JOC The Journal of Organic Chemistry

ARTICLE

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Bromination-Mediated Regioselective Preparation of Cyclopentadienyl-Type [60]Fullerene Derivatives with Alkoxy, Peroxy, and Bromo or Hydro Addends

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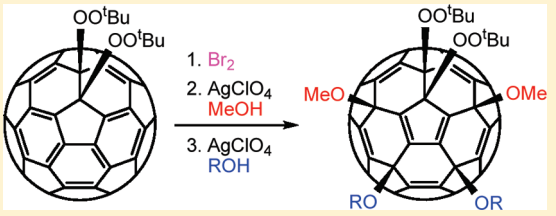
Supporting Information

ABSTRACT: Bromine reacts with the 1,2-bisadduct $C_{60}(OO\mathit{t}Bu)_2$ efficiently to form the cyclopentadienyl-type compound **4** ($C_{60}(OO\mathit{t}Bu)_2Br_4$). In the presence of $AgClO_4$, the four bromine atoms can be replaced regioselectively by methoxyl groups in a stepwise fashion to form $C_{60}(OO\mathit{t}Bu)_2Br_{4-x}(OMe)_x$. A second alcohol may be introduced by treating partially methoxylated compound **6** ($C_{60}(OO\mathit{t}Bu)_2Br_2(OMe)_2$) with ROH/$AgClO_4$. Other related reactions have been investigated to explore the reactivity patterns. The structure of compound **6** was confirmed by single crystal X-ray analysis.



INTRODUCTION

Many methods have been developed for the selective synthesis of fullerene monoadducts such as the Bingel reaction[1] and the Prato reaction.[2] Compared to the numerous fullerene monoadducts known in the literature, isomerically pure fullerene multiadducts are relatively rare.[3] Most fullerene reactions can produce monoadduct effectively, but give complicated mixtures of various adducts with a different number of addends and regioisomers. Tether-directed cycloaddition reactions have been proven a useful strategy for regioselective synthesis of fullerene bis- and trisadducts.[4] A number of isomerically pure fullerene multiadducts have been prepared by this method.

The cyclopentadienyl fullerene adduct is another type of well-known fullerene multiadduct, in which the addends are attached around the same pentagon forming an isolated cyclopentadiene moiety on the fullerene surface. Reactions of C_{60} with ICl or Br_2,[5] radicals,[6] secondary amines,[7] and certain organometallic reagents[8,9] afford cyclopentadienyl-type fullerene derivatives. These reactions usually result in high yield of either $C_{60}X_6$ with just one type of addend or $C_{60}(O)X_4$ with 4 of the same addends and an epoxide. Starting from the 1,4-adduct $C_{60}(PhCH_2)_2$, Nakamura et al.[10] prepared the unsymmetric cyclopentadienide $[C_{60}Ph_3(PhCH_2)_2]^{-1}$.[11] Later a series of unsymmetric bucky ferrocenes such as $CpFe[C_{60}(PhCH_2)_2PhMe_2]$ have been reported. In spite of these successful achievements, new methods are still needed to fully explore the chemical reactivity pattern of fullerene and to prepare fullerene multiadducts for practical application research.[12]

In our previous study, we have prepared $C_{60}(O)(OO\mathit{t}Bu)_4$[13] and $C_{60}(OO\mathit{t}Bu)_6$.[14] Further reactions of the fullerene-mixed peroxides transformed the epoxide and some of the peroxo groups into amino, halo, hydroxyl, aryl, and hydro groups.[15] Here we report the efficient synthesis of cyclopentadienyl adducts with different addends through bromination of fullerene-mixed peroxide and subsequent replacement reactions.

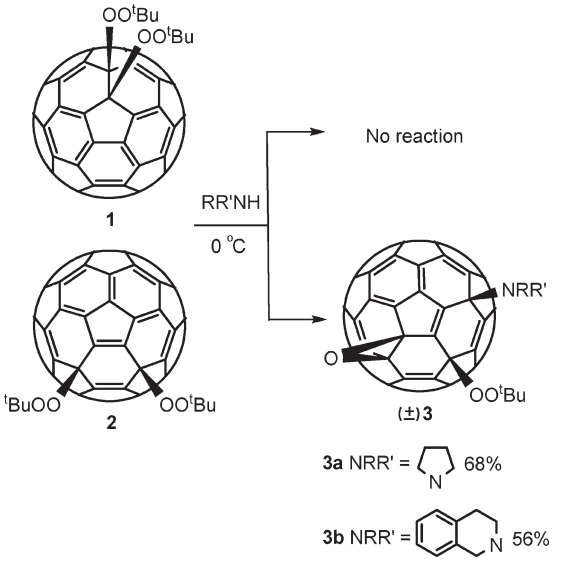
RESULTS AND DISCUSSION

Amination Reactions. In an effort to prepare unsymmetric multiadducts, we treated the bisadducts **1** and **2** with various reagents. Secondary amines[16] reacted with the 1,4-adduct **2** effectively to form compound **3** with an epoxide moiety. But the 1,2-adduct remained unchanged under the condition (Scheme 1). Separation of **1** and **2** is quite difficult by column chromatography. After the reaction, it is easy to separate the unreacted **1** and product **3**. So this amine reaction provides a purification method for compound **1**.

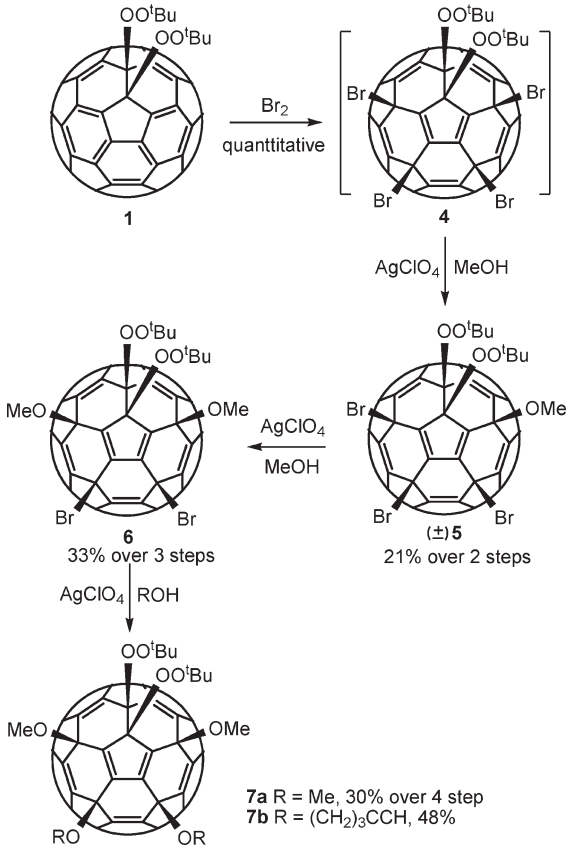
Formation of **3** should follow a S_N2'' pathway. The presence of the double bond on the pentagon is essential in the process. A second amine may add to **3** through the same mechanism to form another epoxide moiety. But the product containing two epoxy moieties on the same hexagon is probably too reactive toward further epoxide-opening reactions and was not detected. There is no double bond on the pentagon in the 1,2-bisadduct **1**, so it is stable under this condition. Similar to the amine reaction, sodium methoxide reacted with **2** to form epoxide product $C_{60}(O)(OMe)(OO\mathit{t}Bu)$ with analogous structure to **3**.[14]

Received: December 1, 2010
Published: February 11, 2011

Scheme 1. Selective Amination of 1,4-Bisadduct

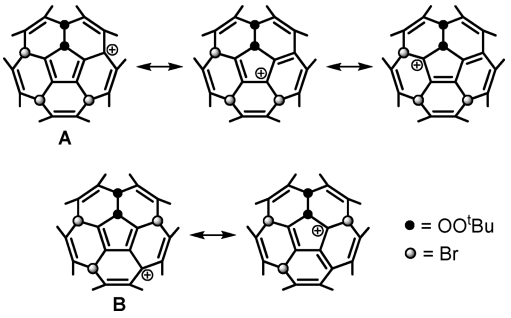


Scheme 2. Cyclopentadienyl-Type Reactions

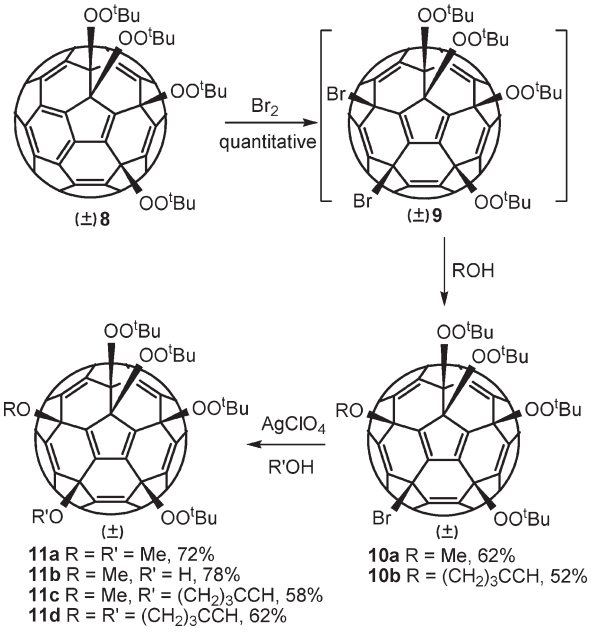


Bromination and Alcohol Replacement. Unlike the above amination reactions, treatment of the bisadduct with bromine results in the cyclopentadienyl adduct. Clear product spots could be observed for both compounds **1** and **2** in the bromination reaction. Attempted purification of the brominated products failed because of decomposition on the silica gel column. The brominated product from the 1,4-bisadduct gave complicated mixtures. But the tetrabromo derivative **4** from the 1,2-bisadduct served as an excellent precursor for alkoxyl derivatives as shown in Scheme 2. In the presence of $AgClO_4$, methanol replaces the bromine addends selectively to form compounds **5**, **6**, and **7** in a stepwise pattern. The degree of replacement may be controlled by the amount of bromine added and the reaction time. The reaction could be monitored by TLC. All four bromine atoms are replaced to form compound **7a** with excess methanol in extended reaction time. A second alcohol such as pent-4-yn-1-ol could be introduced treating purified **6** with $AgClO_4$/ROH. Brominated product from the 1,4-adduct gave complicated mixtures under the same conditions.

Scheme 3. Resonance Structures of Two Possible Cationic Intermediates



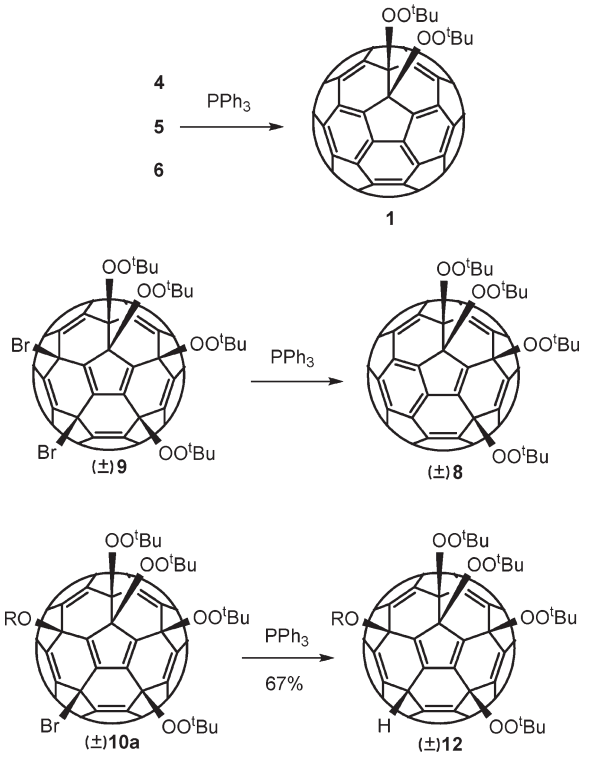
Scheme 4. Reactions of Tetrakisadduct



Selective formation of **5** and **6** with the methoxyl group near the peroxo may be explained by resonance theory (Scheme 3). Cleavage of the bromine atom near the peroxo group results in the carbon cation species **A** with three resonance structures. Only two resonance structures are possible for the carbon cation species **B** resulting from the cleavage of the other bromine further away from the peroxo group. Steric hindrance should

dx.doi.org/10.1021/jo102377r |*J. Org. Chem.* 2011, 76, 1735–1741

Scheme 5. Reduction Reactions with PPh_3



also favor cleavage of the bromine atom near the peroxo group, assuming formation of cation **A** is the rate-limiting step and addition of methanol to **A** in the second step is relatively fast.

The above bromination-mediated strategy was also applied to the tetrakisadduct **8**. Excess bromine converted **8** into **9**. Just like the tetrabromo derivative **4**, compound **9** slowly decomposed upon purification on silica gel column. Addition of alcohol to **9** replaces one bromine atom to form compound **10** (Scheme 4). The remaining bromine atom in **10** could be replaced by another alkoxy group or OH group upon further reaction with $AgClO_4$/ROH.

The cyclopentadienyl fullerene derivatives prepared above exhibit facile reactivity toward triphenylphosphine. All the compounds with more than one bromo addend undergo reductive elimination, cleaving the bromo and alkoxyl groups, whereas the *tert*-butylperoxo groups remained unchanged. Compounds **4**, **5**, and **6** all gave the bisadduct **1** when treated with PPh_3 (Scheme 5). Similarly compound **9** elimiated two bromine atoms to give back its precursor **8**. But unlike the multibromo adducts, the monobromo adduct **10a** formed the hydro derivative **12**. In our previous study, we have observed the conversion of C_{60}(Br)(OH)(OO*t*Bu)$_4$ to C_{60}(H)(OH)(OO*t*Bu)$_4$ when treated with PPh_3.[17]

Replacement reactions of halofullerene derivatives have been reported before. Taylor et al. have converted $C_{60}Cl_6$ into $C_{60}ClPh_5$, $C_{60}ClMe_5$, and $C_{60}Cl(OMe)_5$ by treating it with $FeCl_3$/PhH, LiMe, and NaOMe/MeOH, respectively.[18] The remaining Cl addend in $C_{60}ClPh_5$ could be further substituted with a 4-MeC_6H_4 group by treatment with $FeCl_3$/toluene or reduced to a hydro group by PPh_3. We have reported that the bromo addend in C_{60}Br(OH)(OO*t*Bu)$_4$ can be replaced by OR to form C_{60}(OR)(OH)(OO*t*Bu)$_4$.[19] All these reactions correspond to a S_N1 mechanism, involving a fullerene cation intermediate.

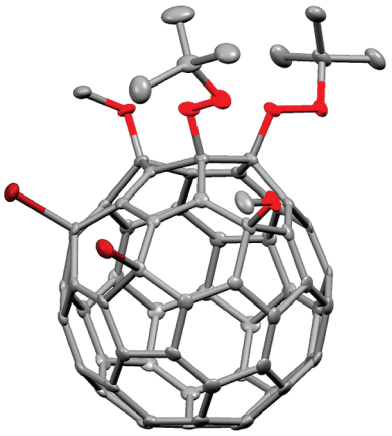


Figure 1. X-ray structure of compound **6**. Ellipsoids were drawn at the 50% level; for clarity hydrogen atoms were not shown. Color key: gray, carbon; red, oxygen; and dark red, bromine.

Characterization by Spectroscopic Data and Single Crystal X-ray Analysis. Single crystals of **6** (Figure 1) were obtained from slow evaporation of its solution in a mixture of CS_2/$CHCl_3$/EtOH. The structure clearly shows a typical cyclopentadienyl structure. The two methoxyl groups are located near the two adjacent *tert*-butyl peroxo groups and the two bromo atoms are at the para-position of the methoxyl groups. Double bonds on the isolated pentagon are the shortest at 1.35 Å. The five double bonds surrounding the pentagon are slightly longer ranging from 1.36 to 1.37 Å. The bond length of other double bonds on the fullerene cage ranges from 1.38 to 1.40 Å.

On the basis of the above X-ray structure and spectroscopic data, structures of other compounds can be assigned as shown in the schemes. Both compounds **6** and **7** are C_s symmetric. Their NMR spectra showed the expected number of ^{1}H and ^{13}C signals. For example, the ^{1}H NMR spectrum of compound **7a** showed two sets of ^{1}H signals at 1.33, 1.56, 3.94, and 3.99 ppm corresponding to the 4 OMe and 2 OO*t*Bu groups, respectively. Its ^{13}C NMR spectrum showed 28 sp^2 signals (two of which are overlapped) and 4 sp^3 signals for the fullerene skeleton carbons. Compound **5** is the precursor of **6**. The chemical shift of the OMe group is the same as that of compound **6** at 4.04 ppm, indicating that the OMe group should be near the *tert*-butylperoxo group. The ^{13}C NMR spectrum of **5** showed 50 sp^2 signals (four of which are overlapped) and 6 sp^3 signals for the fullerene skeleton carbons, in agreement with its C_1 symmetry. Other C_1 symmetric compounds exhibit similar spectra. Satisfactory HRMS spectra are obtained for all the new compounds.

In summary, an efficient method has been developed for the preparation of cyclopentadienyl-type fullerene derivatives with mixed addends through a bromination-mediated process. Compared to other double bonds on the fullerene cage, double bonds on the hexagons adjacent to the two OO*t*Bu groups of the 1,2-bisadduct **1** (C_{60}(OO*t*Bu)$_2$) show much enhanced reactivity toward bromine addition, affording the tetrabrominated derivative **4** (C_{60}(OO*t*Bu)$_2$Br$_4$). Subsequent bromine replacement of **4** by alkoxy groups starts from the position closer to the OO*t*Bu group in a one by one sequence. The regioselectivity can be explained by the relative stability of carbocation. Further work is in progress to prepare fullerene derivative for materials investigation such as solar cell using the present strategy.[20]

dx.doi.org/10.1021/jo102377r |*J. Org. Chem.* 2011, 76, 1735–1741

EXPERIMENTAL SECTION

All reagents were used as received. Dichloromethane was distilled over phosphorus pentaoxide. Toluene and benzene were distilled from sodium. Other solvents were used as received. The reactions were carried out in air. Compounds **1** and **2** were prepared according to the reported procedure.[14]

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

Compound 3a. A mixture of compound **1** and compound **2** (ratio 2:1, 110 mg) was dissolved in 100 mL of benzene. The solution was cooled with an ice bath. Pyrolidine (2 mg, 0.028 mmol) in benzene (5 mL) was added dropwise by a syringe. After the solution was stirred for 20 min, the solution was directly chromatographed on silica gel eluting with toluene. The first band was unreacted compound **1** (70 mg). The second band was collected and evaporated to give compound **3a** as a brown solid (25.1 mg, 0.028 mmol, 68%).

^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 3.52 (m, 4H), 2.08 (m, 4H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) (all signals represent 1C except as noted) δ 153.33, 151.91, 151.01, 149.54, 149.20, 148.70, 148.68, 148.11, 147.22, 147.13 (3C), 146.99, 146.52 (2C), 146.37 (2C), 146.20, 146.04, 145.96, 145.76, 145.73, 145.69 (3C), 145.65, 145.61, 145.01, 144.91, 144.85, 144.76, 144.70, 144.59 (2C), 144.43, 144.18, 143.85, 143.81, 143.75, 143.49, 143.13, 143.02, 142.98 (2C), 142.79, 142.76, 142.70, 142.58, 142.29, 141.76, 141.62, 141.29, 140.58, 140.20, 137.57, 137.17, 86.01, 82.49, 81.37, 77.68, 69.03, 49.64 (2C), 26.70 (3C), 23.84 (2C); FT-IR (microscope) 3362, 2971, 2922, 2851, 1660, 1633, 1514, 1470, 1461, 1435, 1363, 1241, 1189, 1036, 818 cm^{-1}; HRMS (ESI) for $C_{68}H_{18}NO_3$ [M + H$^+$] calcd 896.12867, found 896.12689.

Compound 3b. A mixture of compound **1** and compound **2** (ratio 2:1, 100 mg) was dissolved in 100 mL of benzene. The solution was cooled with an ice bath. Tetrahydroisoquinoline (5 mg, 0.038 mmol) in benzene (5 mL) was added dropwise by a syringe. After the solution was stirred for 20 min, the solution was directly chromatographed on silica gel eluting with toluene. The first band was unreacted compound **1** (62 mg). The second band was collected and evaporated to give compound **3b** as a brown solid (20 mg, 0.021 mmol, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 4H), 4.82 (q, 2H), 3.97 (m, 1H), 3.75 (m, 1H), 3.20 (m, 2H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 152.74, 151.38, 151.30, 149.78, 149.49, 148.93, 148.67, 148.35, 147.44, 147.34, 147.22, 146.85, 146.78, 146.58 (3C), 146.39, 146.36, 146.23 (2C), 146.98, 145.95, 145.90 (4C), 145.79, 145.69, 145.48, 145.20, 145.13, 145.03, 144.99, 144.94, 144.82, 144.75, 144.68, 144.39, 144.10, 144.07, 143.98, 143.66, 143.46, 143.22, 143.18, 142.98, 142.92, 142.73, 142.51, 142.05, 141.83, 141.51, 140.71, 140.38, 138.20, 137.38, 134.53, 134.18, 128.78, 126.84, 126.40, 125.92, 86.29, 82.60, 81.91, 77.95, 71.41, 52.43, 47.33, 30.08, 26.91 (3C); FT-IR (microscope) 3361, 2958, 2921, 2851, 1660, 1633, 1514, 1474, 1424, 1362, 1190, 1092, 1021, 818, 742 cm^{-1}; HRMS (ESI) for $C_{73}H_{20}NO_3$ [M + H$^+$] calcd 958.14432, found 958.14436.

Compound 5. Br_2 (15 drops) was added to a solution of compound **1** (400 mg, 0.445 mmol) in benzene (400 mL). After the solution was stirred in the dark at room temperature for 30 min, compound **1** was almost completely converted to compound **4**. Methanol (20 mL) and $AgClO_4$ (120 mg, 0.578 mmol) were added to the solution. After the solution was stirred in the dark at room temperature for 15 min, the solution was washed with water (5 × 200 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum; the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:5). The first band was a trace amount of compound **4**. The second band was collected and evaporated to give compound **5** as a reddish solid (106 mg, 0.091 mmol, 21%). The third band was collected and evaporated to give compound **6** (142 mg, 0.127 mmol, 28%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 153.70, 151.15, 150.59, 150.08, 149.81, 149.02 (2C), 148.82, 148.77, 148.44 (2C), 148.30, 148.25 (2C), 148.21, 148.19, 148.11, 147.78, 147.72, 147.51, 147.35, 147.16, 147.12, 147.08, 147.03, 146.97, 146.90, 146.82, 145.88, 145.63, 145.58, 145.50, 144.69, 144.66, 144.50, 144.44, 144.37, 144.23 (2C), 144.08, 143.92, 143.61, 143.50, 143.42, 143.13, 143.08, 142.52, 142.18, 141.48, 141.40, 141.24, 141.13, 140.13, 139.76, 89.38, 85.58, 82.50, 81.80, 81.31, 80.17, 57.29, 45.48, 43.56, 26.86 (3C), 26.79 (3C); FT-IR (microscope) 2977, 2926, 2852, 1728, 1456, 1363, 1194, 1090, 1013, 877, 829, 750 cm^{-1}; HRMS (ESI) for $C_{69}H_{21}Br_3NaO_5$ [M + Na$^+$] calcd 1188.88368, found 1188.88313.

Compound 6. Br_2 (10 drops) was added to a solution of compound **1** (200 mg, 0.223 mmol) in benzene (200 mL). After the solution was stirred in the dark at room temperature for 30 min, the staring material was almost completely converted to compound **4**. Methanol (10 mL) and $AgClO_4$ (150 mg, 0.723 mmol) were added to the solution. After the solution was stirred in the dark at room temperature for 30 min, the solution was washed with water (5 × 100 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum; the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:3). The first band was a trace amount of compound **4**. The second band was collected and evaporated to give compound **6** as a reddish solid (82.5 mg, 0.074 mmol, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (s, 6H), 1.60 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 2C except as noted) δ 151.30, 150.46, 150.10, 149.16, 148.83, 148.56, 148.34, 148.25 (1C), 148.20, 147.66, 147.60, 147.16, 147.09, 147.02 (3C), 146.83, 145.67, 144.65, 144.60, 144.55, 144.47, 144.43, 143.40 (4C), 142.85, 141.09, 141.01, 139.37, 90.00 (1C), 85.53 (1C), 81.48 (1C), 81.15 (1C), 80.37, 57.05, 43.90, 26.71 (3C), 26.56 (3C); FT-IR (microscope) 2978, 2927, 1465, 1363, 1194, 1124, 1101, 1086, 813, 731 cm^{-1}; HRMS (ESI) for $C_{70}H_{28}Br_2NO_6$ [M + NH_4^+] calcd 1136.02834, found 1136.02688.

Single crystals were obtained from slow evaporation of **6** in CS_2/$CHCl_3$/EtOH. Crystal data for **6**: $C_{70}H_{24}Br_2O_6$, M_w = 1120.71 g mol^{-1}, T = 113(2) K, orthorhombic, space group P 21 21 21. Unit cell dimensions: a = 12.0065(12) Å, b = 17.5800(18) Å, c = 20.214(2) Å, V = 4266.7(7) Å^3. Z = 4, ρ_{calcd} = 1.745 Mg m^3, μ = 1.970 mm^{-1}. Reflections collected/unique 44026/10142 [R(int) = 0.0370]. Final R indices [$I > 2\sigma(I)$], R_1 = 0.0286, wR_2 = 0.0602. The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre, deposition number CCDC-802118. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/conts/retrieving.html.

Compound 7a. Method A:. Br_2 (10 drops) was added to a solution of compound **1** (204 mg, 0.227 mmol) in benzene (200 mL). After the solution was stirred in the dark at room temperature for 30 min, methanol (10 mL) and $AgClO_4$ (200 mg, 0.964 mmol) were added to the solution. After the solution was stirred in the dark at room temperature for 45 min, the solution was washed with water (5 × 200 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum; the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:1). The only band was collected and evaporated to give compound **7a** as a reddish solid (70.1 mg, 0.069 mmol, 30%).

Method B:. Methanol (5 mL) and $AgClO_4$ (80 mg, 0.386 mmol) were added to a solution of compound **6** (94 mg, 0.084 mmol) in dicholormethane (45 mL). After the solution was stirred in the dark at room temperature for 25 min, the solution was washed with water (5 × 50 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum; the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:1). The first band was a trace amount of compound **6**. The second band was collected and evaporated to give compound **7a** as a reddish solid (28.2 mg, 0.028 mmol, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (s, 6H), 3.94 (s, 6H), 1.56 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 2C except as noted) δ 152.13, 150.99, 149.14, 149.04, 148.61, 148.45, 148.32 (3C), 147.78, 147.73 (4C), 147.59, 147.47 (1C), 147.34, 146.92, 146.22, 145.85, 145.49, 144.95, 144.83, 144.49, 143.67 (4C), 143.30, 142.66, 142.60, 141.97, 138.57, 89.99 (1C), 85.68 (1C), 81.28, 80.82, 79.97, 77.50, 56.17, 55.53, 26.72 (6C); FT-IR (microscope) 2977, 2928, 1458, 1363, 1195, 1104, 1079, 1010, 878, 737 cm^{-1}; HRMS (ESI) for $C_{72}H_{30}NaO_8$ [M + Na$^+$] calcd 1045.18384, found 1045.18329.

Compound 7b. Pent-4-yn-1-ol (10 drops) and $AgClO_4$ (56 mg, 0.270 mmol) were added to a solution of compound **6** (92 mg, 0.082 mmol) in dicholormethane (35 mL). After the solution was stirred in the dark at room temperature for 30 min, the solution was washed with water (5 × 50 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum; the residue was chromatographed on silica gel eluting with dichloromethane. The first band was a trace amount of compound **6**. The second band was collected and evaporated to give compound **7b** as a reddish solid (44 mg, 0.039 mmol, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (m, 2H), 4.30 (m, 2H), 3.93 (s, 6H), 2.46 (m, 4H), 2.07 (m, 4H), 1.97 (t, 2H), 1.56 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 2C except as noted) δ 151.85, 150.78, 149.13, 149.03, 148.62, 148.45, 148.31 (3C), 148.14, 147.72, 147.61, 147.59, 147.46 (1C), 147.34, 146.96, 146.81, 145.89, 145.43, 144.97, 144.78, 144.47, 143.73, 143.68, 143.34, 142.69, 142.49, 142.00, 138.64, 90.09 (1C), 85.62 (1C), 83.75, 81.32 (1C), 80.83 (1C), 79.99, 68.69, 66.41, 55.15, 56.14 (1C), 29.34, 26.78 (3C), 26.73 (3C), 15.46; FT-IR (microscope) 3306, 2975, 2927, 1458, 1363, 1194, 1104, 874, 632 cm^{-1}; HRMS (ESI) for $C_{80}H_{38}O_8$ [M$^+$] calcd 1126.25667, found 1126.25607.

Compound 9 and 10a. Br_2 (5 drops) was added to a solution of compound **8** (103 mg, 0.096 mmol) in dicholormethane (40 mL). After the solution was stirred in the dark at room temperature for 5 min, compound **8** was completely converted to compound **9**. At this stage methanol (5 mL) was added to this solution. After stirring at room temperature for 24 h, the solution was washed with saturated $Na_2S_2O_3$ aqueous solution. The organic layer was dried over Na_2SO_4, and then the solvent was removed under vacuum, the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:4). The first band was a trace amount of compound **9**. The second band was collected and evaporated to give compound **10a** as a reddish solid (70.5 mg, 0.059 mmol, 62%).

Characterization data for compound **9**: HRMS (ESI) for $C_{76}H_{36}Br_2O_8$ [M$^+$] calcd 1234.07669, found 1234.07533.

Characterization data for compound **10a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 3H), 1.59 (s, 9H), 1.52 (s, 9H), 1.36 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 151.84, 151.02, 150.90, 150.52, 150.36, 149.07, 148.99, 148.93, 148.75, 148.55, 148.47, 148.33 (2C), 148.16 (3C), 147.92, 147.67, 147.62, 147.59, 147.52, 147.45, 147.27, 147.24, 147.14, 146.99, 146.96, 146.91, 146.74, 146.05, 145.84, 145.73 (2C), 145.26, 145.06, 144.61 (2C), 144.41, 144.38, 144.22, 144.03, 143.96, 143.81, 143.31, 143.28, 143.18, 143.15, 142.90, 142.82, 142.18, 140.85, 139.89, 139.76, 137.56, 89.99, 85.45, 82.76, 81.81, 81.22, 81.20, 80.94, 80.25, 80.10, 57.05, 44.29, 26.95 (3C), 26.72 (3C), 26.69 (3C), 26.67 (3C); FT-IR (microscope) 2979, 2929, 1458, 1364, 1195, 1098, 1021, 875, 757 cm^{-1}; HRMS (ESI) for $C_{77}H_{39}BrO_9$ [M$^+$] calcd 1186.17775, found 1186.17665.

Compound 10b. Br_2 (5 drops) was added to a solution of compound **8** (154 mg, 0.143 mmol) in CH_2Cl_2 (50 mL). After the solution was stirred in the dark at room temperature for 5 min, compound **8** was converted completely to compound **9**. At this stage pent-4-yn-1-ol (0.5 mL) was added to this solution. After stirring at room temperature for 24 h, the solution was washed with saturated $Na_2S_2O_3$ aqueous solution. The organic layer was dried over Na_2SO_4, and then the solvent was removed under vacuum. The residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:3). The first band was a trace amount of compound **9**. The second band was collected and evaporated to give compound **10b** as a reddish solid (92 mg, 0.074 mmol, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 (m, 1H), 4.31 (m, 1H), 2.50 (m, 2H), 2.08 (m, 2H), 1.96 (t, 1H) 1.59 (s, 9H), 1.49 (s, 9H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 151.90, 151.26, 150.43, 150.26, 149.87, 149.06, 148.96, 148.91, 148.76, 148.53, 148.41, 148.33 (2C), 148.16, 148.13, 148.11, 147.71, 147.68, 147.63, 147.59, 147.46, 147.26, 147.22, 147.14, 147.03 (2C), 146.94, 146.93, 146.85, 146.06, 145.80 (2C), 145.54, 145.24, 145.02, 144.75, 144.53, 144.52, 144.20, 144.00, 143.93, 143.73, 143.28 (4C), 143.07, 142.86, 142.81, 142.19, 140.88, 140.15, 139.85, 137.86, 89.74, 85.60, 84.35, 83.53, 82.90, 81.72, 81.23, 81.17, 80.90, 80.25, 68.40, 68.02, 53.37, 29.61, 26.88 (3C), 26.67 (9C), 15.56; FT-IR (microscope) 3306, 2978, 2930, 1473, 1363, 1195, 1100, 1070, 1024, 874 cm^{-1}; HRMS (ESI) for $C_{81}H_{43}BrNaO_9$ [M + Na$^+$] calcd 1261.19882, found 1261.19627.

Compound 11a. Methanol (2 mL) and $AgClO_4$ (40 mg, 0.193 mmol) were added to a solution of compound **10a** (60 mg, 0.051 mmol) in dichloromethane (25 mL). After the solution was stirred in the dark at room temperature for 5 min, the solution was washed with water (5 × 25 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:1). The only band was collected and evaporated to give compound **11a** as a reddish solid (41.1 mg, 0.036 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 6H), 1.57 (s, 9H), 1.43 (s, 9H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 152.25, 152.19, 151.75, 149.10 (2C), 149.04, 148.99, 148.96, 148.60, 148.50, 148.48, 148.41, 148.31, 148.22 (2C), 147.76 (2C), 147.71, 147.65, 147.62, 147.59, 147.47, 147.40, 147.30 (2C), 147.28, 147.00, 146.93, 146.85, 146.79, 146.30, 146.04, 145.88, 145.72, 145.57, 145.36, 144.98, 144.79, 144.70, 144.47, 144.43, 144.24, 143.71, 143.58 (2C), 143.33, 143.08, 142.81, 142.56, 142.15, 142.02, 141.56, 138.80, 138.09, 89.93, 85.63, 82.81, 81.34, 81.19, 81.06, 80.79, 80.43, 79.82, 77.60, 56.39, 55.54, 26.74 (6C), 26.73 (6C); FT-IR (microscope) 2977, 2929, 1457, 1386, 1363, 1195, 1123, 1195, 1100, 1022, 875 cm^{-1}; HRMS (ESI) for $C_{78}H_{46}NO_{10}$ [M + NH_4^+] calcd 1156.31217, found 1156.30857.

Compound 11b. Water (2 drops) and $AgClO_4$ (35 mg, 0.169 mmol) were added to a solution of compound **10a** (53 mg, 0.045 mmol) in dichloromethane (25 mL). After the solution was stirred in the dark at room temperature for 5 h, the solution was washed with water (4 × 25 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:1). The only band was collected and evaporated to give compound **11b** as a reddish solid (39 mg, 0.035 mmol, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (s, 3H), 1.58 (s, 9H), 1.51 (s, 9H), 1.35 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 152.60, 151.05, 149.47 (2C), 149.32, 148.96, 148.89, 148.82, 148.79, 148.72, 148.46, 148.33, 148.25, 148.18 (2C), 148.11, 148.04, 147.59 (2C), 147.42 (2C), 147.35, 147.32, 147.27, 147.22, 147.19, 147.15, 146.84, 146.64, 145.80, 145.67 (2C), 145.51, 145.17, 144.95, 144.81, 144.52, 144.46 (2C), 144.27, 144.09, 143.71, 143.64, 143.59, 143.55, 143.09, 143.04, 142.96, 142.58, 142.43, 142.00, 140.35, 138.24, 137.35, 89.91, 85.29, 82.75, 81.88, 81.04, 80.98, 80.75, 80.12, 79.46, 71.48, 64.13, 26.70 (3C), 26.60 (9C); FT-IR (microscope) 3385, 2977, 1728, 1456, 1387, 1364, 1195, 1095, 1050, 1024, 876, 756 cm^{-1}; HRMS (ESI) for $C_{77}H_{40}NaO_{10}$ [M + Na$^+$] calcd 1147.25192, found 1147.24832.

Compound 11c. Pent-4-yn-1-ol (4 drops) and $AgClO_4$ (40 mg, 0.193 mmol) were added to a solution of compound **10a** (92 mg, 0.078

mmol) in dichloromethane (40 mL). After the solution was stirred in the dark at room temperature for 1 h, the solution was washed with water (5 × 50 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:1). The only band was collected and evaporated to give compound **11c** as a reddish solid (53.4 mg, 0.045 mmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (m, 1H), 4.27 (m, 1H), 3.98 (s, 3H), 2.45 (m, 2H), 2.06 (m, 2H), 1.97 (t, 1H), 1.57 (s, 9H), 1.43 (s, 9H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 152.18, 151.84, 151.47, 149.38, 149.08, 149.04, 148.99, 148.95, 148.59, 148.49, 148.47, 148.40, 148.28, 148.22, 148.20, 148.15, 147.74, 147.64, 147.61, 147.58, 147.49, 147.46, 147.38, 147.29, 147.24, 147.19, 146.92, 146.87, 146.62, 146.45, 146.06, 145.89, 145.74, 145.48, 145.35, 144.94, 144.78, 144.67, 144.51, 144.36, 144.29, 143.73, 143.64, 143.57, 143.35, 143.05, 143.02, 142.81, 142.48, 142.13, 142.07, 141.20, 138.88, 138.07, 89.95, 85.64, 83.96, 82.75, 81.30, 81.20, 81.05, 80.80, 80.44, 79.86, 68.57, 66.72, 56.28, 56.25, 29.44, 26.73 (12C), 15.38 ; FT-IR (microscope) 3309, 2977, 2928, 2854, 1738, 1457, 1364, 1194, 1104, 1021, 873 cm^{-1}; HRMS (ESI) for $C_{82}H_{50}NO_{10}$ [M + NH_4^+] calcd 1208.34347, found 1208.34020.

Compound 11d. Pent-4-yn-1-ol (4 drops) and $AgClO_4$ (40 mg, 0.193 mmol) were added to a solution of compound **10b** (67 mg, 0.054 mmol) in dichloromethane (35 mL). After the solution was stirred in the dark at room temperature for 15 min, the solution was washed with water (5 × 35 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:1). The only band was collected and evaporated to give compound **11d** as a reddish solid (37 mg, 0.030 mmol, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (m, 4H), 2.46 (m, 4H), 2.06 (m, 4H), 1.98 (m, 2H), 1.57 (s, 9H), 1.43 (s, 9H), 1.33 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 152.21, 152.18, 151.12, 149.31, 149.06, 149.03, 148.97, 148.95, 148.55, 148.48 (2C), 148.41, 148.27, 148.22, 148.19, 147.94, 147.74, 147.70, 147.66, 147.60, 147.54, 147.44, 147.37, 147.29, 147.16, 146.90, 146.88, 146.86, 146.40, 146.21, 146.02, 145.89, 145.74, 145.51, 145.33, 144.87, 144.82, 144.76, 144.52, 144.34, 144.25, 143.69, 143.61, 143.59, 143.34, 143.02, 143.01, 142.78, 142.54, 142.18, 142.14, 141.19, 139.00, 138.26, 89.79, 85.71, 84.33, 84.02, 82.80, 81.33, 81.14, 81.07, 80.81, 80.42, 69.46, 68.60, 68.44, 68.42, 67.26, 66.69, 29.50, 29.47, 26.74 (6C), 26.72 (6C), 15.59, 15.51; FT-IR (microscope) 3306, 2978, 2931, 1472, 1387, 1364, 1194, 1104, 1055, 1023, 874, 633 cm^{-1}; HRMS (ESI) for $C_{86}H_{50}O_{10}$ [M^+] calcd 1242.34040, found 1242.33640.

Reduction of Compound 5 with PPh_3. PPh_3 (1 mg, 0.004 mmol) dissolved in dichloromethane (1 mL) was added to a solution of compound **5** (20 mg, 0.017 mmol) in dichloromethane (10 mL). After the solution was stirred in the dark at room temperature for 5 min, the solution was directly chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:6). The only band was collected and evaporated to give compound **1** as a brown solid (6 mg, 0.007 mmol, 39%).

Compound 12. PPh_3 (10 mg, 0.038 mmol) was added to a solution of compound **10a** (54 mg, 0.045 mmol) in dichloromethane (20 mL). After the solution was stirred in the dark at room temperature for 10 min, the solvent was removed under vacuum, and the residue was chromatographed on silica gel eluting with dichloromethane/petroleum ether (1:3). The first band was collected and evaporated to give compound **8** as a brown solid (8 mg, 0.007 mmol, 16%). The second band was collected and evaporated to give compound **12** as a reddish solid (34 mg, 0.031 mmol, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (s, 1H), 3.89 (s, 3H), 1.58 (s, 9H), 1.46 (s, 9H), 1.35 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 152.70, 151.01, 150.07, 149.95, 149.43, 149.06, 148.97, 148.84, 148.46 (2C), 148.35, 148.28 (2C), 148.20, 148.13, 148.04 (2C), 147.82, 147.73, 147.63 (2C), 147.56, 147.51, 147.38, 147.31, 147.27, 147.15, 147.06, 146.90 (2C), 146.67, 146.06 (2C), 145.53, 145.34, 145.04, 144.50, 144.37 (2C), 144.30, 144.25, 143.95, 143.88 (2C), 143.67, 143.59, 143.32, 143.24 (2C), 142.74, 142.40, 142.12, 140.59, 137.75, 89.95, 85.45, 83.04, 81.43, 81.13, 81.08, 80.99, 80.73, 80.70, 55.48, 43.94, 26.80 (6C), 26.74 (6C); FT-IR (microscope) 2978, 2930, 1457, 1386, 1363, 1195, 1088, 907, 875, 733 cm^{-1}; HRMS (ESI) for $C_{77}H_{44}NO_9$ [M + NH_4^+] calcd 1126.30161, found 1126.29707.

■ ASSOCIATED CONTENT

Supporting Information. Selected spectroscopic data for all new compounds and crystallographic data for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work is supported by NSFC and the Major State Basic Research Development Program.

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