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SUPPLEMENTARY INFORMATION

The synergy of different solid-state techniques to elucidate the supramolecular assembly of two 1*H*-benzotriazole polymorphs

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SI1) X-ray powder diffraction

Diffraction patterns of samples recrystallized in different solvents

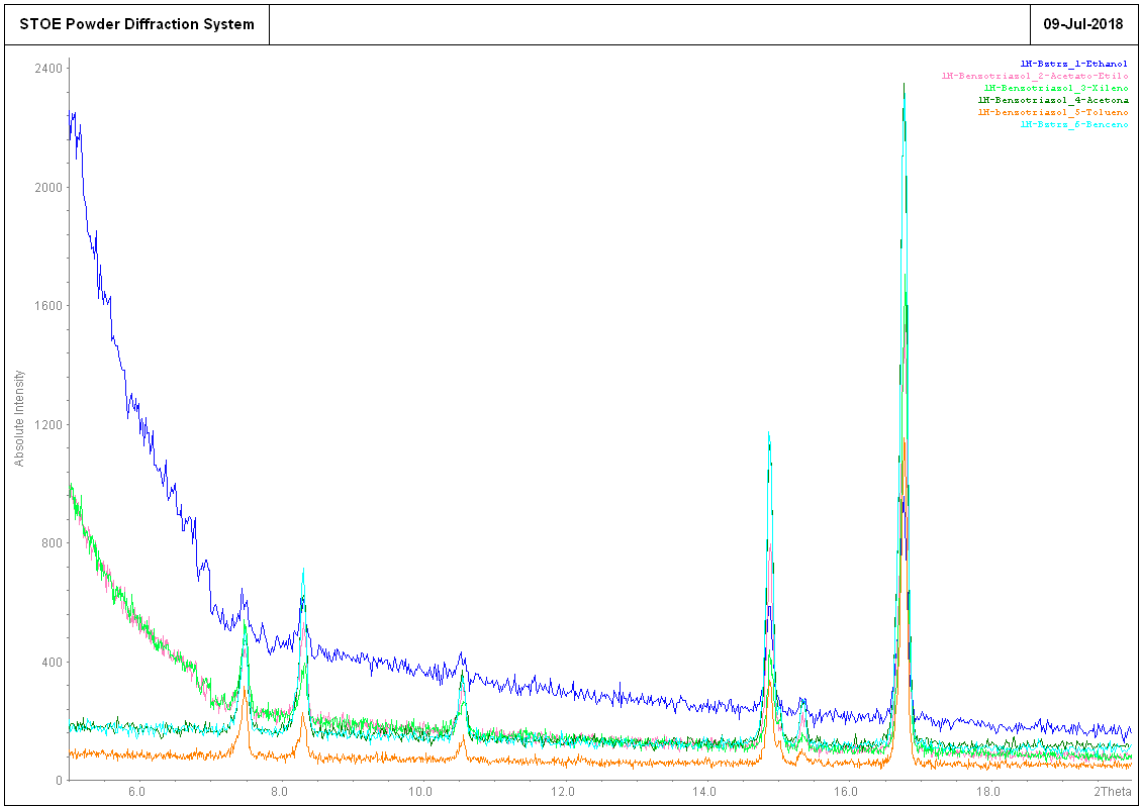

Figure S1. XRPD patterns of 1H-Benzotriazole recrystallized in different solvents.

Rietveld analysis of commercial sample (Madrid)

X-ray powder diffraction (XRPD) pattern of the commercial sample (Madrid) was obtained on a Stoe Stadip diffractometer equipped with a linear position sensitive detector. Data were collected using radiation Cukα1 monochromatized with a curved Ge(111), Debye-Scherrer geometry, scans from 5º to 80º with step-size of 0.01º and measuring time of 40 sec./step.

Fraction of α/β phases present in the sample was determined from Rietveld refinement using the software program JANA2006. Structural models of both phases were obtained from CCDC database. (BZTRAZ and BZTRAZ01).

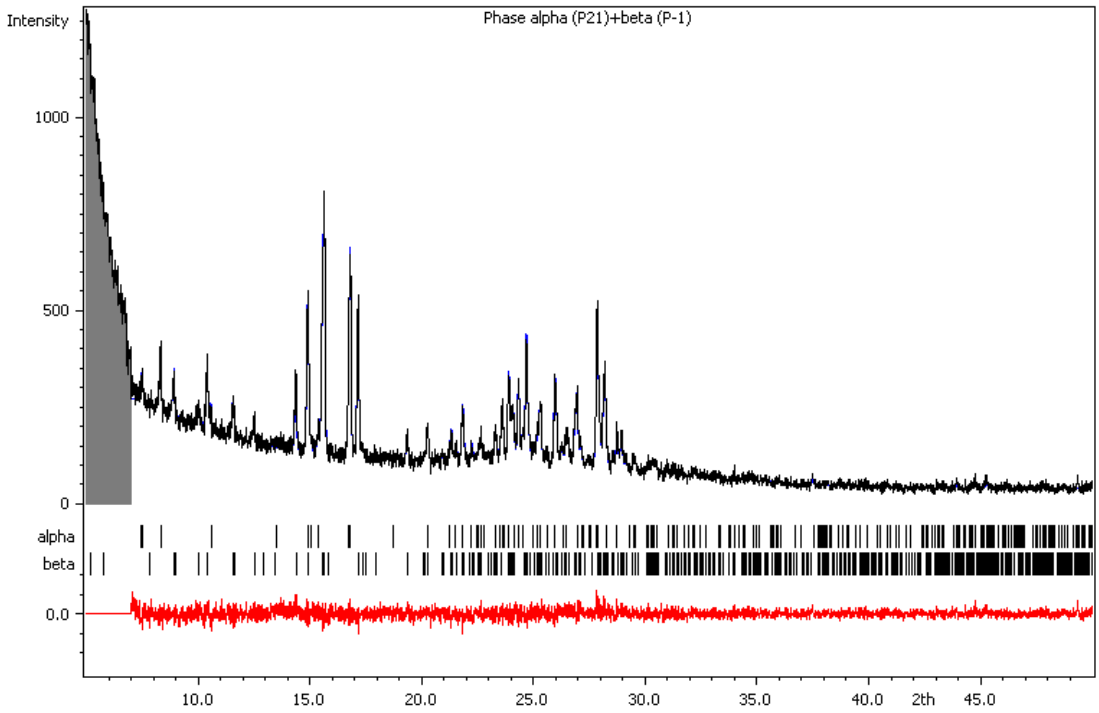

Figure S2. Rietveld refinement of the XRPD pattern of the commercial sample containing both polymorphic forms.

SI2) Optimized geometry and chemical shielding of the decamers at the B3LYP/6-31G(d) computational level.

Polymorph **4a**α

Geometry (Å)	Chemical shielding (ppm)		
Atom, X, Y, Z	Atom	Abs.	Rel.
C,0,0.0969976861,6.6760390822,1.3880272402	1C	75.90	102.61
C,0,-1.2539963974,6.6250200051,1.607032319	2C	76.20	102.32
C,0,-2.1370155848,7.5969770165,1.1249673295	3C	72.45	105.93
C,0,-1.7189967121,8.6759787543,0.3879948725	4C	84.34	94.48
C,0,-0.3309760704,8.7249617141,0.1490018012	5C	62.79	115.23
C,0,0.551022053,7.7809657495,0.6210494755	6C	52.95	124.71
H,0,0.785874043,5.9256743908,1.7592829498	7H	23.68	8.03
H,0,-1.6635690206,5.8026859638,2.1889871131	8H	24.62	7.12
H,0,-3.1958435364,7.4876802922,1.347536297	9H	24.78	6.96
H,0,-2.3963026842,9.4319888927,0.0060874257	10H	24.16	7.56
N,0,0.4457447435,9.6115832897,-0.5701767569	11N	22.87	-173.64
N,0,1.7420634231,9.2199854458,-0.4919864077	12N	-127.08	-31.78
N,0,1.8322750552,8.1264820697,0.2139562553	13N	-68.23	-87.46
C,0,5.9199919822,3.4780128758,-1.8780895188	14C	75.38	103.11
C,0,7.1790091224,4.0360412563,-1.7990688667	15C	73.76	104.67
C,0,7.4099947039,5.2800021226,-1.2110139435	16C	73.31	105.10
C,0,6.4150190731,6.0309992588,-0.6589997641	17C	89.12	89.87
C,0,5.1390406626,5.4818626763,-0.720739459	18C	67.11	111.07

C,0,4.8810619006,4.2299275985,-1.2859164424	19C	54.54	123.18
H,0,3.55835718,6.7986609782,0.0278439029	20H	18.20	13.34
H,0,5.7298307194,2.5143331627,-2.3377615084	21H	23.92	7.79
H,0,8.0224210401,3.4989381945,-2.2252412759	22H	24.81	6.94
H,0,8.4282992817,5.6606648829,-1.1916338686	23H	24.81	6.93
H,0,6.6029324225,7.0022606718,-0.2125145069	24H	24.54	7.19
N,0,3.9086561959,5.8995616825,-0.3252213629	25N	41.36	-191.13
N,0,2.9660628652,4.9949757487,-0.6020584332	26N	-115.37	-42.86
N,0,3.5479225492,3.9707915638,-1.1847950828	27N	-65.60	-89.94
C,0,-1.700988748,0.9230107731,-1.1060016286	28C	79.30	99.34
C,0,-2.2690344907,1.9780071187,-0.4469844796	29C	77.38	101.18
C,0,-1.5369963415,3.1349479125,-0.1220272886	30C	73.90	104.54
C,0,-0.204969378,3.2690734684,-0.4159998165	31C	83.26	95.52
C,0,0.3689533905,2.1709530733,-1.089960397	32C	61.47	116.50
C,0,-0.341997209,1.028966521,-1.4229664509	33C	55.61	122.14
H,0,2.4543374032,2.5708124263,-1.5272127067	34H	16.03	15.45
H,0,-2.2641571915,0.0336858807,-1.3725109738	35H	24.60	7.13
H,0,-3.3223835922,1.9384711366,-0.1794079442	36H	25.24	6.52
H,0,-2.0497995055,3.9506559982,0.3819608277	37H	25.14	6.61
H,0,0.3647219856,4.1619869591,-0.1840745415	38H	24.04	7.68
N,0,1.6381143332,1.945123763,-1.574107449	39N	30.27	-180.63
N,0,1.6899638996,0.7389988179,-2.1610198603	40N	-122.87	-35.76
N,0,0.4999940141,0.1789922748,-2.0940107356	41N	-89.64	-67.20
C,0,2.0209568628,12.6980112313,-3.0120363881	42C	79.24	99.39
C,0,2.5900370829,13.7529922008,-3.6710231643	43C	74.72	103.75
C,0,1.8570092726,14.9099556357,-3.9959513766	44C	71.48	106.87
C,0,0.5249808465,15.0440854061,-3.7020055283	45C	83.10	95.67
C,0,-0.0479623979,13.9460242945,-3.028038003	46C	61.64	116.34
C,0,0.662937154,12.8040486938,-2.6940422449	47C	56.57	121.23
H,0,-2.1392870258,14.3476730604,-2.5937862784	48H	15.48	15.99
H,0,2.5852167929,11.8103707301,-2.7413799875	49H	24.01	7.71
H,0,3.6428128714,13.7114392258,-3.9375793592	50H	24.93	6.82
H,0,2.3679130676,15.7261590839,-4.5000915024	51H	24.87	6.87
H,0,-0.047372256,15.9351647436,-3.9335328902	52H	23.84	7.88
N,0,-1.317146244,13.7201325392,-2.5440268599	53N	27.08	-177.62
N,0,-1.3700340391,12.5140407542,-1.9569756141	54N	-121.26	-37.29
N,0,-0.1797364958,11.9535197816,-2.022731415	55N	-61.26	-94.05
C,0,-5.599991393,15.2530106281,-2.2389069496	56C	75.89	102.62
C,0,-6.8580082266,15.8110428575,-2.3189290492	57C	73.25	105.16
C,0,-7.0889954098,17.0550014189,-2.9069895653	58C	72.89	105.51
C,0,-6.0950182111,17.805993157,-3.459006487	59C	88.68	90.30
C,0,-4.818040693,17.256854495,-3.3972678003	60C	66.93	111.25
C,0,-4.5610600169,16.0049305597,-2.8320811755	61C	54.43	123.28
H,0,-3.2361867193,18.5737090217,-4.1461131586	62H	18.12	13.42
H,0,-5.4112463416,14.2892437133,-1.7789364988	63H	23.87	7.84
H,0,-7.7017629353,15.2743602513,-1.8931209487	64H	24.72	7.02
H,0,-8.1073814462,17.4350572143,-2.926450878	65H	24.75	6.99
H,0,-6.2829647683,18.7770026838,-3.905774562	66H	24.51	7.23
N,0,-3.5876523349,17.6745753036,-3.7927647273	67N	40.98	-190.77
N,0,-2.6460537479,16.7699799421,-3.5159301875	68N	-113.97	-44.18
N,0,-3.2269341296,15.7458158594,-2.9331958298	69N	-61.59	-93.74
C,0,0.2230038219,18.4510452895,-5.5060243831	70C	76.21	102.31
C,0,1.5739976617,18.4000156058,-5.7250386751	71C	76.07	102.45

C,0,2.4570133858,19.3719767073,-5.2419612926	72C	72.50	105.88
C,0,2.0399979629,20.4509776876,-4.5049921821	73C	83.80	95.00
C,0,0.650975919,20.4999666122,-4.267009181	74C	62.66	115.35
C,0,-0.2310250588,19.5559665392,-4.7380543262	75C	52.69	124.96
H,0,-0.4669563068,17.7037419882,-5.881695469	76H	23.69	8.02
H,0,1.9836355882,17.5807400433,-6.3114638531	77H	24.63	7.11
H,0,3.5156121119,19.2630558326,-5.465767392	78H	24.73	7.02
H,0,2.7172059141,21.207288039,-4.1237169879	79H	24.11	7.62
N,0,-0.1257434778,21.38658176,-3.5478230812	80N	22.63	-173.41
N,0,-1.4210660563,20.9949899586,-3.6250195905	81N	-127.74	-31.16
N,0,-1.5122753805,19.9014649068,-4.3319460821	82N	-67.84	-87.82
C,0,-1.7009557551,24.4730112067,-1.1059640695	83C	79.22	99.41
C,0,-2.2690392088,25.527992103,-0.4469762355	84C	74.68	103.78
C,0,-1.5370074658,26.684956659,-0.1220485575	85C	71.55	106.79
C,0,-0.2049832299,26.8190843908,-0.4159977301	86C	83.29	95.49
C,0,0.3689634174,25.7210226746,-1.0899591901	87C	61.78	116.21
C,0,-0.341936961,24.5790464428,-1.422954759	88C	56.73	121.07
H,0,2.4606528036,26.1222947891,-1.5244725077	89H	15.47	15.99
H,0,-2.2653576676,23.5855665314,-1.3766942737	90H	23.97	7.75
H,0,-3.3218633662,25.4865449008,-0.180484479	91H	24.92	6.83
H,0,-2.0485432199,27.5005724177,0.3823522019	92H	24.89	6.85
H,0,0.3677793421,27.7098456068,-0.1843126235	93H	23.87	7.85
N,0,1.6381546624,25.4951444288,-1.5739775643	94N	27.15	-177.69
N,0,1.6900325416,24.2890383483,-2.1610249256	95N	-121.13	-37.41
N,0,0.4997338088,23.7285204959,-2.0942697772	96N	-60.49	-94.78
C,0,5.9199919276,27.0280097955,-1.8780943394	97C	75.79	102.71
C,0,7.179006894,27.5860450375,-1.7990718587	98C	72.91	105.49
C,0,7.4099965421,28.8300019468,-1.2110094319	99C	72.62	105.77
C,0,6.4150190527,29.580988821,-0.6589883858	100C	88.74	90.25
C,0,5.1390409434,29.0318575165,-0.7207396972	101C	66.93	111.25
C,0,4.8810608209,27.7799330231,-1.2859213401	102C	54.57	123.15
H,0,3.5607848663,30.3472313323,0.0323808435	103H	18.22	13.33
H,0,5.731557303,26.0640102688,-2.3377005411	104H	23.84	7.88
H,0,8.0223922291,27.048808524,-2.2246777635	105H	24.69	7.05
H,0,8.4282333582,29.2102153233,-1.1909991286	106H	24.74	7.00
H,0,6.6033500358,30.5515020998,-0.2112863659	107H	24.53	7.21
N,0,3.9086563566,29.4495763926,-0.3252446407	108N	41.30	-191.07
N,0,2.9660551084,28.544985491,-0.6020773779	109N	-113.53	-44.61
N,0,3.547926364,27.5207967014,-1.1847814532	110N	-61.70	-93.63
C,0,0.0969960017,30.2260420599,1.388019574	111C	75.97	102.54
C,0,-1.2539966348,30.1750154001,1.6070371623	112C	75.34	103.14
C,0,-2.1370141207,31.1469764292,1.1249623045	113C	72.00	106.36
C,0,-1.7189990489,32.2259761697,0.3879901433	114C	84.24	94.58
C,0,-0.3309828272,32.2749806558,0.1490148512	115C	62.96	115.07
C,0,0.5510251782,31.330970488,0.6210604102	116C	52.39	125.25
H,0,0.7868953368,29.4786704657,1.7634287785	117H	23.64	8.07
H,0,-1.6632952885,29.3555751658,2.1931807773	118H	24.60	7.14
H,0,-3.1954688537,31.0389518156,1.3490444815	119H	24.69	7.05
H,0,-2.3980634017,32.9813475575,0.0079977491	120H	24.25	7.48
N,0,0.4457775434,33.1615403378,-0.5701639351	121N	26.12	-176.71
N,0,1.7420615993,32.7700009858,-0.4919607588	122N	-125.68	-33.11
N,0,1.8322658418,31.6764734815,0.2139343824	123N	-70.29	-85.51
C,0,2.020961329,36.2480082285,-3.0120308961	124C	77.68	100.90

C,0,2.5900219469,37.302988617,-3.6710046712	125C	72.55	105.83
C,0,1.8570057403,38.4600015377,-3.9959836852	126C	69.14	109.12
C,0,0.5249992922,38.5940206758,-3.7020064637	127C	86.69	92.22
C,0,-0.0479830374,37.4960603585,-3.0279577522	128C	63.69	114.37
C,0,0.6629478922,36.3540610628,-2.6940161855	129C	57.20	120.62
H,0,-2.1528285235,37.8352758525,-2.5904192559	130H	21.36	10.28
H,0,2.5832921276,35.3596865712,-2.7410369689	131H	23.75	7.96
H,0,3.6415839276,37.2618508749,-3.9394196611	132H	24.71	7.03
H,0,2.3681847314,39.2691417839,-4.510829349	133H	24.74	7.01
H,0,-0.0432021584,39.4828737854,-3.9541644961	134H	24.72	7.02
N,0,-1.3170461859,37.2700510197,-2.5441202632	135N	47.83	-197.25
N,0,-1.3700365667,36.0640551869,-1.9569490043	136N	-122.29	-36.31
N,0,-0.1798031413,35.5035243717,-2.0228378687	137N	-69.54	-86.22
H,0,0.1920521098,10.4645520885,-1.1091753906	138H	14.96	16.49
H,0,0.1280725287,22.2399467502,-3.0084832483	139H	14.90	16.54
H,0,0.1922780767,34.0084564222,-1.1048154281	140H	15.50	15.96

Polymorph **4a**β

Geometry (Å)	Chemical shielding (ppm)		
Atom, X, Y, Z	Atom	Abs.	Rel.
N,0,0.3156426946,2.5887159875,-7.4607136067	1N	34.80	-184.92
H,0,-0.1487313773,1.7450198222,-7.8372572555	2H	16.52	14.97
N,0,0.1887505542,2.8761486533,-6.1531550114	3N	-117.88	-40.48
N,0,0.7838504946,4.0135137001,-5.9288935425	4N	-62.04	-93.31
C,0,1.9991202712,5.6456978588,-7.4019545957	5C	80.70	97.99
H,0,2.2402048497,6.3584689543,-6.6190872139	6H	24.22	7.51
C,0,2.3553174261,5.8418970692,-8.6928427133	7C	76.68	101.86
H,0,2.9026272668,6.7402872402,-8.9670924098	8H	24.90	6.84
C,0,2.0344460121,4.9248544537,-9.6926787431	9C	72.78	105.61
H,0,2.3396313852,5.1351974443,-10.7144992181	10H	24.84	6.90
C,0,1.3607994754,3.7707196717,-9.424876506	11C	87.97	90.99
H,0,1.1057654187,3.0564711574,-10.201401491	12H	24.43	7.31
C,0,0.9917720884,3.5730920086,-8.1060266661	13C	67.47	110.73
C,0,1.2910649468,4.4794708121,-7.1110611991	14C	57.47	120.36
N,0,0.8653289571,4.3068528216,-3.1143721108	15N	33.53	-183.72
H,0,0.7416158007,4.4387244057,-4.1328300205	16H	15.94	15.53
N,0,0.4141785179,5.1981235399,-2.2184772429	17N	-113.87	-44.28
N,0,0.7088723256,4.7579304387,-1.0208686844	18N	-56.76	-98.31
C,0,1.8950054872,2.6794307513,-0.1934247727	19C	80.24	98.43
H,0,1.8193738558,2.8977252545,0.8676852199	20H	24.54	7.20
C,0,2.4844964623,1.5471919821,-0.6656269167	21C	76.63	101.91
H,0,2.9032214398,0.8328359998,0.0387054053	22H	25.62	6.15
C,0,2.5681691368,1.2729739543,-2.0298056881	23C	75.12	103.35
H,0,3.0351915925,0.3446701977,-2.3468545153	24H	25.57	6.20
C,0,2.0694481271,2.1093929466,-2.9614077632	25C	89.37	89.64
H,0,2.1083451806,1.8813918441,-4.0208957154	26H	24.99	6.76
C,0,1.4621938883,3.2657465499,-2.4974027222	27C	67.39	110.80
C,0,1.3596409193,3.5568451473,-1.1483070207	28C	56.07	121.70

N,0,-0.3464363447,5.9408717674,1.3532017752	29N	32.26	-182.52
H,0,0.0383502175,5.5164705377,0.4815326475	30H	15.38	16.08
N,0,-0.2379979435,5.2807638586,2.5104481182	31N	-116.55	-41.74
N,0,-0.7439628577,6.0206367017,3.4625962493	32N	-58.11	-97.02
C,0,-1.7689938773,8.3196470459,3.4617822406	33C	80.13	98.54
H,0,-1.9609358696,8.3808162293,4.5286304288	34H	24.26	7.46
C,0,-2.0836483557,9.3315185057,2.6062337746	35C	77.24	101.32
H,0,-2.5423572579,10.2359244147,2.9984170898	36H	24.98	6.77
C,0,-1.8391294761,9.2447902383,1.244581838	37C	76.18	102.34
H,0,-2.1209924339,10.0851758978,0.6139572446	38H	24.96	6.79
C,0,-1.2748208259,8.163219257,0.6806699273	39C	89.91	89.12
H,0,-1.0812511116,8.0948064565,-0.3857814757	40H	24.35	7.38
C,0,-0.9318754291,7.1352506411,1.5418306591	41C	68.49	109.74
C,0,-1.1787943949,7.1858406382,2.8994541833	42C	57.03	120.78
N,0,-1.2318227735,3.9156959313,5.4768223806	43N	32.53	-182.77
H,0,-1.1028849348,4.7816219977,4.9236627761	44H	16.73	14.77
N,0,-0.3300200315,3.6275371918,6.4454011208	45N	-124.97	-33.78
N,0,-0.5727340551,2.410774186,6.8679030377	46N	-62.86	-92.54
C,0,-2.2486041294,0.6569286357,6.2003562763	47C	79.94	98.71
H,0,-1.9048399658,-0.1042605062,6.8940457703	48H	24.13	7.59
C,0,-3.2798855324,0.4346838896,5.3488222476	49C	77.83	100.75
H,0,-3.796353295,-0.5211186043,5.3618348665	50H	25.20	6.56
C,0,-3.7166040783,1.4273917136,4.472716277	51C	74.39	104.06
H,0,-4.5627941764,1.2121700988,3.8240549089	52H	25.08	6.67
C,0,-3.1259838672,2.6432512125,4.3939031581	53C	89.11	89.89
H,0,-3.4639092457,3.4040730044,3.6974628797	54H	25.17	6.59
C,0,-2.0549444327,2.8709591623,5.2564419994	55C	67.06	111.12
C,0,-1.6274436273,1.9033185808,6.1502867996	56C	55.66	122.09
N,0,-1.1472916891,-0.99470028,-8.6303805852	57N	35.98	-186.04
H,0,-0.5142477608,-1.5281671531,-7.9994722183	58H	15.18	16.28
N,0,-1.0913855237,0.3428626803,-8.6747675121	59N	-88.92	-67.88
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C,0,-3.6706516637,-0.3760215647,-10.9729309544	61C	77.89	100.70
H,0,-4.0928115442,0.5191633238,-11.4175455001	62H	24.28	7.45
C,0,-4.1020369808,-1.6281205191,-11.287755754	63C	77.14	101.41
H,0,-4.9054482191,-1.7434013594,-12.0118529609	64H	25.00	6.75
C,0,-3.5642076781,-2.7679387131,-10.7102410209	65C	74.90	103.58
H,0,-3.9598396667,-3.7380737578,-11.0009698609	66H	24.91	6.84
C,0,-2.5644394743,-2.7070598709,-9.8040175884	67C	88.98	90.01
H,0,-2.1430889073,-3.5980321174,-9.3475503361	68H	24.32	7.41
C,0,-2.1062127912,-1.4428780041,-9.4742786252	69C	67.89	110.32
C,0,-2.6298133733,-0.2951959539,-10.0365127373	70C	55.58	122.17
N,0,1.2318227735,-3.9156959313,-5.4768223806	71N	32.53	-182.77
H,0,1.1028849348,-4.7816219977,-4.9236627761	72H	16.73	14.77
N,0,0.3300200315,-3.6275371918,-6.4454011208	73N	-124.97	-33.78
N,0,0.5727340551,-2.410774186,-6.8679030377	74N	-62.86	-92.54
C,0,2.2486041294,-0.6569286357,-6.2003562763	75C	79.94	98.71
H,0,1.9048399658,0.1042605062,-6.8940457703	76H	24.13	7.59
C,0,3.2798855324,-0.4346838896,-5.3488222476	77C	77.83	100.75
H,0,3.796353295,0.5211186043,-5.3618348665	78H	25.20	6.56
C,0,3.7166040783,-1.4273917136,-4.472716277	79C	74.39	104.06
H,0,4.5627941764,-1.2121700988,-3.8240549089	80H	25.08	6.67
C,0,3.1259838672,-2.6432512125,-4.3939031581	81C	89.11	89.89

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C,0,2.0549444327,-2.8709591623,-5.2564419994	83C	67.06	111.12
C,0,1.6274436273,-1.9033185808,-6.1502867996	84C	55.66	122.09
N,0,0.3464363447,-5.9408717674,-1.3532017752	85N	32.26	-182.52
H,0,-0.0383502175,-5.5164705377,-0.4815326475	86H	15.38	16.08
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N,0,0.7439628577,-6.0206367017,-3.4625962493	88N	-58.11	-97.02
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H,0,1.9609358696,-8.3808162293,-4.5286304288	90H	24.26	7.46
C,0,2.0836483557,-9.3315185057,-2.6062337746	91C	77.24	101.32
H,0,2.5423572579,-10.2359244147,-2.9984170898	92H	24.98	6.77
C,0,1.8391294761,-9.2447902383,-1.244581838	93C	76.18	102.34
H,0,2.1209924339,-10.0851758978,-0.6139572446	94H	24.96	6.79
C,0,1.2748208259,-8.163219257,-0.6806699273	95C	89.91	89.12
H,0,1.0812511116,-8.0948064565,0.3857814757	96H	24.35	7.38
C,0,0.9318754291,-7.1352506411,-1.5418306591	97C	68.49	109.74
C,0,1.1787943949,-7.1858406382,-2.8994541833	98C	57.03	120.78
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H,0,-0.7416158007,-4.4387244057,4.1328300205	100H	15.94	15.53
N,0,-0.4141785179,-5.1981235399,2.2184772429	101N	-113.87	-44.28
N,0,-0.7088723256,-4.7579304387,1.0208686844	102N	-56.76	-98.31
C,0,-1.8950054872,-2.6794307513,0.1934247727	103C	80.24	98.43
H,0,-1.8193738558,-2.8977252545,-0.8676852199	104H	24.54	7.20
C,0,-2.4844964623,-1.5471919821,0.6656269167	105C	76.63	101.91
H,0,-2.9032214398,-0.8328359998,-0.0387054053	106H	25.62	6.15
C,0,-2.5681691368,-1.2729739543,2.0298056881	107C	75.12	103.35
H,0,-3.0351915925,-0.3446701977,2.3468545153	108H	25.57	6.20
C,0,-2.0694481271,-2.1093929466,2.9614077632	109C	89.37	89.64
H,0,-2.1083451806,-1.8813918441,4.0208957154	110H	24.99	6.76
C,0,-1.4621938883,-3.2657465499,2.4974027222	111C	67.39	110.80
C,0,-1.3596409193,-3.5568451473,1.1483070207	112C	56.07	121.70
N,0,-0.3156426946,-2.5887159875,7.4607136067	113N	34.80	-184.92
H,0,0.1487313773,-1.7450198222,7.8372572555	114H	16.52	14.97
N,0,-0.1887505542,-2.8761486533,6.1531550114	115N	-117.88	-40.48
N,0,-0.7838504946,-4.0135137001,5.9288935425	116N	-62.04	-93.31
C,0,-1.9991202712,-5.6456978588,7.4019545957	117C	80.70	97.99
H,0,-2.2402048497,-6.3584689543,6.6190872139	118H	24.22	7.51
C,0,-2.3553174261,-5.8418970692,8.6928427133	119C	76.68	101.86
H,0,-2.9026272668,-6.7402872402,8.9670924098	120H	24.90	6.84
C,0,-2.0344460121,-4.9248544537,9.6926787431	121C	72.78	105.61
H,0,-2.3396313852,-5.1351974443,10.7144992181	122H	24.84	6.90
C,0,-1.3607994754,-3.7707196717,9.424876506	123C	87.97	90.99
H,0,-1.1057654187,-3.0564711574,10.201401491	124H	24.43	7.31
C,0,-0.9917720884,-3.5730920086,8.1060266661	125C	67.47	110.73
C,0,-1.2910649468,-4.4794708121,7.1110611991	126C	57.47	120.36
N,0,1.1472916891,0.99470028,8.6303805852	127N	35.98	-186.04
H,0,0.5142477608,1.5281671531,7.9994722183	128H	15.18	16.28
N,0,1.0913855237,-0.3428626803,8.6747675121	129N	-88.92	-67.88
N,0,1.9821834241,-0.7905012377,9.5180177995	130N	-80.89	-75.48
C,0,3.6706516637,0.3760215647,10.9729309544	131C	77.89	100.70
H,0,4.0928115442,-0.5191633238,11.4175455001	132H	24.28	7.45
C,0,4.1020369808,1.6281205191,11.287755754	133C	77.14	101.41
H,0,4.9054482191,1.7434013594,12.0118529609	134H	25.00	6.75

C,0,3.5642076781,2.7679387131,10.7102410209	135C	74.90	103.58
H,0,3.9598396667,3.7380737578,11.0009698609	136H	24.91	6.84
C,0,2.5644394743,2.7070598709,9.8040175884	137C	88.98	90.01
H,0,2.1430889073,3.5980321174,9.3475503361	138H	24.32	7.41
C,0,2.1062127912,1.4428780041,9.4742786252	139C	67.89	110.32
C,0,2.6298133733,0.2951959539,10.0365127373	140C	55.58	122.17

SI3) Theoretical and experimental FarIR, IR and Raman of 4aα crystals crystallized from acetone and toluene

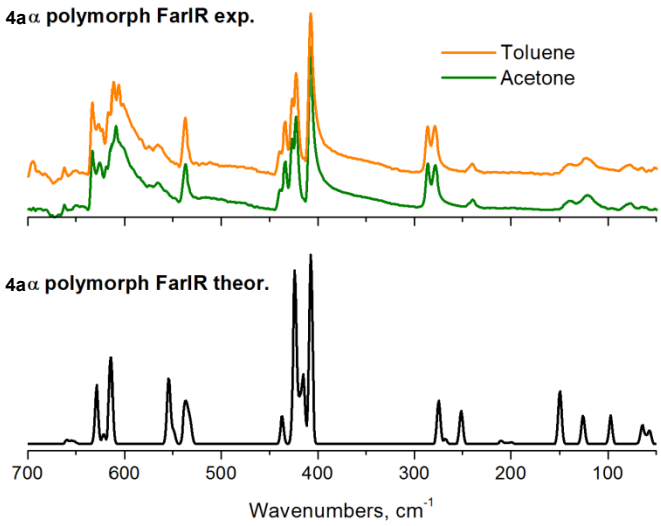

Figure S3. Experimental (top) and scaled predicted (bottom) FarIR spectra of the samples of **4a**α polymorph crystallized in toluene (orange) and acetone (green) in the solid phase (powder) in the 700–50 cm^{-1} spectral region. A scaling frequency factor of 0.97 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 4 cm^{-1}. All the FarIR experimental spectra have been normalized.

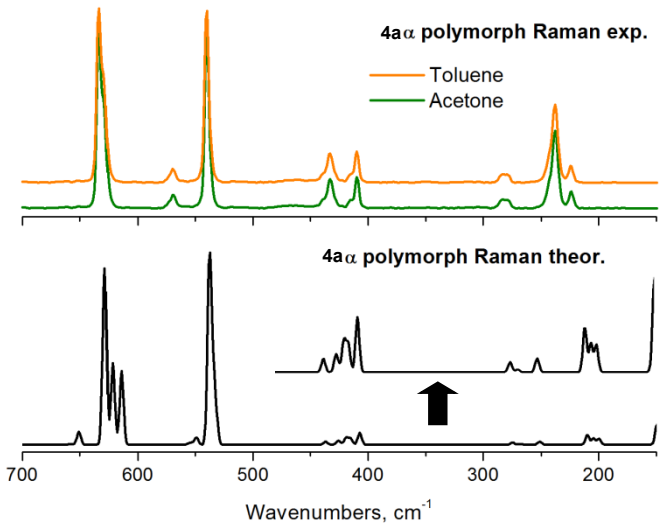

Figure S4. Experimental (top) and scaled predicted (bottom) Raman spectra of the samples of **4a**α polymorph crystallized in toluene (orange) and acetone (green) in the solid phase (powder) in the 700–150 cm^{-1} spectral region. A scaling frequency factor of 0.97 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 4 cm^{-1}. All the Raman experimental spectra have been normalized.

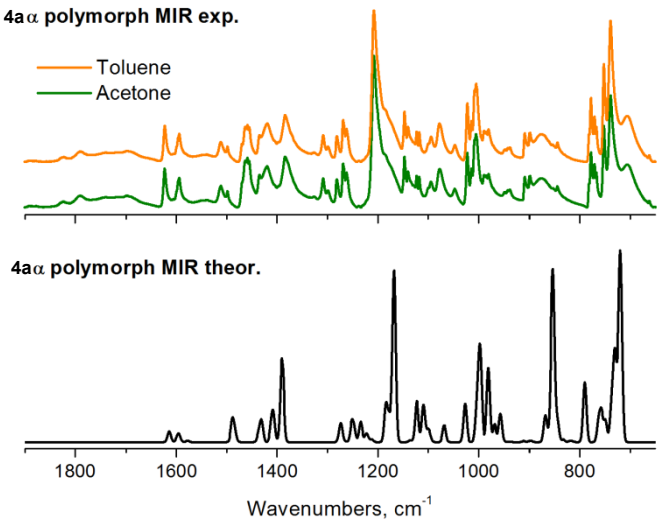

Figure S5. Experimental (top) and scaled predicted (bottom) IR spectra of the samples of **4a**α polymorph crystallized in toluene (orange) and acetone (green) in the solid phase (powder) in the 1900–650 cm^{-1} spectral region. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 8 cm^{-1}. All the IR experimental spectra have been normalized.

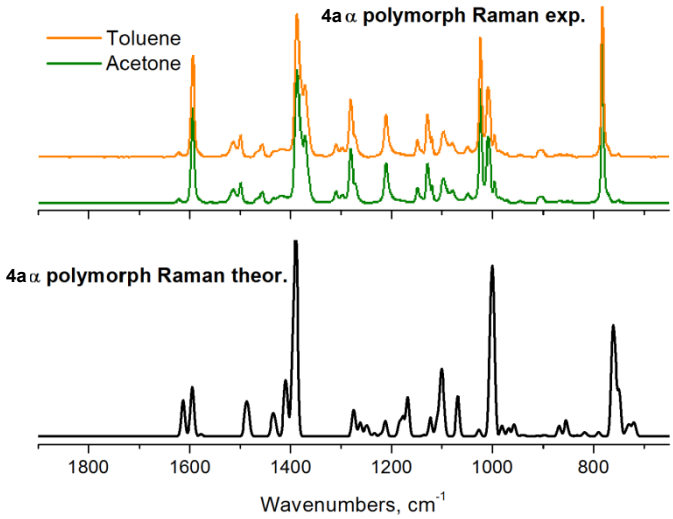

Figure S6. Experimental (top) and scaled predicted (bottom) Raman spectra of the samples of **4a**α polymorph crystallized in toluene (orange) and acetone (green) in the solid phase (powder) in the 1900–650 cm^{-1} spectral region. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 8 cm^{-1}. All the Raman experimental spectra have been normalized.

SI4) Experimental comparison of FarIR, IR and Raman spectra of 4aα and 4aβ polymorphs and those of the Madrid commercial sample

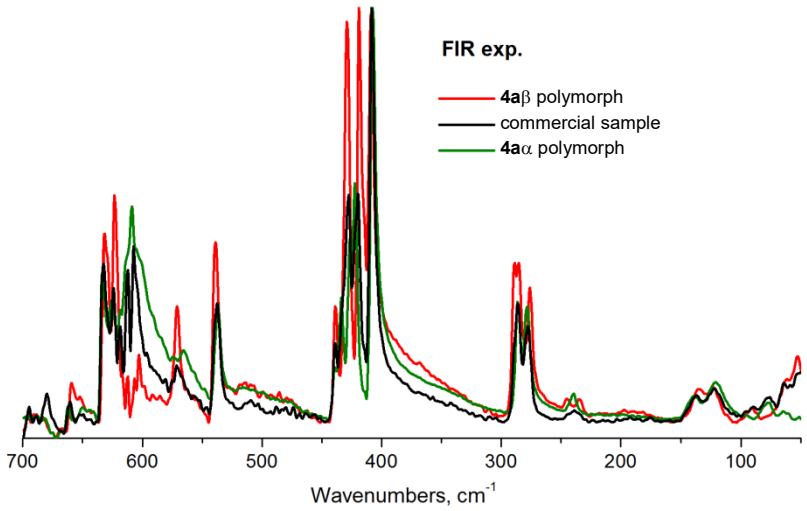

Figure S7. Experimental FarIR spectra of **4a**β polymorph (red), Madrid commercial sample (black) and **4a**α polymorph (green) in the solid phase (powder) in the 700-50 cm^{-1} spectral region. The three spectra have been normalized.

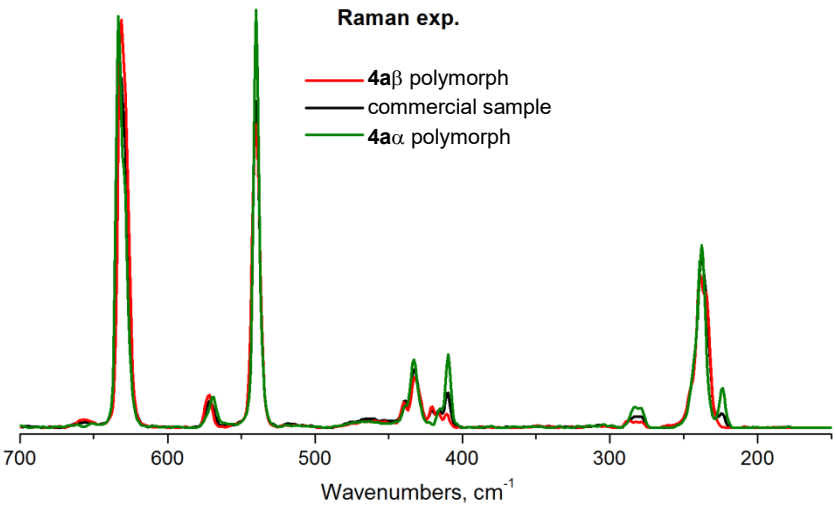

Figure S8. Experimental Raman spectra of **4a**β polymorph (in red), Madrid commercial sample (black) and **4a**α polymorph (green) in the solid phase (powder) in the 700-150 cm^{-1} spectral region. The three spectra have been normalized.

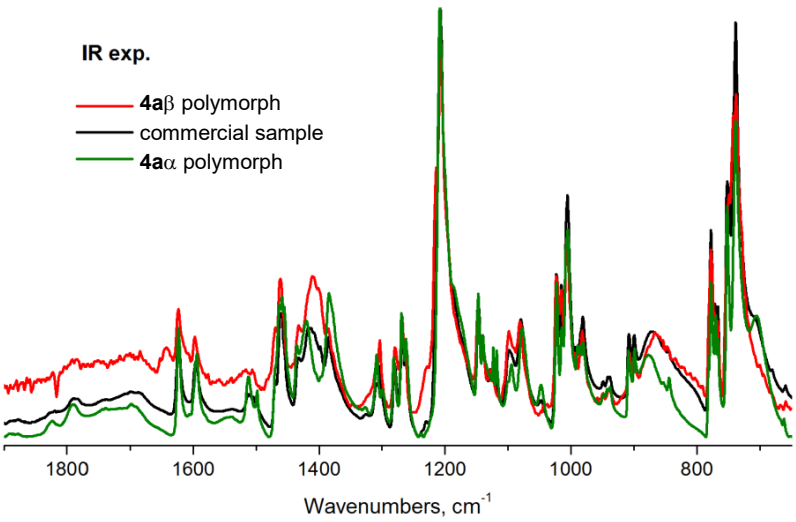

Figure S9. Experimental IR spectra of **4a**β polymorph (in red), Madrid commercial sample (black) and **4a**α polymorph (green) in the solid phase (powder) in the 1900-650 cm^{-1} spectral region. The three spectra have been normalized.

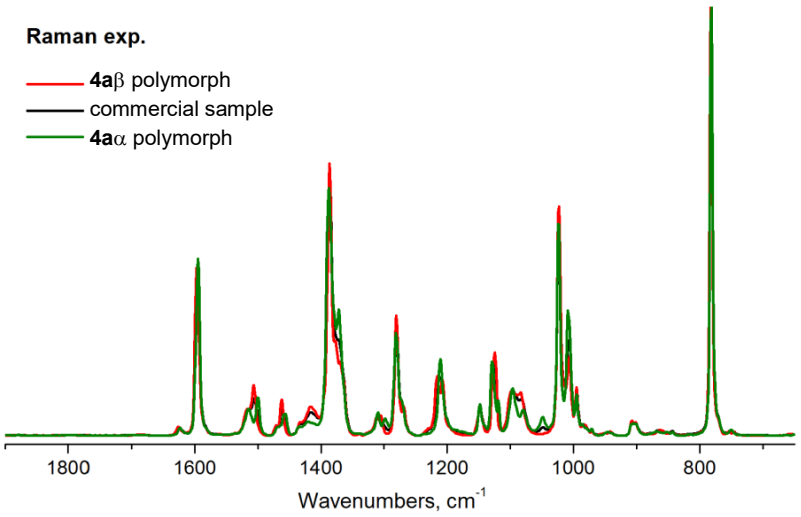

Figure S10. Experimental Raman spectra of **4a**β polymorph (in red), Madrid commercial sample (black) and **4a**α polymorph (green) in the solid phase (powder) in the 1900-650 cm^{-1} spectral region. The three spectra have been normalized.

SI5) Experimental VCD spectra of the 4aα polymorph sample crystallized from toluene, 4aβ polymorph and Madrid commercial sample (4aα + 4aβ) compared with the theoretical VCD spectrum of 4aα polymorph

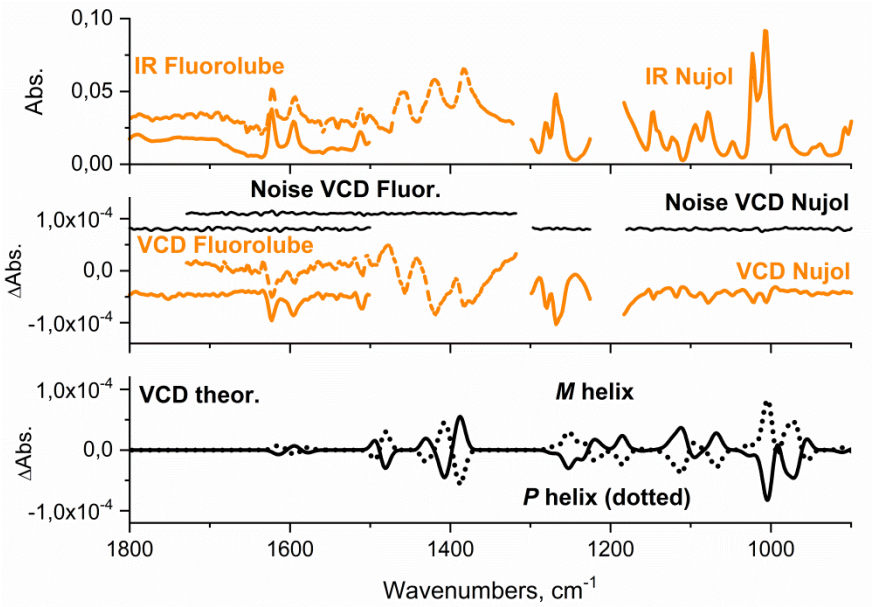

Figure S11. Experimental IR spectra (top) and experimental (middle) and theoretical (bottom) VCD spectra of the **4a**α polymorph sample crystallized in toluene, in fluorolube and nujol mulls in the 1800–900 cm^{-1} spectral region. In the middle graphic, the VCD noise is also shown. The raw VCD spectra were corrected by subtracting nujol or fluorolube signals. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 16 cm^{-1}.

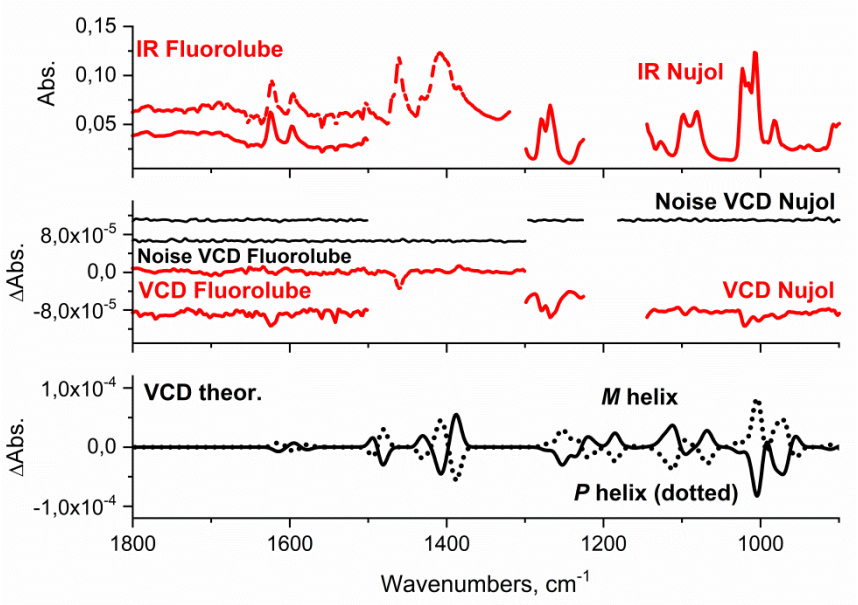

Figure S12. Experimental IR (top) and VCD (middle) spectra of **4a**β polymorph sample in fluorolube and nujol mulls in the 1800–900 cm^{-1} spectral region. In the middle graphic, the VCD noise is also shown. The raw VCD spectra were corrected by subtracting nujol or fluorolube signals. At the bottom, the theoretical VCD spectrum of **4a**α polymorph is shown. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 16 cm^{-1}.

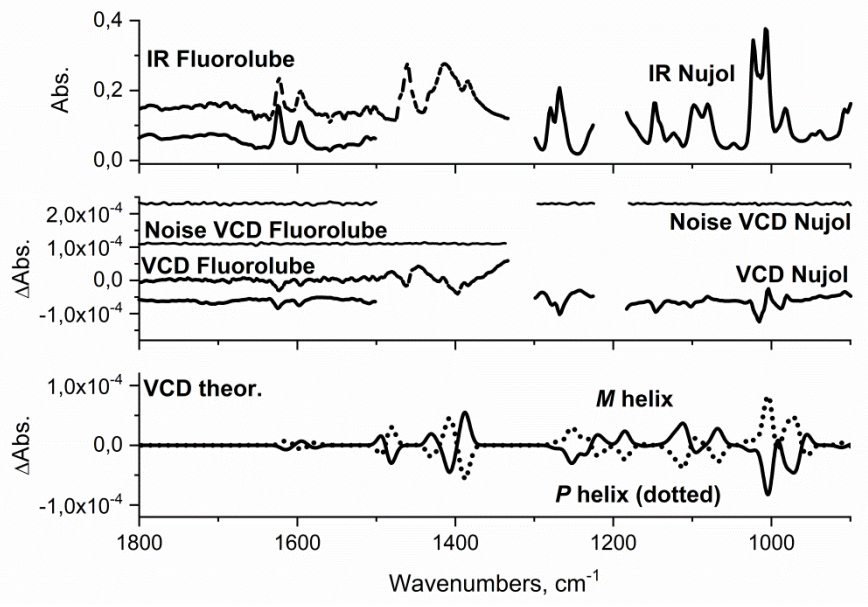

Figure S13. Experimental IR (top) and VCD (middle) spectra of Madrid commercial sample (**4a**α + **4a**β) in fluorolube and nujol mulls in the 1800–900 cm^{-1} spectral region. In the middle graphic, the VCD noise is also shown. The raw VCD spectra were corrected by subtracting nujol or fluorolube signals. At the bottom, the theoretical VCD spectrum of **4a**α polymorph is shown. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 8 cm^{-1}.

SI6) Experimental VCD spectra of the four orientations recorded for the 4aα polymorph sample crystallized from acetone

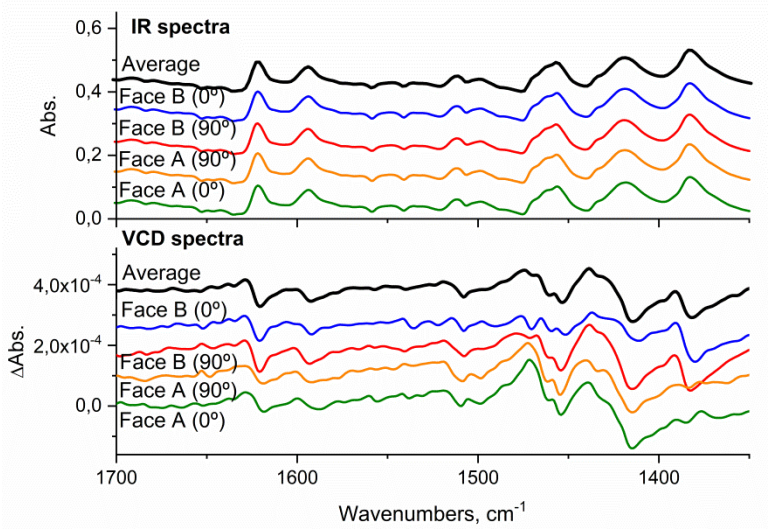

Figure S14. Experimental IR spectra (top) and VCD (bottom) of **4a**α polymorph in fluorolube mineral oil, showing the spectra recorded in selected orientations, face A (0 °), face A (90 °), face B (90 °) and face B (0 °), and the average VCD spectrum.

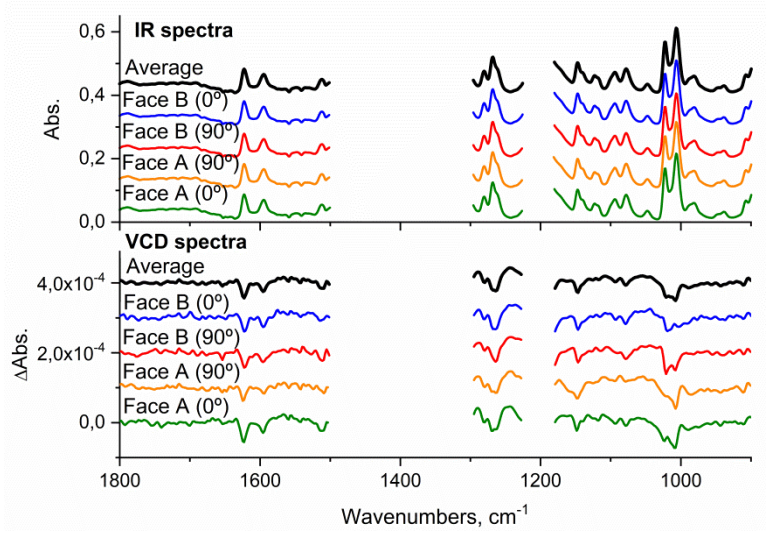

Figure S15. Experimental IR spectra (top) and VCD (bottom) of **4a**α polymorph in nujol mineral oil, showing the spectra recorded in selected orientations, face A (0 °), face A (90 °), face B (90 °) and face B (0 °), and the average VCD spectrum.

SI7) Experimental VCD spectra of the 4aα polymorph sample crystallized from acetone compared with the theoretical VCD spectra of 4aα polymorph (trimer 4-6, trimer 5-7 and tetramer 4-7)

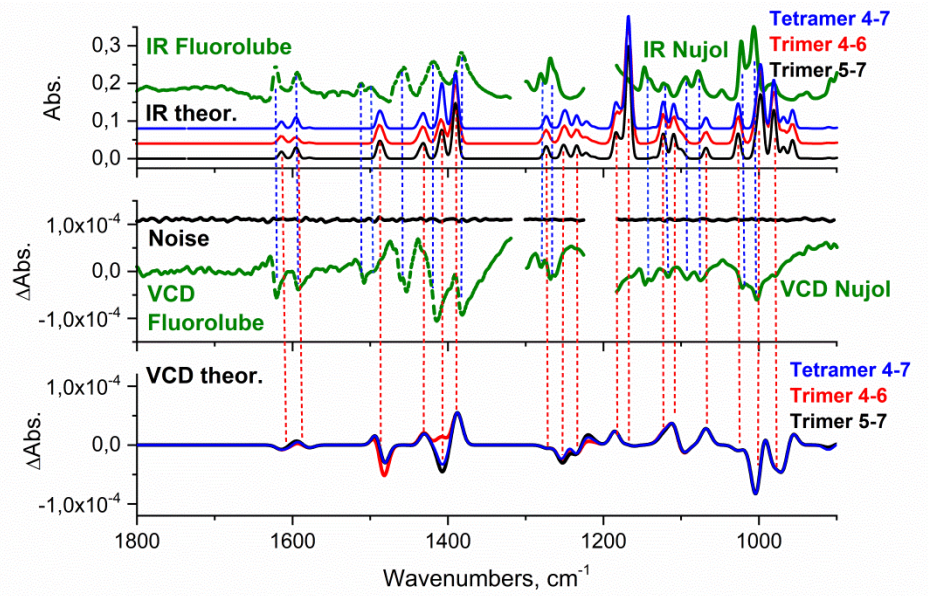

Figure S16. Experimental and theoretical IR spectra (top) and experimental (middle) and theoretical (bottom, *M* helix) VCD spectra of polymorph **4a**α in fluorolube and nujol mulls in the 1800–900 cm^{-1} spectral region. The VCD noise is also shown the middle graphic. The VCD spectra were corrected by subtracting the nujol or fluorolube signals. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 8 cm^{-1} (IR spectrum) and 16 cm^{-1} (VCD spectrum).

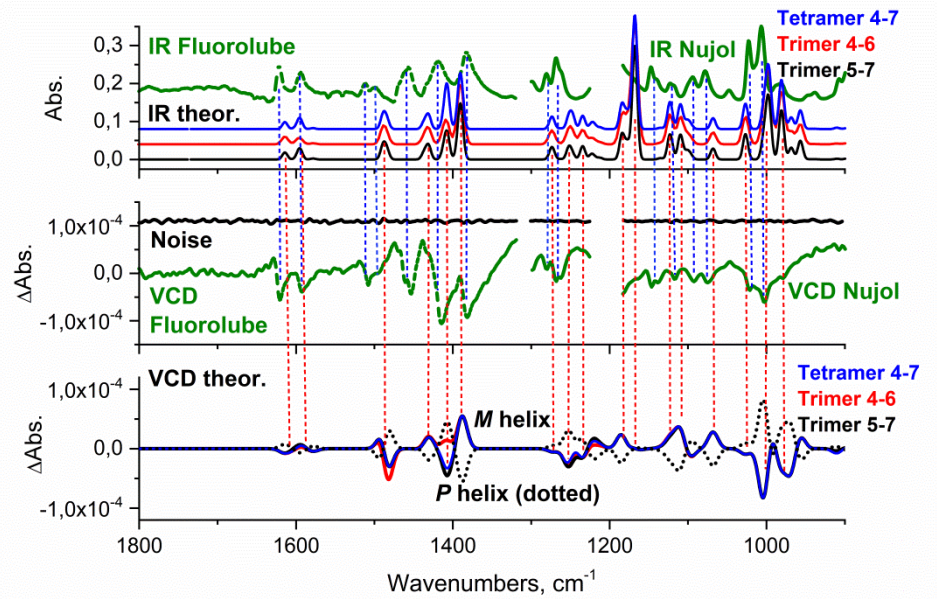

Figure S17. Experimental and theoretical IR spectra (top) and experimental (middle) and theoretical (bottom, *P* and *M* helices) VCD spectra of polymorph **4a**α in fluorolube and nujol mulls in the 1800–900 cm^{-1} spectral region. The VCD noise is also shown the middle graphic. The VCD spectra were corrected by subtracting the nujol or fluorolube signals. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 8 cm^{-1} (IR spectrum) and 16 cm^{-1} (VCD spectrum).

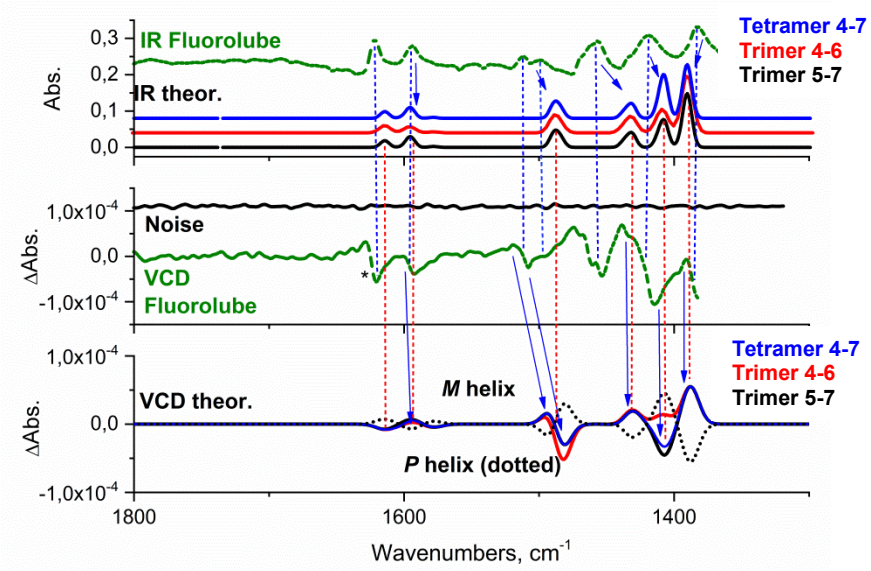

Figure S18. Experimental and theoretical IR spectra (top) and experimental (middle) and theoretical (bottom) VCD spectra of polymorph **4a**α in fluorolube mull in the 1800–1300 cm^{-1} spectral region. The VCD noise is also shown the middle graphic. The VCD spectra were corrected by subtracting the fluorolube signals. A scaling frequency factor of 0.94 was used. Gaussian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 8 cm^{-1} (IR spectrum) and 16 cm^{-1} (VCD spectrum). The band marked with a "*" was not analyzed because it also appeared in the VCD spectrum for the **4a**β sample (see Fig. S12).