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Preparation of Orthogonal π-Conjugated Aryl Alkynes and Cyclophanes

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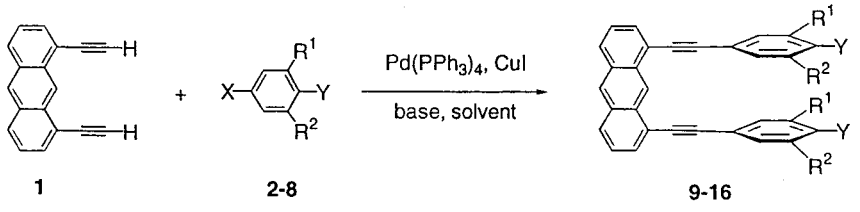
Abstract—A series of anthracene based orthogonal π-conjugated aryl alkynes was prepared using palladium-catalyzed couplings. Thia- and azacyclophanes were prepared from anthracene based orthogonal π-conjugated aryl alkynes.

Introduction

Cyclophane structures continue to generate interest due to their unique physical properties and their ability to act as model compounds for the study of intramolecular processes[1] and host–guest chemistry.[2] Cyclophanes containing extended π-conjugation have been investigated as mimics for the solid-state interactions involving photoexcitation[3] and for electron transfer processes involving extended orthogonal π-systems.[4] The spatial proximity of extended π-conjugated frameworks influences the optical and electronic properties of the resulting bulk materials. Well-defined systems, where the cofacial overlap of aromatic rings is enforced in oligomeric systems, are rare. The emission spectra of such compounds exhibit features that are related to the ability of closely spaced chromophores to interact electronically through space.[4] By controlling the distance between adjacent strands of oligomeric cyclophanes it should be possible to model interchromophore contacts in bulk π-conjugated polymers. We required a series of π-conjugated cyclophanes in order to investigate the relationship between aromatic rings in close proximity and their optoelectronic properties and report herein methodologies for the preparation of precursors to oligomeric cyclophanes. We have previously reported the preparation of the monomeric precursors to the orthogonal



1 **2-8** **9-16**

2, 9	$R^1 = R^2 = H$, X = I, Y = CH_3	**1 + 2 → 9**	piperidine, CH_3CN (92%)
3, 10	$R^1 = R^2 = H$, X = I, Y = OH	**1 + 3 → 10**	piperidine, CH_3CN (NI)
		10 → 11	TDSCl, imidazole (52%, 2 steps)
4, 12	$R^1 = H$, $R^2 = CO_2CH_3$, X = I, Y = H	**1 + 4 → 12**	Et_3N, benzene (99%)
5, 13	$R^1 = R^2 = CO_2CH_3$, X = Br, Y = H	**1 + 5 → 13**	DBU, DMSO (100%)
6, 14	$R^1 = R^2 = CH_2OTBDMS$, X = Br, Y = H	**1 + 6 → 14**	piperidine, CH_3CN (16%)
7, 15	$R^1 = R^2 = CO_2CH_3$, X = I, Y = OTDS	**1 + 7 → 15**	Et_3N, CH_3CN (60%)
8, 16	$R^1 = R^2 = CO_2CH_3$, X = I, Y = OTf	**1 + 8 → 16**	Et_3N, CH_3CN (43%)

NI = not isolated

Scheme 1.

Keywords: cyclophanes; arylalkenes; π-conjugated.

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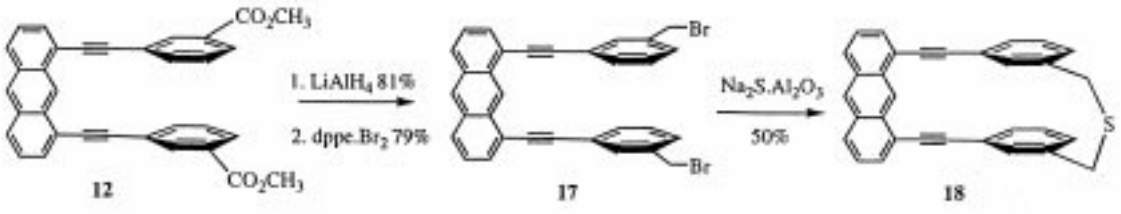


Scheme 2.

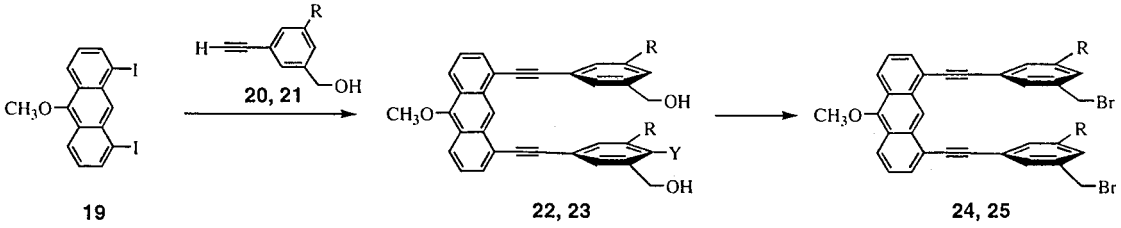
π-conjugated aryl alkynes.[5] In this paper we report their conversion to cyclophanes and extended π-conjugated aryl alkynes.

Results and Discussion

In order to compare the ground state electronic properties of π-conjugated aryl alkynes with their cyclophane analogues, a series of model compounds was initially prepared. Thus, 4-iodotoluene **2** was coupled to 1,8-diethynylanthracene **1**[6] using standard palladium-catalyzed coupling conditions[7] ($Pd(PPh_3)_4$, CuI, piperidine in acetonitrile) to give the desired bis-coupled material **9** in 92% (Scheme 1, base and solvent as indicated). The product was readily soluble in halogenated solvents and could be purified by chromatography on normal phase silica gel without streaking. 4-Iodophenol **3** was then coupled to **1** using these same conditions, and upon workup, the resultant bis-coupled product **10** streaked significantly on both normal phase silica and alumina. The introduction of the phenolic hydroxyl group had had a dramatic effect on the solubility of the product. To improve the isolated yield of **10** the crude reaction material was silylated with thexyldimethylsilyl chloride (TDSCl) and the resulting product **11** (R^1=R^2=H, Y=OTDS) was isolated in 52% (Scheme 1).

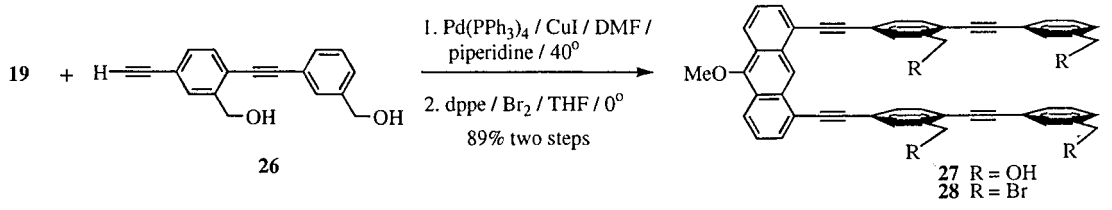
The coupling of methyl ester **4** with **1** was performed using $Pd(PPh_3)_4$ and CuI in a mixture of benzene and triethylamine at 50°, since at lower temperatures the mono-coupled complex precipitated from solution and prevented further progress of the reaction. The product **12** was isolated in 99% after purification on normal phase silica gel. Attempted coupling of dimethyl ester **5** with **1** under these standard conditions gave little coupled product, however, changing the solvent to DMSO and using DBU as the base gave **13** in a quantitative yield. Coupling of silyloxy protected **6** with **1** could be achieved under the standard conditions but the desired product **14** was only isolated in a low 16% after purification using reverse phase silica. Both **7** and **8** could be coupled with **1** under the standard conditions and the respective products **15** and **16** were isolated using reverse phase silica in 60 and 43% (Scheme 1).

Reduction of diester **12** with LAH in THF at 0–25° gave the desired diol in 81% after an acidic workup and purification on reverse phase silica. This diol was not characterized but converted directly into the corresponding bromomethyl compound **17** with dppe and Br_2[8] in 79% (Scheme 2). The alkyne functionality was not affected by either of these two steps. Reaction of **17** with sodium sulfide adsorbed on alumina (2.5 mmol/g)[9] gave the desired cyclophane **18** in 50% after purification on reverse phase silica.

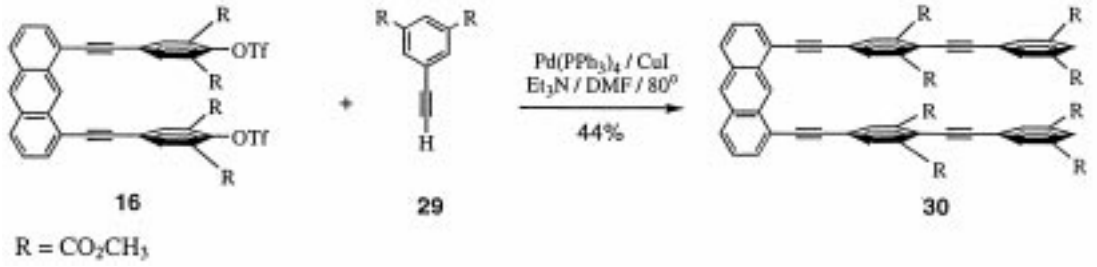


20, 22, 24	R = H	**19 + 20 → 22**	(100%)	$Pd(PPh_3)_4$, CuI, piperidine, DMF
21, 23	R = CH_2OH	**19 + 21 → 23**	(100%)	$Pd(PPh_3)_4$, CuI, piperidine, DMF
25	R = CH_2Br	**22 → 24**	(56%)	PPh_3, NBS, THF
		23 → 25	(64%)	PPh_3, NBS, THF

Scheme 3.



Scheme 4.



Scheme 5.

In order to increase the solubility of the π-conjugated aryl alkynes, 1,8-diiodo-10-methoxyanthracene **19**[10] was used as the orthogonal template. The aryl substrates **20** and **21** both contained unprotected benzyl alcohols and coupled readily with **19** using the standard palladium-catalyzed coupling conditions to give **22** and **23** in a quantitative yield (Scheme 3). Compounds **22** and **23** were converted into the corresponding bromomethyl derivatives by the addition of PPh_3 and NBS to a THF solution of either at low temperature.[11] No addition to the alkyne group was observed under these conditions and the required products **24** and **25** were isolated in 56 and 64%, respectively (Scheme 3).

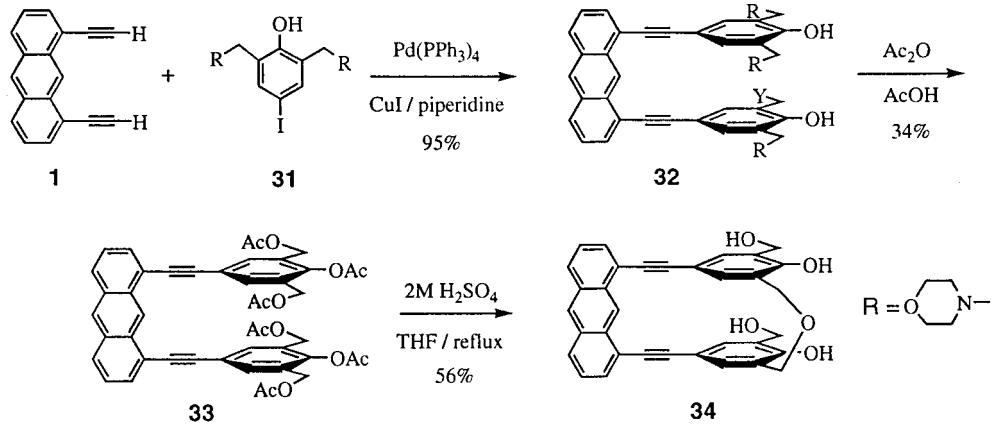
This procedure was applied to the preparation of the extended complex **28** through the palladium-catalyzed coupling of bis(hydroxymethyl)alkyne **26**[5] with **19** and subsequent transformation of the hydroxyl groups of **27** to bromides with dppe and Br_2 as shown in Scheme 4. The tetra(bromomethyl) derivative **28** was obtained in 89% from **19** over the two steps.

The bis-coupled system **16** was extended further by a palladium-catalyzed coupling with 2 equiv. of terminal alkyne **29** (Scheme 5). Standard coupling conditions were used except that the reaction temperature was increased to 80° to aid in the oxidative addition of the hindered triflate. Under these conditions the two-unit oligomer **30** could be produced in a reasonable yield of 44% after purification on normal phase silica. Solubility problems were encountered with **30**, nevertheless, the reactions outlined in Schemes 1 and 5 highlighted the regioselective coupling of iodoaryl triflates with terminal alkynes and indicated that further coupling of the hindered triflate was possible.

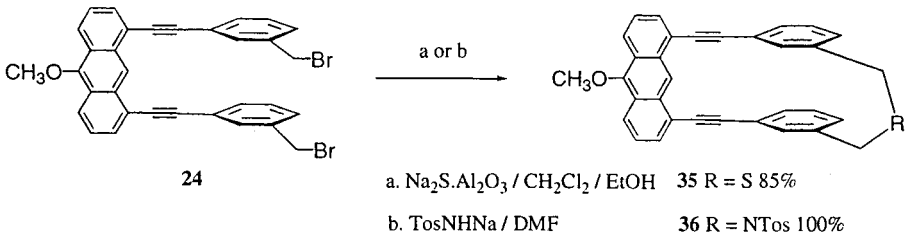
The preparation of a bis-strapped cyclophane was then attempted as outlined in Scheme 6. Coupling of **1** with 2,6-bis(morpholinylmethyl)-4-iodophenol **31**[5] in the presence of $Pd(PPh_3)_4$, CuI in piperidine gave the bis-coupled product **32** after one hour in 95%. The Mannich base **32** was heated at reflux in acetic anhydride with a small amount of acetic acid[5] to give the hexa-acetate **33** in a modest 34% after purification by chromatography on normal phase silica.

Complete hydrolysis of the acetate groups of **33** could not be achieved under basic conditions (guanidine/MeOH[12], K_2CO_3/H_2O/MeOH or LiOH/H_2O/MeOH). Under acidic conditions the reaction proceeded beyond complete hydrolysis to give the mono-strapped cyclophane **34** in 56% through the displacement of a protonated hydroxymethyl group by the oxygen of an adjacent hydroxymethyl substituent. The ^1H NMR spectrum for **34** showed two singlets at δ 4.88 and δ 5.07 of equal intensity for the two types of benzylic methylene protons, and two doublets at δ 7.93 and δ 7.65 (J=1.8 Hz) corresponding to the two distinct aromatic protons of the benzylic ring. The ^{13}C NMR spectrum for **34** showed the expected 14 aromatic signals, and the accurate mass was in agreement with the calculated value. Cyclophane **34** was the sole product isolated from the reaction, with no bis-strapped cyclophane being observed. The cyclophane streaked extensively on normal phase silica gel and had limited solubility in common organic solvents, resulting in the modest isolated yield.

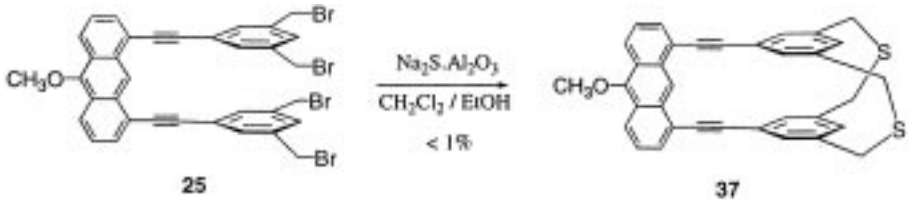
The formation of the mono-strapped thiacyclophane **35** was accomplished by the addition of 3 equiv. of $Na_2S{\cdot}Al_2O_3$



Scheme 6.



Scheme 7.



Scheme 8.

(2.5 mmol/g)[9] to **24** in dichloromethane/ethanol (20.2 mM, 5:1 v/v) as outlined in Scheme 7. After stirring at room temperature for 1 h the crude product was purified on alumina to afford **35** in 85%. The ^{1}H NMR spectrum showed a characteristic upfield shift in the singlet methylene protons for **35** (δ 3.43) compared to **24** (δ 4.31). Variable temperature ^{1}H NMR spectra for **35** obtained at 5° intervals between 25° and −55° in $CDCl_3$ showed no splitting, or even broadening, of the benzylic methylene protons as the temperature was lowered.

Formation of azacyclophane **36** was possible by the addition of 1.5 equiv. of TosNHNa to **24** in DMF under nitrogen with heating. The reaction was complete in 1 h and an extractive workup followed by chromatography on normal silica yielded **36** in a quantitative yield. The azacyclophane **36** was observed to decompose in solution over several hours in the sunlight, over several days in the dark and in the solid state over several weeks. No identifiable decomposition products could be isolated and characterized.

The bis-strapped thiacyclophane **37** was prepared in very low yield from the reaction of **25** with $Na_2S{\cdot}Al_2O_3$ (Scheme 8). The ^{1}H NMR spectrum for **37** showed the benzylic methylene protons as an AB quartet (J=15.0 Hz) which suggested that the structure was more rigid than the mono-strapped compounds **35** and **36**.

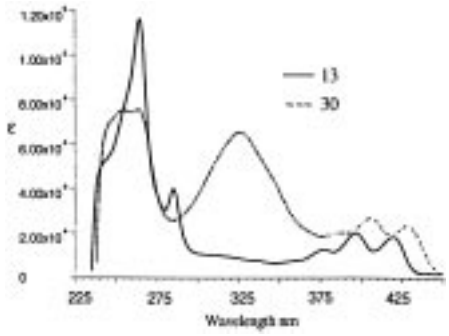


Figure 1. The UV–Vis spectra of **13** and **30**.

Molecular modeling (semi-empirical method using Spartan) indicated that for **35** and **36** the effect of the strapping arm of the cyclophane would be to introduce strain resulting in rotation about the aryl–alkyne bonds. For **37** a significant degree of strain to the cyclophane structure would result in a bending of the anthracene–alkyne–aryl bond. The three atom strapping arm, $-CH_2SCH_2$, was shown to be too short to allow the formation of a strain free cyclophane.

The single crystal X-ray structure of **35** showed that the two aromatic rings were not parallel to one-another, but that one was approximately parallel to the anthracene and the other was approximately perpendicular.[13] This conformation was probably due to intermolecular $\pi-\pi$ stacking between adjacent molecules in the crystal lattice. The distance between one of the aryl rings of the cyclophane and the anthracene ring of an adjacent molecule in the crystal lattice was 3.5 Å, typical for intermolecular $\pi-\pi$ stacking interactions.[14]

The ultra-violet and fluorescence spectra of cyclophanes have been studied in detail, as these compounds possess interesting transannular interactions between the cyclophane rings.[15] These interactions arise when the linker-arms are

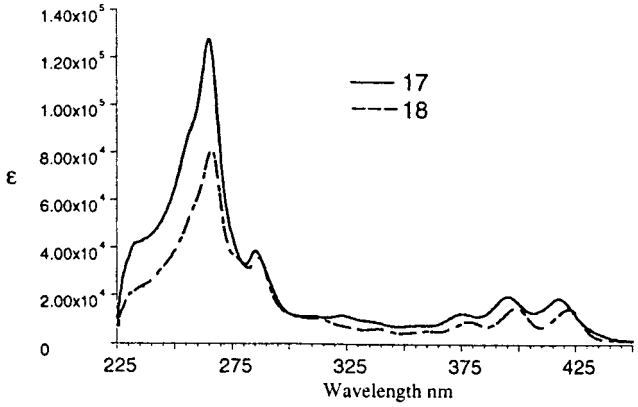


Figure 2. Ultra-violet spectra of **17** and **18**.

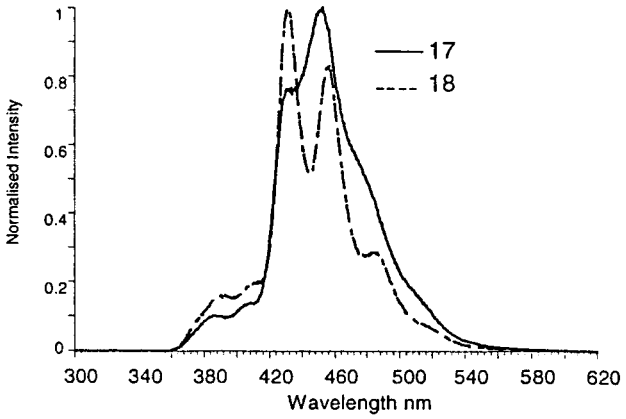


Figure 3. Fluorescence spectra of **17** and **18**.

short, typically two or three methylene units long, thereby introducing deformations to the aromatic rings and so reducing the fine structure observed. All the anthracene containing compounds showed a broad series of absorptions centered around 390 nm resulting from $\pi-\pi^*$ transitions to low excited states (primary band) for the anthracene portion of the molecule, and a quite sharp peak centered about 265 nm resulting from higher energy $\pi-\pi^*$ transitions (secondary band) for the aryl alkyne portion of the molecule.[16] In general, the primary band contained more vibrational fine structure than the secondary.

A small bathochromic shift was observed for the primary band between **13** (λ_{max} 424 nm) and **30** (λ_{max} 428 nm) but a significant bathochromic shift for the secondary band was observed between **13** (λ 285 nm) and **30** (λ_{max} 324 nm), as expected for an extension in the aryl alkyne portion of the molecule, (Fig. 1).

The ultra-violet and fluorescence spectra for the mono-strapped cyclophane **18** and its immediate precursor **17** were very similar as shown in Figs. 2 and 3, respectively. The only difference was to be seen in the fluorescence spectrum (Fig. 3), where more vibrational structure was observed in the spectrum of the cyclophane **18** compared to that of the precursor **17**, although the Stokes shift in both compounds was small.

In conclusion, we have developed an approach to novel, extended orthogonal π-systems and shown that mono-strapped cyclophanes containing an orthogonal anthracene could be readily prepared using standard palladium-catalyzed coupling and intramolecular nucleophilic substitution.

Experimental

^{1}H NMR spectra were recorded at 600 MHz on a Varian Nova or at 300 MHz on a Varian Gemini NMR spectrometer or at 200 MHz on a Varian Gemini spectrometer using a dual 5 mm ^{13}C/^{1}H probe. All spectra were recorded as dilute solutions in $CDCl_3$. Melting points were determined on a Kofler hot-stage micro-melting point apparatus equipped with a Reichart microscope. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded at 70 eV on a Vacuum Generators ZAB 2HF mass spectrometer. Liquid secondary ionization mass spectrometry (LSIMS) and accurate mass spectra were performed by the University of Tasmania mass spectrometric service. Infrared spectra were recorded on an ATI Mattson Genesis FTIR as nujol mulls between sodium chloride plates. Elemental analyses were performed at the University of Otago, New Zealand. The UV–Vis spectra were recorded as dilute solutions ($\sim 10^{-5}$ M) in HPLC grade THF. Thin layer chromatography (tlc) was carried out using Merck Silica gel (Kieselgel) $60F_{254}$ on aluminum backed plates. Solvents were purified and dried using standard laboratory procedures. All organic extracts were dried over anhydrous magnesium sulphate. All solvents for palladium catalyzed coupling reactions were degassed by the freeze–pump–thaw method and kept under an atmosphere of nitrogen. All reactions involving anhydrous solvents were also kept under an atmosphere of nitrogen.

The following compounds were all prepared by literature procedures: 1,8-diethynylanthracene **1**,[6] methyl 3-iodobenzoate **4**,[5] dimethyl-5-bromoisophthalate **5**,[5] 2,6-bis-(morpholinomethyl)-4-iodophenol **6**,[5] dimethyl 5-iodo-2-{[(trifluoromethyl)sulphonyl]oxy}isophthalate **8**,[5] 1,8-diiodo-10-methoxyanthracene **19**,[10] 3-(hydroxymethyl)-ethynylbenzene **20**,[17] 3,5-bis(hydroxymethyl)ethynylbenzene **21**,[18] and $Na_2S{\cdot}Al_2O_3$ (2.5 mmol/g)[9].

3,5-Bis[(*t*-butyldimethyl)silyloxymethyl]bromobenzene 6. Prepared according to the general procedure outlined in Ref. 19 from 1,3-bis(hydroxymethyl)-5-bromobenzene and 2.2 equiv. of both *tert*-butyldimethylsilyl chloride and imidazole. The reaction mixture was stirred at 50°C for 4 h, and purified by flash chromatography [hexane/dichloromethane 5/1 (v/v), R_f 0.33] to give **6** as a colourless oil (93%); Anal. Calcd for $C_{20}H_{37}O_2BrSi_2$: C, 53.91; H, 8.37, Found: C, 54.28; H, 8.52; δ_H (300 MHz) 0.07 (12H, s, $ArCH_2OSi(CH_3)_2tBu$), 0.92 (18H, $ArCH_2OSi(CH_3)_2C(CH_3)_3$), 4.67 (4H, s, $ArCH_2OR$), 7.18 (1H, br s, Ar*H*), 7.31 (2H, br s, Ar*H*); δ_C (75.47 MHz) −5.4, 18.3, 25.8, 64.2 ($ArCH_2OR$), 122.1, 122.3, 127.5, 143.7; *m/z* (EI) 446 (M^+, ^{81}Br, 14%), 444 (M^+, ^{79}Br, 12%), 389 (8), 387(8).

1,8-Di[2-(4-methylphenyl)-1-ethynyl]anthracene 9. A solution containing 4-iodotoluene (0.043 g, 0.195 mmol), $Pd(PPh_3)_4$ (0.010 g, 0.00929 mmol), **1** (0.021 g, 0.0929 mmol) and CuI (0.004 g, 0.0186 mmol) in a degassed solvent system of piperidine (0.5 mL)/acetonitrile (2 mL) was stirred for 0.5 h at room temperature. An extractive workup with dichloromethane (25 mL) gave an orange solid. Purification by squat column chromatography [dichloromethane, R_f 0.38] followed by recrystallization from ethanol gave the title compound as a fine golden needles (0.034 g, 92%); mp 170.5–172.0°C; Anal. Calcd for $C_{32}H_{22}O$: C, 94.55; H, 5.46, Found: C, 94.63; H, 5.41; δ_H (200 MHz) 2.38 (6H, s, $ArCH_3$), 6.99 (4H, d, J=7.8 Hz, Ar*H*), 7.44–7.51 (6H, m, Ar*H*), 7.79 (2H, d, J=6.2 Hz, Anthryl*H*), 8.01 (2H, d, J=8.4 Hz, Anthryl*H*), 8.47 (1H, s, Anthryl*H*), 9.63 (1H, s, Anthryl*H*); δ_C (75.47 MHz) 21.6, 87.0 (*C*≡C), 95.1 (*C*≡C), 120.2, 121.7, 124.2, 125.2, 127.4, 128.7, 129.1, 130.3, 131.4, 131.5, 131.7, 138.2; *m/z*

(FAB) 407 ($(M+H)^+$, 56%), 406 (M^+, 100); ν_{max} (cm^{-1}) 2203 (C≡C); UV–Vis (nm) 257 (97 000), 264 (141 000), 285 (38 000), 308 (11 000), 323 (12 000), 355 (7 000), 375 (14 000), 395 (23 000), 418 (22 000); Fluorescence (nm) 386, 407, 429, 453, 480.

1,8-Di{2-[4-(dimethylthexyl)silyloxyphenyl]-1-ethynyl}-anthracene 11. The procedure was analogous to that for **9** except for the use of 4-iodophenol in place of 4-iodotoluene, and the reaction mixture was stirred for 1 h. After the extractive workup, the crude material was redissolved into dry THF (3 mL) along with dimethythexylsilyl chloride (0.10 mL, 0.508 mmol) and imidazole (0.040 g, 0.588 mmol). The resulting solution was refluxed for 4.5 h. The reaction mixture was cooled to room temperature, diluted with ether (10 mL) and washed with water (10 mL). The aqueous layer was re-extracted with ether (10 mL), the organic layers combined, dried and the solvent removed. Purification by flash chromatography [hexane/dichloromethane 5/1 (v/v), R_f 0.25] gave the title compound as a yellow oil that solidified on standing (0.016 g, 52%); mp 124.0–128.0 °C; Exact Mass Calcd for $C_{46}H_{55}O_2Si_2$: 695.3742, Found: 695.3757; δ_H (300 MHz) 0.26 (6H, s, ArOSi(C*H*$_3$)$_2$R), 0.96 (6H, d, *J*=6.8 Hz, (C*H*$_3$)$_2$CHR), 0.97 (6H, s overlap with 0.96, (CH$_3$)$_2$CHC(C*H*$_3$)$_2$SiR), 1.75 (1H, septet, *J*=6.8 Hz), 6.74 (4H, AA′ portion of AA′XX′, Ar*H*), 7.46 (2H, dd, *J*=6.9, 8.4 Hz, Anthryl*H*), 7.54 (4H, XX′ portion of AA′XX′, Ar*H*), 7.78 (2H, d, *J*=6.9 Hz, Anthryl*H*), 7.99 (2H, d, *J*=8.4 Hz, Anthryl*H*), 8.46 (1H, s, Anthryl*H*), 9.62 (1H, s, Anthryl*H*); δ_C (75.47 MHz) −2.3, 18.6, 20.1, 25.1, 34.0, 86.6 (*C*≡C), 95.0 (*C*≡C), 116.1, 120.3, 121.9, 124.2, 125.1, 127.3, 128.5, 130.2, 131.3, 131.5, 133.2, 156.0; *m/z* (LSIMS) 695 ($(M+H)^+$, 100%), 694 (M^+, 99); UV–Vis (nm) 258 (77 000), 266 (99 000), 287 (38 000), 314 (18 000), 357 (7 000), 377 (11 000), 397 (17 000), 420 (17 000); Fluorescence (nm) 387, 408, 432, 457, 485.

1,8-Di{2-[3-(methoxycarbonyl)phenyl]-1-ethynyl}anthracene 12. A solution containing methyl 3-iodobenzoate (0.331 g, 1.27 mmol), $Pd(PPh_3)_4$ (0.066 g, 0.06 mmol), **1** (0.130 g, 0.58 mmol) and CuI (0.011 g, 0.06 mmol) in a degassed solvent system of triethylamine (2 mL)/benzene (5 mL) was stirred at 50°C for 5 h. An extractive workup with THF (50 mL) gave an orange oil. Purification by squat column chromatography [dichloromethane, R_f 0.32] yielded the title compound as a yellow solid (281 mg, 99%). A small quantity was recrystallized from a THF/methanol mixture to give fine golden needles; mp 188.0–191.5 °C; Anal. Calcd for $C_{34}H_{22}O_4$: C, 82.58; H, 4.48, Found: C, 82.62; H, 4.42; δ_H (300 MHz) 3.85 (6H, s, ArCO$_2$C*H*$_3$), 7.16 (2H, t, *J*=7.8 Hz, Ar*H*), 7.50 (2H, dd, *J*=7.2, 8.7 Hz, Anthryl*H*), 7.67 (2H, dt, *J*=7.8, 1.8 Hz, Ar*H*), 7.83 (2H, dd, *J*=7.2, 1.2 Hz, Anthryl*H*), 7.96 (2H, dt, *J*=7.8, 1.8 Hz, Ar*H*), 8.04 (2H, d, *J*=8.7 Hz, Anthryl*H*), 8.26 (2H, t, *J*=1.8 Hz, Ar*H*), 8.49 (1H, s, Anthryl*H*), 9.58 (1H, s, Anthryl*H*); δ_C (75.47 MHz) (only 17 signals observed) 52.1, 88.6 (*C*≡C), 93.9 (*C*≡C), 121.2, 123.8, 124.0, 125.3, 127.7, 128.5, 129.3 (br), 130.6, 130.8, 131.5, 131.6, 132.8, 135.9; *m/z* (EI) 494 (M^+, 100%), 463 (3); ν_{max} (cm^{-1}) 1737 (C=O); UV–Vis (nm) 265 (109 000), 283 (29 000), 356 (4 000), 375 (9 000), 395 (16 000), 417 (16 000); Fluorescence (nm) 385, 407, 429, 453, 481.

1,8-Di{2-[3,5-di(methoxycarbonyl)phenyl]-1-ethynyl}-anthracene 13. A solution containing **5** (0.068 g, 0.0251 mmol), $Pd(PPh_3)_4$ (0.014 g, 0.0121 mmol), **1** (0.027 g, 0.114 mmol), DBU (0.20 mL, 1.34 mmol) and CuI (0.005 g, 0.0263 mmol) in degassed DMSO (5 mL) was stirred at 50°C for 40 min. An extractive workup with chloroform (30 mL) gave a yellow/orange solid. Purification by squat column chromatography [dichloromethane/ethyl acetate 5/1 (v/v), R_f ~0.50] yielded the title compound as a yellow solid (73 mg, 100%); mp 254.0–258.0 °C; Exact Mass Calcd for $C_{38}H_{26}O_8$: 610.1628, Found: 610.1583; δ_H (300 MHz) 3.83 (12H, s, ArCO$_2$C*H*$_3$), 7.51 (2H, dd, *J*=6.9, 8.4 Hz, Anthryl*H*), 7.83 (2H, d, *J*=6.9 Hz, Anthryl*H*), 8.06 (2H, d, *J*=8.4 Hz, Anthryl*H*), 8.30 (4H, d, *J*=1.8 Hz, Ar*H*), 8.49 (2H, t, *J*=1.8 Hz, Ar*H*), 8.50 (1H, s, Anthryl*H*), 9.57 (1H, s, Anthryl*H*); δ_C (75.47 MHz) (15 signals only) 52.3, 89.4 (*C*≡C), 93.1 (*C*≡C), 120.7, 123.9, 124.2, 125.2, 127.6, 129.5, 129.9, 130.8, 131.4, 131.5, 136.3, 165.1 (*C*=O); *m/z* (LSIMS) 611 ($(M+H)^+$, 69%), 610 (M^+, 100), 579 (39); ν_{max} (cm^{-1}) 2208 (C≡C), 1723 (C=O); UV–Vis (nm) 244 (53 000), 265 (116 000), 285 (40 000), 357 (7 000), 376 (13 000), 396 (20 000), 419 (18 000); Fluorescence (nm) 386, 407, 431, 456, 484.

1,8-Di{2-[3,5-bis([*tert*-butyldimethyl]siloxymethyl)phenyl]-1-ethynyl}anthracene 14. A solution containing **6** (0.134 g, 0.301 mmol), $Pd(PPh_3)_4$ (0.031 g, 0.0265 mmol), **1** (0.030 g, 0.133 mmol), triethylamine (0.10 mL, 1.38 mmol) and CuI (0.002 g, 0.0105 mmol) in degassed acetonitrile (3 mL) was stirred at 50°C for 1.5 h. An extractive workup with ether (20 mL) gave an orange oil. Purification by flash chromatography on reverse phase silica [acetonitrile/dichloromethane 2/1 (v/v), R_f 0.20] yielded the title compound as a yellow oil (20 mg, 16%); Exact Mass Calcd for $C_{58}H_{82}O_4Si_4$: 954.5290, Found: 954.5284; δ_H (200 MHz) 0.07 (6H, s, Si(C*H*$_3$)$_2$), 0.92 (9H, s, SiC(C*H*$_3$)$_3$), 4.47 (8H, s, ArC*H*$_2$OR), 7.37 (6H, br s, Ar*H*), 7.48 (2H, dd, *J*=7, 8.4 Hz, Anthryl*H*), 7.82 (2H, d, *J*=7 Hz, Anthryl*H*), 8.02 (2H, d, *J*=8.4 Hz, Anthryl*H*), 8.47 (1H, s, Anthryl*H*), 9.67 (1H, s, Anthryl*H*); δ_C (75.47 MHz) −5.6, 18.3, 25.9, 64.3 (Ar*C*H$_2$OR), 87.3 (*C*≡C), 95.6 (*C*≡C), 121.7, 122.8, 124.0, 124.3, 125.3, 127.4, 127.9, 128.5, 130.6, 131.5, 131.6, 141.8; *m/z* (LSIMS) 955 ($(M+H)^+$, 100%), 954 (M^+, 98%), 897 (24), 823 (31).

1,8-Di{2-[4-(dimethylthexyl)siloxy-3,5-(methoxycarbonyl)-phenyl]-1-ethynyl}anthracene 15. The procedure was analogous to that for **14** using **1** and **7**, and the reaction mixture was stirred at 50°C for 0.5 h. Instead of an extractive workup, the reaction mixture was filtered through a short squat column of silica, and the residue was washed with a 1:1 dichloromethane:ethyl acetate solution. The filtrate was concentrated in vacuo and further purification by flash chromatography on reverse phase silica [acetone/methanol (v/v), R_f 0.42] gave the title compound as a yellow solid (60%). A small quantity was reprecipitated from *i*-PrOH as a fine yellow powder; mp 190.0–196.0°C; Exact Mass Calcd for $C_{54}H_{63}O_{10}Si_2$: 927.3961, Found: 927.3886; δ_H (300 MHz) 0.00 (6H, s, Si(C*H*$_3$)$_2$), 0.96 (6H, d, *J*=6.6 Hz, SiC(CH$_3$)$_2$CH(C*H*$_3$)$_2$), 1.03 (6H, s, SiC(C*H*$_3$)$_2$), 1.76 (1H, septet, *J*=6.6 Hz, SiC(CH$_3$)$_2$C*H*(CH$_3$)$_2$), 3.77 (12H, s, ArCO$_2$C*H*$_3$), 7.49 (2H, dd, *J*=6.9, 8.4 Hz,

Anthrylʜ), 7.80 (2H, dd, J=0.9, 6.9 Hz, Anthrylʜ), 8.03 (2H, d, J=8.4 Hz, Anthrylʜ), 8.10 (4H, s, Arʜ), 8.49 (1H, s, Anthrylʜ), 9.57 (1H, s, Anthrylʜ); δ_C (75.47 MHz) −2.9, 18.3, 19.9, 25.1, 33.6, 52.0, 88.4 (C≡C), 93.1 (C≡C), 116.4, 121.2, 123.9, 125.3, 126.3, 127.6, 129.1, 130.8, 131.2, 137.9, 153.8, 165.9 (C=O); *m/z* (EI) 418 (M^+, 44%), 331 (98); ν_{max} (cm^{-1}) 1735 (C=O); UV–Vis (nm) 243 (44 000), 265 (12 000), 285 (40 000), 379 (13 000), 400 (21 000), 423 (20 000); Fluorescence (nm) 389, 409, 432, 456, 486.

1,8-Di{2-[3,5-di(methoxycarbonyl)-4-{[(trifluoromethyl)-sulphonyl]oxy}phenyl]-1-ethynyl}anthracene 16. A solution containing **8** (0.128 g, 0.272 mmol), $Pd(PPh_3)_4$ (0.016 g, 0.0138 mmol), **1** (0.030 g, 0.132 mmol), triethylamine (0.40 mL, 2.86 mmol) and CuI (0.002 g, 0.0100 mmol) in degassed DMF (2 mL) was stirred at 50°C for 9 h. An extractive workup with ether (40 mL) gave a yellow oil. Purification by flash chromatography on reverse phase silica [acetonitrile, R_f 0.38] yielded the title compound as a yellow solid (81 mg, 68%); mp 87.0–89.0 °C; Exact Mass Calcd for $C_{40}H_{24}O_{14}S_2F_6$: 906.0545, Found: 906.0539; δ_H (300 MHz) 3.90 (12H, s, $ArCO_2CH_3$), 7.53 (2H, dd, J=7.2, 8.4 Hz, Anthrylʜ), 7.86 (2H, dd, J=7.2, 0.9 Hz, Anthrylʜ), 8.09 (2H, d, J=8.4 Hz, Anthrylʜ), 8.32 (4H, s, Arʜ), 8.52 (1H, s, Anthrylʜ), 9.42 (1H, s, Anthrylʜ); δ_C (75.47 MHz) 53.0 ($ArCO_2CH_3$), 91.3 (C≡C), 91.7 (C≡C), 118.6 (q, J=324.5 Hz, $ArOSO_2CF_3$), 120.0, 123.2, 125.0, 125.2, 126.4, 128.0, 130.1, 131.1, 131.4, 131.9, 138.4, 145.3, 163.3 (C=O); *m/z* (LSIMS) 906 (M^+, 100%), 875 (19); ν_{max} (cm^{-1}) 1734 (C=O).

1,8-Di{2-[3-(bromomethyl)phenyl]-1-ethynyl}anthracene 17. A solution of **12** (0.085 g, 0.172 mmol) in dry THF (10 mL) was added dropwise with stirring to a cooled suspension of $LiAlH_4$ (0.020 g, 0.526 mmol) in dry THF (3 mL) at 0°C. The resulting suspension was allowed to warm to room temperature over 3 h with further stirring. The reaction mixture was quenched with 'wet' ether and then added to 1% HCl (10 mL). The organic layer was separated, and the aqueous layer re-extracted with ether (2×10 mL). The organic layers were combined, dried and the solvent removed. Purification by flash chromatography on reverse phase silica [acetonitrile/acetone 9/1 (v/v), R_f 0.41] gave 1,8-di{2-[3-(hydroxymethyl)phenyl]-1-ethynyl}-anthracene as a yellow solid (0.050 g, 81%); The compound was not characterized, but converted directly to **17**. A solution of dppe (0.032 g, 0.0795 mmol) in dry dichloromethane (2 mL) was cooled to 0°C before 0.2 M bromine in dichloromethane (0.80 mL, 0.159 mmol) was added over 10 mins with stirring. 1,8-di{2-[3-(hydroxymethyl)phenyl]-1-ethynyl}anthracene (0.029 g, 0.0662 mmol) in dry dichloromethane (3 mL) was then added and the reaction mixture allowed to warm to room temperature over 45 min. The reaction mixture was then diluted with dichloromethane (20 mL) and washed with sat. $Na_2S_2O_3$ (20 mL). The aqueous layer was re-extracted with dichloromethane (20 mL), the organic layers combined, dried and the solvent removed. Purification by flash chromatography [hexane/dichloromethane 2/1 (v/v), R_f 0.48] gave the title compound as a yellow solid (29 mg, 78%); mp 129.0–131.5°C; Exact Mass Calcd for $C_{32}H_{20}{}^{79}Br_2$: 561.9933, Found: 561.9910; δ_H (300 MHz) 4.31 (4H, s, $ArCH_2Br$), 7.12 (2H, t, J=7.5 Hz, Arʜ), 7.36 (2H, dd, J=1.8, 7.5 Hz, Arʜ), 7.49 (2H, dd, J=6.9, 8.4 Hz, Anthrylʜ), 7.60 (2H, t, J=1.8 Hz, Arʜ), 7.82 (2H, dd, J=1.2, 6.9 Hz, Anthrylʜ), 8.04 (2H, d, J=8.4 Hz, Anthrylʜ), 8.49 (1H, s, Anthrylʜ), 9.58 (1H, s, Anthrylʜ); δ_C (50.28 MHz) 32.6 ($ArCH_2Br$), 88.3 (C≡C), 94.2 (C≡C), 121.3, 123.9, 124.0, 125.3, 127.6, 129.0, 129.1, 129.2, 130.8, 131.5, 131.6, 131.8, 132.0, 138.2; *m/z* (EI) 566 (M^+, $^{81}Br^{81}Br$, 61%), 564 (M^+, $^{81}Br^{79}Br$, 100%), 562 (M^+, $^{79}Br^{79}Br$, 48%), 404 (27); UV–Vis (nm) 235 (43 000), 264 (127 000), 285 (38 000), 322 (11 000), 356 (8 000), 375 (13 000), 395 (20 000), 418 (19 000); Fluorescence (nm) 386, 406, 432, 451, 477.

6-Thia-1(1,8)-anthacena-4,8(1,3)-dibenzacyclodeca-2,9-diynaphane 18. To a solution of **17** (0.010 g, 0.0177 mmol) in a solvent mixture of dichloromethane (5 mL) and ethanol (1 mL), was added $Na_2S{\cdot}Al_2O_3$ (0.030 g, 0.0750 mmol) and the resulting suspension stirred at room temperature for 3 h. The reaction mixture was filtered and the solvent removed in vacuo. Purification by gravity column chromatography on reverse phase silica [acetonitrile/dichloromethane 4/1 (v/v), R_f 0.44] gave the title compound as a yellow solid (0.004 g, 50%); mp 230.0–233.0°C; Exact Mass Calcd for $C_{32}H_{20}S$: 436.1303, Found: 436.1299; δ_H (300 MHz) 3.45 (4H, s, $ArCH_2SCH_2Ar$), 7.44–7.62 (8H, m, Arʜ), 7.86 (2H, dd, J=1.8, 6.9 Hz, Anthrylʜ), 8.03 (2H, d, J=8.4 Hz, Anthrylʜ), 8.49 (1H, s, Anthrylʜ), 9.59 (1H, s, Anthrylʜ); δ_C (75.47 MHz) (only 16 signals observed) 33.1, 87.8 (C≡C), 94.6 (C≡C), 121.4, 122.9, 123.9, 125.2, 127.7, 129.1, 129.4, 129.5, 130.7, 131.3, 131.6, 132.6, 138.7; *m/z* (EI) 436 (M^+, 100%); ν_{max} (cm^{-1}) no significant absorption; UV–Vis (nm) 235 (24 000), 266 (80 000), 287 (35 000), 313 (10 000), 339 (6 000), 360 (5 000), 378 (9 000), 399 (15 000), 422 (14 000); Fluorescence (nm) 289, 410, 430, 456, 484.

1,8-Di{2-[3-(hydroxymethyl)phenyl]-1-ethynyl}-10-methoxyanthracene 22. A solution containing **19** (0.100 g, 0.217 mmol), $Pd(PPh_3)_4$ (0.025 g, 0.0217 mmol), **20** (0.060 g, 0.456 mmol) and CuI (0.004 g, 0.0217 mmol) in a degassed solvent system of piperidine (1 mL)/DMF (1 mL) was stirred at 40°C for 2 h. An extractive workup with ether (20 mL) gave an orange oil. Purification by squat column chromatography [ethyl acetate/dichloromethane 2/1 (v/v), R_f 0.40] yielded the title compound as a yellow solid (0.102 g, 100%). A small quantity was reprecipitated from a dichloromethane/hexane mixture to give a fluffy yellow powder; mp 91.5–93.0 °C; Exact Mass Calcd for $C_{33}H_{24}O_3$: 468.1725, Found: 468.1713; δ_H (200 MHz) 4.13 (3H, s, $ArOCH_3$), 4.33 (4H, s, $ArCH_2OH$), 7.17 (2H, t, J=8 Hz, Arʜ), 7.25–7.49 (8H, m, Arʜ), 7.75 (2H, dd, J=7.0, 1.0 Hz, Anthrylʜ), 8.27 (2H, d, J=6.8 Hz, Anthrylʜ), 9.37 (1H, s, Anthrylʜ); δ_C (50.28 MHz) 63.6, 64.3, 87.8 (C≡C), 94.5 (C≡C), 119.8, 121.7, 123.0, 123.4, 124.5, 125.0, 127.0, 128.6, 130.1, 130.8, 130.9, 132.0, 141.3, 153.3; *m/z* (LSIMS) 468 (M^+, 100%); ν_{max} (cm^{-1}) no significant absorption; UV–Vis (nm) 268 (118 000), 284 (36 000), 307 (15 000), 327 (12 000), 366 (6 000), 386 (11 000), 407 (18 000), 431 (17 000); Fluorescence (nm) 381, 396, 420, 447, 470, 497.

1,8-Di{2-[3,5-bis(hydroxymethyl)phenyl]-1-ethynyl}-10-methoxyanthracene 23. A solution containing **19** (0.100 g,

0.217 mmol), $Pd(PPh_3)_4$ (0.025 g, 0.0217 mmol), **21** (0.072 g, 0.446 mmol) and CuI (0.004 g, 0.0210 mmol) in a degassed solvent system of piperidine (1 mL)/DMF (2 mL) were stirred together at 50°C for 3 h. An extractive workup with ether (30 mL) gave a yellow solid. Purification by flash chromatography [ethylacetate/methanol 9/1 (v/v), R_f 0.49] yielded the title compound as a yellow solid (0.114 g, 100%); mp 174.0–177.0 °C; Exact Mass Calcd for $C_{35}H_{28}O_5$: 528.1936, Found: 528.1942; δ_H (300 MHz, $CDCl_3$/d_6-DMSO) 3.94 (3H, s, ArOCH_3), 4.18 (8H, d, J=5.7 Hz, ArCH_2OH), 7.19 (4H, br s, ArH), 7.30 (2H, dd, J=8.4, 6.6 Hz, Anthryl$H$), 7.56 (2H, d, J=6.6 Hz, Anthryl$H$), 7.77 (2H, br s, ArH), 8.08 (2H, d, J=8.4 Hz, Anthryl$H$), 9.15 (1H, s, Anthryl$H$); δ_C (75.47 MHz, $CDCl_3$/d_6-DMSO) 62.6, 62.8, 86.3 (C≡C), 94.7 (C≡C), 118.6, 120.8, 121.7, 122.2, 123.5, 124.3, 124.8, 127.7, 130.1, 131.0, 141.7, 152.5; m/z (EI) 528 (M^+, 100%); ν_{max} (cm^{-1}) (film) 2203 (C≡C); UV–Vis (nm) 268 (59 000), 286 (27 000), 309 (14 000), 366 (4 000), 386 (6 000), 408 (9 000), 433 (8 000); Fluorescence (nm) 398, 422, 445, 468, 502.

1,8-Di{2-[3-(bromomethyl)phenyl]-1-ethynyl}-10-methoxyanthracene 24. A solution of **22** (0.050 g, 0.107 mmol) in dry THF (5 mL) was cooled to −20°C before PPh_3 (0.059 g, 0.214 mmol) and NBS (0.040 g, 0.224 mmol) were added. The reaction mixture was then allowed to warm to room temperature over 2 h with stirring. The reaction was quenched by addition to sat. $NaHCO_3$ (20 mL), followed by extraction with ether (2x20 mL). The organic layers were combined, dried and the solvent removed. Purification by flash chromatography [hexane/dichloromethane 2/1 (v/v), R_f 0.30] gave the title compound as a yellow solid (0.035 g, 56%); mp 135.0–137.0 °C; Exact Mass Calcd for $C_{33}H_{22}O^{79}Br_2$: 592.0038, Found: 592.0016; δ_H (200 MHz) 4.18 (3H, s, ArOCH_3), 4.31 (4H, s, ArCH_2Br), 7.14 (2H, t, J=7.6 Hz, ArH), 7.34–7.38 (2H, m, ArH), 7.45–7.59 (4H, m, ArH), 7.81 (2H, dd, J=1 and 6.8 Hz, Anthryl$H$), 8.34 (2H, dt, J=1, 7.8 Hz, Anthryl$H$), 9.40 (1H, s, Anthryl$H$); δ_C (50.28 MHz) 32.6, 63.7, 88.3 (C≡C), 94.4 (C≡C), 119.8, 121.6, 123.4, 123.9, 124.6, 125.1, 129.0, 129.1, 130.9, 131.8, 132.0, 132.1, 138.2, 153.5; m/z (LSIMS) 596 (M^+, $^{81}Br^{81}Br$, 58%), 594 (M^+, $^{81}Br^{79}Br$, 100%), 592 (M^+, $^{79}Br^{79}Br$, 44%); UV–Vis (nm) 268 (141 000), 287 (32 000), 312 (12 000), 327 (12 000), 366 (7 000), 386 (14 000), 408 (22 000), 432 (21 000); Fluorescence (nm) 381, 396, 420, 447, 470, 497.

1,8-Di{2-[3,5-bis(bromomethyl)phenyl]-1-ethynyl}-10-methoxyanthracene 25. The procedure was analogous to that for **24** using **23**, and allowing the reaction mixture to warm to room temperature over 1.5 h. Purification by flash chromatography [hexane/dichloromethane 3/2 (v/v), R_f 0.38] gave the title compound as a yellow solid (64%); mp 182.5–186.5 °C; Exact Mass Calcd for $C_{35}H_{24}O^{79}Br_4$: 775.8563, Found: 775.8587; δ_H (300 MHz) 4.18 (3H, s, ArOCH_3), 4.21 (8H, s, ArCH_2Br), 7.38 (2H, t, J=1.5 Hz, ArH), 7.48 (4H, d, J=1.5 Hz, ArH), 7.52 (2H, dd overlap with 7.48, J=6.9, 8.7 Hz, Anthryl$H$), 7.82 (2H, d, J=6.9 Hz, Anthryl$H$), 8.35 (2H, d, J=8.7 Hz, Anthryl$H$), 9.37 (1H, s, Anthryl$H$); δ_C (50.28 MHz) 32.0, 63.7, 88.9 (C≡C), 93.8 (C≡C), 119.6, 121.3, 123.5, 124.4, 124.5, 125.0, 129.7, 131.0, 131.9, 132.0, 138.9, 153.5; m/z (LSIMS) 780 (within M^+ and $(M+H)^+$ cluster) (M^+, 100%); UV–Vis (nm) 238 (55 000), 268 (122 000), 290 (32 000), 313 (11 000), 328 (10 000), 367 (6 000), 388 (12 000), 409 (20 000), 433 (18 000); Fluorescence (nm) 381, 396, 422, 450, 471, 505.

1,8-Di{2-[2-(4-[2-{3-(hydroxymethyl)phenyl}-1-ethynyl]-3-(hydroxymethyl)phenyl)-1-ethynyl]-1-ethynyl}-10-methoxyanthracene 27. A solution of **19** (0.050 g, 0.108 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.0113 mmol), 26 (0.058 g, 0.221 mmol) and CuI (0.002 g, 0.0105 mmol) in a degassed solvent system of piperidine (0.5 mL)/DMF (2 mL) was stirred at 40°C for 1 h. An extractive workup with a 3:1 ether/THF mixture (20 mL) gave a yellow solid. Purification by squat column chromatography [ethyl acetate, R_f 0.40] yielded the title compound as a yellow solid. The compound was not characterized but converted directly to the tetra-bromomethyl compound **30**.

1,8-Di{2-[2-(4-[2-{3-(bromomethyl)phenyl}-1-ethynyl]-3-(bromomethyl)phenyl)-1-ethynyl]-1-ethynyl}-10-methoxyanthracene 28. A solution of dppe (0.130 g, 0.326 mmol) in dry THF (10 mL) was cooled to 0°C before 0.2 M bromine in chloroform (2.72 mL, 0.543 mmol) was added over 10 min with stirring. Crude **27** dissolved in dry THF (6 mL) was then added and the reaction mixture allowed to warm to room temperature over 1 h. The reaction mixture was then diluted with chloroform (20 mL) and washed with sat. $Na_2S_2O_3$ (20 mL). The aqueous layer was re-extracted with chloroform (20 mL), the organic layers combined, dried and the solvent removed. Purification by flash chromatography [hexane/dichloromethane 1/1 (v/v), R_f 0.45] gave the title compound as a yellow solid (0.093 g, 89% 2 steps); mp 180.0–183.0°C; Exact Mass Calcd for $C_{51}H_{32}O^{79}Br_4$: 975.9189, Found: 975.9147; δ_H (300 MHz) 4.19 (3H, s, ArOCH_3), 4.37 (4H, s, ArCH_2Br), 4.55 (4H, s, ArCH_2Br), 7.18 (2H, t, J=8.1 Hz, ArH), 7.31–7.56 (10H, m, ArH), 7.64 (2H, d, J=1.5 Hz, ArH), 7.82 (2H, dd, J=0.9, 6.9 Hz, Anthryl$H$), 8.35 (2H, d, J=9 Hz, Anthryl$H$), 9.37 (1H, s, Anthryl$H$); δ_C (75.47 MHz) 31.2, 32.6, 63.8, 86.7 (C≡C), 90.1 (C≡C), 94.3 (C≡C), 96.5 (C≡C), 119.7, 121.3, 123.0, 123.3, 123.6, 123.7, 124.5, 125.0, 128.9, 129.4, 120.9, 131.5, 131.6, 131.9, 132.1, 132.6, 132.7, 138.1, 139.6, 153.5; m/z (LSIMS) 980 (within M^+ isotope cluster) (M^+, 100%); UV–Vis (nm) 245 (60 000), 267 (96 000), 319 (71 000), 391 (19 000), 414 (27 000), 438 (25 000); Fluorescence (nm) 397, 430, 457, 480.

Dimethyl 5-ethynylisophthalate 29. A solution of dimethyl 5-(trimethylsilylethynyl)isophthalate[20] (0.200 g, 0.690 mmol) in methanol (10 mL) was stirred with potassium carbonate (0.010 g, 0.0725 mmol) at room temperature for 2 h. The suspension was filter and the solvent removed in vacuo to give a fawn solid. The crude product was sublimed at 120°C/0.02 mmHg to give the title compound as a colourless solid (0.130 g, 87%); mp 130.0–131.0°C with rapid heating; Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62, Found: C, 65.96; H, 4.60; δ_H (200 MHz) 3.18 (1H, s, ArC≡CH), 3.96 (6H, s, ArCO$_2$CH_3), 8.32 (2H, d, J=1.8 Hz, ArH), 8.65 (1H, t, J=1.8 Hz, ArH); δ_C (50.28 MHz) 52.5 (ArCO$_2$CH_3), 79.1 (C≡C), 81.5 (C≡C), 123.2, 130.7, 131.0, 137.0, 165.5 (C=O); m/z (EI) 218 (M^+, 63%), 187 (100), 159 (18),

144 (19); ν_{max} (cm^{-1}) 3249 (C–H of ArC≡C–H), 2104 (C≡C), 1727 (C=O).

1,8-Di{2-[2-(4-[2-{3,5-di(methoxycarbonyl)phenyl}-1-ethynyl]-3,5-di(methoxycarbonyl)phenyl)-1-ethynyl]-1-ethynyl}anthracene 30. A solution containing 16 (0.069 g, 0.0762 mmol), $Pd(PPh_3)_4$ (0.018 g, 0.0156 mmol), 29 (0.035 g, 0.161 mmol), triethylamine (0.11 mL, 0.791 mmol) and CuI (0.003 g, 0.0158 mmol) in degassed DMF (3 mL) was stirred at 80°C for 7 h. An extractive workup with dichloromethane (40 mL) gave a yellow solid. Purification by flash chromatography [dichloromethane/ethylacetate 9/1 (v/v), R_f 0.37] yielded the title compound as a yellow solid (0.035 g, 44%); mp 294.0–296.0 °C; Exact Mass Calcd for $C_{62}H_{43}O_{16}$: 1043.2553, Found: 1043.2511; δ_H (300 MHz) 3.94 (12H, s, $ArCO_2CH_3$), 3.95 (12H, s, $ArCO_2CH_3$), 7.54 (2H, dd, J=7.2, 8.7 Hz, Anthryl*H*), 7.84 (2H, d, J=7.2 Hz, Anthryl*H*), 8.09 (2H, d, J=8.7, Anthryl*H*), 8.18 (8H, m, Ar*H*), 8.44 (2H, t, J=1.8 Hz, Ar*H*), 8.53 (1H, s, Anthryl*H*), 9.58 (1H, s, Anthryl*H*); δ_C (75.47 MHz) 52.4 ($ArCO_2CH_3$), 52.6 ($ArCO_2CH_3$), 87.6 (*C*≡C), 91.4 (*C*≡C), 93.3 (*C*≡C), 99.4 (*C*≡C), 120.7, 121.6, 123.0, 123.9, 124.3, 125.3, 127.7, 129.8, 130.3, 130.7, 130.8, 131.4, 131.5, 134.7, 135.8, 136.5, 165.2 (*C*=O), 165.4 (*C*=O); *m/z* (LSIMS) 1043 ($(M+H)^+$, 100%); ν_{max} (cm^{-1}) (CH_2Cl_2 solution) 1730 (broad C=O); UV–Vis (nm) 250 (74 000), 260 (75 000), 324 (65 000), 386 (20 000), 406 (27 000), 428 (23 000); Fluorescence (nm) 395, 445, 469.

1,8-Di{2-[3,5-bis(morpholinomethyl)-4-hydroxyphenyl]-1-ethynyl}anthracene 32. A solution of **31**[5] (1.22 g, 2.92 mmol), $Pd(PPh_3)_4$ (0.16 g, 0.29 mmol), **1** (0.32 g, 1.39 mmol) and CuI (26 mg, 0.29 mmol) in degassed piperidine (15 mL) was stirred at room temperature for 1 h. An extractive workup with dichloromethane (200 mL) gave an orange oil. Purification by flash chromatography on silica gel [acetone, R_f 0.43] yielded the title compound as a light orange oil (1.07 g, 95%); Exact Mass Calcd for $C_{50}H_{55}N_4O_6$: 807.4123, Found: 807.4246; δ_H (300 MHz) 2.46 (16H, t, J=4.2 Hz), 3.39 (8H, s, $ArCH_2R$), 3.71 (16H, t, J=4.2 Hz), 7.34 (4H, s, Ar*H*), 7.45 (2H, dd, J=6.9 and 8.4 Hz, Anthryl*H*), 7.77 (2H, d, J=6.9 Hz, Anthryl*H*), 7.97 (2H, d, J=8.4 Hz, Anthryl*H*), 8.44 (1H, s, Anthryl*H*), 9.62 (1H, s, Anthryl*H*); δ_C (75.47 MHz) 53.1, 58.7, 66.7 ($ArCH_2R$), 86.3 (*C*≡C), 95.2 (*C*≡C), 113.6, 121.9, 122.6, 124.2, 125.2, 127.3, 128.5, 130.0, 131.3, 131.6, 132.6, 156.7 (*Ar*OH); *m/z* (FAB) 807 ($(M+H)^+$, 5%), 806 (7); ν_{max} (cm^{-1}) 2192 (C≡C).

1,8-Di{2-[3,5-bis(acetoxymethyl)-4-acetoxyphenyl]-1-ethynyl}anthracene 33. A solution of **32** (1.12 g, 1.39 mmol) in acetic anhydride (20 mL) and acetic acid (0.5 mL) was refluxed for 17 h. The reaction mixture was concentrated in vacuo and taken up into dichloromethane (100 mL), washed with sat. Na_2CO_3 (2x50 mL) and water (50 mL). The solvent was dried and removed to give an orange oil. Purification by flash chromatography on silica gel [dichloromethane/ethyl acetate 5/1 (v/v), R_f 0.36] gave the title compound as an orange solid (0.37 g, 34%); mp 52.5–55.0°C; Exact Mass Calcd for $C_{40}H_{38}O_{12}$: 782.2363, Found: 782.2378; δ_H (300 MHz) 2.04 (12H, s, $ArCH_2OCOCH_3$), 2.36 (6H, s, $ArOCOCH_3$), 4.83 (8H, s, $ArCH_2$OAc), 7.46 (2H, dd, J=7.2 and 8.7 Hz, Anthryl*H*), 7.65 (4H, s), 7.80 (2H, d, J=7.2 Hz, Anthryl*H*), 7.98 (2H, d, J=8.7 Hz, Anthryl*H*), 8.41 (1H, s), 9.54 (1H, s); δ_C (75.47 MHz) 20.2 (CH_3OR), 20.4 (CH_3OR), 60.6 ($ArCH_2OAc$), 88.6 (*C*≡C), 93.6 (*C*≡C), 121.1, 121.7, 123.9, 125.2, 127.6, 129.3, 130.0, 130.8, 131.4, 131.5, 133.0, 147.4 (*Ar*OAc), 168.6(*C*=O), 170.3 (*C*=O) *m/z* (EI) 782 (M^+, 24%); ν_{max} (cm^{-1}) 1764, 1747, 1731 (C=O); UV–Vis (nm) 266 (109 000), 274 (37 000), 286 (48 000), 358 (7 000), 377 (12 000), 399 (19 000), 420 (18 000); Fluorescence (nm) 387, 410, 429, 454, 484.

1^2,5^2-Dihydroxy-1^3,5^3-bis(hydroxymethyl)-3-oxa-8(1,8)-anthracena-1,5(1,5)-dibenzacyclodeca-6,9-diynaphane 34. A solution of **33** (0.050 g, 0.0639 mmol) in THF (3 mL) and 2 M H_2SO_4 (1 mL) was refluxed for 48 h. The reaction mixture was diluted with ether (10 mL) and washed with water (20 mL). The aqueous layer was then extracted with ether (3×10 mL) and the organic layers combined, dried and the solvent removed. Purification by squat column chromatography [ethyl acetate, R_f 0.56] gave the title compound as a yellow solid (0.019 g, 56%); mp >307.0°C with decomposition; Exact Mass Calcd for $C_{34}H_{24}O_5$: 512.1624, Found: 512.1597; δ_H (600 MHz, d_6-acetone) 4.88 (4H, s), 5.07 (4H, s), 7.65 (2H, d, J=1.8 Hz, Ar*H*), 7.72 (2H, dd, J=7.2, 8.4 Hz, Anthryl*H*), 7.93 (2H, d, J=1.8 Hz, Ar*H*), 8.03 (2H, d, J=7.2 Hz, Anthryl*H*), 8.28 (2H, d, J=8.4 Hz, Anthryl*H*). 8.84 (1H, s, Anthryl*H*), 9.61 (1H, s, Anthryl*H*); δ_C (75.47 MHz) 62.6, 65.75, 86.4 (*C*≡C), 95.7 (*C*≡C), 114.4, 122.3, 123.8, 125.1, 125.9, 127.7, 128.7, 129.3, 131.2, 131.6, 131.7, 132.3, 133.1, 155.8; *m/z* (LSIMS) 512 (M^+, 30%), 495 (7); UV–Vis (nm) 235 (34 000), 259 (61 000), 268 (66 000), 290 (34 000), 361 (6 000), 382 (9 000), 403 (13 000), 427 (12 000); Fluorescence (nm) 446, 467, 490.

1^{10}-Methoxy-6-thia-1(1,8)-anthracena-4,8(1,3)-dibenzacyclodeca-2,9-diynaphane 35. To a suspension of $Na_2S{\cdot}Al_2O_3$ (0.060 g, 0.152 mmol) in ethanol (3 mL) was added **24** (0.030 g, 0.0505 mmol) in CH_2Cl_2 (5 mL) via a syringe pump over 2.5 h. After addition was complete, the reaction mixture was allowed to stir for 0.5 h before an extra quantity of $Na_2S{\cdot}Al_2O_3$ (0.030 g, 0.0760 mmol) was added and the suspension stirred for a further 1 h. The reaction mixture was filtered and the solvent removed in vacuo. Purification by flash chromatography on alumina [hexane/ethyl acetate 20/1 (v/v), R_f 0.50] gave the title compound as a yellow solid (85%). A small sample was recrystallized from an ethyl acetate/hexane mixture as small orange prisms; mp 236.0–238.5°C; Exact Mass Calcd for $C_{33}H_{22}OS$: 466.1391, Found: 466.1386; δ (300 MHz) 3.43 (4H, s, $ArCH_2SCH_2Ar$), 4.16 (3H, s, $ArOCH_3$), 7.42–7.59 (10H, m, Ar*H*), 7.84 (2H, d, J=6.9 Hz, Anthryl*H*), 8.31 (2H, d, J=8.7 Hz, Anthryl*H*), 9.39 (1H, s, Anthryl*H*); δ_C (75.47 MHz) 32.9, 63.6, 87.9 (*C*≡C), 94.8 (*C*≡C), 119.7, 121.8, 122.9, 123.2, 124.6, 125.0, 129.4, 129.5, 130.8, 131.5, 131.9, 132.7, 138.7, 153.5; *m/z* (EI) 466 (M^+, 98%), 451 (100); ν_{max} (cm^{-1}) no significant absorption; UV–Vis (nm) 269 (11 000), 289 (40 000), 343 (7 000), 369 (7 000), 390 (13 000), 411 (21 000), 436 (21 000); Fluorescence (nm) 380, 398, 423, 449, 473, 503.

1^{10}-Methoxy-6^1-(4-methylphenyl)sulphonyl-6-aza-1(1,8)-

anthracena-4,8(1,3)-dibenzacyclodeca-2,9-diynaphane 36. To a solution of **24** (0.022 g, 0.0370 mmol) in dry DMF (3 mL) was added TosNHNa (0.011 g, 0.0555 mmol) and the resulting solution stirred at 50°C for 1 h. The reaction mixture was added to water (20 mL) and extracted with ether (20 mL). The organic layers were combined, dried and the solvent removed. Purification by flash chromatography on silica [hexane/dichloromethane 1/1 (v/v), R_f 0.30] gave the title compound as a yellow solid (0.022 g, 100%); mp 155.0–160.0°C; Exact Mass Calcd for $C_{40}H_{29}O_3NS$: 603.1885, Found: 603.1927; δ_H (200 MHz) 2.48 (3H, s, ArCH_3), 4.17 (3H, s, ArOCH_3), 4.24 (4H, s, ArCH_2R), 7.18 (2H, dt, J=1.5, 7.8 Hz, ArH), 7.29–7.39 (4H, m, ArH), 7.48–7.58 (6H, m, ArH), 7.82–7.84 (4H, m, ArH), 8.32 (2H, dt, J=1.2, 8.7 Hz, Anthryl$H$), 9.34 (1H, s, Anthryl$H$); δ_C (105.87 MHz) (22 signals only) 21.6, 49.3, 63.7, 88.0 (C≡C), 94.4 (C≡C), 119.6, 121.6, 123.1, 123.2, 124.5, 124.9, 127.3, 129.2, 129.8, 131.2, 131.5, 131.9, 132.6, 135.8, 137.9, 143.6, 153.4; m/z (LSIMS) 604 $((M+H)^+$ and isotopes of M^+, 73%), 603 (M^+, 100).

4(1,8)-Anthracena-1,7(1,3,5)-dibenza-9,12-dithiabicyclo-[5.3.3]trideca-2,5-diynaphane 37. The procedure was analogous to that for **35** using **25**, and purification by flash chromatography on silica [chloroform/hexane 3/5 (v/v), R_f 0.48] gave the title compound as a yellow solid (trace <1 mg); Exact Mass Calcd for $C_{35}H_{24}OS_2$: 524.1269, Found: 524.1263; δ_H (300 MHz, $CDCl_3$/d_6-DMSO) 3.83 (4H, A portion of AB, J=15 Hz, ArCH_AH$_B$SR), 3.87 (4H, B portion of AB, J=15.0 Hz, ArCH$_A$$H_B$SR), 4.18 (3H, s, ArOC$H_3$), 7.10 (2H, br s, Ar$H$), 7.35 (4H, br s, Ar$H$), 7.50 (2H, dd, J=6.9, 9.0 Hz, Anthryl$H$), 7.66 (2H, d, J=6.9 Hz, Anthryl$H$), 8.31 (2H, d, J=9.0 Hz, Anthryl$H$), 9.29 (1H, s, Anthryl$H$); m/z (EI) 524 (M^+, 100%).

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