

# Fullerene tectonics. Part 2.<sup>1</sup> Synthesis and pyrolysis of halogenated benzo[*c*]phenanthrenes

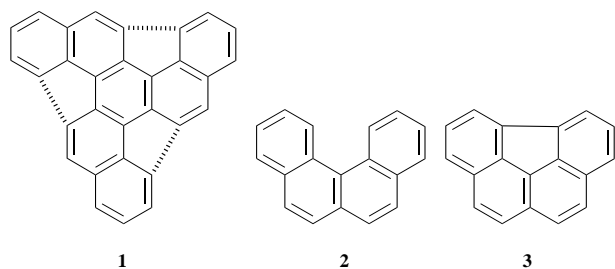
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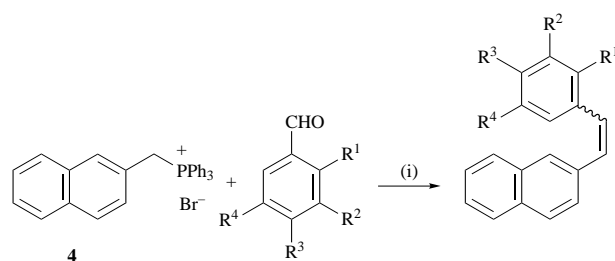
Halogenated benzo[*c*]phenanthrenes with a halogen in the hindered fiord region are prepared by the photochemical cyclisation of appropriately substituted stilbenes. Pyrolysis gives the corresponding benzo[*ghi*]fluoranthrenes in moderate yields. At higher temperatures a competing rearrangement pathway to cyclopenta[*cd*]pyrene occurs.

In the preceding part of this series we reported the synthesis of some large polycyclic tectons or building blocks for C<sub>60</sub> and C<sub>60</sub> fragments.<sup>1</sup> This paper reports our studies on tribenzotriphenylene **1** for which the three ring coupling reactions shown



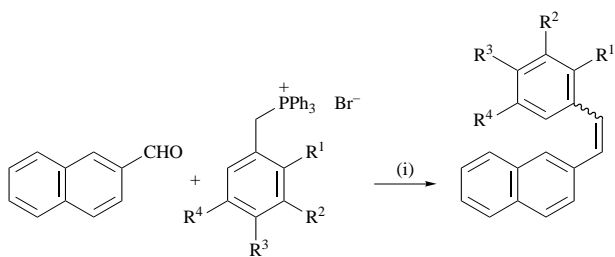
would give the half bowl semibuckminsterfullerene.<sup>2</sup> This is a key optically active fragment of C<sub>60</sub> which has been considered as a potential precursor to C<sub>60</sub> by a stepwise or concerted dimerisation reaction.<sup>3</sup>

Tribenzotriphenylene<sup>4</sup> can be prepared in small quantities by photochemical methods but is difficult to purify so we chose to study the one third sub-unit benzo[*c*]phenanthrene **2** in the first instance. Flash vacuum pyrolysis at high vacuum at 1000 °C gave none of the cyclised material benzo[*ghi*]fluoranthrene **3** but only recovered starting material. This reaction has since been shown to be pressure dependent and indeed at higher pressures, where collisional activation may occur, some cyclised product does form in low yield.<sup>5</sup> A series of halogenated precursors were prepared which were anticipated to be more reactive to ring closure.<sup>6</sup> A chlorine or bromine in the hindered fiord region is sterically compressed and upon pyrolysis could break generating an aryl radical which would provide a strong driving force for ring closure. Furthermore successful syntheses of corannulene have used halogenated precursors or relied upon the generation and cyclisation of a reactive intermediate.<sup>7</sup> 1-Bromobenzo[*c*]phenanthrene has been prepared previously in a lengthy 11 step synthesis<sup>8</sup> so a more convenient photochemical route was developed. The stilbenes shown in Schemes 1 and 2 were prepared as a mixture of *E* and *Z* isomers by the base catalysed condensation of an aryl phosphonium salt with an appropriate aromatic aldehyde in EtOH or THF.<sup>9</sup> The halogen substituted benzylic phosphonium salts are more acidic and reacted very rapidly within minutes at room temperature with 2-naphthaldehyde. For convenience the base sodium methoxide was bought as a dry powder although a fresh jar should be used every few months or so. These reactions can fail drastically and suddenly presumably because the base has absorbed moisture. EtOH was rigorously dried by distillation from an excess of magnesium ethoxide. Sodium ethoxide powder was also used but was a much finer powder that was unpleasant to weigh out.



Aldehyde	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Stilbene ( <i>E/Z</i> mixture)
<b>5</b>	H	Cl	H	Cl	<b>9</b>
<b>6</b>	H	F	H	F	<b>10</b>
<b>7</b>	H	F	F	F	<b>11</b>
<b>8</b>	F	F	F	H	<b>12</b>

**Scheme 1** Reagents and conditions: (i) NaOMe, EtOH, heat, 10 h or KOBu<sup>t</sup>, THF, room temp., 1 h



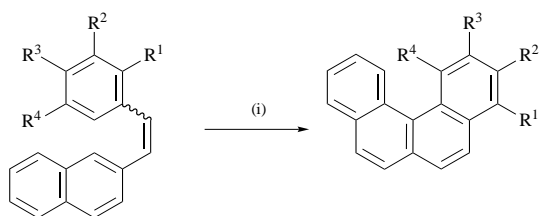
Wittig salt	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Stilbene ( <i>E/Z</i> mixture)
<b>13</b>	Cl	H	H	Cl	<b>20</b>
<b>14</b>	Br	H	H	Cl	<b>21</b>
<b>15</b>	F	H	H	Cl	<b>22</b>
<b>16</b>	Cl	H	H	Br	<b>23</b>
<b>17</b>	F	H	H	F	<b>24</b>
<b>18</b>	H	Br	H	Br	<b>25</b>
<b>19</b>	Cl	H	H	OMe	<b>26</b>

**Scheme 2** Reagents and conditions: (i) NaOMe, EtOH, room temp., 1 h

The yields quoted are based on the quantity of aldehyde. Additional aliquots (0.2 equiv.) of base and phosphonium salt were sometimes needed to drive the reactions to completion. Initially the *E-Z* isomer mixtures were isomerised to the (*E*)-stilbene by refluxing with iodine in xylene. However good microanalyses could not be obtained suggesting that a small amount of iodination had occurred. Each (*E*)-stilbene isomer was therefore purified from the more soluble *Z* isomer by repeated trituration

with light petroleum. The trifluorinated stilbenes **11** and **12** were prepared using the base KOBu<sup>t</sup> in THF at room temperature.

The *E-Z* mixtures of stilbenes were photocyclised to benzo[*c*]phenanthrenes at high dilution in a quartz immersion well reactor using iodine as oxidant and propylene oxide as an acid scavenger (Scheme 3). The introduction by Katz *et al.*<sup>10</sup>



Stilbene	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Benzo[ <i>c</i> ]phenanthrene
<b>9</b>	H	Cl	H	Cl	<b>27</b>
<b>10</b>	H	F	H	F	<b>28</b>
<b>11</b>	H	F	F	F	<b>29</b>
<b>12</b>	F	F	F	H	<b>30</b>
<b>20</b>	Cl	H	H	Cl	<b>31</b>
<b>21</b>	Br	H	H	Cl	<b>32</b>
<b>22</b>	F	H	H	Cl	<b>33</b>
<b>23</b>	Cl	H	H	I (Br)	<b>34*</b>
<b>24</b>	F	H	H	F	<b>35</b>
<b>25</b>	H	Br	H	I (Br)	<b>36*</b>
<b>26</b>	Cl	H	H	OMe	<b>37</b>

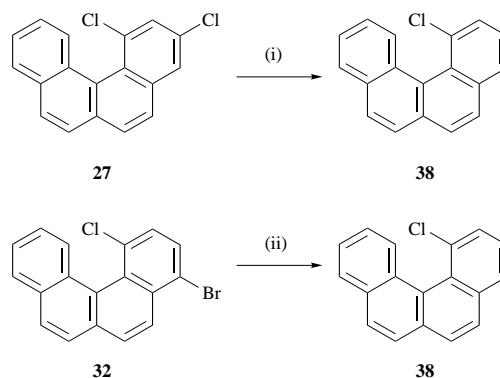
\* The bromine substituent R<sup>4</sup> is replaced by iodine during the photochemical cyclisation.

**Scheme 3** Reagents and conditions: (i) *hν*, I<sub>2</sub>, propylene oxide, N<sub>2</sub>, 1.5–2.5 h

of propylene oxide as an acid scavenger for photochemical cyclisations, which improves the yield and gives much cleaner reactions, represents a long overdue improvement in the methodology particularly considering the vast literature on helicenes and related compounds reported previously.<sup>11</sup> Stilbenes **9**, **10** and **25** must photocyclise, owing to symmetry, to give a halogen in the 1 position. In the remaining stilbenes the halogen substituent at R<sup>1</sup> directs halogen R<sup>4</sup> into the fiord region. Photochemical cyclisation of stilbenes **23** and **25** were problematic and gave products in lower yields which were harder to purify. However one major product was formed in each case which gave good proton and carbon spectra but carbon and hydrogen microanalysis fitted closely for the iodinated compounds **34** and **36** which they are tentatively assigned as. The mass spectra gave a weak molecular ion for the iodinated compounds. No problems were encountered in the synthesis of 4-bromo-1-chlorobenzo[*c*]phenanthrene **32** so presumably the sterically compressed bromine in the fiord region of the benzo[*c*]phenanthrenes formed from stilbenes **23** and **25** is sufficiently weakened to fragment photochemically generating an aryl radical. This would then react rapidly with molecular iodine or an iodine radical at a faster rate than an intramolecular cyclisation. Hence in the final products **34** and **36** the bromine substituent has been replaced by iodine.

The structure of the benzo[*c*]phenanthrene core was proven unambiguously for the non-fluorinated derivatives by complete dehalogenation with formic acid and palladium on carbon.<sup>12</sup> By careful TLC monitoring the outer less hindered chlorine of precursor **27** was selectively reduced to give 1-chlorobenzo[*c*]phenanthrene **38** (Scheme 4). The best route to 1-chlorobenzo[*c*]phenanthrene **38** involved debromination of polycyclic **32** by metal-halogen exchange with Bu<sup>t</sup>Li at low temperature.

A comparative flash vacuum pyrolysis (FVP) study was then made on selected precursors. Pyrolysis of 1-chlorobenzo[*c*]phenanthrenes **38**, **31** and **33** gave benzo[*ghi*]fluoranthenes **3**,



**Scheme 4** Reagents and conditions: (i) HCO<sub>2</sub>H, Et<sub>3</sub>N, 10% Pd/C; (ii) BuLi<sup>t</sup>, –78 °C, 2 min then HOAc, –78 °C to room temp.

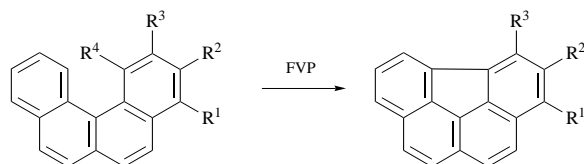
**39** and **40** respectively in moderate yields (Scheme 5). These precursors cyclise more readily than unhalogenated benzo[*c*]phenanthrene **2** although disappointingly high pyrolysis temperatures of 1000–1030 °C were needed to drive the reaction to completion. At these temperatures soot forms along the quartz tube which probably lowers the yields as the reactive edges of free radicals will react with both product and starting material passing along the tube. However the iodinated precursor **34** gave 3-chlorobenzo[*ghi*]fluoranthene **39** at the lower temperature of 950 °C in a higher yield of 75%. A characteristic dark band of iodine formed in the cold trap during the pyrolysis. The fluorinated precursors required a high pyrolysis temperature of 1150 °C and only partially cyclised. They are however more easily cyclised than the parent compound benzo[*c*]phenanthrene **2**. The formation of a distinct yellow product was also observed during pyrolyses at high temperatures. Careful pyrolysis of benzo[*ghi*]fluoranthene **3**<sup>13</sup> gave recovered starting material (35%) and the isomer cyclopenta[*cd*]pyrene **41**<sup>14</sup> (12%) formed by a molecular rearrangement (Scheme 6). This rearrangement is similar to the five- and six-membered ring interconversions studied by Scott and Roelofs<sup>15</sup> and is clearly a potential side reaction which may occur during the formation of large buckybowls such as semibuckminsterfullerene.

The mass spectrum of each benzo[*c*]phenanthrene also showed spontaneous ring coupling to occur much more readily than in the unhalogenated benzo[*c*]phenanthrene. Peaks owing to the loss of halogen and hydrogen halide were observed. In the case of difluorinated precursors **28** and **35** a molecular ion peak was observed followed by the loss of HF (25 and 24% respectively) and not fluorine (19) alone. The carbon–fluorine bond is very strong so presumably these precursors are undergoing an electrocyclisation reaction followed by the elimination of HF. The positively charged molecular ion is probably more reactive owing to the electronegativity of the fluorine groups. This explanation is supported by the mass spectrum of trifluorinated precursor **29** which shows a stronger fragment owing to the loss of HF (60%). Trifluorinated benzo[*c*]phenanthrene **30**, which is not substituted with fluorine in the fiord region, also fragments losing hydrogen (30%) more readily than benzo[*c*]phenanthrene. Our studies on the synthesis of fluorinated derivatives of tribenzotriphenylene have been reported.<sup>16,17</sup>

In conclusion halogenated benzo[*c*]phenanthrenes undergo ring closure to benzo[*ghi*]fluoranthrenes by FVP. Further studies on large halogenated tectons are in progress. Fluorinated precursors are thermally stable to sublimation, have a lower molecular weight and may close up into C<sub>60</sub> by gas phase activation.

## Experimental

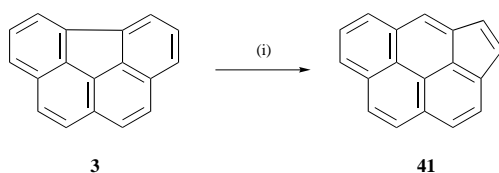
For general details see preceding paper in the series.<sup>1</sup> *J* values are given in Hz. For compounds containing phosphorous or



Benzo[c]phenanthrene	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	I/°C	Benzo[ghi]fluoranthene*
<b>38</b>	H	H	H	Cl	1030	<b>3</b> (53%)
<b>31</b>	Cl	H	H	Cl	1000	<b>39</b> (38%)
<b>33</b>	F	H	H	Cl	1030	<b>40</b> (46%)
<b>34</b>	Cl	H	H	I	950	<b>39</b> (75%)
<b>35</b>	F	H	H	F	1150	<b>35</b> (32%) <b>40</b> (23%)

\* Yields are given in parentheses.

Scheme 5



Scheme 6 Reagents and conditions: (i) FVP 1175 °C to give **41** 12% and **3** 35%

fluorine the <sup>13</sup>C spectrum has either been interpreted or a full listing of peaks given. The number of bonds through which coupling occurs has been reported where possible.

#### Phosphonium salts

**General procedure: (2,5-dichlorobenzyl)triphenylphosphonium bromide 13.** 2,5-Dichlorotoluene (10.0 g, 62 mmol) and *N*-bromosuccinimide (NBS) (11.1 g, 62 mmol) in CCl<sub>4</sub> (50 ml) were treated with a catalytic amount of dibenzoyl peroxide and refluxed for 6 h or until the reaction had gone to completion as monitored by TLC. The reaction mixture was then allowed to cool, washed twice with H<sub>2</sub>O, dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The crude oil was used directly in the next step without any purification assuming a 100% yield. The above oil in xylene (50 ml) was treated with Ph<sub>3</sub>P (16.3 g, 62 mmol) and refluxed for 3 h. The mixture was cooled and the product filtered. The salt was purified by washing with toluene to remove excess Ph<sub>3</sub>P and xylene followed by washing with light petroleum to remove toluene and facilitate rapid drying. The *title compound* (18.4 g, 59%) was obtained as a colourless solid, mp >300 °C (from dichloromethane–light petroleum) (Found: C, 60.0; H, 4.0. C<sub>25</sub>H<sub>20</sub>Cl<sub>2</sub>P requires C, 59.7; H, 4.0%); λ<sub>max</sub>(EtOH)/nm 272 (log ε 5.7); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2850s, 2800s, 1600s, 1460vs, 1440vs, 1120vs, 1110vs and 880vs; δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 5.55 (2H, d, *J* 14.6), 7.0–7.2 (2H, m), 7.4 (1H, s) and 7.45–7.8 (15H, m); δ<sub>C</sub>(62.9 MHz; CDCl<sub>3</sub>) 29.2 (d, <sup>1</sup>J<sub>PC</sub> 48.0), 118.0 (d, <sup>1</sup>J<sub>PC</sub> 85.8), 128.6 (d, *J*<sub>PC</sub> 8.7), 130.4 (d, *J*<sub>PC</sub> 4.3), 130.6 (d, *J*<sub>PC</sub> 12.6), 130.9 (d, *J*<sub>PC</sub> 3.2), 133.4 (d, *J*<sub>PC</sub> 5.0), 133.9 (d, *J*<sub>PC</sub> 4.2), 134.5 (d, *J*<sub>PC</sub> 6.6), 134.7 (d, *J*<sub>PC</sub> 10.0) and 135.5 (d, *J*<sub>PC</sub> 3.0); *m/z* (FAB) 421 (M<sup>+</sup> – Br, 100%).

**(2-Bromo-5-chlorobenzyl)triphenylphosphonium bromide 14.** Yield 63%; colourless solid, mp >300 °C (from dichloromethane–light petroleum) (Found: C, 54.8; H, 3.4. C<sub>25</sub>H<sub>20</sub>-BrCl<sub>2</sub>P requires C, 54.9; H, 3.7%); λ<sub>max</sub>(EtOH)/nm 267 (log ε 5.1); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3050vs, 2845vs, 2760vs, 1590vs, 1430vs, 1120vs, 870vs and 840; δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 5.82 (2H, d, *J* 14.6) and 7.0–7.8 (18H, m); δ<sub>C</sub>(62.9 MHz; CDCl<sub>3</sub>) 29.1 (d, <sup>1</sup>J<sub>PC</sub> 48.8), 117.1 (d, *J*<sub>PC</sub> 86.3), 124.5 (d, *J*<sub>PC</sub> 6.8), 130.1 (d, *J*<sub>PC</sub> 12.7), 132.7 (d, *J*<sub>PC</sub> 4.7), 133.7 (d, *J*<sub>PC</sub> 3.3), 134.2, 134.2 (d, *J*<sub>PC</sub> 10.0) and 135.1 (d, <sup>4</sup>J<sub>PC</sub> 2.7) (two peaks are not resolved); *m/z* (FAB) 467 (M<sup>+</sup> – Br, 100%).

**(5-Chloro-2-fluorobenzyl)triphenylphosphonium bromide 15.** Yield 56%; colourless solid, mp >300 °C (from dichloromethane–light petroleum); λ<sub>max</sub>(EtOH)/nm 267 (log ε 5.36); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2860s, 2800s, 1580m, 1490vs, 1440vs, 1245vs, 1120vs and 840vs; δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 5.49 (2H, d, *J* 14.5), 6.75 (1H, m), 7.14 (1H, m), 7.34 (1H, m) and 7.60–7.82 (15H, m); δ<sub>C</sub>(62.9 MHz; CDCl<sub>3</sub>) 24.4 (d, <sup>1</sup>J<sub>PC</sub> 49.3), 116.4, 117.1 (d, *J*<sub>PC</sub> 86.0), 129.8, 130.2 (d, *J*<sub>PC</sub> 12.7), 130.4 (d, *J*<sub>PC</sub> 3.9), 132.8, 134.0 (d, *J*<sub>PC</sub> 10.6), 135.2 (d, *J*<sub>PC</sub> 2.6) and 159.4 (dd, *J*<sub>FC</sub> 248.0, *J*<sub>PC</sub> 6.0) (one peak is not resolved); *m/z* (FAB) 405 (M<sup>+</sup> – Br, 100%).

**(5-Bromo-2-chlorobenzyl)triphenylphosphonium bromide 16.** Yield 68%; colourless solid, mp >300 °C (from dichloromethane–light petroleum) (Found: C, 55.1; H, 3.6. C<sub>25</sub>H<sub>20</sub>-BrCl<sub>2</sub>P requires C, 54.9; H, 3.7%); λ<sub>max</sub>(EtOH)/nm 266 (log ε 5.03); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2820m, 2750m, 1460s, 1430vs, 1120vs, 1090vs, 860vs and 840vs; δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 5.83 (2H, d, *J* 14.7), 7.06 (1H, d, *J* 8.5), 7.27 (1H, s), 7.34 (1H, d, *J* 8.5) and 7.45–7.90 (15H, m); δ<sub>C</sub>(62.9 MHz; [<sup>2</sup>H<sub>6</sub>]DMSO) 26.7 (d, *J*<sub>PC</sub> 48.0), 116.3 (d, *J*<sub>PC</sub> 86.0), 120.5 (d, *J*<sub>PC</sub> 4.9), 128.6 (d, *J*<sub>PC</sub> 8.6), 130.2 (br), 133.6, 134.1 (d, *J*<sub>PC</sub> 6.8) and 135.5 (br) (three peaks are not resolved); *m/z* (FAB) 467 (M<sup>+</sup> – Br, 100%).

**(2,5-Difluorobenzyl)triphenylphosphonium bromide 17.** Yield 52%; colourless solid, mp >300 °C (from dichloromethane–light petroleum) (Found: C, 63.8; H, 4.1. C<sub>25</sub>H<sub>20</sub>F<sub>2</sub>P requires C, 64.0; H, 4.3%); λ<sub>max</sub>(EtOH)/nm 268 (log ε 5.66); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2850m, 2790m, 1500vs, 1440vs, 1160s, 1110vs, 860vs and 835vs; δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 5.48 (2H, d, *J* 14.6), 6.76 (1H, m), 6.90 (1H, m), 7.19 (1H, m) and 7.60–7.81 (15H, m); δ<sub>C</sub>(62.9 MHz; CDCl<sub>3</sub>) 24.0 (d, *J*<sub>PC</sub> 49.0), 116.2 (m), 116.6 (m), 116.9 (m), 117.1 (d, *J*<sub>PC</sub> 86.0), 119.8 (m), 130.1 (d, *J*<sub>PC</sub> 12.6), 134.0 (d, *J*<sub>PC</sub> 10.0) and 135.2 (d, <sup>4</sup>J<sub>PC</sub> 3.0) (two CF carbons were not detected); *m/z* (FAB) 389 (M<sup>+</sup> – Br, 100%).

**(3,5-Dibromobenzyl)triphenylphosphonium bromide 18.** Yield 62%; colourless solid, mp >300 °C (from dichloromethane–light petroleum); λ<sub>max</sub>(EtOH)/nm 267 (log ε 5.5); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2875m, 2800m, 1580s, 1550s, 1430s, 1115vs, 1000m, 875vs, 740vs and 690vs; δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 5.55 (2H, *J* 14.9), 7.23–7.25 (2H, m), 7.61 (1H, s) and 7.69–7.87 (15H, m); δ<sub>C</sub>(62.9 MHz; CDCl<sub>3</sub>) 30.1 (d, <sup>1</sup>J<sub>PC</sub> 46.7), 117.6 (d, *J*<sub>PC</sub> 85.9), 122.7 (d, *J*<sub>PC</sub> 3.9), 130.0 (d, *J*<sub>PC</sub> 12.7), 131.7 (d, *J*<sub>PC</sub> 8.6), 133.1 (d, *J*<sub>PC</sub> 5.7), 133.8 (d, *J*<sub>PC</sub> 3.9), 134.4 (d, *J*<sub>PC</sub> 9.9) and 134.8 (d, *J*<sub>PC</sub> 3.0); *m/z* 511 (M<sup>+</sup> – Br, 100%).

#### Halogenated stilbenes

Yields for all stilbenes are based on the quantity of aldehyde used. See the text for general comments.

**(*E*)-1-(3,5-Dichlorophenyl)-2-(2-naphthyl)ethene 9.** (2-Naphthylmethyl)triphenylphosphonium bromide **4** (0.558 g, 1.15 mmol) and 3,5-dichlorobenzaldehyde (200 mg, 1.14 mmol) in dry EtOH (20 ml) were treated with sodium methoxide powder (74 mg, 1.37 mmol) and refluxed for 10 h. The reaction

mixture was then cooled, acidified with dil. aq. HCl and extracted into  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed twice with water to remove EtOH, dried over  $\text{MgSO}_4$ , concentrated *in vacuo* and purified by flash chromatography on silica gel. Elution with light petroleum–dichloromethane (90:10) gave a mixture of (E)- and (Z)-1-(3,5-dichlorophenyl)-2-(2-naphthyl)ethene (85%). Repeated trituration with light petroleum washed out the more soluble (Z) isomer to give the *title compound* as a colourless solid, mp 138–139 °C (from light petroleum–dichloromethane) (Found: C, 71.9; H, 3.6.  $\text{C}_{18}\text{H}_{12}\text{Cl}_2$  requires C, 72.2; H, 4.0%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  227 (log  $\epsilon$  4.21), 280 (4.21) and 318 (4.33);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2350vw, 1575s, 1550vs, 1430w, 960vs, 850vs, 800vs and 740;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.05 (1H, d,  $J$  16), 7.28 (1H, d,  $J$  16), 7.29–7.41 (1H, m), 7.41 (2H, d,  $J$  1.7), 7.51 (2H, m), 7.70 (1H, dd,  $J$  1.4 and 8.7) and 7.84–7.86 (4H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  123.1, 124.6, 125.9, 126.3, 126.4, 127.1, 127.4, 127.6, 128.0, 128.4, 131.4, 133.2, 133.5, 133.7, 135.1 and 140.3;  $m/z$  298/300 ( $\text{M}^+$ , 100%), 262/263 ( $\text{M}^+ - \text{Cl}$ , 50) and 226/228 ( $\text{M}^+ - 2\text{Cl}$ ).

**General procedure for stilbenes 20–25: (E)-1-(2,5-Dichlorophenyl)-2-(2-naphthyl)ethene 20.** (2,5-Dichlorobenzyl)triphenylphosphonium bromide **13** (1.9 g, 3.78 mmol) in dry EtOH (20 ml) was treated with NaOMe (208 mg, 3.85 mmol) followed by 2-naphthaldehyde (0.5 g, 3.2 mmol) and stirred at room temp. for 1 h. The yellow coloured ylide decolourised instantly on addition of the aldehyde. The mixture was then diluted with water, acidified with dil. aq. HCl and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with  $\text{H}_2\text{O}$ , dried over  $\text{MgSO}_4$  and purified by flash chromatography on silica gel. Light petroleum–dichloromethane (90:10) eluted a mixture of (E)- and (Z)-1-(2,5-dichlorophenyl)-2-(2-naphthyl)ethene (835 mg, 87%). Repeated trituration with light petroleum washed out the more soluble (Z) isomer to give the *title compound* as a colourless solid, mp 131–132 °C (from light petroleum–dichloromethane) (Found: C, 72.1; H, 3.8.  $\text{C}_{18}\text{H}_{12}\text{Cl}_2$  requires C, 72.2; H, 4.0%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  225 (log  $\epsilon$  4.52), 278 (4.43) and 314 (4.51);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3050w, 1600w, 1460m, 1450m, 1400m, 1100vs, 1050vs, 960vs and 800vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.18 (1H, d,  $J$  8.5), 7.27 (1H, s), 7.34 (1H, d,  $J$  8.5), 7.40–7.59 (3H, m) and 7.72–7.89 (6H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  123.4, 123.6, 126.1, 126.3, 126.4, 127.5, 127.6, 128.1, 128.2, 128.4, 130.8, 131.5, 132.4, 132.8, 133.3, 133.4, 133.9 and 136.8;  $m/z$  298/300 ( $\text{M}^+$ , 30%) and 228 ( $\text{M}^+ - 2\text{Cl}$ , 100).

**General procedure for stilbenes 10–12 and 30: (E)-1-(3,4,5-Trifluorophenyl)-2-(2-naphthyl)ethene 11.** (2-Naphthylmethyl)triphenylphosphonium bromide **4** (1.53 g, 3.14 mmol) was stirred vigorously in dry THF (20 ml) and treated with KOBu<sup>t</sup> powder (360 mg, 3.20 mmol) followed by 3,4,5-trifluorobenzaldehyde (500 mg, 3.13 mmol) and stirred at room temp. for 1 h. The reaction mixture was then acidified with dil. aq. HCl and extracted into  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed twice with water to remove EtOH, dried over  $\text{MgSO}_4$ , concentrated *in vacuo* and purified by flash chromatography on silica gel. Elution with light petroleum–dichloromethane (90:10) gave a mixture of (E)- and (Z)-1-(3,4,5-trifluorophenyl)-2-(2-naphthyl)ethene (489 mg, 56%). Repeated trituration with light petroleum washed out the more soluble (Z) isomer to give the *title compound* as a colourless solid, mp 127–128 °C (from light petroleum–dichloromethane) (Found: C, 76.3; H, 3.7.  $\text{C}_{18}\text{H}_{11}\text{F}_3$  requires C, 76.1; H, 3.9%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  248 (log  $\epsilon$  4.14), 270 (4.45) and 314 (4.56);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2850w, 1440m, 1190s, 730vs and 700vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  6.95–7.20 (4H, m), 7.45–7.49 (2H, m), 7.65 (1H, d,  $J$  8.5) and 7.79–7.82 (4H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  109.8, 109.9, 110.0, 110.1, 123.1, 125.7, 125.7, 125.8, 125.8, 126.3, 126.5, 127.3, 127.6, 128.0, 128.4, 130.9, 131.0, 133.2, 133.4, 133.5, 136.7, 136.9, 137.2, 140.7, 140.9, 141.2, 149.2, 149.3, 149.4, 149.5, 153.2, 153.3, 153.4 and 153.4;  $m/z$  284 ( $\text{M}^+$ , 100%), 283 ( $\text{M}^+ - \text{H}$ , 25%), 282 ( $\text{M}^+ - 2\text{H}$ , 20) and 262 ( $\text{M}^+ - 2\text{H} - \text{HF}$ ).

**(Z)-1-(2,3,4-Trifluorophenyl)-2-(2-naphthyl)ethene 12.** (E)-

and (Z)-1-(2,3,4-Trifluorophenyl)-2-(2-naphthyl)ethene (51%). *Title compound:* colourless solid, mp 130–132 °C (from light petroleum–dichloromethane) (Found: C, 76.5; H, 3.7.  $\text{C}_{18}\text{H}_{11}\text{F}_3$  requires C, 76.1; H, 3.9%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  269 (log  $\epsilon$  4.30), 277 (4.31) and 311 (4.37);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3055w, 1520vs, 1460vs, 1400s, 1140vs, 960vs, 830vs and 750vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  6.91–7.01 (1H, m), 7.25–7.34 (3H, m), 7.45–7.51 (2H, m), 7.70 (1H, d,  $J$  8.5) and 7.79–7.84 (4H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  112.1 (dd,  $J_{\text{FC}}$  17.6 and 3.9), 119.2 (dd,  $J_{\text{FC}}$  5.7 and 2.8), 120.1–120.4 (m, 5 peaks), 122.9 (d,  $J_{\text{FC}}$  3.8), 123.1, 126.2, 126.4, 127.2, 127.6, 128.0, 128.4, 131.8 (dd,  $J_{\text{FC}}$  5.0 and 2.6), 133.2, 133.5, 134.0, 140.1 (dt,  $^{1,2,3}J_{\text{FC}}$  251.6, 15.2 and 15.5), 149.1 (qd,  $^{1,2,3}J_{\text{FC}}$  251.6, 9.4 and 3.0) and 150.2 (qd,  $^{1,2,3}J_{\text{FC}}$  251.6, 9.4 and 3.0);  $m/z$  284 ( $\text{M}^+$ , 100%) and 264 ( $\text{M}^+ - \text{HF}$ , 29).

**(E)-1-(2-Bromo-5-chlorophenyl)-2-(2-naphthyl)ethene 21.** (E)- and (Z)-1-(2-Bromo-5-chlorophenyl)-2-(2-naphthyl)ethene (91%). *Title compound:* colourless solid, mp 138–140 °C (from light petroleum–dichloromethane) (Found: C, 62.8; H, 3.3.  $\text{C}_{18}\text{H}_{12}\text{BrCl}$  requires C, 62.9; H, 3.5%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  226 (log  $\epsilon$  4.40), 272 (4.33) and 314 (4.36);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3050w, 1450m, 1190s, 1030vs, 960vs, 820vs and 750vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.09–7.16 (1H, m), 7.23 (1H, s), 7.48–7.55 (4H, m), 7.70 (1H, d,  $J$  2.5), 7.77 (1H, dd,  $J$  1.6 and 8.9) and 7.83–7.89 (4H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  121.8, 123.4, 126.3, 126.3, 126.4, 127.5, 127.6, 128.1, 128.4, 128.5, 132.6, 133.3, 133.5, 133.5, 133.9, 134.0 and 138.5;  $m/z$  344 ( $\text{M}^+$ , 20%), 342 ( $\text{M}^+$ , 14), 228 ( $\text{M}^+ - \text{Cl} - \text{Br}$ , 100).

**(E)-1-(5-Bromo-2-chlorophenyl)-2-(2-naphthyl)ethene 23.** (E)- and (Z)-1-(5-Bromo-2-chlorophenyl)-2-(2-naphthyl)ethene (77%). *Title compound:* colourless solid, mp 119–120 °C (from light petroleum–dichloromethane) (Found: C, 62.8; H, 3.4.  $\text{C}_{18}\text{H}_{12}\text{BrCl}$  requires C, 62.9; H, 3.5%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  225 (log  $\epsilon$  4.79), 272 (4.49) and 314 (4.51);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3075w, 1190m, 1145s, 950vs, 875s, 870s, 800vs and 740vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.21–7.40 (3H, m), 7.49–7.57 (3H, m) and 7.75–7.89 (6H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  120.6, 123.4, 123.5, 126.3, 126.4, 127.5, 127.6, 128.1, 128.4, 129.0, 131.1, 131.1, 132.2, 132.5, 133.3, 133.4, 133.9 and 137.2;  $m/z$  344 ( $\text{M}^+$ , 25%), 342 ( $\text{M}^+$ , 21), 228 ( $\text{M}^+ - \text{Cl} - \text{Br}$ , 100).

**(E)-1-(2,5-Difluorophenyl)-2-(2-naphthyl)ethene 24.** (E)- and (Z)-1-(2,5-Difluorophenyl)-2-(2-naphthyl)ethene (77%). *Title compound:* colourless solid, mp 101–102 °C (from light petroleum–dichloromethane) (Found: C, 81.25; H, 4.4.  $\text{C}_{18}\text{H}_{12}\text{F}_2$  requires C, 81.2; H, 4.5%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  220 (log  $\epsilon$  4.67), 271 (4.53) and 319 (4.60);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3050w, 1490vs, 1195m, 960m, 850vs, 800vs and 780vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  6.88–7.15 (2H, m), 7.30–7.59 (5H, m) and 7.71–7.93 (5H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  112.5 (dd,  $^{2,3}J_{\text{FC}}$  25.8 and 4.0), 115.0 (dd,  $^{2,3}J_{\text{FC}}$  23.9 and 8.8), 116.6 (dd,  $^{2,3}J_{\text{FC}}$  25.2 and 8.9), 119.9 (dd,  $J_{\text{FC}}$  3.1 and 2.3), 123.3, 126.2, 126.4, 126.5 (m), 127.3, 127.6, 128.0, 128.4, 131.9 (d,  $J_{\text{FC}}$  4.4), 133.2, 133.5, 134.1, 156.3 (dd,  $^{1,4}J_{\text{FC}}$  252.0 and 2.3) and 158.8 (dd,  $^{1,4}J_{\text{FC}}$  242.2 and 2.3);  $m/z$  266 ( $\text{M}^+$ , 100%) and 246 ( $\text{M}^+ - \text{HF}$ , 30).

**(E)-1-(3,5-Difluorophenyl)-2-(2-naphthyl)ethene 10.** (E)- and (Z)-1-(3,5-Difluorophenyl)-2-(2-naphthyl)ethene (72%). *Title compound:* colourless solid, mp 111–113 °C (from light petroleum–dichloromethane) (Found: C, 80.9; H, 4.4.  $\text{C}_{18}\text{H}_{12}\text{F}_2$  requires C, 81.2; H, 4.5%);  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  222 (log  $\epsilon$  4.37), 248 (4.12), 270 (4.43), 278 (4.46) and 314 (4.57);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3100w, 1620m, 1590vs, 1110vs, 960vs, 850vs and 745vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  6.71–6.79 (1H, m), 7.09–7.31 (4H, m), 7.49–7.56 (2H, m) and 7.70–7.87 (5H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  102.2, 102.6, 103.0, 108.7, 108.9, 109.0, 109.1, 123.2, 126.2, 126.4, 126.6, 126.6, 126.7, 127.3, 127.6, 128.0, 128.4, 131.2, 133.2, 133.5, 133.7, 140.5, 140.7, 140.8 and 163.2 (dd,  $^{1,3}J_{\text{FC}}$  248.5 and 13.2);  $m/z$  266 ( $\text{M}^+$ , 100%) and 246 ( $\text{M}^+ - \text{HF}$ , 28).

**(E)-1-(5-Chloro-2-fluorophenyl)-2-(2-naphthyl)ethene 22.** (E)- and (Z)-1-(5-Chloro-2-fluorophenyl)-2-(2-naphthyl)ethene (93%). *Title compound:* colourless solid, mp 108–109 °C (from

light petroleum-dichloromethane) (Found: C, 76.8; H, 4.2.  $C_{18}H_{12}ClF$  requires C, 76.5; H, 4.25%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  222 (log  $\epsilon$  4.78), 275 (4.53) and 318 (4.53);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3050w, 1490m, 965s, 820vs and 740vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.02 (1H, d,  $J$  8.80), 7.07 (1H, d,  $J$  8.80), 7.18–7.53 (5H, m) and 7.63–7.88 (5H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  117.0 (d,  $^2J_{\text{FC}}$  24.3), 119.6 (d,  $J_{\text{FC}}$  3.5), 123.2, 126.2, 126.4, 126.5, 126.7 (d,  $J_{\text{FC}}$  13.8), 127.3, 127.6, 128.1, 128.2, 128.4, 129.4 (d,  $J_{\text{FC}}$  3.2), 132.0 (d,  $J_{\text{FC}}$  4.6), 133.2, 133.5, 134.0 and 158.7 (d,  $^1J_{\text{FC}}$  249.4);  $m/z$  282 ( $M^+$ , 100%) and 246 ( $M^+ - \text{HCl}$ , 80).

**(E)-1-(2-Chloro-5-methoxyphenyl)-2-(2-naphthyl)ethene 26.** (E)- and (Z)-1-(2-Chloro-5-methoxyphenyl)-2-(2-naphthyl)ethene (74%). *Title compound*: colourless solid, mp 103–104 °C (from light petroleum-dichloromethane) (Found: C, 77.7; H, 5.1.  $C_{19}H_{15}ClO$  requires C, 77.4; H, 5.1%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  227 (log  $\epsilon$  4.54), 271 (4.42) and 316 (4.48);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3040w, 1600vs, 950vs, 820vs and 790vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  3.88 (3H, s), 6.80 (1H, dd,  $J$  3.0 and 8.8), 7.24 (1H, d,  $J$  16.2), 7.28 (1H, s), 7.33 (1H, d,  $J$  3.0), 7.45–7.55 (2H, m), 7.62 (1H, d,  $J$  16.2) and 7.82–7.91 (5H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  55.5, 111.1, 114.6, 123.5, 124.9, 125.1, 126.0, 126.3, 127.1, 127.6, 128.0, 128.3, 130.4, 131.3, 133.1, 133.5, 134.4, 136.0 and 158.3;  $m/z$  294 ( $M^+$ , 50%), 259 (100), 244 (60) and 228 (31).

**(E)-1-(3,5-Dibromophenyl)-2-(2-naphthyl)ethene 25.** (E)- and (Z)-1-(3,5-Dibromophenyl)-2-(2-naphthyl)ethene (78%). *Title compound*: colourless solid, mp 154–155 °C (from light petroleum-dichloromethane);  $\lambda_{max}(\text{EtOH})/\text{nm}$  228 (log  $\epsilon$  4.2), 280 (4.3) and 319 (4.4);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3050w, 1575s, 1540vs, 1420s, 1130w, 955vs, 850vs, 815vs and 750vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.04 (1H, d,  $J$  16.3), 7.24 (1H, d,  $J$  16.3), 7.20–7.78 (6H, m) and 7.85 (4H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  123.1, 125.7, 126.3, 126.4, 127.4, 127.6, 127.9, 128.0, 128.4, 131.5, 132.5, 133.2, 133.4, 133.6 and 140.9 (one quaternary carbon is not resolved);  $m/z$  388 ( $M^+$ , 50%), 386 ( $M^+$ , 24), 308 ( $M^+ - \text{Br}$ , 20) and 228 ( $M^+ - \text{Br}$ , 100).

## Benzo[c]phenanthrenes

**General procedure: 4-Bromo-1-chlorobenzo[c]phenanthrene 32.** An *E-Z* mixture of 1-(2-bromo-5-chlorophenyl)-2-(2-naphthyl)ethene **21** (400 mg, 1.17 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.  $I_2$  (325 mg, 1.28 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* (319 mg, 80%) as a colourless solid, mp 155–156 °C (from light petroleum-dichloromethane) (Found: C, 63.2; H, 2.8.  $C_{18}H_{10}BrCl$  requires C, 63.3; H, 2.9%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  290 (log  $\epsilon$  4.3);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3045w, 1465m, 1400m, 1240m, 1170m, 1140m, 1110m, 1090m, 975m, 830vs and 810vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.43–7.62 (3H, m), 7.80–7.95 (3H, m), 8.00–8.05 (2H, m), 8.16 (1H, d,  $J$  9.6) and 8.28 (1H, d,  $J$  8.7);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  121.4, 124.7, 125.1, 125.6, 125.7, 126.1, 127.3, 128.5, 128.8, 128.8, 129.2, 130.0, 131.1, 131.7, 132.2, 132.3 and 133.7 (one quaternary carbon is not resolved; peak at 128.0 is more intense);  $m/z$  340/342/344 ( $M^+$  6, 20 and 16%), 260/261 ( $M^+ - \text{Br}$ , 14 and 27) and 226 ( $M^+ - \text{Br} - \text{Cl}$ , 100).

**1,4-Dichlorobenzo[c]phenanthrene 31.** Yield 83%; colourless solid, mp 161–162 °C (from light petroleum-dichloromethane) (Found: C, 73.0; H, 3.4.  $C_{18}H_{10}Cl_2$  requires C, 72.7; H, 3.4%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  222 (log  $\epsilon$  4.3) and 289 (4.6);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3050w, 1475m, 1400m, 1175m, 1150m, 1120m, 840vs and 815vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.60–7.75 (4H, m), 7.84 (1H, d,  $J$  8.5), 7.90 (1H, d,  $J$  8.8), 8.03 (2H, m), 8.18 (1H, d,  $J$  9.6) and 8.32 (1H, d,  $J$  8.8);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  122.8, 124.7, 125.2, 125.8, 126.1, 126.5, 127.3, 128.3, 128.5, 128.6, 128.9, 129.2,

130.8, 130.9, 131.2, 132.2 and 132.3 (one  $^{13}\text{C}$  resonance is not resolved);  $m/z$  296/298/300 ( $M^+$ , 30, 44, 20%), 262 ( $M^+ - \text{Cl}$ , 40) and 226 ( $M^+ - 2\text{Cl}$ , 100).

**1,3-Dichlorobenzo[c]phenanthrene 27.** Yield 73%; colourless solid, mp 132–133 °C (from light petroleum-dichloromethane) (Found: C, 73.0; H, 3.7.  $C_{18}H_{10}Cl_2$  requires C, 72.7; H, 3.4%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  222 (log  $\epsilon$  4.5) and 289 (4.7);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3050w, 1580m, 1350m, 1180m, 860vs, 830vs, 800vs and 760vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.59–7.65 (2H, m), 7.72–7.73 (2H, m), 7.83 (2H, d,  $J$  8.3), 7.91 (1H, d,  $J$  2.1), 8.02 (2H, d,  $J$  8.1) and 8.17 (1H, d,  $J$  9.6);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  124.6, 125.4, 125.7, 125.7, 125.8, 125.9, 126.2, 127.3, 128.3, 128.7, 128.8, 128.9, 131.1, 131.2, 132.2, 132.4, 132.9 and 135.5;  $m/z$  296/298 ( $M^+$ , 70 and 46%), 261 ( $M^+ - \text{Cl}$ , 20) and 226 ( $M^+ - 2\text{Cl}$ , 100).

**1-Chloro-4-fluorobenzo[c]phenanthrene 33.** Yield 81%; colourless solid, mp 152–153 °C (from light petroleum-dichloromethane) (Found: C, 76.8; H, 3.4.  $C_{18}H_{10}ClF$  requires C, 77.0; H, 3.6%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  218 (log  $\epsilon$  4.6) and 280 (4.7);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3060w, 1610m, 1490m, 1420s, 1235s, 840vs and 825vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.27–7.36 (1H, m), 7.61–7.65 (3H, m), 7.85–7.91 (2H, m), 8.00–8.06 (2H, m) and 8.14–8.22 (2H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  110.9 (d,  $^2J_{\text{FC}}$  22.1), 118.7 (d,  $^3J_{\text{FC}}$  7.4), 124.5, 124.7 (d,  $^2J_{\text{FC}}$  16.9), 125.4, 125.5 (d,  $J_{\text{FC}}$  2.5), 126.1, 127.0 (d,  $J_{\text{FC}}$  3.5), 127.1, 127.6 (d,  $^4J_{\text{FC}}$  2.0), 128.3 (d,  $J_{\text{FC}}$  4.0), 128.7 (d,  $^3J_{\text{FC}}$  8.7), 129.0, 131.2, 132.4 (d,  $^3J_{\text{FC}}$  10.7) and 157.6 (d,  $^1J_{\text{FC}}$  251.3) (two quaternary carbons are not resolved);  $m/z$  280/282 ( $M^+$ , 45 and 25%), 245 ( $M^+ - \text{Cl}$ , 100), 244 ( $M^+ - \text{HCl}$ , 95).

**1,4-Difluorobenzo[c]phenanthrene 35.** Yield 71%; colourless solid, mp 134–135 °C (from light petroleum-dichloromethane) (Found: C, 81.6; H, 3.5.  $C_{18}H_{10}F_2$  requires C, 81.8; H, 3.8%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  214 (log  $\epsilon$  4.6) and 276 (4.8);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3075w, 1640m, 1560m, 1530m, 1280m, 1130s, 1090s, 1000vs, 850vs and 750;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.30–7.36 (2H, m), 7.63–7.67 (2H, m), 7.83–7.92 (2H, m), 8.01–8.04 (2H, m), 8.16–8.20 (1H, m) and 8.27–8.37 (1H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  110.4 (dd,  $^2,^3J_{\text{FC}}$  25.2 and 9.4), 111.8 (dd,  $^2,^3J_{\text{FC}}$  25.2 and 9.1), 119.0 (dd,  $^3,^4J_{\text{FC}}$  6.3 and 2.1), 119.2 (m), 124.2 (m), 125.0 (d,  $^4J_{\text{FC}}$  3.0), 125.7, 126.2, 127.3, 128.0, 128.9, 129.4, 129.6, 129.7, 131.9, 132.9, 154.8 (dd,  $^1,^4J_{\text{FC}}$  248.5 and 2.6) and 155.1 (dd,  $^1,^4J_{\text{FC}}$  248.5 and 2.6);  $m/z$  264 ( $M^+$ , 100%) and 244 ( $M^+ - \text{HF}$ , 24).

**1,3-Difluorobenzo[c]phenanthrene 28.** Yield 76%; colourless solid, mp 129–130 °C (from light petroleum-dichloromethane) (Found: C, 81.4; H, 3.7.  $C_{18}H_{10}F_2$  requires C, 81.8; H, 3.8%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  214 (log  $\epsilon$  4.6) and 276 (4.7);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3055w, 1630m, 1560m, 1530m, 1275m, 1000s, 850vs, 825vs and 745vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.18–7.27 (1H, m), 7.48–7.52 (1H, m), 7.63–7.68 (2H, m), 7.80–7.87 (3H, m), 7.98–8.03 (2H, m) and 8.25–8.36 (1H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  102.7 (t,  $^2,^2J_{\text{FC}}$  27.7 and 27.8), 108.1 (dd,  $^2,^4J_{\text{FC}}$  19.5 and 3.6), 124.6, 124.9 (d,  $^4J_{\text{FC}}$  4.8), 125.7, 126.1, 126.3 (m, 4 peaks), 127.4, 128.2, 128.7, 129.2, 129.5, 129.5, 131.0, 132.9, 135.6 (m), 159.6 (dd,  $^1,^3J_{\text{FC}}$  257.0 and 12.3) and 160.0 (dd,  $^1,^3J_{\text{FC}}$  251.6 and 13.1);  $m/z$  264 ( $M^+$ , 100%) and 244 ( $M^+ - \text{HF}$ , 25).

**4-Chloro-1-methoxybenzo[c]phenanthrene 37.** Yield 78%; colourless solid, mp 140–141 °C (from light petroleum-dichloromethane) (Found: C, 78.2; H, 4.4.  $C_{19}H_{13}ClO$  requires C, 78.0; H, 4.4%);  $\lambda_{max}(\text{EtOH})/\text{nm}$  280 (log  $\epsilon$  4.6) and 308 (4.1);  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  2990w, 1600w, 1440w, 1400w, 1250s, 1100s, 840vs, 795vs and 675s;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  3.84 (3H, s), 7.04 (1H, d,  $J$  8.4), 7.53–7.60 (2H, m), 7.70 (1H, d,  $J$  8.4), 7.82–8.00 (4H, m), 8.09 (1H, d,  $J$  8.3) and 8.33 (1H, d,  $J$  8.8);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  54.6, 107.1, 121.4, 122.9, 123.6, 123.8, 125.5, 125.6, 125.7, 126.6, 127.1, 128.2, 128.2, 129.9, 130.7, 131.5, 131.7, 132.4 and 155.4;  $m/z$  292/294 ( $M^+$ , 80 and 25%) and 242 ( $M^+ - \text{Me} - \text{Cl}$ , 100).

**3-Bromo-1-iodobenzo[c]phenanthrene 36.** Yield 58%; colourless solid which was purified by repeated trituration with light petroleum (Found: C, 49.3; H, 2.1.  $C_{18}H_{10}BrI$  requires C, 49.8;

H, 2.3%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  290 (log  $\epsilon$  4.4);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3050w, 1600m, 1500m, 1360w, 1195vs, 1120s, 1100s, 930vs, 820vs and 790vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.40 (1H, t,  $J$  7.74 and 7.68), 7.69 (1H, d,  $J$  9.0), 7.80 (1H, d,  $J$  8.4), 7.85 (1H, d,  $J$  8.4), 7.94 (2H, s), 8.06 (1H, d,  $J$  8.0), 8.21 (1H, s) and 8.26–8.33 (2H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  95.2, 120.4, 126.7, 127.4, 127.4, 127.8, 128.5, 128.7, 128.9, 130.1, 132.3, 132.6, 134.0, 135.2, 135.8 and 141.6 (one  $^{13}\text{C}$  resonance is not resolved; the peak at 127.4 is more intense);  $m/z$  (CI) 432/434 ( $\text{M}^+$ , 12 and 12%), 306 ( $\text{M}^+ - \text{I}$ , 10) and 226 ( $\text{MH}^+ - \text{Br} - \text{I}$ , 100).

**4-Chloro-1-iodobenzo[c]phenanthrene 34.** Yield 51%; colourless solid which was purified by repeated trituration with light petroleum, mp 113–116 °C (Found: C, 57.7; H, 2.4.  $\text{C}_{18}\text{H}_{10}\text{ClI}$  requires C, 55.6; H, 2.6%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  222 (log  $\epsilon$  4.5) and 290 (4.6);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3050w, 1470w, 1400w, 1120s, 980s, 840vs, 820vs and 760s;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.59–7.68 (3H, m), 7.84–7.92 (3H, m), 7.99–8.15 (2H, m) and 8.21–8.30 (2H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  119.9, 122.5, 124.8, 125.1, 126.1, 126.7, 127.3, 128.2, 128.3, 129.1, 130.1, 131.5, 131.7, 132.2, 132.3 and 132.4 (two  $^{13}\text{C}$  quaternary resonances are not resolved; the peak at 132.2 is more intense);  $m/z$  (CI) 388/390 ( $\text{M}^+$ , 8 and 3%) 340/342/344 ( $\text{C}_{18}\text{H}_{10}\text{BrCl}$ , 21, 33 and 13), 260/262 ( $\text{M}^+ - \text{HI}$  or  $\text{C}_{18}\text{H}_{10}\text{BrCl} - \text{HBr}$ , 29 and 23), 261/263 ( $\text{M}^+ - \text{I}$  or  $\text{C}_{18}\text{H}_{10}\text{BrCl} - \text{Br}$ , 37 and 14) and 226 ( $\text{M}^+ - \text{I} - \text{Cl}$  or  $\text{C}_{18}\text{H}_{10}\text{BrCl} - \text{Br} - \text{Cl}$ , 100).

**1,2,3-Trifluorobenzo[c]phenanthrene 29.** Yield 75%; colourless solid, mp 154–156 °C (from light petroleum–dichloromethane) (Found: C, 77.0; H, 2.9.  $\text{C}_{18}\text{H}_9\text{F}_3$  requires C, 76.6; H, 3.2%);  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.50–7.69 (3H, m), 7.70–7.84 (3H, m), 7.93–8.00 (2H, m) and 8.20–8.31 (1H, m);  $m/z$  282 ( $\text{M}^+$ , 100%) and 262 ( $\text{M}^+ - \text{HF}$ , 60).

**2,3,4-Trifluorobenzo[c]phenanthrene 30.** Yield 71%; colourless solid, mp 135–136 °C (from light petroleum–dichloromethane) (Found: C, 76.7; H, 2.9.  $\text{C}_{18}\text{H}_9\text{F}_3$  requires C, 76.6; H, 3.2%);  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.60–7.95 (5H, m), 7.98–8.08 (2H, m), 8.59–8.68 (1H, m) and 8.87 (1H, d,  $J$  7.7);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  118.1–118.3 (m, 7 peaks), 120.8 (d,  $J_{\text{FC}}$  12.9) 126.3, 126.5, 126.7, 127.6 (t), 128.4, 128.7, 129.6, 131.2 and 133.5 (three quaternary C–F carbons were not detected and two quaternarys were not resolved; two CH carbons are not resolved; peak at 126.7 is more intense);  $m/z$  282 ( $\text{M}^+$ , 100%), 181 ( $\text{M}^+ - \text{H}$ , 32), 280 ( $\text{M}^+ - 2\text{H}$ , 30) and 262 ( $\text{M}^+ - \text{HF}$ , 26).

**1-Chlorobenzo[c]phenanthrene 38.** Method 1.—4-Bromo-1-chlorobenzo[c]phenanthrene **32** (400 mg, 1.17 mmol) in THF (20 ml) was cooled to  $-78$  °C in a dry ice–acetone bath under nitrogen and treated with  $\text{Bu}^t\text{Li}$  (0.64 ml, 1.18 mmol, 2.0 M in hexanes). The mixture was stirred at  $-78$  °C for 3 min and then acidified at low temperature with HOAc (1.0 ml). The mixture was then allowed to warm to room temp., diluted with  $\text{H}_2\text{O}$ , extracted with  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$  and purified by flash chromatography on silica. Light petroleum eluted the title compound (260 mg, 85%) as a colourless solid, mp 147–148 °C (from light petroleum–dichloromethane) (Found: C, 82.0; H, 4.1.  $\text{C}_{18}\text{H}_{11}\text{Cl}$  requires C, 82.3; H, 4.2%);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  222 (log  $\epsilon$  4.2) and 289 (4.5);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3020w, 1610w, 1500w, 1355m, 820s and 760s;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.61–7.65 (3H, m), 7.75 (1H, d,  $J$  7.5), 7.84–7.88 (3H, m), 7.90–8.15 (3H, m) and 8.25 (1H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  124.4, 125.4, 125.7, 125.8, 126.2, 126.7, 126.7, 127.0, 127.1, 127.2, 128.5, 128.9, 129.0, 131.2, 132.1, 132.2 and 135.3 (one  $^{13}\text{C}$  quaternary resonance is not resolved);  $m/z$  262/264 ( $\text{M}^+$ , 60 and 24%), 227 ( $\text{M}^+ - \text{Cl}$ , 95) and 226 ( $\text{M}^+ - \text{HCl}$ , 100).

Method 2.—1,3-Dichlorobenzo[c]phenanthrene **27** (15 mg, 0.005 mmol) was cooled using an ice bath and treated with 10% Pd/C (15 mg) followed by an excess of  $\text{Et}_3\text{N}$  (0.1 ml) and formic acid (0.02 ml). The mixture was heated under argon at 95 °C for about 1 h and monitored by TLC. TLC analysis showed the presence of some unreacted starting material and benzo[c]phenanthrene. After cooling the reaction was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered, washed with water, dried over  $\text{MgSO}_4$  and the residue

purified by chromatography on silica. Light petroleum eluted the title compound (8.3 mg, 63%) identical to the previous sample. The reaction is temperamental, suffers from catalyst poisoning and over reduction to benzo[c]phenanthrene occurs easily. Repeating the reaction with heating for 3 h followed by an identical work up procedure gave benzo[c]phenanthrene **2** (9 mg, 73%).

#### Pyrolysis reactions

**Benzo[ghi]fluoranthene 3.** 1-Chlorobenzo[c]phenanthrene **38** (100 mg, 0.38 mmol) was sublimed under vacuum through an unpacked 30 cm quartz tube heated to 1030 °C. The pyrolysis products condensed outside of the furnace before the liquid nitrogen cold trap. The residue was purified by chromatography on silica. Elution with light petroleum gave the title compound (53 mg, 53%) which had identical spectroscopic properties to the literature material,<sup>13</sup>  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.71 (2H, dd,  $J$  8.0 and 7.0), 7.94–8.10 (6H, m) and 8.15 (2H, d,  $J$  7.0);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  123.3, 124.9, 126.3, 126.5, 126.6, 127.5, 128.2, 132.9, 133.1 and 137.2.

**Cyclopenta[cd]pyrene 41.** Benzo[ghi]fluoranthene **3** (35 mg, 0.15 mmol) was sublimed under vacuum through an unpacked 30 cm quartz tube heated to 1175 °C. The residue was purified by chromatography on silica. Elution with light petroleum gave the title compound (4 mg, 12%) which had identical spectroscopic properties to the literature material<sup>14</sup> followed by starting material (13 mg, 35%).

**3-Chlorobenzo[ghi]fluoranthene 39.** Method 1.—1,4-Dichlorobenzo[c]phenanthrene **31** (50 mg, 0.17 mmol) was sublimed under vacuum through an unpacked 30 cm quartz tube heated to 1030 °C. The residue was purified by chromatography on silica. Elution with light petroleum gave the title compound (17.0 mg, 38%) as a pale yellow solid, mp 139–140 °C (from light petroleum–dichloromethane) (Found:  $\text{M}^+$ , 260.0393.  $\text{C}_{18}\text{H}_9\text{Cl}$  requires  $M$ , 260.0393);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  288 (log  $\epsilon$  4.3) 334 (4.0) and 352 (4.0);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2950w, 1460m, 1420m, 1195m, 1145m, 1000s and 810vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.67 (1H, d,  $J$  8.0), 7.72 (1H, d,  $J$  8.0), 7.93–8.10 (5H, m) and 8.12–8.15 (2H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  123.4, 123.8, 124.8, 125.7, 125.8, 126.4, 126.8, 127.1, 127.6, 128.4, 131.5, 132.4, 133.2, 134.3, 134.7, 135.9 and 136.4 (one  $^{13}\text{C}$  resonance is not resolved; the peak at 123.4 is more intense);  $m/z$  260/262 ( $\text{M}^+$ , 100 and 34%), 224 ( $\text{M}^+ - \text{HCl}$ , 38).

Method 2.—4-Chloro-1-iodobenzo[c]phenanthrene **34** (30 mg, 0.08 mmol) was sublimed under vacuum through an unpacked 30 cm quartz tube heated to 950 °C. The pyrolysis products condensed outside of the furnace before the liquid nitrogen cold trap. A dark band of iodine also formed in the cold trap. The residue was purified by chromatography on silica. Elution with light petroleum gave the title compound (15 mg, 75%) which had identical spectroscopic properties to the previously prepared material.

**3-Fluorobenzo[ghi]fluoranthene 40.** Method 1.—1-Chloro-4-fluorobenzo[c]phenanthrene **33** (50 mg, 0.18 mmol) was sublimed under vacuum through an unpacked 30 cm quartz tube heated to 1030 °C. The residue was purified by chromatography on silica. Elution with light petroleum gave the title compound (23.0 mg, 46%) as a pale yellow solid, mp 165–167 °C (from light petroleum–dichloromethane) (Found:  $\text{M}^+$ , 244.0688.  $\text{C}_{18}\text{H}_9\text{F}$  requires  $M$ , 244.0688);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  227 (log  $\epsilon$  4.8) 244 (4.6), 286 (4.3), 330 (3.9) and 348 (3.9);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3050w, 1460s, 1230s, 810vs and 750vs;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  7.20–7.25 (1H, m), 7.60–7.65 (1H, m) and 7.82–8.10 (7H, m);  $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CDCl}_3)$  112.4 (d,  $^2J_{\text{FC}}$  22.7), 117.1 (d,  $^2J_{\text{FC}}$  18.8), 120.6, 122.9, 124.3 (d,  $^3J_{\text{FC}}$  8.0), 124.7, 125.1 (d,  $J_{\text{FC}}$  1.5), 125.8, 126.8, 127.1, 127.7, 128.4, 131.9, 133.0 (d,  $J_{\text{FC}}$  4.2), 133.4 (d,  $J_{\text{FC}}$  1.4), 135.1 (d,  $J_{\text{FC}}$  8.1), 136.5 and 159.3 (d,  $J_{\text{FC}}$  260.6);  $m/z$  244 ( $\text{M}^+$ , 100%).

Method 2.—1,4-Difluorobenzo[c]phenanthrene **35** (50 mg, 0.20 mmol) was sublimed under vacuum through an unpacked

30 cm quartz tube heated to 1150 °C. The residue was purified by chromatography on silica. Elution with light petroleum gave the *title compound* (11 mg, 23%) with spectroscopic properties identical to the previously reported sample and recovered starting material (16 mg, 32%).

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