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Supporting Information

## **Electronic Modification of a Sterically Demanding Anionic Pyridine Ligand**

Nadja M. C. Schmidlin, Valentin Radtke, Alexei Schmidt, Märt Lõkov, Ivo Leito, and  
Tobias Böttcher\*

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## 1. NMR spectra

Compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}]$ .

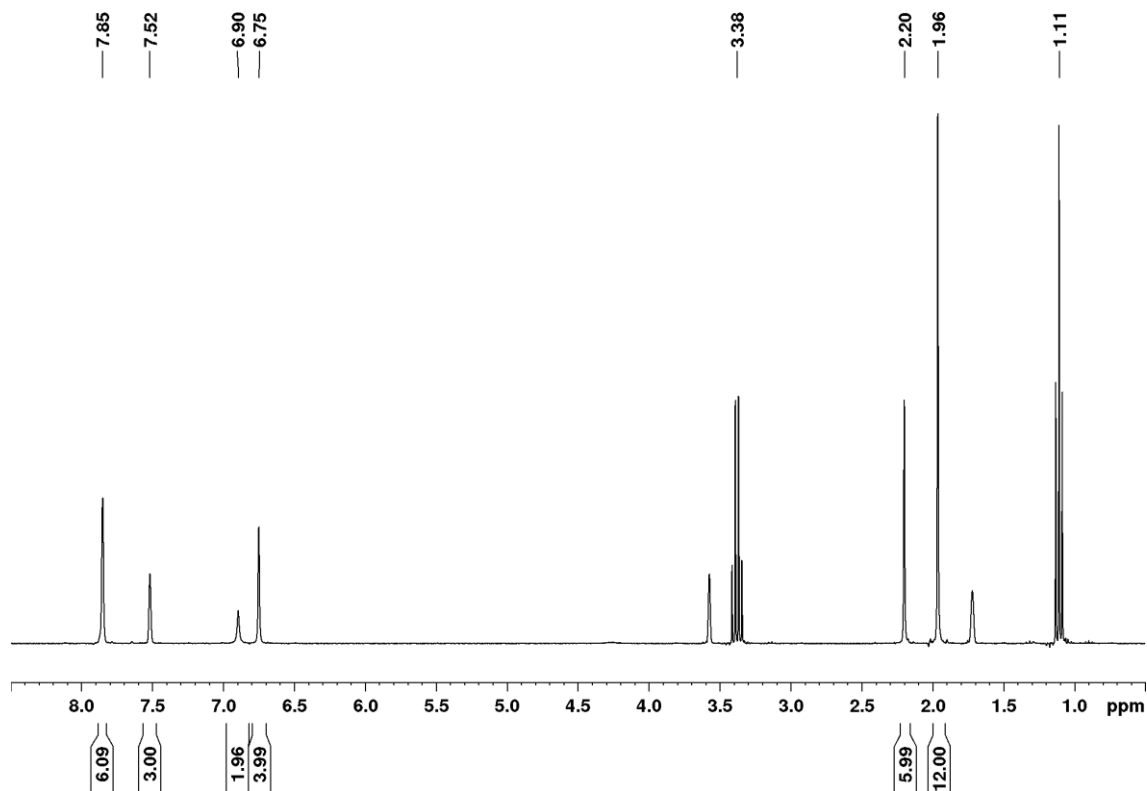


Figure S1.  $^1\text{H}\{^{11}\text{B}\}$  NMR (300 MHz,  $\text{THF-d}_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}]$ .

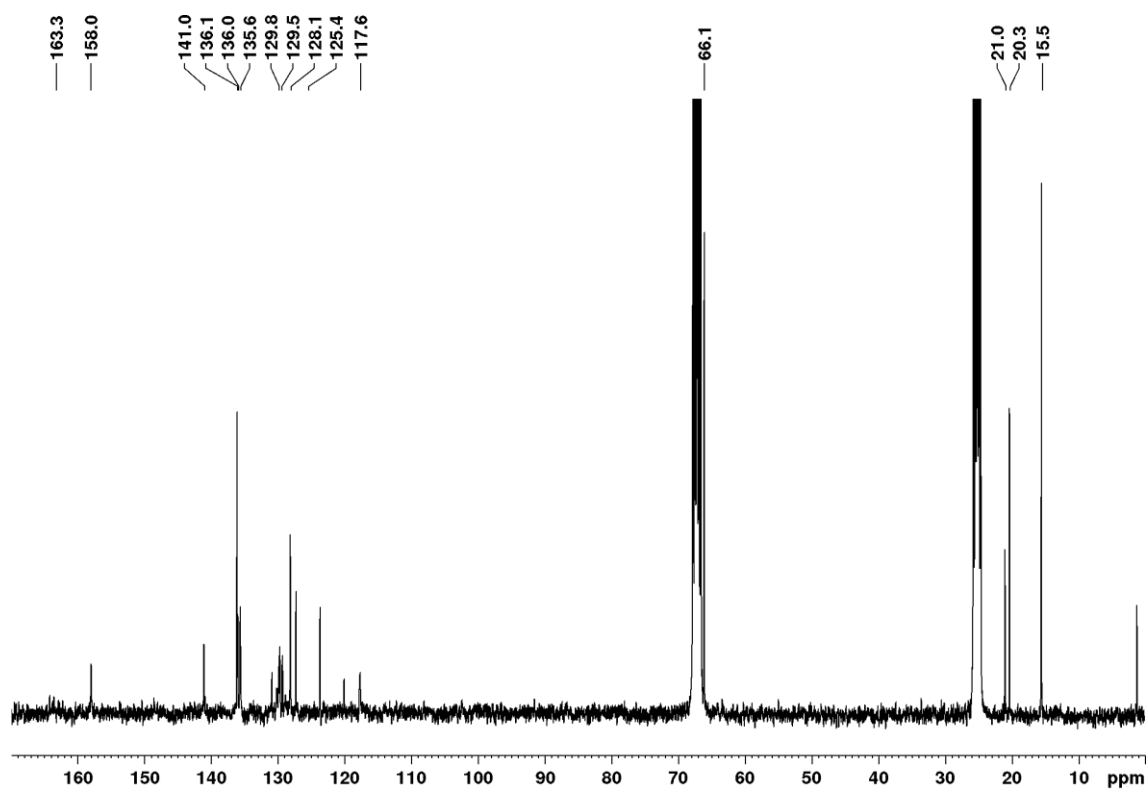
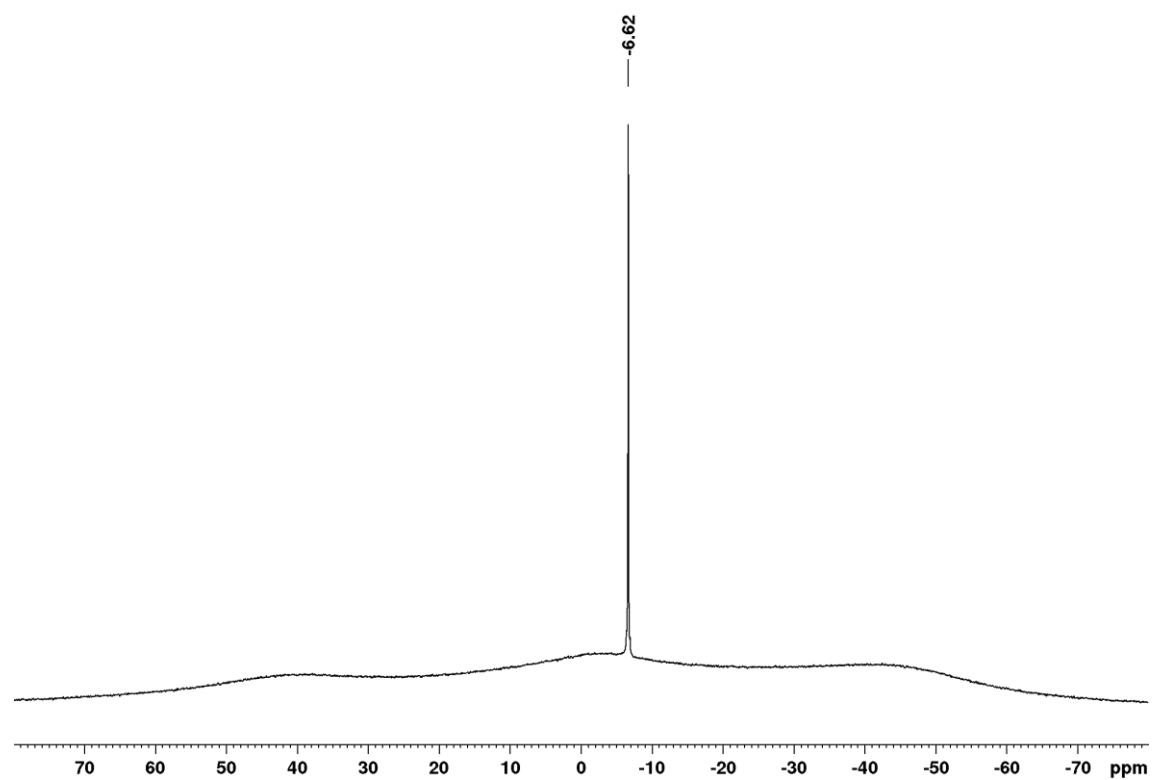
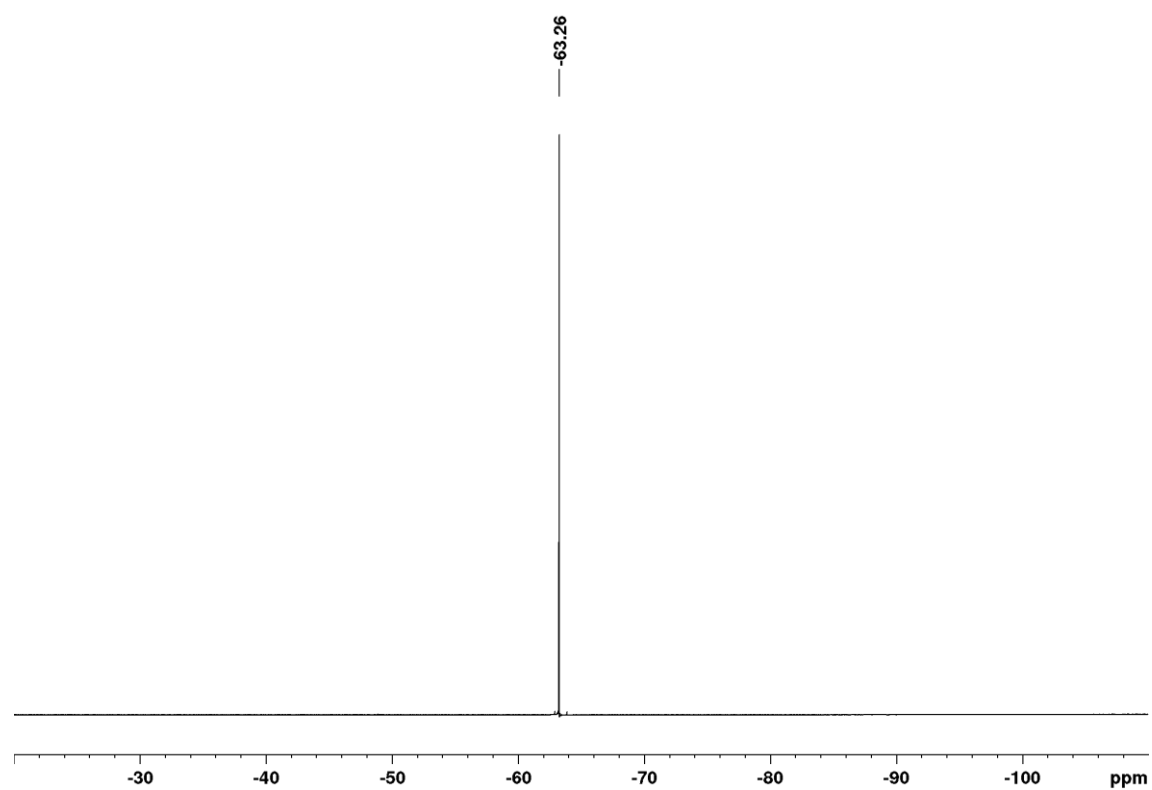


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{THF-d}_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}]$ .



**Figure S3.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz, THF- $\text{d}_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}]$ .



**Figure S4.**  $^{19}\text{F}$  NMR (282 MHz, THF- $\text{d}_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}]$ .

Compound [NEt<sub>4</sub>][1<sup>F</sup>].

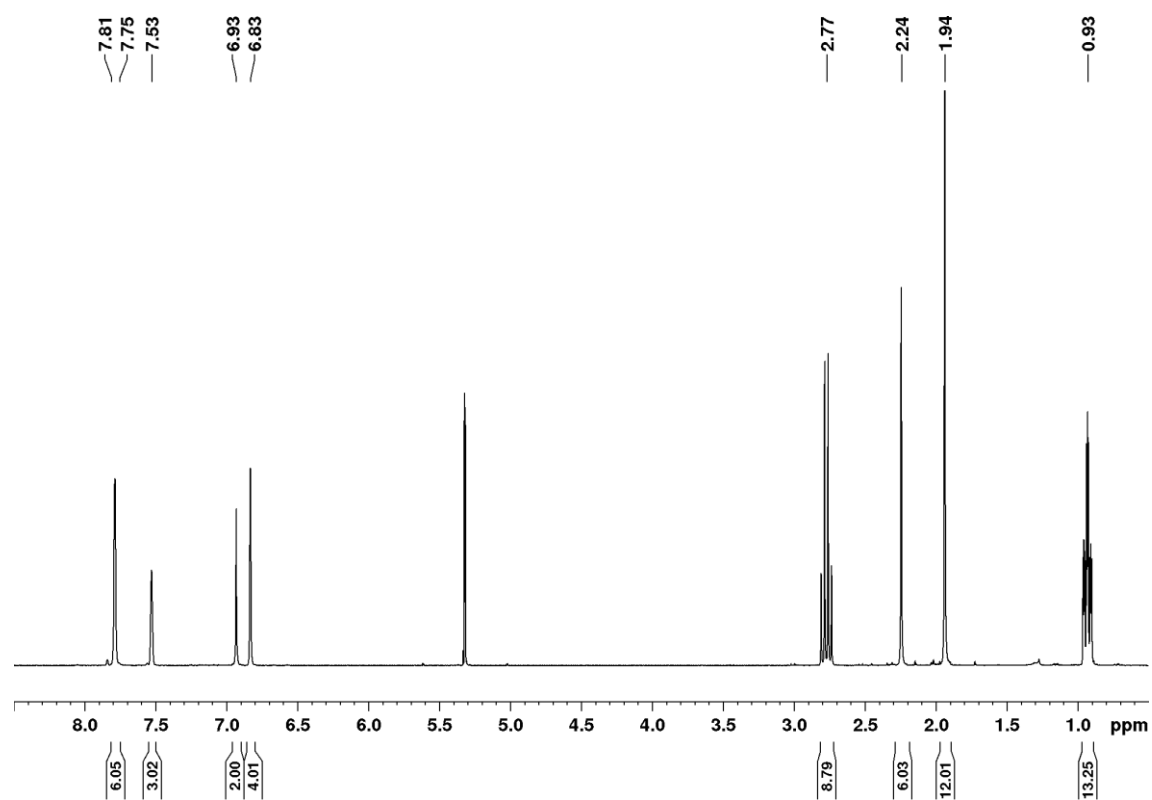


Figure S5. <sup>1</sup>H{<sup>11</sup>B} NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of compound [NEt<sub>4</sub>][1<sup>F</sup>].

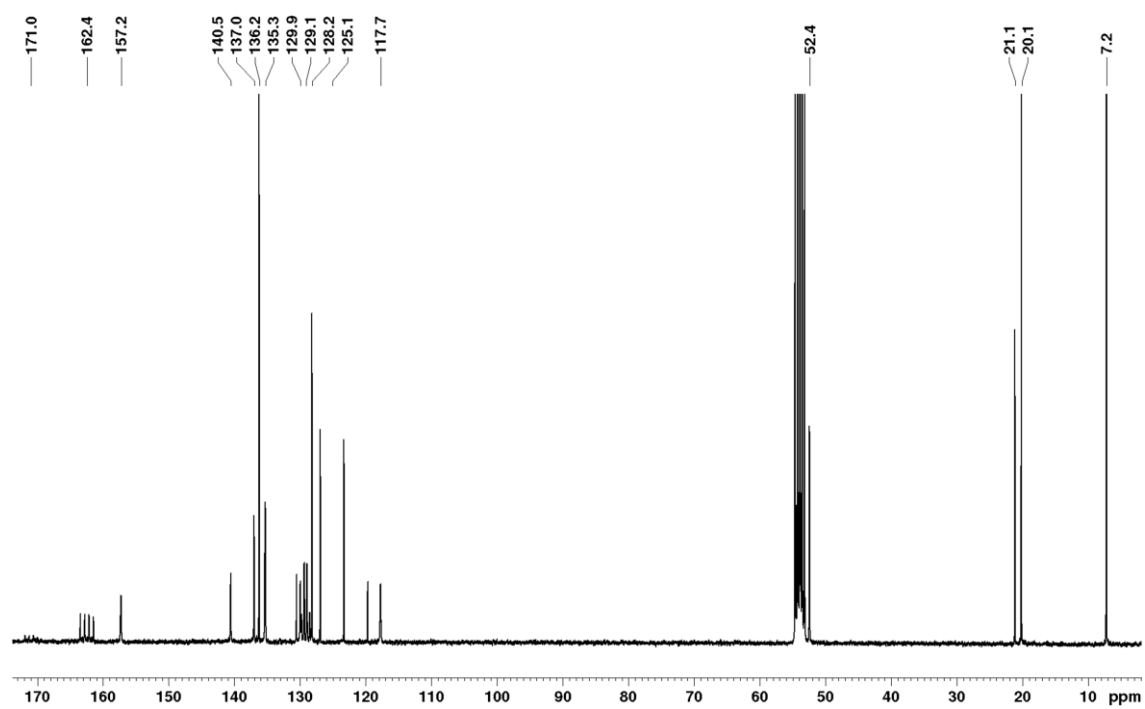
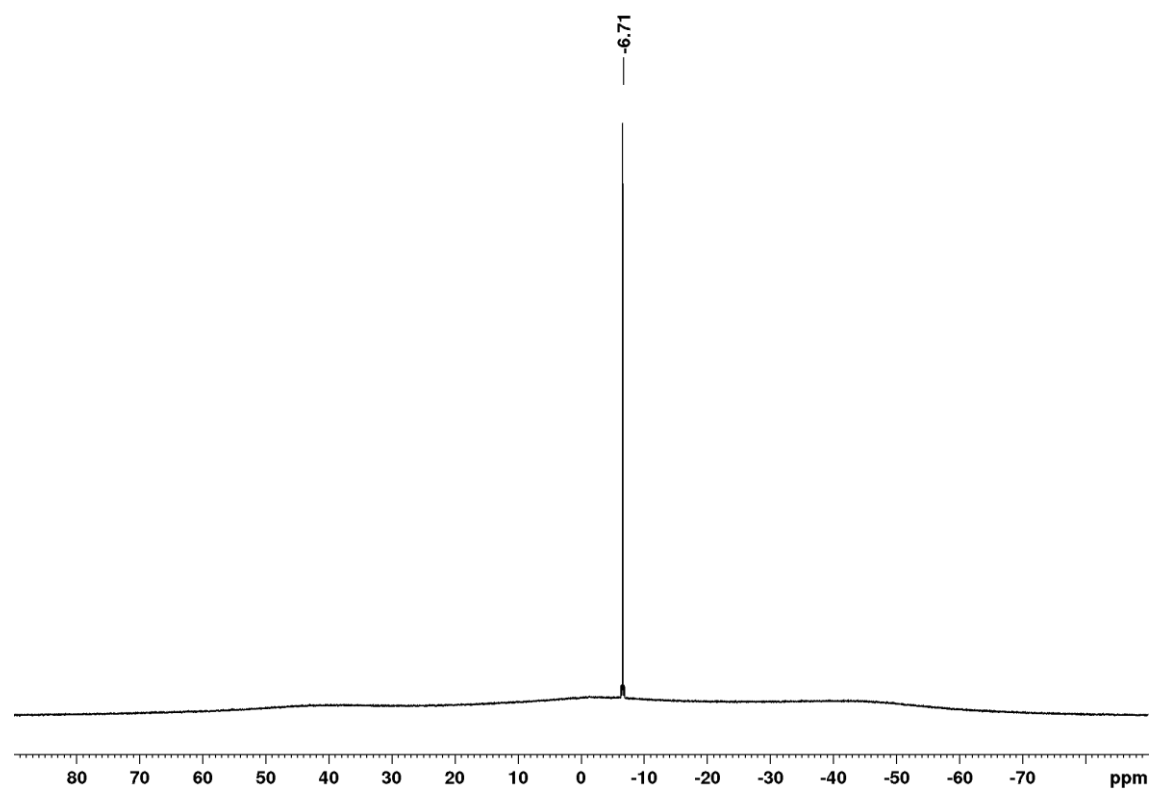
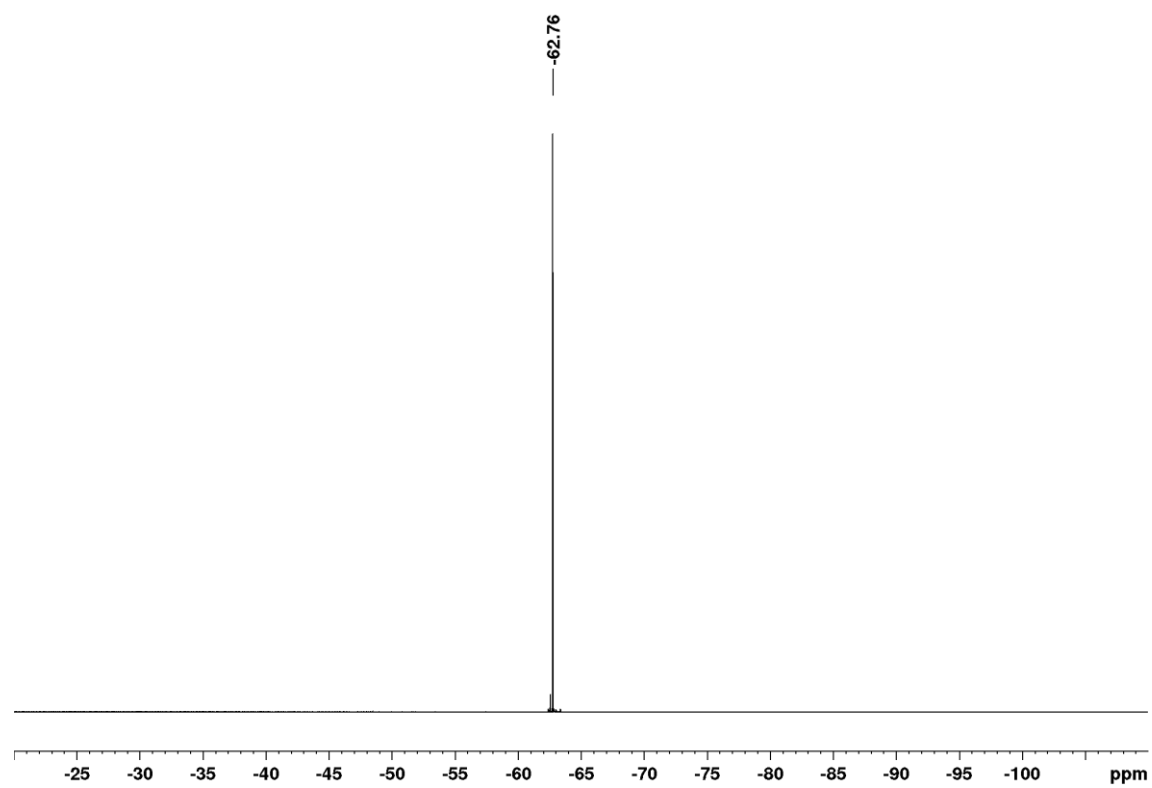


Figure S6. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of compound [NEt<sub>4</sub>][1<sup>F</sup>].



**Figure S7.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound  $[\text{NEt}_4][\mathbf{1}^{\text{F}}]$ .



**Figure S8.**  $^{19}\text{F}$  NMR (282 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound  $[\text{NEt}_4][\mathbf{1}^{\text{F}}]$ .

Compound **1<sup>F</sup>**-H.

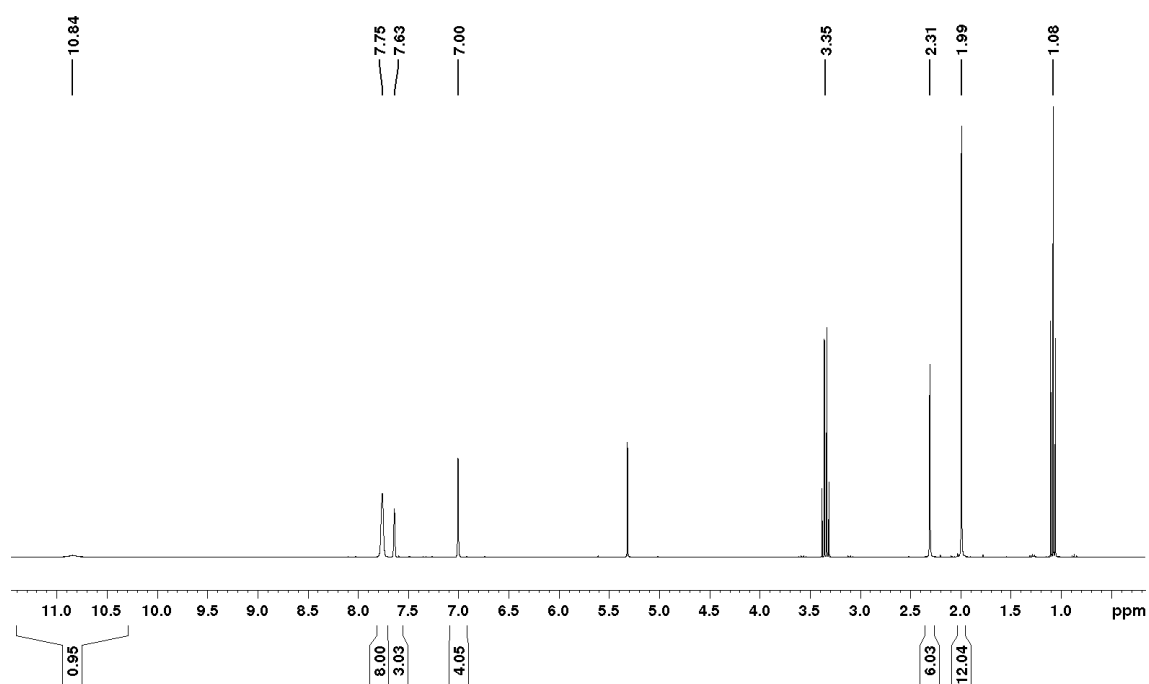


Figure S9. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of compound **1<sup>F</sup>**-H.

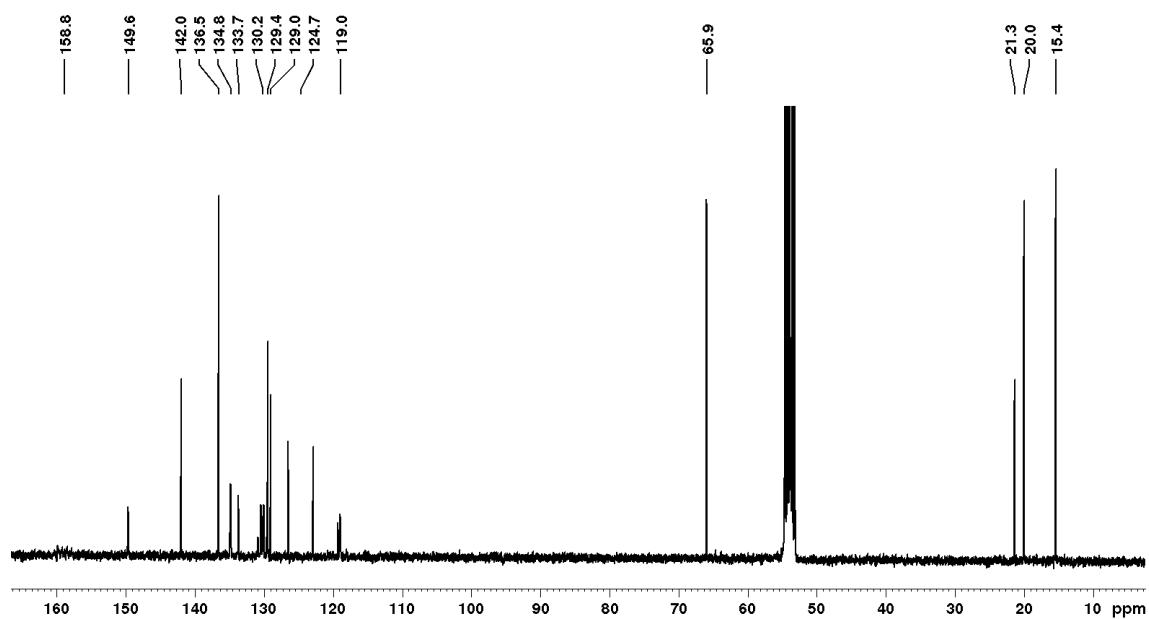
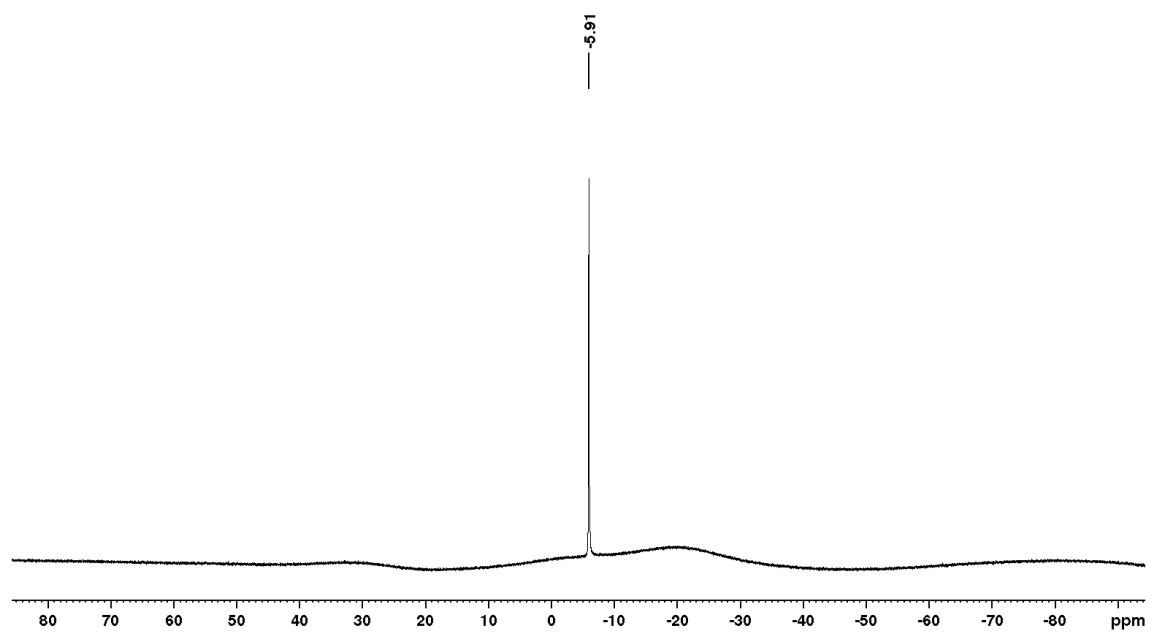
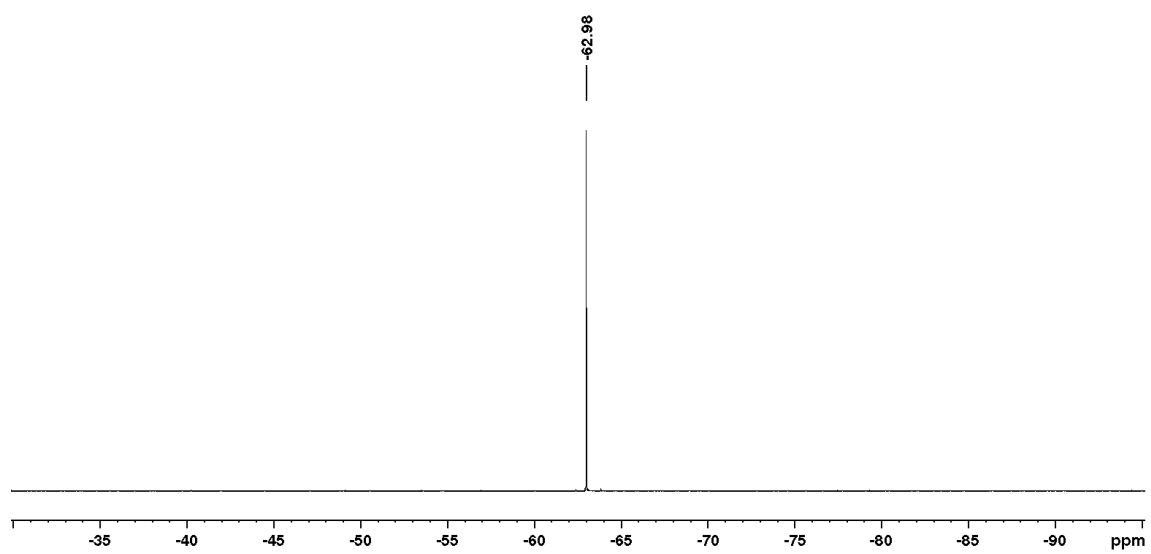


Figure S10. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of compound **1<sup>F</sup>**-H.

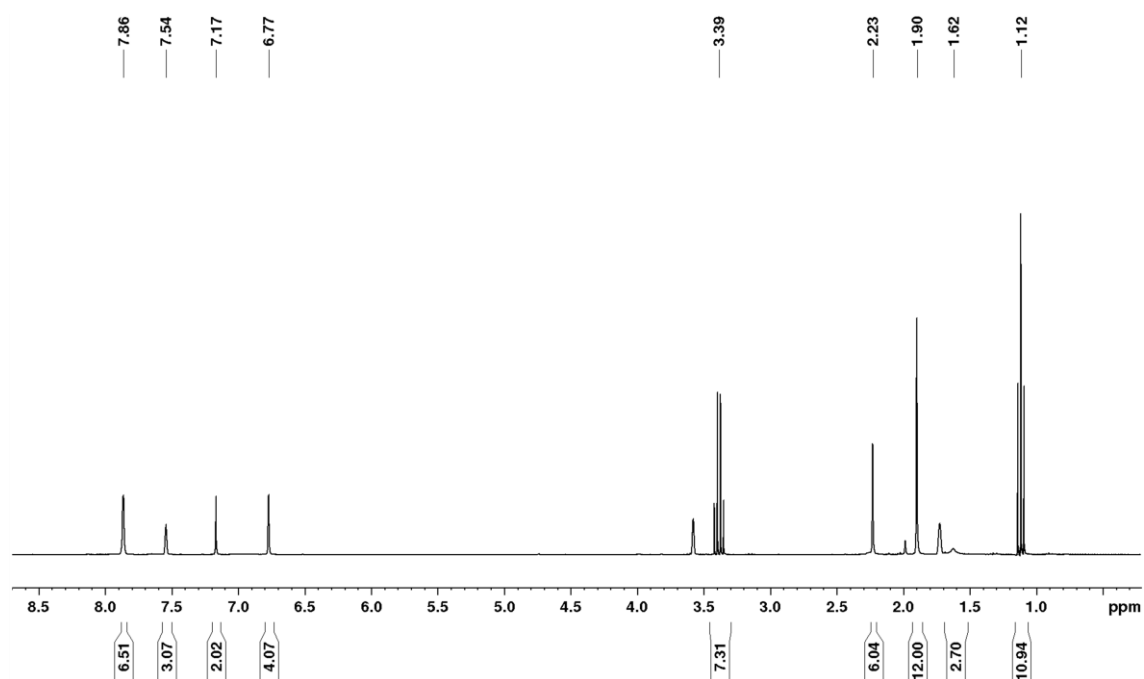


**Figure S11.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound  $1^{\text{F}}\text{-H}$ .

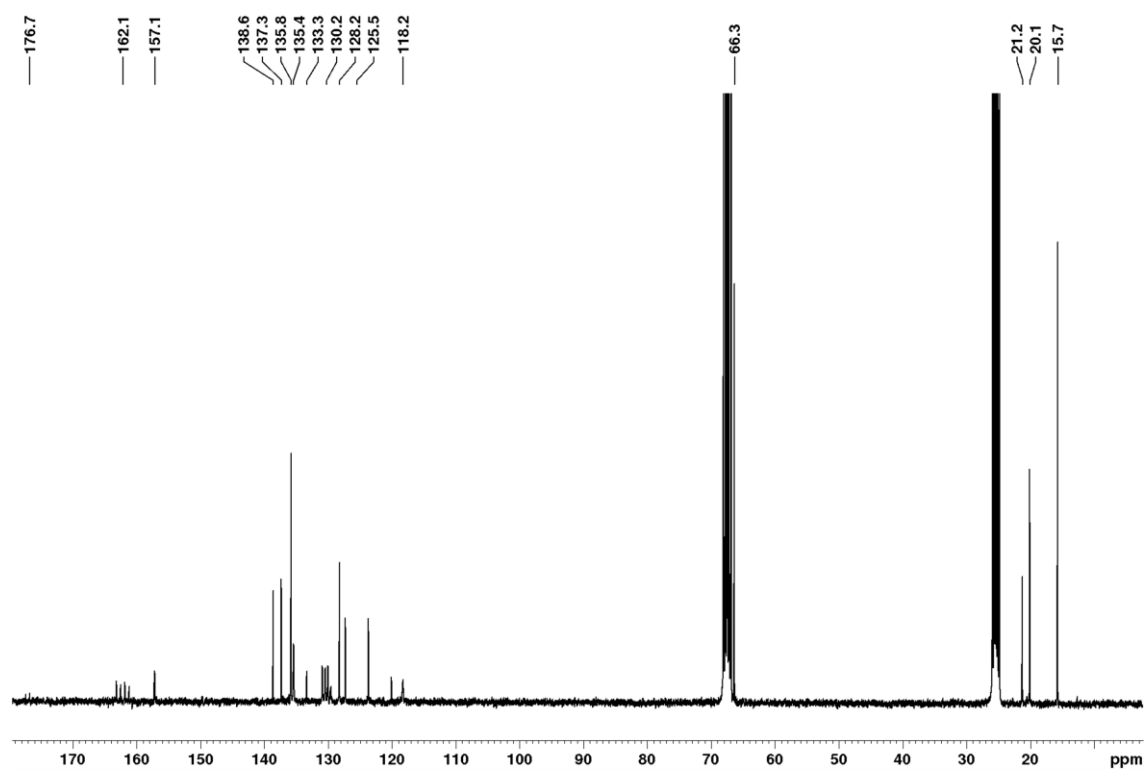


**Figure S12.**  $^{19}\text{F}$  NMR (188 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectrum of compound  $1^{\text{F}}\text{-H}$ .

Compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}\text{-BH}_3]$ .



**Figure S13.**  $^1\text{H}\{^{11}\text{B}\}$  NMR (300 MHz,  $\text{THF-}d_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}\text{-BH}_3]$ .



**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{THF-}d_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\mathbf{1}^{\text{F}}\text{-BH}_3]$ .

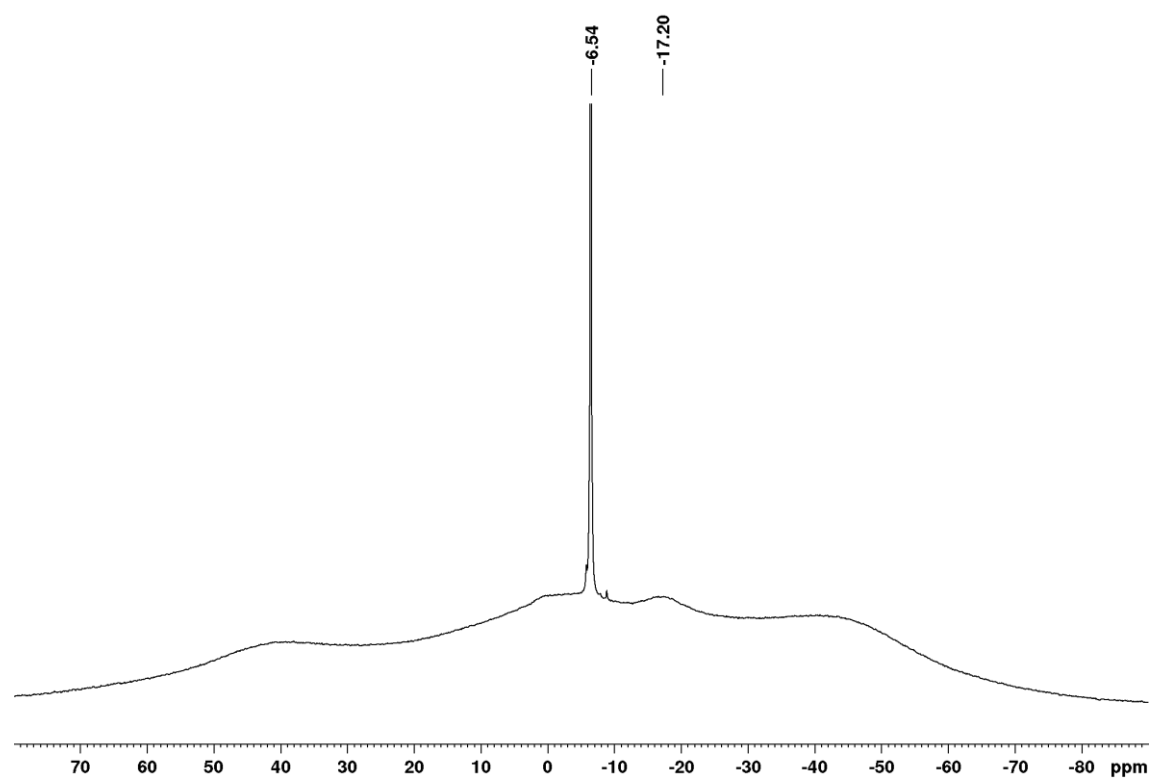


Figure S15.  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{THF-}d_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\text{1}^{\text{F}}\text{-BH}_3]$ .

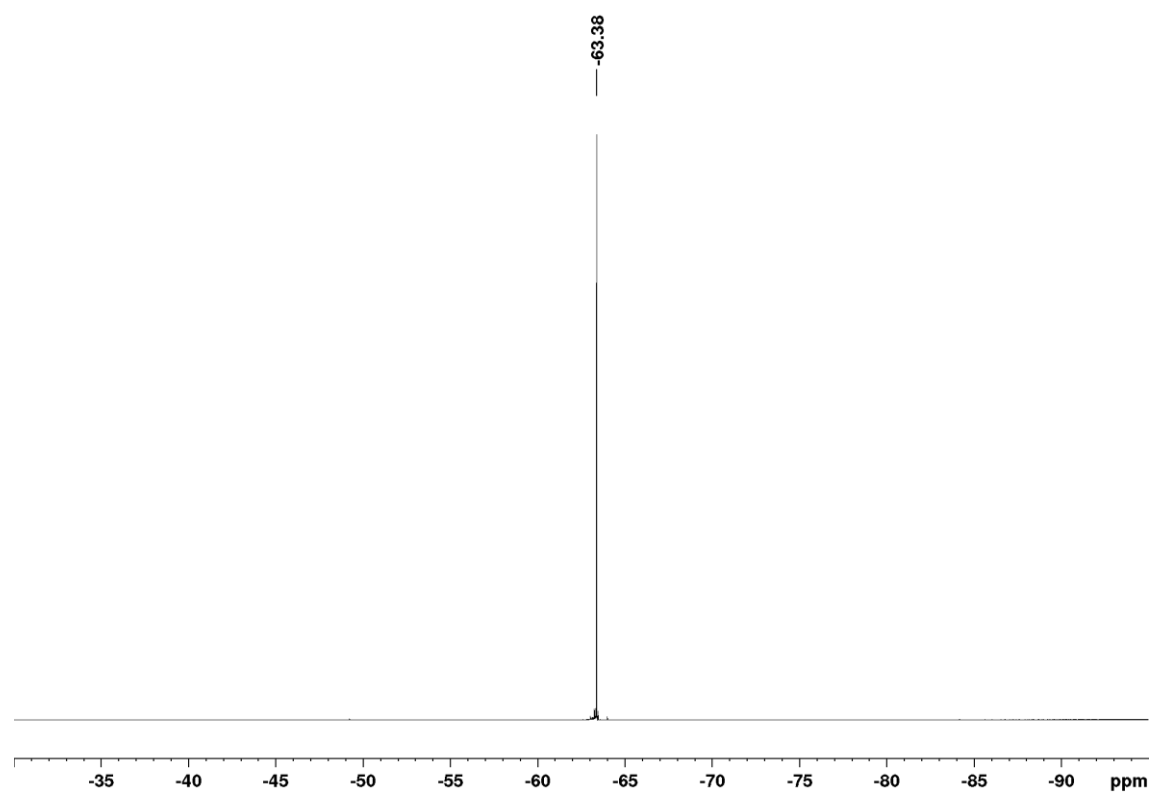


Figure S16.  $^{19}\text{F}$  NMR (282 MHz,  $\text{THF-}d_8$ , 298 K) spectrum of compound  $[\text{Li}(\text{Et}_2\text{O})_2][\text{1}^{\text{F}}\text{-BH}_3]$ .

## 2. $pK_a$ Measurements

The experimental setup and methodology used for the spectrophotometric determination of the  $pK_a$  values in acetonitrile is the same as described in previous papers.<sup>[1]</sup> A brief description is given here. The  $pK_a$  determination in acetonitrile is based on the determination of differences of the  $pK_a$  values of two acids. In this case one was our protonated sample and the other one a reference acid with a previously determined and published  $pK_a$  value. Both compounds are individually spectrophotometrically titrated in order to obtain the UV-vis spectra of the protonated and fully deprotonated forms. The same is then done with the mixture of the two compounds. Using the spectral data from these titrations the dissociation levels  $\alpha = [A^-]/([A^-] + [HA])$  of both acids in all the mixtures formed during titration are calculated which can be used to calculate the difference of  $pK_a$  values ( $\Delta pK_a$ ) of **1<sup>F</sup>**-H and the used reference acid according the following equation:

$$\Delta pK_a = \log \frac{\alpha_1(1 - \alpha_2)}{\alpha_2(1 - \alpha_1)}$$

The  $pK_a$  values were estimated as a result of  $\Delta pK_a$  measurements against three different reference acids. The spectrophotometric titrations were carried out using a Perkin-Elmer Lambda 40 UV-Vis spectrophotometer connected with optical fiber cables to an external cell compartment inside a MBraun Unilab glovebox filled with 99.999 % pure argon. This setup ensured that during the experiments the moisture and oxygen contents in the glovebox atmosphere were always below 10 ppm. Triflic acid (Aldrich, 99+%) and *tert*-butyliminotris(pyrrolidino)phosphorane (Aldrich, ≥97 %) were used to prepare the acidic and basic titrant solutions, respectively. Acetonitrile (Romil 190 SpS far UV/gradient quality) was used as solvent after drying with molecular sieves (3 Å), which lowered its water content to the range of 2–6 ppm. Compounds with previously published  $pK_a$  values were used as reference acids.<sup>[1a]</sup> The accuracy of the  $pK_a$  values is estimated as ±0.05  $pK_a$  units.

**Table S1:** Data of  $pK_a$  measurements (in acetonitrile).

Acid	Reference Acid	$pK_a$ (Ref)	$\Delta pK_a$	$pK_a$ (acid)	assigned $pK_a$
<b>1<sup>F</sup></b> -H	(4-NC <sub>5</sub> F <sub>4</sub> )-(C <sub>6</sub> F <sub>5</sub> )CHCN	16.40	−0.05	16.45	16.44
	(4-Cl-C <sub>6</sub> F <sub>4</sub> )CH(CN)-COOEt	17.39	0.96	16.43	
	(4-NC <sub>5</sub> F <sub>4</sub> )(2-C <sub>10</sub> F <sub>7</sub> )-CHCN	16.02	−0.42	16.44	

### 3. Electrochemical Measurements

Cyclic voltammetry (CV) measurements were carried out using a VMP3 potentiostat from Bio-Logic Science Instruments. All measurements were conducted within a glove box under Ar-atmosphere. The CV measurements of [NEt<sub>4</sub>][1] and [NEt<sub>4</sub>][1<sup>F</sup>] (typically about 0.0035 mol L<sup>-1</sup>) were carried out in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 mol L<sup>-1</sup> [nBu<sub>4</sub>N][PF<sub>6</sub>] (supplied in battery grade from Sigma-Aldrich, dried at 100 °C at 1 mbar for 24 h) as supporting electrolyte. The working electrode was a glassy carbon disc electrode with a diameter d = 2 mm supplied by Deutsche Metrohm GmbH & Co. KG, the counter electrode was a Pt-wire and the reference electrode was a Pt-wire as quasi-reference electrode (q-Pt) (Pt wire 99.9 % supplied by MaTeck GmbH). Before each measurement, the working electrode was polished with MetaDi<sup>®</sup> diamond polishing compounds from Buehler with the smallest grid size of 0.25 μm, thoroughly rinsed with water and isopropanol and dried. The sweep rate was 0.1 V s<sup>-1</sup>. Addition of ferrocene (same concentration as the analyte, *i.e.* about 0.0035 mol L<sup>-1</sup>) and repeating the measurement supplied potential values relatively to the Fc/Fc<sup>+</sup> redox couple.

Cyclic voltammetry measurements (see Figure 2, manuscript) allowed us to determine the redox potentials of the redox pairs [1]<sup>•</sup>/[1]<sup>-</sup> and [1<sup>F</sup>]<sup>•</sup>/[1<sup>F</sup>]<sup>-</sup>, respectively, in CH<sub>2</sub>Cl<sub>2</sub>. The addition of ferrocene neither changed the signal of [NEt<sub>4</sub>][1] nor of [NEt<sub>4</sub>][1<sup>F</sup>]. The CVs of both compounds show two anodic peaks and no cathodic peak. The variation of reverse potential did not result in observable cathodic peaks. We assume homogeneous reactions after the heterogenous electron transfer steps. The multisweep experiment (not shown) revealed a fast degradation of the electrode surface condition manifesting by shifting peak potentials and decreasing peak currents in the successive cycles indicating a decreasing electron transfer kinetics. In Figure 2 the CVs of [NEt<sub>4</sub>][1] (black) and that of [NEt<sub>4</sub>][1<sup>F</sup>] (blue) are shown in the presence of ferrocene. The oxidation waves of ferrocene are marked with A<sub>Fc</sub>. The anodic waves A I are assigned to the oxidation of [1]<sup>-</sup> and [1<sup>F</sup>]<sup>-</sup>. Although we estimated the half wave potentials *E*<sub>1/2</sub> for the sake of completeness, in the main text we refer to the peak potentials of the oxidation *E*<sub>p</sub><sup>ox</sup>, as the literature value for the redox potential of the redox pair [Ph<sub>3</sub>Sn]<sup>+</sup>/Ph<sub>3</sub>Sn<sup>•</sup> is also given as peak potential.<sup>[2]</sup> As approximation to *E*<sub>1/2</sub> we chose *E*<sub>p,3/4</sub> obtained with the current at the minimum between the ferrocene peak and the analyte peak as current offset. The values are listed in Table S2.

**Table S2.** Data extracted from CV measurements of this work and selected literature data in CH<sub>2</sub>Cl<sub>2</sub>. Potentials are given in V vs. Fc<sup>+</sup>/Fc, current densities in μA mm<sup>-2</sup>.

	<i>E</i> <sub>p</sub> <sup>ox</sup>	<i>j</i> <sub>offset</sub>	<i>j</i> <sub>p</sub>	<i>j</i> <sub>p,3/4</sub>	<i>E</i> <sub>p,3/4</sub> ≈ <i>E</i> <sub>1/2</sub>
[1] <sup>•</sup> /[1] <sup>-</sup>	0.56	10.28	4.26	13.48	0.51
[1 <sup>F</sup> ] <sup>•</sup> /[1 <sup>F</sup> ] <sup>-</sup>	1.32	5.09	4.80	8.60	1.22
[Ph <sub>3</sub> C] <sup>+</sup> /Ph <sub>3</sub> C <sup>•</sup>	0.66 <sup>[3],a,c</sup>	--	--	0.62 <sup>[3],b,c</sup>	

<sup>a</sup> *E*<sub>p</sub><sup>ox</sup> was estimated from Figs. 3 and 4 of that publication.

<sup>b</sup> *E*<sub>rev</sub> (as approximation of *E*<sub>1/2</sub>). The value was estimated from Figs. 3 and 4 of that publication.

<sup>c</sup> The measurements were performed at 208 K and the potentials were referenced vs. Ag<sup>+</sup>/Ag (concentration not explicitly specified). *E*<sup>o</sup>(Ag<sup>+</sup>/Ag, CH<sub>2</sub>Cl<sub>2</sub>) vs. *E*<sup>o</sup>(Fc<sup>+</sup>/Fc, CH<sub>2</sub>Cl<sub>2</sub>) is given as 0.65 V.<sup>[4]</sup>

#### 4. Crystallographic Section

The data for  $[\text{Li}(\text{THF})_4][\mathbf{1}^{\text{F}}]$ ,  $[\text{NEt}_4][\mathbf{1}^{\text{F}}]$  and  $[\text{Li}(\text{THF})_4][\mathbf{1}^{\text{F}}\text{--BH}_3]$  were collected from a shock-cooled single crystal at 150(2) K for  $[\text{Li}(\text{THF})_4][\mathbf{1}^{\text{F}}]$ , at 108(2) K for  $[\text{NEt}_4][\mathbf{1}^{\text{F}}]$  and at 100(2) K for  $[\text{Li}(\text{THF})_4][\mathbf{1}^{\text{F}}\text{--BH}_3]$  on a Bruker APEX2 QUAZAR three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker APEXII detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data were integrated with SAINT<sup>[5]</sup> and a multi-scan absorption correction using SADABS<sup>[6]</sup> was applied. The structure were solved by direct methods using SHELXT<sup>[7]</sup> and refined by full-matrix least-squares methods against  $F^2$  by SHELXL-2018/3.<sup>[8]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their  $U_{\text{iso}}$  values constrained to 1.5 times the  $U_{\text{eq}}$  of their pivot atoms for terminal  $\text{sp}^3$  carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.<sup>[9]</sup>

The data for  $\mathbf{1}^{\text{F}}\text{--H}(\text{CH}_2\text{Cl}_2)$  and  $\mathbf{1}^{\text{F}}\text{--H}(\text{Et}_2\text{O})$  were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data were integrated with SAINT<sup>[5]</sup> and a multi-scan absorption correction using SADABS<sup>[6]</sup> was applied. The structure were solved by direct methods using SHELXT<sup>[7]</sup> and refined by full-matrix least-squares methods against  $F^2$  by SHELXL-2018/3.<sup>[10]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their  $U_{\text{iso}}$  values constrained to 1.5 times the  $U_{\text{eq}}$  of their pivot atoms for terminal  $\text{sp}^3$  carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.<sup>[9]</sup>

**Table S3.** Crystallographic data for compounds **1<sup>F</sup>**-H(CH<sub>2</sub>Cl<sub>2</sub>), **1<sup>F</sup>**-H(Et<sub>2</sub>O), [Li(THF)<sub>4</sub>][**1<sup>F</sup>**] and [NEt<sub>4</sub>][**1<sup>F</sup>**].

	<b>1<sup>F</sup></b> -H(CH <sub>2</sub> Cl <sub>2</sub> )	<b>1<sup>F</sup></b> -H(Et <sub>2</sub> O)	[Li(THF) <sub>4</sub> ][ <b>1<sup>F</sup></b> ]	[NEt <sub>4</sub> ][ <b>1<sup>F</sup></b> ]
Empirical formula	C <sub>48</sub> H <sub>36</sub> BCl <sub>2</sub> F <sub>18</sub> N	C <sub>51</sub> H <sub>44</sub> BF <sub>18</sub> NO	C <sub>63</sub> H <sub>65</sub> BF <sub>18</sub> LiNO <sub>4</sub>	C <sub>58</sub> H <sub>59</sub> BCl <sub>6</sub> F <sub>18</sub> N <sub>2</sub>
Formula weight	1050.48	1039.68	1259.90	1349.58
Temperature [K]	100(2)	100(2)	150(2)	108(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> (4)	<i>P</i> 2 <sub>1</sub> (4)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	11.233(2)	11.4981(9)	13.326(9)	13.460(6)
<i>b</i> [Å]	16.877(3)	16.6844(12)	14.251(9)	13.552(6)
<i>c</i> [Å]	12.604(2)	12.8462(10)	17.343(11)	20.435(10)
$\alpha$ [°]	90	90	104.870(12)	75.625(7)
$\beta$ [°]	95.827(15)	97.346(3)	93.355(12)	80.662(15)
$\gamma$ [°]	90	90	99.951(12)	60.682(8)
Volume [Å <sup>3</sup> ]	2377.2(8)	2444.2(3)	3117(3)	3145(3)
<i>Z</i>	2	2	2	2
$\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]	1.468	1.413	1.342	1.425
$\mu$ [mm <sup>-1</sup> ]	0.243	0.131	0.119	0.365
<i>F</i> (000)	1064	1064	1304	1380
Crystal size [mm <sup>3</sup> ]	0.314×0.192×0.184	0.100×0.040×0.030	0.260×0.220×0.100	0.260×0.260×0.200
Crystal color	colorless	colorless	colorless	colorless
Crystal shape	block	block	block	block
Radiation	MoK $\alpha$ ( $\lambda$ =0.71073 Å)	MoK $\alpha$ ( $\lambda$ =0.71073 Å)	MoK $\alpha$ ( $\lambda$ =0.71073 Å)	MoK $\alpha$ ( $\lambda$ =0.71073 Å)
2 $\theta$ range [°]	3.25 to 57.54 (0.74 Å)	3.20 to 55.19 (0.77 Å)	2.44 to 55.57 (0.76 Å)	2.06 to 55.91 (0.76 Å)
Index ranges	-15 ≤ <i>h</i> ≤ 15 -22 ≤ <i>k</i> ≤ 22 -17 ≤ <i>l</i> ≤ 17	-14 ≤ <i>h</i> ≤ 14 -21 ≤ <i>k</i> ≤ 21 -16 ≤ <i>l</i> ≤ 16	-16 ≤ <i>h</i> ≤ 16 -18 ≤ <i>k</i> ≤ 17 -21 ≤ <i>l</i> ≤ 22	-17 ≤ <i>h</i> ≤ 17 -17 ≤ <i>k</i> ≤ 17 -26 ≤ <i>l</i> ≤ 26
Reflections collected	126060	134481	101166	76680
Independent reflections	12274 <i>R</i> <sub>int</sub> = 0.0488 <i>R</i> <sub>sigma</sub> = 0.0247	11216 <i>R</i> <sub>int</sub> = 0.0523 <i>R</i> <sub>sigma</sub> = 0.0245	12756 <i>R</i> <sub>int</sub> = 0.0715 <i>R</i> <sub>sigma</sub> = 0.0527	15040 <i>R</i> <sub>int</sub> = 0.0358 <i>R</i> <sub>sigma</sub> = 0.0298
Completeness to $\theta$ = 25.242°	100.0 %	100.0 %	97.2 %	100.0 %
Data / Restraints / Parameters	12274/534/755	11216/843/777	12756/1384/1027	15040/1407/1065
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.045	1.067	1.038	1.024
Final <i>R</i> indexes [ $\geq 2\sigma(I)$ ]	<i>R</i> <sub>1</sub> = 0.0380 <i>wR</i> <sub>2</sub> = 0.0936	<i>R</i> <sub>1</sub> = 0.0350 <i>wR</i> <sub>2</sub> = 0.0759	<i>R</i> <sub>1</sub> = 0.0481 <i>wR</i> <sub>2</sub> = 0.0999	<i>R</i> <sub>1</sub> = 0.0589 <i>wR</i> <sub>2</sub> = 0.1562
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0430 <i>wR</i> <sub>2</sub> = 0.0967	<i>R</i> <sub>1</sub> = 0.0426 <i>wR</i> <sub>2</sub> = 0.0803	<i>R</i> <sub>1</sub> = 0.0939 <i>wR</i> <sub>2</sub> = 0.1163	<i>R</i> <sub>1</sub> = 0.0833 <i>wR</i> <sub>2</sub> = 0.1741
Largest peak/hole [eÅ <sup>-3</sup> ]	0.31/-0.34	0.27/-0.27	0.26/-0.23	0.95/-1.08
Flack X parameter	0.009(19)	-0.06(10)		
CCDC number	2033814	2033815	2033813	2033812

Table S4. Crystallographic data for compound [Li(THF)<sub>4</sub>][<sup>F</sup>-BH<sub>3</sub>].

	[Li(THF) <sub>4</sub> ][ <sup>F</sup> -BH <sub>3</sub> ]
Empirical formula	C <sub>63</sub> H <sub>68</sub> B <sub>2</sub> F <sub>18</sub> LiNO <sub>4</sub>
Formula weight	1273.74
Temperature [K]	100(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)
<i>a</i> [Å]	21.347(9)
<i>b</i> [Å]	13.468(7)
<i>c</i> [Å]	22.134(9)
$\alpha$ [°]	90
$\beta$ [°]	98.512(12)
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	6293(5)
<i>Z</i>	4
$\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]	1.344
$\mu$ [mm <sup>-1</sup> ]	0.118
<i>F</i> (000)	2640
Crystal size [mm <sup>3</sup> ]	0.450×0.350×0.300
Crystal color	colorless
Crystal shape	block
Radiation	MoK $\alpha$ ( $\lambda$ =0.71073 Å)
2 $\theta$ range [°]	3.55 to 54.79 (0.77 Å)
Index ranges	-27 ≤ <i>h</i> ≤ 27 -17 ≤ <i>k</i> ≤ 16 -28 ≤ <i>l</i> ≤ 28
Reflections collected	113153
Independent reflections	14153 <i>R</i> <sub>int</sub> = 0.0676 <i>R</i> <sub>sigma</sub> = 0.0526
Completeness to $\theta = 25.242^\circ$	100.0 %
Data / Restraints / Parameters	14153/5549/1365
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.271
Final <i>R</i> indexes [ $\geq 2\sigma(I)$ ]	<i>R</i> <sub>1</sub> = 0.0964 <i>wR</i> <sub>2</sub> = 0.1530
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.1446 <i>wR</i> <sub>2</sub> = 0.1721
Largest peak/hole [eÅ <sup>-3</sup> ]	0.48/-0.31
Flack X parameter	
CCDC number	2163415

Table S5. Atomic coordinates and *U*<sub>eq</sub> [Å<sup>2</sup>] for <sup>F</sup>-H(CH<sub>2</sub>Cl<sub>2</sub>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
B1	0.3589(2)	0.49197(14)	0.58306(18)	0.0187(4)
F1	0.45072(14)	0.78523(10)	0.53530(16)	0.0420(4)
C1	0.19175(18)	0.50713(12)	0.29070(16)	0.0193(4)
N1	0.25351(16)	0.45126(11)	0.24160(15)	0.0201(3)
H1	0.235(3)	0.4407(19)	0.179(3)	0.033(8)
F2	0.28435(14)	0.79148(10)	0.43850(14)	0.0380(4)
C2	0.22648(19)	0.52328(13)	0.39690(17)	0.0197(4)
H2	0.184062	0.562256	0.432346	0.024
F3	0.30812(18)	0.85687(9)	0.58533(16)	0.0467(4)
C3	0.32283(18)	0.48362(12)	0.45389(16)	0.0186(4)
C4	0.38209(19)	0.42765(13)	0.39603(17)	0.0210(4)
H4	0.449026	0.400417	0.430887	0.025
C5	0.34702(19)	0.41061(13)	0.29057(17)	0.0204(4)
C6	0.09165(18)	0.54713(13)	0.22579(17)	0.0197(4)
C8	0.0182(2)	0.65646(15)	0.11598(19)	0.0262(4)
H8	0.031406	0.705928	0.083180	0.031
F8	-0.05442(18)	0.34819(18)	0.7101(2)	0.0795(8)
C7	0.1126(2)	0.61987(14)	0.17765(18)	0.0237(4)
F7	-0.05014(17)	0.34668(16)	0.5416(2)	0.0758(8)
F9	-0.03612(15)	0.23926(11)	0.63020(19)	0.0538(5)
C9	-0.0950(2)	0.62227(15)	0.10130(19)	0.0267(5)
C11	-0.0218(2)	0.51196(14)	0.21406(19)	0.0245(4)
F11	0.49591(18)	0.23055(11)	0.80106(18)	0.0579(6)
C10	-0.1132(2)	0.55068(15)	0.1508(2)	0.0285(5)

H10	-0.190357	0.527122	0.141473	0.034
F10	0.35695(16)	0.14529(10)	0.76657(17)	0.0489(5)
C13	-0.1941(3)	0.66281(18)	0.0315(2)	0.0390(6)
H13A	-0.168959	0.670655	-0.040018	0.059
H13B	-0.211335	0.714294	0.062423	0.059
H13C	-0.266165	0.629772	0.026659	0.059
F13	0.65355(18)	0.49299(16)	0.93341(13)	0.0596(6)
C12	0.2342(2)	0.65874(17)	0.1926(3)	0.0375(6)
H12A	0.293545	0.623718	0.165170	0.056
H12B	0.256374	0.668663	0.268636	0.056
H12C	0.231545	0.709079	0.153663	0.056
F12	0.46840(19)	0.17796(11)	0.64684(17)	0.0536(5)
C14	-0.0454(2)	0.43390(16)	0.2671(3)	0.0366(6)
H14A	-0.130629	0.420870	0.254061	0.055
H14B	-0.022774	0.438202	0.344056	0.055
H14C	0.001965	0.392052	0.237571	0.055
F14	0.7160(2)	0.38406(13)	0.87550(18)	0.0685(7)
C16	0.3643(2)	0.27041(15)	0.2356(2)	0.0328(5)
F16	0.75809(16)	0.53101(12)	0.39731(14)	0.0470(4)
C15	0.40383(19)	0.34854(14)	0.22885(17)	0.0229(4)
F15	0.83102(17)	0.48573(16)	0.88945(15)	0.0642(6)
F17	0.90350(15)	0.52588(14)	0.52025(17)	0.0571(5)
C17	0.4206(3)	0.21213(17)	0.1798(2)	0.0394(6)
H17	0.394620	0.158728	0.183475	0.047
C18	0.5130(3)	0.22994(19)	0.1195(2)	0.0408(7)
F18	0.80143(19)	0.63196(11)	0.49499(18)	0.0553(5)
C19	0.5510(3)	0.3075(2)	0.1160(2)	0.0429(7)
H19	0.614725	0.319995	0.074680	0.051
C20	0.4995(2)	0.36827(17)	0.1707(2)	0.0336(5)
C21	0.2660(4)	0.2489(2)	0.3024(4)	0.0609(10)
H21A	0.193283	0.278336	0.277451	0.091
H21B	0.290343	0.262376	0.377110	0.091
H21C	0.250025	0.191890	0.296422	0.091
C22	0.5702(4)	0.1647(2)	0.0603(3)	0.0603(11)
H22A	0.514486	0.147126	-0.000016	0.090
H22B	0.589628	0.119955	0.108559	0.090
H22C	0.643662	0.184567	0.033821	0.090
C23	0.5466(4)	0.4520(2)	0.1714(3)	0.0578(10)
H23A	0.585415	0.464675	0.242570	0.087
H23B	0.480104	0.488771	0.153281	0.087
H23C	0.604822	0.456970	0.118955	0.087
C24	0.30054(19)	0.57403(12)	0.62306(17)	0.0196(4)
C25	0.33532(19)	0.64445(13)	0.57491(18)	0.0223(4)
H25	0.392180	0.641548	0.524154	0.027
C26	0.2897(2)	0.71768(14)	0.59880(19)	0.0244(4)
C27	0.2070(2)	0.72484(14)	0.6728(2)	0.0289(5)
H27	0.174805	0.774978	0.688742	0.035
C28	0.1730(2)	0.65662(14)	0.7225(2)	0.0268(5)
C29	0.2191(2)	0.58212(13)	0.69819(18)	0.0229(4)
H29	0.193971	0.536392	0.733831	0.027
C30	0.3318(2)	0.78814(14)	0.5405(2)	0.0302(5)
C31	0.0854(3)	0.66106(18)	0.8038(2)	0.0401(6)
F1A	0.0517(8)	0.7330(4)	0.8265(8)	0.059(3)
F2A	0.1290(9)	0.6267(6)	0.8977(6)	0.057(2)
F3A	-0.0154(7)	0.6201(4)	0.7745(6)	0.050(2)
F4A	0.091(3)	0.7281(12)	0.859(2)	0.077(8)
F5A	0.099(3)	0.6055(13)	0.879(2)	0.066(7)
F6A	-0.0264(15)	0.6519(15)	0.759(2)	0.090(8)
F7A	0.1402(13)	0.6779(18)	0.8991(11)	0.082(6)
F8A	0.0136(17)	0.6016(9)	0.8072(17)	0.050(5)
F9A	0.0135(18)	0.7254(10)	0.7812(18)	0.064(5)
C32	0.30435(19)	0.40988(13)	0.62720(16)	0.0198(4)
C33	0.1801(2)	0.39656(13)	0.61957(17)	0.0223(4)
H33	0.127517	0.438426	0.595613	0.027
C34	0.1316(2)	0.32431(14)	0.64586(19)	0.0255(5)
C35	0.2039(2)	0.26132(14)	0.68330(19)	0.0257(5)
H35	0.170461	0.212588	0.703608	0.031
C36	0.3268(2)	0.27251(13)	0.68981(19)	0.0241(4)
C37	0.37554(19)	0.34472(13)	0.66198(17)	0.0212(4)
H37	0.460115	0.349975	0.666759	0.025
C38	-0.0020(2)	0.31443(17)	0.6321(2)	0.0364(6)
C39	0.4110(2)	0.20684(15)	0.7262(2)	0.0310(5)

C40	0.50366(19)	0.49815(13)	0.61351(17)	0.0199(4)
C41	0.5518(2)	0.48271(13)	0.71892(18)	0.0237(4)
H41	0.498988	0.469800	0.770632	0.028
C42	0.6742(2)	0.48575(15)	0.74994(18)	0.0273(5)
C43	0.7542(2)	0.50682(14)	0.6785(2)	0.0283(5)
H43	0.837760	0.508472	0.699473	0.034
C44	0.7086(2)	0.52549(13)	0.57505(19)	0.0246(4)
C45	0.58606(19)	0.52060(13)	0.54315(18)	0.0215(4)
H45	0.557858	0.532911	0.471436	0.026
C46	0.7195(3)	0.46208(19)	0.8613(2)	0.0390(6)
C47	0.7930(2)	0.55264(16)	0.4974(2)	0.0314(5)
Cl1_1	0.2556(2)	0.46085(17)	-0.03866(13)	0.0845(7)
Cl2_1	0.0563(2)	0.36673(8)	0.02114(11)	0.0558(5)
C1_1	0.0947(4)	0.4476(4)	-0.0489(5)	0.0503(13)
H1A_1	0.057220	0.495457	-0.021311	0.060
H1AB_1	0.063857	0.441259	-0.124860	0.060
Cl1_2	0.1214(3)	0.3808(3)	-0.0026(3)	0.0629(12)
Cl2_2	0.3330(4)	0.46544(18)	-0.0435(2)	0.0494(9)
C1_2	0.2628(8)	0.3746(6)	-0.0523(10)	0.043(3)
H1A_2	0.312880	0.334917	-0.010608	0.051
H1AB_2	0.252496	0.357013	-0.127593	0.051
Cl1_3	0.2048(9)	0.4444(10)	0.0325(7)	0.093(4)
Cl2_3	0.3483(17)	0.3708(12)	-0.0758(14)	0.124(5)
C1_3	0.193(2)	0.393(3)	-0.091(2)	0.091(9)
H1A_3	0.141732	0.345032	-0.091244	0.109
H1AB_3	0.168588	0.426904	-0.152963	0.109

$U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table S6.** Bond lengths and angles for  $1^F\text{-H}(\text{CH}_2\text{Cl}_2)$ .

Atom–Atom	Length [Å]
B1–C24	1.634(3)
B1–C32	1.635(3)
B1–C40	1.636(3)
B1–C3	1.643(3)
F1–C30	1.345(3)
C1–N1	1.357(3)
C1–C2	1.383(3)
C1–C6	1.484(3)
N1–C5	1.350(3)
F2–C30	1.342(3)
C2–C3	1.406(3)
F3–C30	1.329(3)
C3–C4	1.402(3)
C4–C5	1.378(3)
C5–C15	1.487(3)
C6–C11	1.400(3)
C6–C7	1.400(3)
C8–C9	1.392(3)
C8–C7	1.394(3)
F8–C38	1.325(4)
C7–C12	1.510(3)
F7–C38	1.328(3)
F9–C38	1.325(3)
C9–C10	1.384(4)
C9–C13	1.511(3)
C11–C10	1.397(3)
C11–C14	1.513(3)
F11–C39	1.333(3)
F10–C39	1.330(3)
F13–C46	1.336(4)
F12–C39	1.336(3)
F14–C46	1.330(4)
C16–C15	1.397(3)
C16–C17	1.398(4)
C16–C21	1.500(4)
F16–C47	1.333(3)
C15–C20	1.401(3)
F15–C46	1.329(3)
F17–C47	1.325(3)
C17–C18	1.380(5)
C18–C19	1.379(5)

C18–C22	1.511(4)
F18–C47	1.343(3)
C19–C20	1.394(4)
C20–C23	1.509(4)
C24–C29	1.389(3)
C24–C25	1.408(3)
C25–C26	1.383(3)
C26–C27	1.387(4)
C26–C30	1.500(3)
C27–C28	1.384(4)
C28–C29	1.405(3)
C28–C31	1.492(4)
C31–F8A	1.291(14)
C31–F1A	1.312(7)
C31–F7A	1.324(12)
C31–F4A	1.328(16)
C31–F6A	1.334(15)
C31–F5A	1.335(17)
C31–F3A	1.346(7)
C31–F2A	1.364(7)
C31–F9A	1.366(14)
C32–C37	1.404(3)
C32–C33	1.408(3)
C33–C34	1.389(3)
C34–C35	1.391(3)
C34–C38	1.502(3)
C35–C36	1.388(3)
C36–C37	1.395(3)
C36–C39	1.498(3)
C40–C45	1.398(3)
C40–C41	1.407(3)
C41–C42	1.392(3)
C42–C43	1.381(4)
C42–C46	1.497(3)
C43–C44	1.387(3)
C44–C45	1.397(3)
C44–C47	1.501(3)
Cl1_1–C1_1	1.813(5)
Cl2_1–C1_1	1.705(5)
Cl1_2–C1_2	1.768(8)
Cl2_2–C1_2	1.723(9)
Cl1_3–C1_3	1.775(13)
Cl2_3–C1_3	1.774(13)

Atom–Atom–Atom	Angle [°]
C24–B1–C32	115.95(17)
C24–B1–C40	107.09(17)
C32–B1–C40	111.84(17)
C24–B1–C3	108.20(16)
C32–B1–C3	101.61(17)
C40–B1–C3	112.14(17)
N1–C1–C2	118.14(19)
N1–C1–C6	117.29(18)
C2–C1–C6	124.57(19)
C5–N1–C1	123.69(19)
C1–C2–C3	121.83(19)
C4–C3–C2	115.88(19)
C4–C3–B1	119.40(18)
C2–C3–B1	124.37(18)
C5–C4–C3	122.6(2)
N1–C5–C4	117.90(19)
N1–C5–C15	118.30(19)
C4–C5–C15	123.8(2)
C11–C6–C7	121.1(2)
C11–C6–C1	119.7(2)
C7–C6–C1	119.12(19)
C9–C8–C7	121.6(2)
C8–C7–C6	118.6(2)
C8–C7–C12	120.3(2)
C6–C7–C12	121.1(2)
C10–C9–C8	118.5(2)
C10–C9–C13	121.6(2)
C8–C9–C13	119.9(2)
C10–C11–C6	118.1(2)
C10–C11–C14	120.5(2)
C6–C11–C14	121.4(2)
C9–C10–C11	122.2(2)
C15–C16–C17	118.1(3)
C15–C16–C21	121.3(2)
C17–C16–C21	120.6(3)
C16–C15–C20	121.4(2)
C16–C15–C5	118.5(2)
C20–C15–C5	119.9(2)
C18–C17–C16	121.9(3)
C19–C18–C17	118.5(2)
C19–C18–C22	121.8(3)
C17–C18–C22	119.7(3)
C18–C19–C20	122.4(3)
C19–C20–C15	117.6(3)
C19–C20–C23	122.0(3)
C15–C20–C23	120.4(2)
C29–C24–C25	116.2(2)
C29–C24–B1	127.34(19)
C25–C24–B1	116.43(19)
C26–C25–C24	122.4(2)
C25–C26–C27	120.8(2)
C25–C26–C30	117.4(2)
C27–C26–C30	121.8(2)
C28–C27–C26	117.9(2)
C27–C28–C29	121.4(2)
C27–C28–C31	120.1(2)
C29–C28–C31	118.5(2)
C24–C29–C28	121.3(2)
F3–C30–F2	107.1(2)
F3–C30–F1	107.2(2)
F2–C30–F1	104.8(2)
F3–C30–C26	113.4(2)
F2–C30–C26	112.9(2)
F1–C30–C26	111.0(2)
F8A–C31–F7A	111.8(13)
F4A–C31–F6A	108.5(16)
F4A–C31–F5A	103.2(16)

F6A–C31–F5A	104.9(14)
F1A–C31–F3A	106.4(5)
F1A–C31–F2A	106.9(6)
F3A–C31–F2A	103.7(5)
F8A–C31–F9A	105.4(12)
F7A–C31–F9A	103.2(12)
F8A–C31–C28	116.2(11)
F1A–C31–C28	114.9(5)
F7A–C31–C28	110.8(7)
F4A–C31–C28	113.8(15)
F6A–C31–C28	111.1(12)
F5A–C31–C28	114.8(14)
F3A–C31–C28	112.3(4)
F2A–C31–C28	111.8(5)
F9A–C31–C28	108.3(10)
C37–C32–C33	115.2(2)
C37–C32–B1	123.30(19)
C33–C32–B1	121.01(18)
C34–C33–C32	122.3(2)
C33–C34–C35	121.5(2)
C33–C34–C38	118.8(2)
C35–C34–C38	119.8(2)
C36–C35–C34	117.3(2)
C35–C36–C37	121.2(2)
C35–C36–C39	120.7(2)
C37–C36–C39	118.1(2)
C36–C37–C32	122.5(2)
F9–C38–F8	106.0(3)
F9–C38–F7	106.5(3)
F8–C38–F7	106.7(3)
F9–C38–C34	113.1(2)
F8–C38–C34	112.4(2)
F7–C38–C34	111.6(2)
F10–C39–F11	106.6(2)
F10–C39–F12	106.0(2)
F11–C39–F12	105.9(2)
F10–C39–C36	113.4(2)
F11–C39–C36	112.3(2)
F12–C39–C36	112.2(2)
C45–C40–C41	115.7(2)
C45–C40–B1	125.11(18)
C41–C40–B1	119.16(19)
C42–C41–C40	122.2(2)
C43–C42–C41	121.0(2)
C43–C42–C46	119.9(2)
C41–C42–C46	119.0(2)
C42–C43–C44	118.0(2)
C43–C44–C45	121.0(2)
C43–C44–C47	119.0(2)
C45–C44–C47	119.9(2)
C44–C45–C40	122.0(2)
F15–C46–F14	107.6(3)
F15–C46–F13	105.9(2)
F14–C46–F13	105.6(3)
F15–C46–C42	113.1(2)
F14–C46–C42	112.2(2)
F13–C46–C42	112.0(2)
F17–C47–F16	106.9(2)
F17–C47–F18	106.1(2)
F16–C47–F18	105.4(2)
F17–C47–C44	113.2(2)
F16–C47–C44	112.9(2)
F18–C47–C44	111.7(2)
Cl2_1–C1_1–Cl1_1	111.4(3)
Cl2_2–C1_2–Cl1_2	110.2(5)
Cl2_3–C1_3–Cl1_3	91.4(10)

Bonds to hydrogen atoms were omitted.

**Table S7.** Atomic coordinates and  $U_{eq}$  [ $\text{\AA}^2$ ] for **1<sup>F</sup>**-H(Et<sub>2</sub>O).

Atom	x	y	z	$U_{eq}$
C1	0.35023(19)	0.58620(13)	0.28920(17)	0.0176(4)
O1	0.20242(17)	0.56854(15)	0.02741(14)	0.0403(5)
B1	0.3592(2)	0.50861(16)	0.57892(19)	0.0188(5)
N1	0.25567(17)	0.54668(12)	0.24013(15)	0.0181(4)
H1	0.230(3)	0.5581(19)	0.173(3)	0.037(9)
F002	0.75570(14)	0.46141(11)	0.41652(12)	0.0407(4)
C2	0.3853(2)	0.57009(14)	0.39382(18)	0.0192(4)
H2	0.452753	0.596472	0.428207	0.023
C3	0.3249(2)	0.51614(13)	0.45122(17)	0.0182(4)
C4	0.2279(2)	0.47790(14)	0.39523(18)	0.0192(4)
H4	0.184531	0.440430	0.430529	0.023
C5	0.19345(19)	0.49323(13)	0.29007(17)	0.0180(4)
F006	0.80411(18)	0.36479(11)	0.52200(15)	0.0499(5)
C6	0.40869(19)	0.64715(14)	0.22902(17)	0.0184(4)
C7	0.5116(2)	0.62747(15)	0.18637(19)	0.0242(5)
F008	0.50163(17)	0.77275(11)	0.78975(17)	0.0538(5)
C8	0.5658(2)	0.68736(18)	0.1342(2)	0.0302(6)
H8	0.634882	0.674829	0.104051	0.036
F009	0.36646(16)	0.85954(10)	0.75669(17)	0.0514(5)
C9	0.5217(2)	0.76462(17)	0.1251(2)	0.0309(6)
F00A	0.47248(19)	0.82727(12)	0.63878(16)	0.0531(5)
F00B	0.89540(14)	0.47638(13)	0.54212(15)	0.0511(5)
C10	0.4215(2)	0.78266(16)	0.1704(2)	0.0294(6)
H10	0.391986	0.835892	0.165813	0.035
C12	0.5628(2)	0.54456(18)	0.1971(2)	0.0334(6)
H12A	0.499378	0.505089	0.193997	0.050
H12B	0.612926	0.539911	0.264556	0.050
H12C	0.609676	0.534626	0.139831	0.050
C50	0.0137(3)	0.6279(2)	0.0155(3)	0.0508(8)
H50A	0.049626	0.678583	0.041422	0.076
H50B	-0.006500	0.596182	0.074795	0.076
H50C	-0.057510	0.639095	-0.032839	0.076
C49	0.0961(3)	0.5833(3)	-0.0393(3)	0.0694(13)
H49A	0.060364	0.531662	-0.064193	0.083
H49B	0.113140	0.614171	-0.101461	0.083
C48	0.3488(3)	0.6227(2)	-0.0738(2)	0.0486(8)
H48A	0.295189	0.639403	-0.135454	0.073
H48B	0.425821	0.610465	-0.094829	0.073
H48C	0.356621	0.666028	-0.021889	0.073
C47	0.3009(3)	0.54940(18)	-0.0266(2)	0.0364(6)
H47A	0.276381	0.510040	-0.082831	0.044
H47B	0.363268	0.524468	0.023252	0.044
C11	0.3635(2)	0.72519(14)	0.22201(19)	0.0243(5)
C13	0.5798(3)	0.8289(2)	0.0666(3)	0.0460(8)
H13A	0.656778	0.810035	0.052034	0.069
H13B	0.589566	0.877588	0.109623	0.069
H13C	0.530688	0.840864	0.000354	0.069
C14	0.2548(3)	0.74661(18)	0.2705(3)	0.0385(7)
H14A	0.240584	0.804393	0.263579	0.058
H14B	0.265790	0.731913	0.344932	0.058
H14C	0.187434	0.717429	0.234342	0.058
C15	0.0921(2)	0.45323(14)	0.22753(17)	0.0194(4)
C17	-0.1140(2)	0.44387(16)	0.1715(2)	0.0275(5)
H17	-0.191426	0.463244	0.173085	0.033
C16	-0.0212(2)	0.48320(14)	0.23056(19)	0.0226(5)
C018	0.3313(2)	0.35505(14)	0.57164(18)	0.0207(5)
H018	0.386902	0.356935	0.523022	0.025
C18	-0.0971(2)	0.37738(16)	0.11053(19)	0.0262(5)
C19	0.0163(2)	0.34884(16)	0.1100(2)	0.0275(5)
H19	0.028633	0.303073	0.068772	0.033
C20	0.1120(2)	0.38536(15)	0.16792(19)	0.0245(5)
C21	-0.0421(2)	0.55620(17)	0.2947(2)	0.0340(6)
H21A	0.003867	0.601230	0.272861	0.051
H21B	-0.018052	0.544846	0.369236	0.051
H21C	-0.125589	0.569985	0.283852	0.051
C22	-0.1985(3)	0.33527(19)	0.0466(2)	0.0386(7)
H22A	-0.268529	0.369199	0.042261	0.058
H22B	-0.213829	0.284310	0.080234	0.058
H22C	-0.178913	0.324985	-0.024249	0.058

C23	0.2336(2)	0.3522(2)	0.1669(3)	0.0411(7)
H23A	0.280590	0.390204	0.131780	0.062
H23B	0.228961	0.301046	0.129011	0.062
H23C	0.270328	0.343651	0.239144	0.062
C24	0.5005(2)	0.50096(14)	0.61524(18)	0.0197(4)
C25	0.5840(2)	0.47861(14)	0.55038(18)	0.0215(5)
H25	0.558863	0.467455	0.478500	0.026
C26	0.7032(2)	0.47220(15)	0.58809(19)	0.0234(5)
C27	0.7433(2)	0.48883(15)	0.6919(2)	0.0259(5)
H27	0.824558	0.486052	0.717258	0.031
C28	0.6617(2)	0.50972(15)	0.75821(18)	0.0244(5)
C29	0.5432(2)	0.51441(14)	0.72031(18)	0.0216(5)
H29	0.489190	0.527286	0.767854	0.026
C30	0.7888(2)	0.44439(17)	0.5175(2)	0.0298(6)
C31	0.7013(3)	0.53081(17)	0.8705(2)	0.0347(6)
F1B	0.70404(19)	0.61003(11)	0.88651(15)	0.0553(5)
F2B	0.80871(15)	0.50329(12)	0.90447(13)	0.0465(5)
F3B	0.62958(16)	0.50103(14)	0.93586(12)	0.0495(5)
C32	0.3071(2)	0.59263(14)	0.61999(17)	0.0191(5)
C33	0.3787(2)	0.65847(14)	0.65184(18)	0.0207(5)
H33	0.461297	0.652952	0.654491	0.025
C34	0.3334(2)	0.73155(14)	0.67970(18)	0.0228(5)
C35	0.2135(2)	0.74367(15)	0.67396(19)	0.0252(5)
H35	0.182512	0.793614	0.692831	0.030
C36	0.1404(2)	0.68025(15)	0.63966(19)	0.0247(5)
C37	0.1864(2)	0.60675(14)	0.61354(18)	0.0220(5)
H37	0.133841	0.564598	0.590456	0.026
C38	0.4174(2)	0.79729(15)	0.7159(2)	0.0301(6)
C39	0.0102(2)	0.69017(17)	0.6285(2)	0.0333(6)
F1D	-0.0380(12)	0.6459(9)	0.6989(11)	0.047(3)
F2D	-0.0387(19)	0.6643(10)	0.5334(9)	0.039(3)
F3D	-0.027(2)	0.7655(7)	0.6359(13)	0.040(3)
F4D	-0.047(4)	0.635(2)	0.678(3)	0.069(10)
F5D	-0.037(4)	0.686(2)	0.5272(18)	0.049(8)
F6D	-0.023(4)	0.7602(15)	0.666(3)	0.048(7)
F7D	-0.048(3)	0.648(2)	0.5528(17)	0.064(8)
F8D	-0.017(4)	0.7678(11)	0.614(3)	0.054(7)
F9D	-0.033(3)	0.6692(15)	0.7190(17)	0.065(7)
C40	0.3000(2)	0.42672(14)	0.61765(17)	0.0196(5)
C41	0.2209(2)	0.41953(14)	0.69074(18)	0.0211(5)
H41	0.198173	0.466216	0.725367	0.025
C42	0.1741(2)	0.34533(15)	0.71441(19)	0.0231(5)
C43	0.2043(2)	0.27572(15)	0.6660(2)	0.0251(5)
H43	0.171415	0.225544	0.681479	0.030
C44	0.2844(2)	0.28161(15)	0.59412(19)	0.0228(5)
C45	0.0883(2)	0.34231(17)	0.7924(2)	0.0329(6)
F1A	-0.0106(8)	0.3832(7)	0.7628(9)	0.053(2)
F2A	0.1303(11)	0.3752(6)	0.8860(6)	0.044(2)
F3A	0.0542(10)	0.2694(5)	0.8172(11)	0.061(3)
F4A	0.030(3)	0.4108(12)	0.794(3)	0.059(8)
F5A	0.135(2)	0.325(2)	0.8867(15)	0.070(8)
F6A	0.007(3)	0.2861(18)	0.762(2)	0.068(7)
F7A	0.115(3)	0.3946(13)	0.8690(17)	0.047(5)
F8A	0.090(2)	0.2696(10)	0.835(2)	0.059(6)
F9A	-0.0191(18)	0.3565(18)	0.748(3)	0.083(9)
C46	0.3213(2)	0.21002(15)	0.5366(2)	0.0286(5)
F1C	0.27502(14)	0.20840(10)	0.43555(12)	0.0361(4)
F2C	0.29307(17)	0.14024(9)	0.57850(15)	0.0435(4)
F3C	0.43835(14)	0.20917(10)	0.53522(16)	0.0428(4)

$U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table S8.** Bond lengths and angles for  $1^F\text{-H}(\text{Et}_2\text{O})$ .

Atom–Atom	Length [Å]
C1–N1	1.356(3)
C1–C2	1.379(3)
C1–C6	1.489(3)
O1–C49	1.422(4)
O1–C47	1.438(3)
B1–C40	1.632(3)
B1–C24	1.637(3)
B1–C32	1.638(3)

B1–C3	1.642(3)
N1–C5	1.355(3)
F002–C30	1.335(3)
C2–C3	1.402(3)
C3–C4	1.402(3)
C4–C5	1.382(3)
C5–C15	1.486(3)
F006–C30	1.340(3)
C6–C11	1.400(3)
C6–C7	1.405(3)

C7–C8	1.394(4)
C7–C12	1.503(4)
F008–C38	1.331(3)
C8–C9	1.385(4)
F009–C38	1.332(3)
C9–C10	1.388(4)
C9–C13	1.514(4)
F00A–C38	1.339(3)
F00B–C30	1.337(3)
C10–C11	1.385(4)
C50–C49	1.455(5)
C48–C47	1.500(5)
C11–C14	1.509(4)
C15–C16	1.401(3)
C15–C20	1.402(3)
C17–C18	1.386(4)
C17–C16	1.392(3)
C16–C21	1.507(4)
C018–C44	1.384(3)
C018–C40	1.401(3)
C18–C19	1.389(4)
C18–C22	1.511(3)
C19–C20	1.389(3)
C20–C23	1.505(4)
C24–C29	1.394(3)
C24–C25	1.399(3)
C25–C26	1.398(3)
C26–C27	1.383(3)
C26–C30	1.496(4)
C27–C28	1.390(4)
C28–C29	1.389(3)
C28–C31	1.498(3)
C31–F1B	1.337(3)
C31–F2B	1.338(3)
C31–F3B	1.344(4)
C32–C37	1.399(3)
C32–C33	1.402(3)
C33–C34	1.391(3)
C34–C35	1.385(4)
C34–C38	1.496(3)
C35–C36	1.388(4)
C36–C37	1.393(3)
C36–C39	1.495(4)
C39–F7D	1.317(17)
C39–F3D	1.335(10)
C39–F6D	1.338(18)
C39–F4D	1.339(18)
C39–F8D	1.341(17)
C39–F1D	1.342(10)
C39–F5D	1.344(18)
C39–F2D	1.349(10)
C39–F9D	1.367(17)
C40–C41	1.394(3)
C41–C42	1.399(3)
C42–C43	1.382(4)
C42–C45	1.494(4)
C43–C44	1.388(4)
C44–C46	1.495(4)
C45–F5A	1.295(16)
C45–F9A	1.312(17)
C45–F7A	1.323(16)
C45–F4A	1.327(17)
C45–F3A	1.329(8)
C45–F8A	1.331(15)
C45–F1A	1.338(7)
C45–F6A	1.348(16)
C45–F2A	1.355(7)
C46–F1C	1.338(3)
C46–F2C	1.340(3)
C46–F3C	1.348(3)

Atom–Atom–Atom	Angle [°]
N1–C1–C2	118.4(2)
N1–C1–C6	118.63(19)
C2–C1–C6	122.9(2)
C49–O1–C47	114.6(2)
C40–B1–C24	106.57(18)
C40–B1–C32	115.72(19)
C24–B1–C32	111.46(19)
C40–B1–C3	108.19(18)
C24–B1–C3	113.18(19)
C32–B1–C3	101.84(18)
C5–N1–C1	122.7(2)
C1–C2–C3	122.3(2)
C4–C3–C2	116.0(2)
C4–C3–B1	123.5(2)
C2–C3–B1	120.2(2)
C5–C4–C3	121.8(2)
N1–C5–C4	118.8(2)
N1–C5–C15	117.68(19)
C4–C5–C15	123.5(2)
C11–C6–C7	121.1(2)
C11–C6–C1	118.7(2)
C7–C6–C1	120.1(2)
C8–C7–C6	118.1(2)
C8–C7–C12	120.6(2)
C6–C7–C12	121.3(2)
C9–C8–C7	121.7(2)
C8–C9–C10	118.8(2)
C8–C9–C13	121.4(3)
C10–C9–C13	119.8(3)
C11–C10–C9	121.8(3)
O1–C49–C50	111.1(3)
O1–C47–C48	111.5(3)
C10–C11–C6	118.5(2)
C10–C11–C14	120.6(2)
C6–C11–C14	120.9(2)
C16–C15–C20	121.4(2)
C16–C15–C5	119.5(2)
C20–C15–C5	119.1(2)
C18–C17–C16	122.2(2)
C17–C16–C15	117.9(2)
C17–C16–C21	121.0(2)
C15–C16–C21	121.2(2)
C44–C018–C40	122.7(2)
C17–C18–C19	118.5(2)
C17–C18–C22	121.7(2)
C19–C18–C22	119.8(2)
C18–C19–C20	121.8(2)
C19–C20–C15	118.2(2)
C19–C20–C23	120.5(2)
C15–C20–C23	121.3(2)
C29–C24–C25	115.8(2)
C29–C24–B1	118.5(2)
C25–C24–B1	125.6(2)
C26–C25–C24	122.0(2)
C27–C26–C25	120.7(2)
C27–C26–C30	118.9(2)
C25–C26–C30	120.4(2)
C26–C27–C28	118.2(2)
C29–C28–C27	120.5(2)
C29–C28–C31	119.2(2)
C27–C28–C31	120.2(2)
C28–C29–C24	122.6(2)
F002–C30–F00B	106.5(2)
F002–C30–F006	105.8(2)
F00B–C30–F006	105.9(2)
F002–C30–C26	113.3(2)
F00B–C30–C26	112.8(2)
F006–C30–C26	111.9(2)
F1B–C31–F2B	106.6(2)
F1B–C31–F3B	105.9(2)
F2B–C31–F3B	106.5(2)

F1B–C31–C28	112.2(2)	F9D–C39–C36	111.1(16)
F2B–C31–C28	112.8(2)	C41–C40–C018	115.8(2)
F3B–C31–C28	112.3(2)	C41–C40–B1	127.7(2)
C37–C32–C33	115.2(2)	C018–C40–B1	116.5(2)
C37–C32–B1	121.7(2)	C40–C41–C42	121.7(2)
C33–C32–B1	122.6(2)	C43–C42–C41	121.3(2)
C34–C33–C32	122.4(2)	C43–C42–C45	119.9(2)
C35–C34–C33	121.2(2)	C41–C42–C45	118.8(2)
C35–C34–C38	120.5(2)	C42–C43–C44	117.8(2)
C33–C34–C38	118.3(2)	C018–C44–C43	120.7(2)
C34–C35–C36	117.6(2)	C018–C44–C46	117.5(2)
C35–C36–C37	121.0(2)	C43–C44–C46	121.8(2)
C35–C36–C39	120.3(2)	F9A–C45–F7A	108.7(17)
C37–C36–C39	118.7(2)	F5A–C45–F4A	109.1(18)
C36–C37–C32	122.6(2)	F9A–C45–F8A	108.1(16)
F008–C38–F009	106.0(2)	F7A–C45–F8A	107.7(14)
F008–C38–F00A	105.8(2)	F3A–C45–F1A	105.6(6)
F009–C38–F00A	105.8(2)	F5A–C45–F6A	108.2(18)
F008–C38–C34	112.2(2)	F4A–C45–F6A	105.7(16)
F009–C38–C34	113.3(2)	F3A–C45–F2A	103.9(7)
F00A–C38–C34	113.1(2)	F1A–C45–F2A	103.8(6)
F6D–C39–F4D	105(2)	F5A–C45–C42	113.7(13)
F7D–C39–F8D	109(2)	F9A–C45–C42	111.7(16)
F3D–C39–F1D	107.8(10)	F7A–C45–C42	111.3(17)
F6D–C39–F5D	107(2)	F4A–C45–C42	111.0(13)
F4D–C39–F5D	105(2)	F3A–C45–C42	115.6(6)
F3D–C39–F2D	105.3(10)	F8A–C45–C42	109.2(10)
F1D–C39–F2D	105.9(9)	F1A–C45–C42	113.7(5)
F7D–C39–F9D	106.4(16)	F6A–C45–C42	108.9(12)
F8D–C39–F9D	104.9(17)	F2A–C45–C42	113.0(6)
F7D–C39–C36	115.0(19)	F1C–C46–F2C	106.6(2)
F3D–C39–C36	115.2(11)	F1C–C46–F3C	105.1(2)
F6D–C39–C36	112.9(19)	F2C–C46–F3C	106.8(2)
F4D–C39–C36	115(2)	F1C–C46–C44	113.1(2)
F8D–C39–C36	109.6(18)	F2C–C46–C44	113.4(2)
F1D–C39–C36	111.7(7)	F3C–C46–C44	111.2(2)
F5D–C39–C36	111(2)		
F2D–C39–C36	110.3(10)		

Bonds to hydrogen atoms were omitted.

**Table S9.** Atomic coordinates and  $U_{eq}$  [ $\text{\AA}^2$ ] for  $[\text{Li}(\text{THF})_4][1^{\dagger}]$ .

Atom	x	y	z	$U_{eq}$
C1	0.79468(15)	0.66422(15)	0.90984(13)	0.0209(4)
O1	0.72398(12)	0.67353(12)	0.19765(10)	0.0334(4)
Li1	0.6125(3)	0.7310(3)	0.2394(2)	0.0323(9)
B1	0.74487(18)	0.75243(18)	0.71392(15)	0.0212(5)
N1	0.81343(13)	0.74812(12)	0.97053(11)	0.0215(4)
C2	0.77834(15)	0.66250(15)	0.82925(13)	0.0213(4)
H2	0.764563	0.600727	0.789455	0.026
O2	0.60013(12)	0.82985(12)	0.18585(10)	0.0369(4)
C3	0.78183(15)	0.75020(15)	0.80564(13)	0.0204(4)
O3	0.65446(12)	0.79256(13)	0.35240(10)	0.0374(4)
C4	0.80539(15)	0.83626(15)	0.86962(13)	0.0206(4)
H4	0.812922	0.898665	0.858164	0.025
O4	0.47640(11)	0.64922(11)	0.22359(10)	0.0301(4)
C5	0.81831(15)	0.83399(15)	0.95000(13)	0.0211(4)
F7	0.41637(12)	0.77484(12)	0.90344(9)	0.0486(4)
C7	0.87593(16)	0.52117(16)	0.91768(13)	0.0244(5)
C6	0.79366(15)	0.56930(15)	0.93241(12)	0.0210(4)
C8	0.87333(17)	0.43148(17)	0.93652(14)	0.0283(5)
H8	0.929296	0.398523	0.926140	0.034
F8	0.43325(11)	0.62462(11)	0.85490(10)	0.0458(4)
C9	0.79096(17)	0.38876(16)	0.97015(13)	0.0266(5)
F9	0.30140(10)	0.67314(11)	0.81505(9)	0.0419(4)
C11	0.71018(16)	0.52815(16)	0.96742(13)	0.0247(5)
F11	0.40254(14)	0.76631(13)	0.52070(9)	0.0585(5)
C10	0.71084(17)	0.43848(16)	0.98530(13)	0.0257(5)
H10	0.654439	0.410558	1.008659	0.031
F10	0.46933(11)	0.91579(12)	0.58437(11)	0.0533(4)
C13	0.79033(19)	0.29169(17)	0.99054(15)	0.0338(6)
H13A	0.722066	0.249642	0.974475	0.051
H13B	0.807537	0.304401	1.048476	0.051

H13C	0.840970	0.258108	0.961869	0.051
C12	0.96732(18)	0.56538(18)	0.88169(16)	0.0340(6)
H12A	0.951871	0.548718	0.823272	0.051
H12B	1.027047	0.538527	0.894805	0.051
H12C	0.982161	0.637488	0.903707	0.051
F12	0.32300(11)	0.85025(13)	0.60980(10)	0.0541(4)
C14	0.62071(18)	0.57850(17)	0.98469(16)	0.0340(6)
H14A	0.635856	0.644021	0.974987	0.051
H14B	0.608172	0.585715	1.040836	0.051
H14C	0.559705	0.538625	0.949509	0.051
C15	0.83761(15)	0.92732(15)	1.01732(12)	0.0209(4)
C17	0.79055(16)	1.08123(16)	1.08597(13)	0.0249(5)
H17	0.744028	1.125393	1.090143	0.030
C16	0.76888(16)	0.99214(16)	1.02450(13)	0.0238(5)
C19	0.94334(16)	1.04082(16)	1.13365(13)	0.0234(5)
H19	1.002504	1.056647	1.171354	0.028
C18	0.87730(16)	1.10697(16)	1.14069(13)	0.0240(5)
C20	0.92630(15)	0.95177(15)	1.07327(12)	0.0205(4)
C21	0.67148(17)	0.96962(18)	0.96815(15)	0.0315(5)
H21A	0.685873	0.993719	0.921079	0.047
H21B	0.619835	1.002604	0.995877	0.047
H21C	0.645655	0.897965	0.950977	0.047
C22	0.90070(19)	1.20449(17)	1.20547(15)	0.0337(6)
H22A	0.974741	1.230297	1.213492	0.051
H22B	0.877336	1.194093	1.255717	0.051
H22C	0.865150	1.252118	1.189071	0.051
C23	1.00434(16)	0.88621(16)	1.06571(14)	0.0262(5)
H23A	1.028122	0.876321	1.012325	0.039
H23B	0.973164	0.822078	1.073175	0.039
H23C	1.062611	0.917503	1.106716	0.039
C25	0.84271(16)	0.60636(16)	0.65282(13)	0.0237(5)
H25	0.888179	0.628863	0.700932	0.028
C24	0.76122(15)	0.65433(15)	0.64545(13)	0.0210(4)
C26	0.86026(16)	0.52645(16)	0.59227(13)	0.0254(5)
C27	0.79722(17)	0.49151(16)	0.52015(14)	0.0269(5)
H27	0.808890	0.437217	0.479042	0.032
C28	0.71697(16)	0.53862(15)	0.51044(13)	0.0247(5)
C29	0.69853(16)	0.61656(15)	0.57181(13)	0.0217(5)
H29	0.641091	0.645487	0.563605	0.026
C30	0.94674(18)	0.47652(18)	0.60745(14)	0.0341(5)
F1C	0.9269(10)	0.4217(14)	0.6605(11)	0.027(3)
F2C	1.0356(10)	0.5400(10)	0.6391(12)	0.029(2)
F3C	0.9689(10)	0.4146(13)	0.5404(6)	0.023(2)
F4C	0.9315(19)	0.4395(18)	0.6707(12)	0.061(6)
F5C	1.0346(15)	0.5462(17)	0.6298(18)	0.064(6)
F6C	0.963(2)	0.4045(18)	0.5453(11)	0.059(6)
F7C	1.027(2)	0.543(3)	0.652(2)	0.052(8)
F8C	0.977(3)	0.432(3)	0.5373(14)	0.048(7)
F9C	0.919(3)	0.407(2)	0.647(2)	0.046(7)
C31	0.64731(18)	0.50421(16)	0.43342(14)	0.0318(5)
F1D	0.6936(8)	0.4588(10)	0.3698(6)	0.025(2)
F2D	0.6162(9)	0.5804(6)	0.4126(7)	0.033(2)
F3D	0.5621(8)	0.4387(9)	0.4349(7)	0.029(2)
F4D	0.692(3)	0.478(2)	0.3662(15)	0.042(6)
F5D	0.5920(18)	0.5732(16)	0.4259(17)	0.053(6)
F6D	0.5756(19)	0.4248(17)	0.436(2)	0.053(7)
F7D	0.634(3)	0.5787(19)	0.402(2)	0.052(7)
F8D	0.5539(18)	0.456(2)	0.441(3)	0.050(8)
F9D	0.690(3)	0.441(2)	0.3783(17)	0.040(7)
C32	0.62247(15)	0.75852(15)	0.71337(13)	0.0210(4)
C33	0.56238(16)	0.72715(15)	0.76944(13)	0.0233(5)
H33	0.594006	0.702680	0.808726	0.028
C34	0.45881(16)	0.73036(16)	0.76992(13)	0.0243(5)
C35	0.40948(16)	0.76485(16)	0.71357(14)	0.0253(5)
H35	0.338654	0.767097	0.713673	0.030
C36	0.46586(16)	0.79611(15)	0.65685(13)	0.0243(5)
C37	0.56993(16)	0.79336(15)	0.65722(13)	0.0229(5)
H37	0.606727	0.815895	0.618017	0.028
C38	0.40276(17)	0.70014(18)	0.83443(15)	0.0315(5)
C39	0.41511(17)	0.83134(18)	0.59377(15)	0.0326(5)
C40	0.81219(15)	0.85094(15)	0.69475(12)	0.0210(4)
C41	0.90454(16)	0.84692(16)	0.65961(13)	0.0245(5)

H41	0.926457	0.785358	0.644782	0.029
C42	0.96487(16)	0.92970(17)	0.64580(14)	0.0287(5)
C43	0.93457(17)	1.02055(17)	0.66516(15)	0.0311(5)
H43	0.975131	1.077102	0.655252	0.037
C44	0.84415(17)	1.02667(16)	0.69912(14)	0.0283(5)
C45	0.78449(16)	0.94320(16)	0.71423(13)	0.0244(5)
H45	0.723148	0.950007	0.738566	0.029
C46	1.06291(18)	0.92200(19)	0.60925(16)	0.0388(6)
F1A	1.0809(8)	0.8300(5)	0.5874(7)	0.0332(19)
F2A	1.1468(7)	0.9776(7)	0.6588(5)	0.0417(16)
F3A	1.0657(7)	0.9544(9)	0.5428(5)	0.046(2)
F4A	1.0966(18)	0.8389(10)	0.6073(13)	0.060(5)
F5A	1.1357(14)	0.9965(13)	0.6559(12)	0.089(7)
F6A	1.0611(17)	0.9334(17)	0.5343(9)	0.086(6)
F7A	1.148(2)	0.950(3)	0.662(2)	0.083(10)
F8A	1.071(4)	0.983(2)	0.5614(19)	0.071(9)
F9A	1.062(3)	0.8300(14)	0.5641(19)	0.063(9)
C47	0.80492(19)	1.12117(18)	0.71779(16)	0.0390(6)
F1B	0.8722(7)	1.1975(6)	0.7077(7)	0.044(2)
F2B	0.7809(10)	1.1490(10)	0.7941(5)	0.048(3)
F3B	0.7178(6)	1.1147(12)	0.6715(7)	0.037(3)
F4B	0.8815(16)	1.2005(16)	0.7333(15)	0.082(7)
F5B	0.754(2)	1.134(3)	0.7836(10)	0.063(6)
F6B	0.7396(14)	1.123(3)	0.6565(13)	0.049(5)
F7B	0.808(2)	1.161(3)	0.7979(8)	0.065(7)
F8B	0.7048(12)	1.106(3)	0.6895(17)	0.051(6)
F9B	0.853(2)	1.1936(19)	0.6881(18)	0.068(7)
C48	0.38736(17)	0.69485(18)	0.23443(16)	0.0329(5)
H48A	0.349368	0.687606	0.181784	0.040
H48B	0.408434	0.766271	0.262155	0.040
C49	0.3202(2)	0.64240(19)	0.28486(19)	0.0432(7)
H49A	0.297194	0.690704	0.328849	0.052
H49B	0.259302	0.597269	0.251502	0.052
C50	0.39009(18)	0.58499(18)	0.31776(15)	0.0348(6)
H50A	0.431284	0.625977	0.368261	0.042
H50B	0.350688	0.524151	0.327223	0.042
C51	0.45646(18)	0.56098(17)	0.25084(15)	0.0312(5)
H51A	0.521157	0.545496	0.270645	0.037
H51B	0.420282	0.503721	0.206940	0.037
C52	0.5968(2)	0.8516(2)	0.40722(18)	0.0486(7)
H52A	0.547771	0.808966	0.430586	0.058
H52B	0.558255	0.888847	0.379173	0.058
C53	0.6756(2)	0.9215(2)	0.47172(16)	0.0422(7)
H53A	0.645629	0.942978	0.522724	0.051
H53B	0.706499	0.980508	0.454995	0.051
C54	0.7529(2)	0.8575(2)	0.47919(15)	0.0433(7)
H54A	0.730937	0.813478	0.513440	0.052
H54B	0.821233	0.898343	0.501805	0.052
C55	0.75415(19)	0.7982(2)	0.39285(15)	0.0378(6)
H55A	0.808732	0.831797	0.367308	0.045
H55B	0.766463	0.731156	0.390837	0.045
C56	0.7554(2)	0.5886(2)	0.21442(17)	0.0431(6)
H56A	0.731747	0.528988	0.168799	0.052
H56B	0.727254	0.575896	0.263158	0.052
C57	0.8703(2)	0.6143(3)	0.22700(18)	0.0542(8)
H57A	0.900814	0.554210	0.216217	0.065
H57B	0.895344	0.655946	0.282119	0.065
C58	0.8934(2)	0.6715(2)	0.16498(17)	0.0502(8)
H58A	0.962127	0.714783	0.178343	0.060
H58B	0.888986	0.626264	0.110497	0.060
C59	0.80972(18)	0.7317(2)	0.17140(16)	0.0386(6)
H59A	0.832918	0.796988	0.210931	0.046
H59B	0.789809	0.742114	0.118783	0.046
C60	0.5486(2)	0.80730(19)	0.10665(15)	0.0387(6)
H60A	0.503771	0.740890	0.092027	0.046
H60B	0.598430	0.809343	0.066706	0.046
C61	0.4861(2)	0.88676(19)	0.11074(17)	0.0430(7)
H61A	0.417058	0.866181	0.126217	0.052
H61B	0.478749	0.902317	0.058483	0.052
C62	0.5479(2)	0.9756(2)	0.17519(18)	0.0497(7)
H62A	0.575792	1.029613	0.151539	0.060
H62B	0.504981	1.000975	0.217436	0.060

C63	0.6334(2)	0.9355(2)	0.20898(18)	0.0527(8)
H63A	0.698047	0.954477	0.186455	0.063
H63B	0.644821	0.961334	0.268152	0.063

$U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_j$  tensor.

**Table S10.** Bond lengths and angles for  $[\text{Li}(\text{THF})_4][1^{\text{F}}]$ .

Atom–Atom	Length [Å]
C1–N1	1.349(3)
C1–C2	1.395(3)
C1–C6	1.500(3)
O1–C56	1.438(3)
O1–C59	1.458(3)
O1–Li1	1.910(4)
Li1–O2	1.899(4)
Li1–O3	1.935(5)
Li1–O4	1.941(4)
B1–C24	1.642(3)
B1–C3	1.647(3)
B1–C32	1.648(3)
B1–C40	1.651(3)
N1–C5	1.352(3)
C2–C3	1.406(3)
O2–C60	1.431(3)
O2–C63	1.436(3)
C3–C4	1.401(3)
O3–C55	1.445(3)
O3–C52	1.449(3)
C4–C5	1.404(3)
O4–C51	1.442(3)
O4–C48	1.448(3)
C5–C15	1.499(3)
F7–C38	1.361(3)
C7–C6	1.393(3)
C7–C8	1.394(3)
C7–C12	1.515(3)
C6–C11	1.409(3)
C8–C9	1.394(3)
F8–C38	1.334(3)
C9–C10	1.382(3)
C9–C13	1.512(3)
F9–C38	1.337(3)
C11–C10	1.391(3)
C11–C14	1.501(3)
F11–C39	1.346(3)
F10–C39	1.346(3)
F12–C39	1.331(3)
C15–C16	1.398(3)
C15–C20	1.418(3)
C17–C18	1.385(3)
C17–C16	1.405(3)
C16–C21	1.513(3)
C19–C18	1.385(3)
C19–C20	1.396(3)
C18–C22	1.516(3)
C20–C23	1.504(3)
C25–C24	1.396(3)
C25–C26	1.400(3)
C24–C29	1.409(3)
C26–C27	1.390(3)
C26–C30	1.499(3)
C27–C28	1.381(3)
C28–C29	1.395(3)
C28–C31	1.499(3)
C30–F6C	1.341(11)
C30–F8C	1.342(13)
C30–F4C	1.345(11)
C30–F2C	1.349(10)
C30–F3C	1.350(9)
C30–F7C	1.351(13)
C30–F9C	1.351(13)
C30–F1C	1.362(9)

C30–F5C	1.362(11)
C31–F4D	1.338(13)
C31–F8D	1.345(13)
C31–F3D	1.346(7)
C31–F7D	1.347(13)
C31–F2D	1.350(7)
C31–F5D	1.354(12)
C31–F9D	1.360(13)
C31–F6D	1.363(12)
C31–F1D	1.367(8)
C32–C37	1.405(3)
C32–C33	1.406(3)
C33–C34	1.389(3)
C34–C35	1.383(3)
C34–C38	1.493(3)
C35–C36	1.388(3)
C36–C37	1.394(3)
C36–C39	1.490(3)
C40–C45	1.390(3)
C40–C41	1.408(3)
C41–C42	1.391(3)
C42–C43	1.388(3)
C42–C46	1.494(3)
C43–C44	1.378(3)
C44–C45	1.405(3)
C44–C47	1.494(4)
C46–F4A	1.330(12)
C46–F1A	1.336(7)
C46–F9A	1.340(14)
C46–F7A	1.343(14)
C46–F8A	1.345(14)
C46–F3A	1.347(7)
C46–F6A	1.349(11)
C46–F5A	1.354(11)
C46–F2A	1.360(7)
C47–F1B	1.340(7)
C47–F4B	1.343(12)
C47–F6B	1.344(12)
C47–F3B	1.347(8)
C47–F9B	1.350(13)
C47–F5B	1.352(13)
C47–F7B	1.354(13)
C47–F8B	1.354(13)
C47–F2B	1.355(8)
C48–C49	1.524(4)
C49–C50	1.518(4)
C50–C51	1.506(4)
C52–C53	1.508(4)
C53–C54	1.510(4)
C54–C55	1.521(4)
C56–C57	1.501(4)
C57–C58	1.523(4)
C58–C59	1.512(4)
C60–C61	1.507(4)
C61–C62	1.528(4)
C62–C63	1.512(4)
Atom–Atom–Atom	Angle [°]
N1–C1–C2	123.52(19)
N1–C1–C6	116.64(19)
C2–C1–C6	119.83(19)
C56–O1–C59	109.19(19)
C56–O1–Li1	125.72(19)
C59–O1–Li1	121.23(19)
O2–Li1–O1	105.5(2)
O2–Li1–O3	109.7(2)

O1–Li1–O3	106.08(19)
O2–Li1–O4	105.11(19)
O1–Li1–O4	119.5(2)
O3–Li1–O4	110.6(2)
C24–B1–C3	112.66(18)
C24–B1–C32	110.62(17)
C3–B1–C32	105.40(17)
C24–B1–C40	107.91(17)
C3–B1–C40	109.24(17)
C32–B1–C40	111.03(17)
C1–N1–C5	116.66(18)
C1–C2–C3	121.4(2)
C60–O2–C63	104.68(18)
C60–O2–Li1	122.57(19)
C63–O2–Li1	132.7(2)
C4–C3–C2	113.75(19)
C4–C3–B1	122.07(19)
C2–C3–B1	123.56(18)
C55–O3–C52	108.99(19)
C55–O3–Li1	125.07(19)
C52–O3–Li1	125.4(2)
C3–C4–C5	122.62(19)
C51–O4–C48	107.38(17)
C51–O4–Li1	121.66(18)
C48–O4–Li1	120.09(19)
N1–C5–C4	121.92(19)
N1–C5–C15	116.84(19)
C4–C5–C15	121.24(19)
C6–C7–C8	119.1(2)
C6–C7–C12	120.7(2)
C8–C7–C12	120.2(2)
C7–C6–C11	119.95(19)
C7–C6–C1	119.30(18)
C11–C6–C1	120.74(19)
C9–C8–C7	121.9(2)
C10–C9–C8	118.0(2)
C10–C9–C13	121.2(2)
C8–C9–C13	120.8(2)
C10–C11–C6	118.9(2)
C10–C11–C14	119.75(19)
C6–C11–C14	121.31(19)
C9–C10–C11	122.1(2)
C16–C15–C20	119.3(2)
C16–C15–C5	120.05(19)
C20–C15–C5	120.61(19)
C18–C17–C16	122.4(2)
C15–C16–C17	119.17(19)
C15–C16–C21	122.2(2)
C17–C16–C21	118.7(2)
C18–C19–C20	122.5(2)
C17–C18–C19	117.6(2)
C17–C18–C22	121.6(2)
C19–C18–C22	120.7(2)
C19–C20–C15	118.98(19)
C19–C20–C23	119.90(19)
C15–C20–C23	121.04(19)
C24–C25–C26	122.8(2)
C25–C24–C29	114.6(2)
C25–C24–B1	122.76(19)
C29–C24–B1	122.45(19)
C27–C26–C25	121.1(2)
C27–C26–C30	120.1(2)
C25–C26–C30	118.8(2)
C28–C27–C26	117.5(2)
C27–C28–C29	121.0(2)
C27–C28–C31	119.6(2)
C29–C28–C31	119.4(2)
C28–C29–C24	123.0(2)
F6C–C30–F4C	108.9(13)
F2C–C30–F3C	105.5(9)
F8C–C30–F7C	108.6(17)
F8C–C30–F9C	108.0(17)

F7C–C30–F9C	107.4(18)
F2C–C30–F1C	104.9(10)
F3C–C30–F1C	106.4(10)
F6C–C30–F5C	108.1(13)
F4C–C30–F5C	105.6(13)
F6C–C30–C26	115.6(13)
F8C–C30–C26	109.6(19)
F4C–C30–C26	109.6(11)
F2C–C30–C26	113.8(8)
F3C–C30–C26	113.1(5)
F7C–C30–C26	111(2)
F9C–C30–C26	112.2(18)
F1C–C30–C26	112.5(6)
F5C–C30–C26	108.6(13)
F8D–C31–F7D	107.7(18)
F3D–C31–F2D	106.8(7)
F4D–C31–F5D	108.3(14)
F8D–C31–F9D	107.7(17)
F7D–C31–F9D	106.5(16)
F4D–C31–F6D	107.7(16)
F5D–C31–F6D	104.2(14)
F3D–C31–F1D	105.3(7)
F2D–C31–F1D	105.4(7)
F4D–C31–C28	116.2(17)
F8D–C31–C28	113(2)
F3D–C31–C28	114.2(5)
F7D–C31–C28	112.8(16)
F2D–C31–C28	111.7(4)
F5D–C31–C28	111.0(13)
F9D–C31–C28	108.9(16)
F6D–C31–C28	108.8(16)
F1D–C31–C28	112.8(6)
C37–C32–C33	115.01(19)
C37–C32–B1	123.40(19)
C33–C32–B1	121.58(19)
C34–C33–C32	122.9(2)
C35–C34–C33	120.5(2)
C35–C34–C38	120.5(2)
C33–C34–C38	118.9(2)
C34–C35–C36	118.4(2)
C35–C36–C37	120.6(2)
C35–C36–C39	120.2(2)
C37–C36–C39	119.2(2)
C36–C37–C32	122.5(2)
F8–C38–F9	106.28(18)
F8–C38–F7	105.6(2)
F9–C38–F7	105.56(18)
F8–C38–C34	113.24(19)
F9–C38–C34	113.5(2)
F7–C38–C34	112.06(19)
F12–C39–F10	105.7(2)
F12–C39–F11	106.86(19)
F10–C39–F11	105.2(2)
F12–C39–C36	112.9(2)
F10–C39–C36	112.60(19)
F11–C39–C36	113.0(2)
C45–C40–C41	115.59(19)
C45–C40–B1	123.10(19)
C41–C40–B1	121.27(19)
C42–C41–C40	122.5(2)
C43–C42–C41	120.6(2)
C43–C42–C46	118.9(2)
C41–C42–C46	120.5(2)
C44–C43–C42	118.3(2)
C43–C44–C45	120.9(2)
C43–C44–C47	120.9(2)
C45–C44–C47	118.2(2)
C40–C45–C44	122.2(2)
F9A–C46–F7A	108.0(17)
F9A–C46–F8A	108.4(17)
F7A–C46–F8A	107.4(19)
F1A–C46–F3A	106.0(7)

F4A–C46–F6A	107.4(12)	F3B–C47–C44	112.4(7)
F4A–C46–F5A	106.1(11)	F9B–C47–C44	116.4(15)
F6A–C46–F5A	106.8(12)	F5B–C47–C44	113.0(16)
F1A–C46–F2A	105.9(6)	F7B–C47–C44	111.7(18)
F3A–C46–F2A	104.9(5)	F8B–C47–C44	111.0(17)
F4A–C46–C42	115.0(11)	F2B–C47–C44	113.2(6)
F1A–C46–C42	114.0(5)	O4–C48–C49	107.11(19)
F9A–C46–C42	111.5(18)	C50–C49–C48	103.6(2)
F7A–C46–C42	115(2)	C51–C50–C49	101.7(2)
F8A–C46–C42	106(2)	O4–C51–C50	104.74(19)
F3A–C46–C42	112.1(5)	O3–C52–C53	105.4(2)
F6A–C46–C42	114.2(10)	C52–C53–C54	101.6(2)
F5A–C46–C42	106.8(10)	C53–C54–C55	102.9(2)
F2A–C46–C42	113.2(5)	O3–C55–C54	105.9(2)
F4B–C47–F6B	109.2(14)	O1–C56–C57	105.2(2)
F1B–C47–F3B	106.6(7)	C56–C57–C58	101.3(2)
F4B–C47–F5B	105.3(14)	C59–C58–C57	102.3(2)
F6B–C47–F5B	106.8(14)	O1–C59–C58	105.4(2)
F9B–C47–F7B	106.2(16)	O2–C60–C61	104.5(2)
F9B–C47–F8B	105.6(14)	C60–C61–C62	103.8(2)
F7B–C47–F8B	105.0(15)	C63–C62–C61	104.4(2)
F1B–C47–F2B	106.4(7)	O2–C63–C62	105.5(2)
F3B–C47–F2B	104.7(7)		
F1B–C47–C44	112.8(5)		
F4B–C47–C44	111.7(13)		
F6B–C47–C44	110.6(16)		

Bonds to hydrogen atoms were omitted.

**Table S11.** Atomic coordinates and  $U_{eq}$  [ $\text{\AA}^2$ ] for  $[\text{NEt}_4][1^{\text{F}}]$ .

Atom	x	y	z	$U_{eq}$
C1	0.25169(18)	0.39471(19)	0.38560(10)	0.0200(4)
N1	0.31641(15)	0.44593(17)	0.35689(9)	0.0207(4)
C2	0.21067(18)	0.34834(19)	0.34933(10)	0.0199(4)
H2	0.164259	0.314201	0.372081	0.024
B2	0.19681(19)	0.2977(2)	0.23210(12)	0.0178(4)
C3	0.23707(17)	0.35151(18)	0.27976(10)	0.0181(4)
F4	-0.13554(15)	0.25544(18)	0.44811(8)	0.0557(5)
C4	0.30529(18)	0.40452(19)	0.25151(10)	0.0206(4)
H4	0.326567	0.409449	0.204623	0.025
C5	0.34259(17)	0.44986(19)	0.28975(10)	0.0200(4)
F5	-0.18960(16)	0.2033(2)	0.37654(14)	0.0723(7)
C6	0.22604(18)	0.3887(2)	0.46047(11)	0.0214(4)
F6	-0.19185(13)	0.36568(16)	0.35329(9)	0.0527(5)
F7	-0.03658(13)	0.32095(13)	0.04382(8)	0.0349(3)
C7	0.2796(2)	0.2838(2)	0.50571(12)	0.0269(5)
C8	0.2565(2)	0.2818(2)	0.57516(12)	0.0325(6)
H8	0.294673	0.211243	0.606077	0.039
F8	-0.18926(13)	0.40412(16)	0.10402(8)	0.0411(4)
C9	0.1791(2)	0.3803(2)	0.60017(12)	0.0319(5)
F9	-0.15656(13)	0.49892(14)	0.00953(7)	0.0343(3)
C11	0.14893(19)	0.4897(2)	0.48453(11)	0.0232(5)
F11	0.03620(15)	0.74763(14)	0.08715(9)	0.0445(4)
C10	0.1257(2)	0.4829(2)	0.55441(12)	0.0287(5)
H10	0.071904	0.550606	0.570856	0.034
F10	-0.14210(15)	0.80064(13)	0.08821(9)	0.0460(4)
C12	0.3625(3)	0.1734(2)	0.48149(13)	0.0373(6)
H12A	0.320113	0.141939	0.466527	0.056
H12B	0.410364	0.117107	0.518568	0.056
H12C	0.410918	0.189399	0.443676	0.056
F12	-0.06160(15)	0.75819(13)	0.18068(7)	0.0387(4)
C13	0.1514(3)	0.3761(3)	0.67518(13)	0.0476(8)
H13A	0.177560	0.422115	0.690608	0.071
H13B	0.189905	0.295949	0.699538	0.071
H13C	0.068767	0.407555	0.684044	0.071
C14	0.0907(2)	0.6045(2)	0.43726(12)	0.0313(5)
H14A	0.144070	0.636172	0.421944	0.047
H14B	0.024159	0.657989	0.460996	0.047
H14C	0.065977	0.594021	0.398098	0.047
C16	0.3654(2)	0.6260(2)	0.23706(12)	0.0292(5)
C15	0.41589(19)	0.5055(2)	0.25887(11)	0.0240(5)
C17	0.4356(3)	0.6767(3)	0.21069(13)	0.0362(6)
H17	0.402001	0.757941	0.195212	0.043

C18	0.5537(3)	0.6112(3)	0.20650(12)	0.0395(7)
C19	0.6012(2)	0.4923(3)	0.22629(12)	0.0387(7)
H19	0.681610	0.446786	0.222056	0.046
C20	0.5343(2)	0.4370(2)	0.25230(11)	0.0291(5)
C21	0.2376(2)	0.6990(2)	0.24308(15)	0.0377(6)
H21A	0.217318	0.780249	0.224763	0.057
H21B	0.211434	0.690089	0.290786	0.057
H21C	0.200926	0.674197	0.217608	0.057
C23	0.5884(2)	0.3077(3)	0.27400(14)	0.0401(7)
H23A	0.556219	0.277282	0.249384	0.060
H23B	0.573316	0.287420	0.322692	0.060
H23C	0.670963	0.274356	0.264052	0.060
C22	0.6284(3)	0.6694(4)	0.18440(15)	0.0595(11)
H22A	0.697240	0.620553	0.159906	0.089
H22B	0.650051	0.681102	0.224268	0.089
H22C	0.586314	0.744188	0.154717	0.089
C24	0.14567(17)	0.21477(19)	0.28042(10)	0.0185(4)
C26	0.1648(2)	0.0300(2)	0.34655(12)	0.0261(5)
C25	0.20896(18)	0.0955(2)	0.30049(11)	0.0221(4)
H25	0.284717	0.057460	0.282187	0.026
C27	0.0544(2)	0.0809(2)	0.37382(12)	0.0257(5)
H27	0.024413	0.036324	0.405256	0.031
C28	-0.01131(18)	0.1996(2)	0.35365(11)	0.0234(5)
C29	0.03336(18)	0.26477(19)	0.30836(11)	0.0206(4)
H29	-0.013497	0.345739	0.295853	0.025
C30	0.2408(2)	-0.0966(2)	0.36764(14)	0.0380(6)
F1C	0.3017(10)	-0.1451(10)	0.3153(5)	0.0500(18)
F2C	0.1846(9)	-0.1571(9)	0.3931(9)	0.071(3)
F3C	0.3158(12)	-0.1223(12)	0.4108(7)	0.078(3)
F4C	0.1963(13)	-0.1454(15)	0.4192(11)	0.082(5)
F5C	0.3354(11)	-0.1150(14)	0.3940(10)	0.065(3)
F6C	0.277(2)	-0.1533(17)	0.3191(8)	0.079(5)
C31	-0.1311(2)	0.2556(2)	0.38269(13)	0.0308(5)
C32	0.09746(17)	0.40119(19)	0.18231(10)	0.0182(4)
C33	0.03834(17)	0.37325(19)	0.14519(10)	0.0196(4)
H33	0.056333	0.294734	0.150298	0.024
C34	-0.04560(17)	0.4570(2)	0.10128(10)	0.0204(4)
C35	-0.07603(18)	0.5732(2)	0.09302(11)	0.0219(4)
H35	-0.133501	0.630403	0.063174	0.026
C36	-0.02021(17)	0.60301(19)	0.12949(10)	0.0198(4)
C37	0.06483(17)	0.51838(19)	0.17322(10)	0.0186(4)
H37	0.101624	0.541612	0.197580	0.022
C38	-0.10621(19)	0.4206(2)	0.06477(11)	0.0249(5)
C39	-0.04769(19)	0.7264(2)	0.12142(11)	0.0243(5)
C40	0.31120(18)	0.22244(19)	0.18748(11)	0.0196(4)
C41	0.31674(18)	0.23023(19)	0.11758(11)	0.0210(4)
H41	0.250447	0.283207	0.093015	0.025
C42	0.41605(19)	0.1630(2)	0.08251(11)	0.0235(4)
C43	0.5147(2)	0.0831(2)	0.11637(12)	0.0282(5)
H43	0.581748	0.035647	0.092903	0.034
C44	0.51187(19)	0.0750(2)	0.18576(12)	0.0268(5)
C45	0.41352(18)	0.1436(2)	0.22007(11)	0.0225(4)
H45	0.415247	0.137162	0.267286	0.027
C46	0.4145(2)	0.1784(2)	0.00749(12)	0.0290(5)
F1B	0.3589(12)	0.2905(7)	-0.0201(6)	0.048(2)
F2B	0.3582(18)	0.131(2)	-0.0077(7)	0.068(3)
F3B	0.5158(8)	0.1383(18)	-0.0228(7)	0.059(3)
F4B	0.5121(7)	0.1032(9)	-0.0199(6)	0.0406(18)
F5B	0.3979(16)	0.2829(9)	-0.0261(5)	0.052(2)
F6B	0.3334(6)	0.1640(8)	-0.0128(5)	0.0328(16)
C47	0.6177(2)	-0.0073(2)	0.22369(14)	0.0403(6)
F1A	0.6676(16)	0.0451(10)	0.2398(14)	0.088(7)
F2A	0.6925(10)	-0.0884(14)	0.1910(6)	0.072(4)
F3A	0.5929(7)	-0.0686(17)	0.2809(6)	0.097(6)
F4A	0.6963(12)	0.0297(16)	0.2063(13)	0.075(6)
F5A	0.6683(18)	-0.1128(9)	0.2108(13)	0.058(5)
F6A	0.6047(13)	-0.017(3)	0.2901(5)	0.060(7)
F7A	0.7129(13)	-0.021(4)	0.1870(11)	0.074(11)
F8A	0.627(3)	-0.1115(15)	0.246(2)	0.065(9)
F9A	0.624(2)	0.024(2)	0.2785(13)	0.064(8)
N1_1	0.4942(10)	0.4923(9)	0.5002(5)	0.0200(13)
C1_1	0.5461(4)	0.5474(4)	0.5312(2)	0.0251(9)

H1A_1	0.576311	0.498076	0.575335	0.030
H1AB_1	0.611357	0.548846	0.501365	0.030
C2_1	0.4647(10)	0.6686(7)	0.5419(7)	0.034(2)
H2A_1	0.433657	0.718466	0.498558	0.051
H2B_1	0.505458	0.698285	0.560207	0.051
H2C_1	0.402182	0.667777	0.573731	0.051
C3_1	0.3987(4)	0.4799(4)	0.5462(2)	0.0248(9)
H3A_1	0.337570	0.557764	0.551447	0.030
H3AB_1	0.366203	0.445822	0.523831	0.030
C4_1	0.4336(6)	0.4065(8)	0.6158(4)	0.0342(17)
H4A_1	0.495701	0.329661	0.611389	0.051
H4B_1	0.368191	0.399340	0.640917	0.051
H4C_1	0.459548	0.442913	0.640137	0.051
C5_1	0.5915(4)	0.3751(4)	0.4907(2)	0.0250(9)
H5A_1	0.647538	0.387027	0.456383	0.030
H5AB_1	0.630317	0.334351	0.533863	0.030
C6_1	0.5556(10)	0.2987(8)	0.4691(6)	0.031(2)
H6A_1	0.508192	0.341846	0.429820	0.047
H6B_1	0.511867	0.274018	0.506370	0.047
H6C_1	0.623562	0.230761	0.456973	0.047
C7_1	0.4425(4)	0.5666(4)	0.4335(2)	0.0255(9)
H7A_1	0.375666	0.639188	0.442467	0.031
H7AB_1	0.414683	0.525728	0.413488	0.031
C8_1	0.5234(6)	0.5969(7)	0.3818(3)	0.0304(15)
H8A_1	0.484851	0.640815	0.339469	0.046
H8B_1	0.591215	0.525798	0.373444	0.046
H8C_1	0.546293	0.643534	0.399310	0.046
N1_2	0.5016(10)	0.4990(10)	-0.0007(6)	0.0217(6)
C1_2	0.4346(4)	0.5724(5)	0.0522(2)	0.0288(10)
H1A_2	0.478150	0.537804	0.093841	0.035
H1AB_2	0.428367	0.650232	0.035431	0.035
C2_2	0.3156(11)	0.585(2)	0.0704(11)	0.037(3)
H2A_2	0.267209	0.632088	0.031864	0.055
H2B_2	0.283006	0.622588	0.109516	0.055
H2C_2	0.319586	0.508565	0.081490	0.055
C3_2	0.5275(4)	0.3743(4)	0.0262(3)	0.0314(10)
H3A_2	0.572293	0.328878	-0.009146	0.038
H3AB_2	0.454685	0.370782	0.034994	0.038
C4_2	0.5936(15)	0.3176(12)	0.0911(8)	0.045(3)
H4A_2	0.611989	0.236073	0.103222	0.067
H4B_2	0.546700	0.356821	0.127870	0.067
H4C_2	0.664272	0.323812	0.083757	0.067
C5_2	0.6109(4)	0.5086(4)	-0.0187(2)	0.0238(9)
H5A_2	0.647809	0.491865	0.023665	0.029
H5AB_2	0.590915	0.589261	-0.041045	0.029
C6_2	0.6972(12)	0.4289(19)	-0.0648(11)	0.034(3)
H6A_2	0.760632	0.447161	-0.077834	0.051
H6B_2	0.660187	0.439881	-0.105425	0.051
H6C_2	0.726344	0.348536	-0.040772	0.051
C7_2	0.4335(4)	0.5415(5)	-0.0634(2)	0.0278(10)
H7A_2	0.481803	0.495172	-0.097713	0.033
H7AB_2	0.367018	0.526805	-0.051315	0.033
C8_2	0.3909(14)	0.6672(10)	-0.0951(7)	0.038(3)
H8A_2	0.455928	0.682430	-0.109656	0.058
H8B_2	0.342148	0.714461	-0.061884	0.058
H8C_2	0.346804	0.686432	-0.134257	0.058
CI1_3	-0.13300(11)	-0.06960(11)	0.46560(6)	0.0633(4)
CI2_3	-0.07249(16)	-0.13813(14)	0.33333(7)	0.0888(6)
C1_3	-0.1770(5)	-0.0425(5)	0.3830(2)	0.0692(15)
H1A_3	-0.247638	-0.049415	0.386172	0.083
H1AB_3	-0.194972	0.037633	0.360445	0.083
CI1_4	-0.0672(11)	-0.0793(10)	0.3141(7)	0.141(4)
CI2_4	-0.2997(11)	0.0312(9)	0.3861(6)	0.156(4)
C1_4	-0.1570(17)	-0.080(3)	0.3872(12)	0.091(7)
H1A_4	-0.120997	-0.078193	0.425195	0.109
H1AB_4	-0.158663	-0.154475	0.397685	0.109
CI1_5	0.21517(13)	0.03005(14)	0.13630(8)	0.0541(4)
CI2_5	0.22308(9)	-0.13092(10)	0.06311(6)	0.0490(4)
C1_5	0.1972(4)	0.0106(3)	0.05785(18)	0.0462(8)
H1A_5	0.118405	0.065345	0.043798	0.055
H1AB_5	0.250418	0.027291	0.023196	0.055
CI1_6	0.1880(16)	0.0268(15)	0.1518(7)	0.106(4)

Cl2_6	0.2394(11)	-0.0842(11)	0.0350(6)	0.104(3)
C1_6	0.227(4)	0.033(2)	0.0649(9)	0.086(4)
H1A_6	0.300599	0.034440	0.056264	0.103
H1AB_6	0.168841	0.105597	0.039100	0.103
Cl1_7	0.9123(2)	0.1284(3)	0.21059(11)	0.0414(9)
Cl2_7	0.90460(19)	0.06347(19)	0.08618(7)	0.0382(10)
C1_7	0.9473(15)	0.0131(7)	0.1715(4)	0.046(2)
H1A_7	0.909136	-0.032269	0.197223	0.055
H1AB_7	1.030717	-0.038229	0.172150	0.055
Cl1_8	0.9178(7)	0.1138(8)	0.2128(4)	0.126(3)
Cl2_8	0.8886(9)	0.0708(7)	0.0844(4)	0.171(5)
C1_8	0.930(2)	0.0112(10)	0.1695(6)	0.067(5)
H1A_8	0.882136	-0.024417	0.193878	0.081
H1AB_8	1.010301	-0.050521	0.169659	0.081

$U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table S12.** Bond lengths and angles for [NEt<sub>4</sub>][1<sup>F</sup>].

Atom–Atom	Length [Å]
C1–N1	1.345(3)
C1–C2	1.397(3)
C1–C6	1.504(3)
N1–C5	1.355(3)
C2–C3	1.403(3)
B2–C3	1.639(3)
B2–C32	1.639(3)
B2–C24	1.642(3)
B2–C40	1.646(3)
C3–C4	1.400(3)
F4–C31	1.328(3)
C4–C5	1.381(3)
C5–C15	1.494(3)
F5–C31	1.326(3)
C6–C7	1.399(3)
C6–C11	1.403(3)
F6–C31	1.333(3)
F7–C38	1.343(3)
C7–C8	1.399(3)
C7–C12	1.511(4)
C8–C9	1.390(4)
F8–C38	1.345(3)
C9–C10	1.385(4)
C9–C13	1.511(3)
F9–C38	1.345(3)
C11–C10	1.401(3)
C11–C14	1.508(3)
F11–C39	1.345(3)
F10–C39	1.333(3)
F12–C39	1.339(3)
C16–C17	1.393(4)
C16–C15	1.406(4)
C16–C21	1.510(4)
C15–C20	1.402(3)
C17–C18	1.391(4)
C18–C19	1.386(5)
C18–C22	1.513(4)
C19–C20	1.400(4)
C20–C23	1.505(4)
C24–C25	1.394(3)
C24–C29	1.407(3)
C26–C27	1.383(3)
C26–C25	1.395(3)
C26–C30	1.495(4)
C27–C28	1.391(3)
C28–C29	1.390(3)
C28–C31	1.498(3)
C30–F6C	1.291(10)
C30–F3C	1.309(8)
C30–F4C	1.320(8)
C30–F2C	1.334(7)
C30–F1C	1.336(7)
C30–F5C	1.350(9)

C32–C37	1.395(3)
C32–C33	1.409(3)
C33–C34	1.392(3)
C34–C35	1.390(3)
C34–C38	1.497(3)
C35–C36	1.383(3)
C36–C37	1.401(3)
C36–C39	1.496(3)
C40–C41	1.399(3)
C40–C45	1.409(3)
C41–C42	1.397(3)
C42–C43	1.390(3)
C42–C46	1.497(3)
C43–C44	1.390(3)
C44–C45	1.388(3)
C44–C47	1.499(3)
C46–F3B	1.305(8)
C46–F2B	1.320(9)
C46–F5B	1.336(7)
C46–F1B	1.336(8)
C46–F6B	1.342(7)
C46–F4B	1.345(7)
C47–F1A	1.310(10)
C47–F2A	1.316(7)
C47–F6A	1.321(10)
C47–F8A	1.321(11)
C47–F9A	1.323(11)
C47–F5A	1.324(9)
C47–F7A	1.327(12)
C47–F4A	1.344(8)
C47–F3A	1.354(8)
N1_1–C7_1	1.516(11)
N1_1–C3_1	1.518(10)
N1_1–C5_1	1.519(11)
N1_1–C1_1	1.528(10)
C1_1–C2_1	1.511(9)
C3_1–C4_1	1.513(8)
C5_1–C6_1	1.512(11)
C7_1–C8_1	1.522(8)
N1_2–C5_2	1.518(12)
N1_2–C3_2	1.519(12)
N1_2–C7_2	1.520(12)
N1_2–C1_2	1.521(12)
C1_2–C2_2	1.519(11)
C3_2–C4_2	1.532(11)
C5_2–C6_2	1.524(11)
C7_2–C8_2	1.504(11)
Cl1_3–C1_3	1.772(5)
Cl2_3–C1_3	1.759(5)
Cl1_4–C1_4	1.764(7)
Cl2_4–C1_4	1.767(7)
Cl1_5–C1_5	1.760(4)
Cl2_5–C1_5	1.751(4)
Cl1_6–C1_6	1.761(7)
Cl2_6–C1_6	1.761(7)

Cl1_7–C1_7	1.754(6)
Cl2_7–C1_7	1.786(5)
Cl1_8–C1_8	1.755(6)
Cl2_8–C1_8	1.779(6)
<b>Atom–Atom–Atom</b>	<b>Angle [°]</b>
N1–C1–C2	123.11(19)
N1–C1–C6	115.84(19)
C2–C1–C6	121.1(2)
C1–N1–C5	116.74(18)
C1–C2–C3	120.9(2)
C3–B2–C32	110.56(18)
C3–B2–C24	109.30(17)
C32–B2–C24	108.87(17)
C3–B2–C40	106.51(17)
C32–B2–C40	110.67(17)
C24–B2–C40	110.92(18)
C4–C3–C2	114.58(19)
C4–C3–B2	119.83(18)
C2–C3–B2	125.58(19)
C5–C4–C3	122.00(19)
N1–C5–C4	122.6(2)
N1–C5–C15	116.05(19)
C4–C5–C15	121.30(19)
C7–C6–C11	120.3(2)
C7–C6–C1	120.3(2)
C11–C6–C1	119.4(2)
C6–C7–C8	118.9(2)
C6–C7–C12	121.7(2)
C8–C7–C12	119.4(2)
C9–C8–C7	121.8(2)
C10–C9–C8	118.3(2)
C10–C9–C13	120.4(3)
C8–C9–C13	121.3(2)
C10–C11–C6	118.8(2)
C10–C11–C14	119.5(2)
C6–C11–C14	121.8(2)
C9–C10–C11	121.8(2)
C17–C16–C15	118.8(2)
C17–C16–C21	120.7(3)
C15–C16–C21	120.5(2)
C20–C15–C16	120.8(2)
C20–C15–C5	119.6(2)
C16–C15–C5	119.7(2)
C18–C17–C16	121.5(3)
C19–C18–C17	118.5(2)
C19–C18–C22	121.0(3)
C17–C18–C22	120.4(3)
C18–C19–C20	122.1(3)
C19–C20–C15	118.2(3)
C19–C20–C23	120.9(2)
C15–C20–C23	120.9(2)
C25–C24–C29	115.7(2)
C25–C24–B2	124.33(19)
C29–C24–B2	119.78(19)
C27–C26–C25	121.1(2)
C27–C26–C30	120.3(2)
C25–C26–C30	118.5(2)
C24–C25–C26	122.2(2)
C26–C27–C28	117.8(2)
C29–C28–C27	120.9(2)
C29–C28–C31	120.8(2)
C27–C28–C31	118.2(2)
C28–C29–C24	122.2(2)
F6C–C30–F4C	111.3(9)
F3C–C30–F2C	108.1(7)
F3C–C30–F1C	105.2(8)
F2C–C30–F1C	102.7(7)
F6C–C30–F5C	105.6(11)
F4C–C30–F5C	101.5(9)
F6C–C30–C26	114.6(9)
F3C–C30–C26	113.9(6)

F4C–C30–C26	112.7(7)
F2C–C30–C26	113.9(5)
F1C–C30–C26	112.1(6)
F5C–C30–C26	109.9(7)
F5–C31–F4	106.6(2)
F5–C31–F6	105.7(2)
F4–C31–F6	105.6(2)
F5–C31–C28	112.3(2)
F4–C31–C28	112.6(2)
F6–C31–C28	113.5(2)
C37–C32–C33	115.68(19)
C37–C32–B2	124.93(18)
C33–C32–B2	119.39(19)
C34–C33–C32	122.1(2)
C35–C34–C33	120.9(2)
C35–C34–C38	120.15(19)
C33–C34–C38	118.9(2)
C36–C35–C34	118.1(2)
C35–C36–C37	120.8(2)
C35–C36–C39	120.35(19)
C37–C36–C39	118.8(2)
C32–C37–C36	122.4(2)
F7–C38–F9	106.36(19)
F7–C38–F8	106.0(2)
F9–C38–F8	106.10(18)
F7–C38–C34	112.84(18)
F9–C38–C34	113.0(2)
F8–C38–C34	112.05(19)
F10–C39–F12	106.60(19)
F10–C39–F11	106.1(2)
F12–C39–F11	105.1(2)
F10–C39–C36	113.5(2)
F12–C39–C36	112.79(18)
F11–C39–C36	112.22(18)
C41–C40–C45	115.36(19)
C41–C40–B2	125.04(18)
C45–C40–B2	119.59(19)
C42–C41–C40	122.5(2)
C43–C42–C41	120.9(2)
C43–C42–C46	120.3(2)
C41–C42–C46	118.8(2)
C42–C43–C44	117.7(2)
C45–C44–C43	121.1(2)
C45–C44–C47	119.6(2)
C43–C44–C47	119.3(2)
C44–C45–C40	122.4(2)
F3B–C46–F2B	109.4(8)
F3B–C46–F1B	106.4(6)
F2B–C46–F1B	105.9(8)
F5B–C46–F6B	104.9(6)
F5B–C46–F4B	105.5(6)
F6B–C46–F4B	104.1(6)
F3B–C46–C42	113.9(7)
F2B–C46–C42	110.9(6)
F5B–C46–C42	113.5(5)
F1B–C46–C42	110.0(5)
F6B–C46–C42	114.6(5)
F4B–C46–C42	113.3(6)
F1A–C47–F2A	109.0(12)
F8A–C47–F9A	104.6(16)
F6A–C47–F5A	107.4(13)
F8A–C47–F7A	106.1(17)
F9A–C47–F7A	105.4(16)
F6A–C47–F4A	103.7(13)
F5A–C47–F4A	105.2(13)
F1A–C47–F3A	108.8(13)
F2A–C47–F3A	102.5(10)
F1A–C47–C44	112.6(6)
F2A–C47–C44	113.1(5)
F6A–C47–C44	115.2(6)
F8A–C47–C44	112.8(8)
F9A–C47–C44	114.0(8)

F5A–C47–C44	114.2(6)
F7A–C47–C44	113.2(10)
F4A–C47–C44	110.1(5)
F3A–C47–C44	110.3(5)
C7_1–N1_1–C3_1	106.7(7)
C7_1–N1_1–C5_1	111.3(7)
C3_1–N1_1–C5_1	111.0(7)
C7_1–N1_1–C1_1	110.9(7)
C3_1–N1_1–C1_1	111.1(7)
C5_1–N1_1–C1_1	105.8(7)
C2_1–C1_1–N1_1	114.9(6)
C4_1–C3_1–N1_1	115.0(6)
C6_1–C5_1–N1_1	114.6(6)
N1_1–C7_1–C8_1	114.8(5)
C5_2–N1_2–C3_2	110.9(8)
C5_2–N1_2–C7_2	110.0(8)
C3_2–N1_2–C7_2	107.1(8)

C5_2–N1_2–C1_2	107.2(8)
C3_2–N1_2–C1_2	110.8(8)
C7_2–N1_2–C1_2	110.9(8)
C2_2–C1_2–N1_2	114.6(8)
N1_2–C3_2–C4_2	114.5(7)
N1_2–C5_2–C6_2	115.2(7)
C8_2–C7_2–N1_2	115.7(7)
Cl2_3–C1_3–Cl1_3	112.5(3)
Cl1_4–C1_4–Cl2_4	118.5(10)
Cl2_5–C1_5–Cl1_5	110.8(2)
Cl1_6–C1_6–Cl2_6	113.4(10)
Cl1_7–C1_7–Cl2_7	111.3(4)
Cl1_8–C1_8–Cl2_8	113.1(7)

Bonds to hydrogen atoms were omitted.

**Table S13.** Atomic coordinates and  $U_{\text{eq}}$  [ $\text{\AA}^2$ ] for  $[\text{Li}(\text{THF})_4][1^{\text{F}}\text{-BH}_3]$ .

Atom	x	y	z	$U_{\text{eq}}$
Li1	0.2541(3)	0.5301(4)	0.7217(3)	0.0479(17)
B1	0.68065(16)	0.6452(3)	0.57397(17)	0.0230(8)
N1	0.87480(12)	0.5198(2)	0.63117(12)	0.0281(6)
C1	0.84858(15)	0.5855(2)	0.66725(15)	0.0251(7)
B2	0.9455(2)	0.4766(4)	0.6524(2)	0.0457(12)
H2A	0.974(3)	0.550(4)	0.659(3)	0.069
H2B	0.961(3)	0.430(4)	0.614(3)	0.069
H2C	0.949(3)	0.433(4)	0.697(3)	0.069
H2D	0.932(6)	0.398(6)	0.652(5)	0.069
H2E	0.966(5)	0.500(9)	0.698(4)	0.069
H2F	0.979(5)	0.490(9)	0.620(5)	0.069
C2	0.78933(15)	0.6244(2)	0.64893(15)	0.0257(7)
H2	0.773236	0.671323	0.674751	0.031
C3	0.75147(14)	0.5983(2)	0.59410(14)	0.0228(7)
C4	0.78007(15)	0.5312(2)	0.55909(14)	0.0243(7)
H4	0.757337	0.510374	0.521046	0.029
C5	0.84003(15)	0.4936(3)	0.57709(15)	0.0264(7)
C6	0.88312(15)	0.6135(3)	0.72857(15)	0.0277(7)
C7	0.87732(16)	0.5537(3)	0.77909(16)	0.0313(8)
C8	0.90679(16)	0.5845(3)	0.83636(16)	0.0365(9)
H8	0.903151	0.544309	0.870954	0.044
C9	0.94122(17)	0.6717(3)	0.84444(17)	0.0389(9)
C11	0.91700(16)	0.7026(3)	0.73548(17)	0.0337(8)
C10	0.94547(16)	0.7303(3)	0.79397(18)	0.0383(9)
H10	0.968357	0.790897	0.799168	0.046
C12	0.84086(19)	0.4578(3)	0.77216(18)	0.0436(10)
H12A	0.798866	0.469617	0.748726	0.065
H12B	0.836227	0.431880	0.812630	0.065
H12C	0.863749	0.409389	0.750595	0.065
C013	0.74667(16)	0.8015(3)	0.54381(15)	0.0283(7)
H013	0.783814	0.770472	0.564303	0.034
C13	0.9734(2)	0.7020(4)	0.90743(19)	0.0556(12)
H13A	0.994450	0.766232	0.904863	0.083
H13B	1.004839	0.651804	0.923123	0.083
H13C	0.941642	0.707687	0.935027	0.083
C14	0.92352(19)	0.7666(3)	0.68116(19)	0.0485(11)
H14A	0.936855	0.725599	0.648774	0.073
H14B	0.955279	0.818260	0.693115	0.073
H14C	0.882673	0.797727	0.666152	0.073
C15	0.86604(14)	0.4208(3)	0.53652(15)	0.0293(8)
C16	0.85194(17)	0.3204(3)	0.54108(17)	0.0356(9)
C18	0.91024(18)	0.2838(4)	0.45822(19)	0.0487(11)
C17	0.87477(18)	0.2531(3)	0.50193(18)	0.0431(10)
H17	0.865699	0.184488	0.505425	0.052
C19	0.92224(17)	0.3838(4)	0.45295(17)	0.0476(11)
H19	0.945628	0.405515	0.422082	0.057
C21	0.8132(2)	0.2848(3)	0.5883(2)	0.0549(12)
H21A	0.772061	0.318593	0.582424	0.082
H21B	0.835581	0.299555	0.629211	0.082
H21C	0.806583	0.212948	0.584017	0.082
C20	0.90090(15)	0.4546(3)	0.49189(16)	0.0360(9)

C23	0.91623(19)	0.5625(3)	0.48700(19)	0.0505(11)
H23A	0.940158	0.572499	0.452966	0.076
H23B	0.941717	0.584694	0.525094	0.076
H23C	0.876857	0.600938	0.479744	0.076
C22	0.9365(2)	0.2086(4)	0.4174(2)	0.0762(17)
H22A	0.907498	0.152050	0.410224	0.114
H22B	0.978030	0.185447	0.437284	0.114
H22C	0.941057	0.239803	0.378247	0.114
C24	0.64389(14)	0.6471(2)	0.63419(14)	0.0222(7)
C27	0.57456(15)	0.6324(3)	0.73469(15)	0.0282(7)
H27	0.551476	0.627745	0.768129	0.034
C26	0.62160(15)	0.5648(3)	0.72755(15)	0.0271(7)
C25	0.65551(14)	0.5729(2)	0.67882(14)	0.0239(7)
H25	0.688076	0.525988	0.675611	0.029
C28	0.56212(14)	0.7068(2)	0.69170(15)	0.0249(7)
C29	0.59607(14)	0.7141(2)	0.64284(14)	0.0225(7)
H29	0.586368	0.766632	0.614323	0.027
C30	0.63764(16)	0.4824(3)	0.77214(16)	0.0349(7)
F1F	0.6619(5)	0.4017(9)	0.7488(7)	0.041(2)
F2F	0.5865(5)	0.4532(13)	0.7964(6)	0.033(2)
F3F	0.6810(4)	0.5118(10)	0.8207(5)	0.042(2)
F4F	0.6437(8)	0.3961(14)	0.7412(11)	0.045(4)
F5F	0.5940(9)	0.465(2)	0.8081(10)	0.043(4)
F6F	0.6932(6)	0.4949(17)	0.8086(8)	0.055(4)
F7F	0.588(2)	0.429(3)	0.786(3)	0.036(6)
F8F	0.664(2)	0.525(4)	0.8254(17)	0.040(7)
F9F	0.6810(19)	0.418(3)	0.757(3)	0.038(6)
C31	0.51069(16)	0.7801(3)	0.69604(15)	0.0314(7)
F1C	0.5319(6)	0.8747(7)	0.7017(5)	0.031(2)
F2C	0.4801(6)	0.7644(14)	0.7444(5)	0.030(2)
F3C	0.4673(5)	0.7779(10)	0.6459(5)	0.034(3)
F4C	0.5377(12)	0.8667(11)	0.7170(11)	0.035(5)
F5C	0.4707(14)	0.753(3)	0.7347(10)	0.053(6)
F6C	0.4745(12)	0.805(2)	0.6430(9)	0.056(6)
F7C	0.4952(17)	0.785(3)	0.7527(9)	0.052(9)
F8C	0.4575(12)	0.751(3)	0.6587(11)	0.034(6)
F9C	0.5211(18)	0.8741(14)	0.6788(15)	0.061(9)
C32	0.68810(15)	0.7547(2)	0.54432(14)	0.0248(7)
C33	0.63561(16)	0.8062(3)	0.51372(15)	0.0279(7)
H33	0.594626	0.778488	0.513277	0.033
C34	0.64102(18)	0.8955(3)	0.48422(15)	0.0320(8)
C35	0.69950(19)	0.9395(3)	0.48416(16)	0.0363(9)
H35	0.703329	1.000925	0.463924	0.044
C36	0.75245(18)	0.8914(3)	0.51450(16)	0.0340(8)
C37	0.58336(19)	0.9406(3)	0.44825(16)	0.0409(8)
F1E	0.5964(18)	1.0362(10)	0.4346(14)	0.049(4)
F2E	0.5314(9)	0.940(3)	0.4745(11)	0.057(5)
F3E	0.5684(14)	0.8958(17)	0.3933(7)	0.040(3)
F4E	0.5308(4)	0.9161(15)	0.4729(6)	0.042(2)
F5E	0.5735(9)	0.9034(13)	0.3910(5)	0.057(3)
F6E	0.5832(10)	1.0395(6)	0.4438(11)	0.053(3)
C38	0.8160(2)	0.9380(3)	0.51545(18)	0.0480(9)
F1B	0.8224(5)	0.9801(5)	0.4608(3)	0.051(2)
F2B	0.8646(4)	0.8722(6)	0.5271(3)	0.054(2)
F3B	0.8281(5)	1.0097(5)	0.5577(3)	0.063(2)
F4B	0.8340(11)	0.9422(14)	0.4601(6)	0.057(4)
F5B	0.8627(8)	0.8959(13)	0.5538(7)	0.059(4)
F6B	0.8126(10)	1.0351(9)	0.5338(7)	0.058(4)
F7B	0.8594(10)	0.8683(13)	0.5047(7)	0.055(3)
F8B	0.8394(11)	0.9778(12)	0.5701(5)	0.061(4)
F9B	0.8173(11)	1.0089(10)	0.4733(6)	0.058(4)
C39	0.63874(14)	0.5706(2)	0.52399(14)	0.0223(7)
C40	0.61844(15)	0.4779(2)	0.54184(15)	0.0267(7)
H40	0.629985	0.458100	0.583177	0.032
C41	0.58221(16)	0.4135(3)	0.50203(16)	0.0297(7)
C42	0.56354(16)	0.4400(3)	0.44141(16)	0.0322(8)
H42	0.537564	0.397327	0.414166	0.039
C43	0.58386(16)	0.5303(3)	0.42189(15)	0.0300(8)
C44	0.62137(15)	0.5931(3)	0.46189(15)	0.0260(7)
H44	0.635795	0.653503	0.446600	0.031
C45	0.56483(17)	0.3145(3)	0.52442(16)	0.0379(8)
F1A	0.6151(3)	0.2561(6)	0.5393(3)	0.054(2)

F2A	0.5236(3)	0.2638(5)	0.4833(3)	0.062(2)
F3A	0.5366(3)	0.3213(6)	0.5744(3)	0.0408(15)
F4A	0.6003(10)	0.2412(14)	0.5080(10)	0.046(4)
F5A	0.5051(7)	0.293(2)	0.4987(12)	0.056(5)
F6A	0.5659(11)	0.3083(19)	0.5849(6)	0.049(4)
F7A	0.5546(8)	0.2452(12)	0.4806(7)	0.056(4)
F8A	0.5176(6)	0.3112(18)	0.5569(7)	0.050(4)
F9A	0.6151(8)	0.2739(16)	0.5626(7)	0.047(4)
C46	0.56605(18)	0.5583(3)	0.35627(16)	0.0405(7)
F1D	0.5763(4)	0.6553(4)	0.3457(5)	0.0403(19)
F2D	0.5053(3)	0.5419(6)	0.3349(4)	0.0417(18)
F3D	0.6002(3)	0.5057(4)	0.3196(3)	0.0447(16)
F4D	0.5603(13)	0.6591(9)	0.3524(16)	0.038(3)
F5D	0.5140(8)	0.5171(18)	0.3257(13)	0.044(3)
F6D	0.6147(9)	0.5351(16)	0.3252(11)	0.045(3)
F7D	0.5010(5)	0.5631(15)	0.3457(11)	0.044(3)
F8D	0.5789(6)	0.4848(10)	0.3170(8)	0.047(3)
F9D	0.5907(9)	0.6421(9)	0.3393(12)	0.045(3)
O1_1	0.2576(3)	0.6297(4)	0.6602(3)	0.0438(14)
C1_1	0.2392(3)	0.7308(4)	0.6669(2)	0.0497(16)
H1A_1	0.258953	0.756898	0.707055	0.060
H1AB_1	0.192659	0.735553	0.664422	0.060
C2_1	0.2610(4)	0.7897(5)	0.6164(3)	0.066(2)
H2A_1	0.224435	0.819259	0.589704	0.079
H2AB_1	0.289982	0.843646	0.633193	0.079
C3_1	0.2946(5)	0.7164(6)	0.5819(4)	0.078(2)
H3A_1	0.285574	0.728821	0.537334	0.094
H3AB_1	0.340988	0.719114	0.595015	0.094
C4_1	0.2682(10)	0.6185(8)	0.5978(4)	0.0562(14)
H4A_1	0.227997	0.603894	0.570787	0.067
H4AB_1	0.298622	0.564175	0.594076	0.067
O1_2	0.2747(18)	0.6300(18)	0.6653(12)	0.056(6)
C1_2	0.2944(16)	0.7324(17)	0.6729(9)	0.067(5)
H1A_2	0.338560	0.736378	0.694169	0.080
H1AB_2	0.266640	0.768725	0.697397	0.080
C2_2	0.2898(18)	0.7762(18)	0.6108(12)	0.073(5)
H2A_2	0.323591	0.825753	0.608607	0.087
H2AB_2	0.248011	0.807861	0.598331	0.087
C3_2	0.298(3)	0.687(3)	0.5721(14)	0.072(5)
H3A_2	0.343446	0.671759	0.572759	0.086
H3AB_2	0.278122	0.698187	0.529310	0.086
C4_2	0.265(4)	0.606(3)	0.6014(16)	0.0562(14)
H4A_2	0.219385	0.604375	0.584958	0.067
H4AB_2	0.283875	0.540465	0.594289	0.067
O1_3	0.2474(5)	0.3952(6)	0.6927(5)	0.055(3)
C1_3	0.1956(5)	0.3682(7)	0.6463(5)	0.062(3)
H1A_3	0.181565	0.425927	0.620042	0.075
H1AB_3	0.159247	0.343360	0.664993	0.075
C2_3	0.2213(7)	0.2890(10)	0.6105(6)	0.073(3)
H2A_3	0.187207	0.244598	0.591160	0.087
H2AB_3	0.243652	0.317620	0.578438	0.087
C3_3	0.2657(6)	0.2352(8)	0.6565(6)	0.073(3)
H3A_3	0.303995	0.215074	0.639210	0.088
H3AB_3	0.245391	0.174900	0.670327	0.088
C4_3	0.2830(8)	0.3059(9)	0.7090(6)	0.054(3)
H4A_3	0.271705	0.277469	0.747182	0.065
H4AB_3	0.329046	0.319961	0.715068	0.065
O1_4	0.2641(8)	0.4049(8)	0.6810(6)	0.042(3)
C1_4	0.2737(14)	0.3188(13)	0.7197(9)	0.056(5)
H1A_4	0.253049	0.328192	0.756466	0.067
H1AB_4	0.319559	0.307871	0.732913	0.067
C2_4	0.2454(11)	0.2320(11)	0.6836(9)	0.084(6)
H2A_4	0.278623	0.182770	0.678256	0.101
H2AB_4	0.213221	0.199406	0.704778	0.101
C3_4	0.2164(14)	0.2708(11)	0.6246(8)	0.080(6)
H3A_4	0.170081	0.259195	0.618955	0.096
H3AB_4	0.233990	0.236377	0.591322	0.096
C4_4	0.2296(8)	0.3792(8)	0.6225(5)	0.047(4)
H4A_4	0.255112	0.394091	0.589734	0.056
H4AB_4	0.189551	0.417157	0.614613	0.056
O1_5	0.3160(2)	0.5558(5)	0.79227(16)	0.0406(11)
C1_5	0.3607(2)	0.6368(3)	0.7957(2)	0.0420(10)

H1A_5	0.344057	0.695762	0.814843	0.050
H1AB_5	0.369279	0.655252	0.754420	0.050
C2_5	0.41979(19)	0.5997(3)	0.83403(19)	0.0401(10)
H2A_5	0.444795	0.655033	0.854865	0.048
H2AB_5	0.446569	0.562074	0.809142	0.048
C3_5	0.3937(2)	0.5326(4)	0.87963(19)	0.0425(11)
H3A_5	0.424944	0.481061	0.895564	0.051
H3AB_5	0.382035	0.571323	0.914294	0.051
C4_5	0.3365(2)	0.4872(4)	0.8425(2)	0.0500(12)
H4A_5	0.347143	0.421758	0.826436	0.060
H4AB_5	0.302437	0.478007	0.867884	0.060
O1_6	0.3160(15)	0.541(5)	0.7936(10)	0.047(4)
C1_6	0.3784(15)	0.582(4)	0.8050(13)	0.050(3)
H1A_6	0.378625	0.650750	0.788479	0.060
H1B_6	0.408573	0.541425	0.785747	0.060
C2_6	0.3959(12)	0.583(4)	0.8732(13)	0.051(3)
H2A_6	0.425564	0.637675	0.886778	0.062
H2B_6	0.415472	0.519027	0.888047	0.062
C3_6	0.3332(15)	0.598(3)	0.8949(13)	0.054(3)
H3A_6	0.333843	0.571792	0.936811	0.065
H3B_6	0.321238	0.668887	0.894002	0.065
C4_6	0.2895(14)	0.539(3)	0.8496(15)	0.052(4)
H4A_6	0.286014	0.470236	0.864032	0.063
H4B_6	0.246693	0.569493	0.843443	0.063
O1_7	0.1742(5)	0.5287(13)	0.7502(6)	0.054(4)
C1_7	0.1176(5)	0.5504(10)	0.7084(5)	0.065(3)
H1A_7	0.092849	0.489312	0.697036	0.078
H1B_7	0.127886	0.582445	0.670789	0.078
C2_7	0.0819(6)	0.6200(11)	0.7436(6)	0.078(4)
H2A_7	0.035811	0.617384	0.728734	0.094
H2B_7	0.096874	0.689171	0.740792	0.094
C3_7	0.0968(6)	0.5809(14)	0.8083(6)	0.068(4)
H3A_7	0.095115	0.634833	0.838469	0.082
H3B_7	0.066747	0.527956	0.815877	0.082
C4_7	0.1631(5)	0.5406(10)	0.8116(4)	0.061(3)
H4A_7	0.194184	0.587409	0.833674	0.073
H4B_7	0.166954	0.476015	0.833218	0.073
O1_8	0.1697(8)	0.5689(16)	0.7338(14)	0.064(6)
C1_8	0.1202(15)	0.5063(16)	0.750(2)	0.071(6)
H1A_8	0.138303	0.450978	0.776881	0.085
H1B_8	0.094214	0.478325	0.713594	0.085
C2_8	0.0809(16)	0.574(2)	0.7844(19)	0.067(6)
H2A_8	0.036479	0.550769	0.780594	0.081
H2B_8	0.098813	0.578430	0.828243	0.081
C3_8	0.0858(11)	0.6709(16)	0.7524(16)	0.074(6)
H3A_8	0.053905	0.675043	0.715130	0.089
H3B_8	0.079453	0.727252	0.779576	0.089
C4_8	0.1513(9)	0.6712(14)	0.7366(13)	0.072(5)
H4A_8	0.152023	0.704115	0.696728	0.086
H4B_8	0.180457	0.706984	0.768191	0.086
O1_9	0.1734(6)	0.5528(16)	0.7497(10)	0.051(5)
C1_9	0.1142(9)	0.4993(15)	0.7386(10)	0.063(4)
H1A_9	0.121577	0.426867	0.742250	0.076
H1B_9	0.091535	0.514028	0.697278	0.076
C2_9	0.0762(8)	0.5355(12)	0.7874(11)	0.065(4)
H2A_9	0.030051	0.531428	0.773180	0.078
H2B_9	0.086588	0.497203	0.825774	0.078
C3_9	0.0980(6)	0.6412(11)	0.7955(9)	0.065(4)
H3A_9	0.089381	0.669016	0.834831	0.078
H3B_9	0.077961	0.683840	0.761558	0.078
C4_9	0.1685(5)	0.6287(11)	0.7943(7)	0.063(4)
H4A_9	0.187411	0.691588	0.782542	0.075
H4B_9	0.190449	0.608155	0.834978	0.075

$U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table S14.** Bond lengths and angles for  $[\text{Li}(\text{THF})_4][1^{\text{F}}-\text{BH}_3]$ .

Atom–Atom	Length [Å]
Li1–O1_7	1.906(10)
Li1–O1_6	1.917(14)
Li1–O1_1	1.921(8)
Li1–O1_5	1.921(6)

Li1–O1_3	1.926(9)
Li1–O1_2	1.930(14)
Li1–O1_8	1.934(13)
Li1–O1_4	1.938(11)
Li1–O1_9	1.940(11)
B1–C32	1.632(5)

B1-C3	1.638(4)
B1-C24	1.644(5)
B1-C39	1.655(5)
N1-C5	1.358(4)
N1-C1	1.367(4)
N1-B2	1.621(5)
C1-C2	1.373(4)
C1-C6	1.494(4)
C2-C3	1.400(4)
C3-C4	1.389(4)
C4-C5	1.380(4)
C5-C15	1.491(5)
C6-C11	1.397(5)
C6-C7	1.399(5)
C7-C8	1.392(5)
C7-C12	1.504(5)
C8-C9	1.384(5)
C9-C10	1.381(5)
C9-C13	1.516(5)
C11-C10	1.397(5)
C11-C14	1.502(5)
C013-C36	1.387(5)
C013-C32	1.401(5)
C15-C16	1.392(5)
C15-C20	1.398(5)
C16-C17	1.391(5)
C16-C21	1.505(6)
C18-C17	1.377(6)
C18-C19	1.379(7)
C18-C22	1.519(6)
C19-C20	1.405(6)
C20-C23	1.498(6)
C24-C29	1.397(4)
C24-C25	1.401(4)
C27-C28	1.381(5)
C27-C26	1.382(5)
C26-C25	1.389(4)
C26-C30	1.491(5)
C28-C29	1.392(4)
C28-C31	1.489(5)
C30-F5F	1.334(12)
C30-F1F	1.341(8)
C30-F6F	1.343(11)
C30-F2F	1.344(8)
C30-F9F	1.349(15)
C30-F7F	1.350(15)
C30-F8F	1.358(15)
C30-F4F	1.365(11)
C30-F3F	1.368(7)
C31-F3C	1.337(8)
C31-F7C	1.344(14)
C31-F5C	1.346(12)
C31-F6C	1.348(12)
C31-F2C	1.350(8)
C31-F9C	1.351(14)
C31-F1C	1.352(8)
C31-F4C	1.353(12)
C31-F8C	1.360(13)
C32-C33	1.404(4)
C33-C34	1.382(5)
C34-C35	1.382(5)
C34-C37	1.492(5)
C35-C36	1.387(5)
C36-C38	1.493(5)
C37-F2E	1.327(12)
C37-F6E	1.335(8)
C37-F5E	1.349(8)
C37-F3E	1.353(11)
C37-F4E	1.358(8)
C37-F1E	1.360(11)
C38-F5B	1.336(11)
C38-F4B	1.338(11)

C38-F9B	1.339(11)
C38-F3B	1.343(7)
C38-F8B	1.350(11)
C38-F2B	1.359(7)
C38-F1B	1.361(7)
C38-F7B	1.364(11)
C38-F6B	1.374(11)
C39-C40	1.397(5)
C39-C44	1.403(4)
C40-C41	1.388(5)
C41-C42	1.389(5)
C41-C45	1.489(5)
C42-C43	1.381(5)
C43-C44	1.390(5)
C43-C46	1.494(5)
C45-F8A	1.323(11)
C45-F4A	1.328(12)
C45-F1A	1.332(6)
C45-F6A	1.337(12)
C45-F3A	1.339(6)
C45-F7A	1.340(11)
C45-F5A	1.347(13)
C45-F2A	1.353(6)
C45-F9A	1.378(11)
C46-F9D	1.323(12)
C46-F2D	1.332(7)
C46-F5D	1.333(13)
C46-F1D	1.350(7)
C46-F6D	1.363(13)
C46-F4D	1.365(13)
C46-F3D	1.366(6)
C46-F8D	1.372(10)
C46-F7D	1.376(11)
O1_1-C1_1	1.431(7)
O1_1-C4_1	1.439(7)
C1_1-C2_1	1.498(7)
C2_1-C3_1	1.497(8)
C3_1-C4_1	1.497(8)
O1_2-C4_2	1.435(15)
O1_2-C1_2	1.445(14)
C1_2-C2_2	1.486(14)
C2_2-C3_2	1.497(14)
C3_2-C4_2	1.501(15)
O1_3-C4_3	1.439(11)
O1_3-C1_3	1.440(9)
C1_3-C2_3	1.482(11)
C2_3-C3_3	1.474(11)
C3_3-C4_3	1.505(10)
O1_4-C4_4	1.433(11)
O1_4-C1_4	1.437(13)
C1_4-C2_4	1.492(13)
C2_4-C3_4	1.458(12)
C3_4-C4_4	1.489(13)
O1_5-C1_5	1.444(6)
O1_5-C4_5	1.462(6)
C1_5-C2_5	1.498(6)
C2_5-C3_5	1.520(6)
C3_5-C4_5	1.498(6)
O1_6-C1_6	1.435(15)
O1_6-C4_6	1.436(14)
C1_6-C2_6	1.500(14)
C2_6-C3_6	1.502(15)
C3_6-C4_6	1.491(15)
O1_7-C4_7	1.423(11)
O1_7-C1_7	1.439(12)
C1_7-C2_7	1.498(12)
C2_7-C3_7	1.515(12)
C3_7-C4_7	1.509(11)
O1_8-C4_8	1.437(14)
O1_8-C1_8	1.441(14)
C1_8-C2_8	1.511(14)
C2_8-C3_8	1.499(14)

C3_8–C4_8	1.491(14)
O1_9–C4_9	1.437(13)
O1_9–C1_9	1.444(13)
C1_9–C2_9	1.523(13)
C2_9–C3_9	1.500(13)
C3_9–C4_9	1.519(12)
<b>Atom–Atom–Atom</b>	<b>Angle [°]</b>
O1_7–Li1–O1_1	111.8(6)
O1_7–Li1–O1_5	105.9(5)
O1_1–Li1–O1_5	110.9(4)
O1_7–Li1–O1_3	94.3(7)
O1_1–Li1–O1_3	115.6(5)
O1_5–Li1–O1_3	116.7(5)
O1_6–Li1–O1_2	106.9(18)
O1_6–Li1–O1_8	114.0(17)
O1_2–Li1–O1_8	102.0(14)
O1_6–Li1–O1_4	110(2)
O1_2–Li1–O1_4	104.8(11)
O1_8–Li1–O1_4	117.9(10)
C32–B1–C3	108.5(3)
C32–B1–C24	113.5(3)
C3–B1–C24	108.5(3)
C32–B1–C39	110.8(3)
C3–B1–C39	109.5(3)
C24–B1–C39	106.0(3)
C5–N1–C1	117.7(3)
C5–N1–B2	121.7(3)
C1–N1–B2	120.5(3)
N1–C1–C2	120.9(3)
N1–C1–C6	120.3(3)
C2–C1–C6	118.8(3)
C1–C2–C3	123.3(3)
C4–C3–C2	113.7(3)
C4–C3–B1	124.3(3)
C2–C3–B1	122.0(3)
C5–C4–C3	122.9(3)
N1–C5–C4	121.5(3)
N1–C5–C15	119.9(3)
C4–C5–C15	118.7(3)
C11–C6–C7	120.8(3)
C11–C6–C1	119.6(3)
C7–C6–C1	119.4(3)
C8–C7–C6	118.4(3)
C8–C7–C12	120.4(3)
C6–C7–C12	121.3(3)
C9–C8–C7	122.0(4)
C10–C9–C8	118.5(3)
C10–C9–C13	121.0(4)
C8–C9–C13	120.5(4)
C10–C11–C6	118.5(3)
C10–C11–C14	120.7(3)
C6–C11–C14	120.8(3)
C9–C10–C11	121.8(3)
C36–C013–C32	122.5(3)
C16–C15–C20	120.7(3)
C16–C15–C5	119.4(3)
C20–C15–C5	119.7(3)
C17–C16–C15	119.2(4)
C17–C16–C21	120.3(4)
C15–C16–C21	120.5(3)
C17–C18–C19	118.7(4)
C17–C18–C22	120.5(5)
C19–C18–C22	120.7(4)
C18–C17–C16	121.5(4)
C18–C19–C20	122.0(4)
C15–C20–C19	117.9(4)
C15–C20–C23	120.8(3)
C19–C20–C23	121.3(4)
C29–C24–C25	114.9(3)
C29–C24–B1	124.6(3)
C25–C24–B1	120.3(3)

C28–C27–C26	117.9(3)
C27–C26–C25	120.5(3)
C27–C26–C30	121.0(3)
C25–C26–C30	118.5(3)
C26–C25–C24	123.1(3)
C27–C28–C29	121.2(3)
C27–C28–C31	120.3(3)
C29–C28–C31	118.5(3)
C28–C29–C24	122.4(3)
F5F–C30–F6F	107.3(11)
F1F–C30–F2F	107.5(8)
F9F–C30–F7F	107(2)
F9F–C30–F8F	106(2)
F7F–C30–F8F	105(2)
F5F–C30–F4F	105.9(13)
F6F–C30–F4F	105.5(10)
F1F–C30–F3F	106.4(6)
F2F–C30–F3F	105.4(7)
F5F–C30–C26	114.6(15)
F1F–C30–C26	114.4(8)
F6F–C30–C26	113.6(11)
F2F–C30–C26	111.2(9)
F9F–C30–C26	115(3)
F7F–C30–C26	116(3)
F8F–C30–C26	107(3)
F4F–C30–C26	109.3(12)
F3F–C30–C26	111.5(7)
F5C–C31–F6C	106.5(15)
F3C–C31–F2C	107.3(7)
F7C–C31–F9C	107.0(18)
F3C–C31–F1C	106.2(7)
F2C–C31–F1C	105.6(8)
F5C–C31–F4C	107.1(15)
F6C–C31–F4C	104.3(12)
F7C–C31–F8C	106.4(16)
F9C–C31–F8C	105.0(15)
F3C–C31–C28	111.0(7)
F7C–C31–C28	112(2)
F5C–C31–C28	113.9(18)
F6C–C31–C28	116.1(15)
F2C–C31–C28	113.3(9)
F9C–C31–C28	116.6(17)
F1C–C31–C28	113.0(6)
F4C–C31–C28	108.2(12)
F8C–C31–C28	109.0(18)
C013–C32–C33	115.1(3)
C013–C32–B1	123.3(3)
C33–C32–B1	121.5(3)
C34–C33–C32	122.8(3)
C33–C34–C35	120.8(3)
C33–C34–C37	119.1(3)
C35–C34–C37	119.9(3)
C34–C35–C36	118.1(3)
C35–C36–C013	120.8(3)
C35–C36–C38	119.0(3)
C013–C36–C38	120.3(3)
F6E–C37–F5E	107.7(10)
F2E–C37–F3E	106.9(14)
F6E–C37–F4E	106.1(7)
F5E–C37–F4E	105.2(9)
F2E–C37–F1E	108.2(11)
F3E–C37–F1E	104.6(13)
F2E–C37–C34	116.3(13)
F6E–C37–C34	116.0(9)
F5E–C37–C34	110.6(8)
F3E–C37–C34	111.3(9)
F4E–C37–C34	110.6(7)
F1E–C37–C34	108.9(15)
F5B–C38–F4B	108.2(10)
F9B–C38–F8B	107.4(9)
F3B–C38–F2B	105.9(5)
F3B–C38–F1B	106.5(5)

F2B-C38-F1B	105.4(5)
F9B-C38-F7B	106.5(10)
F8B-C38-F7B	105.0(9)
F5B-C38-F6B	106.5(9)
F4B-C38-F6B	105.3(9)
F5B-C38-C36	115.0(9)
F4B-C38-C36	112.9(11)
F9B-C38-C36	113.7(10)
F3B-C38-C36	113.2(5)
F8B-C38-C36	113.2(11)
F2B-C38-C36	113.3(5)
F1B-C38-C36	111.9(5)
F7B-C38-C36	110.4(11)
F6B-C38-C36	108.4(9)
C40-C39-C44	114.9(3)
C40-C39-B1	120.8(3)
C44-C39-B1	124.2(3)
C41-C40-C39	123.1(3)
C40-C41-C42	120.4(3)
C40-C41-C45	119.5(3)
C42-C41-C45	120.1(3)
C43-C42-C41	118.0(3)
C42-C43-C44	121.0(3)
C42-C43-C46	118.7(3)
C44-C43-C46	120.3(3)
C43-C44-C39	122.5(3)
F4A-C45-F6A	107.6(13)
F1A-C45-F3A	106.3(5)
F8A-C45-F7A	108.3(10)
F4A-C45-F5A	105.7(12)
F6A-C45-F5A	106.6(13)
F1A-C45-F2A	106.8(5)
F3A-C45-F2A	105.3(4)
F8A-C45-F9A	103.9(11)
F7A-C45-F9A	101.3(10)
F8A-C45-C41	117.3(11)
F4A-C45-C41	113.2(10)
F1A-C45-C41	112.3(5)
F6A-C45-C41	114.8(11)
F3A-C45-C41	112.2(4)
F7A-C45-C41	113.9(9)
F5A-C45-C41	108.3(13)
F2A-C45-C41	113.4(4)
F9A-C45-C41	110.5(11)
F2D-C46-F1D	105.9(6)
F5D-C46-F6D	106.8(12)
F5D-C46-F4D	108.7(15)
F6D-C46-F4D	105.4(13)
F2D-C46-F3D	106.3(4)
F1D-C46-F3D	106.5(5)
F9D-C46-F8D	108.1(10)
F9D-C46-F7D	110.2(12)
F8D-C46-F7D	102.5(9)
F9D-C46-C43	115.9(12)
F2D-C46-C43	113.4(5)
F5D-C46-C43	117.4(14)
F1D-C46-C43	112.8(6)
F6D-C46-C43	109.2(12)
F4D-C46-C43	108.7(15)
F3D-C46-C43	111.4(4)
F8D-C46-C43	112.8(9)
F7D-C46-C43	106.4(11)
C1_1-O1_1-C4_1	106.5(6)

C1_1-O1_1-Li1	123.4(5)
C4_1-O1_1-Li1	129.4(6)
O1_1-C1_1-C2_1	107.9(5)
C3_1-C2_1-C1_1	104.9(5)
C4_1-C3_1-C2_1	103.5(7)
O1_1-C4_1-C3_1	104.6(5)
C4_2-O1_2-C1_2	109.1(13)
C4_2-O1_2-Li1	118(2)
C1_2-O1_2-Li1	133(2)
O1_2-C1_2-C2_2	106.9(13)
C1_2-C2_2-C3_2	102.4(15)
C2_2-C3_2-C4_2	103.6(17)
O1_2-C4_2-C3_2	104.6(16)
C4_3-O1_3-C1_3	106.9(7)
C4_3-O1_3-Li1	134.0(8)
C1_3-O1_3-Li1	119.1(7)
O1_3-C1_3-C2_3	104.8(7)
C3_3-C2_3-C1_3	103.7(8)
C2_3-C3_3-C4_3	106.3(7)
O1_3-C4_3-C3_3	106.0(7)
C4_4-O1_4-C1_4	110.6(10)
C4_4-O1_4-Li1	123.6(9)
C1_4-O1_4-Li1	116.2(12)
O1_4-C1_4-C2_4	107.6(10)
C3_4-C2_4-C1_4	106.5(10)
C2_4-C3_4-C4_4	108.7(10)
O1_4-C4_4-C3_4	106.5(9)
C1_5-O1_5-C4_5	108.4(3)
C1_5-O1_5-Li1	123.3(4)
C4_5-O1_5-Li1	126.6(4)
O1_5-C1_5-C2_5	105.8(4)
C1_5-C2_5-C3_5	102.4(3)
C4_5-C3_5-C2_5	103.1(3)
O1_5-C4_5-C3_5	106.7(4)
C1_6-O1_6-C4_6	109.3(14)
C1_6-O1_6-Li1	133(3)
C4_6-O1_6-Li1	114(2)
O1_6-C1_6-C2_6	105.3(14)
C1_6-C2_6-C3_6	102.8(15)
C4_6-C3_6-C2_6	102.3(15)
O1_6-C4_6-C3_6	106.6(15)
C4_7-O1_7-C1_7	110.5(8)
C4_7-O1_7-Li1	126.7(9)
C1_7-O1_7-Li1	119.6(10)
O1_7-C1_7-C2_7	103.6(9)
C1_7-C2_7-C3_7	102.9(9)
C4_7-C3_7-C2_7	103.6(8)
O1_7-C4_7-C3_7	106.3(8)
C4_8-O1_8-C1_8	109.6(12)
C4_8-O1_8-Li1	122.1(14)
C1_8-O1_8-Li1	127.7(17)
O1_8-C1_8-C2_8	104.9(14)
C3_8-C2_8-C1_8	102.0(15)
C4_8-C3_8-C2_8	104.2(13)
O1_8-C4_8-C3_8	106.2(12)
C4_9-O1_9-C1_9	108.7(9)
C4_9-O1_9-Li1	119.4(10)
C1_9-O1_9-Li1	131.6(12)
O1_9-C1_9-C2_9	105.4(10)
C3_9-C2_9-C1_9	101.5(11)
C2_9-C3_9-C4_9	100.5(10)
O1_9-C4_9-C3_9	105.3(9)

Bonds to hydrogen atoms were omitted.

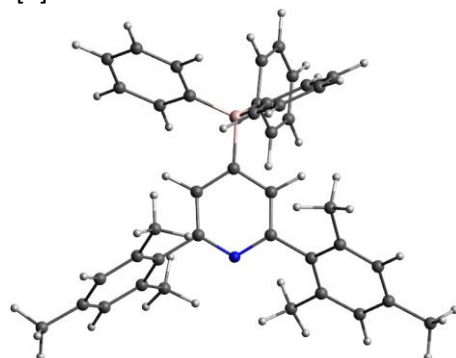
## 5. Computational Section

The quantum chemical calculations were performed with TURBOMOLE<sup>[11]</sup> using the BP86<sup>[12]</sup> functional with def-TZVP<sup>[13]</sup> basis set and D3<sup>[14]</sup>(BJ)<sup>[15]</sup> dispersion correction. Vibrational frequencies were calculated using the AOFORCE<sup>[16]</sup> module. All structures represented true minima without imaginary vibrational frequencies.

Compound	SCF [H]
[1] <sup>-</sup>	-1666.353377340
[1 <sup>F</sup> ] <sup>-</sup>	-3689.634931380

### Cartesian coordinates of the calculated structures in Ångström

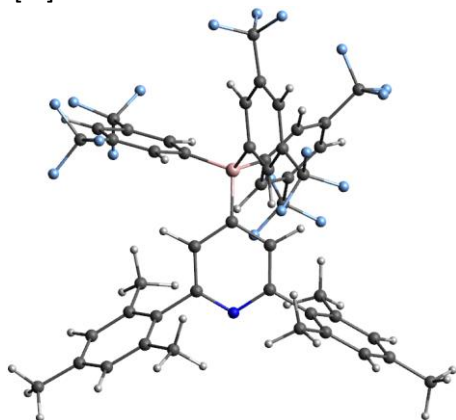
[1]<sup>-</sup>



N	-0.7723679	1.5053438	-1.1210302
B	1.0357171	-1.9174791	1.1616075
C	0.5631301	1.4145378	-0.9663273
C	1.1938281	0.3519792	-0.3031888
H	2.2802368	0.3673976	-0.1911715
C	0.4473070	-0.7083890	0.2306987
C	-0.9427940	-0.6054749	0.0347897
H	-1.5972716	-1.3821659	0.4355572
C	1.3780952	2.5397737	-1.5189194
C	-1.5136771	0.4962246	-0.6028141
C	2.4183457	3.6613258	-3.3975344
H	2.6253503	3.7068723	-4.4711242
C	1.6459795	2.6040878	-2.9000065
C	2.9307917	4.6563910	-2.5566761
C	2.6484892	4.5756368	-1.1881629
H	3.0308368	5.3490486	-0.5151710
C	1.8833391	3.5305332	-0.6540604
C	1.1067291	1.5441307	-3.8263905
H	1.4895611	1.6787163	-4.8475807
H	0.0079714	1.5721400	-3.8557091
H	1.3820882	0.5379349	-3.4767649
C	3.7933029	5.7671825	-3.1057914
H	3.5275518	6.0041034	-4.1462939
H	4.8597958	5.4870802	-3.0955245
H	3.6913221	6.6855292	-2.5094175
C	1.5920545	3.4738730	0.8251645
H	0.5139220	3.3612219	1.0098090
H	1.9431864	4.3847012	1.3297237
H	2.0818279	2.6084493	1.2958094
C	-2.9977187	0.6261525	-0.6864155
C	-3.7643702	0.6533185	0.5009542
C	-5.1587074	0.7689238	0.4052737
H	-5.7467795	0.8057730	1.3272831
C	-5.8142771	0.8473805	-0.8271970
C	-5.0349265	0.8256467	-1.9899919
H	-5.5252378	0.8912558	-2.9661547
C	-3.6401004	0.7216640	-1.9402343
C	-3.1211151	0.5920618	1.8666326
H	-2.8521734	-0.4341170	2.1581505

H	-3.8063287	0.9830051	2.6319217
H	-2.1874880	1.1678084	1.9037249
C	-7.3198905	0.9250388	-0.9035597
H	-7.6484016	1.5031570	-1.7797572
H	-7.7420645	1.3968386	-0.0044664
H	-7.7679948	-0.0791084	-0.9873970
C	-2.8421573	0.7057413	-3.2194050
H	-3.5046968	0.6387619	-4.0938404
H	-2.1430814	-0.1434984	-3.2409448
H	-2.2287685	1.6142307	-3.2996068
C	2.6509121	-1.7753384	1.3681346
C	3.5037400	-1.8770533	0.2475111
H	3.0558582	-2.0514118	-0.7350871
C	4.8928726	-1.7795417	0.3520333
H	5.5154538	-1.8589578	-0.5434606
C	5.4901016	-1.5869683	1.6041868
H	6.5765297	-1.5125170	1.6947150
C	4.6752363	-1.5008613	2.7358483
H	5.1255900	-1.3617761	3.7228886
C	3.2823819	-1.5926532	2.6117202
H	2.6648562	-1.5241316	3.5104125
C	0.1992614	-1.7362274	2.5633459
C	0.2843037	-0.5193455	3.2751891
H	0.9543031	0.2595469	2.9001880
C	-0.4742707	-0.2656915	4.4196527
H	-0.3797821	0.6931340	4.9367940
C	-1.3697433	-1.2317796	4.8955214
H	-1.9753233	-1.0369020	5.7837798
C	-1.4846432	-2.4432837	4.2089701
H	-2.1863865	-3.2047758	4.5607362
C	-0.7093764	-2.6849715	3.0663642
H	-0.8193727	-3.6365061	2.5410342
C	0.7676404	-3.3833993	0.4877173
C	1.2351308	-4.5405009	1.1477673
H	1.7666498	-4.4203387	2.0959066
C	1.0530969	-5.8233277	0.6271238
H	1.4295120	-6.6930936	1.1729163
C	0.3963831	-5.9973923	-0.5979560
H	0.2535451	-6.9979078	-1.0134865
C	-0.0661528	-4.8712153	-1.2830979
H	-0.5741934	-4.9875936	-2.2445953
C	0.1194633	-3.5914013	-0.7430680
H	-0.2519487	-2.7265571	-1.2981759

[1<sup>F</sup>]<sup>-</sup>



C	0.6527300	0.9012929	2.0398858
N	1.7923049	1.3849010	1.5048270
C	-0.3182334	0.2388668	1.2768253
H	-1.2209733	-0.1149272	1.7763045
B	-1.1830696	-0.8221748	-1.0275774
C	-0.1302705	0.0048072	-0.0912410
F	-4.8410714	-0.0589027	3.1539435
C	1.0653352	0.5192871	-0.6262236
H	1.3053523	0.3664283	-1.6811075
C	1.9809133	1.2032028	0.1802625
F	-6.2915484	-1.5817226	2.5372819
C	0.4625732	1.0844655	3.5075673

F	-5.8378960	0.1063642	1.2116487
F	-4.8973628	-1.1568987	-4.8066486
C	0.3221166	-0.0402174	4.3486027
C	0.1366089	0.1597186	5.7237944
H	0.0370159	-0.7143586	6.3737840
F	-6.1591894	-0.2464470	-3.2675963
C	0.0764825	1.4388519	6.2837492
F	-5.6830764	0.8715924	-5.0925240
C	0.4086917	2.3868581	4.0528620
F	-0.9144284	3.9332596	-3.9595562
C	0.2112760	2.5401081	5.4291032
H	0.1555021	3.5508089	5.8440640
F	-2.9862126	4.6073586	-3.7227773
C	0.3845547	-1.4511330	3.8110083
H	-0.5667435	-1.7575160	3.3503770
H	0.6027083	-2.1617799	4.6197816
H	1.1565162	-1.5560556	3.0369282
F	-1.6858604	4.4117188	-1.9672490
C	-0.0974634	1.6297598	7.7705198
H	0.8736999	1.7858368	8.2685953
H	-0.5676909	0.7510197	8.2338027
H	-0.7215452	2.5079727	7.9914688
C	0.5341792	3.6028461	3.1692720
H	1.5267132	3.6430267	2.7002018
H	0.3694432	4.5226058	3.7470525
H	-0.1979478	3.5732469	2.3479190
C	3.2150555	2.8391622	-1.2792970
C	3.2482591	1.7426239	-0.3955035
C	4.4206945	3.3246409	-1.8047833
H	4.3936021	4.1852711	-2.4793755
C	5.6513831	2.7431788	-1.4842791
C	5.6592829	1.6548479	-0.6026012
H	6.6115218	1.1869503	-0.3361929
C	4.4792074	1.1451752	-0.0500835
C	1.9116937	3.5018472	-1.6533783
H	2.0879043	4.4899021	-2.0990849
H	1.2563019	3.6266284	-0.7806531
H	1.3519715	2.9056541	-2.3897355
C	4.5223591	-0.0329850	0.8896691
H	3.9043390	-0.8616278	0.5120402
H	4.1190845	0.2403942	1.8747430
H	5.5502219	-0.4003754	1.0114248
C	6.9342662	3.2546066	-2.0929031
H	7.2112225	2.6701317	-2.9857050
H	7.7718572	3.1828093	-1.3838486
H	6.8382759	4.3043320	-2.4046761
C	-2.2207638	-1.6340418	-0.0546485
C	-2.8989212	-3.6032154	1.2393416
C	-2.0464994	-2.9747285	0.3215060
H	-1.2297752	-3.5516323	-0.1146731
C	-3.9632360	-2.9099218	1.8175274
H	-4.6314094	-3.3994933	2.5231920
C	-4.1652644	-1.5784954	1.4445153
C	-3.3077386	-0.9566244	0.5312689
H	-3.4916251	0.0843174	0.2597732
C	-2.6231310	-5.0249082	1.6462468
F	-2.2175290	-5.7981264	0.5981554
F	-3.7164828	-5.6393423	2.1920757
F	-1.6287918	-5.1028293	2.5891657
C	-5.2778704	-0.7868347	2.0763344
C	-2.0369771	0.1994086	-1.9726713
C	-3.1804132	-0.2582409	-2.6548627
H	-3.4977253	-1.2949144	-2.5212475
C	-3.9325070	0.5772996	-3.4877343
C	-3.5765761	1.9169516	-3.6603011
H	-4.1642995	2.5719099	-4.2996544
C	-2.4545307	2.3949739	-2.9811624
C	-1.6989091	1.5491209	-2.1580567
H	-0.8324515	1.9544626	-1.6329500
C	-5.1566002	0.0203514	-4.1620262
C	-2.0204942	3.8246410	-3.1544963
C	-0.3171828	-1.8697370	-1.9399640
C	-0.5574180	-2.1149165	-3.3003803
H	-1.3481742	-1.5643356	-3.8123140
C	0.2046876	-3.0351882	-4.0337130
C	1.2358610	-3.7541316	-3.4278911

H	1.8275907	-4.4690877	-3.9956066
C	1.4935889	-3.5247157	-2.0738549
C	0.7373684	-2.5959940	-1.3522263
H	0.9799800	-2.4196803	-0.3025958
C	-0.1314433	-3.2760925	-5.4801786
F	-0.3926140	-2.1162121	-6.1515407
F	-1.2453154	-4.0626044	-5.6251836
F	0.8745717	-3.9071770	-6.1585672
C	2.6313996	-4.2315820	-1.3901899
F	2.3019254	-4.6438516	-0.1305979
F	3.7310924	-3.4229975	-1.2523866
F	3.0519659	-5.3390237	-2.0721362

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