Supplementary information

Two different emissions of (2*Z*)-2-(4-bromophenyl)-3-[4-(dimethylamino)phenyl]prop-2-enenitrile due to crystal habit and size: synthesis, optical and supramolecular characterization

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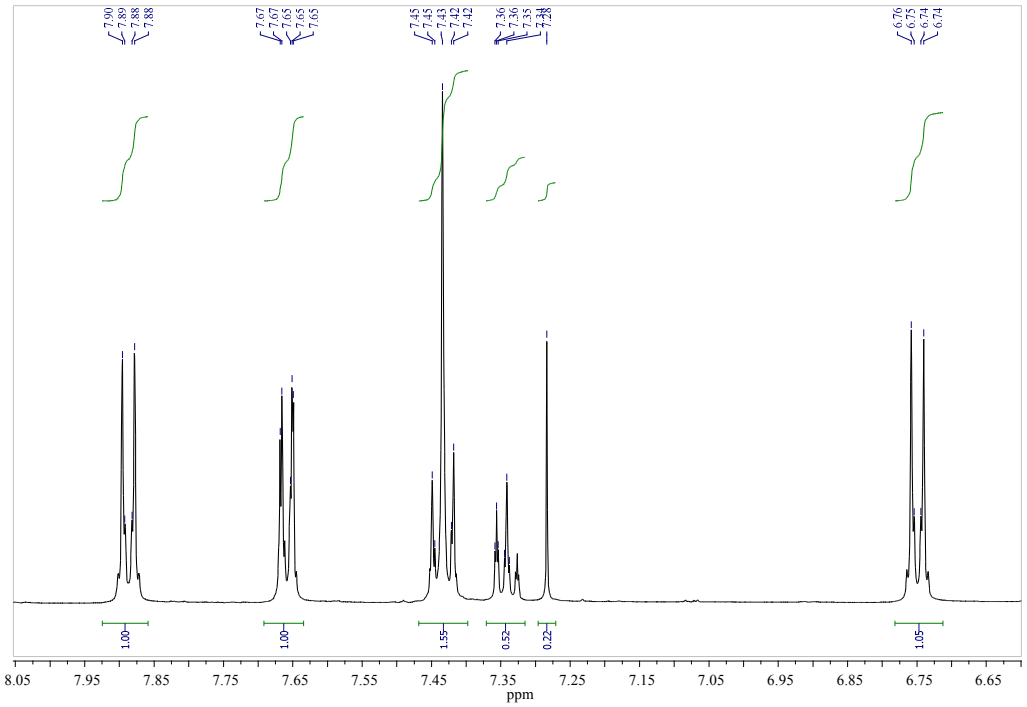
Preparation of crystals I and II

Crystal **I**, the yellow powder, (0.020 g) was dissolved in heated cyclohexane (25 mL) and the vessel was set aside at room temperature and after 18 h the crystals grown from solvent evaporation. The vessel was kept for 12 h more and then the crystals were filtered.

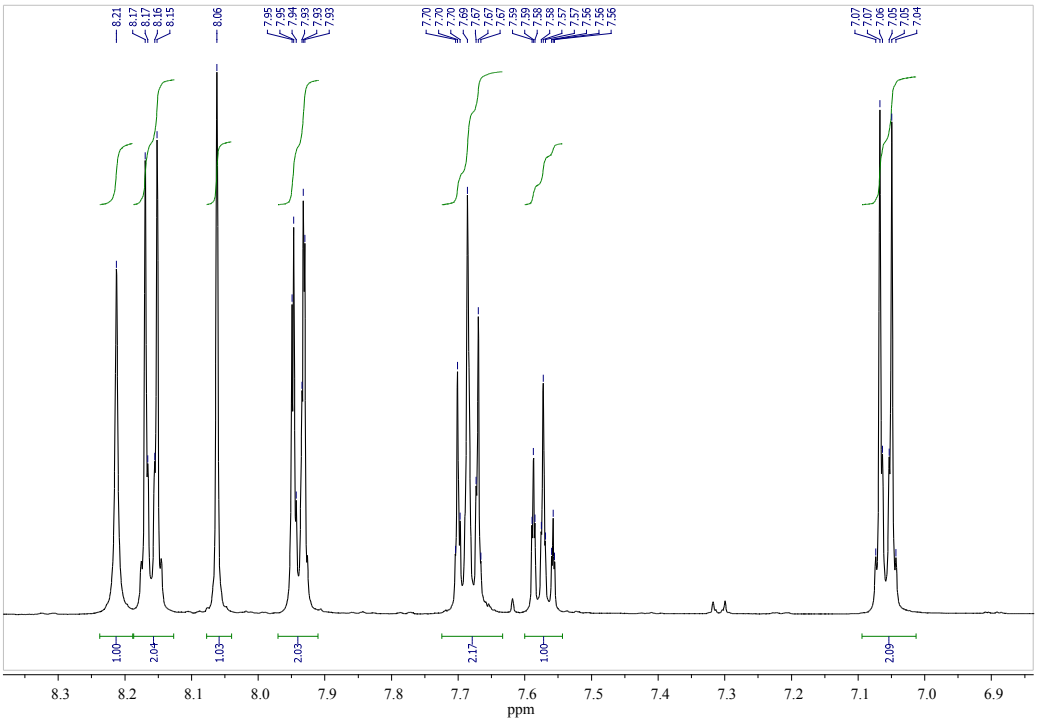
Crystal **II** was obtained as a result in the substitution reaction according to the following conditions: The molar ratio of yellow powder (2*Z*)-2-(4-bromophenyl)-3-[4-(dimethylamino)phenyl]prop-2-enenitrile and *N*-methylaminoethanol was 1:3. To a solution of yellow powder (0.327 g (1.0 mmol)) in DMSO (5 mL) was added of *N*-methylaminoethanol (0.2 mL (3.0 mmol)). The mixture was stirred for 5 min, then K_2CO_3 (0.138 g (1.0 mmol)) was added. After 15 min, CuI (0.019 g, (1.0 mmol)) was added. As the temperature was increased, the color of reaction mixture changed from green →green-yellow → dark-red. The reaction was maintained at reflux for 50 h at 96 °C until a dark-red solution was obtained. A yellow-orange powder was precipitated by treatment with ethanol:water (1:1) at 4 °C. The powder was washed with ethanol followed with hexane in an ice bath. For crystallization, 0.18 g of the yellow-orange powder was treated with 25 mL of warm cyclohexane and the vessel was set aside for 26 h until the orange-yellow crystals grown from solvent evaporation. The m.p. was 192-194 °C and the yield was 87%.

^{1}H NMR spectra

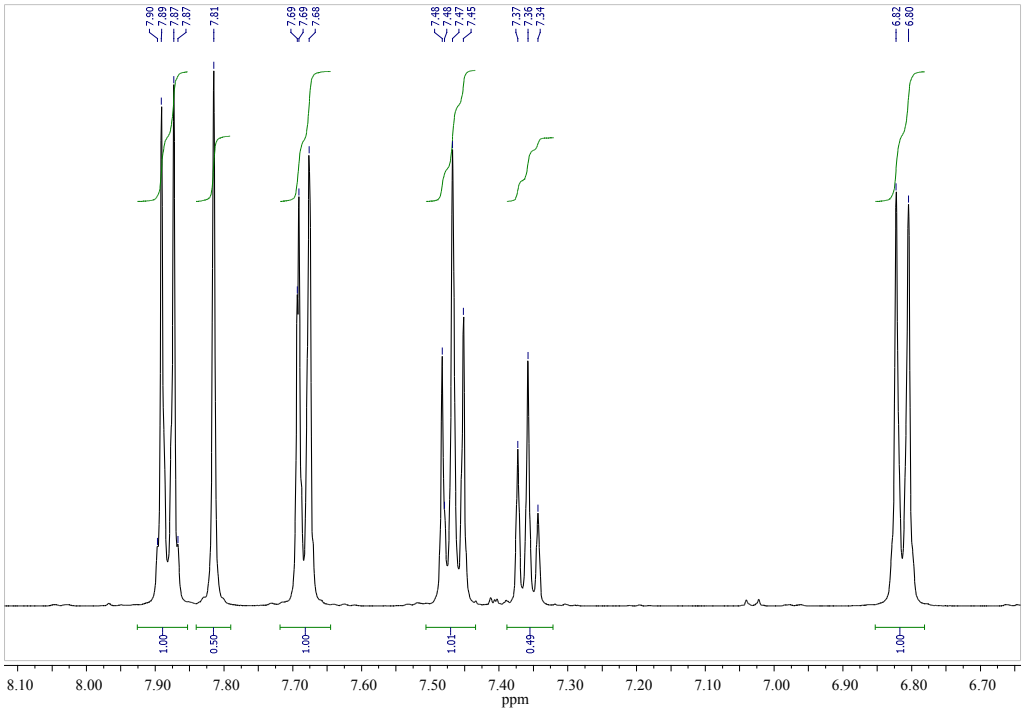
A ($CDCl_3$)



A (DMF)



A (DMSO)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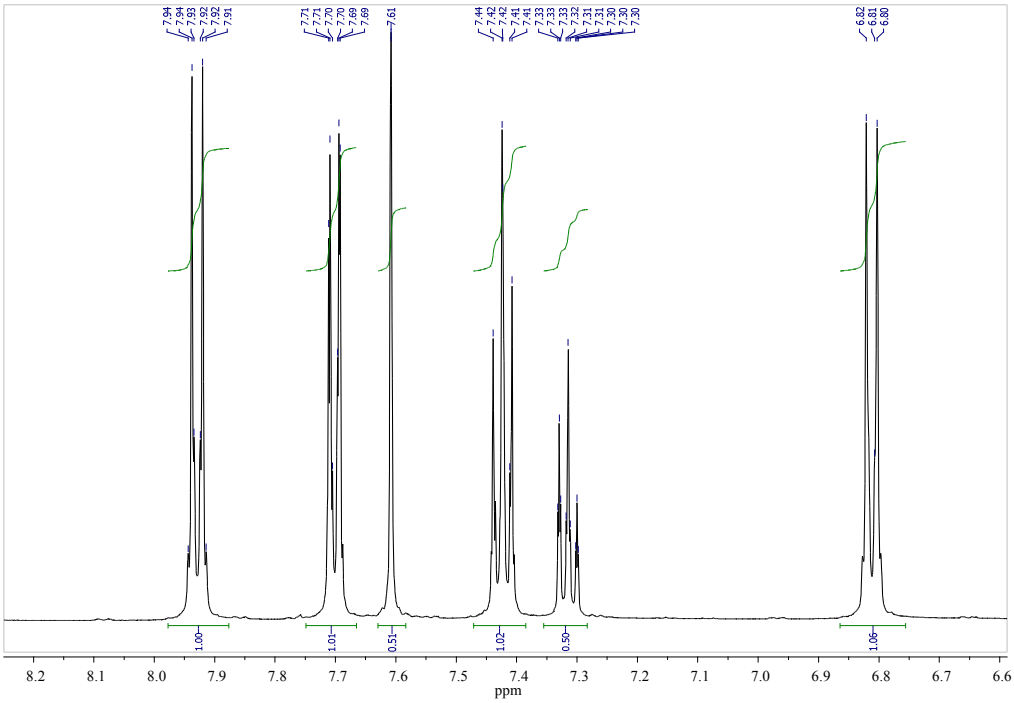
7.37
7.36
7.34
6.82
6.80
1.00
0.50
1.00
1.01
0.49
1.00
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
ppm

A (THF)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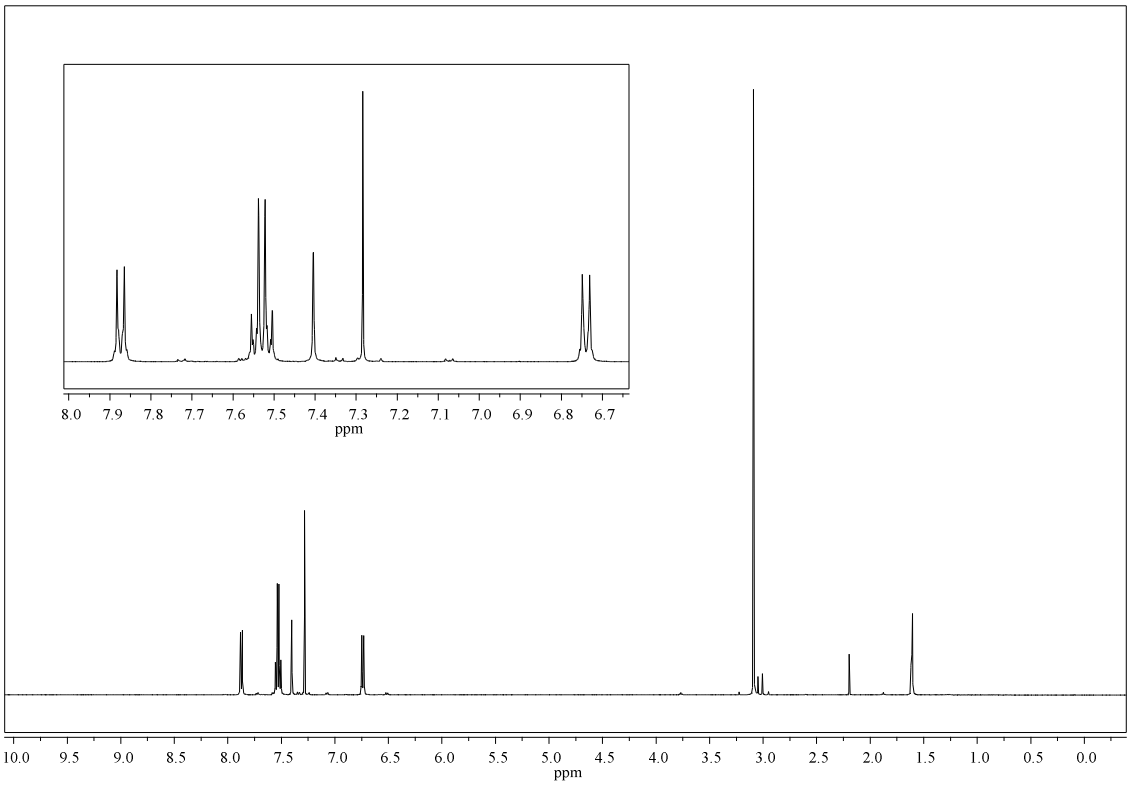
7.42
7.41
7.41
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.30
6.82
6.81
6.80
1.00
1.01
0.51
1.02
0.50
1.06
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm

I ($CDCl_3$)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ppm
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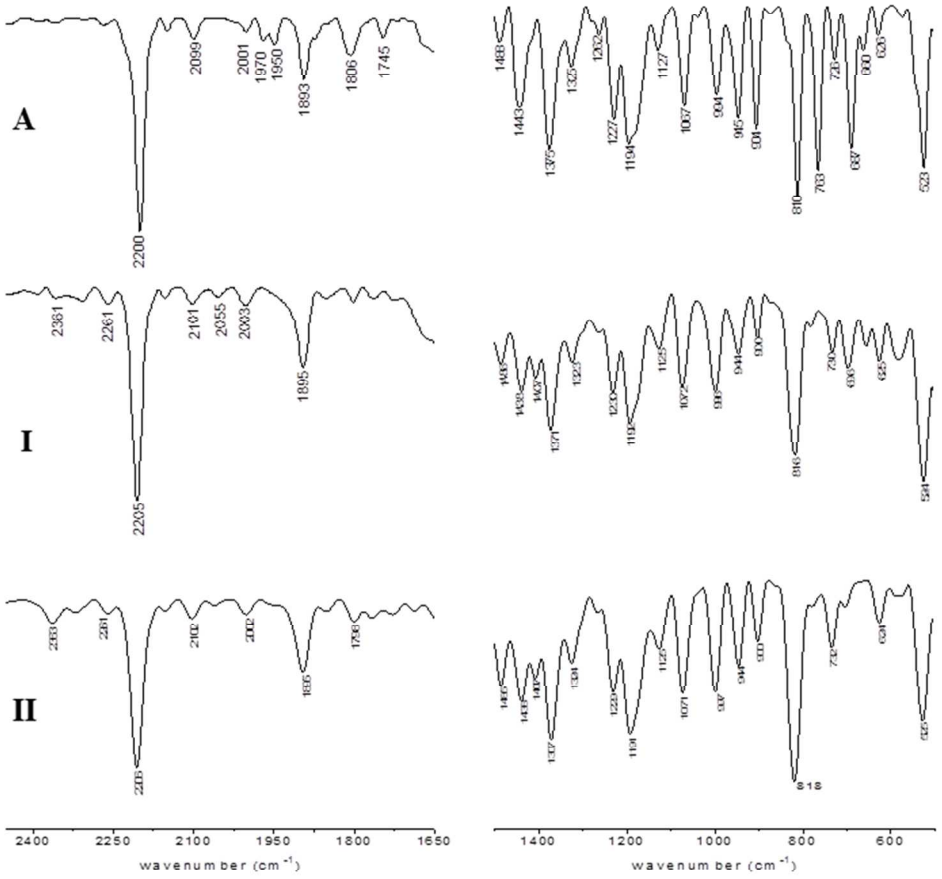
ppm

IR spectra



Comparison of FT-IR spectra of the **A**, **I** and **II**, spectral regions of 2400-1550 cm^{-1} and 1400-500 cm^{-1} at 293 K.

Table S1. Vibrational frequencies in (cm^{-1}) of **A** and the crystals **I** and **II**.

	A	**I**	**II**
assignation	wavenumber (cm^{-1})		
νC-H (Ar)	3090 w	3084 w	3086 w
νC-H (Ar)	3032 w	3038 w	3038 w
ν_{as}C-H (CH_3)	2905 s	2904 s	2903 s
ν_{s}C-H (CH_3)	2819 m	2817 m	2816 m
νC-H overtone	2650 w	2642 w	
νC-H overtone	2548 w	2542 w	
νC≡N	2200 s	2205 s	2205
νC-H overtone (Ar)	2149 w	2102 w	
	2099 w		
	2001 w	2003 w	
νC=C alkene	1611 s		1611 s
νC=C (Ar)	1578 s	1580 s	1580 s
νC=C (Ar)	1529 s 1488 m	1530 s 1485 m	1527 s 1486 m
δ_{as}C-H (CH_3)	1443 m	1438 m	1436 m
δ_{s}C-H (CH_3)	1375 m	1372 s	1372 s
δC-H alkene	1325 m	1323	1323 w
νC-H (CH_3)	1262	1230	1231 m
νC-N [$N(CH_3)_2$]	1194 s	1191	1193.80s
νC-H (CH_3)	1127 m	1126	
δC-H (Ar) (in-plane)	1067 s	1072	1075 s
δC=C-H alkene (out-of plane)	994 s	997	995 s
δC-H (Ar) (in-plane)	945 m	944	944 m
δC-H (Ar) (out-of plane)	904 m	901	900 m
νC=C-H alkene tri-substituted	810 s	815	815 s
δC=C-H (Ar) (in-plane)	726 w	731	731 w
δC=C-H (Ar) (out-of plane)	687 w	695	
δC-H (out-of plane)	626 w	624	626 w
δC=C (out-of plane)	523 m	579; 523	525 s

s = strong, m = medium, w = weak

Table S2. Selected bond lengths (Å) and torsion angles (°) in both crystals **I** and **II** and their comparison with **A**

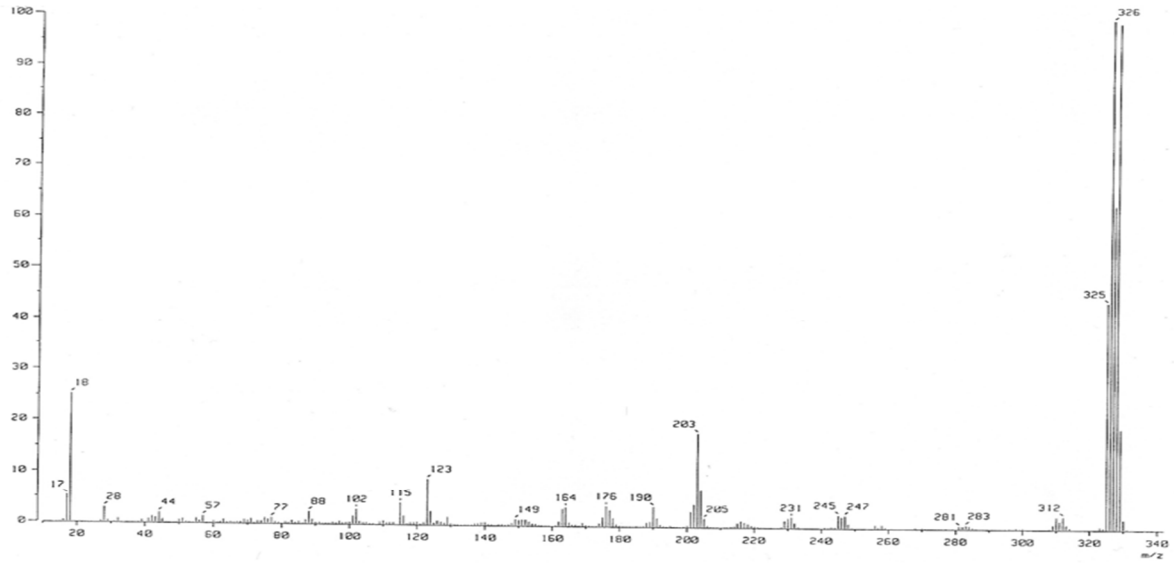
Bond lengths	**I**	**II**	**A**
C(1)-N(1)	1.448(2)	1.443(6)	1.447(3)
C(2)-N(1)	1.4500(19)	1.409(6)	1.454(3)
C(3)-N(1)	1.366(2)	1.369(5)	1.371(3)
C(3)-C(8)	1.412(2)	1.410(7)	1.414(3)
C(3)-C(4)	1.415(2)	1.413(7)	1.407(3)
C(4)-C(5)	1.376(2)	1.385(6)	1.380(3)
C(5)-C(6)	1.408(2)	1.392(7)	1.409(3)
C(6)-C(7)	1.407(2)	1.408(7)	1.406(3)
C(6)-C(9)	1.447(2)	1.462(5)	1.454(3)
C(7)-C(8)	1.380(2)	1.377(6)	1.381(3)
C(9)-C(10)	1.356(2)	1.350(6)	1.356(3)
C(10)-C(11)	1.439(2)	1.436(7)	1.441(3)
C(10)-C(12)	1.484(2)	1.491(6)	1.496(3)
C(11)-N(2)	1.149(2)	1.145(7)	1.151(3)
C(12)-C(13)	1.398(2)	1.386(7)	1.391(3)
C(12)-C(17)	1.401(2)	1.413(6)	1.393(3)
C(13)-C(14)	1.390(2)	1.390(6)	1.392(3)
C(14)-C(15)	1.381(2)	1.357(7)	1.385(4)
C(15)-C(16)	1.386(2)	1.377(7)	1.378(3)
C(15)-Br(1)	1.8961(15)	1.904(4)	
C(16)-C(17)	1.383(2)	1.397(6)	1.393(3)

Torsion angle (°)	**I**	**II**
N(1)-C(3)-C(4)-C(5)	-179.65(14)	-179.0(5)
C(8)-C(3)-C(4)-C(5)	0.0(2)	0.3(8)
C(3)-C(4)-C(5)-C(6)	0.0(2)	-0.8(9)
C(4)-C(5)-C(6)-C(7)	0.0(2)	1.1(8)
C(4)-C(5)-C(6)-C(9)	-178.35(15)	-178.0(5)
C(5)-C(6)-C(7)-C(8)	0.0(2)	-1.0(8)
C(9)-C(6)-C(7)-C(8)	178.51(14)	178.2(5)
C(6)-C(7)-C(8)-C(3)	0.0(2)	0.5(9)
N(1)-C(3)-C(8)-C(7)	179.66(14)	179.1(5)
C(4)-C(3)-C(8)-C(7)	0.0(2)	-0.2(8)
C(7)-C(6)-C(9)-C(10)	-179.84(16)	179.2(6)
C(5)-C(6)-C(9)-C(10)	-1.5(3)	-1.7(10)
C(6)-C(9)-C(10)-C(11)	-1.9(3)	-1.7(10)
C(6)-C(9)-C(10)-C(12)	178.39(15)	178.2(5)
C(9)-C(10)-C(12)-C(13)	-178.84(14)	-178.6(5)

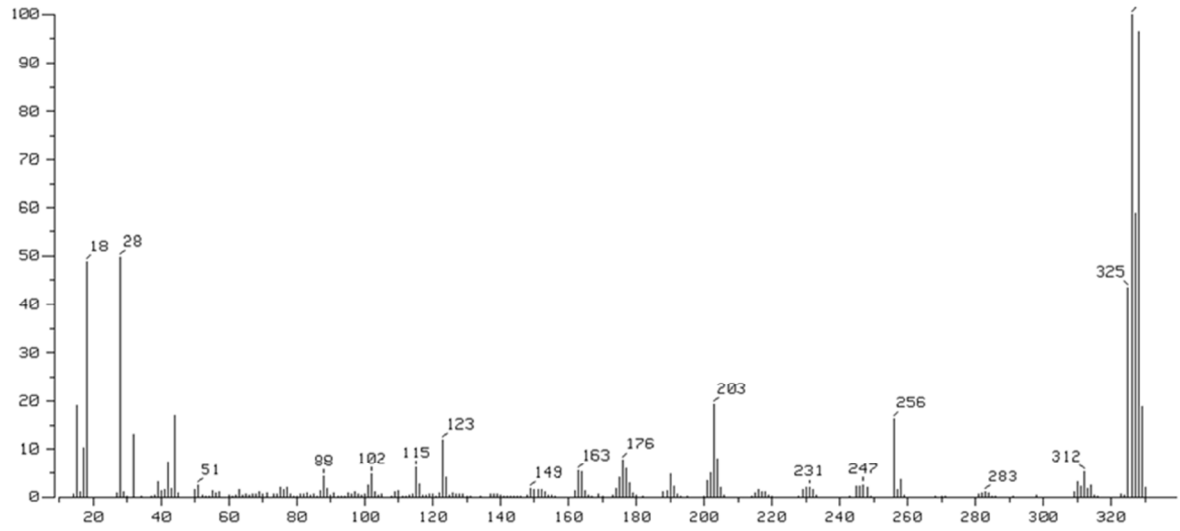
C(11)-C(10)-C(12)-C(13)	1.5(2)	1.4(8)
C(9)-C(10)-C(12)-C(17)	1.4(2)	2.5(9)
C(11)-C(10)-C(12)-C(17)	-178.26(14)	-177.5(5)
C(17)-C(12)-C(13)-C(14)	0.6(2)	-0.2(8)
C(10)-C(12)-C(13)-C(14)	-179.13(14)	-179.1(5)
C(12)-C(13)-C(14)-C(15)	0.1(2)	0.4(9)
C(13)-C(14)-C(15)-C(16)	-0.8(2)	-0.5(9)
C(13)-C(14)-C(15)-Br(1)	178.09(11)	178.0(4)
C(14)-C(15)-C(16)-C(17)	0.9(2)	0.4(9)
Br(1)-C(15)-C(16)-C(17)	-178.02(12)	-178.1(4)
C(15)-C(16)-C(17)-C(12)	-0.2(2)	-0.2(8)
C(13)-C(12)-C(17)-C(16)	-0.5(2)	0.1(8)
C(10)-C(12)-C(17)-C(16)	179.19(14)	179.0(5)
C(8)-C(3)-N(1)-C(1)	-176.94(14)	-176.7(5)
C(4)-C(3)-N(1)-C(1)	2.7(2)	2.5(8)
C(8)-C(3)-N(1)-C(2)	-5.8(2)	-5.2(8)
C(4)-C(3)-N(1)-C(2)	173.89(14)	174.0(5)

Mass Spectra

(I)



(II)



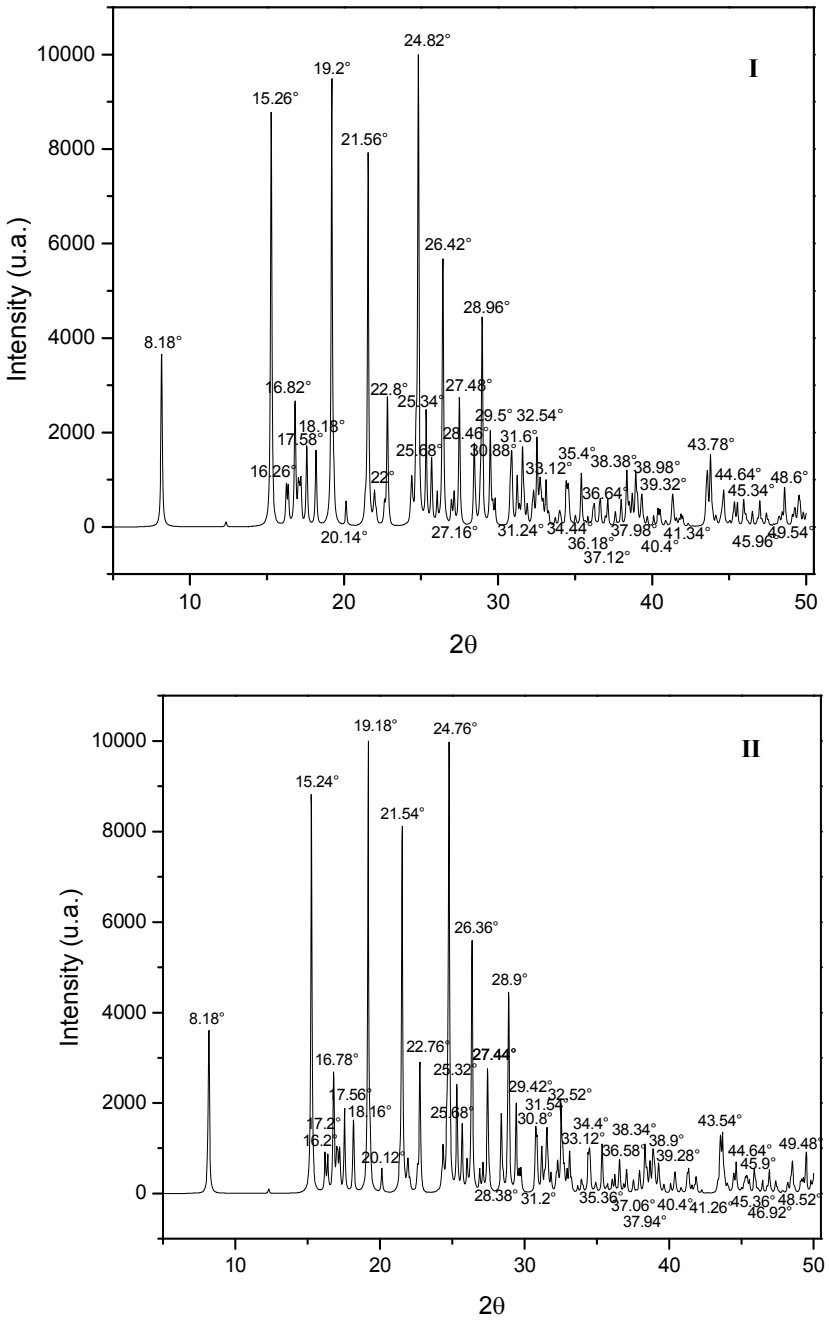


Figure S1. Simulated powder diffraction patterns of **I**, and **II** by mercury software.

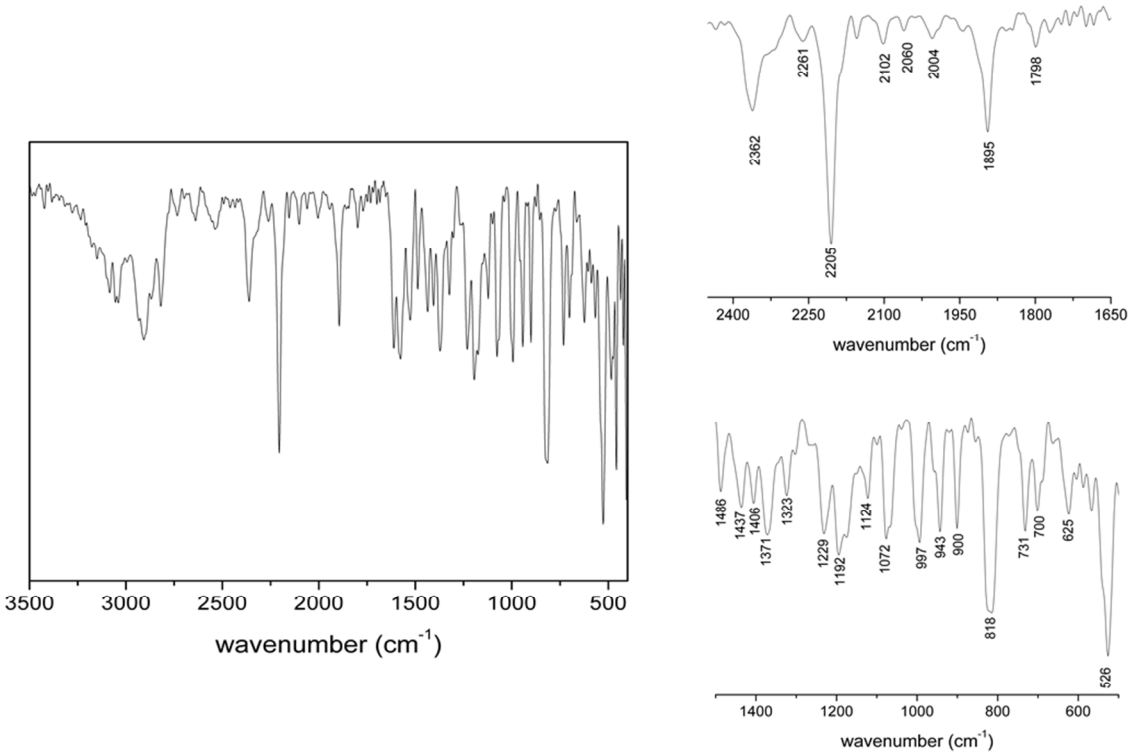


Figure S2. FT-IR spectrum of **I*** in spectral regions of 2400-1550 cm^{-1} and 1400-500 cm^{-1} taken at 293 K

Table S3. Selected data for comparison of the data crystallography for **I**, **II** and **I***.

	I	**II**	**I***
T(K)	110	110	110
a (Å)	11.0169(2)	11.0475(6)	10.995(9)
b (Å)	6.02041(11)	6.0273(3)	6.036(5)
c (Å)	21.8541(4)	21.8533(11)	21.82(2)
α(°)	90	90	90
β(°)	98.4082(18)	98.315(5)	98.35(6)
γ(°)	90	90	90
V $Å^3$	1433.93(5)	1439.84(13)	1433(2)

*I treated with DMF at 100 °C orange crystal

Table S4. Selected data for aliquots at different time A1 (2h), A2 (4h), A3 (6h), A4 (8h), A5 (10h), A6 (12h) and A7 (24h).

	a	b	c	α	β	γ	V
aliquot	Å			°			$Å^3$
A1	11.018(4)	6.021(2)	21.848(9)	90.0	98.42(3)	90.0	1433.7(9)
A2	11.020(3)	6.022(2)	21.847(6)	90.0	98.40(2)	90.0	1434.3(8)
A3	11.020(3)	6.0153(17)	21.852(7)	90.0	98.45(2)	90.0	1432.9(7)
A4	11.024(4)	6.0224(12)	21.832(7)	90.0	98.44(3)	90.0	1433.7(7)
A5	11.017(4)	6.0214(16)	21.847(5)	90.0	98.46(4)	90.0	1433.5(7)
A6	11.010(3)	6.0200(16)	21.816(9)	90.0	98.44(3)	90.0	1430.2(8)
A7	11.025(4)	6.029(2)	21.864(6)	90.0	98.46(3)	90.0	1437.5(8)

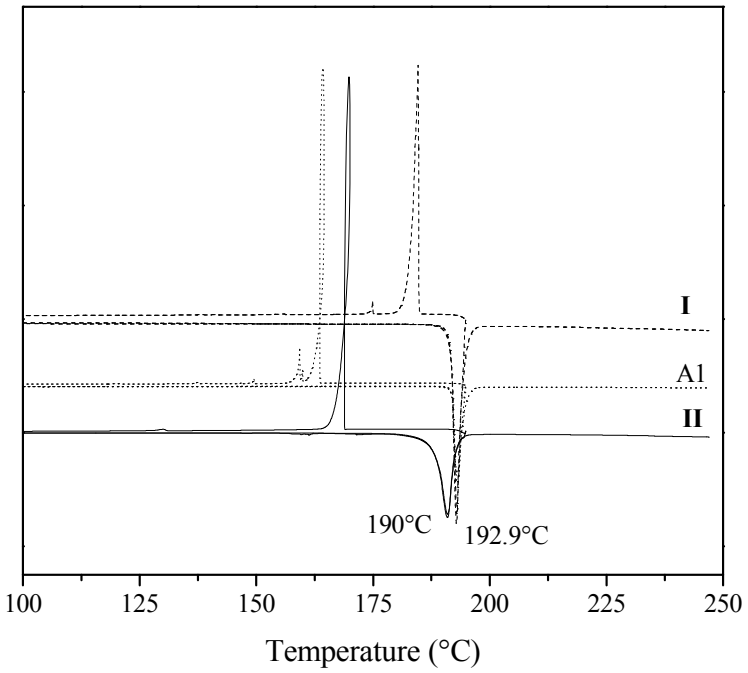


Figure S3. Thermograms of **I**, **II** and **A1 (**aliquot taken at 2 hours) in the experiment using yellow powder of (*Z*)-2-(4-bromophenyl)-3-(4-(dimethylamino)phenyl)acrylonitrile dissolved in DMF at 110 °C for 4 h.

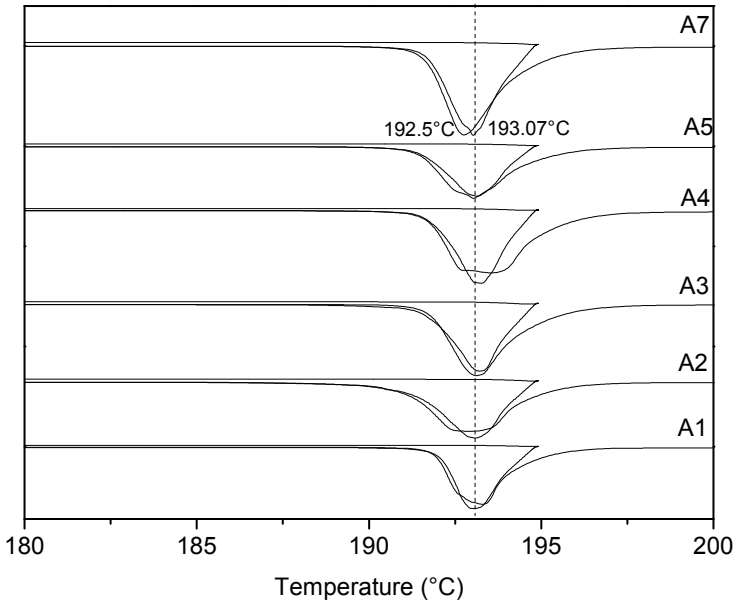


Figure S4. Thermograms of **A1 – A7 (**aliquot taken at 2, 4, 6, 8, 10, 12 and 24 hours) in the experiment using yellow powder of (*Z*)-2-(4-bromophenyl)-3-(4-(dimethylamino)phenyl)acrylonitrile dissolved in DMF at 110 °C for 4 h.