Supporting Information
for DOI: 10.1055/s-0035-1560498
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New reaction of fullerene C$_{60}$ with cyanoacrylates and EtMgBr in the presence of Ti(O$i$-Pr)$_4$

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Supporting Information

General synthetic procedure
Identification of compounds
Commercially available [60]fullerene (99.5% pure, Sigma-Aldrich) was used. The reaction products were analyzed on a HPLC chromatograph Altex (model 330) (USA) equipped with the UV detector at 340 nm. The mixtures were separated on a metal preparative column Cosmosil Buckyprep Waters (250×10 mm) at ~20 °C. Toluene was used as eluent, the flow rate was 3.0 mL•min⁻¹. The ¹H and ¹³C NMR spectra were run on a Bruker Avance-500 spectrometer at 500.17 and 125.78 MHz, respectively. The mixture of CDCl₃ and CS₂ (1:5) was used as a solvent. The mass spectra were obtained on a MALDI TOF/TOF Autoflex-III Bruker operating in a linear mode. S₈ used as a matrix. For the application on a metal target, the toluene solutions of the samples were used.

**General synthetic procedure**

A 50 mL glass reactor was charged with C₆₀ (20 mg, 0.0278 mmol) in dry chlorobenzene (3 mL) and Ti(Oi-Pr)₄ (0.08 mL, 0.278 mmol) under a dried argon atmosphere at 0 °C. The EtMgBr (1 M solution in diethyl ether, 0.417 mmol) was added dropwise during 2—3 min. The resulting solution was heated to 100 °C, cyanoacrylate (0.04 mL, 0.417 mmol) and EtMgBr (1 M solution in diethyl ether, 0.417 mmol) were added. The reaction mixture stirred for 15 min and was quenched with an 8-10% (aq) solution of HCl. The layers were separated and the organic layer passed through a column with small amount of silica gel. The reaction products 1-9, and the starting fullerene C₆₀ were separated by the semi-preparative HPLC, eluent was toluene. Compound 2 was identified by comparing them spectral parameters with previously reported.
Identification of compounds

1'-Amino-1'-ethyl(cyclohexylidene)acetyl-(C_{60}-I_b)[5,6]fullero[2',3':1,9]cyclopropane (1). IR: 527, 1024, 1095, 1262, 1377, 1444, 1476, 1631, 1696, 2855, 2926, 3436 cm⁻¹. UV (CHCl₃), λₘₐₓ, nm: 262, 327, 430. ¹H NMR (500 MHz, CDCl₃): δ 1.58 (t, 3H, CH₃, J = 9.0), 1.8-2.00 (m, 6H, 3CH₂), 2.78 and 3.05 (both m, 2H, CH₂), 4.57 (q, 2H, CH₂, J = 9.0), 6.84 (broad s, 2H, NH₂). ¹³C NMR (125 MHz, CDCl₃): δ 14.86, 24.86, 25.41, 35.36, 58.13, 60.00, 76.42, 102.92, 135.59, 136.09, 138.86, 140.66, 141.68, 141.85, 142.11, 142.36, 142.68, 142.78, 142.93, 143.17, 143.32, 144.41, 144.68, 145.21, 145.31, 145.44, 145.62, 145.80, 146.09, 146.14, 146.19, 146.54, 146.64, 147.35, 147.50, 152.82, 154.36, 156.01, 167.38. MALDI TOF, m/z 915.128 [M]⁺ (C_{71}H_{17}NO₂).

Figure. Mass spectra MALDI TOF/TOF of compound 1 (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 1 (500.17 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The $^{13}$C NMR spectrum of compound 1 (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 1 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The HMBC spectrum of compound 1 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)
1'-Amino-1'-ethyl(cycloheptylidene)acetyl-(C$_{60}$)[5,6]fulleroc[2',3':1,9]cyclopropane (3).

IR: 527, 763, 1101, 1260, 1375, 1430, 1461, 1633, 1741, 2852, 2923, 3436 cm$^{-1}$. UV (CHCl$_3$), $\lambda_{\text{max}}$, nm: 260, 327, 427. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.59 (t, 3H, CH$_3$, $J = 7.0$), 1.70 and 1.80 (both m, 4H, 2CH$_2$), 2.00 and 2.15 (both m, 4H, 2CH$_2$), 3.03 (m, 4H, 2CH$_2$), 4.50 (q, 2H, CH$_2$, $J = 7.0$), 6.85 (broad s, 2H, NH$_2$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 14.92, 26.31, 31.88, 42.78, 59.88, 60.07, 79.25, 104.57, 134.96, 136.30, 139.19, 140.53, 141.73, 141.92, 142.11, 142.22, 142.63, 142.75, 143.17, 144.41, 144.71, 145.11, 145.25, 145.46, 145.55, 145.62, 145.73, 146.11, 146.14, 146.17, 146.30, 146.49, 148.57, 153.70, 155.51, 156.64, 167.65. MALDI TOF, $m/z$ 929.218 [M]$^+$ (C$_{72}$H$_{19}$NO$_2$).

Figure. Mass spectra MALDI TOF/TOF of compound 3 (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 3 (500.17 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The $^{13}$C NMR spectrum of compound 3 (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 3 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The HMBC spectrum of compound 3 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)
1’-Amino-1’-ethyl(cyclooctylidene)acetyl-(C_{60}-I_h)[5,6]fullero[2’,3’:1,9]cyclopropane (4). IR: 527, 791, 1044, 1094, 1262, 1378, 1451, 1666, 1730, 2852, 2924, 3450 cm\(^{-1}\). UV (CHCl\(_3\)), \(\lambda_{\text{max}}\), nm: 257, 329, 427. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.58 (t, 3H, CH\(_3\), \(J = 7.2\)), 1.00-1.80 (m, 6H, 3CH\(_2\)), 2.18 (m, 4H, 2CH\(_2\)), 2.99 and 3.10 (both m, 4H, 2CH\(_2\)), 4.51 (q, 2H, CH\(_2\), \(J = 7.2\)), 6.93 (broad s, 2H, NH\(_2\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 14.89, 24.63, 25.98, 29.81, 30.15, 37.98, 60.05, 63.17, 79.32, 102.12, 135.41, 136.28, 138.94, 140.56, 141.62, 141.84, 141.88, 142.09, 142.19, 142.65, 142.76, 142.91, 143.18, 143.33, 144.42, 144.73, 145.14, 145.26, 145.43, 145.61, 145.77, 146.04, 146.13, 146.21, 146.53, 146.59, 147.18, 147.52, 153.26, 155.42, 157.03, 168.22. MALDI TOF, \(m/z\) 943.184 [M]\(^+\) (C\(_{73}H\(_{21}\)NO\(_2\)).

Figure. Mass spectra MALDI TOF/TOF of compound 4 (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 4 (500.17 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The $^{13}$C NMR spectrum of compound 4 (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 4 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The HMBC spectrum of compound 4 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)
1′-Amino-1′-ethyl(cyclododecanylidene)acetyl-(C\textsubscript{60}-I\textsubscript{4})[5,6]fullerene[2′,3′:1,9]cyclopropane (5). IR: 527, 782, 1031, 1094, 1128, 1262, 1378, 1495, 1528, 1628, 1695, 2856, 2925, 3469 cm\textsuperscript{-1}. UV (CHCl\textsubscript{3}), λ\textsubscript{max}, nm: 260, 330, 429. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 1.55 (t, 3H, CH\textsubscript{3}, J = 6.8), 1.30-1.70 (m, 18H, 9CH\textsubscript{2}), 2.60 and 3.05 (both m, 4H, 2CH\textsubscript{2}), 4.46 (q, 2H, CH\textsubscript{2}, J = 6.8), 6.95 (broad s, 2H, NH\textsubscript{2}). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 14.83, 23.05, 24.13, 24.32, 27.19, 28.78, 38.92, 59.94, 62.69, 78.22, 101.82, 135.62, 136.32, 139.00, 140.51, 141.63, 141.87, 142.13, 142.62, 142.76, 142.91, 143.18, 143.31, 144.43, 144.73, 145.20, 145.27, 145.43, 145.59, 145.61, 145.77, 146.08, 146.14, 146.22, 146.52, 146.79, 153.38, 154.93, 157.32, 168.55. MALDI TOF, m/z 999.395 [M]- (C\textsubscript{77}H\textsubscript{29}NO\textsubscript{2}).

Figure. Mass spectra MALDI TOF/TOF of compound 5 (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 5 (500.17 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The $^{13}$C NMR spectrum of compound 5 (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 5 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The HMBC spectrum of compound 5 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)
1'-Amino-1'-ethyl(fluorenylidene)acetyl-(C₆₀-Ih)[5,6]fullero[2',3':1,9]cyclopropane (6). IR: 527, 740, 1093, 1135, 1285, 1448, 1549, 1632, 1678, 2926, 2966, 3443 cm⁻¹. UV (CHCl₃), λ_max, nm: 257, 328, 432. ¹H NMR (500 MHz, CDCl₃): δ 0.62 (t, 3H, CH₃, J = 7.2), 3.79 (q, 2H, CH₂, J = 7.2), 7.38 (t, 4H, 4CH, J = 5.0), 7.72 (d, 2H, 2CH, J = 5.0), 7.95 (d, 2H, 2CH, J = 5.0). ¹³C NMR (125 MHz, CDCl₃): δ 13.52, 59.20, 71.01, 75.13, 97.67, 119.85, 127.16, 127.23, 128.03, 133.54, 136.82, 139.76, 140.54, 141.64, 141.75, 141.84, 141.92, 142.01, 142.38, 142.70, 142.72, 143.16, 143.24, 144.28, 144.63, 144.93, 145.13, 145.24, 145.41, 145.52, 145.65, 145.79, 145.87, 145.95, 146.09, 146.52, 147.53, 149.76, 152.50, 155.17, 160.42, 166.75. MALDI TOF, m/z 1026.056 [M+S]⁺ (C₇₈H₁₅NO₂).

Figure. Mass spectra MALDI TOF/TOF of compound 6 (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 6 (500.17 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The $^{13}$C NMR spectrum of compound 6 (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 6 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The HMBC spectrum of compound 6 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)
1'-Amino-1'-ethyl(dibutylmethylidene)acetyl-(C\textsubscript{60}−I\textsubscript{h})[5,6]fullero[2',3':1,9]cyclopropane (7).

IR: 527, 1041, 1266, 1379, 1460, 1631, 1672, 2927, 2956, 3436 cm\(^{-1}\). UV (CHCl\(_3\)), \(\lambda\text{max}\), nm: 259, 320, 427. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 0.97 (t, 6H, 2CH\(_3\), \(J = 7.0\)), 1.30-1.40 (m, 8H, 4CH\(_2\)), 1.53 (t, 3H, CH\(_3\), \(J = 7.0\)), 2.59 (t, 6H, 2CH\(_3\), \(J = 7.0\)), 4.48 (q, 2H, CH\(_2\), \(J = 7.5\)), 6.91 (broad s, 2H, NH\(_2\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 14.44, 14.92, 23.88, 29.04, 41.04, 59.74, 62.09, 75.97, 99.92, 135.13, 136.41, 139.41, 140.53, 141.48, 141.74, 141.85, 141.95, 142.14, 142.56, 142.78, 142.88, 143.35, 144.43, 144.71, 145.16, 145.21, 145.48, 145.64, 145.66, 146.05, 146.09, 146.14, 146.44, 146.65, 147.44, 147.49, 153.03, 155.24, 157.25, 167.67. MALDI TOF, \(m/z\) 959.203 [M] (C\textsubscript{74}H\textsubscript{25}NO\textsubscript{2}).

Figure. Mass spectra MALDI TOF/TOF of compound 7 (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 7 (500.17 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The $^{13}$C NMR spectrum of compound 7 (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 7 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The HMBC spectrum of compound 7 (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)
1'-Amino-1'-ethyl(diphenylmethylene)acetyl-(C_{60}I_0)[5,6]fullerol[2',3':1,9]cyclopropane (8). IR: 526, 725, 753, 1110, 1274, 1447, 1542, 1632, 1675, 2925, 2967, 3467 cm\(^{-1}\). UV (CHCl_3), \(\lambda_{\text{max}}, \text{nm}\): 256, 330, 428. \(^1\)H NMR (500 MHz, CDCl_3): \(\delta\) 0.85 (t, 3H, CH_3, \(J = 7.2\)), 3.97 (q, 2H, CH_2, \(J = 7.2\)), 7.27 (t, 4H, 4CH, \(J = 7.2\)), 7.40 (m, 2H, 2CH), 8.13 (d, 4H, 4CH, \(J = 7.2\)). \(^{13}\)C NMR (125 MHz, CDCl_3): \(\delta\) 13.33, 59.41, 73.03, 75.57, 102.90, 126.99, 127.48, 132.01, 135.11, 136.76, 138.88, 140.55, 141.62, 141.69, 141.97, 142.10, 142.58, 142.78, 142.81, 143.06, 143.19, 144.33, 144.59, 144.95, 145.16, 145.39, 145.43, 145.50, 145.63, 145.95, 146.01, 146.04, 146.50, 147.43, 147.56, 152.37, 155.21, 157.79, 167.31. MALDI TOF, \(m/z\) 999.008 [M]\(^-\) (C_{78}H_{17}NO_2).

Figure. Mass spectra MALDI TOF/TOF of compound 8 (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 8 (500.17 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The $^{13}$C NMR spectrum of compound 8 (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 8 (500.17 MHz for ¹H, 125.78 MHz for ¹³C, solvent CS₂ : CDCl₃ = 5:1)

Figure. The HMBC spectrum of compound 8 (500.17 MHz for ¹H, 125.78 MHz for ¹³C, solvent CS₂ : CDCl₃ = 5:1)
Stereoisomeric mixture of 1'-amino-1'-ethyl(heptylmethylidene)acetyl-(C$_{60}$-I$_{h}$)[5,6]fullero[2',3':1,9]cyclopropane (9a,b). IR: 526, 756, 1034, 1106, 1177, 1251, 1460, 1510, 1638, 1679, 2852, 2926, 3435 cm$^{-1}$. UV (CHCl$_3$), $\lambda_{\text{max}}$, nm: 260, 328, 429. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.93-0.95 (m, 6H, 2CH$_3$), 1.30-1.60 (m, 12H, 6CH$_2$), 1.83 and 1.92 (both m, 2H, CH$_2$), 2.51 and 2.64 (both m, 2H, CH$_2$), 4.40-4.60 (m, 4H, 2CH$_2$), 4.86 (m, 4H, 2CH$_2$), 5.40 (m, 2H, 2CH), 6.63 (broad s, 4H, NH$_2$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 14.50, 14.94, 22.35, 22.50, 23.14, 30.09, 30.17, 31.98, 32.03, 34.64, 34.69, 53.65, 55.21, 59.90, 67.06, 71.62, 76.19, 97.01, 97.43, 136.23, 139.51, 140.59, 141.73, 141.76, 141.81, 141.84, 141.98, 142.04, 142.17, 142.21, 142.40, 142.44, 142.69, 142.78, 142.81, 142.93, 143.17, 143.32, 144.27, 144.43, 144.71, 144.78, 145.17, 145.25, 145.31, 145.41, 145.46, 145.49, 145.50, 145.60, 145.64, 145.69, 145.73, 145.81, 145.87, 146.13, 146.29, 146.46, 146.88, 147.47, 150.62, 150.68, 151.28, 153.65, 153.72, 155.84, 156.01, 157.41, 157.46, 167.07, 167.46. MALDI TOF, $m/z$ 945.201 [M] (C$_{73}$H$_{23}$NO$_2$).

Figure. Mass spectra MALDI TOF/TOF of compound 9a,b (matrix – elemental sulfur).
Figure. The $^1$H NMR spectrum of compound 9a,b (500.17 MHz, solvent CS$_2$: CDCl$_3$ = 5:1)
Figure. The $^{13}$C NMR spectrum of compound $9a,b$ (125.78 MHz, solvent CS$_2$ : CDCl$_3$ = 5:1)
Figure. The HSQC spectrum of compound 9a,b (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)

Figure. The HMBC spectrum of compound 9a,b (500.17 MHz for $^1$H, 125.78 MHz for $^{13}$C, solvent CS$_2$ : CDCl$_3$ = 5:1)