

## Supplementary Material

### Trifluoromethylphenylcarbenes. Carbene-Carbene Interconversion on the Singlet Energy Surface and Rearrangement to Trifluorobenzocyclobutene, Trifluorostyrene and Trifluoromethylfulvenallenes.

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**Contents: Figure S1-S10 and Tables S1-S2: GC-MS and NMR data**

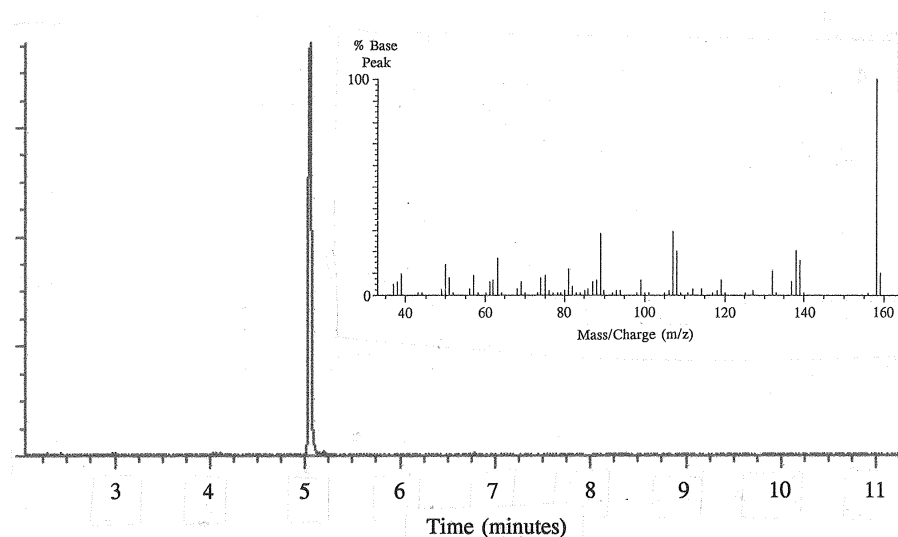


Figure S1. GC-MS of trifluorobenzocyclobutene **14**.

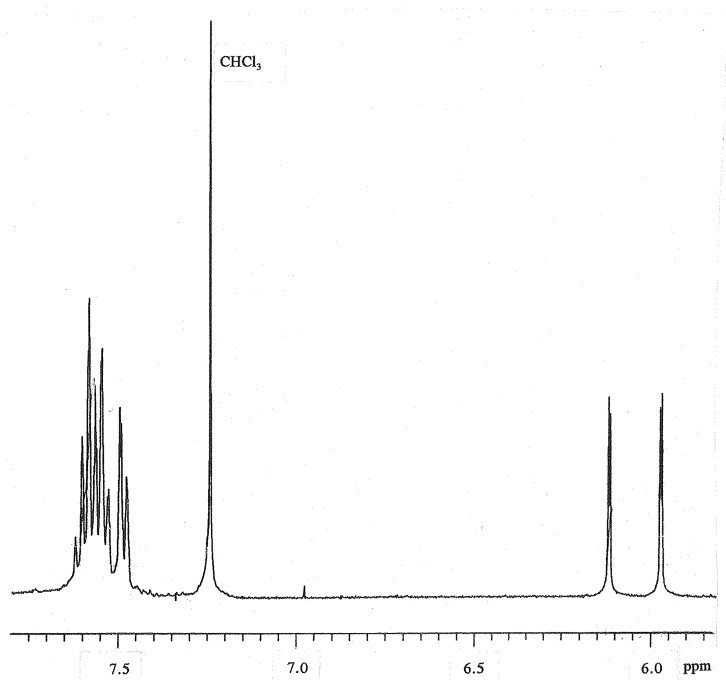


Figure S2.  $^1\text{H}$  NMR spectrum of trifluorobenzocyclobutene **14**.

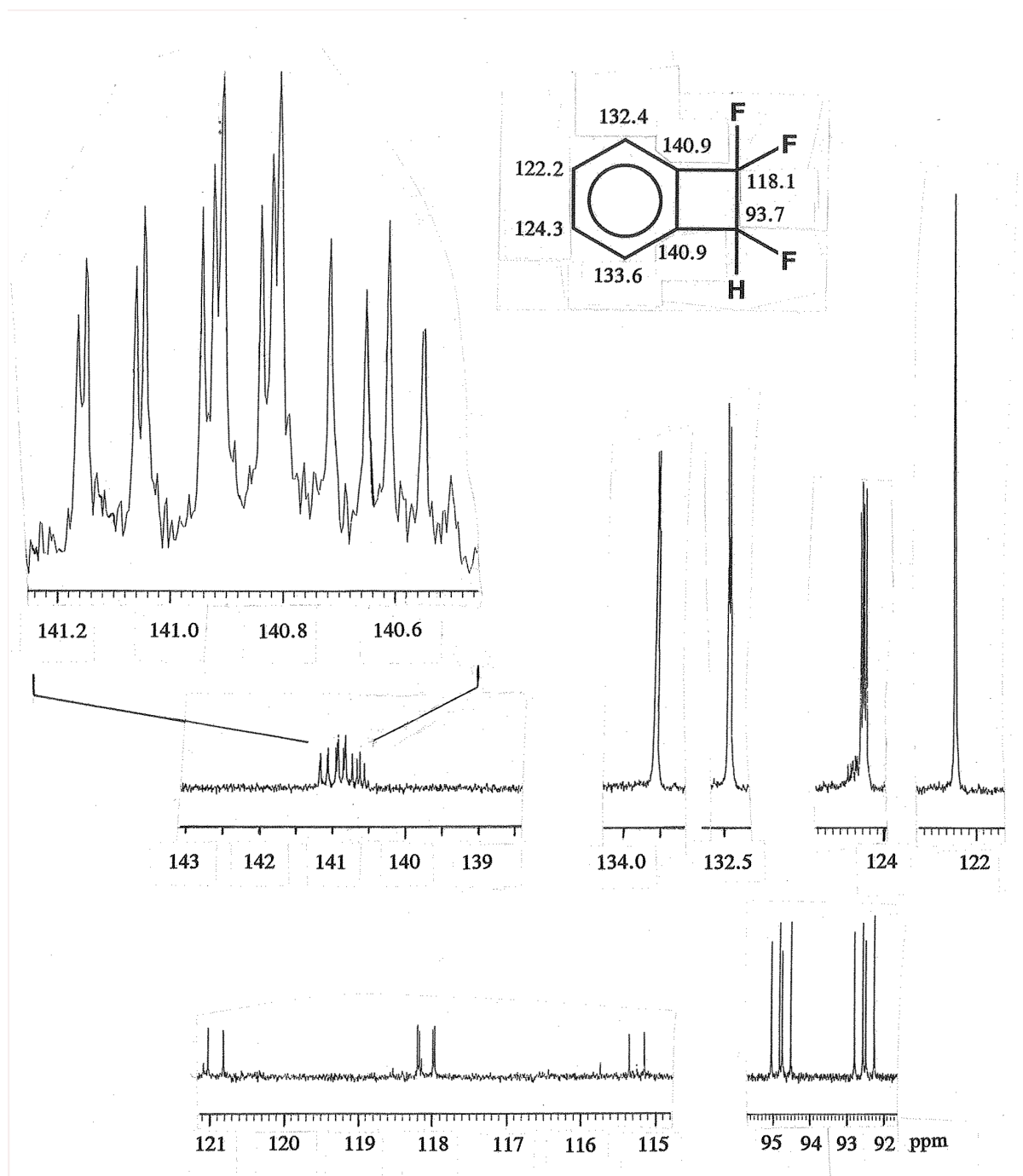


Figure S3.  $^{13}\text{C}$  NMR spectrum of trifluorobenzocyclobutene **14** ( $^1\text{H}$  decoupled).

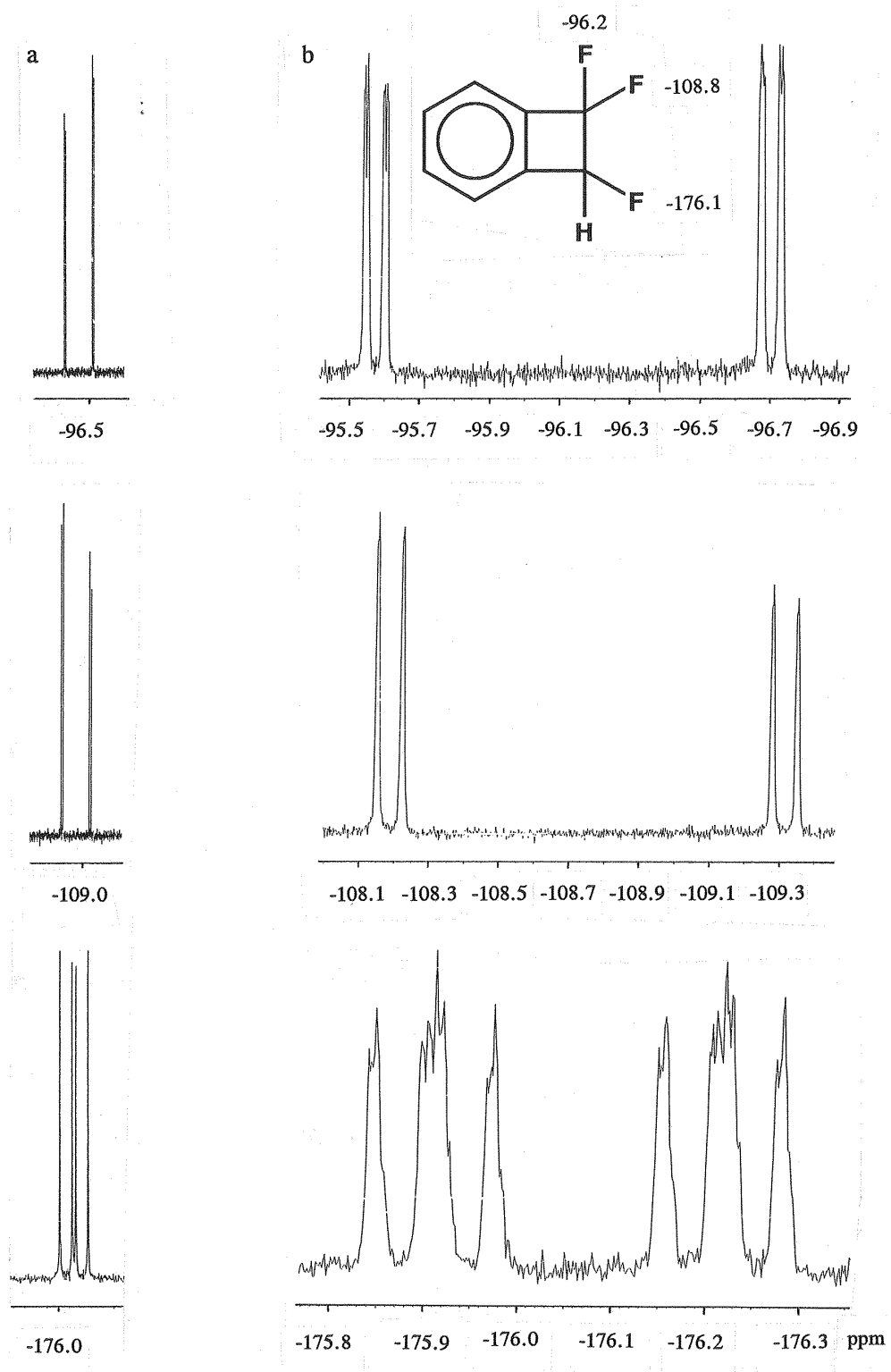


Figure S4.  $^{19}\text{F}$  NMR spectrum of trifluorobenzocyclobutene **14**, (a)  $^1\text{H}$  decoupled, (b) coupled.

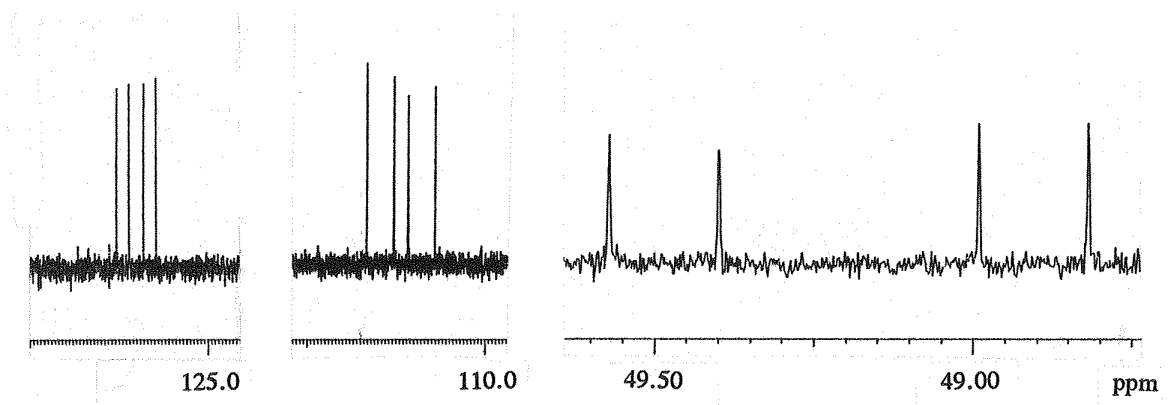


Figure S5.  $^{19}\text{F}$  NMR spectrum of 1',2',2'-trifluorostyrene **15**.

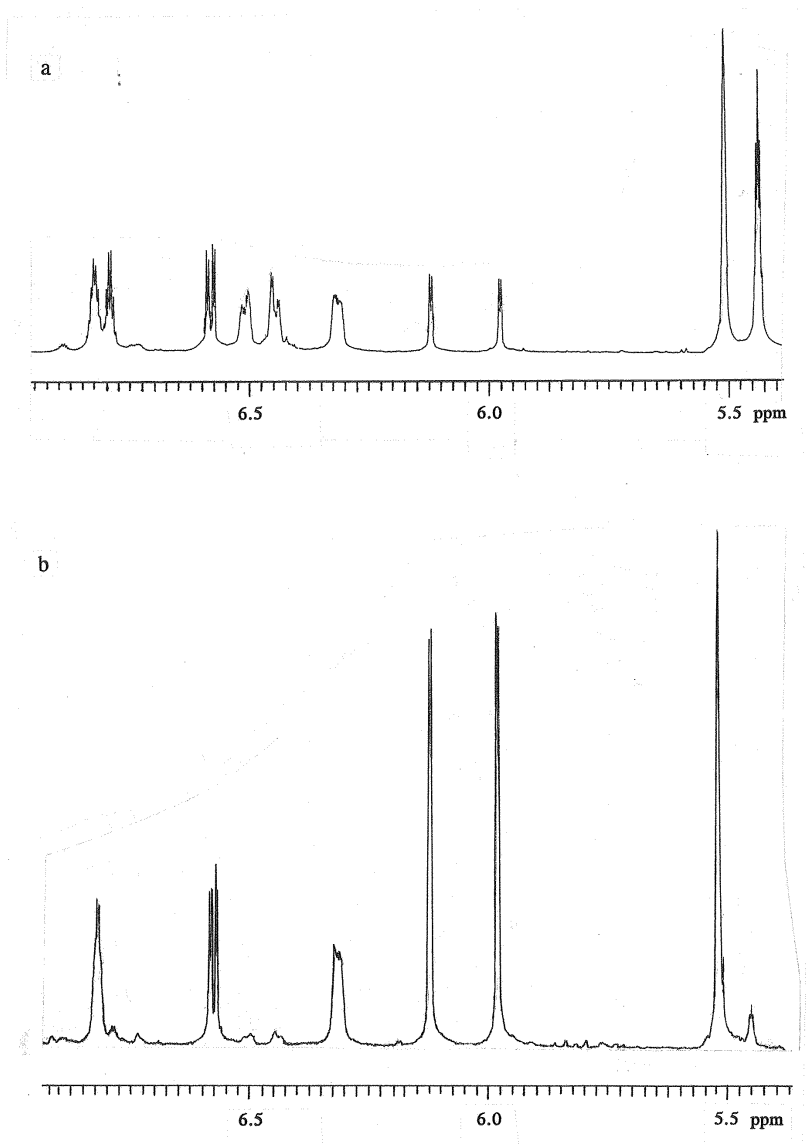


Figure S6.  $^1\text{H}$  NMR spectra of trifluorofulvenallenes **16** and **17**, (a) immediately after collection of the product, (b) after 3 d in  $\text{CDCl}_3$  solution in the NMR tube at room temperature.

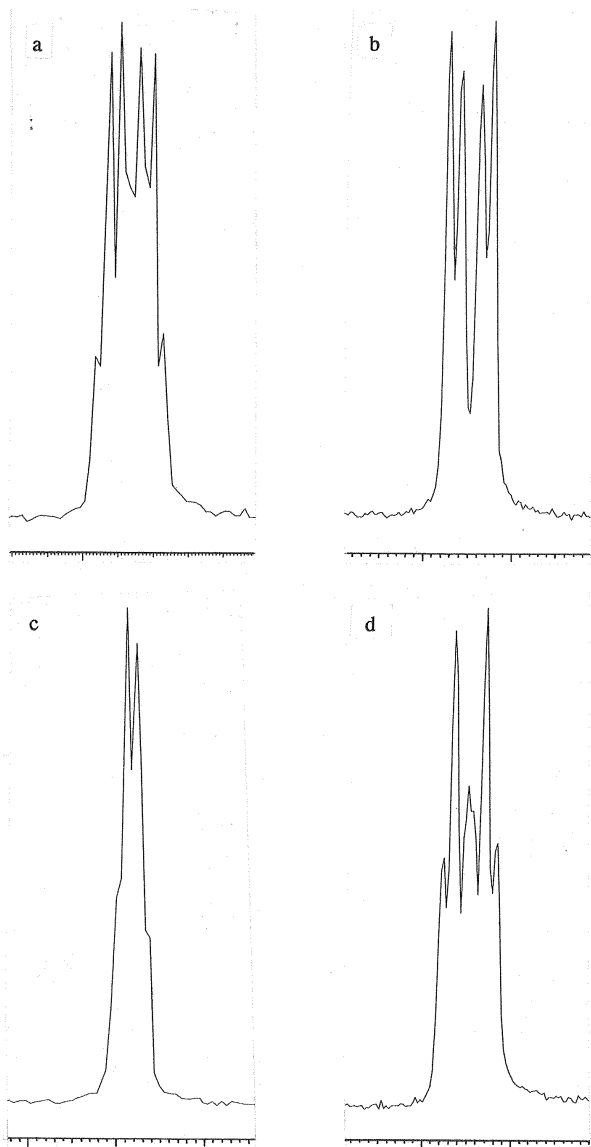


Figure S7.  $^{19}\text{F}$  NMR of 2-trifluorofulvenallene **17**, (a)  $^1\text{H}$  coupled, (b) selective decoupling of protons at 5.51 ppm, (c) decoupling of proton at 6.83 ppm, (d) decoupling of proton at 6.32 ppm.

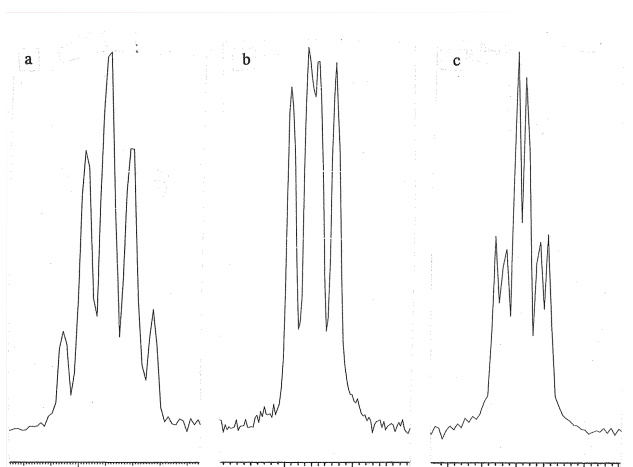


Figure S8.  $^{10}\text{F}$  NMR of 1-trifluoromethylfulvenallene **16**, (a)  $^1\text{H}$  coupled, (b) selective decoupling of protons at 5.45 ppm, (c) decoupling of proton at 6.80 ppm

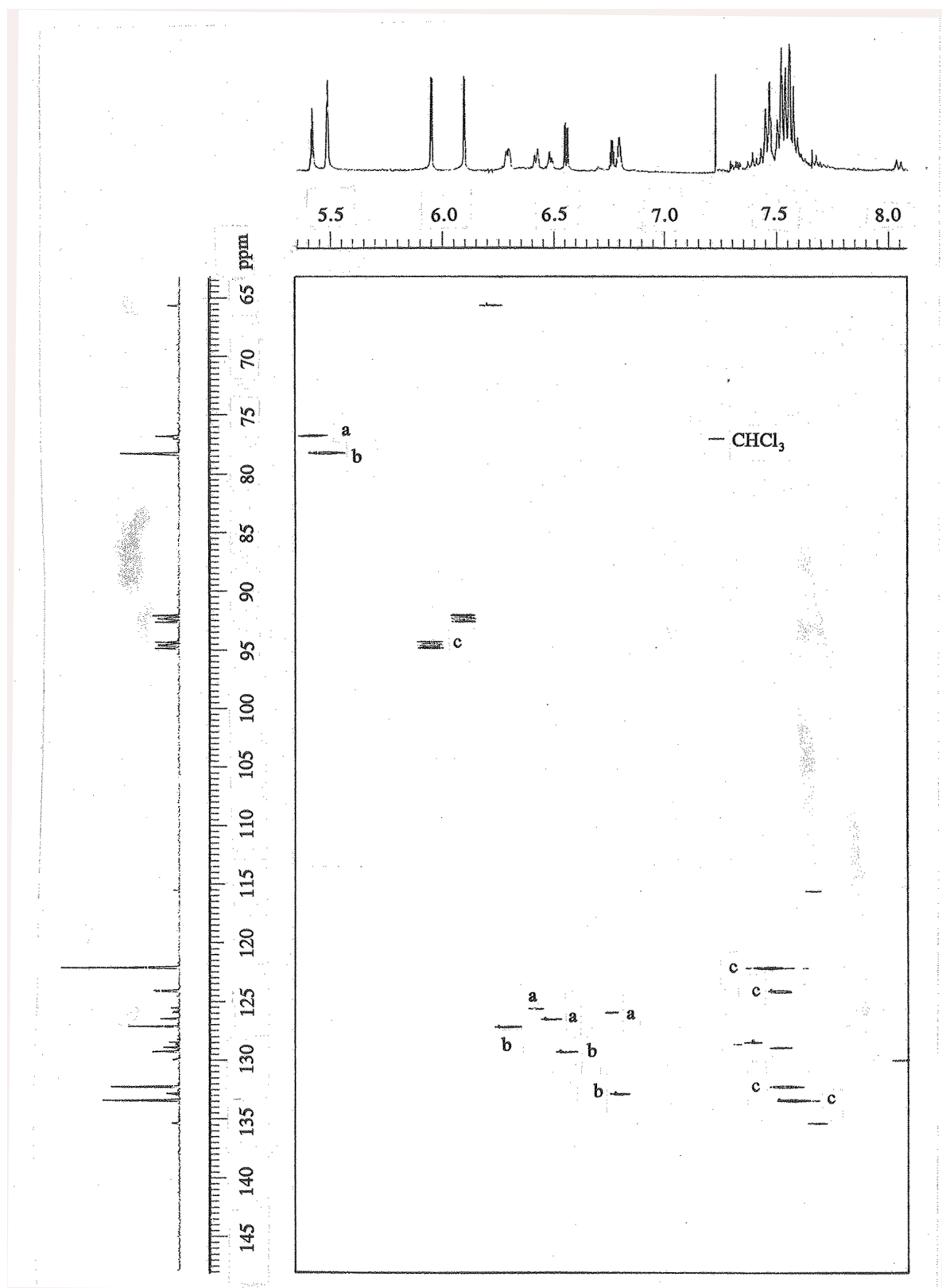


Figure S9. COSY ( $^1\text{H}$ - $^{13}\text{C}$ ) 2D NMR correlation for the FVT product containing **14**, **16** and **17** (a= 1- $\text{CF}_3$ -fulvenallene **16**, b = 2- $\text{CF}_3$ -fulvenallene **17**; c = trifluorobenzocyclobutene **14**).

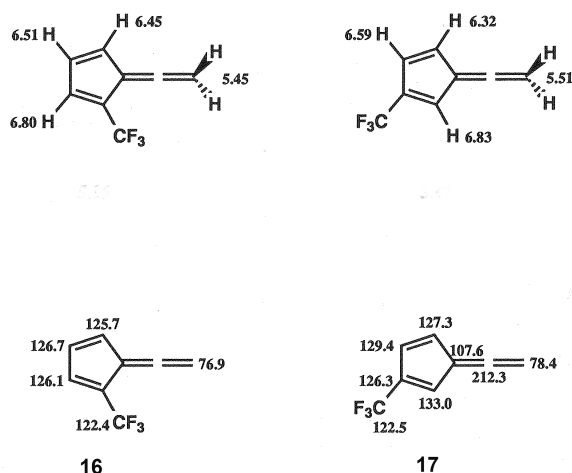


Figure S10. Structural formulas showing  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments for 1- and 2-trifluoromethylfulvenallenes **16** and **17**.

Table S1. GC-MS data for the pyrolyzate from **1** at 500°C.

Retention Time	% Area	Mass Spectrum [ m/z (%) ]
9.255	14.1	316(100), 247(18), 227(64), 178(95)
9.945	0.3	316(56), 247(100), 227(41), 178(97)
10.019	1.2	316(45), 247(100), 227(24), 178(57)
10.440	20.2	316(83), 247(37), 227(47), 178(100)
10.563	0.5	316(56), 247(100), 227(26), 178(55)
10.675	9.6	316(98), 247(32), 227(48), 178(100)
10.837	2.0	316(64), 247(100), 227(35), 178(68)
10.931	1.1	316(82), 247(100), 227(48), 178(76)
11.035	0.9	316(95), 247(100), 227(58), 178(78)
11.118	0.5	316(76), 247(100), 227(35), 178(46)
11.172	1.1	316(100), 247(99), 227(18), 178(54)
11.256	2.4	316(52), 247(100), 227(19), 178(61)
11.358	11.3	316(100), 247(25), 227(26), 178(69)
11.472	1.0	316(86), 247(100), 227(31), 178(47)
11.546	1.5	316(81), 247(100), 227(22), 178(49)
11.649	1.5	316(83), 247(100), 227(29), 178(36)
11.758	10.8	316(100), 227(27), 178(67)
11.868	1.7	316(47), 247(100), 227(14), 178(52)
11.933	1.8	314(100), 295(12), 264(11), 245(10)
12.165	5.1	314(100), 295(16), 245(11), 264(10)
12.223	5.5	316(100), 247(15), 227(29), 178(66)
12.273	1.7	314(100), 295(19), 264(13), 245(11)
12.489	0.6	316(3), 247(22), 246(100), 225(14), 196(17)
12.613	2.7	316(0.5), 247(18), 246(100), 225(9), 196(16)
12.684	1.0	314(100), 295(21), 264(22), 246(49), 245(16)



Table S2. GC-MS data for the pyrolyzate from **1** at 700°C.

Retention Time	% Area	Mass Spectrum [ m/z (%) ]
3.313	6.3	158(100), 138(18), 108(25), 107(31), 89(13)
5.189	22.2	158(100), 138(22), 108(19), 107(33), 89(29)
13.347	0.7	290(100), 271(17), 201(27), 152(15)
13.617	0.9	290(100), 271(27), 201(27), 152(18)
14.293	1.4	316(100), 247(88), 227(48), 178(68)
14.489	1.1	316(100), 247(91), 227(56), 178(91)
14.799	2.7	316(100), 247(50), 227(48), 178(58)
16.058	2.3	316(24), 247(100), 227(15), 178(74)
16.440	5.6	316(35), 247(100), 227(14), 178(92)
16.575	1.0	316(46), 247(100), 227(16), 178(49)
16.850	303	316(57), 247(100), 227(39), 178(63)
16.969	0.9	316(100), 247(29), 227(23), 178(30)
17.041	1.4	316(57), 247(100), 227(66), 178(74)
17.135	1.4	316(100), 247(95), 227(55), 178(56)
17.231	0.7	316(85), 247(100), 227(11), 178(19)
17.271	3.2	316(43), 247(100), 227(16), 178(69)
17.378	4.2	316(36), 247(100), 227(18), 178(58)
17.485	1.3	316(78), 247(100), 227(27), 178(35)
17.514	1.0	316(100), 247(54), 227(46), 178(71)
17.571	0.8	316(64), 247(100), 227(15), 178(21)
17.663	2.9	316(100), 247(100), 227(15), 178(21)
17.779	3.1	316(100), 247(72), 227(30), 178(69)
17.884	4.3	316(47), 247(100), 227(11), 178(61)
17.934	3.0	314(100), 295(20), 264(19), 245(16)
18.185	7.3	314(100), 295(18), 264(14), 245(13)
18.263	4.7	314(68), 295(14), 264(9), 246(100), 245(17)
18.290	2.3	314(100), 295(16), 264(12), 245(9)
18.497	2.1	246(100), 227(10), 225(11), 196(15), 176(13)
18.629	4.2	246(100), 227(9), 225(7), 196(18), 176(9)
18.686	2.5	314(32), 295(5), 264(6), 246(100), 245(19)