Electronic Supplementary Information (ESI)

Switching from positive to negative axial thermal expansion in two organic crystalline compounds with similar packing

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Table of Content

1. Synthesis of compounds 1 and 2

All chemicals were of reagent grade and were used without further purification.

Compound **1** and **2** were synthesized by a procedure already reported in literature.[1] To a three-necked round bottomed flask (100 ml) connected with Schlenk line, 1,4-diiodobenzene (500 mg for Compound **1**)/ 2,6-dibromonaphthalene (434 mg for compound **2**) (1.52 mmol), $Pd(PPh_3)_2Cl_2$ (21.05 mg, 0.03 mmol), CuI (11.61mg, 0.061mmol) and 25 ml triethylamine were added under inert atmosphere and stirred. *S*-(-)-3-butyn-2-ol (0.314 ml, 4 mmol) was added dropwise to a clear solution. The reaction mixture was refluxed overnight under N_2 atmosphere. After cooling to room temperature, solvent was evaporated under vacuum and obtained product was washed with NH_4Cl and brine. Residue was purified by column chromatography using ethyl acetate and hexane as eluent. The isolated products **1** and **2** were recrystallized using $CHCl_3$ and ethyl acetate respectively. Colorless block shaped crystals of **1** and hexagonal prism shaped crystals of **2** were obtained after slow evaporation of solvent. Molecular structures were characterized by ^1H and ^{13}C NMR spectroscopy.

^1H-NMR of **1** (500MHz, DMSO-d_6): δ=7.39 (s, 4H), 5.51 (d, 2H), 4.60 (m, 2H), 1.38 (d, 6H).

^{13}CNMR of **1** (125 MHz, DMSO-d_6): δ= 24.98, 57.14, 82.11, 95.70, 122.80, 131.85.

^1H-NMR of **2** (500MHz, DMSO-d_6): δ= 8.04 (s, 2H), 7.92 (d, 2H), 7.50 (d, 2H), 5.55 (d, 2H), 4.65 (m, 2H), 1.42 (d, 6H).

^{13}C-NMR of **2** (125 MHz, DMSO-d_6): δ= 25.06, 57.21, 94.95, 121.12, 128.57, 129.31, 131.18, 132.33.

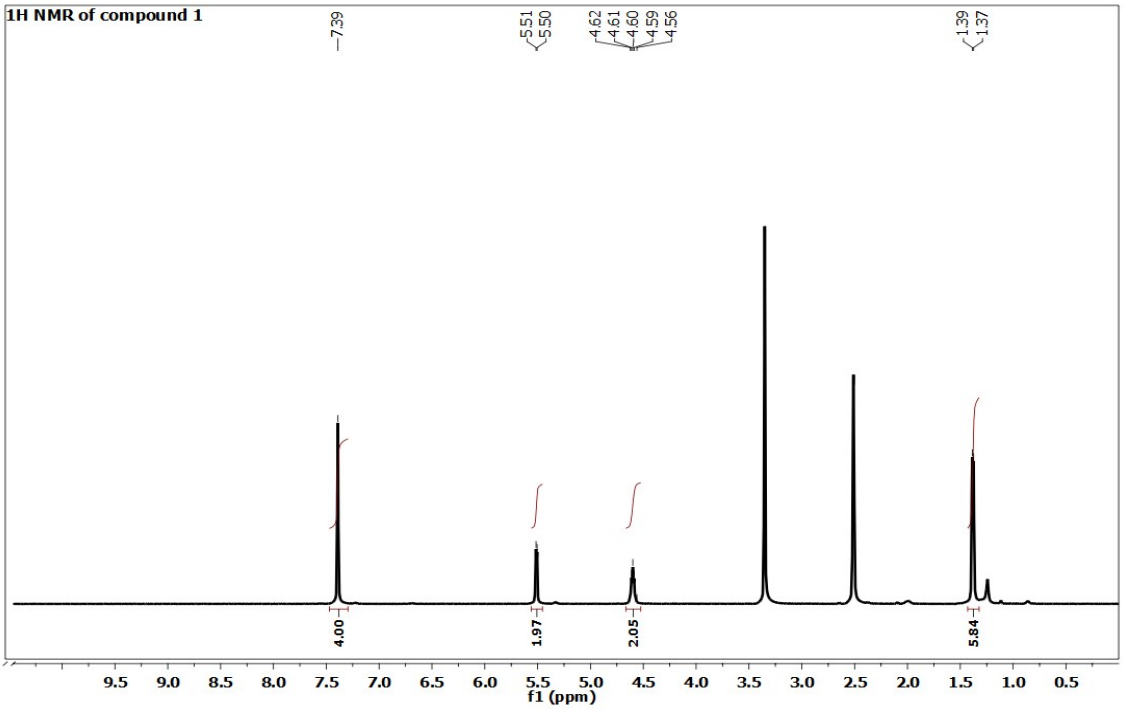


Figure S1. ^{1}H NMR spectrum of compound **1**

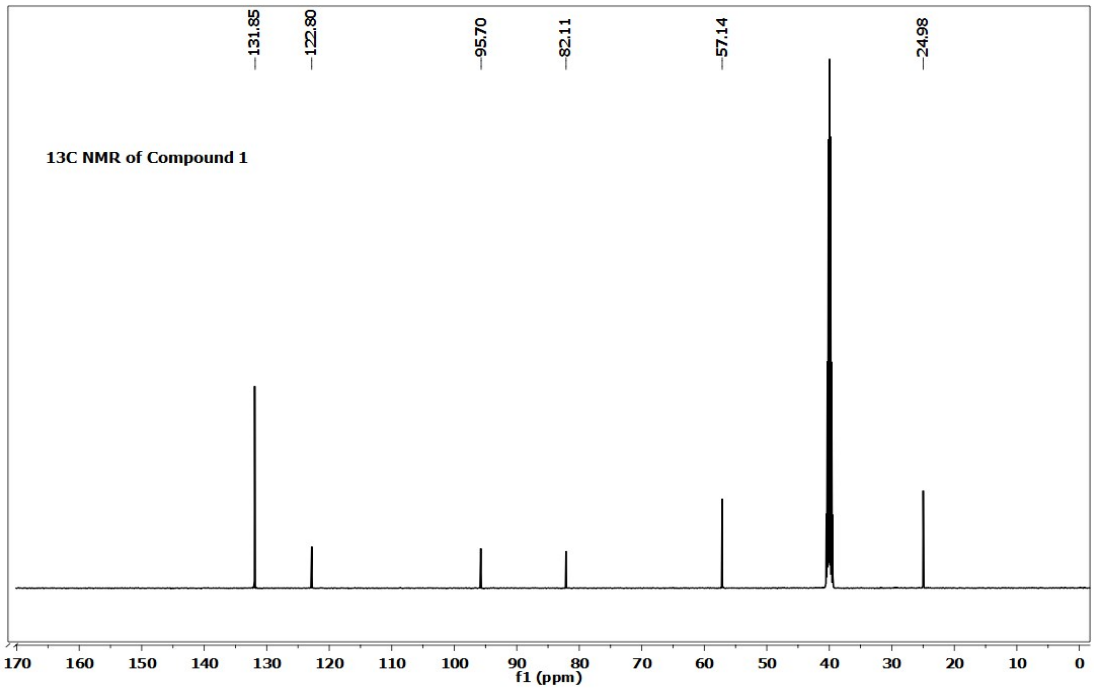


Figure S2. ^{13}C NMR Spectrum of compound **1.**

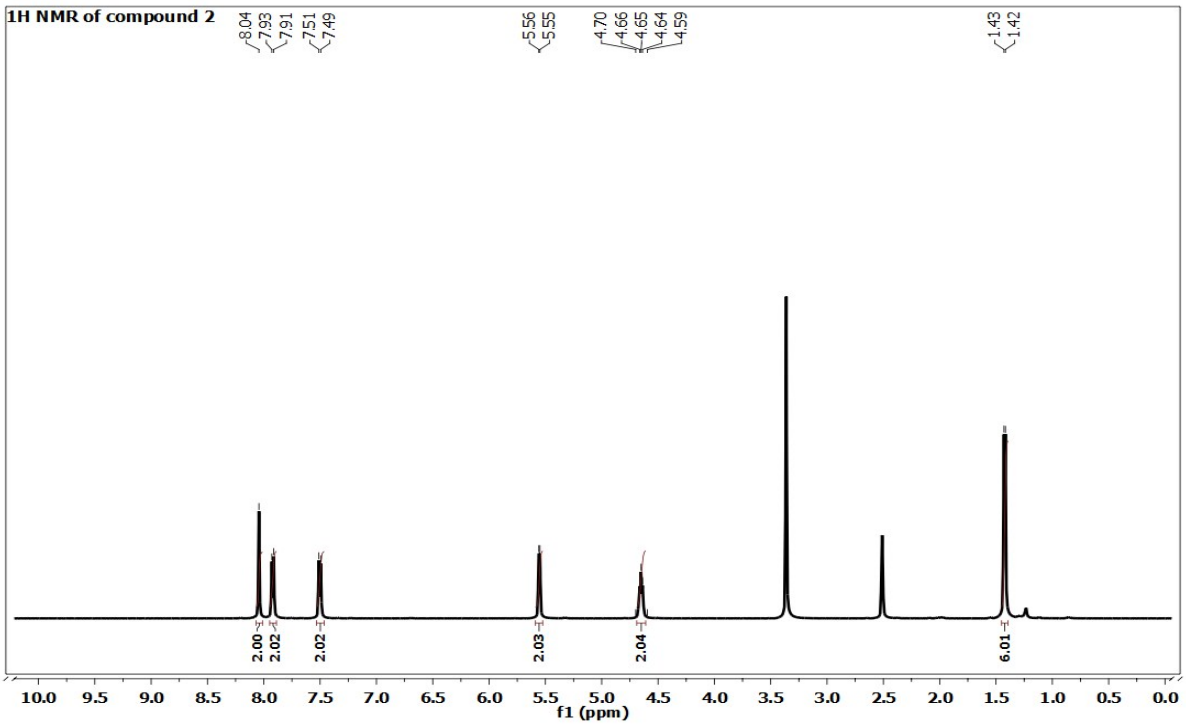


Figure S3. ^{1}H NMR Spectra of compound **2**.

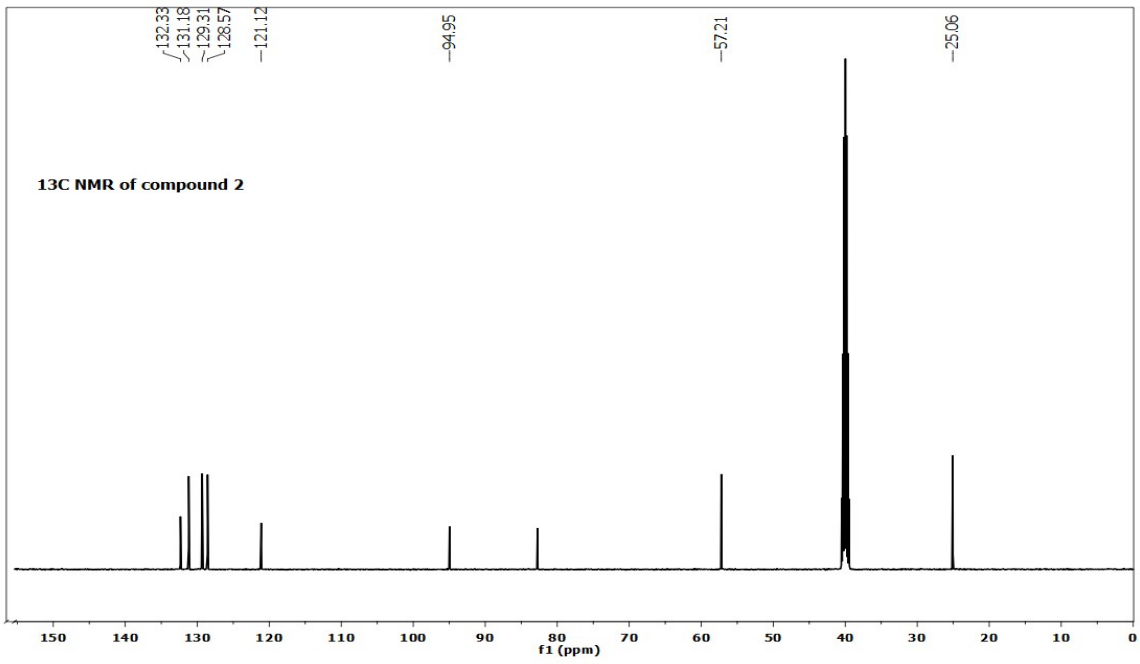


Figure S4. ^{13}C NMR spectrum of compound **2**.

2. Differential Scanning Calorimetry

Differential scanning calorimetric measurements of **1** & **2** were carried out of pure crystalline powdered samples using Mettler-Toledo DSC1 instrument. Approximately 3 to 5 mg of each sample was sealed in aluminium pan and covered with a pierced lid. The samples were heated at the rate of 5 ^{o}C/ min from 25 °C to 160 °C in case of **1** and 25 °C to 200 °C for **2** under flow of N_2 gas with the rate of 40ml/min.

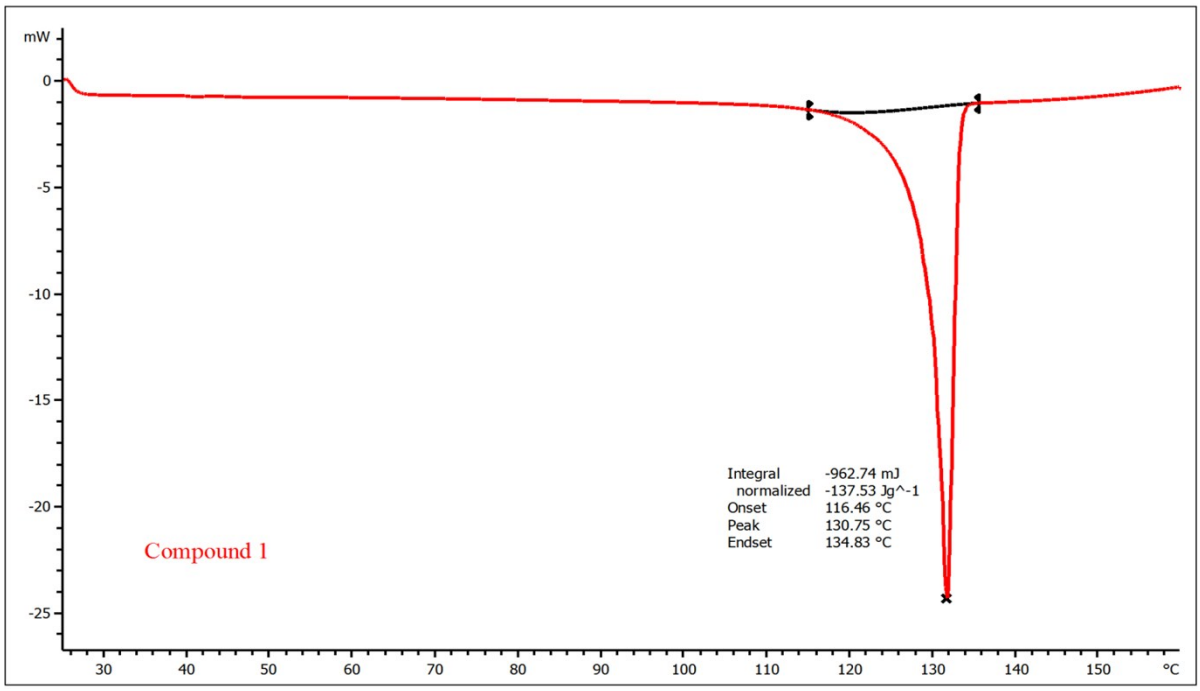


Figure S5a. DSC thermogram shows melting of **1** at 130.75 °C with an onset temperature of 116.46 °C.

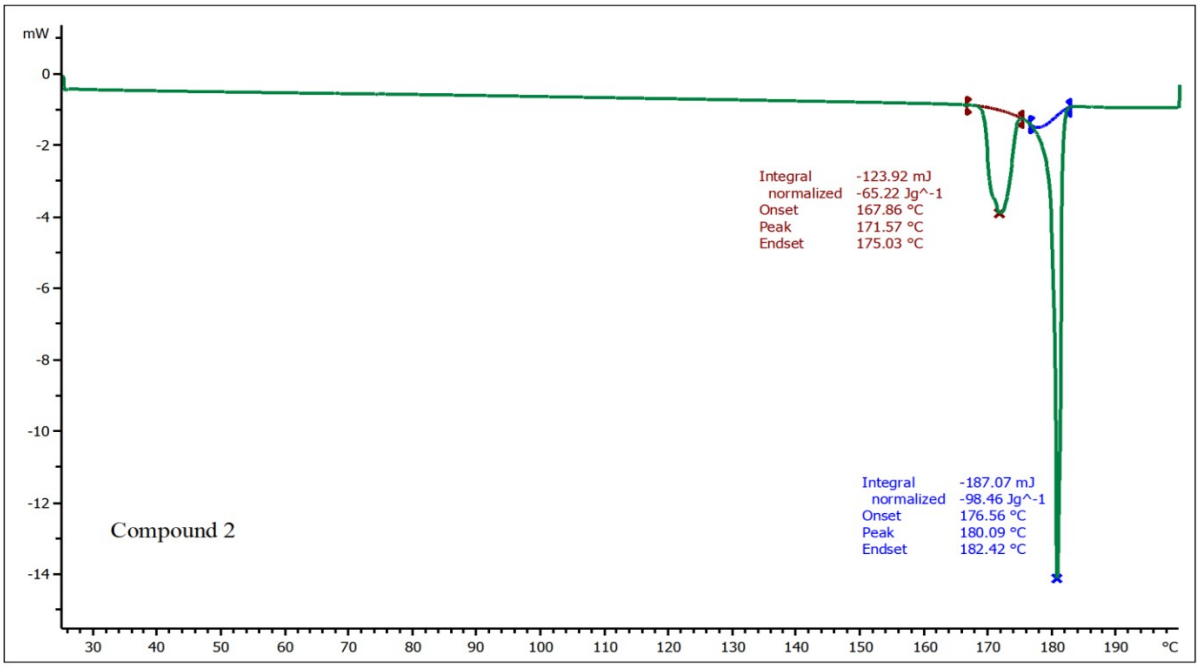
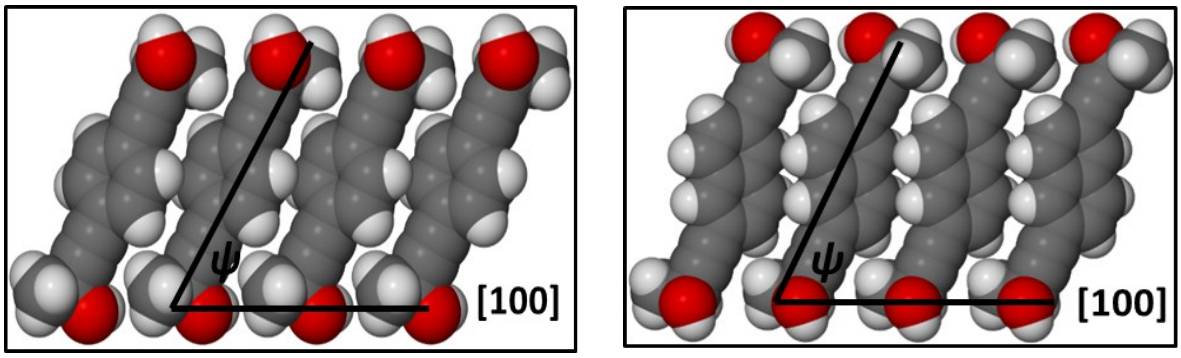


Figure S5b. DSC thermogram of compound **2** shows small endothermic peak at 171.57 °C followed by melting at 180.09 °C. Variable temperature SCD experiment has been performed till 127 °C.

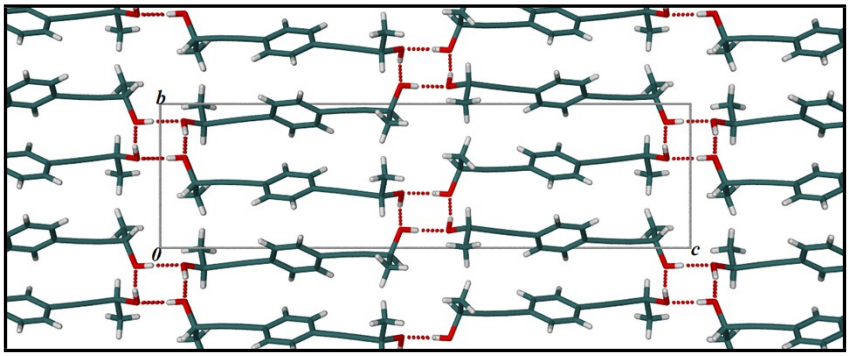
3. Variable Temperature Single Crystal X-ray Diffraction

Single-crystal X-ray data for the compound **1** and **2** in this study were collected on Bruker D8 Quest single crystal X-ray diffractometer equipped with a microfocus anode (MoK_{α}) and a PHOTON 100 CMOS detector. The data were integrated and scaled using the Bruker suite of programs.[2] The structures at each temperature were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-2014.[3] All non-hydrogen atoms were refined anisotropically and all the aromatic hydrogen atoms were placed using calculated positions on riding models. Position of all the hydrogen atoms of hydroxyl groups were assigned using Difference Fourier map. Crystallographic data and final refinement details for the compound **1** and **2** are given in Table **S1** and **S2** respectively.

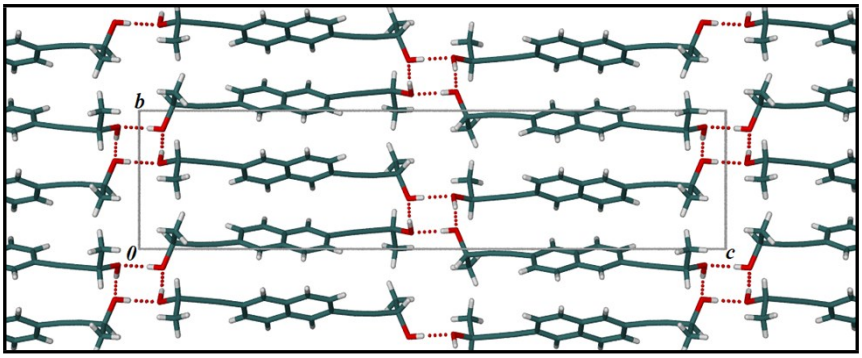


(a) (b)

Figure S6. Molecular stacking of (a) **1** and (b) **2**. Both molecules are tilted with an angle ψ, relative to [100] direction.

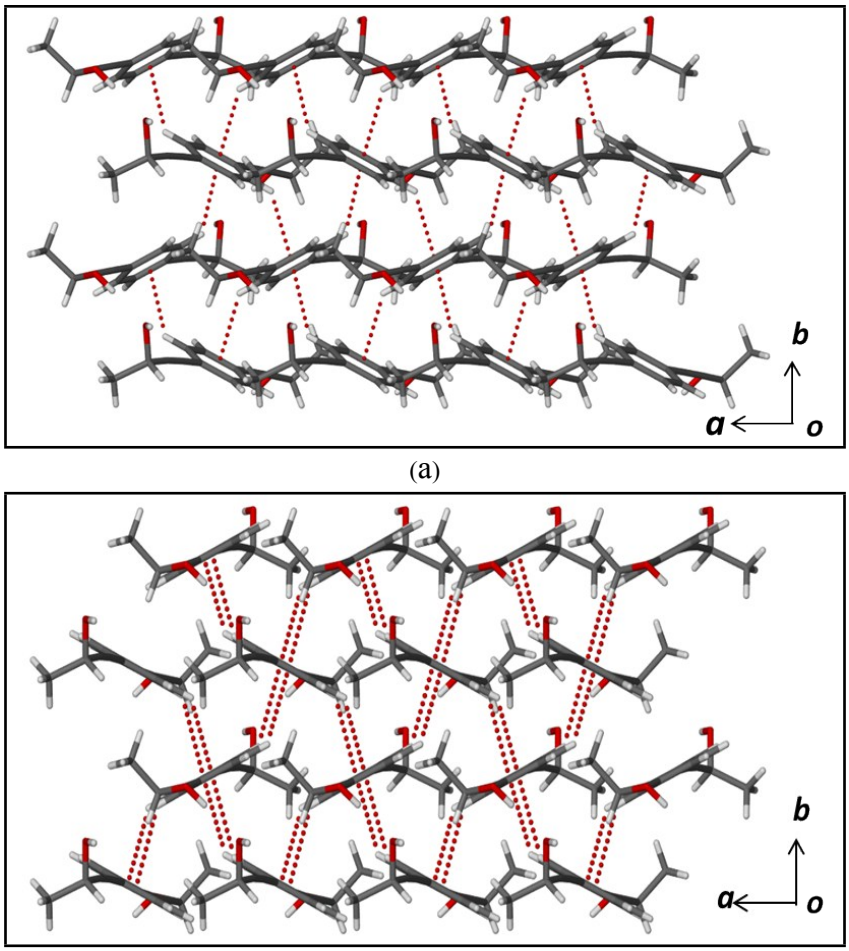


(a)



(b)

Figure S7. Packing diagram of (a) 1 and (b) 2, viewed down the *a* axis. Hydrogen bonding is shown by the red dotted lines.



(a)

(b)

Figure S8. Packing diagram showing C-H···π interactions between the molecules in the crystal structure of (a) **1** and (b) **2** viewed down *c* axis.

Table S1. Crystallographic data and refinement parameters for **1**

Compound	**1_90K**	**1_120K**	**1_150K**	**1_180K**	**1_210K**	**1_240K**	**1_270K**
Empirical formula	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$
T (K)	90(2)	120(2)	150(2)	180(2)	210(2)	240(2)	270(2)
a/(Å)	5.6838(4)	5.6861(4)	5.6883(4)	5.6915(5)	5.6944(5)	5.6982(5)	5.7057(5)
b/(Å)	7.3834(4)	7.4078(5)	7.4343(5)	7.4628(5)	7.4936(6)	7.5247(6)	7.5595(6)
c/(Å)	28.139(2)	28.140(2)	28.140(2)	28.143(3)	28.143(3)	28.143(3)	28.152(3)
α/(deg)	90	90	90	90	90	90	90
β/(deg)	90	90	90	90	90	90	90

γ/(deg)	90	90	90	90	90	90	90
Volume/ Å^3	1180.88(14)	1185.30(14)	1190.00(14)	1195.37(17)	1200.89(18)	1206.69(19)	1214.24(18)
Z	4	4	4	4	4	4	4
D_{cal} /g cm^{-3}	1.205	1.201	1.196	1.190	1.185	1.179	1.172
μ/mm^{-1}	0.080	0.079	0.079	0.079	0.078	0.078	0.077
F_{000}	456	456	456	456	456	456	456
Crystal size/ mm^3	0.222×0.096× 0.077	0.222×0.096× 0.077	0.222×0.096× 0.077	0.222×0.096× 0.077	0.222×0.096× 0.077	0.222×0.096 ×0.077	0.222×0.096× 0.077
Radiation	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
θ range for data collection	2.852-28.292	2.843- 28.299	2.834- 28.305	2.824- 28.298	2.813- 28.318	2.802- 28.351	2.790-28.342
Index ranges	-7 ≤ h ≤7; -9 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -9 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -9 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -9 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -9 ≤ k ≤9; -37 ≤ l ≤34	-7 ≤ h ≤7; -9 ≤ k ≤10; -37 ≤ l ≤34	-7 ≤ h ≤7; -9 ≤ k ≤10; -37 ≤ l ≤34
No. of measured reflections	12631	12587	12671	12778	13087	13197	13376
No. of independent reflections	2922	2935	2951	2977	2988	3010	3030
No. of observed reflections	2481	2386	2301	2164	2051	1885	1746
parameters	156	156	156	156	156	156	156
GOOF (S)	1.066	1.036	1.030	1.041	1.033	1.018	1.007
R_{int}	0.0434	0.0434	0.0466	0.0485	0.0529	0.0582	0.0627
R [I>=2σ (I)]	0.0404	0.0422	0.0431	0.0434	0.0474	0.0496	0.0498
R [all data]	0.0549	0.0638	0.0680	0.0780	0.0921	0.1079	0.1236
CCDC number	1855860	1855848	1855849	1855850	1855851	1855852	1855853

Compound	**1_300K**	**1_310K**	**1_320K**	**1_330K**	**1_340K**	**1_350K**
Empirical formula	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$	$C_{14}H_{14}O_2$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$
T (K)	300(2)	310(2)	320(2)	330(2)	340(2)	350(2)
a/(Å)	5.7073(6)	5.7075(7)	5.7090(7)	5.7113(7)	5.7113(7)	5.7130(8)
b/(Å)	7.5909(7)	7.6016(7)	7.6146(8)	7.6271(8)	7.6398(9)	7.6527(9)
c/(Å)	28.133(3)	28.125(3)	28.123(4)	28.122(4)	28.117(4)	28.116(4)
α/(deg)	90	90	90	90	90	90

β/(deg)	90	90	90	90	90	90
γ/(deg)	90	90	90	90	90	90
Volume/Å^3	1218.8(2)	1220.2(2)	1222.6(2)	1225.0(3)	1226.8(3)	1229.2(3)
Z	4	4	4	4	4	4
D_{cal} /g cm^{-3}	1.168	1.166	1.164	1.162	1.160	1.158
μ/mm^{-1}	0.077	0.077	0.077	0.077	0.077	0.076
F_{000}	456	456	456	456	456	456
Crystal size/ mm^3	0.222×0.096 ×0.077	0.222×0.096× 0.077	0.222×0.096× 0.077	0.222×0.096× 0.077	0.222×0.096× 0.077	0.222×0.096× 0.077
Radiation	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
θ range for data collection	2.779-28.361	2.776-28.291	2.771-28.351	2.767-28.367	2.763-28.297	2.758-28.350
Index ranges	-7 ≤ h ≤7; -9 ≤ k ≤10; -34 ≤ l ≤37	-7 ≤ h ≤7; -10 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -10 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -10 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -10 ≤ k ≤9; -34 ≤ l ≤37	-7 ≤ h ≤7; -10 ≤ k ≤9; -34 ≤ l ≤37
No. of measured reflections	13454	13440	13150	13167	13183	13248
No. of independent reflections	3051	3040	3060	3066	3055	3073
No. of observed reflections	1605	1532	1492	1446	1366	1324
parameters	156	156	156	156	156	156
GOOF (S)	0.999	0.997	0.997	0.997	0.980	0.983
R_{int}	0.0699	0.0711	0.0713	0.0730	0.0769	0.0774
R [I>=2σ (I)]	0.0529	0.0548	0.0529	0.0541	0.0534	0.0530
R [all data]	0.1434	0.1480	0.1593	0.1677	0.1785	0.1840
CCDC number	1855854	1855855	1855856	1855857	1855858	1855859

Table S2. Crystallographic data and refinement parameters for **2**

Compound	**2_100K**	**2_150K**	**2_200K**	**2_250K**	**2_300K**	**2_350K**	**2_400K**
Empirical formula	$C_{18}H_{16}O_2$	$C_{18}H_{16}O_2$	$C_{18}H_{16}O_2$	$C_{18}H_{16}O_2$	$C_{18}H_{16}O_2$	$C_{18}H_{16}O_2$	$C_{18}H_{16}O_2$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$
Temperature	100(2)	150(2)	200(2)	250(2)	300(2)	350(2)	400(2)
a/(Å)	5.8843(4)	5.8912(4)	5.8987(3)	5.9061(3)	5.9146(3)	5.9244(3)	5.9264(11)
b/(Å)	7.2086(5)	7.2496(5)	7.2946(5)	7.3412(5)	7.3912(5)	7.4427(5)	7.4922(18)
c/(Å)	32.936(2)	32.950(2)	32.966(2)	32.9746(19)	32.9799(19)	32.968(2)	32.946(7)
α/(deg)	90	90	90	90	90	90	90
β/(deg)	90	90	90	90	90	90	90

γ/(deg)	90	90	90	90	90	90	90
Volume/ Å^3	1397.04(17)	1407.27(17)	1418.46(15)	1429.71(15)	1441.75(15)	1453.69(15)	1462.9(5)
Z	4	4	4	4	4	4	4
D_{cal} /g cm^{-3}	1.257	1.247	1.238	1.228	1.218	1.208	1.200
μ/mm^{-1}	0.081	0.080	0.080	0.080	0.079	0.079	0.077
F_{000}	560	560	560	560	560	560	560
Crystal size/ mm^3	0.363×0.324×0.085	0.363×0.324×0.085	0.363×0.324×0.085	0.363×0.324×0.085	0.363×0.324×0.085	0.363×0.324×0.085	0.363×0.324×0.085
Radiation	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
θ range for data collection	2.474-28.249	2.472-28.294	2.471-28.321	2.471-28.313	2.470-28.308	2.471-28.349	2.473-28.371
Index ranges	-5 ≤ h ≤7; -6 ≤ k ≤9; -43 ≤ l ≤43	-6 ≤ h ≤7; -6 ≤ k ≤9; -43 ≤ l ≤43	-6 ≤ h ≤7; -6 ≤ k ≤9; -43 ≤ l≤44	-7 ≤ h ≤6; -9 ≤ k ≤6; -43 ≤ l≤44	-7 ≤ h ≤6; -9 ≤ k ≤6; -43 ≤ l≤44	-7 ≤ h ≤6; -9 ≤ k ≤6; -43 ≤ l≤44	-7 ≤ h ≤6; -10 ≤ k ≤6; -43 ≤ l ≤44
No. of measured reflections	8232	8332	8484	8656	8646	8778	8806
No. of independent reflections	2777	2677	2578	2411	2384	2196	1960
No. of observed reflections	3311	3364	3423	3492	3491	3552	3599
parameters	192	192	192	192	192	192	192
GOOF (S)	1.052	1.063	1.071	0.996	1.026	1.033	1.031
R_{int}	0.0277	0.0301	0.0300	0.0327	0.0271	0.0293	0.0310
R [I>=2σ (I)]	0.0396	0.0417	0.0429	0.0433	0.0418	0.0447	0.0437
R [all data]	0.0544	0.0632	0.0720	0.0810	0.0792	0.0956	0.1132
CCDC number	1855861	1855862	1855863	1855864	1855865	1855866	1855867

Table S3. Change of Unit cell parameters in **1** with change of temperature.

T(K)	*a* (Å)	*b*(Å)	*c* (Å)	Vol.(Å^3)
90	5.6838(4)	7.3834(4)	28.139(2)	1180.88(14)
120	5.6861(4)	7.4078(5)	28.140(2)	1185.29(15)
150	5.6883(4)	7.4344(5)	28.143(3)	1190.07(17)
180	5.6915(5)	7.4628(5)	28.143(3)	1195.37(17)
210	5.6944(5)	7.4936(6)	28.143(3)	1200.89(18)
240	5.6982(5)	7.5247(6)	28.143(3)	1206.69(19)

270	5.7057(5)	7.5595(6)	28.152(3)	1214.24(18)
300	5.7073(6)	7.5909(7)	28.133(3)	1218.8(2)
310	5.7075(7)	7.6016(7)	28.125(3)	1220.2(2)
320	5.7090(7)	7.6146(8)	28.123(4)	1226.6(2)
330	5.7113(7)	7.6271(8)	28.122(4)	1225.0(3)
340	5.7113(7)	7.6398(9)	28.117(4)	1226.8(3)
350	5.7130(8)	7.6527(9)	28.116(4)	1229.2(3)

Note: PTE of *c* axis from 90 K to 270 K highlighted by light orange color and NTE of *c* axis from 300 K to 350K highlighted by light blue color.

Table S4. Change of Unit cell parameters in **2** with temperature.

T(K)	***a* (Å)**	***b* (Å)**	***c* (Å)**	**Vol.(Å^3)**
100	5.8843(4)	7.2086(5)	32.936(2)	1397.04(17)
150	5.8912(4)	7.2496(5)	32.950(2)	1407.27(17)
200	5.8987(3)	7.2946(5)	32.966(2)	1418.46(15)
250	5.9061(3)	7.3412(5)	32.975(2)	1429.71(15)
300	5.9146(3)	7.3912(5)	32.980(2)	1441.75(15)
350	5.9244(3)	7.4427(5)	32.968(2)	1453.69(15)
400	5.9264(11)	7.4922(18)	32.946(7)	1462.9(5)

Note: PTE of *c* axis from 100 K to 300 K highlighted by light orange color and NTE of *c* axis from 300 K to 400K highlighted by light blue color.

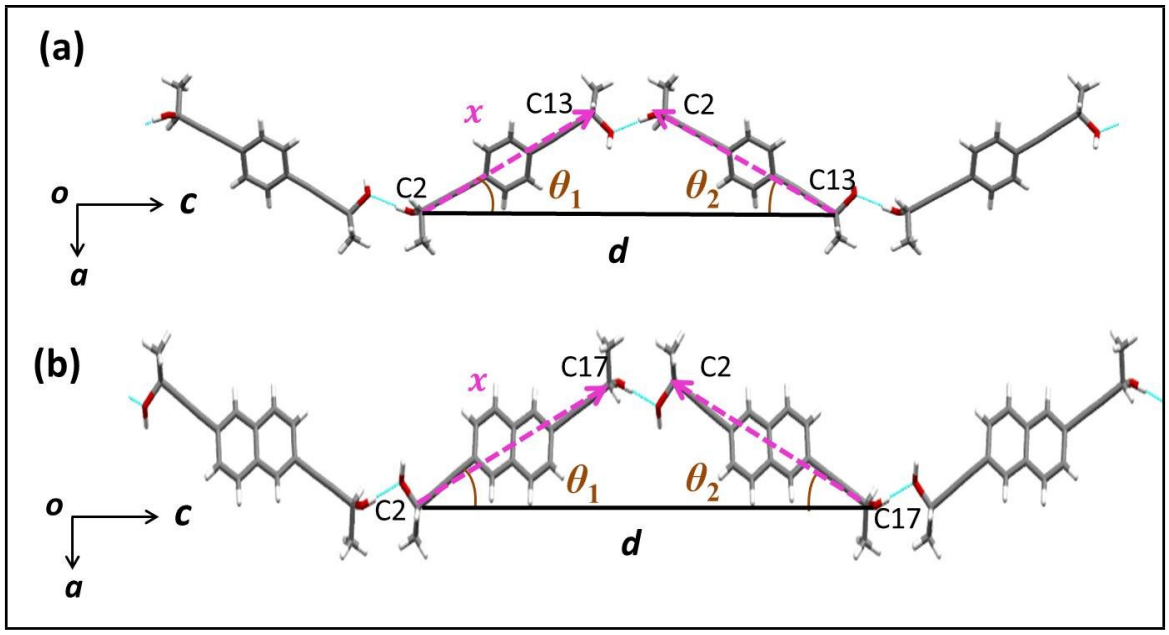


Figure S9. Representation of molecular length (x) between C2-C13 in 1 and C2-C17 in **2** and tilt angle θ_1 and θ_2 in **1** and **2**.

Table S5. Change of Distance between **C2-C13** (distance x, between chiral C atoms positioned at the terminal as shown in Figure S9(a)) in **1** with temperature.

Temperature	**Distance (C2-C13) / Å**
90K	10.997(3)
120K	10.995(3)
150K	10.989(3)
180K	10.985(3)
210K	10.981(3)
240K	10.973(3)
270K	10.964(4)
300K	10.955(4)
310K	10.953(4)
320K	10.947(4)
330K	10.940(4)
340K	10.942(5)

350K	10.937(4)

Table S6. Distance between **C2-C17** (distance *x*, between the chiral C atoms positioned at the terminal as shown in Figure S9(b)) of **2** at different temperature.

Temperature	**Distance (C2-C17) / Å**
100K	13.169(3)
150K	13.165(3)
200K	13.156(3)
250K	13.149(3)
300K	13.136(3)
350K	13.119(3)
400K	13.095(5)

Table S7. Change of Tilt angle (θ_1 and θ_2) with temperature for compound **1 (**Figure S9(a))

Temperature	**Angle (θ_1) ∠C13-C2-C13(°)**	**Angle (θ_2) ∠C2-C13-C2(°)**
90K	26.88(1)	25.36(1)
120K	26.82(1)	25.29(1)
150K	26.75(1)	25.22(1)
180K	26.69(1)	25.14(1)
210K	26.62(1)	25.07(1)
240K	26.58(2)	25.01(2)
270K	26.53(2)	24.94(2)
300K	26.48(2)	24.89(2)
310K	26.46(2)	24.83(2)
320K	26.43(2)	24.79(2)
330K	26.42(2)	24.79(2)

340K	26.41(2)	24.76(2)
350K	26.37(2)	24.73(2)

Table S8. Change of Tilt angle (θ_1 and θ_2) with temperature for compound **2** (Figure S9(b)).

Temperature	**Angle (θ_1) ∠C17-C2-C17(°)**	**Angle (θ_2) ∠C2-C17-C2(°)**
100K	21.76(1)	20.49(1)
150K	21.63(1)	20.33(1)
200K	21.53(1)	20.18(1)
250K	21.40(1)	20.02(1)
300K	21.27(1)	19.87(1)
350K	21.18(2)	19.73(1)
400K	21.07(2)	19.58(2)

Table S9. Change of Hydrogen bonding parameters in compound **1** with Temperature.[4]

T (K)	**Donor – H⋯Acceptor**	**D – H (Å)**	**H⋯A (Å)**	**D⋯A (Å)**	**∠D – H⋯A (°)**
90K	O(1) – H(1) ⋯O(2)	0.85(3)	1.83(3)	2.6752(18)	175(3)
	O(2) – H(2A) ⋯O(1)	0.89(3)	1.84(3)	2.7215(18)	172(2)
120K	O(1) – H(1) ⋯O(2)	0.82(3)	1.86(3)	2.677(2)	174(3)
	O(2) – H(2A) ⋯O(1)	0.90(3)	1.83(3)	2.724(2)	169(3)
150K	O(1) – H(1) ⋯O(2)	0.84(3)	1.84(3)	2.680(2)	175(3)
	O(2) – H(2A) ⋯O(1)	0.94(3)	1.80(3)	2.728(2)	169(2)
180K	O(1) – H(1) ⋯O(2)	0.85(3)	1.83(3)	2.683(2)	176(3)
	O(2) – H(2A) ⋯O(1)	0.93(3)	1.81(3)	2.732(2)	169(3)
210K	O(1) – H(1) ⋯O(2)	0.81(3)	1.88(3)	2.686(2)	178(3)

	O(2) – H(2A) ⋯O(1)	0.91(3)	1.83(3)	2.735(2)	169(3)
240K	O(1) – H(1) ⋯O(2)	0.85(3)	1.84(3)	2.689(3)	177(4)
	O(2) – H(2A) ⋯O(1)	0.91(3)	1.84(3)	2.743(2)	169(3)
270K	O(1) – H(1) ⋯O(2)	0.84(3)	1.85(3)	2.695(3)	179(5)
	O(2) – H(2A) ⋯O(1)	0.91(3)	1.86(3)	2.748(3)	165(3)
300K	O(1) – H(1) ⋯O(2)	0.86(3)	1.84(3)	2.696(3)	179(4)
	O(2) – H(2A) ⋯O(1)	0.91(3)	1.87(3)	2.752(3)	163(3)
310K	O(1) – H(1) ⋯O(2)	0.86(4)	1.84(4)	2.694(3)	179(5)
	O(2) – H(2A) ⋯O(1)	0.91(4)	1.87(4)	2.753(3)	164(3)
320K	O(1) – H(1) ⋯O(2)	0.79(4)	1.91(4)	2.699(3)	174(4)
	O(2) – H(2A) ⋯O(1)	0.90(4)	1.88(4)	2.755(3)	165(3)
330K	O(1) – H(1) ⋯O(2)	0.84(4)	1.86(4)	2.699(3)	175(4)
	O(2) – H(2A) ⋯O(1)	0.92(4)	1.86(4)	2.761(3)	166(3)
340K	O(1) – H(1) ⋯O(2)	0.82(4)	1.89(4)	2.700(3)	177(6)
	O(2) – H(2A) ⋯O(1)	0.88(4)	1.91(4)	2.761(4)	162(4)
350K	O(1) – H(1) ⋯O(2)	0.83(4)	1.87(4)	2.700(3)	178(4)
	O(2) – H(2A) ⋯O(1)	0.88(4)	1.91(4)	2.765(3)	164(3)

Symmetry Code for O(1) – H(1) ⋯O(2) : **1/2-x, 1-y, -1/2+z;**

Symmetry Code for O(2) – H(2A) ⋯O(1)**: 1-x, -1/2+y, 1/2-z.**

Table S10. Change of Hydrogen bonding parameters in compound **2** with Temperature.[4]

T(K)	**Donor – H⋯Acceptor**	**D – H (Å)**	**H⋯A (Å)**	**D⋯A (Å)**	**∠D – H⋯A (°)**
100K	O(1) – H(1A) ⋯O(2)*	0.80(3)	1.87(3)	2.6729(19)	179(5)
	O(2) – H(2A) ⋯O(1)	0.92(3)	1.80(3)	2.7158(18)	175(3)
150K	O(1) – H(1A) ⋯O(2)	0.87(4)	1.81(4)	2.672(2)	175(3)
	O(2) –H(2A) ⋯O(1)	0.85(3)	1.88(3)	2.728(3)	174(3)
200K	O(1) – H(1A) ⋯O(2)	0.85(3)	1.83(3)	2.678(2)	175(3)
	O(2) – H(2A) ⋯O(1)	0.89(4)	1.85(4)	2.733(3)	174(3)
	O(1) – H(1A) ⋯O(2)	0.80(4)	1.89(4)	2.685(2)	173(3)

250K	O(2) – H(2A) ⋯O(1)	0.89(4)	1.85(4)	2.736(3)	175(4)
300K	O(1) – H(1A) ⋯O(2)	0.85(4)	1.84(4)	2.691(2)	174(4)
	O(2) – H(2A) ⋯O(1)	0.88(4)	1.87(4)	2.747(3)	174(3)
350K	O(1) – H(1A) ⋯O(2)	0.89(4)	1.82(4)	2.700(2)	170(3)
	O(2) – H(2A) ⋯O(1)	0.96(4)	1.80(4)	2.753(3)	175(4)
400K	O(1) – H(1A) ⋯O(2)	0.90(4)	1.81(4)	2.705(3)	174(4)
	O(2) – H(2A) ⋯O(1)	0.96(5)	1.81(5)	2.761(4)	173(4)

Symmetry Code for O(1) – H(1A) ⋯O(2): **3/2-x, 1-y, 1/2+z**

Symmetry Code for O(2) – H(2A) ⋯O(1): **1-x, -1/2+y, 3/2-z.**

4. Powder X-ray Diffraction.

The Powder X-Ray diffraction studies of both the compounds were carried on a PANalytical X'pert PRO X-ray Powder Diffractometer using CuKα1 radiation(1.54Å). The crystals of the synthesized compounds were crushed gently and layered on a glass slide. Data were collected at room temperature at scan rate of 2°/ min from 5° to 40°(2θ value).

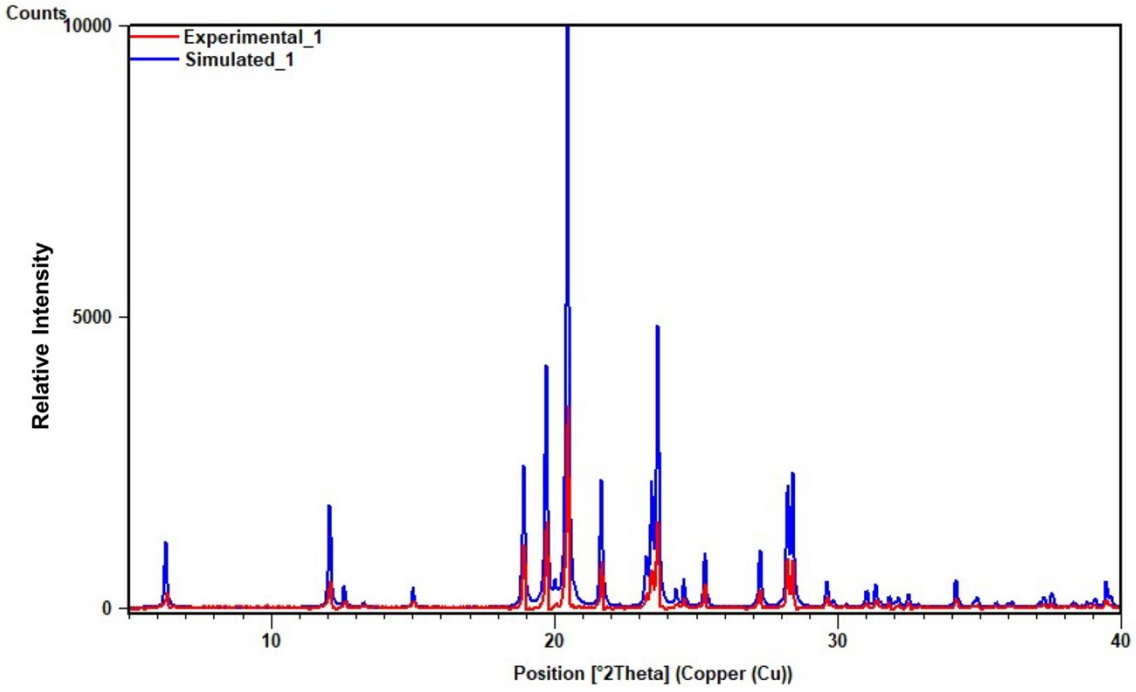


Figure S10. Powder X-ray Diffractogram of bulk sample of compound **1** (red) and simulated pattern obtained from SCXRD data (blue).

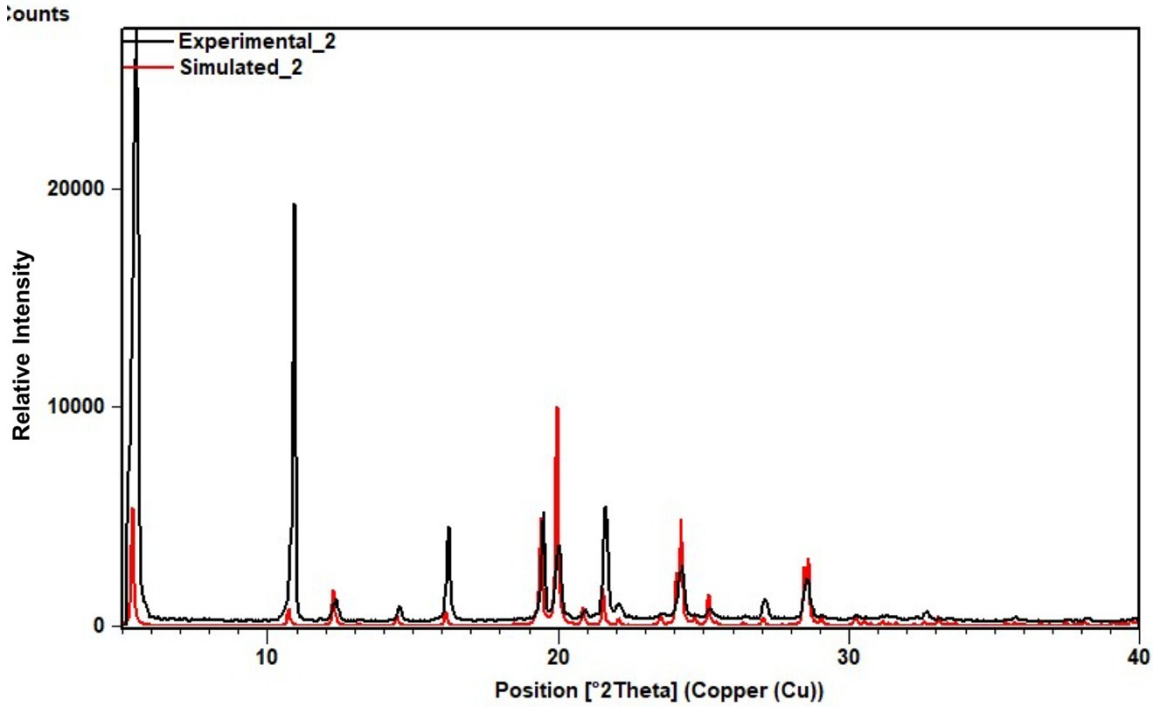


Figure S11. Powder X-ray Diffractogram of bulk sample of compound **2** (black) and simulated pattern obtained from SCXRD data (red).

5. Variation of Atomic Displacement Parameters (U_{11}, U_{22} and U_{33}) of Carbon atoms with Temperature for compound 1 and 2.

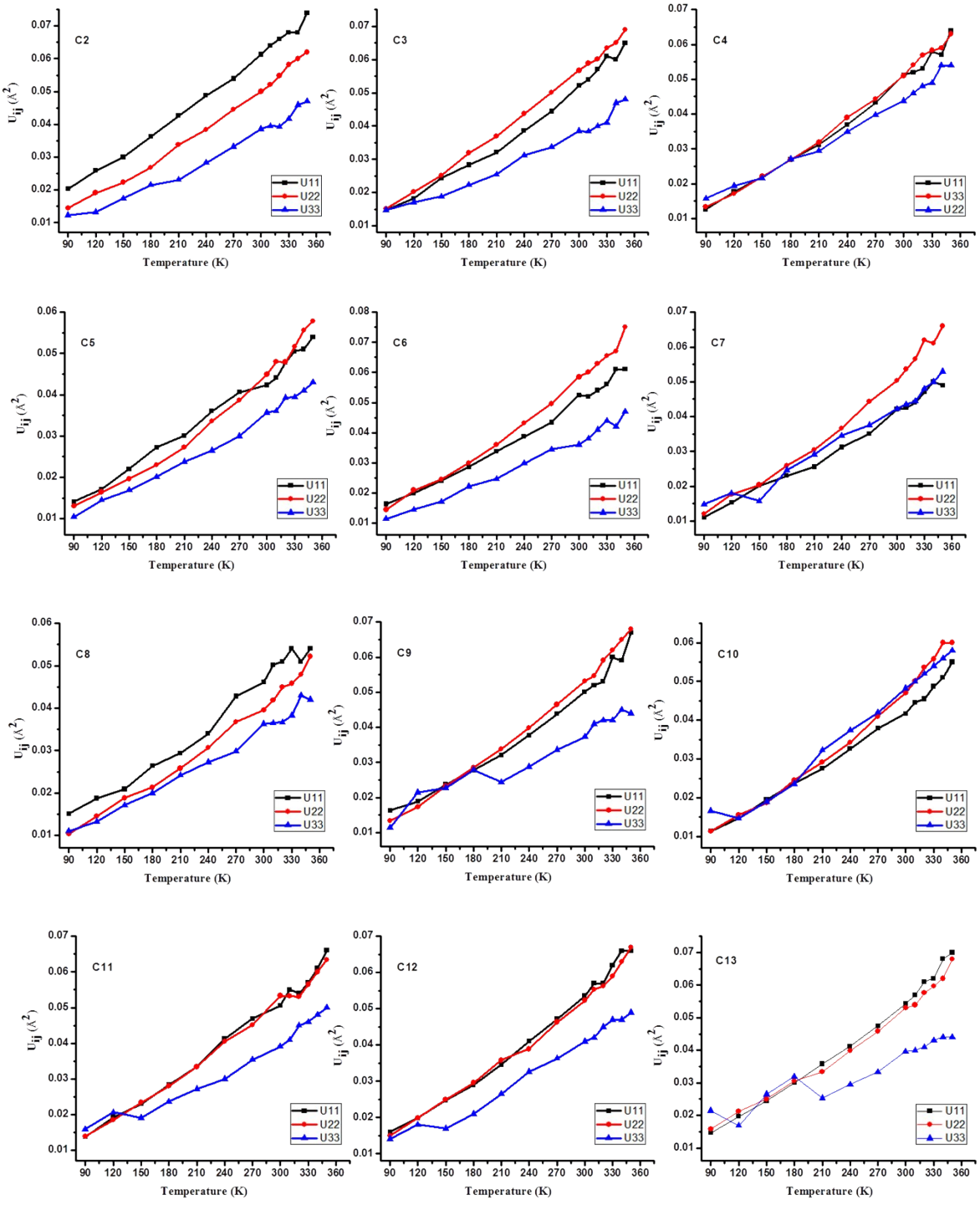
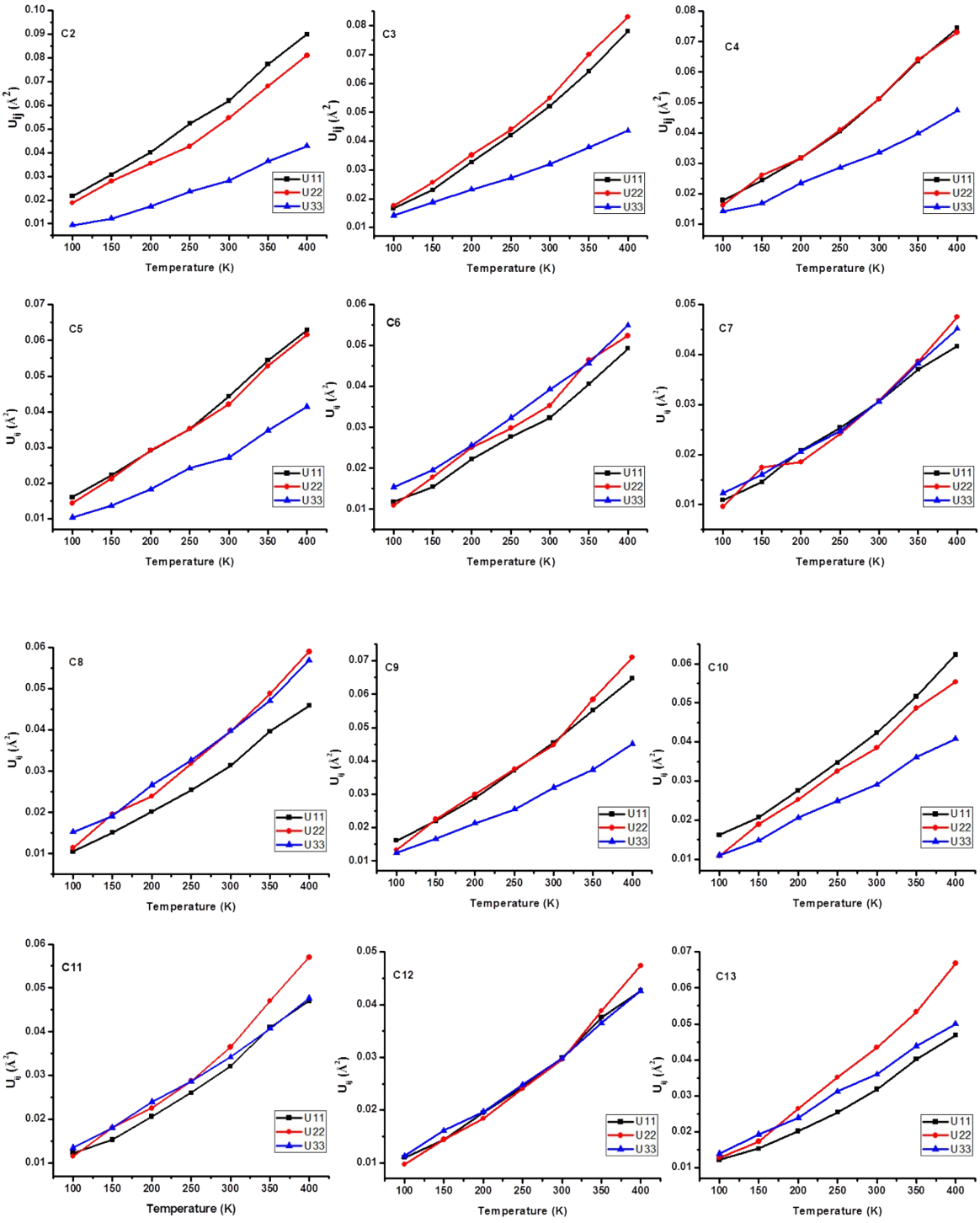


Figure S12. Change of ADPs (U_{11}, U_{22} and U_{33}) of carbon atoms of compound **1** with temperature.


C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
U11
U22
U33
Temperature (K)
U_{ij} ($Å^2$)
U_{ij} ($Å^2$)

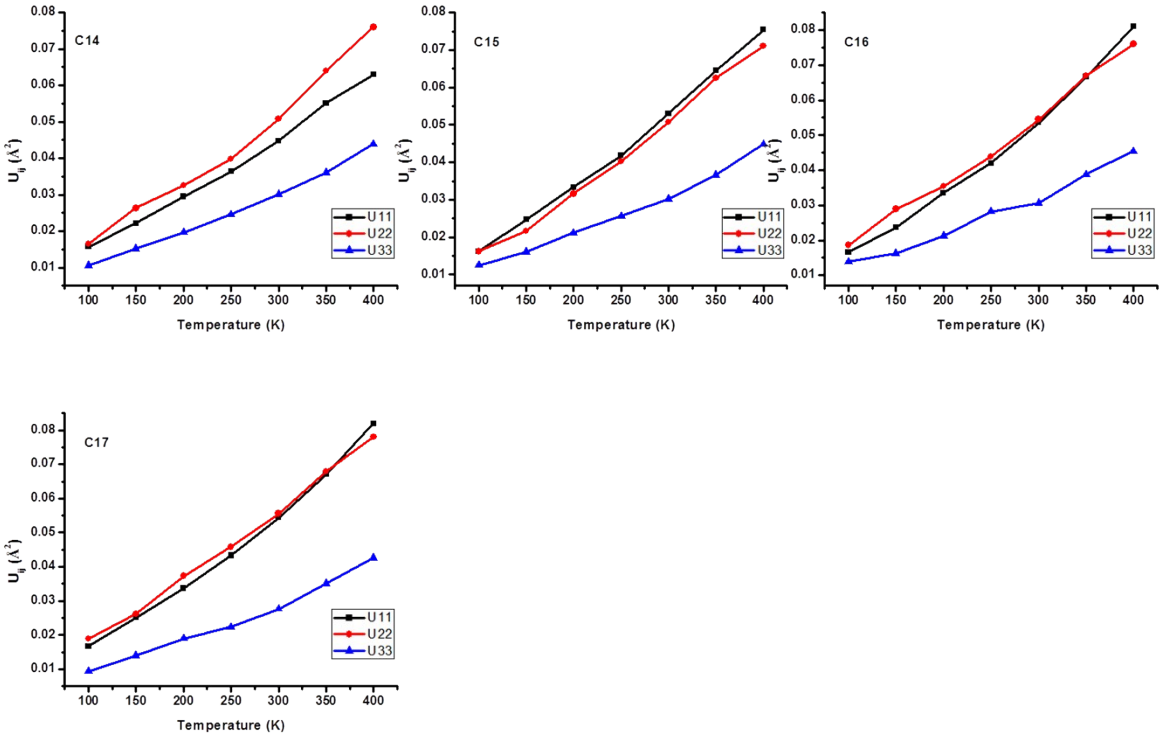
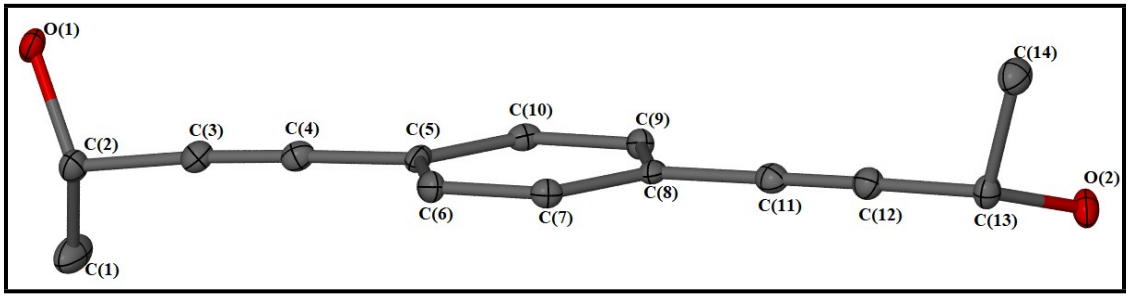
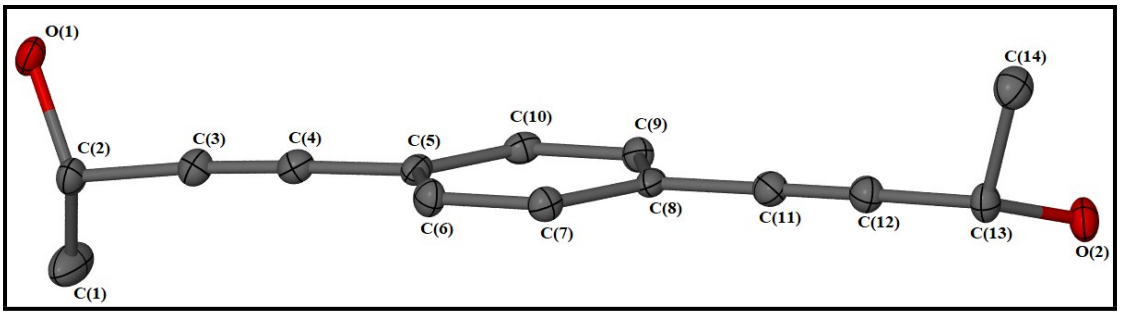


Figure S13. Change of ADPs (U_{11}, U_{22} and U_{33}) of carbon atoms of compound **2** with temperature.

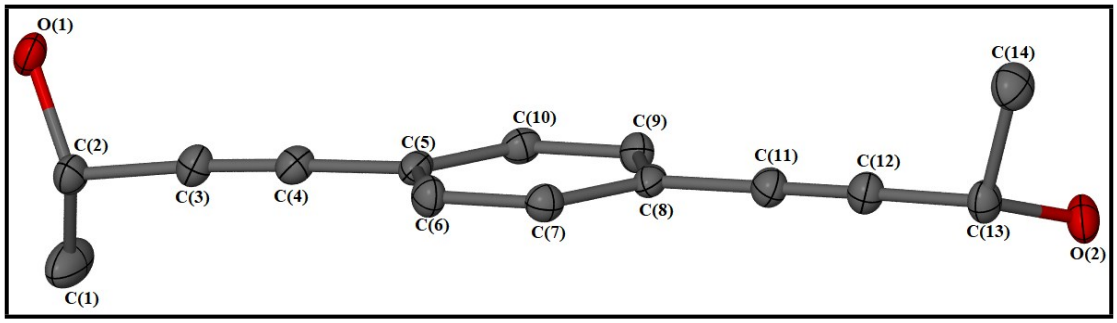
6. Thermal Ellipsoid Plot for compound 1 and 2 at variable temperatures.



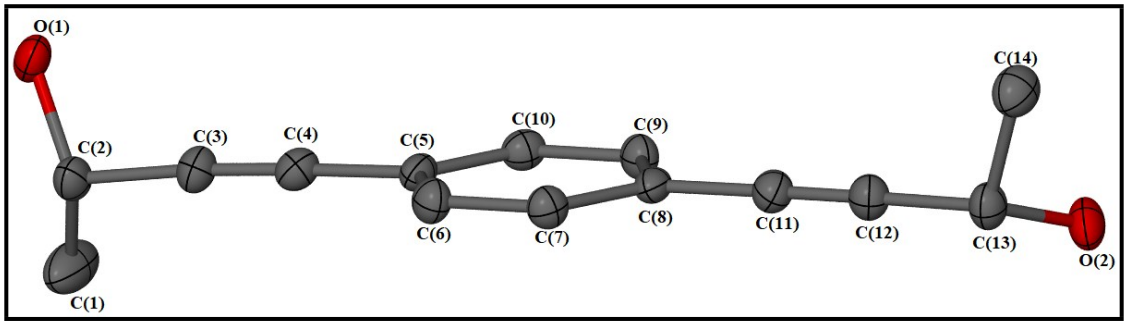
90K



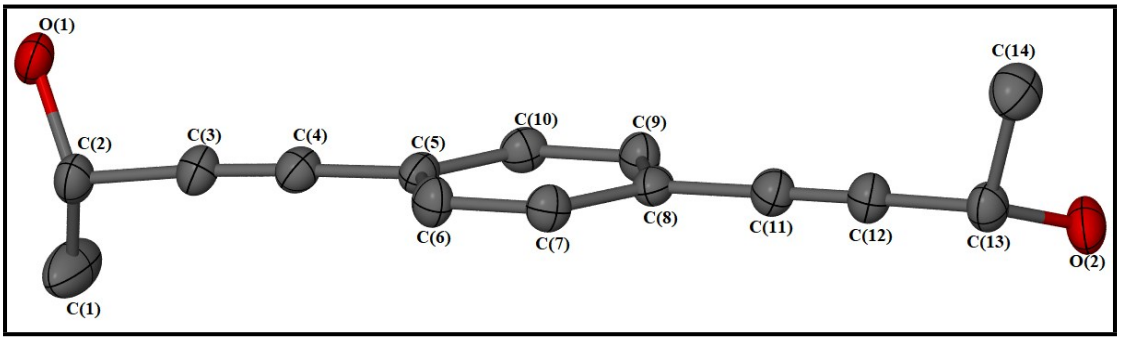
120K



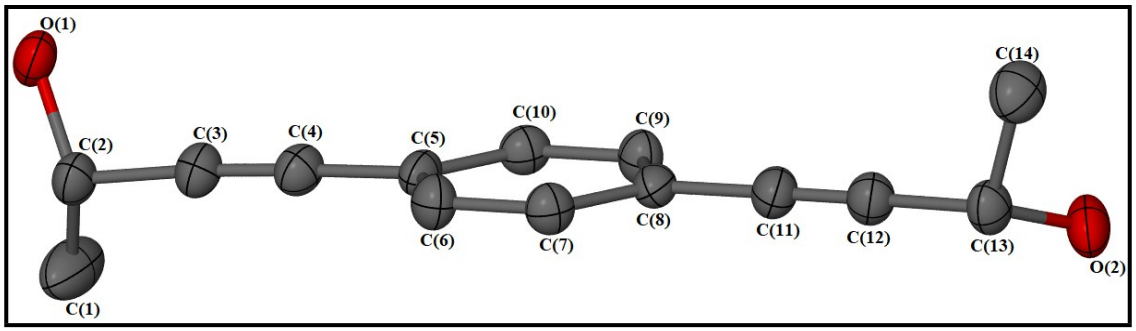
150K



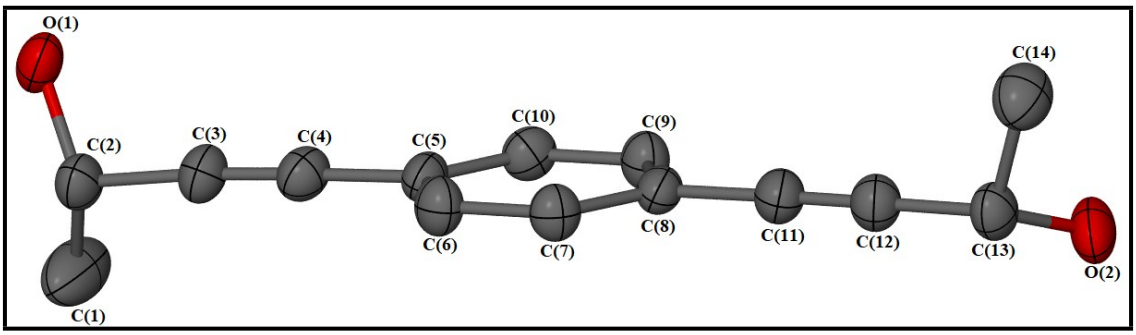
180 K



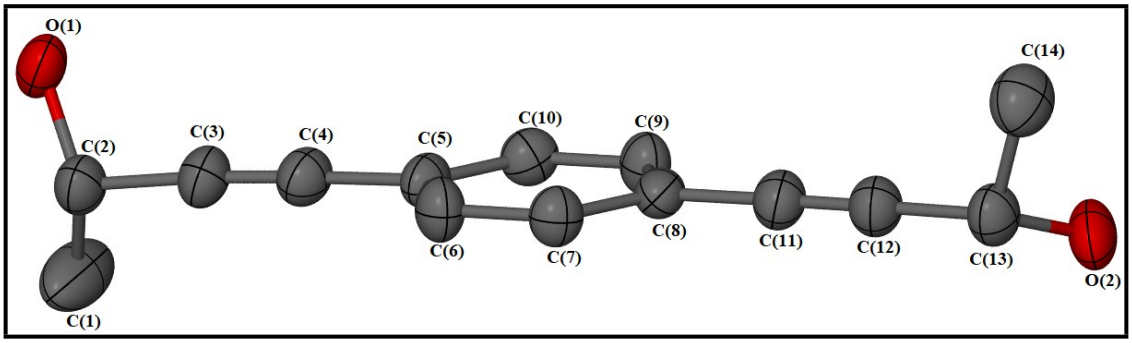
210 K



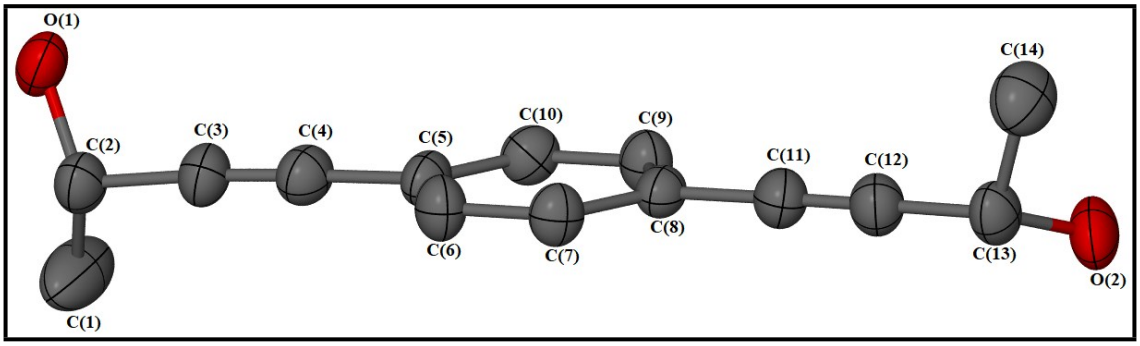
240K



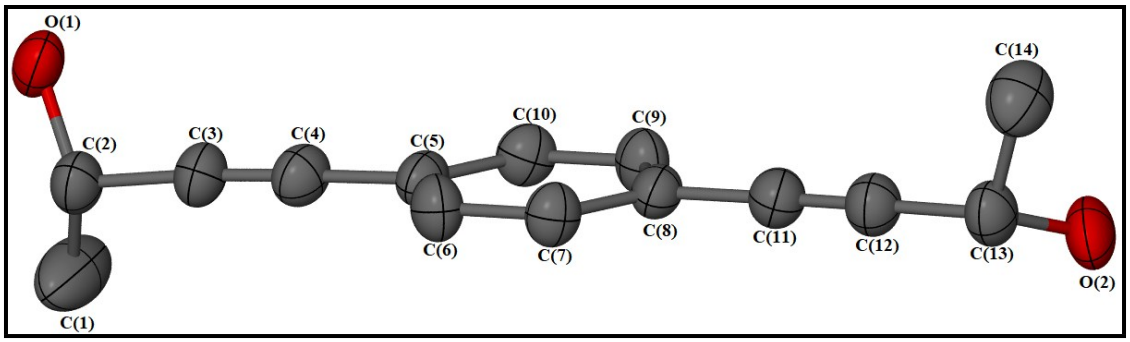
270 K



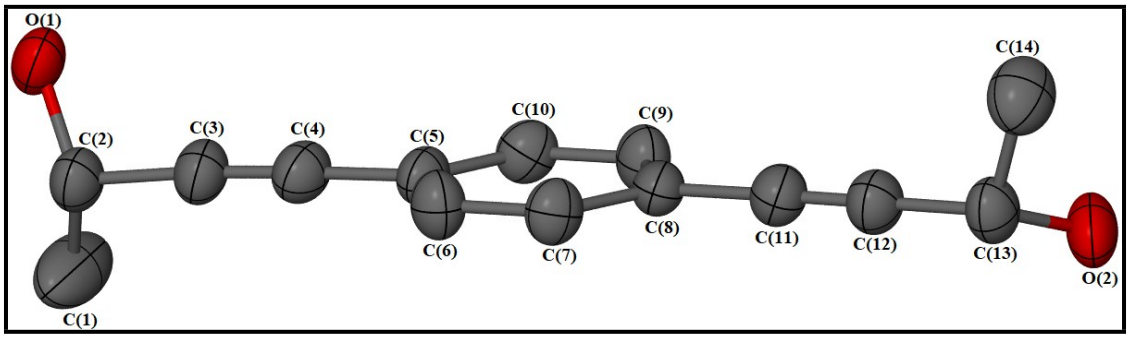
300 K



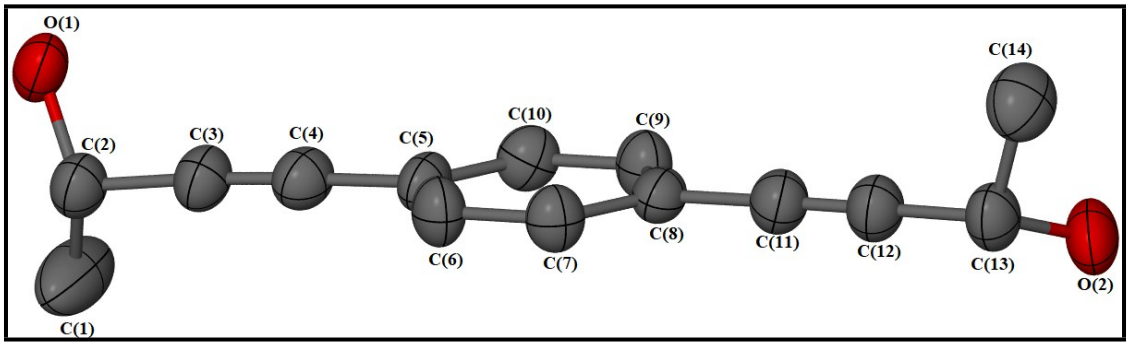
310 K



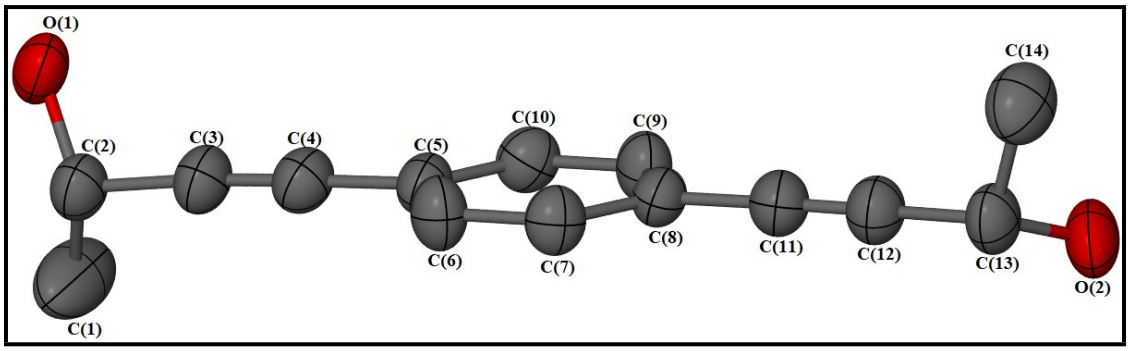
320 K



330 K

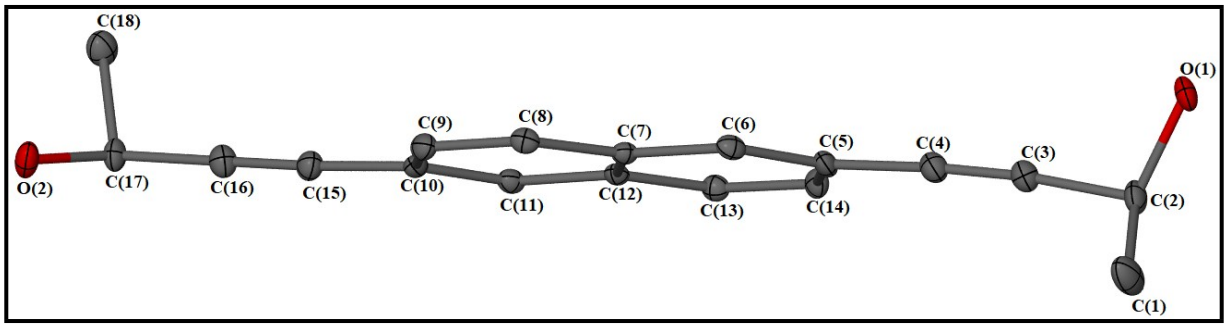


340 K

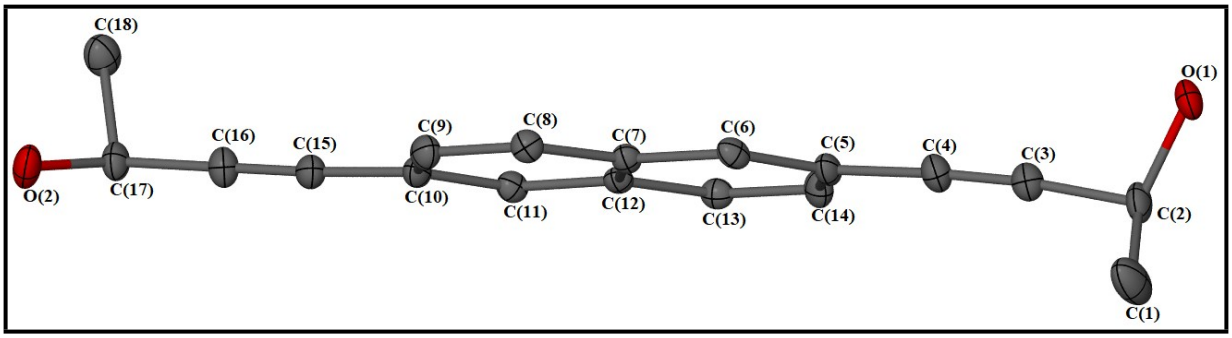


350 K

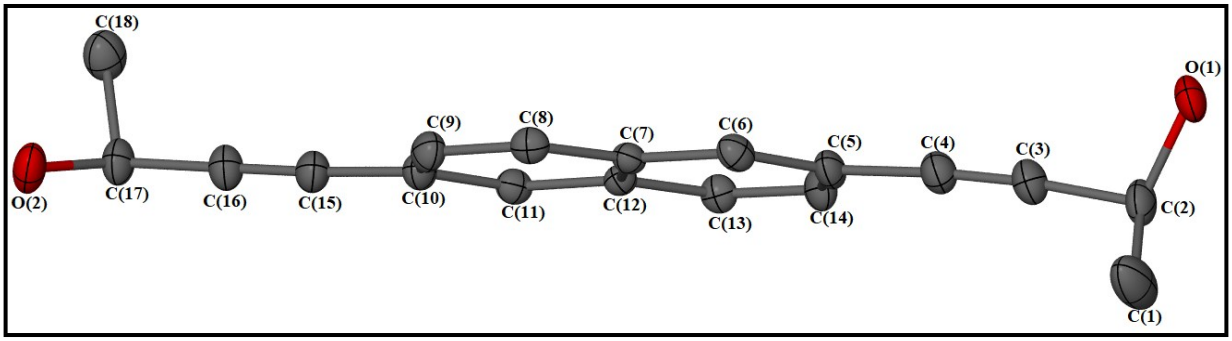
Figure S14. Thermal ellipsoid plot of the molecule in the asymmetric unit of the crystal structure of compound **1** at different temperature. Thermal ellipsoid plots are shown in 50 % probability.



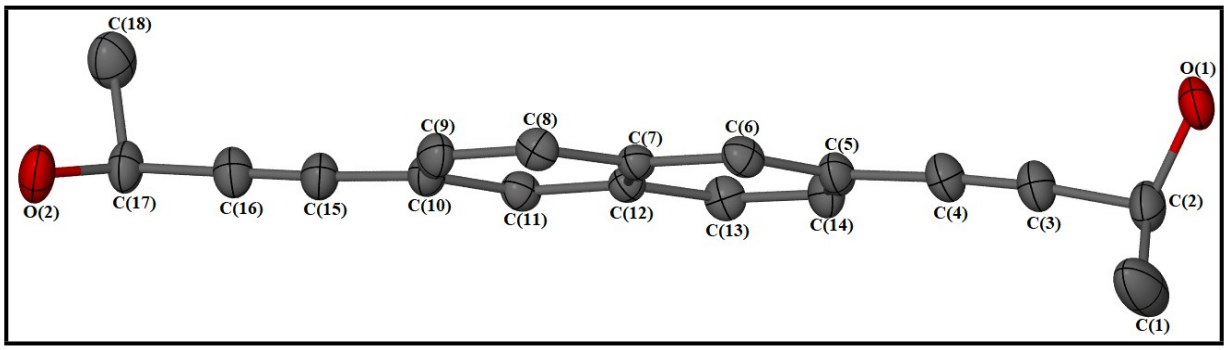
100K



150 K



200 K



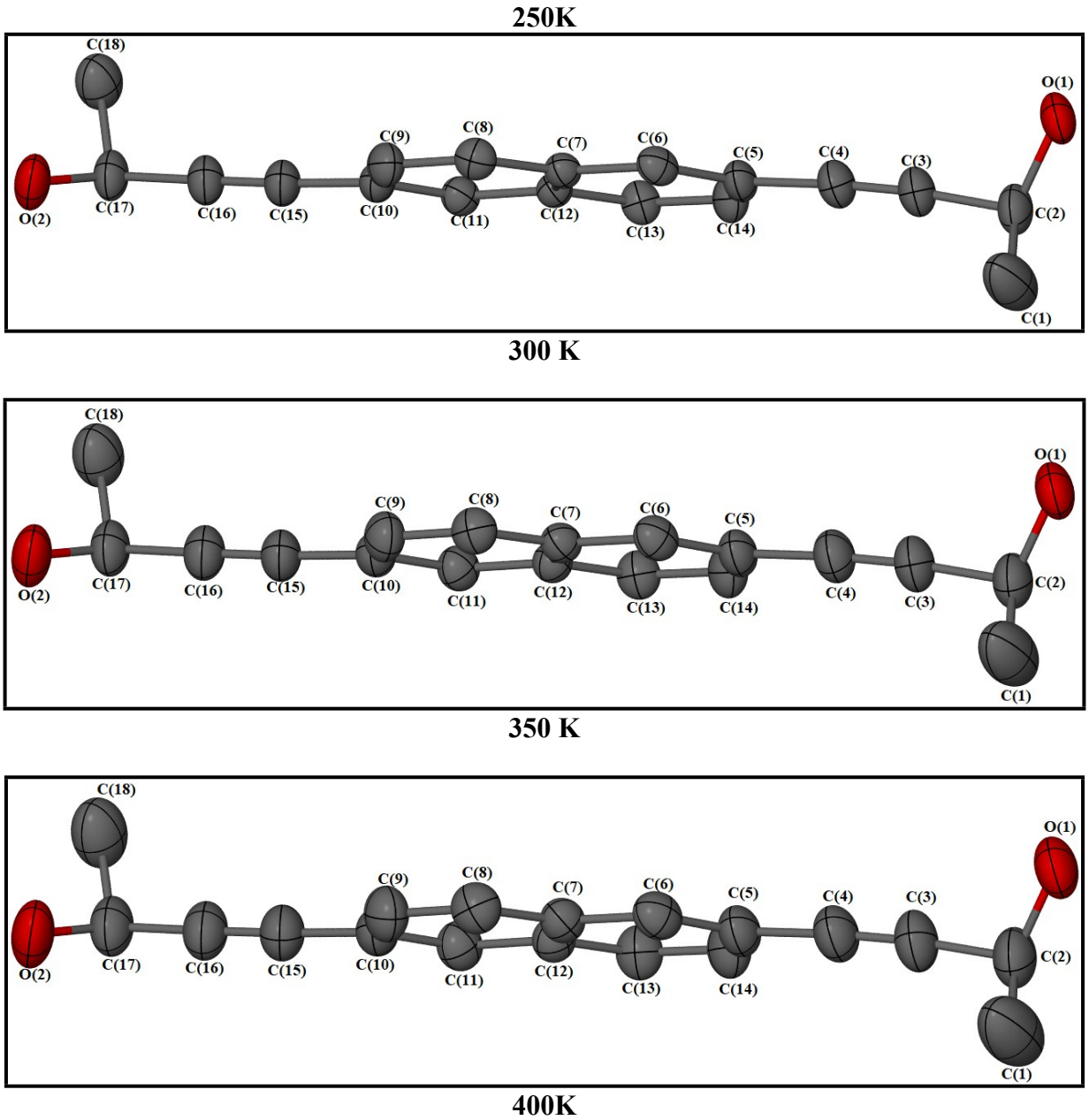


Figure S15. Thermal ellipsoid plot of the molecule in the asymmetric unit of the crystal structure of compound **2** at different temperature. Thermal ellipsoid plots are shown in 50 % probability.

7. References:

1. K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Letters*, 1975, **50**, 4467.

2. SAINT; Bruker AXS Inc., Madison, Wisconsin, USA, 2013. SADABS; Bruker AXS Inc., Madison, Wisconsin, USA, 2012.

3. G. M. Sheldrick, SHELXTL v 2014/7; http://shelx.uni-ac.gwdg.de/SHELX/index.php.

4. PLATON - A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148.