Synthesis of a Macrocycle Bearing a Carbon Framework of [16]Cyclophenacene as a Carbon Nanobelt

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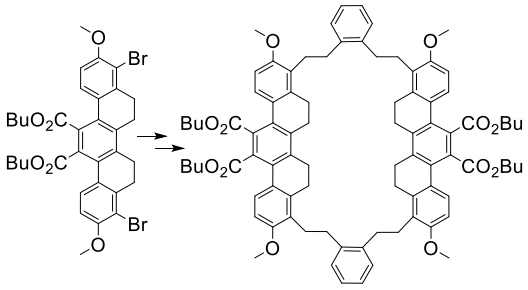
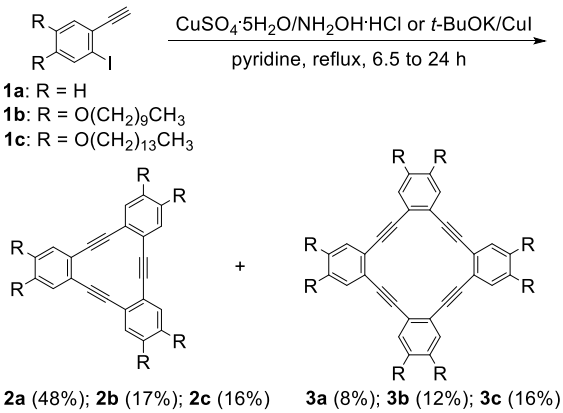
Supporting Information Placeholder



ABSTRACT: A synthetic pathway to a functionalized tetrahydro[5]phenacene was developed, which served as a precursor leading to a dehydrobenzo[32]annulene macrocycle containing four carbon–carbon triple bonds. The high efficiency of the macrocyclization step can be attributed to the structural rigidity of its immediate precursor. Hydrogenation of the four carbon–carbon triple bonds produced a macrocycle bearing a carbon framework of [16]cyclophenacene as the shortest macrocyclic belt-like structure of an (8,8)armchair carbon nanotube.

Dehydrobenzoannulenes (DBAs) continue to attract considerable attention due in part to their interesting chemical reactivities and physical properties for a variety of potential materials applications.[1] Several synthetic methods for DBAs have been developed. The relatively high efficiency of the macrocyclization step can be attributed to the structural rigidity of the precursors leading to DBAs. For example, macrocyclization of **1** was reported to produce hexadehydrotribenzo[12]annulenes **2** in 16 to 48% yields and octadehydrotetrabenzo[16]annulenes **3** in 8 to 16% yields (Scheme 1).[2a-b] Alternative synthetic routes and reaction conditions for hexadehydrotribenzo[12]annulenes were also reported.[2c-j]

Scheme 1. Synthesis of Hexadehydrotribenzo[12]annulenes 2 and Octadehydrotetrabenzo[16]annulenes 3



Our interest in DBAs stems from the possibility of constructing these macrocycles possessing carbon frameworks represented on armchair carbon nanotubes.[3] The use of DBAs to prepare benzoannulenes as potential precursors for the construction of macrocyclic belt-like structures (carbon nanobelts) was recognized previously.[4] Dehydrobenzo[32]annulene **4** containing four carbon–carbon triple bonds was selected as the initial target molecule having two extended tetrahydro[5]phenacene systems to replace two benzene units in **3** to test the validity this synthetic strategy (Figure 1). We were successful in developing a synthetic pathway leading to **4**, which was then hydrogenated to give macrocycle **5**.

The formation of four additional carbon–carbon bonds, depicted in red, of **5** could lead to **6** and, after dehydrogenation by oxidative aromatization, **7** bearing a [16]cyclophenacene ([16]CPA) unit as a carbon nanobelt.[5] The structure of [16]CPA represents the shortest macrocyclic belt-like structure of an (8,8)armchair carbon nanotube. Recently, synthetic pathways leading to three carbon nanobelts, including [12]-, [16]-, and [24]carbon nanobelts as isomers of [12]-, [16]-, and [24]CPAs, respectively, were reported.[5a,b] Synthetic pathways for an armchair and a chiral carbon nanobelts with carbon frameworks represented on the sidewalls of a (12,12)- and a (18,12)carbon nanotubes, respectively, were also reported.[6] The belt-like structures of CPAs can be constructed by fusing together two units of the corresponding cycloparaphenylene (CPP), which consists of a set of *para*-connected benzene rings in a cyclic array. Unlike CPPs, each set of CPP in CPAs has two connections between the adjacent benzene rings. It is anticipated that

CPAs would be thermally more robust, making them more suitable in serving as templates for growing carbon nanotubes of a single diameter and chirality,[7] two factors of critical importance for nanotechnology applications.[8]

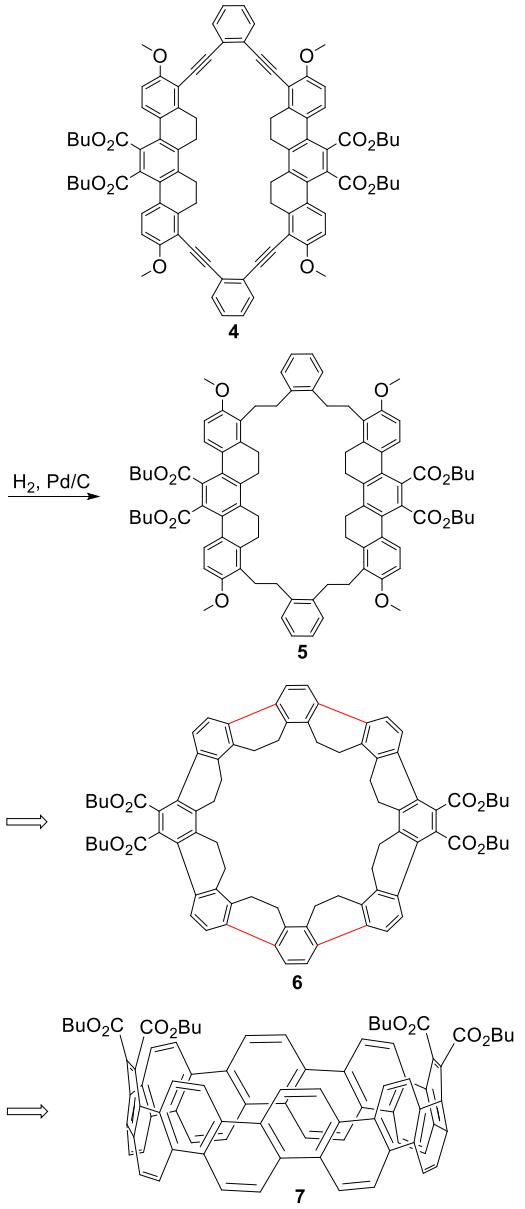
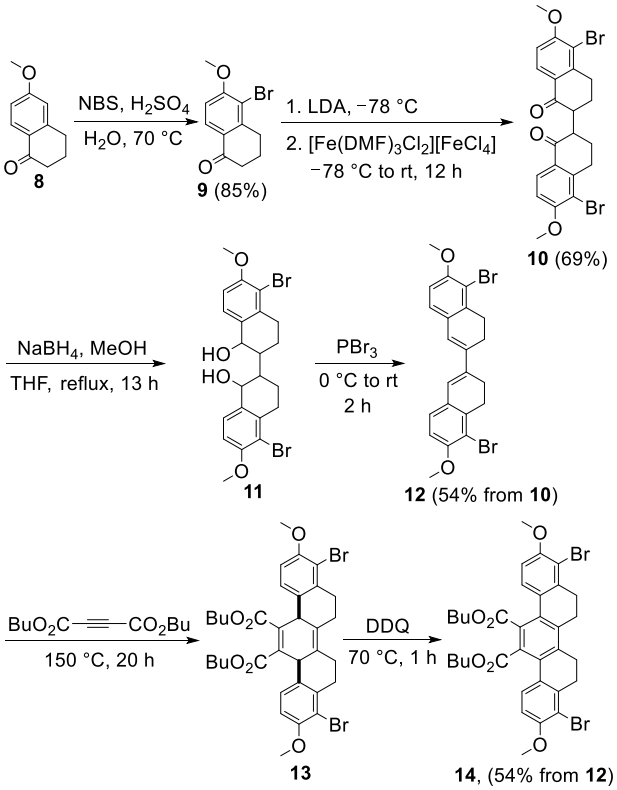


Figure 1. Structures of macrocycles **4** to **6** and [16]CPA **7**.

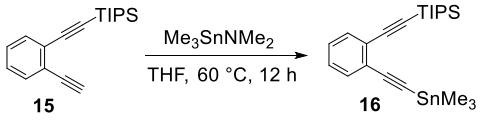
The first stage of the synthetic pathway leading to **5** involved the preparation of functionalized tetrahydro[5]phenacene **14** (Scheme 2). Selective bromination of **8** gave **9** in 85% yield as reported previously.[9] Diketone **10** was successfully synthesized via an iron-promoted oxidative coupling of the enolate of **9** in 69% isolated yield.[10] It is noteworthy that the enolate coupling reaction promoted by $[Fe(DMF)_3Cl_2][FeCl_4]$[10b] appears to be more efficient than by $FeCl_3$. In addition, $[Fe(DMF)_3Cl_2][FeCl_4]$ is not hygroscopic and is stable to water, making it easier to handle when compared to hygroscopic $FeCl_3$.[10] Reduction of **10** with sodium borohydride followed by methanol produced diol **11**, which was used without further purification due to its limited solubility in common organic solvents and the formation of various stereoisomers. The crude mixture of diol **11** was then treated with PBr_3 to provide 1,3-butadiene **12** in 54% isolated yield over two steps from **10**. Diene **12** had very low solubility in common organic solvents, and it was necessary to record its ^1H NMR spectrum in $CDCl_3$ at 60 °C. The Diels–Alder reaction between **12** and dibutyl acetylenedicarboxylate[11] at 150 °C for 20 h produced **13**, which upon treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for oxidative aromatization gave a functionalized and tetrahydrogenated derivative of [5]phenacene **14** in 54% isolated yield over two steps from **12**. It is noteworthy that an excess of dibutyl acetylenedicarboxylate was needed to drive the Diels–Alder reaction toward **13**. It was also important to carefully control the reaction time and temperature to obtain optimal yield because diene **12** was prone to double-bond isomerization to form a 1,4-dihydronaphthyl system and oxidative aromatization to form a naphthyl system.

Scheme 2. Synthesis of Tetrahydro[5]phenacene 14



The synthetic sequence also required the preparation of diacetylene **16**, which was obtained via stannylation of the terminal acetylene in 2-ethynyl-1-[(triisopropylsilyl)ethynyl] benzene (**15**)[12] with Me_3SnNMe_2,[13] a combined base and trimethylstannyl-group transfer reagent (Scheme 3). After 12 h at 60 °C, all volatiles of the reaction mixture were removed in vacuo, and the crude **16** was used without further purification.

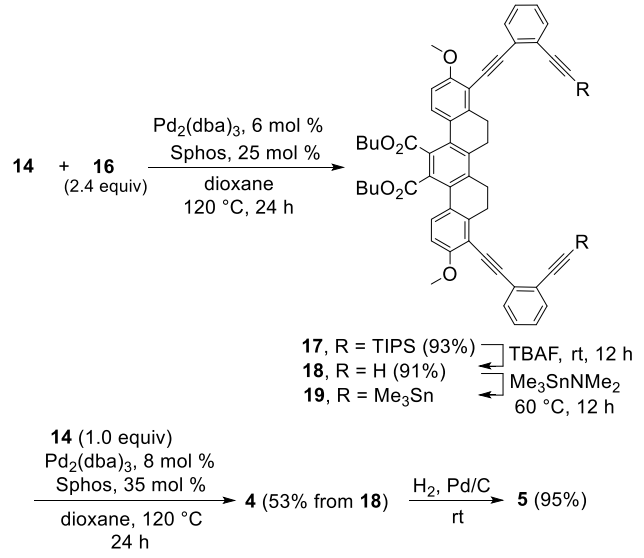
Scheme 3. Synthesis of Diacetylene 16



The next stage of the synthetic sequence involved the Migita–Kosugi–Stille cross-coupling reactions between **14** and 2 equiv of **16** (Scheme 4). After screening several palladium catalysts, ligands, and solvents, the Pd-Sphos-dioxane catalytic system[14]

was found to be most efficient for the cross-coupling reaction between the sterically hindered **14** and **16** in producing **17** in 93% isolated yield. Desilylation of **17** with tetrabutylammonium fluoride (TBAF) then gave **18** in 91% isolated yield. Treatment of **18** with Me_3SnNMe_2 produced the stannylated product **19**. The palladium-catalyzed Migita–Kosugi–Stille cross-coupling reactions between **14** and **19** was again successful in producing dehydrobenzo[32]annulene **4** in 53% isolated yield over two steps from **18**. The structural rigidity of the immediate precursor leading to **4** with limited freedom of rotation likely contributed to the relatively high efficiency of the macrocyclization step. Catalytic hydrogenation of **4** with Pd/C at room temperature afforded macrocycle **5** in 95% isolated yield.

Scheme 4. Synthesis of Macrocycles 4 and 5



In summary, a synthetic pathway leading to macrocycle **5** bearing a carbon framework of [16]CPA as the shortest macrocyclic belt-like structure of an (8,8)armchair carbon nanotube has been developed. The use of $[Fe(DMF)_3Cl_2][FeCl_4]$, instead of hygroscopic $FeCl_3$, to promote the coupling reaction of the enolate of **9** was operationally easier to perform. The macrocyclization step leading to dehydrobenzo[32]annulene **4** is relatively efficiently, presumably due to the structural rigidity of its immediate precursor with limited freedom of rotation. Hydrogenation of **4** then produced macrocycle **5**. The methoxy groups in **5** provide potential handles for converting it to **6** and subsequently, after oxidative aromatization, **7** containing a [16]CPA in its structure. We are developing synthetic pathways to transform **5** and related macrocycles to the corresponding carbon nanobelts.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were conducted in oven-dried (120 °C) glassware under an argon atmosphere. Oil bath was used as the heat source for the reactions that required heating. Chemicals, including 6-methoxy-1,2,3,4-tetrahydronaphthalen-1-one (**8**), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), (dimethylamino)trimethylstannane (Me_3SnNMe_2), tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$], dicyclohexyl[2',6'-dimethoxy(1,1'-biphenyl)-2-yl]phosphine (Sphos), and tetrabutylammonium fluoride (TBAF, 1.0 M in THF) were purchased from chemical suppliers and were used as received. Reported procedures were used to prepare 5-bromo-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-one (**9**),[9] $[Fe(DMF)_3Cl_2][FeCl_4]$,[10b] dibutyl acetylenedicarboxylate,[11] and 2-ethynyl-1-[(triisopropylsilyl)ethynyl]benzene (**15**).[12] Chemical shifts of NMR spectra were reported as parts per million (δ) relative to the signal of $CHCl_3$ at 7.26 ppm for ^1H NMR spectra and center line signal of the $CDCl_3$ triplet at 77.0 ppm for $^{13}C\{^1H\}$ NMR spectra. ^1H NMR spectra and $^{13}C\{^1H\}$ NMR spectra were recorded at 400 and 100 MHz, respectively. Infrared (IR) spectra of solid samples were recorded on a Fourier transform infrared system equipped with a diamond crystal attenuated total reflectance sampling interface. HRMS spectra were obtained on an Orbitrap mass analyzer coupled with electrospray ionization (ESI).

*Experimental Procedure for Dibromide **10**.* To a solution of freshly prepared LDA (14.9 mmol) in THF (20 mL) at −78 °C was added **9**[7] (3.61g, 14.2 mmol) in THF (20 mL) dropwise. After 30 min at −78 °C, a solution of $[Fe(DMF)_3Cl_2][FeCl_4]$[10b] (3.86 g, 7.10 mmol) in 20 mL of DMF under argon was added slowly. The reaction mixture was then warmed to rt. After 12 h, the reaction mixture was quenched with 100 mL of a 1 M aqueous HCl solution. After 30 min of stirring, the reaction mixture was filtered and then washed sequentially with water, ethanol, and hexanes to give **10** (2.50 g, 4.92 mmol, 69% yield) as a white solid: IR 1671, 1586, 1277 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.10 and 8.07 (2 H, two doublets from the two diastereomers, J = 9.0 Hz), 6.90 (2 H, two doublets from the two overlapping diastereomers, J = 9.0 Hz), 3.98 (6 H, s), 3.53–2.88 (6 H, m), 2.16–1.93 (4 H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 197.0, 195.9, 159.8, 159.7, 145.3, 144.8, 128.8, 128.6, 127.7, 127.6, 113.0, 112.8, 109.8, 109.6, 56.5, 47.7, 46.3, 30.5, 30.0, 24.74, 24.66; HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{22}H_{21}Br_2O_4$ 506.9801, 508.9781, 510.9760; found 506.9833, 508.9812, 510.9794.

*Experimental Procedure for **11**.* To a 200-mL flask were added 2.50 g of **10** (4.92 mmol) and 1.70 g of sodium borohydride (44.9 mmol). The flask was flushed with argon before 100 mL of THF was introduced via cannula. The reaction mixture was heated at reflux for 1 h before 6 mL of methanol was added dropwise. The reaction mixture was heated at reflux for an additional 12 h before it was cooled to rt. Then the reaction mixture was quenched with 50 mL of a 3.0 M sodium hydroxide solution. After 10 minutes of stirring, the reaction mixture was filtered and then washed with 20 mL of a 3.0 M sodium hydroxide solution and water (20 mL). After the product was air dried, the crude **11** (2.4 g) was obtained as a white solid, which was used without further purification.

*Experimental Procedure for **12**.* To a 20-mL vial were added 0.300 g of **11**. The vial was capped with a rubber septum and flushed with argon, and then 10 mL of dichloromethane was introduced by a syringe. The reaction mixture was stirred at 0 °C for 5 min before phosphorus tribromide (0.18 mL, 1.9 mmol) was added, and the mixture was warmed to rt. After 2 h of stirring, the reaction mixture was filtered, washed with dichloromethane, a sodium hydroxide solution, water, and acetone to give **12** (0.158 g, 0.33 mmol, 54% yield from **10**) as a white solid: IR 1588, 1475, 1264, 1074 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, 60 °C) δ 7.02 (2 H, d, J = 8.2 Hz), 6.74 (2 H, d, J = 8.2 Hz), 6.61 (2 H, s), 3.90 (6 H, s), 3.07 (4 H, t, J = 8.0 Hz), 2.66 (4 H, t, J = 7.8 Hz); HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{22}H_{21}Br_2O_2$ 474.9903, 476.9882, 478.9862; found 474.9905, 476.9887, 478.9867.

*Experimental Procedure for **13**.* To a mixture of 1,3-butadiene **12** (0.206 g, 0.433 mmol) and an excess of dibutyl acetylenedicarboxylate[9] (0.500 g, 2.21 mmol) in a pressure vessel glass tube was added 2 mL of dry chlorobenzene under argon. The reaction mixture was stirred at 150 °C for 20 h before it was cooled to rt. The reaction mixture including the insoluble materials was filtered and washed with 5 mL of dichloromethane. Solvents were evaporated in vacuo, and the crude residue of **13** was used without further purification.

*Experimental Procedure for **14**.* To a 20-mL flask containing the crude **13** was added 0.150 g (0.661 mmol) of DDQ. The flask was flushed with argon, and then 6 mL of chlorobenzene was introduced by a syringe. The reaction mixture was heated at 70 °C for 1 h before it was cooled to rt. Dichloromethane (10 mL) was added, and the solution was passed through a basic aluminum oxide column (4 cm high, 2.5 cm in diameter). The column was eluted with an additional 100 mL of a mixture of dichloromethane and ethyl acetate (1:1). Solvents were removed in vacuo, and the residue was purified by flash column chromatography (silica gel/dichloromethane:hexanes = 85:15) to produce **14** (0.163 g, 0.233 mmol, 54% yield from **12**) as a white solid: IR 1738, 1725, 1276, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40 (2 H, d, J = 8.6 Hz), 6.79 (2 H, d, J = 8.6 Hz), 4.20 (4 H, t, J = 6.7 Hz), 3.93 (6 H, s), 3.03 (4 H, t, J = 6.5 Hz), 2.78 (4 H, t, J = 6.5 Hz), 1.58 (4 H, quintet, J = 7.0 Hz); 1.26 (4 H, sextet, J = 7.3 Hz), 0.86 (6 H, t, J = 7.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.2, 155.6, 140.3, 137.9, 131.3, 128.9, 127.7, 126.6, 112.8, 109.3, 65.8, 56.4, 30.2, 28.5, 25.9, 19.0, 13.7; HRMS (ESI) *m/z* $[M]^+$ calcd for $C_{34}H_{36}Br_2O_6$ 698.0873, 700.0853, 702.0832; found 698.0874, 700.0853, 702.0826.

*Experimental Procedure for **16**.* To a solution of **15**[10] (0.389 g, 1.38 mmol) in THF (3 mL) was added (dimethylamino)trimethylstannane (0.56 mL, 3.4 mmol). The solution was heated to 60 °C for 16 h, and then all volatiles were removed in vacuo to give the crude **16**, which was used without further purification: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.48–7.44 (2 H, m), 7.22–7.18 (2 H, m), 1.15 (21 H, s), 0.34 (9 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 132.73, 132.72, 127.8, 127.5, 126.1, 125.8, 107.1, 105.5, 97.8, 94.6, 18.8, 11.3, –7.7.

*Experimental Procedure for **17**.* To a mixture of **14** (0.410 g, 0.585 mmol), tris(dibenzylideneacetone)dipalladium (0.030 g, 0.033 mmol), and Sphos ligand (0.060 g, 0.15 mmol) in a pressure vessel glass tube was added 20 mL of dry dioxane under argon. After 10 min of stirring, the crude **16** in 10 mL of dioxane was added to the solution in the glass tube via cannula. The reaction mixture was stirred at 120 °C for 12 h before it was cooled to rt. Dioxane was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/dichloromethane:hexanes = 90:10) to produce **17** (0.601 g, 0.545 mmol, 93% yield) as a white solid: IR 2156, 1717, 1271 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.59 (2 H, d, J = 7.4 Hz), 7.53 (2 H, d, J = 7.4 Hz), 7.43 (2 H, d, J = 8.6 Hz), 7.31–7.24 (4 H, m), 6.76 (2 H, d, J = 8.6 Hz), 4.22 (4 H, t, J = 6.7 Hz), 3.90 (6 H, s), 3.10 (4 H, t, J = 6.3 Hz), 2.76 (4 H, t, J = 6.3 Hz), 1.59 (4 H, quintet, J = 7.3 Hz), 1.28 (4 H, sextet, J = 7.2 Hz), 1.06 (42 H, s), 0.88 (6 H, t, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.5, 160.0, 142.9, 138.1, 132.9, 132.5, 131.2, 128.6, 127.9, 127.8, 126.19, 126.14, 125.6, 111.0, 108.1, 105.6, 96.2, 95.0, 87.7, 65.7, 55.9, 30.2, 26.9, 25.9, 19.0, 18.6, 13.7, 11.3; HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{72}H_{87}Si_2O_6$ 1103.6036, 1104.6069; found 1103.6048, 1104.6078.

*Experimental Procedure for **18**.* To a solution of **17** (0.601 g, 0.545 mmol) in THF (5 mL) at 0 °C was added a solution of TBAF (1.0 M in THF, 1.36 mL, 1.36 mmol). The reaction mixture was then warmed to rt and stirred for 14 h. A saturated aqueous $NaHCO_3$ solution (5.0 mL) was added, and the mixture was poured into water (10 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over sodium sulfate. Solvents were evaporated in vacuo, and the crude residue was purified by flash column chromatography (silica gel/dichloromethane:hexanes = 90:10) to produce **18** (0.391 g, 0.494 mmol, 91% yield) as a white solid: IR 3281, 1718, 1272 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.62 (2 H, d, J = 7.4 Hz), 7.55 (2 H, d, J = 7.4 Hz), 7.44 (2 H, d, J = 8.6 Hz), 7.35 (2 H, t, J = 7.4 Hz), 7.29 (2 H, t, J = 7.4 Hz), 6.79 (2 H, d, J = 9.0 Hz), 4.22 (4 H, t, J = 6.7 Hz), 3.95 (6 H, s), 3.35 (2 H, s), 3.21 (4 H, t, J = 6.7 Hz), 2.82 (4 H, t, J = 6.3 Hz), 1.59 (4 H, quintet, J = 7.2 Hz), 1.27 (4 H, sextet, J = 7.3 Hz), 0.88 (6 H, t, J = 7.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.4, 160.0, 143.2, 138.1, 132.6, 132.0, 131.3, 128.57, 128.53, 128.1, 127.8, 126.8, 126.4, 124.2, 110.8, 108.3, 96.0, 88.3, 82.7, 81.0, 65.7, 56.0, 30.2, 26.8, 25.9, 19.0, 13.7; HRMS (ESI) *m/z* $[M]^+$ calcd for $C_{54}H_{46}O_6$ 790.3289, 791.3323; found 790.3301, 791.3334.

*Experimental Procedure for **19**.* To a solution of **18** (0.380 g, 0.480 mmol) in THF (3 mL) was added (dimethylamino)trimethylstannane (0.40 mL, 2.4 mmol). The solution was heated to 60 °C for 16 h. All volatiles were then removed in vacuo to give the crude **19**, which was used without further purification: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.59 (2 H, d, J = 7.0 Hz), 7.52 (2 H, d, J = 7.4 Hz), 7.44 (2 H, d, J = 9.0 Hz), 7.29–7.22 (4 H, m), 6.79 (2 H, t, J = 8.6 Hz), 4.22 (4 H, t, J = 6.5 Hz), 3.94 (6 H, s), 3.19 (4 H, t, J = 6.3 Hz), 2.80 (4 H, t, J = 6.5 Hz), 1.59 (4 H, quintet, J = 7.1 Hz), 1.28–1.23 (4 H, m), 0.87 (6 H, t, J = 7.2 Hz), 0.32 (18 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.4, 159.9, 142.9, 137.9, 132.7, 132.2, 131.2, 128.5, 127.9, 127.7, 126.2, 126.0, 125.4, 110.9, 108.3, 107.6, 97.9, 96.6, 87.7, 67.0, 65.6, 56.0, 30.1, 26.8, 25.9, 19.0, 13.6, –7.6.

*Experimental Procedure for **4**.* To a mixture of **14** (0.335 g, 0.478 mmol), tris(dibenzylideneacetone)dipalladium (0.034 g, 0.037 mmol), and Sphos ligand (0.068 g, 0.17 mmol) in a pressure vessel glass tube was added 30 mL of dry dioxane under argon. After 10 min of stirring, the crude **19** in 10 mL of dioxane was added to the solution in the glass tube via cannula. The reaction mixture was stirred at 120 °C for 12 h before it was cooled to rt. Dioxane was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/dichloromethane:ethyl acetate = 98:2) to produce **4** (0.336 g, 0.253 mmol, 53% yield) as a white solid: IR 1736, 1710, 1273 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (4 H, dd, J = 5.9, 3.5 Hz), 7.323 (4 H, d, J = 8.6 Hz), 7.322 (4 H, dd, J = 5.9, 3.5 Hz), 6.74 (4 H, d, J = 9.0 Hz), 4.18 (8 H, t, J = 6.8 Hz), 3.87 (12 H, s), 3.05 (8 H, broad), 2.77 (8 H, broad multiplet), 1.57 (8 H, quintet, J = 7.1 Hz), 1.27 (8 H, sextet, J = 7.6 Hz), 0.87 (12 H, *t*, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.2, 160.1, 142.6, 137.4, 132.6, 131.2, 128.5, 128.1, 127.9, 125.9, 125.8, 110.8, 108.5, 96.3, 87.5, 65.7, 55.9, 30.2, 26.7, 26.4, 19.0, 13.7; HRMS (ESI) *m/z* $[M]^+$ calcd for $C_{88}H_{80}O_{12}$ 1328.5644, 1329.5678; found 1328.5671, 1329.5680.

*Experimental Procedure for **5**.* A mixture of **4** (0.100 g, 0.075 mmol), a Pd/C catalyst (0.050 g, 10% Pd on carbon), acetic acid (1.0 mL), methanol (1.0 mL), and ethyl acetate (10 mL) was stirred under a hydrogen atmosphere (25 psi) at rt. After 6 h, the reaction mixture was filtered, and the filtrate was concentrated

in vacuo to give **5** (0.096 g, 0.071 mmol, 95% yield) as a white solid: IR 1720, 1597, 1262 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36 (4 H, dd, J = 5.5, 3.5 Hz), 7.32 (4 H, d, J = 8.6 Hz), 7.22 (4 H, dd, J = 5.5, 3.1 Hz), 6.76 (4 H, d, J = 8.6 Hz), 4.17 (8 H, t, J = 6.7 Hz), 3.87 (12 H, s), 3.02 (8 H, broad multiplet), 2.84 (16 H, two broad overlapping multiplets), 2.76 (8 H, broad multiplet), 1.55 (8 H, quintet, J = 7.1 Hz), 1.19 (8 H, sextet, J = 7.8 Hz), 0.83 (12 H, t, J = 7.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 170.5, 157.4, 140.1, 138.0, 137.1, 131.9, 129.2, 128.7, 127.2, 126.14, 126.11, 125.8, 108.2, 65.5, 55.5, 32.5, 30.2, 27.9, 26.4, 25.2, 19.0, 13.7; HRMS (ESI) *m/z* $[M]^+$ calcd for $C_{88}H_{96}O_{12}$ 1344.6896, 1345.6930; found 1344.6901, 1345.6935.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

^1H and/or ^{13}C NMR spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under CHE – 1464026 and CHE – 1853456. The NMR spectrometer on which this work was carried out was supported by the Major Research Instrumentation Program of the NSF (CHE – 1228336).

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