Supporting information for

Unexpected fullerene dimerization *via* [5,6]-bond upon functionalization of C_s-$C_{70}(CF_3)_8$ by the Bingel reaction

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in Dalton Transactions

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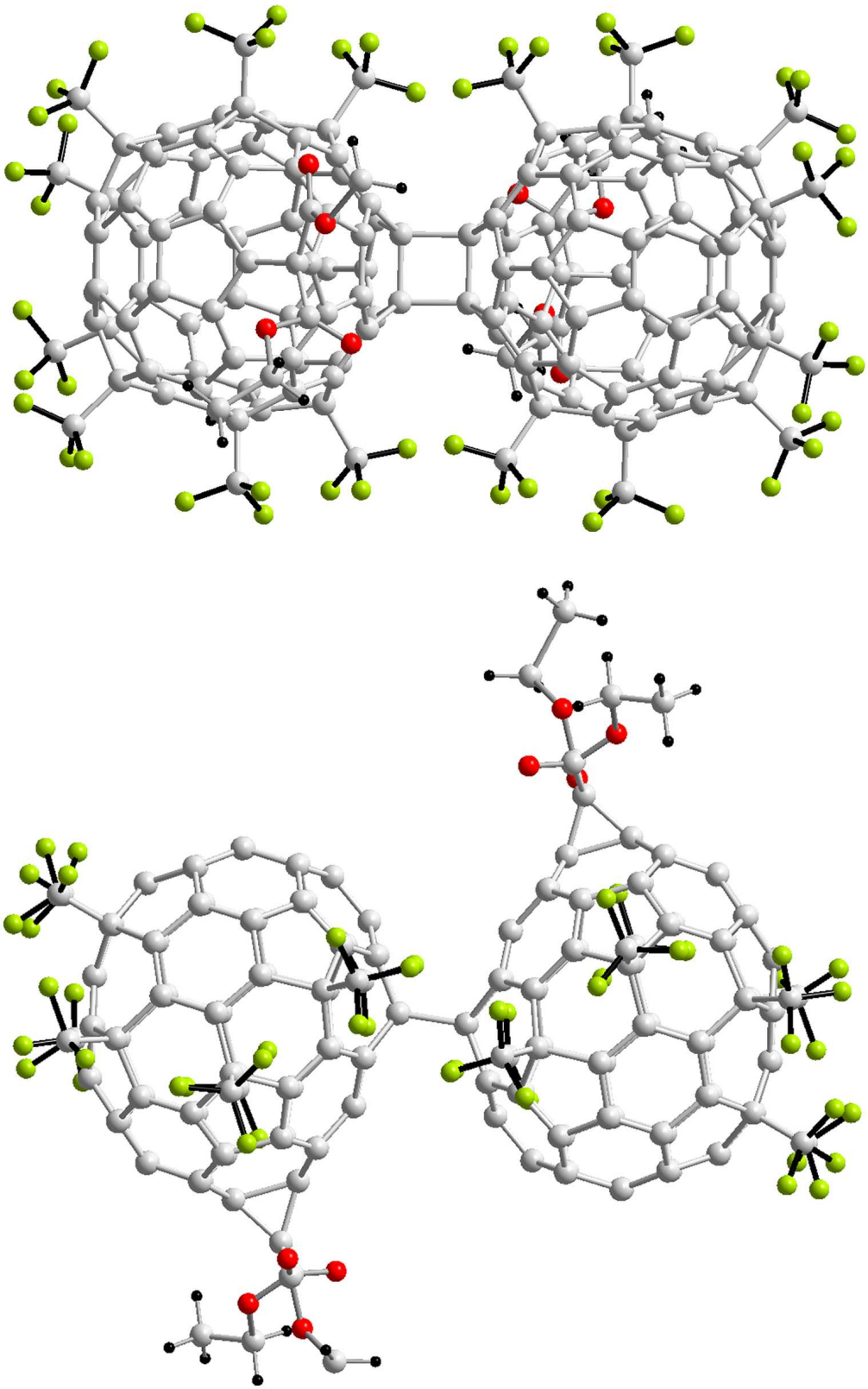


Figure S1.Top and side projections of $\{C_{70}(CF_3)_8[C(CO_2Et)_2]\}_2$*-I.*

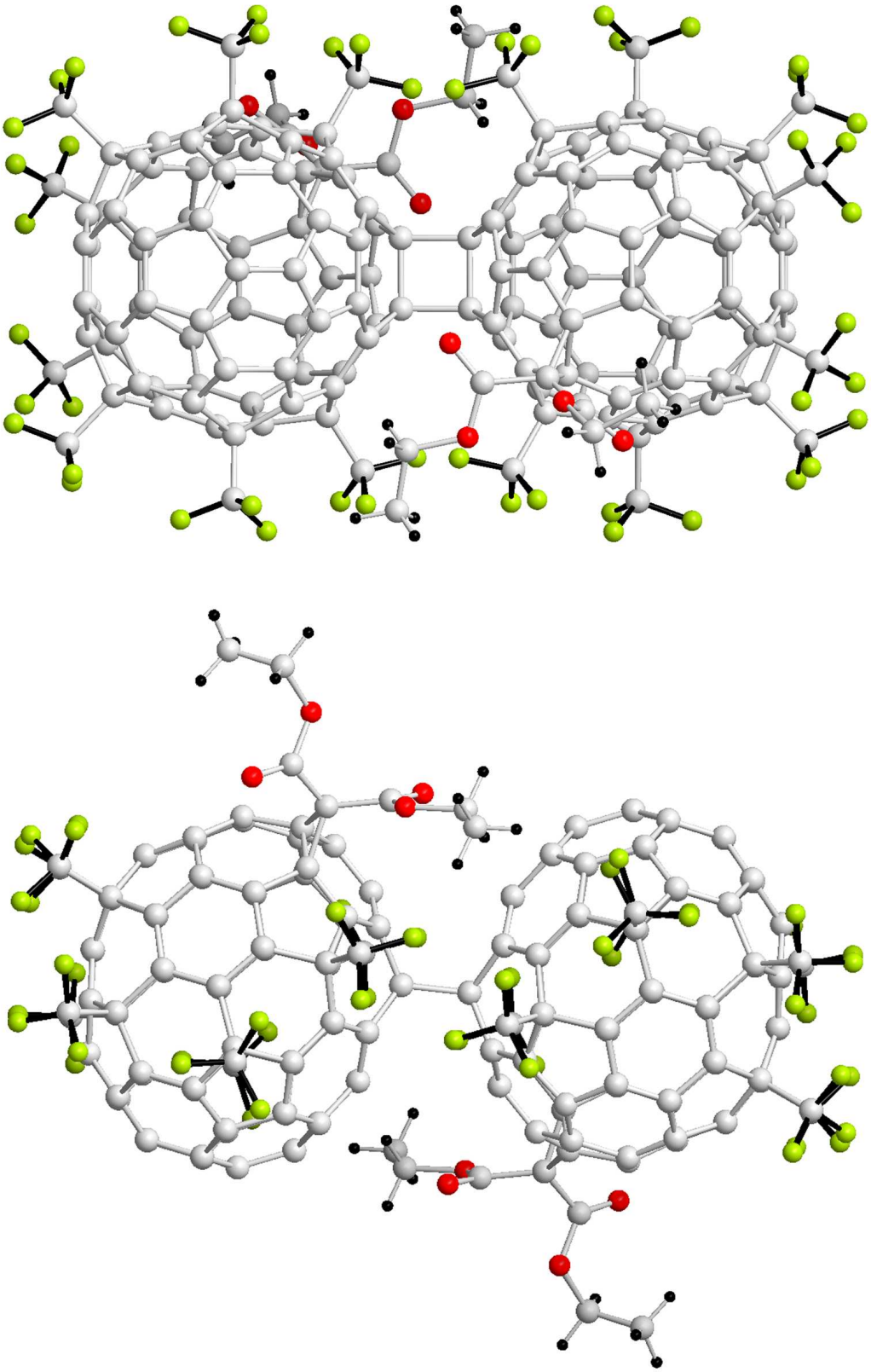


Figure S2. Top and side projections of $\{C_{70}(CF_3)_8[C(CO_2Et)_2]\}_2$*-II.*

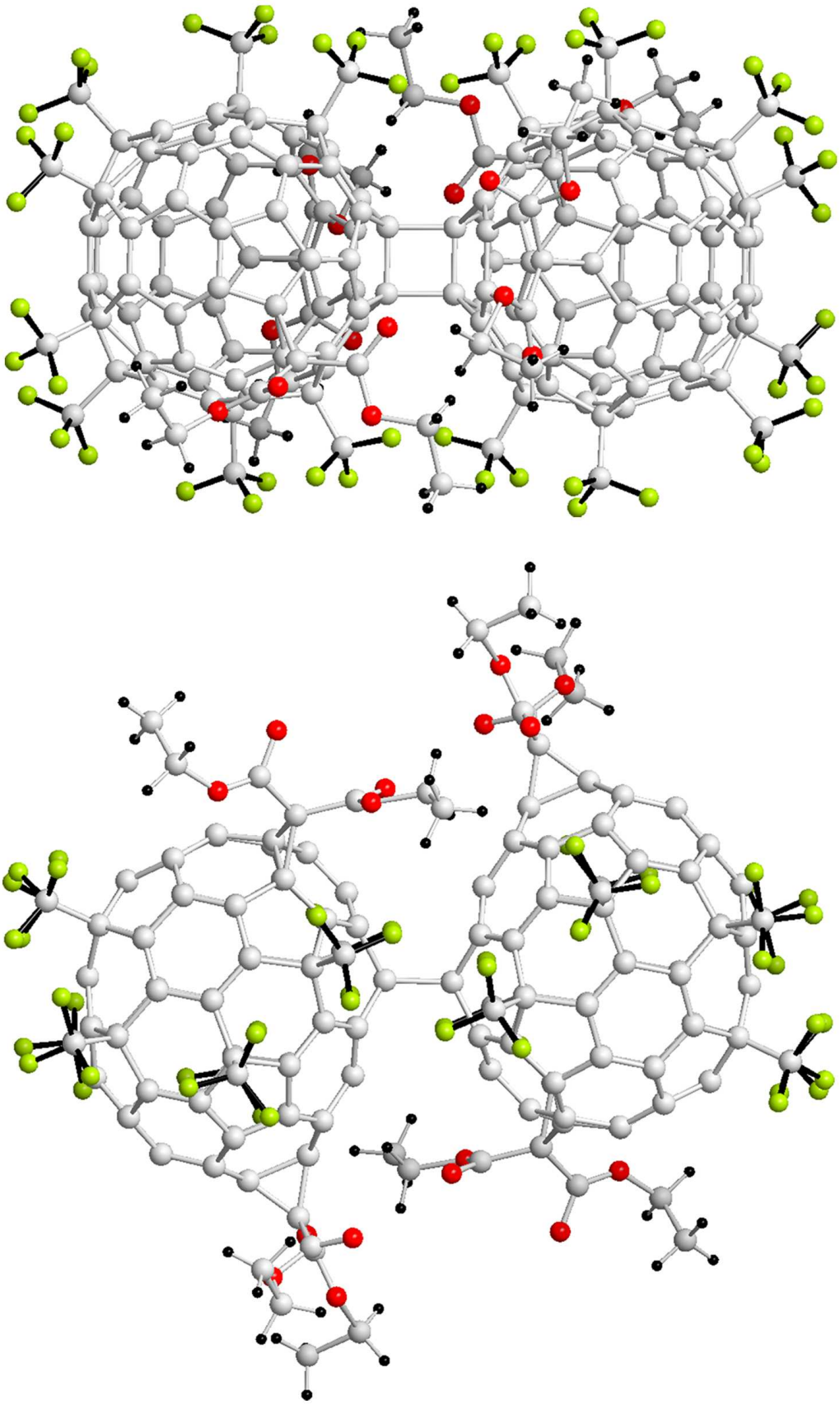


Figure S3. Top and side projections of $\{C_{70}(CF_3)_8[C(CO_2Et)_2]_2\}_2$.

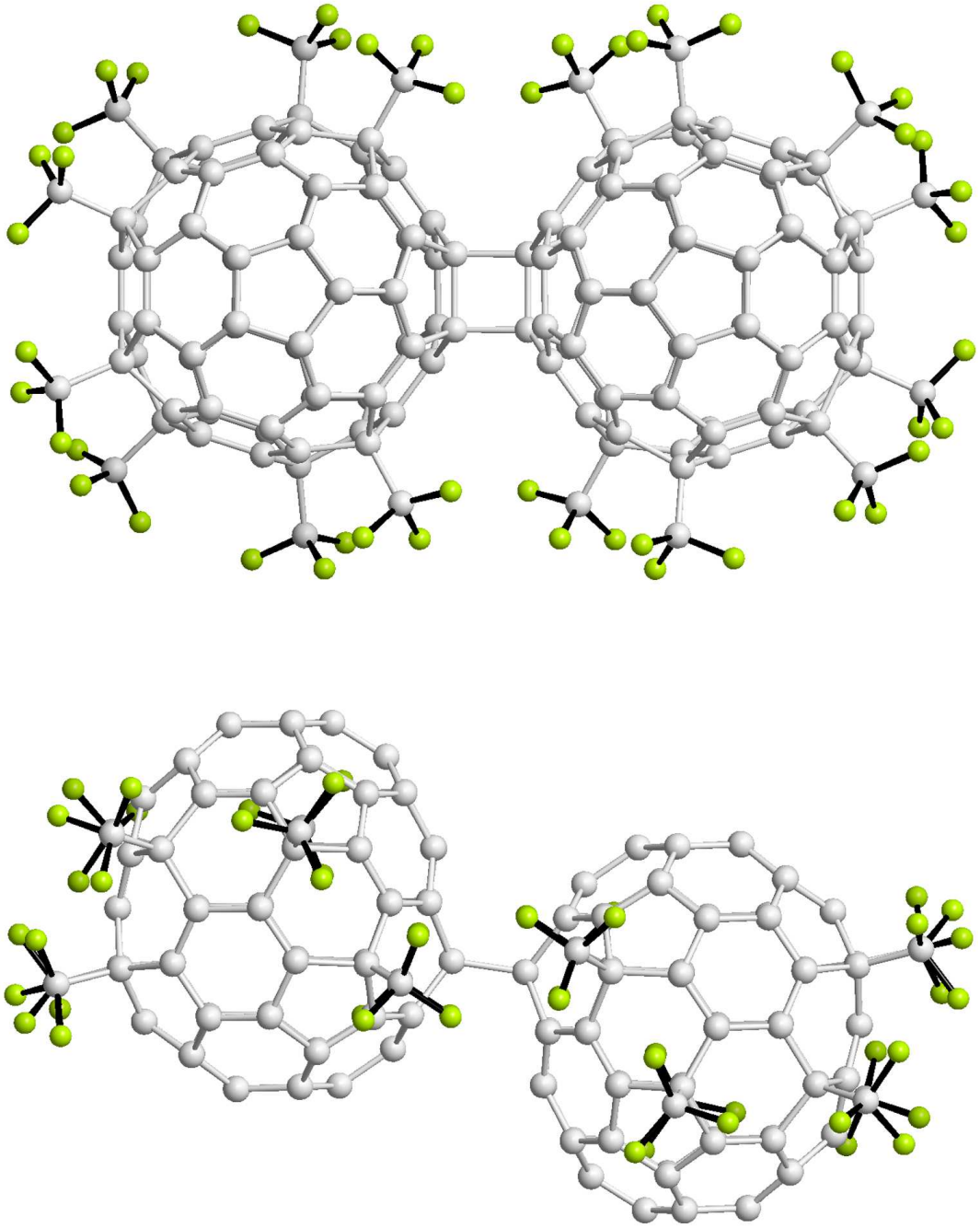


Figure S4. Top and side projections of $\{C_{70}(CF_3)_8\}_2$.

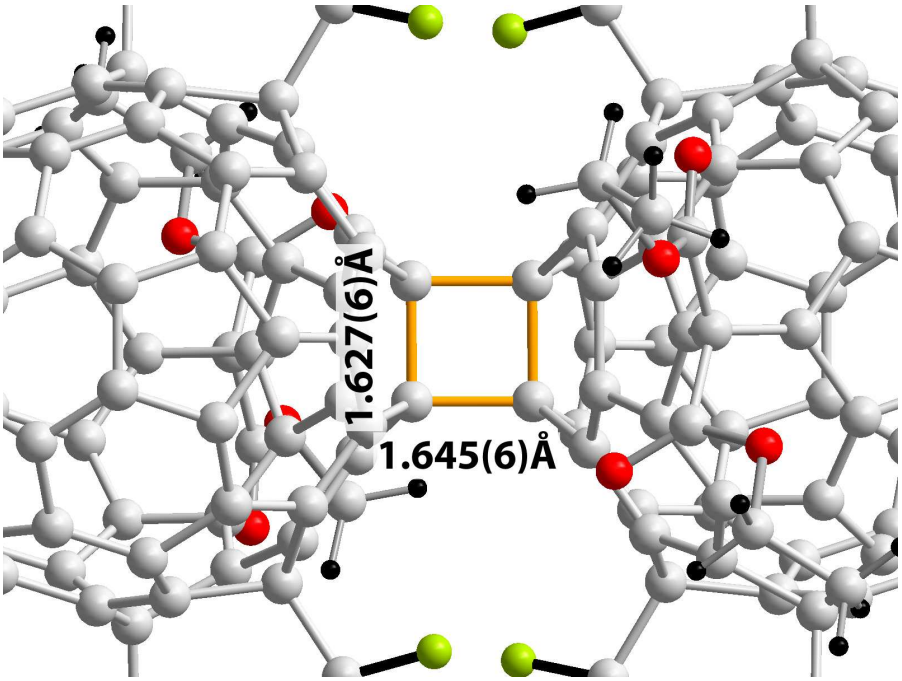


Figure S5.Cyclobutane connection of bispheric $\{C_{70}(CF_3)_8[C(CO_2Et)_2]\}_2$*-I*

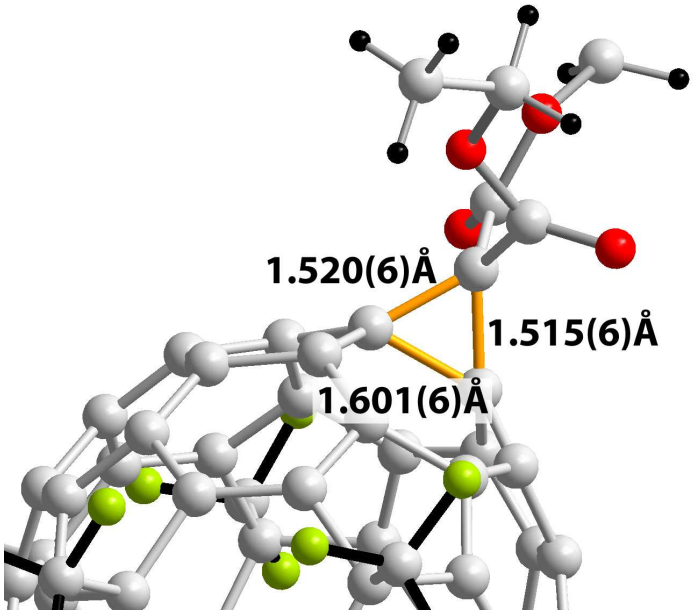


Figure S6. Cyclopropane moiety in the structure $\{C_{70}(CF_3)_8[C(CO_2Et)_2]\}_2$*-I*

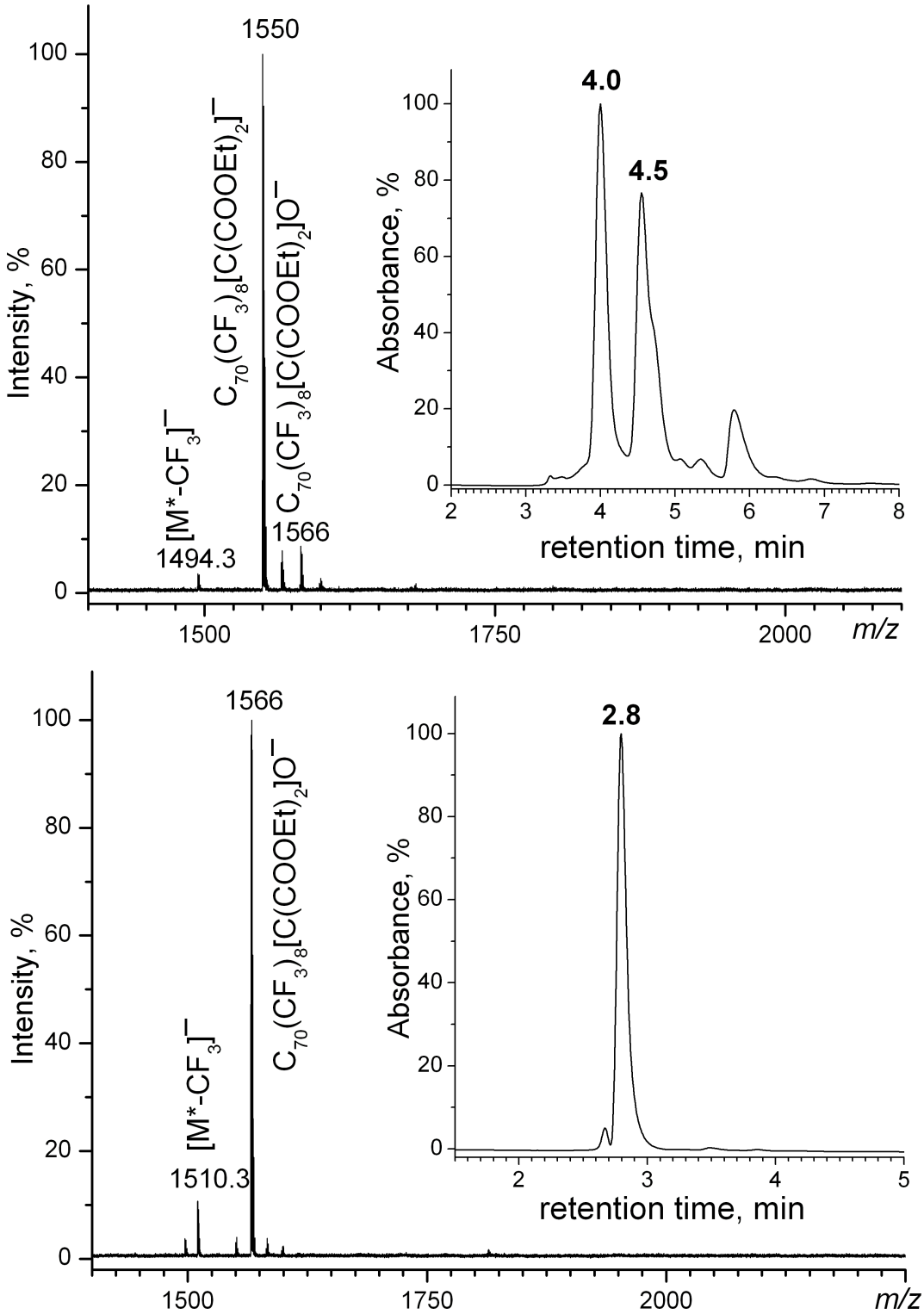


*Figure S7. The negative ion MALDI mass spectrum and the HPLC trace (inset, Cosmosil Buckyprep 10 I.D. mm × 25 cm, toluene, 4.6 mL·min^{-1}) of fraction **p1** after NMR analysis (top). The negative ion MALDI mass spectrum and the HPLC trace (inset, Cosmosil Buckyprep 4.6 I.D. mm × 25 cm, toluene, 2 mL·min^{-1}) of fraction with retention time 4.0 min (bottom).*

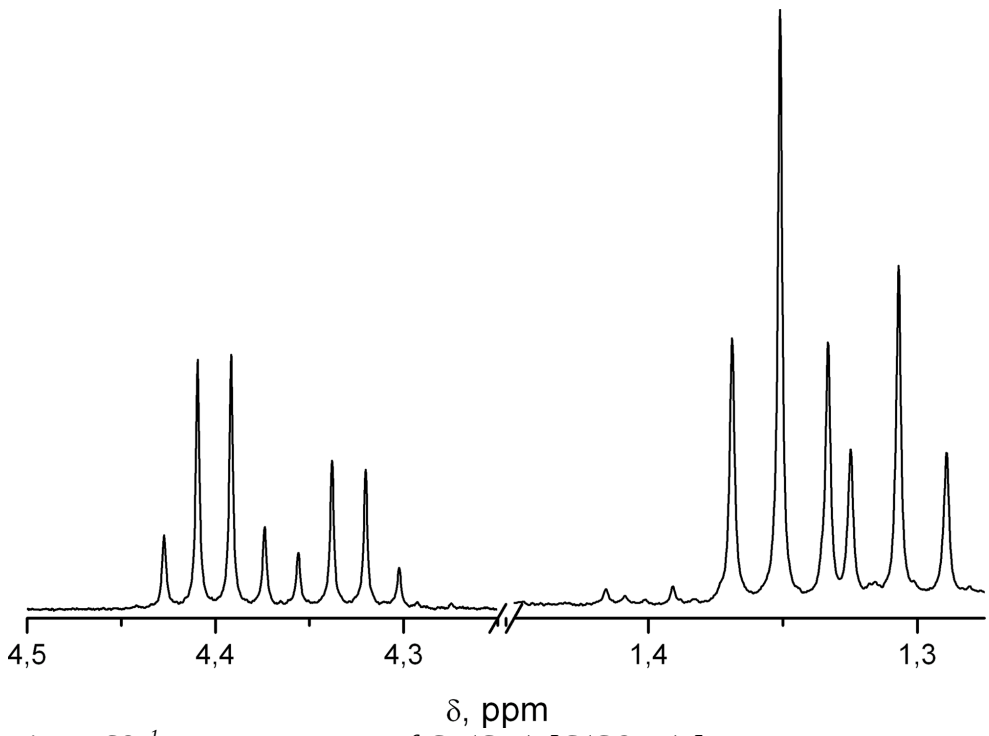


Figure S8. ^{1}H *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-I*

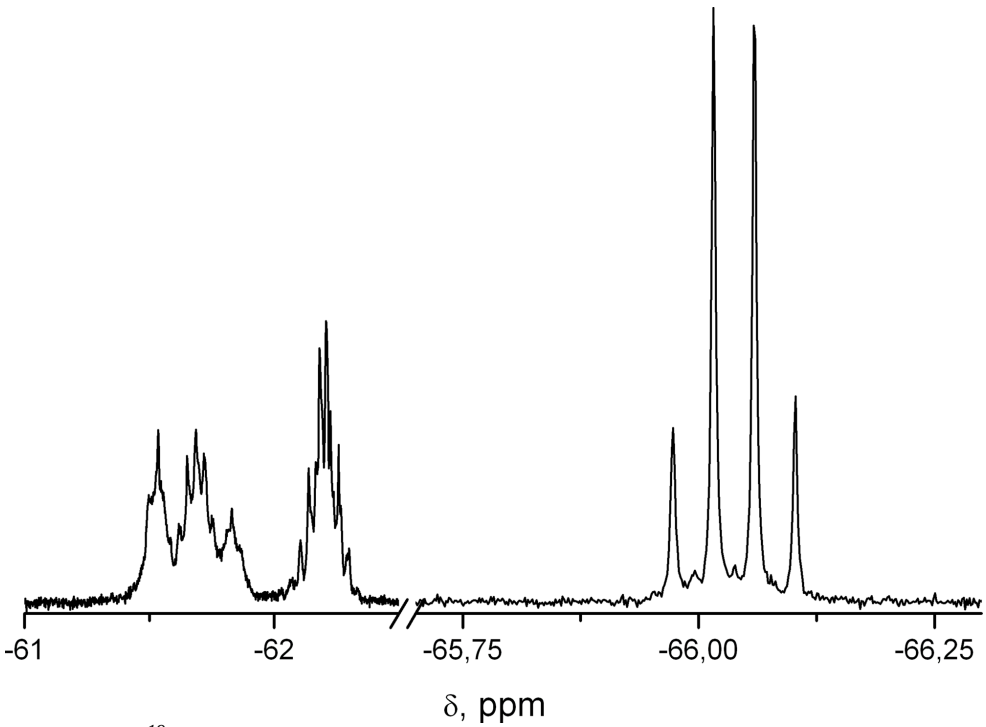


Figure S9. ^{19}F *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-I*

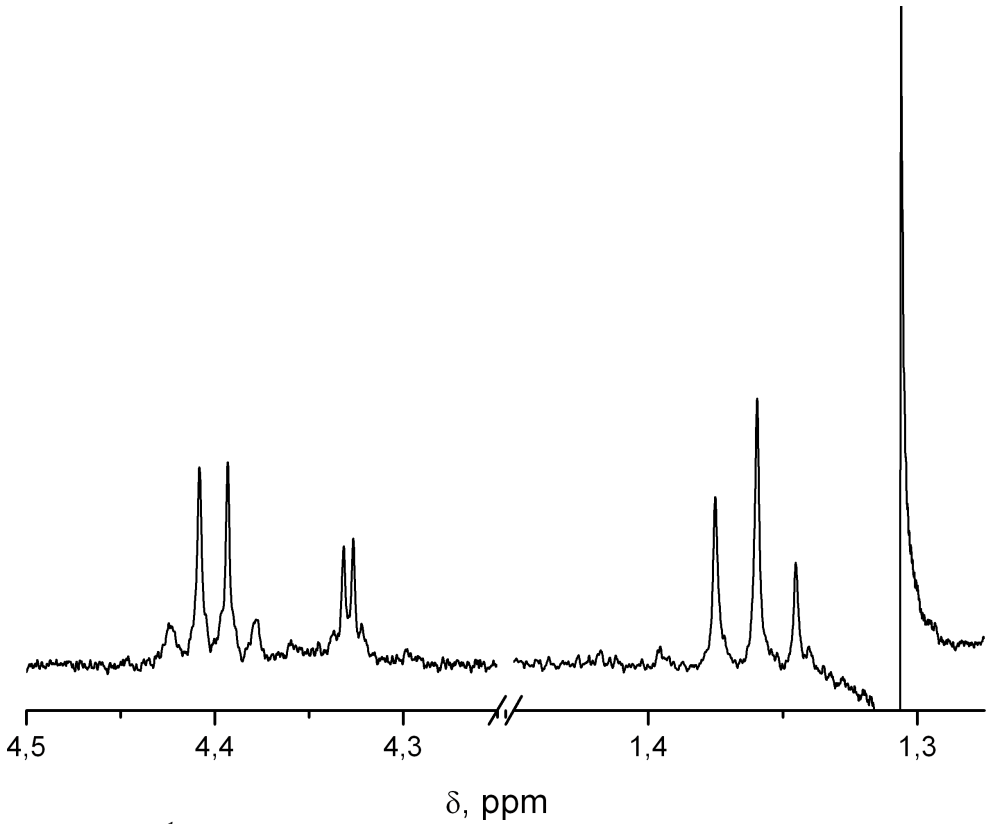


Figure S10. ^{1}H *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-I,* CH_3 *protons (δ=1.31 ppm) decoupled*

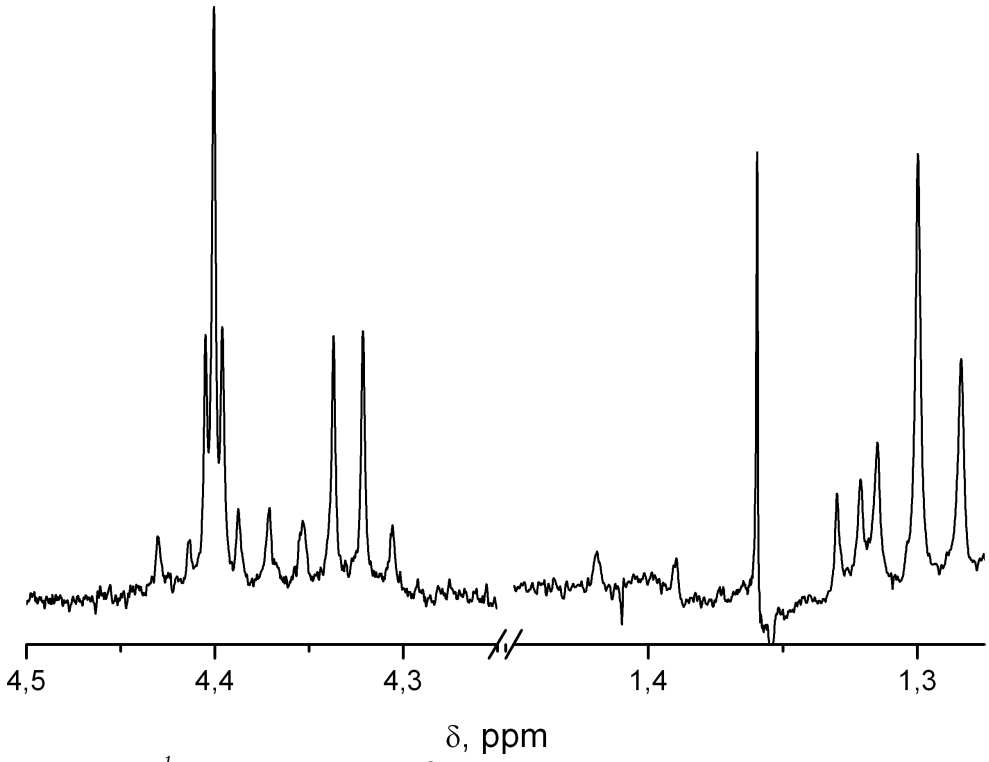


Figure S11. ^{1}H *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-I,* CH_3 *protons (δ=1.36 ppm) decoupled*

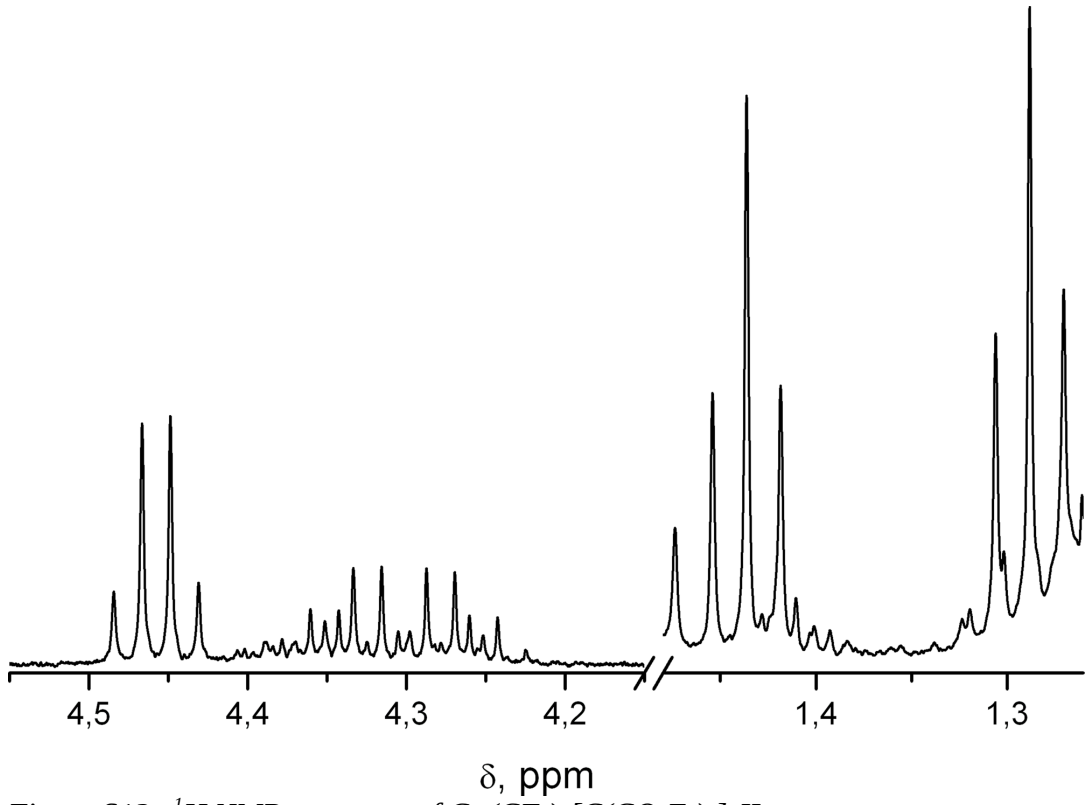


Figure S12. ^{1}H *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-II*

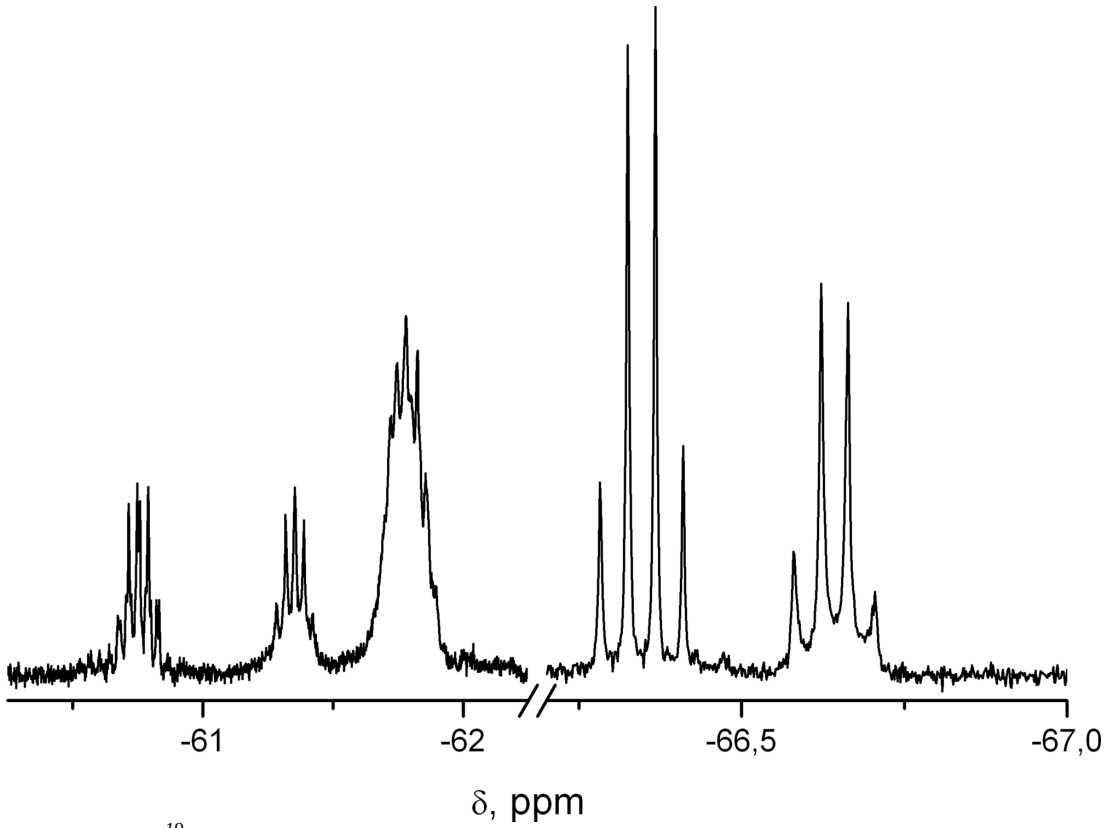


Figure S13. ^{19}F *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-II*

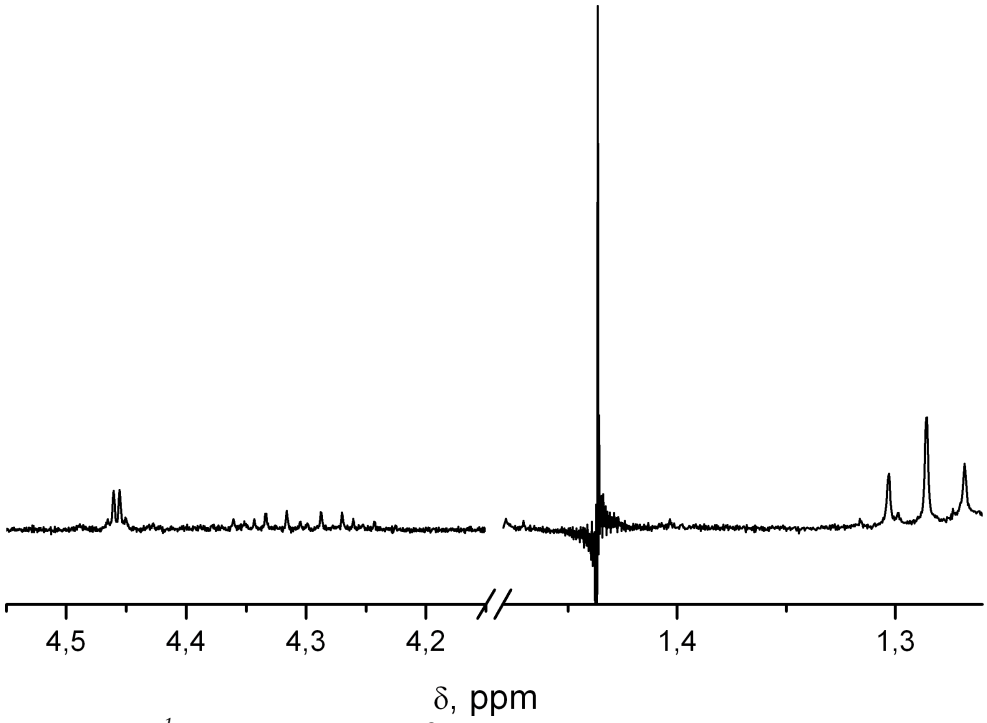


Figure S14. ^{1}H *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-II,* CH_3 *protons (*δ*=1.44 ppm) decoupled*

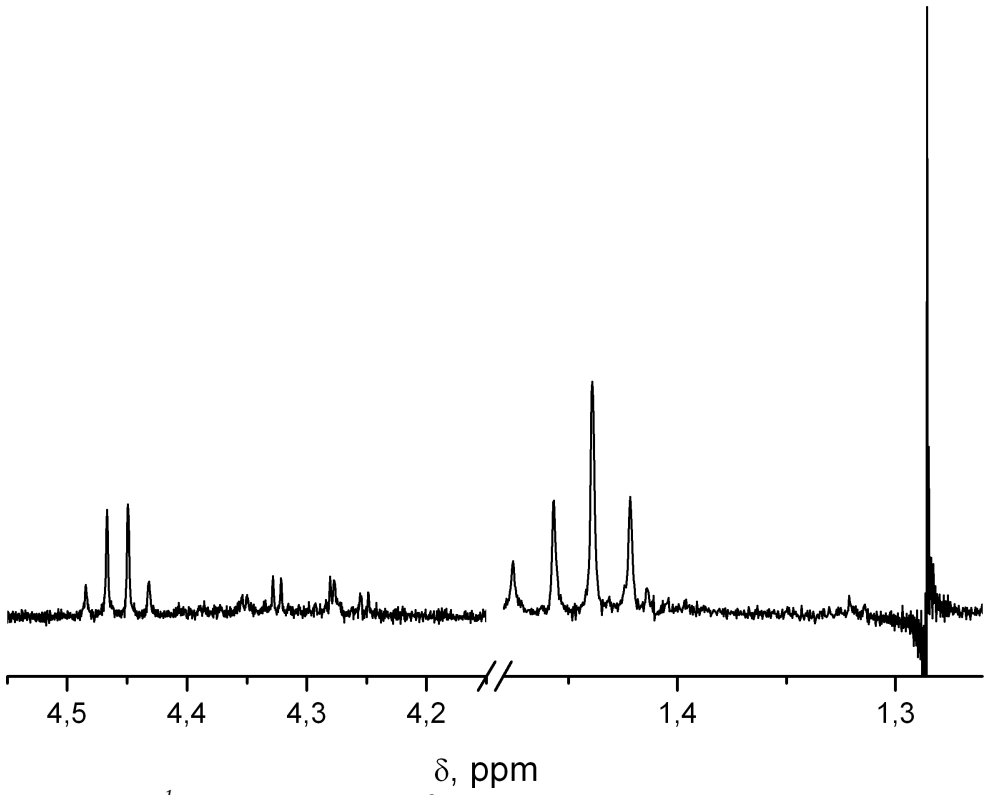


Figure S15. ^{1}H *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]$*-II,* CH_3 *protons (*δ*=1.29 ppm) decoupled*

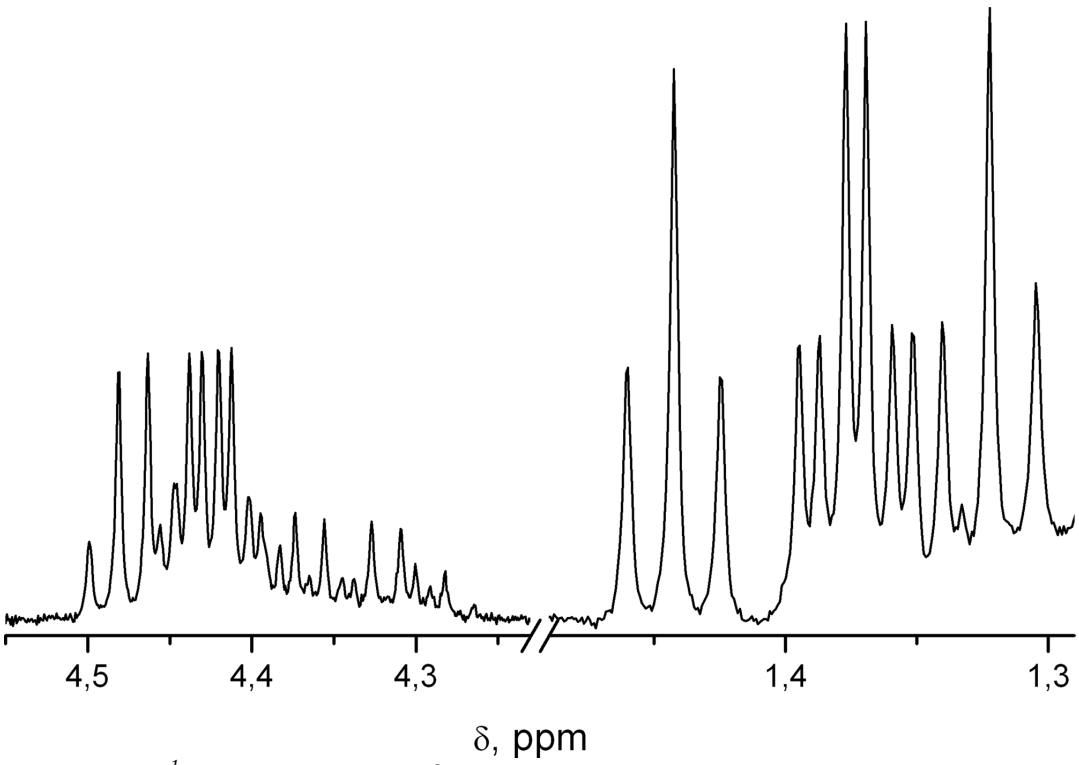


Figure S16. ^{1}H *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$

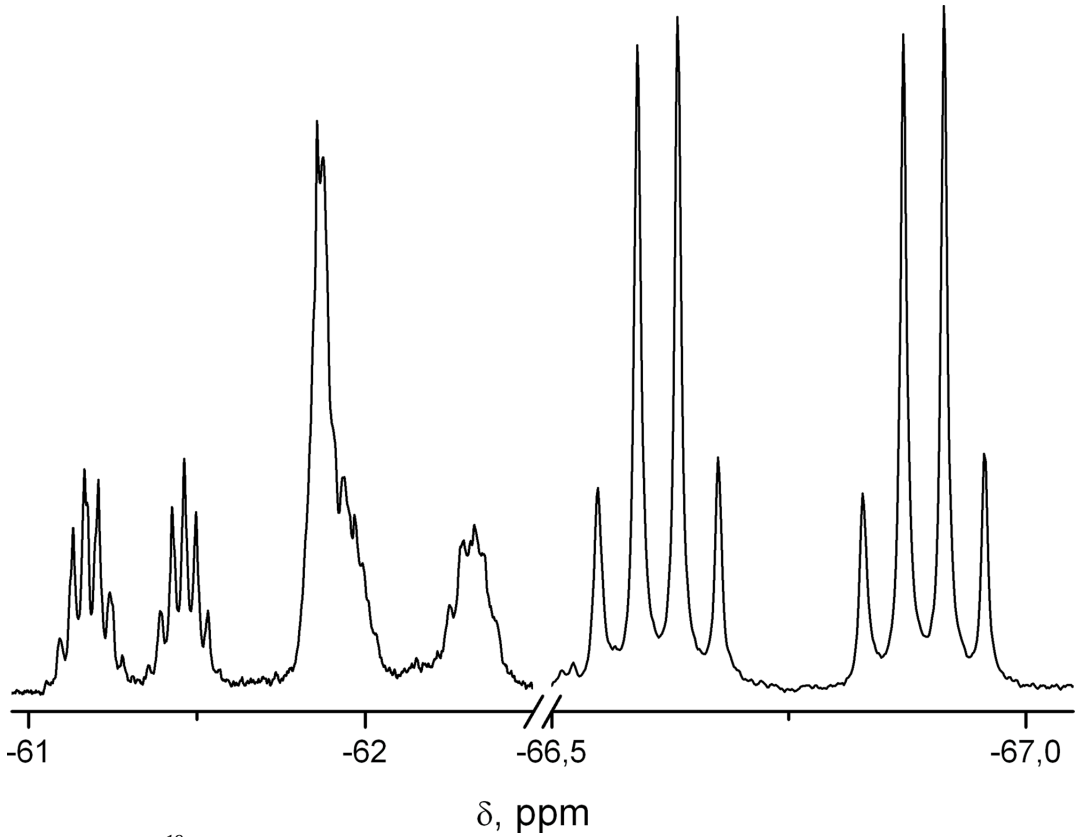


Figure S17. ^{19}F *NMR spectrum of* $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$

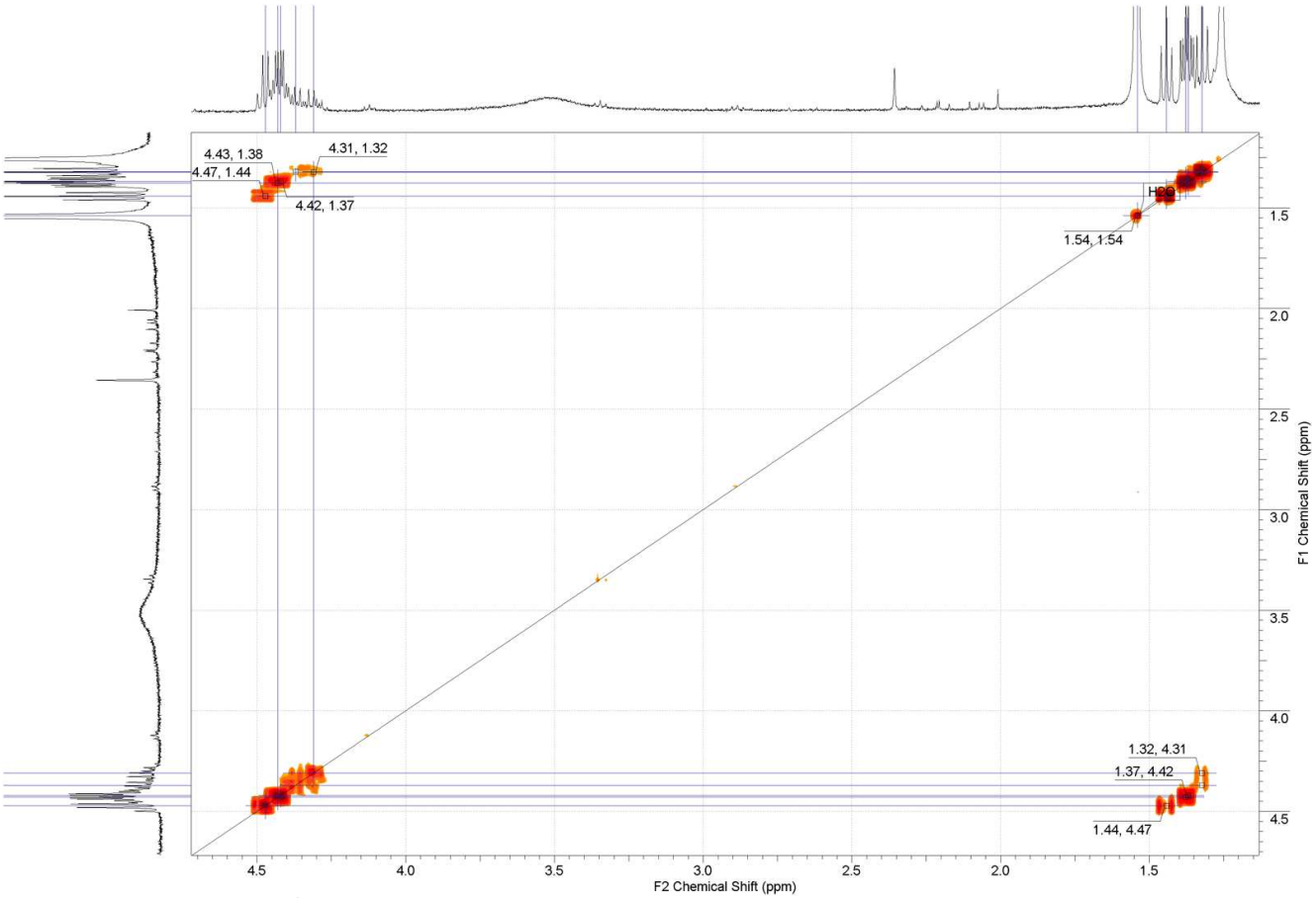


Figure S18. 2D COSY ^{1}H NMR spectrum of $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$

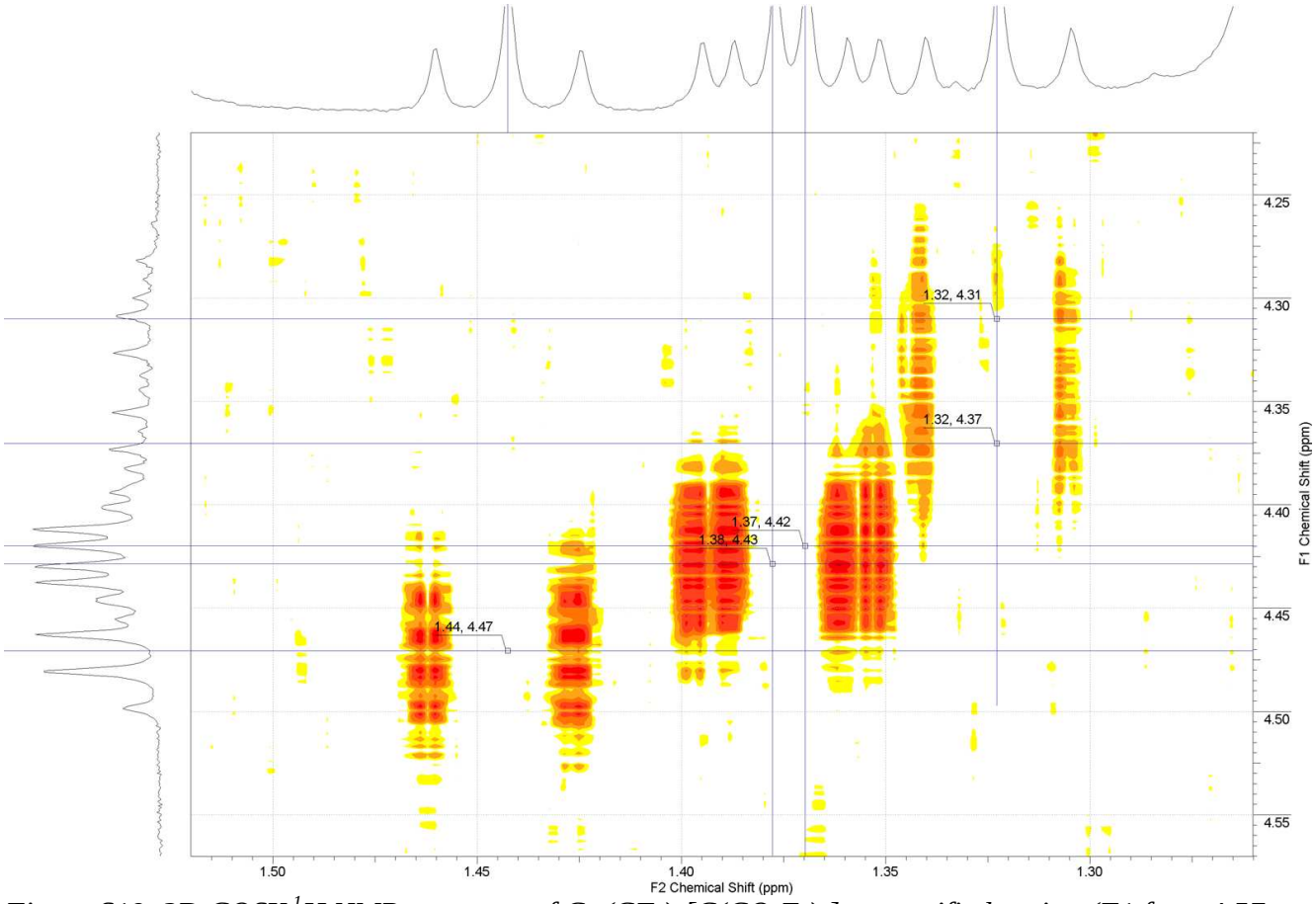


Figure S19. 2D COSY ^{1}H NMR spectrum of $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$, magnified region (F1 from 4.57 to 4.22 ppm × F2 from 1.55 to 1.35 ppm) of Fig.S18.

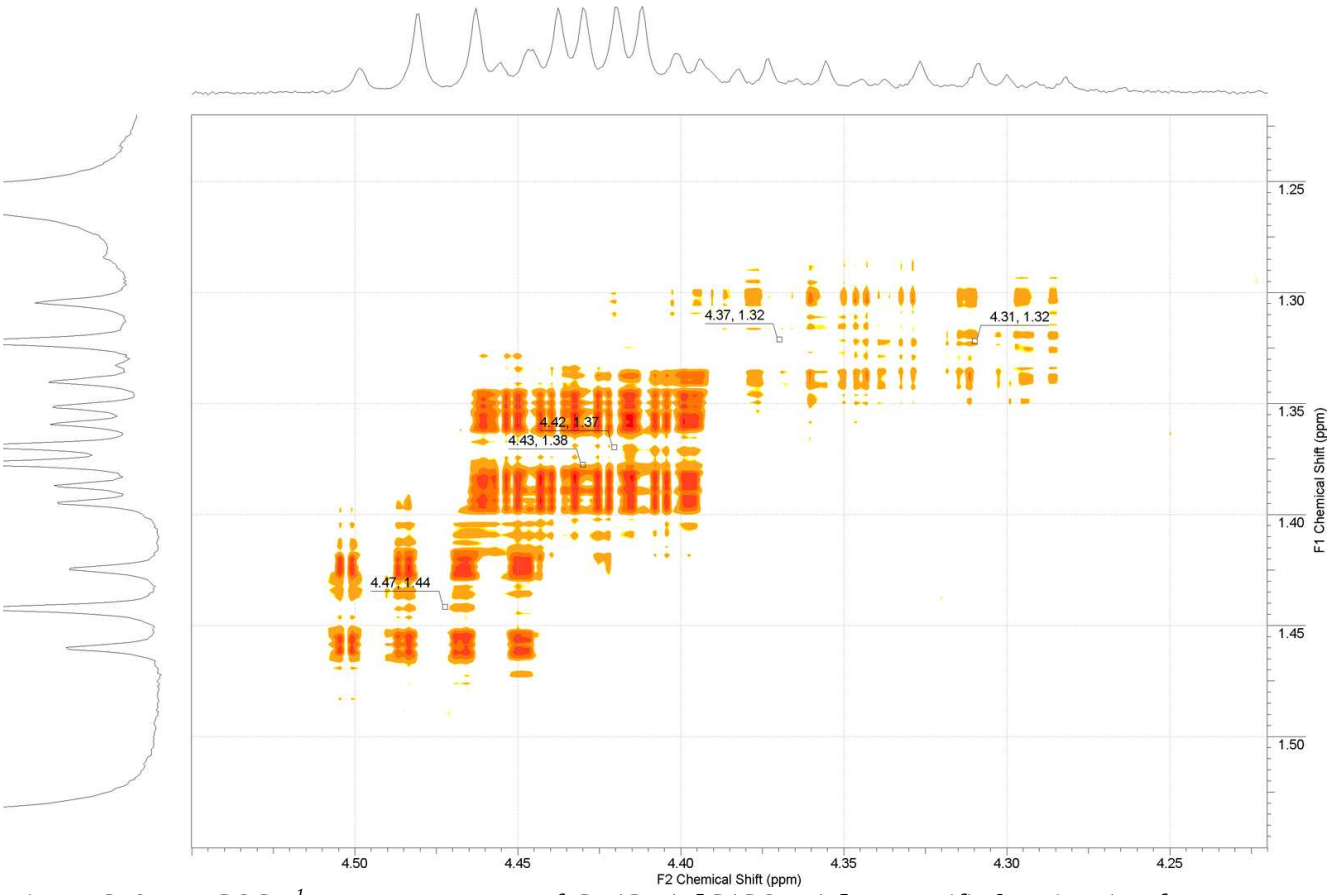


Figure S20. 2D COSY ^{1}H NMR spectrum of $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$, magnified region (F1 from 1.55 to 1.22 ppm × F2 from 4.65 to 4.21 ppm)of Fig.S18.

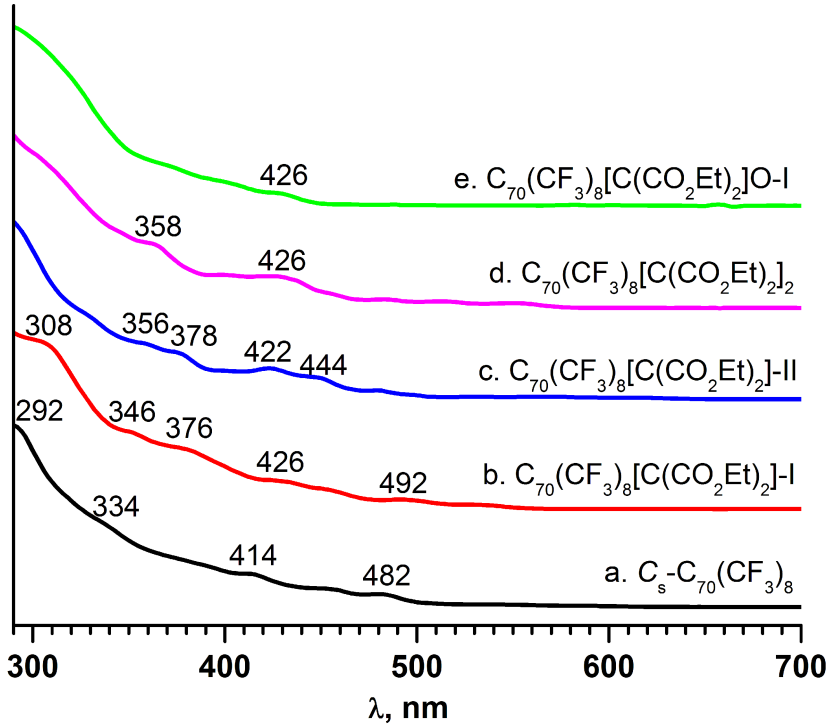


Figure S21. UV/Vis spectra of $C_{70}(CF_3)_8[C(CO_2Et)_2]_n$, n=1,2 and $C_{70}(CF_3)_8[C(CO_2Et)_2]$O-I (290–700 nm, toluene)

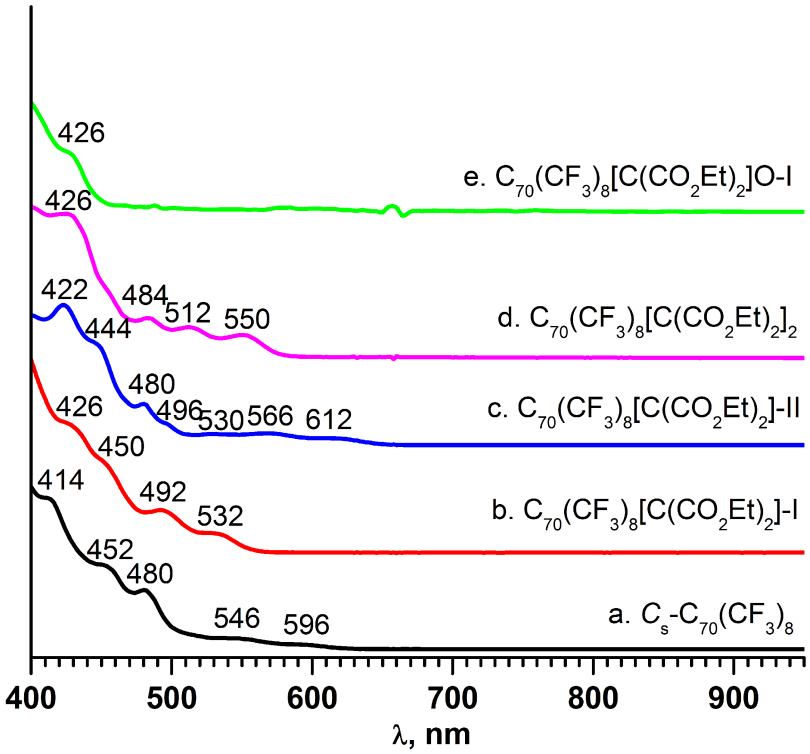


Figure S22. UV/Vis spectra of $C_{70}(CF_3)_8[C(CO_2Et)_2]_n$, n=1,2 and $C_{70}(CF_3)_8[C(CO_2Et)_2]$O-I (400–950 nm, toluene)

Isomer list

The full lists of considered in the work diethyl malonate C_s-$C_{70}(CF_3)_8$ mono- and bisadducts include all possible cycloaddition at pairs of adjacent sp^2 cage carbon atoms of C_s-$C_{70}(CF_3)_8$ molecule. Also possible $C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ intermediates as well as $C_{70}(CF_3)_8H^-$ anionic species were considered. The total isomers counts, count isomers considered at the AM1, single point DFT (spDFT), and DFT levels of theories are given in the Table *S*1.

Initially, molecular geometry of the isomers was optimized by TINKER 4.2 molecular mechanic package with MM2 parameter sets [S1]. Further preliminary geometry optimization for these molecules was carried out at the AM1 level of theory with the use of the Firefly QC software (7.1.C,[S2] partially based on GAMESS (US) source code[S3]). Single point DFT calculation of AM1 optimized geometries, final optimizations and calculation of ^{19}F NMR shielding tensors at the DFT level of theory were performed with the use of the PRIRODA v. 6 software.[S4] PBE exchange-correlation functional[S5] and an original basis set of triple zeta quality with (11s6p2d)/[6s3p2d] contraction scheme for second row atoms were used. Calculation of ^{19}F NMR shielding tensors (GIAO method[S6]) of all species involved was carried out for optimized geometries (10^{-5} Hartree/Å RMS energy gradient).

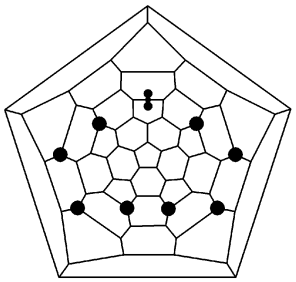
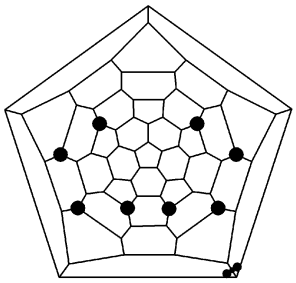
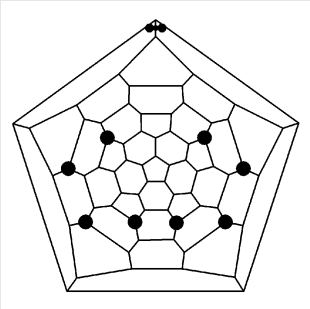
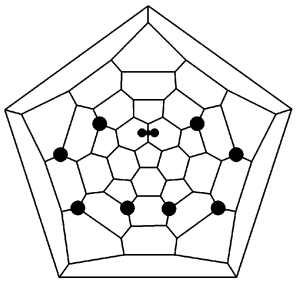
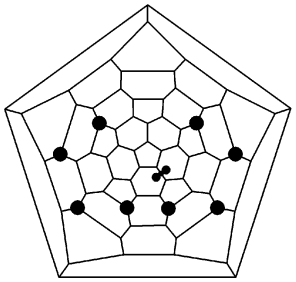
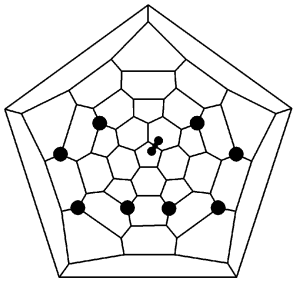
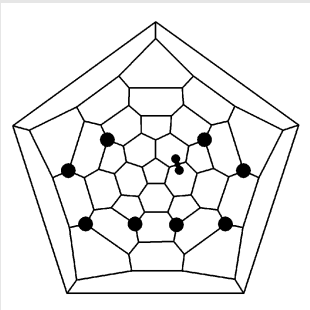
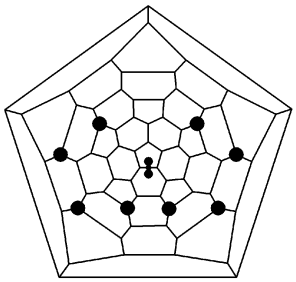
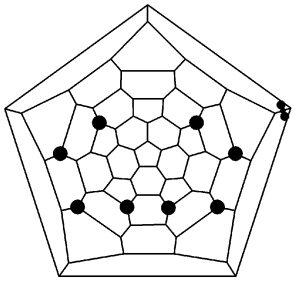
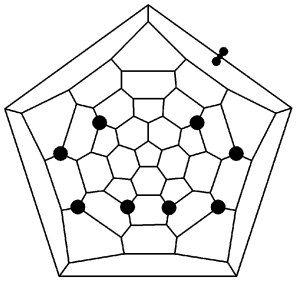
Table S1. Calculation details

$C_{70}(CF_3)_8R_n$,		**Isomer Count**			
R	***n* =**	**Total**	**AM1 considered**	**spDFT**	**DFT considered**
$C[CO_2Et]_2$	**1**	45	45	45	17[b]
	2	1585	1585	214[a]	25[c]
$CBr(CO_2Et)_2^-$	**1**	33	33	12[d]	12
H^-	**1**	33	33	17[d]	–

[a] 100 kJ mol^{-1} AM1 energy gap; [b] 50 kJ mol^{-1} spDFT energy gap; [c] 30 kJ mol^{-1} spDFT energy gap; [d] 50 kJ mol^{-1} AM1 energy gap;

[S1] TINKER molecular modeling software version 4.2, http://dasher.wustl.edu/tinker/index.html
[S2] A. A. Granovsky, Firefly version 7.1.C, http://classic.chem.msu.su/gran/firefly/index.html
[S3] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T., Elbert,M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A., Nguyen, S. Su, T. L.Windus, M. Dupuis and J. A. Montgomery, J. Comput. Chem., 1993, 14, 1347.
[S4] D. N. Laikov, *Chem. Phys. Lett*., 1997, **281**, 151.
[S5] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 38656.
[S6] J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch. J. Chem. Phys., 1996, 104, 5497.

Table S2. Schlegel diagrams, relative energies (at the DFT, single point DFT and AM1 levels of theory) for the most stable isomers of $C_{70}(CF_3)_8C(CO_2Et)_2$ within the DFT energy gap of 40 kJ mol^{-1}. Experimental observed isomers are marked by gray filling.

#	$C_{70}(CF_3)_8[C(CO_2Et)_2]$ Schlegel diagram	ΔE, kJ·mol^{-1}			#	$C_{70}(CF_3)_8[C(CO_2Et)_2]$ Schlegel diagram	ΔE, kJ·mol^{-1}		
		DFT	spDFT	AM1			DFT	spDFT	AM1
1		0.0	0.0	0.0	6		23.7	26.1	13.0
2		12.3	15.2	-1.8	7		26.0	30.6	13.5
3		16.5	17.5	10.1	8		27.5	27.6	-9.4
4		19.4	17.4	5.5	9		27.9	30.6	-0.2
5		23.5	25.4	14.1	10		31.8	29.4	-13.2

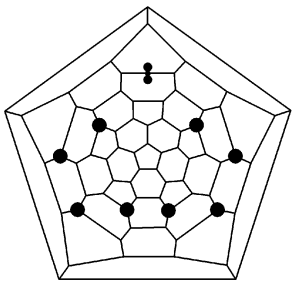
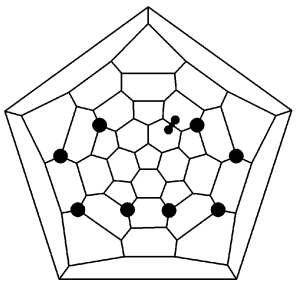
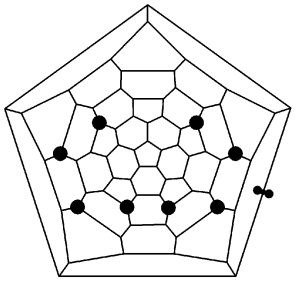
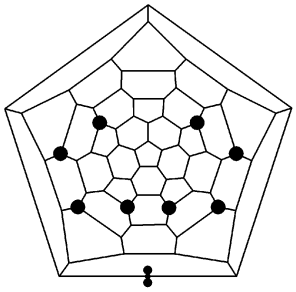
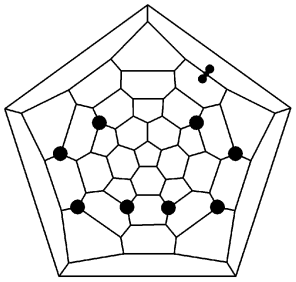
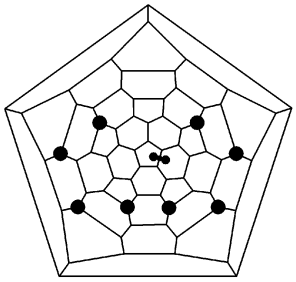
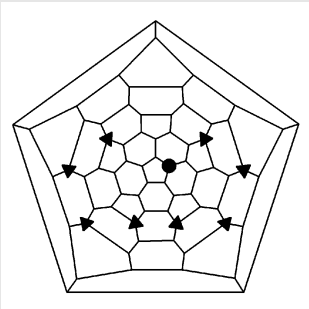
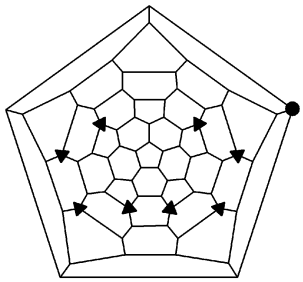
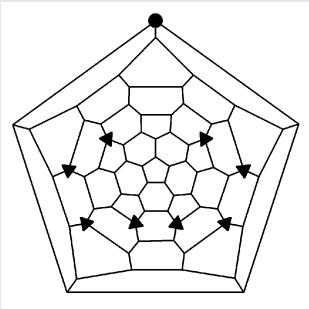
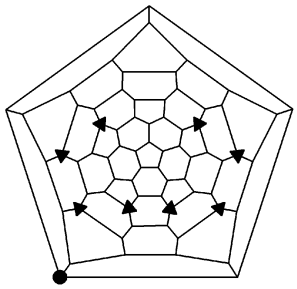
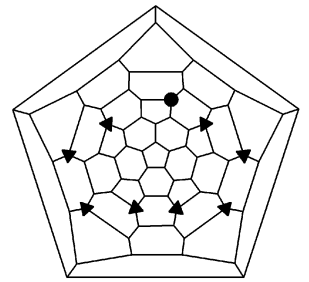
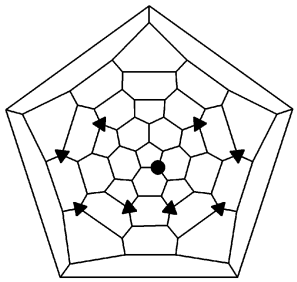
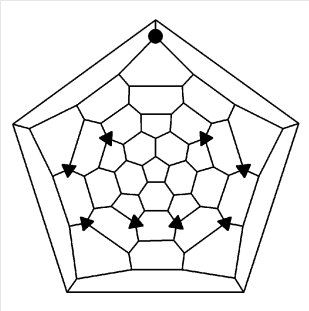
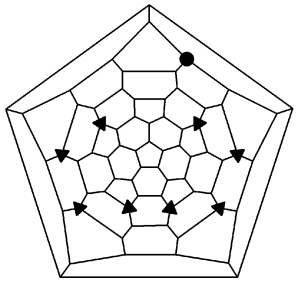
#	$C_{70}(CF_3)_8[C(CO_2Et)_2]$ Schlegel diagram	ΔE, kJ·mol^{-1}			#	$C_{70}(CF_3)_8[C(CO_2Et)_2]$ Schlegel diagram	ΔE, kJ·mol^{-1}		
		DFT	spDFT	AM1			DFT	spDFT	AM1
11		32.7	36.4	-9.7	14		35.5	34.7	39.6
12		32.8	36.4	4.2	15		36.5	34.9	-10.9
13		32.9	43.5	29.5	16		36.8	36.7	-8.5

Table S3. Schlegel diagrams, relative energies (at the DFT, single point DFT and AM1 levels of theory) for the most stable anions $C_{70}(CF_3)_8CBr(CO_2Et)_2^-$ within the DFT energy gap of 50 kJ mol^{-1}.The corresponding energy values of $C_{70}(CF_3)_8H^-$ with same addend moiety are given in the brackets. Intermediates leading to experimental observed isomers are marked by gray filling.

#	$C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ Schlegel diagram	ΔE, kJ·mol^{-1}			#	$C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ Schlegel diagram	ΔE, kJ·mol^{-1}		
		DFT	spDFT	AM1			DFT	spDFT	AM1
1		0.0	0.0 (0.0)	0.0	5		23.4	31.4 (31.8)	30.7
2		7.4	16.2 (18.9)	10.0	6		27.2	37.7 (46.4)	26.1
3		18.4-22.8	29.3 (-9.4)	14.7-27.1	7		29.9	43.5 (44.4)	29.1
4		18.6	15.6 (24.5)	10.5	8		32.7	42.2 (43.4)	31.6

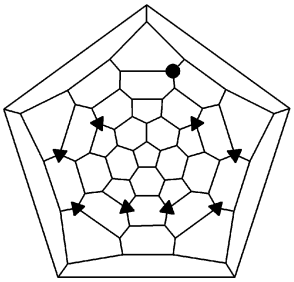
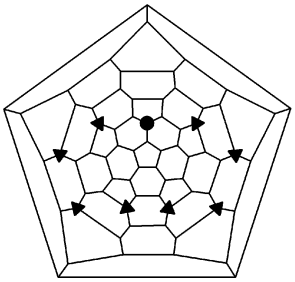
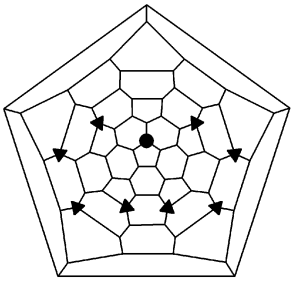
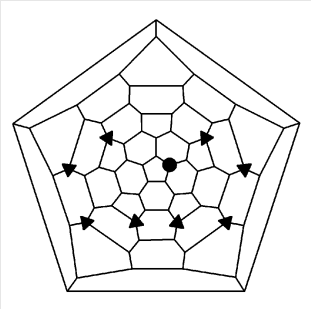
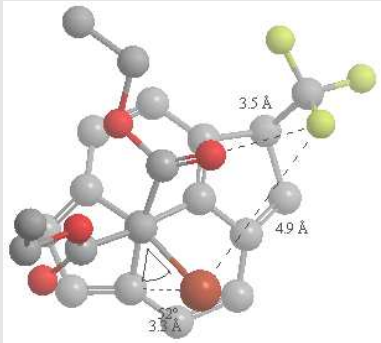
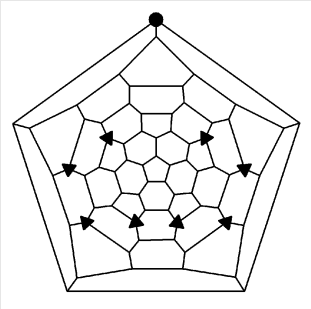
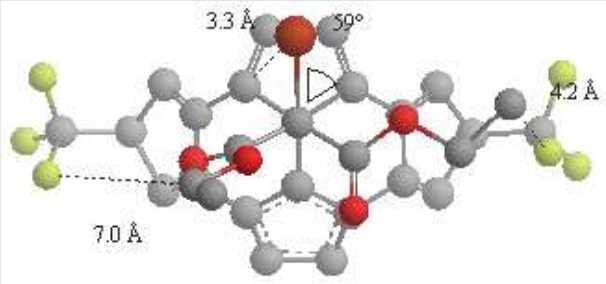
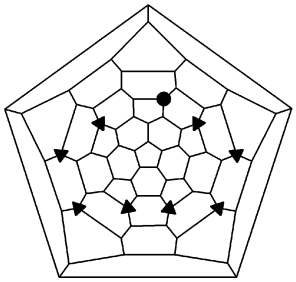
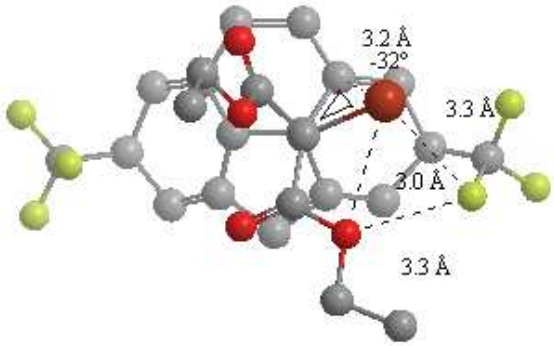
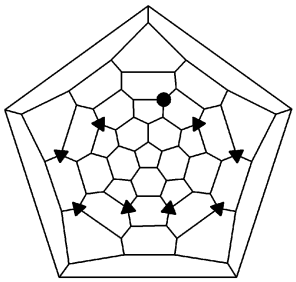
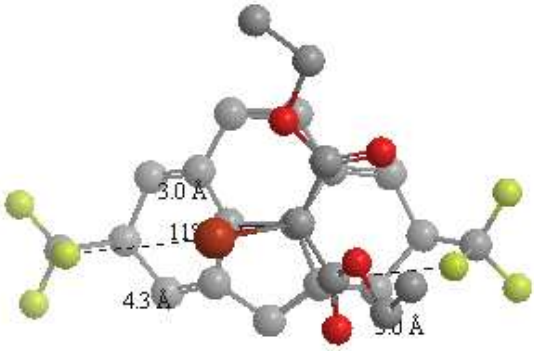
#	$C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ Schlegel diagram	ΔE, kJ·mol^{-1}			#	$C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ Schlegel diagram	ΔE, kJ·mol^{-1}		
		DFT	spDFT	AM1			DFT	spDFT	AM1
9		33.4	44.6 (36.4)	37.1	11		43.4	45.9	43.2
10		34.6	43.4	37.9					

Table S4: Schlegel diagrams, relative DFT energies and fragments of 3D projections of $C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ anionic intermediates. Intermediates leading to experimental observed isomers are marked by gray filling.

#	$C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ Schlegel diagram	DFT ΔE, kJ·mol^{-1}		3D projections of intermediate
		Intermediate	Product	
1		0.0	19.4	
2		7.4	12.3	
3		18.4	0.0	
4		22.8	0.0	

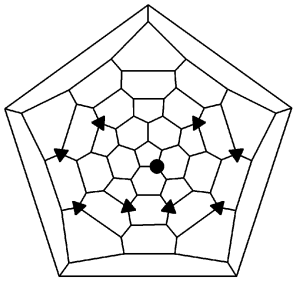
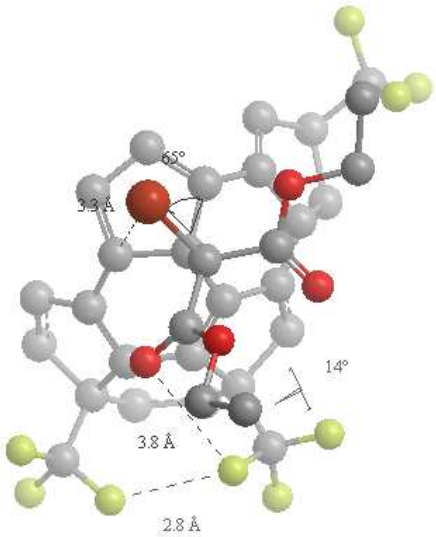
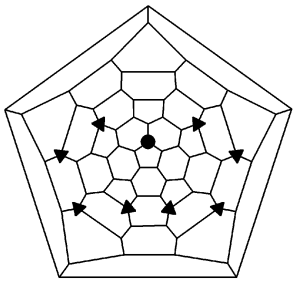
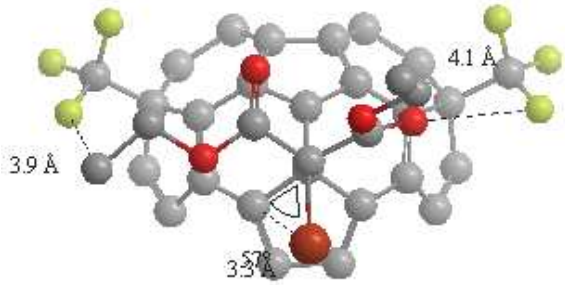
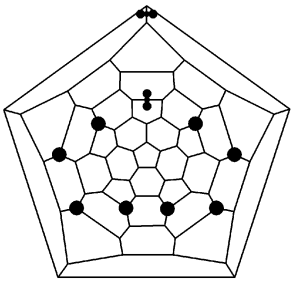
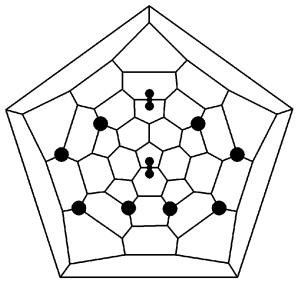
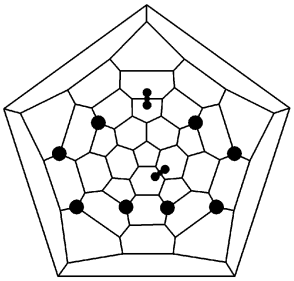
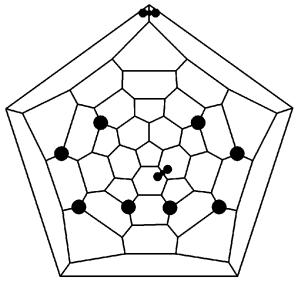
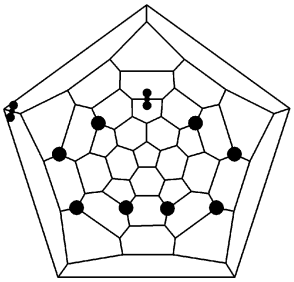
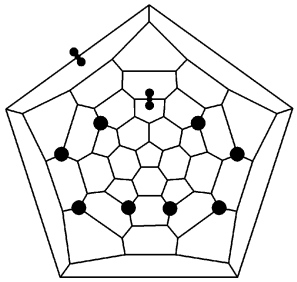
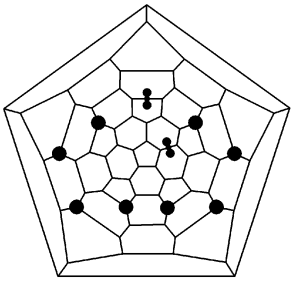
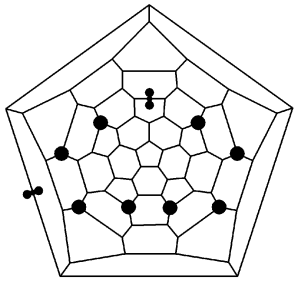
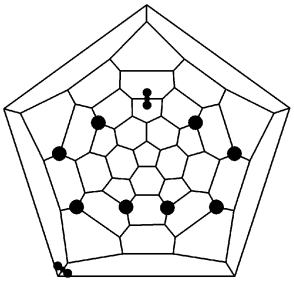
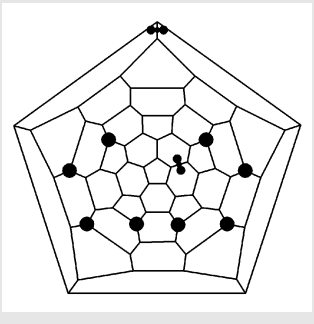
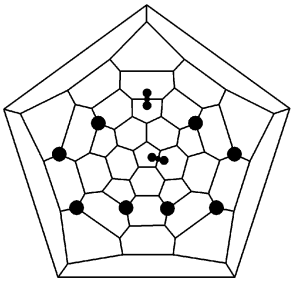
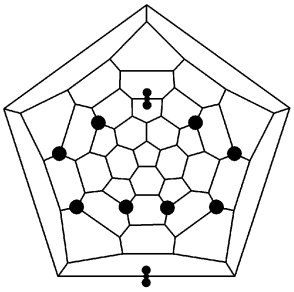
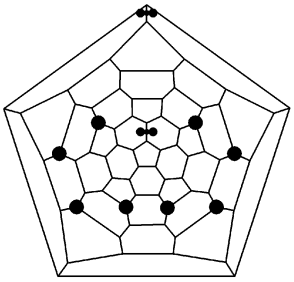
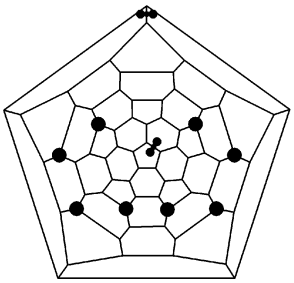
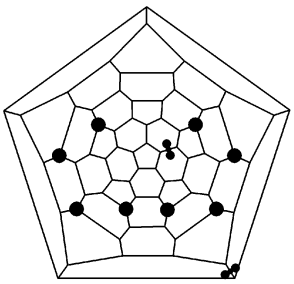
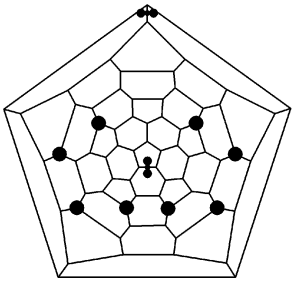
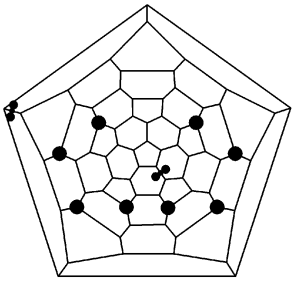
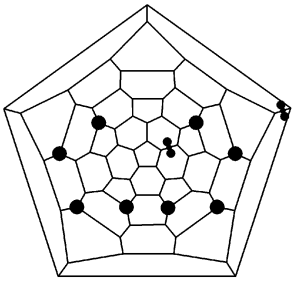
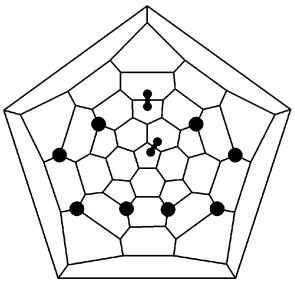
5		29.9	16.2	
6		34.6	25.5	

Table S5. Schlegel diagrams, relative energies (at the DFT, single point DFT and AM1 levels of theory) for the most stable isomers of $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ within the DFT energy gap of 30 kJ mol^{-1}. Experimental observed isomer is marked by gray filling.

#	$C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ Schlegel diagram	ΔE, kJ·mol^{-1}			#	$C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ Schlegel diagram	ΔE, kJ·mol^{-1}		
		DFT	spDFT	AM1			DFT	spDFT	AM1
1		0.0	0.0	0.0	6		17.2	20.4	4.0
2		7.0	3.7	14.7	7		18.4	14.6	12.3
3		8.7	5.3	15.3	8		18.8	14.4	-9.4
4		13.0	10.8	14.5	9		19.7	20.0	8.2
5		14.2	12.2	17.8	10		19.9	14.8	7.8

#	$C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ Schlegel diagram	ΔE, kJ·mol^{-1}		
		DFT	spDFT	AM1
11		23.4	20.2	-6.8
12		25.1	22.3	-6.0
13		26.3	28.8	15.6
14		27.3	27.3	-7.4
15		27.3	21.5	19.9

#	$C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ Schlegel diagram	ΔE, kJ·mol^{-1}		
		DFT	spDFT	AM1
16		28.1	29.5	1.8
17		28.4	26.6	28.9
18		28.8	30.2	23.6
19		29.2	27.7	10.3