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Selective Synthesis of Fullerenol Derivatives with Terminal Alkyne and Crown Ether Addends

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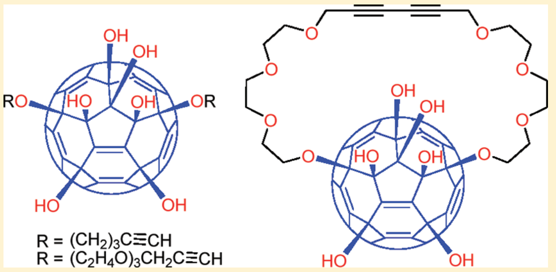
Supporting Information

ABSTRACT: A series of isomerically pure alkynyl-substituted fullerenol derivatives such as $C_{60}(OH)_6(O(CH_2)_3CCH)_2$ were synthesized through Lewis acid catalyzed epoxy ring opening and/or S_N1 replacement reactions starting from the fullerene−mixed peroxide $C_{60}(O)(t\text{-BuOO})_4$. Copper-catalyzed azide−alkyne cycloaddition readily converted the terminal alkynyl groups into triazole groups. Intramolecular oxidative alkyne coupling afforded a fullerenyl crown ether derivative.



■ INTRODUCTION

Fullerenols have been a subject of intensive research in medicine and materials chemistry because of their unique properties such as free-radical scavenging,[1] antioxidizing,[2] photosensitizing,[3] and electrochemical properties.[4] Thus, its synthesis has attracted much attention and a number of methods have been developed, including both acidic[5] and basic hydroxylation methods.[6] However, all these fullerenols are a mixture of fullerene derivatives with different number of hydroxyl groups and different chemical structures. To develop practical functional materials, in particular for fullerene-based medicine, the purity and identity of fullerenols are of crucial importance. Meier and co-workers prepared the simplest fullerene diols, $C_{60}(OH)_2$ and $C_{70}(OH)_2$, by the reaction of C_{60} and C_{70} with RuO_4 followed by acid hydrolysis.[7] A mild and facile process for the preparation of 1,4-fullerenols $C_{60}ArOH$ was achieved by Wang and co-workers.[8] Through peroxide-mediated fullerene reactions, we have obtained a variety of closed-cage and open-cage fullerenols with at least one hydroxyl group and/or hemiketal moiety.[9] Recently, we reported the preparation of the first isomerically pure multihydroxylated fullerene, $C_{60}(OH)_8$.[10]

The combination of fullerenol with other functional moieties could expand possible applications for fullerenols. In the study of photophysical properties, connecting the fullerene cage to other chromophores has been proven to be a very successful strategy to enhance the device performance.[11] However, hydroxyl groups directly bound on the fullerene cage show reactivity quite different from those in classical organic molecules, and it is difficult to attach other functional components onto the fullerenol cage through the fullerenol OH group. The preparation of fullerenol derivatives containing a facile functional group is an alternative method to attach another functional partner onto the fullerenol cage. To prepare such a mixed-fullerenol derivative, we have chosen alkynyl groups as the reactive functional group. Fullerene derivatives with terminal alkynyl addend(s) have been shown to be very useful for further functionalization by Click chemistry.[11] Here we report the synthesis of fullerenol derivatives with various numbers of hydroxyl groups together with one or two terminal alkynyl groups and further reactions of the alkynyl group.

■ RESULTS AND DISCUSSION

Synthesis of Fullerenol Derivatives with Alkynyl Addends. Compound **1** was prepared from C_{60}, as we have reported previously.[12] In the presence of boron trifluoride, the epoxy group of **1** was opened with terminal alkynyl alcohols to form compound **2** (Scheme 1). The yields of **2** decreased as the length of the alcohol increased from **2a** to **2c**. Other Lewis acids such as $FeCl_3$ could also catalyze the reaction, but with lower yields.

To convert the *tert*-butylperoxo groups in **2** into hydroxyl groups, we heated it at 110 °C for 12 h (Scheme 1). Addition of iodine improved the yield in this thermolysis reaction. Iodine probably reacted with radical species, preventing them from adding to the fullerene cage. Only two *tert*-butylperoxo groups were converted into epoxy groups. The other two remained unchanged even after prolonged heating. Raising the temperature resulted in slow conversion into a complex mixture of products. Compounds **3** and **4** are isomers, differing in the relative locations of the two epoxy groups. Treatment of **3** with

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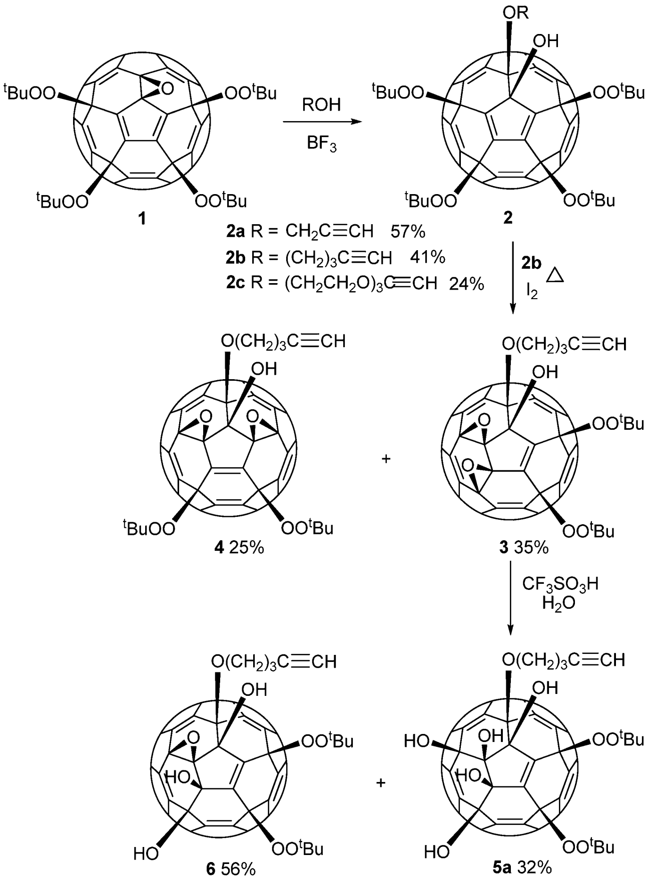
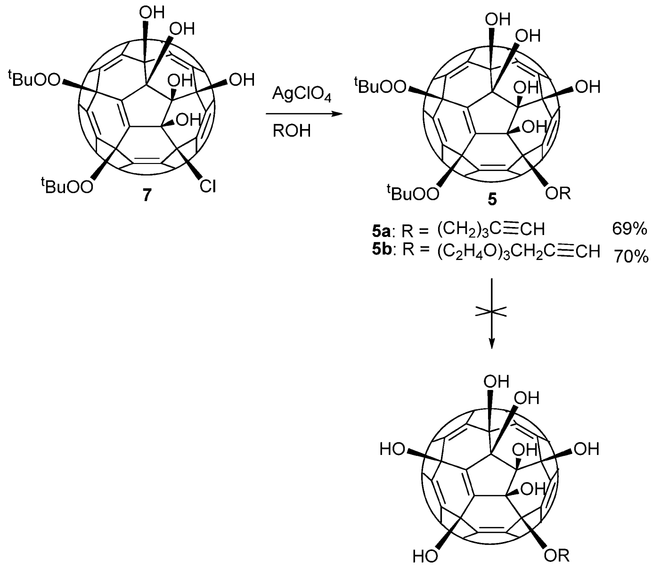
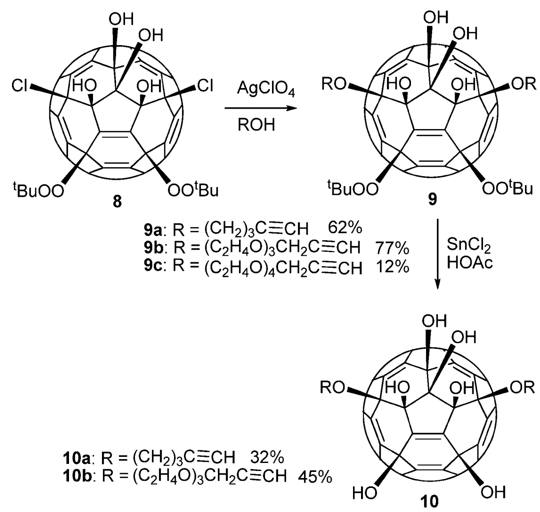
Scheme 1. Formation of Polyhydroxyl Derivatives Containing One Alkynyl Substituent



Scheme 2. Silver Perchlorate Mediated Addition of Terminal Alkynyl Alcohols



Scheme 3. Formation of Polyhydroxyl Derivatives Containing Two Alkynyl Substituents

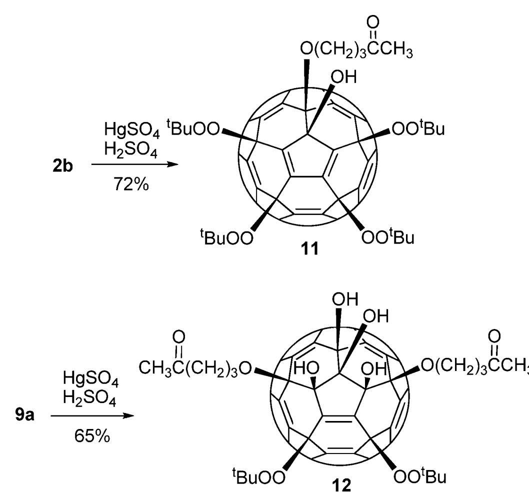


CF_3SO_3H/H_2O opened the epoxy groups to form compounds **5** and **6**. Compound **6** with one epoxy group remaining is an intermediate to **5**. Further treatment of **6** with CF_3SO_3H/H_2O could convert **6** into **5**. Under the same hydrolysis conditions, compound **4** gave very low yields of fullerenol derivatives, indicating that the epoxy group next to the OH group was less reactive because of steric effects.

Another way of making compound **5** is the silver perchlorate mediated S_N1 reaction of the fullerenol derivative **7** with the corresponding alcohol (Scheme 2). Compound **7** was prepared from **1** in four steps as reported before.[10] Efforts to reduce the two *tert*-butylperoxo groups in **5** were unsuccessful. The silver perchlorate mediated S_N1 reaction could also be applied to the C_s-symmetric dichloro fullerenol derivative **8** (Scheme 3), which was prepared from **1** in three steps.[10] The resulting product **9** could be further reduced into compound **10** with six hydroxyl groups.

Hydration, Click Reaction, and Hay Coupling of Alkynyl Groups in Fullerenols. The fullerenol derivatives were very stable and could be stored for months with little change. A sample of **10b** was stored for about 1 year with almost no noticeable decomposition. In an effort to test their reactivity toward further derivatization, compounds **2b** and **9a** were treated with a solution of mercury sulfate (Scheme 4). The alkynyl group was converted into an acetyl group rapidly to give **11** and **12**, respectively. The result is the same as that for classical organic alkyne hydration, yielding a ketone not an aldehyde. Under the hydration conditions, the *tert*-butylperoxo and the hydroxyl groups remained unchanged.

Scheme 4. Hydration of Terminal Alkynyl Groups



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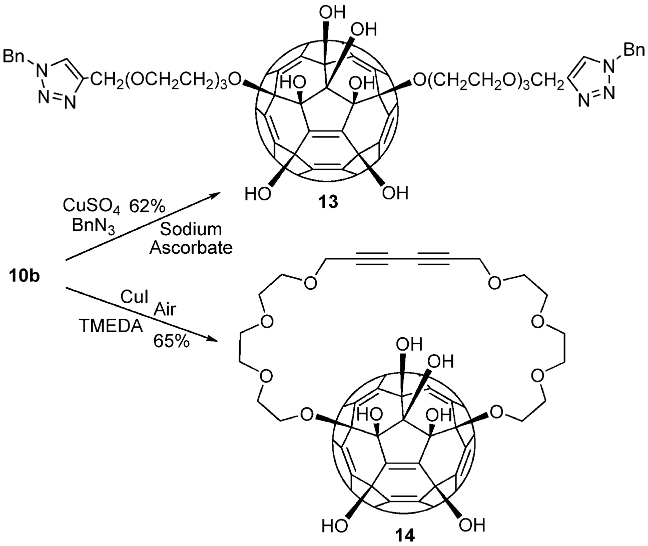
Copper-catalyzed azide–alkyne cycloaddition (CuAAC) is the most widely used click reaction to prepare functional compounds for materials and biological studies. The reaction has also been successfully employed in the preparation of functional fullerene derivatives by the groups of Schuster, Nierengarten, Martin, and others.[11] To test the reactivity of the present alkyne fullerenol derivatives toward click reactions, we treated **10b** with (azidomethyl)benzene (Scheme 5). The bis-triazole derivative **13** was obtained in good yield. The addition should be a stepwise process, but the mono-triazole compound was not detected.

Scheme 5. Click and Hay Coupling Reactions



Another typical reaction for terminal alkyne is the oxidative coupling of two terminal alkyne groups: i.e. Glaser coupling and Hay coupling. Various conditions have been developed recently for cross coupling of terminal alkynes.[13] To prepare a crown ether type product, we tried the intramolecular coupling of **10b** under Hay coupling conditions and obtained compound **14** with a crown size comparable to that of 24-crown-8 (Scheme 5). To avoid intermolecular coupling, the concentration of **10b** was kept at around 1 mg/3 mL in $CHCl_3$, which is relatively dilute compared to the case for other reactions in the present work.

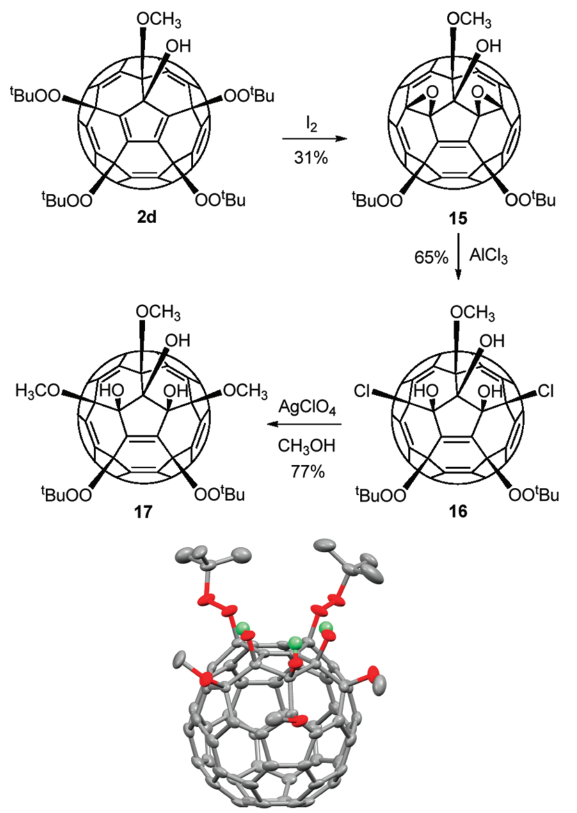
Characterization of Alkynyl Fullerenol Derivatives. Spectroscopic data are in agreement with the structures depicted in the schemes. Compounds **2**, **4**, and **9–13** are C_s symmetric. Their ^1H and ^{13}C NMR spectra showed the expected number of signals. For example, compound **9a** showed three signals at 6.07, 5.64, and 5.55 ppm in a ratio of 1:1:2 corresponding to the four OH groups. Its ^{13}C NMR spectrum showed 25 signals and 2 signals with half intensity in the range from 136 to 149 ppm, assignable to the 52 sp^2 fullerene skeleton carbons. For compounds **11** and **12**, the carbonyl carbon appears at δ 207.95 and 208.20 ppm in the ^{13}C NMR spectra, respectively. Their carbonyl stretching bands appear at 1718 and 1730 cm^{-1} as two intense signals on the IR spectrum.

^1H NMR spectrum of the crown ether derivative **14** is broad at room temperature. Heating the NMR solution to 50 °C improved the resolution. The six hydroxyl groups appear at 6.41, 5.89, and 5.52 ppm in a ratio of 2:1:2, in agreement with its C_s symmetry. Its ^{13}C NMR at room temperature showed 31 signals in the range 136–150 ppm instead of the expected 25 for C_s symmetry for the 52 sp^2 fullerene skeleton carbons, 21 of which are twice the intensity of the other 10 signals. These NMR data indicate that rotation of the crown ether moiety is hindered at room temperature.

Spectroscopic data of compounds **3**, **5**, and **6** indicate that they are C_1 symmetric. It is not difficult to determine what functional groups are present in these molecules through the NMR and HRMS data. However, these data cannot determine the exact locations of the addends. The structures shown in Scheme 1 are mainly induced on the basis of correlations with analogous reaction products reported previously. Mechanistic considerations support the proposed structures with the alkoxy group on the outside in compounds **2** and **9**.[14]

To obtain more conclusive evidence about the structure assignments, we tried to grow crystals under various conditions. The long alkyl and glycol chains present in the above compounds appear to not be suitable for single-crystal formation. We then prepared the methoxyl derivatives **15–17** from **2d**[14a] through essentially the same reaction sequence as above (Scheme 6). In the synthesis of **15**, the isomer **15a** with the epoxy groups next to each other was also obtained, as in the thermolysis reaction of compound **2b**. Yields of the methoxyl derivatives were higher than for the corresponding alkynyl derivatives. Single crystals of **17** were obtained by slow evaporation of its solution in CS_2/hexane/toluene. The X-ray structure showed that the three methoxyl groups are on the outside of the central pentagon. Previously we have reported the single-crystal X-ray structure of an isopropyl analogue of compound **9**.[10] It is unlikely that the methyl and isopropyl

Scheme 6. Synthesis and X-ray Structure of 17[a]



[a]For clarity hydrogen atoms on the methyl groups are not shown.

derivatives follow a different mechanism from the alkynyl derivatives. Therefore, structures of all the new compounds prepared in the present work can be assigned as shown in the schemes.

In summary, fullerenols containing up to six hydroxyl groups and one or two terminal alkynyl groups can be effectively synthesized through Lewis acid catalyzed epoxy ring opening or S_N1 replacement reactions. Terminal alkyne groups in these fullerenol derivatives exhibit reactivity comparable with that of classical organic alkynes such as Click reactions and Hay coupling. Further work will be directed toward attaching specific designed functional groups to the fullerenol moiety and exploring their possible applications.

EXPERIMENTAL SECTION

All reagents were used as received. Toluene used for the reactions was distilled from potassium under nitrogen. Dichloromethane (DCM) was distilled from phosphorus pentoxide. 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. The NMR spectra were obtained at 25 °C unless noted.

Caution: A large amount of peroxides is involved in some of the reactions. Care must be taken to avoid possible explosion.

Compounds 2a–c. To a solution of the alcohol and compound **1** in DCM was added $BF_3 \cdot Et_2O$ at 30 °C in the dark. The reaction was monitored by TLC, and quenched by water. The organic layer was dried over anhydrous sodium sulfate, and concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography using a gradient of toluene and petroleum ether (60–90 °C) to yield the desired compounds **2a–c** (Table 1).

Table 1

product	**1**, mg	alcohol, equiv	time	yield, mg (%)
2a	585	2	15 min	364 (57)
2b	1055	50	30 h	545 (41)
2b	158	2	120 h	41 (24)

*Characterization Data of Compound **2a**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.93 (d, *J* = 2.4 Hz, 2H), 4.75 (s, 1H), 2.49 (t, *J* = 2.5 Hz, 1H), 1.48 (s, 18H), 1.46 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 155.83, 149.65, 149.12, 149.02, 148.67, 148.59, 148.46 (1C), 148.39, 148.37, 147.92, 147.68, 147.49 (1C), 147.45, 147.32, 146.95, 145.81, 145.30, 144.94, 144.75, 144.37, 144.33, 144.03, 143.90, 143.33, 142.87, 142.83, 141.21, 138.80, 82.50 (4C-$(CH_3)_3$), 82.25, 81.88, 81.19(1C), 80.91 (1C), 80.05 (1C), 75.09 (1C), 58.26 (1C), 26.73 (12C). FT-IR (microscope): 3520, 3292, 2979, 2931, 2868, 2130, 1474, 1456, 1387, 1364, 1243, 1192, 1120, 1099, 1089, 1069, 1059, 1050, 1020, 869 cm^{-1}. ESI-HRMS: $C_{79}H_{44}NO_{10}$ (M + NH_4^+) calcd 1166.2960, found 1166.2939.

*Characterization Data of Compound **2b**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (s, 1H), 4.31 (t, *J* = 6.0 Hz, 2H), 2.38 (m, 2H), 2.01 (t, *J* = 6.4 Hz, 2 H), 2.01 (t, *J* = 6.4 Hz, 2 H), 1.99 (s, 1H), 1.48 (s, 9H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 155.52, 150.04, 149.13, 149.00, 148.59 (4C), 148.44 (1C), 148.40, 148.36, 148.34, 147.67, 147.52 (1C), 147.47, 147.35, 146.97, 145.86, 145.32, 144.99, 144.90, 144.38, 144.36, 144.02, 143.87, 143.35, 142.98, 142.71, 141.32, 138.57, 83.53 (1C), 82.66, 82.41, 82.14 ($C(CH_3)_3$), 81.85 ($C(CH_3)_3$), 81.04 (1C), 80.92 (1C), 68.90 (1C), 68.82 (1C), 29.33 (1C), 26.76 (6C), 26.74 (6C), 15.36 (1C). FT-IR (microscope): 3522, 3307, 2979, 2931, 1473, 1387, 1364, 1243, 1193, 1094, 1070, 1049, 1021, 872, 755, 730 cm^{-1}. ESI-HRMS: $C_{81}H_{48}NO_{10}$ (M + NH_4^+) calcd 1194.3273, found 1194.3260.

*Characterization Data of Compound **2c**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.83 (s, 1H), 4.39 (t, *J* = 6.0 Hz, 2H), 4.22 (d, *J* = 4.0 Hz, 2H), 3.84 (t, *J* = 4.0 Hz, 2H), 3.69 (m, 8H), 2.44 (t, *J* = 4.0 Hz, 1H), 1.47 (s, 18H), 1.44 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 155.39, 150.10, 149.12, 149.00, 148.57, 148.56, 148.43 (1C), 148.39, 148.36, 148.27, 147.67, 147.51 (1C), 147.45, 147.34, 146.96, 145.86, 145.40, 144.96, 144.91, 144.37, 144.35, 143.91, 143.83, 143.33, 142.99, 142.71, 141.33, 138.63, 82.67, 82.43, 82.10 ($C(CH_3)_3$), 81.84 ($C(CH_3)_3$), 81.04 (1C), 80.91 (1C), 79.65 (1C), 74.56 (1C), 70.65 (1C), 70.56 (1C), 70.50, 69.45 (1C), 69.14 (1C), 58.42 (1C), 26.76 (8C), 26.72 (8C). FT-IR (microscope): 3517, 3305, 2979, 2929, 2871, 1457, 1388, 1364, 1243, 1193, 1099, 1049, 1022, 872, 733 cm^{-1}. ESI-HRMS: $C_{85}H_{56}NO_{13}$ (M + NH_4^+) calcd 1298.3746, found 1298.3766.

Compounds 3 and 4. To a solution of compound **2b** (545 mg, 0.463 mmol) in 136 mL of toluene was added I_2 (330 mg, 1.30 mmol). After the mixture was stirred overnight at 110 °C, toluene was removed under reduced pressure at 40 °C, and the residue was purified by silica gel column chromatography, giving compound **3** (115 mg, 0.112 mmol, 35%) and compound **4** (161 mg, 0.156 mmol, 25%), both as red solids.

*Characterization Data of Compound **3**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34 (s, 1H), 4.35 (q, *J* = 6.7 Hz, 1H), 4.05 (q, *J* = 7.0 Hz, 1H), 2.40 (m, 2H), 2.03 (t, *J* = 6.4 Hz, 2H), 1.96 (s, 1H), 1.52 (s, 9H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except as noted): δ 150.56, 149.74, 149.57, 149.52, 148.84, 148.80, 148.77, 148.71, 148.60, 148.50, 148.32, 147.87, 147.83, 147.74, 147.64, 147.61, 147.55, 147.40, 147.25, 147.22, 147.15, 146.99 (2C), 146.67, 146.19, 145.93, 145.60, 145.58, 145.26, 145.14, 144.95, 144.83 (2C), 144.65, 144.58, 144.13, 144.05, 143.92, 143.86 (2C), 143.76, 143.59, 143.33, 143.09, 143.04, 142.84, 142.53, 141.60, 141.39, 140.76, 139.50, 139.25, 84.14, 83.42, 83.37 ($C(CH_3)_3$), 82.98, 82.35 ($C(CH_3)_3$), 80.21, 78.04, 71.71, 70.51, 69.41, 68.98, 67.69, 66.85, 29.05, 26.79 (3C), 26.65 (3C), 15.36. FT-IR (microscope): 3495, 3308, 2956, 2850, 1464, 1364, 1152, 1057, 853 cm^{-1}. ESI-HRMS: $C_{73}H_{26}NaO_8$ (M + Na^+) calcd 1053.1520, found 1053.1499.

*Characterization Data of Compound **4**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (s, 1H), 4.19 (t, *J* = 6.0, 2H), 2.42 (m, 2H), 2.02 (m, 3H), 1.44 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 149.93, 149.64, 148.51, 148.25, 148.21 (1C), 148.01, 147.95, 147.78, 147.64 (1C), 147.34, 147.29, 146.68 (4C), 146.06, 145.98, 145.72, 145.25, 145.24, 144.66, 144.24, 144.12, 144.07, 143.96, 143.52, 142.51, 138.94, 138.32, 87.02 (1C), 83.39, 83.11, 82.09 ($C(CH_3)_3$), 78.67 (1C), 74.64 (1C), 69.57 (1C), 69.28 (1C), 65.37, 28.77 (1C), 26.68 (6C), 15.46 (1C). FT-IR (microscope): 3476, 3304, 2976, 2921, 2850, 1725, 1464, 1421, 1387, 1364, 1285, 1262, 1243, 1192, 1175, 1125, 1106, 1061, 1012, 927, 906, 872, 757, 639, 631 cm^{-1}. ESI-HRMS: $C_{73}H_{26}NaO_8$ (M + Na^+) calcd 1053.1520, found 1053.1489.

Synthesis of Compounds 5a and 6. A 7.6 μL amount of TfOH and 7.6 μL of water were added to a solution of compound **3** (76 mg, 0.074 mmol) in 19 mL of $CHCl_3$ at room temperature. After the mixture was stirred for 20 min, the solution was washed with water and the organic layer was dried over anhydrous sodium sulfate. Then $CHCl_3$ was removed under reduced pressure at 35 °C. The residue was purified by silica gel column chromatography, with toluene/petroleum ether/ethyl acetate 10/5/2) as eluent, giving compound **5a** (25 mg, 0.023 mmol, 32%) and **6** (44 mg, 0.042 mmol, 56%), both as red solids.

Compound 5a. Another method for the synthesis of **5a** was the same as described for **9a** (see below) starting from 4-pentyn-1-ol (92 μL, 1.1 mmol) and **7** (40 mg, 0.039 mmol). Yield of compound **5a**: 29 mg (0.027 mmol, 69%, red solid).

*Characterization Data of Compound **5a**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (s, 1H), 6.12 (s, 1H), 5.74 (s, 1H), 5.56 (s, 2H), 4.13 (t, *J* = 4.8 Hz, 2H), 2.42 (t, *J* = 4.8 Hz, 2H), 2.08 (s, 1H), 2.02 (t, *J* = 6.4 Hz, 2H), 1.41 (s, 9H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except as noted): δ 151.19, 148.97, 148.90, 148.86, 148.71, 148.68, 148.65, 148.53 (2C), 148.47, 148.46, 148.33, 148.21, 148.17, 148.12 (4C), 148.09 (4C), 147.77, 147.69, 146.15, 145.87, 145.15, 145.14, 144.54 (2C), 144.47, 144.45, 144.41, 143.87, 143.83, 143.79, 143.66, 143.62, 143.51, 143.24 (2C), 143.00 (2C), 142.76, 142.69, 142.48, 142.40, 142.36, 139.12, 138.84, 137.14, 135.74, 83.40, 83.22, 82.30 (C-$(CH_3)_3$), 82.24 (C-$(CH_3)_3$), 82.06, 81.35, 80.80, 80.73, 80.57, 76.05, 74.30, 69.47, 67.83, 28.67, 26.71 (6C), 15.55. FT-IR (microscope): 3403, 3307, 2975, 2926, 1387, 1364, 1192, 1053, 757 cm^{-1}. ESI-HRMS: $C_{73}H_{34}NO_{10}$ (M + NH_4^+) calcd 1084.2177, found 1084.2158.

*Characterization Data of Compound **6**.* ^1H NMR (400 MHz, $CDCl_3$): δ 6.16 (s, 1H), 5.39 (s, 1H), 5.26 (s, 1H), 4.11 (m, 1H), 3.98 (m, 1H)), 2.38 (m, 2H), 2.02 (s, 1H), 1.98 (t, J = 6.4 Hz, 2H), 1.45 (s, 9H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except as noted): δ 150.99, 149.45, 149.42, 149.37, 149.27, 148.82, 148.59, 148.54 (2C), 148.32, 148.28, 148.01, 147.74, 147.61, 147.42, 147.36, 147.15, 147.01, 146.95, 146.91, 146.85, 146.60, 146.31, 146.25, 146.10, 145.71, 145.53, 145.26, 145.09, 144.58, 144.49, 144.18, 143.90, 143.75, 143.47, 143.32, 143.20, 143.04, 142.93, 142.55, 142.04, 141.92, 141.69, 141.64, 142.29, 140.88, 139.87, 139.06, 138.64, 138.38, 136.82, 132.28, 83.28, 83.02, 82.47, 82.05 ($C(CH_3)_3$), 81.93 ($C(CH_3)_3$), 80.73, 80.31, 75.76, 72.55, 71.42, 69.41, 69.20, 67.86, 28.89, 26.78 (3C), 26.71 (3C), 15.46. FT-IR (microscope): 3373, 3309, 2922, 2851, 1731, 1463, 1388, 1192, 1090, 1056, 912, 871 cm^{-1}. ESI-HRMS: $C_{73}H_{32}NO_9$ (M + NH_4^+) calcd 1066.2072, found 1066.2046.

Compound 5b. The synthesis was carried out as described for **9a** (see below) starting from 2-[2-(2-propargyloxyethoxy)ethoxy]ethanol (1124 mg, 5.98 mmol) and **7** (162 mg, 0.159 mmol). Yield of compound **5b**: 131 mg (0.112 mmol, 70%, red solid).

*Characterization Data of Compound **5b**.* ^1H NMR (400 MHz, $CDCl_3$): δ 4.32 (q, J = 16 Hz, 2H), 3.88 (m, 12H), 2.45 (s, 1H), 1.33 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except as noted): δ 151.31, 148.95, 148.86, 148.85, 148.71, 148.66, 148.59, 148.55 (4C), 148.54, 148.37, 148.35, 148.26, 148.19, 148.16, 148.14, 148.13, 148.09 (2C), 148.06 (2C), 147.79, 146.22, 146.94, 145.45, 145.11, 144.81, 144.62, 144.48, 144.42, 144.35, 143.79, 143.76 (2C), 143.64, 143.52 (2C), 143.47, 143.40, 143.12, 143.04, 142.83, 142.71, 142.70, 142.23, 141.95, 139.17, 138.95, 137.31, 135.42, 82.87, 82.18 ($C(CH_3)_3$), 82.04 ($C(CH_3)_3$), 81.69, 81.08, 80.80, 80.49, 79.65, 76.15, 74.98, 70.61, 70.58, 70.16, 69.87, 69.01, 68.70, 58.21, 26.77 (6C). FT-IR (microscope): 3381, 3305, 2976, 2925, 2871, 2855, 1364, 1192, 1111, 1088, 1065, 1055, 756 cm^{-1}. ESI-HRMS: $C_{77}H_{38}NaO_{13}$ (M + Na^+) calcd 1193.2205, found 1193.2180.

Compound 9a. To a solution of 4-pentyn-1-ol (600 μL, 7.52 mmol) and compound **8** (78 mg, 0.075 mmol) in DCM (16 mL) was added anhydrous silver perchlorate (94 mg, 0.45 mmol) at 30 °C in the dark. The mixture was stirred for 1 h. The solution was washed with water (3 × 50 mL), and the organic layer was dried over anhydrous sodium sulfate. Then the solution was concentrated in vacuo and the residue was purified by silica gel column chromatography with toluene/petroleum ether/ethyl acetate (5/5/1) as eluent, giving compound **9a** (50 mg, 62%) as a red solid.

*Characterization Data of Compound **9a**.* ^1H NMR (400 MHz, $CDCl_3$): δ 6.07 (s, 1H), 5.64 (s, 1H), 5.55 (s, 2H), 4.09 (q, J = 4.0 Hz, 4H), 2.42 (m, J = 2.4 Hz, 4H), 2.05 (s, 2H), 2.02 (m, J = 2.5 Hz, 4H), 1.41 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 148.92, 148.83, 148.72, 148.70 (1C), 148.60, 148.59, 148.52, 148.22, 148.15 (4C), 148.10, 147.99, 147.79 (1C), 146.18, 145.03, 144.61, 144.57, 144.46, 143.81, 143.74, 143.43, 143.24, 142.81, 142.53, 142.24, 139.23, 136.58, 83.49, 83.33, 82.16 (C-$(CH_3)_3$), 81.99, 81.08, 80.64 (1C), 74.09 (1C), 69.20, 67.78, 28.81, 26.66 (6C), 15.52. FT-IR (microscope): 3423, 3304, 2976, 2928, 1387, 1364, 1243, 1217, 1192, 1160, 1059, 756 cm^{-1}. ESI-HRMS: $C_{78}H_{40}NO_{10}$ (M + NH_4^+) calcd 1150.2647, found 1150.2620.

Compound 9b. The synthesis was carried out as described for **9a**, starting from **8** (191 mg, 0.184 mmol) and 2-[2-(2-propargyloxyethoxy)ethoxy]ethanol (1.98 mL, 11.1 mmol) in the presence of anhydrous silver perchlorate (229 mg, 1.10 mmol). Yield of compound **9b**: 191 mg (0.143 mmol, 77%, red solid).

*Characterization Data of Compound **9b**.* ^1H NMR (400 MHz, $CDCl_3$): δ 6.13 (s, 1H), 5.87 (s, 2H), 5.72 (s, 1H), 4.02 (m, 28H), 2.49 (t, J = 2.4 Hz, 2H), 1.39 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 148.95, 148.84, 148.66 (3C), 148.62, 148.51 (4C), 148.38, 148.17, 148.13, 148.08, 148.02, 147.80 (1C), 146.31, 145.02, 144.72, 144.62, 144.39, 143.64, 143.58, 143.49, 143.33, 142.93, 142.42, 142.10, 139.55, 136.69, 82.84, 82.10, 81.62 ($C(CH_3)_3$), 81.10, 80.59 (1C), 79.72, 74.65, 74.12 (1C), 70.68, 70.67, 70.45, 70.17, 69.06, 68.88, 58.39, 26.69 (6C). FT-IR (microscope): 3388, 3301, 2973, 2925, 2871, 1458, 1364, 1192, 1091, 1065, 1102, 943, 870, 757, 667 cm^{-1}. ESI-HRMS: $C_{86}H_{52}NaO_{16}$ (M + Na^+) calcd 1363.3148, found 1363.3128.

Compound 9c. The synthesis was carried out as described for **9a**, starting from **8** (150 mg, 0.145 mmol) and 3,6,9,12-tetraoxapentadec-14-yn-1-ol (2.01 mL, 6.81 mmol) in the presence of anhydrous silver perchlorate (180 mg, 0.867 mmol). Yield of compound **9c**: 25 mg (0.18 mmol, 12%, red solid).

*Characterization Data of Compound **9c**.* ^1H NMR (400 MHz, $CDCl_3$): δ 6.11 (s, 1H), 5.88 (s, 2H), 5.72 (s, 1H), 3.98 (m, 36H), 2.46 (t, J = 2.4 Hz, 2H), 1.39 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 148.98, 148.91, 148.73 (3C), 148.69, 148.58 (4C), 148.42, 148.24, 148.20, 148.15, 148.09, 147.86 (1C), 146.36, 145.08, 144.77, 144.68, 144.46, 143.71, 143.65, 143.55, 143.38, 142.99, 142.48, 142.18, 139.60, 136.75, 82.94, 82.18, 81.72 ($C(CH_3)_3$), 81.18, 80.67 (1C), 79.72 (1C), 74.62, 74.19, 70.76, 70.73, 70.70, 70.66, 70.46, 70.27, 69.16, 68.95, 58.44, 26.75 (6C). FT-IR (microscope): 3403, 3300, 2975, 2925, 2872, 2114, 1457, 1364, 1216,1192, 1093, 1065, 1037, 944, 870, 756 cm^{-1}. ESI-HRMS: $C_{90}H_{60}NaO_{18}$ (M + Na^+) calcd 1451.3672, found 1451.3656.

Compound 10a. To a solution of compound **9a** (75 mg, 0.066 mmol) and AcOH (398 μL, 6.6 mmol) in $CHCl_3$ (50 mL) was added $SnCl_2$ (1.285 g, 6.6 mmol) at 50 °C, and the mixture was stirred for 1 h. The solution was washed with water (3 × 150 mL), HCl (1 moL/L, 3 × 150 mL), and then water (3 × 150 mL). Then the organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo and the residue was purified by silica gel column chromatography with $CHCl_3/CH_3OH$ (100/1) as eluent. Yield of compound **10a**: 21 mg (32%, red solid).

*Characterization Data of Compound **10a**.* ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 3.99 (t, J = 6.0 Hz, 2H), 2.72 (t, J = 2.5 Hz, 1H), 2.31 (m, 2H), 1.88 (m, 2H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$; all signals represent 2C, except as noted): δ 150.93, 149.31, 148.31, 148.26, 148.21, 148.10 (4C), 148.06, 147.85 (4C), 147.80, 147.59, 147.33 (1C), 146.78, 145.12, 144.44, 144.10, 143.71, 143.51, 143.32, 143.30, 142.86, 142.65, 142.55, 142.26, 142.21 (1C), 138.51, 84.22, 83.95 (1C), 82,92, 81.55, 73.86 (1C), 71.69, 71.56, 67.85, 28.90, 14,86. FT-IR (microscope): 3389, 3301, 2953, 2923, 2851, 1721, 1467, 1377, 1130, 1101, 1072, 994 cm^{-1}. ESI-HRMS: $C_{70}H_{24}NO_8$ (M + NH_4^+) calcd 1006.1496, found 1006.1474.

Compound 10b. The synthesis was carried out as described for **10a**, starting from $SnCl_2$ (2.0 g, 10.5 mmol) and **9b** (146 mg, 0.109 mmol). Yield of compound **10b**: 57 mg (0.048 mmol, 45%, red solid).

*Characterization Data of Compound **10b**.* ^1H NMR (400 MHz, $CDCl_3$): δ 4.31 (d, J = 2.4 Hz, 4H), 3.99 (m, 24H), 2.52 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 149.71, 148.91, 148.84 (1C), 148.80, 148.65, 148.62, 148.51 (4C), 148.24, 148.22, 148.10, 148.06, 147.73 (1C), 146.87, 144.78, 144.76, 144.70, 144.47, 144.11, 143.88, 143.39, 143.24, 142.44, 142.33, 142.22, 141.26, 136.36, 83.60, 82.87, 81.37, 79.79, 74.86 (1C), 74.82 (1C), 74.74 (1C), 72.36, 70.83, 70.58, 70.51, 70.07, 69.15, 68.95, 58.50. FT-IR (microscope): 3383, 3298, 2924, 2872, 1458, 1362, 1088, 1068, 940, 923, 667 cm^{-1}. ESI-HRMS: $C_{78}H_{40}NO_{14}$ (M + NH_4^+) calcd 1214.2443, found 1214.2461.

Compound 11. To a solution of compound **2b** (255 mg, 0.217 mmol) and $HgSO_4$ (95 mg, 0.32 mmol) in toluene (26 mL) was added 10% H_2SO_4 (26 mL, 0.65 mmol) at 50 °C, and the mixture was stirred for 4 h. The solution was washed with water (3 × 150 mL). Then the organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo and the residue was purified by silica gel column chromatography with toluene/petrol oil/ethyl acetate (20/10/1) as eluent. Yield of compound **11**: 183 mg (0.153 mmol, 71%, red solid).

*Characterization Data of Compound **11**.* ^1H NMR (400 MHz, $CDCl_3$): δ 4.66 (s, 1H), 4.21 (t, J = 6.4 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 2.16 (s, 3H), 2.05 (m, 2H), 1.48 (s, 18H), 1.44 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 207.95 (C=O, 1C), 155.39, 149.95, 149.07, 148.94, 148.52, 148.50, 148.37 (1C), 148.34, 148.29, 148.18, 147.60, 147.44 (1C), 147.39, 147.28, 146.91, 145.79, 145.17,144.92, 144.82, 144.33, 144.27, 143.98, 143.81, 143.30, 142.92, 142.66, 141.24, 138.48, 82.58, 82.35, 82.08 ($C(CH_3)_3$), 81.81 ($C(CH_3)_3$), 80.87 (1C), 80.85 (1C), 69.28 (1C), 40.07 (1C), 30.06 (1C), 26.72 (6C), 26.70 (6C), 24.24 (1C). FT-IR (microscope): 3520, 2978, 2930, 1718, 1473, 1364, 1242, 1193, 1146, 1098, 1071, 1049, 1021, 871, 755 cm^{-1}. ESI-HRMS: $C_{81}H_{46}NaO_{11}$ (M + Na^+) calcd 1217.2932, found 1217.2926.

Compound 12. The synthesis was carried out as described for **11** ,starting from $HgSO_4$ (95 mg, 0.32 mmol) and **9a** (121 mg, 0.107 mmol) in the presence of 10% H_2SO_4 (12 mL, 0.64 mmol). Yield of compound **12**: 81 mg (0.069 mmol, 65%).

Characterization Data of Compound 12. ^1H NMR (400 MHz, $CDCl_3$): δ 6.02 (s, 1H), 5.62 (s, 1H), 5.48 (s, 2H), 4.01 (m, 4H), 2.66 (m, 4H), 2.20 (s, 6H), 2.07 (m, 4H), 1.41 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 208.20, 148.88, 148.71, 148.68 (3C), 148.56 (4C), 148.48, 148.18, 148.11 (4C), 148.05, 147.94, 147.74 (1C), 146.11, 144.93, 144.57, 144.53, 144.42, 143.78, 143.73, 143.30, 143.20, 142.77, 142.49, 142.19, 139.20, 136.55, 83.29, 82.14 ($C(CH_3)_3$), 81.91, 81.01, 80.60 (1C), 74.04 (1C), 68.24, 40.09, 30.10, 26.64 (6C), 23.93. FT-IR (microscope): 3420, 2976, 2928, 1715, 1471, 1364, 1242, 1191, 1163, 1106, 1059, 1021, 925, 866, 754 cm^{-1}. ESI-HRMS: $C_{78}H_{40}NaO_{12}$ (M + Na^+) calcd 1191.2412, found 1191.2378.

Compound 13. Copper sulfate (23 mg, 0.096 mmol) and sodium ascorbate (38 mg, 0.19 mmol) were added to a solution of compound **10b** (57 mg, 0.048 mmol) and 63 mg of benzyl azide (63 mg, 0.48 mmol) in a mixture of $CHCl_3$ and water (1/1) at 60 °C. After the mixture was stirred for 3 h, the organic layer was abstracted and dried over anhydrous sodium sulfate. $CHCl_3$ was removed under reduced pressure at 35 °C, and the residue was purified by silica gel column chromatography with $CHCl_3/CH_3OH$ (40/1) as eluent. Yield of compound **13**: 43 mg (0.029 mmol, 62%, red solid).

Characterization Data of Compound 13. ^1H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.32 (m, 6H), 7.28 (m, 4H), 6.30 (s, 2H), 6.15 (s, 1H), 5.82 (s, 2H), 5.79 (s, 1H), 5.52 (s, 4H), 4.74 (q, J = 10 Hz, 4H), 4.13 (m, 2H), 4.04 (t, J = 10 Hz, 2H), 3.88 (t, J = 10 Hz, 2H), 3.77 (m, 10H), 3.74 (s, 8H). ^{13}C NMR (125 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 150.02, 148.84, 148.75 (4C), 148.61, 148.57, 148.49, 148.28, 148.20, 148.15, 148.09, 148.04, 147.71 (1C), 146.77, 145.39 (1C), 144.81, 144.79, 144.62, 144.41, 144.02, 143.82, 143.30, 143.28, 142.49, 142.38, 142.26, 141.70, 136.58, 134.60, 129.03 (4C), 128.66, 128.15 (4C), 123.01, 83.41, 82.87 (1C), 81.29, 74.60 (1C), 72.15, 70.77, 70.52, 70.37, 69.99, 69.74, 68.80, 64.51, 54.15. FT-IR (microscope): 3379, 2923, 2871, 1456, 1353, 1292, 1210, 1087, 939, 757, 721 cm^{-1}. ESI-HRMS: $C_{92}H_{49}N_6O_{14}$ (M − H^+) calcd 1461.3312, found 1461.3292.

Compound 14. Cuprous iodide (735 mg, 3.47 mmol) and TMEDA (446 mg, 3.47 mmol) were added to a solution of compound **10b** (23 mg, 0.019 mmol) in $CHCl_3$ (70 mL) at 25 °C. After the mixture was stirred for 3 h in the dark, the solution was washed with 2 M HCl (aq) (3 × 100 mL), followed by water (3 × 100 mL). Then the organic layer was dried over anhydrous sodium sulfate. $CHCl_3$ was removed under reduced pressure at 35 °C, and the residue was purified by silica gel column chromatography with $CHCl_3/CH_3OH$ (100/1) as eluent. Yield of compound **14**: 15 mg (0.013 mmol, 65%, red solid).

Characterization Data of Compound 14. ^1H NMR (500 MHz, $CDCl_3$): δ 6.41 (s, 2H), 5.89 (s, 1H), 5.52 (s, 1H), 4.57 (s, 2H), 4.43 (s, 2H), 4.28 (s, 2H), 4.15 (m, 2H), 4.06 (t, J = 5 Hz, 2H), 3.95 (m, 2H), 3.85 (m, 20H). ^{13}C NMR (126 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 149.85 (1C), 149.83 (1C), 149.02, 148.95 (1C), 148.91, 148.77, 148.73, 148.63, 148.58, 148.36, 148.32, 148.22, 148.18, 147.84 (1C), 147.00 (1C), 146.99 (1C), 144.88, 144.86 (4C), 144.58, 144.23, 143.99, 143.48, 143.35, 142.55 (1C), 142.54 (1C), 142.51, 142.36, 141.44 (1C), 141.43 (1C), 136.47, 90.94 (1C), 83.72, 82.98 (1C), 81.64, 81.51, 74.89 (1C), 72.54 (1C), 71.04 (1C), 70.99 (1C), 70.93 (1C), 70.75 (1C), 70.68, 70.62, 70.26 (1C), 70.21 (1C), 69.61 (1C), 69.50, 69.07, 60.20 (1C), 60.18 (1C). FT-IR (microscope): 3384, 2924, 2872, 1456, 1351, 1291, 1271, 1209, 1087, 995, 908, 731 cm^{-1}. ESI-HRMS: $C_{78}H_{34}NaO_{14}$ (M + Na^+) calcd 1217.1841, found 1217.1813.

Compound 15. The synthesis was carried out as described for **3** and **4**, starting from **2d** ($C_{60}(OH)(OCH_3)(OO^tBu)_4$; 574 mg, 0.511 mmol) and I_2 (366 mg, 1.44 mmol). Yields: compound **15a**, 197 mg (0.202 mmol, 44%); unconverted starting material **2d**, 57 mg; **15**, 140 mg (0.143 mmol, 31%).

Characterization Data of Compound 15a. The structure of **15a** is analogous to that of compound **3**. ^1H NMR (400 MHz, $CDCl_3$): δ 5.35 (s, 1H), 3.91 (s, 3H), 1.52 (s, 9H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except as noted): δ 150.52, 149.75, 149.61, 149.57, 148.86, 148.81, 148.60, 148.53, 148.34, 148.24 (2C), 147.89, 147.85, 147.75, 147.65, 147.63, 147.55, 147.41, 147.29, 147.24, 147.17, 147.02 (2C), 146.67, 146.20, 145.95, 145.68, 145.59, 145.28, 145.17, 144.94 (2C), 144.85, 144.61, 144.56, 144.17, 144.00, 143.97, 143.88 (2C), 143.73, 143.61, 143.38, 143.06, 143.00, 142.86, 142.54, 141.62, 141.42, 140.80, 139.86, 139.48, 84.83, 83.26, 82.99, 82.37, 80.28, 78.03, 71.75, 70.53, 67.69, 66.88, 57.99, 26.72 (3C), 26.65 (3C). FT-IR (microscope): 3498, 2980, 2930, 2829, 1456, 1388, 1364, 1191, 1083, 1058, 1019, 950, 928, 853, 755 cm^{-1}. ESI-HRMS: $C_{69}H_{23}O_8$ (M + H^+) calcd 979.1387, found 979.1388.

Characterization Data of Compound 15. ^1H NMR (400 MHz, $CDCl_3$): δ 4.73 (s, 1H), 3.89 (s, 3H), 1.44 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 149.68, 149.45, 148.53, 148.29, 148.25 (1C), 148.05, 147.98, 147.83, 147.68 (1C), 147.38, 147.31, 146.71 (4C), 146.08, 146.00, 145.79, 145.27, 144.70, 144.32, 144.28, 144.15 (4C), 143.92, 143.56, 142.53, 138.94, 138.62, 87.28, 83.15, 82.15, 78.64 (1C), 74.64 (1C), 65.40, 58.14 (1C), 26.68 (6C). FT-IR (microscope): 3483, 2979, 2930, 2829, 1457, 1420, 1387, 1364, 1192, 1124, 1083, 1062, 1012, 982, 923, 903, 872, 756 cm^{-1}. ESI-HRMS: $C_{69}H_{22}NaO_8$ (M + Na^+) calcd 1001.1207, found 1001.1209.

Compound 16. Aluminum chloride (202 mg, 1.52 mmol) was added to a solution of compound **15** (186 mg, 0.190 mmol) and 1.8 mL of MeOH in 60 mL of $CHCl_3$ and 6 mL of THF at 30 °C. After the mixture was stirred for 24 h, the solution was quenched with 2 mL of HCl and washed with water. Then the organic layer was dried over anhydrous sodium sulfate. $CHCl_3$ was removed under reduced pressure at 35 °C, and the residue was purified by silica gel column chromatography with toluene/petroleum ether/ethyl acetate (8/4/1) as eluent. Yield of compound **16**: 135 mg (0.128 mmol, 65%, red solid). Another minor product was isolated as **16a** (28 mg, 0.027 mmol, 14%).

Characterization Data of Compound 16. ^1H NMR (400 MHz, $CDCl_3$): δ 5.93 (s, 1H), 5.69 (s, 2H), 3.85 (s, 3H), 1.45 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 150.65, 148.96, 148.82 (1C), 148.80, 148.74, 148.62, 148.58, 148.44, 148.27, 148.24, 148.18, 147.75 (1C), 147.65, 145.18, 144.40, 144.31, 144.00, 143.96, 143.77, 143.62, 143.00, 142.86, 141.52, 140.88, 140.69, 140.29, 137.91, 86.42, 83.26, 81.48, 80.58 (1C), 80.43 (1C), 70.13, 58.46 (1C), 26.70 (6C). FT-IR (microscope): 3375, 2978, 2930, 2826, 1388, 1365, 1190, 1116, 1081, 1006, 965, 855, 756 cm^{-1}. ESI-HRMS: $C_{69}H_{24}Cl_2NaO_8$ (M + Na^+) calcd 1073.0740, found 1073.0770.

Characterization Data of Compound 16a. The structure of **16a** is similar to that of compound **16**, except that one Cl was replaced by one OMe group. ^1H NMR (400 MHz, $CDCl_3$): δ 5.72 (s, 1H), 5.65 (s, 1H), 5.49 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 1.44 (s, 9H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except as noted): δ 150.74, 148.96, 148.95, 148.83, 148.76, 148.68 (3C), 148.67, 148.65, 148.60, 148.56, 148.50, 148.43, 148.34, 148.26, 148.20 (4C), 148.15, 147.77, 147.39, 147.31, 146.21, 145.13, 144.75, 144.57, 144.49, 144.43, 144.40, 144.36, 144.08, 143.91 (2C), 143.79, 143.74, 143.59, 143.02, 142.99, 142.96, 142.86, 142.83, 142.61, 141.96, 141.72, 141.59, 140.90, 139.77 (2C), 138.63, 136.79, 85.52, 82.97, 82.85, 81.96, 81.42, 80.83, 80.78, 80.75, 80.45, 70.64, 58.50, 56.27, 26.70 (3C), 26.68 (3C). FT-IR (microscope): 3406, 2978, 2929, 2829, 1455, 1387, 1364, 1191, 1114, 1080, 974, 864, 756 cm^{-1}. ESI-HRMS: $C_{70}H_{31}ClNO_9$ (M + NH_4^+) calcd 1064.1682, found 1064.1689.

Compound 17. Anhydrous silver perchlorate (179 mg, 0.865 mmol) was added to a solution of MeOH (9 mL) and compound **16**

(227 mg, 0.216 mmol) in toluene (36 mL) at 30 °C in the dark, and the mixture was stirred for 2 h. The solution was washed with water (3 × 50 mL), and the organic layer was dried over anhydrous sodium sulfate. Then the solution was concentrated in vacuo and the residue was purified by silica gel column chromatography with toluene/petroleum ether/ethyl acetate (10/5/2) as eluent. Yield of compound **17**: 175 mg (0.168 mmol, 77%, red solid).

*Characterization Data of Compound **17**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31 (s, 2H), 5.28 (s, 1H), 3.91 (s, 6H), 3.80 (s, 3H), 1.38 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 2C, except as noted): δ 148.95, 148.86 (1C), 148.71, 148.69, 148.64, 148.50, 148.36, 148.33, 148.25, 148.18, 148.14, 147.80 (1C), 147.47, 146.44, 144.75, 144.45 (4C), 143.88, 143.74, 143.28, 143.03, 142.93, 142.91, 142.82, 142.06, 140.68, 138.27, 85.08, 83.05, 81.71, 81.11, 80.88 (1C), 58.26 (1C), 56.24, 26.69 (6C). FT-IR (microscope): 3450, 2977, 2930, 2828, 1456, 1387, 1364, 1192, 1112, 1083, 1009, 975, 868, 756 cm^{-1}. ESI-HRMS: $C_{71}H_{34}NO_{10}$ (M + NH_4^+) calcd 1060.2177, found 1060.2180.

*Crystal Data for Compound **17**:* $C_{299}H_{136}O_{40}S_2$, T = 173(2) K, triclinic, space group $P\bar{1}$, unit cell dimensions a = 14.809(2) Å, b = 17.264(3) Å, c = 19.650(4) Å, V = 4780.0 (14) Å^3. Z = 1, ρ_{calcd} = 1.540 Mg/m^3, 49 375/16 833 collected/unique reflections (R(int) = 0.0442). Final R indices ($I > 2\sigma(I)$): R1 = 0.1298, wR2 = 0.3344. CCDC file: No. 818563.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving selected spectroscopic data for all new compounds and a CIF file giving crystallographic data for **17**. 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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