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Portrayal of the Color Polymorphism in the 5-Acetyl-derivative of ROY

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Supporting Information

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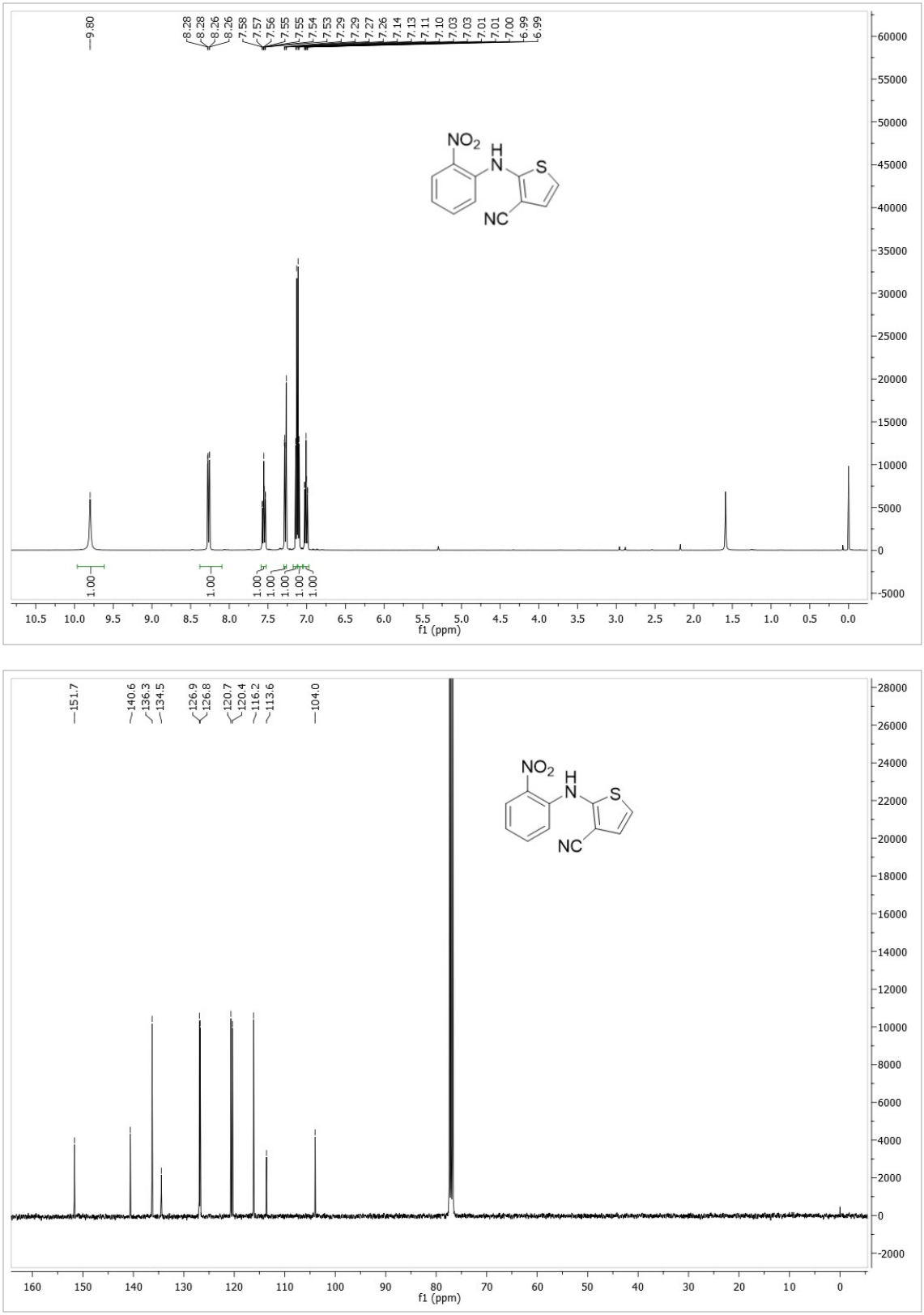


Figure S1. ^{1}H and ^{13}C NMR spectra of 2-((2-nitrophenyl)amino)thiophene-3-carbonitrile in $CDCl_3$.

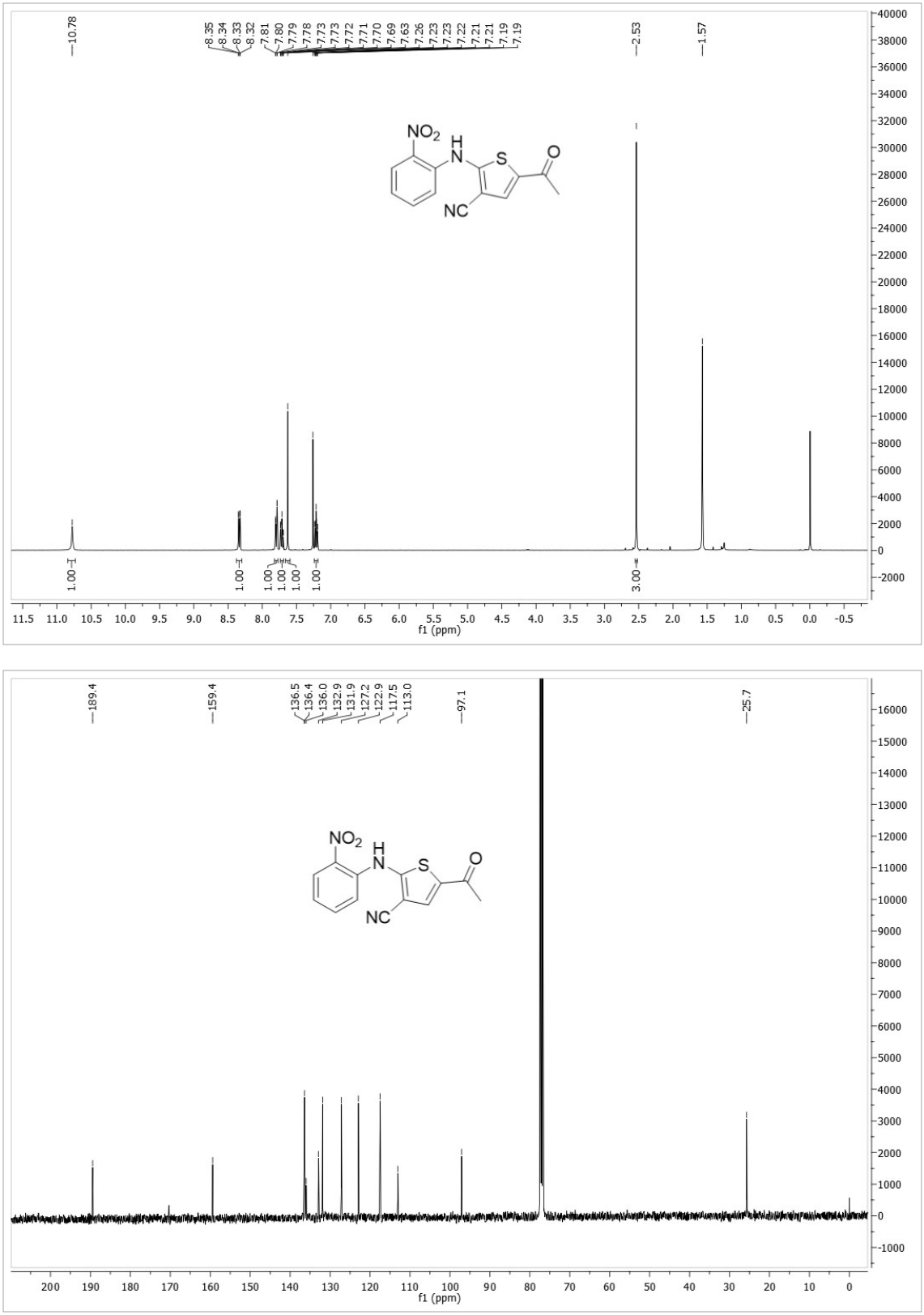


Figure S2. ^{1}H and ^{13}C NMR spectra of AcROY in $CDCl_3$.

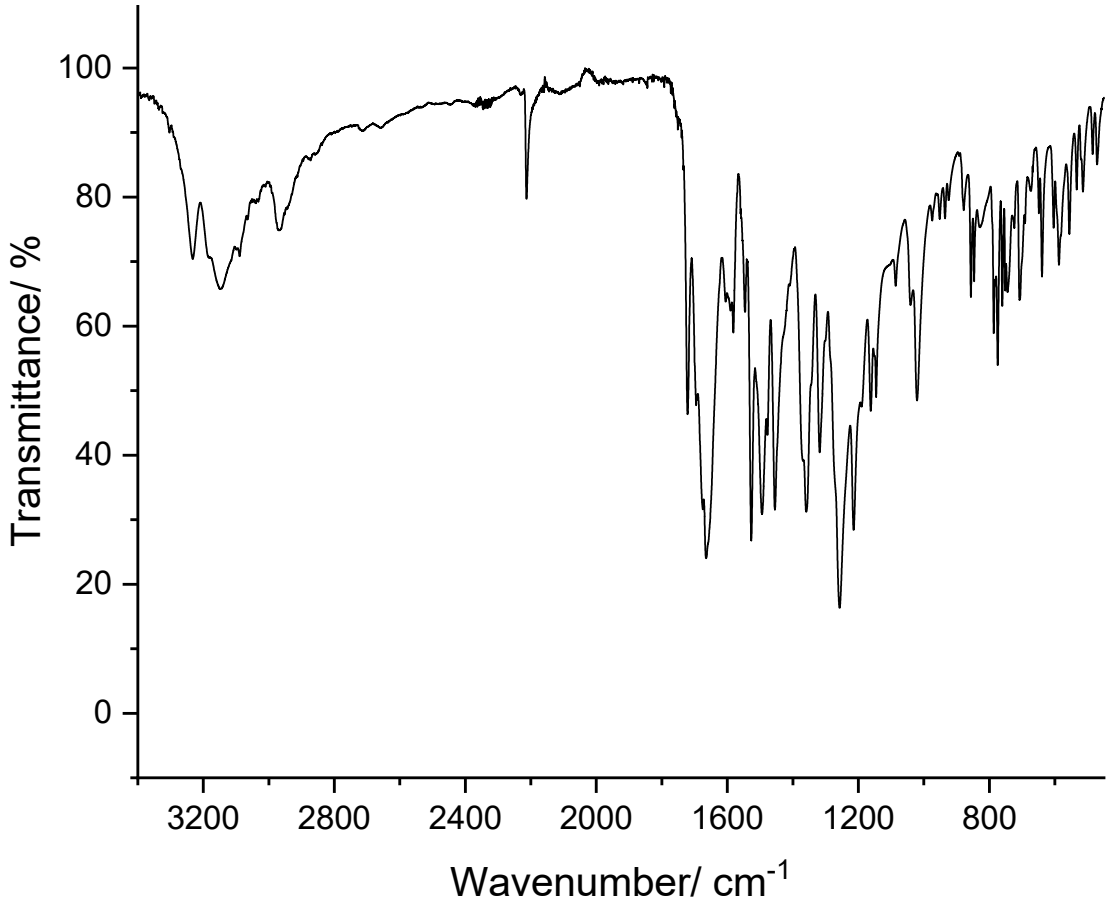


Figure S3. IR-ATR spectrum of the synthesized AcROY material.

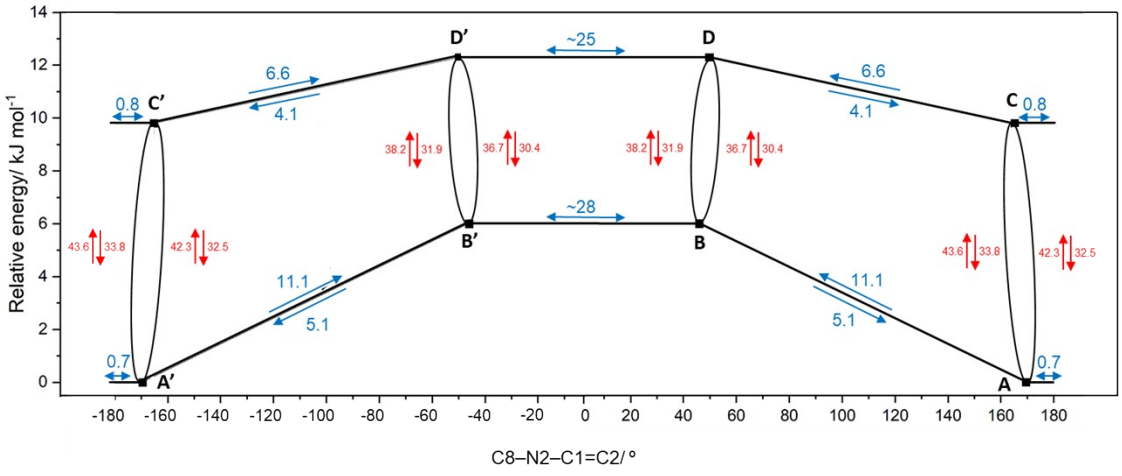


Figure S4. Relative energy plot of the four conformers of AcROY, showing the energy of the transition states for conformational isomerization. Values in blue and red color refer to rotations defined by θ and φ (see Scheme 1).

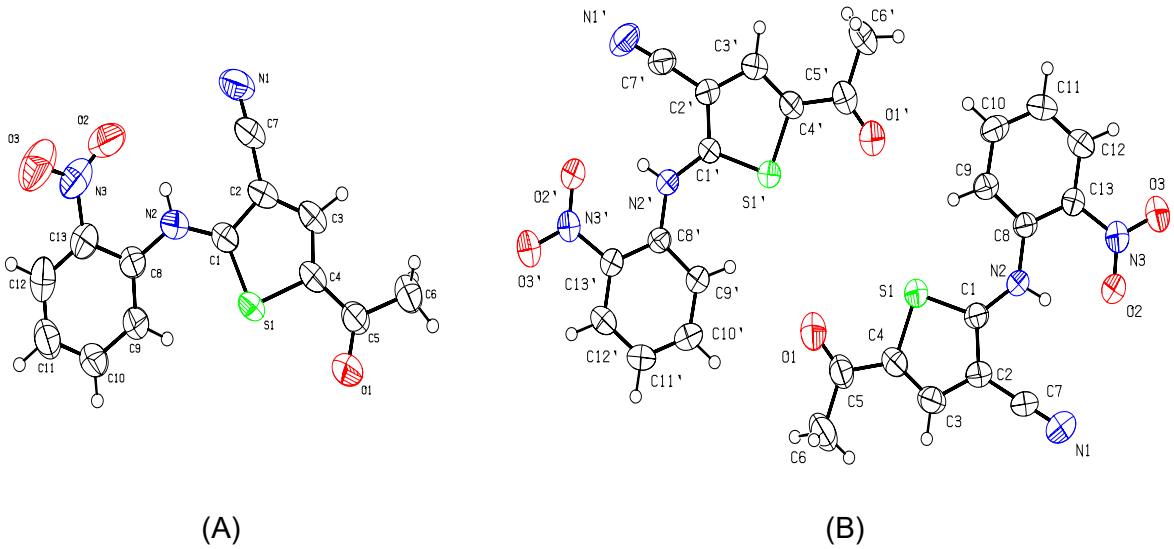


Figure S5. ORTEP plot depicting the anisotropic displacement ellipsoids, drawn at the 50% probability level, for polymorphs **1** (A) and **2** (B).

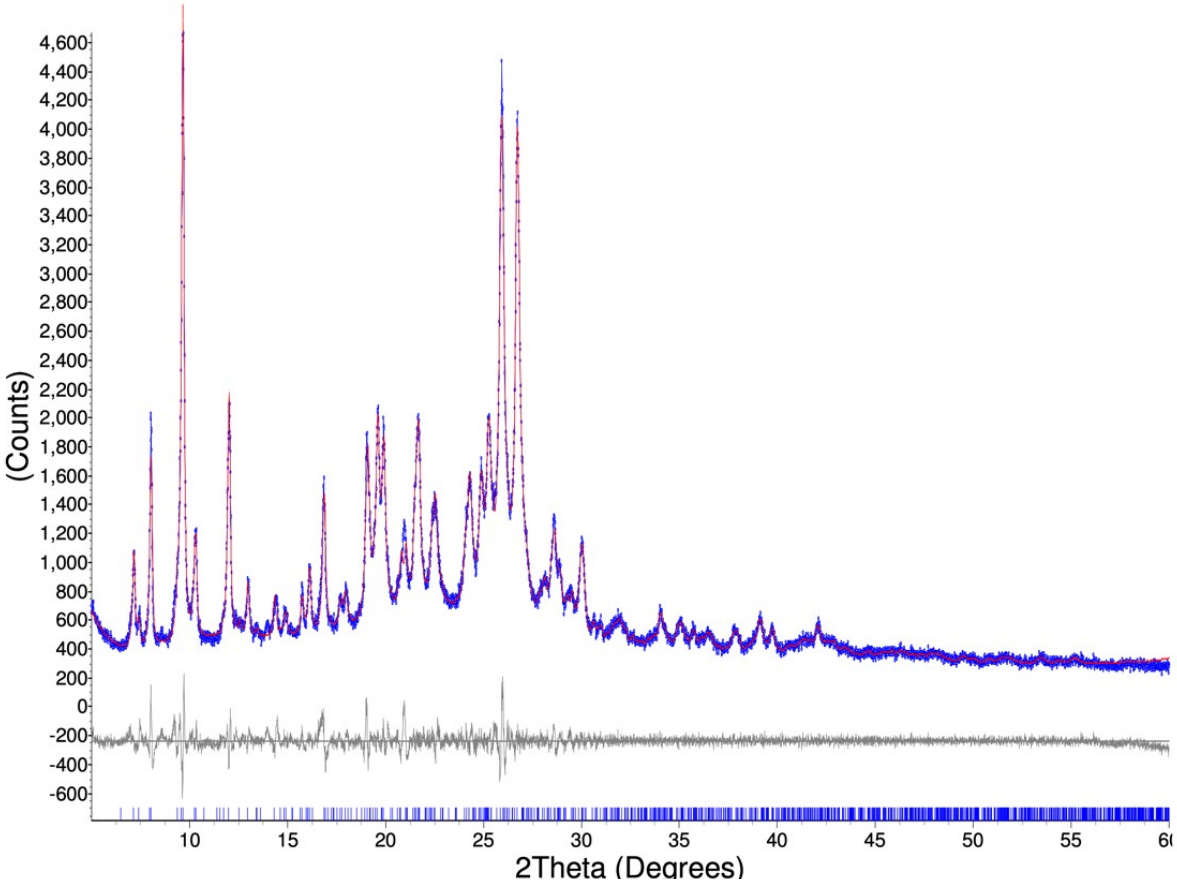
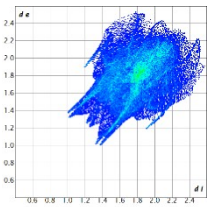
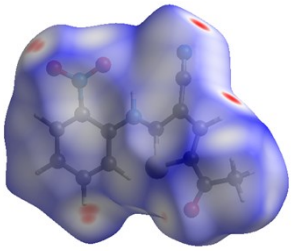


Figure S6. Diffractogram showing the observed (blue), calculated (red) and difference (black, at the bottom) profiles from the Pawley refinement using the monoclinic cell of the best Monte-Carlo solution given by the *LP*-search algorithm.

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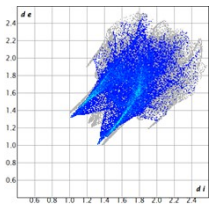
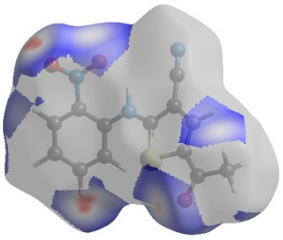

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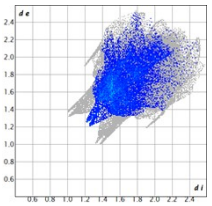
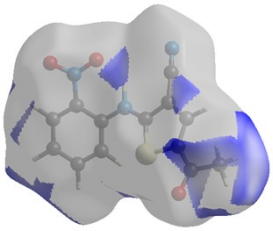

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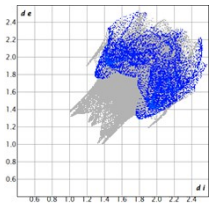
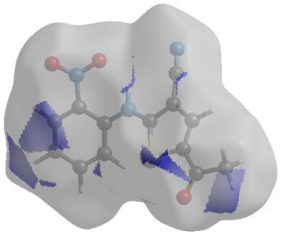

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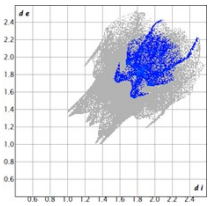
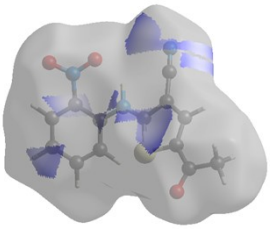

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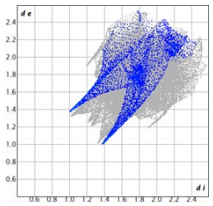
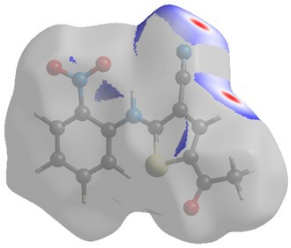

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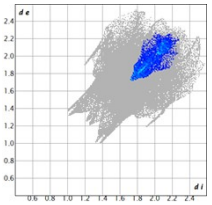
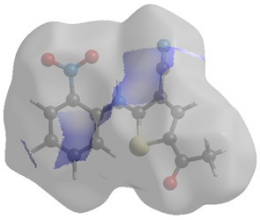

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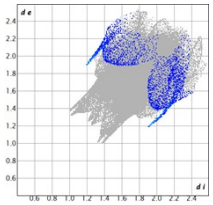
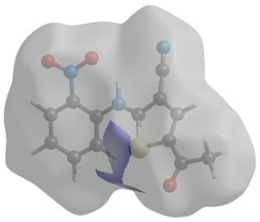

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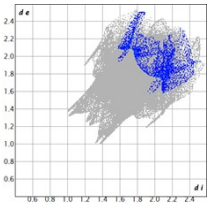
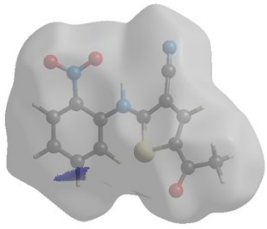

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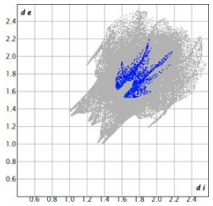
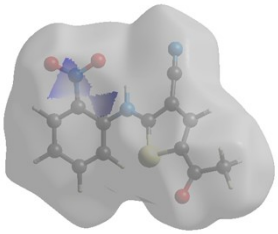

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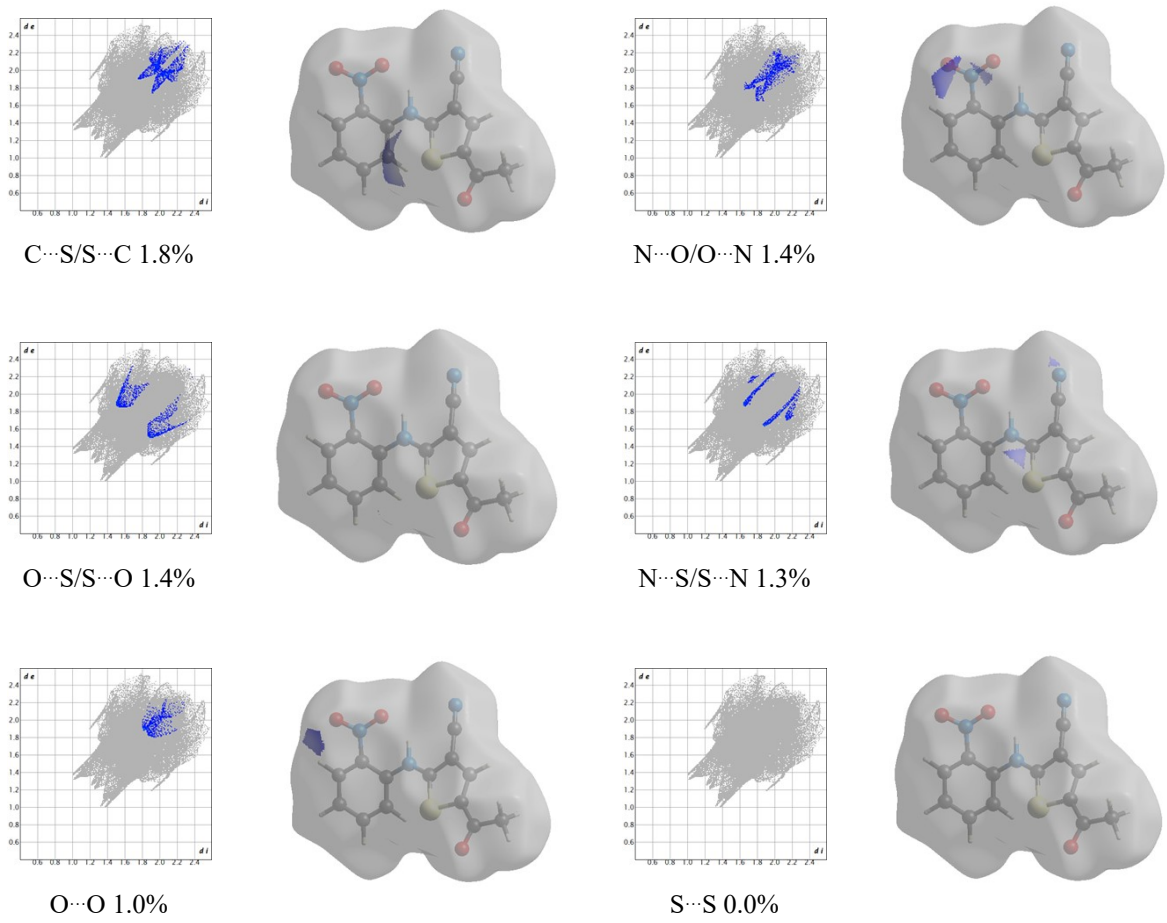
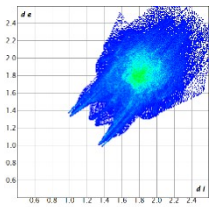
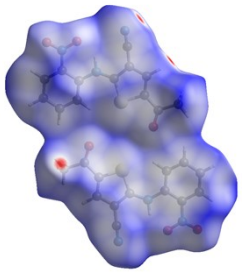


Figure S7 – Two-dimensional d_e vs. d_i fingerprint plots for AcROY polymorph **1** crystal (left) and the respective d_{norm} mapping on the Hirshfeld surfaces of the interactions. The colored areas on the plots represent the contributions of the referred interacting pair of atoms, whereas the non-colored grey areas represent the whole set of interactions. Colors are determined by the fraction of surface points in 0.01 Å bin in both d_e and d_i. The real colors span a continuous range and are mapped using the HSV (Hue, Saturation, Value) scheme, where S ≈ V ≈ 1.0 and H ~ 0.66 (240º, blue) for minimum relative area, and H ≈ 0.0 (0º, red) for more than 0.1% of surface points in the bin.

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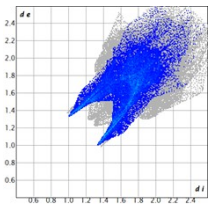
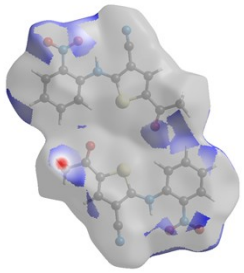

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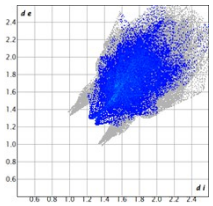
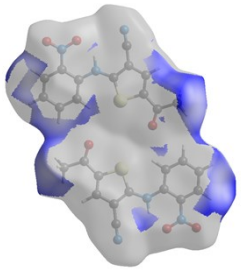

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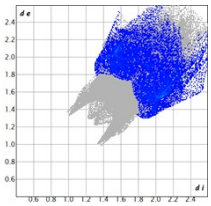
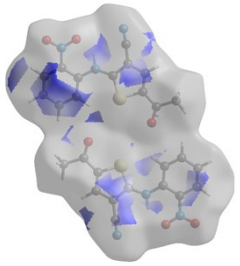

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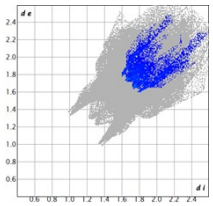
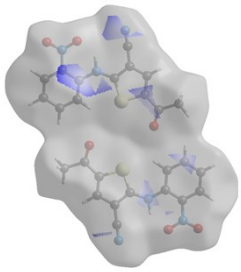

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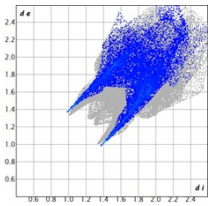
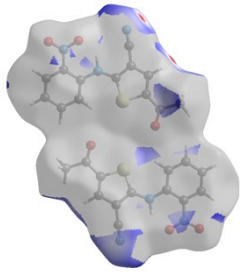

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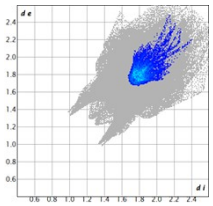
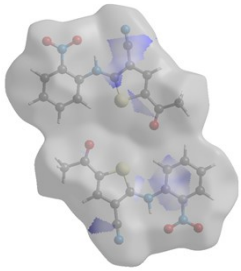

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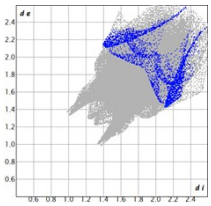
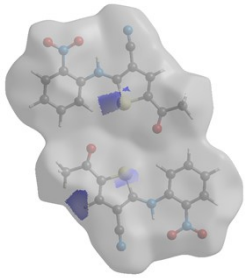

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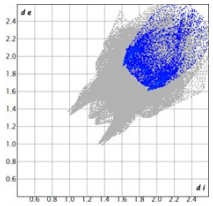
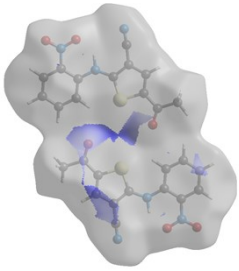

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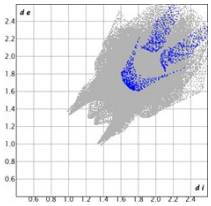
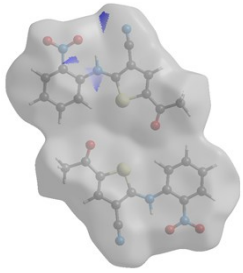

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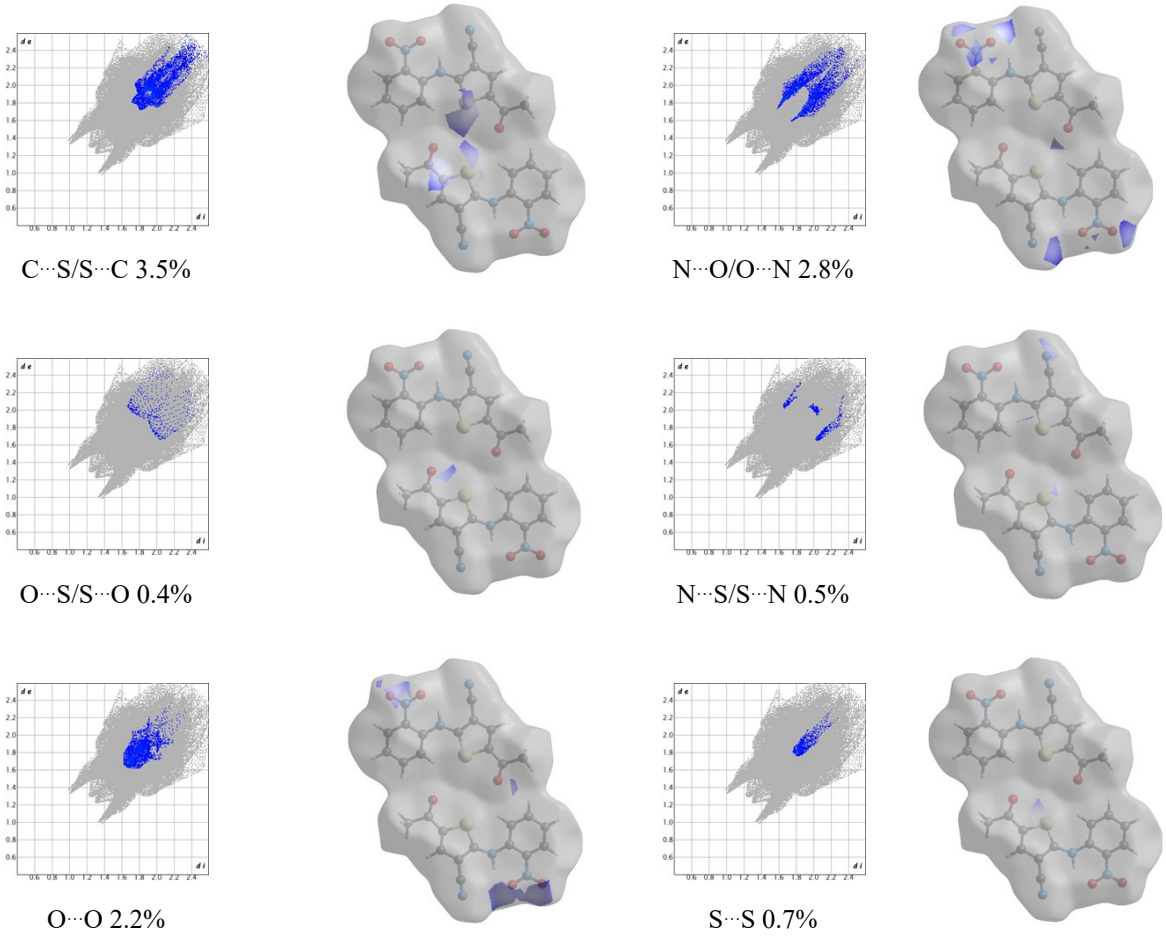

Figure S8 – Two-dimensional d_e vs. d_i fingerprint plots for AcROY polymorph **2** crystal (left) and the respective d_{norm} mapping on the Hirshfeld surfaces of the interactions. The colored areas on the plots represent the contributions of the referred interacting pair of atoms, whereas the non-colored grey areas represent the whole set of interactions. Colors are determined by the fraction of surface points in 0.01 Å bin in both d_e and d_i. The real colors span a continuous range and are mapped using the HSV (Hue, Saturation, Value) scheme, where S ≈ V ≈ 1.0 and H ~ 0.66 (240º, blue) for minimum relative area, and H ≈ 0.0 (0º, red) for more than 0.1% of surface points in the bin.

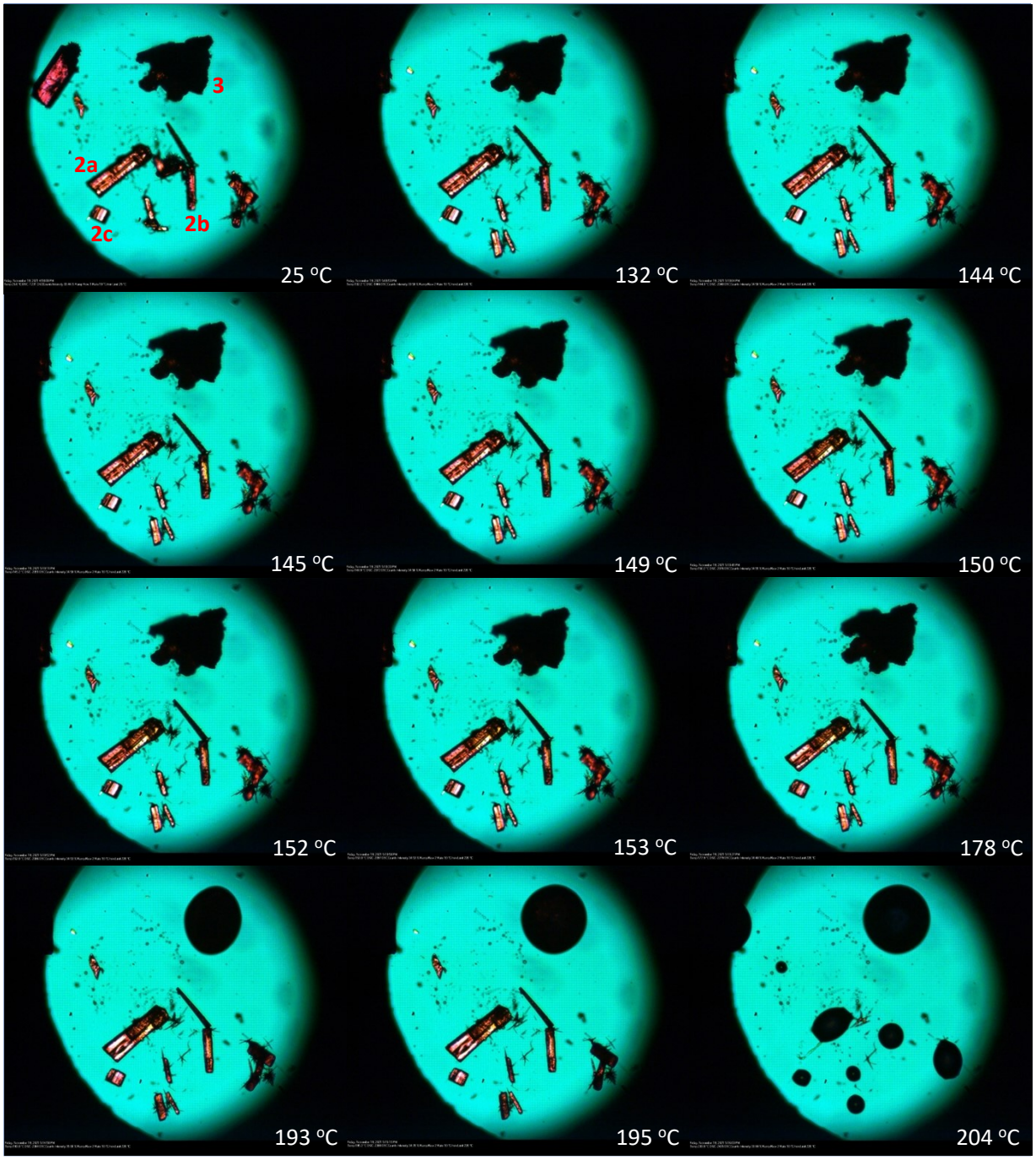

Figure S9 – PLTM images obtained along the heating of crystals of the polymorphs of AcROY (heating rate: 10 ºC min^{-1}). In the first plate of the image (left-top), crystals of polymorphs **2** and **3** are labelled with the corresponding number, while the non-labelled crystals belong to polymorph **1**. Some of the crystals of **1** and **2** are accompanied by small crystals of polymorph **3** (*e.g.*, the crystal of polymorph **1** at the right-bottom corner of the image). These pictures were extracted from the PLTM video submitted as Supporting Information.

Table S1. Polymorphic structures obtained from the room temperature solvent evaporation recrystallization experiments used as polymorph screening method.

Polymorph **1**	Polymorph **2**	Polymorph **3**
1,4-Dioxane	Acetone*	Acetone*
Toluene		DMSO*
Diethyl ether		
Chloroform		
Ethyl acetate		
THF		
Dichloromethane		
Acetone*		
Acetonitrile		
Acetic acid,		
1-Propanol		
Ethanol		
Methanol		
DMF		
DMSO*		
Formic acid		

* Concomitant mixtures.

Table S2. Tentative assignment of the infrared and Raman spectra of AcROY polymorphs.[a]

Polymorph **1**		Polymorph **2**		Polymorph **3**		Isolated molecule (form **A**)[b]			Tentative assignment[c]
ν^{R}	ν^{IR}	ν^{R}	ν^{IR}	ν^{R}	ν^{IR}	ν	a^{R}	I^{IR}	
65						56	3.3	2.4	Skeletal
						62	1.4	3.4	δ(C2–C1– N2)
						69	0.6	1.4	τ(C–NO_2)
						87	0.01	4.0	τ(–CH_3)
89		109		89		101	4.8	9.0	δ(C–C≡N)
104						115	0.2	4.3	Skeletal
122		120		117		124	2.8	1.5	τ(CC) phenyl
						143	0.9	1.3	γ(C–C≡N)
163/185		163/173		165		168	3.2	2.5	δ(C4–C5–C6)
						201	0.4	6.9	δ(S1–C1–N2)
213		213		213		245	2.4	1.4	Skeletal
255		249				270	0.3	4.4	Skeletal
278		282		264		316	8.5	3.9	δ(C–NO_2)
						316	2.6	1.0	Skeletal
		299		320		354	2.2	2.0	δ(C4–C5–C6); δ(C–NO_2)
322		328		344		401	6.8	0.6	δ(CC) phenyl
407	423		404	406	402	427	1.1	2.3	τ(CC) phenyl
422	447	404	420	425	439	433	5.2	0.7	Skeletal
481		474		455/468		468	30.2	0.2	δ(C–S–C)
	472		472		472	477	1.9	2.7	τ(thiophene)
	485		484	480	484	487	2.3	8.6	γ(C–C≡N); γ(C–N)
517	515		516	512	513/520	520	1.2	12.3	τ(CC) phenyl
	537	524	532		539/546	529	1.4	0.5	δ(C–NO_2); δ(C–C≡N)\
564	563	562	571	573	661	563	31.2	0.8	δ(CC) phenyl; δ(C–C≡N)\
598	594	589	589	582	575/584	586	8.5	37.3	δ(C–C=O)
	605		604		604	606	0.4	7.6	γ(C=O)
	640/649	627	628	624	611	639	3.9	13.4	δ(CC) phenyl; γ(NH)\
676	674	651	648/656	640/649	640/649	653	5.0	16.1	δ(CC) phenyl; γ(NH)\
	674	669	672	675	674	660	1.7	7.8	τ(thiophene)
	700	689	680	681	681	699	1.9	4.2	τ(CC) phenyl; γ(NH)
701	700	689	688	700	699	700	11.6	17.2	ν(C4–S); γ(NH)
717	716	716	704	724	716	712	44.8	14.5	ν(C4–S); γ(NH)
728	726	727	729	734	735	731	7.4	39.6	γ(NH)
747	744		741	783	741	746	2.4	50.0	γ(CH) phenyl
	780	813	779		760/780	786	0.5	4.8	γ(NO_2)
842	840	843	839	843	840	841	67.4	16.8	δ(NO_2)
						861	0.6	0.5	γ(CH) phenyl
	848		847		845	868	1.9	14.5	γ(C3–H)
	863		870	860	866	877	3.4	8.2	δ(CC) phenyl
881	879	882	875/878	877/886	877	904	50.9	35.6	ν(C5–C6)

926	925	923	923	932	925/933	959	20.4	9.9	ν(C1–S); γ(CH_3)
	956	957	958	949	950/958	963	0.1	1.8	γ(CH) phenyl
	977		977		979	983	1.4	0.4	γ(CH) phenyl
	1023		1018/1023		1012/1024	1027	0.04	1.9	γ(CH_3)
1053	1043	1056	1041/1050	1062	1040/1061	1032	30.5	49.7	γ(CH_3)
1082	1079	1072	1072	1079	1079	1053	115.4	13.9	ν(CC) phenyl
	1118		1109	1135	1137	1080	53.4	39.1	ν(C13–N3)
1152	1150	1149	1146	1159	1152	1147	153.7	86.3	δ(CH) phenyl
1165	1166	1164	1162	1169	1162	1169	63.1	35.2	δ(CH) phenyl
1209	1188	1197	1196	1208	1210/1230	1186	38.8	112.4	δ(C3–H)
	1194	1207	1211	1235	1210/1230	1210	62.7	11.0	ν(CC) phenyl
1261	1240/1260	1253	1248/1258	1258	1256	1253	81.7	645.1	ν(C4–C5)
1261	1240/1260	1278	1248/1258	1258	1285	1278	656.1	92.5	ν(NO_2) s; ν(C13–N3)
1301	1296	1302	1299	1291/1302	1297	1286	50.0	26.2	δ(CH) phenyl
1319	1317	1322	1319	1320/1322	1316	1316	32.5	21.4	ν(CC) phenyl; δ(CH) phenyl
1345	1341	1347	1344	1344	1342	1341	49.0	128.7	ν(C8–N2; ν(NO_2) s
1380	1364		1357	1399	1408	1365	1.5	49.0	δ(CH_3) s
1387	1387	1388	1387	1374	1373	1385	58.6	7.0	ν(C2–C7)
1409	1409	1408	1405	1356	1360/1367	1405	746.5	229.7	ν(N2–C1); δ(NH)
1423	1434	1430	1436	1418	1426	1444	5.9	12.3	δ(CH_3) as
1450	1456	1451	1456	1425	1435	1451	11.0	11.0	δ(CH_3) as
1450	1456	1451	1456	1451	1449	1453	154.6	30.9	δ(CH) phenyl
1461	1456	1456	1456	1451	1449	1463	686.8	426.8	δ(CH) phenyl; ν(C1=C2); δ(NH)
1494	1498/1509	1506	1498	1500/1511	1495/1500	1511	126.3	800.0	δ(CH) phenyl
1533	1529	1533	1533	1536	1532	1540	319.2	71.2	ν(C3=C4)
1562	1558	1563	1559	1559	1561	1565	57.0	38.6	ν(CC) phenyl; δ(NH); ν(NO_2) as
1595	1590	1600	1595		1591	1594	22.8	249.1	δ(NH)
1610	1606	1612	1605	1606	1605	1619	271.2	127.9	ν(CC) phenyl
1653	1647	1657	1652	1652/1680	1647/1697	1676	250.6	269.2	ν(C=O)
	2214		2211		2213	2267	459.0	65.5	ν(C≡N)
	3011		3009		3010	2981	229.3	2.1	ν(CH_3) s
	3050		3041		3040	3037	51.8	5.1	ν(CH_3) as
	3099		3100		3081	3085	124.8	8.5	ν(CH_3) as
	3116		3112		3109	3123	78.7	2.9	ν(C10–H), ν(C11–H) as
	3143		3140		3139	3142	178.7	4.8	ν(C10–H), ν(C11–H) s
			3169			3158	118.0	0.9	ν(C3–H)
						3159	35.8	0.1	ν(C9–H)
	3176		3173		3176	3167	146.6	3.9	ν(C12–H)
	3233		3216/3272		3230/3275	3339	855.3	242.1	ν(N–H)

[a] Frequencies (ν) in cm^{-1}. [b] Calculated 6-311++G(2d,p) frequencies for conformer **A**, scaled by 0.982; IR intensities (I^{IR}) in km mol^{-1}; Raman activities (a^R) in $Å^4$/a.m.u.. [c] Tentative assignments were made with help of the normal modes animation module of Chemcraft [ChemCraft (version 1.8) - Graphical Software for Visualization of Quantum Chemistry Computations. https://www.chemcraftprog.comt] using the data obtained for the isolated molecule (form **A**). Abbreviations: ν, stretching; γ, out-of-plane rocking; δ, bending; τ, torsion; s, symmetric; as, anti-symmetric.

Table S3. Selected valence angles in the molecules present in polymorphs **1** and **2** of AcROY. The second column corresponds to the molecule of polymorph **2** with unprimed atomic labels, the third column to the molecule with primed labels in the figures.

Bond length (Å)/ Valence angle (°)	Polymorph **1**	Polymorph **2**	
C≡N	1.136(3)	1.132(5)	1.138(5)
N2-C1	1.358(3)	1.358(4)	1.360(4)
N2-C8	1.385(3)	1.383(4)	1.383(4)
N3-O2	1.225(3)	1.225(4)	1.235(4)
N3-O3	1.208(3)	1.216(4)	1.216(4)
C8−C9−C10	121.1(2)	120.9(3)	121.0(3)
C9−C10−C11	121.5(2)	121.4(4)	121.5(4)
C10−C11−C12	118.7(2)	119.5(4)	119.0(4)
C11−C12−C13	120.6(2)	120.2(4)	120.7(4)
C12−C13−C8	121.4(2)	121.5(3)	121.4(3)
C1=C2−C3	113.09(17)	112.6(3)	113.1(3)
C2−C3=C4	113.04(17)	112.7(3)	112.7(3)
C3=C4−S1	111.68(16)	112.3(3)	111.8(3)
C4−S1−C1	91.59(9)	91.39(18)	91.09(17)

C