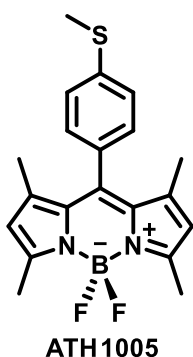


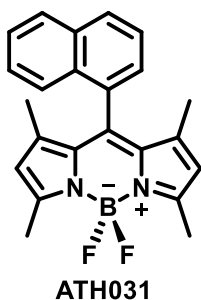
## SUPPLEMENTARY DATAS

### 8-(4-methylthiophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene



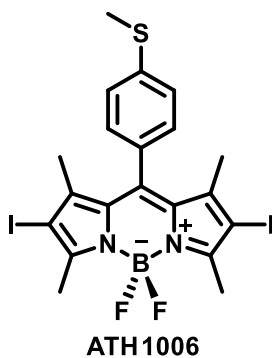
Purification by column chromatography on silica gel (*n*-hexane/CHCl<sub>3</sub> 7:3) yielded (777.6 mg, 42%) as a pink solid. **UV-Vis** (EtOH)  $\lambda$ /nm 499. **m.p.** (°C) = 186-187. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.28 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.91 (s, 2H), 2.48 (s, 6H), 2.47 (s, 3H), 1.36 (s, 6H). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$ : -143.7 (q, *J* = 32.8, 2F). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.6, 143.2, 140.9, 140.2, 131.5, 128.6, 126.6, 121.3, 119.0, 29.8, 15.5, 14.8. **HRMS** (ESI<sup>+</sup>) *m/z* calcd. for C<sub>20</sub>H<sub>21</sub>BF<sub>2</sub>N<sub>2</sub>S [M+H]<sup>+</sup>: 371.1565, found: 371.1563. **ATR-FTIR**  $\nu$  (cm<sup>-1</sup>) = 2969, 2918, 1595, 1535, 1398, 1297, 1181, 1153, 1046, 970, 816, 757, 699, 578, 474.

### 8-(naphthalen-1-yl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene



Purification by column chromatography on silica gel (*n*-hexane/CHCl<sub>3</sub> 8:2) yielded (523.9 mg, 28%) as an orange solid. **UV-Vis** (EtOH)  $\lambda$ /nm 501. **m.p.** (°C) = 223-225. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.87 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.30 (m, 2H), 5.86 (s, 2H), 2.51 (s, 6H), 0.97 (s, 6H). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$ : -143.50 (q, *J* = 31.7 Hz, 2F). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.62, 159.99, 148.27, 143.15, 135.29, 133.86, 131.98, 129.89, 129.21, 126.78, 126.43, 121.23, 114.99, 133.59, 13.35. **HRMS** (ESI<sup>+</sup>) *m/z* calcd. for C<sub>23</sub>H<sub>21</sub>BF<sub>2</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 375.1844, found: 375.1846. **ATR-FTIR**  $\nu$  (cm<sup>-1</sup>) = 3055, 2963, 2919, 1606, 1541, 1504, 1399, 1306, 1190, 1153, 1061, 971, 786, 630, 548, 474.

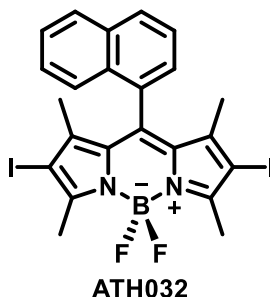
### 8-(4-methylthiophenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene



Purification by column chromatography on silica gel (*n*-hexane/CHCl<sub>3</sub> 3:1) yielded **2a** (78.1 mg, 91%) as a purple solid. **m.p.** (°C) = 204-206. **UV-Vis** (EtOH)  $\lambda$ /nm 511. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.30 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 2.57 (s, 6H), 2.49 (s, 3H), 1.38 (s, 6H). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$ : -145.7 (q, *J* = 32.0, 2F). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 156.9, 145.4, 141.2, 141.0, 131.6, 131.0, 128.4, 128.3, 126.7, 126.6, 85.8, 15.4. **HRMS** (ESI<sup>+</sup>) *m/z* calcd. for

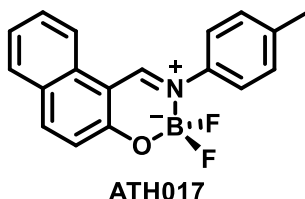
C<sub>20</sub>H<sub>19</sub>F<sub>2</sub>I<sub>2</sub>N<sub>2</sub>S [M+H]<sup>+</sup>: 622.9496 found: 622.9486. **ATR-FTIR**  $\nu$  (cm<sup>-1</sup>) = 2918, 1678, 1523, 1392, 1304, 1174, 1079, 980, 755, 698, 585, 524, 442.

**8-(naphthalen-1-yl)-2,6-diiodo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3*a*,4*a*-diazas-indacene**



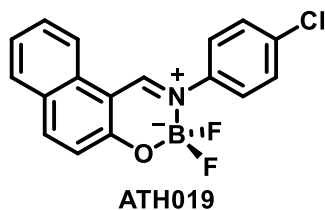
Purification by column chromatography on silica gel (*n*-hexane/CHCl<sub>3</sub> 4:1) yielded (58.7 mg, 68%) as a purple solid. **UV-Vis** (EtOH) $\lambda$ /nm 535. **m.p.** (°C) = 210-211. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (ddd, *J* = 8.3, 2.2, 1.0 Hz, 1H), 8.14 (t, *J* = 1.8 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.60 (dt, *J* = 7.6, 1.4 Hz, 1H), 2.59 (s, 6H), 1.30 (s, 6H). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -142.98 (q, *J* = 32.0, 2F). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.75, 160.03, 148.63, 143.67, 136.07, 132.10, 131.29, 129.25, 129.11, 127.32, 126.50, 120.38, 120.35, 115.12, 13.58, 13.31. **HRMS** (ESI<sup>+</sup>) *m/z* calcd. for C<sub>23</sub>H<sub>19</sub>BF<sub>2</sub>I<sub>2</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 626.9777, found: 626.9767. **ATR-FTIR**  $\nu$  (cm<sup>-1</sup>) = 2970, 1521, 1398, 1307, 1173, 1090, 988, 780, 748, 630, 586, 522.

**3,3-difluoro-2-(*p*-tolyl)-3*H*-2*a*,3*a*-naphtho[1,2-*e*][1,3,2]oxazaborinine**



Purification by column chromatography on silica gel (dichloromethane) yielded (482.2 mg, 78%) as a green solid. **UV-Vis** (EtOH) $\lambda$ /nm 449. **m.p.** (°C) = 158-159. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.01 (s, 1H), 7.99 (dd, *J* = 26.3, 8.7 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 9.1 Hz, 1H), 2.36 (s, 3H). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -132.07 (q, *J* = 13.3, 2F). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.66, 157.88, 140.95, 140.63, 139.46, 131.65, 130.42, 129.91, 129.60, 128.23, 125.23, 123.57, 120.70, 119.26, 108.80, 21.29. **HRMS** (ESI<sup>+</sup>) *m/z* calcd. for C<sub>18</sub>H<sub>14</sub>BF<sub>2</sub>NO [M+H]<sup>+</sup>: 309.1137, found: 309.1138. **ATR-FTIR**  $\nu$  (cm<sup>-1</sup>) = 1625, 1549, 1360, 1204, 1126, 1037, 899, 821, 752, 589, 488, 420.

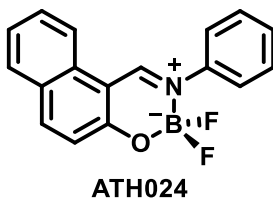
**3,3-difluoro-2-(4-chlorophenyl)-3*H*-2*a*,3*a*-naphtho[1,2-*e*][1,3,2]oxazaborinine**



Purification by column chromatography on silica gel (dichloromethane) yielded (481.1 mg, 73%) as a green solid. **UV-Vis** (EtOH) $\lambda$ /nm 461. **m.p.** (°C) = 162-164. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.00 (s, 1H), 8.04 (d, *J* = 9.1 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 3H), 7.22 – 7.19 (m, 1H). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -131.65 (q, *J* = 13.1, 2F). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.12, 158.27, 141.68, 141.43, 135.26, 131.55, 130.01, 129.82, 128.23, 125.45, 125.14, 120.61, 119.25, 108.81. **HRMS** (ESI<sup>+</sup>) *m/z* calcd. for C<sub>20</sub>H<sub>22</sub>BF<sub>2</sub>N<sub>2</sub>S

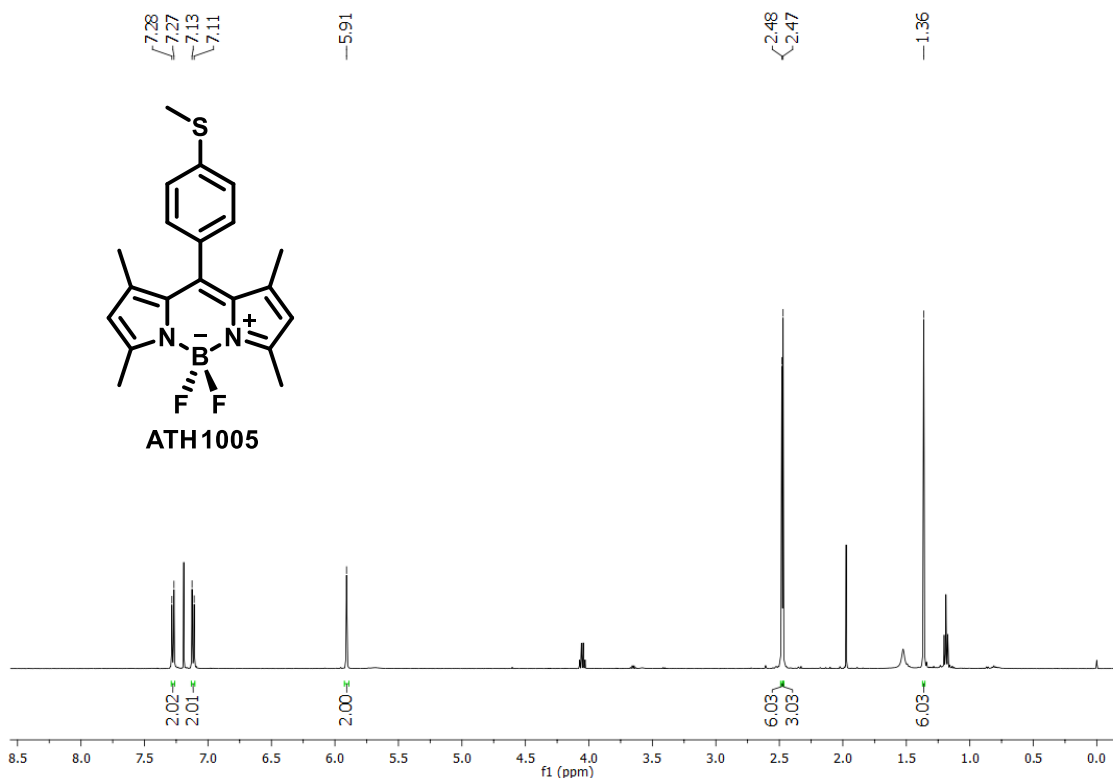
[M+H]<sup>+</sup>: 329.0590, found: 329.0591. **ATR-FTIR**  $\nu$  (cm<sup>-1</sup>) = 1625, 1552, 1466, 1367, 1204, 1078, 1045, 984, 828, 746, 587, 487, 427.

**3,3-difluoro-2-phenyl-3*H*-2a,3a-naphtho[1,2-*e*][1,3,2]oxazaborinine**



Purification by column chromatography on silica gel (dichloromethane) yielded (430.8 mg, 73%) as a yellow solid. **UV-Vis** (EtOH)  $\lambda$ /nm 460. **m.p.** (°C) = 140-141. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.09 (d, *J* = 2.9 Hz, 1H), 8.08 (d, *J* = 9.1 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.65–7.57 (m, 3H), 7.54–7.44 (m, 4H), 7.29–7.25 (m, 1H). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>)  $\delta$ : -131.34 (q, *J* = 13.0, 2F). **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 162.69, 158.30, 143.00, 141.07, 130.00, 129.88, 129.63, 125.24, 124.40, 120.86, 120.63, 119.29, 108.76. **HRMS** (ESI<sup>+</sup>) *m/z* calcd. for C<sub>20</sub>H<sub>22</sub>BF<sub>2</sub>N<sub>2</sub>S [M+H]<sup>+</sup>: 295.0980, found: 295.09802. **ATR-FTIR**  $\nu$  (cm<sup>-1</sup>) = 1606, 1552, 1463, 1395, 1309, 1208, 1046, 987, 824, 748, 583, 511, 419.

**NMR, HRMS and ATR-FTIR spectra**



**Figure S1:** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of compound **ATH1005 (D)**.

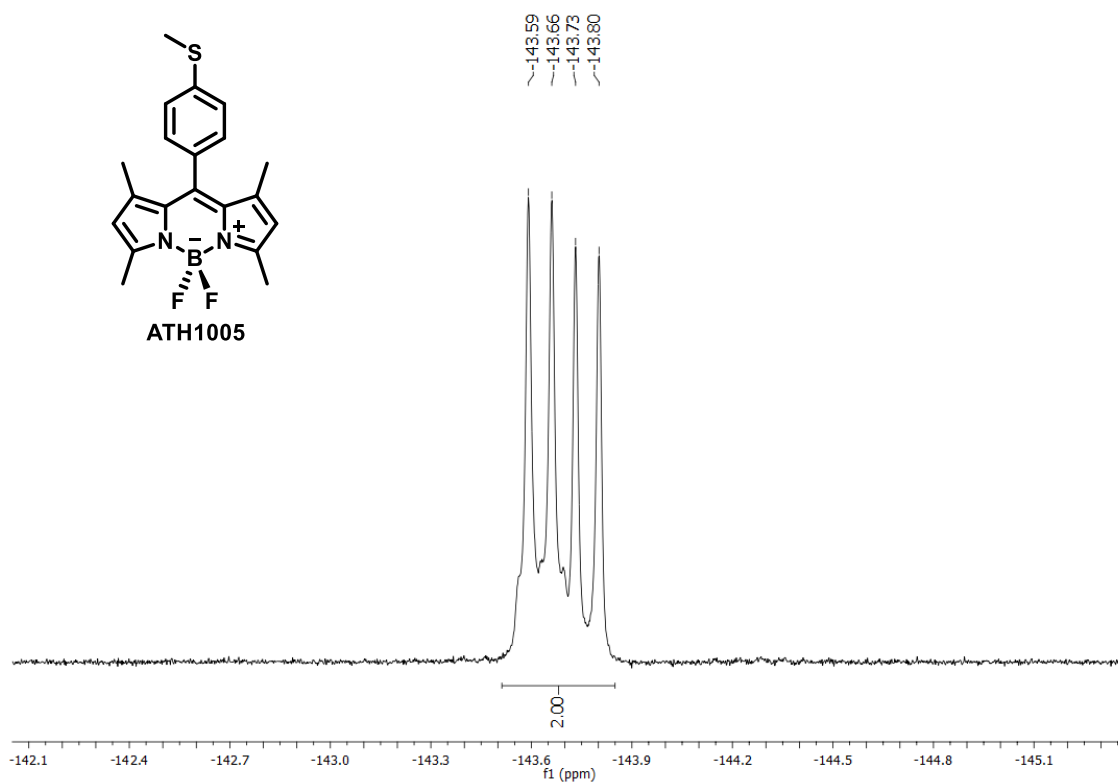


Figure S2: <sup>19</sup>F NMR spectrum (470 MHz, CDCl<sub>3</sub>) for compound ATH1005 (D).

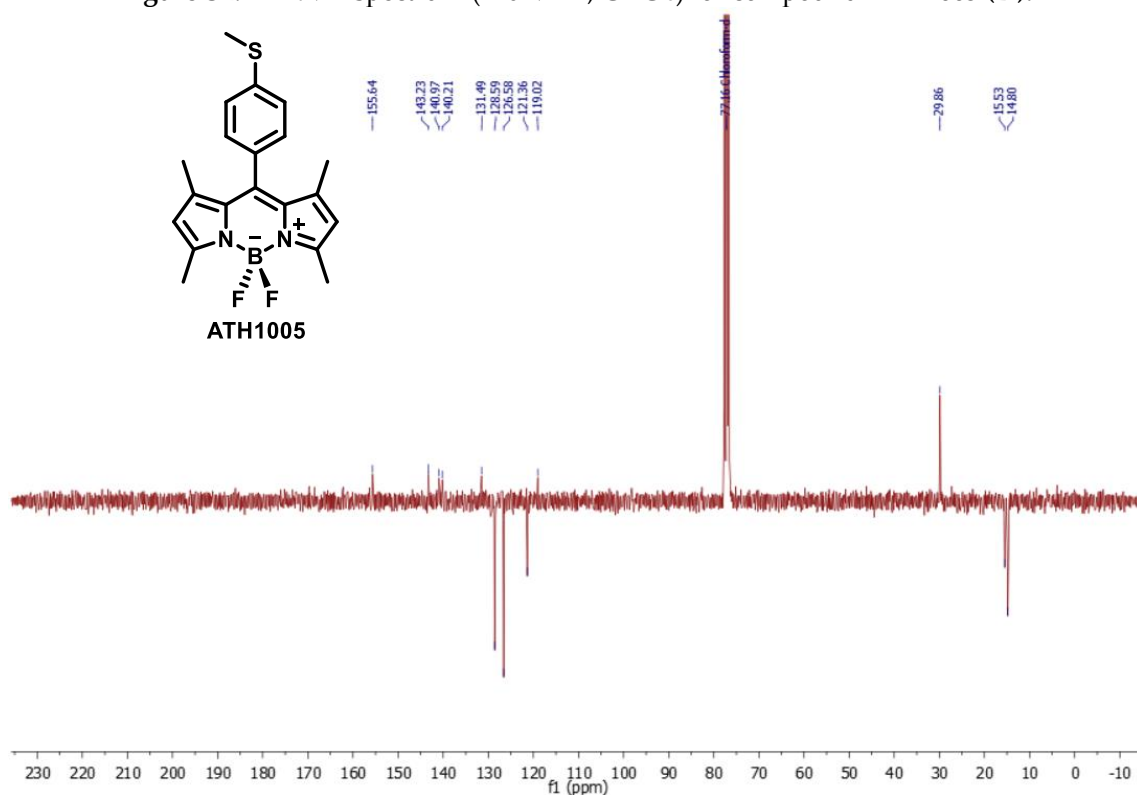


Figure S3: <sup>13</sup>C NMR spectrum (126 MHz, CDCl<sub>3</sub>) for compound ATH1005 (D).

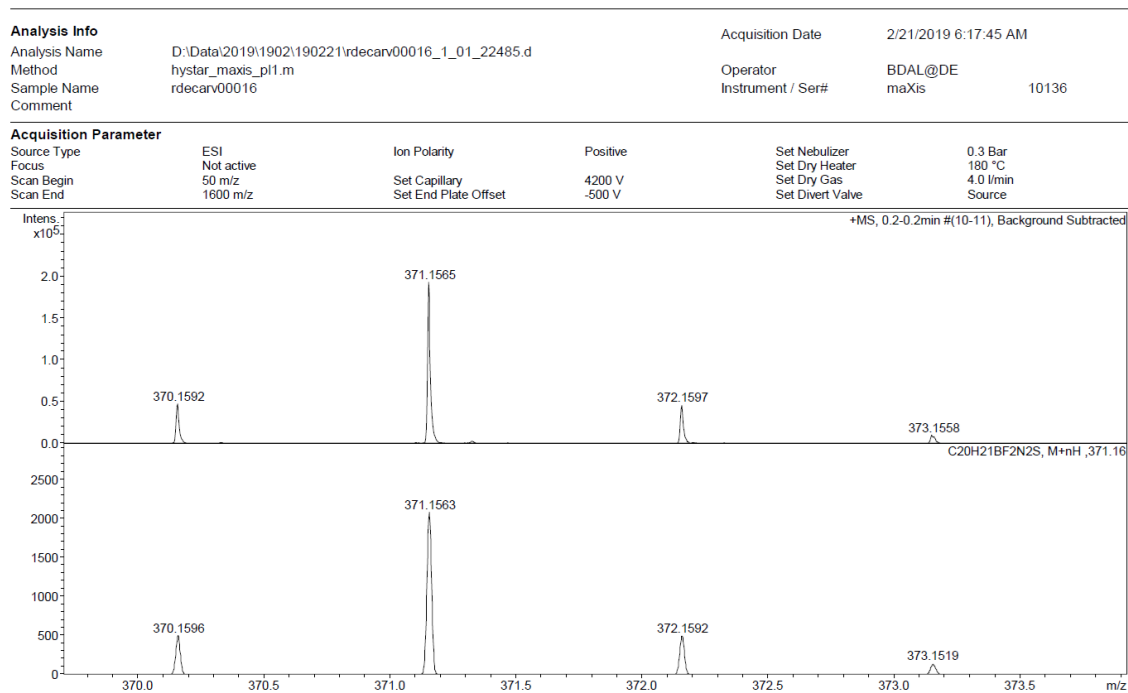


Figure S4: HRMS spectrum for compound ATH1005 (D).

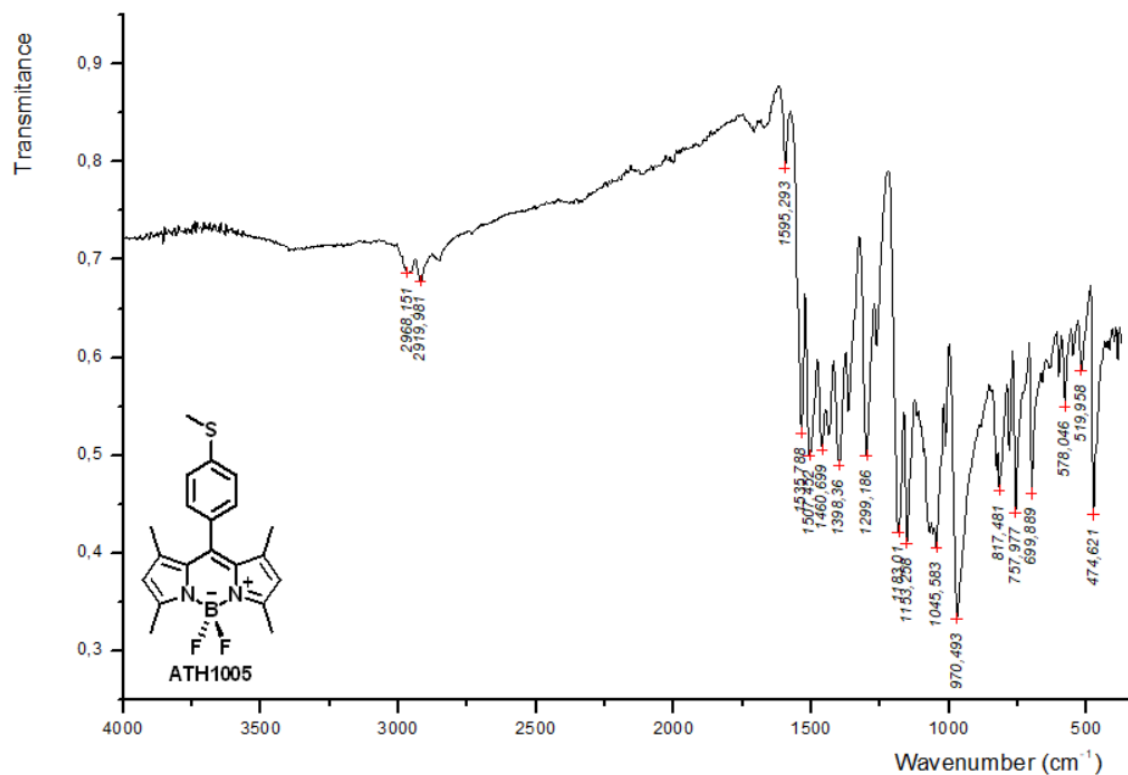
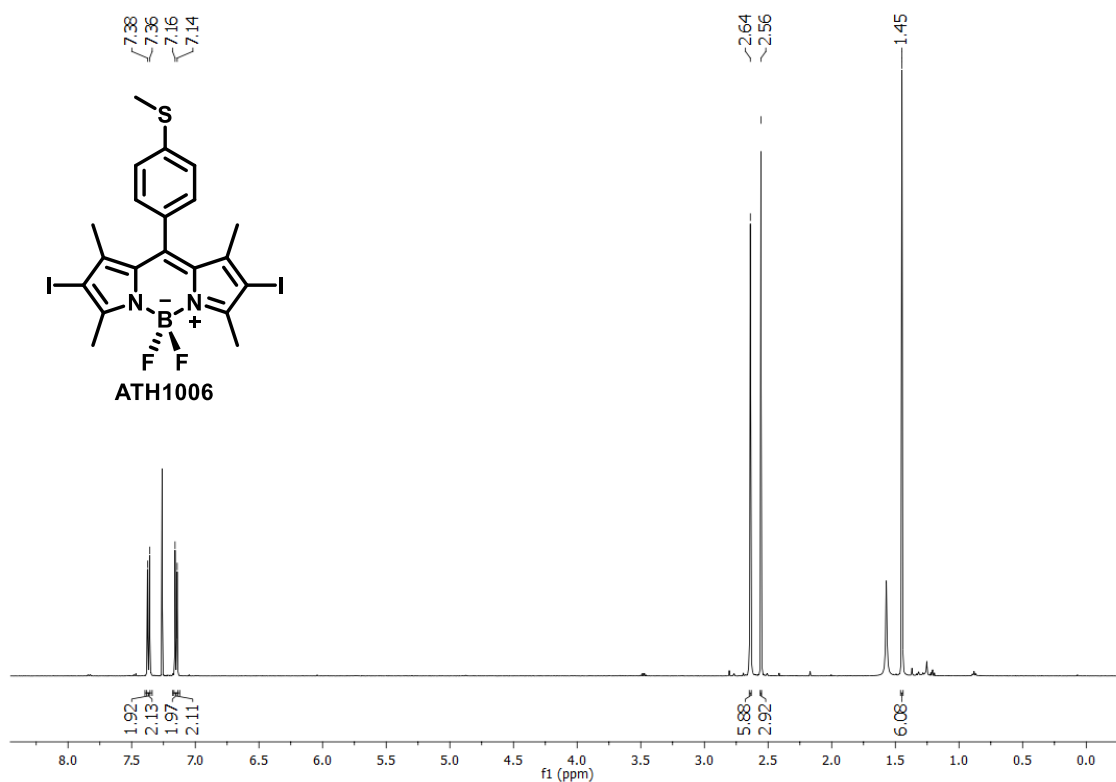
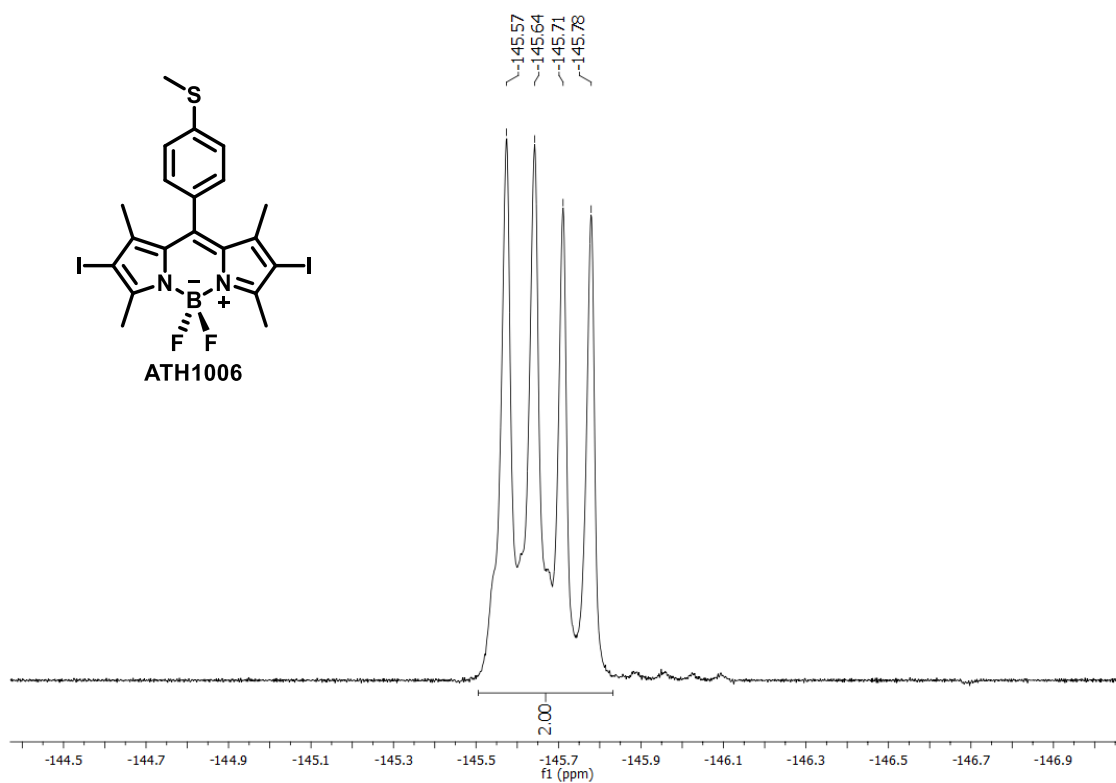


Figure S5: ATR-FTIR spectrum for compound ATH1005 (D).



**Figure S6:**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of compound **ATH1006 (E)**.



**Figure S7:**  $^{19}\text{F}$  NMR spectrum (470 MHz,  $\text{CDCl}_3$ ) for compound **ATH1006 (E)**.

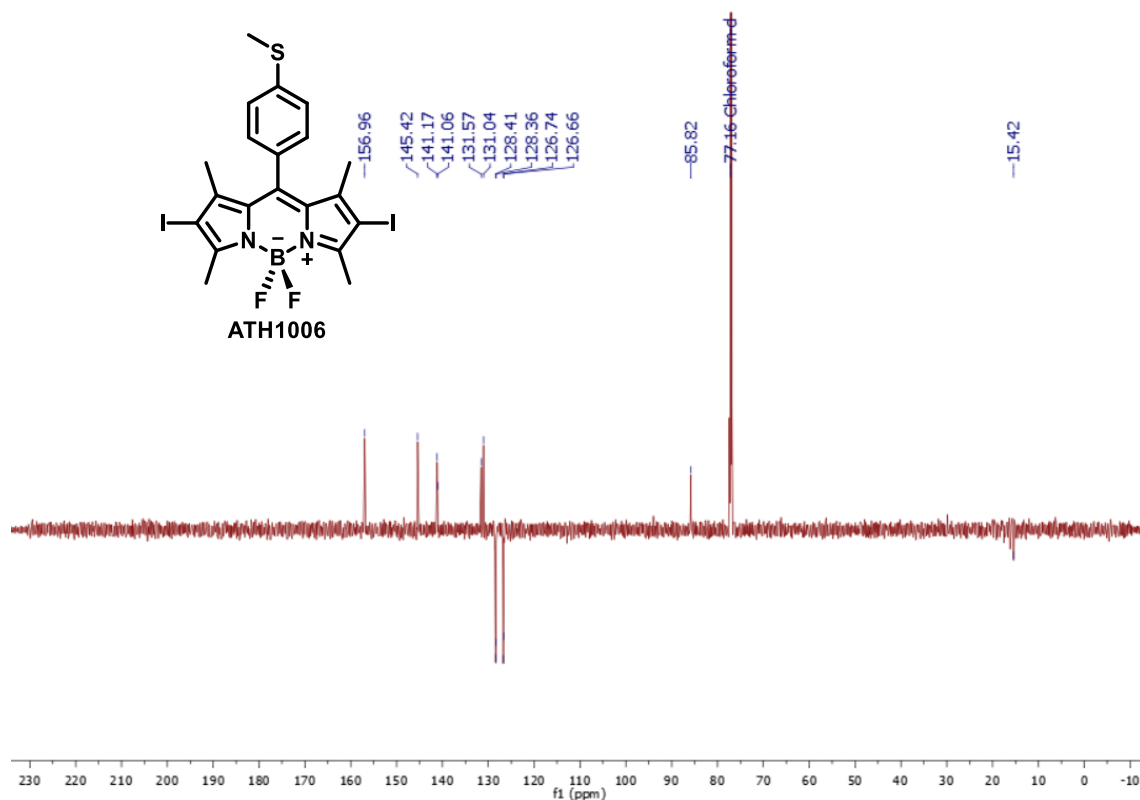


Figure S8:  $^{13}\text{C}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ) for compound ATH1006 (E).

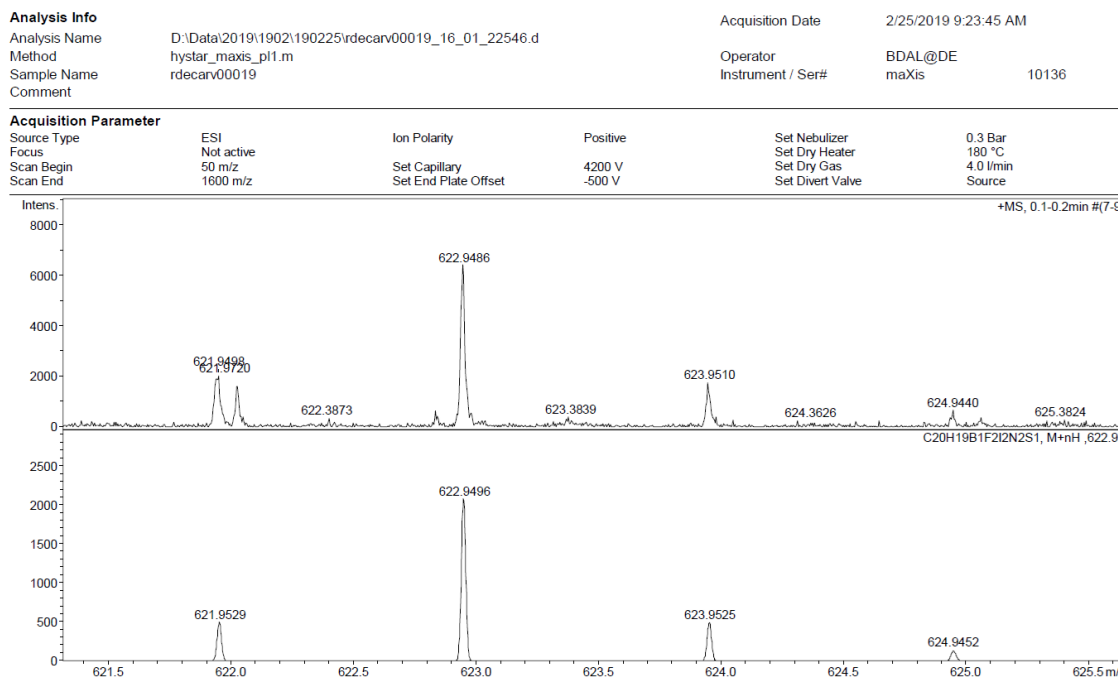


Figure S9: HRMS spectrum for compound ATH1006 (E).

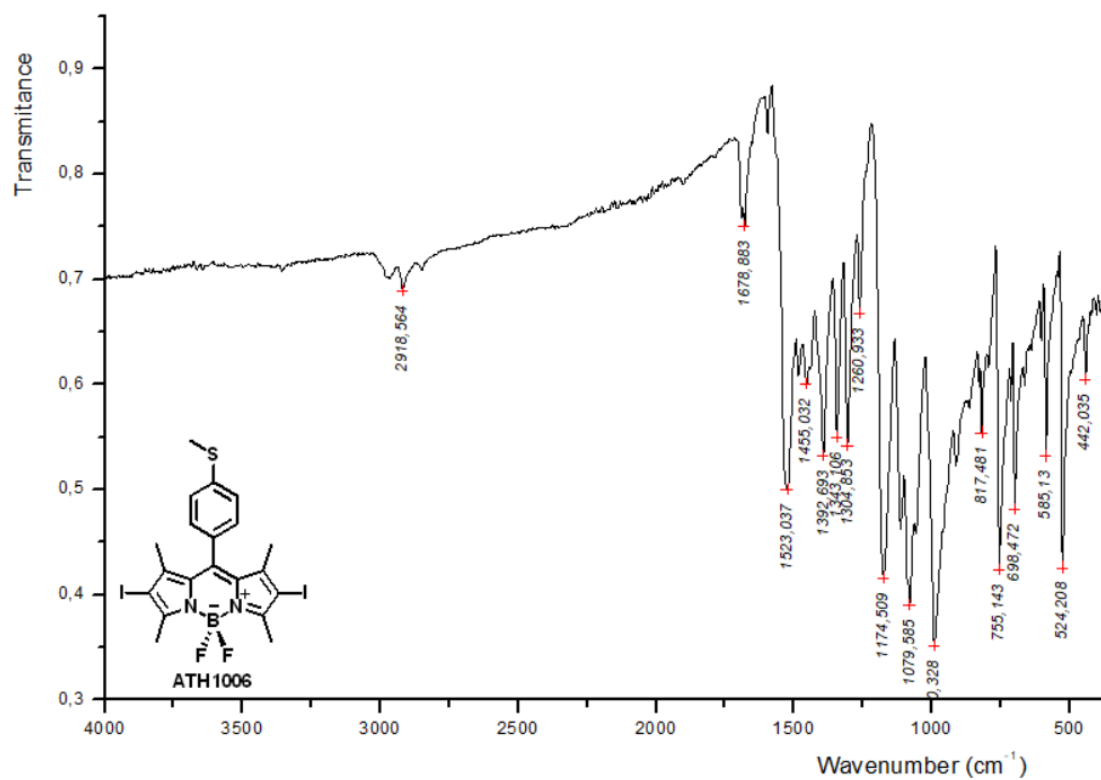


Figure S10: ATR-FTIR spectrum for compound ATH1006 (E).

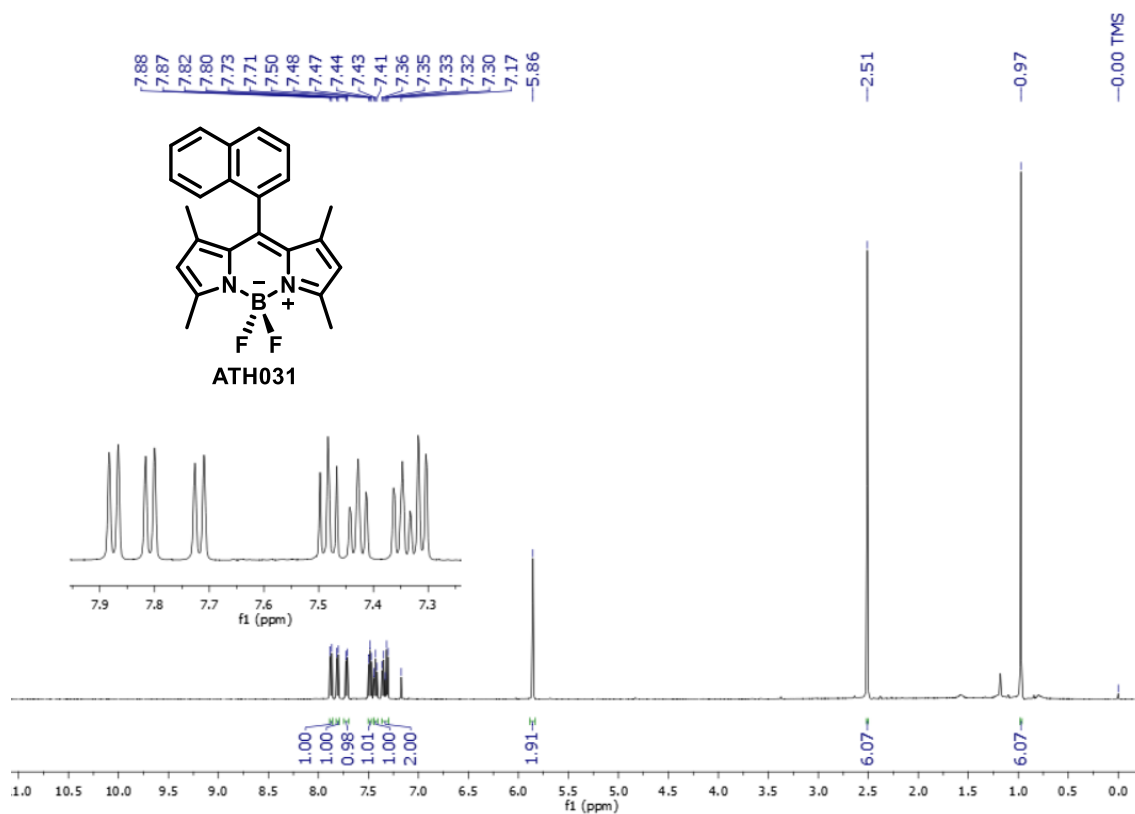
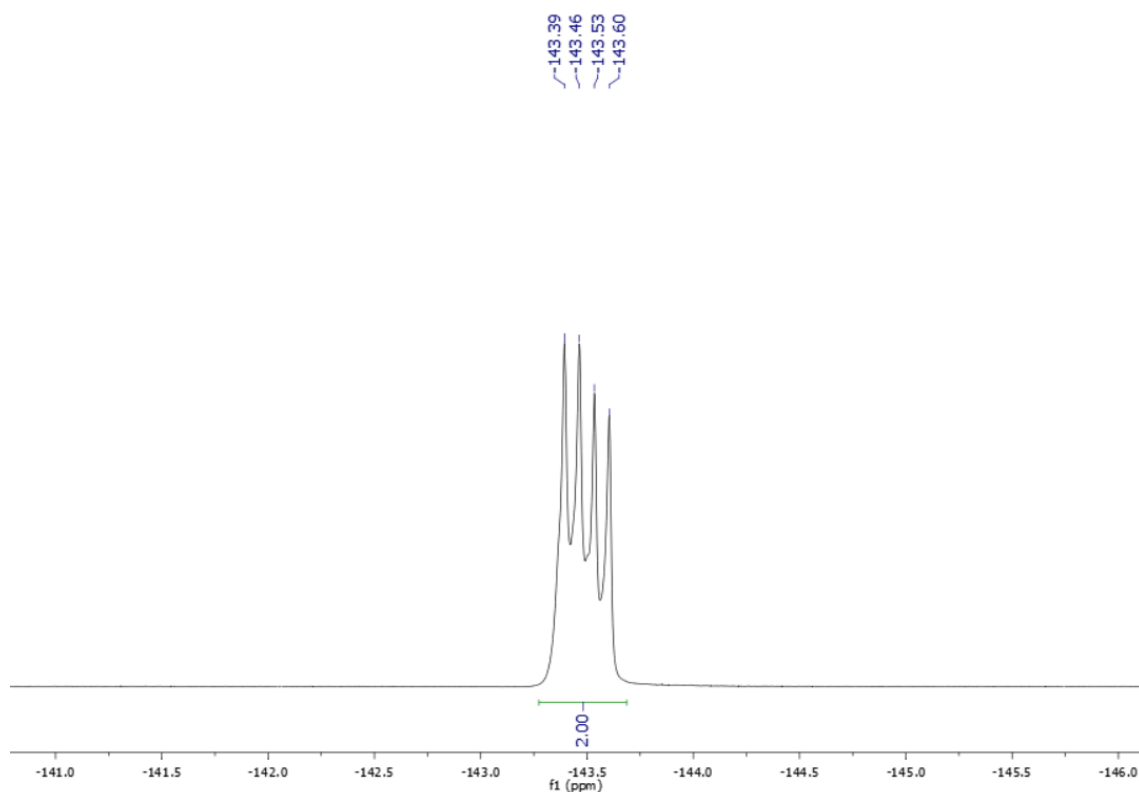
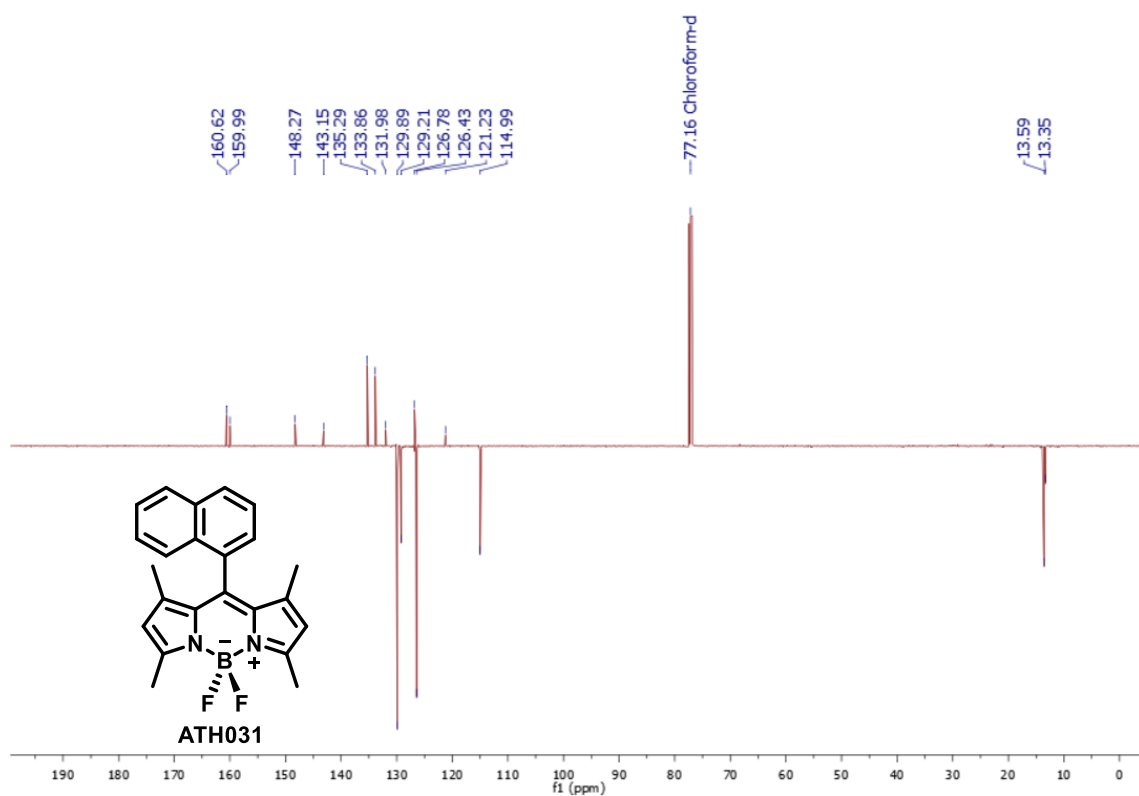


Figure S11: <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of compound ATH031 (F).





**Figure S12:**  $^{19}\text{F}$  NMR spectrum (470 MHz,  $\text{CDCl}_3$ ) for compound ATH031 (F).



**Figure S13:**  $^{13}\text{C}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ) for compound ATH031 (F).

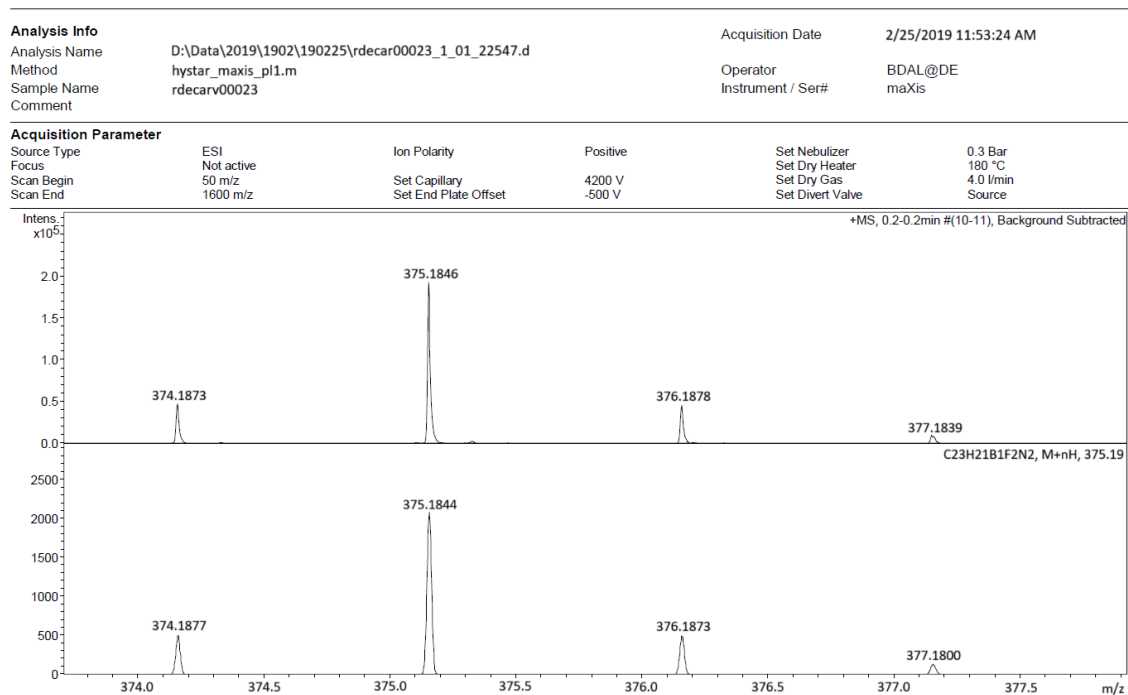


Figure S14: HRMS spectrum for compound ATH031 (F).

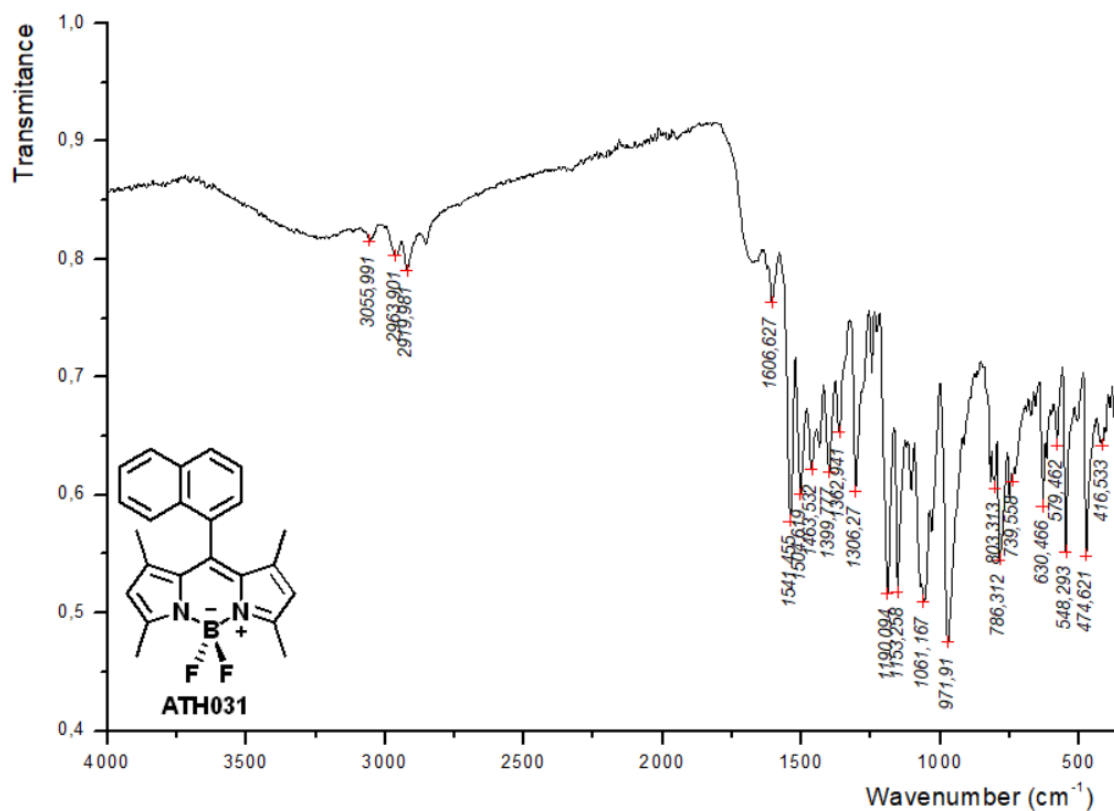
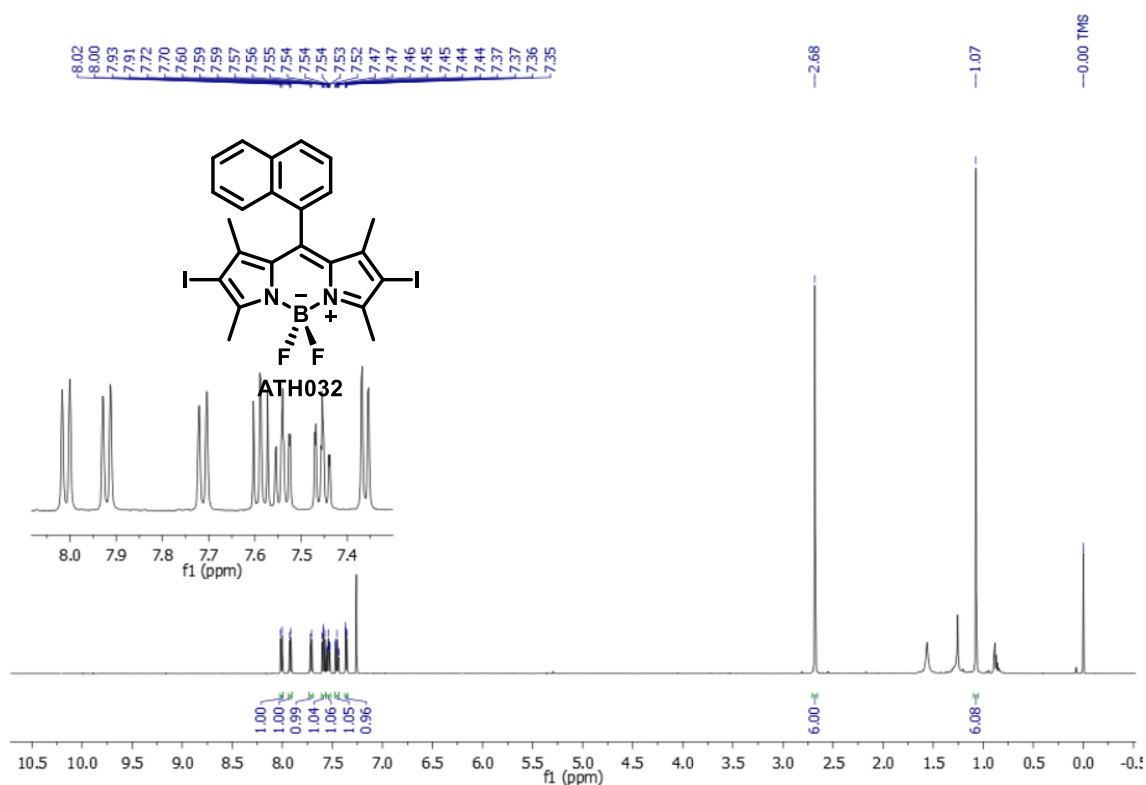
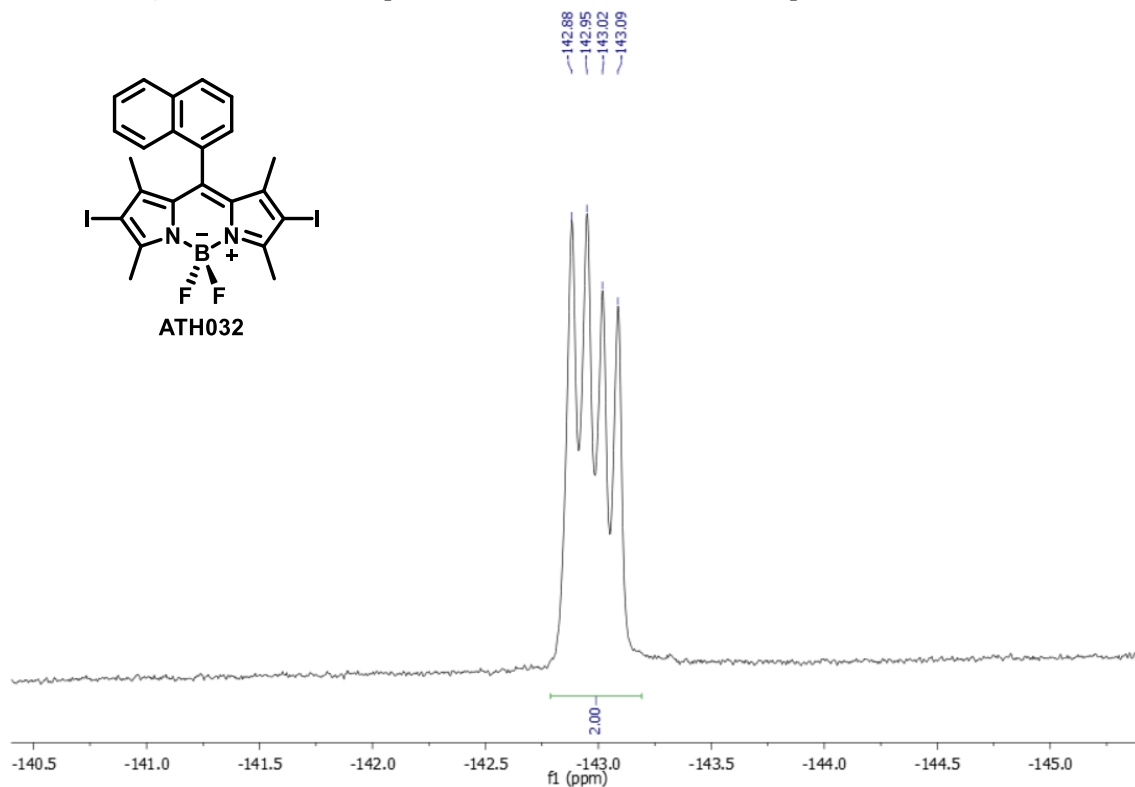


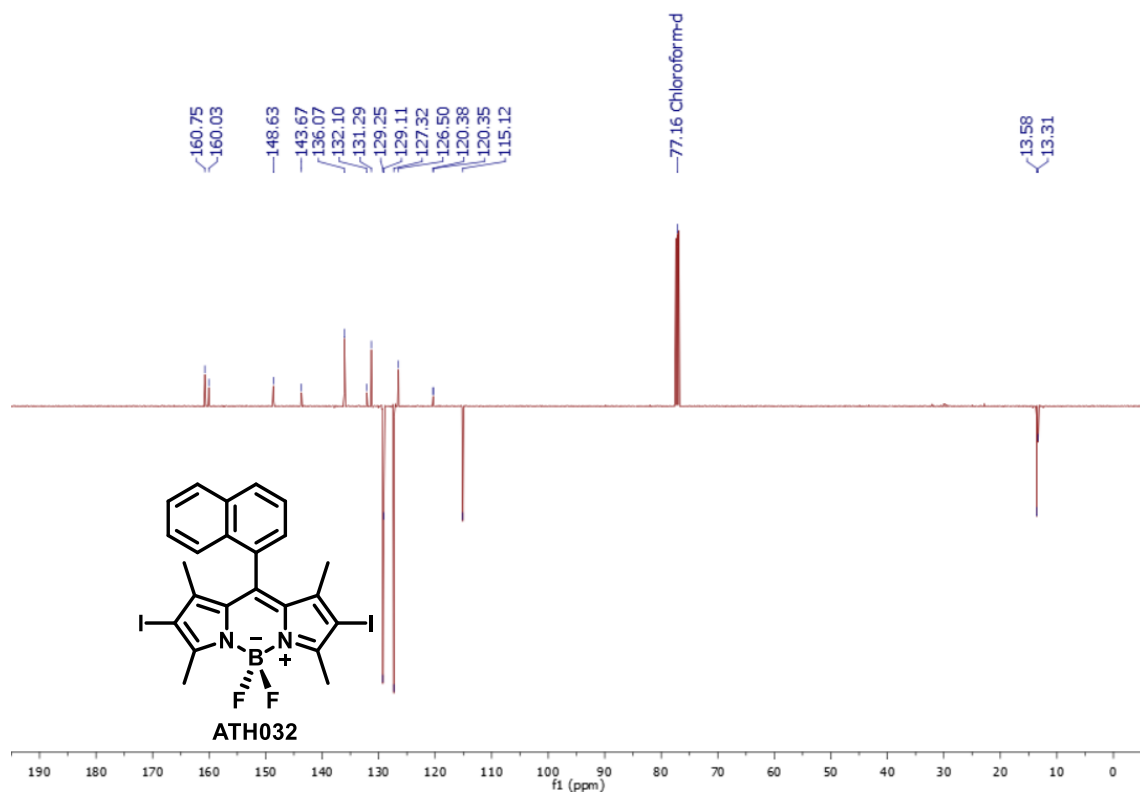
Figure S15: ATR-FTIR spectrum for compound ATH031 (F).



**Figure S16:** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of compound **ATH032 (G)**.



**Figure S17:** <sup>19</sup>F NMR spectrum (470 MHz, CDCl<sub>3</sub>) for compound **ATH032 (G)**.



**Figure S18:** <sup>13</sup>C NMR spectrum (126 MHz, CDCl<sub>3</sub>) for compound ATH032 (G).

#### Analysis Info

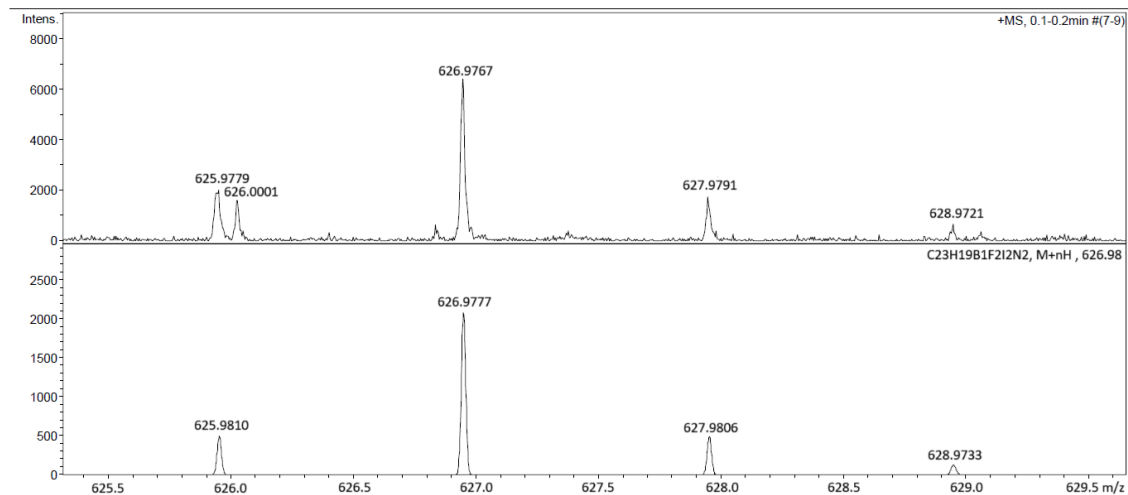
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 Method: hystar\_maxis\_pl1.m  
 Sample Name: rdcarv00021  
 Comment:

Acquisition Date: 2/25/2019 10:01:32 AM

Operator: BDAL@DE  
 Instrument / Ser#: maXis

#### Acquisition Parameter

| Source Type | ESI        | Ion Polarity         | Positive | Set Nebulizer    | 0.3 Bar   |
|-------------|------------|----------------------|----------|------------------|-----------|
| Focus       | Not active |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z     | Set Capillary        | 4200 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 1600 m/z   | Set End Plate Offset | -500 V   | Set Divert Valve | Source    |



**Figure S19:** HRMS spectrum for compound ATH032 (G).

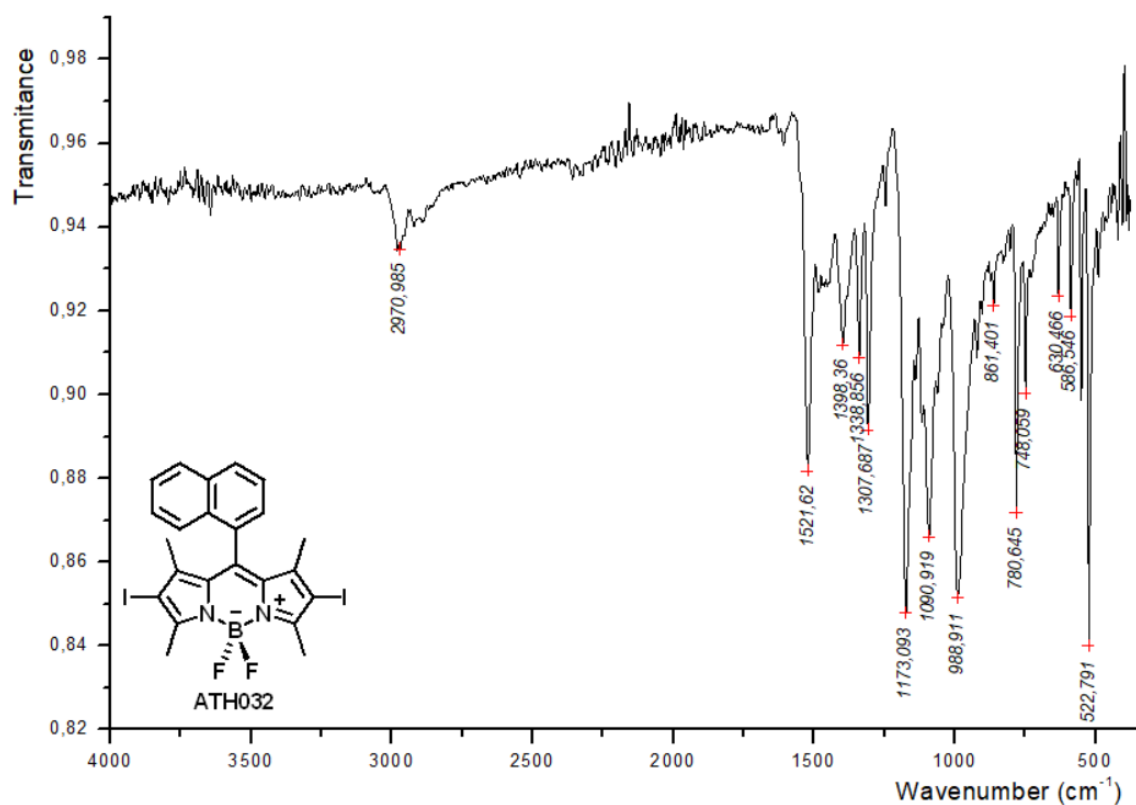


Figure S20: ATR-FTIR spectrum for compound ATH032 (G).

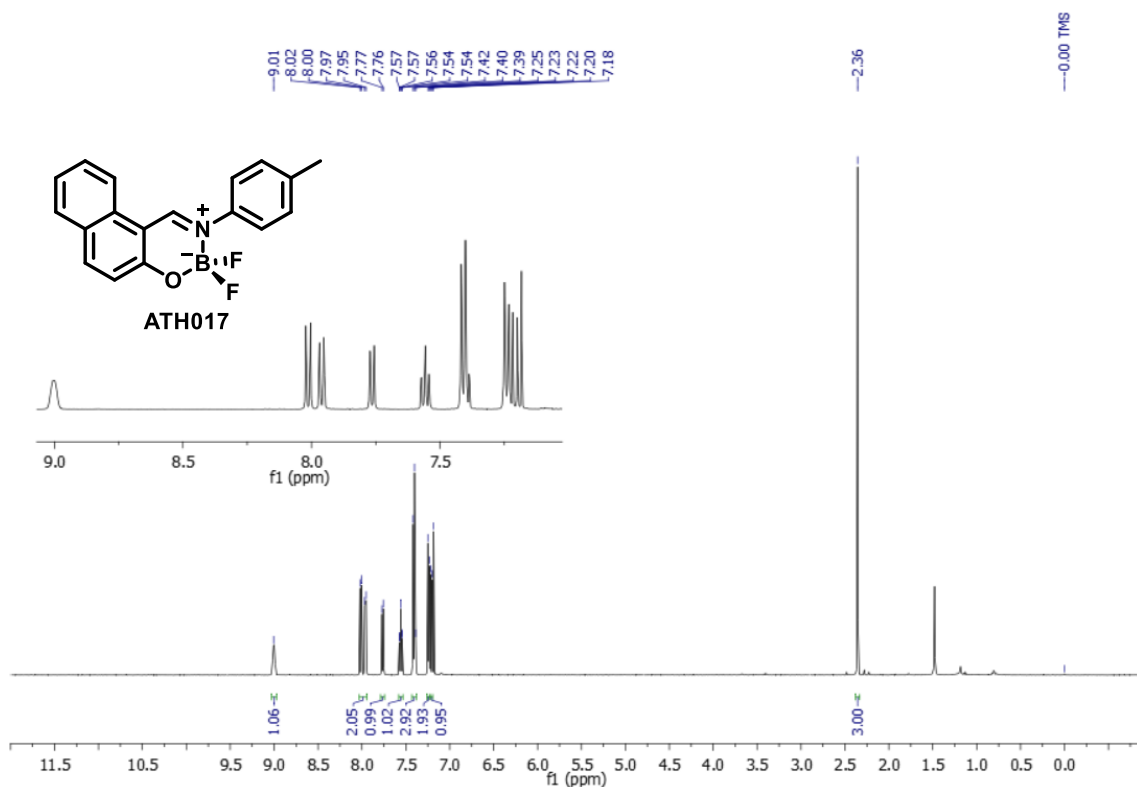
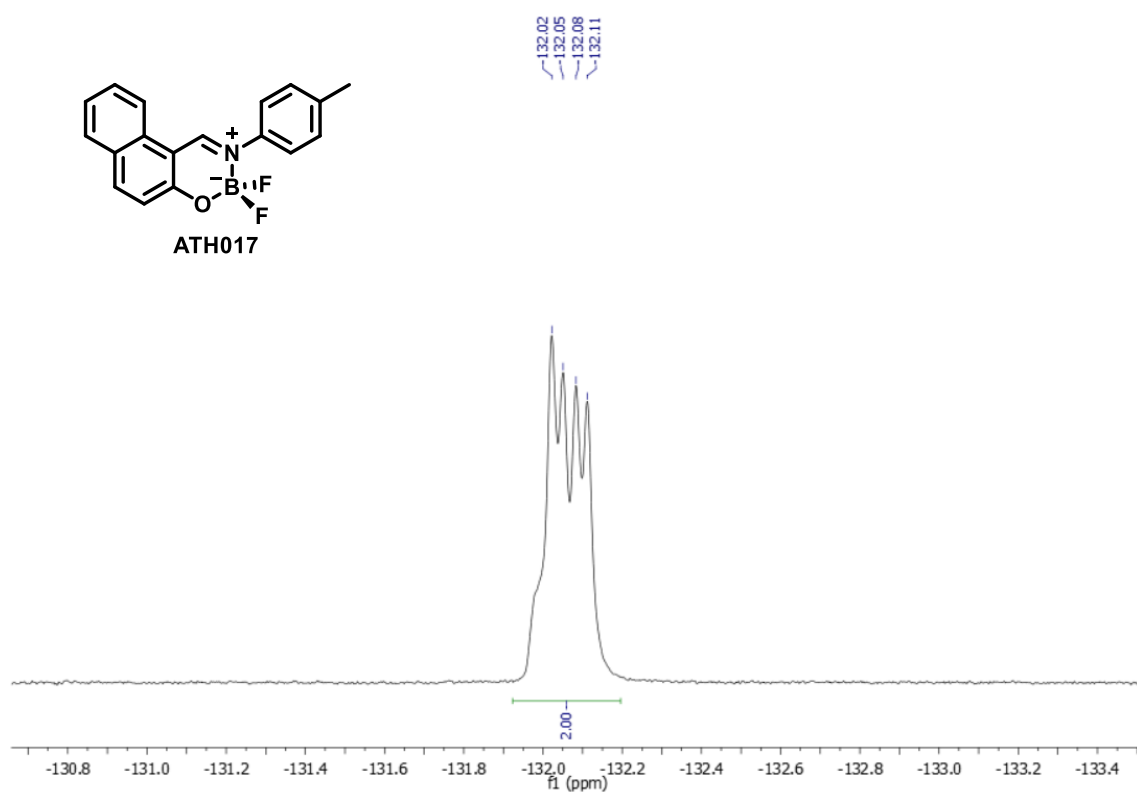
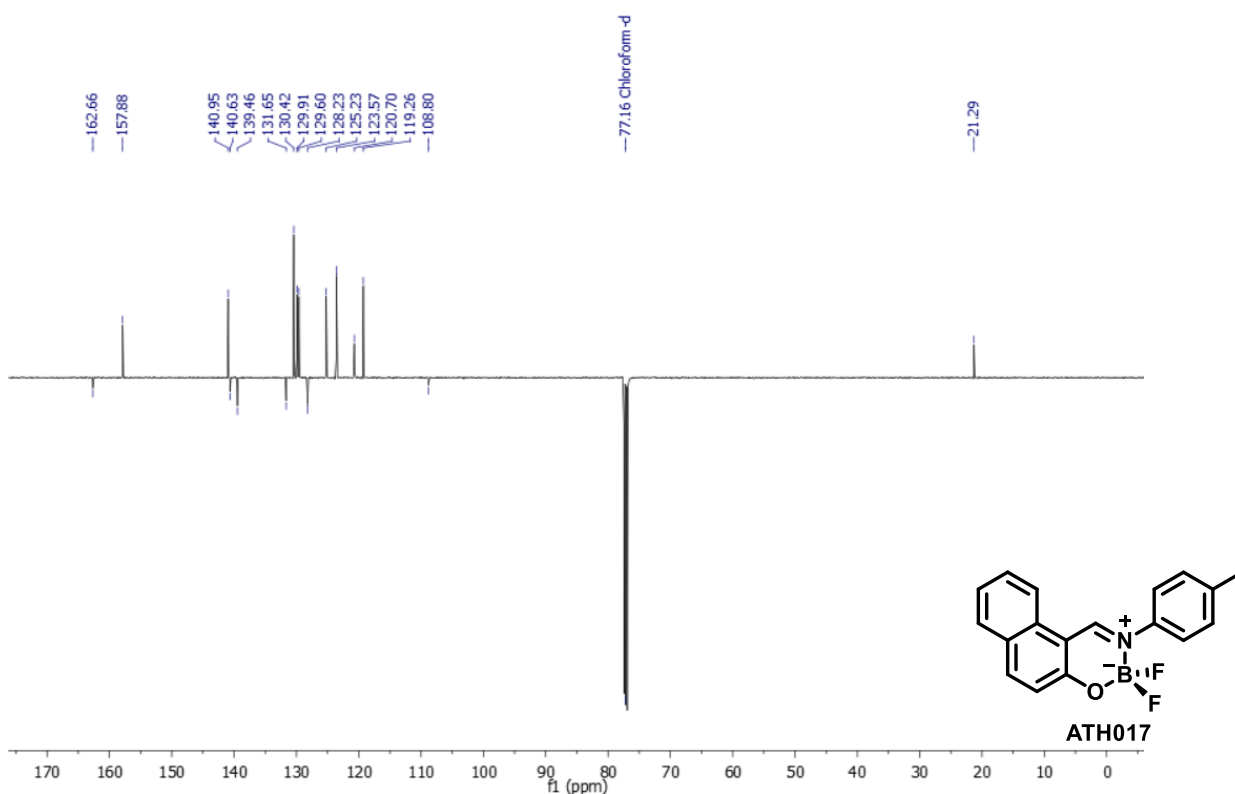


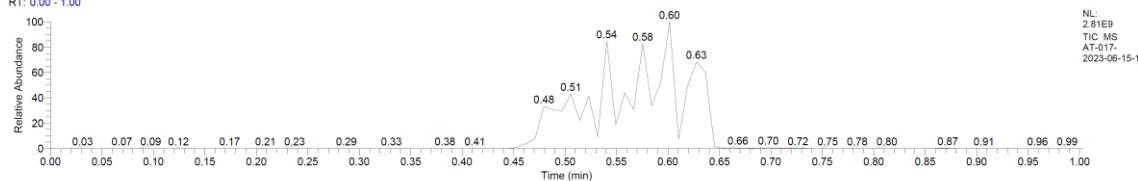
Figure S21: <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of compound ATH017 (A).



**Figure S22:** <sup>19</sup>F NMR spectrum (470 MHz, CDCl<sub>3</sub>) for compound ATH017 (A).



**Figure S23:** <sup>13</sup>C NMR spectrum (126 MHz, CDCl<sub>3</sub>) for compound ATH017 (A).



AT-017-2023-06-15-1 #56-72 RT: 0.49-0.63 AV: 17 NL: 6.41E8

T: FTMS - p APCI corona Full ms [100.0000-400.0000]

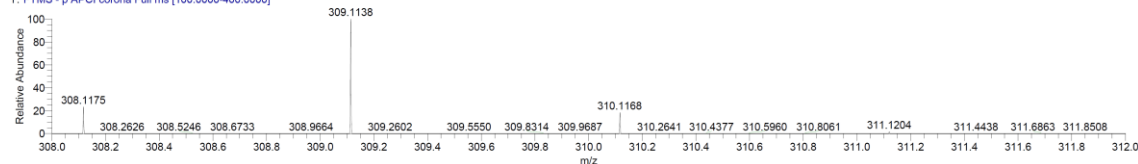


Figure S24: HRMS spectrum for compound ATH017 (A).

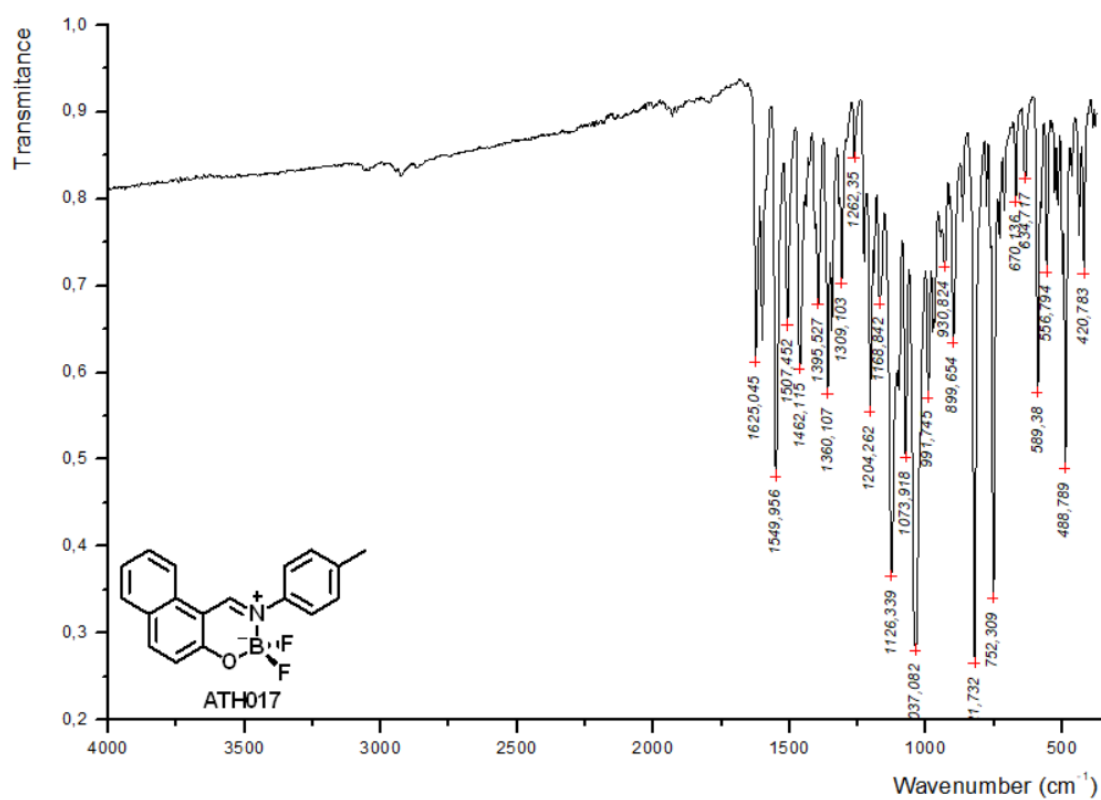


Figure S25: ATR-FTIR spectrum for compound ATH017 (A).

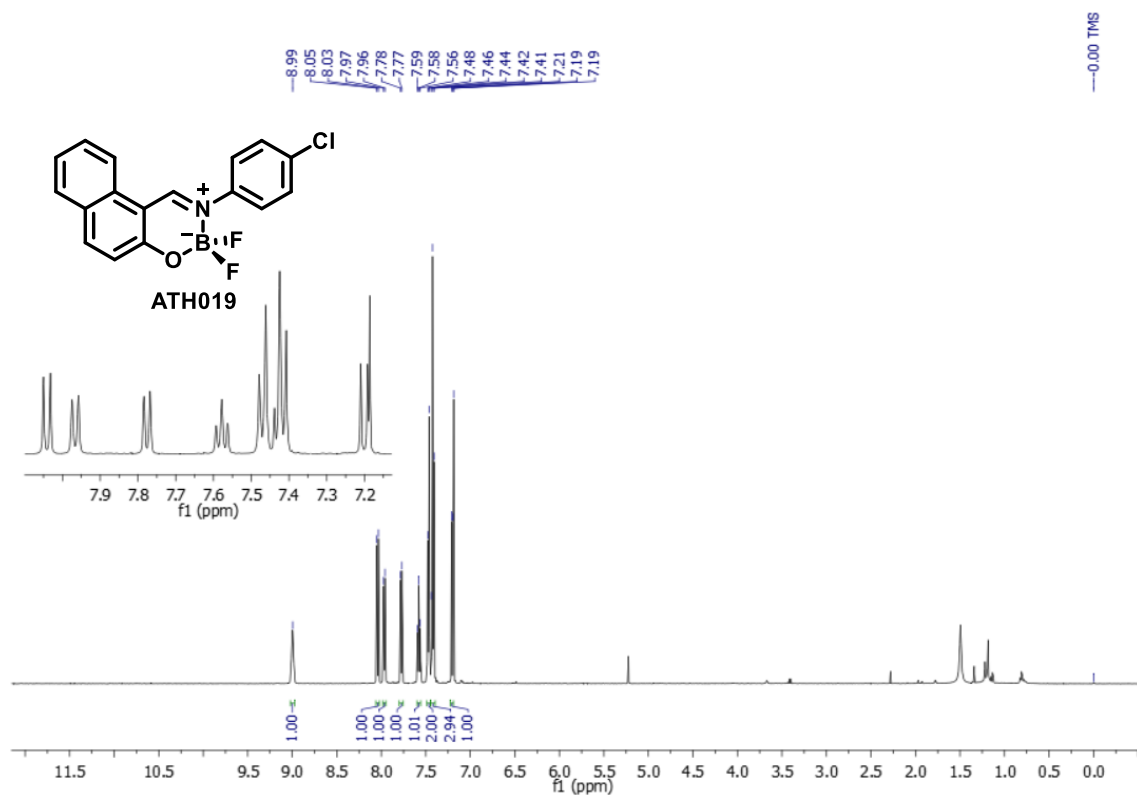


Figure S26: <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of compound ATH019 (B).

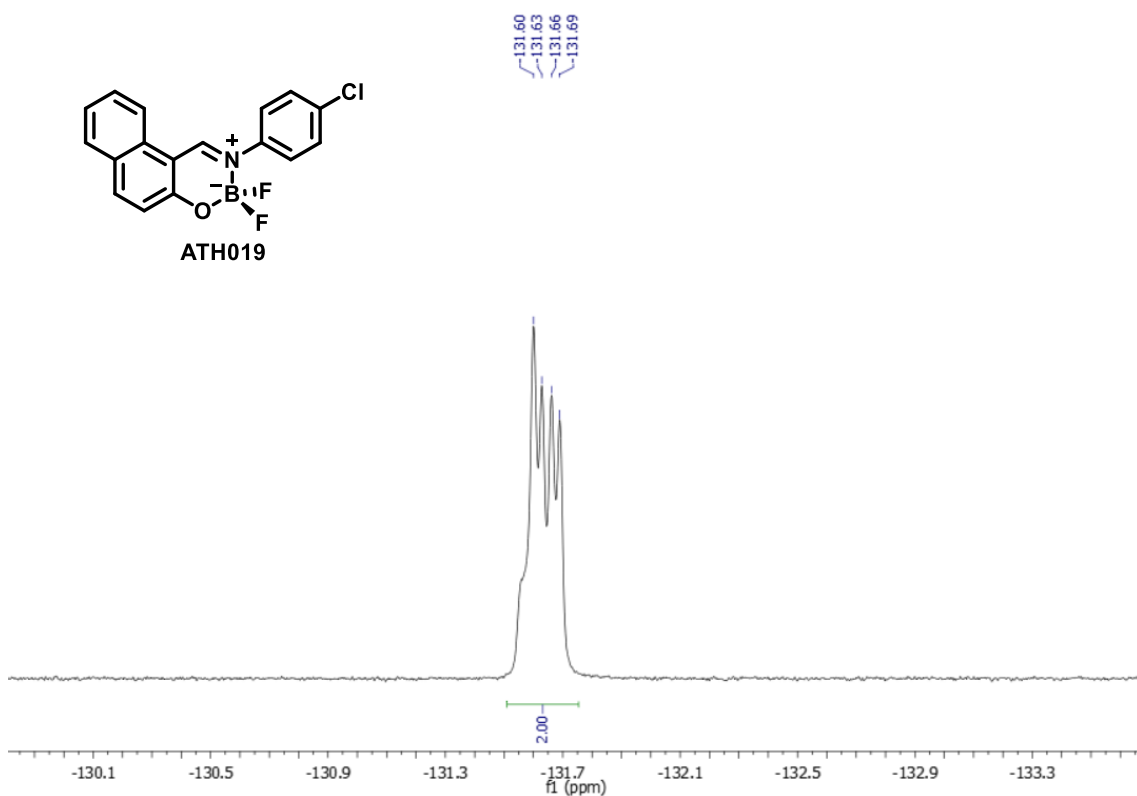


Figure S27: <sup>19</sup>F NMR spectrum (470 MHz, CDCl<sub>3</sub>) for compound ATH019 (B).



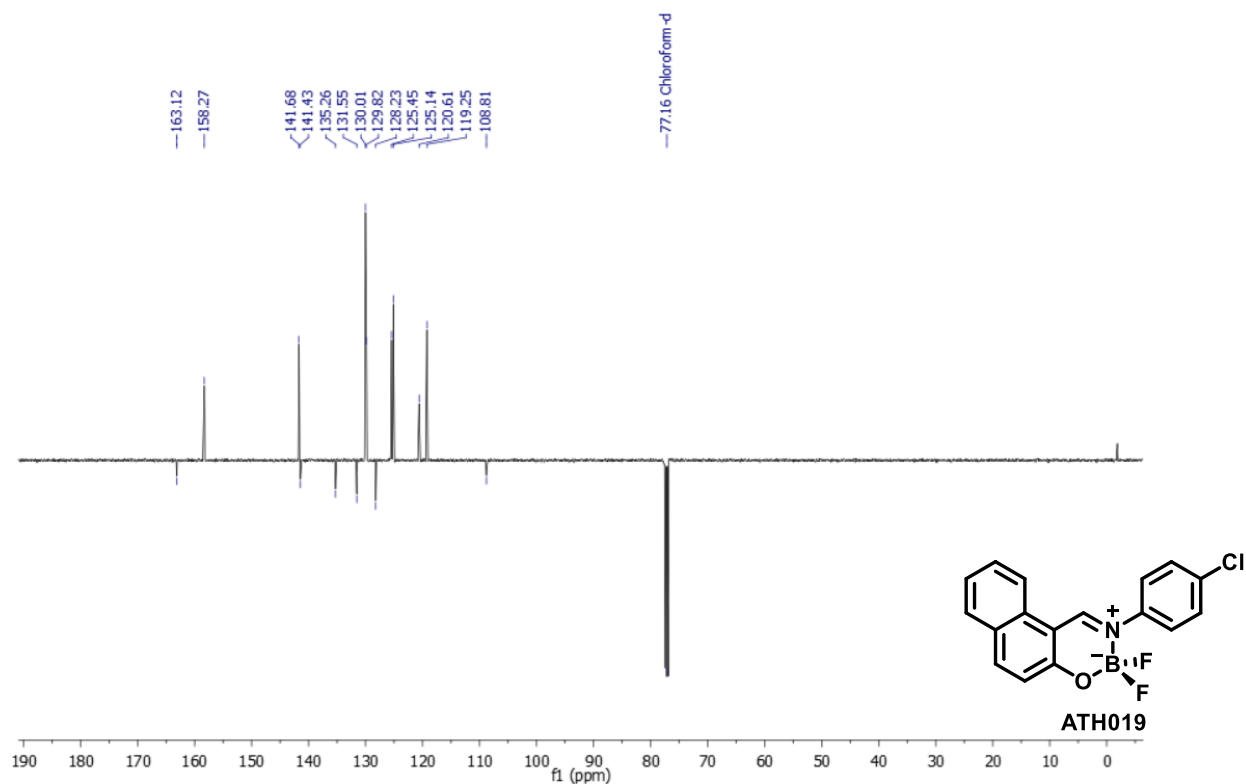


Figure S28: <sup>13</sup>C NMR spectrum (126 MHz, CDCl<sub>3</sub>) for compound ATH019 (B).

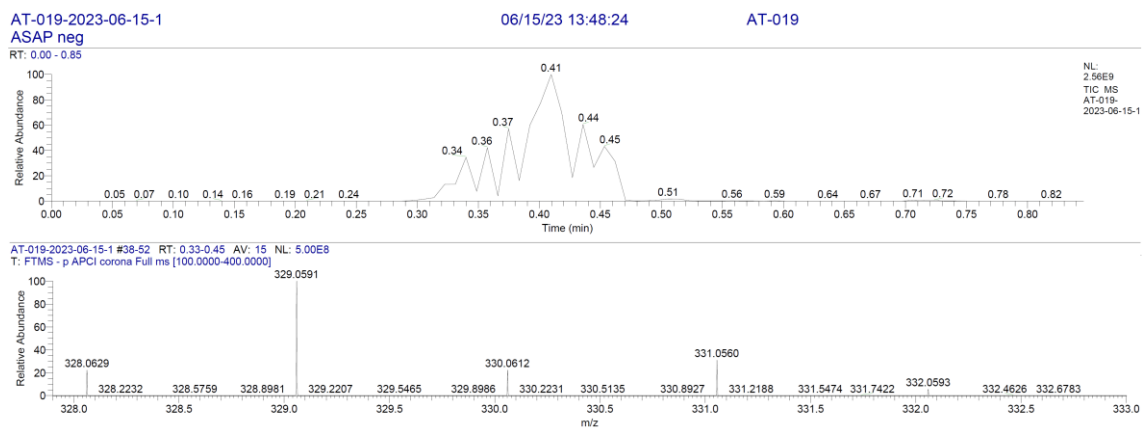


Figure S29: HRMS spectrum for compound ATH019 (B).

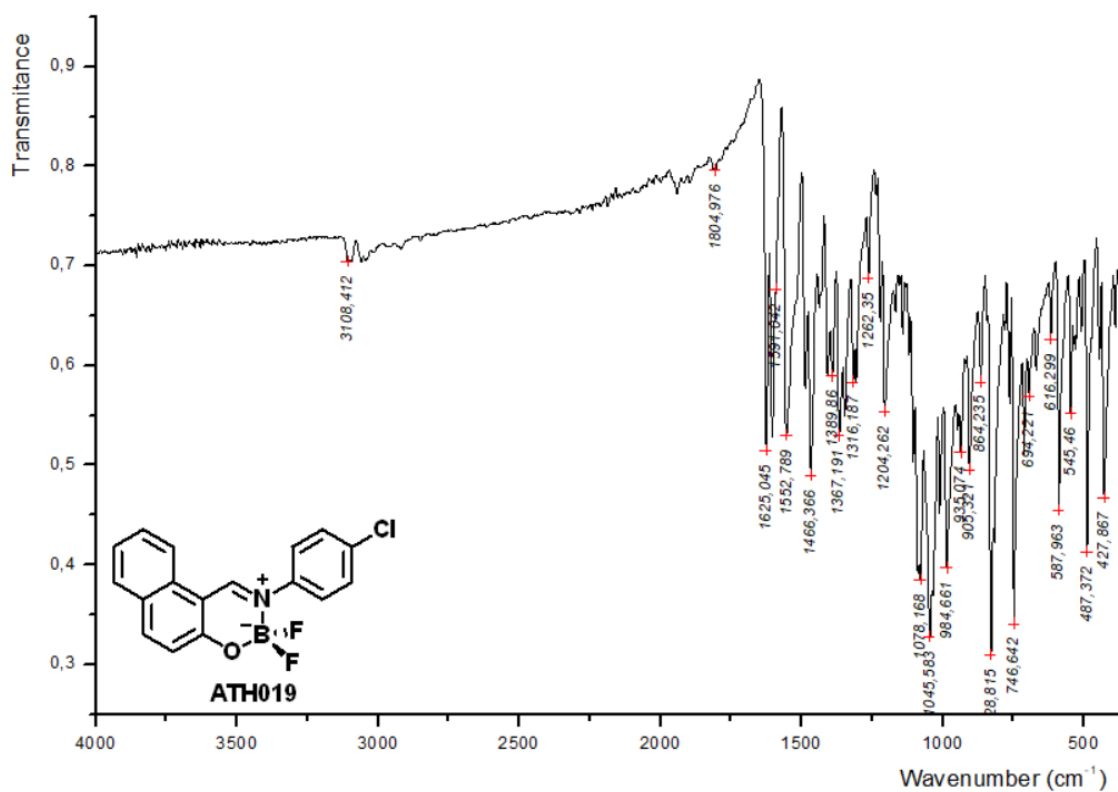


Figure S30: ATR-FTIR spectrum for compound ATH019 (B).

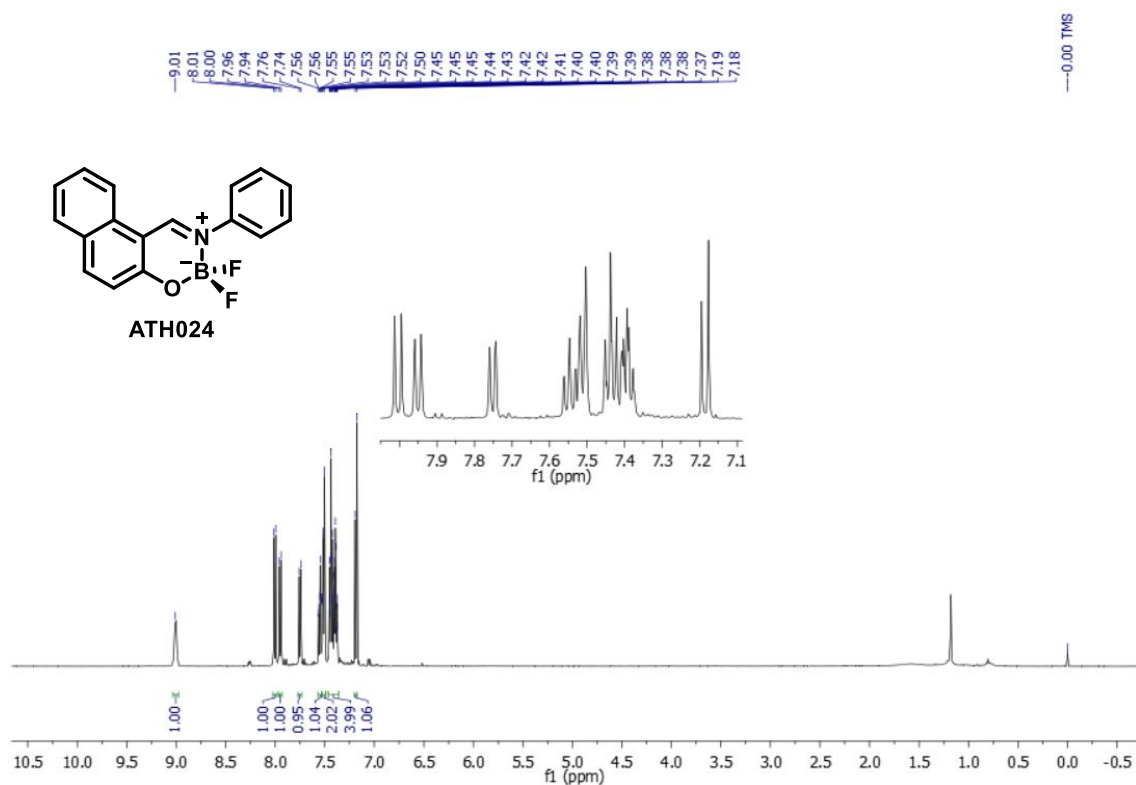
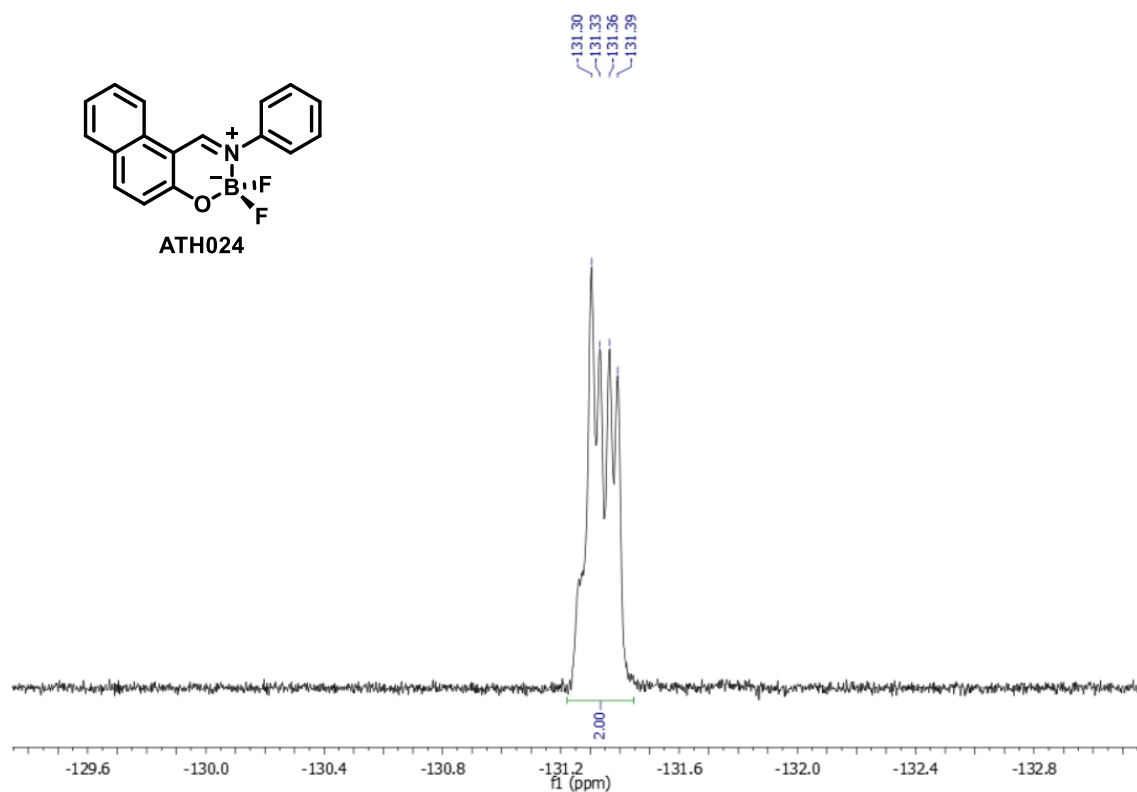
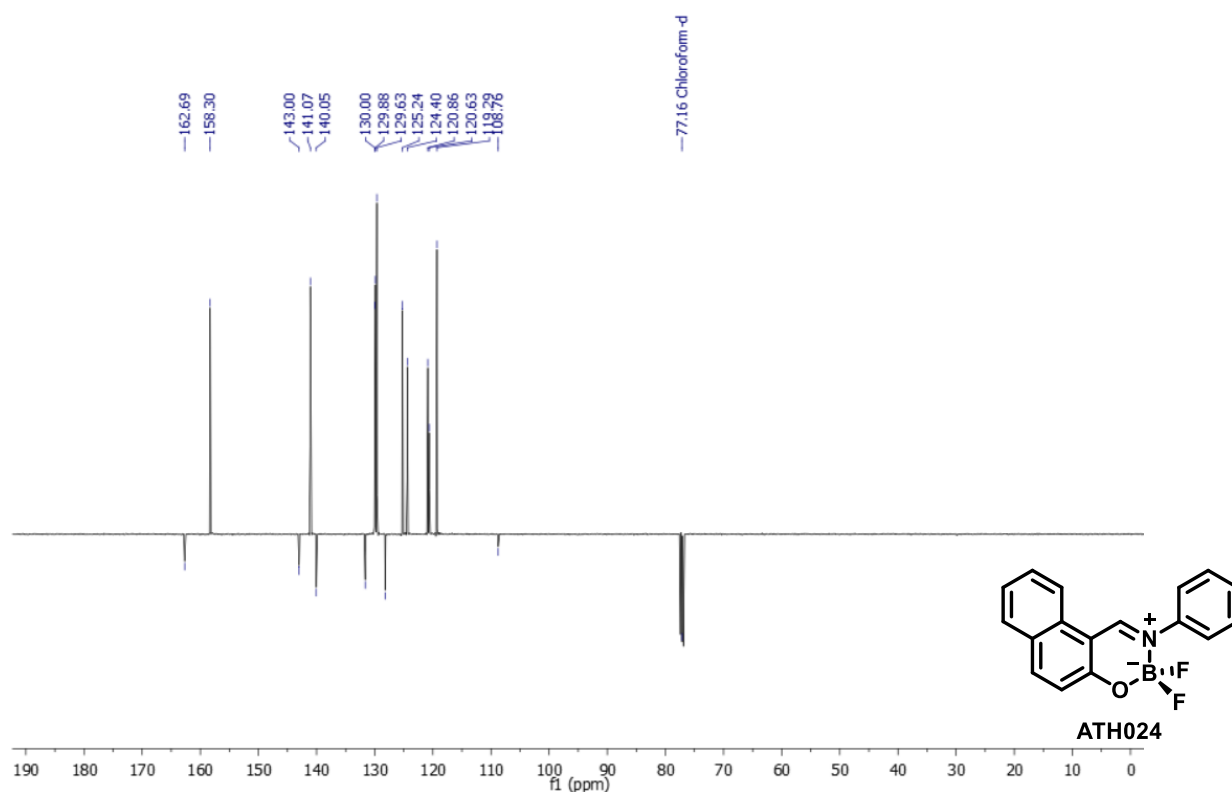


Figure S31: <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of compound ATH024 (C).



**Figure S32:** <sup>19</sup>F NMR spectrum (470 MHz, CDCl<sub>3</sub>) for compound ATH024 (C).



**Figure S33:** <sup>13</sup>C NMR spectrum (126 MHz, CDCl<sub>3</sub>) for compound ATH024 (C).

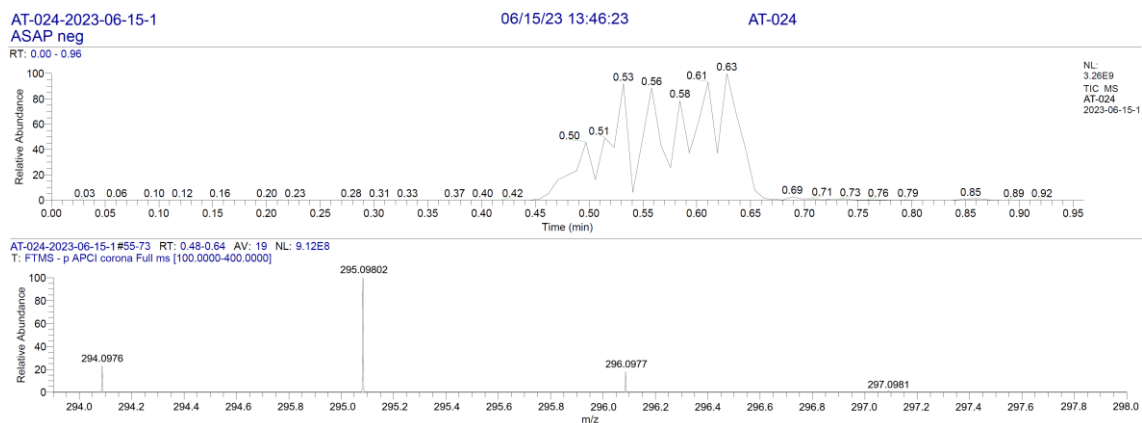


Figure S34: HRMS spectrum for compound ATH024 (C).

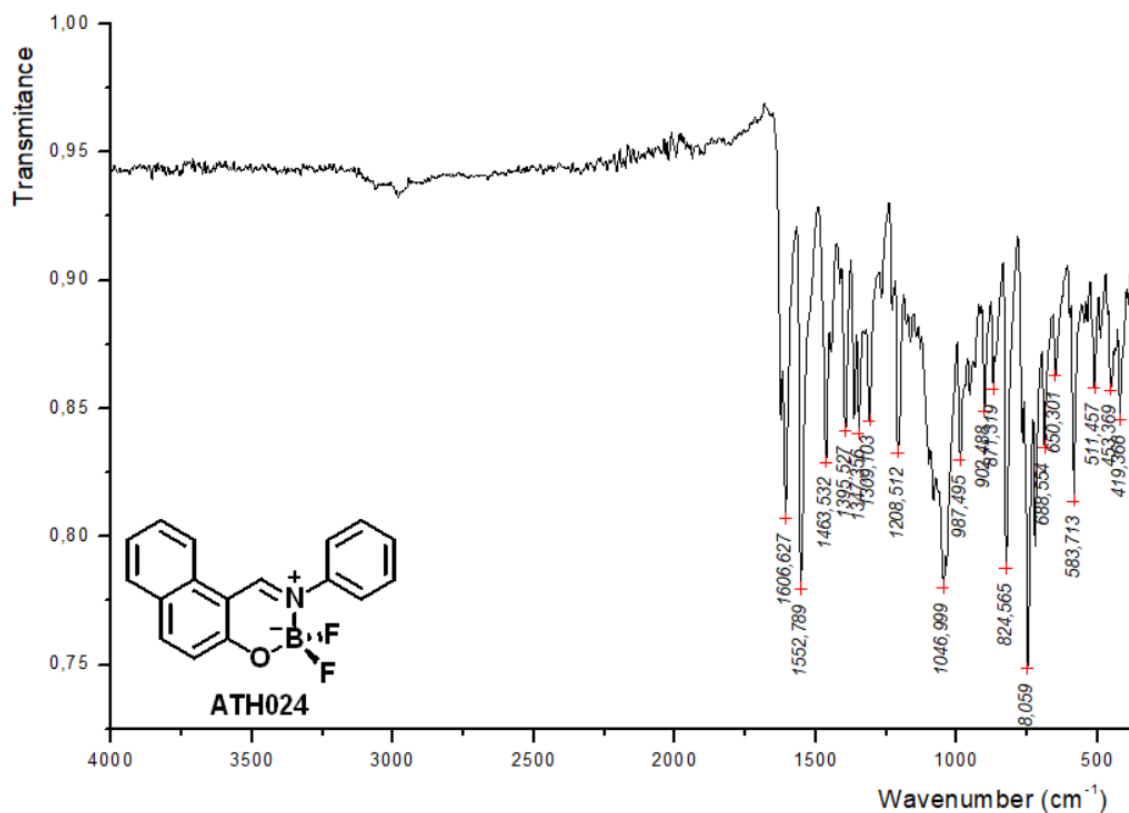


Figure S35: ATR-FTIR spectrum for compound ATH024 (C).