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# Synthesis and Chemical Reactivity of Tetrahydro[60]fullerene Epoxides with Both Amino and Aryl Addends

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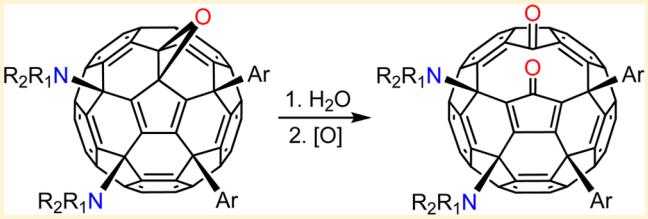
Supporting Information

**ABSTRACT:** Tetrahydro[60]fullerene epoxides $C_{60}(O)$-$Ar_n(NR_2)_{4-n}$, $n$ = 1, 2, have been prepared by treating 1,4-adducts $C_{60}(OH)Ph$ and $C_{60}(Tol)_2$ with cyclic secondary amines. The epoxy moieties in these mixed tetrahydro[60]-fullerene epoxides were hydrolyzed into the corresponding diol derivatives, which were further oxidized into diketone open-cage fullerenes with a 10-membered orifice. A few other reactions also showed that the present tetrahydro[60]fullerene epoxides with both amino and aryl addends exhibit improved chemical reactivity over the tetraamino[60]fullerene epoxide without any aryl group.




## INTRODUCTION

The skew-pentagonal-pyramid addition products $C_s$-$C_{60}X_6$ and $C_s$-$C_{60}YX_5$ are among the extensively studied fullerene multiadducts.[1,2] They are formed through the cyclopentadienyl type addition pattern in which five addends are attached around the same pentagon and another addend on the pentagon. A closely related multiadduct is the tetrahydro[60]fullerene epoxide $C_s$-$C_{60}(O)X_4$. Compared to $C_{60}X_6$ and $C_{60}YX_5$, which have various different types of addends, the tetrahydro[60]-fullerene epoxide is quite limited. The first such epoxide is a tetraamino $C_{60}$ epoxide from the reaction of secondary amine with $C_{60}$ in the presence of oxygen.[3] Later, various other secondary amines have been shown to form this type of adducts with $C_{60}$ in good yields under different conditions.[4] Hydrogen peroxides such as *t*-butylhydrogen peroxide can also react efficiently with $C_{60}$ to form the tetraperoxo epoxy adduct.[5] Even though many different aryl groups can form the pentaaryl adduct $C_{60}Ar_5H$,[1c,6] only the triphenylamine derived adduct can be converted to the epoxide $C_{60}(O)Ar_4$ by deprotonation induced dearylation in the presence of oxygen.[7] Remarkably, the tetraperfluoroalkyl $C_{60}$ epoxides $C_{60}(O)(CF_3)_4$ and $C_{60}(O)(C_2F_5)_4$ were isolated in low yields from the complex reaction mixture between $C_{60}$ and $CF_3I$ or $C_2F_5I$, respectively, at high temperature.[8] Biological activities of the tetraamino $C_{60}$ epoxides have been explored,[9] but further reaction study of the tetrahydro[60]fullerene epoxides is mainly limited to the peroxo adduct.[10] Here, we report the preparation of several new tetrahydro[60]fullerene epoxides and investigation of their chemical reactivity.

## RESULTS AND DISCUSSION

In our previous work, we have shown that the epoxy moiety in $C_{60}(O)(OOtBu)_4$ can be opened selectively by various nucleophiles to form the hexaadduct $C_{60}(OH)Nu(OOtBu)_4$,[11] which can be further converted to other fullerene derivatives including open-cage fullerenes[12] and azafullerenes.[13] In an attempt to extend the epoxy opening reactions to other tetrahydro[60]fullerene epoxides, we tested the reactivity of the tetraamino $C_{60}$ epoxides. All our efforts failed to produce any new compound selectively. The amino addends can be partially eliminated from the fullerene cage under the conditions, thus resulting in a complex mixture of products. To avoid the undesirable side effect of the amino addends, the number of amino addends should be reduced. Therefore, we prepared the tetrahydro epoxy products **3**–**6** starting from 1,4-bisadducts **1** and **2** (Scheme 1).[14,15]

Compounds **1** and **2** were prepared according to the literature procedure.[14] Their reactions with 4-methylpiperidine afforded a mixture of two isomers in both cases. The amination conditions shown in Scheme 1 are the same as those developed by Nakamura et al. for the amination reaction of $C_{60}$.[4c] As expected, the 1,4-bisadducts are more reactive than $C_{60}$. The present reaction time is about 3 h, whereas the reaction of $C_{60}$ needs more than 10 h. Other secondary amines can also react with **1** and **2** to form a mixture of isomers. For example, the reaction of piperidine with **2** afforded **5a** and **6a**, which are analogous to the 4-methylpiperidine products **5** and **6**. We chose the 4-methylpiperidine because of its better solubility and characteristic methyl group for NMR characterization.

Structural assignments of the isomers **5** and **6** were based on their different symmetry shown on the NMR spectra. To assign structures of the $C_1$ symmetric compounds **3** and **4**, single crystals of compound **4** were obtained from slow evaporation of

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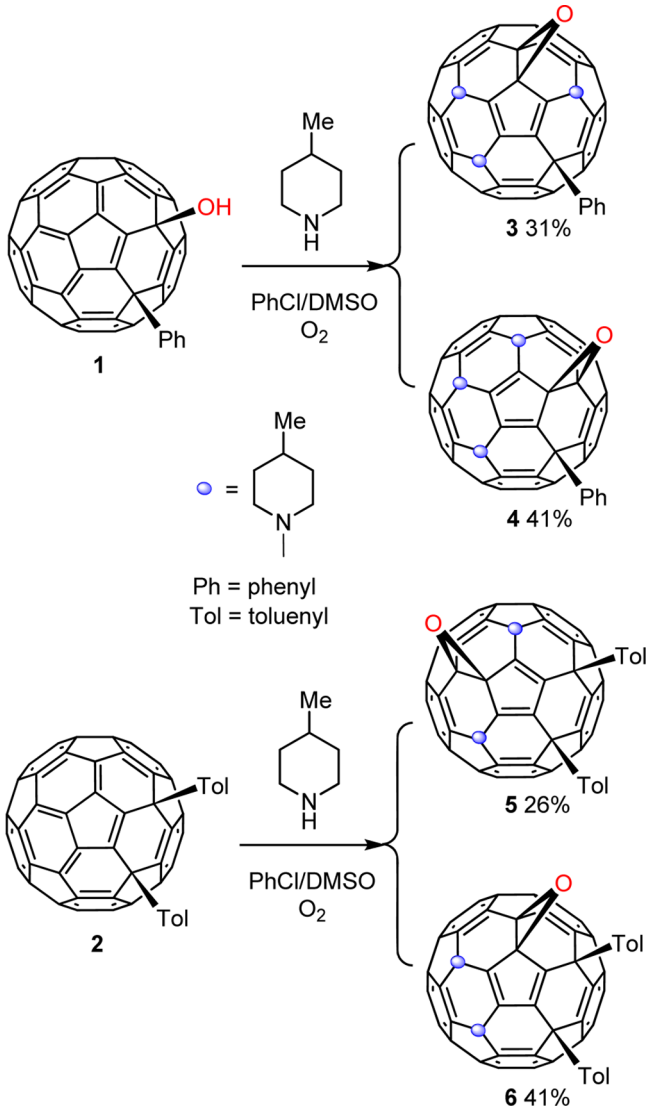
**Scheme 1. Amination Reactions of 1,4-$C_{60}$ Adducts**



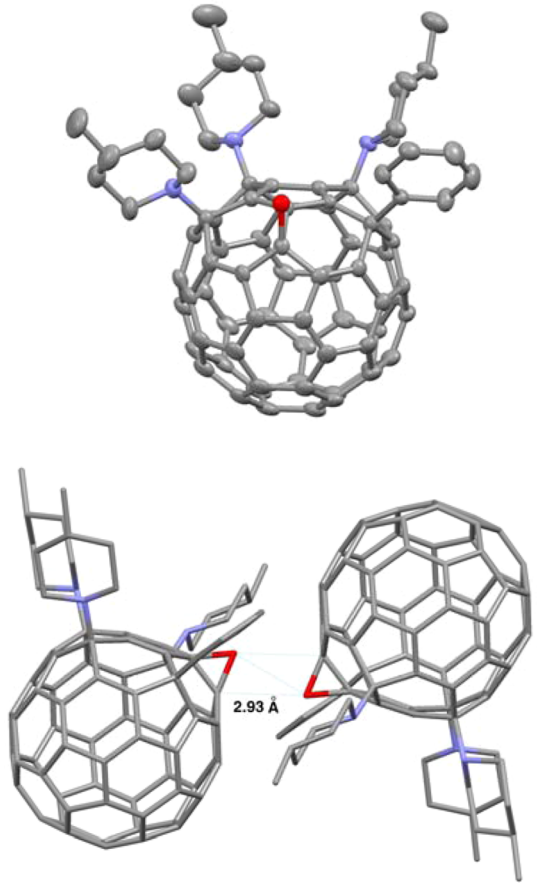




**Figure 1.** X-ray structure of compound **4**. Ellipsoids were drawn at 50%. For clarity, hydrogen atoms were not drawn. Color scheme: gray = C, blue = N, red = O.

its solution in $CDCl_3$. The structure shows four pairs of enantiomers in the unit cell. The epoxy moieties in each pair of enantiomers are in close contact, forming dimeric structures (Figure 1). The bond distances and bond angles are virtually the same between the phenyl bound cage carbon and the corresponding 4-methylpiperidine bound cage carbon next to the epoxy moiety, indicating that the different addends have no effect on the cage structure. The cyclopentadienyl double bonds (3.51 Å) surrounded by the addends are the shortest on the cage.

Possible pathways for the formation of compounds **3**–**6** are shown in Scheme 2. The initial single electron transfer step to form **A** and formation of the aziridinium moiety in intermediates **D** and **F** are the same as in the amination reaction of pristine $C_{60}$.[4c,15c] Formation of compound **3** with the epoxy group far away from the phenyl group may go through intermediates **A**, **B**, and **C**, in which process the hydroxyl group is replaced by an amino group through an $S_N2'$ mechanism. Amino groups could be replaced by more reactive amines through an $S_N2'$ mechanism as reported by Troshin et al.[16] Addition of the aminium group in the *para* position of the OH group in **B** would lead eventually to a hydroxyl group containing tetrahydro[60]fullerene epoxide, but no such product was isolated perhaps due to further reactions to form more complex products. Compound **4** can also be formed through intermediates **D** and **E** besides **C**, which probably is responsible for the higher yield of **4** compared to that of **3**. The formation of compounds **5** and **6** may go through intermediate **F**, which can be formed in a similar pathway to intermediate **D**. The higher yield of **6** indicates that the $S_N2'$ pathway is more efficient than the $S_N2''$ pathway.

With the aryl group mixed aminofullerene epoxides in hand, we then investigated the chemical reactivity of their epoxy moiety (Scheme 3). Indeed, introduction of aryl groups improves the selectivity and results in reactions analogous to those for the tetraperoxo $C_{60}$ epoxide $C_{60}(O)(OOtBu)_4$. Treatment of **6** with ferric chloride in toluene afforded the hexaadduct **7** with the addition of another tolyl addend.[15b,17] Hydroxyl and alkoxyl groups were added by using *p*-toluenesulfonic acid as the catalyst. The epoxide opening reactions are highly regioselective, producing only the product with the hydroxyl group on the central pentagon.[11] The vicinal diol moiety in **8a** can be easily converted to the open-cage diketone **9** with diacetoxyliodobenzene.[18] The 10-membered orifice in **9** could be closed to form isomers **10a** and **10b** by treating it with methanol in the presence of $BF_3$. This orifice closing reaction is different from the analogous reaction of $C_{60}(O)_2(OOtBu)_4$ with methanol, which gave just one product with the hydroxyl group on the central pentagon.[18] Considering such a result, we assigned the major product **10a** with the



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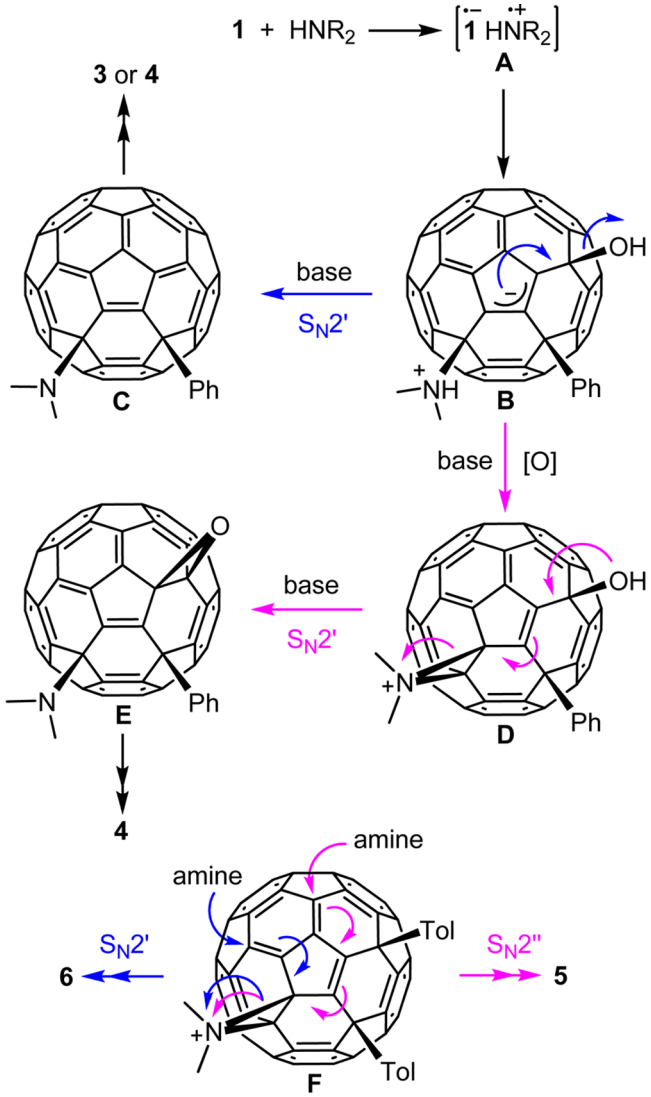
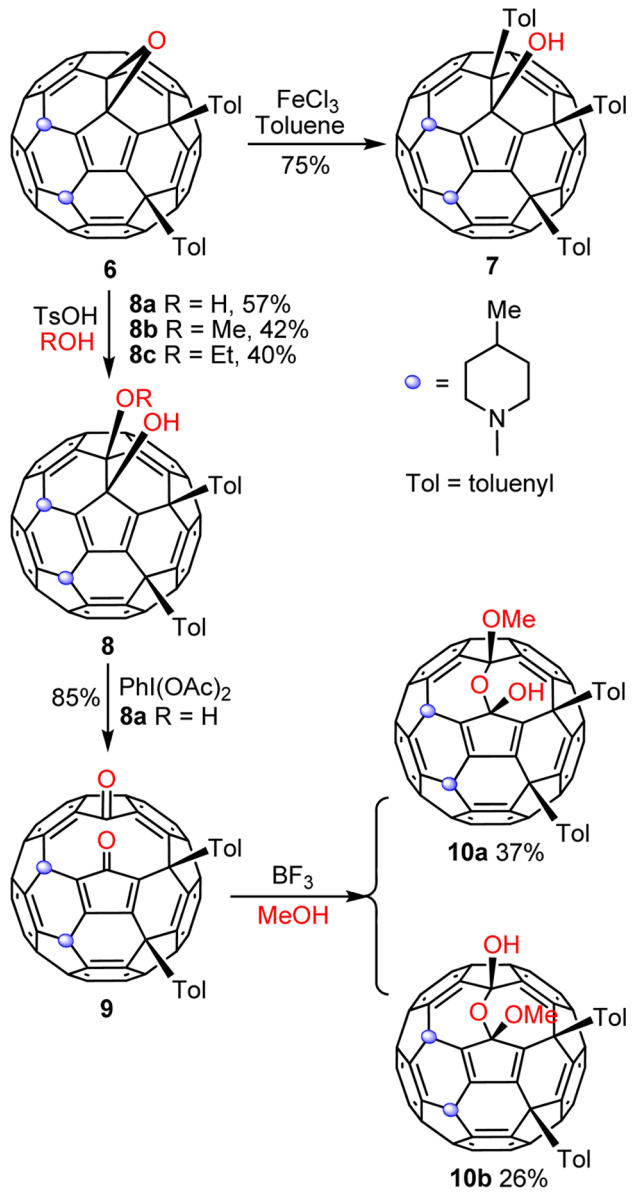
**Scheme 2. Possible Pathways of Amination Reactions of 1,4-$C_{60}$ Adducts**




**Scheme 3. Epoxy Opening Reactions and Preparation of Open-Cage Compounds**[a]




[a]The assignment of **10a** and **10b** is not conclusive and may be reversed.

hydroxyl group on the central pentagon.[19] The epoxy moiety in compounds **3**, **4**, and **5** could also be hydrolyzed to the vicinal diols **11**, **12**, and **13**, and then oxidized into the corresponding open-cage diketone compounds **14**, **15**, and **16**, respectively (Figure 2).

Spectroscopic data of compounds **7**−**16** are in agreement with the structures depicted in Scheme 3 and Figure 2. All the compounds except diol **13** and diketone **16** are $C_1$ symmetric and showed the expected NMR pattern, in particular, on the $^{13}C$ NMR spectra, which showed the expected number of fullerene skeleton carbon signals. Assignments of the hydroxyl group on the central pentagon for compounds **7** and **8** assumed that there is no OH shift in the epoxy opening process. This is well supported by the fact that oxidation of diols **8a**, **11**, **12**, and **13** led to the corresponding diketones. Compounds **10a** and **10b** showed two characteristic acetal signals at 106. 48, 107.73 ppm and 102.94, 110.35 ppm, respectively, confirming the presence of the diacetal moiety. However, the NMR data cannot distinguish the isomers and the assignment could be switched. The open-cage compounds **9**, **14**, **15**, and **16** showed the expected carbonyl carbon signals on the $^{13}C$ NMR spectra. Their IR spectra showed strong carbonyl stretching at around 1743 $cm^{-1}$.

Elimination of the epoxy moiety and partial elimination of the amino addends can be effectively achieved with excess $PPh_3/I_2$ for compounds **3** and **5**, as shown in Scheme 4. Complete removal of all the addends and formation of $C_{60}$ was observed when $C_{60}(O)(NR_2)_4$ ($NR_2$ = 4-methylpiperidinyl) was treated with $PPh_3/I_2$. Triphenylphosphine has been reported before to remove the epoxy moiety in fullerene epoxides $C_{60}(O)_n$.[20] In the present case, triphenylphosphine alone could not eliminate the amino nor epoxy addends. Both iodine and triphenylphosphine are needed for the retroamination addition process. Treating the open-cage compounds such as **9** with $PPh_3/I_2$ yielded a complex mixture of unidentified products. The 1,4-adduct **17**[21] reacted with 4-methylpiperidine



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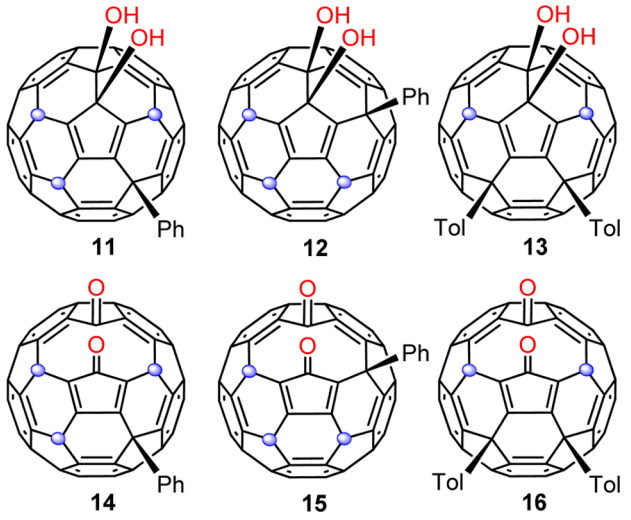
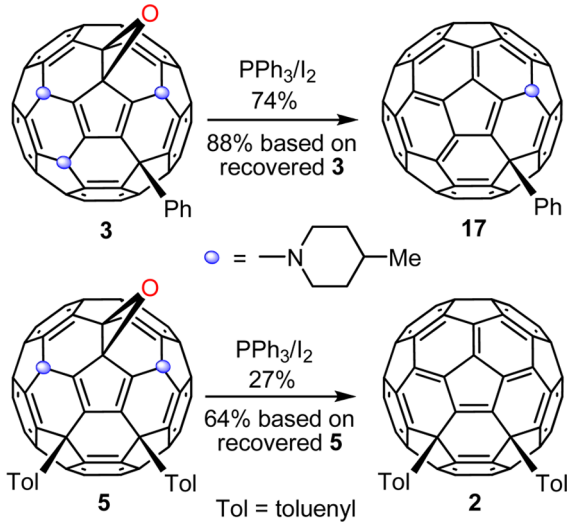



**Figure 2.** Structure of compounds **11**–**16**.

**Scheme 4. Selective Removal of Amino and Epoxy Addends**




to give compounds **3** and **4**, which supports the formation of intermediate **C** in the proposed mechanism in Scheme 2.

## CONCLUSION

Similar to pristine $C_{60}$, aryl 1,4-[60]fullerene adducts react with secondary amines to form amino and aryl-mixed tetrahydro[60]fullerene epoxides in good yields. Introduction of the aryl group greatly improves the chemical reactivity of the epoxy moiety in comparison to the tetraamino[60]fullerene epoxides. Hydrolysis of the epoxy moiety in the mixed tetrahydro[60]fullerene epoxides yields the vicinal diol moiety, which can be oxidized into the open-cage diketones with a 10-membered orifice. In addition, $PPh_3/I_2$ has been shown to facilitate a retroamination process for the tetrahydro[60]-fullerene epoxides. The present method may be applied to prepare other mixed tetrahydro[60]fullerene epoxides.

## EXPERIMENTAL SECTION

All reagents were used as received. Dichloromethane (DCM) was distilled from phosphorus pentoxide. Benzene was distilled from sodium. Other solvents were used as received. The reactions were carried out under atmosphere condition. The NMR spectra were obtained at 25 °C (except noted) with 400 and 500 MHz spectrometers ($^1$H and $^{13}$C NMR spectra of the same compound were obtained with different spectrometers in some cases). Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for $^{13}$C NMR). ESI-FT-ICR-HRMS spectra were recorded in the positive-mode. Chromatographic purifications were carried out with silica gel of 200–300 mesh.

**Preparation of Compounds 3 and 4.** To a solution of compound **1** (132 mg, 0.162 mmol) in 80 mL of PhCl was added DMSO (16 mL), and the mixture was stirred under continuous bubbling of $O_2$ for 10 min. To the solution was then added 4-methylpiperidine (96 mg, 0.97 mmol), and the mixture was stirred under an atmospheric pressure of $O_2$ at 25 °C for 3 h. The mixture was washed with saturated aqueous $NH_4Cl$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The solution was chromatographed on a silica gel column eluting with DCM. Compound **3** was collected and evaporated as an orange solid (56 mg, 0.051 mmol, 31%). The eluting solvent was changed to DCM/ethyl acetate (500:1), and another red band was eluted to give compound **4** (74 mg, 0.067 mmol, 41%) as an orange solid.

*Characterization Data for* ***3****.* $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.31 (d, 2H, $J$ = 7.4 Hz), 7.47 (dd, 2H, $J1$ = 7.1 Hz, $J2$ = 7.4 Hz), 7.38 (t, 1H, $J$ = 7.0 Hz), 3.82 (d, 1H, $J$ = 10.8 Hz), 3.64–3.59 (m, 4H), 3.51 (d, 1H, $J$ = 10.1 Hz), 2.75 (t, 1H, $J$ = 11.3 Hz), 2.68–2.59 (m, 5H), 1.83–1.61 (m, 9H), 1.42–1.32 (m, 6H), 0.97 (s, br, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 152.55, 152.46, 151.91, 151.58, 150.32, 149.95, 149.68, 149.29, 149.12, 149.05, 148.99, 147.82, 147.78, 147.77 (2C), 147.65 (2C), 147.46, 147.37, 147.24 (2C), 147.20, 147.12 (2C), 147.07, 146.97, 146.93, 146.87, 146.46, 146.41, 146.34, 145.73, 145.69, 145.59, 145.37, 145.07, 145.02, 144.62, 144.32, 144.15, 143.78, 143.74, 143.72, 143.71, 143.59, 143.53, 143.47, 143.02, 142.96, 142.85, 141.92, 140.59, 140.38, 140.11, 138.47, 128.92 (2C), 128.58 (2C), 127.58, 76.84, 76.82, 76.19, 72.66, 71.28, 59.64, 51.82, 51.67, 51.44, 51.20, 51.17, 50.76, 35.25 (2C), 35.22 (2C), 35.20, 35.15, 30.84, 30.63, 30.57, 21.97 (3C). ESI-FT-ICR-HRMS-Positive: $C_{84}H_{42}N_3O$ ($M + H^+$) calculated 1108.3322, found 1108.3346.

*Characterization Data for* ***4****.* $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.02 (d, 2H, $J$ = 7.5 Hz), 7.44 (dd, 2H, $J1$ = 7.6 Hz, $J2$ = 7.6 Hz), 7.34 (t, 1H, $J$ = 7.3 Hz), 3.86 (d, 1H, $J$ = 11.1 Hz), 3.78 (d, 1H, $J$ = 10.8 Hz), 3.68–3.65 (m, 3H), 3.48 (d, 1H, $J$ = 10.1 Hz), 2.87–2.61 (m, 6H), 2.37 (t, 1H, $J$ = 10.6 Hz), 1.87–1.70 (m, 6H), 1.57–1.47 (m, 3H), 1.39–1.30 (m, 6H), 1.01 (dd, 6H, $J1$ = 6.5 Hz, $J2$ = 9.0 Hz), 0.94 (d, 3H, $J$ = 6.1 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 154.85, 154.73, 152.14, 150.96, 150.55, 149.31, 149.27, 148.98, 148.86, 147.93, 147.82, 147.77, 147.69, 147.47, 147.39, 147.24, 147.12, 147.05, 147.04, 147.00, 146.97, 146.95, 146.93, 146.84, 146.77, 146.74, 146.63, 146.36, 146.25, 146.18, 146.07, 145.79, 145.44, 145.28, 145.16, 145.12, 145.02, 144.61, 144.24, 143.96, 143.91, 143.90, 143.83, 143.78, 143.63, 143.51, 143.39, 142.98, 142.91, 142.84, 140.50, 140.42, 139.63, 137.96, 128.85 (2C), 128.42 (2C), 127.53, 76.28, 76.00, 72.57, 72.50, 72.12, 62.23, 51.80, 51.42, 51.31, 50.96, 50.92, 50.48, 35.32, 35.22 (4C), 35.15, 35.12, 30.94, 30.77, 30.63, 22.03, 21.98, 21.96. ESI-FT-ICR-HRMS-Positive: $C_{84}H_{42}N_3O$ ($M + H^+$) calculated 1108.3322, found 1108.3333.

Single crystals of **4** were obtained from slow evaporation of its $CDCl_3$ solution. Formula: $C_{84}H_{41}N_3O$, $T$ = 180.00(10) K, monoclinic, space group $C2/c$. Unit cell dimensions: $a$ = 34.1629(8) Å, $b$ = 20.3663(4) Å, $c$ = 19.4299(3) Å, $\alpha = \gamma$ = 90°, $\beta$ = 104.204(2)°. $V$ = 13105.5(5) Å$^3$. $Z$ = 8, $\rho_{calcd}$ = 1.123 Mg/m$^3$. Reflections collected/unique 96995/12884 [$R$(int) = 0.0511]. Final $R$ indices [$I > 2\sigma(I)$], $R_1$ = 0.0817, $wR_2$ = 0.2481 [all data]. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-1046797

**Preparation of Compounds 5 and 6.** To a solution of compound **2** (250 mg, 0.277 mmol) in 90 mL of PhCl was added DMSO (18 mL), and the mixture was stirred under continuous bubbling of $O_2$ for 10 min. To the solution was then added 4-methylpiperidine (165 mg, 1.66 mmol), and the mixture was stirred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under an atmospheric pressure of $O_2$ at 25 °C for 3 h. The mixture was washed with saturated aqueous $NH_4Cl$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The solution was chromatographed on a silica gel column eluting with toluene/$CS_2$ (1:1). Compound **5** was collected and evaporated as an orange solid (79 mg, 0.071 mmol, 26%). The eluting solvent was changed to toluene/ethyl acetate (500:1), and another red band was eluted to give compound **6** (128 mg, 0.115 mmol, 41%) as an orange solid.

*Characterization Data for* ***5****.* $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.89 (d, 4H, $J$ = 8.0 Hz), 7.67 (d, 4H, $J$ = 7.9 Hz), 3.64 (d, 2H, $J$ = 11.0 Hz), 3.54 (d, 2H, $J$ = 12.2 Hz), 2.64−2.58 (m, 4H), 2.37 (s, 6H), 1.77−1.70 (m, 4H), 1.41−1.38 (m, 6H), 0.99 (d, 6H, $J$ = 5.9 Hz). ESI-FT-ICR-HRMS-Positive: $C_{86}H_{39}N_2O$ ($M + H^+$) calculated: 1115.3057, found: 1115.3036. ($^{13}$C NMR for the compound could not be obtained due to low solubility).

*Characterization Data for* ***6****.* $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.82 (d, 2H, $J$ = 8.0 Hz), 7.67 (d, 2H, $J$ = 8.0 Hz), 7.14 (dd, 4H, $J1$ = 7.9 Hz, $J2$ = 13.5 Hz), 3.77 (d, 1H, $J$ = 11 Hz), 3.67 (m, 2H), 3.54 (d, 1H, $J$ = 10.7 Hz), 2.77 (t, 1H, $J$ = 10.6 Hz), 2.71−2.60 (m, 2H), 2.54−2.50 (m, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 1.83 (d, 1H, $J$ = 12.1 Hz), 1.74 (t, 3H, $J$ = 11.4 Hz), 1.62 (d, 1H, $J$ = 12.0 Hz), 1.36−1.30 (m, 5H), 0.97 (dd, 6H, $J1$ = 6.6 Hz, $J2$ = 6.6 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 156.42, 152.39, 152.35, 151.02, 150.89, 150.18, 149.39, 149.29, 149.12, 148.94, 148.90, 148.01, 147.84, 147.77, 147.74 (2C), 147.65, 147.50, 147.34, 147.20, 147.19, 147.17, 147.10, 147.07, 146.99, 146.82, 146.81, 146.61, 146.43, 146.37, 146.28, 146.22, 145.54, 145.43, 145.42, 145.15, 145.04, 144.97, 144.65, 144.55, 144.01, 144.00, 143.77 (2C), 143.61, 143.52, 143.46, 143.34, 142.95, 142.90, 141.09, 140.54, 140.34, 137.78, 137.35, 137.32, 136.85, 136.22, 129.63 (2C), 129.43 (2C), 128.08 (4C), 76.41, 76.06, 72.76, 72.05, 62.39, 59.20, 51.84, 51.46, 51.14, 50.78, 35.20 (3C), 35.16, 30.80, 30.64, 21.96 (2C), 21.15, 21.14. ESI-FT-ICR-HRMS-Positive: $C_{86}H_{39}N_2O$ ($M + H^+$) calculated: 1115.3057, found: 1115.3072.

**Preparation of Compounds 5a and 6a.** To a solution of compound **2** (620 mg, 0.687 mmol) in 200 mL of PhCl was added DMSO (40 mL), and the mixture was stirred under continuous bubbling of $O_2$ for 10 min. To the solution was then added piperidine (350 mg, 4.12 mmol), and the mixture was stirred under an atmospheric pressure of $O_2$ at 25 °C for 3 h. The mixture was washed with saturated aqueous $NH_4Cl$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The solution was chromatographed on a silica gel column eluting with toluene/$CS_2$ (1:1). Compound **5a** was collected and evaporated as an orange solid (209 mg, 0.192 mmol, 28%). The eluting solvent was changed to toluene/ethyl acetate (500:1), and another red band was eluted to give compound **6a** (314 mg, 0.289 mmol, 42%) as an orange solid. Due to poor solubility, characterization data of **5a** could not be obtained. Characterization data for **6a**: $^1$H NMR (500 MHz, $CS_2$/$CDCl_3$) $\delta$: 7.79 (d, 2H, $J$ = 7.9 Hz), 7.61 (d, 2H, $J$ = 7.9 Hz), 7.11 (dd, 4H, $J1$ = 8.4 Hz, $J2$ = 10.2 Hz), 3.19−3.12 (m, 8H), 2.35 (s, 6H), 1.71−1.68 (m, 8H), 1.52−1.51 (m, 4H). $^{13}$C NMR (125 MHz, $CS_2$/$CDCl_3$) (all signals represent 1C except noted) $\delta$: 156.28, 152.50, 152.34, 150.62, 150.51, 149.67, 149.15 (2C), 148.97, 148.81, 148.77, 147.87, 147.77, 147.62, 147.60, 147.49 (2C), 147.34, 147.16, 147.05, 147.04 (2C), 146.95, 146.93, 146.84, 146.65 (2C), 146.49, 146.30, 146.21, 146.12, 146.08, 145.26, 145.24, 145.23, 145.07, 144.99, 144.88, 144.46, 144.43, 143.92, 143.86, 143.67, 143.61, 143.49, 143.36, 143.30, 143.23, 142.81 (2C), 141.03, 140.53, 139.91, 137.64, 137.04, 136.98, 136.69, 135.93, 129.49 (2C), 129.30 (2C), 128.07 (2C), 127.92 (2C), 76.34, 75.88, 72.81, 71.87, 62.20, 59.05, 52.16 (2C), 51.46 (2C), 27.01 (2C), 26.96 (2C), 24.74, 24.57, 21.10 (2C). ESI-FT-ICR-HRMS-Positive: $C_{84}H_{35}N_2O$ ($M + H^+$) calculated: 1087.2744, found: 1087.2730.

**Preparation of Compound 7.** To a solution of compound **6** (290 mg, 0.260 mmol) in 80 mL of toluene was added $FeCl_3$ (253 mg, 1.56 mmol), and the mixture was stirred at 35 °C for 20 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The solution was chromatographed on a silica gel column eluting with toluene. Compound **7** was collected and evaporated as an orange solid (235 mg, 0.195 mmol, 75%).

*Characterization Data for* ***7****.* $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.88 (s, 2H), 7.59 (s, 2H), 7.22−7.17 (m, 6H), 7.00 (s, 2H), 3.92 (s, 2H), 3.53 (s, 1H), 3.10−3.05 (m, 2H), 2.75 (d, 2H, $J$ = 7.4 Hz), 2.57 (s, 1H), 2.38 (s, 6H), 2.27 (s, 3H), 1.96−1.85 (m, 3H), 1.59−1.18 (m, 7H), 1.03 (s, 3H), 0.84 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 154.54, 154.10, 153.72, 153.54, 152.59, 152.41, 150.38, 148.83 (2C), 148.73, 148.67, 148.61 (2C), 148.57, 148.56, 148.54, 148.50, 148.44, 148.25, 148.23, 147.99, 147.90, 147.57, 147.47, 147.43, 147.35, 147.29, 147.27, 147.25, 146.92, 146.66, 145.47, 145.30, 145.28, 145.04, 144.99, 144.96, 144.79, 144.74 (2C), 144.67, 144.54, 144.38, 144.19, 143.72, 143.64, 143.30, 143.24, 143.21, 142.72, 142.08, 141.69, 141.58, 139.63, 138.34, 137.34, 137.07, 137.04, 137.01, 136.47, 130.54, 129.54 (3C), 129.48 (2C), 129.41 (2C), 128.58 (2C), 127.43 (2C), 84.79, 74.04, 71.07, 63.19, 61.07, 58.12, 51.70, 51.65, 50.33, 50.17, 35.67, 35.58, 35.21, 35.14, 31.18, 30.52, 22.14, 21.98, 21.28, 21.20, 21.13. ESI-FT-ICR-HRMS-Positive: $C_{93}H_{47}N_2O$ ($M + H^+$) calculated 1207.3683, found 1207.3651.

**Preparation of Compound 8a.** *p*-Toluenesulfonic acid monohydrate (140 mg, 0.736 mmol) was added to compound **6** (164 mg, 0.147 mmol) in 80 mL of toluene. The resulting solution was stirred at 80 °C for about 18 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The organic layer was directly chromatographed on a silica gel column eluting with toluene to give some compound **2** and some compound **7** (45 mg, 0.037 mmol, 5%). The eluting solvent was changed to toluene/ethyl acetate (50:1) to remove unknown impurities. Then, the eluent was changed to toluene/ethyl acetate (10:1). The first red band was some byproducts. The second red band was eluted with $CS_2$/toluene/ethyl acetate (1:2:4) to afford fullerenol **8a** (95 mg, 0.084 mmol, 57%). Characterization data for **8a**: ESI-FT-ICR-HRMS-Positive: $C_{86}H_{41}N_2O_2$ ($M + H$)$^+$ calculated 1133.3163, found 1133.3133. (NMR spectra for **8a** could not be obtained due to low solubility)

**Preparation of Compound 8b.** *p*-Toluenesulfonic acid monohydrate (316 mg, 1.66 mmol) and $CH_3OH$ (15 mL) were added to compound **6** (185 mg, 0.166 mmol) in 60 mL of chlorobenzene. The resulting solution was stirred at 80 °C for about 10 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The organic layer was directly chromatographed on a silica gel column eluting with toluene to give some compound **2** and some unreacted compound **6** (84 mg, 0.075 mmol). The eluting solvent was still toluene to remove unknown impurities. Then, the eluent was changed to toluene/ethyl acetate (100:1). The first red band was compound **8b** (80 mg, 0.070 mmol, 42%, based on recovered starting material 77%). Characterization data for **8b**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.78 (d, 2H, $J$ = 7.5 Hz), 7.74 (d, 2H, $J$ = 7.5 Hz), 7.17 (d, 2H, $J$ = 7.4 Hz), 7.12 (d, 2H, $J$ = 7.4 Hz), 5.02 (s, 1H), 3.90 (s, 3H), 3.81 (d, 1H, $J$ = 12.9 Hz), 3.72 (d, 1H, $J$ = 10.2 Hz), 3.66 (d, 1H, $J$ = 10.6 Hz), 3.35 (d, 1H, $J$ = 10.2 Hz), 2.75 (t, 1H, $J$ = 10.6 Hz), 2.67−2.58 (m, 2H), 2.37 (s, 6H), 2.17 (t, 1H, $J$ = 10.5 Hz), 1.78 (s, br, 2H), 1.68 (d, 1H, $J$ = 8.1 Hz), 1.47−1.20 (m, 7H), 0.98 (d, 3H, $J$ = 5.7 Hz), 0.91 (d, 3H, $J$ = 4.4 Hz). $^{13}$C NMR (125 MHz, 50 °C, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 154.19, 153.76, 153.67, 152.86, 152.32, 151.30, 149.22, 148.96 (3C), 148.95, 148.86, 148.81 (2C), 148.77, 148.70, 148.69, 148.63, 148.44, 148.31 (2C), 148.16 (2C), 147.75, 147.67, 147.58, 147.49, 147.47, 147.42, 146.61, 146.49, 145.90, 145.81, 145.37, 145.22, 145.04, 144.92, 144.79 (2C), 144.72, 144.48, 144.22, 144.10, 143.99, 143.64, 143.61, 143.50 (2C), 143.28, 143.23, 143.17, 143.14, 142.90, 142.62, 137.39, 137.36, 136.59, 135.87, 129.62 (2C), 129.48 (2C), 128.50 (2C), 128.30 (2C), 83.56, 82.03, 74.64, 71.67, 60.50, 58.25, 56.37, 51.92, 51.54, 51.38, 50.36, 35.54, 35.43, 31.02, 30.83, 22.05 (2C), 21.24 (2C). ESI-FT-ICR-HRMS-Positive: $C_{87}H_{43}N_2O_2$ ($M + H$)$^+$ calculated 1147.3319, found 1147.3336.

**Preparation of Compound 8c.** *p*-Toluenesulfonic acid monohydrate (546 mg, 2.87 mmol) and $C_2H_5OH$ (15 mL) were added to compound **6** (320 mg, 0.287 mmol) in 100 mL of toluene. The



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resulting solution was stirred at 80 °C for about 25 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The organic layer was directly chromatographed on a silica gel column eluting with toluene to give some compound **2** and some unreacted compound **6** (145 mg, 0.130 mmol). The eluting solvent was still toluene to remove unknown impurities. Then, the eluent was changed to toluene/ethyl acetate (100:1). The first red band was compound **8c** (132 mg, 0.114 mmol, 40%, based on recovered starting material 73%). Characterization data for **8c**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.74 (dd, 4H, $J$ = 8.9 Hz), 7.13 (dd, 4H, $J1$ = 7.3 Hz, $J2$ = 19.5 Hz), 5.13 (s, 1H), 4.25−4.22 (m, 1H), 4.16−4.12 (m, 1H), 3.79 (d, 1H, $J$ = 9.5 Hz), 3.72 (d, 1H, $J$ = 9.9 Hz), 3.62 (d, 1H, $J$ = 9.3 Hz), 3.31 (d, 1H, $J$ = 9.2 Hz), 2.76 (t, 1H, $J$ = 10.4 Hz), 2.67−2.51 (m, 2H), 2.36 (s, 6H), 2.13 (t, 1H, $J$ = 9.8 Hz), 1.77 (s, br, 1H), 1.65 (d, 1H, $J$ = 7.1 Hz), 1.42−1.36 (m, 8H), 1.25−1.20 (m, 3H), 0.98 (d, 3H, $J$ = 4.8 Hz), 0.90 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 153.84, 153.62, 153.29, 152.77, 152.03, 151.14, 148.93, 148.68 (3C), 148.59, 148.53 (2C), 148.51, 148.46, 148.45, 148.36, 148.16, 148.04 (2C), 147.87, 147.62, 147.47, 147.39, 147.34, 147.23, 147.20, 147.15, 146.57, 146.30, 146.11, 145.68, 145.06, 144.87, 144.81, 144.74, 144.59, 144.55, 144.51, 144.26, 144.01, 143.91, 143.82, 143.75, 143.42 (2C), 143.21, 143.07, 142.98 (2C), 142.84, 142.64 (2C), 142.32, 137.17, 137.12, 136.27, 135.61, 129.45 (2C), 129.35 (2C), 128.31 (2C), 128.05 (2C), 83.05, 81.41, 74.37, 71.38, 64.59, 60.23, 57.95, 51.79, 51.43, 51.20, 50.16, 35.33, 35.24 (3C), 30.86, 30.65, 22.02 (2C), 21.21 (2C), 15.90. ESI-FT-ICR-HRMS-Positive: $C_{88}H_{45}N_2O_2$ $(M + H)^+$ calculated 1161.3476, found 1161.3469.

**Preparation of Compound 9.** To a solution of compound **8a** (177 mg, 0.156 mmol) in 50 mL of dry benzene was added DIB (diacetocyliodobenzene) (101 mg, 0.313 mmol). The resulting solution was stirred at 35 °C for 45 min. The organic layer was directly chromatographed on a silica gel column eluting with toluene/ethyl acetate (100:1). The first red band was collected as compound **9** (150 mg, 0.133 mmol, 85%). Characterization data for **9**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.76 (d, 2H, $J$ = 7.5 Hz), 7.60 (d, 2H, $J$ = 7.5 Hz), 7.19 (d, 2H, $J$ = 7.4 Hz), 7.11 (d, 2H, $J$ = 7.4 Hz), 3.79 (d, 1H, $J$ = 10.3 Hz), 3.66 (d, 1H, $J$ = 9.2 Hz), 3.53 (d, 1H, $J$ = 9.6 Hz), 3.18 (d, 1H, $J$ = 9.4 Hz), 2.86 (t, 1H, $J$ = 10.5 Hz), 2.73 (t, 1H, $J$ = 11.0 Hz), 2.48 (t, 1H, $J$ = 10.7 Hz), 2.36 (s, 3H), 2.35(s, 3H), 2.28 (t, 1H, $J$ = 11.1 Hz), 1.81 (m, 2H), 1.65−1.62 (m, 1H), 1.49−1.47 (m, 2H), 1.36−1.31 (m, 3H), 1.23−1.18 (m, 2H), 0.97 (d, 3H, $J$ = 5.6 Hz), 0.90 (d, 3H, $J$ = 5.5 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 201.74, 199.53, 152.77, 152.11, 152.04, 150.54, 149.60, 149.27 (2C), 149.24, 149.16, 149.02, 149.00, 148.98, 148.82, 148.73, 148.64, 148.55, 148.47, 148.39, 148.24 (2C), 147.93, 147.85, 147.54, 147.40, 146.74, 146.71, 146.12, 145.19, 145.04, 144.92 (2C), 144.78, 144.64, 144.54, 143.52 (2C), 143.18, 143.09, 142.92, 142.80, 142.70, 142.67, 142.55, 142.53, 141.60, 140.97 (2C), 140.65, 140.23, 140.04, 139.69, 137.88, 137.73, 135.28, 134.62 (2C), 129.66 (4C), 128.39 (2C), 127.52 (2C), 81.89, 69.45, 66.31, 56.24, 52.57, 52.37, 51.43, 50.16, 35.03, 34.96, 34.91, 34.88, 30.52, 30.35, 21.83, 21.77, 21.16, 21.11. FT-IR (microscope): 3025, 2949, 2921, 2870, 2810, 1743, 1722, 1511, 1461, 1377, 1279, 1261, 1205, 1159, 1107, 1105, 1079, 1021, 974, 887, 845, 818, 757, 729, 695 cm$^{-1}$. ESI-FT-ICR-HRMS-Positive: $C_{86}H_{39}N_2O_2$ $(M + H)^+$ calculated 1131.3006, found 1131.3021.

**Preparation of Compound 10a and 10b.** Boron trifluoride ethyl ether complex (678 mg, 9.97 mmol, 0.6 mL) was added to compound **9** (324 mg, 0.287 mmol) in 80 mL of dry DCM and 15 mL of MeOH. The resulting solution was stirred at 40 °C for about 1.5 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The organic layer was directly chromatographed on a silica gel column eluting with toluene/ethyl acetate (100:1) to remove two black bands which could not be characterized. Then, the eluent was changed to toluene/ethyl acetate (40:1). The first red band was compound **10b** (87 mg, 0.075 mmol, 26%). The second red band was eluted with toluene/ethyl acetate (20:1) to afford compund **10a** (124 mg, 0.107 mmol, 37%).

*Characterization Data for **10a**.* $^1$H NMR (500 MHz, $CDCl_3/CS_2$) $\delta$: 7.74 (d, 2H, $J$ = 7.8 Hz), 7.68 (d, 2H, $J$ = 7.8 Hz), 7.15−7.14 (m, 4H), 4.15 (s, 1H, O*H*), 3.80 (s, 3H, OC$H_3$), 3.73 (s, br, 2H), 3.60 (d, 1H, $J$ = 10.2 Hz), 3.35 (d, 1H, $J$ = 10.3 Hz), 2.67 (dd, 2H, $J1$ = 9.9 Hz, $J2$ = 20.7 Hz), 2.53 (t, 1H, $J$ = 10.5 Hz), 2.37 (s, 3H), 2.36 (s, 3H), 2.19 (t, 1H, $J$ = 10.5 Hz), 1.78 (d, 2H, $J$ = 11.6 Hz), 1.68 (d, 1H, $J$ = 11.4 Hz), 1.59−1.46 (m, 2H), 1.39−1.32 (m, 3H), 1.24−1.22 (m, 1H), 0.98 (d, 3H, $J$ = 6.0 Hz), 0.91 (d, 3H, $J$ = 5.7 Hz). $^{13}$C NMR (125 MHz, $CDCl_3/CS_2$) (all signals represent 1C except noted) $\delta$: 159.56, 159.19, 151.82, 150.19, 149.34, 149.30, 149.17, 149.07, 148.97, 148.92, 148.90, 148.86, 148.67, 148.50 (2C), 148.42, 148.40, 148.25, 148.19, 148.17, 148.13, 147.97, 147.89, 147.42, 147.34, 147.05, 147.03, 146.99, 146.65, 146.39, 146.18, 145.95, 145.49, 144.90, 144.70 (2C), 144.60, 144.16, 144.05, 143.61, 143.50, 143.38, 143.32, 143.23, 142.58, 142.55, 142.48, 141.95, 141.64, 141.36 (2C), 140.99, 140.94, 137.41, 137.34, 136.89, 136.18 (2C), 129.83, 129.59, 127.87, 127.71, 107.73, 106.48, 80.99, 69.30, 65.99, 56.28, 54.33, 52.40, 51.81, 51.19, 50.00, 35.33, 35.28, 35.22 (2C), 30.93, 30.81, 22.08, 22.04, 21.26, 21.22. ESI-FT-ICR-HRMS-Positive: $C_{87}H_{43}N_2O_3$ $(M + H)^+$ calculated 1163.3268, found 1163.3261.

*Characterization Data for **10b**.* $^1$H NMR (500 MHz, $CDCl_3/CS_2/CD_3OD$) $\delta$: 7.74 (d, 2H, $J$ = 6.3 Hz), 7.54 (d, 2H, $J$ = 6.2 Hz), 7.21 (d, 2H, $J$ = 6.0 Hz), 7.12 (d, 2H, $J$ = 5.8 Hz), 3.74 (d, 1H, $J$ = 9.3 Hz), 3.67 (d, 1H, $J$ = 8.9 Hz), 3.49 (s, 3H, OC$H_3$), 3.43 (s, 1H, O*H*), 3.25 (d, 1H, $J$ = 8.6 Hz), 2.71−2.65 (m, 2H), 2.49−2.47 (m, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.94−1.92 (m, 1H), 1.78 (dd, 2H, $J1$ = 12.3 Hz, $J2$ = 21.2 Hz), 1.60 (d, 1H, $J$ = 9.4 Hz), 1.47−1.36 (m, 5H), 1.18−1.14 (m, 3H), 0.98 (s, 3H), 0.86 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3/CS_2/CD_3OD$) (all signals represent 1C except noted) $\delta$: 160.87, 158.57, 151.95, 150.19, 149.95, 149.27, 149.21, 149.17, 148.93, 148.92, 148.77 (2C), 148.56, 148.43, 148.42, 148.30 (2C), 148.24, 148.04, 147.98, 147.94, 147.85, 147.71, 147.22 (2C), 147.20 (2C), 147.07, 146.86, 146.50, 146.46, 146.22, 145.67, 145.30, 144.79, 144.67, 144.57, 144.41, 143.92, 143.36, 143.33, 143.17, 143.09, 143.06, 142.42 (2C), 142.32, 141.81, 141.67, 141.34, 140.82, 140.16, 138.39, 137.37, 137.20, 136.46, 135.98, 133.57, 129.41 (2C), 129.35 (2C), 129.01 (2C), 127.55 (2C), 110.35, 102.94, 80.46, 68.91, 66.38, 56.96, 55.86, 52.12, 51.26, 51.19, 49.75, 35.14, 35.07, 34.78, 34.62, 30.61, 30.49, 21.87, 21.82, 21.13, 21.02. ESI-FT-ICR-HRMS-Positive: $C_{87}H_{43}N_2O_3$ $(M + H)^+$ calculated 1163.3268, found 1163.3271.

**Compound 11.** *p*-Toluenesulfonic acid monohydrate (424 mg, 2.23 mmol) was added to compound **3** (247 mg, 0.223 mmol) in 80 mL of toluene. The resulting solution was stirred at 80 °C for about 5 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The organic layer was directly chromatographed on a silica gel column eluting with toluene to give some compound **17** and some unreacted starting material **3** (32 mg, 0.029 mmol). The eluting solvent was changed to toluene/ethyl acetate (50:1) to remove unknown impurities. Then, the eluent was changed to toluene/ethyl acetate (10:1). The first red band was some byproducts. The second red band was eluted with $CS_2$/toluene/ethyl acetate (1:2:4) to afford fullerenol **11** (168 mg, 0.149 mmol, 67%, based on recovered starting material 80%). Characterization data for **11**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.21 (d, 2H, $J$ = 4.8 Hz), 7.43 (s, 2H), 7.35 (d, 2H, $J$ = 4.7 Hz), 5.93 (s, 2H, br, O*H*), 3.79−3.74 (m, 4H), 3.49 (s, 1H), 3.29 (s, 1H), 2.86 (m, 1H), 2.72−2.64 (m, 3H), 2.39 (m, 1H), 2.28 (m, 1H), 1.76 (d, 4H, $J$ = 20.3 Hz), 1.56 (m, 1H), 1.47 (m, 2H), 1.31−1.29 (m, 7H), 1.16 (m, 1H), 0.92 (s, 6H), 0.88 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 154.96, 153.15, 151.27, 151.05, 150.95, 149.59, 149.28, 148.93, 148.86, 148.74 (3C), 148.63, 148.59, 148.48, 148.45, 148.40, 148.28 (3C), 148.21, 147.83 (2C), 147.68, 147.59, 147.51, 147.32 (3C), 147.26, 147.14, 146.06, 145.92, 145.86, 145.19, 145.10, 144.85, 144.74, 144.67, 144.65, 144.54, 144.51, 144.40, 144.10, 143.43, 143.07, 142.94, 142.74, 142.71, 142.66, 142.42, 142.40, 142.13, 141.36, 139.98, 139.82, 128.83 (2C), 128.53 (2C), 127.63 (2C), 82.07, 76.68, 74.37, 73.86, 71.34, 57.65, 51.50 (2C), 51.33, 51.16, 51.08, 50.12, 35.33,



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35.25, 34.94 (3C), 34.84, 30.68, 30.54, 30.41, 22.04, 21.95, 21.93. ESI-FT-ICR-HRMS-Positive: $C_{84}H_{44}N_3O_2$ $(M + H)^+$ calculated 1126.3428, found 1126.3451.

**Preparation of Compound 12.** *p*-Toluenesulfonic acid monohydrate (196 mg, 1.03 mmol) was added to compound **4** (114 mg, 0.103 mmol) in 80 mL of toluene. The resulting solution was stirred at 80 °C for about 12 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$. The organic layer was directly chromatographed on a silica gel column eluting with toluene to give some compound **17**. Then, the eluent was changed to toluene/ethyl acetate (50:1) to remove unknown impurities. Then, the eluent was changed to toluene/ethyl acetate (10:1).The first red band was some byproduct. The second red band was eluted with $CS_2$/toluene/ethyl acetate (1:2:4) to afford fullerenol **12** (79 mg, 0.070 mmol, 68%). Characterization data for **12**: ESI-FT-ICR-HRMS-Positive: $C_{84}H_{44}N_3O_2$ $(M + H)^+$ calculated 1126.3428, found 1126.3425. (NMR spectra for **12** could not be obtained due to low solubility)

**Preparation of Compound 13.** *p*-Toluenesulfonic acid monohydrate (158 mg, 0.831 mmol) was added to compound **5** (185 mg, 0.166 mmol) in 80 mL of toluene. The resulting solution was stirred at 80 °C for about 3 h. The solution was washed with saturated aqueous $NaHCO_3$ (100 mL) twice. The organic layer was washed further with water three times and dried over anhydrous $Na_2SO_4$, and the organic layer was directly chromatographed on a silica gel column eluting with toluene to give some compound **2**. Then, the eluent was changed to toluene/ethyl acetate (50:1) to remove uncharacterizable products. Then, the eluent was changed to toluene/ethyl acetate (10:1); the first red band was some byproducts. The second red band was eluted with $CS_2$/toluene/ethyl acetate (1:2:4) to afford fullerenol **13** (150 mg, 0.133 mmol, 80%). Characterization data for **13**: $^1$H NMR (500 MHz, $C_6D_4Cl_2/CS_2$) $\delta$: 7.58 (s, 4H), 6.89 (s, 4H), 5.64 (s, br, 2H, O*H*), 3.59 (s, 2H), 3.41 (s, 2H), 2.45 (s, 2H), 2.12 (s, 6H), 1.53 (s, 2H), 1.40 (s, 2H), 1.15 (m, 8H), 0.68 (s, 6H). ESI-FT-ICR-HRMS-Positive: $C_{86}H_{41}N_2O_2$ $(M + H)^+$ calculated 1133.3163, found 1133.3195. ($^{13}$C NMR spectrum for the **13** could not be obtained due to low solubility).

**Preparation of Compound 14.** To a solution of compound **11** (198 mg, 0.176 mmol) in 50 mL of dry benzene was added DIB (114 mg, 0.352 mmol). The resulting solution was stirred at 35 °C for 1 h. The organic layer was directly chromatographed on a silica gel column eluting with toluene/ethyl acetate (100:1). The first red band was collected as compound **14** (170 mg, 0.151 mmol, 86%). Characterization data for **14**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 8.10 (s, 2H), 7.44 (s, 2H), 7.37 (s, 1H), 3.85 (s, 1H), 3.63−3.58 (m, 4H), 3.27 (s, 1H), 2.86−2.73 (m, 3H), 2.53−2.51 (d, 2H, *J* = 9.9 Hz), 2.42 (m, 1H), 1.80−1.72 (m, 5H), 1.55−1.28 (m, 10H), 0.94 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 201.39, 199.90, 153.55, 152.29, 151.99, 151.80, 149.74, 149.63, 149.59, 149.53, 149.43, 149.32, 149.31, 149.27, 149.16, 148.81, 148.80, 148.71 (2C), 148.68, 148.62, 148.52, 148.21, 148.20, 148.13, 147.63, 147.62, 147.38, 146.95, 146.78, 145.27, 145.13, 145.12, 145.11, 144.92, 144.66, 144.60, 144.54, 144.51, 143.71, 143.63, 143.36, 142.98, 142.75, 142.72, 142.68, 142.44, 141.84, 141.81, 141.61, 141.36, 140.93, 140.76, 140.41, 139.16, 136.35, 134.90, 128.95 (2C), 128.56 (2C), 128.18, 82.00, 81.65, 69.49, 56.85, 52.69, 52.57, 52.47, 52.23, 51.52, 50.27, 35.29, 35.28, 35.23, 35.17, 35.15, 35.03, 30.82, 30.56, 30.47, 22.04, 22.00 (2C). FT-IR (microscope): 3059, 3026, 2949, 2921, 2871, 2842, 2810, 2757, 2703, 1744, 1720, 1598, 1495, 1461, 1445, 1377, 1320, 1279, 1258, 1235, 1205, 1160, 1105, 1076, 1032, 975, 940, 907, 845, 734, 698, 649 cm$^{-1}$. ESI-FT-ICR-HRMS-Positive: $C_{84}H_{42}N_3O_2$ $(M + H)^+$ calculated 1124.3272, found 1124.3231.

**Preparation of Compound 15.** To a solution of compound **12** (124 mg, 0.11 mmol) in 50 mL of dry benzene and 5 mL of $CS_2$ was added DIB (71 mg, 0.22 mmol). The resulting solution was stirred at 35 °C for 1 h. The organic layer was directly chromatographed on a silica gel column eluting with toluene/ethyl acetate (100:1). The first red band was collected as compound **15** (110 mg, 0.098 mmol, 89%). Characterization data for **15**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.09 (d, 2H, *J* = 7.5 Hz), 7.44 (dd, 2H, *J*1 = 7.3 Hz, *J*2 = 7.3 Hz), 7.34 (t, 1H, *J* = 7.1 Hz), 3.82 (d, 1H, *J* = 10.5 Hz), 3.69−3.54 (m, 4H), 3.22 (d, 1H, *J* = 9.9 Hz), 2.92−2.87 (m, 1H), 2.80−2.54 (m, 4H), 2.20−2.15 (m, 1H), 1.84−1.67 (m, 5H), 1.50−1.30 (m, 8H), 1.33−1.11 (m, 2H), 0.99 (d, 6H, *J* = 3.2 Hz), 0.90 (d, 3H, *J* = 5.9 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) $\delta$: 202.05, 199.46, 153.96, 152.86, 152.00, 150.47, 149.73, 149.45, 149.44, 149.30, 149.24, 149.05, 148.95 (2C), 148.82, 148.79, 148.65, 148.58, 148.51, 148.42, 148.39, 148.32, 148.05, 147.90, 147.47, 147.45, 147.28, 146.76, 146.61, 144.87, 144.75, 144.64, 144.58, 144.49, 144.23, 144.00, 143.95, 143.76, 143.62, 143.49, 143.31, 143.29, 142.98, 142.87, 142.67, 142.60, 142.57, 142.55, 141.71, 141.03, 141.01, 140.82, 140.64, 140.14, 138.42, 138.13, 134.95, 128.95 (2C), 128.59 (2C), 127.92, 81.80, 69.60, 69.36, 66.39, 52.57, 52.45, 51.75, 50.54, 50.45, 49.92, 35.19, 35.15, 35.09 (2C), 34.94 (2C), 30.77, 30.70, 30.42, 21.89 (2C), 21.80. FT-IR (microscope): 2948, 2921, 2870, 2841, 2809, 1744, 1720, 1495, 1460, 1443, 1377, 1320, 1279, 1257, 1205, 1159, 1106, 1079, 1032, 974, 907, 885, 773, 695, 649 cm$^{-1}$. ESI-FT-ICR-HRMS-Positive: $C_{84}H_{42}N_3O_2$ $(M + H)^+$ calculated 1124.3272, found 1124.3264.

**Preparation of Compound 16.** To a solution of compound **13** (150 mg, 0.133 mmol) in 50 mL of dry benzene was added DIB (85 mg, 0.27 mmol). The resulting solution was stirred at 35 °C for 45 min. The organic layer was directly chromatographed on a silica gel column eluting with toluene. The first red band was collected as compound **16** (125 mg, 0.111 mmol, 83%). Characterization data for **16**: $^1$H NMR (500 MHz, $CDCl_3/CS_2$) $\delta$: 7.57 (d, 4H, *J* = 8 Hz), 7.05 (d, 4H, *J* = 7.9 Hz), 3.53 (d, 4H, *J* = 10.6 Hz), 2.73−2.69 (m, 2H), 2.46−2.41 (m, 2H), 2.34 (s, 6H), 1.72 (d, 2H, *J* = 12.5 Hz), 1.66 (d, 2H, *J* = 12.6 Hz), 1.40−1.38 (m, 2H), 1.30−1.28 (m, 4H), 0.94 (s, 3H), 0.93 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3/CS_2$) $\delta$: 152.46, 152.02, 151.34, 149.58, 149.52, 149.37, 149.23, 148.76, 148.71, 148.59, 148.49, 148.18, 147.63, 147.25, 146.99, 145.29, 145.00, 144.82, 144.80, 144.54, 143.41, 142.99, 142.63, 142.60, 141.76, 141.44, 140.85, 137.70, 136.21, 135.47, 129.65 (4C), 128.26 (4C), 81.86 (2C), 56.37 (2C), 52.47 (2C), 52.16 (2C), 35.31 (2C), 35.17 (2C), 30.68 (2C), 22.12 (2C), 21.32 (2C). $^1$H NMR (500 MHz, $C_6D_4Cl_2$) $\delta$: 7.89 (d, 3H, *J* = 6.4 Hz), 7.35−7.34 (m, 5H), 4.03 (d, 2H, *J* = 11.0 Hz), 3.80 (d, 2H, *J* = 10.4 Hz), 2.96 (t, 2H, *J* = 10.5 Hz), 2.82(t, 2H, *J* = 10.6 Hz), 2.44−2.41 (m, 6H), 1.88−1.86 (m, 4H), 1.61−1.59 (m, 6H), 1.09 (s, 6H). $^{13}$C NMR (125 MHz, $C_6D_4Cl_2$) (some signals were hidden in solvent signals) $\delta$: 197.78, 197.73, 151.37, 150.98, 149.82, 148.16, 147.99, 147.39, 147.34, 147.17, 147.14, 146.80, 146.31, 145.62, 143.99, 143.78, 143.70, 143.50, 143.21, 142.18, 141.55, 141.21, 141.19, 140.33, 140.11, 139.45, 136.59, 134.82, 134.40, 80.77, 55.45, 51.33 (2C), 50.78 (2C), 34.09 (2C), 34.00 (2C), 29.38 (2C), 20.62 (2C), 19.78 (2C)). FT-IR (microscope): 2950, 2923, 2852, 1743, 1511, 1463, 1261, 1107, 1072, 1022, 975, 810, 756 cm$^{-1}$. ESI-FT-ICR-HRMS-Positive: $C_{86}H_{39}N_2O_2$ $(M + H)^+$ calculated 1131.3006, found 1131.3012.

**Preparation of Compound 17.** To a solution of compound **3** (124 mg, 0.112 mmol) in 80 mL of $CH_2Cl_2$ were added $PPh_3$ (253 mg, 0.448 mmol) and $I_2$ (455 mg, 1.79 mmol), and the resulting solution was stirred at room temperature for 1 day. Then, the reaction was treated with excess aqueous $Na_2S_2O_3$ (100 mL) twice. The organic layer was washed further with aqueous $NH_4Cl$ (100 mL) twice and dried over anhydrous $Na_2SO_4$, and the solvent was removed under vacuum. The residue was chromatographed on silica gel eluting with $CS_2$. A trace amount of the impurities was eluted out first. Then, the eluent was changed to toluene/$CS_2$ (1:1). The first band was collected and evaporated to give compound **17** (74 mg, 0.083 mmol, 74%, based on recovered starting material 88%) as a black solid. The eluting solvent was changed to toluene to give unreacted compound **3** (20 mg, 0.018 mmol) as an orange solid. Characterization data for **17**: $^1$H NMR (400 MHz, $CDCl_3/CS_2$) $\delta$: 8.42 (d, 2H, *J* = 7.4 Hz), 7.60 (dd, 2H, *J*1 = 7.6 Hz, *J*2 = 7.6 Hz), 7.47 (t, 1H, *J* = 7.4 Hz), 4.07 (dd, 2H, *J*1 = 10.3 Hz, *J*2 = 22.9 Hz), 3.14−3.06 (m, 2H), 1.89 (s, br, 2H), 1.60−1.52 (m, 3H), 1.08 (d, 3H, *J* = 5.2 Hz). $^{13}$C NMR (125 MHz, $CDCl_3/CS_2$) (all signals represent 1C except noted) $\delta$: 155.30, 153.05, 152.44, 149.74, 148.95, 148.69 (2C), 148.45, 147.78, 147.31, 147.25 (2C), 147.17 (3C), 147.15, 146.90, 146.80, 145.79, 145.72, 145.61, 145.55, 145.28, 144.79, 144.67, 144.63, 144.46, 144.42, 144.39 (2C),



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144.25, 144.23, 144.13, 144.02, 143.92, 143.79, 143.64, 143.53, 143.49, 143.40, 143.37, 143.36, 143.29, 143.02 (2C), 142.94, 142.87, 142.68, 142.68, 142.60, 142.50, 142.29, 141.11, 140.93, 140.85, 140.17, 139.17, 138.28, 138.19, 129.42 (2C), 128.44 (2C), 128.29, 74.49, 62.02, 50.69, 49.77, 35.50, 35.44, 31.48, 22.36. ESI-FT-ICR-HRMS-Positive: $C_{72}H_{18}N$ $(M + H)^+$ calculated 896.1450, found 896.1434.

**Reaction of 5 with $PPh_3/I_2$.** To a solution of compound **5** (100 mg, 0.0898 mmol) in 60 mL of $CHCl_3$ were added $PPh_3$ (94 mg, 0.36 mmol) and $I_2$ (365 mg, 1.44 mmol), and the resulting solution was stirred at room temperature for 1 day. Then, the reaction was treated with excess aqueous $Na_2S_2O_3$ (100 mL) twice. The organic layer was washed further with aqueous $NH_4Cl$ (100 mL) twice and dried over anhydrous $Na_2SO_4$, and the solvent was removed under vacuum. The residue was chromatographed on silica gel eluting with $CS_2$. The first band was collected and evaporated to give compound **2** (22 mg, 0.024 mmol, 27%, based on recovered starting material 64%) as a black solid. The eluting solvent was changed to toluene to give unreacted compound **5** (58 mg, 0.052 mmol) as an orange solid.

## ■ ASSOCIATED CONTENT

### Supporting Information

Selected spectroscopic data for all new compounds and crystallographic data for **4**, including CIF file. 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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