STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 76 (2020)

Supporting information for article:

A positive to negative uniaxial thermal expansion crossover in an organic benzothienobenzothiophene structure

Dan G. Dumitrescu, Gilles H. Roche, Joël J. E. Moreau, Olivier J. Dautel and Arie van der Lee

Supporting information for:

A positive to negative uniaxial thermal expansion crossover in an organic benzothienobenzothiophene structure

Authors

Dan G. Dumitrescu[a], Gilles H. Roche[bc], Joël J. E. Moreau[b], Olivier J. Dautel[b] and Arie van der Lee[d]*

[a]Elettra, Sincrotrone Trieste S.C.p.A., Strada Statale 14 - km 163,5 in AREA Science Park, Basovizza, Trieste, 34149, Italy

[b]ICGM, Université de Montpellier, CNRS, ENSCM, Montpellier, France

[c]Université de Bordeaux, IMS, CNRS, UMR 5218, Bordeaux INP, ENSCBP, 33405, Talence, 33405, France

[d]Institut Européen des Membranes, IEM - UMR 5635, ENSCM, CNRS, Université de Montpellier, Montpellier, France

Correspondence email: arie.van-der-lee@umontpellier.fr

Table S1 Single-crystal X-ray diffraction experimental data and refinement results

The prefix ‘A’ in each column head refers to the first run ‘A’ and the number refer to the data collection temperature in K.

	A100	A110	A120	A130	A140	A150	A160
formula	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$
moiety	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$
***T* (K)**	100(2)	110(2)	120(2)	130(2)	140(2)	150(2)	160(2)
spacegroup	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
***a* (Å)**	13.428(2)	13.438(3)	13.450(3)	13.462(2)	13.473(2)	13.484(2)	13.496(3)
***b* (Å)**	5.060(1)	5.061(1)	5.063(1)	5.064(1)	5.066(1)	5.068(1)	5.070(1)
***c* (Å)**	14.255(1)	14.262(1)	14.270(1)	14.278(1)	14.286(1)	14.294(1)	14.303(1)
α (º)	90	90	90	90	90	90	90
β (º)	106.920(16)	106.973(15)	107.026(15)	107.080(14)	107.137(14)	107.194(12)	107.255(14)
γ (º)	90	90	90	90	90	90	90
***V* (Å^3)**	926.6(2)	927.7(3)	929.2(3)	930.4(2)	931.8(2)	933.2(2)	934.6(3)
Z	2	2	2	2	2	2	2
ρ (gcm^{-3})	1.378	1.377	1.374	1.373	1.371	1.369	1.366
M_r (gmol^{-1})	384.53	384.53	384.53	384.53	384.53	384.53	384.53
μ (mm^{-1})	0.291	0.290	0.290	0.289	0.289	0.289	0.288
R_{int}	0.0258	0.0248	0.0234	0.0233	0.0237	0.0231	0.0214
Θ_{max} (º)	29.886	29.894	29.890	29.887	29.884	29.882	29.889
N_{tot} (measured)	8234	8303	8199	8277	8296	8300	8282
N_{ref} (unique)	2730	2748	2739	2748	2749	2741	2741
N_{ref} (I>2σ(I))	2498	2488	2497	2496	2484	2472	2463
N_{ref} (least-squares)	2730	2748	2739	2748	2749	2741	2741
N_{par}	121	121	121	121	121	121	121
<σ(I)/I>	0.0251	0.0234	0.0230	0.0225	0.0225	0.0226	0.0218
R_1 (I>2σ(I))	0.0380	0.0385	0.0389	0.0384	0.0385	0.0391	0.0403
wR_2 (I>2σ(I))	0.1043	0.1059	0.1083	0.1072	0.1064	0.1079	0.1131
R_1 (all)	0.0405	0.0421	0.0421	0.0416	0.0420	0.0429	0.0438
wR_2 (all)	0.1063	0.1090	0.1110	0.1101	0.1092	0.1112	0.1158
GOF	1.081	1.060	1.081	1.073	1.077	1.068	1.093
$\Delta\rho$ (eÅ^{-3})	-0.428/0.951	-0.429/0.946	-0.450/0.930	-0.397/0.907	-0.375/0.909	-0.380/0.874	-0.432/0.830
crystal size (mm^3)	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12

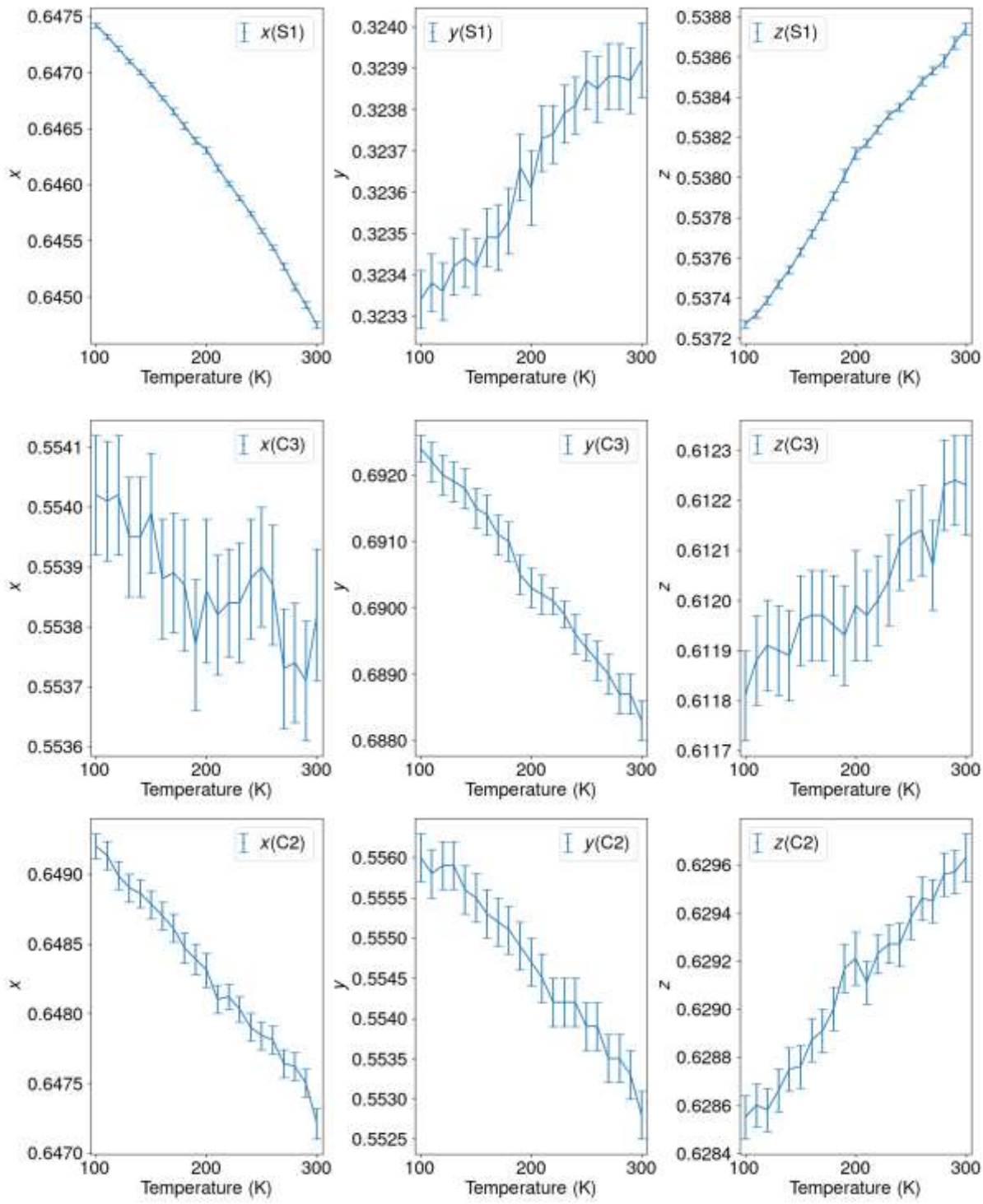
	A170	A180	A190	A200	A210	A220	A230
formula	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$
moiety	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$
***T* (K)**	170(2)	180(2)	190(2)	200(2)	210(2)	220(2)	230(2)
spacegroup	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
***a* (Å)**	13.508(3)	13.521(3)	13.535(3)	13.550(2)	13.569(2)	13.587(2)	13.606(2)
***b* (Å)**	5.073(1)	5.076(1)	5.078(1)	5.078(1)	5.078(1)	5.077(1)	5.077(1)
***c* (Å)**	14.312(1)	14.322(1)	14.332(1)	14.344(2)	14.355(2)	14.368(2)	14.379(2)
α (º)	90	90	90	90	90	90	90
β (º)	107.316(13)	107.384(14)	107.455(15)	107.529(17)	107.612(18)	107.690(16)	107.770(18)
γ (º)	90	90	90	90	90	90	90
***V* (Å^3)**	936.3(3)	938.1(3)	939.7(3)	941.1(2)	942.7(2)	944.3(2)	945.9(2)
Z	2	2	2	2	2	2	2
ρ (gcm^{-3})	1.364	1.361	1.359	1.357	1.355	1.352	1.350
M_r (gmol^{-1})	384.53	384.53	384.53	384.53	384.53	384.53	384.53
μ (mm^{-1})	0.288	0.287	0.287	0.286	0.286	0.285	0.285
R_{int}	0.0228	0.0223	0.0218	0.0226	0.0259	0.0240	0.0244
Θ_{max} (º)	29.878	29.893	29.876	29.893	29.868	29.887	29.880
N_{tot} (measured)	8289	8298	8316	8206	8423	8507	8516
N_{ref} (unique)	2751	2758	2767	2773	2785	2798	2802
N_{ref} (I>2σ(I))	2471	2465	2452	2418	2507	2563	2550
N_{ref} (least-squares)	2751	2758	2767	2773	2785	2798	2802
N_{par}	121	121	121	121	120	121	121
<σ(I)/I>	0.0222	0.0212	0.0212	0.0217	0.0254	0.0234	0.0235
R_1 (I>2σ(I))	0.0404	0.0415	0.0431	0.0476	0.0428	0.0383	0.0391
wR_2 (I>2σ(I))	0.1138	0.1153	0.1200	0.1317	0.1173	0.1134	0.1168
R_1 (all)	0.0440	0.0457	0.0476	0.0531	0.0464	0.0410	0.0422
wR_2 (all)	0.1166	0.1187	0.1243	0.1372	0.1209	0.1166	0.1225
GOF	1.082	1.071	1.092	1.096	1.057	1.040	1.042
$\Delta\rho$ (eÅ^{-3})	-0.407/0.798	-0.451/0.810	-0.499/0.801	-0.640/0.818	-0.543/0.648	-0.296/0.698	-0.297/0.667
crystal size (mm^3)	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12

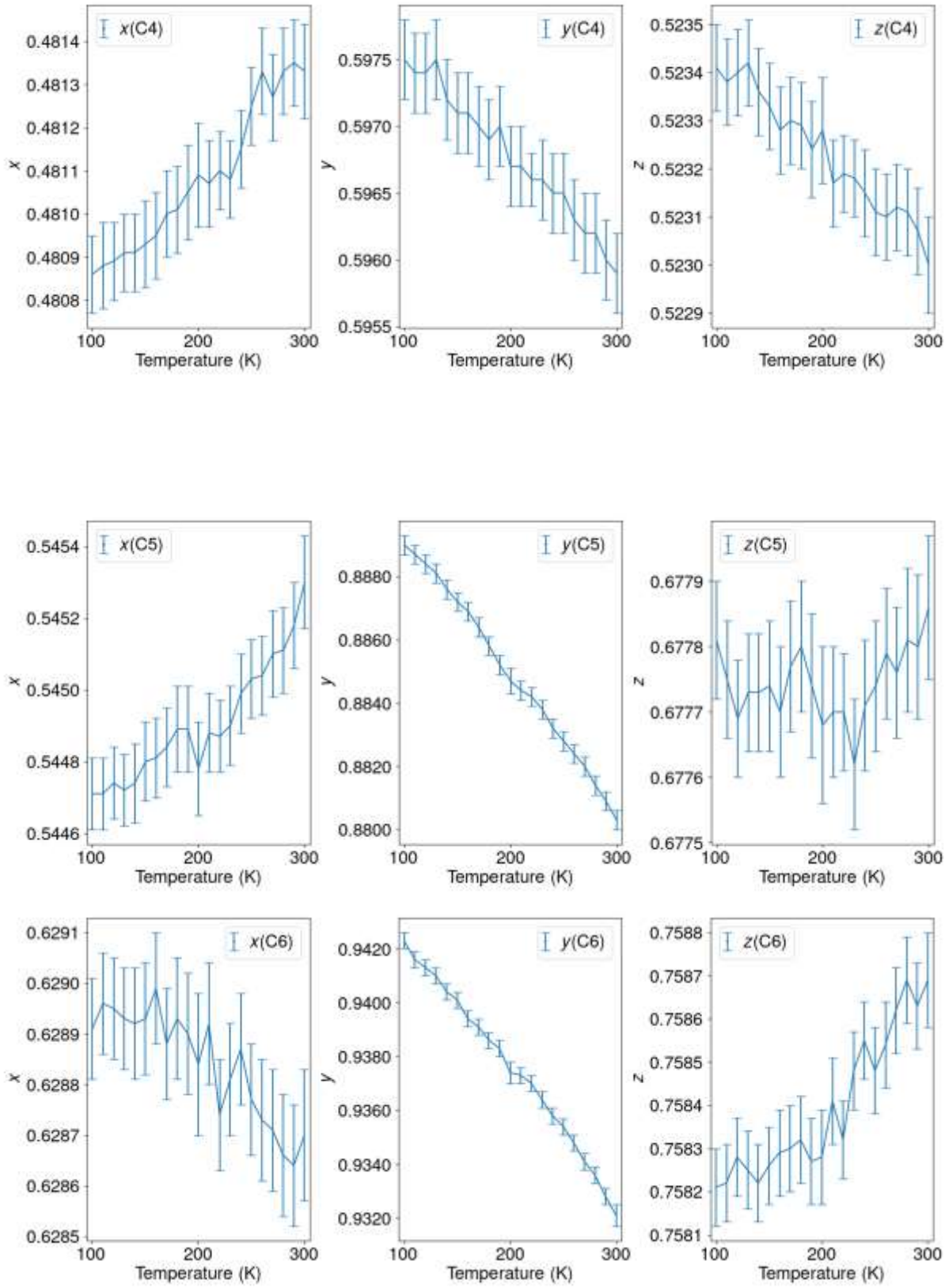
	A240	A250	A260	A270	A280	A290	A300
formula	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$
moiety	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$	$C_{22}H_{24}O_2S_2$
***T* (K)**	240(2)	250(2)	260(2)	270(2)	280(2)	290(2)	300(2)
spacegroup	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
***a* (Å)**	13.625(2)	13.644(3)	13.664(4)	13.684(4)	13.705(3)	13.725(2)	13.748(6)
***b* (Å)**	5.076(1)	5.076(1)	5.075(1)	5.074(1)	5.074(1)	5.073(1)	5.072(1)
***c* (Å)**	14.392(2)	14.405(3)	14.419(4)	14.433(4)	14.447(3)	14.461(2)	14.477(2)
α (º)	90	90	90	90	90	90	90
β (º)	107.852(19)	107.94(2)	108.02(3)	108.11(3)	108.20(2)	108.301(19)	108.402(19)
γ (º)	90	90	90	90	90	90	90
***V* (Å^3)**	947.4(2)	949.2(3)	950.8(4)	952.5(4)	954.4(3)	955.9(2)	957.9(5)
Z	2	2	2	2	2	2	2
ρ (gcm^{-3})	1.348	1.345	1.343	1.341	1.338	1.336	1.333
M_r (gmol^{-1})	384.53	384.53	384.53	384.53	384.53	384.53	384.53
μ (mm^{-1})	0.284	0.284	0.283	0.283	0.282	0.282	0.281
R_{int}	0.0257	0.0244	0.0256	0.0281	0.0239	0.0261	0.0292
Θ_{max} (º)	29.872	29.880	29.892	29.882	29.894	29.885	29.880
N_{tot} (measured)	8471	8491	8501	8556	8550	8549	8661
N_{ref} (unique)	2793	2806	2820	2820	2833	2837	2848
N_{ref} (I>2σ(I))	2534	2530	2523	2505	2496	2459	2430
N_{ref} (least-squares)	2793	2806	2820	2820	2833	2837	2848
N_{par}	121	121	121	121	121	121	121
<σ(I)/I>	0.0250	0.0240	0.0248	0.0274	0.0238	0.0260	0.0287
R_1 (I>2σ(I))	0.0397	0.0392	0.0407	0.0405	0.0415	0.0415	0.0430
wR_2 (I>2σ(I))	0.1179	0.1154	0.1215	0.1216	0.1239	0.1231	0.1101
R_1 (all)	0.0429	0.0427	0.0448	0.0449	0.0463	0.0469	0.0493
wR_2 (all)	0.1214	0.1189	0.1262	0.1268	0.1297	0.1306	0.1161
GOF	1.024	1.002	1.031	1.029	1.007	1.016	0.865
$\Delta\rho$ (eÅ^{-3})	-0.312/0.647	-0.272/0.631	-0.326/0.611	-0.292/0.581	-0.269/0.563	-0.251/0.567	-0.289/0.552
crystal size (mm^3)	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12	0.02x0.06x0.12

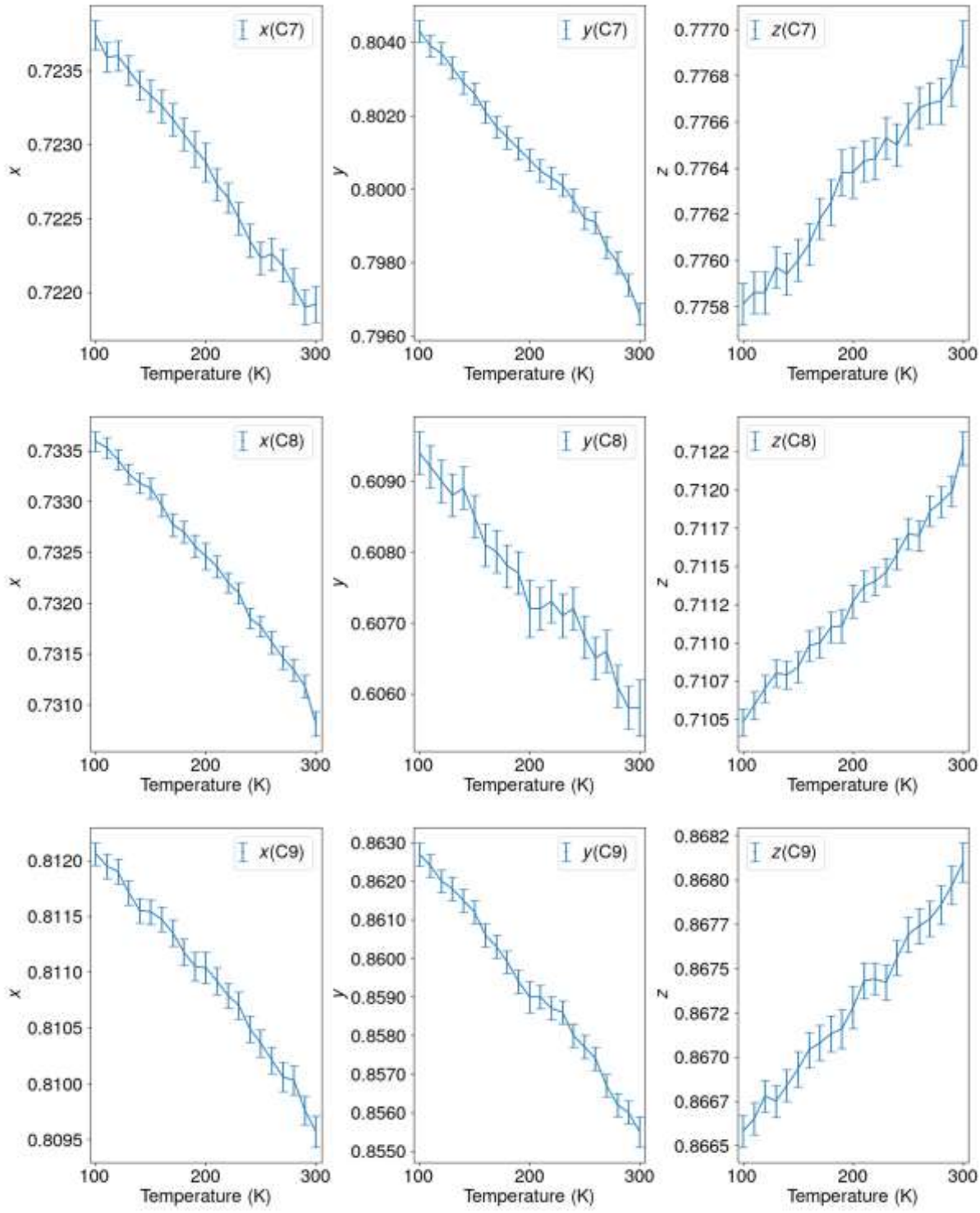
Table S2 Comparison of results obtained by a Hirshfeld atomic refinement (HAR) and by an independent atom model refinement (IAM) on two different crystals of **BTBT-C4OH**.

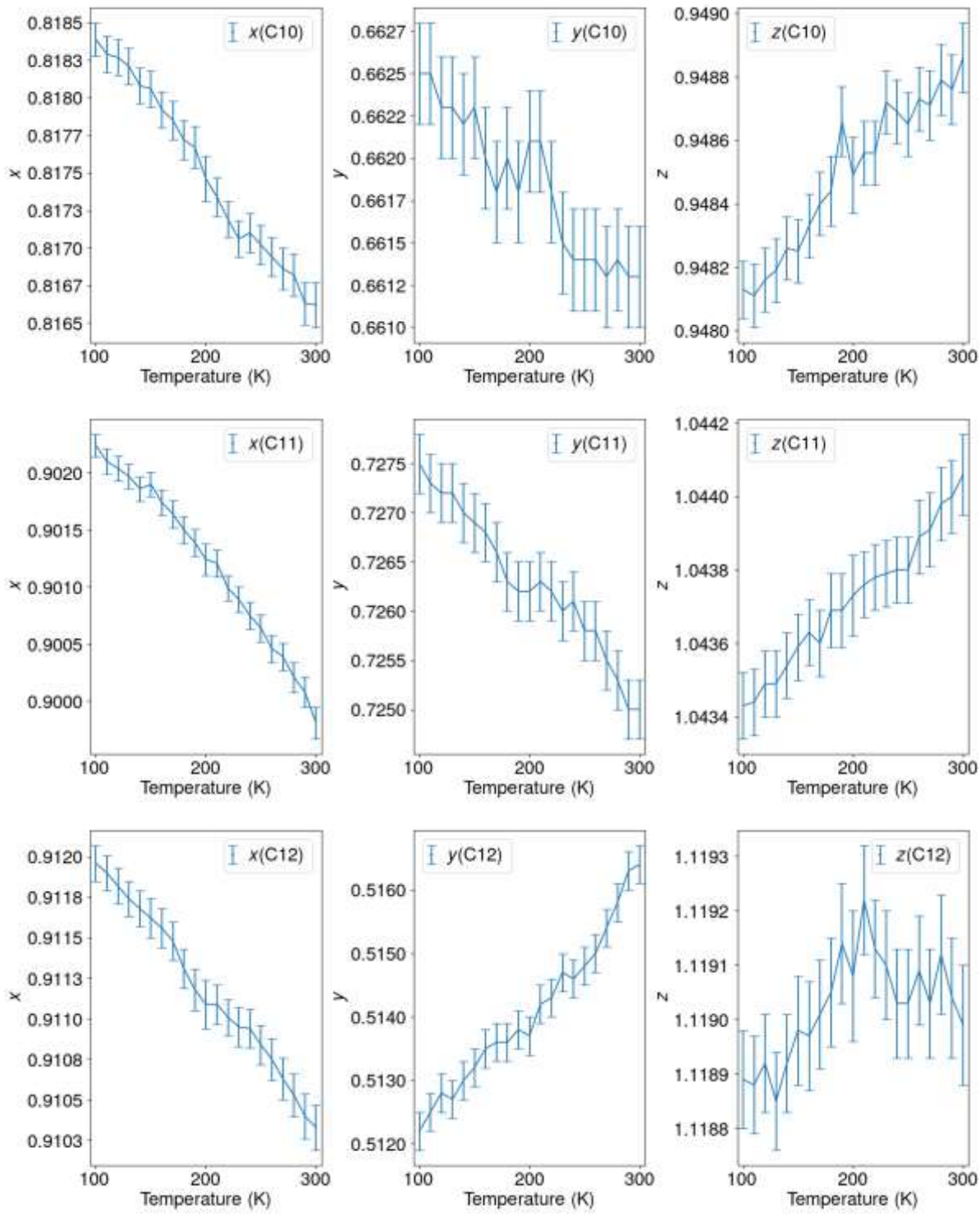
Atom	$\angle(\boldsymbol{v}_{\perp}, \boldsymbol{u}(\lambda_1))$		$\angle(\boldsymbol{v}_{\perp}, \boldsymbol{u}(\lambda_2))$		$\angle(\boldsymbol{v}_{\perp}, \boldsymbol{u}(\lambda_3))$		λ_2/λ_1		λ_3/λ_1	
	HAR	IAM	HAR	IAM	HAR	IAM	HAR	IAM	HAR	IAM
S1	10.3	10.5	89.9	89.1	79.7	79.6	0.6	0.7	0.5	0.5
C2	22.1	81.6	82.4	35.3	69.4	56.0	0.9	0.9	0.7	0.7
C3	46.4	77.7	50.3	39.3	70.0	53.4	0.9	0.9	0.7	0.7
C4	17.8	33.6	84.7	79.0	73.0	58.7	0.8	0.9	0.6	0.7
C5	8.9	14.9	87.6	85.7	81.5	75.8	0.8	0.9	0.5	0.6
C6	16.0	87.2	76.0	11.8	82.3	78.5	1.0	0.8	0.6	0.6
C7	89.4	86.6	16.2	42.2	73.8	48.0	0.8	0.6	0.5	0.5
C8	14.8	40.2	77.0	57.0	83.1	69.8	0.8	0.9	0.6	0.7
C9	81.9	81.8	10.6	8.5	83.3	88.0	0.7	0.7	0.5	0.5
C10	66.5	67.6	23.7	24.4	87.7	80.8	0.5	0.5	0.4	0.4
C11	62.5	67.0	27.5	23.7	89.4	84.6	0.6	0.6	0.4	0.5
C12	58.4	61.8	35.7	29.8	75.1	81.2	0.6	0.6	0.5	0.5
O13	52.2	56.8	42.1	41.5	74.3	68.1	0.7	0.6	0.4	0.4

The HAR was performed on 116 K data and the IAM refinement on 110 K data. The angles between the vector normal v⊥ of the least-squares plane of the BTBT core and the eigenvectors of the non-hydrogen atomic displacement tensors are compared (in degrees) as well as the ratios of the second and third eigenvalues with respect to the first eigenvalue. The results show that quality of the directions of the eigenvectors for a number of atoms is most probably not optimal, but for others a very good agreement is found.


x(S1)
y(S1)
z(S1)
x(C3)
y(C3)
z(C3)
x(C2)
y(C2)
z(C2)
Temperature (K)


x(C4)
y(C4)
z(C4)
x(C5)
y(C5)
z(C5)
x(C6)
y(C6)
z(C6)
Temperature (K)


x(C7)
y(C7)
z(C7)
x(C8)
y(C8)
z(C8)
x(C9)
y(C9)
z(C9)
x
y
z
Temperature (K)
100
200
300
0.7235
0.7230
0.7225
0.7220
0.8040
0.8020
0.8000
0.7980
0.7960
0.7770
0.7768
0.7766
0.7764
0.7762
0.7760
0.7758
0.7335
0.7330
0.7325
0.7320
0.7315
0.7310
0.6090
0.6080
0.6070
0.6060
0.7122
0.7120
0.7117
0.7115
0.7112
0.7110
0.7107
0.7105
0.8120
0.8115
0.8110
0.8105
0.8100
0.8095
0.8630
0.8620
0.8610
0.8600
0.8590
0.8580
0.8570
0.8560
0.8550
0.8682
0.8680
0.8677
0.8675
0.8672
0.8670
0.8667
0.8665


x(C10)
y(C10)
z(C10)
x(C11)
y(C11)
z(C11)
x(C12)
y(C12)
z(C12)
Temperature (K)

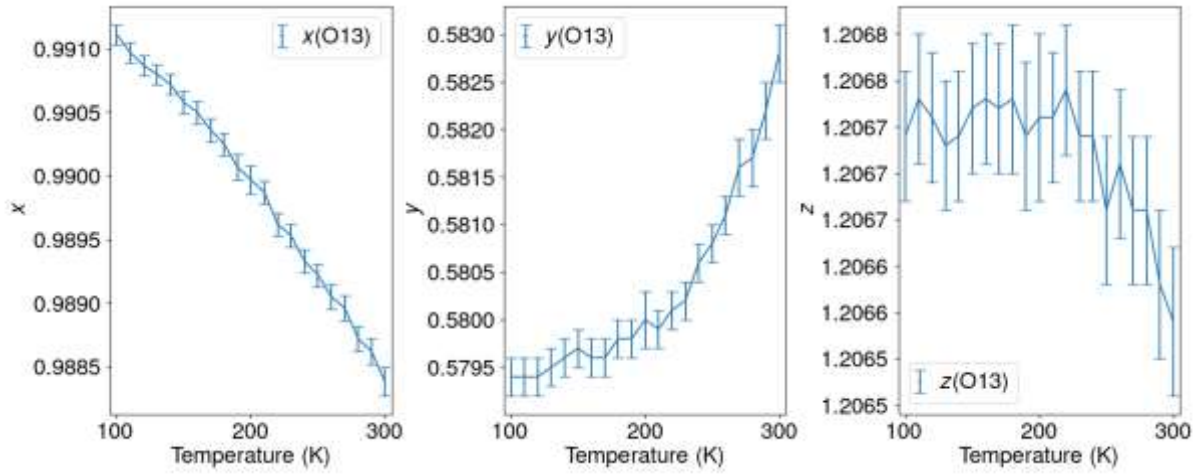


Figure S1 Temperature evolution of fractional crystallographic coordinates for all non-hydrogen atoms

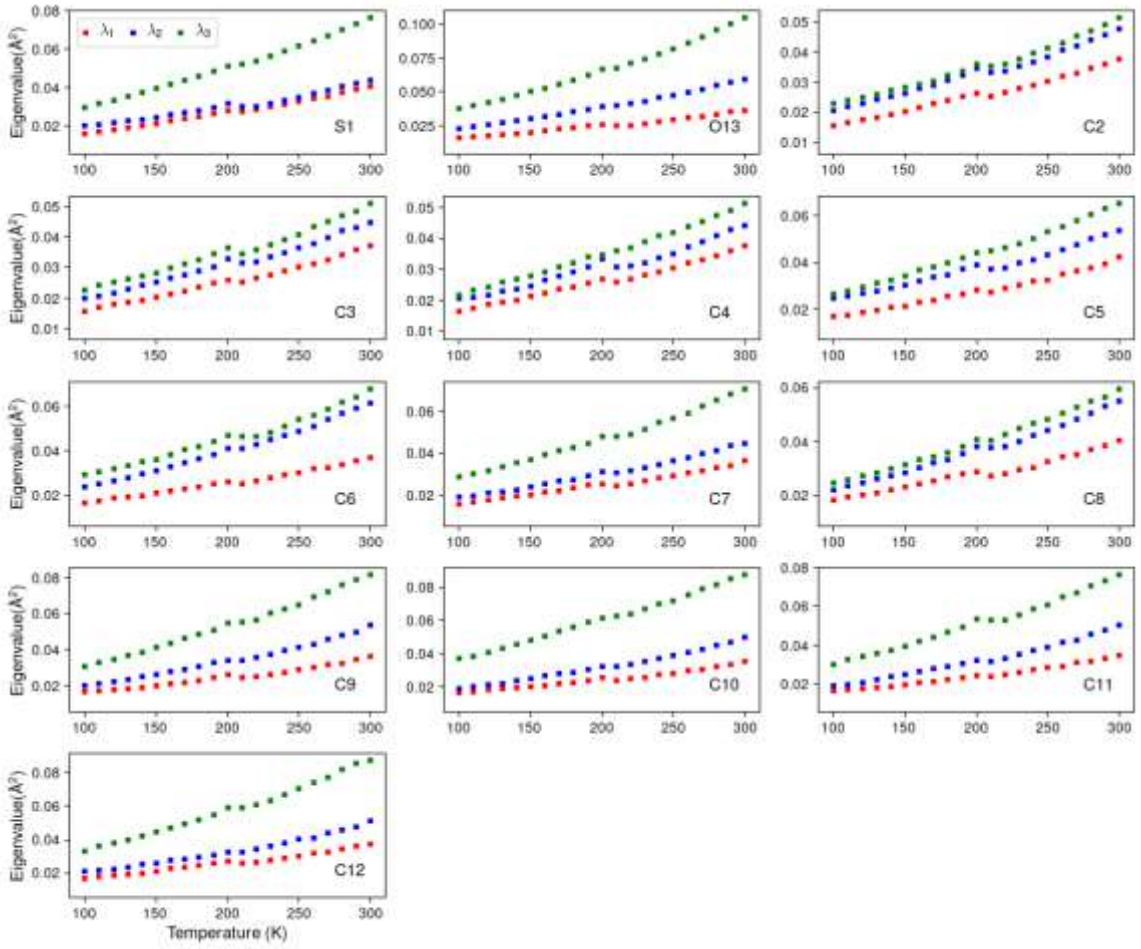
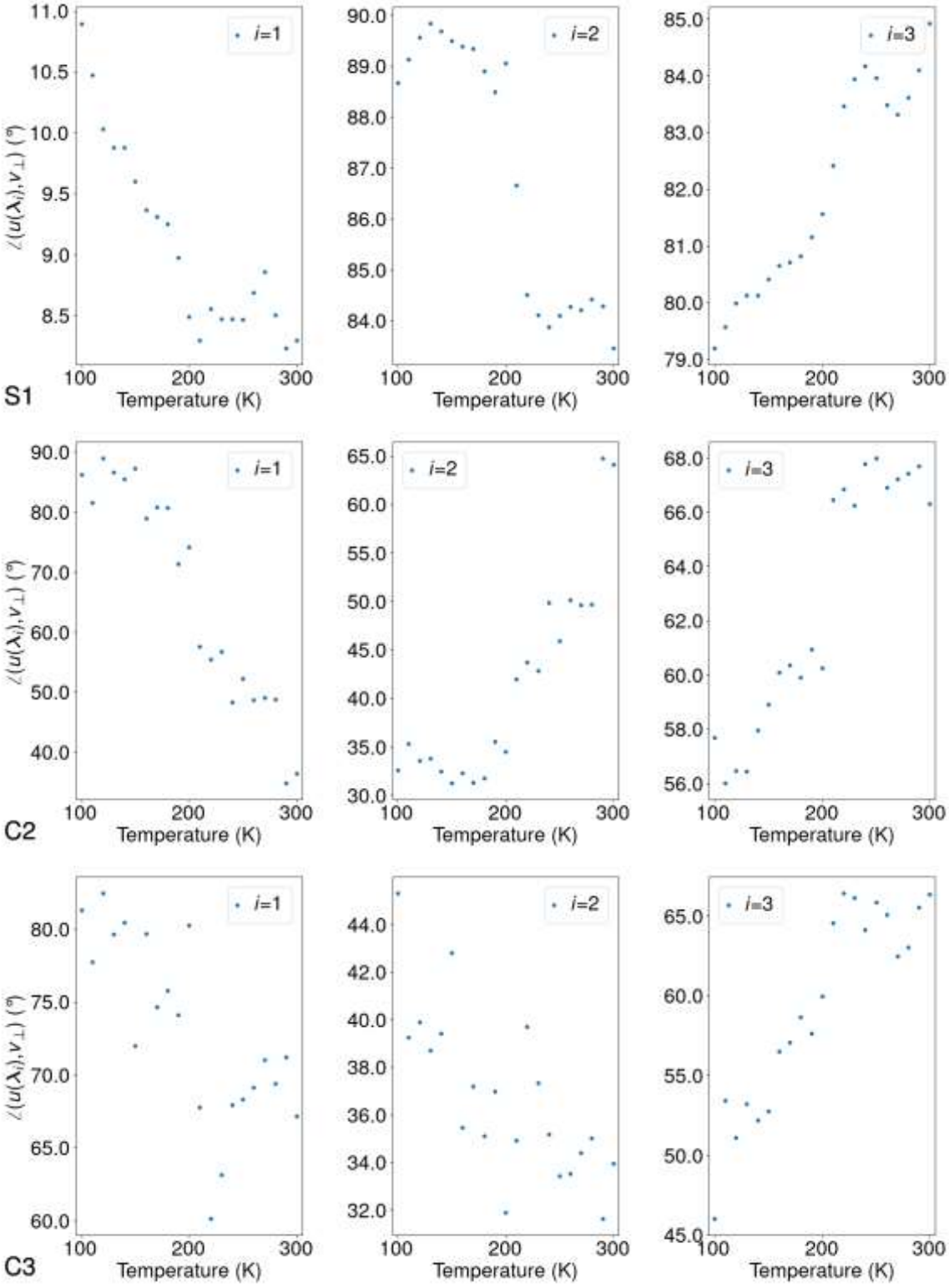
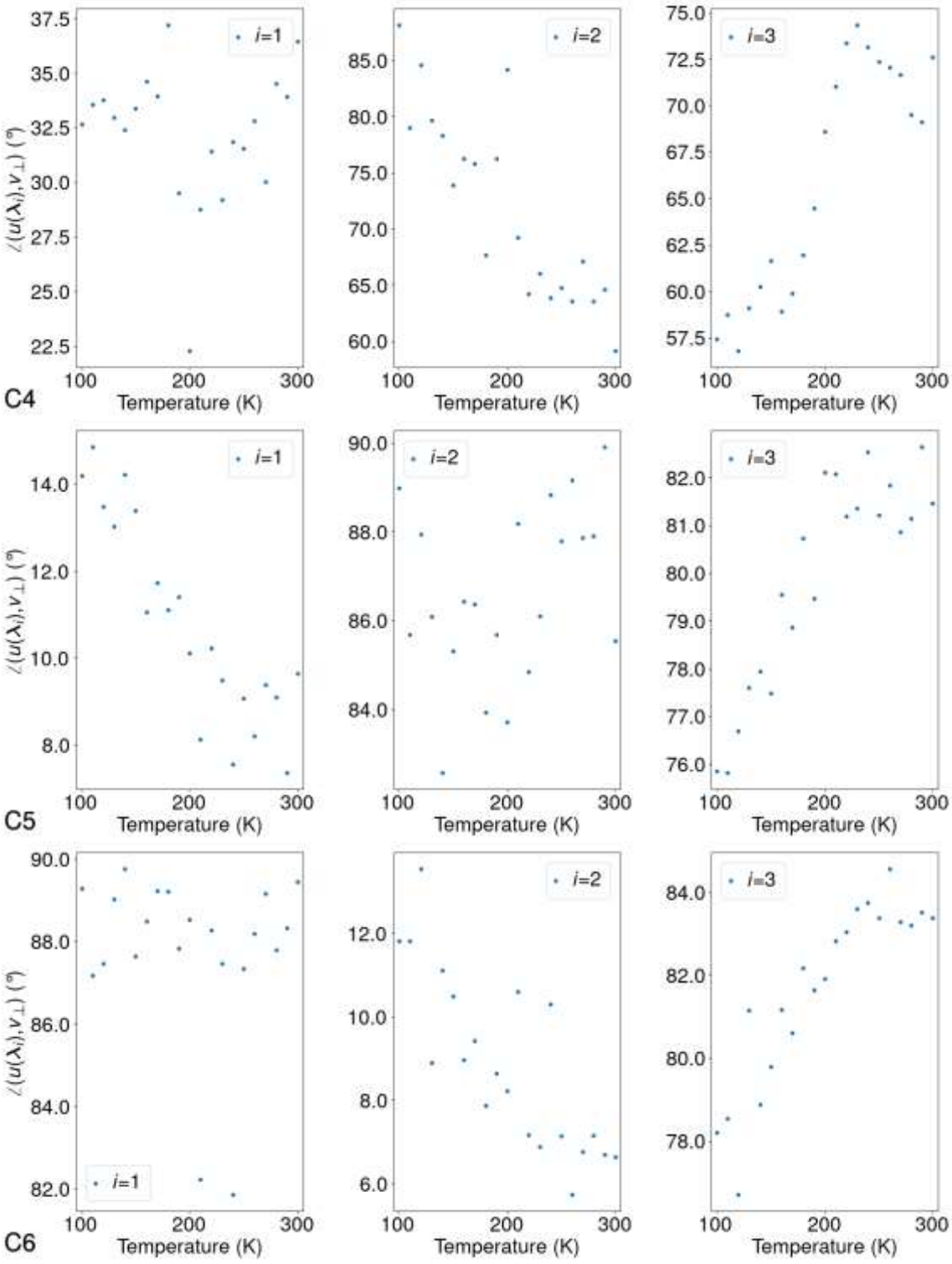
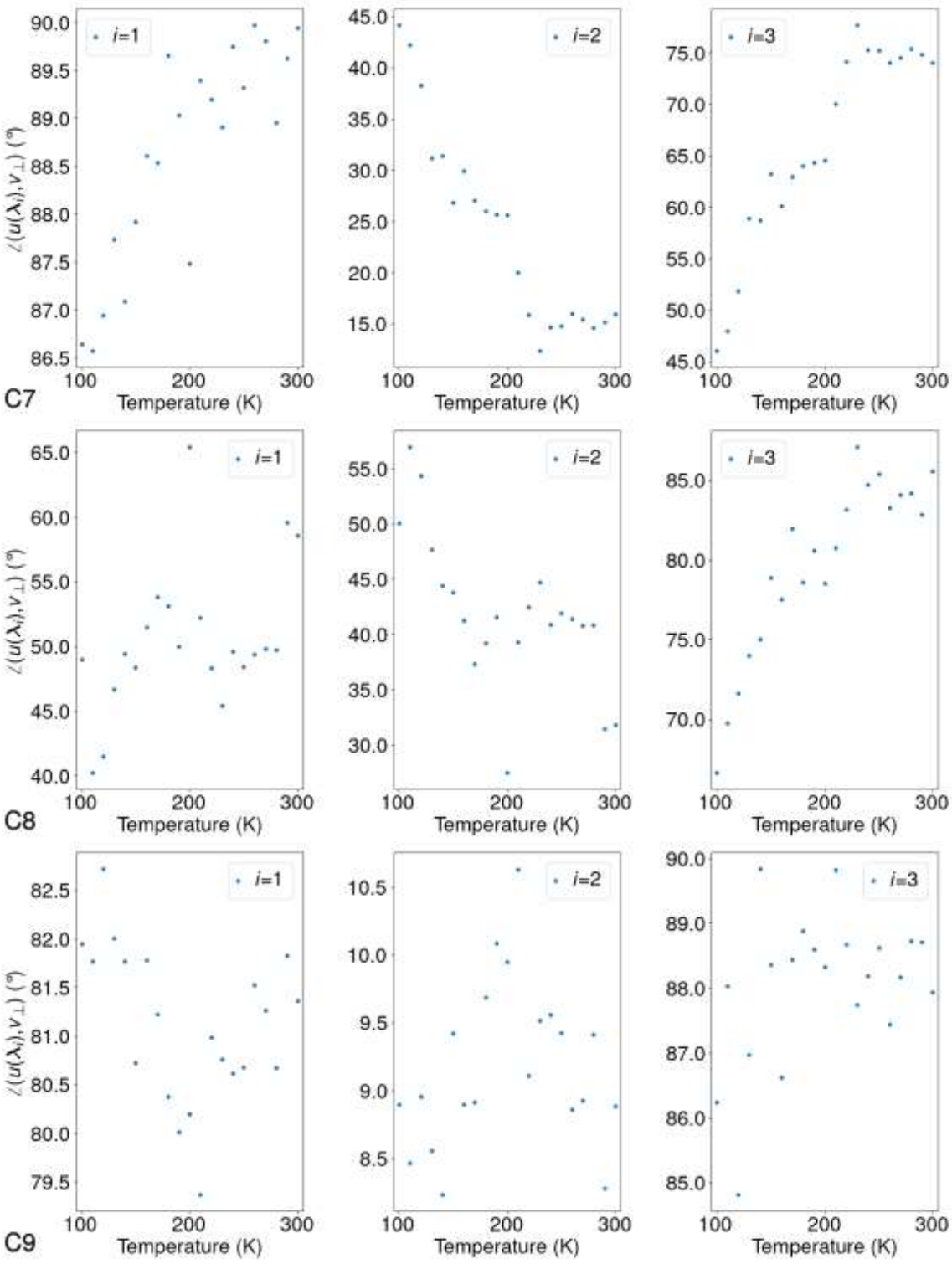
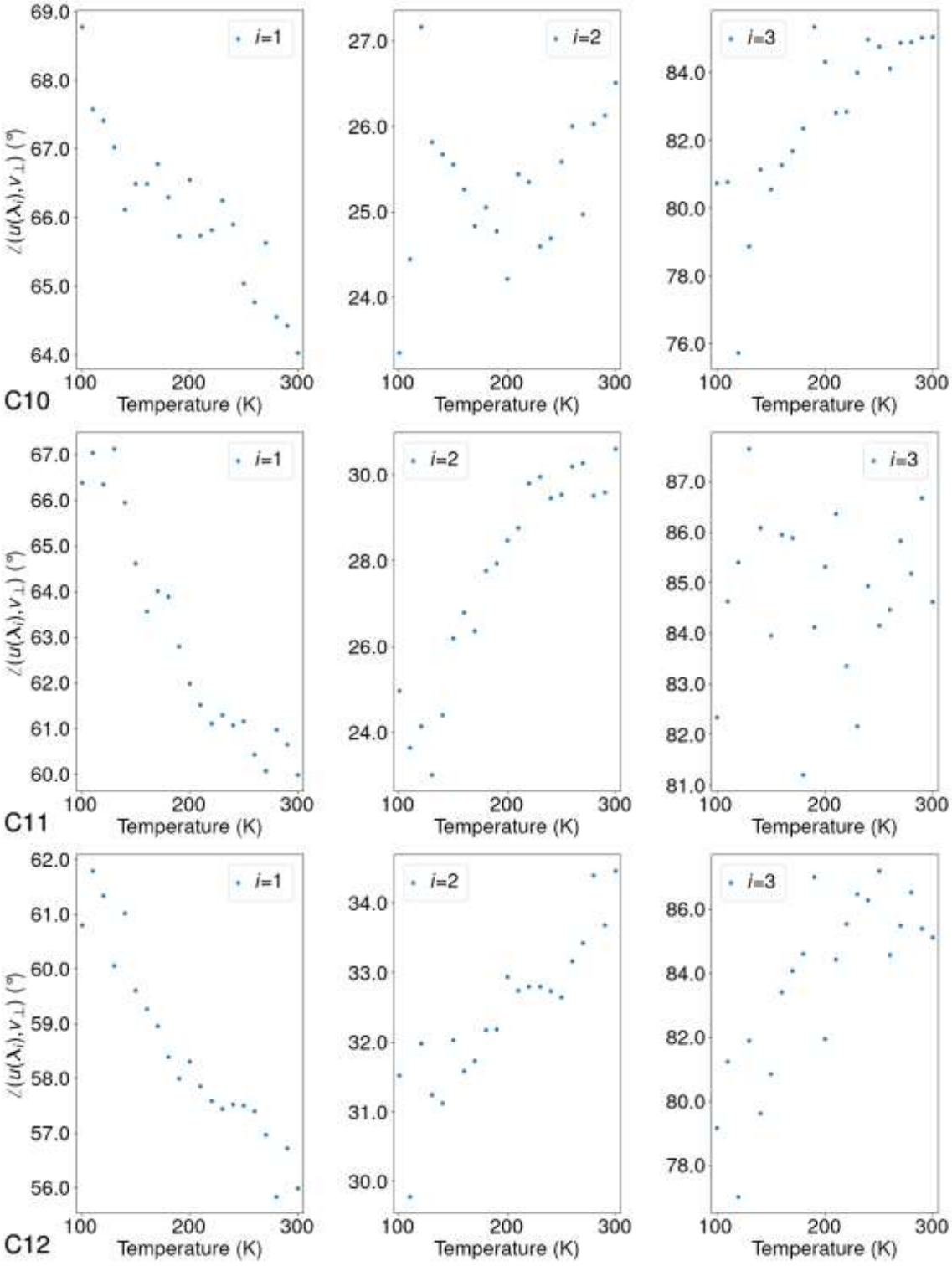


Figure S2 Eigenvalues of the anisotropic atomic displacement tensor for the non-hydrogen atoms in the structure of **BTBT-C4OH** as a function of temperature. The vertical scale of the different plots is not the same.


S1
C2
C3
i=1
i=2
i=3
∠(u(λi),v⊥) (°)
Temperature (K)


C4
C5
C6
i=1
i=2
i=3
∠(u(λi),v⊥) (°)
Temperature (K)
100
200
300


C7
C8
C9
i=1
i=2
i=3
∠(u(λi),v⊥) (°)
Temperature (K)
100
200
300


C10
C11
C12
i=1
i=2
i=3
∠(u(λi),v⊥) (°)
Temperature (K)
100
200
300

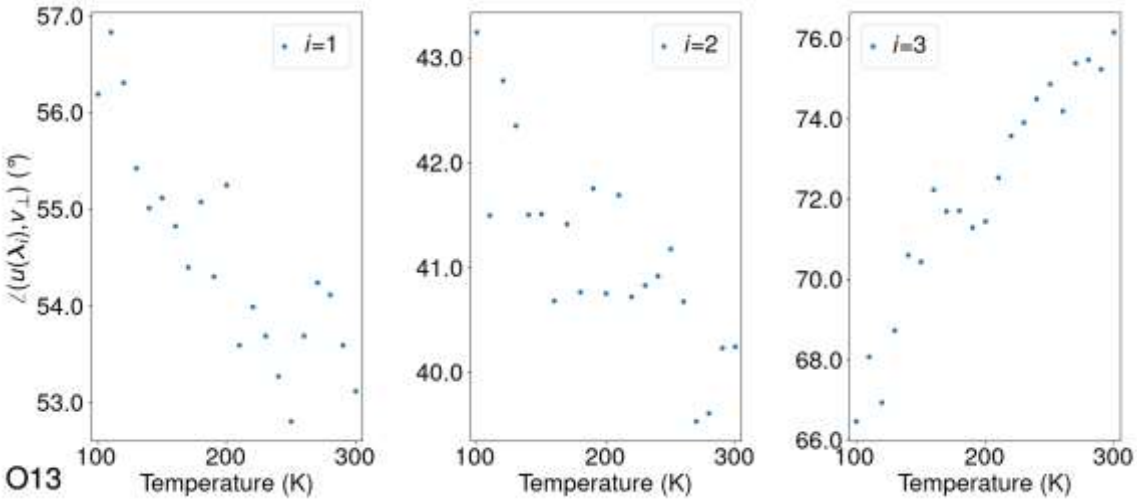
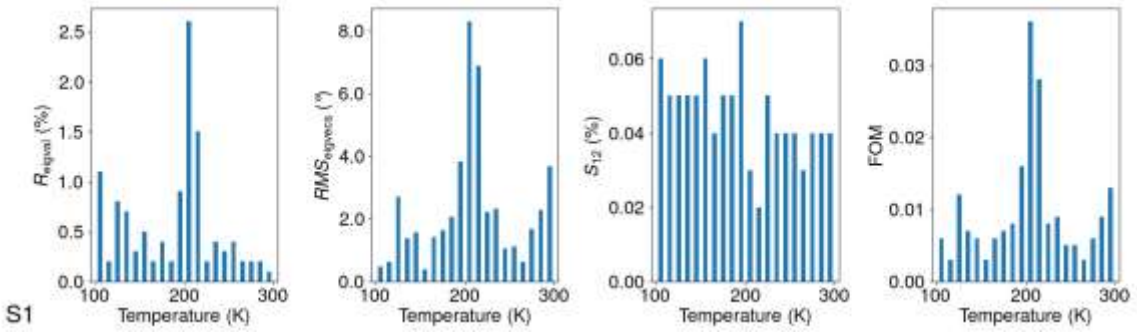
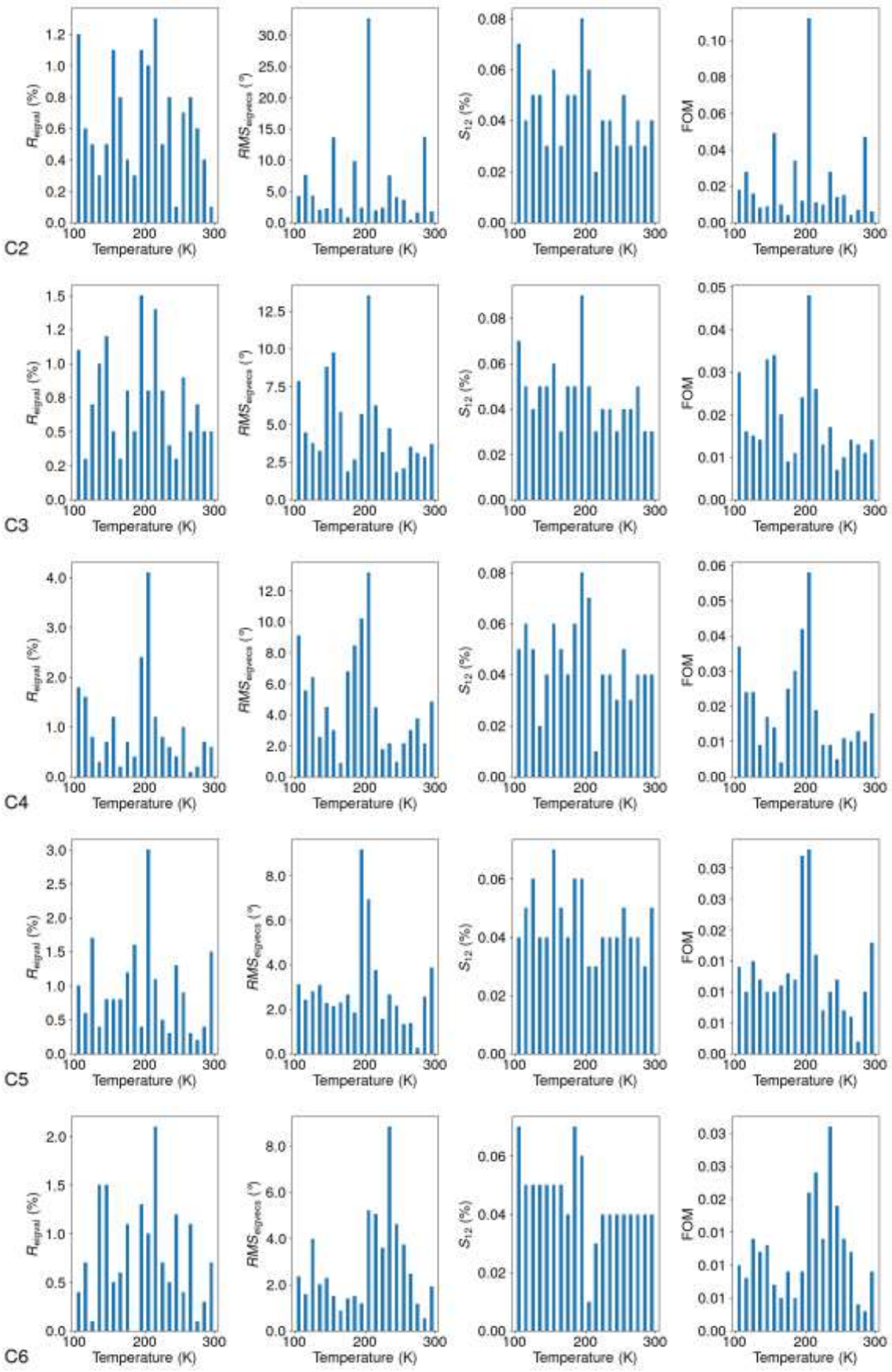
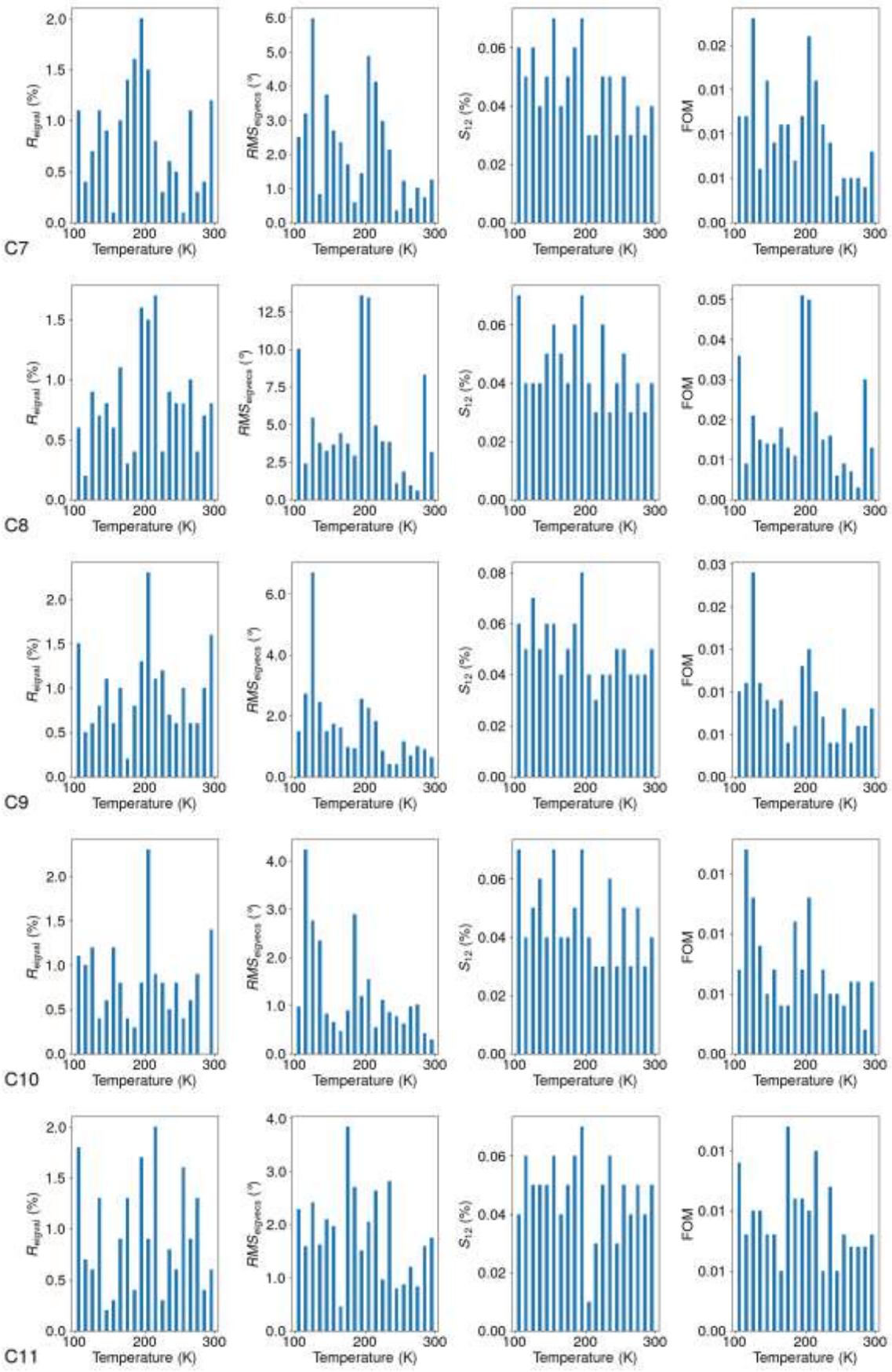


Figure S3 Temperature evolution of angles between the normal vector of the **BTBT** least-squares plane and the atomic principal displacement eigenvectors for all non-hydrogen atoms. The least squares plane of the **BTBT** core has been calculated in a cartesian coordinate system using singular value decomposition followed by least-squares refinement on the obtained solution. The eigenvalues and eigenvectors of the atomic displacement tensors have been determined by solving the eigenvalue problem. The eigenvalues and eigenvectors have then been sorted in decreasing order of the eigenvalues. However, this does not lead always to the correct order in the temperature sequence when the eigenvalues are close to each other. The problem shows up by unnatural large jumps of the angles between successive points. One problem case appeared for atom C2, where the first two eigenvalues and corresponding eigenvectors needed to be swapped in order to obtain a more natural plot. The problem could have been anticipated by inspecting the temperature variation of the two largest eigenvalues in Fig. S2 for C2 which are indeed very close to each other below the phase transition temperature.




C2
C3
C4
C5
C6
R_{eigval} (%)
$RMS_{eigvecs}$ (°)
S_{12} (%)
FOM
Temperature (K)


C7
C8
C9
C10
C11
R_{eigval} (%)
RMS_{eigvecs} (°)
S_{12} (%)
FOM
Temperature (K)

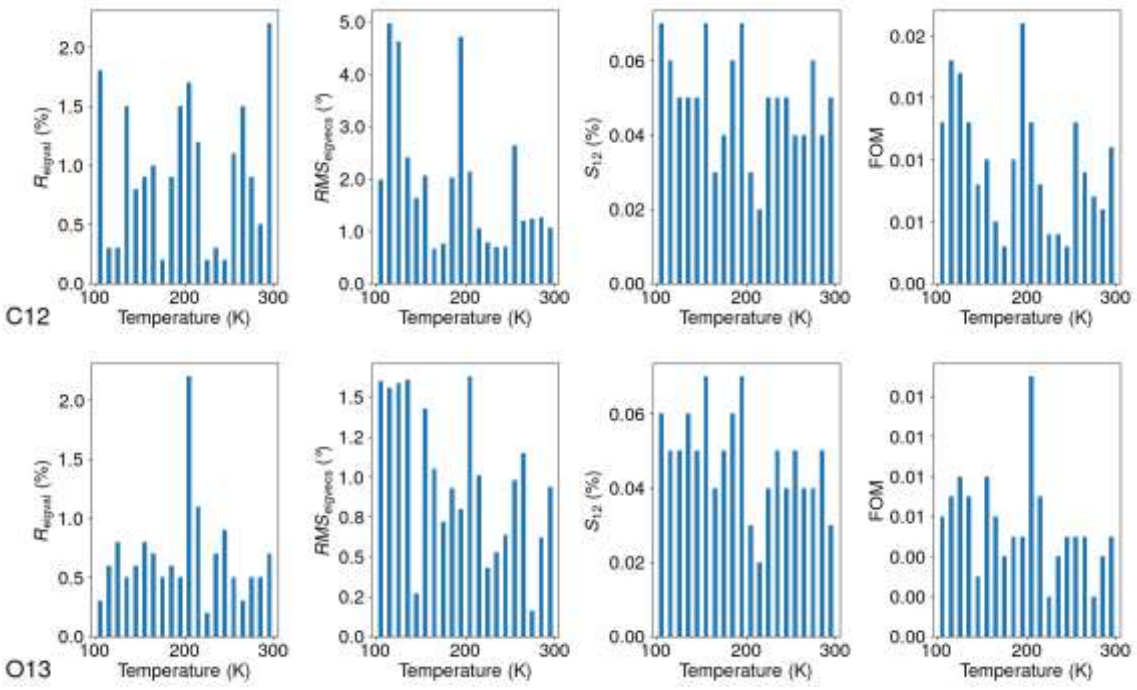


Figure S4 R_{eigval}, RMS_{eigvecs}, S_{12}, and the combined figure of merit FOM for the ADP's of the non hydrogen atoms in the molecule as a function of temperature.

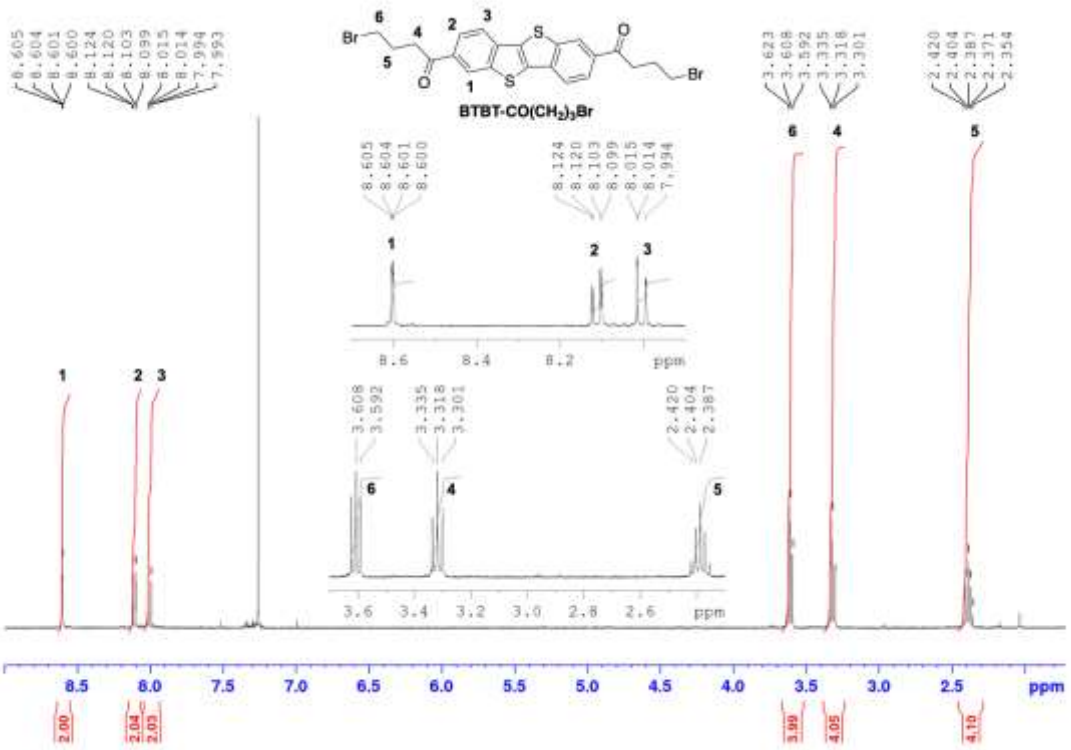
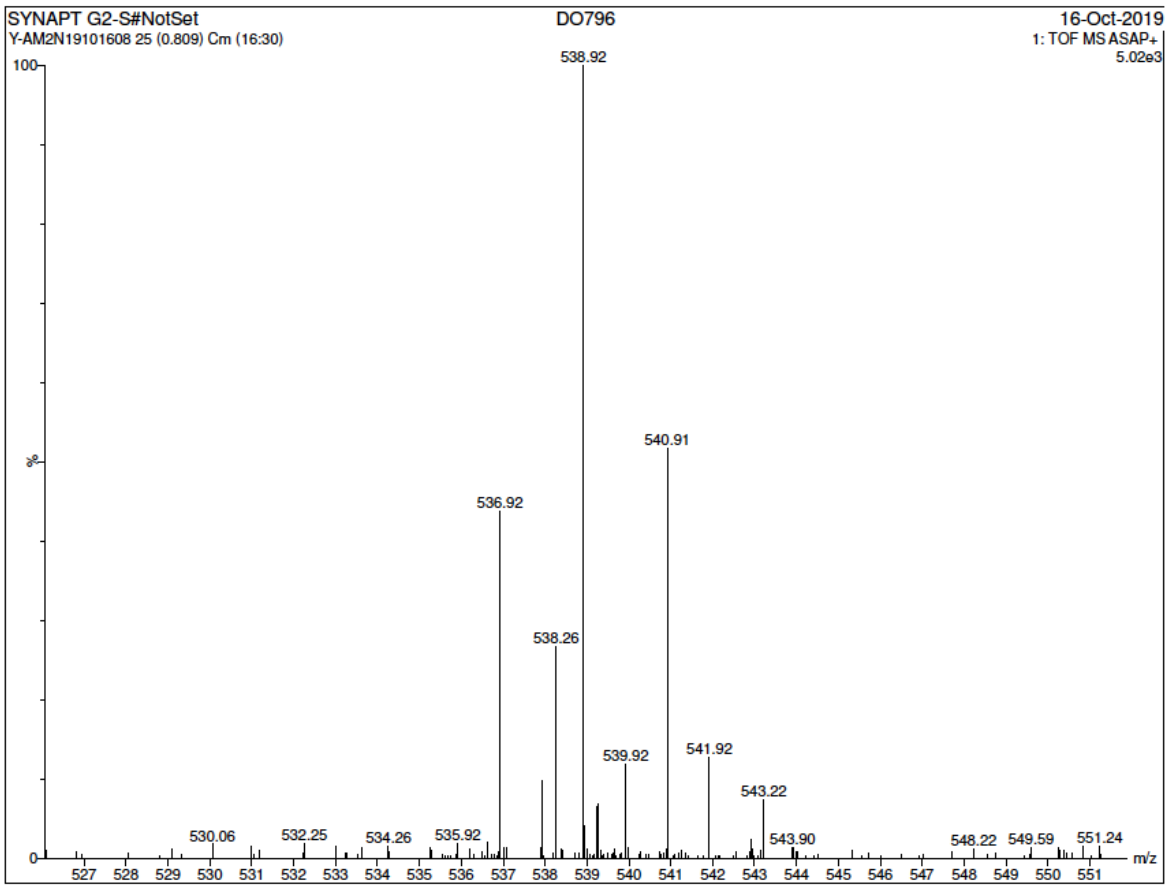


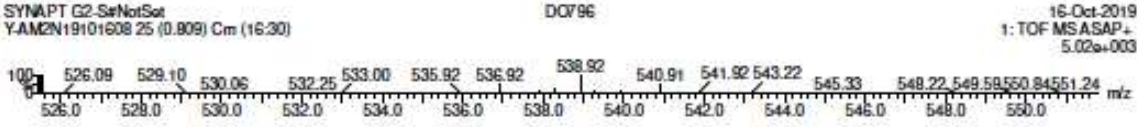
Figure S5 1H NMR ($CDCl_3$) spectrum of **BTBT-CO(CH_2)$_3$Br**



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 mDa / DBE: min = -1.0, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
57 formula(e) evaluated with 3 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-30 S: 2-2 Br: 2-2



Minimum:				-1.0				
Maximum:		10.0	20.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
536.9189	536.9193	-0.4	-0.7	12.5	220.1	0.457	63.29	C22 H19 O2 S2 Br2
	536.9252	-6.3	-11.7	3.5	220.7	1.042	35.29	C15 H23 O7 S2 Br2
	536.9099	9.0	16.8	-0.5	223.9	4.257	1.42	C11 H23 O10 S2 Br2

Figure S6 Masse spectrum of **BTBT-CO(CH$_2$)$_3$Br**

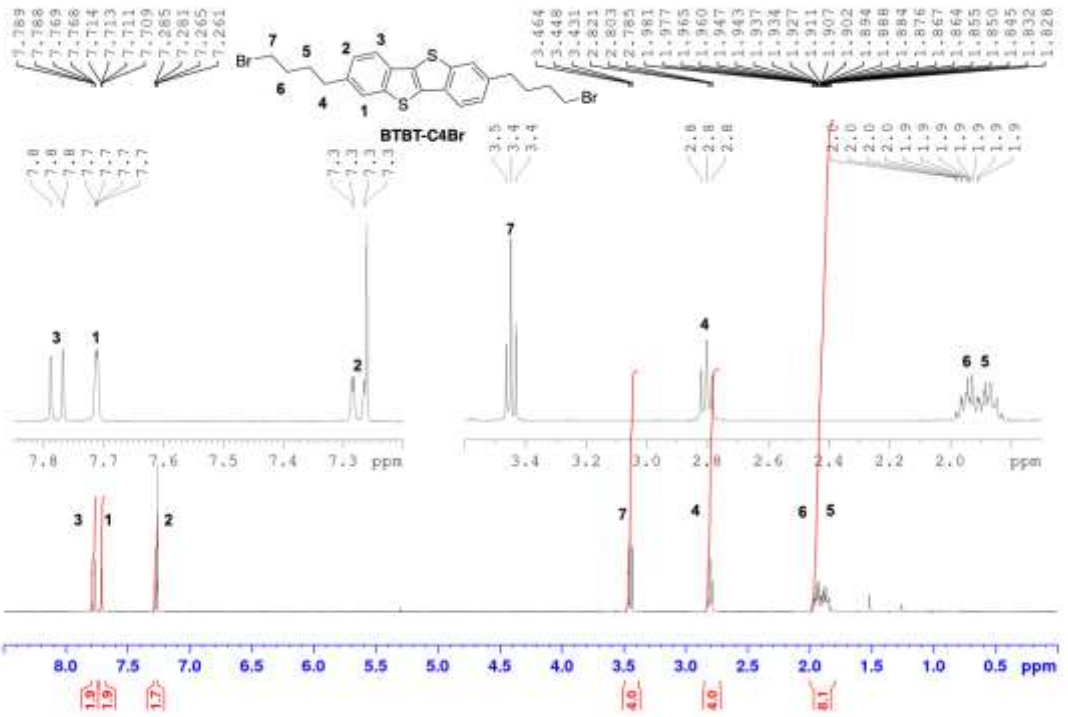


Figure S7 1H NMR ($CDCl_3$) spectrum of **BTBT-C4Br**

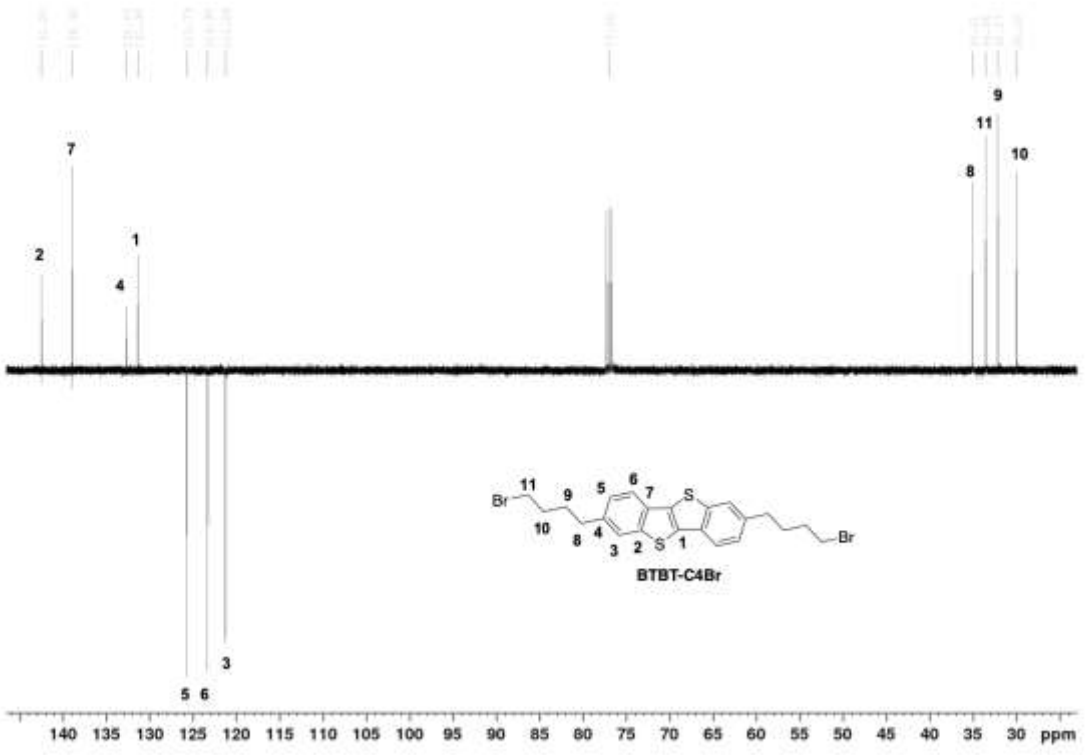
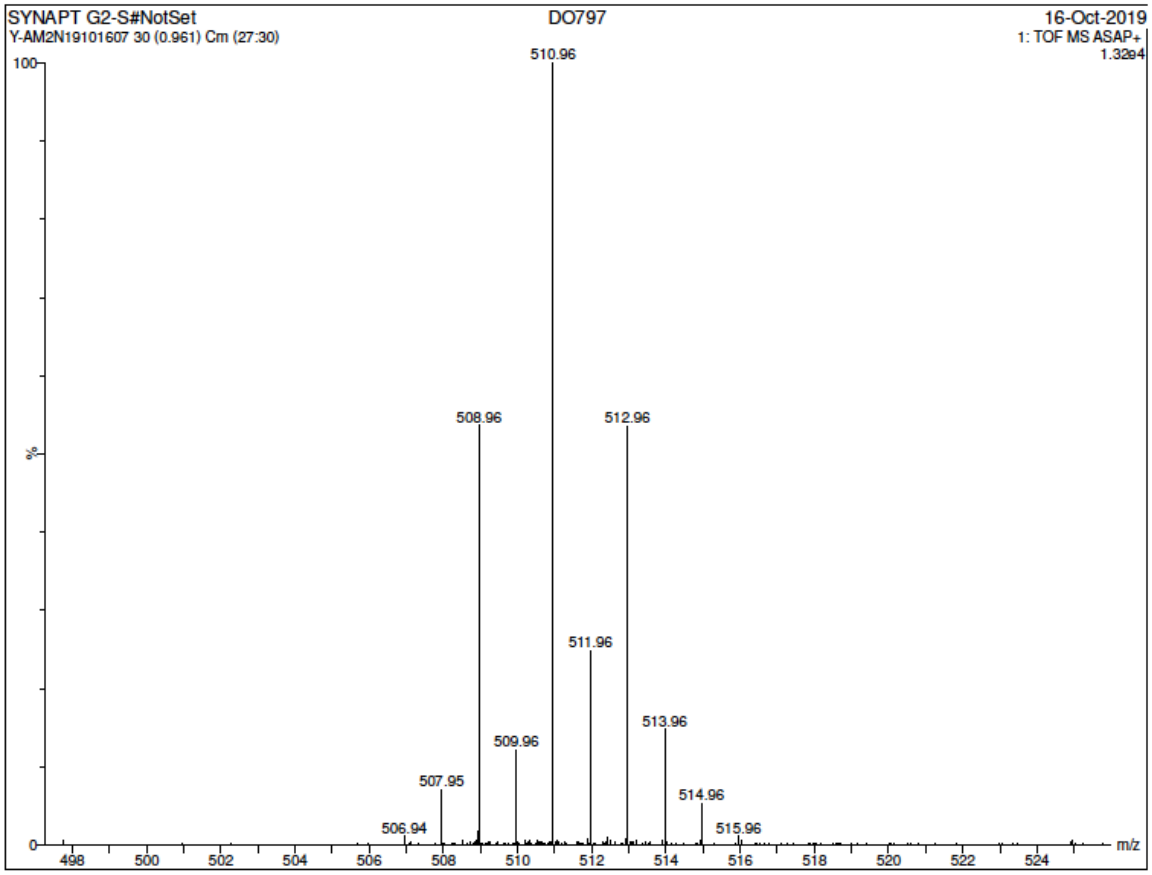


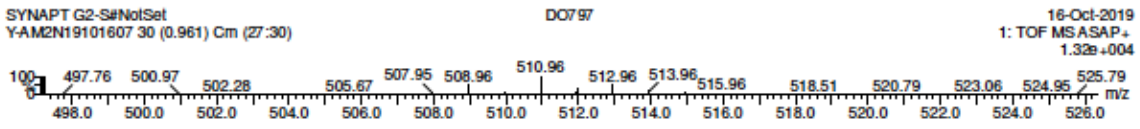
Figure S8 13C NMR ($CDCl_3$) spectrum of **BTBT-C4Br**



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 mDa / DBE: min = -1.0, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
49 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-30 S: 2-2 Br: 2-2



Minimum:				-1.0				
Maximum:		10.0	20.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
508.9593	508.9608	-1.5	-2.9	10.5	328.2	0.032	96.89	C22 H23 S2 Br2
	508.9667	-7.4	-14.5	1.5	331.6	3.471	3.11	C15 H27 O5 S2 Br2

Figure S9 Mass spectrum of **BTBT-C4Br**

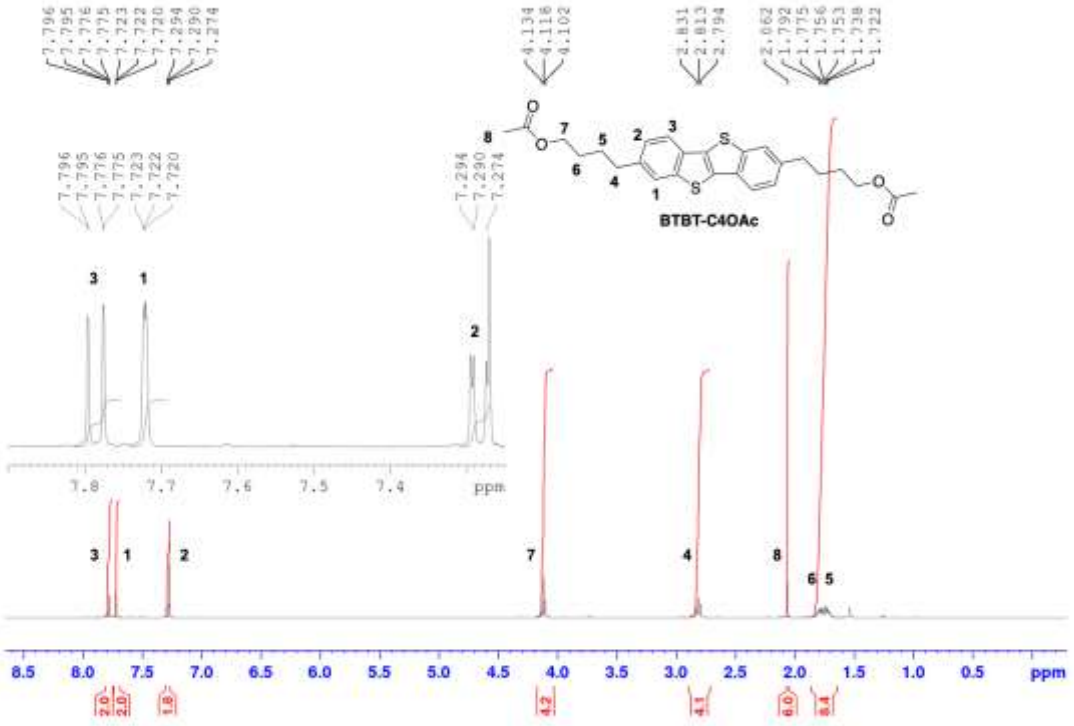


Figure S10 1H NMR ($CDCl_3$) spectrum of **BTBT-C4OAc**

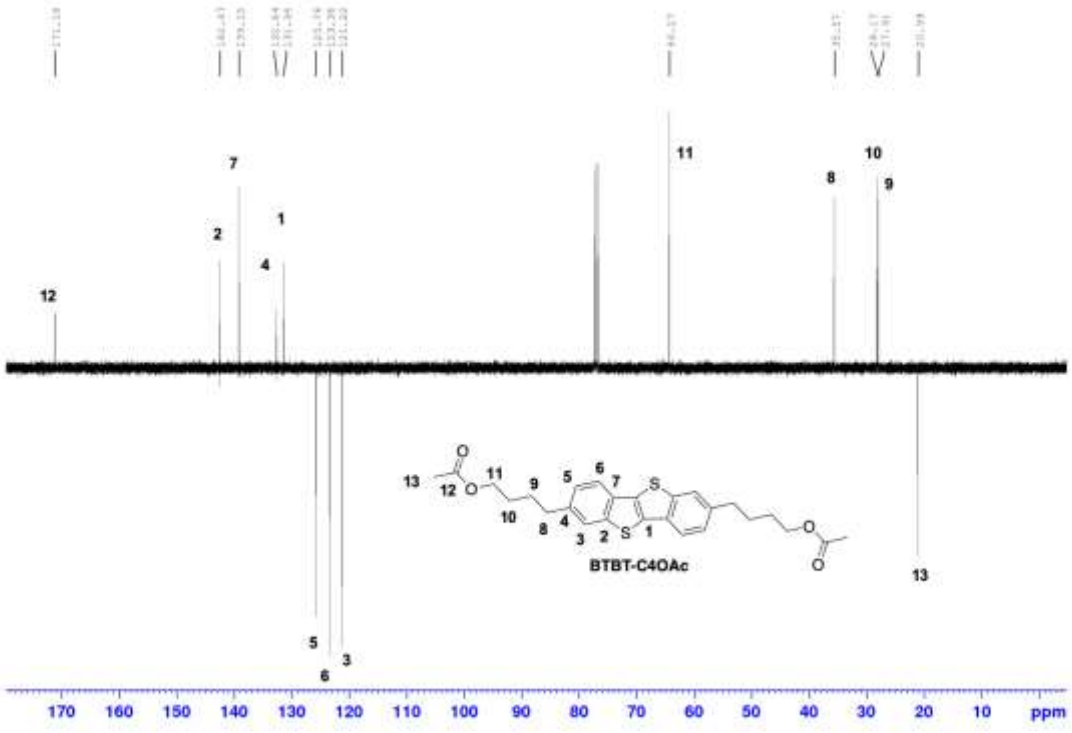
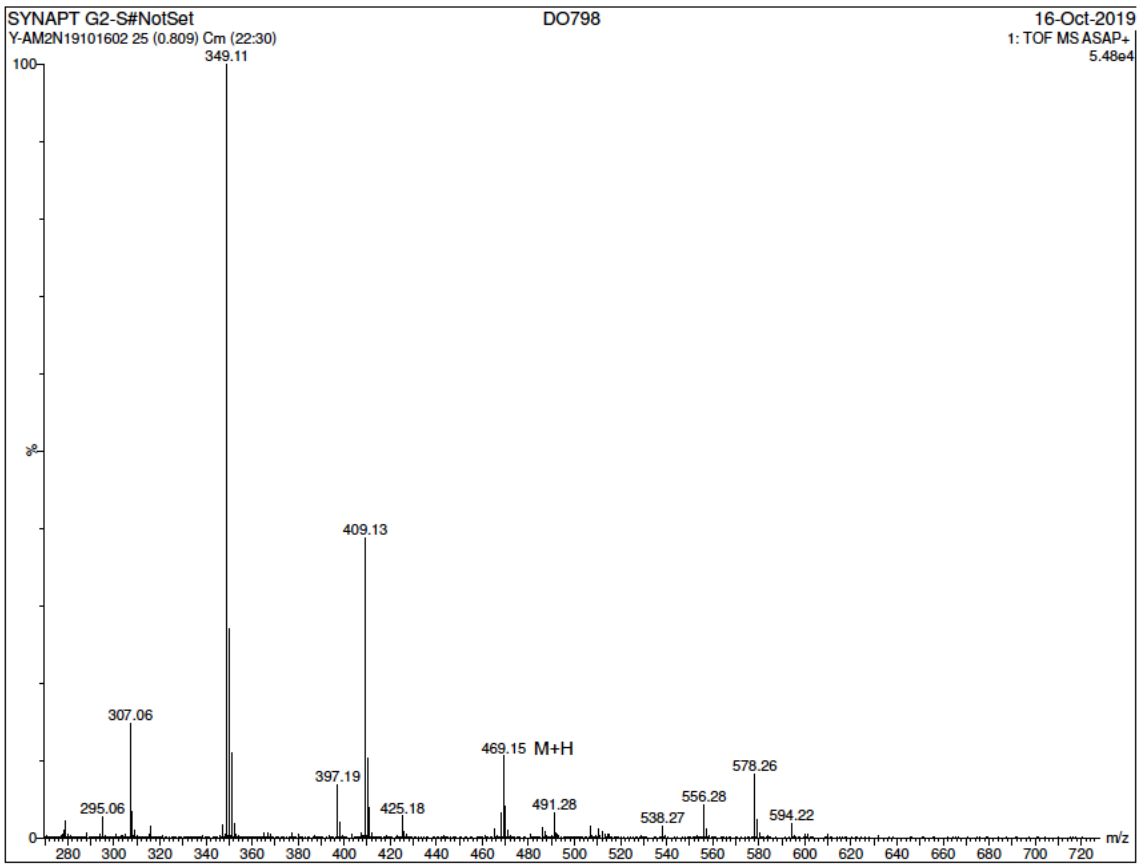


Figure S1113C NMR ($CDCl_3$) spectrum of **BTBT-C4OAc**



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.0, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
86 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-30 S: 2-2

Minimum:				-1.0				
Maximum:		1.0	20.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
469.1500	469.1507	-0.7	-1.5	12.5	208.8	n/a	n/a	C26 H29 O4 S2 M+H

Figure S12 Mass spectrum of **BTBT-C4OAc**

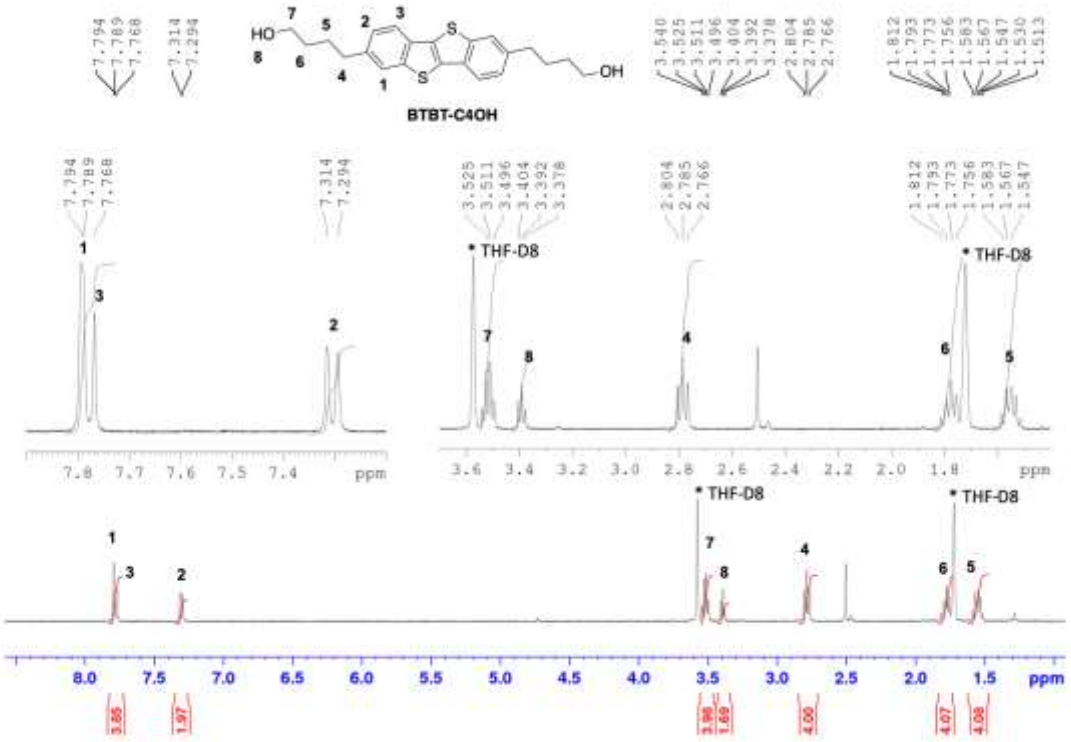


Fig. S12: 1H NMR (THF-D8) spectrum of **BTBT-C4OH**

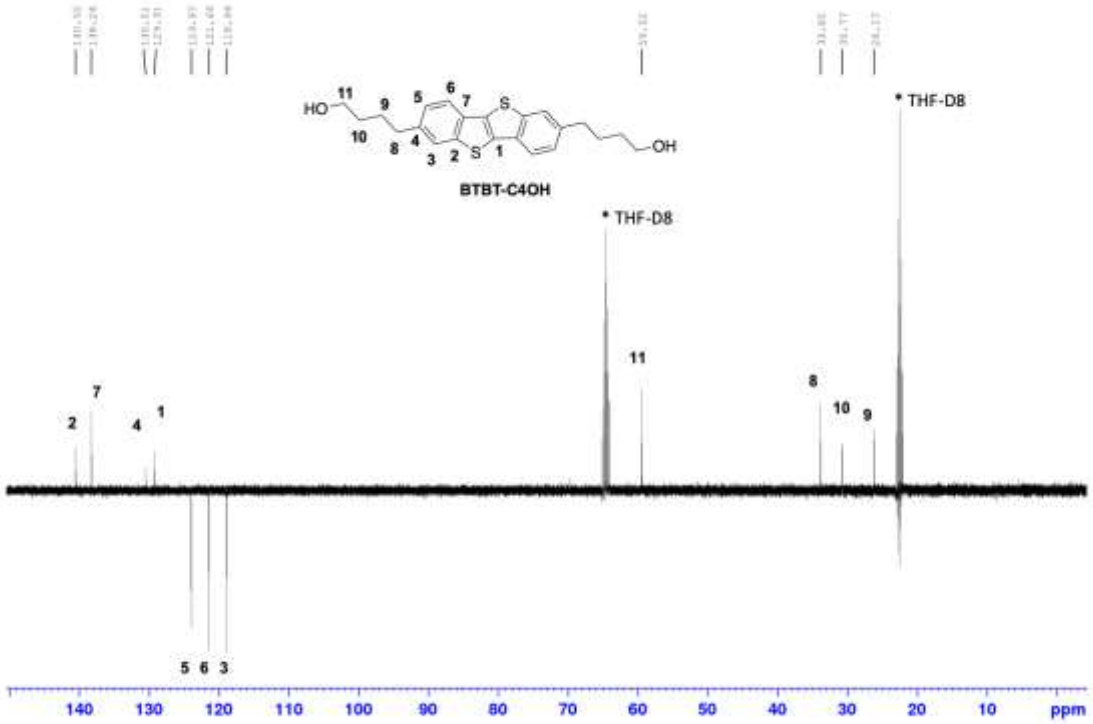


Figure S1313C NMR (THF-D8) spectrum of **BTBT-C4OH**