Supporting Information.

Diels-Alder Reactions of "In-situ" Generated Perfluorinated Thioketones.

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Experimental

NMR spectra were acquired on a Varian 500 MHz VNMRS spectrometer equipped with a 5 mm 13 C- ^{31}P { $^{1}H, ^{19}F$ } probe. ^{1}H spectra were acquired with a 90° flip angle, 3.7 s acquisition time, and 30 s recycle delay. ^{19}F spectra were acquired with a 60 ° flip angle, 0.7 s acquisition time, and 7 s recycle delay. The sample temperature was 298 K. Spectra were typically acquired in chloroform-d. Spectra were acquired in CDCl₃ as lock solvent, using CFCl₃ and TMS as internal standards. High temperature NMR spectra were recorded using CDCl₂CDCl₂ solvent.

GC and GC/MS analyses were carried out on an HP-6890 instrument, using an HP FFAP capillary column and either TCD (GC) or mass- selective (GS/MS) detectors, respectively. Anhydrous DMF (water < 50 ppm), 2,3-dimethylbutadiene-1,3, cyclohexadiene-1,3, cycloheptatriene-1,3,5, anthracene (Aldrich), fluoroolefins **1,2,4** (Chemours Co.), **3,5,6** (SynQuest) were obtained from commercial sources and used without further purification. Same batch of sublimed sulfur (sulfur powder, ~100 mesh, 99.5%, Alfa Aesar) was used in all experiments.

Samples of commercial potassium or caesium fluoride (Aldrich) were grinded, dried under dynamic vacuum at 100-120°C for 5-10 h and were stored and handled inside of nitrogen glove box.

Due to the high ratio of sulfur to fluorine in all compounds, elemental analyses were not attempted for new materials, and the purity of all isolated compounds was established to be at least 99% (GC and NMR spectroscopy) unless specified otherwise (see Table 1).

Preparation of Adducts 1a,b, 2a-f, 3a-b, 4a-c, 5a, 6a,b.

A reaction vessel containing magnetic stir bar was charged with catalytic amount of dry CsF inside of dry box. Dry DMF was added via syringe, followed by addition of sulfur. In case when reaction mixture was kept anhydrous, the addition of sulfur resulted in immediate development of blue colour. The reaction mixture was agitated for 5-15 min at ambient temperature and the corresponding diene (~ 10 mol % excess) was added followed by addition of an olefin and disappearance of blue-brown colour. The reaction vessel was closed and a reaction mixture was agitated at 25-65°C for 1-5 days. The reaction mixture was diluted with 300 ml of water, extracted by hexane (50mlx3), extracts was combined and washed with water (100mlx3) in order to remove residual DMF. Organic phase was dried over MgSO₄, solvent was removed under reduced pressure and the residue was distilled under vacuum or crystallized from hexane.

Reaction of perfluorobutene-2 (6) and CHTr was carried out in three neck round bottomed flask equipped with dry ice-condenser, thermocouple and gas inlet tube. The olefin was condensed in reaction flask containing sulfur, CsF and DMF. The reaction mixture was agitated at ambient temperature for two days. At this point CHPTr was added to reaction mixture and the reaction was continued for another three

days at 25°C. The reaction mixture was diluted with 300 ml of water, extracted by hexane (50mlx3), extract was combined and washed with water (100mlx3) in order to remove residual DMF. Organic phase was dried over MgSO₄, solvent was removed under reduced pressure and product **6a,b** was isolated by column chromatography (silicagel, eluent – hexane).

Reactions of **6** and CHD was carried out in heavy wall glass tube equipped with Teflon^R stopcock, and magnetic stir bar. Dry CsF (0.5 g, 0.03 mol) was loaded inside of dry box and 25 ml of DMF was injected into reaction vessel under nitrogen blanket, followed by addition of 1.0 g (0.03 mol) of sulfur. The colour of the reaction mixture immediately changed to blue. The reaction mixture was agitated for 5 min and 3.1 g (0.038 mol) of CHD was added. Reaction vessel was closed, cooled down to ~ -50°C and F-butene-2 (**6**, 5.8 g , 0.029 mol, precondenced in graduated cold trap) was added to cold reaction mixture as a liquid. The reaction vessel was closed and reaction mixture was agitated at ambient temperature till all sulfur dissolved (3-5 days). The reaction mixture was diluted with 300 ml of water, extracted by hexane (50mlx3), extracts was combined and washed with water (100mlx3) in order to remove residual DMF. Organic phase was dried over MgSO₄, solvent was removed under reduced pressure and the residue was distilled under vacuum.

Reactions involving 2,3-dichlorohexafluorobutene-2 (4) with CDH or ATHR were carried out using excess of dry KF.

Reaction conditions, ratio of reagents, yields, boiling (melting) points of products and NMR data are summarized in Table 1 and Table 2, respectively.

Variable Temperature NMR Spectroscopy

Variable temperature NMR spectra of **2f** were acquired on a Varian 400 MHz VNMRS spectrometer equipped with a 5 mm ¹H, ¹⁹F {¹³C-³¹P} probe. Spectra were acquired in toluene-d₈. The probe temperature was calibrated against standards of methanol (< 303 K) and ethylene glycol (> 303 K). Magnetization transfer experiments were performed at 194.5, 204.6, 214.6, and 224.6 K by selective inversion of each of the nonequivalent ¹⁹F nuclei of the CF₂ adjacent to the bridgehead carbon. Selective inversion was effected by an iburp-2 pulse created by the Pandora's Box utility in Vnmrj 3.2. The integrated intensity of each ¹⁹F nucleus of that CF₂ was plotted against the interval of time between the selective inversion pulse and a hard $\pi/2$ pulse, and the rates of interconversion between rotamers were determined by simple least-squares minimization of a first-order numerical integration over ca. 3,600 time increments.

Spectra were acquired at elevated temperatures as well: 313.2, 322.8, 332.4, 342.0, 351.6, and 361.2 K. The linewidths of the same CF_2 nuclei were measured by a simple FWHM determination. As the multiplets were not simple singlets, but a large doublet (${}^{2}J_{FF}$) of quartets (${}^{4}J_{FF}$), the degree of broadening was determined indirectly. The extent of broadening was much less than the ${}^{2}J_{FF}$, so a simulation of the 12.9 Hz quartet was performed by superposition of four Lorentzians of the appropriate 1:3:3:1 intensity ratio with their center frequencies separated by that same 12.9 Hz. The linewidth parameter of that

superposition of Lorentzians was then varied until the best match to the experimentally determined FWHM was obtained, and that value was taken as the extent of exchange broadening.

Results: NMR Experiments:



Figure SI1. ¹⁹F NMR spectra of **2f** in toluene- d_8 from 303 to 363 K. Expansion around CF_2 moiety nearest bridgehead.



Figure SI2. ¹⁹*F NMR spectra of* **2***f in toluene-d*⁸ *at 204.8K, with selective inversion of doublet at -104 ppm. Interpulse delay for magnetization transfer between selective inversion pulse and hard excitation pulse is arrayed.*



Figure SI3. Plot of integrated signal intensity v. magnetization transfer time at 204.8 K for **2f**. Fitted lines determined as described in Experimental section above.



Figure SI4. Arrhenius plot for interconversion of rotamers of **2f**. Data fitted by linear least-squares regression.



Fig. SI5a. Proposed structure of major rotamer of 2f.



Fig. SI5b. Proposed structure of major rotamer of 2f.







Fig. SI6. Variable temperature ¹⁹F NMR of compound **2f** in CDCl₂CDCl₂ and ¹H NMR of compound **2f** in CDCl₃ (ambient temperature, sample contained anthracene impurity)











ratio 55:45

Fig. SI8.Variable temperature ¹⁹F NMR of compound **4a,b** in CDCl₂CDCl₂

C1158-11 in TCE-d2



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Journal Name



Fig. SI9. Variable temperature ¹⁹F NMR of compound **5a** (in $CDCl_2CDCl_2$) and ¹H and ¹⁹F NMR spectra at ambient temperature ($CDCl_3$) of compound **5a**.



Sample: c1097-159SILICA_PLUG Operator: kn21710			[* 1 e9]
Cost Code: VT91551033 Notebook Number: C1097-159 SILICAPLUG Instrument: rmmr6-vnmrs500 Spectrometer 1H frequency: 499.8 MHz			-
Probe: 5mmCPHF Solvent: cdcl3 Sample temperature: 25 C Date Submitted: 01/05/2018 15:18:04			- 05
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			- 100
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[] 38 []	100 100 11 100 11 100 11 100 11 100 100		
- 50		- 150	- 200 [ppm]



Fig. SI10. ¹⁹F and ¹H NMR of compound **3b** in CDCl₃ (purity 96%)



Table 1. Reaction Conditions, Yields and Boiling (melting) Points of New Materials.

Ent	Reagents,	DMF (ml)	Temp. (°C),	Product(s)	B.p. °C/mm Hg	Isolated
ry	(mmol) ratio		time (h)		(m.p., °C)	yield (%);
No						
1	1 (100),	35	20-28ª (24)	1a + 1b (ratio 80:20)	87-89/10	75
	DMBD(109),					
	Sx (100),					
	CsF(10)					
2	2 (10),	12	22 (96)	2a, 2b	95-108/10	41
	DMBD(11),			Ratio 65:35		
	Sx (10),					
	CsF(3)				-	
3	1 (100),	35	22(72)	2c+2d+2e,	76-77/1;	54
	CHD(11),			Ratio 78:12:10	93-97/10	
	Sx (10),					
	CSF(11)					
	1/10) ATUD	12		26	(120 F 120)b	<u> </u>
4	1(10), ATHK	12	05(72)	21	(128.5-129)*	04
	(11),					
	SX(10),					
5	3 (20)	12	65 (4)	30	84-85 /10	69
	DMBD(22)	12	05 (4)	50	04-03710	05
	$S_{x}(20)$					
	$C_{SF(3)}$					
6	3 (20).	12	22 (8d)	3b	(40.5-41) ^c	60
	CHTr (22).		(00)			
	Sx (20).					
	CsF(5)					
7	3 (11), ATHR	12	65(5)	3c	(151-151.5) ^b	45
	(10),					
	Sx (10),					
	CsF(5)					
8	4 (20),	12	22(5d)	4a+4b,		78 ^d
	CHD(22),			Ratio 55:45		
	Sx (20),					
	KF(45)					

9	4 (30), CHD(35), Sx (30), CsF(4)	25	22-25(3d)	4a+4b, Ratio 55:45	46-48/10	88 ^e
10	4 (22), ATHR(20), Sx (25), KF(45)	12	65(4d)	4c	(56-57) ^e	30
11	5 (25), ATHR(20), Sx (20), CsF(5)	12	65(5d)	5a	(30-31)	64
12	6 (25), CHPTr(20), Sx (22), CsF(10)	50	22(5d)	6a+6b , Ratio 55:45	clear oil ^f	40

^a reaction was slightly exothermic

^b purity 98%, 2% anthracene

 $^{\rm c}$ isolated by column chromatograph, purity 96%, eluent hexane; thermally labile compound

^d calculated yield (NMR); product was identified by comparison of NMR and GC/MS with material obtained in reaction of **6** and CHD (see entry 9)

^e reported value 54-55 °C [1]

^f thermally unstable; isolated by column chromatography (silicagel, eluent – hexane)

[1] W.J. Middleton, Fluorothiocarbonyl compounds. III. Diels-Alder reactions, J. Org. Chem. (1965) 1390-1394.

Table 2. NMR data for New Materials.

No	Product No	¹ H NMR	¹⁹ F NMR (δ, ppm,. J,	¹³ C NMR	MS (<i>m/z</i>)
		(δ, ppm,. J, Hz)ª	Hz) ^a	(δ, ppm,. J, Hz) ª	
1	1a + 1b	1a: 1.81(3H,s),	1a: -77.28(3F,m),		364
	Ratio 80:20	1.84(3H,s),	- 110.45(1F, dm,		(M+,
		2.68(2H,s),	280.0), -110.68(1F,dm,		$C_{11}H_{10}F_{10}S^{+}$
		3.07(2H,s)	280.0)		
		1b: 1.82(3H,s),			
		1.85(3H,s),	1b: -68.94(3F,m),		
		2.64(2H,s),	-80.81(3F, dd, 13.0,		
		3.01(1H,d,	11.5),		
		14.6),	-108.63(1F, dm, 280.0)		
		3.13(1H, d,			
		14.6)			
2	2a, 2b	2a: 1.81(3H,s),	2a+2b: -77.12(3F, sept.,		464
	Ratio 65:35	1.84(3H,s),	5.6), -80.79(3F, tt, 10.5,		(M⁺,
		2.72(2H,s),	3.0),		$C_{13}H_{10}F_{14}S^{+}$)
		3.07(2H,s)	-80.87(6F,13.0),		
			-105.0 to -107.0 (4F,		
		2b: 1.81(3H,s),	m), -109.39(2F, A:B q,		
		1.84(3H,s),	280.7), -118.00(2F,m), -		
		2.67(1H,d,	121.19(2F,m), -		
		16.3),	125.86(2F, AB q, 288.0)		
		2.70(1H,16.3),			
		3.01(1H,d,			
		14.5),			
		3.05(1H, d,			
	2	14.5)			262
3	2c+2d+2e,	2c+2d+2e:	2c : -//.85(6F,m),		362
	Ratio 78:12:10	1.26(1H,M),	-78.43(6F,M),		(IVI ⁺ ,
		1.75(1H,M),	-99./(2F, 0, 283.8), -		$C_{11}H_8F_{10}S')$
		2.20(1H, m),	105.58 (2F, Dr.S,		
		3.57(1H,M),	$\Delta V_{1/2} = 650 HZ$,		
		3.70(1H,M),	20+2e : -62.40 (m),		
		$0.30(1\pi,111),$	-05.00(Dr.S, ΔV _{1/2} =90		
		0.30(10,1,7.8)	ΠΖ], 90 ΛΕ/+ 13 Ε\		
			-00.43(1, 12.3), _80 77(35 + 12.3)		
			-00.77(31,1, 13.3), 101 03/hr c		
			10+.03(01.3, Λν/=660Hz)		
			-105 12(ΔB α 20/ 7) -		
			108 02		
			$(\text{br.s. }\Lambda v_{4/2} = 650 \text{Hz})$		
			-114.32(AB a. 280.6)		
			-123,24(AB a. 288.6).		
3	2c+2d+2e, Ratio 78:12:10	2a. 1.81(3 H , s), 1.84(3 H , s), 2.72(2 H , s), 2b: 1.81(3 H , s), 1.84(3 H , s), 2.67(1 H ,d, 16.3), 2.70(1 H ,16.3), 3.01(1 H ,d, 14.5), 3.05(1 H , d, 14.5), 2c+2d+2e: 1.26(1 H , m), 1.75(1 H , m), 2.20(1 H , m), 3.57(1 H , m), 3.70(1 H , m), 6.36(1 H , t , 7.8)	2a+zu : -77.12(3F, sept., 5.6), -80.79(3F, tt, 10.5, 3.0), -105.0 to -107.0 (4F, m), -109.39(2F, A:B q, 280.7), -118.00(2F,m), - 121.19(2F,m), - 125.86(2F, AB q, 288.0) 2c : -77.85(6F,m), -78.43(6F,m), -99.7(2F, d, 283.8), - 105.58 (2F, br.s, $\Delta V_{1/2}$ =650Hz), 2d+2e : -62.40 (m), -65.66(br.s, $\Delta V_{1/2}$ =90 Hz), -80.45(t, 12.5), -80.77(3F,t, 13.3), 104.03(br.s, $\Delta V_{1/2}$ =660Hz), -105.12(AB q, 294.7), - 108.02 (br.s, $\Delta V_{1/2}$ =650Hz), -114.32(AB q, 280.6), -123.24(AB q, 288.6),		404 (M ⁺ , C ₁₃ H ₁₀ F ₁₄ S ⁺) 362 (M ⁺ , C ₁₁ H ₈ F ₁₀ S ⁺)

			-123,.82 (br.s, Δν _{1/2} =280 Hz)		
4	2f	5.25(1H,s), 5.35(1H,s), 7.20(24H, m), 7.35(3H,m), 7.39(1H,d)	-62.23(3F, qd, 14.2, 5.8), -80.50(1F,t, 12.7), -97.74(1F, br. s, $\Delta V_{1/2}$ =650 Hz), -109.84, 1F, d, 298.4), -123.18(2F, br. s, $\Delta V_{1/2}$ = 66Hz); 100°C: ^c -61.68(3F, m), -80.14(3F, t, 13.1), -97.25(1F,d, 297.5), -104.70(1F, dm, 297.5, 6.3), -122.09(2F, q, 17.3)		b
5	3a	1.78(3H, s), 1.80(3H, s), 2.53(2H, s), 3.20(2H, s)	-117.154, -120.49 (2FF, AB quartet, 252.7),), 124.51(1F, dt, 253.0, 8.0), -124.55(1F, (1F, dt, 253.0, 6.3), - 131.83(1F, d q., 252.2, 4.9)	18.65, 19.72, 29.82 (m), 30.25(t, 3.1), 55.15 (qint., 20.7), 110.57, tm, 275.5), 116.29(tm, 271.2), 123.79, 125.32	326 (M ⁺ , C ₁₁ H ₁₀ F ₈ S ⁺)
6	3b	0.15(1H, m), 0.30 (1H, q, 7.5), 1.3 (1H, m), 1.66, 1H, m), 3.96(1H, ddm, 7.3, 3.8, 1.1), 4.07(1H, m), 5.80(1H, t, 7.2), 6.29(1H, t, 7.3)	-112.80(1F, dd, 243.5, 10.6), -115.05 (2F, AB q, d, 243.0), - 116.46(1F, d sixt., 5.0), -124.18(1F, d m, 250.5), -124.53(1F, dm, 252.0), -129.55(1F, dm, 250.5), -131.66(1F, d q., 252.0, 5.9)		b
7	3c	5.37(1H, s), 5.40 (1H,t, 1.6), 7.25 (2H, dt, 7.4, 1.5), 7.27 (2H, dt, 7.4, 1.5), 7.39 (2H, d, 7.4), 7.40 (2H, d, 7.4),	-115.43(2F, d, 249.0), -118.22(2F,d, 249.0), -123.81(2F, d quint, 253.2, 8.3), -130.47(2F, d quint., 253.2, 3.4)		422(M ⁺ , C ₁₉ H ₁₀ F ₈ S ⁺)
8	4a,b Ratio 55:45	4a,b : 1.27(1H, m), 1.76(1H, m), 2.17(2H,	Major : -63.00(3F, sixt., 12.5), -78.49(3F, q, 9.5),		314 (M ⁺ , C ₁₀ H ₈ F ₁₀ S ⁺)

		m), 3.52(1H,m), 3.68(1H,t, 5.5), 6.32-6.42, 1H, m), 6.58(1H, q)	-108.42(2F, AB q, 289.7) Minor:-66.50(3F, br.s) -70.35(3F, q, 11.3), - 103.53(1F, br.d, ~280.0), -112.17(1F, br.s) Major: ^d -62.56(3F, sixt., 10.9), -78.04(3F, q, 9.8), -107.53(2F, q, 13.0) Minor: ^d -65.66(3F, sixt., 10.5), -78.83(3F,q), - 110.40(1F,d, 283.6), -102.65(1F, dq, 283.6, 11.0)		
9	4c	5.27(1H,s), 5.29(1H,s), 7.22(4H,m), 7.38(4H,m)	-62.83(3F,sixt., 7.3), - 78.60(3F,q, 10.8), -100.89(1F, d, 289.8), - 109.05 (1F, d, 289.8)	46.67, 47.52(m, 1.7), 68.64(m, 28.4), 113.63(td, 264.3, 38.9), 118.86(qt, 290.4,38.4), 123.87(qd, 284.0, 4.0), 126.40(m), 126.54 (m), 126.85, 127.29, 127.50, 38.40, 138.50, 142.62(d, 26.4)	b
10	5a	1.28(1H,m), 1.78(1H,m), 2.22(2H,m), 3.72(1H,t, 5.4), 3.82(1H,dm, J_d =6.7), 6.42(1H, q, 4.2), 6.66(1H,t, 7.3)	-110.35, -113.85, -116.78, -118.20, -120.85, -125.04, -138.7, -141.62 (all broad singlets); 120 °C: ^e -111.03(1F,d,277.7), 113.85(2F, AB quart., 278.0), -115.81(1Fd, 277.7), -112.14(2F,t, 294.0), -126.61(1F,d, 282.5), -135.83(1F,d, 280.7), -137.11(1F, d, 282.5),		374(M ⁺ , C ₁₂ H ₈ F ₁₀ S ⁺)

			-138.99(1F, d, 280.7)	
11	6a+6b , Ratio 55:45	Major: 0.15(1H,m), 1.44(1H,m),	Major: -59.98(3F, m), -79.44(3F,q, 12.0), -	b
		3.85(1H,m), 5.62(2H,m)	104.73(1F, dq, 285.5, 15.1), -106.71(dq, 288.5,7.8) Minor: -64.76(3F, br. s),	
		Minor: 0.05(1H, dm, 16.4), 1.15(1H,dm, 16.2), 3.78(1H,ddd, 15.1, 7.4, 3.8)), 6.02(2H,m)	-82.29 (3F,t, 7.5), , 12.0), -98.59(1F, dq, 283.5, ~11), -109.50 (br.s)	

^a in CDCl₃ as lock solvent, ambient temperature, unless stated otherwise

^b thermally unstable, decomposition on GC column

 $^{\rm c}$ 100°C, in CDCl₂CDCl₂ as a lock solvent

 $^{\rm d}$ 100°C, in CDCl_2CDCl_2 as a lock solvent

^e, in CDCl₂CDCl₂ as a lock solvent