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A Versatile Synthesis of Functionalized Pentahelicenes

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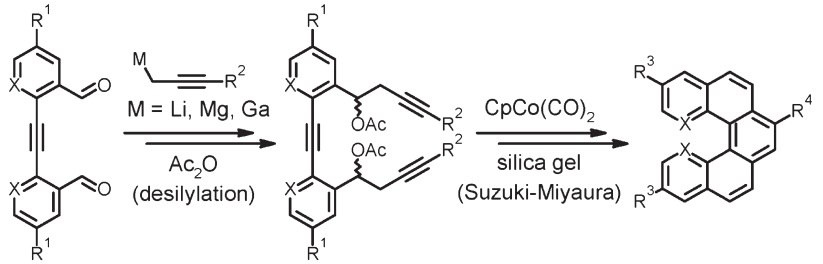

A general synthetic methodology for the preparation of functionalized (hetero)helicenes has been developed. It employs the sequence of a double propargyl organometallics (Li, Mg, Ga/In) addition to a tolan-2,2′-dialdehyde-type intermediate, a cobalt-catalyzed/cobalt-mediated [2 + 2 + 2] cycloisomerization of a triyne intermediate, and a double silica gel-assisted acetic acid elimination to receive pentahelicene, 1,14-diazapentahelicene, and 3,12-dichloro-, 3,12-dichloro-7-trimethylsilyl-, and 3,12-di-*tert*-butylpentahelicene. 3,12-Dichloropentahelicene undergoes a Suzuki−Miyaura coupling with aryl boronic acids (or ester) under palladium catalysis to afford 3,12-diarylpentahelicenes.

Introduction

Intramolecular [2 + 2 + 2] alkyne cycloisomerization catalyzed by Co^{I}, Ni^{0}, or Rh^{I} has been proven to be a powerful method for the synthesis of carbohelicenes,[1] azahelicenes,[2] helquats,[3] and helicene-like compounds.[4] Its strength consists of a simultaneous formation of three,[1−4] five,[5] or six cycles[6] in a single cyclization step, which allows for a rapid construction of (hetero)helicene backbones. The classical or newly developed alternative methods[7] such as photodehydrocyclization of stilbene-type precursors,[7a] Diels−Alder cycloaddition,[7b] ring-closing olefin metathesis,[7c] carbenoid coupling,[7d] McMurry reaction,[7e] Friedel−Crafts cycloacylation[7f] or cycloalkylation,[7g] homolytic aromatic substitution,[7h] C−H arylation reaction,[7i] cycloisomerization of biaryl alkynes,[7j] Stille−Kelly reaction,[7k] rearrangement of benzannulated enediynes,[7l] aromatic oxy-Cope rearrangement,[7m] cycloaddition of aromatic arynes,[7n] binaphthyl bisphosphonium salt conversion,[7o] and Stevens rearrangement[7p] are so far less effective in this regard.

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Although remarkable progress in the preparation of helicenes has recently been accomplished, the modular synthesis of their functionalized derivatives or heteroanalogues remains a challenging task.

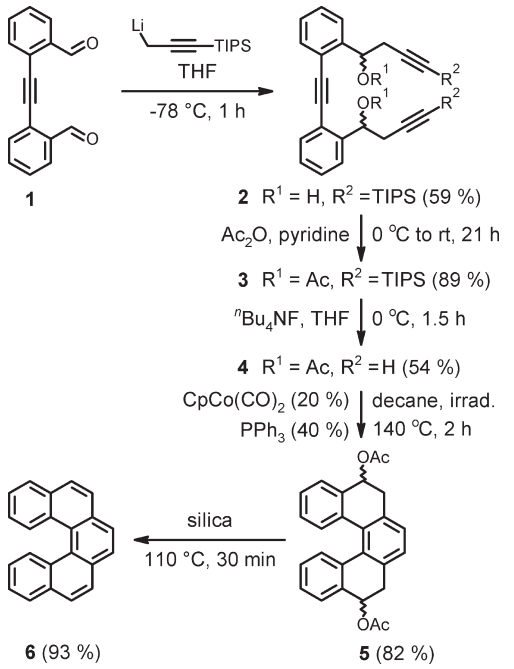
The [2 + 2 + 2] cycloisomerization approach leads directly to fully aromatic helicenes[1a] or to their tetrahydro derivatives,[1b,c,8] which have to be oxidized. Even though such an aromatization step can be done with $Ph_3C^+BF_4^-$ (refs 1b and 1c) or MnO_2 under microwave irradiation,[2a] an alternative is required as serious difficulties occasionally occur. Either a lipophilic helicene compound can be difficult to separate from the Ph_3CH side product or the oxidation depends on the MnO_2 activity, which critically varies from batch to batch. Herein, we report on the innovated synthesis of pentahelicene and its functionalized congeners, which demonstrates facile aromatization of the helical backbone based on an acid-assisted elimination of the acetic acid. This approach is also an alternative way of assembling the key triyne intermediate, which further extends the scope of the [2 + 2 + 2] alkyne cycloisomerization in the synthesis of helicenes. Relying on the results described below, we have recently employed this methodology in the synthesis of [11]helicene.[6]

Results and Discussion

Synthesis of Pentahelicene 6. First, we embarked on the synthesis of the prototypal pentahelicene **6** to check the viability of the proposed approach (Scheme 1). The easily accessible dialdehyde **1** (ref 9) was treated with lithiated 1-(triisopropylsilyl)-propyne to provide triyne **2** as a mixture of diastereomers. We did not detect homoallenyl alcohols arising through a propargylic rearrangement in the material purified by column chromatography. After acetylation of the free hydroxy groups (**2** → **3**) and desilylation of the pendant alkyne units (**3** → **4**), we attempted the key [2 + 2 + 2] cycloisomerization to form the helical scaffold. Upon applying Co^I-catalysis, we obtained a derivative of tetrahydropentahelicene **5** as a mixture of diastereomers difficult to separate by column chromatography. The last step of the synthetic sequence proceeded smoothly. The diacetoxy derivative **5** adsorbed on silica gel underwent spontaneously acetic acid elimination at elevated temperature to provide pure pentahelicene **6**[1a,7p] in a high yield.

Thus, the concept of acetic acid elimination to aromatize tetrahydrohelicene derivatives has been found to be feasible.

SCHEME 1. The Synthesis of Pentahelicene 6



In connection with ongoing projects on helicene-based materials, we further attempted the preparation of the required helicene molecules or building blocks employing this newly developed synthetic methodology described above.

Synthesis of 3,12-Dichloropentahelicene 13. For the sake of preparing suitable pentahelicene derivatives amenable to subsequent functionalization, we focused on the synthesis of the so-far unknown 3,12-dichloropentahelicene **13** (Scheme 2).

We reasoned that the aryl chloride moiety would be, on the one hand, unreactive in order to survive the presence of organometallics during the synthesis and, on the other hand, reactive enough to undergo a Suzuki−Miyaura coupling after the pentahelicene backbone construction. The preparation of **13** started from commercially available 5-chlorosalicylaldehyde **7**, which was converted to the corresponding triflate **8**.[10] Its reaction with gaseous acetylene under Pd^{II}/Cu^I catalysis smoothly led to dialdehyde **9** but the product was only sparingly soluble in nonpolar or slightly polar solvents. Due to this fact, the double addition of $LiCH_2C{\equiv}CTIPS$ in ether solvents at low temperature was rather difficult to pursue (cf. reaction **1** → **2**) except for a very small quantity of the starting material **9**. Thus, we applied an alternative method relying on propargyl bromide addition to **9** in the presence of the stoichiometric amount of gallium and catalytic amount of indium.[11] By adding a hot (50 °C), close-to-saturated solution of dialdehyde **9** in THF to the preformed organogallium reagent in the same solvent kept at 0 °C, the double addition proceeded at room temperature. The required homopropargyl-type triyne **10** was isolated in an acceptable yield as a mixture of diastereomers. It is worth noting that the choice of the propargyl organometallics (Li, Mg, Ga), which were added to the aromatic dialdehydes mentioned in this study, was on an empirical basis in order to minimize the

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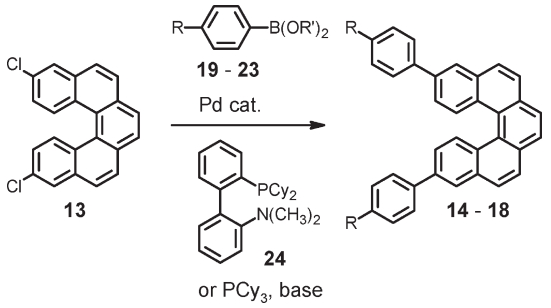
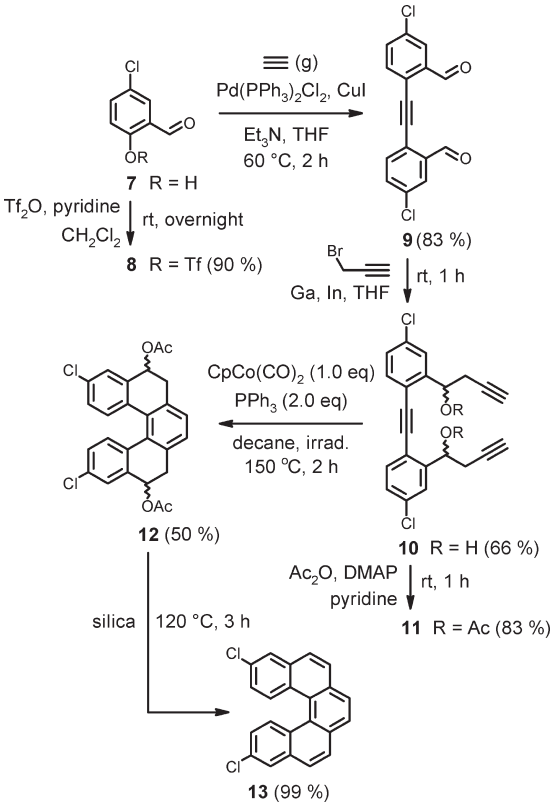
TABLE 1. The Suzuki−Miyaura Coupling between 3,12-Dichloropentahelicene 13 and Arylboronic Acids 19−23



entry	R	conditions (mol %)[a]	product (%)[b]
1	H	**19** (2.4 equiv), $Pd(CH_3CN)_2Cl_2$ (25), PCy_3 (50), TBAF (6 equiv), 90 °C	**14** (88)
2	OH	**20** (4 equiv), $Pd(CH_3CN)_2Cl_2$ (40), PCy_3 (80), TBAF (10 equiv), 85 °C	**15** (98)
3[c]	NH_2	**21** (4 equiv), $Pd(OAc)_2$ (40), **24** (80), Cs_2CO_3 (9 equiv), dioxane, water, 85 °C	**16** (72)
4	CH_3—C≡C	**22** (4 equiv), $Pd(OAc)_2$ (40), **24** (80), Cs_2CO_3 (5 equiv), dioxane, 85 °C	**17** (45)
5	TIPS—C≡C	**23** (4 equiv), $Pd(OAc)_2$ (10), **24** (20), Cs_2CO_3 (4 equiv), dioxane, 80 °C	**18** (50)

[a]Free boronic acid was used unless noted otherwise, the reaction period was 20 h. [b]Isolated yield. [c]Boronic acid pinacol ester was used.

SCHEME 2. The Synthesis of 3,12-Dichloropentahelicene 13



allene-type byproduct(s) formation and to keep the reaction partners soluble under the given conditions. After acetylation (**10** → **11**), no desilylation step was necessary (cf. **3** → **4**) and the material **11** was subjected directly to Co^I-mediated [2 + 2 + 2] cycloisomerization in order to afford functionalized tetrahydropentahelicene **12** (utilizing a catalytic amount of the Co^I catalyst led to an unsatisfactory yield). A smooth aromatization by acetic acid elimination completed the synthesis of 3,12-dichloropentahelicene **13**, whose structure was unambiguously confirmed by a single-crystal analysis (Figure 1).[12]

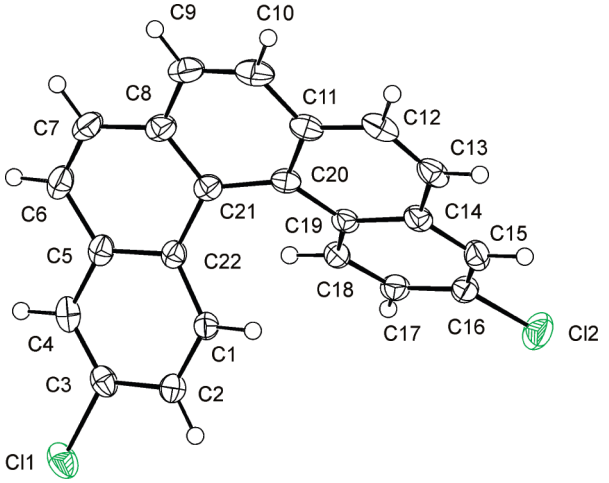


FIGURE 1. The single-crystal molecular structure of **13**.

Suzuki−Miyaura Couplings of 3,12-Dichloropentahelicene 13. Suzuki−Miyaura coupling chemistry with helicene halides has practically been unexplored[13] and, to the best of our knowledge, never reported in connection with helicene chlorides. We found that unactivated dichloropentahelicene **13** reacted with aryl boronic acids **19**, **20** (commercially available), **22**,[14] and **23**[15] or boronic acid pinacol ester **21** (commercially available) under palladium catalysis in the presence of electronically rich, bulky phosphines such as PCy_3 or Buchwald's DavePhos ligand **24** (Table 1).[16]

Depending on the structure of the aryl boronic acid derivatives, we employed either a solvent-free[17] (entries 1 and 2) or

(12) CCDC-784073 and CCDC-784074 contain the supplementary crystallographic data for **13** and **14**, respectively. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax +44(1223) 336033; e-mail deposit@ccdc.cam.ac.uk.

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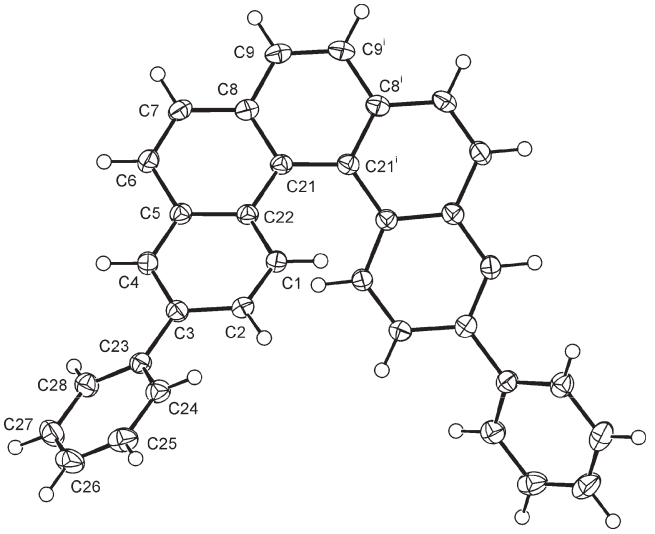


FIGURE 2. The single-crystal molecular structure of **14** with the atom numbering scheme. The second part of the molecule is generated by the operation of its 2-fold axis. Symmetry code (i): $1-x, y, 0.5-z$.

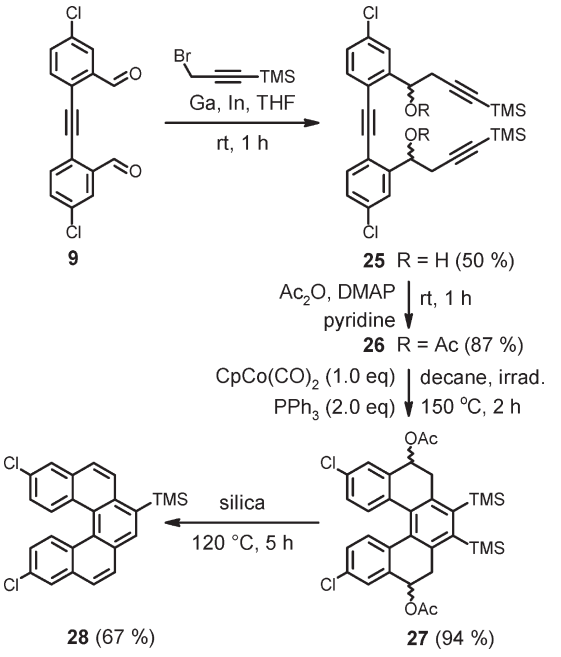
solution[18] (entries 3−5) Suzuki−Miyaura coupling reaction condition to obtain the products **14**−**18** in moderate to excellent yields. The structure of 3,12-diphenylpentahelicene **14** was proven by a single-crystal analysis (Figure 2).[12]

Synthesis of 3,12-Dichloro-7-trimethylsilylpentahelicene 28. Aiming at the synthesis of other functionalized pentahelicene derivatives, we attempted the preparation of TMS-substituted 3,12-dichloropentahelicene **28** (Scheme 3).

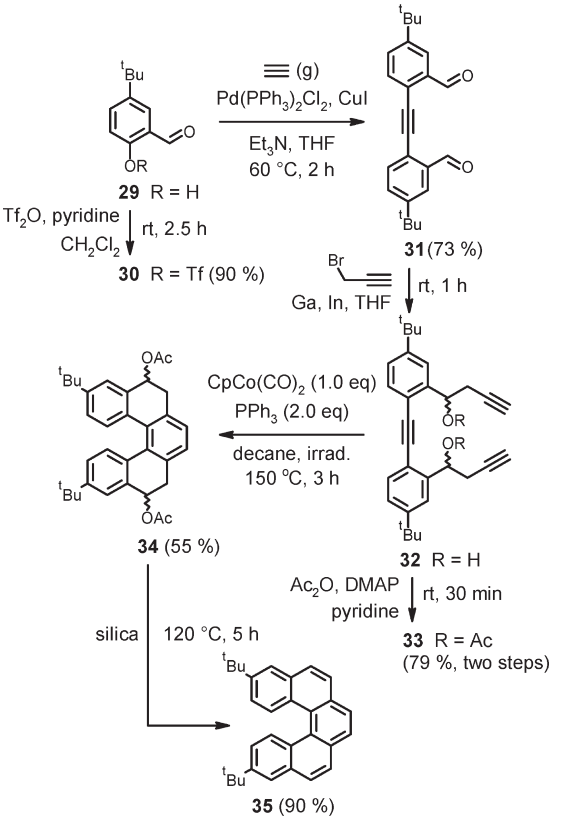
With the exception of the utilization of an organogallium reagent derived from silylated propargyl bromide, the synthetic route followed that developed for **13**. It is worth noting that the homopropargyl-type triyne **25** dominated exclusively over the homoallenyl one. After the acetylation and cycloisomerization steps (**25** → **26** → **27**), we completed the synthesis of **28** by silica gel-assisted aromatization. However, this process was accompanied by a partial desilylation of the product affording the monosilylated product **28**.

Synthesis of 3,12-Di-*tert*-butylpentahelicene 35 and 1,14-Diazapentahelicene 41. While the reaction scheme for the preparation of 3,12-di-*tert*-butylpentahelicene **35** (Scheme 4) was the same as that for **13** regardless of the different electronic nature of the substituents (Cl versus *t*-Bu) (**29** → **35**), the synthesis of the heterocyclic analogue 1,14-diazapentahelicene **41** (refs 2a and 19) required a modification (Scheme 5, **36** → **41**). Dialdehyde **37** was practically insoluble in ether solvents and, therefore, the use of the organogallium reagent generated from propargyl bromide resulted in a low yield of **38**. However, by treating the suspension of **37** with propargyl magnesium bromide in a mixture of ether−THF at low temperature, the homopropargyl-type triyne **38** was readily formed and its acetyl derivative **39** was isolated in a moderate yield. The cyclized product **40** was subjected to the final acetic acid elimination by using silica gel either plain or preferably wetted with triflic acid to afford azahelicene **41**.

SCHEME 3. The Synthesis of Silylated 3,12-Dichloropentahelicene 28



SCHEME 4. The Synthesis of 3,12-Di-*tert*-butylpentahelicene 35



Conclusions

In conclusion, we have developed a general synthetic protocol for the nonphotochemical[20] preparation of pentahelicene **6**, its dichloro derivative **13**, TMS derivative **28**, di-*tert*-butyl

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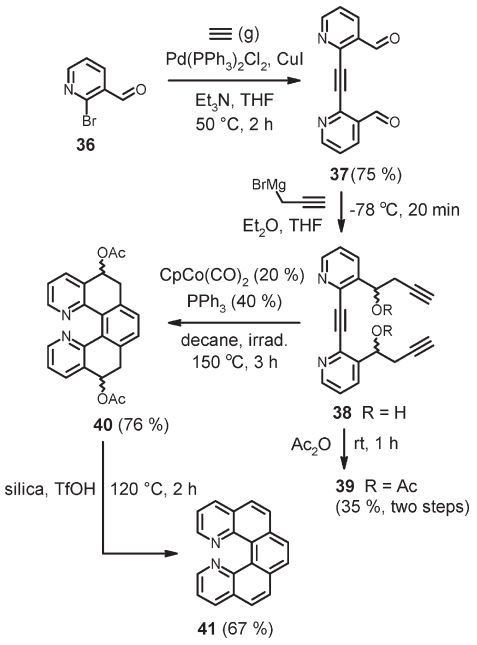
SCHEME 5. The Synthesis of 1,14-Diazapentahelicene 41



derivative **35**, or diaryl derivatives **14**−**18**, and diazapentahelicene **41**. The modular nature of the approach permits variation of the starting building blocks and the uniform employment of the sequence of double propargyl organometallics addition to a tolan-2,2′-dialdehyde-type intermediate, a cobalt-catalyzed/cobalt-mediated [2 + 2 + 2] cycloisomerization of a triyne intermediate, and a silica gel-assisted acetic acid elimination to receive a fully aromatic product. 3,12-Dichloropentahelicene **13** undergoes Suzuki−Miyaura couplings with aryl boronic acids (or ester) under palladium catalysis representing the first successful reaction of this type in helicene chemistry. Thus, we have demonstrated a practical methodology for the preparation of various functionalized pentahelicenes, which can serve as a paradigm for the synthesis of higher[6] or differently functionalized helicenes. Physical and physicochemical studies on the pentahelicene molecules described in this report are in progress.

Experimental Section

General. ^{1}H NMR spectra were measured at 200.04, 400.13, and 499.88 or 500.13 MHz, ^{13}C NMR spectra at 100.6 and 125.8 MHz, in $CDCl_3$ with TMS as an internal standard, and in d_6-DMSO. Chemical shifts are given in δ-scale, coupling constants J are given in Hz. HMBC experiments were set up for $J_{C-H} = 5$ Hz. For correct assignment of both ^{1}H and ^{13}C NMR spectra of key compounds, the COSY, HMQC, and HMBC experiments were performed. IR spectra were measured in $CHCl_3$ or CCl_4. EI mass spectra were determined at an ionizing voltage of 70 eV, m/z values are given along with their relative intensities (%). Standard 70 eV spectra were recorded in the positive ion mode. TOF EI spectra were measured using the orthogonal acceleration time-of-flight mass spectrometer. The sample was dissolved in chloroform, loaded into a quartz cup of the direct probe, and inserted into the ion source. The source temperature was 220 °C. For exact mass measurement, the spectra were internally calibrated with perfluorotri-*n*-butylamine. ESI mass spectra were recorded by using the classic ion trap mass spectrometer equipped with an electrospray ion source. The mobile phase consisted of methanol/water (9:1), flow rate of 200 μL/min. The samples were dissolved in chloroform, diluted with the mobile phase, and injected using a 5-μL loop. The exact mass was measured using the hybrid mass spectrometer equipped with an electrospray ion source. The mobile phase consisted of methanol/water (9:1), flow rate of 100 μL/min. The sample was dissolved in chloroform and diluted with the mobile phase and injected using a 2-μL loop. The mass spectra were internally calibrated using known impurities in the mobile phase. TOF ESI mass spectra were recorded using the micro mass spectrometer. The mobile phase consisted of acetonitrile/water (1:1), flow rate of 25 μL/min. Samples dissolved in chloroform were diluted with the mobile phase and injected using a manual injector (2 μL). For exact mass measurement, the mass spectra were internally calibrated using PEG oligomers. Accurate mass measurements were obtained by the EI, ESI, TOF EI, or TOF ESI MS. Commercially available catalysts and reagent grade materials such as phenyl boronic acid **19**, 4-hydroxyphenylboronic acid **20**, and 4-aminophenylboronic acid pinacol ester **21** were used as received. 4-Tris(1-methylethyl)silane-acetylene boronic acid **23** was prepared according to the literature procedure.[15] Decane and distilled water were degassed by 3 freeze−pump−thaw cycles before use; triethylamine was distilled from calcium hydride under argon; THF was freshly distilled from sodium/benzophenone under nitrogen, and dioxane was distilled from calcium hydride and degassed by 3 freeze−pump−thaw cycles before use. Commercial pure solvents were used directly when growing crystals for the X-ray analysis. TLC was performed on silica gel F_{254}-coated aluminum sheets and spots were detected by the solution of $Ce(SO_4)_2 \cdot 4H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). Flash chromatography was performed on silica gel (0.040−0.063 mm or <0.063 mm) or on silica gel cartridges (0.040−0.063 mm) used in automatic flash purification systems.

X-ray Crystallography. Single-crystal diffraction data for **13** and **14** were obtained from the kappa geometry CCD diffractometer by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The structures were solved by direct methods (SIR92)[21] and refined by full-matrix least-squares based on F^2 (SHELXL97).[22] The hydrogen atoms were found on difference Fourier maps and recalculated into the idealized position; all were fixed into their positions (riding model) with assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(pivot atom).

1,1′-(Ethyne-1,2-diyldibenzene-2,1-diyl)bis{4-[tris(1-methylethyl)-silyl]but-3-yn-1-ol} (2). The Schlenk flask was charged with a solution of 1-triisopropylsilyl-1-propyne (3.0 mL, 12.52 mmol, 2.16 equiv) in THF (30 mL) under argon. The reaction was cooled to −78 °C, a butyllithium solution (1.6 M in hexanes, 8.0 mL, 12.8 mmol, 2.2 equiv) was added, and the reaction mixture was stirred at the same temperature for 2 h. Then a solution of dibenzyl aldehyde **1** (1.358 g, 5.80 mmol) in THF (30 mL) was added and the reaction mixture was stirred at −78 °C for 1 h and then at room temperature for another hour. The reaction mixture was poured into a saturated aqueous solution of NH_4Cl (50 mL) and extracted with diethyl ether (5 × 60 mL), then the combined organic portions were washed with water (2 × 20 mL) and dried over anhydrous $MgSO_4$. The solvents were removed in

(20) The $CpCo(CO)_2/PPh_3$ catalyzed [2 + 2 + 2] cycloisomerization under halogen lamp irradiation is not a truly photochemical process with respect to the triyne substrate. Such an irradiation by visible light usually activates the catalyst to provide a higher preparative yield of the cyclized product but the reaction can technically proceed in the absence of light.

(21) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(22) Sheldrick, G. M. *SHELXL97*; University of Göttingen, Göttingen, Germany, 1997.

vacuo and the residue was purified by flash chromatography on silica gel (petroleum ether−diethyl ether 90:10 to 85:15) to provide triyne **2** (2.127 mg, 59%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): 1.05 (42 H, m), 2.72 (2 H, dd, J = 17.0, 3.2), 2.74 (2 H, dd, J = 17.0, 3.2), 3.04 (4 H, dd, J = 17.0, 4.7), 5.37 (2 H, m), 7.27 (2 H, dt, J = 7.7, 7.7, 1.0), 7.38 (2 H, dt, J = 7.6, 7.6, 1.4), 7.52 (2 H, dd, J = 7.7, 1.4), 7.62 (2 H, d, J = 7.7). ^{13}C NMR (125 MHz, $CDCl_3$): 11.2 (q), 18.6 (q), 29.97 (t), 30.04 (t), 70.4 (d), 84.3 (s), 92.2 (s), 104.1 (s), 120.4 (s), 125.5 (d), 127.5 (d), 128.8 (d), 132.6 (d), 143.8 (s). IR (CCl_4): 3615 w, 3560 w, 3097 vw, 3070 w, 3030 w, 2866 vs, 2170 m, 1601 vw, 1489 w, 1463 m, 1451 m, 1383 w, 1367 w, 1332 w, 1309 w, 1194 w, 1160 vw, 1106 w, 1057 m, 1019 m, 996 m, 883 m, 678 s, 663 m, 607 w, 458 w cm^{-1}. EI MS: 626 ($M^{+\bullet}$, 4), 608 (40), 565 (16), 431 (100), 413 (52), 387 (40), 329 (7), 283 (12), 257 (29), 235 (39), 178 (22), 153 (47), 115 (64), 75 (69), 59 (93). HR EI MS: calcd for $C_{40}H_{58}O_2Si_2$ 626.3975, found 626.3994.

Ethyne-1,2-diylbis{benzene-2,1-diyl-1-[tris(1-methylethyl)silyl]-but-1-yne-4,4-diyl} Diacetate (3). To a solution of dihydroxy derivative **2** (512 mg, 0.817 mmol) in pyridine (6 mL) was added acetanhydride (620 μL, 6.52 mmol, 8.0 equiv) at 0 °C. The reaction mixture was then allowed to slowly reach room temperature while stirring and stirring was continued at the same temperature for an additional 21 h. The mixture was poured into ice and extracted with diethyl ether (4 × 50 mL), then the combined organic portions were washed with a 10% solution of $CuSO_4$ (4 × 15 mL) and a saturated aqueous solution of $KHCO_3$ (3 × 15 mL), dried over anhydrous Na_2SO_4, and evaporated in vacuo to afford the diacetoxy derivative **3** (514 mg, 89%) as a viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): 1.00−1.04 (42 H, m), 2.129 (3 H, s), 2.134 (3 H, s), 2.86 (2 H, dd, J = 17.2, 6.6), 2.89 (2 H, dd, J = 17.1, 6.5), 3.08 (2 H, dd, J = 17.2, 5.2), 3.09 (2 H, dd, J = 17.2, 5.3), 6.40 (1 H, dd, J = 6.6, 5.2), 6.41 (1 H, dd, J = 6.5, 5.3), 7.28 (2 H, dd, J = 7.5, 1.3), 7.33 (2 H, dt, J = 7.5, 7.5, 1.3), 7.52 (2 H, dt, J = 7.5, 7.5, 1.3), 7.57 (2 H, dd, J = 7.5, 1.3). ^{13}C NMR (125 MHz, $CDCl_3$): 11.2 (q), 18.5 (q), 21.0 (q), 26.67 (t), 26.77 (t), 71.89 (d), 71.97 (d), 83.11 (s), 83.17 (s), 92.7 (s), 103.33 (s), 103.36 (s), 120.94 (s), 120.96 (s), 126.1 (d), 126.2 (d), 127.84 (d), 127.86 (d), 128.60 (d), 128.62 (d), 132.6 (d), 140.5 (s), 140.6 (s), 169.7 (s). IR (CCl_4): 3070 w, 3022 w, 2958 s, 2944 s, 2925 m, 2891 m, 2866 s, 2177 m, 1750 s, 1603 vw, 1572 vw, 1493 w, 1464 m, 1453 w, 1428 w, 1383 w, 1372 m, 1289 w, 1234 s, 1216 s, 1102 w, 1030 m, 996 w, 937 w, 884 m, 678 m, 663 m, 644 w, 613 w cm^{-1}. EI MS: 710 ($M^{+\bullet}$, 0.6), 667 (2), 607 (6), 565 (5), 477 (2), 413 (3), 349 (2), 307 (3), 215 (2), 173 (100), 115 (10), 73 (10), 59 (14), 43 (11). HR EI MS: calcd for $C_{44}H_{62}O_4Si_2$ 710.4187; found 710.4176.

Ethyne-1,2-diylbis(benzene-2,1-diylbut-1-yne-4,4-diyl) Diacetate (4). A Schlenk flask was charged with diacetoxy derivative **3** (490 mg, 0.689 mmol) and flushed with argon. THF (10 mL) was added and the resulting solution was cooled to 0 °C. A tetrabutylammonium fluoride solution (0.964 M in THF, 4.3 mL, 4.15 mmol, 6.0 equiv) was added. After stirring at 0 °C for 1.5 h, the solvent was removed in vacuo. The crude product was chromatographed on silica gel (hexane−diethyl ether 80:20 to 60:40) to provide triyne **4** (147 mg, 54%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 1.99 (2 H, t, J = 2.6), 2.146 (3 H, s), 2.151 (3 H, s), 2.85 (2 H, ddd, J = 17.0, 6.6, 2.6), 2.86 (2 H, ddd, J = 17.0, 6.6, 2.6), 2.96 (2 H, ddd, J = 17.0, 5.5, 2.6), 2.97 (2 H, ddd, J = 17.0, 5.5, 2.6), 6.42 (1 H, t, J = 6.2), 6.43 (1 H, t, J = 6.2), 7.32 (2 H, dt, J = 7.5, 7.5, 1.4), 7.38 (2 H, dt, J = 7.5, 7.5, 1.3), 7.51 (2 H, ddd, J = 7.5, 1.3, 0.6), 7.60 (2 H, ddd, J = 7.5, 1.4, 0.6). ^{13}C NMR (125 MHz, $CDCl_3$): 21.0 (q), 25.56 (t), 25.6 (t), 70.8 (d), 71.50 (d), 71.54 (d), 79.4 (s), 91.95 (s), 91.97 (s), 121.09 (s), 121.14 (s), 125.89 (d), 125.92 (d), 128.0 (d), 128.74 (d), 128.75 (d), 132.60 (d), 132.63 (d), 140.5 (s), 169.8 (s). IR ($CHCl_3$): 3310 s, 3070 w, 3030 m, 2215 vw, 2125 w, 1743 vs, 1602 w, 1571 w, 1494 m, 1452 m, 1429 m, 1422 m, 1374 s, 1341 w, 1295 m, 1239 vs, 1163 w, 1103 w, 1049 s, 1032 s, 937 w, 820 w, 650 s, 639 s, 608 w, 566 w, 514 w, 448 w cm^{-1}. EI MS: 398 ($M^{+\bullet}$, 0.4), 356 (1), 314 (1), 295 (10), 278 (44), 257 (100), 239 (26), 228 (68), 215 (6), 202 (14), 189 (6), 178 (12), 43 (85). HR EI MS: not recorded due to a low intensity of the molecular ion.

5,6,9,10-Tetrahydropentahelicene-5,10-diyl Diacetate (5). A two-necked Schlenk flask was charged with triyne **4** (105 mg, 0.264 mmol) and flushed with argon. Decane (2.5 mL) was added and then a solution of PPh_3 (28.0 mg, 0.107 mmol, 40 mol %) in decane (0.5 mL) and a solution of $CpCo(CO)_2$ (7.0 μL, 0.053 mmol, 20 mol %) in decane (0.5 mL) were added. The reaction mixture was heated at 140 °C for 2 h under simultaneous irradiation with a halogen lamp. The solvent was removed in vacuo and the crude product was chromatographed on silica gel (hexane−diethyl ether 100:0 to 80:20) to provide the tetrahydro [5[helicene derivative **5** (86.4 mg, 82%) as an amorphous solid. ^{1}H NMR (200 MHz, $CDCl_3$): 1.96 (3 H, br s), 2.32 (3 H, br s), 2.65−3.37 (6 H, m), 5.89−6.26 (2 H, m), 7.00−7.59 (10 H, m). IR ($CHCl_3$): 3104 w, 3067 w, 3029 m, 1730 vs, 1605 w, 1572 w, 1490 m, 1435 m, 1423 m, 1374 s, 1329 w, 1246 vs, 1175 m, 1161 w, 1136 w, 1113 w, 1038 s, 1023 s, 990 s, 948 m, 813 m, 686 w, 611 m, 536 w, 510 w cm^{-1}. EI MS: 398 ($M^{+\bullet}$, 20), 338 (7), 278 (100), 263 (13), 252 (11), 178 (7), 138 (17), 97 (7), 71 (12), 57 (13), 45 (11). HR EI MS: calcd for $C_{26}H_{22}O_4$ 398.1518, found 398.1521.

Pentahelicene (6). To a solution of tetrahydro [5]helicene derivative **5** (72.0 mg, 0.181 mmol) in dichloromethane (5 mL) was added silica gel (3.6 g). The solvent was evaporated in vacuo and the solvent-free mixture was heated at 110 °C for 30 min. The product was extracted from silica gel by dichloromethane (100 mL). Removal of the solvent in vacuo led to pentahelicene **6** (46.8 mg, 93%) as an amorphous solid.[1a,7p]

2,2′-Ethyne-1,2-diylbis(5-chlorobenzaldehyde) (9). A Schlenk flask was charged with triflate **8** (557 mg, 1.93 mmol), $Pd(PPh_3)_2Cl_2$ (56.1 mg, 0.080 mmol, 4 mol %), and CuI (7.4 mg, 0.040 mmol, 2 mol %) and filled with acetylene. A mixture of Et_3N (2 mL) and THF (1 mL) was added and the flask was filled with acetylene. The reaction mixture was stirred at 60 °C for 2 h. The solvents were removed in vacuo and the crude product was chromatographed on silica gel (hexane−dichloromethane 60:40) to provide dialdehyde **9** (243 mg, 83%) as a pale amorphous solid. Mp: 201 °C (acetone). ^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (2 H, dd, J = 8.4, 2.0), 7.64 (2 H, d, J = 8.4), 7.93 (2 H, d, J = 2.0), 10.51 (1 H, s). ^{13}C NMR (101 MHz, $CDCl_3$): 91.6 (s), 123.2 (s), 128.4 (d), 133.9 (d), 134.8 (d), 136.3 (s), 137.2 (s), 189.5 (d). IR ($CHCl_3$): 3067 vw, 2846 w, 2742 w, 1720 w, 1697 vs, 1592 w, 1586 w, 1554 vw, 1484 m, 1406 w, 1388 w, 1305 vw, 1278 w, 1246 m, 1186 s, 1114 w, 1079 w, 908 m, 900 w, 833 m, 703 vw, 658 w, 630 w cm^{-1}. EI MS: 302 ($M^{+\bullet}$, 88), 274 (16), 267 (74), 246 (45), 239 (94), 210 (41), 176 (100), 160 (3), 150 (15), 105 (15), 98 (9), 87 (10), 74 (8). HR EI MS: calcd for $C_{16}H_8O_2Cl_2$ 301.9901, found 301.9907.

1,1′-[Ethyne-1,2-diylbis(5-chlorobenzene-2,1-diyl)]bisbut-3-yn-1-ol (10). A Schlenk flask was charged with gallium (50.6 mg, 0.730 mmol, 2.2 equiv), indium (3.8 mg, 0.030 mmol, 10 mol %), THF (0.5 mL), and propargyl bromide (146 μL, 1.33 mmol, 80 w % in toluene, 4.0 equiv) under argon and then vigorously stirred at 10 °C for 1 h. After complete consumption of gallium, a solution of the dialdehyde **9** (100 mg, 0.330 mmol, 1.0 equiv) in THF (3 mL) was slowly added and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo and the saturated aqueous solution of $NaHCO_3$ (100 mL) was added to the crude mixture. The product was extracted with dichloromethane (3 × 200 mL) and the combined organic portions were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the crude product was chromatographed on silica gel (hexane−ethyl acetate 70: 30) to provide a mixture of the diastereoisomers of dialdehyde **10** (84.0 mg, 66%) as a pale amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): 2.14 (2 H, t, J = 2.4, one diastereoisomer), 2.15 (2 H, t, J = 2.4, one

diastereoisomer), 2.58−2.65 (2 H, m), 2.83−2.90 (2 H, m), 5.30−5.38 (2 H, m), 7.29 (2 H, dd, J = 8.4, 2.0), 7.44 (2 H, d, J = 8.4), 7.63 (1 H, d, J = 2.0). ^{13}C NMR (101 MHz, $CDCl_3$): 28.4 (t), 28.5 (t), 69.9 (d), 70.0 (d), 71.5 (d), 71.6 (d), 80.1 (s), 80.3 (s), 91.8 (s), 91.9 (s), 118.5 (s), 126.00 (d), 126.02 (d), 128.0 (d), 133.45 (d), 133.47 (d), 135.4 (s), 145.6 (s). IR ($CHCl_3$): 3600 m, 3307 vs, 3069 vw, 2927 m, 2855 m, 2121 vw, 1595 m, 1559w, 1489 s, 1467 m, 1407 m, 1307 w, 1270 m, 1180 m, 1117 m, 1092 vs, 1056 s, 902 m, 898 m, 825 s, 685 w, 642 s, 508 w cm^{-1}. ESI MS: 381 ([M − H]$^-$). HR ESI MS: calcd for $C_{22}H_{15}O_2Cl_2$ 381.0455, found 381.0452.

Ethyne-1,2-diylbis[(5-chlorobenzene-2,1-diyl)but-1-yne-4,4-diyl] Diacetate (11). To a solution of **10** (61.3 mg, 0.160 mmol) and 4-(dimethylamino)pyridine (2.3 mg, 0.020 mmol, 12 mol %) in pyridine (0.25 mL) was added acetic anhydride (0.50 mL) dropwise and the reaction mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo and the crude product was chromatographed on silica gel (hexane−ethyl acetate 70:30) to provide a mixture of two diastereoisomers of diacetoxy derivative **11** (62.0 mg, 83%) as a white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): 2.02 (2 H, t, J = 2.6), 2.16 (6 H, br s), 2.77−2.85 (2 H, m), 2.87−2.96 (2 H, m), 6.34 (2 H, t, J = 6.0, one diastereoisomer), 6.37 (2 H, t, J = 6.0, one diastereoisomer), 7.29 (2 H, dd, J = 8.4, 2.6), 7.48−7.51 (4 H, m). ^{13}C NMR (101 MHz, $CDCl_3$): 21.0 (q), 25.50 (t), 25.53 (t), 70.80 (d), 70.85 (d), 71.2 (d), 78.69 (s), 78.73 (s), 91.7 (s), 119.3 (s), 126.36 (d), 126.38 (d), 128.4 (d), 133.62 (d), 133.64 (d), 135.06 (s), 135.08 (s), 142.3 (s), 169.6 (s). IR ($CHCl_3$): 3309 m, 2927 w, 2855 w, 2125 vw, 1744 vs, 1595 w, 1559 vw, 1490 m, 1468 w, 1408 w, 1374 m, 1279 w, 1270 m, 1236 vs, 1182 w, 1116 w, 1046 m, 1032 m, 1091 m, 908 w, 826 m, 653 m, 641 m, 608 w, 508 w cm^{-1}. EI MS: 466 ($M^{+\bullet}$, 21), 367 (9), 346 (87), 325 (91), 312 (100), 300 (33), 290 (85), 276 (97), 262 (97), 255 (80), 226 (95), 212 (13), 200 (5), 176 (16). HR EI MS: calcd for $C_{26}H_{20}O_4Cl_2$ 466.0739, found 466.0755.

3,12-Dichloro-5,6,9,10-tetrahydropentahelicene-5,10-diyl Diacetate (12). A solution of triyne **11** (336 mg, 0.720 mmol), PPh_3 (378 mg, 1.44 mmol, 2.0 equiv), and $CpCo(CO)_2$ (95 μL, 0.720 mmol, 1.0 equiv) in decane (20 mL) was heated at 150 °C for 2 h under simultaneous irradiation with a halogen lamp. The solvent was then removed in vacuo and the crude product was chromatographed on silica gel (hexane−acetone 90:10) to provide a mixture of two diastereoisomers of helicene diacetoxy derivative **12** (165 mg, 50%) as a yellowish amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.95 (3 H, s), 2.32 (3 H, s), 2.77−2.81 (1 H, m), 2.96−3.00 (1 H, m), 3.14−3.26 (2 H, m), 5.92 (1 H, s), 6.04−6.11 (1 H, m), 7.03−7.07 (2 H, m), 7.14−7.24 (4 H, m), 7.37 (1 H, s), 7.54 (1 H, s). IR ($CHCl_3$): 3029 w, 3013 w, 2954 w, 2929 w, 2895 w, 2853 w, 2840 w, 1734 s, 1599 w, 1590 w, 1564 vw, 1488 w, 1482 w, 1407 w, 1347 m, 1242 vs, 1174 w, 1103 w, 1078 w, 1038 m, 833 m, 688 vw, 603 w, 525 w cm^{-1}. ESI MS: 489 ([M + Na]$^+$). HR ESI MS: calcd for $C_{26}H_{20}O_4NaCl_2$ 489.0636, found 489.0637.

3,12-Dichloropentahelicene (13). Helicene diacetate **12** (70.0 mg, 0.150 mmol) was dissolved in dichloromethane (2.0 mL) and added to silica gel (8.0 g). The solvent was evaporated in vacuo and the resulting solid was put under argon and stirred at 120 °C for 3 h. The silica gel with absorbed product was loaded to the silica gel column and directly chromatographed (hexane) to provide the desired product **13** (51.5 mg, 99%) as a crystalline yellowish solid. Mp: 270 °C (dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$): 7.24 (2 H, dd, J = 9.0, 2.4), 7.84 (2 H, d, J = 8.4), 7.88 (2 H, s), 7.91 (2 H, d, J = 8.4), 7.93 (2 H, d, J = 2.4), 8.38 (2 H, d, J = 9.0). ^{13}C NMR (101 MHz, $CDCl_3$): 125.2 (d), 126.6 (s), 126.7 (d), 127.5 (d), 127.6 (d), 128.9 (s), 130.2 (d), 132.0 (s), 132.4 (s), 133.7 (s). IR ($CHCl_3$): 3056 w, 1618 w, 1597 w, 1554 w, 1507 w, 1485 m, 1455 vw, 1434 m, 1384 vw, 1333 w, 1312 w, 1264 w cm^{-1}. EI MS: 346 ($M^{+\bullet}$, 35), 310 (49), 276 (100), 248 (2), 155 (8), 137 (19). HR EI MS: calcd for $C_{22}H_{12}Cl_2$ 346.0316, found 346.0305. Crystallographic data: Single crystals of **13** were grown by slow evaporation from dichloromethane; $C_{22}H_{12}Cl_2$, M_r = 347.22, orthorhombic, *Pbca* (no. 61), a = 5.91540(10) Å, b = 20.1928(3) Å, c = 26.1972(4) Å, Z = 8, D_x = 1.474 Mg m^{-3}, colorless crystal of dimensions 0.4 × 0.1 × 0.03 mm^3, an absorption was neglected [μ = 0.41 mm^{-1}; 45726 diffraction collected (θ_{max} = 27.5°), 3446 independent (R_{int} = 0.043) and 2786 observed ($I > 2\sigma(I)$)], 217 refined parameters, goodness of fit 1.05, final R indices $R[F^2 > 2\sigma(F^2)]$ = 0.035, $wR(F^2)$ = 0.099, maximal/minimal residual electron density ($\Delta\rho_{max}$ = 0.23, $\Delta\rho_{min}$ −0.34 e·Å^{-3}). CCDC-784073 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_reguest/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44(1223) 336033; e-mail deposit@ccdc.cam.ac.uk.

3,12-Diphenylpentahelicene (14). A mixture of chloro helicene **13** (10.9 mg, 0.032 mmol), phenylboronic acid **19** (9.4 mg, 0.077 mmol, 2.4 equiv), $Pd(MeCN)_2Cl_2$ (2.0 mg, 0.008 mmol, 25 mol %), tricyclohexyl phosphine (4.5 mg, 0.016 mmol, 50 mol %), and TBAF (60.5 mg, 0.192 mmol, 6.0 equiv) was heated under argon at 90 °C overnight. Water (5 mL) was added to the mixture and the product was extracted with dichloromethane (3 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was chromatographed on silica gel (hexane−ethyl acetate 90:10) to provide the diphenyl derivative **14** (12 mg, 88%) as an amorphous white solid. Mp: 246−251 °C (dichloromethane−diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): 7.38−7.42 (2 H, m), 7.49−7.53 (4 H, m), 7.59 (2 H, dd, J = 8.8, 2.0), 7.79−7.82 (4 H, m), 7.89 (2 H, s), 7.92 (2 H, d, J = 8.6), 8.01 (2 H, d, J = 8.6), 8.19 (2 H, d, J = 2.0), 8.64 (2 H, d, J = 8.8). ^{13}C NMR (101 MHz, $CDCl_3$): 123.7 (d), 125.6 (d), 126.8 (d), 127.0 (s), 127.23 (d), 127.26 (d), 127.5 (d), 127.8 (d), 128.9 (d), 129.5 (d), 130.0 (s), 132.4 (s), 133.1 (s), 138.7 (s), 140.6 (s). IR ($CHCl_3$): 3052 m, 1621 w, 1600 m, 1578 w, 1556 w, 1493 m, 1486 m, 1446 m, 1435 w, 1384 w, 1322 w, 1169 w, 1143 w, 1102 w, 1077 w, 1042 w, 1024 w, 890 s, 854 m, 836 vs, 698 vs, 648 w, 581 m, 548 m, 521 w, 440 w. EI MS: 430 ($M^{+\bullet}$, 100), 413 (8), 387 (5), 352 (53), 350 (48), 339 (37), 276 (10), 176 (6). HR EI MS: calcd for $C_{34}H_{22}$ 430.1722, found 430.1712. Crystallographic data: Single crystals of **14** were grown by slow evaporation from the mixture of dichloromethane−diethyl ether; $C_{34}H_{22}$, M_r = 430.52, monoclinic, $C2/c$ (no. 15), a = 20.2803 (8) Å, b = 9.1154(3) Å, c = 12.4619(5) Å, β = 107.3695(18)°, Z = 4, D_x = 1.301 Mg m^{-3}, colorless crystal of dimensions 0.4 × 0.3 × 0.3 mm^3, an absorption was neglected [μ = 0.07 mm^{-1}, 12781 diffraction collected (θ_{max} = 27.5°), 2509 independent (R_{int} = 0.031) and 2039 observed ($I > 2\sigma(I)$)]. 154 parameters, goodness of fit 1.05, final R indices $R[F^2 > 2\sigma(F^2)]$ = 0.040, $wR(F^2)$ = 0.112, maximal/minimal residual electron density ($\Delta\rho_{max}$ = 0.20, $\Delta\rho_{min}$ −0.17 e·Å^{-3}). CCDC-784074 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_reguest/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44(1223) 336033; e-mail deposit@ccdc.cam.ac.uk.

Representative Procedure for Solvent-Free Suzuki−Miyaura Coupling: 4,4′-Pentahelicene-3,12-diyldiphenol (15). A mixture of chloro helicene **13** (103 mg, 0.300 mmol), 4-hydroxyphenylboronic acid **20** (166 mg, 1.20 mmol, 4.0 equiv), $Pd(MeCN)_2Cl_2$ (32.1 mg, 0.120 mmol, 40 mol %), tricyclohexyl phosphine (67.3 mg, 0.240 mmol, 80 mol %), and TBAF (947 mg, 3.01 mmol, 10.0 equiv) was heated under argon at 85 °C overnight. Water (5 mL) was added to the mixture and the product was extracted with dichloromethane (3 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was chromatographed on silica gel

(hexane−acetone 70:30) to provide the diphenol **15** (134 mg, 98%) as an amorphous white solid. ^{1}H NMR (400 MHz, d_6-DMSO): 6.91 (4 H, d, J = 8.4), 7.65 (2 H, dd, J = 8.8, 2.0), 7.73 (4 H, d, J = 8.4), 8.01 (2 H, s), 8.02 (2 H, d, J = 8.8), 8.11 (2 H, d, J = 8.8), 8.29 (2 H, d, J = 2.0), 8.42 (2 H, d, J = 8.8), 9.65 (2 H, s). ^{13}C NMR (101 MHz, d_6-DMSO): 115.7 (d), 122.7 (d), 123.9 (d), 125.8 (s), 126.5 (d), 127.0 (s), 127.8 (d), 128.42 (s), 128.42 (d), 129.9 (s), 131.8 (s), 132.8 (s), 137.7 (s), 157.3 (s). IR ($CHCl_3$): 3433 vs, 1611 m, 1592 w, 1520 w, 1507 w, 1501 w, 1490 w, 1443 w, 1105 w, 1013 vw, 834 w, 821 w, 697 vw cm^{-1}. EI MS: 462 ($M^{+\bullet}$, 51), 368 (29), 355 (20), 337 (11), 313 (2), 276 (4), 186 (100), 157 (32), 128 (16). HR EI MS: calcd for $C_{34}H_{22}O_2$ 462.1620, found 462.1603.

Representative Procedure for Suzuki−Miyaura Coupling in Solution: 4,4′-Pentahelicene-3,12-diyldianiline (16). A mixture of chloro helicene **13** (92.8 mg, 0.270 mmol), 4-aminophenylboronic acid **21** (234 mg, 1.07 mmol, 4.0 equiv), $Pd(OAc)_2$ (24.0 mg, 0.110 mmol, 40 mol %), 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl **24** (84.5 mg, 0.110 mmol, 80 mol %), and cesium carbonate (783 mg, 2.40 mmol, 9.0 equiv) in a mixture of dioxane−water (3:1, 4 mL) was heated under argon at 85 °C overnight. After the removal of salt by filtration through a paper filter using dichloromethane, the crude reaction mixture was chromatographed on silica gel (hexane−ethyl acetate 70:30) providing helicene dianiline **16** (88.5 mg, 72%) an amorphous white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 3.83 (4 H, br s), 6.82 (4 H, d, J = 8.4), 7.53 (2 H, dd, J = 8.8, 2.0), 7.62 (4 H, d, J = 8.4), 7.85 (2 H, s), 7.88 (2 H, d, J = 8.4), 7.95 (2 H, d, J = 8.4), 8.09 (2 H, d, J = 2.0), 8.59 (2 H, d, J = 8.8). ^{13}C NMR (101 MHz, $CDCl_3$): 115.5 (d), 123.2 (d), 124.2 (d), 126.6 (d), 126.97 (d), 127.02 (s), 127.6 (d), 128.1 (d), 129.4 (d), 130.9 (s), 132.2 (s), 133.1 (s), 138.6 (s), 146.1 (s). IR ($CHCl_3$): 3486 w, 3455 w, 3401 w, 3376 w, 3051 w, 1620 vs, 1609 s, 1524 m, 1508 m, 1491 m, 1473 w, 1445 w, 1398 w, 1130 w, 1012 vw, 838 m, 822 m cm^{-1}. EI MS: 460 ($M^{+\bullet}$, 100), 442 (10), 426 (3), 367 (56), 350 (18), 337 (12), 276 (5). HR EI MS: calcd for $C_{34}H_{24}N_2$ 460.1939, found 460.1923.

3,12-Bis(4-prop-1-yn-1-ylphenyl)pentahelicene (17). A mixture of chloro helicene **13** (10.6 mg, 0.030 mmol), 4-prop-1-yn-1-ylphenyl boronic acid **22** (19.5 mg, 0.122 mmol, 4.0 equiv), $Pd(OAc)_2$ (2.7 mg, 0.012 mmol, 40 mol %), 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl **24** (9.5 mg, 0.024 mmol, 80 mol %), and cesium carbonate (49.5 mg, 0.152 mmol, 5.0 equiv) in dioxane (0.5 mL) was heated under argon at 85 °C overnight. After the removal of salt by filtration through a paper filter using dichloromethane, the crude reaction mixture was chromatographed on silica gel (hexane−acetone 70:30) providing diyne **17** (7.1 mg, 45%) as an amorphous white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 2.10 (6 H, s), 7.52 (4 H, d, J = 8.4), 7.56 (2 H, dd, J = 8.8, 2.0), 7.73 (4 H, d, J = 8.4), 7.89 (2 H, s), 7.91 (2 H, d, J = 8.4), 7.98 (2 H, d, J = 8.4), 8.17 (2 H, d, J = 2.0), 8.60 (2 H, d, J = 8.8). ^{13}C NMR (101 MHz, $CDCl_3$): 4.4 (q), 79.7 (s), 86.8 (s), 123.2 (s), 123.4 (d), 125.5 (d), 126.89 (d), 126.94 (d), 127.3 (d), 127.8 (d), 129.6 (d), 130.1 (s), 132.0 (d), 132.5 (s), 133.0 (s), 138.0 (s), 139.6 (s). IR ($CHCl_3$): 3051 m, 2256 vw, 2220 vw, 1621 w, 1601 m, 1518 w, 1503 w, 1487 m, 1468 w, 1446 m, 1409 w, 1380 w, 1322 w, 1168 w, 1143 w, 1103 w, 1078 w, 1024 w, 890 s, 854 m, 846 m, 836 vs, 824 m, 698 m, 582 m, 549 m, 415 w cm^{-1}. EI MS: 506 ($M^{+\bullet}$, 100), 490 (6), 475 (3), 390 (25), 377 (28), 350 (2). HR EI MS: calcd for $C_{40}H_{26}$ 506.2035, found 506.2033.

[Pentahelicene-3,12-diylbis(benzene-4,1-diylethyne-2,1-diyl)]-bis[tris(1-methylethyl)silane] (18). A mixture of chloro helicene **13** (204 mg, 0.588 mmol), 4-tris(1-methylethyl)silane-acetylene boronic acid **23**[15] (350 mg, 2.31 mmol, 4.0 equiv), $Pd(OAc)_2$ (13.2 mg, 0.059 mmol, 10 mol %), 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl **24** (46.7 mg, 0.118 mmol, 20 mol %), and cesium carbonate (766 mg, 2.352 mmol, 4.0 equiv) in dioxane (4 mL) was heated under argon at 80 °C overnight. After the removal of salt by filtration through a paper filter using dichloromethane, the crude reaction mixture was chromatographed on silica gel (hexane−acetone 70:30) providing the compound **18** (238 mg, 50%) as an amorphous white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.21 (42 H, s), 7.54 (2 H, dd, J = 8.8, 1.6), 7.63 (2 H, d, J = 8.6), 7.73 (2 H, d, J = 8.6), 7.87 (2 H, s), 7.89 (2 H, d, J = 8.6), 7.97 (2 H, d, J = 8.6), 8.15 (2 H, d, J = 1.6), 8.59 (2 H, d, J = 8.8). ^{13}C NMR (101 MHz, $CDCl_3$): 11.4 (d), 18.7 (q), 91.6 (s), 107.0 (s), 122.7 (s), 123.4 (d), 125.6 (d), 126.91 (d), 126.94 (d), 127.4 (d), 127.8 (d), 129.6 (d), 130.2 (s), 132.53 (s), 132.59 (d), 133.0 (s), 137.9 (s), 140.4 (s). IR ($CHCl_3$): 3602 w, 2959 s, 2892 m, 2866 vs, 2154 m, 1517 w, 1464 m, 1408 w, 1384 w, 1366 vw, 1321 w, 1184 vw, 1108 w, 1073 w, 1017 w, 997 w, 884 m, 704 m, 679 s, 660 s, 630 w cm^{-1}. EI MS: 790 ($M^{+\bullet}$, 50), 740 (29), 534 (100), 491 (28), 463 (14), 491 (30), 463 (15), 449 (32), 435 (32), 421 (40), 276 (9), 218 (9), 210 (9). HR EI MS: calcd for $C_{56}H_{62}Si_2$ 790.4390, found 790.4391.

(4-Prop-1-yn-1-ylphenyl)boronic Acid (22). A Schlenk flask containing a solution of 1-bromo-4-idophenyl (200 mg, 0.692 mmol), $Pd(PPh_3)_2Cl_2$ (5.0 mg, 0.007 mmol, 1 mol %), and CuI (2.7 mg, 0.014 mmol, 2 mol %) in pyridine (1 mL) was connected with a bottle of prop-1-yne and the mixture was stirred at room temperature for 2 h. After the evaporation of the solvent in vacuo, salt was removed by precipitation using diethyl ether and the crude mixture was chromatographed on silica gel (hexane) to furnish the 1-bromo-4-prop-1-yn-1-ylbenzene[23] (111 mg, 82%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra were in agreement with the published data.[23] IR ($CHCl_3$): 3082 vw, 3056 vw, 2963 w, 2255 m, 2219 w, 1588 w, 1486 vs, 1466 m, 1395 s, 1378 w, 1297 vw, 1299 w, 1266 m, 1177 vw, 1112 w, 1071 vs, 1012 s, 971 m, 826 vs, 704 w, 636 w, 523 s, 485 m, 412 w cm^{-1}. EI MS: 196 ($M^{+\bullet}$ with ^{81}Br, 10), 194 ($M^{+\bullet}$ with ^{79}Br, 10), 167 (8), 147 (30), 115 (15), 75 (28), 73 (100). HR EI MS: calcd for $C_9H_7{}^{79}Br$ 193.9731, found 193.9738. To the solution of 1-bromo-4-prop-1-yn-1-ylbenzene (0.8770 g, 4.50 mmol) in THF (20 mL) at −78 °C under argon was carefully added a butyllithium solution (1.6 M in hexanes, 3.7 mL, 5.85 mmol, 1.3 equiv) and the reaction was stirred at −78 °C for 20 min. The mixture was transferred by a syringe into a cold solution of triisopropyl borate (3.1 mL, 13.50 mmol, 3.0 equiv) at −78 °C, and the reaction was stirred at the same temperature for 20 min and 2 h at room temperature. After the evaporation of the solvent in vacuo, the crude mixture was poured into aq HCl (1 N, 20 mL) and stirred for 20 min. Then the water phase was extracted with dichloromethane (3 × 20 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The flash chromatography on silica gel mixture (hexane−acetone 70:30) of the crude mixture yielded boronic acid **22**[16] (561 mg, 78%) as a white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): 2.09 (3 H, s), 7.49 (2 H, d, J = 8.0), 8.09 (2 H, d, J = 8.0). ^{13}C NMR (101 MHz, $CDCl_3$): 4.4 (q), 79.98 (s), 88.4 (s), 128.4 (s), 131.0 (d), 135.4 (d). IR ($CHCl_3$): 3212 vw, 3078 w, 3038 vw, 2254 w, 2217 vw, 1605 s, 1511 w, 1402 s, 1380 s, 1369 s, 1345 vs, 1309 s, 1298 m cm^{-1}. ESI MS: 159 ([M − H]$^-$). HR ESI MS: calcd for $C_9H_8O_2B$ 159.0623, found 159.0620.

1,1′-[Ethyne-1,2-diylbis(5-chlorobenzene-2,1-diyl)]bis[4-(trimethylsilyl)but-3-yn-1-ol] (25). A Schlenk flask was charged with gallium (101 mg, 1.45 mmol, 2.2 equiv), indium (8.0 mg, 0.070 mmol, 10 mol %), trimethylsilyl propargyl bromide (0.42 mL, 2.64 mmol, 4.0 equiv), and THF (1 mL) under argon. The reaction mixture was then vigorously stirred at 10 °C for 1 h. After complete consumption of gallium, a solution of dialdehyde **9** (200 mg, 0.660 mmol) in THF (4 mL) was slowly added and the reaction mixture was stirred at room temperature for 1 h. After removal of the solvent in vacuo, sat. $NaHCO_3$ (100 mL) was added to the crude reaction mixture, the product was extracted with dichloromethane (3 × 200 mL) and the

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organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the crude product was chromatographed on silica gel (hexane−ethyl acetate 70:30) providing a mixture of two diastereosiomers of the hydroxy derivative **25** (176 mg, 50%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 0.15 (18 H, s, one diastereoisomer), 0.15 (18 H, s, one diastereoisomer), 2.60−2.68 (2 H, m), 2.83 (2 H, br s), 2.87−2.94 (2 H, m), 5.27−5.33 (2 H, m), 7.22−7.26 (2 H, m), 7.40−4.43 (2 H, m), 7.61 (2 H, m). ^{13}C NMR (101 MHz, $CDCl_3$): −0.04 (q), 29.9 (t), 30.0 (t), 69.78 (d), 69.84 (d), 88.67 (s), 88.74 (s), 91.9 (s), 92.0 (s), 102.0 (s), 102.1 (s), 118.47 (s), 118.50 (s), 126.16 (d), 126.19 (d), 127.8 (d), 133.3 (d), 135.2 (s), 145.8 (s). IR ($CHCl_3$): 3602 w, 2962 m, 2901 w, 2174 m, 1595 w, 1558 vw, 1488 m, 1408 w, 1308 vw, 1278 w, 1252 s, 1180 w, 1116 w, 1092 m, 1057 m, 908 m, 896 w, 846 vs, 825 m, 700 w, 651 w, 506 w cm^{-1}. ESI MS: 525 ([M − H]$^-$). HR ESI MS: calcd for $C_{28}H_{31}O_2Cl_2Si_2$ 525.1245, found 525.1242.

Ethyne-1,2-diylbis[(5-chlorobenzene-2,1-diyl)-1-(trimethylsilyl)-but-1-yne-4,4-diyl] Diacetate (26). To the solution of **25** (124 mg, 0.200 mmol) and 4-(dimethylamino)pyridine (2.4 mg, 0.020 mmol, 10 mol %) in pyridine (0.5 mL) was slowly added acetic anhydride (1.0 mL, 11.0 mmol, 55 equiv) and the reaction mixture was stirred at room temperature for 1 h. Solvent was then removed in vacuo and the crude product was chromatographed on silica gel (hexane−ethyl acetate 70:30) to provide a mixture of two diastereoisomers of the diacetate **26** (0.126 mg, 87%) as yellowish oil. One diastereoisomer of **26** was isolated in a pure form by precipitation in hexane. Mixture of diastereoisomers of **26**: ^{1}H NMR (400 MHz, $CDCl_3$): 0.109 and 0.113 (18 H, 2 × s), 2.15 and 2.16 (6 H, 2 × s), 2.78−2.85 (2 H, m), 2.93−3.01 (2 H, m), 6.31−6.36 (2 H, m), 7.28 (2 H, dd, J = 8.4, 2.2), 7.47−7.51 (4 H, m). ^{13}C NMR (101 MHz, $CDCl_3$): −0.2 (q), 20.9 (q), 26.7 (t), 26.9 (t), 70.9 (d), 88.20 (s), 88.24 (s), 91.83 (s), 91.85 (s), 100.97 (s), 101.01 (s), 119.2 (s), 126.7 (d), 126.8 (d), 128.2 (d), 133.5 (d), 134.83 (s), 134.85 (s), 142.36 (s), 142.39 (s), 169.5 (s). IR ($CHCl_3$): 2961 w, 2902 w, 2179 w, 1744 s, 1596 w, 1559 vw, 1491 w, 1421 w, 1408 w, 1374 m, 1250 s, 1238 vs, 1181 w, 1116 w, 1091 w, 1032 m, 900 w, 846 vs, 826 m, 701 w, 638 w, 606 vw cm^{-1}. ESI MS: 1243 ([2M + Na]$^+$), 633 ([M + Na]$^+$). HR ESI MS: calcd for $C_{32}H_{36}O_4Cl_2NaSi_2$ 633.1421, found 633.1426. Pure diastereoisomer of **26**: ^{1}H NMR (400 MHz, $CDCl_3$): 0.11 (18 H, s), 2.15 (6 H, s), 2.82 (2 H, dd, J = 17.2, 6.0), 2.97 (2 H, dd, J = 17.2, 6.0), 6.33 (2 H, t, J = 6.0), 7.28 (2 H, dd, J = 8.4, 2.2), 7.48 (2 H, d, J = 8.4), 7.50 (2 H, d, J = 2.2). ^{13}C NMR (101 MHz, $CDCl_3$): −0.2 (q), 21.0 (q), 26.8 (t), 70.9 (d), 88.3 (s), 91.9 (s), 101.3 (s), 119.2 (s), 126.9 (d), 128.2 (d), 133.5 (d), 134.9 (s), 142.4 (s), 169.5 (s). IR ($CHCl_3$): 2961 w, 2902 w, 2179 w, 1744 s, 1596 w, 1559 vw, 1491 w, 1421 w, 1408 w, 1374 m, 1250 s, 1238 vs, 1181 w, 1116 w, 1091 w, 1032 m, 900 w, 846 vs, 826 m, 701 w, 638 w, 606 vw cm^{-1}. ESI MS: 633 ([M + Na]$^+$). HR ESI MS: calcd for $C_{32}H_{36}O_4Cl_2NaSi_2$ 633.1421, found 633.1426.

3,12-Dichloro-7,8-bis(trimethylsilyl)-5,6,9,10-tetrahydropentahelicene-5,10-diyl Diacetate (27). The solution of triyne **26** (35.0 mg, 0.066 mmol), PPh_3 (31.3 mg, 0.133 mmol, 2.0 equiv), and $CpCo(CO)_2$ (8.7 μL, 0.066 mmol, 1.0 equiv) in decane (20 mL) under agon was stirred at 150 °C for 2 h under simultaneous irradiation with a halogen lamp. The solvent was then removed in vacuo and the crude product was chromatographed on silica gel (hexane) to provide a mixture of two diastereoisomers of diacetate **27** (33.0 mg, 94%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 0.41 (18 H, s), 1.95−2.34 (6 H, m), 2.63−2.84 (2 H, m), 3.40−3.80 (2 H, m), 6.00−6.20 (2 H, m), 6.94−7.02 (4 H, m), 7.34 (2 H, br s), 7.50 (2 H, br s). IR ($CHCl_3$): 2960 m, 2902 w, 1736 vs, 1596 w, 1571 w, 1484 w, 1421 w, 1411 w, 1374 m, 1252 vs, 1237 vs, 1182 w, 1034 m, 846 vs, 697 w, 612 w cm^{-1}. ESI MS: 1243 ([2M + Na]$^+$), 633 ([M + Na]$^+$). TOF EI MS: 610 (M$^{+\bullet}$, 15), 550 (25), 490 (68), 455 (17), 418 (63), 403 (20), 382 (41), 73 (100). HR TOF EI MS: calcd for $C_{32}H_{36}O_4Cl_2Si_2$ 610.1529, found 610.1528.

(3,12-Dichloropentahelicen-7-yl)(trimethyl)silane (28). The compound **27** (33.0 mg, 0.053 mmol) was dissolved in dichloromethane and added to silica gel 60 (2 g). The solvent was evaporated in vacuo and the resulting solid was put under argon and stirred at 120 °C for 5 h. The silica gel with absorbed product was loaded to the silica gel column and directly chromatographed (hexane) to provide the desired silylated pentahelicene **28** (14.9 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 0.56 (9 H, s), 7.20 (1 H, dd, J = 8.8, 2.0), 7.22 (1 H, dd, J = 8.8, 2.0), 7.82−7.93 (5 H, m), 8.05 (1 H, s), 8.18 (1 H, d, J = 8.8), 8.26 (1 H, d, J = 2.0), 8.29 (1 H, d, J = 2.0). ^{13}C NMR (101 MHz, $CDCl_3$): 0.4 (q), 125.1 (d), 125.3 (d), 125.9 (d), 126.3 (d), 126.5 (s), 126.7 (d), 127.1 (s), 127.4 (d), 127.6 (d), 128.8 (s), 129.3 (s), 130.3 (d), 130.8 (d), 131.3 (s), 131.9 (s), 132.0 (s), 132.9 (s), 133.8 (s), 135.2 (d), 135.6 (s), 137.5 (s). IR ($CHCl_3$): 3052 w, 2958 w, 2900 w, 1607 w, 1596 w, 1573 w, 1553 w, 1507 w, 1493 w, 1479 w, 1464 w, 1434 w, 1412 w, 1380 vw, 1255 m, 866 vs, 876 s, 841 s, 824 m, 812 m, 692 w, 631 w cm^{-1}. TOF EI MS: 418 (M$^{+\bullet}$, 98), 403 (28), 383 (22), 353 (21), 348 (27), 310 (100), 289 (30), 275 (55), 167 (5), 73 (25). HR TOF EI MS: calcd for $C_{25}H_{20}Cl_2Si$ 418.0711, found 418.0710.

4-*tert*-Butyl-2-formylphenyl Trifluoromethanesulfonate (30). To a solution of alcohol **29** (235 mg, 1.32 mmol) and pyridine (0.32 mL, 3.96 mmol, 3.0 equiv) in dichloromethane (6 mL) was carefully added trifluoromethanesulfonic anhydride (0.24 mL, 1.45 mmol, 1.1 equiv) at 0 °C over 10 min. After 2.5 h of vigorous stirring at room temperature, the solvent was removed in vacuo, diethyl ether (5 mL) was added, and the precipitation was filtered off. Flash chromatography of the crude mixture on silica gel (dichloromethane) provided triflate **30** (369 mg, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.36 (9 H, s), 7.32 (1 H, d, J = 8.8), 7.72 (1 H, dd, J = 8.8, 2.8), 7.99 (1 H, d, J = 2.8), 10.27 (1H, s). ^{13}C NMR (101 MHz, $CDCl_3$): 31.1 (q), 35.1 (s), 118.7 (q, J = 322), 122.0 (d), 127.5 (d), 127.9 (s), 133.0 (d), 147.9 (s), 152.5 (s), 186.8 (d). IR ($CHCl_3$): 3033 m, 2969 s, 2936 m, 2908 m, 2873 m, 2816 w, 2768 w, 1603 m, 1589 w, 1479 m, 1464 m, 1429 vs, 1400 s, 1367 m, 1249 vs, 1230 vs, 1176 s, 1118 s, 1077 s, 961 w, 929 m, 838 m, 573 w, 510 m cm^{-1}. EI MS: 310 (M$^{+\bullet}$, 18), 295 (100), 231 (6), 203 (20), 175 (8), 134 (13), 105 (7). HR EI MS: calcd for $C_{12}H_{13}F_3O_4S$ 310.0486, found 310.0486.

2,2′-Ethyne-1,2-diylbis(5-*tert*-butylbenzaldehyde) (31). A Schlenk flask was charged with triflate **30** (364 mg, 1.17 mmol), $Pd(PPh_3)_2Cl_2$ (34.0 mg, 0.050 mmol, 4 mol %), and CuI (5.0 mg, 0.025 mmol, 2 mol %) and filled with acetylene. A mixture of Et_3N (2 mL) and THF (1 mL) was added and reaction mixture was stirred for 2 h at 60 °C. The solvents were removed in vacuo and the crude product was chromatographed on silica gel (hexane−acetone 90:10) to provide dialdehyde **31** (151 mg, 73%) as a pale amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.36 (18 H, s), 7.62 (2 H, d, J = 8.4), 7.65 (2 H, dd, J = 8.4, 2.0), 7.99 (2 H, d, J = 2.0), 10.61 (2 H, s). ^{13}C NMR (101 MHz, $CDCl_3$): 31.0 (q), 35.1 (s), 91.3 (s), 123.1 (s), 124.6 (d), 131.2 (d), 133.3 (d), 135.8 (s), 153.0 (s), 191.5 (d). IR ($CHCl_3$): 2968 m, 2933 w, 2909 w, 2870 w, 2845 w, 2749 w, 2208 vw, 1694 vs, 1602 m, 1550 w, 1502 w, 1477 w, 1465 w, 1412 vw, 1397 w, 1390 w, 1366 m, 1284 w, 1253 w, 1192 m, 1126 w, 1105 vw, 1094 vw, 933 w, 841 m, 638 w cm^{-1}. ESI MS: 369 ([M + Na]$^+$). HR ESI MS: calcd for $C_{24}H_{26}NaO_2$ 369.1825, found 369.1827.

1,1′-[Ethyne-1,2-diylbis(5-*tert*-butylbenzene-2,1-diyl)]bisbut-3-yn-1-ol (32). Purification by chromatography on silica gel (hexane−acetone 90:10) provided two diastereoisomers of dihydroxy derivative **32** (98.5 mg, 30%) as oil containing some traces of unknown impurities (for experimental details see the preparation of **33**). The degradation seems to occur during the purification on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): 1.34 (18 H, br s), 2.11 (2 H, br s), 2.63−2.69 (2 H, m), 2.86−2.93 (2 H, m), 5.34−5.43 (2 H, m), 7.31−7.34 (2 H, m), 7.46−7.48 (2 H, m), 7.64−7.65 (2 H, m). ^{13}C NMR (101 MHz, $CDCl_3$): 28.5 (t), 28.6

(t), 31.2 (q), 35.1 (s), 70.7 (d), 70.8 (d), 70.96 (d), 71.03 (d), 80.9 (s), 81.0 (s), 91.6 (s), 91.7 (s), 117.6 (s), 122.4 (d), 124.7 (d), 132.2 (d), 143.3 (s), 152.3 (s). IR ($CHCl_3$): 3602 w, 3308 s, 2967 vs, 2933 m, 2908 m, 2870 m, 2210 vw, 2120 vw, 1606 w, 1505 m, 1477 w, 1464 w, 1419 w, 1396 w, 1365 m, 1261 m, 1185 w, 1128 w, 1105 w, 1083 w, 1054 m, 834 m, 643 m, 525 w cm^{-1}. ESI MS: 449 ($[M + Na]^+$), 875 ($[2M + Na]^+$). HR ESI MS: calcd for $C_{30}H_{34}NaO_2$ 449.2451, found 449.2454.

Ethyne-1,2-diylbis[(5-*tert*-butylbenzene-2,1-diyl)but-1-yne-4,4-diyl] Diacetate (33). A Schlenk flask was charged with gallium (118 mg, 1.69 mmol, 2.2 equiv), indium (10.0 mg, 0.080 mmol, 10 mol %), propargyl bromide (360 μL, 3.23 mmol, 3.0 equiv), and THF (1 mL) under argon. The reaction mixture was then vigorously stirred at 10 °C for 1 h. After complete consumption of gallium, a solution of dialdehyde **31** (267 mg, 0.770 mmol) in hot THF (4 mL) was slowly added and the reaction mixture was stirred at room temperature for 1 h. After removal of the solvent in vacuo, sat. $NaHCO_3$ (100 mL) was added to the crude mixture and the product was extracted with dichloromethane (3 × 200 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo affording the dihydroxy derivative **32**. The crude product was dissolved in pyridine (1 mL) and 4-(dimethylamino)pyridine (20.8 mg, 0.170 mmol, 10 mol %) was added, then acetic anhydride (2 mL, 22.0 mmol, 29 equiv) was carefully added over 5 min. The mixture was left to react at room temperature for 30 min and then the solvent was removed in vacuo. Flash chromatography on silica gel (hexane−acetone 80:20) of the crude mixture provided the desired diacetate **33** (311 mg, 79%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.34 (18 H, s), 1.99 (2 H, t, J = 2.7), 2.15 (6 H, s), 2.79−2.87 (2 H, m), 2.93−3.01 (2 H, m), 6.41−6.44 (2 H, m), 7.32−7.34 (2 H, m), 7.50−7.54 (4 H, m). ^{13}C NMR (101 MHz, $CDCl_3$): 21.0 (q), 25.5 (t), 31.1 (q), 34.9 (s), 70.7 (d), 71.77 (d), 71.79 (d), 79.7 (s), 91.42 (s), 91.45 (s), 118.3 (s), 118.4 (s), 123.2 (d), 125.0 (d), 132.3 (d), 139.80 (s), 139.83 (s), 151.79 (s), 151.82 (s), 169.7 (s). IR ($CHCl_3$): 3309 m, 2967 m, 2933 w, 2908 w, 2870 w, 2124 vw, 1741 s, 1608 w, 1507 w, 1478 w, 1463 w, 1422 w, 1395 w, 1374 m, 1368 m, 1240 vs, 1191 w, 1128 w, 1103 w, 1078 w, 1044 m, 1031 m, 834 w, 647 m, 606 w, 523 vw cm^{-1}. ESI MS: 533 ($[M + Na]^+$). HR ESI MS: calcd for $C_{34}H_{38}NaO_4$ 533.2662, found 533.2666.

3,12-Di-*tert*-butyl-5,6,9,10-tetrahydropentahelicene-5,10-diyl Diacetate (34). A solution of **33** (132 mg, 0.259 mmol), triphenylphosphine (136 mg, 0.517 mmol, 2.0 equiv), and $CpCo(CO)_2$ (35 μL, 259 mmol, 1.0 equiv) in decane (7 mL) under argon was heated at 150 °C for 3 h under simultaneous irradiation with a halogen lamp. The solvent was then removed in vacuo and the crude product was chromatographed on silica gel (hexane−acetone 90:10) to provide two diastereoisomers of helicene diacetate **34** (72.1 mg, 55%) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.34 (18 H, s), 1.95−2.33 (6 H, m), 2.97−3.25 (4 H, m), 5.99 (2 H, m), 7.01 (4 H, m), 7.31−7.48 (4 H, m). IR ($CHCl_3$): 2966 m, 2933 w, 2906 w, 2870 w, 1739 m, 1726 s, 1611 w, 1595 vw, 1501 w, 1478 w, 1465 w, 1425 w, 1412 w, 1395 w, 1373 m, 1366 m, 1248 vs, 1240 s, 1182 w, 1123 vw, 1102 vw, 1077 w, 1035 w, 1023 m, 842 w, 693 vw, 610 w, 527 vw, 457 vw cm^{-1}. EI MS: 510 ($M^{+\bullet}$, 9), 450 (3), 390 (90), 375 (14), 333 (36), 277 (100), 263 (10), 180 (5), 152 (7), 57 (28). HR EI MS: calcd for $C_{34}H_{38}O_4$ 510.2770, found 510.2769.

3,12-Di-*tert*-butylpentahelicene (35). To the solution of helicene diacetate **34** (72.1 mg, 0.140 mmol) in dichloromethane was added silica gel (7 g). The solvent was evaporated in vacuo, then the solid was put under argon and stirred at 120 °C for 5 h. The silica gel with absorbed product was loaded to the silica gel column and directly chromatographed (hexane) providing the desired pentahelicene **35** (49.5 mg, 90%) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.48 (18 H, s), 7.38 (2 H, dd, J = 9.0, 2.4), 7.83 (2 H, s), 7.85 (2 H, d, J = 9.0), 7.90−7.92 (4 H, m), 8.53 (2 H, d, J = 9.0). ^{13}C NMR (101 MHz, $CDCl_3$): 31.4 (q), 34.8 (s), 122.7 (d), 123.2 (d), 126.3 (d), 126.8 (d), 127.0 (s), 127.6 (d), 128.7 (d), 128.9 (s), 132.0 (s), 132.6 (s). IR ($CHCl_3$): 3051 w, 2966 vs, 2932 m, 2907 m, 2869 m, 1621 w, 1606 w, 1513 w, 1496 w, 1478 w, 1464 w, 1444 w, 1394 w 1386 w, 1363 m, 888 m, 839 s cm^{-1}. EI MS: 390 ($M^{+\bullet}$, 26), 333 (11), 317 (6), 300 (11), 277 (100). HR EI MS: calcd for $C_{30}H_{30}$ 390.2348, found 390.2342.

2,2′-Ethyne-1,2-diyldipyridine-3-carbaldehyde (37). A Schlenk flask was charged with bromide **36** (300 mg, 1.61 mmol), Pd-$(PPh_3)_2Cl_2$ (45.0 mg, 0.060 mmol, 4 mol %), and CuI (6.0 mg, 0.030 mmol, 2 mol %) and filled with acetylene. A mixture of Et_3N (8 mL) and THF (2 mL) was added and the reaction mixture was stirred at 50 °C for 2 h. The solvents were removed in vacuo and the crude product was chromatographed on silica gel (hexane−acetone 80:20) to provide dialdehyde **37** (143 mg, 75%) as a pale amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.53 (1 H, ddd, J = 7.9, 4.7, 0.9), 8.29 (1 H, dd, J = 7.9, 1.8), 8.90 (1 H, dd, J = 4.7, 1.8), 10.71 (1 H, d, J = 0.9). ^{13}C NMR (125 MHz, $CDCl_3$): 89.7 (s), 124.5 (d), 132.8 (s), 135.2 (d), 144.2 (s), 154.6 (d), 189.9 (d). IR ($CHCl_3$): 3054 w, 2805 w, 2743 w, 2230 vw, 1701 vs, 1578 s, 1566 s, 1440 s, 1390 m cm^{-1}. EI MS: 236 ($M^{+\bullet}$, 64), 208 (24), 179 (100), 153 (37), 126 (13), 99 (14), 87 (6), 75 (17), 69 (8), 62 (11), 55 (11), 51 (29), 41 (15). HR EI MS: calcd for $C_{14}H_8N_2O_2$ 236.0586, found 236.0581.

Ethyne-1,2-diylbis(pyridine-2,3-diylbut-1-yne-4,4-diyl) Diacetate (39). A solution of propargyl magnesiumbromide (freshly prepared from magnesium turnings (83.0 mg, 3.41 mmol, 2.40 equiv) and propargyl bromide (441 mg, 3.71 mmol, 2.61 equiv) in Et_2O (15 mL)) was placed in a Schlenk flask under argon and cooled to −78 °C. Dialdehyde **37** (336 mg, 1.42 mmol) in THF (40 mL) was added dropwise to the solution of Grignard reagent and the resulting mixture was stirred at −78 °C for 20 min to provide **38**. Then acetic anhydride (432 mg, 4.23 mmol, 2.98 equiv) was added and the mixture was stirred at room temperature for 1 h. After quenching the reaction with EtOH (5 mL), ethyl acetate (50 mL) was added and the mixture was washed with brine (3 × 20 mL) and dried over anhydrous $MgSO_4$. The solvents were removed in vacuo and the crude product was chromatographed on silica gel (hexane−acetone 80:20) to provide the desired triyne **39** (200 mg, 35%) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$): 2.01 (2 H, t, J = 2.7), 2.15 (2 H, s), 2.93 (2 H, ddd, J = 17.1, 5.4, 2.7), 3.01 (2 H, ddd, J = 17.1, 5.7, 2.7), 6.40 (1 H, br t, J = 5.6), 6.43 (1 H, br t, J = 5.6), 7.35 (2 H, ddd, J = 8.0, 4.8, 0.5), 7.88 (2 H, dd, J = 8.0, 1.7), 8.62 (2 H, br dd, J = 4.8, 1.7). ^{13}C NMR (125 MHz, $CDCl_3$): 20.9 (q), 25.30 (t), 25.31 (t), 69.9 (d), 70.0 (d), 71.65 (d), 71.68 (d), 78.4 (s), 78.5 (s), 89.90 (s), 89.93 (s), 123.4 (d), 134.2 (d), 137.29 (s), 137.31 (s), 140.0 (s), 149.7 (d), 149.8 (d), 169.46 (s), 169.48 (s). IR ($CHCl_3$): 3309 s, 3055 w, 2234 vw, 2124 w, 1746 vs, 1583 m, 1569 s, 1444 vs, 1420 m, 1373 s, 1341 w, 1236 vs, 1044 s, 1029 s, 651 s, 640 s, 604 w cm^{-1}. EI MS: 400 ($M^{+\bullet}$, 1), 357 (11), 341 (11), 319 (14), 297 (43), 281 (68), 269 (31), 259 (43), 247 (13), 231 (36), 209 (11), 181 (17), 149 (10), 128 (9), 112 (6), 97 (8), 71 (26), 57 (24), 43 (100). HR EI MS: calcd for $C_{24}H_{20}N_2O_4$ 400.1423, found 400.1427.

5,6,9,10-Tetrahydrobenzo[1,2-*h*:4,3-*h*′]diquinoline-5,10-diyl Diacetate (40). A solution of triyne **39** (150 mg, 0.380 mmol), PPh_3 (39.0 mg, 0.150 mmol, 40 mol %), and $CpCo(CO)_2$ (10 μL, 0.080 mmol, 20 mol %) in decane (7 mL) under argon was heated at 150 °C for 3 h under simultaneous irradiation with a halogen lamp. After removal of solvent, the flash chromatography of the crude mixture on silica gel (hexane−acetone 70:30) afforded helicene diacetate **40** (114 mg, 76%) as an amorphous yellowish solid. ^{1}H NMR (500 MHz, $CDCl_3$): 2.14 (1 H, s), 2.18 (1 H, s), 2.98−3.10 (1 H, m), 3.16 (1 H, dd, J = 15.1, 4.9), 3.19 (1 H, dd, J = 15.1, 4.9), 6.15 (1 H, br s), 6.17 (1 H, br dd, J = 8.8, 4.9), 7.13 (2 H, dd, J = 7.6, 4.7), 7.26 (2 H, s), 7.73 (1 H, ddd, J = 7.6, 1.7, 0.9), 7.75 (1 H, br dd, J = 7.6, 1.7), 8.24 (1 H, ddd, J = 4.7, 1.8, 0.5), 8.25 (1 H, br dd, J = 4.7, 1.7). ^{13}C NMR (125 MHz, $CDCl_3$): 21.28 (q), 21.32 (q), 34.7 (t), 34.8 (t), 69.66 (d), 69.73 (d),

122.0 (d), 129.0 (d), 130.1 (s), 133.0 (s), 133.2 (d), 135.05 (s), 135.09 (s), 147.7 (d), 148.0 (d), 152.8 (s), 153.1 (s), 170.7 (s), 170.8 (s). IR ($CHCl_3$): 3060 w, 1732 s, 1587 w, 1571 m, 1461 m, 1435 m, 1374 s, 1241 vs, 1035 s, 614 w cm^{-1}. EI MS: 400 ($M^{+\bullet}$, 17), 297 (6), 280 (100), 269 (13), 252 (17), 178 (23), 161 (12), 140 (27), 97 (9), 81 (12), 69 (32), 57 (29), 41 (36). HR EI MS: calcd for $C_{24}H_{20}N_2O_4$ 400.1423, found 400.1426.

Benzo[1,2-*h*:4,3-*h*′]diquinoline (1,14-Diaza[5]helicene) (41). Helicene diacetate **40** (90.0 mg, 0.225 mmol) was dissolved in dichloromethane (10 mL) and trifluoromethanesulfonic acid coated silica gel (10 wt % of trifluoromethanesulfonic acid on silica gel, 5.5 g) was added. The solvent was evaporated in vacuo, and the resulting solid was put under argon and stirred at 120 °C for 2 h. The silica gel with absorbed product was loaded to the silica gel column and directly chromatographed (hexane−acetone−triethylamine 80:20:1) to provide the desired diazapentahelicene **41** (42.1 mg, 67%) as an amorphous yellowish solid.[2a,21] Mp (toluene), ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), IR ($CHCl_3$ or CCl_4), and EI MS spectra were in agreement with the published data.[2a]

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Supporting Information Available: Crystallographic data for **13** and **14**, copies of ^{1}H NMR and ^{13}C NMR spectra for the compound **22** and the new compounds **2**−**5**, **9**−**18**, **25**−**28**, **30**−**35**, **37**, **39**, **40** (for **3**, **5**, **12**, **27**, and **34** only ^{1}H NMR spectra), and CIF files for **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.