Electronic Supplementary Information for

Difluoromethylenation of fullerene C_{70} provides isomeric diversity and availability of equatorial [5,6]-homofullerene $C_{70}(CF_2)$

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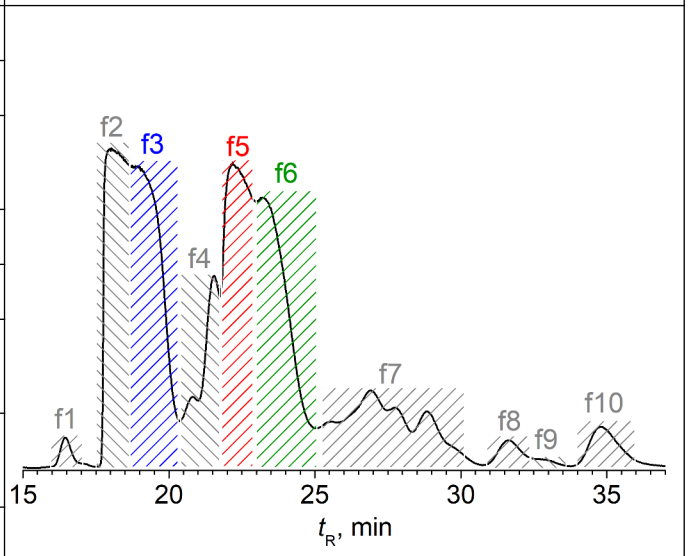
Table *S*1. HPLC separation and mass spectrometry analysis of the isolated fractions.

Fraction	t_R, min[a]	Composition[b]	HPLC trace[a]
f1	16.1–16.8	$C_{70}(CF_2)_2$	
f2	17.6–18.6	C_{70}	
f3	18.7–20.2	**$C_{70}(CF_2)$ [isomer I]**, C_{70}	
f4	20.4–21.7	$C_{70}(CF_2)_n$, n=2–3	
f5	21.9–22.8	**$C_{70}(CF_2)$ [isomer II]**	
f6	23.0–24.8	**$C_{70}(CF_2)$ [isomer III]**, $C_{70}(CF_2)_n$, n=2–3	
f7	25.2–30.0	$C_{70}(CF_2)_nO_m$, n=2–4, m=0–2	
f8	31.0–32.2	$C_{70}(CF_2)_2$	
f9	32.4–33.6	$C_{70}(CF_2)_n$, n=2–3	
f10	34.1–35.9	$C_{70}(CF_2)_2$	

[a] The retention time, t_R (Cosmosil Buckyprep 20 mm I.D. × 25 cm, toluene, 15 mL min^{-1}); [b] According to MALDI mass spectrometry data.

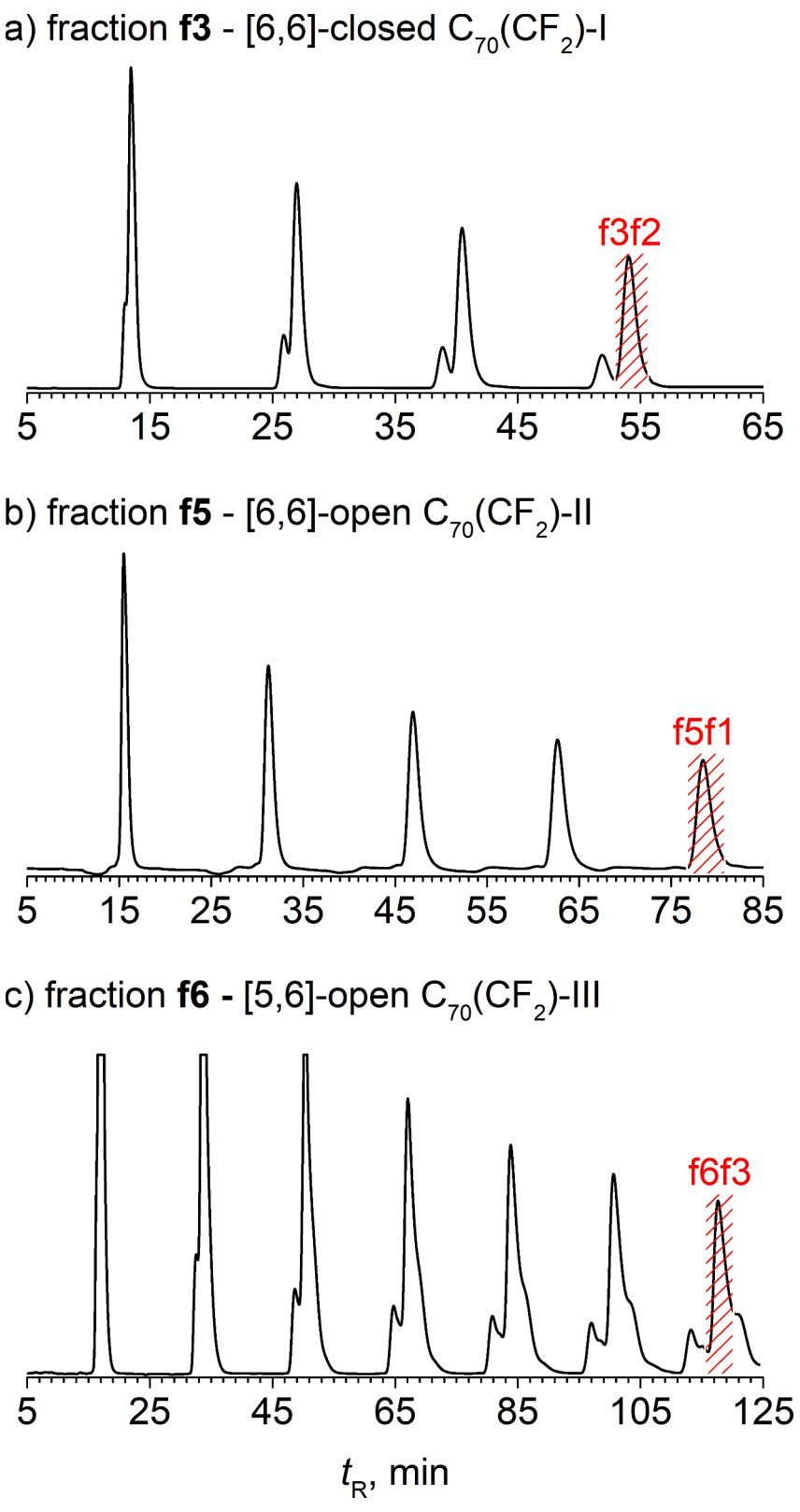


Figure *S*1. Purification of the isolated fractions using semi-preparative HPLC (Cosmosil Buckyprep column 10 mm I.D. × 25 cm) equipped with recycling system.

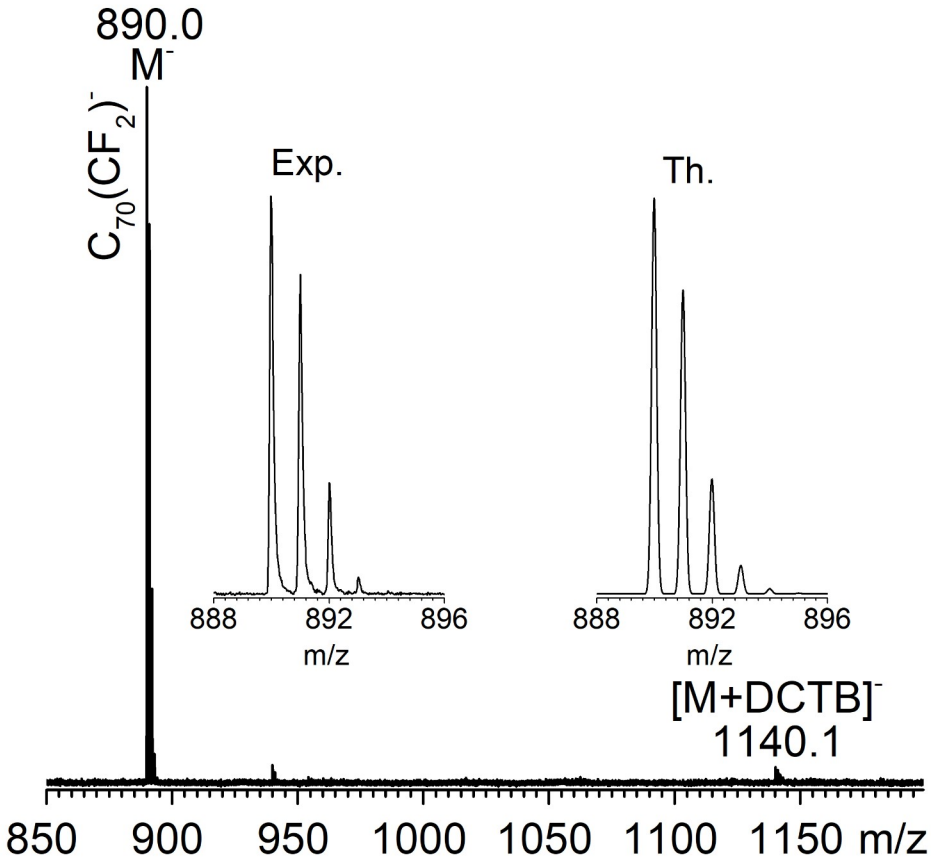


Figure *S*2. MALDI mass spectrum of $C_{70}(CF_2)$ isomer III.

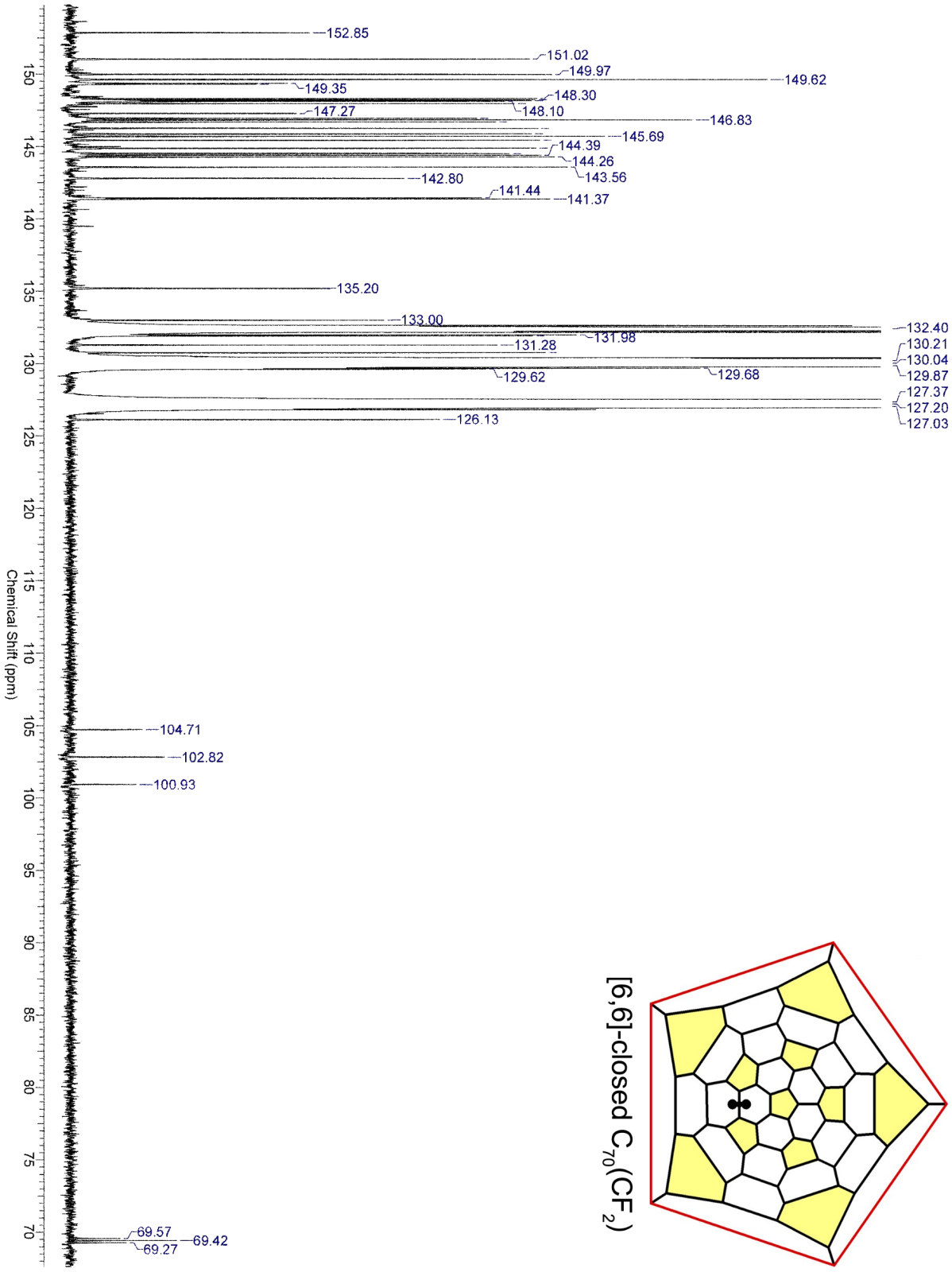


Figure *S3.* ^{13}C NMR spectrum of [6,6]-closed $C_{70}(CF_2)$ isomer I.

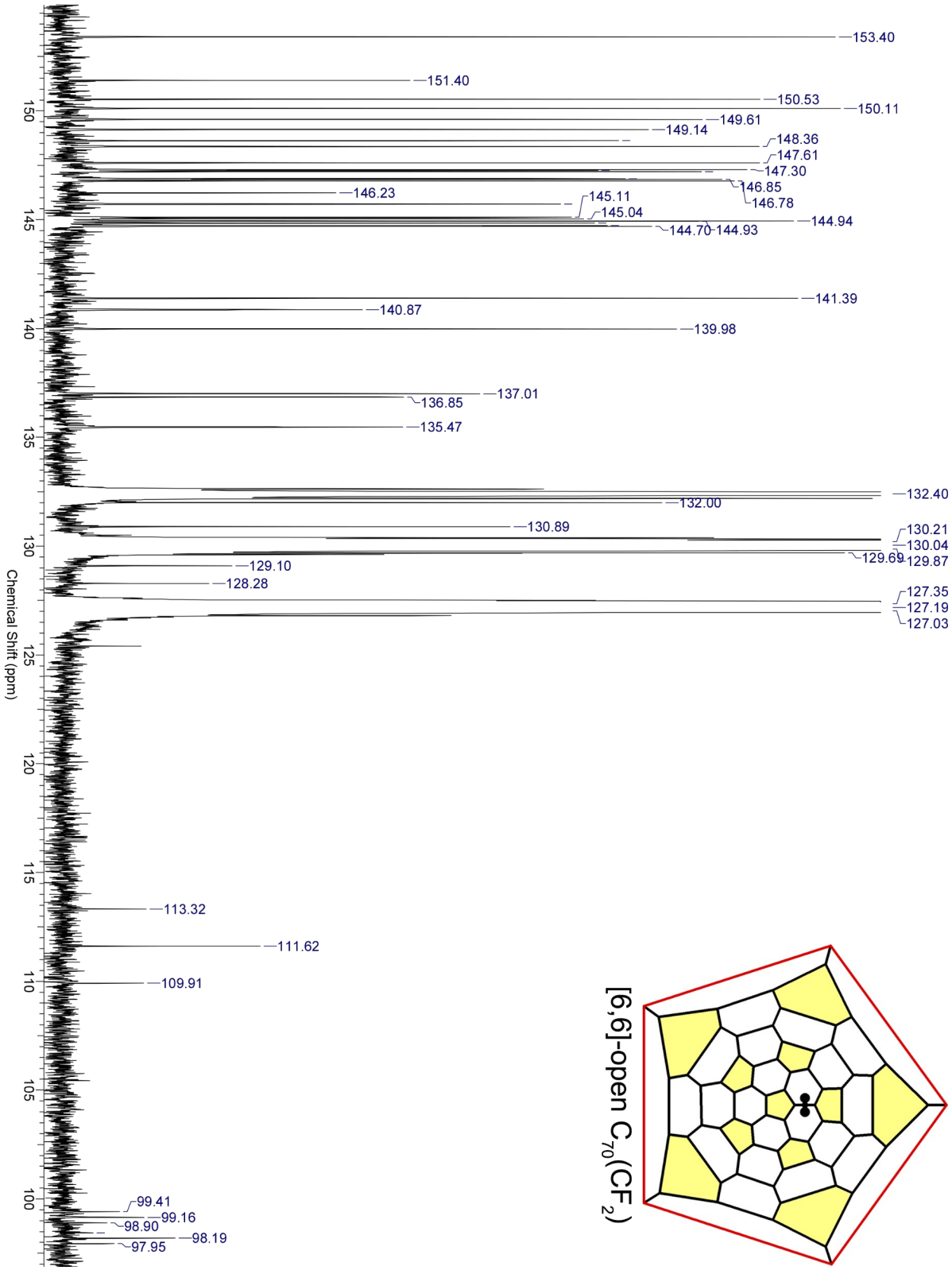


Figure *S4.* ^{13}C NMR spectrum of [6,6]-open $C_{70}(CF_2)$ isomer II.

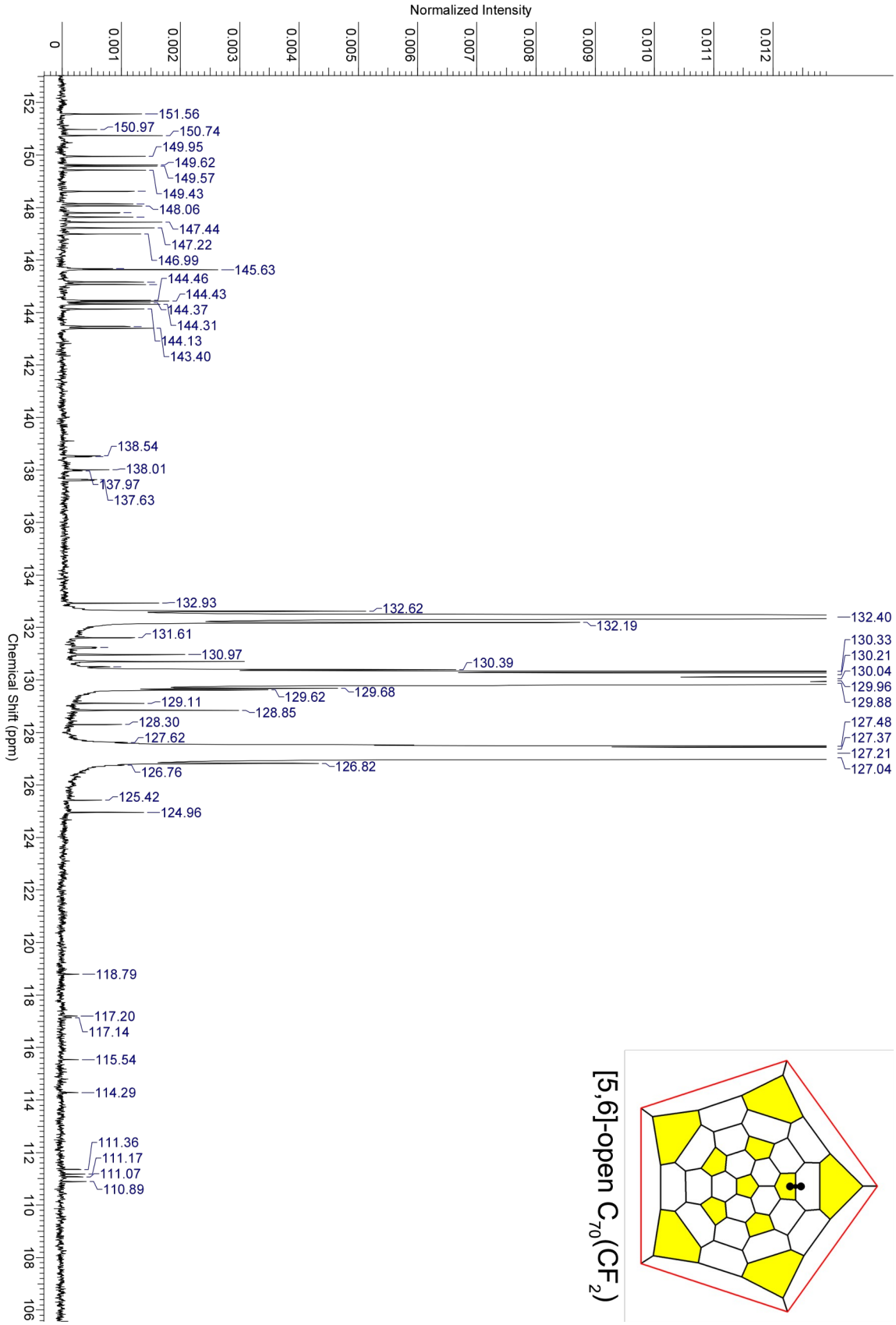


Figure *S*5. ^{13}C NMR spectrum of [5,6]-open $C_{70}(CF_2)$ isomer III.

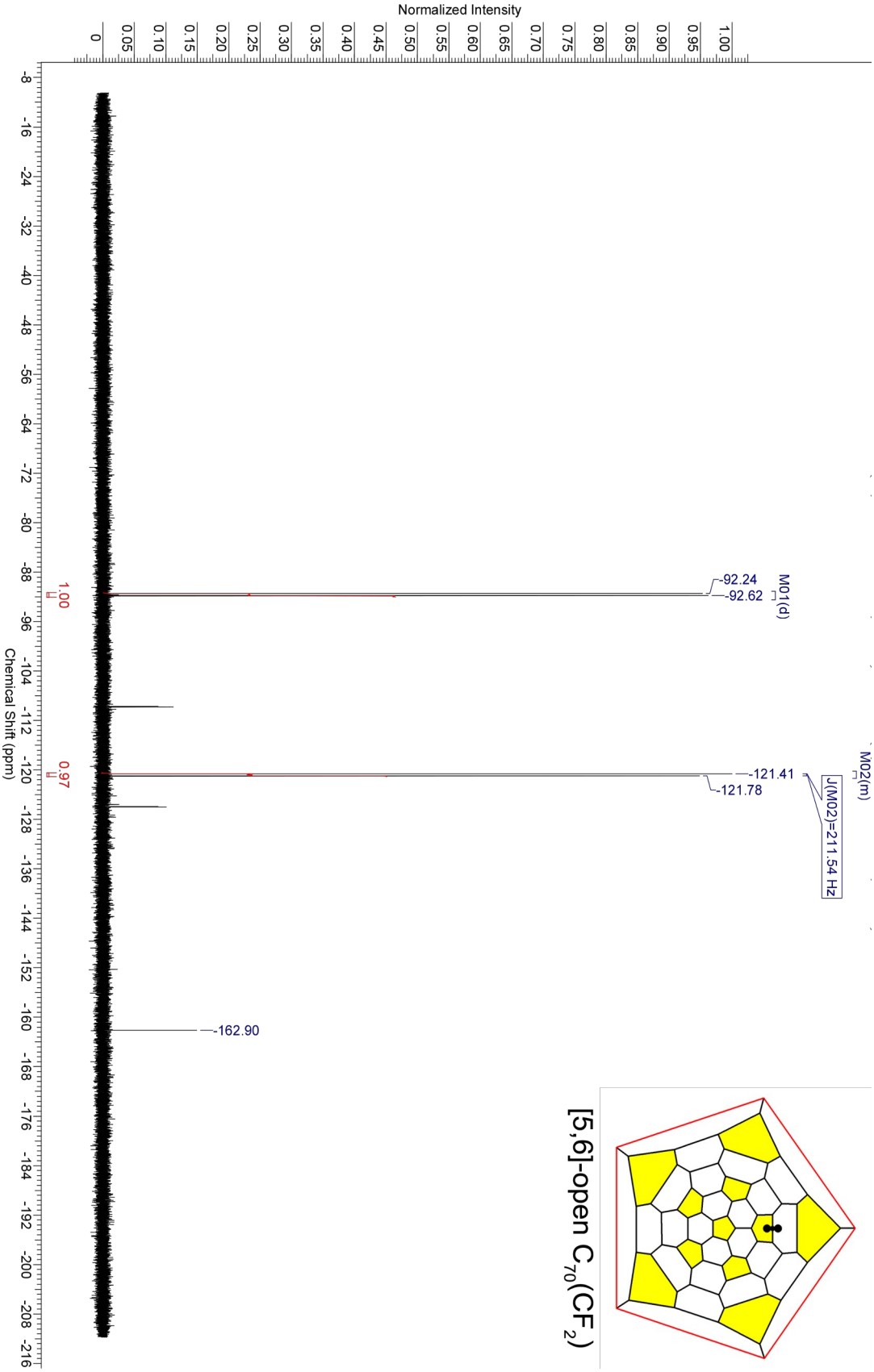
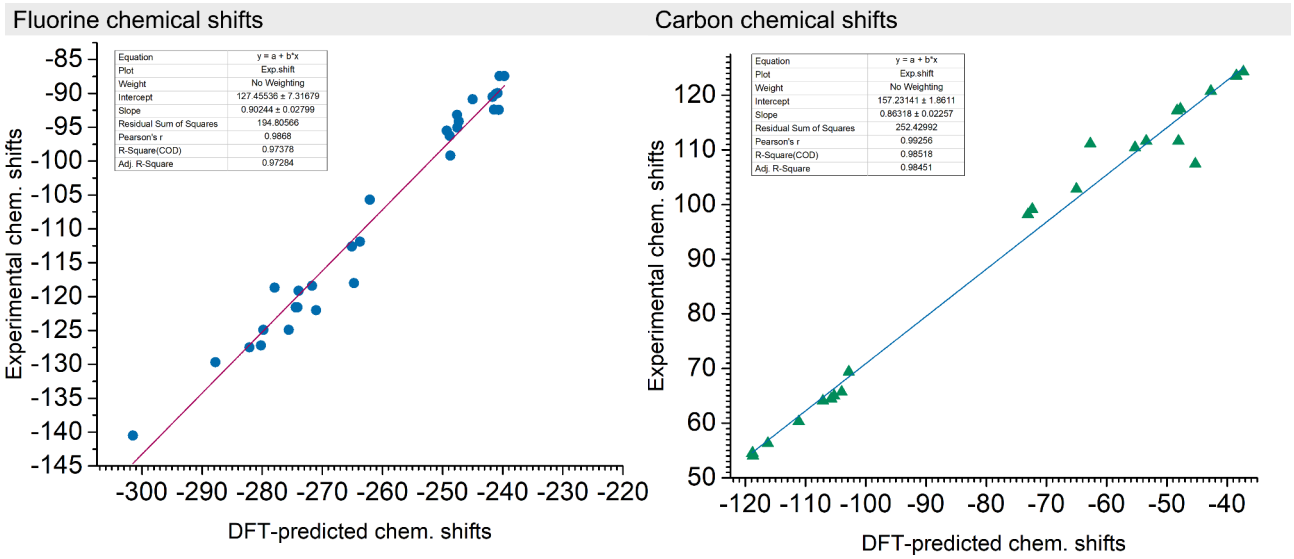


Figure *S*6. ^{19}F NMR spectrum of [5,6]-open $C_{70}(CF_2)$.



List of considered compounds: $C_{60}(CF_2)$, $C_{70}(CF_2)$ (3 isomers), $C_{60}(CF_2)H_2$, $C_{60}(CF_2)R_2$ (*R*=Bn, allyl, pentafluorobenzyl, carbomethoxy, H, 6 compounds) [1–4].

Figure *S*7. NMR chemical shifts correlations.

Table *S*2. Experimental and DFT-predicted NMR chemical shifts, the relative formation energies and configurations for $C_{60}(CF_2)$ as well as $C_{70}(CF_2)$ isomers.[a]

Compound	Bond/ Symmetry	*r*(C…C), [b] Å	ΔE [c] / kJ mol^{-1}	Number of expected NMR resonances		$-\delta_F$, ppm		δ_C, ppm				*RMS* [d]
				^{19}F	^{13}C	C<u>*F*$_2$</u>		<u>*C*</u>F$_2$		<u>*C*</u>-CF$_2$-<u>*C*</u>		
						Exp.	Th.	Exp.	Th.	Exp.	Th.	
[6,6]-open $C_{60}(CF_2)$	[6,6]/ C_{2v}	2.06 [1.67]	–	1×2F	sp^2: 13×4C+ 4×2C	118.94	118	107.42	110	110.44	118	2.7
[6,6]-closed $C_{70}(CF_2)$ I	**5**/C_s	1.72 [1.63]	19.6	2×1F	sp^2: 32×2C+ 4×1C sp^3: 1×2C+ 1×1C	124.9 127.5	125 127	102.8	101	69.4	69	0.5
[6,6]-open $C_{70}(CF_2)$ II	**7**/C_s	2.09 [1.67]	2	1×2F	sp^2: 33×2C+ 4×1C sp^3: 1×1CF$_2$	111.9	111	111.6	111	99.2 98.2	94 95	1.6
[5,6]-open $C_{70}(CF_2)$ III	**4**/C_s	2.19 [2.16]	0	2×1F	sp^2: 33×2C+ 4×1C sp^3: 1×1CF$_2$	92.4 121.6	90 (*p*) 122 (*h*)	117.2	116	111.1	103	2.1
	8/C_s	2.21	2.3	2×1F	sp^2: 33×2C+ 4×1C sp^3: 1×1CF$_2$	92.4 121.6	79 96	117.2	117	111.1	106	7.3
	1/C_{2v}		–42	1×2F	sp^2: 14×4C+ 7×2C	–	100	–	113	–	109	–
	2/C_1		42.8	2×1F	sp^2: 70×1C	–	97 111	–	111	–	81 101	–
	3/C_1		38.9	2×1F	sp^2: 70×1C	–	94 99	–	116	–	94 103	–
	6/C_1		10.9	2×1F	sp^2: 70×1C	–	98.7 99.1	–	116	–	101 106	–

[a] The experimental chemical shifts are given according to works: $C_{60}(CF_2)$ [3], $C_{70}(CF_2)$ I and II [1], isomer III – this work (*p*, *h* – fluorine atoms over pentagon and hexagon faces). Bonds are specified at the Schlegel diagram in Figure 3. [b] DFT-calculated distances between bridgehead carbon atoms at the PBE/tz2p level and PBE0/def2-svp (in square brackets). [c] The relative formation energies of $C_{70}(CF_2)$ isomers at the PBE/tz2p level are given according to works [1,5]. [d] The root-mean-square (RMS) deviations between the experimental and DFT predicted ^{19}F and ^{13}C chemical shifts.

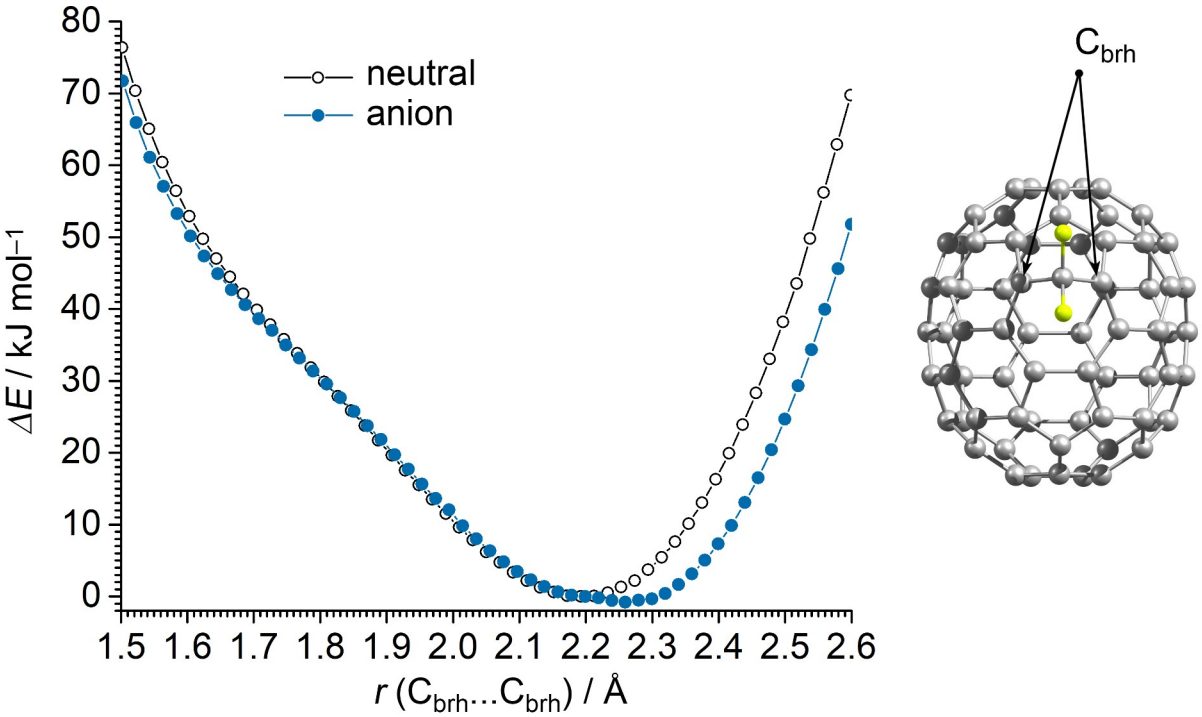


Figure *S*8.The potential energy surfaces (PES) cross-sections for neutral and anionic [5,6]-open $C_{70}(CF_2)$ isomer III along C...C stretching coordinate between the bridgehead carbon atoms (PBE/tz2p).

Table *S3*. Electronic features of $C_{70}(CF_2)$ isomers.

Compound	Energies[a] / eV			E_G^{Opt} [b] / eV	EA[c] / eV		λ[d] / eV
	HOMO	LUMO	E_G		PBE/tz2p	PBE0/def2-svp	
C_{70}	–5.93 [–6.02]	–3.77 [–4.32]	2.16	1.82 [1.70]	2.77		0.21
[6,6]-closed $C_{70}(CF_2)$ (I)	–5.89 [–5.91]	–3.78 [–4.35]	2.11	1.77 [1.56]	2.81	2.62	0.21
[6,6]-open $C_{70}(CF_2)$ (II)	–5.97 [–6.09]	–3.90 [–4.43]	2.07	1.69 [1.66]	2.90	2.84	0.17
[5,6]-open $C_{70}(CF_2)$ (III)	–5.87 [–6.07]	–3.87 [–4.42]	2.0 0	1.76 [1.65]	2.91	2.97	0.14

[a] Electrochemical and DFT-calculated (PBE/tz2p) energies of boundary orbitals and LUMO–HOMO (E_G) gaps (the DFT values are given in square brackets). The electrochemical HOMO and LUMO energies were estimated from onsets of the oxidation and reduction peaks with reference to the $Fc^{+/0}$ potential of –4.8 eV w.r.t. the vacuum level: $E(HOMO)^{EC} = -e(E_{ox} + 4.8)$ eV and $E(LUMO)^{EC} = -e(E_{1/2} + 4.8)$ eV [6–8]. [b] The optical band gaps (E_g^{opt}) estimated from the UV-vis spectra and DFT-calculated at the PBE/tz2p level (in square brackets). [c] DFT-estimated electron affinities (EA) values. The experimental EA(C_{70}) value of 2.765±0.010 eV was used to scale calculated data [9]. [d] Reorganization energies, λ (PBE/tz2p).

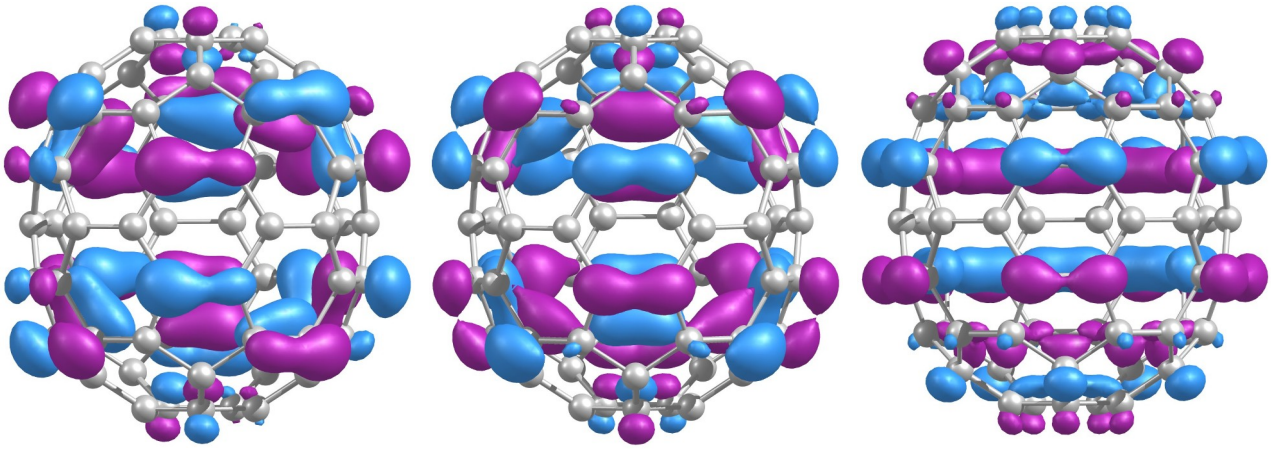


Figure *S9*.The doubly degenerated HOMO (left and center) and HOMO–1 (right) density distributions in C_{70} fullerene (PBE0/tzvpp).

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