

25. Methanofullerene Molecular Scaffolding: Towards C₆₀-Substituted Poly(triacetylenes) and Expanded Radialenes, Preparation of a C₆₀–C₇₀ Hybrid Derivative, and a Novel Macrocyclization Reaction

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The synthesis of (*E*)-hex-3-ene-1,5-diynes and 3-methylidenepenta-1,4-diynes with pendant methano[60]-fullerene moieties as precursors to C₆₀-substituted poly(triacetylenes) (PTAs, *Fig. 1*) and expanded radialenes (*Fig. 2*) is described. The *Bingel* reaction of diethyl (*E*)-2,3-dialkynylbut-2-ene-1,4-diyl bis(2-bromopropanedioates) **5** and **6** with two C₆₀ molecules (*Scheme 2*) afforded the monomeric, silyl-protected PTA precursors **9** and **10** which, however, could not be effectively desilylated (*Scheme 4*). Also formed during the synthesis of **9** and **10**, as well as during the reaction of C₆₀ with the desilylated analogue **16** (*Scheme 5*), were the macrocyclic products **11**, **12**, and **17**, respectively, resulting from double *Bingel* addition to one C-sphere. Rigorous analysis revealed that this novel macrocyclization reaction proceeds with complete regio- and diastereoselectivity. The second approach to a suitable PTA monomer attempted *N,N'*-dicyclohexylcarbodiimide(DCC)-mediated esterification of (*E*)-2,3-diethynylbut-2-ene-1,4-diol (**18**, *Scheme 6*) with mono-esterified methanofullerene-dicarboxylic acid **23**; however, this synthesis yielded only the corresponding decarboxylated methanofullerene-carboxylic ester **27** (*Scheme 7*). To prevent decarboxylation, a spacer was inserted between the reacting carboxylic-acid moiety and the methano C-atom in carboxymethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (**28**, *Scheme 8*), and DCC-mediated esterification with diol **18** afforded PTA monomer **32** in good yield. The formation of a suitable monomeric precursor **38** to C₆₀-substituted expanded radialenes was achieved in 5 steps starting from dihydroxyacetone (*Schemes 9 and 10*), with the final step consisting of the DCC-mediated esterification of **28** with 2-[1-ethynyl(prop-2-ynylidene)]propane-1,3-diol (**33**). The first mixed C₆₀–C₇₀ fullerene derivative **49**, consisting of two methano[60]fullerenes attached to a methano[70]fullerene, was also prepared and fully characterized (*Scheme 13*). The C_s-symmetrical hybrid compound was obtained by DCC-mediated esterification of bis[2-(2-hydroxyethoxy)ethyl] 1,2-methano[70]fullerene-71,71-dicarboxylate (**46**) with an excess of the C₆₀-carboxylic acid **28**. The presence of two different fullerenes in the same molecule was reflected by its UV/VIS spectrum, which displayed the characteristic absorption bands of both the C₇₀ and C₆₀ mono-adducts, but at the same time indicated no electronic interaction between the different fullerene moieties. Cyclic voltammetry showed two reversible reduction steps for **49**, and comparison with the corresponding C₇₀ and C₆₀ mono-adducts **46** and **30** indicated that the three fullerenes in the composite fullerene compound behave as independent redox centers.

1. Introduction. – Conjugated polymers are widely explored as advanced materials for electronic [1], photonic [2], and nonlinear optical applications [3]. For many years, polyacetylenes [4] and poly(diacetylenes) [5] were the only known single-strand conjugated polymers with a non-aromatic all-C-atom backbone; however, recently we succeeded in preparing first oligomers [6] and polymers [7] with a poly(triacetylene) (PTA) back-

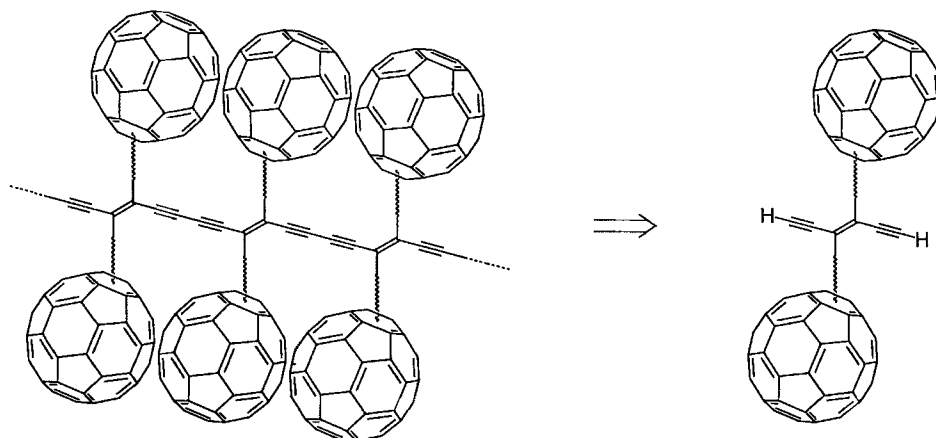


Fig. 1. Proposed synthesis of C_{60} -substituted poly(triacetylenes) (PTAs) by oxidative acetylenic couplings of (*E*)-hex-3-ene-1,5-diyne precursors with two pendant fullerene spheres

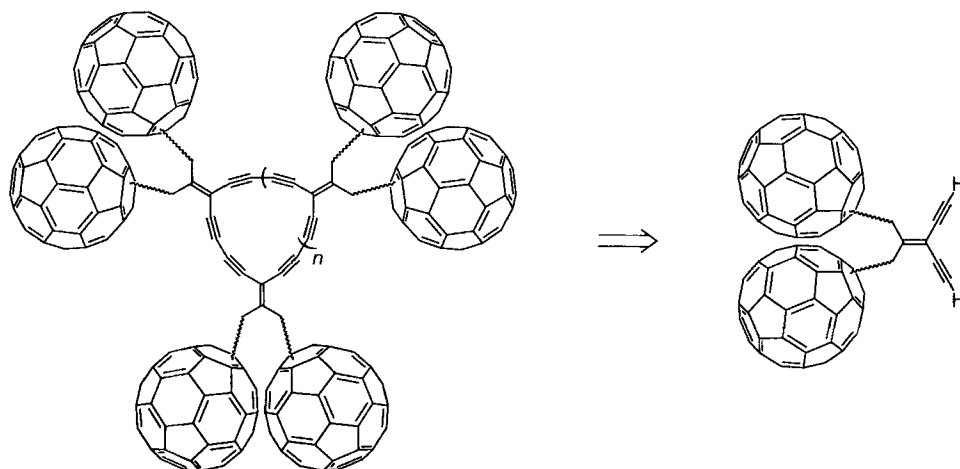


Fig. 2. Proposed synthesis of C_{60} -substituted expanded radialenes by oxidative cyclization of 3-methylenepenta-1,4-diyne precursors

bone. As part of our research in C-scaffolding and the construction of C-rich nanomaterials [8], we became interested in the preparation of PTA oligomers and polymers with laterally appended C_{60} spheres (Fig. 1). In view of the many intriguing properties of C_{60} , such as large nonlinear optical effects [9], superconductivity of the alkali metal salts M_3C_{60} [10a–d], and ferromagnetism of charge-transfer complexes with amines [10e,f], conjugated polymers with pendant fullerene spheres were also expected to display a variety of interesting material features [11].

Whereas oxidative coupling of C_{60} -substituted (*E*)-hex-3-ene-1,5-diyne should yield linearly conjugated molecular rods with the PTA backbone, the corresponding geminally ethynylated 3-methylenepenta-1,4-diyne should give C_{60} -substituted macrocycles, namely expanded radialenes (Fig. 2). Recently, first examples of these robust, multi-

Herein, we report the synthesis of C₆₀-substituted monomeric precursors for the construction of fullerene-containing PTAs and expanded radialenes, as depicted in *Figs. 1* and *2*, respectively. We also describe some of the interesting reactivity encountered during the synthesis of these molecules, specifically, a new, direct regio- and diastereoselective bis-functionalization of C₆₀ and a new synthesis of methanofullerene-carboxylic esters. As part of this research program on oligomeric and polymeric fullerene materials, we also communicate the preparation of a mixed C₆₀–C₇₀ fullerene compound which consists of a C₇₀ derivative bearing two C₆₀ substituents. This hybrid is the first member of a new class of mixed fullerene oligomers.

Dibromides **5** and **6** were added to C_{60} by *Bingel* reaction (DBU, PhMe) to form the bis(1,2-methanofullerene) derivatives **9** and **10**, respectively (*Scheme 2*). Their solubility

Reaction scheme showing the synthesis of **1** and **2** from **3** and **4**, and their subsequent conversion to **5**, **6**, **7**, and **8**.

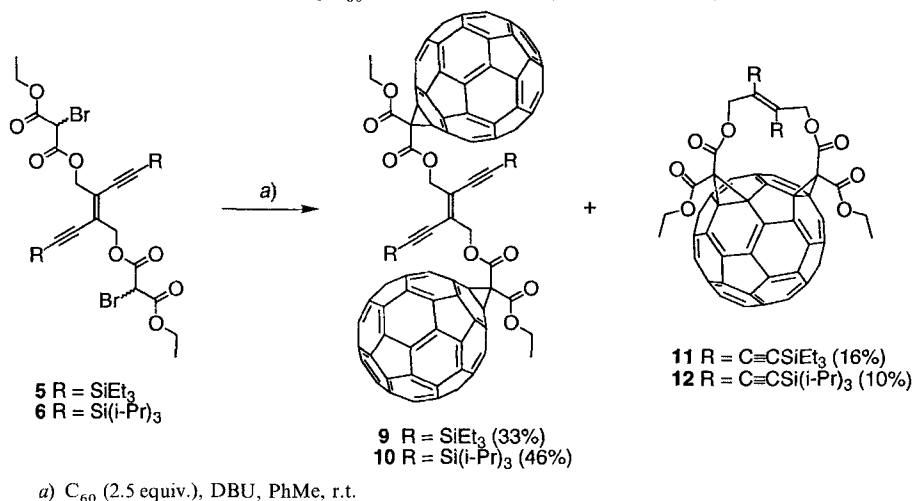
1 R = SiEt₃
2 R = Si(i-Pr)₃

3 R = SiEt₃ (50%)
4 R = Si(i-Pr)₃ (65%)

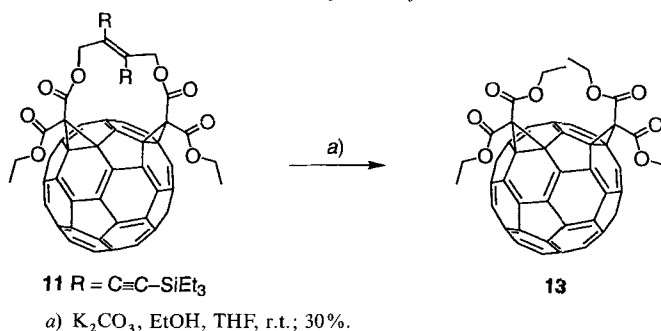
5 R = SiEt₃ (52%)
6 R = Si(i-Pr)₃ (48%)

7 R = SiEt₃ (11%)
8 R = Si(i-Pr)₃ (18%)

a) $\text{EtO}_2\text{CCH}_2\text{COCl}$, $\text{C}_5\text{H}_5\text{N}$, CH_2Cl_2 , 0° to r.t. b) DBU (2 equiv.), THF, 0° to r.t., then -78° , CBr_4 (2 equiv.).

Scheme 2. Reactions of C_{60} with the Tethered Bis(2-bromomalonates) **5** and **6**

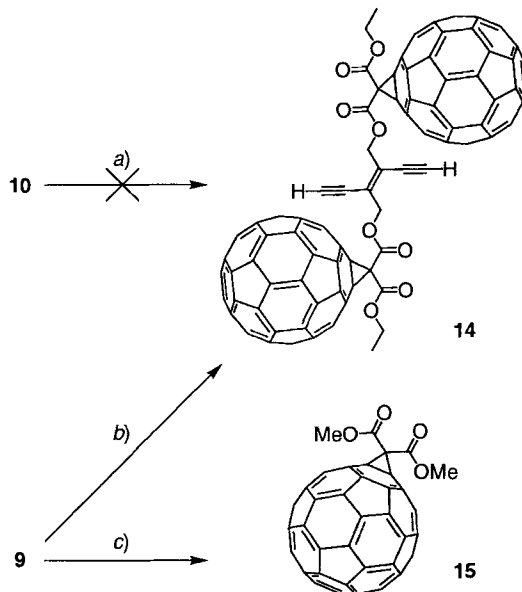
in aromatic and chlorinated organic solvents was sufficient to allow for complete spectroscopic characterization. The UV/VIS spectra of **9** and **10** displayed similar absorption bands and end absorptions (λ 690 nm) to those measured for diethyl 1,2-methano[60]-fullerene-61,61-dicarboxylate [15a]. As previously reported for other bis-fullerene derivatives [18] [19], there exists no electronic communication between the two fullerene moieties. Interestingly, the C_{60} bis-adducts **11** and **12**, resulting from a macrocyclization reaction on the C_{60} core, were also isolated as major side products. When the reaction between **6** and C_{60} was performed under high dilution conditions, only a trace amount of **10** was formed, and bis-adduct **12** was isolated in 15% yield. This new, direct bis-functionalization of C_{60} was highly regioselective. In effect, the linker between the two malonate moieties acted as a directing tether [20], and only one out of nine possible, constitutionally isomeric bis-adducts [21] [22] was formed. The relative position of the two cyclopropane rings on the C_{60} core was unambiguously determined by transformation of **11**, via transesterification, into the known C_s -symmetrical *cis*-2 tetraethyl ester **13** [21] (Scheme 3). Although there exist a total of four possible C_1 -symmetrical *cis*-2

Scheme 3. Transesterification of Bis-adduct **11**

diastereoisomers [22], compounds **11** and **12** were formed with complete diastereoselectivity. Due to the in/out stereoisomerism [23], the two ethoxycarbonyl residues in **11** and **12** can either adopt an 'out-out' (as shown in *Scheme 2*), an 'in-out', or an 'in-in' orientation with respect to each other. Furthermore, due to the restricted rotation of the *trans*-alkene moiety in the 13-membered ring, two 'in-out' diastereoisomers are possible. Steric considerations derived from molecular and computer modeling strongly suggested that the two bis-adducts **11** and **12** should adopt the 'out-out'-configuration, in analogy to a related macrocyclic *cis*-2 bis-adduct for which an X-ray crystal structure was obtained [22]. Following the isolation of **11** and **12**, the general character of this facile methodology for the selective preparation of C_{60} bis-adducts was established and recently reported in a preliminary communication [22].

All efforts to efficiently deprotect the bis-fullerene derivatives **9** or **10** toward formation of the desired PTA monomer **14** were disappointing (*Scheme 4*). Reaction of **10** with Bu_4NF under various conditions led to polymerization and/or decomposition, as had been previously reported for the attempted F^- -mediated deprotection of $(i\text{-}Pr)_3Si-C\equiv C$ -substituted methanofullerenes [24]. Removal of the more labile Et_3Si -protecting groups in **9** by protodesilylation ($K_2CO_3/MeOH/THF$) did not give **14** but rather dimethyl ester **15** (65% yield), resulting from remarkably facile transesterification. On a very small, preparatively impractical scale (0.003 mm runs), Et_3Si -protected **9** could be transformed with a catalytic amount of Bu_4NF on SiO_2 in wet THF into the free *trans*-enediynes **14** in 94% yield. All attempts, however, to scale up this reaction failed, and only decomposition products were observed.

Scheme 4. Attempted Desilylation of Bis-fullerene Derivatives **9** and **10**

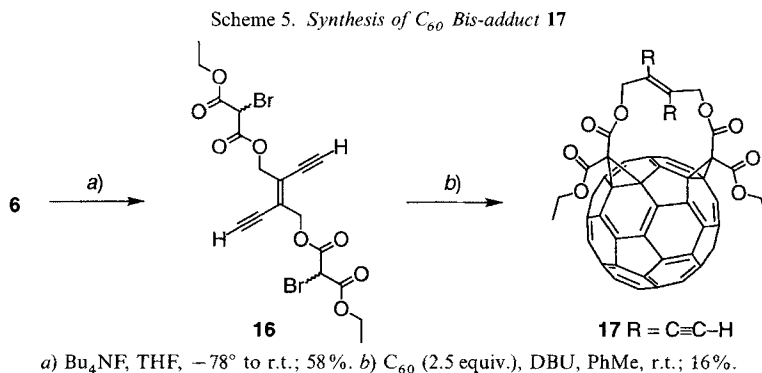


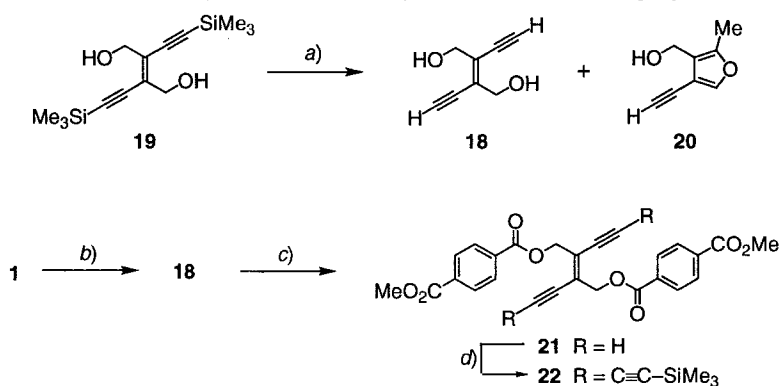
a) Bu_4NF , THF, -78° or r.t.; or Bu_4NF on SiO_2 , THF, -78° or r.t. b) 0.0034 mm **9**, Bu_4NF on SiO_2 , THF, r.t.; 94%. c) K_2CO_3 , MeOH, THF, r.t.; 65%.

To avoid the problematic removal of the R_3Si -protecting groups in **9** and **10**, deprotection of the *trans*-enediynes was performed before the coupling reaction with C_{60} . Actually, protection of terminal alkynes in substrates for the *Bingel* addition to C_{60} is *a priori* not necessary, since DBU (pK_a 24.3 in MeCN) [25] is not sufficiently basic to deprotonate a terminal ethynyl group. Also, previous experience [7a] suggested that unprotected *trans*-enediynes **16** would have sufficient stability for isolation and further reaction. Deprotection of **6** with Bu_4NF in THF indeed afforded **16** in 58% yield; the subsequent *Bingel* addition, however, gave none of the desired bis-fullerene derivative **14** but rather, as the only isolable product, the macrocyclic bis-adduct **17** (16%, *Scheme 5*). The product distribution in the *Bingel* reaction of **5**, **6**, and **16** with C_{60} (*Schemes 2* and *5*) is clearly dependent upon the nature of the alkyne substituents (R), with bulky groups apparently retarding the macrocyclization due to unfavorable steric demands. Thus, the bis-adduct/bis-fullerene product ratio increases from 1:5 ($R = (i\text{-}Pr)_3Si$), to 1:2 ($R = Et_3Si$), to bis-adduct formation only ($R = H$).

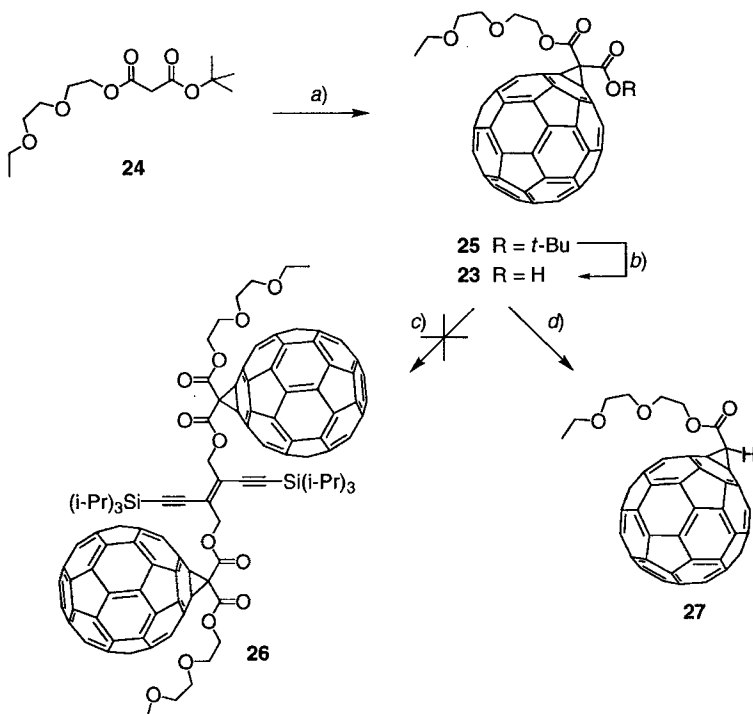
2.2. A PTA Monomer by Esterification of 1,2-Methano[60]fullerene-carboxylic Acids. To avoid the problems of alkyne deprotection and competing macrocyclization encountered in the synthesis of **14** (*Sect. 2.1*), an alternative route to PTA monomers was pursued by esterification of 1,2-methano[60]fullerene carboxylic-acid derivatives with (*E*)-2,3-diethynylbut-2-ene-1,4-diol (**18**). This diol was obtained in low yield (6%) by protodesilylation ($K_2CO_3/MeOH/THF$) of **19** [7a] [26], with the major product formed being furan **20** resulting from *exo-dig* cyclization of **19** under the basic conditions [18b] [27] (*Scheme 6*). Fortunately, the undesired furan formation could be avoided by preparing **18** via deprotection of **1** with Bu_4NF in THF. In model reactions to support the feasibility of the new route towards PTA monomers and polymers, diol **18** was transformed in 61% yield into diester **21** by N,N' -dicyclohexylcarbodiimide(DCC)-mediated esterification [28] with terephthalic acid. Subsequently, the potential of *trans*-enediynes diesters in oxidative coupling reactions was successfully demonstrated by reacting **21** under *Hay* conditions [29] with $Me_3Si-C\equiv C-H$ giving **22** in 72% yield.

As the second component in the 'esterification route' towards a PTA monomer, methanofullerene-carboxylic acid **23** was prepared starting from the mixed malonate ester **24** (*Scheme 7*). Reaction of malonyl dichloride with *t*-BuOH and diethyleneglycol monoethyl ether in CH_2Cl_2 in the presence of C_5H_5N afforded **24**, which was treated with C_{60} in PhMe in the presence of DBU and I_2 [15b] to give highly soluble **25**, of which



Scheme 6. Synthesis of Diol **18**, Model Esterification, and Oxidative Coupling Reactions


a) K_2CO_3 , MeOH, THF, r.t.; 6% (**18**) and 60% (**20**). b) Bu_4NF , THF, r.t. c) Methyl hydrogen terephthalate, DCC, 4-(dimethylamino)pyridine (DMAP), CH_2Cl_2 , r.t.; 61% (from **1**). d) $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$ (100 equiv.), CuCl , N,N,N',N' -tetramethylethylenediamine (TMEDA), O_2 , CH_2Cl_2 , r.t.; 72%.

 Scheme 7. Synthesis of Methanofullerene-carboxylic Acid **23** and Decarboxylation to **27**


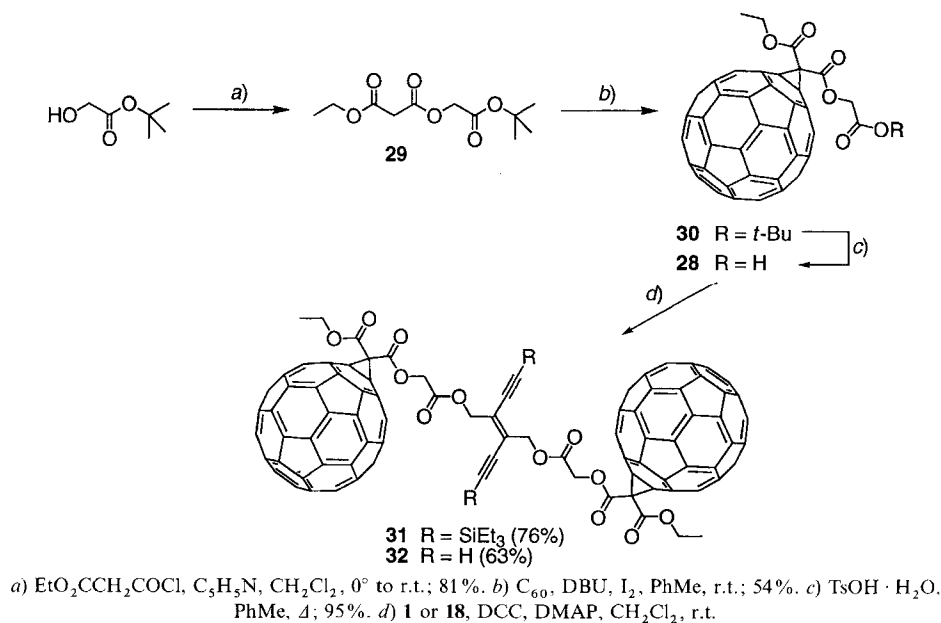
a) C_{60} , DBU, I_2 , PhMe, r.t.; 51%. b) $\text{TsOH} \cdot \text{H}_2\text{O}$, PhMe, Δ ; 95%. c) **2**, DCC, DMAP, CH_2Cl_2 , r.t. d) DMAP, CH_2Cl_2 , r.t.; 85%.

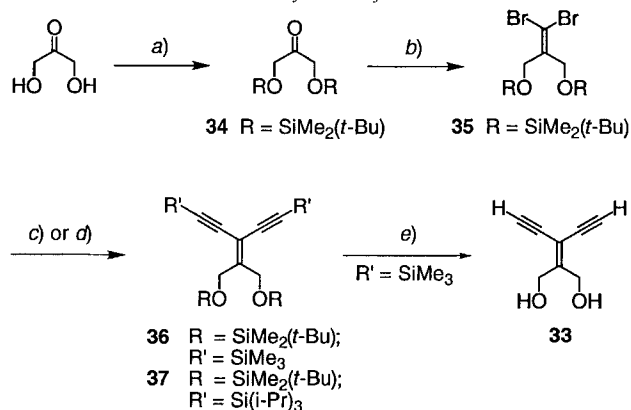
350 mg could be dissolved in *ca.* 1 ml of CDCl_3 . Selective hydrolysis of the *t*-Bu ester moiety with toluene-4-sulfonic acid (TsOH) in refluxing PhMe [30] gave **23** which also was readily soluble in chlorinated organic solvents. DCC-Mediated esterification of **23** with diol **2** in CH_2Cl_2 , however, was not successful and afforded methanofullerene **27** by rapid decarboxylation rather than desired **26**. It was subsequently determined that decarboxylation of **23** readily occurs in the presence of a catalytic amount of DMAP in CH_2Cl_2 at r.t., affording **27** in high yield (85%).

Methanofullerene-monocarboxylic esters such as **27** were previously prepared in generally modest yields by 1,3-dipolar cycloaddition of the corresponding diazo esters to C_{60} , followed by elimination of N_2 [16a] [31]. In addition, these reactions led to mixtures of 6,6-closed and 6,5-open (addition to bonds shared by a 5- and a 6-membered ring) isomers which had to be subsequently equilibrated to the thermodynamically more stable 6,6-closed product. The *Bingel* addition of mixed malonate esters such as **24** to C_{60} , followed by hydrolysis of the *t*-Bu ester moiety and decarboxylation appears to be a mild, efficient alternative for the preparation of methanofullerene-monocarboxylic esters.

To prevent decarboxylation reactions under the conditions of DCC/DMAP-mediated esterifications, a spacer was introduced between the bridging C-atom of the methanofullerene and the reacting carboxylic-acid group. The synthesis of the targeted acid **28** started with the reaction of *tert*-butyl 2-hydroxyacetate [32] with ethyl 3-chloro-3-oxopropanoate to give the mixed malonate ester **29** (Scheme 8). Methanofullerene **30** was obtained by *Bingel* reaction of C_{60} with **29** in the presence of DBU and I_2 in PhMe, and selective cleavage of the *tert*-butyl ester (TsOH, PhMe) yielded the desired carboxylic acid **28**. DCC-Mediated esterification of **28** with diols **1** and **18** subsequently afforded the

Scheme 8. Synthesis of *trans*-Enediyne **32**, a Direct Precursor for the Oxidative Cyclization to C_{60} -Appended Poly(triacetylenes)



Scheme 9. *Synthesis of Diol 33*

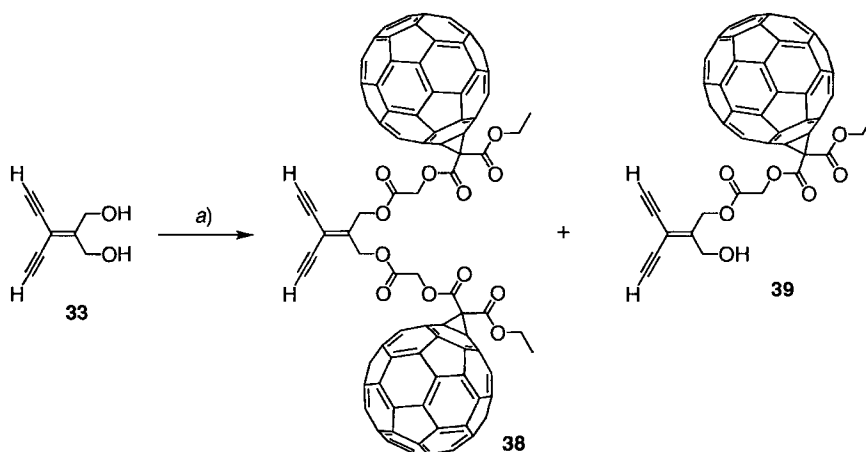
a) 1*H*-Imidazol, $\text{Me}_2(t\text{-Bu})\text{SiCl}$, DMF, r.t. b) CBr_4 , PPh_3 , PhH, r.t.; 38 %. c) $\text{Me}_3\text{Si}-\text{C}\equiv\text{CH}$, $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI, Et_3N , r.t.; 73 %. d) $(i\text{-Pr})_3\text{Si}-\text{C}\equiv\text{CH}$, $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI, Et_3N , r.t.; 86 %. e) Bu_4NF (5 equiv.), wet THF, 0°; 66 %.

protected and deprotected PTA monomers **31** and **32**, respectively, in good yields. It should be noted that the described route readily provides access to multigram quantities of **32** that are required for the exploration of the oxidative coupling to C_{60} -appended PTA oligomers and polymers. Compound **32** displays low solubility in common organic solvents but is remarkably stable and does not melt or decompose below 280°.

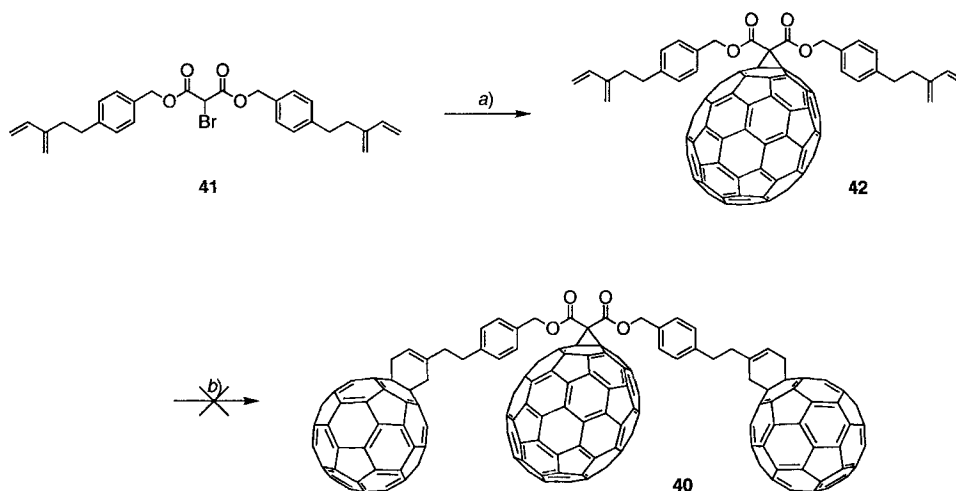
2.3. Synthesis of a Monomer for the Preparation of C_{60} -Substituted Expanded Radialenes. The synthesis of a direct monomer for the oxidative cyclization to expanded radialenes with pendant methano[60]fullerene residues followed the 'esterification route' employed for the preparation of PTA monomer **32** (Sect. 2.2). To obtain diol **33** required for this route (Scheme 9), protected dihydroxyacetone **34** was synthesized as reported by Tamm and coworkers [33], and subsequent Corey-Fuchs dibromoolefination ($\text{CBr}_4/\text{PPh}_3$) [34] afforded **35** as a stable oil. Pd-Catalyzed coupling of **35** with either $\text{Me}_3\text{Si}-$ or $(i\text{-Pr})_3\text{Si}$ -protected acetylene gave the geminal diynes **36** and **37** in high yields, respectively [35]. Deprotection of **36** with Bu_4NF in THF at 0° led to diol **33** as an unstable oily solid. Under these conditions, **33** did not react further under undesirable furan formation.

Because of its instability, diol **33** was quickly carried on to the next step without further purification. Under the DCC-mediated esterification conditions, methano[60]fullerene-carboxylic acid **28** reacted with **33** to yield the bis- and mono-adducts **38** and **39** in 25 and 23 % yields, respectively (Scheme 10). The solubility of both products was sufficient to allow full spectroscopic characterization. Similar to the isomeric PTA monomer **32**, the direct precursor **38** to the expanded radialenes is highly stable under normal laboratory conditions.

2.4. Synthesis of a Mixed C_{60} - C_{70} Fullerene Derivative: a Member of a New Class of Fullerene-Based Oligomers. The first target in our attempts to prepare mixed fullerene oligomers was compound **40** with two C_{60} Diels-Alder adducts attached to a central methano[70]fullerene (Scheme 11). Bingel addition of the anchor-tether-reactive-group conjugate **41** [20a] to C_{70} was expected to occur selectively at the most curved bond near

Scheme 10. Synthesis of the Direct Precursor **38** to C_{60} -Substituted Expanded Radialenes

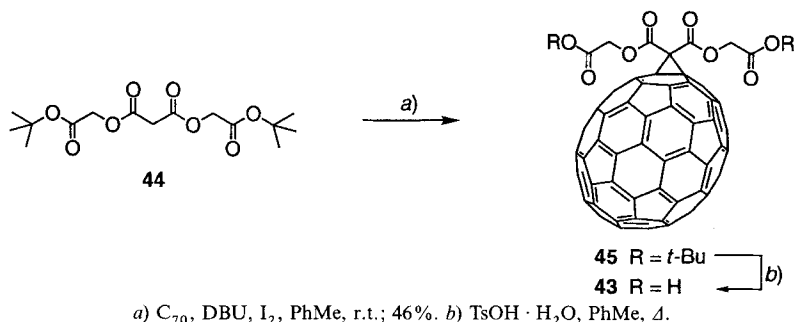
a) **28**, DCC, DMAP, CH_2Cl_2 , r.t.; 25 % (**38**) and 23 % (**39**).

Scheme 11. Attempted Synthesis of Mixed Fullerene Compound **40**

a) C_{70} , DBU, PhMe, r.t. b) C_{60} , PhMe, Δ .

the pole, yielding **42**. In contrast to the previous findings with C_{60} [20a], however, regioselective double intramolecular *Diels-Alder* addition of **42** should be disfavored, because the tether directs the two reactive 1,3-diene groups to 6,6-bonds of low reactivity [36] in the flatter equator region of the C_{70} sphere. Hence, intermolecular additions of **42** to C_{60} molecules present in solution should preferentially occur under formation of the mixed fullerene compound **40**.

Cyclopropanation of C_{70} with **41** [20a] in PhMe with DBU as base yielded mono-adduct **42** which is stable in dilute solution but polymerizes rapidly in the neat state. The

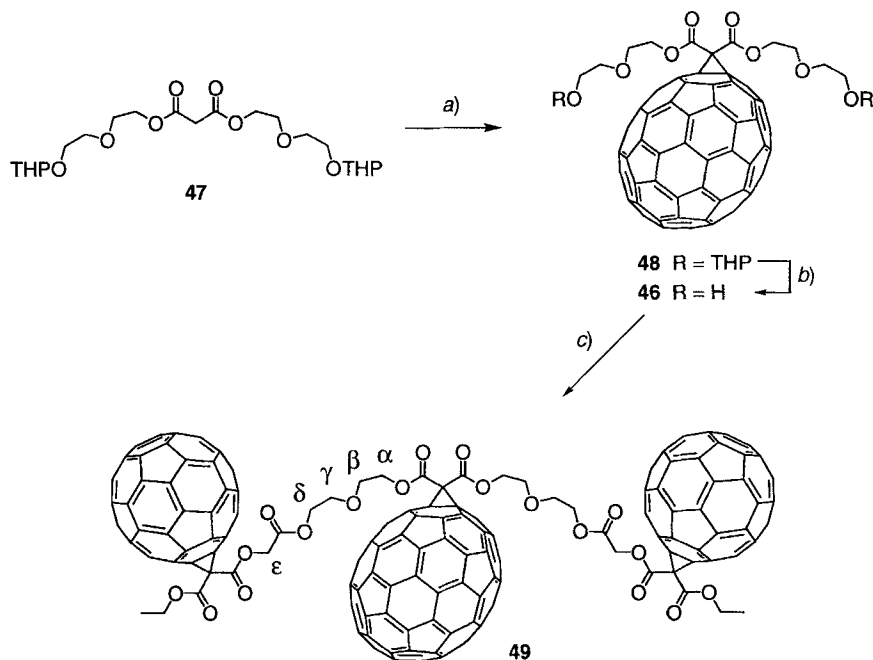
Scheme 12. Synthesis of 1,2-Methano[70]fullerene Dicarboxylic Acid **43**

subsequently attempted intermolecular *Diels-Alder* addition between the two buta-1,3-diene moieties of **42** and two C_{60} molecules [37], however, did not produce isolable amounts of hybrid compound **40**.

We subsequently intended to prepare a mixed fullerene compound by DCC-mediated esterification of methano[70]fullerene-dicarboxylic acid **43** (Scheme 12) with two equiv. of a suitable methano[60]fullerenol derivative. For the synthesis of **43**, malonate **44** was prepared by reacting *tert*-butyl 2-hydroxyacetate [32] with malonyl dichloride and subsequently added by *Bingel* reaction regioselectively [15a] [38] to the 1,2-bond at the pole of C_{70} under formation of **45**. The ^{13}C -NMR spectrum confirmed the C_s symmetry, displaying the 36 out of the 37 expected fullerene resonances (34 between 130 and 150 ppm, two of which showed half intensity, and 2 at 66.03 and 66.55 ppm), as well as 6 non-fullerenic signals (162.49 and 165.35 (C=O), 63.29 (CH_2), 28.10 and 83.00 (CMe_3), and 36.24 ppm (methano bridge)). Cleavage of the *t*-Bu ester groups in **45** (TsOH, PhMe) afforded diacid **43** as a very insoluble compound. Due to the low solubility, attempted DCC-mediated esterifications with **43** in CH_2Cl_2 failed and, therefore, the synthesis of a mixed fullerene compound needed to be changed again.

It was now planned to prepare the fullerene hybrid by esterification of methano[70]fullerenediol **46** with 2 equiv. of methano[60]fullerene-carboxylic acid **28**, which was already in hand (Scheme 13). On this, ultimately, successful route, malonate **47** was obtained by reacting 2-[2-(3,4,5,6-tetrahydro-2*H*-pyran-2-yloxy)ethoxy]ethanol [39] with malonyl dichloride and subsequently added to C_{70} under formation of 1,2-mono-adduct **48** which was obtained as a mixture of diastereoisomers. Deprotection (TsOH/EtOH/PhMe) afforded the readily soluble diol **46** which was doubly esterified with **28** to give the desired C_{60} - C_{70} hybrid **49** as a dark brown solid in 23% yield. Due to the low solubility of **28**, the esterification required high dilution and prolonged reaction times, which led to partial decomposition. The low yield of **49** was due to this decomposition as well as due to the difficulties in separating the target compound from the degradation products.

The structure of **49** was confirmed by matrix-assisted laser-desorption time-of-flight (MALDI-TOF) mass spectrometry, which depicted a strong molecular ion peak at m/z 2900 (M^+ , $C_{215}H_{30}O_{18}$ requires 2900.6). The C_s -symmetrical compound **49** was poorly soluble in CH_2Cl_2 and $CHCl_3$ but sufficiently soluble in $Cl_2DCCDCl_2$ to record both its 1H - and ^{13}C -NMR spectra.

Scheme 13. Synthesis of the C_{60} - C_{70} Hybrid Compound **49**

a) C_{70} , DBU, I_2 , PhMe, r.t.; 65%. b) $TsOH \cdot H_2O$, PhMe, EtOH, 60° ; 60%. c) **28** (3 equiv.), DCC, DMAP, CH_2Cl_2 , r.t.; 23%.

The 1H -NMR spectrum of **49** displayed seven signals between 1.4 and 5.0 ppm corresponding to the 5 different CH_2 groups α – ϵ (Scheme 13) and the t and q for the ethyl-ester groups. The $CH_2(\epsilon)$ protons are diastereotopic; however, they appeared as a sharp s resulting from a pseudo-plane of symmetry perpendicular to the mirror plane of the C_s -symmetrical compound. This pseudo-symmetry was also revealed in the ^{13}C -NMR spectrum, and both the C_{60} and C_{70} core resonances appeared with the typical pattern of C_s -symmetrical fullerenes. Of the 37 core resonances expected for a C_s -symmetrical C_{70} and the 32 ones for two identical, pseudo- C_s -symmetrical C_{60} moieties in **49**, a total of 60 were observed. As a result of this pseudo-symmetry, there is a large difference in intensity between the C_{70} and C_{60} signals, with the latter having twice the relative intensity of the former, and they are, therefore, easily distinguishable.

The electronic absorption spectra of **30**, **46**, and **49** are shown in Fig. 3. In the range between 430 nm and the end absorption above 700 nm, the spectrum of **49** closely resembles that of the C_{70} derivative **46**. As a result of the domination of the C_{70} chromophore in the visible absorption range, solutions of **49** have the classical brown-red color generally observed for C_{70} mono-adducts [36] [38]. Below 430 nm, the characteristic absorption bands of a methano[60]fullerene at 257, 325, and 425 nm [40], dominate the spectrum of hybrid **49**. Thus, the UV/VIS spectrum of **49** clearly reflects the presence of the two different fullerenes. Since the spectrum of **49** is remarkably similar in shape and intensity to a calculated UV/VIS spectrum resulting from addition of the spectra of **46** and **30** in a 1:2 ratio, there exists no special electronic interaction between the different fullerene sub-units in **49**. This is not surprising since the three fullerene moieties in the hybrid compound are separated by rather long tethers.

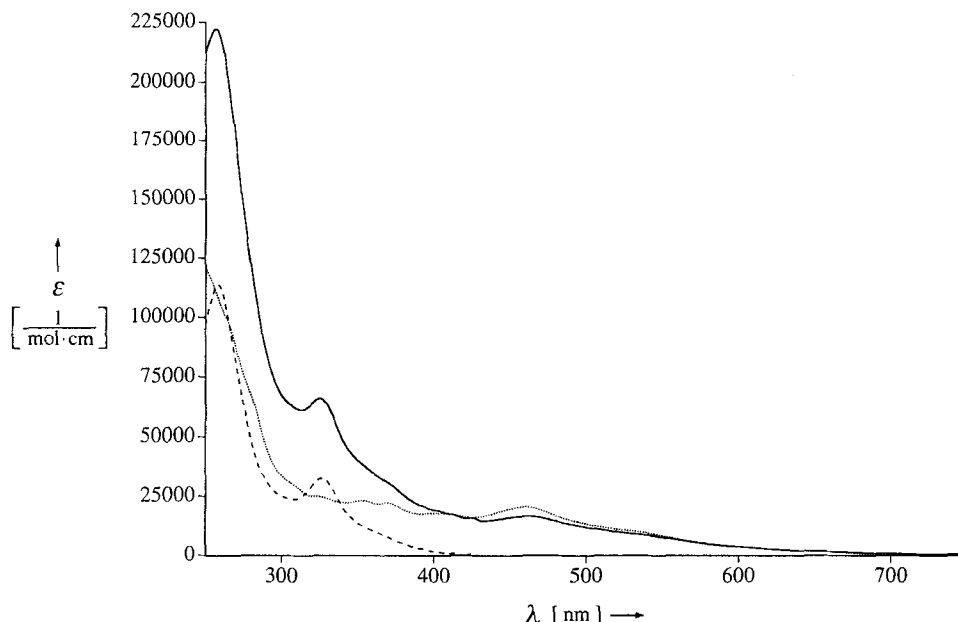


Fig. 3. UV/VIS Spectra of **30** (---), **46** (····), and **49** (—) in CH_2Cl_2

2.5. Electrochemical Studies. The redox behavior of **30**, **46**, and **49** is summarized in the Table. On the available potential range, **30** and **46** gave in CH_2Cl_2 several reduction steps [14a], the first two being reversible on the time scale of the cyclic voltammetry. Indeed, for all sweep rates, the current ratio $I_{\text{pc}}/I_{\text{pa}}$ was unity, and the peak potential difference, for sweep rates lower than 0.2 Vs^{-1} , was close to 90 mV for **30** and 70 mV for **46**, respectively (uncorrected for ohmic drop). All these features are characteristic of a reversible one-electron charge transfer.

For the mixed fullerene derivative **49**, only two reversible reduction steps were observed in the solvent mixture $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ 95:5. The cyclic voltammograms were not well defined for sweep rates higher than 0.2 Vs^{-1} due to adsorption phenomena. For sweep rates lower than 0.2 Vs^{-1} , the voltammogram showed reversible couples. Rotating disk electrode (RDE) experiments gave rise to two well defined reduction waves, each having the same amplitude. The slopes of these waves, by plotting E vs. $\log(I/I_d - I)$ were equal to 70 mV.

Table. Reduction Characteristics of the Fullerene Derivatives **30**, **46**, and **49** Observed by Cyclic Voltammetry on a Glassy Carbon Electrode in CH_2Cl_2 (+ 0.1M $(\text{Bu}_4\text{N})\text{PF}_6$)

	E_{red1}^0 ([V] vs. Fc/Fc^+) ^{a)}	E_{red2}^0 ([V] vs. Fc/Fc^+) ^{a)}
30	−1.00(86)	−1.38(93)
46	−1.02(68)	−1.39(82)
49 ^{b)}	−1.00(66)	−1.40(83)

^{a)} In parentheses, ΔE_p in mV at $v = 0.1 \text{ V s}^{-1}$.

^{b)} $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ 95:5 was used instead of CH_2Cl_2 for solubility reasons.

As the number and the reduction potentials are quite identical in the mixed fullerene derivative **49**, as compared to the separate C_{60} and C_{70} adducts (*Table*), it is clear that the three fullerenes in **49** behave as independent redox centers. The resulting voltammogram is consistent with the sum of the individual constituents. It can, therefore, be assumed that each of the two reversible reduction steps of **49** involves three electrons, namely one for each independent redox center on each fullerene. The near identity of the potentials at which the first three one-electron reductions occur in C_{60} and C_{70} [41] had been established shortly after the discovery of the bulk preparation method for fullerenes in 1990 [42]. The presence of three independent redox centers in **49** was, to some extent, expected as the fullerene sub-units in **49** are separated by rather long, saturated chains. These results are also in agreement with the UV/VIS spectra discussed above.

3. Conclusions. – (*E*)-Hex-3-ene-1,5-diynes and 3-methylidenepenta-1,4-diynes with pendant C_{60} moieties were synthesized as precursors to fullerene-substituted poly(tri-acylenes) (PTAs) and expanded radialenes, respectively. The direct precursors to PTAs, *i.e.*, **32**, and to expanded radialenes, *i.e.*, **38**, each contain two terminal free alkyne groups, yet both constitutionally isomeric compounds are remarkably stable. Other attractive features are their relatively good solubility, despite two appended C_{60} moieties and molecular weights above 1900 D, as well as their potential availability in multigram quantities. Investigations into the formation of the targeted C_{60} -substituted PTAs and expanded radialenes are now further pursued in our laboratory.

During the development of suitable PTA monomers in this study, a new macrocyclization reaction, consisting of a double *Bingel* addition of a tethered bis-malonate to C_{60} was discovered. Thus, reactions of bis-bromomalonates **5**, **6**, and **16** yielded the macrocyclic products **11**, **12**, and **17**, respectively, with complete regio- and diastereoselectivity. In the meantime, the versatility of this simple bis-functionalization of C_{60} was further established, and bis-malonates with optically active tethers were even applied to the enantioselective preparation of optically active C_{60} bis-adducts [22] whose chirality exclusively results from the chiral addition pattern [43].

Also during the search for suitable monomers for C_{60} -substituted expanded radialenes, a new synthesis of methano[60]fullerene-monocarboxylic esters was discovered which should hold distinct advantages, such as high yields and versatile access, over the established preparation of these compounds by 1,3-dipolar cycloaddition of diazo esters followed by N_2 elimination. The new synthetic sequence consists of *i*) the *Bingel* addition of mixed *tert*-butyl malonate esters (such as **24**) to C_{60} , *ii*) selective hydrolysis of the *tert*-butyl ester moiety, and *iii*) decarboxylation of the resulting acid (such as **23**) by stirring with DMAP in CH_2Cl_2 under formation of the desired monoester (such as **27**).

Finally, with **49**, the first mixed C_{60} – C_{70} fullerene derivative, which is composed of a C_{70} -mono-adduct bearing two C_{60} substituents, was prepared and fully characterized. Compound **49** can be viewed as the first representative of a new family of mixed fullerene oligomers, and this work demonstrates that by choosing the right building blocks and coupling conditions, soluble fullerene composites with $M_w \approx 3000$ D and above can be prepared.

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Mr. Hans-Ulrich Hediger for recording the MALDI-TOF mass spectra, and Dr. Monika Šebova, Mr. Rainer Martin, Dr. Berthold Hinzen, Mr. Jens Cuntze, Dr. Esther Martinborough, Ms. Francesca Cardullo, Dr. Ulf Neidlein, and Dr. Peter Walliman for high-field NMR measurements.

Experimental

General. Reagents and solvents were purchased reagent grade and used without further purification. Fullerene soot extract was purchased from *MER Corporation*, Tucson, Arizona (AZ) 85706, USA. THF was distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled over CaH_2 or dried over molecular sieves (4 Å). C_{60} [40] and C_{70} [38b] were purified as previously reported. *tert*-Butyl 2-hydroxyacetate [32], 2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethanol [39], compounds **1** [17b], **2** [17a], **19** [7a] [26], **34** [33], and **41** [20a] were prepared as previously reported. All reactions were performed in standard glassware under an inert atmosphere of N_2 or Ar. Evaporation and concentration was done at water-aspirator pressure, and compounds were dried at 10^{-2} Torr. Column chromatography (CC): SiO_2 -60 (230–400 mesh, 0.040–0.063 mm) from *E. Merck*. Thin-layer chromatography (TLC): glass sheets coated with SiO_2 -60 F_{254} from *E. Merck*; visualization by UV light. Melting points: *Büchi Smp-20*; uncorrected. UV/VIS Spectra (λ_{max} in nm (ϵ)): *Varian Cary-5*-spectrophotometer. IR spectra (cm^{-1}): *Perkin-Elmer 1600-FTIR*. NMR Spectra: *Bruker AM 500* and *Varian Gemini 300* or 200 at 296 or 300 K, with solvent peaks as reference. EI-MS (m/z (%)): *VG Tribrid* instrument; 70 eV. FAB-MS: *VG ZAB 2SEQ* instrument; 3-nitrobenzyl alcohol as matrix. MALDI-TOF-MS: measured with reflectron detection in the positive- or negative-ion mode, acceleration voltage 15–20 kV, on a *Bruker-REFLEX* spectrometer; 2,5-dihydroxybenzoic acid (DHB, 0.1M in MeCN/EtOH/ H_2O 50:45:5), α -cyano-4-hydroxycinnamic acid (CCA, 0.1M in MeCN/EtOH/ H_2O 50:45:5) or 1,8,9-anthracenetriol (dithranol; 0.05M in $\text{CHCl}_3/\text{MeOH}$ 1:1) were used as matrices. Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für Organische Chemie, ETH-Zürich*.

(*E*)-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Dipropanedioate (**3**). Ethyl 3-chloro-3-oxopropanoate (4.0 ml, 31 mmol) was added to a stirred soln. of **1** (4.55 g, 12.5 mmol) and $\text{C}_5\text{H}_5\text{N}$ (5 ml, 63 mmol) in CH_2Cl_2 (400 ml) at 0° . The mixture was allowed to warm slowly to r.t. (over 1 h) and stirred for 12 h, then washed with H_2O (2 $\times$), dried (MgSO_4), and evaporated. CC (SiO_2 , CH_2Cl_2 /hexane 4:3) yielded **3** (3.67 g, 50%). Colorless oil. IR (neat): 2148 ($\text{C}\equiv\text{C}$), 1759 ($\text{C}=\text{O}$), 1741 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 200 MHz): 0.59 (*m*, 12H); 0.95 (*t*, $J = 7.8$, 18H); 1.23 (*t*, $J = 7.2$, 6H); 3.35 (*s*, 4H); 4.16 (*q*, $J = 7.2$, 4H); 4.91 (*s*, 4H). ^{13}C -NMR (CDCl_3 , 50 MHz): 3.84; 7.07; 13.69; 40.88; 61.14; 64.29; 100.11; 107.15; 127.25; 165.65; 165.75. FAB-MS: 563 (18, $[\text{M} - \text{Et}]^+$), 461 (65, $[\text{M} - \text{O}_2\text{CCH}_2\text{CO}_2\text{Et}]^+$), 115 (100, SiEt_3^+). Anal. calc. for $\text{C}_{30}\text{H}_{48}\text{O}_8\text{Si}_2$ (592.88): C 60.78, H 8.17; found: C 60.94, H 8.27.

(*E*)-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Dipropanedioate (**4**). Ethyl 3-chloro-3-oxopropanoate (2.0 ml, 15.6 mmol) was added to a stirred soln. of **2** (2.80 g, 6.25 mmol) and $\text{C}_5\text{H}_5\text{N}$ (2.5 ml, 31 mmol) in CH_2Cl_2 (200 ml) at 0° . The mixture was allowed to slowly warm to r.t. (over 1 h) and stirred for 10 h, then washed with H_2O (2 $\times$), dried (MgSO_4), and evaporated. CC (SiO_2 , CH_2Cl_2 /hexane 4:3) afforded **4** (2.75 g, 65%). Colorless oil. IR (neat): 2148 ($\text{C}\equiv\text{C}$), 1759 ($\text{C}=\text{O}$), 1742 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 200 MHz): 1.05 (*s*, 42H); 1.24 (*t*, $J = 7.0$, 6H); 3.36 (*s*, 4H); 4.17 (*q*, $J = 7.0$, 4H); 4.96 (*s*, 4H). ^{13}C -NMR (CDCl_3 , 50 MHz): 10.81; 13.72; 18.25; 40.90; 61.17; 64.47; 100.92; 106.30; 127.26; 165.65; 165.76. FAB-MS: 633 (44, $[\text{M} - \text{i-Pr}]^+$), 545 (100, $[\text{M} - \text{O}_2\text{CCH}_2\text{CO}_2\text{Et}]^+$).

(*E*)-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(2-bromopropanedioate) (**5**) and (*E*)-3-[(3-Ethoxy-1,3-dioxopropoxy)methyl]-5-(triethylsilyl)-2-[(triethylsilyl)ethynyl]pent-2-en-4-ynyl Ethyl-2-Bromopropanoate (**7**). DBU (1.05 ml, 7.08 mmol) was added under N_2 to a stirred soln. of **3** (2.10 g, 3.54 mmol) in dry THF (200 ml) at 0° . The mixture was allowed to warm slowly to r.t. (over 30 min) and then cooled to -78° . CBr_4 (2.35 g, 7.08 mmol) was added, and stirring under N_2 at -78° was continued for 3 h. After addition of sat. aq. NH_4Cl soln. (40 ml) and hexane, the mixture was extracted with sat. aq. NaCl soln. (2 $\times$), dried (MgSO_4), and evaporated. CC (SiO_2) eluting with hexane/ CH_2Cl_2 5:4 gave **5** (1.39 g, 52%) and eluting with hexane/ CH_2Cl_2 1:1 yielded **7** (263 mg, 11%).

5: Colorless oil. IR (neat): 2147 ($\text{C}\equiv\text{C}$), 1771 ($\text{C}=\text{O}$), 1748 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 200 MHz): 0.63 (*m*, 12H); 0.98 (*t*, $J = 7.8$, 18H); 1.29 (*t*, $J = 7.1$, 6H); 4.27 (*q*, $J = 7.1$, 4H); 4.84 (*s*, 2H); 5.01 (*AB*, $J = 12.3$, 4H). ^{13}C -NMR (CDCl_3 , 50 MHz): 4.31; 7.59; 14.02; 42.05; 63.47; 66.25; 100.29; 108.55; 127.69; 164.47; 164.65. FAB-MS: 723/721/719 (4/6/3, $[\text{M} - \text{Et}]^+$), 541/539 (22/19, $[\text{M} - \text{O}_2\text{CCHBrCO}_2\text{Et}]^+$), 115 (100, SiEt_3^+). Anal. calc. for $\text{C}_{30}\text{H}_{46}\text{Br}_2\text{O}_8\text{Si}_2$ (750.68): C 48.00, H 6.18; found: C 47.83, H 6.01.

7: Colorless oil. IR (neat): 2148 ($\text{C}\equiv\text{C}$), 1747 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 300 MHz): 0.63 (*m*, 12H); 0.98 (*m*, 18H); 1.27 (*t*, $J = 7.2$, 3H); 1.29 (*t*, $J = 7.2$, 3H); 3.39 (*s*, 2H); 4.19 (*q*, $J = 7.2$, 2H); 4.27 (*q*, $J = 7.2$, 2H);

4.84 (s, 1 H); 4.95 (s, 2 H); 5.01 (AB, $J = 12.4$, 2 H). ^{13}C -NMR (CDCl_3 , 50 MHz): 4.16; 7.42; 13.85; 14.04; 41.22; 41.87; 61.53; 63.21; 64.55; 66.11; 100.16; 100.24; 107.88 (2 $\times$); 126.51; 128.40; 164.09; 164.28; 166.00; 166.11. FAB-MS: 643/641 (25/24, $[\text{M}-\text{Et}]^+$), 541/539 (66/61, $[\text{M}-\text{O}_2\text{CCH}_2\text{CO}_2\text{Et}]^+$), 461 (100, $[\text{M}-\text{O}_2\text{CCHBrCO}_2\text{Et}]^+$). Anal. calc. for $\text{C}_{30}\text{H}_{47}\text{BrO}_8\text{Si}_2 \cdot 1.8 \text{CH}_2\text{Cl}_2$ (824.66): C 46.32, H 6.18; found: C 46.46, H 6.15.

(E)-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(2-bromopropanedioate) (**6**) and (E)-3-[(3-Ethoxy-1,3-dioxopropoxy)methyl]-5-(triisopropylsilyl)-2[(triisopropylsilyl)ethynyl]pent-2-en-4-ynyl Ethyl 2-Bromopropanoate (**8**). DBU (0.88 ml, 5.9 mmol) was added under N_2 to a stirred soln. of **4** (2.00 g, 2.95 mmol) in dry THF (200 ml) at 0° . The mixture was warmed slowly to r.t. (over 30 min) and then cooled to -78° . CBr_4 (1.96 g, 5.90 mmol) was added, and stirring was continued for 5 h under N_2 at -78° . After addition of sat. aq. NH_4Cl soln. (30 ml) and dilution with hexane, the mixture was extracted with sat. aq. NaCl soln. (2 $\times$), dried (MgSO_4), and evaporated. CC (SiO_2) eluting with CH_2Cl_2 /hexane 1:1 yielded **6** (1.18 g, 48%) and eluting with CH_2Cl_2 /hexane 2:1 gave **8** (410 mg, 18%).

6: Colorless oil. IR (neat): 2149 ($\text{C}\equiv\text{C}$), 1769 ($\text{C}=\text{O}$), 1749 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 200 MHz): 1.07 (s, 42 H); 1.28 (t, $J = 7.1$, 6 H); 4.26 (q, $J = 7.1$, 4 H); 4.82 (s, 2 H); 5.04 (AB, $J = 12.9$, 4 H). ^{13}C -NMR (CDCl_3 , 50 MHz): 10.84; 13.56; 18.30; 41.50; 62.92; 65.96; 100.58; 106.99; 127.11; 163.76; 163.93. FAB-MS: 793/791/789 (80/100/82 $[\text{M} - \text{i-Pr}]^+$). Anal. calc. for $\text{C}_{36}\text{H}_{58}\text{Br}_2\text{O}_8\text{Si}_2$ (834.84): C 51.79, H 7.00; found: C 51.75, H 6.98.

8: Colorless oil. IR (neat): 2144 ($\text{C}\equiv\text{C}$), 1744 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 300 MHz): 1.07 (s, 42 H); 1.25 (t, $J = 7.1$, 3 H); 1.28 (t, $J = 7.1$, 3 H); 3.37 (s, 2 H); 4.18 (q, $J = 7.1$, 2 H); 4.25 (q, $J = 7.1$, 2 H); 4.82 (s, 1 H); 4.98 (s, 2 H); 5.03 (AB, $J = 12.3$, 2 H). ^{13}C -NMR (CDCl_3 , 75 MHz): 11.11; 13.83; 14.03; 18.56; 41.20; 41.82; 61.51; 63.18; 64.68; 66.36; 101.04 (2 $\times$); 106.92; 106.98; 126.41; 128.56; 164.07; 164.24; 165.96; 166.07. FAB-MS: 713/711 (100/87, $[\text{M} - \text{i-Pr}]^+$). Anal. calc. for $\text{C}_{36}\text{H}_{59}\text{BrO}_8\text{Si}_2$ (755.94): C 57.20, H 7.87; found: C 57.33, H 7.84.

(E)-2,3-bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**9**) and ($\pm$)-(E)-endo,endo-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(1,2,7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate) (**11**). DBU (0.2 ml, 1.4 mmol) was added under N_2 at r.t. to C_{60} (500 mg, 0.694 mmol) and **5** (209 mg, 0.278 mmol) in PhMe (600 ml), and the mixture was stirred under N_2 at r.t. for 4 h, then filtered over a short plug of SiO_2 (PhMe), and evaporated. CC (SiO_2) eluting with hexane/PhMe 2:1 yielded unreacted C_{60} (108 mg), with hexane/ CH_2Cl_2 2:1 **11** (59 mg, 16%), and with hexane/ CH_2Cl_2 5:3 to 5:4 **9** which was recrystallized from pentane/ CH_2Cl_2 (184 mg, 33%).

9: Dark-red solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 258 (250400), 303 (sh, 79800), 327 (76000), 426 (4810), 488 (2890), 688 (390). IR (KBr): 2146 ($\text{C}\equiv\text{C}$), 1749 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 200 MHz): 0.69 (m, 12 H); 1.04 (t, $J = 7.5$, 18 H); 1.51 (t, $J = 7.1$, 6 H); 4.58 (q, $J = 7.1$, 4 H); 5.35 (s, 4 H). ^{13}C -NMR (CDCl_3 , 125 MHz): 4.33; 7.70; 14.31; 51.82; 63.41; 66.37; 71.47; 100.75; 108.54; 128.17; 138.75; 139.59; 140.85; 140.92; 141.82; 141.92; 142.19; 142.91; 142.99; 143.00; 143.08; 143.86; 143.89; 144.59; 144.60; 144.63; 144.66; 144.68; 144.89; 145.08; 145.16; 145.18; 145.19; 145.26; 145.31; 145.49; 163.18; 163.20. FAB-MS: 2028 (1, M^+), 1308 (7, $[\text{M}-\text{C}_{60}]^+$), 720 (100, C_{60}^+). Anal. calc. for $\text{C}_{150}\text{H}_{44}\text{O}_8\text{Si}_2 \cdot \text{CH}_2\text{Cl}_2$ (2115.12): C 85.75, H 2.19; found: C 85.68, H 2.36.

11: Dark red solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 260 (118700), 290 (sh, 62900), 308 (sh, 54100), 374 (sh, 10100), 409 (sh, 3270), 437 (2530), 469 (2300). IR (KBr): 2152 ($\text{C}\equiv\text{C}$), 1752 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 200 MHz): 0.68 (m, 6 H); 0.76 (m, 6 H); 1.03 (t, $J = 7.5$, 9 H); 1.11 (t, $J = 7.5$, 9 H); 1.34 (t, $J = 7.1$, 3 H); 1.35 (t, $J = 7.1$, 3 H); 4.25–4.55 (m, 4 H); 4.52 (d, $J = 10.3$, 1 H); 5.09 (d, $J = 10.7$, 1 H); 5.29 (d, $J = 10.7$, 1 H); 6.11 (d, $J = 10.3$, 1 H). ^{13}C -NMR (CDCl_3 , 125 MHz): 4.21; 4.37; 7.64; 14.08; 48.73; 49.38; 62.88; 62.92; 65.73; 65.89; 67.29; 67.45; 70.22; 70.42; 102.46; 102.63; 107.83; 107.94; 129.53; 130.75; 135.59; 135.86; 136.42; 136.70; 137.24; 137.43; 139.89; 140.52; 141.03; 141.11; 141.20; 141.22; 142.21; 142.31; 142.96; 143.08; 143.16; 143.30; 143.58; 143.59; 143.62; 143.91; 143.93; 144.22; 144.52; 144.53; 144.59; 144.61; 144.67; 145.14; 145.18; 145.19; 145.20; 145.22; 145.39; 145.46; 145.56; 145.59; 145.70; 145.73; 145.87; 145.99; 146.00; 146.08; 146.10; 147.27; 147.46; 147.53; 161.56; 161.86; 162.42; 162.46. FAB-MS: 1309 (20, MH^+), 720 (100, C_{60}^+). Anal. calc. for $\text{C}_{90}\text{H}_{44}\text{O}_8\text{Si}_2$ (1309.52): C 82.55, H 3.39; found: C 82.50, H 3.49.

(E)-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**10**) and ($\pm$)-(E)-endo,endo-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Diethyl Bis(1,2,7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate) (**12**). DBU (0.2 ml, 1.4 mmol) was added under N_2 at r.t. to C_{60} (500 mg, 0.694 mmol) and **6** (232 mg, 0.278 mmol) in PhMe (600 ml), and the soln. was stirred under N_2 at r.t. for 4 h, then filtered over a short plug of SiO_2 (PhMe) and evaporated. CC (SiO_2) eluting with hexane/PhMe 4:1 yielded unreacted C_{60} (110 mg), with hexane/ CH_2Cl_2 3:1 **12** (39 mg, 10%), and with hexane/ CH_2Cl_2 2:1 to 4:3 **10** which was recrystallized from hexane/ CH_2Cl_2 (272 mg, 46%).

10: Dark-red solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 258 (249300), 304 (sh, 68800), 327 (67700), 426 (4130), 488 (2520), 688 (290). IR (CHCl_3): 2144 ($\text{C}\equiv\text{C}$), 1745 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 200 MHz): 1.13 (s, 42 H); 1.49 (t, $J = 7.1$, 6 H); 4.56 (q, $J = 7.1$, 4 H); 5.37 (s, 4 H). ^{13}C -NMR (CDCl_3 , 125 MHz): 11.38; 14.31; 18.79; 51.93;

63.36; 66.59; 71.56; 101.65; 107.73; 128.28; 138.88; 139.51; 140.85; 140.92; 141.87; 141.96; 142.24; 142.95; 143.01; 143.04; 143.11; 143.12; 143.91; 143.93; 144.62; 144.64; 144.70; 144.71; 144.93; 145.03; 145.14; 145.20; 145.21; 145.26; 145.30; 145.53; 163.15; 163.18. FAB-MS: 2114 (2, MH^+), 1393 (6, $[M-C_{60}]^+$), 720 (100, C_{60}^+). Anal. calc. for $C_{156}H_{56}O_8Si_2$ (2114.35): C 88.62, H 2.67; found: C 88.50, H 2.95.

12: Dark-red solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 260 (113700), 292 (61300), 309 (53800), 374 (sh, 10600), 409 (sh, 3300), 437 (2650), 469 (2380). IR ($CHCl_3$): 2144 ($C\equiv C$), 1748 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 1.13 (s, 21 H); 1.19 (s, 21 H); 1.32 (t, $J = 7.1$, 3 H); 1.33 (t, $J = 7.1$, 3 H); 4.25–4.55 (m, 4 H); 4.46 (d, $J = 10.5$, 1 H); 5.01 (d, $J = 10.9$, 1 H); 5.35 (d, $J = 10.9$, 1 H); 6.21 (d, $J = 10.5$, 1 H). ^{13}C -NMR ($CDCl_3$, 125 MHz): 11.11; 11.37; 14.07; 14.08; 18.68; 18.74; 18.77; 18.79; 48.30; 48.89; 62.80; 62.86; 66.00; 66.12; 67.25; 67.42; 70.12; 70.29; 103.18; 103.27; 106.58; 106.72; 129.41; 130.48; 135.60; 136.03; 136.61; 137.05; 137.35; 137.65; 137.93; 139.80; 140.62; 141.02; 141.10; 141.16; 141.19; 142.19; 142.34; 142.84; 143.00; 143.10; 143.26; 143.59; 143.61; 143.86; 144.19; 144.20; 144.22; 144.24; 144.50; 144.62; 144.69; 145.16; 145.21; 145.31; 145.39; 145.46; 145.52; 145.56; 145.70; 145.72; 145.74; 145.89; 145.96; 146.07; 146.08; 147.25; 147.45; 147.53; 148.19; 148.68; 161.35; 161.66; 162.24; 162.27. FAB-MS: 1393 (21, MH^+), 720 (100, C_{60}^+). Anal. calc. for $C_{96}H_{56}O_8Si_2 \cdot 1/3 CH_2Cl_2$ (1421.99): C 81.37, H 4.02; found: C 81.06, H 4.41.

Preparation of 12 under High Dilution Conditions. A mixture of C_{60} (258.7 mg, 0.359 mmol) and **6** (300 mg, 0.359 mmol) in PhMe (500 ml) was added dropwise over 36 h under vigorous stirring to a N_2 -flushed soln. of DBU (1 ml, 7.2 mmol) in PhMe (250 ml), and the soln. turned orange-yellow, then orange-red. Filtration over a short plug of SiO_2 (PhMe), evaporation, and CC (SiO_2) yielded unreacted C_{60} (19 mg; with hexane/toluene 4:1) and **12** (with hexane/ CH_2Cl_2 3:1). Recrystallization from hexane/ $CHCl_3$ /PhH gave **12** (76 mg, 15%).

Tetraethyl 1,2:7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate (13). K_2CO_3 (17.9 mg, 0.130 mmol) was added to **11** (17 mg, 0.013 mmol) in THF/EtOH 1:1 (100 ml), and the mixture was stirred at r.t. for 4 h, then evaporated. The residue was filtered through a pad of SiO_2 (CH_2Cl_2), and CC (SiO_2 , CH_2Cl_2 /hexane 2:1) yielded **13** (4 mg, 30%). Dark-red solid. M.p. $> 280^\circ$. IR, UV/VIS, 1H - and ^{13}C -NMR, and FAB-MS: identical to those reported previously [21].

(E)-2,3-Diethynylbut-2-ene-1,4-diyl Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (14). Bu_4NF on SiO_2 (0.2 mg, 0.0017 mmol) was added to **9** (7 mg, 0.0034 mmol) in wet THF (15 ml), and the soln. was stirred for 48 h at r.t. Sat. aq. NH_4Cl soln. (20 ml) was added, and the mixture was diluted with CH_2Cl_2 , extracted with sat. aq. NaCl soln. (2 $\times$), dried ($MgSO_4$), and evaporated. CC (SiO_2 , CH_2Cl_2 /hexane 3:2) afforded **14** (5.8 mg, 94%) which was not fully characterized due to its insolubility. Dark-red solid. M.p. $> 280^\circ$. IR (KBr): 3289 ($\equiv C-H$), 2194 ($C\equiv C$), 1743 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 1.51 (t, $J = 7.2$, 6 H); 3.74 (s, 2 H); 4.58 (q, $J = 7.2$, 4 H); 5.35 (s, 4 H). FAB-MS: 1800 (3, M^+), 720 (100, C_{60}^+).

Dimethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (15). K_2CO_3 (102 mg, 0.738 mmol) was added to **9** (250 mg, 0.123 mmol) in THF/PhMe/MeOH 25:10:8 (430 ml), and the mixture was stirred at r.t. for 2 h. After addition of AcOH (0.2 ml) and evaporation, the dark-red solid was dissolved in PhMe, filtered through a pad of SiO_2 (PhMe), and purified by CC (SiO_2 , hexane/ CH_2Cl_2 5:4): **15** (135 mg, 65%). Dark-red solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 258 (147000), 326 (41200), 426 (2410), 487 (1440), 686 (160). IR ($CHCl_3$): 1745 ($C=O$). 1H -NMR ($CDCl_3$, 300 MHz): 4.11 (s, 6 H). ^{13}C -NMR ($CDCl_3$, 125 MHz): 51.95; 54.07; 71.42; 139.01; 140.96; 141.92; 142.19; 142.98; 143.01; 143.06; 143.87; 144.62; 144.63; 144.68; 144.90; 145.11; 145.15; 145.18; 145.26; 164.05. FAB-MS: 850 (14, M^+), 720 (100, C_{60}^+).

(E)-2,3-Diethynylbut-2-ene-1,4-diyl Diethyl Bis(2-bromopropanedioate) (16). Bu_4NF (1M) in THF (0.75 ml, 0.75 mmol) was added to **6** (152 mg, 0.182 mmol) in THF (50 ml) at -78° ; then the mixture was warmed slowly to r.t. (over 1 h). After evaporation to 10 ml, CH_2Cl_2 was added and the soln. was filtered through a pad of SiO_2 (CH_2Cl_2) and evaporated. CC (SiO_2 , CH_2Cl_2) gave **16** (55 mg, 58%) as a colorless glassy product which was used without further purification. IR (neat): 3277 ($\equiv C-H$), 2101 ($C\equiv C$), 1741 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 1.31 (t, $J = 7.3$, 6 H); 3.67 (s, 2 H); 4.29 (q, $J = 7.3$, 4 H); 4.89 (s, 2 H); 5.04 (s, 4 H). ^{13}C -NMR ($CDCl_3$, 50 MHz): 14.07; 42.10; 63.83; 65.83; 91.75; 101.42; 127.93; 164.59 (2 $\times$).

($\pm$)-(E)-endo,endo-2,3-Diethynylbut-2-ene-1,4-diyl Diethyl 1,2:7,21-Bismethano[60]fullerene-61,61,62,62-tetracarboxylate (17). DBU (0.06 ml, 0.42 mmol) was added under N_2 at r.t. to C_{60} (189 mg, 0.262 mmol) and **16** (55 mg, 0.105 mmol) in PhMe (200 ml), and the soln. was stirred under N_2 at r.t. for 5 h. Filtration over a short plug of SiO_2 (PhMe) and CC (SiO_2) yielded unreacted C_{60} (141 mg, with hexane/PhMe 4:1) and **17** (with CH_2Cl_2) which was recrystallized from hexane/ CH_2Cl_2 (18 mg, 16%). Dark-red solid. M.p. $> 280^\circ$. IR (KBr): 3285 ($\equiv C-H$), 2098 ($C\equiv C$), 1744 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 1.35 (t, $J = 7.2$, 3 H); 1.36 (t, $J = 7.2$, 3 H); 3.85 (s, 1 H); 3.97 (s, 1 H); 4.42 (m, 4 H); 4.58 (d, $J = 10.9$, 1 H); 5.19 (AB, $J = 11.4$, 2 H); 6.02 (d, $J = 10.9$, 1 H). ^{13}C -NMR ($CDCl_3$, 125 MHz): 15.09; 64.11; 66.31; 66.50; 68.21; 68.22; 71.32; 71.34; 80.52; 81.07; 92.57; 93.11; 129.79; 130.66; 135.09; 136.02; 136.19; 136.59; 137.73; 139.99; 140.23; 141.04; 141.08; 141.24; 142.35; 143.04;

143.14; 143.26; 143.30; 143.60; 143.73; 143.76; 144.14; 144.24; 144.52; 144.55; 144.64; 145.19; 145.26; 145.46; 145.64; 145.75; 145.83; 145.95; 146.17; 147.32; 147.49; 147.54; 148.50; 148.73; 162.05; 162.33; 162.54; 162.69. FAB-MS: 1081 (100, MH^+), 720 (78, C_{60}^+).

(E)-2,3-Diethynylbut-2-ene-1,4-diol (**18**) and 4-Ethynyl-2-methylfuran-3-methanal (**20**). K_2CO_3 (2.46 g, 17.8 mmol) was added to **19** (1.00 g, 3.57 mmol) in THF/MeOH 7:3 (100 ml), and the mixture was stirred at r.t. for 75 min. Evaporation to 10 ml, dilution with CH_2Cl_2 , and extraction with sat. aq. NaCl soln. ($2 \times$) afforded an org. layer which was dried ($MgSO_4$) and evaporated. Recrystallization from hexane/ CH_2Cl_2 1:1 yielded colorless crystals of **18** (31 mg, 6%) which were collected by filtration and used without further purification. 1H -NMR ($CDCl_3$, 200 MHz): 1.89 (m, 2 H); 3.66 (s, 2 H); 4.44 (d, $J = 4.6$, 4 H).

The filtrate was evaporated, and recrystallization from hexane/ CH_2Cl_2 10:1 provided **20** (291 mg, 60%). Colorless crystals. M.p. 71° . IR (KBr): 3293 (O–H), 3254 ($\equiv C-H$), 2115 ($C\equiv C$). 1H -NMR ($CDCl_3$, 200 MHz): 1.90 (br. s, 1 H); 2.27 (s, 3 H); 3.15 (s, 1 H); 4.50 (d, $J = 4.3$, 2 H); 7.48 (s, 1 H). ^{13}C -NMR ($CDCl_3$, 50 MHz): 11.37; 54.79; 80.97; 88.57; 107.06; 119.88; 144.25; 149.90. EI-MS: 136 (100, M^+), 121 (4, $[M-Me]^+$), 118 (52, $[M-H_2O]^+$), 105 (6, $[M-CH_2OH]^+$). Anal. calc. for $C_8H_8O_2$ (136.15): C 70.58, H 5.92; found: C 70.60, H 5.90.

Dimethyl (E)-2,3-Diethynylbut-2-ene-1,4-diyl Bis(benzene-1,4-dicarboxylate) (**21**). Bu_4NF (1M) in THF (14.7 ml, 14.7 mmol) was added to **1** (1.34 g, 3.68 mmol) in THF/ H_2O 10:1 (110 ml) at r.t., and the mixture was stirred for 1 h. After addition of sat. aq. NH_4Cl soln. (100 ml), the mixture was diluted with CH_2Cl_2 , extracted with sat. aq. NaCl ($2 \times$), dried ($MgSO_4$), and evaporated to yield crude **18** as a pale yellow solid which was directly used in the next step. DCC (1.67 g, 8.10 mmol) and DMAP (150 mg, 1.23 mmol) were added to crude **18** followed by methyl hydrogen benzene-1,4-dicarboxylate (1.46 g, 8.10 mmol) in CH_2Cl_2 (150 ml) at r.t., and the mixture was stirred for 5 h, then filtered through a pad of SiO_2 (CH_2Cl_2). After cooling to 0° , the colorless crystals of dicyclohexylurea (DCU) were removed by filtration and evaporation afforded a pale-yellow solid which was dissolved in a minimum amount of CH_2Cl_2 and cooled at -20° overnight. After filtration of residual DCU and evaporation, recrystallization from hexane/ CH_2Cl_2 yielded **21** (1.03 g, 61%). Colorless crystals. M.p. 171° (dec.). IR (KBr): 3238 ($\equiv C-H$), 2097 ($C\equiv C$), 1714 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 3.66 (s, 2 H); 3.95 (s, 6 H); 5.24 (s, 4 H); 8.14 (AB, $J = 8.5$, 8 H). ^{13}C -NMR ($CDCl_3$, 50 MHz): 52.19; 64.15; 78.05; 90.63; 127.77; 129.31; 129.50; 133.17; 133.89; 165.00; 165.95. FAB-MS: 460 (100, M^+), 445 (13, $[M-Me]^+$). Anal. calc. for $C_{26}H_{20}O_8 \cdot 0.5 H_2O$ (468.45): C 66.52, H 4.51; found: C 66.61, H 4.66.

(E)-2,3-Bis[4-(trimethylsilyl)buta-1,3-diyne]but-2-ene-1,4-diyl Dimethyl Bis(benzene-1,4-dicarboxylate) (**22**). $CuCl$ (1.4 g, 14.1 mmol) and TMEDA (2.1 ml, 14 mmol) were added to $Me_3SiC\equiv CH$ (4.0 ml, 28 mmol) and **21** (130 mg, 0.282 mmol) in CH_2Cl_2 (100 ml), and the soln. was vigorously stirred for 5 h in the presence of dry air. After evaporation to 10 ml and addition of hexane, the mixture was filtered over a short plug of SiO_2 , first with hexane to remove bis(trimethylsilyl)butadiyne, then with CH_2Cl_2 . Recrystallization from CH_2Cl_2 /hexane gave **22** (132 mg, 72%). Pale-yellow crystals. M.p. 96° (dec.). IR (KBr): 2093 ($C\equiv C$), 1727 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 0.19 (s, 18 H); 3.95 (s, 6 H); 5.15 (s, 4 H); 8.14 (AB, $J = 8.5$, 8 H). ^{13}C -NMR ($CDCl_3$, 50 MHz): -0.47 ; 52.68; 64.76; 71.48; 86.97; 89.33; 98.30; 129.94 ($2 \times$); 130.23; 133.71; 134.55; 165.60; 166.64. FAB-MS: 653 (MH^+). Anal. calc. for $C_{36}H_{36}O_8Si_2$ (652.85): C 66.23, H 5.56; found: C 66.52, H 5.51.

tert-Butyl 2-(2-Ethoxyethoxy)ethyl Propanedioate (**24**). Malonyl dichloride (6 ml, 62 mmol) was added to *t*-BuOH (5.9 ml, 62 mmol), 2-(2-ethoxyethoxy)ethanol (8.4 ml, 62 mmol), and C_3H_5N (10.9 ml, 136 mmol) in CH_2Cl_2 (400 ml) at 0° and, after warming slowly to r.t. (over 1 h), the soln. was stirred for 5 h. Washing with sat. aq. NH_4Cl soln. ($4 \times$) and drying ($MgSO_4$), followed by distillation afforded as the first fraction di(tert-butyl) malonate (2.86 g, 21%). Colorless oil. B.p. $60^\circ/0.2$ Torr. 1H - and ^{13}C -NMR: identical to those of the commercial product.

The second fraction contained **24** (7.30 g, 43%). Colorless oil. B.p. $135^\circ/0.2$ Torr. IR (neat): 1749, 1730 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 1.09 (t, $J = 7.0$, 3 H); 1.36 (s, 9 H); 3.20 (s, 2 H); 3.41 (q, $J = 7.0$, 2 H); 3.50 (m, 4 H); 3.63 (t, $J = 4.9$, 2 H); 4.18 (t, $J = 4.9$, 2 H). ^{13}C -NMR ($CDCl_3$, 50 MHz): 15.22; 27.99; 42.86; 64.51; 66.78; 69.06; 69.95; 70.81; 82.10; 165.90; 167.23. FAB-MS: 277 (100, MH^+), 219 (59, $[M-t-Bu]^+$). Anal. calc. for $C_{13}H_{24}O_6$ (276.33): C 56.51, H 8.75; found: C 56.47, H 8.58.

tert-Butyl 2-(2-Ethoxyethoxy)ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**25**). DBU (0.2 ml, 1.4 mmol) was added under N_2 at r.t. to C_{60} (500 mg, 0.694 mmol), I_2 (176 mg, 0.694 mmol), and **24** (192 mg, 0.694 mmol) in PhMe (600 ml), and the soln. was stirred for 4 h. Filtration over a short plug of SiO_2 , first with PhMe to remove unreacted C_{60} (48 mg), then with CH_2Cl_2 followed by $CC(SiO_2, CH_2Cl_2)$ and recrystallization from pentane/ CH_2Cl_2 provided **25** (351 mg, 51%). Dark-red solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 258 (125000), 326 (38000), 393 (sh, 4370), 401 (sh, 3170), 413 (sh, 2240), 426 (2340), 493 (1390), 688 (180). IR (KBr): 1742 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 1.20 (t, $J = 7.0$, 3 H); 1.67 (s, 9 H); 3.52 (q, $J = 7.0$, 2 H); 3.60 (m, 2 H); 3.68 (m, 2 H); 3.88 (t, $J = 4.8$, 2 H); 4.63 (t, $J = 4.8$, 2 H). ^{13}C -NMR ($CDCl_3$, 50 MHz): 15.00; 27.80; 52.76;

65.80; 66.49; 68.59; 69.58; 70.50; 71.55; 84.85; 138.60; 138.82; 140.58; 140.63; 141.59; 141.91; 142.70; 142.77; 143.58; 144.26; 144.37; 144.54; 144.85; 144.93; 145.09; 145.31; 161.84; 163.64. FAB-MS: 995 (100, MH^+), 720 (72, C_{60}^+). Anal. calc. for $C_{73}H_{22}O_6$ (994.99): C 88.12, H 2.23; found: C 88.11, H 2.02.

2-(2-Ethoxyethoxy)ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (23). A soln. of **25** (320 mg, 0.322 mmol) and TsOH · H₂O (306 mg, 1.61 mmol) in PhMe (150 ml) was heated to reflux for 4 h, then cooled to r.t., washed with H₂O (5 ×), dried (MgSO₄), and evaporated. The residue was washed with acetone and hexane, then dried under high vacuum and recrystallized from CHCl₃/hexane to give **23** (282 mg, 95%). Dark-red solid. M.p. > 280°. UV/VIS (CH₂Cl₂): 258 (74900), 327 (22700), 393 (sh, 3420), 402 (sh, 2460), 413 (sh, 1830), 426 (1810), 488 (1060), 686 (140). IR (KBr): 3384 (O–H), 1740 (C=O). ¹H-NMR (CDCl₃, 200 MHz): 1.34 (t, *J* = 7.0, 3 H); 3.65–3.80 (m, 6 H); 3.92 (m, 2 H); 4.68 (m, 2 H). ¹³C-NMR (CDCl₃, 75 MHz): 14.90; 52.41; 65.85; 67.34; 68.57; 70.21; 70.36; 71.71; 138.99; 139.03; 140.97; 141.97; 142.08; 142.23; 143.00; 143.05; 143.87; 144.58; 144.70; 144.82; 145.16; 145.23; 145.24; 145.46; 163.77; 164.14. FAB-MS: 939 (75, MH^+), 720 (100, C_{60}^+). Anal. calc. for $C_{69}H_{14}O_6$ · CHCl₃ (1058.26): C 79.45, H 1.43; found: C 79.32, H 1.63.

2-(2-Ethoxyethoxy)ethyl 1,2-Methano[60]fullerene-61-carboxylate (27). A soln. of DMAP (0.6 mg, 0.005 mmol) and **25** (10 mg, 0.011 mmol) in CH₂Cl₂ (10 ml) was stirred for 5 h at r.t., then filtered over a short plug (SiO₂, CH₂Cl₂), and recrystallization from pentane/CH₂Cl₂ gave **27** (8.2 mg, 85%). Dark-red solid. M.p. > 280°. UV/VIS (CH₂Cl₂): 259 (107800), 327 (31600), 394 (sh, 3990), 402 (sh, 2910), 414 (sh, 2000), 427 (2220), 491 (1230), 690 (140). IR (KBr): 1741 (C=O). ¹H-NMR (CDCl₃, 200 MHz): 1.24 (t, *J* = 7.0, 3 H); 3.57 (q, *J* = 7.0, 2 H); 3.68 (m, 2 H); 3.76 (m, 2 H); 3.94 (t, *J* = 4.7, 2 H); 4.62 (t, *J* = 4.7, 2 H); 4.84 (s, 1 H). ¹³C-NMR (CDCl₃, 50 MHz): 15.45; 39.09; 65.62; 67.08; 69.31; 70.15; 70.82; 71.12; 136.78; 141.02; 141.30; 141.53; 142.46; 142.59; 142.81; 143.20; 143.36; 143.47; 143.66; 144.12; 144.36; 144.81; 144.99; 145.07; 145.47; 145.60; 145.98; 146.05; 148.63; 166.80. FAB-MS: 895 (72, MH^+), 720 (100, C_{60}^+). Anal. calc. for $C_{68}H_{14}O_4$ · 0.4 CH₂Cl₂ (928.84): C 88.45, H 1.61; found: C 88.32, H 1.72.

2-(tert-Butoxy)-2-oxoethyl Ethyl Propanedioate (29). Ethyl 3-chloro-3-oxopropanoate (4.0 g, 26.6 mmol) was added to *tert*-butyl 2-hydroxyacetate (3.50 g, 26.6 mmol) and C₅H₅N (2.6 ml, 32 mmol) in CH₂Cl₂ (200 ml) at 0°, then the soln. was allowed to warm slowly to r.t. (over 1 h) and stirred for an additional 6 h. Washing with sat. aq. NH₄Cl soln. (4 ×), drying (MgSO₄), and distillation under reduced pressure afforded **29** (5.27 g, 81%). Colorless oil. B.p. 115–120°/0.2 Torr. IR (neat): 1747 (C=O). ¹H-NMR (CDCl₃, 200 MHz): 1.18 (t, *J* = 7.1, 3 H); 1.37 (s, 9 H); 3.36 (s, 2 H); 4.10 (q, *J* = 7.1, 2 H); 4.44 (s, 2 H). ¹³C-NMR (CDCl₃, 50 MHz): 13.62; 27.56; 40.66; 61.16; 61.41; 82.13; 165.55; 165.62; 165.78. FAB-MS: 247 (37, MH^+), 191 (100, $[M-t-Bu]^+$). Anal. calc. for C₁₁H₁₈O₆ (246.26): C 53.65, H 7.37; found: C 53.48, H 7.16.

2-(tert-Butoxy)-2-oxoethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (30). DBU (0.2 ml, 1.4 mmol) was added under N₂ at r.t. to C₆₀ (500 mg, 0.694 mmol), I₂ (176 mg, 0.694 mmol), and **29** (171 mg, 0.694 mmol) in PhMe (600 ml), and the soln. was stirred under N₂ at r.t. for 7 h. Filtration over a plug of SiO₂ (PhMe) yielded first unreacted C₆₀ (48 mg), then the crude product which was recrystallized from hexane/CH₂Cl₂ to give **30** (361 mg, 54%). Dark-red solid. M.p. > 280°. UV/VIS (CH₂Cl₂): 258 (113800), 327 (32600), 393 (sh, 4300), 402 (sh, 2970), 413 (sh, 2150), 426 (2150), 490 (1310), 686 (130). IR (KBr): 1747 (C=O). ¹H-NMR (CDCl₃, 200 MHz): 1.50 (t, *J* = 7.1, 3 H); 1.54 (s, 9 H); 4.60 (q, *J* = 7.1, 2 H); 4.86 (s, 2 H). ¹³C-NMR (CDCl₃, 50 MHz): 14.39; 28.33; 52.04; 63.40; 63.94; 71.68; 83.35; 139.13; 139.76; 141.34; 142.28; 142.29; 142.60; 143.35; 143.41; 144.27; 145.03; 145.04; 145.28; 145.57; 145.66; 145.79; 163.47; 163.53; 165.79. FAB-MS: 964 (55, M^+), 720 (100, C_{60}^+). Anal. calc. for C₇₁H₁₆O₆ (964.92): C 88.38, H 1.67; found: C 88.12, H 1.69.

Carboxymethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (28). A soln. of **30** (300 mg, 0.311 mmol) and TsOH · H₂O (296 mg, 1.56 mmol) in PhMe (300 ml) was refluxed for 5 h, then cooled to r.t., washed with H₂O (4 ×), dried (MgSO₄), and evaporated. The residue was washed with Et₂O and hexane, then dried at 10^{–5} Torr to yield **28** (268 mg, 95%) as a dark-red solid which was used without further purification. M.p. > 280°. IR (KBr): 3355 (O–H), 1734 (C=O). ¹H-NMR (CDCl₃, 200 MHz): 1.50 (t, *J* = 7.2, 3 H); 4.59 (q, *J* = 7.2, 2 H); 5.05 (s, 2 H). FAB-MS: 909 (55, MH^+), 720 (100, C_{60}^+).

2,2'-(E)-2,3-Bis[(triethylsilyl)ethynyl]but-2-ene-1,4-diylbis[2-oxoethan-2,1-yl] Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (31). DCC (97 mg, 0.472 mmol) and DMAP (10 mg, 0.082 mmol) were added to **28** (268 mg, 0.295 mmol) and **1** (43 mg, 0.118 mmol) in CH₂Cl₂ (150 ml) at r.t., and the mixture was stirred for 24 h. After addition of SiO₂ (10 g) and evaporation, CC (SiO₂, CH₂Cl₂/hexane 6:5) followed by recrystallization from hexane/CHCl₃ yielded **31** (192 mg, 76%). Dark-red solid. M.p. > 280°. UV/VIS (CH₂Cl₂): 258 (248500), 299 (sh, 78100), 327 (70700), 393 (sh, 9460), 402 (sh, 6770), 413 (sh, 5020), 426 (4820), 487 (2790), 687 (250). IR (CHCl₃): 2117 (C≡C), 1750 (C=O). ¹H-NMR (CDCl₃, 300 MHz): 0.66 (m, 12 H); 1.02 (t, *J* = 7.7, 18 H); 1.50 (t, *J* = 7.1, 6 H); 4.59 (q, *J* = 7.1, 4 H); 5.03 (s, 4 H); 5.07 (s, 4 H). ¹³C-NMR (CDCl₃, 125 MHz): 4.26; 7.61; 14.21; 51.56; 62.23; 63.68; 64.44; 71.27; 100.05; 108.43; 127.38; 139.08; 139.20; 140.92; 140.95; 141.88;

142.21; 142.97; 143.00; 143.06; 143.87; 144.63; 144.65; 144.68; 144.89; 145.12; 145.14; 145.18; 145.27; 162.90; 162.99; 165.84. FAB-MS: 2145 (100, M^+), 720 (20, C_{60}^+). Anal. calc. for $C_{154}H_{48}O_{12}Si_2$ (2146.26): C 86.18, H 2.25; found: C 86.02, H 2.51.

2,2'-[(E)-2,3-Diethynylbut-2-ene-1,4-diyl]bis[2-oxoethan-2,1-yl] Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**32**). DCC (188 mg, 0.912 mmol) and DMAP (10 mg, 0.082 mmol) were added to **28** (659 mg, 0.725 mmol) and **18** (31 mg, 0.228 mmol) in CH_2Cl_2 (250 ml), and the soln. was stirred at r.t. for 24 h. After addition of SiO_2 (15 g) and evaporation, CC (SiO_2 , PhMe/ CH_2Cl_2 5:2) followed by recrystallization from pentane/ $CHCl_3$ afforded **32** (276 mg, 63%) which was not fully characterized due to its limited solubility. Dark-red solid. M.p. > 280°. IR (KBr): 3288 ($\equiv C-H$), 2101 ($C\equiv C$), 1746 ($C=O$). 1H -NMR ($CDCl_3$, 200 MHz): 1.50 (*t*, *J* = 7.2, 6 H); 3.73 (*s*, 2 H); 4.59 (*q*, *J* = 7.2, 2 H); 5.06 (*s*, 4 H); 5.07 (*s*, 4 H). FAB-MS: 1917 (100, M^+), 720 (52, C_{60}^+). Anal. calc. for $C_{142}H_{20}O_{12} \cdot 2.5 CHCl_3$ (2216.18): C 78.32, H 1.02; found: C 78.34, H 1.37.

1,1-Dibromo-3-[(tert-butyl)dimethylsilyloxy]-2-[(tert-butyl)dimethylsilyloxymethyl]propene (**35**). To **34** (3.0 g, 9.4 mmol) and CBR_4 (4.11 g, 12.4 mmol) in PhH (150 ml) was added PPh_3 (6.48 g, 24.7 mmol), and the soln. was stirred at 20° for 48 h. After addition of hexane (100 ml) and filtration through a large pad of Celite, CC (SiO_2 , hexanes/ CH_2Cl_2 2:1) yielded **34** (1.85 g, 38%). Light-yellow oil. IR (neat): 2930, 1472, 1253, 1078, 837. 1H -NMR (200 MHz, $CDCl_3$): 0.11 (*s*, 12 H); 0.92 (*s*, 18 H); 4.38 (*s*, 4 H). ^{13}C -NMR (50 MHz, $CDCl_3$): -5.25; 18.37; 25.92; 62.57; 90.29; 143.71. FAB-MS: 473/475/471 (65/100/50, M^+). Anal. calc. for $C_{16}H_{34}Br_2O_2Si_2$ (474.42): C 40.51, H 7.22; found: C 40.33, H 7.07.

5-[(tert-Butyl)dimethylsilyloxy]-4-[(tert-butyl)dimethylsilyloxymethyl]-1-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-3-en-1-yne (**36**). A mixture of **35** (0.829 g, 1.75 mmol), $Me_3SiC\equiv CH$ (0.514 g, 5.24 mmol), $[PdCl_2(PPh_3)_2]$ (80 mg, 0.11 mmol), and CuI (40 mg, 0.21 mmol) in degassed Et_3N (30 ml) was stirred at r.t. for 16 h. Additional $Me_3SiC\equiv CH$ (0.20 g, 2.0 mmol) and $[PdCl_2(PPh_3)_2]$ (25 mg, 0.036 mmol) were added, and the mixture was stirred for 12 more h. Evaporation and CC (SiO_2 , hexanes/ CH_2Cl_2 10:1) provided **36** (0.647 g, 73%). Light-yellow oil. IR (neat): 2956, 2153 ($C\equiv C$), 1250. 1H -NMR (200 MHz, $CDCl_3$): 0.01 (*s*, 18 H); 0.12 (*s*, 12 H); 0.82 (*s*, 18 H); 4.42 (*s*, 4 H). ^{13}C -NMR (50.3 MHz, $CDCl_3$): -5.25; -0.15; 18.42; 25.98; 60.24; 98.14; 99.89; 103.23; 157.90. EI-MS: 508 (4, M^+), 73 (100, $SiMe_3^+$). Anal. calc. for $C_{26}H_{52}O_2Si_4$ (509.04): C 61.35, H 10.30; found: C 61.24, H 10.38.

5-[(tert-Butyl)dimethylsilyloxy]-4-[(tert-butyl)dimethylsilyloxymethyl]-1-(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]pent-3-en-1-yne (**37**). A mixture of **35** (2.00 g, 4.22 mmol), $(i-Pr)_3SiC\equiv CH$ (1.75 g, 9.62 mmol), $[PdCl_2(Ph_3P)_2]$ (150 mg, 0.21 mmol), and CuI (75 mg, 0.39 mmol) in degassed Et_3N (35 ml) was stirred at r.t. for 24 h. After evaporation, the residue was dissolved in Et_2O , washed with sat. aq. NH_4Cl soln., dried ($MgSO_4$), and chromatographed (SiO_2 , hexanes/ CH_2Cl_2 10:1): **37** (2.46 g, 86%). Light-yellow oil. IR (CCl_4): 2944, 2151 ($C\equiv C$), 1464, 1256, 1066, 838. 1H -NMR (200 MHz, $CDCl_3$): 0.06 (*s*, 12 H); 0.88 (*s*, 18 H); 1.06 (*s*, 42 H); 4.53 (*s*, 4 H). ^{13}C -NMR (50.3 MHz, $CDCl_3$): -5.31; 11.27; 18.43; 18.63; 25.94; 60.35; 94.93; 102.21; 103.97; 155.75. EI-MS: 676 (4, M^+), 619 (20, $[M-(t-Bu)]^+$), 532 (100, $[M-(t-Bu)Me_2Si]^+$). HR-MS: 676.4931 (M^+ , $C_{38}H_{76}O_2Si_4^+$; calc. 676.4922).

2-(1-Ethynylprop-2-ynylidene)propane-1,3-diol (**33**). Bu_4NF (1M) in THF (2.28 ml, 2.28 mmol) was added to **36** (0.230 g, 0.456 mmol) in wet THF (25 ml) at 0°, and the mixture was stirred for 8 h. Dilution with Et_2O , washing with sat. aq. NH_4Cl soln., drying ($MgSO_4$), and evaporation gave **33** (41 mg, 66%) as an unstable oily solid that was used without further purification. IR (neat): 3364 (O-H), 3289 ($\equiv C-H$), 2925, 2100 ($C\equiv C$), 1436.

2,2'-[2-(1-Ethynylprop-2-ynylidene)propane-1,3-diyl]bis[2-oxoethan-2,1-diyl] Diethyl Bis(1,2-methano[60]fullerene-61,61-dicarboxylate) (**38**) and Ethyl 2-[3-Ethynyl-2-(hydroxymethyl)pent-2-en-4-ynyl]-2-oxoethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**39**). A mixture of **28** (0.450 g, 0.500 mmol), **33** (30 mg, 0.221 mmol), DCC (0.188 g, 0.912 mmol), and DMAP (10 mg, 0.082 mmol) in CH_2Cl_2 was stirred at r.t. for 24 h. After addition of SiO_2 (10 g) and evaporation, CC (2 ×; SiO_2 , PhMe, → PhMe/ CH_2Cl_2 1:1 → CH_2Cl_2 ; then SiO_2 , CH_2Cl_2) afforded **38** (0.106 g, 25%) and **39** (0.052 g, 23%).

38: Dark-brown solid. M.p. > 250°. UV/VIS ($CHCl_3$): 258 (241700), 326 (70600), 412 (5800), 426 (5300), 479 (2800). IR (CCl_4): 3292 ($\equiv C-H$), 2933, 2108 ($C\equiv C$), 1746 ($C=O$), 1233. 1H -NMR (500 MHz, $CDCl_3$): 1.50 (*t*, *J* = 7.1, 6 H); 3.39 (*s*, 2 H); 4.59 (*q*, *J* = 7.1, 4 H); 5.05 (*s*, 4 H); 5.20 (*s*, 4 H). ^{13}C -NMR (125 MHz, $CDCl_3$): 14.23; 51.46; 62.41; 62.80; 63.74; 71.22; 84.74; 108.59; 135.98; 139.03; 139.23; 140.94; 140.96; 141.87; 142.20; 142.96; 143.00; 143.87; 144.62; 144.65; 144.67; 144.79; 144.89; 145.08; 145.13; 145.17; 145.27; 146.85; 162.98; 163.13; 166.11. FAB-MS: 1917 (100, M^+), 720 (32, C_{60}^+). Anal. calc. for $C_{142}H_{20}O_{12}$ (1917.74): C 88.94, H 1.05; found: C 88.80, H 1.35.

39: Dark-brown solid. M.p. > 250°. UV/VIS ($CHCl_3$): 258 (210700), 326 (57000), 413 (11900), 425 (3800), 485 (2400). IR (CCl_4): 3427 (O-H), 3294 ($\equiv C-H$), 3000, 2933, 2105 ($C\equiv C$), 1749 ($C=O$), 1235, 906. 1H -NMR (500 MHz, $CDCl_3$): 1.50 (*t*, *J* = 7.2, 3 H); 2.31 (*s*, 1 H); 3.31 (*s*, 2 H); 4.56 (*s*, 2 H); 4.59 (*q*, *J* = 7.2, 2 H); 5.04

(s, 2 H); 5.22 (s, 2 H). ^{13}C -NMR (125 MHz, CDCl_3): 14.20; 51.46; 60.91; 61.58; 62.49; 63.81; 71.91; 77.78; 77.94; 82.93; 83.27; 105.76; 138.93; 139.23; 140.97; 140.99; 141.86; 142.20; 142.97; 143.02; 143.05; 143.07; 143.87; 144.60; 144.65; 144.69; 144.92; 145.09; 145.11; 145.18; 145.20; 145.29; 152.75 163.13; 163.25; 166.60. FAB-MS: 1027 (36, M^+), 720 (100, C_{60}^+). HR-MS: 1027.0785 (MH^+ , $\text{C}_{75}\text{H}_{15}\text{O}_7^+$, calc. 1027.0818).

Bis[2-(tert-butoxy-2-oxoethyl)] Propanedioate (44). A soln. of *tert*-butyl 2-hydroxyacetate (1.029 g, 7.8 mmol) and $\text{C}_5\text{H}_5\text{N}$ (0.63 ml, 7.8 mmol) in dry CH_2Cl_2 (15 ml) was purged with Ar and cooled with an ice bath. Malonyl dichloride (0.38 ml, 3.9 mmol) was added dropwise within 5 min ($\rightarrow$ yellow, then dark-violet). After 2.5 h, the ice bath was removed, and stirring was continued for 14 h at r.t. Extraction with H_2O , filtration, and evaporation, followed by CC (SiO_2 , CH_2Cl_2) gave **44** (0.827 g, 64%). Yellow oil. IR (neat): 1749 (C=O). ^1H -NMR (200 MHz, CDCl_3): 1.27 (s, 18 H); 3.38 (s, 2 H); 4.35 (s, 4 H). ^{13}C -NMR (50 MHz, CDCl_3): 27.43; 39.94; 61.36; 81.91; 164.93; 165.62. FAB-MS: 333 (MH^+). Anal. calc. for $\text{C}_{15}\text{H}_{24}\text{O}_8$ (332.35): C 54.21, H 7.28, O 38.51; found: C 54.10, H 7.38, O 38.59.

Bis[2-(tert-butoxy-2-oxoethyl)] 1,2-Methano[70]fullerene-71,71-dicarboxylate (45). A soln. of C_{70} (60 mg, 0.071 mmol) in dry PhMe (70 ml) was sonicated and purged with Ar, after which **44** (0.026 g, 0.079 mmol), I_2 (0.020 g, 0.079 mmol), and DBU (0.027 g, 0.178 mmol), each dissolved in PhMe, were added. After 1 h, more I_2 (0.005 g, 0.020 mmol) in PhMe was added, and stirring was continued for 14 h at r.t. Evaporation and CC (SiO_2 , CH_2Cl_2 /hexane 2:1) gave **45** (39 mg, 46%). Black solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 265 (sh, 96700), 323 (24700), 353 (23100), 369 (21800), 402 (17700), 460 (20300), 540 (sh, 9400), 661 (sh, 1000). IR (KBr): 1749 (C=O). ^1H -NMR (CDCl_3 , 500 MHz): 1.53 (s, 18 H); 4.85 (s, 4 H). ^{13}C -NMR (CDCl_3 , 125 MHz): 28.10; 36.24; 63.29; 66.03; 66.55; 83.00; 130.79; 130.93; 132.79; 133.53; 136.65; 140.94; 141.59; 142.38; 142.56; 142.84; 143.53; 143.82; 143.93; 144.91; 145.88; 145.93; 146.45; 146.98; 147.27; 147.49; 147.57; 148.45; 148.47; 148.56; 148.75; 149.08; 149.23; 149.31; 150.55; 150.68; 151.14; 151.31; 151.33; 155.07; 162.49; 165.30. MALDI-TOF-MS (CCA): 1170.9 (M^-), 1115.3, 840.7 (C_{70}^-).

Bis(carboxymethyl) 1,2-Methano[70]fullerene-71,71-dicarboxylate (43). A soln. of **45** (33 mg, 0.029 mmol) and $\text{TsOH} \cdot \text{H}_2\text{O}$ (43 mg, 0.228 mmol) in PhMe (50 ml) was heated to reflux for 5 h. Additional $\text{TsOH} \cdot \text{H}_2\text{O}$ (44 mg) was added and, after refluxing for 14 h, the soln. was evaporated and the solid washed with H_2O . Dissolution in THF, drying (MgSO_4), followed by evaporation yielded crude **43** which was dried at 10^{-2} Torr and used without further purification. Dark-red solid. M.p. $> 280^\circ$. ^1H -NMR ($(\text{D}_8)\text{THF}$, 200 MHz): 4.06 (s, 4 H).

Bis[2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethyl] Propanedioate (47). Malonyl dichloride (0.5 ml, 5.11 mmol) was added to 2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethanol [39] (1.94 g, 10.22 mmol) and $\text{C}_5\text{H}_5\text{N}$ (0.9 ml, 11.15 mmol) in CH_2Cl_2 (200 ml) at 0° , and the soln. was allowed to warm slowly to r.t. (over 1 h) and stirred for 3 h at this temperature. After washing with sat. aq. NH_4Cl soln. (2 $\times$) and drying (MgSO_4), CC (SiO_2 , CH_2Cl_2 /MeOH 97:3) afforded **47** as a mixture of diastereoisomers (1.42 g, 62%). Colorless oil. IR (neat): 1739 (C=O). ^1H -NMR (CDCl_3 , 200 MHz): 1.40–1.80 (m, 12 H); 3.36 (s, 2 H); 3.40–3.85 (m, 16 H); 4.19–4.25 (m, 4 H); 4.55 (br. s, 2 H). ^{13}C -NMR (CDCl_3 , 50 MHz): 19.10; 25.07; 30.19; 40.91; 61.82; 64.27; 66.26; 68.45; 70.19; 98.56; 166.10. FAB-MS: 449 (MH^+). Anal. calc. for $\text{C}_{21}\text{H}_{36}\text{O}_{10}$ (448.52): C 56.24, H 8.09; found: C 56.08, H 8.00.

Bis[2-[2-(3,4,5,6-tetrahydro-2H-pyran-2-yloxy)ethoxy]ethyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate (48). A soln. of C_{70} (61.1 mg, 0.073 mmol) in dry PhMe (70 ml) was sonicated and purged with Ar, after which **47** (0.036 g, 0.080 mmol), I_2 (0.021 g, 0.080 mmol), and DBU (0.028 g, 0.182 mmol), each dissolved in PhMe, were added. After stirring for 14 h at r.t., CC (SiO_2) eluting with CH_2Cl_2 gave unreacted C_{70} and with CH_2Cl_2 /MeOH 99.5:0.5 **48** (61 mg, 65%) as a mixture of diastereoisomers. Black solid. M.p. $> 280^\circ$. ^1H -NMR (CDCl_3 , 200 MHz): 1.20–1.90 (m, 12 H); 3.46–3.93 (m, 16 H); 4.57–4.64 (m, 6 H). MALDI-TOF-MS (DHB): 1287.0 (M^-).

Bis[2-(2-hydroxyethoxy)ethyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate (46). A soln. of **48** (0.061 g, 0.047 mmol) in PhMe/EtOH 1:3 (80 ml) was purged with Ar and, after addition of $\text{TsOH} \cdot \text{H}_2\text{O}$ (0.091 g, 0.472 mmol) was stirred at 60° for 2 h. Evaporation and CC (SiO_2 , $\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2$ /MeOH 98:2) gave **46** (32 mg, 60%). Black solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 265 (sh, 97400), 324 (24900), 353 (23300), 369 (22100), 403 (17900), 461 (20700), 538 (sh, 9900), 654 (sh, 1600). IR (KBr): 2920 (O–H), 1744 (C=O). ^1H -NMR (CDCl_3 , 500 MHz): 2.78 (br. s, 2 H); 3.68–3.70 (m, 4 H); 3.77–3.81 (m, 4 H); 3.89–3.92 (m, 4 H); 4.61–4.64 (m, 4 H). ^{13}C -NMR (CDCl_3 , 125 MHz): 36.81; 61.76; 66.17; 66.22; 66.79; 68.68; 72.68; 130.80; 130.91; 130.93; 132.81; 133.54; 136.80; 140.86; 141.61; 142.28; 142.74; 142.85; 143.55; 143.84; 143.94; 144.85; 145.89; 145.96; 146.45; 147.00; 147.29; 147.50; 147.59; 148.47; 148.49; 148.58; 148.75; 149.12; 149.26; 149.34; 150.57; 150.70; 151.15; 151.33 (2 $\times$); 155.01; 163.49. MALDI-TOF-MS (DHB): 1118.8 (M^-).

Bis[2-{2-[2-(61-(Ethoxycarbonyloxy)-1,2-methano[60]fulleren-61-ylcarbonyloxy]-1-oxoethoxy}ethoxy]ethyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate (49). DCC (13.2 mg, 0.064 mmol) and DMAP (2.6 mg,

0.0214 mmol) were added at r.t. to a stirred soln. of **46** (24 mg, 0.0214 mmol) and **28** (58.3 mg, 0.0642 mmol) in CH_2Cl_2 (100 ml). The mixture was stirred for 36 h, and an additional portion of **28** (39 mg, 0.0428 mmol) was added each 12 h. Evaporation followed by CC ($2 \times$; SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 99.5:0.5 $\rightarrow$ 99:1) and recrystallization from $\text{CHCl}_3/\text{MeOH}$ provided **49** (14 mg, 23%). Dark-brown solid. M.p. $> 280^\circ$. UV/VIS (CH_2Cl_2): 257 (222200), 325 (66000), 408 (sh, 18000), 425 (16000), 462 (16600), 551 (sh, 7700), 598 (sh, 3900). IR (KBr): 1748 ($\text{C}=\text{O}$). ^1H -NMR (CDCl_3 , 500 MHz): 1.41 (t, $J = 7.1$, 6 H); 3.70 (t, $J = 4.5$, 4 H); 3.80 (t, $J = 4.5$, 4 H); 4.32 (t, $J = 4.5$, 4 H); 4.50 (q, $J = 7.1$, 4 H); 4.54 (m, 4 H); 4.97 (s, 4 H). ^{13}C -NMR (CDCl_3 , 125 MHz): 14.63 (Me); 39.43 (methano bridge); 39.47 (methano bridge); 62.92; 64.22; 64.88; 65.67; 66.45; 68.96; 69.09; 71.52; 75.18; 130.97 (C_{70}); 131.07 (C_{70}); 131.12 (C_{70}); 133.02 (C_{70}); 133.71 (C_{70}); 137.03 (C_{70}); 139.12 (C_{60}); 139.50 (C_{60}); 141.04 (C_{70}); 141.14 (C_{60}); 141.17 (C_{60}); 141.78 (C_{70}); 142.08 (C_{60}); 142.10 (C_{60}); 142.41 (C_{60}); 142.49 (C_{60}); 142.96 (C_{70}); 143.03 (C_{70}); 143.18 (C_{60}); 143.21 (C_{60}); 143.23 (C_{60}); 143.30 (C_{60}); 143.73 (C_{70}); 144.03 (C_{70}); 144.08 (C_{60}); 144.13 (C_{70}); 144.81 (C_{60}); 144.86 (C_{60}); 144.88 (C_{60}); 144.90 (C_{60}); 145.01 (C_{60}); 145.03 (C_{70}); 145.11 (C_{60}); 145.31 (C_{60}); 145.37 (C_{60}); 145.39 (C_{60}); 145.49 (C_{60}); 146.11 (C_{70}); 146.17 (C_{70}); 146.63 (C_{70}); 147.21 (C_{70}); 147.49 (C_{70}); 147.69 (C_{70}); 147.77 (C_{70}); 148.65 (C_{70}); 148.68 (C_{70}); 148.74 (C_{70}); 148.96 (C_{70}); 149.35 (C_{70}); 149.44 (C_{70}); 149.52 (C_{70}); 150.76 (C_{70}); 150.91 (C_{70}); 151.34 (C_{70}); 151.52 (C_{70}); 151.54 (C_{70}); 155.22 (C_{70}); 163.31 ($\text{C}=\text{O}$); 163.36 ($\text{C}=\text{O}$); 163.66 ($\text{C}=\text{O}$); 166.76 ($\text{C}=\text{O}$). MALDI-TOF-MS (dithranol): 2900 (M^+).

Electrochemistry. The electrochemical experiments were carried out in a classical three-electrode cell in CH_2Cl_2 or in $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ 95:5 containing 0.1M (Bu_4N)PF₆. The working electrode was a glassy carbon disk electrode ($\varnothing$ 2 mm, EDI-type, SOLEA-Tacussel, Villeurbanne, France) used either motionless (for cyclic voltammetry from 0.01 to 10 V/s) or as a rotating disk electrode (RDE). The auxiliary electrode was a Pt wire, and a Ag wire was used as a pseudo-reference electrode. The electrochemical cell was connected to a computerized multipurpose electrochemical device DACFAMOV (Microtec-CNRS, Toulouse, France) interfaced with an Apple II microcomputer. The accessible range of potentials was +1.2 to -2.2 V vs Fc/Fc^+ in CH_2Cl_2 and +1.2 to -1.9 V vs Fc/Fc^+ in $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ 95:5. All the potentials given are referred to the ferrocene/ferrocenium (Fc/Fc^+) couple used as internal standard.

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