Electronic supplementary information for the manuscript

“Synthesis of different types of alkoxy fullerene derivatives from chlorofullerene C₆₀Cl₆”

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Fig. S101. ESR spectrum of the reaction mixture $C_{60}Cl_6+DMPO+MeOH+[NBu_4]I$ in toluene proving radical nature of the investigated reaction.
Experimental procedures and selected spectroscopic data

Chloro fullerene C$_{60}$Cl$_6$ was prepared as described in P. A. Troshin et al., *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2003, 11, 165 and stored in dark.

*General procedure for the synthesis of alkoxyfullerenes C$_{60}$(OR)$_5$H and C$_{60}$(OR)$_5$Br using Bu$_4$NBr as a reagent*

Compounds 1a,d, 2e-f,h-j and 3a-b,d,g,i-j were synthesized according to the following procedure. A triple-neck round-bottom 100 mL flask was evacuated and filled with argon three times. Afterwards, 100 mg of C$_{60}$Cl$_6$ (0.11 mmol) and 50 mL of dry chlorobenzene were introduced into the flask in a stream of argon. The mixture was stirred magnetically until complete dissolving of C$_{60}$Cl$_6$ with the formation of a transparent orange solution and then an appropriate amount of the corresponding alcohol (1.1-110 mmol, 10-1000 eq.) was added in one portion. Afterwards, a solution of the Bu$_4$NBr (1.1 mmol, 10 eq.) in 30 ml of dry chlorobenzene was added dropwise to the stirred reaction mixture. In order to obtain compounds 1a,d the reaction mixture was stirred 30 minutes at room temperature and then diluted by toluene and poured on top of a silica gel column. The target products 1a,d were eluted using toluene-acetonitrile mixtures (97-99%:1-3% v/v). The obtained solutions of 1a,d were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds 1a,d were obtained as dark-orange powders.

For preparation of compounds 3a-b, d,g, i-j, the reaction mixture was stirred 1 h at 55°C after addition of Bu$_4$NBr solution. Then the reaction mixture was concentrated at the rotary evaporator, the residue was dissolved in toluene and poured on the top of a silica gel column. The target products 3a-b, d, g, i-j were eluted using toluene-acetonitrile mixtures (97-99% : 1-3% v/v). Compounds 3g, i-j were eluted using toluene-THF mixtures (70-90% : 10-30% v/v). The obtained solutions of 3a-b, d, g, i-j were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds 3a-b, d, g, i-j were obtained as dark-orange powders.

Compounds 2e-f, h-j were isolated as byproducts or even the main products in the reactions between C$_{60}$Cl$_6$ and the corresponding alcohols under the reaction conditions specified above.
General procedure for the DMSO-promoted synthesis of alkoxyfullerenes $C_{60}(OR)_5Br$

Compounds 3a-b, d, g, i-j were also prepared using the DMSO-promoted synthesis according to the following procedure. A corresponding alcohol (1.61 mmol) and 3 ml of dry DMSO were added to the stirred solution of $C_{60}$Cl6 (100 mg, 0.11 mmol) in 150 ml of dry chlorobenzene. Afterwards, a solution of the Bu₄NBr (207 mg, 0.6 mmol) in 50 ml of dry chlorobenzene was added dropwise. The reaction mixture was stirred 30 minutes at room temperature and then diluted by hexanes and poured on top of a silica gel column. The target products 3a-b, d, g, i-j were eluted using toluene-acetonitrile mixtures (98-99% : 1-2% v/v). The obtained solutions were concentrated at the rotary evaporator, the residues were washed with hexanes and dried in air. The target compounds were obtained as dark-orange powders with 53-70% isolated yields.

1a (Yield 45%). ¹H NMR (500 MHz, CDCl₃:CS₂ 1:1, δ, ppm): 3.87 (s, 3H), 3.95 (s, 6H), 3.96 (s, 6H), 4.81 (s, 1H).

¹³C NMR (125 MHz, CDCl₃:CS₂ 1:1, δ, ppm): 55.44 (OCH₃), 55.61 (OCH₃), 55.88 (OCH₃), 59.53 (Csp₃ fullerene cage-H), 78.13 (Csp₃ fullerene cage -O), 80.38 (Csp₃ fullerene cage -O), 82.34 (Csp₃ fullerene cage -O), 140.47, 140.87, 142.97, 143.00, 143.11, 143.49, 143.53, 143.98, 144.43, 144.63, 145.21, 145.65, 146.08, 146.48, 146.81, 147.19, 147.26, 147.72, 147.92, 148.11, 148.18, 148.25, 148.46, 149.18, 149.34, 149.75, 152.07, 154.01.

APCI MS: m/z=875 ([M-H]-).

C₆₅H₁₆O₅ (876.82): calcd. C 89.04, H 1.84; found C 89.29, H 1.84.

1d (Yield 43%). ¹H NMR (600 MHz, CDCl₃, δ, ppm): 0.97-1.06 (m, 15H), 1.47-1.61 (m, 10H), 1.75-1.85 (m, 10H), 4.12 (t, 2H, J = 6.4 Hz), 4.16-4.44 (m, 8H), 4.80 (s, 1H).

¹³C NMR (150 MHz, CDCl₃, δ, ppm): 14.00 (CH₃), 14.03 (CH₃), 14.07 (CH₃), 19.47 (CH₂CH₃), 19.51 (CH₂CH₃), 19.54 (CH₂CH₃), 32.23 (OCH₂CH₂), 32.28 (OCH₂CH₂), 32.34 (OCH₂CH₂), 59.49 (Csp₃ fullerene cage-H), 67.18 (OCH₂), 67.89 (OCH₂), 68.18 (OCH₂), 77.60 (Csp₃ fullerene cage-O), 79.81 (Csp₃ fullerene cage-O), 81.78 (Csp₃ fullerene cage-O), 140.66, 140.81, 142.86, 143.12, 143.35, 143.36, 143.39, 144.05, 144.26, 144.60, 145.25, 145.66, 146.19, 146.55, 146.78, 147.04, 147.15, 147.25, 147.67, 148.07, 148.14, 148.18, 148.57, 148.86, 149.06, 149.22, 152.47, 154.10.

APCI MS: m/z=1086 ([M-H]-).

C₈₀H₄₆O₅ (1087.22): calcd. C 88.38, H 4.26; found C 88.15, H 4.27.

2e (Yield 90%). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 1.37-1.39 (m, 12H), 4.96-5.04 (m, 2H).

ESI MS: m/z=838 ([M]+).

**2f** (Yield 73%). $^1$H NMR (600 MHz, CDCl$_3$, δ, ppm): 1.18-1.22 (m, 12H), 1.98-2.07 (m, 8H), 4.85 (p, 2H, $J$ = 5.8 Hz).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ, ppm): 10.03 (CH$_3$), 10.06 (CH$_3$), 28.00 (CH$_2$), 28.15 (CH$_2$), 79.35 (C$_{sp3}$ fullerene cage-O), 79.62 (CH), 138.54, 139.40, 140.50, 141.27, 142.28, 142.31, 143.02, 143.11, 143.17, 143.29, 143.30, 143.32, 143.37, 143.88, 144.22, 144.31, 144.34, 144.48, 145.60, 145.81, 146.53, 146.82, 146.99, 147.38, 147.49, 148.91, 149.32, 150.78.

ESI MS: m/z=894 ([M$^+$]).

**2h** (Yield 34%). $^1$H NMR (500 MHz, CDCl$_3$, δ, ppm): 3.46 (s, 6H), 3.68 (dd, 4H, $J$ = 5.5; 3.9 Hz), 3.88 (dd, 4H, $J$ = 5.5; 3.9 Hz), 4.11 (t, 4H, $J$ = 4.9 Hz), 4.78-4.86 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ, ppm): 59.18 (CH$_3$), 67.32 (CH$_2$), 70.86 (CH$_2$), 70.92 (CH$_2$), 72.14 (CH$_2$), 79.75 (C$_{sp3}$ fullerene cage-O), 138.57, 139.88, 140.73, 141.23, 142.25, 142.32, 142.90, 143.15, 143.27, 143.31, 143.35, 143.39, 143.64, 143.77, 143.80, 144.22, 144.30, 144.45, 144.48, 145.76, 145.87, 146.58, 146.69, 146.88, 146.99, 147.05, 147.40, 148.21, 149.00, 149.62.

ESI MS: m/z=958 ([M$^+$]).

C$_{70}$H$_{22}$O$_6$ (958.92): calcd. C 87.68, H 2.31; found C 87.42, H 2.32.

**2i** (Yield 36%). $^1$H NMR (500 MHz, CDCl$_3$, δ, ppm): 3.40 (s, 6H), 3.59 (dd, 4H, $J$ = 5.6; 3.8 Hz), 3.72 (dd, 4H, $J$ = 5.6; 3.8 Hz), 3.77-3.79 (m, 4H), 3.88-3.90 (m, 4H), 4.08-4.10 (t, 4H, $J$ = 4.8 Hz), 4.75-4.83 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ, ppm): 59.13 (CH$_3$), 67.30 (CH$_2$), 70.81 (CH$_2$), 70.82 (CH$_2$), 71.00 (CH$_2$), 72.03 (CH$_2$), 79.74 (C$_{sp3}$ fullerene cage-O), 138.57, 139.87, 140.73, 141.23, 142.25, 142.31, 142.89, 143.12, 143.15, 143.27, 143.30, 143.35, 143.39, 143.63, 143.76, 143.80, 144.22, 144.44, 144.48, 145.75, 145.87, 146.58, 146.68, 146.87, 146.97, 147.05, 147.39, 148.22, 148.99, 149.62.

ESI MS: m/z=1053 ([M+Li$^+$]).

C$_{74}$H$_{30}$O$_8$ (1047.03): calcd. C 84.89, H 2.89; found C 84.67, H 2.91.

**2j** (Yield 21%). $^1$H NMR (500 MHz, CDCl$_3$, δ, ppm): 1.54 (s, 18H), 2.95-2.98 (t, 4H, $J$ = 6.4 Hz), 4.81-4.90 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ, ppm): 28.27 (COOC(CH$_3$)$_3$), 36.75 (CH$_2$), 63.70 (CH$_2$), 79.73 (COOC(CH$_3$)$_3$), 80.92 (C$_{sp3}$ fullerene cage-O), 138.57, 139.84, 140.72, 141.26, 142.25, 142.31, 142.90, 143.14, 143.29, 143.31, 143.34, 143.38, 143.63, 143.82, 144.23, 144.30, 144.43, 144.49, 145.75, 145.86, 146.58, 146.66, 146.89, 146.96, 147.05, 147.39, 148.26, 148.99, 149.62, 170.54 (COO).
ESI MS: m/z=1033 ([M+\text{Na}]^+).

3a (Yield 25%). $^1$H NMR (500 MHz, CDCl$_3$, $\delta$, ppm): 3.94 (s, 3H), 3.98 (s, 6H), 4.06 (s, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$, ppm): 55.50 (CH$_3$), 56.00 (CH$_3$), 58.34 (CH$_3$), 65.69 (C$_{sp^3}$ fullerene cage-Br), 77.57 (C$_{sp^3}$ fullerene cage-O), 80.05 (C$_{sp^3}$ fullerene cage-O), 81.51 (C$_{sp^3}$ fullerene cage-O), 138.02, 142.22, 142.42, 142.60, 142.94, 143.35, 143.56, 143.86, 144.37, 144.49, 144.92, 145.02, 145.36, 146.77, 146.95, 147.18, 147.34, 147.35, 147.71, 148.23, 148.33, 148.34, 148.45, 149.02, 149.18, 151.24, 154.65.

ESI MS: m/z=875 ([M-Br]).

C$_{65}$H$_{15}$BrO$_5$ (955.72): calcd. C 81.69, H 1.58, Br 8.36; found C 81.47, H 1.59, Br 8.33.

3b (Yield 38%). $^1$H NMR (600 MHz, CDCl$_3$, $\delta$, ppm): 1.45-1.48 (m, 9H), 1.53 (t, 6H, $J$ = 7.0 Hz), 4.22-4.32 (m, 8H), 4.46-4.51 (m, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$, ppm): 15.35 (CH$_3$), 15.84 (CH$_3$), 16.08 (CH$_3$), 63.76 (OCH$_2$), 64.24 (OCH$_2$), 66.16 (C$_{sp^3}$ fullerene cage-Br), 66.95 (OCH$_2$), 79.54 (C$_{sp^3}$ fullerene cage-O), 81.46 (C$_{sp^3}$ fullerene cage-O), 138.28, 142.50, 142.67, 142.81, 143.24, 143.47, 143.59, 144.13, 144.36, 144.73, 145.08, 145.26, 145.49, 146.94, 147.32, 147.46, 147.79, 147.81, 148.31, 148.44, 148.56, 148.76, 149.07, 149.21, 151.88, 154.66.

ESI MS: m/z=945 ([M-Br$^+$]).

3d (Yield 30%). $^1$H NMR (600 MHz, CDCl$_3$, $\delta$, ppm): 0.96-1.05 (m, 15H), 1.46-1.63 (m, 10H), 1.78-1.89 (m, 10H), 4.15-4.24 (m, 8H), 4.39-4.43 (m, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$, ppm): 13.96 (CH$_3$), 14.06 (CH$_3$), 14.14 (CH$_3$), 19.31 (CH$_2$CH$_3$), 19.56 (CH$_2$CH$_3$), 19.58 (CH$_2$CH$_3$), 31.86 (OCH$_2$CH$_2$), 32.28 (OCH$_2$CH$_2$), 32.39 (OCH$_2$CH$_2$), 66.29 (C$_{sp^3}$ fullerene cage-Br), 67.88 (OCH$_2$), 68.50 (OCH$_2$), 70.98 (OCH$_2$), 79.57 (C$_{sp^3}$ fullerene cage-O), 81.35 (C$_{sp^3}$ fullerene cage-O), 138.34, 142.58, 142.65, 142.87, 143.11, 143.15, 143.47, 143.59, 144.14, 144.36, 144.79, 145.02, 145.26, 145.53, 146.93, 147.32, 147.46, 147.79, 148.31, 148.43, 148.53, 148.56, 148.84, 149.05, 149.19, 151.95, 154.80.

APCI MS: m/z=1086 ([M-Br$^+$]), 1166 ([M$^+$]), 866 ([M-3(O$^-$Bu)-Br$^+$]).

C$_{80}$H$_{45}$BrO$_5$ (1166.11): calcd. C 82.40, H 3.89, Br 6.86; found C 82.23, H 3.91, Br 6.84.

3g (Yield 33%). $^1$H NMR (500 MHz, CDCl$_3$:CD$_3$OD 10:1, $\delta$, ppm): 3.40 (s, 3H), 3.44 (s, 6H), 3.47 (s, 6H), 3.75-3.90 (m, 10H), 4.30-4.44 (m, 8H), 4.48-4.56 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$:CD$_3$OD 10:1, $\delta$, ppm): 58.89 (OCH$_3$), 58.99 (OCH$_3$), 59.17 (OCH$_3$), 65.94 (C$_{sp^3}$ fullerene cage-Br), 67.38 (CH$_2$), 67.88 (CH$_2$), 69.94 (CH$_2$), 71.49 (CH$_2$), 71.84 (CH$_2$), 71.91 (CH$_2$), 77.28 (C$_{sp^3}$ fullerene cage-O), 79.51 (C$_{sp^3}$ fullerene cage-O), 81.48 (C$_{sp^3}$ fullerene cage-O), 137.90, 142.34, 142.38, 142.66, 143.03, 143.48, 143.63, 143.99, 144.45, 144.71, 145.07, 145.09,
145.40, 146.93, 147.29, 147.32, 147.46, 147.47, 147.81, 148.30, 148.45, 148.57, 148.58, 149.12, 149.27, 151.49, 154.63.

ESI MS: m/z=1095 ([M-Br]+).

C_{75}H_{35}BrO_{10} (1175.98): calcd. C 76.60, H 3.00, Br 6.79; found C 76.51, H 3.03, Br 6.77.

3i (Yield 11%). 1H NMR (500 MHz, CDCl3, δ, ppm): 3.36-3.39 (m, 15H), 3.52-3.81 (m, 40H), 3.87-3.98 (m, 10H), 4.33-4.44 (m, 8H), 4.51-4.62 (m, 2H).

13C NMR (125 MHz, CDCl3, δ, ppm): 59.14 (OCH3), 66.05 (Csp3 fullerene cage-Br), 67.59 (CH2), 67.92 (CH2), 68.14 (CH2), 70.11 (CH2), 70.25 (CH2), 70.36 (CH2), 70.53 (CH2), 70.66 (CH2), 70.76 (CH2), 70.87 (CH2), 71.93 (CH2), 72.02 (CH2), 72.49 (CH2), 79.50 (Csp3 fullerene cage-O), 81.54 (Csp3 fullerene cage-O), 137.99, 142.36, 142.42, 142.43, 142.68, 143.03, 143.49, 143.63, 144.01, 144.44, 144.71, 145.05, 145.17, 145.42, 146.94, 146.99, 147.32, 147.46, 147.49, 147.83, 148.34, 148.42, 148.46, 148.59, 149.14, 149.28, 151.56, 154.66.

APCI MS: m/z=1536 ([M-Br]+), 1389 ([M-Br+OR+H2O]+).

3j. 1H NMR (500 MHz, CDCl3, δ, ppm): 1.42 (s, 9H), 1.45-1.46 (m, 36H), 2.73-2.82 (m, 10H), 4.36-4.58 (m, 10H).

13C NMR (125 MHz, CDCl3, δ, ppm): 28.26 (CH3), 28.30 (CH3), 28.34 (CH3), 36.39 (CH2), 36.43 (CH2), 36.72 (CH2), 63.90 (CH2), 64.56 (CH2), 65.73 (Csp3 fullerene cage-Br), 66.49 (CH2), 77.01 (Csp3 fullerene cage-O), 79.52 (Csp3 fullerene cage-O), 80.67 (C(CH3)3), 80.75 (C(CH3)3), 80.78 (C(CH3)3), 81.29 (Csp3 fullerene cage-O), 138.12, 142.55, 142.59, 142.79, 143.00, 143.59, 143.73, 144.07, 144.55, 144.79, 145.11, 145.22, 145.54, 147.01, 147.32, 147.40, 147.56, 147.57, 147.91, 148.42, 148.47, 148.54, 148.65, 149.19, 149.34, 151.68, 154.91, 170.46 (COO), 170.50 (COO), 170.62 (COO).

APCI MS: m/z=1446 ([M-Br]+).

C_{95}H_{65}BrO_{15} (1526.43): calcd. C 74.75, H 4.29, Br 5.23; found C 74.73, H 4.30, Br 5.21.

**General procedure for the synthesis of epoxide-type alkoxyfullerenes C_{60}(OR)_{4}O**

Compounds 4b-c,i were synthesized according to the following procedure. A triple-neck round-bottom 100 mL flask was evacuated and filled with argon three times. Afterwards, 100 mg of C_{60}Cl_{6} (0.11 mmol) and 50 mL of toluene were introduced into the flask in a stream of argon. The mixture was stirred magnetically until complete dissolving of C_{60}Cl_{6} with the formation of transparent orange solution. Afterwards, an excess of the corresponding alcohol (11 mmol, 100 eq.) and 0.1 ml of distilled water were added in one portion. Then a solution of the Bu_{4}NBr (345 mg, 1.1 mmol) in 30 ml of toluene was added dropwise. The reaction mixture was stirred 12 hours at room temperature and then diluted by toluene and poured on top of a silica gel column.
The target products 4b-c,i were eluted using toluene-acetonitrile mixtures (97-99% : 1-3% v/v) after elution of corresponding bromides. The obtained solutions of 4b-c,i were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds 4b-c,i were obtained as dark-orange powders.

**4b** (Yield 31%). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 1.46 (t, 6H, J = 7.0 Hz), 1.52 (t, 6H, J = 7.0 Hz), 4.23-4.33 (m, 6H), 4.45-4.51 (m, 2H).

¹³C NMR (125 MHz, CDCl₃, δ, ppm): 15.83 (CH₃), 16.07 (CH₃), 63.81 (CH₂), 64.46 (CH₂), 76.19 (C₃sp fullerene cage-O), 76.98 (C₃sp fullerene cage-O), 77.24 (C₃sp fullerene cage-O), 79.46 (C₃sp fullerene cage-O), 137.25, 142.43, 142.69, 142.75, 143.45, 143.59, 143.62, 144.11, 144.39, 144.85, 145.03, 145.26, 145.42, 146.93, 147.28, 147.43, 147.49, 147.77, 148.29, 148.33, 148.43, 148.58, 148.61, 148.68, 149.10, 149.19, 151.55, 154.40.

APCI MS: m/z=916 ([M]+).

C₆₈H₂₀O₅ (916.88): calcd. C 89.08, H 2.20; found C 88.94, H 2.21.

**4c** (Yield 17%). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 1.09-1.14 (m, 12H), 1.82-1.96 (m, 8H), 4.13-4.22 (m, 6H), 4.35-4.40 (m, 2H).

¹³C NMR (150 MHz, CDCl₃, δ, ppm): 10.90 (CH₃), 11.04 (CH₃), 23.46 (CH₂), 23.63 (CH₂), 69.85 (CH₂), 70.47 (CH₂), 76.17 (C₃sp fullerene cage-O), 79.49 (C₃sp fullerene cage-O), 137.34, 142.51, 142.73, 142.77, 143.46, 143.60, 143.62, 144.11, 144.39, 144.90, 145.02, 145.25, 145.45, 146.93, 147.28, 147.43, 147.50, 147.77, 148.16, 148.33, 148.43, 148.56, 148.61, 148.71, 149.10, 149.18, 151.64, 154.40.

APCI MS: m/z=972 ([M]+).

**4i** (Yield 25%). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 3.37 (s, 12H), 3.55 (dd, 8H, J = 5.5; 3.8 Hz), 3.65-3.70 (m, 16H), 3.76-3.78 (m, 8H), 3.89 (dt, 8H, J = 9.9; 4.9 Hz), 4.27-4.46 (m, 8H).

¹³C NMR (125 MHz, CDCl₃, δ, ppm): 59.07 (CH₃), 67.79 (CH₂), 68.66 (CH₂), 70.51 (CH₂), 70.59 (CH₂), 70.68 (CH₂), 70.70 (CH₂), 70.80 (CH₂), 71.97 (CH₂), 76.65 (C₃sp fullerene cage-O), 77.24 (C₃sp fullerene cage-O), 77.51 (C₃sp fullerene cage-O), 81.86 (C₃sp fullerene cage-O), 140.44, 142.15, 143.09, 143.20, 143.61, 143.70, 144.37, 144.43, 144.77, 145.17, 145.20, 146.37, 146.47, 146.71, 146.85, 147.05, 147.10, 147.18, 147.22, 147.26, 147.42, 147.73, 148.02, 149.50, 149.66, 150.00, 150.71.

APCI MS: m/z=1411 ([M+Na]+).

C₈₈H₆₀O₁₇ (1389.41): calcd. C 76.07, H 4.35; found C 76.04, H 4.36.

**General procedure for the synthesis of alkoxyfullerenes C₆₀(OR)₅Cl using triethylamine as a base**
Compounds 5a-e,g-i were synthesized according to the following procedure. An excess of the corresponding alcohol (1.1-110 mmol, 10-1000 eq.) and triethylamine (542 mg, 5.36 mmol) were added to the stirred solution of C_{60}Cl_{6} (100 mg, 0.11 mmol) in 70 ml of toluene. The reaction mixture was kept under stirring at room temperature for 30 minutes and then concentrated at the rotary evaporator. The residue was dissolved in toluene and poured on top of a silica gel column. The target products 5a-e were eluted using toluene-acetonitrile mixtures (97-99% : 1-3% v/v). Compounds 5g-i were eluted using toluene-tetrahydrofuran mixtures (70-90% : 10-30% v/v). The obtained solutions of 5a-e,g-i were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds 5a-e,g-i were obtained as dark-orange powders with 38-52% yields.

5a. 1H NMR (600 MHz, bromobenzene-D5, δ, ppm): 3.83 (s, 6H), 3.86 (s, 3H), 3.94 (s, 6H).

13C NMR (150 MHz, bromobenzene-D5, δ, ppm): 55.44 (CH3), 55.91 (CH3), 58.45 (CH3), 73.90 (C_{sp3} fullerene cage-Cl), 77.64 (C_{sp3} fullerene cage-O), 80.10 (C_{sp3} fullerene cage-O), 82.07 (C_{sp3} fullerene cage-O), 138.08, 142.10, 142.39, 142.64, 143.40, 143.62, 143.77, 144.39, 144.44, 144.49, 145.05, 145.09, 145.36, 146.76, 147.15, 147.31, 147.33, 147.63, 147.73, 148.19, 148.30, 148.38, 148.43, 148.94, 149.07, 151.38, 154.43.

ESI MS: m/z=875 ([M-Cl]-).


5b. 1H NMR (500 MHz, CDCl3, δ, ppm): 1.43-1.51 (m, 15H), 4.20-4.43 (m, 10H).

ESI MS: m/z=945 ([M-Cl]-).


5c. 1H NMR (500 MHz, CDCl3, δ, ppm): 1.02 (t, 3H, J = 7.4 Hz), 1.09-1.13 (m, 12H), 1.81-1.94 (m, 10H), 4.13-4.20 (m, 8H), 4.27-4.31 (m, 2H).

13C NMR (125 MHz, CDCl3, δ, ppm): 10.59 (CH3), 10.89 (CH3), 10.99 (CH3), 23.30 (CH2), 23.45 (CH2), 23.62 (CH2), 69.94 (CH2O), 70.27 (CH2O), 72.97 (CH2O), 73.86 (C_{sp3} fullerene cage-Cl), 79.41 (C_{sp3} fullerene cage-O), 81.67 (C_{sp3} fullerene cage-O), 138.21, 142.52, 142.57, 142.69, 143.11, 143.51, 143.62, 144.04, 144.36, 144.51, 144.74, 145.15, 145.31, 145.50, 146.98, 147.36, 147.51, 147.79, 148.18, 148.34, 148.45, 148.52, 148.61, 148.82, 149.05, 149.19, 151.85, 154.27.

APCI MS: m/z=1015 ([M-Cl]-).
C\textsubscript{75}H\textsubscript{35}ClO\textsubscript{5} (1051.53): calcd. C 85.67, H 3.35, Cl 3.37; found C 85.74, H 3.37, Cl 3.35.

\textbf{5d}. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 0.96-1.04 (m, 15H), 1.45-1.63 (m, 10H), 1.78-1.87 (m, 10H), 4.16-4.22 (m, 8H), 4.30-4.35 (m, 2H).

\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 13.97 (CH\textsubscript{3}), 14.08 (CH\textsubscript{3}), 19.29 (CH\textsubscript{2}), 19.54 (CH\textsubscript{2}), 32.06 (CH\textsubscript{2}), 32.27 (CH\textsubscript{2}), 32.40 (CH\textsubscript{2}), 67.92 (CH\textsubscript{2}O), 68.43 (CH\textsubscript{2}O), 71.22 (CH\textsubscript{2}O), 73.86 (C\textsubscript{sp3} fullerene cage-Cl), 79.43 (C\textsubscript{sp3} fullerene cage-O), 81.68 (C\textsubscript{sp3} fullerene cage-O), 138.23, 142.54, 142.59, 142.69, 143.52, 143.63, 144.04, 144.38, 144.48, 144.75, 145.15, 145.32, 145.51, 146.98, 147.37, 147.51, 147.53, 147.80, 148.21, 148.34, 148.46, 148.52, 148.62, 148.83, 149.05, 149.19, 151.89, 154.34.

APCI MS: m/z=1085 ([M-Cl]-).

C\textsubscript{80}H\textsubscript{45}ClO\textsubscript{5} (1121.66): calcd. C 85.66, H 4.04, Cl 3.16; found C 85.50, H 4.05, Cl 3.18.

\textbf{5e}. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 1.44 (dd, 18H, \(J = 11.1; 5.7 \text{ Hz}\)), 1.47 (d, 6H, \(J = 6.0 \text{ Hz}\)), 1.51 (d, 6H, \(J = 6.1 \text{ Hz}\)), 4.69-4.77 (m, 1H), 4.84-4.97 (m, 4H).

\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 24.02 (CH\textsubscript{3}), 24.32 (CH\textsubscript{3}), 24.43 (CH\textsubscript{3}), 24.46 (CH\textsubscript{3}), 70.32 (CH), 70.59 (CH), 72.76 (CH), 74.20 (C\textsubscript{sp3} fullerene cage-Cl), 76.52 (C\textsubscript{sp3} fullerene cage-O), 78.57 (C\textsubscript{sp3} fullerene cage-O), 81.86 (C\textsubscript{sp3} fullerene cage-O), 138.28, 142.60, 142.94, 143.43, 143.53, 143.77, 143.95, 144.29, 144.46, 144.60, 144.86, 145.06, 145.19, 145.41, 146.98, 147.40, 147.55, 147.57, 147.80, 148.31, 148.44, 148.48, 148.50, 148.60, 149.03, 149.15, 152.72, 154.90.

APCI MS: m/z=1015 ([M-Cl]-).

C\textsubscript{75}H\textsubscript{35}ClO\textsubscript{10} (1131.53): calcd. C 79.61, H 3.12, Cl 3.13; found C 79.58, H 3.39, Cl 3.38.

\textbf{5g}. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 3.41 (s, 3H), 3.46 (s, 6H), 3.47 (s, 6H), 3.76-3.87 (m, 10H), 4.35-4.42 (m, 8H), 4.46-4.49 (m, 2H).

\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 59.04 (CH\textsubscript{3}), 59.16 (CH\textsubscript{3}), 59.21 (CH\textsubscript{3}), 67.48 (CH\textsubscript{2}O), 67.85 (CH\textsubscript{2}O), 70.24 (CH\textsubscript{2}O), 71.64 (CH\textsubscript{2}O), 71.85 (CH\textsubscript{2}O), 71.89 (CH\textsubscript{2}O), 73.64 (C\textsubscript{sp3} fullerene cage-Cl), 76.90 (C\textsubscript{sp3} fullerene cage-O), 79.36 (C\textsubscript{sp3} fullerene cage-O), 81.82 (C\textsubscript{sp3} fullerene cage-O), 137.78, 142.08, 142.35, 142.68, 143.51, 143.66, 143.90, 144.40, 144.45, 144.69, 145.19, 145.39, 146.98, 147.34, 147.50, 147.52, 147.76, 147.81, 148.29, 148.33, 148.47, 148.54, 148.64, 149.11, 149.25, 151.44, 154.14.

APCI MS: m/z=1095 ([M-Cl]-).

C\textsubscript{75}H\textsubscript{35}ClO\textsubscript{10} (1131.53): calcd. C 79.61, H 3.12, Cl 3.13; found C 79.37, H 3.15, Cl 3.12.

\textbf{5h}. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 3.35 (s, 3H), 3.39 (s, 6H), 3.40 (s, 6H), 3.51-3.52 (m, 2H), 3.57-3.59 (m, 8H), 3.69-3.70 (m, 2H), 3.72-3.74 (m, 4H), 3.76-3.78 (m, 4H), 3.85-3.89 (m, 6H), 3.92-3.94 (m, 4H), 4.35-4.41 (m, 8H), 4.45-4.48 (m, 2H).

\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}, \(\delta\), ppm): 59.05 (CH\textsubscript{3}), 59.08 (CH\textsubscript{3}), 67.61 (CH\textsubscript{2}O), 68.05 (CH\textsubscript{2}O), 70.33 (CH\textsubscript{2}O), 70.57 (CH\textsubscript{2}O), 70.59 (CH\textsubscript{2}O), 70.66 (CH\textsubscript{2}O), 70.72 (CH\textsubscript{2}O), 72.00
(CH₂O), 72.03 (CH₂O), 72.06 (CH₂O), 73.66 (C₃sp fullerene cage-Cl), 76.93 (C₃sp fullerene cage-O), 79.32 (C₃sp fullerene cage-O), 81.83 (C₃sp fullerene cage-O), 137.82, 142.08, 142.36, 142.69, 143.49, 143.64, 143.88, 144.35, 144.42, 144.63, 145.13, 145.19, 145.36, 146.97, 147.34, 147.51, 147.68, 147.81, 148.34, 148.35, 148.46, 148.54, 148.62, 149.11, 149.24, 151.41, 154.13.

APCI MS: m/z=1373 ([M+Na]+).

5i. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 3.36 (s, 3H), 3.37-3.38 (m, 12H), 3.50-3.57 (m, 10H), 3.60-3.71 (m, 20H), 3.73-3.79 (m, 10H), 3.83-3.93 (m, 10H), 4.33-4.47 (m, 10H).

¹³C NMR (125 MHz, CDCl₃, δ, ppm): 59.06 (CH₃), 67.58 (CH₂O), 68.02 (CH₂O), 68.66 (CH₂O), 70.32 (CH₂O), 70.55 (CH₂O), 70.58 (CH₂O), 70.59 (CH₂O), 70.63 (CH₂O), 70.69 (CH₂O), 70.71 (CH₂O), 70.77 (CH₂O), 70.80 (CH₂O), 71.93 (CH₂O), 71.96 (CH₂O), 73.69 (C₃sp fullerene cage-Cl), 76.93 (C₃sp fullerene cage-O), 79.32 (C₃sp fullerene cage-O), 81.87 (C₃sp fullerene cage-O), 137.81, 142.08, 142.35, 142.69, 143.49, 143.63, 143.88, 144.37, 144.42, 144.63, 145.14, 145.20, 145.36, 146.97, 147.05, 147.34, 147.52, 147.69, 147.81, 148.34, 148.47, 148.55, 148.62, 149.11, 149.25, 151.42, 154.10.

APCI MS: m/z=1536 ([M-Cl]-).

C₉₅H₇₅ClO₂₀ (1572.05): calcd. C 72.58, H 4.81, Cl 2.26; found C 72.49, H 4.85, Cl 2.24.

Synthesis of 3j-H and 3j-K

Compound 3j (80 mg, 0.05 mmol) was dissolved in 15 mL of CH₂Cl₂ and quenched with trifluoroacetic acid (1 mL) at room temperature. The solvent and excess of CF₃COOH were removed in vacuo; the residue was washed with ethyl acetate and then dried in air. Acid 3j-H was obtained as an orange powder with 98% yield.

Afterwards, 3j-H (62 mg, 0.05 mmol) was suspended in distilled water (10 mL) and then aqueous solution of K₂CO₃ (17 mg, 0.125 mmol, in 3 mL of water) was added. The obtained solution was filtered via syringe PES filter and freeze-dried. Compound 3j-K was obtained as an orange light powder with virtually quantitative yield.

3j-H. ¹H NMR (500 MHz, acetone-D₆, δ, ppm): 2.73-2.83 (m, 10H), 4.35-4.60 (m, 10H).

¹³C NMR (125 MHz, acetone-D₆, δ, ppm): 34.42 (CH₂), 34.71 (CH₂), 34.80 (CH₂), 64.18 (CH₂), 64.25 (CH₂), 64.32 (CH₂), 64.46 (CH₂), 66.55 (C₃sp fullerene cage-Br), 76.88 (C₃sp fullerene cage-O), 79.40 (C₃sp fullerene cage-O), 79.45 (C₃sp fullerene cage-O), 81.43 (C₃sp fullerene cage-O), 137.01, 138.34, 142.50, 142.60, 142.73, 142.79, 142.84, 142.92, 143.21, 143.49, 143.51, 143.66, 143.71, 144.12, 144.16, 144.46, 144.51, 144.69, 145.04, 145.18, 145.22, 145.31, 145.36, 145.60, 146.92, 146.96, 147.35, 147.47, 147.49, 147.72, 147.84, 148.32, 148.35, 148.43, 148.46, 148.55, 148.76,
Synchrotron X-ray data for single crystal of 3b·

Synchrotron X-ray data for single crystal of 3b (0.03 × 0.03 × 0.01 mm³) were collected at 100 K on BL14.2 at the BESSY storage ring (Berlin, Germany) using a MAR225 detector, \( \lambda = 0.8551 \) Å. The structures was solved and anisotropically refined using SHELX package. Absorption correction was not applied. Crystal data for 3b: C\(_{70}\)H\(_{25}\)BrO\(_5\), \( M = 1025.81 \), orthorhombic, \( Pnma \), \( a = 19.765(1) \), \( b = 17.350(1) \), \( c = 24.003(2) \) Å, \( V = 8231.2(9) \) Å\(^3\), \( Z = 8 \), \( D_{calc} = 1.656 \) g cm\(^{-3}\). Anisotropic refinement with 9880 reflections and 866 parameters yielded a conventional \( R_1 = 0.104 \) for 4087 reflections with \( I > 2\sigma (I) \) and \( wR_2 = 0.269 \) for all reflections. All methylene and methyl hydrogen atoms were placed into geometrically calculated positions and refined in the riding mode. Both C\(_{60}(OC_2H_5)\)Br molecules are located on a mirror plane so that two halves are independent. Due to approximate fivefold symmetry, both molecules are disordered around pseudo C\(_5\) axes with OC\(_2\)H\(_5\) groups disordered over two positions each. Br atoms are disordered over 2-4 positions. For more details see CCDC 1496548.
**Fig. S1.** UV-VIS spectra of the C$_{60}$Cl$_6$+ Bu$_4$NI+MeOH reaction mixture and solutions of C$_{60}$[OMe]$_5$H and Bu$_4$NI$_3$ in chlorobenzene

**Fig. S2.** HPLC profile of compound 5g (Orbit C18 column, 150 x 4.6 mm, acetonitrile/toluene 70/30 v/v, flow rate 1 mL min$^{-1}$)

**Fig. S3.** APCI MS spectrum of compound 1a
Fig. S4. $^1$H NMR spectrum of compound 1a (* denotes signals of the hydrolysis products)

Fig. S5. $^{13}$C NMR spectrum of compound 1a (* denotes signals of toluene impurity)

Fig. S6. APCI MS spectrum of compound 1d
Fig. S7 $^1$H NMR spectrum of compound 1d

Fig. S8. High-field part of the $^{13}$C NMR spectrum of compound 1d

Fig. S9. Low-field part of the $^{13}$C NMR spectrum of compound 1d
Fig. S10. H-H COSY NMR spectrum of compound 1d

Fig. S11. H-C HSQC NMR spectrum of compound 1d
Fig. S12. APCI mass spectrum of compound 2f

Fig. S13. $^1$H NMR spectrum of compound 2f

Fig. S14. $^{13}$C NMR spectrum of compound 2f
Fig. S15. H-H COSY NMR spectrum of compound 2f

Fig. S16. H-C HSQC NMR spectrum of compound 2f

Fig. S17. APCI mass spectrum of compound 2h
**Fig. S18** $^1$H NMR spectrum of compound 2h

**Fig. S19** $^{13}$C NMR spectrum of compound 2h
Fig. S20  H-H COSY NMR spectrum of compound 2h

Fig. S21  H-C HSQC NMR spectrum of compound 2h
Fig. S22. APCI mass spectrum of compound 2i ([M+Li]+)

Fig. S23. $^1$H NMR spectrum of compound 2i

Fig. S24. $^{13}$C NMR spectrum of compound 2i
Fig. S25. H-H COSY NMR spectrum of compound 2i

Fig. S26. H-C HSQC NMR spectrum of compound 2i
Fig. S27. APCI mass spectrum of compound 2j ([M+Na]+)

Fig. S28. ¹H NMR spectrum of compound 2j

Fig. S29. ¹³C NMR spectrum of compound 2j
Fig. S30. H-C HSQC NMR spectrum of compound 2j

Fig. S31. ESI MS spectrum of compound 3a

Fig. S32. $^1$H NMR spectrum of compound 3a
Fig. S33. $^{13}$C NMR spectrum of compound 3a

Fig. S34 ESI MS spectrum of compound 3b

Fig. S35 $^1$H NMR spectrum of compound 3b
Fig. S36. $^{13}$C NMR spectrum of compound 3b

Fig. S37. APCI mass spectrum of compound 3d

Fig. S38. $^1$H NMR spectrum of compound 3d ("*" denotes signals of C$_{60}$(OC$_4$H$_9$)$_2$ impurity)
Fig. S39. High-field part of the $^{13}$C NMR spectrum of compound 3d

Fig. S40. Low-field part of the $^{13}$C NMR spectrum of compound 3d

Fig. S41. H-C HSQC NMR spectrum of compound 3d
Fig. S42. ESI mass spectrum of compound 3g

Fig. S43. $^1$H NMR spectrum of compound 3g

Fig. S44. $^{13}$C NMR spectrum of compound 3g
**Fig. S45.** H-C HSQC NMR spectrum of compound 3g

**Fig. S46.** APCI mass spectrum of compound 3i: 1536 ([M-Br]), 1389 ([M-Br-OR+H2O])

**Fig. S47** $^1$H NMR spectrum of compound 3i
Fig. S48 $^{13}$C NMR spectrum of compound 3i

Fig. S49 H-H COSY NMR spectrum of compound 3i
**Fig. S50.** H-C HSQC NMR spectrum of compound 3i

![H-C HSQC NMR spectrum of compound 3i](image)

**Fig. S51.** APCI mass spectrum of compound 3j (1446 [M-Cl]+, 1404 [M-Cl-C(CH3)3]+, 1317 [M-Cl-OC2H4COOC(CH3)3]+).

![APCI mass spectrum of compound 3j](image)

**Fig. S52.** $^1$H NMR spectrum of compound 3j

![$^1$H NMR spectrum of compound 3j](image)
Fig. S53. $^{13}$C NMR spectrum of compound 3j

Fig. S54. H-H COSY NMR spectrum of compound 3j (left) and H-C HSQC NMR spectrum of compound 3j (right)

Fig. S55. APCI MS spectrum of compound 4b
Fig. S56. $^1$H NMR spectrum of compound 4b

Fig. S57. $^{13}$C NMR spectrum of compound 4b (* denotes signals of unknown impurity)
**Fig. S58.** H-C HSQC NMR spectrum of compound 4b

**Fig. S59.** H-C HMBC NMR spectrum of compound 4b
Fig. S60. APCI MS spectrum of compound 4c

Fig. S61. ¹H NMR spectrum of compound 4c

Fig. S62. ¹³C NMR spectrum of compound 4c
Fig. S63. H-H COSY NMR spectrum of compound 4c

Fig. S64. H-C HSQC NMR spectrum of compound 4c
Fig. S65. APCI MS spectrum of compound 4i ([M+Na]⁺)

Fig. S66. ¹H NMR spectrum of compound 4i
Fig. S67. $^{13}$C NMR spectrum of compound 4i

Fig. S68. H-C HSQC NMR spectrum of compound 4i
Fig. S69. APCI MS spectrum of compound 5c

Fig. S70. $^1$H NMR spectrum of compound 5c

Fig. S71. $^{13}$C NMR spectrum of compound 5c
**Fig. S72.** H-H COSY NMR spectrum of compound 5c

**Fig. S73.** H-C HSQC NMR spectrum of compound 5c
Fig. S74. APCI MS spectrum of compound 5d

Fig. S75. $^1$H NMR spectrum of compound 5d

Fig. S76. High-field part of the $^{13}$C NMR spectrum of compound 5d
**Fig. S77.** Low-field part of the $^{13}$C NMR spectrum of compound 5d

**Fig. S78.** APCI MS spectrum of compound 5e

**Fig. S79.** $^1$H NMR spectrum of compound 5e
Fig. S80. $^{13}$C NMR spectrum of compound 5e

Fig. S81. APCI MS spectrum of compound 5g
Fig. S82. $^1$H NMR spectrum of compound 5g

Fig. S83. High-field part of the $^{13}$C NMR spectrum of compound 5g
Fig. S84. Low-field part of the $^{13}$C NMR spectrum of compound 5g

Fig. S85. H-H COSY NMR spectrum of compound 5g
Fig. S86. H-C HSQC NMR spectrum of compound 5g

Fig. S87. APCI MS spectrum of compound 5h ([M+Na]⁺)

Fig. S88. ¹H NMR spectrum of compound 5h
Fig. S89. $^{13}$C NMR spectrum of compound 5h

Fig. S90. H-H COSY NMR spectrum of compound 5h
Fig. S91. H-C HSQC NMR spectrum of compound 5h

Fig. S92. APCI mass spectrum of compound 5i

Fig. S93. $^1$H NMR spectrum of compound 5i
Fig. S94. $^{13}$C NMR spectrum of compound 5i

Fig. S95. $^1$H NMR spectrum of compound 3j-H

Fig. S96. $^{13}$C NMR spectrum of compound 3j-H
**Fig. S97.** Comparison of the selected areas in the $^{13}$C NMR spectra of compounds $C_60(OnBu)_5X$ (X=H (1), Br (2) and Cl (3))

**Fig. S98.** Comparison of the selected areas in the $^{13}$C NMR spectra of compounds $C_{60}(OEt)_5Br$ (1) and $C_{60}(OEt)_4O$ (2)
Fig. S99. ESR spectrum of the reaction mixture $\text{C}_{60}\text{Cl}_6 + \text{DMPO} + \text{MeOH} + [\text{NBu}_4]\text{Br}$ in toluene proving radical nature of the investigated reaction.

Fig. S100. ESR spectrum of the reaction mixture $\text{C}_{60}\text{Cl}_6 + \text{DMPO} + \text{MeOH} + \text{NEt}_3$ in toluene proving radical nature of the investigated reaction.

Fig. S101. ESR spectrum of the reaction mixture $\text{C}_{60}\text{Cl}_6 + \text{DMPO} + \text{MeOH} + [\text{NBu}_4]\text{I}$ in toluene proving radical nature of the investigated reaction.