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Ring expansion of 11*H*-benzo[*b*]fluorene-11-methanols and related compounds leading to 17,18-diphenyldibenzo[*a*,*o*]pentaphene and related polycyclic aromatic hydrocarbons with extended conjugation and novel architectures

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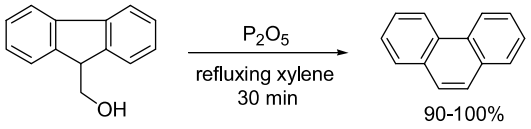
Abstract—Condensation between 7-(1,1-dimethylethyl)-13-phenyl-8*H*-indeno[2,1-*b*]phenanthrene and paraformaldehyde produced the corresponding 9-fluorenylmethanol derivative, which on treatment with P_2O_5 to promote a Wagner–Meerwein rearrangement for ring expansion furnished 14-phenyldibenzo[*a*,*j*]anthracene in 88% yield. Similarly, 17,18-diphenyldibenzo[*a*,*o*]pentaphene possessing a helical twist and bearing two phenyl substituents at the most sterically congested C17 and C18 positions and other related compounds were likewise synthesized. Subsequent intramolecular arylation reactions involving the phenyl substituents produced polycyclic aromatic hydrocarbons with novel architectures.

1. Introduction

The Wagner–Meerwein rearrangement of 9-fluorenylmethanols and related fluorene derivatives provides an efficient pathway for ring expansion to form phenanthrenes.[1] Specifically, the phosphorous pentoxide-induced rearrangement of the parent 9-fluorenylmethanol occurs in refluxing xylene to produce phenanthrene in excellent yield (Eq. 1).[2] We recently reported the synthesis of a variety of 11*H*-benzo[*b*]fluorenes and related derivatives via the benzannulated enediynyl propargylic alcohols.[3–10] We now report the use of these benzofluorenyl derivatives to prepare 11*H*-benzo[*b*]fluorene-11-methanols for the subsequent Wagner–Meerwein rearrangement leading to phenanthrenes having extended conjugation and bearing one or two aryl substituents at the sterically most hindered positions. The presence of these aryl substituents also allows intramolecular electrophilic aromatic substitution reactions to occur, producing polycyclic aromatic hydrocarbons with novel architectures.



(1)

2. Results and discussion

Indenophenanthrene **8** was prepared by a synthetic sequence reported previously[3] involving condensation between *tert*-butyl 2-naphthyl ketone (**1**) and the benzannulated enediynyl lithium acetylide **2** to form the benzannulated enediynyl propargylic alcohol **3** followed by reduction with triethylsilane in the presence of trifluoroacetic acid to give **4** (Scheme 1). Treatment of **4** with potassium *tert*-butoxide in refluxing toluene for 3 h then provided 7-(1,1-dimethylethyl)-13-phenyl-8*H*-indeno[2,1-*b*]phenanthrene (**8**) in 89% yield. Presumably, a cascade sequence of reactions occurred as reported previously[3] involving an initial 1,3-prototropic rearrangement to form the benzannulated enyne-allene **5** followed by a Schmittel cyclization reaction[11–15] to generate biradical **6** for the subsequent intramolecular radical–radical coupling to furnish **7** and, after a second prototropic rearrangement, indenophenanthrene **8**. It is

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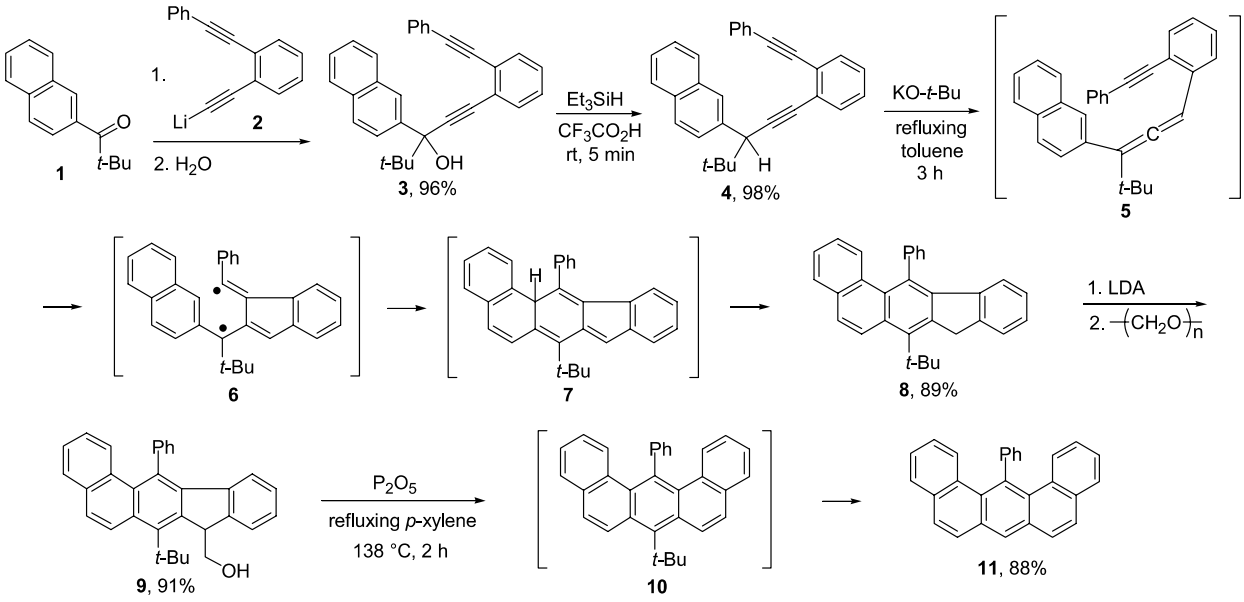
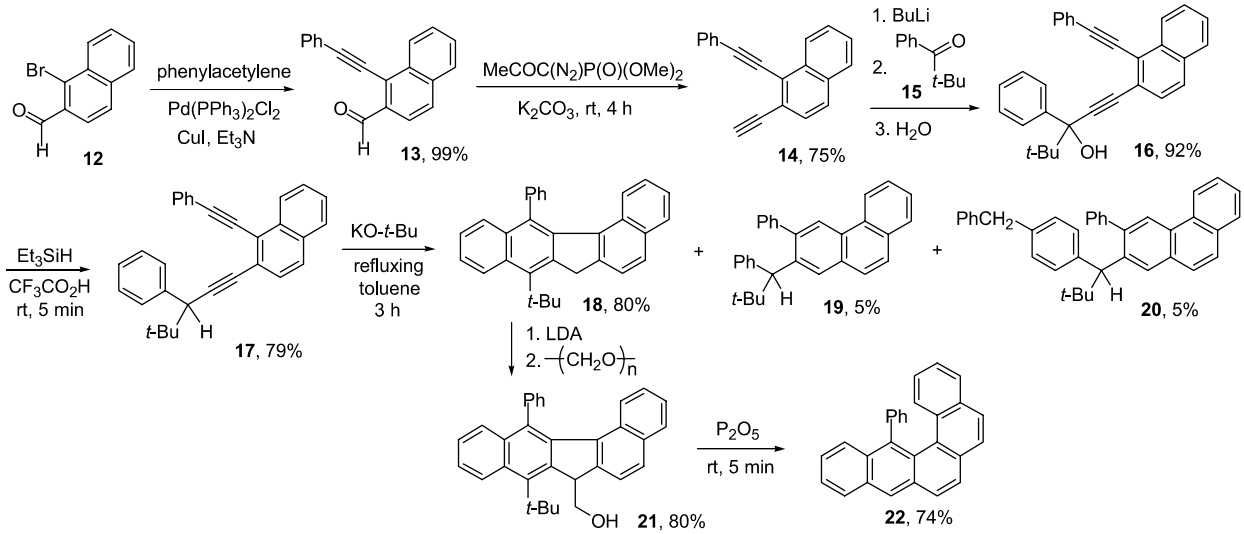


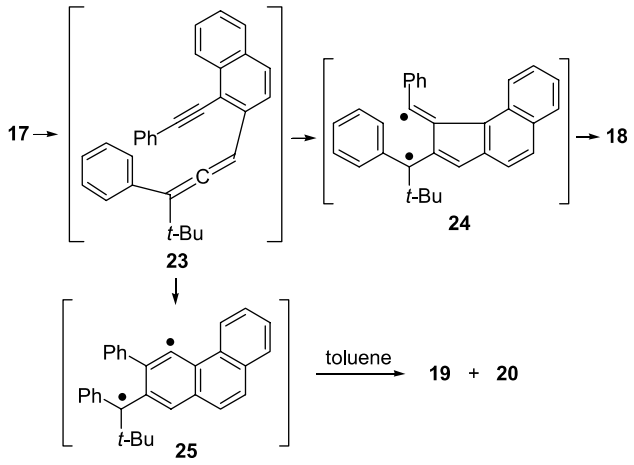
Scheme 1.

worth noting that the intramolecular radical–radical coupling reaction of biradical **6** involved only the α-position of the naphthyl ring to produce **7** preferentially. Attaching the β-position to form an indeno-fused anthracene derivative did not appear to occur. The higher reactivity of the α-position than the β-position of naphthalene in homolytic addition may be responsible for the regioselectivity.[16–17] Conversion of **8** to the 9-fluorenylmethanol derivative **9** was readily accomplished by treatment of **8** with lithium diisopropylamide (LDA) followed by paraformaldehyde.[18] Unlike the parent 9*H*-fluorene, the presence of a sterically demanding *tert*-butyl group in **9** appeared to prevent it from condensation with a second molecule of formaldehyde even in the presence of excess LDA and paraformaldehyde. On exposure to P_2O_5, **9** was transformed smoothly via the Wagner–Meerwein rearrangement to form **10** in situ followed by the loss of the *tert*-butyl group to give 14-phenyldibenzo[*a*,*j*]anthracene (**11**) in 88% yield. The *tert*-butyl group is removed from **10** by protonation of the C7 carbon followed by dealkylation as observed previously in other aromatic systems.[19–22] It is also possible that the *tert*-butyl group was first removed from **9** followed by a Wagner–Meerwein rearrangement to furnish **11**.

Similarly, the benzannulated enediynyl propargylic alcohol **16** was synthesized by condensation between 2,2-dimethylpropiophenone (**15**) and the benzannulated enediyne **14**, which was readily prepared by the Sonogashira reaction between phenylacetylene and **12** to form **13** followed by treatment of **13** with dimethyl (1-diazo-2-oxopropyl)-phosphonate[23] (Scheme 2). Reduction of **16** followed by treatment of the resulting **17** with potassium *tert*-butoxide in refluxing toluene then afforded 8-(1,1-dimethylethyl)-13-phenyl-7*H*-dibenzo[*b*,*g*]fluorene (**18**) in 80% yield along with two minor adducts **19** and **20**. Presumably, a 1,3-prototropic rearrangement of **17** gave the benzannulated enyne-allene **23**, which could undergo either a Schmittel cyclization reaction to give biradical **24** leading to **18** or a



Scheme 2.

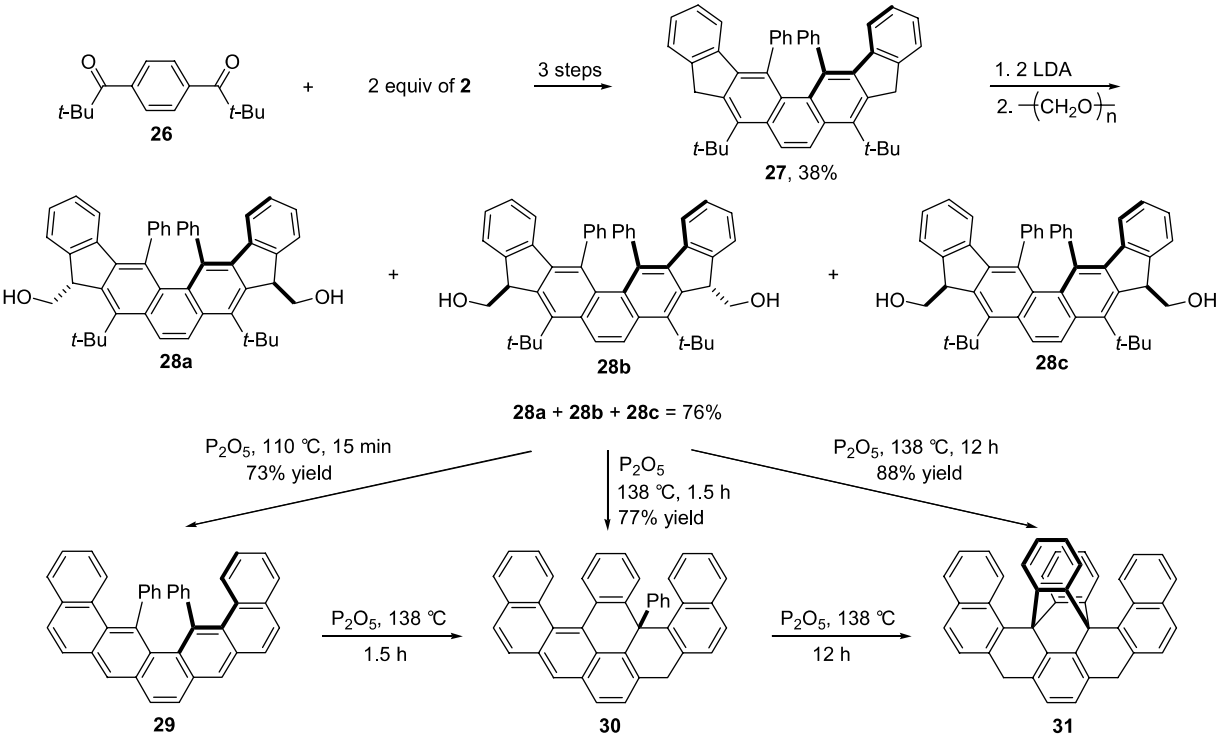


Scheme 3.

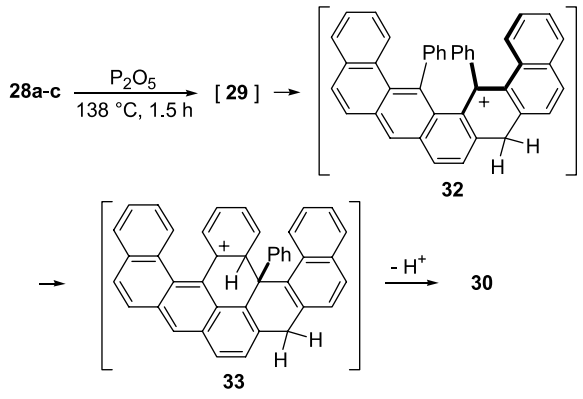
Myers–Saito cyclization reaction[24–27] to form biradical **25** leading to **19** and **20** (Scheme 3). Treatment of **18** with LDA followed by paraformaldehyde then produced **21** for the subsequent Wagner–Meerwein rearrangement to furnish 14-phenylnaphth[1,2-*a*]anthracene (**22**) with the phenyl substituent at one of the most sterically hindered positions in 74% yield. Because of steric hindrance, the rotation of the carbon–carbon bond attaching the phenyl substituent to the naphth[1,2-*a*]anthracene system is restricted. As a result, the ^{1}H NMR signals (600 MHz) of the *ortho* and *meta* hydrogens of the phenyl substituent appeared as broad humps at δ 8.2, 7.5, 6.7, and 6.1 at 25 °C. However, at −20 °C two doublets at δ 8.24/6.14 for the *ortho* hydrogens and two triplets at δ 7.49/6.67 for the *meta* hydrogens could be clearly discerned. The coalescence temperatures were determined to be at 50 °C for the *ortho* hydrogens and at 40 °C for the *meta* hydrogens on a 270 MHz spectrometer, corresponding to rotational barriers of 14.4 and 14.5 kcal/mol at these two temperatures, which are slightly higher than those of 1-phenylbenzo[*a*]phenanthrenes ($\Delta G^{\ddagger}_{rot}$ = ca. 13 kcal/mol) reported earlier.[28]

The diindeno-fused phenanthrene **27** was synthesized previously from diketone **26** and 2 equiv of **2** in three steps in 38% overall yield (Scheme 4).[6] The X-ray structure of **27** showed that the presence of the two phenyl substituents at the congested C4 and C5 positions of the phenanthrene moiety caused a severe helical twist of the diindeno-fused phenanthrene system. Treatment of **27** with 2 equiv of LDA followed by paraformaldehyde produced **28a–c** as a mixture of three diastereomers in a 63 (**28a** or **28b**): 34 (**28c**): 3 (**28a** or **28b**) ratio in 76% combined yield. The major isomer (**28a** or **28b**) having a C_2 symmetry and **28c** without a C_2 symmetry were separated by silica gel chromatography to allow structural elucidation. The use of a mixture of **28a–c** containing all three diastereomers for two consecutive Wagner–Meerwein rearrangements, promoted by P_2O_5 in *p*-xylene at 110 °C for 15 min, was also successful, giving rise to 17,18-diphenyldibenzo[*a*,*o*]pentaphene (**29**) with the two phenyl substituents at the most sterically congested C17 and C18 positions.

Interestingly, when a mixture of **28a–c** was exposed to P_2O_5 at a higher temperature (138 °C) in refluxing *p*-xylene for 1.5 h, compound **30** was produced in 77% yield. Treatment of **29** with P_2O_5 under the same condition (refluxing *p*-xylene, 1.5 h) also produced **30**. Apparently under this reaction condition, the transformation from **28a–c** to **30** proceeds via an initial formation of **29** in situ followed by protonation of the C7 carbon of **29** to furnish **32** (Scheme 5). A subsequent intramolecular electrophilic aromatic substitution reaction involving the phenyl substituent at the C17 position to form



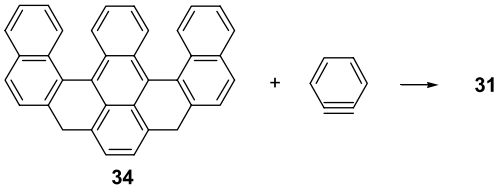
Scheme 4.



Scheme 5.

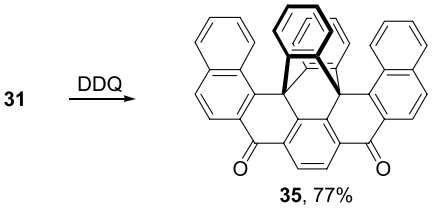
33 followed by deprotonation then gave **30**. The reaction sequence of protonation followed by an intramolecular electrophilic aromatic substitution reaction is reminiscent of what was reported previously in the transformation of 1-phenylbenzo[*a*]anthracene to dibenzo[*a*,*l*]pyrene.[29]

It was also possible to promote a second intramolecular electrophilic aromatic substitution reaction involving the phenyl substituent of **30** by protonation of the C10 carbon. Treatment of either **28a–c** or **30** with P_2O_5 in refluxing *p*-xylene over a longer period of time (12 h) furnished **31** having a C_2 symmetry and two vertical planes of symmetry and thus belonging to the group C_{2v}. It is interesting to note that **31** can be regarded as the Diels–Alder adduct of the cycloaddition reaction between the central benzene ring of the central anthracene unit of **34** and benzyne to produce the triptycene moiety in **31** (Eq. 2).[30–32]



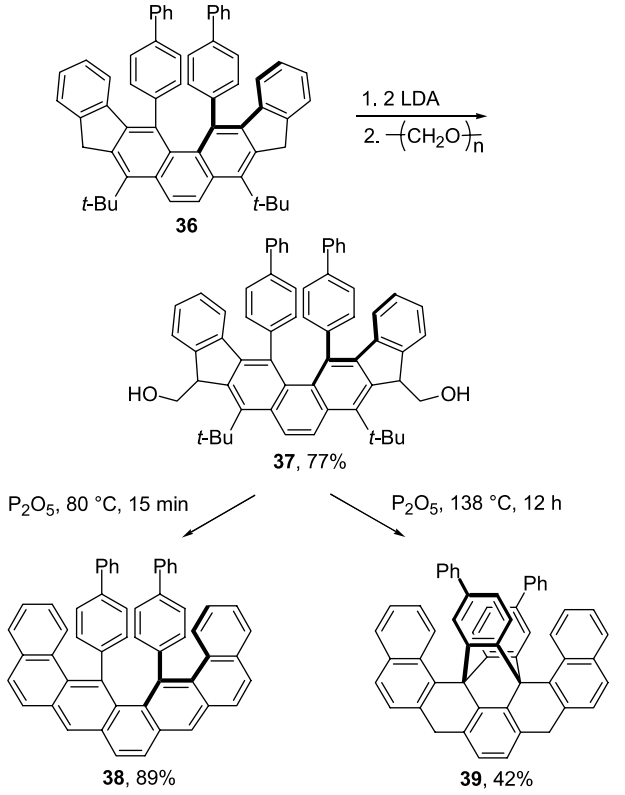
(2)

Compare to **30** in which an AB quartet of ^{1}H NMR signals at δ 4.83 (J=22.8 Hz) and δ 4.77 (J=23.0 Hz) were observed for the two methylene hydrogens because of the lack of symmetry, a singlet ^{1}H NMR signal at δ 4.42 was observed for the four methylene hydrogens of **31**. Oxidation of **31** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) produced **35** (Eq. 3), which has its structure established by X-ray structure analysis.



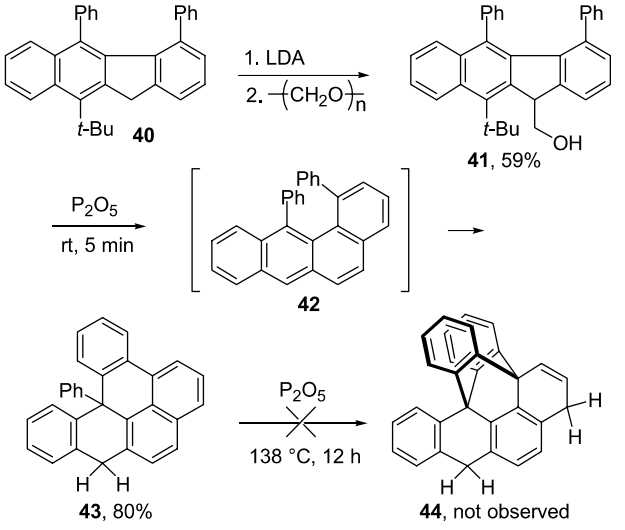
(3)

Similarly, treatment of **36**[6] with 2 equiv of LDA and paraformaldehyde gave **37** as a mixture of two diastereomers (isomer ratio=55:45), which on exposure to P_2O_5 in refluxing benzene at 80 °C for 15 min underwent two Wagner–Meerwein rearrangements to give **38** (Scheme 6). Under a harsher reaction condition (P_2O_5, *p*-xylene at 138 °C, 12 h), **39** was likewise produced. Compared to **31**, which belongs to the group C_{2v}, the structure of **39** retains the C_2 symmetry but no longer has the two planes of symmetry and thus belongs to the group C_2. The chirality of the helical structure is lost in the transformation from **27** to **31**, whereas the chirality of **36** is retained in **39**. As a result, the ^{1}H NMR signals of the diastereotopic methylene hydrogens of **39**, recorded on a 600 MHz NMR spectrometer, were observed as an AB quartet at δ 4.46 (J=21.6 Hz) and δ 4.43 (J=21.0 Hz).



Scheme 6.

The benzo[*b*]fluorene derivative **40**[9] was also successfully employed to produce **41** (Scheme 7). However, attempts to promote the Wagner–Meerwein rearrangement to give **42**



Scheme 7.

resulted in the formation of **43** even under mild reaction conditions (P_2O_5, 25 °C, 5 min). The structure of **43** was established by X-ray structure analysis. Apparently, protonation of the initially formed **42** and the subsequent intramolecular electrophilic aromatic substitution reaction are very facile under the reaction condition, preventing **42** from being isolated. However, the resulting **43** is resistant to further transformation to **44** on heating in refluxing *p*-xylene at 138 °C for 12 h. Apparently, it is difficult to protonate the naphthalene moiety of **43** for the subsequent intramolecular electrophilic aromatic substitution reaction.

3. Conclusion

The Wagner–Meerwein rearrangement was successfully applied to a variety of 11*H*-benzo[*b*]fluorene-11-methanols and related fluorene derivatives leading to highly conjugated aromatic systems bearing one or two aryl substituents at the most sterically hindered positions. These sterically congested aromatic systems are prone to protonation for subsequent intramolecular electrophilic aromatic substitution reactions, leading to polycyclic aromatic hydrocarbons with novel architectures not easily attainable by other synthetic methods. The synthetic sequence is simple and straightforward, making it easily adoptable for the synthesis of other polycyclic aromatic compounds.

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, lithium diisopropylamide (LDA, 2.0 M) in heptane/THF/ethylbenzene, triethylsilane, trifluoroacetic acid, potassium *tert*-butoxide (1.0 M) in THF, 2-naphthoyl chloride, 1-bromo-2-naphthalenecarboxaldehyde (**12**), phenylacetylene, $Pd(PPh_3)_2Cl_2$, copper(I) iodide, $CuBr \cdot SMe_2$, triethylamine, 2,2-dimethylpropiophenone (**15**), paraformaldehyde, and phosphorus pentoxide were purchased from chemical suppliers and were used as received. 1,2-Bis[(2-ethynylphenyl)ethynyl]benzene was prepared as reported previously.[6] Melting points were uncorrected. ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^1H δ 7.26) and $CDCl_3$ (^{13}C δ 77.0) as internal standards unless otherwise indicated for those recorded on a 600-MHz NMR spectrometer.

4.1.1. 7-(1,1-Dimethylethyl)-13-phenyl-8*H*-indeno[2,1-*b*]phenanthrene-8-methanol (9). To a solution of 0.317 g (0.796 mmol) of **8** in 8 mL of THF under a nitrogen atmosphere at 0 °C was added 0.53 mL of a 2.0 M solution of LDA (1.06 mmol) in heptane/tetrahydrofuran/ethylbenzene. After 10 min at 0 °C, 0.030 g (1.00 mmol) of paraformaldehyde was introduced via a 120° angle glass tubing fitted with ground joints at both ends. The reaction mixture was then allowed to warm to room temperature. After an additional 15 min, 5 mL of a saturated sodium bicarbonate solution was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/20% diethyl ether in hexanes) to afford 0.311 g of **9** (0.727 mmol, 91%) as a white solid: mp 207–209 °C; IR 3401 (br), 832, 750, 697 cm^{-1}; ^1H δ 8.50 (1H, d, J=9.6 Hz), 7.79 (1H, dd, J=7.9, 1.5 Hz), 7.69–7.52 (7H, m), 7.41–7.31 (2H, m), 7.21 (1H, td, J=7.4, 1.0 Hz), 7.04–6.93 (2H, m), 5.94 (1H, d, J=7.9 Hz), 5.02 (1H, dd, J=7.5, 3.8 Hz), 4.43 (1H, m), 3.53 (1H, m), 1.91 (9H, s), 1.50 (1H, OH); ^{13}C δ 146.3, 143.3, 142.9, 140.8, 139.9, 139.4, 134.2, 132.8, 132.5, 131.4, 130.2, 130.0, 129.9, 128.7, 127.9, 127.6, 126.9, 126.8, 126.2, 125.6, 124.5, 124.28, 124.25, 123.6, 67.8, 51.4, 38.5, 34.6; MS *m*/*z* 429 (MH^+), 415, 355.

4.1.2. 14-Phenyldibenzo[*a*,*j*]anthracene (11). To a flask containing 0.069 g (0.161 mmol) of **9** were added 0.256 g (1.80 mmol) of phosphorus pentoxide and 10 mL of *p*-xylene. The reaction mixture was heated under reflux for 2 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of a saturated sodium bicarbonate solution was introduced, and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/10% methylene chloride in hexanes) to provide 0.050 g of **11** (0.141 mmol, 88%) as a white solid: mp 259–261 °C; IR 1443, 878, 790, 743, 696 cm^{-1}; ^1H δ 8.35 (1H, s), 7.82 (2H, d, J=8.9 Hz), 7.79 (2H, dd, J=8.2, 1.5 Hz), 7.69 (2H, d, J=8.7 Hz), 7.66–7.58 (3H, m), 7.52–7.48 (2H, m), 7.39 (2H, ddd, J=7.9, 6.9, 1.0 Hz), 7.21 (2H, d, J=8.7 Hz), 6.99 (2H, ddd, J=8.7, 6.9, 1.7 Hz); ^{13}C δ 145.4, 138.8, 134.2, 131.5, 131.3, 131.2, 130.6, 129.0, 128.4, 128.2, 128.13, 128.10, 127.8, 126.9, 125.9, 124.5; MS *m*/*z* 354 (M^+), 337, 313; HRMS calcd for $C_{28}H_{18}$ 354.1409, found 354.1402.

4.1.3. Diols 28a–c. To a solution of 0.344 g (0.557 mmol) of **27** in 60 mL of benzene and 50 mL of THF under a nitrogen atmosphere at 0 °C was added 1.80 mL of a 2.0 M solution of LDA (3.60 mmol) in heptane/tetrahydrofuran/ethylbenzene. After 20 min at 0 °C, 0.220 g (7.33 mmol) of paraformaldehyde was transferred into the reaction mixture via a 120° angle glass tubing fitted with ground joints at both ends. The reaction mixture was then allowed to warm to room temperature. After an additional 30 min, 10 mL of a saturated sodium bicarbonate solution was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/50% diethyl ether in hexanes) to afford 0.287 g of **28a–c** (0.423 mmol, 76%, a mixture of three isomers, isomer ratio=63:34:3) as a pale yellow solid. The ^1H NMR spectrum suggested that all three diastereomers, **28a** and **28b** having a C_2 symmetry (63 and 3% not necessarily respectively) and **28c** without a C_2 symmetry (34%), were produced. The major isomer (**28a** or **28b**) and **28c** were further separated by column chromatography on a silica gel

column. **28a–c**: mp 221–225 °C; IR 3412 (br), 1052, 704 cm^{-1}; ^1H (**28a** or **28b**) δ 7.81 (2H, s), 7.49 (2H, d, J=7.5 Hz), 7.13 (2H, tm, J=7.5, 1 Hz), 7.10 (2H, tm, J=7.5, 1 Hz), 6.99 (4H, t, J=7.5 Hz), 6.78 (2H, t, J=7.2 Hz), 6.46 (4H, d, J=6.9 Hz), 6.22 (2H, d, J=7.9 Hz), 4.70 (2H, dd, J=5.9, 3.0 Hz), 4.47 (2H, m), 3.82 (2H, m), 1.82 (18H, s), 1.13 (2H, OH); ^{13}C (**28a** or **28b**) δ 146.6, 140.7, 140.6, 138.7, 137.4, 135.1, 134.9, 132.1, 131.2, 128.2, 126.56, 126.51, 126.0, 123.8, 122.9, 121.9, 67.0, 50.7, 37.7, 34.3; ^1H (**28c**) δ 7.97 (1H, d, J=9.7 Hz), 7.88 (1H, d, J=9.3 Hz), 7.50 (1H, d, J=7.5 Hz), 7.45 (1H, d, J=7.1 Hz), 7.19–6.91 (8H, m), 6.83–6.74 (2H, m), 6.47 (4H, t, J=8.1 Hz), 6.32 (2H, t, J=6.9 Hz), 4.85 (1H, dd, J=7.7, 3.8 Hz), 4.73 (1H, dd, J=6.1, 3.2 Hz), 4.47 (1H, m), 4.36 (1H, m), 3.74 (1H, m), 3.47 (1H, t, J=8 Hz), 1.86 (9H, s), 1.85 (9H, s), 1.64 (1H, OH), 1.17 (1H, OH); ^{13}C (**28c**) δ 146.7, 146.6, 140.8, 140.5, 140.4, 139.0, 138.9, 138.5, 138.4, 137.3, 135.9, 134.9, 134.6, 133.3, 133.0, 132.5, 132.2, 127.7, 126.9, 126.6, 126.1, 123.8, 123.5, 123.3, 123.0, 122.8, 122.1, 69.6, 67.2, 52.2, 50.7, 38.3, 37.8, 34.5, 34.2; The ^1H NMR signals attributable to the minor isomer having a C_2 symmetry (**28a** or **28b**) were observed at δ 8.05 (2H, s) and 1.90 (18H, s); MS m/z 678 (M^+), 664, 647, 605; HRMS calcd for $C_{50}H_{46}O_2$ 678.3492, found 678.3496.

4.1.4. 17,18-Diphenyldibenzo[*a*,*o*]pentaphene (29). To a flask containing 0.0134 g (0.0198 mmol) of a mixture of **28a–c** were added 0.100 g (0.704 mmol) of phosphorus pentoxide and 10 mL of *p*-xylene. The reaction mixture was heated at 110 °C for 15 min. After the reaction mixture was allowed to cool to room temperature, 10 mL of a saturated sodium bicarbonate solution was introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/10% methylene chloride in hexanes) to provide 0.0076 g of **29** (0.014 mmol, 73%) as a light yellow solid: mp 272–275 °C; IR 1437, 879, 797, 744, 697 cm^{-1}; ^1H δ 8.03 (2H, s), 7.71 (2H, d, J=8.9 Hz), 7.65 (2H, d, J=7.7 Hz), 7.61 (2H, d, J=8.9 Hz), 7.44 (2H, s), 7.19 (2H, td, J=7.9, 1.0 Hz), 7.00 (2H, tt, J=7.4, 1.0 Hz), 6.81 (4H, t, J=7.7 Hz), 6.62 (2H, td, J=7.8, 1.5 Hz), 6.51 (2H, d, J=8.7 Hz), 6.40 (4H, d, J=8.0 Hz); ^{13}C δ 141.2, 139.3, 133.9, 132.52, 132.45, 132.3, 130.9, 128.90, 128.84, 128.2, 127.7, 127.2, 127.0, 126.37, 126.35, 126.0, 125.5, 123.6, 122.8; MS m/z 530 (M^+), 453, 437, 424; HRMS calcd for $C_{42}H_{26}$ 530.2035, found 530.2035.

4.1.5. Hydrocarbon 30. To a flask containing 0.083 g (0.12 mmol) of a mixture of **28a–c** were added 0.310 g (2.2 mmol) of phosphorus pentoxide and 15 mL of *p*-xylene. The reaction mixture was heated under reflux for 1.5 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of a saturated sodium bicarbonate solution was introduced. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. The residue was allowed to precipitate out from hexanes to provide 0.050 g of **30** (0.094 mmol, 77%) as a bright yellow solid: mp 260–262 °C; IR 1443, 873, 738, 703 cm^{-1}; ^1H δ 9.50 (1H, dd, J=6.4, 3.5 Hz), 8.31 (2H, d, J=8.2 Hz), 8.12 (1H, s), 7.90–7.70 (6H, m), 7.64–7.58 (3H, m), 7.45 (1H, d, J=8.4 Hz), 7.36 (1H, td, J=7.1, 1.0 Hz), 7.31–7.22 (3H, m), 7.06–6.92 (3H, m), 6.61 (3H, br s), 4.83 (1H, d, J=22.8 Hz), 4.77 (1H, d, J=23.0 Hz); ^{13}C δ 149.1, 139.5, 136.1, 133.7, 133.3, 133.0, 132.4, 131.9, 131.8, 130.5, 130.4, 130.1, 129.3, 129.2, 128.72, 128.65, 128.4, 128.2, 127.9, 127.63, 127.58, 127.0, 126.9, 126.3, 126.2, 125.7, 125.6, 125.2, 125.1, 124.6, 53.4, 35.8; MS m/z 530 (M^+), 453, 435, 424; HRMS calcd for $C_{42}H_{26}$ 530.2035, found 530.2030.

4.1.6. Hydrocarbon 31. To a flask containing 0.048 g (0.071 mmol) of a mixture of **28a–c** were added 0.496 g (3.49 mmol) of phosphorus pentoxide and 20 mL of *p*-xylene. The reaction mixture was heated under reflux for 12 h before it was allowed to cool to room temperature. A saturated sodium bicarbonate solution (10 mL) was introduced, and the organic layer was separated. The aqueous layer was back extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. The residue was allowed to precipitate out from hexanes to provide 0.033 g of **31** (0.062 mmol, 88%) as a light brown solid: mp > 380 °C; IR 1455, 797, 779, 744 cm^{-1}; ^1H δ 8.02 (2H, d, J=8.2 Hz), 7.99 (2H, d, J=8.7 Hz), 7.75 (2H, d, J=8.4 Hz), 7.60 (2H, d, J=8.4 Hz), 7.49 (2H, td, J=7.7, 0.9 Hz), 7.27 (2H, td, J=8, 1 Hz), 6.85 (2H, s), 6.79–6.71 (8H, m), 4.42 (4H, s); ^{13}C δ 146.0, 134.8, 133.4, 132.5, 130.5, 128.8, 128.6, 128.2, 126.7, 125.6, 124.9, 124.7, 124.1, 123.7, 54.1, 33.8; MS m/z 530, 453; HRMS calcd for $C_{42}H_{26}$ 530.2035, found 530.2025.

4.1.7. Diketone 35. To a flask containing 0.021 g (0.040 mmol) of **31** were added 0.101 g (0.445 mmol) of DDQ and 25 mL of benzene. The reaction mixture was heated under reflux for 72 h before it was allowed to cool to room temperature. The reaction mixture and then diethyl ether solvent were allowed to flow through an aluminum oxide column. The effluent was concentrated, and the residue was purified by flash column chromatography (silica gel/10% diethyl ether in hexanes) to provide 0.017 g of **35** (0.030 mmol, 77%) as a light yellow solid: mp >370 °C; IR 1654, 758 cm^{-1}; ^1H δ 8.82 (2H, d, J=8.7 Hz), 8.31 (2H, d, J=8.9 Hz), 8.17 (2H, d, J=8.2 Hz), 8.12 (2H, s), 7.88 (2H, d, J=8.7 Hz), 7.74 (2H, ddd, J=8.0, 6.8, 1.2 Hz), 7.45 (2H, ddd, J=8.4, 6.9, 1.2 Hz), 6.84 (4H, dd, J=5.7, 3.2 Hz), 6.72 (4H, dd, J=5.7, 3.2 Hz); ^{13}C δ 182.6, 150.8, 143.6, 136.7, 136.5, 132.5, 131.7, 131.4, 130.3, 129.9, 129.2, 128.5, 125.79, 125.75, 125.70, 124.5, 122.9, 53.3; MS m/z 558 (M^+), 529, 498, 479, 464; HRMS calcd for $C_{42}H_{22}O_2$ 558.1620, found 558.1603. Recrystallization of **35** from CH_2Cl_2/2-propanol produced a single crystal suitable for X-ray structure analysis.

4.1.8. Diol 37. The same procedure was repeated as described for **28** except that 0.094 g (0.122 mmol) of **36** in a mixture of 30 mL of benzene and 20 mL of THF was treated with 0.50 mL of a 2.0 M solution of LDA (1.0 mmol) in heptane/tetrahydrofuran/ethylbenzene followed by 0.050 g (1.67 mmol) of paraformaldehyde to afford 0.078 g of **37** (0.094 mmol, 77%, a mixture of two isomers, isomer ratio=55:45) as a bright yellow solid. The major isomer does not possess a C_2 symmetry, whereas

the minor isomer has a C_2 symmetry. Compound **37**: mp 235–238 °C; IR 3416 (br), 768, 728, 696 cm^{-1}; ^1H δ 8.00 (major isomer, 0.55H, d, $J=9.4$ Hz), 7.90 (major isomer, 0.55H, d, $J=9.4$ Hz), 7.85 (minor isomer, 0.9H, s), 7.68–7.62 (4H, m), 7.51–7.25 (12H, m), 7.13–7.05 (2H, m), 6.80–6.73 (2H, m), 6.62–6.58 (4H, m), 6.47–6.34 (2H, m), 4.88–4.71 (2H, m), 4.54–4.38 (2H, m), 3.92–3.73 and 3.54–3.46 (2H, m), 1.88 (major isomer, s, *t*-Bu), 1.87 (major isomer, s, *t*-Bu), 1.84 (minor isomer, s, *t*-Bu), 1.10 (br, OH); ^{13}C δ (two isomers) 146.8, 146.6, 141.1, 141.00, 140.8, 140.73, 140.67, 140.6, 140.5, 140.4, 139.3, 139.15, 139.08, 138.91, 138.87, 137.9, 137.7, 137.56, 137.53, 137.4, 136.1, 134.9, 134.6, 134.5, 134.3, 133.0, 132.6, 132.2, 132.0, 131.2, 131.0, 128.85, 128.76, 127.2, 126.8, 126.7, 126.6, 126.4, 126.2, 126.1, 126.0, 123.9, 123.6, 123.3, 123.0, 122.9, 122.8, 122.3, 122.0, 69.6, 67.1, 66.9, 52.3, 50.7, 38.3, 37.8, 37.7, 34.5, 34.3, 34.2; MS *m/z* 830 (M^+), 799, 681, 656; HRMS calcd for $C_{62}H_{54}O_2$ 830.4118, found 830.4073.

4.1.9. Hydrocarbon 38. The same procedure was repeated as described for **29** except that 0.0085 g (0.0102 mmol) of **37**, 0.100 g (0.704 mmol) of phosphorus pentoxide, and 10 mL of benzene were used. The reaction mixture was heated under refluxing benzene at 80 °C for 15 min to afford 0.0062 g of **38** (0.0091 mmol, 89%) as a yellow solid: mp 264–267 °C; IR 1449, 732, 697 cm^{-1}; ^1H δ 8.06 (2H, s), 7.73 (2H, d, $J=8.7$ Hz), 7.65–7.54 (8H, m), 7.47 (2H, s), 7.40 (4H, t, $J=7.3$ Hz), 7.33–7.26 (2H, m), 7.17 (2H, tt, $J=7.9$, 1.3 Hz), 7.12 (4H, d, $J=8.4$ Hz), 6.68–6.59 (4H, m), 6.54 (4H, d, $J=8.2$ Hz); ^{13}C δ 140.7, 140.5, 138.8, 138.6, 134.0, 132.7, 132.5, 132.4, 130.9, 129.0, 128.7, 128.1, 127.9, 127.5, 127.3, 127.2, 126.7, 126.5, 125.9, 125.6, 123.9, 122.9; MS *m/z* 682 (M^+), 528, 448, 425; HRMS calcd for $C_{54}H_{34}$ 682.2661, found 682.2687.

4.1.10. Hydrocarbon 39. The same procedure was repeated as described for **31** except that 0.038 g (0.046 mmol) of **37**, 0.300 g (2.11 mmol) of phosphorus pentoxide, and 40 mL of *p*-xylene were used. The reaction mixture was heated under reflux for 12 h to afford 0.013 g of **39** (0.019 mmol, 42%) as a yellow solid: mp 186–189 °C; ^1H δ (600 MHz) 8.034 (2H, d, $J=7.8$ Hz), 8.021 (2H, d, $J=7.2$ Hz), 7.90 (2H, d, $J=9.0$ Hz), 7.61 (2H, d, $J=8.4$ Hz), 7.54 (2H, ddd, $J=8.1$, 6.6, 1.2 Hz), 7.35 (2H, ddd, $J=7.8$, 6.6, 1.2 Hz), 7.17–7.08 (6H, m), 7.03–7.01 (4H, m), 6.983 (2H, s), 6.976 (2H, dd, $J=7.2$, 2.4 Hz), 6.89 (2H, s), 6.86 (2H, d, $J=8.4$ Hz), 4.46 (2H, d, $J=21.6$ Hz), 4.43 (2H, d, $J=21.0$ Hz); ^{13}C δ (150 MHz) 146.6, 145.3, 142.2, 141.0, 137.2, 134.9, 133.5, 132.6, 130.4, 129.0, 128.8, 128.4, 128.2, 127.0, 126.9, 126.7, 126.5, 125.9, 125.1, 124.8, 124.1, 123.1, 54.1, 33.9; MS *m/z* 682 (M^+), 529, 425; HRMS calcd for $C_{54}H_{34}$ 682.2661, found 682.2663.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2006.02.066. Experimental procedures and spectroscopic data for **1**, **3**, **4**, **8**, **13**, **14**, **16**–**22**, **41**, and **43**; ^1H and ^{13}C NMR spectra of compounds **1**, **3**, **4**, **8**, **9**, **11**, **13**, **14**, **16**–**22**, **28a** or **28b**, **28c**, **29**–**31**, **35**, **37**–**39**, **41**, and **43**; ORTEP drawings of the crystal structures of **18**, **35**, **41**, and **43**. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC nos. 292502, 292503, 292504, and 292505 have been assigned for the compounds **18**, **41**, **43**, and **35**, 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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