Additions of Azomethine Ylides to Fullerene C_{60} Assisted by a Removable Anchor

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The addition of nitrile oxides to [60]fullerene, leading to isoxazolinofullerenes, can be reversed using reducing agents such as $Mo(CO)_6$ or DIBALH. Thus, this reaction can be used, in principle, for protection/deprotection of [60]fullerene or for solubilization purposes. The tether-controlled tandem addition of nitrile oxides and azomethine ylides provides mainly cis-1 patterns. The determination of the structure of bisadducts was obtained by NMR spectroscopy with the help of HMQC, HMBC, and NOEDS techniques. The isoxazoline moiety could be removed using $Mo(CO)_6$ leaving a fulleropyrrolidine derivative.

The control of multiple additions to fullerene C_{60} is an issue of current high interest.[1,2] With its several reactive double bonds, C_{60} can be considered an ideal framework for the construction of complex architectures. In fact, this concept has been successfully developed by the Hirsch and Diederich groups and applied to the synthesis of very complex molecules with perfect control of fullerene stereochemistry. The approach of the German and Swiss groups is different. Hirsch has investigated in deep detail the stepwise multiple additions of bromomalonates to C_{60} providing an excellent statistical means and taking advantage of the high propensity of malonate anions to attack equatorial and trans-3 sites.[3−9]

The Diederich strategy is based on the template-directed multifunctionalization: by careful choice of the length of the arm, exclusively equatorial or cis-2 addends have been obtained. The base reaction used for these studies is again a cyclopropanation reaction, which offers the advantage of being remarkably selective.[10−16]

Instead, the cycloaddition of azomethine ylides to C_{60},[17] another widely used fullerene functionalization methodology, is much less selective. For instance, five bisadducts in the reaction of sarcosine and formaldehyde are formed in approximately the same amounts. Furthermore, when bisadducts start to be formed, trisadducts also appear, thus making the whole reaction mixture very complex and the separation of pure isomers very difficult.[18,19]

To study the possibility of controlling the reactivity of these dipoles, we have carried out a systematic study based on the use of a reversible anchorage. First, an anchor (**A**) is attached to C_{60}, then the azomethine ylide is generated, which attacks intramolecularly a second double bond of the same fullerene spheroid. The length of the arm between the anchor and the pyrrolidine ring can be varied to check its influence on regioselectivity. Eventually, the anchor is removed and a fulleropyrrolidine is obtained (Scheme 1).[20]

Results and Discussion

The reaction used to provide a reversible anchorage to C_{60} is the cycloaddition of nitriloxides. This reaction has been extensively studied by the groups of Meier and Irngartinger.[21−25] Among other methods, these reactive species are easily generated in situ by dehydrohaloge-

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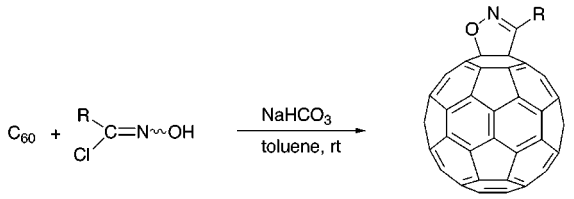
Scheme 1

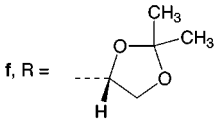
Scheme 2



a, R = C_6H_4-4-OCH_2Ph; **b**, R = COOEt; **c**, R = COPh; **d**, R = 9-anthryl;

e, R = $CH_2OCH_2CH_2OCH_2CH_2OCH_3$;

f, R =

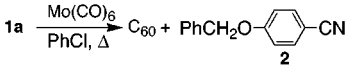


nation of chloroximes, obtained by chlorination of oximes. The cycloaddition step can be performed at room temperature in toluene, using $NaHCO_3$ as the base (Scheme 2). Isolated yields were typically in the 20−40% range, with a wide variety of substitutions allowed. Fullerene-fused isoxazolines (colloquially termed isoxazolinofullerenes) are relatively thermally stable and revert back to [60]fullerene only at very high temperatures (280−400 °C).[25]

Compounds **1** are also stable to acids. Addition of 10 equiv of trifluoroacetic acid to a solution of **1b** in chlorobenzene at reflux gave only traces of [60]fullerene after 10 days. Addition of *N*-phenylmaleimide as retrocycloaddition trapping agent did not produce any formation of the corresponding adduct, even in chlorobenzene at reflux.

However, when $Mo(CO)_6$ was added to a refluxing chlorobenzene solution of **1**, C_{60} was recovered in virtually quantitative yield. The same happened when adducts **1** were treated with excess DIBALH (diisobutylaluminum hydride) in toluene at room temperature.

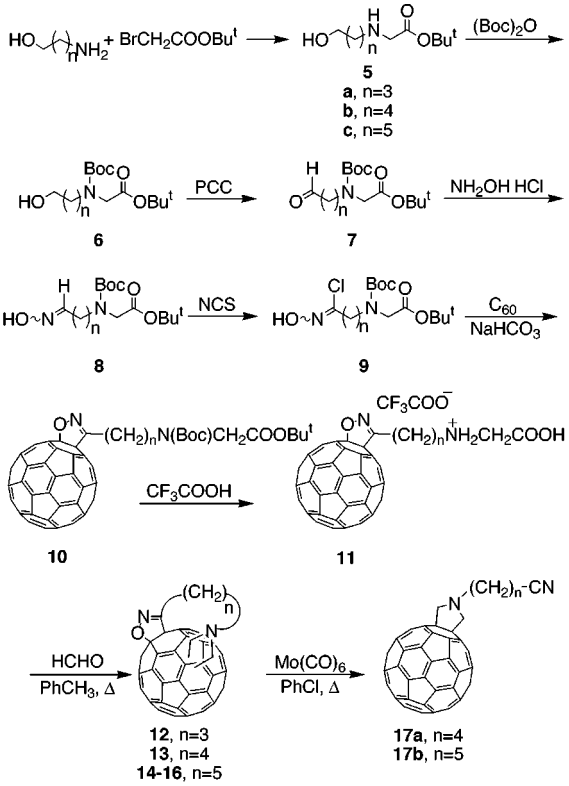
The reactions were followed by TLC, and at the end C_{60} was isolated and characterized by ^{13}C NMR. The reaction of **1a** with $Mo(CO)_6$ or DIBALH was studied in detail. In the reaction with $Mo(CO)_6$, compound **2** was isolated in 91% yield and identified with an authentic sample along with C_{60} (eq 1).



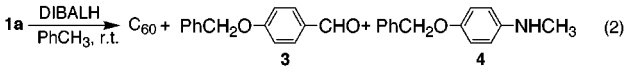
(1)

A plausible mechanism would envision $Mo(CO)_6$-induced retrocycloaddition.[26] This reaction would generate C_{60} and the corresponding nitrile oxide, which would in turn be reduced to nitrile by excess $Mo(CO)_6$.

Scheme 3



C_{60} was also obtained in the treatment of **1** with DIBALH (10 equiv) at room temperature in toluene. In this case, the reaction of **1a**, besides the quantitative production of [60]fullerene, yielded aldehyde **3** and amine **4** in 31 and 64% isolated yield, respectively (eq 2). Both compounds were identified by comparison with authentic samples. Also in the case of DIBALH, retrocycloaddition to the nitrile oxide, followed by reduction, would give nitrile **2**. This latter compound can be further reduced by DIBALH to aldehyde **3**. Amine **4** may form from rearrangement of the nitrile oxide to the corresponding isocyanate,[27] which is then reduced to **4**. All attempts to trap the transient nitrile oxide under reductive conditions using strong dipolarophiles (*N*-phenylmaleimide) failed.



(2)

Once the reversibility of the anchorage was established, the stage was set for the controlled cycloaddition of azomethine ylides. The first step was the alkylation of amino alcohols by *tert*-butyl bromoacetate to give esters **5** (Scheme 3). Then, the amine function was protected: at this stage, it was possible to oxidize the alcohol by PCC. The resulting aldehydes **7** were converted to oximes by hydroxylamine hydrochloride in water and then to chloroximes using *N*-chlorosuccinimide (NCS) in acetonitrile. The cycloaddition to C_{60} produced isoxazolines **10**, in which the carboxylic acid and amine groups of the glycine moiety were protected as *tert*-butyl ester and *tert*-butyl carbamate, respectively. Treatment of **10** with

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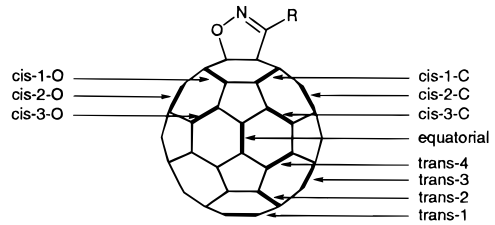


Figure 1. Labeling of different isomers in the bisaddition to isoxazolinofullerenes.

trifluoroacetic acid liberated both functionalities generating salts **11**. These protonated glycines, suspended in toluene, were heated to reflux in the presence of formaldehyde, inducing the intramolecular cycloaddition of azomethine ylides. In the reactions of derivatives **11a** and **11b** one main product was isolated (respectively **12** and **13**), whereas three different compounds were produced in the case of **11c**.

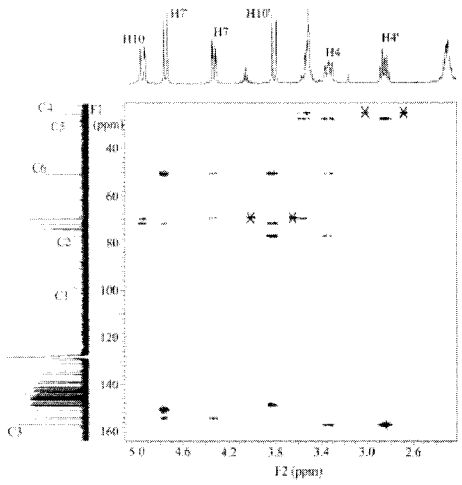
The complete characterization of the different isomers and the determination of the exact structure were made difficult by the absence of symmetry elements. Structural assignments relied on UV−vis spectra, electrospray mass spectrometry (ES-MS), elemental analysis, but especially NMR techniques, such as ^{1}H NMR, ^{13}C NMR, HMQC, HMBC, HH-COSY, and NOE, assisted by geometrical optimizations with semiempirical PM3 procedure.[28]

Figure 1 provides a pictorial description of bis-addition patterns. Since the isoxazoline ring is asymmetric we distinguish between additions of the azomethine ylide on the side of the imine carbon of isoxazoline (designated by the suffix -*C*) and additions on the side of oxygen (designated by the suffix -*O*).

In the course of these investigations, the most profitable diagnostic technique was the detection of long-range correlations between proton and carbon atoms by means of HMBC technique. Whenever this correlation was found, a firm structural assignment was possible, whereas when this interaction was missing the task was much more difficult. The following is a succinct description of the structural assignment of compounds **12**−**16**. The description refers to the HMBC of compounds **12**−**14** reported in Figures 2, 3, and 4, respectively. The structural determinations also allow the assignment (reported in the Experimental Section) of most ^{1}H resonances and of many ^{13}C resonances.

Compound 12. The pyrrolidine protons show different ^{1}H resonances, which have been assigned (with HMQC and HMBC) as indicated in the upper trace of Figure 2. The H4 and H4′ protons α to the imine carbon C3 are assigned from the ^2J correlation with this same carbon. The H4 proton also shows ^3J correlations with methylenic carbons C5 and C6 and with the quaternary aliphatic carbon C2. This same carbon C2 also gives ^3J coupling with the pyrrolidine proton H10′. This constitutes the most convincing proof for structure **12**. The attack of the azomethine ylide is then of type cis-1-C with respect to the original isoxazoline anchor, on the side of the imine carbon. The aliphatic chain separating the isoxazoline ring and the reactive azomethine ylide is too short to allow a reaction to far sites. The UV−vis spectrum of **12** is reported in Figure 5a.

(28) Spartan 4.0 program package, 1995, distributed by Wavefunction, Inc., Irvine, CA 92715.



C	ppm
1	99.3
2	77.0
3	157.0
4	25.3
5	27.7
6	50.7
7	70.1
8	72.0
9	74.1
10	69.7
11	150.9
12	148.8
13	154.1

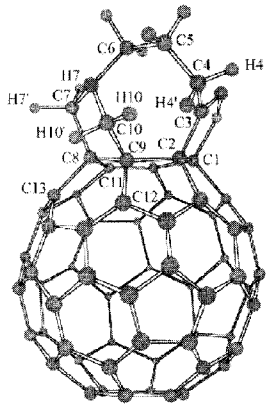
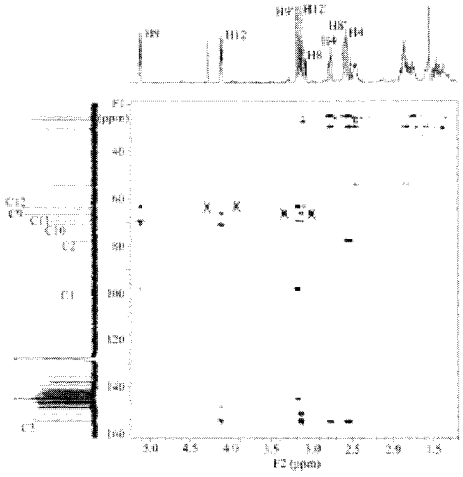


Figure 2. HMBC spectrum of bisadduct **12**. The resonance labels refer to the structures reported in Scheme 3. Crosses indicate cross peaks deriving from an incomplete suppression of the $^1J_{CH}$ correlations.

Compound 13. The four pyrrolidine protons give again distinct resonances, assigned as indicated in Figure 3. The H4 and H4′ resonances are attributed from the ^2J correlation with the imine carbon C3. However, no further correlation could be detected with carbon C2. The structural assignment therefore rests upon the following considerations. The pyrrolidine protons H8, H8′, H11, and H11′ correlate with the three methylenic carbons C7, C8, and C11 and also with three quaternary aliphatic carbons not bound to oxygen. The ^{13}C resonances correlating with H8 and H8′ necessarily belong to C9 and C10, so that the last correlation of H11′ is with carbon C2 of the isoxazoline ring. This set of correlations again points to the cis-1-C structure. The UV−vis is reported in Figure 5b.

Compounds 14−**16.** The longer aliphatic chain can in principle allow for a different type of bisaddition. In fact, the increased freedom of the arm brings about the formation of three products.

Compound 14. The ^{1}H NMR shows again four signals for the pyrrolidine protons, which could be assigned as indicated in Figure 4. The structural assignment is straightforward from the inspection of the HMBC spectrum. The pyrrolidine H9′ proton shows a ^3J correlation with the high-field aliphatic resonance at 98.39 ppm, unambiguously attributed to the quaternary carbon C1 bound to oxygen. Thus, the structure of the bisadduct corresponds to the cis-1-O type, with the pyrrolidine ring oriented toward the oxygen of the isoxazoline moiety. The



C	ppm
1	99.2
2	77.3
3	158.7
4	30.4
5	27.7
6	28.6
7	50.2
8	65.1
9	70.8
10	69.2
11	65.8
12	149.7
13	147.1
14	152.8

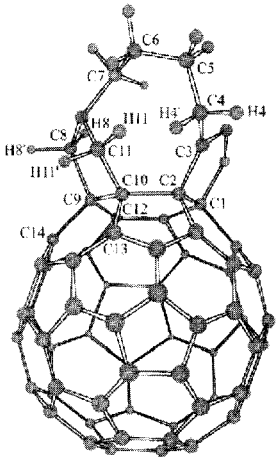
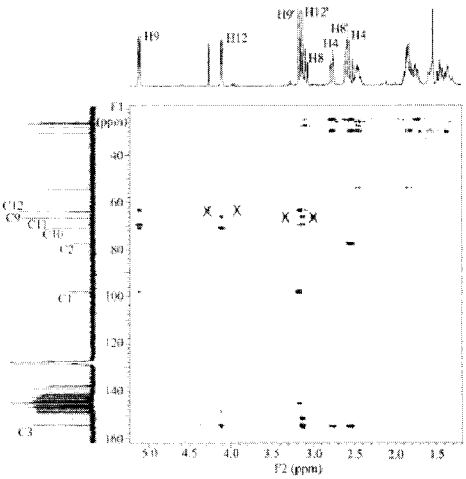


Figure 3. HMBC spectrum of bisadduct **13**. See caption of Figure 2.



C	ppm
1	98.4
2	77.8
3	154.4
4	26.0
5	29.7
6	25.0
7	27.5
8	54.0
9	66.4
10	71.2
11	69.7
12	63.5
13	151.5
14	154.3

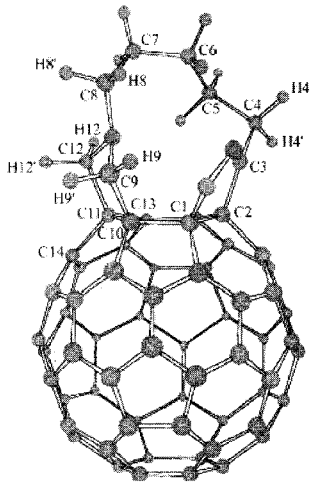


Figure 4. HMBC spectrum of bisadduct **14**. See caption of Figure 2

UV−Vis spectrum reported in Figure 5c, very similar to that of compound **13**, shows that two different cis-1 adducts give similar absorption patterns.

Compound 15. The determination of the structure in the present case is based more on the absence than on the detection of diagnostic scalar or dipolar interactions, and is therefore more speculative than the previous examples. The discussion also rests upon the semiempirical PM3 optimizations of the potential configurations and conformations related to this compound. The cis-1-C structures of compounds **12** and **13** and the cis-1-O structure of compound **14** have been revealed by the detection of ^3J correlations between one pyrrolidine proton and carbons C1 or C2 of the isoxazoline ring. No such correlation was detected in the HMBC spectrum of **15** (not shown), suggesting junctions of the cis-2 or cis-3 type. The geometry optimizations reveal that the cis-2-C and cis-3-C structures are by far more stable than the corresponding cis-2-O and cis-3-O structures. One remarkable feature of compound **15** is the absence in the NOEDS spectra of dipolar interactions between any of the methylenic protons α to the pyrrolidine nitrogen (H8, H8′, H9, H9′, H12, and H12′) and any of the methylenic proton α to the isoxazoline ring (H4 and H4′), indicating that the minimal distance between protons of one set and protons of the other is above 3.2 Å. In every conformer of the cis-2-C structure such distances are below the threshold, while in the conformer of the cis-3-C structure (also the most stable conformer) all distances are above 5 Å. Thus, the analysis of the dipolar interaction net will point toward the cis-3-C structure. The UV−vis spectrum of **15** is reported in Figure 5d and is reminiscent of that recorded for a cis-3 pattern by Taki et al.,[29] thus corroborating our tentative assignment.

Compound 16. This isomer was formed in very low yields (2%) and was only characterized by ES-MS and UV−vis spectrophotometry. The mass spectrum confirmed that **16** is an isomer of **14** and **15**, whereas the UV−vis spectrum, reported in Figure 5e, is similar to that obtained by Taki et al. for a cis-2 isomer.[29] Accordingly, we tentatively assign a cis-2-C structure to isomer **16**.

Compounds **12**−**15** were subjected to treatment by $Mo(CO)_6$ in chlorobenzene at reflux. Except for derivatives **12**, which gave mainly decomposition products, in all cases the reaction gave the corresponding nitriles **17a**,**b** as the only isolated products.

The reactions of **14** and **15** produced the same nitrile derivative, thus confirming the isomeric nature of the two reactants. The structure of nitrile **17a** was also confirmed by an independent synthesis. Nitrile-amine **18**, prepared according to the literature,[30] was alkylated by *t*-butyl bromoacetate to give aminoester **19**, which was hydro-

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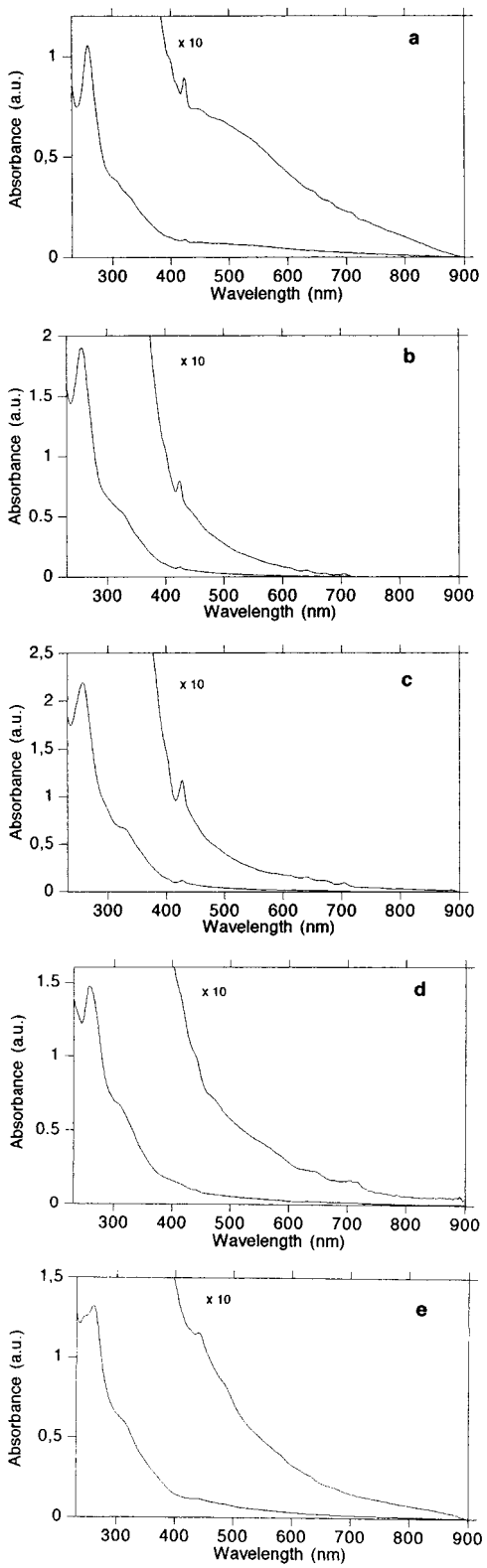
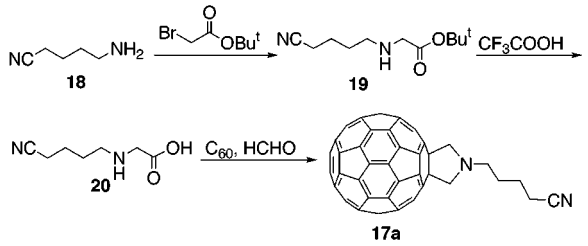


Figure 5. UV−vis spectra of compounds **12**−**16**, registered in cyclohexane.

lyzed to amino acid **20**. The latter was condensed with formaldehyde in the presence of C_{60} to produce **17a** in 34% isolated yield (Scheme 4).

In conclusion, the intramolecular cycloaddition of azomethine ylides to an isoxazolinofullerene appears to be determined by the length of the tether. With relatively short tethers (three or four methylene units), only cis-1-C bisadducts are obtained, characterized by relatively small distances between the imine carbon and the pyrrolidine nitrogen. This parallels the tendency on unhindered additions to proceed in a *cis*-1 fashion as observed by Hirsch and Djojo.[7,9] With the longer 5-methylene tether, the cis-1-O and cis-3-C bis bisadducts are obtained. It is remarkable that in this case no cis-1-C compound was observed, probably because this addition modality requires an energetically unfavored twisting of the long methylenic chain.

Scheme 4



In all cases, nitrile oxide cycloaddition could be reversed, allowing the isolation of monopyrrolidine derivatives.

The methodology reported in this paper has the potential of allowing a reversible tether-controlled cycloaddition of azomethine ylides in complex fullerene architectures. Since cis-1 bisadducts were never observed in the addition of azomethine ylides to C_{60}, as a matter of fact, the possibility of generating cis-1 structures might be helpful for the exploitation of unusual multiple addition patterns.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 200 or 400 MHz and ^{13}C spectra at 50 or 100 MHz. Chemical shifts (δ) are given in parts per million relative to tetramethylsilane. The NOE spectra have been obtained in the differential mode (NOEDS).[31] The heterocorrelated reverse-mode HMQC[32−34] and HMBC[34,35] (multiple bond HMQC) spectra have been acquired from a total of 256 t1 measurements in the phase sensitive acquisition mode, with 16 (HMQC) or 32 (HMBC) scans for each t1 value. The delay for the BIRD filter is matched to the average $^1J_{CH}$ = 140 Hz. The fixed delay for the detection of multiple bond correlations is tuned to $^nJ_{CH}$ = 5 Hz. FT-IR spectra were recorded using NaCl cells or mixtures compound/KBr (DRIFT system). C_{60} was purchased from Bucky-USA (99.5%), all other reagents and solvents were used as purchased from Fluka, Aldrich, J. T. Baker, and Cambridge Isotope Laboratories; silica gel NM Kieselgel 60 (70−230 mesh ASTM) was obtained from Macherey-Nagel and Merck.

General Synthesis of 3′-Substituted [5,6]Fullerene-C_{60}-I_h-[1,9-*d*]isoxazole (1). The syntheses of oximes and chloroximes were performed according to the literature.[36−39]

Hydroxylamine hydrochloride (321 mg, 4.6 mmol) and Na_2CO_3·10 H_2O (1.32 g, 4.6 mmol) were added to a cold solution

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of aldehyde (3.1 mmol) in water. The mixture was stirred for 45 min at 0 °C, the water was removed, and the crude was washed with ethyl acetate. The crude oximes, obtained by evaporation of the solvent under reduced pressure, were sufficiently pure (^{1}H NMR) and were used without further purification. *N*-Chlorosuccinimide (283 mg, 2.1 mmol) was added to a solution of oxime (2.1 mmol) in acetonitrile (5 mL) in 30 min. The mixture was stirred for 2 h, the solvent was removed, and the crude was washed with CCl_4. The chloroximes were used without further purification. Addition of nitrile oxides to C_{60} were carried out according to reported methodology.[21,22,24,25] Compounds **1b** and **1d** were synthesized according to the literature.[21]

To a solution of C_{60} (200 mg, 0.278 mmol) in toluene (150 mL) were added 0.556 mmol of hydroximoyl chloride and 150 mg (1.8 mmol) of $NaHCO_3$. The suspension was stirred at room temperature, washed with water, dried over anhydrous Na_2SO_4, and purified by chromatography.

***N*-Hydroxy-4-(phenylmethoxy)benzenecarboximidoyl Chloride.** $C_{14}ClH_{12}NO_2$ (MW 261.710) 544 mg, 2.07 mmol. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.80 (m, 2H), 7.41 (m, 5H), 6.99 (m, 2H), 5.11 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 174.3, 136.3, 128.7, 128.6, 128.2, 127.4, 114.7, 70.1.

3′-[4-(Phenylmethoxy)phenyl][5,6]fullereno-C_{60}-I_h-[1,9-*d*]isoxazole (1a). $C_{74}H_{11}NO_2$ (MW 945.918). Yield: 37% (97.5 mg, 0.10 mmol, yield on C_{60} reacted: 60%). Reaction time: 4 h; eluant toluene/petroleum ether 4/1; precipitated by CS_2/diethyl ether. ^{1}H NMR (200 MHz, $CDCl_3/CS_2$): δ 8.15 (m, 2H), 7.43 (m, 4H), 7.38 (m, 1H), 7.13 (m, 2H), 5.14 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3/CS_2$): δ 160.4, 152.3, 147.5, 147.1, 146.3, 146.1, 145.8, 145.4, 145.3, 145.1, 145.0, 144.9, 144.7, 144.3, 144.0, 142.9, 142.7, 142.4, 142.2, 142.0, 141.6, 140.2, 136.9, 136.5, 136.2, 130.3, 128.6, 128.1, 127.2, 121.6, 115.3, 69.9. UV−vis (cyclohexane): λ_{max} nm 685, 550 (sh), 458 (sh), 425, 402 (sh), 315, 256, 219. Anal. Calcd for $C_{74}H_{11}NO_2$: C, 93.96; H, 1.17; N, 1.48. Found: C, 91.7; H, 0.95; N, 1.49.

[5,6]Fullereno-C_{60}-I_h-[1,9-*d*]isoxazol-3′-ylphenylmethanone (1c). $C_{68}H_5NO_2$ (MW 867.804). Yield: 36% (86.32 mg, 0.1 mmol). Reaction time: 30 min; eluant toluene/petroleum ether 4/1; precipitated by CS_2/diethyl ether. IR (KBr): (cm^{-1}) 1653, 575. ^{1}H NMR (200 MHz, $CDCl_3/CS_2$): δ 8.54 (m, 2H), 7.68 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3/CS_2$): δ 184.7, 151.1, 147.6, 147.0, 146.9, 146.2, 146.1, 145.8, 145.8, 145.5, 145.1, 145.0, 144.5, 144.1, 144.0, 142.9, 142.7, 142.6, 142.4, 142.3, 142.2, 142.0, 141.6, 140.1, 140.0, 136.9, 136.0, 135.9, 134.0, 130.6, 128.5, 128.1. UV−vis (cyclohexane): λ_{max} nm 673, 460, 426, 314, 254. Anal. Calcd for $C_{68}H_5NO_2$: C, 94.12; H, 0.58; N, 1.61. Found: C, 92.92; H, 0.61; N, 1.38.

***N*-Hydroxy-2-[2-(2-methoxyethoxy)ethoxy]ethanimidoyl Chloride. Oxime.** $C_7H_{15}NO_4$ (MW 177.202). Yield: 87% (476 mg, 2.7 mmol). ^{1}H NMR (200 MHz, $CDCl_3$), two isomers: 9.22 and 9.07 (bs, 1H), 7.45 and 6.87 (t, J = 5.7, 3.6 Hz respectively, 1H), 4.34 and 4.09 (d, J = 3.6, 5.6 Hz, respectively, 2H), 3.61 (m, 6H), 3.54 (m, 2H), 3.34 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.7, 147.9, 71.6, 70.3, 70.2, 70.2, 70.1, 69.6, 67.6, 64.9, 58.8. EI-MS: 177 (M^+, 2), 103 (15), 89 (60), 59 (100). **Chloroxime.** $C_7ClH_{14}NO_4$ (MW 211.647) 270 mg, 1.3 mmol (quantitative yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.11 (bs, 1H), 4.28 (s, 2H), 3.66 (m, 6H), 3.55 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.0, 71.8, 71.2, 70.5, 70.3, 70.1, 70.0, 69.5, 68.7, 5 9.0.

3′-[(2-(2-Methoxyethoxy)ethoxy]methyl[5,6]fullereno-C_{60}-I_h-[1,9-*d*]isoxazole (1e). $C_{67}H_{13}NO_4$ (MW 895.855). Yield: 30% (74.0 mg, 0.084 mmol). Reaction time: 6 h; eluant toluene/ethyl acetate 9/1; precipitated by dichloromethane/methanol. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.96 (s, 2H), 3.82 (m, 2H), 3.57 (m, 2H), 3.51 (m, 2H), 3.42 (m, 2H), 3.29 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.7, 147.6, 146.1, 146.1, 146.0, 145.8, 145.7, 145.7, 145.3, 145.1, 145.0, 144.7, 144.7, 144.0, 143.9, 143.8, 142.7, 142.6, 142.6, 142.2, 142.2, 142.1, 141.9, 141.6, 140.3, 134.0, 136.6, 136.1, 103.2, 78.0, 71.8, 70.5, 70.4, 70.4, 70.1, 65.6, 58.8. UV−vis (cyclohexane): λ_{max} nm 460, 425, 401 (sh), 314, 254. Anal. Calcd for $C_{67}H_{13}NO_4$: C, 89.83; H, 1.46; N, 1.56. Found: C, 86.53; H, 1.30; N, 1.31.

3′-(2,2-Dimethyl-1,3-dioxolan-4-yl)-(*S*)-[5,6]fullereno-C_{60}-I_h-[1,9-*d*]isoxazole (1f). $C_{66}H_9NO_3$ (MW 863.813). Yield: 34% (82.0 mg, 0.094 mmol). Reaction time: 4 h; eluant toluene/petroleum ether 4/1; precipitated by CS_2/diethyl ether. ^{1}H NMR (200 MHz, $CDCl_3/CS_2$): δ 5.54 (dd, J = 5.8, 6.6 Hz, 1H), 4.82 (dd, J = 5.9, 8.5 Hz, 1H), 4.52 (dd, J = 6.6, 8.4 Hz, 1H), 1.51 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3/CS_2$): δ 153.2, 147.7, 147.1, 146.3, 146.2, 146.2, 146.0, 145.9, 145.9, 145.8, 145.5, 145.4, 145.3, 145.2, 145.2, 145.1, 144.8, 144.6, 144.2, 144.1, 144.1, 144.0, 143.9, 143.6, 142.9, 142.8, 142.7, 142.7, 142.3, 142.3, 142.2, 142.1, 142.0, 141.8, 141.7, 141.6, 140.3, 140.1, 136.8, 136.5, 135.9, 111.2, 103.7, 78.2, 72.1, 67.3, 26.1, 25.4. UV−vis (cyclohexane): λ_{max} nm 678, 459, 425, 315, 254. Anal. Calcd for $C_{66}H_9NO_3$: C, 91.77; H, 1.05; N, 1.62. Found: C, 91.3; H, 1.00; N, 1.58.

Reactions with $Mo(CO)_6$: General Procedure. To a solution of **1a** (20 mg, 2.1×10^{-2} mmol) in chlorobenzene (10 mL) were added 16.6 mg (6.3×10^{-2} mmol) of $Mo(CO)_6$ and 80 μL of methanol. The mixture was heated to reflux for 1.5 h, and the products were purified by chromatography (toluene). There were recovered C_{60} (10.91 mg, 1.5×10^{-2} mmol, yield 71%) and 4-benzyloxy-benzonitrile **2** (4 mg, $1.9 \cdot 10^{-2}$ mmol, yield 91%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.59 (m, 2H), 7.41 (m, 5H), 7.02 (m, 2H), 5.12 (s, 2H).

Reactions with DIBALH: General Procedure. To a cold solution of **1a** (20 mg, 2.1×10^{-2} mmol) in anhydrous toluene (10 mL), under nitrogen, were added 210 μL of DIBALH (1M solution in hexane). The solution was stirred for 2 h at room temperature, and then the mixture was washed with water and the organic layer dried over anhydrous Na_2SO_4. The products were purified by chromatography (petroleum ether/ethyl acetate 9/1). Aldehyde **3**. Yield: 31% (1.36 mg, 6.4×10^{-3} mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.84 (m, 2H), 7.40 (m, 5H), 7.08 (m, 2H), 5.16 (s, 2H). Amine **4**. Yield: 64% (2.86 mg, 1.34×10^{-2} mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.37 (m, 5H), 6.89 (m, 2H), 6.58 (m, 2H), 5.00 (s, 2H), 2.81 (s, 3H).

Experiments performed with both procedures on all compounds **1** gave yields of C_{60} ranging between 70 and 90%.

Synthesis of 4-(Phenylmethoxy)benzonitrile (2).[40] To a solution of 4-cyanophenol (100 mg, 0.84 mmol) in anhydrous acetonitrile (2 mL) were added 116 mg (0.42 mmol) of silver carbonate and benzyl bromide (100 μL, 144 mg, 0.84 mmol). The mixture was stirred under N_2 in the dark for 18 h at room temperature and was filtered on Celite, and the product was purified by chromatographic column (petroleum ether/ethyl acetate 9/1). $C_{14}H_{11}NO$ (MW 209.250). Yield: 85% (150 mg, 0.72 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.39 (m, 5H), 6.98 (m, 2H), 5.18 (s, 2H).

Synthesis of *N*-Methyl-4-(phenylmethoxy)benzenamine (4).[41] To a cold solution of 4-benzyloxyaniline hydrochloride (500 mg, 2.12 mmol) in methanol (5 mL) were added paraformaldehyde (57.2 mg, 1.9 mmol) and sodium cyanoborohydride (133 mg, 2.11 mmol). After 2.5 h, the solvent was evaporated, water (10 mL) was added to the crude, and the crude was then washed with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by chromatography (petroleum ether/ethyl acetate 9/1). $C_{14}H_{15}NO$ (MW 213.282). Yield: 11% (50 mg, 0.23 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.28 (m, 5H), 6.78 (m, 2H), 6.48 (m, 2H), 4.90 (s, 2H), 2.70 (s, 3H).

Synthesis of Glycine *N*-(ω-Hydroxyalkyl)-1,1-dimethylethyl Esters (5). To a solution of amino alcohol (100 mmol) in 100 mL of diethyl ether at 0 °C, *tert*-butyl bromoacetate (3.8 mL, 25.6 mmol) in diethyl ether (25 mL) was dropped over a period of 2 h. The solution was brought to room temperature and stirred for 3 h. The mixture was washed with water, and the organic phase was dried over anhydrous Na_2SO_4. The solvent was concentrated at reduced pressure, and the product was purified by chromatography (ethyl acetate /methanol 9/1).

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5a. $C_{10}H_{21}NO_3$ (MW 203.284). Yield: 25% (1.3 g, 6.4 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.59 (t, J = 5.3 Hz, 2H), 3.28 (s, 2H), 3.16 (broad s, 2H), 2.64 (t, J = 5.7 Hz, 2H), 1.63 (m, 4H), 1.45 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.0, 81.5, 62.4, 50.9, 49.2, 31.7, 28.0, 27.9. EI-MS: 203 (M^+, 2), 102 (100), 88 (25).

5b. $C_{11}H_{23}NO_3$ (MW 217.311). Yield: 89% (4.9 g, 22.8 mmol). IR (NaCl): (cm^{-1}) 3369, 1735. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.62 (t, J = 6.1 Hz, 2H), 3.29 (s, 2H), 2.60 (t, J = 6.9 Hz, 2H), 1.92 (bs, 2H) 1.56 (m, 6H), 1.46 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.2, 81.7, 62.0, 50.7, 48.9, 32.1, 28.6, 28.0, 23.1. EI-MS: 217 (M^+, 5), 116 (100), 88 (60).

5c. $C_{12}H_{25}NO_3$ (MW 231.338). Yield: 84% (5.0 g, 21.6 mmol). IR (NaCl): (cm^{-1}) 3320, 1733. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.49 (t, J = 6.5 Hz, 2H), 3.18 (s, 2H), 2.49 (t, J = 6.9 Hz, 2H), 2.38 (broad s, 2H), 1.49−1.38 (m, 4H), 1.38 (s, 9H), 1.30−1.25 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.6, 81.1, 62.3, 51.5, 49.3, 32.6, 29.8, 28.0, 26.9, 25.5. EI-MS: 231 (M^+, 2), 130 (100), 88 (90).

Synthesis of Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-(ω-hydroxyalkyl)-1,1-dimethylethyl Esters (6). To a solution of **5** (9.3 mmol) in dioxane were added 2.03 g (9.3 mmol) of di-*tert*-butyl dicarbonate and a water solution of sodium acetate (790 mg, 9.3 mmol). The mixture was stirred at room temperature for 3 h. After the solvent was removed at reduced pressure, water was added and the mixture extracted with ethyl acetate. The organic phase, dried over anhydrous Na_2SO_4, was concentrated and the product was purified by chromatography (petroleum ether/ethyl acetate 4/1).

6a. $C_{15}H_{29}NO_5$ (MW 303.402). Yield: 92% (2.6 g, 8.6 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.83 and 3.74 (s, 2H), 3.66 (broad t, 2H), 3.29 (m, 2H), 1.56 (m, 4H), 1.46 (s, 9H), 1.42 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 155.5, 81.4, 79.9, 62.4, 50.2, 49.6, 48.1, 29.8, 29.6, 28.3, 28.0, 24.8, 24.7. EI-MS: 303 (M^+, 1), 146 (40), 102 (100).

6b. $C_{16}H_{31}NO_5$ (MW 317.429). Yield: 98% (2.9 g, 9.1 mmol). IR (NaCl): (cm^{-1}) 3451, 1747, 1697. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.82 and 3.73 (s, 2H), 3.62 (t, J = 6.2 Hz, 2H), 3.25 (m, 2H), 1.65 (m, 6H), 1.45 (s, 9H), 1.42 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 155.7, 155.4, 81.3, 79.8, 62.2, 50.2, 49.6, 48.4, 48.3, 32.2, 28.3, 28.2, 28.0, 27.9, 22.9, 22.8. EI-MS: 317 (M^+, 5), 261 (10), 204 (30), 117 (100).

6c. $C_{17}H_{33}NO_5$ (MW 331.456). Yield: 97% (3.0 g, 9.0 mmol). IR (NaCl): (cm^{-1}) 1747, 1698. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.76 and 3.67 (s, 2H), 3.56 (dt, J = 2.7, 6.2 Hz, 2H), 3.18 (dt, J = 2.5, 7.1 Hz, 2H), 2.23 (broad s, 1H), 1.55−1.43 (m, 4H), 1.41 (s, 9H), 1.37 (s, 9H), 1.34−1.24 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 155.5, 155.4, 81.3, 79.8, 62.5, 62.3, 50.1, 49.5, 48.2, 48.0, 32.5, 28.2, 28.0, 26.5, 26.1, 25.4, 25.1. EI-MS: 331 (M^+, 3), 230 (10), 202 (20), 174 (20), 130 (100).

Synthesis of Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-(ω-oxyalkyl)-1,1-dimethylethyl Esters (7). To a dichloromethane solution of **6** (3.15 mmol in 50 mL) was added PCC (3.4 g, 15.8 mmol) in one portion. The mixture was stirred at room temperature for 1 day. Celite and ethyl ether (25 mL) were added, and the mixture was stirred for 15 min and then filtered on silica gel. The eluted was reduced to a small volume, and the product was loaded on top of a SiO_2 column and purified by chromatography (petroleum ether/ethyl acetate 7/3).

7a. $C_{15}H_{27}NO_5$ (MW 301.386). Yield: 40% (380 mg, 1.26 mmol). IR (NaCl): (cm^{-1}) 1750, 1700, 1655. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.75 (s, 1H), 3.79 and 3.71 (s, 2H), 3.26 (m, 2H), 2.52 (m, 2H), 1.81 (m, 2H), 1.44 (s, 9H), 1.40 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.9, 201.5, 169.1, 155.4, 81.4, 80.2, 80.0, 50.3, 49.7, 47.6, 41.1, 40.9, 28.2, 28.0, 20.9, 20.8. EI-MS: 301 (M^+, 1), 257 (10), 172 (35), 100 (100).

7b. $C_{16}H_{29}NO_5$ (MW 315.413). Yield: 43% (430 mg, 1.36 mmol). IR (NaCl): (cm^{-1}) 1746, 1696. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.70 (t, J = 1.5 Hz, 1H), 3.82 and 3.72 (s, 1H), 3.23 (m, 2H), 2.47 (t, J = 6.6 Hz, 2H), 1.56 (m, 4H), 1.46 (s, 9H), 1.42 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 202.2, 201.9, 169.1, 155.3, 81.3, 79.8, 50.1, 49.6, 48.0, 47.9, 43.4, 28.2, 28.0, 27.6, 19.1. EI-MS: 214 (10), 186 (40), 114 (100).

7c. $C_{17}H_{31}NO_5$ (MW 329.440). Yield: 55% (570 mg, 1.73 mmol). IR (NaCl): (cm^{-1}) 1745, 1700. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.66 (s, 1H), 3.72 and 3.64 (s, 2H), 3.15 (m, 2H), 2.35 (t, J = 7.2 Hz, 2H), 1.54 (m, 4H), 1.37 (s, 9H), 1.33 (s, 9H), 1.25 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 202.6, 169.1, 155.8, 155.2, 81.2, 79.8, 79.8, 50.1, 49.5, 48.1, 48.1, 43.7, 33.8, 28.3, 28.2, 28.0, 27.8, 26.2, 24.4, 21.7.

Synthesis of Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-[ω-(*N*′-hydroxyalkanimidoyl)-1,1-dimethylethyl Esters (8). A water solution of hydroxylamine hydrochloride (106 mg, 1.5 mmol) and Na_2CO_3·10 H_2O (440 mg, 1.5 mmol) was added to a solution of **7** (1.0 mmol) in dioxane (10 mL). The mixture was stirred for 18 h, the solvent was evaporated at reduced pressure, and the crude was extracted by ethyl acetate. The oximes were sufficiently pure to be used without further purification.

8a. $C_{15}H_{28}N_2O_5$ (MW 316.401). Yield: 88% (280 mg, 0.88 mmol). ^{1}H NMR (200 MHz, $CDCl_3$), two isomers: δ 7.80 (broad s, 1H), 7.40 and 6.70 (broad t, J = 5.7 Hz, 1H), 3.83 and 3.74 (d, J = 1.8 Hz, 2H), 3.28 (m, 2H), 2.38 and 2.22 (m, 2H), 1.72 (m, 2H), 1.46 (s, 9H), 1.43 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 151.3, 81.5, 80.1, 67.1, 50.4, 49.8, 48.2, 47.9, 47.6, 28.3, 28.1, 26.9, 25.2, 24.8.

8b. $C_{16}H_{30}N_2O_5$ (MW 330.428). Yield 99% (330 mg, 1.0 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.60 (bs, 1H), 7.40 and 6.70 (t, J = 6.0, 5.5 Hz, 1H), 3.82 and 3.77 (s, 2H), 3.46 (m, 2H), 2.39 and 2.22 (m, 2H), 1.52 (m, 4H), 1.46 (s, 9H), 1.42 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 155.7, 155.4, 152.3, 152.1, 151.7, 151.5, 81.4, 79.9, 50.2, 49.6, 48.0, 29.2, 28.3, 28.1, 27.7, 24.6, 23.7, 23.3.

8c. $C_{17}H_{32}N_2O_5$ (MW 344.455). Yield: 99% (340 g, 0.99 mmol). IR (NaCl): (cm^{-1}) 3380, 1746, 1697. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.82 (broad s, 1H), 7.39 and 6.69 (t, J = 6.0, 5.5 Hz, respectively, 1H), 3.82 and 3.72 (s, 2H), 3.23 (m, 2H), 2.36 and 2.20 (m, 2H), 1.55−1.24 (m, 6H), 1.46 (s, 9H), 1.42 (s, 9H). EI-MS: 344 (M^+).

Synthesis of Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-[ω-*N*′-hydroxy-ω-chloroalkanimidoyl)-1,1-dimethylethyl Esters (9). An acetonitrile solution of **8** (0.36 mmol in 3 mL) and NCS (48.6 mg, 0.36 mmol) was stirred for 2 h, and then the solvent was evaporated and the crude residue was washed with CCl_4. The mixture was filtered, and the solvent was removed affording the product.

9a. $C_{15}ClH_{27}N_2O_5$ (MW 350.846), 126 mg, 0.36 mmol. IR (NaCl): (cm^{-1}) 3310, 1745, 1710. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.56 and 9.26 (broad s, 1H), 3.77 and 3.69 (s, 2H), 3.22 (m, 2H), 2.47 (t, J = 7.3 Hz, 2H), 1.80 (m, 2H), 1.39 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.4, 169.1, 155.6, 155.4, 81.5, 81.4, 80.3, 80.0, 50.3, 50.1, 47.5, 47.3, 33.9, 29.4, 28.1, 27.9, 25.0, 24.8.

9b. $C_{16}ClH_{29}N_2O_5$ (MW 364.873), 84 mg, 0.23 mmol. IR (NaCl): (cm^{-1}) 3257, 1740, 1630. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.57 and 9.51 (broad s, 1H), 3.78 and 3.69 (s, 2H), 3.21 (m, 2H), 2.46 (t, J = 6.8 Hz, 2H), 1.56 (m, 4H), 1.41 (s, 9H), 1.37 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.3, 169.2, 155.4, 81.5, 80.2, 50.1, 49.5, 47.8, 36.1, 29.5, 28.1, 27.9, 27.1, 26.9, 23.3.

9c. $C_{17}ClH_{31}N_2O_5$ (MW 378.900), 130 mg, 0.34 mmol. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.37 and 9.12 (broad s, 1H), 3.78 and 3.70 (s, 2H), 3.19 (m, 2H), 2.44 (t, J = 6.9 Hz, 2H), 1.59 (m, 4H), 1.42 (s, 9H), 1.38 (s, 9H), 1.28 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.3, 169.2, 155.4, 81.7, 79.9, 60.2, 50.2, 50.0, 49.5, 47.9, 36.4, 29.6, 28.1, 27.9, 27.1, 26.9, 21.3, 14.2.

Synthesis of Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-(ω-[5,6]fullereno-C_{60}-I_h-[1,9-*d*]isoxazol-3′-ylalkyl)-1,1-dimethylethyl Esters (10). A toluene solution of C_{60} (200 mg, 0.28 mmol in 100 mL), hydroximoyl chlorides **9** (0.74 mmol), and $NaHCO_3$ (150 mg, 1.8 mmol) was stirred for 4 h. The reaction mixture was loaded on top of a column, and the product was purified by chromatography (toluene/ethyl acetate 9/1).

Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-(3-[5,6]-fullereno-C_{60}-I_h-[1,9-*d*]isoxazol-3′-ylpropyl)-1,1-dimethylethyl Ester (10a). $C_{75}H_{26}N_2O_5$ (MW 1035.054). Yield: 34% (98.54 mg, 0.095 mmol, yield on reacted fullerene: 54%). IR (KBr): (cm^{-1}) 1741, 1700, 526. ^{1}H NMR (200 MHz, $CDCl_3$): δ

3.94 and 3.86 (s, 2H), 3.59 (m, 2H), 3.11 (m, 2H), 2.36 (m, 2H), 1.50 (s, 9H), 1.46 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 169.1, 155.7, 155.6, 154.9, 154.8, 147.8, 147.2, 146.3, 146.2, 146.0, 145.9, 145.6, 145.6, 145.3, 145.2, 145.1, 145.0, 144.9, 144.7, 144.3, 144.1, 143.0, 142.8, 142.4, 142.2, 142.1, 141.8, 140.7, 140.1, 136.9, 136.9, 136.8, 136.7, 81.6, 81.5, 80.5, 80.6, 80.5, 80.3, 80.1, 50.6, 50.0, 48.2, 48.0, 28.5, 28.3, 28.2, 26.2, 26.1, 25.6, 25.3. UV−vis (cyclohexane): λ_{max} nm 685, 456, 426, 412 (sh), 402 (sh), 313, 255. Anal. Calcd for $C_{75}H_{26}N_2O_5$: C, 87.03; H, 2.53; N, 2.71. Found: C, 86.9; H, 2.75; N, 2.62.

Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-(4-[5,6]-fullereno-C$_{60}$-I$_h$-[1,9-*d*]isoxazol-3′-ylbutyl)-1,1-dimethylethyl Ester (10b). $C_{76}H_{28}N_2O_5$ (MW 1049.081). Yield: 34% (101.0 mg, 0.096 mmol, yield on reacted fullerene: 79%). IR (NaCl): (cm^{-1}) 1741, 1693. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.90 and 3.82 (s, 2H), 3.40 (m, 2H), 3.11 (t, J = 7.4 Hz, 2H), 2.15 (m, 2H), 1.86 (m, 2H), 1.50 (s, 9H), 1.44 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 155.6, 155.4, 154.9, 154.7, 147.8, 147.2, 146.3, 146.2, 145.9, 145.6, 145.4, 145.3, 145.2, 145.2, 145.1, 144.8, 144.7, 144.3, 144.1, 144.1, 142.9, 142.7, 142.3, 142.2, 142.1, 141.8, 140.7, 140.1, 136.8, 136.7, 81.4, 80.5, 80.5, 80.0, 79.9, 50.3, 49.6, 48.0, 29.7, 28.4, 28.3, 28.1, 27.7, 23.9, 23.8. UV−vis (cyclohexane): λ_{max} nm 686, 459, 424, 316, 255. Anal. Calcd for $C_{76}H_{28}N_2O_5$: C, 87.01; H, 2.69; N, 2.67. Found: C, 86.40; H, 2.42; N, 2.57.

Glycine *N*-[(1,1-Dimethylethoxy)carbonyl]-*N*-(5-[5,6]-fullereno-C$_{60}$-I$_h$-[1,9-*d*]isoxazol-3′-ylpentil)-1,1-dimethylethyl Ester (10c). $C_{77}H_{30}N_2O_5$ (MW 1063.108). Yield: 38% (112.1 mg, 0.105 mmol, yield on reacted fullerene: 74%). IR (NaCl): (cm^{-1}) 1740, 1695. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.87 and 3.78 (s, 2H), 3.32 (m, 2H), 3.07 (t, J = 7.6 Hz, 2H), 2.15 (m, 2H), 1.66−1.58 (m, 4H), 1.48 (s, 9H), 1.43 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.3, 155.8, 155.4, 155.1, 155.0, 147.9, 147.3, 146.4, 146.4, 146.3, 146.1, 146.0, 145.7, 145.5, 145.4, 145.3, 145.2, 145.0, 145.0, 144.8, 144.4, 144.2, 143.0, 142.9, 142.5, 142.5, 142.3, 142.3, 142.2, 141.9, 140.8, 140.2, 137.0, 136.8, 81.5, 81.5, 80.7, 80.0, 79.9, 50.4, 49.8, 48.5, 48.3, 29.8, 28.7, 28.6, 28.4, 28.3, 28.3, 28.2, 26.9, 26.8, 26.6, 26.4. UV−vis (cyclohexane): λ_{max} nm 688, 460, 425, 314, 255. ES-MS (THF/methanol 4/1): m/z 950 (M − 2 isobutene). Anal. Calcd for $C_{77}H_{30}N_2O_5$: C, 87.0; H, 2.84; N, 2.64. Found: C, 85.6; H, 2.90; N, 2.53.

Synthesis of *N*-(ω-[5,6]fullereno-C$_{60}$-I$_h$-[1,9-*d*]isoxazol-3′-ylalkyl)glycine Trifluoroacetic Salts (11). A dichloromethane solution of **10** (0.05 mmol in 5 mL) and trifluoroacetic acid (5 mL) was stirred for 18 h, the solvent was evaporated, and the residue was washed with toluene (three times).

***N*-(3-[5,6]Fullereno-C$_{60}$-I$_h$-[1,9-*d*]isoxazol-3′-ylpropyl)-glycine Trifluoroacetic Salt (11a).** $C_{68}F_3H_{11}N_2O_5$ (MW 992.851). Yield: 99% (49.54 mg, 0.05 mmol). ES-MS (CH_3CN/trifluoroacetic acid 1/0.01): m/z 879 (MH^+), 901 $(M + Na)^+$.

***N*-(4-[5,6]Fullereno-C$_{60}$-I$_h$-[1,9-*d*]isoxazol-3′-ylbutyl)-glycine Trifluoroacetic Salt (11b).** $C_{69}F_3H_{13}N_2O_5$ (MW 1006.879). Yield: 99% (50.23 mg, 0.05 mmol). ES-MS (CH_3-CN/trifluoroacetic acid 1/0.01): m/z 893 (MH^+), 915 $(M + Na)^+$.

***N*-(5-[5,6]Fullereno-C$_{60}$-I$_h$-[1,9-*d*]isoxazol-3′-ylpentyl)-glycine Trifluoroacetic Salt (11c).** $C_{70}F_3H_{15}N_2O_5$ (MW 1020.906). Yield: 99% (50.93 mg, 0.05 mmol). ES-MS (CH_3-CN /trifluoroacetic acid 1/0.01): m/z 907 (MH^+), 929 $(M + Na)^+$.

Synthesis of 12−16. In 150 mL of toluene, **11** (0.03 mmol) and paraformaldehyde (18 mg, 0.6 mmol) were suspended and the mixture was heated to reflux for 4 h. After concentration at reduced pressure, the products were purified by chromatography (toluene/ethyl acetate 9/1).

Bisadduct 12. $C_{66}H_{10}N_2O$ (MW 846.828). Yield: 65% (16.63 mg, 0.019 mmol). ^{1}H NMR (400 MHz, CS_2/benzene-d_6): δ 4.95 (dd, H10, $J_{10,10'}$ = 14.9 Hz, $J_{7,10'}$ = 2.8 Hz), 4.74 (d, H7′, $J_{7,7'}$ = 12.3 Hz), 4.32 (dd, H7), 3.80 (dd, H10), 3,51 (m, H6 and H6′), 3.33 (m, H4), 2.85 (m, H4′), 2.31 (m, H5 and H5′).^{13}C NMR (100 MHz, CS_2/benzene-d_6): δ 156.96 (C3), 154.12 (C13), 150.93 (C11), 149.15, 148.97, 148.81 (C12), 148.70, 148.66, 147.91, 147.88, 147.06, 147.02, 146.58, 146.44, 146.25, 146.12, 145.99, 145.85, 145.79, 145.62, 145.47, 145.24, 145.20, 145.03, 144.97, 144.93, 144.92, 144.90, 144.87, 144.62, 144.58, 144.38 (two carbons), 144.37, 143.63, 143.61, 143.52, 143.30, 143.10, 142.99, 142.91, 142.87, 142.66, 142.38, 142.17, 141.53, 141.44, 141.16, 141.08, 140.86, 139.51, 139.12, 138.92, 138.72, 135.49, 134.18, 130.73, 99.31 (C1), 77.02 (C2), 74.10 (C9), 72.00 (C8), 70.12 (C7), 69.71 (C10), 50.74 (C6), 27.68 (C5), 25.26 (C4). UV−vis (cyclohexane): λ_{max} nm 705 (sh), 668 (sh), 647 (sh), 485 (sh), 424, 448, 401 (sh), 325 (sh), 303, 256. ES-MS (toluene/methanol/trifluoroacetic acid 4/1/0.01): m/z 847 (MH^+). Anal. Calcd for $C_{66}H_{10}N_2O$: C, 93.61; H, 1.19; N, 3.31. Found: C, 90.1; H, 1.14; N, 3.18.

Bisadduct 13 (3′,1″-Butano-1″*H*-pyrrolo[3″,4″:10,11]-[5,6]fullereno-C$_{60}$-I$_h$-[1,9-*d*]isoxazole). $C_{67}H_{12}N_2O$ (MW 860.855). Yield: 67% (17.29 mg, 0.020 mmol). ^{1}H NMR (400 MHz, CS_2/benzene-d_6): δ 4.88 (dd, H11, $J_{11,11'}$ = 11.9 Hz, $J_{8,11}$ = 2.5 Hz), 4.31 (dd, H8, $J_{8,8'}$ = 9.1 Hz), 4.00 (d, H8′), 3.39 (m, one H7 proton), 3.24 (d, H11′), 3.12 (m, H4), 2.87 (m, one H7 proton), 2.71 (m, H4′), 2.65 (m, one H5 proton), 2.31 (m, one H5 proton), 2.27 (m, one H8 proton), 2.02 (one H6 proton). ^{13}C NMR (100 MHz, CS_2/benzene-d_6): δ 158.17 (C3), 152.78 (C14), 149.65 (C12), 149.46, 149.17, 148.85, 148.66, 148.16, 147.86, 147.27, 147.09 (C13), 146.96, 146.57, 146.52, 146.45, 146.30, 146.26, 145.99 (two carbons), 145.77, 145.45, 145.17, 145.06, 145.04, 145.02, 144.98, 144.93, 144.82, 144.80, 144.70, 144.62, 144.60, 144.47, 144.20, 143.61, 143.42, 143.35, 143.32, 142.95, 142.79, 142.77, 142.75, 142.48, 142.39, 142.30, 141.53, 141.36, 141.26, 141.10, 140.85, 140.68, 139.88, 139.10, 139.03, 136.70, 135.25, 132.53, 99.24 (C1), 77.31 (C2), 70.75, 69.15 (C10), 65.80 (C11), 65.13 (C8), 50.17 (C7), 32.64, 30.44 (C5), 28.63 (C6), 27.89 (C4). UV−Vis (cyclohexane): λ_{max} nm 706, 671, 642, 519 (sh), 425, 400 (sh), 329 (sh), 257. MALDI-MS: m/z 860 (M^+). Anal. Calcd for $C_{67}H_{12}N_2O$: C, 93.48; H, 1.41; N, 3.25. Found: C, 91.78; H, 1.57; N, 3.06.

Bisadducts 14−16. $C_{68}H_{14}N_2O$ (MW 874.882), three isomers, total yield 87%. The derivative **16** was obtained in very low quantity and was only partially characterized.

Bisadduct 14. Yield: 54% (14.16 mg, 0.016 mmol). ^{1}H NMR (400 MHz, CS_2/benzene-d_6): δ 5.11 (dd, H9, $J_{9,9'}$ = 8.8 Hz, $J_{9,12}$ = 2.7 Hz), 4.11 (dd, H12, $J_{12,12'}$ = 8.5 Hz), 3.17 (d, H9′), 3.13 (d, H12′), 3.09 (m, H8), 2.76 (m, one H4 proton), 2.59 (m, H8′), 2.55 (m, one H4 proton), 2.45 (m, one H6 proton), 1.86 (m, one H5 proton), 1.82 (m, one H6 proton), 1.75 (m, one H5 proton), 1.57 (m, one H7 proton), 1.46 (m, one H7 proton). ^{13}C NMR (100 MHz, CS_2/benzene-d_6): δ 154.39 (C3), 154.28 (C14), 151.47 (C13), 149.32, 149.05, 148.90, 148.77, 148.52, 147.83, 147.47, 147.41, 147.29, 146.92, 146.87, 146.85, 146.59, 146.53, 146.22, 146.01, 145.22, 145.19 (two carbons), 145.15 (two carbons), 145.04, 154.01, 144.98, 144.82, 144.79, 144.75, 144.49, 144.22, 144.15, 144.08, 143.99, 143.93, 143.77, 143.68, 143.14, 143.12, 142.95, 142.70, 142.68, 142.38, 142.31, 142.26, 142.13, 142.76, 141.35, 141.18, 140.70, 139.20, 139.15, 138.12, 137.60, 137.37, 135.70, 98.39 (C1), 77.85 (C2), 71.17 (C10), 69.68 (C11), 66.43 (C9), 63.51 (C12), 53.98 (C8), 29.73 (C5), 27.52 (C7), 25.99 (C4), 25.00 (C6). UV−Vis (cyclohexane): λ_{max} nm 704, 666 (sh), 634 (sh), 488 (sh), 427, 402 (sh), 325 (sh), 255. MALDI-MS: m/z 874 (M^+).

Bisadduct 15. Yield: 31% (8.13 mg, 0.009 mmol). ^{1}H NMR (400 MHz, CS_2/benzene-d_6): δ 4.54 (d, H12′, $J_{12,12'}$ = 11.9 Hz), 4.34 (dd, H9, $J_{9,12}$ = 2.7 Hz), 4.31 (dd, H12), 4.15 (d, H9′, $J_{9,9'}$ = 12.5 Hz), 3.41 (m, H8′), 3.10 (m, H8), 3.02 (m, H4′), 2.60 (m, H4′), 1.69−1.56 (multiplets, the six H5, H6 and H7 protons). ^{13}C NMR (100 MHz, CS_2/benzene-d_6): δ 154.10 (C3), 153.35 (C15), 150.77 (C16), 149.32, 148.94, 148.66, 148.33, 148.20, 148.02, 147.97, 147.80 (C13), 147.76, 147.49, 147.10, 146.71, 146.53, 146.46, 146.37, 146.31, 146.26, 146.15, 145.91, 145.88, 145.86, 145.63, 145.09, 144.95, 144.92, 144.68, 144.50, 144.17, 144.13, 143.17, 143.04 (two carbons), 142.74, 142.67, 142.60, 142.55, 142.50, 142.43, 142.38, 142.18, 142.10, 140.29, 140.00, 139.89, 139.35, 138.88, 138.37, 137.66, 136.04, 135.85, 135.49, 143.82, 131.38 (C14), 123.61, 99.30 (C1), 75.52 (C2), 73.82 (C11), 69.99 (C12), 69.05 (C10), 65.90 (C9), 50.69 (C8), 30.45, 30.35, 27.18, 25.68 (C4). UV−vis (cyclohexane): λ_{max} nm 715, 634, 554 (sh), 470 (sh), 442 (sh), 310 (sh), 258. MALDI-MS: m/z 874 (M^+).

Bisadduct 16. Yield: 2% (0.52 mg, 6×10^{-4} mmol). UV−vis (cyclohexane): λ_{max} nm 668 (sh), 631 (sh), 580 (sh), 493

(sh), 445 (sh), 375 (sh), 315, 258, 240. ES-MS (toluene/methanol/trifluoroacetic acid 4/1/0.01): *m*/*z* 875 (MH^+).

General Reaction with $Mo(CO)_6$. To a solution of bis-adduct (5.8×10^{-3} mmol) in chlorobenzene (5 mL) $Mo(CO)_6$ (2.3 mg, 8.7×10^{-3} mmol) was added. The mixture was heated to reflux for 4 h. After cooling, the product was purified by chromatography (toluene/ethyl acetate 9/1) and precipitated by $CHCl_3$/methanol.

2′*H*-[5,6]Fullereno-C_{60}-I_h-[1,9-*d*]pyrrole-1′(5′*H*)-pentanenitrile 17b. $C_{67}H_{12}N_2$ (MW 844.856). Yield: 21% (1.04 mg, 1.23×10^{-3} mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.42 (s, 4H), 3.16 (t, J = 6.6 Hz, 2H), 2.63 (t, J = 6.5 Hz, 2H), 2.10 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.8, 149.9, 147.2, 146.2, 146.0, 145.3, 145.2, 144.5, 143.0, 142.6, 142.2, 142.0, 141.8, 140.2, 140.1, 136.1, 119.7, 70.5, 67.9, 53.7, 29.7, 23.6, 14.2. ES-MS (toluene/methanol/trifluoroacetic acid 4/1/0.01): *m*/*z* 845 (MH^+).

2′*H*-[5,6]Fullereno-C_{60}-I_h-[1,9-*d*]pyrrole-1′(5′H)-esanenitrile (17c) from 14 or 15. $C_{68}H_{14}N_2$ (MW 858.883). ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.42 (s, 4H), 3.14 (t, J = 7.0 Hz, 2H), 2.50 (t, J = 6.4 Hz, 2H), 2.02 (m, 2H), 1.89 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.8, 146.1, 145.9, 145.3, 144.4, 142.5, 142.1, 141.8, 140.1, 136.1, 119.5, 70.5, 67.9, 54.5, 28.1, 26.9, 25.5, 17.3. ES-MS (toluene/methanol/formic acid 4/1/0.01): *m*/*z* 859 (MH^+).

Synthesis of 5-Aminovaleronitrile (18).[30] Sodium azide (600 mg, 9.25 mmol) was added to a solution of 5-bromovaleronitrile (720 μL, 6.17 mmol) in DMSO (10 mL). After 18 h of stirring at room temperature, 20 mL of water was added, and the solution was extracted by diethyl ether. $C_5H_8N_4$ (MW 124.075). Yield: 99% (764 mg, 6.16 mmol). IR (NaCl): (cm^{-1}) 2240, 1250. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.35 (bt, J = 5.4 Hz, 2H), 2.39 (m, 2H), 1.74 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 119.1, 50.4, 27.8, 22.7, 16.8. Triphenylphosphine (3.24 g, 12.3 mmol) and water (300 μL) were added to the azide (1.5 g, 12.3 mmol) dissolved in THF (12.3 mL). After 18 h at room temperature, the solvent was removed and the residue washed with petroleum ether/diethyl ether 1/1 (50 mL). Ethyl acetate was added to the crude product, and an acid−basic double extraction was performed. $C_5H_{10}N_2$ (MW 98.084). Yield: 99% (1.2 g, 12.2 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.70 (t, J = 6.1 Hz, 2H), 2.33 (t, J = 6.1 Hz, 2H), 1.64 (m, 4H).

Synthesis of Glycine *N*-(5-Cyanopentyl)-1,1-dimethylethyl Ester (19). To a cold solution of **18** (250 mg, 2.55 mmol) and TEA (530 μL, 3.8 mmol) in 5 mL of diethyl ether *tert*-butyl bromoacetate (188 μL, 1.28 mmol) was dropped in 2 h. The mixture was stirred at room temperature for 20 h. The product was purified by chromatography (ethyl acetate). $C_{11}H_{20}N_2O_2$ (MW 212.152). Yield: 43% (115 mg, 0.54 mmol). IR (NaCl): (cm^{-1}) 2260, 1740, 1680. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.28 (s, 2H), 2.63 (t, J = 6.5 Hz, 2H), 2.38 (t, J = 6.8 Hz, 2H), 1.68 (m, 4H), 1.46 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.6, 119.5, 81.2, 51.4, 48.2, 29.6, 28.8, 28.0, 23.0, 16.9.

Synthesis of N−(5-Cyanopentyl)glycine (20). Trifluoroacetic acid (1 mL) was added to a solution of **19** (58 mg, 0.27 mmol) in dichloromethane (3 mL) and the mixture was stirred at room temperature for 6 h. The solvent and the excess of trifluoroacetic acid were removed by evaporation and the product washed four times by toluene. The product was used without further purification. $C_9F_3H_{11}N_2O_4$ (MW 270.083), 72.9 mg, 0.27 mmol.

Synthesis of 2′*H*-[5,6]Fullereno-C_{60}-I_h-[1,9-*d*]pyrrole-1′-(5′*H*)-pentanenitrile (17b). To a solution of C_{60} (100 mg, 0.139 mmol) in toluene (50 mL) were added **20** (72 mg, 0.27 mmol) and paraformaldehyde (12.5 mg, 0.417 mmol). The mixture was heated to reflux for 45 min. The cold solution was washed with a basic solution, the organic layer was dried over anhydrous Na_2SO_4, and the product was purified by chromatography (toluene). The compound was precipitated by dichloromethane/methanol. $C_{67}H_{12}N_2$ (MW 844.856). Yield: 34% (39.43 mg, 0.047 mmol). IR (KBr): (cm^{-1}) 2244, 524. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.42 (s, 4H), 3.17 (t, J = 6.1 Hz, 2H), 2.64 (t, J = 6.8 Hz, 2H), 2.10 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.0, 154.4, 153.6, 150.9, 146.8, 146.2, 146.0, 145.9, 145.3, 144.5, 143.0, 142.5, 142.3, 141.8, 140.1, 136.1, 135.2, 119.9, 70.7, 68.0, 53.6, 30.0, 23.7, 16.9. UV−vis (cyclohexane): λ_{max} nm 700, 462, 430, 403 (sh), 327, 308, 255. ES-MS (toluene/methanol/formic acid 4/1/0.01): *m*/*z* 845 (MH^+).

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Supporting Information Available: Copies of ^{1}H and/or ^{13}C NMR spectra for compounds *N*-hydroxy-4-(phenylmethoxy)-benzenecarboximidoyl chloride, **1a**,**c**, 3,6,9-trioxadecanaldehyde-oxime, *N*-hydroxy-2-[2-(2-methoxy-ethoxy)-ethoxy]ethanimidoyl chloride, **1e**,**f**, **2**, **4**, **5a**−**c**, **6a**−**c**, **7a**−**c**, **8a**−**c**, **9a**−**c**, **17a**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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