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Preparation of Sterically Constrained Arylalkynes

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Abstract: The preparation of a series of sterically constrained phenyleneethynylenes is described. Restricting the interannular rotation significantly narrows the lowest energy absorption and increases its extinction coefficient in the UV/VIS spectrum. © 1997 Elsevier Science Ltd.

INTRODUCTION

Poly(phenyleneethynylenes) are highly conjugated, organic polymers exhibiting interesting optoelectronic properties and the potential to be incorporated into nonlinear optical devices and chemical probes. Numerous publications have described the synthesis and physical properties of poly(phenyleneethynylenes) and their corresponding second[1]- and third-order[2,3] nonlinearities. Modifications to the poly(phenyleneethynylene) template have involved the use of solubilising side-chains to improve the processing of the polymer and the addition of donor-acceptor groups to increase the polarizability of the π-electrons within the polymer. In addition, oligo(phenyleneethynylenes) have been used for the construction of fluorescent chemosensors[4], cyclophanes[5] and molecular turnstiles[6].

Several theoretical studies of conjugation length and optical nonlinearity indicate a saturation response at finite length, that is, the effective conjugation length is observed to approach a maximum after a specified number of repeat units, rather than continuing to increase with molecular weight.[7] The optimum effective conjugation length for poly(thiophene) has been reported to be 9-10 repeat units[8] (corresponding to a similar maxima in the response for the third order optical nonlinearity), while the UV/VIS absorption spectra for a series of oligo(*p*-phenylenes) demonstrated no increase in the position of the maximum wavelength after 3 repeat units[9,10]. This restriction on the effective conjugation length has been attributed to rotations around single bonds in the materials which disrupts the conjugation.[11] It has been shown for poly(ethenylthiophene) that introduction of side-chains which restrict the interannular rotations around the single bond result in a significant reduction in the bandgap of the resulting conducting polymer.[12]

For a tolane containing a donor and an acceptor group in the para positions, the phenyl rings were

observed to be coplanar with respect to each other in the solid state.[13] Calculations have shown that twisting around the ethyne linkage from a planar to orthogonal geometry requires 0.3 kcal/mol, and in the gas and solution phase the actual conformation is an equilibrium mixture somewhere between coplanar and orthogonal.[14]

We wish to report in this paper the preparation and physical properties of a number of sterically constrained *o*, *o*'-dihydroxytolane derivatives based on the template shown in Figure 1. In the following paper we report on the synthesis of a series of oligo(phenyleneethynylenes) with dioxaalkyl linker arms also based on the template in Figure 1.

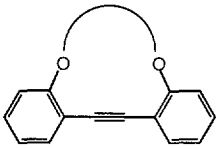


Figure 1

RESULTS AND DISCUSSION

Low level geometry optimizations[15] were performed on a variety of structures based on *o*, *o*'-dihydroxytolane. The two parameters which were of interest in terms of the influence of geometry on the physical properties where the dihedral angle β, which gives a measure of the distortion in the linear alkyne unit, and the angle α, which measures the internal distortion from coplanarity between the two aromatic rings (Figure 2). The results of these theoretical studies, combined with synthetic feasibility and chemical stability, suggested that the compounds shown in Figure 3 should display near planarity of the two aromatic rings with varying degrees of bending of the alkynyl unit. These calculations for geometry optimizations are only approximations and in solution at room temperature a variety of conformations would be available. Compounds that exist predominantly in a conformation with $\alpha = 0°$ and $\beta = 180°$ would be of particular interest as their UV/VIS spectra should display a narrow, low energy absorption with a significant extinction coefficient.

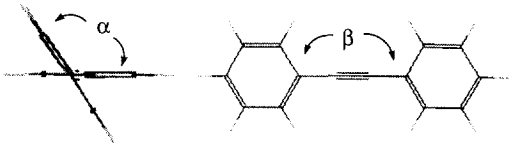
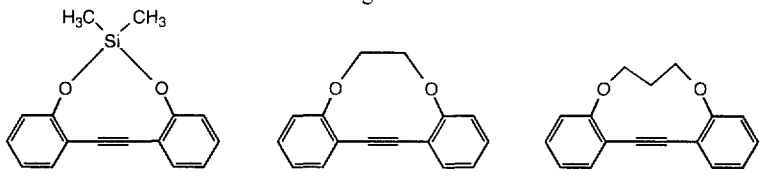


Figure 2



α = 2°
β = 167°

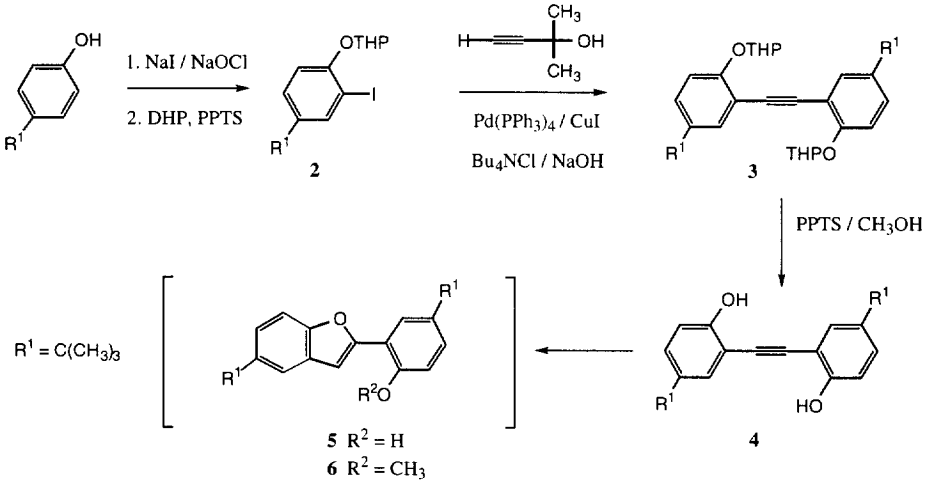
α = 13.5°
β = 172.5°

α = 1.1°
β = 178.3°

Figure 3

Initially a common tolane template was to be used with the expectation that subsequent derivatization could be accomplished with suitable length linker groups. This would allow for a comparison of the chemical and physical differences of various linker units and their effect on the electronic properties of the tolane. A key feature in the preparation of these materials was the synthesis of a common, functionalised tolane precursor with a *tert*-butyl substituent on the aromatic ring to improve material solubility. In recent years, the most favoured method for the preparation of tolanes has been palladium mediated reaction using either copper (I) catalysed terminal alkyne coupling[16] or Stille coupling[17].

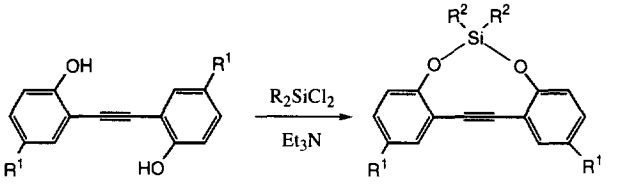
4-*tert*-Butylphenol was iodinated[18] in moderate yield, 61%, and protected as the THP ether in 96% to give **2** (Scheme 1). 2-Methyl-3-butyn-2-ol was coupled with two equivalents of **2** in a "single pot" reaction using a standard palladium catalysed coupling protocol[19] and gave the tolane derivative **3** as a pale yellow solid in moderate yield (58%, Scheme 1) which could be deprotected to give **4** as a white solid in high yield (88%). Appreciable quantities (up to 24%) of the benzofuran **5** were obtained when reaction times longer than 12 hours were used. Benzofuran **5** was converted into the corresponding methyl ether for complete characterization and X-ray diffraction analysis showed that the phenyl ring was coplanar with the benzofuran substituent.[20] This unwanted cyclisation could be minimised by constant monitoring of the reaction mixture by tlc and immediate workup when **3** had all been deprotected.



Scheme 1

Silylene Bridges

Silylene ethers of diols have been prepared by reacting the diol with diorganosilyl halides in the presence of a suitable base[21]. *o*, *o*'-Dihydroxytolanes, **4** and **7**, were treated with either dimethyldichlorosilane or diphenyldichlorosilane in the presence of triethylamine and gave the desired silylenes, **8**, **9** or **10**, in good yield (Scheme 2). Each of the silylenes was hydrolysed to the corresponding starting diol on silica and alumina, however chromatography employing a Florisil support allowed removal of amine salts and other polar impurities with minimal hydrolysis.

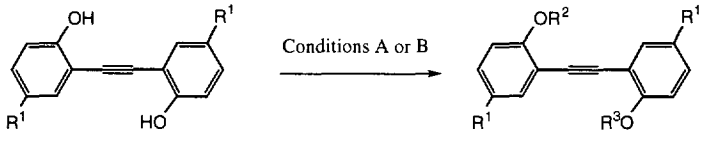


4 $R^1 = C(CH_3)_3$
7 $R^1 = H$

8 $R^1 = C(CH_3)_3$ $R^2 = CH_3$
9 $R^1 = H$ $R^2 = CH_3$
10 $R^1 = H$ $R^2 = Ph$

Scheme 2

Based on steric hindrance, the larger di-*tert*-butyl substituted silylenes should be more resistant to hydrolysis than the corresponding dimethyl or diphenylsilyl derivatives. In an attempt to improve product stability, di-*tert*-butylsilylbistriflate was reacted with **4** but afforded the silynol **11** in 71% as the only isolated product (Condition A, Scheme 3). This material was observed to be stable on exposure to silica and was purified by chromatography. In order to compare the spectroscopic properties of sterically constrained tolanes with analogous non-constrained materials, **4** was reacted with dimethylthexylsilyl chloride in the presence of hydroxybenzotriazole[22] and triethylamine and gave **12** in quantitative yield (Condition B, Scheme 3). Compound **12** was stable to silica and could be purified by chromatography. Attempts to improve the silylene bridge stability were not successful, presumably because steric hindrance and strain associated with the bridge disfavoured their formation.



4 $R^1 = C(CH_3)_3$

Condition A ⟶ **11**
Condition B ⟶ **12**

Condition A **4**, $[(CH_3)_3C]_2Si(OTf)_2$, dimethylpyridine
Condition B **4**, thexyl$(CH_3)_2SiCl$, hydroxybenztriazole

11 $R^2 = H$ $R^3 = Si(OH)(C(CH_3)_3)_2$
12 $R^2 = R^3 = Si(CH_3)_2$thexyl

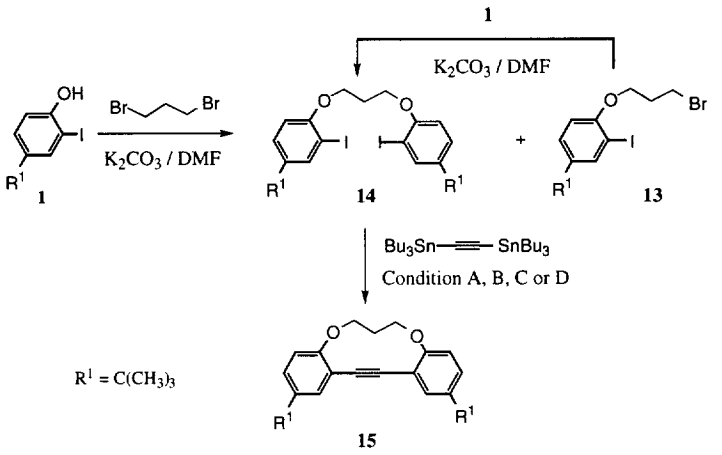
Scheme 3

Dioxaalkyl Bridges

The Williamson ether synthesis has traditionally been used to prepare cyclophane alkyl-aryl ethers.[23] Attempts to react **4** with 1,2-dichloro or dibromoethane in the presence of potassium carbonate in DMF/water gave, as the only isolated product, benzofuran **5** (65-70%). It was clear that this route was not appropriate due to competing base-catalysed eliminations and benzofuran cyclizations.[24]

An alternate route was pursued for the dioxaalkyl tolanes with the linker arm in place prior to the introduction of the triple bond (Scheme 4). Alkylation of 2-iodo-4-*tert*-butylphenol **1** with 1,3-dibromo propane gave **13** in 53% yield and **14** in 5% yield. The bromoether **13** was converted into the desired diether **14** in 38% yield on subsequent treatment with excess **1**. Stille coupling between bis(tributylstannyl) acetylene and **14** was carried out under a variety of conditions (Scheme 4). While $Pd(AsPh_3)_4$ has been reported to enhance some Stille couplings[25], only polymeric byproducts, presumably formed from intermolecular coupling between **14** and the stannane, were observed (Condition A, Scheme 4). The

ligandless catalyst $(CH_3CN)_2PdCl_2$ decomposed rapidly and only starting material was isolated on workup (Condition B, Scheme 4). Coupling with $Pd(PPh_3)_4$ in DMF failed to afford **15**, with intermolecular polymeric byproducts forming (Condition C, Scheme 4). $Pd(PPh_3)_4$ in THF was the most suitable system affording **15** in low yield at either 0.002M (25%) or 0.03M (18%), (Condition D, Scheme 4).



Condition A: $Pd(AsPh_3)_4$, 60°C, THF (0.03M) → 15 in 0%, polymer formation

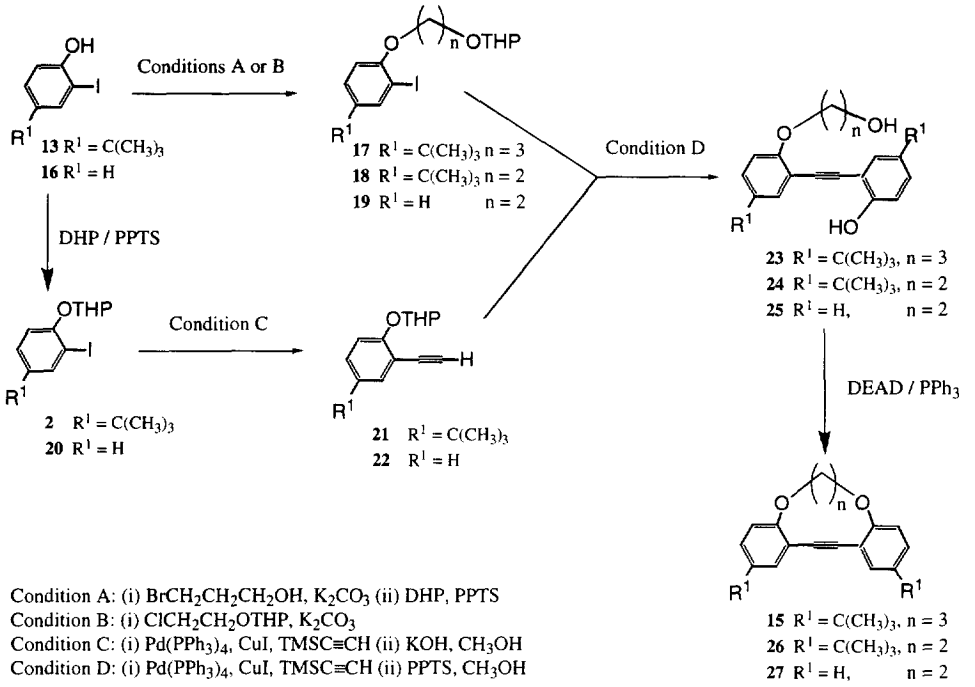
Condition B: $(CH_3CN)_2PdCl_2$, RT, DMF (0.03M) → 15 in 0%, catalyst decomposed

Condition C: $Pd(PPh_3)_4$, 80°C, DMF (0.03M) → 15 in 0%, polymer formation

Condition D: $Pd(PPh_3)_4$, 70°C, THF (either 0.0002M or 0.03M) → 15 in 18 – 25%

Scheme 4

An alternative method for the preparation of **15** was sought which would be generally applicable for different ring sizes and provide higher yields of the cyclophane (Scheme 5). Alkylation of **1** with 3-bromopropanol gave the unprotected analogue of **17** in 87% yield. Subsequent protection of the primary hydroxyl as a THP ether was smoothly accomplished in 98% (Condition A, Scheme 5). $Pd(PPh_3)_4$/CuI catalysed coupling between **2** and trimethylsilylacetylene was complete in 3 hours at room temperature and delivered a quantitative yield of the trimethylsilyl analogue of **21** which was subsequently deprotected to give **21** in 99% yield (Scheme 5). $Pd(PPh_3)_4$/CuI catalysed coupling between **17** and **21** for 5 hours at 70°C afforded the bis-THP analogue of **23** in 76% yield. Both of the THP protecting groups were readily cleaved under mildly acidic conditions and gave **23** in quantitative yield (Scheme 5). The Mitsunobu reaction[26] presented a particularly attractive method to instigate the desired ring closure as this reaction has been used previously for generating aryl-alkyl ethers,[27] with literature reports indicating that intramolecular cyclisation could occur under neutral conditions[28]. Application of standard Mitsunobu conditions to effect the intramolecular cyclisation of **23** using DEAD and PPh_3 at a 0.009M concentration afforded **15** in 67% yield (Scheme 5). Cyclophane **15** was isolated as a white solid and was recrystallised from hexane to give crystals suitable for an X-ray diffraction structure which showed the angle α was 26.3° and the angle β was 172.8°.[29]

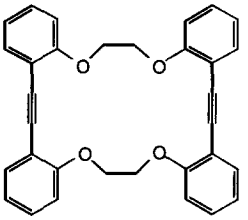


Condition A: (i) $BrCH_2CH_2CH_2OH$, K_2CO_3 (ii) DHP, PPTS
Condition B: (i) $ClCH_2CH_2OTHP$, K_2CO_3
Condition C: (i) $Pd(PPh_3)_4$, CuI, TMSC≡CH (ii) KOH, CH_3OH
Condition D: (i) $Pd(PPh_3)_4$, CuI, TMSC≡CH (ii) PPTS, CH_3OH

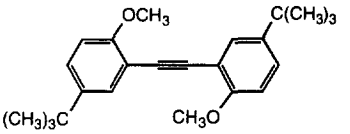
Scheme 5

The preparation of the analogous two carbon linked cyclophane **26** followed a similar route. Thus **18** was prepared on a large scale in 81% yield from 2-iodo-4-*tert*-butylphenol, **1** and 2(2-chloroethoxy) tetrahydropyran (Condition B, Scheme 5). At 70°C a facile $Pd(PPh_3)_4$/CuI catalysed coupling between **18** and **21** took place and the THP protected analogue of **24** was isolated in 96% yield. The THP protecting groups were readily cleaved under mildly acidic conditions resulting in the isolation of **24** as a white solid in 92% yield. Employing Mitsunobu reaction conditions, **24** was cyclized to **26** in good yield (82%), (Scheme 5). A low concentration of **24** (approximately 0.003M) was essential to optimise the yield and higher concentrations resulted in lower yields of **26** and impurities arising from intermolecular reactions. Exhaustive attempts to recrystallise **26** in a form suitable for X-ray diffraction studies proved fruitless. In summary this 7 step synthetic route demonstrated the facile preparation of **15** and **26** from 2-iodo-4-*tert*-butylphenol.

The conditions developed in this sequence were directly applicable for the development of **27** with only minor modifications. A monomer lacking the *tert*-butyl substituents was prepared in the hope that it would crystallize in a form suitable for X-ray analysis. 2-Iodophenol, **16**, was alkylated with 2(2-chloroethoxy)tetrahydropyran and gave **19** in 88% yield (Condition B, Scheme 5). $Pd(PPh_3)_4$/CuI catalysed coupling between **19** and **22** (prepared from **20** under Condition C, Scheme 5) took place and, after removal of the THP protecting groups, gave **25** in 83% yield. Intramolecular coupling of **25** under Mitsunobu conditions gave the expected product **27** in 62% yield as well as the unexpected dimer **28** in 29% yield. The identity of **28** was confirmed by an X-ray structure.[30] Attempts to recrystallise the unsubstituted **27** furnished well formed crystals, but investigation found them unsuitable for X-ray diffraction experiments.



28



29

Mitsunobu techniques were readily applied to the common precursor **4** and a mixture containing methanol, DEAD and triphenylphosphine to give the dimethyl derivative **29** in 79% yield. An X-ray diffraction structure of **29**[31] and **12**[32] showed coplanarity of the aromatic rings with the ether substituents in an *anti* conformation.

The π to π^* transitions associated with benzenoid chromophores show broad absorption features usually in the region between 230 and 270nm. Substitution with a bathochromic substituent such as an ethyne linkage will result in a small shift (23nm for an ethyne substituent on benzene) of the absorption maxima to longer wavelength. Absorptions due to acetylenic chromophores tend to be complex, but are generally characterised by the main features of an intense π to π^* transitions at similar wavelengths as that seen for the benzenoid chromophores, and second less intense absorptions at slightly longer wavelengths.[33] Thus for the aryl-alkyne systems the absorption features at wavelengths longer than approximately 300nm are associated with π to π^* transitions arising from the molecular orbitals associated with a conjugated polyene/yne type system, formed from orbital overlap between the aromatic rings and the triple bond.

The UV/VIS spectrum of the sterically constrained silylene **8** demonstrated a clear sharpening of the absorption features and improved resolution in its associated fine structure, when compared to the corresponding unconstrained dimethylthexyl derivative **12**. The principle lower energy absorption feature of **8** occurred at 330nm (ε_{max} 30000), this being 6nm lower than **12**, which occurred at 325nm (ε_{max} 14000), Table. An increase in the absorption intensity of this feature in **8** indicated steric constrainment resulted in an increased probability of this transition and a possible increase in the transition dipole of **8**. Consistent with the silylene bridge systems, the UV/VIS spectra of ether bridge compounds **26** and **15** demonstrated a narrowing of the lower energy absorption feature with improvement in fine structure, when compared with the unconstrained derivative **29**. Unlike the silylene system the lower energy π to π^* transition presumably associated with the conjugated triple bond, occurred at 320nm (ε_{max} 26000) and 313nm (ε_{max} 38000) for **26** and **15** respectively, as compared to 332nm (ε_{max} 16000) for the unconstrained derivative **29**. The higher energy absorption feature presumably arises from π to π^* transitions associated with the aromatic ring. These features remains reasonably invariant of linker arm substituent, with compounds **15**, **26** and **29** displaying absorptions between 282 and 285nm.

While these linker units do not allow optimum molecular orbital overlap and associated maximum conjugation, a substantial increase in the absorption probability (ε_{max}) was observed relative to the unconstrained system.

Table. UV/VIS data for compounds **8**, **12**, **15**, **26** and **29**

Compound	λ_{max}	ε_{max}
8	330	30 000
12	325	14 000
15	313	38 000
26	320	26 000
29	332	16 000

EXPERIMENTAL

All reactions were performed in oven dried glassware under a nitrogen atmosphere (unless in aqueous solution). Melting points were recorded on a Reichhert hot stage apparatus and are uncorrected. Proton and carbon NMR spectra were recorded on a Bruker ACP-300 or a Varian Gemini 200 spectrometer in $CDCl_3$ as solvent with tetramethylsilane as an internal standard. Mass spectra were recorded on VG ZAB 2HF mass spectrometer with either electron impact (EI) or fast atom bombardment (FAB) ionisation, or on an AEI-GEC MS 3074 instrument with EI ionisation. Ultraviolet spectra were recorded on a Pye Unicam SP8-100 spectrometer. Fluorescence spectra were recorded on a Perkin Elmer 3000 spectrometer. IR spectra were recorded on a Hitachi 270-30 spectrometer. Dihydro-2H-pyran (DHP) was distilled from sodium and stored over anhydrous potassium carbonate. Tetrahydrofuran (THF) was freshly distilled from sodium/ benzophenone prior to use. Dry dichloromethane was freshly distilled from phosphorous pentoxide. Unless otherwise stated all organic extracts and washings were dried using anhydrous magnesium sulfate. Unless otherwise stated Merck Kieselgel 60 (230-400 mesh) was used as the adsorbant for all silica flash[34] and squat[35], (dry column flash) column chromatgraphy and Merck Kieselgel 60 PF_{254} gipshaltig, for radial chromatography. Thin layer chromatography (tlc) was conducted on either Merck DC-Alufolien Kieselgel 60 F_{254} or Merck DC-Alufolien Aluminium Oxid 150 F_{254} plates, and both were visualised using ultraviolet light (254nm), 5% ethanolic phosphomolybdic acid or iodine vapour. Ultraviolet-visible (UV/VIS) spectra were recorded using a Carey 5E UV/VIS-NIR spectrophotometer, in THF unless otherwise indicated. Fluorescence spectra were recorded on a Perkin Elmer 3000 spectrophotometer in THF. Elemental analysis was performed by Chemical and Microanalytical Services Pty. Ltd., Essendon, Nth. Melbourne.
The following compounds were prepared according to literature procedures: $Pd(PPh_3)_4$[36], pyridinium -*p*-toluene sulfonate[37] and 2-(2-chloroethoxy)tetrahydropyran[38].

2-[4-(*tert*-Butyl)-2-iodophenoxy)]tetrahydro-2H-pyran (2)

Following a modification to a literature procedure,[18] a 7.5% aqueous sodium hypochlorite solution (160mL, 160mmol) was added slowly over 3 hours to a solution of 4-*tert*-butylphenol (25g, 170mmol), potassium hydroxide (9.5g, 170mmol) and sodium iodide (25g, 170mmol) in methanol (500mL), with the mixture maintained below 2°C during this addition. The mixture was allowed to stir at ambient temperature for 48 hours, methanol was removed and the residue adjusted to pH 1 with conc. HCl. The product was extracted into dichloromethane (2x250mL) and dried. The iodide **1** was isolated as a clear oil after column chromatography employing eluants grading from hexanes to dichloromethane (28.3g, 61%). FTIR (solid film) : 3411 br; 3164; 2960; 2904; 2864; 1673; 1597; 1573; 1503 cm^{-1}. ^1H NMR: δ 1.26 (s, 9H, $C(CH_3)_3$);

6.55 (brs, 1H, O**H**); 6.91 (d, *J*8.7Hz, 1H, Ar); 7.24 (dd, *J*2.4,8.4Hz, 1H, Ar); 7.62 (d, *J*2.3Hz, 1H, Ar). ^{13}C NMR: δ 31.4; 33.9; 85.5; 114.5; 127.2; 134.9; 145.4; 152.4. EIMS m/e 276, (M^+, 30%); 260. PPTS (0.5g, 2mmol) was added to a nitrogen blanketed solution of **1** (8.1g, 29mmol) and freshly distilled DHP (8.5mL, 93mmol) and the mixture was maintained at 50°C for 12 hours. Excess solvent was removed and the residue subject to chromatography employing 10:90 dichloromethane:hexanes as eluant. Compound **2** was isolated as a pale yellow oil (10.2g, 96%). ^{1}H NMR: δ 1.27 (s, 9H, C(C**H**$_3$)$_3$); 1.33-2.12 (m, 6H); 3.56-3.59 (m, 1H, OC**H**$_2$); 3.87 (dt, *J*3.1,11.1Hz, 1H, OC**H**$_2$); 5.49 (t, *J*2.81Hz, 1H, OC**H**O); 6.99 (d, *J*8.6Hz, 1H, Ar); 7.27 (dd, *J*2.4,8.6Hz, 1H, Ar); 7.75 (d, *J*2.4Hz, 1H, Ar). ^{13}C NMR: δ 18.2; 25.2; 30.1; 31.3; 33.9, ; 61.5; 87.3; 96.3; 114.4; 126.2; 136.0; 146.1; 153.1. EIMS m/e 360 (M^+, 16%); 276; 260; 233.

1,2-Di[5-(*tert*-butyl)-2-tetrahydro-2H-2-pyranyloxy)phenyl]acetylene (3)

Following a modified literature procedure[19], nitrogen was bubbled through a mixture of benzene (150mL) and potassium hydroxide (25g) in water (100mL) for 30 minutes. 3-Methylbut-3-yn-2-ol (2.5mL, 26mmol), **2** (18g, 50mmol), copper(I)iodide (460mg, 2.4mmol), tetrabutylammonium chloride (300mg, 1mmol) and $Pd(PPh_3)_4$ (1.9g, 1.6mmol), were added sequentially, and the mixture heated at 80°C for 24 hours. The cooled mixture was filtered through kenite, the organic layer was separated, washed with water (3x50mL) and dried. The dark brown tar was purified by chromatography, employing eluants grading from 10:90 to 30:70 dichloromethane:hexanes. The title compound was isolated as a yellow solid (7.12g, 58%). FTIR (solid film): 2951; 2869; 1601; 1499; 1457; 1392; 1362; 1319; 1239; 1201 cm^{-1}. ^{1}H NMR: δ 1.31 (s, 18H, C(C**H**$_3$)$_3$); 150-2.21 (m, 12H); 3.56-3.62 (m, 2H, OC**H**$_2$); 4.05 (dt, *J*2.9,10.9Hz, 2H, OC**H**$_2$); 5.86 (t, *J*2.7Hz, 2H, OC**HO**); 7.06 (d, *J*8.7Hz, 2H, Ar); 7.28 (dd, *J*2.6,8.7Hz, 2H, Ar); 7.51 (d, *J*2.5Hz, 2H, Ar). ^{13}C NMR: δ 18.3; 25.4; 30.3; 31.5; 34.1; 61.6; 88.7; 96.5; 114.0; 115.7; 126.4; 130.1; 144.2; 154.9. EIMS m/e 490, (M^+, 0.5%), 446; 405; 346; 322; 307; 150; 135; 85.

4-(*tert*-Butyl)-2-{2-[5-(*tert*-butyl)-2-hydroxyphenyl]-1-ethynyl}phenol (4)

A nitrogen blanketed solution of PPTS (0.5g, 2mmol) and **3** (5.78g, 12mmol) in methanol (200mL), was heated at 50°C for 12 hours. Solvent was removed and the residue purified via flash chromatography, employing dichloromethane as eluant. The title compound was isolated as a yellow/orange solid (3.35g, 88%). Recrystallisation from hexanes afforded pure white fluffy crystals. M.p. 113-116°C. FTIR (solid film) : 3382 br; 2960; 2904; 2887; 1604; 1493; 1462; 1406; 1363; 1285; 1270; 1248; 1212 cm^{-1}. ^{1}H NMR: δ 1.30 (s, 18H, C(C**H**$_3$)$_3$); 6.31 (brs, 2H, O**H**); 6.91 (d, *J*8.6Hz, 2H, Ar); 7.30 (dd, *J*2.4,8.6Hz, 2H, Ar); 7.43 (d, *J*2.4Hz, 2H, Ar). ^{13}C NMR: δ 31.4; 34.1; 90.5; 108.7; 114.5; 127.9; 128.0; 143.4; 154.3. EIMS m/e 322, (M^+, 100%), 307, 290, 250.

Minor product was **5** as a cream solid. A sample was recrystallised from hexanes as white plates. M.p. 113-116°C. FTIR (solid film) : 3524 br; 2959; 2904; 2867; 1598; 1510; 1498; 1477; 1394; 1364; 1327; 1297 cm^{-1}. ^{1}H NMR: δ 1.33 (s, 9H, C(C**H**$_3$)$_3$; 1.37 (s, 9H, C(C**H**$_3$)$_3$; 6.92 (d, *J*8.5Hz, 1H); 7.07 (s, 1H); 7.12 (s, 1H); 7.26 (dd, *J*2.4,8.6Hz, 1H); 7.32 (dd, *J*1.9,8.7Hz, 1H); 7.41 (d, *J*8.7Hz, 1H); 7.58 (d, *J*1.7Hz, 1H); 7.70 (d, *J*2.4Hz, 1H). ^{13}C NMR: δ 31.2; 31.4; 34.1; 34.7; 103.4; 110.2; 115.5; 116.9; 117.1; 122.2; 123.5; 127.4; 128.3; 143.3; 146.3; 151.0; 152.2; 154.7. EIMS m/e 322 (M^+,100%); 307; 251; 146; 118. UV/VIS (λ_{max}) : 332; 318; 292; 280; 243 nm.

4-(*tert*-Butyl)-2-[5-(*tert*-butyl)benzo[b]furan-2-yl]phenyl methyl ether (6)

A nitrogen blanketed solution of **5** (0.15g, 0.47mmol) potassium carbonate (0.30g, 1.8mmol) and methyl iodide (100μL, 1.6mmol) in DMF (30mL) was stirred for 30 min at ambient temperature. The reaction was diluted with ethyl acetate (75mL), washed with dilute aqueous sodium bicarbonate solution (4×50mL) and dried. Purification via flash column chromatography using hexanes as eluant followed by recrystallisation from the same solvent affords the title compound as large white plates (120mg, 77%). M.p. 173-174°C. FTIR (solid film): 2955; 2903; 2865; 2840; 1609; 1508; 1477; 1462; 1440; 1392; 1363; 1327; 1303 cm^{-1}. ^1H NMR: δ 1.38 (s, 18H, $C(CH_3)_3$); 3.06 (s, 3H, OCH_3); 6.93 (d, *J*8.7Hz, 1H, OCC**H**); 7.33 (dd, *J*1.8,8.7Hz, 2H, OCCHC**H**); coincident with 7.31 (s, 1H, =C**H**); 7.45 (d, *J*8.7Hz, 1H); 7.59 (d, *J*1.9Hz, 1H); 8.06 (d, *J*2.5Hz, 1H). ^{13}C NMR: δ 31.55; 31.9; 34.3; 34.7; 55.5; 106.4; 110.1; 110.7; 117.2; 119.0; 121.9; 124.0; 125.9; 129.5; 143.4,145.5; 152.1; 152.6; 154.4. Calculated M^+ for $C_{23}H_{28}O_2$ m/e 336.2089; found 336.2095. EIMS m/e 336, (M^+, 100%); 321. Calculated analysis for $C_{23}H_{28}O_2$:C 82.09, H 8.39; found: C 82.20, H 8.20. UVVIS (λ_{max}) : 332; 317; 294; 281 nm.

2,10-Di(*tert*-butyl)-6,6-dimethyl-12,13-didehydrobenzo[d,h][1,3,2]dioxasilonine (8)

Dichlorodimethylsilane (200μL, 1.7mmol) was added to a nitrogen blanketed stirred solution containing **4** (0.37g, 1.15mmol) and triethylamine (1.6mL, 11.5mmol) in dry dichloromethane (10mL) at ambient temperature. Solvent was removed after 12 hours and the residue purified via rapid vacuum filtration through florisil, employing dichloromethane as eluant. The title compound was isolated as a white solid in 96% yield. Recrystallisation from hexanes afforded a fine powdery solid. M.p. 152.5-154°C. IR (solid film): 3036; 2956; 2904; 2864; 1600; 1494; 1464; 1398; 1366; 1318; 1260; 1232; 1202 cm^{-1}. ^1H NMR: δ 0.32 (s, 6H, $Si(CH_3)_2$); 1.31 (s, 18H $C(CH_3)_3$); 6.93 (d, *J*8.5Hz, 2H, Ar); 7.28 (dd, *J*2.5, 8.5Hz, 2H, Ar); 7.34 (d, *J*2.4Hz, 2H, Ar). ^{13}H NMR: δ -1.1, ($Si(CH_3)_2$); 31.4; 34.2; 95.4 (C≡C); 113.3; 119.5; 125.2; 127.2; 144.5; 154.5. Calculated M^+ for $C_{24}H_{30}O_2Si$: m/e 378.2015; found: 378.2029. EIMS m/e 378 (M^+, 80%); 363; 261. UV/VIS (λ_{max}, ε_{max}): 330 (30000); 317 (17000); 309 (14000); 282 (22000); 273 (15000); 267 (13000) nm.

6,6-Dimethyl-12,13-didehydrobenzo[d,h][1,3,2]dioxasilonine (9)

As described for **8** using dichlorodimethylsilane (560μL, 4.3mmol) and **7** (0.80g, 3.8mmol) to afford the title compound as a clear oil (1.01g, 99%) FTIR (solid film): 2966; 1595; 1569; 1485; 1446; 1260 cm^{-1}. ^1H NMR: δ 0.46 (s, 6H, $Si(CH_3)_2$); 6.93 (t, *J*7.5Hz, 2H); 7.04 (d, *J*8.1Hz, 2H); 7.13 (dt, *J*1.7,7.7Hz, 2H); 7.43 (dd, *J*1.5,7.7Hz, 2H). ^{13}C NMR: δ -2.0, ($Si(CH_3)_2$); 90.1 (C≡C); 115.9; 120.2; 122.1; 129.6; 133.1; 154.8. Calculated: M^+ for $C_{16}H_{14}O_2Si$ m/e 266.0763; found: 266.0767. EIMS m/e 266, (M^+, 22%); 251; 210; 181; 85; 84.

6,6-Diphenyl-12,13-didehydrobenzo[d,h][1,3,2]dioxasilonine (10)

As described for **8** using dichlorodiphenylsilane (120μL, 0.55mmol) and **7** (0.10g, 4.8mmol) to afford the title compound as a waxy white solid (0.14g, 73%). M.p. 155-157.5°C. Attempts to recrystallise this material from hexanes were unsuccessful. IR (nujol mull): 2924; 2852; 1494; 1452; 1432; 1378; 1286; 1252; 1224 cm^{-1}. ^1H NMR: δ 6.94-7.00 (m, 2H); 7.22-7.35 (m, 12H); 7.59-7.62 (m, 4H). ^{13}C NMR: δ 95.1 (C≡C); 114.2; 119.5; 122.2; 127.9; 128.7; 130.3; 130.4; 133.0; 133.8; 156.5. EIMS m/e 390 (M^+, 100%); 313.

1-(2-(Hydroxy-di-*tert*-butylsiloxy)-5-*tert*-butylphenyl)-2-(2-hydroxy-5-*tert*-butylphenyl)ethyne (11)

4 (0.15g, 0.47mmol) and 2,6-dimethylpyridine (0.32mL, 2.8mmol) were dissolved in dry dichloromethane (10mL) and cooled to 5°C under a nitrogen atmosphere. Di-*tert*-butylsilylbis(trifluromethanesulfonate) (200mL, 0.55mmol) was added and the mixture was maintained at ambient temperature for 12 hours, then 65°C for 6 days. The mixture was diluted with 20:80 ethyl acetate:hexanes (100mL) and vacuum filtered through florisil using the same solvent system. Florisil chromatography employing 50:50 dichloromethane:hexanes as eluant afforded the title compound as a waxy semi-solid (0.16g, 71%). FTIR (film): 3408 br; 2956; 2862; 1712; 1604; 1495; 1464; 1391; 1360; 1283 cm^{-1}. ^1H NMR: δ 1.10 (s, 18H, $(tBu)_2Si$); 1.29 (s, 9H, $CC(CH_3)_3$); 1.31 (s, 9H, $CC(CH_3)_3$); 6.69 (brs, 1H, CO**H**); 6.86 (d, *J*8.6Hz, 1H); 7.04 (d, *J*8.7Hz, 1H); 7.23 (dd, *J*2.6,8.7Hz, 1H); coincident with 7.24 (dd, *J*2.6,8.7Hz,1H); 7.43 (d, *J*2.4Hz, 1H); 7.48 (d, *J*2.5Hz, 1H). ^{13}C NMR: δ 20.7; 27.4; 31.4; 34.1; 34.1; 87.4, 93.3 (C≡C); 109.4; 113.4; 114.6; 119.6; 127.1; 127.3; 128.8; 130.2; 142.9; 144.0; 153.9; 154.2. Calculated: M^+ for $C_{30}H_{44}O_3Si$ m/e 480.3060; found: 480.3073. EIMS m/e 480, (M^+, 67%); 423; 363; 307.

1,2-Bis(2-dimethylthexylsiloxy-5-*tert*-butylphenyl)ethyne (12)

Dimethylthexylsilyl chloride (250μL, 1.3mmol) was added to a nitrogen blanketed solution of **4** (0.17g, 0.53mmol), hydroxybenzotriazole (10mg, 0.1mmol) and triethylamine (0.75mL, 5.3mmol) in dry dichloromethane (15mL). The mixture was heated at gentle reflux for 12 hours, solvent was removed and the residue filtered through a pad of silica, employing 50:50 dichloromethane:hexanes as eluant. The residue was purified via silica flash column chromatography employing 10:90 dichloromethane:hexanes as eluant. The title compound was isolated as a waxy solid in quantitative yield. M.p. 99-101°C. FTIR (solid film): 2958; 2869; 1499; 1465; 1410; 1363; 1279; 1252 cm^{-1}. ^1H NMR: δ 0.29 (s, 12H, $Si(CH_3)_2$); 0.96 (d, *J*6.8Hz, 12H, $(CH_3)_2CH$); 1.03 (s, 12H, $(CH_3)_2C$); 1.78 (sept, *J*6.9Hz, 2H, $(CH_3)_2CH$); 6.76 (d, *J*8.6Hz, 2H, Ar); 7.19 (dd, *J*2.6,8.7Hz, 2H, Ar); 7.49 (d, *J*2.5Hz, 2H, Ar). ^{13}C NMR: δ -2.2, $((CH_3)_2Si)$; 18.6; 20.2; 25.2; 31.4; 34.0; 43.1; 90.3 (C≡C); 115.7; 119.1; 126.0; 130.3; 143.5; 153.8. Calculated: M^+ for $C_{38}H_{62}O_2Si_2$ m/e 606.4288; found: 606.4244. EIMS m/e 606 (M^+, 33%); 591; 521; 463; 437; 379; 362. UV/VIS (λ_{max}, ε_{max}) : 325 (14000); 314 (18000); 282 (25000); 275 (14000) nm.

1-(3-Bromopropoxy)-4-(*tert*-butyl)-2-iodobenzene (13)

A nitrogen blanketed solution of **1** (1.5g, 5.4mmol) 1,3-dibromopropane (2.75mL, 27mmol) and potassium carbonate (9g, 54mmol) in DMF (50mL) was stirred at ambient temperature for 2 days. The cream suspension was diluted with diethyl ether (100mL), washed with water (4x100mL) and dried. The residue was separated via flash chromatography, employing eluants grading from hexanes to 40:60 dichloromethane:hexanes. The title compound was isolated as an oil in 53% yield. FTIR (solid film): 2959; 2870; 1594; 1490; 1387; 1284; 1255; 1206cm^{-1}. ^1H NMR: δ 1.27 (s, 9H, $C(CH_3)_3$); 2.31 (p, *J*6.0Hz, 2H, CH_2CH_2Br); 3.68 (t, *J*6.4Hz, 2H, CH_2Br); 4.09 (t, *J*5.6Hz, 2H, OCH_2); 6.74 (d, *J*8.6Hz, 1H, Ar); 7.28, (dd, *J*2.4,8.4Hz, 1H, Ar); 7.76, (d, *J*2.4Hz, 1H, Ar). ^{13}C NMR: δ 30.3; 31.3; 32.2; 33.9; 66.4; 86.6; 111.6; 126.2; 136.4; 145.7; 154.8. Calculated: M^+ for $C_{13}H_{18}BrOI$ m/e 395.9586; found: 395.9597. EIMS m/e 398, 396 (M^+, 33%, 1:1); 383, 381; 317; 302; 260. A second component was isolated and identified as 1,3-bis(2-iodo-4-*tert*-butylphenoxy)propane (**14**) (0.08g, 5%).

4-(*tert*-Butyl)-1-{3-[4-(*tert*-butyl)-2-iodophenoxy]propoxy}-2-iodobenzene (14)

14 was also prepared by reaction of **13** and excess **1** in the presence of potassium carbonate in DMF. The title compound was obtained in 38% yield. FTIR (solid film): 2958; 1595; 1491; 1466; 1388; 1254 cm^{-1}. ^1H NMR: δ 1.27 (s, 18H, $C(CH_3)_3$); 2.32 (p, *J*5.6Hz, 2H, CH_2CH_2O); 4.26 (t, *J*5.9Hz, 4H, CH_2CH_2O); 6.80 (d, *J*8.6Hz, 2H, Ar); 7.29 (dd, *J*2.4,8.6Hz, 2H, Ar); 7.74 (d, *J*2.4Hz, 2H, Ar). ^{13}C NMR: δ 29.2; 31.4; 34.0; 65.7; 86.6; 111.8; 126.3; 136.4; 145.7; 155.1. Calculated: M^+ for $C_{23}H_{30}I_2O_2$ 592.0335; found: 592.0352. EIMS m/e 592, (M^+, 100%); 577; 467; 352; 317; 302; 261.

2,12-di(*tert*-Butyl)-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecine (15)

DEAD (440μL, 2.8mmol) was added to a nitrogen blanketed stirred solution of **23** (0.51g, 1.3mmol) and triphenylphosphine (0.73g, 2.8mmol) in dry THF (150mL) at room temperature. Solvent was removed after 12 hours and the residue purified via flash column chromatography, employing 20:80 dichloromethane :hexanes as eluant. The title compound was isolated as a white solid (326mg, 67%), and recrystallised from hexanes, to yield well formed white crystals. M.p. 156.5-158.5°C. FTIR (solid film) : 2956; 2873; 1485; 1464; 1381; 1252; 1210 cm^{-1}. ^1H NMR: δ 1.32, (s, 18H, $C(CH_3)_3$); 2.11, (p, *J*5.0Hz, 2H, OCH_2CH_2); 4.38, (t, *J*4.9Hz, 4H, OCH_2); 7.05, (d, *J*8.4Hz, 2H, OCCH); 7.30, (dd, *J*2.5,8.6Hz, 2H, OCCH=CH); 7.50, (d, *J*2.5Hz, 2H, CHCJ). ^{13}C NMR: δ 30.9; 31.3; 34.4; 69.6; 91.2, (C≡C); 116.9; 121.8; 126.9; 128.6; 146.9; 158.9. Calculated M^+ for $C_{25}H_{30}O_2$ m/e 362.2246; found 362.2236. EIMS m/e 362, (M^+, 100%); 347; 319; 290. Calculated analysis for $C_{25}H_{30}O_2$, C 82.82, H 8.35; found C 82.60, H 8.13. UV/VIS (λ_{max}, ε_{max}) : 313, (38000); 304, (25000); 285, (41000); 271, (25000) nm. Fluorescence (λ_{max}) : 340 nm.

This compound was also prepared by the following palladium-catalysed coupling route:
Nitrogen was bubbled through a solution of THF (200mL) for 10 minutes, then **14** (0.225g, 0.38mmol), $Pd(PPh_3)_4$ (0.08g, 0.038mmol) and bis(tributylstannyl)acetylene (0.01ml, 0.19mmol) were added. The reaction was heated at reflux for 45 minutes and further bis(tributylstannyl)acetylene (0.01ml, 0.19mmol) was added over an hour. The mixture was heated at reflux for 2 days and the solvent was removed, the residue dissolved in diethylether (100mL) and washed with a 5% aqueous KF solution and finally dried over $MgSO_4$. The resulting brown oil was purified via flash chromatography employing 0:80 dichloromethane :hexanes as eluant. The product was isolated as a yellow gum in 25% yield.

1-([4-(*tert*-Butyl)-2-iodophenoxy]-3-tetrahydro-2H-2-pyranyloxy)propane (17)

As described for **13** using **1** (25g, 91mmol) and 3-bromopropan-1-ol (15g, 108 mmol) to afford the deprotected analogue of **17** as a clear oil (26.3g, 87%). ^1H NMR: δ 1.28 (s, 9H, $C(CH_3)_3$); 2.09 (p, *J*5.7Hz, 2H, CH_2CH_2OH); 2.35 (br s, 1H, OH); 3.92 (t, *J*5.6Hz, 2H, CH_2OH); 4.15 (t, *J*5.8Hz, 2H, $ArOCH_2$); 6.76 (d, *J*8.5Hz, 1H, Ar); 7.30, (dd, *J*2.4,8.4Hz, 1H, Ar); 7.75, (d, *J*2.4Hz, 1H, Ar). ^{13}C NMR: δ 31.3; 31.7; 34.0; 60.8; 67.5; 86.4; 111.4; 126.3; 136.4; 145.8; 155.0. Calculated: M^+ for $C_{13}H_{19}O_2I$ m/e 334.0430; found: 334.0439. EIMS m/e 334 (M^+, 100%); 319; 260; 207. Protected as the THP ether as described for **20** using PPTS (0.05g, 0.2mmol) and the deprotected analogue of **17** (1.55g, 4.6mmol) and DHP (10mL) to afford **17** as a colourless oil (1.9g, 98%). ^1H NMR: δ 1.27 (s, 9H, $(CH_3)_3C$); 1.50-1.74 (m, 6H); 2.13 (p, *J*6.3Hz, 2H, $ArOCH_2CH_2$); 3.47-3.55 (m, 2H); 3.83-3.90 (m, 2H); 4.11 (t, *J*6.1Hz, 2H, $ArOCH_2$); 4.59-4.62

(m, 1H, OC**H**O); 6.75 (d, *J*8.6Hz, 1H, Ar); 7.28, (dd, *J*2.3,8.6Hz, 1H, Ar); 7.75, (d, *J*2.4Hz, 1H, Ar). ^{13}C NMR: δ 19.4; 25.3; 30.5; 31.3; 32.75; 33.8; 62.1; 63.8; 65.9; 86.5; 98.7; 111.4; 126.1; 136.2; 145.2; 155.1. Calculated: M^+ for $C_{18}H_{27}O_3I$ m/e 418.1005; found: 418.1013. EIMS m/e 418, (M^+, 100%); 334; 319; 260.

1-([4-(*tert*-Butyl)-2-iodophenoxy]-3-tetrahydro-2H-2-pyranyloxy)ethane (18)

As described for **13** using **1** (0.5g, 1.8mmol) and 2-(2-chloroethoxy)tetrahydropyran (400μL, 2.7mmol) to afford **18** as a colourless oil (600mg, 82%). IR (neat film): 2952; 2864; 1738; 1594; 1558; 1498; 1456; 1392; 1362; 1322; 1288; 1260; 1200 cm^{-1}. ^{1}H NMR: δ 1.28 (s, 9H, C(C**H**$_3$)$_3$); 1.51-1.86 (m, 6H); 3.53-3.68 (m, 1H); 3.84-3.98 (m, 2H); 4.04-4.15 (m, 1H); 4.18 (t, *J*2.7Hz, 2H, OC**H**$_2$); 4.83 (t, *J*3.3Hz, 1H, OC**H**O); 6.78 (d, *J*8.6Hz, 1H, Ar); 7.29 (dd, *J*2.4,8.6Hz, 1H, Ar); 7.76 (d, *J*2.4Hz, 1H, Ar). ^{13}C NMR: δ 19.2; 25.4; 30.5; 31.3; 33.9; 62.0, 65.5, 68.8; 86.6; 99.0; 111.9; 126.2; 136.4; 146.0; 155.3. Calculated: M^+ for $C_{17}H_{25}O_3I$ m/e 404.0849; found: 404.0855. EIMS m/e 404, (M^+, 25%); 320; 305; 286; 262; 163; 129.

1-(2-Iodophenoxy)-2-(tetrahydro-2H-2-pyranyloxy)ethane (19)

As described for **13** using 2-iodophenol (3.0g, 13.6mmol) and 2-(2-chloroethoxy)tetrahydropyran to afford the title compound as a clear oil (4.2g, 88%). IR (neat oil): 2936; 2868; 1582; 1474; 1440; 1384; 1352; 1322; 1276; 1248; 1200 cm^{-1}. ^{1}H NMR: δ 1.50-1.83 (m, 6H); 3.50-3.55 (m, 1H); 3.84-3.94 (m, 2H); 4.04-4.09 (m, 1H); 4.15-4.18 (m, 2H); 4.81 (t, *J*3.3Hz, 1H, OC**H**O); 6.69 (dt, *J*1.1,7.6Hz, 1H, Ar); 6.82 (dd, *J*1.0,8.1Hz, 1H, Ar); 7.26 (dt, *J*1.1,8.1Hz, 1H, Ar); 7.75 (dd, *J*1.6,7.8Hz, 1H, Ar). ^{13}C NMR: δ 19.1; 25.3; 30.3; 61.9; 65.3; 68.6; 86.5; 98.8; 112.2; 122.5; 129.2; 139.2; 157.3. Calculated: M^+ for $C_{13}H_{17}IO_3$ m/e 348.0223; found: 348.0214. EIMS m/e 348, (M^+, 16%); 264,; 247; 219; 203; 129; 85.

2-(2-Iodophenoxy)tetrahydro-2H-2-pyran (20)

PPTS (0.050g, 0.2mmol) was added to a nitrogen blanketed solution of 2-iodophenol (4.0g, 18mmol) in DHP (10mL). The mix was heated at 50°C and monitored via tlc (10:90 ethyl acetate:hexanes) until all starting material was consumed. Solid potassium hydroxide (1g) was added and excess DHP removed under vaccum. The residue was purified by flash chromatography employing 5:95 ethyl acetate:hexanes as eluant. The title compound was isolated as a colourless oil (5.40g, 98%). FTIR (neat film): 2942; 2874; 1580; 1467; 1439; 1355; 1276; 1238; 1201 cm^{-1}. ^{1}H NMR: δ 1.61-2.17 (m, 6H); 3.55-3.61 (m, 1H, OC**H**$_2$); 3.85 (dt, *J*2.9,11.0Hz, 1H, OC**H**$_2$); 5.52 (t, *J*2.5Hz, 1H, OC**H**O); 6.70 (dt, *J*1.4,7.6Hz, 1H); 7.06 (dd, *J*1.3,8.3Hz, 1H); 7.25 (dt, *J*1.3,7.8Hz, 1H); 7.75 (dd, *J*1.4,7.8Hz, 1H). ^{13}C NMR: δ 18.2; 25.1; 30.1; 61.5; 87.3; 96.3; 115.0; 123.1; 129.2; 139.1; 155.3. Calculated: M^+ for $C_{11}H_{13}IO_2$ m/e 303.9960; found: 303.9948. EIMS m/e 304, (M^+, 14%); 220.

2-[4-(*tert*-Butyl)-2-(1-ethynyl)phenoxy]tetrahydro-2H-pyran (21)

Nitrogen was bubbled through a solution of triethylamine (70mL) for 40 minutes, then **2** (10.2g, 28mmol), $Pd(PPh_3)_4$ (0.26g, 0.23mmol), triphenylphosphine (0.13g, 0.5mmol), and copper(I)iodide (0.1g, 0.53mmol) were added. Trimethylsilylacetylene (4.4mL, 31mmol) was finally added and the reaction allowed to stir at room temperature for 3 hours. Solvent was removed from the cream suspension and the residue passed through a pad of silica employing 50:50 dichloromethane:hexanes as eluant. The resulting brown oil was purified via flash chromatography employing 20:80 then 40:60 dichloromethane:hexanes as eluants. The

trimethylsilyl derivative of **21** was isolated as a yellow oil in quantitative yield (9.62g). FTIR (solid film): 2954; 2156; 1494; 1460; 1394.4; 1359; 1248; 1202 cm^{-1}. ^1H NMR: δ .26 (s, 9H, $Si(CH_3)_3$); 1.28 (s, 9H, $C(CH_3)_3$); 1.58-2.14 (m, 6H); 3.56-3.60 (m, 1H, OCH_2); 4.01 (dt, *J*2.9,11.0Hz, 1H, OCH_2); 5.54 (t, *J*5.3Hz, 1H, OCHO); 7.01 (d, *J*8.7Hz, 1H, Ar); 7.27 (dd, *J*2.7,8.6Hz, 1H, Ar); 7.43 (d, *J*2.5Hz, 1H, Ar). ^{13}C NMR: δ 0.1 ($Si(CH_3)_3$); 18.2; 25.3; 30.2; 31.3; 34.1; 61.5; 96.6; 97.4 (C≡CSi); 102.1 (C≡CSi); 113.23; 115.9; 127.0; 130.3; 144.3; 155.8. Calculated: M^+ for $C_{20}H_{30}O_2Si$ m/e 330.2015; found: 330.2005. EIMS m/e 330 (M^+, 3%); 246; 231; 216; 85.

Dichloromethane (10mL) was added slowly to a nitrogen blanketed solution of the trimethylsilyl derivative of **21** (1.01g, 3mmol) in methanol (70mL) until all insoluble material had dissolved. Potassium hydroxide (0.26g, 5mmol) was added and the bright yellow solution allowed to stir at room temperature for 4 hours. Solvent was removed and the residue disolved in 20:80 dichloromethane:hexanes then filtered through a pad of silica using the same eluant. Solvent removal afforded **21** as a mobile oil (780mg, 99%). FTIR (solid film): 3285; 2952; 2871; 2107; 1602; 1496; 1461; 1392; 1359; 1249; 1202 cm^{-1}. ^1H NMR: δ 1.29 (s, 9H, $C(CH_3)_3$); 1.58-2.11 (m, 6H); 3.22 (s, 1H, CCH); 3.55-3.61 (m, 1H, OCH_2); 3.96 (dt, *J*3.0,10.5Hz, 1H, OCH_2); 5.51 (t, *J*2.9Hz, 1H, OCHO); 7.04 (d, *J*8.8Hz, 1H, Ar); 7.29 (dd, *J*2.5,8.8Hz, 1H, Ar); 7.46 (d, *J*2,5Hz, 1H, Ar). ^{13}C NMR: δ 18.3; 25.3; 30.2; 31.4; 34.0; 61.7; 80.2 (C≡CH); 80.6 (C≡CH); 96.4; 111.9; 115.2; 118.7; 127.1; 130.7; 144.1; 155.8. Calculated: M^+ for $C_{17}H_{22}O_2$ m/e 258.16198; found: 258.1614. EIMS m/e 258, (M^+, 10%); 174; 159; 85.

2-(1-Ethynyl)phenyltetrahydro-2H-2-pyranyl ether (22)

As described for **21** using **20** (5.20g, 17.1mmol) and trimethylsilylacetylene (2.9mL, 21mmol) to afford the trimethylsilyl derivative of **22** as a pale straw oil (3.46g, 82%). FTIR (neat film) : 2950; 2158; 1596; 1485; 1447; 1356; 1285; 1246; 1201 cm^{-1}. ^1H NMR: δ .25, (s, 9H, $Si(CH_3)_3$); 1.58-2.14, (m, 6H); 3.53-3.57, (m, 1H, CH_2O); 3.96, (dt, *J*2.9,11.9Hz, 1H, CH_2O); 5.53, (t, *J*2.5Hz, 1H, OCHO); 6.88, (dt, *J*.7,7.5Hz, 1H, Ar); 7.07, (d, *J*8.1Hz, 1H, Ar); 7.20, (dt, *J*1.3,7.8Hz, 1H, Ar); 7.40, (dd, *J*1.6,7,6Hz, 1H, Ar). ^{13}C NMR: δ -0.2, ($Si(CH_3)_3$); 17.9; 25.2; 30.0; 61.2; 96.1; 97.8, (C≡CSi); 101.4, (C≡CSi); 113.8; 115.6; 121.3; 129.6; 133.2; 157.8. Calculated M^+ for $C_{16}H_{22}SiO_2$ m/e 274.1389; found 274.1447. EIMS m/e 274,(M^+, 11%); 190; 175; 159; 115; 85.

Deprotection as described for **21** yielded the title compound as a pale yellow oil (1.55g, 94%). FTIR (neat film) : 3285; 2944; 2875; 1596; 1485; 1446; 1356; 1283; 1242; 1202 cm^{-1}. ^1H NMR: δ .1.60-2.10, (m, 6H); 3,25, (s, 1H, CCH); 3.54-3.60, (m, 1H, OCH_2); 3.92, (dt, *J*10.8,3.0Hz 1H, OCH_2); 5.51, (t, *J*2.9Hz, 1H, OCHO); 6.90, (dt, *J*7.5,1.1Hz, 1H); 7.10, (dd, *J*.8,8.3Hz, 1H, Ar); 7.25, (dt, *J*8.6,1.4Hz, 1H, Ar); 7.44, (dd, *J*1.7,7.6Hz, 1H, Ar). ^{13}C NMR: δ 18.2; 25.1; 30.0; 61.5; 79.9, (C≡CH); 80.8, (C≡CH); 96.2; 112.5; 115.3; 121.2; 129.9; 133.7; 157.9. Calculated M^+ for $C_{13}H_{14}O_2$ m/e 202.0994; found 202.1000. EIMS m/e 202, (M^+, 2%); 118; 85.

3-(4-(*tert*-Butyl)2-{2-[5-(*tert*-butyl)-2-hydroxyphenyl]-1-ethynyl}phenoxy)-1-propanol (23)

Nitrogen was bubbled through a nitrogen blanketed solution of **17** (1.2g, 2.9mmol) in triethylamine (40mL) for 40 minutes. $Pd(PPh_3)_4$ (0.10g, 0.1mmol), triphenylphosphine (50mg, 0.19mmol), and copper(I)iodide (40mg, 0.2mmol) was added and allowed to stir at ambient temperature for 10 minutes. **21** (0.50g, 1.9mmol) was added and the mixture allowed to stir for 5 hours at 70°C. Solvent was removed and the residue purified

via flash chromatography, employing eluants grading from 40:60 dichloromethane:hexanes to dichloromethane. The THP protected analogue of **23** was isolated as a yellow oil (805mg, 76%). FTIR (film): 2950; 2870; 1600; 1499; 1463; 1360; 1243; 1202 cm^{-1}. ^1H NMR: δ 1.30 (s, 9H, $C(CH_3)_3$); 1.31 (s, 9H, $C(CH_3)_3$); 1.42-2.01 (m, 12H); 2.13 (p, *J*6.3Hz, 2H); 3.40-3.50 (m, 1H); 3.58-3.85 (m, 3H); 3.95-4.16 (m, 2H); 4.16-4.21 (m, 2H, $ArOCH_2$); 4.58 (t, *J*3.5Hz, 1H); 5.59 (t, *J*2.6Hz, 1H, ArOCHO); 6.86 (d, *J*8.7Hz, 1H, Ar); 7.06 (d, *J*8.7Hz, 1H, Ar) 7.27 (dd, *J*2.4,8.8Hz, 1H, Ar); 7.28 (dd, *J*2.5,8.7Hz, 1H, Ar); 7.52 (d, *J*2.3Hz, 1H, Ar); 7.58 (d, *J*2.1Hz, 1H, Ar). ^{13}C NMR: δ 18.3; 19.6; 25.4; 29.6; 30.2; 31.3; 33.1, 34.0; 61.5; 62.3; 63.9; 65.7; 89.7, 89.8 (C≡C); 96.5, 99.0; 112.0; 112.8; 114.0; 115.6; 126.2; 126.3; 130.0; 130.4; 143.0, 144.2; 155.0; 157.0. Calculated: M^+ for $C_{35}H_{48}O_5$ m/e 548.3502; found: 548.3520. EIMS m/e 548, (M^+, 8%); 464; 380; 375; 299. Deprotection as described for **4** gave the title compound as a colourless film in quantitative yield. FTIR (solid film): 3428 br; 2958; 1602; 1495; 1458; 1398; 1364; 1254 cm^{-1}. ^1H NMR: δ 1.29 (s, 9H, $C(CH_3)_3$); 1.30 (s, 9H, $C(CH_3)_3$); 2.30 (p, *J*12.9Hz, 2H, CH_2CH_2OH) coincident with (s, 1H CH_2OH); 3.87 (t, *J*11.5Hz, 2H, CH_2OH); 4.12 (t, *J*11.7Hz, 2H, CH_2OAr); 6.84 (d, *J*8.7Hz, 1H, CHCO); 6.90 (d, *J*8.6Hz, 1H, CHCO); 7.26 (dd, *J*2.2,8.4Hz, 1H, Ar); 7.30 (dd, *J*2.4,8.6Hz, 1H, Ar); 7.43 (d, *J*2.4Hz, 1H, Ar); 7.51 (d, *J*2.5Hz, 1H, Ar). ^{13}C NMR (300MHz): δ 31.3; 31.4; 60.4; 66.9; 89.1 (C≡C); 92.3 (C≡C); 109.3; 110.9; 111.5; 114.8; 126.7; 127.4; 127.7; 129.0; 142.7; 143.3; 154.7; 156.4. Calculated: M^+ for $C_{25}H_{32}O_3$ m/e 380.2351; found: 380.2350. EIMS m/e 380, (M^+, 100%); 365; 335; 306; 290.

2-(4-(*tert*-Butyl)-2-{2-[5-(*tert*-butyl)-2-hydroxyphenyl]-1-ethynyl}phenoxy)-1-ethanol (24)

Coupling between **18** (4.5g, 11mmol) and **21** (2.55g, 10mmol), as described for **23** gave the THP protected analogue of **24** as a pale yellow oil and as a mixture of diastereoisomers (5.02g, 95%). FTIR (solid film): 2951; 2871; 1500; 1455; 1361; 1280; 1241; 1201 cm^{-1}. ^1H NMR: δ 1.33 (s, 9H, $C(CH_3)_3$); 1.34 (s, 9H, $C(CH_3)_3$); 1.44-2.23 (m, 12H); 3.46-3.52 (m, 1H); 3.60-3.65 (m, 1H); 3.88-3.96 (m, 2H); 4.04-4.13 (m, 2H); 4.29 (t, *J*5.2Hz, 2H, $ArOCH_2$); 4.83 (t, *J*3.4Hz, 1H, CH_2OCHO); 5.61 (t, *J*2.1Hz, 1H, ArOCHO); 6.91 (d, *J*8.7Hz, 1H); 7.09 (d, *J*8.7Hz, 1H, Ar); 7.30 (dd, *J*2.2, 8.4Hz, 1H, Ar); 7.31 (dd, *J*2.2, 8.4Hz, 1H, Ar); 7.55 (d, *J*2.4Hz, 1H, Ar); 7.56 (d, *J*2.4Hz, 1H, Ar). ^{13}C NMR: δ 18.3; 19.2; 25.4; 30.3; 30.5; 31.2; 31.3; 34.0, 34.1; 61.6; 61.9; 65.6; 68.6; 89.7, 89.8 (C≡C); 96.5; 96.6; 99.0; 112.46; 113.0; 113.9; 114.0; 115.5; 115.6; 126.3; 126.4; 123.0; 130.6; 143.4, 144.3; 155.1; 156.0. Calculated: M^+ for $C_{34}H_{46}O_5$ m/e 534.33452; found: 534.3364. EIMS m/e 534, (M^+, 3%); 450; 366; 351; 307; 84. Deprotection as described for **4** and recrystallisation from hexanes afforded the title compound as fine white needles (0.87g, 92%). M.p. 51-54°C. FTIR (solid film): 3442 br; 2958; 1495; 1456; 1399; 1364; 1255 cm^{-1}. ^1H NMR: δ 1.33 (s, 9H, $C(CH_3)_3$); 1.35 (s, 9H, $C(CH_3)_3$); 2.99 (br s, 1H, CH_2OH); 4.09 (t, *J*4.1Hz, 2H, CH_2OH); 4.21 (t, *J*4.2Hz, 2H, CH_2CH_2OH); 6.90 (d, *J*8.7Hz, 1H); 6.96 (d, *J*8.7Hz, 1H); 7.12 (br s, 1H, Ar); 7.32 (dd, *J*2.5,8.6Hz, 1H, Ar); 7.36 (dd, *J*2.6,8.8Hz, 1H, Ar); 7.44 (d, *J*2.4Hz, 1H, Ar); 7.53 (d, *J*2.5Hz, 1H, Ar). ^{13}C NMR: δ 31.3, 31.4; 34.1, 34.1; 61.2; 70.7; 89.1, 93.7 (C≡C); 109.3; 111.2; 111.4; 114.0; 126.4; 126.9; 127.5; 128.5; 143.0, 143.9; 154.8; 156.7. Calculated: M^+ for $C_{24}H_{30}O_3$ m/e 366.2195; found: 366.2202. EIMS m/e 366, (M^+, 100%); 351; 306; 291; 250.

2-{2-[2-(2-Hydroxyphenyl)-1-ethynyl]phenoxy}-1-ethanol (25)

Coupling between **19** (3.6g, 10mmol) and **22** (1.1g, 5.3mmol), as described for **23** gave the THP protected analogue of **25** as a pale yellow oil. (2.1g, 94%). ^1H NMR: δ 1.23-2.13 (m, 12H); 3.43-3.47 (m, 1H); 3.57-

3.60 (m, 1H); 3.83-4.11 (m, 4H); 4.24 (t, *J*5.1Hz, 2H, ArOC**H**$_2$); 4.76 (t, *J*3.3Hz, 1H, OC**H**O); 5.58 (m, 1H, OC**H**O); 6.92-6.95 (m, 2H, Ar); 7.14-7.31 (m, 4H, Ar); 7.48-7.49 (m, 2H, Ar). ^{13}C NMR: δ 18.1; 19.0; 25.1; 25.2; 30.1; 30.3; 61.4; 61.8; 65.5; 68.2; 89.5, 89.7 (C≡C); 96.3, 98.8; 112.5; 113.4; 114.3; 115.7; 120.6; 121.3; 128.3; 129.2; 133.1; 133.7; 157.1; 159.1. Calculated: M$^+$ for $C_{26}H_{30}O_5$ m/e 422.2093; found: 422.2075. EIMS m/e 422, (M$^+$,6%); 338; 254. Deprotection as described for **4** gave the title compound as a pale yellow oil (0.88g, 70%). ^{1}H NMR: δ 3.04 (brs, 1H, CH$_2$O**H**); 4.07 (t, *J*4.2Hz, 2H, C**H**$_2$O); 4.18 (t, *J*4.2Hz, 2H, C**H**$_2$O); 6.87-7.00 (m, 4H, Ar); 7.22-7.33 (m, 3H, Ar); 7.38 (dd, *J*1.6,7.6Hz, 1H, Ar); 7.47 (dd, *J*1.7,7.6Hz, 1H, Ar). ^{13}C NMR: δ 60.9; 70.3; 89.0; 93.1 (C≡C); 110.0; 111.6; 112.0; 114.5; 120.1; 120.9; 129.8; 130.1; 131.5; 156.9; 158.7. Calculated: M$^+$ for $C_{16}H_{14}O_3$ m/e 254.0943; found: 254.0933. EIMS m/e 254, (M$^+$, 100%); 209; 181.

2,11-Di(*tert*-butyl)-13,14-didehydro-6,7-dihydrodibenzo[e,l][1,4]dioxecine (26)

24 (1.65g, 3.1mmol) and DEAD (1.45mL, 9.2mmol) were both added in 4 equal portions over 5 hours, to a nitrogen blanketed solution of triphenylphosphine (2.3g, 9mmol) in THF (300mL) at room temperature. Solvent was removed after 12 hours and the residue purified via flash chromatography, employing 25:75 dichloromethane:hexanes as eluant. Recrystallisation from pentane afforded white crystals (1.29g, 82%). M.p. 109-110.5°C. FTIR (solid film): 2956; 2873; 1485; 1386; 1360; 1262; 1210 cm^{-1}. ^{1}H NMR: δ 1.31 (s, 18H, C(C**H**$_3$)$_3$); 4.44 (s, 4H, OC**H**$_2$); 7.07 (d, *J*8.6Hz, 2H, Ar); 7.31 (dd, *J*2.5,8.5Hz, 2H, Ar); 7.41 (d, *J*2.5Hz, Ar). ^{13}C NMR: δ 31.3; 34.3; 73.65; 95.47 (C≡C); 116.2; 121.6; 126.8; 126.9; 146.6; 160.3. Calculated: M$^+$ for $C_{24}H_{28}O_2$ m/e 348.2089; found: 348.2105. EIMS m/e 348, (M$^+$, 100%); 333; 276. Calculated analysis for $C_{24}H_{28}O_2$, C 82.71, H 8.10; found C 82.49, H 7.93. UV/VIS (λ_{max}, ε_{max}) : 320 (26000); 310 (20000); 301 (17000) 285 (22000); 272 (16000) nm. Fluorescence (λ_{max}) : 335 nm.

13,14-Didehydro-6,7-dihydrodibenzo[e,l][1,4]dioxecine (27)

DEAD (1.1mL, 6.0mmol) dissolved in THF (10mL), was added via syringe pump over 20 hours to a nitrogen blanketed solution of **25** (0.88g, 3.5mmol) and triphenylphosphine (1.82g, 7mmol) at room temperature. Solvent was removed after 2 days and the residue separated into components via flash chromatography using 40:60 dichloromethane:hexanes as the eluant. The title compound was isolated as a white solid and was recrystallised from hexane as well formed white crystals (0.51g, 62%). M.p. 76-77.5°C. FTIR (solid film): 1476; 1444; 1390; 1272; 1251; 1208 cm^{-1}. ^{1}H NMR: δ 4.45 (s, 4H, OC**H**$_2$); 7.09 (dt, *J*.6,7.6Hz, 2H); 7.13 (d, *J*7.9Hz, 2H); 7.28 (dt, *J*1.5,7.9Hz, 2H); 7.39 (dd, *J*1.4,7.6Hz, 2H). ^{13}C NMR: δ 73.7; 95.4 (C≡C); 117.0; 122.2; 123.8; 129.8; 129.9; 162.5. Calculated: M$^+$ for $C_{16}H_{12}O_2$ m/e 236.0837; found: 236.0829. EIMS m/e 236, (M$^+$, 100%); 221; 202. A second component identified as the dimer (**28**) was also isolated (0.24g, 29%). M.p 128.5-130°C. FTIR (solid film): 2931; 1587; 1480; 1437; 1271; 1239; cm^{-1}. ^{1}H NMR: δ 4.56 (s, 8H, OC**H**$_2$); 6.91 (d, *J*8.2Hz, 4H); coincident with 6.95 (dt, *J*.6,7.4Hz, 4H); 7.24 (dt, *J*1.6,7.9Hz, 4H); 7.46 (dd, *J*1.6,7.6Hz, 4H). ^{13}C NMR: δ 68.7; 90.1 (C≡C); 114.2; 114.9; 121.6; 129.5; 133.5; 159.4. Calculated: M$^+$ for $C_{32}H_{24}O_4$ m/e 472.1675; found: 472.1665. EIMS m/e 472, (M$^+$, 2%); 446; 254; 236; 221; 210; 181.

4-(*tert*-Butyl)-2-{2-[5-(*tert*-butyl)-2-methoxyphenyl]-1-ethynyl}-1-methoxybenzene (29)

Mitsunobu coupling between **4** (0.38g, 1.2mmol) and methanol (250μL, 6.2mmol) in dry THF (100mL) as

described for **26** gave the title compound as a white solid (324mg, 79%), which was recrystallised from pentane as large white cubic crystals. M.p. 139.5-141°C. IR (nujol mull): 2924; 2852; 1506; 1464; 1412; 1366; 1282; 1256; 1242 cm^{-1}. ^1H NMR: δ 1.31 (s, 18H, $C(CH_3)_3$); 3.91 (s, 6H, OCH_3); 6.85 (d, *J*8.6Hz, 2H, Ar); 7.29 (dd, *J*2.5,8.6Hz, 2H, Ar); 7.56, (d, *J*2.6Hz, 2H, Ar). ^{13}C NMR: δ 31.4; 34.1; 56.0; 89.7 (C≡C); 110.3; 112.1; 126.4; 130.7; 143.1; 157.7. Calculated: M^+ for $C_{24}H_{30}O_2$ m/e 350.2246; found: 350.2255. EIMS m/e 350, (M^+, 100%); 335; 320; 305; 160. Calculated analysis for $C_{24}H_{30}O_2$, C 82.23, H 8.63; found C 82.38, H 8.49. UV/VIS (λ_{max}, ε_{max}): 332 (16000); 321 (18000); 313 (19000); 282 (18000); 274 (16000); 268 (14000) nm. Fluorescence (λ_{max}): 348 nm.

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