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The Bergman reaction as a synthetic tool: advantages and restrictions

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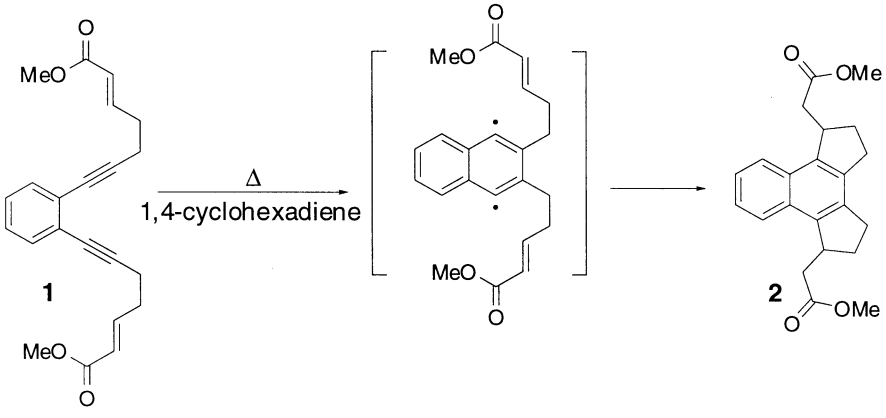
Abstract—The Bergman cycloaromatization reaction efficiently converts easily prepared acyclic enediynes into aromatic rings. In order to prepare larger, functionalized fused aromatic systems using this reaction, a thorough understanding of how functionalization affects cycloaromatization is necessary. We present here our studies on the influence of substituents at three different functionalization sites on cycloaromatization, and how these functional groups can be tailored to prepare more complex systems.

First reported in the early 1970s, the cycloaromatization that eventually became known as the Bergman reaction[1] received little attention until the early 1990s, when it was discovered that this reaction formed the DNA-cleaving 'warhead' of a series of marine antitumor antibiotics.[2] As efforts to control the activity of these potential drugs proved less than successful, a few researchers began to investigate the Bergman cyclization as a synthetic tool. Recent examples include the exploitation of the diradical nature of the *p*-benzyne, formed through cycloaromatization, for the synthesis of poly(*p*-phenylenes),[3] as well as the polymerization and crosslinking reaction for the formation of a series of arene-rich polymers.[4] A recent application of cycloaromatization to the synthesis of fused-ring systems involved tethering alkenes to the enediyne unit, allowing them to react with the cycloaromatized species to form additional (saturated) rings (Scheme 1).[5]

We recently began a series of projects applying the Bergman reaction to the synthesis of fused aromatic systems. Effective use of this reaction required us to develop an understanding of not only the functional group tolerances of this reaction, but also the geometric parameters required for successful ring closures initiated by the Bergman radical. Because we are particularly interested in synthetic applications, rather than detailed mechanistic considerations, our focus in exploring the scope of this reaction has been to determine how substitution affects the isolated yield and purity of products of these reactions, rather than how substituents alter the kinetics or rate of reaction.



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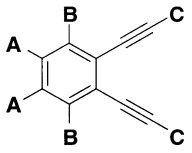
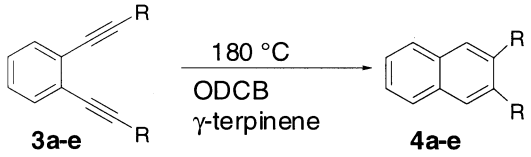


Figure 1. The three distinct functionalization sites of an arenediyne.



Cpd	R	Yield of naphthalene
a	Cl	90%
b	Br	85%
c	CHO	80%
d	C(O)Me	0%
e	CCTMS	0%

Scheme 2.

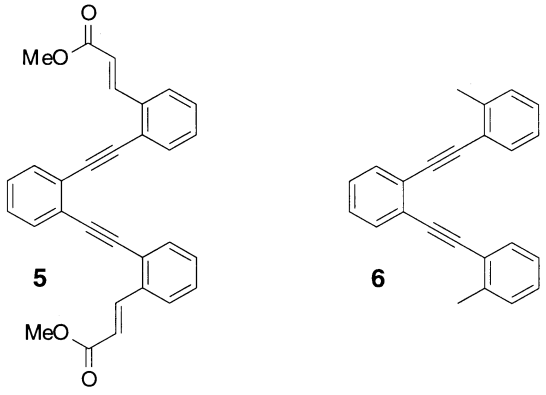


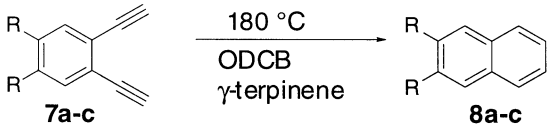
Figure 2. Substituted arenediynes which do not undergo cycloaromatization.

An aromatic enediyne can be substituted at three distinct positions (Fig. 1): On the positions *para* to the alkynes (**A**), on the positions *ortho* to the alkynes (**B**), or on the alkynes themselves (**C**). Because the chemistry of alkyne functionalization is both well optimized and diverse, substitution of the alkynes is particularly straightforward. Unfortunately, this sort of substitution typically has a detrimental impact on the cycloaromatization reaction, with the majority of disubstituted enediynes showing no cycloaromatization products formed at temperatures in excess of 250°C.[6] A few exceptions to this trend are the dichlorodibromo- and diformyl-enediynes **3a–c**, which undergo cycloaromatization in very good yields at much more synthetically amenable temperatures (180°C, refluxing *o*-dichlorobenzene/γ-terpinene).[7] However, even relatively subtle changes to these systems appear to shut down the Bergman reaction (Scheme 2).

For example, while diformyl derivative (**3c**) forms diformyl naphthalene (**4c**) cleanly upon cycloaromatization, the sterically more demanding diketone **3d** shows no cycloaromatization product even at temperatures as high as 220°C. Electronic factors also appear to play an important role in this reaction, since the tetrayne **3e** (the alkyne substituent is no more sterically encumbering across the enediyne than a halogen) also failed to undergo cycloaromatization.

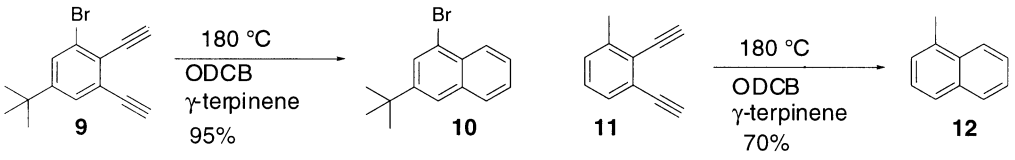
The only hydrocarbon-substituted enediynes which have been shown to cycloaromatize in good yield have been those with substituents which 'trap' the resulting radical.[8] Such systems do have rather severe limitations. They require very high temperatures (>220°C) to induce cyclization, and they are restricted to the formation of five-membered *saturated* ring systems. Attempts at forming six-membered rings by this method were not successful. Numerous efforts to extend this concept to compounds with a more rigid radical acceptor (e.g. **5**), or to quench the Bergman radical by hydrogen abstraction rather than cyclization (e.g. **6**) were unsuccessful in our hands, with such systems showing no reaction below 250°C (Fig. 2).

The dramatic effect of alkyne substitution on the cycloaromatization reaction has led us to investigate whether similar functionalization on the final product can be attained by substitution on the aromatic ring, rather than the alkynes. Substituents on the positions *para* to the alkynes have *no* steric impact on the cycloaromatization reaction, and are located far enough from the developing radical centers that interactions with these reactive species are negligible. Such characteristics make these the ideal positions for attachment of large solubilizing groups. Although they are remote from the enediyne, we have found that substituents at these positions do have a significant influence on the yield of the Bergman reaction. While several researchers have reported that electron-donating groups decrease the *rate* of cycloaromatizations,[9] we have found that along with lowering the temperature at which cycloaromatization takes place, such groups also have a salutary effect on the *yield* of the reaction (Scheme 3). Unlike other enediynes we have studied, dialkoxy arenediynes[10] even undergo quantitative cycloaromatization in the injection port of the GC/MS! A possible explanation for this result could lie in an increased reactivity of the *p*-benzyne unit toward hydrogen-atom abstraction,[11] making it a more competitive alternative to unproductive intermolecular radical couplings.

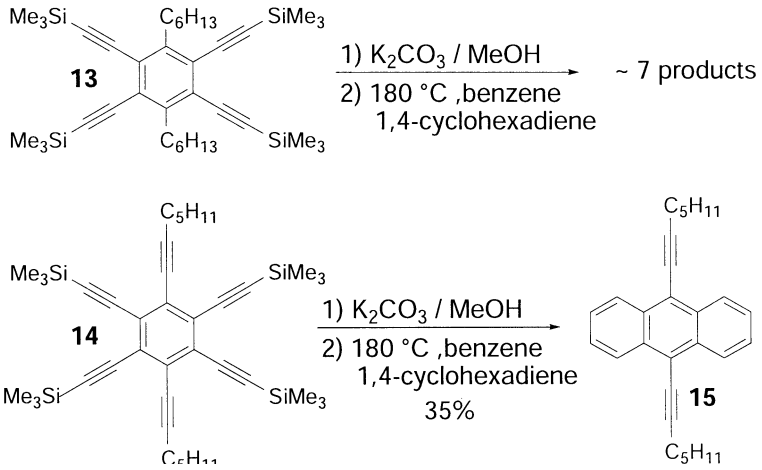


Cpd	R	Yield
a	n-hexyl	73%
b	OEt	95%
c	O(n-Octyl)	89%

Scheme 3.



Scheme 4.



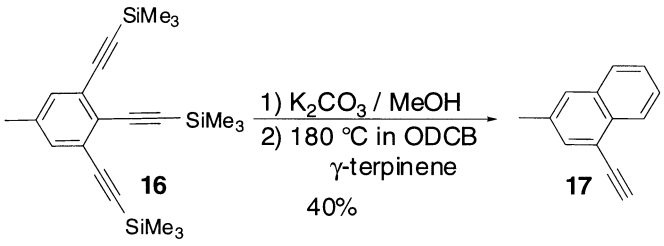
Scheme 5.

The positions *ortho* to the alkynes reveal both the benefits and disadvantages of the use of cycloaromatization as a synthetic tool. While substituents at these positions have little *direct* impact on the cycloaromatization reaction, they are close enough to the radical centers generated by cycloaromatization to react with them. This confluence of attributes can be a double-edged sword: While further cyclization initiated by the Bergman radical can be a useful synthetic tool, it can also be a serious competing side-reaction when further cyclization is not desired.

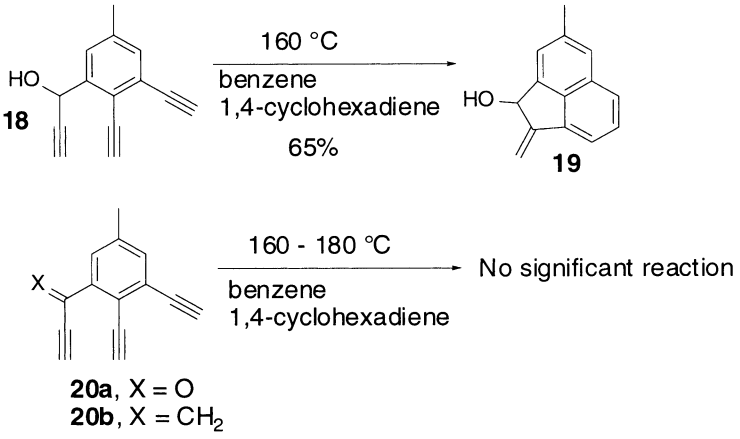
We began our investigations of *ortho*-substituted systems by preparing two simple arenediynes with small groups in the *ortho* position, and discovered that the cycloaromatization reaction proceeded quite rapidly and in good yield (Scheme 4).[12] Early reports on the cycloaromatization reaction related ease of cycloaromatization to the distance between the ends of the two alkynes.[2] Calculations on the bromo- and methyl-substituted enediynes **9** and **11** show that this distance is slightly decreased (from 4.07 to 4.03 Å) by the buttressing *ortho* substituents.[13]

Unfortunately, increasing the length of an *ortho* alkyl chain beyond methyl leads to cycloaromatization reactions which produce complicated mixtures. For example the double-cycloaromatization of desilylated **13** showed complete reaction within 2 h. However, GC/MS analysis of the reaction mixture showed *seven* products in relatively equal amounts, all of which appear to have arisen from various side-chain reactions such as hydrogen abstraction, elimination and fragmentation (Scheme 5).

In an attempt to avoid such adverse side-reactions we prepared hexayne **14**, which underwent an unprecedented double cycloaromatization smoothly to yield anthracene **15** in 35% yield. Because double cycloaromatization represents a new entry into the rapid synthesis of acenes, the low yield for this cycloaromatization reaction is as disconcerting as it is puzzling: The alkyl chains are remote enough that hydrogen abstraction is unlikely, and the geometry of the system should preclude reaction of the *p*-benzyne radicals with the adjacent alkynes. In order to further investigate the cycloaromatization chemistry of such systems with a simpler model, triyne **16** was prepared and subjected to cycloaromatization at 180°C. The yield of the expected ethynyl naphthalene **17** was only 40%; the bulk of the remaining material (an additional ~40%) appeared to be an inseparable mixture of dimeric species (a broad peak on the GC trace, with a mass corresponding to dimerized **17**). Although the actual structure of this by-product could not



Scheme 6.

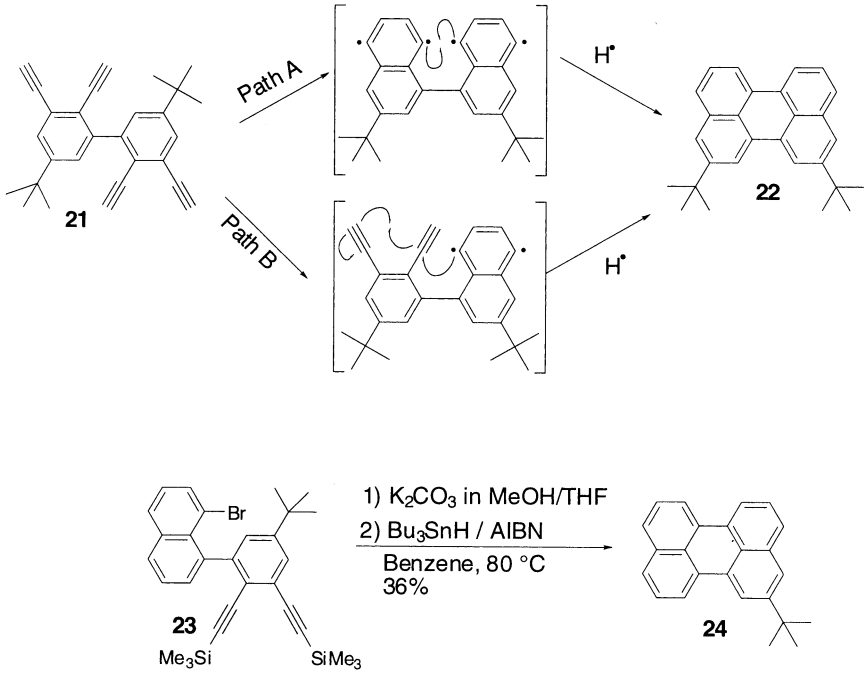


Scheme 7.

be determined by further spectroscopic analysis, the absence of acetylenic carbons in this material led us to believe that the dimerization occurred Diels–Alder reactions between the alkyne and the naphthalene ring. In order to prevent such reactions in future materials, we are currently preparing derivatives of **14** with significantly bulkier groups on the solubilizing alkynes (Scheme 6).

Of course, interactions between the Bergman radical and functional groups on the aromatic core can also be beneficial, since reactions of the *ortho* side-chain with the newly generated radical centers are a rapid and efficient way to construct multiple fused rings. Our first efforts in this vein focused on the preparation of acenaphthene derivatives. Triyne **18** underwent cycloaromatization followed by 5-*exo* cyclization in excellent yield, providing **19** as the only significant product. This second cyclization step appears to be highly dependent on the geometry of the pendant alkyne, since neither the ketone **20a** nor the alkene **20b** yielded characterizable products following cycloaromatization (Scheme 7).

We next shifted our attention to a slightly longer pendant group, which would lead to a 6-*exo* cyclization reaction with the Bergman radical. While *ortho*-linked arenediynes cycloaromatize in parallel to form substituted perylenes,[14] whether this reaction occurred by the coupling of two Bergman radicals (Scheme 8, Path A) or by a radical cascade mechanism (Path B) was not clear. Because the viability of the radical cascade is critical to the successful formation of larger fused aromatic systems, we further investigated this reaction by preparing bromonaphthyl arenediyne **23**. Reaction of this compound with tributyltin hydride/AIBN generates a radical species, which mimics the geometry and reactivity of the Bergman radical, and induces a cycloaromatization reaction with the adjacent enediyne. While the yield of perylene is not high (36%), the significant side product is hydrostannylated enediyne—an unfortunate



Scheme 8.

result of the need to use tin-based reagents for this type of cyclization. Thus the modest yield for this reaction can be viewed as a minimum yield for such a radical cascade, and in the absence of tin reagents Bergman-induced radical cascades should prove effective synthetic tools for the formation of *peri*-fused aromatic systems.

1. Conclusions

Methodologies involving cycloaromatization are efficient routes to substituted and fused aromatic systems. This thermal reaction tolerates a wide range of functional groups, many of which also increase the yield of the cycloaromatization reaction. The reactive radical generated from cycloaromatization can be employed to form further rings, yielding either acenaphthenes or perylene derivatives.

2. Experimental

2.1. General data

^{1}H and ^{13}C NMR spectra were recorded on Varian (Gemini 200 MHz/Unity 400 MHz) spectrometers with tetramethylsilane as the internal standard. Mass spectral analyses were performed in the EI-mode on a Varian Saturn GC/MS spectrometer.

2.2. Techniques and materials

All experiments were carried out under nitrogen in freshly distilled solvents under anhydrous conditions unless otherwise noted. Commercial chemicals were used as supplied. Tetrahydrofuran (THF) and diethyl ether were purified by passage through a column of activated alumina. Preparative column chromatography was performed with silica gel (230–425 mesh) from Fisher Scientific Company. Thin layer chromatography (TLC) was performed on glass-backed silica gel 60 F_{254} plates from Fisher Scientific Company. Radial chromatography was performed on a Harrison Research Chromatotron, using 4 mm silica plates. γ-terpinene was purchased from Acros Organics. Because desilylated enediynes are often prone to decomposition, silylated enediynes were typically desilylated immediately prior to cycloaromatization. Deprotection is assumed to be quantitative, unless otherwise noted.

2.3. General conditions used for cycloaromatization

A 0.01 M solution of the enediyne in *o*-dichlorobenzene/γ-terpinene (10:1 v/v) was sparged with dry nitrogen for 20 min. For large scale reactions, a condenser was added to the flask, and the mixture heated to 180°C for 2 h. For small scale reactions, this mixture was poured into a thick-walled glass tube which was then capped with a teflon screw cap, and heated to 180°C for 2 h. After reaction, the high-boiling solvents were removed on a rotary evaporator (connected to a high-vacuum pump), and the residue purified by chromatography or recrystallization.

2.3.1. 2,3-Dihexylnaphthalene (8a). 2.0 g of 1,2-dihexyl-4,5-bis(trimethyl-silylethynyl)benzene (4.5 mmol)[10] was desilylated by stirring with potassium carbonate in methanol/THF overnight. The resulting compound was extracted into hexanes, dried, and the solvent removed. The resulting dark oil was immediately treated to the cyclization conditions described above (sealed tube method). Evaporation of solvents left a dark oil, which was purified by flushing through a thin pad of silica (hexanes) to yield (after evaporation of solvent) 0.95 g (73%) of 2,3-dihexylnaphthalene as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.8 (t, 6H, J=6.6 Hz), 1.27 (m, 8H); 1.65 (m, 8H), 2.1 (t, 4H, J=6.8 Hz), 7.42 (dd, 2H, J=9.3, 2.5 Hz); 7.75 (s, 2H), 7.82 (dd, 2H, J=9.6, 2.1 Hz);. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.07, 22.64, 28.58, 29.59, 31.88, 36.41, 125.23, 126.82, 127.25, 132.18, 138.94 ppm. FTIR (neat) 3058, 2975 cm^{-1}. MS (EI 70 eV) *m/z* 296 (100%, M^+).

2.3.2. 2,3-Dioctyloxynaphthalene (8c). 1,2-dioctyloxy-4,5-bis(trimethylsilylethynyl)benzene (2.0 g, 3.8 mmol)[10] was desilylated by stirring with tetrabutylammonium fluoride in wet THF for 2 h. The compound was extracted into hexanes, dried, and the solvent removed. The resulting oil was subjected to cycloaromatization as described above (sealed tube method, but only 1 h *reaction time*) to yield after purification (silica plug, 3:1 hexanes/methylene chloride) 1.3 g (89%) of **8c** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.86 (t, J=6.6 Hz, 6H), 1.5–1.2 (broad m, 20H), 2.12 (quintet, J=6.6 Hz, 4H), 4.26 (t, J=6.6 Hz, 4H), 7.11 (s, 2H), 7.46 (m, 2H), 7.78 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.94, 22.55, 25.91, 26.00, 28.98, 29.14, 31.71, 69.18, 108.02, 127.67, 129.33, 130.53, 149.55 ppm. MS (EI 70 eV) *m/z* 384 (25%, M^+), 272 (20%, M^+−octyl), 160 (100%).

2.3.3. 1-Methylnaphthalene (12). 1.0 g (3.5 mmol) of 2,3-bis(trimethylsilylethynyl)toluene[15] was desilylated by treatment with potassium carbonate in methanol. The resulting enediyne was extracted into methylene chloride, dried, and subjected to the cyclization conditions described above (sealed tube). Chromatography on silica gel (hexanes) led to 0.35 g of a colorless liquid (70%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.11 (s, 3H), 7.70 (m, 1H), 7.76 (d, J=4.2 Hz, 1H), 7.888 (m, 2H), 8.08 (d, J=8.0 Hz, 1H), 8.22 (d, J=8.0 Hz, 1H), 8.36 (d, J=7.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 19.14 124.07, 125.49, 125.53, 125.67, 126.38, 126.55, 128.52, 133.61, 134.19 ppm. GC retention time and MS fragmentation identical to a commercial sample.

2.3.4. 1,4-Di-hept-1-ynyl-2,3,5,6-tetrabromobenzene. To a flame dried 100 mL two-neck flask was added a solution of 1-heptyne (1.92 g, 20 mmol, 4 equiv.) in 30 mL THF. After the solution was cooled to 0°C, butyllithium (19.9 mmol, 2.5 M in Et_2O), was added dropwise. The suspension was allowed to warm to 25°C and stirred for 1 h, after which bromanil (2.12 g, 5 mmol) was added. The solution was stirred at this temperature for 12 h, then quenched with 10 mL saturated NH_4Cl. The solution was extracted with three portions of 100 mL hexanes, and the organic layer dried and poured onto a thick pad of silica gel. After flushing the silica with 200 mL hexanes (to remove excess heptyne), the desired compounds were flushed off the silica with 250 mL ethyl acetate. The solvent was removed to yield 3.0 g of a brown powder (two spots by TLC in 3:1 hexanes/EtOAc). The two crude enantiomers and 3.79 g

(20 mmol, 4 equiv.) of $SnCl_2$ were taken up in 25 mL acetonitrile and two drops of H_2O in a 100 mL flask fitted with a reflux condenser. The reaction was heated to reflux for 12 h, and after cooling, the precipitate was filtered away. The solvent was removed, and the oily residue passed through a pad of silica gel (hexanes) to remove any unreacted starting material. Evaporation of solvent yielded 2.8 g of an orange oil (96% yield). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.45 (t, J=8 Hz, 3H), 1.87 (m, 2H), 2.01 (m, 2H), 2.19 (m, 2H), 3.15 (t, J=8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 13.97, 19.79, 22.49, 28.09, 31.23, 80.99, 103.12, 127.75, 128.96. FTIR (neat) 2952, 2141 cm^{-1}. MS (EI 70 eV) *m/z* 582 (80%, M^+), 525 (100%, M^+-Bu).

2.3.5. 1,4-Di-hept-1-ynyl-2,3,5,6-tetrakis(trimethylsilylethynyl)benzene (14). 2.9 g (5.0 mmol) of 1,4-di-hept-1-ynyl-2,3,5,6-tetrabromobenzene was dissolved in 20 mL piperidine and sparged under N_2 for 30 min. Bis[triphenylphosphine]palladium(II) chloride (70 mg, 2 mol%), CuI (95 mg, 10 mol%), and trimethylsilylacetylene (7.0 g, 50 mmol) were added and the reaction was heated to 50°C for 48 h. After cooling, the solvent was removed under vacuum and the residue was taken up in 20 mL hexanes, which purified by silica gel chromatography (hexane eluent) to yield 2.8 g (86%) of hexa-yne as an orange oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.11 (m, 36H), 0.88 (m, 6H), 1.24 (m, 12H), 1.65 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ −0.11, 13.90, 19.82, 22.15, 28.37, 31.15, 77.80, 100.75, 101.57, 104.13, 127.48, 128.45 ppm. FTIR (neat) 3050, 2105, 1954, 1758, 1496, 1205 cm^{-1}. MS (EI 70 eV) *m/z* 650 (80% M^+), 635(100%, M^+-CH_3).

2.3.6. 9,10-Di-hept-1-ynylanthracene (15). 0.8 g (1.2 mmol) of 1,4-di-hept-1-ynyl-2,3,5,6-tetrakis-(trimethylsilylethynyl)benzene was desilylated by stirring in methanolic K_2CO_3 for 1 h. The resulting desilylated material was extracted into hexanes, dried, evaporated, and immediately taken up in 50 mL of benzene. After this solution was sparged with nitrogen for 20 min, 5 mL of 1,4-cyclohexadiene was added, the solution was transferred under N_2 into a steel reaction vessel and heated to 180°C for 2 h. The vessel was cooled to room temperature and the solvent was removed via rotary evaporation to give an orange greasy solid. Recrystallization (MeOH) gave 0.15 g (35%) of **15** as a waxy yellow–orange solid (mp 205–206°C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95 (t, J=7.4 Hz, 6H), 1.44 (m, 8H), 1.80 (m, 4H), 2.73 (t, J=6.9 Hz, 4H), 7.56 (t, J=8.3 Hz, 4H), 8.52 (d, J=8.3 Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.91, 20.12, 22.18, 28.68, 31.26, 65.78, 103.37, 126.26, 127.31, 132.20, 141.68 ppm. FTIR (neat) 3100, 2900, 1590, 1500, 1120, 610, 590 cm^{-1}. MS (EI 70 eV) *m/z* 366 (100%, M^+), 309 (25%, M^+-butyl).

2.3.7. 1-Ethynyl-3-methylnaphthalene (17). 0.75 g (2 mmol) of 5-methyl-1,2,3-tris(trimethylsilylethynyl)benzene (**16**, obtained as a by-product as described below) was desilylated by stirring in methanolic KOH overnight. The compound was extracted into hexanes, then subjected to cycloaromatization conditions as described above (sealed tube method). The solvent was removed, and the compound purified by chromatography on silica (hexanes eluent) to give 133 mg (40%) ethynylnaphthalene **17** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.49 (s, 3H), 3.44 (s, 1H), 7.44 (s, 1H), 7.62 (s, 1H), 7.81 (m, 2H), 8.38 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.23, 81.49, 81.82, 119.59, 125.82, 126.03, 126.31, 126.50, 127.62, 128.43, 131.87, 133.35, 134.73 ppm. FTIR (neat) 3345, 3050, 2920, 2250 cm^{-1}. MS (EI 70 eV) *m/z* 166 (80%, M^+), 151 (100%, M^+-CH_3).

2.3.8. 3-Bromo-4,5-bis(trimethylsilylethynyl)toluene and 3,4,5-tris(trimethylsilylethynyl) toluene (16). A solution of 4.23 g (10.0 mmol) of 3-bromo-4,5-diiodotoluene (prepared as described in Ref. 14) in 50 mL of piperidine was placed in a 100 mL screw cap glass tube. The solution was sparged under N_2 for 30 min, and bis[triphenylphosphine]palladium(II) chloride (300 mg, 2 mol%), CuI (190 mg, 10 mol%), and trimethylsilylacetylene (3.11 mL, 2.2 equiv.) were added sequentially. The tube was then sealed, and heated at 60°C for 12 h. After cooling, the resulting amine salts were removed by filtration, and the clear solution was evaporated to dryness. The resulting dark oil was taken up in 20 mL hexanes, poured onto a thick pad of silica gel, and separated into its two components with hexanes eluent. Evaporation of the solvent from the first-eluted fraction afforded 2.5 g (70%) of desired diyne as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.10 (s, 9H), 0.12 (s, 9H), 0.39 (s, 1H), 1.98 (s, 3H), 7.10 (s, 1H), 7.39 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 0.19, 0.07, 20.77, 98.82, 101.68, 102.81, 102.85, 124.58, 125.62, 127.15, 131.56, 132.95, 139.12 ppm. FTIR (neat) 3300, 2923, 2150, 1711, 1592, 1534, 1249, 853 cm^{-1}. MS (EI 70 eV) *m/z* 362 (15%, M^+), 267 (10%), 73 (100%). Solvent removal from the second chromatographic fraction gave 0.4 g (10%) of the triyne as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.285 (three overlapping peaks, 27H), 2.27 (s, 3H), 7.23 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ −0.13, 0.01, 20.76, 98.18, 101.74, 101.93, 103.08, 125.35, 126.19, 132.81, 137.66. FTIR (neat) 3005, 2958, 2210, 2106, 1621, 1490, 1428, 1299, 632 cm^{-1}. MS (EI 70 eV) *m/z* 380 (20%, M^+), 365 (100% M^+-CH_3).

2.3.9. 2,3-Bis(trimethylsilylethynyl)-5-methylbenzaldehyde. A flame dried 100 mL two-neck flask under N_2 was cooled to −78°C and charged with 0.88 g (2.42 mmol) of 3-bromo-4,5-bis-(trimethylsilylethynyl)-toluene in 50 mL dry THF. The solution was stirred for 5 min, after which 3.7 mL *sec*-BuLi (4.8 mmol, 1.3 M in Et_2O) was added dropwise, and was stirred for 10 min. *N*-formyl morpholine (0.7 g, 6.1 mmol, 2.5 equiv.) was then added and the solution was allowed to stir until no further evidence of starting material could be detected by TLC (1:1 hexanes/CH_2Cl_2). The reaction was quenched with 10 mL of 10% HCl, extracted into hexanes, washed with H_2O, dried, and passed through a pad of silica gel (1:1 hexanes/CH_2Cl_2). The solvent was evaporated to yield 0.76 g (100%) of the benzaldehyde as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.02 (s, 9H), 0.03 (s, 9H), 1.99 (s, 3H), 7.02 (s, 1H), 7.21 (s, 1H), 10.10 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 0.48, 0.40, 98.16, 99.10, 101.86, 105.39, 125.79, 126.85, 126.90, 135.86, 137.43, 138.11 ppm. FTIR (neat) 3050, 2410, 2350, 1693, 1265, 749 cm^{-1}. MS (EI 70 eV) *m/z* 312 (20%, M^+), 297 (100%, M^+-CH_3), 269 (25%) 238 (25%), 73 (50%).

2.3.10. *R,S*-1-[5-Methyl-2,3-bis(trimethylsilylethynyl)-phenyl]-prop-2-yn-1-ol. 0.60 g (1.92 mmol) of 2,3-bis(trimethylsilylethynyl)-5-methylbenzaldehyde in 10 mL dry ether was added to an ethereal solution of ethynyl Grignard(20 mL of a 0.5 M solution) at 0°C, and stirred at this temperature for 20 min. The reaction was then quenched with 10 mL of a saturated aqueous NH_4Cl, extracted into hexanes, washed with water, dried, and passed through a thin pad of silica gel with CH_2Cl_2. The solvent was removed by rotary evaporation to yield 0.64 g (99%) of a racemic mixture of triyne alcohols as a yellow solid, mp 70–72°C (MeOH). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.13 (s, 18H), 2.10 (s, 3H), 2.40 (d, J=2.2 Hz, 1H), 5.62 (s, 1H), 6.99 (s, 1H), 7.21 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 0.36, 0.45, 20.90, 61.99, 73.86, 82.58, 97.66, 100.638, 103.25, 103.65, 120.32, 125.68, 126.77, 132.04, 138.30, 142.56 ppm. FTIR (neat) 3111, 2995, 2407, 2219, 1355, 810, 755 cm^{-1}. MS (EI 70 eV) m/z 338 (25%, M^+), 323 (100%, M^+-CH_3).

2.3.11. *R,S*-1-(5-Methyl-2,3-diethynylphenyl)-prop-2-yne-1-ol (18). To a racemic mixture of 1-[5-methyl-2,3-bis(trimethylsilylethynyl)phenyl]-prop-2-yn-1-ol (0.95 g, 2.3 mmol) in 2 mL THF and 10 mL MeOH was added one KOH pellet. After no evidence of starting material could be detected by TLC (5:1 hexanes/CH_2Cl_2), the reaction mixture was extracted into 500 mL hexanes, washed with water, brine, dried, and passed through a pad of silica gel with 5:1 hexanes/CH_2Cl_2 eluent. The solvent was removed to yield 0.43 g (96%) of a racemic mixture of **18** as a (marginally stable) yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.99 (s, 3H), 2.42 (s, 1H), 3.15 (s, 1H), 3.42 (s, 1H), 4.10 (broad s, 1H), 5.89 (s, 1H), 6.97 (s, 1H), 7.26 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.68, 61.38, 74.35, 78.61, 81.16, 81.55, 82.52, 86.32, 119.60, 124.91, 127.16, 132.47, 138.77, 142.46 ppm. FTIR (neat) 3090, 2955, 2460, 2210, 1290, 700, 605 cm^{-1}. MS (EI 70 eV) m/z 194 (100, M^+), 169 (10%).

2.3.12. 7-Methyl-2-methylene-acenaphthen-1-ol (19). 1-(5-Methyl-2,3-diethynylphenyl)prop-2-yne-1-ol **18** (0.34 g, 1.74 mmol) in 50 mL benzene was sparged with N_2 for 1 h. 1,4-Cyclohexadiene (5 mL, 10%/vol) was added and the solution was sealed under N_2 in a steel pressure apparatus. The reaction mixture was heated to 160°C for 1.5 h. After cooling, the solvent was removed under vacuum and the residue was dissolved in 5 mL 1:1 hexanes/CH_2Cl_2 and separated into its components via radial chromatography (2:1 hexanes/CH_2Cl_2). Compound **19** was isolated as a yellow solid (0.23 g, 65%), mp 105–106°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.35 (s, 3H), 5.44 (s, 1H), 5.46 (s,1H), 5.70 (s,1H), 7.11 (s, 1H), 7.38 (m,3H), 7.42 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.61, 75.25, 109.01, 115.29, 122.03, 123.64, 124.10, 128.19, 130.96, 135.85, 137.43, 138.23, 142.22, 151.10 ppm. FTIR (neat) 3350, 3100, 2990, 1750,1410, 600 cm^{-1}. MS (EI 70 eV) m/z 196 (100%, M^+), 181 (8%, M^+-CH_3).

2.3.13. 1-Bromo-8-(5-*tert*-butyl-2,3-bis(trimethylsilylethynyl)phenyl)naphthalene (23). To 2.0 g (5 mmol) of 1-bromo-5-*tert*-butyl-2,3-bis(trimethylsilylethynyl)benzene[13] in 50 mL dry THF at −78°C was slowly added 2.5 mL of *n*-BuLi (2.0 M in hexanes). After 20 min, 0.7 g (5 mmol) of dry zinc chloride was added, and the solution warmed to 0°C. 1-Bromo-8-iodonaphthalene (1.66 g, 5 mmol) and bis[triphenylphosphine]palladium(II) chloride (0.35 g, 10 mol%) were added, and the solution allowed to warm to room temperature overnight. The solution was then poured into hexanes, extracted with water, dried, and passed through a plug of silica (hexanes). Recrystallization from methanol led to pure **23** (1.6 g, 60%), mp 138–139°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ −0.24 (s, 9H), 0.27 (s, 9H), 1.32 (s, 12H), 7.4 (m, 4H), 7.8 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ −0.64, −0.03, 30.96, 34.64, 97.08, 101.39, 102.63, 104.41, 120.12, 124.35, 124.44, 125.32, 125.86, 127.83 (two overlapping peaks), 128.82, 129.15, 129.99, 130.85, 133.28, 135.73, 138.89, 146.23, 150.38 ppm. FTIR (KBr) 3052.4, 2959.2, 2893.2, 2147.6, 1242.7, 842.7, 753.4 cm^{-1}. MS (EI 70 eV) m/z 532 (30%, M^+), 517 (100%, M^+-CH_3). The compound was desilylated by treatment with potassium carbonate in methanol immediately prior to cyclization.

2.3.14. 2-*tert*-Butyl-perylene (24). 1.0 g (2 mmol) of compound **23** was dissolved in a mixture of 15 mL methanol and 5 mL THF, to which a catalytic amount of potassium carbonate had been added. Upon complete desilylation (as determined by GC/MS analysis), the mixture was poured into hexanes, and extracted with water. Drying and evaporation of the hexanes led to the crude desilylated diyne, which was immediately dissolved in 200 mL of dry, degassed benzene. The benzene solution was heated at reflux, and a solution of tributyltin hydride (1.1 equiv.) and AIBN (4 equiv.) in benzene (40 mL) was added by syringe pump over a period of 6 h. The reaction mixture was allowed to reflux for an additional 10 h and then cooled to room temperature. The benzene was evaporated under vacuum, and the resulting residue was dissolved in hexanes. Silica gel chromatography (hexanes) gave **24** as a yellow oil in 36% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.47 (s, 9H), 7.45 (m, 4H), 7.65 (m, 3H), 8.11 (d, J=7.2 Hz, 1H), 8.16 (d, J=7.6 Hz, 1H), 8.21 (d, J=6.8 Hz, 1H), 8.29 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.59, 35.13, 119.15, 119.79, 120.15, 120.29, 123.60, 126.64, 126.69, 126.75, 127.32, 127.90, 127.93, 128.09, 129.00, 130.99, 131.12, 131.56, 131.76, 135.01, 135.05, 149.21 ppm. FTIR (KBr) 3048, 2959, 2924, 2850, 1464, 1258, 838, 768 cm^{-1}. MS (EI 70 eV) m/z 308 (75%, M^+), 293 (100%, M^+-CH_3).

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