Supporting Information for

Synthesis of a class of 5-((5-(pyrrol-2-yl-methylene)-pyrrol-2-yl)methylene)furan-2-ones and the formation of a furanone dipyrren imino ether

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**Fig. S2** $^{13}$C NMR (100 MHz) spectrum of 1a.
Fig. S3 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of 1a.

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Fig. S26 $^1$H NMR (400 MHz) spectrum of 3.
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Fig. S28 HR ESI(+) TOF mass spectrum of 3: calculated and observed spectra.
<Crystallographic data>

Crystallographic data of 2b-1

A crystalline red plate of C_{22}H_{8}N_{3}O_{3}F_{5}Cl_{2} having approximate dimensions of 0.12 × 0.25 × 0.40 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 56.0º. Data were collected in a series of φ and ω scans in 0.50º oscillations with 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 20418 reflections that were collected, 4938 were unique (R_{int} = 0.024); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT^{S1} software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 3.91 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABSS^{S2}), with minimum and maximum transmission coefficients of 0.890 and 0.954, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods^{S3}. All non-hydrogen atoms were refined anisotropically. All C-H hydrogen atoms were placed in calculated positions but were not refined. The N-H hydrogen atom was located in a difference map and refined isotropically. The final cycle of full-matrix least-squares refinement^{S4} on F² was based on 4938 reflections and 321 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.046 and wR2 = 0.102).

The standard deviation of an observation of unit weight^{S5} was 0.99. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.41 and -0.32 e/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber^{S6}. Anomalous dispersion effects were included in Fcalc^{S7}; the values for Δf' and Δf'' were those of Creagh and McAuley^{S8}. The values for the mass attenuation coefficients are those of Creagh and Hubbell^{S9}. All refinements were performed using the SHELXTL^{S10} crystallographic software package from Bruker-AXS.

Table S1. Parameters for the hydrogen-bonds of 2b-1.

<table>
<thead>
<tr>
<th>Donor --- H...Acceptor</th>
<th>D – H (Å)</th>
<th>H...A (Å)</th>
<th>D...A (Å)</th>
<th>D – H...A (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1) --H(1n) ..N(2)</td>
<td>0.84(3)</td>
<td>2.18(2)</td>
<td>2.76(18)</td>
<td>127(2)</td>
</tr>
<tr>
<td>N(1) --H(1n) ..O(2)</td>
<td>0.84(3)</td>
<td>2.39(2)</td>
<td>2.86(18)</td>
<td>116.3(18)</td>
</tr>
</tbody>
</table>

Fig. S29 ORTEP structure of 2b-1. Thermal ellipsoids are scaled to the 50% probability level.
Crystallographic data of 2a-2

A crystalline black prism of C_{25}H_{17}N_{3}O_{3}Cl_{4} having approximate dimensions of 0.40 × 0.45 × 0.55 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 56.2°. Data were collected in a series of φ and ω scans in 0.5° oscillations with 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 38352 reflections that were collected, 5806 were unique (R_{int} = 0.028); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 5.16 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS), with minimum and maximum transmission coefficients of 0.674 and 0.814, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All C-H hydrogen atoms were placed in calculated positions but were not refined. The N-H hydrogen atom was located in a difference map and refined isotropically. The final cycle of full-matrix least-squares refinement on F² was based on 5806 reflections and 321 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.057 and wR2 = 0.118).

The standard deviation of an observation of unit weight was 1.08. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.51 and -0.38 e/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in Fcalc; the values for Δρ and Δρ'' were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbell. All refinements were performed using the SHELXTL crystallographic software package from Bruker-AXS.

Table S2. Parameters for the hydrogen-bonds of 2a-2.

<table>
<thead>
<tr>
<th>Donor --- H...Acceptor</th>
<th>D – H (Å)</th>
<th>H...A (Å)</th>
<th>D...A (Å)</th>
<th>D – H...A (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1) --H(1n) ..N(2)</td>
<td>0.88(2)</td>
<td>2.08(2)</td>
<td>2.730(2)</td>
<td>130(2)</td>
</tr>
<tr>
<td>C(7) --H(7c) ..O(2)</td>
<td>0.95</td>
<td>2.49</td>
<td>2.889(3)</td>
<td>111</td>
</tr>
</tbody>
</table>

Fig. S30 ORTEP structure of 2a-2. Thermal ellipsoids are scaled to the 50% probability level.
Table S3. Crystallographic data of 2a-2 and 2b-1.

<table>
<thead>
<tr>
<th></th>
<th>2a-2</th>
<th>2b-1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{25}$H$</em>{17}$Cl$_4$N$_3$O$_3$</td>
<td>C$_{22}$H$_8$Cl$_2$F$_5$N$_3$O$_3$</td>
</tr>
<tr>
<td><strong>Mw</strong></td>
<td>549.22</td>
<td>528.21</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a / Å</strong></td>
<td>7.5524(4)</td>
<td>7.0689(13)</td>
</tr>
<tr>
<td><strong>b / Å</strong></td>
<td>12.9084(7)</td>
<td>9.6348(19)</td>
</tr>
<tr>
<td><strong>c / Å</strong></td>
<td>13.1120(7)</td>
<td>16.0743(3)</td>
</tr>
<tr>
<td><strong>α / deg</strong></td>
<td>102.326(2)</td>
<td>94.959(7)</td>
</tr>
<tr>
<td><strong>β / deg</strong></td>
<td>94.333(2)</td>
<td>95.467(7)</td>
</tr>
<tr>
<td><strong>γ / deg</strong></td>
<td>98.378(2)</td>
<td>106.429(7)</td>
</tr>
<tr>
<td><strong>V / Å$^3$</strong></td>
<td>1227.94(11)</td>
<td>1037.93(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>D$_c$ / g cm$^{-1}$</strong></td>
<td>1.485</td>
<td>1.690</td>
</tr>
<tr>
<td><strong>μ(MoKα) cm$^{-1}$</strong></td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>Number of observed data (I &gt; 0.00σ(I))</strong></td>
<td>5806</td>
<td>4938</td>
</tr>
<tr>
<td><strong>Reflection / Parameter Ratio</strong></td>
<td>18.09</td>
<td>15.38</td>
</tr>
<tr>
<td><strong>R1; wR2</strong></td>
<td>0.0574; 0.1179</td>
<td>0.0456; 0.1019</td>
</tr>
<tr>
<td><strong>GOF</strong></td>
<td>1.075</td>
<td>0.990</td>
</tr>
<tr>
<td><strong>Number of observed data (I &gt; 2σ(I))</strong></td>
<td>4685</td>
<td>4046</td>
</tr>
<tr>
<td><strong>(R1; wR2)</strong></td>
<td>0.0409; 0.1008</td>
<td>0.0347; 0.0926</td>
</tr>
</tbody>
</table>

* R1 = Σω|Fo| - |Fc|/Σω|Fo|,  
  b wR2 = √Σω(Fo$^2$ - Fc$^2$)/Σω(Fo$^2$),  
  c refined on F, I>2σ(I)

**Reference**

S4. Least Squares function minimized: Σω(Fo$^2$ - Fc$^2$)$^2$
S5. Standard deviation of an observation of unit weight: [Σω(Fo$^2$ - Fc$^2$)$^2$ / (No - Nv)]$^{1/2}$
Where:  
  N$_o$ = number of observations  
  N$_v$ = number of variables