# Electronic Supporting Information - Synthesis of Fused-ring Aza-dipyrromethenes from Aromatic Nitriles

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## Experimental

### **General Information**

All reagents were used as received unless otherwise noted. 1,3-dicyanobenzene, 1,4dicyanobenzene, 3-thiophenecarbonitrile, benzonitrile, 4-cyanophenol, 2-ethyl-1-iodohexane, zinc (ii) acetate dihyrdate, n-butanol, n-butyllithium (1.6 M in hexanes), diisopropylamine, 2,2,6,6tetramethylpiperidine, n-butyllitium (1.6 M in hexanes) and lithium diisopropylamide (LDA, 2.0 M in THF/heptane/ethylbenzene) were purchased from Sigma-Aldrich. Formamide and tetrahydrofuran were purchased from Fisher Scientific, the latter was dried over 4 Å molecular sieves.

### Instrumentation

Absorption spectra were recorded using a Varian Cary 5000 spectrometer in DCM. NMR spectra were splot between an Agilent DD2 600 spectrometers (600 MHz) and an Agilent DD2 500 spectrometer (500 MHz).

### Notes

- For very large scale reactions with 1,3-dicyanobenzene, LDA was prepared from diisopropylamine and <sup>n</sup>BuLi and is cooled to -98°C before adding 1,3-dicyanobenzene to it. This method prevents addition products from forming during lithiation, due to local temperature fluctuations. For smaller scale reactions, commercially available LDA solution can simply be added to the 1,3-dicyanobenzene solution as usual.
- 2. When adding lithiated aromatic nitriles via cannula to another solution, it is imperative that a very high flow rate is maintained and no breaks in flow are allowed to happen. Visually, the colour of the solution should not change after travelling through the cannula, though it is unavoidable that the first few millilitres will be purple/black.
- 3. Time limits for the reductive amination in formamide are approximations. The ideal time will change depending on the molecule, scale, and size of heating mantle. The colour of the reaction is the best indicator of completion, and past a certain point the products will start to degrade.

### **Synthesis**

### Synthesis of 1a



A flame dried, argon filled 500 mL 3-neck flask was charged with diisopropylamine (6.0 mL, 4.3 g, 42 mmol), THF (150 mL), and a stir bar. The flask was placed in an ice bath and <sup>n</sup>BuLi (1.6 M in hexanes, 24.5 mL, 39.2 mmol) was slowly added. The mixture was cooled to -98°C and 1,3-dicyanobenzene (10.5 g, 81.9 mmol) in THF (200 mL) was added using an addition funnel over 2 h while maintaining the temperature at -98°C. The dark yellow mixture was slowly warmed to RT and stirred for 2 h, at which point the solution was dark red/violet. The solvent was removed under vacuum, then formamide (100 mL) was added and the mixture was heated to reflux on a heating mantle for roughly 20 minutes, until the mixture had changed from purple to green/blue. The mixture was rapidly cooled back to RT with an ice bath. The reaction mixture was then poured into water (300 mL) and vacuum filtered. After washing with methanol (500 mL) The solid material was added to a soxhlet thimble and washed with methanol for 24 h, acetone for 24 h, and DCM for 2 h to yield a purple solid (4.90 g, 50%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.42 (d, 2H), 8.17 (s, 2H), 8.13 (d, 2H), 7.88 (d, 2H), 7.80 (d, 2H), 7.76 (t, 2H), 7.59 (t, 2H); <sup>13</sup>C NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 148.95, 144.14, 136.33, 134.96, 134.31, 134.03, 133.35, 132.77, 130.18, 128.59, 126.72, 118.51, 117.76, 113.63, 105.61; HRMS-DART calcd for C<sub>32</sub>H<sub>16</sub>N<sub>7</sub> [M+H]<sup>+</sup> 498.1467, found: 498.1472

### Synthesis of 1b



A flame dried, argon filled 500 mL 3-neck flask was charged with THF (250 mL), 1,4dicyanobenzene (10.5 g, 81.9 mmol) and a stir bar. After stirring for 10 min to dissolve the solid, LDA (2.0 M in THF/heptane/ethylbenzene, 20.4 mL, 40.8 mmol) was slowly added over 10 min. The mixture was then stirred at RT for 1 h before evaporating the solvent under inert atmosphere. Formamide (100 mL) was added and the mixture was heated to reflux on a heating mantle for approximately 20 min. The green mixture was rapidly cooled back to RT in an ice bath and filtered. The solid was washed with methanol (500 mL) before adding to a soxhlet thimble and washed with methanol for 24 h, acetone for 24 h, and DCM for 2 h to yield a purple solid (5.08 g, 50%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.34 (s, 2H), 8.27 (d, 2H), 8.10 (d, 4H), 7.95 (d, 4H), 7.73 (d, 2H); HRMS-ESI calcd for C<sub>32</sub>H<sub>14</sub>N<sub>7</sub> [M-H]<sup>-</sup> 496.1316, found: 496.1308

#### Synthesis of 1c



A flame dried, argon filled 100 mL 3-neck flask was charged with THF (12 mL) and 3thiophenecarbonitrile (1.16 g, 10.6 mmol). The flask was cooled to -98°C and methylmagnesium chloride (2 M in THF, 2.6 mL, 5.2 mmol) was added dropwise. After stirring at -98°C for 5 minutes, the flask was removed from the bath and allowed to warm to RT. After stirring at RT for 2 h, the solvent was evaporated under inert atmosphere. Formamide (10 mL) as added and the mixture was heated at maximum power on a heating mantle for 5 minutes after the first sign of gas evolution. The flask was taken off the heating mantle and cooled to RT using a water bath. The mixture was filtered, washed with MeOH three times followed by DCM, to give a gold coloured solid (17 mg, 2%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.88 (dd, 2H), 7.68 (dd, 2H), 7.60 (dd, 2H), 7.52 (d, 2H), 7.40 (d, 2H); HRMS-DART calcd for C<sub>20</sub>H<sub>12</sub>N<sub>3</sub>S<sub>4</sub> [M+H]<sup>+</sup> 421.9914, found: 421.9906

#### Synthesis of 1d



A flame dried, argon filled 250 mL 3-neck flask was charged with THF (100 mL), 2,2,6,6-tetramethylpiperidine (733 mg, 5.20 mmol) and a stir bar. The flask was cooled to  $-98^{\circ}$ C and n-butyllithium (1.6 M in hexanes, 3.25 mL, 5.20 mmol) was added dropwise. After stirring at  $-98^{\circ}$ C for 5 minutes, a solution of benzonitrile (1.125 g, 10.9 mmol) in THF (10 mL) was added dropwise while maintaining the temperature. After stirring for 5 minutes, the flask was removed from the MeOH/N<sub>2</sub> bath and allowed to warm to RT. After stirring at RT for 2 h, the solvent was evaporated under inert atmosphere. Formamide (15 mL) as added and the mixture was heated at maximum power on a heating mantle until the solution was greenish-blue. The flask was taken off the heating mantle and cooled to RT using a water bath. The mixture was filtered, washed with MeOH/H<sub>2</sub>O (2:1), and purified by silica column chromatography using a DCM/hexanes gradient to give a shiny purple solid (103 mg, 10%). <sup>1</sup>H NMR matches previously reported.<sup>1</sup>

#### Synthesis of 2a



A flame dried, argon filled 500 mL 3-neck flask was charged with LDA (2.0 M in THF/heptane/ethylbenzene, 19.5 mL, 39 mmol), THF (150 mL), and a stir bar. The mixture was cooled to -98°C and 1,3-dicyanobenzene (5.0 g, 39 mmol) in THF (100 mL) was added using an addition funnel over 1 h while maintaining the temperature at -98°C. After stirring for 10 min, the mixture was transferred by cannula (under static vacuum) to another 500 mL 3-neck flask containing benzonitrile (5.0 g, 49 mmol) in THF (100 mL). This flask was kept in a 40°C water bath to prevent it from cooling too much during the addition of lithiated 1,3-dicyanobenzene. The dark red mixture was warmed to RT and stirred for 2 h. The solvent was removed under vacuum, then formamide (50 mL) was heated at maximum power on a heating mantle for 10 min after the first sign of gas evolution. The green mixture was cooled back to RT and filtered. The solid was washed vigourously with methanol followed by a single DCM wash to give a purple/brown lustrous powder (4.1 g, 47%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.39 (d, 2H), 7.93 (d, 2H), 7.91 (t, 2H), 7.74 (d, 2H), 7.61, (dd, 6H), 7.54 (t, 2H); HRMS-DART calcd for C<sub>30</sub>H<sub>18</sub>N<sub>5</sub> [M+H]<sup>+</sup> 448.1562, found: 448.1556

### Synthesis of 2b



A flame dried, argon filled 100 mL 3-neck flask was charged with a stir bar, THF (50 mL), and 1,3-dicyanobenzene (1.77 g, 13.8 mmol). The mixture was cooled to -98°C and LDA (2.0 M in THF/heptane/ethylbenzene, 6.90 mL, 13.8 mmol) over 15 min while maintaining the temperature at -98°C. After stirring for 10 min, the mixture was transferred by cannula (under static vacuum) to 500 mL 3-neck flask containing 4-((2-ethylhexyl)oxy)benzonitrile (3.47 g, 15.0 mmol) in THF (150 mL). This flask was kept in a 40°C water bath to prevent it from cooling too much during the addition of lithiated 1,3-dicyanobenzene. The dark red mixture was warmed to RT and stirred for 2 h. The solvent was removed under vacuum, then formamide (50 mL) was heated at maximum

power on a heating mantle for approximately 20 minutes before cooling in an ice bath. The mixture was filtered and washed with 2:1 MeOH/water. The solid was redissolved in DCM and purified on a silica column with a DCM/hexanes gradient to give a shiny gold-coloured solid (201 mg, 4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 (d, 2H), 7.83 (d, 4H), 7.66 (d, 2H), 7.43 (t, 2H), 7.07 (d, 4H), 3.95 (d, 4H), 1.78 (m, 2H), 1.52 (m, 8H), 1.35 (m, 8H), 0.97 (m, 12H); HRMS-DART calcd for C<sub>46</sub>H<sub>50</sub>N<sub>5</sub>O<sub>2</sub> [M+H]<sup>+</sup> 704.3965, found: 704.3961

#### Synthesis of zinc aza-diisoindolmethines



This procedure was adapted from the microwave procedure from Bessette et al.<sup>2</sup> The azadiisoindolmethine (40-100 mg), DIPEA (2 eq),  $Zn(OAc)_2$  (1.2 eq), n-butanol (3 mL) and a stir bar. The mixture was heated in a microwave reactor at 140°C for 5 minutes before cooling to RT and evaporating the solvent. Soluble products (**1b-Zn**, **1d-Zn**, **2a-Zn**, and **2b-Zn**) were purified on a silica column, whereas **1a-Zn** was purified by filtration and washing with MeOH and DCM sequentially.

**1a-Zn**: Washed with MeOH and DCM to give a gold-coloured product (29 mg, 67%). MALDI-MS calcd for  $C_{64}H_{28}N_{14}Zn$  [M]<sup>-</sup> 1056.19, found: 1056.0

**1b-Zn**: Purified by silica column with DCM/MeOH gradient to give a gold-coloured product (24 mg, 64%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (d, 4H), 7.95 (s, 4H), 7.87 (d, 4H), 7.43 (d, 8H), 7.34 (d, 8H); MALDI-MS calcd for C<sub>64</sub>H<sub>28</sub>N<sub>14</sub>Zn [M]<sup>-</sup> 1056.19, found: 1056.0

**1d-Zn**: Purified by silica column with DCM to give a violet product (68 mg, 73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d, 4H), 7.58 (d, 4H), 7.41 (d, 8H), 7.39 (t, 4H), 7.19 (t, 4H), 6.92 (t, 8H), 6.82 (t, 4H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  153.24, 141.53, 137.24, 132.80, 130.36, 128.59, 128.04, 127.48, 127.30, 124.89, 121.58, 120.62; MALDI-MS calcd for C<sub>56</sub>H<sub>36</sub>N<sub>6</sub>Zn [M]<sup>-</sup> 856.23, found: 856.1

**2a-Zn**: Purified by silica column with DCM to give a copper-coloured product (89 mg, 82%). <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ )  $\delta$  8.32 (d, 4H), 7.67 (d, 4H), 7.54 (t, 4H), 7.29 (d, 8H), 6.96 (t, 4H), 6.92 (t, 8H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  153.85, 140.62, 137.83, 133.01, 130.88, 130.04, 128.68, 128.16, 127.66, 127.47, 125.66, 117.25, 105.01; MALDI-MS calcd for C<sub>60</sub>H<sub>32</sub>N<sub>10</sub>Zn [M]<sup>-</sup> 956.21, found: 956.1

**2b-Zn**: Purified by silica column with a DCM/hexanes gradient to give a violet product (60 mg, 91%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (d, 4H), 7.65 (d, 4H), 7.46 (t, 4H), 7.24 (d, 8H), 6.35 (d, 8H), 3.46(d, 8H), 1.55 (m, 4H), 1.38 (m, 16H), 1.33 (m, 16H), 0.97 (t, 12H), 0.92 (t, 12H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  160.76, 153.23, 140.62, 137.85, 132.74, 130.18, 128.17, 126.85, 125.27, 122.98, 117.69, 113.47, 104.89, 70.41, 39.20, 30.56, 29.14, 23.85, 23.12, 14.16, 11.21; MALDI-MS calcd for C<sub>92</sub>H<sub>96</sub>N<sub>10</sub>O<sub>4</sub>Zn [M]<sup>+</sup> 1468.69, found: 1468.6

### Synthesis of Aza-BODIPYs



The aza-BODIPYs generated from every aza-diisoindolmethine (with the exception of 2b) suffered from extremely poor solubility, which hindered their purification and characterization. Due to this lmiitation, only the aza-BODIPY of 2b is reported. This procedure was adapted from Gresser et. al.<sup>1</sup>

**2b-BF2**: Purified by silica column chromatography with DCM/hexanes gradient (44 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (d, 2H), 7.71 (d, 2H), 7.68 (d, 4H), 7.57 (t, 2H), 7.02 (d, 4H), 3.92 (d, 4H), 1.74 (m, 2H), 1.45 (m, 8H), 1.35 (m, 8H), 0.96 (m, 12H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  162.10, 153.51, 144.58, 138.97, 134.83, 134.10, 132.31, 129.58, 129.07, 125.93, 120.07, 116.21, 114.21, 107.42, 70.55, 39.41, 30.50, 29.09, 23.84, 23.03, 14.06, 11.15; <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) 129.86 (q, 2F). DART calcd for C<sub>46</sub>H<sub>48</sub>N<sub>5</sub>O<sub>2</sub>BF<sub>2</sub> [M+H]<sup>+</sup> 752.39, found: 752.4

## **NMR Data**

### Notes

Compound **1a-Zn** is not soluble enough for any NMR characterization. Compounds **1b** and **1c** are not soluble enough for <sup>13</sup>C NMR spectra. Proton and carbon NMR assignments are based on a combination of COSY, HSQC, and HMBC spectra, where possible. Unassigned spectra are given in cases of low solubility compounds. In compounds with poor solubility, a CHCl<sub>3</sub> is seen in <sup>1</sup>H NMR spectra taken in  $CD_2Cl_2$  because of signal amplification.

### **Aza-diisoindolmethines**



Figure S1: <sup>1</sup>H NMR Spectrum of 1a

500 MHz, CD<sub>2</sub>Cl<sub>2</sub>



Figure S2: <sup>1</sup>H COSY NMR Spectrum of 1a



Figure S3: <sup>13</sup>C NMR Spectrum of 1a



Figure S4: <sup>1</sup>H NMR Spectrum of 1b

500 MHz, CD<sub>2</sub>Cl<sub>2</sub>



Figure S5: <sup>1</sup>H COSY NMR Spectrum of 1b



Figure S6: <sup>1</sup>H NMR Spectrum of 1c

500 MHz, CD<sub>2</sub>Cl<sub>2</sub>



Figure S7: <sup>1</sup>H COSY NMR Spectrum of 1c

500 MHz,  $CD_2Cl_2$ 



Figure S8: <sup>1</sup>H NMR Spectrum of 2a



Figure S9: <sup>1</sup>H COSY NMR Spectrum of 2a



Figure S10: <sup>1</sup>H NMR Spectrum of 2b

400 MHz, CDCl<sub>3</sub>



Figure S11: <sup>1</sup>H NMR Spectrum of 2b

## Zinc Aza-diisoindolmethines



Figure S12: <sup>1</sup>H NMR Spectrum of 1b-Zn

600 MHz, CDCl<sub>3</sub>



Figure S13: <sup>1</sup>H COSY NMR Spectrum of 1b-Zn

600 MHz, CDCl<sub>3</sub>



Figure S14: <sup>1</sup>H NMR Spectrum of 2b-Zn

600 MHz, CDCl<sub>3</sub>



Figure S15: <sup>1</sup>H COSY NMR Spectrum of 1d-Zn



Figure S16: <sup>13</sup>C NMR Spectrum of 1d-Zn



Figure S17: <sup>1</sup>H NMR Spectrum of 2a-Zn



Figure S18: <sup>1</sup>H COSY NMR Spectrum of 2a-Zn



Figure S19: <sup>13</sup>C NMR Spectrum of 2a-Zn



Figure S20: <sup>13</sup>C NMR Spectrum of 2b-Zn



Figure S21: <sup>1</sup>H NMR Spectrum of 2b-Zn



Figure S22: <sup>1</sup>H COSY NMR Spectrum of 2b-Zn



Figure S23: <sup>13</sup>C NMR Spectrum of 2b-Zn



Figure S24: <sup>1</sup>H-<sup>13</sup>C HSQC NMR Spectrum of 2b-Zn



Figure S25: <sup>1</sup>H-<sup>13</sup>C HMBC NMR Spectrum of 2b-Zn

## **Aza-BODIPY**



Figure S26: <sup>1</sup>H NMR Spectrum of 2b-BF<sub>2</sub>



Figure S27: <sup>13</sup>C NMR Spectrum of 2b-BF<sub>2</sub>



Figure S28: <sup>19</sup>F NMR Spectrum of 2b-BF<sub>2</sub>

## **Mass Spectrometry Data**

DART MS is used for aza-diisoindolmethines, MALDI is used for Zn(II) complexes

### Aza-diisoindolmethines



Figure S29: HR-MS of 1a

#### **DART** Ionization

#### AIMS Mass Spectrometry Laboratory Department of Chemistry - U of T

AccuTOF







#### **DART** Ionization

#### AIMS Mass Spectrometry Laboratory Department of Chemistry - U of T

AccuTOF





Figure S31: HR-MS of 2a

**DART** Ionization

#### AIMS Mass Spectrometry Laboratory Department of Chemistry - U of T

AccuTOF



Figure S32: HR-MS of 2b

## Zinc Aza-diisoindolmethines



MALDI Mass Spectrum

Figure S33: MALDI Mass Spectrum of 1a-Zn



Figure S34: MALDI Mass Spectrum of 1b-Zn



Figure S35: MALDI Mass Spectrum of 1d-Zn



Figure S36: MALDI Mass Spectrum of 2a-Zn



Figure S37: MALDI Mass Spectrum of 2b-Zn

## **Aza-BODIPY**



ION MODE: POSITIVE

Figure S38: MALDI Mass Spectrum of 2b-BF<sub>2</sub>

# **Absorption Data**



Figure S39: Normalized absorbance spectrum of aza-BODIPY 2b-BF<sub>2</sub>

## **Electrochemical Data**

CV was used to compare the redox properties of **1a**, **1d**, and **2a**. These molecules can be considered to be the same aza-diisoindolmethine frameworks with 4, 0, and 2 cyano groups, respectively.

Compound	$E_{1/2}$ [ox] (V) <sup>(a)</sup>	$E_{1/2}$ [red] (V) <sup>(a)</sup>	HOMO (eV) <sup>(b)</sup>	LUMO (eV) <sup>(b)</sup>
1a	0.6	-0.9	-5.4	-3.9
1d	$0.1 (0.17)^{(c)}$	-1.3 (-1.42) <sup>(c)</sup>	-4.9 (-4.97) <sup>(c)</sup>	-3.5 (-3.38) <sup>(c)</sup>
2a	0.5	-1.0	-5.3	-3.8

**Table S1: Electrochemical Properties of Aza-diisoindolmethines** 

<sup>(a)</sup>Half-wave potentials were measured in  $CH_2Cl_2/TBAPF_6$  (0.1 M) vs. Ag/Ag<sup>+</sup>, scan rate 100 mV/s, using Fc/Fc<sup>+</sup> as an internal standard. <sup>(b)</sup>HOMO and LUMO values were calculated using Fc/Fc<sup>+</sup> as -4.8 eV. <sup>(c)</sup>Values previously reported by Gresser et al.<sup>1</sup>



Figure S40: Reduction of aza-diisoindolmethines in DCM



Figure S41: Oxidation of aza-diisoindolmethines in DCM

## **Organic Photovoltaic Device Data**

Test OPVs were made from a blend of P3HT and 2b-Zn (1:0.7 weight ratio). Table S2 includes the average metrics over 5 devices.



Figure S42: a) J-V curve and b) EQE plot for OPVs with P3HT/2b-Zn

**Table S2: Device Metrics** 

	V <sub>OC</sub> (V)	$J_{SC}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
P3HT:2b-Zn	$0.54\pm0.01$	$1.40\pm0.01$	$47.4\pm0.7$	$0.36 \pm 0.01$



Figure S43: Absorbance of OPV device from S42

ITO slides were washed with aqueous detergent, followed by ultrasonic cleaning in deionized water, acetone and isopropanol for 20 minute cycles. Slides were then plasma cleaned using air plasma for 10 minutes. Slides were then coated with ZnO oxide as described in a previous report and were transferred to a N<sub>2</sub> glovebox ( $O_2 < 5ppm$ ).<sup>3</sup>

Device solutions were prepared in the glovebox. Briefly, a 20 mg/mL solution (total mass) of poly(3-hexylthiophene) (P3HT) (Rieke metals: RMI-001EE) and 2b-Zn was prepared in orthodichlorobenzene at a 1:0.7 ratio (P3HT:2b-Zn). Solutions were stirred overnight at 80 C. Device solutions were filtered through 0.45  $\mu$ m PTFE syringe filters immediately prior to use and were spin cast at 1000 rpm for 40s followed by 2000 rpm for 2s. Devices were then annealed at 120 ° C for 30 minutes. After annealing a 5 nm layer of MoO<sub>3</sub> and an 80 nm layer of Ag were thermally evaporated using an Angstrom Engineering (Kitchener, ON) Covap II at 10<sup>-6</sup> Torr. Device area was defined by shadow masking as 0.07 cm<sup>2</sup>.

J-V curves were collected using a Keithley 2400 source meter under simulated AM 1.5G at a power intensity of 100 mW/cm<sup>2</sup>. Spectral mismatch was calibrated using a Si diode with a KG-5 filter. EQE spectra were recorded using a 300 W Xe arc lamp and an Oriel cornerstone 260 1/4 m monochromator referenced to a Si cell traceable to the National Institute of Standards and Technology.

# X-ray Crystallography Data

Crystals grown from slow evaporation in  $CHCl_3$  with 5 eq TFA



Figure S44: Supramolecular Structure of 1c with TFA

	X	у	Z	U (eq)
S(1A)	550(2)	9759(1)	3871(1)	74(1)
S(2A)	-414(2)	7412(1)	4219(1)	45(1)
S(3A)	8358(2)	7154(1)	5222(1)	50(1)
S(4A)	8578(3)	9601(1)	5094(1)	66(1)
C(19A)	9657(9)	9044(5)	5097(3)	42(3)
S(4F)	9567(17)	9239(7)	5159(6)	38(6)
C(19F)	8139(19)	9602(11)	5130(20)	40(20)
N(1A)	3990(4)	7456(2)	4719(1)	36(1)
N(2A)	2689(4)	8248(2)	4480(1)	35(1)
N(3A)	5632(4)	8173(2)	4875(1)	36(1)
C(1A)	1508(6)	9285(3)	4096(2)	50(2)
C(2A)	-668(5)	9322(3)	3865(2)	43(2)
C(3A)	-354(6)	8823(3)	4031(2)	43(2)
C(4A)	928(5)	8794(3)	4166(2)	38(2)
C(5A)	1482(5)	8292(2)	4327(2)	34(1)
C(6A)	967(5)	7746(2)	4341(2)	35(2)
C(7A)	238(6)	6779(3)	4363(2)	45(2)
C(8A)	1441(6)	6816(3)	4498(2)	42(2)
C(9A)	1870(5)	7377(3)	4484(2)	36(2)
C(10A)	2970(6)	7689(2)	4574(2)	37(2)
C(11A)	5106(5)	7629(2)	4842(2)	34(2)
C(12A)	6075(5)	7253(3)	4963(2)	35(2)
C(13A)	6257(6)	6666(3)	5033(2)	46(2)
C(14A)	7438(6)	6562(3)	5177(2)	50(2)
C(15A)	7126(6)	7564(3)	5052(2)	38(2)
C(16A)	6856(5)	8139(3)	4991(2)	37(2)
C(17A)	7678(5)	8623(3)	5030(2)	41(2)
C(18A)	8989(6)	8555(3)	5077(2)	49(2)
C(20A)	7317(6)	9175(3)	5039(2)	50(2)

Table S3: Atomic coordinates (10<sup>4</sup>) and equivalent isotropic displacement parameters ( $\mathring{A}^2 \times 10^3$ ) for 3. U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

## References

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