

**Supporting Information for:**

**Selective one- and two-electron reductions of a haloborane enabled by a  $\pi$ -withdrawing carbene ligand**

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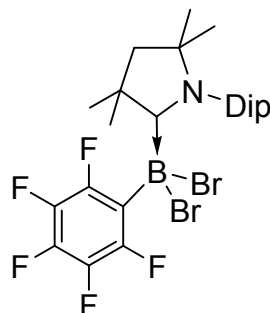
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## Experimental Details

### General information

All reactions were performed under an atmosphere of dry argon using standard Schlenk line or glovebox techniques. Deuterated benzene and tetrahydrofuran were degassed by three freeze-pump-thaw cycles and dried over molecular sieves. All other solvents were distilled and degassed from appropriate drying agents. Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves. NMR spectra were obtained from a Bruker Avance 500 NMR spectrometer ( $^1\text{H}$  and  $^1\text{H}\{^{11}\text{B}\}$ : 500.1 MHz,  $^{13}\text{C}\{^1\text{H}\}$ : 125.8 MHz) or a Bruker Avance 400 ( $^1\text{H}$  and  $^1\text{H}\{^{11}\text{B}\}$ : 400.1 MHz,  $^{13}\text{C}\{^1\text{H}\}$ : 100.6 MHz;  $^{11}\text{B}$ : 128.4 MHz,  $^{19}\text{F}$ : 376.5 MHz) at 298 K. Chemical shifts ( $\delta$ ) are given in ppm and internally referenced to the carbon nuclei ( $^{13}\text{C}\{^1\text{H}\}$ ) or residual protons ( $^1\text{H}$ ) of the solvent.  $^{11}\text{B}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra were referenced to external standard  $[\text{BF}_3\cdot\text{OEt}_2]$  or  $\text{CFCl}_3$ , respectively. High-resolution mass spectrometry was obtained from a Thermo Scientific Exactive Plus spectrometer in LIFDI or ESI mode. EPR measurements at X-band (9.38 GHz) were carried out at room temperature using a Bruker ELEXSYS E580 CW EPR spectrometer. The continuous wave (CW) EPR spectrum was measured using 0.5 mW microwave power and 0.5 G field modulation at 100 kHz, with a conversion time of 80 ms. The spectral simulations were performed using MATLAB 8.6 and the EasySpin 5.2.11 toolbox.<sup>1</sup> Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocenium ( $[\text{Cp}_2\text{Fe}]^{+/0}$ ) redox couple by using ferrocene as an internal standard. Tetra-*n*-butylammonium hexafluorophosphate ( $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ ) was employed as the supporting electrolyte. Compensation for resistive losses (iR drop) was employed for all measurements. Pentafluorophenylboron dibromide<sup>2</sup> ( $\text{C}_6\text{F}_5\text{BBr}_2$ ), CAAC<sup>3</sup> and DAC-carbene<sup>4</sup> were synthesized according to the literature procedures.

## Preparation of [(CAAC)B(C<sub>6</sub>F<sub>5</sub>)Br<sub>2</sub>] (1)



Hexane solution of CAAC (1.95 g, 6.81 mmol) was slowly added by cannula to a solution of C<sub>6</sub>F<sub>5</sub>BBR<sub>2</sub> (2.06 g, 6.78 mmol) in hexane at 30 °C with vigorous stirring. The reaction mixture was then allowed to warm to room temperature and stirred for three hours. A white precipitate was subsequently formed. After removal of all volatiles the residual solid was washed twice with pentane to yield the adduct **1** as a white powder (3.36 g, 85% yield). Colorless single crystals suitable for X-ray crystallography were obtained from a saturated benzene solution.

<sup>1</sup>H{<sup>11</sup>B} NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.11 (t, *J* = 7.8 Hz, 1H, Dip(Ar)), 7.01 (d, *J* = 7.7 Hz, 2H, Dip(Ar)), 2.92 (sept, *J* = 6.6 Hz, 2H, Dip(CH(Me)<sub>2</sub>)), 1.53 (s, 2H, CAAC(CH<sub>2</sub>)), 1.51 (d, *J* = 6.5 Hz, 6H, Dip(CHMe<sub>2</sub>)), 1.45 (br, 6H, CAAC(BCCMe<sub>2</sub>)), 1.13 (d, *J* = 6.5 Hz, 6H, Dip(CHMe<sub>2</sub>)), 0.95 (s, 6H, CAAC (DipNC(Me)<sub>2</sub>)).

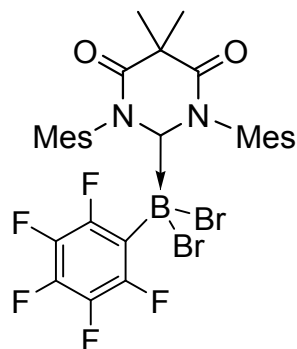
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 215.1 (br, *C* carbene), 145.9 (br, Dip(C<sup>Ar</sup>)), 141.0 (br, C<sup>C6F5</sup>), 132.9 (C<sup>Ar(i-Pr)2</sup>), 129.9 (C<sup>ArH</sup>), 125.4 (Dip(C<sup>ArH</sup>)), 79.9 (DipNC(Me)<sub>2</sub>), 54.4 (BCC(Me)<sub>2</sub>), 51.4 (NC(Me)<sub>2</sub>CH<sub>2</sub>), 29.1 (d, *J* = 3.6 Hz), 28.3 (DipNC(Me)<sub>2</sub>), 26.7 (BCC(Me)<sub>2</sub>), 24.7 (Dip(CH(Me)<sub>2</sub>)).

<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ -126.7 (d, *J* = 18.9 Hz, 2F), -161.4 (t, *J* = 20.5 Hz, 1F), -166.3 (br, 2F).

<sup>11</sup>B NMR (128.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ = -10.4 (s).

HRMS (LIFDI): calculated for C<sub>26</sub>H<sub>31</sub>BBrF<sub>5</sub>N ([M-Br]<sup>+</sup>): 542.1648; found: 542.1656.

## Preparation of [(DAC)B(C<sub>6</sub>F<sub>5</sub>)Br<sub>2</sub>] (**2**)



A benzene solution of DAC (2.0 g, 5.31 mmol) was slowly added by cannula to a solution of C<sub>6</sub>F<sub>5</sub>BBr<sub>2</sub> (1.82 g, 5.41 mmol) in hexane at 30 °C with vigorous stirring. The reaction mixture was then allowed to warm to room temperature and stirred for three hours. A light yellow precipitate was subsequently formed. After removal of all volatiles the residual solid was washed twice with pentane to yield the adduct **2** as a yellow powder (3.52 g, 92% yield). Single crystals suitable for X-ray crystallography were obtained from a saturated benzene solution.

<sup>1</sup>H{<sup>11</sup>B} NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.50 (br, 4H, (ArH)), 2.22 (br s, 12H, Mes(Me<sub>4</sub>)), 1.97 (br s, 6H, Mes(Me<sub>2</sub>)), 1.36 (s, 6H, DAC(Me<sub>2</sub>)).

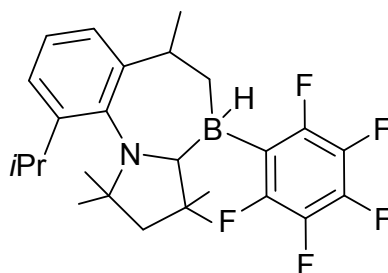
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 195.6 (C, carbene) 171.3 (MesNCO), 147.2 (C<sup>C<sub>6</sub>F<sub>5</sub></sup>), 145.2 (C<sup>C<sub>6</sub>F<sub>5</sub></sup>), 140.3 (C<sup>ArMe</sup>), 136.3 (C<sup>ArH</sup>), 129.4 (C<sup>ArMe</sup>), 128.2 (C<sup>ArH</sup>), 51.7 (NC(O)C(Me)<sub>2</sub>), 22.2 (NC(O)C(Me)<sub>2</sub>), 19.1 (d, J = 3.9 Hz).

<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ -124.7 (dd, J = 17.3 Hz, 6.6 Hz, 2F), -160.2 (t, J = 20.4 Hz, 1F), -164.7 (m, 2F).

<sup>11</sup>B NMR (128.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ = -9.3 (br).

HRMS (LIFDI): calculated for C<sub>30</sub>H<sub>28</sub>BBrF<sub>5</sub>N<sub>2</sub>O<sub>2</sub> ([M-Br]<sup>+</sup>): 633.1349; found: 633.1342.

### Preparation of the C-H activation product **3**



Benzene was slowly added to a mixture of **1** (100 mg, 0.16 mmol) and  $\text{KC}_8$  (47.8 mg, 0.35 mmol) by cannula with stirring. The reaction mixture was then allowed to stir at room temperature for four hours. The excess graphite was filtered off and all the volatiles of the filtrate were removed under vacuum, resulting in an off-white solid. The residual solid was washed twice with pentane to yield **3** as a white powder (58 mg, 70% yield). Colorless single crystals suitable for X-ray crystallography were obtained from a saturated benzene solution.

$^1\text{H}\{^{11}\text{B}\}$  NMR (500.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.12-7.08 (m, 3H, Dip(Ar)), 2.79 (sept,  $J$  = 6.7 Hz, 1H, Dip( $\text{CHMe}_2$ )), 2.46 (m,  $\text{BCH}_2\text{CHMe}$ ), 2.25 (br, 1H, BH), 2.12 (m, 1H,  $\text{BCH}_2\text{CHMe}$ ), 1.43 (d,  $J$  = 6.8 Hz, 3H, Dip( $\text{CHMe}_2$ )), 1.35 (s, 1H, CAAC( $\text{CH}_2$ )), 1.31 (s, 1H, CAAC( $\text{CH}_2$ )), 1.23 (d,  $J$  = 6.9 Hz, 3H, Dip( $\text{CHMe}_2$ )), 1.19 (s, 6H, CAAC(DipNC( $\text{Me}$ ) $_2$ )), 0.99 (s, 3H,  $\text{BCH}_2\text{CHMe}$ ), 0.83 (s, 3H, CAAC(DipNC( $\text{Me}$ ) $_2$ )), 0.79 (s, 3H, CAAC(DipNC( $\text{Me}$ ) $_2$ )).

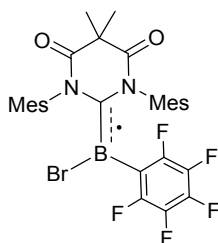
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  148.1 (br,  $\text{C}^{\text{C}_6\text{F}_5}$ ), 143.2 ( $\text{C}^{\text{Ar}}$ ), 142.6 ( $\text{C}^{\text{Ar}(i\text{-Pr})_2}$ ), 139.6 (br,  $\text{C}^{\text{C}_6\text{F}_5}$ ), 136.1 (br,  $\text{C}^{\text{C}_6\text{F}_5}$ ), 134.1 ( $\text{C}^{\text{ArC}(\text{Me})}$ ), 129.3 ( $\text{C}^{\text{ArH}}$ ), 123.9 ( $\text{C}^{\text{ArH}}$ ), 122.0 ( $\text{C}^{\text{ArH}}$ ), 75.8 ( $\text{NC}(\text{Me})_2$ ), 51.5 ( $\text{NC}(\text{Me})_2\text{CH}_2$ ), 34.7 ( $\text{BCH}_2$ ), 29.8, 28.9 (DipNC( $\text{Me}$ ) $_2$ ), 27.9, 26.7, 25.4, 22.3, 21.6, 21.1, 13.9 ( $\text{BCC}(\text{Me})_2$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -129.8 (br, 1F), -161.2 (t,  $J$  = 20.8 Hz, 2F), -165.2 (br, 2F).

$^{11}\text{B}$  NMR (128.4 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 20.5 (d,  $J$  = 93 Hz).

HRMS (LIFDI): calculated for  $\text{C}_{26}\text{H}_{31}\text{BF}_5\text{N}$  ( $[\text{M}-\text{H}]^+$ ): 463.2464; found: 463.2475.

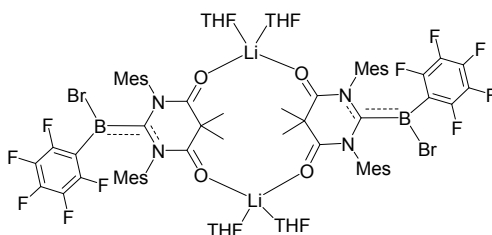
## Preparation of boryl radical **4**



Benzene (15 mL) was added to a mixture of **2** (120 mg, 0.16 mmol) and KC<sub>8</sub> (91 mg, 0.67 mmol) at room temperature. After two hours of vigorous stirring, pentane (20 mL) was added and the reaction mixture was filtered through Celite. All volatiles were removed under reduced pressure, and the crude product was recrystallized from pentane at room temperature to afford **4** as a red solid (51 mg, 48%). X-ray quality single crystals were obtained by slow evaporation of a pentane solution.

**HRMS (LIFDI):** calculated for C<sub>30</sub>H<sub>28</sub>BBrF<sub>5</sub>N<sub>2</sub>O<sub>2</sub> ([M-Br]<sup>+</sup>): 633.1349; found: 633.1342.

## Preparation of **5**



THF (15 mL) was added to a mixture of **2** (100 mg, 0.14 mmol) and Li (4 mg, 0.57 mmol) at room temperature. After twelve hours of stirring, excess Li was filtered off and all the volatiles were removed under reduced pressure to afford **5** as a yellow solid (148 mg, 67%). X-ray quality single crystals were obtained by slow evaporation of a THF solution.

$^1\text{H}\{^{11}\text{B}\}$  NMR (400 MHz,  $d_8$ -THF):  $\delta$  6.63 (s, 4H, Mes(Ar)), 6.35 (s, 4H, Mes(Ar)) 2.22 (s, 12H, Mes( $Me_4$ )), 2.08 (s, 6H, Mes( $Me_2$ )), 2.01 (s, 12H, Mes( $Me_4$ )), 1.95 (s, 6H, Mes( $Me_2$ )), 1.40 (s, 12H, DAC( $Me_4$ )).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $d_8$ -THF):  $\delta$  165.8, 165.1 (MesNCO), 138.6 ( $C^{C6F5}$ ), 136.9 ( $C^{C6F5}$ ), 136.4 ( $C^{C6F5}$ ), 136.2 ( $C^{ArMe}$ ), 136.1 ( $C^{C6F5}$ ), 135.5, 128.8, 128.4, 128.0, 127.4 ( $C^{ArMe}$  or  $C^{ArH}$ ), 47.1 (NC(O)C( $Me$ ) $_2$ ), 19.9, 19.6, 19.4, 18.8, 18.7.

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.5 MHz,  $d_8$ -THF):  $\delta$  -129.2 (d,  $J$  = 19.4 Hz, 2F), -165.5 (t,  $J$  = 19.1 Hz, 1F), -167.6 (m, 2F).

$^{11}\text{B}$  NMR (128.4 MHz,  $d_8$ -THF):  $\delta$  = 17.2 (br).

**HRMS (ESI-MS negative mode):** calculated for  $[\text{C}_{30}\text{H}_{28}\text{BBrF}_5\text{LiN}_2\text{O}_2]^-$ : 633.1347; found: 633.1338.

**Preparation of **5** from **4**:** A mixture of radical **4** (20 mg, 0.03 mmol) and Li (2 mg, 0.28 mmol) in THF (1 mL) was stirred for four hours at room temperature. Once the red colour had diminished and formed a yellow solution, excess Li was removed by filtration. A slow evaporation of the solution resulted in yellow crystals of **5** (23mg, 53%). The compound was characterized by multinuclear NMR spectroscopy.

## X-ray Crystallographic Details

### Crystal structure determination

The crystal data of **1** were collected on a Bruker SMART-APEX diffractometer with a CCD area detector and graphite monochromated  $\text{Mo}_{K\alpha}$  radiation. The structure was solved using intrinsic phasing method,<sup>5</sup> refined with the ShelXL program<sup>6</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **1**:  $\text{C}_{26}\text{H}_{31}\text{BBr}_2\text{F}_5\text{N}$ ,  $M_r = 623.15$ , colourless block,  $0.3 \times 0.2 \times 0.1 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 11.6404(4) \text{ \AA}$ ,  $b = 15.7259(5) \text{ \AA}$ ,  $c = 14.2888(5) \text{ \AA}$ ,  $\beta = 99.812(2)^\circ$ ,  $V = 2577.39(15) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.606 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 3.197 \text{ mm}^{-1}$ ,  $F(000) = 1256$ ,  $T = 100(2) \text{ K}$ ,  $R_I = 0.0399$ ,  $wR^2 = 0.0784$ , 6463 independent reflections [ $2\theta \leq 56.81^\circ$ ] and 324 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1839159**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)



## Crystal structure determination

The crystal data of **2** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo<sub>Kα</sub> radiation. The structure was solved using intrinsic phasing method,<sup>5</sup> refined with the ShelXL program<sup>6</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **2**: C<sub>30</sub>H<sub>28</sub>BBr<sub>2</sub>F<sub>5</sub>N<sub>2</sub>O<sub>2</sub>,  $M_r = 714.17$ , colourless plate, 0.444×0.286×0.15 mm<sup>3</sup>, orthorhombic space group  $P2_12_12_1$ ,  $a = 8.492(5) \text{ \AA}$ ,  $b = 15.351(7) \text{ \AA}$ ,  $c = 22.229(11) \text{ \AA}$ ,  $V = 2898(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.637 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 2.862 \text{ mm}^{-1}$ ,  $F(000) = 1432$ ,  $T = 103(2) \text{ K}$ ,  $R_I = 0.0572$ ,  $wR^2 = 0.0838$ , 5708 independent reflections [ $2\theta \leq 52.044^\circ$ ] and 387 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1839162**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

## Crystal structure determination

The crystal data of **3** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated Mo<sub>K</sub>α radiation. The structure was solved using intrinsic phasing method,<sup>5</sup> refined with the ShelXL program<sup>6</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except H1 were assigned to idealised positions. The coordinates of H1 was refined freely.

Crystal data for **3**: C<sub>29</sub>H<sub>34</sub>BF<sub>5</sub>N,  $M_r = 502.38$ , colourless needle, 0.40×0.10×0.09 mm<sup>3</sup>, monoclinic space group  $P2_1/n$ ,  $a = 7.7509(4)$  Å,  $b = 10.5075(7)$  Å,  $c = 31.1985(19)$  Å,  $\beta = 91.565(2)^\circ$ ,  $V = 2539.9(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.314$  g·cm<sup>-3</sup>,  $\mu = 0.101$  mm<sup>-1</sup>,  $F(000) = 1060$ ,  $T = 100(2)$  K,  $R_1 = 0.0790$ ,  $wR^2 = 0.1369$ , 5185 independent reflections [ $2\theta \leq 52.744^\circ$ ] and 336 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1839161**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

## Crystal structure determination

The crystal data of **4** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo<sub>K</sub>α radiation. The structure was solved using intrinsic phasing method,<sup>5</sup> refined with the SHELXL program<sup>6</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **4**: C<sub>30</sub>H<sub>28</sub>BBrF<sub>5</sub>N<sub>2</sub>O<sub>2</sub>,  $M_r = 634.26$ , red block, 0.20×0.20×0.20 mm<sup>3</sup>, triclinic space group  $P\bar{1}$ ,  $a = 7.394(2)$  Å,  $b = 11.982(4)$  Å,  $c = 16.917(6)$  Å,  $\alpha = 104.90(2)^\circ$ ,  $\beta = 102.465(12)^\circ$ ,  $\gamma = 99.493(19)^\circ$ ,  $V = 1375.2(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.532$  g·cm<sup>-3</sup>,  $\mu = 1.561$  mm<sup>-1</sup>,  $F(000) = 646$ ,  $T = 100(2)$  K,  $R_I = 0.0463$ ,  $wR^2 = 0.0922$ , 5920 independent reflections [ $2\theta \leq 53.798^\circ$ ] and 378 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1839160**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

## Crystal structure determination

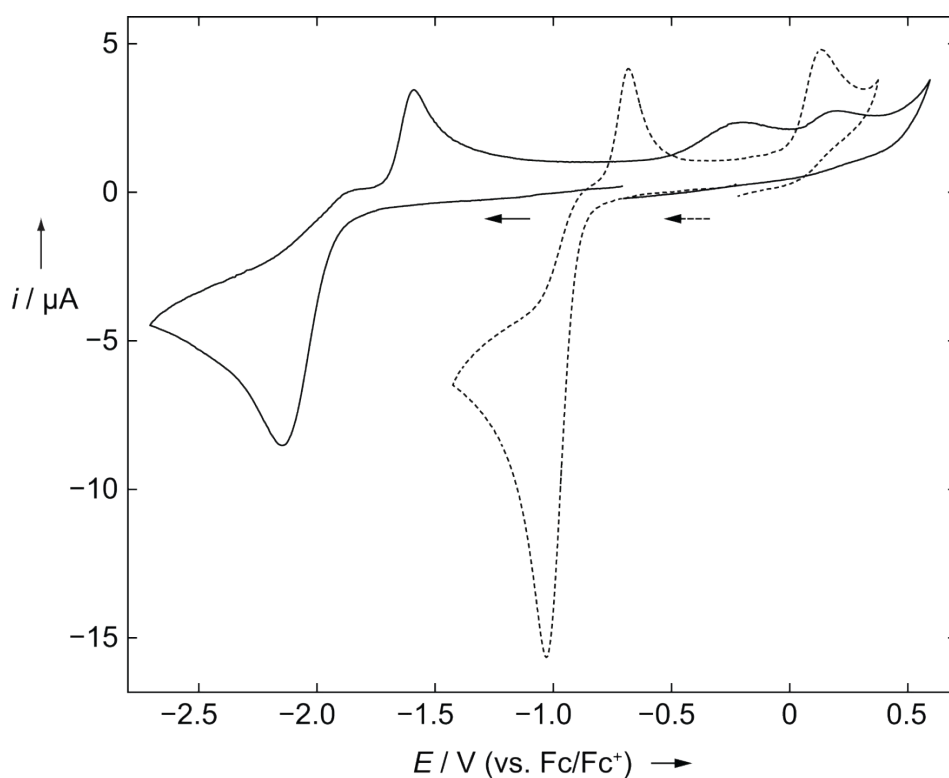
The crystal data of **5** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated Mo<sub>K $\alpha$</sub>  radiation. The structure was solved using intrinsic phasing method,<sup>5</sup> refined with the ShelXL program<sup>6</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **5**: C<sub>84</sub>H<sub>104</sub>B<sub>2</sub>Br<sub>2</sub>F<sub>10</sub>Li<sub>2</sub>N<sub>4</sub>O<sub>10</sub>,  $M_r = 1715.03$ , yellow block, 0.21×0.11×0.06 mm<sup>3</sup>, monoclinic space group  $P2_1/c$ ,  $a = 10.2637(10)$  Å,  $b = 24.161(3)$  Å,  $c = 16.6779(17)$  Å,  $\beta = 97.972(4)^\circ$ ,  $V = 4095.8(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.391$  g·cm<sup>-3</sup>,  $\mu = 1.073$  mm<sup>-1</sup>,  $F(000) = 1784$ ,  $T = 100(2)$  K,  $R_I = 0.0853$ ,  $wR^2 = 0.1031$ , 8075 independent reflections [ $2\theta \leq 52.04^\circ$ ] and 542 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1839163**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

## Electrochemical details

Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a *Vycor* tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocenium ( $[\text{Cp}_2\text{Fe}]^{+/0}$ ) redox couple by using ferrocene as an internal standard. Tetra-*n*-butylammonium hexafluorophosphate ( $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ ) was employed as the supporting electrolyte. Compensation for resistive losses ( $iR$  drop) was employed for all measurements.



**Fig. S1.** Cyclic voltammograms of **1** (solid line) and **2** (dashed line) in THF/0.1 M  $[\text{n-Bu}_4\text{N}][\text{PF}_6]$  measured at  $250 \text{ mV s}^{-1}$ . Formal potentials: **1**:  $E_{\text{pc}} = -2.15 \text{ V}$ ,  $E_{\text{pa}} = -1.59 \text{ V}$ ,  $E_{\text{pa}} = -0.21 \text{ V}$ ,  $E_{\text{pa}} = 0.19 \text{ V}$ ; **2**:  $E_{\text{pc}} = -1.01 \text{ V}$ ,  $E_{\text{pa}} = -0.68 \text{ V}$ ;  $E_{\text{pa}} = 0.13 \text{ V}$  (relative to the  $\text{Fc}/\text{Fc}^+$  couple).

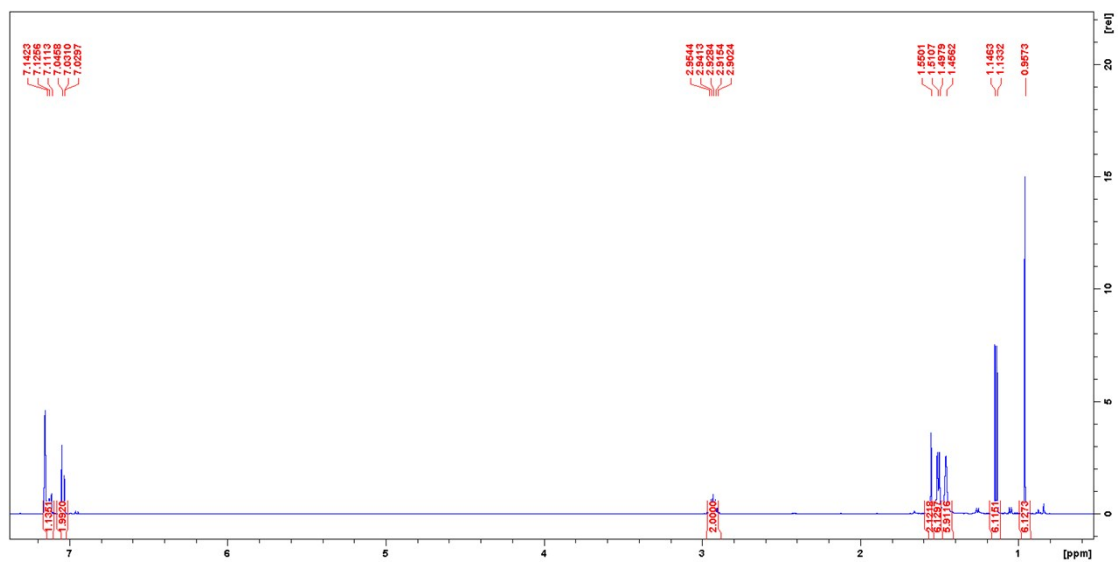


Fig. S2.  $^1\text{H}$  NMR of compound **1** in  $\text{C}_6\text{D}_6$  at  $70\text{ }^\circ\text{C}$ .

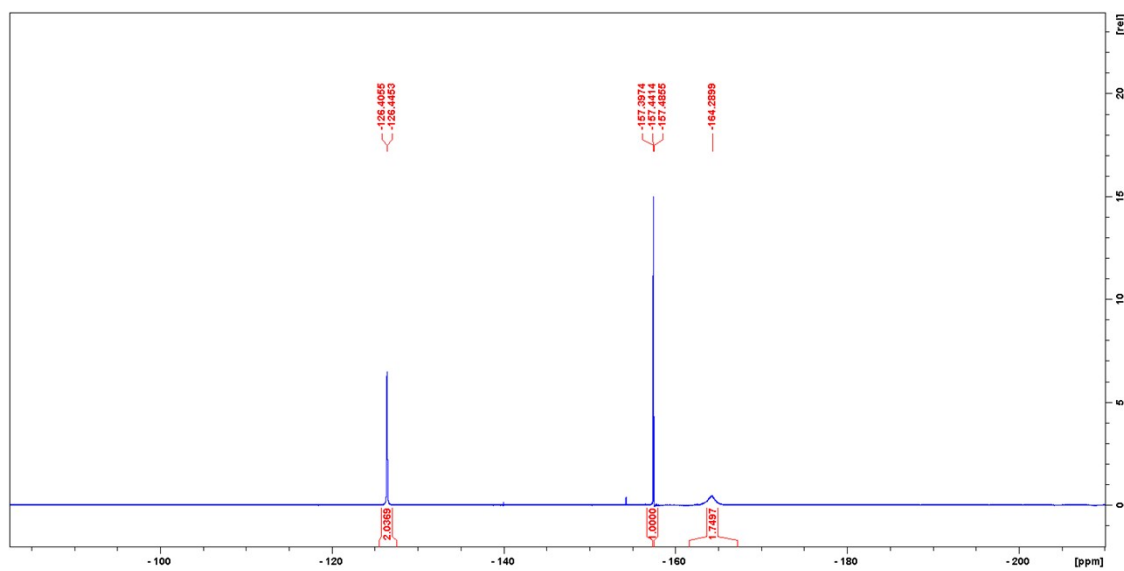
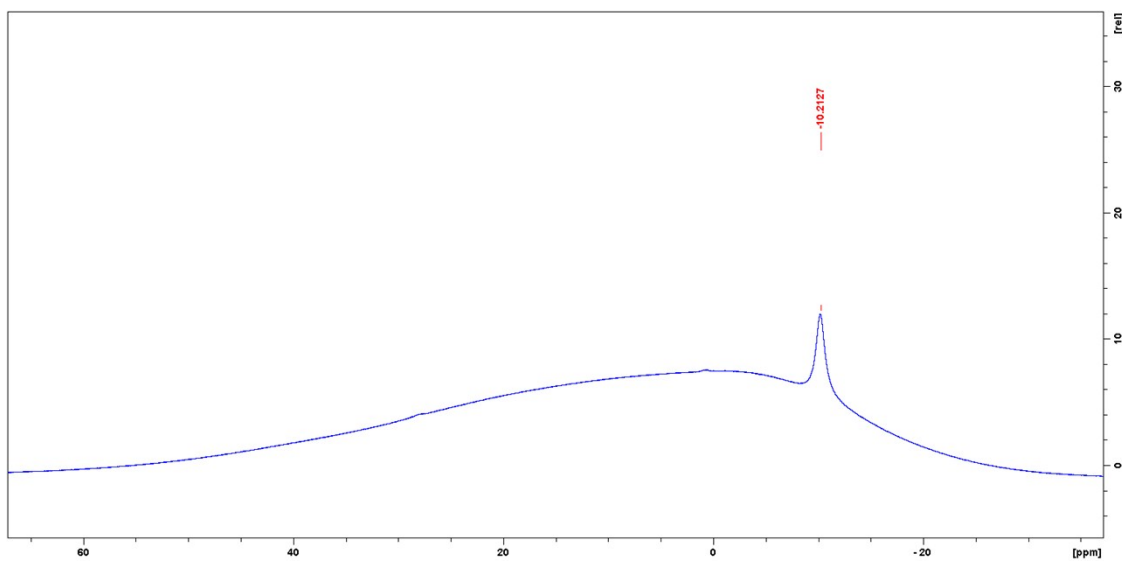
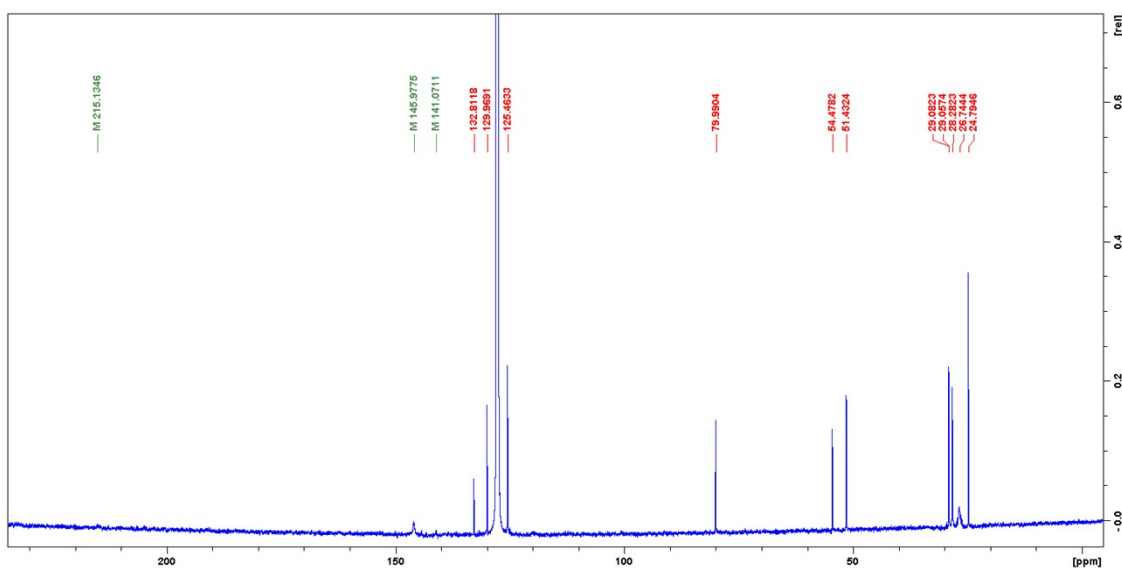


Fig. S3.  $^9\text{F}\{^1\text{H}\}$  NMR of compound **1** in  $\text{C}_6\text{D}_6$ .



**Fig. S4.**  $^{11}\text{B}$  NMR of compound **1** in  $\text{C}_6\text{D}_6$ .



**Fig. S5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR of compound **1** in  $\text{C}_6\text{D}_6$ .

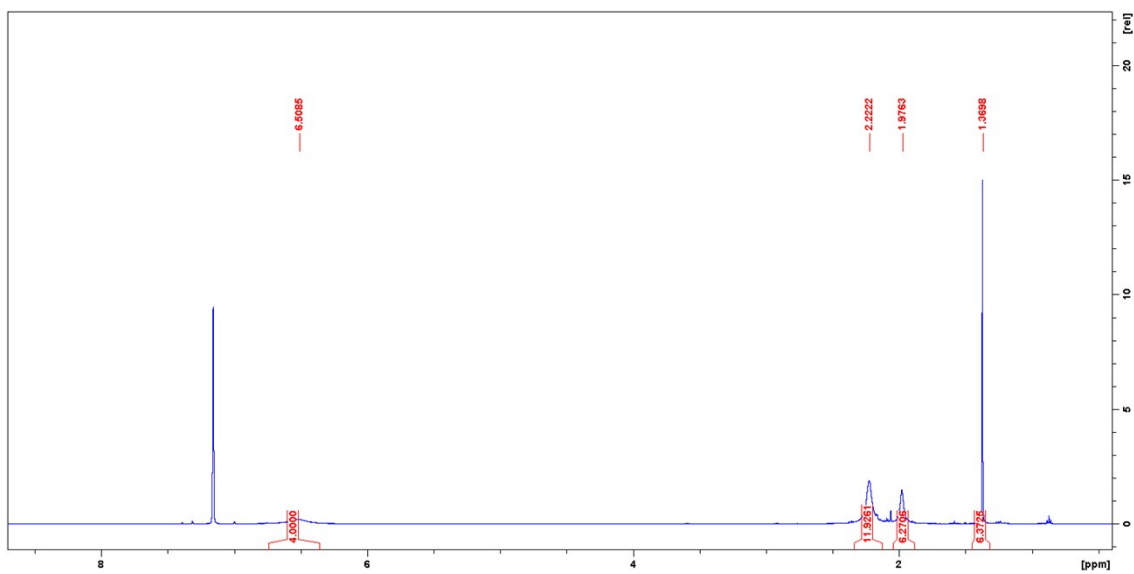


Fig. S6. <sup>1</sup>H NMR of compound 2 in C<sub>6</sub>D<sub>6</sub>.

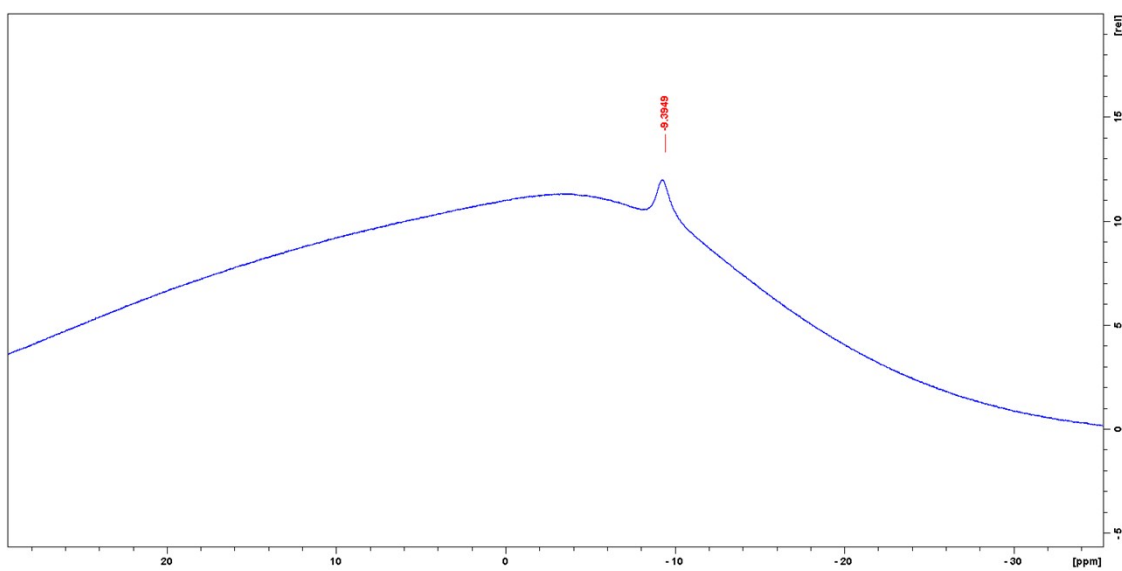


Fig. S7. <sup>11</sup>B NMR of compound 2 in C<sub>6</sub>D<sub>6</sub>.



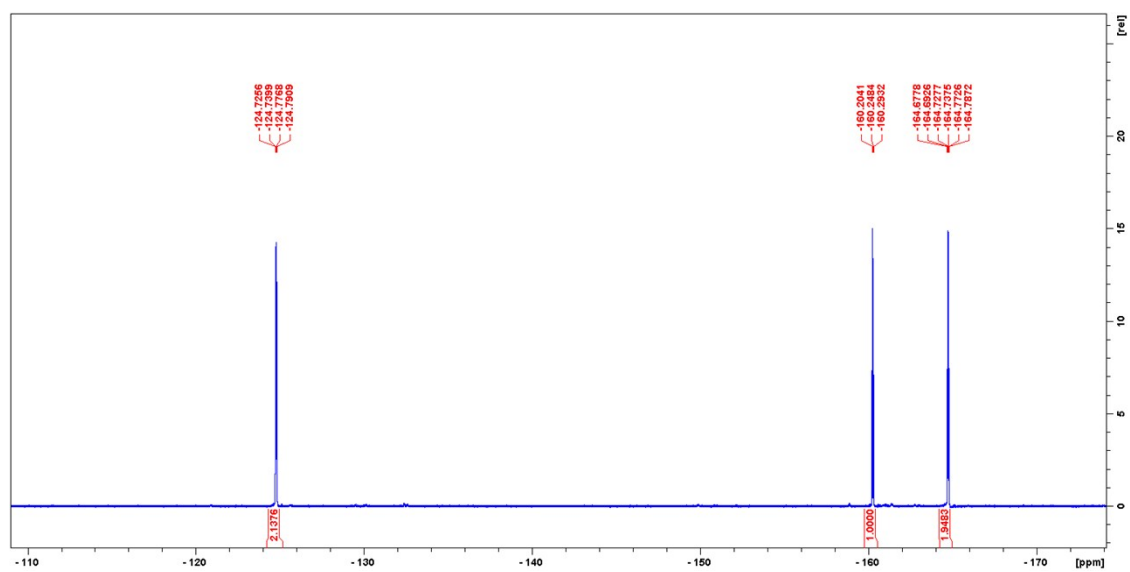


Fig. S8.  $^9\text{F}\{^1\text{H}\}$  NMR of compound 2 in  $\text{C}_6\text{D}_6$ .

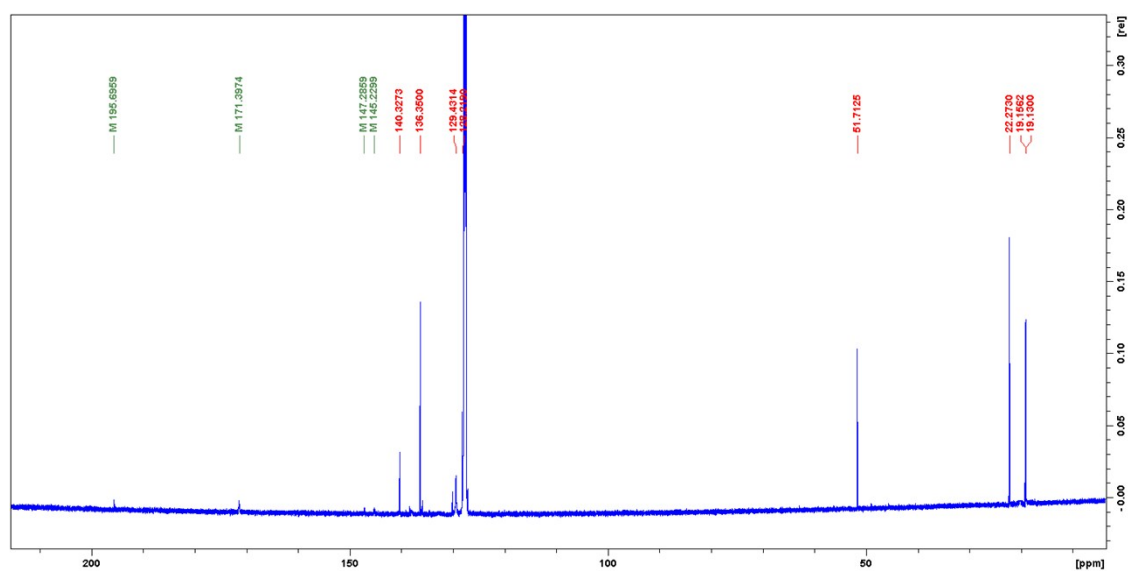


Fig. S9.  $^{13}\text{C}\{^1\text{H}\}$  NMR of compound 2 in  $\text{C}_6\text{D}_6$ .

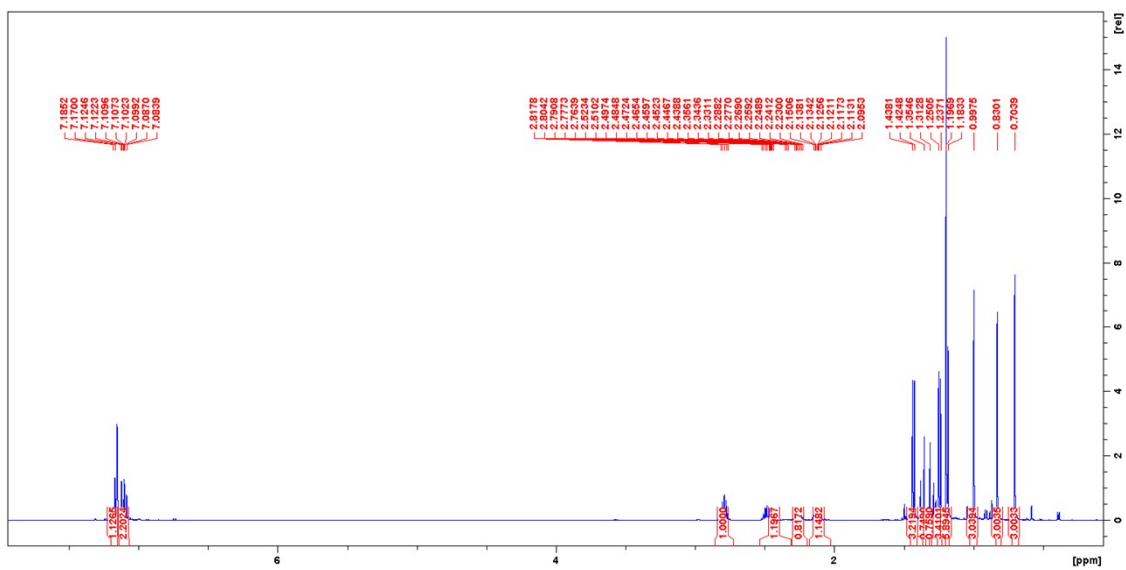


Fig. S10.  $^1\text{H}\{^{11}\text{B}\}$  NMR of compound **3** in  $\text{C}_6\text{D}_6$

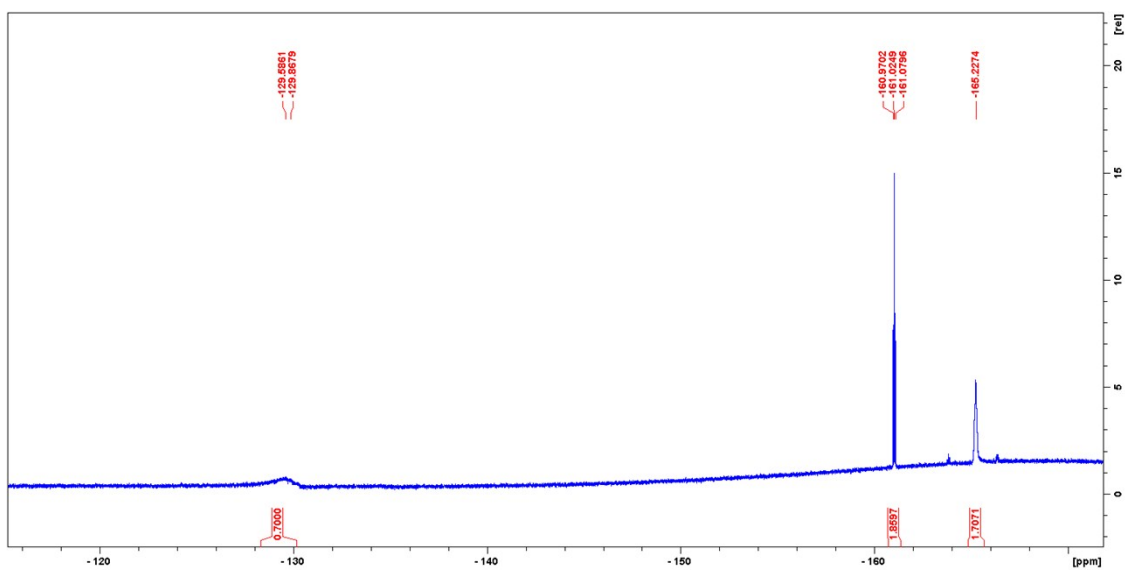


Fig. S11.  $^9\text{F}\{^1\text{H}\}$  NMR of compound **3** in  $\text{C}_6\text{D}_6$

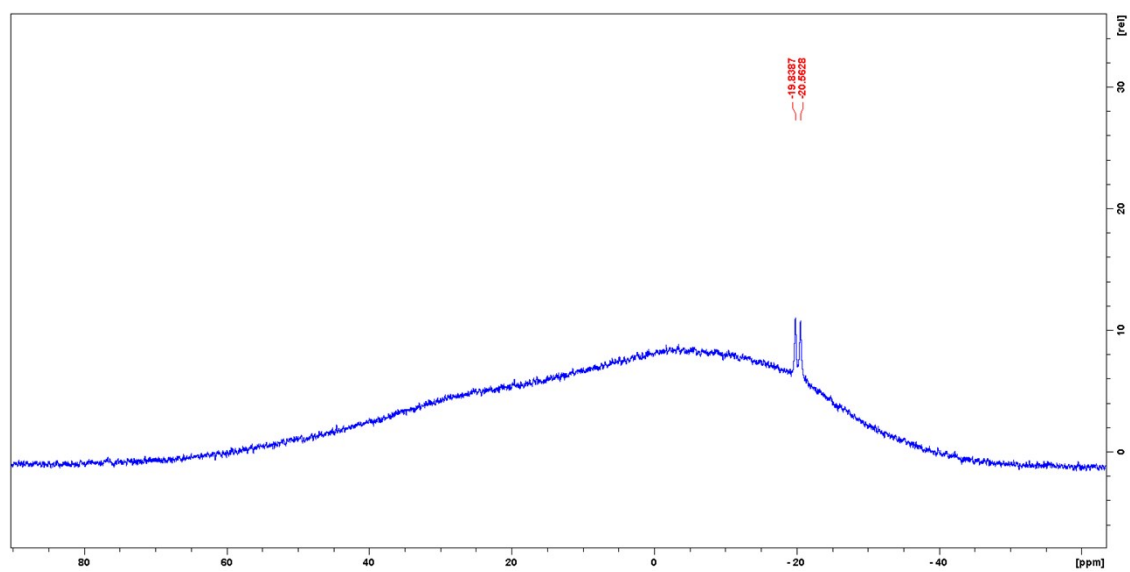


Fig. S12. <sup>11</sup>B NMR of compound 3 in C<sub>6</sub>D<sub>6</sub>.

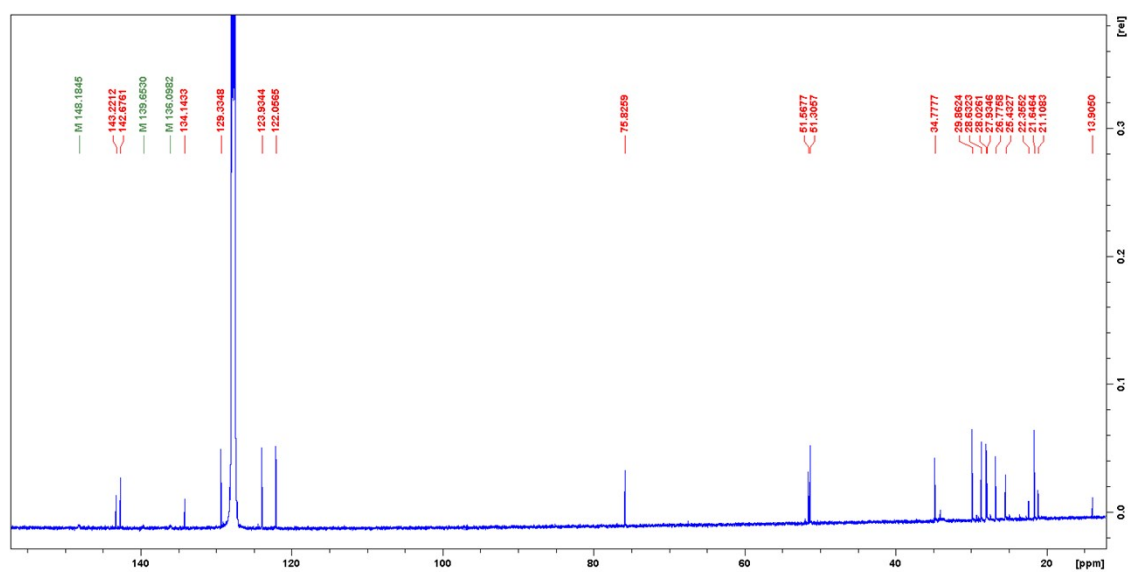


Fig. S13. <sup>13</sup>C{<sup>1</sup>H} NMR of compound 3 in C<sub>6</sub>D<sub>6</sub>.

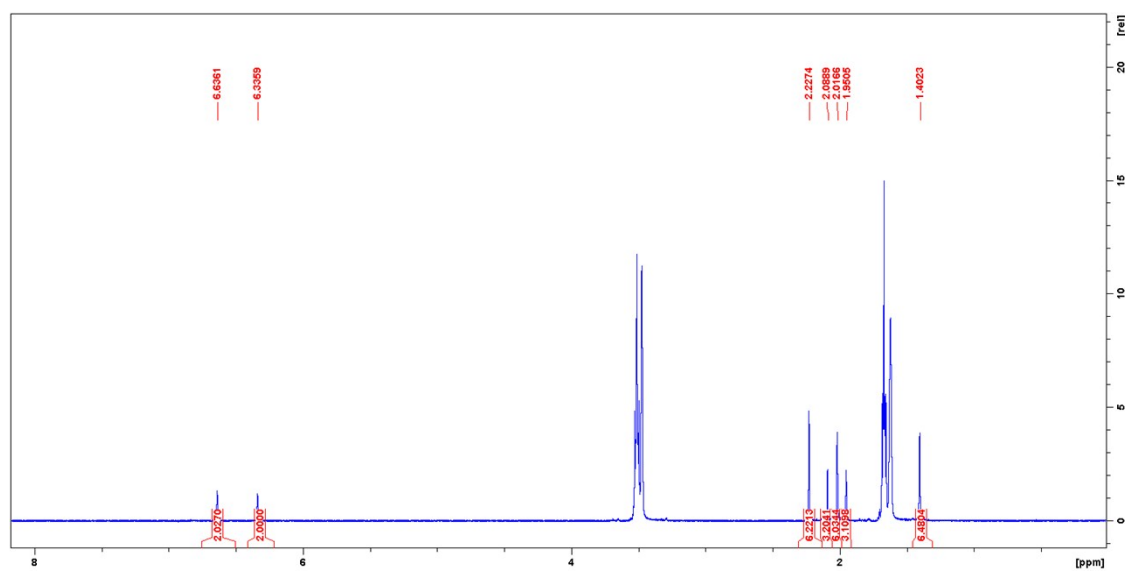


Fig. S14.  $^1\text{H}$  NMR of compound **5** in  $d_8$ -THF.

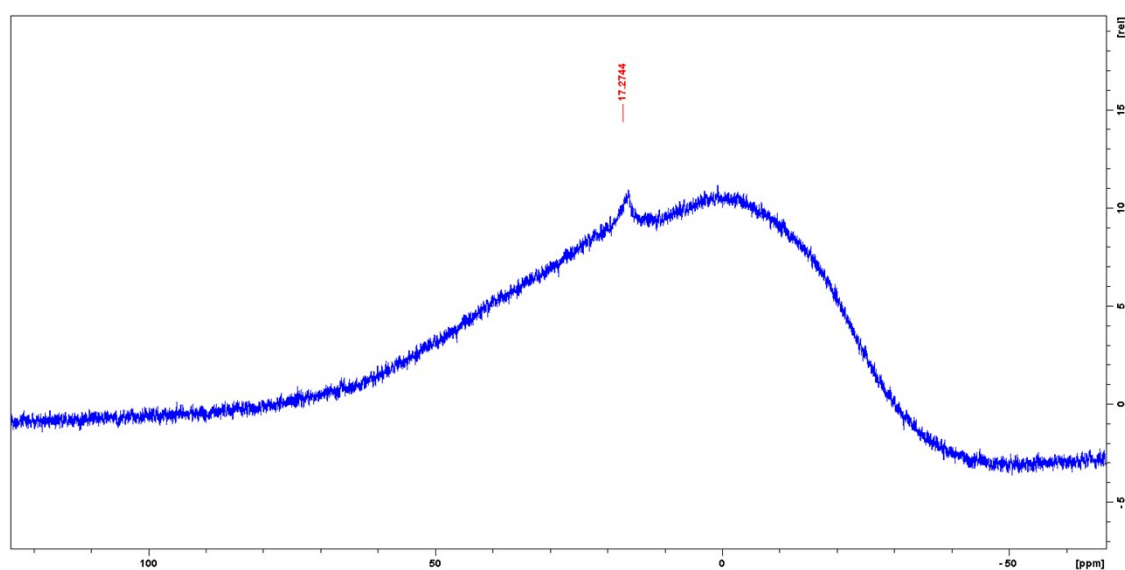
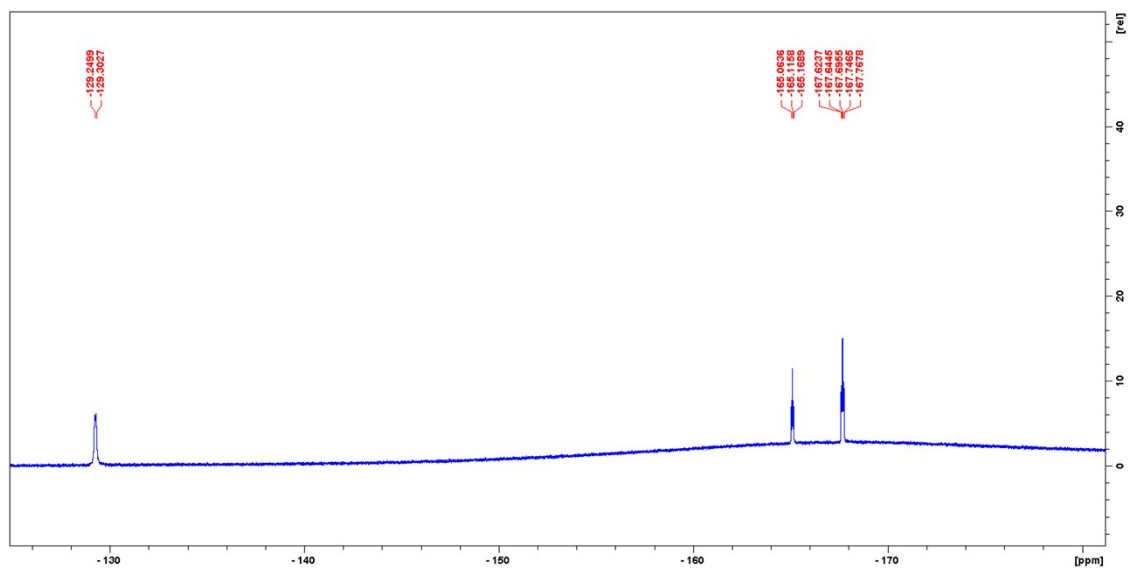
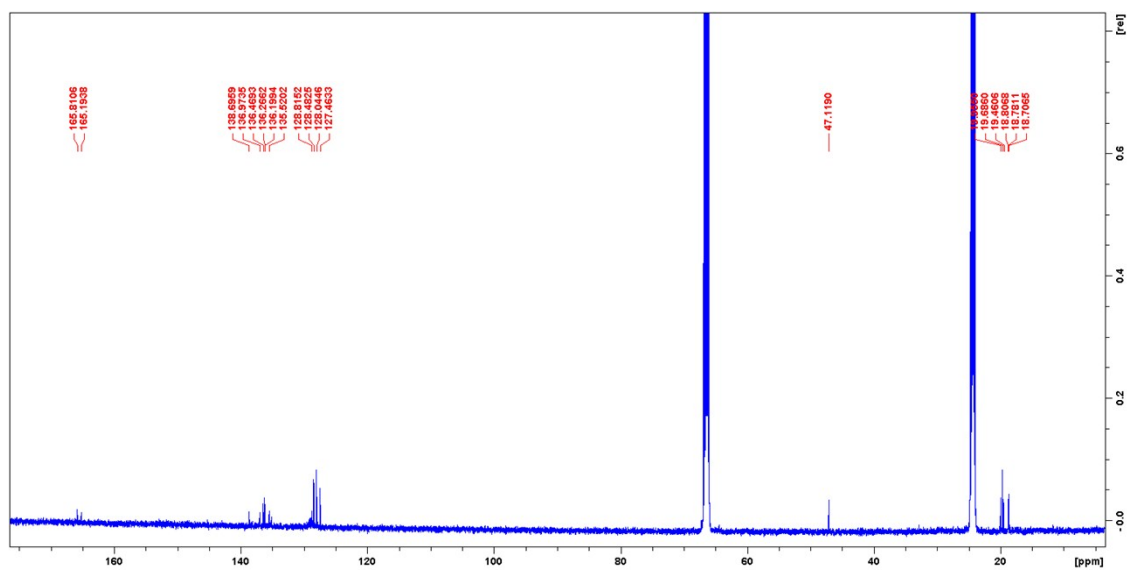


Fig. S15.  $^{11}\text{B}\{^1\text{H}\}$  NMR of compound **5** in  $d_8$ -THF.



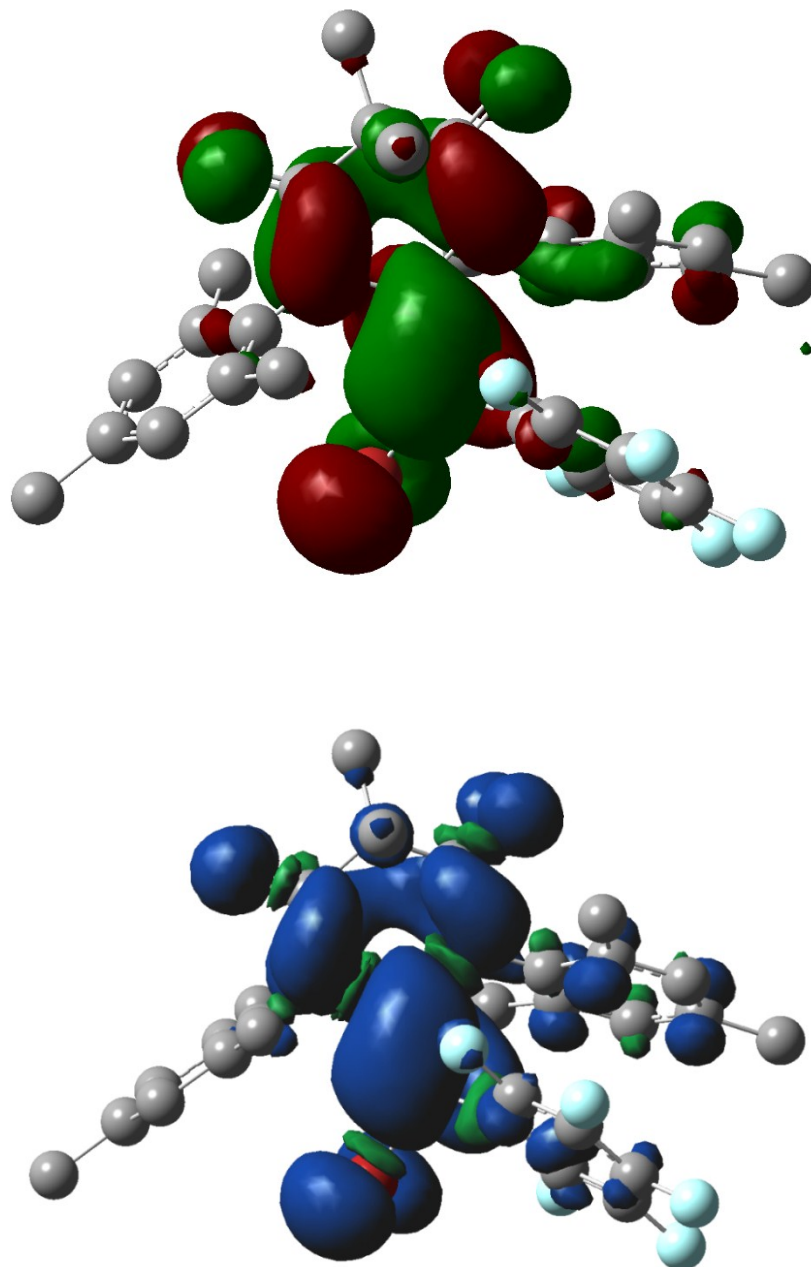
**Fig. S16.**  $^9\text{F}\{^1\text{H}\}$  NMR of compound **5** in  $d_8$ -THF.



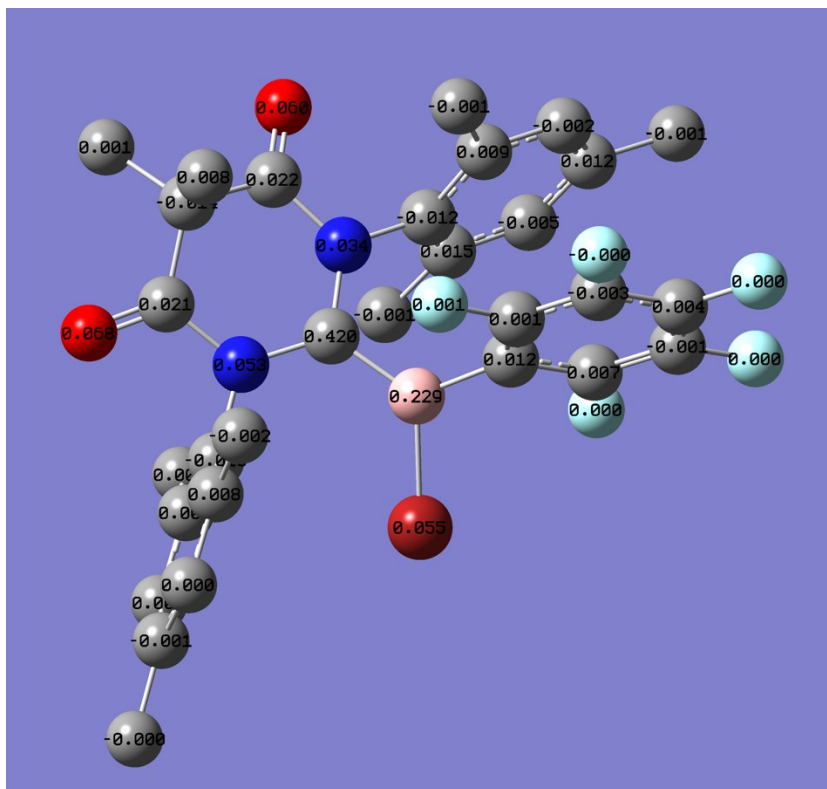
**Fig. S17.**  $^{13}\text{C}\{^1\text{H}\}$  NMR of compound **5** in  $d_8$ -THF.

## Computational Details

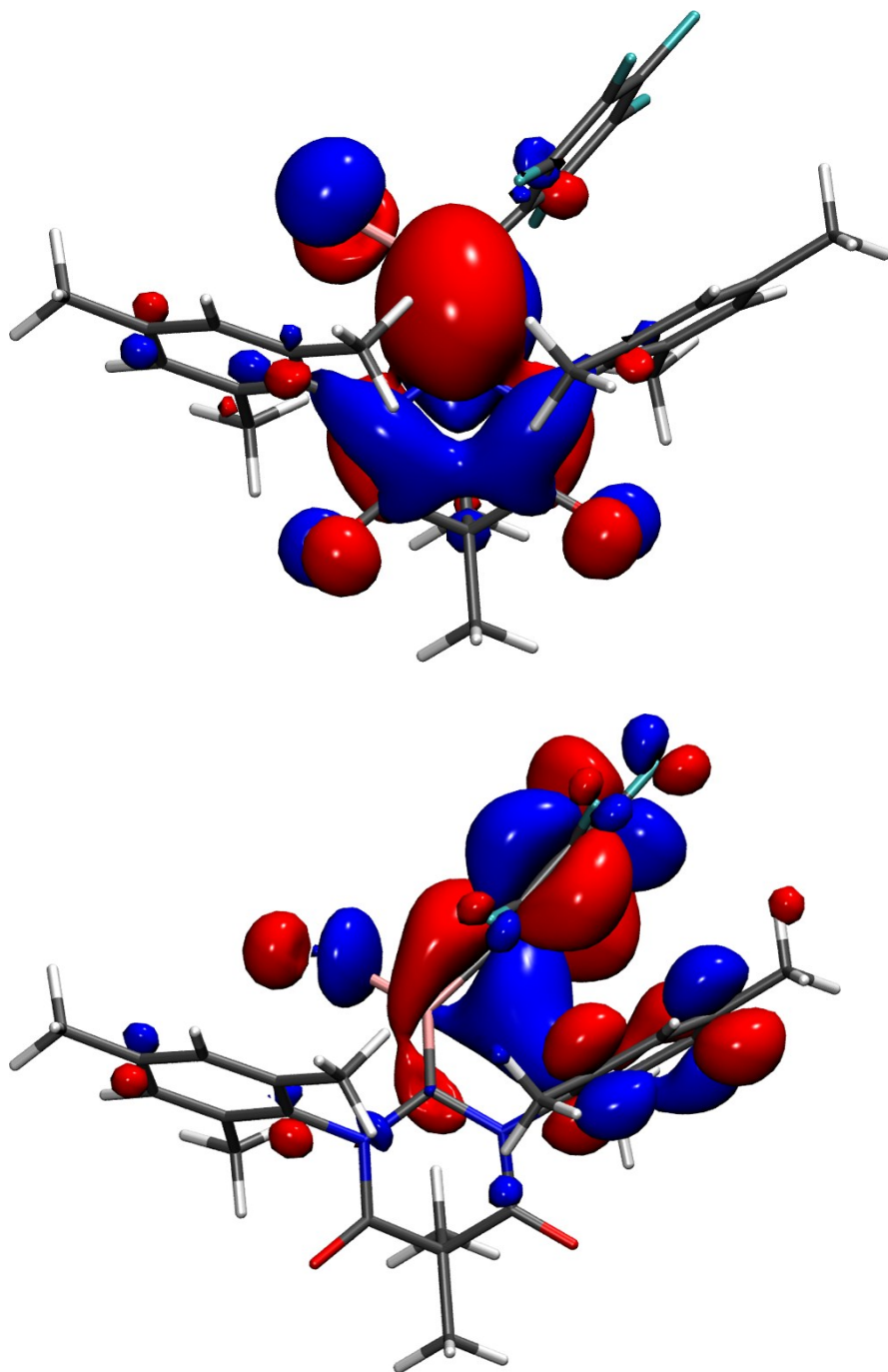
All calculations were performed using the Gaussian 09<sup>7</sup> suite of programs and unrestricted methods. The uB3LYP hybrid functional<sup>8</sup> was used in conjunction with the Def2-TZVP(P) basis set for all atoms.<sup>9</sup> The optimized geometry was confirmed to have all-real frequencies by vibrational analysis at the same level of theory.



**Fig. S18.** Kohn-Sham SOMO of **4** (top) and spin density (SCF, bottom). Hydrogen atoms omitted for clarity.



**Fig. S19.** Values for the spin density of **4** obtained from a Mulliken spin population analysis.



**Fig. S20.** Kohn-Sham HOMO (top) and LUMO (bottom) of **5**.



### Cartesian Coordinates of 4

C	-2.17514800	2.20271500	11.61553400
N	-2.36366000	0.86808400	11.24889600
C	-3.11764400	-0.04878700	12.00097500
C	-3.61262800	0.40443400	13.36338500
C	-3.89029700	1.89424700	13.37560100
N	-3.03711800	2.69581200	12.60403700
O	-3.29647700	-1.17637900	11.59933600
O	-4.76907400	2.38714000	14.04608600
C	-2.48825300	0.11452400	14.39597500
H	-2.28555200	-0.95556200	14.41309400
H	-2.82123100	0.42157800	15.38662400
H	-1.56376700	0.64001200	14.16193300
C	-4.87751700	-0.37027500	13.74677800
H	-5.68515500	-0.18048300	13.04101700
H	-5.21281700	-0.06156200	14.73355500
H	-4.66748400	-1.43648000	13.74533900
C	-1.69564000	0.26397100	10.10082300
C	-0.43327700	-0.30836400	10.26770400
C	0.16255700	-0.91210500	9.16250700
H	1.14792400	-1.34704800	9.27781700
C	-0.47427100	-0.98547400	7.92858900
C	-1.75567400	-0.45158000	7.82065600
H	-2.28367100	-0.52441700	6.87733900
C	-2.38913000	0.16995200	8.89147300
C	0.27569700	-0.31615500	11.59429200
H	1.26797500	-0.75186900	11.49249800
H	-0.27191100	-0.91276700	12.32690100
H	0.39297000	0.68358300	12.00975600
C	0.20168900	-1.61720300	6.74087000
H	-0.51357900	-2.14896000	6.11283600
H	0.97307000	-2.32217800	7.04979100
H	0.68129200	-0.85886900	6.11670100
C	-3.78560900	0.70250700	8.72984700
H	-3.83301700	1.77584100	8.91288200
H	-4.47537300	0.21606400	9.42152800
H	-4.14599800	0.52198500	7.71879100
C	-3.25556000	4.12820600	12.73958200
C	-3.94098300	4.81846400	11.73122100
C	-4.14905500	6.18631700	11.89463600
H	-4.67383900	6.72551700	11.11544500
C	-3.72078600	6.87087000	13.02622700

C	-3.09832800	6.13860300	14.03383800
H	-2.79046900	6.64312700	14.94200500
C	-2.86918400	4.77081800	13.92425100
C	-4.48655900	4.13721800	10.50504700
H	-5.25243400	4.75767400	10.04298100
H	-4.93699100	3.17427000	10.74453500
H	-3.71136300	3.96423100	9.75650700
C	-3.91996900	8.35689900	13.15685400
H	-3.05990600	8.90019100	12.75707000
H	-4.03691600	8.65324200	14.19920500
H	-4.79953400	8.68995900	12.60618700
C	-2.27007400	4.03455000	15.09134700
H	-1.60158800	3.23220600	14.78714300
H	-3.06224900	3.58646700	15.69467900
H	-1.71090200	4.71688200	15.72970700
Br	-0.53313000	3.08299400	9.15927000
B	-1.12197200	3.14989400	11.01843200
C	-0.36694400	4.26472400	11.84533100
C	0.40855200	3.93996400	12.95490500
C	1.18229900	4.86202200	13.64261500
C	1.19207000	6.18320000	13.22376700
C	0.43360800	6.55691500	12.12282600
C	-0.31808700	5.60455000	11.45464000
F	0.44327300	2.66798100	13.40263800
F	1.91017400	4.49161200	14.69990100
F	1.91907800	7.08871300	13.87580200
F	0.42969400	7.83180300	11.72564400
F	-1.03752700	6.02478600	10.40769900

### Cartesian Coordinates of 5

C	-1.930338	2.044267	11.867712
N	-2.221070	0.707580	11.377414
C	-3.095621	-0.132459	12.019387
C	-3.566295	0.326817	13.397723
C	-3.911641	1.812891	13.345585
N	-3.073939	2.593574	12.596261
O	-3.469216	-1.197538	11.541706
O	-4.874138	2.269986	13.954548
C	-2.415702	0.117687	14.412927
H	-2.166288	-0.942549	14.469014
H	-2.734219	0.448689	15.402050
H	-1.520261	0.669576	14.131377
C	-4.789679	-0.479649	13.832357
H	-5.613309	-0.355118	13.131413
H	-5.124169	-0.140290	14.810586
H	-4.539003	-1.537878	13.871121
C	-1.627551	0.167769	10.172004
C	-0.737019	-0.913755	10.274711
C	-0.202362	-1.456872	9.111967
H	0.492208	-2.285128	9.200319
C	-0.516510	-0.963294	7.849610
C	-1.411550	0.094983	7.776442
H	-1.690837	0.490589	6.806048
C	-1.983074	0.664154	8.914735
C	-0.337105	-1.493899	11.602083
H	0.537320	-2.134569	11.488087
H	-1.148461	-2.091781	12.021260
H	-0.090149	-0.710451	12.317359
C	0.115525	-1.541103	6.609523
H	-0.489889	-1.340255	5.724501
H	0.243416	-2.621934	6.693051
H	1.105518	-1.110584	6.432453
C	-2.967691	1.782807	8.758365
H	-2.553621	2.718112	9.133645
H	-3.879461	1.585753	9.321446
H	-3.234323	1.917256	7.709892
C	-3.274143	4.015930	12.768528
C	-4.015212	4.753883	11.841026
C	-4.185197	6.123336	12.053443
H	-4.752978	6.692413	11.325525
C	-3.670783	6.768907	13.169052
C	-3.006719	5.994176	14.116866

H	-2.633884	6.463338	15.020587
C	-2.814559	4.627490	13.947446
C	-4.675007	4.125676	10.646501
H	-5.611064	4.639706	10.424707
H	-4.893724	3.075193	10.818169
H	-4.042030	4.194760	9.761959
C	-3.821241	8.256975	13.350292
H	-2.935426	8.787868	12.990539
H	-3.951893	8.519768	14.401347
H	-4.678355	8.640297	12.795252
C	-2.176651	3.831506	15.052843
H	-1.477986	3.088690	14.675938
H	-2.948083	3.304066	15.618984
H	-1.640332	4.486372	15.739216
Br	0.987822	1.949646	10.849566
B	-0.675370	2.758342	11.680315
C	-0.298963	4.272776	12.008214
C	0.525982	4.618609	13.075837
C	0.967601	5.910813	13.311976
C	0.594254	6.927483	12.447422
C	-0.208286	6.629998	11.359033
C	-0.629353	5.323709	11.157978
F	0.933754	3.675664	13.945231
F	1.746724	6.193936	14.370344
F	1.004667	8.187260	12.664027
F	-0.566861	7.610684	10.513228
F	-1.379603	5.098145	10.063630

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