Electronic Supporting Information for Publication

Intermolecular benzoyl group transfer reactivity in crystals of racemic 2,6-di-*O*-benzoyl-*myo*-inositol 1,3,5-orthobenzoate: Controlling reactivity by solvate (pseudopolymorph) formation

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Table of Contents

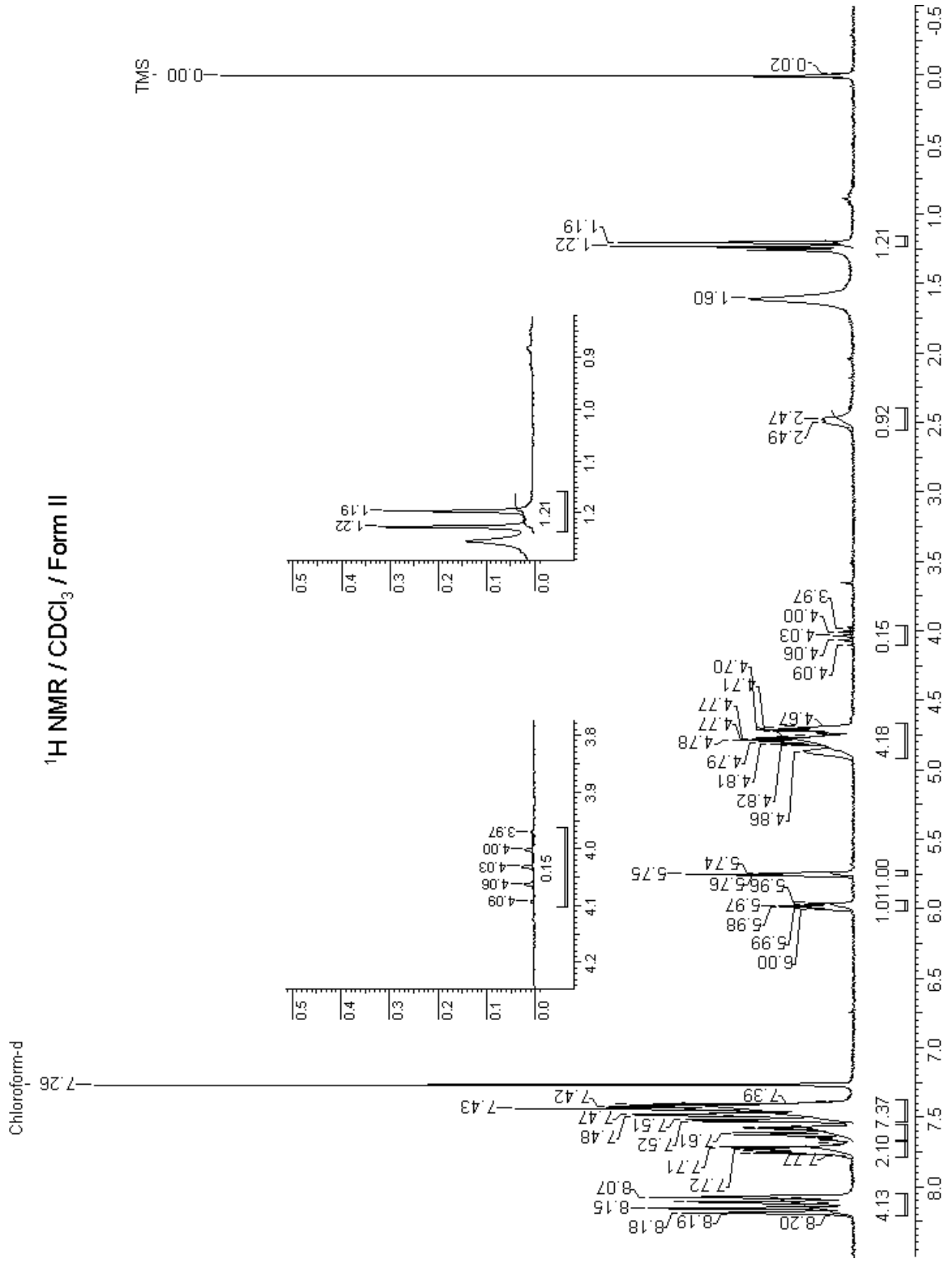


Fig. S1 Proton NMR spectrum of Form II crystals of **rac-3**. Inset shows the solvent (2-propanol) peaks.

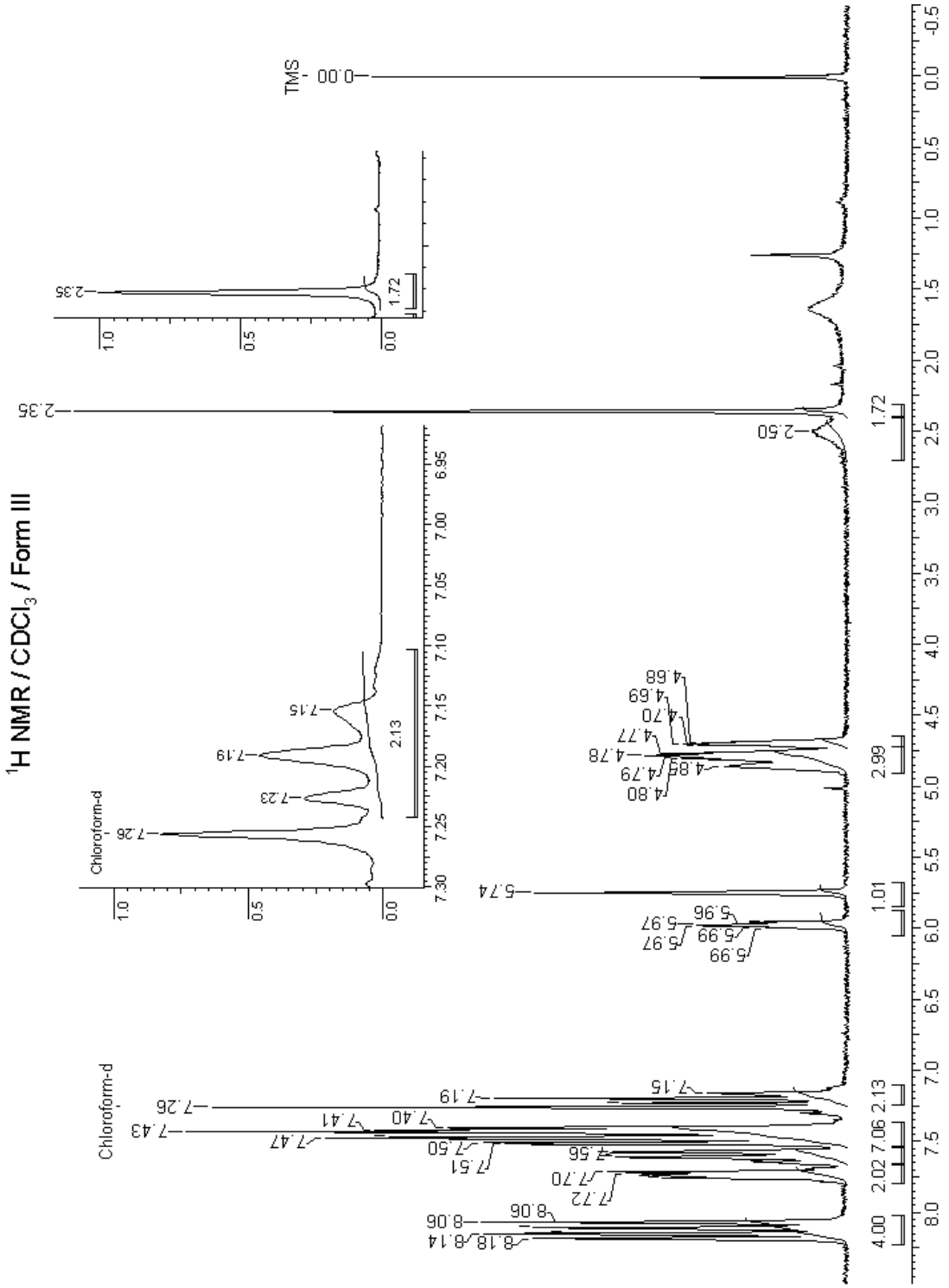


Fig. S2 Proton NMR spectrum of Form III crystals of **rac-3**. Inset shows the solvent (toluene) peaks.

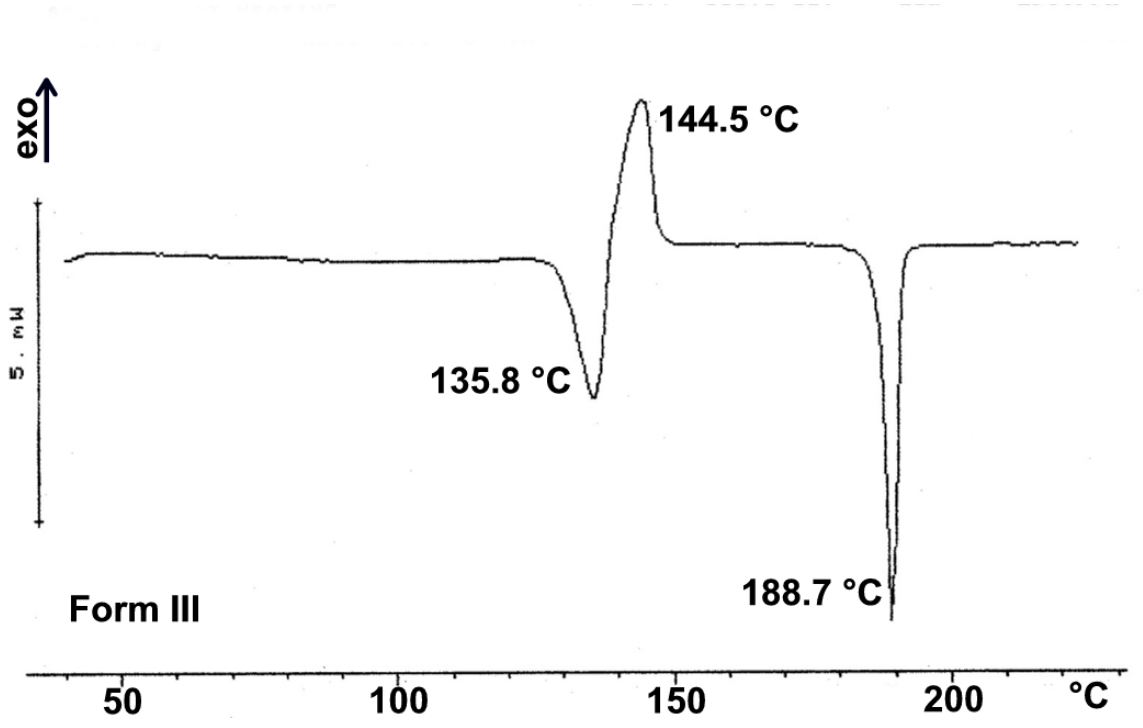


Fig. S3 DSC curve for Form III crystals of **rac-3**.

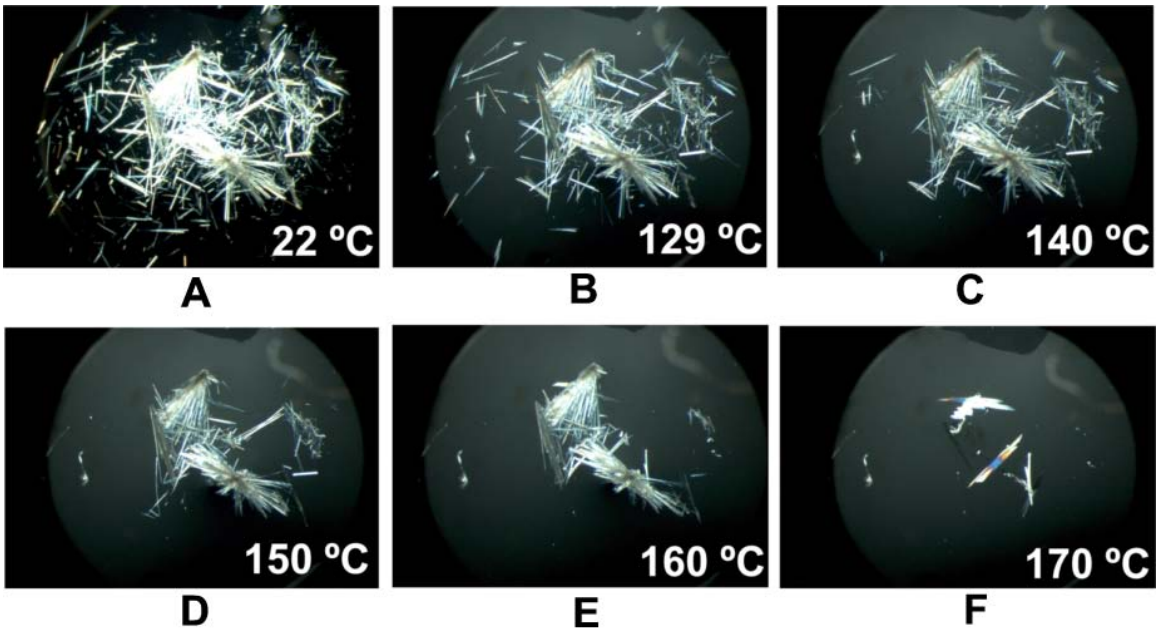


Fig. S4 Hot stage microscopy images for Form II crystals of **rac-3**.

Table 1 Crystal data table for Form II crystals of **rac-3**.

	rac-3 - Form II
Chemical formula	$C_{27}H_{22}O_8 \cdot [0.25(C_3O); 0.125 (C_3O) \cdot 0.25 (O); 0.125 (O)]$
M_r	489.22
Crystal size	0.10×0.01×0.01
Crystal system	Triclinic
Space group	*P*-1
a (Å)	6.1780(12)
b (Å)	15.941(3)
c (Å)	28.069(6)
α (°)	84.21(3)
β (°)	87.52(3)
γ (°)	85.76(3)
V (Å^3)	2740.9(9)
Z, D_{calc} (g cm^{-3})	4, 1.186
μ (mm^{-1}), *F(000)*	0.088, 1025
T_{min} , T_{max}	0.9913, 0.9991
h, *k*, *l* (min, max)	(-6,6), (-18,18), (-32,33)
Reflns collected	10041
Unique reflns	6869
Observed reflns	2306
No. of parameters	673
GoF	0.922
$R_1[I > 2\sigma(I)]$	0.2157
$wR_2[I > 2\sigma(I)]$	0.4424
R_1_all data	0.2992
wR_2_all data	0.5000
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.47, -0.42
CCDC dep. No.	787939

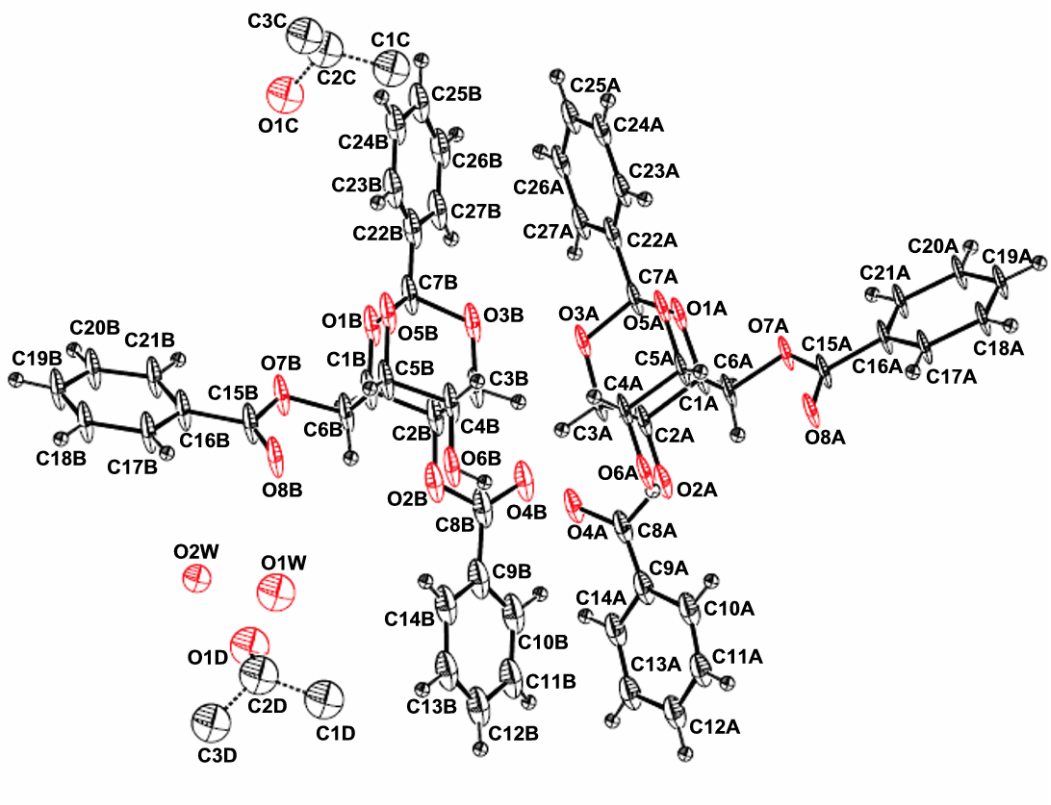


Fig. S5 Representative ORTEP for molecules in Form II crystals of **rac-3**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii.

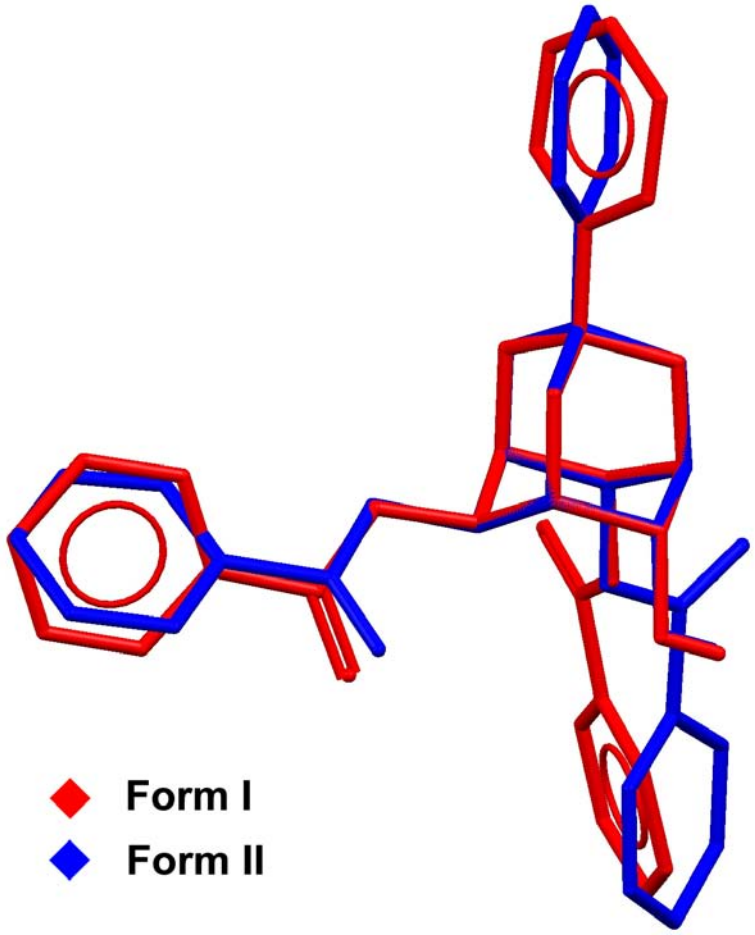
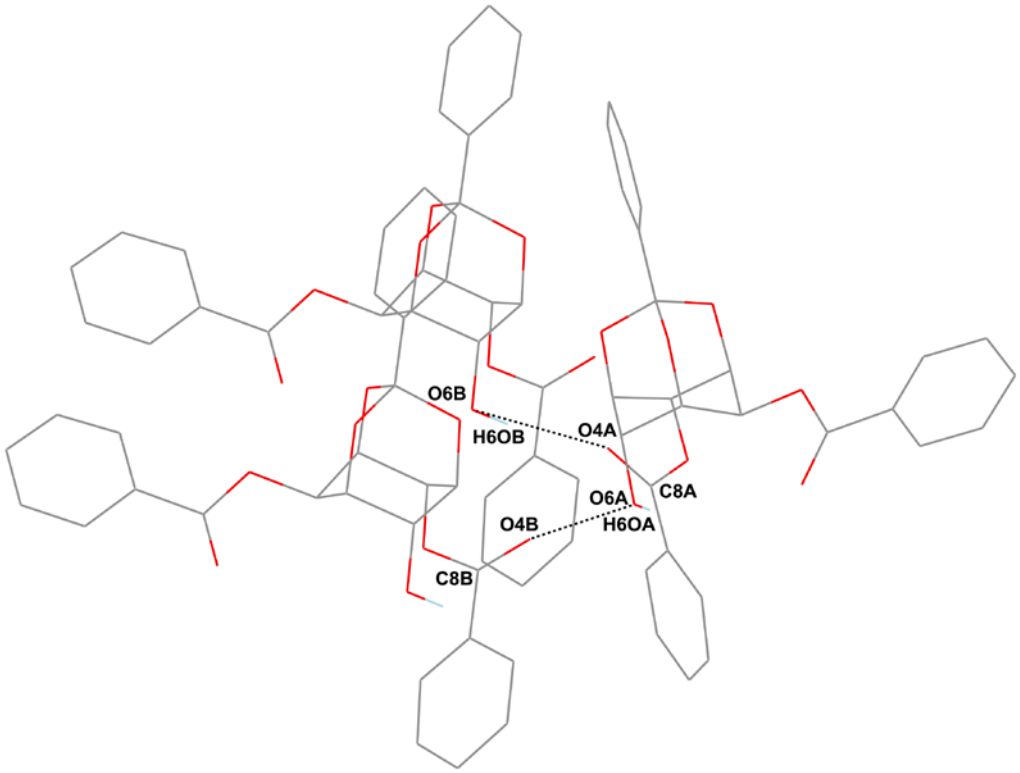


Fig. S6 Molecular overlap of Form I and Form II crystals showing the conformational differences.

Table S2 Hydrogen bonding interactions in Form II crystals forming chain along the *a*-axis

D-H···A	D-H /Å	H···A /Å	D···A /Å	D-H···A /°
O6B-H6OB···H4A^{i}	0.82	2.12	2.934(12)	170
C4A-H4A···O3B^{ii}	0.98	2.51	3.417(14)	153
C4B-H4B···O3A^{i}	0.98	2.54	3.422(16)	149
C2A-H2A···O6A^{iii}	0.98	2.33	3.203(15)	148
C2B-H2B···O6B^{iii}	0.98	2.37	3.233(16)	146
C5B-H5B···O1B^{ii}	0.98	2.57	3.450(16)	150

Symmetry codes: (i) *x*, *y*, *z*; (ii) 1+*x*, *y*, *z*; (iii) -1+*x*, *y*, *z*.



O=C…O-H	d (C…O) /Å	∠ (O=C…O) /°
O4B=C8B…O6A	3.891	34.93
O4A=C8A…O6B	3.947	30.24

Fig. S7 Closely interacting molecules in the chain along *a*-axis with the El-Nu parameters which are not conducive for acyl transfer reaction in the solid-state.

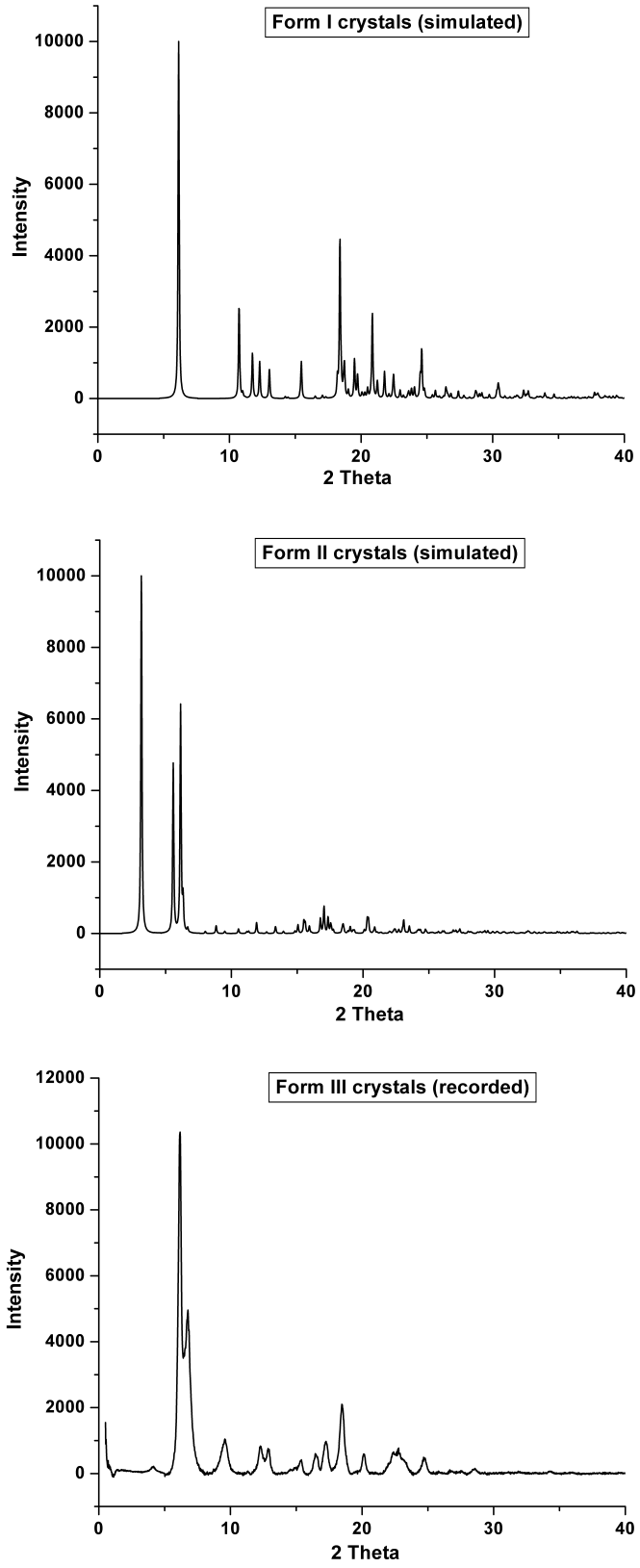


Fig. S8 Simulated (Form I, Form II) and recorded (Form III) PXRD patterns of crystals of **rac-3**.