Contents

1   NMR Spectra

**Figure S1.** ^{19}F NMR spectra of hexafluoroisopropylborane adducts.
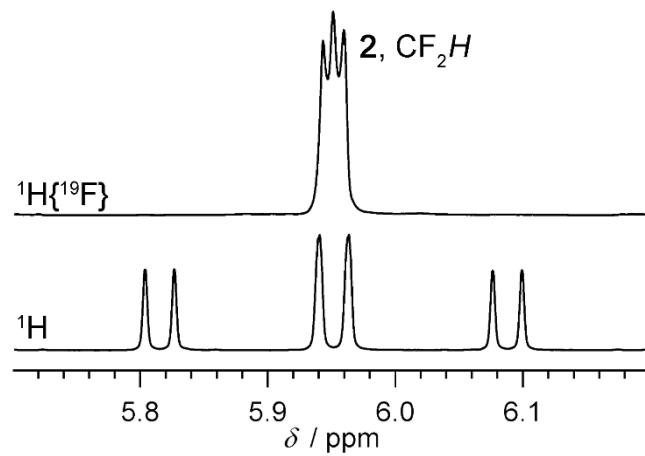
Figure S2. Section of the ^{19}F and $^{19}F\{^1H\}$ spectrum of **2**.
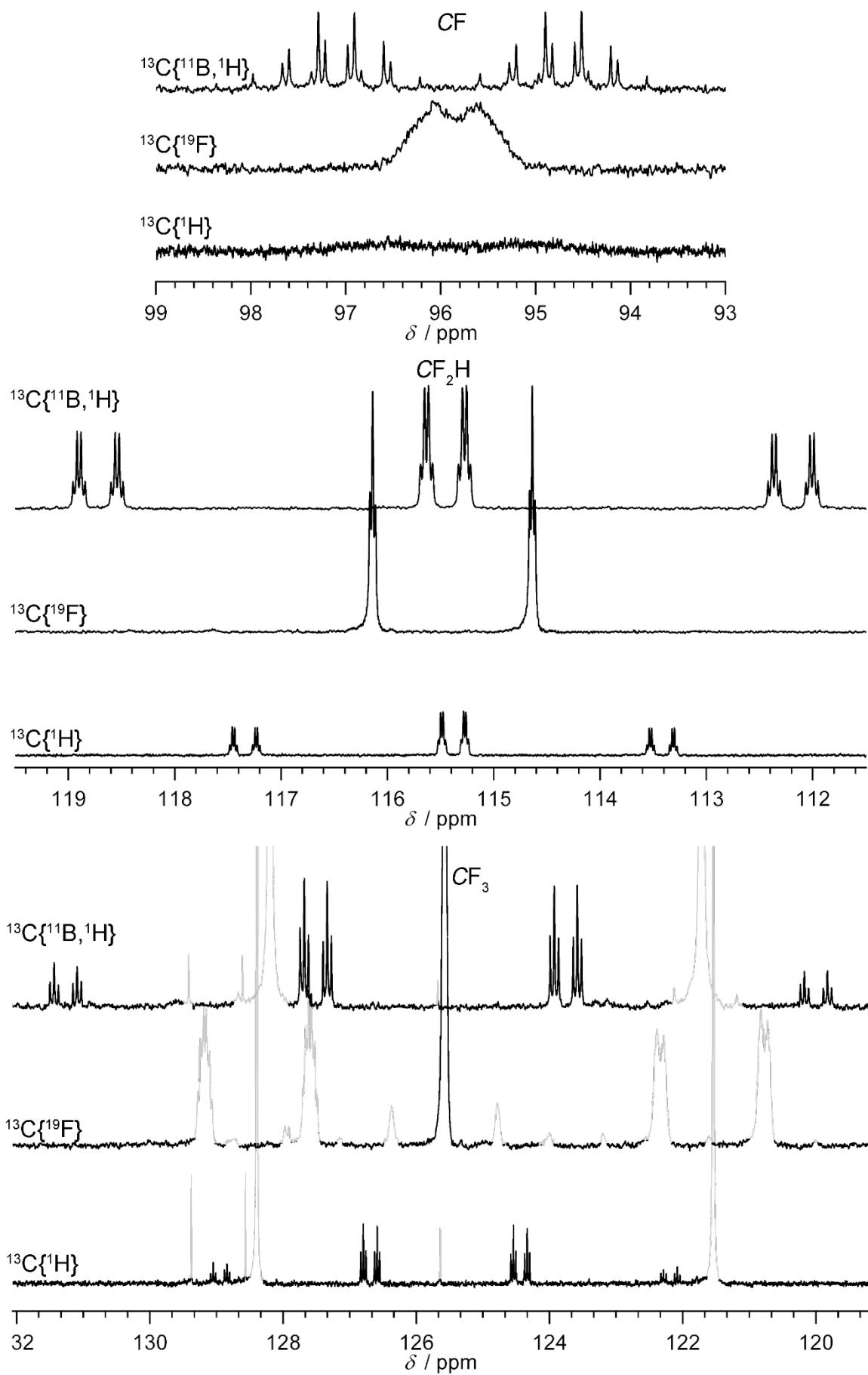
**Figure S3.** $^{13}C\{^1H\}$ (bottom), $^{13}C\{^{19}F\}$ (middle), and $^{13}C\{^{11}B,^1H\}$ NMR spectra (top) of **3b** ($^{13}C\{^1H\}$ NMR (125.76 MHz), $^{13}C\{^{19}F\}$ NMR (125.76 MHz), and $^{13}C\{^{11}B,^1H\}$ NMR (75.48 MHz)).
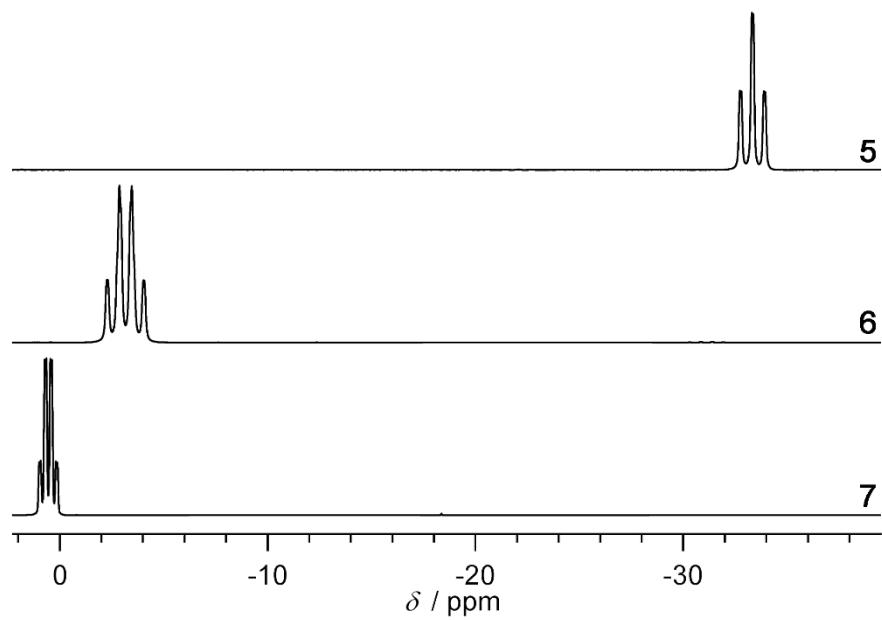
Figure S4. ^{11}B NMR spectra of hexafluoroisopropylborates.
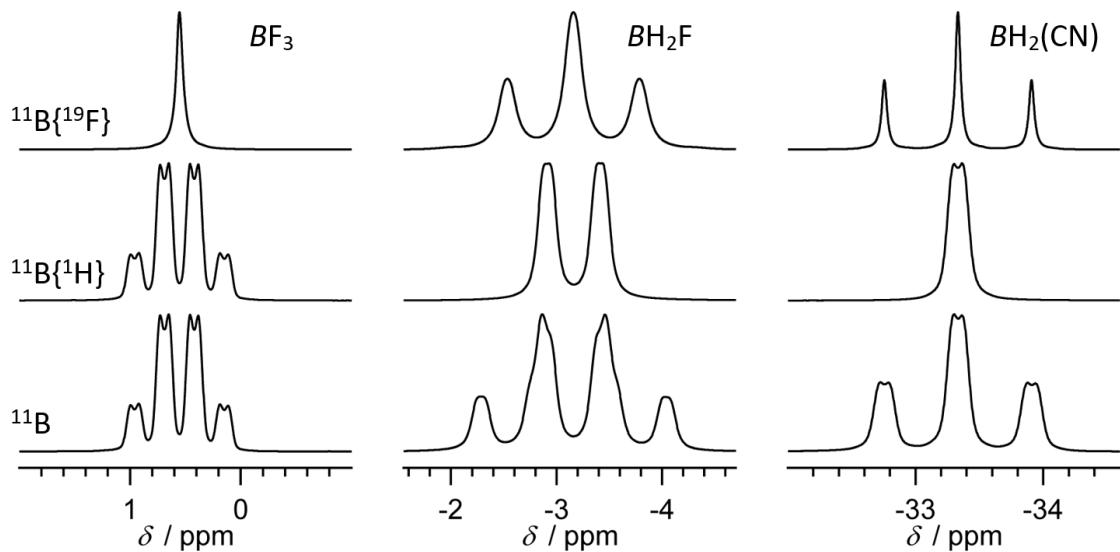
Figure S5. ^{11}B (top), ^{11}B{^{1}H} (middle), and ^{11}B{^{19}F} NMR spectra (top) of **7** (left), **6** (middle), and **5** (right).
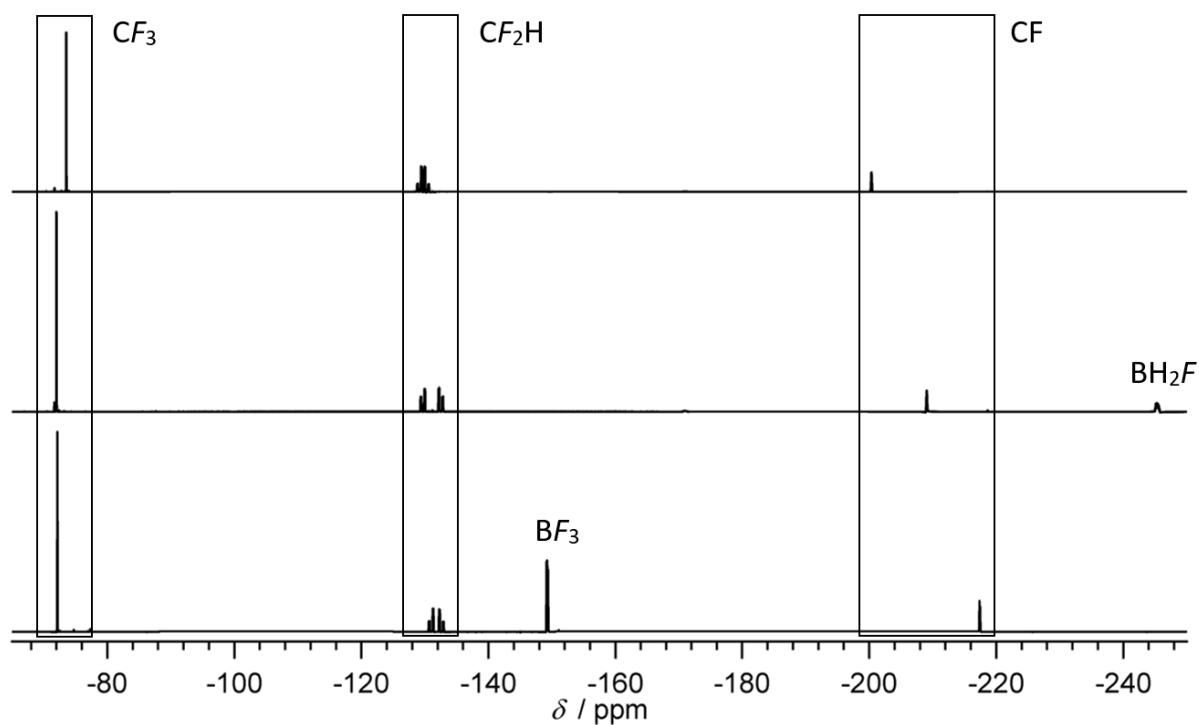
Figure S6. ^{19}F NMR spectra of **5** (top), **6** (middle), and **7** (bottom).
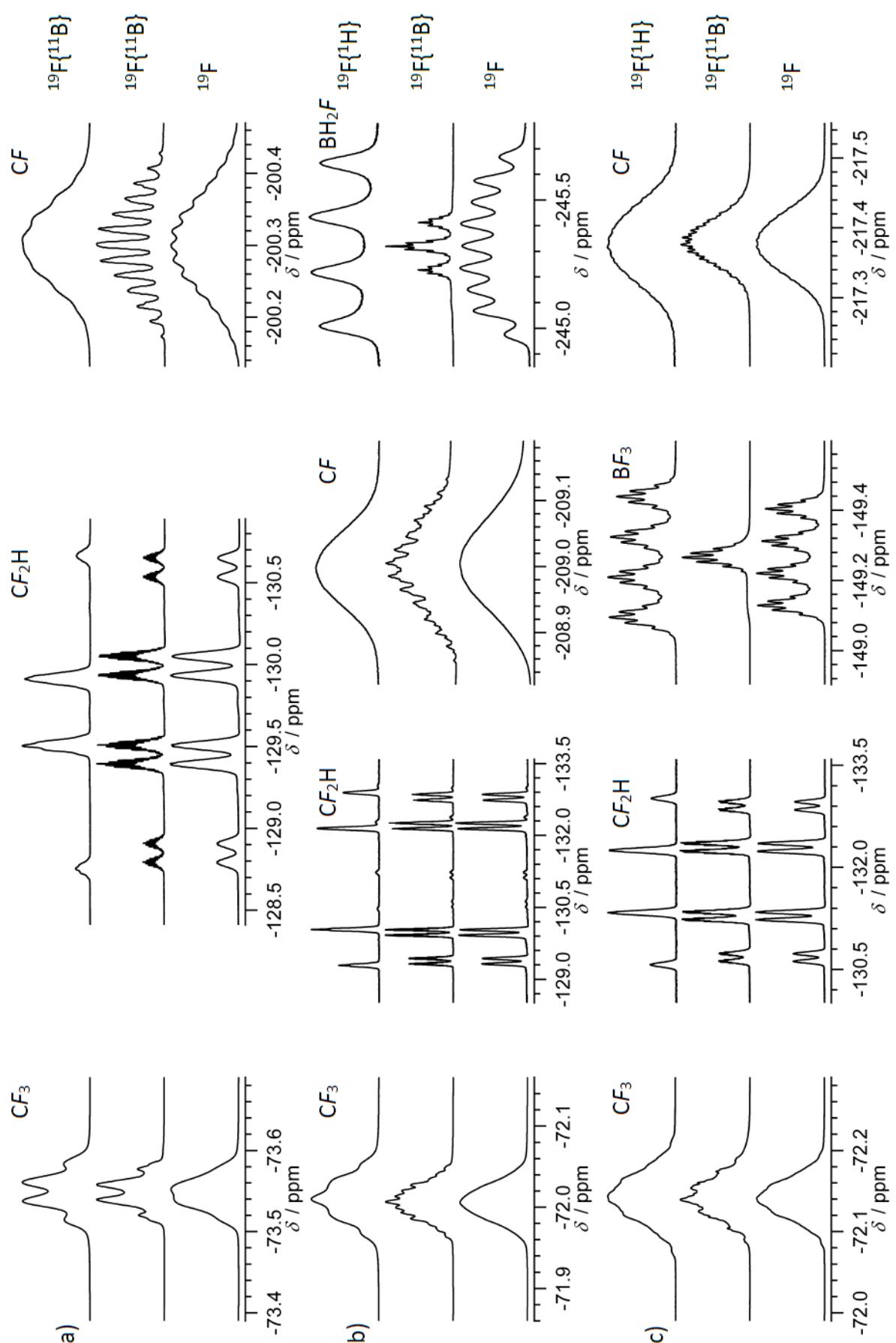
Figure S7. 19F, 19F{11B}, and 19F{1H} NMR spectra of **5** (a, top), **6** (b, middle), and **7** (c, bottom, 19F-NMR (470.59 MHz), 19F{11B}-NMR (470.59 MHz), 19F{1H}-NMR (376.82 MHz)).
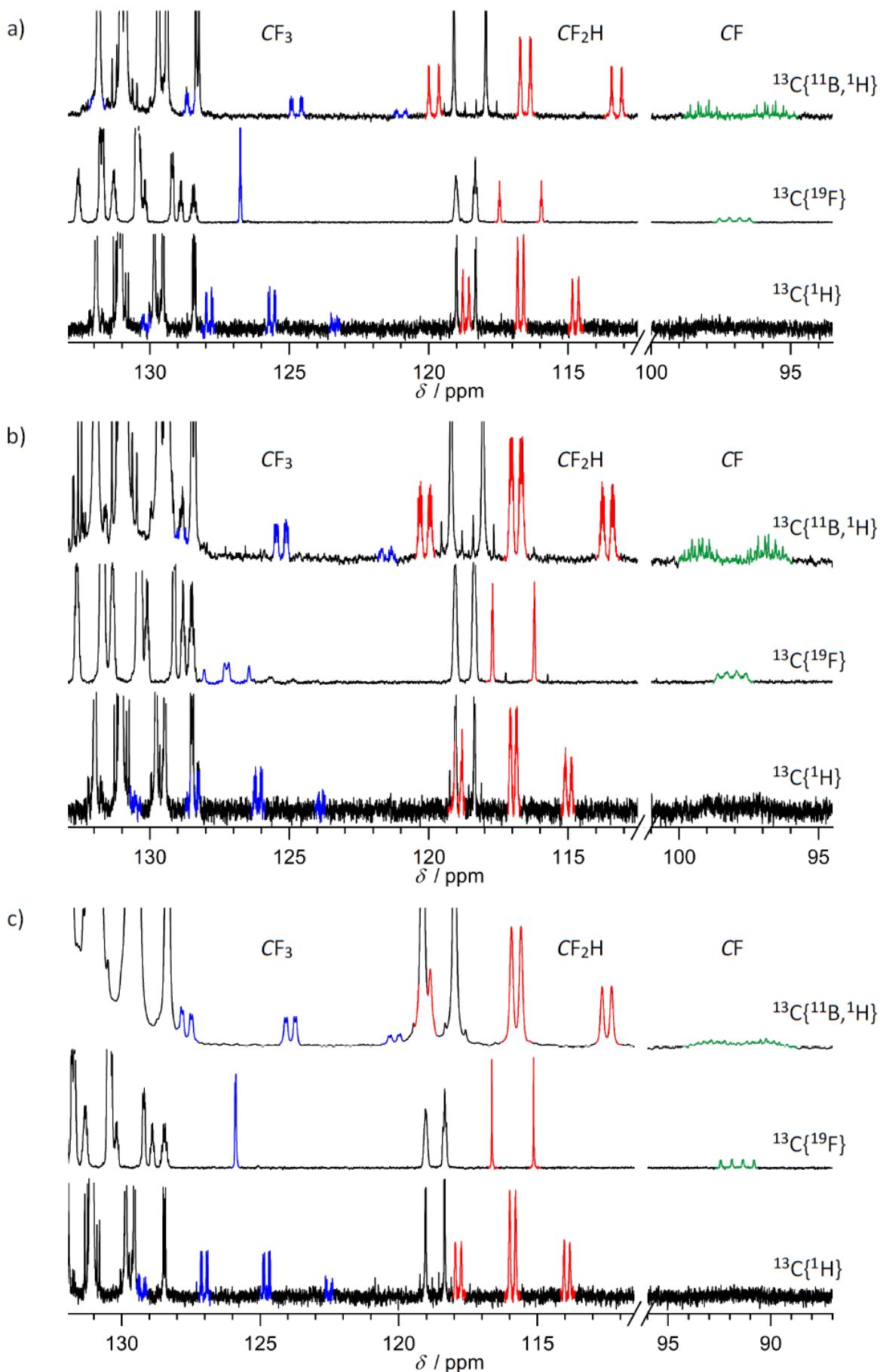
Figure S8. $^{13}C\{^1H\}$, $^{13}C\{^{19}F\}$, and $^{13}C\{^{11}B,^1H\}$ NMR spectra of **5** (a, top), **6** (b, middle), and **7** (c, bottom, $^{13}C\{^1H\}$-NMR (125.76 MHz), $^{13}C\{^{19}F\}$-NMR (125.76 MHz), $^{13}C\{^{11}B,^1H\}$-NMR (75.48 MHz)).

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2 Details on Quantum Chemical Calculations

Density functional calculations (DFT) [1] were carried out using the B3LYP functional [2-5] with the Gaussian16 program suite [6]. Geometries were optimized, and energies were calculated with the 6-311++G(d,p) basis sets. Diffuse functions were incorporated because improved energies are obtained for the anion [7]. All calculated structures represent true minima with no imaginary frequency on the respective hypersurface. Calculated energies are summarized in Table S1.

Table S1. Calculated electronic energies (EE), energies with zero-point corrections (E_0), enthalpies (H), and free energies(G) at the B3LYP/6-311++G(d,p) level of theory.

Species	Symmetry	EE / a.u.	E_0 / a.u.	H / a.u.	G / a.u.
2	C_1	−1080.89911	−1080.73974	−1080.72253	−1080.78564
3a	C_1	−966.57734	−966.43386	−966.41901	−966.47638
3b	C_1	−1005.89848	−1005.72750	−1005.71087	−1005.77279
3c	C_1	−1123.87527	−1123.61918	−1123.59857	−1123.67102
3d	C_1	−1043.98865	−1043.81295	−1043.79570	−1043.85920
3e	C_1	−1120.26023	−1120.06999	−1120.05263	−1120.11567
4	C_1	−1900.65146	−1900.01209	−1899.97043	−1900.08602
5	C_1	−833.24283	−833.16622	−833.15355	−833.20496
6	C_1	−840.26139	−840.19155	−840.17977	−840.22926
7	C_1	−1038.96175	−1038.90384	−1038.89051	−1038.94363

3 Cyclic Voltammetry

Cyclic voltammetry experiments were performed with a Metrohm PGSTAT30 potentiostat under an argon atmosphere with the software Nova 2.0. A standard three electrode cell configuration was employed with an ESA EE047 glassy carbon working electrode ($\emptyset$ = 3 mm), a Pt wire counter electrode, and an Ag/AgNO$_3$ reference electrode (0.01 mol·L^{-1} AgNO$_3$ in acetonitrile containing 0.1 mol·L^{-1} [nBu$_4$N][PF$_6$]) separated from the solution by a vigor Vycor tip. Experiments on 4-CN-py, **2**, and **4** were conducted in acetonitrile containing 0.1 mol·L^{-1} [nBu$_4$N][PF$_6$]. The concentrations of 4-CN-py, **2**, and **4** were about 0.01 mol·L^{-1}. Experiments on [BnPPh$_3$]**5**, [BnPPh$_3$]**6**, and [BnPPh$_3$]**7** were conducted as 0.05 M acetonitrile solutions. The experimental results are referenced against ferrocene as internal standard, which was added to the solution in the course of the CV experiment.

4   Single Crystal X-Ray Diffraction

All single-crystals were studied on a XtaLAB Synergy Dualflex, HyPix diffractometer using Cu-K$_\alpha$ radiation (micro-focus sealed X-ray tube, λ = 1.54184 Å).

All structures were solved by intrinsic phasing methods (SHELXT) and refinement is based on full-matrix least-squares calculations on F^2 (SHELXL) [8-11]. All non-hydrogen atoms were refined anisotropically. For CH idealized bond lengths and angles were used. Calculations were carried out using the ShelXle graphical interface [12] or the Olex2 program package [13]. Molecular structure diagrams were drawn with the program Diamond 4.6.4 [14]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Experimental details, crystal data, and CCDC numbers are collected in Table S2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S2: Selected crystal data and details of the refinement of the crystal structures of **2**, (*S*)-**3b**, (*S*)-**3b**, **4**, [BnPPh$_3$]**5**, [BnPPh$_3$]**6**, and [BnPPh$_3$]**7**.

Compound	**2**	(*S*)-**3b**	(*R*)-**3b**	**4**	[BnPPh$_3$]**5**	[BnPPh$_3$]**6**	[BnPPh$_3$]**7**
Chemical formula	C$_9$H$_7$BF$_6$N$_2$	C$_7$H$_9$BF$_6$N$_2$	C$_7$H$_9$BF$_6$N$_2$	C$_{30}$H$_{39}$BF$_6$N$_2$	C$_{29}$H$_{25}$BF$_6$NP	C$_{28}$H$_{25}$BF$_7$P	C$_{28}$H$_{23}$BF$_9$P
M [g·mol^{-1}]	267.98	245.97	245.97	552.42	543.28	536.25	572.24
T [K]	100.0(20)	100.0(1)	99.9(1)	100.0(1)	100.0(20)	95.0(20)	100.0(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P1$	$P1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	6.9476(3)	5.3235(3)	5.3211(2)	9.18820(10)	11.5147(2)	11.18190(10)	11.09140(10)
b [Å]	10.3117(5)	7.0486(4)	7.0515(3)	9.6919(2)	15.5359(2)	14.9172(2)	15.00700(10)
c [Å]	15.4000(5)	7.2349(4)	7.2263(3)	18.0035(3)	14.8098(2)	15.3878(2)	15.48890(10)
α [°]	86.644(3)	79.091(4)	79.093(3)	88.8120(10)	90	90	90
β [°]	88.402(3)	73.788(4)	73.742(4)	88.4840(10)	92.8730(10)	90.0640(10)	91.1140(10)
γ [°]	83.768(4)	73.518(4)	73.522(4)	68.367(2)	90	90	90
Volume [Å^3]	1094.62(8)	248.18(3)	247.83(2)	1489.68(5)	2646.01(7)	2566.72(5)	2577.62(3)
Z	4	1	1	2	4	4	4
D_{calc} [Mg·m^{-3}]	1.626	1.646	1.646	1.232	1.364	1.388	1.475
μ [mm^{-1}]	1.531	1.616	1.618	0.819	1.467	1.549	1.697
$F(000)$ [e]	536	124	124	584	1120	1104	1168
Reflections collected	10778	5072	9853	61302	37719	113721	52773
Independent reflections	3964	1667	1962	5388	5402	5237	5270
R(int)	0.0379	0.0380	0.0500	0.0430	0.0467	0.0789	0.0418
Parameters / restraints	469 / 618	154 / 3	154 / 3	533/ 846	415 / 322	593 / 1615	2395 / 707
$R1[I>2\sigma(I)]$[a]	0.0532	0.0398	0.0327	0.0502	0.0483	0.0542	0.0396
$wR2$ (all)[b]	0.1274	0.1033	0.0734	0.1048	0.1091	0.1092	0.0821
GooF on F^2[c]	1.195	0.868	1.160	1.007	1.067	1.022	1.113
Largest diff. peak / hole [e·Å^{-3}]	0.474 / −0.539	0.314 / −0.249	0.207 / −0.212	0.280 / −0.531	0.469 / −0.468	0.567 / −0.585	0.378 / −0.369
CCDC no.	2304957	2304958	2304959	2304960	2304961	2304962	2304963

5   Literature

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