Highly Selective Synthesis of Tetrahydronaphthaleno[60]fullerenes *via* Fullerene-Cation-Mediated Intramolecular Cyclization

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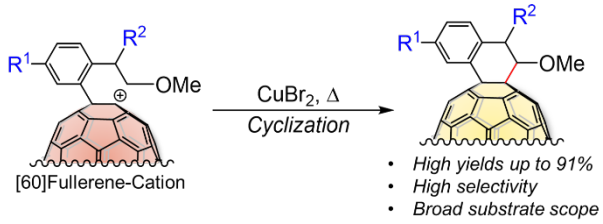


ABSTRACT: High-yielding protocol to construct six-membered carbon rings on fullerene is presented. This methodology with in-situ fullerene-cation-mediated intramolecular cyclization provides high selectivity and efficient access to six-membered tetrahydronaphthaleno[60]fullerenes with remarkable functional group tolerance and excellent yields. Furthermore, high solubilities of tetrahydronaphthaleno[60]fullerenes are reported.

Cyclo[60]fullerenes are widely used [60]fullerene derivatives with applications in several types of photovoltaic devices, including organic thin-film solar cells,[1] polymer solar cells,[2] and recently improved perovskite solar cells.[3] In particular, cyclo[60]fullerenes with six-membered carbon rings, namely, tetrahydronaphthaleno[60]fullerenes, such as indene-C_{60} bis-adduct[4] and methanoindene fullerene,[5] play a dominant role in photovoltaics. Consequently, substantial effort has been devoted to constructing cyclo[60]fullerenes and several synthetic strategies have been established.[6]

Among the reported strategies, Diels–Alder cycloaddition is the most commonly used method for constructing tetrahydronaphthaleno[60]fullerenes.[4a,5a,7] However, this approach suffers from several limitations, such as inevitable multi-addition by-products, high reaction temperature, and low yield. Furthermore, heteroaromatic substituents are incompatible with this method, limiting the functional group tolerance. Accordingly, more efficient synthetic strategies with broader applicability would be of great value.

In our previous studies, fullerene-cation-mediated reactions displayed impressive performance compared with fullerene-radical-mediated and fullerene-anion-mediated approaches,[8] suggesting the possibility of using fullerene-cation-mediated reactions to construct tetrahydronaphthaleno[60]fullerenes. Fullerene cations have a newly formed lowest unoccupied molecular orbital (LUMO) with a lower energy level,[8d,9] permitting a facile and highly efficient intramolecular cyclization via a quasi-E2 pathway (Figure. 1).

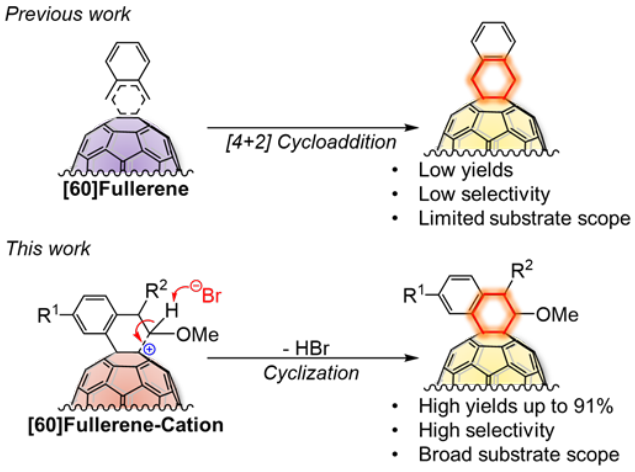
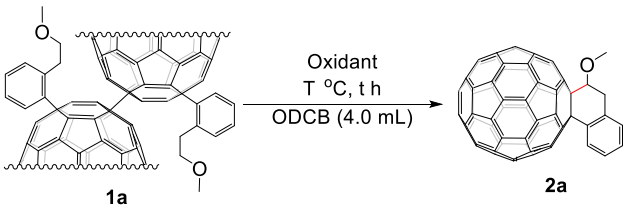


Figure. 1. Concept of the synthetic strategy adopted in this work.

In this work, we report a versatile and scalable Cu(II)-promoted fullerene-cation-mediated strategy to access tetrahydronaphthaleno[60]fullerenes in high yields of up to 91%. Notably, thanks to the excellent functional group tolerance, dimethyl-substituted tetrahydronaphthaleno[60]fullerene **2e** was successfully obtained and found to possess a remarkably high solubility of 34.8 mg/mL in chlorobenzene (CB) and 10.9 mg/mL in $CHCl_3$, which should enable this compound to be fabricated into photovoltaics through the facile spin-coating method rather than costly thermal deposition.[10]

Table 1. Optimization of Reaction Conditions[a]

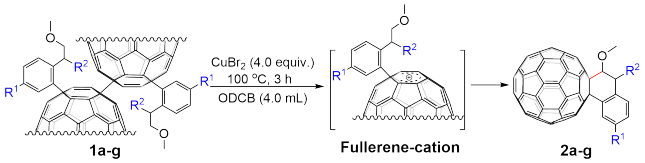


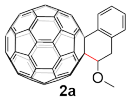
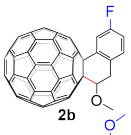
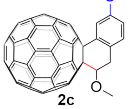
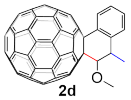
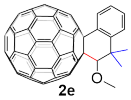
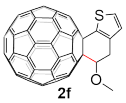
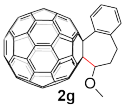
Entry	Oxidant	Temp. (°C)	Time (h)	Yield (%)[b]
1	–	100	3.0	–
2	$K_2S_2O_8$	100	3.0	N.D.[c]
3	Ag_2O	100	3.0	<5
4	AgOAc	100	3.0	<5
5	$Cu(OAc)_2$	100	3.0	10
6	$CuCl_2$	100	3.0	24
7	$Cu(BF_4)_2$	100	3.0	32
8	**$CuBr_2$**	**100**	**3.0**	**89**
9	$CuBr_2$	80	3.0	61
10	$CuBr_2$	120	3.0	75
11	$CuBr_2$	100	2.0	63
12	$CuBr_2$	100	4.0	81
13[d]	$CuBr_2$	100	3.0	74
14[e]	$CuBr_2$	100	3.0	58
15[f]	$CuBr_2$	100	3.0	89

[a] Unless otherwise specified, all reactions were performed using 0.02 mmol of **1a** and oxidant (4.0 equiv.) in 4.0 mL of ortho-dichlorobenzene (*o*-DCB) under ambient atmosphere. [b] Isolated yield. [c] No desired product (N.D.). [d] 2.0 equiv. of CuBr2. [e] 6.0 equiv. of CuBr2. [f] Under argon atmosphere.

The investigation started with screening the reaction conditions using the aryl[60]fullerenyl dimer **1a** as a model substrate, which was synthesized according to our previously reported procedure and summarized in Table 1.[8a–d] First, **1a** (0.03 mmol) was directly heated to 100 °C under ambient atmosphere for 3 h, but the desired product **2a** was not obtained (Table 1, entry 1). Therefore, the fullerene radical intermediate did not promote the intramolecular cyclization. Subsequently, to examine the feasibility of fullerene-cation-mediated intramolecular cyclization, oxidants such as $K_2S_2O_8$, Ag(I) and Cu(II) salts were screened for the *in situ* generation of the fullerene cation accessing the intramolecular cyclization (Table 1, entries 2–8). To our delight, 4.0 equiv. of $CuBr_2$ efficiently generated the fullerene cation intermediate, affording the desired product in 89% yield (Table 1, entry 8). Decreasing the temperature to 80 °C or increasing the temperature to 120 °C did not improve the outcome (Table 1, entries 9 and 10). Decreasing the reaction time to 2.0 h afforded **2a** in 63% yield with residual unreacted dimer **1a** (Table 1, entry 11). However, prolonging the reaction time to 4.0 h also led to a lower yield of **2a** and the formation of by-products due to overoxidation (Table 1, entry 12). Similarly, varying the amount of $CuBr_2$ to 2.0 or 6.0 equiv. decreased the yield of **2a** (Table 1, entries 13 and 14). Intriguingly, when the reaction was conducted under argon atmosphere, the same yield of **2a** was obtained as under ambient atmosphere (Table 1, entry 15). This result demonstrates the extremely high reactivity of fullerene cations compared with fullerene anions and fullerene radicals, which are conventionally prone to oxidation via a single-electron-transfer (SET) pathway in the presence of oxygen.[11] Thus, the reaction proceeded best under the following conditions: aryl[60]dimer **1a** was heated at 100 °C in the presence of 4.0 equiv. of $CuBr_2$ as oxidant for 3.0 h under ambient atmosphere, affording tetrahydronaphthaleno[60]fullerene **2a** in 89% yield.

Table 2. Fullerene-Cation-Mediated Intramolecular Cyclization with Broad Functional Group Tolerance[a]



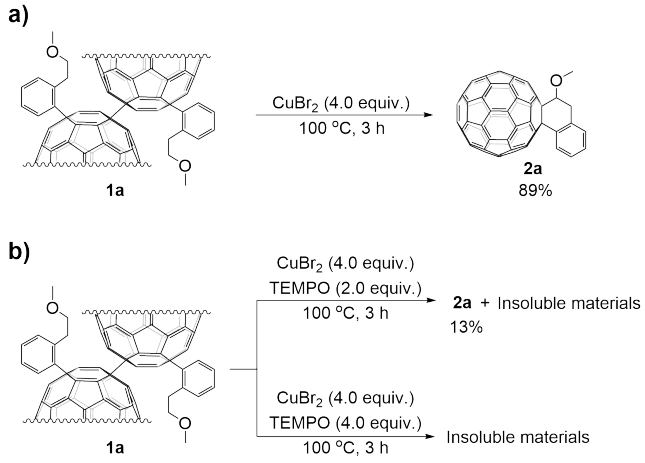
Entry	R^1	R^2	Products 2	Yield (%)[b]
1	H-	H-	 2a	89
2	F-	H-	 2b	78
3	CH_3O-	H-	 2c	91
4	H-	CH_3-	 2d	81
5	H-	CH_3- CH_3-	 2e	76
6	H-	H-	 2f	75
7[c]	H-	H-	 2g	48

[a] Unless otherwise specified, all reactions were performed using 0.02 mmol of aryl[60]fullerenyl dimers **1a**–**g** and 4.0 equiv. of $CuBr_2$ in 4.0 mL *o*-DCB solution at 100 °C for 3.0 h under ambient atmosphere. [b] Isolated yield. [c] The reaction was conducted at 120 °C.

With the optimized reaction conditions in hand, the substrate scope and generality of this protocol were explored (Table 2). To examine the influence of electronegativity on the proposed method, fluoro- and methoxy-substituted aryl[60]fullerenyl dimers **1b** and **1c** were selected as representative compounds containing electron-withdrawing and electron-donating groups, respectively (Table 2, entries 2 and 3). The former compound **2b** was obtained in a lower yield (78%) than the latter compound **2c** (91%). Subsequently, the influence of steric effects was examined by incorporating one or two methyl groups at the benzylic position. The monomethyl- and dimethyl-functionalized products **2d** and **2e** were obtained in yields of 81% and 76%, respectively, indicating slight steric effects (Table 2, entries 4 and 5). Furthermore, the substrate scope also included heteroaromatic compounds, and thiophene-functionalized cyclo[60]fullerene **2f** was obtained in 75% yield (Table 2, entry 6). It should be noted that **2f** is the first six-membered-ring-containing cyclo[60]fullerene including a thiophene structure, and this compound could represent a useful build-

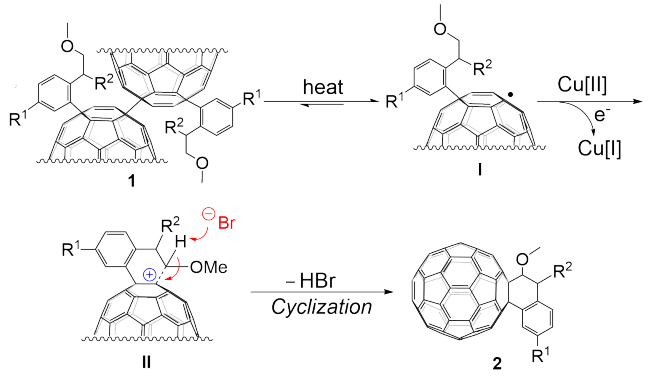
ing block for thiophene functionalization at the 5-position for thin-film organic electronics.[12] More intriguingly, the fullerene-cation-mediated protocol provided access to a seven-membered-ring-containing cyclo[60]fullerene, and the desired product **2g** was obtained in 48% yield (Table 2, entry 7). This relatively low yield is presumably attributable to the instability of seven-membered rings compared with six-membered rings according to Baeyer ring-strain theory.[13] In addition, the scale-up synthesise was exemplified by applying 0.3 g of **1a** under the same conditions, producing **2a** in a high yield of 82%, which demonstrates a facile and scalable way for the production of tetrahydronaphthaleno[60]fullerenes used in photovoltaics.

Scheme 1. Preliminary Mechanistic Studies



To gain further insight into the reaction mechanism, additional experiments were conducted using the conventional radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Scheme 1). The addition of 2.0 equiv. of TEMPO to the reaction dramatically decreased the yield of **2a** to 13%. Further increasing the amount of TEMPO to 4.0 equiv. terminated the reaction and produced large amounts of insoluble materials that precipitated from the solution. These results conclusively demonstrate that fullerene radicals are the precursor of the fullerene cations during this reaction (Scheme 1b).

Scheme 2. Plausible Mechanism for The Formation of Tetrahydronaphthaleno[60]fullerenes



Based on the above experimental results and previous studies,[8b–d] a plausible reaction mechanism involving a fullerene cation intermediate was proposed (Scheme 2). First, the aryl[60]fullerenyl dimer **1** (ArC_{60}-$C_{60}Ar$) undergoes homolysis upon heating at 100 °C to generate the aryl[60]fullerenyl radical intermediate **I** ($ArC_{60}^{\bullet}$). Subsequently, the radical **I** is oxidized by Cu(II) through a SET process, resulting in the *in situ* generation of the key species, [60]fullerene cation **II** (ArC_{60}^{+}). Finally, cation **II** undergoes intramolecular cyclization to afford the tetrahydronaphthaleno[60]fullerene derivative **2** with the concomitant loss of one molecule of HBr, that is generated by the deprotonation by a bromide anion.

Table 3. Solubility of Selected Products at 298.0 K[a]

Product	Solubility in CB (mg/mL)	Solubility in $CHCl_3$ (mg/mL)
C_{60}[b]	6.4	0.3
2a	29.1	18.9
2d	24.7	15.5
2e	34.8	21.8
$PC_{61}BM$[c]	40.0	27.6

[a] All solubilities were measured under the same conditions. [b] The reported solubility of C_{60} is 6.5 mg/mL in CB and 0.3 mg/mL in $CHCl_3$.[14] [c] The reported solubility of $PC_{61}BM$ is 45.0 mg/mL in CB and 27.0 mg/mL in $CHCl_3$.[15]

As the solubility of fullerenes is a crucial parameter for photovoltaic applications,[1c,12a,16] the solubility of selected potential photovoltaic fullerene candidates was measured in the conventionally used solvents CB and $CHCl_3$ (Table 3). The introduction of long aliphatic chain moieties, such as hexyl or 2-ethylhexyl groups, is a widely employed strategy for improving solubility.[17] Intriguingly, the dimethyl-functionalized compound **2e** displayed a similar solubility to $PC_{61}BM$ in both CB and $CHCl_3$, demonstrating the possibility of improving the solubility without introducing bulky long aliphatic chains.

Table 4. Half-Wave Reduction Potentials[a]

Fullerene	E_1 (V)	E_2 (V)
C_{60}	–1.10	–1.52
$PC_{61}BM$	–1.17	–1.56
2a	–1.19	–1.57
2b	–1.17	–1.56
2c	–1.18	–1.56
2d	–1.20	–1.60
2e	–1.20	–1.59
2f	–1.17	–1.57
2g	–1.18	–1.57

[a] The CVs of fullerenes (1.0 mM) were measured in *o*-DCB containing 0.1 M of n-Bu_4NClO_4 versus ferrocene/ferrocenium as internal reference.

Finally, cyclic voltammograms (CVs) of compounds **2a**–**g** were measured to evaluate their reduction potentials (Table 4). As expected, tetrahydronaphthaleno[60]fullerenes displayed similar LUMO levels to $PC_{61}BM$, which can be reasonably attributed to the same π-electron system (58 π electrons) smaller than C_{60} (60 π electrons).[1b,5a,18] The remarkably low LUMO levels of these compounds could permit their application as electron-transporting materials in perovskite solar cells.[19]

In summary, a highly selective and efficient synthesis of tetrahydronaphthaleno[60]fullerenes based on fullerene-cation-mediated intramolecular cyclization has been successfully developed. This protocol features remarkably high yields, excellent selectivity, and broad substrate scope, and not only represents a novel alternative to conventional synthetic methods but also generates fullerene materials with potential photovoltaic applications.

EXPERIMENTAL PROCEDURES AND CHARACTERIZATIONS

General Information. Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware with standard vacuum-line techniques. All reactions that require heating use an oil bath as the heat source. All NMR spectra were taken at 400 MHz (Bruker AVANCE III 400 spectrometer). Unless otherwise specified, all the NMR spectra were recorded in parts per million (ppm, scale) with the proton of $CDCl_3$ (7.26 ppm) or the proton of 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) (6.00 ppm) for ^1H NMR and carbon of $CDCl_3$ (77.16 ppm) or carbon of TCE-d_2 (73.78 ppm) for $^{13}C\{^1H\}$ NMR as internal reference, respectively. The data were presented as following order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, hept = heptet, m = multiplet and/or multiplet resonances), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (*italic*). High-resolution mass spectra (HRMS) were obtained by MALDI or ESI using a time-of-flight mass analyzer on a Bruker Ultra exTOF/TOF spectrometer.

Experimental procedures for synthesis of the starting materials. The starting materials, aryl bromides used for the synthesis of monoarylated fullerenes necessary in this work was prepared from esters **3**, which were converted to carboxylic acids **4**, alcohols **5**, and then methyl ethers **6**. When intermediate compounds are commercially available, we can start synthesis from those compounds. As for the conversion from **5** to **6**, we used a general procedure A.

General Procedure **A**: To a solution of **5** (10.0 mmol) in dry *N*,*N*-dimethylformamide (20.0 mL) was cooled to 0 °C in an ice water bath. And sodium hydride (60% in oil, 480 mg, 12.0 mmol) was slowly added and stirred for 10 min at 0 °C. Then methyl iodide (2.13 g, 15.0 mmol) was added to the reaction mixture. After stirring at room temperature for 3 h, it was carefully quenched with water and the aqueous phase was extracted with AcOEt (3 × 30.0 mL). The combined organic layers were washed with brine (40.0 mL) and dried over sodium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (20:1 = PE:EA) to afford the product **6**.

Synthesis of Grignard reagents An anhydrous tetrahydrofuran (THF) (5.0 mL) solution of aryl bromides **6a**–**g** (10 mmol) was slowly dropped into another anhydrous THF (5.0 mL) solution with polished Mg powder (360.0 mg, 15 mmol) and a trace amount of $BrCH_2CH_2Br$ under an argon atmosphere at 0 °C. After vigorously stirred 1 hour, the prepared Grignard solution was transferred by Schlenk operation and stocked in a Schlenk bottle. The concentration was confirmed before using through anhydrous titration by using menthol as titrant with a trace amount of 1,10-phenanthroline as indicator under an argon atmosphere.

Synthesis of organo(hydro)[60]fullerenes precursors ($ArC_{60}H$). To a solution of C_{60} (100 mg, 0.139 mmol) in *ortho*-dichlorobenzene (*o*-DCB) (25.0 mL) containing 1,3-dimethyl-2-imidazolidinone (476 mg, 4.17 mmol) was added a tetrahydrofuran (THF) solution of different Grignard reagents (ArMgBr, 0.556 mmol) under the argon atmosphere at 25 °C. After vigorously stirring for 20 min, CH_3COOH solution (0.4 mL) was added to quench the reaction for 10 min at room temperature. The resulting dark red solution was filtrated through a pad of gel plug to remove the insoluble salts and then volatile components were removed under reduced pressure. The residue ($ArC_{60}H$) was further purified by a silica gel column with the CS_2 as the eluent, producing hydroaryl[60]fullerenes with isolated yields of 83–90%.

Synthesis of aryl[60]fullerenyl dimers (ArC_{60}-$C_{60}Ar$). To a solution of organo(hydro)[60]fullerenes precursors ($ArC_{60}H$) (0.100 mmol, 1.00 equiv.) in *o*-DCB (10.0 mL) was added a THF solution of *t*-BuOK (0.120 mmol, 1.20 equiv., 1.00 mol/L) under the argon atmosphere at room temperature. After vigorously stirring for 20 min, NBS (0.40 mmol, 4.00 equiv.) was added under the argon atmosphere at room temperature for further 1 hour. Later, the resulting mixture was quenched by 0.2 mL water, and then evaporated in vacuo to remove the volatile solvent. Finally, the residue was further separated on a silica gel column with CS_2 as the eluent to afford aryl[60]fullerenyl dimers in 86–98%.

Synthesis of tetrahydronaphthaleno[60]fullerene derivatives. To a solution of aryl[60]fullerenyl dimer (ArC_{60}-$C_{60}Ar$) (0.0200 mmol, 1.00 equiv.) in *o*-DCB (4.0 mL) was added anhydrous $CuBr_2$ (0.0800 mmol, 4.00 equiv.) under an air atmosphere. After stirring for 3 hours at 100 °C, the resulting mixture was filtrated through a silica gel plug to remove insoluble materials, and then evaporated in vacuo to remove the solvent. Finally, the residue was further separated on a silica gel column with CS_2 as the eluent to afford tetrahydronaphthaleno[60]fullerenes with isolated yields of 48–91%.

Synthesis of 1-bromo-2-(2-methoxyethyl)benzene (6a). 6a was synthesized from commercially sourced **5a** (2-(2-bromophenyl)ethan-1-ol) according to General Procedure **A**. (2.01 g, 9.40 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.27–7.20 (m, 2H), 7.07–7.03 (m, 1H), 3.60 (t, J = 7.2 Hz, 2H), 3.35 (s, 3H), 3.02 (t, J = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.3, 132.9, 131.1, 128.1, 127.5, 124.7, 71.8, 58.7, 36.4. HRMS (ESI-TOF) (m/z): $[M^+]$ calcd for $C_9H_{11}BrO$, 213.9993; found, 213.9996.

Synthesis of 2-(2-bromo-4-fluorophenyl)ethan-1-ol (5b). To a solution of 2-(2-bromo-4-fluorophenyl)acetic acid (4.62 g, 20.0 mmol, 1.00 equiv.) in dry THF (80.0 mL) cooled in an ice water bath were added $NaBH_4$ pellets (1.52 g, 40.0 mmol, 2.00 equiv.) under a flow of nitrogen over 15 min. To the resulting mixture was added $BF_3{\cdot}Et_2O$ (2.66 mL, 21.0 mmol, 1.05 equiv.) dropwise by syringe over 15 min. The mixture was allowed to stir at 60 °C for 1 h. Upon completion, the mixture was quenched by addition of MeOH (30.0 mL) and was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the residue was extracted with ethyl acetate (150 mL), and the mixture was washed with brine (2 × 50.0 mL). The organic layer was further dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to afford the product **5b** (4.26 g, 19.6 mmol, 98%).[20] ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 7.22–7.18 (m, 1H), 6.94 (ddd, J_1 = 10.8 Hz, J_2 = 8.4 Hz, J_3 = 2.4 Hz, 1H), 3.77 (t, J = 6.8 Hz, 2H), 3.39 (br, 1H), 2.93 (t, J = 6.8 Hz, 2H). literature data: ^1H

NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.23–7.20 (m, 1H), 7.00 (ddd, J_1 = 8.0 Hz, J_2 = 7.5 Hz, J_3 = 1.5 Hz, 1H), 3.73 (t, J = 7.1 Hz, 2H), 3.34 (s, 1H), 2.89 (t, J = 7.1 Hz, 2H).

Synthesis of 2-bromo-4-fluoro-1-(2-methoxyethyl)benzene (6b). 6b was synthesized from **5b** (2.18 g, 10.0 mmol) according to General Procedure **A**. (2.16 g, 9.30 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 2H), 6.95 (ddd, J_1 = 10.8 Hz, J_2 = 8.0 Hz, J_3 = 2.4 Hz, 1H), 3.57 (t, J = 6.8 Hz, 2H), 3.35 (s, 3H), 2.98 (t, J = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.1 (d, J = 249.9 Hz), 134.2 (d, J = 3.5 Hz), 131.8 (d, J = 8.3 Hz), 124.3 (d, J = 9.4 Hz), 119.9 (d, J = 24.2 Hz), 114.5 (d, J = 20.8 Hz), 71.7, 58.7, 35.6. HRMS (ESI-TOF) (m/z): [M$^+$] calcd for $C_9H_{10}BrFO$, 231.9899; found, 231.9895.

Synthesis of 2-(2-bromo-4-methoxyphenyl)ethan-1-ol (5c). 5c was synthesized from commercially sourced **4c** (4.88 g, 20.0 mmol) according to the procedure from **4b** to **5b.** (4.32 g, 18.8 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 2.8 Hz, 1H), 6.80 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 3.81 (t, J = 6.8 Hz, 2H), 3.76 (s, 3H), 2.94 (t, J = 6.8 Hz, 2H), 2.03 (br, 1H). literature data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 2.6 Hz, 1H), 6.84 (dd, J_1 = 8.4 Hz, J_2 = 2.6 Hz, 1H), 3.87 (t, J = 6.7 Hz, 2H), 3.81 (s, 3H), 2.99 (t, J = 6.7 Hz, 2H), 2.05 (s, 1H).

Synthesis of 2-bromo-4-methoxy-1-(2-methoxyethyl)benzene (6c). 6c was synthesized from **5c** (2.30 g, 10 mmol) according to General Procedure **A**. (2.27 g, 9.30 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.4 Hz, 1H), 7.09 (d, J = 2.8 Hz, 1H), 6.79 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 3.76 (s, 3H), 3.56 (t, J = 7.2 Hz, 2H), 3.36 (s, 3H), 2.96 (t, J = 6.8 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.7, 131.4, 130.1, 124.7, 118.0, 113.7, 72.1, 58.7, 55.6, 35.5. HRMS (ESI-TOF) (m/z): [M−OCH_3]$^+$ calcd for $C_9H_{10}BrO$, 212.9915; found, 212.9900.

Synthesis of methyl 2-(2-bromophenyl)propanoate (3d'). NaHMDS (17.5 mL of a 2.00 M solution in THF, 35.0 mmol, 1.00 equiv.) was added dropwise at 0 °C to a stirred solution of the ester **3d** (7.98 g, 35.0 mmol, 1.00 equiv.) in freshly distilled THF (110.0 mL). The mixture was stirred at 20°C for 45 min and iodomethane (2.2 mL, 35.0 mmol, 1.00 equiv.) was added dropwise. After stirring at 20°C for 3 h, the reaction mixture was quenched with a saturated aq. solution of NH_4Cl and the aqueous phase was extracted with AcOEt (3 x 20.0 mL). The combined organic layers were washed with brine (40.0 mL). The extracts were then dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography (heptanes/AcOEt: 9/1) to afford **3d'** as colorless oil (7.04 g, 29.1 mmol, 83%).[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 1H), 7.32–7.26 (m, 2H), 7.13–7.09 (m, 1H), 4.23 (q, J = 6.8 Hz, 1H), 3.68 (s, 3H), 1.49 (d, J = 7.2 Hz, 3H). literature data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 1H), 7.30 (m, 2H), 7.11 (m, 1H), 4.22 (q, J = 7.0 Hz, 1H), 3.69 (s, 3H), 1.49 (d, J = 7.0 Hz, 3H).

Synthesis of 2-(2-bromophenyl)propan-1-ol (5d). In a 250 mL round bottom flask, 4.84 g (20.0 mmol, 1.00 equiv.) of the ester (**3d'**) was taken up in 100.0 mL of dry THF under an atmosphere of N_2. The reaction solution was cooled to 0°C in a wet ice bath. To this was slowly added 11.0 mL (22.0 mmol, 1.10 equiv.) of the LAH solution (2.00 M in THF). The reaction was allowed to stir for 1 h. The wet ice bath was recharged with more ice and the reaction was then slowly and carefully quenched with 20.0 mL of 2.00 M HCl solution. Once the reaction was quenched, the mixture was poured into 50.0 mL of H_2O. The aqueous phase was extracted with AcOEt (3 x 50.0 mL). The combined organic layers were washed with brine (50.0 mL). The extracts were then dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography (heptanes/AcOEt: 8/1) to afford **5d** as a colorless oil (4.06 g, 19.0 mmol, 95%).[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.30–7.23 (m, 2H), 7.08–7.04 (m, 1H), 3.78–3.74 (m, 1H), 3.67–3.62 (m, 1H), 3.48 (dt, J_1 = 13.2 Hz, J_2 = 6.4 Hz, 1H), 1.93 (br, 1H), 1.27 (d, J = 7.2 Hz, 3H). literature data: ^{1}H NMR (400 MHz, acetone-d_6) δ 1.25 (s, 3H), 3.50–3.64 (m, 1H), 3.67–3.81 (m, 2H), 7.01–7.14 (m, 1H), 7.27–7.41 (m, 2H), 7.55 (d, J = 7.86 Hz, 1H).

Synthesis of 1-bromo-2-(1-methoxypropan-2-yl)benzene (6d). 6d was synthesized from **5d** (2.14 g, 10.0 mmol) according to General Procedure **A**. (2.14 g, 9.40 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 4.4 Hz, 2H), 6.98–6.92 (m, 1H), 3.52–3.42 (m, 2H), 3.32–3.27 (m, 1H), 3.25 (s, 3H), 1.18 (d, J = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.1, 133.0, 127.8, 127.7, 127.6, 124.9, 77.1, 58.8, 38.3, 17.7. HRMS (ESI-TOF) (m/z): [M$^+$] calcd for $C_{10}H_{13}BrO$, 228.0150; found, 228.0152.

Synthesis of methyl 2-(2-bromophenyl)-2-methylpropanoate (3e'). To a stirred solution of HMDS (8.5 mL, 40.0 mmol, 2.00 equiv.) in THF (50.0 mL) was added n-BuLi (22.0 mL, 1.60 M in hexane, 40.0 mmol, 2.00 equiv.) at 0 °C. After the mixture was stirred for 1.5 h, a solution of **3e** (4.56 g, 20.0 mmol, 1.00 equiv.) in THF (50.0 mL) was added, and the mixture was stirred for 2 h at room temperature. Then MeI (2.5 mL, 40.0 mmol, 2.00 equiv.) was added at 0 °C, and the mixture was stirred for 12 h at room temperature. The reaction was quenched by addition of 1.00 M HCl at 0 °C. The crude mixture was extracted with EtOAc (3 x 50.0 mL) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to afford the product **3e'** (4.50 g, 17.6 mmol, 88%).[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.42 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.32 (ddd, J_1 = 8.8 Hz, J_2 = 7.6 Hz, J_3 = 1.2 Hz, 1H), 7.11 (ddd, J_1 = 9.6 Hz, J_2 = 8.0 Hz, J_3 = 1.6 Hz, 1H), 3.68 (s, 3H), 1.64 (s, 6H). literature data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.45 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H), 7.33 (ddd, J_1 = 8.6 Hz, J_2 = 7.6 Hz, J_3 = 1.2 Hz, 1H), 7.14 (ddd, J_1 = 8.6 Hz, J_2 = 8.0 Hz, J_3 = 1.6 Hz, 1H), 3.70 (s, 3H), 1.65 (s, 6H).

Synthesis of 2-(2-bromophenyl)-2-methylpropan-1-ol (5e). 5e was synthesized from **3e'** (3.84 g, 15.0 mmol) according to the procedure from **3d'** to **5d.** (3.17 g, 13.9 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.32–7.24 (m, 1H), 7.22–7.17 (m, 1H), 7.01–6.97 (m, 1H), 3.94 (s, 2H), 3.52 (s, 1H), 1.42 (s, 6H). literature data: ^{1}H NMR (400 MHz, acetone-d_6) δ 1.48 (s, 6H), 3.94 (d, J = 5.71 Hz, 2H), 7.04–7.15 (m, 1H), 7.26–7.35 (m, 1H), 7.50–7.65 (m, 2H).

Synthesis of 1-bromo-2-(1-methoxy-2-methylpropan-2-yl)benzene (6e). 6e was synthesized from **5e** (2.28 g, 10.0 mmol) according to General Procedure **A**. (2.30 g, 9.50 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.33 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.18–7.14 (m, 1H), 6.94 (ddd, J_1 = 9.2 Hz, J_2 = 8.0 Hz, J_3 = 1.2 Hz, 1H), 3.68 (s, 2H), 3.24 (s, 3H), 1.42 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.7, 135.8, 129.6, 127.8, 127.4, 122.5, 80.0, 59.3, 41.2, 25.5 (2C). HRMS (ESI-TOF) (m/z): [M$^+$] calcd for $C_{11}H_{15}BrO$, 242.0306; found, 242.0303.

Synthesis of methyl 2-(2-bromothiophen-3-yl)ethan-1-ol (5f'). In the absence of light, a solution of NBS (3.56 g, 20.0 mmol,

1.00 equiv.) in DMF (20.0 mL) was added dropwise to a solution of **5f** (2.56 g, 20.0 mmol, 1.00 equiv.) in DMF (20.0 mL). After stirring for 3 h, the reaction mixture was quenched with ice-water and extracted with dichloromethane. Combined organic phases were washed with water, dried over magnesium sulfate, and concentrated under vacuum. Distillation of the crude product gave 3.75 g (18.2 mmol, 91%) of desired product.[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 5.6 Hz, 1H), 6.87 (d, J = 5.6 Hz, 1H), 3.83 (t, J = 6.8 Hz, 2H), 2.86 (t, J = 6.8 Hz, 2H), 1.69 (s, 1H). literature data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 5.6 Hz, 1H), 6.87 (d, J = 5.6 Hz, 1H), 3.84 (t, J = 6.6 Hz, 2H), 2.87 (t, J = 6.6 Hz, 2H), 1.53 (s, 1H).

Synthesis of 2-bromo-3-(2-methoxyethyl)thiophene (6f). 6f was synthesized from **5f'** (2.06 g, 10 mmol) according to General Procedure **A**. (2.11 g, 9.60 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 5.6 Hz, 1H), 6.86 (d, J = 5.6 Hz, 1H), 3.57 (t, J = 6.8 Hz, 2H), 3.36 (s, 3H), 2.86 (t, J = 6.8 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.4, 128.7, 125.5, 110.0, 71.7, 58.7, 30.0. HRMS (ESI-TOF) (m/z): [M$^+$] calcd for C_7H_9BrSO, 219.9557; found, 219.9556.

Synthesis of 3-(2-bromophenyl)propan-1-ol (5g). 5g was synthesized from commercially sourced **4g** (4.56 g, 20.0 mmol) according to the procedure from **4b** to **5b.** (3.94 g, 18.4 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 1H), 7.24–7.20 (m, 2H), 7.07–7.02 (m, 1H), 3.68 (t, J = 6.4 Hz, 2H), 2.84–2.80 (m, 2H), 2.57 (br, 1H), 1.92–1.85 (m, 2H). literature data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.25–7.22 (m, 2H), 7.07–7.03 (m, 1H), 3.65 (t, J = 6.4 Hz, 2H), 2.86–2.81 (m, 2H), 2.59 (s, 1H), 1.94–1.88 (m, 2H).

Synthesis of 1-bromo-2-(3-methoxypropyl)benzene (6g). 6g was synthesized from **5g** (2.14 g, 10.0 mmol) according to General Procedure **A**. (2.10 g, 9.20 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 1H), 7.22–7.18 (m, 2H), 7.06–7.00 (m, 1H), 3.40 (t, J = 6.4 Hz, 2H), 3.34 (s, 3H), 2.82–2.78 (m, 2H), 1.92–1.85 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.3, 132.9, 130.5, 127.6, 127.4, 124.5, 71.8, 58.6, 32.8, 29.7. HRMS (ESI-TOF) (m/z): [M$^+$] calcd for $C_{10}H_{13}BrO$, 228.0150; found, 228.0145.

Synthesis of monoadduct 7a ((2-$CH_3OCH_2CH_2C_6H_4$)C_{60}H) By following the general procedure, the chromatography with the CS_2 as eluent provided an air-stable dark brown solid **7a** in a yield of 90% (107.1 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.41 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.74 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.60–7.52 (m, 2H), 6.88 (s, 1H), 4.25 (t, J = 6.8 Hz, 2H), 4.02 (t, J = 6.8 Hz, 2H), 3.48 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 153.5 (1C), 147.7 (1C), 147.4 (1C), 146.9 (3C), 146.5 (3C), 146.4, 146.30 (3C), 146.29 (3C), 146.1, 145.9, 145.63, 145.55, 145.53, 145.51, 144.9, 144.7, 143.5, 142.8 (3C), 142.7, 142.25 (3C), 142.21 (3C), 141.8 (4C), 141.5 (3C), 140.5, 140.0, 138.6 (3C), 132.6 (1C), 130.3 (1C), 128.8 (1C), 127.5 (1C), 73.9 (1C, sp^3-C of C_{60}), 68.6 (1C, sp^3-C of C_{60}), 63.0 (1C), 59.1 (1C), 33.7 (1C); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{69}H_{12}O$, 856.0888; found, 856.0899.

Synthesis of monoadduct 7b ((2-$CH_3OCH_2CH_2$-5-F-C_6H_3)C_{60}H). By following the general procedure, the chromatography with the CS_2 as eluent provided an air-stable dark brown solid **7b** in a yield of 83% (100.8 mg). ^{1}H NMR (400 MHz, TCE-d_2/CS_2) δ 8.16 (dd, J_1 = 10.8 Hz, J_2 = 2.4 Hz, 1H), 7.77 (dd, J_1 = 7.4 Hz, J_2 = 6.0 Hz, 1H), 7.32 (ddd, J_1 = 10.0 Hz, J_2 = 8.4 Hz, J_3 = 2.8 Hz, 1H), 6.92 (s, 1H), 4.24 (t, J = 6.4 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 3.52 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 161.2 (d, J = 247.8 Hz, 1C), 152.7 (1C), 147.3 (1C), 147.2 (3C), 146.9, 146.4 (3C), 146.1 (3C), 146.0, 145.89 (3C), 145.87 (3C), 145.4, 145.3, 145.1 (6C), 144.4, 144.2, 143.0 (3C), 142.7 (1C), 142.4 (3C), 142.3 (3C), 141.83 (3C), 141.80 (3C), 141.4 (3C), 141.0, 140.1, 139.6 (1C), 134.1 (d, J = 3.4 Hz, 1C), 133.6 (d, J = 7.7 Hz, 1C), 117.0 (d, J = 23.7 Hz, 1C), 115.0 (d, J = 20.5 Hz, 1C), 73.3 (1C, sp^3-C of C_{60}), 67.7 (1C, sp^3-C of C_{60}), 62.3 (1C), 58.6 (1C), 32.6 (1C); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{69}H_{11}OF$, 874.0794; found, 874.0790.

Synthesis of monoadduct 7c ((2-$CH_3OCH_2CH_2$-5-CH_3O-C_6H_3)C_{60}H). By following the general procedure, the chromatography with the CS_2 as eluent provided an air-stable dark brown solid **7c** in a yield of 88% (108.3 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.90 (d, J = 2.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.07 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.87 (s, 1H), 4.13 (t, J = 6.8 Hz, 2H), 3.97–3.94 (m, 5H), 3.46 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 158.4 (1C), 153.2 (1C), 147.4 (1C), 147.1 (1C), 146.7 (4C), 146.3 (3C), 146.2, 146.08 (3C), 146.07 (3C), 145.7 (3C), 145.4, 145.35 (3C), 145.34 (3C), 145.30 (3C), 144.7, 144.4, 143.3 (3C), 142.6 (3C), 142.5, 142.1 (3C), 142.0 (3C), 141.6 (3C), 141.3, 140.3, 139.8, 133.4 (1C), 130.2 (1C), 117.4 (1C), 112.6 (1C), 74.0 (1C, sp^3-C of C_{60}), 68.3 (1C, sp^3-C of C_{60}), 62.7 (1C), 58.8 (1C), 55.1 (1C), 32.8 (1C); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{70}H_{14}O_2$, 886.0994; found, 886.0990.

Synthesis of monoadduct 7d ((2-$CH_3OCH_2CH(CH_3)$-C_6H_4)C_{60}H). By following the general procedure, the chromatography with the CS_2 as eluent provided an air-stable dark brown solid **7d** in a yield of 89% (107.6 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.28 (d, J = 8.4 Hz, 1H), 7.70 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.56–7.51 (m, 1H), 7.44–7.40 (m, 1H), 7.20 (s, 1H), 5.37–7.34 (m, 1H), 4.00–3.90 (m, 1H), 3.70–3.57 (m, 1H),3.44 (s, 3H), 1.39 (d, J = 9.6 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.9 (1C), 147.5 (3C), 147.2 (3C), 146.93 (1C), 146.86 (1C), 146.40 (3C), 146.37, 146.2 (6C), 145.8 (1C), 145.7 (1C), 145.6 (4C), 145.5 (3C), 145.42 (3C), 145.39 (3C), 144.8, 143.4 (1C), 143.3 (1C), 142.68 (3C), 142.66 (3C), 142.6 (1C), 142.15 (4C), 142.14 (3C), 142.11, 141.8 (1C), 141.7 (1C), 141.4 (1C), 140.4 (1C), 140.3 (1C), 130.0 (1C), 129.0 (1C), 128.4 (1C), 127.1 (1C), 68.5 (1C, sp^3-C of C_{60}), 62.7 (1C, sp^3-C of C_{60}), 59.4 (1C), 50.8 (1C), 35.3 (1C), 20.1 (1C); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{70}H_{14}O$, 870.1045; found, 870.1043.

Synthesis of monoadduct 7e ((2-$CH_3OCH_2C(CH_3)_2$-C_6H_4)C_{60}H). By following the general procedure, the chromatography with the CS_2 as eluent provided an air-stable dark brown solid **7e** in a yield of 86% (105.6 mg). ^{1}H NMR (400 MHz, TCE-d_2/CS_2) δ 9.23 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.89 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.73–7.69 (m, 1H), 7.54–7.50 (m, 1H), 6.88 (s, 1H), 4.05 (s, 2H), 3.45 (s, 3H), 1.97 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, TCE-d_2/CS_2, all 2C unless indicated) δ 153.5 (1C), 147.2 (1C), 146.8 (1C), 146.5 (3C), 146.1 (3C), 146.0, 145.88, 145.87, 145.5, 145.4, 145.2 (3C), 145.15, 145.08, 145.0, 144.9 (3C), 144.4 (3C), 144.2 (3C), 143.1, 142.41, 142.40, 142.0, 141.8, 141.6, 141.5, 141.3, 140.7, 140.1, 138.9, 136.7 (1C), 135.2 (1C), 130.0 (1C), 127.3 (1C), 127.2 (1C), 81.5 (1C, sp^3-C of C_{60}), 69.6 (1C, sp^3-C of C_{60}), 65.4 (1C), 58.7 (1C), 40.7 (1C), 29.5 (2C); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{71}H_{16}O$, 884.1201; found, 884.1187.

Synthesis of monoadduct 7f ((3-$CH_3OCH_2CH_2$-C_4SH_2)C_{60}H). By following the general procedure, the chromatog-

raphy with the CS_2 as eluent provided an air-stable dark brown solid **7f** in a yield of 89% (106.6 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.42–7.37 (m, 2H), 7.03 (s, 1H), 4.02 (t, J = 6.4 Hz, 2H), 3.92 (t, J = 6.4 Hz, 2H), 3.52 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 153.0 (1C), 152.7, 147.6 (1C), 147.3 (1C), 146.7, 146.41, 146.39, 146.23, 146.18, 145.84, 145.81, 145.7, 145.5, 145.45, 145.40, 145.1 (1C), 144.7, 144.5, 143.3, 142.65, 142.61, 142.13 (4C), 142.10, 141.8, 141.7, 141.5, 140.4, 140.2, 137.2, 136.1, 135.6, 131.0 (1C), 123.4 (1C), 72.8 (1C, sp^3-C of C_{60}), 63.5 (1C, sp^3-C of C_{60}), 63.0 (1C), 58.9 (1C), 29.9 (1C); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{67}H_{10}SO$, 862.0452; found, 862.0450.

Synthesis of monoadduct 7g ((2-$CH_3OCH_2CH_2CH_2$-C_6H_4)C_{60}H). By following the general procedure, the chromatography with the CS_2 as eluent provided an air-stable dark brown solid **7g** in a yield of 88% (106.3 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.37 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.68 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.58–7.48 (m, 2H), 6.77 (s, 1H), 4.03 (br, 2H), 3.67 (t, J = 6.0 Hz, 2H), 3.40 (s, 3H), 2.34–2.27 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 153.2 (1C), 147.5 (1C), 147.2 (1C), 146.7 (3C), 146.4 (3C), 146.3, 146.1 (4C), 145.7 (3C), 145.54, 145.49, 145.44, 145.40, 145.3, 144.7, 144.5 (1C), 143.3 (3C), 142.62 (3C), 142.59 (3C), 142.13 (3C), 142.07 (3C), 141.7 (3C), 141.6 (3C), 141.4 (3C), 140.3 (3C), 139.9, 132.25 (1C), 130.16 (1C), 128.8 (1C), 127.0 (1C), 72.2 (1C, sp^3-C of C_{60}), 68.4 (1C, sp^3-C of C_{60}), 63.0 (1C), 58.6 (1C), 32.6 (1C), 30.0 (1C); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{70}H_{14}O$, 870.1045; found, 870.1043.

Synthesis of compound 2a. By following the general procedure, the chromatography with the CS_2 as eluent provided a brownish shinning powder **2a** in a yield of 89% (30.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ for *R* isomer: 8.51–8.49 (m, 1H), 7.71–7.60 (m, 1H), 7.58–7.48 (m, 2H), 5.40 (d, J = 3.6 Hz, 1H), 4.47 (d, J = 15.6 Hz, 1H), 3.89 (dd, J_1 = 16.0 Hz, J_2 = 3.6 Hz, 1H), 3.84 (s, 3H); δ for *S* isomer: 8.51–8.49 (m, 1H), 7.71–7.60 (m, 1H), 7.58–7.48 (m, 2H), 4.96 (d, J = 10.8 Hz, 1H), 4.18 (t, J = 12.4 Hz, 1H), 3.79 (d, J = 14.4 Hz, 1H), 3.62 (s, 3H); ^{1}H NMR (400 MHz, TCE-d_2, 373 K) δ 8.54 (br, 1H), 7.68 (br, 1H), 7.57 (br, 2H), 5.23 (br, 1H), 4.11 (br, 2H), 3.78 (br, 3H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 1C unless indicated) δ 155.4, 154.3, 152.3, 147.6, 147.1, 146.4 (2C), 146.42 (2C), 146.40, 146.2, 146.15 (2C), 146.12, 146.10, 146.0, 145.44 (2C), 145.40, 145.3, 145.2 (2C), 145.1, 144.7, 144.6, 144.4, 143.1 (2C), 142.71, 142.69, 142.64, 142.62, 142.3, 142.2, 142.18, 142.16, 142.1, 141.9, 141.8, 141.64 (2C), 141.62 (2C), 141.44, 141.39 (2C), 141.37, 140.6, 140.4, 138.4, 137.7, 136.9, 136.8, 136.5, 130.5, 129.9, 128.8, 128.3, 128.0, 127.74 (2C), 127.71, 127.65, 127.63, 84.6, 84.4 (*dr*)*, 74.4 (sp^3-*C* of C_{60}), 70.1 (sp^3-*C* of C_{60}), 58.7, 56.5 (*dr*), 34.2, 31.9 (*dr*); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{69}H_{10}O$, 854.0732; found, 854.0721. (*dr = diastereomer)

Synthesis of compound 2b. By following the general procedure, the chromatography with the CS_2 as eluent provided a brownish shinning powder **2b** in a yield of 78% (27.2 mg). ^{1}H NMR (400 MHz, TCE-d_2/CS_2) δ for *R* isomer: 8.22–8.18 (m, 1H), 7.70–7.60 (m, 1H), 7.29–7.24 (m, 1H), 5.45–5.41 (m, 1H), 4.43 (d, J = 14.8 Hz, 1H), 3.93 (d, J = 1.2 Hz, 1H), 3.88 (s, 3H); δ for *S* isomer: 8.22–8.18 (m, 1H), 7.70–7.60 (m, 1H), 7.29–7.24 (m, 1H), 4.95 (d, J = 11.6 Hz, 1H), 4.14 (t, J = 12.8 Hz, 1H), 3.82 (d, J = 14.8 Hz, 1H), 3.64 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, TCE-d_2/CS_2, all 1C unless indicated) δ 153.5 (d, J = 94.1 Hz, 1C), 147.2, 146.9, 146.4 (2C), 146.03 (2C), 145.96 (2C), 145.82 (2C), 145.81 (2C), 145.5 (2C), 145.4 (2C), 145.2 (2C), 145.09 (2C), 145.07 (2C), 145.0 (2C), 144.4 (2C), 144.2 (2C), 143.0 (2C), 142.30 (3C), 142.26 (2C), 141.79 (3C), 141.75 (3C), 141.4 (4C), 141.1 (2C), 140.0 (2C), 139.6, 138.4 (3C), 134.4 (3C), 132.3, 129.9, 128.4, 127.1, 116.4 (3C), 72.8, 71.1 (sp^3-*C* of C_{60}), 68.1 (sp^3-*C* of C_{60}), 62.6, 33.4; HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{69}H_9FO$, 872.0637; found, 872.0635.

Synthesis of compound 2c. By following the general procedure, the chromatography with the CS_2 as eluent provided a brownish shinning powder **2c** in a yield of 91% (32.2 mg). ^{1}H NMR (400 MHz, TCE-d_2/CS_2) δ for *R* isomer: 8.00 (s, 1H), 7.60–7.54 (m, 1H), 7.08 (d, J = 8.0 Hz 1H), 5.40 (d, J = 3.2 Hz, 1H), 4.41 (d, J = 15.6 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 3.85 (d, J = 4.0 Hz, 1H); δ for *S* isomer: 8.00 (s, 1H), 7.60–7.54 (m, 1H), 7.08 (d, J = 8.0 Hz 1H), 4.94 (d, J = 10.8 Hz, 1H), 4.10 (t, J = 13.6 Hz, 1H), 3.94 (s, 3H), 3.78 (d, J = 14.4 Hz, 1H), 3.64 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, TCE-d_2/CS_2, all 1C unless indicated) δ 159.2, 158.8, 154.0, 153.5, 147.4, 146.14 (2C), 146.12 (2C), 145.84 (2C), 145.81 (2C), 145.75, 145.73, 145.15, 145.13, 145.10 (2C), 144.99, 144.9 (4C), 144.83 (2C), 144.81 (2C), 144.7 (2C), 144.3 (3C), 142.8 (3C), 142.4 (3C), 142.3 (3C), 142.1 (2C), 142.0 (2C), 141.9 (2C), 141.83 (2C), 141.79 (2C), 141.75, 141.3 (2C), 141.11 (2C), 141.07, 131.0, 130.5, 115.4, 114.7, 112.6, 112.1, 84.5, 84.1 (*dr*)*, 69.7 (sp^3-*C* of C_{60}), 68.7 (sp^3-*C* of C_{60}), 58.4, 56.1 (*dr*), 54.9, 33.1, 30.7 (*dr*); HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{70}H_{12}O_2$, 884.0837; found, 884.0835. (*dr = diastereomer)

Synthesis of compound 2d. By following the general procedure, the chromatography with the CS_2 as eluent provided a brownish shinning powder **2d** in a yield of 81% (28.1 mg). ^{1}H NMR (400 MHz, TCE-d_2/CS_2) δ 8.54 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.64–7.54 (m, 2H), 4.60 (d, J = 10.4 Hz, 1H), 4.46–4.38 (m, 1H), 3.86 (s, 3H), 2.01 (d, J = 6.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, TCE-d_2/CS_2, all 1C unless indicated) δ 155.0, 153.8, 152.2, 148.7, 147.4, 147.2 (2C), 147.1, 146.2 (4C), 146.0, 145.9 (2C), 145.82 (3C), 145.77, 145.6, 145.11 (2C), 145.08, 145.0, 144.93 (3C), 144.87, 144.5 (2C), 144.3 (2C), 144.2, 144.0, 142.8 (3C), 142.5, 142.4 (2C), 142.3 (2C), 142.1 (2C), 142.0 (2C), 141.9 (2C), 141.53, 141.50, 141.41, 141.36, 141.18, 141.14, 141.08, 140.1, 139.5, 138.5, 138.4, 135.8, 128.3, 127.8, 127.7, 125.8, 89.5, 69.1 (sp^3-C of C_{60}), 62.4 (sp^3-C of C_{60}), 38.8, 29.7, 13.9; HRMS (MALDI-TOF) (m/z): [M$^+$] calcd for $C_{70}H_{12}O$, 868.0888; found, 868.0888.

Synthesis of compound 2e. By following the general procedure, the chromatography with the CS_2 as eluent provided a brownish shinning powder **2e** in a yield of 76% (26.8 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ for *R* isomer: 8.73 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.86 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.57–7.50 (m, 2H), 4.84 (s, 1H), 3.84 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H); δ for *S* isomer: 8.70 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.78 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.49–7.41 (m, 2H), 4.89 (s, 1H), 3.77 (s, 3H), 2.22 (s, 3H), 2.06 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 1C unless indicated, diastereomer, 142C) δ 160.1, 159.8, 157.9, 157.3, 156.0, 155.6, 155.3, 153.8, 149.0, 148.0, 147.74, 147.67, 147.55, 147.53, 147.4, 146.7, 146.5, 146.45 (2C), 146.44 (2C), 146.39, 146.36, 146.3, 146.22, 146.16, 146.1, 146.05 (4C), 146.02 (2C), 145.9, 145.8 (2C), 145.7, 145.6, 145.5, 145.40, 145.37, 145.34, 145.31 (2C), 145.27 (2C), 145.23, 145.21, 145.17, 145.15 (2C), 145.06, 145.04, 145.00 (2C), 144.8 (2C), 144.72, 144.66 (2C), 144.6, 144.5, 144.4, 144.3, 143.6, 143.3, 143.2, 143.1 (2C), 142.75, 142.72 (2C), 142.67, 142.61, 142.57 (2C), 142.5, 142.4, 142.35, 142.32, 142.27 (2C), 142.20, 142.16, 142.1, 141.8, 141.71,

141.65 (4C), 141.6, 141.5, 141.39, 141.38, 141.34, 141.31 (2C), 141.2, 141.14, 141.09, 140.3, 140.1, 140.0, 139.9, 139.5, 138.7, 138.3, 138.2, 137.7, 137.2, 135.6, 135.3, 134.6, 134.1, 134.0, 133.7, 133.6, 133.4, 130.6, 130.4, 129.8, 128.1, 127.9, 127.55, 127.50, 126.9, 126.6, 95.6, 90.3, 69.6 (sp^3-C of C_{60}), 68.4 (sp^3-C of C_{60}), 67.1 (sp^3-C of C_{60}), 64.5 (sp^3-C of C_{60}), 63.8, 62.6, 42.2, 42.1, 31.6, 28.5, 27.2, 25.7; HRMS (MALDI-TOF) (m/z): [M^+] calcd for $C_{71}H_{14}O$, 882.1045; found, 882.1041.

Synthesis of compound 2f. By following the general procedure, the chromatography with the CS_2 as eluent provided a brownish shinning powder **2f** in a yield of 75% (25.8 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ for *R* isomer: 7.49 (d, J = 5.2 Hz, 1H), 7.24 (d, J = 4.8 Hz, 1H), 5.16–5.11 (m, 1H), 3.99–3.94 (m, 2H), 3.79 (s, 3H); δ for *S* isomer: 7.61 (d, J = 5.2 Hz, 1H), 7.33 (d, J = 5.2 Hz, 1H), 6.20 (d, J = 3.2 Hz, 1H), 3.90 (s, 3H), 3.48 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, TCE-d_2/CS_2, all 1C unless indicated) δ 147.2, 146.9, 146.4 (3C), 146.04 (3C), 145.96 (2C), 145.83 (3C), 145.81 (3C), 145.78 (2C), 145.4 (3C), 145.2 (2C), 145.1 (2C), 145.0 (3C), 144.4 (2C), 144.20 (2C), 144.16, 143.0 (3C), 142.31 (3C), 142.27 (3C), 141.8 (3C), 141.7 (3C), 141.4 (3C), 141.1 (2C), 140.0, 139.6, 135.7 (3C), 133.1, 129.9, 128.2, 127.3, 104.8, 68.0 (sp^3-C of C_{60}), 65.0 (sp^3-C of C_{60}), 62.3, 37.5; HRMS (MALDI-TOF) (m/z): [M^+] calcd for $C_{67}H_8SO$, 860.0296; found, 860.0293.

Synthesis of compound 2g. By following the general procedure, the chromatography with the CS_2 as eluent provided a brownish shinning powder **2g** in a yield of 48% (16.7 mg). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.13–8.11 (m, 1H), 7.81–7.79 (m, 1H), 7.61–7.58 (m, 2H), 5.44 (t, J = 6.4 Hz, 1H), 4.03–3.97 (m, 2H), 3.06 (dt, J_1 = 14.4 Hz, J_2 = 7.2 Hz, 1H), 2.75 (dt, J_1 = 14.4 Hz, J_2 = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, CS_2/$CDCl_3$, all 1C unless indicated) δ 158.3, 154.9, 154.7, 153.7, 147.5, 147.3, 146.5, 146.3, 146.25, 146.22, 146.12, 146.09, 146.08, 146.05, 146.03 (2C), 145.94, 145.88, 145.8, 145.5, 145.4, 145.35, 145.30, 145.27, 145.25 (2C), 145.16, 145.1, 144.9, 144.6, 144.5 (2C), 144.1, 143.25, 143.21, 142.73, 142.69, 142.66, 142.6, 142.4, 142.33, 142.32, 142.28, 142.2, 142.10 (2C), 142.08, 142.0, 141.9, 141.85, 141.78, 141.76, 140.7, 140.6, 140.0, 139.3, 136.7, 135.2, 134.9, 134.5, 129.1, 128.7, 126.6, 126.0, 77.4, 74.6 (sp^3-C of C_{60}), 70.8 (sp^3-C of C_{60}), 58.7, 54.0, 37.5; HRMS (MALDI-TOF) (m/z): [M^+] calcd for $C_{70}H_{12}O$, 868.0888; found, 868.0888.

ASSOCIATED CONTENT

Supporting Information

Experimental section including ^{1}H and ^{13}C NMR spectra, and CV. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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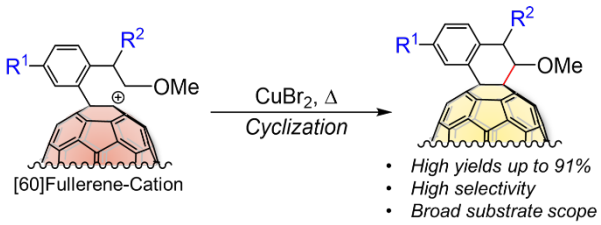

Fullerene-cation-mediated synthesis of tetrahydronaphthaleno[60]fullerenes with high yields, selectivity and broad substrate scope .