Synthesis and properties of new triazole methanofullerenes under the "click-chemistry" conditions

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The "click-chemistry" methods were used for the first time to synthesize new 1,2,3-triazole derivatives of fullerene, promising for the study of their biological activity, as well as for the preparation of new fullerene-containing materials on their basis. The purity and composition of the compounds synthesized were confirmed by MALDI-TOF mass spectrometry and HPLC, their structures were confirmed by a combination of 2D NMR homo- and heteronuclear correlation.

Key words: "click-chemistry", alkyne methanofullerenes, 1,2,3-triazole derivatives of fullerene, high-performance liquid chromatography, 2D NMR homo- and heteronuclear correlation.

In the last years, the so-called "click-chemistry" reactions attracted great attention of researchers. In the works,[1,2] it was independently shown that the reactions of azides with alkynes[3] in the presence of Cu^{I} as a catalyst proceeded under mild conditions by the pattern of 1,3-dipolar cycloaddition and exclusively furnished 1,4-disubstituted 1,2,3-triazoles in high yields. The practical interest to these reactions is explained by the fact that many known 1,2,3-triazoles possess various biological activity, including the anti-HIV activity.[4—7]

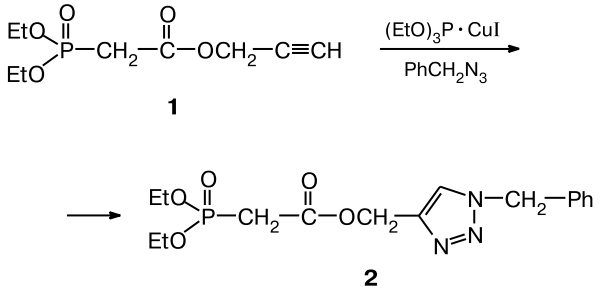
A possibility of the formation of fullerene derivatives containing 1,2,3-triazole fragments is studied poorly. While the "click-chemistry" approach turned out to be a powerful method for the preparation of different triazole-containing organic compounds, its compatibility with the fullerene derivatives was not so obvious, since organic azides can also undergo a [3+2] cycloaddition at the double bonds of fullerene.[8,9] Among seldom examples are the works,[10,11] in which efficient methods for the synthesis of fullerene triazole hexakis-adducts and triazole-porphirine-fullerene diads were developed using the "click-chemistry" reactions. A number of unique triazole derivatives of fullerene were obtained, promising for the practical application.

Taking into account the actuality of development of new materials and biologically active compounds based on fullerene, we applied the "click-chemistry" method for the preparation of new phosphorylated and malonate methanofullerenes containing 1,2,3-triazole fragments. To accomplish this, we used two approaches: 1) the synthesis of 1,2,3-triazole fullerene derivatives by the Bingel—Hirsch reaction, starting from fullerene C_{60} and triazole derivatives containing active methylene groups; 2) the synthesis of methanofullerene derivatives containing acetylenic bonds with subsequent formation of the heterocycle under the "click-chemistry" conditions.

Results and Discussion

The starting phosphorylated alkyne **1** was obtained by the reaction of propargyl chloroacetate with triethyl phosphite in the benzene solution upon reflux. Subsequent heterocyclization of compound **1** was carried out under the "click-chemistry" conditions using benzylazide and CuI as a catalyst. The reaction course was monitored by IR spectra of the reaction mixture. The disappearance of the band at 2096 cm^{-1} characteristic of the azide group indicated the conversion of the starting alkyne **1** to the corresponding triazole **2** (Scheme 1).

Scheme 1



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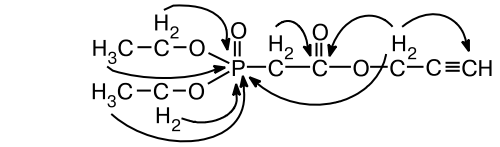

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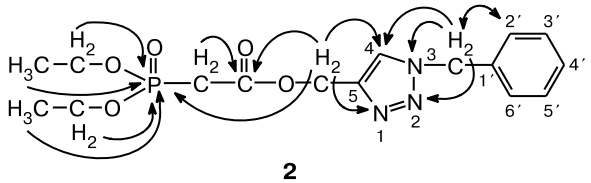


2

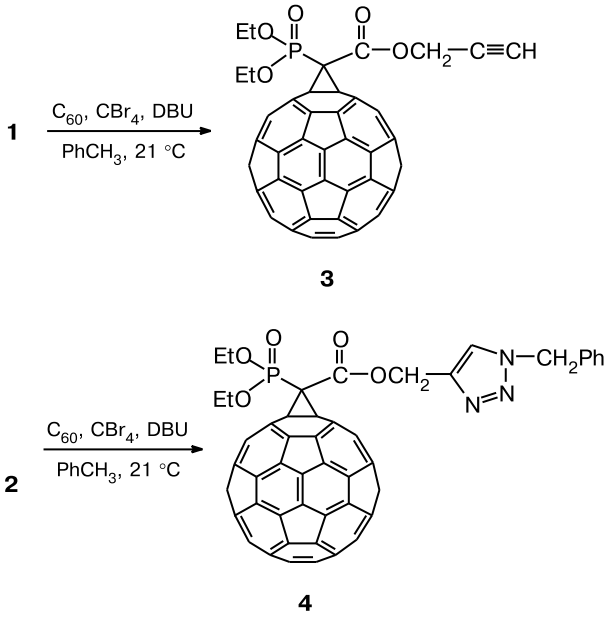
^{13}C: R^2 = 0.994 (**1**), 0.996 (**2**); ^{15}N: R^2 = 0.995 (**2**)

Fig. 1. The principal heteronuclear correlations (shown with arrows from the ^1H to the X nucleus). The correlation coefficients between the experimental and calculated chemical shifts are given.

The structure of compounds **1** and **2** unambiguously was established using a number of 2D NMR correlation methods ($^1H—^1H$, $^1H—^{13}C$, $^1H—^{15}N$, and $^1H—^{31}P$)[12]. The principal HMBC correlations for compounds **1** and **2** are shown in Fig. 1. Besides this, the agreement between the experimental and the calculated[13] ^{13}C and ^{15}N (GIAO DFT) chemical shifts for compound **2** (see Figs 1 and 2) additionally confirms the structure suggested.

The reaction of fullerene C_{60} and compounds **1** and **2** in the presence of tetrabromomethane and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under the Bingel—Hirsch reaction conditions[14,15] furnished the corresponding phosphorylated methanofullerenes **3** and **4** containing the alkyne and the triazole fragments, respectively (Scheme 2).

Scheme 2



These reactions take place at room temperature. The yields of compounds **3** and **4** after their isolation by column chromatography on SiO_2 were 41 and 25.2%, respectively, if calculated based on the converted fullerene.

Compound **4** was also obtained by an alternative method from methanofullerene **3** containing acetylene bonds and benzylazide in the presence of a $(EtO)_3P \cdot CuI$ catalyst, *i.e.* under the "click-chemistry" reaction conditions (Scheme 3).

The reaction course was monitored by high-performance liquid chromatography (HPLC) (Fig. 3). As it is

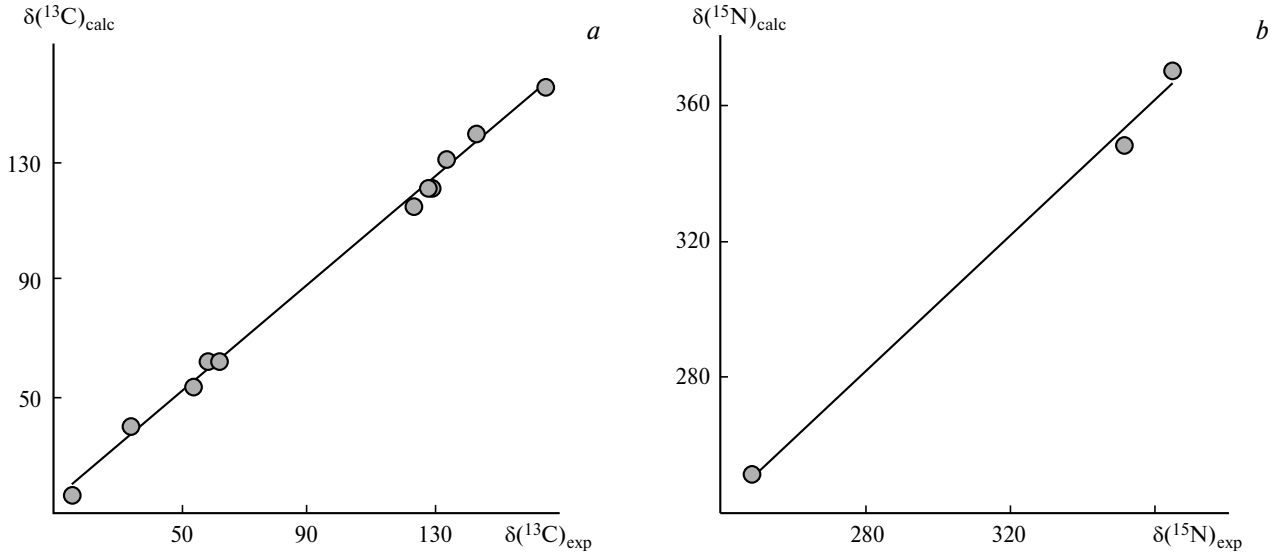


Fig. 2. The correlation of the experimental and the calculated chemical shifts ^{13}C (*a*) and ^{15}N (*b*) for compound **2**; R^2 = 0.996 (*a*) and 0.995 (*b*).

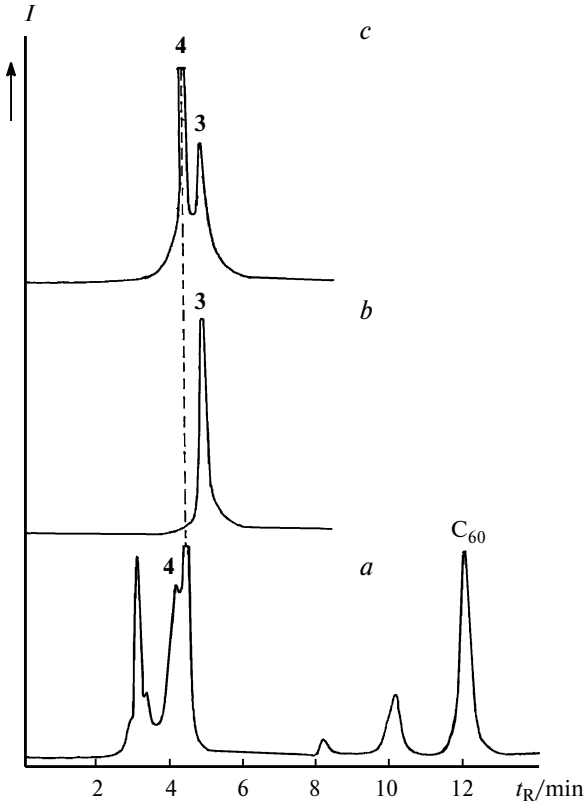
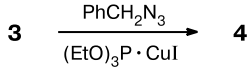


Fig. 3. The chromatogram (HPLC) for the reaction mixture obtained in the synthesis of compound **4** by the Bingel—Hirsch reaction (*a*) and for the starting compound **3** (*b*), as well as for the reaction mixture in the synthesis of product **4** by the "click-chemistry" (*c*) (a Partisil5-ODS(C_{18}) column; eluent toluene—acetonitrile (1 : 1); UV detector, λ = 328 nm); *I* is the intensity.

Scheme 3



seen from Fig. 3, *a*, the Bingel—Hirsch reaction, besides the main product **4**, formed many polycycloaddition products, which decreased the yield of compound **4** (25%).

The reaction of methanofullerene **3** with benzylazide under the "click-chemistry" conditions required only mild conditions and gave high yield of compound **4** (~89%). An increase in the reaction time led to a complete conversion of phosphorylated alkyne methanofullerene **3** to the triazole methanofullerene **4**, with the benzylazide itself being unreactive with fullerene C_{60} under these conditions.

The structures of compounds obtained were confirmed by the spectral data, their composition was confirmed by MALDI-TOF mass spectrometry.

The UV spectra of methanofullerenes **3** and **4** exhibit absorption bands of the fullerene framework at 258, 326, 431, 492, and 696 nm. The absorption band at 431 nm is characteristic of the addition of the methano fragment at the closed 6,6-bond of the fullerene sphere.

The IR spectra of compounds **3** and **4** exhibit an absorption band in the region 527 cm^{-1} characteristic of vibrations of the bonds of the fullerene framework, whereas vibrational bands of the carbonyl and the phosphoryl groups are found in the region 1733 and 1262 cm^{-1}, respectively. A vibrational band at 2121 cm^{-1} characteristic of the CH group at the triple bond was found for methanofullerene **3** containing an alkyne fragment, for methanofullerene **4**, a weak vibrational band of the CH group in the triazole ring was found at 3140 cm^{-1}.

In the MALDI-TOF mass spectra of compounds **3** and **4**, peaks of the protonated molecular ions $[MH]^+$ with *m/z* 953.05 and 1086.1, respectively, are present, which confirms the composition of the molecules under study.

Finally, the structures of compounds **3** and **4** were confirmed based on the data of 1D and 2D NMR correlation experiments.[12] The principal HMBC-correlations, which allowed us to establish the structures of the addends in compounds **3** and **4**, are shown in Fig. 4.

The ^{13}C NMR spectra of compounds **3** and **4**, besides the signals of the addend, exhibit a number of lines in the region indicative for the C atoms of the fullerene sphere (δ 148—136 and ~70). The presence of the spin-spin coupling constants from the phosphorus nuclei to the carbon nuclei of the fullerene C(1)/C(6) atoms[16] indicates the addition of the addend to the fullerene sphere. In this case, the chemical shifts for C(1)/C(6) (δ 70.10 and 70.24 for **3** and **4**, respectively) allows us to suggest a close character of the cycloaddition at the 6—6 bond.

We also obtained dipropargyl malonate **5** (see Ref. 17) and a derived from it alkyne methanofullerene **6**. The re-

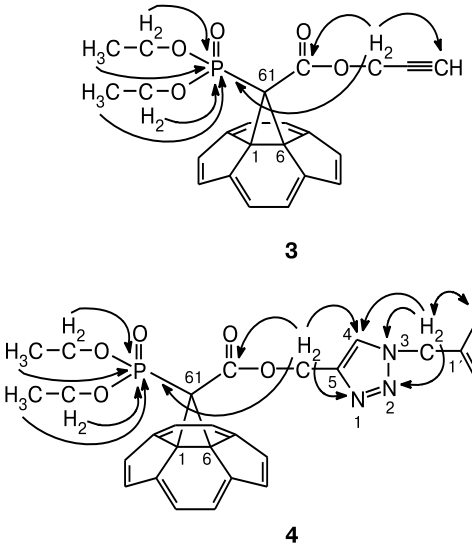
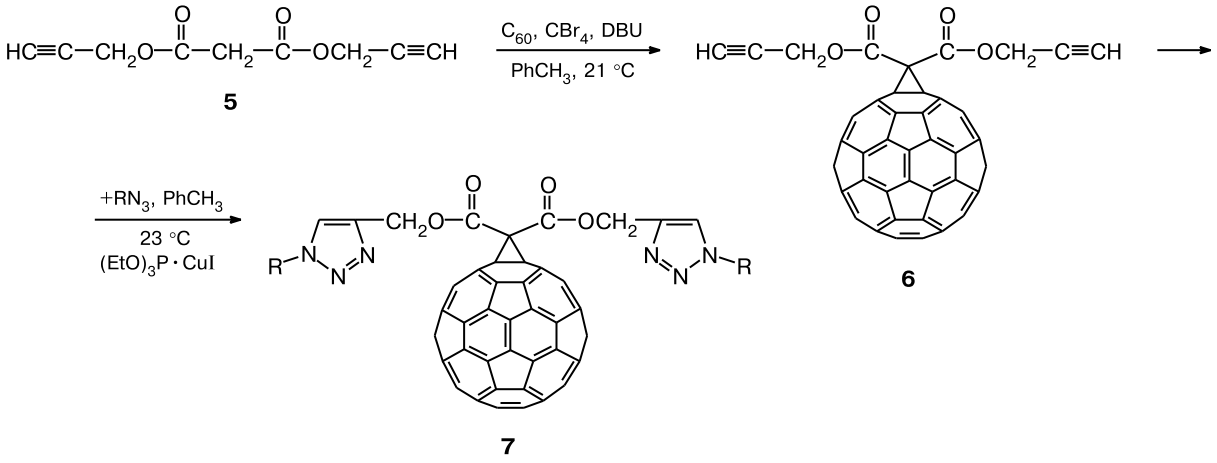


Fig. 4. The principal heteronuclear correlations (shown with arrows from the ^1H to the X nucleus) for compounds **3** and **4** (the upper part of the fullerene sphere is shown schematically).

Scheme 4



R = CH_2Ph

action of compound **6** with benzylazide in the presence of the catalyst $(EtO)_3P \cdot CuI$ led to the formation of the triazole methanofullerene **7** (Scheme 4). Compounds **6** and **7** were isolated by column chromatography on silica gel in 46 and 44% yields, respectively. Spectral characteristics of compound **5** corresponded to the literature data.[17] The structures of the obtained compounds **6** and **7** were also confirmed by a combination of spectroscopic methods.

The mass spectra of compounds **6** and **7** exhibited peaks of the molecular ions with m/z 898.02 and 1065.1 $[M + H]^+$, respectively, which confirmed the composition of the methanofullerenes under study.

A number of 1D and 2D NMR correlation experiments were used to confirm the structures of compounds **6** and **7**, as well.

The 1D ^{13}C NMR spectra of compounds **6** and **7** exhibited 17 signals with δ 145—136 in the region indicative for the sp^2-hybridized C atoms of the fullerene sphere, as well as the signals for the sp^3-hybridized atoms C(1)/C(6) (δ ~71). The chemical shift for the C(1)/C(6) (70.9 and 71.2 for **6** and **7**, respectively) indicated a closed character of cycloaddition at the 6—6-bond. The ^1H NMR spectra of compounds **6** and **7** and the principal HMBC correlations characteristic of them, which allowed us to establish the structures of the addends, are shown in Fig. 5.

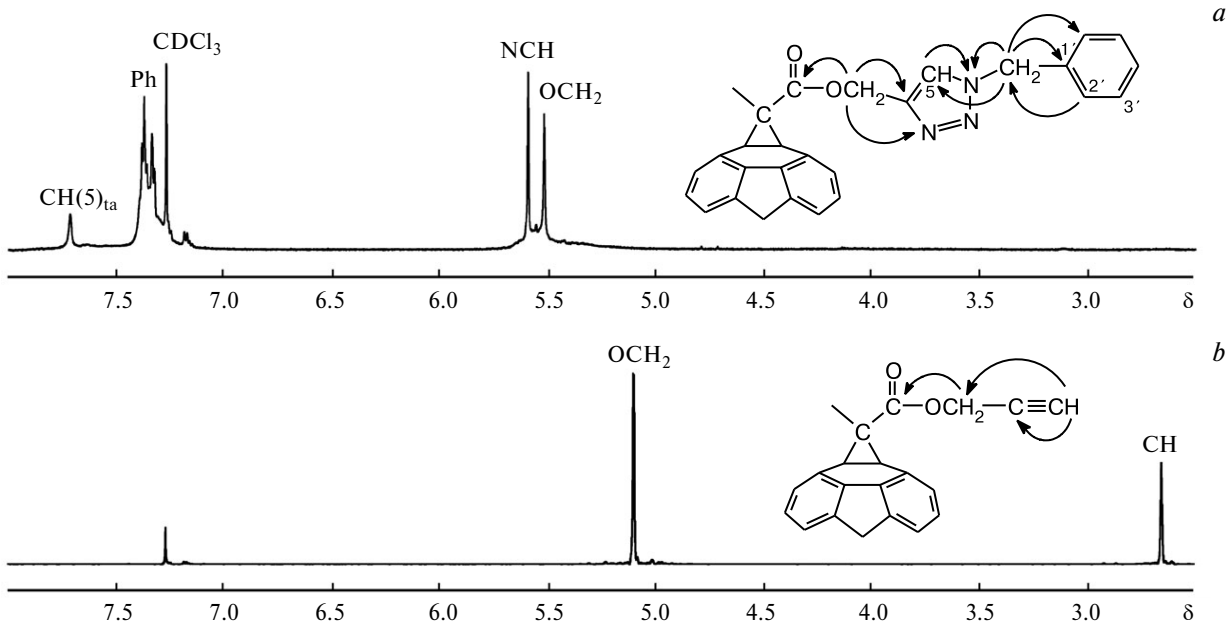


Fig. 5. The ^1H NMR spectra and the principal heteronuclear correlations for compounds **6** (*a*) and **7** (*b*) (only the upper part of the fullerene sphere and a one part of the attached fragment are shown schematically); $CH(5)_{ta}$ is the signal for triazole.

In conclusion, we obtained new alkyne and triazole derivatives of fullerene C_{60} and showed that in the preparation of triazole-containing methanofullerenes, the cycloaddition of azides and alkynes by the "click-chemistry" reaction was preferable as compared to the Bingel—Hirsch reaction, since it led to the formation of only the target compound in high yield. In this case, fullerene did not react with azide under the indicated conditions.

Experimental

Analysis by HPLC was performed on an Agilent Technologies 1200 Series chromatograph with a UV detector, using columns with a C18 reversed phase (Partisil-5 ODS-3) and toluene—MeCN (1 : 1, v/v) as an eluent. Organic solvents were dried and distilled before use. Fullerene C_{60} (99.9%) was purchased from Fulleren Tsentr Inc., Nizhny Novgorod. All chemical manipulations were performed under dry argon.

UV spectra were recorded on a Specord M-40 spectrophotometer in dichloromethane, IR spectra were recorded on a Bruker-Vector 22 Fourier-transform spectrometer (Bruker).

Mass spectra were recorded on a MALDI-TOF mass spectrometer.

1D and 2D NMR experiments (^1H, ^{13}C, and ^{31}P) were performed on an Avance-400 (Bruker) (^1H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{15}N, 40.5 MHz; ^{31}P, 161.9 MHz) spectrometer at 30 °C, using residual signals of $CDCl_3$ as a reference (δ_H 7.26 and δ_C 77.0). Chemical shifts of ^{15}N and ^{31}P were determined relative to the signals of the external standard CD_3CN (δ_N 0.0) or H_3PO_4 (δ_P 0.0), respectively.

NMR chemical shifts for compounds **1** and **2** were calculated by the GIAO B3LYP/6-31G(d) method, using the GAUSSIAN 98 program package.[18]

Diethyl (propargyloxycarbonylmethyl)phosphonate (1). Propargyl chloroacetate (5 g, 0.037 mol) in anhydrous benzene (5 mL) was added dropwise to a refluxed solution of triethyl phosphite (6.3 g, 0.037 mol) in benzene (5 mL) and the reflux was continued for 6 h. Then, the solvent was evaporated to obtain a crude product (7.8 g), which after distillation *in vacuo* at 126—130 °C (2 Torr) yielded compound **1** (5 g, 57%) as a dense oil, n_D^{20} 1.4550, d_4^{20} 1.1715. IR (in KBr pellet), ν/cm^{-1}: 494, 617, 708, 784, 887, 975, 1027, 1114, 1164, 1261 (P=O); 1370, 1394, 1444, 1479, 1642, 1744 (C=O); 2126 (—C=CH); 2912, 2936, 2986. ^{31}P NMR, δ: 18.75. ^1H NMR ($CDCl_3$), δ: 1.24 (t, 6 H, J = 7.3 Hz); 2.45 (t, 1 H, J = 2.7 Hz); 2.93 (d, 2 H, J = 21.7 Hz); 4.075 (m, 4 H); 4.62 (d, 2 H, J = 2.9 Hz).

Diethyl [(1-benzyl-1,2,3-triazol-4-yl)methoxycarbonylmethyl]phosphonate (2). Compound **1** (0.5 g, 2.1 mmol) in anhydrous benzene (10 mL) was placed into a flat-bottom flask, followed by addition of benzylazide (0.28 g, 2 mmol) and a triethyl phosphite complex with CuI (0.15 g, 4.2 mmol). The reaction mixture was stirred at ~20 °C for 7 days using a magnetic stirrer. The reaction progress was monitored recording IR spectra of the reaction mixture and observing decrease in intensity of the band characteristic of the azide group (2098 cm^{-1}). Compound **2** was purified by column chromatography on SiO_2. Unreacted benzylazide and the CuI complex were isolated by elution with a mixture of benzene—ethyl acetate (5 : 2). Elution with ethyl alcohol gave compound **2** (0.5 g, 64.1%). MS (MALDI-TOF), found: m/z 367.370 $[M]^+$. $C_{16}H_{22}N_3O_5P$. Calculated: M = 367.373. IR (in KBr pellet), ν/cm^{-1}: 490, 606, 725, 810, 889, 973, 1029, 1117, 1164, 1262 (P=O), 1369, 1394, 1456, 1498, 1559, 1608, 1733 (C=O), 2912, 2940, 2985, 3140. ^{31}P NMR, δ: 18.88. ^1H NMR ($CDCl_3$), δ: 1.35 (t, 6 H, J = 7.2 Hz); 3.10 (d, 2 H, J_{PCH} = 21.5 Hz); 4.14 (m, 4 H); 5.32 (s, 2 H); 5.67 (s, 2 H); 7.48 (m, 5 H); 7.97 (s, 1 H).

61-(Propargyloxycarbonyl)-61-(diethoxyphosphoryl)methano[60]fullerene (3). A solution of compound **1** (0.1053 g, 0.45 mmol) in toluene, CBr_4 (0.1494 g, 0.45 mmol) in toluene, and DBU (0.0685 g, 0.45 mmol) were sequentially added to a solution of fullerene C_{60} (0.216 g, 0.3 mmol) in toluene (150 mL). The reaction mixture was stirred for 9 h at 28—30 °C. The reaction progress was monitored by HPLC. Then, the reaction mixture was acidified with three drops of 1 M H_2SO_4 and the solution obtained was washed with water (2×30 mL). The organic layer was concentrated *in vacuo* and the residue was deposited on a column with SiO_2. Unreacted C_{60} (15.7 mg) was isolated by elution with a mixture of toluene—hexane (20 : 20, v/v). Elution with a mixture of toluene—acetonitrile (40 : 0.5, v/v) led to the isolation of compound **3** (99.3 mg, 42%, the yield was calculated based on the consumed fullerene C_{60}), as well as to a mixture of bis-adducts. MS (MALDI-TOF): m/z 952.02. $C_{69}H_{13}O_5P$. Calculated: M = 952.05. UV (CH_2Cl_2), λ_{max}/nm (ε): 327 (15 905), 430 (3848), 492 (2107), 696 (142). IR (in KBr pellet), ν/cm^{-1}: 488, 525, 573, 669, 708, 740, 800, 950, 1010, 1042, 1173, 1220, 1259 (P=O), 1367, 1428, 1534, 1738 (C=O), 2922, 2980. ^1H NMR ($CDCl_3$), δ: 1.58 (t, 6 H, J = 7.2 Hz); 2.61 (t, 1 H, J = 2.7 Hz); 4.37 (m, 4 H); 5.06 (d, 2 H, J = 2.3 Hz). ^{31}P {^1H} NMR ($CDCl_3$), δ: 10.76. ^{13}C NMR ($CDCl_3$), δ: 15.26, 16.11, 16.95, 17.80, 47.71—48.79 (J = 164 Hz); 53.33, 54.35, 55.35, 63.55, 64.65, 65.64, 70,04, 75.39, 76.32, 77.89, 77.07, 70.75, 137.08, 140.82, 140.85, 140.92, 141.82, 141.98, 142.14, 142.18, 142.70, 142.94, 142.95, 143.05, 143.13, 143.81, 143.96, 144.49, 144.59, 144.70, 144.81, 144.86, 144.89, 144.93, 144.98, 145.13, 145.24, 145.28, 147.08 ($^3J_{CP}$ = 3 Hz); 163.55.

61-[(1-Benzyl-1,2,3-triazol-4-yl)methoxycarbonyl]-61-(diethoxyphosphoryl)methano[60]fullerene (4). Method *A* (the Bingel—Hirsch reaction). A solution of compound **2** (0.1519 g, 0.41 mmol) in toluene, CBr_4 (0.1375 g, 0.41 mmol) in toluene, and DBU (0.0630 g, 0.41 mmol) were sequentially added to a solution of fullerene C_{60} (0.198 g, 0.27 mmol) in toluene (200 mL). The reaction mixture was stirred for 42 h at ~20 °C. The reaction progress was monitored by HPLC. Then, the reaction mixture was acidified with three drops of 1 M H_2SO_4, the solution obtained was washed with water (2×30 mL). The organic layer was concentrated *in vacuo*, and the residue was deposited on a column with SiO_2. Unreacted C_{60} (15.7 mg) was isolated by elution with a mixture of toluene—hexane (30 : 10, v/v). Elution with a mixture of toluene—acetonitrile (38 : 2, v/v) led to the isolation of compound **4** (58 mg, 25%, the yield was calculated based on the consumed fullerene C_{60}), as well as a mixture of bis-adducts.

Method *B* (click-chemistry). A mixture of compound **3** (0.04 g, 0.04 mmol), benzylazide ($PhCH_2N_3$) (5.6 mg, 0.04 mmol), and the catalyst $(EtO)_3P \cdot CuI$ (2.9 g, 0.008 mmol) in anhydrous toluene (20 mL) was stirred for 74 h at ~20 °C. The reaction progress was monitored by HPLC. Compound **4** (33.9 mg, 89%) was isolated by column chromatography on silica gel with a mixture of toluene—acetonitrile (38 : 2, v/v). MS (MALDI-TOF): m/z 1086.12 $[M + H]^+$. $C_{76}H_{20}O_5PN_3$. Calculated: M = 1085.11.

UV (CH_2Cl_2), λ_{max}/nm (ε): 326 (14 803), 429 (4127), 491 (2087), 696 (132). IR (in KBr pellet), ν/cm^{-1}: 525, 575, 588, 703, 725, 801, 979, 1016, 1044, 1095, 1176, 1220, 1264 (P=O), 1367, 1428, 1495, 1737 (C=O), 2923, 3140. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 11.00. ^1H NMR ($CDCl_3$), δ: 1.45 (t, 6 H, J = 7.0 Hz); 4.45 (m, 4 H); 5.51 (s, 2 H); 5.59 (s, 2 H); 7.28—7.78 (m, 5 H); 7.67 (s, 1 H). ^{13}C NMR ($CDCl_3$), δ: 16.46, 22.59, 31.52, 47.52, 49.14, 54.36, 60.04, 64.53, 64.59, 70.12, 70.16, 109.94, 128.22, 128.95, 129.20, 130.00, 132.34, 136.62, 137.58, 140.78, 140.82, 140.85, 141.67, 141.79, 142.07, 142.15, 142.21, 142.64, 142.92, 142.94, 143.03, 143.05, 143.11, 143.77, 143.94, 144.25, 144.55, 144.60, 144.62, 144.65, 144.79, 144.83, 144.89, 145.11, 145.21, 145.24, 147.14 ($^3J_{P,C}$ = 3 Hz), 163.55.

61-Bis(propargyloxycarbonyl)methano[60]fullerene (6). A solution of freshly distilled dipropargyl malonate **5** (0.113 g, 0.63 mmol) in toluene, CBr_4 (0.208 g, 0.63 mmol) in toluene, and DBU (0.095 g, 0.63 mmol) were sequentially added to a solution of fullerene C_{60} (0.3 g, 0.42 mmol) in anhydrous dichlorobenzene (35 mL) with stirring. The reaction mixture was stirred for 10 h at ~20 °C. The reaction progress was monitored by HPLC. Then, the reaction mixture was acidified with three drops of 1 M H_2SO_4, the solution was washed with water (2×10 mL). The organic layer was concentrated *in vacuo* and the residue was deposited on a column with SiO_2. Unreacted C_{60} (121.5 mg) was isolated by elution with hexane. Elution with a mixture of toluene—hexane (1 : 1) gave compound **6** (102.3 mg, 46%, the yield was calculated based on the consumed fullerene C_{60}), as well as a mixture of bis-adducts (93 mg). MS (MALDI-TOF): m/z 898.02. $C_{69}H_{13}O_5P$. Calculated: M = 898.05. UV (CH_2Cl_2), λ_{max}/nm (ε): 327 (15 905), 430 (3848), 492 (2107), 696 (142). IR (a suspension in Nujol), ν/cm^{-1}: 527, 579, 672, 724, 970, 1001, 1059, 1096, 1182, 1199, 1225, 1266, 1367, 1428, 1539, 1649, 1747 (C=O), 2129, 3291. ^1H NMR ($CDCl_3$), δ: 2.65 (t, 2 H, J = 2.4 Hz); 5.10 (d, 4 H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 50.63 (C_{61}), 54.52 (OCH_2), 70.90 (sp^3), 76.28, 76.55, 139.25, 140.96, 141.81, 142.18, 142.98, 143.00, 143.04, 143.86, 144.60, 144.67, 144.69, 144.93, 145.04, 145.18, 145.28, 162.55.

61-Bis[(1-benzyl-1,2,3-triazol-4-yl)methoxycarbonyl]methano[60]fullerene (7). A mixture of compound **6** (0.059 g, 0.066 mmol), benzylazide ($PhCH_2N_3$) (0.017 g, 0.065 mmol), and the catalyst $(EtO)_3P \cdot CuI$ (0.0047 g, 0.013 mmol) in anhydrous toluene (25 mL) was stirred for 105 h at ~20 °C. The reaction progress was monitored by HPLC. Compound **6** (4.02 mg) was isolated by column chromatography on silica gel eluting with a mixture of toluene—hexane (30 : 10, v/v), compound **7** (31.4 mg, 44%) was isolated by eluting with a mixture of toluene—hexane—MeCN (40 : 4 : 2.5, v/v). MS (MALDI-TOF): m/z 1165.49 $[M + H]^+$. $C_{83}H_{20}N_6O_4$. Calculated: M = 1164.16. UV (CH_2Cl_2), λ_{max}/nm (ε): 3268 (14 950), 428 (4104), 492 (2093), 697 (112). IR (a suspension in Nujol), ν/cm^{-1}: 526, 580, 723, 817, 997, 1026, 1050, 1113, 1156, 1182, 1205, 1228, 1263, 1745 (C=O), 3141. ^1H NMR ($CDCl_3$), δ: 5.52 (s, 4 H, OCH_2); 5.59 (s, 4 H, NCH_2); 7.33—7.37 (m, 5 H, Ar); 7.72 (s, 2 H, CH of triazole ring). ^{13}C NMR ($CDCl_3$), δ: 51.20 (C_{61}); 54.41 (N—CH_2); 60.10 (OCH_2); 71.20 (sp^3-hybridized C atoms, C_{60}); 124.51, 128.30, 128.91, 129.20, 134.40, 139.02, 140.92, 141.70, 141.81, 142.21, 142.37, 143.03, 143.07, 143.90, 144.50, 144.66, 144.68, 144.80, 144.90, 145.01, 145.20, 145.31, 163.20.

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