Copper-Mediated Simple and Efficient Synthesis of Tribenzohexadehydro[12]annulene and Its Derivatives

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This article is dedicated to Professor Teruaki Mukaiyama for his 77th birthday.

Abstract: A simple and efficient synthesis of tribenzohexadehydro[12]annulene and its derivatives was carried out using coupling reaction of acetylenes with iodoarenes in the presence of catalytic amounts of CuI and PPh_3, together with three equivalents of K_2CO_3 in DMF. This synthetic procedure was applied to the synthesis of a large annulenoannulene derivative.

Key words: annulenes, cross-coupling, cyclizations, macrocycles, oligomerization

There has been a considerable interest in cyclic phenylacetylenes such as dehydroannulenes,[1] cyclynes,[2] and phenylacetylene macrocycles,[3] because of their π-conjugation, all-carbon networks,[4,5] formation of unusual metal complexes,[2] self-association[6] and inclusion properties.[7] Tribenzohexadehydro[12]annulene (tribenzocyclyne) (**1a**) is a unit structure of graphyne.[4] Since **1a** is one of the most useful cyclic acetylenes, a variety of synthetic methods for **1a** have been developed. Annulene **1a** can be prepared by Stephens–Castro coupling of copper (2-iodophenyl)acetylide,[8] palladium-catalyzed trimerization of 4-(2-bromophenyl)-2-methylbutyn-2-ol,[9] palladium-catalyzed co-cyclization of 1,2-diiodobenzene with acetylene,[10] a combination of Wittig reaction and bromination/dehydrobromination procedures[11] or recently reported alkyne metathesis.[12] However, the synthesis of **1a** still remains troublesome, especially for medium to large scale reactions. Here we report a practical procedure for the synthesis of **1a** and related compounds.

Although the Sonogashira reaction of phenylacetylene with bromo- or iodobenzene using $Pd(PPh_3)_2Cl_2$ and CuI in Et_3N produces diphenylacetylene in a quantitative yield,[13] cyclotrimerization of (2-bromophenyl)acetylene under similar conditions affords **1a** in a very low yield due to homo-coupling of (2-bromophenyl)acetylene as a preferable reaction.[14] The cyclotrimerization of (2-iodophenyl)acetylene under similar Sonogashira conditions also formed only a trace amount of **1a**. Thus, the homo-coupling of acetylene units takes place more easily than the normal Sonogashira coupling in the case of (2-bromophenyl)- and (2-iodophenyl)acetylenes.

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A copper-catalyzed cross-coupling of phenylacetylene with iodobenzene in an aprotic solvent such as DMF and DMSO was reported to produce diphenylacetylene in a quantitative yield.[15] Since this reaction proceeds smoothly to produce no homo-coupling product, we tried to apply the cyclotrimerization of (2-iodophenyl)acetylene (**3a**) and its derivatives with catalytic amounts of CuI and PAr_3 (Ar = Ph or 2-furyl) in the presence of K_2CO_3 as a base in DMF. Although the reaction takes place at high temperatures (160−165 °C), the desired product **1a** and related annulenes **1b**−**d** can be prepared in moderate to good yields (Figure 1). Additionally, the annulenoannulene derivative **2c** can be synthesized in a short pathway.

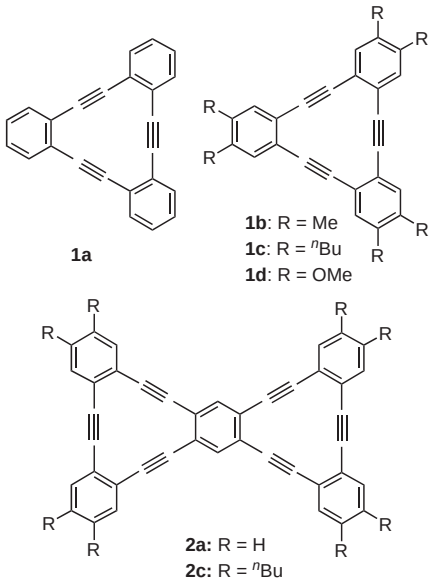
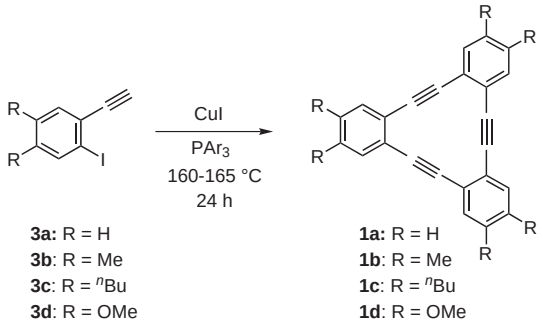


Figure 1 The structures of the annulenes **1a**−**d** and **2a**,**c**

For the construction of the [12]annulene framework, the cyclotrimerization of **3a**−**d** was first investigated under various conditions using CuI and PAr_3 (Scheme 1 and Table 1). The reaction of **3a** with CuI (30−50 mol%) and PPh_3 (30−50 mol%) in DMF proceeded smoothly at 160−165 ºC for 24 hours to afford **1a** in 54−55% yields (entries 1 and 2). A similar reaction of **3a** in DMSO, however, resulted in the formation of a complex mixture of unidentified products (entry 3). As the ligand, tri(2-furyl)phosphine can be employed for the cyclotrimerization to give **1a** in 41% yield (entry 4).



Scheme 1 Synthesis of **1**–**4**

Although the reaction of phenylacetylene with iodobenzene in the presence of CuI (5 mol%) and PPh_3 (10 mol%) proceeded smoothly at 120 °C to produce diphenylacetylene, **3a** was recovered unchanged under similar conditions. As other ligands, P(*o*-tolyl)$_3$, $AsPh_3$ and $Ph_2PCH_2CH_2PPh_2$ can be employed for the cyclotrimerization of **3a** to afford **1a** in lower yields. Additionally, the reaction of **3a** with a stoichiometric amount of CuI and PPh_3 (1 equivalent) also leads to **1a** in 44% yield.

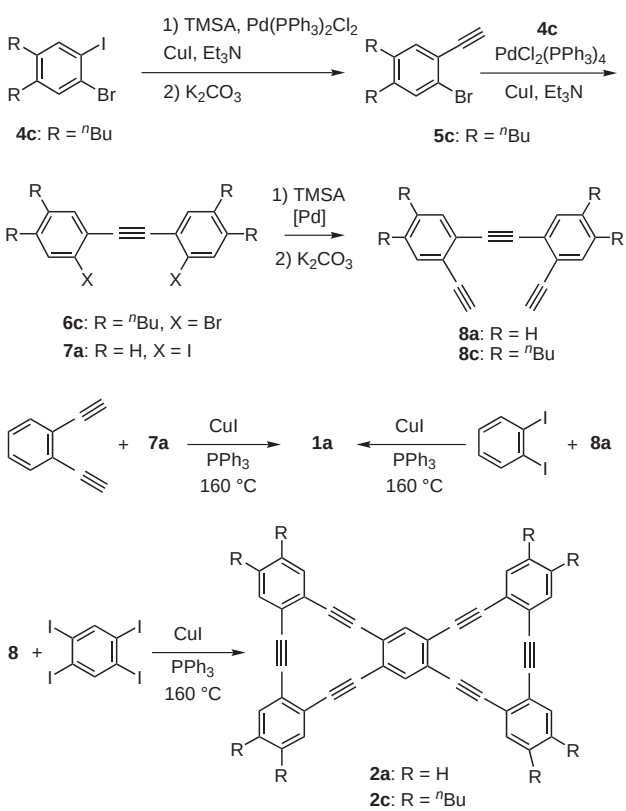
The cyclotrimerization of **3a** can be applied for the preparation of substituted tribenzohexadehydro[12]annulenes **1b**–**d**. (2-Iodoaryl)acetylenes **3b**–**d** were prepared by the Sonogashira reaction of the corresponding 1,2-diiodoarenes, followed by deprotection with K_2CO_3 in methanol. As shown in Table 1, the reactions of **3b**–**d** with CuI (30 mol%) and P(2-furyl)$_3$ (30 mol%) in DMF at 160 °C for 24 hours produced **1b**–**d** in 28%, 37% and 17% yields (entries 5, 6 and 8). In the case of **3c**, the reaction with 30 mol% of CuI and PPh_3 under similar conditions afforded **1c** in 31% yield (entry 7). Although the copper-catalyzed cyclotrimerization of **3b**–**d** with PPh_3 yielded **1b**–**d**, the reaction with P(2-furyl)$_3$ afforded **1b**–**d** in better yields (entries 5–8).

Table 1 Cyclotrimerization of **3a**–**d** with CuI and PAr_3[a]

Entry	**3**	CuI (mol%)	Ligand (mol%)	Solvent	Product (%)[b]
1	**3a**	30	PPh_3 (30)	DMF	**1a** (55)
2	**3a**	50	PPh_3 (50)	DMF	**1a** (54)
3	**3a**	30	PPh_3 (30)	DMSO	**1a** (0)
4	**3a**	30	P(2-furyl)$_3$ (30)	DMF	**1a** (41)
5	**3b**	30	P(2-furyl)$_3$ (30)	DMF	**1b** (28)
6	**3c**	30	P(2-furyl)$_3$ (30)	DMF	**1c** (37)
7	**3c**	30	PPh_3 (30)	DMF	**1c** (31)
8	**3d**	30	P(2-furyl)$_3$ (30)	DMF	**1d** (17)

[a] Conditions: 160–165 °C, 24 h.
[b] Isolated yield.

For the construction of the [12]annulene framework, we next tried the [6+6] or [10+2] cyclization using the copper-mediated cross-coupling strategy. As shown in Scheme 2, the reaction of **7a** with 1.5 equivalents of 1,2-diethynylbenzene in the presence of CuI (30 mol%), PPh_3 (30 mol%) and K_2CO_3 (3 equivalents) in DMF at 160 °C for 24 hours afforded **1a** in 33% yield, whereas a similar reaction of **8a** with 1 equivalent of 1,2-diiodobenzene produced **1a** in 51% yield. Since the annulenoannulene **2a** is an interesting target molecule,[1,16] the synthesis of **2a** was tried using our [10+2] coupling reaction. Thus, the cross-coupling of **8a** with 0.5 equivalents of 1,2,4,5-tetraiodobenzene was carried out using CuI and PPh_3 in DMF. However, the reaction gave a complex mixture, and only a trace amount of **2a** was detected by MS analysis, presumably due to an extremely low solubility of **2a** and its precursors.



Scheme 2 Synthesis of **1a**, **2a** and **2c**

Taking into account the low solubility of **2a**, the synthesis of **2c** was attempted, because eight butyl groups may increase the solubility of **2c** enough to isolate a pure compound. The precursor **8c** was prepared starting from **4c**.[17] The Sonogashira reaction of **4c** with trimethylsilylacetylene (TMSA), followed by deprotection yields **5c** (two steps, 80%). The cross-coupling of **5c** with **4c** in the presence of $PdCl_2(PPh_3)_2$ and CuI in Et_3N afforded **6c** (93%). The Sonogashira reaction of **6c** with TMSA, followed by deprotection produced the diethynyl precursor **8c** in 64% overall yield. The reaction of **8c** with 1,2,4,5-tetraiodobenzene (0.5 equivalents) in the presence of CuI (1 equiv-

alent) and PPh_3 (1 equivalent) in DMF at 160−165 °C for 24 hours produced the desired product **2c** in 1% yield. The annulenoannulene **2c** is a stable yellow crystalline compound and has a moderate solubility in CH_2Cl_2, THF and CS_2.

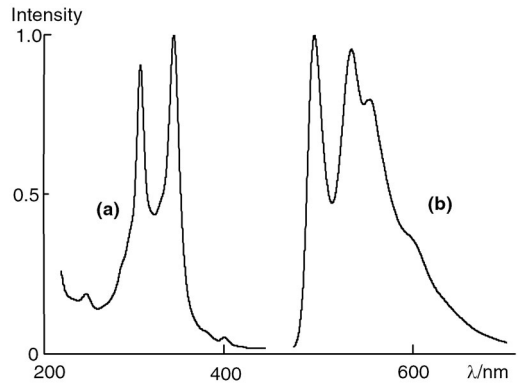


Figure 2 Electronic (a) and fluorescence spectra (b) of **2c** in CH_2Cl_2

Interestingly, **2c** shows an intense fluorescence at 495, 535 and 555 nm (Figure 2) with a large Storks shift of 190 nm, reflecting the tribenzohexadehydro[12]annulene structure. The fluorescence quantum yield (Φ = 0.21) of **2c** is fairly large. Additionally, **2c** forms a 2:1 silver complex with $AgBF_4$ at equilibrium (Figure 3), although we assume a partial formation of the 2:1 complex after mixing **2c** and $AgBF_4$. The formation of the $(\mathbf{2c})_2$-$AgBF_4$ complex was confirmed by TOF-MS and ^{1}H NMR analysis.[18]

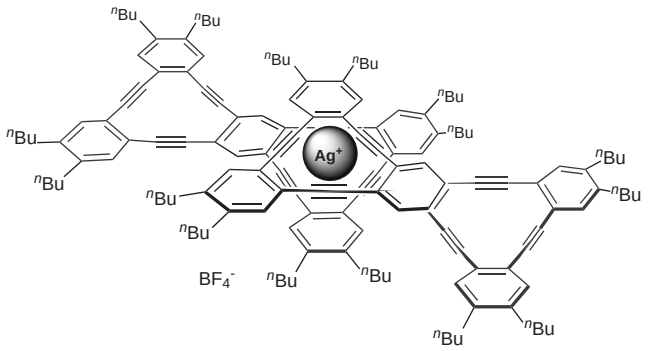


Figure 3 The silver complex $(\mathbf{2c})_2$-$AgBF_4$

^{1}H and ^{13}C NMR spectra were recorded on JEOL LA-500 and JEOL LA-400 instruments. Spectra are reported (in δ) referenced to Me_4Si. Mass spectra were recorded on JEOL JMS-AX 500 and KRATOS AXIMA-CFR instruments. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. High-Resolution MS was determined on JEOL JMS-SX102A instrument. Electronic spectra were recorded on a SHIMADZU UV-VIS-NIR scanning spectrophotometer (Model UV-3101-PC). Melting points were determined with a Rigaku DSC8230L differential scanning calorimetry apparatus and a Yanaco MP-500D melting point apparatus. Elemental analyses were performed in the microanalysis laboratory of Tokyo Metropolitan University. Column chromatography was carried out with use of EM reagents silica gel 60, 70−230 mesh ASTM, Daiso silica gel 1001W, or neutral alumina activity II-III, 70−230 mesh ASTM. All solvents were dried by conventional procedures and distilled before use. 1,2-Diiodo-4,5-dimethylbenzene,[19] 4,5-dibutyl-1,2-diiodo-benzene,[20] 1,2-diiodo-4,5-dimethoxybenzene[21] and (2-iodophenyl)-acetylene[8b,22] were prepared according to literature procedures.

(2-Iodoaryl)acetylenes 3; General Procedure

To a 50 mL two-necked flask equipped with an argon balloon, 1,2-diiodoarene (10 mmol), trimethylsilylacetylene (1.17 g, 12 mmol), Et_3N (20 mL), CuI (38 mg, 0.2 mmol) and $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) were added. The reaction mixture was stirred for 6−15 h at r.t. The solvent was removed under reduced pressure. The residue was passed through a short column of Al_2O_3 and eluted with hexane−CH_2Cl_2 to give the crude product which was purified by column chromatography on silica gel (hexane−CH_2Cl_2) to afford 1-iodo-2-trimethylsilylethynylarene.

To a solution of 1-iodo-2-trimethylsilylethynylarene (5 mmol) in MeOH (20 mL) was added K_2CO_3 (69 mg, 0.5 mmol), and the mixture was stirred for 1−5 h at r.t. The mixture was poured into H_2O and extracted with Et_2O. The organic phase was washed with sat. aq NH_4Cl solution, and dried over $MgSO_4$. After removal of the drying reagent, the solvent was evaporated under reduced pressure to give a residue which was passed through a silica gel column (hexane−CH_2Cl_2) to afford **3**.

1-Ethynyl-2-iodo-4,5-dimethylbenzene (3b)

Colorless crystals; yield: 43%; mp 71.5–72 °C.

^{1}H NMR ($CDCl_3$): δ = 2.18 (s, 3 H), 2.21 (s, 3 H), 3.31 (s, 1 H), 7.27 (s, 1 H), 7.60 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 19.17, 19.31, 79.78, 85.25, 96.60, 125.83, 134.29, 136.68, 139.40, 139.65.

MS (EI): *m*/*z* (%) = 256 (100, M^+), 129 (30), 128 (53).

HRMS–FAB: *m*/*z* calcd for $C_9H_{10}I$: 255.9749; found: 255.9750.

1,2-Dibutyl-4-ethynyl-5-iodobenzene (3c)

Colorless oil; yield: 51%.

^{1}H NMR ($CDCl_3$): δ = 0.92−0.96 (m, 6 H), 1.35−1.40 (m, 4 H), 1.49−1.55 (m, 4 H), 2.50−2.55 (m, 4 H), 3.31 (s, 1 H), 7.28 (s, 1 H), 7.59 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 13.93, 22.62, 22.68, 31.71, 31.89, 32.94, 33.02, 79.67, 85.39, 96.78, 125.75, 134.02, 139.06, 140.71, 143.73.

MS (EI): *m*/*z* (%) = 340 (81, M^+), 255 (100), 170 (20).

HRMS–FAB: *m*/*z* calcd for $C_{16}H_{21}I$: 340.0688; found: 340.0688.

1-Ethynyl-2-iodo-4,5-dimethoxybenzene (3d)

Colorless crystals; yield: 40%; mp 107.4−107.6 °C.

^{1}H NMR ($CDCl_3$): δ = 3.31 (s, 1 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 6.99 (s, 1 H), 7.21 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 55.97, 56.16, 79.29, 85.30, 89.64, 115.41, 120.79, 120.88, 148.85, 150.01.

MS (EI): *m*/*z* (%) = 288 (100, M^+), 273 (19), 118 (49).

HRMS–FAB: *m*/*z* calcd for $C_{10}H_9IO_2$: 287.9647; found: 287.9646.

Cyclotrimerization of 3; General Procedure (Table 1)

To a solution of (2-iodoaryl)acetylene **3** (1.5 mmol) and PPh_3 (118 mg, 0.45 mmol) or P(2-furyl)$_3$ (104.5 mg, 0.45 mmol) in DMF (5 mL) were added CuI (86 mg, 0.45 mmol) and K_2CO_3 (622 mg, 4.5 mmol). The mixture was heated with stirring for 24 h in an oil bath at 160 °C under argon atmosphere. The mixture was poured into H_2O and extracted with toluene. The combined organic phase was washed with sat. aq NH_4Cl solution, and dried over $MgSO_4$. The

drying reagent was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was passed through a short column on Al_2O_3 and eluted with hexane–CH_2Cl_2 to give the crude product which was purified by column chromatography on silica gel (hexane–CH_2Cl_2, 10:1 to 5:1) to afford **1** together with a small amount of a cyclic tetramer (tetrabenzooctadehydro[16]annulene or its derivatives).

Hexadehydrotribenzo[12]annulene (1a)[8–12]
Yellow plates; yield: 55%; mp 208.5–210 °C.

^{1}H NMR ($CDCl_3$): δ = 7.19 (m, 6 H), 7.39 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 92.99, 126.35, 128.39, 132.10.

Hexamethylhexadehydrotribenzo[12]annulene (1b)[10,12]
Yellow crystals; yield: 28%; mp ca. 340 °C (dec.).

^{1}H NMR (CD_2Cl_2): δ = 2.21 (s, 18 H), 7.10 (s, 6 H).

^{13}C NMR (CD_2Cl_2): δ = 19.70, 92.42, 124.29, 133.15, 138.22.

MS (EI): *m*/*z* (%) = 384 (100, M^+), 192 (14).

HRMS (EI): *m*/*z* calcd for $C_{30}H_{24}$: 384.1878; found: 384.1832.

Hexabutylhexadehydrotribenzo[12]annulene (1c)
Yellow crystals; yield: 37%; mp 153–154.5 °C.

^{1}H NMR ($CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 18 H), 1.37–1.41 (m, 12 H), 1.51–1.57 (m, 12 H), 2.52 (t, *J* = 7.9 Hz, 12 H), 7.11 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 14.00, 22.74, 32.05, 32.89, 92.18, 124.08, 132.33, 141.18.

MS (EI): *m*/*z* (%) = 636 (100, M^+), 551 (17), 318 (13).

HRMS–FAB: *m*/*z* calcd for $C_{48}H_{60}$: 636.4695; found: 636.4687.

Hexamethoxyhexadehydrotribenzo[12]annulene (1d)[12]
Yellow crystals; yield: 17%; mp > 250 °C.

^{1}H NMR ($CDCl_3$): δ = 3.87 (s, 18 H), 6.74 (s, 6 H).

^{13}C NMR (CD_2Cl_2): δ = 55.89, 91.91, 113.78, 119.81, 149.06.

MS (EI): *m*/*z* (%) = 480 (100, M^+), 335 (13), 281 (5).

HRMS–FAB: *m*/*z* calcd for $C_{30}H_{24}O_6$: 480.1573; found: 480.1573.

Coupling of 7a with 1,2-Diethynylbenzene
To a mixture of CuI (63 mg, 0.33 mmol), PPh_3 (87 mg, 0.33 mmol) and K_2CO_3 (414 mg, 3 mmol) in DMF (10 mL) was added **7a**[23] (430 mg, 1 mmol) and 1,2-diethynylbenzene (189 mg, 1.5 mmol) under argon. The mixture was stirred for 24 h at 160 °C. The mixture was poured into H_2O and extracted with Et_2O. The organic phase was washed with sat. aq NH_4Cl solution, and dried over $MgSO_4$. After removal of the solvent, **1a** was isolated by silica gel column chromatography (99 mg, 33%).

Coupling of 8a with 1,2-Diiodobenzene
In a similar manner to the reaction of **7a** with 1,2-diethynylbenzene, the reaction of **8a** (226 mg, 1 mmol), 1,2-diiodobenzene (330 mg, 1 mmol), CuI (63 mg, 0.33 mmol), PPh_3 (87 mg, 0.33 mmol) and K_2CO_3 (414 mg, 3 mmol) in DMF (10 mL) afforded **1a** (153 mg, 51%).

1-Bromo-4,5-dibutyl-2-ethynylbenzene (5c)
To a 20 mL-flask, 1-bromo-2-iodo-4,5-dibutylbenzene (2.53 g, 6.4 mmol), trimethylsilylacetylene (1.0 mL, 7.09 mmol), Et_3N (12 mL), CuI (121.7 mg, 0.64 mmol) and $PdCl_2(PPh_3)_2$ (453.3 mg, 0.64 mmol) were added. The reaction mixture was stirred overnight at r.t. under argon. The mixture was poured into sat. aq NH_4Cl solution (20 mL) and extracted with Et_2O (3 × 20mL). The combined organic phase was washed with sat. aq NaCl solution (20 mL) and dried over $MgSO_4$. After filtration, solvent was removed under reduced pressure, and the residue was separated by column chromatography on silica gel (hexane) to afford 1-bromo-4,5-dibutyl-2-trimethylsilylethynyl benzene (2.26 g, 96%).

To a 20 mL-flask, 1-bromo-4,5-dibutyl-2-trimethylsilylethynyl benzene (2.26 g, 6.2 mmol), K_2CO_3 (857.5 mg, 6.2 mmol) and MeOH (15 mL) were added. The mixture was stirred for 30 min at r.t. The mixture was poured into sat. aq NaCl solution (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phase was dried over $MgSO_4$. After filtration, solvent was evaporated, and the residue was separated by column chromatography on Al_2O_3 (hexane) to afford **5c** (1.59 g, 88%) as a yellow oil.

^{1}H NMR ($CDCl_3$): δ = 0.92–0.96 (m, 6 H), 1.37–1.41 (m, 4 H), 1.51–1.54 (m, 4 H), 2.51–2.57 (m, 4 H), 3.30 (s, 1 H), 7.30 (s, 1 H), 7.34 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 13.94, 22.64, 22.68, 31.64, 32.09, 32.97, 32.99, 80.43, 82.27, 121.16, 122.20, 132.69, 134.58, 139.88, 143.73.

Bis(2-bromo-4,5-dibutylphenyl)acetylene (6c)
To a 10 mL-flask were added 1-bromo-4,5-dibutyl-2-ethylnyl benzene (1.44 g, 4.9 mmol), 1-bromo-2-iodo-4,5-dibutylbenzene (1.94 g, 4.9 mmol), Et_3N (8.8 mL), CuI (93.4 mg, 0.49 mmol) and $PdCl_2(PPh_3)_2$ (346.8 mg, 0.49 mmol). The mixture was stirred overnight at r.t. The mixture was poured into sat. aq NH_4Cl solution (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phase was washed with sat. aq NaCl solution (20 mL) and dried over $MgSO_4$. After filtration, solvent was evaporated, and the residue was passed through a short Al_2O_3 column and eluted (hexane–benzene, 9:1). The crude product was purified by column chromatography on silica gel (hexane–benzene, 9:1) to give **6c** (2.56 g, 93%).

^{1}H NMR ($CDCl_3$): δ = 0.95 (2 t, *J* = 7.3 Hz, 2 × 6 H), 1.36–1.43 (m, 8 H), 1.51–1.58 (m, 8 H), 2.53–2.59 (m, 8 H), 7.36 (s, 2 H), 7.37 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 13.96, 22.69, 22.70, 31.75, 32.12, 33.03, 33.11, 91.44, 122.21, 122.32, 132.74, 134.00, 139.81, 143.17.

MS (EI): *m*/*z* (%) = 562 (52, M^+ + 4), 560 (100, M^+ + 2), 558 (51, M^+), 477 (21), 475 (40), 473 (20).

HRMS–FAB: *m*/*z* calcd for $C_{30}H_{40}Br_2$: 558.1497; found: 558.1490.

Bis(2-ethynyl-4,5-butylphenyl)acetylene (8c)
Bis(2-bromo-3,4-dibutylphenyl)acetylene (**6c**, 2.51 g, 4.48 mmol), trimethylsilylacetylene (2.5 mL, 17.7 mmol), PPh_3 (117.6 mg, 0.49 mmol), CuI (42.7 mg, 0.22 mmol), $PdCl_2(PPh_3)_2$ (158.8 mg, 0.23 mmol) and piperidine (20 mL) were placed in a 50 mL-flask. The mixture was evacuated with argon and stirred overnight at 80 °C. The mixture was poured into sat. aq. NH_4Cl solution (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phase was washed with sat. aq NaCl solution (20 mL) and dried over $MgSO_4$. After filtration, solvent was evaporated, and the residue was separated by column chromatography on silica gel (hexane–benzene, 4:1) to afford bis(2-trimetylsilylethynyl-4,5-dibutylphenyl)acetylene (2.07 g, 78%) as a viscous oil.

To a solution of bis(2-trimetylsilylethynyl-4,5-dibutylphenyl)acetylene (1.47 g, 2.47 mmol) in THF (10 mL) and MeOH (10 mL) was added K_2CO_3 (341.5 mg, 2.47 mmol) under argon. The mixture was stirred for 1 h at r.t. The mixture was poured into sat. aq NaCl solution (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was separated by column chromatography on Al_2O_3 (hexane–benzene, 4:1) to afford **8c** (916 mg, 82%) as a viscous oil.

^{1}H NMR ($CDCl_3$): δ = 0.951 (t, *J* = 7.3 Hz, 6 H), 0.954 (t, *J* = 7.3 Hz, 6 H), 1.37−1.42 (m, 8 H), 1.52−1.59 (m, 8 H), 2.56−2.60 (m, 8 H), 3.26 (s, 2 H), 7.31 (s, 2 H), 7.35 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 13.98, 22.70, 22.72, 32.06, 32.12, 33.01, 33.03, 79.99, 82.64, 91.00, 121.52, 123.60, 132.84, 133.20, 141.11, 141.64.

MS (EI): *m*/*z* (%) = 450 (100, M^+), 365 (25), 293 (6).

HRMS–FAB: *m*/*z* calcd for $C_{34}H_{42}$: 450.3287; found: 450.3291.

Annulenoannulene 2c

To a mixture of 1,2,4,5-tetraiodobenzene (227 mg, 0.39 mmol), K_2CO_3 (324 mg, 2.34 mmol), CuI (148 mg, 0.78 mmol) and PPh_3 (614 mg, 2.34 mmol) was added a solution of **8c** (352 mg, 0.78 mmol) in DMF (2 mL) under argon. The mixture was stirred for 20 h at 160 °C. The mixture was poured into sat. aq NH_4Cl solution (25 mL) and extracted with CS_2 (3 × 30 mL). The combined organic phase was washed with sat. aq NaCl solution (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was separated by column chromatography on Al_2O_3 (hexane−benzene, 4:1) to give **2c** (3 mg, 1%) as yellow crystals; mp >250 °C.

^{1}H NMR (CS_2/CD_2Cl_2, 1:1): δ = 1.02−1.05 (m, 24 H), 1.44−1.51 (m, 16 H), 1.58−1.64 (m, 16 H), 2.60 (t, *J* = 7.6 Hz, 16 H), 7.08 (s, 4 H), 7.09 (s, 4 H), 7.17 (s, 2 H).

^{13}C NMR (CS_2/CD_2Cl_2, 1:1): δ = 13.97, 22.58, 22.67, 31.91, 31.97, 32.88, 32.89, 79.98, 82.53, 91.00, 121.57, 123.61, 132.70, 133.07, 140.89, 141.41.

UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 252 (4.32), 310 (4.98), 345 (5.03), 399 (3.81), 440 (3.49), 454 (3.41), 486 nm (3.11).

LDTOF-MS: *m*/*z* 970 (M^+).

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(17) 1-Iodo-2-bromo-4,5-dibutylbenzene was prepared by bromination of 1,2-dibutylbenzene with Br_2 (63%), followed by iodination with I_2 and H_5IO_6 in AcOH−H_2SO_4−H_2O (64%).

(18) The silver complex (**2c**)$_2$$AgBF_4$: ^{1}H NMR ($CD_2Cl_2$): δ = 0.87 (m, 24 H), 1.02 (m, 16 H), 1.48 (m, 16 H), 2.39 (m, 8 H), 2.54 (m, 8 H), 7.09 (s, 4 H), 7.14 (s, 4 H), 7.69 (s, 2 H); LDTOF-MS: *m*/*z* calcd for $C_{148}H_{164}Ag$: 2048.19; found: 2049.5.

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