Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary information for:

Forced topochemistry of a solid-state Diels-Alder reaction by encapsulation in epoxy glue

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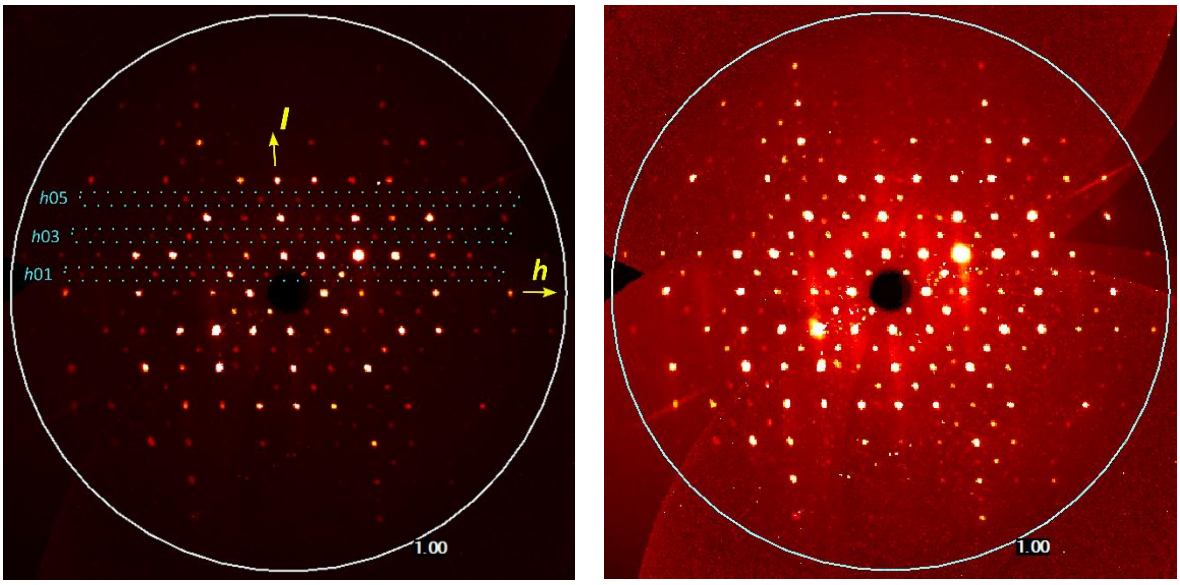
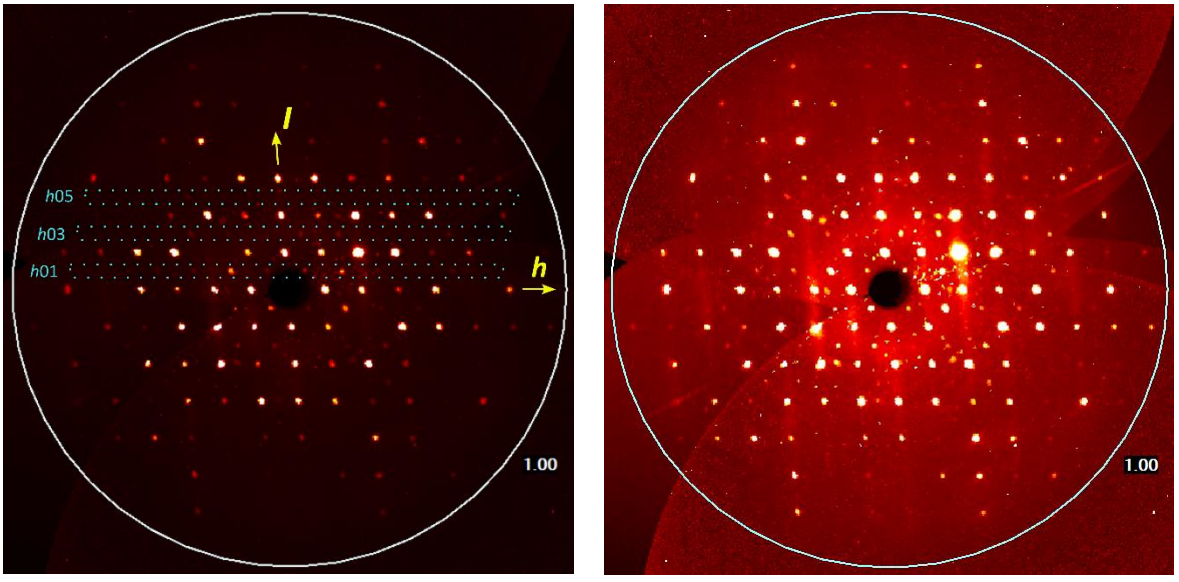
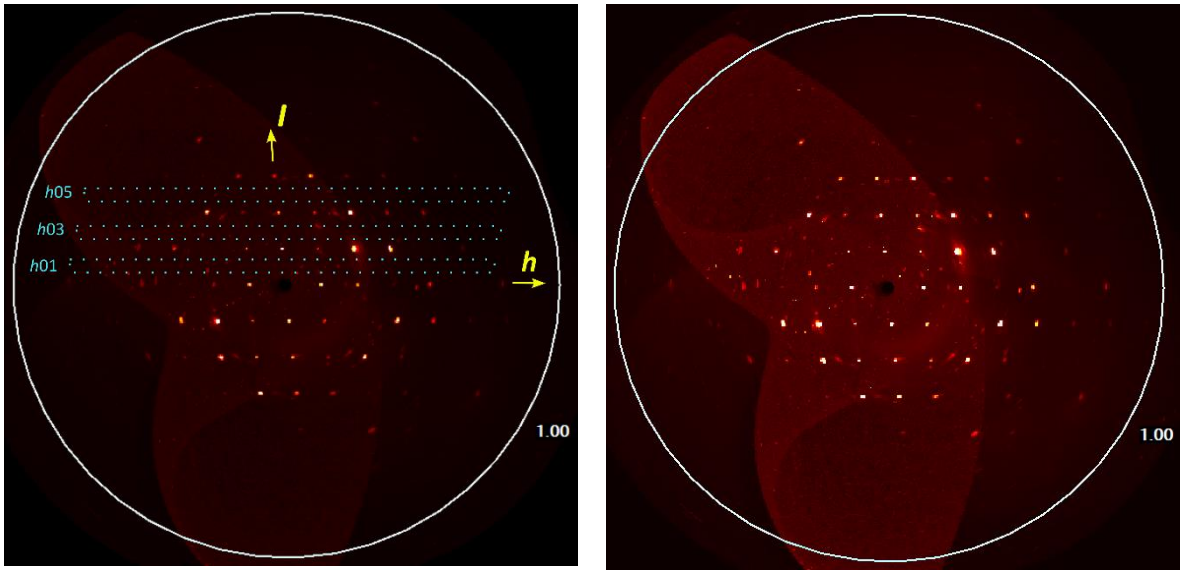
1. Supplementary information associated with the results and discussion



(a)



(b)



(c)

Fig. S1. Pseudo [*h*0*l*] precession images for (a) the room temperature reacted crystal at 64% (just before unit cell transformation), and after the *P*-1 to *C*2/*c* transformation at (b) 79% and (c) 89% conversion. The [*h01*], [*h03*], and [*h05*] reflections enclosed in doted lines are allowed in the triclinic *P*-1 space group (a) but are weaker in (b) and absent in (c) as required for *C*2/*c*. The right and left image are the same image by at differing intensity contrasts.

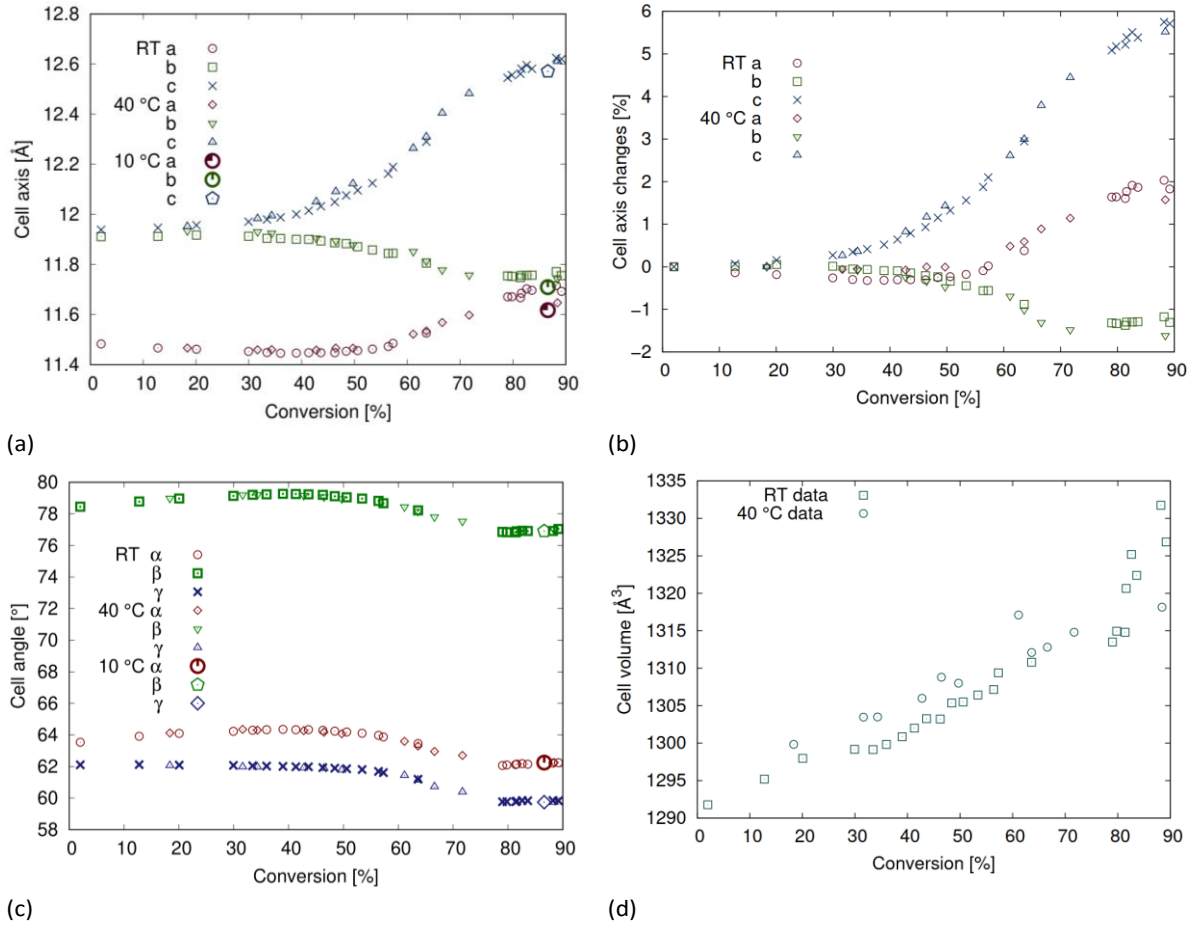


Fig. S2. Changes in the unit cell parameters for epoxy encapsulated crystals during the reaction at room temperature (20 °C) and at 40 °C. (a) Changes in unit cell lengths, (b) percent change in unit cell lengths compared to initial unreacted crystal, (c) changes in unit cell angles, and (d) changes in cell volume with percent conversion. Unit cell parameters for a single crystal that was reacted freely (no epoxy encapsulation) for 2 years and 77 days in a fridge at 10 °C (86.6% conversion) has also been included on plots (a) and (c).

2. Supplementary information associated with reacted crystal structures

Table S1 Crystallographic and refinement data for the solid-state reaction at room temperature.

Identification code	22talb05_90C_DC49B_Freezer_Glue_0f	22talb09_90C_DC49Br_FzGRT_6d7h_0f	22talb11_90C_DC49B_FzGRT_12d9h_0f	22talb14_90C_DC49B_FzGRT_22d2h_0f	22talb16_90C_DC49B_FzGRT_27d19h_0f	22talb17_90C_DC49B_FzGRT_32d11h_0f	22talb18_90C_DC49B_FzGRT_39d14h_0f
Time reacted (Conversion)	0 h (2.0 %)	6d 7h (12.8 %)	12d 9h (20.0 %)	22d 2h (29.9 %)	27d 19h (33.4 %)	32d 11h (36.0 %)	39d 14h (39.0 %)
Empirical formula	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$
Formula weight	619.53	619.53	619.53	619.53	619.53	309.77	619.53
Temperature/K	173.15	173.15	173.15	173.15	173.15	173.15	173.15
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	11.4827(5)	11.4667(6)	11.4616(6)	11.4528(6)	11.4482(6)	11.4457(6)	11.4464(6)
b/Å	11.9111(5)	11.9120(6)	11.9174(6)	11.9126(6)	11.9046(6)	11.9037(6)	11.9005(7)
c/Å	11.9382(5)	11.9462(6)	11.9565(6)	11.9707(6)	11.9797(6)	11.9878(6)	12.0001(7)
α/°	63.532(2)	63.912(2)	64.094(2)	64.230(2)	64.297(2)	64.330(2)	64.352(2)
β/°	78.453(2)	78.782(2)	78.975(2)	79.138(2)	79.211(2)	79.237(2)	79.266(2)
γ/°	62.107(2)	62.114(2)	62.088(2)	62.067(2)	62.040(2)	62.027(2)	62.005(2)
Volume/Å3	1291.78(10)	1295.20(12)	1297.97(12)	1299.18(12)	1299.14(12)	1299.83(12)	1300.85(13)
Z	2	2	2	2	2	4	2
ρcalcg/cm3	1.593	1.589	1.585	1.584	1.584	1.583	1.582
μ/mm-1	1.795	1.79	1.786	1.785	1.785	1.784	1.782
F(000)	632	632	632	632	632	632	632
Crystal size/mm3	0.289 × 0.09 × 0.076	0.319 × 0.288 × 0.21	0.322 × 0.08 × 0.065	0.305 × 0.079 × 0.078	0.297 × 0.08 × 0.076	0.283 × 0.08 × 0.072	0.297 × 0.082 × 0.064
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.812 to 56.69	3.796 to 55	3.788 to 56.64	3.778 to 56.654	4.028 to 56.662	3.77 to 56.7	3.766 to 56.76
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	55192	66091	49988	76415	57104	54540	55707
Independent reflections	6382 [Rint = 0.0460, Rsigma = 0.0286]	5941 [Rint = 0.0482, Rsigma = 0.0269]	6432 [Rint = 0.0600, Rsigma = 0.0355]	6440 [Rint = 0.0682, Rsigma = 0.0314]	6442 [Rint = 0.0642, Rsigma = 0.0336]	6449 [Rint = 0.0611, Rsigma = 0.0332]	6461 [Rint = 0.0676, Rsigma = 0.0354]
Data/restraints/parameters	6382/2/378	5941/2/378	6432/2/377	6440/1090/701	6442/1061/700	6449/1093/716	6461/1093/716
Goodness-of-fit on F2	1.106	1.068	1.115	1.185	1.135	1.146	1.141
Final R indexes [I>=2σ (I)]	R1 = 0.0434, wR2 = 0.1425	R1 = 0.0535, wR2 = 0.1561	R1 = 0.0693, wR2 = 0.1928	R1 = 0.0640, wR2 = 0.1768	R1 = 0.0651, wR2 = 0.1893	R1 = 0.0677, wR2 = 0.2016	R1 = 0.0709, wR2 = 0.2071
Final R indexes [all data]	R1 = 0.0455, wR2 = 0.1439	R1 = 0.0575, wR2 = 0.1588	R1 = 0.0816, wR2 = 0.2008	R1 = 0.0776, wR2 = 0.1853	R1 = 0.0788, wR2 = 0.1992	R1 = 0.0831, wR2 = 0.2158	R1 = 0.0867, wR2 = 0.2185
Largest diff. peak/hole / e Å-3	1.20/-0.43	1.00/-0.58	1.21/-0.69	0.91/-0.54	0.98/-0.51	0.99/-0.47	1.04/-0.50

Table S1 Continued.

Identification code	22talb19_90C_DC49B_Fz GRT_46d6h_0f	22talb22_90C_DC49B_Fz GRT_52d21h_0f	22talb24_90C_DC49B_Fz GRT_59d_12h_0f	22talb29_90CDC49B_Fz GRT_66d3h_0f	22talb30_90C_DC49B_Fz GRT_72d19h_0f	22talb31_90C_DC49B_Fz GRT_78d20h_0f	22talb32_90C_DC49B_Fz GRT_85d23h_0f
Time reacted (Conversion)	46d 6h (41.3 %)	52d 21h (43.6 %)	59d 12h (46.2 %)	66d 3h (48.4 %)	72d 19h (50.6 %)	78d 20h (53.4 %)	85d 23h (56.4 %)
Empirical formula	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$
Formula weight	309.77	619.53	619.53	619.53	619.53	619.53	619.53
Temperature/K	173.15	173.15	173.15	173.15	173.15	173.15	173.15
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	11.4476(6)	11.4477(7)	11.4476(7)	11.4534(8)	11.4561(8)	11.4623(7)	11.4723(8)
b/Å	11.9000(7)	11.8940(7)	11.8865(7)	11.8830(9)	11.8710(8)	11.8581(7)	11.8443(8)
c/Å	12.0147(7)	12.0324(7)	12.0495(7)	12.0758(8)	12.0961(8)	12.1246(7)	12.1622(8)
α/°	64.330(2)	64.336(2)	64.292(2)	64.240(2)	64.184(2)	64.105(2)	63.971(3)
β/°	79.260(2)	79.235(2)	79.202(2)	79.120(3)	79.051(2)	78.968(2)	78.820(3)
γ/°	61.983(2)	61.976(2)	61.928(2)	61.892(2)	61.856(2)	61.809(2)	61.688(3)
Volume/Å3	1302.00(13)	1303.27(14)	1303.22(14)	1305.36(16)	1305.50(16)	1306.43(14)	1307.15(16)
Z	4	2	2	2	2	2	2
ρcalcg/cm3	1.58	1.579	1.579	1.576	1.576	1.575	1.574
μ/mm-1	1.781	1.779	1.779	1.776	1.776	1.775	1.774
F(000)	632	632	632	632	632	632	632
Crystal size/mm3	0.279 × 0.078 × 0.074	0.293 × 0.076 × 0.072	0.319 × 0.075 × 0.072	0.312 × 0.083 × 0.062	0.191 × 0.142 × 0.057	0.191 × 0.142 × 0.057	0.278 × 0.077 × 0.074
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.762 to 56.818	3.756 to 56.71	3.752 to 56.73	4.032 to 56.656	3.742 to 56.696	3.734 to 56.822	4.034 to 53.998
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	53281	77550	59062	52122	74409	59993	49387
Independent reflections	6479 [Rint = 0.0661, Rsigma = 0.0356]	6471 [Rint = 0.0778, Rsigma = 0.0357]	6468 [Rint = 0.0776, Rsigma = 0.0404]	6463 [Rint = 0.0809, Rsigma = 0.0479]	6477 [Rint = 0.0718, Rsigma = 0.0615]	6527 [Rint = 0.0723, Rsigma = 0.0638]	5700 [Rint = 0.0731, Rsigma = 0.0710]
Data/restraints/parameters	6479/1087/716	6471/1093/716	6468/1093/716	6463/1087/716	6477/1122/721	6527/1116/721	5700/1113/716
Goodness-of-fit on F2	1.144	1.145	1.129	1.102	1.083	1.073	1.687
Final R indexes [I>=2σ (I)]	R1 = 0.0790, wR2 = 0.2191	R1 = 0.0803, wR2 = 0.2195	R1 = 0.0850, wR2 = 0.2377	R1 = 0.0913, wR2 = 0.2546	R1 = 0.0968, wR2 = 0.2762	R1 = 0.1074, wR2 = 0.3036	R1 = 0.1182, wR2 = 0.3764
Final R indexes [all data]	R1 = 0.0942, wR2 = 0.2289	R1 = 0.1010, wR2 = 0.2348	R1 = 0.1106, wR2 = 0.2586	R1 = 0.1205, wR2 = 0.2789	R1 = 0.1161, wR2 = 0.2952	R1 = 0.1351, wR2 = 0.3318	R1 = 0.1450, wR2 = 0.4042
Largest diff. peak/hole / e Å-3	1.08/-0.46	1.07/-0.55	1.03/-0.55	1.06/-0.67	1.14/-0.68	1.08/-0.86	1.22/-0.81

Table S1 Continued.

Identification code	22talb33_90C_DC49B_Fz GRT_91d_0f	22talb35_90C_DC49B_Fz GRT_103d4h_0f	22talb36_90C_DC49B_Fz GRT_133d5h_0f_1	22talb37_90C_DC49B_Fz GRT_138d2h_c2c_0f	22talb39_90C_DC49B_Fz GRT_144d1h_monoc_0f	22talb40_90C_DC49B_Fz GRT_153d_0f	22talb41_90C_DC49B_Fz GRT_156d7h_mono_0f
Time reacted (Conversion)	91d 0h (57.3 %)	103d 4h (63.6 %)	133d 5h (79.0 %)	138d 2h (79.8 %)	144d 1h (81.4 %)	153d 0h (81.6 %)	156d 7h (83.6 %)
Empirical formula	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$
Formula weight	619.53	619.53	619.53	619.53	619.53	619.53	619.53
Temperature/K	173.15	173.15	173	173	173	173	173
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*-1	*P*-1	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a/Å	11.4850(8)	11.5260(10)	20.1661(11)	20.1678(16)	20.1614(14)	20.1992(11)	20.2248(11)
b/Å	11.8448(8)	11.8060(11)	11.7540(11)	11.7525(16)	11.7473(14)	11.7561(11)	11.7573(11)
c/Å	12.1888(8)	12.2903(11)	14.9001(12)	14.9159(17)	14.9224(14)	14.9433(12)	14.9500(12)
α/°	63.868(3)	63.453(4)	90	90	90	90	90
β/°	78.672(3)	78.220(4)	131.943(5)	131.937(7)	131.925(6)	131.896(6)	131.928(6)
γ/°	61.607(3)	61.190(3)	90	90	90	90	90
Volume/Å3	1309.39(16)	1310.8(2)	2627.0(4)	2629.9(6)	2629.6(5)	2641.3(4)	2644.8(4)
Z	2	2	4	4	4	4	4
ρcalcg/cm3	1.571	1.57	1.566	1.565	1.565	1.558	1.556
μ/mm-1	1.771	1.769	1.765	1.763	1.763	3.94	3.934
F(000)	632	632	1264	1264	1264	1264	1264
Crystal size/mm3	0.288 × 0.075 × 0.072	0.273 × 0.093 × 0.065	0.286 × 0.078 × 0.074	0.281 × 0.071 × 0.066	0.286 × 0.059 × 0.055	0.29 × 0.076 × 0.075	0.304 × 0.076 × 0.069
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	3.722 to 53.994	3.704 to 49.998	4.402 to 49.986	4.402 to 49.992	4.404 to 49.988	9.55 to 131.534	9.546 to 131.184
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-23 ≤ h ≤ 23, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17	-23 ≤ h ≤ 23, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17	-23 ≤ h ≤ 23, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17	-23 ≤ h ≤ 23, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17	-23 ≤ h ≤ 23, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	49987	40827	52117	52818	46341	34736	35750
Independent reflections	5705 [Rint = 0.0716, Rsigma = 0.0541]	4609 [Rint = 0.0681, Rsigma = 0.0437]	2305 [Rint = 0.1477, Rsigma = 0.0401]	2307 [Rint = 0.1745, Rsigma = 0.0466]	2304 [Rint = 0.1512, Rsigma = 0.0428]	2280 [Rint = 0.1223, Rsigma = 0.0448]	2278 [Rint = 0.1261, Rsigma = 0.0446]
Data/restraints/parameters	5705/1122/721	4609/1122/709	2305/709/343	2307/709/343	2304/709/343	2280/714/348	2278/714/348
Goodness-of-fit on F2	1.75	1.913	1.119	1.128	1.081	1.057	1.63
Final R indexes [I>=2σ (I)]	R1 = 0.1232, wR2 = 0.3847	R1 = 0.1331, wR2 = 0.4123	R1 = 0.1083, wR2 = 0.2905	R1 = 0.1215, wR2 = 0.2906	R1 = 0.1124, wR2 = 0.2778	R1 = 0.1099, wR2 = 0.2934	R1 = 0.1410, wR2 = 0.3797
Final R indexes [all data]	R1 = 0.1508, wR2 = 0.4140	R1 = 0.1635, wR2 = 0.4426	R1 = 0.1316, wR2 = 0.3158	R1 = 0.1682, wR2 = 0.3412	R1 = 0.1604, wR2 = 0.3299	R1 = 0.1588, wR2 = 0.3475	R1 = 0.2017, wR2 = 0.4432
Largest diff. peak/hole / e Å-3	1.30/-0.78	0.84/-0.75	0.83/-0.43	0.93/-0.37	0.85/-0.36	0.83/-0.34	0.97/-0.34

Table S1 Continued.

Identification code	22talb42_90C_DC49B_Fz GRT_162d8h_c2c_0f	22talb43_90C_DC49B_Fz GRT_168d6h_c2c_0f	22talb46_90C_DC49B_Fz GRT_186d20h_mono_0f
Time reacted (Conversion)	162d 8h (82.6 %)	168d 6h (88.2 %)	186d 20h (89.2 %)
Empirical formula	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$
Formula weight	619.53	619.53	619.53
Temperature/K	173	173	173
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a/Å	20.2382(10)	20.261(2)	20.2158(9)
b/Å	11.7565(10)	11.7713(12)	11.7554(9)
c/Å	14.9692(10)	15.002(3)	14.9649(9)
α/°	90	90	90
β/°	131.914(5)	131.889(5)	131.738(6)
γ/°	90	90	90
Volume/Å3	2650.4(4)	2663.5(7)	2653.7(3)
Z	4	4	4
ρcalcg/cm3	1.553	1.545	1.551
μ/mm-1	3.926	3.907	3.921
F(000)	1264	1264	1264
Crystal size/mm3	0.325 × 0.087 × 0.071	0.309 × 0.076 × 0.058	0.328 × 0.081 × 0.074
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.544 to 133.988	9.53 to 133.996	9.538 to 118.534
Index ranges	-24 ≤ h ≤ 24, -13 ≤ k ≤ 14, -17 ≤ l ≤ 17	-24 ≤ h ≤ 24, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17	-22 ≤ h ≤ 22, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	38113	30734	34235
Independent reflections	2346 [Rint = 0.1096, Rsigma = 0.0404]	2354 [Rint = 0.1439, Rsigma = 0.0538]	1916 [Rint = 0.1820, Rsigma = 0.0639]
Data/restraints/parameters	2346/714/348	2354/714/348	1916/714/348
Goodness-of-fit on F2	1.618	1.452	1.593
Final R indexes [I>=2σ (I)]	R1 = 0.1378, wR2 = 0.3763	R1 = 0.1648, wR2 = 0.3852	R1 = 0.1899, wR2 = 0.4059
Final R indexes [all data]	R1 = 0.1877, wR2 = 0.4337	R1 = 0.2660, wR2 = 0.4627	R1 = 0.2881, wR2 = 0.4778
Largest diff. peak/hole / e Å-3	1.02/-0.35	1.05/-0.44	0.94/-0.34

Table S2 Crystallographic and refinement data for the solid-state reaction at 40 °C.

Identification code	21tal_TAL16_TAL090C_React_Fridge_0s	21tal_TAL18_TAL090C_RF_1d15h_0s	21tal_TAL20_TAL090C_RF_2d16h_0s	21tal_TAL22_TAL090C_RF_4d22h_0s	21tal_TAL25_TAL090C_RF_5d22h_0s	21tal_TAL26_TAL090C_RF_6d18h_0s	21tal_TAL27_TAL090C_RF_8d16h_0s
Time reacted (Conversion)	0 h (18.3 %)	1d 5h (31.6 %)	2d 16h (34.3 %)	4d 22h (42.8 %)	5d 22h (46.5 %)	6d 18h (49.7 %)	8d 16h (61.1 %)
Empirical formula	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$
Formula weight	619.53	619.53	619.53	619.53	619.53	619.53	619.53
Temperature/K	173.15	173.15	173.15	173.15	173.15	173.15	173.15
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	11.4664(6)	11.4592(3)	11.4600(6)	11.4577(6)	11.4659(9)	11.4655(8)	11.5217(9)
b/Å	11.9345(6)	11.9307(3)	11.9251(6)	11.9051(7)	11.8945(11)	11.8783(9)	11.8519(10)
c/Å	11.9516(6)	11.9831(4)	11.9945(7)	12.0500(7)	12.0911(12)	12.1224(10)	12.2638(11)
α/°	64.124(2)	64.3521(17)	64.302(2)	64.269(3)	64.173(4)	64.074(4)	63.591(5)
β/°	78.987(2)	79.2012(19)	79.216(3)	79.164(3)	79.075(4)	78.958(4)	78.447(6)
γ/°	62.060(2)	61.9785(14)	61.968(2)	61.909(2)	61.881(3)	61.774(3)	61.432(5)
Volume/Å3	1299.84(12)	1303.47(7)	1303.50(13)	1305.98(13)	1308.8(2)	1308.01(18)	1317.1(2)
Z	2	2	2	2	2	2	2
ρcalcg/cm3	1.593	1.578	1.585	1.575	1.572	1.573	1.562
μ/mm-1	1.784	1.779	1.779	1.775	1.771	1.773	1.760
F(000)	632	632	632	632	632	632	632
Crystal size/mm3	0.319 × 0.288 × 0.21	0.383 × 0.268 × 0.172	0.363 × 0.275 × 0.134	0.319 × 0.288 × 0.21	0.319 × 0.288 × 0.21	0.344 × 0.3 × 0.186	0.363 × 0.299 × 0.142
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.788 to 56.766	3.772 to 55.996	3.77 to 52.938	3.752 to 52.856	3.744 to 50.07	3.736 to 50.078	3.708 to 50
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -14 ≤ l ≤ 15	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -14 ≤ l ≤ 15	-12 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-10 ≤ h ≤ 13, -14 ≤ k ≤ 13, -14 ≤ l ≤ 14	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	17394	23336	16189	15185	8044	9196	13684
Independent reflections	6458 [Rint = 0.0645, Rsigma = 0.0901]	6296 [Rint = 0.0765, Rsigma = 0.0908]	5353 [Rint = 0.0793, Rsigma = 0.0902]	5344 [Rint = 0.0790, Rsigma = 0.1037]	4529 [Rint = 0.0552, Rsigma = 0.1337]	4506 [Rint = 0.0718, Rsigma = 0.1366]	4636 [Rint = 0.1407, Rsigma = 0.2176]
Data/restraints/parameters	6458/2/378	6296/1073/700	5353/1073/697	5344/1067/697	4529/1073/697	4506/1110/709	4636/1230/697
Goodness-of-fit on F2	0.884	0.904	0.980	0.966	0.947	0.961	0.933
Final R indexes [I>=2σ (I)]	R1 = 0.0503, wR2 = 0.1125	R1 = 0.0479, wR2 = 0.1062	R1 = 0.0559, wR2 = 0.1414	R1 = 0.0642, wR2 = 0.1680	R1 = 0.0736, wR2 = 0.1838	R1 = 0.0765, wR2 = 0.2017	R1 = 0.1091, wR2 = 0.2948
Final R indexes [all data]	R1 = 0.0958, wR2 = 0.1246	R1 = 0.1005, wR2 = 0.1191	R1 = 0.0998, wR2 = 0.1535	R1 = 0.1252, wR2 = 0.1864	R1 = 0.1560, wR2 = 0.2140	R1 = 0.1635, wR2 = 0.2321	R1 = 0.2513, wR2 = 0.3549
Largest diff. peak/hole / e Å-3	0.61/-0.42	0.64/-0.34	0.60/-0.33	0.67/-0.40	0.57/-0.44	0.58/-0.42	0.53/-0.47

Table S2 Continued.

Identification code	mo_21talv_TALv6_TAL090C_RF_9d16h_0s	21tal_TAL18_TAL090C_RF_1d15h_0s	21talv_TALv8_TAL090CRF_12d17hs	22talb03_90C_DiC49Br_T3_Final_0f
Time reacted (Conversion)	9d 16h (63.6 %)	10d 20h (66.6 %)	12d 17h (71.7 %)	4d 22h (88.4 %)
Empirical formula	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$
Formula weight	619.53	619.53	619.53	619.53
Temperature/K	173.15	173.15	173.15	173.15
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	*P*-1	*C*2/*c*
a/Å	11.534(2)	11.568(2)	11.5975(19)	20.1182(19)
b/Å	11.814(2)	11.778(2)	11.758(2)	11.7417(11)
c/Å	12.309(2)	12.404(2)	12.483(2)	14.9309(14)
α/°	63.291(5)	62.950(5)	62.699(5)	90
β/°	78.160(5)	77.807(6)	77.538(5)	131.630(4)
γ/°	61.139(4)	60.720(5)	60.382(4)	90
Volume/Å3	1312.1(4)	1312.8(4)	1314.8(4)	2636.3(4)
Z	2	2	2	4
ρcalcg/cm3	1.568	1.567	1.564	1.561
μ/mm-1	1.767	1.766	1.763	3.947
F(000)	632	632	632	1264
Crystal size/mm3	0.423 × 0.263 × 0.244	0.397 × 0.296 × 0.259	0.363 × 0.275 × 0.134	0.4 × 0.352 × 0.287
Radiation/Å	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.74 to 49.994	5.428 to 39.998	5.422 to 49.998	9.556 to 133.038
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-23 ≤ h ≤ 23, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	24992	31780	49215	23399
Independent reflections	4599 [Rint = 0.1150, Rsigma = 0.0768]	2440 [Rint = 0.3193, Rsigma = 0.1034]	4608 [Rint = 0.3530, Rsigma = 0.1167]	2254 [Rint = 0.0764, Rsigma = 0.0401]
Data/restraints/parameters	4599/1221/692	2440/1236/692	4608/1324/709	2254/701/355
Goodness-of-fit on F2	1.740	2.116	1.684	1.114
Final R indexes [I>=2σ (I)]	R1 = 0.1612, wR2 = 0.4402	R1 = 0.1536, wR2 = 0.4312	R1 = 0.1930, wR2 = 0.4435	R1 = 0.1238, wR2 = 0.3284
Final R indexes [all data]	R1 = 0.2334, wR2 = 0.4806	R1 = 0.1993, wR2 = 0.4718	R1 = 0.2981, wR2 = 0.5038	R1 = 0.1580, wR2 = 0.3687
Largest diff. peak/hole / e Å-3	0.80/-0.70	1.11/-0.76	1.64/-0.76	1.07/-0.41

Table S3 Crystallographic and refinement data for a crystal that was reacted at 10 °C for 2 years and 77 days (86.6% conversion). The crystal data was first collected at 25 °C and then repeated at -100 °C.

Identification code	23talb01_90C_DC49B_NoGFr_2y_0f Collected at 298.15 K	23talb02_90C_DC49B_NoGFr_2y77f Collected at 173 K
Empirical formula	$C_{30}H_{23}BrN_2O_4S_2$	$C_{30}H_{23}BrN_2O_4S_2$
Formula weight	619.53	619.53
Temperature/K	298.15	173
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a/Å	20.168(3)	20.0690(16)
b/Å	11.8017(16)	11.7091(9)
c/Å	14.918(2)	14.9014(12)
α/°	90	90
β/°	131.298(4)	131.712(2)
γ/°	90	90
Volume/Å3	2667.7(6)	2614.0(4)
Z	4	4
ρcalcg/cm3	1.543	1.574
μ/mm-1	1.738	1.774
F(000)	1264	1264
Crystal size/mm3	0.487 × 0.161 × 0.138	0.487 × 0.161 × 0.138
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.374 to 49.99	4.416 to 49.978
Index ranges	-23 ≤ h ≤ 23, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17	-23 ≤ h ≤ 23, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	58708	34285
Independent reflections	2334 [Rint = 0.1237, Rsigma = 0.0411]	2295 [Rint = 0.0890, Rsigma = 0.0486]
Data/restraints/parameters	2334/709/343	2295/709/343
Goodness-of-fit on F2	1.138	1.095
Final R indexes [I>=2σ (I)]	R1 = 0.0963, wR2 = 0.2621	R1 = 0.1024, wR2 = 0.2696
Final R indexes [all data]	R1 = 0.1263, wR2 = 0.3012	R1 = 0.1245, wR2 = 0.3015
Largest diff. peak/hole / e Å-3	0.85/-0.40	1.16/-0.54