Steric Hindrance Facilitated Synthesis of Enynes and Their Intramolecular [4 + 2] Cycloaddition with Alkynes

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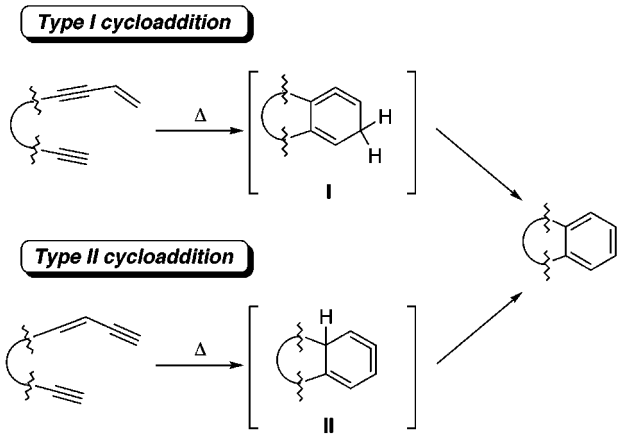
The palladium-catalyzed insertion of 1-alkynes into internal alkynes which are bent out of linearity by the interference with a peri or ortho substituent led to enynes regioselectively. The resulting enynes undergo a new type of intramolecular thermal cycloaddition, which can be used for the annulation of an aryl ring onto naphthalene derivatives to afford fluranthenes. The cyclization of (*E*)-1-(1-buten-3-ynyl)-8-ethynylnaphthalene could also be performed in the presence of a Cu(I) catalyst at room temperature.

New thermal cyclization processes such as the Bergman cyclizations of enediynes and the Myers cyclization of enyne−allenes have received great attention because of their involvement as key steps in the activation of some complex natural antibiotics.[1,2] Additionally, these transformations show promise as methods for the sequential construction of elaborate polycyclic systems.[1] Recently, Danheiser has reported an attractive alternative to the cyclizations of conjugated systems by using the intramolecular [4 + 2] cycloaddition of 1-en-3-ynes with alkynes (type I dehydro-Diels−Alder cycloaddition, Scheme 1).[3,4] Although this intramolecular cycloaddition most probably proceeds through formation of a highly strained allene intermediate **I**,[5,6] the reaction is thermodynamically favorable.[3,7] We report here the first examples of the alternative type II cycloaddition, which should proceed through a 1,2,4-cyclohexatriene **II**. Although the same aromatized product is expected in both processes, their differences may not be insubstantial with regard to the outcome of the elaboration of the strained intermediates with the appropriate reagents.[5,8] This new type of cycloaddition was uncovered as part of a study on the regioselective palladium-catalyzed insertion of 1-alkynes into internal alkynes which are bent out of linearity by the interference with a peri or ortho substituent.

The palladium-catalyzed cross-coupling of haloarenes with alkynyl coppers generated in situ from 1-alkynes (Sonogashira reaction) has been extensively used as a tool for the rapid assemblage of a variety of natural and nonnatural products.[9] Thus, Pd(0)- and Cu(I)-catalyzed coupling of 1,8-diiodonaphthalene (**1**)[10] with acetylene **2** proceeds smoothly in the presence of diisopropylamine or piperidine to give diyne **3** in almost quantitative yield (Scheme 2). Surprisingly, when pyrrolidine was used as the solvent, enediyne **4** was formed as the major product (51% yield).[11,12] The best yield of **4** (82%) was realized by using Ag(I)[13] instead of Cu(I). Under the conditions required for the deprotection of the acetylenes of **4**,[14] intermediate **5** suffered a type II cycloaddition and aromatization to give fluoranthene **6** (63% yield). Therefore, annulation of an aromatic ring onto naphthalene **1** was achieved in 52% yield by formation of five carbon−carbon bonds in just two steps.[15]

Scheme 1



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(11) The *Z* configuration of **4** was assigned by a NOESY spectrum and by comparison with its *E* isomer, which was available by isomerization of **4**, via the (η^3-allyl)palladium complex [$Pd(PPh_3)_4$ cat., 90 °C, acetonitrile or pyrrolidine].

(12) (a) Self-coupling of **2** gave variable amounts of regioisomeric butenynes and the diyne as byproducts. (b) Enediyne **4** incorporated the deuterium label at the alkenyl position (ca. 50%) when the reaction was carried out with **2**-*4,O-d*$_2$ (80% D) in pyrrolidine-*N-d* (65% D).

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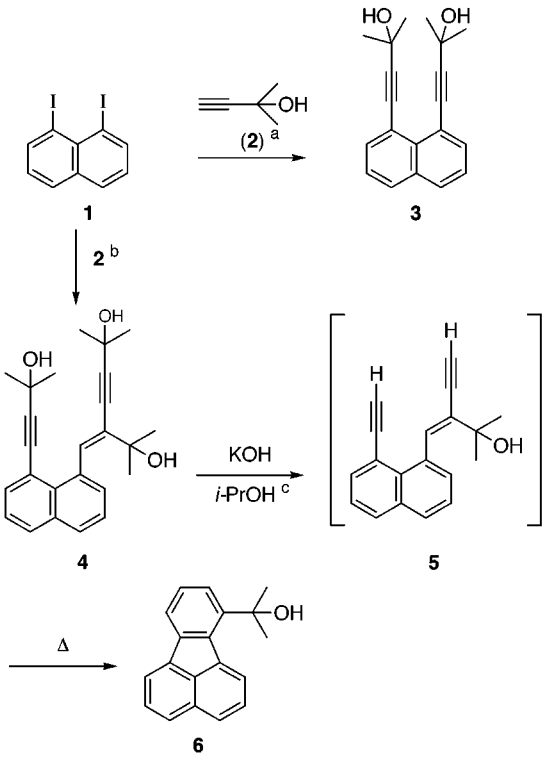
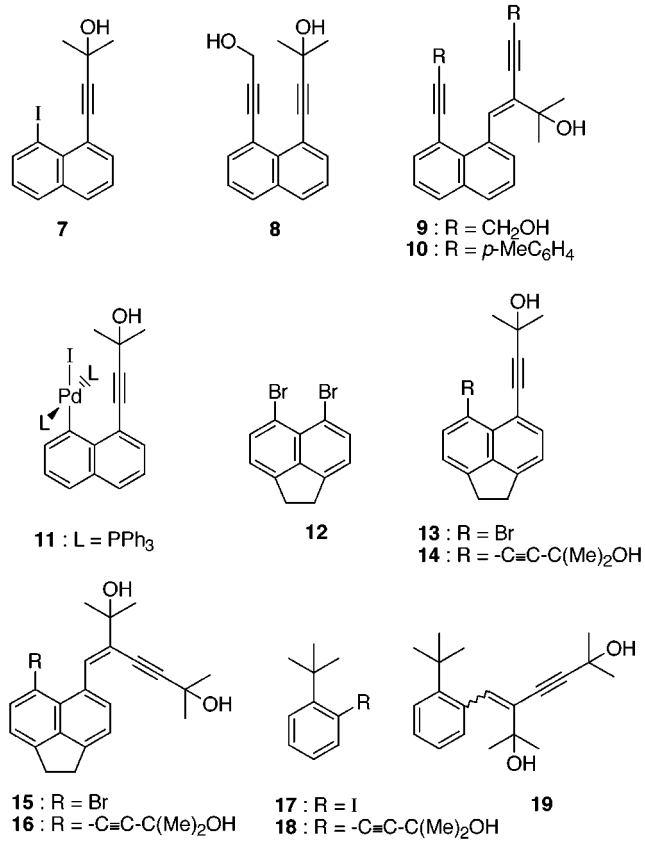
Scheme 2[a]



[a] (a) [$Pd(PPh_3)_4$] (5%), CuI (10%), *i*-Pr_2NH, 23 °C, 16 h, 99%; (b) [$Pd(PPh_3)_4$] (5%), Ag_2O (5%), pyrrolidine, 50 °C, 16 h, 82%; (c) reflux, 12 h, 63%.

The insertion of an alkyne involved in the formation of **4** is catalyzed by palladium. Thus, **7**[16] reacted with **2** in the presence of $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ as the catalysts to give **4**. Reaction of **7** with a second alkyne such as propargyl alcohol, under the conditions used for the conversion of **1** into **4**, provided a mixture of **8** (24%) and **9** (42%). A similar reaction between **7** and *p*-tolylacetylene gave enediyne **10** (76% yield).[17] None of the alternative regioisomeric enediynes could be detected in the reaction mixtures. Treatment of **7** with 1 equiv of $Pd(PPh_3)_4$ afforded complex **11** (95%), which reacted with excess **2** to give exclusively diyne **3**. This result suggest that the insertion of the alkyne to form the enyne precedes the second coupling reaction. The precise sequence of events was demonstrated by using 5,6-dibromoacenaphthene **12**[10b] as the electrophile. Coupling between **12** and alkyne **2** (3 equiv) with $Pd(PPh_3)_4$ (5 mol %) and CuI (10 mol %) in pyrrolidine (35 °C, 24 h) gave **13** (85% yield). By using a large excess of **2** (15 equiv), a mixture of diyne **14** (44%) and enediyne **16** (56%) was obtained.[17b] With Ag_2O as the cocatalyst, intermediate **15** could be isolated (28%). As observed before for **1**, the coupling of **12** and **2** in piperidine [$Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), reflux, 24 h] led cleanly to dialkyne **14** (97% yield).



The facile insertion into the disubstituted alkynes is related to the presence of a bulky peri or ortho substituent, probably as an effect of the bending of the alkyne out of linearity.[18] Thus, in contrast with **1** and **12**, iodobenzene reacted with **2** [$Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), pyrrolidine, 30−35 °C, 18−20 h] to give exclusively the arylalkyne (100%).[19] However, *o*-*tert*-butyliodobenzene (**17**), with a bulky ortho substituent, afforded enyne **19** (25% yield),[17c,20] along with arylalkyne **18** (75% yield). Although insertion of alkynylpalladium complexes into terminal alkynes has been previously observed under catalytic conditions,[21] the facile insertion into an internal alkyne and the observed regioselectivity are unprecedented.[22]

Benzannulation using an alternative synthesis of enynes by successive palladium-catalyzed cross-coupling reaction is illustrated in Scheme 3. Selective Stille

(15) (a) Cyclization of 1,8-bis(phenylethynyl)naphthalene also gives rise to a fluoranthene.[15b] However, this process could be considered as a type I cyclization. (b) See ref 10a and the following: Staab, H. A.; Ipaktschi, J. *Chem. Ber.* **1971**, 1170.

(16) Iodoalkyne **7** was prepared by reaction of **1** with **2** [$Pd_2(dba)_3$·dba (1.7 mol %), PPh_3 (6 mol %), CuI (6 mol %), Et_3N (1 equiv), toluene, 23 °C, 12 h; 60%, 83% based on unrecovered **1**].

(17) (a) The configurations of **9** and **10** were tentatively assigned as shown by comparison of their ^1H NMR spectra with that of **4**. (b) The configurations of **15** and **16** were assigned as *E* on the basis of NOESY experiments. These compounds are probably formed from the *Z*-enynes by a palladium-catalyzed isomerization.[11] (c) The configuration of enyne **19**, isolated as a single isomer, was not determined.

(18) (a) Gleiter, R.; Herger, R. In *Modern Acetylenic Chemistry*; Stang, P. J., Diederich, F. Eds.; VCH: Weinheim, 1995. Chapter 8.4. (b) Balasubramaniyan, V. *Chem. Rev.* **1966**, *66*, 567.

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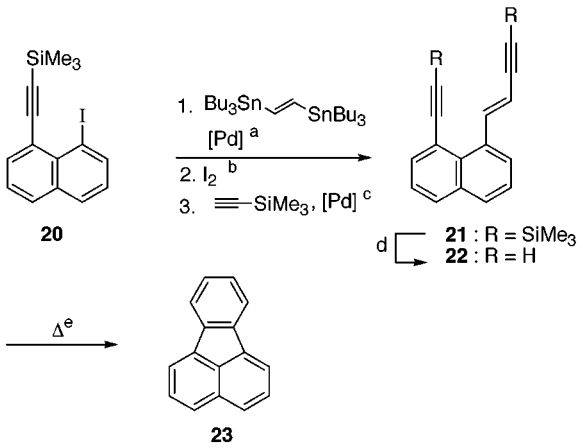
(20) 1-Iodo-8-phenylnaphthalene and alkyne **2** also led to an enyne [$Pd(PPh_3)_4$ (5 mol %), Ag_2O (5 mol %), pyrrolidine, 50 °C, 16 h] although the isolated yield was low (8%). See Experimental Section for details.

(21) (a) Sabourin, E. T. *J. Mol. Catal.* **1984**, *26*, 363. (b) Trost, B. M.; Chan, C.; Rühter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486. (c) Trost, B. M.; Matsubara, S.; Caringi, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 8745. (d) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266. (e) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698. (f) Trost, B. M.; McIntosh, M. C. *Tetrahedron Lett.* **1997**, *38*, 3207.

(22) The regiochemistry of the insertion is contrary to that observed in the Heck reaction between iodoarenes and disubstituted alkynes similar to those used in this work: Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron* **1985**, *41*, 5121.

Scheme 3[a]



[a] (a) $[Pd_2(dba)_3 \cdot dba]$ (3%) + $AsPh_3$ (6%) NMP, 50 °C, 2 h; (b) THF, −78 °C, 0.5 h; (c) $[Pd_2(dba)_3 \cdot dba]$ (2%) + PPh_3 (4%), CuI, (9%), piperidine, 23 °C, 12 h, 66% (three steps); (d) $Bu_4NF \cdot H_2O$, CH_2Cl_2, 23 °C, 4 h, 100%; (e) xylenes, hydroquinone (ca. 1%), 150 °C, 6 h, 65%.

coupling of iodoarylalkyne **20**[23] and (*E*)-bis(tributylstannyl)ethene under Farina's conditions[24] followed by iodolysis of the alkenylstannane and Sonogashira coupling with trimethylsilylacetylene yielded enediyne **21** (66%, three steps).[25] Desilylation of **21** gave quantitatively **22,** which underwent intramolecular cycloaddition at 150 °C in xylenes to afford fluoranthene **(23**) in 65% yield. Remarkably, this cyclization also can be performed at room temperature with CuCl or CuI as the catalysts (20 mol %) (pyridine or pyrrolidine, 5 h, 50% yield).[26]

In summary, we have found that the presence of bulky substituents ortho or peri to an arylalkyne enhances its propensity to suffer regioselective palladium-catalyzed insertion reactions. Several mechanistic aspects of this reaction, such as the exact role played by pyrrolidine, deserve further study.[27] The availability of conjugated enynes[28] coupled to type II cycloaddition provides a useful tool for the ready construction of polycyclic aromatics.

Experimental Section

Only the most significant IR absortions and the molecular ions and/or base peaks in the MS are given. "Usual workup" means aqueous treatment, extraction with EtOAc or CH_2Cl_2, drying with Na_2SO_4, filtration, and evaporation. Chromatography was performed with flash grade silica gel. All reactions were carried out under an atmosphere of Ar.

The following compounds were prepared according to the described procedures: 1,8-diiodonaphthalene (**1**),[29] 5,6-dibromoacenaphthene (**12**),[30] 1-*tert*-butyl-2-iodobenzene (**17**),[31] 2-methyl-3-butyn-2-ol-*4,O-d*$_2$ (**2**-*d*$_2$),[32] pyrrolidine-*N*-*d*,[33] 1-phenyl-8-iodonaphthalene.[34] (*E*)-1-(Trimethylstannyl)-4-(trimethylsilyl)-1-buten-3-yne was prepared in 56% by a modification of the described procedure for the synthesis of the *Z* isomer[35] by using (*E*)-bis(tributylstannyl)ethene[36] as the starting material: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.95 (d, J = 13.9 Hz, 1H), 5.99 (d, J = 13.9 Hz, 1H), 1.89−1.15 (m, 12H), 1.11−0.65 (m, 15H), 0.19 (s, 9H).

1,8-Bis(3-hydroxy-3-methyl-1-butynyl)naphthalene (3). To a mixture of **1** (100 mg, 0.26 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and CuI (5 mg, 0.026 mmol) in *i*-Pr_2NH was added alkyne **2** (250 μL, 2.6 mmol), and the mixture was stirred at 50 °C for 16 h. After the usual workup (EtOAc), the residue was chromatographed (5:1 hexanes−EtOAc) to give **3** as a white solid (75 mg, 99%): mp (toluene) 120−121 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.81 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.43 (dd, J = 8.6, 7.8 Hz, 2H), 3.99 (br s, 2H, OH), 1.69 (s, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz; DEPT) δ 134.9 (2C, d, ArH), 133.9 (2C, s, Ar), 131.0 (1C, s, Ar), 129.3 (2C, d, ArH), 125.3 (2C, d, ArH), 120.4 (1C, s, Ar), 100.4 (2C, s, Ar*C*≡*C*C(CH$_3$)$_2$OH), 82.2 (2C, s, Ar*C*≡CC(CH$_3$)$_2$OH), 65.9 (2C, s, ArC≡C*C*(CH$_3$)$_2$OH), 31.6 (4C, q, ArC≡CC(*C*H$_3$)$_2$OH); EI-MS *m*/*z* 292 (M$^+$, 35), 215 (100). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.06; H, 6.92.

(*Z*)-5-[(8-(3-Hydroxy-3-methyl-1-butynyl)-1-naphthyl)methylidene]-2,6-dimethyl-3-heptyne-2,6-diol (4).[37] **Method a.** To a solution of **1** (1.30 g, 3.4 mmol), $Pd(PPh_3)_4$ (150 mg, 0.13 mmol), and CuI (50 mg, 0.27 mmol) in pyrrolidine (20 mL) was added alkyne **2** (2.00 mL, 20.8 mmol) and the mixture was stirred at 50 °C for 16 h. After the usual workup (EtOAc), the residue was chromatographed (5:1 hexanes−EtOAc) to yield **3** (360 mg, 36%) and (eluting with 1:1 hexanes−EtOAc) **4** as a white solid (652 mg, 51%).[38]

Method b. To a suspension of **1** (100 mg, 0.26 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Ag_2O (3 mg, 0.013 mmol) in pyrrolidine (1.5 mL) was added alkyne **2** (250 μL, 2.6 mmol) and the mixture was stirred at 50 °C for 16 h. After the usual workup (EtOAc), the residue was chromatographed (1:1 hexanes−EtOAc) to yield **4** as a white solid (80 mg, 82%): mp (toluene) 115−116 °C; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 7.89 (dd, J = 8.2, 1.3 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.60 (dd, J = 7.2, 1.4 Hz, 1H), 7.45−7.31 (m, 4H), 5.28 (s, 1H, OH), 5.27 (s, 1H, OH), 4.10 (s, 1H, OH), 1.59 (s, 6H), 1.43 (s, 6H), 1.27 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz; DEPT) δ 137.29 (1C, d, Ar*C*HCRR′), 135.21 (1C, s, Ar), 134.10 (1C, d, ArH), 134.08 (1C, s, Ar), 130.76 (1C, s, ArCH*C*RR′), 130.42 (1C, s, Ar), 129.35 (1C, d, ArH), 128.89 (1C, d, ArH), 128.02 (1C, d, ArH), 125.26 (1C, d, ArH), 125.16 (1C, d, ArH), 120.09 (1C, s, Ar), 100.15 (1C, s, =CRC≡*C*C(CH$_3$)$_2$OH), 95.90 (1C, s, ArC≡*C*C(CH$_3$)$_2$OH), 83.81 (1C, s, =CR*C*≡CC(CH$_3$)$_2$OH), 83.20 (1C, s, Ar*C*≡CC(CH$_3$)$_2$OH), 73.50 (1C, s, R(CH$_3$)$_2$*C*OH), 65.56 (1C, s, R(CH$_3$)$_2$*C*OH), 65.05 (1C, s, R(CH$_3$)$_2$*C*OH), 31.41 (2C, q,

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(25) (*E*)-1-Tributylstannyl-4-trimethylsilyl-1-buten-3-yne[25b] (60% yield). (b) Burke, S. D.; Piscopio, A. D.; Kort, M. E.; Matulenko, M. A.; Parker, M. H.; Armistead, D. M.; Shankaran, K. J. *J. Org. Chem.* **1994**, *59*, 332.

(26) The reaction failed with Ag(I) salts or when MeCN or THF was used as the solvent. The cyclization also failed with $Cu(BF_4)_2$ or $Cu(BF_4)_2$/LiCl (pyridine solutions), which suggests that Cu(I) is the actual catalyst.

(27) Protonation of the alkyne by the pyrrolidinium salts, which are soluble under the reaction conditions, may play a role in the process. Piperidinium iodide is insoluble in neat piperidine at room temperature.

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(36) Renaldo, A. F.; Labadie, J. W.; Stille, J. K. *Org. Synth.* **1988**, *67*, 86.

(37) The regiochemistry of **4** was determined on the basis of HMQC and HMBC experiments. Its configuration was determined on the basis of NOESY experiments (800 and 400 ms mixing time).

(38) 2,6-Dimethyl-5-methylidene-3-heptyne-2,6-diol, obtained as a byproduct in some of the couplings of alkyne **2**, was prepared according to the published procedure: Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698.

R(CH_3)$_2$COH), 31.26 (2C, q, R(CH_3)$_2$COH), 30.07 (2C, q, R(CH_3)$_2$COH); EI-MS *m*/*z* 376 (M^+, 7), 59 (100). Anal. Calcd for $C_{25}H_{28}O_3$: C, 79.76; H, 7.50. Found: C, 79.64; H, 7.74. When the reaction was carried out in the presence of 2-methyl-3-butyn-2-ol-*4,O-d*$_2$ and pyrrolidine-*N-d* deuterated **4**-d_1(C-6) was obtained (50% D).

7-(1-Hydroxy-1-methylethyl)fluoranthene (6). A suspension of **4** (300 mg, 0.8 mmol) and KOH (450 mg, 8 mmol) in *i*-PrOH (10 mL) was stirred at 80 °C for 12 h. The reaction mixture was poured into H_2O and extracted (EtOAc). The organic extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed (5:1 hexanes−EtOAc) to yield **6** as a brownish solid (131 mg, 63%): mp 114−115 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.82 (d, J = 7.3 Hz, 1H), 7.94−7.81 (m, 4H), 7.69−7.56 (m, 2H), 7.41−7.27 (m, 2H), 2.11 (s, 1H, OH), 1.86 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz; DEPT) δ 144.33 (1C, s, Ar), 141.22 (1C, s, Ar), 136.44 (2C, s, Ar), 132.44 (1C, s, Ar), 129.78 (1C, s, Ar), 128.63 (1C, d, ArH), 128.10 (1C, d, ArH), 127.25 (1C, d, ArH), 127.17 (1C, d, ArH), 126.91 (1C, d, ArH), 126.45 (1C, d, ArH), 124.53 (1C, d, ArH), 120.45 (1C, d, ArH), 119.23 (1C, d, ArH), 76.60 (1C, s, Ar*C*(CH_3)$_2$OH), 29.90 (2C, q, ArC(CH_3)$_2$OH) (one of the signals corresponding to a quaternary carbon was not observed); EI-MS *m*/*z* 260 (M^+, 100). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.32; H, 6.33.

1-Iodo-8-(trimethylsilylethynyl)naphthalene (20).[23] To a solution of **1** (1.00 g, 2.6 mmol), $Pd(PPh_3)_4$ (150 mg, 0.13 mmol), and CuI (47 mg, 0.26 mmol) in piperidine (5 mL) was added trimethylsilylacetylene (375 μL, 2.7 mmol) and the mixture was stirred at 23 °C for 12 h. After the usual workup (Et_2O), the residue was chromatographed (hexane) to yield **20** as a colorless oil (0.60 g, 65%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.28 (dd, J = 7.3, 1.3 Hz, 1H), 7.88 (dd, J = 7.2, 1.3 Hz, 1H), 7.79 (dd, J = 7.0, 1.6 Hz, 1H), 7.78 (dd, J = 7.8, 1.6 Hz, 1H), 7.38 (dd, J = 7.8, 7.3 Hz, 1H), 7.07 (dd, J = 7.8, 7.7 Hz, 1H), 0.32 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz; DEPT) δ 142.78 (1C, d, ArH), 137.14 (1C, d, ArH), 134.71 (1C, s, Ar), 131.89 (1C, s, Ar), 130.62 (1C, d, ArH), 130.09 (1C, d, ArH), 127.02 (1C, d, ArH), 125.28 (1C, d, ArH), 122.75 (1C, s, Ar), 107.52 (1C, s, C≡C), 104.19 (1C, s, C≡C), 93.14 (1C, s, Ar), −0.56 (3C, q, (CH_3)$_3$Si); EI-MS *m*/*z* 350 (M^+, 90), 165 (100). Anal. Calcd for $C_{15}H_{15}ISi$: C, 51.44; H, 4.32. Found: C, 51.47; H, 4.37.

(*E*)-1-(4-Trimethylsilyl-1-buten-3-ynyl)-8-(trimethylsilylethynyl)naphthalene (21). Method a. To a solution of **20** (119 mg, 0.34 mmol), $Pd_2(dba)_3$·dba (20 mg, 0.03 mmol) and $AsPh_3$ (27.2 mg, 0.07 mmol) in NMP (2 mL) was added a solution of (*E*)-bis(tributylstannyl)ethene (280 mg, 0.68 mmol) in NMP (0.5 mL) and the mixture was stirred at 50 °C for 16 h. After the usual workup (Et_2O), the residue was chromatographed (250:1 hexane−CH_2Cl_2) to yield **21** as a yellow oil (70 mg, 60%).

Method b. (i) A solution of **20** (300 mg, 0.86 mmol), $Pd_2(dba)_3$·dba (15 mg, 0.026 mmol), and $AsPh_3$ (21 mg, 0.05 mmol) in NMP (5 mL) was treated with (*E*)-1,2-bis(tributylstannyl)ethene (784 mg, 1.3 mmol) at 50 °C for 2 h. The mixture was dissolved in THF (30 mL) and was treated at −78 °C with a solution of I_2 (870 mg, 3.4 mmol) in THF (10 mL). After 30 min the mixture was warmed to 23 °C, diluted with Et_2O, and treated with a saturated aqueous $Na_2S_2O_3$ solution and a 10% aqueous HCl solution. The organic extract was dried ($MgSO_4$) and the solvent was evaporated. The residue was chromatographed (hexane) to yield (*E*)-1-(2-iodoethenyl)-8-(trimethylsilylethynyl)naphthalene mixed with Bu_3SnI. (ii) This crude derivative and $Pd_2(dba)_3$·dba (25 mg, 0.02 mmol, 2.5 mol %), CuI (15 mg, 0.09 mmol), and PPh_3 (11 mg, 0.04 mmol) in piperidine (5 mL) were treated with trimethylsilylacetylene (120 μL, 0.9 mmol) a 23 °C for 12 h. After the usual workup (Et_2O), the residue was chromatographed (hexane) to yield **21** as yellow solid (180 mg, 66%): mp (hexane) 56−57 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.57 (d, J = 16.1 Hz, 1H), 7.73−7.68 (m, 3H), 7.43−7.26 (m, 3H), 5.91 (d, J = 16.1 Hz, 1H), 0.29 (s, 9H), 0.16 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz; DEPT) δ 143.79 (1C, d, CH), 135.89 (1C, s, Ar), 135.22 (1C, d, CH), 134.16 (1C, s, Ar), 130.31 (1C, s, Ar), 129.97 (1C, d, CH), 129.84 (1C, d, CH), 127.36 (1C, d, CH), 125.94 (1C, d, CH), 125.06 (1C, d, CH), 119.59 (1C, s, Ar), 109.04 (1C, d, CH), 106.45 (1C, s, C≡C), 105.15 (1C, s, C≡C), 105.04 (1C, s, C≡C), 101.26 (1C, s, C≡C), 0.14 (3C, q, (CH_3)$_3$Si), 0.06 (3C, q, (CH_3)$_3$-Si); EI-MS *m*/*z* 346 (M^+, 63), 73 (100). Anal. Calcd for $C_{22}H_{26}Si_2$: C, 76.23; H, 7.56. Found: C, 76.22; H, 7.86.

(*E*)-1-(1-Buten-3-ynyl)-8-ethynylnaphthalene (22). A solution of **21** (0.90 g, 2.6 mmol) in CH_2Cl_2 (10 mL) was treated with *n*-Bu_4NF·*x*H_2O (1.80 g, ca. 6.5 mmol) in CH_2Cl_2 (20 mL) a 23 °C for 4 h. The mixture was partitioned between CH_2Cl_2 and H_2O. The organic extract was dried (Na_2SO_4) and the solvent was evaporated. The residue was chromatographed (hexane) to yield **22** as a yellow solid (530 mg, 100%): mp 66−67 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.63 (d, J = 15.9 Hz, 1H), 7.87−7.78 (m, 3H), 7.48−7.37 (m, 3H), 5.90 (dd, J = 15.9, 2.5 Hz, 1H), 3.58 (s, 1H), 3.04 (d, J = 2.5 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz; DEPT) δ 145.32 (1C, d, ArH), 135.50 (1C, s, Ar), 135.23 (1C, d, ArH), 134.09 (1C, s, Ar), 130.52 (1C, s, Ar), 130.19 (1C, d, ArH), 129.85 (1C, d, ArH), 127.20 (1C, d, ArH), 125.97 (1C, d, ArH), 125.15 (1C, d, ArH), 118.59 (1C, s, Ar), 108.07 (1C, d, ArH), 85.18 (1C, s, R*C*≡CH), 83.63 (1C, d, RC≡*C*H), 83.14 (1C, s, R*C*≡CH), 78.13 (1C, d, RC≡*C*H); EI-MS *m*/*z* 202 (M^+, 100). EI−HRMS *m*/*z* Calcd for $C_{16}H_{10}$: 202.0783. Found: 202.0786.

Fluoranthene (23). Method a. A solution of **21** (100 mg, 0.5 mmol) and hydroquinone (ca. 1 mg) in xylene (10 mL) was stirred at 150 °C for 6 h. The solvent was evaporated, and the residue was chromatographed (hexane) to yield **23** as a white solid (65 mg, 65%).

Method b. A solution of **21** (50 mg, 0.25 mmol) and CuCl (5 mg, 0.05 mmol) in pyridine (3 mL) was stirred at 23 °C for 5 h. The reaction mixture was partitioned between Et_2O and 10% aqueous HCl solution. The organic extract was dried ($MgSO_4$) and the solvent was evaporated. The residue was chromatographed (hexane) to yield **23** as a yellow solid (25 mg, 50%): mp 107−109 °C (lit.[39] mp 110−111 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.98−7.82 (m, 6H), 7.70−7.60 (m, 2H), 7.43−7.35 (m, 2H).

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Supporting Information Available: Full experimental details and characterization data for ***E*-4**, **7**−**11**, **13**−**16**, **18**, **19**, **24**, and the products of the reaction of 1-iodo-8-phenylnaphthalene with alkyne **2** and copies of the ^{1}H and ^{13}C NMR spectra of **8**, **10**, **18**, **19**, **22** (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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