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Preparation of Sterically Constrained Arylalkyne Oligomers

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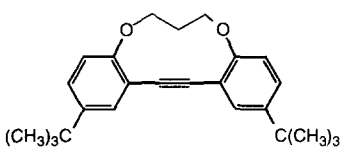
Abstract: The preparation and physical properties of a series of dioxapropylphenylethynylene oligomers is described. Restricting the interannular rotation narrows the lowest energy absorption and increases its extinction coefficient in the UV/VIS spectrum. The fluoresence spectrum of oligomers **2** and **3** are consistent with molecules possessing restricted degrees of rotation

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(phenylene ethynylenes) and their corresponding nonlinearities[1,2,3]. In addition, oligo(phenyleneethynylenes) have been used for the construction of fluorescent chemosensors[4], cyclophanes[5] and molecular turnstiles[6].

We have reported in the preceding paper[7] on the preparation of a series of sterically constrained arylalkynes where the length of the linker arm was varied in order to probe the relationship between the interannular angle of the phenyl rings and the spectroscopic properties of the compounds. The conclusion from this study was that a dioxapropyl linker arm (as in **1**) was synthetically accessible and significantly restricted the intraannular rotation. On the basis of this work we have developed a general strategy for the preparation of oligomers **2** and **3** as well as a potential route to the extended oligomer **4** .



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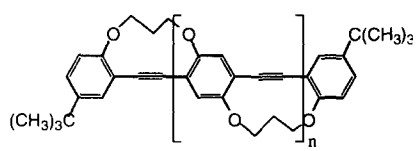
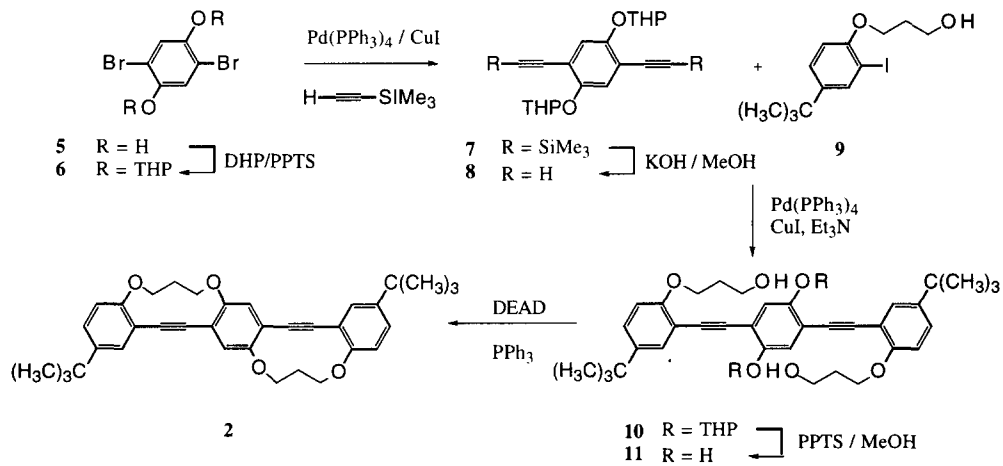


2, n = 1; **3**, n = 2; **4**, n = 4

RESULTS AND DISCUSSION

Oligomer 2

The main structural requirement for oligomer **2** was the central 2,5-diethynyl-1,4-hydoquinone and 2,5-dibromo-1,4-hydroquinone[8] **5** was employed as a convenient precursor as outlined in Scheme 1. In order to avoid problems associated with the formation of benzofurans from intramolecular, base-catalysed cyclization of 2-alkynylphenols[9], **5** was as the THP ether **6** in 94% yield (Scheme 1). A Sonogashira[10] coupling of **6** with excess trimethylsilylacetylene gave the coupled alkyne **7** in 99% yield. Deprotection of the trimethylsilyl group was accomplished under mild conditions by treatment with potassium hydroxide in a mixture of methanol and dichloromethane to afford **8** in quantitative yield. Compound **8** was reacted with 2 equivalents of **9**[7]in the presence of a Pd(0)/CuI/PPh_3 catalyst system to give **10** as a highly UV fluorescent yellow solid in 71% yield. Under these conditions partially coupled material was also observed as a minor by-product (~7%) which could be readily separated by flash chromatography. The THP protecting groups of **10** were conveniently cleaved by application of PPTS in methanol and gave **11** in excellent yield (96%). Complete conversion was essential as **11** could not be separated from **10** by flash chromatography.



Scheme 1

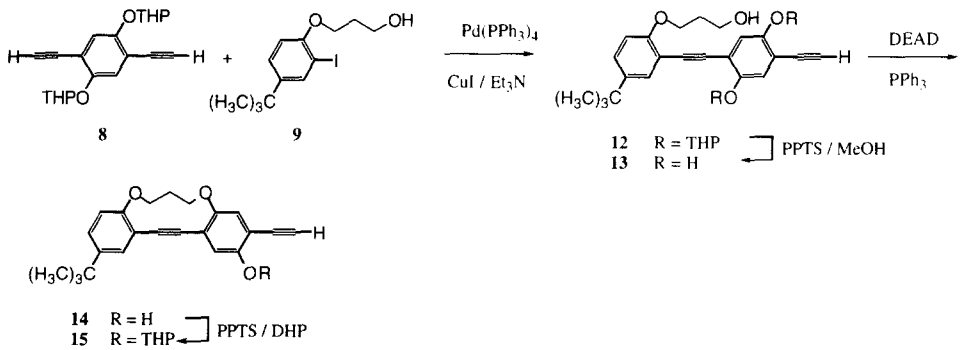
Preparation of **2** was accomplished by the application of two intramolecular Mitsunobu[11] reactions on **11** (Scheme 1). Both DEAD and **11** were added under high dilution conditions in an attempt to suppress competing, intermolecular reactions. Even with this precaution the title compound was isolated in a moderate yield of 41%, with considerable quantities of unidentified polymeric materials also being formed.

In conclusion, the synthetic path outlined in Scheme 1 demonstrated that oligomeric dioxapropylphenylethynylenes could be readily prepared from 2,5-dibromo-1,4-hydroquinone (**5**) in an overall yield of 26%.

Oligomer 3

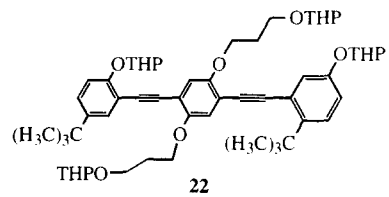
In order to prepare higher homologues of the dioxapropylphenylethynylenes a similar path was followed, the key compounds being the bridged alkyne **15** (Scheme 2) and bridged iodide **23** (Scheme 3).

Hence, one equivalent of **9** was added over 20 hours to a solution of **8** and $Pd(PPh_3)_4/CuI/PPh_3$ and the mixture was allowed to react for a total of 2 days at ambient temperature to give **12** in 56% yield. The minor products **10** (22% yield) and unreacted starting material **8** (20% yield) were also isolated and could be readily separated by flash chromatography. Tolane **12** was deprotected and gave **13** in 75% yield (Scheme 2). In order to close the bridge, DEAD was added slowly over 10 hours to a 0.01 molar solution of **13** and PPh_3 in THF at ambient temperature for a total of 12 hours and gave **14** in moderate yield (60%). In order to suppress benzofuran formation **14** was converted to the THP ether **14** in 89% yield. The overall yield in the 4 step synthesis of **15** from **8** and **9** was 22%.



Scheme 2

In order to prepare **23** a complementary route was followed (Scheme 3). Alkylation of 2.5-diiodo-1.4-hydroquinone **16** with 3-bromopropanol furnished **17** as a white solid in 69% yield (Scheme 3). While the primary hydroxyl functionality was expected to support subsequent synthetic methodology, purification would be more readily achieved with THP protected ethers and so **17** was reacted with DHP to give **18** in quantitative yield. Palladium-catalysed coupling was achieved when **19** was added in two portions over a 4 hour period to excess **18** (2.8 molar equivalence) at 70°C (Scheme 3). The reaction was complete after 7 hours and the desired material **20** was isolated as the major product (65% yield based on **19**) along with unreacted **18** (57% yield based on **19**) and doubly coupled product **22** (20%yield).



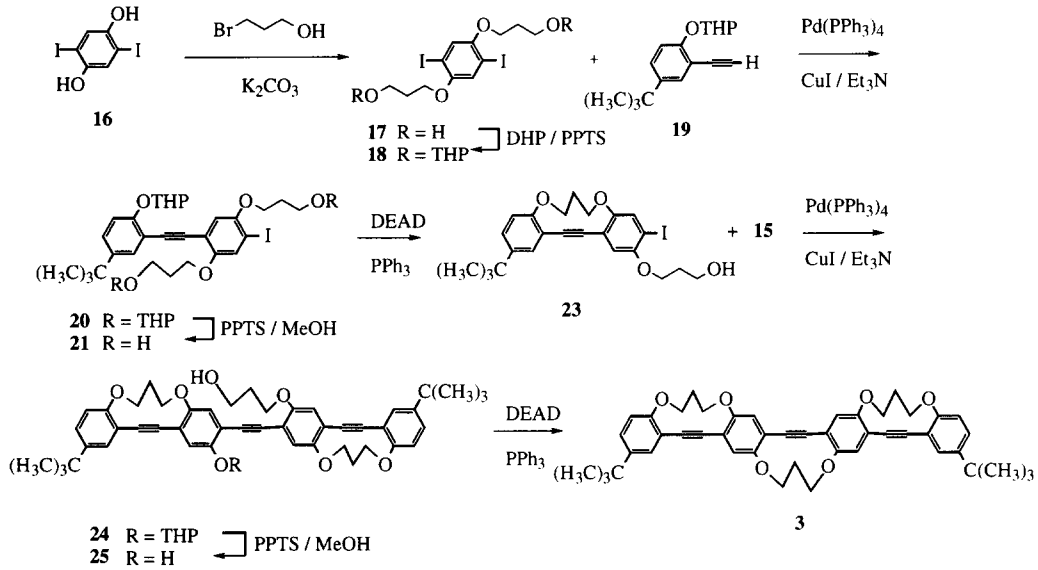
22

In order to carry out the Mitsunobu ring closure **20** was deprotected with PPTS in methanol and furnished **21** in excellent yield (98%). DEAD reagent was then added dropwise over 7 hours to a 0.01 molar solution of **21** and PPh_3 in THF with **23** being isolated as the only product in 65% yield (Scheme 3). The two subunits **15** and **23** were coupled effectively using a $Pd(PPh_3)_4/CuI/PPh_3$ system with **24** being isolated in 96% yield a (Scheme 3). The THP protecting group on **24** was cleaved and **25** was isolated in moderate

yield (64%) as a sparingly soluble solid (Scheme 3).

Under Mitsunobu conditions DEAD was added slowly over 6 hours to a 0.002 molar solution of **25** and PPh_3 in THF at ambient temperature. The reaction was terminated after 14 hours and **3** was isolated as a pale yellow solid in 71% yield (Scheme 6.22).

In conclusion, we have developed a suitable route for the preparation of **3** from simple precursors with the application of modified, routine literature procedures.



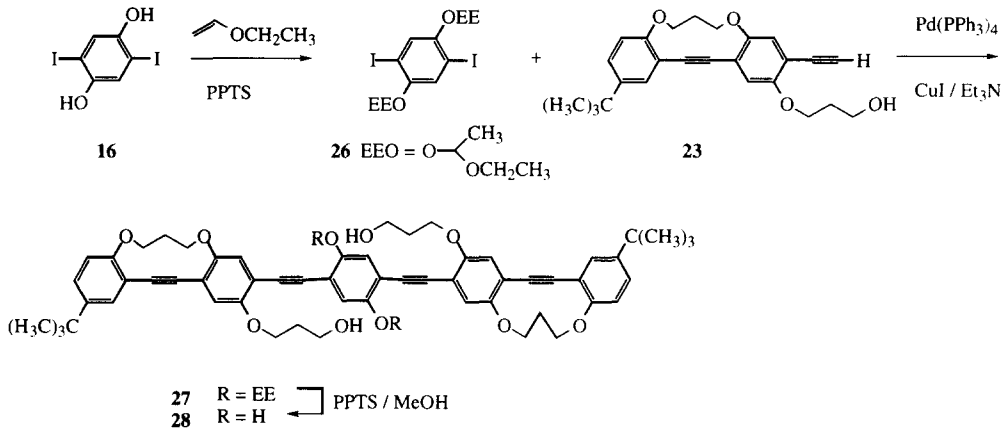
Scheme 3

Oligomer 4

A route to the target material **4** was proposed starting from precursors developed in the preceding sections (Schemes 2 and 3). The removal of the THP protecting groups required conditions which were becoming incompatible with the oligomeric aryl alkynes so the more readily cleaved ethoxyethyl (OEE) protecting group was employed. Thus the protected derivative **26** was prepared in high yield (88%) by treatment of 2,5-diiodo-1,4-hydroquinone (**16**) with ethyl vinyl ether and PPTS. Coupling between **26** and **23** afforded **27** as a solid film in quantitative yield (Scheme 4). A trace impurity in **27** was detected by ^{13}C NMR and was identified as the competing homocoupled product. This material could not be separated by standard chromatographic methods as **27** and the dimer had identical R_f values by tlc. The free phenol functions were regenerated by deprotection of **27** with **28** being isolated as a sparingly soluble yellow film in 43% yield (Scheme 4). Manipulations and purification of **28** proved arduous due to the intractable nature and limited solubility of the material.

Preliminary attempts to induce a double intramolecular Mitsunobu ring closure on **28** were not successful. Under the standard conditions DEAD reagent was added to a THF solution of **28** and PPh_3 over 10 hours at room temperature, with the reaction being worked up after 12 hours. The product mixture obtained was sparingly soluble in common organic solvents and could not be purified by chromatographic

methods because of severe "tailing and streaking" of components. Further analysis of the reaction mixture was not possible due to its very limited solubility.



Scheme 4

Spectroscopic Properties

We have discussed in the preceding paper[7] the general characteristics of the ultraviolet-visible spectra for constrained arylalkynes. The oligomers **2** and **3** show a substantial increase in the absorption probability (ε_{max}) (Table) compared to the unconstrained compounds **10** and **24** (although the difference between **24** and **3** is smaller since two of the links are already constrained). In addition, the small Stokes-loss between the absorption maxima in the ultraviolet-visible spectra and the corresponding fluorescence spectra for **2** and **3** again reflects the restricted conformations around the tolane subunits (Table). The ^{13}C nmr spectra show a characteristic downfield shift for the alkyne carbons in the constrained materials (Table).

Table. UV/VIS and ^{13}C nmr data for compounds **10**, **2**, **24**, **3** and **27**

Compound	UV/VIS maxima (ε_{max})	Fluorescence maxima	^{13}C δ C≡C
10	360 (63 000)		89.7, 91.5
2	358 (110 000)	409	90.3, 93.7
24	397 (100 000)		90.5, 90.7, 91.6, 93.3, 93.5
3	382 (140 000)	427	90.1, 92.4, 93.8
27	412 (106 000)		90.4, 90.7, 91.8, 93.5

In conclusion, these two papers have described routes to sterically constrained tolane monomers and oligomers in which the restricted conformations around the arylalkyne unit has led to a significant narrowing of the absorption bands in the ultraviolet-visible spectra and a corresponding increase in the extinction coefficient.

EXPERIMENTAL

The experimental protocols have been described in the previous paper.[7] The following compounds were prepared according to literature procedures: $Pd(PPh_3)_4$[12], 2,5-dibromo-1,4-hydroquinone (**5**)[8] and 2,5-diiodo-1,4-hydroquinone (**16**)[13].

7,22-di(*tert*-butyl)-11,15,26,30-tetraoxapentacyclo[15.13.1.1^{2,16}.0^{5,10}.0^{20,25}]dotriaconta-1,5(10),6,8,16(32),17(31),20(25),21,23-nonaen-3,18-diyne (2)

THF (10mL) solutions of compound **11** (1.29g, 2.3mmol) and DEAD reagent (1.43mL, 9.0mmol) were added simultaneously over 4 hours, under high dilution conditions, to a nitrogen blanketed solution of PPh_3 (2.4g, 9.2mmol) in THF (120mL), at ambient temperature. Solvent was removed after 12 hours, and the residue purified via silica flash column chromatography, employing 50:50 dichloromethane:hexanes as eluant. The title compound was isolated as a white solid (0.49g, 41%), and was recrystallised from hexanes, as fine white needles. M.p. >275°C. IR (nujol mull) : 2924; 2852; 1488; 1462; 1378; 1350; 1260; 1224; 1210 cm^{-1}. ^{1}H NMR δ 1.32, (s, 18H, $C(CH_3)_3$); 2.12, (p, *J*5.0Hz, 4H, OCH_2CH_2); 4.36, (t, *J*4.8Hz, 8H, OCH_2); 7.06, (d, *J*8.5Hz, 2H, Ar); 7.21, (s, 2H, Ar); 7.33, (dd, *J*2.5,8.5Hz, 2H, Ar); 7.49, (d, *J*2.4Hz, 2H, Ar). ^{13}C NMR δ 30.9; 31.5; 34.6; 69.8; 70.0; 90.3; 93.7, (C≡C); 116.7; 119.1; 122.1; 125.1; 127.5; 128.9; 147.3; 157.4, 159.2. FABMS m/e 535, ($M+H^+$, 50%); 534, (M^+, 100%). Calculated analysis for $C_{36}H_{38}O_4$ C 80.86, H 7.17; found C 81.03, H 7.14. UV/VIS (λ_{max}, ε_{max}) : 358, (110000); 341, (70000); 314, (50000); 303 (35000) n.m. Fluorescence (λ_{max}) : 409; 391nm.

3,17-di(*tert*-butyl)-5,6,14,15,26,27-hexadehydro-10,11,21,22,23,30,31,32-octahydro-9H-benzo[10^{1,11},11^{1,11}][1,5]dioxacycloundecino[7^{1,11},6^{1,11}:4^{11},5^{11}]benzo[10^1,11^1][1,5]dioxacycloundecino[6^1,7^1:4,5]benzo[f]benzo[j][1,5]dioxacycloundecine (3)

A THF solution (10mL) of DEAD reagent (85μL, 0.54mmol) was added dropwise over 6 hours to a nitrogen blanketed solution of **25** (0.26g, 0.36mmol) and PPh_3 (0.14g, 0.54mmol), in THF (200mL) at ambient temperature. After 12 hours solvent was removed and the residue purified via silica squat column chromatography employing 50:50 dichloromethane:hexanes then dichloromethane as eluant. The title compound was isolated as a yellow solid (0.18g, 71%). M.p. >230°C. FTIR (solid film) : 2956; 2871; 1595; 1477; 1371; 1261 cm^{-1}. ^{1}H NMR δ 1.33, (s, 18H, $C(CH_3)_3$); 2.10-2.20, (m, 6H, OCH_2CH_2); 4.3 0-4.40, (m, 12H, OCH_2); 7.06, (d, *J*8.4Hz, 2H, OC=CH); 7.21, (s, 2H); 7.22, (s, 2H); 7.34, (dd, *J*2.5,8.6Hz, 2H, Ar); 7.49, (d, *J*2.4Hz, 2H, Ar). ^{13}C NMR δ 30.6; 30.7; 31.3; 34.4; 69.6; 69.8; 69.9; 90.1; 92.4; 93.8; 116.4; 118.4; 119.4; 121.9; 125.0; 125.1; 127.4; 128.7; 147.1; 157.2; 157.3; 159.0. EIMS m/e 706, (M^+, 8%); 646; 420; 362; 143; 85. UV/VIS (λ_{max}, ε_{max}) : 382, (140000); 362, (86000); 319, (30000); 262, (33000) n.m. Fluorescence (λ_{max}): 427; 407 nm.

2-[2,5-dibromo-4-(tetrahydro-2H-2-pyranyloxy)phenoxy]tetrahydro-2H-pyran (6)

PPTS (0.10g, 0.4mmol) was added to a nitrogen blanketed solution of 2,5-dibromo-1,4-hydroquinone (**5**) (15g, 56mmol) in dihydropyran (DHP) (20mL, 220mmol). A mildly exothermic reaction ensued, and the suspension obtained was allowed to stir at room temperature for 2.5 hours. Excess DHP was removed under vacuum and the residue was quenched into saturated sodium bicarbonate (150mL), extracted into

dichloromethane (2×150mL) washed with water (2×150mL) and dried. This mixture was filtered through a pad of silica and solvent removal yielded a cream white solid (24.27g, 99%). Recrystallisation from hexanes/dichloromethane afforded the title compound as an off white solid. Mp. 159-163°C. FTIR (solid film) : 2946; 1475; 1346 cm^{-1}. ^1H NMR δ 1.62-1.74, (m, 8H); 1.84-2.08, (m, 4H); 3.59-3.65, (m, 2H, OCH_2CH_2); 3.90, (dt, *J*2.9.10.8Hz, 2H, OCH_2CH_2); 5.37, (t, *J*2.6Hz, 2H, OCHO); 7.36, (s, 2H, Ar). ^{13}C NMR δ 18.2; 25.1; 30.1; 61.9; 97.6; 112.2; 121.3; 148.7. Calculated M^+ for $C_{16}H_{20}Br_2O_4$ m/z 435.9708, found 435.9695. EIMS m/e 438,436,434, (M^+, 9%, 1:2:1); 353,351,349, (93%, 1:2:1); 269,267,265, (1:2:1); 189,187, (1:1); 169.

2-[2,5-di(2-trimethylsilyl-1-ethynyl)-4-(tetrahydro-2H-2-pyranyloxy)phenoxy]tetrahydro-2H-pyran (7)

Nitrogen was bubbled through a solution of piperidine (25mL) and triethylamine (70mL) for 30 minutes. Compound **6** (6.3g, 14mmol) followed by CuI (0.10g, 0.52mmol), PPh_3 (0.13g, 0.5mmol) and $Pd(PPh_3)_4$ (0.26g, 0.23mmol) were then added and allowed to stir at room temperature for 10 minutes. Trimethylsilylacetylene (5mL, 36mmol) was added and the mixture was heated at 80°C for 3 hours. Solvent was removed and the residue filtered through a short pad of silica with 50:50 dichloromethane:hexanes, to yield a orange/red solid. This crude product was purified via silica flash column chromatography, employing a gradient of 30:70 to 60:40 dichloromethane:hexanes as the eluant. The title compound was obtained as a pure cream yellow solid (6.75g, 99%). Mp. 162-165°C. FTIR (solid film) : 2952; 2154; 1735; 1489; 1351 cm^{-1}. ^1H NMR δ .24, (s, 18H, $Si(CH_3)_3$); 1.63-2.33, (m, 12H); 3.59-3.62, (m, 2H, OCH_2CH_2); 3.99, (dt, *J*2.7,11.1Hz, 2H, OCH_2CH_2); 5.45, (t, *J*2.6Hz, 2H, OCHO); 7.15, (s, 2H, Ar). ^{13}C NMR δ -0.13; 18.1; 25.3; 30.2; 61.5; 97.2; 99.9; 100.9; 115.4, (≡CC); 120.9; 152.5. Calculated M^+ for $C_{26}H_{38}O_4Si_2$ m/e 470.2309; found 470.2323. EIMS m/e 470, (M^+, 15%); 386; 385; 374; 371; 327; 325; 302; 287; 269.

2-[2,5-di(1-ethynyl)-4-(tetrahydro-2H-2-pyranyloxy)phenoxy]tetrahydro-2H-pyran (8)

Compound **7** (5.9g, 13mmol) was dissolved in a nitrogen blanketed solution of dichloromethane (150mL), containing methanol (50mL) and potassium hydroxide (2.1g, 38mmol). The mixture was heated at gentle reflux for 10 minutes and solvent was removed under vacuum. The residue was purified via squat chromatography employing 30:70 dichloromethane:hexanes grading to 100% dichloromethane as eluants. Solvent removal yielded the desired product as a pale yellow solid (4.03g, 99%). Mp. 165-168.5°C. FTIR (solid film) : 3265; 2943; 2873; 1489; 1396; 1351 cm^{-1}. ^1H NMR δ 1.59-2.07, (m, 12H); 3.30, (s, 2H, CCH); 3.57-3.64, (m, 2H, OCH_2CH_2); 3.94, (dt, *J*3.0,10.8Hz, 2H, OCH_2CH_2); 5.42, (t, *J*2.9Hz, 2H, OCHO); 7.21, (s, 2H). ^{13}C NMR δ 18.4; 25.2; 30.2; 61.8; 79.6, (C≡CH); 82.3, (C≡CH); 97.4; 114.5; 121.1; 152.5. Calculated M^+ for $C_{20}H_{22}O_4$ m/e 326.1518, found 326.1528. EIMS m/e 326, (M^+, 13%); 242; 158.

3-(4-(*tert*-butyl)-2-{2-[4-[5-(*tert*-butyl)-2-(3-hydroxypropoxy)phenyl]-1-ethynyl}-2,5-di(tetrahydro-2H-2-pyranyloxy)phenyl]-1-ethynyl}phenoxy)-1-propanol (10)

Nitrogen was bubbled through a solution of **9** (4.1g, 12.3mmol) in triethylamine (30mL) and dichloromethane (120mL) for 15 minutes. A catalyst system consisting of $Pd(PPh_3)_4$ (0.37g, 0.4mmol), PPh_3 (0.18g, 0.7mmol), and CuI (0.15g, 0.8mmol) was added and allowed to stir for 15 minutes at ambient

temperature. Alkyne **8** (2g, 6.1mmol) was added and the mixture heated at gentle reflux for 18 hours. Solvent was removed and the residue separated into components via silica flash column chromatography, employing eluants grading from dichloromethane to 80:20 ethyl acetate:dichloromethane. The title compound was isolated (3.2g, 71%) and recrystallised from hexanes/dichloromethane as pale yellow crystals. Mp. 147-150°C. FTIR (solid film) : 3418 br; 2952; 2873; 2201; 1594; 1502; 1419; 1357; 1274 cm^{-1}. ^1H NMR δ 1.30, (s, 18H, $C(CH_3)_3$); 1.61-2.20, (m, 12H); 2.09, (p, *J*5.8Hz, 4H, CH_2CH_2OH); 2.84, (t, *J*5.3Hz, 2H, **OH**); 3.60-3.70, (m, 2H, OCH_2:THP); 3.93, (q, *J*5.5Hz, 4H, CH_2OH); 4.06, (dt, *J*2.8,10.9Hz, 2H, OCH_2:THP); 4.20, (t, *J*5.7Hz, 4H, $ArOCH_2$); 5.56, (t, *J*2.6Hz, 2H, OC**H**O); 6.85, (d, *J*8.7Hz, 2H, OCC**H**CH); 7.30, (dd, *J*2.5,8.7Hz, 2H, Ar); 7.33, (s, 2H, Ar); 7.49, (d, *J*2.5Hz, Ar). ^{13}C NMR δ 18.2; 25.3; 30.2; 31.3; 31.9; 34.0; 61.0; 61.7; 67.4; 89.7, 91.5, (**C≡C**); 97.2; 111.8; 112.6; 115.3; 120.3; 126.7; 130.1; 143.6; 151.7; 157.0. EIMS m/e 738, (M^+, 4%); 570; 85; 57. UV/VIS (λ_{max}, ε_{max}) : 360, (63000); 325, (35000); 297, (35000) n.m.

2,5-di{2-[5-(*tert*-butyl)-2-(3-hydroxypropoxy)phenyl]-1-ethynyl}-1,4-benzenediol (11)

PPTS (0.10g, 0.4mmol) was added to a nitrogen blanketed solution of compound **10** (3.1g, 4.2mmol) in dichloromethane (50mL) and methanol (100mL). The mixture was maintained at gentle reflux for 12 hours. Solvent was removed and the residue purified via silica flash column chromatography, employing 20:80 then 40:60 ethyl acetate:dichloromethane as eluants. The title compound was isolated as a yellow solid (2.30g, 96%) and recrystallised from hexanes/dichloromethane as fine yellow needles. Mp. 189-193°C. FTIR (solid film) : 3436 br; 2957; 2873; 2201; 1600; 1495; 1362; 1338; 1276 cm^{-1}. ^1H NMR δ 1.35, (s, 18H, $C(CH_3)_3$); 2.17, (p *J*5.7Hz, 4H, OCH_2CH_2); 2.81, (t, *J*5.5Hz, 2H, CH_2OH); 3.95, (q, *J*5.5Hz, 4H, CH_2OH); 4.31, (t, *J*5.8Hz, 4H, $ArOCH_2$); 6.90, (d, *J*8.7Hz, 2H, OCC**H**CH); 7.01, (br s, 2H, ArO**H**); 7.05, (s, 2H, Ar); 7.37, (dd, *J*2.5,8.7Hz, 2H, Ar); 7.53, (d, *J*2.4Hz, 2H, Ar). ^{13}C NMR δ 31.4; 31.5; 34.2; 61.0; 67.4; 88.8, 94.3, (**C≡C**); 111.0; 111.4; 112.0; 116.9; 127.2; 129.3; 144.0; 150.4; 156.6. FABMS m/e 571, ($M+H^+$, 41%); 570, (M^+, 100%).

3-(4-(*tert*-butyl)-2-{2-[4-(1-ethynyl)-2,5-di(tetrahydro-2H-2-pyranyloxy)phenyl]-1-ethynyl}phenoxy)-1-propanol (12)

Nitrogen was bubbled through a mixture containing **8** (4.26g, 13mmol) triethylamine (25mL) and dichloromethane (120mL), for 15 minutes, and a catalyst system consisting of $Pd(PPh_3)_4$ (0.15g, 0.13mmol), PPh_3 (0.070g, 0.27mmol), and CuI (0.055g, 0.29mmol) was added. Compound **9** (4.36g, 13mmol) in degassed dichloromethane (10mL) was added via syringe pump over 20 hours at room temperature. Solvent was removed after 48 hours, and the residue separated into components via silica flash column chromatography, employing dichloromethane then 30:70 ethyl acetate:dichloromethane as eluants. Starting terminal acetylene was recovered unreacted (1.26g, 29%), and the title compound was isolated as a red oil, solidifiying upon standing to a yellow solid (3.90g, 56%) and was identified as a mixture of diastereoisomers. IR (neat film) : 3456 br; 3288; 2952; 2244; 1738; 1600; 1504; 1418; 1396; 1358; 1324; 1270 cm^{-1}. ^1H NMR δ 1.29, (s, 9H, $C(CH_3)_3$); 1.60-2.00, (m, 12H); 2.07, (p, *J*5.8Hz, 2H, CH_2CH_2OH); 2.88, (br s, 1H, **OH**); 3.31, (s, 1H, ≡**CH**); 3.60-3.65, (m, 2H, CH_2OH); 3.85-4.03, (m, 4H); 4.17, (t, *J*5.7Hz, 2H, $ArOCH_2$); 5.48, (s, 2H, OC**H**O); 6.83, (d, *J*8.7Hz, 1H, OCC**H**CH); 7.22, (s, 1H); 7.29, (dd, *J*2.5,8.7Hz, 1H, Ar); 7.32, (s, 1H): 7.48, (d, *J*2.5Hz, 1H, Ar). ^{13}C NMR δ 18.2; 25.2; 25.2; 30.1; 30.1; 31.2; 31.9; 33.9;

60.7; 61.6; 61.7; 67.3; 79.8; 82.0/82.1; 89.3; 91.7; 96.9/97.0; 97.3/97.4; 111.7; 112.3; 113.4; 116.3; 120.0; 121.4/121.4; 126.8; 130.0; 143.4; 151.5; 152.6; 157.0. EIMS m/e 533, ($M+H^+$, 1%); 532, (M^+, 1%); 450; 367; 366; 291; 85; 84.

Dimer (**10**) was also isolated as a red oil, solidifying on standing to a yellow solid (2.12g, 22%).

2-{2-[5-(*tert*-butyl)-2-(3-hydroxypropoxy)phenyl]-1-ethynyl}-5-(1-ethynyl)-1,4-benzenediol (13)

A nitrogen blanketed solution containing compound **12** (0.18g, 0.34mmol), PPTS (10mg, 0.04mmol) and dichloromethane (35mL), in methanol (20mL), was stirred at ambient temperature for 12 hours. Solvent was removed and the residue purified via silica squat chromatography, employing 10:90 ethyl acetate: dichloromethane as eluants. The title compound was isolated as a yellow oil (92mg, 75%). IR (neat film) : 3296 br; 2956; 2248; 2200; 2104; 1728; 1600; 1500; 1272 cm^{-1}. ^1H NMR δ 1.29, (s, 9H, $C(\mathbf{CH_3})_3$); 2.10, (p, *J*5.6Hz, 2H, $C\mathbf{H_2}CH_2O$); 3.47, (s, 1H, **H**C≡C); 3.90, (t, *J*5.5Hz, 2H, $C\mathbf{H_2}OH$); 4.21, (t, *J*5.8Hz, 2H, $ArOC\mathbf{H_2}$); 6.83, (d, *J*8.7Hz, 1H, OCC**H**CH); 6.97, (s, 2H, Ar**O**H); coincident with 6.97, (s, 2H, Ar); 7.31, (dd, *J*2.4,8.7Hz, 1H, Ar); 7.48, (d, *J*2.4Hz, 1H, Ar). ^{13}C NMR δ 31.3; 34.1; 60.8; 67.2; 78.5, (C≡**C**); 84.7, (≡**C**H); 88.2, 94.7, (**C**≡C); 110.0; 111.0; 112.7; 116.4; 118.1; 127.4; 129.2; 143.8; 150.1; 150.7; 156.6. EIMS m/e 366, ($M+2^+$, 88%); 291; 84.

12-(*tert*-butyl)-3-(1-ethynyl)-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecin-2-ol (14)

DEAD reagent (520μL, 33mmol) in THF (10mL) was added via syringe pump over 10 hours to a nitrogen blanketed solution of compound **13** (1.10g, 3.1mmol) and PPh_3 in THF (250mL) at ambient temperature. Solvent was removed after 14 hours, and the residue purified via silica flash column chromatography, employing 60:40 dichloromethane:hexanes as eluant. The title compound was isolated as a white solid (640mg, 60%). Mp. 153-157°C. IR (neat film) : 3292 br; 2960; 2208; 2100; 1616; 1546; 1486; 1386; 1264cm^{-1}. ^1H NMR δ 1.33. (s, 9H, $C(\mathbf{CH_3})_3$); 2.10, (p, *J*4.4Hz, 2H, $C\mathbf{H_2}CH_2O$); 3.54, (s, 1H, **HC**≡); 4.29-4.37, (m, 4H, $C\mathbf{H_2}O$); 7.04, (s, 1H); 7.06, (d, *J*8.3Hz, 1H, OCC**H**CH); 7.14, (s, 1H); 7.34, (dd, *J*2.5,8.5Hz, 1H, OCCHC**H**); coincident with 7.35, (br s, 1H, O**H**); 7.50, (d, *J*2.4Hz, 1H, *t*BuCC**H**C≡). ^{13}C NMR δ 30.7; 31.4; 34.4; 69.7, 69.9; 78.0, (C≡**C**); 85.5, (≡**C**H); 90.0, 93.6, (**C**≡**C**); 109.0; 116.4; 117.3; 120.6; 122.0; 125.2; 127.5; 128.8; 147.1; 153.7; 154.1; 159.1. EIMS m/e 346, (M^+, 27%); 84, (100%).

12-(*tert*-butyl)-3-(1-ethynyl)-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecin-2-yl tetrahydro-2H-2-pyranyl ether (15)

PPTS (0.10g, 0.4mmol) was added to a nitrogen blanketed room temperature solution containing, cyclophane **14** (0.81g, 2.3mmol), freshly distilled DHP (8mL) and dry dichloromethane (80mL). Solvent was removed after 1.5 hours and the residue purified via silica squat chromatography, employing 50:50 dichloromethane:hexanes as eluant. The title compound was isolated as a fluffy white solid (0.90g, 89%). Mp. FTIR (solid film) : 3288; 2953; 2874; 1488; 1379; 1261 cm^{-1}. ^1H NMR δ 1.31, (s, 9H, $C(\mathbf{CH_3})_3$); 1.62-1.95, (m, 6H); 2.09, (p, *J*4.5Hz, 2H, $ArOCH_2C\mathbf{H_2}$); 3.33, (s, 1H, **HC**≡); 3.62-3.67, (m, 1H, $OC\mathbf{H_2}$:THP); 3.96, (dt, *J*2.8,10.8Hz, 1H, $OC\mathbf{H_2}$,THP); 4.31-4.36, (m, 4H, $OC\mathbf{H_2}$); 5.47, (t, *J*2.8Hz, 1H, OC**H**O); 7.05, (d, *J*8.5Hz, 1H, Ar); 7.21, (s, 1H); 7.23, (s,1H); 7.32, (dd, *J*2.5,8.6Hz, 1H, Ar); 7.47, (d, *J*2.5Hz, 1H, Ar). ^{13}C NMR δ 18.3; 25.2; 30.2; 30.7; 31.3; 34.4; 61.8; 69.6; 69.7; 79.4; 82.4, (≡**C**H); 90.3; 93.3; 97.1; 113.7; 116.5;

118.4; 119.3; 121.9; 127.1; 127.3; 128.7; 147.0; 154.4; 155.0; 159.0.

3-[4-(3-hydroxypropoxy)-2,5-diiodophenoxy]-1-propanol (17)

A nitrogen blanketed DMF (50mL) solution of **16** (5.5g, 15mmol), 3-bromopropanol (8mL, 89mmol) potassium carbonate (20g, 120mmol), and water (15mL), was maintained at ambient temperature. Solvent was removed under high vacuum, the residue dissolved in ethyl acetate (400mL), washed with water (2×100mL) and dried. The residue was recrystallised from dichloromethane:acetone to afford the title compound as a white solid (4.99g, 69%). FTIR (solid film) : 3268 br; 2947; 2875; 1486; 1462; 1400; 1351; 1264; 1211 cm^{-1}. ^1H NMR ($CDCl_3$/d^6DMSO) : δ 2.02, (p, *J*6.1Hz, 4H, C**H**$_2$CH$_2$OH); 3.80, (q, *J*5.7Hz, 4H, CH$_2$**O**H); 4.02, (t, *J*5.3Hz, 2H, **O**H); 4.08, (t, *J*6.2Hz, 4H, ArOC**H**$_2$); 7.23, (s, 2H). ^{13}C NMR ($CDCl_3$/d^6DMSO) : δ 31.6; 58.0; 66.8; 85.6, (=**C**I); 122.0; 152.0.

1-{2,5-diiodo-4-[3-(tetrahydro-2H-2-pyranyloxy)propoxy]phenoxy}-3-(tetrahydro-2H-2-pyranyloxy)propane (18)

A nitrogen blanketed solution containing **17** (4.8g, 10mmol), PPTS (0.10g, 0.4mmol) and freshly distilled DHP (25mL), was heated at 50°C for 2 hours. Solvent was removed and the residue filtered through a silica squat column, employing 50:50 ethyl acetate:hexanes as eluant. The title compound was isolated as a pure straw oil in quantitative yield. FTIR (film) : 2938; 2871; 1458; 1348; 1262; 1205 cm^{-1}. ^1H NMR δ 1.52-1.78, (m, 12H); 2.10, (p, *J*6.2Hz, 4H, C**H**$_2$CH$_2$O); 3.51-3.70, (m, 4H); 3.80-4.03, (m, 4H); 4.08, (t, *J*6.2Hz, 4H, ArOC**H**$_2$); 4.61-4.65, (m, 2H, OC**H**O); 7.22, (s, 2H). ^{13}C NMR δ 19.4; 25.2; 29.4; 30.5; 62.1; 63.6; 66.9; 86.1, (=**C**I); 98.7; 122.5; 152.5. Calculated M^+ for $C_{22}H_{32}O_6I_2$ m/e 646.0292; found 646.0289. EIMS m/e 646, (M^+, 8%); 563; 169; 143; 85.

1-[5-(*tert*-butyl)-2-(tetrahydro-2H-2-pyranyloxy)phenyl]-2-{4-iodo-2,5-di[3-(tetrahydro-2H-2-pyranyloxy)propoxy]phenyl}acetylene (20)

Nitrogen was bubbled through a solution of **18** (6.8g, 11.1mmol) in triethylamine (25mL) for 30 minutes. A catalyst system consisting of $Pd(PPh_3)_4$ (0.10g, 0.09mmol), PPh_3 (0.05g, 0.19mmol) and CuI (0.04g, 0.21mmol) was added. The mixture was heated to 70°C and **19** (1.0g, 3.9mmol) was added over 4 hours. Solvent was removed after 7 hours and the residue separated into components via silica flash chromatography, employing 15:85 grading to 25:75 ethyl acetate: hexanes as eluants. Unreacted starting **18** was recovered (3.85g, 57%), and the title compound isolated as a clear oil (1.95g, 65%). FTIR (film) : 2943; 2871; 1495; 1464; 1373; 1265; 1205 cm^{-1}. ^1H NMR δ 1.31, (s, 9H, C(C**H**$_3$)$_3$); 1.47-1.82, (m, 18H); 2.06-2.12, (m, 4H); 3.50-3.67, (m, 4H); 3.80-3.83, (m, 2H); 3.94-4.04, (m, 4H); 4.09, (t, *J*6.1Hz, 2H); 4.15, (t, *J*6.4Hz, 2H); 4.57, (t, *J*3.5Hz, 1H); 4.62, (t, *J*3.3Hz, 1H); 5.56, (brs, 1H, OC**H**O:ArOTHP); 6.96, (s, 1H); 7.06, (d, *J*8.8Hz, 1H, Ar); 7.29, (dd, *J*2.5,8.7Hz, 1H, Ar); 7.36, (s, 1H); 7.51, (d, *J*2.5Hz, 1H, Ar). ^{13}C NMR δ 18.1; 19.3; 19.4; 25.1; 25.2; 29.4; 30.0; 30.4; 31.1; 33.8; 61.3; 61.9; 63.5, 63.6; 66.5; 66.7; 86.7, (=**C**I); 88.4, 91.2, (**C**≡**C**); 96.3, 98.6; 113.2; 114.2; 115.4; 115.8; 124.0; 126.5; 129.8; 144.0; 151.5; 153.8; 154.9. EIMS m/e 775, (M-H^+, 22%); 703; 622; 555; 486; 143; 85.

A second product was isolated and identified as (**22**) (.36g, 20%). ^1H NMR δ 1.31, (s, 18H, C(C**H**$_3$)$_3$); 1.44-2.03, (m, 24H); 2.13, (p, *J*6.2Hz, 4H, ArOCH$_2$C**H**$_2$); 3.43-3.45, (m, 2H); 3.59-3.69, (m, 4H); 3.78-3.84, (m, 2H); 3.94-4.07, (m, 4H); 4.18, (t, *J*6.1Hz, 4H, ArOC**H**$_2$); 4.58, (t, *J*3.4Hz, 2H,

OC**H**O:CH_2OTHP); 5.57, (t, *J*2.6Hz, 2H OC**H**O:ArOTHP); 7.07, (d, *J*8.7Hz, 2H, Ar); coincident with 7.07, (s, 2H); 7.29, (dd, *J*2.5,8.8Hz, 2H, Ar); 7.52, (d, *J*2.5Hz, 2H, Ar). ^{13}C NMR δ 18.3; 19.5; 25.2; 25.3; 29.6; 30.2; 30.6; 31.2; 34.0; 61.5; 62.2; 63.8; 66.4; 89.0, 91.9, (C≡C); 96.5, 98.9; 113.4; 114.3; 115.4; 117.3; 126.6; 130.0; 144.2; 153.2, 155.0,. EIMS m/e 906, (M^+, 1%); 628; 143; 85; 84.

3-[2-{2-[5-(*tert*-butyl)-2-tetrahydro-2H-2-pyranyloxy)phenyl]-1-ethynyl}-4-(3-hydroxypropoxy)-5-iodophenoxy]-1-propanol (21)

A nitrogen blanketed solution of **20** (0.36g, 0.46mmol), PPTS (0.050g, 0.2mmol), dichloromethane (15mL) and methanol (30mL) was heated at gentle reflux for 12 hours. Solvent was removed and the residue vacuum filtered through silica employing 40:60 ethyl acetate:hexanes as eluant. The title compound was isolated as a pale yellow oil (0.24g, 98%). FTIR (film) : 3325 br; 2955; 2879; 1486; 1465; 1378; 1270; 1210 cm^{-1}. ^{1}H NMR δ 1.29, (s, 9H, C(CH_3)$_3$); 2.02-2.10, (m, 4H, OCH_2CH_2); 3.08, (brs, 2H, CH_2OH); 3.84-3.89, (m, 4H, CH_2OH); 4.04-4.16, (m, 4H, ArOCH_2); 6.89, (d, *J*8.6Hz, 1H, Ar); 6.91, (s, 1H); 7.27, (dd, *J*2.5,8.6Hz, 1H, Ar); 7.28, (s, 1H); coincident with 7.28, (s, 1H, ArO**H**); 7.43, (d, *J*2.9Hz, 1H, Ar). ^{13}C NMR δ 31.2; 31.4, 31.7; 33.8; 59.8, 59.9; 67.4, 67.5; 87.0, (=CI); 90.7, 90.9, (**C**≡**C**); 108.8; 112.9; 114.5; 114.8; 122.1; 122.7; 127.7; 127.8; 142.7; 151.5; 153.2; 154.7.

3-{[12-(*tert*-butyl)-3-iodo-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecin-2-yl]oxy}-1-propanol (23)

A THF solution (10mL) of DEAD reagent (560μL, 3.6mmol) was added over 7 hours to a nitrogen blanketed solution of **21** (0.85g, 1.6mmol) and PPh_3 (0.94g, 3.6mmol) in THF (150mL), at room temperature. Water (1mL) was added after 12 hours, and the solvent removed. The residue was purified via silica flash column chromatoghraphy employing 50:50 dichloromethane:hexanes then dichloromethane as eluants. The title compound was isolated as a tacky oil (0.53g, 65%). FTIR (film) : 3397 br; 2956; 2875; 1466; 1372; 1258 cm^{-1}. ^{1}H NMR δ 1.31, (s, 9H, C(CH_3)$_3$); 2.08, (p, *J*5.7Hz, 4H, OCH_2CH_2); 2.40, (brs, 1H, O**H**); 3.88-3.92, (m, 2H, CH_2OH); 4.12, (t, *J*5.8Hz, 2H, $CH_2CH_2CH_2OH$); 4.30-4.35, (m, 4H); 6.89, (s, 1H); 7.05, (d, *J*8.5Hz, 1H, Ar); 7.32, (dd, *J*2.5,8.5Hz, 1H, Ar); 7.48, (d, *J*2.4Hz, 1H, Ar); 7.56, (s, 1H). ^{13}C NMR δ 30.5; 31.2; 31.7; 34.3; 60.3; 67.5; 69.5; 69.9; 86.4, (=CI); 90.0, 92.8, (**C**≡**C**); 113.2; 116.3; 118.1; 121.9; 127.3; 128.5; 133.0; 147.0; 153.7; 155.3; 158.8. Calculated M^+ for $C_{24}H_{27}O_4I$ m/e 506.0956; found 506.0964. EIMS m/e 506, (M^+, 58%); 262; 188,; 85; 84.

12-(*tert*-butyl)-3-{2-[12-(*tert*-butyl)-2-(3-hydroxypropoxy)-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecin-3-yl]-1-ethynyl}-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecin-2-yl tetrahydro-2H-2-pyranyl ether (24)

Nitrogen was bubbled through a solution of cyclophane **23** (0.53g, 1mmol) in triethylamine (25mL) for 20 minutes. A catalyst system consisting of $Pd(PPh_3)_4$ (0.060g, 0.05mmol), PPh_3 (0.025g, 0.10mmol), and CuI (0.020g, 0.11mmol) was added, followed by **13** (0.50g, 1.2mmol). Solvent was removed after 14 hours at room temperature, and the thick yellow suspension was purified via silica flash chromatography employing 5:95 ethyl acetate:dichloromethane as eluant. The title compound was isolated as a yellow solid (0.81g, 96%). M.p. 175°C partial dec. FTIR (solid film) : 3502 br; 2954; 2867; 1489; 1420; 1379; 1263 cm^{-1}. ^{1}H NMR δ 1.32, (s, 18H, C(CH_3)$_3$); 1.64-2.04, (m, 6H); 2.11, (p, *J*5.5Hz, 6H); 2.53, (t, *J*5.6Hz, 1H,

OH); 3.60-3.70, (m, 1H, OCH_2:THP); 3.92, (q, *J*5.5Hz, 2H, CH_2OH); 3.95-4.08, (m, 1H, OCH_2:THP); 4.22, (t, *J*5.8Hz, 2H, $ArOCH_2CH_2CH_2OH$); 4.30-4.40, (m, 8H); 5.52, (t, *J*2.8Hz, 1H, OCHO); 7.00, (s, 1H); 7.05, (d, *J*8.5Hz, 1H); 7.07, (d, *J*8.5Hz, 1H); 7.24, (s, 1H); 7.25, (s, 1H); 7.30, (s, 1H); 7.29-7.36, (m, 2H); 7.49, (d, *J*2.2Hz, 1H); 7.50, (d, *J*2.2Hz, 1H). ^{13}C NMR 18.4; 15.2; 30.3; 30.7; 31.3; 31.8; 34.3; 60.8; 61.8; 68.0; 69.6; 69.8; 90.5; 90.7; 91.6; 93.3; 93.5; 97.3; 114.2; 114.3; 114.9; 116.4; 116.6; 118.5; 118.6; 118.9; 121.9; 121.9; 126.4; 126.6; 127.2; 127.4; 128.6; 128.6; 146.9, 147.0; 153.7; 154.8; 155.3; 159.0. EIMS m/e 809, ($M+H^+$, 100%); 725; 446; 143; 85. UV/VIS (THF) λ_{max} 266; 315; 377; 397 nm.

12-(*tert*-butyl)-3-{2-[12-(*tert*-butyl)-2-(3-hydroxypropoxy)-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecin-3-yl]-1-ethynyl}-14,15-didehydro-7,8-dihydro-6H-dibenzo[f,j][1,5]dioxacycloundecin-2-ol (25)

Compound **24** (0.78g, 0.9mmol) was dissolved in dichloromethane (40mL), followed by the addition of methanol (100mL) and PPTS (0.10g, 0.4mmol). The mixture was heated at gentle reflux under nitrogen for 12 hours. Solvent was removed and the residue purified via silica squat chromatography, employing near boiling dichloromethane then 95:5 dichloromethane:ethyl acetate as eluants. The title compound was isolated as a unstable yellow solid film (0.45g, 64%). FTIR (solid film) : 3441 br; 2956; 2874; 1769; 1487; 1420; 1379; 1263 cm^{-1}. ^1H NMR δ 1.32, (s, 18H, $C(CH_3)_3$); 2.10-2.23, (m, 6H, OCH_2CH_2); 2.98, (brs, 1H, OH); 3.85-3.95, (m, 2H, CH_2OH); 4.23, (t, *J*5.8Hz, 2H, $ArOCH_2CH_2CH_2OH$); 4.30-4.50, (m, 8H); 6.98, (s, 1H); 7.05, (d, *J*8.4Hz, 1H); 7.04, (s, 1H); coincdent with 7.06, (d, *J*8.4Hz, 1H); 7.15, (s, 1H); 7.22, (s, 1H); 7.24, (brs. 1H ArOH); 7.30-7.35, (m, 2H); 7.48, (d, *J*2.4Hz, 1H); 7.49, (d, *J*2,5Hz, 1H). ^{13}C NMR δ 30.6; 31.3; 31.4; 34.3; 60.5; 67.7; 69.6; 69.8; 90.3; 90.6; 93.3; 93.4; 93.9; 110.6; 112.8; 113.7; 116.3; 116.5; 117.8; 119.1; 119.8; 121.8; 121.9; 124.2; 125.5; 127.2; 127.4; 128.5; 128.7; 146.9, 147.0; 153.4; 154.0; 154.8; 154.9; 159.0. EIMS m/e 724, (M^+, 18%); 143; 85.

1,4-di(1-ethoxyethoxy)-2,5-diiodobenzene (26)

PPTS (0.050g, 0.2mmol) was added to a nitrogen blanketed solution of 2,5-diiodo-1,4-hydroquinone (3.0g, 8mmol) and ethylvinyl ether (4mL, 42mmol) in dry dichloromethane (20mL). The mixture was heated at gentle reflux for 2.5 hours, solvent was removed and the residue purified via silica squat chromatography employing 50:50 dichloromethane:hexanes as eluant. The title compound was isolated as a cream solid (3.68g, 88%). Mp. 83-89°C. FTIR (solid film) : 2978; 2932; 1463; 1382; 1338; 1259 cm^{-1}. ^1H NMR δ 1.23, (t, *J*7.1Hz, 6H, OCH_2CH_3); 1.52, (d, *J*5.1Hz, 6H, CH_3CHO); 3.54-3.62, (m, 2H, OCH_2); 3.76-3.84, (M, 2H, OCH_2); 5.28-5.31, (m, 2H, OCHO); 7.43, (s, 2H, Ar). ^{13}C NMR δ 15.1; 20.1; 61.6; 88.6, (=CI); 101.4; 127.2; 151.6. EIMS m/e 505.2, (M^+, 49%); 433.4; 73; 45.

2,5-di{2-[12-(*tert*-butyl)-2-(3-hydroxypropoxy)-14,15-didehydro-7,8-dihydro-6H-dibenzo [f,j][1,5]dioxacycloundecin-3-yl]-1-ethynyl}-1,4-di(1-ethoxyethoxy)benzene (27)

Nitrogen was bubbled through a solution of **26** (0.13g, 0.25mmol) and triethylamine (5mL) for 15 minutes. A catalyst system consisting of $Pd(PPh_3)_4$ (0.050g, 0.04mmol), PPh_3 (0.025g, 0.1mmol), and CuI (0.02g, 0.1mmol) was added and allowed to stir for 15 minutes at ambient temperature. Compound **23** (0.20g, 0.5mmol) in degassed dichloromethane (10mL) was added via syringe pump over 8 hours and the mixture allowed to stir for 40 hours. Solvent was removed and the residue purified via silica squat chromatography,

employing dichloromethane then 60:40 ethyl acetate:hexanes as eluants. The title compound was isolated as a moderate purity yellow green oil in quantitative yield. FTIR : 2957; 2874; 1489; 1468; 1422; 1378; 1264; cm^{-1}. ^1H NMR δ 1.26, (t, *J*7.0Hz, 6H, $OCH_2C\mathbf{H}_3$); 1.32, (s, 18H, $C(C\mathbf{H}_3)_3$); 1.59, (d, *J*5.2Hz, 6H, $CHC\mathbf{H}_3$); 2.09-2.13, (m, 8H, $OCH_2C\mathbf{H}_2$); 2.98, (t, *J*4.9Hz,~2H, O**H**); 3.63-3.68, (m, 2H); 3.91-3.98, (m, 6H); 4.21, (t, *J*5.7Hz, 4H, $C\mathbf{H}_2CH_2CH_2OH$); 4.34-4.36, (m, 8H); 5.43, (q, *J*5.2Hz, 2H, OC**H**O); 6.99, (s, 2H); 7.07, (d, *J*8.5Hz, 2H, Ar); 7.26, (s, 2H); 7.28, (s, 2H); 7.33, (dd, *J*2.5,8.5Hz, 2H, Ar); 7.49, (d, *J*2.5Hz, 2H, Ar). ^{13}C NMR δ 15.1; 20.4; 30.6; 31.2; 31.8; 34.2; 60.4; 62.2; 67.4; 69.5; 69.7; 90.4, 90.7, 91.8, 93.5, (C≡C); 101.7; 113.8; 114.0; 116.1; 116.3; 118.7; 121.9; 122.0; 126.5; 127.3; 132.0; 146.9; 151.9; 154.6; 155.3; 159.0. FABMS m/e 1060, ($M+2H^+$, 29%); 1015; 942; 916. UV/VIS (λ_{max}, ε_{max}) : 412, (106000); 392, (92000); 318, (50000); 289, (34000) nm. Fluorescence (λ_{max}) : 480; 454 nm.

2,5-di{2-[12-(*tert*-butyl)-2-(3-hydroxypropoxy)-14,15-didehydro-7,8-dihydro-6H-dibenzo [f,j][1,5]dioxacycloundecin-3-yl]-1-ethynyl}-1,4-benzenediol (28)

PPTS (0.05g, 0.2mmol) was added to a nitrogen blanketed solution of **27** (0.19g, 0.18mmol) and methanol (20mL) in dichloromethane (10mL) at ambient temperature. After 48 hours solvent was removed and the residue purified via silica flash column chromatography employing eluants grading from 2:98 to 10:90 acetone:dichloromethane. The title compound was isolated as a moderate purity yellow film (0.070g, 43%) contaminated with inseparable impurities which made NMR assignment problematic. ^1H NMR (d^6DMSO/$CDCl_3$) δ 1.33, (s, 18H, $C(CH_3)_3$); 1.96-2.12, (m, 8H, $OCH_2C\mathbf{H}_2$); 3.72, (q, *J*5.5Hz, 4H, $C\mathbf{H}_2OH$); 4.17, (t, *J*5.8Hz, 4H, $OC\mathbf{H}_2$); 4.24-4.30, (m, 8H); 4.54, (t, *J*5.1Hz, 4H, $OC\mathbf{H}_2$); 6.90, (s, 2H); 7.12, (d, *J*7.8Hz, 2H, Ar); 7.12, (s, 2H); 7.27, (s, 2H); 7.41, (dd, *J*1.8,8.3Hz, 2H, Ar); 7.48, (d, *J*1.8Hz, 2H, Ar); 9.42, (s, 2H, ArO**H**). ^{13}C NMR (d^6DMSO/$CDCl_3$) : δ 27.4; 29.4; 30.4; 32.4; 60.0; 64.2, 67.6, 67.7; 88.4, 88.7, 90.6, 91.3, (**C**≡C); 110.0; 112.1; 112.5; 114.2; 116.1; 116.7; 120.3; 124.4; 125.7; 126.2; 145.0; 149.0, 152.3, 153.7, 157.0. FABMS m/e 915, ($M+1^+$, 27%); 446, (100%).

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