

Supporting Information  
for  
Synthesis, Mechanism of Formation, and Dynamics of a Highly Fluorinated  
Methylenecyclobutene  
by  
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General experimental information:

NMR spectra were obtained on 300 and 500 MHz machines.  $^{19}\text{F}$  NMR spectra were recorded at 282.2 and 470.3 MHz, with trichlorofluoromethane as internal reference.

Hexafluorobenzene was used as an internal area standard for  $^{19}\text{F}$  NMR.  $^{13}\text{C}$  NMR spectra were recorded at 125.7 MHz. Acetonitrile was purified by distillation from  $\text{P}_4\text{O}_{10}$ . Other solvents were used as obtained from commercial sources.

Z Matrix for Rotamer **6a** (B3LYP/6-31G\*)

F1	-2.878	0.631	-1.603	2				
C2	-2.577	0.266	-0.350	1	5	4	3	
C3	-1.099	0.325	-0.092	2	7	6		
F4	-3.241	1.065	0.503	2				
F5	-3.040	-0.995	-0.169	2				
C6	-0.176	-0.643	0.107	3	9	10		
C7	-0.137	1.427	0.037	3	8	9		
C8	-0.050	2.756	-0.003	7	16	17		
C9	0.974	0.378	0.279	6	7	11	12	
C10	-0.306	-2.143	0.061	6	14	15	13	
C11	2.041	0.370	-0.829	9	23	19	18	
C12	1.591	0.500	1.684	9	21	20	22	
C13	0.600	-2.894	1.045	10	28	29	27	
C14	-0.167	-2.669	-1.385	10	25	24	26	
H15	-1.328	-2.388	0.356	10				
C16	-1.171	3.718	-0.251	8	30	32	31	
H17	0.910	3.227	0.180	8				
F18	2.876	-0.673	-0.718	11				
F19	2.779	1.499	-0.789	11				
F20	0.631	0.429	2.622	12				
F21	2.211	1.691	1.820	12				
F22	2.496	-0.458	1.934	12				
F23	1.452	0.308	-2.036	11				
F24	1.064	-2.473	-1.879	14				
F25	-1.045	-2.028	-2.181	14				
F26	-0.440	-3.982	-1.446	14				
F27	0.454	-2.369	2.278	13				
F28	1.896	-2.824	0.706	13				
F29	0.255	-4.191	1.112	13				
F30	-0.730	4.749	-1.003	16				
F31	-1.636	4.235	0.905	16				
F32	-2.211	3.155	-0.896	16				

Total energy: -2255.5780915 a.u.

Z Matrix for Rotamer **6b** (B3LYP/6-31G\*)

C1	0.158	2.739	-0.407	4	3	2			
C2	0.065	1.421	-0.238	1	6	5			
H3	1.134	3.212	-0.355	1					
C4	-0.982	3.675	-0.688	1	9	7	8		
C5	-0.913	0.321	-0.218	2	13	10			
C6	1.165	0.395	0.089	2	12	11	10		
F7	-1.257	3.748	-2.006	4					
F8	-2.112	3.309	-0.052	4					
F9	-0.661	4.918	-0.272	4					
C10	0.014	-0.619	0.092	5	6	23			
C11	2.184	0.184	-1.041	6	17	15	16		
C12	1.835	0.606	1.455	6	19	18	14		
C13	-2.393	0.308	-0.486	5	20	21	22		
F14	2.587	-0.464	1.793	12					
F15	1.559	0.078	-2.224	11					
F16	2.888	-0.950	-0.845	11					
F17	3.052	1.207	-1.121	11					
F18	0.908	0.773	2.410	12					
F19	2.632	1.689	1.454	12					
F20	-2.668	1.087	-1.550	13					
F21	-3.079	0.777	0.571	13					
F22	-2.836	-0.930	-0.756	13					
C23	0.104	-2.089	0.398	10	24	25	26		
H24	1.140	-2.297	0.671	23					
C25	-0.727	-2.473	1.634	23	30	32	31		
C26	-0.173	-3.003	-0.813	23	28	29	27		
F27	0.353	-4.221	-0.600	26					
F28	0.417	-2.488	-1.910	26					
F29	-1.478	-3.155	-1.072	26					
F30	-0.273	-1.788	2.702	25					
F31	-0.614	-3.784	1.899	25					
F32	-2.030	-2.186	1.485	25					

Total energy: -2255.5776487 a.u.

Z Matrix for (Z)-Anion (B3LYP/6-31G\*)

C1	-2.202	1.592	-0.219	4	3	2			
C2	-1.172	0.711	-0.214	1	5	6			
H3	-3.200	1.176	-0.125	1					
C4	-2.199	3.067	-0.149	1	9	7	8		
C5	-1.090	-0.711	-0.109	2	13	10			
C6	0.381	0.779	-0.233	2	12	11	10		
F7	-2.155	3.548	1.136	4					
F8	-1.192	3.691	-0.800	4					
F9	-3.362	3.563	-0.669	4					
C10	0.315	-0.768	0.006	5	6	14			
C11	0.960	1.208	-1.607	6	18	17	16		
C12	0.968	1.584	0.936	6	20	19	15		
C13	-2.196	-1.690	-0.067	5	21	22	23		
C14	1.281	-1.707	0.310	10	24	25			
F15	2.276	1.345	1.149	12					
F16	1.101	0.147	-2.425	11					
F17	2.167	1.808	-1.505	11					
F18	0.159	2.078	-2.252	11					
F19	0.324	1.280	2.080	12					
F20	0.838	2.914	0.739	12					
F21	-3.271	-1.217	-0.767	13					
F22	-2.677	-1.959	1.181	13					
F23	-1.869	-2.884	-0.617	13					
C24	0.905	-3.067	0.790	14	29	31	30		
C25	2.746	-1.501	0.170	14	28	27	26		
F26	3.358	-2.592	-0.381	25					
F27	3.404	-1.287	1.348	25					
F28	3.066	-0.456	-0.628	25					
F29	-0.232	-3.060	1.530	24					
F30	1.869	-3.604	1.590	24					
F31	0.701	-3.987	-0.196	24					

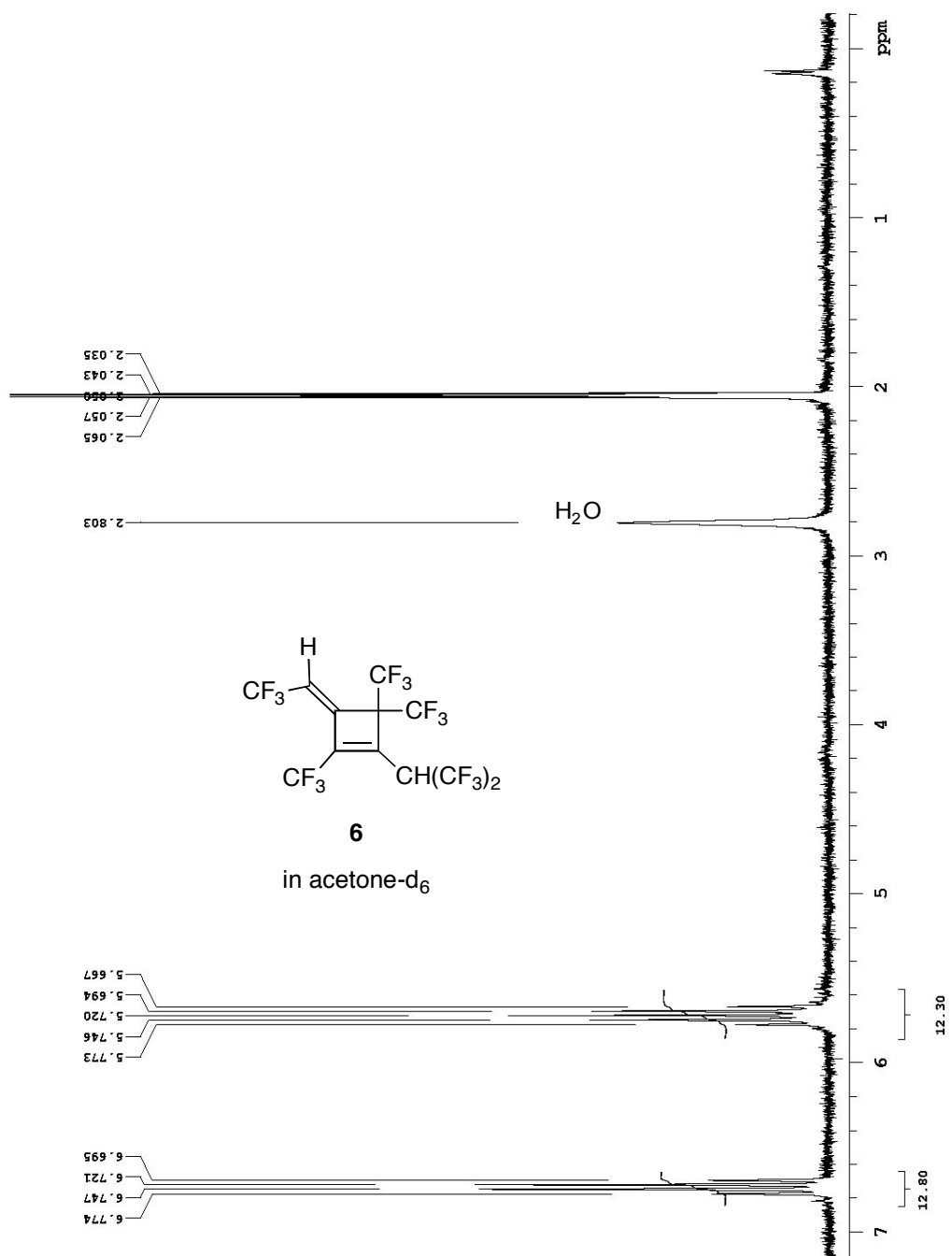
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Z Matrix for (E)-Anion (B3LYP/6-31G\*)

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C2	-0.999	0.866	-0.249	1	6	5			
H3	-1.541	2.903	-0.360	1					
C4	-3.361	1.737	-0.253	1	9	7	8		
C5	-0.906	-0.558	-0.185	2	13	10			
C6	0.543	0.965	-0.158	2	12	11	10		
F7	-3.944	1.526	-1.471	4					
F8	-3.793	0.726	0.542	4					
F9	-3.940	2.881	0.223	4					
C10	0.495	-0.590	0.014	5	6	14			
C11	1.141	1.535	-1.461	6	18	16	17		
C12	1.028	1.751	1.065	6	20	19	15		
C13	-1.944	-1.591	-0.383	5	21	22	23		
C14	1.447	-1.525	0.368	10	24	25			
F15	2.345	1.606	1.306	12					
F16	1.038	0.649	-2.469	11					
F17	2.436	1.901	-1.365	11					
F18	0.480	2.655	-1.846	11					
F19	0.377	1.364	2.175	12					
F20	0.802	3.081	0.907	12					
F21	-2.893	-1.153	-1.254	13					
F22	-2.617	-1.963	0.739	13					
F23	-1.429	-2.730	-0.913	13					
C24	1.063	-2.884	0.846	14	29	31	30		
C25	2.914	-1.287	0.352	14	28	27	26		
F26	3.600	-2.384	-0.083	25					
F27	3.457	-0.990	1.571	25					
F28	3.272	-0.271	-0.467	25					
F29	-0.153	-2.904	1.443	24					
F30	1.946	-3.354	1.776	24					
F31	1.025	-3.844	-0.123	24					

Total energy: -2255.0591465 a.u.

<sup>1</sup>H NMR of 6

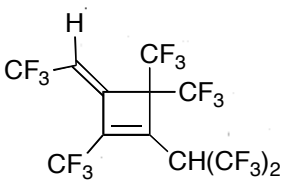


<sup>13</sup>C NMR of 6

STANDARD CARBON PARAMETERS (500)

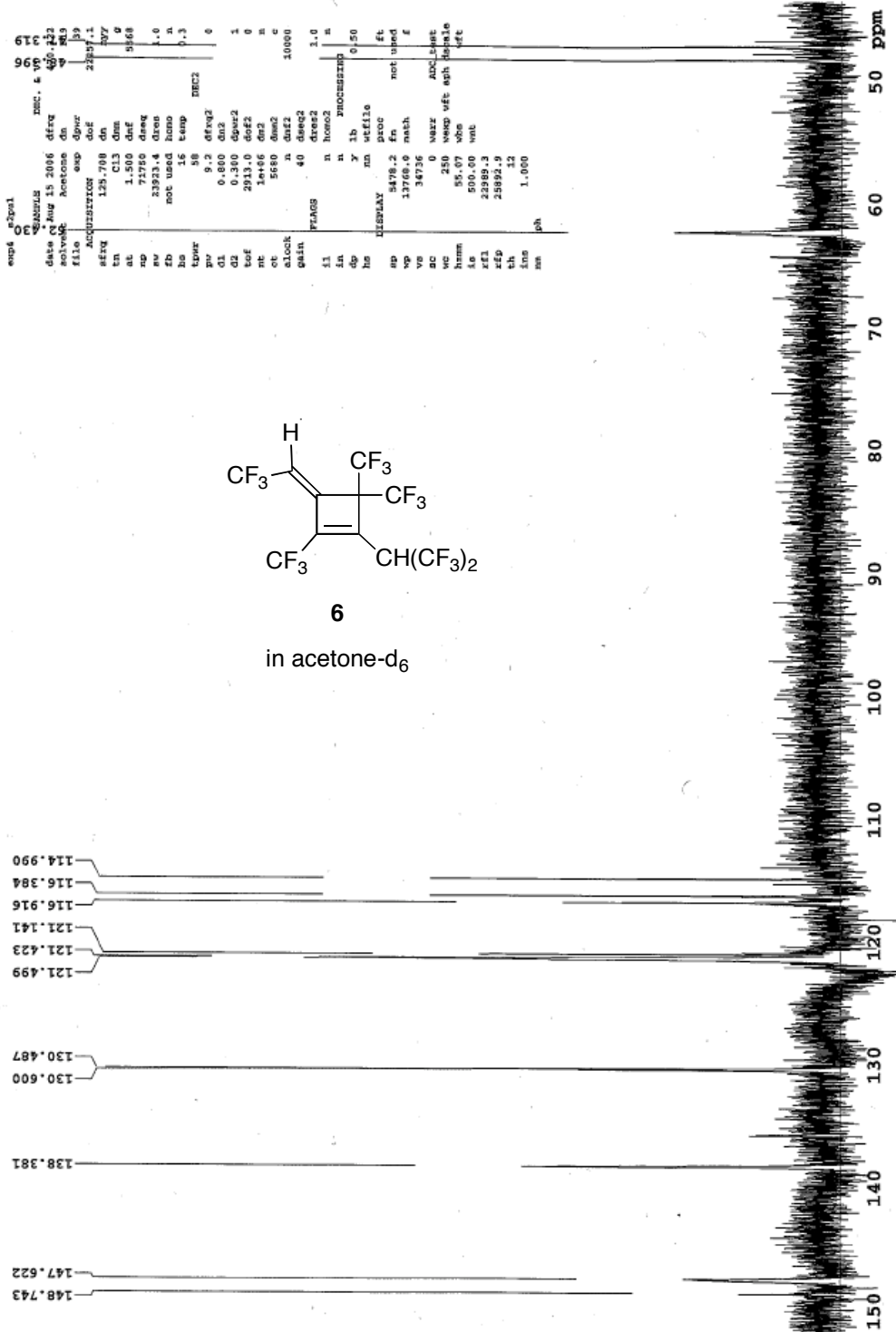
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dl 21370 dseg2
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ct 5680 dm2
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ia n PHOSPHOR
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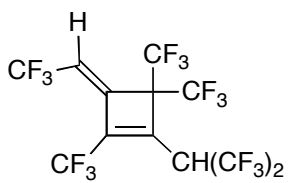
6

in acetone-d<sub>6</sub>



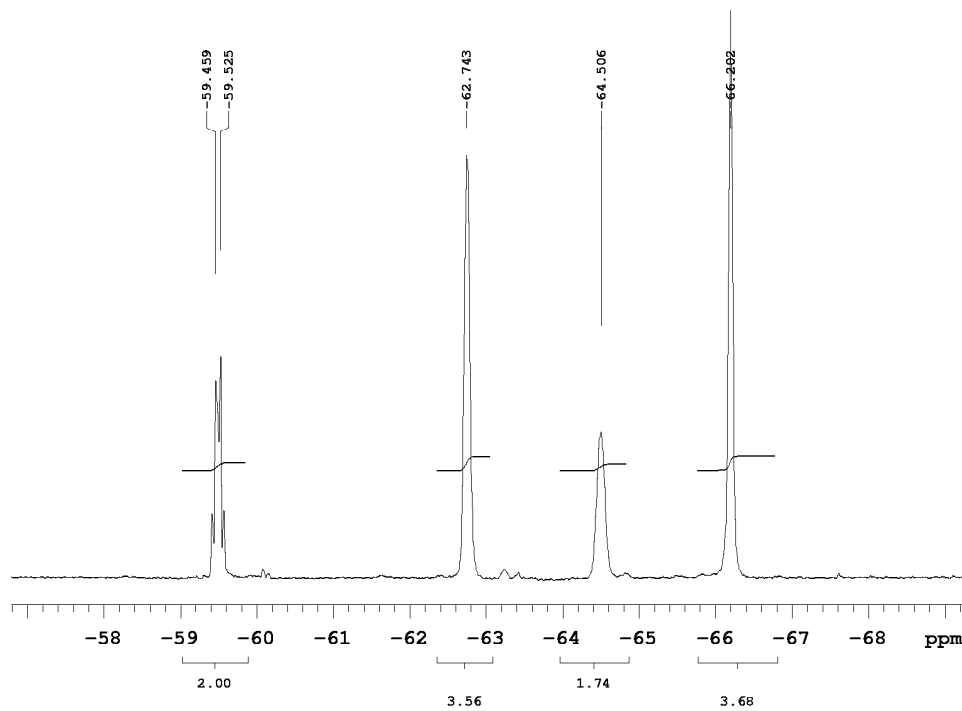


$^{19}\text{F}$  NMR spectrum of **6**



**6**

in acetone-d<sub>6</sub>



(F, H) NOESY spectrum of **6** in CD<sub>3</sub>CN

