Fullerene tectonics. Part 1. A programmed precursor to C_{60}

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Soluble polycyclic tectonic building blocks for C_{60} have been prepared by the cyclotrimerisation of aromatic ketones. Electron impact fragmentation pathways are described.

The identification of C_{60} in 1985 [1] by the laser vapourisation of graphite, for which Kroto, Smalley and Curl have received the Nobel prize, followed by the production of C_{60}, [2,3] has provided some intriguing challenges and opportunities. Retrosynthetic analysis of C_{60} leads to a whole series of bowl shaped polycyclic aromatic hydrocarbons [4,5] which would be predicted to be air stable and isolable given the stability of C_{60}. Graphite is planar carbon and so by analogy to the formation of C_{60}, planar polycyclic aromatic hydrocarbons on activation in the gas phase would be expected to close up into fullerene fragments and even C_{60} itself. Indeed numerous 'buckybowls' have now been isolated and characterised by flash vacuum pyrolysis. [5] Fullerene fragments and fullerenes have also been detected by the laser desorption of novel cyclic acetylene precursors by Diederich and co-workers. [6] We now report some of our studies aimed at the detection of C_{60} fragments and C_{60} by the electron impact activation of large polycyclic fullerene precursors. [7] We have called these 'tectons' because they are potential building blocks for C_{60}. These studies might help to elucidate the order in which endothermic ring coupling reactions occur. The molecular ion or individual daughter ions, produced by EI, CI or FAB, can be selected, activated by argon ion bombardment, followed by detection and analysis of the fragmentation patterns.

Retrosynthetic analysis of C_{60} reveals the series of three robust polycyclic precursors **1**, **2** and **3**. The desired ring coupling reactions that would lead to either fullerene fragments or in the case of precursor **3** to C_{60} itself are shown. The formation of C_{60} from tecton **3** would require the formation of 15 new carbon–carbon bonds. The EI spectrum of decacyclene **1** showed a strong molecular ion at m/z 450 (100%) and a weak fragment at m/z 448 ($M^+ - 2H$, 20%). The argon ion fragmentation of decacyclene and subsequent daughter ion analysis was encouraging because it showed weak molecular ion at m/z 450 (10%), a fragment at 448 ($M^+ - 2H$, 100%), 446 ($M^+ - 4H$, 36%) and a very weak peak at 444 ($M^+ - 6H$, 1%). The spectrum was perfectly clean with no other fragmentations apparent. Hence simply in a mass spectrometer, and not unexpectedly, the molecule appears to be spontaneously folding into a buckybowl! [8] Decacyclene **1** is an insoluble C_{36} precursor which is commercially available and can be easily prepared by the cyclotrimerisation of acenaphthene **4** and acenaphthylene **5** by cyclodehydrogenation with sulfur [9] or by the acid catalysed trimerisation of ketone **6**. [10] Fragments **11** and **12** were prepared, followed by an attempted trimerisation to the C_{60} precursor **3** (Scheme 1). Condensation of (2-naphthylmethyl)-phosphonium salts **7** or **8** with indan-1-one **9** gave a mixture of *E* and *Z* isomers of stilbene **10**. The (tributyl)phosphonium salt **8** is more reactive than the (triphenyl)phosphonium salt **7** and gave the stilbene isomer mixture in a higher yield of 56%. The mixture of stilbenes was photocyclised to 4,5-dihydrobenzo-[*l*]acephenanthrylene **11** using I_2 as an oxidant and propylene oxide [11] as an acid scavenger. Dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene gave precursor **12**. The high dilution photocyclisation


1

2

3

4   **5**   **6**
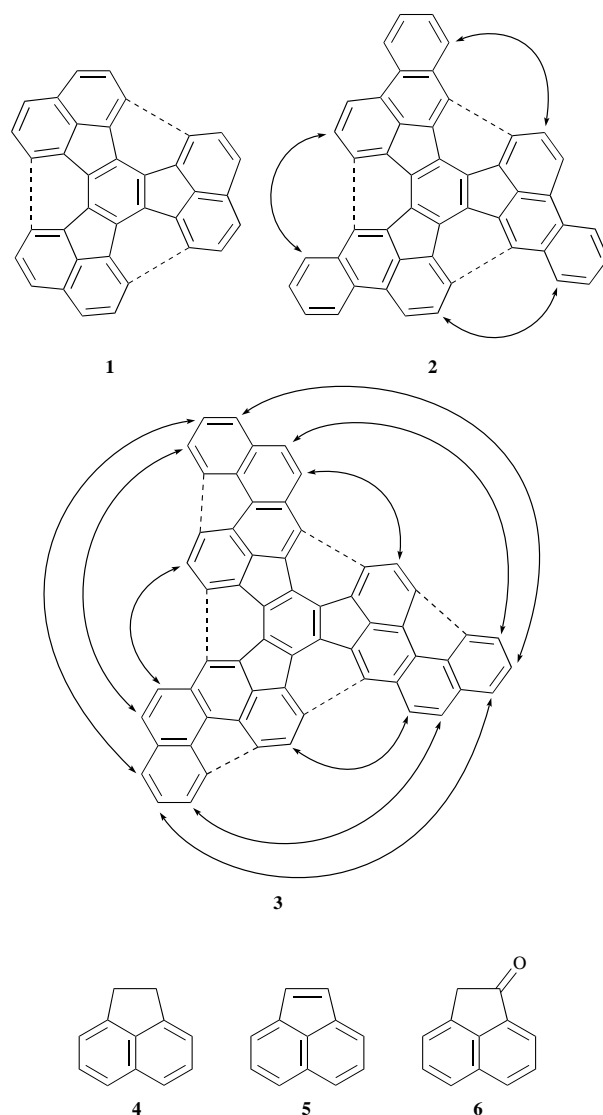
was successful although the strain of the five-membered ring frequently prevents the ring closure reaction. [12] For example stilbene **13**, [13] prepared in an analogous manner to stilbene **10**, in 38% yield, and stilbenes **14** (19%) and **15** (24%) prepared by the NaOEt catalysed condensation of indene with benzaldehyde and 2-naphthaldehyde respectively, failed to photocyclise. With precursors **11** and **12** in hand an attempt was made to cyclotrimerise these into the unimolecular C_{60} precursor **3**. However upon heating with sulfur in an analogous manner to the preparation of decacyclene no products were successfully purified and characterised, possibly because of the insolubility of this hydrocarbon.

Owing to the difficulty of preparing large polycyclic pre-

Table 1 Cyclotrimerisation of aryl ketones

Ketone	Conditions	Products	Yield (%)
16	(i)	**17**	42
16	(iii)	**17**	39
16	(iv)	**17**	29
18	(i)	**19**	54
18	(ii)	**19**	51
18	(iv)	**19**	8
20	(i)	**21**	32
20	(ii)	**21**	30
20	(iv)	**21**	0

7 R = Ph
8 R = Bu
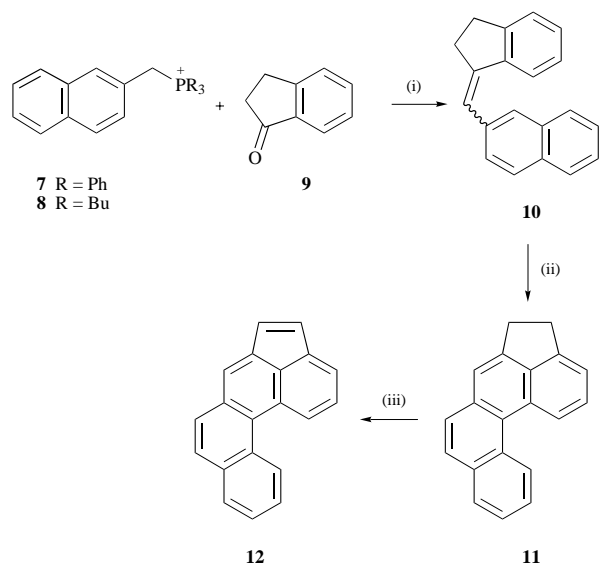
Scheme 1 *Reagents and conditions:* (i) Bu^{n}Li, THF, −78 °C to room temp. then heat, R = Ph 32%, R = Bu 56%; (ii) *hv*, I$_2$, propylene oxide, 2 h, 75%; (iii) DDQ, benzene, heat, 3 h, 60%

13 **14** **15**
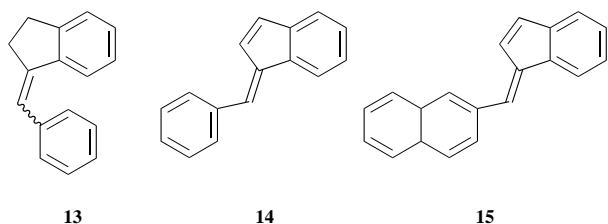
cursors that were not functionalised with solubilising groups, our attention turned to the preparation of the related series of soluble precursors **17**, **19** and **21** (Scheme 2). 1,3,5-Tri-(1-naphthyl)benzene **17** was first prepared by Wirth *et al.* *via* the triethyl orthoformate catalysed trimerisation of 1-acetyl-naphthalene.[14] This compound, in contrast to decacyclene, is freely soluble in organic solvents. 9-Acetylphenanthrene **18** is commercially available[15] and 5-acetylbenzo[*c*]phenanthrene **20** was prepared by Friedel–Crafts acylation of benzo[*c*]phenan-threne with acetic anhydride and AlCl$_3$ in chlorobenzene.[16] Friedel–Crafts acylations frequently give different isomers depending upon the reaction conditions. The authenticity of 5-acetylbenzo[*c*]phenanthrene **20** was originally proved by oxida-tion to the carboxylic acid, which had an identical melting point with a sample of 6-carboxybenzo[*c*]phenanthrene pre-pared by unambiguous methods.[16] These precursors were cyclotrimerised on a small scale using SiCl$_4$ in EtOH[17] or using either HC(OEt)$_3$ or Si(OEt)$_4$ in EtOH saturated with dry HCl. The reaction conditions are shown in Table 1. Unimolecular precursor **21** can only be prepared using SiCl$_4$ in EtOH and did not form by the Wirth method. The precursors **19** and **21** are soluble in organic solvents as expected and were purified by chromatography and fully characterised. The ^{1}H NMR spectra
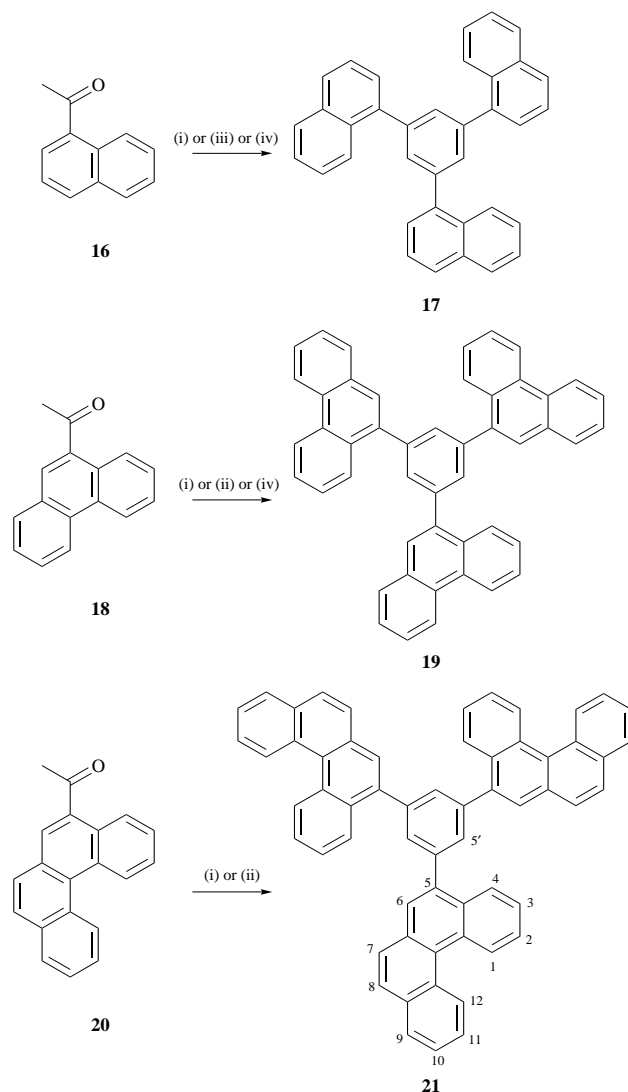
Scheme 2 *Reagents and conditions:* (i) SiCl$_4$, EtOH (1:4), heat, 2 h; (ii) Si(OEt)$_4$, EtOH (1:4), dry HCl, heat, 2 h; (iii) Si(OEt)$_4$, EtOH (1:4), dry HCl, room temp.; (iv) HC(OEt)$_3$, EtOH (1:4), dry HCl, room temp., 1 h

are well resolved owing to the different chemical shifts of the aromatic protons. Considering trimer **21**, one third of the molecule showed multiplets at 7.6–7.8 ppm (4H), two clearly coupled doublets at 7.8–8.0 ppm (H7 and H8,† $J = 8.6$ Hz), a doublet (H9) overlapping with two singlets (H6 and H5′) at 8.0–8.2 ppm, a characteristic doublet at 8.5 ppm for H4 ($J = 8.2$ Hz) which is deshielded owing to steric compression with the adjacent peri phenyl ring and two doublets at 9.2–9.4 ppm (H1 and H12). Fiord region protons on benzo[*c*]phenanthrene show a characteristic doublet in this region. If the authenticity of 5-acetylbenzo[*c*]phenanthrene been incorrect, and the 6-substituted isomer had been cyclotrimerised by mistake, in the ^{1}H NMR spectrum H7 would be deshielded by the peri phenyl ring which is not the case in this spectrum. The spectrum of trimer **19** also showed characteristic doublets at 8.8 ppm owing to the deshielded bay region phenanthrene protons, and a doub-let at 8.4 ppm owing to H4 being deshielded by the peri phenyl ring.

Each of the precursors **17**, **19** and **21** showed a strong molecular ion in the FAB spectrum. However in contrast to the fragmentation pattern observed for decacyclene the electron impact fragmentation of trimer **17** was very disappointing. It showed a strong molecular ion at *m/z* 456 (100%) with no evi-dence for the loss of hydrogen from this molecular ion. Peaks

† See structure of **21** for numbering system used.

at m/z 329 ($M^+ - C_{10}H_7$, 20%), 328, 327 and 326 (30–50%) showed that the molecule was primarily fragmenting by the initial loss of a naphthyl group. Strong peaks at m/z 128 ($C_{10}H_8$, 80%) and 127 ($C_{10}H_7$, 25%) were also present.

The flexible but weaker aryl–aryl link in these compounds, required for solubility and ease of synthesis, leads to an alternative undesirable fragmentation pathway upon activation in a mass spectrometer. A solution to this problem *via* the preparation of more reactive halogenated precursors is reported in the following paper.

Experimental

NMR spectra were recorded on a Bruker 250 MHz instrument. J values are given in Hz. Infrared spectra were recorded on a Perkin Elmer FTIR instrument using KBr discs and ultraviolet spectra were recorded on a Perkin Elmer Lambda 15 UV/VIS spectrophotometer. Mass spectra were obtained with a VG Quattro II triple quadrupole mass spectrometer. Melting points were recorded with an Austrian Reichertz microscopic melting point apparatus and are uncorrected. Solvents were dried by standard methods. Light petroleum refers to the fraction boiling in the range 40–60 °C.

2-(Indan-1-ylidenemethyl)naphthalene 10

Method 1. A suspension of (2-naphthylmethyl)triphenylphosphonium bromide **7** (10.0 g, 0.021 mmol) in dry THF (60 ml) was cooled to -78 °C and treated with Bu^{n}Li in hexanes (13 ml, 1.6 M, 0.021 mmol) under nitrogen with stirring. After 5 min indan-1-one (2.0 g, 0.015 mmol) was added. The mixture was refluxed for 15 h and then cooled, diluted with water, acidified with dil. aq. HCl, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and purified by flash chromatography on silica gel. Elution with light petroleum–dichloromethane (75:25) gave firstly (Z)-2-(*indan-1-ylidenemethyl*)*naphthalene* (255 mg, 7%) as a colourless solid, mp 76–77 °C (from light petroleum–dichloromethane) (Found: C, 93.4; H, 6.4. $C_{20}H_{16}$ requires C, 93.75; H, 6.25%); λ_{max}(cyclohexane)/nm 220 (log ε 4.26), 271 (4.36) and 329 (4.46); ν_{max}(KBr)/cm^{-1} 3050m, 2950m, 2850m, 1640m, 1590m, 1510m, 1460m, 860vs and 755vs; δ_H(250 MHz; CDCl$_3$) 3.08–3.14 (4H, m), 6.87 (1H, s), 6.97–7.03 (1H, m), 7.22–7.28 (1H, m), 7.37–7.41 (2H, d, J 9.0), 7.55–7.59 (2H, m), 7.62–7.65 (1H, d, J 9.0) and 7.87–7.95 (4H, m); δ_C(62.9 MHz; CDCl$_3$) 30.1, 34.3, 121.4, 124.3, 125.3, 125.5, 125.7, 125.9, 126.8, 127.2, 127.6, 127.7, 127.8, 128.2, 132.3, 133.5, 135.8, 139.5, 143.7 and 148.8; m/z 256 (M^+, 100%); followed by (E)-2-(*indan-1-ylidenemethyl*)*naphthalene* (950 mg, 25%) as a colourless solid, mp 112–113 °C (from light petroleum–dichloromethane) (Found: C, 93.8; H, 6.35. $C_{20}H_{16}$ requires C, 93.75, H, 6.25%); λ_{max}(cyclohexane)/nm 225 (log ε 5.22), 274 (4.64) and 330 (4.38); ν_{max}(KBr)/cm^{-1} 3060w, 2950w, 1640w, 1620w, 900vs, 820vs and 740vs; δ_H(250 MHz; CDCl$_3$) 3.23 (4H, s), 7.18–7.94 (11H, m) and 7.99 (1H, s); δ_C(62.9 MHz; CDCl$_3$) 30.7, 30.8, 119.0, 120.2, 125.2, 125.5, 126.0, 126.6, 126.9, 127.5, 127.7, 127.9, 128.1, 131.9, 133.6, 135.8, 142.5, 144.6 and 145.8 (one ^{13}C resonance was not resolved); m/z 256 (M^+, 100%).

Method 2. A suspension of (2-naphthylmethyl)tributylphosphonium bromide **8** (3.53 g, 8.3 mmol) in dry THF (40 ml) was cooled to -78 °C and treated with Bu^{n}Li in hexanes (5.7 ml, 1.6 M, 9.1 mmol) under nitrogen with stirring. After 5 min indan-1-one (1.10 g) was added and the reaction refluxed for 5 h. The mixture was then cooled, diluted with water, acidified with dil. aq. HCl, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and purified by flash chromatography on silica gel. Elution with light petroleum–dichloromethane (75:25) gave an E/Z mixture of the *title compounds* (1.2 g, 56%).

4,5-Dihydrobenzo[*l*]acephenanthrylene 11

An E/Z mixture of 2-(indan-1-ylidenemethyl)naphthalene **10** (200 mg, 0.781 mmol) was dissolved in benzene (20 ml) and added to light petroleum (600 ml) containing propylene oxide (10 ml) in a 500 W water cooled quartz photochemical immersion well reactor. I_2 (218 mg, 0.852 mmol) dissolved in benzene (30 ml) was then added and the mixture was deoxygenated with N_2 for 15 min. After irradiation for 2 h the I_2 colour had disappeared. The mixture was concentrated *in vacuo*, washed with sat. aq. $Na_2S_2O_4$ to remove residual traces of I_2 and then purified by flash chromatography on silica gel. Light petroleum eluted the *title compound* (149 mg, 75%) as a colourless solid, mp 123–124 °C (from light petroleum–dichloromethane) (Found: C, 94.7; H, 5.7. $C_{20}H_{14}$ requires C, 94.5; H, 5.5%); λ_{max}(cyclohexane)/nm 217 (log ε 4.73), 274 (4.96) and 283 (5.03); ν_{max}(KBr)/cm^{-1} 3040w, 2910w, 1610m, 1430w, 880vs and 750vs; δ_H(250 MHz; CDCl$_3$) 3.49–3.52 (4H, m), 7.53 (1H, d, J 6.98), 7.65 (1H, s), 7.68–7.92 (5H, m), 8.08 (1H, d, J 8.0), 8.99 (1H, d, J 9.0) and 9.36 (1H, d, J 9.0); δ_C(62.9 MHz; CDCl$_3$) 29.3, 30.6, 120.1, 120.4, 123.4, 124.7, 125.2, 126.1, 126.9, 127.2, 127.6, 128.2, 128.5, 128.9, 131.2, 132.7, 133.6, 139.1, 145.0 and 146.0; m/z 254 (M^+, 100%).

Benzo[*l*]acephenanthrylene 12

4,5-Dihydrobenzo[*l*]acephenanthrylene **11** (80 mg, 0.315 mmol) in benzene (10 ml) was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (150 mg, 0.661 mmol) and refluxed for 2 h. The reaction mixture was cooled, concentrated *in vacuo* and the product purified by chromatography on silica gel. Elution with light petroleum–dichloromethane (75:25) gave the *title compound* (48 mg, 60%) as a pale yellow solid, mp 101–104 °C (from light petroleum–dichloromethane) (Found: C, 95.3; H, 5.1. $C_{20}H_{12}$ requires C, 95.2; H, 4.8%); λ_{max}(cyclohexane)/nm 219 (log ε 4.67), 288 (4.70) and 338 (3.97); ν_{max}(KBr)/cm^{-1} 2920w, 1460w, 1010m, 830vs, 800vs and 740vs; δ_H(250 MHz; CDCl$_3$) 7.16 (1H, d, J 5.3), 7.26 (1H, d, J 5.3), 7.65–8.06 (8H, m), 8.97 (1H, dd, J 6.0 and 3.0) and 9.23 (1H, d, J 8.5); δ_C(62.9 MHz; CDCl$_3$) 122.5, 126.0, 126.4, 126.4, 126.5, 127.2, 127.9, 128.0, 128.3, 128.6, 128.9, 129.2, 131.2, 131.8, 133.2, 133.9, 138.8 and 139.9 (two ^{13}C resonances are not resolved); m/z 252 (M^+, 100%).

(E)-2-(Indan-1-ylidenemethyl)benzene 13

Indan-1-one (1.0 g, 7.58 mmol) was added to a mixture of (benzyl)triphenylphosphonium chloride (3.5 g, 9.0 mmol) treated with Bu^{n}Li (3.7 ml, 2.5 M) in dry THF at -78 °C. The reaction was stirred and refluxed for 14 h. The reaction mixture was allowed to cool, diluted with H_2O, extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, filtered and purified by chromatography on silica gel. Elution with light petroleum gave firstly (Z)-2-(*indan-1-ylidenemethyl*)*benzene* (161 mg, 10%) followed by the *title compound* (432 mg, 28%) as a pale yellow solid, mp 73–74 °C (lit.,[13] 73–74 °C) (from light petroleum–dichloromethane) (Found: C, 93.5; H, 7.0. $C_{16}H_{14}$ requires C, 93.2; H, 6.8%); λ_{max}(EtOH)/nm 315 (log ε 4.38); δ_H(250 MHz; CDCl$_3$) 3.15 (4H, s), 7.02 (1H, s), 7.25–7.47 (6H, m), 7.54 (2H, d, J 7.6) and 7.66–7.69 (1H, m); δ_C(62.9 MHz; CDCl$_3$) 30.6, 30.8, 118.9, 120.1, 125.2, 126.1, 126.5, 128.1, 128.3, 128.4, 138.2, 142.5, 144.0 and 145.7; m/z 206 (M^+, 100%).

(E)-2-(Inden-1-ylidenemethyl)benzene 14

Indene (1 ml, 0.996 g, 8.59 mmol) and benzaldehyde (0.91 g, 8.59 mmol) in EtOH (20 ml) were treated with NaOEt powder (1.17 g, 17.0 mmol) and refluxed for 20 h. The mixture was then diluted with H_2O, extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$ and purified by chromatography on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (334 mg, 19%) as a yellow solid, mp 84–86 °C (from light petroleum–dichloromethane); δ_H(250 MHz; CDCl$_3$) 7.11 (2H, s), 7.24–7.60 (7H, m), 7.68 (2H, d, J 7.6) and 7.70 (1H, d, J 5.5); δ_C(62.9 MHz; CDCl$_3$) 119.1, 120.9, 125.1, 126.1, 127.5, 128.3, 128.6, 128.7, 130.2, 134.5, 136.9, 137.4, 140.0 and 142.0.

(E)-2-(Inden-1-ylidenemethyl)naphthalene 15

Indene (372 mg, 3.21 mmol) and 2-naphthaldehyde (0.50 g, 3.21 mmol) in EtOH (20 ml) were treated with NaOEt powder (436 mg, 6.4 mmol) and refluxed for 20 h. The mixture was then diluted with H_2O, extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$ and purified by chromatography on silica. Light petroleum–dichloromethane (50:50) eluted the *title compound* (195 mg, 24%) as a yellow solid, mp 153–157 °C (from light petroleum–dichloromethane); δ_H(250 MHz; CDCl$_3$) 7.12 (1H, d, J 5.5), 7.21 (1H, d, J 5.5), 7.24–7.60 (5H, m), 7.70 (1H, s), 7.79–8.00 (5H, m) and 8.10 (1H, s); δ_C(62.9 MHz; CDCl$_3$) 119.2, 121.0, 125.2, 126.1, 126.5, 126.7, 127.3, 127.5, 127.7, 128.3, 128.3, 128.8, 130.2, 133.0, 133.4, 134.4, 134.7, 137.5, 140.2 and 142.0; m/z 254 (M$^+$, 100%).

(2-Naphthylmethyl)tributylphosphonium bromide 8

2-(Bromomethyl)naphthalene (5.0 g, 22.6 mmol) in xylene (20 ml) was treated with tributylphosphine (5.03 g, 24.9 mmol) and refluxed for 3 h. The mixture was cooled and the resultant oil slurried with toluene followed by light petroleum. The oil was left to stand and eventually crystallised after a few weeks as a pale fawn solid (6.80 g, 71%) which was used in Wittig couplings without further purification, δ_H(250 MHz; CDCl$_3$) 0.80–0.90 (9H, m), 1.34–1.41 (12H, m), 2.33–2.45 (6H, m), 4.45 (2H, d, J 15.3), 7.41–7.44 (2H, m), 7.51 (1H, d, J 8.6), 7.72–7.76 (3H, m) and 7.87 (1H, s); δ_C(62.9 MHz; CDCl$_3$) 13.4, 18.4, 19.2, 23.7, 23.8, 23.8, 24.1, 26.9, 27.6, 125.9, 126.1, 126.7, 126.8, 127.5, 127.5, 127.7, 129.2, 129.3, 129.4, 132.7, 132.7, 133.3 and 133.3; m/z (FAB) 343.3 (M$^+$ − Br, 100%).

1,3,5-Tris(benzo[c]phenanthren-5-yl)benzene 21

Method 1. A suspension of 5-acetylbenzo[c]phenanthrene **20** (85 mg, 0.32 mmol) in EtOH (1 ml) under nitrogen was treated with SiCl$_4$ (0.25 ml) injected carefully by syringe. The reaction of SiCl$_4$ with ethanol is exothermic and the reaction mixture turned deep red. The mixture was refluxed for 1$\frac{3}{4}$ h during which time the red colour faded to leave a yellow precipitate. The mixture was saturated with dry HCl gas and refluxed for a further 15 min. The reaction was then cooled, diluted with CH_2Cl_2, extracted twice with dil. aq. HCl, dried over $MgSO_4$, filtered and purified by flash chromatography on silica. Elution with light petroleum–dichloromethane (75:25) gave the *title compound* (26 mg, 32%) as a colourless solid, mp 184–187 °C (from light petroleum–dichloromethane); λ_{max}(cyclohexane)/nm 218 (log ε 5.03), 289 (5.18) and 345sh (4.58); ν_{max}(KBr)/cm^{-1} 3015m, 2931m, 2895m, 1594m and 1380m; δ_H(250 MHz; CDCl$_3$) 7.70 (12H, m), 7.89 (3H, d, J 8.6), 7.96 (3H, d, J 8.6), 8.04 (3H, m), 8.08 (3H, s), 8.09 (3H, s), 8.51 (3H, d, J 7.8), 9.17 (3H, d, J 8.2) and 9.24 (3H, d, J 8.0); δ_C(62.9 MHz; CDCl$_3$) 125.9, 126.1, 126.1, 126.3, 126.6, 126.7, 127.1, 127.8, 127.9, 127.9, 128.4, 130.0, 130.4, 130.8, 130.9, 132.1, 133.6, 138.5 and 140.9; m/z (FAB) 757 (M$^+$ + H, 100%) and 756 (M$^+$, 94%).

Method 2. A suspension of 5-acetylbenzo[c]phenanthrene **20** (75 mg, 0.278 mmol) in EtOH (0.8 ml) and Si(OEt)$_4$ (0.25 ml) was cooled to 0 °C and saturated with dry HCl gas. After refluxing for 3 h the mixture was cooled, diluted with CH_2Cl_2, extracted twice with dil. aq. HCl, dried over $MgSO_4$, filtered and purified by flash chromatography on silica. Elution with light petroleum–dichloromethane (75:25) gave the *title compound* (21 mg, 30%) with identical spectroscopic properties to the previous sample.

1,3,5-Tri(phenanthren-9-yl)benzene 19

Method 1. A suspension of 9-acetylphenanthrene **18** (200 mg, 0.091 mmol) in EtOH (2 ml) under nitrogen was treated carefully with SiCl$_4$ (0.5 ml) injected by syringe. The mixture was refluxed for 2 h and then allowed to cool. The reaction mixture was diluted with CH_2Cl_2, extracted twice with dil. aq. HCl,

dried over $MgSO_4$, filtered and purified by flash chromatography on silica. Elution with light petroleum–dichloromethane (75:25) gave the *title compound* (93 mg, 53%) as a colourless solid, mp 174–176 °C (from light petroleum–dichloromethane) (Found: C, 95.1; H, 5.3. C$_{48}$H$_{30}$ requires C, 95.05; H, 4.5%); λ_{max}(cyclohexane)/nm 256 (log ε 4.91) and 299 (4.63); ν_{max}(KBr)/cm^{-1} 3030w, 3000w, 1600w, 1450w, 890w, 750vs and 730vs; δ_H(250 MHz; CDCl$_3$) 7.70 (12H, m), 7.95 (3H, m), 7.96 (3H, s), 7.98 (3H, s), 8.37 (3H, d, J 7.6), 8.77 (3H, d, J 7.80) and 8.83 (3H, d, J 7.6); δ_C(62.9 MHz; CDCl$_3$) 122.6, 123.0, 126.6, 126.7, 126.8, 126.9, 128.0, 128.7, 130.8, 131.0, 131.0, 131.6, 138.3 and 141.0 (two ^{13}C resonances are not resolved); m/z 606 (M$^+$, 100%).

Method 2. A suspension of 9-acetylphenanthrene **18** (100 mg, 0.454 mmol) in EtOH (0.6 ml) and Si(OEt)$_4$ (0.4 ml) was cooled to 0 °C and saturated with dry HCl gas. After refluxing for 2 h the mixture was cooled, diluted with CH_2Cl_2, extracted twice with dil. aq. HCl, dried over $MgSO_4$, filtered and purified by flash chromatography on silica. Elution with light petroleum–dichloromethane (75:25) gave the *title compound* (47 mg, 51%) with identical spectroscopic properties to the previous sample.

1,3,5-Tri(1-naphthyl)benzene 17

Method 1. A solution of 1-acetylnaphthalene **16** (250 mg, 1.469 mmol) in EtOH (4 ml) under nitrogen was treated carefully with SiCl$_4$ (1 ml) injected by syringe. After refluxing for 2 h the mixture was cooled, diluted with CH_2Cl_2, extracted twice with dil. aq. HCl, dried over $MgSO_4$, filtered and purified by flash chromatography on silica. Elution with light petroleum–dichloromethane (75:25) gave the *title compound* (93 mg, 42%) as a colourless solid, mp 187–188 °C (from light petroleum–dichloromethane) (lit.,[14] 195–196 °C) (Found: C, 94.7; H, 5.5. C$_{36}$H$_{24}$ requires C, 94.7; H, 5.3%); λ_{max}(cyclohexane)/nm 223 (log ε 5.15) and 293 (4.49); ν_{max}(KBr)/cm^{-1} 2060w, 2970w, 1600w, 1580w, 1520w, 1400m, 800vs and 1775vs; δ_H(250 MHz; CDCl$_3$) 7.50–7.65 (12H, m), 7.82 (3H, s), 7.90–8.00 (6H, m) and 8.27 (3H, dd, J 3.36 and 6.10); δ_C(62.9 MHz; CDCl$_3$) 125.6, 126.0, 126.1, 126.3, 127.4, 128.0, 128.5, 130.8, 131.7, 134.0, 139.9 and 140.9; m/z 456 (M$^+$, 100%).

Method 2. A solution of 1-acetylnaphthalene **16** (1.2 g, 7.05 mmol) in EtOH (4 ml) and Si(OEt)$_4$ (2.5 ml) was cooled to 0 °C and saturated with dry HCl gas. The mixture was then allowed to warm to room temp. and stirred for 1 h. The reaction was then diluted with CH_2Cl_2, extracted twice with dil. aq. HCl, dried over $MgSO_4$, filtered and purified by flash chromatography on silica. Elution with light petroleum–dichloromethane (75:25) gave the *title compound* (420 mg, 39%) with identical spectroscopic properties to the previous sample.

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