# Supporting Information

# Polymorphism and Psuedopolymorphism of an Aromatic Amide: Spontaneous Resolution and Crystal to Crystal Phase Transition

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**Contents**

## X-ray Crystallographic Analysis.

**Crystal data for 1 (Form I)**. $C_{22}H_{18}F_2N_2O_2$; $M_r$ = 380.38 g mol$^{-1}$, colorless prism measuring 0.40 × 0.40 × 0.40 mm, orthorhombic, *Aba*2, $a$ = 13.82(2), $b$ = 15.56(1), $c$ = 8.99(1) Å, $V$ = 1932(4) Å$^3$, $Z$ = 4, $D_c$ = 1.458 Mg m$^{-3}$, $T$ = 298 K, $\mu$ = 0.098 mm$^{-1}$, $2\theta_{max}$ = 54.44°, 4541 reflections, 1610 unique ($R_{int}$ = 0.0144), $R_1$ = 0.0319, $wR_2$ = 0.1060 (all data) $R_1$ = 0.0294, $wR_2$ = 0.1011 ($I > 2\sigma(I)$) for 129 parameters.

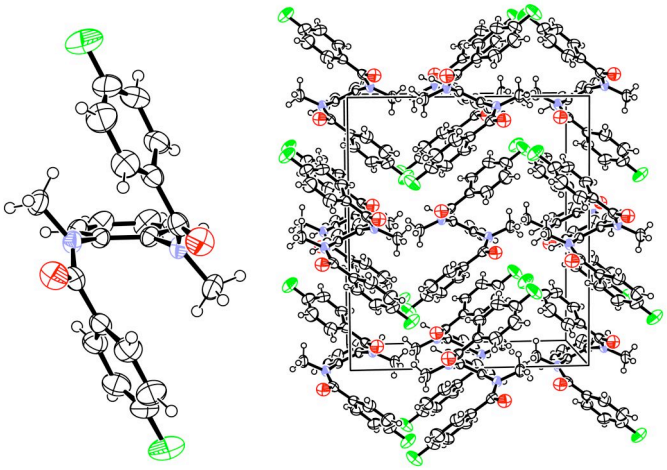

**Figure S1**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form I.

**Crystal data for 1 (Form II)**. $C_{22}H_{18}F_2N_2O_2$; $M_r$ = 380.38 g mol$^{-1}$, colorless prism, orthorhombic, *Aba*2, $a$ = 17.830(2), $b$ = 7.4296(7), $c$ = 13.522(1) Å, $V$ = 1791.2(3) Å$^3$, $Z$ = 4, $D_c$ = 1.411 Mg m$^{-3}$, $T$ = 90 K, $\mu$ = 0.105 mm$^{-1}$, $2\theta_{max}$ = 56.42°, 4705 reflections, 1963 unique ($R_{int}$ = 0.0185), $R_1$ = 0.0325, $wR_2$ = 0.0558 (all data) $R_1$ = 0.0308, $wR_2$ = 0.0555 ($I > 2\sigma(I)$) for 128 parameters.

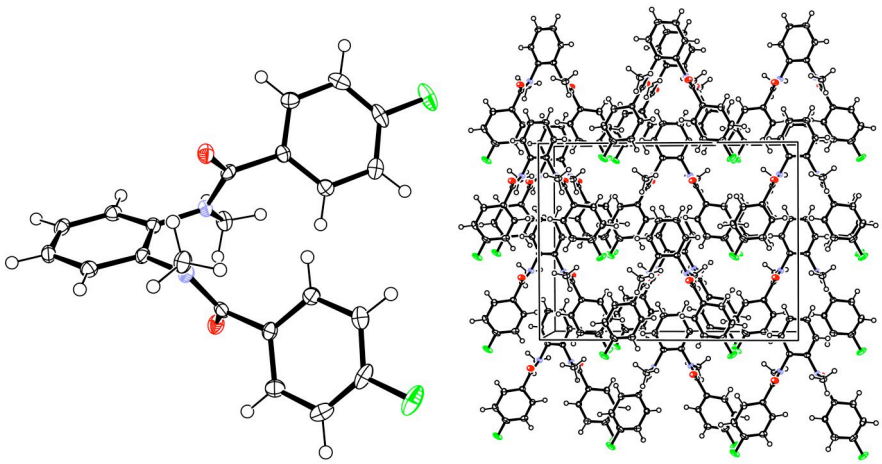

**Figure S2**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form II.

**Crystal data for 1 (Form III)**. $C_{22}H_{18}F_2N_2O_2 \cdot 2(CHCl_3)$; $M_r$ = 619.12 g mol$^{-1}$, colorless prism measuring 0.40 × 0.40 × 0.20 mm, triclinic, *P*-1, $a$ = 8.905(5), $b$ = 11.135(6), $c$ = 14.695(8) Å, $\alpha$ = 68.790(7), $\beta$ = 88.629(7), $\gamma$ = 87.128(7)°, $V$ = 1357(1) Å$^3$, $Z$ = 2, $D_c$ = 1.516 Mg m$^{-3}$, $T$ = 150 K, $\mu$ = 0.673 mm$^{-1}$, $2\theta_{max}$ = 56.06°, 7024 reflections, 5493 unique ($R_{int}$ = 0.0278), $R_1$ = 0.1110, $wR_2$ = 0.3052 (all data) $R_1$ = 0.0955, $wR_2$ = 0.2948 ($I > 2\sigma(I)$) for 327 parameters.

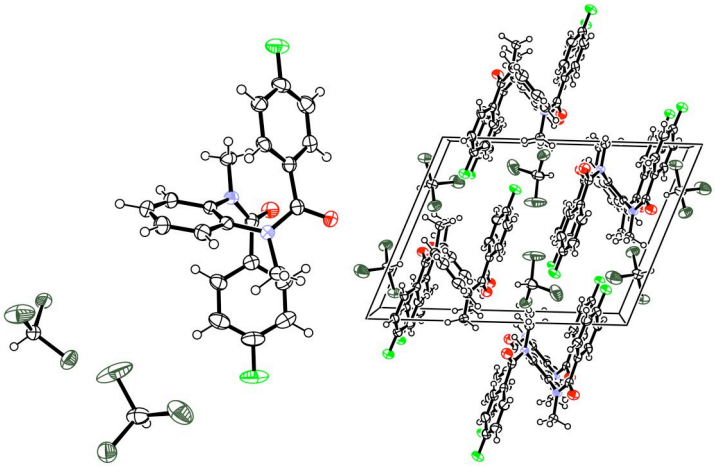

**Figure S3**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form III.

**Crystal data for 1 (Form IV)**. $C_{22}H_{18}F_2N_2O_2 \cdot 0.5(CH_2Cl_2)$; $M_r$ = 619.12 g mol$^{-1}$, colorless prism measuring 0.40 × 0.20 × 0.05 mm, orthorhombic, *Aba2*, $a$ = 28.459(3), $b$ = 8.985(1), $c$ = 15.498(2) Å, $V$ = 3963.1(8) Å$^3$, $Z$ = 8, $D_c$ = 1.417 Mg m$^{-3}$, $T$ = 90 K, $\mu$ = 0.233 mm$^{-1}$, $2\theta_{max}$ = 56.32°, 10612 reflections, 3279 unique ($R_{int}$ = 0.0503), $R_1$ = 0.0598, $wR_2$ = 0.0952 (all data) $R_1$ = 0.0421, $wR_2$ = 0.0836 ($I > 2\sigma(I)$) for 269 parameters.

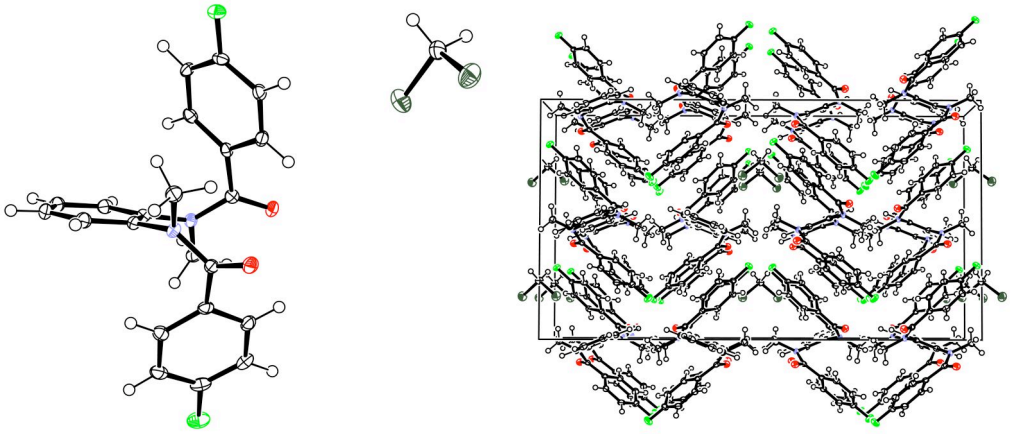

**Figure S4**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form IV.

**Crystal data for 1 (Form V)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_3H_6O$; $M_r$ = 438.46 g mol$^{-1}$, colorless prism measuring 0.20 × 0.10 × 0.10 mm, monoclinic, *Cc*, $a$ = 10.900(2), $b$ = 14.745(2), $c$ = 13.823(2) Å, $\beta$ = 97.187(2)°, $V$ = 2204.1(6) Å$^3$, $Z$ = 4, $D_c$ = 1.321 Mg m$^{-3}$, $T$ = 120 K, $\mu$ = 0.098 mm$^{-1}$, $2\theta_{max}$ = 54.54°, 5046 reflections, 3240 unique ($R_{int}$ = 0.0253), $R_1$ = 0.0454, $wR_2$ = 0.1087 (all data) $R_1$ = 0.0360, $wR_2$ = 0.1006 ($I > 2\sigma(I)$) for 293 parameters.

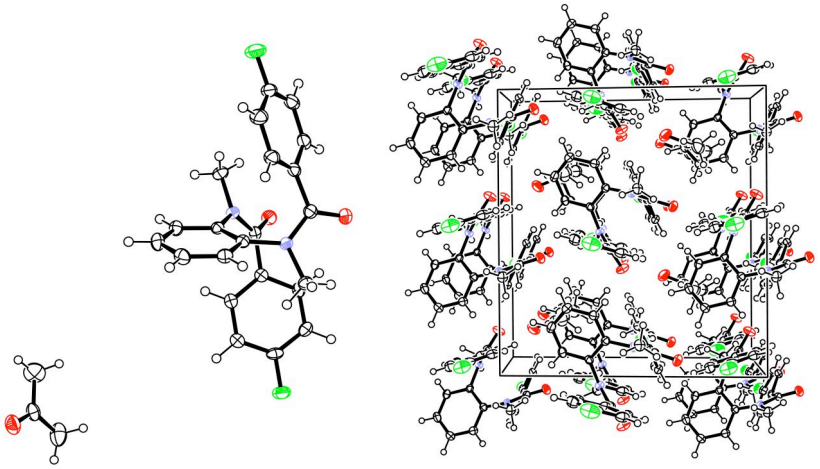

**Figure S5**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form V.

**Crystal data for 1 (Form VI)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_4H_8O$; $M_r$ = 452.49 g mol$^{-1}$, colorless prism measuring 0.40 × 0.30 × 0.20 mm, monoclinic, *Pn*, $a$ = 9.038(2), $b$ = 10.645(3), $c$ = 11.762(3) Å, $\beta$ = 91.078(3)°, $V$ = 1131.5(5) Å$^3$, $Z$ = 2, $D_c$ = 1.328 Mg m$^{-3}$, $T$ = 120 K, $\mu$ = 0.098 mm$^{-1}$, $2\theta_{max}$ = 51.68°, 5113 reflections, 3576 unique ($R_{int}$ = 0.0203), $R_1$ = 0.0558, $wR_2$ = 0.0653 (all data) $R_1$ = 0.0423, $wR_2$ = 0.0630 ($I > 2\sigma(I)$) for 300 parameters.

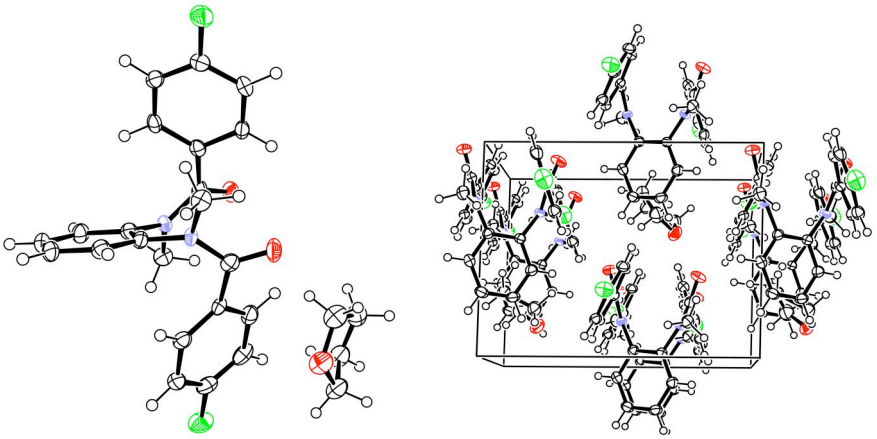

**Figure S6**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form VI.

**Crystal data for 1 (Form VII)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_4H_8O_2$; $M_r$ = 468.49 g mol$^{-1}$, colorless prism measuring 0.20 × 0.20 × 0.10 mm, monoclinic, *C*2/*c*, $a$ = 12.763(2), $b$ = 9.163(2), $c$ = 20.309(5) Å, $\beta$ = 103.286(3)°, $V$ = 2311.5(8) Å$^3$, $Z$ = 4, $D_c$ = 1.346 Mg m$^{-3}$, $T$ = 90 K, $\mu$ = 0.102 mm$^{-1}$, $2\theta_{max}$ = 54.64°, 4522 reflections, 2278 unique ($R_{int}$ = 0.0880), $R_1$ = 0.0772, $wR_2$ = 0.1694 (all data) $R_1$ = 0.0450, $wR_2$ = 0.1223 ($I > 2\sigma(I)$) for 156 parameters.

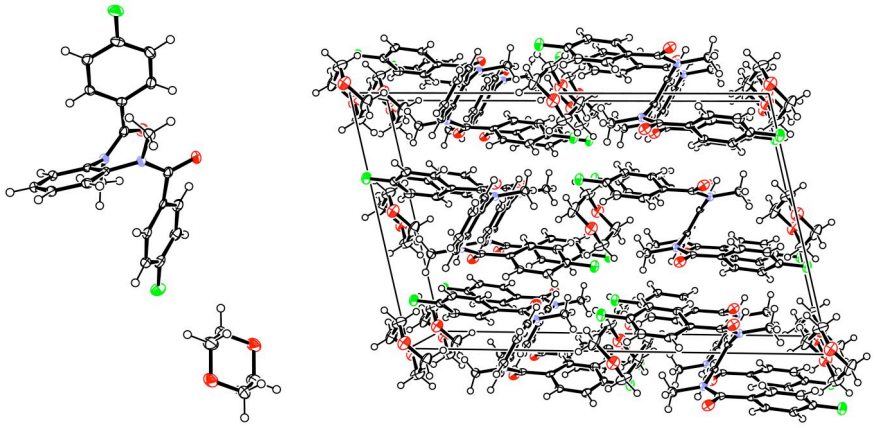

**Figure S7**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form VII.

**Crystal data for 1 (Form VIII)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_6H_6$; $M_r$ = 458.49 g mol$^{-1}$, colorless prism measuring 0.20 × 0.10 × 0.10 mm, monoclinic, *C*2/*c*, $a$ = 12.804(1), $b$ = 8.9673(8), $c$ = 21.308(2) Å, $\beta$ = 104.445(1)°, $V$ = 2369.2(4) Å$^3$, $Z$ = 4, $D_c$ = 1.285 Mg m$^{-3}$, $T$ = 120 K, $\mu$ = 0.092 mm$^{-1}$, $2\theta_{max}$ = 52.50°, 5618 reflections, 2339 unique ($R_{int}$ = 0.0232), $R_1$ = 0.0567, $wR_2$ = 0.0923 (all data) $R_1$ = 0.0385, $wR_2$ = 0.0845 ($I > 2\sigma(I)$) for 155 parameters.

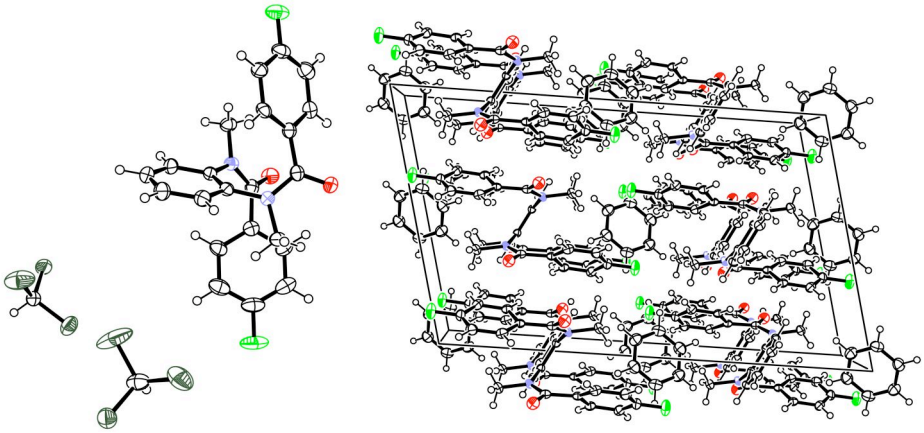

**Figure S8**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form VIII.

**Crystal data for 1 (Form IX)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_3H_6O_3$; $M_r$ = 470.46 g mol$^{-1}$, colorless prism measuring 0.20 × 0.20 × 0.20 mm, monoclinic, *C*2/*c*, $a$ = 15.585(1), $b$ = 9.0737(7), $c$ = 16.639(1) Å, $\beta$ = 104.404(1)°, $V$ = 2279.0(3) Å$^3$, $Z$ = 4, $D_c$ = 1.371 Mg m$^{-3}$, $T$ = 120 K, $\mu$ = 0.107 mm$^{-1}$, $2\theta_{max}$ = 53.90°, 5427 reflections, 2299 unique ($R_{int}$ = 0.0179), $R_1$ = 0.0478, $wR_2$ = 0.1061 (all data) $R_1$ = 0.0394, $wR_2$ = 0.0997 ($I > 2\sigma(I)$) for 183 parameters.

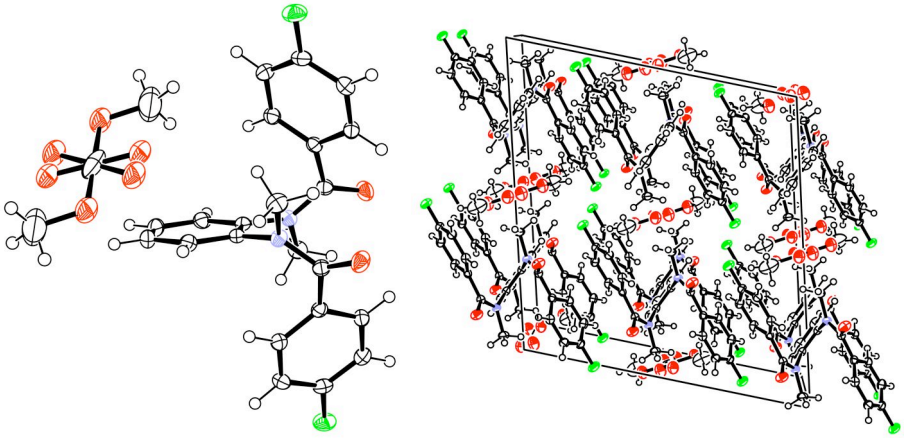

**Figure S9**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form IX.

**Crystal data for 1 (Form X)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_4H_8O_2$; $M_r$ = 468.50 g mol$^{-1}$, colorless prism measuring 0.40 × 0.40 × 0.10 mm, trigonal, $P3_1$, $a = b$ = 9.0756(5), $c$ = 24.324(2) Å, $V$ = 1735.1(2) Å$^3$, $Z$ = 3, $D_c$ = 1.345 Mg m$^{-3}$, $T$ = 298 K, $\mu$ = 0.851 mm$^{-1}$, $2\theta_{max}$ = 135.60°, 4995 reflections, 4104 unique ($R_{int}$ = 0.039), $R_1$ = 0.0545, $wR_2$ = 0.1496, $R_1$ = 0.0534, $wR_2$ = 0.1479 ($I > 2\sigma(I)$) for 309 parameters. Flack parameter = 0.1 (2).

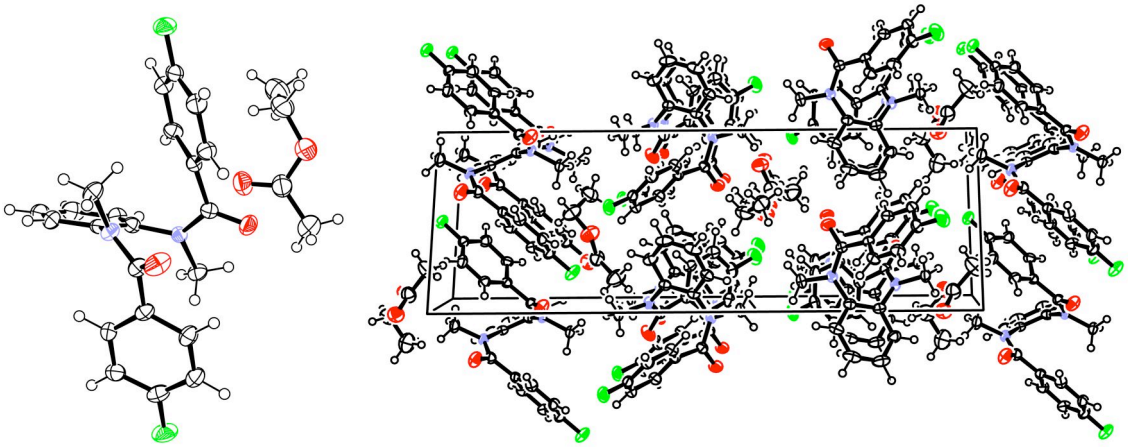

**Figure S10**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form X.

**Crystal data for 1 (Form XI)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_4H_8O_2$; $M_r$ = 468.49 g mol$^{-1}$, colorless prism measuring 0.20 × 0.10 × 0.10 mm, trigonal, $P3_2$, $a = b$ = 9.0311(4), $c$ = 24.502(3) Å, $V$ = 1730.7(2) Å$^3$, $Z$ = 3, $D_c$ = 1.349 Mg m$^{-3}$, $T$ = 150 K, $\mu$ = 0.851 mm$^{-1}$, $2\theta_{max}$ = 53.92°, 8575 reflections, 4475 unique ($R_{int}$ = 0.0261), $R_1$ = 0.0593, $wR_2$ = 0.1152 (all data) $R_1$ = 0.0460, $wR_2$ = 0.1058 ($I > 2\sigma(I)$) for 311 parameters. Flack parameter = 0.2(8) (indeterminate).

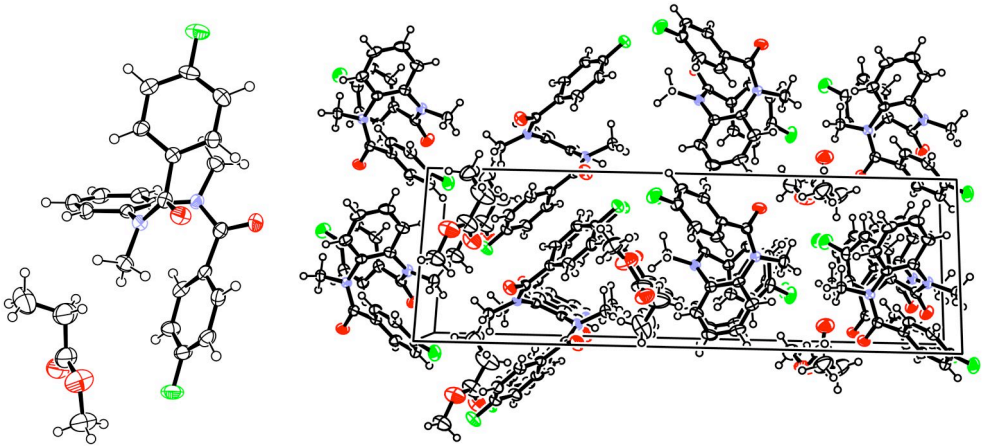

**Figure 11**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form XI.

**Crystal data for 1 (Form XII)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_4H_80_2$; $M_r$ = 466.47 g mol$^{-1}$, colorless prism measuring 0.60 × 0.40 × 0.40 mm, trigonal, $P3_2$, $a = b$ = 8.9987(3), $c$ = 24.529(2) Å, $V$ = 1720.2(2) Å$^3$, $Z$ = 3, $D_c$ = 1.351 Mg m$^{-3}$, $T$ = 150 K, $\mu$ = 0.102 mm$^{-1}$, $2\theta_{max}$ = 54.28°, 8482 reflections, 3941 unique ($R_{int}$ = 0.0175), $R_1$ = 0.0447, $wR_2$ = 0.1165 (all data) $R_1$ = 0.0427, $wR_2$ = 0.1153 ($I > 2\sigma(I)$) for 310 parameters. Flack parameter = -0.3(7) (indeterminate).

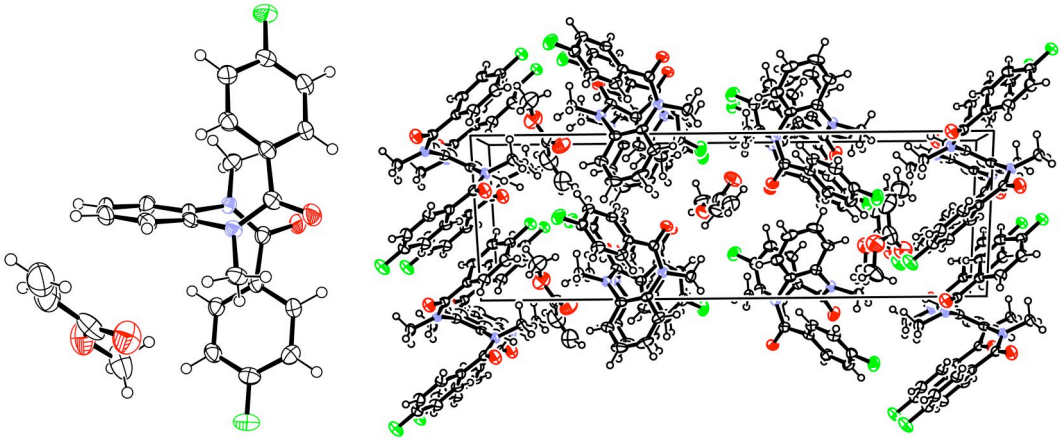

**Figure S12**. ORTEP diagram of asymmetric unit (left) and packing structure (right) in a crystal of Form XII.

**Crystal data for 1 (Form XIII)**. $C_{22}H_{18}F_2N_2O_2 \cdot C_7H_8$; $M_r$ = 472.51 g mol$^{-1}$, colorless prism measuring 0.10 × 0.10 × 0.02 mm, monoclinic, *C*2/*c*, $a$ = 22.531(5), $b$ = 13.650(3), $c$ = 23.223(5) Å, $\beta$ = 91.193(4)°, $V$ = 7141(3) Å$^3$, $Z$ = 12, $D_c$ = 1.318 Mg m$^{-3}$, $T$ = 90 K, $\mu$ = 0.093 mm$^{-1}$, $2\theta_{max}$ = 55.14°, 21126 reflections, 8104 unique ($R_{int}$ = 0.0725), $R_1$ = 0.2233, $wR_2$ = 0.3805 (all data) $R_1$ = 0.0882, $wR_2$ = 0.3008 ($I > 2\sigma(I)$) for 518 parameters. 1.5 molecules of **1** and 1.5 molecules of toluene are included in an asymmetric unit of the crystal. The positions of hydrogen atoms included in the toluene molecules were not calculated.

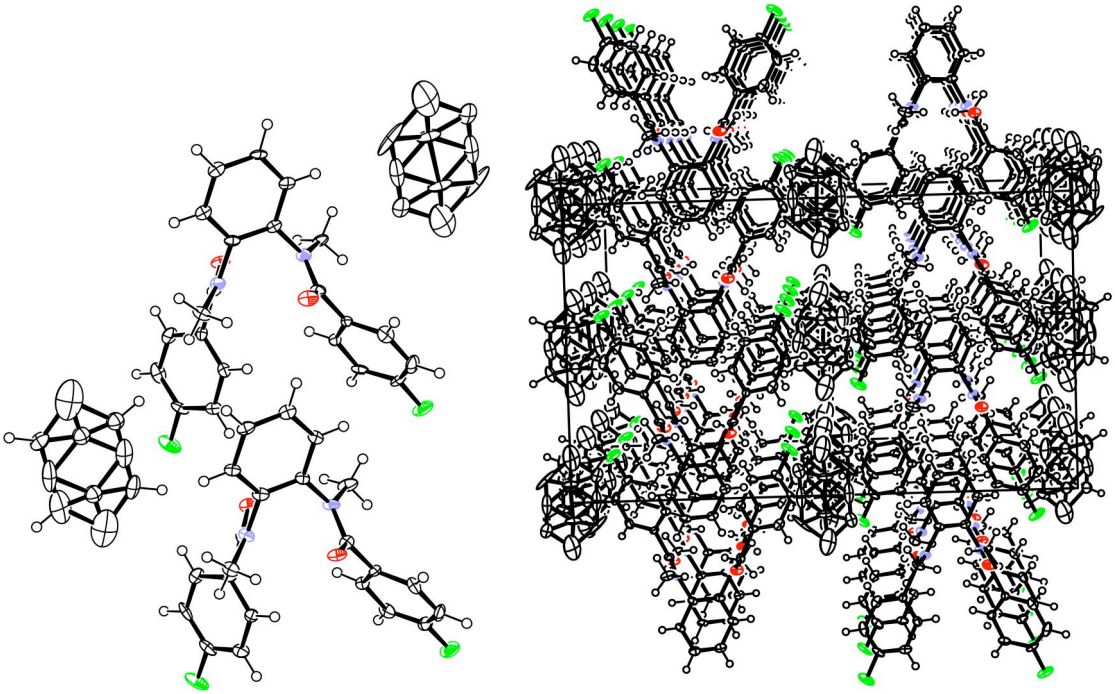

**Figure S13**. ORTEP diagram of included molecules after treatment of symmetry-expansion (left) and packing structure (right) in a crystal of Form XIII. An asymmetric unit includes 1.5 molecules of **1** and 1.5 molecules of toluene.

**Intermolecular C–H···F interactions.**

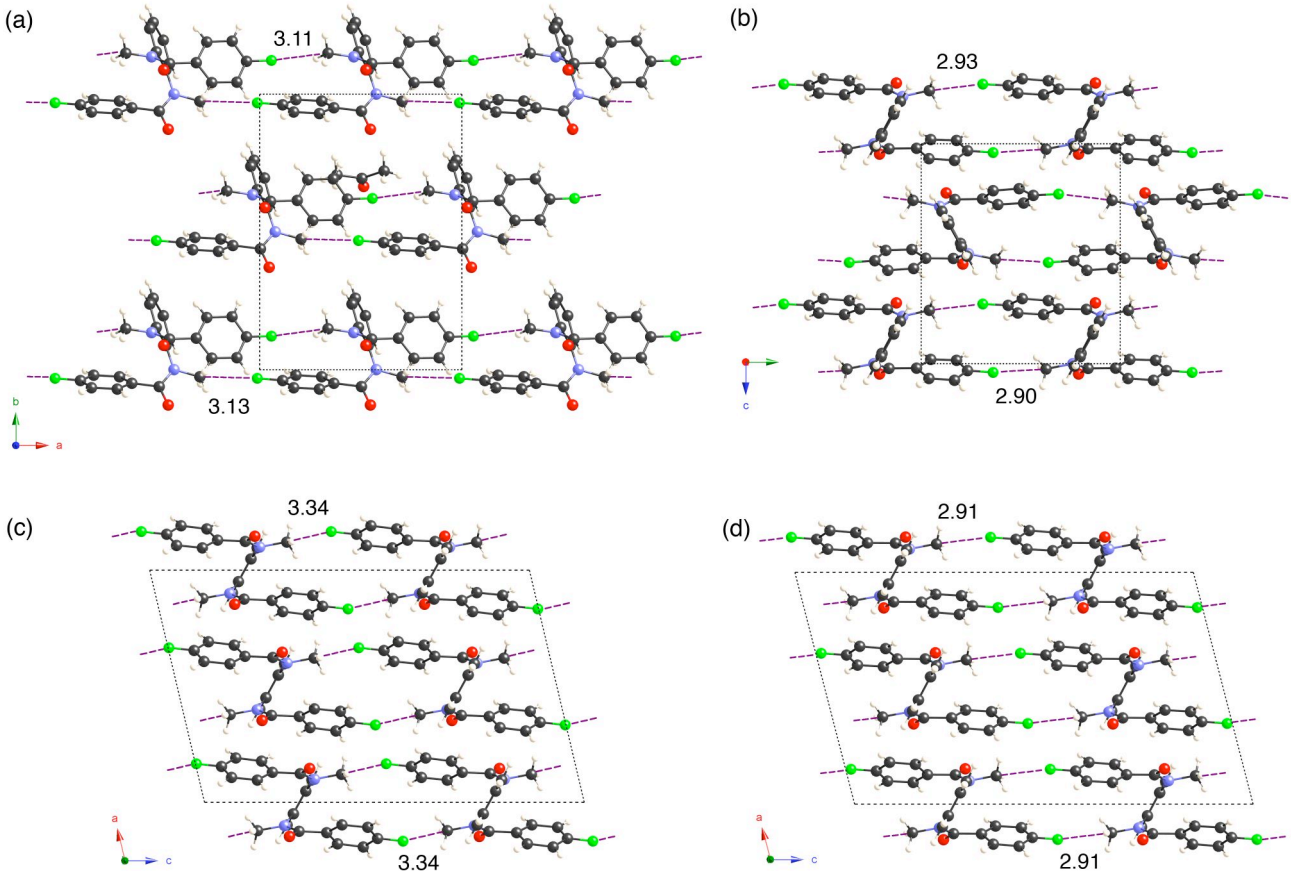


**Figure S14.** Intermolecular C–H···F interactions in crystals of Form V (a) , VI (b) VII (c) and IIX (d). C–H···F interactions are indicated with purple dot lines. Distances between F and C (methyl) are indicated in Å.

**DSC analysis for Form I–VII, X and XIII.**

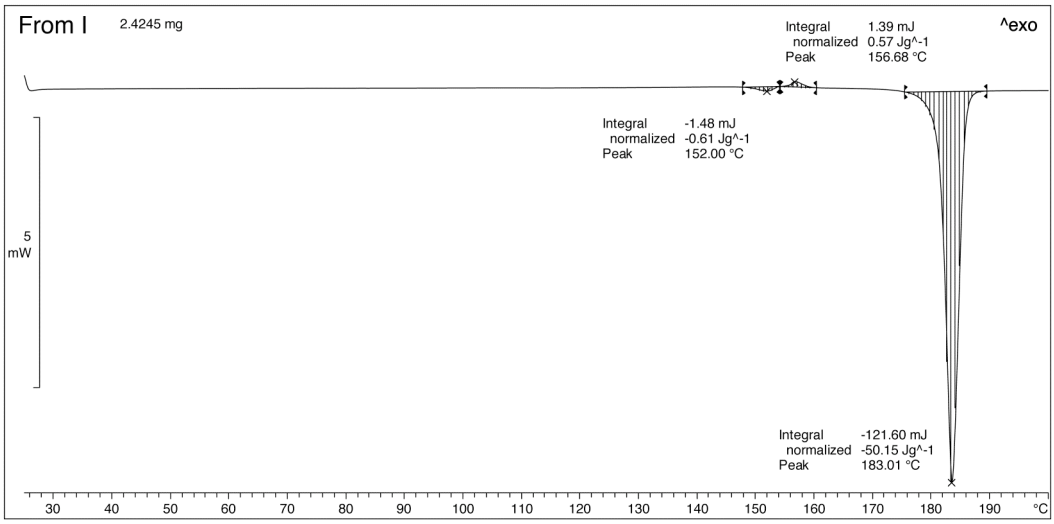


**Figure S15**. DSC chart of Form I.

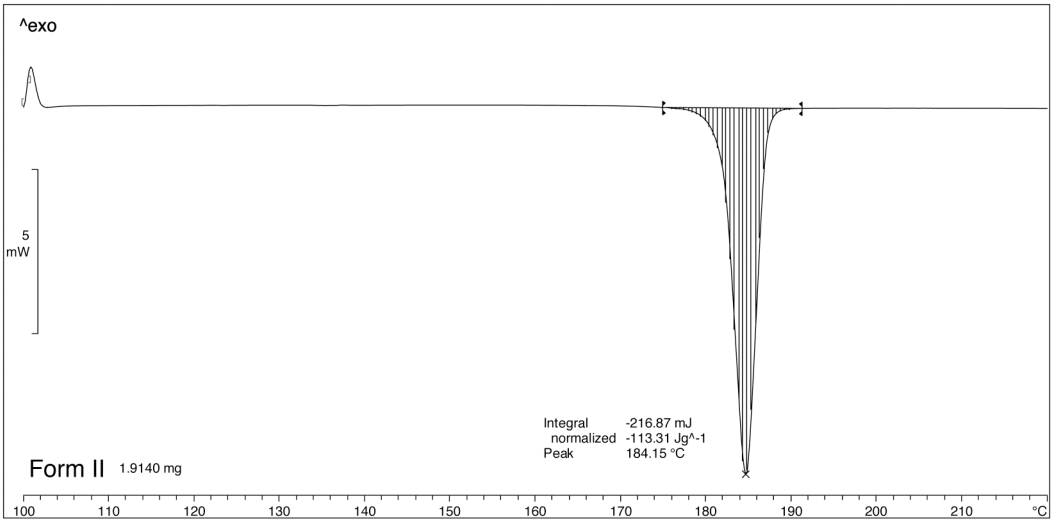


**Figure S16**. DSC chart of Form II.

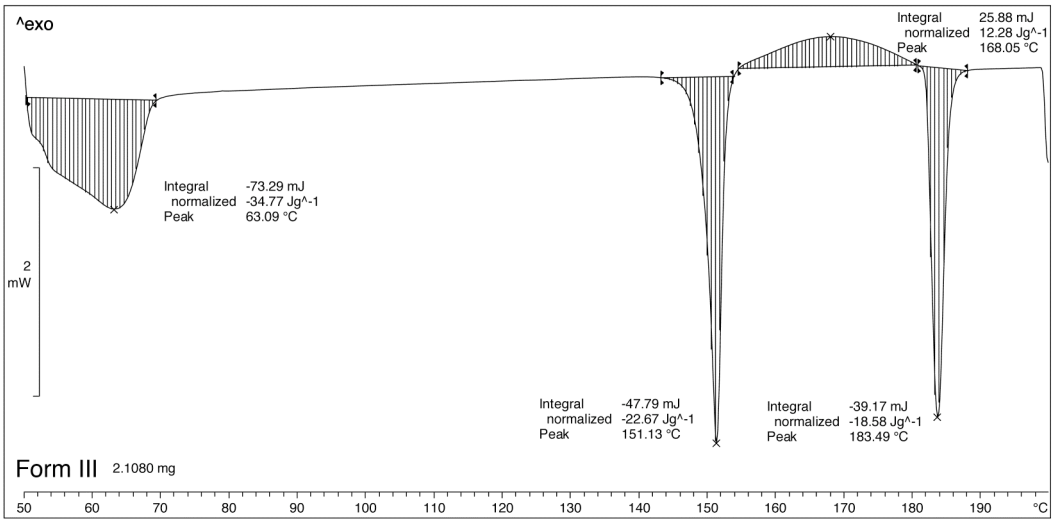


**Figure S17**. DSC chart of Form III.

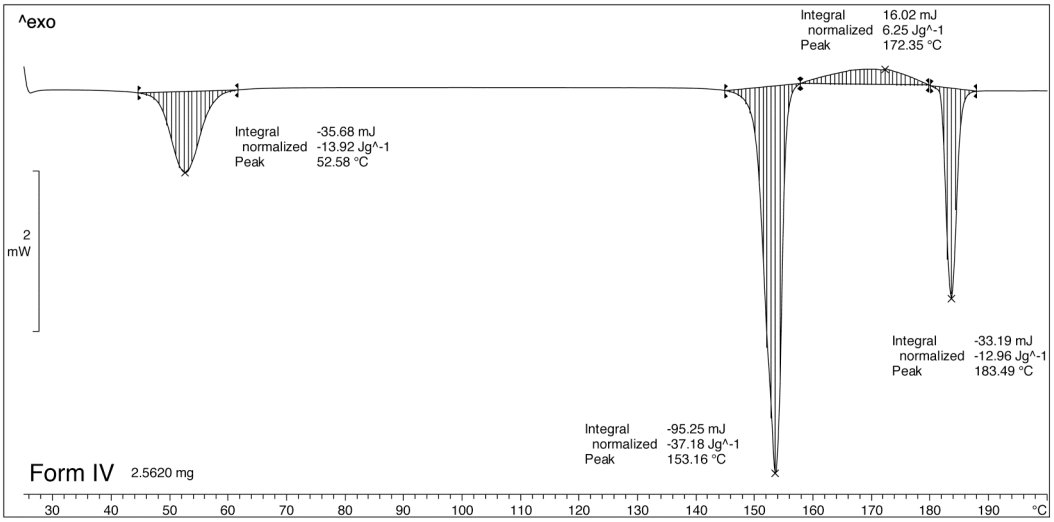


**Figure S18**. DSC chart of Form IV.

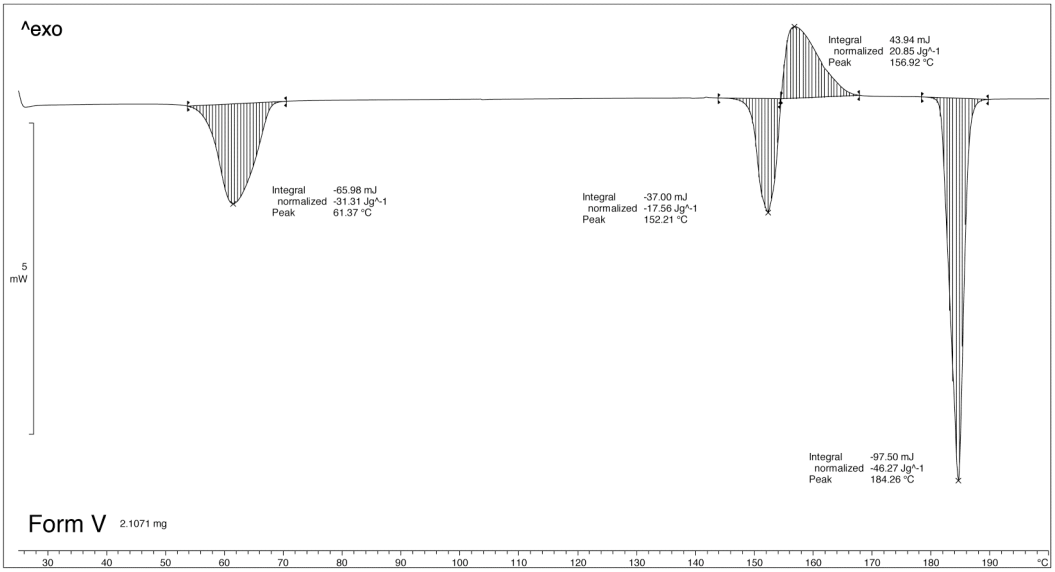


**Figure S19**. DSC chart of Form V.

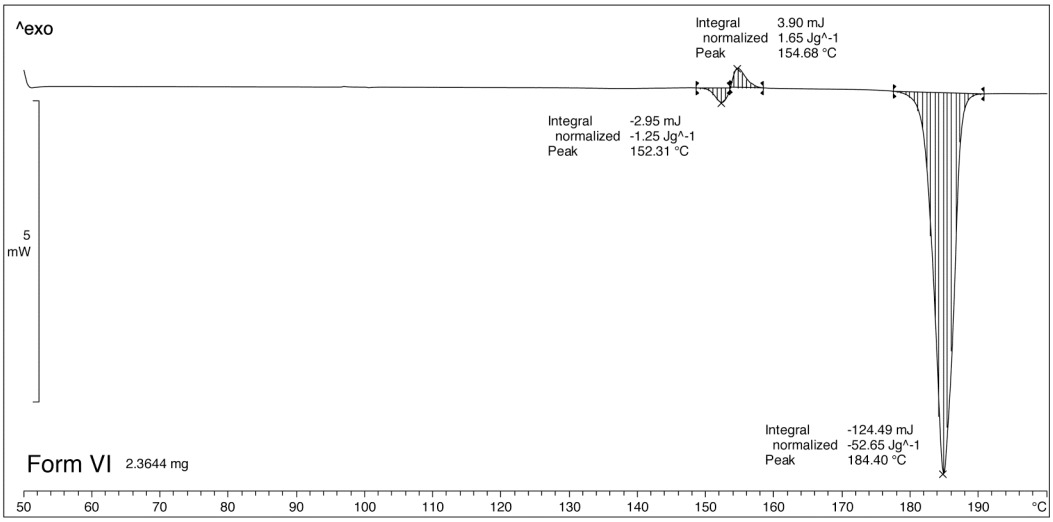


**Figure S20**. DSC chart of Form VI.

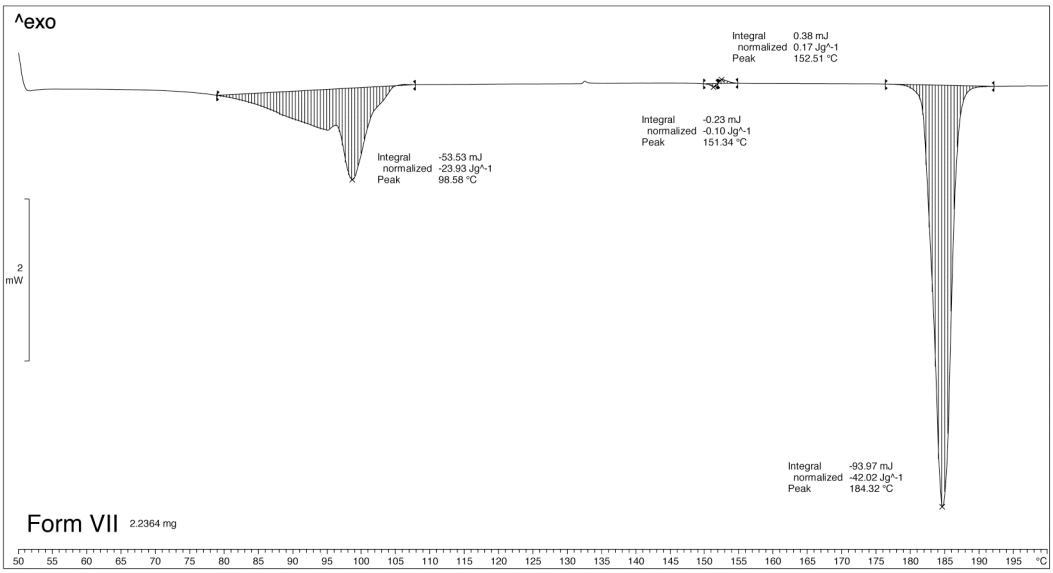


**Figure S21**. DSC chart of Form VII.

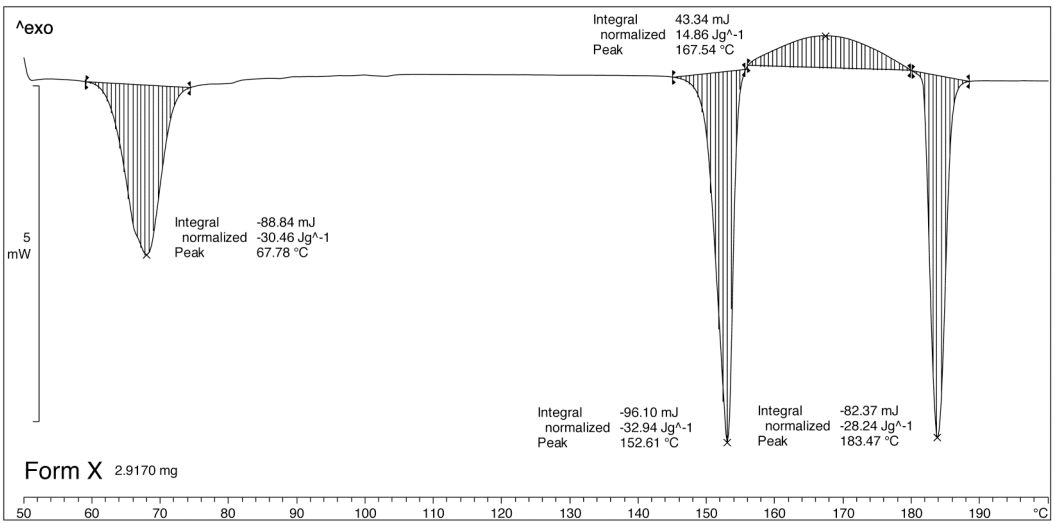


**Figure S22**. DSC chart of Form X.

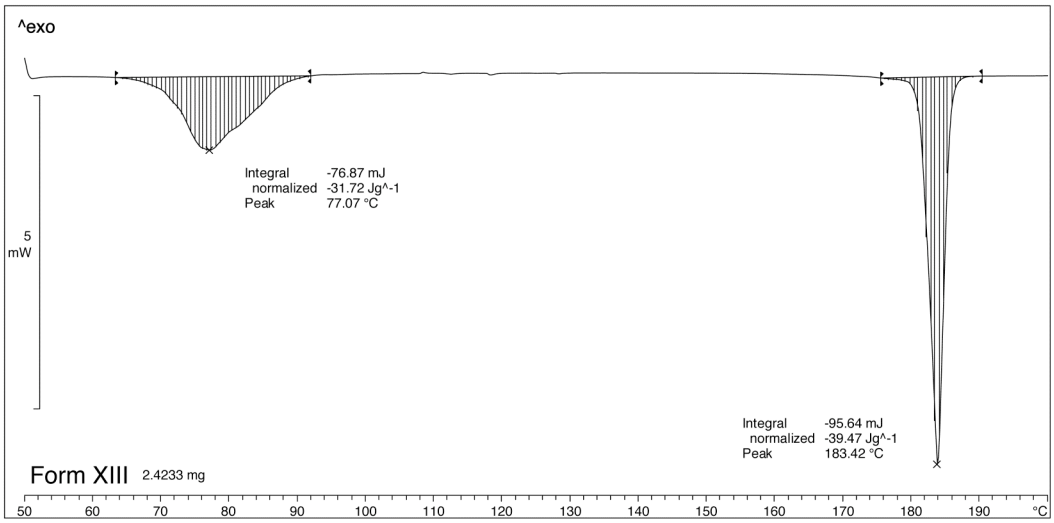


**Figure S23**. DSC chart of Form XIII.