Synthesis of a $C_{44}H_{26}$ Hydrocarbon Having a Carbon Framework Represented on the Surface of C_{60} via Benzoenyne-Allenes

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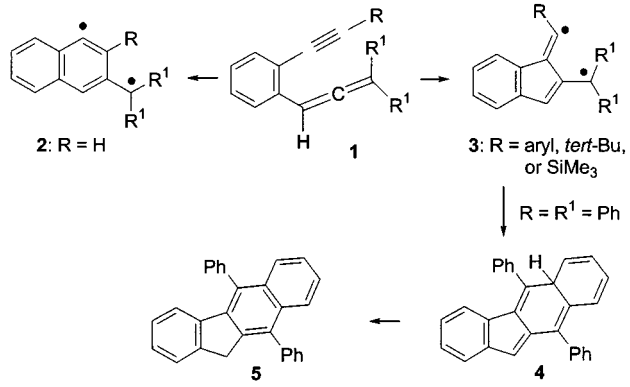
The $C_{44}H_{26}$ hydrocarbon **20** was synthesized in 13% overall yield in eight steps from acenaphthenequinone (**6**) and 2 equiv of 1-(2-ethynylphenyl)-2-phenylethyne. Condensation of the monoketal **7** with the lithium acetylide **8** afforded the benzoenediynyl propargylic alcohol **9**. On exposure to thionyl chloride, **9** underwent a cascade of reactions with the formation of the chloro-substituted benzoenyne-allene **11** in situ followed by a C2−C6 cyclization to produce the biradical **12**, leading to the formal Diels−Alder adduct **13** and subsequently, after tautomerization, the chloride **14**. Reduction with sodium borohydride then gave **15**. Deprotection of the ketal group produced **16** to allow a repeat of condensation with the acetylide **17** followed by the cascade transformation to afford the chloride **19**. Subsequent reduction then furnished the $C_{44}H_{26}$ hydrocarbon **20** having a carbon framework represented on the surface of C_{60}.

Introduction

Thermal cyclization of the benzoenyne-allenes **1** provides easy access to the naphthalene biradicals **2**[1] and the benzofulvene biradicals **3**[2] (Scheme 1). The nature of the substituent at the acetylenic terminus is responsible for directing the reaction toward either the Myers cyclization reaction to generate the naphthalene biradicals **2** or the C2−C6 cyclization reaction to furnish the benzofulvene biradicals **3**. With an aryl substituent or a sterically demanding group, such as the *tert*-butyl group and the trimethylsilyl group, at the acetylenic terminus, the C2−C6 cyclization reaction becomes the preferred pathway. The effect of the aryl substituent is attributed to its ability to stabilize the alkenyl radical center in **3**.[2c,i] The sterically demanding group inhibits the Myers cyclization reaction because of the emergence of severe nonbonded steric interactions in the biradicals **2**.[2c,f,j] If R^1 is a phenyl group, the biradical **3** undergoes an intramolecular radical−radical coupling to form **4** and subsequently, after tautomerization, the benzofluorene **5**.[1h,2] Although the transformation from **1** to **4** could also be regarded as a Diels−Alder reaction, mechanistic[2e] and DNA-cleaving[2h] studies suggest a two-step biradical pathway. Several synthetic methods have been reported for the preparation of benzoenyne-allenes to allow generation of biradicals for subsequent synthetic elaborations.[1,2] We now report a simple and efficient route to these highly unsaturated compounds for the C2−C6 cyclization reaction. This synthetic pathway was successfully adopted for the preparation of a $C_{44}H_{26}$ hydrocarbon having a carbon framework represented on the surface of C_{60}.

Scheme 1



Results and Discussion

Treatment of the commercially available acenaphthenequinone (**6**) with 2,2-dimethyl-1,3-propanediol in the presence of *p*-TsOH according to the reported procedure produced the monoketal **7** in 90% yield (Scheme 2).[3] Condensation of **7** with the lithium acetylide **8**, obtained by lithiation of 1-(2-ethynylphenyl)-2-phenylethyne[2b,4] with *n*-butyllithium, followed by hydrolytic workup, then furnished the propargylic alcohol **9**. Treatment of **9** with

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(2) (a) Engels, B.; Hanrath, M. *J. Am. Chem. Soc.* **1998**, *120*, 6356−6361. (b) Schmittel, M.; Strittmatter, M. *Tetrahedron* **1998**, *54*, 13751−13760. (c) Engels, B.; Lennartz, C.; Hanrath, M.; Schmittel, M.; Strittmatter, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1960−1963. (d) Schmittel, M.; Steffen, J.-P.; Auer, D.; Maywald, M. *Tetrahedron Lett.* **1997**, *38*, 6177−6180. (e) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843−1845. (f) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett.* **1996**, *37*, 7691−7694. (g) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (h) Schmittel, M.; Maywald, M.; Strittmatter, M. *Synlett* **1997**, 165−166. (i) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, *36*, 4975−4978. (j) Gillmann, T.; Hulsen, T.; Massa, W.; Wocadlo, S. *Synlett* **1995**, 1257−1259. (k) Garcia, J. G.; Ramos, B.; Pratt, L. M.; Rodriguez, A. *Tetrahedron Lett.* **1995**, *36*, 7391−7394.

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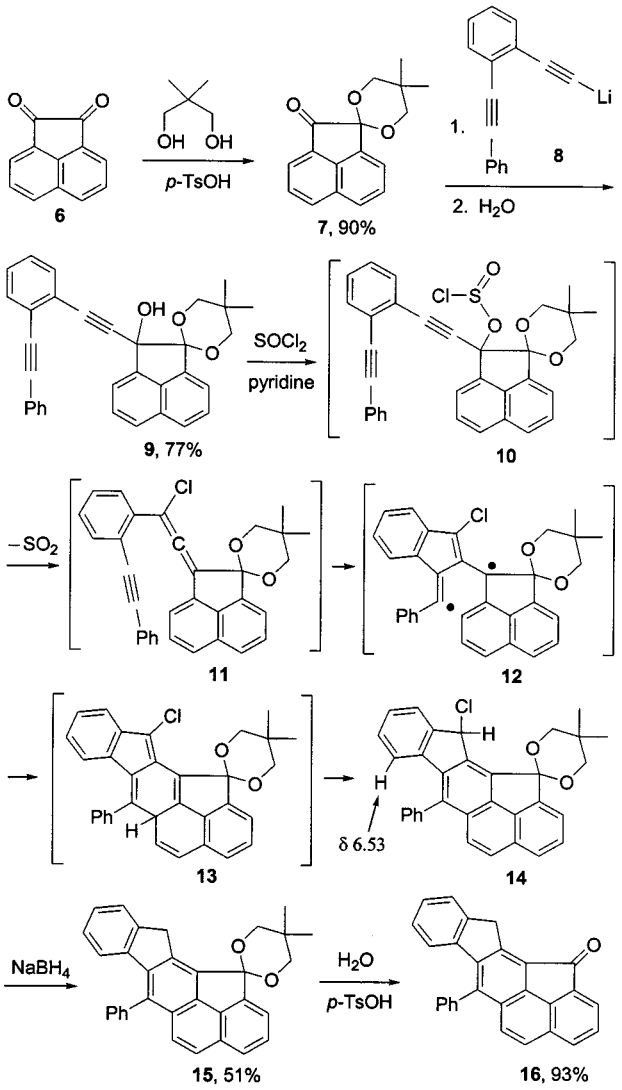
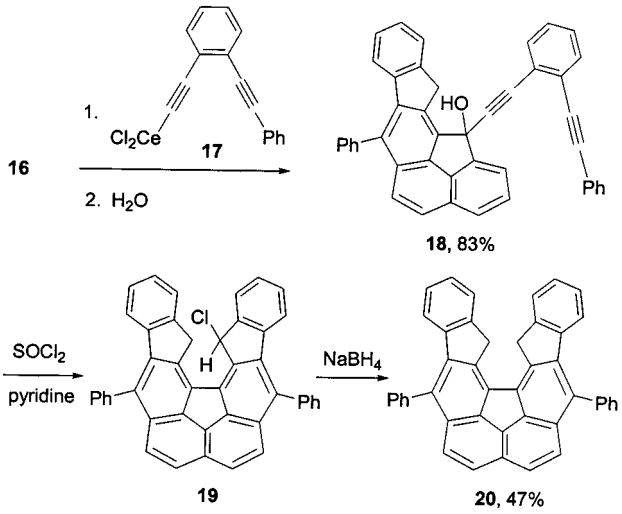
Scheme 2



thionyl chloride promoted a sequence of reactions with an initial formation of the chlorosulfite **10** followed by an S_Ni' reaction[5] to produce in situ the chlorinated benzoenyne-allene **11**. A C2−C6 cyclization reaction generated the biradical **12**, which in turn underwent a radical−radical coupling to afford the formal Diels−Alder adduct **13** and, subsequently after tautomerization, the chloride **14**. The chloride **14** was prone to hydrolysis, and attempts to purify it on silica gel resulted in the transformation to the corresponding alcohol. Fortunately, recrystallization of **14** from benzene afforded a pure sample (35% yield) to allow structural elucidation.

The use of thionyl chloride to induce the transformation from **9** to **11** represents a new and convenient way to prepare in situ the chlorinated benzoenyne-allenes for subsequent cascade radical cyclizations. In addition, the transformation from **9** to **14** is very facile and can be carried out at ambient and subambient temperatures. This is perhaps of critical importance because 1-chloro-1,3,3-triphenylallene is known to undergo facile dimerization.[6] The simplicity of the procedure and the mildness of the reaction conditions are especially attractive features of this synthetic pathway.

Scheme 3



Because of the presence of a chiral center in **14**, the two methylene carbons of the protective group are diastereotopic, as are the two methyl carbons. They exhibit different ^{13}C NMR chemical shifts. Interestingly, the DEPT experiment gives 13 distinct signals for the aromatic methine carbons (CH) with the peak at δ 125.93 having twice the intensity. This is one more signal than expected if the rotation of the phenyl substituent is not restricted. The observation of 13 signals for the aromatic methine carbons suggests that **14** prefers the conformation with the phenyl substituent perpendicular to the remaining aromatic ring system and the rate of rotation of the phenyl substituent is slower than the NMR time scale, making the two ortho carbons diastereotopic and the two meta carbons also diastereotopic. The perpendicular orientation of the phenyl ring was also observed previously in other similar structures by X-ray[1h] and is most likely responsible for shielding the neighboring aromatic hydrogen located on the top of the phenyl substituent, causing its ^1H NMR signal to shift upfield to δ 6.53 (doublet). The appearance of this upfield doublet signal is indicative of a successful formal intramolecular Diels−Alder reaction of the benzoenyne-allene moiety in **11**.

Because the chloride **14** was prone to hydrolysis, it was operationally convenient to treat the crude **14** without further purification with $NaBH_4$[7] to furnish **15** in 51% overall yield from **9**. Hydrolysis of the ketal group in **15** gave **16** having a carbonyl group to allow a repeat of the condensation and C2−C6 cyclization sequence.

Initial attempts to try to prepare **18** from condensation of **16** with the lithium acetylide **8** were unsuccessful, presumably because the hydrogen atoms on the five-membered ring of **16** are very acidic.[8] Fortunately, by first converting **8** to the corresponding cerium derivative **17**,[9] the condensation reaction went smoothly to afford **18** in 83% yield (Scheme 3). Further treatment of **18** with thionyl chloride gave **19** in a manner similar to the transformation from **9** to **14**. The chloride **19** was also prone to hydrolysis to the corresponding alcohol on silica

(5) Jacobs, T. L.; Fenton, D. M. *J. Org. Chem.* **1965**, *30*, 1808−1812.
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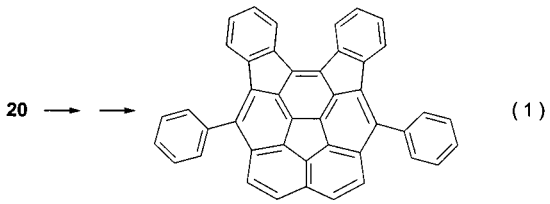
gel. It was possible to regenerate **19** for structural elucidation by treatment of the resulting alcohol with thionyl chloride. Reduction of the crude **19** with $NaBH_4$ then gave the $C_{44}H_{26}$ hydrocarbon **20** in 47% yield from **18**. The overall yield from **6** to **20** was 13% in eight steps.

The lack of symmetry in **19** is apparent on its ^1H and ^{13}C NMR spectra. For example, the two hydrogens of the methylene carbon give two sets of doublets at δ 5.38 and 4.49 with a large geminal coupling constant of 22.4 Hz. In addition, 40 distinct ^{13}C NMR signals are discernible. The two upfield aromatic hydrogen signals at δ 6.76 (doublet) and 6.66 (doublet) are again indicative of a successful second formal intramolecular Diels−Alder reaction. In contrast, the ^1H NMR spectrum of the hydrocarbon **20** exhibits a singlet for the four methylene hydrogens at δ 4.69. Moreover, only 20 distinct ^{13}C NMR signals are discernible (one less than expected presumably as a result of low signal intensity and/or overlapping). The presence of an upfield ^1H NMR signal at δ 6.78 (doublet) again suggests that the two pendent phenyl substituents are perpendicular to the central aromatic rings.

It is worth noting that **20** has a carbon framework represented on the surface of C_{60}. Although the molecular model of **20** shows that its central aromatic system has essentially a planar geometry,[10] **20** could serve as a precursor to the $C_{44}H_{22}$ hydrocarbon **21** containing a curved corannulene unit (eq 1).[11] Development of new



(1)

21, $C_{44}H_{22}$

synthetic pathways to such nonplanar polycyclic aromatic hydrocarbons is a subject of intense current interest because they could serve as precursors to C_{60} and larger carbon cages and may possess useful physical properties and chemical reactivities.[12]

Conclusions

A new synthetic pathway to generate the chloro-substituted benzoenyne-allenes in situ for the subsequent cascade radical cyclizations was established. This pathway was adopted for the preparation of the $C_{44}H_{26}$ hydrocarbon **20** having a carbon framework represented on the surface of C_{60}. Using different combinations of benzoenediynes and diaryl ketones for condensation, it is possible that a variety of other polycyclic aromatic hydrocarbons could also be likewise synthesized.

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere except in the case of **16**. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, 2,2-dimethyl-1,3-propanediol, cerium(III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$), dichlorobis(triphenylphosphine)-palladium, CuI, piperidine, pyridine (anhydrous), sulfolane, thionyl chloride, and triethylamine were purchased from Aldrich and were used as received. Phenylacetylene and (trimethylsilyl)acetylene were purchased from GFS Chemicals, Inc. and were used without further purification. 1-Bromo-2-iodobenzene and acenaphthenequinone were purchased from Alfa and Lancaster, respectively. The 2,2-dimethylpropylene monoketal **7** of acenaphthenequinone was prepared in 90% yield according to the reported procedure.[3] Silica gel for flash column chromatography was purchased from ICN. Melting points were uncorrected. ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^1H δ 7.26) and $CDCl_3$ (^{13}C δ 77.00) as internal standards.

Propargylic Alcohol 9. To a solution of 1.666 g of 1-(2-ethynylphenyl)-2-phenylethyne[2b,4] (8.247 mmol) in 80 mL of diethyl ether was added 3.3 mL of a 2.5 M solution of *n*-butyllithium (8.25 mmol) in hexanes at 0 °C. The reaction mixture was then allowed to warm to room temperature. After 15 min at room temperature, a solution of 2.01 g of **7** (7.50 mmol) in 100 mL of diethyl ether was added via cannula, and the mixture was stirred at room temperature for 12 h. Water (30 mL) was introduced, and the organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated to furnish a brown solid. Recrystallization from ethanol/water afforded 2.735 g (5.819 mmol, 77% yield) of **9** as a white solid: R_f 0.53 (hexanes/diethyl ether = 1:1); mp 157−159 °C; IR (KBr) 3494, 778, 756 cm^{-1}; ^1H NMR δ 7.84 (1 H, d, J = 8.3 Hz), 7.78−7.71 (3 H, m), 7.62−7.41 (6 H, m), 7.34−7.22 (5 H, m), 4.25 (1 H, d, J = 11.5 Hz), 4.13 (1 H, d, J = 11.1 Hz), 4.00 (1 H, d, J = 10.9 Hz), 3.84 (1 H, d, J = 11.5 Hz), 3.75 (1 H, s), 1.23 (3 H, s), 1.05 (3 H, s); ^{13}C NMR δ 142.92, 139.42, 134.37, 132.09, 131.82, 131.76, 130.98, 128.57, 128.23, 128.14, 127.89, 127.75, 126.17, 126.02, 125.29, 125.24, 123.17, 120.61, 106.86, 93.32, 92.32, 88.09, 86.10, 79.78, 73.60, 72.18, 30.78, 22.82, 22.56; MS m/z 470 (M^+), 453, 442, 385, 369, 339, 326; HRMS calcd for $C_{33}H_{26}O_3$ 470.1882, found 470.1871. Anal. Calcd for $C_{33}H_{26}O_3$: C, 84.23; H, 5.57. Found: C, 84.18; H, 5.60.

Chloride 14. To 0.352 g of the propargylic alcohol **9** (0.749 mmol) in 8 mL of THF at 0 °C was added via cannula a solution of 0.095 g of thionyl chloride (0.80 mmol) and 0.119 g of anhydrous pyridine (1.5 mmol) in 2 mL of THF at 0 °C. The reaction mixture was then allowed to warm to room temperature. After 4 h, the reaction mixture was concentrated, and 20 mL of water and 100 mL of methylene chloride were added. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated to furnish a light brown solid. Recrystallization from benzene afforded 0.127 g (0.260 mmol, 35% yield) of **14** as a light brown solid: IR 3053, 1470, 1025 cm^{-1}; ^1H NMR δ 7.94 (1 H, d, J = 7.1 Hz), 7.82 (1 H, d, J = 8.1 Hz), 7.71−7.52 (7 H, m), 7.42−7.36 (2 H, m), 7.27 (1 H, t, J = 7.5 Hz), 7.07 (1 H, t, J = 7.6 Hz), 6.53 (1 H, d, J = 7.9 Hz), 6.44 (1 H, s), 4.64 (1 H, d, J = 11.7 Hz), 4.62 (1 H, d, J = 11.7 Hz), 3.95 (1 H, dd, J = 11.7 and 2.0 Hz), 3.85 (1 H, dd, J = 11.6 and 2.0 Hz), 1.85 (3 H, s), 1.11 (3 H, s); ^{13}C NMR δ 144.85, 141.22, 139.86, 138.66, 138.22, 137.32, 137.17, 135.62, 135.06, 134.92, 129.85, 129.51, 129.16, 129.00, 128.87, 128.42, 128.33, 128.10, 127.85, 127.35, 125.93, 125.83, 123.92, 123.39, 123.28, 109.14, 72.68, 72.30, 54.65, 30.51, 24.38, 22.87; MS m/z 490 and 488 (M^+), 453, 369, 367; HRMS calcd for $C_{33}H_{25}ClO_2$ 488.1543, found 488.1525.

(10) For the structure of a related compound, see: Attar, S.; Forkey, D. M.; Olmstead, M. M.; Balch, A. L. *Chem. Commun.* **1998**, 1255−1256.

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Ketal 15. The propargylic alcohol **9** (2.312 g, 4.92 mmol) was converted to the chloride **14**, and the resulting crude product was concentrated and then used directly for reduction without further purification by recrystallization from benzene. To a flask maintained at 45 °C were added 0.673 g (17.8 mmol) of sodium borohydride, 24 mL of sulfolane, and the crude product **14**. The resulting mixture was heated at 100 °C for 1 h before it was allowed to cool to room temperature. The mixture was poured into a beaker containing 50 mL of water, and the resulting solution was extracted with diethyl ether. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (silica gel/3% diethyl ether in hexanes) to afford 1.144 g (2.52 mmol, 51% yield from **9**) of **15** as a yellow solid: R_f 0.31 (hexanes/diethyl ether = 8:1); mp 252−253 °C; IR 3050, 1471 cm^{-1}; ^1H NMR δ 7.93 (1 H, d, J = 7.1 Hz), 7.82 (1 H, d, J = 8.1 Hz), 7.65−7.42 (9 H, m), 7.24 (1 H, t, J = 7.5 Hz), 7.04 (1 H, t, J = 7.6 Hz), 6.68 (1 H, d, J = 7.9 Hz), 4.61 (2 H, d, J = 11.5 Hz), 4.42 (2 H, s), 3.84 (2 H, d, J = 11.9 Hz), 1.75 (3 H, s), 1.10 (3 H, s); ^{13}C NMR δ 144.29, 141.80, 141.63, 140.51, 138.20, 137.27, 136.61, 135.63, 134.15, 134.02, 129.88, 128.97, 128.29, 127.81, 126.96, 126.67, 126.23, 125.95, 125.00, 124.56, 124.22, 123.30, 123.08, 108.79, 72.56, 33.97, 30.67, 23.91, 22.60; MS m/z 454 (M^+), 368, 339; HRMS calcd for $C_{33}H_{26}O_2$ 454.1933, found 454.1919. Anal. Calcd for $C_{33}H_{26}O_2$: C, 87.20: H, 5.77. Found: C, 87.23; H, 5.76.

Ketone 16. To a mixture of 0.538 g of **15** (1.19 mmol), 50 mL of acetone, 5 mL of THF, and 4 mL of water was added 0.047 g of *p*-toluenesulfonic acid monohydrate (0.25 mmol). The resulting mixture was heated at 56 °C, and the progress of the reaction was monitored by TLC. After 23 h, the reaction mixture was allowed to cool to room temperature and concentrated in vacuo. The yellow solid residue was dissolved in 100 mL of methylene chloride, and water (50 mL) was added. The organic layer was separated, washed with a saturated aqueous $NaHCO_3$ solution and water, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (silica gel/2% diethyl ether in hexanes) to afford 0.407 g (1.11 mmol, 93% yield) of **16** as a yellow solid: R_f 0.26 (hexanes/diethyl ether = 8:1); mp 277−279 °C; IR 1706, 823, 728 cm^{-1}; ^1H NMR δ 7.87 (1 H, d, J = 8.1 Hz), 7.81 (1 H, d, J = 6.9 Hz), 7.67−7.46 (8 H, m), 7.41 (1 H, d, J = 9.1 Hz), 7.26 (1 H, td, J = 7.5 and 0.9 Hz), 7.05 (1 H, t, J = 7.5 Hz), 6.65 (1 H, d, J = 7.9 Hz), 4.34 (2 H, s); ^{13}C NMR δ 193.94, 143.88, 141.57, 141.43, 140.58, 138.72, 138.28, 137.71, 137.27, 133.67, 130.69, 129.29, 129.23, 128.84, 128.33, 127.36, 127.19, 127.12, 126.59, 125.20, 124.54, 124.29, 123.33, 122.32, 34.86; MS m/z 368 (M^+), 339; HRMS calcd for $C_{28}H_{16}O$ 368.1201, found 368.1195.

Propargylic Alcohol 18. Cerium(III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$, 0.596 g, 1.60 mmol) was heated in a flask with stirring at 150 °C in vacuo (0.2 Torr) for 2 h. The flask was then allowed to cool to room temperature, and THF (6 mL) was introduced. After 2 h of stirring, the resulting white suspension was cooled to −78 °C. In a separate flask, a solution of the lithium acetylide **8** was prepared by adding 0.63 mL of a 2.5 M solution of *n*-butyllithium (1.58 mmol) in hexanes to a solution of 0.323 g of 1-(2-ethynylphenyl)-2-phenylethyne (1.60 mmol) in 3 mL of THF at −78 °C. After 0.5 h of stirring, the resulting lithium acetylide **8** was introduced via cannula to the cerium(III) chloride suspension at −78 °C. After an additional 0.5 h of stirring, a solution of 0.295 g of the ketone **16** (0.80 mmol) in 165 mL of THF was added via cannula, and the mixture was allowed to warm to room temperature. After 16 h, 6 mL of water was introduced, and the reaction mixture was concentrated in vacuo. Water (100 mL) and diethyl ether (200 mL) were added, and the organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (silica gel/10% diethyl ether in hexanes) to afford 0.376 g (0.66 mmol, 83% yield) of **18** as a yellow solid: R_f 0.46 (hexanes/diethyl ether = 1:1); mp 130−132 °C; IR 3526, 2215, 1494, 756 cm^{-1}; ^1H NMR δ 7.91 (1 H, d, J = 7.1 Hz), 7.83 (1 H, d, J = 7.9 Hz), 7.71 (1 H, d, J = 9.1 Hz), 7.65−7.43 (10 H, m), 7.38−7.12 (8 H, m), 7.02 (1 H, t, J = 7.6 Hz), 6.69 (1 H, d, J = 7.9 Hz), 4.55 (1 H, d, J = 22.6 Hz), 4.33 (1 H, d, J = 22.6 Hz), 2.97 (1 H, s); ^{13}C NMR δ 146.56, 144.04, 141.51, 140.56, 139.11, 137.98, 137.55, 135.19, 134.04, 133.90, 132.36, 131.84, 131.56, 129.88, 129.03, 128.45, 128.42, 128.26, 128.19, 127.99, 127.90, 127.85, 127.00, 126.76, 126.29, 126.10, 125.53, 125.11, 124.66, 124.53, 123.32, 122.78, 120.54, 93.58, 91.32, 87.86, 83.16, 77.64, 33.56; MS m/z 570 (M^+), 554, 368, 339, 202; HRMS calcd for $C_{44}H_{26}O$ 570.1984, found 570.1959.

Chloride 19. The same procedure was repeated as described for **14** except that 0.205 g of **18** (0.360 mmol) was used. Attempts to purify the crude product of **19** by flash column chromatography (silica gel/10% diethyl ether in hexanes) resulted in the conversion of **19** to the corresponding alcohol (0.083 g, 0.146 mmol, 41% yield from **18**). A small sample of pure **19** was obtained by treatment of the alcohol in methylene chloride with thionyl chloride (rt, 2 h) followed by removal of the volatile materials in vacuo (0.2 Torr). **Data for the corresponding alcohol**: ^1H NMR δ 7.81−7.75 (3 H, m), 7.70 (1 H, d, J = 7.3 Hz), 7.64−7.51 (12 H, m), 7.31 (1 H, d, J = 6.7 Hz), 7.29 (1 H, t, 7 Hz), 7.12 (1 H, t, J = 7.8 Hz), 7.09 (1 H, t, J = 7.3 Hz), 6.77 (1 H, d, J = 7.9 Hz), 6.65 (1 H, d, J = 7.7 Hz), 6.25 (1 H, d, J = 10.7 Hz), 5.30 (1 H, d, J = 23.1 Hz), 4.56 (1 H, d, J = 23.1 Hz), 2.17 (1 H, d, J = 10.9 Hz); ^{13}C NMR δ 145.68, 144.00, 143.09, 142.29, 141.73, 140.89, 140.55, 138.13, 137.68, 135.31, 134.95, 133.71, 133.10, 132.94, 132.42, 130.73, 130.12, 130.02, 129.84, 129.15, 128.88, 128.85, 128.37, 128.07, 127.93, 127.85, 127.11, 126.87, 126.52, 126.36, 125.78, 125.45, 125.36, 125.12, 124.12, 123.56, 123.51, 73.70, 36.56; MS m/z 570 (M^+), 568, 552. **Data for 19**: IR 3056, 1601 cm^{-1}; ^1H NMR δ 7.81−7.75 (3 H, m), 7.69 (1 H, d, J = 7.5 Hz), 7.64−7.49 (12 H, m), 7.31 (1 H, t, J = 7.1 Hz), 7.29 (1 H, t, J = 6.7 Hz), 7.14 (1 H, d, J = 8.1 Hz), 7.10 (1 H, d, J = 7.9 Hz), 6.76 (1 H, d, J = 7.9 Hz), 6.66 (1 H, d, J = 7.7 Hz), 6.54 (1 H, s), 5.38 (1 H, d, J = 22.4 Hz), 4.49 (1 H, d, J = 22.4 Hz); ^{13}C NMR δ 143.62, 143.46, 142.60, 141.63, 140.74, 140.60, 139.83, 137.98, 137.36, 135.67, 135.44, 133.82, 133.12, 133.09, 132.41, 130.63, 130.08, 129.91, 129.40, 128.99, 128.89, 128.80, 128.54, 128.19, 127.97, 127.91, 127.21, 126.92, 126.65, 126.52, 125.98, 125.84, 125.69, 125.40, 124.99, 124.20, 123.67, 123.57, 57.47, 36.56; MS m/z 590 and 588 (M^+), 553; HRMS calcd for $C_{44}H_{25}Cl$ 588.1645, found 588.1621.

Hydrocarbon 20. The propargylic alcohol **18** (0.196 g, 0.344 mmol) was converted to the chloride **19**, and the resulting crude product was concentrated and then used directly for reduction without further purification. Reduction by sodium borohydride was carried out by using the procedure described for the ketal **15** to afford 0.090 g (0.16 mmol, 47% yield) of **20** as a yellow solid: R_f 0.32 (hexanes/diethyl ether = 8:1); mp (sealed tube) 318−320 °C; IR (KBr) 1598, 1422, 1363, 773, 735, 698 cm^{-1}; ^1H NMR δ 7.79 (2 H, d, J = 8.7 Hz), 7.68−7.54 (14 H, m), 7.29 (2 H, t, J = 7.3 Hz), 7.10 (2 H, t, J = 7.5 Hz), 6.78 (2 H, d, J = 7.9 Hz), 4.69 (4 H, s); ^{13}C NMR δ 143.13, 142.05, 140.49, 140.05, 138.15, 134.88, 132.64, 131 68, 130.11, 128.79, 127.89, 127.07, 126.80, 126.66, 126.42, 125.52, 125.02, 124.41, 123.58, 36.80; MS m/z 554 (M^+), 477; HRMS calcd for $C_{44}H_{26}$ 554.2035, found 554.2035.

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Supporting Information Available: Experimental procedures and spectroscopic data for 1-(2-bromophenyl)-2-phenylethyne, 1-phenyl-2-[2-(trimethylsilylethynyl)phenyl]ethyne, and 1-(2-ethynylphenyl)-2-phenylethyne and ^1H and ^{13}C NMR spectra for 1-(2-bromophenyl)-2-phenylethyne, 1-phenyl-2-[2-(trimethylsilylethynyl)phenyl]ethyne, 1-(2-ethynylphenyl)-2-phenylethyne and compounds **9**, **14**−**16**, **18**−**20,** and the corresponding alcohol of **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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