

# Synthesis and Properties of Chiral Fluorescent Helicene-BODIPY Conjugates

## Supporting Information

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Supporting Information Placeholder

## Contents

1. General Information and Apparatus	S2
2. Synthesis and characterization of compounds	S6
3. Optimization of the two-step one-pot procedure	S48
4. (Chir)optical properties	S49
5. Electrochemical properties	S52
6. Computed energies and Cartesian coordinates of compounds <b>4a</b>	S53
7. Vertical excitations of BODIPY compounds <b>4a</b>	S65
8. Frontier Molecular Orbitals of BODIPYs <b>4a</b>	S83
9. Computed spin densities of compound <b>4aA</b>	S84
10. Crystal data and structure refinement for compound <b>4aE</b>	S88
11. References	S90

# 1. General Information and Apparatus

## Reagents

Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. All reactions involving air sensitive compounds were carried out under N<sub>2</sub> *via* an inert gas/vacuum double manifold line and standard Schlenk techniques using dry solvents. Reactions involving oxygen-sensitive reagents were performed using degassed solvents.

## Microwaves

MW reactions were performed in a Biotage Initiator Robot with Robot Sixty set up for high absorption solvent without previous stirring.

## Chromatography

**Analytical thin-layer chromatographies** (TLCs) were performed with Silica gel 60 F<sub>254</sub> aluminium plates purchased from Merck. **Flash column chromatographies** were performed with Silica SiliaFlash P60, 40-63 μm (230-400 mesh) and with CombiFlash® R<sub>f</sub> 200 on SiO<sub>2</sub> 4 g, 12 g and 24 g cartridges. **Retardation factors** (*R<sub>f</sub>*) were measured on TLC Aluminium oxide 60 F<sub>254</sub>, neutral or basic plates purchased from Merck. Enantiopure materials were obtained by chiral stationary phase **HPLC** resolution on an Agilent 1260 Infinity II apparatus (quaternary pump, auto sampler, column thermostat and diode array detector) using a semi-preparative CHIRALPAK® IG column (250 x 10 mm, 5 mic) and HPLC grade solvents.

## Infrared

IR spectra were recorded with a Perkin-Elmer 100 FT-IR spectrometer using a diamond ATR Golden Gate sampling and are reported in wavenumbers ( $\text{cm}^{-1}$ ).

## Nuclear Magnetic Resonance

NMR spectra were recorded on a Bruker AVANCE I 300 MHz spectrometer (equipped with a 5 mm QNP D133 probe), on a Bruker AVANCE III HD-*NanoBay* 300 MHz spectrometer (equipped with a 5 mm BB(F)-H-D probe), on a Bruker AVANCE III HD-*NanoBay* 400 MHz spectrometer (equipped with a 5 mm CryoProbe Prodigy) or on a Bruker II 500 MHz spectrometer (equipped with a 5 mm Cryogenic DCH ( $^1\text{H}/^{13}\text{C}$ ) probe).  **$^1\text{H}$  NMR**: chemical shifts are given in ppm relative to  $\text{Me}_4\text{Si}$  with solvent resonances used as internal standards ( $\text{CD}_2\text{Cl}_2$   $\delta = 5.32$  ppm). Data are reported as follows: chemical shift (ppm) on the  $\delta$  scale, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, td = triplet of doublets and m = multiplet), coupling constant (Hz) and integration.  **$^{13}\text{C}$  NMR**: chemical shifts are given in ppm relative to  $\text{Me}_4\text{Si}$  with solvent resonances used as internal standards ( $\text{CD}_2\text{Cl}_2$   $\delta = 54.00$  ppm).  **$^{19}\text{F}$  NMR** chemical shifts are given in ppm.

## Mass Spectrometry

**ESI-MS** spectra were obtained in methanol solutions on an API 150EX (AB/MDS Sciex) spectrometer in positive polarity. **HRMS** spectra were obtained in methanol solutions on a QSTAR Pulsar (AB/MDS Sciex) spectrometer in positive polarity by the Department of Mass Spectroscopy at the University of Geneva.

## Cyclic Voltammetry

Potentiodynamic electrochemical measurements were carried out on an Electrochemical Analyzer with Picoamp booster and Faraday cage (CH Instruments 660C).

## (Chir)optical measurements

**Optical rotations** were measured on a Perkin Elmer 241 polarimeter at 20 °C using a Hg lamp (365 nm). **UV-Vis** absorption spectra were recorded on a JASCO V-650 spectrophotometer at 20 °C. Measurements were performed in acetonitrile analytical grade at precise concentrations. **Electronic Circular Dichroism** (ECD) spectra were recorded on a JASCO J-815 spectrophotometer at 20 °C. Measurements were performed in analytical grade acetonitrile at precise concentrations. **Circularly Polarized Luminescence** (CPL) measurements were carried out with a home-built apparatus,<sup>[1]</sup> on acetonitrile diluted solutions with an optical density < 0.1, under 517 nm irradiation from a LED source (90° geometry). **Steady-state fluorescence** spectra were measured using a Varian Cary 50 Eclipse spectrofluorimeter in analytical grade acetonitrile at precise concentrations. All fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection. **Fluorescence quantum yields** ( $\Phi_F$ ) were measured in a diluted solution with an optical density < 0.1 using the following equation:

$$\Phi_s = \Phi_r \cdot \left(\frac{A_r}{A_s}\right) \cdot \left(\frac{D_s}{D_r}\right) \cdot \left(\frac{\eta_s}{\eta_r}\right)^2$$

where “r” and “s” stand for reference and sample respectively, A is the absorbance at the excitation wavelength, D is the integrated intensity and  $\eta$  is the refractive index of the solvent. The fluorescence quantum yields were measured relative to cresyl violet ( $\Phi_F = 54\%$  in methanol). Excitations of reference and sample compounds were performed at the same wavelength.

## Computational details

DFT calculations were performed with the Gaussian 09 software package, revision D.01.<sup>[2]</sup> All optimized **geometries** were assigned to a minimum by frequency calculations with the Berny algorithm<sup>[3]</sup> at the hybrid B3LYP<sup>[4]</sup> or CAM-B3LYP<sup>[5]</sup> level of theory. Optimizations were carried out in gas phase without any constraints at 298 K and 1 atm. Chlorine atom was represented by the Relativistic Effective Core Potential (RECP) of the Stuttgart group and the associated

basis sets<sup>[6]</sup> augmented by a d-polarization function.<sup>[7]</sup> The remaining atoms (C, H, O, N, B, F) were represented by the 6-311G(d,p) Pople basis set.<sup>[8]</sup> All **energies** are reported in Hartrees as Self-Consistent Field (SCF) energies along with their corrections. **Solvent** effects were assessed through the integral equation formalism variant of the Polarizable Continuum Model (IEFPCM)<sup>[9]</sup> with default parameters for acetonitrile. **Electronic vertical excitations** were calculated with TD-DFT at the B3LYP/6-311G(d,p) level of theory in gas phase. Data are reported as follows: transition number, wavelength (nm), energy (eV), oscillator strength (cgs), Molecular Orbitals involved in the transition, CI coefficient and contribution (%). Only transitions with  $\geq 25\%$  contribution are reported. **Frontier Molecular Orbitals** were computed at the B3LYP/6-311G(d,p) level of theory in gas phase and the pictures rendered with Visual Molecular Dynamics (VMD) software, version 1.9.1.<sup>[10]</sup> **Electrostatic Potential Surfaces** were computed at the B3PW91<sup>[11]</sup>/6-311G(d,p) level of theory in gas phase. **Spin densities** are reported with hydrogens summed into heavy atoms.

## Crystallography

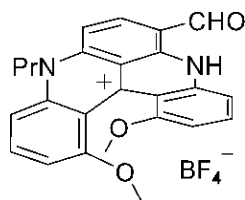
All data were collected on an Agilent supernova using Cu K $\alpha$ 1 radiation. Refinements were carried out in the SHELXL<sup>[12]</sup> program, within the *Olex2*<sup>[13]</sup> graphical software. Details for the refinement of each structure are reported along with a representation of the cation and the content of the asymmetric units shown as displacement ellipsoids (drawn at 50 percent probability). For disordered structures, comments on the modeling of the disorder are included.

## 2. Synthesis and characterization of compounds

### General procedure for the formylation of quinacridinium salts **5**

To a solution of quinacridinium salt **5** (1.0 equiv) in DMF (12 equiv) is slowly added POCl<sub>3</sub> (24 equiv). The reaction mixture is allowed to stir for 17 h at 40 °C. After complete consumption of quinacridinium **5** (monitored by ESI-MS analysis of the crude sample), the reaction mixture is brought to 0 °C and stirred for 5 min. Then, small pieces of ice are carefully and slowly added one by one until bubbling is no longer observed, and the reaction mixture is allowed to stir for 1 h at 25 °C. The product is extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed several times with a solution of LiCl (10 wt%) until the organic phase is no longer colorful. Then, the organic phase is washed with a solution of HBF<sub>4</sub> 1 M and subsequently washed with a solution of NaOH 1.5 M. The organic phase is dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. Flash chromatography using silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (100:0 to 98:2 gradient) affords formylated derivatives in the neutral form. Finally, dissolution of the compounds in CH<sub>2</sub>Cl<sub>2</sub> and acidification with a solution of HBF<sub>4</sub> 1 M affords the desired derivatives **6** as dark purple solids.

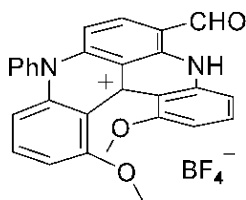
**8-Formyl-1,13-dimethoxy-5-propyl-5,9-dihydro-13bH-quinolino[2,3,4-kl]acridin-13b-ylum tetrafluoroborate (6a)**



Prepared according to the general procedure, using 1.99 g (4.34 mmol) of quinacridinium salt **5a**, 4 mL (52.1 mmol) of DMF and 9.8 mL (104 mmol) of POCl<sub>3</sub>. The desired compound was isolated as a dark purple solid (1.67 g, 3.42 mmol, 79%).

**R<sub>f</sub>** (neutral Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.45. **UV/Vis** (CH<sub>3</sub>CN, C = 5·10<sup>-6</sup> M, λ<sub>abs</sub> (ε)): 561 nm (12900 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR** (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$  2926, 1597, 1509, 1468, 1350, 1264, 1232, 1166, 1057, 784, 543, 527, 511 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 10.19 (s, 1H, CHO), 8.51 (d, *J* = 8.8 Hz, 1H, CH), 8.05 (t, *J* = 8.5 Hz, 1H, CH), 7.98 (t, *J* = 8.2, 1H, CH), 7.52 (dd, *J* = 8.9, 4.2 Hz, 2H, 2 x CH), 7.46 (d, *J* = 8.4 Hz, 1H, CH), 7.04 (d, *J* = 8.1 Hz, 1H, CH), 7.00 (d, *J* = 8.1 Hz, 1H, CH), 4.78-4.68 (m, 1H, CH<sub>2</sub>), 4.60-4.50 (m, 1H, CH<sub>2</sub>), 3.83 (d, *J* = 6.0 Hz, 6H, 2 x OCH<sub>3</sub>), 2.25-2.11 (m, 2H, CH<sub>2</sub>), 1.28 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 193.21, 160.84, 159.88, 143.76, 143.29, 142.74, 142.34, 140.16, 139.45, 138.88, 138.31, 117.40, 114.11, 113.51, 110.97, 110.29, 107.98, 105.41, 105.27, 56.49, 56.42, 20.67, 11.38 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -152.27 (brs, 20%), -152.32 (brs, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>25</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M<sup>+</sup>)]: 399.1703 m/z; found: 399.1708 m/z.

**8-Formyl-1,13-dimethoxy-5-phenyl-5,9-dihydro-13bH-quinolino[2,3,4-kl]acridin-13b-ylidium tetrafluoroborate (6b)**



Prepared according to the general procedure, using 100 mg (0.25 mmol) of quinacridinium salt **5b**, 0.23 mL (2.97 mmol) of DMF and 0.65 mL (6.92 mmol) of POCl<sub>3</sub>. The reaction was allowed to stir for 1 h at 90 °C. The desired compound was isolated as a dark purple solid (88 mg, 0.19 mmol, 75%).

**R<sub>f</sub>** (neutral Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.60. **UV/Vis** (CH<sub>3</sub>CN, C = 5·10<sup>-6</sup> M, λ<sub>abs</sub> (ε)): 563 nm (6000 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (CH<sub>2</sub>Cl<sub>2</sub>)**:  $\bar{\nu}$  1652, 1597, 1504, 1468, 1405, 1346, 1263, 1228, 1179, 1061, 1038, 816, 785, 753, 703, 547 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 10.14 (s, 1H, CHO), 8.24 (d, *J* = 8.9 Hz, 1H, CH), 8.02 (t, *J* = 8.3 Hz, 1H, CH), 7.89-7.83 (m, 3H, 3 x CH), 7.79 (dd, *J* = 8.8, 8.1 Hz, 1H, CH), 7.54-7.51 (m, 1H, CH), 7.50 (dd, *J* = 8.4, 0.9 Hz, 1H, CH), 7.45-7.42 (m, 1H, CH), 7.04 (d, *J* = 11.2 Hz, 1H, CH), 7.02 (d, *J* = 11.2 Hz, 1H, CH), 6.73 (d, *J* = 8.8 Hz, 1H, CH), 6.69 (dd, *J* = 8.7, 0.8 Hz, 1H, CH), 3.87 (d, *J* = 8.3 Hz, 6H, 2 x OCH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 193.22, 160.65, 160.14, 144.77, 144.55, 143.96, 142.22, 140.73, 139.34, 138.77, 138.39, 137.60, 132.93, 132.12, 131.92, 129.37, 128.19, 116.92, 113.78, 113.57, 111.15, 110.40, 109.86, 106.89, 105.55, 105.45, 56.53 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -152.70 (brs, 20%), -152.76 (brs, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>28</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> (M<sup>+</sup>)]: 433.1547 m/z; found: 433.1547 m/z.

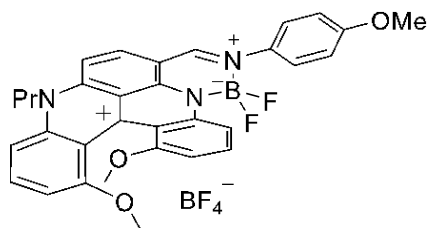


## General procedure for the synthesis of BODIPYs of type 4a

To a solution of quinacridinium salt **6** (1.0 equiv) and a spatula tip of powder molecular sieves (4 Å) in CH<sub>3</sub>CN (0.05 M), the corresponding amine (1.1 equiv) is added. Pyrrolidine (10 mol%), is finally added and the reaction mixture is allowed to stir for 6 h at 25 °C. After complete consumption of quinacridinium **6a** (monitored by ESI-MS analysis of the crude sample), the solvent is evaporated and the crude used for the next step.

To a solution of the crude imine in dry and degassed CH<sub>2</sub>Cl<sub>2</sub> (0.05 M), DIPEA (5.5 equiv) is added. After 5 min of stirring, BF<sub>3</sub>·OEt<sub>2</sub> (48 wt% solution) (7.0 equiv) is slowly added and the reaction mixture is allowed to stir at 25 °C for 8 hours. After complete consumption of iminium intermediate **7** (monitored by ESI-MS analysis of the crude sample), H<sub>2</sub>O is added and the product is extracted with CH<sub>2</sub>Cl<sub>2</sub> (x3). The combined organic phases are assembled and a final wash with a solution of NaBF<sub>4</sub> 0.2 M is done. The organic layer is dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Flash chromatography using silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (100:0 to 98:2 gradient), followed by selective precipitations with Et<sub>2</sub>O affords the title BODIPY derivatives **4a** as dark red solids.

**6,6-Difluoro-1,15-dimethoxy-7-(4-methoxyphenyl)-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -  
[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate  
(4aA)**



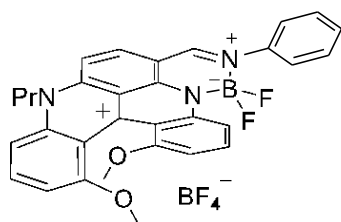
Prepared according to the general procedure, using 51 mg (0.10 mmol) of quinacridinium salt **6a**, 14.1 mg (0.11 mmol) of *p*-anisidine and 0.9  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 101  $\mu$ L of DIPEA (0.57 mmol) and 192  $\mu$ L (0.73 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. The desired compound was isolated as a dark red solid (43 mg, 0.07 mmol, 65%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.28. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 559 nm (12700 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  1599, 1583, 1554, 1506, 1469, 1454, 1377, 1334, 1279, 1255, 1207, 1170, 1023, 1009, 834, 821, 786, 756, 680, 659, 609, 563 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.88 (brs, 1H, CH), 8.56 (d, *J* = 9.0 Hz, 1H, CH), 8.34 (dt, *J* = 9.1, 3.2 Hz, 1H, CH), 8.02 (t, *J* = 8.5 Hz, 1H, CH), 7.95 (dd, *J* = 9.1, 7.9 Hz, 1H, CH), 7.68-7.63 (m, 2H, 2  $\times$  CH), 7.54 (dd, *J* = 9.0, 6.8 Hz, 2H, 2  $\times$  CH), 7.11-7.06 (m, 2H, 2  $\times$  CH), 7.02 (t, *J* = 8.4 Hz, 2H, 2  $\times$  CH), 4.78-4.67 (m, 1H, CH<sub>2</sub>), 4.63-4.51 (m, 1H, CH<sub>2</sub>), 3.89 (s, 3H, OCH<sub>3</sub>), 3.78 (d, *J* = 3.4 Hz, 6H, 2  $\times$  OCH<sub>3</sub>), 2.27-2.14 (m, 2H, CH<sub>2</sub>), 1.28 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  161.05, 160.99, 160.49, 159.61, 145.36, 142.96, 141.21, 140.18, 138.09, 137.18, 135.76, 126.04, 117.05, 117.02, 115.42, 115.23, 114.22, 114.11, 114.03, 103.92, 108.01, 106.92, 106.36, 105.48, 105.16, 56.38, 56.26, 56.19, 52.82, 20.84, 11.37 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -(116.27-117.02) (m, 1F, BF<sub>2</sub>), -(120.66-121.38) (m, 1F, BF<sub>2</sub>), -151.74 (s, 20%), -151.80 (s, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>32</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>3</sub> (M<sup>+</sup>): 552.2265 m/z; found: 552.2264 m/z.



**6,6-Difluoro-1,15-dimethoxy-7-phenyl-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -**

**[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate  
(4aC)**

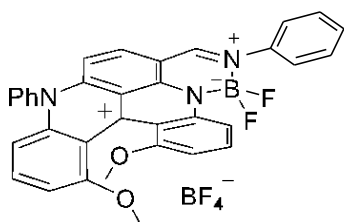


Prepared according to the general procedure, using 50 mg (0.10 mmol) of quinacridinium salt **6a**, 10  $\mu$ L (0.11 mmol) of aniline and 0.9  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 100  $\mu$ L of DIPEA (0.57 mmol) and 192  $\mu$ L (0.73 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. The desired compound was isolated as a dark red solid (49 mg, 0.08 mmol, 78%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.28. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 555 nm (10300 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  1597, 1580, 1549, 1512, 1493, 1469, 1378, 1332, 1279, 1262, 1208, 1107, 1055, 1024, 1007, 867, 823, 781, 754, 732, 698, 658, 617, 578 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.88 (brs, 1H, CH), 8.55 (d, *J* = 9.1 Hz, 1H, CH), 8.37 (dt, *J* = 9.2, 3.2 Hz, 1H, CH), 8.04 (t, *J* = 8.5 Hz, 1H, CH), 7.97 (dd, *J* = 9.1, 8.0 Hz, 1H, CH), 7.75-7.69 (m, 2H, 2  $\times$  CH), 7.64-7.53 (m, 5H, 5  $\times$  CH), 7.03 (dd, *J* = 9.7, 8.1 Hz, 1H, CH), 4.80-4.69 (m, 1H, CH<sub>2</sub>), 4.65-4.54 (m, 1H, CH<sub>2</sub>), 3.79 (d, *J* = 3.9 Hz, 6H, 2  $\times$  OCH<sub>3</sub>), 2.29-2.15 (m, 2H, CH<sub>2</sub>), 1.29 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  161.13, 159.94, 159.05, 145.08, 142.49, 142.44, 142.40, 142.25, 140.60, 137.58, 136.73, 129.85, 129.56, 124.42, 113.73, 113.56, 113.50, 113.48, 113.41, 107.47, 105.94, 105.02, 104.70, 55.83, 55.64, 52.33, 20.32, 10.82 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -(116.44-117.18) (m, 1F, BF<sub>2</sub>), -(120.81-121.54) (m, 1F, BF<sub>2</sub>), -152.57 (s, 20%), -(152.61-152.63) (m, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>31</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>2</sub> (M<sup>+</sup>): 522.2159 m/z; found: 522.2166 m/z.

**6,6-Difluoro-1,15-dimethoxy-7,11-diphenyl-6,11-dihydro-15bH-6λ<sup>4</sup>,7λ<sup>4</sup>-**

**[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate**  
**(4bC)**

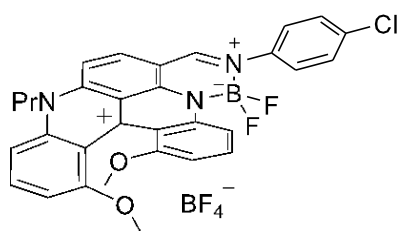


To a solution of quinacridinium salt **6b** (40 mg, 0.08 mmol) and a spatula tip of powder molecular sieves (4 Å) in CH<sub>3</sub>CN (2 mL, 0.04 M), aniline (7.7 μL, 85 μmol, 1.1 equiv) was added and the reaction mixture was allowed to stir for 1 h at 60 °C. After complete consumption of quinacridinium **6b** (monitored by ESI-MS analysis of the crude sample), the crude reaction mixture was cooled down to 25 °C and the solvent evaporated. To this mixture, dry and degassed CH<sub>2</sub>Cl<sub>2</sub> (4 mL, 0.02 M) and DIPEA (74 μL, 0.43 mmol, 5.5 equiv) were added. After 5 min of stirring, BF<sub>3</sub>·OEt<sub>2</sub> (48 wt% solution) (66 μL, 0.54 mmol, 7.0 equiv) was slowly added and the reaction mixture was allowed to stir at 25 °C for 12 hours. After complete consumption of iminium intermediate **7** (monitored by ESI-MS analysis of the crude sample), H<sub>2</sub>O was added and the product extracted with CH<sub>2</sub>Cl<sub>2</sub> (x3). The combined organic phases were assembled and a final wash with a solution of NaBF<sub>4</sub> 0.2 M was done. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Flash chromatography using silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (100:0 to 98:2 gradient), followed by selective precipitations with Et<sub>2</sub>O afforded BODIPY derivative **4bC** as a dark red solid (39 mg, 0.06 mmol, 82%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 98:2): 0.50. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M, λ<sub>abs</sub> (ε)): 559 nm (5600 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR** (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$  2921, 2852, 1712, 1598, 1550, 1506, 1463, 1377, 1318, 1264, 1202, 1058, 1021, 860, 751, 721, 699, 590, 569, 552, 539, 528, 520 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.86 (brs, 1H, CH), 8.40 (dt, J = 9.1, 3.2 Hz, 1H, CH), 8.30 (d, J = 9.1, 1H, CH), 8.01 (dd, J = 9.1, 8.0 Hz, 1H, CH), 7.90-7.83 (m, 3H, 3 x CH), 7.79 (t, J = 8.5 Hz, 1H, CH), 7.74-7.69 (m, 2H, 2 x CH), 7.64-7.54 (m, 4H, 4 x CH), 7.50-7.45 (m, 1H, CH), 7.04 (dd, J = 15.9, 8.0 Hz, 2H, 2 x CH), 6.79 (d, J = 9.0, 1H, CH), 6.73 (d, J = 8.8 Hz, 1H, CH), 3.83 (d, J = 2.3 Hz, 6H, 2 x OCH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 160.5, 159.0, 158.6, 145.5, 142.5, 142.2, 141.5, 141.4, 141.2, 139.1, 136.4, 136.3, 131.5, 130.7, 130.7, 129.1, 128.8, 128.0, 126.8, 123.6, 115.15,

114.1, 112.8, 112.7, 112.7, 112.4, 108.7, 106.8, 105.7, 104.4, 104.0 ppm.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -(115.87-116.62) (m, 1F,  $\text{BF}_2$ ), -(119.83-120.54) (m, 1F,  $\text{BF}_2$ ), -151.79 (s, 20%), -151.84 (s, 80%) (4F,  $\text{BF}_4$ ) ppm. **HRMS (ESI)** calculated for  $[\text{C}_{34}\text{H}_{25}\text{B}_2\text{F}_6\text{N}_3\text{O}_2 (\text{M}^+)]$ : 556.2002 m/z; found: 556.2000 m/z.

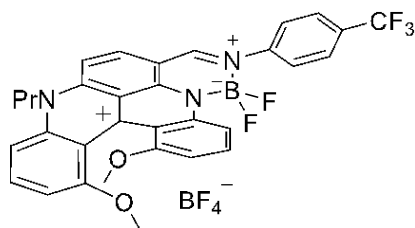
**7-(4-Chlorophenyl)-6,6-difluoro-1,15-dimethoxy-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate (4aD)**



Prepared according to the general procedure, using 52 mg (0.11 mmol) of quinacridinium salt **6a**, 15.3 mg (0.12 mmol) of *p*-chloroaniline and 0.9  $\mu\text{L}$  (0.01 mmol) of pyrrolidine in 2 mL of  $\text{CH}_3\text{CN}$ , and 102  $\mu\text{L}$  of DIPEA (0.59 mmol) and 197  $\mu\text{L}$  (0.75 mmol) of  $\text{BF}_3\cdot\text{OEt}_2$  (48 wt%) in 2 mL of dry and degassed  $\text{CH}_2\text{Cl}_2$ . The desired compound was isolated as a light red solid (56 mg, 0.09 mmol, 82%).

$R_f$  (basic  $\text{Al}_2\text{O}_3$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 97:3): 0.30. **UV/Vis** ( $\text{CH}_3\text{CN}$ ,  $\text{C} = 10^{-5}$  M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 553 nm (11200  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). **IR (neat)**:  $\bar{\nu}$  1599, 1549, 1510, 1487, 1469, 1380, 1334, 1262, 1205, 1171, 1149, 1026, 1009, 822, 784, 754, 658, 578  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.92 (brs, 1H, CH), 8.59 (d,  $J = 9.1$  Hz, 1H, CH), 8.36 (dt,  $J = 9.1, 3.2$  Hz, 1H, CH), 8.03 (dd,  $J = 8.8, 8.1$  Hz, 1H, CH), 7.97 (dd,  $J = 9.1, 7.9$  Hz, 1H, CH), 7.72-7.68 (m, 2H, 2  $\times$  CH), 7.60-7.53 (m, 4H, 4  $\times$  CH), 7.03 (dd,  $J = 10.9, 8.0$  Hz, 2H, 2  $\times$  CH), 4.79-4.70 (m, 1H,  $\text{CH}_2$ ), 4.66-4.53 (m, 1H,  $\text{CH}_2$ ), 3.79 (d,  $J = 4.9$  Hz, 6H, 2  $\times$   $\text{OCH}_3$ ), 2.29-2.15 (m, 2H,  $\text{CH}_2$ ), 1.29 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  161.71, 160.51, 159.61, 145.75, 143.32, 142.95, 141.27, 141.13, 140.52, 138.15, 137.33, 136.04, 130.53, 126.39, 116.95, 115.28, 114.31, 114.10, 114.02, 113.95, 108.03, 106.65, 105.63, 105.33, 56.40, 56.20, 52.94, 20.90, 11.38 ppm.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -(116.37-117.11) (m, 1F,  $\text{BF}_2$ ), -(120.80-121.49) (m, 1F,  $\text{BF}_2$ ), -152.32 (brs, 20%), -(152.36-152.38) (brs, 80%) (4F,  $\text{BF}_4$ ) ppm. **HRMS (ESI)** calculated for  $[\text{C}_{31}\text{H}_{26}\text{BClF}_2\text{N}_3\text{O}_2 (\text{M}^+)]$ : 556.1769 m/z; found: 556.1792 m/z.

**6,6-Difluoro-1,15-dimethoxy-11-propyl-7-(4-(trifluoromethyl)phenyl)-6,11-dihydro-15bH-6λ<sup>4</sup>,7λ<sup>4</sup>-[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate (4aE)**



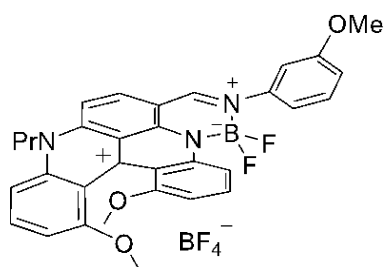
Prepared according to the general procedure, using 50 mg (0.10 mmol) of quinacridinium salt **6a**, 28  $\mu$ L (0.22 mmol) of *p*-(trifluoromethyl)aniline and 0.8  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN at 40 °C, and 99  $\mu$ L of DIPEA (0.56 mmol) and 189  $\mu$ L (0.71 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. The desired compound was isolated as a dark red solid (20 mg, 0.03 mmol, 28%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.30. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M, λ<sub>abs</sub> (ε)): 550 nm (10900 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  1599, 1549, 1510, 1468, 1378, 1324, 1281, 1261, 1209, 1170, 1052, 1025, 849, 822, 782, 753, 727, 660, 585 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 9.05 (brs, 1H, CH), 8.67 (d, *J* = 9.1 Hz, 1H, CH), 8.36 (dt, *J* = 9.1, 3.2 Hz, 1H, CH), 8.04 (t, *J* = 8.5 Hz, 1H, CH), 7.97 (dd, *J* = 9.1, 8.0 Hz, 1H, CH), 7.94-7.85 (m, 4H, 4 × CH), 7.57 (dd, *J* = 11.5, 9.0 Hz, 2H, 2 × CH), 7.04 (t, *J* = 8.4 Hz, 2H, 2 × CH), 4.80-4.69 (m, 1H, CH<sub>2</sub>), 4.65-4.54 (m, 1H, CH<sub>2</sub>), 3.79 (d, *J* = 3.7 Hz, 6H, 2 × OCH<sub>3</sub>), 2.29-2.15 (m, 2H, CH<sub>2</sub>), 1.29 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 162.28, 160.53, 159.65, 145.96, 145.60, 143.80, 142.95, 142.86, 141.12, 140.70, 138.21, 137.35, 131.82, 131.49, 127.60, 127.57, 127.53, 127.49, 125.70, 123.01, 116.89, 115.30, 114.35, 114.11, 114.02, 113.93, 108.09, 106.87, 105.76, 105.44, 56.43, 56.23, 52.96, 30.26, 20.95, 11.37 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -62.94 (s, 3F, CF<sub>3</sub>), -(115.78-116.53) (m, 1F, BF<sub>2</sub>), -(120.39-121.10) (m, 1F, BF<sub>2</sub>), -151.96 (s, 20%), -152.02 (m, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>32</sub>H<sub>26</sub>BF<sub>5</sub>N<sub>3</sub>O<sub>2</sub> (M<sup>+</sup>)]: 590.2033 m/z; found: 590.2060 m/z.





**6,6-Difluoro-1,15-dimethoxy-7-(3-methoxyphenyl)-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate (4aH)**



Prepared according to the general procedure, using 50 mg (0.10 mmol) of quinacridinium salt **6a**, 13  $\mu$ L (0.11 mmol) of *m*-anisidine and 0.8  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 100  $\mu$ L of DIPEA (0.57 mmol) and 190  $\mu$ L (0.72 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. The desired compound was isolated as a dark red solid (45 mg, 0.07 mmol, 69%).

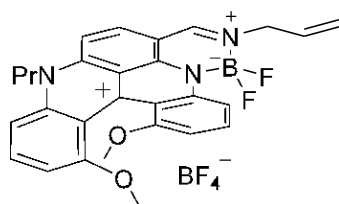
**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.30. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 555 nm (9200 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  1596, 1546, 1510, 1486, 1467, 1376, 1331, 1260, 1023, 781, 751, 718, 692, 618 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.89 (brs, 1H, CH), 8.55 (d, *J* = 9.1 Hz, 1H, CH), 8.37 (dt, *J* = 9.1, 3.2 Hz, 1H, CH), 8.03 (t, *J* = 8.4 Hz, 1H, CH), 7.96 (dd, *J* = 9.1, 7.9 Hz, 1H, CH), 7.56 (t, *J* = 8.7 Hz, 2H, 2 x CH), 7.50 (t, *J* = 8.1 Hz, 1H, CH), 7.30-7.25 (m, 2H, 2 x CH), 7.10 (ddd, *J* = 8.5, 2.5, 0.9 Hz, 1H, CH), 7.06-7.00 (m, 2H, 2 x CH), 4.80-4.69 (m, 1H, CH<sub>2</sub>), 4.65-4.54 (m, 1H, CH<sub>2</sub>), 3.92 (s, 3H, OCH<sub>3</sub>), 3.79 (d, *J* = 3.8 Hz, 6H, 2 x OCH<sub>3</sub>), 2.30-2.13 (m, 2H, CH<sub>2</sub>), 1.29 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  161.71, 161.23, 160.53, 159.64, 145.68, 143.88, 143.16, 142.98, 141.19, 138.14, 137.29, 131.17, 117.05, 115.75, 114.32, 110.92, 108.06, 106.54, 105.61, 105.28, 56.41, 56.29, 56.21, 20.91, 11.38 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -(116.44-117.20) (m, 1F, BF<sub>2</sub>), -(120.77-121.47) (m, 1F, BF<sub>2</sub>), -(152.48-152.51) (m, 20%), -152.55 (s, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>32</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>3</sub> (M<sup>+</sup>)]: 552.2265 m/z; found: 552.2286 m/z.



**7-Allyl-6,6-difluoro-1,15-dimethoxy-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -**

**[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate**

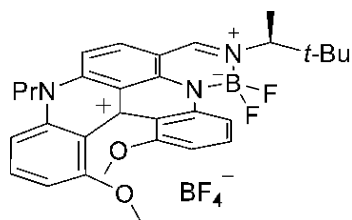
**(4aJ)**



Prepared according to the general procedure, using 50 mg (0.10 mmol) of quinacridinium salt **6a**, 9  $\mu$ L (0.11 mmol) of allylamine and 0.8  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 100  $\mu$ L of DIPEA (0.57 mmol) and 191  $\mu$ L (0.72 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. The desired compound was isolated as a dark red solid (22 mg, 0.04 mmol, 38%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.26. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 554 nm (13200 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  1650, 1587, 1559, 1510, 1459, 1375, 1334, 1277, 1259, 1250, 1172, 1025, 1005, 926, 822, 782, 753, 678, 651, 634, 531 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.83 (brs, 1H, CH), 8.49 (d, *J* = 9.0 Hz, 1H, CH), 8.32 (dt, *J* = 9.2, 3.2 Hz, 1H, CH), 7.97 (dt, *J* = 20.0, 8.6 Hz, 2H, 2 x CH), 7.55-7.44 (m, 2H, 2 x CH), 6.99 (dd, *J* = 8.1, 6.1 Hz, 2H, 2 x CH), 6.16 (ddt, *J* = 16.8, 9.9, 6.6 Hz, 1H, CH), 5.56 (dd, *J* = 27.6, 13.6 Hz, 2H, 2 x CH), 4.74-4.65 (m, 1H, CH<sub>2</sub>), 4.62 (d, *J* = 6.6 Hz, 2H, CH<sub>2</sub>), 4.58-4.47 (m, 1H, CH<sub>2</sub>), 3.77 (d, *J* = 2.3 Hz, 6H, 2 x OCH<sub>3</sub>), 2.26-2.10 (m, 2H, CH<sub>2</sub>), 1.27 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  162.77, 160.51, 159.63, 145.07, 143.17, 142.99, 142.40, 141.32, 140.00, 137.98, 137.11, 132.14, 122.71, 117.22, 115.15, 114.14, 114.00, 113.97, 107.92, 105.76, 105.24, 104.94, 56.34, 56.16, 55.37, 52.73, 20.75, 11.37 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -(123.28-124.03) (m, 1F, BF<sub>2</sub>), -(126.38-127.11) (m, 1F, BF<sub>2</sub>), -152.28 (brs, 20%), -(152.32-152.34) (m, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>28</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>2</sub> (M<sup>+</sup>)]: 486.2159 m/z; found: 486.2177 m/z.

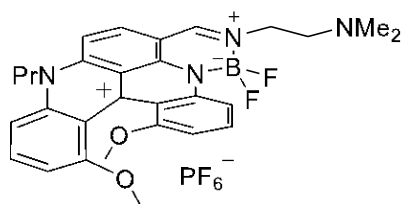
**(S)-7-(3,3-Dimethylbutan-2-yl)-6,6-difluoro-1,15-dimethoxy-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum tetrafluoroborate (4aK)**



Prepared according to the general procedure, using 50 mg (0.10 mmol) of quinacridinium salt **6a**, 15  $\mu$ L (0.11 mmol) of (*S*)-(+)-3,3-dimethyl-2-butylamine and 0.8  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 100  $\mu$ L of DIPEA (0.57 mmol) and 191  $\mu$ L (0.72 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. The desired compound was isolated as a dark red solid (19 mg, 0.03 mmol, 30%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.40. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 561 nm (13500 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  2962, 1644, 1597, 1583, 1557, 1510, 1453, 1374, 1330, 1274, 1258, 1170, 1051, 1023, 1006, 822, 781, 752, 651 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.87 (brs, 1H, CH), 8.54 (dd, *J* = 9.0, 3.5 Hz, 1H, CH), 8.34 (ddd, *J* = 13.2, 9.2, 3.0 Hz, 1H, CH), 8.00 (td, *J* = 8.5, 2.3 Hz, 1H, CH), 7.93 (t, *J* = 8.5 Hz, 1H, CH), 7.57-7.47 (m, 2H, 2  $\times$  CH), 6.99 (td, *J* = 9.5, 8.8, 2.5 Hz, 1H, CH), 4.76-4.64 (m, 1H, CH<sub>2</sub>), 4.61-4.49 (m, 1H, CH<sub>2</sub>), 4.28-4.18 (m, 1H, CH), 3.81-3.74 (m, 6H, 2  $\times$  OCH<sub>3</sub>), 2.25-2.11 (m, 2H, CH<sub>2</sub>), 1.62 (dd, *J* = 10.2, 7.1 Hz, 3H, CH<sub>3</sub>), 1.27 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>), 1.13 (d, *J* = 24.3 Hz, 9H, 3  $\times$  CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  161.58, 161.49, 160.50, 160.47, 159.71, 159.43, 144.98, 144.94, 143.40, 143.08, 142.80, 142.60, 142.48, 141.33, 141.31, 139.69, 137.99, 137.94, 137.02, 136.98, 117.19, 114.18, 114.09, 113.98, 113.91, 107.94, 107.93, 105.85, 105.59, 105.23, 105.20, 105.01, 104.78, 56.35, 56.32, 56.17, 56.14, 52.65, 36.33, 27.89, 27.60, 20.75, 18.25, 20.72, 18.03, 11.34 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -(119.98-120.76) (m, 1F, BF<sub>2</sub>), -(122.54-123.34) (m, 50%), -(126.36-127.10) (m, 50%) (1F, BF<sub>2</sub>), -152.24 (brs, 20%), -(152.28-152.30) (m, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>31</sub>H<sub>35</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>2</sub> (M<sup>+</sup>)]: 530.2785 m/z; found: 530.2785 m/z.

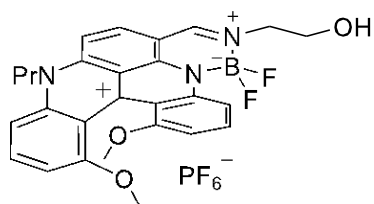
**7-(2-(Dimethylamino)ethyl)-6,6-difluoro-1,15-dimethoxy-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum hexafluorophosphate (4aL)**



Prepared according to the general procedure, using 49 mg (0.10 mmol) of quinacridinium salt **6a**, 12  $\mu$ L (0.11 mmol) of *N,N*-dimethylethylenediamine and 0.8  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 98  $\mu$ L of DIPEA (0.56 mmol) and 188  $\mu$ L (0.71 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. Ion metathesis with a solution of KPF<sub>6</sub> 0.2 M was done before flash chromatography. The desired compound was isolated as a dark red solid (67 mg, 0.07 mmol, 73%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.41. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 553 nm (11600 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  1649, 1598, 1560, 1511, 1458, 1376, 1352, 1332, 1258, 1171, 1111, 1094, 1050, 1023, 1009, 831, 781, 753, 657, 555 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.71 (brs, 1H, CH), 8.39 (d, *J* = 9.0 Hz, 1H, CH), 8.30 (dt, *J* = 9.1, 3.1 Hz, 1H, CH), 8.00 (dd, *J* = 8.9, 8.1 Hz, 1H, CH), 7.94 (dd, *J* = 9.1, 7.9 Hz, 1H, CH), 7.48 (dd, *J* = 10.6, 8.8 Hz, 2H, 2  $\times$  CH), 6.99 (t, *J* = 8.0 Hz, 2H, 2  $\times$  CH), 4.75-4.64 (m, 1H, CH<sub>2</sub>), 4.58-4.45 (m, 1H, CH<sub>2</sub>), 4.01 (brs, 2H, CH<sub>2</sub>), 3.77 (d, *J* = 2.3 Hz, 6H, 2  $\times$  OCH<sub>3</sub>), 2.87 (td, *J* = 6.0, 1.4 Hz, 2H, CH<sub>2</sub>), 2.37 (s, 6H, 2  $\times$  CH<sub>3</sub>), 2.31-2.05 (m, 2H, CH<sub>2</sub>), 1.27 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  163.40, 160.50, 159.64, 144.92, 143.15, 143.03, 142.12, 141.32, 139.95, 138.03, 137.11, 117.26, 115.10, 114.12, 113.99, 113.92, 113.82, 107.88, 105.52, 105.23, 104.90, 58.93, 56.34, 56.15, 52.66, 50.29, 45.54, 30.26, 20.72, 11.35 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -71.73 (s), -74.25 (s) (6F, PF<sub>6</sub>), - (123.00-123.80) (m, 1F, BF<sub>2</sub>), -(126.52-127.29) (m, 1F, BF<sub>2</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>29</sub>H<sub>32</sub>BF<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (M<sup>+</sup>)]: 517.2581 m/z; found: 517.2576 m/z.

**6,6-Difluoro-7-(2-hydroxyethyl)-1,15-dimethoxy-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylium hexafluorophosphate (4aM)**



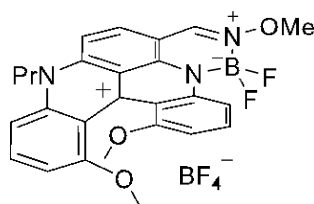
Prepared according to the general procedure, using 51 mg (0.10 mmol) of quinacridinium salt **6a**, 9  $\mu$ L (0.11 mmol) of 2-aminoethanol and 0.9  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 101  $\mu$ L of DIPEA (0.57 mmol) and 193  $\mu$ L (0.73 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. Ion metathesis with a solution of KPF<sub>6</sub> 0.2 M was done before flash chromatography. The desired compound was isolated as a dark red solid (43 mg, 0.07 mmol, 65%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.20. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 560 nm (17200 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  3605, 2924, 1643, 1597, 1559, 1510, 1457, 1374, 1331, 1259, 1242, 1172, 1083, 1051, 1023, 1007, 828, 820, 780, 753, 733, 656, 618, 555 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.81 (brs, 1H, CH), 8.39 (d, *J* = 9.0 Hz, 1H, CH), 8.36-8.28 (m, 1H, CH), 7.97 (dt, *J* = 16.9, 8.5 Hz, 2H, 2 x CH), 7.46 (dd, *J* = 18.1, 9.0 Hz, 2H, 2 x CH), 6.99 (dd, *J* = 8.1, 5.4 Hz, 2H, 2 x CH), 4.74-4.65 (m, 1H, CH<sub>2</sub>), 4.57-4.45 (m, 1H, CH<sub>2</sub>), 4.17-4.08 (m, 4H, 2 x CH<sub>2</sub>), 3.77 (d, *J* = 3.2 Hz, 6H, 2 x OCH<sub>3</sub>), 2.24-2.14 (m, 2H, CH<sub>2</sub>), 0.88 (t, *J* = 6.6 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  142.19, 142.17, 138.02, 137.23, 128.20, 107.86, 105.52, 105.26, 104.98, 61.50, 56.36, 56.16, 55.80, 32.50, 30.26, 29.93, 23.27, 14.45, 11.40 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -71.70 (s), -74.21 (s) (6F, PF<sub>6</sub>), -(122.83-123.61) (m, 1F, BF<sub>2</sub>), -(126.27-127.03) (m, 1F, BF<sub>2</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>27</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>3</sub> (M<sup>+</sup>)]: 490.2108 m/z; found: 490.2122 m/z.

**6,6-Difluoro-1,7,15-trimethoxy-11-propyl-6,11-dihydro-15bH-6 $\lambda^4$ ,7 $\lambda^4$ -**

**[1,3,2]diazaborinino[5,4,3-de]quinolino[4,3,2-mn]acridin-15b-ylum      tetrafluoroborate**

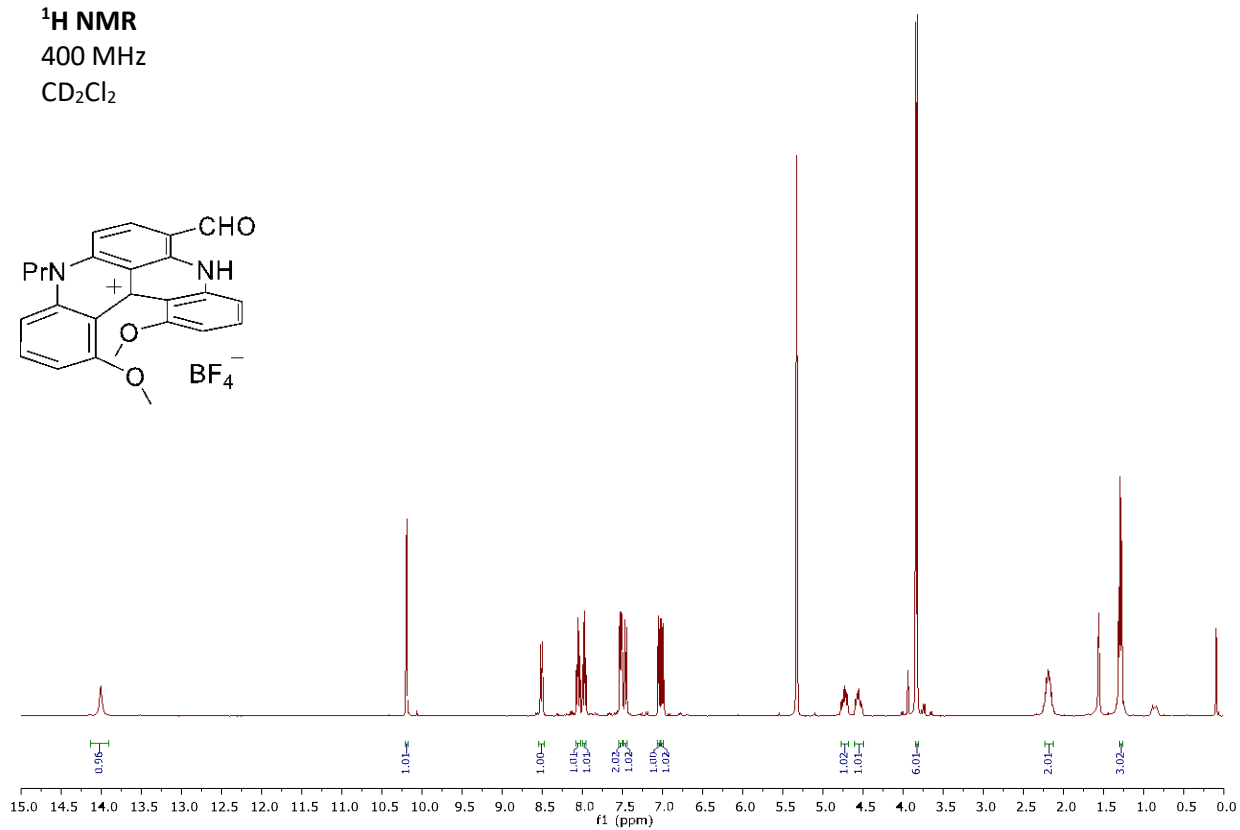
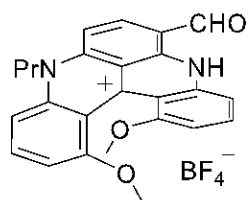
**(4aN)**



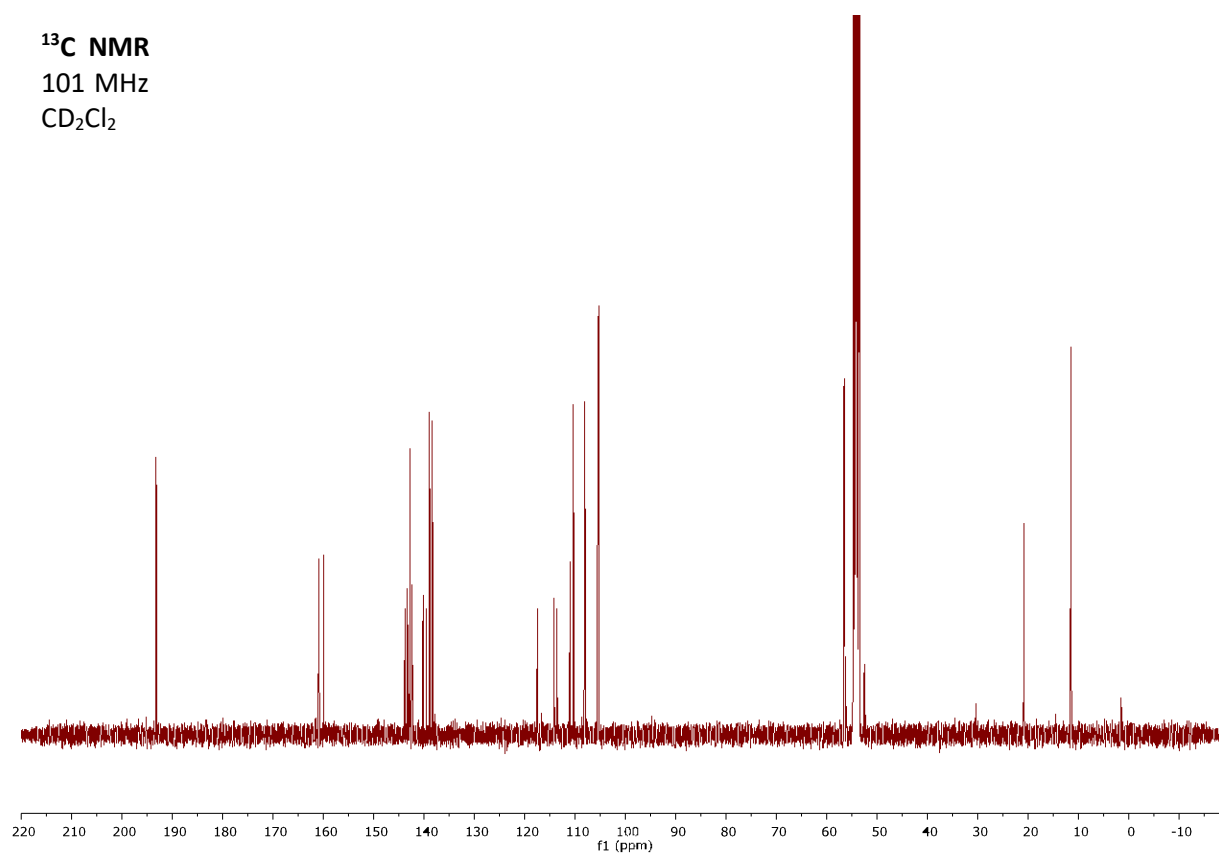
Prepared according to the general procedure, using 51 mg (0.10 mmol) of quinacridinium salt **6a**, 9.8 mg (0.11 mmol) of methoxyammonium chloride, 16  $\mu$ L (0.11 mmol) of Et<sub>3</sub>N (stirring for 10 min) and 0.9  $\mu$ L (0.01 mmol) of pyrrolidine in 2 mL of CH<sub>3</sub>CN, and 101  $\mu$ L of DIPEA (0.57 mmol) and 192  $\mu$ L (0.73 mmol) of BF<sub>3</sub>·OEt<sub>2</sub> (48 wt%) in 2 mL of dry and degassed CH<sub>2</sub>Cl<sub>2</sub>. The desired compound was isolated as a dark red solid (43 mg, 0.08 mmol, 74%).

**R<sub>f</sub>** (basic Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3): 0.34. **UV/Vis** (CH<sub>3</sub>CN, C = 10<sup>-5</sup> M,  $\lambda_{\text{abs}}$  ( $\epsilon$ )): 556 nm (10600 L·mol<sup>-1</sup>·cm<sup>-1</sup>). **IR (neat)**:  $\bar{\nu}$  1596, 1554, 1510, 1495, 1468, 1427, 1371, 1327, 1264, 1238, 1169, 1126, 1048, 1022, 946, 852, 822, 780, 750, 656, 590 cm<sup>-1</sup>. **<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.24 (brs, 1H, CH), 8.56 (d, *J* = 9.1 Hz, 1H, CH), 8.29 (dt, *J* = 9.1, 3.3 Hz, 1H, CH), 7.99 (ddd, *J* = 17.2, 8.9, 8.0 Hz, 2H, 2 x CH), 7.55 (d, *J* = 9.1 Hz, 1H, CH), 7.51 (d, *J* = 8.8 Hz, 1H, CH), 7.00 (dd, *J* = 8.0, 3.2 Hz, 2H, 2 x CH), 4.76-4.66 (m, 1H, CH<sub>2</sub>), 4.60-4.49 (m, 1H, CH<sub>2</sub>), 4.34 (s, 3H, OCH<sub>3</sub>), 3.77 (d, *J* = 3.2 Hz, 6H, 2 x OCH<sub>3</sub>), 2.27-2.12 (m, 2H, CH<sub>2</sub>), 1.28 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  160.50, 159.68, 156.57, 144.92, 143.15, 142.11, 141.28, 139.42, 138.14, 137.32, 115.05, 114.21, 107.92, 106.34, 105.26, 105.11, 103.30, 67.01, 56.37, 56.19, 52.88, 20.79, 11.38 ppm. **<sup>19</sup>F NMR** (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -(124.74-125.45) (m, 1F, BF<sub>2</sub>), -(128.02-128.70) (m, 1F, BF<sub>2</sub>), -152.02 (s, 20%), -(152.06-152.08) (m, 80%) (4F, BF<sub>4</sub>) ppm. **HRMS (ESI)** calculated for [C<sub>26</sub>H<sub>25</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>3</sub> (M<sup>+</sup>)]: 476.1952 m/z; found: 476.1953 m/z.

**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>

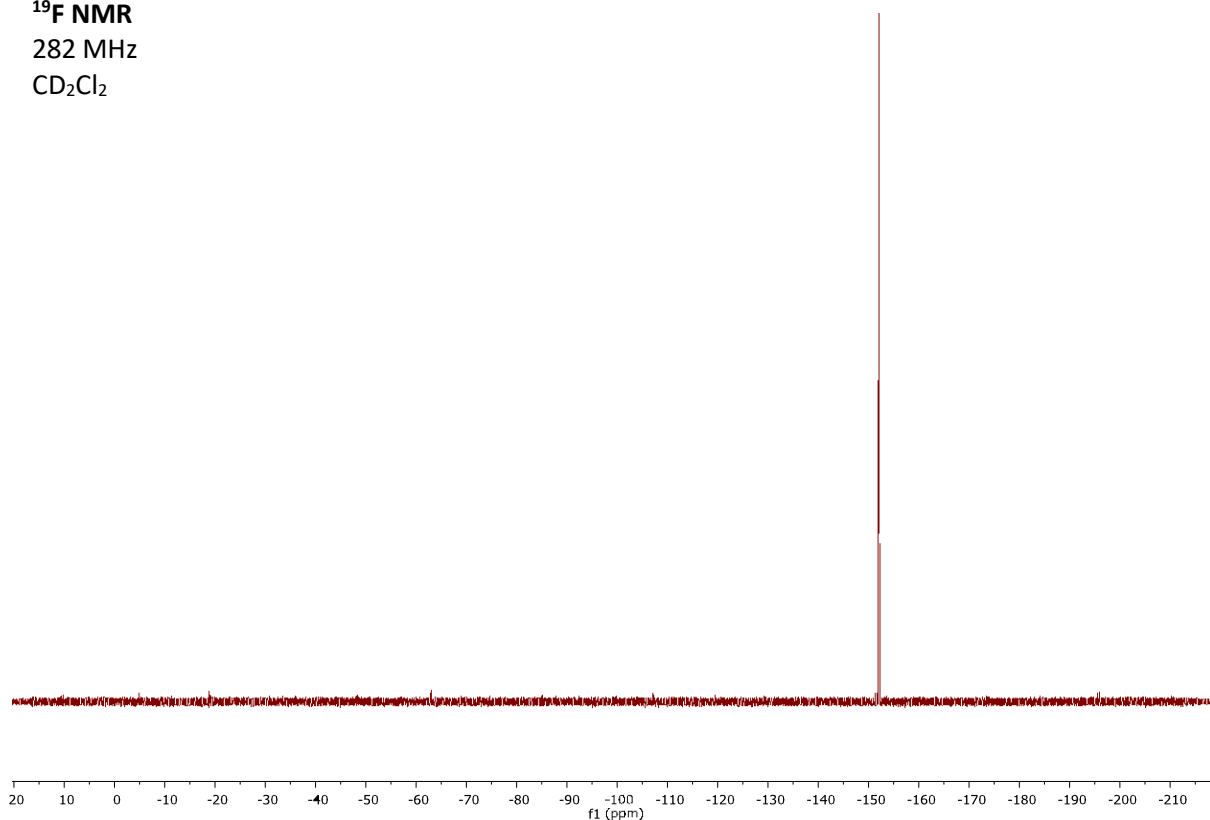


**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>

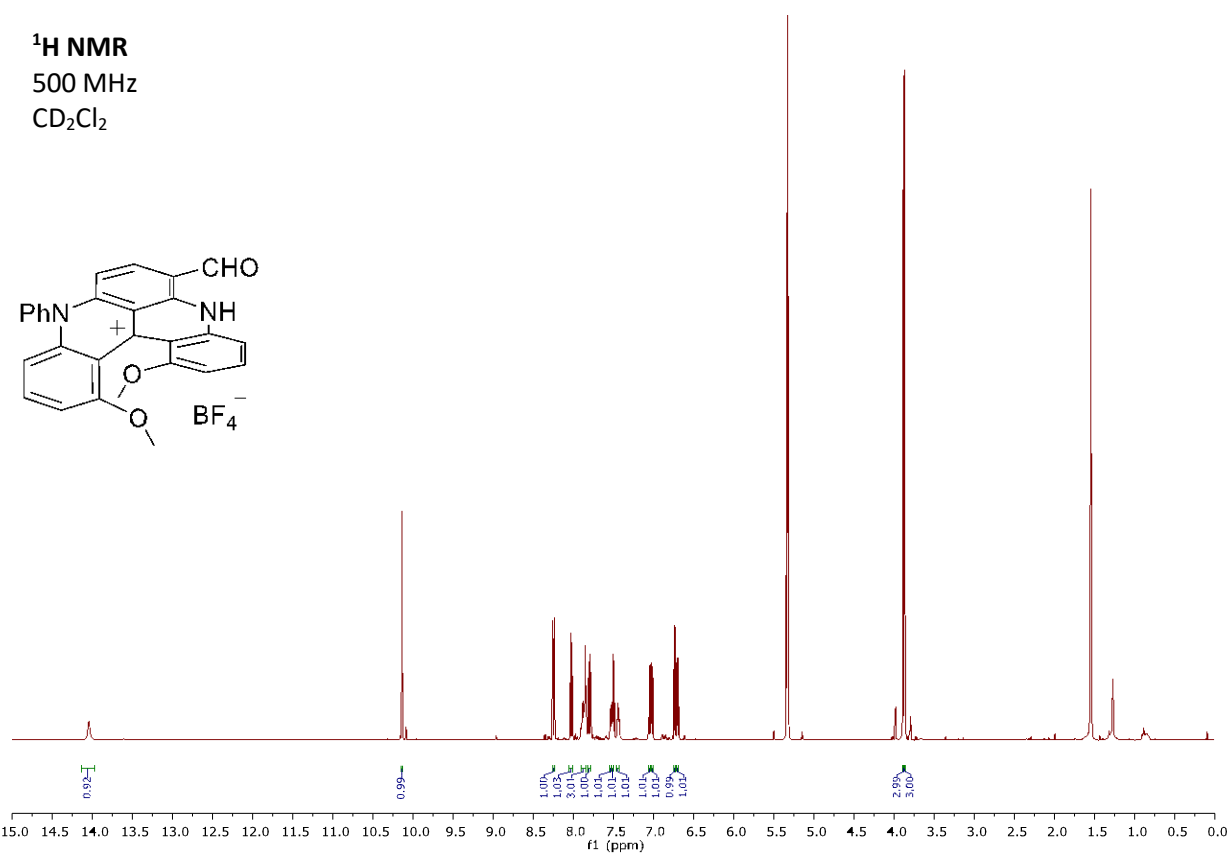




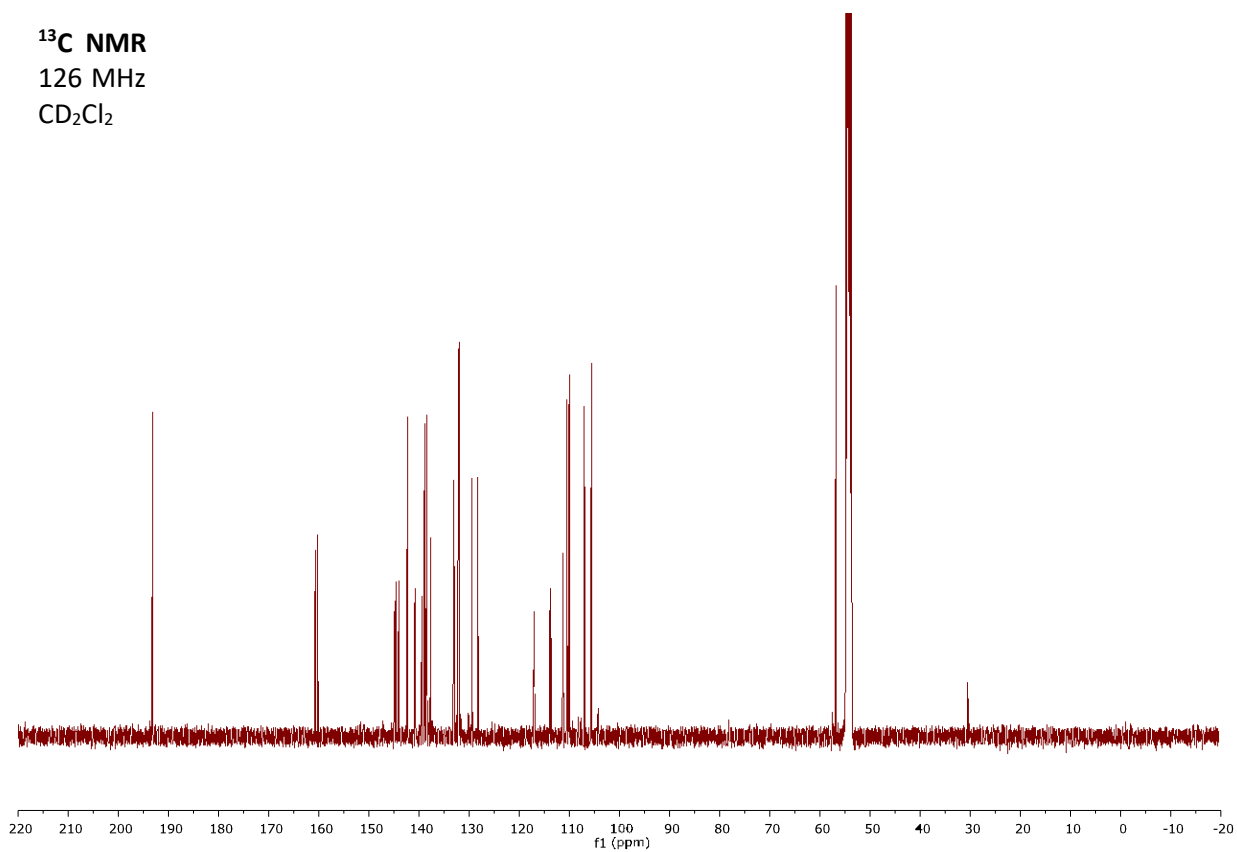
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



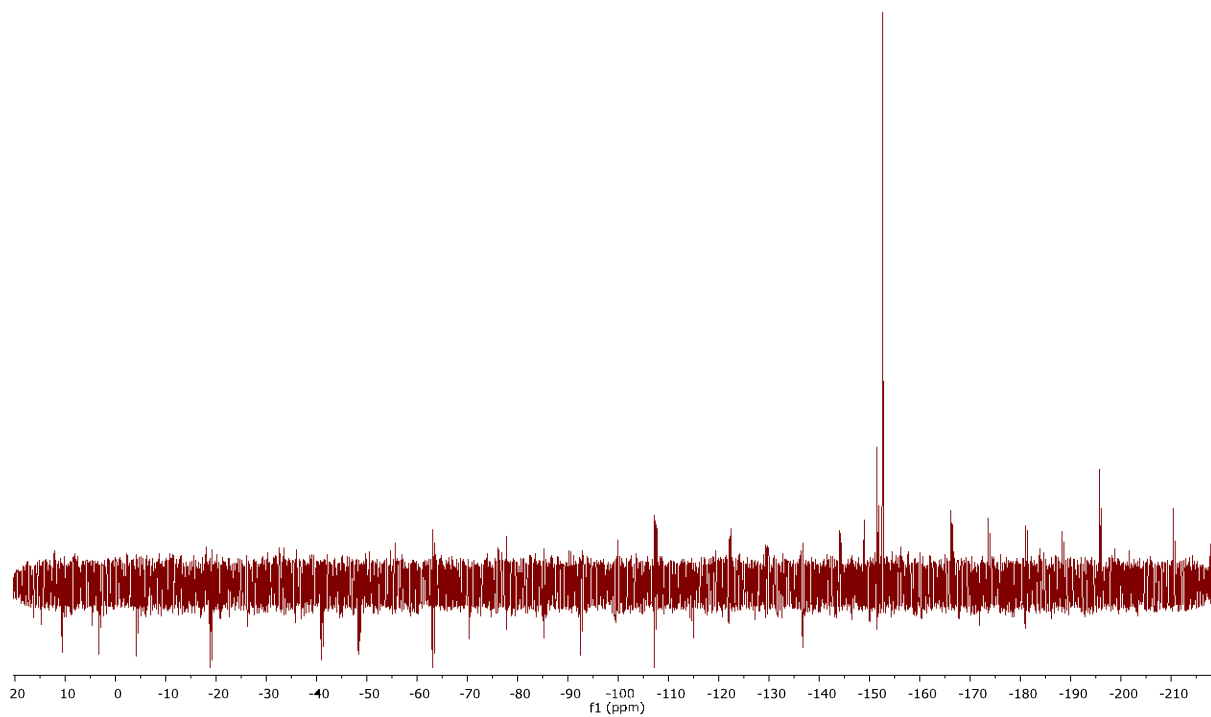
**<sup>1</sup>H NMR**  
500 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



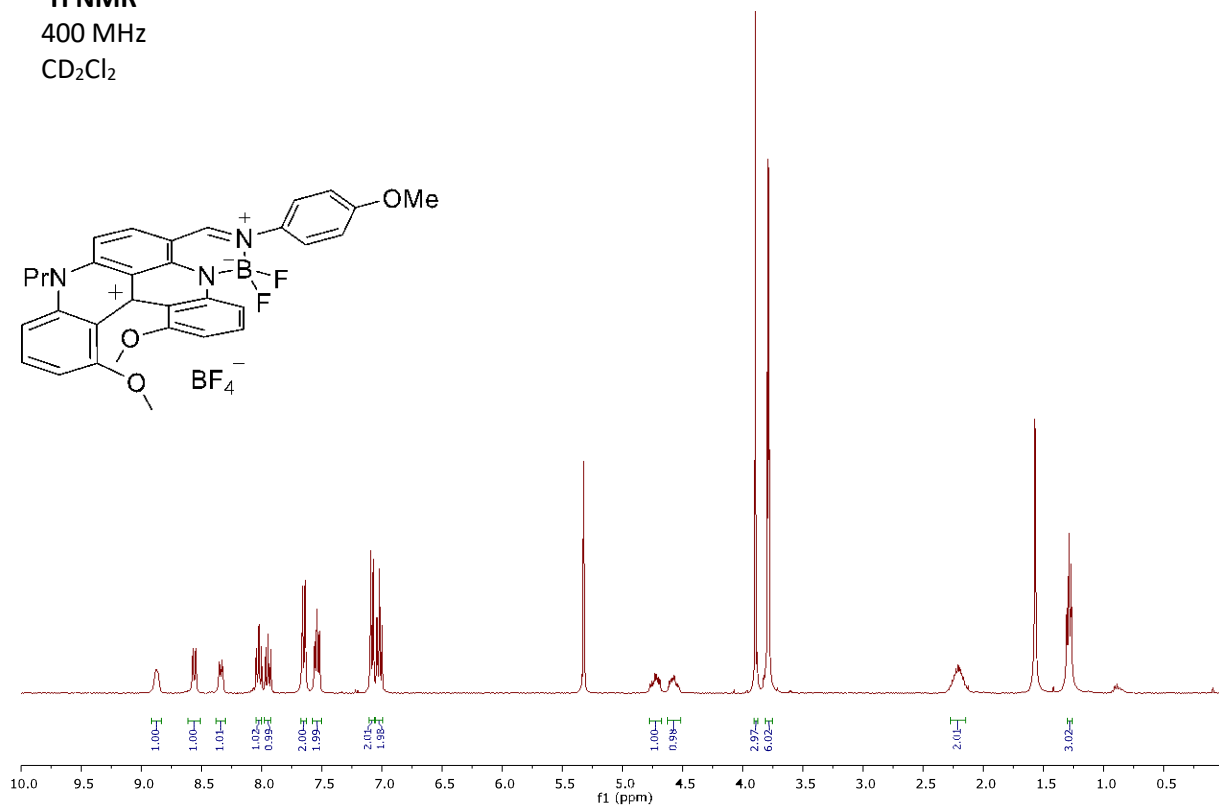
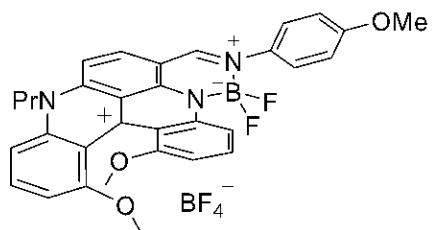
**$^{13}\text{C}$  NMR**  
126 MHz  
 $\text{CD}_2\text{Cl}_2$



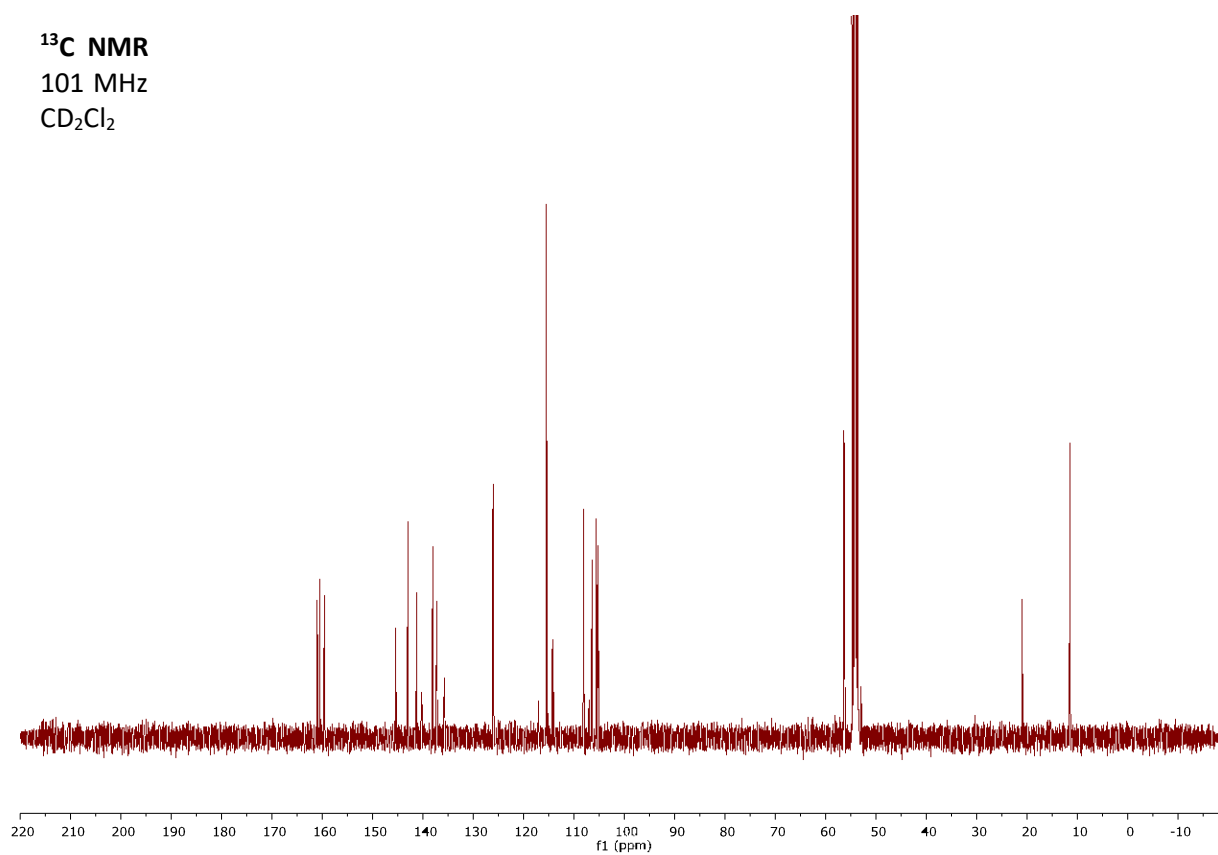
**$^{19}\text{F}$  NMR**  
282 MHz  
 $\text{CD}_2\text{Cl}_2$



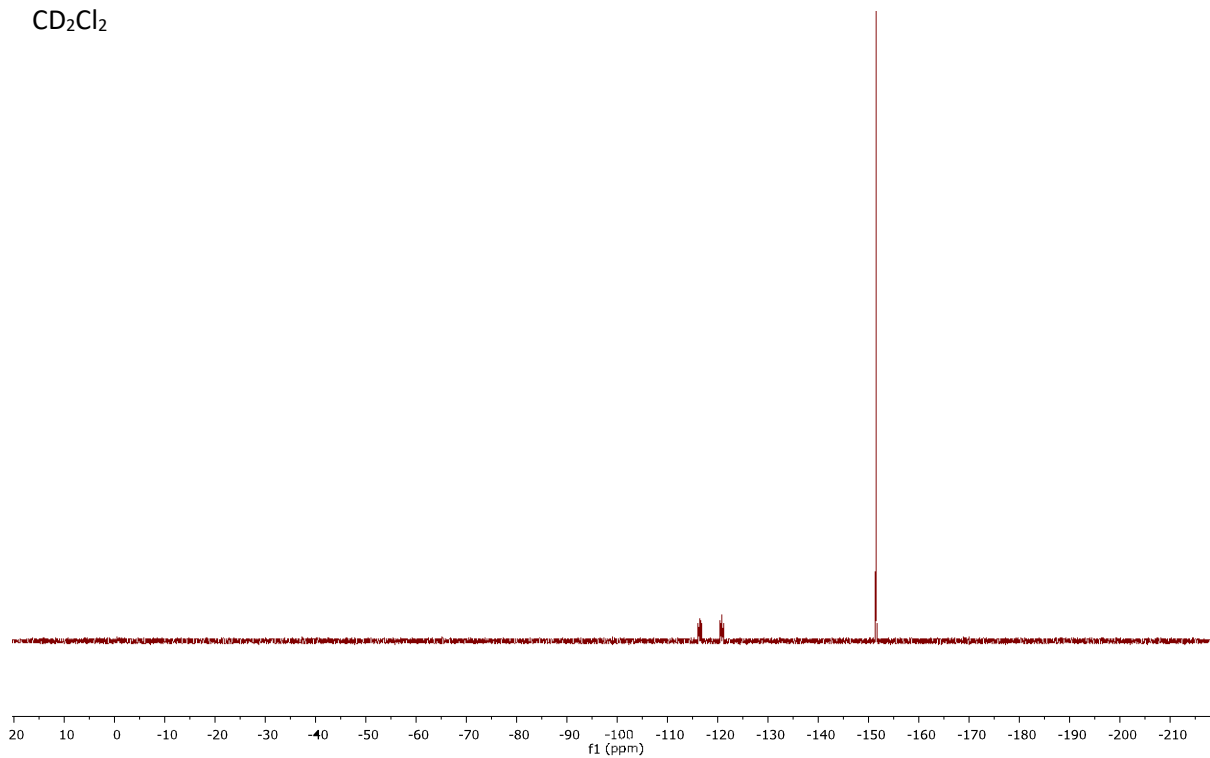
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



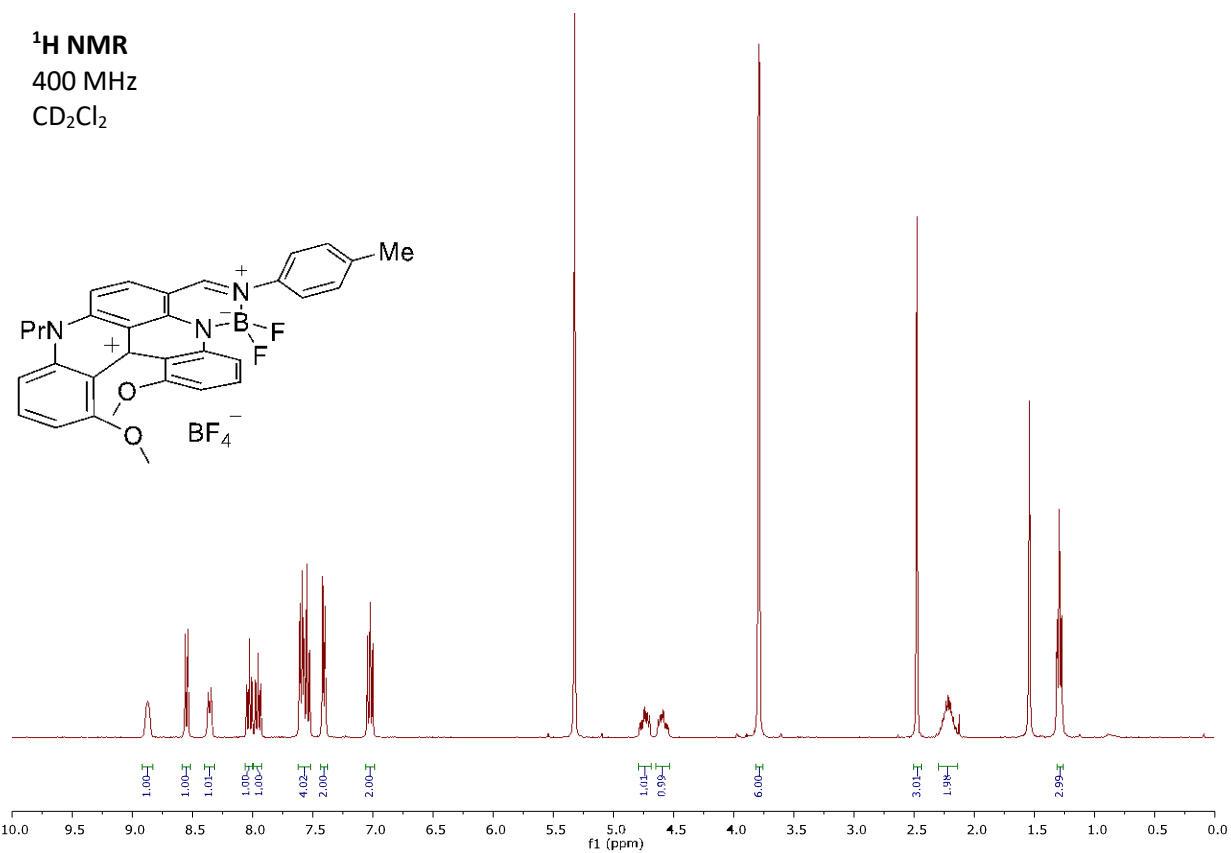
**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



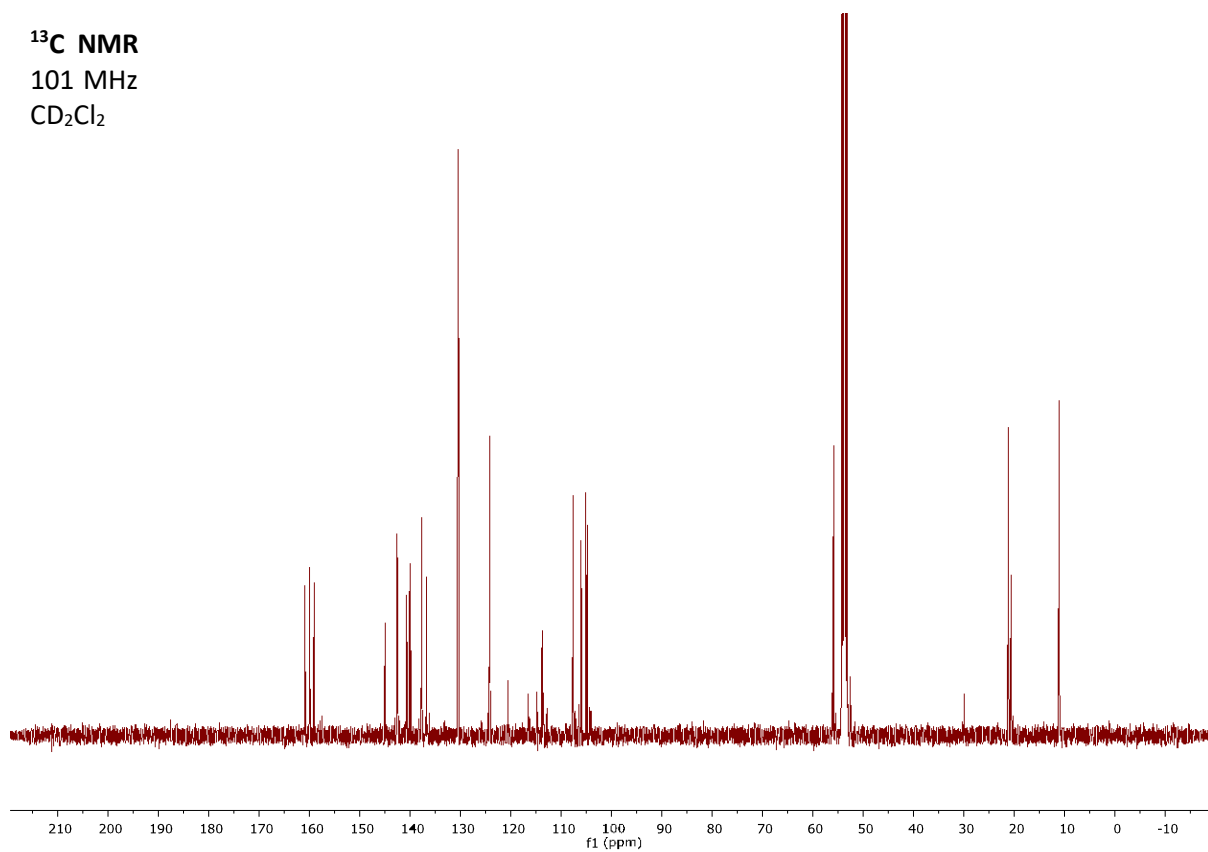
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



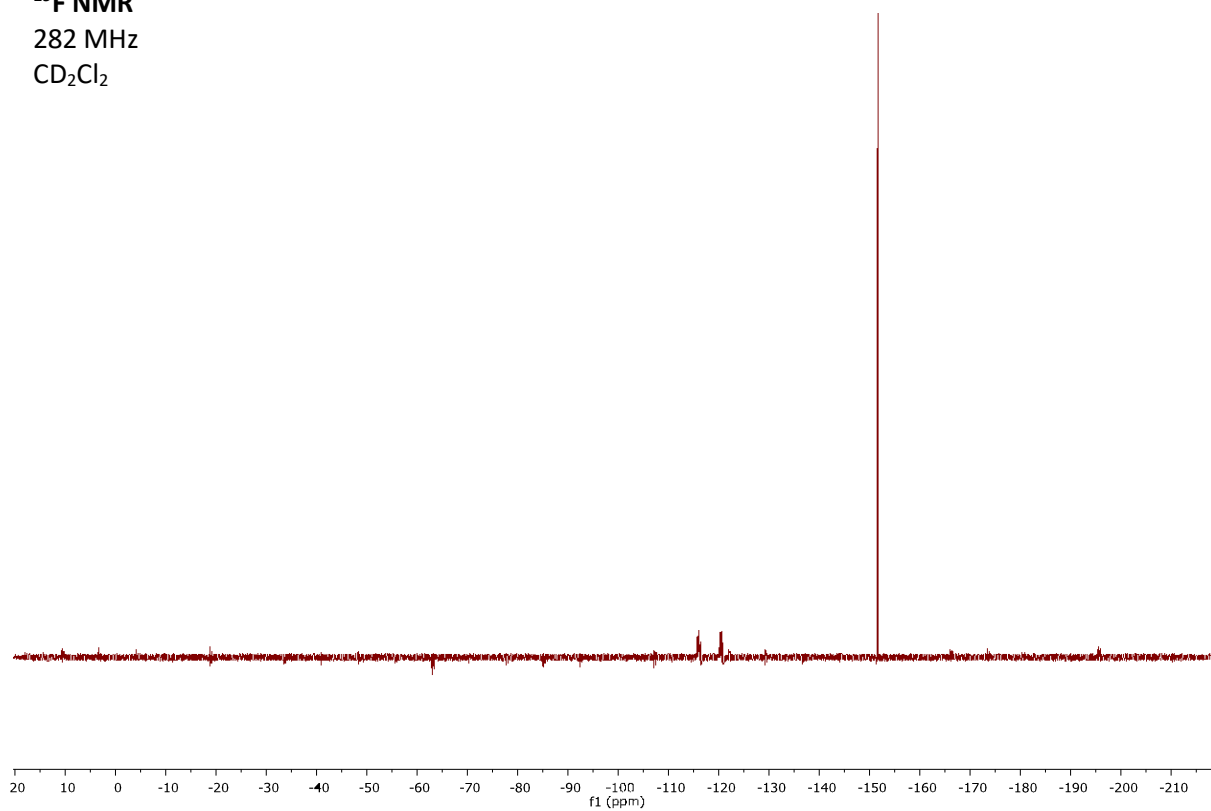
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



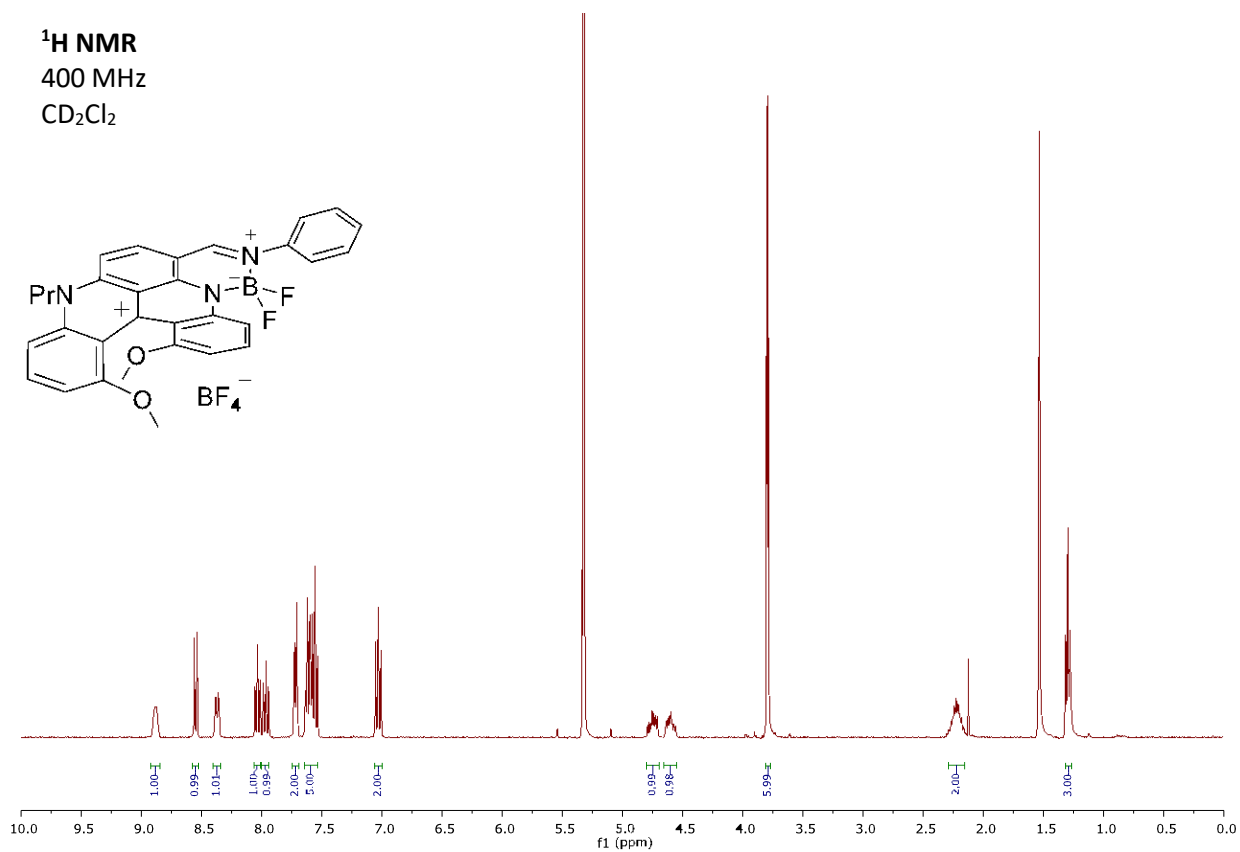
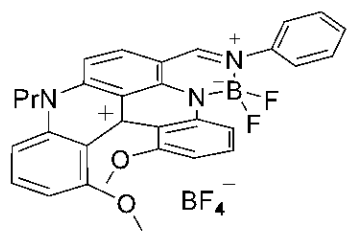
**$^{13}\text{C}$  NMR**  
101 MHz  
 $\text{CD}_2\text{Cl}_2$



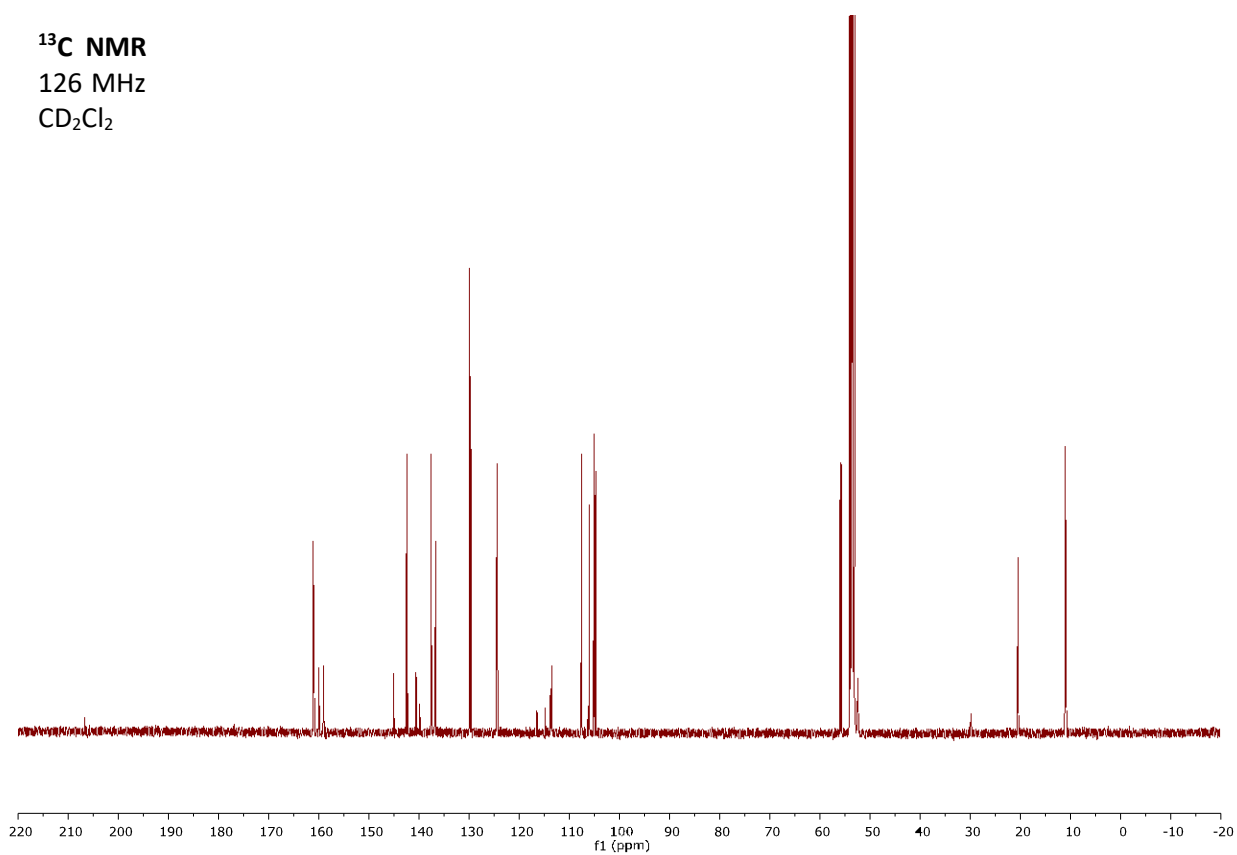
**$^{19}\text{F}$  NMR**  
282 MHz  
 $\text{CD}_2\text{Cl}_2$



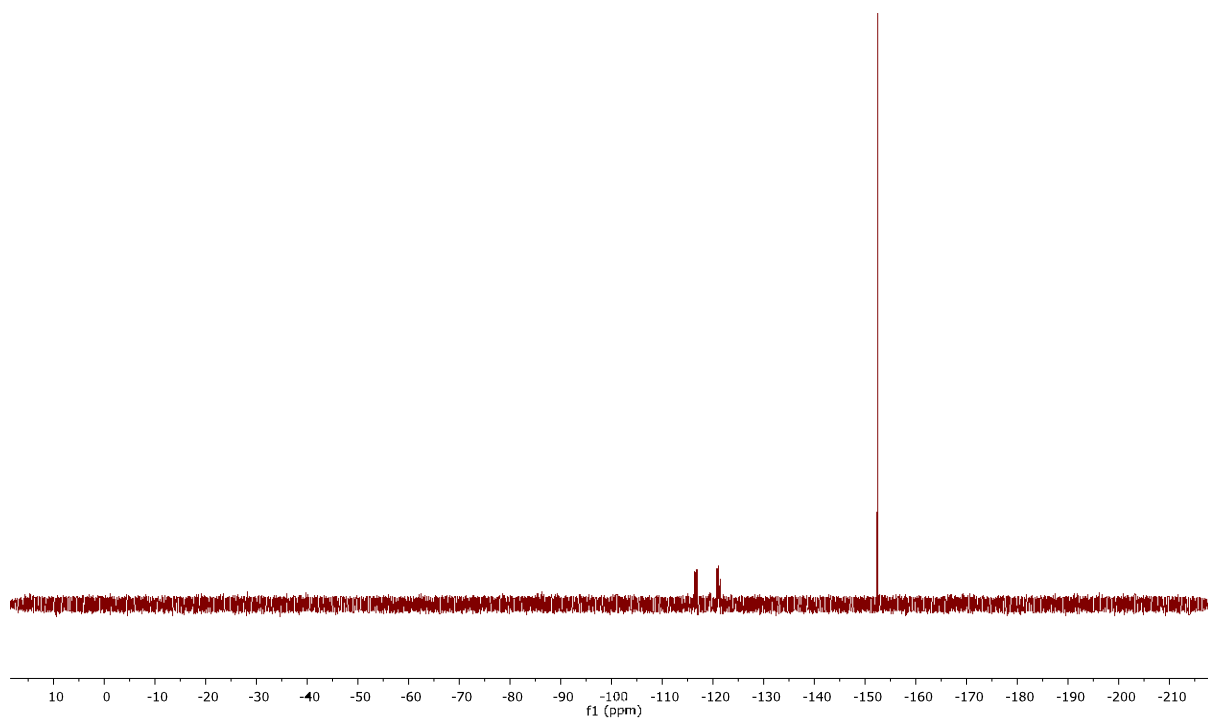
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



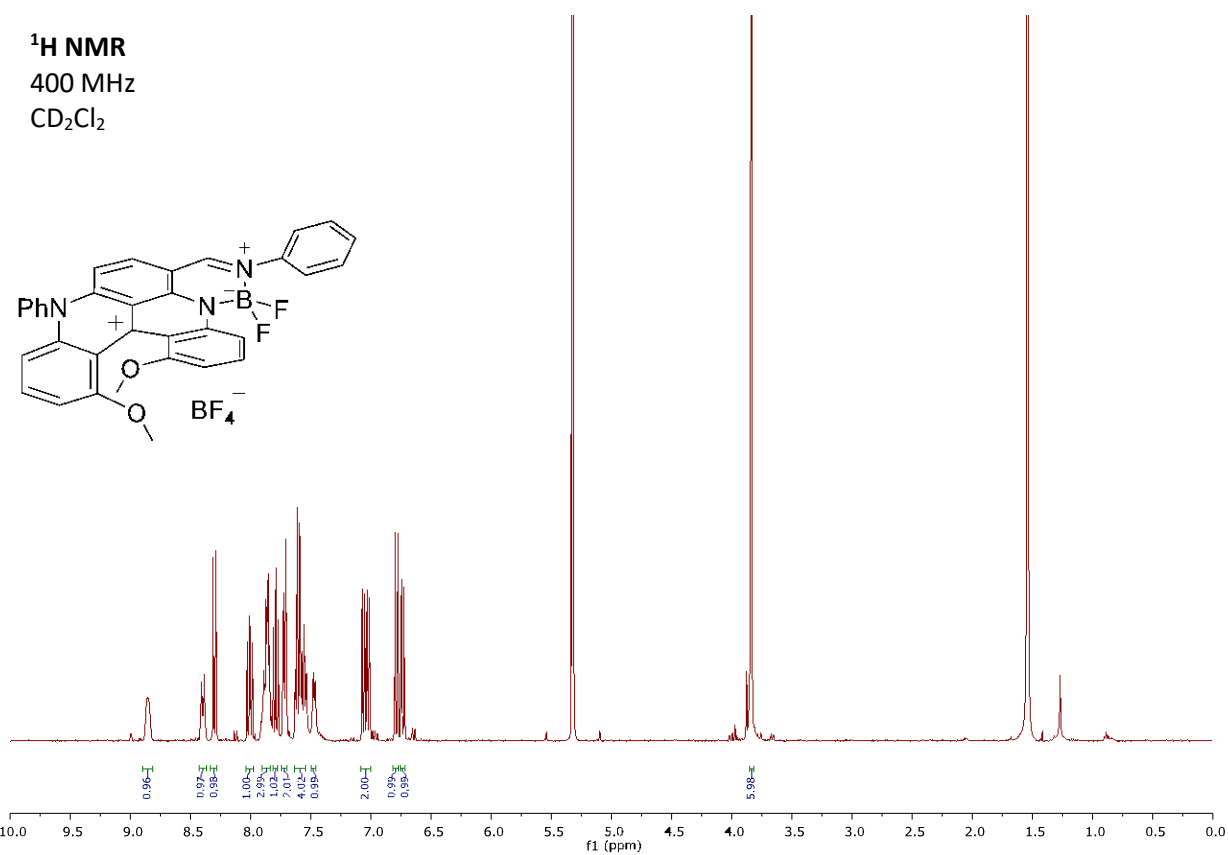
**<sup>13</sup>C NMR**  
126 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



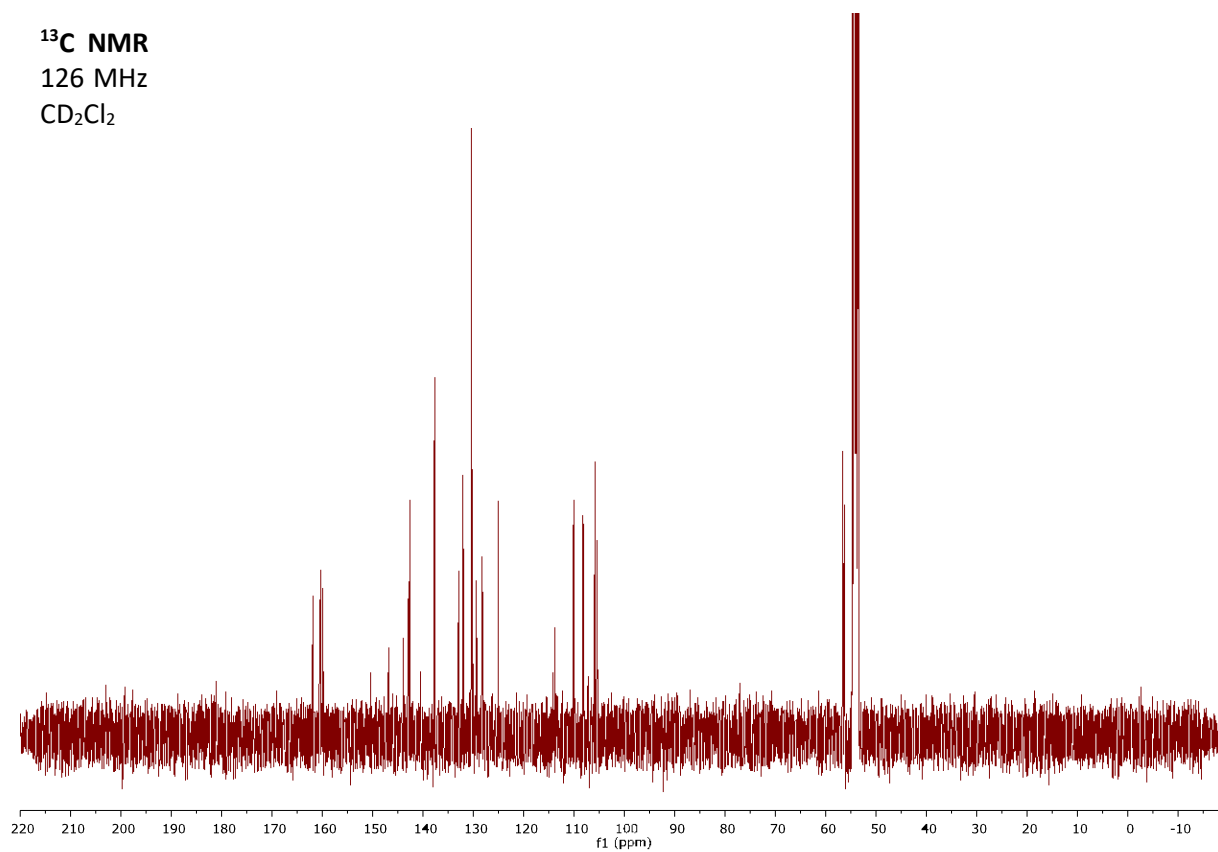
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



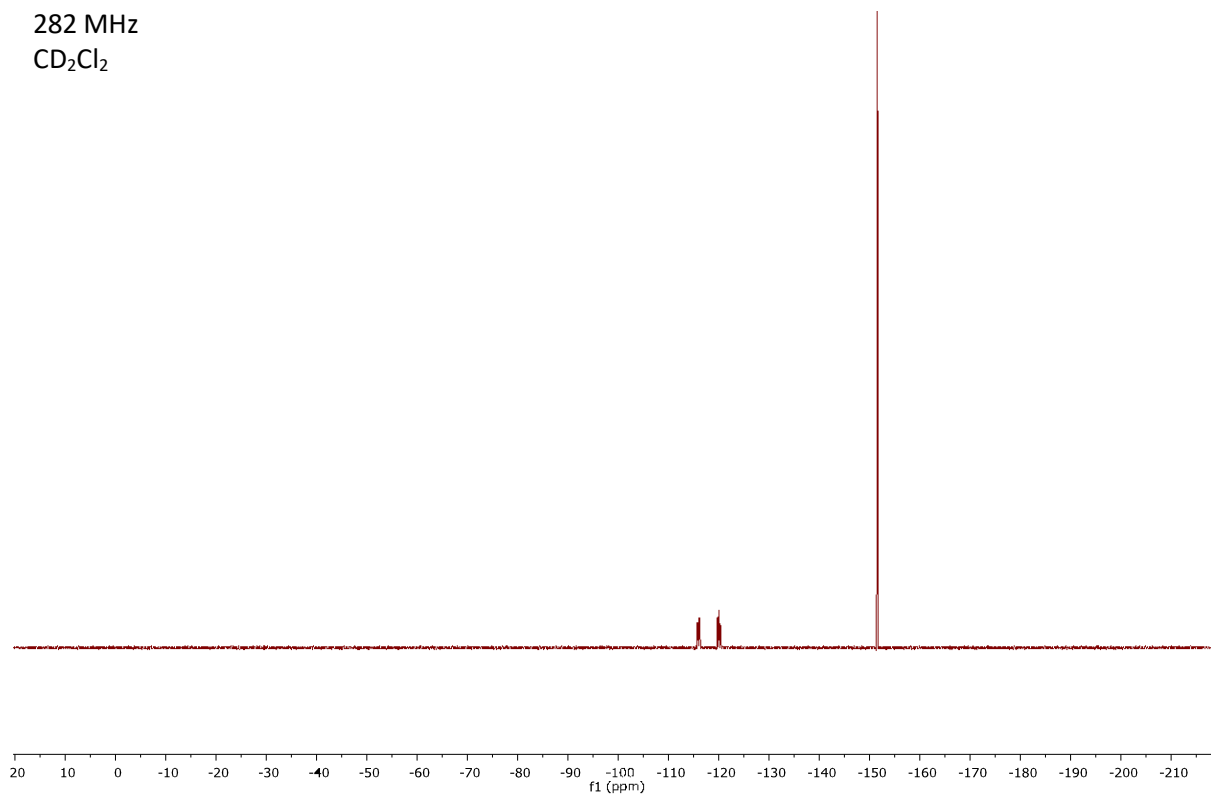
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



**$^{13}\text{C}$  NMR**  
126 MHz  
 $\text{CD}_2\text{Cl}_2$

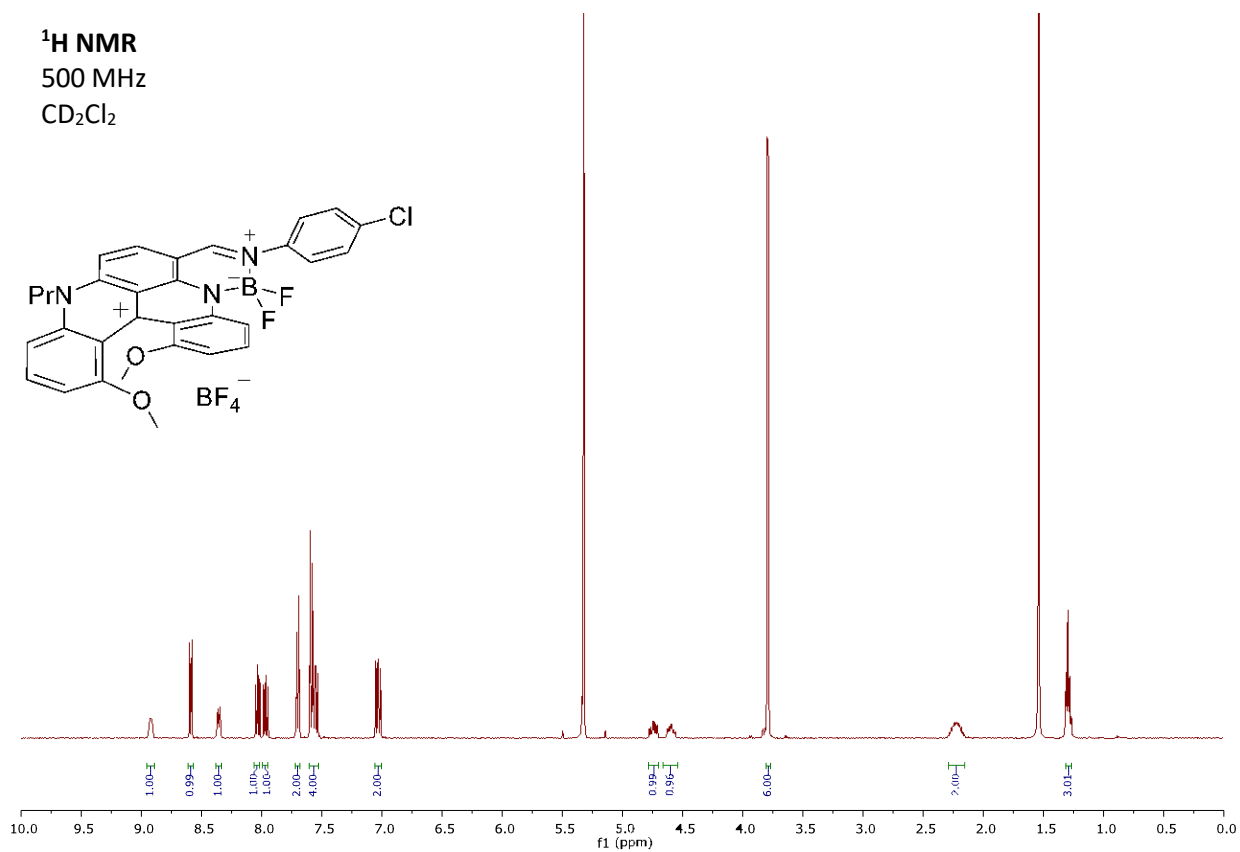
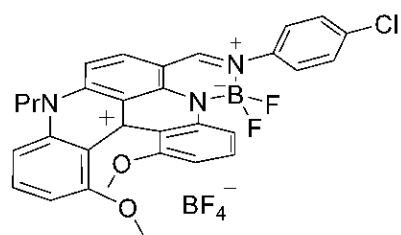


**$^{19}\text{F}$  NMR**  
282 MHz  
 $\text{CD}_2\text{Cl}_2$

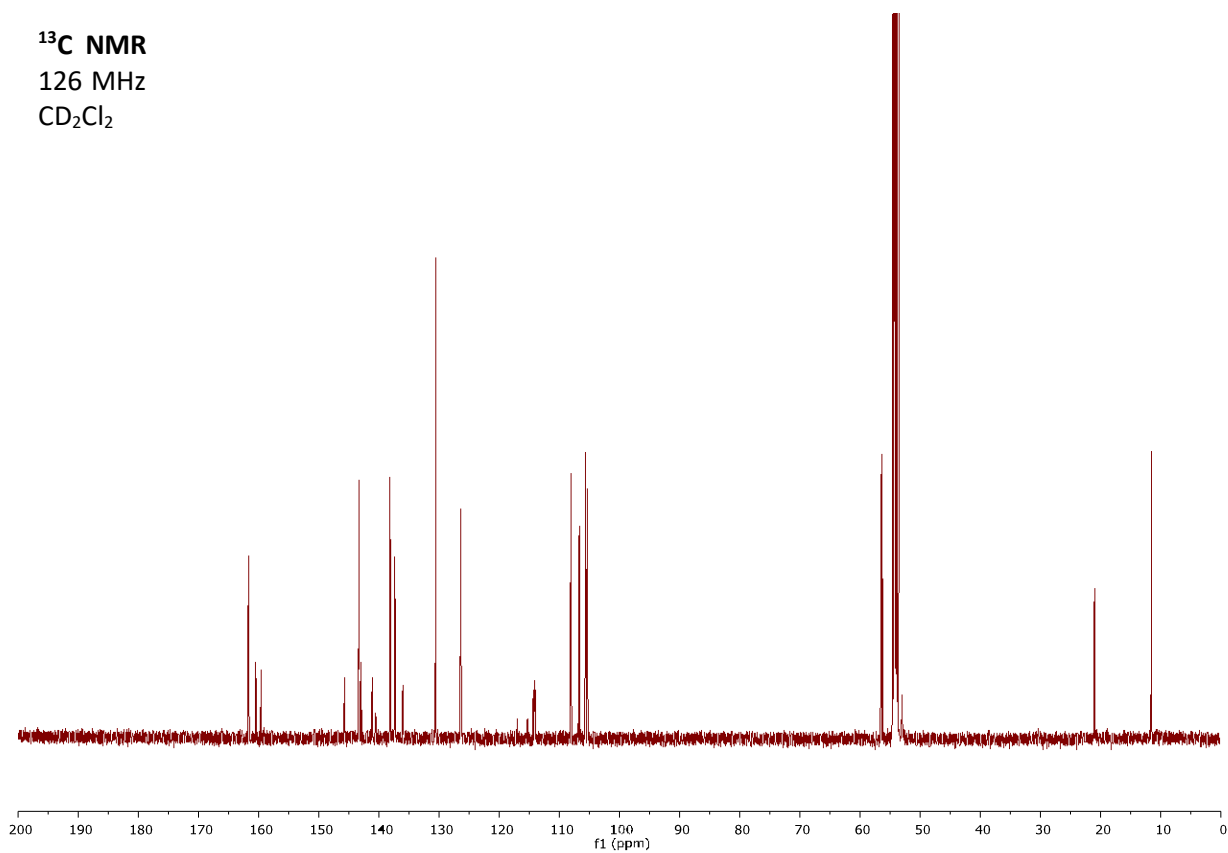




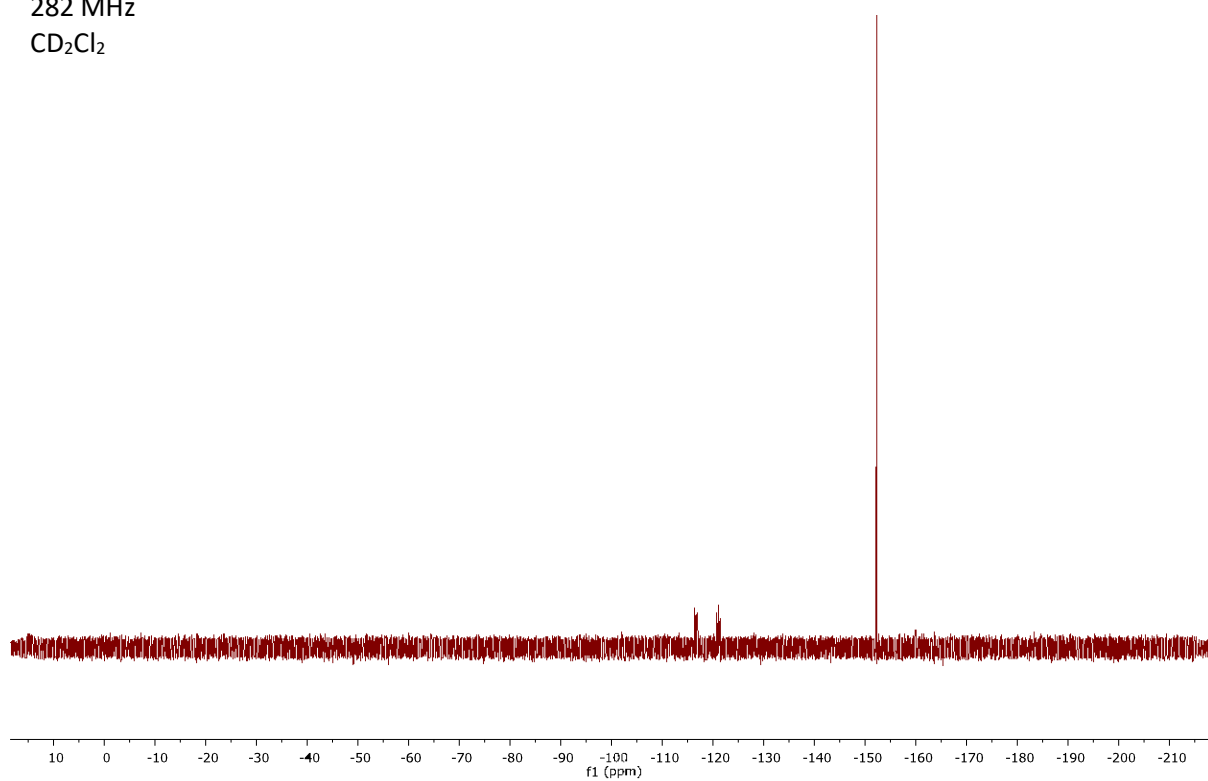
**<sup>1</sup>H NMR**  
500 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



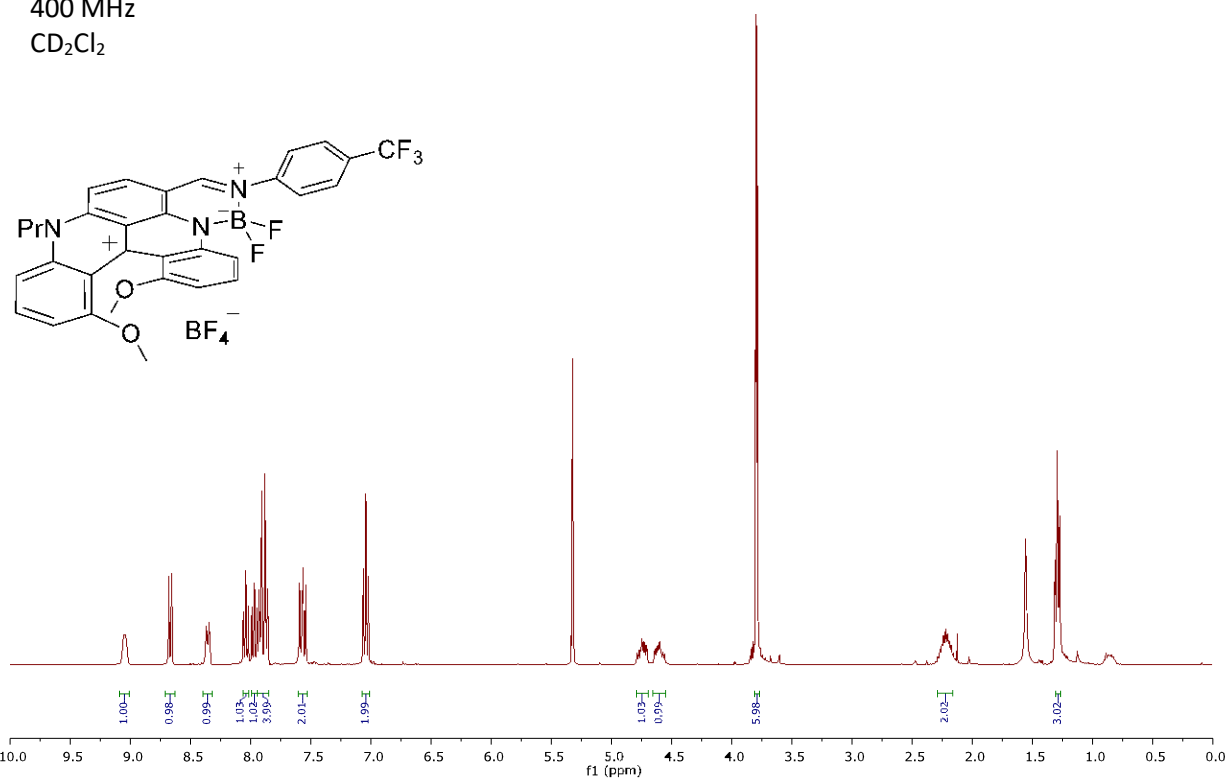
**<sup>13</sup>C NMR**  
126 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



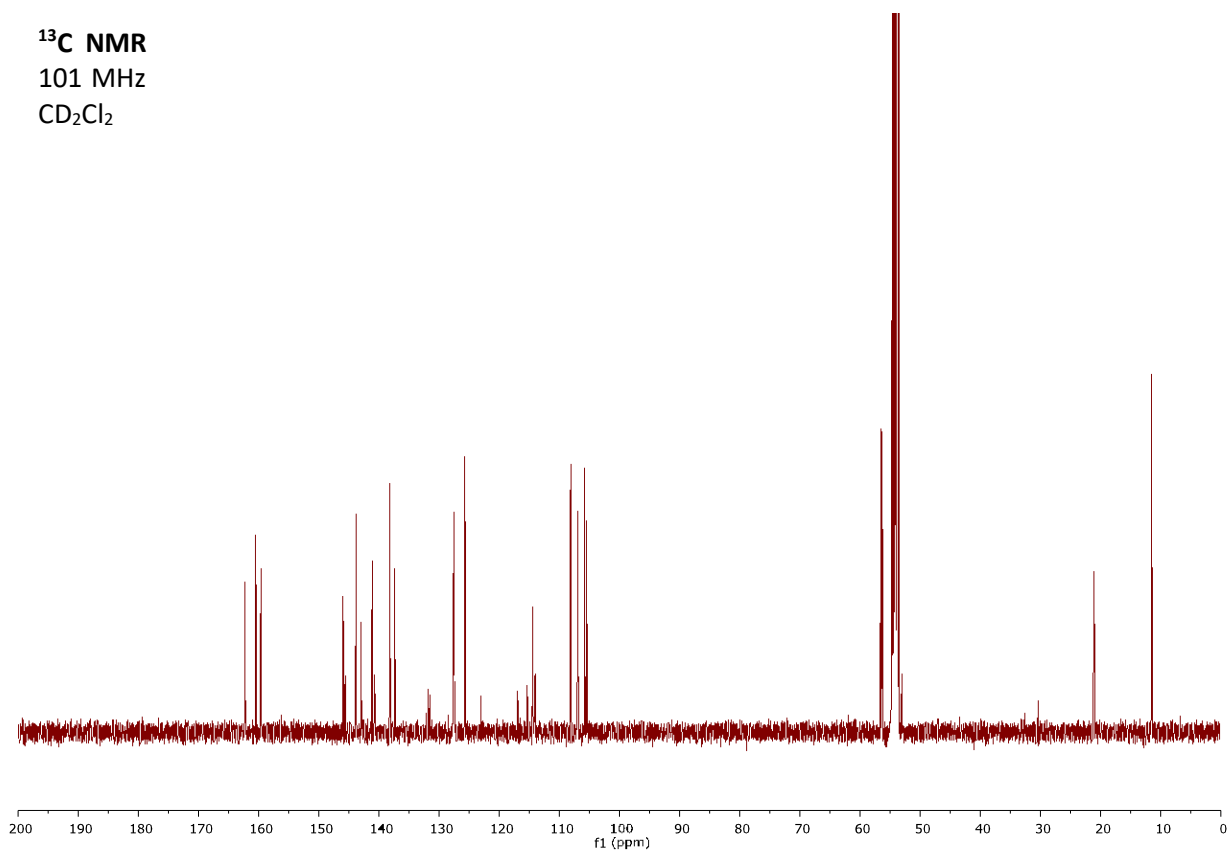
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



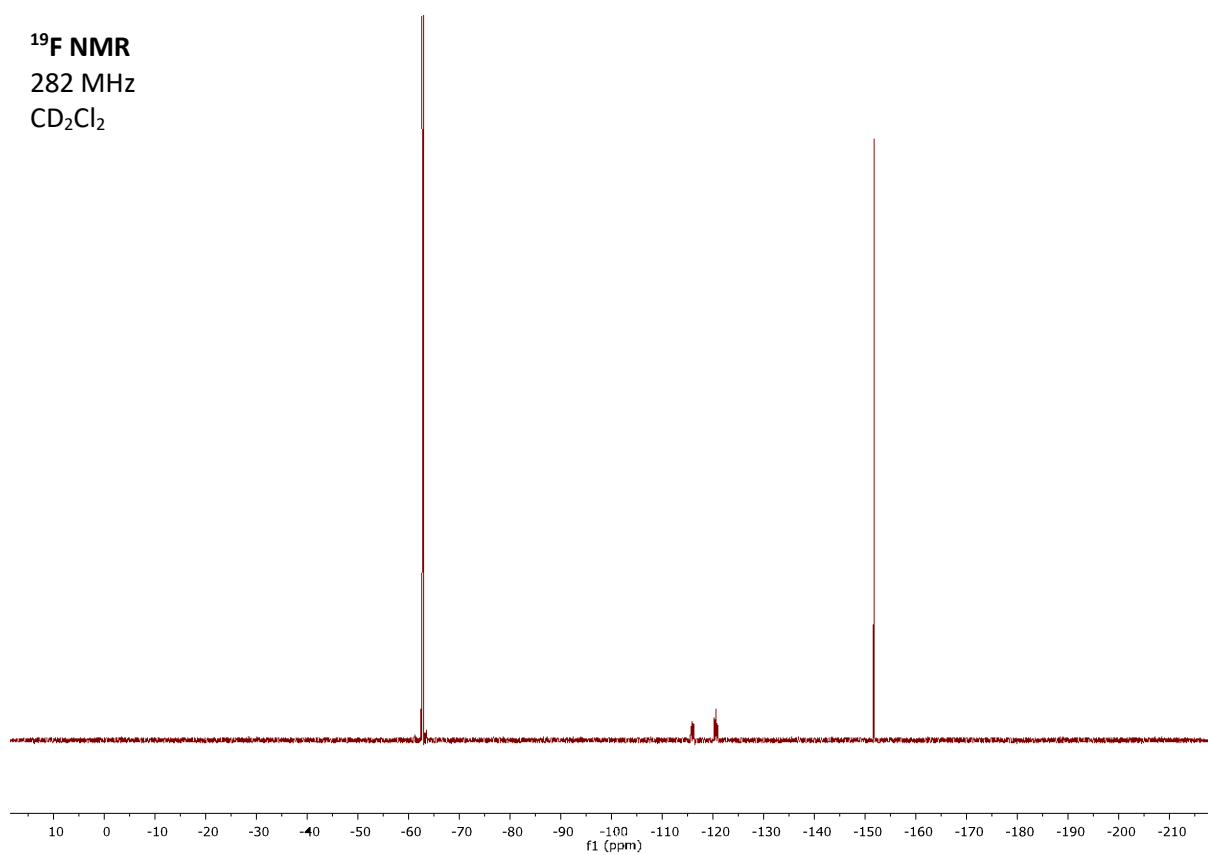
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



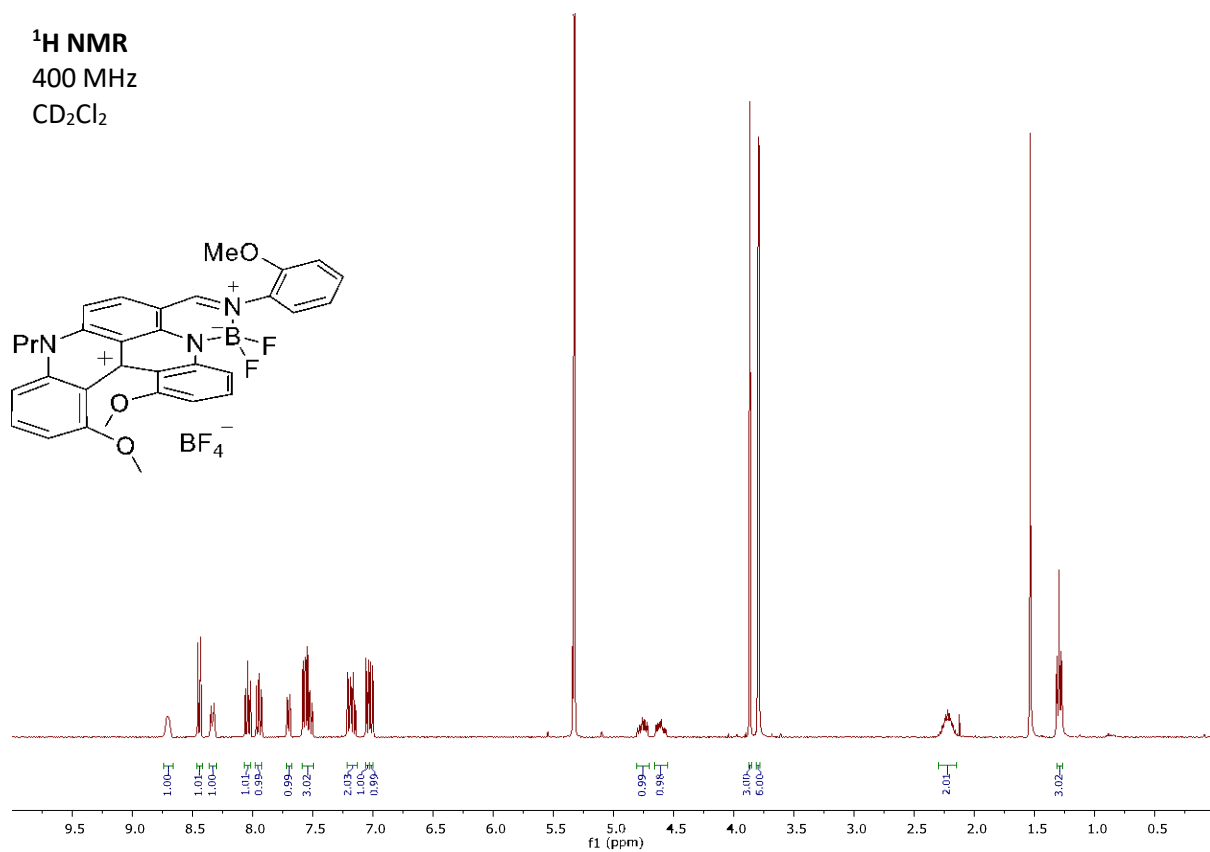
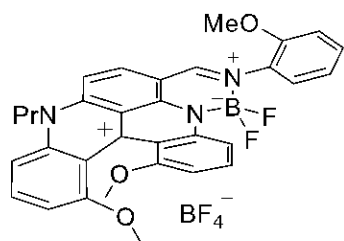
**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



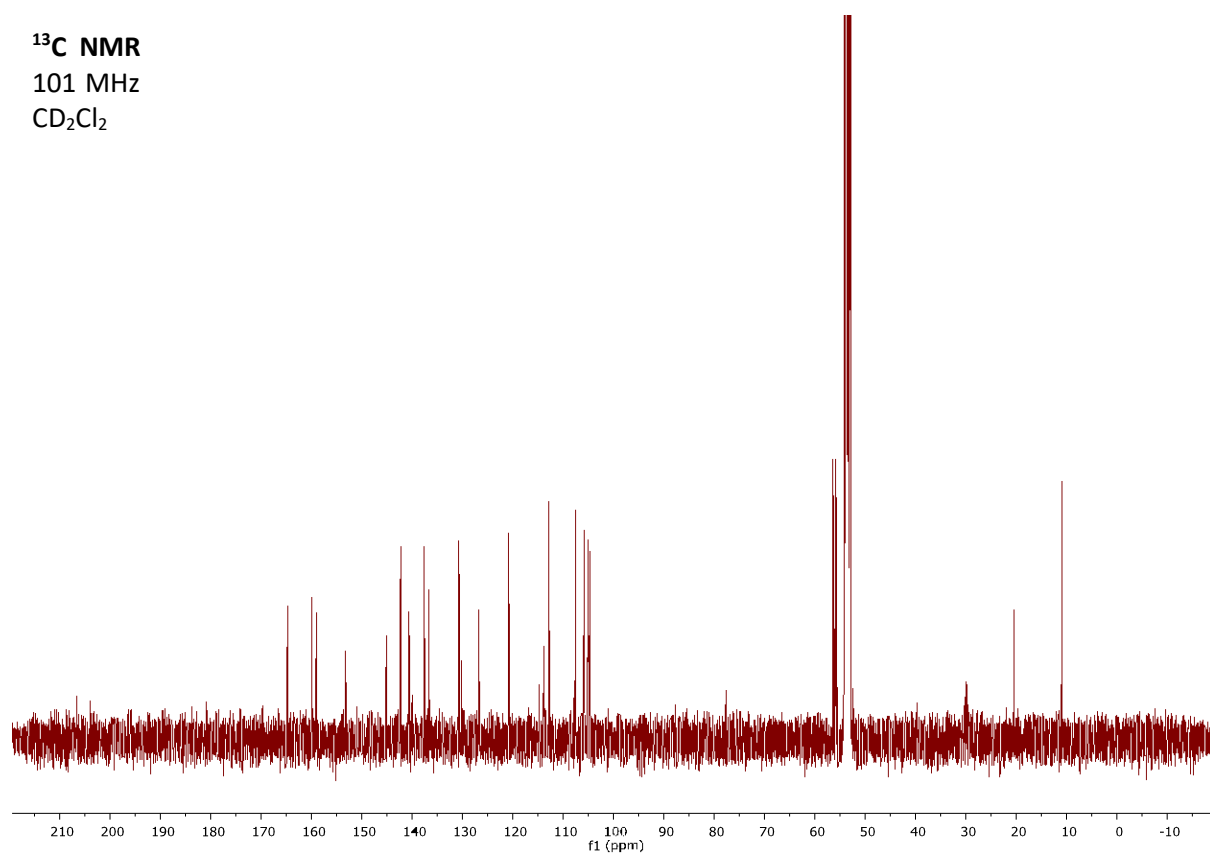
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



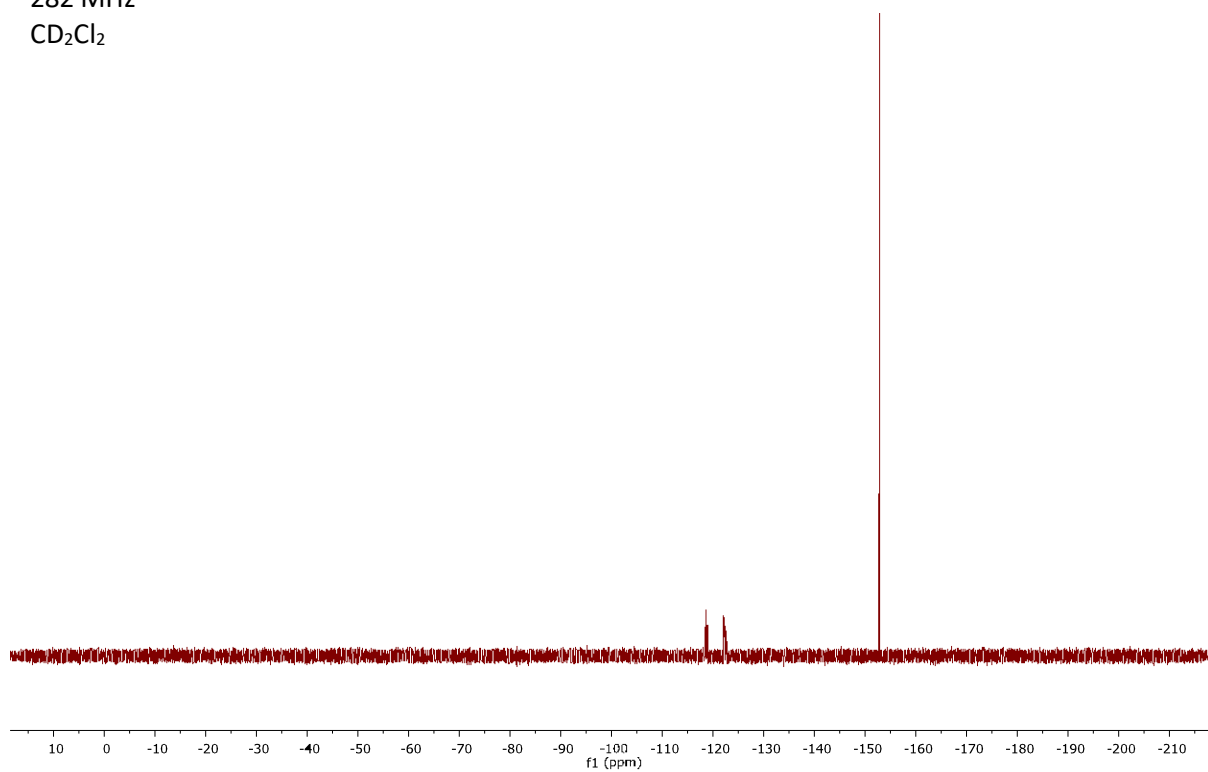
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



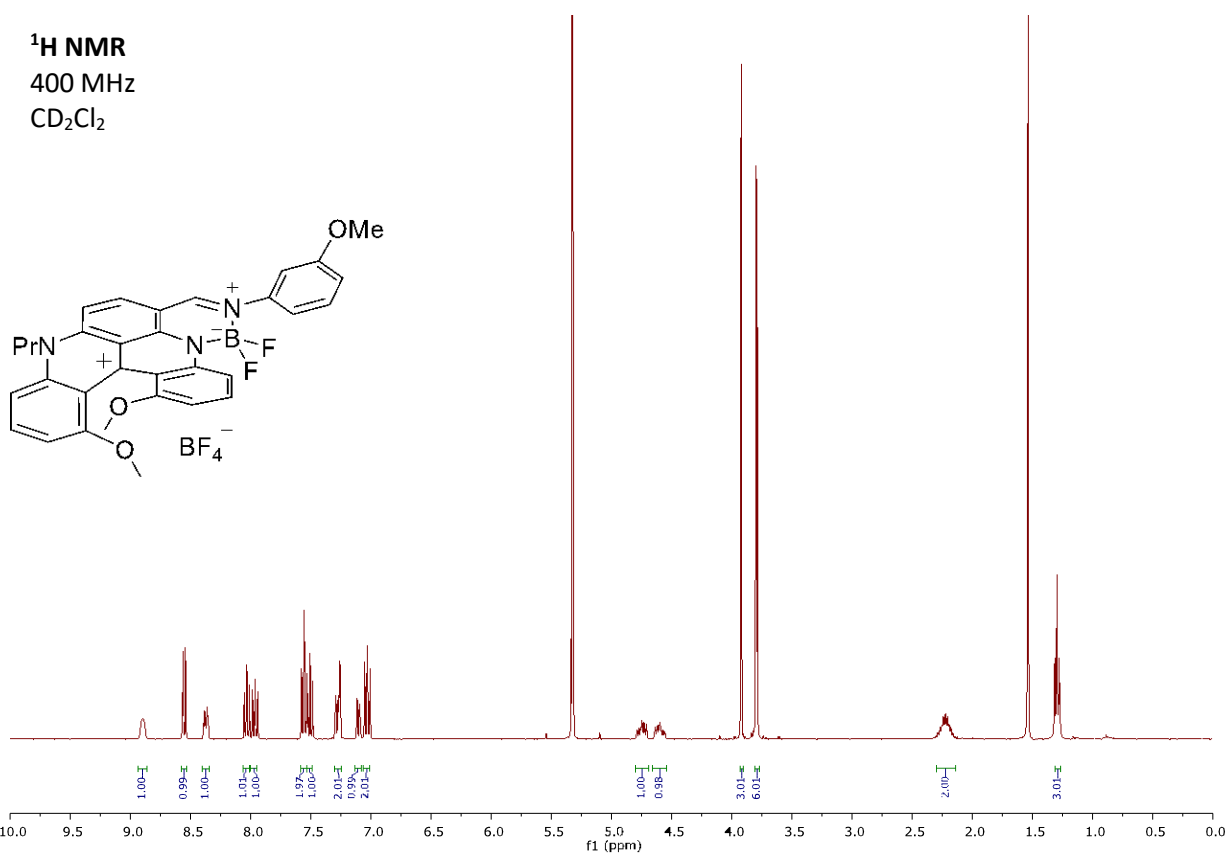
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101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



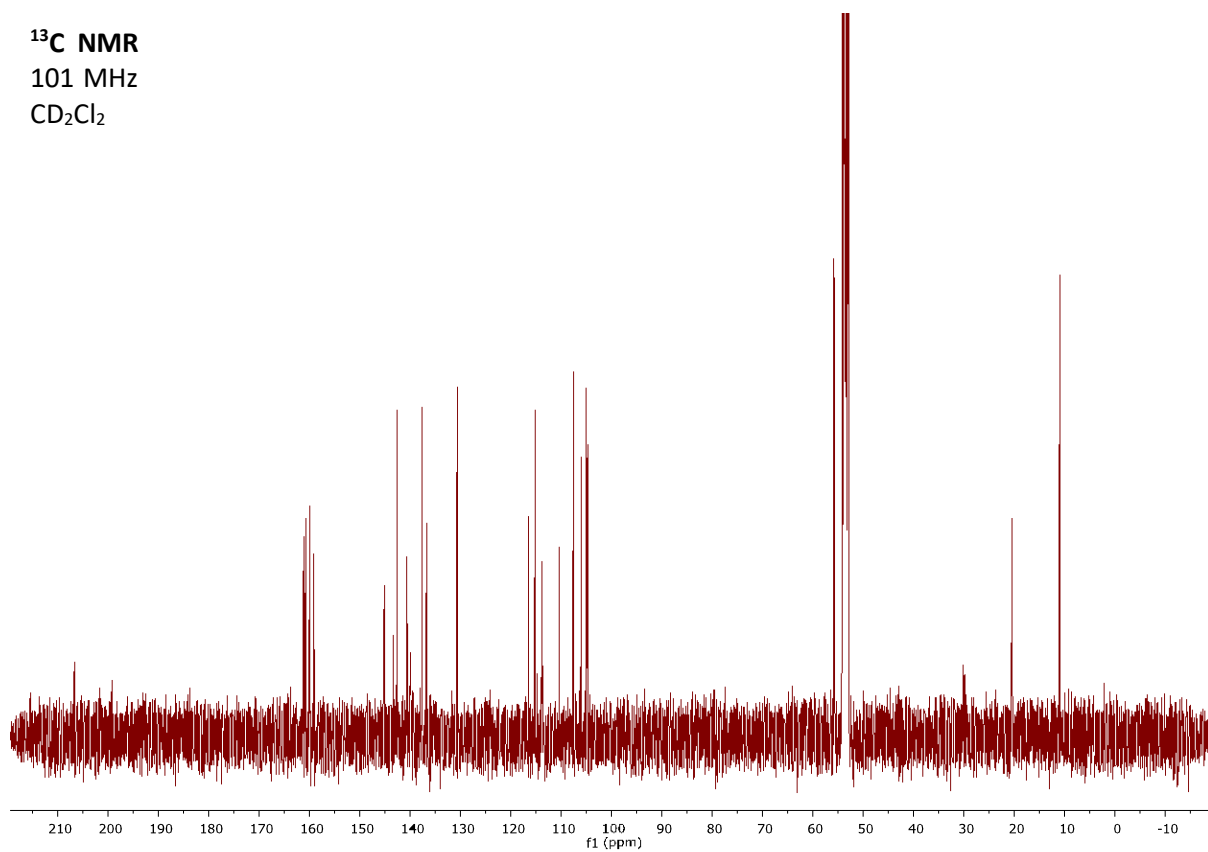
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



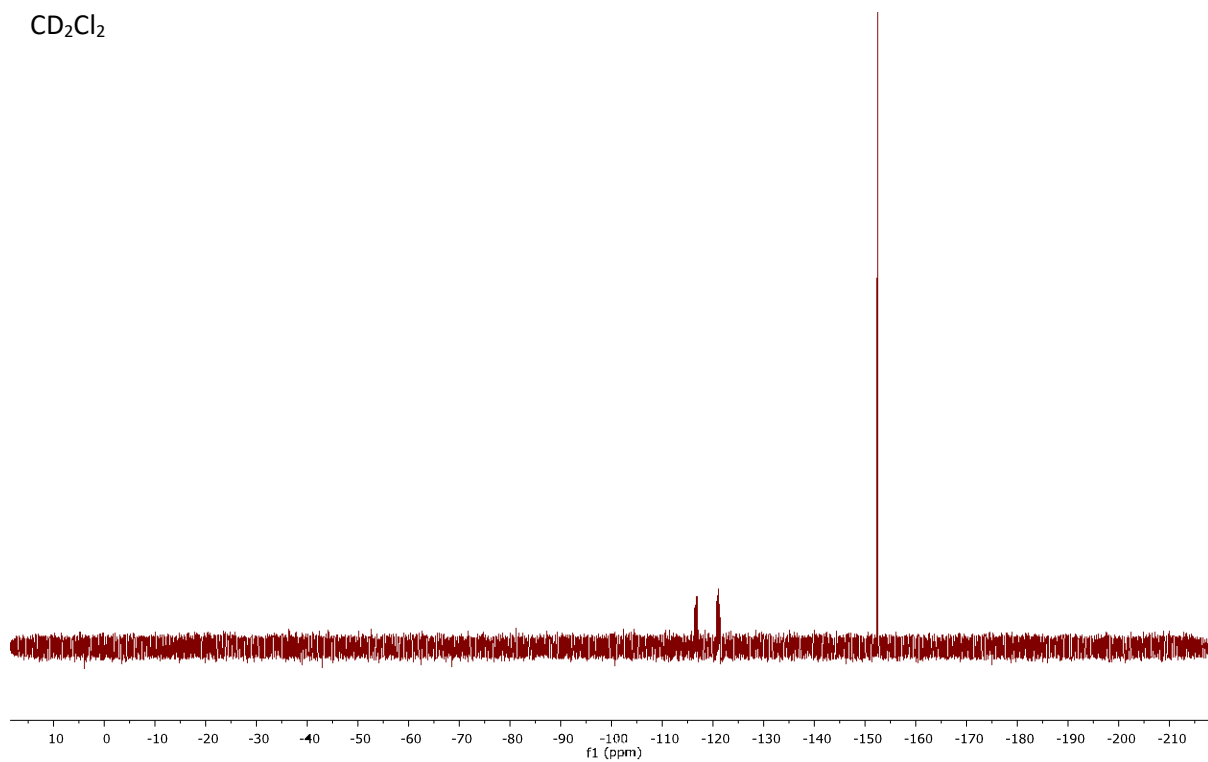
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



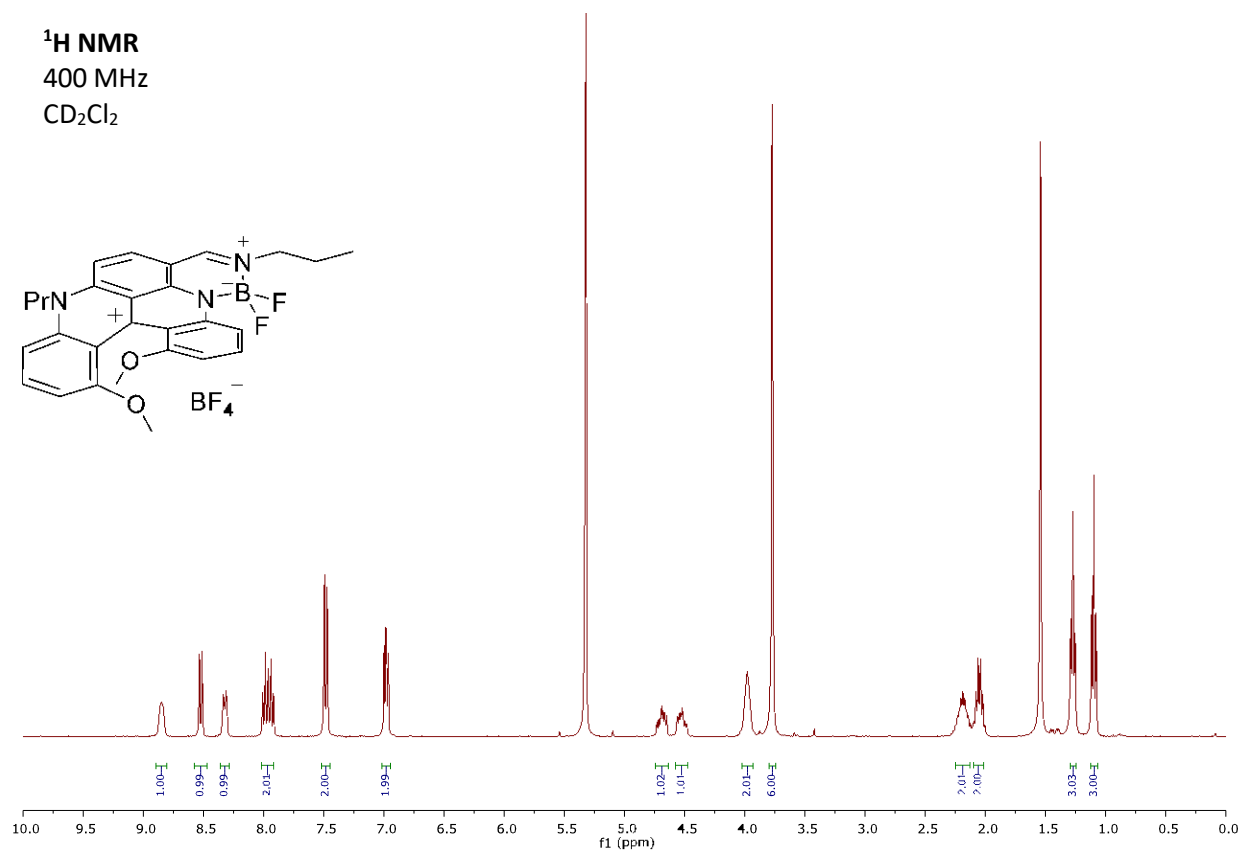
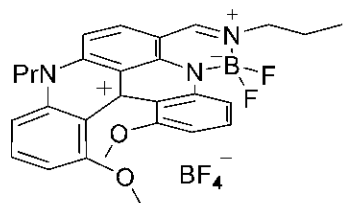
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101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



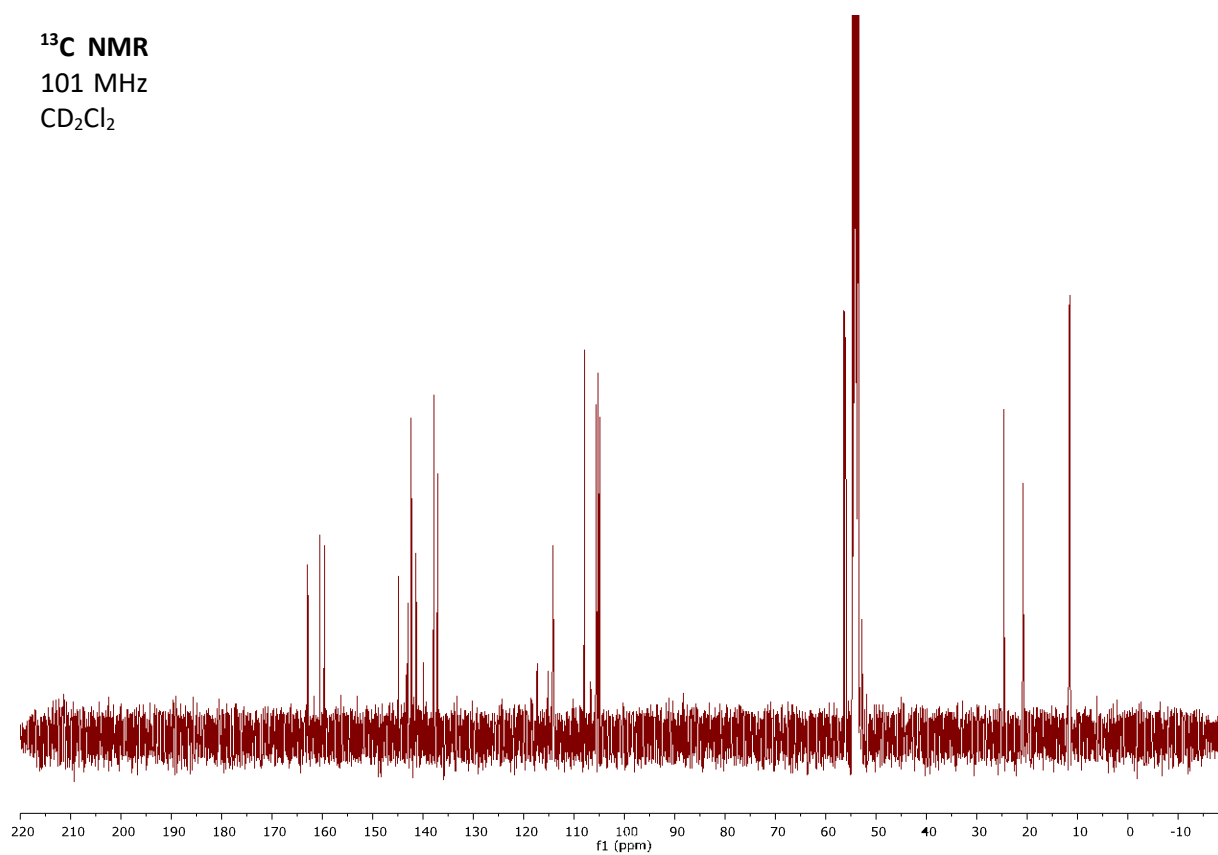
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



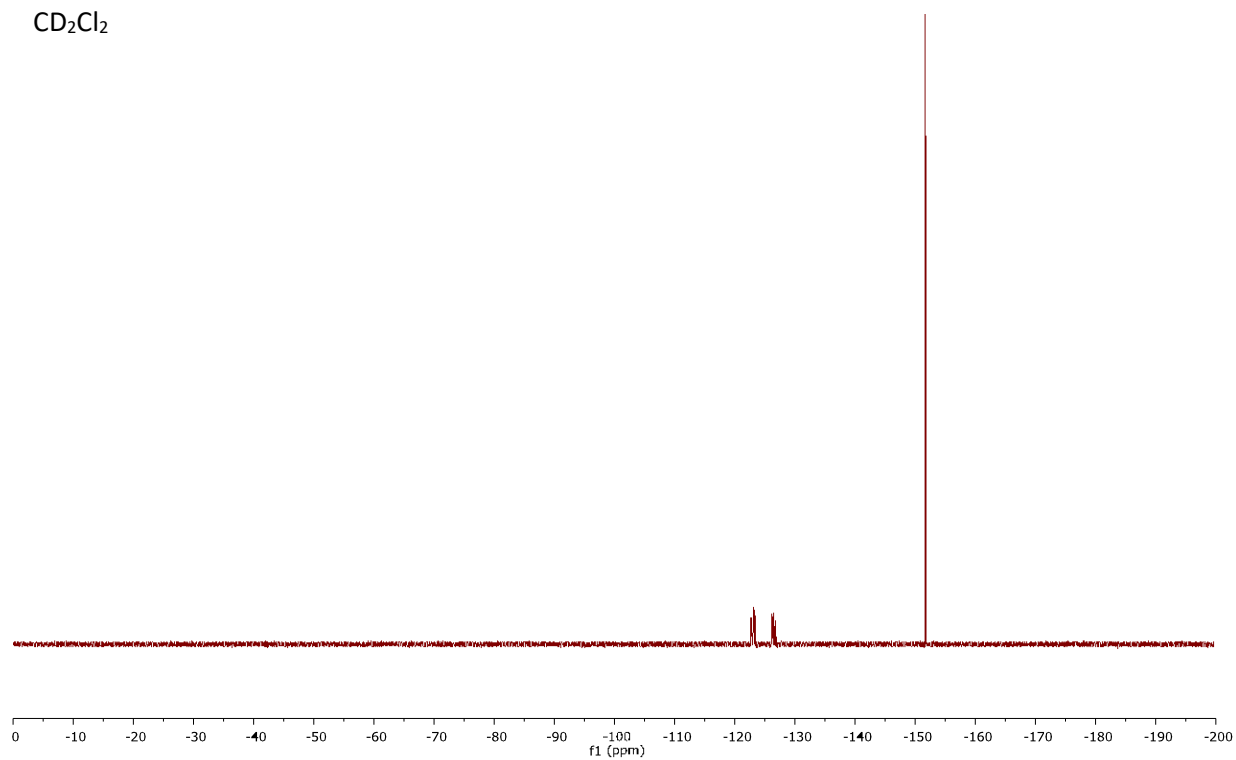
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



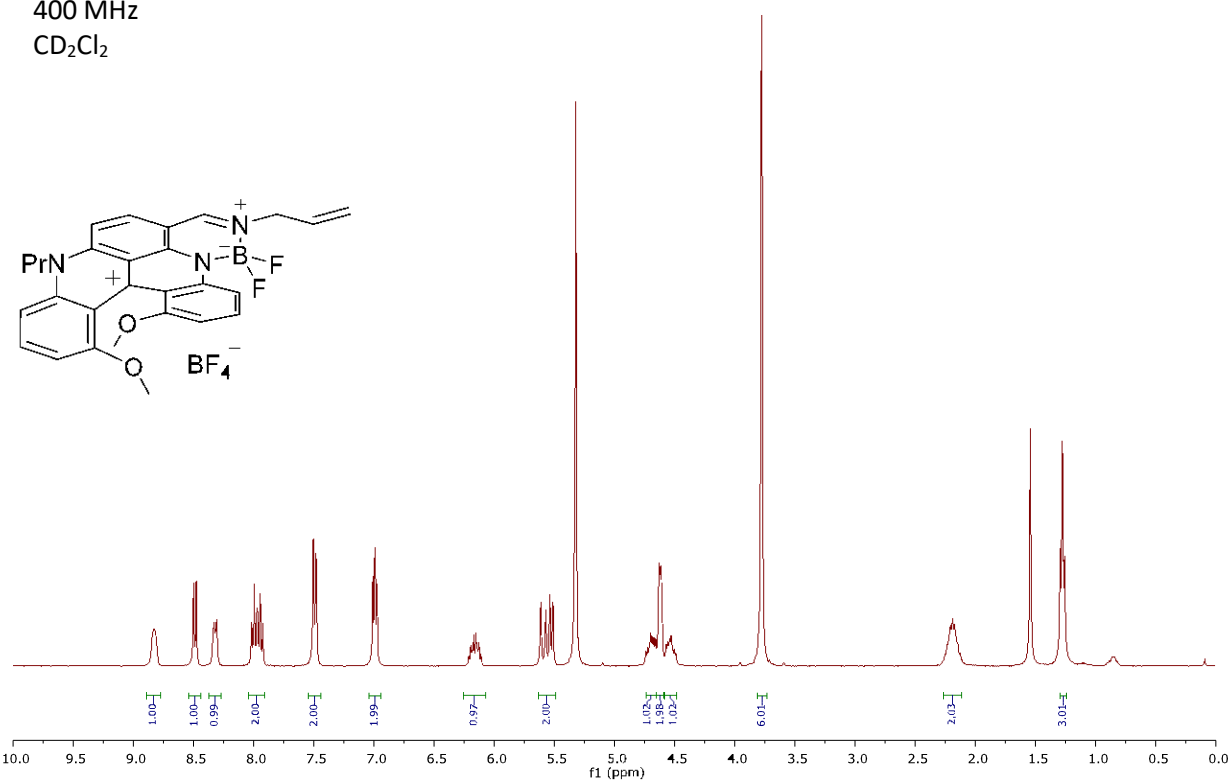
**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



**$^{19}\text{F}$  NMR**  
282 MHz  
 $\text{CD}_2\text{Cl}_2$

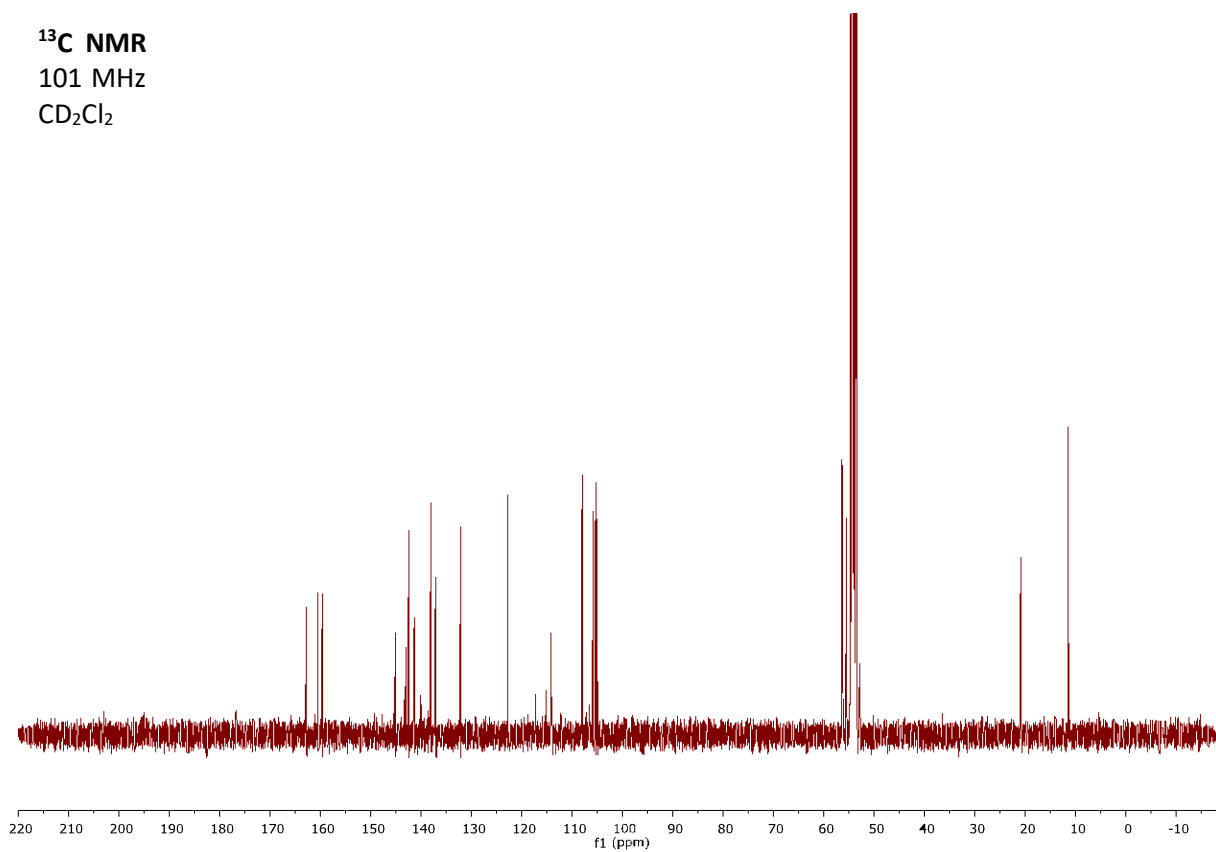


**$^1\text{H}$  NMR**  
400 MHz  
 $\text{CD}_2\text{Cl}_2$

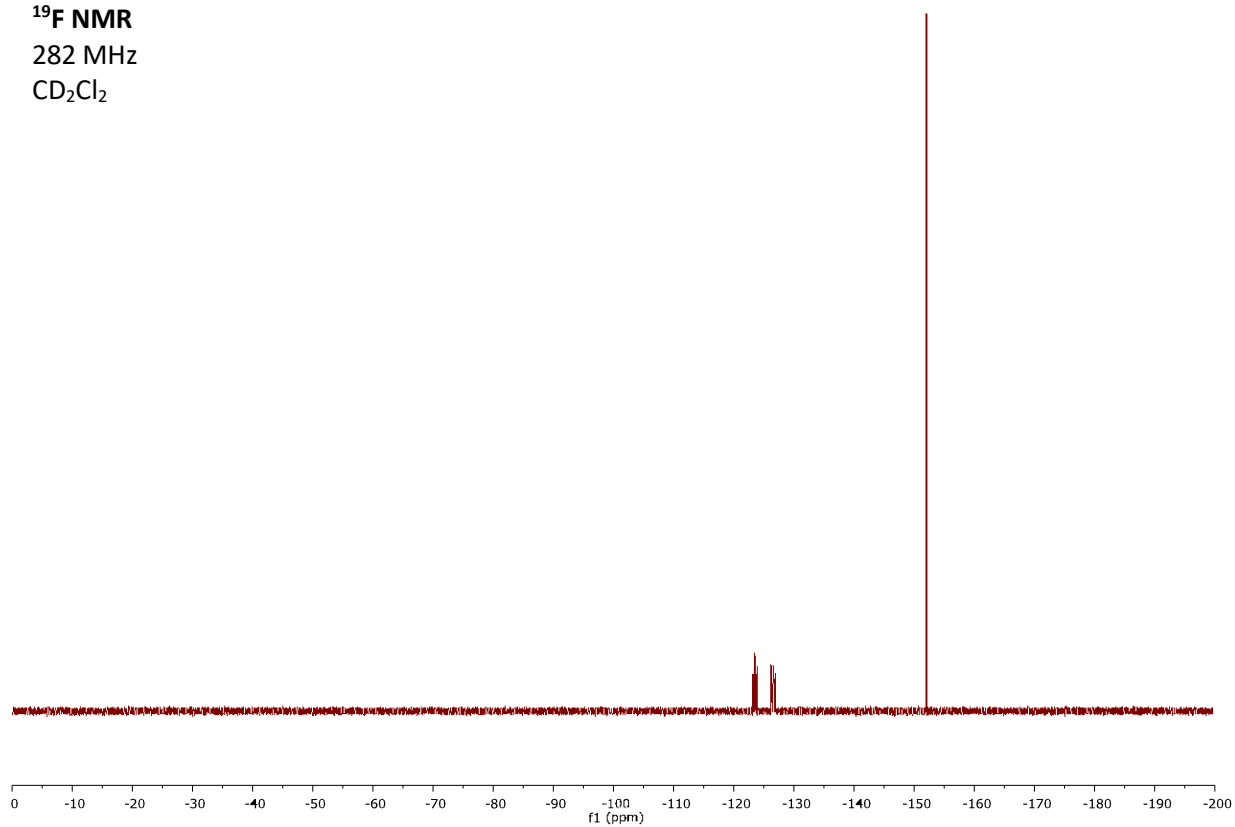




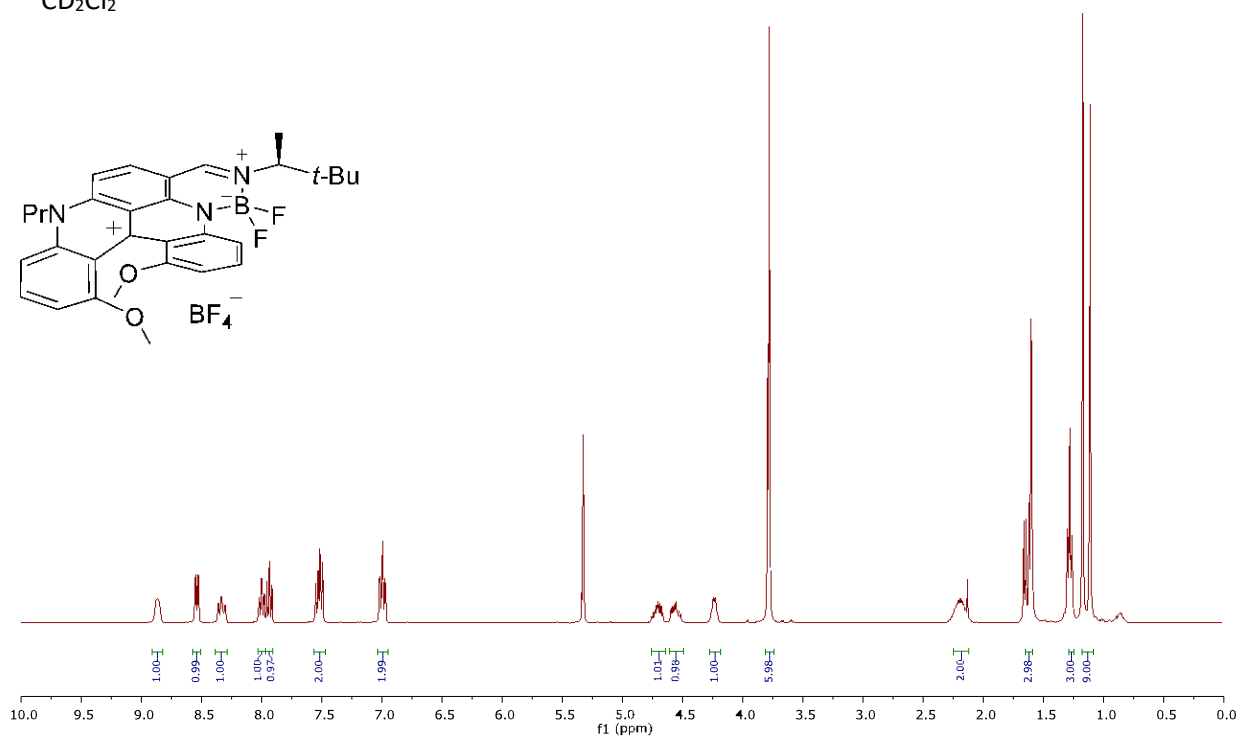
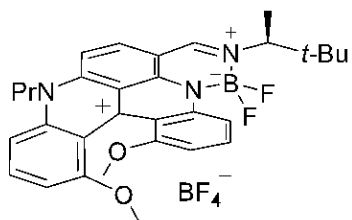
**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



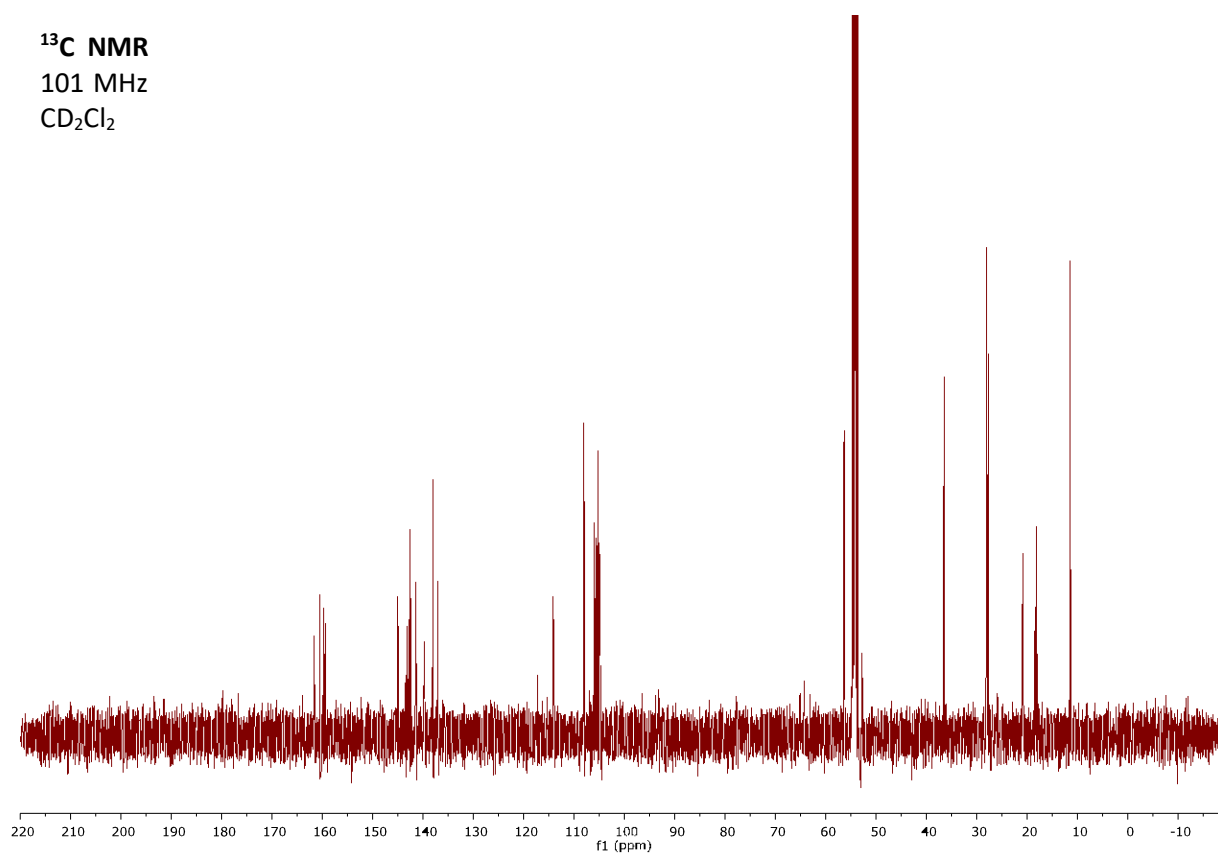
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



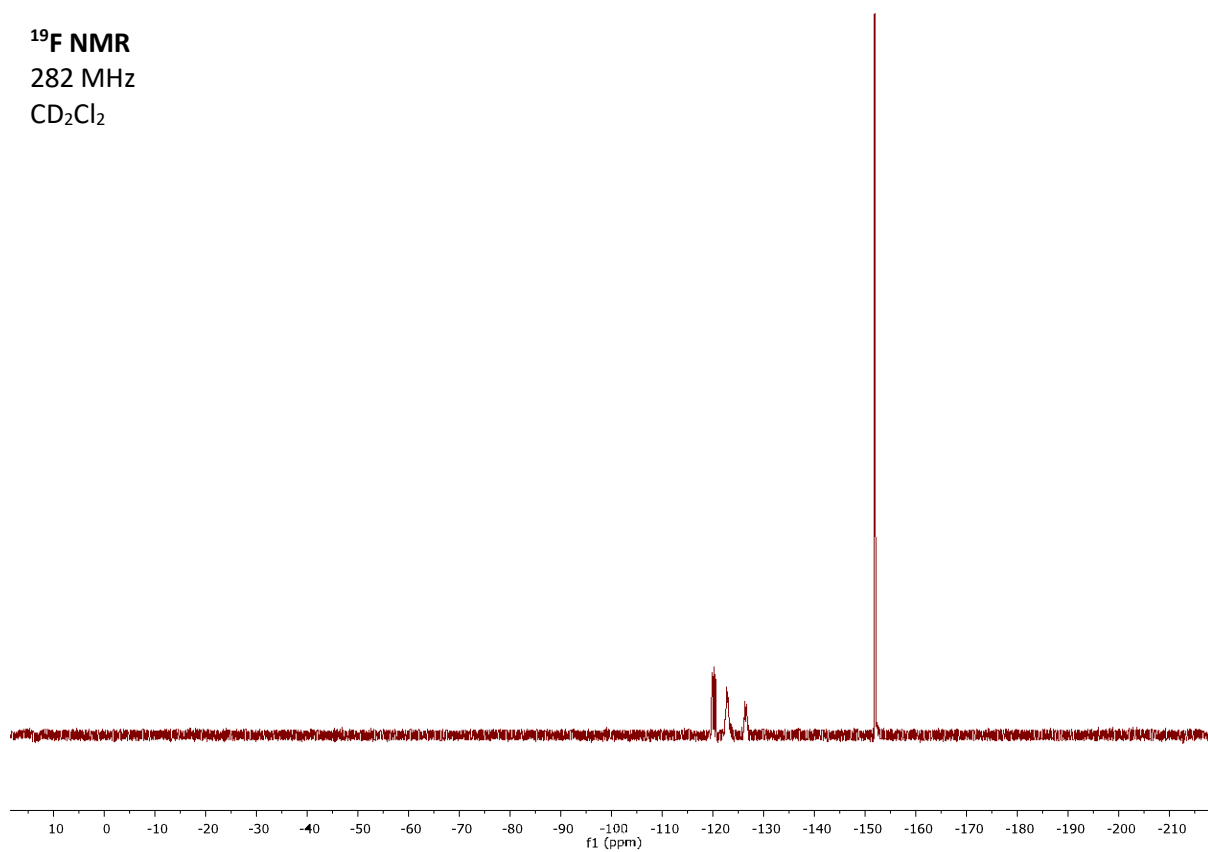
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



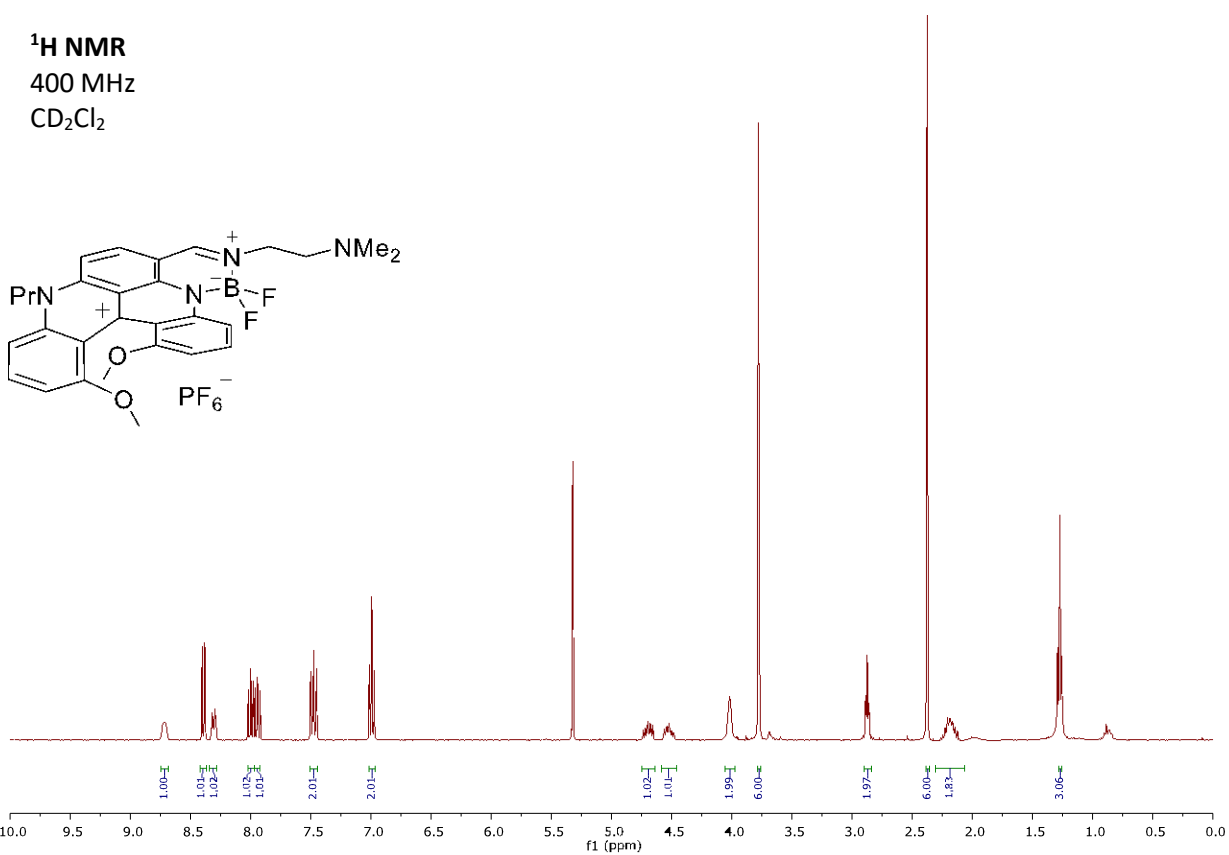
**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



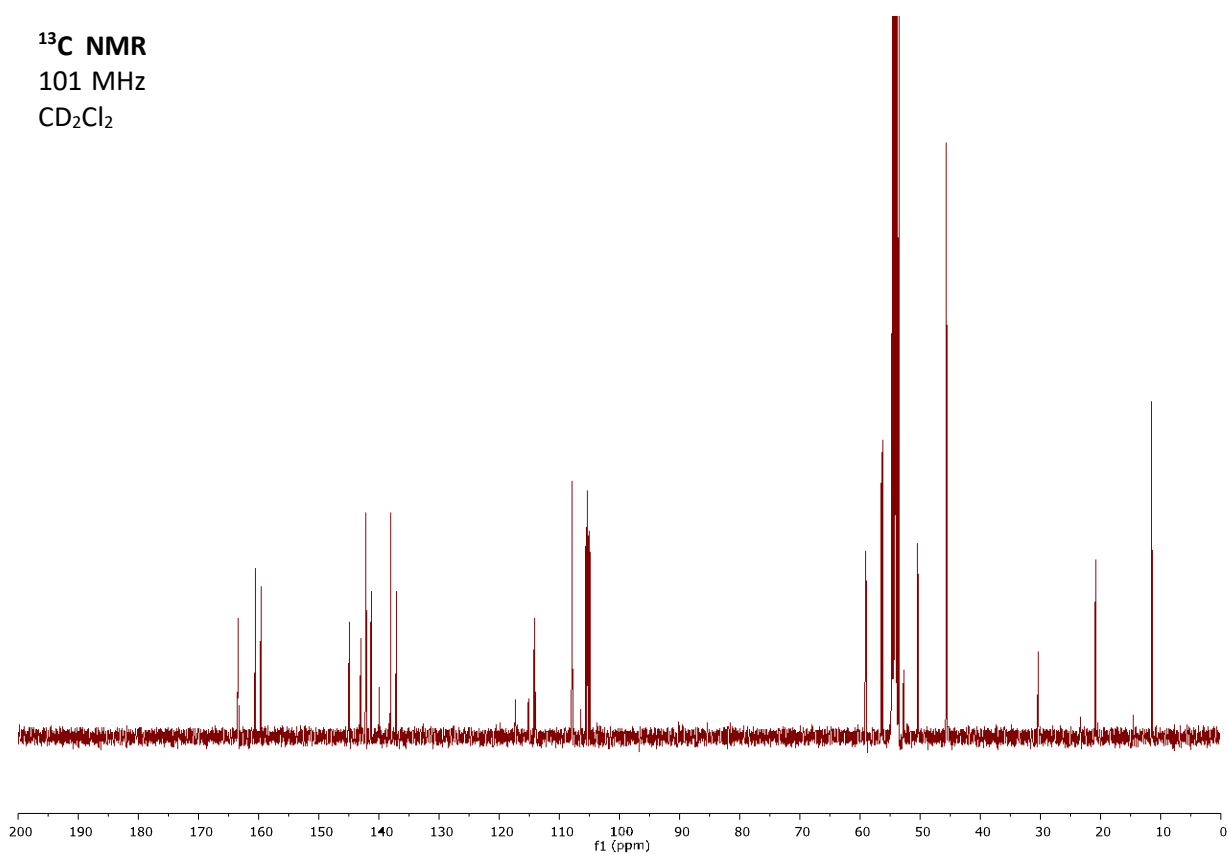
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



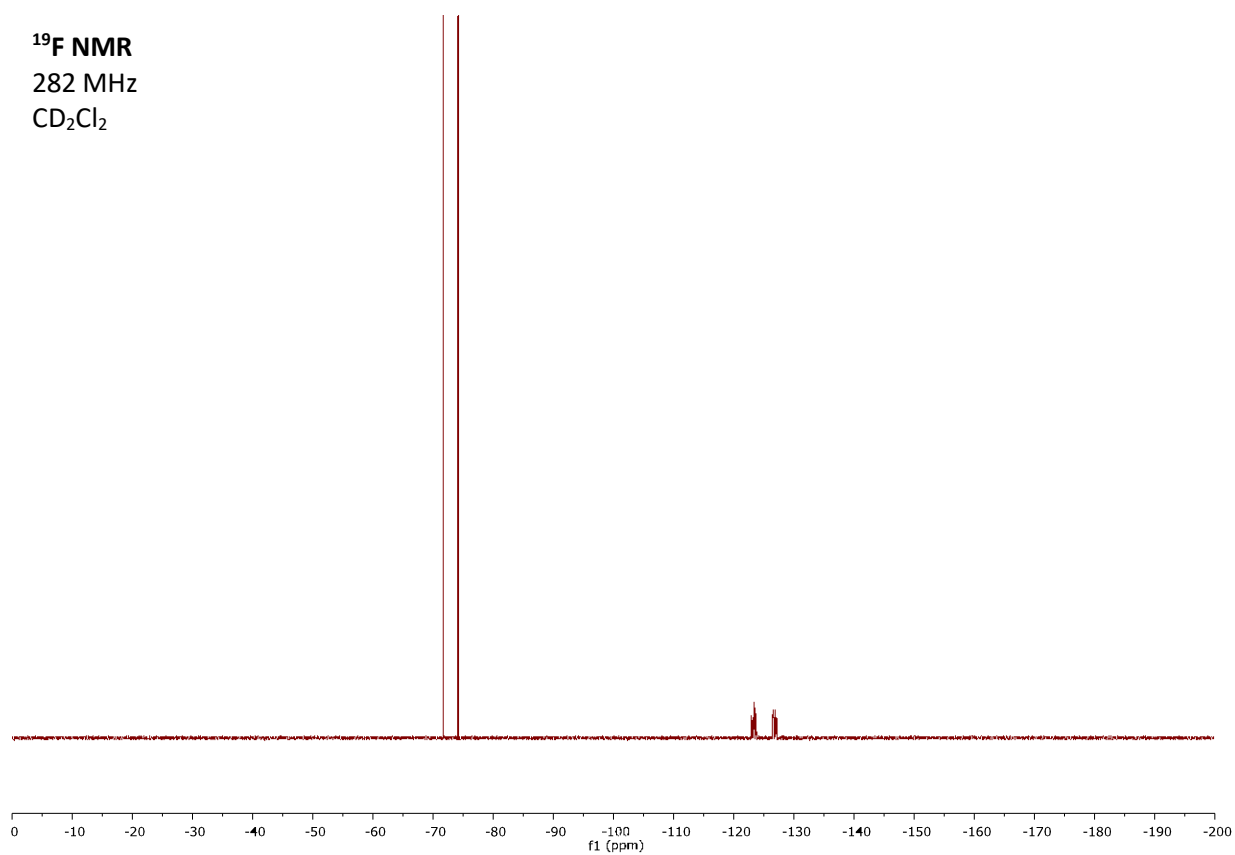
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



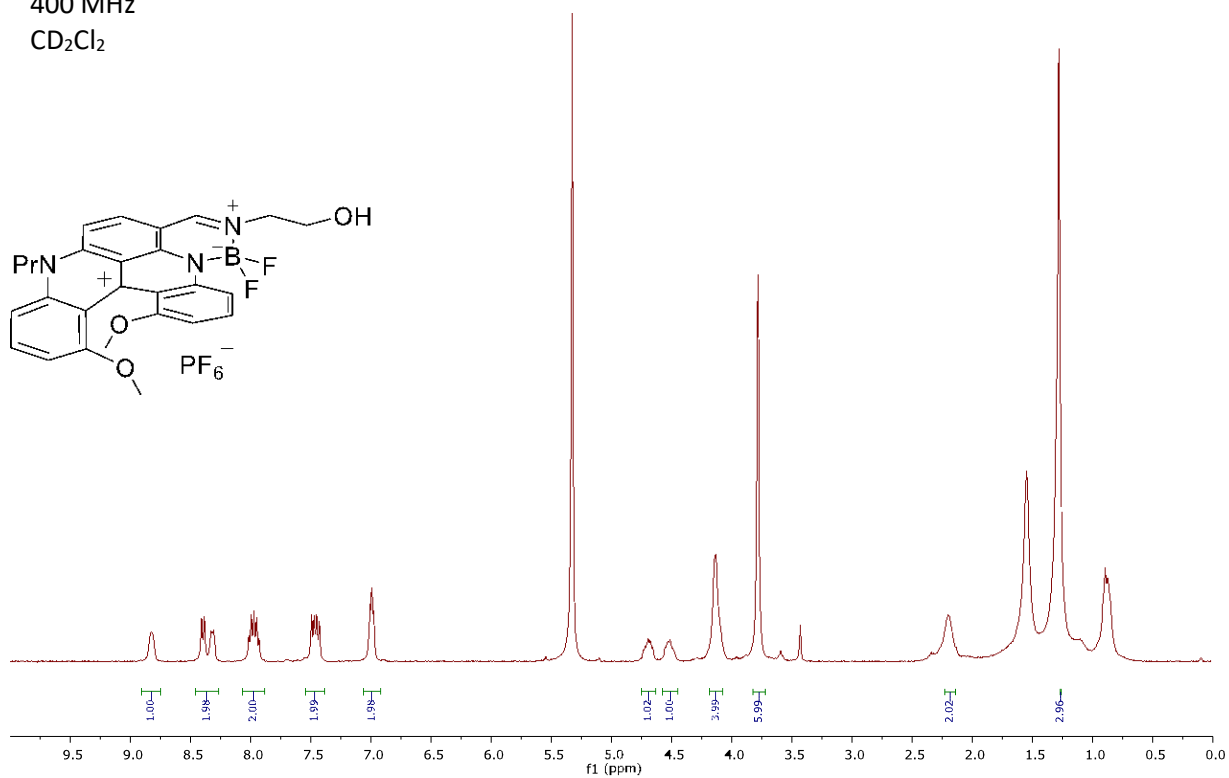
**$^{13}\text{C}$  NMR**  
101 MHz  
 $\text{CD}_2\text{Cl}_2$



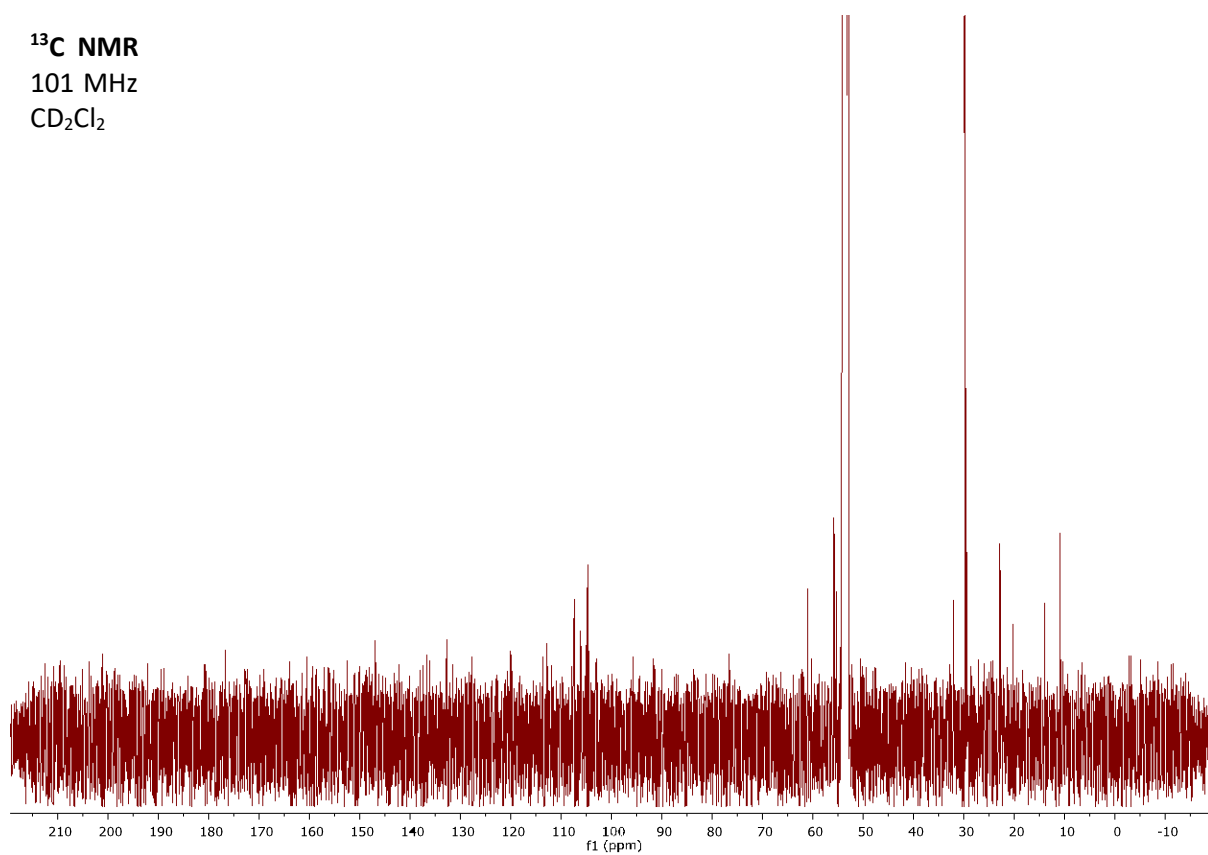
**$^{19}\text{F}$  NMR**  
282 MHz  
 $\text{CD}_2\text{Cl}_2$



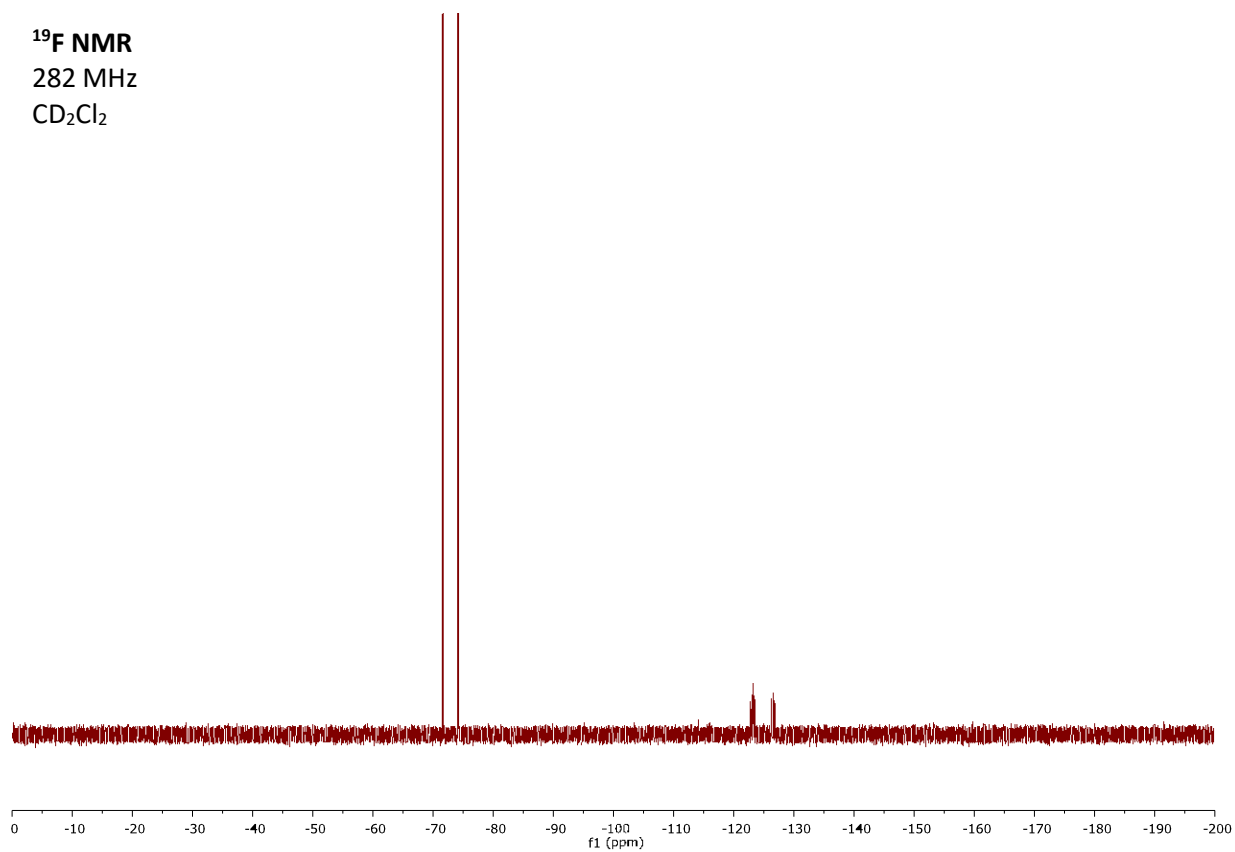
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



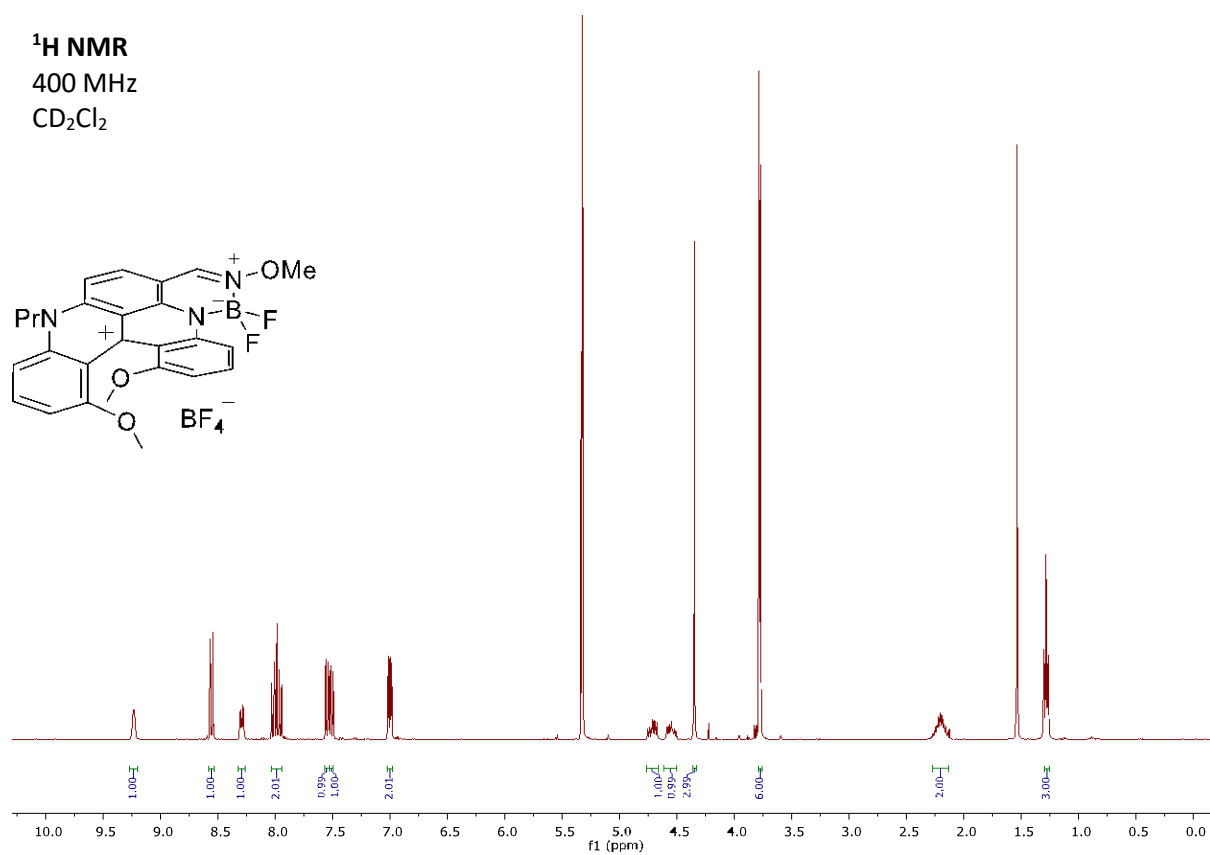
**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



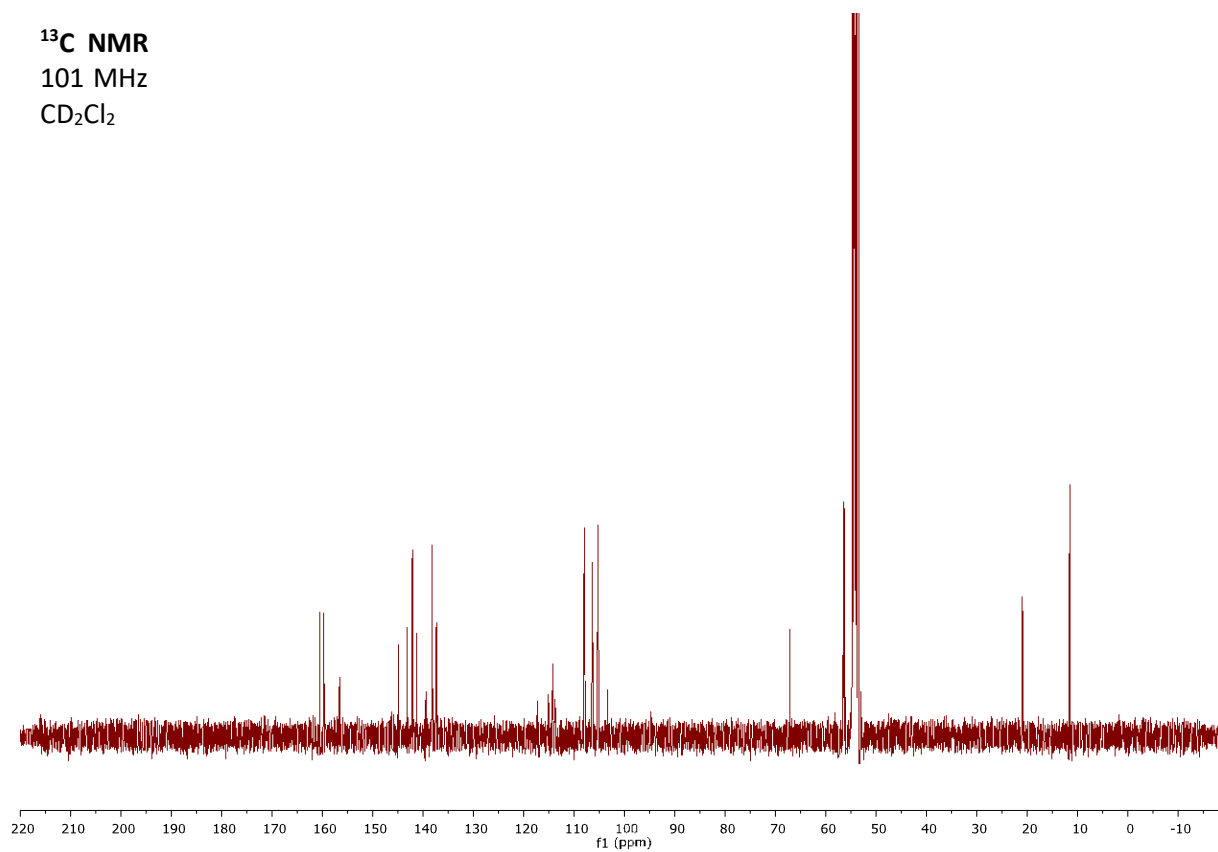
**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



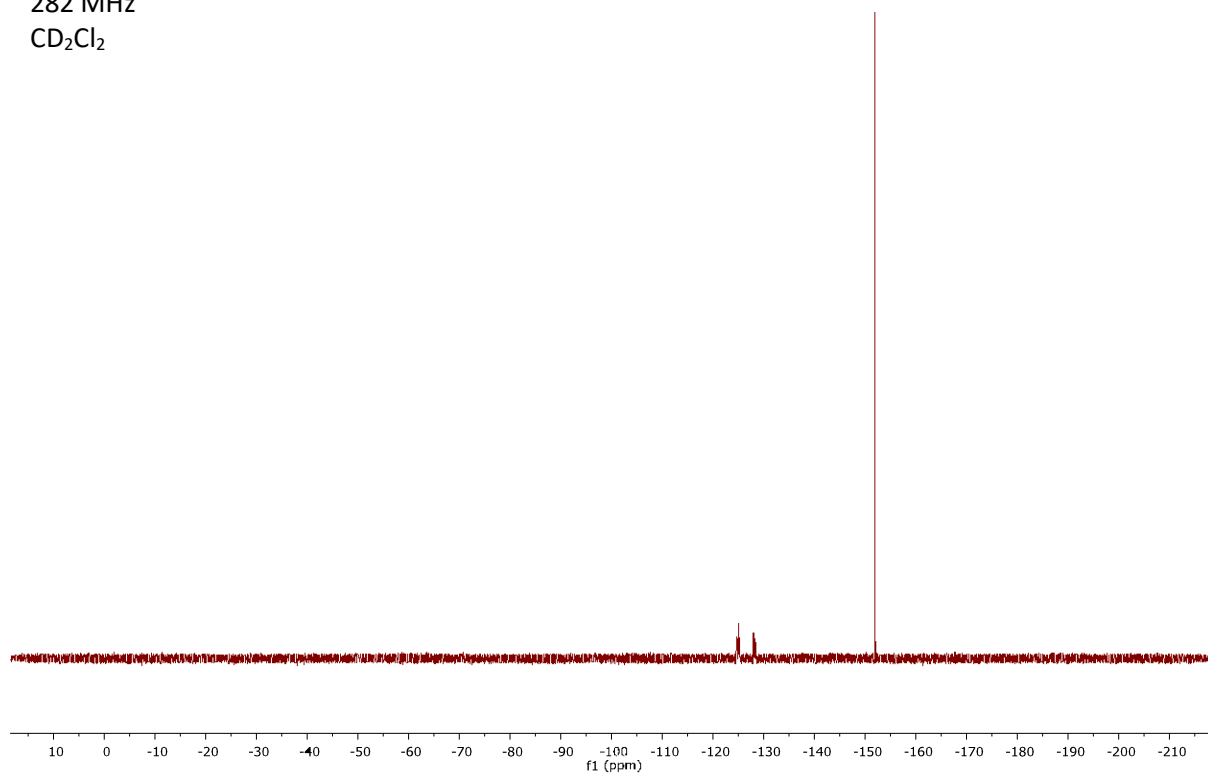
**<sup>1</sup>H NMR**  
400 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



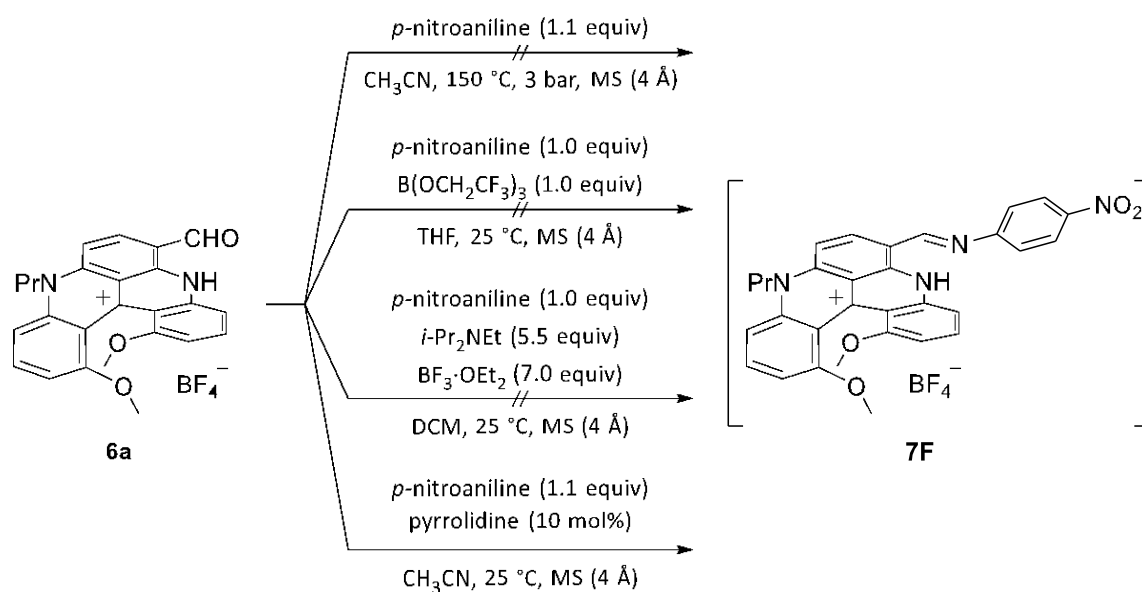
**<sup>13</sup>C NMR**  
101 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



**<sup>19</sup>F NMR**  
282 MHz  
CD<sub>2</sub>Cl<sub>2</sub>



### 3. Optimization of the two-step one-pot procedure

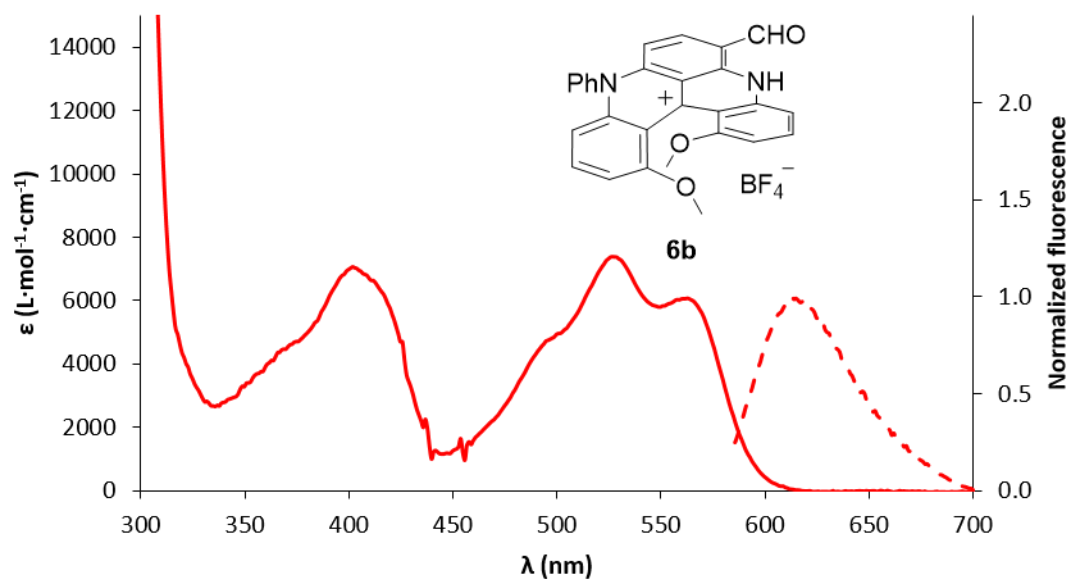


**Scheme S1.** Optimization of the imine formation step with formylated **6a** and *p*-nitroaniline **F**.

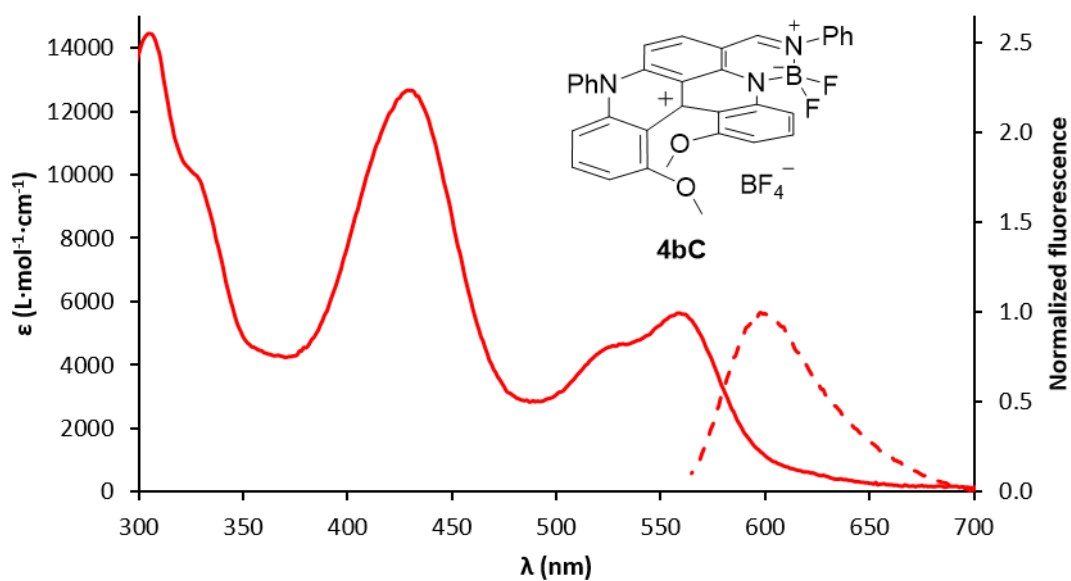
Initially, the reaction was attempted at 150 °C under MW irradiation, but no conversion was observed. Other attempts were then conducted in the presence of Lewis acids. For instance, Reeves and co-workers recently reported the use of tris(2,2,2-trifluoroethyl)borate as an effective reagent for promoting the condensation of sulfinamides with all types of aldehydes.<sup>[14]</sup> In our case, nonetheless, these conditions led to a very messy reaction crude in which **7F** could not be detected. Still, with boron-based Lewis acids in mind, we wondered whether boron trifluoride etherate could play a dual role, being the Lewis acid that would favor the first step but also the chelating agent in the second. As discussed, BF<sub>3</sub>·OEt<sub>2</sub> was added altogether with **6a**, *p*-nitroaniline **F** and Hünig's base. Once again, the outcome of the reaction was a very messy reaction crude. Finally, the desired result was obtained by using an organocatalytic method that involves the presence of an iminium ion as a key *in situ* intermediate. Indeed, García Ruano and Cid reported in 2014 the use of pyrrolidine as a catalyst for the synthesis of a large variety of imines.<sup>[15]</sup> To our delight, these conditions turned out to be applicable to our substrates and an instantaneous formation of intermediate **7F** was observed at room temperature.



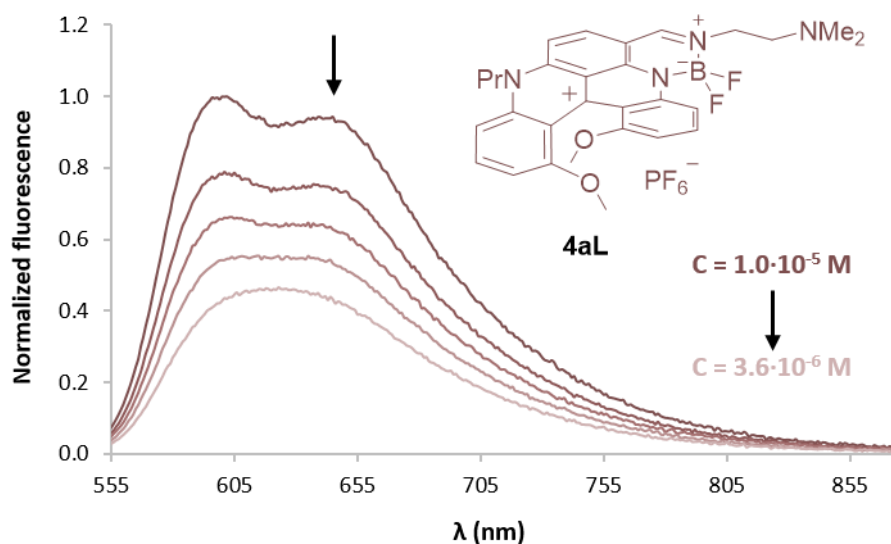
## 4. (Chir)optical properties



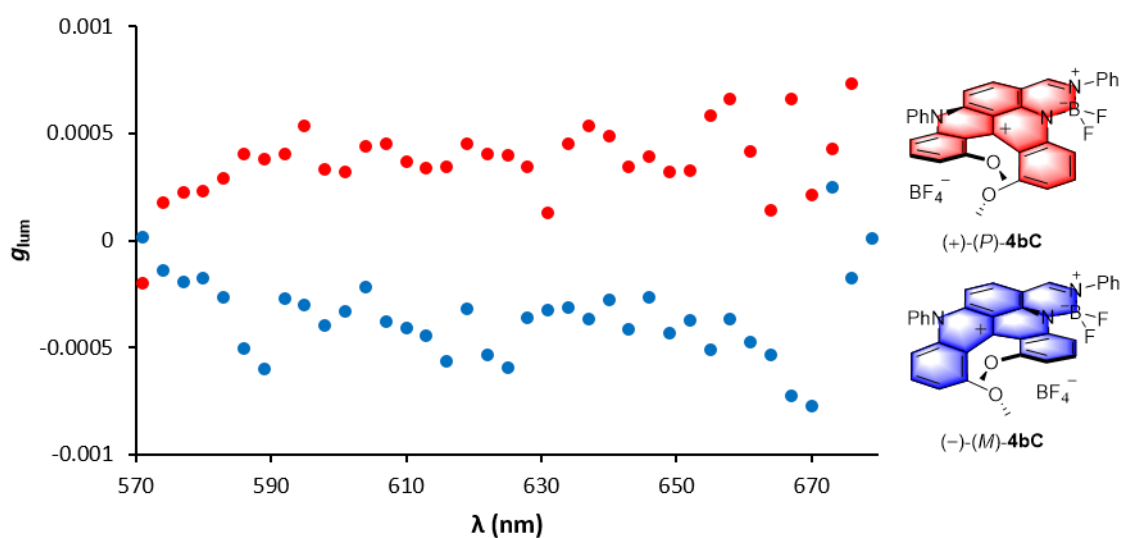
**Figure S1.** Absorption (solid line) and fluorescence (dashed line) of **6b**. Solutions in  $\text{CH}_3\text{CN}$  ( $5 \cdot 10^{-6}$  M).



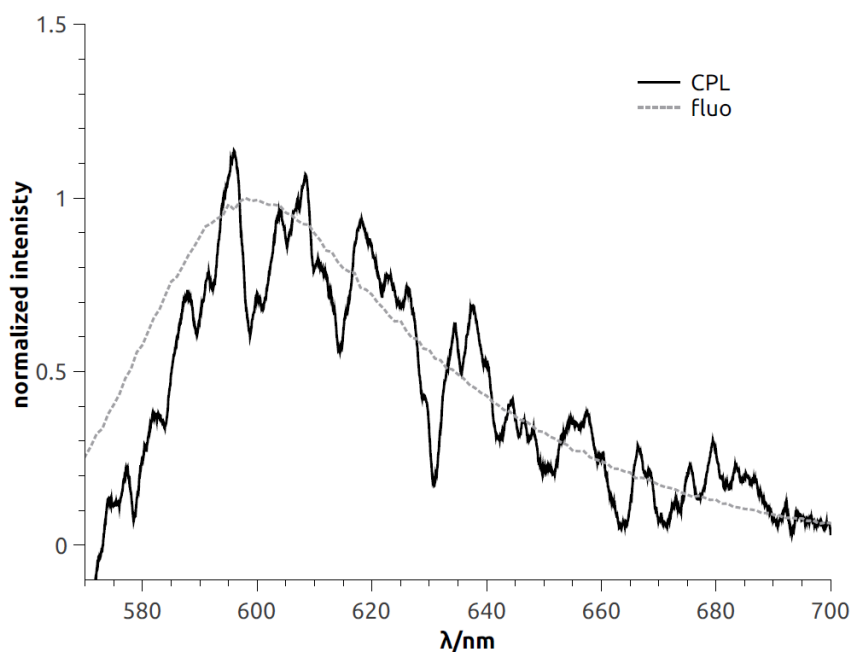
**Figure S2.** Absorption (solid line) and fluorescence (dashed line) of **4bC**. Solutions in  $\text{CH}_3\text{CN}$  ( $1 \cdot 10^{-5}$  M).



**Figure S3.** Normalized fluorescence spectra of BODIPY **4aL** at various concentrations ( $\text{CH}_3\text{CN}$ ,  $1.0 \cdot 10^{-5} \text{ M}$   $\rightarrow$   $7.6 \cdot 10^{-6} \text{ M}$   $\rightarrow$   $6.1 \cdot 10^{-6} \text{ M}$   $\rightarrow$   $4.7 \cdot 10^{-6} \text{ M}$   $\rightarrow$   $3.6 \cdot 10^{-6} \text{ M}$ ).

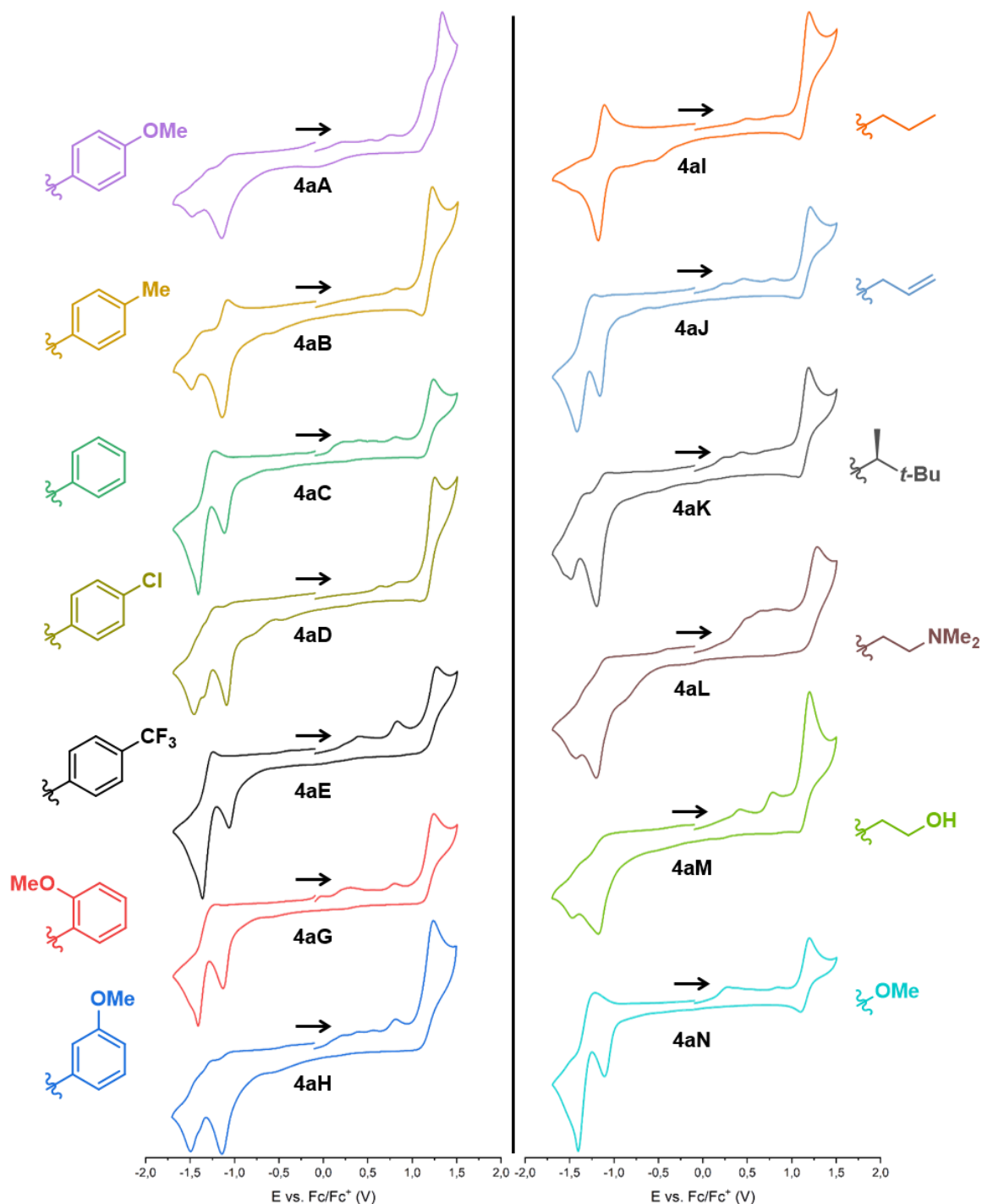


**Figure S4.**  $g_{\text{lum}}$  response of (+)-(P)-**4bC** (red dots) and (-)(M)-**4bC** (blue dots). Average of 6 accumulations. Solutions in  $\text{CH}_3\text{CN}$  ( $6.7 \cdot 10^{-6} \text{ M}$ ).



**Figure S5:** comparison between CPL (solid line) of (+)-(P)-**4bC** and fluorescence (dotted line) spectra. The spectra are normalized for an easier visual comparison.

## 5. Electrochemical properties



**Figure S6.** Cyclic voltammograms of compounds **4a** in  $CH_3CN$  ( $C = 10^{-3}$  M) recorded vs.  $Fc/Fc^+$  at a Pt working electrode ( $\varnothing = 3$  mm,  $\nu = 0.1$  V $\cdot$ s $^{-1}$ ) and containing  $[TBA][PF_6]$  as supporting electrolyte ( $C = 10^{-1}$  M). The potential was scanned first toward positive values and then toward negative ones. Voltammograms with the ferrocene reference added *in situ* are not represented.

## 6. Computed energies and Cartesian coordinates of compounds 4a

### Compound 4aA

SCF Done: E(RB3LYP) = -1851.781084

Zero-point correction = 0.557006

Enthalpy correction = 0.592814

Gibbs Free Energy correction = 0.490425

O	3.478919	-2.506669	-1.242533
O	3.483317	-2.180322	1.485133
N	3.111270	2.191096	-0.342361
C	1.175974	0.756041	-0.218483
C	1.744094	2.066796	-0.314310
C	3.928526	1.154915	0.109803
C	5.290619	1.381150	0.379701
H	5.750132	2.335319	0.179619
C	3.365980	-0.133841	0.325136
C	0.010525	-1.774377	-0.371132
C	-0.242403	0.585140	-0.239834
C	2.014179	-0.375168	-0.115958
C	5.471572	-0.831093	1.355626
H	6.067051	-1.552295	1.895580
C	-0.569498	-3.054827	-0.488550
H	-1.630847	-3.186674	-0.374718
C	1.433166	-1.639570	-0.442240
C	0.893194	3.183503	-0.424124
H	1.290542	4.182354	-0.499878
C	3.715895	3.480457	-0.752804
C	1.593655	-3.993728	-1.074442
H	2.157348	-4.847374	-1.421177
C	4.140928	-1.087316	1.061546
C	-1.069033	1.744219	-0.256421
C	2.195942	-2.762910	-0.913976
C	-0.470804	3.007983	-0.365252
H	-1.112988	3.881293	-0.396003
C	6.040431	0.385333	0.972366
H	7.084766	0.571846	1.192941
C	0.221929	-4.130766	-0.812972
H	-0.236844	-5.106705	-0.918790
C	4.269295	-3.546955	-1.820348
H	4.393849	-4.383410	-1.126111
H	5.237446	-3.096178	-2.026613
H	3.824908	-3.904059	-2.753558

C	4.154650	-3.131937	2.314716
H	3.410426	-3.891762	2.541116
H	4.499296	-2.667188	3.242459
H	4.999039	-3.588908	1.790751
N	-0.793258	-0.651684	-0.199526
C	-2.478136	1.646499	-0.135379
N	-3.113821	0.519664	0.003127
B	-2.371868	-0.874253	-0.038599
C	-4.552319	0.515972	0.043570
C	-5.278326	1.275674	-0.883361
C	-6.659485	1.296995	-0.836826
C	-7.346702	0.552392	0.134230
C	-6.619694	-0.218120	1.049975
C	-5.229698	-0.238780	0.999718
H	-4.762120	1.815761	-1.668718
H	-7.236134	1.863778	-1.556628
H	-7.122636	-0.803104	1.807200
H	-4.672558	-0.831833	1.710668
F	-2.863972	-1.549162	-1.138205
F	-2.581354	-1.552879	1.149805
H	-3.060867	2.563250	-0.132527
C	3.935768	4.481588	0.389776
C	4.554716	5.784781	-0.124451
O	-8.693469	0.638235	0.093733
H	3.069812	3.906790	-1.520552
H	4.656927	3.249907	-1.251358
H	2.983790	4.689486	0.886259
H	4.581160	4.034703	1.150359
H	4.710659	6.487385	0.696013
H	5.525017	5.608427	-0.597596
H	3.909830	6.273442	-0.860564
C	-9.465832	-0.118759	1.025590
H	-10.504715	0.102995	0.792211
H	-9.287001	-1.191990	0.907853
H	-9.252142	0.183146	2.055665

**Compound 4aB**

SCF Done: E(RB3LYP) = -1776.554185

Zero-point correction = 0.551851

Enthalpy correction = 0.586936

Gibbs Free Energy correction = 0.485707

O	3.206919	-2.499469	-1.263258
O	3.256723	-2.161705	1.462362
N	2.826583	2.200549	-0.374910
C	0.902955	0.754333	-0.212961
C	1.461484	2.067882	-0.324583
C	3.658060	1.170880	0.067428
C	5.022699	1.406864	0.314281
H	5.472930	2.363160	0.103667
C	3.107215	-0.120408	0.296865
C	-0.249562	-1.783590	-0.333841
C	-0.514696	0.574967	-0.209500
C	1.749554	-0.371596	-0.119795
C	5.233995	-0.800764	1.294565
H	5.842946	-1.516363	1.826913
C	-0.824795	-3.067199	-0.436618
H	-1.883248	-3.204491	-0.303252
C	1.170685	-1.640824	-0.430534
C	0.602166	3.179782	-0.426373
H	0.992783	4.180320	-0.513252
C	3.416740	3.493131	-0.797181
C	1.333017	-3.996251	-1.057057
H	1.895281	-4.848063	-1.410598
C	3.900203	-1.066473	1.023680
C	-1.347933	1.730068	-0.218801
C	1.931443	-2.761603	-0.911476
C	-0.759140	2.996997	-0.344280
H	-1.406970	3.866327	-0.368612
C	5.788587	0.417831	0.897939
H	6.835193	0.611776	1.100574
C	-0.033092	-4.139990	-0.771109
H	-0.488194	-5.118804	-0.865480
C	3.991872	-3.536353	-1.854871
H	4.134685	-4.370942	-1.161972
H	4.953212	-3.080409	-2.080667
H	3.531337	-3.897304	-2.778703
C	3.947667	-3.105607	2.284957
H	3.212001	-3.868950	2.526847
H	4.304534	-2.634440	3.204766

H	4.786097	-3.559583	1.749024
N	-1.056896	-0.664501	-0.153656
C	-2.753606	1.624447	-0.072066
N	-3.376768	0.494251	0.086199
B	-2.632224	-0.896710	0.029720
C	-4.816738	0.483756	0.169086
C	-5.569652	1.173855	-0.781150
C	-6.956907	1.185685	-0.686356
C	-7.617973	0.509514	0.343505
C	-6.840318	-0.184529	1.278735
C	-5.453831	-0.209954	1.199327
H	-5.078231	1.667005	-1.612097
H	-7.533362	1.717263	-1.435309
H	-7.328295	-0.714855	2.089214
H	-4.867442	-0.749438	1.929293
F	-3.135868	-1.568132	-1.066812
F	-2.824019	-1.579167	1.217467
H	-3.344069	2.536524	-0.063968
C	3.647635	4.497149	0.340644
C	4.249676	5.803845	-0.184659
C	-9.123067	0.495784	0.427612
H	-9.463568	0.549162	1.464075
H	-9.562314	1.331490	-0.119827
H	-9.525824	-0.428109	-0.000486
H	2.756417	3.914046	-1.555690
H	4.351380	3.267535	-1.309732
H	2.702101	4.699246	0.851657
H	4.307746	4.055476	1.091582
H	4.414574	6.508028	0.632688
H	5.213184	5.633376	-0.673558
H	3.589601	6.287763	-0.910344

Compound **4aC**

SCF Done: E(RB3LYP) = -1737.225295

Zero-point correction = 0.524736

Enthalpy correction = 0.557902

Gibbs Free Energy correction = 0.461603

O	2.877122	-2.533583	-1.281988
O	2.959522	-2.200106	1.443012
N	2.585305	2.171700	-0.384330
C	0.639462	0.757914	-0.205968
C	1.219133	2.061894	-0.321765
C	3.403642	1.127207	0.048531
C	4.774289	1.339755	0.282414
H	5.238707	2.288603	0.068887
C	2.833213	-0.154902	0.281741
C	-0.557076	-1.760037	-0.317620
C	-0.780955	0.602711	-0.188932
C	1.467681	-0.382432	-0.122010
C	4.957818	-0.872659	1.257616
H	5.559793	-1.599293	1.782898
C	-1.155012	-3.033344	-0.415601
H	-2.214341	-3.152875	-0.272298
C	0.864321	-1.641273	-0.428362
C	0.377786	3.188909	-0.414764
H	0.784664	4.182661	-0.504682
C	3.193736	3.455315	-0.808798
C	0.980356	-3.998610	-1.058054
H	1.524648	-4.859550	-1.417565
C	3.617119	-1.115392	0.999592
C	-1.594272	1.772340	-0.189933
C	1.601072	-2.774295	-0.917799
C	-0.985166	3.029564	-0.320215
H	-1.618342	3.909776	-0.338029
C	5.528999	0.336993	0.857284
H	6.580645	0.512962	1.049926
C	-0.384944	-4.119328	-0.758539
H	-0.857650	-5.090133	-0.848926
C	3.639397	-3.583766	-1.880036
H	3.773417	-4.420626	-1.188167
H	4.606507	-3.144274	-2.113622
H	3.165256	-3.936575	-2.800090
C	3.641856	-3.156537	2.258540
H	2.895125	-3.906677	2.507673
H	4.016251	-2.692082	3.174760

H	4.466573	-3.625225	1.714061
N	-1.343608	-0.627242	-0.128925
C	-2.999592	1.690472	-0.032074
N	-3.639649	0.570517	0.132116
B	-2.920454	-0.833331	0.070519
C	-5.079896	0.585881	0.230830
C	-5.826140	1.269220	-0.731191
C	-7.212998	1.306792	-0.624963
C	-7.850483	0.659898	0.431105
C	-7.097911	-0.031964	1.378319
C	-5.710559	-0.078645	1.283668
H	-5.329383	1.732820	-1.575611
H	-7.793578	1.828095	-1.376543
H	-7.591142	-0.538991	2.198922
H	-5.120101	-0.614299	2.013057
F	-3.447407	-1.496856	-1.019762
F	-3.112821	-1.509930	1.261234
H	-3.575109	2.612123	-0.020385
C	3.452643	4.451134	0.330137
C	4.071898	5.749344	-0.196115
H	2.533801	3.889682	-1.559957
H	4.119406	3.214981	-1.330814
H	2.515684	4.667292	0.851103
H	4.112414	3.995283	1.072897
H	4.256183	6.447552	0.622205
H	5.027912	5.564433	-0.694373
H	3.413568	6.247169	-0.913932
H	-8.930602	0.686633	0.510318

Compound **4aD**

SCF Done: E(RB3LYP) = -1751.623099

Zero-point correction = 0.515133

Enthalpy correction = 0.549537

Gibbs Free Energy correction = 0.449944

O	3.498514	-2.480143	-1.249434
O	3.527635	-2.139688	1.475864
N	3.065514	2.217069	-0.367895
C	1.155935	0.752206	-0.217519
C	1.702595	2.070748	-0.327521
C	3.904550	1.195829	0.081014
C	5.264724	1.445996	0.336722
H	5.706755	2.406572	0.128443
C	3.364922	-0.100761	0.307983
C	0.029490	-1.797554	-0.343927
C	-0.259809	0.559199	-0.223250
C	2.012971	-0.365597	-0.117383
C	5.491889	-0.758828	1.319954
H	6.104704	-1.467853	1.856659
C	-0.532971	-3.085924	-0.450339
H	-1.590932	-3.233855	-0.324444
C	1.448733	-1.640752	-0.431020
C	0.833111	3.175473	-0.437146
H	1.215630	4.179200	-0.522674
C	3.646478	3.515027	-0.788631
C	1.637695	-3.994673	-1.055553
H	2.210547	-4.841256	-1.404607
C	4.162673	-1.038576	1.040658
C	-1.103905	1.707305	-0.239617
C	2.223635	-2.754179	-0.906410
C	-0.525781	2.980685	-0.363509
H	-1.181566	3.843848	-0.393297
C	6.036683	0.465014	0.926206
H	7.079887	0.669656	1.135657
C	0.271419	-4.151483	-0.779129
H	-0.173674	-5.134584	-0.876360
C	4.297253	-3.509192	-1.837383
H	4.444602	-4.342421	-1.143908
H	5.255068	-3.043394	-2.057778
H	3.845147	-3.874058	-2.763758
C	4.222564	-3.075857	2.304627
H	3.493043	-3.846419	2.542048
H	4.567800	-2.599880	3.226325

H	5.069308	-3.521526	1.774977
N	-0.790072	-0.685206	-0.170089
C	-2.507480	1.589157	-0.103043
N	-3.120449	0.451484	0.052611
B	-2.362214	-0.933116	0.000812
C	-4.559233	0.424575	0.126368
C	-5.313409	1.091279	-0.840689
C	-6.701369	1.088549	-0.765070
C	-7.324277	0.409693	0.277283
C	-6.579156	-0.271120	1.236050
C	-5.191600	-0.268792	1.159776
H	-4.823293	1.580002	-1.674410
H	-7.293785	1.593322	-1.516428
H	-7.080319	-0.796924	2.037766
H	-4.602610	-0.794775	1.897277
F	-2.854793	-1.607122	-1.099095
F	-2.560706	-1.616577	1.187128
H	-3.106821	2.495579	-0.100591
C	3.859800	4.523627	0.348543
C	4.454175	5.834211	-0.175964
H	2.987720	3.927932	-1.552809
H	4.586612	3.296788	-1.294124
H	2.908657	4.718832	0.851819
H	4.518023	4.089929	1.105701
H	4.605361	6.542355	0.640560
H	5.423402	5.671219	-0.655941
H	3.795869	6.309651	-0.908792
Cl	-9.073091	0.402027	0.377060



Compound **4aE**

SCF Done: E(RB3LYP) = -2074.359294

Zero-point correction = 0.529218

Enthalpy correction = 0.566083

Gibbs Free Energy correction = 0.459467

O	4.045949	-2.449145	-1.221929
O	4.036821	-2.101493	1.502494
N	3.527324	2.242857	-0.358131
C	1.639957	0.748379	-0.226740
C	2.167121	2.075014	-0.333627
C	4.377296	1.235907	0.103037
C	5.730158	1.508263	0.373554
H	6.159465	2.475076	0.167682
C	3.855555	-0.068495	0.327134
C	0.555585	-1.819216	-0.362041
C	0.227590	0.533124	-0.249203
C	2.513279	-0.355674	-0.113639
C	5.980833	-0.690340	1.365054
H	6.598696	-1.388242	1.910486
C	0.014192	-3.115850	-0.474095
H	-1.042881	-3.280027	-0.361458
C	1.973128	-1.640246	-0.431353
C	1.281757	3.166494	-0.456120
H	1.650252	4.175642	-0.539084
C	4.093145	3.548386	-0.777292
C	2.206251	-3.991793	-1.049626
H	2.796614	-4.829933	-1.389727
C	4.659429	-0.991883	1.071478
C	-0.633989	1.668526	-0.277827
C	2.771259	-2.742181	-0.894945
C	-0.074127	2.951097	-0.397790
H	-0.742934	3.803828	-0.436956
C	6.510708	0.540918	0.974293
H	7.548107	0.762485	1.195028
C	0.839190	-4.169405	-0.790942
H	0.410653	-5.159381	-0.892556
C	4.867497	-3.466089	-1.800000
H	5.020801	-4.295871	-1.103729
H	5.819942	-2.985120	-2.010769
H	4.431082	-3.839242	-2.730544
C	4.737429	-3.025448	2.340464
H	4.017678	-3.807196	2.570960
H	5.064696	-2.542649	3.265130

H	5.596922	-3.458132	1.820771
N	-0.283483	-0.719064	-0.200668
C	-2.036067	1.528930	-0.158612
N	-2.632464	0.381386	-0.007251
B	-1.853268	-0.992128	-0.051453
C	-4.071821	0.333888	0.053680
C	-4.823510	0.974263	-0.932458
C	-6.211524	0.950383	-0.865792
C	-6.843759	0.279799	0.178810
C	-6.088234	-0.374648	1.151355
C	-4.700445	-0.355189	1.091953
H	-4.329233	1.454403	-1.768458
H	-6.800087	1.432111	-1.635539
H	-6.584389	-0.905292	1.953748
H	-4.108039	-0.863371	1.838860
F	-2.321635	-1.669556	-1.159689
F	-2.058321	-1.681143	1.130040
H	-2.649981	2.425595	-0.165791
C	4.278505	4.564819	0.357812
C	4.859860	5.881479	-0.166231
H	3.436757	3.948320	-1.550318
H	5.041919	3.342261	-1.271571
H	3.318734	4.748668	0.848891
H	4.933886	4.144446	1.124819
H	4.989935	6.595950	0.648386
H	5.837438	5.730659	-0.633010
H	4.203847	6.343141	-0.909822
C	-8.348425	0.295195	0.285257
F	-8.934213	0.459628	-0.916698
F	-8.822186	-0.846632	0.819882
F	-8.768340	1.307807	1.074950

Compound **4aG**

SCF Done: E(RB3LYP) = -1851.779712

Zero-point correction = 0.557200

Enthalpy correction = 0.592977

Gibbs Free Energy correction = 0.491066

O	-3.262592	-2.375393	1.441324
O	-3.485080	-2.175889	-1.287847
N	-2.753032	2.251665	0.281087
C	-0.904592	0.716259	0.069315
C	-1.400537	2.057283	0.147931
C	-3.653060	1.239116	-0.052824
C	-5.020119	1.523155	-0.223810
H	-5.415162	2.508434	-0.037783
C	-3.172533	-0.085346	-0.247519
C	0.150181	-1.859479	0.254420
C	0.501684	0.475186	-0.013385
C	-1.800459	-0.374633	0.092190
C	-5.388398	-0.720647	-1.065103
H	-6.061345	-1.434577	-1.516475
C	0.680027	-3.159828	0.390340
H	1.720572	-3.348397	0.193561
C	-1.253850	-1.650364	0.433168
C	-0.492406	3.133553	0.136592
H	-0.835688	4.153321	0.195804
C	-3.260785	3.585288	0.680327
C	-1.467470	-3.960622	1.197240
H	-2.038559	-4.767705	1.632204
C	-4.051128	-1.031218	-0.868175
C	1.379869	1.591475	-0.117647
C	-2.024665	-2.710775	1.022742
C	0.852730	2.886912	-0.021536
H	1.536095	3.726616	-0.083125
C	-5.864015	0.540725	-0.701166
H	-6.912917	0.770883	-0.845759
C	-0.129787	-4.178327	0.832792
H	0.290869	-5.169874	0.951199
C	-4.049058	-3.346025	2.133971
H	-4.270717	-4.206511	1.495621
H	-4.974313	-2.837572	2.395674
H	-3.544898	-3.681422	3.044621
C	-4.273404	-3.131892	-2.001321
H	-3.590200	-3.940211	-2.250902
H	-4.678925	-2.697123	-2.918916

H	-5.087201	-3.516214	-1.379669
N	0.988214	-0.787854	-0.034902
C	2.768569	1.418822	-0.345687
N	3.328201	0.255023	-0.485596
B	2.543506	-1.094546	-0.275598
C	4.755702	0.162326	-0.664093
C	5.618344	0.757935	0.280009
C	6.997032	0.618815	0.113312
C	7.504339	-0.092691	-0.972034
C	6.650289	-0.677835	-1.899771
C	5.273722	-0.554829	-1.738614
O	5.031000	1.439391	1.300624
H	7.046803	-1.231132	-2.741454
H	4.589552	-1.017924	-2.435602
F	3.074027	-1.699334	0.846943
F	2.652620	-1.877817	-1.411503
H	3.393074	2.301574	-0.427856
C	-3.531821	4.547875	-0.484359
C	-4.050630	5.897587	0.020481
H	-2.532959	4.011162	1.371379
H	-4.165640	3.422640	1.265315
H	-2.616403	4.691459	-1.065167
H	-4.256354	4.100207	-1.169629
H	-4.244995	6.572882	-0.814567
H	-4.984525	5.784382	0.578567
H	-3.326760	6.385798	0.679421
H	8.577867	-0.186445	-1.085313
H	7.678574	1.061072	0.826596
C	5.846016	1.889576	2.384638
H	5.157903	2.317187	3.110914
H	6.386597	1.055831	2.841024
H	6.553265	2.657780	2.057894

Compound **4aH**

SCF Done: E(RB3LYP) = -1851.780351

Zero-point correction = 0.557101

Enthalpy correction = 0.592838

Gibbs Free Energy correction = 0.491025

O	3.507628	-2.315866	-1.418962
O	3.706469	-2.052730	1.307080
N	2.860037	2.318807	-0.359291
C	1.054703	0.735894	-0.128919
C	1.513197	2.088392	-0.232245
C	3.786174	1.339462	0.001769
C	5.143165	1.665942	0.176326
H	5.512125	2.657845	-0.027234
C	3.341950	0.006029	0.220807
C	0.075058	-1.873246	-0.260226
C	-0.344717	0.456591	-0.052075
C	1.981367	-0.329216	-0.121825
C	5.569082	-0.549090	1.065499
H	6.258996	-1.234276	1.535397
C	-0.413657	-3.192587	-0.361554
H	-1.448656	-3.408786	-0.163953
C	1.473489	-1.627124	-0.437280
C	0.574954	3.139318	-0.249709
H	0.890389	4.166844	-0.326564
C	3.332647	3.657680	-0.784670
C	1.760208	-3.948304	-1.141373
H	2.357257	-4.748408	-1.553741
C	4.242588	-0.901619	0.866657
C	-1.254877	1.549971	0.018690
C	2.278554	-2.678010	-0.997164
C	-0.763401	2.858559	-0.098435
H	-1.470396	3.679958	-0.060339
C	6.011144	0.717774	0.679160
H	7.052012	0.980685	0.825886
C	0.428895	-4.197261	-0.774253
H	0.039160	-5.204052	-0.866873
C	4.323829	-3.277571	-2.089909
H	4.568997	-4.117813	-1.433506
H	5.234428	-2.747857	-2.360593
H	3.831451	-3.646140	-2.994116
C	4.515953	-2.968921	2.048909
H	3.854094	-3.790627	2.311838
H	4.900872	-2.501224	2.959111

H	5.345710	-3.343788	1.442853
N	-0.796059	-0.818798	-0.004347
C	-2.640338	1.341869	0.229871
N	-3.175647	0.166827	0.380451
B	-2.342024	-1.166867	0.245236
C	-4.607649	0.056350	0.533803
C	-5.432077	0.726832	-0.361869
C	-6.823315	0.657037	-0.215433
C	-7.368952	-0.095094	0.829406
C	-6.519788	-0.768158	1.707376
C	-5.138608	-0.709430	1.575304
H	-5.030421	1.273467	-1.205833
O	-7.537935	1.341464	-1.140330
H	-6.950089	-1.349586	2.514057
H	-4.484917	-1.231741	2.257338
F	-2.847717	-1.838905	-0.849190
F	-2.427957	-1.895377	1.417427
H	-3.292119	2.208813	0.293075
C	3.565613	4.653915	0.359623
C	4.048751	6.006510	-0.172353
H	2.598932	4.046363	-1.491229
H	4.246737	3.507914	-1.358531
H	2.641628	4.784023	0.929969
H	4.297093	4.243836	1.060787
H	4.215561	6.706227	0.648410
H	4.990504	5.908504	-0.719964
H	3.316607	6.457661	-0.848321
H	-8.439393	-0.169330	0.960933
C	-8.963074	1.289620	-1.084193
H	-9.310988	1.891160	-1.921088
H	-9.327347	0.263820	-1.197256
H	-9.339873	1.715896	-0.149093

**Compound 4aI**

SCF Done: E(RB3LYP) = -1624.097439

Zero-point correction = 0.529102

Enthalpy correction = 0.561905

Gibbs Free Energy correction = 0.466630

O	2.291815	-2.700949	-1.144730
O	2.249069	-2.278754	1.566648
N	2.304341	2.040996	-0.417315
C	0.250372	0.781566	-0.302961
C	0.931844	2.034532	-0.429365
C	3.016036	0.956371	0.096547
C	4.384157	1.075470	0.400794
H	4.930057	1.979389	0.185269
C	2.339259	-0.271591	0.337861
C	-1.123222	-1.644918	-0.406717
C	-1.176592	0.732071	-0.359002
C	0.984893	-0.412875	-0.135627
C	4.349194	-1.110142	1.450864
H	4.866797	-1.860025	2.030528
C	-1.810333	-2.871946	-0.508497
H	-2.882058	-2.907081	-0.422054
C	0.306650	-1.634495	-0.438223
C	0.184287	3.215219	-0.608769
H	0.668864	4.172334	-0.710592
C	3.031139	3.257943	-0.851410
C	0.278383	-4.011831	-0.999780
H	0.775506	-4.920989	-1.304780
C	3.009431	-1.261790	1.127211
C	-1.897285	1.957892	-0.439692
C	0.981758	-2.833804	-0.852779
C	-1.190660	3.159733	-0.583776
H	-1.753741	4.082905	-0.666838
C	5.029619	0.040349	1.046703
H	6.079726	0.145465	1.292207
C	-1.107142	-4.021807	-0.779505
H	-1.646316	-4.956876	-0.874505
C	3.006762	-3.824571	-1.662258
H	3.029049	-4.646910	-0.941049
H	4.018573	-3.467904	-1.841215
H	2.567681	-4.168942	-2.602671
C	2.819366	-3.264711	2.431337
H	2.008104	-3.952210	2.658423
H	3.185020	-2.809442	3.355670

H	3.630952	-3.803959	1.934603
N	-1.831776	-0.452442	-0.294006
C	-3.314283	1.978468	-0.346956
N	-4.029662	0.913637	-0.185968
B	-3.425204	-0.531126	-0.204722
C	-5.500013	1.011078	-0.045479
F	-3.929819	-1.158031	-1.334151
F	-3.777994	-1.188280	0.961105
H	-3.822111	2.939946	-0.395405
C	3.303925	4.275347	0.264859
C	4.069290	5.491728	-0.264414
H	2.447971	3.710363	-1.653698
H	3.962563	2.928974	-1.311346
H	2.358481	4.593791	0.712906
H	3.871154	3.796099	1.067032
H	4.256014	6.208021	0.537598
H	5.038203	5.204819	-0.683011
H	3.509423	6.010978	-1.047711
C	-5.949373	1.080152	1.419599
H	-5.835672	1.895538	-0.594203
H	-5.921940	0.134478	-0.538155
C	-7.474816	1.141111	1.533002
H	-5.562082	0.207182	1.947943
H	-5.503322	1.964666	1.888403
H	-7.778912	1.198969	2.579904
H	-7.883633	2.016696	1.020086
H	-7.941283	0.251161	1.101953

Compound 4aJ

SCF Done: E(RB3LYP) = -1622.855966

Zero-point correction = 0.505436

Enthalpy correction = 0.537689

Gibbs Free Energy correction = 0.443332

O 2.039180 -2.788196 -1.176828  
O 2.032767 -2.394213 1.538423  
N 2.355318 1.934649 -0.400551  
C 0.225682 0.807749 -0.289911  
C 0.985467 2.015787 -0.406049  
C 2.998439 0.801406 0.098989  
C 4.372225 0.830345 0.398992  
H 4.973159 1.700436 0.191666  
C 2.245479 -0.383359 0.330132  
C -1.300251 -1.524129 -0.420935  
C -1.201708 0.850061 -0.342134  
C 0.882919 -0.433141 -0.138956  
C 4.202142 -1.359906 1.425285  
H 4.672843 -2.147885 1.994328  
C -2.065646 -2.702388 -0.540279  
H -3.137393 -2.669577 -0.452625  
C 0.127423 -1.605280 -0.453653  
C 0.314820 3.244009 -0.570280  
H 0.860337 4.168554 -0.663963  
C 3.156199 3.106594 -0.828564  
C -0.054688 -3.968129 -1.047291  
H 0.382285 -4.903231 -1.365503  
C 2.854112 -1.422505 1.106004  
C -1.842598 2.121050 -0.406866  
C 0.723610 -2.840353 -0.884581  
C -1.060539 3.276761 -0.540726  
H -1.563315 4.235029 -0.612194  
C 4.953065 -0.250783 1.030798  
H 6.008587 -0.215321 1.272997  
C -1.438246 -3.891359 -0.827430  
H -2.036634 -4.788179 -0.935708  
C 2.682131 -3.950103 -1.704061  
H 2.652429 -4.778265 -0.989804  
H 3.714450 -3.656145 -1.879952  
H 2.222691 -4.258125 -2.647346  
C 2.542727 -3.417773 2.397364  
H 1.690105 -4.052100 2.627624  
H 2.942372 -2.989497 3.320493

H 3.314999 -4.006785 1.894479  
N -1.930687 -0.290483 -0.291099  
C -3.254540 2.231659 -0.309581  
N -4.035410 1.212604 -0.155172  
B -3.528146 -0.270055 -0.205225  
C -5.502793 1.403641 -0.014526  
F -4.063615 -0.827593 -1.358074  
F -3.928207 -0.932783 0.935315  
H -3.699057 3.224502 -0.348857  
C 3.502003 4.094652 0.293924  
C 4.336036 5.266211 -0.233099  
H 2.598114 3.603278 -1.622469  
H 4.061529 2.722826 -1.298200  
H 2.582613 4.467426 0.754356  
H 4.046267 3.574132 1.086262  
H 4.574227 5.962500 0.572873  
H 5.281266 4.924066 -0.664007  
H 3.801468 5.825780 -1.006240  
C -5.934574 1.505500 1.423847  
H -5.767592 2.313425 -0.562434  
H -5.983794 0.560998 -0.509777  
C -6.795689 0.672223 1.994056  
H -5.517520 2.335128 1.990355  
H -7.109281 0.800493 3.023154  
H -7.217401 -0.168568 1.453637

Compound **4aK**

SCF Done: E(RB3LYP) = -1742.060976

Zero-point correction = 0.613399

Enthalpy correction = 0.649824

Gibbs Free Energy correction = 0.548335

O	2.982081	-2.652383	-1.055507
O	2.800213	-2.172613	1.639193
N	2.734052	2.098224	-0.448411
C	0.742501	0.741069	-0.390046
C	1.365296	2.023279	-0.519204
C	3.474031	1.061622	0.122399
C	4.820077	1.255268	0.481825
H	5.329950	2.180037	0.266421
C	2.847869	-0.192850	0.365141
C	-0.512302	-1.748547	-0.499690
C	-0.675710	0.619731	-0.504510
C	1.523725	-0.411659	-0.161772
C	4.844905	-0.904741	1.584084
H	5.371940	-1.614534	2.204320
C	-1.133230	-3.009227	-0.616482
H	-2.204425	-3.095774	-0.580670
C	0.916350	-1.670341	-0.464652
C	0.567129	3.159196	-0.759964
H	1.006464	4.137414	-0.866920
C	3.418468	3.339792	-0.881022
C	1.028317	-4.055179	-0.984410
H	1.582041	-4.944031	-1.248789
C	3.529602	-1.129909	1.207276
C	-1.454137	1.800915	-0.640919
C	1.666764	-2.842522	-0.824293
C	-0.803872	3.034243	-0.786627
H	-1.408409	3.925829	-0.912247
C	5.486020	0.268357	1.180337
H	6.518088	0.430761	1.467609
C	-0.364256	-4.127867	-0.833134
H	-0.853768	-5.088687	-0.939511
C	3.772160	-3.748087	-1.520714
H	3.797283	-4.559343	-0.787081
H	4.774021	-3.346842	-1.655954
H	3.395544	-4.124841	-2.475714
C	3.380153	-3.112615	2.547327
H	2.594632	-3.835657	2.753619
H	3.682338	-2.622885	3.477008

H	4.238230	-3.619680	2.096969
N	-1.279772	-0.588279	-0.440183
C	-2.871955	1.755155	-0.580226
N	-3.572891	0.677068	-0.414599
B	-2.879094	-0.739137	-0.438295
F	-3.255229	-1.380441	-1.606615
F	-3.227334	-1.449935	0.697442
H	-3.402438	2.702156	-0.649483
C	3.589449	4.396310	0.219212
C	4.311291	5.639134	-0.309872
H	2.849898	3.743614	-1.718991
H	4.384690	3.047883	-1.291399
H	2.609924	4.674023	0.618533
H	4.145995	3.967740	1.056592
H	4.426635	6.383252	0.480155
H	5.310432	5.394676	-0.681847
H	3.757716	6.108723	-1.128184
C	-5.071090	0.838691	-0.313575
C	-5.784048	-0.017234	-1.363062
H	-5.224917	1.885544	-0.590424
C	-5.653056	0.714986	1.150183
H	-6.850243	0.214557	-1.348046
H	-5.403681	0.203624	-2.361608
H	-5.659981	-1.083077	-1.185102
C	-6.893130	1.637473	1.199130
C	-6.097971	-0.712617	1.520556
C	-4.635514	1.220437	2.189080
H	-7.366174	1.571550	2.181646
H	-6.623385	2.684747	1.030172
H	-7.645122	1.356382	0.457497
H	-6.480389	-0.713339	2.544867
H	-6.906466	-1.063402	0.875568
H	-5.277730	-1.425416	1.468170
H	-5.106483	1.259298	3.174168
H	-3.770112	0.559293	2.260906
H	-4.284673	2.232784	1.960395

Compound **4aL**

SCF Done: E(RB3LYP) = -1718.765639

Zero-point correction = 0.573985

Enthalpy correction = 0.609288

Gibbs Free Energy correction = 0.507947

O 3.071176 -2.557102 -1.013400  
O 2.788581 -2.108720 1.679732  
N 2.617298 2.175754 -0.371360  
C 0.676800 0.743195 -0.384117  
C 1.254804 2.049699 -0.480165  
C 3.380468 1.163040 0.210658  
C 4.707478 1.404659 0.609599  
H 5.186513 2.350546 0.416584  
C 2.796006 -0.116408 0.423768  
C -0.468832 -1.794865 -0.555163  
C -0.732210 0.568586 -0.545292  
C 1.497682 -0.380752 -0.144954  
C 4.783584 -0.763261 1.693361  
H 5.319508 -1.458677 2.322201  
C -1.038081 -3.077617 -0.690708  
H -2.106277 -3.204689 -0.685569  
C 0.952945 -1.660023 -0.477051  
C 0.423163 3.159075 -0.729158  
H 0.829552 4.153891 -0.809521  
C 3.266679 3.443496 -0.782232  
C 1.172414 -4.035910 -1.001563  
H 1.767623 -4.901317 -1.253185  
C 3.489083 -1.034928 1.277249  
C -1.548976 1.726183 -0.693287  
C 1.758668 -2.799983 -0.820129  
C -0.940223 2.984125 -0.801219  
H -1.573441 3.854196 -0.935970  
C 5.390878 0.437034 1.318051  
H 6.407512 0.635557 1.636003  
C -0.219989 -4.164506 -0.888535  
H -0.667650 -5.143751 -1.009965  
C 3.918011 -3.620022 -1.454430  
H 3.953529 -4.429998 -0.719833  
H 4.906562 -3.178838 -1.559796  
H 3.585273 -4.010866 -2.419988  
C 3.375868 -3.030400 2.602018  
H 2.611464 -3.782077 2.783792  
H 3.633196 -2.533164 3.541146

H 4.264394 -3.504673 2.175512  
N -1.284773 -0.668376 -0.515016  
C -2.965289 1.623259 -0.704751  
N -3.595721 0.499037 -0.594454  
B -2.867598 -0.886598 -0.555789  
C -5.071514 0.466835 -0.553011  
F -3.220229 -1.557469 -1.715567  
F -3.256003 -1.570003 0.585134  
H -3.549701 2.536694 -0.796485  
C 3.376327 4.501478 0.324495  
C 4.059343 5.772877 -0.188361  
H 2.703481 3.830829 -1.631517  
H 4.251722 3.187270 -1.171282  
H 2.379879 4.740472 0.706733  
H 3.933654 4.092006 1.170845  
H 4.132974 6.517742 0.605900  
H 5.073066 5.567995 -0.544351  
H 3.501922 6.224130 -1.014323  
C -5.606005 0.505059 0.892806  
H -5.448306 1.310522 -1.134463  
H -5.398582 -0.451343 -1.037172  
N -7.057225 0.461152 0.899086  
H -5.217584 -0.369332 1.414770  
H -5.204403 1.398748 1.408582  
C -7.598594 -0.174033 2.097579  
C -7.672632 1.760273 0.655125  
H -8.755367 1.644657 0.578809  
H -7.459850 2.490877 1.457132  
H -7.325345 2.182353 -0.290741  
H -8.682457 -0.265076 2.000756  
H -7.185563 -1.178927 2.203915  
H -7.385443 0.391114 3.022363

**Compound 4aM**

SCF Done: E(RB3LYP) = -1660.002783

Zero-point correction = 0.505723

Enthalpy correction = 0.538358

Gibbs Free Energy correction = 0.443283

O	2.257560	-2.706690	-1.166666
O	2.243058	-2.298105	1.547092
N	2.311617	2.032132	-0.413454
C	0.249940	0.786931	-0.288487
C	0.939548	2.035682	-0.412660
C	3.020232	0.939044	0.086952
C	4.391966	1.046399	0.378652
H	4.942449	1.947463	0.162984
C	2.336536	-0.285200	0.327781
C	-1.142496	-1.629160	-0.393544
C	-1.177670	0.748310	-0.334359
C	0.977094	-0.413901	-0.134576
C	4.350603	-1.144527	1.417201
H	4.868125	-1.901417	1.987761
C	-1.838599	-2.851447	-0.489309
H	-2.909604	-2.880131	-0.392685
C	0.287170	-1.628834	-0.437374
C	0.199413	3.223692	-0.577239
H	0.690745	4.177639	-0.676251
C	3.043565	3.245925	-0.848781
C	0.237213	-4.004759	-1.003502
H	0.725051	-4.916670	-1.315166
C	3.006719	-1.284541	1.105598
C	-1.889717	1.980071	-0.402233
C	0.949933	-2.831648	-0.861668
C	-1.175113	3.178389	-0.542570
H	-1.732191	4.105979	-0.615967
C	5.035830	0.002956	1.012688
H	6.088989	0.098874	1.248658
C	-1.145791	-4.005813	-0.768577
H	-1.692204	-4.937140	-0.858769
C	2.960511	-3.834220	-1.692505
H	2.985432	-4.657077	-0.972004
H	3.972432	-3.483297	-1.881791
H	2.509566	-4.175199	-2.628485
C	2.813684	-3.291411	2.403317
H	1.999238	-3.973385	2.635594
H	3.191298	-2.841993	3.325684

H	3.616453	-3.835275	1.897394
N	-1.841508	-0.431342	-0.273046
C	-3.305224	2.011434	-0.310611
N	-4.031429	0.950689	-0.158752
B	-3.434076	-0.498650	-0.166989
C	-5.497402	1.063080	-0.051088
F	-3.957589	-1.138327	-1.278570
F	-3.772581	-1.135478	1.016193
H	-3.806039	2.976247	-0.358389
C	3.337255	4.254920	0.269748
C	4.106762	5.467685	-0.261938
H	2.455319	3.707324	-1.642145
H	3.967040	2.911728	-1.320819
H	2.399702	4.578995	0.730221
H	3.909578	3.766745	1.062896
H	4.308470	6.178092	0.541658
H	5.068451	5.175006	-0.692956
H	3.542425	5.995759	-1.036056
C	-5.997307	0.947449	1.392148
H	-5.810947	2.028480	-0.453446
H	-5.940428	0.275834	-0.660083
O	-7.383578	1.233234	1.317710
H	-5.795866	-0.055706	1.776552
H	-5.465746	1.675337	2.022957
H	-7.800844	0.968395	2.142283



Compound **4aN**

SCF Done: E(RB3LYP) = -1620.61940188

Zero-point correction = 0.475931

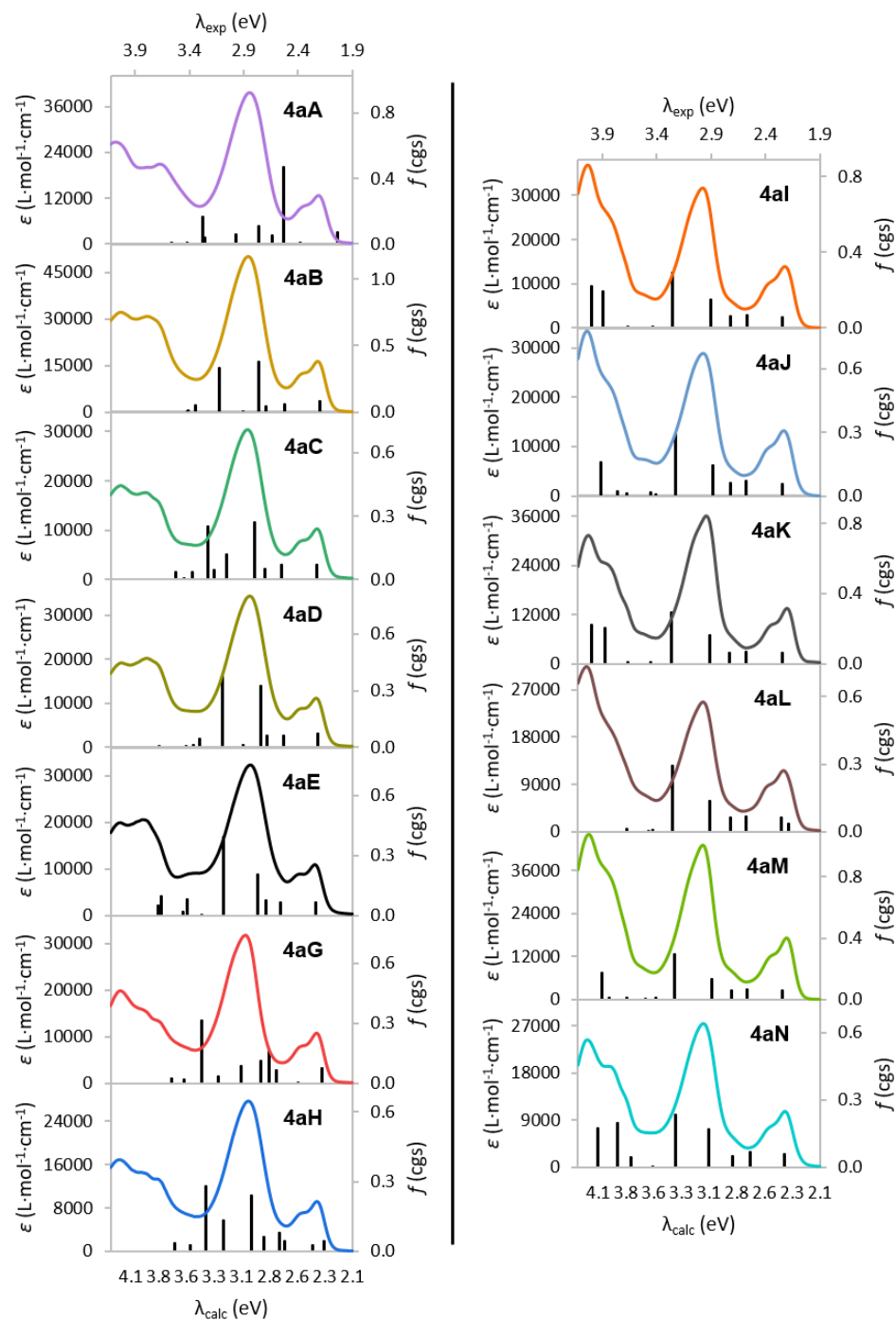
Enthalpy correction = 0.507139

Gibbs Free Energy correction = 0.415822

O	1.601621	-2.826962	-1.300591
O	1.799305	-2.526419	1.424895
N	2.294796	1.833039	-0.407434
C	0.101739	0.848907	-0.190753
C	0.935528	2.006111	-0.321398
C	2.888195	0.644307	0.015176
C	4.277550	0.570411	0.223224
H	4.923132	1.403787	-0.000385
C	2.070965	-0.494538	0.261988
C	-1.583276	-1.376481	-0.270046
C	-1.319695	0.988291	-0.148908
C	0.681852	-0.436965	-0.117872
C	4.021693	-1.634522	1.199153
H	4.472080	-2.469386	1.715257
C	-2.424492	-2.505794	-0.337092
H	-3.482325	-2.413934	-0.165838
C	-0.170344	-1.546796	-0.410232
C	0.343675	3.280927	-0.406772
H	0.944262	4.169842	-0.508485
C	3.145411	2.962128	-0.854424
C	-0.542916	-3.883011	-1.020047
H	-0.190568	-4.837624	-1.382087
C	2.655477	-1.597204	0.966812
C	-1.871923	2.300254	-0.147790
C	0.312894	-2.806214	-0.906266
C	-1.021948	3.405363	-0.295842
H	-1.462153	4.395974	-0.316036
C	4.821073	-0.566538	0.785765

H	5.889843	-0.610057	0.958630
C	-1.895852	-3.726391	-0.686486
H	-2.555145	-4.583680	-0.753243
C	2.130765	-4.017960	-1.887198
H	2.110183	-4.850952	-1.178324
H	3.160731	-3.782087	-2.144929
H	1.578814	-4.287433	-2.791817
C	2.289800	-3.598107	2.235751
H	1.411898	-4.179673	2.506785
H	2.770344	-3.214602	3.139731
H	2.990449	-4.226616	1.678774
N	-2.122139	-0.106288	-0.074560
C	-3.267597	2.511026	-0.003144
N	-4.089081	1.531025	0.183363
B	-3.694308	-0.004642	0.172432
O	-5.421514	1.900806	0.137930
F	-4.407471	-0.574948	-0.860043
F	-3.986332	-0.560655	1.400951
H	-3.691086	3.509003	-0.054396
C	3.627678	3.889558	0.269645
C	4.500676	5.021677	-0.279814
H	2.573713	3.519786	-1.596347
H	3.990636	2.534228	-1.392667
H	2.766012	4.304773	0.799919
H	4.186065	3.310424	1.009529
H	4.834851	5.676401	0.526851
H	5.391882	4.633675	-0.781288
H	3.954889	5.637100	-1.000861
C	-6.281595	1.161557	1.038175
H	-5.923105	1.237366	2.065135
H	-7.240805	1.663102	0.928547
H	-6.361158	0.120427	0.730144

## 7. Vertical excitations of BODIPY compounds 4a



**Figure S7.** Computed excited states and experimental absorption spectra of BODIPY derivatives **4a**. 0.15 eV offset applied to all  $\lambda_{\text{calc}}$  axes. Computed at the B3LYP/6-311G(d,p) level of theory in gas phase.

**Table S1. Ten first transitions of BODIPY derivative 4aA computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	564	2.20	0.0695	144	145	0.693	96.0
2	488	2.54	0.0074	143	145	0.653	85.3
3	460	2.70	0.4707	144	146	0.681	92.8
4	442	2.80	0.0526	142	145	0.622	77.4
5	424	2.93	0.1110	141	145	0.610	74.5
6	395	3.14	0.0558	143	146	0.669	89.5
7	362	3.42	0.0403	140	145	0.631	79.7
8	360	3.44	0.1678	142	146	0.586	68.6
9	346	3.58	0.0097	141	146	0.686	94.1
10	333	3.73	0.0015	140	146	0.694	96.4

**Table S2. Ten first transitions of BODIPY derivative 4aA computed at the B3LYP/6-311G(d,p) level of theory in acetonitrile as implicit solvent.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	538	2.30	0.1100	144	145	0.688	94.8
2	465	2.67	0.0582	143	145	0.645	83.1
3	451	2.75	0.1453	141	145	0.387	29.9
				142	145	0.513	52.7
4	445	2.79	0.5435	144	146	0.658	86.6
5	415	2.99	0.0891	141	145	0.477	45.5
				142	145	-0.373	27.8
6	385	3.22	0.2740	143	146	0.653	85.3
7	369	3.36	0.0343	142	146	0.671	90.1
8	355	3.49	0.0062	141	146	0.694	96.2
9	326	3.81	0.0292	139	145	0.490	48.0
				144	147	0.444	39.5
10	321	3.87	0.0010	140	145	0.694	96.3

**Table S3. Ten first transitions of BODIPY derivative 4aB computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	524	2.36	0.0797	140	141	0.676	91.4
2	461	2.69	0.0582	139	141	0.662	87.7
3	434	2.86	0.0463	137	141	-0.447	40.0
				138	141	0.530	56.1
4	424	2.93	0.3746	140	142	0.687	94.3
5	405	3.06	0.0078	137	141	0.419	35.2
				138	141	0.413	34.2
6	378	3.28	0.3311	139	142	0.590	69.5
7	377	3.29	0.0091	136	141	0.689	95.0
8	353	3.51	0.0509	138	142	0.658	86.7
9	347	3.57	0.0102	137	142	0.649	84.2
10	346	3.59	0.0030	136	142	0.651	84.7

**Table S4. Ten first transitions of BODIPY derivative 4aB computed at the B3LYP/6-311G(d,p) level of theory in acetonitrile as implicit solvent.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	524	2.37	0.1066	140	141	0.688	94.6
2	464	2.67	0.0602	139	141	0.695	96.7
3	442	2.80	0.0647	138	141	0.675	91.2
4	429	2.89	0.5713	140	142	0.693	95.9
5	387	3.21	0.1356	139	142	0.619	76.7
6	366	3.39	0.2452	137	141	0.622	77.5
7	361	3.44	0.0103	138	142	0.664	88.3
8	337	3.68	0.1083	137	142	0.669	89.5
9	331	3.74	0.0003	136	141	0.697	97.0
10	324	3.83	0.0302	135	141	0.518	53.6
				140	143	0.417	34.7

**Table S5. Ten first transitions of BODIPY derivative 4aC computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	519	2.39	0.0711	136	137	0.676	91.5
2	457	2.72	0.0689	135	137	0.673	90.6
3	432	2.87	0.0511	134	137	0.674	90.8
4	419	2.96	0.2725	136	138	0.686	94.2
5	385	3.22	0.1190	135	138	0.508	51.6
6	372	3.34	0.0448	133	137	0.594	70.4
7	365	3.40	0.2496	132	137	0.532	56.6
				135	138	0.368	27.0
8	350	3.54	0.0354	134	138	0.662	87.6
9	343	3.61	0.0031	133	138	0.663	87.8
10	336	3.68	0.0361	132	138	0.656	86.1

**Table S6. Ten first transitions of BODIPY derivative 4aC computed at the B3LYP/6-311G(d,p) level of theory in acetonitrile as implicit solvent.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	520	2.38	0.1013	136	137	0.687	94.3
2	465	2.67	0.0589	135	137	0.695	96.6
3	441	2.81	0.0694	134	137	0.676	91.3
4	425	2.92	0.4888	136	138	0.691	95.4
5	385	3.22	0.2434	135	138	0.658	86.6
6	361	3.43	0.0192	134	138	0.693	96.2
7	346	3.58	0.1447	133	137	0.679	92.1
8	327	3.79	0.0005	132	137	0.695	96.7
9	325	3.81	0.1539	131	137	0.552	60.9
10	320	3.88	0.0681	133	138	0.533	56.8
				136	139	0.376	28.2



**Table S7. Ten first transitions of BODIPY derivative 4aC computed at the CAM-B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	433	2.86	0.1858	136	137	0.674	90.8
2	393	3.15	0.1423	135	137	0.600	72.1
3	373	3.33	0.0183	134	137	0.598	71.4
4	360	3.44	0.5686	136	138	0.630	79.5
5	305	4.07	0.1206	135	138	0.431	37.1
6	294	4.22	0.0580	131	137	0.428	36.6
				135	138	0.383	29.4
7	284	4.36	0.1756	134	138	0.313	<b>19.6</b>
8	278	4.46	0.0322	133	137	0.412	33.9
				133	138	-0.388	30.1
9	271	4.58	0.0049	132	138	0.531	56.3
10	269	4.61	0.2022	134	138	0.473	44.8

**Table S8. Ten first transitions of BODIPY derivative 4aD computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	521	2.38	0.0758	139	140	0.670	89.9
2	460	2.70	0.0650	138	140	0.654	85.5
3	436	2.85	0.0637	136	140	-0.453	41.1
				137	140	0.507	51.4
4	426	2.91	0.3271	139	141	0.683	93.2
5	404	3.07	0.0117	136	140	0.369	27.3
				137	140	0.421	35.4
				138	141	-0.380	28.9
6	380	3.26	0.3771	138	141	0.552	60.9
7	358	3.47	0.0470	137	141	0.660	87.2
8	352	3.52	0.0109	136	141	0.693	95.9
9	345	3.60	0.0005	135	140	0.694	96.2
10	323	3.84	0.0015	135	141	0.689	94.9

**Table S9. Ten first transitions of BODIPY derivative 4aE computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	516	2.40	0.0666	152	153	0.674	90.7
2	456	2.72	0.0671	151	153	0.667	89.1
3	434	2.86	0.0750	150	153	0.649	84.2
4	422	2.93	0.2045	152	154	0.668	89.3
5	382	3.25	0.3924	151	154	0.624	78.0
6	359	3.46	0.0042	150	154	0.676	91.3
7	346	3.58	0.0785	149	153	0.664	88.0
8	342	3.63	0.0186	148	153	0.682	93.0
9	324	3.82	0.0971	149	154	0.645	83.1
10	322	3.86	0.0496	147	153	0.437	38.1
				148	154	-0.396	31.4

**Table S10. Ten first transitions of BODIPY derivative 4aG computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	529	2.34	0.0752	144	145	0.664	88.1
2	483	2.57	0.0050	143	145	0.626	78.3
3	449	2.76	0.0649	142	145	0.634	80.3
4	438	2.83	0.1566	144	146	0.616	75.8
5	427	2.90	0.1106	141	145	0.643	82.8
6	401	3.09	0.0842	143	146	0.661	87.5
7	376	3.30	0.0365	140	145	0.567	64.4
				142	146	-0.376	28.3
8	360	3.45	0.3154	140	145	0.400	32.0
				142	146	0.542	58.7
9	343	3.61	0.0163	141	146	0.677	91.6
10	333	3.73	0.0246	140	146	0.687	94.3

**Table S11. Ten first transitions of BODIPY derivative 4aH computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	534	2.32	0.0427	144	145	0.655	85.8
2	510	2.43	0.0283	143	145	0.627	78.7
3	462	2.68	0.0450	144	146	0.660	87.0
4	453	2.74	0.0778	142	145	0.640	81.8
5	431	2.88	0.0598	141	145	0.673	90.7
6	415	2.99	0.2394	143	146	0.681	92.8
7	381	3.25	0.1329	140	145	-0.438	38.3
				142	146	0.507	51.4
8	364	3.41	0.2802	140	145	0.529	55.9
				142	146	0.413	34.1
9	349	3.56	0.0267	141	146	0.668	89.4
10	336	3.69	0.0363	140	146	0.684	93.7

**Table S12. Ten first transitions of BODIPY derivative 4aI computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	515	2.41	0.0589	128	129	0.678	92.0
2	453	2.74	0.0690	127	129	0.681	92.6
3	430	2.88	0.0603	126	129	0.677	91.5
4	404	3.07	0.1477	128	130	0.678	92.0
5	363	3.41	0.2942	127	130	0.646	83.5
6	345	3.60	0.0076	126	130	0.690	95.3
7	323	3.83	0.0086	125	129	0.545	59.3
				128	131	-0.436	38.0
8	305	4.06	0.1907	124	129	0.634	80.3
9	298	4.16	0.2182	125	129	0.368	27.2
				128	131	0.484	46.9
10	282	4.40	0.0895	125	130	0.505	51.0
				127	131	0.414	34.3

**Table S13. Ten first transitions of BODIPY derivative 4aJ computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	515	2.41	0.0591	127	128	0.678	91.9
2	453	2.74	0.0689	126	128	0.679	92.1
3	430	2.88	0.0610	125	128	0.674	90.8
4	407	3.05	0.1436	127	129	0.679	92.2
5	366	3.39	0.2986	126	129	0.641	82.3
6	347	3.58	0.0066	125	129	0.683	93.3
7	342	3.62	0.0159	124	128	0.687	94.4
8	323	3.84	0.0102	123	128	0.540	58.4
				127	130	0.438	38.4
9	315	3.93	0.0231	124	129	0.690	95.3
10	304	4.08	0.1607	122	128	0.637	81.2

**Table S14. Ten first transitions of BODIPY derivative 4aK computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	515	2.41	0.0647	140	141	0.680	92.5
2	452	2.74	0.0689	139	141	0.683	93.2
3	429	2.89	0.0598	138	141	0.680	92.4
4	403	3.08	0.1650	140	142	0.683	93.2
5	361	3.43	0.2953	139	142	0.651	84.8
6	342	3.62	0.0067	138	142	0.689	94.9
7	324	3.83	0.0076	137	141	0.542	58.8
				140	143	-0.432	37.3
8	306	4.05	0.2021	136	141	0.607	73.8
9	298	4.16	0.2243	140	143	0.485	47.0
10	281	4.41	0.0929	137	142	0.484	46.9
				139	143	0.435	37.8



**Table S15. Ten first transitions of BODIPY derivative 4aL computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	637	1.95	0.0059	136	137	0.705	99.5
2	527	2.35	0.0340	136	138	0.702	98.5
3	514	2.41	0.0649	135	137	0.675	91.3
4	453	2.74	0.0682	134	137	0.680	92.4
5	430	2.89	0.0628	133	137	0.675	91.1
6	404	3.07	0.1368	135	138	0.678	92.0
7	363	3.42	0.2925	134	138	0.647	83.6
8	345	3.60	0.0067	133	138	0.681	92.7
9	341	3.64	0.0028	136	139	0.690	95.3
10	323	3.84	0.0109	132	137	0.544	59.3
				135	139	-0.426	36.2

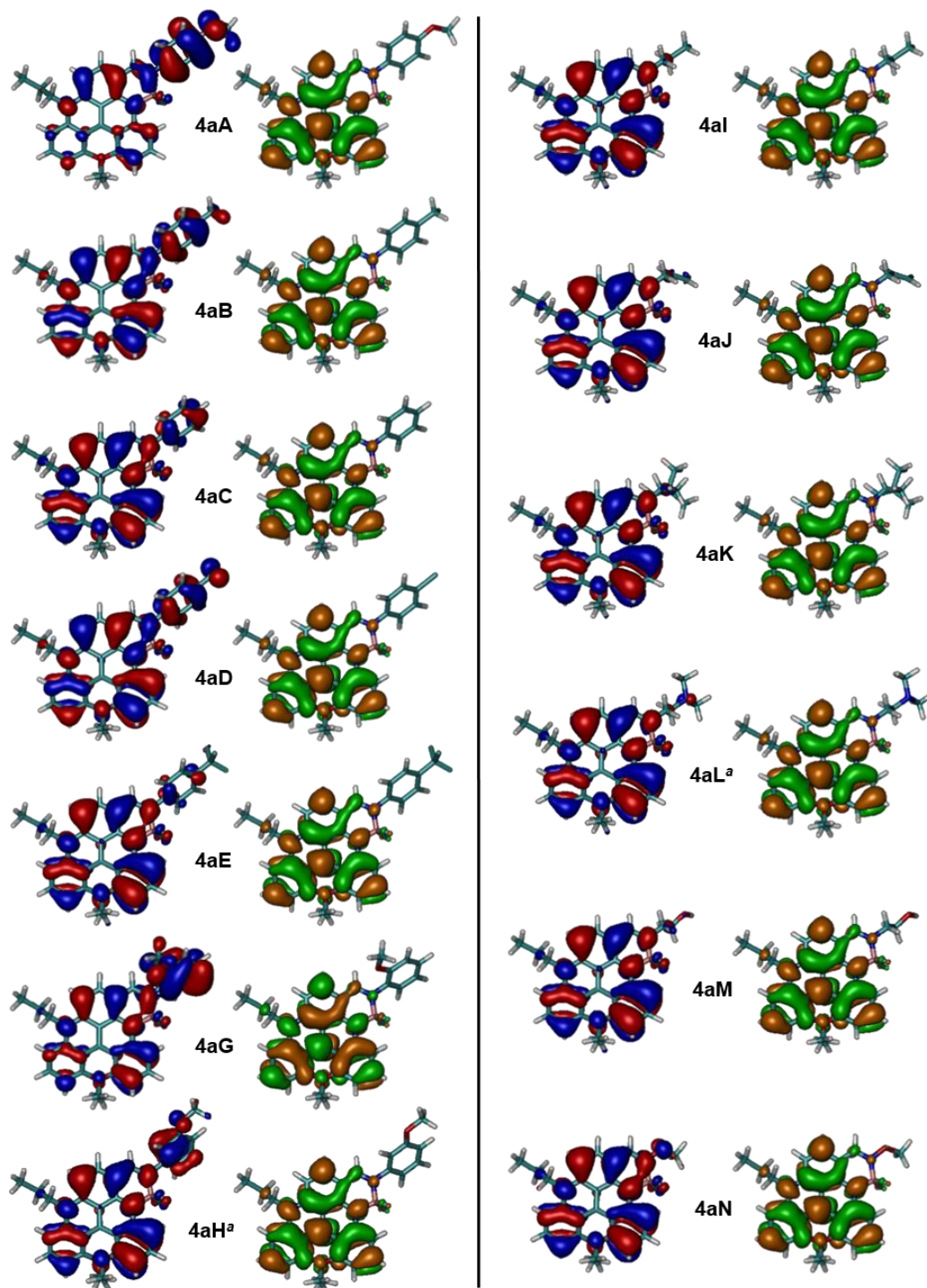
**Table S16. Ten first transitions of BODIPY derivative 4aM computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	514	2.41	0.0559	128	129	0.677	91.7
2	453	2.74	0.0681	127	129	0.679	92.1
3	431	2.88	0.0614	126	129	0.673	90.5
4	405	3.06	0.1351	128	130	0.676	91.4
5	365	3.40	0.2973	127	130	0.642	82.4
6	347	3.57	0.0085	126	130	0.690	95.3
7	338	3.67	0.0018	125	129	0.701	98.4
8	323	3.84	0.0093	124	129	0.544	59.2
				128	131	-0.435	37.9
9	310	4.00	0.0103	125	130	0.694	96.4
10	305	4.07	0.1732	123	129	0.635	80.6

**Table S17. Ten first transitions of BODIPY derivative 4aN computed at the B3LYP/6-311G(d,p) level of theory in gas phase.**

Transition	$\lambda$ (nm)	Energy (eV)	$f$ (cgs)	From MO	To MO	CI Coefficient	Contribution (%)
1	519	2.39	0.0567	124	125	0.679	92.3
2	458	2.71	0.0689	123	125	0.683	93.4
3	433	2.86	0.0486	122	125	0.683	93.3
4	402	3.09	0.1695	124	126	0.672	90.3
5	365	3.39	0.2324	123	126	0.639	81.7
6	344	3.60	0.0039	122	126	0.686	94.2
7	327	3.80	0.0436	121	125	0.490	48.0
				124	127	-0.354	25.1
8	316	3.92	0.1986	120	125	-0.376	28.3
				121	125	0.443	39.3
9	302	4.11	0.1759	120	125	0.395	31.3
				124	127	0.461	42.5
10	283	4.38	0.0894	121	126	0.388	30.1
				123	127	0.447	40.0

## 8. Frontier Molecular Orbitals of BODIPYs 4a



**Figure S8.** HOMO (red and blue lobes) and LUMO (orange and green lobes) representations of compounds **4a** computed at the B3LYP/6-311G(d,p) level of theory in gas phase. Isovalues  $\pm 0.02$ . <sup>a</sup>HOMO-1 and LUMO are represented.

## 9. Computed spin densities of compound 4aA

SCF Done: E(RB3LYP) = -1851.946427	32 C	0.000678
Charge: 0	36 C	0.000627
Multiplicity: 2	40 N	0.046352
Unpaired e <sup>-</sup> :	41 C	0.027493
1	42 N	-0.001625
Spin state: doublet	43 B	0.001098
1 O	44 C	0.000302
2 O	45 C	0.000134
3 N	46 C	-0.000272
4 C	47 C	0.000379
5 C	48 C	-0.000221
6 C	49 C	0.000544
7 C	54 F	0.000980
9 C	55 F	0.000975
10 C	57 C	0.003651
11 C	58 C	0.000516
<b>12 C 0.424937</b>	59 O	-0.000089
13 C	67 C	0.000009
15 C		
17 C		
18 C		
20 C		
21 C		
23 C		
24 C		
25 C		
26 C		
28 C		
30 C		

SCF Done: E(RB3LYP) = -1851.986376	<b>41 C 0.375530</b>
Charge: -1	42 N 0.155608
Multiplicity: 3	43 B -0.008470
Unpaired e <sup>-</sup> :	44 C -0.009199
2	45 C 0.028596
Spin state: triplet	46 C -0.016375
1 O 0.007226	47 C 0.039665
2 O 0.009216	48 C -0.017404
3 N 0.068577	49 C 0.039230
4 C -0.095436	54 F 0.002874
<b>5 C 0.285057</b>	55 F 0.003000
6 C 0.084568	57 C 0.002648
7 C -0.025739	58 C 0.000787
9 C -0.076986	59 O 0.003776
10 C 0.065767	67 C 0.001012
<b>11 C 0.203452</b>	
<b>12 C 0.471610</b>	
13 C -0.036082	
15 C -0.005146	
17 C -0.080216	
18 C -0.133382	
20 C 0.002780	
21 C -0.017649	
23 C 0.109488	
24 C -0.112132	
25 C 0.091330	
<b>26 C 0.258092</b>	
28 C 0.126596	
30 C 0.078948	
32 C 0.000754	
36 C 0.001537	
40 N 0.116494	

SCF Done: E(RB3LYP) = -1851.443736	41 C	-0.070005
Charge: +2	42 N	0.082121
Multiplicity: 2	43 B	-0.002895
Unpaired e <sup>-</sup> :	<b>44 C</b>	<b>0.135857</b>
1	45 C	-0.024997
Spin state: doublet	46 C	0.066254
1 O	47 C	0.081644
2 O	48 C	0.039515
3 N	49 C	0.004692
4 C	54 F	0.007199
5 C	55 F	0.003101
6 C	57 C	0.005214
7 C	58 C	0.000673
9 C	59 O	0.122090
10 C	67 C	0.008908
11 C		
12 C		
13 C		
15 C		
17 C		
<b>18 C</b>		<b>0.137771</b>
20 C		
21 C		
23 C		
<b>24 C</b>		<b>0.149915</b>
25 C		
26 C		
28 C		
30 C		
32 C		
36 C		
40 N		

SCF Done: E(RB3LYP) = -1850.992763	41 C -0.013043
Charge: +3	42 N 0.028704
Multiplicity: 3	43 B -0.003952
Unpaired e <sup>-</sup> :	<b>44 C 0.275114</b>
2	45 C -0.068216
Spin state: triplet	46 C 0.138670
1 O 0.126156	47 C 0.122928
2 O 0.077308	48 C 0.089172
3 N 0.059093	49 C -0.021117
4 C 0.096902	54 F 0.005423
5 C -0.017617	55 F 0.004960
6 C -0.043539	57 C 0.004804
7 C 0.116373	58 C 0.000940
9 C 0.044748	59 O 0.208327
10 C -0.033531	67 C 0.014108
11 C -0.034397	
12 C -0.036868	
13 C 0.045266	
<b>15 C 0.291367</b>	
17 C 0.005025	
18 C 0.075464	
20 C -0.000568	
21 C 0.208137	
23 C 0.044241	
24 C 0.081991	
25 C 0.074615	
26 C -0.036237	
28 C -0.018670	
30 C -0.093467	
32 C 0.008105	
36 C 0.006374	
40 N 0.166909	

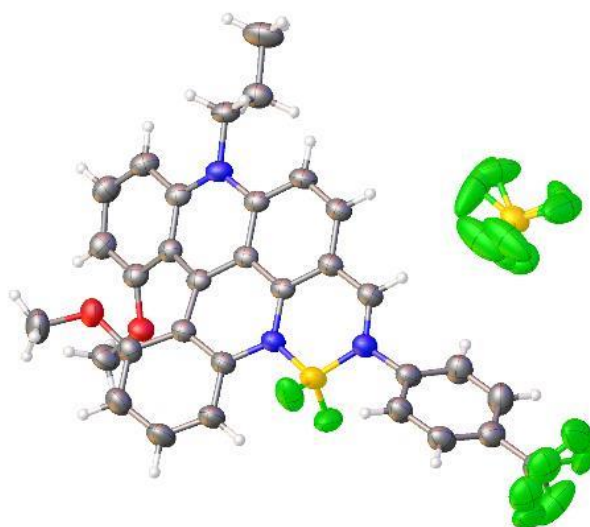


## 10. Crystal data and structure refinement for compound 4aE

Empirical formula	C <sub>32</sub> H <sub>26</sub> B <sub>2</sub> F <sub>9</sub> N <sub>3</sub> O <sub>2</sub>	
Formula weight	677.18	
CCDC number	2024041	
Temperature	180.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.2245(5) Å	α = 92.741(3)°
	b = 13.0227(5) Å	β = 106.371(3)°
	c = 13.7251(5) Å	γ = 107.992(3)°
Volume	1810.66(12) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.242 Mg/m <sup>3</sup>	
Absorption coefficient	0.948 mm <sup>-1</sup>	
F(000)	692	
Crystal size	0.28 x 0.162 x 0.014 mm <sup>3</sup>	
Theta range for data collection	3.393 to 73.657°	
Index ranges	-13 ≤ h ≤ 12, -15 ≤ k ≤ 15, -14 ≤ l ≤ 16	
Reflections collected	17797	
Independent reflections	7062 [R(int) = 0.0201]	
Completeness to theta = 67.684°	99.8%	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.488	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7062 / 172 / 489	
Goodness-of-fit on F <sup>2</sup>	1.045	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0516, wR <sub>2</sub> = 0.1506	
R indices (all data)	R <sub>1</sub> = 0.0602, wR <sub>2</sub> = 0.1593	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.496 and -0.350 e.Å <sup>-3</sup>	

## Comments

The tetrafluoroborate was refined using two components. Restraints were used, same distances (SADI) restraints on 1-2 and 1-3 distances and rigid bond restraints (RIGU) on displacement parameters. An EADP constraint was also used between two close fluorine atoms. The  $\text{CF}_3$  group is also disordered and was refined using six fluorine atoms. Same distances (SADI) restraints were used on C–F distances and on the F–F distances of the low occupancy part. Rigid bond restraints were used on the displacement parameters. One EADP constraint was used between two close fluorine atoms. The squeeze/bypass<sup>[16]</sup> procedure was used to take care of disordered solvent. R before squeezing:  $R_1$  29.26% and  $wR_2$  0.6984. Both the electronic density before squeezing and the number of electrons found during the squeeze/bypass procedure hinted towards disordered dichloromethane molecules. One hole representing about 22 percent of the volume of the unit-cell was located containing 129 electrons, which could correspond to about 3 dichloromethane molecules. The solvent molecules were not added to the formula.



**Figure S9.** View of the asymmetric unit (displacement ellipsoids at 50 percent probability)

## 11. References

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