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Synthesis and structures of helical polycyclic aromatic hydrocarbons bearing aryl substituents at the most sterically hindered positions

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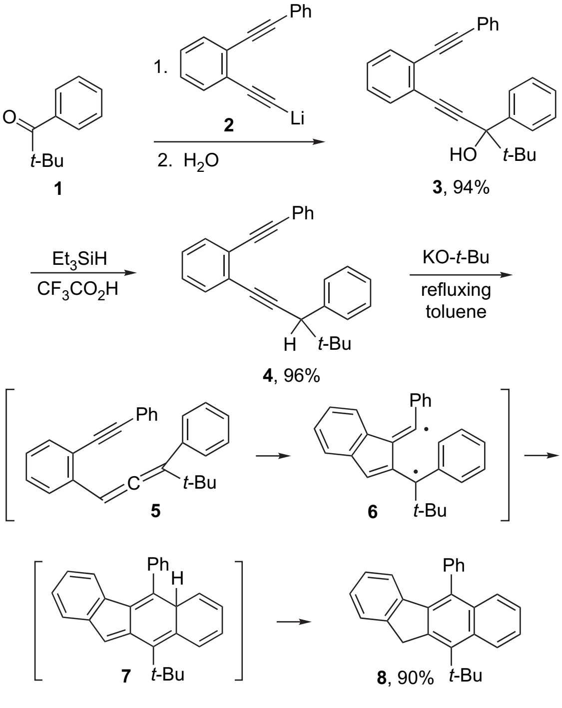
Abstract

A three-step synthetic sequence starting from condensation between a benzannulated enediyne and an aryl *tert*-butyl ketone was established to provide easy access to angularly fused polycyclic aromatic hydrocarbons bearing one or two aryl substituents at the most sterically hindered positions to cause helical twists. The dynamic behaviors involving the helix inversion and the restricted rotation of the aryl substituents were investigated by temperature-dependent NMR studies. The X-ray structure of an indeno-fused 1-phenylpentahelicene derivative showed severe distortion of the [5]helicene system from planarity.

Keywords: Helical polycyclic aromatic hydrocarbons; Benzannulated enyne–allenes; Cascade biradical cyclization

1. Introduction

We recently reported an efficient synthetic pathway outlined in Scheme 1 to produce **8** as an indeno-fused 11*H*-benzo[*b*]fluorene derivative.[1] Condensation between pivalophenone (**1**) and lithium acetylide **2** furnished the benzannulated enediynyl alcohol **3**, which was then reduced with triethylsilane in the presence of trifluoroacetic acid to give the benzannulated enediyne **4**. Treatment of **4** with potassium *tert*-butoxide in refluxing toluene then produced **8** via a sequence of cascade reactions. Presumably, an initial 1,3-prototropic rearrangement of **4** furnished the benzannulated enyne–allene **5**, which then underwent a Schmittel cyclization reaction to generate benzofulvene biradical **6**.[2–7] A subsequent intramolecular radical–radical coupling then gave the formal Diels–Alder adduct **7**



Scheme 1.

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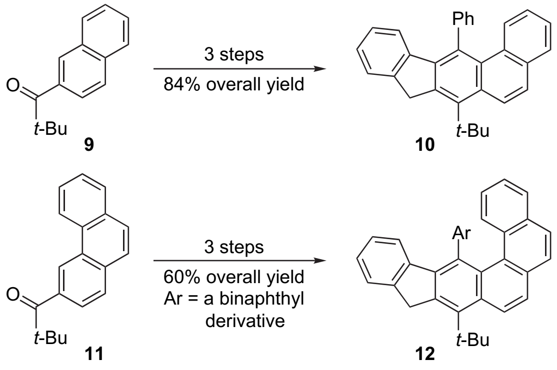
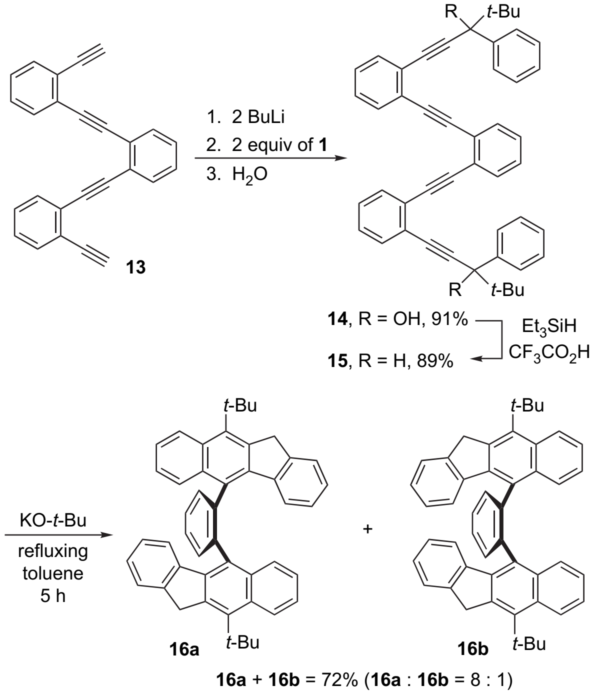
and, after a prototropic rearrangement, the indeno-fused 11*H*-benzo[*b*]fluorene **8** in excellent yield. Similarly, by using ketones **9** and **11** for condensation with **2** and a related binaphthyl derivative, the synthetic sequence led to polycyclic aromatic compounds **10** and **12**, respectively (Scheme 2).[8,9] In addition, this synthetic pathway was also adopted for the preparation of helical 4,5-diarylphenanthrenes and related derivatives.[10–12] Furthermore, by using tetraacetylene **13** for condensation with 2 equiv of **1**, the reaction sequence led to 1,2-bis[5-(11*H*-benzo[*b*]fluorenyl)]benzenes **16a** and **16b** as atropisomers (Scheme 3).[13] We envisioned that by replacing the 3-phenanthryl group of **11** with a 2-benzo[*c*]phenanthryl group, the synthetic sequence could lead to a dibenzo[*c*,*g*]phenanthrene ([5]helicene) derivative bearing a phenyl substituent at the most sterically hindered position to cause a helical twist. Helicenes and related compounds have continued to attract considerable attention due in part to their unusual structures and interesting optical and electronic properties.[14–25] The highly efficient assembly of two benzo[*b*]fluorenyl units by employing tetraacetylene **13** to initiate the reaction sequence also prompted us to explore the use of other tetraacetylenes for the construction of helical polycyclic aromatic hydrocarbons.



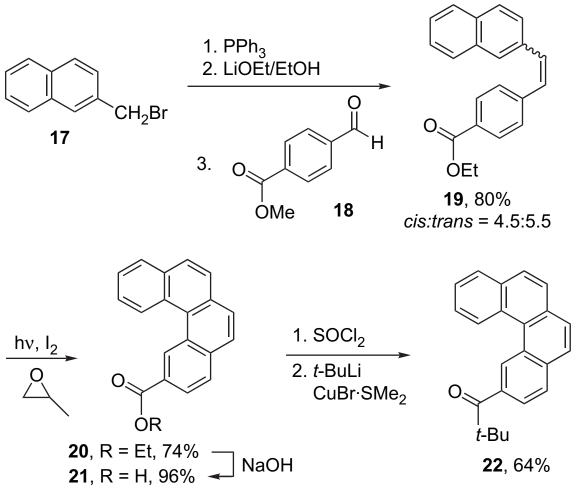
Scheme 2.



Scheme 3.

2. Results and discussion

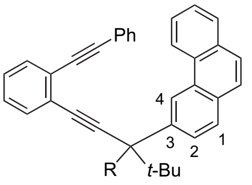
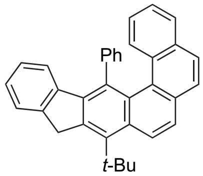
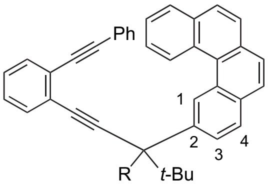
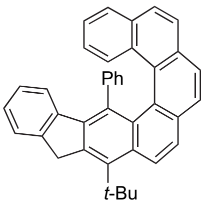
The requisite 2-benzo[*c*]phenanthryl *tert*-butyl ketone (**22**) was prepared as outlined in Scheme 4. Treatment of benzo[*c*]phenanthrene-2-carboxylic acid (**21**) with thionyl chloride to produce the corresponding acid chloride followed by *tert*-butylcopper, prepared from *tert*-butyllithium and $CuBr\cdot SMe_2$, produced **22** in 64% yield. A synthetic procedure for carboxylic acid **21** involving oxidation of 2-methylbenzo[*c*]phenanthrene was reported previously.[26] We used an alternative synthetic sequence to prepare **21**. The Wittig reaction between 2-(bromomethyl)naphthalene (**17**) and methyl 4-formylbenzoate (**18**), using lithium ethoxide as the base, produced ethyl 4-[2-(2-naphthalenyl)ethenyl]benzoate (**19**) as a mixture of the cis and trans isomers (cis/trans=4.5:5.5). A subsequent photocyclization reaction[27,28] furnished ethyl benzo[*c*]phenanthrene-2-carboxylate (**20**), which then was hydrolyzed to give **21**.



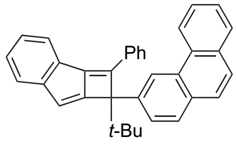
Scheme 4.

The use of **11** and **22** for condensation with **2** furnished the benzannulated enediynyl alcohols **23** and **25**, respectively, which were reduced with triethylsilane in the presence of trifluoroacetic acid to afford the benzannulated enediynes **24** and **26** (Table 1). Treatment of **24** and **26** with potassium *tert*-butoxide in refluxing toluene converted them to the indeno-fused benzo[*c*]phenanthrene **27** and dibenzo[*c*,*g*]phenanthrene ([5]helicene]) **28**, respectively, with a phenyl substituent at the most sterically hindered position in a single operation. The parent 1-phenylbenzo[*c*]phenanthrene[29,30] and 10-phenyldibenzo[*c*,*g*]phenanthrene (1-phenylpentahelicene)[31] and related compounds[29–33] were prepared previously by photocyclization reactions. Minor amounts of **29** (ca. 2%) and **30** (ca. 12%), derived from the intramolecular [2+2] cycloaddition reactions of the corresponding

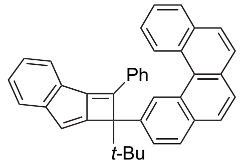
Table 1
Synthesis of benzo[*c*]phenanthrene **27** and dibenzo[*c*,*g*]phenanthrene **28**

Benzannulated enediynyl alcohols and enediynes	Phenanthrenes
 **23**, R = OH, 94% **24**, R = H, 98%	 **27**, 83%
 **25**, R = OH, 87% **26**, R = H, 89%	 **28**, 78%

benzannulated enyne–allene precursors, were also produced as observed previously.[1,10,11]



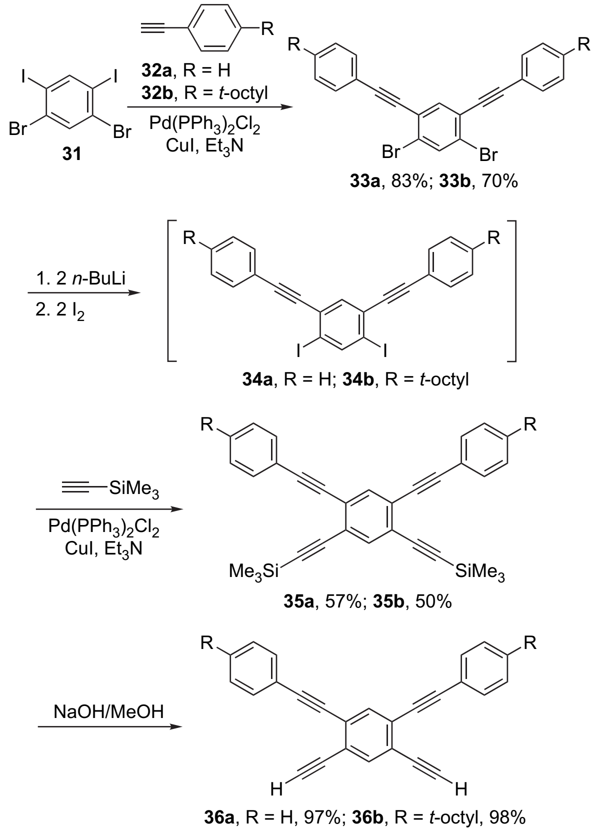
29



30

It is worth noting that the intramolecular radical–radical coupling reaction of the biradicals derived from **24** and **26** involved preferentially the 4-position of the phenanthryl ring[9] and the 1-position of the benzo[*c*]phenanthryl ring to produce the angularly fused **27** and **28**, respectively. Such a preference is reminiscent of what was observed in **10** in which only the α-position of the naphthyl ring was attacked. Attaching the β-position to form an indeno-fused anthracene derivative did not appear to occur. The regioselectivity was attributed to the higher reactivity of the α-position than the β-position of naphthalene in radical addition.[34,35] A similar preference could also account for the formation of the angularly fused **27** and **28**.

Tetraacetylene **36a** was prepared from 1,5-dibromo-2,4-diiodobenzene (**31**)[36,37] to test the feasibility of assembling two benzannulated enediynyl alcohol units for the synthesis of helical polycyclic aromatic hydrocarbons (Scheme 5). The Sonogashira reactions between **31** and 2 equiv of phenylacetylene (**32a**) produced **33a** as reported previously.[38] Transformation of **33a** to diiodide **34a** followed by Sonogashira reactions with 2 equiv of (trimethylsilyl)acetylene furnished, after desilylation, **36a**. Similarly, tetraacetylene **36b** bearing two sterically demanding 1,1,3,3-tetramethylbutyl (*tert*-octyl) groups was prepared by using **32b**[39] for the initial Sonogashira reactions with **31**.

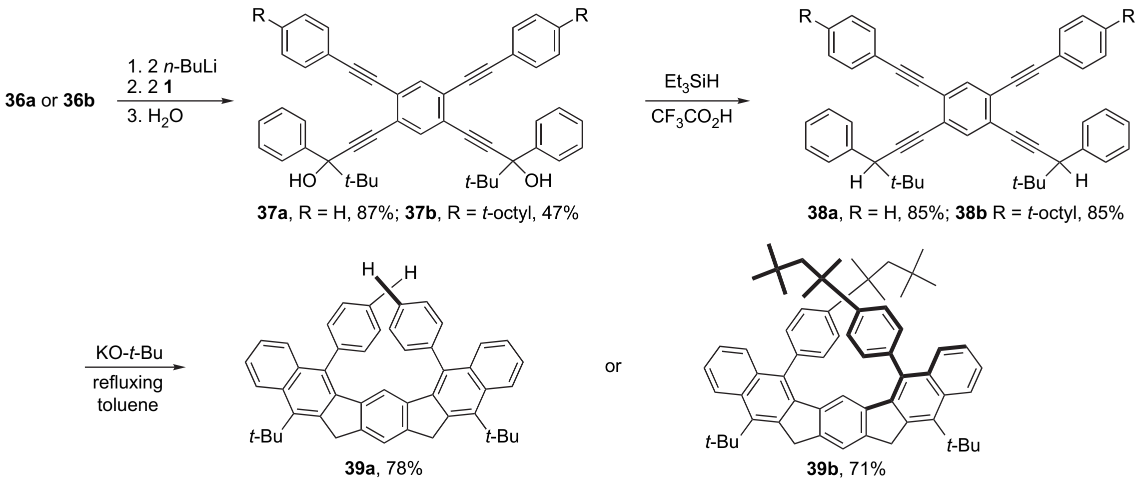


Scheme 5.

Condensation between **36a** and 2 equiv of pivalophenone (**1**) produced the benzannulated enediynyl diol **37a**, which was readily reduced with triethylsilane in the presence of trifluoroacetic acid to give **38a** bearing two benzannulated enediynyl units (Scheme 6). Treatment of **38a** with potassium *tert*-butoxide in refluxing toluene promoted two rounds of the cascade cyclization reactions leading to polycyclic aromatic hydrocarbon **39a** having a 7-fused-ring system. Similarly, **39b** was produced from **36b** in three steps. Polycyclic aromatic hydrocarbons **44a/b** and **45a** containing a 9-fused-ring system and an 11-fused-ring system, respectively, were likewise synthesized by employing 2 equiv of ketones **9** and **11** for condensation (Table 2).

Recorded on a 600 MHz NMR spectrometer, the proton signal of the two hydrogens on the five-membered ring of **10** in $CDCl_3$ appeared as a singlet at δ 4.45.[8] This observation is consistent with the planar geometry of the indeno[2,1-*b*]phenanthrene ring system of **10** with the phenyl substituent oriented roughly perpendicular to the phenanthrene ring as observed in the X-ray structure (Fig. 1).[40]

Interestingly, the proton signals of the methylene hydrogens of **27** in $CDCl_3$, also recorded on a 600 MHz NMR spectrometer at 25 °C, appeared as an AB quartet at δ 4.55 and 4.34 with a coupling constant of 20.7 Hz, indicating that the indeno-fused benzo[*c*]phenanthrene ring system with the phenyl substituent at the most sterically hindered position is nonplanar, and the rate of racemization is relatively slow on the NMR time scale. As a result, the methylene hydrogens are diastereotopic, exhibiting

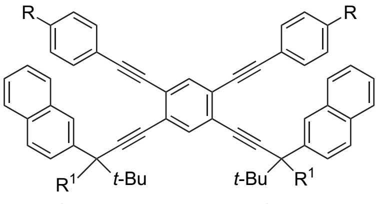
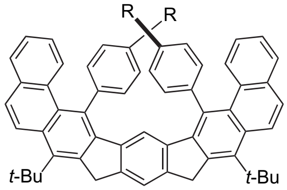
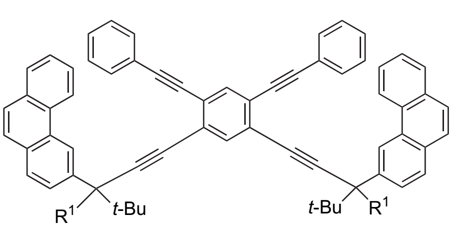
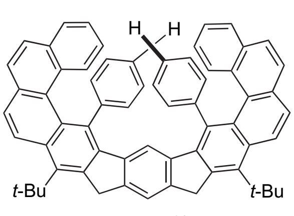


Scheme 6.

a large geminal coupling constant. The helical nature of the structures of several 1-phenylbenzo[*c*]phenanthrene derivatives was established by temperature-dependent NMR studies earlier.[30] The rate of racemization with the phenyl group moving from one side of the helical twist to the other side was determined to be ca. 16 kcal/mol. The well resolved AB quartet of the proton signals of the methylene hydrogens of **27** also provided an opportunity to determine the activation barrier of racemization by temperature-dependent NMR studies. However, the AB signals of **27** in 1,1,2,2-tetrachloroethane-d_2, recorded on a 270 MHz NMR spectrometer, remained well separated and exhibited essentially no line broadening at 125 °C, indicating that the rate of the helix inversion is relatively slow on the NMR time scale. $\Delta G^{\ddagger}_{rac}$ of **27** is estimated to be at least 19.4 kcal/mol on the basis of the AB signals at δ 4.60 and 4.39 ($\delta_A-\delta_B$=56.6 Hz) with a coupling constant of 20.7 Hz at 125 °C. The higher energy barrier for racemization than those of the earlier cases may be attributed to the buttressing effect of the fused indeno group and the *tert*-butyl substituent in **27** as observed previously in related systems.[10]

The ^{1}H NMR spectrum of **27** in CDCl$_3$ recorded on a 600 MHz NMR spectrometer at 25 °C also showed four broad humps at δ 8.01, 7.33, 6.72, and 6.07. At −20 °C, the signals at δ 8.01 and 6.07 became doublets and the signals at δ 7.33 and 6.72 became triplets, attributable to the *ortho* and *meta* hydrogens on the phenyl substituent, respectively. The fact that four separate signals were observed suggests that rotation around the carbon−carbon single bond attaching the phenyl substituent to the benzo[*c*]phenanthrene ring system is restricted on the NMR time scale. The signals of the *ortho* hydrogens coalesced at ca. 60 °C and the signals of the *meta* hydrogens coalesced at ca. 50 °C, corresponding to a rotational barrier of ca. 14.5 kcal/

Table 2
Synthesis of helical polycyclic aromatic hydrocarbons **44a**, **44b**, and **45a**

Benzannulated enediynyl diols and enediynes	Polycyclic aromatic hydrocarbons
 **40a**, R = H, R^1 = OH, 74%; **41a**, R = R^1 = H, 85% **40b**, R = *t*-octyl, R^1 = OH, 46%; **41b**, R = *t*-octyl, R^1 = H, 78%	 **44a**, R = H, 72% **44b**, R = *t*-octyl, 71%
 **42a**, R^1 = OH, 73%; **43a**, R^1 = H, 84%	 **45a**, 70%

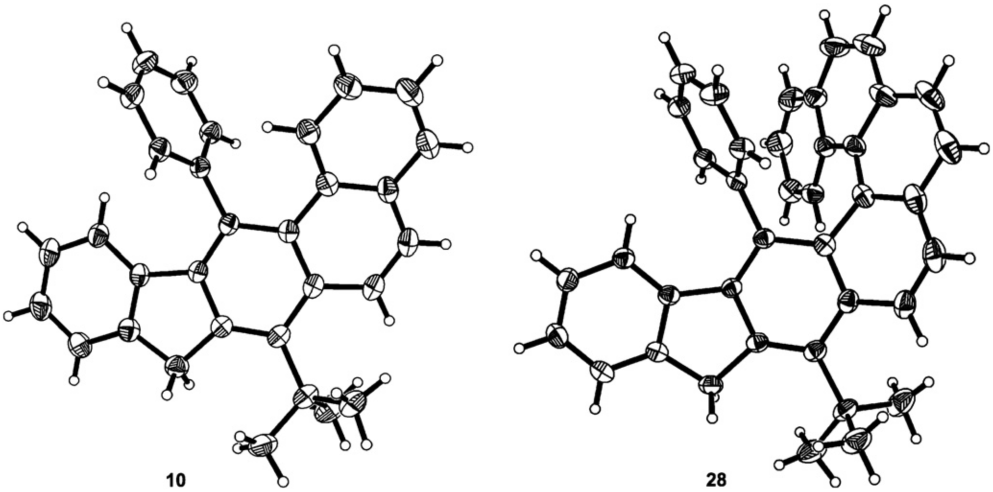


Figure 1. Perspective view of the molecular structures of **10** and **28** with the thermal ellipsoids scaled to enclose 30% probability.

mol, which is slightly higher than the rotational barriers of ca. 13 kcal/mol of several other 1-phenylbenzo[*c*]phenanthrene derivatives reported earlier.[30]

Compared to **27**, the structural distortion of **28** with an additional fused benzene ring could be expected to be even more profound. The X-ray structure of **28** (Fig. 1)[40] shows that the indeno-fused dibenzo[*c*,*g*]phenanthrene ([5]helicene) skeleton is severely twisted to minimize unfavorable van der Waals contact with the π electrons of the phenyl substituent at the most sterically hindered position. The acute dihedral angle between the mean planes of the benzene ring bearing the phenyl substituent and the benzene ring at the other end of the [5]helicene system is a pronounced 58.4° from planarity. The phenyl substituent is oriented at an angle of 60.6° from the mean plane of the benzene ring where it is attached.

As observed in **27** the AB quartet signals of the methylene hydrogens of **28** in 1,1,2,2-tetrachloroethane-d_2 at δ 4.63 and 4.35 ($\delta_A-\delta_B$=77.8 Hz, J=21.1 Hz), recorded on a 270 MHz NMR spectrometer, remained well separated and exhibited essentially no line broadening at 125 °C, corresponding to a $\Delta G^{\ddagger}_{rac}$ of at least 19.3 kcal/mol. The proton signals of the *ortho* hydrogens on the phenyl substituent appeared as doublets at δ 6.43 and 5.75, whereas those of the *meta* hydrogens appeared as overlapping triplets at δ 6.56 and 6.54. The coalescence temperature of the *ortho* hydrogens was determined to be at 100 °C, corresponding to a higher rotational barrier of 17.5 kcal/mol than the rotational barrier of 14.5 kcal/mol of **27**.

Recorded on a 600 MHz NMR spectrometer, the proton signal of the methylene hydrogens on the five-membered rings of **39a** in $CDCl_3$ appeared as a singlet at δ 4.52, indicating that the rate of racemization is relatively fast on the NMR time scale. Apparently, the two phenyl substituents in **39a** are relatively far apart, allowing them to move pass each other easily from one side of the helical twist to the other side. As a result, the proton signal of the methylene hydrogens appeared as a singlet. In addition, only one proton signal from the four *ortho* hydrogens on the phenyl substituents was observed as a doublet at δ 7.06 (J=7.8 Hz) and one proton signal from the four *meta* hydrogens appeared as a triplet at δ 7.35 (J=7.2 Hz), indicating relatively free rotation around the carbon–carbon single bonds attaching the phenyl substituents to the 7-fused-ring system. However, in the case of **39b** having two *tert*-octyl groups at the *para* positions of the phenyl substituents, the proton signals of the methylene hydrogens on the five-membered rings appeared as an AB quartet at δ 4.58 (J=21.6 Hz) and 4.44 (J=21.6 Hz), indicating that the rate of racemization is slow on the NMR time scale. Apparently, the sterically demanding *tert*-octyl groups impede the helix inversion. In addition, rotation around the carbon–carbon single bonds attaching the two 4-*tert*-octylphenyl substituents to the 7-fused-ring system is also restricted on the NMR time scale, and the proton signals from the *ortho* and *meta* hydrogens became too broad to be detected at 25 °C. However, at −25 °C, four additional signals appearing at δ 6.70, 7.08, 7.20, and 7.55, attributable to the two *ortho* hydrogens and the two *meta* hydrogens on each of the 4-*tert*-octylphenyl substituent, were clearly discernible.

As in the case of **39a**, the methylene hydrogens on the five-membered rings of **44a** in $CDCl_3$ appeared as a singlet at δ 4.47, indicating that the rate of racemization is also relatively fast on the NMR time scale. Again, only one proton signal from the *ortho* hydrogens and one proton signal from the *meta* hydrogens on the phenyl substituents were observed at δ 6.99 (d, J=8.4 Hz) and 7.17 (t, J=7.5 Hz), respectively. As expected, the methylene hydrogens on the five-membered rings of **44b** in $CDCl_3$ appeared as an AB quartet at δ 4.45 (J=21.6 Hz) and 4.43 (J=21.6 Hz) at 25 °C. Two broad humps at δ 6.95 and 7.28 attributable to the *ortho* and *meta* hydrogens on the 4-*tert*-octylphenyl substituents were also observed.

In the case of **45a**, one set of an AB quartet signals of the methylene hydrogens on the five-membered rings at δ 4.53 (J=21.0 Hz) and 4.44 (J=21.0 Hz) was observed. This is reminiscent of what was observed in **27**, which possesses a relatively stable helical configuration of 1-phenylbenzo[*c*]phenanthryl group on the NMR time scale. On the other hand, the helical configuration due to the steric interactions between the two phenyl substituents is less likely to be stable, and the helix inversion could occur rapidly as observed in the cases of **39a** and **44a**.

The presence of two helical subunits of 1-phenylbenzo[*c*]phenanthryl group in **45a** makes it possible for **45a** to exist as a P,M-(*meso*) compound with the two phenyl substituents on the same side of the 11-fused-ring system or as a P,P- and M,M-racemic mixture with the two phenyl substituents on the opposite sides. The fact that only one set of AB quartet signals was observed indicates that either the *meso* compound or the racemic mixture was produced preferentially. At 25 °C, very broad humps of the *ortho* and *meta* hydrogens of the phenyl substituents were observed. At −20 °C, two signals at δ 5.71 (d, J=7.2 Hz,) and 7.72 (overlapping signal) attributable to the *ortho* hydrogens and two signals at δ 6.13 (t, J=7.2 Hz) and 6.60 (t, J=7.2 Hz) attributable to the *meta* hydrogens could be clearly discerned.

3. Conclusion

Several helical polycyclic aromatic hydrocarbons bearing aryl substituents at the most sterically hindered positions were synthesized. The efficiency of the three-step synthetic sequence coupled with the ready availability of the starting benzannulated enediynes and aryl *tert*-butyl ketones make the process especially attractive for the construction of helical molecules. The convergent approach could also allow the synthetic sequence to be easily adopted for the preparation of other helical molecules bearing diverse structural features.

4. Experimental

4.1. General

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, *tert*-butyllithium (1.7 M) in pentane, $CuBr\cdot SMe_2$, triethylsilane, trifluoroacetic acid, potassium *tert*-butoxide, 2-naphthoyl chloride, 3-acetylphenanthrene, 2-(bromomethyl)naphthalene (**17**), triphenylphosphine, methyl 4-formylbenzoate (**18**), phenylacetylene (**32a**), and (trimethylsilyl)acetylene were purchased from chemical suppliers and were used as received. 1,5-Dibromo-2,4-diiodobenzene (**31**),[36,37] 1-ethynyl-2-(2-phenylethynyl)-benzene,[10] and 1-ethynyl-4-(1,1,3,3-tetramethylbutyl)benzene (**32b**)[39] were prepared according to the reported procedures. 3-Phenanthrenecarboxylic acid was prepared from 3-acetylphenanthrene as reported previously.[41] Melting points were uncorrected. Recrystallization of **10** from CH_2Cl_2/hexanes produced a single crystal suitable for X-ray structure analysis. ^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 77.0) as internal standards unless otherwise indicated.

4.2. *tert*-Butyl 3-phenanthryl ketone (**11**)

To a flask containing 0.500 g (2.25 mmol) of 3-phenanthrenecarboxylic acid[41] was introduced 39 mL of thionyl chloride. The reaction mixture was heated under reflux for 12 h. The excess thionyl chloride was removed in vacuo to furnish the crude 3-phenanthrenecarbonyl chloride. To a suspension of 0.562 g of $CuBr\cdot SMe_2$ (2.71 mmol) in 17 mL of THF was added 1.6 mL of a 1.7 M solution of *tert*-butyllithium (2.71 mmol) in pentane at −50 °C. After 30 min of stirring, a solution of the crude 3-phenanthrenecarbonyl chloride in 15 mL of THF was introduced dropwise via cannula. After an additional 4 h at −50 °C, the reaction mixture was allowed to warm to room temperature and treated with 20 mL of a saturated aqueous ammonium chloride solution. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 0.558 g of **11** (2.13 mmol, 95%) as an orange solid. Mp 57–59 °C; IR 1667, 842 cm^{-1}; ^1H NMR δ 9.13 (1H, s), 8.64 (1H, d, J=7.9 Hz), 7.93 (1H, dd, J=8.2, 1.4 Hz), 7.76 (2H, t, J=8.7 Hz), 7.67–7.51 (4H, m), 1.50 (9H, s); ^{13}C NMR δ 209.0, 136.2, 133.4, 132.2, 130.5, 129.6, 128.85, 128.78, 128.1, 127.09, 127.03, 126.2, 125.6, 123.2, 122.6, 44.4, 28.3; MS *m/z* 262 (M^+), 205, 177.

4.3. 2-Benzo[*c*]phenanthryl *tert*-butyl ketone (**22**)

The same procedure was repeated as described for **11** except that 0.264 g (0.97 mmol) of benzo[*c*]phenanthrene-2-carboxylic acid (**21**) was heated with 17 mL of thionyl chloride under reflux for 12 h to furnish the crude benzo[*c*]-phenanthrene-2-carbonyl chloride. The acid chloride was treated with *tert*-butylcopper, prepared from 0.241 g of $CuBr\cdot SMe_2$ (1.16 mmol) and 0.68 mL of a 1.7 M solution of *tert*-butyllithium (1.16 mmol) in pentane, to afford 0.193 g of **22** (0.62 mmol, 64%) as an orange solid. Mp 68–70 °C; IR 1668, 848 cm^{-1}; ^1H NMR δ 9.57 (1H, s), 9.03 (1H, d, J=8.4 Hz), 8.07–7.97 (3H, m), 7.94 (1H, d, J=8.4 Hz), 7.90 (2H, s), 7.84 (1H, d, J=8.6 Hz), 7.77–7.63 (2H, m), 1.49 (9H, s); ^{13}C NMR δ 208.8, 135.4, 134.6, 133.6, 131.2, 129.9, 129.2, 128.73, 128.66, 128.5, 128.2, 127.9, 127.7, 126.8, 126.7, 126.5, 126.2, 125.1, 44.2, 28.2; MS *m/z* 255 (M^+-57), 226.

4.4. Benzannulated enediynyl alcohol **23**

To a solution of 0.516 g of 1-ethynyl-2-(2-phenylethynyl)-benzene (2.56 mmol) in 15 mL of THF at 0 °C was added 1.0 mL of a 2.5 M solution of *n*-butyllithium (2.5 mmol) in hexanes. After 30 min of stirring, a solution of 0.558 g of **11** (2.13 mmol) in 20 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 20 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/20% diethyl ether in hexanes) afforded 0.931 g of **23** (2.01 mmol, 94%) as a white solid. IR 3546, 2213, 753 cm^{-1}; ^1H NMR δ 9.32 (1H, s), 8.96 (1H, d, J=7.7 Hz), 8.25 (1H, d, J=8.2 Hz), 7.99 (1H, d, J=6.9 Hz), 7.90–7.70 (7H, m), 7.60 (2H, d,

J=7.4 Hz), 7.44–7.28 (5H, m), 3.17 (1H, s), 1.44 (9H, s); ^{13}C NMR δ 140.3, 132.14, 132.10, 131.9, 131.5, 131.1, 130.4, 129.1, 128.4, 128.2, 128.03, 127.98, 127.86, 127.0, 126.9, 126.7, 126.4, 126.3, 125.8, 124.9, 122.75, 122.68, 121.4, 96.4, 93.4, 88.3, 84.8, 79.8, 39.9, 25.6.

4.5. Benzannulated enediyne **24**

To a solution of 0.114 g of **23** (0.25 mmol) and 0.043 g of triethylsilane (0.37 mmol) in 10 mL of methylene chloride was added 0.08 mL of trifluoroacetic acid (1 mmol). After 10 min of stirring at room temperature, a solution of 0.068 g of sodium carbonate (0.64 mmol) in 10 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes) afforded 0.107 g of **24** (0.24 mmol, 98%) as a yellow solid. IR 2214, 1493, 842, 756 cm^{-1}; ^{1}H NMR δ 8.90 (2H, m), 8.04–7.97 (1H, m), 7.94–7.81 (4H, m), 7.77–7.69 (4H, m), 7.55 (2H, d, J=6.9 Hz), 7.44–7.22 (5H, m), 4.18 (1H, s), 1.35 (9H, s); ^{13}C NMR δ 137.6, 132.1, 132.0, 131.6, 130.8, 130.2, 129.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.4, 126.53, 126.50, 126.4, 126.2, 125.7, 123.5, 123.1, 122.6, 95.7, 93.0, 88.6, 82.8, 51.1, 35.7, 27.9; MS m/z 448 (M$^+$), 391, 207.

4.6. Benzannulated enediynyl alcohol **25**

The same procedure was repeated as described for **23** except that 0.102 g of **22** (0.33 mmol) was treated with **2**, prepared from 0.079 g of 1-ethynyl-2-(2-phenylethynyl)benzene (0.39 mmol) and 0.16 mL of a 2.5 M solution of n-butyllithium in hexanes, to afford 0.146 g of **25** (0.28 mmol, 87%) as a white solid. IR 3556, 2217, 730 cm^{-1}; ^{1}H NMR δ 9.58 (1H, s), 9.23 (1H, d, J=8.4 Hz), 8.09 (1H, dd, J=8.4, 1.7 Hz), 8.01 (1H, d, J=7.9 Hz), 7.95–7.82 (5H, m), 7.67–7.61 (2H, m), 7.57 (1H, t, J=7.4 Hz), 7.44–7.32 (5H, m), 7.28–7.12 (3H, m), 2.74 (1H, s), 1.24 (9H, s); ^{13}C NMR δ 140.1, 133.4, 132.7, 132.3, 132.1, 131.5, 131.1, 130.2, 129.1, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 127.07, 126.96, 126.91, 126.7, 126.2, 126.1, 125.9, 125.8, 125.1, 122.7, 96.5, 93.4, 88.3, 84.9, 80.0, 40.2, 25.7.

4.7. Benzannulated enediyne **26**

The same procedure was repeated as described for **24** except that 0.140 g of **25** (0.27 mmol) was treated with 0.048 g of triethylsilane (0.41 mmol) and 0.90 mL of trifluoroacetic acid (1.08 mmol) in 10 mL methylene chloride to afford 0.121 g of **26** (0.24 mmol, 89%) as a yellow solid. IR 2217, 844 cm^{-1}; ^{1}H NMR δ 9.23–9.17 (2H, m), 8.01 (1H, J=7.9 Hz), 7.93–7.75 (6H, m), 7.63–7.54 (3H, m), 7.45 (1H, tm, J=7.8, 1.2 Hz), 7.36–7.27 (4H, m), 7.21 (1H, m), 7.16–7.08 (2H, m), 4.06 (1H, s), 1.17 (9H, s); ^{13}C NMR δ 137.4, 133.4, 132.4, 132.2, 132.0, 131.5, 131.0, 130.3, 129.7, 128.4, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 127.0, 126.7, 126.5, 126.3, 126.1, 125.7, 123.1, 95.8, 93.0, 88.6, 82.9, 51.2, 36.0, 27.9; MS m/z 498 (M$^+$), 441.

4.8. 9-(1,1-Dimethylethyl)-15-phenyl-10H-benz[c]indeno[1,2-h]phenanthrene (**27**)

To 0.280 g of **24** (0.63 mmol) in 10 mL of anhydrous toluene under a nitrogen atmosphere were added 0.077 g of potassium *tert*-butoxide (0.69 mmol) and 0.48 mL of 2-methyl-2-propanol (5.0 mmol). The reaction mixture was then heated under reflux for 3 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 20 mL of methylene chloride were introduced. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes) afforded 0.232 g of **27** (0.52 mmol, 83%) as a yellow solid. Mp 169–171 °C; IR 1366, 831 cm^{-1}; ^{1}H NMR δ (600 MHz, $CDCl_3$, −20 °C) 8.34 (1H, d, J=8.4 Hz), 8.01 (1H, d, J=7.8 Hz), 7.84 (1H, d, J=7.8 Hz), 7.76 (1H, t, J=8.4 Hz), 7.75 (1H, t, J=8.4 Hz), 7.62 (1H, d, J=7.8 Hz), 7.55 (1H, d, J=8.4 Hz), 7.52 (1H, d, J=7.8 Hz), 7.33 (1H, t, J=7.5 Hz), 7.18 (1H, t, J=7.2 Hz), 7.16 (1H, t, J=7.2 Hz), 7.02 (1H, t, J=7.5 Hz), 6.97 (1H, t, J=7.2 Hz), 6.88 (1H, t, J=7.2 Hz), 6.72 (1H, t, J=7.8 Hz), 6.27 (1H, d, J=8.4 Hz), 6.07 (1H, d, J=7.8 Hz), 4.545 (1H, d, J=21.6 Hz), 4.331 (1H, d, J=21.0 Hz), 1.84 (9H, s); ^{13}C NMR δ (150 MHz, $CDCl_3$, 25 °C) 144.4, 140.9, 140.7, 140.6, 139.0, 138.6, 134.6, 133.2, 131.5, 130.9, 130.6, 130.4, 130.1, 128.0, 127.7, 127.1, 126.8, 126.5, 126.0, 125.9, 125.5, 124.8, 124.4, 124.3, 124.2, 123.9, 122.3, 40.0, 38.2, 33.5; MS m/z 448 (M$^+$), 433, 391; HRMS calcd for $C_{35}H_{28}$ 448.2191, found 448.2193.

In addition to **27**, the formation of a minor amount (ca. 2%) of the intramolecular [2+2] cycloaddition adduct **29** was also detected with characteristic ^{1}H NMR signals (600 MHz, $CDCl_3$) at δ 8.84 (1H, s), 8.40 (1H, d, J=9.0 Hz), 8.12 (2H, d, J=8.4 Hz), 7.84 (1H, d, J=7.8 Hz), 6.49 (1H, s, vinylic), and 1.29 (9H, s) and a ^{13}C NMR signal (150 MHz, $CDCl_3$) at δ 76.1 attributable to the sp^3 carbon on the four-membered ring as observed previously in similar systems.[10,11]

4.9. Indeno-fused dibenzo[c,g]phenanthrene **28**

The same procedure was repeated as described for **27** except that 0.120 g of **26** (0.24 mmol) was treated with a mixture of 0.030 g of potassium *tert*-butoxide (0.26 mmol) and 0.18 mL of 2-methyl-2-propanol (1.92 mmol) in 10 mL of anhydrous toluene under reflux for 3 h to afford 0.094 g of **28** (0.19 mmol, 78%) as a yellow solid. Mp>250 °C; IR 1366, 839 cm^{-1}; ^{1}H NMR δ (600 MHz, $CDCl_3$) 8.42 (1H, d, J=8.4 Hz), 7.85 (1H, d, J=8.4 Hz), 7.81 (1H, d, J=7.8 Hz), 7.76 (1H, d, J=8.4 Hz), 7.618 (1H, d, J=6.0 Hz), 7.605 (1H, d, J=9 Hz), 7.52 (1H, d, J=8.4 Hz), 7.45 (1H, d, J=7.8 Hz), 7.40 (1H, d, J=8.4 Hz), 7.32 (1H, td, J=7.5, 1.2 Hz), 7.12 (1H, ddd, J=7.8, 6.6, 1.2 Hz), 7.08 (1H, td, J=7.8, 0.8 Hz), 6.73 (2H, t, J=7.5 Hz), 6.558 (1H, t, J=8.4 Hz), 6.546 (1H, t, J=7.8 Hz), 6.42 (1H, d, J=7.8 Hz), 6.04 (1H, d, J=8.4 Hz), 5.76 (1H, d, J=7.8 Hz), 4.58 (1H, d, J=21.0 Hz), 4.28 (1H, d, J=21.0 Hz), 1.97 (9H, s); ^{13}C NMR δ (150 MHz, CDCl$_3$) 144.3, 141.0, 140.8, 139.3, 139.2, 138.3, 134.5, 132.7, 132.0, 131.8, 131.5, 131.4, 131.3, 129.5, 129.22, 129.18, 127.7, 127.0, 126.8, 126.6, 126.5, 126.4, 126.0, 125.74, 125.70, 125.67, 125.59, 125.45, 125.3, 125.04, 125.03, 123.82, 123.80, 122.1, 40.1, 38.3, 33.8; MS *m/z* 498 (M$^+$), 441, 363; HRMS calcd for $C_{39}H_{30}$ 498.2348, found 498.2351. Recrystallization of **28** from CH$_2$Cl$_2$/hexanes produced a crystal suitable for X-ray structure analysis.

In addition to **28**, the formation of a minor amount (ca. 12%) of the intramolecular [2+2] cycloaddition adduct **30** was also detected with characteristic ^{1}H NMR signals (600 MHz, CDCl$_3$) at δ 9.28 (1H, s), 8.88 (1H, d, J=8.4 Hz), 8.12 (2H, d, J=8.4 Hz), 7.99 (1H, d, J=7.8 Hz), 6.51 (1H, s, vinylic), and 1.27 (9H, s) and a ^{13}C NMR signal (150 MHz, CDCl$_3$) at δ 76.3 attributable to the sp^3 carbon on the four-membered ring as observed previously in similar systems.[10,11]

4.10. Polycyclic aromatic hydrocarbon *39a*

The same procedure was repeated as described for **27** except that a solution of 0.076 g of **38a** (0.12 mmol) in 10 mL of anhydrous toluene was treated with 0.25 mL of a 1.0 M solution of potassium *tert*-butoxide (0.25 mmol) in 2-methyl-2-propanol and 0.18 mL of 2-methyl-2-propanol (1.93 mmol). The resulting mixture was heated under reflux for 3 h to afford 0.059 g of **39a** (0.09 mmol, 78%) as a yellow solid. IR 1368, 761 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.54 (2H, d, J=8.4 Hz), 7.63 (1H, s), 7.41 (2H, t, J=7.2 Hz), 7.35 (6H, t, J=7.2 Hz), 7.30 (2H, d, J=8.4 Hz), 7.20 (2H, t, J=7.5 Hz), 7.06 (4H, d, J=7.8 Hz), 6.65 (1H, s), 4.52 (4H, s), 1.89 (18H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 144.1, 140.3, 138.7, 138.5, 138.1, 137.7, 134.7, 132.5, 131.2, 130.3, 129.3, 127.7, 127.2, 127.0, 123.9, 123.1, 120.1, 119.4, 40.0, 38.8, 34.3; MS *m/z* 618 (M$^+$), 561; HRMS calcd for $C_{48}H_{42}$ 618.3281, found 618.3295.

4.11. Polycyclic aromatic hydrocarbon *39b*

The same procedure was repeated as described for **27** except that a solution of 0.024 g of **38b** (0.028 mmol) in 10 mL of anhydrous *p*-xylene was treated with 0.03 mL of a 1.0 M solution of potassium *tert*-butoxide (0.03 mmol) in 2-methyl-2-propanol and 0.02 mL of 2-methyl-2-propanol (0.16 mmol). The resulting mixture was heated under reflux for 5 h to afford 0.017 g of **39b** (0.020 mmol, 71%) as a yellow solid. IR 1466, 1365 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.53 (2H, d, J=9.0 Hz), 7.59 (1H, s), 7.55 (2H, d, J=7.8 Hz, at −25 °C), 7.40 (2H, dd, J=8.4, 1.2 Hz), 7.34 (2H, td, J=7.8, 1.2 Hz), 7.20 (2H, d, J=7.2 Hz, at −25 °C), 7.17 (2H, t, J=7.5 Hz), 7.08 (2H, d, J=7.2 Hz, at −25 °C), 6.85 (1H, s), 6.70 (2H, d, J=7.2 Hz, at −25 °C), 4.58 (2H, d, J=21.6 Hz), 4.44 (2H, d, J=21.6 Hz), 1.88 (18H, s), 1.81 (2H, d, J=15 Hz), 1.79 (2H, d, J=15 Hz), 1.72 (6H, s), 1.45 (6H, s), 0.77 (18H, s); MS *m/z* 842 (M$^+$), 785; HRMS calcd for $C_{64}H_{74}$ 842.5785, found 842.5751.

4.12. Polycyclic aromatic hydrocarbon *44a*

The same procedure was repeated as described for **27** except that a solution of 0.209 g of **41a** (0.29 mmol) in 10 mL of anhydrous toluene was treated with 0.61 mL of a 1.0 M solution of potassium *tert*-butoxide (0.61 mmol) in 2-methyl-2-propanol and 0.43 mL of 2-methyl-2-propanol (4.64 mmol). The resulting mixture was heated under reflux for 3 h to afford 0.150 g of **44a** (0.21 mmol, 72%) as a yellow solid. IR 1459, 822, 699 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.24 (2H, d, J=9.6 Hz), 7.69 (2H, d, J=7.8 Hz), 7.68 (1H, s), 7.47 (2H, d, J=9.0 Hz), 7.26 (2H, t, J=8 Hz) 7.21 (2H, t, J=7.8 Hz), 7.17 (4H, t, J=7.5 Hz), 6.99 (4H, d, J=8.4 Hz), 6.74 (2H, t, J=7.8 Hz), 6.58 (2H, d, J=7.8 Hz), 6.44 (1H, s), 4.47 (4H, s), 1.83 (18H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 143.6, 140.7, 140.4, 139.2, 139.0, 138.7, 132.9, 132.4, 131.3, 131.0, 130.7, 130.3, 129.2, 127.3, 126.4, 125.7, 125.1, 122.8, 39.9, 38.5, 34.0; MS *m/z* 718 (M$^+$); HRMS calcd for $C_{56}H_{46}$ 718.3594, found 718.3594.

4.13. Polycyclic aromatic hydrocarbon *44b*

The same procedure was repeated as described for **27** except that a solution of 0.024 g of **41b** (0.025 mmol) in 10 mL of anhydrous *p*-xylene was treated with 0.03 mL of a 1.0 M solution of potassium *tert*-butoxide (0.03 mmol) in 2-methyl-2-propanol and 0.02 mL of 2-methyl-2-propanol (0.16 mmol). The resulting mixture was heated under reflux for 5 h to afford 0.017 g of **44b** (0.018 mmol, 71%) as a yellow solid. IR 1464, 1365 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.25 (2H, d, J=9.6 Hz), 7.69 (2H, d, J=7.8 Hz), 7.64 (1H, s), 7.48 (2H, d, J=9.6 Hz), 7.29 (2H, d, J=8.4 Hz), 7.28 (4H, br), 6.95 (4H, br), 6.92 (2H, d, J=8.4 Hz), 6.72 (2H, td, J=7.5, 1.2 Hz), 6.64 (1H, s), 4.45 (2H, d, J=21.6 Hz), 4.43 (2H, d, J=21.6 Hz), 1.84 (2H, d, J=15 Hz), 1.83 (18H, s), 1.70 (2H, d, J=15 Hz), 1.50 (6H, s), 1.28 (6H, s), 0.85 (18H, s); MS *m/z* 942 (M$^+$); HRMS calcd for $C_{72}H_{78}$ 942.6098, found 942.6150.

4.14. Polycyclic aromatic hydrocarbon *45a*

The same procedure was repeated as described for **27** except that a solution of 0.155 g of **43a** (0.19 mmol) in 10 mL of anhydrous toluene was treated with 0.40 mL of a 1.0 M solution of potassium *tert*-butoxide (0.40 mmol) in 2-methyl-2-propanol and 0.15 mL of 2-methyl-2-propanol (3.03 mmol). The resulting mixture was heated under reflux for 3.5 h to afford 0.109 g of **45a** (0.13 mmol, 70%) as a yellow solid. IR 1365, 830 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.26 (2H, d, J=9.0 Hz), 7.72 (2H, d, J=7.2 Hz, at −20 °C), 7.71 (1H, s), 7.68 (2H, d, J=9.0 Hz), 7.67 (2H, d, J=9.0 Hz), 7.48 (2H, d, J=7.2 Hz), 7.47 (2H, d, J=9.0 Hz), 7.18 (2H, d, J=8.4 Hz), 6.94 (2H, td, J=7.2, 1.2 Hz), 6.60 (2H, t, J=7.2 Hz, at −20 °C), 6.57 (2H, td, J=7.5, 1.2 Hz), 6.40 (1H, s), 6.35 (2H, t, J=7.2 Hz), 6.13 (2H, t, J=7.2 Hz, at −20 °C), 5.71 (2H, d, J=7.2 Hz, at −20 °C), 4.53 (2H, d, J=21.0 Hz), 4.44 (2H, d, J=21.0 Hz), 1.84 (18H, s); ^{13}C NMR (150 MHz, CDCl$_3$)

δ 143.7, 139.3, 138.98, 138.89, 138.4, 138.1, 133.4, 132.8, 130.5, 130.3, 130.20, 130.17, 130.09, 127.5, 126.9, 125.6, 125.3, 124.6, 124.0, 123.8, 121.8, 120.8, 119.4, 39.6, 38.2, 33.6; MS *m/z* 818 (M^+), 761, 650; HRMS calcd for $C_{64}H_{50}$ 818.3907, found 818.3916.

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Supplementary data

Experimental procedures and spectroscopic data for **19–21**, **33a/b**, **35a/b**, **36a/b**, **37a/b**, **38a/b**, **40a/b**, **41a/b**, **42a**, and **43a**, ^{1}H and/or ^{13}C NMR spectra of compounds **11**, **19–28**, **33a/b**, **35a/b–41a/b**, **42a**, **43a**, **44a/b**, and **45a**, and the ORTEP drawings of the crystal structures of **10** and **28**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.11.073.

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40. Crystallographic data of **10** and **28** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC nos. 661596 and 661597 have been assigned for the compounds **10** and **28**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
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