Supplementary Information for

Single-crystalline photochromism of diarylethenes: reactivity-structure relationship

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Table S1. Crystal data and structure refinement for **2a**.

Identification code	compd2a	
Empirical formula	$C_{31}H_{26}F_6O_2S_2$	
Formula weight	608.64	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.564(3) Å	α = 90°
	b = 9.771(2) Å	β = 96.368(4)°
	c = 23.797(5) Å	γ = 90°
Volume	2903.2(10) Å^3	
Z	4	
Density (calculated)	1.392 g/cm^3	
Absorption coefficient	0.249 mm^{-1}	
F(000)	1256	
Crystal size	0.6 x 0.3 x 0.2 mm^3	
Theta range for data collection	1.63 to 21.97°.	
Index ranges	-13 <= h <= 13, -10 <= k <= 10, -25 <= l <= 21	
Reflections collected	10956	
Independent reflections	3545 [R(int) = 0.0592]	
Completeness to theta = 21.97°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3545 / 9 / 438	
Goodness-of-fit on F^2	1.080	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0453, $wR2$ = 0.1075	
R indices (all data)	$R1$ = 0.0640, $wR2$ = 0.1151	
Largest diff. peak and hole	0.223 and -0.197 e Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6598(1)	3538(1)	2169(1)	49(1)
S(2)	1530(1)	5276(1)	1481(1)	65(1)
F(1A)	4696(12)	-745(18)	1609(6)	82(4)
F(2A)	5118(7)	137(15)	837(5)	76(2)
F(3A)	3120(4)	-1718(7)	924(6)	100(3)
F(4A)	3269(4)	-107(11)	313(2)	92(2)
F(5A)	2028(10)	-162(14)	1524(4)	81(2)
F(6A)	1640(8)	790(13)	713(5)	87(3)
C(7A)	3291(8)	-377(13)	859(7)	61(3)
F(1B)	4830(30)	140(50)	675(17)	118(13)
F(2B)	4930(30)	-770(50)	1502(17)	78(10)
F(3B)	3107(16)	-1130(40)	535(15)	140(18)
F(4B)	3125(11)	-1610(20)	1412(18)	124(11)
F(5B)	1770(30)	830(30)	660(13)	120(14)
F(6B)	1700(30)	90(40)	1498(14)	113(13)
C(7B)	3210(20)	-590(30)	1054(12)	53(12)
C(1)	5601(2)	2326(3)	2113(1)	45(1)
C(2)	5010(3)	2425(3)	1597(1)	45(1)
C(3)	5373(3)	3461(4)	1237(1)	48(1)
C(4)	6243(3)	4154(3)	1498(1)	46(1)
C(5)	4119(3)	1494(3)	1396(1)	45(1)
C(6)	4343(3)	108(4)	1179(2)	59(1)
C(8)	2443(3)	513(4)	1120(2)	61(1)
C(9)	3063(3)	1751(3)	1349(1)	46(1)
C(10)	2065(3)	3938(4)	1136(2)	57(1)
C(11)	2513(2)	3009(4)	1513(2)	46(1)
C(12)	2393(2)	3340(3)	2088(1)	43(1)
C(13)	1867(2)	4558(4)	2139(1)	47(1)
C(14)	5505(3)	1364(4)	2592(2)	59(1)
C(15)	1963(4)	3937(5)	501(2)	84(1)
C(16)	4910(3)	3688(5)	636(2)	79(1)
C(17)	2740(3)	2401(4)	2572(2)	66(1)
C(18)	6859(2)	5270(3)	1275(1)	44(1)
C(19)	6352(3)	6393(4)	994(2)	52(1)
C(20)	6929(3)	7433(4)	784(2)	52(1)
C(21)	8034(3)	7390(4)	851(1)	48(1)
C(22)	8558(3)	6300(4)	1128(2)	53(1)
C(23)	7960(3)	5264(4)	1336(2)	52(1)
C(24)	1595(2)	5269(4)	2645(2)	48(1)
C(25)	2271(3)	5276(4)	3147(2)	53(1)

C(26)	2033(3)	5964(4)	3621(2)	57(1)
C(27)	1092(3)	6701(4)	3603(2)	57(1)
C(28)	406(3)	6719(4)	3112(2)	71(1)
C(29)	644(3)	6022(4)	2642(2)	65(1)
C(30)	9658(3)	8580(5)	754(2)	94(2)
C(31)	1469(4)	7443(5)	4557(2)	94(2)
O(1)	8537(2)	8455(3)	618(1)	65(1)
O(2)	767(2)	7412(3)	4051(1)	78(1)

Table S3. Bond lengths [Å] and angles [°] for **2a**.

S(1)-C(1)	1.718(3)
S(1)-C(4)	1.718(4)
S(2)-C(10)	1.720(4)
S(2)-C(13)	1.723(3)
F(1A)-C(6)	1.356(15)
F(2A)-C(6)	1.337(12)
F(3A)-C(7A)	1.340(12)
F(4A)-C(7A)	1.323(19)
F(5A)-C(8)	1.320(10)
F(6A)-C(8)	1.347(10)
C(7A)-C(6)	1.525(11)
C(7A)-C(8)	1.557(11)
F(1B)-C(6)	1.41(4)
F(2B)-C(6)	1.32(4)
F(3B)-C(7B)	1.34(2)
F(4B)-C(7B)	1.32(3)
F(5B)-C(8)	1.34(3)
F(6B)-C(8)	1.42(3)
C(7B)-C(8)	1.46(3)
C(7B)-C(6)	1.58(2)
C(1)-C(2)	1.367(5)
C(1)-C(14)	1.493(5)
C(2)-C(3)	1.433(5)
C(2)-C(5)	1.480(5)
C(3)-C(4)	1.375(5)
C(3)-C(16)	1.499(5)
C(4)-C(18)	1.469(5)
C(5)-C(9)	1.343(4)
C(5)-C(6)	1.487(5)
C(8)-C(9)	1.507(5)
C(9)-C(11)	1.484(5)
C(10)-C(11)	1.354(5)
C(10)-C(15)	1.503(5)
C(11)-C(12)	1.431(5)
C(12)-C(13)	1.373(5)
C(12)-C(17)	1.499(5)
C(13)-C(24)	1.465(5)
C(18)-C(23)	1.375(4)
C(18)-C(19)	1.401(5)
C(19)-C(20)	1.373(5)
C(20)-C(21)	1.380(5)
C(21)-O(1)	1.367(4)
C(21)-C(22)	1.382(5)
C(22)-C(23)	1.384(5)
C(24)-C(25)	1.386(5)
C(24)-C(29)	1.402(5)
C(25)-C(26)	1.374(5)
C(26)-C(27)	1.381(5)

C(27)-O(2)	1.371(4)
C(27)-C(28)	1.374(5)
C(28)-C(29)	1.370(5)
C(30)-O(1)	1.415(5)
C(31)-O(2)	1.413(5)

C(1)-S(1)-C(4)	93.33(16)
C(10)-S(2)-C(13)	93.12(17)
F(4A)-C(7A)-F(3A)	108.7(9)
F(4A)-C(7A)-C(6)	110.6(9)
F(3A)-C(7A)-C(6)	112.8(11)
F(4A)-C(7A)-C(8)	109.9(9)
F(3A)-C(7A)-C(8)	112.0(10)
C(6)-C(7A)-C(8)	102.8(6)
F(4B)-C(7B)-F(3B)	107(2)
F(4B)-C(7B)-C(8)	112.9(16)
F(3B)-C(7B)-C(8)	113.4(19)
F(4B)-C(7B)-C(6)	109.6(17)
F(3B)-C(7B)-C(6)	109.4(17)
C(8)-C(7B)-C(6)	104.7(14)
C(2)-C(1)-C(14)	130.5(3)
C(2)-C(1)-S(1)	109.9(3)
C(14)-C(1)-S(1)	119.7(2)
C(1)-C(2)-C(3)	114.2(3)
C(1)-C(2)-C(5)	124.3(3)
C(3)-C(2)-C(5)	121.4(3)
C(4)-C(3)-C(2)	111.6(3)
C(4)-C(3)-C(16)	124.3(3)
C(2)-C(3)-C(16)	124.0(3)
C(3)-C(4)-C(18)	128.8(3)
C(3)-C(4)-S(1)	111.0(3)
C(18)-C(4)-S(1)	120.2(2)
C(9)-C(5)-C(2)	128.1(3)
C(9)-C(5)-C(6)	111.4(3)
C(2)-C(5)-C(6)	120.4(3)
F(2A)-C(6)-F(1A)	105.8(8)
F(2B)-C(6)-F(1B)	104(2)
F(2B)-C(6)-C(5)	120(2)
F(2A)-C(6)-C(5)	111.8(7)
F(1A)-C(6)-C(5)	110.8(8)
F(1B)-C(6)-C(5)	113(2)
F(2A)-C(6)-C(7A)	110.6(8)
F(1A)-C(6)-C(7A)	112.2(9)
C(5)-C(6)-C(7A)	105.6(5)
F(2B)-C(6)-C(7B)	105.4(19)
F(1B)-C(6)-C(7B)	108.8(17)
C(5)-C(6)-C(7B)	104.7(9)
F(5A)-C(8)-F(6A)	107.4(7)
F(5B)-C(8)-F(6B)	101.0(17)
F(5B)-C(8)-C(7B)	116.4(16)
F(6B)-C(8)-C(7B)	109.5(17)

F(5A)-C(8)-C(9)	111.6(6)
F(5B)-C(8)-C(9)	111.1(15)
F(6A)-C(8)-C(9)	114.5(7)
F(6B)-C(8)-C(9)	110.7(17)
C(7B)-C(8)-C(9)	108.1(10)
F(5A)-C(8)-C(7A)	110.8(9)
F(6A)-C(8)-C(7A)	108.5(8)
C(9)-C(8)-C(7A)	104.1(5)
C(5)-C(9)-C(11)	128.2(3)
C(5)-C(9)-C(8)	110.2(3)
C(11)-C(9)-C(8)	121.5(3)
C(11)-C(10)-C(15)	130.4(4)
C(11)-C(10)-S(2)	110.4(3)
C(15)-C(10)-S(2)	119.2(3)
C(10)-C(11)-C(12)	113.7(3)
C(10)-C(11)-C(9)	123.6(3)
C(12)-C(11)-C(9)	122.7(3)
C(13)-C(12)-C(11)	112.5(3)
C(13)-C(12)-C(17)	124.4(3)
C(11)-C(12)-C(17)	123.0(3)
C(12)-C(13)-C(24)	129.9(3)
C(12)-C(13)-S(2)	110.3(3)
C(24)-C(13)-S(2)	119.8(3)
C(23)-C(18)-C(19)	116.9(3)
C(23)-C(18)-C(4)	121.5(3)
C(19)-C(18)-C(4)	121.6(3)
C(20)-C(19)-C(18)	121.5(3)
C(19)-C(20)-C(21)	120.0(3)
O(1)-C(21)-C(20)	115.8(3)
O(1)-C(21)-C(22)	124.3(3)
C(20)-C(21)-C(22)	119.9(3)
C(21)-C(22)-C(23)	119.0(3)
C(18)-C(23)-C(22)	122.6(3)
C(25)-C(24)-C(29)	116.3(3)
C(25)-C(24)-C(13)	122.3(3)
C(29)-C(24)-C(13)	121.4(3)
C(26)-C(25)-C(24)	122.7(3)
C(25)-C(26)-C(27)	119.6(3)
O(2)-C(27)-C(28)	116.2(4)
O(2)-C(27)-C(26)	124.7(4)
C(28)-C(27)-C(26)	119.1(4)
C(29)-C(28)-C(27)	121.0(4)
C(28)-C(29)-C(24)	121.3(4)
C(21)-O(1)-C(30)	117.8(3)
C(27)-O(2)-C(31)	117.5(3)

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	43(1)	47(1)	56(1)	-3(1)	-4(1)	-3(1)
S(2)	62(1)	64(1)	64(1)	11(1)	-5(1)	21(1)
F(1A)	102(8)	50(4)	93(4)	0(4)	2(4)	18(5)
F(2A)	62(3)	74(4)	96(5)	-27(4)	23(3)	1(2)
F(3A)	96(3)	44(3)	158(10)	-14(4)	2(5)	-20(2)
F(4A)	97(3)	106(5)	69(3)	-24(3)	-2(2)	-1(3)
F(5A)	70(6)	80(4)	93(4)	7(3)	18(3)	-28(4)
F(6A)	54(4)	99(7)	102(6)	-12(4)	-16(4)	-22(3)
C(7A)	65(5)	52(5)	66(8)	-5(8)	3(5)	-6(4)
F(1B)	160(30)	93(14)	110(20)	-33(14)	56(19)	-30(20)
F(2B)	61(11)	58(12)	110(20)	-24(14)	-32(15)	30(9)
F(3B)	124(13)	150(40)	130(20)	-100(30)	-47(17)	10(20)
F(4B)	85(8)	97(11)	190(30)	58(14)	-2(11)	-11(7)
F(5B)	130(20)	57(14)	150(30)	8(14)	-109(16)	-4(14)
F(6B)	64(17)	100(20)	190(20)	-34(14)	52(13)	-50(14)
C(7B)	61(13)	40(20)	50(20)	-5(15)	-2(11)	-23(10)
C(1)	39(2)	43(2)	53(2)	2(2)	4(2)	3(2)
C(2)	39(2)	40(2)	55(2)	-1(2)	2(2)	1(2)
C(3)	44(2)	46(2)	53(2)	2(2)	-3(2)	-2(2)
C(4)	39(2)	40(2)	58(2)	-4(2)	3(2)	2(2)
C(5)	42(2)	41(2)	51(2)	1(2)	2(2)	0(2)
C(6)	56(3)	52(3)	71(3)	-2(2)	7(2)	-2(2)
C(8)	47(3)	65(3)	68(3)	3(2)	-8(2)	-14(2)
C(9)	41(2)	46(2)	50(2)	3(2)	0(2)	-6(2)
C(10)	53(2)	60(2)	57(2)	5(2)	-1(2)	12(2)
C(11)	30(2)	48(2)	58(2)	6(2)	-5(2)	-1(2)
C(12)	30(2)	48(2)	51(2)	7(2)	-1(2)	-2(2)
C(13)	34(2)	54(2)	53(2)	4(2)	-2(2)	1(2)
C(14)	50(2)	56(2)	70(3)	2(2)	2(2)	1(2)
C(15)	94(3)	100(4)	56(3)	9(2)	-7(2)	23(3)
C(16)	83(3)	80(3)	69(3)	12(2)	-16(2)	-31(2)
C(17)	81(3)	58(3)	61(2)	13(2)	9(2)	18(2)
C(18)	34(2)	43(2)	54(2)	-4(2)	4(2)	-1(2)
C(19)	36(2)	52(2)	66(2)	-1(2)	2(2)	-1(2)
C(20)	47(2)	51(2)	58(2)	5(2)	2(2)	3(2)
C(21)	50(2)	47(2)	49(2)	-6(2)	11(2)	-10(2)
C(22)	37(2)	55(2)	67(2)	-8(2)	7(2)	-2(2)
C(23)	46(2)	46(2)	62(2)	-3(2)	3(2)	2(2)
C(24)	35(2)	47(2)	62(2)	8(2)	1(2)	0(2)
C(25)	42(2)	53(2)	62(2)	6(2)	3(2)	6(2)

C(26)	53(2)	58(2)	58(3)	7(2)	1(2)	-1(2)
C(27)	58(2)	52(2)	65(3)	0(2)	15(2)	-2(2)
C(28)	50(2)	73(3)	90(3)	-3(3)	12(2)	15(2)
C(29)	44(2)	74(3)	74(3)	-5(2)	-7(2)	12(2)
C(30)	59(3)	83(3)	144(4)	4(3)	31(3)	-20(3)
C(31)	123(4)	89(4)	71(3)	-9(3)	22(3)	5(3)
O(1)	62(2)	63(2)	71(2)	0(1)	16(1)	-18(1)
O(2)	83(2)	76(2)	79(2)	-11(2)	22(2)	7(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **2a**.

	x	y	z	U(eq)
H(14A)	4902	770	2499	88
H(14B)	5405	1876	2927	88
H(14C)	6146	826	2659	88
H(15A)	2406	3227	372	127
H(15B)	2188	4807	369	127
H(15C)	1230	3775	356	127
H(16A)	4294	4272	629	119
H(16B)	4702	2825	465	119
H(16C)	5436	4112	431	119
H(17A)	3470	2596	2714	99
H(17B)	2684	1469	2445	99
H(17C)	2289	2537	2868	99
H(19A)	5608	6436	948	62
H(20A)	6575	8166	598	63
H(22A)	9302	6263	1175	64
H(23A)	8317	4534	1524	62
H(25A)	2912	4794	3164	63
H(26A)	2503	5934	3951	68
H(28A)	-230	7212	3098	85
H(29A)	166	6048	2315	78
H(30A)	9910	9370	569	141
H(30B)	10005	7776	631	141
H(30C)	9820	8678	1156	141
H(31A)	1154	7975	4835	141
H(31B)	2137	7849	4486	141
H(31C)	1593	6527	4695	141

Table S6. Torsion angles [°] for **2a**.

C(4)-S(1)-C(1)-C(2)	-1.1(3)
C(4)-S(1)-C(1)-C(14)	178.1(3)
C(14)-C(1)-C(2)-C(3)	-177.8(3)
S(1)-C(1)-C(2)-C(3)	1.3(4)
C(14)-C(1)-C(2)-C(5)	-2.2(6)
S(1)-C(1)-C(2)-C(5)	176.9(3)
C(1)-C(2)-C(3)-C(4)	-0.9(4)
C(5)-C(2)-C(3)-C(4)	-176.6(3)
C(1)-C(2)-C(3)-C(16)	175.0(4)
C(5)-C(2)-C(3)-C(16)	-0.7(5)
C(2)-C(3)-C(4)-C(18)	179.3(3)
C(16)-C(3)-C(4)-C(18)	3.4(6)
C(2)-C(3)-C(4)-S(1)	0.0(4)
C(16)-C(3)-C(4)-S(1)	-175.9(3)
C(1)-S(1)-C(4)-C(3)	0.7(3)
C(1)-S(1)-C(4)-C(18)	-178.7(3)
C(1)-C(2)-C(5)-C(9)	105.5(4)
C(3)-C(2)-C(5)-C(9)	-79.2(5)
C(1)-C(2)-C(5)-C(6)	-78.5(5)
C(3)-C(2)-C(5)-C(6)	96.7(4)
C(9)-C(5)-C(6)-F(2B)	-126(2)
C(2)-C(5)-C(6)-F(2B)	58(2)
C(9)-C(5)-C(6)-F(2A)	133.0(6)
C(2)-C(5)-C(6)-F(2A)	-43.5(7)
C(9)-C(5)-C(6)-F(1A)	-109.2(8)
C(2)-C(5)-C(6)-F(1A)	74.3(8)
C(9)-C(5)-C(6)-F(1B)	111(2)
C(2)-C(5)-C(6)-F(1B)	-66(2)
C(9)-C(5)-C(6)-C(7A)	12.6(8)
C(2)-C(5)-C(6)-C(7A)	-163.9(8)
C(9)-C(5)-C(6)-C(7B)	-7.6(11)
C(2)-C(5)-C(6)-C(7B)	175.8(11)
F(4A)-C(7A)-C(6)-F(2A)	-25.9(10)
F(3A)-C(7A)-C(6)-F(2A)	96.1(13)
C(8)-C(7A)-C(6)-F(2A)	-143.2(10)
F(4A)-C(7A)-C(6)-F(1A)	-143.9(10)
F(3A)-C(7A)-C(6)-F(1A)	-21.9(14)
C(8)-C(7A)-C(6)-F(1A)	98.9(13)
F(4A)-C(7A)-C(6)-C(5)	95.2(7)
F(3A)-C(7A)-C(6)-C(5)	-142.8(9)
C(8)-C(7A)-C(6)-C(5)	-22.0(11)
F(4B)-C(7B)-C(6)-F(2B)	15(3)
F(3B)-C(7B)-C(6)-F(2B)	-101(3)
C(8)-C(7B)-C(6)-F(2B)	137(3)

F(4B)-C(7B)-C(6)-F(1B)	126(3)
F(3B)-C(7B)-C(6)-F(1B)	10(3)
C(8)-C(7B)-C(6)-F(1B)	-112(3)
F(4B)-C(7B)-C(6)-C(5)	-112.4(19)
F(3B)-C(7B)-C(6)-C(5)	131(2)
C(8)-C(7B)-C(6)-C(5)	9.0(17)
F(4B)-C(7B)-C(8)-F(5B)	-122(2)
F(3B)-C(7B)-C(8)-F(5B)	-1(3)
C(6)-C(7B)-C(8)-F(5B)	118(2)
F(4B)-C(7B)-C(8)-F(6B)	-9(3)
F(3B)-C(7B)-C(8)-F(6B)	113(3)
C(6)-C(7B)-C(8)-F(6B)	-128(2)
F(4B)-C(7B)-C(8)-C(9)	112(2)
F(3B)-C(7B)-C(8)-C(9)	-127(2)
C(6)-C(7B)-C(8)-C(9)	-7.4(17)
F(4A)-C(7A)-C(8)-F(5A)	145.8(8)
F(3A)-C(7A)-C(8)-F(5A)	24.8(13)
C(6)-C(7A)-C(8)-F(5A)	-96.5(11)
F(4A)-C(7A)-C(8)-F(6A)	28.1(9)
F(3A)-C(7A)-C(8)-F(6A)	-92.8(13)
C(6)-C(7A)-C(8)-F(6A)	145.8(10)
F(4A)-C(7A)-C(8)-C(9)	-94.2(7)
F(3A)-C(7A)-C(8)-C(9)	144.9(9)
C(6)-C(7A)-C(8)-C(9)	23.5(11)
C(2)-C(5)-C(9)-C(11)	-3.4(6)
C(6)-C(5)-C(9)-C(11)	-179.6(3)
C(2)-C(5)-C(9)-C(8)	179.4(3)
C(6)-C(5)-C(9)-C(8)	3.2(4)
F(5A)-C(8)-C(9)-C(5)	102.3(7)
F(5B)-C(8)-C(9)-C(5)	-125.7(17)
F(6A)-C(8)-C(9)-C(5)	-135.5(6)
F(6B)-C(8)-C(9)-C(5)	123.0(17)
C(7B)-C(8)-C(9)-C(5)	3.1(13)
C(7A)-C(8)-C(9)-C(5)	-17.3(8)
F(5A)-C(8)-C(9)-C(11)	-75.2(7)
F(5B)-C(8)-C(9)-C(11)	56.9(17)
F(6A)-C(8)-C(9)-C(11)	47.1(7)
F(6B)-C(8)-C(9)-C(11)	-54.4(17)
C(7B)-C(8)-C(9)-C(11)	-174.3(12)
C(7A)-C(8)-C(9)-C(11)	165.3(8)
C(13)-S(2)-C(10)-C(11)	-2.0(3)
C(13)-S(2)-C(10)-C(15)	176.9(3)
C(15)-C(10)-C(11)-C(12)	-176.4(4)
S(2)-C(10)-C(11)-C(12)	2.3(4)
C(15)-C(10)-C(11)-C(9)	2.6(6)
S(2)-C(10)-C(11)-C(9)	-178.6(3)
C(5)-C(9)-C(11)-C(10)	105.4(4)

C(8)-C(9)-C(11)-C(10)	-77.7(5)
C(5)-C(9)-C(11)-C(12)	-75.7(5)
C(8)-C(9)-C(11)-C(12)	101.2(4)
C(10)-C(11)-C(12)-C(13)	-1.5(4)
C(9)-C(11)-C(12)-C(13)	179.4(3)
C(10)-C(11)-C(12)-C(17)	174.5(3)
C(9)-C(11)-C(12)-C(17)	-4.5(5)
C(11)-C(12)-C(13)-C(24)	-179.1(3)
C(17)-C(12)-C(13)-C(24)	4.9(6)
C(11)-C(12)-C(13)-S(2)	0.0(3)
C(17)-C(12)-C(13)-S(2)	-176.0(3)
C(10)-S(2)-C(13)-C(12)	1.1(3)
C(10)-S(2)-C(13)-C(24)	-179.7(3)
C(3)-C(4)-C(18)-C(23)	-133.6(4)
S(1)-C(4)-C(18)-C(23)	45.6(4)
C(3)-C(4)-C(18)-C(19)	46.7(5)
S(1)-C(4)-C(18)-C(19)	-134.1(3)
C(23)-C(18)-C(19)-C(20)	0.5(5)
C(4)-C(18)-C(19)-C(20)	-179.7(3)
C(18)-C(19)-C(20)-C(21)	-0.3(5)
C(19)-C(20)-C(21)-O(1)	178.7(3)
C(19)-C(20)-C(21)-C(22)	0.0(5)
O(1)-C(21)-C(22)-C(23)	-178.5(3)
C(20)-C(21)-C(22)-C(23)	0.1(5)
C(19)-C(18)-C(23)-C(22)	-0.5(5)
C(4)-C(18)-C(23)-C(22)	179.8(3)
C(21)-C(22)-C(23)-C(18)	0.2(5)
C(12)-C(13)-C(24)-C(25)	36.8(5)
S(2)-C(13)-C(24)-C(25)	-142.2(3)
C(12)-C(13)-C(24)-C(29)	-145.2(4)
S(2)-C(13)-C(24)-C(29)	35.7(4)
C(29)-C(24)-C(25)-C(26)	0.6(5)
C(13)-C(24)-C(25)-C(26)	178.6(3)
C(24)-C(25)-C(26)-C(27)	-0.9(6)
C(25)-C(26)-C(27)-O(2)	179.2(3)
C(25)-C(26)-C(27)-C(28)	0.7(6)
O(2)-C(27)-C(28)-C(29)	-178.8(3)
C(26)-C(27)-C(28)-C(29)	-0.2(6)
C(27)-C(28)-C(29)-C(24)	-0.2(6)
C(25)-C(24)-C(29)-C(28)	0.0(6)
C(13)-C(24)-C(29)-C(28)	-178.1(4)
C(20)-C(21)-O(1)-C(30)	169.6(3)
C(22)-C(21)-O(1)-C(30)	-11.7(5)
C(28)-C(27)-O(2)-C(31)	-178.3(4)
C(26)-C(27)-O(2)-C(31)	3.1(5)

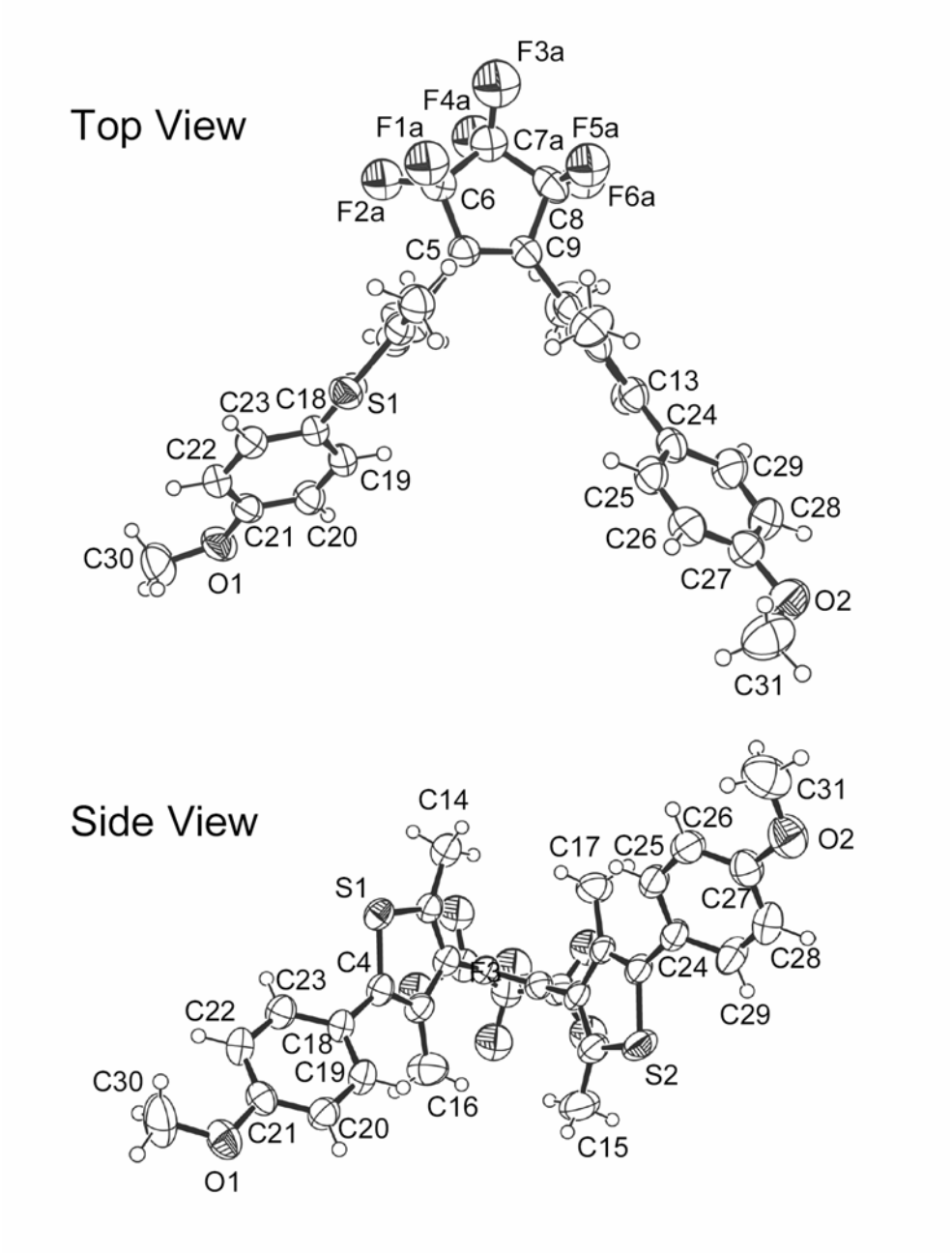

Figure S1. ORTEP drawings of **2a**, showing 50% probability displacement ellipsoids. The fluorinated cyclopentene ring was disordered (74:26). Only the major structure is illustrated for clarity.

Table S7. Crystal data and structure refinement for **3a**.

Identification code	compd3a	
Empirical formula	$C_{33}H_{30}F_6S_2$	
Formula weight	604.69	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	*a* = 23.546(4) Å	α = 90°
	b = 8.3164(15) Å	β = 127.235(3)°
	c = 19.233(4) Å	γ = 90°
Volume	2998.4(9) $Å^3$	
Z	4	
Density (calculated)	1.340 g/cm^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	1256	
Crystal size	0.5 x 0.4 x 0.4 mm^3	
Theta range for data collection	2.17 to 23.25°.	
Index ranges	-26 <= *h* <= 26, -9 <= *k* <= 9, -19 <= *l* <= 21	
Reflections collected	6489	
Independent reflections	2151 [*R*(int) = 0.0763]	
Completeness to theta = 23.25°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2151 / 3 / 214	
Goodness-of-fit on F^2	0.999	
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0440, *wR*2 = 0.1061	
R indices (all data)	*R*1 = 0.0621, *wR*2 = 0.1152	
Largest diff. peak and hole	0.300 and -0.254 e $Å^{-3}$	

Table S8. Atomic coordinates (x 10^{-4}) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	754(1)	9460(1)	1657(1)	52(1)
F(1A)	1014(3)	3641(8)	2535(4)	73(2)
F(2A)	-63(3)	3614(8)	1364(4)	71(1)
C(6A)	305(4)	3922(8)	2186(5)	42(2)
F(1B)	340(4)	3757(8)	1582(5)	100(3)
F(2B)	1092(4)	3487(8)	2990(5)	94(2)
C(6B)	456(4)	3962(9)	2375(5)	48(3)
F(3)	160(7)	1494(4)	2712(8)	110(5)
F(4)	674(2)	2592(6)	3485(3)	94(1)
C(1)	212(1)	7928(3)	1542(2)	43(1)
C(2)	557(1)	7036(3)	2288(1)	41(1)
C(3)	1272(1)	7559(3)	2957(2)	46(1)
C(4)	1444(1)	8892(3)	2703(2)	48(1)
C(5)	230(1)	5634(3)	2402(1)	40(1)
C(7)	117(3)	2883(5)	2664(4)	50(1)
C(8)	-510(1)	7695(3)	693(2)	51(1)
C(9)	-456(2)	7174(4)	-30(2)	80(1)
C(10)	-973(2)	9190(4)	413(2)	81(1)
C(11)	1788(1)	6707(3)	3807(2)	64(1)
C(12)	2116(1)	9839(3)	3200(2)	54(1)
C(13)	2365(2)	10539(4)	3986(2)	73(1)
C(14)	2987(2)	11423(4)	4450(2)	86(1)
C(15)	3368(2)	11620(4)	4134(2)	83(1)
C(16)	3131(2)	10932(4)	3357(2)	85(1)
C(17)	2508(2)	10047(4)	2889(2)	71(1)

Table S9. Bond lengths [Å] and angles [°] for **3a**.

S(1)-C(4)	1.718(2)
S(1)-C(1)	1.720(2)
F(1A)-C(6A)	1.392(8)
F(2A)-C(6A)	1.287(9)
C(6A)-C(7)#1	1.470(9)
C(6A)-C(5)	1.524(7)
C(6A)-C(7)	1.511(9)
F(1B)-C(6B)	1.388(9)
F(2B)-C(6B)	1.286(10)
C(6B)-C(7)#1	1.582(10)
C(6B)-C(5)	1.502(8)
C(6B)-C(7)	1.513(10)
F(3)-C(7)	1.159(5)
F(3)-C(7)#1	1.309(8)
F(4)-C(7)	1.329(6)
F(4)-C(7)#1	1.852(7)
C(1)-C(2)	1.363(3)
C(1)-C(8)	1.494(3)
C(2)-C(3)	1.435(3)
C(2)-C(5)	1.485(3)
C(3)-C(4)	1.368(3)
C(3)-C(11)	1.498(3)
C(4)-C(12)	1.486(3)
C(5)-C(5)#1	1.344(4)
C(7)-F(3)#1	1.309(8)
C(7)-C(6A)#1	1.470(9)
C(7)-C(6B)#1	1.582(10)
C(7)-F(4)#1	1.852(7)
C(8)-C(10)	1.520(4)
C(8)-C(9)	1.534(4)
C(12)-C(13)	1.378(4)
C(12)-C(17)	1.380(4)
C(13)-C(14)	1.380(4)
C(14)-C(15)	1.362(4)
C(15)-C(16)	1.365(5)
C(16)-C(17)	1.381(4)

C(4)-S(1)-C(1)	92.85(11)
F(2A)-C(6A)-C(7)#1	95.2(6)
F(2A)-C(6A)-F(1A)	106.2(6)
C(7)#1-C(6A)-F(1A)	124.2(6)
F(2A)-C(6A)-C(5)	114.7(6)
C(7)#1-C(6A)-C(5)	107.0(5)
F(1A)-C(6A)-C(5)	109.2(5)

F(2A)-C(6A)-C(7)	114.0(6)
F(1A)-C(6A)-C(7)	108.6(6)
C(5)-C(6A)-C(7)	104.1(5)
F(2B)-C(6B)-F(1B)	108.5(7)
F(2B)-C(6B)-C(7)#1	110.8(6)
F(1B)-C(6B)-C(7)#1	106.4(6)
F(2B)-C(6B)-C(5)	119.5(6)
F(1B)-C(6B)-C(5)	108.3(6)
C(7)#1-C(6B)-C(5)	102.5(5)
F(2B)-C(6B)-C(7)	93.5(6)
F(1B)-C(6B)-C(7)	122.3(6)
C(5)-C(6B)-C(7)	105.0(5)
C(2)-C(1)-C(8)	129.7(2)
C(2)-C(1)-S(1)	110.11(17)
C(8)-C(1)-S(1)	120.08(17)
C(1)-C(2)-C(3)	114.1(2)
C(1)-C(2)-C(5)	123.4(2)
C(3)-C(2)-C(5)	122.53(19)
C(4)-C(3)-C(2)	111.4(2)
C(4)-C(3)-C(11)	123.6(2)
C(2)-C(3)-C(11)	124.9(2)
C(3)-C(4)-C(12)	129.0(2)
C(3)-C(4)-S(1)	111.53(17)
C(12)-C(4)-S(1)	119.49(18)
C(5)#1-C(5)-C(2)	128.26(12)
C(5)#1-C(5)-C(6B)	111.9(3)
C(2)-C(5)-C(6B)	119.7(3)
C(5)#1-C(5)-C(6A)	108.8(3)
C(2)-C(5)-C(6A)	122.5(3)
F(3)-C(7)-C(6A)#1	127.4(11)
F(3)#1-C(7)-C(6A)#1	117.3(9)
F(3)#1-C(7)-F(4)	107.4(5)
C(6A)#1-C(7)-F(4)	100.0(5)
F(3)-C(7)-C(6B)#1	126.9(10)
F(3)#1-C(7)-C(6B)#1	110.5(8)
F(4)-C(7)-C(6B)#1	111.2(5)
F(3)-C(7)-C(6A)	125.0(10)
F(3)#1-C(7)-C(6A)	113.5(9)
C(6A)#1-C(7)-C(6A)	105.4(6)
F(4)-C(7)-C(6A)	112.6(5)
C(6B)#1-C(7)-C(6A)	101.7(3)
F(3)-C(7)-C(6B)	125.4(11)
F(3)#1-C(7)-C(6B)	121.1(10)
C(6A)#1-C(7)-C(6B)	107.1(3)
F(4)-C(7)-C(6B)	100.5(5)
C(6B)#1-C(7)-C(6B)	105.7(6)
F(3)-C(7)-F(4)#1	86.6(6)

C(6A)#1-C(7)-F(4)#1	90.0(4)
C(6B)#1-C(7)-F(4)#1	78.7(4)
C(6A)-C(7)-F(4)#1	78.6(4)
C(6B)-C(7)-F(4)#1	90.7(4)
C(1)-C(8)-C(10)	112.3(2)
C(1)-C(8)-C(9)	111.3(2)
C(10)-C(8)-C(9)	110.2(2)
C(13)-C(12)-C(17)	118.1(2)
C(13)-C(12)-C(4)	120.6(2)
C(17)-C(12)-C(4)	121.3(2)
C(12)-C(13)-C(14)	121.0(3)
C(15)-C(14)-C(13)	120.2(3)
C(14)-C(15)-C(16)	119.7(3)
C(15)-C(16)-C(17)	120.5(3)
C(12)-C(17)-C(16)	120.6(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Table S10. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	56(1)	45(1)	59(1)	8(1)	37(1)	-1(1)
F(1A)	71(3)	52(2)	117(5)	6(3)	69(4)	14(2)
F(2A)	108(4)	60(3)	66(3)	-9(2)	64(3)	-2(3)
F(1B)	199(8)	55(3)	139(7)	-11(3)	150(7)	-1(5)
F(2B)	64(3)	62(3)	138(6)	6(4)	52(4)	22(2)
F(3)	178(13)	41(2)	200(14)	56(5)	161(11)	49(5)
F(4)	96(3)	87(3)	87(3)	38(2)	48(2)	22(2)
C(1)	48(1)	39(1)	51(1)	2(1)	34(1)	3(1)
C(2)	46(1)	38(1)	48(1)	1(1)	33(1)	1(1)
C(3)	44(1)	51(2)	49(1)	1(1)	32(1)	0(1)
C(4)	49(1)	48(1)	57(2)	-2(1)	37(1)	-5(1)
C(5)	44(1)	38(1)	40(1)	1(1)	27(1)	-1(1)
C(8)	51(1)	49(2)	51(2)	4(1)	30(1)	-1(1)
C(9)	88(2)	84(2)	62(2)	-11(2)	42(2)	0(2)
C(10)	56(2)	73(2)	83(2)	3(2)	27(2)	14(2)
C(11)	55(2)	72(2)	59(2)	10(1)	31(1)	-1(1)
C(12)	51(1)	50(2)	65(2)	6(1)	38(1)	-3(1)
C(13)	69(2)	85(2)	79(2)	-23(2)	52(2)	-27(2)
C(14)	75(2)	94(3)	83(2)	-24(2)	45(2)	-32(2)
C(15)	66(2)	75(2)	101(3)	-7(2)	47(2)	-23(2)
C(16)	81(2)	87(2)	115(3)	0(2)	75(2)	-21(2)
C(17)	75(2)	74(2)	81(2)	-7(2)	57(2)	-22(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3a**.

	x	y	z	U(eq)
H(8)	-747	6828	773	61
H(9A)	-236	8015	-133	121
H(9B)	-925	6965	-556	121
H(9C)	-172	6215	148	121
H(10A)	-1022	9475	857	121
H(10B)	-1435	8977	-124	121
H(10C)	-753	10061	328	121
H(11A)	1934	5717	3702	96
H(11B)	1562	6482	4077	96
H(11C)	2198	7376	4186	96
H(13)	2108	10415	4207	88
H(14)	3148	11886	4981	103
H(15)	3786	12219	4447	100
H(16)	3391	11062	3142	102
H(17)	2351	9586	2360	85

Table S12. Torsion angles [°] for **3a**.

C(4)-S(1)-C(1)-C(2)	0.38(18)
C(4)-S(1)-C(1)-C(8)	-176.92(19)
C(8)-C(1)-C(2)-C(3)	175.6(2)
S(1)-C(1)-C(2)-C(3)	-1.4(3)
C(8)-C(1)-C(2)-C(5)	-3.8(4)
S(1)-C(1)-C(2)-C(5)	179.21(17)
C(1)-C(2)-C(3)-C(4)	1.9(3)
C(5)-C(2)-C(3)-C(4)	-178.6(2)
C(1)-C(2)-C(3)-C(11)	-174.4(2)
C(5)-C(2)-C(3)-C(11)	5.0(4)
C(2)-C(3)-C(4)-C(12)	178.4(2)
C(11)-C(3)-C(4)-C(12)	-5.3(4)
C(2)-C(3)-C(4)-S(1)	-1.6(3)
C(11)-C(3)-C(4)-S(1)	174.8(2)
C(1)-S(1)-C(4)-C(3)	0.71(19)
C(1)-S(1)-C(4)-C(12)	-179.2(2)
C(1)-C(2)-C(5)-C(5)#1	-80.0(4)
C(3)-C(2)-C(5)-C(5)#1	100.6(3)
C(1)-C(2)-C(5)-C(6B)	105.4(4)
C(3)-C(2)-C(5)-C(6B)	-73.9(4)
C(1)-C(2)-C(5)-C(6A)	91.6(4)
C(3)-C(2)-C(5)-C(6A)	-87.8(4)
F(2B)-C(6B)-C(5)-C(5)#1	-107.7(7)
F(1B)-C(6B)-C(5)-C(5)#1	127.4(6)
C(7)#1-C(6B)-C(5)-C(5)#1	15.2(6)
C(7)-C(6B)-C(5)-C(5)#1	-4.8(6)
F(2B)-C(6B)-C(5)-C(2)	67.7(7)
F(1B)-C(6B)-C(5)-C(2)	-57.2(7)
C(7)#1-C(6B)-C(5)-C(2)	-169.4(3)
C(7)-C(6B)-C(5)-C(2)	170.6(3)
F(2B)-C(6B)-C(5)-C(6A)	174(3)
F(1B)-C(6B)-C(5)-C(6A)	50(2)
C(7)#1-C(6B)-C(5)-C(6A)	-63(2)
C(7)-C(6B)-C(5)-C(6A)	-83(2)
F(2A)-C(6A)-C(5)-C(5)#1	100.2(5)
C(7)#1-C(6A)-C(5)-C(5)#1	-4.0(6)
F(1A)-C(6A)-C(5)-C(5)#1	-140.8(5)
C(7)-C(6A)-C(5)-C(5)#1	-25.0(6)
F(2A)-C(6A)-C(5)-C(2)	-72.9(6)
C(7)#1-C(6A)-C(5)-C(2)	-177.1(3)
F(1A)-C(6A)-C(5)-C(2)	46.1(7)
C(7)-C(6A)-C(5)-C(2)	161.9(3)
F(2A)-C(6A)-C(5)-C(6B)	-153(3)
C(7)#1-C(6A)-C(5)-C(6B)	103(3)

F(1A)-C(6A)-C(5)-C(6B)	-34(2)
C(7)-C(6A)-C(5)-C(6B)	82(2)
F(2A)-C(6A)-C(7)-F(3)	60.1(10)
F(1A)-C(6A)-C(7)-F(3)	-58.0(10)
C(5)-C(6A)-C(7)-F(3)	-174.3(8)
F(2A)-C(6A)-C(7)-F(3)#1	25.4(9)
F(1A)-C(6A)-C(7)-F(3)#1	-92.7(9)
C(5)-C(6A)-C(7)-F(3)#1	151.0(7)
F(2A)-C(6A)-C(7)-C(6A)#1	-104.3(7)
F(1A)-C(6A)-C(7)-C(6A)#1	137.6(7)
C(5)-C(6A)-C(7)-C(6A)#1	21.4(4)
F(2A)-C(6A)-C(7)-F(4)	147.7(6)
F(1A)-C(6A)-C(7)-F(4)	29.6(8)
C(5)-C(6A)-C(7)-F(4)	-86.7(6)
F(2A)-C(6A)-C(7)-C(6B)#1	-93.3(6)
F(1A)-C(6A)-C(7)-C(6B)#1	148.6(6)
C(5)-C(6A)-C(7)-C(6B)#1	32.4(6)
F(2A)-C(6A)-C(7)-C(6B)	156(3)
F(1A)-C(6A)-C(7)-C(6B)	38(2)
C(5)-C(6A)-C(7)-C(6B)	-78(2)
F(2A)-C(6A)-C(7)-F(4)#1	-17.5(6)
F(1A)-C(6A)-C(7)-F(4)#1	-135.6(6)
C(5)-C(6A)-C(7)-F(4)#1	108.2(4)
F(2B)-C(6B)-C(7)-F(3)	-59.7(10)
F(1B)-C(6B)-C(7)-F(3)	54.9(12)
C(5)-C(6B)-C(7)-F(3)	178.5(8)
F(2B)-C(6B)-C(7)-F(3)#1	-98.0(8)
F(1B)-C(6B)-C(7)-F(3)#1	16.5(12)
C(5)-C(6B)-C(7)-F(3)#1	140.2(7)
F(2B)-C(6B)-C(7)-C(6A)#1	123.8(6)
F(1B)-C(6B)-C(7)-C(6A)#1	-121.6(8)
C(5)-C(6B)-C(7)-C(6A)#1	2.0(7)
F(2B)-C(6B)-C(7)-F(4)	19.8(6)
F(1B)-C(6B)-C(7)-F(4)	134.3(7)
C(5)-C(6B)-C(7)-F(4)	-102.0(5)
F(2B)-C(6B)-C(7)-C(6B)#1	135.5(6)
F(1B)-C(6B)-C(7)-C(6B)#1	-109.9(9)
C(5)-C(6B)-C(7)-C(6B)#1	13.8(4)
F(2B)-C(6B)-C(7)-C(6A)	-152(3)
F(1B)-C(6B)-C(7)-C(6A)	-38(2)
C(5)-C(6B)-C(7)-C(6A)	86(2)
F(2B)-C(6B)-C(7)-F(4)#1	-146.0(5)
F(1B)-C(6B)-C(7)-F(4)#1	-31.4(8)
C(5)-C(6B)-C(7)-F(4)#1	92.2(5)
C(2)-C(1)-C(8)-C(10)	126.1(3)
S(1)-C(1)-C(8)-C(10)	-57.2(3)
C(2)-C(1)-C(8)-C(9)	-109.9(3)

S(1)-C(1)-C(8)-C(9)	66.8(3)
C(3)-C(4)-C(12)-C(13)	-58.5(4)
S(1)-C(4)-C(12)-C(13)	121.4(3)
C(3)-C(4)-C(12)-C(17)	121.7(3)
S(1)-C(4)-C(12)-C(17)	-58.4(3)
C(17)-C(12)-C(13)-C(14)	0.0(4)
C(4)-C(12)-C(13)-C(14)	-179.8(3)
C(12)-C(13)-C(14)-C(15)	0.1(5)
C(13)-C(14)-C(15)-C(16)	-0.2(5)
C(14)-C(15)-C(16)-C(17)	0.2(5)
C(13)-C(12)-C(17)-C(16)	0.0(5)
C(4)-C(12)-C(17)-C(16)	179.8(3)
C(15)-C(16)-C(17)-C(12)	-0.1(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

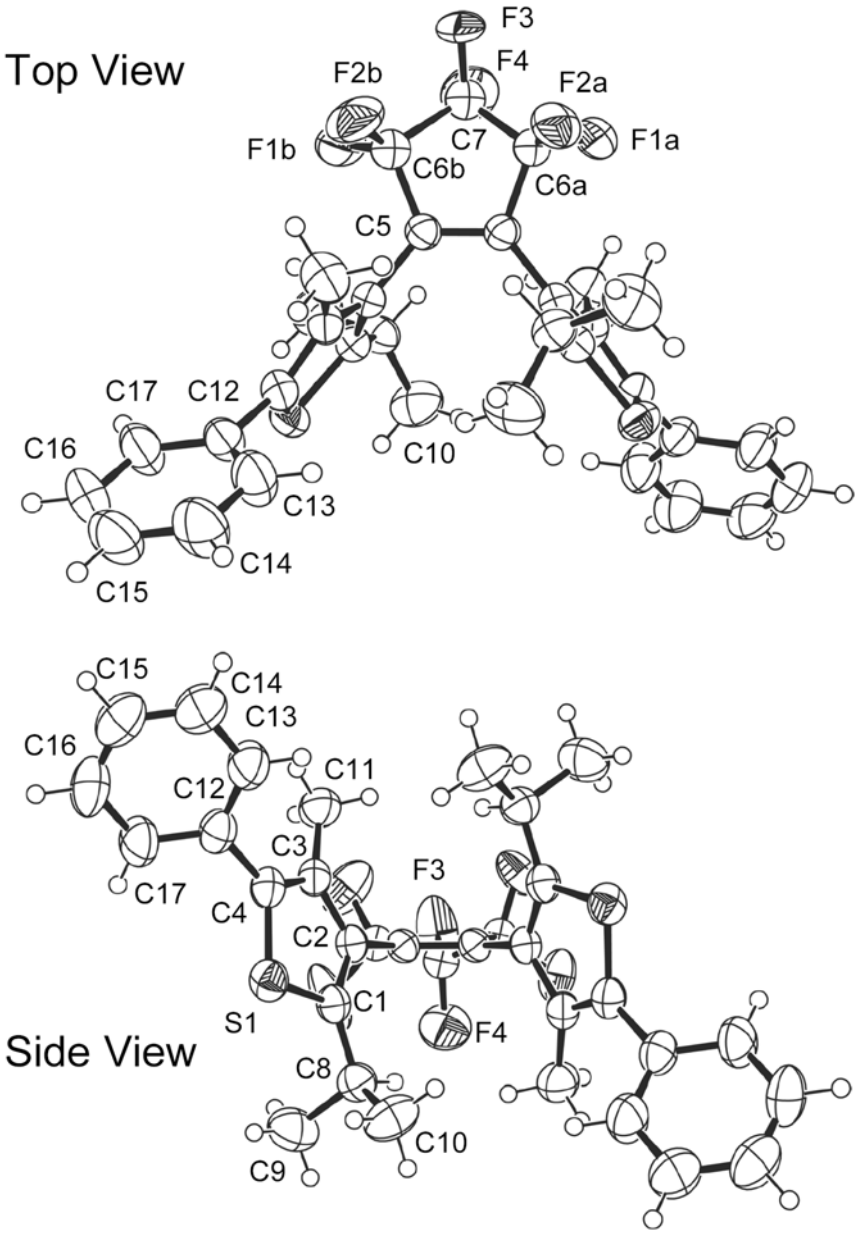

Figure S2. ORTEP drawings of **3a** showing 50% probability displacement ellipsoids. Only a half of the molecule is independent. The fluorinated cyclopentene ring was disordered. Only the major structure is illustrated for clarity.

Table S13. Crystal data and structure refinement for **4a**.

Identification code	compd4a	
Empirical formula	$C_{35}H_{34}F_6O_2S_2$	
Formula weight	664.74	
Temperature	304(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	*a* = 13.5668(11) Å	α = 90°
	b = 14.7276(12) Å	β = 111.9480(10)°
	c = 18.0976(14) Å	γ = 90°
Volume	3353.9(5) Å^3	
Z	4	
Density (calculated)	1.316 g/cm^3	
Absorption coefficient	0.222 mm^{-1}	
F(000)	1384	
Crystal size	0.45 x 0.4 x 0.3 mm^3	
Theta range for data collection	2.13 to 28.00°.	
Index ranges	-17 <= *h* <= 17, -19 <= *k* <= 19, -23 <= *l* <= 23	
Reflections collected	29012	
Independent reflections	3887 [*R*(int) = 0.0334]	
Completeness to theta = 28.00°	95.8 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3887 / 8 / 248	
Goodness-of-fit on F^2	1.056	
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0447, *wR*2 = 0.1220	
R indices (all data)	*R*1 = 0.0691, *wR*2 = 0.1345	
Largest diff. peak and hole	0.303 and -0.188 e Å^{-3}	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2727(1)	498(1)	7062(1)	64(1)
C(6A)	4066(4)	-2692(4)	7214(2)	61(3)
F(1A)	3255(3)	-2854(2)	6525(3)	91(1)
F(2A)	3700(3)	-2880(3)	7789(2)	98(1)
C(6B)	4058(4)	-2680(5)	7116(3)	74(3)
F(1B)	3841(4)	-2977(2)	6372(2)	121(2)
F(2B)	3193(3)	-2788(3)	7297(4)	136(2)
F(3)	5136(3)	-3332(2)	6589(2)	101(1)
F(4)	4980(20)	-4094(1)	7564(10)	108(1)
O(1)	-176(1)	2081(1)	3526(1)	105(1)
C(1)	3608(1)	-336(1)	7560(1)	52(1)
C(2)	3747(1)	-938(1)	7030(1)	45(1)
C(3)	3128(1)	-726(1)	6207(1)	47(1)
C(4)	2541(1)	47(1)	6137(1)	52(1)
C(5)	4473(1)	-1722(1)	7292(1)	46(1)
C(7)	5039(5)	-3255(2)	7297(2)	70(1)
C(8)	4050(2)	-345(1)	8455(1)	62(1)
C(9)	3216(2)	-661(2)	8776(1)	103(1)
C(10)	4508(2)	564(2)	8802(1)	101(1)
C(11)	3162(2)	-1250(1)	5503(1)	63(1)
C(12)	1829(1)	544(1)	5427(1)	56(1)
C(13)	1111(1)	115(1)	4771(1)	62(1)
C(14)	422(2)	604(2)	4123(1)	68(1)
C(15)	459(2)	1533(2)	4138(1)	73(1)
C(16)	1171(2)	1970(2)	4777(2)	98(1)
C(17)	1842(2)	1489(2)	5416(1)	85(1)
C(18)	-1035(2)	1697(2)	2920(2)	104(1)

Table S15. Bond lengths [Å] and angles [°] for **4a**.

S(1)-C(1)	1.7157(16)
S(1)-C(4)	1.7294(17)
C(6A)-F(2A)	1.3399(10)
C(6A)-F(1A)	1.3404(10)
C(6A)-C(7)	1.517(7)
C(6A)-C(5)	1.518(5)
C(6B)-F(2B)	1.3403(10)
C(6B)-F(1B)	1.3406(10)
C(6B)-C(5)	1.509(7)
C(6B)-C(7)#1	1.540(8)
F(3)-C(7)	1.3408(10)
F(4)-C(7)	1.3403(10)
O(1)-C(15)	1.382(2)
O(1)-C(18)	1.387(3)
C(1)-C(2)	1.371(2)
C(1)-C(8)	1.502(2)
C(2)-C(3)	1.444(2)
C(2)-C(5)	1.476(2)
C(3)-C(4)	1.367(2)
C(3)-C(11)	1.505(2)
C(4)-C(12)	1.480(2)
C(5)-C(5)#1	1.344(3)
C(7)-C(6A)#1	1.464(9)
C(7)-C(6B)#1	1.540(8)
C(8)-C(10)	1.511(3)
C(8)-C(9)	1.526(3)
C(12)-C(13)	1.376(2)
C(12)-C(17)	1.392(3)
C(13)-C(14)	1.395(3)
C(14)-C(15)	1.368(3)
C(15)-C(16)	1.360(3)
C(16)-C(17)	1.372(3)

C(1)-S(1)-C(4)	93.17(8)
F(2A)-C(6A)-F(1A)	105.7(4)
F(2A)-C(6A)-C(7)	111.8(4)
F(1A)-C(6A)-C(7)	112.1(4)
F(2A)-C(6A)-C(5)	110.5(3)
F(1A)-C(6A)-C(5)	113.4(4)
C(7)-C(6A)-C(5)	103.5(3)
F(2B)-C(6B)-F(1B)	108.9(5)
F(2B)-C(6B)-C(5)	110.6(4)
F(1B)-C(6B)-C(5)	116.1(5)
F(2B)-C(6B)-C(7)#1	108.1(5)
F(1B)-C(6B)-C(7)#1	109.4(5)
C(5)-C(6B)-C(7)#1	103.3(3)
C(15)-O(1)-C(18)	118.9(2)
C(2)-C(1)-C(8)	130.16(15)

C(2)-C(1)-S(1)	110.25(12)
C(8)-C(1)-S(1)	119.50(12)
C(1)-C(2)-C(3)	113.70(14)
C(1)-C(2)-C(5)	122.10(15)
C(3)-C(2)-C(5)	124.20(13)
C(4)-C(3)-C(2)	111.77(14)
C(4)-C(3)-C(11)	123.28(15)
C(2)-C(3)-C(11)	124.86(15)
C(3)-C(4)-C(12)	131.38(16)
C(3)-C(4)-S(1)	111.10(12)
C(12)-C(4)-S(1)	117.50(12)
C(5)#1-C(5)-C(2)	128.48(8)
C(5)#1-C(5)-C(6B)	110.7(2)
C(2)-C(5)-C(6B)	120.8(3)
C(5)#1-C(5)-C(6A)	109.0(2)
C(2)-C(5)-C(6A)	122.0(2)
F(4)-C(7)-F(3)	107.8(5)
F(4)-C(7)-C(6A)#1	116.9(12)
F(3)-C(7)-C(6A)#1	105.6(4)
F(4)-C(7)-C(6A)	112.0(11)
F(3)-C(7)-C(6A)	110.1(4)
C(6A)#1-C(7)-C(6A)	104.1(3)
F(4)-C(7)-C(6B)#1	113.4(12)
F(3)-C(7)-C(6B)#1	111.5(4)
C(6A)-C(7)-C(6B)#1	101.9(2)
C(1)-C(8)-C(10)	112.14(17)
C(1)-C(8)-C(9)	111.05(16)
C(10)-C(8)-C(9)	111.1(2)
C(13)-C(12)-C(17)	117.04(17)
C(13)-C(12)-C(4)	122.97(17)
C(17)-C(12)-C(4)	119.96(17)
C(12)-C(13)-C(14)	121.61(19)
C(15)-C(14)-C(13)	119.42(19)
C(16)-C(15)-C(14)	120.00(19)
C(16)-C(15)-O(1)	115.8(2)
C(14)-C(15)-O(1)	124.1(2)
C(15)-C(16)-C(17)	120.5(2)
C(16)-C(17)-C(12)	121.4(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, y, -z+3/2

Table S16. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	68(1)	62(1)	56(1)	-7(1)	15(1)	22(1)
C(6A)	73(7)	25(3)	80(4)	-12(3)	23(4)	-21(3)
F(1A)	80(2)	62(2)	112(3)	-23(2)	13(2)	-27(2)
F(2A)	103(3)	80(2)	129(3)	14(2)	65(2)	-28(2)
C(6B)	56(6)	77(6)	83(5)	16(4)	19(4)	2(4)
F(1B)	182(4)	54(2)	82(2)	-22(1)	-3(3)	0(3)
F(2B)	78(3)	68(2)	273(8)	32(4)	77(3)	-14(2)
F(3)	128(2)	77(2)	104(2)	-25(2)	50(2)	10(2)
F(4)	133(2)	38(1)	143(5)	27(4)	39(4)	1(6)
O(1)	101(1)	93(1)	89(1)	24(1)	0(1)	8(1)
C(1)	48(1)	54(1)	50(1)	-4(1)	15(1)	7(1)
C(2)	41(1)	42(1)	52(1)	-3(1)	18(1)	-1(1)
C(3)	45(1)	47(1)	49(1)	-5(1)	17(1)	-4(1)
C(4)	49(1)	52(1)	51(1)	-3(1)	14(1)	2(1)
C(5)	50(1)	37(1)	53(1)	-2(1)	23(1)	-4(1)
C(7)	86(3)	36(2)	91(5)	-4(2)	37(4)	-2(2)
C(8)	62(1)	72(1)	48(1)	-6(1)	15(1)	14(1)
C(9)	101(2)	152(2)	58(1)	0(1)	32(1)	-11(2)
C(10)	125(2)	90(2)	63(1)	-23(1)	7(1)	-9(2)
C(11)	69(1)	63(1)	55(1)	-10(1)	23(1)	5(1)
C(12)	53(1)	58(1)	54(1)	2(1)	16(1)	4(1)
C(13)	59(1)	63(1)	60(1)	1(1)	16(1)	2(1)
C(14)	58(1)	84(1)	55(1)	-2(1)	13(1)	-3(1)
C(15)	69(1)	71(1)	70(1)	16(1)	16(1)	9(1)
C(16)	111(2)	58(1)	93(2)	9(1)	3(2)	7(1)
C(17)	95(2)	59(1)	73(1)	2(1)	-1(1)	4(1)
C(18)	67(1)	140(2)	87(2)	29(2)	8(1)	4(2)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4a**.

	x	y	z	U(eq)
H(8A)	4632	-787	8628	75
H(9A)	2973	-1257	8576	154
H(9B)	2627	-246	8608	154
H(9C)	3523	-678	9348	154
H(10A)	5030	748	8591	151
H(10B)	4836	515	9371	151
H(10C)	3950	1008	8665	151
H(11A)	3029	-845	5060	94
H(11B)	2629	-1715	5362	94
H(11C)	3850	-1522	5638	94
H(13A)	1084	-516	4758	75
H(14A)	-57	302	3685	81
H(16A)	1204	2601	4780	117
H(17A)	2317	1800	5850	102
H(18A)	-1395	2157	2538	157
H(18B)	-1516	1440	3139	157
H(18C)	-787	1230	2662	157

Table S18. Torsion angles [°] for **4a**.

C(4)-S(1)-C(1)-C(2)	-0.11(13)
C(4)-S(1)-C(1)-C(8)	-177.00(15)
C(8)-C(1)-C(2)-C(3)	176.14(17)
S(1)-C(1)-C(2)-C(3)	-0.32(18)
C(8)-C(1)-C(2)-C(5)	-4.2(3)
S(1)-C(1)-C(2)-C(5)	179.31(11)
C(1)-C(2)-C(3)-C(4)	0.7(2)
C(5)-C(2)-C(3)-C(4)	-178.89(14)
C(1)-C(2)-C(3)-C(11)	177.42(16)
C(5)-C(2)-C(3)-C(11)	-2.2(2)
C(2)-C(3)-C(4)-C(12)	177.43(16)
C(11)-C(3)-C(4)-C(12)	0.7(3)
C(2)-C(3)-C(4)-S(1)	-0.80(18)
C(11)-C(3)-C(4)-S(1)	-177.54(13)
C(1)-S(1)-C(4)-C(3)	0.54(14)
C(1)-S(1)-C(4)-C(12)	-177.96(14)
C(1)-C(2)-C(5)-C(5)#1	-60.4(3)
C(3)-C(2)-C(5)-C(5)#1	119.2(2)
C(1)-C(2)-C(5)-C(6B)	118.0(2)
C(3)-C(2)-C(5)-C(6B)	-62.4(3)
C(1)-C(2)-C(5)-C(6A)	110.4(2)
C(3)-C(2)-C(5)-C(6A)	-70.0(2)
F(2B)-C(6B)-C(5)-C(5)#1	131.8(5)
F(1B)-C(6B)-C(5)-C(5)#1	-103.5(5)
C(7)#1-C(6B)-C(5)-C(5)#1	16.3(3)
F(2B)-C(6B)-C(5)-C(2)	-46.9(5)
F(1B)-C(6B)-C(5)-C(2)	77.8(4)
C(7)#1-C(6B)-C(5)-C(2)	-162.40(19)
F(2B)-C(6B)-C(5)-C(6A)	56(3)
F(1B)-C(6B)-C(5)-C(6A)	-180(100)
C(7)#1-C(6B)-C(5)-C(6A)	-60(3)
F(2A)-C(6A)-C(5)-C(5)#1	94.9(4)
F(1A)-C(6A)-C(5)-C(5)#1	-146.5(4)
C(7)-C(6A)-C(5)-C(5)#1	-24.9(3)
F(2A)-C(6A)-C(5)-C(2)	-77.5(4)
F(1A)-C(6A)-C(5)-C(2)	41.0(4)
C(7)-C(6A)-C(5)-C(2)	162.66(19)
F(2A)-C(6A)-C(5)-C(6B)	-159(4)
F(1A)-C(6A)-C(5)-C(6B)	-40(3)
C(7)-C(6A)-C(5)-C(6B)	81(3)
F(2A)-C(6A)-C(7)-F(4)	35.8(10)
F(1A)-C(6A)-C(7)-F(4)	-82.7(9)
C(5)-C(6A)-C(7)-F(4)	154.7(9)
F(2A)-C(6A)-C(7)-F(3)	155.7(3)

F(1A)-C(6A)-C(7)-F(3)	37.2(5)
C(5)-C(6A)-C(7)-F(3)	-85.3(4)
F(2A)-C(6A)-C(7)-C(6A)#1	-91.4(4)
F(1A)-C(6A)-C(7)-C(6A)#1	150.1(3)
C(5)-C(6A)-C(7)-C(6A)#1	27.5(2)
F(2A)-C(6A)-C(7)-C(6B)#1	-85.8(3)
F(1A)-C(6A)-C(7)-C(6B)#1	155.7(4)
C(5)-C(6A)-C(7)-C(6B)#1	33.2(3)
C(2)-C(1)-C(8)-C(10)	132.5(2)
S(1)-C(1)-C(8)-C(10)	-51.3(2)
C(2)-C(1)-C(8)-C(9)	-102.5(2)
S(1)-C(1)-C(8)-C(9)	73.7(2)
C(3)-C(4)-C(12)-C(13)	42.9(3)
S(1)-C(4)-C(12)-C(13)	-138.93(16)
C(3)-C(4)-C(12)-C(17)	-139.2(2)
S(1)-C(4)-C(12)-C(17)	38.9(2)
C(17)-C(12)-C(13)-C(14)	-0.3(3)
C(4)-C(12)-C(13)-C(14)	177.56(17)
C(12)-C(13)-C(14)-C(15)	0.0(3)
C(13)-C(14)-C(15)-C(16)	0.8(3)
C(13)-C(14)-C(15)-O(1)	179.2(2)
C(18)-O(1)-C(15)-C(16)	-169.3(2)
C(18)-O(1)-C(15)-C(14)	12.2(3)
C(14)-C(15)-C(16)-C(17)	-1.3(4)
O(1)-C(15)-C(16)-C(17)	-179.8(2)
C(15)-C(16)-C(17)-C(12)	1.0(4)
C(13)-C(12)-C(17)-C(16)	-0.2(3)
C(4)-C(12)-C(17)-C(16)	-178.1(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, y, -z+3/2

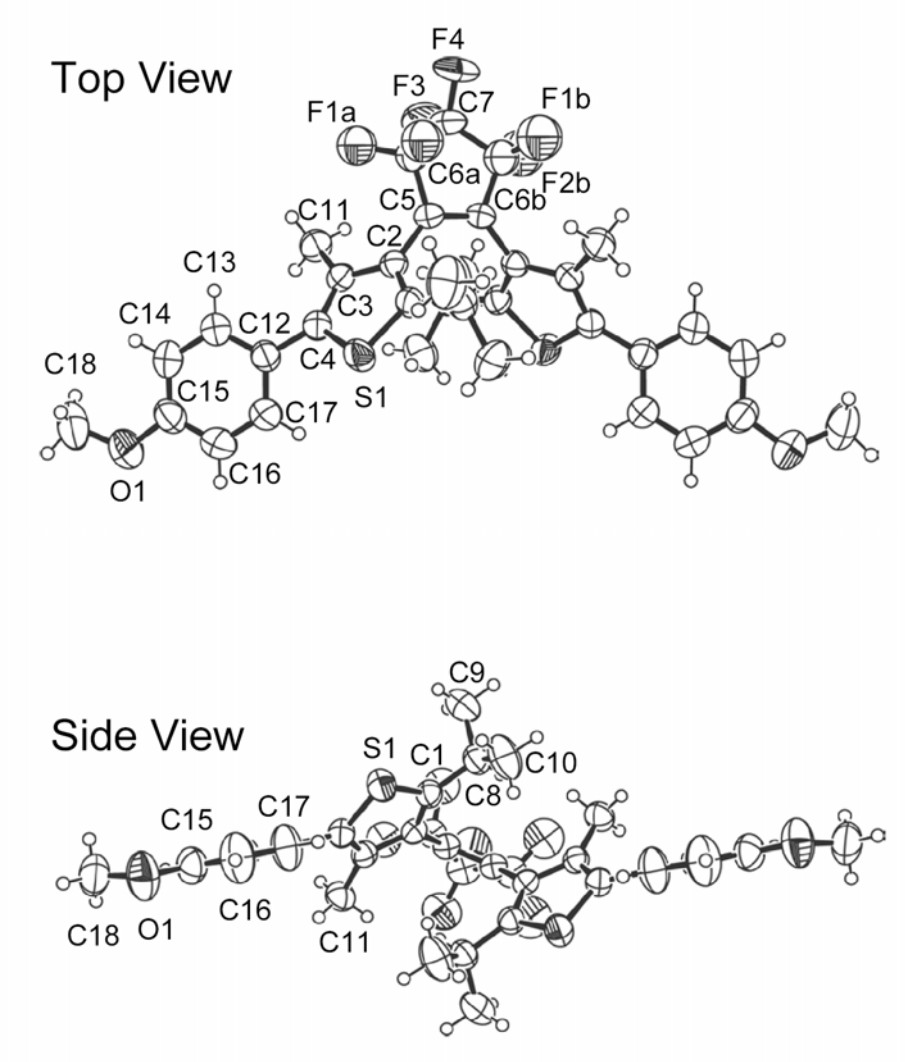

Figure S3. ORTEP drawings of **4a** showing 50% probability displacement ellipsoids. Only a half of the molecule is independent. The fluorinated cyclopentene ring was disordered. Only the major structure is illustrated for clarity.