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Preparation of a 12-Membered Open-Cage Fullerendione through Silane/Borane-Promoted Formation of Ketal Moieties and Oxidation of a Vicinal Fullerendiol

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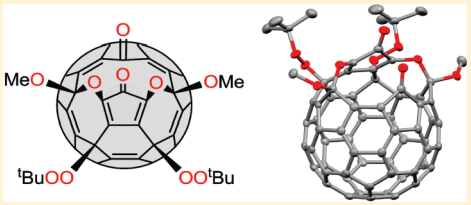
Supporting Information

ABSTRACT: [60]Fullerene mixed peroxide C_{60} (OH)(Cl)(OO*t*Bu) reacts with $PhMe_2SiH/B(C_6F_5)_3$ to give oxahomofullerene. Mechanistic investigation indicates that the hydroxyl group in the central pentagon ring is essential to convert the *tert*-butylperoxo group into a ketal moiety. Migration of the silyl group and transformation of the siloxy group into a phenyl group are observed in the deprotection of the fullerene bound siloxy group. A 12-membered open-cage fullerendione was obtained through oxidation of a [6,6]-fullerendiol. This orifice could be closed to form ketal/hemiketal moieties by BF_3-catalyzed reaction with methanol. All of the new fullerene derivatives were characterized by spectroscopic data, and structure of the open-cage fullerendione was also confirmed by single-crystal X-ray analysis.



INTRODUCTION

The open-cage fullerene is of great interest for its role as host for small molecules to form endohedral fullerene.[1] The first synthesis of a fullerene derivative with a hole was reported by Wudl and co-workers.[2] So far remarkable progress has been made in this area, especially the preparation of $H_2@C_{60}$ through molecular surgery in which the orifice of fullerene was closed after insertion of hydrogen.[3] In most cases the key hole formation reaction involves oxidation with singlet oxygen. We have reported that peroxide-mediated hole formation is also an effective method.[4] Open-cage fullerenes with water inside the carbon cage and a switchable open-cage compound have also been prepared starting from fullerene mixed peroxides.[4]

Unlike the above fully opened fullerene derivatives, fullerene derivatives with hemiketal and/or ketal moieties do not contain a hole because the oxygen atom effectively blocks the opening by bonding to the two disconnected fullerene carbon atoms. These fullerene derivatives are called oxahomofullerene according to IUPAC recommendations.[5] Formation of hemiketals in the fullerene cage was first conjectured by Chiang in the study of fullerenols.[6] Later, Taylor reported the [6,6]-open fluorooxahomofullerene derivative and Weisman described [5,6]-open oxahomo[60]fullerene.[7] We have prepared several fullerene derivatives with hemiketal functions based on fullerene mixed peroxides.[8,9] An interesting isomerization process was observed between the [5,6]- and [6,6]-oxahomofullerene.[8] A recent case is a metallofullerene derivative with an oxygen atom inserted at a [5,6] junction reported by Wang and co-workers.[10]

Despite various successful examples reported in the literature, methods for preparing open-cage fullerene derivatives remain limited. It is not possible to rationally design the size of an orifice with proper functional groups on the rim of the orifice. New methods are still needed to modify the fullerene skeleton bonds efficiently. Here we report the synthesis of an open-cage fullerendione with symmetrical bisketal moieties through silane/borane-induced hemiketal formation and subsequent oxidation of a vicinal fullerendiol.

RESULTS AND DISCUSSION

During the course of our exploration of cage-opening methods, we turned our attention to silanes for protection of hydroxyl groups on the fullerene cage surface. The reaction between fullerenol and silane has not been well studied.[11] Silyl ether is among the most frequently used protective groups for alcohols.[12] The classic method is to use chlorosilane in the presence of base. However, sometimes it does not work well, especially for sterically hindered alcohols.[13] Another route is the utilization of silane (R_3SiH) with the aid of a catalyst.[14] Piers and co-workers found that Lewis acid $B(C_6F_5)_3$ could be used to promote the reaction between silane and alcohol to form silyl ether, and the more hindered the alcohol is, the quicker the reaction is.[15]

We found that the silane/Lewis acid protection method developed by Piers[15] can also be applied to fullerenols. In the presence of $B(C_6F_5)_3$, dimethylphenylsilane $PhMe_2SiH$ reacted with **1** to form ketal **2** in moderate yield (Scheme 1). Other silanes, such as triethylsilane and diphenylmethylsilane, could also give similar results. Silyl groups of the ketal moieties in **2**

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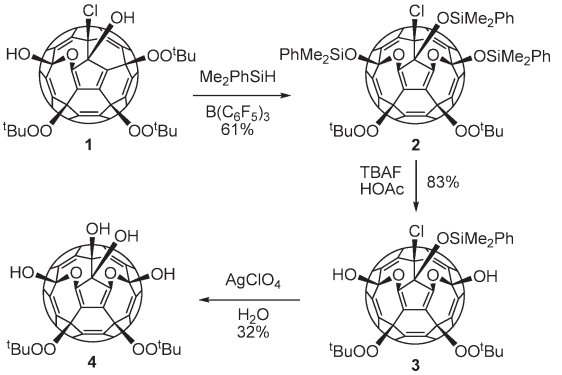
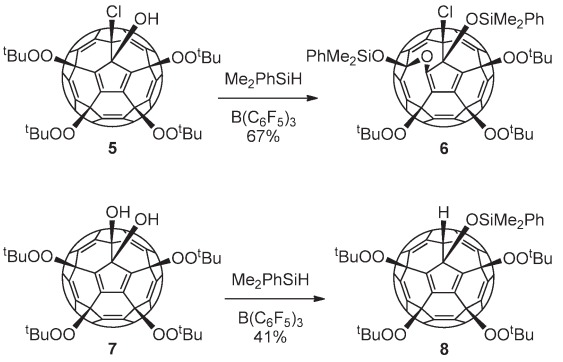
Scheme 1. Silane/Borane-Promoted Formation of Ketal 2 and Preparation of Fullerenol 4



Scheme 2. Reactions of 5 and 7 with Silane/Borane

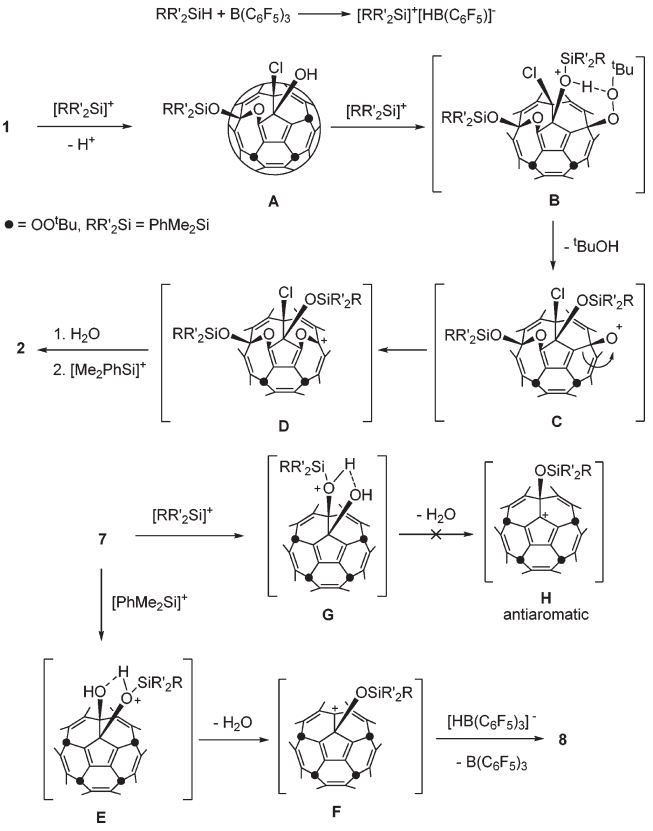


could be removed readily by TBAF with the exception of the central silyl group, which could not be deprotected under this condition. Interestingly, fullerenol **4** with two hemiketal moieties was obtained when compound **3** was treated with silver perchlorate and water. Both the Cl and siloxy groups were replaced by hydroxyl groups. However, the reaction of silver perchlorate with **2** gave complex mixture. Fullerenol **4** is different from fullerenols that we have reported before,[16] such as $C_{60}(OH)_6(OOtBu)_2$, in that **4** contains two hemiketal moieties at the [6,6] junctions.

In order to understand the mechanism of ketal formation promoted by silane/borane, we also studied the reaction of compound **5**[8] with $PhMe_2SiH/B(C_6F_5)_3$ (Scheme 2). In addition to the protection of the hydroxyl group, the reaction transformed a *tert*-butylperoxo group into a ketal moiety to form compound **6**. Unlike the ketal formation process with **5**, reaction of the dihydroxyl derivative **7**[17] afforded compound **8** with the *tert*-butylperoxo groups unchanged. Attempts to convert compound **6** and **8** into a bisketal derivative failed even at elevated temperatures with excess $PhMe_2SiH/B(C_6F_5)_3$. So presence of the OH group is essential for the conversion of the *tert*-butylperoxo group into a ketal moiety.

On the basis of the above results, a possible mechanism is proposed for the silane-promoted ketal formation reaction as shown in Scheme 3. The key step is the combination of the strong Lewis acid $B(C_6F_5)_3$ and hydride in silane giving an ion pair. The active and less hindered hemiketal hydroxyl group is first protected with silane to form intermediate **A**. Then the silylium

Scheme 3. Proposed Mechanisms for the Formation of 2 and 8



cation bonds to the other hydroxyl group on the central pentagon to form intermediate **B**. Because of steric hindrance the resulting proton on this OH group could not be easily removed by a base. Instead this proton combines with the *tert*-butoxyl group of the adjacent *tert*-butylperoxo group to form *tert*-butanol and the oxonium intermediate **C**. Following the general rearrangement pathway observed before,[7] the oxonium **C** rearranges into carbocation **D**. Finally, addition of water to **D** and protection of the resulting hemiketal hydroxyl group gives compound **2**.

The same mechanism can be used to explain the formation of compound **6** from **5**. Compound **8** probably formed through a slightly different process. In this case, the neighboring OH group interacts with the silane bound OH proton more strongly than the *tert*-butylperoxo group and form the carbocation **F**, which is then reduced by $[HB(C_6F_5)_3]^{-1}$ or silane to form **8**. Regioselectivity of the reaction of **7** may be due to the unfavorable antiaromatic nature of the carbocation **H**.

Oxidation of the vicinal diol moiety in **4** with various oxidizing agents provided no compounds that could be characterized probably due to the interference of the active hemiketal OH groups. To avoid the interference, we treated compound **3** with methyl iodide in the presence of silver oxide and obtained the methylated ketal **9** (Scheme 4). Then Cl in **9** was converted to a hydroxyl group by treating it with silver perchlorate and water. The silyl group in **9** could not be removed under standard conditions. Instead it migrated from the central pentagon to the adjacent hydroxyl oxygen to form compound **11** in the presence of hydrofluoric acid. Migration of the silyl group from one hydroxyl group to another is often observed in the deprotection

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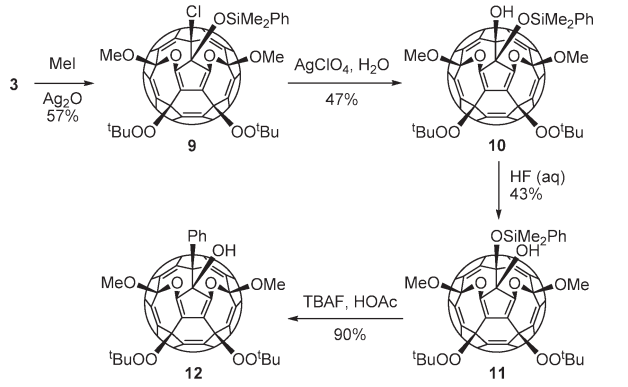
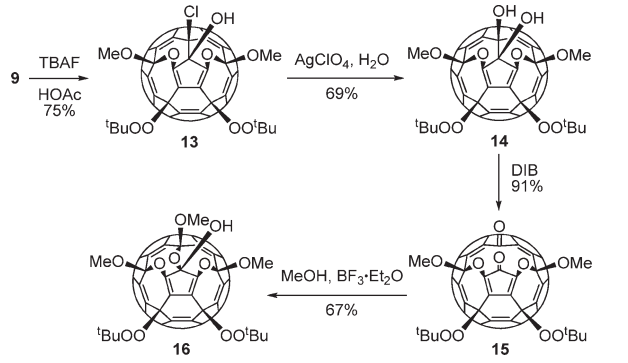
Scheme 4. Migrations of Silyl and Phenyl Groups To Form Compound 12



Scheme 5. Preparation of Open-Cage Fullerendione 15 and Close of the Orifice To Give 16



of other organic molecules.[18] Further treatment of **11** with TBAF removed the silyl group, but surprisingly a phenyl group was attached at the siloxy position. The phenyl group in **12** should originate from the cleavage of the Si−Ph bond and subsequent addition to the fullerene cage. In agreement with these results, the MS spectrum of compound **10** showed the molecular ion signal as the most intense peak, but the MS spectrum of compound **11** showed a signal corresponding to the Ph loss as the most intensive peak. Silyl ether has been converted directly to other functional groups, such as aldehydes, bromides.[19] The present intramolecular transformation from dimethylphenylsiloxy to phenyl is quite rare.

To prepare the vicinal diol derivative, we then switched the reaction sequence slightly. After the protection of the hydroxyl groups with iodomethane, the silyl group in **9** was first removed with TBAF and acetic acid to form **13** (Scheme 5). Then the Cl in **13** was replaced with a hydroxyl group to form **14**. Compound **14** shows poor solubility in benzene and dichloromethane but dissolves well in chloroform. Oxidation of **14** in chloroform with diacetoxyiodobenzene (DIB) in 5 min afforded bisketal fullerendione **15** with a 12-membered orifice in almost quantitive yields.[17] The excellent reactivity of **14** may due to the presence of the two ketal oxygen atoms which increase the tension of the carbon skeleton and thus facilitate the cage opening. Treatment of compound **15** with $BF_3 \cdot Et_2O$ in the presence of methanol resulted in **16** containing three oxygen atoms inserted at the [6,6] junction of the original fullerene skeleton.[17] This process provides a possible method for the preparation of endohedral-fullerenes if atoms such as helium could be pressed into the cage.

NMR spectra of most of these novel compounds are relatively simple due to the C_s symmetry. All of the hemiketal/ketal moieties showed characteristic peak ranging from 107.5 to 112.5 ppm. The FTIR spectrum of **15** exhibits a strong C═O stretching band at 1750 cm^{-1}, which is similar to our previously reported fullerendione[17] and other open-cage fullerene derivatives reported by Komatsu et al.[20] To further confirm the open-cage structure, single crystals of **15** were obtained by slow evaporation of its solution in a mixture of chloroform and isopropyl alcohol at 5 °C. X-ray analysis confirmed our structural assignment. Pentagons containing carbonyl groups and ketal groups adopt an envelope shape. The ketal carbons are positioned out of the cage surface by about 0.6 Å. This is longer than for carbonyl carbons (about 0.4 Å). The distances between the two carbonyl oxygen atoms and the two carbonyl carbon atoms are 2.608 and 2.989 Å, respectively, which are also a little farther apart than those of the fullerene dione derivative without the ketal moieties.[21]

CONCLUSION

In summary, silane/borane has been shown to be an effective reagent not only for the protection of fullerenols but also for the formation of oxahomofullerenes from fullerene-mixed peroxides. Adjacent functional groups have significant effect on the reactions involving silane and silyl fullerene derivatives. An open-cage fullerene with a 12-membered orifice has been prepared through oxidation of a vicinal fullerendiol. The two carbonyl groups on the rim of the orifice can be readily coupled into ketal moieties, thus closing the orifice effectively. Further work is underway to enlarge the hole and study its encapsulation of small molecules.

EXPERIMENTAL SECTION

All reagents were used as received. Toluene was distilled from sodium. Dichloromethane was distilled over phosphorus pentaoxide. Chloroform was treated with concentrated H_2SO_4, washed with water to remove ethanol, and dried with anhydrous K_2CO_3. Other solvents were used as received. The reactions were carried out in air. Compound **1** was prepared as in ref 8. NMR spectra were recorded at room temperature (298 K). Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESI-HRMS spectra were recorded with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent; positive-mode spectra were recorded, unless otherwise noted. FTIR spectra were recorded in the microscope mode. Chromatographic purifications were carried out with silica gel of mesh 200−300. **Caution:** a large amount of peroxides is involved in some of the reactions; care must be taken to avoid possible explosion.

Compound 2. To a stirred solution of compound **1** (170 mg, 0.158 mmol) and dimethylphenylsilane (118 mg, 0.866 mmol) in toluene (6 mL) at 25 °C was added $B(C_6F_5)_3$ (12 mg, 0.023 mmol). The resulting solution turned black quickly with hydrogen bubbling out of the solution. The reaction was monitored by TLC and quenched by filtering through a short silica gel column eluting with toluene. Then toluene was removed under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with petroleum ether to remove unreacted silane. Then the solvent was changed to toluene/petroleum ether (v/v) = 1:3 and the first red band was collected giving compound **2** (138 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.92−7.94 (m, 2H), 7.59−7.61 (m, 4H), 7.46−7.48 (m, 2H), 7.28−7.30 (m, 7H), 1.37 (s, 18H), 0.74 (s, 6H), 0.64 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 150.22, 149.98, 149.76, 149.72, 149.30, 149.02 (1C), 148.73, 148.42,

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148.03, 147.99, 147.93, 147.65 (1C), 147.48, 146.96, 146.44, 144.56, 144.23, 143.31, 142.56, 142.34, 142.32, 141.84, 140.81, 139.57, 139.13, 138.37, 138.17, 137.97, 137.24, 133.74, 133.55 (4C), 129.70, 129.61 (1C), 127.72 (5C), 127.70, 125.96 (1C), 108.53, 82.54 (1C), 82.21, 81.51, 77.80 (1C), 26.69 ($6CH_3$), 0.33 ($2CH_3$), 0.18 ($2CH_3$), 0.05 ($2CH_3$). IR (microscope): 3069, 3048, 2978, 2928, 1683, 1648, 1473, 1454, 1428, 1364, 1254, 1195, 1118, 1065, 1028, 1013, 997,961, 907, 868, 835, 817, 791, 732, 697 cm^{-1}. ESI-HRMS: $C_{92}H_{55}ClNO_9Si_3$ (M + NH_4^+) calcd 1436.2868, found 1436.2849.

Compound 3. To a stirred solution of compound **2** (388 mg, 0.273 mmol) and acetic acid (134 μL) in dichloromethane (30 mL) at 25 °C was added tetrahydrofuran (3 mL) containing tetrabutylammonium fluoride (211 mg, 0.807 mmol). The reaction was monitored by TLC. After about 3 min, the reaction was quenched by adding water. The solution was washed by water three times. The organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with toluene/petroleum ether (v/v) = 1:1 to remove some unknown impurities. Then the solvent was changed to toluene/ethyl acetate (v/v) = 50:1 giving compound **3** (260 mg, 83%). (The eluting process should be done quickly. Otherwise the yield would be low.) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93−7.96 (m, 2H), 7.49−7.50 (m, 3H), 4.76 (s, 2H), 1.37 (s, 18H), 0.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 150.13, 149.96, 149.78, 149.40, 149.02 (1C), 148.86, 148.57, 148.16, 148.08, 148.01, 147.90 (1C), 147.74, 147.56, 147.04, 146.35, 144.63, 143.38, 143.27, 142.73, 142.53, 142.17, 142.00, 141.29, 139.89, 139.50, 139.00, 138.39, 137.75, 133.83, 129.75 (1C), 127.76, 125.64 (1C), 107.57, 82.70 (1C), 82.34, 81.78, 77.94 (1C), 26.71 ($6CH_3$), 0.25 ($2CH_3$). IR (microscope): 3483, 3421, 3069, 2978, 2928, 1683, 1650, 1472, 1454, 1427, 1364, 1257, 1192, 1154, 1114, 1066, 855, 837, 809, 789, 735, 700 cm^{-1}. ESI-HRMS: $C_{76}H_{35}ClNO_9Si$ (M + NH_4^+) calcd 1168.1764, found 1168.1741.

Compound 4. To a stirred solution of compound **3** (40 mg, 0.043 mmol) in toluene (8 mL) at 25 °C was added water (6 μL). Then silver perchlorate hydrate (23 mg, 0.102 mmol) was added. The resulting solution was stirred in the dark and monitored by TLC. About 10 min later, the reaction was quenched by adding water. The solution was washed three times with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with chloroform/methanol (v/v) = 100:1 giving compound **4** (11 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$/d_8-dioxane) δ: 7.65 (s,1H), 6.50 (br,s,2H), 3.49 (s,1H), 1.36 (s,18H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 151.04, 149.97, 149.83, 149.42, 149.18, 148.87, 148.70 (4C), 148.03, 147.92 (5C), 147.69, 147.15, 146.43, 145.73 (1C), 145.07 (4C), 143.24, 142.51 (4C), 142.25, 141.94, 140.99, 140.16, 139.57, 139.32, 139.21, 107.47, 84.29, 82.62 (1C), 81.81, 80.94 (1C), 26.74 ($6CH_3$). IR (microscope): 3384, 2979, 2930, 1647, 1388, 1365, 1188, 1154, 1110, 1052, 1027, 1007, 867, 791, 749 cm^{-1}. ESI-HRMS: $C_{68}H_{26}NO_{10}$ (M + NH_4^+) calcd 1016.1551, found 1016.1555.

Compound 6. To a stirred solution of compound **5** (81 mg, 0.072 mmol) and dimethylphenylsilane (75 mg, 0.550 mmol) in toluene (6 mL) at 25 °C was added $B(C_6F_5)_3$ (9 mg, 0.017 mmol). The resulting solution turned black quickly with hydrogen bubbling out of the solution. The reaction was monitored by TLC and quenched by filtering through a short silica gel column eluting with toluene. Then toluene was removed under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with petroleum ether to remove unreacted silane. Then the solvent was changed to toluene/petroleum ether (v/v) = 1:2 and the first red band was collected giving compound **6** (64 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95−7.98 (m, 2H), 7.61−7.64 (m,2H), 7.45−7.47 (m, 3H), 7.27−7.32 (m, 3H), 1.40 (s, 9H), 1.39 (s, 9H), 1.25 (s, 9H), 0.88 (s, 3H), 0.80 (s, 3H), 0.68 (s, 3H), 0.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 1C except noted. δ: 158.88, 150.48, 149.78, 149.45, 149.43, 149.31, 148.99, 148.91, 148.72, 148.58, 148.45, 148.39, 148.30, 148.18, 143.03, 147.92 (2C), 147.79, 147.76, 147.73, 147.65 (2C), 147.52, 147.22, 147.20, 146.64, 146.44, 146.12, 145.58, 145.12, 144.45, 144.34, 144.12, 143.93, 143.79, 143.56, 143.25, 143.09, 142.74, 142.56 (2C), 142.19, 141.99, 141.89, 141.78, 141.17, 140.32, 139.77, 139.39, 138.83, 138.76, 138.73, 137.76, 137.23, 136.83, 133.77 (2C), 133.58 (2C), 129.71, 129.38, 128.31, 127.72 (2C), 127.67, 127.60 (2C), 108.70, 83.85, 82.89, 82.00, 81.60, 81.58, 81.56, 81.53, 78.61, 74.16, 26.71 ($6CH_3$), 26.58 ($3CH_3$), 1.32 (CH_3), 0.62 (CH_3), 0.21 (CH_3), 0.07 (CH_3). ESI-HRMS: $C_{88}H_{53}NO_9ClSi_2$ (M + NH_4^+) calcd 1358.2942, found 1358.2921.

Compound 8. To a stirred solution of compound **7** (87 mg, 0.078 mmol) and dimethylphenylsilane (75 mg, 0.550 mmol) in toluene (6 mL) at 25 °C was added $B(C_6F_5)_3$ (11 mg, 0.021 mmol). The resulting solution turned black quickly with hydrogen bubbling out of the solution. The reaction was monitored by TLC and finished in 1 min. Then it was quenched by filtering through a short silica gel column eluting with toluene. Then toluene was removed under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with petroleum ether to remove unreacted silane. Then the solvent was changed to toluene/petroleum ether (v/v) = 1:2 and the first red band was collected giving compound **8** (39 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86−7.89 (m, 2H), 7.44−7.46 (m, 3H), 5.35 (s, 1H), 1.43 (s, 18H), 1.32 (s, 18H), 0.94 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 152.27, 151.92, 149.39, 149.08, 148.85, 148.57, 148.26, 148.12, 148.04 (1C), 147.55, 147.43, 147.17, 147.06 (4C), 146.54, 146.32 (1C), 146.08, 145.84, 145.63, 145.17, 144.56, 144.24, 143.61, 143.46, 142.78, 141.85, 141.61, 140.10, 136.96, 133.42, 129.22, 127.65, 85.90, 83.49, 81.54, 81.32, 80.79 (1C), 55.27 (1C), 26.78 ($6CH_3$), 26.69 ($6CH_3$), 1.64 ($2CH_3$). ESI-HRMS: $C_{84}H_{52}NO_9Si$ (M + NH_4^+) calcd 1246.3406, found 1246.3424.

Compound 9. To a stirred solution of compound **3** (114 mg, 0.099 mmol) and iodomethane (6 mL) in dichloromethane (20 mL) at 25 °C was added silver oxide (148 mg, 0.023 mmol). The reaction was stirred in the dark and monitored by TLC. After 3 days, the reaction was stopped, and the solvent was removed under reduced pressure. The obtained residue was chromatographed on a silica gel column eluting with toluene/petroleum ether (v/v) = 1:1 and the first red band was collected giving compound **9** (66 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94−7.96 (m,2H), 7.48−7.51 (m,3H), 3.86 (s,6H), 1.36 (s,18H), 0.81 (s,6H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 150.28, 149.89, 149.68, 149.25, 148.92 (1C), 148.75, 148.46, 148.04, 147.92, 147.89, 147.78, 147.75 (1C), 147.71, 146.98, 146.45, 144.52, 143.22, 143.09, 142.58, 142.41, 142.32, 141.98, 141.86, 140.93, 139.75, 138.97, 138.26, 137.56, 133.53, 129.51 (1C), 127.63, 125.47 (1C), 111.28, 82.19, 81.43, 54.41, 26.56, 0.004. IR (microscope): 3069, 3047, 2976, 2925, 2850, 1683, 1650, 1456, 1428, 1386, 1363, 1255, 1194, 1162, 1105, 1068, 1022, 1001, 962, 856, 789, 748, 699 cm^{-1}. ESI-HRMS: $C_{78}H_{39}ClNO_9Si$ (M + NH_4^+) calcd 1196.2077, found 1196.2047.

Compound 10. To a stirred solution of compound **9** (52 mg, 0.044 mmol) in dichloromethane (10 mL) at 30 °C was added water (30 μL). After stirring for 15 min, silver perchlorate hydrate (25 mg, 0.111 mmol) was added. The resulting solution was stirred in the dark and monitored by TLC. About 2 h later, the solution was directly chromatographed on a short silica gel column eluting with toluene to remove unknown impurities, and then the solvent was changed to toluene/petroleum ether/ethyl acetate (v/v) = 30:15:2 giving compound **10** (24 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, J = 7.20 Hz, 2H), 7.36−7.38 (m,3H), 4.04 (s,6H), 2.81 (s,1H), 1.39 (s,18H), 0.12 (s,6H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 151.41, 150.11, 149.95, 149.71, 149.23, 148.98, 148.59, 148.33 (1C), 148.06, 148.03, 147.89, 147.59 (1C), 147.54, 147.18, 146.16, 144.05, 143.67, 143.50, 142.67, 142.62, 142.06, 141.88, 141.68, 141.55, 139.60, 138.94,

138.75, 130.79, 127.65, 127.05 (1C), 124.49 (1C), 111.87, 83.15 (1C), 82.52, 81.78, 81.58, 73.27 (1C), 55.12, 26.69 ($6CH_3$), −0.78 ($2CH_3$). ESI-HRMS: $C_{78}H_{40}NO_{10}Si$ (M + NH_4^+) calcd 1178.2416, found 1178.2400.

Compound 11. To a stirred solution of compound **10** (60 mg, 0.052 mmol) in dichloromethane (6 mL) at 25 °C was added hydrofluoric acid (40%, 3 mL). The reaction was monitored by TLC. After 25 min, the reaction was quenched by adding water. The solution was washed by water three times. The organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with toluene/petroleum ether (v/v) = 2:1 giving compound **11** (26 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 7.62 Hz, 2H), 7.38 (t, J = 7.69 Hz, 2H), 7.27 (t, J = 7.20 Hz, 1H), 4.04 (s,6H), 2.31 (s,1H), 1.38 (s,18H), 0.18 (s,3H), 0.16 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 150.88, 150.06, 149.91, 149.59, 149.18, 148.94, 148.56, 148.32 (1C), 148.02 (4C), 147.87, 147.54 (1C), 147.49, 147.12, 146.12, 144.84, 144.08, 143.45, 143.34, 142.61, 142.58, 142.02, 141.79, 141.59, 141.51, 139.56, 138.84, 138.79, 130.79, 127.74, 127.06 (1C), 124.57 (1C), 111.81, 83.46 (1C), 82.45, 81.42, 73.16 (1C), 55.03, 26.61 ($6CH_3$), −2.02 (CH_3), −2.20 (CH_3). ESI-HRMS: $C_{74}H_{42}NO_{13}Si$ (M + $2CH_3OH$ + H_2O + NH_4^+ − C_6H_6) calcd 1180.2420, found 1180.2361.

Compound 12. To a stirred solution of compound **11** (25 mg, 0.022 mmol) and acetic acid (15 μL) in dichloromethane (5 mL) at 25 °C was added tetrahydrofuran (1 mL) containing tetrabutylammonium fluoride (17 mg, 0.065 mmol). The reaction was monitored by TLC. After 10 min, the reaction was quenched by adding water. The solution was washed with water for three times. The organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with toluene/petroleum ether/ethyl acetate (v/v) = 20:10:1 giving compound **12** (21 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J = 7.55 Hz, 2H), 7.51 (t, J = 7.83 Hz, 2H), 7.38 (t, J = 7.40 Hz, 1H), 4.05 (s,6H), 2.55 (s,6H), 1.41 (s,18H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 151.16, 150.11, 149.98, 149.32, 149.28, 149.04, 148.60, 148.44 (1C), 148.16, 148.07, 147.97, 147.66 (1C), 147.43, 147.24, 146.21, 144.89, 144.39, 143.54, 142.70, 142.65 (4C), 142.19, 142.12, 141.78, 139.84, 139.67, 138.91, 138.65, 130.42, 129.24, 128.29 (1C), 124.47 (1C), 112.09, 82.72 (1C), 81.81, 71.93, 65.58 (1C), 55.26, 26.74 ($6CH_3$). ESI-HRMS: $C_{76}H_{34}NO_9$ (M + NH_4^+) calcd 1104.2228, found 1104.2213.

Compound 13. To a stirred solution of compound **9** (170 mg, 0.144 mmol) and acetic acid (100 μL) in dichloromethane (30 mL) at 25 °C was added tetrahydrofuran (3 mL) containing tetrabutylammonium fluoride (110 mg, 0.421 mmol). The reaction was monitored by TLC. After 2 h, another portion of tetrahydrofuran (3 mL) containing tetrabutylammonium fluoride (53 mg, 0.421 mmol) was added to the above solution; 35 min later, the reaction was quenched by adding water. The solution was washed with water three times. The organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with toluene/petroleum ether (v/v) = 1:1 to remove unknown impurities. Then the solvent was changed to toluene/petroleum ether/ethyl acetate (v/v) = 50:25:1 giving compound **13** (113 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.15 (s,1H), 3.96 (s,6H), 1.40 (s,18H). ^{13}C NMR (75 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 149.98, 149.79, 149.63, 149.44, 149.12 (1C), 148.93, 148.54, 148.23, 148.12, 148.05, 147.94 (1C), 147.52, 147.30, 147.16, 146.16, 144.64, 143.47, 143.02, 142.71, 142.52, 142.07, 141.68 (4C), 141.57, 140.02, 139.17, 137.35, 111.63, 82.42 (1C), 81.99, 81.35, 77.79 (1C), 54.96, 26.68 ($6CH_3$). IR (microscope): 3514, 2978, 2932, 1684, 1651, 1455, 1387, 1364, 1230, 1191, 1157, 1103, 1052, 1021, 935, 870, 824, 756, 730, 695 cm^{-1}. ESI-HRMS: $C_{70}H_{29}ClNO_9$ (M + NH_4^+) calcd 1062.1525, found 1062.1507.

Compound 14. To a stirred solution of compound **13** (144 mg, 0.138 mmol) in dichloromethane (25 mL) at 30 °C was added dimethyl sulfoxide (2.5 mL) containing water (23 μL). After 15 min of stirring, silver perchlorate hydrate (93 mg, 0.413 mmol) was added. The resulting solution was stirred in the dark and monitored by TLC. About 1 h and 15 min later, the reaction was quenched by filtering through a short silica gel column eluting with dichloromethane/methanol (v/v) = 100:1. The solution was washed several times with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained residue was chromatographed on a silica gel column eluting with toluene/petroleum ether/ethyl acetate (v/v) = 10:5:2 giving compound **14** (98 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.16 (s,1H), 4.57 (s,1H), 3.96 (s,6H), 1.40 (s,18H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 150.21, 149.94, 149.80, 149.43, 149.13 (1C), 148.90, 148.63, 148.17, 148.07, 147.99, 147.97 (1C), 147.46, 147.14, 147.00, 146.21, 144.87, 143.78, 143.33, 142.68, 142.50, 142.12, 141.72, 141.69, 141.57, 140.26, 139.26, 139.23, 111.41, 84.64, 82.47 (1C), 81.87, 81.26, 77.41 (1C), 54.98, 26.72 ($6CH_3$). IR (microscope): 3448, 2977, 2931, 1681, 1649, 1455, 1387, 1363, 1231, 1190, 1157, 1101, 1050, 1019, 925, 870, 756, 730, 695 cm^{-1}. ESI-HRMS: $C_{70}H_{30}NO_{10}$ (M + NH_4^+) calcd 1044.1864, found 1044.1840.

Compound 15. To a stirred solution of compound **14** (79 mg, 0.077 mmol) in chloroform (25 mL) at 35 °C was added iodobenzene diacetate (37 mg, 0.115 mmol). The reaction was monitored by TLC. After 5 min, the solution was chromatographed on a silica gel column eluting with toluene/petroleum ether/ethyl acetate (v/v) = 30:15:1 giving compound **15** (72 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.90 (s,6H), 1.38 (s,18H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 194.16, 189.75, 150.48, 149.92 (1C), 149.75, 149.23, 148.95 (1C), 148.93, 148.83, 148.31, 148.23, 148.02, 147.55, 147.36, 145.82, 144.99, 144.85, 144.48, 143.71, 142.80, 141.96, 141.63, 140.61, 140.43, 140.38, 139.08, 138.70, 131.37, 115.46, 82.23, 80.91, 55.52, 26.62 ($6CH_3$). IR (microscope): 2975, 2935, 1750, 1664, 1634, 1512, 1456, 1387, 1364, 1193, 1135, 1083, 1049, 997, 959, 754 cm^{-1}. ESI-HRMS: $C_{70}H_{28}NO_{10}$ (M + NH_4^+) calcd 1042.1708, found 1042.1682.

Single crystals were obtained from slow evaporation of **15** in $CHCl_3$/*i*PrOH. Crystal data for **15** ($C_{70}H_{24}O_{10}$, M_r = 1024.89): crystal size 0.40 mm × 0.30 mm × 0.10 mm, monoclinic, space group $P2(1)/c$, a = 13.2045(18), b = 19.022(3), c = 18.615(3) Å, α = 90, β = 98.097(2), γ = 90°, V = 4629.2(11) Å^3, Z = 4, ρ_{calcd} = 1.471 Mg/m^3, T = 173(2) K; 41141 reflections collected, 10574 independent (R_{int} = 0.0545) included in the refinement; max/min transmission 0.9902/0.9615; refinement by full-matrix least-squares method on F^2 ; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0688, $wR2$ = 0.1618, R indices (all data): $R1$ = 0.0793, $wR2$ = 0.1682. CCDC-825991.

Compound 16. To a stirred solution of compound **15** (35 mg, 0.034 mmol) and methanol (170 μL) in dichloromethane (7 mL) at 25 °C was added boron trifluoride ether solution (48%, 150 μL). The reaction was monitored by TLC. After 2 h, the reaction was quenched by adding water. The organic solution was washed with water three times and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed on a short silica gel column eluting with toluene/petroleum ether/ethyl acetate (v/v) = 10: 5:2 giving compound **16** (24 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.08 (s,1H), 3.94 (s,6H), 3.80 (s,3H), 1.41 (s,18H). ^{13}C NMR (75 MHz, $CDCl_3$) all signals represent 2C except noted. δ: 150.84, 150.01, 149.58 (1C), 149.06, 148.90, 148.73, 148.54, 148.38 (3C), 148.12, 147.43, 147.16, 146.17, 145.92, 145.78, 143.76, 142.74, 142.21, 142.02, 141.13, 140.34, 140.21, 140.18, 139.95, 139.45, 139.03, 134.90, 121.92, 112.48, 111.55 (1C), 96.34, 81.96, 81.58, 55.28, 54.17 (1C), 26.66 ($6CH_3$). IR (microscope): 3385, 2977, 2927, 2852, 1690, 1659, 1459, 1386, 1364, 1214, 1184, 1160, 1091, 1055, 1000, 971,

908, 871, 733 cm^{-1}. ESI-HRMS: $C_{71}H_{32}NO_{11}$ ($M + NH_4^+$) calcd 1074.1970, found 1074.1944.

■ ASSOCIATED CONTENT

Supporting Information. Selected spectroscopic data for all new compounds and crystallographic data for **15** including CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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