Supporting Information

Isomeric and isostructural oligothienylsilanes – structurally similar, physicochemically different – the effect of interplay between C–H…C(π), S…C(π) and chalcogen S…S interactions

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1. Thermal analysis:

Table S1. The summary of DSC measurements for selected compounds. Melting points (T_m), crystallization temperatures (T_c) and enthalpy (ΔH).

	mass / mg	T_m / ^{0}C	T_c / ^{0}C	ΔH / J·g^{-1}	heating cycle
I	4.27	28.6	-24	-61.8	first
		17.2	--	-56.7	second
II	3.38	71.3	23.0	-72.9	first
		71.4	--	-74.1	second
III	2.44	131.5	67.1	-74.6	first
		131.8	69.8	-74.8	second
IV	4.46	221.4	152.2	-81.1	first
		221.2	152.1	-81.0	second
III+IV	0.94	180-210	131.4	77.7	first

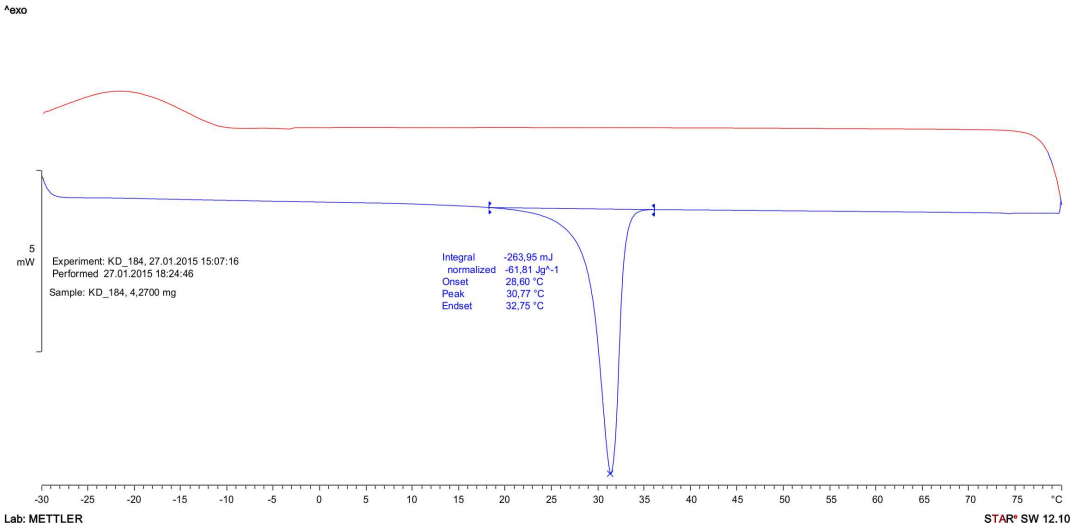


Figure S1. DSC curve of **I**.

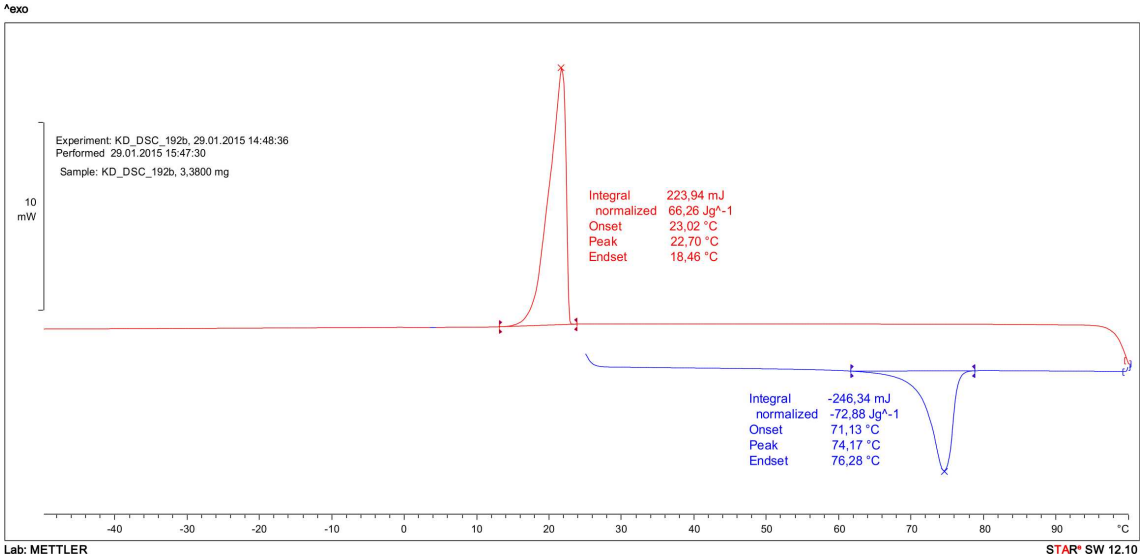


Figure S2. DSC curve of **II**.

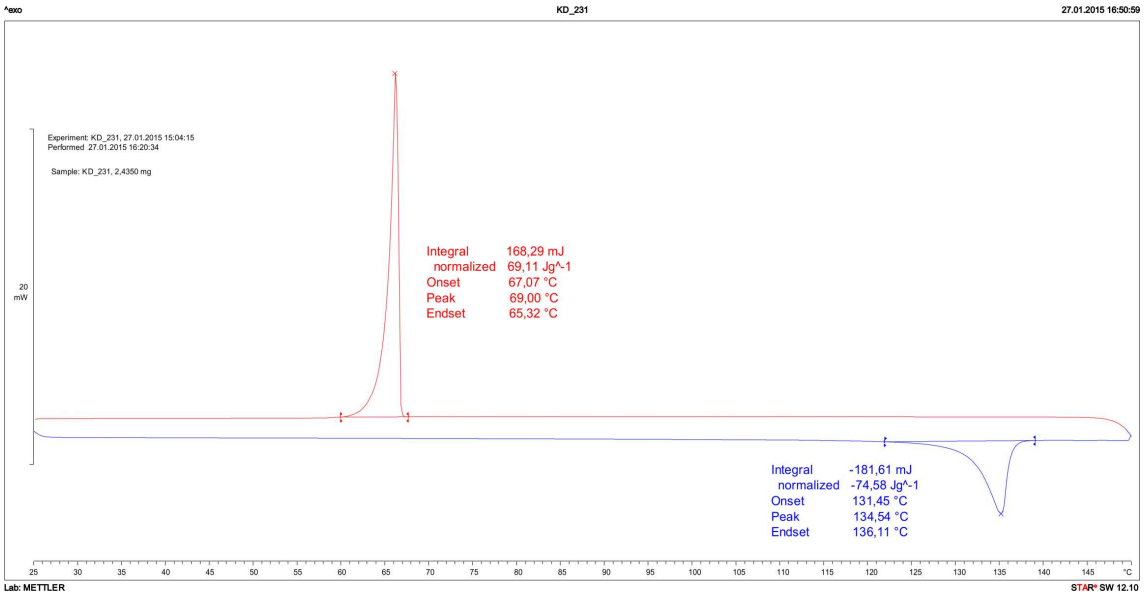


Figure S3. DSC curve of **III**.

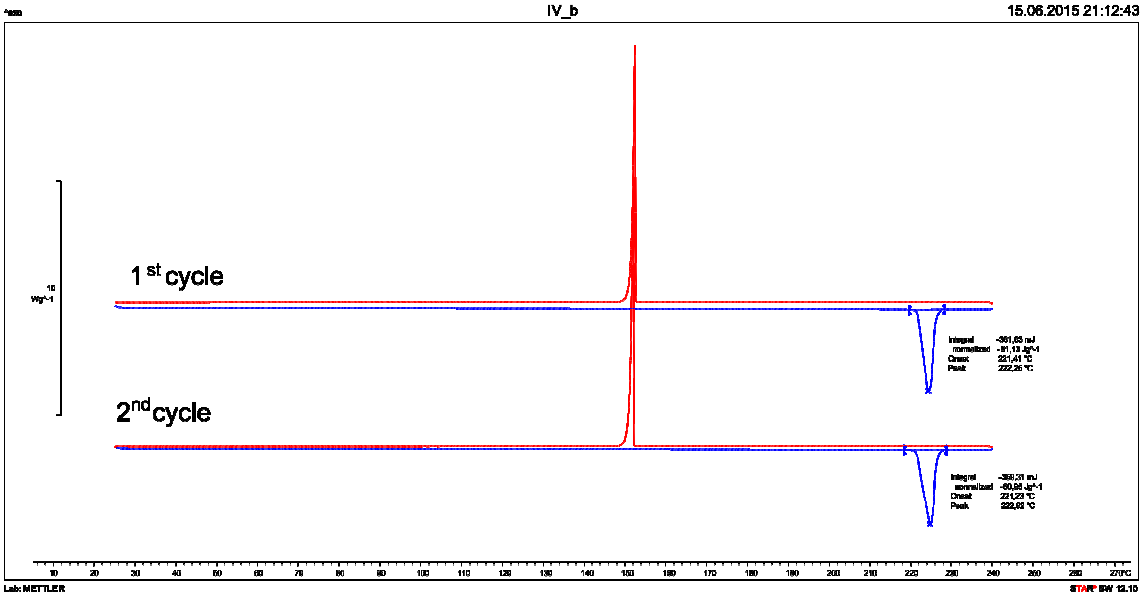


Figure S4. DSC curve of **IV**.

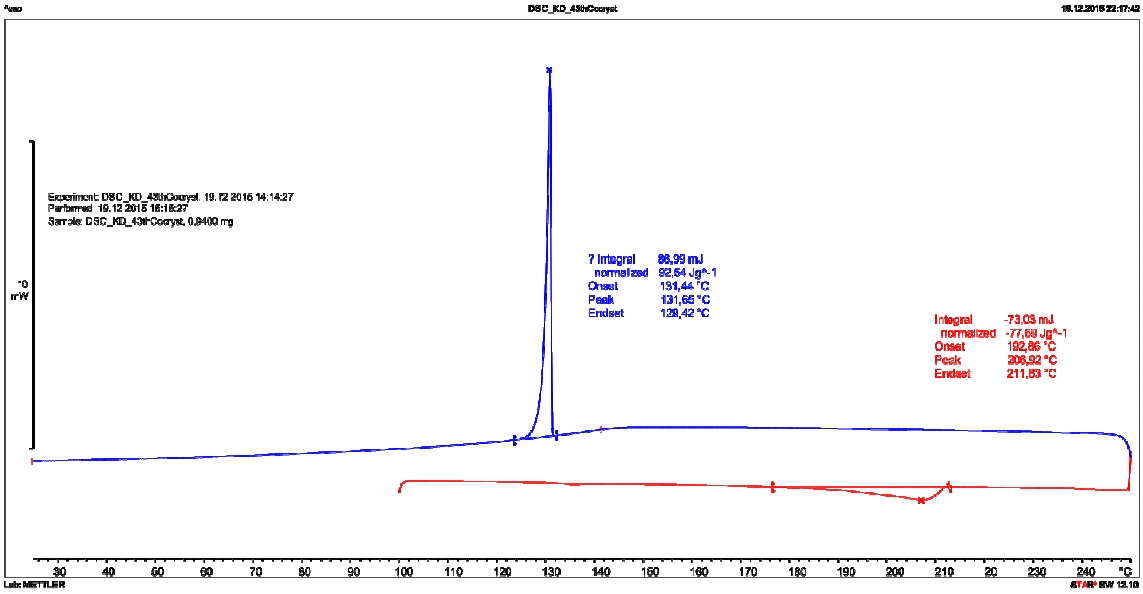


Figure S5. DSC curve of cocrystal **III** + **IV**.

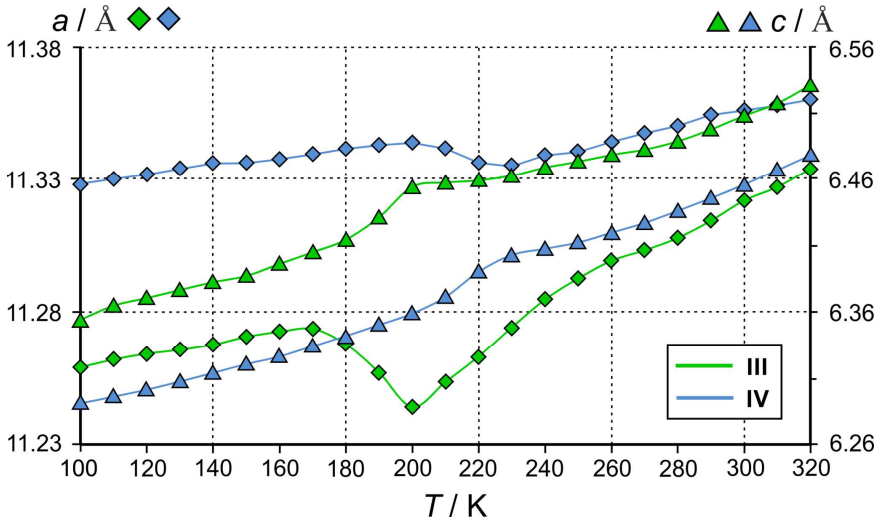
2. Solubility studies.

Table S2. Solid-liquid equilibria (SLE) for binary mixtures of **III** and **IV** with toluene, thiophene and 1,4-dioxane determined by a dynamic method in the temperature range of 293-363 K. *x* stands for the molar fraction.

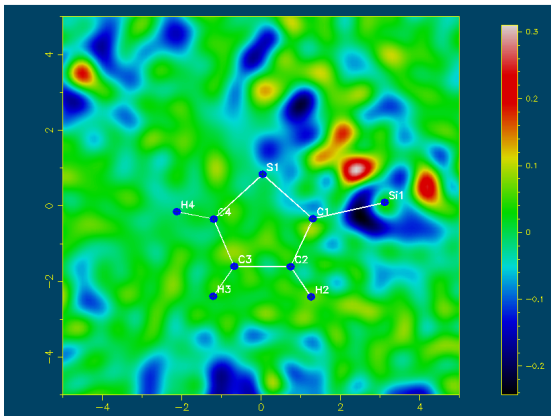
III + toluene		**IV** + toluene		**III** + thiophene		**IV** + thiophene		**III** + 1,4-dioxane		**IV** + 1,4-dioxane	
T / °C	*x*	*T* / °C	*x*	*T* / °C	*x*	*T* / °C	*x*	*T* / °C	*x*	*T* / °C	*x*
56.6	0.09985	96.6	0.02896	47.1	0.10799	88.8	0.03956	67.7	0.19015	92.5	0.04011
53.8	0.08854	95.4	0.02795	42.0	0.09342	86.5	0.03657	58.2	0.14652	90.5	0.03798
50.4	0.07873	94.2	0.02694	38.7	0.08669	83.5	0.03346	44.2	0.09858	88.6	0.03580
46.7	0.06908	93.2	0.02593	37.2	0.08309	80.5	0.03057	39.3	0.08537	86.7	0.03388
42.4	0.05932	92.0	0.02486	32.3	0.07116	77.5	0.02759	36.1	0.07729	85.2	0.03204
36.8	0.04928	91.0	0.02384	28.3	0.06264	74.6	0.02473	33.3	0.07077	83.6	0.02993
34.4	0.04477	89.8	0.02282	25.7	0.05793	71.4	0.02174	30.1	0.06411	81.8	0.02790
31.6	0.03959	88.6	0.02177	23.3	0.05347	67.1	0.01875	27.6	0.05911	79.7	0.02560
27.9	0.03475	87.4	0.02071	20.4	0.04828	61.9	0.01581	24.4	0.05367	77.2	0.02396
23.4	0.02951	86.2	0.01968	18.2	0.04513	56.8	0.01287	20.9	0.04792	74.5	0.02212
18.5	0.02448	85.0	0.01865			50.2	0.00991	18.0	0.04364	71.8	0.02001
12.5	0.01984	83.8	0.01761			44.5	0.00791			69.0	0.01793
										65.4	0.01600

3. Single-crystal X-ray diffraction analysis

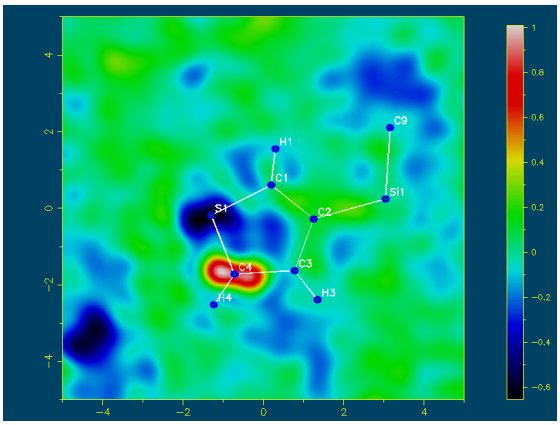
Table S3. Unit-cell parameters for **III** and **IV** measured in the temperature range 100 – 320 K.



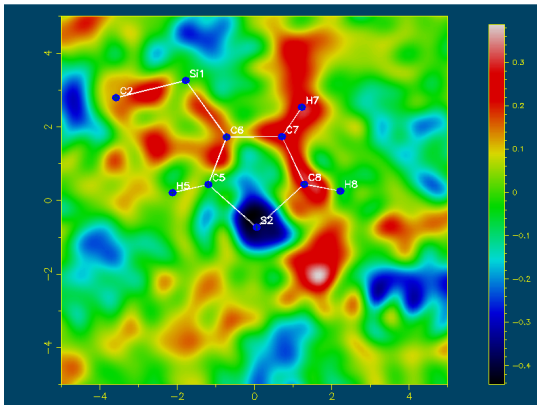
	III			**IV**		
T / K	a / Å	c / Å	V / Å^3	a / Å	c / Å	V / Å^3
100	11.259(1)	6.354(1)	805.5(1)	11.328(1)	6.291(1)	806.9(1)
110	11.262(1)	6.365(1)	807.3(1)	11.330(1)	6.296(1)	808.2(1)
120	11.264(1)	6.371(1)	808.3(1)	11.332(1)	6.301(1)	809.1(1)
130	11.266(1)	6.377(1)	809.3(1)	11.334(1)	6.307(1)	810.2(1)
140	11.268(1)	6.383(1)	810.3(1)	11.336(1)	6.314(1)	811.4(1)
150	11.271(1)	6.387(1)	811.4(1)	11.336(1)	6.321(1)	812.3(1)
160	11.273(1)	6.396(1)	812.8(1)	11.338(1)	6.326(1)	813.2(1)
170	11.274(1)	6.405(1)	814.1(1)	11.340(1)	6.334(1)	814.5(1)
180	11.268(1)	6.415(1)	814.4(1)	11.342(1)	6.342(1)	815.8(1)
190	11.257(1)	6.431(1)	815.0(1)	11.343(1)	6.350(1)	817.1(1)
200	11.244(1)	6.454(1)	816.0(1)	11.344(1)	6.359(1)	818.3(1)
210	11.254(1)	6.458(1)	817.8(1)	11.342(1)	6.372(1)	819.6(1)
220	11.263(1)	6.459(1)	819.4(1)	11.336(1)	6.390(1)	821.3(1)
230	11.274(1)	6.463(1)	821.5(1)	11.335(1)	6.403(1)	822.7(1)
240	11.285(1)	6.469(1)	823.8(1)	11.339(1)	6.408(1)	823.9(1)
250	11.293(1)	6.474(1)	825.5(1)	11.341(1)	6.412(1)	824.7(1)
260	11.299(1)	6.479(1)	827.2(1)	11.344(1)	6.420(1)	826.2(1)
270	11.303(1)	6.483(1)	828.3(1)	11.348(1)	6.427(1)	827.6(1)
280	11.308(1)	6.489(1)	829.8(1)	11.350(1)	6.436(1)	829.2(1)
290	11.314(1)	6.498(1)	831.9(1)	11.355(1)	6.446(1)	831.0(1)
300	11.322(1)	6.508(1)	834.3(1)	11.356(1)	6.456(1)	832.6(1)
310	11.327(1)	6.518(1)	836.3(1)	11.358(1)	6.467(1)	834.3(1)
320	11.334(1)	6.532(1)	839.0(1)	11.360(1)	6.479(1)	836.1(1)



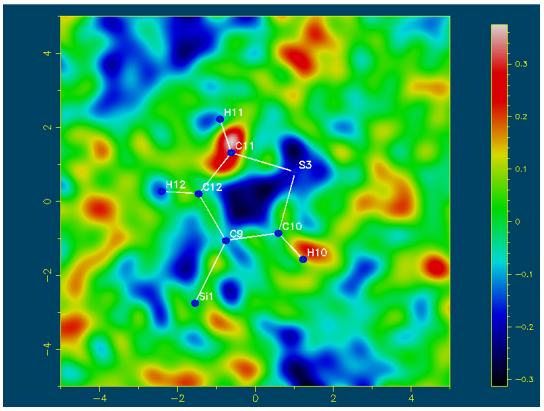
I_S1



II_S1



II_S2



II_S3

Figure S5. Difference-Fourier map in the thienyl ring planes generated for **I** and **II**. Map was prepared with MAPVIEW program within WinGX (L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837–838).

Table S4. Geometrical parameters for intermolecular interactions in studied systems. *d* - distance; θ – angle.

	Dimer	Conformation	Groups involved in interaction	Interactions	$d_{H\cdots A}$ / Å	d_{D-H} / Å	$d_{D\cdots A}$ / Å	$\theta_{D-H\cdots A}$ / °
I	**D1**	**S1S2S3**	**S3 - S2**	C10A-H10A…C8A	2.742	1.080	3.784	162.05
				C10A-H10A…S2A	2.743		3.735	152.49
			S2 - S1	S2A…C4	-	-	3.497	-
		S1S2*S3	**S3 - S2***	C10A-H10A…C6B	2.762	1.083	3.737	149.78
				C10A-H10A…C7B	2.702		3.776	171.33
				C10A-H10A…C8B	2.878		3.811	144.31
			S2* - S1	C6B-H6B…C3	2.832	1.082	3.696	136.82
				C6B-H6B…C4	2.898		3.897	153.52
		S1S2S3*	**S3* - S2**	S3B…C5	-	-	3.426	-
				S3B…S2A	-	-	3.593	-
			S2 - S1	S2A…C4	-	-	3.568	-
		S1S2*S3*	**S3* - S2***	S3B…C5	-	-	3.458	-
				S3B…C6B	-	-	3.425	-
			S2* - S1	C6B-H6B…C3	2.816	1.079	3.666	135.64
				C6B-H6B…C4	2.855		3.857	154.45
	D2	**S1S2S3**	**S1 – S1**	C4-H4…C1	2.838	1.076	3.812	150.43
				C4-H4…C2	2.735		3.776	162.66
				C4-H4…C3	2.653		3.677	158.85
				C4-H4…C4	2.694		3.640	146.45
				C4-H4…S1	2.900		3.775	138.56
		S1S2*S3	**S1 – S1**	C4-H4…C1	2.843	1.082	3.814	149.38
				C4-H4…C2	2.735		3.792	165.50
				C4-H4…C3	2.657		3.691	159.84
				C4-H4…C4	2.700		3.633	144.18
				C4-H4…S1	2.904		3.757	135.90
		S1S2S3*	**S1 – S1**	C4-H4…C1	2.862	1.078	3.820	148.09
				C4-H4…C2	2.749		3.782	160.59
				C4-H4…C3	2.638		3.675	161.16
				C4-H4…C4	2.689		3.655	148.93

			C4-H4…S1	2.913		3.792	138.82
	S1S2*S3*		C4-H4…C1	2.844		3.813	149.60
			C4-H4…C2	2.733		3.779	163.51
		S1 – S1	C4-H4…C3	2.663	1.078	3.693	159.84
			C4-H4…C4	2.704		3.647	145.89
			C4-H4…S1	2.902		3.766	137.30
D3	**S1S2S3**	**S2 – S2**	C8A-H8A…C8A	2.893	1.080	3.937	162.78
			C8A-H8A…C7A	2.805		3.862	166.25
		S1 – S2	C2- H2…S2A	2.868	1.078	3.693	133.42
	S1S2*S3	**S2* – S2***	C7B-H7B…C8B	2.910	1.083	3.948	160.62
	S1S2S3*	**S2 – S2**	C8A-H8A…C8A	2.831	1.082	3.873	161.82
			C8A-H8A…C7A	2.779		3.839	166.45
		S1 – S2	C2- H2…S2A	2.768	1.079	3.577	131.60
	S1S2*S3*	**S2* – S2***	C7B-H7B…C8B	2.902	1.084	3.949	162.23
D4	**S1S2S3**	**S3 – S3**	C11A-H11A…C12A	2.827	1.083	3.701	137.79
	S1S2*S3	**S3 – S3**	C11A-H11A…C12A	2.803	1.082	3.679	137.99
	S1S2S3*	**S3* – S3***	C12B-H12B…C10B	2.780	1.076	3.582	131.27
			C12B-H12B…C11B	2.464		3.476	156.36
	S1S2*S3*	**S3* – S3***	C12B-H12B…C10B	2.757	1.077	3.579	133.06
			C12B-H12B…C11B	2.445		3.464	157.51
D5	**S1S2S3**	**CH_3 – S3**	C13-H13B…C12A	2.671	1.091	3.741	166.38
	S1S2*S3	**CH_3 – S3**	C13-H13B…C12A	2.691	1.083	3.759	168.86
	S1S2S3*	**CH_3 – S3***	C13-H13B…C11B	2.791	1.090	3.870	170.53
			C13-H13B…C12B	2.764		3.809	160.42
	S1S2*S3*	**CH_3 – S3***	C13-H13B…C11B	2.850	1.090	3.926	169.03
			C13-H13B…C12B	2.800		3.847	160.72
II	**D1**	**S1S2S3**	**S1 – S2**	C3-H3…S2	2.753	1.081	3.638	139.01
				C3-H3…C8	2.871		3.774	141.19

			S3 – S1	C10-H10…C2	2.748	1.078	3.650	141.15
				C10-H10…C3	2.618		3.667	164.36
				C10-H10…C4	2.905		3.792	139.77
	D2	**S1S2S3**	**S1 – S2**	C1-H1…C8	2.690	1.079	3.636	146.14
				C1-H1…C7	2.906		3.939	160.41
			S2 – S3	C8-H8…S3	2.918	1.076	3.746	136.87
				C8-H8…C10	2.888		3.803	139.72
	D3	**S1S2S3**	**S2 – S2**	C4-H4…C4	2.947	1.079	3.994	163.52
	D5	**S1S2S3**	**S3 – S3**	C11-H11…C9	2.862	1.079	3.798	157.33
				C11-H11…C10	2.780		3.915	165.34
				C11-H11…C12	2.947		3.893	146.69
	D6	**S1S2S3**	**S1 – S2**	S1…S2	-	-	3.550	-
III	**D1**	**S1S2S3S4**	**S1 – S1**	S1…C4	-	-	3.616	-
				S1…S1	-	-	3.696	-
		S1*S2S3S4	**S1* – S3**	C2-H2…S3	2.909	1.082	3.758	135.46
				C2-H2…C12	2.723		3.787	167.42
			S3 – S4	S3…S4	-	-	3.668	-
				S3…C14	-	-	3.574	-
				S3…C15	-	-	3.567	-
				S3…C16	-	-	3.589	-
			S4 – S2	S4…S2	-	-	3.668	-
				S4…C6	-	-	3.589	-
				S4…C7	-	-	3.567	-
				S4…C8	-	-	3.574	-
			S2 – S1*	S2…S1	-	-	3.632	-
				S2…C2	-	-	3.541	-
				S2…C3	-	-	3.506	-
				S2…C4	-	-	3.502	-
		S1*S2*S3S4	**S1* - S3**	C2-H2…S3	2.909	1.082	3.758	135.46
				C2-H2…C12	2.723		3.787	167.42
			S4 – S2*	S3…S4	-	-	3.668	-
				S3…C14	-	-	3.574	-
				S3…C15	-	-	3.567	-
				S3…C16	-	-	3.589	-

		S2* – S1*	C14-H14…C6	2.823	3.769	132.65
			C14-H14…C7	2.622	3.669	1.082	162.67
			C14-H14…C8	2.776	3.644	152.36
		S3 – S4	S2…S1	-	-	3.668	-
			S2…C2	-	-	3.567	-
			S2…C3	-	-	3.589	-
			S2…C4	-	-	3.574	-
	S1*S2*S3*S4	**S1* – S3***	C2-H2…S3	2.909	1.082	3.758	135.46
			C2-H2…C12	2.723		3.787	167.42
		S3* – S4	C10-H10…S4	2.823	1.082	3.769	132.65
			C10-H10…C15	2.622		3.669	162.67
		S4 – S2*	S4…S2	-	-	3.632	-
			S4…C6	-	-	3.541	-
			S4…C7	-	-	3.506	-
			S4…C8	-	-	3.502	-
		S2*– S1*	C6-H6…S1	2.901	1.082	3.751	135.12
			C6-H6…C4	2.727		3.793	167.03
	S1*S2*S3*S4*	**S1* – S1***	C1-H1…C2	2.9658	1.081	3.6881	124.56
			C1-H1…C1	2.622		3.515	139.52
			C1-H1…S1	2.680		3.761	177.77
D2	**S1S2S3S4**	**S1 – S1**	C4-H4…C3	2.612	1.081	3.668	165.41
			C4-H4…C4	2.741		3.783	161.65
	S1*S2S3S4	**S1* - S3**	C3-H3…C12	2.796	1.080	3.783	161.65
		S3 - S1*	C12-H12…C4	2.663	1.081	3.728	168.43
		S4 – S2	C16-H16…C7	2.612	1.081	3.668	165.41
			C16-H16…C8	2.741		3.782	161.65
		S2 – S4	C8-H8…C15	2.612	1.081	3.668	165.41
			C8-H8…C16	2.741		3.782	161.65
	S1*S2*S3S4	**S1* - S3**	C3-H3…C12	2.796	1.080	3.813	156.89
		S3 - S1*	C12-H12…C4	2.663	1.081	3.728	168.43
		S4 – S2*	C16-H16…C8	2.663	1.081	3.728	168.43
		S2* – S4	C8-H8…C16	2.796	1.080	3.813	156.89
	S1*S2*S3*S4	**S1* - S3***	C3-H3…C12	2.882	1.080	3.937	165.62
		S3* - S1*	C12-H12…C3	2.882	1.080	3.937	165.62

			S4 – S2*	C16-H16…C8	2.663	1.080	3.728	168.43
			S2* – S4	C7-H7…C16	2.796	1.080	3.813	156.89
		S1*S2*S3*S4*	**S1* – S1***	C3-H3…C3	2.882	1.080	3.937	165.62
IV	**D1**	**S1S2S3S4**	**S1 – S1**	C3-H3…C3	2.652	1.087	3.678	156.93
				C3-H3…S1	2.841		3.774	143.82
		S1*S2S3S4	**S1* – S2**	C1-H1…C8	2.725	1.083	3.713	151.58
				C1-H1…S2	2.860		3.831	149.32
			S2 – S4	C7-H7…C16	2.653	1.087	3.678	156.94
				C7-H7…S4	2.841		3.774	143.82
			S4 – S3	C15-H15…C12	2.653	1.087	3.678	156.94
				C15-H15…S3	2.841		3.774	143.82
			S3– S1*	C11-H11…C4	2.729	1.087	3.598	136.68
				C11-H11…S1	2.584		3.645	164.86
		S1*S2*S3S4	**S1* – S2***	C1-H1…C8	2.648	1.083	3.657	141.79
				C1-H1…S2	2.744		3.682	159.72
			S2* – S4	C5-H5…C16	2.725	1.083	3.713	151.58
				C5-H5…S4	2.860		3.831	149.32
			S4 – S3	C15-H15…C12	2.653	1.087	3.678	156.94
				C15-H15…S3	2.841		3.774	143.82
			S3– S1*	C11-H11…C4	2.729	1.087	3.598	136.68
				C11-H11…S1	2.584		3.645	164.86
		S1*S2*S3*S4	**S1* – S2***	C1-H1…C8	2.648	1.083	3.657	141.79
				C1-H1…S2	2.744		3.682	159.72
			S2* – S4	C5-H5…C16	2.725	1.083	3.713	151.58
				C5-H5…S4	2.860		3.831	149.32
			S4 – S3	C15-H15…C12	2.584	1.087	3.598	136.68
				C15-H15…S3	2.728		3.645	164.87
			S3– S1*	C9-H9…C4	2.744	1.083	3.682	141.79
				C9-H9…S1	2.648		3.657	159.72
		S1*S2*S3*S4*	**S1* – S1***	C1-H1…C3	2.744	1.083	3.660	141.79
				C1-H1…S1	2.648		3.682	159.72
	D2	**S1S2S3S4**	**S1 – S1**	C4-H4…C4	2.744	1.078	3.781	161.23
				C4-H4…S1	2.982		3.752	128.70
		S1*S2S3S4	**S1*- S2**	S1…S2	-	-	3.416	-

			S1…C8	-	-	3.571	-
		S2 - S1*	C8-H8…S1	2.877	1.078	3.874	153.82
		S4 – S3	C16-H16…C9	2.744	1.078	3.781	161.23
			C16-H16…S3	2.982		3.752	128.70
		S3 – S4	C12-H12…C16	2.744	1.078	3.781	161.23
			C12-H12…S4	2.982		3.752	128.70
	S1*S2*S3S4	**S1*- S2***	S1…S2	-	-	3.638	-
			S1…C8	-	-	3.545	-
		S2* - S1*	S2…S1	-	-	3.638	-
			S2…C4	-	-	3.545	-
		S4 – S3	C16-H16…C9	2.744	1.078	3.781	161.23
			C16-H16…S3	2.982		3.752	128.70
		S3 – S4	C12-H12…C16	2.744	1.078	3.781	161.23
			C12-H12…S4	2.982		3.752	128.70
	S1*S2*S3*S4	**S1*- S2***	S1…S2	-	-	3.638	-
			S1…C8	-	-	3.545	-
		S2* - S1*	S2…S1	-	-	3.638	-
			S2…C4	-	-	3.545	-
		S4 – S3*	C16-H16…C9	2.877	3.958	1.078	165.09
			C16-H16…S3	2.906	3.874		153.82
		S3* – S4	S2…S4	-	-	3.416	-
			S3…C16	-	-	3.571	-
	S1*S2*S3*S4*	**S1* – S1***	S1…C4	-	-	3.752	-
			S1…S1	-	-	3.545	-
D6	**S1S2S3S4**	**S1 – S1**	S1…S1	-	-	3.541	-
	S1*S2S3S4	**S1* - S4**	C4-H4…S4	2.862	1.084	3.781	142.67
		S2 – S3	S2…S3	-	-	3.541	-

4. Theoretical calculations

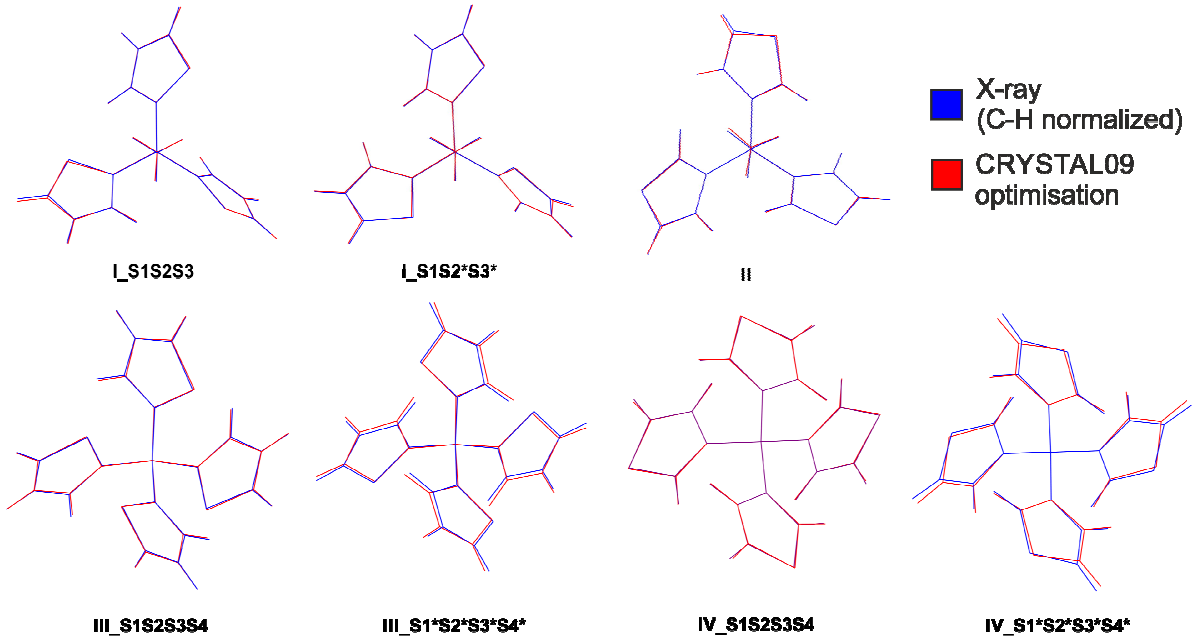
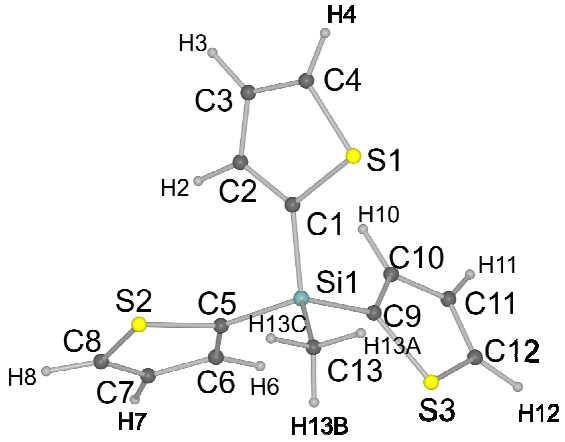
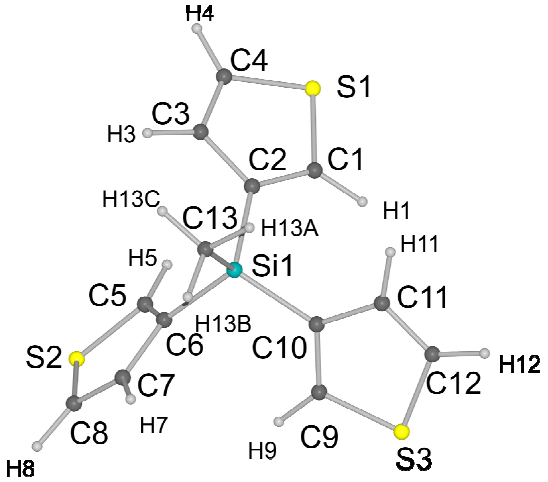


Figure S6. Overlay of molecular geometries taken from crystal structures with standardized X-H (blue) distances and geometries optimized with *CRYSTAL09* program (red). Note that in the case of structures derived from atomic positions with higher occupancy factors (**III_S1S2S3S4** and **IV_S1S2S3S4**), the differences between experimental and optimized geometries are very small, while in the case of **III_S1*S2*S3*S4*** and **IV_S1*S2*S3*S4*** the differences are much more pronounced.

Table S5. The positions of symmetrically non-equivalent atoms obtained from CRYSTAL09 optimisation of **I** and **II**. Unit cell parameters were constrained during optimisation procedure (**I**: a = 15.1565 Å, b = 27.9888 Å, c = 6.6148 Å, α = 90 °, β = 90 °, γ = 90 °; Space group: *Pccn*; **II**: a = 9.2813 Å, b = 28.5568 Å, c = 6.5767 Å, α = 90 °, β = 125.384 °, γ = 90 °; Space group: *Cc*).

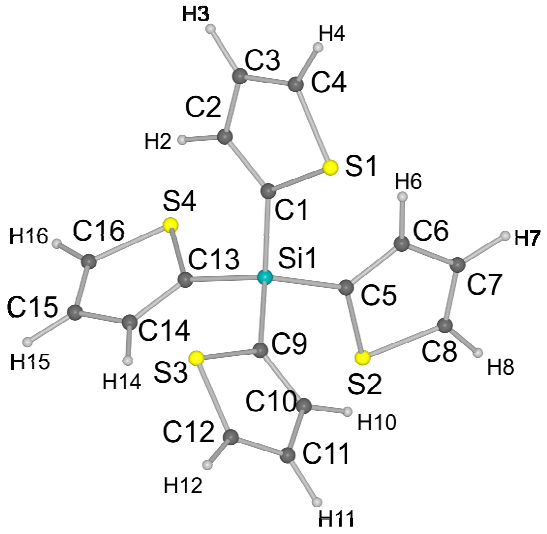




	I													**II**		
Atom	**S1S2S3**			**S1S2*S3**			**S1S2S3***			**S1S2*S3***			*Atom*	**S1S2S3**		
	X	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*		*X*	*Y*	*Z*
Si	0.4955	-0.3930	0.2354	0.4955	-0.3930	0.2354	0.4955	-0.3930	0.2354	0.4955	-0.3930	0.2354	Si1	0.3365	-0.1403	0.4826
S1	0.3354	-0.3835	-0.4517	0.3364	-0.3827	-0.4572	0.3365	-0.3831	-0.4488	0.3356	-0.3832	-0.4524	S1	-0.3237	-0.0457	0.1187
S2	-0.4839	-0.3114	-0.1016	-0.3340	-0.3443	0.0859	-0.4848	-0.3071	-0.0801	-0.3286	-0.3404	0.0911	S2	-0.0069	-0.1974	-0.3160
S3	-0.3902	-0.4843	0.3568	-0.3907	-0.4828	0.3577	-0.3925	-0.4048	-0.3619	-0.3899	-0.4034	-0.3690	S3	-0.0326	-0.0515	-0.1618
C1	0.4173	-0.3576	0.3925	0.4173	-0.3576	0.3925	0.4173	-0.3576	0.3925	0.4173	-0.3576	0.3925	C1	-0.4831	-0.0628	-0.1902
C2	0.4141	-0.3084	0.4127	0.4141	-0.3084	0.4127	0.4141	-0.3084	0.4127	0.4141	-0.3084	0.4127	C2	0.4978	-0.1100	-0.2169

C3	0.3477	-0.2917	-0.4532	0.3467	-0.2922	-0.4541	0.3478	-0.2916	-0.4535	0.3484	-0.2918	-0.4511	C3	-0.3875	-0.1335	0.0167
C4	0.3002	-0.3273	-0.3673	0.2996	-0.3285	-0.3730	0.3013	-0.3273	-0.3646	0.3007	-0.3276	-0.3660	C4	-0.2846	-0.1046	0.2126
C5	-0.4394	-0.3490	0.0864	-0.4394	-0.3490	0.0864	-0.4394	-0.3490	0.0864	-0.4394	-0.3490	0.0864	C5	0.1544	-0.1622	-0.3001
C6	-0.3465	-0.3436	0.0889	-0.4804	-0.3158	-0.0730	-0.3465	-0.3436	0.0889	-0.4804	-0.3158	-0.0730	C6	0.1727	-0.1714	-0.4868
C7	-0.3153	-0.3090	-0.0492	-0.4124	-0.2885	-0.1667	-0.3154	-0.3081	-0.0458	-0.4145	-0.2886	-0.1671	C7	0.0537	-0.2081	0.3506
C8	-0.3799	-0.2881	-0.1617	-0.3334	-0.3001	-0.0953	-0.3809	-0.2860	-0.1511	-0.3315	-0.2976	-0.0977	C8	-0.0486	-0.2257	0.4171
C9	-0.4277	-0.4257	0.4047	-0.4277	-0.4257	0.4047	-0.4277	-0.4257	0.4047	-0.4277	-0.4257	0.4047	C9	0.2198	-0.0968	0.2242
C10	-0.3880	-0.4088	-0.4186	-0.3880	-0.4088	-0.4186	-0.3922	-0.4705	0.3652	-0.3922	-0.4705	0.3652	C10	0.0406	-0.0931	0.0744
C11	-0.3305	-0.4418	-0.3253	-0.3294	-0.4419	-0.3246	-0.3354	-0.4868	-0.4793	-0.3341	-0.4861	-0.4803	C11	0.1861	-0.0397	-0.0550
C12	-0.3232	-0.4837	-0.4282	-0.3244	-0.4834	-0.4316	-0.3273	-0.4551	-0.3245	-0.3263	-0.4539	-0.3274	C12	0.3018	-0.0660	0.1481
C13	0.4371	-0.4350	0.0632	0.4375	-0.4347	0.0631	0.4376	-0.4361	0.0667	0.4373	-0.4356	0.0650	C13	0.4550	-0.1827	0.4103
H2	0.4596	-0.2852	0.3346	0.4587	-0.2845	0.3344	0.4607	-0.2853	0.3374	0.4580	-0.2847	0.3320	H1	0.4460	-0.0360	-0.3299
H3	0.3358	-0.2544	-0.4206	0.3344	-0.2549	-0.4212	0.3363	-0.2543	-0.4204	0.3366	-0.2544	-0.4189	H3	-0.3782	-0.1712	0.0376
H4	0.2470	-0.3248	-0.2598	0.2456	-0.3243	-0.2674	0.2494	-0.3243	-0.2540	0.4021	-0.4627	0.1516	H4	-0.1840	-0.1134	0.4038
H6	-0.3045	-0.3645	0.1867	0.4501	-0.3141	-0.1098	-0.3041	-0.3656	0.1815	0.4501	-0.3150	-0.1088	H5	0.2229	-0.1365	-0.1539
H7	-0.2463	-0.2997	-0.0658	-0.4237	-0.2620	-0.2830	-0.2464	-0.2993	-0.0642	-0.4267	-0.2634	-0.2884	H7	0.0447	-0.2199	0.1874
H8	-0.3737	-0.2613	-0.2778	-0.2729	-0.2833	-0.1452	-0.3742	-0.2596	-0.2694	-0.2713	-0.2821	-0.1522	H8	0.3527	0.2472	0.3264
H10	-0.4004	-0.3736	-0.3590	-0.4007	-0.3736	-0.3579	-0.4067	-0.4909	0.2307	-0.4071	-0.4912	0.2317	H10	-0.0554	-0.1111	0.0885
H11	-0.2960	-0.4351	-0.1847	-0.2938	-0.4351	-0.1857	-0.3009	0.4794	-0.4825	-0.2986	0.4804	-0.4829	H11	0.2119	-0.0155	-0.1563
H12	-0.2831	0.4858	-0.3913	-0.2835	0.4865	-0.3902	-0.2883	-0.4586	-0.1894	-0.2862	-0.4571	-0.1940	H12	0.4428	-0.0644	0.2384
H13A	0.3914	-0.4157	-0.0351	0.3931	-0.4148	-0.0336	0.3894	-0.4177	-0.0277	0.3910	-0.4167	-0.0321	H13A	-0.4579	-0.2058	-0.4330
H13B	0.3996	-0.4617	0.1470	0.4002	-0.4603	0.1512	0.4043	-0.4638	0.1537	0.2472	-0.3243	-0.2596	H13B	-0.4650	-0.1639	0.3643
H13C	0.4840	-0.4531	-0.0359	0.4854	-0.4535	-0.0290	0.4853	-0.4529	-0.0340	0.4854	-0.4532	-0.0323	H13C	0.3621	-0.2042	0.2490

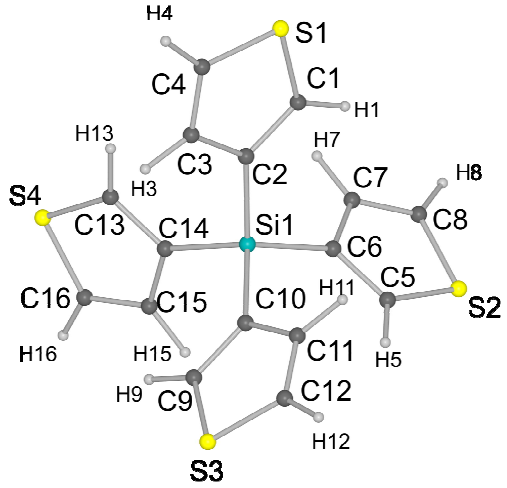
Table S6. The positions of symmetrically non-equivalent atoms obtained from CRYSTAL09 optimisation of **III**. Unit cell parameters were constrained during optimisation procedure (a = 11.2609 Å, b = 11.2609 Å, c = 6.3487 Å, α = 90 °, β = 90 °, γ = 90 °; Space group: **S1S2S3S4**, **S1*S2*S3*S4***: $P\text{-}42_1c$; **S1*S2S3S4**, **S1*S2*S3S4**, **S1*S2*S3*S4**: $P2_1$).



Atom	**S1S2S3S4**			**S1*S2S3S4**			**S1*S2*S3S4**			**S1*S2*S3*S4**			**S1*S2*S3*S4***		
	X	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*
Si1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S1	0.1216	0.1599	0.3587	0.0786	-0.2552	0.1410	0.0786	-0.2552	0.1410	0.0786	-0.2552	0.1410	-0.0786	0.2552	0.1410
C1	0.0126	0.1374	0.1620	-0.0180	-0.1328	0.1703	-0.0180	-0.1328	0.1703	-0.0180	-0.1328	0.1703	0.0180	0.1328	0.1703
C2	-0.0580	0.2358	0.1482	-0.0981	-0.1547	0.3279	-0.0981	-0.1547	0.3279	-0.0981	-0.1547	0.3279	0.0856	0.2682	0.4245
C3	-0.0272	0.3294	0.2887	0.0053	-0.3323	0.3411	0.0053	-0.3323	0.3411	-0.0856	-0.2682	0.4245	-0.0053	0.3323	0.3411
C4	0.0681	0.3027	0.4116	-0.0856	-0.2682	0.4245	-0.0856	-0.2682	0.4245	0.0053	-0.3323	0.3411	0.0981	0.1547	0.3279
H2	-0.1317	0.2411	0.0394	-0.1632	-0.0899	0.3783	-0.1632	-0.0899	0.3783	-0.1632	-0.0899	0.3783	0.1632	0.0899	0.3783

H3	-0.0745	0.4130	0.2974	-0.1399	-0.2989	0.5538	-0.1399	-0.2989	0.5538	-0.1399	-0.2989	0.5538	0.1399	0.2989	-0.4462
H4	0.1097	0.3568	-0.4686	0.0380	-0.4181	0.3881	0.0380	-0.4181	0.3881	0.0380	-0.4181	0.3881	-0.0380	0.4181	0.3881
S2				0.1216	0.1599	0.3587	0.2552	0.0786	-0.1410	0.2552	0.0786	-0.1410			
C5				0.0126	0.1374	0.1620	0.1328	-0.0180	-0.1703	0.1328	-0.0180	-0.1703			
C6				-0.0580	0.2358	0.1482	0.1547	-0.0981	-0.3279	0.1547	-0.0981	-0.3279			
C7				-0.0272	0.3294	0.2887	0.2682	-0.0856	-0.4245	0.2682	-0.0856	-0.4245			
C8				0.0681	0.3027	0.4116	0.3323	0.0053	-0.3411	0.3323	0.0053	-0.3411			
H6				-0.1317	0.2411	0.0394	0.0899	-0.1632	-0.3783	0.0899	-0.1632	-0.3783			
H7				-0.0745	0.4130	0.2974	0.2989	-0.1399	-0.5538	0.2989	-0.1399	-0.5538			
H8				0.1097	0.3568	0.5314	0.4181	0.0380	-0.3881	0.4181	0.0380	-0.3881			
S3				0.1374	-0.0126	-0.1620	0.1216	0.1599	0.3587	-0.2552	-0.0786	-0.1410			
C9				0.1599	-0.1216	-0.3587	0.0126	0.1374	0.1620	-0.1328	0.0180	-0.1703			
C10				0.2358	0.0580	-0.1482	-0.0580	0.2358	0.1482	-0.1547	0.0981	-0.3279			
C11				0.3294	0.0272	-0.2887	-0.0272	0.3294	0.2887	-0.2682	0.0856	-0.4245			
C12				0.3027	-0.0681	-0.4116	0.0681	0.3027	0.4116	-0.3323	-0.0053	-0.3411			
H10				0.2411	0.1317	-0.0394	-0.1317	0.2411	0.0394	-0.0899	0.1632	-0.3783			
H11				0.4130	0.0745	-0.2974	-0.0745	0.4130	0.2974	-0.2989	0.1399	-0.5538			
H12				0.3568	-0.1097	-0.5314	0.1097	0.3568	0.5314	-0.4181	-0.0380	-0.3881			
S4				-0.1599	0.1216	-0.3587	-0.1599	0.1216	-0.3587	0.1216	0.1599	0.3587			
C13				-0.1374	0.0126	-0.1620	-0.1374	0.0126	-0.1620	0.0126	0.1374	0.1620			
C14				-0.2358	-0.0580	-0.1482	-0.2358	-0.0580	-0.1482	-0.0580	0.2358	0.1482			
C15				-0.3027	0.0681	-0.4116	-0.3294	-0.0272	-0.2887	-0.0272	0.3294	0.2887			
C16				-0.3294	-0.0272	-0.2887	-0.3027	0.0681	-0.4116	0.0681	0.3027	0.4116			
H14				-0.2411	-0.1317	-0.0394	-0.2411	-0.1317	-0.0394	-0.1317	0.2411	0.0394			
H15				-0.4130	-0.0745	-0.2974	-0.4130	-0.0745	-0.2974	-0.0745	0.4130	0.2974			
H16				-0.3568	0.1097	-0.5314	-0.3568	0.1097	-0.5314	0.1097	0.3568	0.5314			

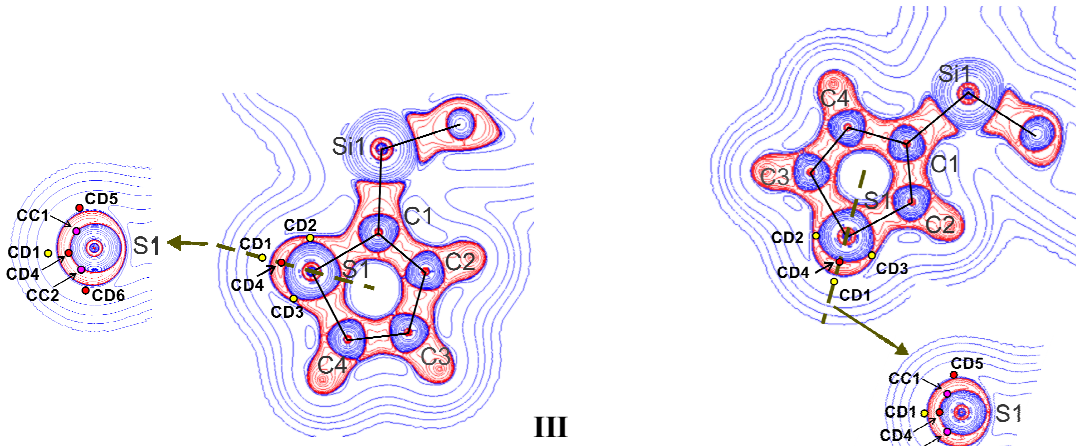
Table S7. The positions of symmetrically non-equivalent atoms obtained from CRYSTAL09 optimisation of **IV**. Unit cell parameters were constrained during optimisation procedure (a = 11.3206 Å, b = 11.3206 Å, c = 6.3023 Å, α = 90 °, β = 90 °, γ = 90 °; Space group: **S1S2S3S4**, **S1*S2*S3*S4***: $P\text{-}42_1c$; **S1*S2S3S4**, **S1*S2*S3S4**, **S1*S2*S3*S4**: $P2_1$).



Atom	**S1S2S3S4**			**S1*S2S3S4**			**S1*S2*S3S4**			**S1*S2*S3*S4**			**S1*S2*S3*S4***		
	X	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*
Si1	0.0000	0.0000	0.0000	0.2500	0.0000	0.2500	0.2500	0.0000	0.2500	0.2500	0.0000	0.2500	0.0000	0.0000	0.0000
S1	-0.0525	0.3384	0.3399	0.3601	-0.2763	0.7052	0.3601	-0.2763	0.7052	0.3601	-0.2763	0.7052	-0.0802	0.2908	0.4455
C1	0.0070	0.2373	0.1570	0.3642	-0.1420	0.5676	0.3642	-0.1420	0.5676	0.3642	-0.1420	0.5676	-0.0869	0.1499	0.3288
C2	-0.0443	0.1282	0.1694	0.2782	-0.1329	0.4168	0.2782	-0.1329	0.4168	0.2782	-0.1329	0.4168	-0.0082	0.1367	0.1675
C3	-0.1340	0.1243	0.3303	0.2061	-0.2382	0.4128	0.2061	-0.2382	0.4128	0.2061	-0.2382	0.4128	0.0607	0.2424	0.1364
C4	-0.1499	0.2283	0.4339	0.2378	-0.3223	0.5547	0.2378	-0.3223	0.5547	0.2378	-0.3223	0.5547	0.0338	0.3318	0.2706

H1	0.0782	0.2653	0.0545	0.4302	-0.0774	0.6125	0.4302	-0.0774	0.6125	0.4302	-0.0774	0.6125	-0.1475	0.0855	0.3935
H3	-0.1825	0.0445	0.3696	0.1317	-0.2487	0.3068	0.1317	-0.2487	0.3068	0.1317	-0.2487	0.3068	0.1284	0.2500	0.0164
H4	-0.2086	0.2482	-0.4362	0.1963	-0.4069	0.5852	0.1963	-0.4069	0.5852	0.1963	-0.4069	0.5852	0.0734	0.4187	0.2809
S2				0.2391	0.3440	0.5805	0.5263	0.1101	-0.2052	0.5263	0.1101	-0.2052			
C5				0.2867	0.2344	0.4024	0.3920	0.1142	-0.0676	0.3920	0.1142	-0.0676			
C6				0.2218	0.1329	0.4168	0.3829	0.0282	0.0832	0.3829	0.0282	0.0832			
C7				0.1315	0.1424	0.5750	0.4882	-0.0439	0.0873	0.4882	-0.0439	0.0873			
C8				0.1285	0.2480	0.6768	0.5723	-0.0122	-0.0547	0.5723	-0.0122	-0.0547			
H5				0.3611	0.2529	0.3004	0.3274	0.1802	-0.1125	0.3274	0.1802	-0.1125			
H7				0.0733	0.0696	0.6159	0.4987	-0.1183	0.1932	0.4987	-0.1183	0.1932			
H8				0.0725	0.2757	0.8059	0.6569	-0.0537	-0.0852	0.6569	-0.0537	-0.0852			
S3				0.5940	0.0109	-0.0805	0.2391	0.3440	0.5805	-0.0263	-0.1101	-0.2052			
C9				0.4844	-0.0367	0.0976	0.2867	0.2344	0.4024	0.1080	-0.1142	-0.0676			
C10				0.3829	0.0282	0.0832	0.2218	0.1329	0.4168	0.1171	-0.0282	0.0832			
C11				0.3924	0.1185	-0.0750	0.1315	0.1424	0.5750	0.0118	0.0439	0.0873			
C12				0.4980	0.1215	-0.1768	0.1285	0.2480	0.6768	-0.0723	0.0122	-0.0547			
H9				0.5029	-0.1111	0.1996	0.3611	0.2529	0.3004	0.1726	-0.1802	-0.1125			
H11				0.3196	0.1767	-0.1159	0.0733	0.0696	0.6159	0.0013	0.1183	0.1932			
H12				0.5257	0.1776	-0.3059	0.0725	0.2757	0.8059	-0.1569	0.0537	-0.0852			
S4				-0.0940	-0.0109	-0.0805	-0.0940	-0.0109	-0.0805	0.2391	0.3440	0.5805			
C13				0.0156	0.0367	0.0976	0.0156	0.0367	0.0976	0.2867	0.2344	0.4024			
C14				0.1171	-0.0282	0.0832	0.1171	-0.0282	0.0832	0.2218	0.1329	0.4168			
C15				0.1076	-0.1185	-0.0750	0.1076	-0.1185	-0.0750	0.1315	0.1424	0.5750			
C16				0.0020	-0.1215	-0.1768	0.0020	-0.1215	-0.1768	0.1285	0.2480	0.6768			
H13				-0.0029	0.1111	0.1996	-0.0029	0.1111	0.1996	0.3611	0.2529	0.3004			
H15				0.1805	-0.1767	-0.1159	0.1805	-0.1767	-0.1159	0.0733	0.0696	0.6159			
H16				-0.0257	-0.1776	-0.3059	-0.0257	-0.1776	-0.3059	0.0725	0.2757	0.8059			

Table S8. The results of topological analysis of electron density around sulphur atom. $\rho(\mathbf{r})$ donates to electron density, $L(\mathbf{r})$ – negative Laplacian of electron density, $L(\boldsymbol{r}_{CP}) / \rho(\boldsymbol{r}_{CP})$ indicates nucleophilic/electrophilic powers of CC/CD).



III **IV**

	$\rho(\boldsymbol{r}_{CP})$ / $e\cdot$Å^{-3}	$L(\boldsymbol{r}_{CP})$ / $e\cdot$Å^{-5}	$(L(\boldsymbol{r}_{CP})$ / $\rho(\boldsymbol{r}_{CP}))$ / Å^{-2}		$\rho(\boldsymbol{r}_{CP})$ / $e\cdot$Å^{-3}	$L(\boldsymbol{r}_{CP})$ / $e\cdot$Å^{-5}	$(L(\boldsymbol{r}_{CP})$ / $\rho(\boldsymbol{r}_{CP}))$ / Å^{-2}
CC1 (3,-3)	1.25	11.45	9.19	CC1 (3,-3)	1.24	11.31	9.12
CC2 (3,-3)	1.24	11.42	9.17	CC2 (3,-3)	1.24	11.32	9.13
CD1 (3,+1)	0.35	-1.69	-4.84	CD1 (3,+1)	0.35	-1.69	-4.85
CD2 (3,+1)	0.86	0.94	1.09	CD2 (3,+1)	0.86	1.01	1.17
CD3 (3,+1)	0.86	0.84	0.98	CD3 (3,+1)	0.86	0.84	0.97
CD4 (3,-1)	1.23	10.68	8.71	CD4 (3,-1)	1.22	10.59	8.66
CD5 (3,-1)	0.34	-1.43	-4.26	CD5 (3,-1)	0.33	-1.42	-4.23
CD6 (3,-1)	0.34	-1.40	-4.17	CD6 (3,-1)	0.34	-1.42	-4.23

5. NMR spectra of cocrystals III + IV

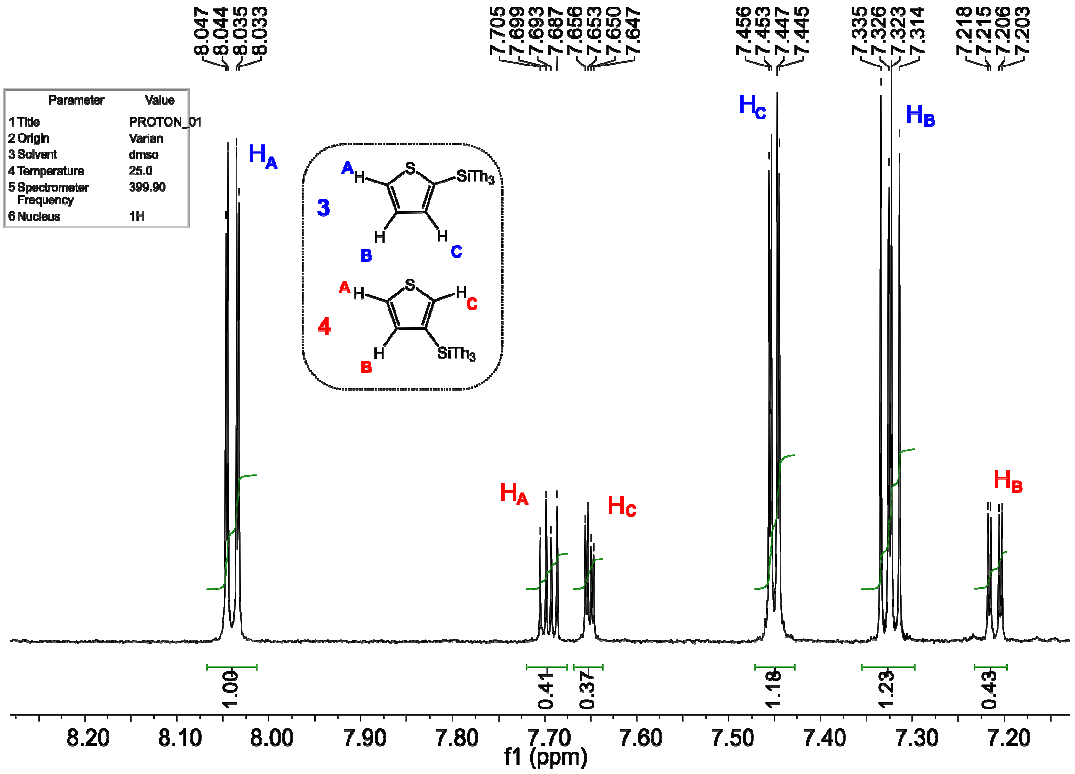


Figure S7. ^{1}H NMR spectrum of cocrystal **III+IVa.**

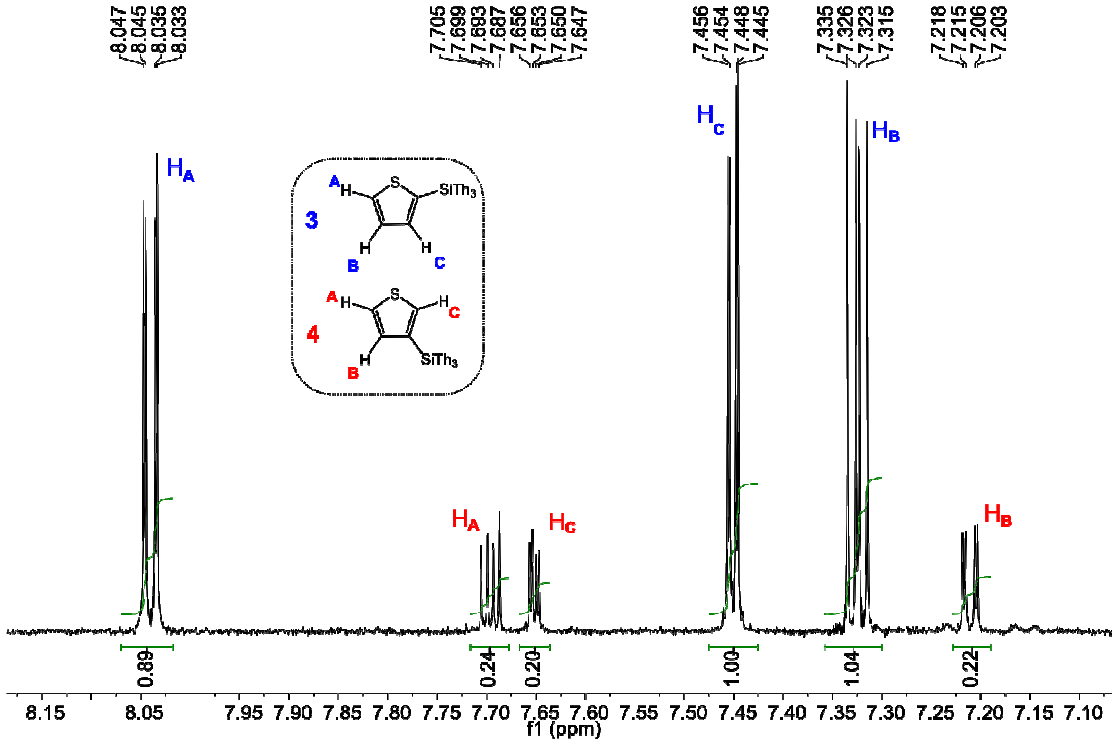


Figure S8. ^{1}H NMR spectrum of cocrystal **III+IVb.**

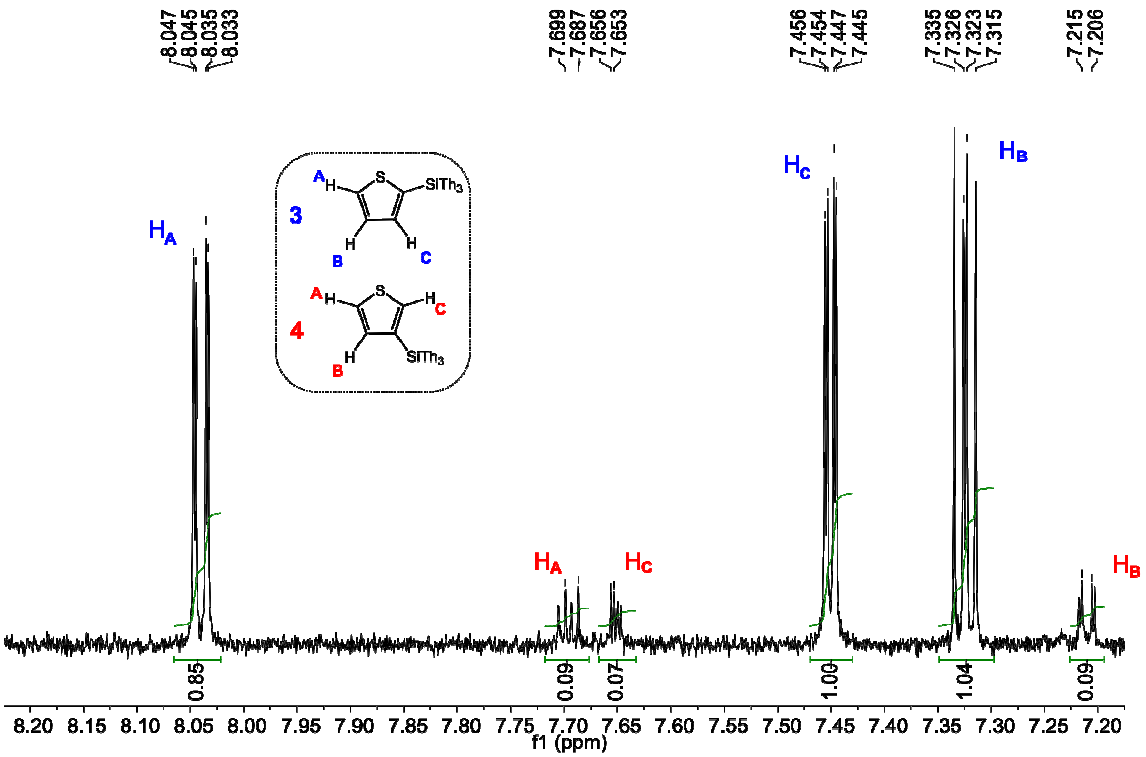


Figure S9. ^{1}H NMR spectrum of cocrystal **III+IVc.**