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Synthesis of 18-Membered Open-Cage Fullerenes through Controlled Stepwise Fullerene Skeleton Bond Cleavage Processes and Substituent-Mediated Tuning of the Redox Potential of Open-Cage Fullerenes

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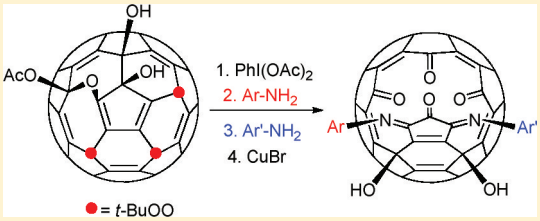
Supporting Information

ABSTRACT: Oxidation of the fullerenediol $C_{60}(OH)_2(O)(OAc)(OOtBu)_3$ with $PhI(OAc)_2$ yields the open-cage fullerene derivative $C_{60}(O)_2(O)(OAc)(OOtBu)_3$ **2** with an 11-membered orifice. Compound **2** reacts with aniline to form a new open-cage derivative with a 14-membered orifice, which yields an 18-membered open-cage fullerene derivative upon addition of another molecule of aniline. Two different types of aniline derivatives with either electron-donating or electron-withdrawing substituents can be added sequentially, affording an unsymmetrical moiety in the open-cage structure. Reduction potentials of the 18-membered open-cage fullerene derivatives can be fine-tuned by changing the substituents on the aniline. The results provide new insights about the mechanism of open-cage reactions of fullerene-mixed peroxide.



INTRODUCTION

Several methods have been reported for the synthesis of open-cage fullerene derivatives.[1] Most of the known methods employ singlet oxygen oxidation as a key step, which undergoes a 2 + 2 cycloaddition to form a dioxetane intermediate followed by ring-opening rearrangement to form fullerenediones. This process is well-established and successfully applied to the synthesis of a number of open-cage fullerene derivatives.[2−7] Opening of the fullerene cage results in remarkable change of the physical properties, such as their redox potentials. Recently, Murata and co-workers found that open-cage fullerenes can improve the open-circuit voltage of fullerene-based solar cells.[8] Fine-tuning the elctronic property of fullerene derivatives is a promising approach in creating suitable acceptors for efficient solar cells.[9]

We have reported a fullerene-mixed peroxide procedure for the preparation of open-cage fullerenes.[10] This method can generate orifices large enough for a water molecule to go into the cavity of the C_{60} cage.[10c,e,g] Unlike the well-studied singlet oxygen reaction, the mechanism of this procedure is quite complex and not well understood. To further explore fullerene peroxide chemistry, we have been investigating details of the reactions involving fullerene-mixed peroxides. Here, we report the isolation of a key intermediate in the cage-opening process and its application in tuning the redox potentials of open-cage fullerenes.

RESULTS AND DISCUSSION

Preparation of Open-Cage Fullerenes. Fullerendiol **1** was prepared from C_{60} in five steps.[10e] In our previous study, we found that compound **1** could be oxidized by DIB (diacetoxyliodobenzene) into the diketone derivative **2** with an 11-membered orifice. We also reported that compound **2** reacted with excess anilines efficiently to form compound **3** with an 18-membered orifice, which was characterized by single crystal X-ray analysis (Scheme 1).[10e] Careful examination of the reaction indicates that reactive intermediates could be detected in the aniline reaction. To isolate the intermediate, 2 equiv of aniline was added slowly into a solution of compound **2** instead of adding excess aniline (15 equiv) in one portion as in the original procedure. Progress of the reaction was monitored by TLC. Quenching of the reaction by flash column chromatography afforded compound **4** as a relatively stable intermediate. Under the same conditions as originally reported for the formation of **3** from **2**, compound **4** also gave **3** in about the same yield; i.e., addition of aniline to isolated compound **4**, followed by reduction with CuBr, afforded compound **3** (Scheme 1).

The HRMS of compound **4** from the 3,4,5-trimethoxy aniline reaction is in agreement with the depicted structure. Its

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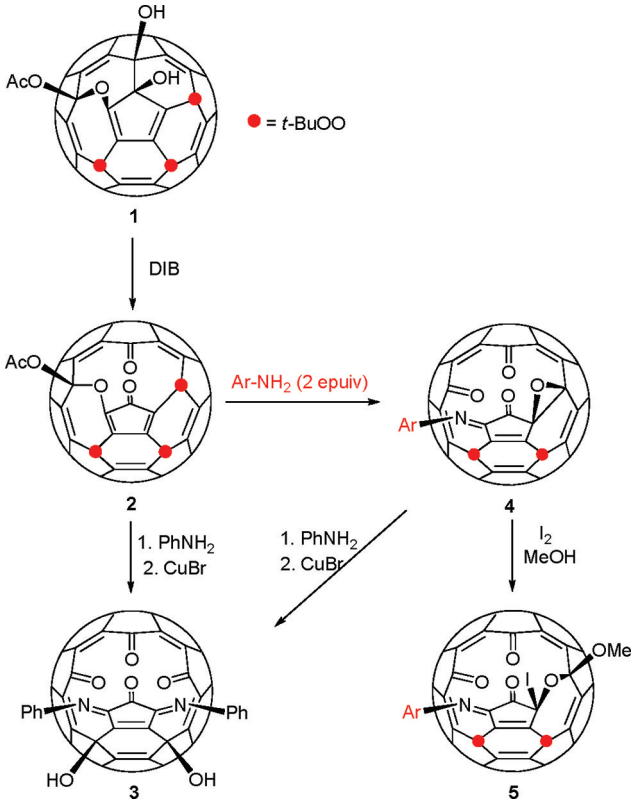
Scheme 1. Preparation of Compounds 4 and 5



^{1}H NMR spectrum also agrees with the structure, which showed only two OO*t*Bu groups and one 3,4,5-trimethoxy aniline group. Compound **4** decomposed into complex mixtures when we tried to measure its ^{13}C NMR spectrum overnight. These characterization data can not assign the structure of **4** conclusively, as many isomers are possible. To obtain more structural information about compound **4**, we treated it with iodine and methanol. Compound **5** was obtained as a stable product. The C−C bond of epoxide moiety in **4** was cleaved, and the two carbons were converted into a ketal and an iodoketal group, respectively. Spectroscopic data are in agreement with the structure as depicted in Scheme 1. The ^{13}C NMR spectrum of **5** showed two characteristic signals for the ketal (112.9 ppm) and iodoketal (58.2 ppm) carbons. The three carbonyl carbons appear at 186.4, 184.6, and 180.1 ppm. Single crystal X-ray analysis of **5** (Figure 1) further confirmed its structure. The seven-membered ring containing the bridging ketal oxygen atom adopts an envelope conformation with the iodoketal carbon projecting out of the plane. The pentagon containing the carbonyl and the imino groups is slightly twisted as a result of the presence of the iodoketal carbon.

Further treatment of **4** with aniline followed by reduction with CuBr could give compound **3** as mentioned above. Following the same procedure compounds **7a** and **7b** were prepared by using *p*-methoxyl aniline and ethyl *p*-aminobenzoate, respectively. Another different aniline could also react with **4** to give compound **6** (Scheme 2). Reduction of **6** with CuBr converted the remaining *t*-butylperoxo group into a hydroxyl group and afforded compounds **7c**−**i** as unsymmetrical analogues of compound **3**. By using such a procedure, we have prepared various aniline adducts containing both electron-donating and -withdrawing groups.

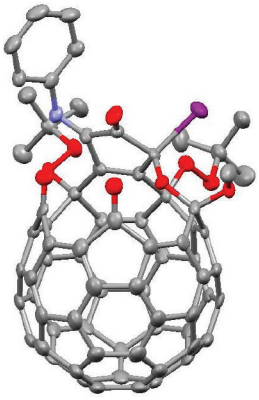
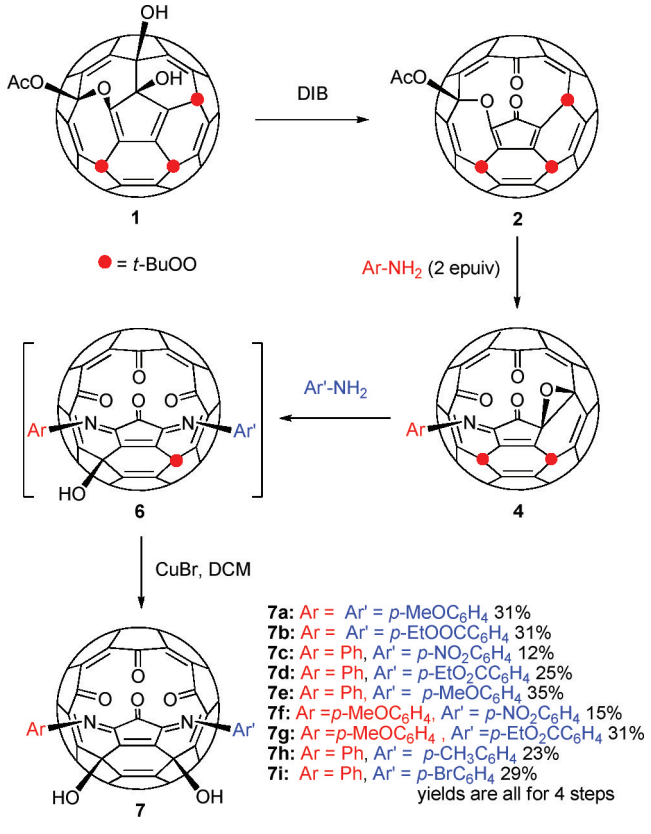


Figure 1. Single-crystal X-ray structure of **5**. Ellipsoids were drawn at the 50% level; for clarity, hydrogen atoms were not shown. Color key: gray, carbon; red, oxygen; blue, nitrogen; purple, iodine.

Scheme 2. Preparation of Compound 7



Spectroscopic data of compounds **7c**−**i** are comparable to the symmetric compound **3**. For example, compounds **7c**−**i** showed three carbonyl carbons in the range of 183−185 ppm. Another signal at 175 ppm could be assigned to the carbonyl with two adjacent imino groups on the lifted pentagon. These chemical shifts are almost the same as those of compound **3**, which appear at 175.3, 182.7, and 184.2 ppm. The signal at 184.2 ppm is twice the intensity of 182.7 ppm, reflecting the C_s symmetry of **3**. The carbonyl stretching frequency appears at around 1744 cm^{-1} for both the symmetric compounds **3**, **7a**, and **7b** and the unsymmetric compounds **7c**−**i**.

Mechanism Consideration. The aniline-induced hole-enlargement process was an unexpected reaction. In our previous report, a mechanism was proposed to involve a

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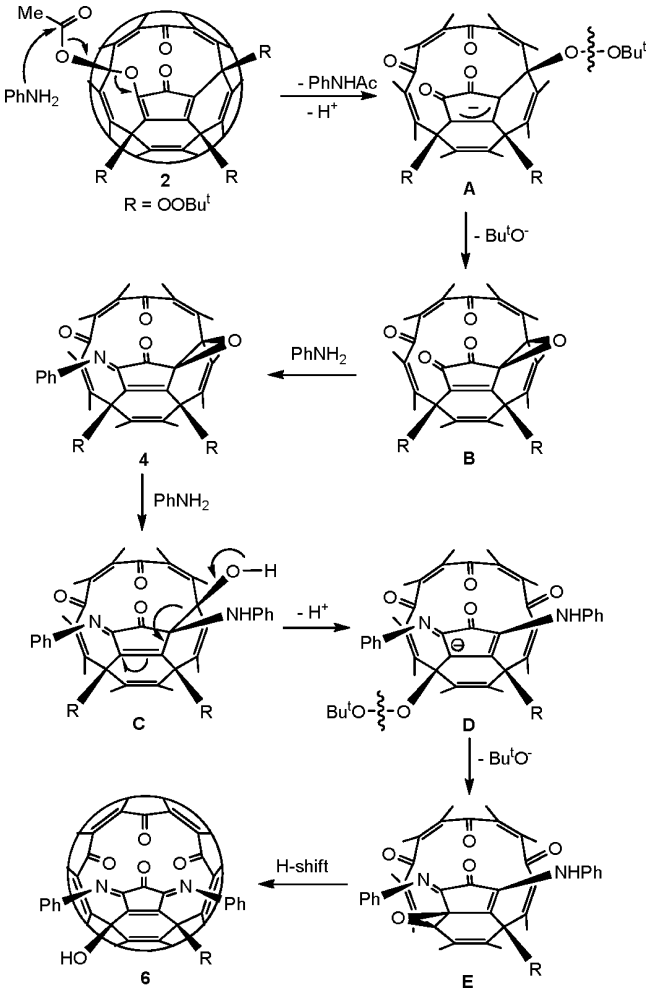
cascade sequence including a deketalization, an S_N2' epoxide opening reaction, and a formal 3,3-σ rearrangement.[10e] At the time, none of the intermediates were isolated or detected. On the basis of the present results, a revised mechanism is proposed for the reaction between aniline and compound **2** as shown in Scheme 3. The first step is still the aminolysis of the

Scheme 3. Revised Mechanism for Formation of 6



hemiketal ester to form the allyl anion intermediate **A** with four carbonyl groups. Release of ring string should be responsible for the mild C–C bond cleavage in the step from **C** to **D**. The conversion of **4** to **5** in the presence of I_2/MeOH also involves the cleavage of the same fullerene C–C bond. The hydroxyl group in compound **6** forms a strong H-bond with the imino nitrogen atom, which may partially explain its facile formation from the *t*-butylperoxo group in the step from **E** to **6**.

In the proposed mechanism, addition of aniline to **4** occurred to the α-position of the α,β-epoxyketone moiety. In contrast, in Scheme 1, addition of methanol to **4** occurred to the β-position of the α,β-epoxyketone moiety. The difference may be explained by the following: In the aniline addition, single electron transfer from aniline to **4** may be involved to form a radical ion pair precursor for intermediate **C**. It is well-known that the addition of amines to fullerenes involves single electron transfer processes.[11] With the negative charge present, the epoxy moiety in the radical ion pair precursor prefers to cleave at the α-position. In the reaction of **4** with I_2/MeOH, an iodonium-induced opening of the epoxy moiety is probably involved as the first step.[12] In this case, cleavage at the β-position to form a cation intermediate with the positive charge further away from the carbonyl is more favorable. Addition of methanol to the cation leads to the observed β-regioselectivity in compound **5**. This process is reminecent of the ring-opening addition reaction of cyclopropane.

UV Absorption Spectra and Differential Pulse Voltammograms. To study the substituent effect of the aniline on the fullerene cage, we have measured the UV–vis spectra and the redox properties of compounds **3** and **7**. The UV spectra of compounds **7** are all very similar with two major absorption bands at 252 and 305 nm. So, presence of electron-donating or -withdrawing groups on the aniline does not affect the absorption properties significantly.

Unlike the UV–vis spectra, differential pulse voltammetry (DPV) showed remarkable differences for compounds **7a–g** as shown in Figure 2 and Table 1. Six peaks were observed for

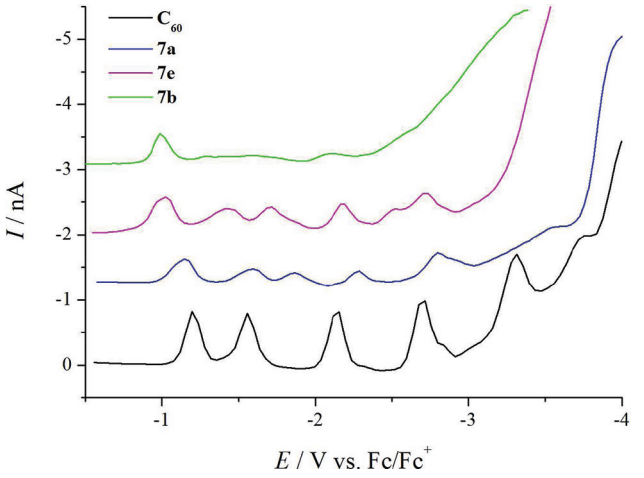


Figure 2. DPVs of C_{60}, **7a**, **7b**, **7e** in toluene.

Table 1. Redox Potentials (E_{red}/V vs Fc^+/Fc) of C_{60} and 7[a]

compd	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^5_{red}	E^6_{red}
C_{60}	−1.200	−1.562	−2.164	−2.724	−3.322	−3.745
3	−1.022	−1.479	−1.739	−2.167	−2.759	−3.505
7a	−1.149	−1.596	−1.874	−2.292	−2.801	−3.563
7b	−0.994	−1.287				
7c	−1.059	−1.357	−1.715	−2.128	−2.349	
7d	−1.025	−1.421	−1.715	−2.200	−2.506	−2.737
7e	−1.031	−1.455	−1.846	−2.203	−2.768	−3.563
7f	−1.060	−1.335	−1.629	−2.107	−2.335	−2.797
7g	−1.033	−1.418	−1.723	−2.143		

[a]Conditions for DPV measurements: toluene solution containing C_{60} or **7** (2.0×10^{-4} mol/L) and 0.05 mol/L of tetrahexylammonium bis (trifluoromethylsulfonyl) imide (THA-Tf_2N) as supporting electrolyte, ferrocene (Fc) as an internal standard, a platinum microelectrode (diameter 25 μm) as the working electrode, a platinum wire and a Ag wire as the counter and quasi-reference electrodes, respectively. Scan rate: 20 mV s^{-1}.

most of the compounds. Aniline derivatives containing a NO_2 or COOEt group exhibit more complicated behavior due to the reduction of these groups themselves. Comparison of the reduction potentials indicates that substituents on the phenyl ring have a remarkable effect on the reduction potential of these open-cage fullerenes. Compared to the parent C_{60}, all the

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open-cage fullerenes have a stronger tendency to obtain electrons, probably due to the presence of the carbonyl groups on the rim of the orifice. As expected, values of reduction potentials for **7a** with two strong electron-donating *p*-methoxyphenyl groups are the lowest, whereas those of **7b** with two electron-withdrawing *p*-ethoxycarbonylphenyl groups are the highest; i.e., the presence of electron-withdrawing groups enhances the oxidation ability of the open-cage fullerenes, and electron donating groups have the opposite effect. In the case of compounds **7c** and **7d** with just one electron-withdrawing group, the effect is relatively weak, and only potentials of multielectron reductions were slightly enhanced. The first reduction potential can be fine-tuned in the range of −1.15 to −0.99 V by changing substitutes on the phenyl ring. This should be helpful in the optimization of organic solar cells, in which a good match between the energy level of the HOMO of the donor and the energy level of the LUMO of the acceptor is a key factor.[9]

CONCLUSION

A key intermediate has been isolated for the cage-opening reaction mediated by fullerene-mixed peroxide. Further reactions of the intermediate led to a revised mechanism for the reaction. On the basis of the new findings, a one-pot cascade procedure has been developed to prepare open-cage fullerene derivatives with two different aniline groups containing either electron-donating or -withdrawing substituents. UV−vis absorption spectra show that substituents on the phenyl ring have little effect on the absorption bands. Reduction potentials of the open-caged fullerene derivatives are positively shifted compared with C_{60}, and the value of reduction potential could be adjusted by the substituent on the phenyl group.

EXPERIMENTAL SECTION

All the reagents were used as received. Dichloromethane was distilled over phosphorus pentaoxide. Benzene and toluene were distilled over sodium. Other solvents were used as received. Compound **1** was prepared according to reported procedure.[10e] The reactions were carried out in air. NMR spectra were recorded at room temperature (298 K). Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESI-HRMS spectra were recorded with $CHCl_3$/CH_3OH or $CDCl_3$/CH_3OH as the solvent; positive-mode spectra were recorded, unless otherwise noted. FTIR spectra were recorded in the microscope mode. Chromatographic purifications were carried out with silica gel of mesh 200−300. **Caution**: Peroxides are potentially explosive compounds; care must be taken to avoid possible explosion.

Electrochemical Measurements. A conventional three-electrode system is used, with a platinum ultramicroelectrode (Pt UME, diameter: 25 μm) as the working electrode and a platinum wire and a Ag wire as the counter and quasi-reference electrodes, respectively. Ferrocene served as an internal standard. Before being used, the Pt UME was polished using alumina powder with 0.05 μm and then sonicated in ethanol and water for 3 min, respectively. DPV measurements were carried out in toluene solution containing 2.0×10^{-4} mol/L of C_{60} or **7** and 0.05 mol/L THA-Tf_2N as supporting electrolyte (scan rate: 20 mVs^{-1}). All the solutions were purged with argon for at least 25 min to remove oxygen prior to experiments. All experiments were carried out at room temperature (22 ± 2 °C).

Compound ***4***. To the solution of compound **1** (102.5 mg, 0.094 mmol) in benzene (28 mL) was added iodobenzene diacetate (55.8 mg, 0.168 mmol) at 20 °C. Progress of the reaction was monitored by TLC. After **1** was completely consumed, 3,4,5-*tri*-methoxyaniline (34.2 mg, 0.188 mmol) dissolved in benzene was slowly dropped into the reaction mixture. The desired product **4** reached its maximum yield in about 15 min. The reaction mixture was rapidly chromatographed on a silica gel column eluting with toluene/ethyl acetate (v/v) = 20:1. The red band was collected and evaporated to give **4** (93 mg, 0.081 mmol, 87%).

Spectral data: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.68 (s, 2H), 4.06 (s, 6H), 3.89 (s, 3H), 1.48 (s, 9H), 1.33 (s, 9H); ESI-HRMS $C_{77}H_{30}NO_{11}$ ($M + H^+$) calcd 1144.1813, found 1144.1804.

Compound ***5***. To the solution of compound **1** (77 mg, 0.070 mmol) in benzene (25 mL) was added iodobenzene diacetate (39.6 mg, 0.119 mmol) at 30 °C. Progress of the reaction was monitored by TLC. After **1** was completely consumed, aniline (13.0 mg, 0.140 mmol) dissolved in benzene was slowly dropped into the reaction mixture. After the desired product **4** reached its maximum yield, 0.5 mL of methanol and 1.0 g of iodine were added into the reaction mixture. After compound **5** reached its maximum yield as indicated by TLC (within 5 min), the reaction mixture was chromatographed on a silica gel column eluting with toluene/ethyl acetate (v/v) = 100:1. The first red band was collected and evaporated to give **5** (38.4 mg, 0.032 mmol, 45%).

Spectral data: ^1H NMR ($CDCl_3$, CS_2, 400 MHz) δ 7.47−7.41 (4H), 7.26−7.25 (1H), 3.87 (s, 3H), 1.30 (s, 9H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$, CS_2, 100 MHz, all signals represent 1C except noted) δ 186.41, 184.60, 180.10, 151.21, 149.80, 149.70, 149.63 (2C), 149.53, 149.31, 149.19, 149.14, 149.10, 149.07, 148.81, 148.54, 148.10, 148.06, 148.01, 147.79 (2C), 147.76, 147.58, 147.52, 146.87, 146.61, 146.48, 145.51, 145.27, 144.99, 144.85, 144.63, 144.43, 144.22, 144.09, 143.96, 143.49, 143.31, 143.19, 143.17, 142.84, 142.32, 141.79, 141.69, 141.41 (2C), 141.21, 140.82, 140.77, 140.52, 139.41, 138.57, 138.54, 135.76, 134.66, 133.28, 131.14, 128.46 (2C), 125.58, 120.46 (2C), 112.96, 86.99, 82.36, 81.76, 81.67, 58.17, 54.16, 26.89 (3C), 26.63 (3C); FT-IR (microscope) 3362, 2923, 2852, 1748, 1591, 1469, 1364, 1192, 1152, 1119, 1059, 1006, 874, 748, 692 cm^{-1}; ESI-HRMS $C_{75}H_{27}INO_9$ ($M + H^+$) calcd 1212.0725, found 1212.0750. Crystal of **5** suitable for X-ray diffraction was obtained by slow evaporation in toluene. Crystal data: triclinic, space group *P*1. Unit cell dimensions: a = 11.5500 (10) Å, α = 95.160 (10)°, b = 12.4940 (11) Å, β = 104.400 (10)°, c = 19.908 (3) Å, γ = 112.710 (8)°, volume = 2510.6 (5) $Å^3$. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0707, wR_2 = 0.1392. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-837676.

Compounds ***7a, 7b***. These compounds were prepared according to reported procedure.[10e]

Compound ***7a***. Spectral data: ^1H NMR ($CDCl_3$, CS_2, 400 MHz) δ 8.00 (s, 2H), 7.69 (d, J = 8.8 Hz, 4H), 6.97 (d, J = 8.8 Hz, 4H), 3.87 (s, 6H); ^{13}C NMR ($CDCl_3$, CS_2, 125 MHz, all signals represent 2C except noted) δ 184.77, 183.57 (1C), 175.32 (1C), 159.90, 154.27, 149.69 (1C), 149.54 (1C), 149.49, 149.34, 149.31, 149.23, 148.17 (4C), 148.07, 147.83, 147.00, 146.33, 145.86, 145.82, 145.37, 144.83, 144.79, 144.34, 144.29, 143.34 (4C), 143.17, 142.52, 140.48, 138.46, 136.35, 136.20, 126.77, 126.39 (4C), 113.61 (4C), 77.88, 55.42; FT-IR (microscope) 3237, 2922, 2851, 1743, 1501, 1301, 1252, 1167, 1110, 1036, 1016, 833, 737, 729 cm^{-1}; ESI-HRMS $C_{74}H_{17}N_2O_8$ ($M + H^+$) calcd 1061.0979, found 1061.0981.

Compound ***7b***. Spectral data: ^1H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, J = 8.3 Hz, 4H), 7.54 (d, J = 8.3 Hz, 4H), 7.24 (s, 2H), 4.40 (q, J = 7.0 Hz, 4H), 1.41 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, all signals represent 2C except noted) δ 184.95, 183.74 (1C), 175.95 (1C), 166.06, 155.79, 149.85 (1C), 149.62, 149.59 (1C), 149.47, 149.43 (6C), 148.42, 148.29, 148.24, 148.12, 147.97, 147.16, 146.55, 145.47, 145.44, 144.70, 144.36 (4C), 144.29, 143.52 (4C), 142.79, 142.56, 140.72, 136.96, 135.67, 130.25 (4C), 128.79, 126.81, 121.33 (4C), 77.67, 61.00, 14.38; FT-IR (microscope) 3323, 2924, 2852, 1743, 1716, 1599, 1237, 1169, 1108, 1017, 872, 770, 737, 700 cm^{-1}; ESI-HRMS $C_{78}H_{21}N_2O_{10}$ ($M + H^+$) calcd 1145.1190, found 1145.1182.

General Procedure for Preparation of Compounds 7c−i. Iodobenzene diacetate (42.1 mg, 0.131 mmol) was added to the solution of compound **1** (77.3 mg, 0.070 mmol) in benzene (27 mL) at 20 °C. Progress of the reaction was monitored by TLC. After **1** was completely consumed, aniline (13.2 mg, 0.141 mmol) dissolved in benzene was slowly dropped into the reaction mixture. After comound

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4 reached its maximum yield, 4-methoxyaniline (24.6 mg, 0.2 mmol) was added. After the desired compound **6e** reached its maximum yield as indicated by TLC (about 15 min), the solution was directly chromatographed on a silica gel column eluting with toluene. The first brown band was collected and evaporated to give crude product **6e**. CuBr (10.0 mg, 0.140 mmol, 2 equiv of **1**) was added to a solution of **6e** in CH_2Cl_2 (10 mL) at r.t. When the desired product **7e** reached its maximum yield (about 3 h), the solution was directly chromatographed on a silica gel column and eluted with toluene. The first red band was collected and evaporated to give **7e** (27.5 mg). The overall yield from **1** to **7e** was 35% (Table 2).

Table 2. Yields of Compounds 7c–i

entry	**1** (mg)	product	Ar	Ar′	mg, (yield %)
1	116	**7c**	Ph	*p*-$NO_2C_6H_4$	10.9 (12)
2	86.8	**7d**	Ph	*p*-$EtO_2CC_6H_4$	21 (25)
3	77.3	**7e**	Ph	*p*-$MeOC_6H_4$	27.5 (35)
4	60	**7f**	*p*-$MeOC_6H_4$	*p*-$NO_2C_6H_4$	8.3 (15)
5	68	**7g**	*p*-$MeOC_6H_4$	*p*-$EtO_2CC_6H_4$	21.1 (31)
6	77.8	**7h**	Ph	*p*-$CH_3C_6H_4$	16.8 (23)
7	81.3	**7i**	Ph	*p*-BrC_6H_4	23.1 (29)

Compound ***6e***. Spectral data: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (s, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.45–7.41 (2H), 7.37 (d, J = 8.3 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 1.29 (s, 9H); ESI-HRMS $C_{77}H_{23}N_2O_8$ (M + H^+) calcd 1103.1449, found 1103.1442.

Compound ***7c***. Spectral data: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.33 (d, J = 8.7 Hz, 2H), 7.64 (s, 1H), 7.61–7.57 (4H), 7.51–7.47 (2H), 7.34 (t, J = 7.3 Hz, 1H), 6.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except noted) δ 185.22, 184.86, 183.84, 175.89, 156.15, 154.95, 151.93, 150.62, 149.81, 149.52, 149.43 (2C), 149.40 (4C), 148.25, 148.22, 148.18 (3C), 148.13, 148.08, 148.06, 147.92 (2C), 147.12, 147.09, 146.48, 146.46, 145.99, 145.62, 145.44, 145.42, 145.36 (2C), 145.09, 144.64, 144.62, 144.37, 144.27 (2C), 144.23, 144.16, 144.10, 143.49 (4C), 142.74 (2C), 142.62, 142.32, 140.68, 140.65, 136.89, 136.75, 135.72, 135.56, 128.62 (2C), 128.18, 126.77, 126.71, 124.52 (2C), 122.87 (2C), 121.32 (2C), 77.79, 77.45; FT-IR (microscope) 3514, 3315, 2924, 2850, 1742, 1587, 1514, 1340, 1108, 1037, 1015, 909, 750, 736, 693 cm^{-1}; ESI-HRMS $C_{72}H_{12}N_3O_8$ (M + H^+) calcd 1046.0619, found 1046.0598.

Compound ***7d***. Spectral data: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, J = 8.3 Hz, 2H), 7.68 (s, 1H), 7.59 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.49–7.45 (2H), 7.32 (t, J = 6.1 Hz, 1H), 7.28 (s, 1H), 4.40 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, all signals represent 1C except noted) δ 184.97, 184.87, 183.81, 175.86, 166.14, 155.87, 155.24, 149.85 (2C), 149.83, 149.59, 149.50, 149.47, 149.43 (4C), 149.40 (2C), 149.16, 148.28 (2C), 148.24 (2C), 148.13 (2C), 147.95 (2C), 147.14, 147.12, 146.73, 146.52 (2C), 145.55, 145.52, 145.47 (2C), 145.27, 144.74 (2C), 144.57, 144.44, 144.34 (2C), 144.33 (2C), 143.49 (3C), 142.79, 142.75 (2C), 142.67, 140.68, 140.66, 136.89, 136.83, 135.85, 135.75, 130.24 (2C), 128.59 (2C), 128.52, 127.85, 126.81, 126.77, 122.79 (2C), 121.23 (2C), 77.85, 77.66, 60.98, 14.40; FT-IR (microscope) 3517, 3308, 2920, 2850, 1742, 1714, 1599, 1495, 1274, 1109, 1036, 1016, 870, 762, 752, 693 cm^{-1}; ESI-HRMS $C_{75}H_{17}N_2O_8$ (M + H^+) calcd 1073.0979, found 1073.0958.

Compound ***7e***. Spectral data: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (s, 1H), 7.75 (s, 1H), 7.74 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 7.4 Hz, 2H), 7.50–7.47 (2H), 7.31 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except noted) δ 184.95 (2C), 183.88, 175.65, 160.26, 155.59, 154.04, 149.80, 149.61, 149.58, 149.51, 149.44, 149.43, 149.42, 149.40, 149.36, 149.34, 148.36, 148.27 (2C), 148.25 (2C), 148.15 (2C), 147.93 (2C), 147.10, 147.09, 146.47, 146.42, 145.81, 145.71, 145.61, 145.46, 145.45, 145.05, 144.87, 144.80, 144.74, 144.71, 144.38, 144.35 (2C), 144.31, 143.46 (2C), 143.44 (2C), 143.06, 143.06, 142.67, 142.65, 140.61, 140.56, 138.51, 136.64, 136.54, 136.20, 136.03, 128.51 (2C), 127.19, 126.85, 126.80, 126.74 (2C), 122.38 (2C), 113.79 (2C), 78.00, 77.81, 55.59; FT-IR (microscope) 3279, 2925, 2851, 1743, 1561, 1501, 1254, 1109, 1036, 1015, 871, 737 cm^{-1}; ESI-HRMS $C_{73}H_{15}N_2O_7$ (M + H^+) calcd 1031.0874, found 1031.0895.

Compound ***7f***. Spectral data: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (d, J = 8.7 Hz, 2H), 7.98 (s, 1H), 7.74 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.90 (s, 1H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, all signals represent 1C except noted) δ 185.32, 184.94, 183.87, 175.77, 160.88, 156.34, 153.29, 152.41, 151.63, 149.84, 149.59, 149.57, 149.46 (2C), 149.44 (3C), 149.43 (2C), 149.40, 148.29, 148.26, 148.24 (2C), 148.15, 148.12, 147.97, 147.96, 147.16, 147.12, 146.48, 146.44, 145.61, 145.54, 145.50, 145.48 (2C), 144.75, 144.70, 144.52, 144.34, 144.32, 144.27, 144.25, 144.22, 143.52 (2C), 143.51 (2C), 143.45, 142.86, 142.73 (2C), 142.55, 140.71, 140.63, 138.46, 136.80, 136.54, 136.09, 135.75, 127.21 (2C), 126.87, 124.56 (2C), 121.16 (2C), 113.93 (2C), 78.00, 77.47, 55.63; FT-IR (microscope) 3343, 2926, 2837, 1743, 1586, 1514, 1502, 1339, 1254, 1108, 1036, 1015, 876, 737 cm^{-1}; ESI-HRMS $C_{73}H_{14}N_3O_9$ (M + H^+) calcd 1076.0725, found 1076.0733.

Compound ***7g***. Spectral data: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15 (d, J = 8.2 Hz, 2H), 8.02 (s, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.27 (s, 1H), 6.99 (d, J = 8.6 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, all signals represent 1C except noted) δ 185.00, 184.89, 183.80, 175.69, 166.19, 160.53, 155.97, 153.69, 150.17, 150.05, 149.78, 149.57, 149.54, 149.44, 149.40 (5C), 149.36, 149.33, 148.25 (2C), 148.21 (2C), 148.12 (2C), 147.92 (2C), 147.10, 147.07, 146.47, 146.41, 145.70, 145.57, 145.43 (2C), 144.81, 144.72, 144.62, 144.45, 144.32 (2C), 144.28 (2C), 144.22, 143.45 (4C), 142.92, 142.79, 142.67, 142.65, 140.63, 140.55, 138.49, 136.72, 136.55, 136.11, 135.85, 130.23 (2C), 128.26, 126.97 (2C), 126.83, 121.04 (2C), 113.86 (2C), 77.98, 77.60, 60.94, 55.59, 14.42; FT-IR (microscope) 3285, 2956, 2925, 2851, 1743, 1716, 1598, 1501, 1272, 1255, 1169, 1108, 1036, 1017, 875, 737 cm^{-1}; ESI-HRMS $C_{76}H_{19}N_2O_9$ (M + H^+) calcd 1103.1085, found 1103.1107.

Compound ***7h***. Spectral data: ^{1}H NMR ($CDCl_3$, CS_2, 400 MHz) δ 7.90 (s, 1H), 7.74 (s, 1H), 7.60–7.54 (4H), 7.49–7.45 (2H), 7.34–7.26 (3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, CS_2, 100 MHz, all signals represent 1C except noted) δ 184.52, 184.48, 183.29, 175.46, 155.49, 155.06, 149.72, 149.56, 149.48, 149.46, 149.36 (2C), 149.32 (2C), 149.27 (2C), 148.22 (2C), 148.20 (2C), 148.07 (2C), 147.86 (2C), 147.69, 147.05 (2C), 146.48, 146.46, 146.37, 145.73, 145.70, 145.45, 145.39 (2C), 144.84, 144.82, 144.81, 144.78, 144.43 (2C), 144.37 (2C), 143.38 (2C), 143.01, 142.98, 142.82, 142.62 (2C), 140.58, 140.56, 138.06 (2C), 136.72, 136.67, 135.93, 135.87, 129.09 (2C), 129.07, 128.45 (2C), 127.27, 126.70, 123.51 (2C), 123.40, 122.56 (2C), 77.87, 77.79, 21.50; FT-IR (microscope) 3519, 3261, 2922, 2852, 1743, 1570, 1561, 1495, 1448, 1110, 1037, 1015, 909, 764, 732, 693 cm^{-1}; ESI-HRMS $C_{73}H_{15}N_2O_6$ (M + H^+) calcd 1015.0925, found 1015.0916.

Compound ***7i***. Spectral data: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (s, 1H), 7.61–7.57 (4H), 7.51–7.47 (5H), 7.33 (t, J = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except noted) δ 185.02, 184.87, 183.84, 175.76, 155.74, 155.19, 149.78, 149.55, 149.45 (2C), 149.38 (4C), 149.34 (2C), 148.23 (2C), 148.19 (2C), 148.08 (2C), 148.03, 147.90 (2C), 147.13, 147.07 (2C), 146.45, 146.42, 145.54, 145.52, 145.41 (2C), 145.27 (2C), 144.72, 144.70, 144.51, 144.44, 144.28 (4C), 143.44 (4C), 142.78, 142.68 (3C), 140.60 (2C), 136.72, 136.69, 135.84, 135.82, 131.65 (2C), 128.56 (2C), 127.69, 126.74 (2C), 124.26 (2C), 122.65 (2C), 121.18, 77.80, 77.72; FT-IR (microscope) 3513, 3360, 2921, 2851, 1742, 1660, 1634, 1479, 1109, 1037, 1015, 870, 764, 692 cm^{-1}; ESI-HRMS $C_{72}H_{12}BrN_2O_6$ (M + H^+) calcd 1078.9873, found 1078.9850.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected spectroscopic data for all new compounds and crystallographic data for **5**, including a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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