Figure S1. DSC thermograms of xH-R melting temperatures (exo up) recorded at 5 °C/min from ambient temperature, or from equilibrated elevated temperature with >50 °C established baseline, over three heating and cooling cycles. All traces are intensity-normalized to the melt peak. All traces displayed are from second heating cycles, with the exception of 5H-NMe₂, 5H-CO₂Me, and 6H-CO₂Me, which display first heat traces due to significant decomposition following initial melt. 6H-NMe₂ Tm manually recorded by SRS Digimelt MPA 160 (in triplicate) only.
Table S1. Summarized melting temperatures of xH-R isomers.

<table>
<thead>
<tr>
<th>xH-R</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4H-NMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>204-205 (dec)</td>
</tr>
<tr>
<td>5H-NMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>283 (dec)</td>
</tr>
<tr>
<td>6H-NMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>212-213 (dec)</td>
</tr>
<tr>
<td>4H-OMe</td>
<td>223</td>
</tr>
<tr>
<td>5H-OMe</td>
<td>195</td>
</tr>
<tr>
<td>6H-OMe</td>
<td>189</td>
</tr>
<tr>
<td>4H-H</td>
<td>193</td>
</tr>
<tr>
<td>5H-H</td>
<td>163</td>
</tr>
<tr>
<td>6H-H</td>
<td>190</td>
</tr>
<tr>
<td>4H-CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>252 (dec)</td>
</tr>
<tr>
<td>5H-CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>226 (dec)</td>
</tr>
<tr>
<td>6H-CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>234 (dec)</td>
</tr>
</tbody>
</table>

Figure S2. (Left) Excitation spectra of xH-NMe<sub>2</sub> single crystals (λ<sub>em</sub> = 650 nm for 4H-NMe<sub>2</sub>, 560 nm for 5H-NMe<sub>2</sub>, 610 nm for 6H-NMe<sub>2</sub> (I), 640 nm for 6H-NMe<sub>2</sub> (II) 6H-NMe<sub>2</sub>, 560 nm for 5H-NMe<sub>2</sub>). (Right) Emission spectra of xH-NMe<sub>2</sub> single crystals (λ<sub>ex</sub> = 430 nm for 5H-NMe<sub>2</sub> and 6H-NMe<sub>2</sub> (I), 480 nm for 4H-NMe<sub>2</sub> and 6H-NMe<sub>2</sub> (II)).
Figure S3. (Left) Crystal structure of non-emissive red polymorph 6H-NMe2 (II), hydrogens omitted for clarity. (Right) Intermolecular ArF-ArH stacking between ArF ring and terephthalate, as well as ArF ring and terminal dimethylaniline.

Figure S4. (Left) Excitation spectra of xH-OMe single crystals ($\lambda_{em} =$540 nm for 4H-OMe, 520 nm for 5H-OMe and 6H-OMe polymorphs). (Right) Emission spectra of xH-OMe single crystals ($\lambda_{ex} = 380$ nm).
Figure S5. View of a partial structure for 6H-OMe (II) displayed as thermal ellipsoids, showing only modest variations in packing relative to 6H-OMe (I). Disorder modeled in ArF pendant of second PE molecule. Hydrogens omitted for clarity.

Figure S6. (Left) Excitation spectra of xH-H single crystals ($\lambda_{em} = 500, 470, and 500$ nm for 4H-H, 5H-H, and 6H-H, respectively). (Right) Emission spectra of xH-H single crystals ($\lambda_{ex} = 350, 310, 350$ nm for 4H-H, 5H-H, and 6H-H, respectively).
Figure S7. (Top) single point calculated energies of xH-R HOMO (left) and LUMO (right) using atomic coordinates taken from crystal structures at the B3LYP / 6-311+G(d,p) level of theory. (Bottom) Visualization of frontier orbitals HOMO (left) and LUMO (right) as a function of ArF fluorine regiochemistry for xH-OMe isomers using atomic coordinates from crystal structures.
Figure S8. Intensity normalized excitation spectra (top) and emission spectra (bottom) of xH-NMe2 MFC response.

Figure S9. Excitation spectra (top) and emission spectra (bottom) of xH-OMe MFC response.
Figure S10. Excitation spectra (top) and emission spectra (bottom) of xH-H MFC response.

Figure S11. Excitation spectra (top) and emission spectra (bottom) of xH-CO₂Me MFC response.
Figure S12. Additional plots summarizing optical properties of xH-R regioisomers, showing optical shifts of annealed film emission maxima relative to solution. a) Optical shifts plotted according to ArF substitution pattern and ArH substituent. b) Optical shifts plotted as a function of Hammett $\sigma_m$. Dashed line in plots ($\Delta\lambda = 25$ nm) indicates empirical boundary beyond which notable shifts typically indicate the presence of planarized / aggregated PE chromophores.
2. Crystallographic Tables

Table S1. Crystal data and structure refinement for 4H-NMe₂

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<thead>
<tr>
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<tr>
<td>Empirical formula</td>
<td>C42H28F8N2O4</td>
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<tr>
<td>Formula weight</td>
<td>776.66</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 4.4959(3) Å</td>
</tr>
<tr>
<td></td>
<td>b = 13.0881(9) Å</td>
</tr>
<tr>
<td></td>
<td>c = 15.9017(11) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>849.16(10) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.519 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.127 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>398</td>
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<tr>
<td>Crystal size</td>
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<tr>
<td>Theta range for data collection</td>
<td>2.799 to 32.453°.</td>
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<td>-6&lt;=h&lt;=6, -19&lt;=k&lt;=19, -23&lt;=l&lt;=23</td>
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<td>Reflections collected</td>
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<td>Independent reflections</td>
<td>6095 [R(int) = 0.0241]</td>
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<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
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<td>Extinction coefficient</td>
<td>n/a</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.554 and -0.242 e.Å⁻³</td>
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Table S2. Crystal data and structure refinement for 5H-NMe2

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</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.6598(7) Å, b = 9.1930(9) Å, c =12.4157(12) Å</td>
</tr>
<tr>
<td></td>
<td>α = 89.665(2)°, β = 81.654(2)°, γ = 84.678(2)°</td>
</tr>
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<td>Volume</td>
<td>861.26(14) Å³</td>
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<td>Z</td>
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<td>F(000)</td>
<td>398</td>
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<tr>
<td>Crystal size</td>
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<td>Theta range for data collection</td>
<td>2.699 to 27.058°.</td>
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<td>-9&lt;=h&lt;=9, -11&lt;=k&lt;=11, -15&lt;=l&lt;=15</td>
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<td>Independent reflections</td>
<td>3778 [R(int) = 0.0185]</td>
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<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.9 %</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
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<td>Extinction coefficient</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.367 and -0.169 e.Å⁻³</td>
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**Table S3. Crystal data and structure refinement for 6H-NMe₂ (I)**

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<td>Empirical formula</td>
<td>C42 H28 F8 N2 O4</td>
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<td>Formula weight</td>
<td>776.66</td>
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<td>Temperature</td>
<td>278(2) K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.5445(10) Å, b = 16.744(2) Å, c = 16.820(2) Å</td>
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<tr>
<td>Volume</td>
<td>1803.5(4) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
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<tr>
<td>Density (calculated)</td>
<td>1.430 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.120 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>796</td>
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<tr>
<td>Crystal size</td>
<td>0.2 x 0.1 x 0.1 mm³</td>
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<td>Theta range for data collection</td>
<td>1.398 to 22.062°.</td>
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<tr>
<td>Index ranges</td>
<td>-7&lt;=h&lt;=7, -17&lt;=k&lt;=17, -17&lt;=l&lt;=17</td>
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<td>Refractions collected</td>
<td>20104</td>
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<tr>
<td>Independent reflections</td>
<td>4423 [R(int) = 0.0253]</td>
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<tr>
<td>Completeness to theta = 22.062°</td>
<td>99.7%</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>4423 / 0 / 506</td>
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<td>Goodness-of-fit on F²</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0842, wR2 = 0.2265</td>
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<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.497 and -0.353 e.Å⁻³</td>
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Table S4. Crystal data and structure refinement for 6H-NMe₂ (II)

Identification code: SS161012_0ma_a
Empirical formula: C₈₄ H₅₆ F₁₆ N₄ O₈
Formula weight: 1553.32
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: P2₁/c
Unit cell dimensions:
\[ a = 13.1980(13) \text{ Å} \]
\[ b = 9.1099(9) \text{ Å} \]
\[ c = 15.1637(14) \text{ Å} \]
\[ \alpha = 90^\circ \]
\[ \beta = 107.904(2)^\circ \]
\[ \gamma = 90^\circ \]
Volume: 1734.9(3) Å³
Z: 2
Density (calculated): 2.974 Mg/m³
Absorption coefficient: 0.498 mm⁻¹
F(000): 1592
Crystal size: 2.000 x 1.000 x 1.000 mm³
Theta range for data collection: 1.621 to 36.439°.
Index ranges: -21 <= h <= 22, -13 <= k <= 13, -19 <= l <= 19
Reflections collected: 39560
Independent reflections: 5568 [R(int) = 0.0359]
Completeness to theta = 25.242°: 100.0 %
Absorption correction: Semi-empirical from equivalents
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 5568 / 0 / 255
Goodness-of-fit on F²: 1.053
Final R indices [I>2sigma(I)]: R1 = 0.0708, wR2 = 0.1949
R indices (all data): R1 = 0.0891, wR2 = 0.2180
Extinction coefficient: n/a
Largest diff. peak and hole: 0.853 and -0.578 e.Å⁻³
Table S5. Crystal data and structure refinement for 4H-OMe

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<th>Identification code</th>
<th>cu_P8_18007_0m_a</th>
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<td>Empirical formula</td>
<td>C40 H22 F8 O6</td>
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<td>Formula weight</td>
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<tr>
<td>Temperature</td>
<td>100(2) K</td>
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<tr>
<td>Wavelength</td>
<td>1.54184 Å</td>
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<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>C2/c</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td>a</td>
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<td>b</td>
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<td>c</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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<tr>
<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
<td>382</td>
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<tr>
<td>Crystal size</td>
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<tr>
<td>Independent reflections</td>
<td>6599 [R(int) = 0.0601]</td>
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<td>Completeness to theta = 67.684°</td>
<td>100.0 %</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole</td>
<td>0.269 and -0.218 e.Å⁻³</td>
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Table S6. Crystal data and structure refinement for 5H-OMe.

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<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
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<td>Unit cell dimensions</td>
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<td>b = 9.2589(5) Å, β= 100.4840(10)°.</td>
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<tr>
<td></td>
<td>c = 11.7819(7) Å, γ = 94.6500(10)°.</td>
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<tr>
<td>Volume</td>
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<td>Z</td>
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<tr>
<td>Density (calculated)</td>
<td>1.528 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
<td>382</td>
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<tr>
<td>Crystal size</td>
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<td>Theta range for data collection</td>
<td>2.947 to 30.264°</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.8 %</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
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<td>R indices (all data)</td>
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<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.528 and -0.178 e.Å⁻³</td>
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**Table S7. Crystal data and structure refinement for 6H-OMe (I)**

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<td>Empirical formula</td>
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<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 6.8850(7) Å, α = 90.762(2)°, b = 7.0203(7) Å, β = 90.770(2)°, c = 17.4630(18) Å, γ = 109.465(2)°</td>
</tr>
<tr>
<td>Volume</td>
<td>795.61(14) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.562 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.136 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>380</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.300 x 0.300 x 0.100 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.078 to 40.291°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12&lt;=h&lt;=12, -12&lt;=k&lt;=12, -31&lt;=l&lt;=31</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>28316</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9950 [R(int) = 0.0442]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>9950 / 0 / 245</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.096</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.1257, wR2 = 0.3429</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1577, wR2 = 0.3659</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>3.234 and -0.843 e.Å⁻³</td>
</tr>
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</table>
### Table S8. Crystal data and structure refinement for 4H-H

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>Identification code</td>
<td>SS170508_0m_a</td>
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<tr>
<td>Empirical formula</td>
<td>C38 H18 F8 O4</td>
</tr>
<tr>
<td>Formula weight</td>
<td>690.52</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 40.925(4) Å, b = 40.925(4) Å, c = 4.6169(6) Å, α = 90°, β = 90°, γ = 120°</td>
</tr>
<tr>
<td>Volume</td>
<td>6696.8(16) Å</td>
</tr>
<tr>
<td>Z</td>
<td>9</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.541 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.133 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>3150</td>
</tr>
<tr>
<td>Crystal size</td>
<td>1.000 x 0.100 x 0.100 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.986 to 24.427°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-47&lt;=h&lt;=47, -47&lt;=k&lt;=47, -5&lt;=l&lt;=5</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>27719</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2459 [R(int) = 0.0591]</td>
</tr>
<tr>
<td>Completeness to theta = 24.427°</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2459 / 0 / 226</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.123</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0467, wR2 = 0.1553</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0574, wR2 = 0.1640</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.128 and -0.250 e.Å⁻³</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>Identification code</td>
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</tr>
<tr>
<td>Empirical formula</td>
<td>C38 H18 F8 O4</td>
</tr>
<tr>
<td>Formula weight</td>
<td>690.52</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.7154(7) Å, α = 101.159(2°), b = 9.1759(8) Å, β = 96.904(2°), c = 11.2358(10) Å, γ = 95.288(2°)</td>
</tr>
<tr>
<td>Volume</td>
<td>769.29(12) Å³</td>
</tr>
<tr>
<td>Z</td>
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</tr>
<tr>
<td>Density (calculated)</td>
<td>1.491 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.129 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>350</td>
</tr>
<tr>
<td>Crystal size</td>
<td>1.000 x 1.000 x 0.500 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.041 to 40.918°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14&lt;=h&lt;=14, -16&lt;=k&lt;=16, -20&lt;=l&lt;=20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>28044</td>
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<tr>
<td>Independent reflections</td>
<td>9932 [R(int) = 0.0207]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>98.9 %</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>9932 / 0 / 226</td>
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<td>Goodness-of-fit on F²</td>
<td>1.071</td>
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<td>Final R indices [l&gt;2sigma(I)]</td>
<td>R1 = 0.0459, wR2 = 0.1287</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0572, wR2 = 0.1377</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.758 and -0.257 e.Å⁻³</td>
</tr>
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</table>
**Table S10.** Crystal data and structure refinement for 6H-H

![Structure Diagram]

<table>
<thead>
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<th>Value</th>
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<tbody>
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<tr>
<td><strong>Empirical formula</strong></td>
<td>C38 H18 F8 O4</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>690.52</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2₁/n</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>6.8439(8) Å</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>b</td>
<td>31.466(4) Å</td>
</tr>
<tr>
<td>β</td>
<td>109.878(2)°</td>
</tr>
<tr>
<td>c</td>
<td>7.0224(8) Å</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>1422.2(3) Å</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
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<td><strong>Density (calculated)</strong></td>
<td>1.613 Mg/m³</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>0.139 mm⁻¹</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>700</td>
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<tr>
<td><strong>Crystal size</strong></td>
<td>0.200 x 0.100 x 0.100 mm³</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>3.152 to 25.042°.</td>
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<tr>
<td><strong>Index ranges</strong></td>
<td>-8&lt;=h&lt;=8, -37&lt;=k&lt;=37, -8&lt;=l&lt;=8</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>19394</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>2516 [R(int) = 0.0335]</td>
</tr>
<tr>
<td><strong>Completeness to theta = 25.042°</strong></td>
<td>99.7 %</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>2516 / 0 / 226</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.085</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
<td>R1 = 0.0384, wR2 = 0.0860</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.0453, wR2 = 0.0896</td>
</tr>
<tr>
<td><strong>Extinction coefficient</strong></td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>0.537 and -0.180 e.Å⁻³</td>
</tr>
</tbody>
</table>
3. High Resolution Mass Spectrometry Data
HRMS of 5H-CO₂Me

SS-8
Qtof_70254b 41 (1.571) AM (Cen,3, 80.00, Ar,14000.0, 734.47, 0.70, LS 5); Sm (SG, 2x5.00), Cm (37.42) 1: TOF MS ES+

1.2263

807.1278

808.1316

809.1356

815.5046

885.1486

948.5102

m/z

200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950

263.9730 359.2512 413.2677 441.2988 507.3320 587.1933 617.1241 639.4070 677.1075 809.1356 815.5046 885.1486 948.5102
HRMS of 6H-CO$_2$Me
### HRMS reports

#### 4H-CO₂Me

**Elemental Composition Report**

**Single Mass Analysis**
- Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron ions**
- 163 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

<table>
<thead>
<tr>
<th>Elements Used:</th>
<th>C: 0-200</th>
<th>H: 0-200</th>
<th>O: 0-10</th>
<th>Na: 0-1</th>
<th>F: 8-8</th>
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</table>

<table>
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<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Formula</th>
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<tr>
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<td>C₄₂ H₂₃ O₈ F₆</td>
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#### 5H-CO₂Me

**Elemental Composition Report**

**Single Mass Analysis**
- Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron ions**
- 163 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

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<th>H: 0-200</th>
<th>O: 0-10</th>
<th>Na: 0-1</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>807.1278</td>
<td>807.1265</td>
<td>1.3</td>
<td>1.6</td>
<td>27.5</td>
<td>1.6</td>
<td>C₄₂ H₂₃ O₈ F₆</td>
</tr>
<tr>
<td>807.1241</td>
<td>3.7</td>
<td>4.6</td>
<td>24.5</td>
<td>1.7</td>
<td>C₄₀ H₂₄ O₈ F₆ Na</td>
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</tr>
</tbody>
</table>
**Elemental Composition Report**

**Single Mass Analysis**
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
163 formula(s) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-200  H: 0-200  O: 0-10  F: 0-1  Na: 0-1

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1</td>
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<td>807.1241</td>
<td></td>
<td>1.5</td>
<td>1.9</td>
<td>24.5</td>
<td>1.3</td>
<td>C40 H24 O8 F9 Na</td>
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</table>
4. NMR Data

$^1$H-NMR of 2-4
$^{19}$F-NMR of 2-4
$^{13}$C-NMR of 2-4
$^{1}H$-NMR of 2-5
$^{19}$F-NMR of 2-5
$^{13}$C-NMR of 2-5
$^1$H-NMR of 2-6
$^{19}$F-NMR of 2-6
$^{13}$C-NMR of 2-6
$^1$H-NMR of 4H-NMe$_2$
$^{19}$F-NMR of $4\text{H-NMe}_2$

![NMR Spectrum and Molecular Structure](image)
$^{13}$C-NMR of $\text{4H-NMe}_2$
$^1$H-NMR of 5H-NMe$_2$
$^{19}$F-NMR of 5H-NMe$_2$
$^{13}$C-NMR of 5H-NMe$_2$
$^1$H-NMR of 6H-NMe$_2$
$^{19}$F-NMR of 6H-NMe$_2$
$^{13}$C-NMR of 6H-NMe$_2$
$^{19}$F-NMR of $4\text{H-OMe}$

$^{13}$C-NMR of $4\text{H-OMe}$
$^1$H-NMR of 5H-OMe
$^{19}$F-NMR of 5H-OMe
$^{13}$C-NMR of 5H-OMe
$^1$H-NMR of 6H-OMe
$^{19}$F-NMR of 6H-OMe
$^{13}$C-NMR of 6H-OMe
$^1$H-NMR of $4H$-H
$^{19}$F-NMR of 4H-H
$^{13}$C-NMR of 4H-H
$^1$H-NMR of 5H-H
$^{19}$F-NMR of 5H-H
$^{13}$C-NMR of 5H-H
$^1$H-NMR of 6H-H
$^9$F-NMR of 6H-H

[Chemical structure image]

f1 (ppm)

$^{13}$C-NMR of 6H-H
$^1$H-NMR of 4H-CO$_2$Me
$^{19}$F-NMR of 4H-CO$_2$Me
$^{13}$C-NMR of $4H$-CO$_2$Me
$^1$H-NMR of 5H-CO$_2$Me
$^{19}$F-NMR of 5H-CO$_2$Me
$^{13}$C-NMR of $5\text{H-CO}_2\text{Me}$
$^1$H-NMR of $6\text{H-CO}_2\text{Me}$
$^{19}$F-NMR of 6H-CO$_2$Me
$^{13}$C-NMR of $6\text{H-CO}_2\text{Me}$