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Hydrolysis Rate of Functionalized Fullerenes Bearing Alkoxysilanes: A Comparative Study

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Soluble fulleropyrrolidines bearing a trialkoxysilyl functionality (methoxy, ethoxy, butoxy, and isopropoxy) have been prepared and characterized. The hydrolysis rate constant for each fulleropyrrolidine was measured with ^{1}H NMR spectroscopy by following the disappearance of selected resonances of the fullerene substrate under the conditions (HCl/H_2O/THF) used for the preparation of fullerene-doped sol–gel glasses. It has been found that fulleropyrrolidine **1**, bearing the trimethoxysilyl group, hydrolyzes faster than substrates **2**–**7** and should be the reagent of choice to minimize aggregation of the fullerene spheroid in sol–gel glassy matrices. The triethoxysilyl derivative **2**, our benchmark fulleropyrrolidine for incorporation in sol–gel glasses, has the second fastest hydrolysis rate.

Introduction

[60]Fullerene and its derivatives are among the most efficient materials for optical limiting known to date, operating on the basis of a reverse saturable absorption mechanism.[1] They display a ground-state absorption extending from the UV region of the spectrum to almost the entire visible region that triggers an efficient pumping to excited states. These states could be either the first singlet or the lowest energy, triplet excited states. From these states, further photons can be absorbed with absorption cross-sections that are larger than that of the ground state.[2]

In order to develop practical fullerene-based optical limiters, one must face a number of complicated issues related to the operational conditions of the device. These issues include fullerene aggregation, nonlinear scattering and refraction, thermo-optical effects, and high-energy laser damage to the fullerene or to its hosting medium must also be considered. To limit these phenomena, a series of functionalized fullerenes bearing a trialkoxysilyl group for the covalent bonding to silica networks of hybrid organic/inorganic sol–gel glasses[3–11] have been introduced, although other approaches have been reported.[12–14] Our benchmark derivative, triethoxysilyl fulleropyrrolidine **2**,[3,15] and other fulleropyrrolidines that exhibit the common feature of a covalently linked silicon alkoxide end group,[3] are fairly soluble in the polar solvents (HCl/H_2O/THF) employed for sol–gel processing and bind to the silica network, thus preventing the formation of fullerene aggregates that would have detrimental effects on the optical behavior and quality of the samples. However, the presence of residual linear scattering, likely due to structural inhomogeneities, somehow affected the measurements of the optical-limiting properties on thick glassy slabs,[3] despite the fact that the covalent linking of the fullerene derivatives to the silica matrix should have avoided the formation of clusters.

It is reasonable to assume that acid-catalyzed hydrolysis of fulleropyrrolidine-alkoxysilane groups would play an important role during sol–gel processing of the hosting glassy matrix because a low hydrolysis rate would translate into aggregation and clustering of the fullerene component in the matrix. In order to avoid these unfavorable phenomena during the sol–gel process, the silicon alkoxide functionality on the fullerene should hydrolyze and condense at a rate comparable to that of the tetraalkoxysilane reagent [tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS)] commonly employed to prepare sol–gel matrices. To this aim, a series of soluble fulleropyrrolidines, bearing a trialkoxysilyl group, have been prepared and characterized in this work, where the alkoxysilyl functionality varied from methoxy, ethoxy, butoxy, and isopropoxy (Scheme 1). The hydrolysis rate constant for each fulleropyrrolidine was measured under the conditions employed in the sol–gel process by ^{1}H NMR spectroscopy. The influence of the different alkoxysilane moieties on the hydrolysis rate constants is discussed, and the results compared with those obtained for TEOS and TMOS. With regard to established results,[3–6] this comparative kinetic study sets, on a quantitative basis, the different reactivities towards hydrolysis of a series of

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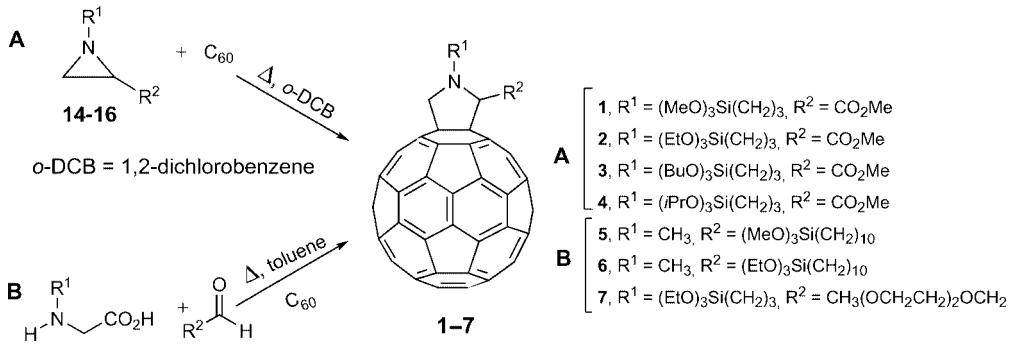


Scheme 1. Fulleropyrrolidines studied.

fulleropyrrolidine-alkoxysilanes, in view of the optimization of the optical-limiting properties of [60]fullerenes through an improvement of the optical quality of sol–gel materials.

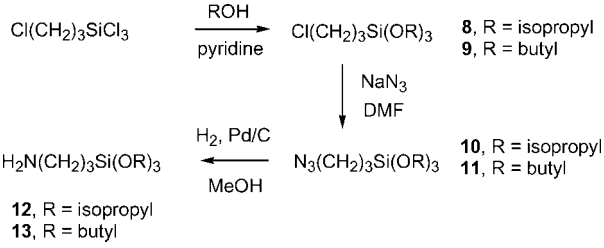
Results and Discussion

Synthesis

Two synthetic strategies have been employed to prepare fulleropyrrolidines **1**–**7** considered in this work. Both pathways, illustrated in Scheme 1, are based on the well-established 1,3-dipolar cycloaddition reaction of azomethine ylides to [60]fullerene.[16,17]

Compounds **1**–**4** have the trialkoxysilyl group attached to the pyrrolidine nitrogen through a propyl spacer. They were prepared by thermal ring-opening, in the presence of [60]fullerene, of suitably functionalized aziridines substituted at the 2-position with a methoxycarbonyl group.[16] The aziridines were in turn synthesized starting from methyl 2,3-dibromopropanoate and a proper 3-(trialkoxysilyl)propan-1-amine.[15] 3-(Triisopropoxysilyl)propan-1-amine (**12**) and 3-(tributoxysilyl)propan-1-amine (**13**) were synthesized in three steps starting from trichloro(3-chloropropyl)silane and the appropriate alcohol, as illustrated in Scheme 2.

The decarboxylation route to the azomethine ylides was used for the preparation of compounds **5**–**7**.[14] This is a more flexible method than that for compounds **1**–**4** since it allows for the location of the trialkoxysilyl group either on the amino acid residue (compound **7**) or on the aldehyde reagent (compounds **5** and **6**) and tolerates the presence of



Scheme 2. Synthesis of 3-(trialkoxysilyl)propan-1-amines **12** and **13**.

other functional groups, such as solubilizing groups. Pyrrolidine **7**, which contains a triethylene glycol (TEG) chain at the 2-position of the five-membered ring, displays a higher solubility in tetrahydrofuran (THF) than **5** and **6** (Table 1). The solubility of compounds **1**–**7** was measured in THF – a good solvent for our fulleropyrrolidine-alkoxysilanes that is also compatible with water and the alcohols employed for the sol–gel synthesis. Interestingly, the solubility increases from **1** to **4** as the number of carbon atoms and the size of the alkoxysilane increases. In particular, compound **4**, with a triisopropoxysilyl group, is the most soluble.

Hydrolysis Rate Determination

The knowledge of the hydrolysis rate constants of alkoxysilane derivatives is of fundamental importance for the development of kinetic models that elucidate the sol–gel

Table 1. Solubility and kinetic data for fulleropyrrolidine-alkoxysilanes **1**–**7**.[a]

	R^1	R^2	Solubility in THF [mg/mL]	$k_{obsd.}$ [s^{-1}]
1[b]	$(MeO)_3Si(CH_2)_3$	CO_2Me	29	$(3.14\pm0.29)\times10^{-4}$
2[b]	$(EtO)_3Si(CH_2)_3$	CO_2Me	43[d]	$(7.34\pm0.09)\times10^{-5}$
3[b]	$(BuO)_3Si(CH_2)_3$	CO_2Me	80	$(2.36\pm0.07)\times10^{-5}$
4[b]	$(iPrO)_3Si(CH_2)_3$	CO_2Me	100	$(6.36\pm0.14)\times10^{-6}$
5[c]	CH_3	$(MeO)_3Si(CH_2)_{10}$	27[d]	$(1.49\pm0.03)\times10^{-5}$
6[c]	CH_3	$(EtO)_3Si(CH_2)_{10}$	34	too slow
7[c]	$(EtO)_3Si(CH_2)_3$	$CH_3(OCH_2CH_2)_2OCH_2$	78	$(6.32\pm0.29)\times10^{-6}$
8	TEOS		–	$(5.40\pm0.17)\times10^{-3}$
9	TMOS		–	too fast

[a] The initial concentration of **1**–**9** was in the $7–14\times10^{-3}$ M range. The concentration of D^+ and D_2O was 4.5×10^{-4} M and 2.12 M, respectively, for all kinetic experiments. [b] Synthesis outlined in Scheme 1 (route A). [c] Synthesis outlined in Scheme 1 (route B). [d] ref.[3]

processing steps.[16,17] To this end, the hydrolysis and condensation processes of the sol–gel starting materials, TEOS and TMOS, has been extensively studied.[18–23]

^{29}Si NMR spectroscopy[18] has been commonly employed to follow hydrolysis evolution. It is preferred over ^{1}H NMR spectroscopy because of the simplicity of the spectra. However, the use of ^{29}Si NMR spectroscopy requires lengthy experiments because of the intrinsic low sensitivity and long relaxation time of the silicon nucleus. For TEOS, TMOS, and other silicon alkoxysilanes, the analysis by ^{29}Si NMR spectroscopy is feasible because high concentrations of the substrate (around 1 M) and relaxation agents can be used.[18] This is not feasible with fulleropyrrolidine-alkoxysilanes whose solubility in polar solvents is orders of magnitude lower than that of TEOS and TMOS. We therefore turned our attention to ^{1}H NMR spectroscopy. Each experiment was carried out by dissolving the alkoxysilane in [D_8]THF (ca. 10 mM) in the presence of 1,4-dinitrobenzene as an internal standard. The intensity change of selected proton resonances of the starting alkoxysilane was monitored immediately after the addition of a catalytic amount of deuterated hydrochloric acid. Because of the complexity of the NMR spectra of **1**–**7**, a suitable isolated proton signal was selected for each substrate. In particular, the methine proton (δ = 5.3 ppm) of the pyrrolidine ring was chosen for compounds **1**–**4**; the singlet of the methoxy group (δ = 3.5 ppm) was preferred for **5**, while the variation of one of the methylene hydrogens (δ = 4.8 and 4.2 ppm for **6**; δ = 4.9 and 4.3 ppm for **7**) at the 5-position of the pyrrolidine heterocycle was monitored for **6** and **7**.

It is important to note that hydrolysis of the first silicon alkoxide group in fulleropyrrolidine-alkoxysilanes makes the resulting intermediate highly insoluble in [D_8]THF, thus hampering the determination of its concentration. Therefore this first hydrolysis has to be considered irreversible.

The kinetic study began with the determination of the reaction order for the hydrolysis of the representative fulleropyrrolidine-ethoxysilane **2**. To this end, excess D_2O and a catalytic amount of DCl were added to a [D_8]THF solution of **2** whose time evolution during the hydrolysis process was monitored by ^{1}H NMR spectroscopy. The linear interpolation of the data, corresponding to 10–15% decay of **2**, provided its initial hydrolysis rate at that concentration. Figure 1 shows the plot of the initial rate versus concentration for four experiments in which only the amount of **2** in [D_8]THF was changed.

A first order kinetic reaction, relative to the substrate, is inferred from the linearity of the data, the interpolation of which gave the pseudo-first-order rate constant $k_{obsd.}$ = $(1.12 \pm 0.03) \times 10^{-4}$ s^{-1} for fulleropyrrolidine-ethoxysilane **2**.

Figure 2 displays the disappearance of **2** with time as a result of its hydrolysis, monitored over the course of about 15 h. A clear slope change, after ca. 3.2 h (11800 s) is evident from the diagram.

The change could be ascribed to an inhibition process, which, in turn, could be related to several reasons such as formation and accumulation of hydrolyzed intermediates, as observed earlier for alkoxysilanes lacking the fullerene

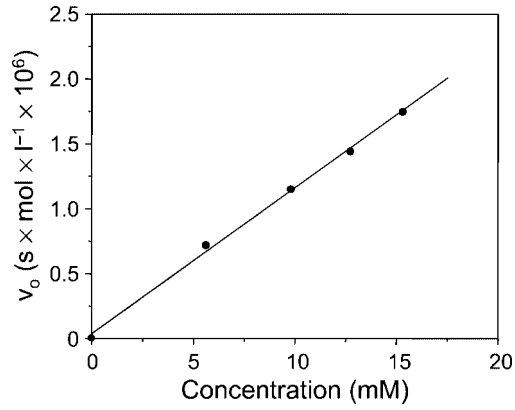


Figure 1. Initial hydrolysis rate vs. concentration for derivative **2**.

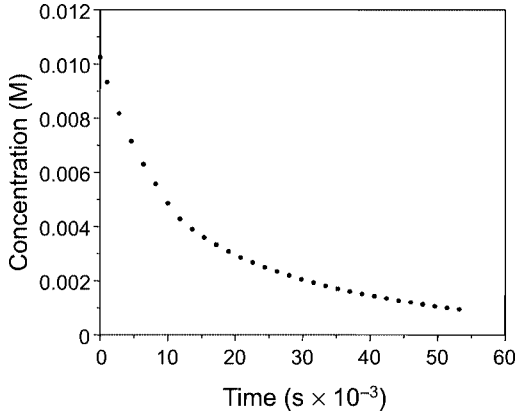


Figure 2. Plot of concentration of **2** vs. time.

moiety,[18] or the release of ethanol, which changes the medium composition and/or affects the catalyst action. An important issue here is the fulleropyrrolidine nitrogen that could be involved in acid–base equilibria with the DCl catalyst. It has been found, however, that fulleropyrrolidines are almost six orders of magnitude less basic than the corresponding pyrrolidines,[24] thus supporting the view that the fulleropyrrolidine nitrogen should not have a major influence on the activity of the acid catalyst.

Three different experiments for the hydrolysis of **2**, with the same concentrations of the substrate, water, and the catalyst, gave very close $k_{obsd.}$ values (mean $k_{obsd.}$ = $(7.34 \pm 0.09) \times 10^{-5}$ s^{-1}) by fitting the initial part of the curve, as illustrated in the representative example shown in Figure 2. It should be noted that this hydrolysis rate constant is slightly lower than that calculated with the initial rates method (Figure 1). Although the latter would minimize complications by interfering byproducts, it is worth mentioning that the calculations are made from a smaller set of data points. Furthermore, the evaluation of the time-zero rate constant is not always an easy task. We therefore used the linearization method of the first set of data from the total kinetic plot (Figure 2) to evaluate the hydrolysis rate constant $k_{obsd.}$. This was employed for a comparative evaluation of the relative reactivity, toward hydrolysis, of the fulleropyrrolidine-alkoxysilanes **1**–**7**.

Figure 3 displays the concentration versus time profile for substrates **1**–**4** under the hydrolysis conditions mentioned earlier. The respective rate constant decreases following the order: MeO > EtO > BuO > *i*PrO. This trend could be explained on the basis of the steric hindrance that the silicon alkoxide group exerts towards nucleophilic attack of the water.

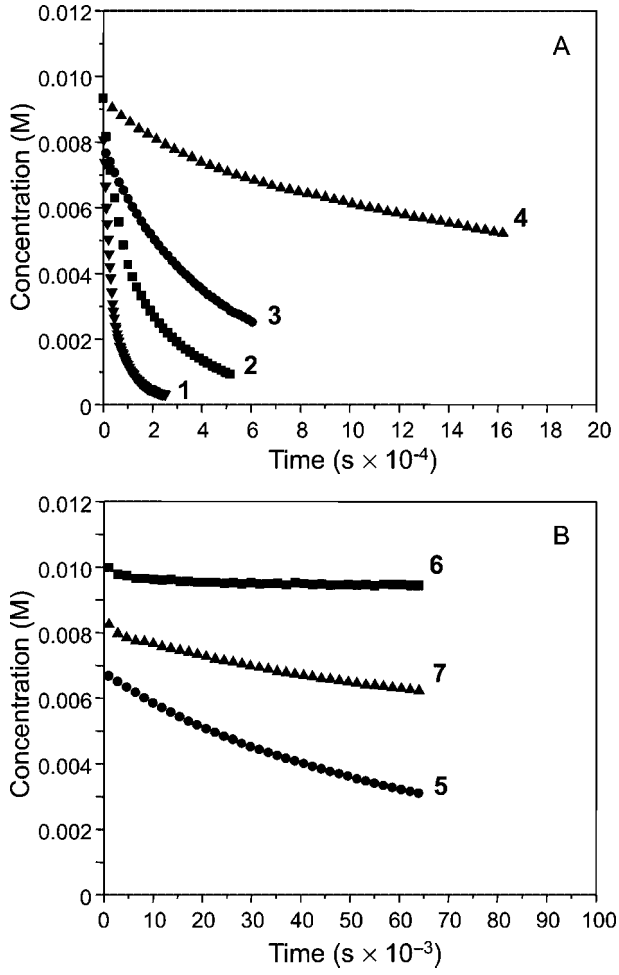


Figure 3. A) Concentration of derivatives **1**–**4** vs. time. B) Concentration of derivatives **5**–**7** vs. time.

Derivatives **5**–**7** present a hydrolysis kinetic profile that is much slower than that of derivatives **1**–**4** (Figure 3B). The hydrolysis of **6** was so slow that a value for the rate constant was not determined.

To the best of our knowledge, kinetic studies of the acid-catalyzed hydrolysis of alkoxysilanes are reported in ethanol, methanol, and dioxane,[18–23] while data in THF are not available. For this reason, we performed the kinetic analysis for TEOS (**8**) and TMOS (**9**) under the hydrolysis conditions used for fulleropyrrolidines **1**–**7**. The rate constants are shown in Table 1.

It is worth mentioning that the addition of the acid catalyst produces an almost instantaneous hydrolysis of TMOS. The first NMR spectrum, collected after 2 min, showed that the substrate was completely hydrolyzed. On the other hand, TEOS had a $k_{obsd.}$ value that was comparable to that of fulleropyrrolidine-ethoxysilane **2**.

Next we examined the effect of increasing the amount of acid on the hydrolysis rate constant. The plot of $k_{obsd.}$ versus $[D^+]$ is shown in Figure 4; a deviation from linearity is observed for $[D^+] > 10^{-3}$ M. This result could be explained within the framework of the Debye–Hückel limit:[25] in [D_8]-THF/water (96:4), it is reasonable to assume that the activity of D^+ does not coincide with its concentration. Furthermore, an increase in the rate constant is expected upon increasing the ionic strength of the medium, induced by D^+ ions. A similar behavior was described earlier for other alkoxysilanes.[18,19]

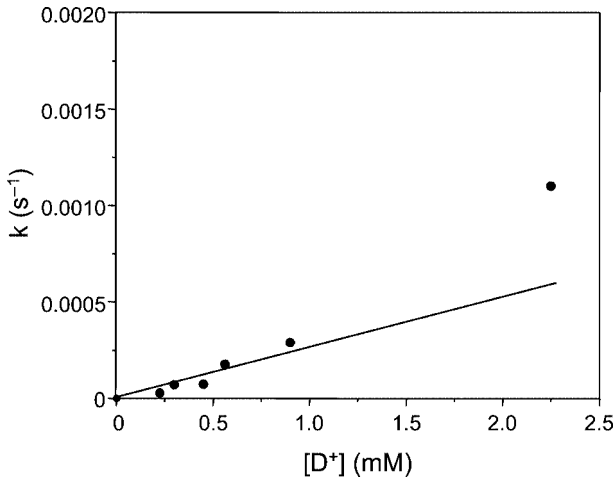


Figure 4. Relationship between DCl concentration and $k_{obsd.}$ for derivative **2** in [D_8]THF/water.

Conclusions

The evaluation of the hydrolysis rate constant of a series of fulleropyrrolidines bearing different silicon alkoxide groups and solubilizing chains was achieved following the disappearance of selected ^{1}H-NMR resonances of the pyrrolidine ring under the conditions (HCl/H_2O/THF) reported earlier for the preparation of fullerene-doped sol–gel glasses. It has been found that fulleropyrrolidine **1**, bearing the trimethoxysilyl group, hydrolyzes faster than substrates **2**–**7** and should be the reagent of choice to minimize aggregation of the fullerene spheroid in sol–gel glassy matrices. Interestingly, the presence of solubilizing chains on the pyrrolidine ring of derivatives **5**–**7** slows down the hydrolysis process. A good balance between solubility in THF and the rate of hydrolysis is reached with fulleropyrrolidine-ethoxysilane **2**, a thoroughly characterized reverse saturable absorption material with a very low threshold for nonlinear transmission. Derivative **2** hydrolyzes at a rate comparable to that of TEOS, one of the most common reagents for the preparation of sol–gel glasses. If a more reactive substrate is needed, fulleropyrrolidine-trimethoxysilane **1** should be used, although special care must be observed because of its reactivity towards humidity and towards SiO_2 during purification by column chromatography.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF), dichloromethane, dimethylformamide (DMF), cyclohexane, and pyridine were carefully distilled prior to use. [60]-Fullerene was obtained from Bucky USA (99.5%). *N*-(3-Triethoxysilylpropyl)glycine,[4] 3,6,9-trioxadecanal,[26] fulleropyrrolidine **2**,[15] and fulleropyrrolidine **5**[3] were prepared as described in the literature. ^{1}H- and ^{13}C NMR spectra were recorded with AC 250 and AM 400 Bruker instruments. In all NMR spectra, chemical shifts were referenced to the solvent resonance. MS spectra were measured with a GC Hewlett–Packard 5890 instrument, equipped with a capillary column (15 m × 0.2 mm) on silica functionalized with polymethylsiloxane, and interfaced to a Hewlett–Packard 5970 Mass Selective Detector. The mass of high-molecular-weight derivatives was detected with a MALDI-TOF (Matrix Assisted Laser Desorption Ionization Time-of-Flight) instrument (Bruker), and 2,5-dihydroxybenzoic acid was used as the matrix. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 5 spectrophotometer. Infrared spectra were recorded with a FT-IR Perkin–Elmer 1600 instrument. Thin layer chromatography (TLC) was performed on silica gel Poligram Sil G/UV$_{254}$ (Macherey–Nagel) plates. Analytical and preparative HPLC were performed with a Shimadzu LC-8A instrument, equipped with a Shimadzu SPD-6A UV/Vis detector working at 340 nm, by using a Primesphere 5-Sil (250 × 10 mm, 5 μm, flow rate: 2 mL/min) or a Primesphere 10-Sil (250 × 21 mm, 10 μm, flow rate: 7 mL/min) column, respectively. The solubility of the fullerene derivatives was determined as follows. A saturated solution of pyrrolidine in THF was subjected to centrifugation for 5 min at 12000 rpm to separate any solid residue and to obtain a clear solution. This solution was diluted with THF and the pyrrolidine concentration determined by UV/Vis from a calibration curve.

Preparation of the Samples for Kinetic Measurements

The fullerene derivatives were dissolved in [D$_8$]THF containing 1,4-dinitrobenzene as the internal standard (ca. 10 mM), to have an initial concentration of ca. 10 mM. The exact concentrations were calculated from the integration of the proton signal followed during the hydrolysis relative to the integration value of the standard. To start the hydrolysis process, a solution of DCl (11.7 mM) in water (20 μL) was added to the substrate in [D$_8$]THF. For kinetic experiments at different concentrations of acid, the DCl solutions were prepared by dilution with deuterated water from a stock (0.117 M) solution of DCl.

General Procedure for the Synthesis of 3-Chloropropyltrialkoxysilanes

Trichloro(3-chloropropyl)silane in pentane was carefully added dropwise, under a nitrogen atmosphere, to a solution of the appropriate alcohol and freshly distilled pyridine in dry pentane, cooled to 0 °C. The mixture was stirred at room temperature for 1 h and then filtered. The solvent was evaporated, and the desired product distilled under reduced pressure.

3-Chloropropyltriisopropoxysilane (8): Starting materials: Propan-2-ol (1.5 mL, 20 mmol) and pyridine (1.5 mL, 20 mmol) in pentane (100 mL), trichloro(3-chloropropyl)silane (1.0 mL, 6.4 mmol) in pentane (15 mL). Product **8** was obtained as a colorless oil. Yield: 1.04 g (58%). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.62 (m, 2 H), 1.12 (d, J = 7.6 Hz, 18 H), 1.80 (m, 2 H), 3.46 (t, J = 8.8 Hz, 2 H), 4.14 (hept, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, CDCl$_3$, 25 °C): δ = 9.67, 25.49, 26.80, 47.61, 64.97 ppm. GC-MS (M_W = 282): m/z (%) = 43 (47), 79 (95), 97 (100), 121 (55), 139 (51), 181 (58), 205 (57), 223 (53).

3-Chloropropyltributoxysilane (9): Starting materials: Butan-1-ol (3.9 mL, 42 mmol) and pyridine (3.5 mL, 43 mmol) dissolved in pentane (250 mL), trichloro(3-chloropropyl)silane (2.22 mL, 14 mmol) in pentane (30 mL). Product **9** was obtained as a colorless oil. Yield: 3.32 g (75%). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.71 (m, 2 H), 0.89 (t, J = 6.8 Hz, 9 H), 1.35 (m, 6 H), 1.51 (m, 6 H), 1.85 (m, 2 H) 3.50 (t, J = 6.3 Hz, 2 H) 3.71 (t, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR (62.5 MHz, CDCl$_3$, 25 °C): δ = 7.85, 13.73, 18.83, 26.49, 34.54, 47.39, 62.44 ppm. GC-MS (M_W = 324): m/z (%) = 55 (72), 79 (43), 97 (48), 135 (31), 209 (34), 247 (100), 281 (17).

General Procedure for the Synthesis of 3-Azidopropyltrialkoxysilanes

A solution of the appropriate 3-chloropropyltrialkoxysilane and NaN_3 in DMF was heated at 60 °C for 3 h. After concentration, diethyl ether was added, and the precipitated NaN_3 was filtered off. The solvent was evaporated affording the desired product, which was used without further purification.

3-Azidopropyltriisopropoxysilane (10): Starting materials: 3-Chloropropyltriisopropoxysilane (**8**, 3.5 g, 12.4 mmol) and NaN_3 (3.8 g, 58.5 mmol) in DMF (200 mL). Product **10** was obtained as a colorless oil. Yield: 3.1 g (89%). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.60 (m, 2 H), 1.17 (d, J = 3.9 Hz, 18 H), 1.69 (m, 2 H), 3.25 (t, J = 6.8 Hz, 2 H), 4.20 (sept, J = 5.9 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, CDCl$_3$, 25 °C): δ = 9.17, 22.88, 25.50, 53.92, 64.99 ppm. GC-MS (M_W = 289): m/z (%) = 43 (29), 45 (44), 63 (43), 79 (100), 118 (95), 163 (42), 205 (81), 230 (53). IR (neat): $\tilde{\nu}$ = 2097 cm^{-1}.

3-Azidopropyltributoxysilane (11): Starting materials: 3-Chloropropyltributoxysilane (**9**, 3.0 g, 9.26 mmol) and NaN_3 (3.0 g, 46.15 mmol) in DMF (200 mL). Product **11** was obtained as a colorless oil. Yield 2.8 g (91%). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.65 (m, 2 H), 0.91 (t, J = 6.8 Hz, 9 H), 1.36 (m, 6 H), 1.53 (m, 6 H), 1.70 (m, 2 H), 3.25 (t, J = 6.8 Hz, 2 H), 3.73 (t, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR (62.5 MHz, CDCl$_3$, 25 °C): δ = 7.44, 13.76, 18.85, 22.66, 34.55, 53.78, 62.49 ppm. GC-MS (M_W = 331): m/z (%) = 63 (49), 79 (76), 93 (24), 118 (35), 135 (40), 246 (25), 247 (100), 274 (21). IR (neat): $\tilde{\nu}$ = 2096 cm^{-1}.

General Procedure for the Synthesis of 3-(Trialkoxysilyl)propan-1-amines

3-Azidopropyltrialkoxysilanes were hydrogenated at atmospheric pressure in MeOH for 2 h with 5% Pd/C as a catalyst. After filtration of the catalyst, the solvent was evaporated affording the desired product, which was used without further purification.

3-(Triisopropoxysilyl)propan-1-amine (12): Starting materials: 3-Azidopropyltriisopropoxysilane (**10**, 1.88 g, 6.5 mmol), H_2 and Pd/C (100 mg) in MeOH (250 mL). Product **12** was obtained as a colorless oil. Yield 1.7 g (99%). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.45 (m, 2 H), 1.08 (d, J = 5.9 Hz, 18 H), 1.42 (m, 2 H), 2.02 (m, 2 H), 2.55 (t, J = 6.3 Hz, 2 H), 4.09 (hept, J = 5.9 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, CDCl$_3$, 25 °C): δ = 8.95, 25.39, 27.13, 44.80, 49.80, 64.80 ppm. GC-MS (M_W = 263): m/z (%) = 28 (62), 30 (45), 45 (27), 63 (33), 78 (37), 79 (91), 102 (32), 120 (58), 162 (67), 203 (63), 204 (100).

3-(Tributoxysilyl)propan-1-amine (13): Starting materials: 3-Azidopropyltributoxysilane (**11**, 2.64 g, 7.95 mmol), H_2 and Pd/C (100 mg) in MeOH (250 mL). Product **13** was obtained as a colorless oil. Yield 2.3 g (95%). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 0.62 (m, 2 H), 0.94 (t, J = 6.8 Hz, 9 H), 1.34 (m, 6 H), 1.52 (m, 8 H), 2.67 (t, J = 6.9 Hz, 2 H) 3.71 (t, J = 6.8 Hz, 6 H) ppm. ^{13}C

NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 7.41, 13.83, 18.89, 27.26, 34.63, 45.08, 62.53 ppm. GC-MS (M_W = 263): *m/z* (%) = 79 (57), 135 (29), 176 (63), 190 (92), 232 (100), 247 (79).

General Procedure for the Synthesis of Methyl *N*-[3-(Trialkoxysilyl)-propyl]aziridine-2-carboxylates

A solution of the appropriate 3-(trialkoxysilyl)propan-1-amine and triethylamine in dry benzene was slowly added to a solution of methyl 2,3-dibromopropanoate in benzene, and cooled to 5 °C. The mixture was heated to reflux for 2 h, and after cooling to room temperature, the precipitated salts were filtered. The solvent was evaporated affording the desired product, which was used without further purification.

Methyl *N*-[3-(Triisopropoxysilyl)propyl]aziridine-2-carboxylate (14): Starting materials: 3-(Triisopropoxysilyl)propan-1-amine (**12**, 980 mg, 3.72 mmol) and triethylamine (1.2 mL, 8.61 mmol) in benzene (5 mL), methyl 2,3-dibromopropanoate (910 mg, 3.69 mmol) in benzene (3.5 mL). Product **14** was obtained as a pale yellow oil. Yield 898 mg (70%). ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ = 0.56 (m, 2 H), 1.14 (d, *J* = 5.9 Hz, 18 H), 1.54 (m, 1 H), 1.67 (m, 2 H), 2.02 (m, 1 H), 2.12 (m, 1 H), 2.28 (m, 2 H), 3.68 (s, 3 H), 4.15 (hept, *J* = 5.9 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, C_6D_6, 25 °C): δ = 9.96, 23.71, 25.77, 34.03, 37.41, 51.34, 63.86, 65.06, 170.95 ppm. GC-MS (M_W = 347): *m/z* (%) = 45 (36), 63 (35), 79 (100), 121 (40), 202 (30), 230 (33), 260 (57). IR (neat): $\tilde{\nu}$ = 1752 cm^{-1}.

Methyl *N*-[3-(Tributoxysilyl)propyl]aziridine-2-carboxylate (15): Starting materials: 3-(Tributoxysilyl)propan-1-amine (**13**, 806 mg, 3.27 mmol) and triethylamine (1.2 mL, 8.61 mmol) in benzene (5 mL), methyl 2,3-dibromopropanoate (900 mg, 3.63 mmol) in benzene (3.5 mL). Product **15** was obtained as a pale yellow oil. Yield 900 mg (71%). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 0.58 (m, 2 H), 0.88 (t, *J* = 6.8 Hz, 9 H), 1.33 (m, 6 H), 1.51 (m, 7 H), 1.69 (m, 2 H), 2.01 (m, 1 H), 2.13 (m, 1 H), 2.21 (m, 1 H), 2.35 (m, 1 H), 3.67 (s, 3 H), 3.69 (t, *J* = 6.8 Hz, 6 H) ppm. ^{13}C NMR (62.5 MHz, C_6D_6, 25 °C): δ = 7.79, 13.75, 18.82, 22.80, 34.46, 34.53, 37.08, 52.08, 62.40, 63.62, 171.41 ppm. GC-MS (M_W = 389) *m/z* (%) = 79 (42), 93 (22), 247 (18), 302 (100), 316 (43), 389 (1). IR (neat): $\tilde{\nu}$ = 1751 cm^{-1}.

Methyl *N*-[3-(Trimethoxysilyl)propyl]aziridine-2-carboxylate (16): Starting materials: 3-(Trimethoxysilyl)propan-1-amine (764 mg, 4.27 mmol) and triethylamine (1.2 mL, 8.61 mmol) in benzene (5 mL), methyl 2,3-dibromopropanoate (1.05 g, 4.27 mmol) in benzene (3.5 mL). Product **16** was obtained as a pale yellow oil. Yield 843 mg (80%). ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ = 0.67 (m, 2 H), 1.14 (d, *J* = 1.46 Hz, 1 H), 1.68 (m, 2 H), 1.81 (m, 1 H), 2.05 (m, 3 H), 3.36 (s, 3 H), 3.42 (s, 9 H) ppm. ^{13}C NMR (62.5 MHz, C_6D_6, 25 °C): δ = 7.06, 23.17, 33.99, 37.24, 50.21, 51.38, 63.44, 170.96 ppm. GC-MS (M_W = 263): *m/z* (%) = 59 (29), 91 (59), 121 (100), 172 (21), 176 (38), 204 (28), 263 (1). IR (film): $\tilde{\nu}$ = 1736 cm^{-1}.

General Procedure for the Synthesis of Methyl *N*-[3-(Trialkoxysilyl)-propyl]fullero[*c*]pyrrolidine-2-carboxylates

A solution of [60]fullerene and the appropriate methyl *N*-[3-(trialkoxysilyl)propyl]aziridine-2-carboxylate in 1,2-dichlorobenzene was heated to reflux for 2–5 h. After evaporation of the solvent, the product was purified by flash chromatography (SiO_2, 63–100 μm) with toluene to remove unreacted [60]fullerene, and then with a mixture of toluene/ethyl acetate. The compound was dissolved with a minimum amount of toluene, precipitated by the addition of CH_3CN, washed several times with CH_3CN, and dried under reduced pressure.

Methyl *N*-[3-(Trimethoxysilyl)propyl]fullero[*c*]pyrrolidine-2-carboxylate (1): Starting materials: [60]Fullerene (101 mg, 140 μmol) and methyl *N*-[3-(trimethoxysilyl)propyl]aziridine-2-carboxylate (**16**, 85 mg, 322 μmol) in 1,2-dichlorobenzene (100 mL), heated to reflux for 3 h. Product **1** was obtained as a brown solid. Yield 40 mg (29%), recovered [60]fullerene: 50 mg (49%). R_f = 0.7, toluene/ethyl acetate, 9:1. ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ = 0.88 (m, 2 H), 1.98 (m, 2 H), 2.89 (m, 1 H), 3.23 (m, 1 H), 3.53 (s, 9 H), 3.61 (s, 3 H), 4.18 (d, *J* = 9.1 Hz, 1 H), 5.01 (d, *J* = 9.1 Hz, 1 H), 5.06 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3/CS_2$, 1:1, 25 °C): δ = 6.83, 21.59, 50.32, 51.73, 54.82, 64.87, 69.25, 72.43, 135.22, 135.87, 136.37, 137.55, 139.47, 139.66, 140.08, 141.60, 141.68, 141.75, 141.79, 141.92, 142.02, 142.41, 142.45, 142.88, 144.22, 144.26, 144.34, 144.44, 145.04, 145.08, 145.22, 145.27, 145.38, 145.43, 145.51, 145.56, 145.61, 145.84, 145.97, 146.02, 146.06, 146.14, 147.06, 147.15, 150.82, 153.44, 154.40, 154.55, 169.81 ppm. IR (KBr): $\tilde{\nu}$ = 1755, 1735, 1166, 1102, 1076, 575, 526 cm^{-1}. MALDI-MS (M_W = 984): *m/z* = 985 [M + H]$^+$. UV/Vis (THF): λ_{max} (ε, mol^{-1} dm^3 cm^{-1}) = 254 (124100), 307 (42650), 430 (4800), 698 (520) nm. $C_{70}H_{21}NO_5Si$ (984): calcd. C 85.44, H 2.15, N 1.42; found C 79.35, H 2.13, N 1.23. HPLC (toluene/ethyl acetate, 9:1): R_T = 9.58 min, purity 98%.

Methyl *N*-[3-(Tributoxysilyl)propyl]fullero[*c*]pyrrolidine-2-carboxylate (3): Starting materials: [60]Fullerene (260 mg, 361 μmol) and methyl *N*-[3-(tributoxysilyl)propyl]aziridine-2-carboxylate (**15**, 300 mg, 700 μmol) in 1,2-dichlorobenzene (220 mL), heated to reflux for 2 h. Product **3** was obtained as a brown solid. Yield 119 mg (30%), recovered [60]fullerene: 127 mg (49%). R_f = 0.5, toluene/ethyl acetate, 95:5. ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ = 0.82 (m, 2 H), 0.92 (t, *J* = 6.8 Hz, 9 H), 1.36 (m, 6 H), 1.53 (m, 6 H), 1.98 (m, 2 H), 2.92 (m, 1 H), 3.25 (m, 1 H), 3.74 (t, *J* = 6.8 Hz, 6 H), 3.79 (s, 3 H), 4.30 (d, *J* = 9.1 Hz, 1 H), 5.04 (d, *J* = 9.1 Hz, 1 H), 5.06 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 7.91, 14.00, 19.17, 21.86, 34.73, 51.44, 54.59, 62.21, 64.66, 69.16, 127.12, 127.51, 127.89, 135.70, 136.01, 136.44, 137.35, 139.75, 139.94, 140.33, 140.41, 141.80, 141.87, 142.19, 142.30, 142.37, 142.75, 142.77, 142.82, 143.18, 143.32, 144.49, 144.54, 144.73, 144.88, 145.29, 145.38, 145.57, 145.69, 145.92, 146.05, 146.14, 146.20, 146.27, 146.28, 146.36, 146.41, 146.54, 146.73, 146.95, 147.29, 147.32, 153.79, 154.62, 154.70, 156.82, 169.05 ppm. IR (KBr): $\tilde{\nu}$ = 1757, 1739, 1166, 1116, 1089, 575, 527 cm^{-1}. MALDI-MS (M_W = 1110): *m/z* = 1111 [M + H]$^+$. UV/Vis (THF): λ_{max} (ε, mol^{-1} dm^3 cm^{-1}) = 254 (135400), 308 (44700), 430 (4480), 699 (390) nm. $C_{79}H_{39}NO_5Si$ (1110): calcd. C 85.46, H 3.54, N 1.26; found C 82.40, H 3.63, N 1.10. HPLC (toluene/ethyl acetate, 95:5): R_T = 5.95 min, purity 98%.

Methyl *N*-[3-(Triisopropoxysilyl)propyl]fullero[*c*]pyrrolidine-2-carboxylate (4): Starting materials: [60]Fullerene (195 mg, 270 μmol) and methyl *N*-[3-(triisopropoxysilyl)propyl]aziridine-2-carboxylate (**14**, 205 mg, 590 μmol) in 1,2-dichlorobenzene (150 mL), heated to reflux for 2 h. Product **4** was obtained as a brown solid. Yield 135 mg (47%), recovered [60]fullerene: 89 mg (45%). R_f = 0.6, toluene/ethyl acetate, 95:5. ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ = 0.93 (m, 2 H), 1.27 (d, *J* = 5.9 Hz, 18 H), 2.14 (m, 2 H), 2.94 (m, 1 H), 3.33 (m, 1 H), 3.56 (s, 3 H), 4.21 (d, *J* = 9.2 Hz, 1 H), 4.31 (hept, *J* = 5.9 Hz, 3 H) 5.06 (d, *J* = 9.2 Hz, 1 H), 5.14 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, CD_2Cl_2, 25 °C): δ = 9.96, 22.45, 22.83, 25.83, 51.81, 65.10, 69.67, 72.81, 77.38, 135.59, 136.23, 136.69, 137.85, 139.82, 139.98, 140.39, 140.44, 141.94, 141.99, 142.13, 142.21, 142.26, 142.39, 142.73, 142.77, 143.20, 144.57, 144.61, 144.70, 144.76, 145.38, 145.54, 145.60, 145.75, 145.80, 145.90, 146.04, 146.07, 146.17, 146.35, 146.46, 147.38, 147.48, 151.44, 154.04, 154.88, 155.14, 169.90 ppm. IR (KBr): $\tilde{\nu}$ = 1767, 1738, 1166, 1119,

1031, 575, 527 cm^{-1}. MALDI-MS (M_W = 1068): *m/z* = 1069 $[M+H]^+$. UV/Vis (THF): λ_{max} (ε, $mol^{-1}\,dm^3\,cm^{-1}$) = 254 (108600), 306 (36000), 430 (3720), 698 (340) nm. $C_{76}H_{33}NO_5Si$ (1068): calcd. C 85.46, H 3.11, N 1.31; found C 82.31, H 3.11, N 1.13. HPLC (toluene/ethyl acetate, 9:1): R_T = 6.17 min, purity 97%.

11-Triethoxysilylundecanal (17): Hexachloroplatinic acid in cyclohexanone [20 μL of a solution prepared by dissolving the acid (10 mg) in cyclohexanone (1 mL)] was added to a solution of 10-undecenal (400 μL, 1.92 mmol) and triethoxysilane (370 μL, 1.97 mmol), and the mixture was heated to 55 °C for 4 h. The product was purified by flash chromatography (SiO_2, eluant: petroleum ether/ethyl acetate, 8:2) affording 189 mg (30%) of the product as a pale yellow oil. R_f = 0.6, petroleum ether/ethyl acetate, 8:2. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 0.57 (m, 2 H), 1.20 (t, *J* = 7.0 Hz, 9 H), 1.24 (m, 14 H), 1.62 (m, 2 H), 2.37 (td, *J* = 1.8, *J* = 7.3 Hz, 2 H), 3.80 (q, *J* = 7.0 Hz, 6 H), 9.75 (t, *J* = 1.8 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 10.35, 18.26, 22.69, 22.71, 24.67, 29.18, 29.31, 29.42, 33.13, 33.90, 43.89, 58.27, 178.91 ppm. GC-MS (M_W = 332): *m/z* (%) = 79 (19), 119 (31), 163 (100), 219 (15), 240 (13). IR (neat): $\tilde{\nu}$ = 2660, 1710 cm^{-1}.

***N*-Methyl 2-[10-(Triethoxysilyl)decyl]fullero[*c*]pyrrolidine (6):** A solution of [60]fullerene (96 mg, 130 μmol), *N*-methylglycine (26 mg, 260 μmol), and 11-triethoxysilylundecanal (**17**, 44 mg, 332 μmol) in toluene (100 mL) was heated to reflux for 5 h. After evaporation of the solvent, the product was purified by flash chromatography (SiO_2, 32–63 μm) with toluene to remove the unreacted [60]fullerene, and then with a mixture of toluene/ethyl acetate. The compound was dissolved with a minimum amount of toluene and precipitated by the addition of acetonitrile to yield 29 mg (21%) of **6** along with unreacted [60]fullerene (48 mg, 51%). R_f = 0.38, toluene/ethyl acetate, 9:1. ^1H NMR (250 MHz, CD_2Cl_2, 25 °C): δ = 0.55 (m, 2 H), 1.20 (t, *J* = 7.0 Hz, 9 H), 1.41 (m, 14 H), 1.92 (m, 2 H), 2.43 (m, 2 H), 2.98 (s, 3 H), 3.75 (q, *J* = 7.0 Hz, 6 H), 3.80 (t, *J* = 5.6 Hz, 1 H), 4.18 (d, *J* = 9.8 Hz, 1 H), 4.80 (d, *J* = 9.8 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz, CD_2Cl_2/CS_2, 1:5, 25 °C): δ = 10.91, 18.70, 23.26, 27.92, 29.84, 30.05, 30.18, 30.88, 31.44, 33.61, 58.31, 70.28, 70.53, 76.47, 78.36, 135.69, 136.0, 137.34, 139.74, 140.40, 141.79, 141.85, 142.18, 142.29, 142.35, 142.74, 142.76, 142.81, 144.53, 145.37, 145.55, 145.67, 145.91, 146.04, 146.07, 146.13, 146.26, 146.40, 146.53, 146.72, 146.94, 147.31, 153.78, 154.62, 156.81 ppm. IR (KBr): $\tilde{\nu}$ = 1164, 1102, 1171, 956, 575, 527 cm^{-1}. MALDI-MS (M_W = 1080): *m/z* = 1081 $[M+H]^+$. UV/Vis (THF): λ_{max} (ε, $mol^{-1}\,dm^3\,cm^{-1}$) = 254 (104400), 308 (31450), 431 (4230), 704 (530) nm. $C_{79}H_{41}NO_3Si$ (1080): calcd. C 87.84, H 3.83, N 1.30; found C 80.14, H 3.95, N 1.21. HPLC (toluene/ethyl acetate, 95:5): R_T = 16.50 min, purity 96%.

***N*-[3-(Triethoxysilyl)propyl]-2-[(2-methoxyethoxy)ethoxymethyl]fullero[*c*]pyrrolidine (7):** A solution of [60]fullerene (100 mg, 140 μmol), *N*-(3-triethoxysilylpropyl)glycine (38.5 mg, 130 μmol), and 3,6,9-trioxadecanal (30 mg, 180 μmol) in toluene (100 mL) was heated to reflux for 40 min. After evaporation of the solvent, the product was purified by flash chromatography (SiO_2, 32–63 μm) with toluene to remove the unreacted [60]fullerene, and then with a mixture of toluene/ethyl acetate. The compound was dissolved with a minimum amount of toluene and precipitated by addition of acetonitrile to yield 42 mg (30%) of **7** along with unreacted [60]-fullerene (40 mg, 40%). R_f = 0.5, toluene/ethyl acetate, 8:2. ^1H NMR (250 MHz, CD_2Cl_2, 25 °C): δ = 0.89 (m, 2 H), 1.29 (t, *J* = 7.0 Hz, 9 H), 2.00 (m, 2 H), 2.88 (m, 1 H), 3.32 (s, 3 H), 3.58 (m, 9 H), 3.87 (q, *J* = 7.0 Hz, 6 H), 4.10 (d, *J* = 9.2 Hz, 1 H), 4.32 (m, 1 H), 4.52 (m, 1 H), 4.90 (d, *J* = 9.2 Hz, 1 H) ppm. ^{13}C NMR (62.5 MHz CD_2Cl_2, 25 °C): δ = 8.61, 18.80, 21.64, 55.90, 58.56, 58.81, 67.04, 69.78, 70.78, 70.82, 72.54, 74.04, 75.01, 135.80, 136.01, 136.54, 137.57, 139.41, 139.41, 139.76, 140.33, 140.44, 141.79, 141.86, 142.17, 142.27, 142.35, 142.76, 143.17, 144.55, 144.74, 144.88, 145.29, 145.38, 145.42, 145.55, 145.63, 145.76, 145.83, 145.97, 146.13, 146.32, 146.44, 146.46, 146.95, 147.29, 147.33, 147.48, 152.83, 154.48, 154.82, 156.39 ppm. IR (KBr): $\tilde{\nu}$ = 1164, 1105, 1078, 575, 527 cm^{-1}. MALDI-MS (M_W = 1099): *m/z* = 1100 $[M+H]^+$. UV/Vis (THF): λ_{max} (ε, $mol^{-1}\,dm^3\,cm^{-1}$) = 254 (113600), 323 (37000), 430 (3980) nm. $C_{77}H_{36}NO_6Si$ (1099): calcd. C 84.14, H 3.30, N 1.27; found C 83.94, H 3.09, N 1.10. HPLC (toluene/ethyl acetate, 96:4): R_T = 7.40 min, purity 98%.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of derivatives **1**, **3**, **4**, **6**–**17** are included.

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