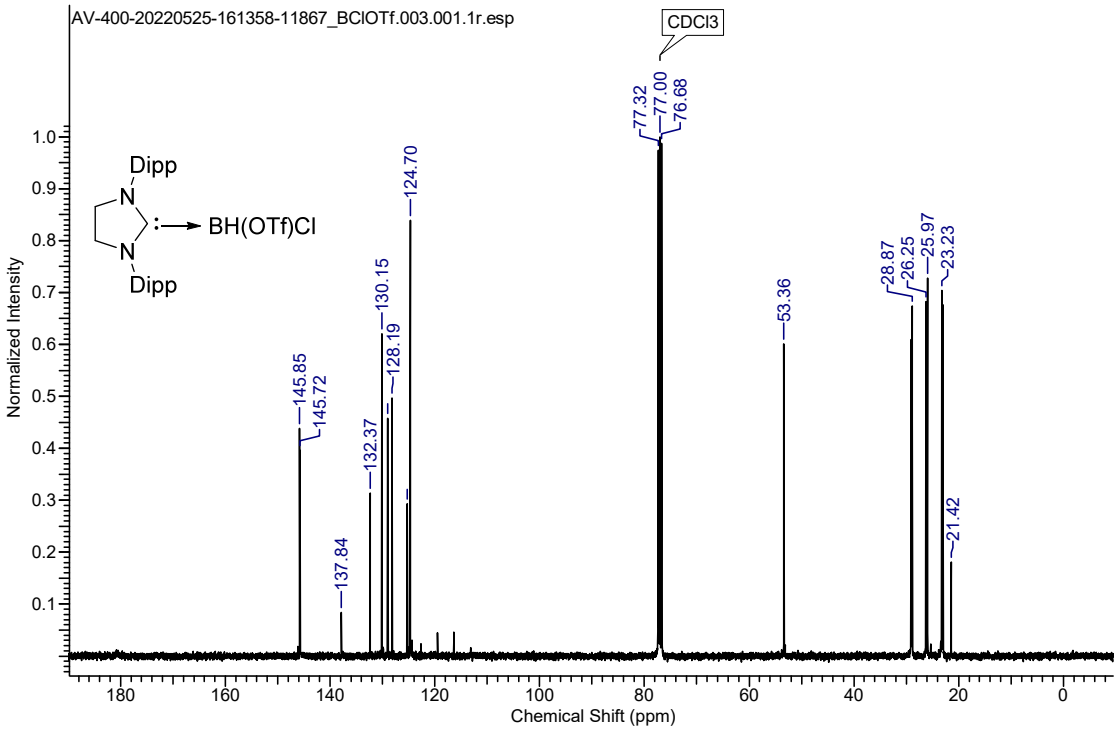


Figure S11.[13]C NMR spectrum of **4**.

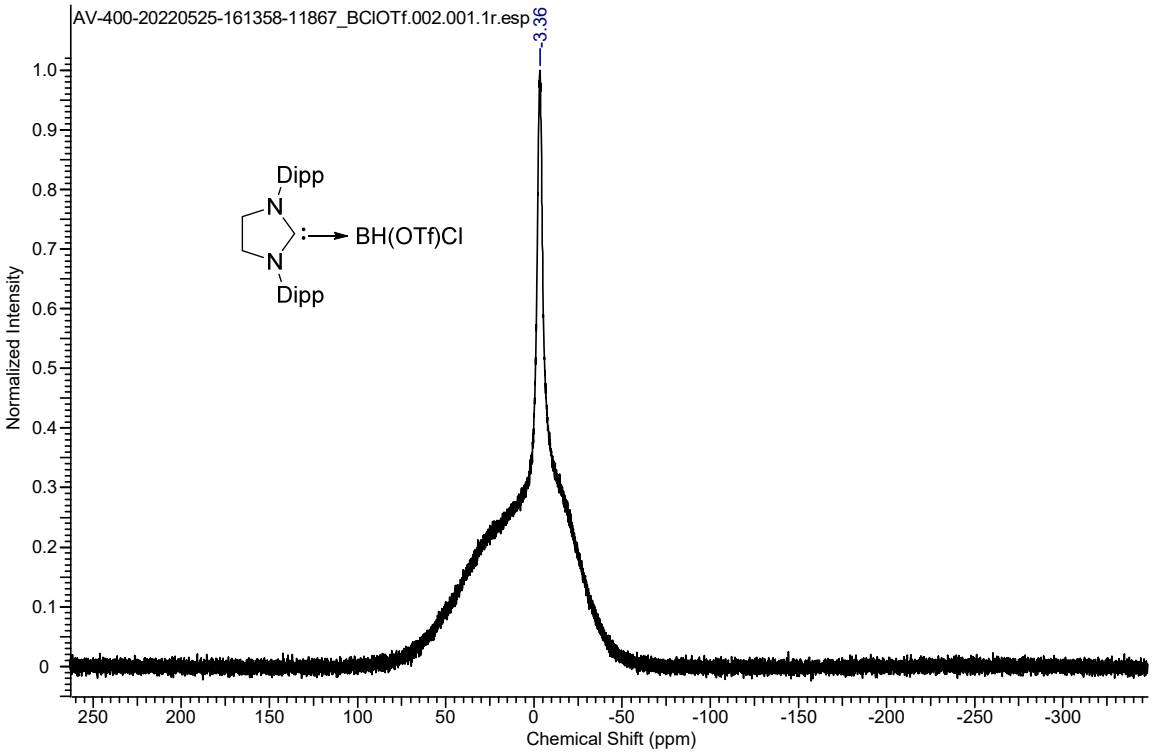


Figure S12.[11]B NMR spectrum of **4**.

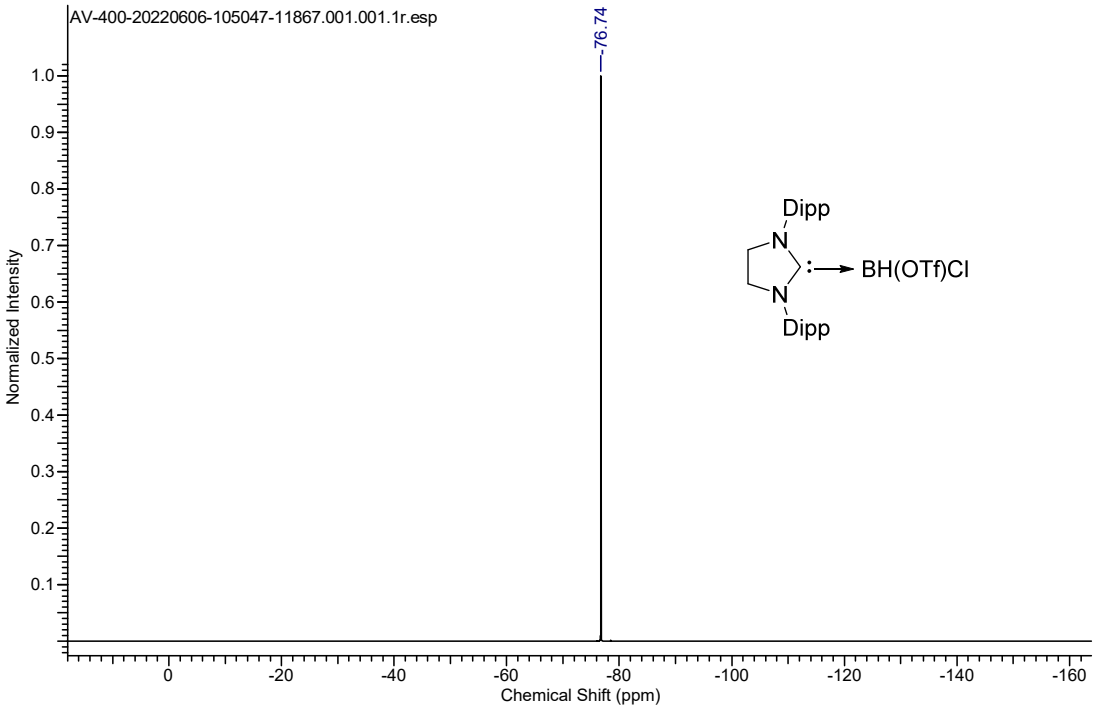


Figure S13.[19]F NMR spectrum of **4**.

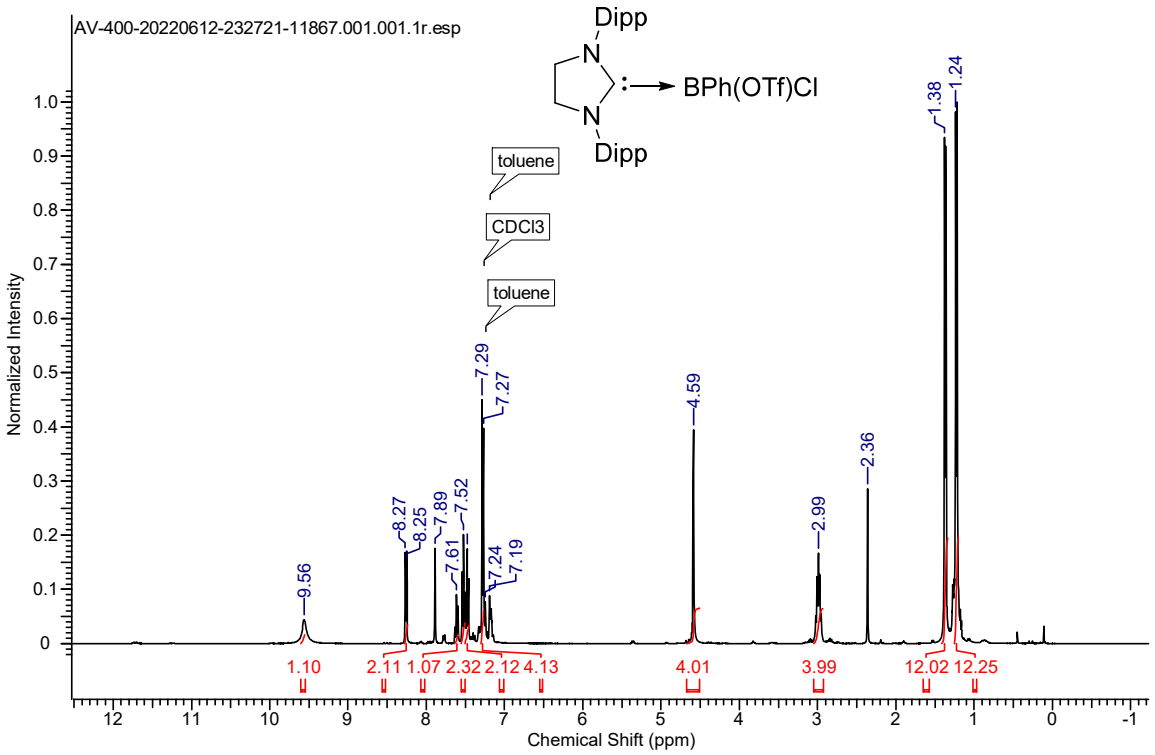


Figure S14. [1]H NMR spectrum of **5b**.

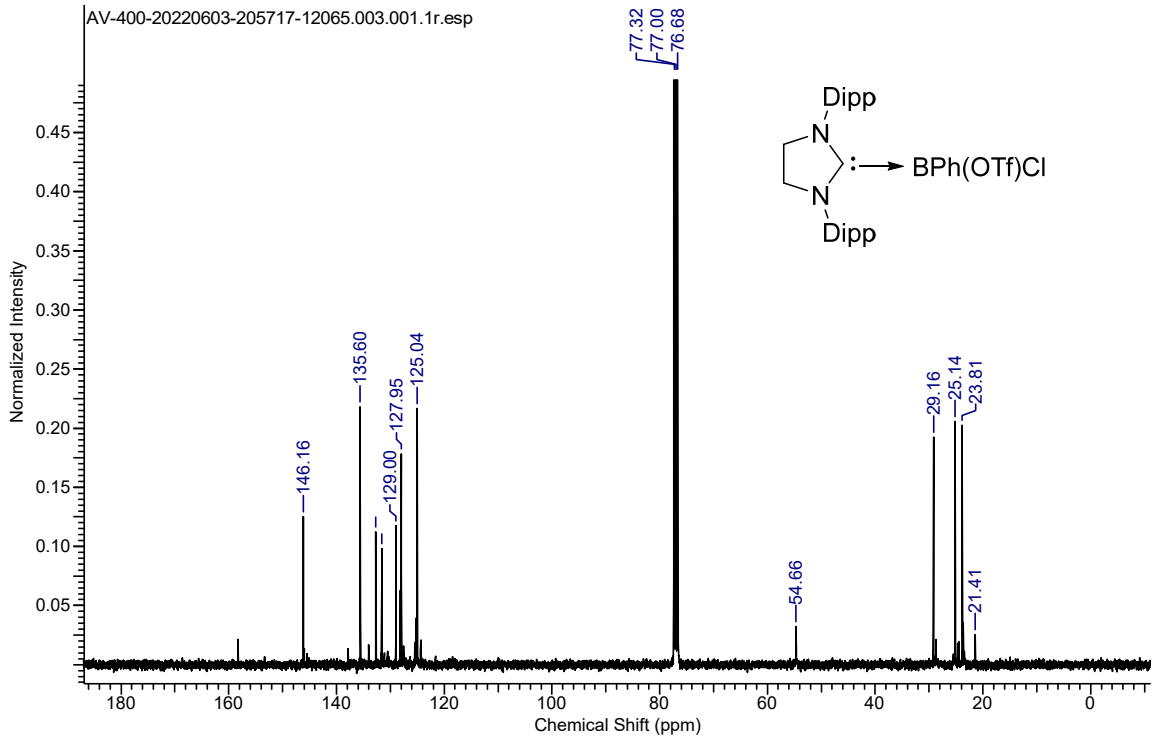


Figure S15. ^{13}C NMR spectrum of **5b**.

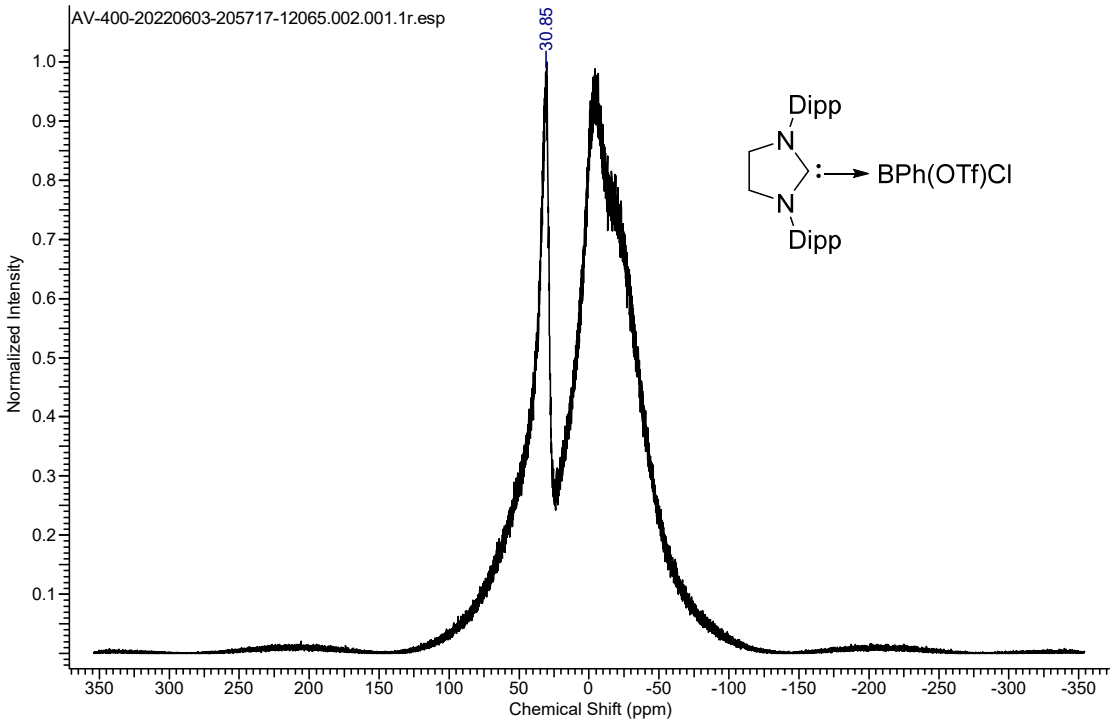


Figure S16. ^{11}B NMR spectrum of **5b**.

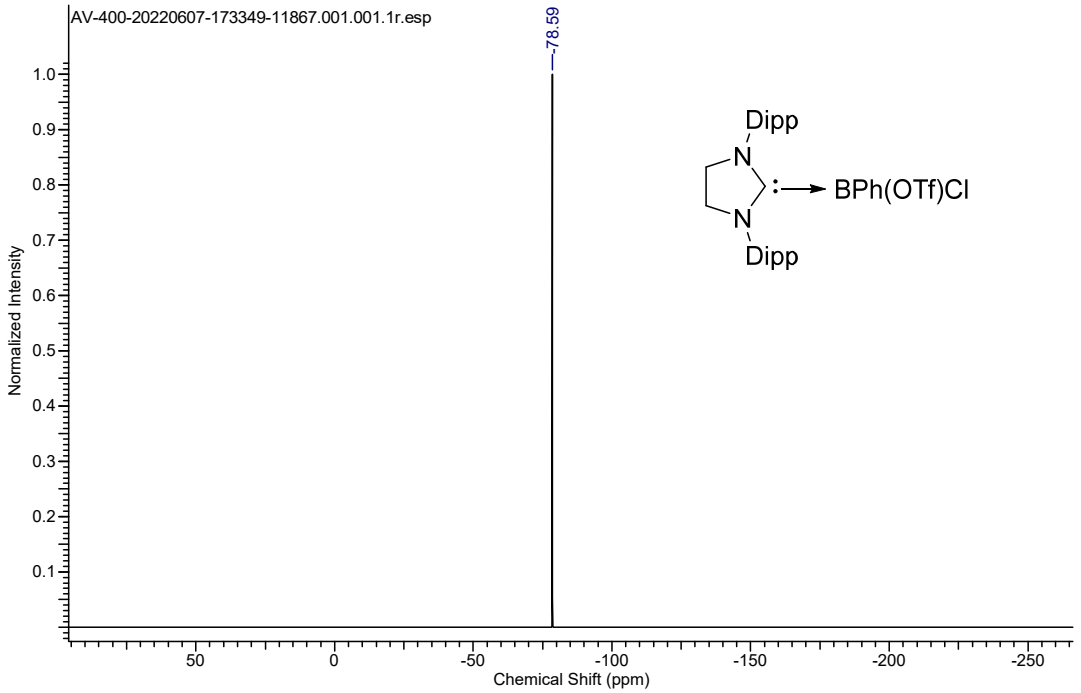


Figure S17. ^{19}F NMR spectrum of **5b**.

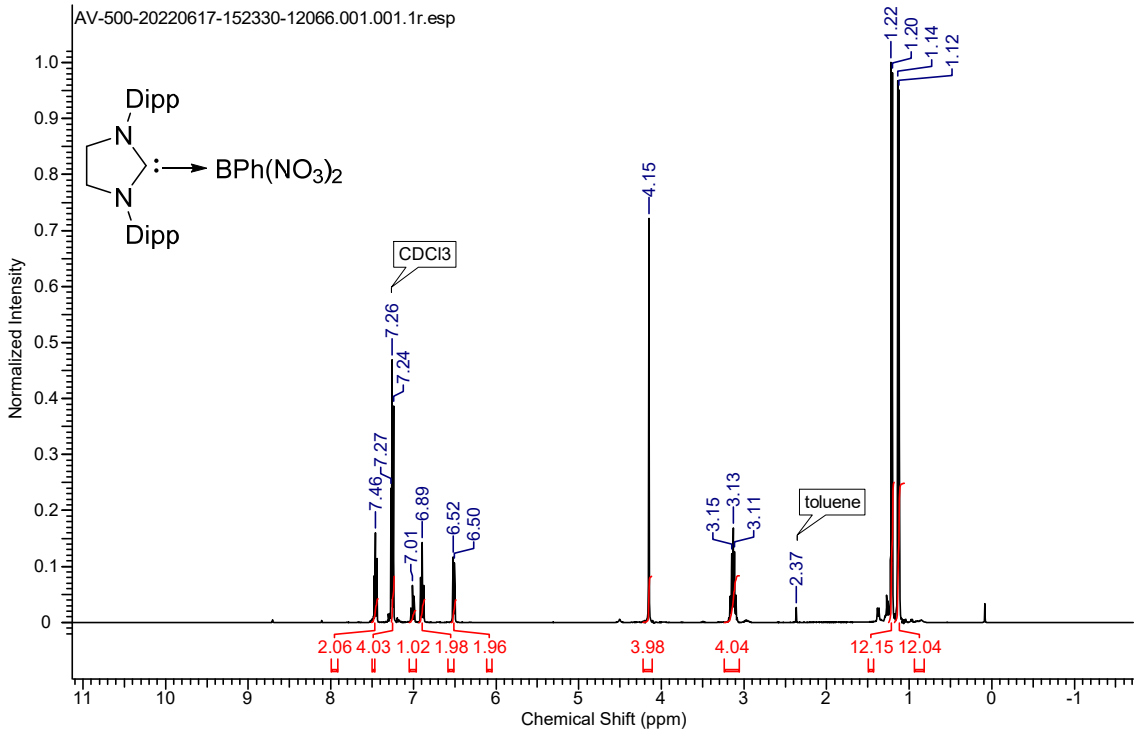


Figure S18. ^{1}H NMR spectrum of **6**.

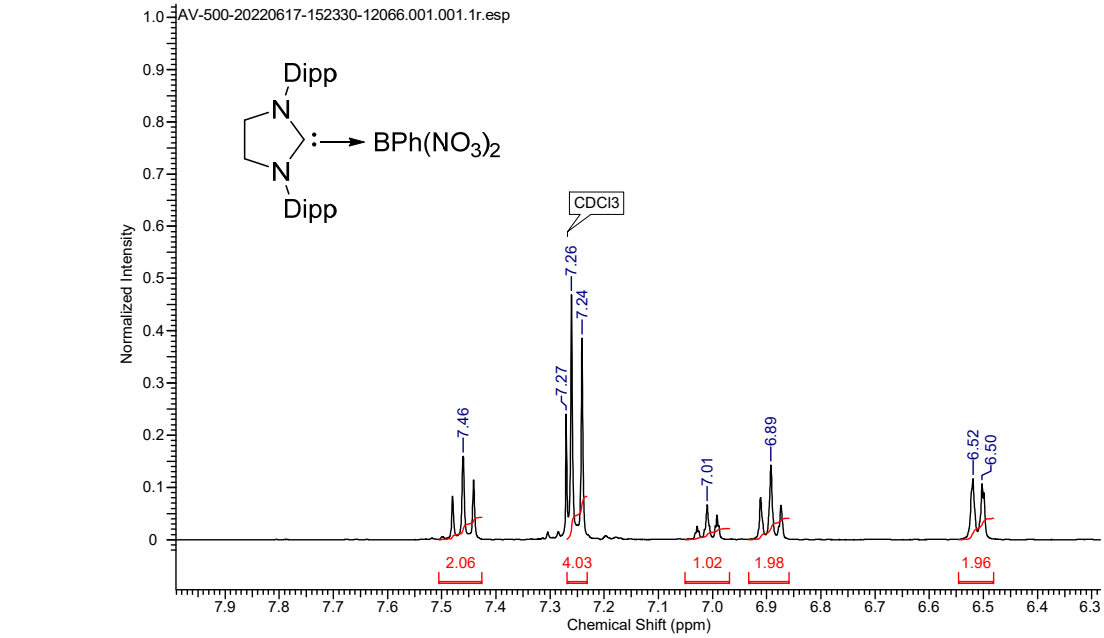


Figure S19. Enlarged version of the aromatic region of ^{1}H NMR spectrum of **6**.

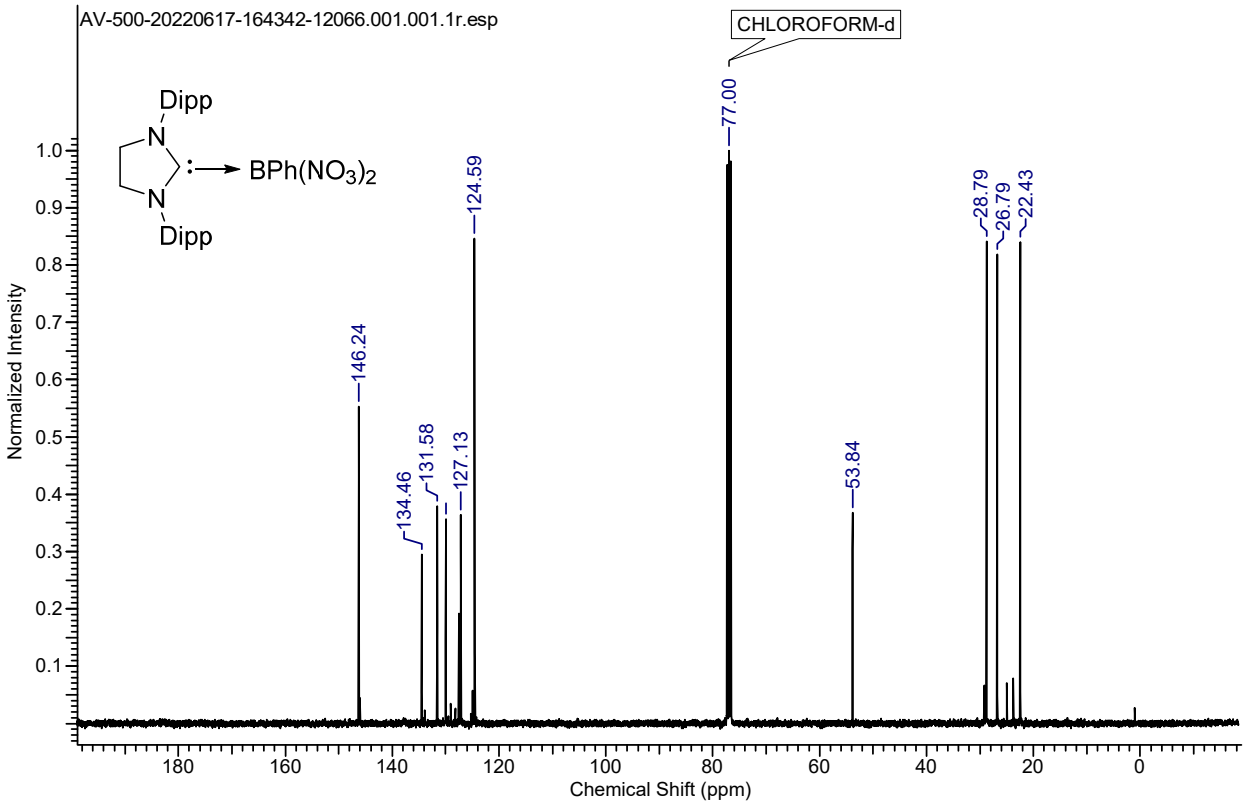


Figure S20. ^{13}C NMR spectrum of **6**.

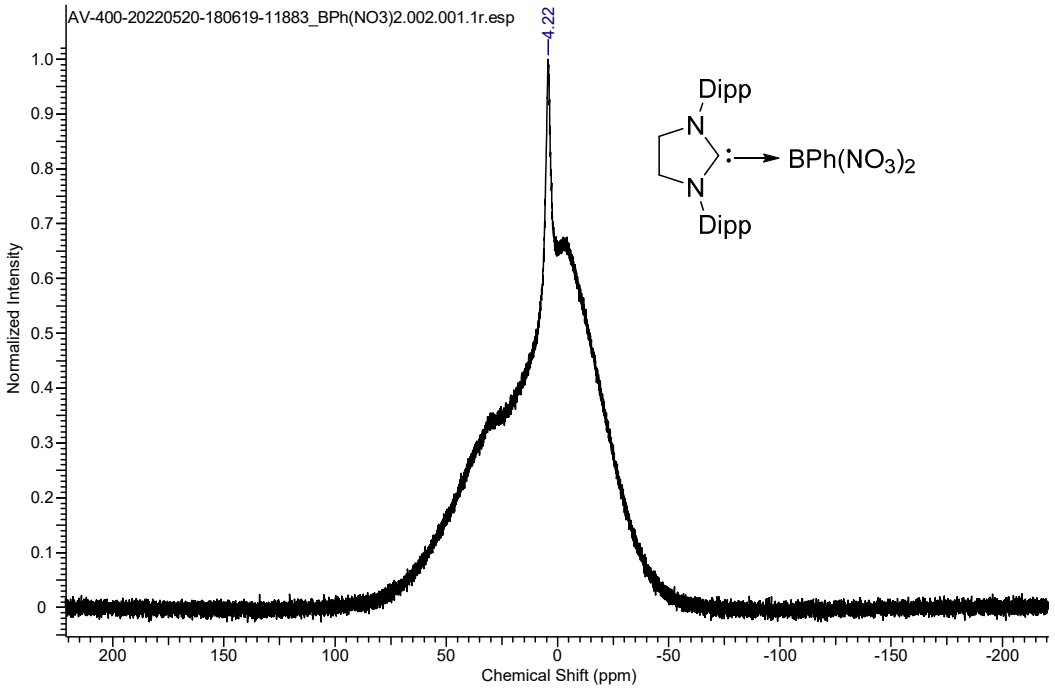


Figure S21. ^{11}B NMR spectrum of **6**.

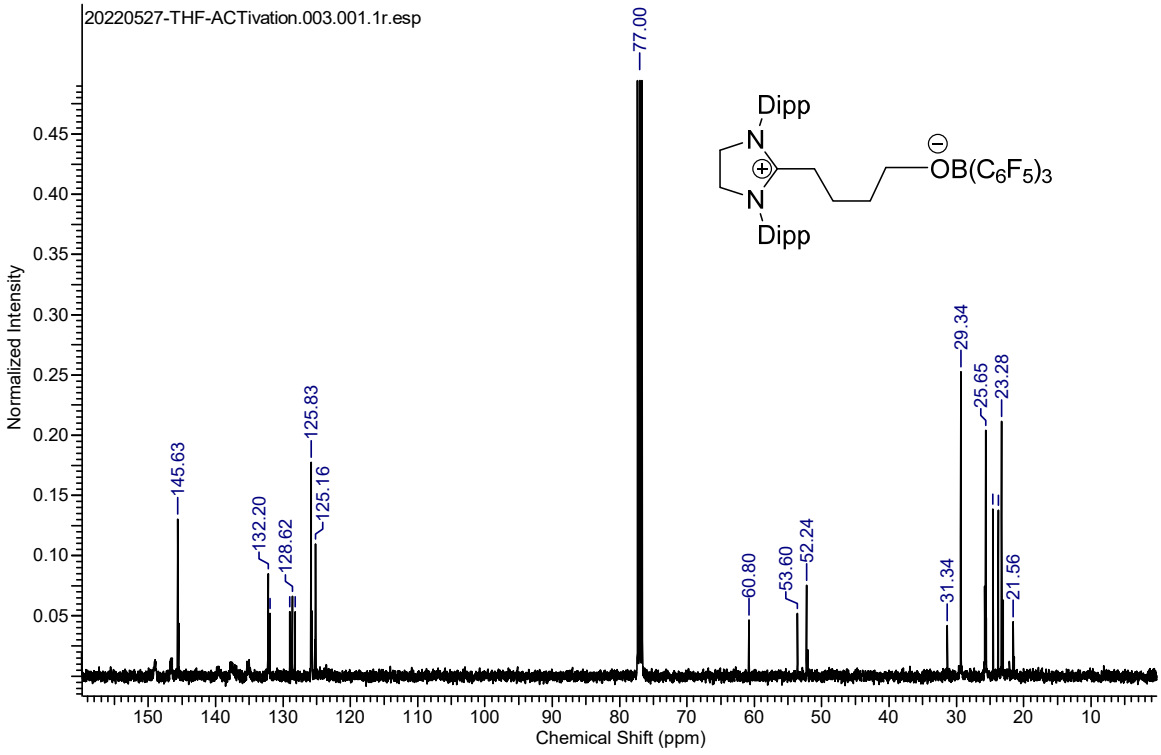


Figure S22.^{13}C NMR spectrum of **7**.

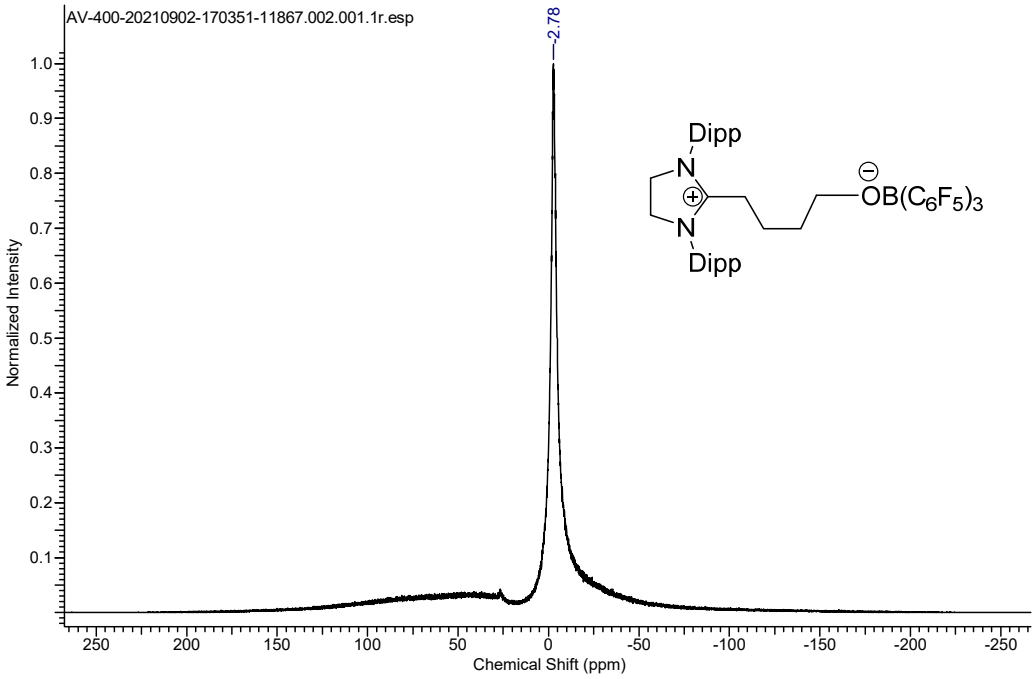


Figure S23.[11]B NMR spectrum of **7**.

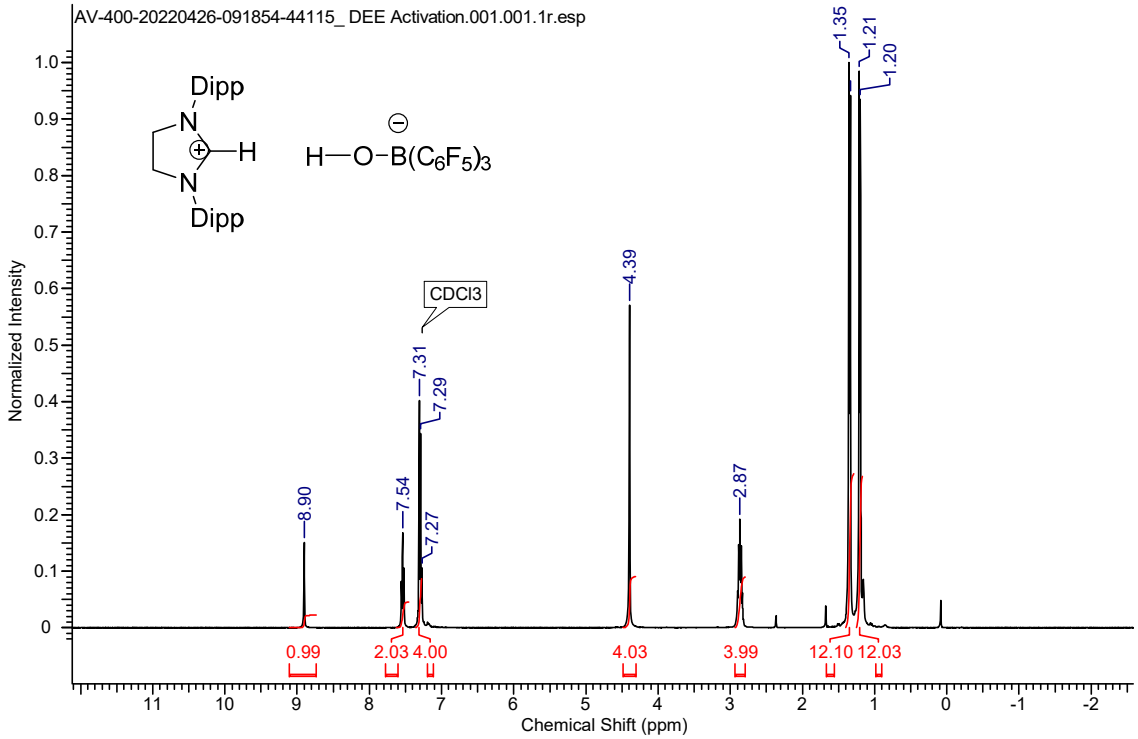


Figure S24.[1]H NMR spectrum of **8**.

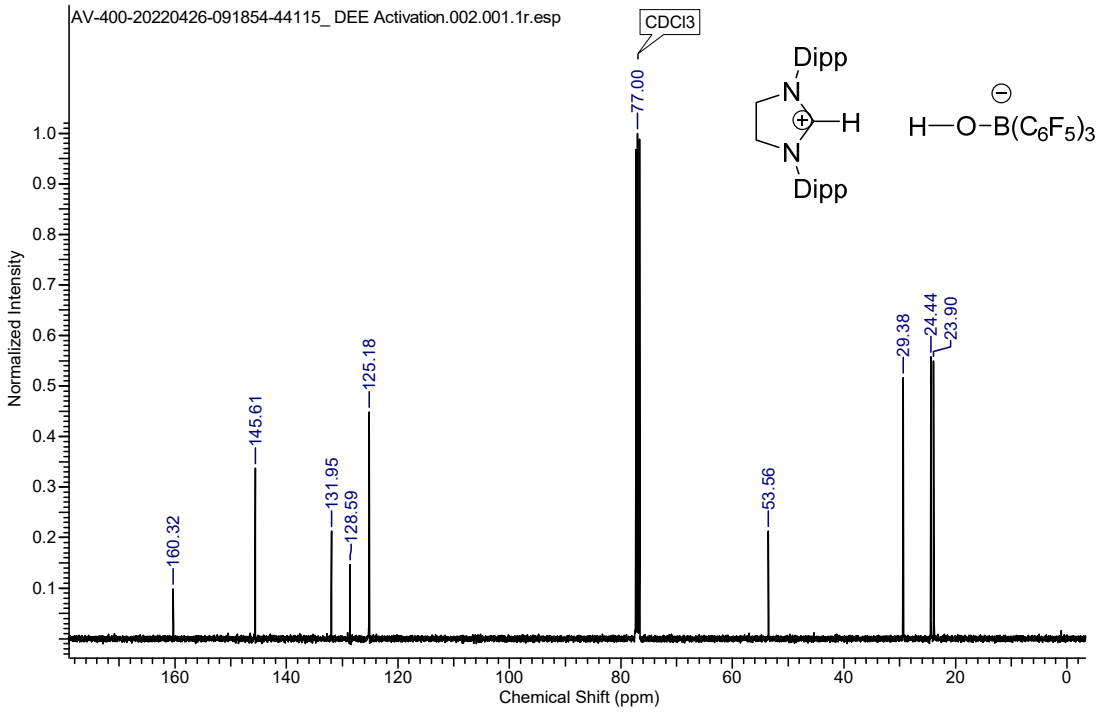


Figure S25.[13]C NMR spectrum of **8**.

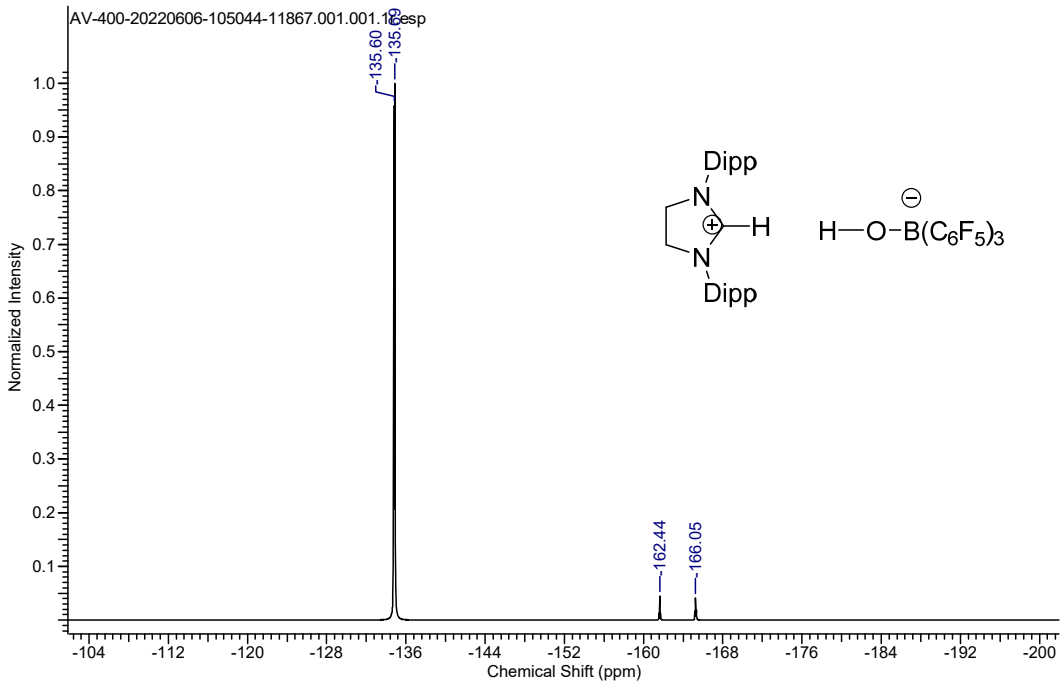


Figure S26. [19]F NMR spectrum of **8**.

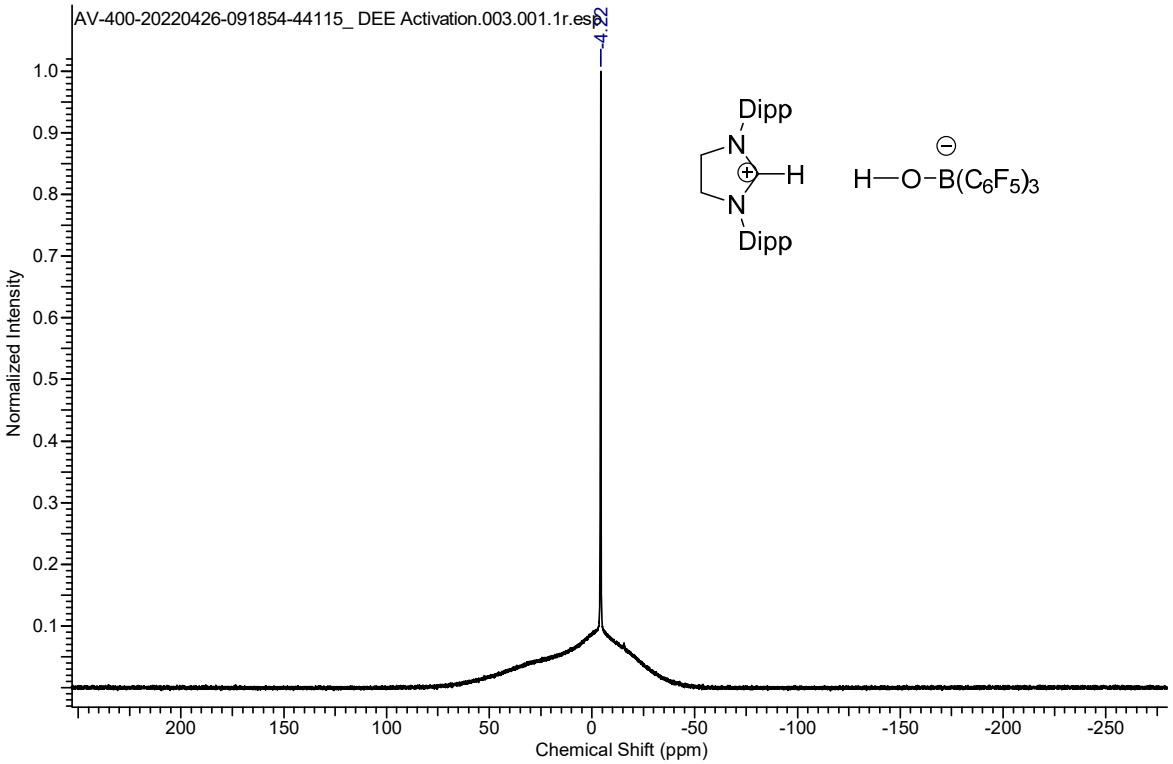
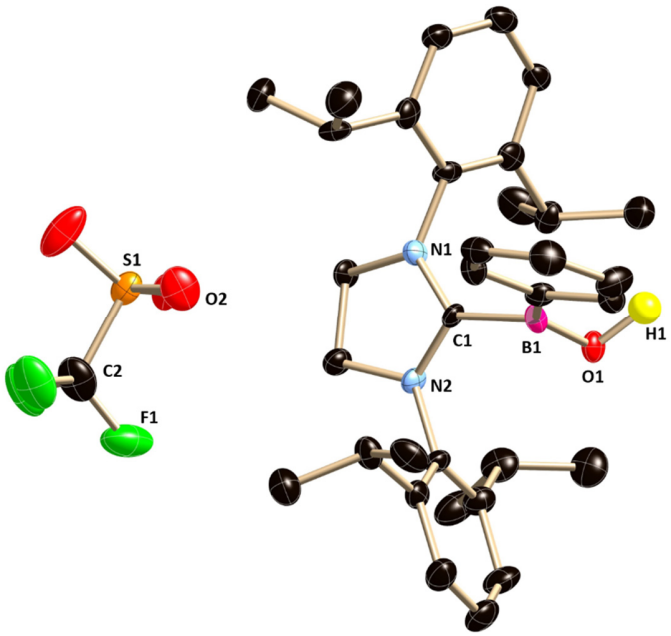


Figure S27. ^{11}B NMR spectrum of **8**.

S2. Molecular Structure of **5b**



S3. Crystallographic data for the structural analysis of compounds 1-8

Single crystals of **1-8** were mounted on a Bruker SMART APEX II single crystal X-ray CCD diffractometer having graphite monochromatised (Mo-Kα = 0.71073 Å) radiation at low temperature 100 K and 298 K. The X-ray generator was operated at 50 kV and 30 mA. The X-ray data acquisition was monitored by APEX2 program suit. The data were corrected for Lorentz-polarization and absorption effects using SAINT and SADABS programs which are an integral part of APEX2 package.[1,2] The structures were solved by direct methods and refined by full matrix least squares, based on F^2, using SHELXL Crystal structures were refined using Olex2-1.0 software. Anisotropic refinement was performed for all non-H atom. The C-H hydrogen atoms were calculated using the riding model.[3–5] The structures were examined using the ADSYM subroutine of PLATON to assure that no additional symmetry could be applied to the models. The molecular weight of each structure mentioned herein has been calculated considering the solvent molecules trapped in the crystal. Crystallographic information is available at www.ccdc.cam.ac.uk/data or as part of Supporting Information.

	1	**2**	**3**	**4**
Empirical formula	$C_{39}H_{51}BCl_2N_2$	$C_{33}H_{43}BCl_2N_2$	$C_{27}H_{42}BN_2O_3$	$C_{35}H_{47}BClF_3N_2O_3S$
Formula weight	629.53	549.40	452.43	679.06
Temperature/K	100.0	100.0	296.15	100.0
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	12.3193(19)	11.8231(7)	12.8167(19)	12.286(3)
b/Å	14.797(3)	18.7331(11)	15.081(2)	14.731(3)
c/Å	20.094(3)	14.2604(8)	14.264(2)	20.644(4)
α/°	90	90	90.00	90
β/°	94.984(5)	106.906(2)	108.660(3)	104.789(9)
γ/°	90	90	90.00	90
Volume/Å^3	3649.0(10)	3021.9(3)	2612.1(6)	3612.8(13)
Z	4	4	4	4

ρ_{calc}g/cm^3	1.146	1.208	1.153	1.248
μ/mm^{-1}	0.206	0.239	0.074	0.215
F(000)	1352.0	1176.0	988.0	1440.0
Crystal size/mm^3	0.14 × 0.13 × 0.06	0.12 × 0.12 × 0.08	0.2 × 0.2 × 0.2	0.15 × 0.12 × 0.09
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.738 to 49.996	3.952 to 72.752	4.04 to 56.96	4.082 to 52.998
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -23 ≤ l ≤ 23	-19 ≤ h ≤ 19, -31 ≤ k ≤ 31, -23 ≤ l ≤ 23	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -19 ≤ l ≤ 19	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -25 ≤ l ≤ 25
Reflections collected	156159	134803	113995	53931
Independent reflections	6392 [R_{int} = 0.1716, R_{sigma} = 0.0535]	14650 [R_{int} = 0.0564, R_{sigma} = 0.0270]	6560 [R_{int} = 0.3107, R_{sigma} = 0.1569]	7489 [R_{int} = 0.0481, R_{sigma} = 0.0288]
Data/restraints/parameters	6392/0/405	14650/0/351	6560/0/310	7489/0/424
Goodness-of-fit on F^2	1.151	1.107	1.043	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0933, wR_2 = 0.2291	R_1 = 0.0349, wR_2 = 0.0984	R_1 = 0.0985, wR_2 = 0.1721	R_1 = 0.0541, wR_2 = 0.1529
Final R indexes [all data]	R_1 = 0.1166, wR_2 = 0.2441	R_1 = 0.0424, wR_2 = 0.1074	R_1 = 0.2309, wR_2 = 0.2185	R_1 = 0.0580, wR_2 = 0.1580
Largest diff. peak/hole / e Å^{-3}	0.42/-0.52	0.61/-0.53	0.32/-0.42	1.35/-0.84
CCDC No	2180189	2180190	2180191	2180197

Identification code	**5a**	**6**	**7**	**8**
Empirical formula	$C_{41}H_{51}BClF_3N_2O_3S$	$C_{33}H_{43}BN_4O_6$	$C_{52}H_{49}BF_{15}N_2O$	$C_{45}H_{40}BF_{15}N_2O$
Formula weight	755.15	602.52	1013.74	920.60
Temperature/K	100.0	160.0	100.0	100.0
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	P-1	$P2_1/n$
a/Å	16.0556(5)	10.1256(5)	9.4393(13)	10.0450(7)
b/Å	22.2837(7)	16.8204(13)	14.568(2)	22.3914(17)
c/Å	23.3059(7)	18.9207(16)	17.814(3)	18.9077(15)
α/°	90	90	97.195(6)	90
β/°	107.6690(10)	98.178(2)	97.145(5)	90.037(3)
γ/°	90	90	99.872(5)	90
Volume/Å^3	7945.0(4)	3189.7(4)	2367.6(6)	4252.7(6)
Z	8	4	2	4
ρ_{calc}g/cm^3	1.263	1.255	1.422	1.438
μ/mm^{-1}	0.203	0.086	0.125	0.131
F(000)	3200.0	1288.0	1046.0	1888.0

Crystal size/mm^3	0.26 × 0.22 × 0.2	0.19 × 0.12 × 0.08	0.3 × 0.15 × 0.1	0.26 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.094 to 49.998	4.35 to 59.156	4.43 to 62.2	4.228 to 66.4
Index ranges	-19 ≤ h ≤ 19, -26 ≤ k ≤ 26, -27 ≤ l ≤ 27	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -25 ≤ l ≤ 26	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -25 ≤ l ≤ 25	-15 ≤ h ≤ 15, -34 ≤ k ≤ 34, -29 ≤ l ≤ 29
Reflections collected	196375	21918	155747	334120
Independent reflections	13881 [R_{int} = 0.0508, R_{sigma} = 0.0187]	7552 [R_{int} = 0.1113, R_{sigma} = 0.1409]	15134 [R_{int} = 0.0813, R_{sigma} = 0.0392]	16241 [R_{int} = 0.0606, R_{sigma} = 0.0200]
Data/restraints/parameters	13881/0/975	7552/0/405	15134/0/648	16241/0/589
Goodness-of-fit on F^2	1.136	0.995	1.090	1.166
Final R indexes [I>=2σ (I)]	R_1 = 0.0463, wR_2 = 0.1329	R_1 = 0.0693, wR_2 = 0.1688	R_1 = 0.0572, wR_2 = 0.1425	R_1 = 0.0478, wR_2 = 0.1324
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1386	R_1 = 0.1607, wR_2 = 0.2175	R_1 = 0.0841, wR_2 = 0.1643	R_1 = 0.0573, wR_2 = 0.1463
Largest diff. peak/hole / e Å^{-3}	1.11/-0.43	0.51/-0.76	0.53/-0.54	0.56/-0.54
CCDC No:	2180198	2180199	2180200	2180457

S4. References

1. *APEX3, SAINT-Plus and SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2006.
2. *Apex CCD and SAINT v8.30C*; Bruker AXS Inc.: Madison, WI, USA, 2013.
3. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
4. Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **2015**, *48*, 3–10.
5. Krause, L.; Herbst-Irmer, R.; Stalke, D. An empirical correction for the influence of low-energy contamination. *J. Appl. Crystallogr.* **2015**, *48*, 1907–1913.