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Bisaziridine Tetracarboxylates as Building Blocks in the Stereoselective Synthesis of C_{60}-Fullerene Diads and Dumbbell-like Bis-C_{60}-fullerene Triads

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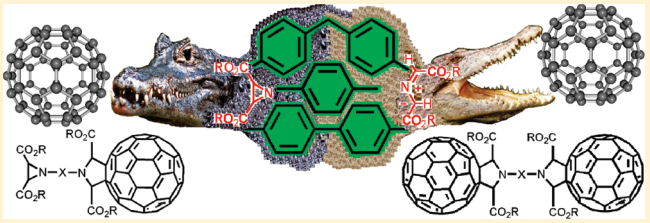
Supporting Information

ABSTRACT: The synthesis of alkoxycarbonyl-substituted bisaziridines with the two aziridine units connected by conjugated *p*-phenylene, partly conjugated 1,1′-biphenyl-4,4′-diyl, and nonconjugated 4,4′-methylenediphenyl linkers was developed. The reaction of azomethine ylides derived from the bisaziridines with fullerene C_{60} was optimized and used for the stereoselective preparation of both the monoadducts (C_{60}—linker—aziridine dicarboxylate), and the dumbbell bisadducts (C_{60}—linker—C_{60}). The reasons for the observed selectivity of the azomethine ylide formation and cycloaddition were theoretically studied at the DFT B3LYP/6-31G(d) level or at the ONIOM B3LYP/6-31G(d):B3LYP/STO-3G level for fullerene-containing molecules.



INTRODUCTION

Dumbbell-like compounds containing two fullerene C_{60} moieties draw attention as candidates for applications in molecular electronics[1] and in the construction of photovoltaic devices.[2] Thus, fullerene-based compounds with fullerenes as anchoring groups have been recently designed and applied as a single-molecule junction for molecular electronic devices. These junctions showed a lower spread in low-bias conductance and increased stretching length before breaking compared to commonly used thiol-based junctions.[1] Significant interest has been also developed in fullerene-containing diads and triads for photovoltaic applications. It is marked that the rates of forward and back electron transfer in fullerene-containing hybride donor—acceptor systems depend on the molecular geometry, i.e., it is possible to modulate these properties by varying the separation or spatial orientation of the donor and acceptor units by means of the appropriate linker.[3] Fullerenes C_{60} are known to form stable monolayers on Au surfaces.[4] This, along with the reported increased stability of bisfullerene junctions,[1] allows us to imagine a possible application of dumbbell-like fullerene molecules as seeds for growing gold nanorods, such as in the published experiments with thiol derivatives.[5] Application of rigid fullerene-capped linkers-seeds would provide a synthesis of nanostructures of predefined architecture.

A number of dumbbell-like fullerene compounds have been previously synthesized by reaction of fullerene, carbonyl compounds, and suitable diamines.[1] Unfortunately, the yields of the products were only about 5—14%, presumably due to the harsh reaction conditions. The described reaction of bisaziridines with fullerene C_{60} resulted in low yields of 5% for bisfullerene-adduct as well.[1b] Extremely low solubility of the synthesized bisadducts was another problem, which could be overcome by the incorporation of long aliphatic chains into the aromatic core of the linker.[1b] These difficulties, along with the increasing interest to dumbbell-like bisfullerene triads,[1b] stimulate the search for other routes for their synthesis. A good methodology for the synthesis of linkers of different geometry and molecular conductance, which can be effectively fastened to fullerene, could contribute to the development of the aforementioned fields of nanoscience.

The Prato reaction, 1,3-dipolar cycloaddition of azomethine-ylides across the [6,6]-juncture of the fullerene core to form fulleropyrrolidine derivatives, is one of the most widely used methods for the construction of fullerene diads and triads.[6] Three methods are mostly used for the generation of azomethine-ylides in this reaction: (1) condensation of carbonyl compounds with α-amino acids followed by decarboxylation and dehydration of the primary products,[2,6,7] (2) condensation of carbonyl compounds with amines followed by imine—ylide tautomerization or dehydration of the primary products,[6e,7l,8] and (3) thermal electrocyclic ring-opening of aziridines.[1b,7a,9] This last approach is less investigated than the other two, but this method can be expected to provide a stereoselective route to fulleropyrrolidine derivatives, because the configuration of the aziridine determines the configuration of the ylide resulting from the ring-opening,[10] while prediction of the configuration of the ylide is rather difficult in the first two cases. Relatively mild conditions for the ring-opening of suitably substituted aziridines can be an additional advantage of the aziridine approach to fulleropyrrolidines.

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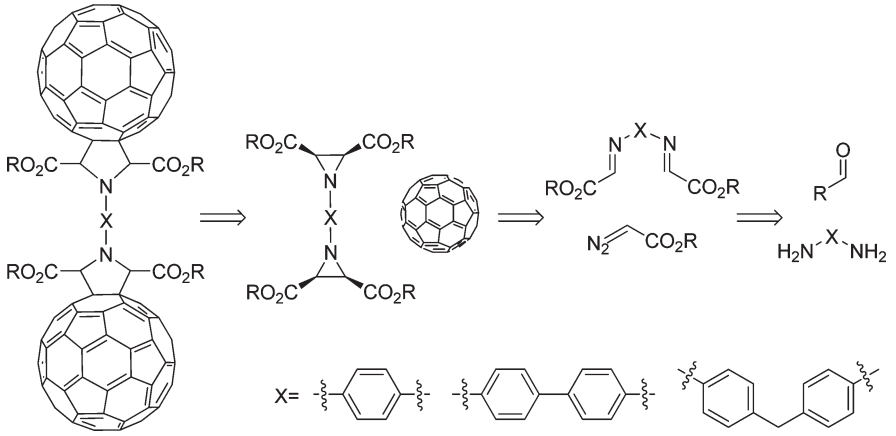
Scheme 1



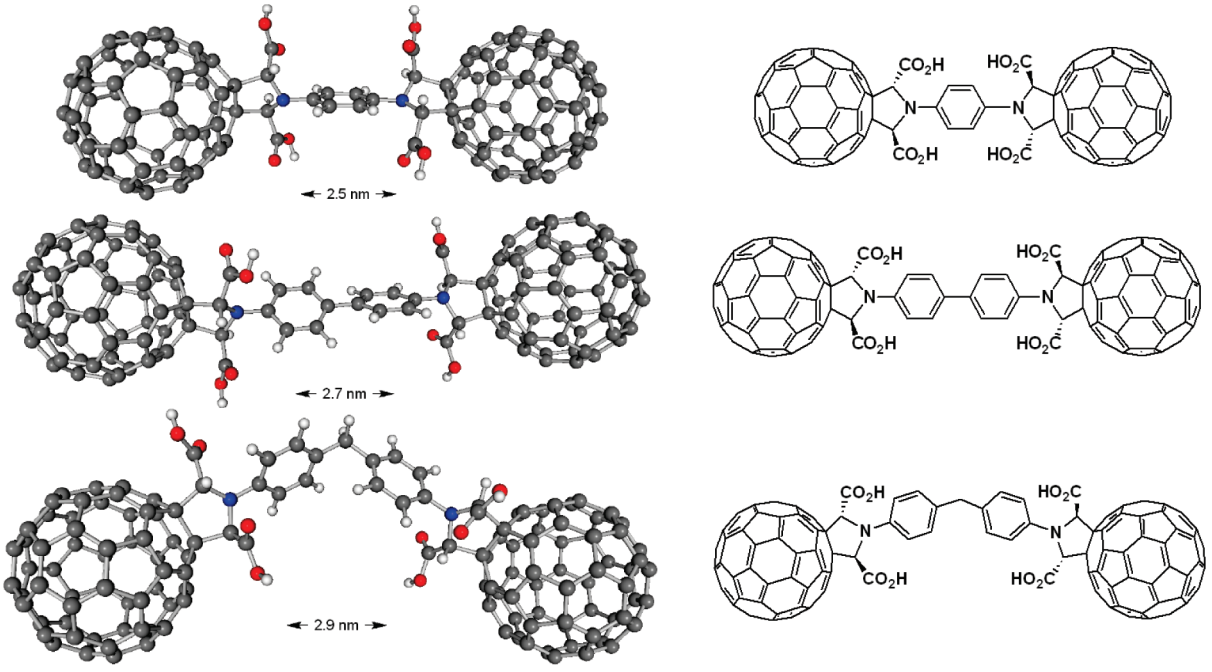


Figure 1. Geometry of some dumbbell-like fullerene ensembles available via the bisaziridine synthetic approach optimized at the DFT ONIOM B3LYP/6-31G(d):B3LYP/STO-3G level.

In the framework of our research concerning the synthesis of heterocycles via N-ylide reactions,[9f,g,11] compounds with two aziridine units connected by different linkers have been developed, which allow the construction of dumbbell-like fullerene ensembles with predefined geometry and variable conjugation. We have chosen conjugated *p*-phenylene, partly conjugated 1,1′-biphenyl-4,4′-diyl, and nonconjugated 4,4′-methylenediphenyl as the linkers that allow the creation of products with linear or bent geometry and with different molecular conductance (Figure 1, Scheme 1).

Varying the substituents on the aziridine ring allows the solubility of the fullerene ensembles to be modified and also provides the additional possibility of modulating their shape. The developed approach is also potentially suitable for the preparation of unsymmetrical fullerene-containing diads using fullerene—bisaziridine monoadducts.

We present here the synthesis and characterization of alkyl bisaziridine tetracarboxylates, the reaction of azomethine ylides generated from them with fullerene C_{60}, and the preparation and characterization of new fullerene-containing diads and dumbbell-like triads.

RESULTS AND DISCUSSION

The target bisaziridines were prepared according to the sequence presented in the retrosynthetic Scheme 1. Freshly prepared aldehyde **1a** from the oxidation of diethyl tartrate with periodic acid[12] was condensed with *p*-phenylene diamine **2a** to give bisimine **3a**. After simple workup, the crude imine was immediately reacted with ethyl diazoacetate **4a** in the presence of a catalytic amount of $BF_3 \cdot OEt_2$ to yield a mixture of the bisaziridines **5a** and **6a** (Table 1, Scheme 2). The bisaziridines

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decompose slowly under the reaction conditions, and a prolonged reaction time in the second step decreases the product yields (Table 1, entries 1−4). The best results were obtained in experiments where a benzene solution of 3 equiv of **1a** was stirred with 1 equiv of **2a** in the presence of anhyd Na_2SO_4 for 0.5 h at rt and then reacting the resulting imine with the catalyst and 2.2 equiv of **4a** in ether for 4 h at rt (Table 1, entry 5), yielding **5a** (55%) and **6a** (27%). The preferred formation of *cis*-aziridines in $BF_3 \cdot OEt_2$-catalyzed reactions of diazo compounds with imines is well documented.[13]

Having found the optimal conditions, we next synthesized a number of *cis,cis*- and *cis,trans*-bisaziridines **5** and **6** (Table 2). Octyl glyoxylate **1b** and octyl diazoacetate **4b**, which are required for the preparation of aziridines **5d**−**f** and **6d**−**f**, were prepared analogously to published procedures.[12,14] The structures of bisaziridines **5a**−**f** and **6a**−**f** were verified by ^1H and ^{13}C NMR and IR spectroscopy, elemental analysis, and HRMS. The ^1H NMR spectra of compounds **5** contain only one set of signals for the protons of the aziridine rings, alkyl chains, and aromatic cores, meaning either a cis,cis or trans,trans configuration of aziridine fragments. The ^1H NMR spectra of compounds **5** show the doublet−doublet satellite signals for the aziridine protons with the $^3J_{HH}$ constant in the range 6.2−7.0 Hz, proving cis,cis-configuration of **5**, after taking into consideration that $^3J_{HH}$ are 0−3 Hz in *trans*-aziridines and 6−7 Hz in *cis*-aziridines.[13b,15] In contrast, the ^1H NMR spectra of compounds **6** contain two sets of signals for the protons of aziridine rings, alkyl chains, and aromatic cores, unambiguously attesting to nonequivalence of the aziridine rings and C_1 symmetry of the molecules, which therefore are *cis,trans*-bisaziridines. Thus, compounds **6a**−**f** show a singlet signal at 3.04−3.11 ppm, which corresponds well to the value of the chemical shift for aziridine protons of *cis,cis*-bisaziridines **5** (3.05−3.12 ppm), and it can thus be attributed to the *cis*-aziridine ring in **6**. The characteristic value of a spin−spin coupling constant of 6.9 Hz found for the satellite signals of *cis*-aziridine protons (at 3.06 ppm) in **6c** provides independent proof. Along with the signal for the *cis*-aziridine rings, a singlet at 3.43−3.50 ppm for the protons of the *trans*-aziridine ring was observed in compounds **6** having the characteristic trans-$^3J_{HH}$ = 2.4 Hz for the satellite signals.

Table 1. Optimization of the Synthesis of Bisaziridines 5a, 6a

			yield, %	
entry	ratio **1a**:**4a**:**2a**	reaction time, h	**5a**	**6a**
1	4:3:1	24; 6	39	–
2	4:2.2:1	24; 6	36	–
3	2.2:2.2:1	24; 12	30	11
4	2.2:2.2:1 ("old" aldehyde)	24; 6	2	–
5	3:2.2:1	0.5; 4	55	27

A further goal was to find optimal conditions for the synthesis of the monoadducts of bisaziridines **5**, **6** to fullerene C_{60}, because the aziridine moiety, remaining in the monoadduct, can also be used as a joining tool for the construction of C_{60}-based hybrid ensembles. The thermally allowed conrotatory opening of one aziridine ring in the bisaziridine **5** leads to the formation of only the S-ylide[10b] ***cis*-A-SY**. Provided no isomerization of the S-ylide ***cis*-A-SY** occurs under the reaction conditions, cycloaddition of this ylide to C_{60} should give the adduct **7** as the sole stereoisomer (Scheme 3).

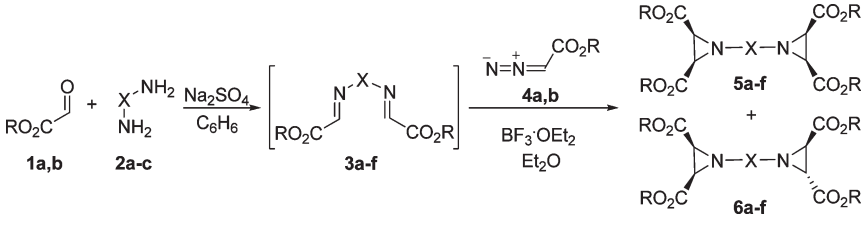
In contrast, the thermally allowed conrotatory opening of one aziridine ring in the bisaziridine **6** can lead to the formation of three ylides: the S-ylide ***trans*-A-SY**, the W-ylide ***cis*-A-WY**, and the U-ylide ***cis*-A-UY** (Scheme 4). The cycloaddition of the W-ylide ***cis*-A-WY** and the U-ylide ***cis*-A-UY** to C_{60} will lead to two conformers of adduct **8**, which can interconvert via the nitrogen inversion. The cycloaddition of the S-ylide ***trans*-A-SY** to C_{60} will lead to the two stereoisomeric adducts **9**, **10**.

To evaluate the possible selectivity of the discussed reactions, we performed DFT B3LYP/6-31G(d) model calculations of energy profiles for transformations of diethyl 1-phenylaziridin-2,3-dicarboxylates ***cis*-** and ***trans*-A** and the corresponding ylides **SY**, **UY**, and **WY** (Figure 2). According to the results obtained, the barriers to the conrotatory opening of the aziridine ring in model compound ***cis*-A**, leading to S-ylide **SY**, and compound ***trans*-A**, leading to U-ylide **UY** and W-ylide **WY**, are very close. The barriers to interconversion of the ylides **SY**, **UY**, and **WY** have the same order of values as the barriers to the ring-opening. The reaction of fullerene with the above-mentioned aziridines will, therefore, be selective only if the barriers to cycloaddition of the ylides to C_{60} are lower than the barriers to interconversion of the ylides. The barriers to cycloaddition of the ylides **SY**, **UY**, and **WY** to C_{60} were computed at the ONIOM B3LYP/6-31G(d):B3LYP/STO-3G level.[16] Earlier we found[9f] for similar systems that the ONIOM simplification for the fullerene moiety, excepting common atoms of fullerene and pyrrolidine rings, is valid. The calculated barrier to cycloaddition of the ylides **SY**, **UY**, and **WY** to C_{60} ($\Delta G^{\ddagger}$ kcal·mol^{-1}) are 20.3, 19.5, 19.2, respectively. The barrier to cycloaddition of the ylide **SY** to ethylene calculated at the B3LYP/6-31G(d) level for comparison equals 22.3 kcal·mol^{-1}. From this data one can conclude that the reaction of

Table 2. Synthesis of Bisaziridines 5 and 6

R	X	**1**	**2**	**4**	yield of **5**, %	yield of **6**, %
Et	1,4-C_6H_4	**1a**	**2a**	**4a**	**5a**, 55	**6a**, 27
Et	4,4′-$(C_6H_4)_2$	**1a**	**2b**	**4a**	**5b**, 24	**6b**, -
Et	4,4′-$(C_6H_4)_2CH_2$	**1a**	**2c**	**4a**	**5c**, 38	**6c**, 20
oct-1-yl	1,4-C_6H_4	**1b**	**2a**	**4b**	**5d**, 61	**6d**, 14
oct-1-yl	4,4′-$(C_6H_4)_2$	**1b**	**2b**	**4b**	**5e**, 38	**6e**, 10
oct-1-yl	4,4′-$(C_6H_4)_2CH_2$	**1b**	**2c**	**4b**	**5f**, 58	**6f**, 25

Scheme 2



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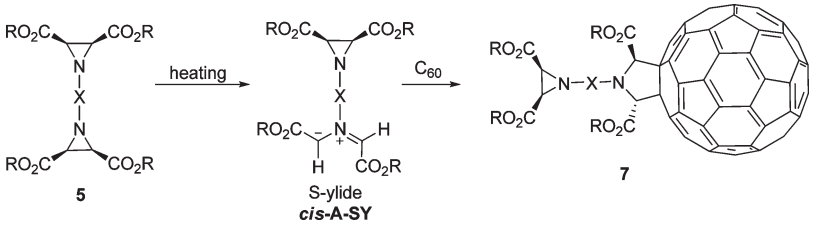
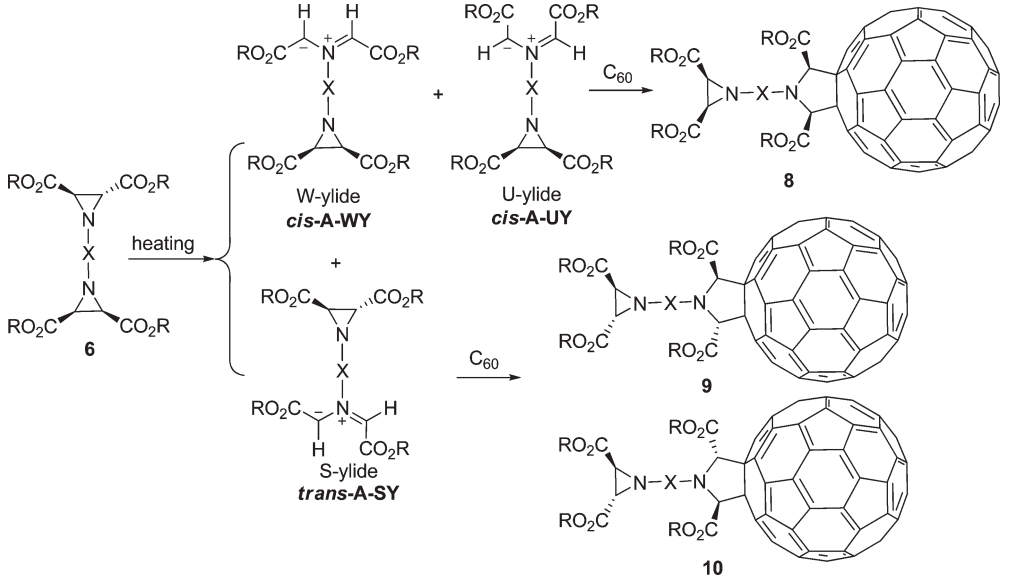
Scheme 3



Scheme 4



bisaziridines **5** in not very harsh conditions will give only one cycloadduct **7**, whereas the reaction of bisaziridines **6** under the same conditions will give a mixture of monoadducts **8**−**10**. After analysis of these computation results, we have chosen bisaziridine **5a** as the best candidate for finding optimal conditions of the synthesis of monoadducts.

The reaction of the bisaziridine **5a** with C_{60} was performed at various temperatures under conventional heating or under microwave irradiation, in *o*-dichlorobenzene (*o*-DCB) or 1-methylnaphthalene (1MN) (Table 3). The conditions of choice are the slow dropwise addition of the *o*-DCB solution of the bisaziridine **5a** to the solution of 3.3 equiv of C_{60} in *o*-DCB at 80 °C followed by stirring the reaction mixture at this temperature for several hours until all the aziridine is consumed. Under these conditions, monoadduct **7a** was isolated in 65% yield. No products were detected at lower temperatures (Table 3, entries 1, 2). Increasing the temperature decreases the yield significantly (Table 3, entries 4−6). Thus, though the reaction proceeded at 100 °C much faster than at 80 °C, the yield of the monoadduct **7a** was only 32%. The soluble polymer of unknown composition was the only product when the reaction was performed at 120 °C. Analogously, only polymerization occurred when the reaction was conducted under microwave irradiation. But the polymerization seems to proceed to a higher degree in this case, as the reaction yielded a substance insoluble in any solvent and swelling in *o*-DCB without solution. The opening of aziridine rings does not occur at low temperatures, while at temperatures higher than 80 °C, further reactions of the aziridine ring in the primary product lead to the formation of bisadducts or polymers. Changing *o*-DCB to 1MN has only a minor effect on the yield. The optimized reaction conditions were used for the synthesis of monoadducts **7a**−**d**,**f** (Table 4).

The ^{1}H NMR spectra of compounds **7a**−**f** contain signals for *cis*-aziridine protons at 3.11−3.18 and signals for the pyrrolidine protons at 6.49−6.60 ppm. The constant $^3J_{HH}$ = 6.7 Hz for the $C_{aziridine}$-2/3 satellite signals in the ^{1}H NMR spectrum of compound **7b** also suggests a cis-configuration of the aziridine fragment. This means that the configuration of the surviving aziridine ring was not changed. The ^{1}H NMR spectra of compounds **7a**−**f** also demonstrate nonequivalence of the alkoxycarbonyl group at the pyrrolidine ring. This then implies C_1 symmetry for the molecules that can be possible only if the configurations of the pyrrolidine and aziridine rings are different, that is the pyrrolidine fragment of **7a**−**f** has trans-configuration. Formation of the trans-adduct in the reaction of *cis*,*cis*-bisaziridines **5** with C_{60} suggests that the cycloaddition reaction of the S-ylide, resulting from thermally allowed conrotatory opening of a *cis*-aziridine ring, proceeds with a higher rate than the isomerization of the formed ylide. Thus, the experimental results agree completely with the model calculations.

The reaction of bisaziridine **6a** with fullerene C_{60} gave predictably three isomeric monoadducts **8** (11%), **9**, and **10** (the last two are inseparable, common yield 34%) (Scheme 4, X = 1,4-C_6H_4, R = Et) under the same conditions. The cis,cis-adduct

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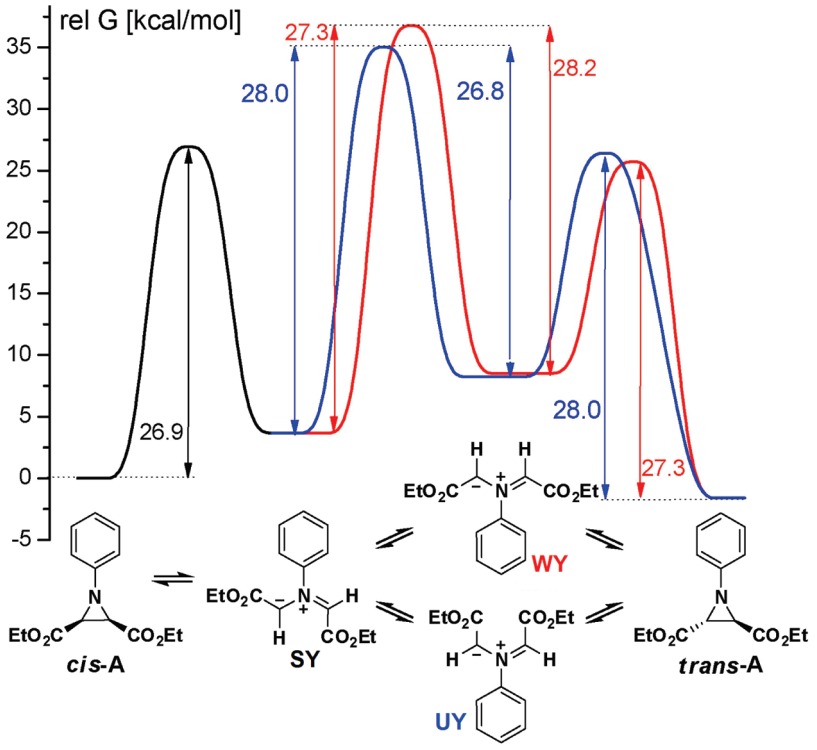

Figure 2. Energy profiles for transformations of diethyl 1-phenylaziridin-2,3-dicarboxylates *cis*- and *trans*-**A** and the corresponding ylides **SY**, **UY**, and **WY**. Relative free energies [kcal·mol^{-1}, 298 K] computed at the DFT B3LYP/6-31G(d) level.

Table 3. Optimization of Monoadduct 7a Synthesis

entry	**5a**: C_{60}	solvent	*T*, °C	time, h	yield, %
1	1: 1.67	*o*-DCB	20	48	no reaction
2	1: 1.67	*o*-DCB	50	10	no reaction
3	1: 1.67	*o*-DCB	mw, 160 W	1	insoluble polymer
4	1:6.7	*o*-DCB	120	5	soluble polymer
5	1:3.3	*o*-DCB	100−110	5	35
6	1:10	*o*-DCB	100−110	4	20
7	1:3.3	*o*-DCB	100	6	32
8	1:3.3	*o*-DCB	80	19	65
9	1:3.3	*o*-DCB	80	31	59
10	1:3.3	*o*-DCB	80	36	53
11	1:3.3	1MN	80	26	59

Table 4. Synthesis of Monoadducts 7a−d,f

5a−d, f $\xrightarrow[o\text{-DCB, }80\ ^\circ C]{C_{60}}$ **7a−d, f**

R	X	**5**	yield of **7**, %
Et	1,4-C_6H_4	**5a**	**7a**, 65
Et	4,4′-$(C_6H_4)_2$	**5b**	**7b**, 50
Et	4,4′-$(C_6H_4)_2CH_2$	**5c**	**7c**, 53
oct-1-yl	1,4-C_6H_4	**5d**	**7d**, 44
oct-1-yl	4,4′-$(C_6H_4)_2CH_2$	**5f**	**7f**, 44

8 possesses C_s symmetry and characteristic signals for the *cis*-aziridine protons at 3.21 ppm, and those for the pyrrolidine protons at 5.80 ppm are visible in its ^{1}H NMR spectrum. The cis, trans-adducts **9** and **10** possess C_2 symmetry and show characteristic signals for the *trans*-aziridine protons at 3.54 ppm and 3.55 ppm, and for the pyrrolidine protons signal at 6.50 ppm. The signal corresponding to the pyrrolidine protons of trans-cycloadducts is significantly shifted downfield with respect to that of cis-cycloadducts, and this corresponds well to literature data.[17] Thus, the reaction of bisaziridine **6a** with fullerene C_{60} leads to the cycloaddition products of S/U/W-ylides, in perfect consistence with the aforementioned calculation results.

Our next task was the optimization of the synthesis of the dumbbell-like fullerene triads. The bisadducts formed in the reaction of bisaziridine **5a** with fullerene C_{60} were almost insoluble in organic solvents and could not be properly characterized, although their formation was detected by TLC analysis. The presence of a carbonyl group was indicated by the intensive bands at 1757, 1735, and 1730 cm^{-1} in the IR spectra of the brown solid isolated by column chromatography from the reaction mixture. Fortunately, the substitution of the ethyl group by an octyl group in the ester moiety of the starting aziridine allowed us to solve this problem of solubility. The reaction of bisaziridines **5d**,**f** with C_{60} in *o*-DCB at 80 °C gave mixtures of the monoadduct **7d** (44%) with the bisadducts **11a**, **12a** (total yield 26%) and of the monoadduct **7f** (44%) with the bisadducts **12a**,**c** (total yield 16%), respectively (Scheme 5).

The bisadducts become the main reaction products at higher temperatures. Thus, the reaction of aziridine **5d** with fullerene C_{60} at 100 °C yielded isomeric trans,trans-bisadducts **11a** and **12a** in 27% and 34% yield, respectively, along with monoadduct **7d** in 31% yield, which means a total conversion of aziridine into fullerene adducts of more than 90% (Scheme 5, Table 5). The reaction of **6d** with C_{60} under the same conditions yielded only cis,trans-bisadduct **13a** (R = oct-1-yl, X = 1,4-C_6H_4) in 32% yield (Scheme 5).

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Scheme 5

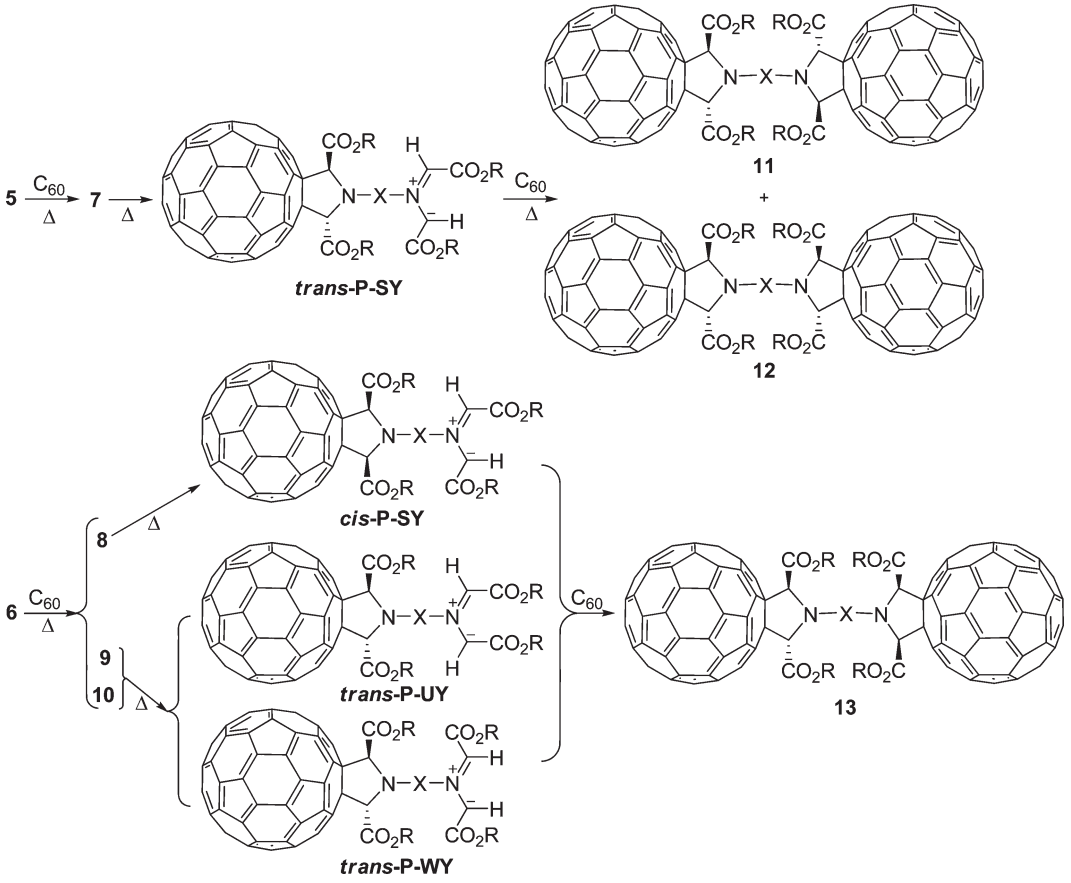

Table 5. Yields of the Products of Reaction the Bisaziridines 5 with Fullerene C_{60} in *o*-DCB at 100 °C

R	X	5	yield of **11**, **12**, %	yield of **7**, %
oct-1-yl	1,4-C_6H_4	**d**	27,[a] **11a**; 34,[a] **12a**	31, **7d**
oct-1-yl	4,4′-$(C_6H_4)_2$	**e**	12,[a] **11b**; 12,[a] **12b**	30, **7e**
oct-1-yl	4,4′-$(C_6H_4)_2$	**e**	33,[a] **11b** + **12b**	30, **7e**
oct-1-yl	4,4′-$(C_6H_4)_2$	**e**	47,[b] **11b** + **12b**	—[b]
oct-1-yl	4,4′-$(C_6H_4)_2CH_2$	**f**	15,[a] **11c**; 16,[a] **12c**	54,[a] **7f**
oct-1-yl	4,4′-$(C_6H_4)_2CH_2$	**f**	56,[b] **11c** + **12c**	—[b]

[a] Reaction time 8 h. [b] Reaction time 20 h.

Whereas the fullerene monoadducts of bisaziridines could be measured by electrospray mass spectrometry using dichloromethane and methanol with formic acid as solvents, ionization of the dumbbell-like fullerene bisadducts could not be achieved by ESI. Field desorption (FD) ionization was, therefore, applied for mass spectrometric detection of these compounds. Under the soft ionization conditions used for field desorption, $M^{+\cdot}$ molecular ions were formed by removal of an electron under exposure to a high voltage (10 kV) without extensive fragmentation.[18] This technique proves to be suitable even for the mass spectrometric characterization of the fullerene bisadducts with molecular weights above 2000 u and represents a promising alternative for such kinds of compounds. Thus, the molecular ion peaks of the fullerene bisadducts **11**, **12**, and **13** were obtained by field desorption mass spectrometry (FD-MS, see Experimental Section and Supporting Information).

The formation of two isomers of the bisadduct from the *cis*,*cis*-aziridine **5** and only one isomer of the bisadduct from the *cis*, *trans*-aziridine **6** is in full accordance with the expected stereochemical outcome of the reactions when taking into account the aforementioned results of the model calculation. Indeed, addition of fullerene C_{60} to the ylide ***trans*-P-SY**, resulting from the thermally allowed conrotatory opening of the *cis*-aziridine ring of the monoadduct **7**, leads to the stereoisomeric bisadducts **11**, **12** (Scheme 5). At the same time, in the reaction of the *cis*,*trans*-aziridine **6**, the primary product **8** gives the ylide ***cis*-P-SY**, whereas the primary products **9**, **10** give the ylide ***trans*-P-UY** and ***trans*-P-WY**. The addition of these ylides to fullerene C_{60}, however, leads to only one bisadduct (bisadduct **13**), the same one from each ylide (Scheme 5).

Hence, already the number of products in each case permits the partial assignment of the stereochemistry of the bisadducts. Additional proof was obtained by comparing proton NMR spectra of the compounds **11a**, **12a**, and **13a**. The ^1H NMR spectrum of compound **13a** contains three singlets for pyrrolidine protons at 5.92, 5.96, and 6.64 ppm and an AB system for the aromatic protons. This unequivocally proves nonequivalence of the pyrrolidine fragments and aromatic protons and suggests C_1 symmetry and cis,trans-configuration of the product. A comparison with the data for the compounds **7a**–**f** allows the assignment of the singlets at 5.92 and 5.96 ppm to the cis-substituted

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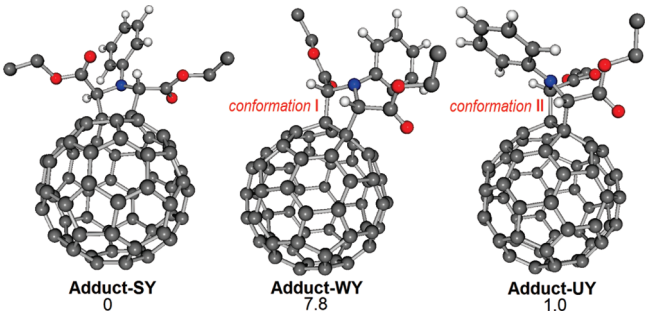


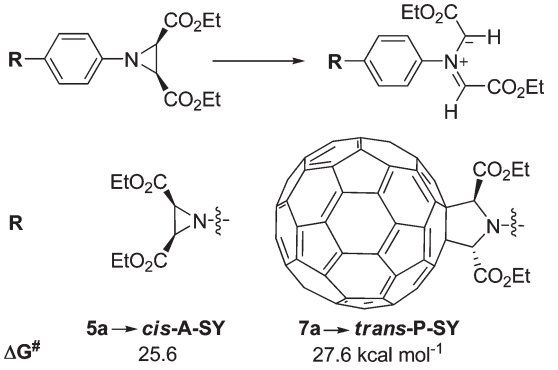
Figure 3. Geometry of the adducts of fullerene C_{60} and ylides **SY**, **UY**, and **WY**, derived from diethyl 1-phenylaziridine-2,3-dicarboxylates *cis*- and *trans*-**A** (see Figure 2), and relative free energies ($\Delta\Delta G$ [kcal·mol^{-1}, 298 K] computed at the DFT ONIOM B3LYP/6-31G(d):B3LYP/STO-3G level. Hydrogen atoms on ethyl groups are omitted for clarity.

pyrrolidine ring, and the singlet at 6.64 ppm to the trans-substituted pyrrolidine ring.

The *cis*-pyrrolidine ring in compound **13a** can be formed by addition to fullerene of the U- or W-ylides that, according to model calculations at the DFT ONIOM B3LYP/6-31G(d):B3LYP/STO-3G level, leads to adducts with different conformations of one of the pyrrolidine rings (**Adduct-WY** and **Adduct-UY**, conformations **I**, **II**, Figure 3). The calculated barrier to cycloaddition of the U- and W-ylides to C_{60} are practically equal (vide supra), but **Adduct-WY** is less stable than **Adduct-UY** by 6.8 kcal·mol^{-1} (Figure 3) and the barrier to transformation of the first to the second via inversion is only 1.5 kcal·mol^{-1}. Therefore, according to the calculations, the *cis*-pyrrolidine ring in all adducts should have conformation **II**, such as in **Adduct-UY**. There are two possible characteristic through-space interactions shown by the 2D ^{1}H-NOESY spectra of the adducts containing the *cis*-pyrrolidine stereochemistry which can be used for distinguishing between conformations of type **I** and **II**. Namely, in conformation **I** an interaction between the pyrrolidine protons (distance 2.5 Å) should be present, while the interaction of these protons and ortho-protons of the Ph ring should be absent; in conformation **II** the contary should be true, that is, the interaction of the pyrrolidine protons with ortho-protons of the Ph ring should be present, while that between the pyrrolidine protons (distance 4.0 Å) should be absent. The analysis of the 2D ^{1}H-NOESY spectrum of compound **13a** (see Supporting Information) shows that the *cis*-pyrrolidine ring of compound **13a** has the conformation of type **II**.

^{1}H NMR spectra of compounds **11a** and **12a** contain a sole singlet for the pyrrolidine protons at 6.91 ppm and singlets for aromatic protons at 7.63 and 7.67 ppm, suggesting high symmetry of the compounds and equivalence of the aromatic protons and pyrrolidine ring protons. This can be true either for a cis,cis- or a trans,trans-configuration, but only one cis,cis-bisadduct can exist, while two trans,trans-bisadducts are possible. As the ^{1}H NMR and ^{13}C NMR spectra of **11a** and **12a** are almost identical, supposition that they constitute cis,cis- and trans,trans-pair seemed to be improbable, while their being a pair of trans, trans-bisadducts seemed to be most possible. The value of 6.91 ppm for the signal of the pyrrolidine protons, which is shifted downfield with respect to the value of 5.92−5.96 ppm in the *cis*-pyrrolidine ring, further supports this assignment. The attempts to determine the relative configuration of the two

Scheme 6



fulleropyrrolidine fragments in the trans,trans-bis-adducts **11** and **12** by recording their ^{1}H NMR spectra using tris[3-(heptafluorpropyl-hydroxymethylene)-D-camphorato]praseodymium as a shift reagent were unsuccessful, as the spectra revealed no difference. Chromatography on a chiral column, however, allowed them to be distinguished. Thus, chromatography of compound **11a** shows two peaks of equal intensity with retention times of 6.3 and 5.9 min, suggesting that **11a** is a *dl*-pair, 1:1 mixture of enantiomers (*S*,*S*,*S*,*S*) and (*R*,*R*,*R*,*R*). There is only one peak, however, with retention time of 7.2 min, in the case of compound **12a**, suggesting that this is the meso-isomer of C_s symmetry. The configuration of bisadducts **11b**,**c** (*dl*-pair) and **12b**,**c** (meso) was established in the same way.

Analogously, the reaction of aziridines **5e**,**f** with C_{60} under the same conditions yielded a pair of isomeric trans,trans-bisadducts **11b**,**c** and **12b**,**c** (Scheme 5, Table 5). The yields are significantly decreased after the chromatographic separation of the trans, trans-bisadducts **11** and **12**. The mixtures of compounds **11b**, **12b** and **11c**, **12c** can be isolated in a larger common yield of 33% (50% based on reacted fullerene C_{60}) and 29% (54% based on reacted fullerene C_{60}), respectively. The corresponding monoadducts **7** were also isolated in all cases, with 30% yield for **7e** and 54% yield for **7f**, when the reaction time was 8 h. A prolonged reaction time of 20 h permits the completion of the reaction of monoadduct with fullerene, yielding the desired isomeric trans, trans-bisadducts in 47% yield (**11b**, **12b**) and 56% yield (**11c**, **12c**, 97% based on consumed C_{60}).

Thus, the synthesized bisaziridines represent the starting material that allows us to direct the reaction with fullerene C_{60} toward formation of monoadduct, bisadduct, or polymer by changing the reaction temperature. The theoretical calculations are in agreement with experimental observations (Scheme 6). The calculated barrier to conrotatory opening of the *cis*-aziridine ring in the bisaziridine **5a** is lower than the corresponding barrier in the monoadduct **7a** by 2 kcal·mol^{-1}. To the best of our knowledge, such selectivity can hardly be achieved by implication of either amino- or imino-based variants of the Prato reaction.

■ CONCLUSIONS

The synthesis of alkoxycarbonyl-substituted bisaziridines with two aziridine units connected by different linkers (conjugated *p*-phenylene, partly conjugated 1,1′-biphenyl-4,4′-diyl, and non-conjugated group 4,4′-methylenediphenyl) was optimized. It was demonstrated that the reaction of the bisaziridines with fullerene C_{60} can be used for selective preparation of both monoadducts and bisadducts in moderate to good yields with a high degree of

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stereocontrol. The reasons for the observed selectivity of the azomethine ylide formation and cycloaddition have been theoretically studied at the DFT B3LYP/6-31G(d) level or at the ONIOM B3LYP/6-31G(d):B3LYP/STO-3G level for fullerene-containing molecules. The developed synthetic approach makes possible the construction of dumbbell-like fullerene ensembles with predefined geometry, variable conjugation, and good solubility in common organic solvents.

EXPERIMENTAL SECTION

General Methods. Melting points were determined on a hot stage microscope and are uncorrected. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were determined in $CDCl_3$ or C_6D_6 with a DPX 300 spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. ESI-HRMS was performed using a 7T-FTICR mass spectrometer equipped with an electrospray ion source applying an electrospray voltage of 4.2 kV and micrOTOF 10223 mass spectrometer. Samples were injected via syringe pump injection. Field desorption (FD) measurements were carried out on a TOF mass spectrometer AccuTOF GCv using an FD emitter with an emitter voltage of 10 kV. The reactions under microwave irradiation at 160 W were carried out in a sealed flask in a Minotavr-2 microwave oven for laboratory experiments. Chiral chromatography was performed on a Chiralpak IA HPLC column (250 mm × 4.6 mm, particle size 5 μm) with a CH_2Cl_2/hexane mixture (50/50) as eluent and a flow of 0.8 mL/min.

General Procedure for the Synthesis of Bisaziridines 5, 6. As a representative example, the synthesis of **diethyl *cis,cis*- and *cis, trans*-1-[4-[2,3-di(ethoxycarbonyl)aziridin-1-yl]phenyl]-2,3-aziridinedicarboxylate 5a, 6a** is described here. A mixture of aldehyde **1a** (306 mg, 3 mmol), amine **2a** (108 mg, 1 mmol), and anhyd Na_2SO_4 (1.0 g) in dry C_6H_6 (25 mL) was stirred at rt for 30 min and filtered, and the solvent was removed in vacuo. The resulting yellowish oil consisting mostly of the imine **3a** was dissolved in dry Et_2O (18 mL). A catalytic amount of $BF_3 \cdot OEt_2$ (2 drops, ca. 14 mg) was added to the imine solution followed by dropwise addition of an ethyl diazoacetate (251 mg, 2.2 mmol) solution in Et_2O (2 mL). The reaction mixture was stirred at rt for 4 h and quenched with Et_3N (4 drops, ca. 0.3 mL) and water (1 mL), the water layer was pipetted off, and the reaction mixture was dried over Na_2SO_4. The desiccant was filtered off, the solvent was removed in vacuo, and the crude product was purified by column chromatography (silica gel, hexane−ethyl acetate), to give bisaziridines **5a** (251 mg, 55%) and **6a** (122 mg, 27%).

Bisaziridine 5a. Colorless crystals: mp 88−91 °C. IR ($CHCl_3$, NaCl): 1736 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.33 (t, J = 7.1 Hz, 12H, CH_3), 3.05 (4H, CH) (satellite signals: 3.05 (dd, $^1J_{CH}$ = 172.3 Hz, $^3J_{HH}$ = 6.5 Hz)), 4.28 (q, J = 7.1 Hz, 8H, CH_2), 6.94 (4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 43.1 (CHN), 61.8 (CH_2), 120.7 (C_{arom}-C), 147.1 (C_{arom}-N), 166.8 (C═O). Anal. Calcd for $C_{22}H_{28}N_2O_8$: C, 58.92; H, 6.29; N, 6.25. Found: C, 58.77; H, 6.25; N, 6.14.

Bisaziridine 6a. Yellow oil. IR ($CHCl_3$, NaCl): 1750 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23 (t, J = 7.3 Hz, 6H, CH_3), 1.34 (t, J = 7.3 Hz, 6H, CH_3), 3.06 (2H, CH), 3.44 (2H, CH), 4.10−4.25 (m, 4H, CH_2), 4.29 (q, J = 7.3 Hz, 4H, CH_2), 6.82 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 6.93 (pseudo d, J = 8.7, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.98 (CH_3), 14.02 (CH_3), 42.1 (CHN), 43.0 (CHN), 61.7 (CH_2), 61.8 (CH_2), 120.42 (C_{arom}-C), 120.44 (C_{arom}-C), 143.4 (C_{arom}-N), 146.4 (C_{arom}-N), 166.7 (C═O), 166.9 (C═O). HR-ESI-MS: 449.1929 (MH^+, $C_{22}H_{29}N_2O_8^+$; calcd 449.1918).

Diethyl *cis,cis*-1-[4′-[2,3-Bis(ethoxycarbonyl)aziridin-1-yl][1,1′-biphenyl]-4-yl]-2,3-aziridinedicarboxylate 5b. Yield: 24% (139 mg from 205 mg of **2b**). Reaction time: 8 h. Yellow oil. IR (KBr): 1730, 1712 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.35 (t, J = 7.3 Hz, 12H, CH_3), 3.12 (4H, CH) (satellite signals: 3.12 (dd, $^1J_{CH}$ = 172.9 Hz, $^3J_{HH}$ = 6.5 Hz), 4.31 (q, J = 7.3 Hz, 8H, CH_2), 7.09 (pseudo d, J = 8.0 Hz, 4H, H_{arom}), 7.45 (pseudo d, J = 8.0 Hz, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ, 14.1 (CH_3), 43.0 (CHN), 61.9 (CH_2), 120.4 (HC_{arom}), 127.5 (HC_{arom}), 136.3 (C_{arom}-C),150.0 (C_{arom}-N), 166.9 (C═O). HR-ESI-MS: 525.2239 (MH^+, $C_{28}H_{33}N_2O_8$; calcd 525.2231), 547.2055 (MNa^+, $C_{28}H_{32}N_2O_8Na^+$; cacld 547.2051.

Diethyl *cis,cis*-1-[4-[[4-[2,3-Bis(ethoxycarbonyl)aziridin-1-yl]-phenyl]methyl]phenyl]-2,3-aziridinedicarboxylate 5c. Yield: 38% (103 mg from 99 mg of **2c**). Reaction time: 3.5 h. Colorless crystals: mp 106−110 °C. IR ($CHCl_3$, NaCl): 1750 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (t, J = 7.1 Hz, 12H, CH_3), 3.07 (4H, CH) (satellite signals: 3.06 dd ($^1J_{CH}$ = 172.6 Hz, $^3J_{HH}$ = 7.0 Hz), 3.88 (2H, CH_2C), 4.30 (q, J = 7.1 Hz, 8H, CH_2O), 6.96 (pseudo d, J = 8.3, 4H, H_{arom}), 7.05 (pseudo d, J = 8.3, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 40.4 (CH_2C), 42.9 (CHN), 61.7 (CH_2O), 120.0 (HC_{arom}), 129.5 (HC_{arom}), 136.7 (C_{arom}-C), 149.0 (C_{arom}-N), 166.9 (C═O). HR-ESI-MS: 539.2388 (MH^+, $C_{29}H_{35}N_2O_8^+$; calcd 539.2388), 561.2221 (MNa^+, $C_{29}H_{34}N_2O_8Na^+$; calcd 561.2207).

Diethyl *cis,trans*-1-[4-[[4-[2,3-Bis(ethoxycarbonyl)aziridin-1-yl]-phenyl]methyl]phenyl]-2,3-aziridinedicarboxylate 6c. Yield: 20% (54 mg from 99 mg of **2c**). Reaction time: 3.5 h. Yellow oil. IR ($CHCl_3$, NaCl): 1750 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 1.19 (t, J = 7.3 Hz, 6H, CH_3), 1.33 (t, J = 7.3 Hz, 6H, CH_3), 3.06 (2H, CH) (satellite signals: 3.06 (dd, $^1J_{CH}$ = 172.5 Hz, $^3J_{HH}$ = 6.9 Hz), 3.45 (2H, CH) (satellite signals: 3.45 (dd, $^1J_{CH}$ = 181.3 Hz, $^3J_{HH}$ = 2.4 Hz), 3.85 (2H, CH_2C), 4.15 (q, J = 7.3 Hz, 4H, CH_2O), 4.28 (q, J = 7.3 Hz, 4H, CH_2O), 6.82 (pseudo d, J = 8.0 Hz, 2H, H_{arom}), 6.93 (pseudo d, J = 8.0 Hz, 2H, H_{arom}), 7.00−7.15 m (4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 14.1 (CH_3), 40.4 (CH_2C), 42.1 (CHN), 42.9 (CHN), 61.72 (CH_2O), 61.74 (CH_2O), 119.8 (HC_{arom}), 120.0 (HC_{arom}), 129.3 (HC_{arom}), 129.5 (HC_{arom}), 136.0 (C_{arom}-C), 137.0 (C_{arom}-C), 145.3 (C_{arom}-N), 148.9 (C_{arom}-N), 166.9 (C═O), 167.0 (C═O). HR-ESI-MS: 539.2393 (MH^+, $C_{29}H_{35}N_2O_8^+$; calcd 539.2388), 561.2222 (MNa^+, $C_{29}H_{34}N_2O_8Na^+$; calcd 561.2207).

Dioctyl *cis,cis*-1-[4-[2,3-Bis(octyloxycarbonyl)aziridin-1-yl]-phenyl]-2,3-aziridinedicarboxylate 5d. Yield 61% (120 mg from 27 mg of **2a**). Reaction time: 4 h. Colorless crystals: mp 33−35 °C. IR (KBr): 1754, 1734 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.90 (t, J = 6.7 Hz, 12H, CH_3), 1.20−1.45 (m, 40H, CH_2), 1.60−1.80 (m, 8H, CH_2CH_2O), 3.05 (4H, CH), 4.21 (t, J = 6.9 Hz, 8H, CH_2), 6.94 (4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0 (CH_3), 22.6, 25.7, 28.4, 29.12, 29.15, 31.7 (CH_2), 43.1 (CHN), 66.0 (CH_2O), 120.7 (C_{arom}-C), 147.1 (C_{arom}-N), 166.9 (C═O). Anal. Calcd for $C_{46}H_{76}N_2O_8$: C, 70.37; H, 9.76; N, 3.57. Found: C, 70.44; H, 9.74; N, 3.66.

Dioctyl *cis,trans*-1-[4-[2,3-Bis(octyloxycarbonyl)aziridin-1-yl]phenyl]-2,3-aziridinedicarboxylate 6d. Yield 14% (28 mg from 27 mg of **2a**). Reaction time: 4 h. Yellow oil. IR (KBr): 1730 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85−0.95 (m, 12H, CH_3), 1.20−1.45 (m, 40H, CH_2), 1.55−1.64 (m, 4H, CH_2CH_2O), 1.64−1.75 (m, 4H, CH_2CH_2O), 3.04 (2H, CH), 3.43 (2H, CH), 4.00−4.20 (m, 4H, CH_2O), 4.20 (t, J = 6.9 Hz, 4H, CH_2O), 6.80 (pseudo d, J = 8.4 Hz, 2H, H_{arom}), 6.91 (pseudo d, J = 8.4 Hz, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.6, 25.7, 28.36, 28.43, 29.10, 29.13, 29.17, 31.72, 31.75 (CH_2), 42.2, 43.1 (CHN), 65.99, 66.02 (CH_2O), 120.4, 120.5 (C_{arom}-C), 143.5, 146.6 (C_{arom}-N), 166.91, 166.96 (C═O). HR-ESI-MS: 785.5660 (MH^+, $C_{46}H_{77}N_2O_8^+$; calcd 785.5674), 807.5497 (MNa^+, $C_{46}H_{76}N_2O_8Na^+$; 807.5494).

Dioctyl *cis,cis*-1-[4′-[2,3-Bis(octyloxycarbonyl)aziridin-1-yl]-[1,1′-biphenyl]-4-yl]-2,3-aziridinedicarboxylate 5e. Yield 38% (82 mg from 46 mg of **2b**). Reaction time: 4 h. Oily crystals. IR (KBr): 1748 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.90 (t, J = 6.5 Hz, 12H, CH_3), 1.20−1.45 (m, 40H, CH_2), 1.60−1.80 (m, 8H, CH_2CH_2O), 3.12 (4H, CH) (satellite signals: 3.12 (dd, $^1J_{CH}$ = 172.1 Hz, $^3J_{HH}$ = 6.5 Hz), 4.23 (t, J = 6.9 Hz, 8H, CH_2), 7.09 (pseudo d, J = 8.7 Hz, 4H, H_{arom}), 7.45

(pseudo d, J = 8.7 Hz, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.6, 25.8, 28.4, 29.15, 29.17, 31.8 (CH_2), 43.1 (CHN), 66.1 (CH_2O), 120.4, 127.5 (HC_{arom}), 136.3 (C_{arom}-C), 150.1 (C_{arom}-N), 166.9 (C═O). HR-ESI-MS: 861.5985 (MH^+, $C_{52}H_{80}N_2O_8^+$; calcd 861.5987), 883.5809 (MNa^+, $C_{52}H_{80}N_2O_8Na^+$; calcd 883.5807).

Dioctyl *cis,trans*-1-[4′-[2,3-Bis(octyloxycarbonyl)aziridin-1-yl][1,1′-biphenyl]-4-yl]-2,3-aziridinedicarboxylate 6e. Yield 10% (21 mg from 46 mg of **2b**). Reaction time: 4 h. Yellow oil. IR (KBr): 1740 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.80−0.95 (m, 12H, CH_3), 1.20−1.45 (m, 40H, CH_2), 1.50−1.65 (m, 4H, CH_2CH_2O), 1.65−1.80 (m, 4H, CH_2CH_2O), 3.11 (2H, CH), 3.50 (2H, CH), 4.05−4.25 (m, 4H, CH_2), 4.24 (t, J = 6.9 Hz, 4H, CH_2,), 6.95 (pseudo d, J = 8.4 Hz, 2H, H_{arom}), 7.08 (pseudo d, J = 8.4 Hz, 2H, H_{arom}), 7.35−7.50 (m, 4H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.6, 25.74, 25.78, 28.38, 28.47, 29.11, 29.16, 31.73, 31.76 (CH_2), 42.2, 43.1 (CHN), 66.1 (CH_2O), 120.1, 120.3, 127.3, 127.5 (HC_{arom}), 135.6(C_{arom}-C), 136.5 (C_{arom}-C), 146.5 (C_{arom}-N), 149.9 (C_{arom}-N), 166.97, 167.03 (C═O). HR-ESI-MS: 861.5989 (MH^+, $C_{52}H_{81}N_2O_8^+$; calcd 861.5987), 883.5826 (MNa^+, $C_{52}H_{80}N_2O_8Na^+$; calcd 883.5807), 899.5565 (MK^+, $C_{52}H_{80}N_2O_8K^+$; calcd 899.5546).

Dioctyl *cis,cis*-1-[4-[[4-[2,3-Bis(octyloxycarbonyl)aziridin-1-yl]phenyl]methyl]phenyl]-2,3-aziridinedicarboxylate 5f. Yield 58% (125 mg from 50 mg of **2c**). Reaction time: 4 h. Yellow oil. IR (KBr): 1757, 1735 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, J = 6.5 Hz, 12H, CH_3), 1.20−1.45 (m, 40H, CH_2), 1.60−1.75 (m, 8H, CH_2CH_2O), 3.06 (4H, CH) (satellite signals: 3.06 (dd, $^1J_{CH}$ = 172.5 Hz, $^3J_{HH}$ = 6.2 Hz), 3.87 (2H, CH_2C), 4.21 (t, J = 6.5 Hz, 8H, CH_2), 6.95 (pseudo d, J = 8.0 Hz, 4H, H_{arom}), 7.04 (pseudo d, J = 8.0 Hz, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0 (CH_3), 22.6, 25.8, 28.4, 29.14, 29.17, 31.7 (CH_2), 40.4 (CH_2Ar), 43.0 (CHN), 66.0 (CH_2O), 120.1, 129.5 (HC_{arom}), 136.7 (C_{arom}-C), 149.1 (C_{arom}-N), 167.0 (C═O). HR-ESI-MS. 875.6134 (MH^+, $C_{53}H_{83}N_2O_8$; calcd 875.6144).

Dioctyl *cis,trans*-1-[4-[[4-[2,3-Bis(octyloxycarbonyl)aziridin-1-yl]phenyl]methyl]phenyl]-2,3-aziridinedicarboxylate 6f. Yield 25% (55 mg from 50 mg of **2c**). Reaction time: 4 h. Yellow oil. IR (KBr): 1738 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.80−1.00 (m, 12H, CH_3), 1.20−1.45 (m, 40H, CH_2), 1.55−1.65 (m, 4H, CH_2CH_2O), 1.65−1.80 (m, 4H, CH_2CH_2O), 3.06 (2H, CH), 3.44 (2H, CH), 3.86 (2H, CH_2C), 4.00−4.20 (m, 4H, CH_2O), 4.21 (t, J = 6.9 Hz, 4H, CH_2O), 6.81 (pseudo d, J = 8.3 Hz, 2H, H_{arom}), 6.94 (pseudo d, J = 8.3 Hz, 2H, H_{arom}), 7.01 (pseudo d, J = 8.5 Hz, 2H, H_{arom}), 7.04 (pseudo d, J = 8.5 Hz, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0 (CH_3), 22.6, 25.71, 25.73, 28.3, 28.4, 29.08, 29.11, 29.15, 31.7 (CH_2), 40.4 (CH_2Ar), 42.1, 43.0 (CHN), 65.9, 66.0 (CH_2O), 119.8, 120.0, 129.3, 129.5 (HC_{arom}), 135.9, 136.9 (C_{arom}-C), 145.4, 149.0 (C_{arom}-N), 167.0, 167.1 (C═O). HR-ESI-MS. 875.6148 (MH^+, $C_{53}H_{83}N_2O_8$; calcd 875.6144).

General Procedure for the Synthesis of Monoadducts 7−10. As a representative example, the synthesis of **7a** is described here. A solution of bisziridine **5a** (13 mg, 0.03 mmol) in *o*-DCB (1−2 mL) was added dropwise very slowly (during 4−7 h) to a stirred solution of C_{60} (72 mg, 1 mmol) in *o*-DCB (3−4 mL) at 80 °C, and the heating was continued until the aziridine disappeared (TLC). In this case, it took 19 h of overall heating. The reaction mixture was separated by column chromatography (silica gel, benzene), which yielded monoadduct **7a** (22 mg) in 65% yield along with 50 mg of unreacted C_{60}.

Compound 7a. Yield: 65%. Brown solid. IR ($CHCl_3$, NaCl): 1736(C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.18 (t, J = 7.1 Hz, 6H, CH_3), 1.39 (t, J = 7.1 Hz, 6H, CH_3), 3.18 (2H, CH_{az}), 4.15−4.30 (m, 4H, CH_2O), 4.34 (q, J = 7.1 Hz, 4H, CH_2O), 6.50 (2H, CH_{pyr}), 7.17 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 7.29 (pseudo d, J = 8.7 Hz, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.17, 14.21 (CH_3), 43.1, 43.2 (C_{az}), 61.9 (CH_2O), 71.1 (C_{pyr}), 74.5 (HC_{pyr}), 120.0, 121.1 (HC_{arom}), 136.2, 136.9, 139.7, 140.2, 141.77, 141.82, 141.90, 141.95, 142.17, 142.23, 142.7, 142.8, 143.08, 143.13, 144.5, 144.6, 145.3, 145.4, 145.60, 145.64, 145.67, 145.8, 146.1, 146.4, 146.5, 147.5, 150.4, 153.2 (C_{sp2}), 166.98, 167.00, 170.1 (C═O). HR-ESI-MS: 1169.1923 (MH^+, $C_{82}H_{29}N_2O_8$; calcd: 1169.1918).

Compound 8. Yield from **6a**: 11% (4 mg from 13 mg of **6a**). Reaction time: 36 h. Brown solid. IR (KBr): 1739 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.18 (t, J = 7.2 Hz, 6H, CH_3), 1.39 (t, J = 7.1 Hz, 6H, CH_3), 3.21 (2H, CH_{az}), 4.25 (q, J = 7.1 Hz, 4H, CH_2O), 4.35 (q, J = 7.2 Hz, 4H, CH_2O), 5.80 (2H, CH_{pyr}), 7.20 (pseudo d, J = 8.7, 2H, H_{arom}), 7.63 (pseudo d, J = 8.7 Hz, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.18, 14.20 (CH_3), 43.1 (C_{az}), 61.92, 61.94 (CH_2O), 67.2 (C_{pyr}), 71.3 (HC_{pyr}), 121.0, 124.1 (HC_{arom}), 135.3, 137.7, 140.0, 141.80, 141.88, 141.96, 141.99, 142.21, 142.24, 142.74, 142.76, 143.1, 144.4, 144.6, 145.3, 145.4, 145.5, 145.6, 145.8, 145.9, 146.11, 146.13, 146.3, 146.5, 147.5, 148.0, 150.6, 152.6, (C_{sp2}), 166.9, 168.5 (C═O). HR-ESI-MS: 1169.1914 (MH^+, $C_{82}H_{29}N_2O_8^+$; calcd 1169.1918), 1191.1729 (MNa^+, $C_{82}H_{28}N_2O_8Na^+$; calcd 1191.1738).

Compounds 9 + 10. Yield from **6a**: 34% (12 mg from 13 mg of **6a**). Reaction time: 36 h. Brown solid. ^1H NMR ($CDCl_3$ + C_6D_6), 300 MHz): δ 1.18 (t, J = 7.1 Hz,12H, CH_3), 1.26 (t, J = 7.2 Hz, 6H, CH_3), 1.29 (t, J = 7.2 Hz, 6H, CH_3), 3.546 (2H, CH_{az}), 3.551 (2H, CH_{az}), 4.15−4.35 (m, 16H, CH_2O), 6.50 (4H, CH_{pyr}), 7.04 (pseudo d, J = 8.6 Hz, 2H, H_{arom}), 7.06 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 7.27 (pseudo d, J = 8.7 Hz, 4H, H_{arom}). HR-ESI-MS: 1169.1916 (MH^+, $C_{82}H_{29}N_2O_8^+$; calcd 1169.1918).

Compound 7b. Yield: 50% (19 mg from 16 mg of **5b**). Reaction time: 75 h. Brown solid. IR (KBr): 1753 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.20 (t, J = 6.9 Hz, 6H, CH_3), 1.38 (t, J = 7.3 Hz, 6H, CH_3), 3.17 (2H, CH_{az}) (satellite signals: 3.17 (dd, $^1J_{CH}$ = 172.4 Hz, $^3J_{HH}$ = 6.7 Hz), 4.20−4.40 (m, 4H, CH_2O), 4.35 (q, J = 7.3 Hz, 4H, CH_2O), 6.59 (2H, CH_{pyr}), 7.16 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 7.39 (pseudo d, J = 8.4 Hz, 2H, H_{arom}), 7.59 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 7.67 (pseudo d, J = 8.4 Hz, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 14.2 (CH_3), 43.1 (C_{az}), 61.90, 61.92 (CH_2O), 71.0 (C_{pyr}), 74.4 (HC_{pyr}), 119.2, 120.5, 127.4, 127.8 (HC_{arom}), 134.2, 136.2, 136.4, 136.9, 139.6, 140.2, 141.75, 141.81, 141.90, 141.94, 142.16, 142.23, 142.7, 142.8, 143.1, 144.49, 144.55, 144.60, 145.3, 145.4, 145.60, 145.64, 145.66, 145.8, 146.1, 146.39, 146.44, 147.5, 149.9, 150.4, 153.2 (C_{sp2}), 166.9, 170.1 (C═O). HRMS: 1245.2226 (MH^+, $C_{88}H_{33}N_2O_8^+$; calcd 1245.2231), 1267.2042 (MNa^+, $C_{88}H_{32}N_2O_8Na^+$; 1267.2051).

Compound 7c. Yield: 53% (20 mg from 16 mg of **5c**). Reaction time: 36 h. Brown solid. IR (KBr): 1756 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.16 (t, J = 7.3 Hz, 6H, CH_3), 1.36 (t, J = 6.9 Hz, 6H, CH_3), 3.12 (2H, CH_{az}), 3.98 (2H, CH_2Ar), 4.20−4.40 (m, 4H, CH_2O), 4.31 (q, J = 6.9 Hz, 4H, CH_2O), 6.52 (2H, CH_{pyr}), 7.01 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 7.15 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 7.2−7.4 (m, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.14, 14.16 (CH_3), 40.5 (CH_2Ar), 43.0 (C_{az}), 61.8 (CH_2O), 71.1 (C_{pyr}), 74.4 (HC_{pyr}), 119.0, 120.1, 129.7, 129.9 (HC_{arom}), 134.9, 136.2, 136.9, 137.1, 139.6, 140.2, 141.78, 141.81, 141.92, 141.94, 142.17, 142.23, 142.7, 142.8, 143.1, 143.5, 144.5, 144.6, 145.3, 145.4, 145.63, 145.69, 145.71, 145.76, 146.1, 146.40, 146.44, 147.5, 149.0, 150.5, 153.3 (C_{sp2}), 167.0, 170.2 (C═O). HR-ESI-MS: 1259.2384 (MH^+, $C_{89}H_{35}N_2O_8^+$; calcd 1259.2388), 1276.2657 (MNH_4^+, $C_{89}H_{38}N_3O_8^+$; calcd 1276.2653), 1281.2207 (MNa^+, $C_{89}H_{34}N_2O_8Na^+$; 1281.2207).

Compound 7d. Yield: 44% (19 mg from 23 mg of **5d**). Brown solid. IR (KBr): 1753, 1730 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.86 (t, J = 6.7 Hz, 6H, CH_3), 0.92 (t, J = 6.9 Hz, 6H, CH_3), 1.15−1.50 (m, 40H, CH_2), 1.50−1.65 (m, 4H, CH_2CH_2O), 1.65−1.80 (m, 4H, CH_2-CH_2O), 3.17 (2H, CH_{az}), 4.10−4.20 (m, 4H, CH_2O), 4.25 (t, J = 6.9 Hz, 4H, CH_2O), 6.51 (2H, CH_{pyr}), 7.15 (pseudo d, J = 8.7 Hz, 2H, H_{arom}), 7.27 (pseudo d, J = 8.7 Hz, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.6, 25.8, 25.9, 28.49, 28.51, 29.10, 29.16, 29.17, 29.22, 31.73, 31.79 (CH_2), 43.1, 43.3 (C_{az}), 66.1 (CH_2O), 71.1 (C_{pyr}),

74.6 (HC_{pyr}), 120.0, 121.1 (HC_{arom}), 136.2, 136.9, 139.7, 140.2, 141.75, 141.79, 141.90, 141.93, 142.16, 142.22, 142.7, 142.8, 143.1, 144.5, 144.6, 145.3, 145.4, 145.60, 145.62, 145.64, 145.70, 145.75, 146.1, 146.40, 146.45, 147.5, 150.4, 153.2 (C_{sp2}), 167.03, 167.04, 170.2 (C═O). HR-ESI-MS: 1505.5681 (MH^+, $C_{106}H_{77}N_2O_8^+$; calcd 1505.5674).

Compound 7e. Yield: 30% (13 mg). (**7e** was obtained as a byproduct when **5e** (23 mg, 0.026 mmol) was heated with C_{60} (72 mg, 0.1 mmol) in *o*-DCB at 100 °C for 8 h). Brown solid. IR (KBr): 1728 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 0.84 (t, J = 6.7 Hz, 6H, CH_3), 0.92 (t, J = 6.4 Hz, 6H, CH_3), 1.15−1.50 (m, 40H, CH_2), 1.50−1.65 (m, 4H, CH_2CH_2O), 1.65−1.80 (m, 4H, CH_2CH_2O), 3.16 (2H, CH_{az}), 4.10−4.30 (m, 4H, CH_2O), 4.26 (t, J = 7.0 Hz, 4H, CH_2O), 6.60 (2H, CH_{pyr}), 7.15 (pseudo d, J = 8.4 Hz, 2H, H_{arom}), 7.38 (pseudo d, J = 8.5 Hz, 2H, H_{arom}), 7.58 (pseudo d, J = 8.4 Hz, 2H, H_{arom}), 7.66 (pseudo d, J = 8.5 Hz, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.62, 22.65, 25.8, 25.9, 28.5, 28.6, 29.13, 29.15, 29.18, 29.22, 31.7, 31.8 (CH_2), 43.1 (C_{az}), 66.1 (CH_2O), 71.1 (C_{pyr}), 74.6 (HC_{pyr}), 119.2, 120.5, 127.4, 127.8 (HC_{arom}), 134.2, 136.2, 136.4, 136.9, 139.7, 140.2, 141.8, 141.9, 142.0, 142.18, 142.25, 142.7, 142.8, 143.1, 144.51, 144.57, 144.63, 145.3, 145.4, 145.62, 145.64, 145.67, 145.71, 145.79, 146.2, 146.4, 146.5, 147.5, 150.0, 150.5, 153.3 (C_{sp2}), 167.0, 170.3 (C═O). HR-ESI-MS: 1603.5821 (MNa^+, $C_{112}H_{80}N_2O_8Na^+$; 1603.5807).

Compound 7f. Yield: 44% (15 mg from 19 mg of **5f**). Brown solid. IR (KBr): 1755, 1735 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.8−0.95 (m, 12H, CH_3), 1.15−1.45 (m, 40H, CH_2), 1.50−1.65 (m, 4H, CH_2CH_2O), 1.65−1.80 (m, 4H, CH_2CH_2O), 3.11 (2H, CH_{az}), 3.97 (2H, CH_2Ar), 4.15−4.25 (m, 4H, CH_2O), 4.23 (t, J = 7.3 Hz, 4H, CH_2O), 6.54 (2H, CH_{pyr}), 7.01 (pseudo d, J = 8.0 Hz, 2H, H_{arom}), 7.16 (pseudo d, J = 8.0 Hz, 2H, H_{arom}), 7.20−7.30 (m, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.07, 14.10, 22.62, 22.64, 25.8, 25.9, 28.47, 28.50, 29.09, 29.15, 29.19, 31.7, 31.8 (CH_2), 40.5 (CH_2Ar)), 43.1 (C_{az}), 66.0 (CH_2O), 71.1 (C_{pyr}), 74.5 (HC_{pyr}), 118.9, 120.1, 129.7, 129.8 (HC_{arom}), 134.7, 136.2, 136.8, 136.9, 139.7, 140.1, 141.77, 141.79, 141.92, 142.15, 142.22, 142.7, 142.8, 143.1, 143.5, 144.49, 144.55, 145.29, 145.35, 145.60, 145.65, 145.70, 146.1, 146.39, 146.43, 147.5, 149.1, 150.6 (C_{sp2}), 153.3, 167.1, 170.3 (C═O). HR-ESI-MS: 1617.5962 (MNa^+, $C_{113}H_{82}N_2O_8Na^+$; 1617.5964).

General Procedure for Synthesis of Bisadducts 11−13. As a representative example, the synthesis of bisadducts **11a**, **12a** is described here. A solution of aziridine **5d** (20 mg, 0.026 mmol) in *o*-DCB (2 mL) was added dropwise very slowly (during 7−8 h) to a stirred solution of C_{60} (72 mg, 1 mmol) in *o*-DCB (3 mL) at 100 °C, and the heating was continued for an additional 1 h. The reaction mixture was separated by column chromatography (silica gel, benzene−petroleum ether) to yield bisadducts **11a** (16 mg) and **12a** (20 mg) in 27% and 34% yield, respectively, along with 12 mg (31%) of monoadduct **7d** and 40 mg of unreacted C_{60}.

Compound 11a. IR (KBr): 1757, 1730 (C═O). Brown solid. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.92 (t, J = 6.9 Hz, 12H, CH_3), 1.10−1.40 (m, 40H, CH_2), 1.40−1.60 (m, 8H, CH_2CH_2O), 4.16 (t, J = 6.5 Hz, 8H, CH_2O), 6.91 (4H, CH_{pyr}), 7.63 (4H, H_{arom}). ^{13}C NMR (C_6D_6, 75 MHz): δ 14.5 (CH_3), 23.2, 26.5, 29.1, 29.6, 29.8, 32.3 (CH_2), 66.1 (CH_2O), 72.0 (C_{pyr}), 75.2 (HC_{pyr}), 121.0, (HC_{arom}), 136.8, 137.5, 140.2, 140.6, 141.1, 142.2, 142.31, 142.37, 142.45, 142.51, 142.57, 143.1, 143.2, 143.3, 143.6, 144.9, 145. 0, 145.6, 145.7, 145.98, 146.03, 146.2, 146.36, 146.38, 146.44, 146.75, 146.83, 147.8, 151.6, 154.1 (C_{sp2}), 170.3 (C═O). FD-MS: 2224.6 (M^+, $C_{166}H_{76}N_2O_8^+$; calcd 2224.6).

Compound 12a. Brown solid. IR (KBr): 1730 (C═O).^{1}H NMR (C_6D_6, 300 MHz): δ 0.91 (t, J = 6.9 Hz, 12H, CH_3), 1.10−1.60 (m, 48H, CH_2), 4.0−4.3 (m, 8H, CH_2O), 6.91 (4H, CH_{pyr}), 7.67 (4H, H_{arom}). ^{13}C NMR (C_6D_6, 75 MHz): δ 14.4 (CH_3), 23.1, 26.4, 29.0, 29.6, 29.7, 30.2 (CH_2), 66.0 (CH_2O), 71.9 (C_{pyr}), 75.4 (HC_{pyr}), 121.3, (HC_{arom}), 136.8, 137.5, 140.1, 140.6, 141.3, 142.1, 142.2, 142.3, 142.38, 142.44, 142.5, 143.0, 143.1, 143.2, 143.5, 144.8, 144.9, 145.56, 145.60, 145.92, 145.96, 146.1, 146.3, 146.4, 146.7, 146.8, 147.7, 151.5, 154.0 (C_{sp2}), 170.3 (C═O). FD-MS: 2224.6 (M^+, $C_{166}H_{76}N_2O_8^+$; calcd 2224.6).

Compound 13a. Yield from **6d**: 32% (23 mg from 25 mg of **6d**). Brown solid. IR (KBr): 1755, 1732 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J = 6.5 Hz, 12H, CH_3), 1.20−1.40 (m, 40H, CH_2), 1.50−1.80 (m, 8H, CH_2CH_2O), 4.10−4.40 (m, 8H, CH_2O), 5.92 (1H, CH_{pyr}), 5.96 (1H, CH_{pyr}), 6.64 (2H, CH_{pyr}), 7.47 (pseudo d, J = 8.4 Hz, 2H, H_{arom}), 7.76 (pseudo d, J = 8.4 Hz, 2H, H_{arom}). ^{13}C NMR (C_6D_6, 75 MHz): δ 14.5 (CH_3), 23.2, 26.41, 28.99, 29.07, 29.56, 29.63, 29.70, 29.72, 29.75, 32.24, 32.27 (CH_2), 66.1, 66.2 (CH_2O), 71.98, 72.05, 72.13 (C_{pyr}), 75.3, 77.1, 77.5 (HC_{pyr}), 121.0, 123.7, (HC_{arom}), 135.8, 136.8, 137.5, 138.4, 140.1, 140.4, 140.6, 140.7, 142.15, 142.19, 142.28, 142.34, 142.38, 142.43, 142.50, 142.56, 142.93, 143.07, 143.11, 143.17, 143.52, 143.55, 143.59, 144.62, 144.81, 144.85, 144.94, 144.96, 145.61, 145.66, 145.67, 145.93, 145.97, 146.01, 146.11, 146.20, 146.32, 146.36, 146.39, 146.44, 146.50, 146.70, 146.75, 146.83, 147.75, 147.79, 151.5, 151.74, 151.75, 153.50, 153.53, 154.1 (C_{sp2}), 168.86, 168.91, 170.3 (C═O). FD-MS: 2224.6 (M^+, $C_{166}H_{76}N_2O_8^+$; calcd 2224.6).

Compound 11b. Brown solid. Yield: 12% (7 mg from 22.5 mg of **5e**). IR (KBr): 1740 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.86 (t, J = 6.5 Hz, 12H, CH_3), 1.10−1.40 (m, 40H, CH_2), 1.50−1.70 (m, 8H, CH_2CH_2O), 4.10−4.30 (m, 8H, CH_2O), 6.624 (4H, CH_{pyr}), 7.42 (pseudo d, J = 8.3 Hz, 4H, H_{arom}), 7.76 (pseudo d, J = 8.3 Hz, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.7, 26.0, 28.6, 29.15, 29.19 31.8 (CH_2), 66.2 (CH_2O), 71.1 (C_{pyr}), 74.6 (HC_{pyr}), 119.2, (HC_{arom}), 127.7, 134.4, 136.3, 136.9, 139.7, 140.2, 141.8, 141.95, 141.98, 142.19, 142.26, 142.7, 142.8, 143.2, 144.46, 144.53, 144.58, 145.3, 145.4, 145.64, 145.69, 145.74, 145.8, 146.2, 146.4, 146.5, 147.5, 150.5, 153.3 (C_{sp2}), 170.4 (C═O). FD-MS: 2300.6 (M^+, $C_{172}H_{80}N_2O_8^+$; calcd 2300.6).

Compound 12b. Brown solid. Yield: 12% (7 mg from 22.5 mg of **5e**).IR (KBr): 1735 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 0.86 (t, J = 6.5 Hz, 12H, CH_3), 1.10−1.40 (m, 40H, CH_2), 1.50−1.70 (m, 8H, CH_2CH_2O), 4.10−4.30 (m, 8H, CH_2O), 6.623 (4H, CH_{pyr}), 7.44 (pseudo d, J = 8.3 Hz, 4H, H_{arom}), 7.78 (pseudo d, J = 8.3 Hz, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.7, 26.0, 28.6, 29.14, 29.17, 31.7 (CH_2), 66.1 (CH_2O), 71.1 (C_{pyr}), 74.6 (HC_{pyr}), 119.2, (HC_{arom}), 127.7, 134.4, 136.3, 136.9, 139.7, 140.2, 141.8, 141.95, 141.97, 142.19, 142.26, 142.7, 142. 8, 143.2, 144.47, 144.53, 144.59, 145.3, 145.4, 145.64, 145.66, 145.69, 145.7, 145.8, 146.2, 146.4, 146.5, 147.5, 150.5, 153.3 (C_{sp2}), 170.4 (C═O). FD-MS: 2300.6 (M^+, $C_{172}H_{80}N_2O_8^+$; calcd 2300.6).

Compounds 11b + 12b. Reaction time: 20 h. Common yield: 47% (28 mg from 19 mg of **5e**).

Compound 11c. Brown solid. Yield: 16% (10 mg from 23 mg of **5f**). IR (KBr), cm^{-1}: 1757, 1735 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J = 6.6 Hz, 12H, CH_3), 1.15−1.40 (m, 40H, CH_2), 1.50−1.70 (m, 8H, CH_2CH_2O), 4.07 (2H, CH_2Ar), 4.15−4.30 (m, 8H, CH_2O), 6.586 (4H, CH_{pyr}), 7.30 (pseudo d, J = 10.1 Hz, 4H, H_{arom}), 7.34 (pseudo d, J = 10.1 Hz, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.7, 26.0, 28.6, 29.15, 29.19, 31.8 (CH_2), 40.5 (CH_2Ar), 66.1 (CH_2O), 71.1 (C_{pyr}), 74.5 (HC_{pyr}), 118.9, (HC_{arom}), 130.1, 134.9, 136.3, 136.9, 139.7, 140.2, 141.78, 141.82, 141.9, 142.17, 142.24, 142.70, 142.77, 143.1, 143.5, 144.5, 144.6, 145.3, 145.4, 145.6, 145.7, 145.8, 146.1, 146.41, 146.45, 147.5, 150.6, 153.3 (C_{sp2}), 170.4 (C═O). FD-MS: 2314.7 (M^+, $C_{173}H_{82}N_2O_8^+$; calcd 2314.6).

Compound 12c. Brown solid. Yield: 15% (9 mg from 23 mg of **5f**). IR (KBr), cm^{-1}: 1757, 1734 (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J = 6.7 Hz, 12H, CH_3), 1.15−1.45 (m, 40H, CH_2), 1.50−1.70 (m, 8H, CH_2CH_2O), 4.07 (2H, CH_2Ar), 4.15−4.35 (m, 8H, CH_2O), 6.589 (4H, CH_{pyr}), 7.20−7.40 (m, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 22.7, 26.0, 28.6, 29.16, 29.19, 31.8 (CH_2), 40.4 (CH_2Ar), 66.1 (CH_2O), 71.1 (C_{pyr}), 74.5 (HC_{pyr}), 118.9, (HC_{arom}),

130.1, 134.9, 136.3, 136.9, 139.7, 140.2, 141.79, 141.82, 141.9, 142.17, 142.24, 142.70, 142.78, 143.1, 143.5, 144.5, 144.6, 145.3, 145.4, 145.6, 145.7, 145.8, 146.1, 146.41, 146.45, 147.52, 150.6, 153.3 (C_{sp2}), 170.4 (C═O). FD-MS: 2314.6 (M^+, $C_{173}H_{82}N_2O_8^+$; calcd 2314.6).

Compounds 11c + 12c. Reaction time: 20 h. Common yield: 56% (34 mg from 23 mg of **5e**).

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for all new compounds, the 2D-^{1}H-NOESY spectrum of compound **13a**, and mass spectra of compounds **7**−**13a**. Computation details: Energies of the reactants, transition states, and their Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Martin, C. A.; Ding, D.; Sørensen, J. K.; Bjørnholm, T.; van Ruitenbeek, J. M.; van der Zant, H. S. J. *J. Am. Chem. Soc.* **2008**, *130*, 13198. (b) Sørensen, J. K.; Fock, J.; Pedersen, A. H.; Jennum, K.; Bechgaard, K.; Kilså, K.; Geskin, V.; Cornil, J.; Bjørnholm, T.; Nielsen, M. B. *J. Org. Chem.* **2011**, *76*, 245.

(2) Van der Pol, C.; Bryce, M. R.; Wielopolski, M.; Atienza-Castellanos, C.; Guldi, D. M.; Filippone, S.; Martín, N. *J. Org. Chem.* **2007**, *72*, 6662.

(3) (a) Guldi, D. M.; Luo, C.; Prato, M.; Troisi, A.; Zerbetto, F.; Scheloske, M.; Dietel, E.; Bauer, W.; Hirsch, A. *J. Am. Chem. Soc.* **2001**, *123*, 9166. (b) Imahori, H.; Tkachenko, N. V.; Vehmanen, V.; Tamaki, K.; Lemmetyinen, H.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 1750.

(4) (a) Yoshimoto, S.; Narita, R.; Tsutsumi, E.; Matsumoto, M.; Itaya, K.; Ito, O.; Fujiwara, K.; Murata, Y.; Komatsu, K. *Langmuir* **2002**, *18*, 8518. (b) Uemura, S.; Samori, P.; Kunitake, M.; Hirayama, C.; Rabe, J. P. *J. Mater. Chem.* **2002**, *12*, 3366.

(5) Jain, T.; Westerlund, F.; Johnson, E.; Moth-Pulsen, K.; Bjørnholm, T. *ACS Nano* **2009**, *3*, 828.

(6) (a) Prato, M. *Acc. Chem. Res.* **1998**, *31*, 519.(b) Hirsch, A.; Brettreich, M.; Wudl, F. *Fullerenes: Chemistry and Reactions*; Wiley-VCH: Weinhem, Germany, 2005. (c) Langa, F., Nierengarten, J.-F., Ed. *Fullerenes: Principles and Applications*; Royal Society of Chemistry: London, 2007. (d) Kramer, C. N., Ed. *Fullerene Research Advances*; Nova Science: Hauppauge, NY, 2007. (e) Kharisov, B. I.; Kharissova, O. V.; Gomez, M. J.; Mendez, U. O. *Ind. Eng. Chem. Res.* **2009**, *48*, 545.

(7) (a) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798. (b) Thomas, K. G.; Biju, V.; George, M. V.; Guldi, D. M.; Kamat, P. V. *J. Phys. Chem. A* **1998**, *102*, 5341. (c) Zheng, D. G.; Lia, C.-W.; Li, Y.-L. *Synth. Commun.* **1998**, *28*, 2007. (d) Shi, Z.; Jin, J.; Li, Y.; Guo, Z.; Wang, S.; Jiang, L.; Zhu, D. *New J. Chem.* **2001**, *25*, 670. (e) Conti, F.; Corvaja, C.; Maggini, M.; Scorrano, G.; Ceroni, P.; Paolucci, F.; Roffia, S. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3518. (f) Hua, J. L.; Ding, F.; Meng, F. S.; Tian, H. *Chin. Chem. Lett.* **2004**, *15*, 1373. (g) Hua, J.; Meng, F.; Ding, F.; Li, F.; Tian, H. *J. Mater. Chem.* **2004**, *14*, 1849. (h) Gu, T.; Whitesell, J. K.; Fox, M. A. *J. Org. Chem.* **2004**, *69*, 4075. (i) Enes, R. F.; Tomé, A. C.; Cavaleiro, J. A. S.; Amoratti, R.; Fumo, M. G.; Pedulli, G. F.; Valgimigli, L. *Chem.—Eur. J.* **2006**, *12*, 4646. (j) de la Escosura, A.; Martnez-Daz, M. V.; Guldi, D. M.; Torres, T. *J. Am. Chem. Soc.* **2006**, *128*, 4112. (k) Zhou, Z.; Schuster, D. I.; Wilson, S. R. *J. Org. Chem.* **2006**, *71*, 1545. (l) Troshin, P. A.; Peregudov, A. S.; Troyanov, S. I.; Lyubovskaya, R. N. *Russ. Chem. Bull.* **2008**, *57*, 887.

(8) (a) Kawamura, Y. *Int. J. Modern Phys. B* **2003**, *17*, 1910. (b) Wu, S.-H.; Sun, W.-Q.; Zhang, D.-W.; Shu, L.-H.; Wu, H.-M.; Xu, J.-F.; Lao, X.-F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1733.

(9) (a) Bianco, A.; Gasparrini, F.; Maggini, M.; Misiti, D.; Polese, A.; Prato, M.; Scorrano, G.; Toniolo, C.; Villani, C. *J. Am. Chem. Soc.* **1997**, *119*, 7550. (b) Schergna, S.; Ros, T. D.; Linda, P.; Ebert, C.; Gardossi, L.; Prato, M. *Tetrahedron Lett.* **1998**, *39*, 7791. (c) Gasparrini, F.; Misiti, D.; Negra, F. D.; Maggini, M.; Scorrano, G.; Villani, C. *Tetrahedron.* **2001**, *57*, 6997. (d) Bianco, A.; Maggini, M.; Nogarole, M.; Scorrano, G. *Eur. J. Org. Chem.* **2006**, 2934. (e) Brunetti, F. G.; Herrero, M. A.; Muñoz, J. d. M.; Giordani, S.; Díaz-Ortiz, A.; Filippone, S.; Ruaro, G.; Meneghetti, M.; Prato, M.; Vázquez, E. *J. Am. Chem. Soc.* **2007**, *129*, 14580. (f) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Konev, A. S.; Yufit, D. S.; Selivanov, S. I.; Frauendorf, H. *J. Org. Chem.* **2010**, *75*, 5211. (g) Khlebnikov, A. F.; Novikov, M. S.; Golovkina, M. V.; Petrovskii, P. P.; Konev, A. S.; Yufit, D. S.; Stoeckli-Evans, H. *Org. Biomol. Chem.* **2011**, *9*, 3886.

(10) (a) *Synthetic Application of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Padwa, A., Pearson, W. H., Eds.; John Wiley & Sons: New York, 2002. (b) Tsuge, O.; Kanemasa, S. *Adv. Heterocycl. Chem.* **1989**, *45*, 231.

(11) (a) Khlebnikov, A. F.; Novikov, M. S.; Kostikov, R. R. *Russ. Chem. Rev.* **2005**, *74*, 171. (b) Khlebnikov, A. F.; Novikov, M. S.; Kostikov, R. R.; Kopf, J. *Russ. J. Org. Chem.* **2005**, *41*, 1341. (c) Voznyi, I. V.; Novikov, M. S.; Khlebnikov, A. F. *Synlett* **2005**, 1006. (d) Konev, A. S.; Novikov, M. S.; Khlebnikov, A. F. *Tetrahedron Lett.* **2005**, *46*, 8337. (e) Khlebnikov, A. F.; Novikov, M. S.; Amer, A. A.; Kostikov, R. R.; Magull, J.; Vidovic, D. *Russ. J. Org. Chem.* **2006**, *42*, 515. (f) Voznyi, I. V.; Novikov, M. S.; Khlebnikov, A. F.; Kostikov, R. R. *Russ. J. Org. Chem.* **2006**, *42*, 689. (g) Shinkevich, E. Yu.; Novikov, M. S.; Khlebnikov, A. F. *Synthesis* **2007**, *2*, 225. (i) Novikov, M. S.; Amer, A. A.; Khlebnikov, A. F. *Tetrahedron Lett.* **2006**, *47*, 639. (j) Konev, A. S.; Novikov, M. S.; Khlebnikov, A. F. *Russ. J. Org. Chem.* **2007**, *43*, 286. (k) Khlebnikov, A. F.; Novikov, M. S.; Dolgikh, S. A.; Magull, J. *ARKIVOC (Gainesville, FL, U. S.)* **2008**, 94. (l) Kadina, A. P.; Novikov, M. S.; Khlebnikov, A. F.; Magull, J. *Chem. Heterocycl. Compd.* **2008**, *44*, 576. (m) Konev, A. S.; Khlebnikov, A. F. *Collect. Czech. Chem. Commun.* **2008**, 1553. (n) Shinkevich, E. Y.; Abbaspour Tehrani, K.; Khlebnikov, A. F.; Novikov, M. S. *Tetrahedron* **2008**, *64*, 7524. (o) Khistiaev, K. A.; Novikov, M. S.; Khlebnikov, A. F.; Magull, J. *Tetrahedron Lett.* **2008**, *49*, 1237. (p) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Magull, J.; Ringe, A. *Org. Lett.* **2009**, *11*, 979. (q) Khlebnikov, V. A.; Novikov, M. S.; Khlebnikov, A. F.; Rostovskii, N. V. *Tetrahedron Lett.* **2009**, *50*, 6509. (r) Khlebnikov, A. F.; Novikov, M. S. *Russ. J. Gen. Chem.* **2010**, *80*, 1652. (s) Kobylianskii, I. J.; Novikov, M. S.; Khlebnikov, A. F. *J. Fluorine Chem.* **2011**, *132*, 175. (t) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Stoeckli-Evans, H. *J. Org. Chem.* **2011**, *76*, 5384.

(12) Kelly, T. R.; Schmidt, T. E.; Haggerty, J. G. *Synthesis* **1972**, 544.

(13) (a) Casarrubious, L.; Pérez, J. A.; Brookhart, M.; Templeton, J. L. *J. Org. Chem.* **1996**, *61*, 8358. (b) Rasmussen, K. G.; Jørgensen, R. G. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1287. (c) Akiyama, T.; Ogi, S.; Fuchibe, K. *Tetrahedron Lett.* **2003**, *44*, 4011.

(14) Searle, N. E. US 2490714, 1949; *Chem. Abstr.* **1950**.

(15) (a) De Kimpe, N.; Verhé, R.; Buyck, L.; Schamp, N. *J. Org. Chem.* **1980**, *45*, 5319. (b) Chervin, I. I.; Fomichev, A. A.; Moskalenko, A. S.; Zaichenko, N. L.; Aliev, A. E.; Prosyanik, A. V.; Voznesenskii, V. N.; Kostyanovskii, R. G. *Russ. Chem. Bull.* **1988**, *37*, 972.

(16) (a) Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 19357. (b) Dapprich, S.; Komáromi, I.; Byu, K. S.; Morokuma, K.; Frisch, M. J. *J. Mol. Struct. (THEOCHEM)* **1999**, *461*−*462*, 1.

(17) (a) Vedejs, E.; Grissom, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 3238. (b) Kuznetsov, M. A.; Ushkov, A. V.; Selivanov, S. I.; Pan'kova, A. S.; Linden, A. *Russ. J. Org. Chem.* **2009**, *45*, 1200.

(18) de Hoffmann, E.; Stroobant, V. *Mass Spectrometry Principles and Applications*, 2nd ed.; John Wiley & Sons: New York, 2002.