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Supporting Information

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Efficient Phenanthrene, Helicene and Azahelicene Syntheses.

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X-RAY ANALYSIS OF [5]HELICENES 18B, 18C AND 20.

There are 8 distinct species within the unit cell of 2,3,7,8,12,13-hexamethoxy[5]helicene **18b** (Figure 2), with the (*M*)- and (*P*)-enantiomers each having four conformational forms (distinguished by colour in Figures 2 and 3). The orientation of the methoxy substituents at C7 and C8 provides a means of differentiating between the conformational isomers. In two of the conformations (red and blue), the O–CH_3 bonds are oriented in the same sense (*cisoid*) relative to the plane of the central arene. The torsion angles C7–C8–O–CH_3 are 84.5° (red) and 79.9° (blue) and for C8–C7–O–CH_3 are 104.7° (red) and 107.5° (blue) respectively. In the other conformers (yellow and green), the O–CH_3 bonds are oriented in an opposed sense (*transoid*) relative to the plane of the central arene. The torsion angles C7–C8–O–CH_3 are 82.4° (green) and 82.1° (yellow) respectively while for C8–C7–O–CH_3 they are 40.3° (green) and 42.4° (yellow) respectively (Figure 2).

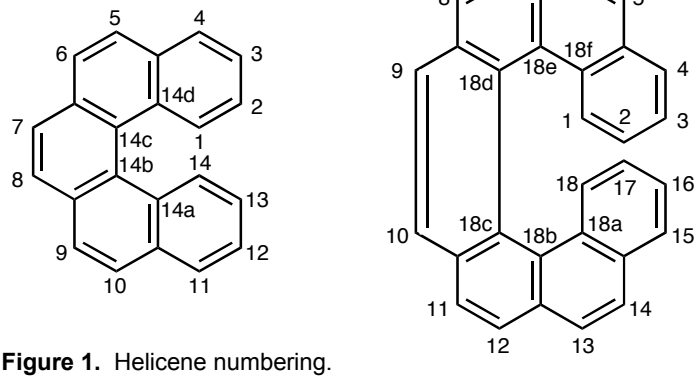


Figure 1. Helicene numbering.

In each conformer the torsion angle C14a–C14b–C14c–C14d was in the range 32.0° to 35.5° and substantially greater than the torsion angles for C1–C14d–C14c–C14b/C14–C14a–C14b–C14c which ranged from 9.8° to 20.4°. Thus, in stark contrast to **18c** and **20**, it is the central arene that accommodates most of the torsional strain in this case. The helicenes form stacks of symmetrically equivalent molecules within the extended crystal structure, as shown in Figure 3.

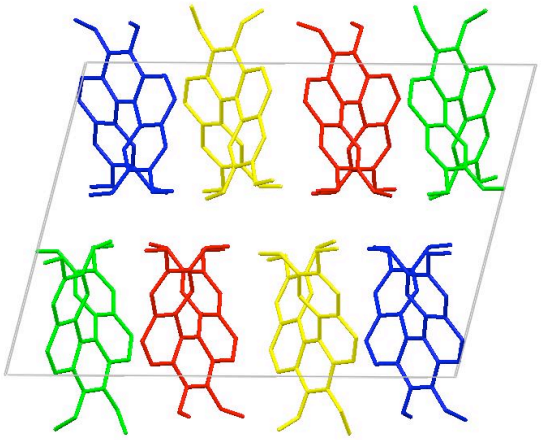


Figure 2. Unit cell for **18b**.

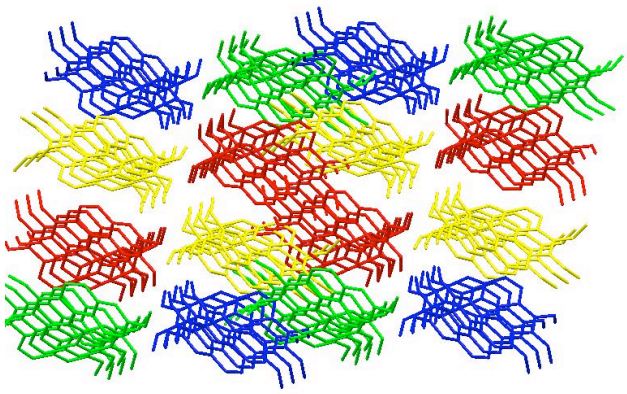


Figure 3. Stacking of symmetrically equivalent conformers in crystals of **18b**.

Only the (*P*)-enantiomer was observed in a crystal of 1,7,8,14-tetramethoxy[5]helicene following recrystallization of *rac*-**18c** from ethyl acetate/hexane. All four molecules within the unit cell were equivalent (Figure 4) and the torsion angle for C14a–

C14b–C14c–C14d (25.5°) was found to be similar to that of C14–C14a–C14b–C14c (23.5°) and C1–C14d–C14c–C14b (22.6°). This suggests that the burden of strain is shared more evenly between the aromatic rings in this case. The methoxy substituents at C7 and C8 were opposed (*transoid*) relative to the plane of the central arene and again, the helicene formed stacks within the extended crystal structure (Figure 5).

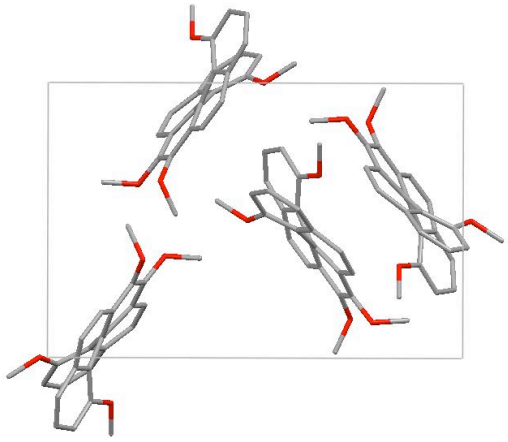


Figure 4. Unit cell for (*P*)-**18c**.

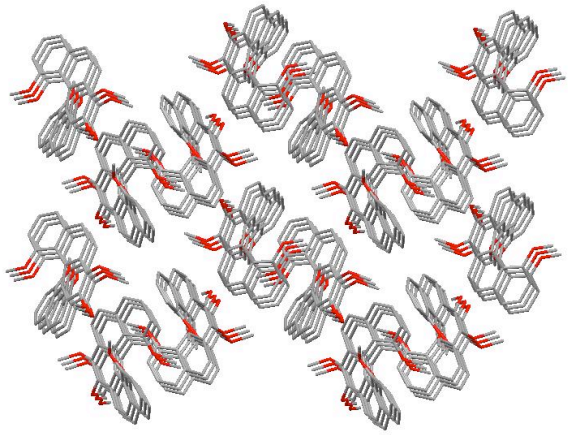


Figure 5. Stacking in crystals of (*P*)-**18c**.

Recrystallization of 9,10-dimethoxy[7]helicene **20** from ethyl acetate produced a racemic crystal form, with the unit cell comprised of four molecules of each of the (*M*)- and (*P*)-enantiomers (coloured in red and blue respectively, Figure 6). As with the preceding example, torsion angles show that strain is accommodated in each of the arenes [torsion angles of 20.6° for C18–C18a–C18b–C18c, 25.0° for C18a–C18b–C18c–C18d, 23.7° for C18b–C18c–C18d–C18e, 24.8° for C18c–C18d–C18e–C18f and 17.2° for C1–C18f–C18e–C18d, having been measured.] Again, the methoxy substituents on the central arene (C9 and C10) are opposed (*transoid*) relative to the central arene and the helicene form stacks within the extended crystal structure (Figure 7).

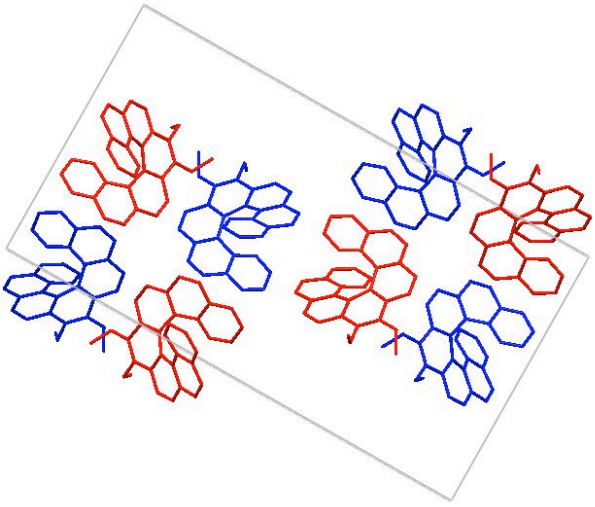


Figure 6. Unit cell for **20**.

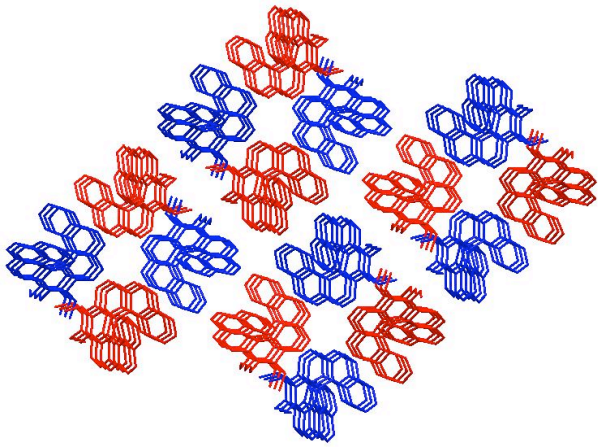
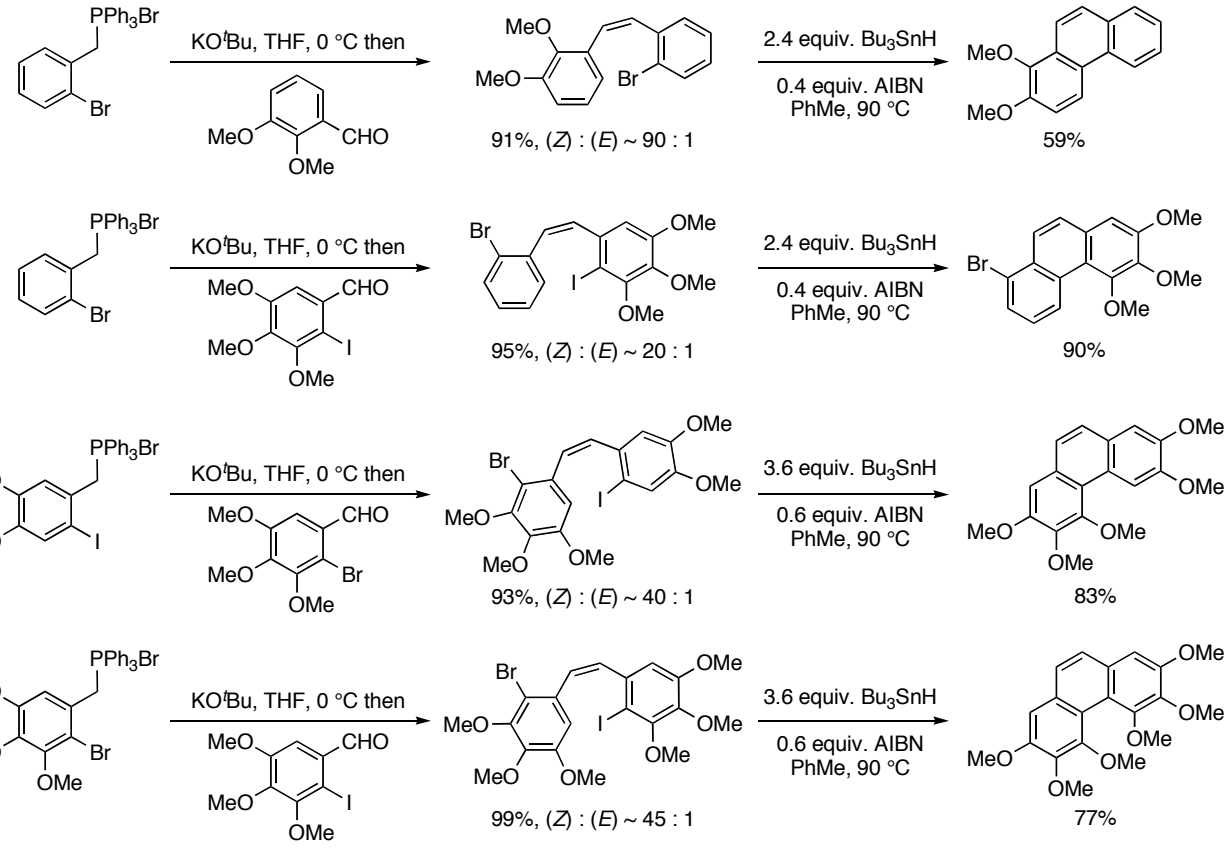


Figure 7. Stacking in crystals of **20**.

FURTHER EXAMPLES OF REGIOCONTROLLED PHENANTHRENE SYNTHESES.

Four additional examples of regiocontrolled phenanthrene syntheses are outlined below. It can be seen that with 2-bromo-2'-iodostilbenes, substitution at C3 promotes reduction of the carbon-to-bromine bond (though it is still outpaced by carbon-to-iodine bond homolysis).[1] In such cases, product mixtures containing both brominated and debrominated phenanthrenes were obtained when using 2.4 equiv. tributyltin hydride and 0.4 equiv. AIBN while complete reduction was achieved using 3.6 equiv. tributyltin hydride and 0.6 equiv. AIBN. When C3 is unsubstituted, the corresponding 1-bromophenanthrene is given in high yield when employing 2.4 equiv. tributyltin hydride and 0.4 equiv. AIBN.



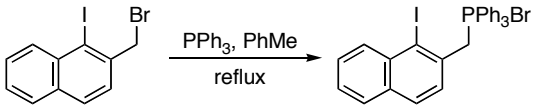
DETERMINATION OF (*Z*) : (*E*) RATIOS.

(*Z*) : (*E*) ratios for each of the Wittig reactions were determined by comparing integrals for related resonances in ^{1}H NMR spectra recorded on crude product mixtures prior to purification by column chromatography, in accord with the procedure adopted by Gilheany *et al.*[2] The alkene resonances for the (*Z*)-stilbenes appear in the region δ_H 6.5 – 7.1 ppm with J = 11.9 ± 0.3 Hz, while those for the (*E*)-stilbenes appear in the region δ_H 7.2 – 7.8 ppm with J ~ 16.5 Hz. Where these signals were obscured, comparison was made between other well-separated resonances attributed to the two isomers.

EXPERIMENTAL PROCEDURES AND COMPOUND CHARACTERIZATION.

The data quoted in the following accounts was recorded on samples purified by column chromatography and/or recrystallization as stated and is limited to the major product/diastereoisomer. Where ^{1}H and ^{13}C NMR spectra were recorded on diastereoisomeric mixtures, we have assumed that the more intense resonances correspond to the major isomer and that less intense resonances were due to the minor isomer, as indicated. 2-Bromomethyl-1-iodonaphthalene **1**,[3] (2-chlorobenzyl)triphenylphoshonium bromide (**5**),[4] (2-bromobenzyl)triphenylphoshonium bromide (**6**),[5] 2-bromo-4,5-dimethoxybenzaldehyde (**12a**),[6] (2-iodobenzyl)triphenylphosphonium bromide (**15a**),[7] 2-iodo-4,5-dimethoxybenzyl bromide[8] and 1-bromomethyl-2-iodo-3,5-dimethoxybenzene[9] were each prepared according to the referenced procedure.

(1-Iodonaphthalen-2-ylmethyl)triphenylphosphonium bromide (2)



1 **2**, 94%

2-Bromomethyl-1-iodonaphthalene **1** (1.0 g, 2.88 mmol) and triphenylphosphine (786 mg, 3.0 mmol) were heated at 90 °C in toluene (30 mL) for 16 h. After cooling to RT, the solid was collected by filtration and washed with petrol (2 x 20 mL) to afford phosphonium salt **2** (1.65 g, 2.70 mmol, 94%) as a white solid.

MP >250 °C (EtOH).

IR ν_{max} (neat, cm^{-1}) 3001 w, 2924 w, 2800 w, 2738 w, 1584 w, 1481 m, 1433 s, 1394 m, 1192 w, 1098 s, 994 m.

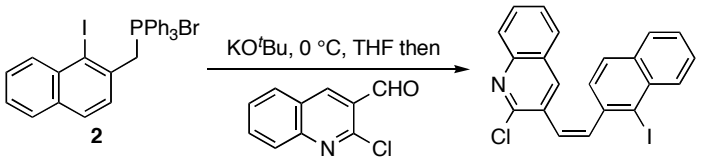
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.89 (1H, m), 7.78 – 7.68 (4H, m), 7.67 – 7.46 (16H, m), 5.88 (2H, d, *J* 14.3 Hz).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 135.3 (d, *J* 3.3 Hz, 3 x CH), 135.0 (d, *J* 3.3 Hz, C), 134.6 (d, *J* 10.0 Hz, 6 x CH), 133.4 (d, *J* 2.2 Hz, C), 133.1 (CH), 130.5 (C), 130.3 (d, *J* 12.2 Hz, 6 x CH), 129.8 (d, *J* 3.3 Hz, CH), 128.6 (2 x CH), 128.2 (d, *J* 3.3 Hz, CH), 127.5 (CH), 117.4 (d, *J* 85.1 Hz, 3 x C), 111.8 (d, *J* 10.0 Hz, CI), 38.2 (d, *J* 47.5 Hz, CH_2).

Mass $^m/_z$ (ES+) 529 ($[M\text{-}Br]^+$, 100).

CHN Found C 57.10, H 3.78. $C_{29}H_{23}BrIP$ requires C 57.17, H 3.80.

(*Z*)-3-(1-Iodonaphth-2-yl)-ethen-2-yl)-2-chloroquinoline (3)



2 **3**, 97%, (*Z*) : (*E*) ~ 16 : 1

To a cooled (0 °C) suspension of phosphonium salt **2** (731 mg, 1.2 mmol) in THF (10 mL) was added potassium *tert*-butoxide (157 mg, 1.4 mmol). After 30 min, 2-chloroquinoline 3-carboxaldehyde (192 mg, 1.0 mmol) in THF (10 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (30 mL) was added. The aqueous phase was separated and extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 10 - 20% ether / petrol) to yield firstly (*Z*)-**3** (414 mg, 0.94 mmol, 94%) as a yellow solid followed by fractions containing both (*Z*)-**3** and (*E*)-**3** (13 mg, 0.03 mmol, 3%). Data for (*Z*)-**3**:

MP 140-143 °C (hexanes).

IR ν_{max} (neat, cm^{-1}) 3053 w, 2994 w, 1580 w, 1543 w, 1483 m, 1363 w, 1328 m, 1319 m, 1129 m, 1034 s, 958 s.

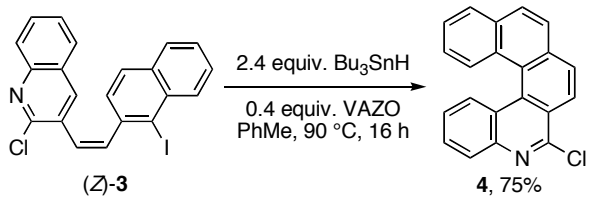
^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.30 (1H, dd, *J* 8.5, 1.0 Hz), 7.98 (1H, dd, *J* 8.5, 1.0 Hz), 7.69 – 7.63 (3H, m), 7.60 (1H, ddd, *J* 8.5, 7.0, 1.5 Hz), 7.50 (1H, ddd, *J* 8.0, 6.8, 1.3 Hz), 7.49 (1H, d, *J* 9.0 Hz), 7.38 – 7.35 (2H, m), 7.10 (1H, d, *J* 11.8 Hz), 7.06 (1H, d, *J* 8.3 Hz), 6.98 (1H, dd, *J* 11.8, 1.0 Hz).

^{13}C NMR δ_C (100 MHz, $CDCl_3$) 150.6 (C), 147.0 (C), 139.8 (C), 138.9 (CH), 138.8 (CH), 135.2 (C), 133.2 (C), 132.4 (CH), 130.6 (CH), 129.2 (C), 128.9 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.6 (CH), 127.1 (CH), 127.1 (CH), 127.0 (C), 126.5 (CH), 105.5 (C).

Mass $^m/_z$ (ES^+) 444 ($[M(^{37}Cl)H]^+$, 10), 442 ($[M(^{35}Cl)H]^+$, 35).

CHN Found C 57.52, H 2.94, N 3.03. $C_{21}H_{13}ClIN$ requires C 57.10, H 2.97, N 3.17.

6-Chloro-5-aza[5]helicene (4)



(*Z*)-**3** **4**, 75%

A solution of azastilbene (*Z*)-**3** (221 mg, 0.5 mmol), tributyltin hydride (0.16 mL, 0.60 mmol) and VAZO (24 mg, 0.10 mmol) in toluene (25 mL) was heated at 90 °C for 16 h then cooled to RT. Additional tributyltin hydride (0.16 mL, 0.60 mmol) and VAZO (24 mg, 0.10 mmol) were added and the reaction heated for a further 16 h at 90 °C. After cooling to RT and concentration *in vacuo*, the crude product mixture was purified by recrystallization from toluene to afford the title compound **4** (118 mg, 0.37 mmol, 75%) as a yellow solid.

MP 238-241 °C (toluene).

IR ν_{max} (neat, cm^{-1}) 3051 w, 2953 w, 2920 w, 1568 m, 1485 m, 1444 w, 1328 m, 1265 m, 1125 m, 1085 w, 1034 m.

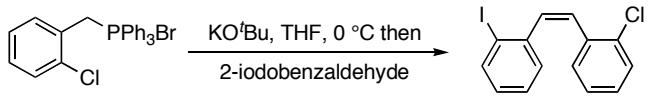
^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.48 (1H, d, *J* 8.5 Hz), 8.41 (1H, d, *J* 8.3 Hz), 8.41 (1H, d, *J* 8.3 Hz), 8.14 (1H, dd, *J* 8.3, 1.0 Hz), 8.02 (1H, d, *J* 8.5 Hz), 7.98 (1H, d, *J* 8.4 Hz), 7.97 (1H, d, *J* 8.2 Hz), 7.86 (1H, d, *J* 8.5 Hz), 7.66 (1H, ddd, *J* 8.3, 7.0, 1.5 Hz), 7.58 (1H, ddd, *J* 8.0, 7.0, 1.0 Hz), 7.33 (1H, ddd, *J* 8.5, 7.0, 1.5 Hz), 7.30 (1H, ddd, *J* 8.5, 7.0, 1.5 Hz).

^{13}C NMR δ_C (100 MHz, $CDCl_3$) 151.4 (C), 144.2 (C), 135.0 (C), 133.2 (C), 133.1 (C), 130.6 (C), 130.4 (CH), 129.5 (CH), 129.2 (CH), 128.8 (CH), 128.7 (CH), 128.2 (CH), 128.1 (CH), 127.4 (CH), 126.1 (CH), 125.8 (C), 125.3 (2 x CH), 125.0 (C), 124.8 (C), 124.6 (CH).

Mass $^m/_z$ (ES+) 316 ([M(^{35}Cl)+H]$^+$, 33), 314 ([M(^{37}Cl)+H]$^+$, 100).

CHN Found C 79.90, H 3.95, N 4.20. $C_{21}H_{12}ClN$ requires C 80.38, H 3.85, N 4.46.

1-((*Z*)-2-(2-Chlorophenyl)-1-ethenyl)-2-iodobenzene (7)



5 **7**, 92%, (*Z*) : (*E*) ~ 9 : 1

To a cooled (0 °C) suspension of phosphonium salt **5** (1.77 g, 3.6 mmol) in THF (25 mL) was added potassium *tert*-butoxide (470 mg, 4.2 mmol). After 30 min, 2-iodobenzaldehyde (696 mg, 3.00 mmol) in THF (25 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and re-extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 5% ether / petrol) to yield an inseparable 9 : 1 mixture of (*Z*)- and (*E*)-**7** (938 mg, 2.75 mmol, 92%) as a pale yellow oil.

IR ν_{max} (neat, cm^{-1}) 3058 w, 3021 w, 1582 w, 1556 w, 1474 m, 1458 m, 1432 s, 1050 s, 1035 s, 1012 s, 947 m.

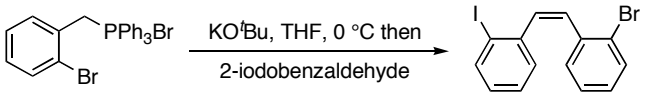
^{1}H NMR (*Z*)-isomer δ_H (300 MHz, $CDCl_3$) 7.87 (1H, dd, *J* 8.0, 1.3 Hz), 7.38 (1H, d, *J* 7.8 Hz), 7.16-7.05 (2H, m), 7.00 (1H, dd, *J* 7.5, 1.3 Hz), 6.98-6.93 (2H, m), 6.89 (1H, td, *J* 7.5, 1.8 Hz), 6.83 (1H, d, *J* 11.9 Hz), 6.69 (1H, d, *J* 11.9 Hz).

^{13}C NMR (*Z*)-isomer δ_C (75 MHz, $CDCl_3$) 141.0 (C), 139.2 (CH), 135.6 (CH), 135.1 (C), 134.0 (C), 131.0 (CH), 130.5 (CH), 129.6 (CH), 129.0 (CH), 128.7 (CH), 128.4 (CH), 128.0 (CH), 126.4 (CH), 99.9 (CI). Residual signals attributed to (*E*)-**7**: 139.8 (CH), 130.0 (CH), 129.1 (CH), 127.8 (CH), 127.2 (CH), 127.1 (CH), 126.9 (CH), 126.7 (CH).

Mass $^m/_z$ (EI) 342 ([M(^{37}Cl)]$^+$, 35), 340 ([M(^{35}Cl)]$^+$, 98), 214 ([M(^{37}Cl)-HI]$^+$, 26), 212 ([M(^{35}Cl)-HI]$^+$, 49), 176 (100).

Accurate $^m/_z$ (EI) Found M$^+$ 339.9516. $C_{14}H_{10}{}^{35}ClI$ requires 339.9516.

1-((*Z*)-2-(2-Bromophenyl)-1-ethenyl)-2-iodobenzene (8)



6 **8**, 91%, (*Z*) : (*E*) ~ 9 : 1

To a cooled (0 °C) suspension of phosphonium salt **6** (1.84 g, 3.6 mmol) in THF (25 mL) was added potassium *tert*-butoxide (470 mg, 4.2 mmol). After 30 min, 2-iodobenzaldehyde (696 mg, 3.00 mmol) in THF (25 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and re-extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 5% ether / petrol) to yield an inseparable 9 : 1 mixture of (*Z*)- and (*E*)-**8** (1.05 g, 2.73 mmol, 91%) as a pale yellow oil.

IR ν_{max} (neat, cm^{-1}) 3053 w, 3017 w, 1582 w, 1557 w, 1470 m, 1457 m, 1430 s, 1043 m, 1025 s, 1012 s.

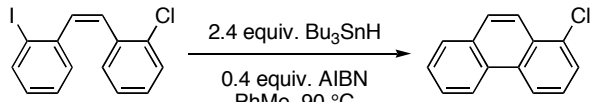
^{1}H NMR (*Z*)-isomer δ_H (300 MHz, $CDCl_3$) 7.87 (1H, dd, *J* 7.9, 1.1 Hz), 7.57 (1H, dd, *J* 7.3, 1.8 Hz), 7.11 – 6.93 (5H, m), 6.89 (1H, td, *J* 7.7, 1.9 Hz), 6.76 (1H, d, *J* 11.8 Hz), 6.68 (1H, d, *J* 11.8 Hz).

^{13}C NMR (*Z*)-isomer δ_C (75 MHz, $CDCl_3$) 140.9 (C), 139.2 (CH), 137.0 (C), 135.4 (CH), 132.8 (CH), 131.1 (CH), 130.8 (CH), 130.6 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 127.1 (CH), 124.3 (C), 100.0 (C). Residual signals attributed to (*E*)-**8**: 133.3 (CH), 132.5 (CH), 131.0 (CH), 129.6 (CH), 129.4 (CH), 128.7 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH).

Mass $^m/_z$ (EI) 386 ([M(^{81}Br)]$^+$, 73), 384 ([M(^{79}Br)]$^+$, 62), 258 ([M(^{81}Br)-HI]$^+$, 30), 256 ([M(^{79}Br)-HI]$^+$, 26), 176 (100).

Accurate $^m/_z$ (EI) Found M^+ 383.9010. $C_{14}H_{10}{}^{79}BrI$ requires 383.9011.

1-Chlorophenanthrene (9)[10]



9 : 1 (*Z*)-**7** and (*E*)-**7** **9**, 90%
*100% based on (Z)-**7***

A solution of stilbene **7** (9 : 1 mixture of (*Z*)- and (*E*)-isomers, 340 mg, 1.0 mmol), tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) in toluene (25 mL) was heated at 90 °C for 16 h then cooled to RT. Additional tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) were added and the reaction heated for a further 8 h at 90 °C. After cooling to RT and concentration *in vacuo*, the product mixture was purified by column chromatography (10% KF/SiO_2, 4% ether / petrol) to afford the title compound **9** (191 mg, 0.90 mmol, 90%) as a white solid.

MP 121-124 °C (EtOH), lit.[10] 118-119 °C (EtOH).

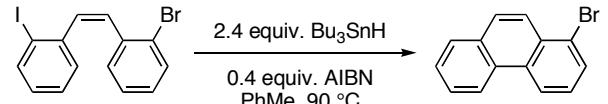
IR ν_{max} (neat, cm^{-1}) 3054 w, 3031 w, 1592 m, 1439 m, 1296 m, 1205 m, 1106 m, 1044 m, 1020 m

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.66 (1H, d, *J* 7.9 Hz), 8.63 (1H, d, *J* 8.4 Hz), 8.25 (1H, dd, *J* 9.2, 0.6 Hz), 7.92 (1H, dd, *J* 7.9, 2.0 Hz), 7.85 (1H, d, *J* 9.2 Hz), 7.72 – 7.62 (3H, m), 7.55 (1H, dd, 8.3, 7.6 Hz).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 132.9 (C), 132.1 (2 x C), 130.1 (C), 129.5 (C), 128.8 (CH), 128.4 (CH), 127.3 (CH), 127.2 (2 x CH), 126.6 (CH), 123.1 (CH), 122.6 (CH), 121.8 (CH).

Mass $^m/_z$ (EI) 214 ([M(^{37}Cl)]$^+$, 38), 212 ([M(^{35}Cl)]$^+$, 88), 176 ([M-HCl]$^+$, 100).

1-Bromophenanthrene (10)[11]



9 : 1 (*Z*)-**8** and (*E*)-**8**

10, 86%
*95% based on (Z)-**8***

A solution of stilbene **8** (9 : 1 mixture of (*Z*)- and (*E*)-isomers, 385 mg, 1.0 mmol), tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) in toluene (25 mL) was heated at 90 °C for 16 h then cooled to RT. Additional tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) were added and the reaction heated for a further 8 h at 90 °C. After cooling to RT and concentration *in vacuo*, the product mixture was purified by column chromatography (10% KF/SiO_2, 4% ether / petrol) to afford the title compound **10** (221 mg, 0.86 mmol, 86%) as a white solid. Recorded data was in accord with literature values:

MP 110-112 °C (EtOH), lit.[11] 109-110 °C.

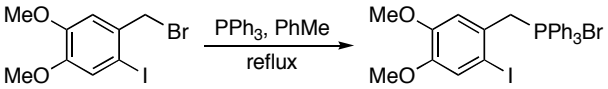
IR ν_{max} (neat, cm^{-1}) 3053 w, 1592 w, 1450 m, 1438 m, 1295 m, 1204 m, 1040 m, 1012 w, 863 m.

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.68 (2H, d, *J* 8.2 Hz), 8.23 (1H, d, *J* 9.2 Hz), 7.95 – 7.89 (2H, m), 7.86 (1H, d, *J* 9.2 Hz), 7.73 – 7.62 (2H, m), 7.50 (1H, dd, *J* 8.2, 7.9).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 132.2 (C), 132.1 (C), 130.9 (CH), 130.8 (C), 130.1 (C), 128.9 (CH), 128.7 (CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 125.5 (CH), 123.9 (C), 123.1 (CH), 122.5 (CH).

Mass $^m/_z$ (EI) 258 ([M(^{81}Br)]$^+$, 99), 256 ([M(^{79}Br)]$^+$, 87), 176 ([M-HBr]$^+$, 100).

(2-Iodo-4,5-dimethoxybenzyl)triphenylphosphonium bromide (11)



11, 93%

2-Iodo-4,5-dimethoxybenzyl bromide (8.5 g, 23.8 mmol) and triphenylphosphine (6.38 g, 24.3 mmol) were heated at reflux in toluene (80 mL) for 16 h. After cooling to RT, the resulting precipitated was collected by filtration and washed with petrol (2 x 40 mL) to afford **11** as a white solid (13.70 g, 22.13 mmol, 93%).

MP >250 °C (EtOH).

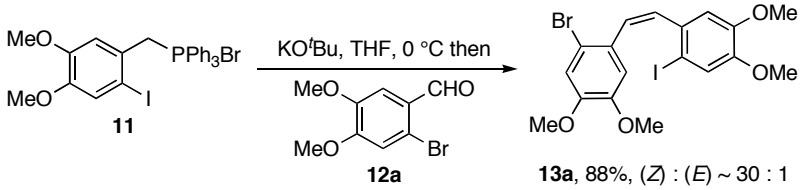
IR ν_{max} (neat, cm^{-1}) 3008 w, 2838 w, 2775 w, 1503 s, 1438 s, 1376 m, 1258 s, 1211 s, 1164 m, 1112 s, 1018 s.

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.79 – 7.72 (3H, m), 7.64 – 7.57 (12H, m), 7.02 (1H, d, *J* 2.2 Hz), 6.97 (1H, s), 5.33 (2H, d, *J* 13.4 Hz), 3.74 (3H, s), 3.45 (3H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 149.5 (2 x C), 135.2 (d, *J* 3.0 Hz, 3 x CH), 134.5 (d, *J* 8.9 Hz, 6 x CH), 130.2 (d, *J* 12.9 Hz, 6 x CH), 122.4 (d, *J* 8.9 Hz, C), 121.2 (d, *J* 3.0 Hz, CH), 117.2 (d, *J* 85.2 Hz, 3 x C), 115.0 (d, *J* 4.0 Hz, CH), 92.5 (d, *J* 7.9 Hz, C), 56.3 (CH_3), 56.2 (CH_3), 35.2 (d, *J* 47.6 Hz, CH_2).

Mass $^m/_z$ (ES+) 539 ([M-Br]$^+$, 100).

1-((*Z*)-2-(2-Bromo-4,5-dimethoxyphenyl)-1-ethenyl)-2-iodo-4,5-dimethoxybenzene (13a)



To a cooled (0 °C) suspension of phosphonium salt **11** (2.23 g, 3.6 mmol) in THF (25 mL) was added potassium *tert*-butoxide (470 mg, 4.2 mmol). After 30 min, 2-bromo-4,5-dimethoxybenzaldehyde (**12a**) (735 mg, 3.0 mmol) in THF (25 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and re-extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, gradient elution, 30-40% ether / petrol) to yield a 30 : 1 mixture of (*Z*)- and (*E*)-**13a** (1.33 g, 2.63 mmol, 88%). Recrystallization from hexane gave (*Z*)-**13a** in pure form for analysis.

MP 109-111 °C (hexanes).

IR ν_{max} (neat, cm^{-1}) 2955 w, 2835 w, 1596 w, 1494 m, 1453 m, 1432 m, 1370 w, 1257 m, 1203 s, 1159 s, 1020 m.

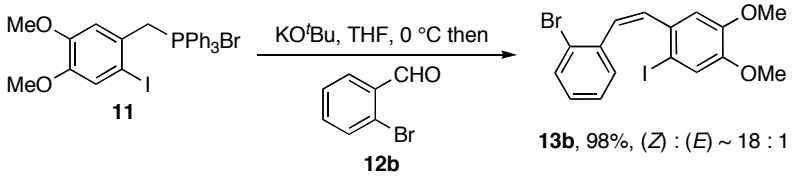
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.25 (1H, s), 7.02 (1H, s), 6.64 (1H, d, *J* 11.6 Hz), 6.59 (1H, s), 6.56 (1H, d, *J* 11.6 Hz), 6.55 (1H, s), 3.85 (6H, s), 3.51 (3H, s), 3.48 (3H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 149.1 (C), 149.0 (C), 148.9 (C), 148.0 (C), 134.1 (CH), 133.4 (C), 129.7 (CH), 129.0 (C), 121.2 (CH), 115.2 (CH), 114.6 (C), 113.3 (CH), 113.1 (CH), 88.3 (C), 56.3 (2 x CH_3), 55.9 (2 x CH_3).

Mass $^m/_z$ (EI) 506 ([M(^{81}Br)]$^+$, 49), 504 ([M(^{79}Br)]$^+$, 41), 298 (100).

CHN Found C 42.87, H 3.57. $C_{18}H_{18}BrIO_4$ requires C 42.80, H 3.59.

1-((*Z*)-2-(2-Bromophenyl)-1-ethenyl)-2-iodo-4,5-dimethoxybenzene (13b)



To a cooled (0 °C) suspension of phosphonium salt **11** (1.49 g, 2.4 mmol) in THF (20 mL) was added potassium *tert*-butoxide (313 mg, 2.8 mmol). After 30 min, 2-bromobenzaldehyde (**12b**) (370 mg, 2.0 mmol) in THF (20 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (30 mL) was added. The aqueous phase was separated and re-extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 20% ether / petrol) to yield a 18 : 1 mixture of (*Z*)- and (*E*)-**13b** (872 mg, 1.96 mmol, 98%) as a colourless oil.

FT - IR ν_{max} (neat, cm^{-1}) 2998 w, 2952 w, 1589 w, 1557 w, 1497 s, 1462 m, 1434 m, 1369 m, 1253 s, 1205 s, 1023 s.

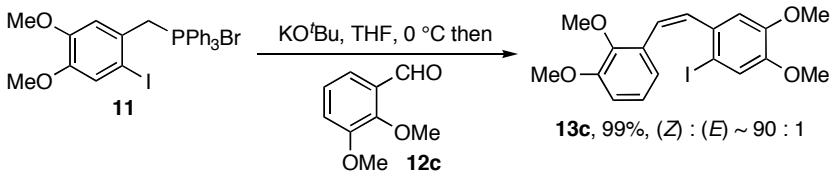
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.59 (1H, m), 7.24 (1H, s), 7.10-7.02 (3H, m), 6.68 (1H, d, J 11.7 Hz), 6.63 (1H, d, J 11.7 Hz), 6.46 (1H, s), 3.85 (3H, s), 3.39 (1H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 149.0 (C), 148.8 (C), 137.6 (C), 135.1 (CH), 132.7 (CH), 132.7 (C), 131.3 (CH), 129.9 (CH), 128.8 (CH), 127.2 (CH), 124.1 (C), 121.2 (CH), 113.2 (CH), 88.5 (C), 56.2 (CH_3), 55.6 (CH_3). Residual signals attributed to (*E*)-**13b**: 133.2 (CH), 129.1 (CH), 127.9 (CH), 121.8 (CH), 121.6 (CH), 112.9 (CH), 109.2 (CH), 56.4 (CH_3), 56.1 (CH_3).

Mass $^m/_z$ (EI) 446 ([M(^{81}Br)]$^+$, 85), 444 ([M(^{79}Br)]$^+$, 93), 318 ([M(^{81}Br)-HI]$^+$, 19), 316 ([M(^{79}Br)-HI]$^+$, 16), 238 (100), 223 (76), 195 (78), 177 (61), 165 (71), 152 (91), 119 (90).

Accurate $^m/_z$ (EI) Found M$^+$ 443.9220. $C_{16}H_{14}O_2{}^{79}BrI$ requires 443.9222.

1-((*Z*)-2-(2,3-Dimethoxyphenyl)-1-ethenyl)-2-iodo-4,5-dimethoxybenzene (13c)



To a cooled (0 °C) suspension of phosphonium salt **11** (2.23 g, 3.6 mmol) in THF (25 mL) was added potassium *tert*-butoxide (470 mg, 4.2 mmol). After 30 min, 2,3-dimethoxybenzaldehyde (**12c**) (825 mg, 3.0 mmol) in THF (25 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and re-extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, gradient elution, 30-40% ether / petrol) to yield a 90 : 1 mixture of (*Z*)- and (*E*)-**13c** (1.27 mg, 2.98 mmol, 99%) as a pale yellow oil.

IR ν_{max} (neat, cm^{-1}) 2933 w, 2835 w, 1592 w, 1499 m, 1465 s, 1426 m, 1255 s, 1209 s, 1068 m, 1026 m, 1007 m.

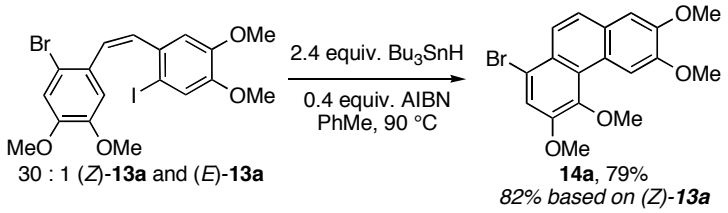
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.24 (1H, s), 6.84 – 6.73 (3H, m), 6.64 (1H, s), 6.62 (1H, dd, *J* 7.1, 1.8 Hz), 6.56 (1H, d, *J* 11.9 Hz), 3.86 (3H, s), 3.85 (6H, s), 3.44 (3H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 152.9 (C), 148.8 (C), 148.7 (C), 147.3 (C), 134.3 (CH), 133.5 (C), 131.1 (C), 125.7 (CH), 123.7 (CH), 122.3 (CH), 121.1 (CH), 113.2 (CH), 111.5 (CH), 88.4 (C), 60.9 (CH_3), 56.2 (CH_3), 55.9 (CH_3), 55.6 (CH_3).

Mass $^m/_z$ (EI) 426 ([M]$^+$, 100), 299 ([M-I]$^+$, 82), 284 (71), 268 (99).

Accurate $^m/_z$ (EI) Found M$^+$ 449.0214. $C_{18}H_{19}IO_4$ requires 449.0220.

1-Bromo-3,4,6,7-tetramethoxyphenanthrene (14a)



A solution of stilbene **13a** (30 : 1 mixture of (*Z*)- and (*E*)-isomers, 505 mg, 1.0 mmol), tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) in toluene (25 mL) was heated at 90 °C for 16 h then cooled to RT. Additional tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) were added and the reaction heated for a further 14 h at 90 °C. After cooling to RT and concentration *in vacuo*, the product mixture was purified by column chromatography (10% KF/SiO_2, 4% ether / petrol) to afford the title compound **14a** (297 mg, 0.788 mmol, 79%).

MP 152-155 °C (ether / petrol).

IR ν_{max} (neat, cm^{-1}) 2935 w, 1587 m, 1510 m, 1473 m, 1411 m, 1268 m, 1238 s, 1221 m, 1160 m, 1108 s, 1051 m.

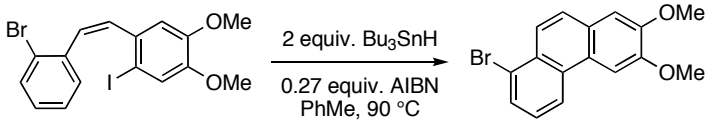
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 9.24 (1H, s), 7.98 (1H, d, *J* 9.0 Hz), 7.60 (1H, s), 7.59 (1H, d, *J* 9.0 Hz), 7.22 (1H, s), 4.08 (3H, s), 4.06 (3H, s), 4.03 (3H, s), 3.94 (3H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 150.8 (C), 149.4 (C), 148.9 (C), 145.9 (C), 128.7 (C), 126.4 (CH), 126.0 (C), 125.7 (C), 124.1 (CH), 123.8 (C), 118.6 (C), 117.0 (CH), 108.9 (CH), 108.1 (CH), 60.3 (CH_3), 56.9 (CH_3), 55.9 (2 x CH_3).

Mass $^m/_z$ (EI) 378 ([M(^{81}Br)]$^+$, 100), 376 ([M(^{79}Br)]$^+$, 88), 363 ([M(^{81}Br)-Me]$^+$, 41), 361 ([M(^{79}Br)-Me]$^+$, 37).

CHN Found C 57.51, H 4.63. $C_{18}H_{17}BrO_4$ requires C 57.31, H 4.54.

1-Bromo-6,7-dimethoxyphenanthrene (14b)



18 : 1 (*Z*)-**13b** and (*E*)-**13b**

14b, 82%
*87% based on (Z)-**13b***

A solution of stilbene **13b** (18 : 1 mixture of (*Z*)- and (*E*)-isomers, 150 mg, 0.34 mmol), tributyltin hydride (91 μL, 0.34 mmol) and AIBN (8 mg, 0.04 mmol) in toluene (5 mL) was heated at 90 °C for 2 h then cooled to RT. Additional tributyltin hydride (91 μL, 0.34 mmol) and AIBN (8 mg, 0.04 mmol) were added and the reaction heated at 90 °C for a further 4 h. After cooling to RT and concentration *in vacuo*, the product mixture was purified by column chromatography (10% K_2CO_3/SiO_2, 20% ether/petrol) to afford the title compound **14b** as a white solid (88 mg, 0.28 mmol, 82%).

MP 169-171 °C (EtOAc / hexanes).

FT - IR ν_{max} (neat, cm^{-1}) 3006 w, 2928 w, 2827 w, 1615w, 1593 w, 1500 m, 1469 m, 1456 m, 1397 m, 1374 m, 1267 m, 1221 s, 1191 m, 1159 s, 1113 m, 1028 s, 968 m.

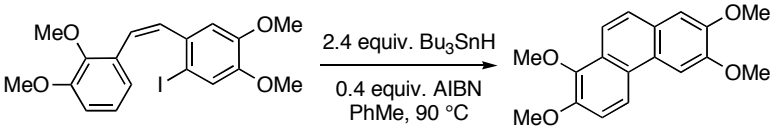
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.51 (1H, d, J 8.4 Hz), 8.11 (1H, d, J 9.1 Hz), 7.97 (1H, s), 7.83 (1H, dd, J 7.5, 0.7 Hz), 7.74 (1H, d, J 9.1 Hz), 7.44 (1H, dd, J 8.4, 7.5 Hz), 7.25 (1H, s), 4.12 (3H, s), 4.06 (3H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 150.0 (C), 149.9 (C), 131.5 (C), 130.0 (C), 129.9 (CH), 127.7 (CH), 127.4 (C), 126.6 (CH), 124.8 (C), 124.0 (C), 123.9 (CH), 122.1 (CH), 108.4 (CH), 103.6 (CH), 56.2 (CH_3), 56.1 (CH_3).

Mass $^m/_z$ (EI) 318 ([M(^{81}Br)]$^+$, 97), 316 ([M(^{79}Br)]$^+$, 100), 194 (96), 176 (65), 163 (74), 151 (88).

CHN Found C 60.51, H 4.11. $C_{16}H_{13}BrO_2$ requires C 60.59, H 4.13.

1,2,6,7-Tetramethoxyphenanthrene (14c)



90 : 1 (*Z*)-**13c** and (*E*)-**13c**

14c, 74%

A solution of stilbene **13c** (40 : 1 mixture of (*Z*)- and (*E*)-isomers, 426 mg, 1.0 mmol), tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) in toluene (25 mL) was heated at 90 °C for 16 h then cooled to RT. Additional tributyltin hydride (0.32 mL, 1.2 mmol) and AIBN (32 mg, 0.2 mmol) were added and the reaction heated for a further 16 h at 90 °C. After cooling to RT and concentration *in vacuo*, the crude product mixture was purified by recrystallization from toluene to afford the title compound **14c** (221 mg, 0.742 mmol, 74%) as a cream solid.

MP 198-200 °C (toluene), lit.[12] 183-185 °C (EtOH / acetone).

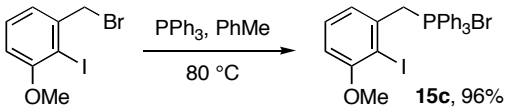
IR ν_{max} (neat, cm^{-1}) 2962 w, 2835 w, 1614 w, 1599 w, 1482 m, 1443 m, 1263 s, 1224 s, 1154 s, 1059 s, 1014 s.

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.26 (1H, d, *J* 9.0 Hz), 8.01 (1H, d, *J* 9.0 Hz), 7.91 (1H, s), 7.65 (1H, d, *J* 9.0 Hz), 7.34 (1H, d, *J* 9.0 Hz), 7.22 (1H, s), 4.11 (3H, s), 4.04 (9H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 149.5 (C), 149.1 (C), 149.0 (C), 144.1 (C), 127.0 (C), 126.6 (CH), 126.2 (C), 125.4 (C), 125.0 (C), 118.7 (CH), 118.5 (CH), 113.7 (CH), 108.6 (CH), 103.2 (CH), 61.4 (CH_3), 56.8 (CH_3), 56.2 (CH_3), 56.1 (CH_3).

Mass $^m/_z$ (EI) 298 ([M]$^+$, 100), 283 ([M-CH_3]$^+$, 58), 255 (51), 240 (54), 224 (47), 197 (45), 149 (58), 140 (62).

(2-Iodo-3-methoxybenzyl)triphenylphosphonium bromide (15c)



15c, 96%

2-Iodo-3-methoxybenzyl bromide (1.35 g, 4.14 mmol) and triphenylphosphine (1.19 g, 4.55 mmol) were heated at 80 °C in toluene (20 mL) for 24 h. The reaction was cooled to RT and the solid collected by filtration and washed with petrol (2 x 40 mL) to afford **15c** as a white solid (2.33 g, 3.96mmol, 96%).

MP > 250 °C (ethanol).

FT - IR ν_{max} (neat, cm^{-1}) 2930 w, 2821 w, 2763 w, 1583 w, 1566 m, 1461 m, 1435 m, 1423 m, 1401 w, 1294 w, 1260 s, 1157 w, 1109 s, 1058 s, 1016 w, 994 m.

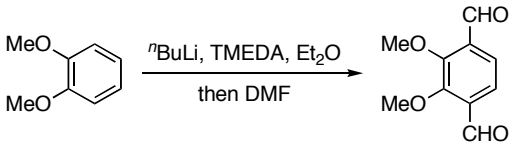
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.81-7.72 (3H, m), 7.63-7.55 (12H, m), 7.13 (1H, dd, J 8.1, 7.7 Hz), 7.02 (1H, ddd, J 7.7, 1.3, 1.3 Hz), 6.73 (1H, dd, J 8.1, 1.3 Hz), 5.57 (2H, d, J 14.1 Hz), 3.78 (3H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 158.6 (C), 135.2 (d, J 2.2 Hz, 3 x CH), 135.2 (CH), 134.3 (d, J 9.8 Hz, 6 x CH), 132.4 (d, J 8.9 Hz, C), 130.1 (d, J 12.2 Hz, 6 x CH), 124.2 (d, J 4.4 Hz, CH), 117.2 (d, J 85.1 Hz, 3 x C), 110.9 (d, J 3.3 Hz, CH), 97.5 (d, J 7.7 Hz, C), 56.8 (CH_3), 36.0 (d, J 47.6 Hz, CH_2).

Mass $^m/_z$ (ES+) 509 ([M-Br]$^+$, 100).

CHN Found C 52.78, H 3.94. $C_{26}H_{23}BrIOP$ requires C 53.00, H 3.93.

2,3-Dimethoxybenzene-1,4-dicarbaldehyde (16)



16, 42%

A solution of veratrole (1.27 mL, 10.0 mmol) and TMEDA (7.56 mL, 50.0 mmol) in diethyl ether (50 mL) was cooled to –78 °C and *n*-BuLi (2.39 M in hexanes, 20.9 mL, 50.0 mmol) added dropwise over 15 min. The reaction was allowed to warm to RT then heated under reflux for 4 h. After re-cooling –78 °C, DMF (3.9 mL) was added *via* syringe over 5 min. After 1 h at –78 °C, the reaction was allowed to warm to RT and water (50 mL), then HCl (2 M aq. 10 mL) were added. The aqueous phase was separated and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 25% EtOAc / petrol) to give **16** (814 mg, 4.20 mmol, 42%) as a pale yellow solid.

MP 95-97 °C (EtOAc / hexanes) lit.[13] 99-100 °C.

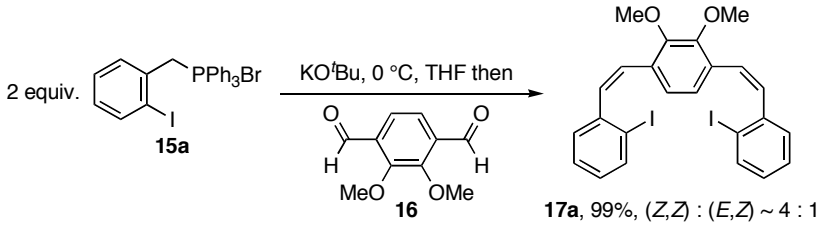
IR ν_{max} (neat, cm^{-1}) 2953 w, 2873 w, 1680 vs, 1569 m, 1461 s, 1382 s, 1243 vs, 1219 s, 1038 s, 1006 s.

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 10.43 (2H, s), 7.62 (2H, s), 4.06 (6H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 189.4 (2 x CH), 156.8 (2 x C), 134.4 (2 x C), 123.0 (2 x CH), 62.6 (2 x CH_3).

Mass $^m/_z$ (EI) 194 (M$^+$, 100), 179 (57), 119 (53), 51 (54).

(*Z*,*Z*)-1-(1-1-(1-((2-Iodophen-1-yl)-ethen-2-yl)-2,3-dimethoxyphen-4-yl)-ethen-2-yl)-2-iodobenzene (17a)



To a cooled (0 °C) suspension of phosphonium salt **15a** (1.34 g, 2.4 mmol) in THF (20 mL) was added potassium *tert*-butoxide (313 mg, 2.8 mmol). After 30 min, 2,3-dimethoxybenzene-1,4-dicarbaldehyde (**16**) (194 mg, 1.0 mmol) in THF (20 mL) was added over 10 min. The mixture was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and extracted with diethyl ether (2 x 40 mL) and ethyl acetate (2 x 40 mL). The combined organic extracts were washed with brine (40 mL), dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 10% ether / petrol) to give an inseparable 4 : 1 mixture of (*Z*,*Z*)-**17a** and (*E*,*Z*)-**17a** (588 mg, 0.99 mmol, 99%) as a yellow oil.

IR ν_{max} (neat, cm^{-1}) 3049 w, 2927 w, 2855 w, 2820 w, 1734 m, 1581 m, 1554 m, 1449 s, 1430 m, 1400 s, 1275 m, 1224 m, 1173 w, 1047 s, 1011 s.

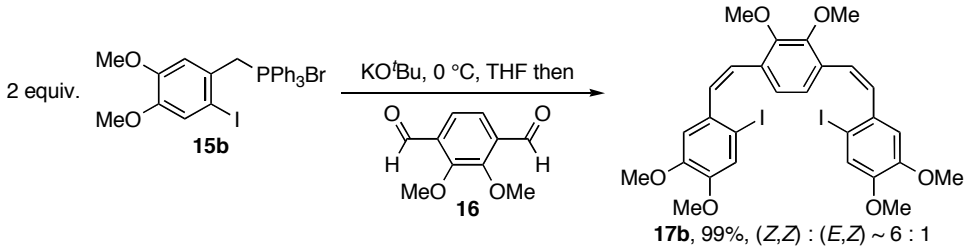
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.83 (2H, d, *J* 7.8 Hz), 7.09 (4H, m), 6.87 (2H, m), 6.76 (2H, d, *J* 12.0 Hz), 6.56 (2H, d, *J* 12.0 Hz), 6.39 (2H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 151.6 (2 x C), 141.6 (2 x C), 139.2 (2 x CH), 134.5 (2 x CH), 130.4 (2 x C), 130.3 (2 x CH), 128.8 (2 x CH), 127.9 (2 x CH), 126.0 (2 x CH), 124.6 (2 x CH), 99.9 (2 x C), 61.1 (2 x CH_3). Residual signals attributed to (*E*,*Z*)-**17a**: 151.9 (C), 151.3 (C), 141.9 (C), 140.8 (C), 139.8 (CH), 134.7 (CH), 133.6 (CH), 132.8 (CH), 130.9 (CH), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.1 (CH), 127.0 (CH), 126.6 (CH), 125.8 (CH), 125.3 (CH), 121.1 (CH), 100.7 (C), 61.3 (CH_3).

Mass $^m/_z$ (ES+) 595 (MH^+, 95).

Accurate Found $[M+Na]^+$ 616.9447. $C_{24}H_{20}I_2O_2Na$ requires 616.9444.

(*Z*,*Z*)-1-(1-1-(1-((2-Iodo-4,5-dimethoxyphen-1-yl)-ethen-2-yl)-2,3-dimethoxyphen-4-yl)-ethen-2-yl)-2-iodo-4,5-dimethoxybenzene (17b)



To a cooled (0 °C) suspension of phosphonium salt **15b** (1.49 g, 2.4 mmol) in THF (20 mL) was added potassium *tert*-butoxide (313 mg, 2.8 mmol). After 30 min, 2,3-dimethoxybenzene-1,4-dicarbaldehyde (**16**) (194 mg, 1.0 mmol) in THF (20 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and extracted with diethyl ether (2 x 40 mL) and ethyl acetate (2 x 40 mL). The combined organic phases were washed with brine (40 mL), dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 30% ether / petrol) to give firstly (*Z*,*Z*)-**17b** (415 mg, 0.58 mmol, 58%) as a yellow oil, then a 2 : 1 mixture of (*Z*,*Z*)-**17b** and (*E*,*Z*)-**17b** (290 mg, 0.41 mmol, 41%) as a yellow oil.

IR ν_{max} (neat, cm^{-1}) 3000 w, 2933 w, 2837 w, 1591 w, 1559 w, 1497 s, 1452 m, 1398 m, 1253 m, 1205 vs, 1022 s.

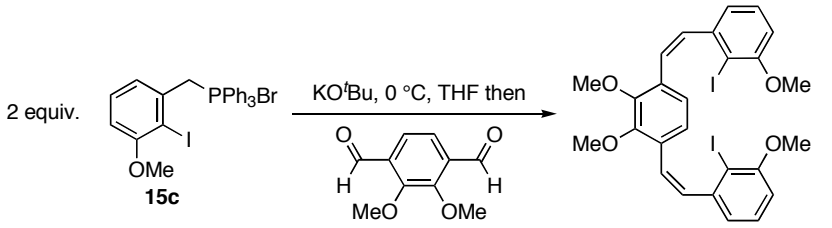
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.22 (2H, s), 6.68 (2H, d, *J* 12.1 Hz), 6.64 (2H, s), 6.55 (2H, s), 6.52 (2H, d, *J* 12.1 Hz), 3.88 (6H, s), 3.85 (6H, s), 3.49 (6H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 151.7 (2 x C), 148.8 (2 x C), 149.1 (2 x C), 134.5 (2 x CH), 133.9 (2 x C), 130.9 (2 x C), 125.2 (2 x CH), 124.7 (2 x CH), 121.5 (2 x CH), 112.5 (2 x CH), 88.4 (2 x C), 61.3 (2 x CH_3), 56.4 (2 x CH_3), 56.0 (2 x CH_3).

Mass $^m/_z$ (ES^+) 714 (M^+, 26), 588 ([MH-I]$^+$, 27), 460 (12), 267 (77), 145 (100).

Accurate Found [M+Na]$^+$: 736.9854. $C_{28}H_{28}O_6I_2Na$ requires 736.9867.

(*Z*,*Z*)-1-(1-1-(1-((2-Iodo-3-methoxyphen-1-yl)-ethen-2-yl)-2,3-dimethoxyphen-4-yl)-ethen-2-yl)-2-iodo-3-methoxy-benzene (17c)



17c, 99%, (*Z*,*Z*) : (*E*,*Z*) ~ 7 : 1

To a cooled (0 °C) suspension of phosphonium salt **15c** (2.12 g, 3.6 mmol) in THF (20 mL) was added potassium *tert*-butoxide (470 mg, 4.2 mmol). After 30 min, 2,3-dimethoxybenzene-1,4-dicarbaldehyde (**16**) (291 mg, 1.5 mmol) in THF (20 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and extracted with diethyl ether (2 x 40 mL) and ethyl acetate (2 x 40 mL). The combined organic extracts were washed with brine (40 mL), dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 10% ether / petrol) to give firstly (*Z*,*Z*)-**17c** (722 mg, 1.10 mmol, 74%) as a white solid followed by a 1 : 1 mixture of (*Z*,*Z*)- and (*E*,*Z*)-**17c** (249 mg, 0.38 mmol, 25%) as a pale yellow solid.

FT - IR ν_{max} (neat, cm^{-1}) 2926 w, 2839 w, 1583 w, 1560 m, 1452 m, 1416 m, 1277 m, 1262 s, 1062 s, 1011 s, 964 m.

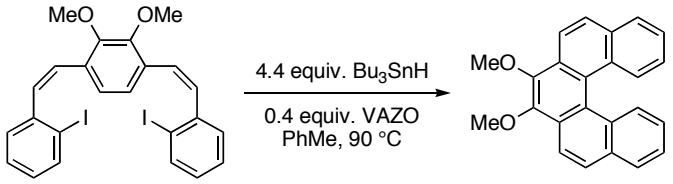
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.04 (2H, dd, J 8.1, 7.7 Hz, 2 x CH), 6.75 (2H, d, J 12.1 Hz, 2 x HC=CH), 6.70 (2H, dd, J 7.7, 1.3 Hz, 2 x CH), 6.62 (2H, dd, J 8.1, 1.3 Hz, 2 x CH), 6.58 (2H, d, J 12.1 Hz, 2 x HC=CH), 6.35 (2H, s, 2 x CH), 3.89 (12H, s, 4 x CH_3).

^{13}C NMR δ_C (100 MHz, $CDCl_3$) 158.2 (2 x C), 151.3 (2 x C), 143.6 (2 x C), 134.7 (2 x CH), 130.2 (2 x C), 128.7 (2 x CH), 125.4 (2 x CH), 124.4 (2 x CH), 122.7 (2 x CH), 109.0 (2 x CH), 91.4 (2 x C), 60.9 (2 x CH_3), 56.4 (2 x CH_3).

Mass $^m/_z$ (ES+) 677 ([M+Na]$^+$, 100).

CHN Found C 47.68, H 3.76. $C_{26}H_{24}I_2O_4$ requires C 47.73, H 3.70.

7,8-Dimethoxy[5]helicene (18a)



(*Z*,*Z*)-**17a** + (*E*,*Z*)-**17a**
4 : 1 mixture

18a, 60%
*80% based on (Z,Z)-**17a***

A solution of *bis*-stilbene **17a** (4 : 1 mixture of (*Z*,*Z*)- and (*E*,*Z*)-isomers, 300 mg, 0.51 mmol), tributyltin hydride (0.30 mL, 1.11 mmol) and VAZO (25 mg, 0.10 mmol) in toluene (10 mL) was heated at 90 °C for 16 h then cooled to RT. Additional tributyltin hydride (0.30 mL, 1.11 mmol) and VAZO (25 mg, 0.10 mmol) were added and the reaction heated for a further 8 h at 90 °C. After cooling to RT and concentration *in vacuo*, the crude product mixture was purified by column chromatography (10% KF/SiO_2, 5% EtOAc / petrol) to give [5]helicene **18a** as a pale yellow solid (103 mg, 0.31 mmol, 60%).

MP 122-125 °C (EtOH).

IR ν_{max} (neat, cm^{-1}) 3055 w, 2935 w, 2837 w, 1599 m, 1582 m, 1413 m, 1232 w, 1255 m, 1094 m, 1045 s, 1022 m.

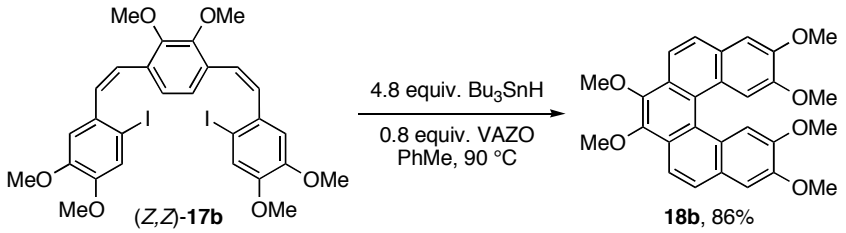
^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.39 (2H, d, *J* 8.5 Hz), 8.27 (2H, d, *J* 9.0 Hz), 7.93 (2H, d, *J* 9.0 Hz), 7.92 (2H, dd, *J* 8.0, 1.3 Hz), 7.47 (2H, ddd, *J* 8.0, 6.8, 1.0 Hz), 7.23 (2H, ddd, *J* 8.5, 6.8, 1.3 Hz), 4.12 (6H, s).

^{13}C NMR δ_C (100 MHz, $CDCl_3$) 145.1 (2 x C), 132.0 (2 x C), 130.7 (2 x C), 129.0 (2 x CH), 128.3 (2 x C), 127.8 (2 x CH), 127.6 (2 x CH), 126.0 (2 x CH), 124.5 (2 x C), 124.5 (2 x CH), 119.7 (2 x CH), 61.1 (2 x CH_3).

Mass $^m/_z$ (ES+) 361 ([M+Na]$^+$, 100)

CHN Found C 85.04, H 5.33. $C_{24}H_{18}O_2$ requires C 85.18, H 5.36.

2,3,7,8,12,13-Hexamethoxy[5]helicene (18b)



(*Z*,*Z*)-**17b**

18b, 86%

A solution of *bis*-stilbene (*Z*,*Z*)-**17b** (190 mg, 0.27 mmol), tributyltin hydride (86 μL, 0.32 mmol) and VAZO (13 mg, 0.05 mmol) in toluene (10 mL) was heated at 90 °C, with further tributyltin hydride (86 μL, 0.32 mmol) and VAZO (13 mg, 0.05 mmol) added after 4, 8 and 24 h. After 30 h, the reaction was cooled to RT, concentrated *in vacuo* and purified by column chromatography (10% KF/SiO_2, 30% EtOAc / petrol) to afford [5]helicene **18b** (105 mg, 0.23 mmol, 86%) as a pale yellow solid.

MP 248-251 °C (EtOH).

IR ν_{max} (neat, cm^{-1}) 2997 w, 2949 w, 2900 w, 1611 m, 1509 s, 1477 s, 1459 s, 1416 s, 1252 s, 1166 s, 1000 s.

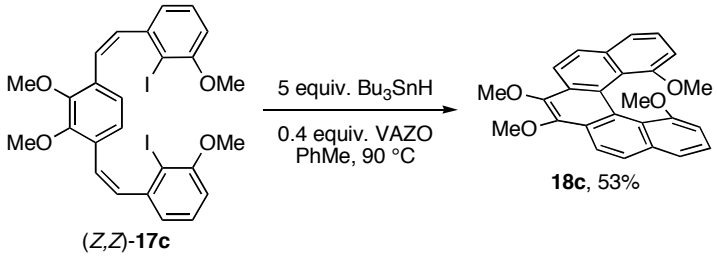
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.22 (2H, d, *J* 8.7 Hz), 7.87 (2H, d, *J* 8.7 Hz), 7.74 (2H, s), 7.30 (2H, s), 4.14 (6H, s), 4.07 (6H, s), 3.59 (6H, s).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 148.8 (2 x C), 147.7 (2 x C), 144.6 (2 x C), 127.9 (2 x C), 127.8 (2 x C), 126.5 (2 x CH), 125.3 (2 x C), 123.7 (2 x C), 118.5 (2 x CH), 110.3 (2 x CH), 107.4 (2 x CH), 61.3 (2 x CH_3), 56.0 (2 x CH_3), 55.7 (2 x CH_3).

Mass $^m/_z$ (ES$^+$) 482 ([MH+Na]$^+$, 28), 481 ([M+Na]$^+$, 100), 459 ([MH]$^+$, 37).

CHN Found C 73.35, H 5.77. $C_{28}H_{26}O_6$ requires C 73.35, H 5.72.

1,7,8,14-Tetramethoxy[5]helicene (18c)



(*Z*,*Z*)-**17c** **18c**, 53%

A solution of *bis*-stilbene (*Z*,*Z*)-**17c** (251 mg, 0.38 mmol), tributyltin hydride (0.26 mL, 0.96 mmol) and VAZO (18 mg, 0.075 mmol) in toluene (7 mL) was heated at 90 °C, with further tributyltin hydride (0.26 mL, 0.96 mmol) and VAZO (18 mg, 0.075 mmol) added after 4 h. After 48 h, the reaction was cooled to RT, concentrated *in vacuo* and purified by column chromatography (10% K_2CO_3/SiO_2, 5% EtOAc / petrol) to afford [5]helicene **18c** (81 mg, 0.20 mmol, 53%) as a yellow solid.

MP 175-179 °C (EtOH).

FT - IR ν_{max} (neat, cm^{-1}) 2932 w, 2831 w, 1736 m, 1612 w, 1556 m, 1446 m, 1260 s, 1109 m, 1094 s, 1058 s, 1029 s.

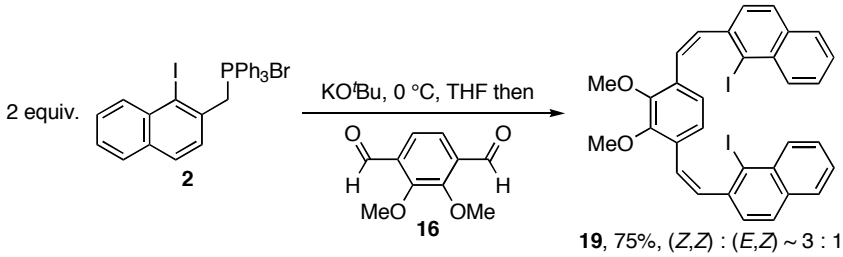
^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.35 (2H, d, 8.8 Hz), 7.94 (2H, d, J 8.8 Hz), 7.64 (2H, dd, J 7.9, 0.9 Hz), 7.48 (2H, t, J 7.9 Hz), 6.71 (2H, dd, J 7.9, 0.9 Hz), 4.20 (6H, s), 2.86 (6H, s).

^{13}C NMR δ_C (100 MHz, $CDCl_3$) 155.7 (2 x C), 144.4 (2 x C), 132.0 (2 x C), 127.1 (2 x C), 126.9 (2 x CH), 125.3 (2 x CH), 124.5 (2 x C), 122.8 (2 x C), 119.7 (4 x CH), 104.9 (2 x CH), 61.2 (2 x CH_3), 53.5 (2 x CH_3).

Mass $^m/_z$ (ES+) 421 ([M+Na]$^+$, 100), 399 (MH^+, 21).

CHN Found C 78.32, H 5.56. $C_{26}H_{22}O_4$ requires C 78.37, H 5.57.

(*Z*,*Z*)-1-(1-1-(1-((1-Iodo-naphth-2-yl)-ethen-2-yl)-2,3-dimethoxyphen-4-yl)-ethen-2-yl)-1-iodo-naphthalene (19)



19, 75%, (*Z*,*Z*) : (*E*,*Z*) ~ 3 : 1

To a cooled (0 °C) suspension of phosphonium salt **2** (2.19 g, 3.6 mmol) in THF (25 mL) was added potassium *tert*-butoxide (470 mg, 4.2 mmol). After 30 min, 2,3-dimethoxybenzene-1,4-dicarbaldehyde (**16**) (291 mg, 1.5 mmol) in THF (25 mL) was added over 10 min. The reaction was allowed to warm to RT and after 16 h water (40 mL) was added. The aqueous phase was separated and re-extracted with diethyl ether (2 x 40 mL) and ethyl acetate (2 x 40 mL). The combined organic phases were washed with brine (40 mL), dried ($MgSO_4$), concentrated *in vacuo* and purified by column chromatography (SiO_2, 5% EtOAc / petrol) to give firstly (*Z*,*Z*)-**19** (619 mg, 0.89 mmol, 59%) as a pale yellow solid, then a 6 : 11 mixture of (*Z*,*Z*)-**19** and (*E*,*Z*)-**19** (271 mg, 0.39 mmol, 26%) as a yellow solid and finally a 7 : 5 mixture of (*E*,*Z*)-**19** and (*E*,*E*)-**19** (169 mg, 0.24 mmol, 7%) as a yellow solid. Data for (*Z*,*Z*)-**19**:

MP 171-173 °C (EtOAc / hexanes).

IR ν_{max} (neat, cm^{-1}) 3050 w, 2927 w, 2822 w, 1543 m, 1448 m, 1403 s, 1276 s, 1218 s, 1046 s, 1018 vs, 963 s,

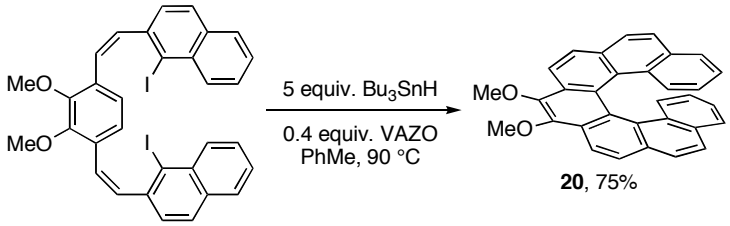
^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.18 (2H, d, *J* 8.4 Hz), 7.65 (2H, dd, *J* 7.7, 1.3 Hz), 7.55 – 7.41 (6H, m), 7.12 (2H, d, *J* 8.4 Hz), 6.87 (2H, d, *J* 12.1 Hz), 6.80 (2H, d, *J* 12.1 Hz), 6.23 (2H, s), 3.95 (6H, s).

^{13}C NMR δ_C (100 MHz, $CDCl_3$) 151.5 (2 x C), 141.2 (2 x C), 136.2 (2 x CH), 135.1 (2 x C), 133.1 (2 x C), 132.4 (2 x CH), 130.6 (2 x C), 128.3 (4 x CH), 127.9 (2 x CH), 127.8 (2 x CH), 126.7 (2 x CH), 125.7 (2 x CH), 124.9 (2 x CH), 105.1 (2 x C), 61.2 (2 x CH_3).

Mass $^m/_z$ (ES^+) 694 (M^+, 67), 568 ([MH-I]$^+$, 100).

CHN Found C 55.53, H 3.44. $C_{32}H_{24}I_2O_2$ requires C 55.35, H 3.48.

9,10-Dimethoxy[7]helicene (20)



(*Z,Z*)-**19** **20**, 75%

A solution of *bis*-stilbene (*Z,Z*)-**19** (175 mg, 0.25 mmol), tributyltin hydride (0.17 mL, 0.63 mmol) and VAZO (12 mg, 0.05 mmol) in toluene (5 mL) was heated at 90 °C, with further tributyltin hydride (0.17 mL, 0.63 mmol) and VAZO (12 mg, 0.05 mmol) added after 4 h. After 24 h, the reaction was cooled to RT, concentrated *in vacuo* and purified by column chromatography (10% KF/SiO_2, 10% ether / petrol) to afford [5]helicene **20** (83 mg, 0.19 mmol, 75%) as orange needles.

MP >250 °C (EtOAc / hexanes).

IR ν_{max} (neat, cm^{-1}) 3045 w, 2944 w, 1737 w, 1600 m, 1470 m, 1375 s, 1276 m, 1246 m, 1096 s, 1048 s, 987 m.

^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.40 (2H, d, *J* 8.3 Hz), 7.96 (2H, d, *J* 8.3 Hz), 7.74 (2H, d, *J* 8.5 Hz), 7.48 (2H, d, *J* 8.5 Hz), 7.30 (2H, d, *J* 8.3 Hz), 7.15 (2H, d, *J* 8.5 Hz), 6.91 (2H, ddd, *J* 8.3, 7.0, 1.3 Hz), 6.41 (2H, ddd, *J* 8.3, 7.0, 1.3 Hz), 4.27 (6H, s).

^{13}C NMR δ_C (100 MHz, $CDCl_3$) 144.5 (2 x C), 131.8 (2 x C), 130.2 (2 x C), 129.4 (2 x C), 128.3 (2 x C), 128.3 (2 x C), 127.6 (2 x CH), 127.0 (2 x CH), 126.5 (2 x CH), 125.6 (2 x CH), 124.9 (2 x CH), 124.4 (2 x CH), 123.5 (2 x CH), 123.2 (2 x C), 120.3 (2 x CH), 61.3 (2 x CH_3).

Mass $^m/_z$ (ES^+) 461 (M^+, 100).

CHN Found C 87.70, H 5.07. $C_{32}H_{22}O_2$ requires C 87.65, H 5.06.

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