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# Selective Surface Decoration of Corannulene

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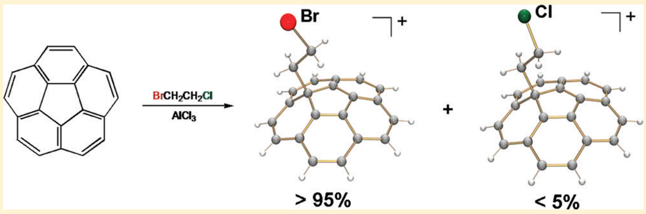
Supporting Information



**ABSTRACT:** The reaction of corannulene ($C_{20}H_{10}$) with 1,2-$C_2H_4Hal_2$ (Hal = Cl or Br) in the presence of $AlCl_3$ affords stable nonplanar carbocations $C_{20}H_{10}CH_2CH_2Hal^+$ (Hal = Cl (**1**) and Br (**2**)) with an $-CH_2CH_2Hal$ moiety attached to the interior carbon atom of the bowl. In the analogous reaction with 1-bromo-2-chloroethane, the selective (up to 98%) abstraction of chloride is observed with the formation of cation **2**. The molecular structures of bowl-shaped carbocations **1** and **2** crystallized as salts with $AlCl_4^-$ counterions are revealed by single-crystal X-ray diffraction. The reaction of **2** with methanol or ethanol provides further decoration of the nonplanar polyarene upon the nucleophilic addition of alkoxy groups to the exterior carbon atom of the corannulene moiety. The $^1$H NMR investigation of the corresponding products, $C_{20}H_{10}(CH_2CH_2Br)(OCH_2R)$ (R = H (**3**) and $CH_3$ (**4**)), shows the formation of intramolecular H···O and H···Br hydrogen bonds.

## INTRODUCTION

The functionalization of aromatic compounds by electrophilic substrates was discovered almost 135 years ago by Friedel and Crafts.[1] Today, the corresponding Friedel−Crafts reaction serves as one of the most powerful synthetic tools providing a great variety of derivatives, important for industry and medicine.[2] Great knowledge has been accumulated on the reactivity of planar aromatic hydrocarbons toward different alkylation/acylation substrates under Friedel−Crafts reaction conditions.[3] In contrast, much less is known about the relative reactivity of bowl-shaped polyarenes (buckybowls).[4] At the same time, decoration of curved carbon surfaces of fullerenes and nanotubes by electrophilic and nucleophilic substrates plays an important role in the preparation of functionalized materials for different applications.[5] It was established that under Friedel−Crafts reaction conditions, fullerenes $C_{60}$ and $C_{70}$ undergo the 1,4-addition of $CHCl_3$ or $Cl_2CHCHCl_2$ in the presence of $AlCl_3$ with the formation of neutral products (Scheme 1, top).[6] Upon their hydrolysis and subsequent elimination of an OH-group under superacidic conditions, the formation of functionalized fullerene cations has been observed in solution.[6]

In contrast, corannulene ($C_{20}H_{10}$), which can be considered as a 1/3 subunit of the $C_{60}$ surface, gives the corresponding functionalized cations directly in the reaction with halogenated hydrocarbons and $AlCl_3$ (Scheme 1, bottom). The in situ formation of these unusual products of Friedel−Crafts alkylation upon the electrophilic addition of $CDCl_2^+$ and $CCl_3^+$ cations to corannulene was postulated by Scott et al. based on $^1$H NMR spectroscopy back in 1999.[7] Recently, we have isolated a series of functionalized corannulene cations with several attached $CH_xCl_{3-x}$ ($x$ = 0−3) groups (Scheme 1, bottom) as pure bulk crystalline compounds, and that allowed us to accomplish their first structural characterization.[8]

Herein, we set out to test 1,2-$C_2H_4Hal_2$ (Hal = Cl or/and Br) substrates as to add new members to the family of corannulene cations with longer substituents at the interior carbon sites. The attachment of longer alkyl chains to the corannulene core should allow one to tune properties of $\pi$-bowls, for example, to increase solubility of the resulting species. It should also facilitate further surface-anchored functionalization,[9] which remains largely undeveloped for bowl-shaped polyarenes.

## RESULTS AND DISCUSSION

We found that corannulene readily reacts with 1,2-dichloroethane or 1,2-dibromoethane in the presence of $AlCl_3$ with the formation of blue-purple functionalized corannulene cations, $C_{20}H_{10}CH_2CH_2Hal^+$ (**1** and **2**), at ambient conditions (Scheme 2).

The $^1$H NMR spectra of both cations show characteristic splitting of the resonance signals for aromatic protons,[8] consistently with their $C_s$ symmetry (Figure 1). The corresponding resonances appear as four doublets and one singlet in the 9.23−8.52 ppm range, similarly to those observed previously for the series of $C_{20}H_{10}R^+$ cations (R ranging from $CH_3$ through $CCl_3$).[8] Owing to the strong shielding from the aromatic system of the corannulene core, the proton resonances of the $-CH_2CH_2Hal$ moieties are high-field shifted and appear as two triplets at 2.33/0.81 ppm for **1** and 2.17/0.89 ppm for **2**. The corresponding resonance signals of the parent

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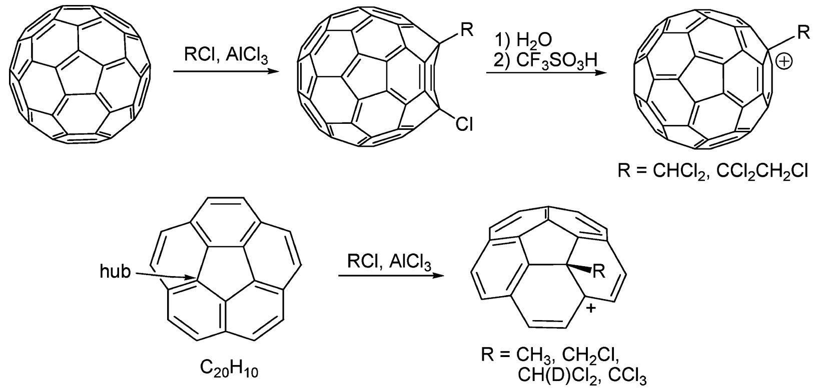
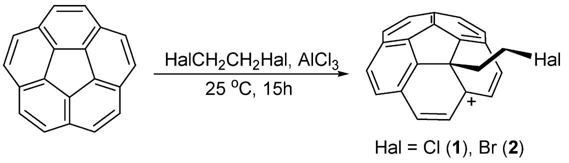
Scheme 1. Alkylation of the $C_{60}$-Fullerene (Top) and Corannulene (Bottom) by Halocarbons



Scheme 2. Preparation of Cations 1 and 2



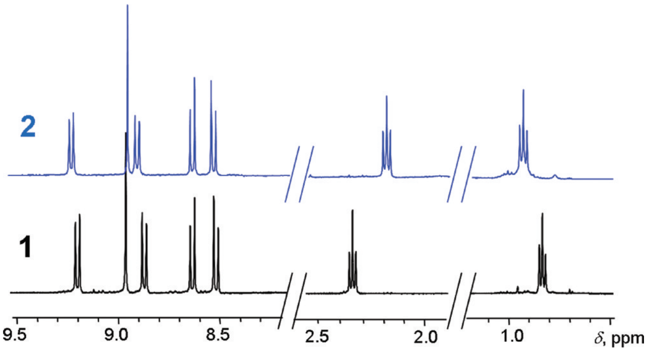


**Figure 1.** $^1H$ NMR spectra of cations **1** and **2**.

halogenated hydrocarbons $ClCH_2CH_2Cl$ and $BrCH_2CH_2Br$ appear at 3.73 and 3.67 ppm, respectively.

In the $^{13}C$ NMR spectra of **1** and **2**, the chemical shift of the cationic center ($\delta = 195$ ppm) is close to that for the previously observed corannulene cation with an attached methyl group ($\delta = 196$ ppm).[8] It indicates an absence of intramolecular interactions between the chlorine atom of the $-CH_2CH_2Cl$ moiety and the cationic center in **1**. The chemical shift of the hub carbon atom having an attached $-CH_2CH_2Cl$ group ($\delta = 56$ ppm) shows the exclusion of this carbon atom from the aromatic system of corannulene. The UV−vis spectra of cations **1** and **2** in chloroform demonstrate very close values of the absorption band maxima of the $\pi-\pi^*$ electron transition ($\lambda_{max} = 569$ and 575 nm for **1** and **2**, respectively), owing to their similar electronic structures. These maxima lie almost in between the corresponding values previously found for the $C_{20}H_{10}CH_3^+$ ($\lambda_{max} = 560$ nm) and $C_{20}H_{10}CH_2Cl^+$ ($\lambda_{max} = 582$ nm) cations.[8]

When the mixed halogenated substrate, $ClCH_2CH_2Br$, is used for the reaction with corannulene and $AlCl_3$, cation **2** is formed as a major product (95−98%), as estimated by $^1H$ NMR spectroscopy. This observation is consistent with the preferential reactivity of the C−Cl bond over C−Br bonds, previously found for Friedel−Crafts alkylation of planar arenes.[10] However, after the initial in situ formation of $R^+$ cations, the reactions proceed differently for planar and nonplanar hydrocarbons. In planar systems, the electrophilic attack at the $\pi$-surface and formation of a $\pi$-complex is followed by the attachment of R group at the rim ($\sigma$-complex) and extrusion of a proton to afford alkylbenzenes. As a result, the Lewis acid catalyst is regenerated at the final step. Notably, the product is often more nucleophilic than the starting arene and as such can react further to give mixtures of polyalkylated species. Thus, the yield of the monoalkylated product is often found to be low or medium. The electrophilic attack at the nonplanar surface of corannulene occurs at the hub C-atom that possesses the largest atomic coefficient of the highest occupied molecular orbital.[11] The alkyl group does not slip to the rim of corannulene and remains trapped at the hub-site due to the release of strain energy stored within its nonplanar surface. Thus, the reaction equilibrium is greatly shifted toward the hub-functionalized cationic product, providing an excellent site-selectivity that is different from planar arenes. There is no catalyst regeneration in this case, as all involved $AlHal_3$ is utilized as a counterion $AlHal_4^-$ to balance the charge for the resulting corannulene cations. This formation of more positively charged and thus less active in electrophilic reactions nonplanar polyaromatic species provides great selectivity toward a specific monoalkylated corannulene product. Plus, the absence of competing reactions results in excellent product yields.

The $^1H$ NMR monitoring of the reaction of $C_{20}H_{10}$ with $AlCl_3$ or $AlBr_3$ in $ClCH_2CH_2Br$ ($CDCl_3$ as an external standard) also indicates the preferential formation of cation **2**. When the $ClCH_2CH_2Cl/BrCH_2CH_2Br$ mixture (1:1, v/v) is used for the reaction of $C_{20}H_{10}$ with $AlCl_3$ in a 1:1 ratio, cation **1** is formed as the major product according to the $^1H$ NMR data.

Cation **1** crystallizes in the form of its salt with the $AlCl_4^-$ counterion by slow diffusion of hexanes vapors into the $CHCl_3$ solution as dark purple plates. The X-ray diffraction study of [**1**]·[$AlCl_4$] revealed the essentially $C_s$ symmetry of **1** within the limit of experimental errors. Strong pyramidalization at the interior C3-atom of the corannulene core (Figure 2) is indicative of the $sp^3$-character of this atom. The C2−C3 bond length between the $-CH_2CH_2Cl$ moiety and the bowl core (1.607(7) Å) is significantly elongated compared to the corresponding C−C bond in the $C_{20}H_{10}CH_2Cl^+$ cation (1.577(5) Å).[8] The deviation between the C3 atom and the plane passing through the three neighboring C-atoms of the corannulene core (0.492(8) Å) is larger than the values for four

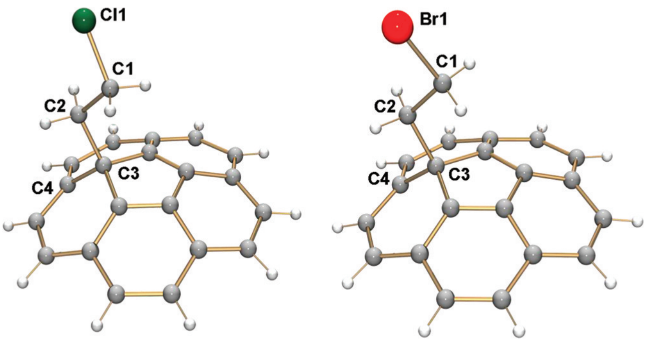


**Figure 2.** Molecular structures of cations **1** (left) and **2** (right).

other interior carbon atoms of the five-membered ring, unaffected by electrophilic addition (avg 0.176(7) Å). The deviation for the cationic center C4 (0.018(8) Å) is indicative of its essential sp$^2$-character. The bowl depth of the corannulene core in **1** is notably increased (1.009(7) Å vs 0.876(2) Å in the parent corannulene[12]), similarly to the previously crystallographically characterized corannulene cations.[8] An increase of the bowl depth in buckybowls upon addition of metal complexes to their interior has been previously documented.[13] On the other hand, rim substitution generally provides some flattening effect of the bowl.[14]

The X-ray diffraction analysis of the [**2**]·[$AlCl_4$] salt, grown by layering the $CH_2Cl_2$ solution with hexanes, showed very close geometrical parameters of **2** compared to **1** (Figure 2, Table 1).

Cations **1** and **2** exhibit a similar aggregation pattern in the solid state. The chlorine or bromine ends of the $-CH_2CH_2Hal$ groups interact with the concave face of the neighboring cations (Figure 3). In contrast to the previously observed symmetrical *endo*-coordination of the chlorine atom of $AlCl_4^-$ within the cationic corannulene cavitiy,[8] the electrostatic Cl···C$_{bowl}$ interactions in **1** and **2** are shifted to the cationic C3 center of the neighboring bowl (Figure 3, left). The Cl···C3 and Br···C3 contacts (3.428(7) and 3.382(4) Å) show the shortest intermolecular Hal···C separations. For comparison, the Cl···C$^+$ contacts for $C_{20}H_{10}CHCl_2^+$ and $C_{20}H_{10}CCl_3^+$ carbocations measure at 3.769(3) and 3.422(7) Å.[8] These electrostatic intermolecular Hal···C interactions lead to the 1D columnar stacking of cations **1** and **2** in the solid state (Figure 3). Additionally, the $\pi-\pi$ interactions (ca. 3.5 Å) between the convex faces of neighboring carbocations link these 1D columns into a 2D network. Similar convex−convex $\pi-\pi$ interactions (ca. 3.5−3.8 Å) were previously seen in the crystal structures of corannulene cations with the shorter $CH_xCl_{3-x}$ ($x$ = 0−2) groups.[8]

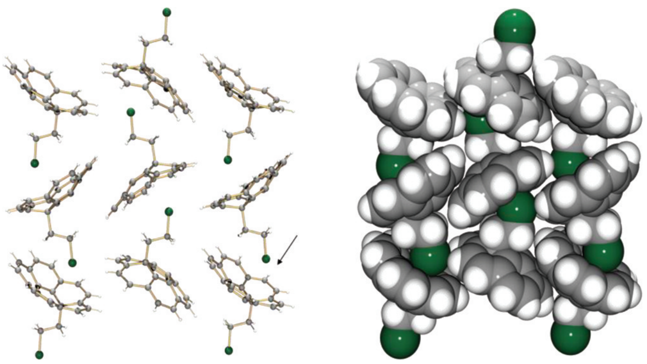
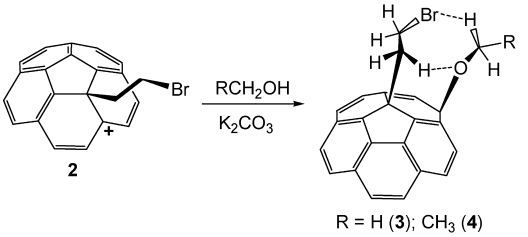


**Figure 3.** Packing of **1** in the solid state (left, arrow shows the shift of the Cl atom toward the cationic center) and the corresponding space-filling model (right).

### Scheme 3. Preparation of 3 and 4



The interior attachment of the $-CH_2CH_2Hal$ group makes the exterior of corannulene to be positively charged and thus susceptible to nucleophilic attack. This surface charge redistribution allows further decoration of corannulene cations at their rim using subsequent nucleophilic reactions with alcohols (methanol and ethanol, Scheme 3). Starting from **2**, the corresponding ethers **3** (with $-OCH_3$) and **4** (with $-OC_2H_5$) are isolated in the form of only one stereoisomer, as identified by $^1$H NMR spectroscopy. Their formation is attributed to the nucleophilic attack of the alkoxy groups to the exterior carbon of the corannulene core in a 1,4-addition fashion. The $^1$H NMR study of similar reactions involving cation **1** shows the formation of the related products, but it also indicates significant amounts of unidentified species. Compounds **3** and **4** are yellowish solids that liberate the parent alcohols upon prolonged drying in vacuo to give the blue-purple cation **2**. The $^1$H NMR monitoring of their solutions demonstrates slow decomposition of **3** and **4** with the formation of $CH_3OH$ and $C_2H_5OH$, respectively.

The chemical shifts of the corannulene proton resonances in **3** and **4** indicate the presence of six aromatic ($\delta$ = 7.68−7.11 ppm), three olefinic ($\delta$ = 6.70−5.92 ppm), and one aliphatic ($\delta$ = 4.97 and 5.09 ppm) protons (Figure 4). Interesting conclusions can be drawn from the multiplicities of the resonance signals for the groups attached to the corannulene core in **3** and **4**. The proton resonances of the $-CH_2CH_2Br$ group in **3** demonstrate additional splitting compared to those measured in the parent cation **2** (Figure 1). They appear as a multiplet at 3.42 ppm for the $-C\boldsymbol{H}_2Br$ moiety and two multiplets at 2.79/2.59 ppm for the $-C\boldsymbol{H}_2CH_2Br$ protons (Figure 4). Surprisingly, the resonance signals for the $-OC\boldsymbol{H}_2CH_3$ protons appear as two multiplets ($\delta_H$ 4.01/3.87 ppm) in the NMR spectrum of **4**. In contrast, only one sharp singlet at 3.70 ppm is detected for the $-OCH_3$ protons in the

### Table 1. Selected Bond Length Distances (in Å) for 1 and 2

| | C−Hal | C1−C2 | C2−C3 | C3−C | C3···X[a] | C4···X[a] |
|---|---|---|---|---|---|---|
| **1** | 1.796(5) | 1.488(8) | 1.607(7) | 1.457(8)− 1.506(8) | 0.492(8) | 0.018(8) |
| **2** | 1.941(4) | 1.509(6) | 1.607(6) | 1.483(6)− 1.507(6) | 0.488(6) | 0.009(6) |

[a] Distance between the C-atom and the plane passing through three neighboring atoms.

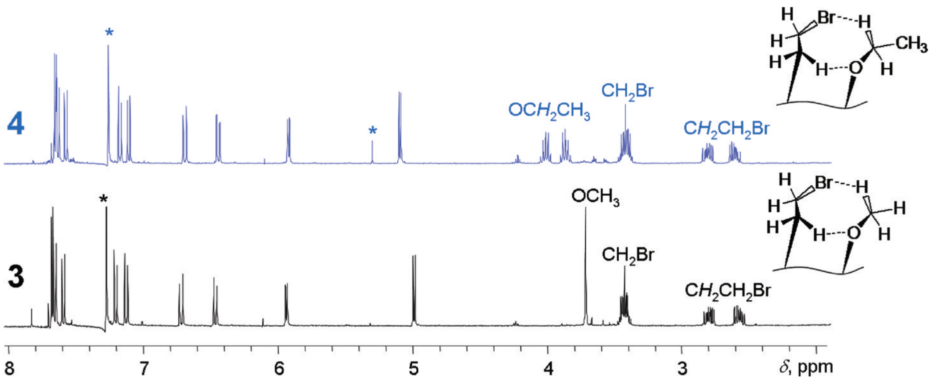


**Figure 4.** $^1$H NMR spectra of **3** and **4** (* = $CHCl_3$ or $CH_2Cl_2$ signals).

spectrum of **3**. The hindered rotation about the C−C and C−O bonds of the surface-bound groups in **4** most likely makes their protons nonequivalent at the NMR time-scale and results in the additional splitting of the $-CH_2CH_2Br$ and $-O\boldsymbol{CH_2}CH_3$ proton resonances. The formation of the seven-membered ring with two O···H and Br···H hydrogen bonds over the corannulene moiety may explain this observation (Figure 4). One singlet for the $-OCH_3$ proton resonance demonstrates a nonhindered rotation about the O−$CH_3$ bond in **3**. In contrast to that, the O−$CH_2$ rotation in **4** is obstructed because it would lead to the breakage of the Br···H intramolecular contact. The intramolecular hydrogen bond stabilization was previously postulated for the reaction product of $C_{20}H_{10}CHCl_2^+$ with methanol; however, only one O···H hydrogen bond was identified in the resulting product.[15]

In conclusion, we have isolated and structurally characterized two new stable bowl-shaped carbocations with the $-CH_2CH_2Hal$ alkyl chains attached to the interior carbon sites of the corannulene core. The selective (up to 98%) abstraction of chloride over bromide from the mixed-halogen substrate, 1-bromo-2-chloroethane, was observed by using a corannulene and $AlCl_3$ mixture. Further decoration of nonplanar corannulene cations at the rim site was achieved by addition of alcohols as nucleophilic substrates. The formation of a single stereoisomer is postulated due to the formation of multiple intramolecular hydrogen bonds in the resulting corannulene-based products.

## ■ EXPERIMENTAL SECTION

**Materials and Methods.** All manipulations were carried out using Schlenk and glovebox techniques under an atmosphere of high-purity dinitrogen or argon. All solvents were degassed and stored over activated molecular sieves (4 Å). Corannulene was prepared as previously described[16] and doubly sublimed at 175 °C prior to use. Purchased aluminum(III) chloride and bromide (99.99+%) were additionally purified by sublimation in vacuo. $^1$H and $^{13}$C NMR spectra were measured at 400 MHz for $^1$H and 100.6 MHz for $^{13}$C and were referenced to the resonances of the corresponding solvent used. Crystal data collections were performed on an CCD-based X-ray diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at $T$ = 173(2) K. Data were corrected for absorption effects using the empirical method SADABS.[17] The structures were solved by direct methods and refined using the Bruker SHELXTL (Version 6.14) software package.[18] Hydrogen atoms were included at idealized positions using the riding model.

**General Procedure for the Preparation of [1]·[AlCl$_4$], [2]·[AlCl$_4$] ([2]·[AlCl$_3$Br]).** A solution of corannulene (15 mg, 0.06 mmol) in the appropriate halogenated solvent ($ClCH_2CH_2Cl$, $ClH_2CH_2Br$, or $BrCH_2CH_2Br$) (3 mL) was added to a suspension of $AlCl_3$ (9 mg, 0.07 mmol) in the same solvent (2 mL). The resulting intensely colored mixture was stirred for 15 h at ambient conditions. Filtration and subsequent evaporation of the solvent afford a solid product that was dried in vacuo for 2 h.

**[1]·[AlCl$_4$]:** yield 70%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.20 (d, 2H, $J_{H,H}$ = 8.4 Hz), 8.96 (s, 2H), 8.87 (d, 2H, $J_{H,H}$ = 8.4 Hz), 8.63 (d, 2H, $J_{H,H}$ = 8.9 Hz), 8.52 (d, 2H, $J_{H,H}$ = 8.9 Hz), 2.33 (t, 2H, $J_{H,H}$ = 6.3 Hz), 0.81 (t, 2H, $J_{H,H}$ = 6.3 Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 194.6, 168.8, 149.8, 143.3, 135.4, 133.9, 133.6, 131.8, 130.0, 129.9, 55.7, 48.1, 38.7; UV−vis ($CHCl_3$, nm) 343, 569; ESI 313.0780 (**1**) (calcd 313.0779) (correct isotope pattern). Anal. Calcd: C, 54.75; H, 2.92. Found: C, 54.79; H, 2.85. Crystal data for [**1**]·[$AlCl_4$]: $C_{22}H_{14}AlCl_5$, $M$ = 482.56, monoclinic, $a$ = 11.930(4) Å, $b$ = 14.202(5) Å, $c$ = 12.708(4) Å, $\beta$ = 105.706(5)°, $V$ = 2072.7 (12) Å$^3$, $P2_1/n$, $Z$ = 4, $\rho_{calcd}$ = 1.546 g/cm$^3$, $\mu$ = 0.749 mm$^{-1}$, $\lambda$ = 0.71073 Å, 15523 measured intensities (4.56° ≤ $2\theta$ ≤ 52.34°), 4167 unique intensities ($R_{int}$ = 0.0731), $R_1$ = 0.0795, w$R_1$ = 0.1597 for 4167 intensities with $I \geq 2\sigma(I)$, w$R_2$ = 0.1772 (for all data), refinement of 253 parameters against $|F^2|$ of all unique reflections with hydrogen atoms on calculated position.

**[2]·[AlCl$_3$Br]:** yield 65%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.23 (d, 2H, $J_{H,H}$ = 8.1 Hz), 8.95 (s, 2H), 8.90 (d, 2H, $J_{H,H}$ = 8.1 Hz), 8.63 (d, 2H, $J_{H,H}$ = 8.4 Hz), 8.52 (d, 2H, $J_{H,H}$ = 8.4 Hz), 2.17 (t, 2H, $J_{H,H}$ = 7.3 Hz), 0.89 (t, 2H, $J_{H,H}$ = 7.3 Hz); $^{13}$C NMR (100.6 MHz, $CH_2Cl_2$ + $CDCl_3$ {10:1, v/v, respectively}) $\delta$ 194.5, 168.9, 150.1, 143.7, 135.3, 134.3, 133.1, 132.2, 130.3, 130.3, 56.1, 38.1, 30.6; UV−vis ($CHCl_3$, nm) 345, 575; ESI 357.0277 (calcd 357.0279) (correct isotope pattern). Crystal data for [**2**]·[$AlCl_4$]: $C_{22}H_{14}AlBrCl_4$, $M$ = 527.02, monoclinic, $a$ = 9.7555(14) Å, $b$ = 14.481(2) Å, $c$ = 15.035(2) Å, $\beta$ = 93.891(3)°, $V$ = 2119.1(5) Å$^3$, $P2_1/c$, $Z$ = 4, $\rho_{calcd}$ = 1.652 g/cm$^3$, $\mu$ = 2.492 mm$^{-1}$, $\lambda$ = 0.71073 Å, 18213 measured intensities (5.04° ≤ $2\theta$ ≤ 56.14°), 4983 unique intensities ($R_{int}$ = 0.0582), $R_1$ = 0.0590, w$R_1$ = 0.1331 for 4983 intensities with $I \geq 2\sigma(I)$, w$R_2$ = 0.1513 (for all data), refinement of 262 parameters against $|F^2|$ of all unique reflections with hydrogen atoms on calculated position.

**General Procedure for the Preparation of 3 and 4.** Vicinal dibromoethane (3 mL) was added to a mixture of corannulene (20 mg, 0.08 mmol) and $AlBr_3$ (21 mg, 0.08 mmol). The resulting purple solution was stirred at ambient conditions for 25 h and then filtered. The filtrate was added dropwise to a degassed suspension of the appropriate alcohol (4 mL) and $K_2CO_3$ (30 mg, 0.217 mmol). The resulting yellow solution was then poured into distilled water (100 mL), and the product was extracted into chloroform (3 × 30 mL). The combined organic fraction was dried over $Na_2SO_4$ and passed through a silica gel plug. The solution was evaporated, and further purification of the crude product is achieved by column chromatography ($SiO_2$, eluent $CH_2Cl_2$/hexanes, 1:1, v/v). The evaporation of the solvents gives yellowish solids of **3** or **4**.

**$C_{20}H_{10}(CH_2CH_2Br)(OCH_3)$ (3):** yield 26%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.67−7.57 (m, 4H), 7.19 (d, 1H, $J_{H,H}$ = 8.4 Hz), 7.11 (d, 1H, $J_{H,H}$ = 8.4 Hz), 6.70 (d, 1H, $J_{H,H}$ = 9.5 Hz), 6.45 (d, 1H, $J_{H,H}$ = 9.5 Hz), 5.92 (d, 1H, $J_{H,H}$ = 5.6 Hz), 4.97 (d, 1H, $J_{H,H}$ = 5.6 Hz), 3.70 (s, 3H), 3.42 (m, 2H), 2.79 (m, 1H), 2.59 (m, 1H). Satisfactory $^{13}$C NMR spectrum could not be collected owing to the sample decomposition during long acquisition times. ESI: 411.0355 ($C_{23}H_{17}O^{79}BrNa$, [**3** + Na]$^+$) and 413.0335 ($C_{23}H_{17}O^{81}BrNa$, [**3** + Na]$^+$) (calcd 411.0355 and 413.0335).

**$C_{20}H_{10}(CH_2CH_2Br)(OCH_2CH_3)$ (4):** yield 20%; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.68−7.56 (m, 4H), 7.17 (d, 1H, $J_{H,H}$ = 8.3 Hz), 7.11 (d, 1H, $J_{H,H}$ = 8.3 Hz), 6.68 (d, 1H, $J_{H,H}$ = 9.8 Hz), 6.44 (d, 1H, $J_{H,H}$ = 9.8 Hz), 5.92 (d, 1H, $J_{H,H}$ = 5.3 Hz), 5.09 (d, 1H, $J_{H,H}$ = 5.3 Hz), 4.01 (m, 1H), 3.87 (m, 1H), 3.42 (m, 2H), 2.80 (m, 1H), 2.61 (m, 1H), 1.37 (t, 3H, $J_{H,H}$ = 7.0 Hz); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 146.8, 142.8, 142.4, 131.3, 131.1, 129.5, 127.7, 126.9, 126.8, 126.5, 126.4, 126.3, 126.1, 124.1, 124.0, 123.8, 75.5, 64.1, 50.5, 43.2, 29.8, 15.8 (22 signals seen of 24 expected); ESI 425.0511 ($C_{24}H_{19}O^{79}BrNa$, [**4** + Na]$^+$) and 427.0489 ($C_{24}H_{19}O^{81}BrNa$, [**4** + Na]$^+$) (calcd 425.0511 and 427.0491).

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystallographic data for compounds **1** and **2** (CIF) and all spectroscopic data (NMR, UV−vis, and HRMS) for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENTS

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