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Orienting effect of the cage addends: the case of nucleophilic cyclopropanation of C_2-$C_{70}(CF_3)_8$

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Abstract: C_2-$C_{70}(CF_3)_8$ was found to be a very promising substrate in the Bingel and the Bingel-Hirsch reactions combining perfect regioselectivity with much higher reactivity compared to its analogs. The reactions with diethyl malonate yield a single isomer of the monoadduct $C_{70}(CF_3)_8[C(CO_2Et)_2]$ and a single C_2-symmetrical bisadduct $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$. The Bingel-Hirsch variation is particularly interesting in that it additionally affords, in a similar regioselective manner, the unexpected alkylated derivatives $C_{70}(CF_3)_8[CH(CO_2Et)_2]H$ and $C_{70}(CF_3)_8[C(CO_2Et)_2][CH(CO_2Et)_2]H$. The novel compounds have been isolated and structurally characterized by means of ^1H and ^{19}F NMR spectroscopy, single crystal X-ray diffraction. The mechanistic and regiochemical aspects of the reaction are explained with the aid of the DFT calculations.

Introduction

Trifluoromethylated [70]fullerenes, a vast family of compounds with different arrangements of 2 to 20 CF_3 addends,[1–4] show a potential for application in organic electronic devices. They remain chemically stable upon electron transfer and demonstrate good acceptor properties, their first reduction potentials varying within the range of –0.11 to 0.34 V vs $C_{70}^{0/-}$.[2] Moreover, it has been shown recently that the CF_3 addition pattern of C_s-p^7-$C_{70}(CF_3)_8$[‡] confers regioselectivity to a range of addition reactions. In particular, chlorination[5] and cyanation[6] of C_s-p^7-$C_{70}(CF_3)_8$ proceed selectively at its near-equatorial [5,6]-double bond while nucleophilic addition of the bulky diethyl bromomalonate carbanion results in likewise selective cyclopropanation but now at more sterically accessible [6,6]-bonds at the poles of the C_{70} cage.[7] Similarly, the related C_1-p^7mp-$C_{70}(CF_3)_{10}$ demonstrates regioselectivity towards its less sterically hindered pole in the reactions of nucleophilic alkylation[6,8] and [4+2]-cycloaddition.[9] Thus, further functionalization of trifluoromethylated fullerenes is a promising way to selectively introduce predefined regiochemistry and, consequently, chemical and electronic properties.

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C_2-p^7-$C_{70}(CF_3)_8$, the second most abundant isomer, is related to C_s-p^7-$C_{70}(CF_3)_8$ via relocation of only one CF_3 group (Figure 1).[3,4,10] However, this turns out to be enough to effect significant variations between their properties. C_2-p^7-$C_{70}(CF_3)_8$ reveals a dramatic anodic shift of 0.34 V vs $C_{70}^{0/-}$ in its first reduction potential compared to only 0.04 V in C_s-p^7-$C_{70}(CF_3)_8$.[2] Undoubtedly, this difference in electronic properties should be reflected in the reactivity of the compounds, in particular, in the common organic functionalization reactions of fullerenes like nucleophilic addition and [4+2]-cycloaddition.

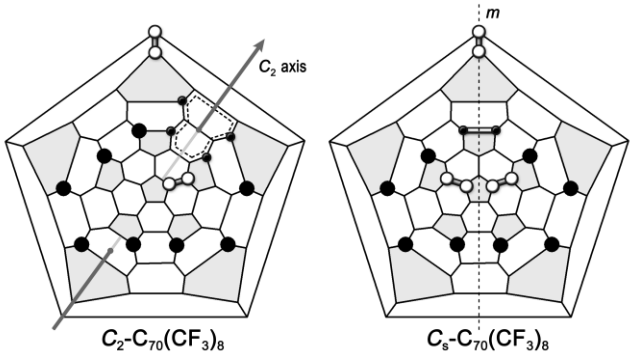


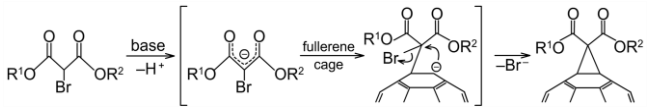
Figure 1. Schlegel diagrams of C_2- and C_s-$C_{70}(CF_3)_8$ where large black circles denote CF_3 groups. Marked otherwise are preferable addition sites of sterically unhindered (small black circles) and bulky (large white circles) addends as revealed by the experimental and theoretical findings of the present paper and of ref. 7.

Here we present our first results on the nucleophilic addition to the C_2-p^7-$C_{70}(CF_3)_8$ (hereinafter C_2-$C_{70}(CF_3)_8$). The Bingel reaction and its modification due to Hirsch were used to determine the most reactive sites in the molecule. We report the major reaction products obtained, the cycloadducts $C_{70}(CF_3)_8[C(CO_2Et)_2]_n$, n=1–2, and the less expected alkylated derivatives with $CH(CO_2Et)_2$ addend.

Results and Discussion

To prepare the precursory C_2-$C_{70}(CF_3)_8$, we used a two-step ampoule protocol.[4,10] Initially, C_{70} was reacted with CF_3I in a sealed ampoule placed in a temperature gradient to give a mixture of $C_{70}(CF_3)_n$ compounds (n=12–20). Then, the mixture was ground with a further portion of C_{70} and heated in a glass ampoule at 450 °C to give, via comproportionative transalkylation, the material enriched with $C_{70}(CF_3)_8$. The yield of the HPLC isolated individual C_2-$C_{70}(CF_3)_8$ isomer was 8%.

Nucleophilic cyclopropanation of C_2-$C_{70}(CF_3)_8$ was carried out following the two conventional alternative routes: (*i*) the Bingel reaction[11] with diethyl bromomalonate in the presence of *t*-BuOK as a base and (*ii*) the variation of the Bingel reaction involving diethyl malonate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base and I_2 (reported by Diederich et al.[12] and labeled as Bingel-Diederich reaction hereinafter) or CBr_4 (suggested by Hirsch et al.[13] and designated as Bingel-Hirsch reaction hereinafter) as a source of halogen. The Bingel reaction starts with nucleophilic addition of a stabilized α-halogenated carbanion to the fullerene cage, which is followed by intramolecular nucleophilic substitution to yield a cyclopropane moiety (Scheme 1).



Scheme 1. The Bingel reaction mechanism.

In all cases, according to the HPLC data, the conversion of C_2-$C_{70}(CF_3)_8$ was largely complete within several minutes. The product compositions, however, were different (Figure 2*a*). The Bingel reaction gave a single major product while the Bingel-Hirsch modification afforded at least three in comparable yields (and the same set of major products was observed upon replacement of CBr_4 with iodine under Bingel-Diederich conditions, see Figure *S*2 in the SI). Compared to C_s-$C_{70}(CF_3)_8$ and C_1-p^7mp-$C_{70}(CF_3)_{10}$ where the Bingel-Hirsch reaction requires several hours to complete, C_2-$C_{70}(CF_3)_8$ demonstrates much higher reactivity. Apparently, its stronger electron-withdrawing properties translate into higher affinity to the anionic bromomalonate intermediate.

The reaction products (compounds **I**–**IV** in the increasing order of retention times) and unreacted C_2-$C_{70}(CF_3)_8$ (compound **V**) were isolated from the reaction by means of multistep HPLC using toluene and toluene-hexane mixtures (1:1 and 3:7 v/v) as eluents. The molecular compositions of the isolated compounds as determined by means of MALDI MS are shown in Figure 2*b* and in Table 1. Compounds **IV** and **II** common to both reaction variations were found to be the expected mono- and biscyclopropanated adducts of C_2-$C_{70}(CF_3)_8$. Products **III** and **I** specific to the Bingel-Hirsch reaction turned out to be the alkylated rather than cyclopropanated $C_{70}(CF_3)_8[CH(CO_2Et)_2]H$ and the mixed $C_{70}(CF_3)_8[C(CO_2Et)_2][CH(CO_2Et)_2]H$.

Unexpected observation of the alkylated products **I** and **III** under the Bingel-Hirsch conditions prompted us to investigate a similar system with malonate and DBU but without any halogen compounds. Remarkably, C_2-$C_{70}(CF_3)_8$ still turned out to be reactive and selectively gave compound **III** (Figure 2*a, bottom*), i.e. the product of alkylation without cycloaddition. For the pristine fullerenes, we observed no interaction (see Figure *S*3,4 in SI), which correlates with the lack of alkylated products already under the Bingel-Hirsch and Bingel-Diederich conditions.

The MALDI mass spectra (negative ion mode) of the cyclopropanated adducts **IV** and **II** were dominated by the molecular anions $C_{70}(CF_3)_8[C(CO_2Et)_2]^-$ and $C_{70}(CF_3)_8[C(CO_2Et)_2]_2^-$ (Figure 2*b*, left and Figure *S*1*d* in SI), respectively, with several minor signals due to the CF_3 loss and impurities. Such MS behavior, which is quite typical for the Bingel derivatives of trifluoromethylated fullerenes,[7,8] demonstrates high stability of the doubly linked malonate moieties under the MALDI conditions. On the contrary, compound **III** with its singly linked addends gave rise to $C_{70}(CF_3)_8H^-$ as the major MS signal (Figure 2*b*, right) accompanied by much weaker peaks of $C_{70}(CF_3)_8^-$ and $C_{70}(CF_3)_8[CH(CO_2Et)_2]^-$. Interpretation of $C_{70}(CF_3)_8H^-$ as a fragment of the missing molecular anion $C_{70}(CF_3)_8[CH(CO_2Et)_2]H^-$ was supported by detection of an additional weak metastable peak due to fragmentation in the drift region. Accordingly, $C_{70}(CF_3)_8[CH(CO_2Et)_2]^-$ is the pseudomolecular ion formed via deprotonation, which is typical for fullerene compounds with cage-linked hydrogens.[14] Compound **I** demonstrated the same principal fragmentation channels as **III**, i.e. loss of $[CH(CO_2Et)_2]$ or a proton (see Figure *S*1*c* in SI).

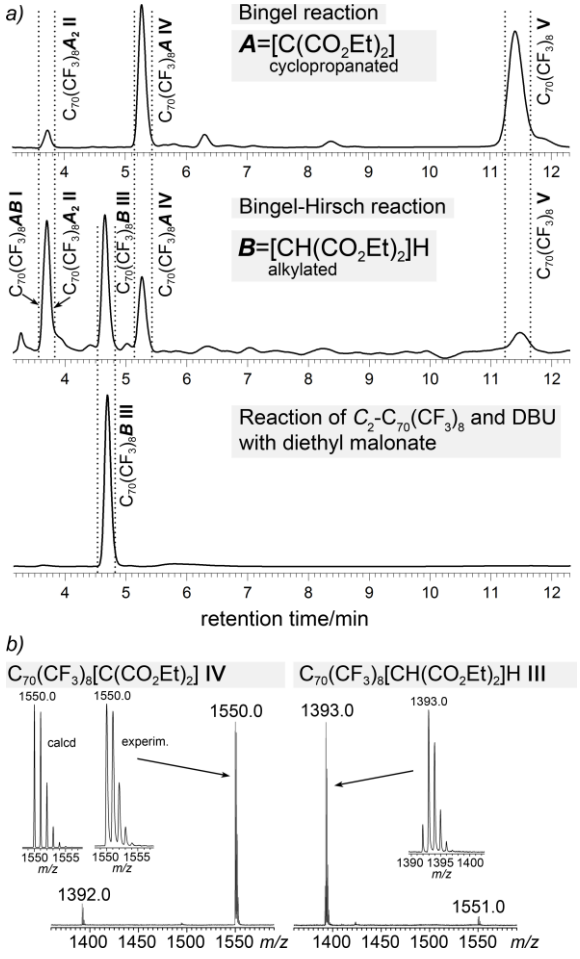


Figure 2. *a*) HPLC traces of the product mixtures from the Bingel, Bingel-Hirsch reactions of C_2-$C_{70}(CF_3)_8$, and the reaction with diethyl malonate and DBU only (Cosmosil Buckyprep, 4.6 mm I.D. × 25 cm, toluene:hexane=1:1 v./v., 1 mL min^{-1}). *b*) Negative ion MALDI mass spectra of compounds **IV** and **III** with enlarged major peaks and theoretical isotopic pattern of $C_{70}(CF_3)_8[C(CO_2Et)]^-$.

Table 1. HPLC isolated compounds **I–V**: retention times, molecular compositions, and yields in the Bingel (B) and Bingel-Hirsch (B-H) reactions.

Id	t_R, min[a], toluene:hexane, v/v			Composition,[b] R = CO_2Et	Yield,[c] %	
	10:0	1:1[d]	3:7[d]		B	B-H
I	1.44	3.7	5.1	$C_{70}(CF_3)_8[CR_2][CHR_2]H$	0	11
II	1.44	3.7	5.4	$C_{70}(CF_3)_8[CR_2]_2$	10	25
III	1.58	4.6	7.8	$C_{70}(CF_3)_8[CHR_2]H$	0	31
IV	1.62	5.3	9.7	$C_{70}(CF_3)_8[CR_2]$	47	16
V	2.38	11.5	27.4	$C_{70}(CF_3)_8$	38	7

[a] Cosmosil Buckyprep column, 4.6 mm I.D. × 25 cm, 290 nm, 25 °C, at flow rate of 2 mL min^{-1}. [b] According to MS MALDI data. [c] According to HPLC trace integration. [d] 1 mL min^{-1}.

Interestingly, the previously reported Bingel-Hirsch reactions of C_s-$C_{70}(CF_3)_8$ and C_1-$C_{70}(CF_3)_{10}$ have not been observed to yield any non-cyclized products.[7,8] It is likely that the peculiarity of the C_2-$C_{70}(CF_3)_8$ case is due to its higher electron affinity. We will discuss the possible formation mechanisms of the alkylated compounds **I** and **III** in more detail in the respective section below.

Structural determination of the cyclopropanated adducts II and IV

Slow evaporation of a toluene solution of **II** gave pink crystalline material. Single crystal X-ray diffraction study using synchrotron radiation revealed formation of a C_2-symmetric bisadduct $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$. Cyclopropanation occurs at the symmetrically equivalent [6,6]-bonds ***a*** and ***a'*** at the poles of the fullerene cage (see Figure 3 and Table 2 for bond labeling) and results in elongation of these bonds from 1.391(4) Å in the parent trifluoromethylated fullerene[10] to 1.582(4) and 1.588(5) Å, which is typical for methanofullerenes.[15] The lengths of neighboring C–C bonds are also slightly elongated from ~1.45 to ~1.48 Å.

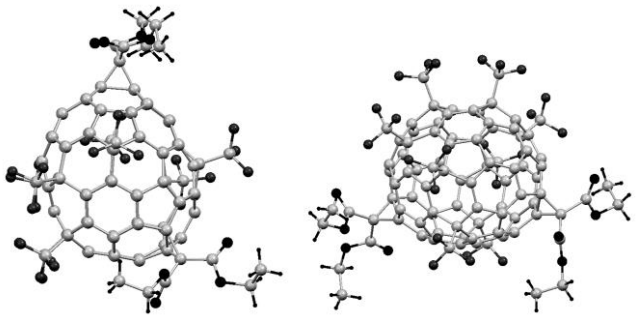


Figure 3. X-ray structure of the $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ bisadduct (**II**). Two projections of the molecule are shown.

NMR spectroscopic data for the compound **II** are fully consistent with the X-ray structure. The ^{19}F NMR spectrum contains four CF_3 multiplets of equal intensity (Figure 4*a*). The quartet signal at δ_F –69.6 ppm with J_{FF} 10.6 Hz, 1.3 ppm upfield with respect to the parent C_2-$C_{70}(CF_3)_8$, corresponds to the terminal pair of CF_3 groups (**A**). The other unresolved quartet (**D**) is characteristic of the central pair of CF_3 addends, and the two multiplet signals in between are due to the rest two pairs of CF_3 groups. The ^1H NMR spectrum of **II** consists of two ABX_3 spin systems of equal intensity due to the two inequivalent pairs of ethoxy groups with diasteretopic methylene protons (Figure 4*b*). The CH_3 protons give rise to the triplet signals at δ_H 1.35 and 1.41 ppm while the protons of the methylene moieties can be found at δ_H 4.48, 4.45, 4.39 and 4.35 ppm (A and B doublets of quartets). Rather large spacing between the CF_3 and the malonate moieties makes their mutual influence on the NMR pattern quite weak.

The structure of the $C_{70}(CF_3)_8[C(CO_2Et)_2]$ monoadduct (**IV**) has been determined on the basis of the ^{19}F and ^1H NMR spectroscopic data and DFT calculations. The ^{19}F NMR spectrum of compound **IV** consists of four CF_3 signals of equal and two of doubled intensity (Figure 4*c*), which indicates the lack of molecular symmetry. The two quartet signals at δ_F –68.8 and –69.1 ppm (J_{FF} 11.0 and 10.4 Hz) can be attributed to the two terminal CF_3 groups (**H** and **A**), now inequivalent. The ^1H spectrum of **IV** is quite similar to that of **II** in that it comprises two ABX_3 systems due to the two ethoxy moieties (Figure 4*d*). The methyl protons are observed at δ_H 1.32 and 1.41 ppm (triplets, $^3J_{HH}$ 7.1 Hz) while the methylene ones – at δ_H 4.45 and 4.49 ppm (AB quartets of quartets, $^2J_{HH}$ 10.6 Hz, $^3J_{HH}$ 7.1 Hz).

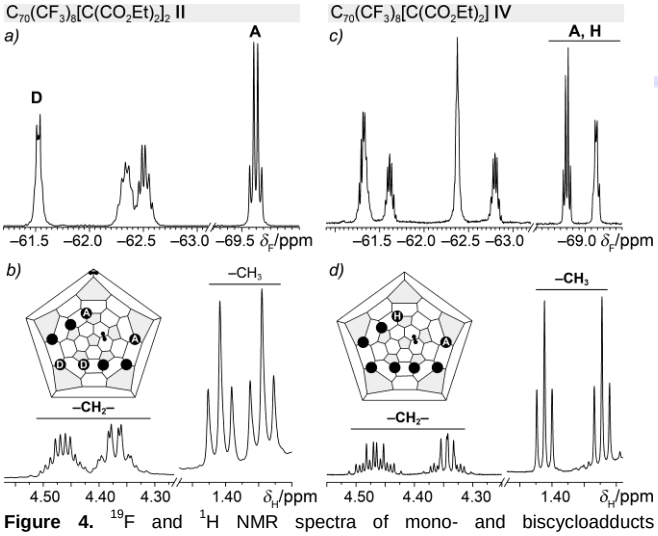
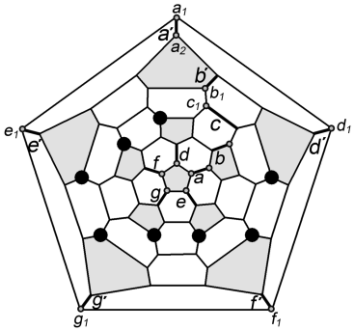


Figure 4. ^{19}F and ^1H NMR spectra of mono- and biscycloadducts $C_{70}(CF_3)_8[C(CO_2Et)_2]_n$ (n=1, 2) **II** (*a*, *b*) and **IV** (*c*, *d*). Schlegel diagrams are shown on insets.

As was shown previously, regioselectivity in the nucleophilic cyclopropanation of C_s-p^7-$C_{70}(CF_3)_8$ and C_1-p^7mp-$C_{70}(CF_3)_{10}$ correlates with the relative formation energy of the anionic intermediates and cyclopropanated products.[7,8] This correlation is likely based on the Bell-Evans-Polanyi (BEP) relationship

between the activation energy and the enthalpy for a series of isomeric reactions. Applicability of BEP-based kinetic model for prediction of isomeric composition in fullerene chemistry was recently verified on example of trifluoromethylation of fullerenes possessing rich isomeric and compositional product complexity.[16] In order to determine the possible cyclopropanation position in **IV**, we have carried out the DFT relative energy calculations of all theoretically possible isomeric intermediates $C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$ and final compounds $C_{70}(CF_3)_8[C(CO_2Et)_2]$. The most energetically favorable intermediates and cycloadducts are listed in the Table 2.

Table 2. The DFT relative energies of the most energetically favorable isomers of $C_{70}(CF_3)_8[C(CO_2Et)_2]$ and their anionic precursors $C_{70}(CF_3)_8[CBr(CO_2Et)_2]^-$.



Anionic intermediate		Monoadduct	
at site[a]	Δ*E*, kJ mol^{-1}	at bond[a]	Δ*E*, kJ mol^{-1}
a1	0	***a***	0
a2	17		
b1	35	***b***	14
c1	102	***c***	14
d1	30	***d***	16
e1	60	***e***	17
f1	37	***f***	18
g1	34	***g***	21

[a] In the Schlegel diagram of C_2-$C_{70}(CF_3)_8$ (left) black circles denote the CF_3 groups, the ***a***–***g*** indices denote the bonds at which cycloaddition occurs and the indices with subscript numerals denote the possible anionic intermediate attachment sites.

As one can see, the most favorable anionic intermediates involve the $\boldsymbol{a_1}$ and $\boldsymbol{a_2}$ sites and both lead to the likewise most favorable cycloadduct ***a***. Even though the six alternative cycloadduct isomers ***b***–***g*** are characterized by comparatively low relative energy, their anionic precursors can be found no less than 30 kJ mol^{-1} above $\boldsymbol{a_1}$. Thus, our quantum chemical data predicts the nucleophilic cyclopropanation of C_2-$C_{70}(CF_3)_8$ to occur at the [6,6]-bond ***a***. This conclusion, being perfectly corroborated by the above discussed bisaddict **II** with attachment to ***a*** and ***a'***, makes the structural assignment of **IV** unambiguous.

It was interesting to verify the validity our theoretical analysis by applying it to the possible isomeric bisadducts based on **IV**. The detailed results, which perfectly agree with the experimental findings, are given in Tables *S*4 and *S*5 of the SI. Briefly, both the experimental compound **II** and its $\boldsymbol{a_1}$ intermediate turned out to be the most stable. The next stable isomeric bisadduct with ***a*** and ***b*** attachment of the malonate moieties is only 11 kJ mol^{-1} higher; however, similarly to the monoadduct case, its anionic intermediate $\boldsymbol{b_1}$ was observed 30+ kJ mol^{-1} above $\boldsymbol{a_1}$. Thus, regioselective formation of **II** and **IV** is governed by the same energy-based BEP criteria.

Structure of the alkylated compounds $C_{70}(CF_3)_8[CH(CO_2Et)_2]H$ (III) and $C_{70}(CF_3)_8[C(CO_2Et)_2][CH(CO_2Et)_2]H$ (I)

The structure of the $C_{70}(CF_3)_8[CH(CO_2Et)_2]H$ (**III**) was deduced from the ^{19}F and ^1H NMR data. The ^{19}F NMR spectrum contains eight signals of the equal intensity within the range of –58 to –72 ppm demonstrating inevitable asymmetry of the compound (Figure 5*a*). All eight signals were unambiguously attributed to corresponding CF_3 groups **A**–**H** on the basis of the ^{19}F COSY NMR spectrum (see Figure *S*5 in the SI). Most importantly, the quartet **A** at δ_F –71.8 (J_{FF} 12.1 Hz) and the doublet of quartets **H** at δ_F –63.9 ppm (J_{FF} 13.2 Hz and J_{HF} 2.7 Hz) are clearly due to the terminal CF_3 groups. To understand the structure of **III**, it was material to find out, which of the protons gives rise to the doublet splitting of **H**. The ^1H NMR spectrum of **III** contained two already familiar ABX_3 patterns due to the ethoxy groups plus a broadened singlet signal at δ_H 5.91 ppm and a quartet signal at δ_H 4.91 ppm (J_{HF} 2.7 Hz) (Figure 5*b*). Knowing the typical chemical shift ranges for various types of protons in the fullerene compounds,[14,17] the quartet signal is to be assigned to the malonate C*H*$(CO_2Et)_2$ proton while the singlet – to the C_{70}-*H* one. Thus, CF_3 group **H** interacts with the malonate proton, which can be possible only if the two groups are attached in the same ring of the C_{70} cage. The broadening of the singlet at 5.91 ppm is also indicative of interaction of the cage linked hydrogen with, most probably, some CF_3 group and, consequently their close proximity to each other. Although the said coupling does not give rise to any additional splitting in the ^{19}F spectrum, a considerable upfield shift of the signal **A** by 3.5 ppm with respect to the parent C_2-$C_{70}(CF_3)_8$ can be viewed as an evidence that the interaction involves the fluorine atoms of **A**.

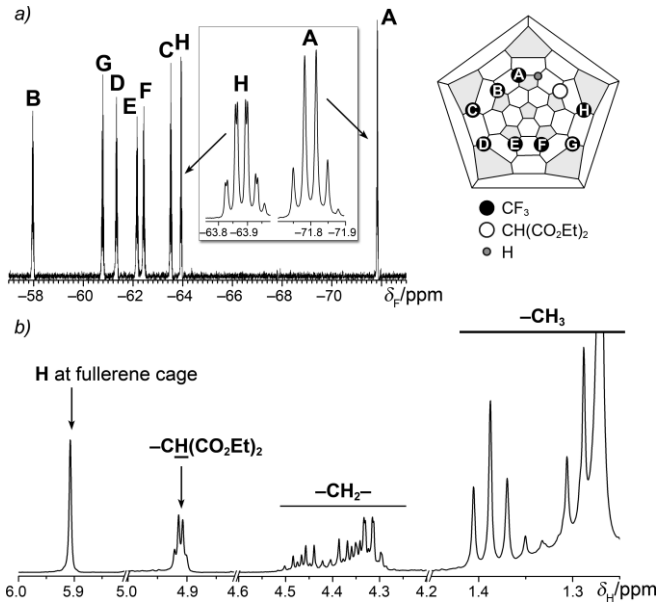


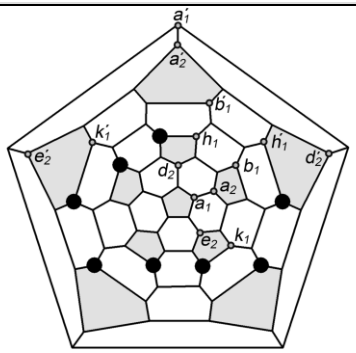
Figure 5. ^{1}H and ^{19}F NMR spectra and Schlegel diagram of alkylated product $C_{70}(CF_3)_8[CH(CO_2Et)_2]H$ **III**.

Theoretically, formation of **III** can occur via two alternative pathways: through either $C_{70}(CF_3)_8[CH(CO_2Et)_2]^-$ or $C_{70}(CF_3)_8H^-$ anionic intermediates. In the former case, $[CH(CO_2Et)_2]^-$ anions form in minor quantities in a proton-exchange equilibrium between DBU and non-brominated diethyl malonate, alongside with more stable $[CBr(CO_2Et)_2]^-$, and then become captured by the electron-withdrawing C_2-$C_{70}(CF_3)_8$ molecules. Subsequent protonation will afford the final product **III**. Alternatively, $C_{70}(CF_3)_8^{-\bullet}$ anions form upon single electron transfer from DBU and detach a hydrogen atom from a malonate molecule to give a closed shell $C_{70}(CF_3)_8H^-$ intermediate. $C_{70}(CF_3)_8H^-$ will then attach the dehydrogenated $^{\bullet}CH(CO_2Et)_2$ radical and return the extra electron to neutral C_2-$C_{70}(CF_3)_8$ or $DBU^{+\bullet}$. Obviously, formation of **III** without CBr_4 means that the reduction-hydrogen transfer pathway is implicated anyway. However, it was interesting to analyze, whether it would still remain predominant in presence of CBr_4. Therefore, we have carried out a theoretical analysis of the possible intermediates for both reaction pathways in question.

As shown in Table 3, the most stable isomeric $C_{70}(CF_3)_8[CH(CO_2Et)_2]^-$ intermediates have the malonate moiety attached at the sites $\boldsymbol{a_1}$ or $\boldsymbol{b_1}$. Unlike the case of bulkier bromomalonate intermediate (see Table 2), the two structures are virtually isoenergetic. The NMR-based conclusion regarding proximity to a terminal CF_3 group would clearly suggest $\boldsymbol{b_1}$, but $\boldsymbol{a_1}$ has an obvious advantage of better steric accessibility. Therefore, formation of **III** via the malonate pathway would likely result in a mixture of two isomers rather than a single one. On the contrary, the hydrogen transfer pathway clearly favors the hydrogenated intermediate $\boldsymbol{h_1}$ over all the others. Furthermore, hydrogen attachment to the site $\boldsymbol{h_1}$ should give rise to an interaction with a terminal CF_3 group as suggested by the NMR data. Thus, formation of **III** as a single isomer of $C_{70}(CF_3)_8[CH(CO_2Et)_2]H$ demonstrates that the hydrogen transfer pathway must be at least much faster than the malonate one.

To analyze the regiochemistry of alkylation of the $\boldsymbol{h_1}$ isomer of $C_{70}(CF_3)_8H^-$, we have considered the energetics of the isomeric $C_{70}(CF_3)_8[CH(CO_2Et)_2]H^{-\bullet}$ anions with varied site of malonate attachment. The experimental isomer **III** was found to be 18 kJ mol^{-1} more stable than any alternative structures (see Table *S*10 in the SI). Thus, we arrive at the structure of **III** as shown in Figure 5, which demonstrates perfect agreement with the NMR observations. Note that **III** is isostructural to a number of C_{70} derivatives including $C_{70}X_{10}$, X=H, Cl, Br, CH_3,[18] as well as some bisadducts of C_s-$C_{70}(CF_3)_8$,[5,6] its highly favorable addition pattern separating the initial spherical π-system of C_{70} into the two disjoint corannulene-based subsystems of 28 and 32 electrons.

Table 3. The DFT relative energies of most energetically favorable isomers of anionic intermediates $C_{70}(CF_3)_8[CH(CO_2Et)_2]^-$ and $C_{70}(CF_3)_8H^-$



Anionic intermediate $C_{70}(CF_3)_8R^-$, *R*=, Δ*E*, kJ mol^{-1}		
at site	**$CH(CO_2Et)_2$**	**H**
$\boldsymbol{h_1}$	28	0
$\boldsymbol{b_1}$	0	71
$\boldsymbol{a_1}$	2	37
$\boldsymbol{a_2}$	18	46
$\boldsymbol{e_2}$	18	42
$\boldsymbol{d_2}$	25	41
$\boldsymbol{k_1}$	69	22

Turning now to the compound **I**, its low quantity made us impossible to acquire sufficiently accurate NMR data. However, we have acquired its ^{19}F NMR spectrum which turned out to be quite similar to that of **III** and the ^{1}H spectrum containing a signal at 5.8 ppm due to the cage-linked hydrogen. Thus, the NMR and MALDI MS data available predict **I** to be a mixed $C_{70}(CF_3)_8[C(CO_2Et)_2][CH(CO_2Et)_2]H$ adduct with hydrogen and $CH(CO_2Et)_2$ attachment like in **III** and cyclopropanation most probably as in **II** and **IV**. Indeed, our DFT data demonstrates this hypothetic structure of **I** to be the most favorable, 11 kJ mol^{-1} below the next stable isomer.

Orienting effect of trifluoromethylation and the electronic structure aspects

As is shown above, while the bulky α-bromomalonate carbanion tends to attach to the poles of the C_2-$C_{70}(CF_3)_8$, the more compact species like non-brominated malonate carbanion may prefer the equatorial region of the molecule. The closely related C_s-$C_{70}(CF_3)_8$ is known to show the similar trends both for the bulkier α-bromomalonate carbanion[7] and the smaller groups of Cl and CN.[5,6] This is different from pristine C_{70} where both

nucleophilic addition and cycloaddition preferably occur at the polar region,[11,14,19] (the only exclusion is a highly thermodynamically stable equatorial adduct C_{2v}-$C_{70}(CH_2)$ obtainable only under extreme conditions via pyrolysis of C_{70} with CH_4 at 1100 °C or via the Krätschmer–Huffman method in the presence of methane[20] due to poor kinetics). So far, we have demonstrated that the products reported in the present paper can be predicted on the basis of the energetic criteria. It is interesting to find out, whether our findings correlate with the common reactivity criteria like orbital localization approaches.

The eight CF_3 groups drastically alter the geometry of the equatorial region of the molecule. Thus, bond lengths of equatorial naphthalenoid moiety of C_2-$C_{70}(CF_3)_8$ fall within much narrower range of 1.40–1.42 Å[10] (except for the bond ***c*** of 1.460(3) Å, see Figure 6) compared to the pristine C_{70} (1.476(16) Å for ***c*** and 1.37–1.45 Å for the rest of the bonds[21]). In the related C_s-$C_{70}(CF_3)_8$, the near-equatorial [5,6]-bond ***d*** became likewise shortened to 1.418(6) Å[3] from 1.437(9) Å in the pristine C_{70}.[21] Pronounced shortening of the bonds ***b*** and ***d*** in C_2- and C_s-$C_{70}(CF_3)_8$, respectively, reflects the increase in their bond orders and, consequently, in their reactivity toward cycloaddition, as well as nucleophilic, electrophilic, and radical addition.

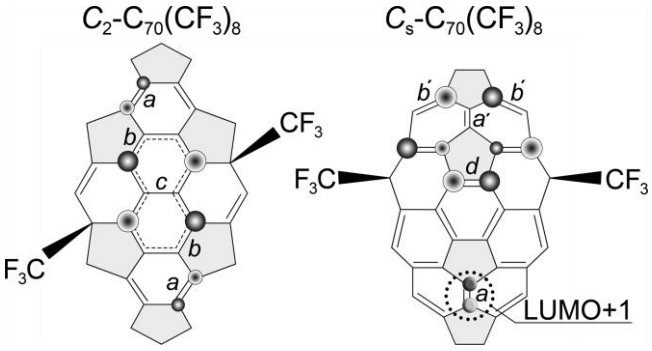


Figure 6. LUMO and LUMO+1 localization in C_2-$C_{70}(CF_3)_8$ (left) and C_s-$C_{70}(CF_3)_8$ (right). The bonds are labelled according to Table 2 and to ref. 7 (C_s isomer).

The DFT-calculated LUMO localization in C_2-$C_{70}(CF_3)_8$ and C_s-$C_{70}(CF_3)_8$ is shown in Figure 6. Both molecules have the highest LUMO contributions at the carbon atoms in *ortho*- and *para*-positions with respect to the terminal CF_3 groups and, to a somewhat lesser extent, in the polar pentagons. Hence, the orienting effects of the LUMO localization should direct the smaller anionic species to the equatorial sites, mostly to the *para*-positions with respect to the CF_3 addends since the *ortho*-positions are strongly screened, while the bulky nucleophiles will attack the poles of the fullerene cage. Thus, the equatorial belts of the CF_3 groups effect such alteration of the electronic structure of C_{70} that the LUMO induces regioselective nucleophilic addition to the equatorial region of the molecule.

The difference in the overall addition patterns between the compounds **I–V** turns out to have quite discernible effect on the electronic properties as evidenced by the UV/Vis spectra shown in Figure 7. Mono- and biscyclopropanation of C_2-$C_{70}(CF_3)_8$ withdraws, respectively, two and four electrons from the π-system, which results in a blue shift of the first absorption band by *ca*. 55 nm per each cyclopropane moiety. Transition to a disjoint π-system in **III** has much deeper consequences – the first absorption band blueshifts by as much as 220 nm with respect to C_2-$C_{70}(CF_3)_8$. A further 35 nm shift is observed in **I** in accordance with reduction of π-system during cyclopropanation of **III**. Noteworthy, the experimental data show a good correlation with the calculated HOMO–LUMO gap (Table 4).

Table 4. DFT-calculated electron affinities and HOMO–LUMO gaps as well wavelengths of the most red shifted peaks and estimated optical gaps of compounds **I–V**

Compound	EA, eV	E_{HOMO}, eV	E_{LUMO}, eV	Gap^{DFT}, eV[a]	λ_{peak}, nm	Gap^{opt}, eV[b]
C_2-$C_{70}(CF_3)_8$ **V**	3.1	–6.09	–4.83	1.26	670	1.8
$C_{70}(CF_3)_8[C(CO_2Et)_2]$ **IV**	2.8	–5.90	–4.47	1.43	612	2.0
$C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ **II**	2.6	–5.72	–4.10	1.62	558	2.2
$C_{70}(CF_3)_8[CH(CO_2Et)_2]H$ **III**	2.5	–6.21	–4.06	2.15	452	2.7
$C_{70}(CF_3)_8[C(CO_2Et)_2][CH(CO_2Et)_2]H$ **I**	2.2	–6.00	–3.68	2.31	416	3.0

[a] DFT-predicted HOMO–LUMO gap. [b] Optical gaps determined from UV-Vis data.

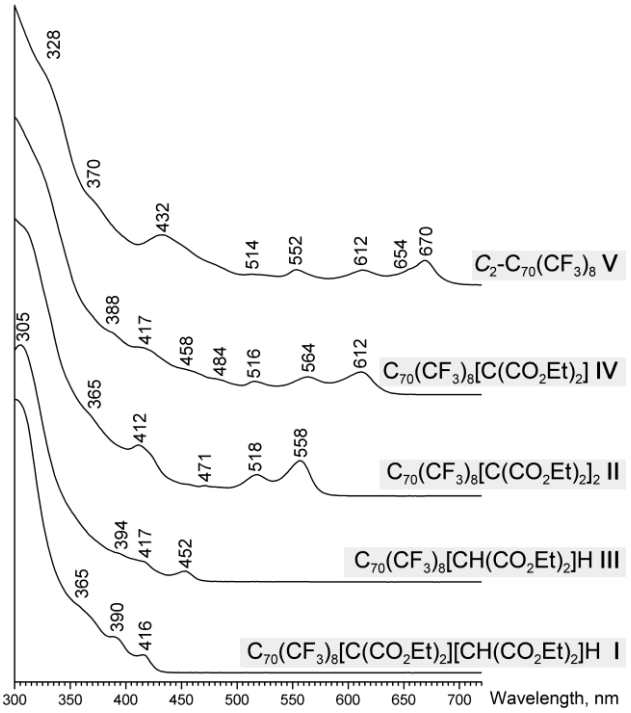


Figure 7. UV/Vis spectra of compounds **I–V** (toluene as a solvent).

Reduction of the π-system also leads to a significant decrease in the calculated electron affinity (EA). EA values drop from 3.1 eV for the parent C_2-$C_{70}(CF_3)_8$ to 2.8 and 2.6 eV for mono- and bis-cycloadduct, respectively, and even further for the compounds **III** and **I**. Note the 0.3 eV difference between the EA of compounds **IV** and **III** despite the same overall size of the conjugated system, which can be regarded as a measure of the effect of its partition into the two disjoint fragments in **III**.

Conclusions

The increased electron affinity of C_2-$C_{70}(CF_3)_8$ endows it with enhanced reactivity toward nucleophilic addition compared to its analogs. Moreover, it also gives rise to the alternative reaction pathways in the Bingel-Hirsch reaction affording alkylation alongside with cyclopropanation. What is even more interesting, it further enables pure alkylation when one completely removes any sources of halogen, and it involves the equatorial, normally less reactive, region of the C_{70} cage. Together with remarkable regioselectivity due to the orienting effects of the CF_3 groups, this gives a family of novel fullerene derivatives employable as acceptors in charge transfer systems.

In this regard, the malonate moieties can provide a very convenient way of chemically linking these compounds to the donor substances.

It is to be noted that, compared to other classes of electron withdrawing fullerene derivatives, the trifluoromethylated fullerene compounds are particularly advantageous due to stability of the CF_3 groups towards nucleophilic substitution. Hence, the Bingel and Bingel-Hirsch functionalization of the trifluoromethylated fullerene compounds may evolve in a promising approach in the field of design of novel fullerene materials. Of special interest would be a broader comparison of reactivity and regioselectivity as a function of the addition pattern and electron affinity.

Experimental Section

General information

Mass spectrometry. The negative ion MALDI mass spectra were recorded using a Bruker AutoFlex II (Bruker Daltonik GmbH) Rf-TOF mass spectrometer equipped with an N_2 laser (337 nm, 2.5 ns pulse). *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, ≥98%, Sigma-Aldrich) was used as a matrix, matrix-to-analyte molar ratio in probes being above 1000/1. The high resolution positive ion ESI mass spectra were registered using a LTQ Orbitrap XLTM instrument (resolving power above 50000). The acetonitrile (HPLC grade) with 0.1% of formic acid was used as a solvent.

High performance liquid chromatography. HPLC analyses were carried out using an Agilent 1100 System equipped with a diode array detector (DAD) and a temperature-controlled Cosmosil Buckyprep 4.6 mm I.D. × 25 cm column (Nacalai Tesque, Inc.). HPLC separation was carried out using a Waters 1500 chromatographic system equipped with a dual wavelength UV/Vis detector and Cosmosil Buckyprep 10 mm I.D. × 25 cm column (Nacalai Tesque, Inc.). Toluene (99.8%, Khimmed, Russia), hexane (99.7%, Khimmed, Russia) and mixtures thereof were used as eluents. The UV/Vis spectra of the toluene solutions were obtained via a DAD in the 290–950 nm range with resolution of 2 nm.

NMR spectroscopy. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded at 400.3, 376.5 and 150 MHz, respectively, using a Bruker Avance-400 spectrometer. The samples were dissolved in chloroform-d and spiked with small amounts of hexafluorobenzene (δ_F –162.9 ppm) and TMS (δ_H and δ_C 0.0 ppm) as internal standards.

Quantum chemical calculations. The complete sets of the cyclopropanated mono- (41 structures) and bisadducts (1571 structures), i.e. $C_{70}(CF_3)_8[C(CO_2Et)_2]_n$ with n=1 or 2, considered herein include all theoretically possible isomers with cycloaddition to the pairs of adjacent sp^2 atoms in C_2-p^7-$C_{70}(CF_3)_8$. The complete sets of the anionic intermediates $C_{70}(CF_3)_8R^-$, R= H, -$CBr(CO_2Et)_2$, -$CH(CO_2Et)_2$, (31 structures for each) include all inequivalent additions to the sp^2 atoms of the C_2-p^7-$C_{70}(CF_3)_8$ molecule. In the cases of attachment of the -$CBr(CO_2Et)_2$ and -$CH(CO_2Et)_2$ moieties, we additionally performed preliminary conformational analysis with respect to the internal rotation at the AM1 level of theory. See the SI for further details.

Initially, molecular geometry of the each structure in question was optimized using the TINKER 4.2 molecular mechanic package with MM2 force field.[22] In the next step, the geometry was refined at the AM1 level of theory with the use of the Firefly 8.1 software[23] partly based on the GAMESS (US) source code.[24] This was followed by single point DFT calculations and final DFT optimizations of the subsets of most stable structures. The latter were carried out with the use of the PRIRODA v. 6 software implementing efficient RI approximation.[25] PBE exchange-correlation functional[26] and a built-in basis set of triple zeta quality with

(11s6p2d)/[6s3p2d] contraction scheme for first row atoms and (5s1p)/[3s1p] for hydrogens were used.

X-ray crystallography. Single crystals of $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$ **II** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from an HPLC purified fraction. Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PFS, Berlin, Germany) using a MAR225 CCD detector, λ = 0.9050 Å. Structure was solved and anisotropically refined using the SHELX package.[27] $C_{92}H_{20}F_{24}O_8$: monoclinic, $P2_1/n$, a = 14.4300(9) Å, b = 21.615(2) Å, c = 20.064(1) Å, β = 92.027(6)°, V = 6254.1(8) Å^3, Z = 4, $R_1(F)/wR_2(F^2)$ = 0.072/0.162 for 13121/11862 reflections and 1234 parameters. One CF_3 group is disordered over two positions around a C–CF_3 bond. Two $CO_2(C_2H_5)$ groups are disordered over two positions each with an occupancy ratio of 0.535/0.465(4). CCDC 1043212 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of C_2-p^7-$C_{70}(CF_3)_8$

Fullerene C_{70} (Fullerene-center, 99.8%; 50 mg) was loaded into a glass ampoule and an excess of CF_3I (P&M-Invest, 98%; ca. 1 mL) was then condensed into it under cooling with liquid nitrogen. The sealed ampoule was placed into a gradient furnace at 420 °C for 72 h. As was evidenced by MALDI MS, the resulting mixture consisted of higher trifluoromethylated compounds with 12 to 20 CF_3 addends. Annealing of the said mixture (40 mg) with pristine C_{70} (15 mg) in a sealed glass ampoule at 450 °C for 40 h yielded a mixture of lower CF_3 derivatives, with 2 to 10 CF_3 groups. Isolation of the individual C_2-$C_{70}(CF_3)_8$ isomer was carried out by means of HPLC using a Cosmosil Buckyprep 10 mm I.D. × 25 cm column and toluene as an eluent (flow rate 4.6 mL min^{-1}). Additional HPLC purification of the isolated fraction with the use of the 1:1 (v/v) toluene–hexane mixture as an eluent gave ca. 4 mg of pure individual C_2-$C_{70}(CF_3)_8$. Over 10 mg of the pure C_2-$C_{70}(CF_3)_8$ have been accumulated after several synthetic runs, which was sufficient for further chemical reactions.

Compound V, C_2-p^7-$C_{70}(CF_3)_8$, 1,4,11,19,31,41,51,60-$C_{70}(CF_3)_8$: t_R 2.38 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene, 2 mL min^{-1}); ^{19}F NMR (376.5 MHz, $CDCl_3$, 25 °C, C_6F_6): δ=–61.10 (m, 6F; CF_3), –61.64 (m, 6F; CF_3), –62.66 (m, 6F; CF_3), –68.32 ppm (q, J(F,F)=11.5 Hz, 6F; CF_3); UV/Vis (toluene): λ_{max}=328, 370, 432, 514, 552, 612, 654, 670 nm; MALDI MS: m/z (%): 1392.0 (100) [M^-].

The Bingel-Hirsch reaction with C_2-p^7-$C_{70}(CF_3)_8$

Diethyl malonate (Acros Organics, 99+%; 4.3 μL, 28 μmol), carbon tetrabromide (Acros Organics, 9.3 mg, 28 μmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; Acros Organics, 98%; 4.2 μL, 28 μmol) in toluene (400 μL) were stirred at 40 °C for 20 min. In each synthetic run, 100 μL of the said solution was added to the solution of C_2-$C_{70}(CF_3)_8$ (7.5 mg, 5 μmol) in 10 mL of toluene. Then an additional portion of DBU (1 μL, 7 μmol) in toluene (100 μL) was added dropwise under stirring. The reaction mixture was stirred at room temperature for further 15 min and then filtered through silica using toluene as an eluent. The four fractions containing reaction products **I–IV** as well as starting C_2-$C_{70}(CF_3)_8$ **V** were isolated by means multi-step HPLC separation (Cosmosil Buckyprep 10 mm I.D. × 25 cm column and toluene–hexane, 1:1 and 3:7 v/v, as eluents with flow rate of 4.6 mL min^{-1}).

The Bingel reaction with C_2-p^7-$C_{70}(CF_3)_8$

1. Synthesis of the diethyl bromomalonate. Several drops of the liquid bromine were added to diethyl malonate (30 mL, 0.198 mol) in chloroform (30 mL) and the mixture was then briefly heated to 80 °C to initiate the reaction. Then an additional amount of bromine (10.2 mL, 0.198 mol) was added dropwise at room temperature. The brown-red reaction mixture was then refluxed until coming to a residual pale color stable in time. The cooled mixture was washed 5 times with 15 mL of aqueous Na_2CO_3 (5%), the organic layer was then separated and evaporated at 40 °C under low pressure. Finally, the resulting diethyl bromomalonate was purified by distillation at 10 Torr, b.p. 106 °C; ^{1}H NMR (400.3 MHz, $CDCl_3$, 25 °C, TMS): δ=4.81 (s, 1H; CH), 4.29 (q, ^3J(H,H)= 7.15 Hz, 4H; CH_2), 1.30 ppm (t, ^3J(H,H) = 7.15 Hz, 6H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ=164.60 (C=O), 63.25 (CH_2), 42.44 (CH), 13.90 ppm (CH_3); HRMS (ESI): m/z calcd for $C_7H_{11}BrO_4$+H$^+$: 238.9913 [M+H$^+$]; found: 238.9907.

2. The Bingel reaction. To a solution of C_2-$C_{70}(CF_3)_8$ (4.9 mg, 3.5 μmol) and diethyl bromomalonate (0.8 μL, 4.9 μmol) in toluene, potassium *tert*-butoxide (0.55 mg, 4.9 μmol) in toluene (1 mL) was added. The reaction was stirred at 40 °C for 20 min and then filtered through silica using toluene as eluent. Two fractions containing compounds **II** and **IV** as well as starting C_2-$C_{70}(CF_3)_8$ **V** were isolated via HPLC (Cosmosil Buckyprep 10 mm I.D. × 25 cm column and toluene–hexane, 1:1 v/v, as an eluent with flow rate of 4.6 mL min^{-1}).

Alkylation of C_2-p^7-$C_{70}(CF_3)_8$ with diethyl malonate in the presence of DBU

DBU (0.2 μL, 1.3 μmol) in toluene (20 μL) was added to the solution of C_2-$C_{70}(CF_3)_8$ (2 mg, 1.3 μmol) in toluene (3 mL) and the resulting mixture was stirred at 40°C for 5 min under an inert atmosphere. Then diethyl malonate (0.2 μL, 1.3 μmol) in toluene (20 μL) was added. After 10 min of further stirring at 40°C, few drops of CF_3COOH were added, and the reaction mixture was filtered through silica using toluene as an eluent. According to the HPLC, MALDI MS, and UV/Vis spectra, there was only a single reaction product, which was identified as compound **III**.

The Bingel-Diederich reaction with C_2-p^7-$C_{70}(CF_3)_8$

To the solution of C_2-$C_{70}(CF_3)_8$ (0.9 mg, 0.6 μmol) in toluene (1.5 mL), DBU (0.09 μL, 0.6 μmol), I_2 (0.15 mg, 0.6 μmol) and diethyl malonate (0.09 μL, 0.6 μmol) in toluene (60 μL) were added. The reaction mixture was stirred at 40°C for 10 min under an inert atmosphere. Then a few drops of CF_3COOH were added, and the mixture was filtered through silica using toluene as an eluent. According to HPLC, MS MALDI and UV/Vis data, the product composition was the same as in the reaction under the Bingel-Hirsch conditions.

Compound I, $C_{70}(CF_3)_8[C(CO_2Et)_2][CH(CO_2Et)_2]H$: t_R 5.1 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene–hexane, 3:7 (v/v), 1 mL min^{-1}); ^{19}F NMR (564.7 MHz, $CDCl_3$, 25 °C, C_6F_6): δ=–57.7 (m, 3F; CF_3), –61.0 (m, 3F; CF_3), –61.5 (m, 3F; CF_3), –62.4 (m, 3F; CF_3), –62.6 (m, 3F; CF_3), –64.3 (m, 3F; CF_3), –64.5 (q, J(F,F)=13.8 Hz, 3F; CF_3), –71.9 ppm (q, J(F,F)=12.1 Hz, 3F; CF_3); UV/Vis (toluene): λ_{max}=365, 390, 416 nm; MALDI MS: m/z (%): 1551.0 (100) [M–{$C(CO_2Et)_2$}$^-$], 1709.0 (6) [M^-].

Compound II, $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$: t_R 5.4 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene–hexane, 3:7 (v/v), 1 mL min^{-1}); ^{1}H NMR (400.3 MHz, $CDCl_3$, 25 °C, TMS): δ=4.48 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.8 Hz, 2H; $2CH_2$), 4.45 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.8 Hz, 2H; $2CH_2$), 4.39 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.8 Hz, 2H; $2CH_2$), 4.35 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.8 Hz, 2H; $2CH_2$), 1.41 (t, ^3J(H,H)=7.1 Hz, 6H; $2CH_3$), 1.35 ppm (t, ^3J(H,H)=7.1 Hz, 6H; $2CH_3$); ^{19}F NMR (376.5 MHz,

$CDCl_3$, 25 °C, C_6F_6): δ=–61.52 (m, 6F; CF_3), –62.33 (br. sept, J(F,F)=11.0, 6F; CF_3), –62.50 (m, 6F; CF_3), –69.60 ppm (q, J(F,F)=10.6 Hz, 6F; CF_3); UV/Vis (toluene): λ_{max}=365, 412, 471, 518, 558 nm; MALDI MS: *m/z* (%): 1639.0 (5) [*M*–CF_3^-], 1652.3 (11) [*M**–CF_3^-], 1708.0 (100) [*M*$^-$].

Compound III, $C_{70}(CF_3)_8[CH(CO_2Et)_2]H$: t_R 4.7 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene–hexane, 1:1 (v/v), 1 mL min^{-1}); ^{1}H NMR (400.3 MHz, $CDCl_3$, 25 °C, TMS): δ=5.91 (s, 1H, C_{cage}–*H*), 4.91 (q, J(H,F)=2.7 Hz, 1H; C*H*$(CO_2Et)_2$), 4.46 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.8 Hz, 1H; CH_2), 4.36 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.8 Hz, 1H; CH_2), 4.33 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=11.0 Hz, 1H; CH_2), 4.31 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=11.0 Hz, 1H; CH_2), 1.39 (t, ^3J(H,H)=7.1 Hz, 3H; CH_3), 1.29 (t, ^3J(H,H)=7.1 Hz, 3H; CH_3); ^{19}F NMR (376.5 MHz, $CDCl_3$, 25 °C, C_6F_6): δ=–57.95 (sept, J(F,F)=13.1, 3F; CF_3), –60.75 (3F, sept, J(F,F)=13.7 Hz, CF_3), –61.30 (sept, J(F,F)=13.2 Hz, 3F; CF_3), –62.11 (sept, J(F,F)=12.8 Hz, 6F; CF_3), –62.39 (sept, J(F,F)=12.8 Hz, 3F; CF_3), –63.45 (sept, J(F,F)=13.2 Hz, 3F; CF_3), –63.87 (dq, J(F,F)=13.2 Hz and J(H,F)=2.7 Hz, 3F; CF_3), –71.80 ppm (q, J(F,F)=12.1 Hz, 3F; CF_3); UV/Vis (toluene): λ_{max}=305, 394, 417, 452 nm; MALDI MS: *m/z* (%): 1393.0 (100) [*M*–{$CH(CO_2Et)_2$}$^-$], 1552.0 (5) [*M*$^-$].

Compound IV, $C_{70}(CF_3)_8[C(CO_2Et)_2]$: t_R 5.3 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene–hexane, 1:1 (v/v), 1 mL min^{-1}); ^{1}H NMR (400.3 MHz, $CDCl_3$, 25 °C, TMS): δ=4.49 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.6, 2H; CH_2), 4.45 (dq, ^3J(H,H)=7.1 Hz, ^2J(H,H)=10.6 Hz, 2H; CH_2), 1.41 (t, ^3J(H,H)=7.1 Hz, 3H; CH_3), 1.32 ppm (t, ^3J(H,H)=7.1 Hz, 3H; CH_3); ^{19}F NMR (376.5 MHz, $CDCl_3$, 25 °C, C_6F_6): δ=–61.30 (m, 6F; CF_3), –61.60 (sept, J(F,F)=13.5 Hz, 3F; CF_3), –62.36 (m, 6F; CF_3), –62.78 (sept, J(F,F)=12.4 Hz, 3F; CF_3), –68.83 (q, J(F,F)=11.0 Hz, 3F; CF_3), –69.07 ppm (br. q, J(F,F)=10.4 Hz, 3F; CF_3); UV/Vis (toluene): λ_{max}=388, 417, 458, 484, 516, 564, 612 nm; MALDI MS: *m/z* (%): 1481.0 (4) [*M*–CF_3^-], 1494.3 (6) [*M**–CF_3^-], 1550.0 (100) [*M*$^-$].

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Notes

‡ Hereinafter, the isomeric names are given in the following format: "symmetry–notation of the addittion pattern–composition", *e.g.* C_s-p^7-$C_{70}(CF_3)_8$. Abbrevations used in the notation for the addition patterns: *p*, *para*, and *m*, *meta*, denote $C_6(CF_3)_2$ hexagon with 1,4- and 1,3-situated CF_3 groups, respectively; superscript denotes the number of similar edge-sharing fragments in a chain, a discontinuity in an addition pattern is denoted by comma.

Keywords: nucleophilic cyclopropanation • reaction mechanism • trifluoromethylfullerenes • DFT calculations • structure elucidation

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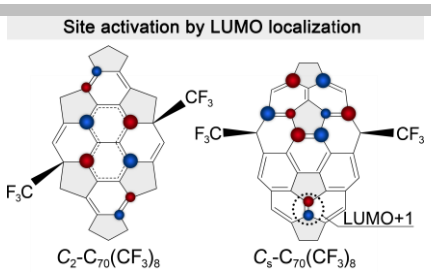
Entry for the Table of Contents

FULL PAPER

Acceptor derivatized fullerene substrates can exhibit enhanced reactivity and regioselectivity in the important organic reactions. We report Bingel and Bingel-Hirsch functionalization of C_2-$C_{70}(CF_3)_8$, which affords rapid and LUMO-directed regioselective formation of both conventional cyclopropanated and unusual alkylated products. The mechanistic and regiochemical aspects of the reaction are explained with the aid of the DFT calculations.



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Page No. – Page No.

Orienting effect of the cage addends: the case of nucleophilic cyclopropanation of C_2-$C_{70}(CF_3)_8$