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Synthesis of annulated dioxins as electron-rich donors for cation radical salts

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Abstract—The synthesis of a series of new alkoxylated linearly annulated dioxins is described together with their cyclic voltammetric behavior and some preliminary result on their ability to form cation radical salts. Of these dioxins, seven (**8**, **12**, **19**, **21**, **27**, **33**, **34**) are the first representatives of entirely new heterocyclic systems. Dioxins **8**, **21**, **22** and **27** gave good quality cation radical salts upon electrocrystallization.

1. Introduction

In the field of organic electroactive materials, many different interesting applications can be envisaged and realized with slight alterations in the molecular structure. By designing and substituting the constituting π-system, properties like solubility, crystallinity, intramolecular π-overlap etc can be manipulated.

Low crystallinity together with high charge carrier mobility is a prerequisite for obtaining LED-characteristics. A good solubility together with large π-overlap is needed to get a good candidate for liquid phase processable materials for field-effect transistors.[1]

We have previously presented alkoxylated dibenzofurans[2] and naphthalenes[3] as donors for cation radical salts. These systems have in general generated interesting results, although conductivities have been modest and electron–electron repulsion high. ESR-signals have on the other hand been very narrow and intense, indicative of a high stability of the cation radical, a low spin–orbit coupling due to the presence of only lighter elements (C, H, O), and a good charge-carrier mobility because of regular π-stacking.

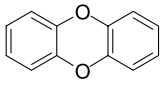
In order to reduce the electron–electron repulsion one must enlarge the communicative π-system (keep it planar), but one side effect is that the system usually gets more insoluble and therefore less useful.

We anticipated that a possible solution to this problem was to use annulated benzodioxins as the core π-system.

Dibenzodioxin **1** is a heterocyclic system whose halogenated derivatives form a notorious class of compounds, infamous for their ecotoxicity. Less is known about more electron-rich derivatives, although the stability of the corresponding cation radicals had been noted quite early.[4] This stability and the planarity of the dibenzodioxin[5] system prompted us to synthesize a series of substituted dibenzodioxins for evaluation of this class of compounds as potential donors for cation radical salts and as candidates for the active electrolyte in field-effect transistors. We were also encouraged by initial calculations,[6] that showed that dibenzodioxins should be more flexible than the corresponding anthracenes, thereby making them more soluble and easier to study.

Furthermore, recent interest in pharmacological applications of dihydrodioxins[7] and dibenzodioxins[8] should render the synthesis of these products interest to a larger audience.

We have previously published a preliminary report on these systems[9] and now want to present more results on our synthetic efforts in this project.



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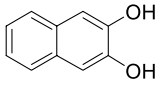

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2. Results and discussion

Published syntheses of dibenzodioxins are either aimed at preparing electron-poor halogenated structures[10] or use

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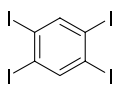
carcinogenic hexamethylphosphoramide (HMPA) as solvent.[11] Low yields are common when the substrate is not activated towards nucleophilic aromatic substitution.[12]

Our first strategy is based on the use of 2,3-dihydroxynaphthalene **2** as a nucleophile in a modification of the Ullmann ether synthesis.[13] Diiodinated electrophiles were readily available by Suzuki iodination[14] or the corresponding dibromo-derivatives by bromination with bromine in dichloromethane. We chose 1,3-dimethyl-3,4,5,6-tetrahydro2(1*H*)-pyrimidinone (DMPU) as a non-carcinogenic alternative to HMPA and copper(I) iodide as catalyst. No optimizations were made for each substrate. The yields and structures of dioxins **8**-**12** prepared from the diiodinated electrophiles are given in Table 1 and the corresponding dioxins **11**, **12** and **19**-**22** from the dibrominated electrophiles in Table 2.

As seen from the tables a series of new annulated dioxins could be synthesized in low to modest yields.

Although this method is relatively inefficient, it provides a fast way into highly substituted pentacyclic dioxins. All of these (except dinaphthodioxin **9**) are new compounds, and structures **8**, **12**, **19**, **20** and **21** are representatives of entirely new heterocyclic systems. Both sterically demanding and very electron-rich electrophiles (like **5** and **6**) can be forced to react under this protocol. We could not identify any clear difference between diiodinated or dibrominated electrophiles in terms of yield.

Attempts to make a fourfold etherification with substrates like 1,2,4,5-tetraiodobenzene **23** or 2,3,4,5-tetrabromothiophene **24** were unsuccessful.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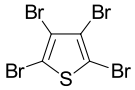
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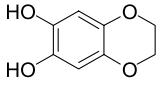
Although useful, 2,3-naphthalenediol (**2**) as the nucleophilic part is limiting the target structure to a napththodioxin, rendering all these donors a limited solubility and an 'unused' side for substitution. We therefore wished to explore the possibility of using other nucleophiles in the reaction protocol used for 2,3-naphthalenediol **2**.

Unfortunately, we were unsuccessful when applying this procedure with nucleophiles other than 2,3-dihydroxynaphthalene (**2**). Thus, 6,7-dihydroxybenzo-1,4-dioxane **25** failed to react with 2,3-diiodonaphthalene (**4**) and also with both 6,7-dibromo or 6,7-diiodobenzo-1,4-dioxane (**26** and **3** respectively).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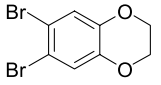
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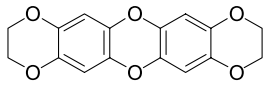
The latter reaction should have given access to a very interesting, symmetrical and electron-rich tri-dioxin **27**, that we envisaged to have interesting properties.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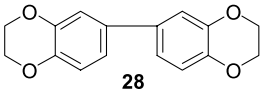
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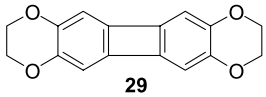
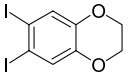
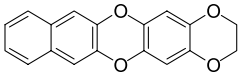
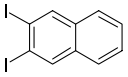
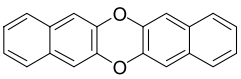
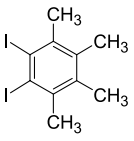
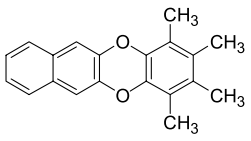
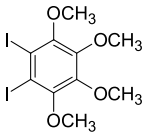
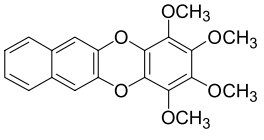
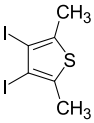
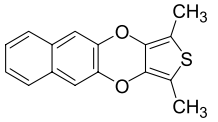

29

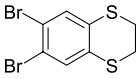
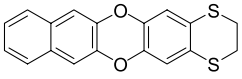
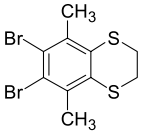
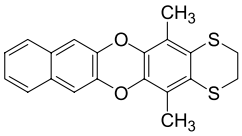
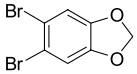
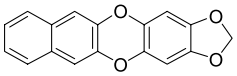
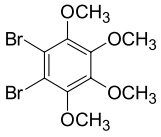
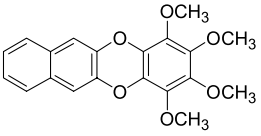
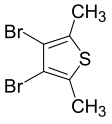
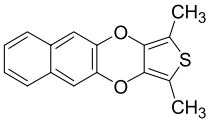
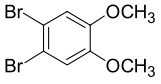
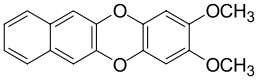
However, the only products that we could find in the reaction mixture had spectroscopic properties indicating

Table 1. Products **8**-**12** yielded from reaction of 2,3-dihydoxynaphthalene (**2**) with various diiodinated electrophiles[a]

Electrophile		Product		Yield (%)
	**3**		**8**	8
	**4**		**9**	25
	**5**		**10**	21
	**6**		**11**	2
	**7**		**12**	9

[a] The reaction was conducted in anoxic conditions.

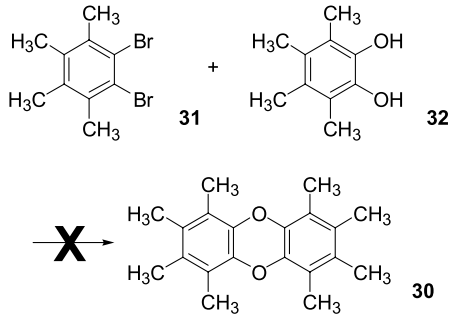
Table 2. Products **11**, **12** and **19**-**22** yielded from reaction of 2,3-dihydoxy-naphthalene (**2**) with various dibrominated electrophiles[a]

Electrophile		Product		Yield (%)
	**13**		**19**	34
	**14**		**20**	8
	**15**		**21**	4
	**16**		**11**	1
	**17**		**12**	9
	**18**		**13**	43

[a] The reaction was conducted in anoxic conditions.

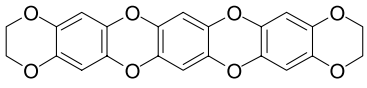
mainly dimer of benzo(1,4)dioxane, **28**, and traces of the biphenylene structure **29**.

Similarly unsuccessful was the attempt to synthesize the permethylated dibenzodioxin **30**, from dibromoprehnitene **31** and dihydroxyprehnitene **32** (Scheme 1).

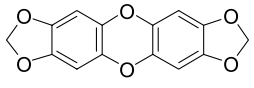


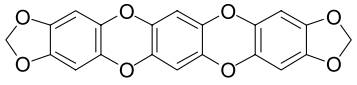
Scheme 1. Unsuccessful attempt to prepare compound **30**.

The results gained so far clearly showed that we needed heavier chalcogen substitution to get more electron-rich and thereby more easily oxidized donors. There was also an obvious need to alter the nucleophile to be able to synthesize dioxins other than ones with naphthalene substitution, since this substitution pattern led to more insoluble donor structures. Furthermore, we wished to synthesize both electron-rich and symmetrical structures since these reduce the risk for structural disorder in the solid state.

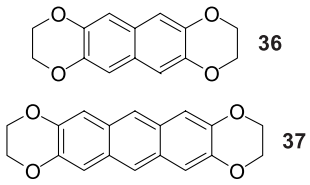


Inspired by the results so far we set up a new series of target molecules. We chose the highly symmetric tri-dioxin **27** and its higher homologue tetra-dioxin **33** as the prime targets.



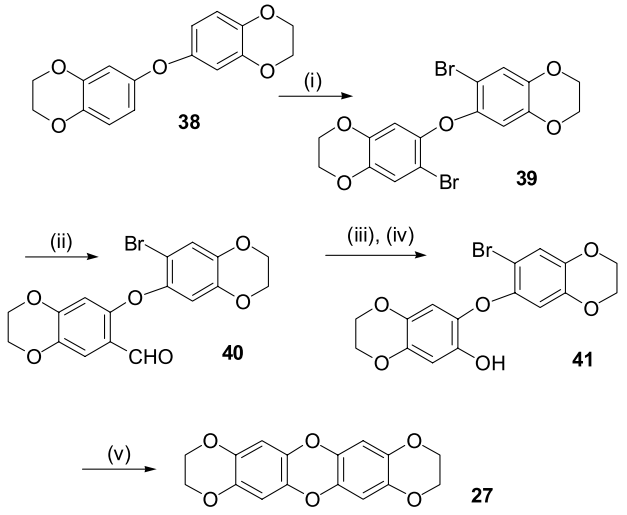


The ethylenedioxo substitution is often a good compromise between donating ability and steric demand. In comparison the methoxy group lowers the oxidation potential more effectively, but prevents good stacking of the π-donors in the cation radical salt, due to its relatively unrestricted rotation of the methoxy group. The methylenedioxy group is even less sterically demanding and has been shown to provide possibilities for hydrogen-bonding in the solid state.[15] Compounds **34** and **35** were therefore also included as target structures as a valuable isomer that should be possible to synthesize by the methodology we developed for the ethylenedioxy-analogues.



If our hypothesis was right, these structures should be both soluble and have a comparably low oxidation potential as well as a lower separation between the first and second half-wave in their cyclic voltammograms. In order to effectively compare the effect of one dioxin moiety inserted into the linear acene, we decided to synthesize the corresponding bis(dihydrodioxino)-substituted naphthalene and anthracene (**36** and **37**) respectively.

The first goal was the elusive tri-dioxin **27**. The synthesis is shown in Scheme 2.

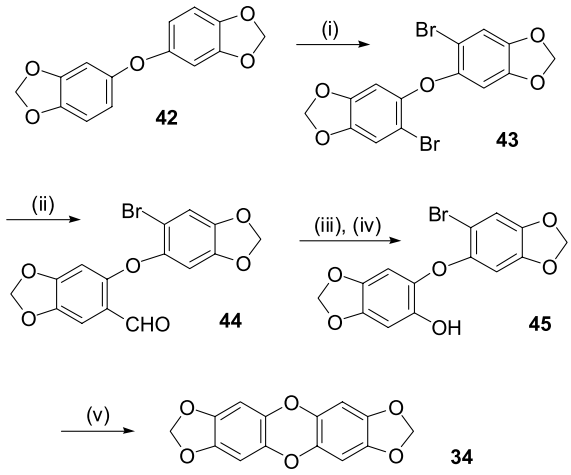


Scheme 2. Reagents and conditions: (i) Br_2, CH_2Cl_2, rt, 94% (ii) *n*-BuLi, THF, −70 °C, DMF, 49% (iii) MCPBA, CH_2Cl_2, reflux, 84% (iv) KOH, MeOH, rt, quant. (v) NaH, Cu(I)I, DMPU, 140 °C 31%.

The corresponding diaryl ether of benzodioxane, (or 6,6′-oxybis[2,3-dihydroyl-1,4-benzodioxin]) **38** could be conveniently dibrominated to give compound **39** in 94% yield. Monolithiation with n-butyllithium in THF and quenching with DMF gave the monoaldehyde **40** in 49% yield after chromatography. Bayer–Villiger oxidation with MCPBA gave the formate in 84% yield, which was hydrolyzed without purification in quantitative yield to the corresponding phenol **41**.

When treated with our standard Ullmann conditions we could isolate the target tri-dioxin **27** in 42% yield.

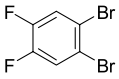
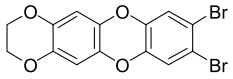
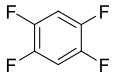
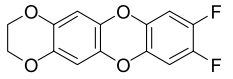
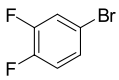
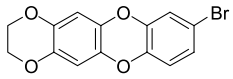
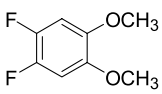
Analogously, we could synthesize the dioxolo-derivative **34** from the corresponding diaryl ether **42** in five steps and 14% yield (Scheme 3).



Scheme 3. Reagents and conditions: (i) Br_2, CH_2Cl_2, rt, quant. (ii) *n*-BuLi, THF, −70 °C, DMF, 47% (iii) MCPBA, CH_2Cl_2, reflux, quant (iv) KOH, MeOH, rt, 86% (v) NaH, Cu(I)I, DMPU, 140 °C, 36%.

Although successful for the construction of the pentacyclic structures **27** and **34**, we thought that this stepwise procedure would be impractical when constructing the higher homologues, and decided therefore to adopt another strategy for these structures. We envisaged that aromatic nucleophilic substitution could be useful in the construction of these systems and that proved to be correct. The results are shown in Table 3.

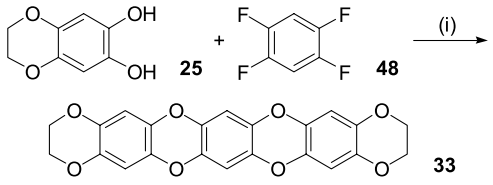
Table 3. Products **47**, **49** and **51** yielded from reaction[a] of 6,7-dihydroxy-benzo-1,4-dioxane (**25**) with some electrophiles

Electrophile		Product		Yield (%)
	**46**		**47**	Quant.
	**48**		**49**	72
	**50**		**51**	43
	**52**	No reaction		—

[a] Reactants and conditions: NaH, DMPU, 140 °C.

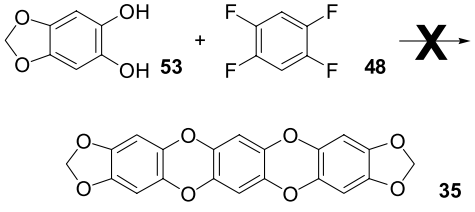
Reaction of 6,7-dihydroxybenzo-1,4-dioxane **25** with 1,2-dibromo-4,5-difluorobenzene **46** proceeded smoothly to give a quantitative yield of the dibrominated dibenzodioxin **47**, a reaction that nicely demonstrates the difference in reactivity of the halogen substituents. Analogously the difluorodibenzodioxin **49** could be synthesized in useful yields from 6,7-dihydroxybenzo-1,4-dioxane **25** and 1,2,4,5-tetrafluorobenzene **48**. However, when we used 4,5-difluorobromobenzene **50** for this reaction, we could isolate the monobromodibenzodioxin **51** in a modest 43% yield, and 4,5-difluoroveratrol **52** was completely unreactive under these conditions, once again showing the importance of the para-substituents influence on the reactivity.

By replacing the DMPU with N-methylpyrrolidinone (NMP), increasing the temperature to 205 °C, and using 2 equiv. of 6,7-dihydroxybenzo-1,4-dioxane (**25**) versus 1,2,4,5-tetrafluorobenzene (**48**), we could perform a fourfold aromatic nucleophilic substitution, and isolate the higher homologous tetra-dioxin **33** in 81% yield (Scheme 4).



Scheme 4. Reagents and conditions: (i) NaH, NMP, 205 °C, 81%.

In accordance with our expectations, product **33** was rather soluble, although being a linear heptacycle; for example, ^{1}H NMR could be recorded in deuterated chloroform without any problem. Surprisingly enough, extension of this protocol to the analogous dioxolo-derivative **35** was not successful (Scheme 5).

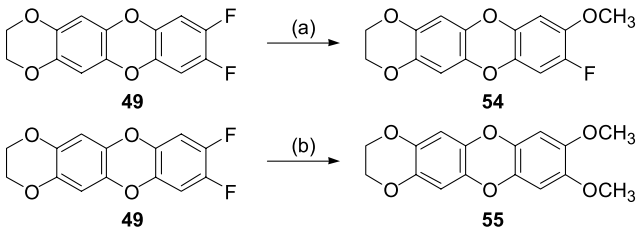


Scheme 5. Reagents and conditions: (i) NaH, NMP, 205 °C.

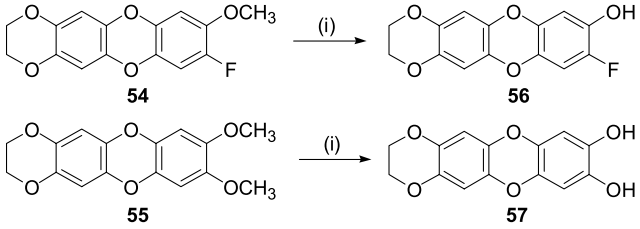
We then investigated the application of this methodology for the higher analogues of linear benzodioxins.

Selective methoxylation of the difluoro-derivative **49** to either the fluoromethoxy- or the dimethoxy-analogue (**54** and **55**) proceeded in useful yields, 81 and 63%, respectively (Scheme 6).

These could then be conveniently demethylated using the boron tribromide dimethylsulfide complex,[16] yielding the corresponding phenols (**56** and **57**) in 93 and 86% respectively (Scheme 7).



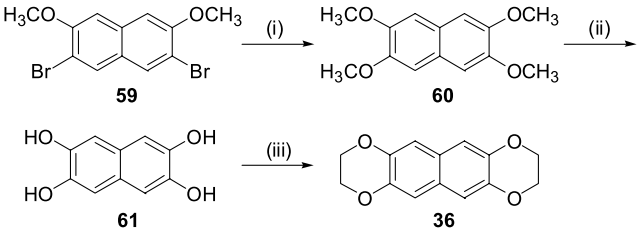
Scheme 6. Reagents and conditions: (a) NaOMe (1.1 equiv.), NMP, 90 °C, 83% (b) NaOMe (4 equiv.), NMP, 140 °C, 61%.



Scheme 7. Reagents and conditions: (i) $BBr_3(CH_3)_2S$, 1,2-dichloroethane, reflux. 93 and 86% respectively.

Our attempts to synthesize longer homologues of **33** have so far been unsuccessful. All attempts to dimerize **56** under basic conditions, or **57** under acidic conditions failed. Also, much to our disappointment, the dihydroxyderivative **58** seemed to be more or less useless as a nucleophile; all attempts to react this compound with 1,2-dibromo-4,5-difluorobenzene, or even iodomethane, failed.[17] Similarly, all attempts to substitute the dibromodibenzodioxin **47** were unsuccessful or, as in the case of methoxylation, less rewarding than the corresponding reactions for the fluoro-derivative **49**.

Bis(dihydrodioxino)naphthalene **36** could be synthesized from commercially available 2,7-dihydroxynaphthalene via 2,7-dibromo-3,6-dimethoxynaphthalene (**59**) (Scheme 8). Methoxylation of 2,7-dibromo-3,6-dimethoxynaphthalene[18] (**59**) with sodium methoxide in the presence of copper(I) iodide in DMF gave 2,3,6,7-tetramethoxynaphthalene[19] (**60**) in up to 80% yield. By refluxing 2,3,6,7-tetramethoxy-naphthalene in concentrated hydrobromic acid in the presence of a catalytical amount of tetra-*n*-butylammonium bromide,[20] a fourfold demethylation occured to give 2,3,6,7-tetrahydroxynaphthalene (**61**) in quantitative yield. 2,3,6,7-tetrahydroxynaphthalene was used immediately in the next step without further purification. 2,3,6,7-Tetra-hydroxynaphthalene **61** seemed to be quite unstable, since the primary off-white material turned green and then

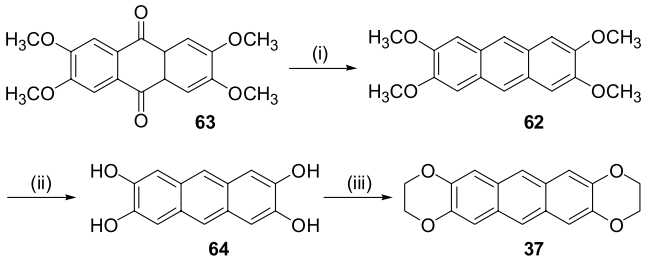


Scheme 8. Reagents and conditions: (i) NaOMe, Cu(I)I, DMF, 64% (ii) conc. HBr, n-Bu_4NBr, reflux, quant (iii) 1-chloro-2-bromoethane, K_2CO_3, DMSO, 100 °C 23%.

darkened further within minutes when exposed to ambient laboratory atmosphere.

Treatment of 2,3,6,7-tetrahydroxynaphthalene **61** with 1-chloro-2-bromoethane in DMSO in the presence of potassium carbonate gave the desired 2,3,6,7-bis(ethylenedioxy)-naphthalene **36** in 23% yield.

The 2,3,6,7-bis(ethylenedioxy)-anthracene **37** was prepared from 2,3,6,7-tetramethoxyanthracene **62**, which was synthesized from the corresponding anthraquinone **63**[21] by reduction with tetra-*n*-butylammonium borohydride/iodomethane (Scheme 9). Demethylation of 2,3,6,7-tetramethoxyanthracene **62** yielded 2,3,6,7-tetrahydroxy-anthracene **64** in 85% and subsequent fourfold alkylation then gave the desired compound **37**.[22]



Scheme 9. Reagents and conditions: (i) *n*-Bu_4NBH_4, CH_3I; (ii) conc. HBr, *n*-Bu_4NBr, reflux; (iii) 1-chloro-2-bromo-ethane, K_2CO_3, DMSO, 100 °C.

2.1. Cyclic voltammetry

All compounds except **9** and **36** showed one quasi-reversible oxidation–reduction couple (Table 4).

Table 4. Cyclic voltammetric results from synthesized dibenzodioxins[a]

Compound	$E^{1/2}$	Compound	$E^{1/2}$
8	1.12	**22**	1.02
9	>1.6	**27**	0.93
10	1.24	**33**	1.03
11	1.24	**34**	0.93
12	1.46	**36**	1.35
19	1.14	**37**[b]	1.08
20	1.05	**60**	1.08
21	1.04	**62**	0.83

[a] 1 mM in $TBAPF_6$ (0.15 M) CH_2Cl_2, scan rate 100 mV/s, E versus SCE.
[b] 1 mM in $TBABF_4$ (0.15 M) CH_2Cl_2, scan rate 100 mV/s, E versus SCE.

Several features are noteworthy. The bis-alkoxysubstituted dibenzodioxins **27** and **34** have the lowest oxidation potentials, as could be expected but the mono-annulated (**8**, **20**, **21**, **22**) derivatives were only roughly 100 mV higher.

Also apparent is the inefficiency of more than two methoxy substituents in lowering the oxidation potential; donor **11** has an oxidation potential 200 mV higher than **22**.

The addition of one more benzodioxin unit is not lowering the oxidation potential, as seen by the comparison between **27** and **33**. The interpretation of the cyclic voltammetry of **33** is not trivial since the rather low solubility makes comparison difficult, so we cannot rule out that the oxidation potential at 1.03 V is a two-electron process, but we have no reasons to believe this. Furthermore, it is also evident that the dibenzodioxin core is a better donor than the corresponding anthracene (**27** and **37**). The hypothesis that longer π-systems should give lower electron–electron repulsion is however not supported by the current CV-data.

2.2. Electrocrystallization

Some of the target dioxins were tested as donors to cation radical salts in a constant current electrolysis in a divided cell.

Donors **9**, **10**, **11**, **12**, and **19** did not yield any cation radical salts under these conditions. This is perhaps not surprising in the case of **9**, since it is either very insoluble or very hard to oxidize. In the case of **10**, **11** and **12**, they are substituted with steric demanding substituents that should make precipitation less favorable. In these cases we did observe a strongly colored solution under electrolysis, which supports the hypothesis that the cation radicals of these donors are too soluble under these conditions. Electrolysis in a freezer did not improve the situation for donor **10**.

Donors **33** and **36** gave to our disappointment only polycrystalline materials that were difficult to analyze.

More rewarding was the electrolysis of donors **8**, **21**, **22** and **27**. Well-formed crystals with the composition $(\mathbf{8})_2AsF_6$ (2:1-salt), $(\mathbf{21})AsF_6$ (1:1-salt), and $(\mathbf{27})_2AsF_6$, $(\mathbf{27})_2PF_6$, $(\mathbf{27})_2ClO_4$, (2:1-salts), could be harvested after approximately one week of electrolysis. The dimethoxy-substituted donor **22** formed a non-stoicheometric salt with AsF_6, with a donor equivalent of 1.1–1.2.

The salt $(\mathbf{8})_2AsF_6$ is a semiconductor with a room temperature conductivity of $\approx 6\times10^{-3}$ S/cm and a very high number of spins as measured by ESR (0.25 spins/molecular unit). Details of the solid-state properties of these salts will be published elsewhere.

The results from the cyclovoltammetry and electrolysis experiments clearly show the superiority of the ethylenedioxy substituent as a good compromise between donor strength and good crystallinity through low steric demands.

2.3. Other applications

An unforeseen application for the symmetric dioxins **27** and **33** as substrates in matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) has also been investigated. The dioxins combination of robust MS-properties (low fragmentation) and electroactivity render them with interesting properties, and make them useful as substrates for sensitizing other low molecular weight compounds, which are otherwise impossible to analyze with standard techniques.[23]

Linear acenes like pentacene have been demonstrated to work as an active component in field-effect transistors.[24] We are now pursuing experiments to establish whether our longer dioxins could work in these applications as well,

albeit being more soluble. Results of this work will be published in due course.

3. Conclusion

We have synthesized a series of new alkoxylated dibenzodioxin donors. Several of these are the first representatives of entirely new heterocyclic systems. The more alkoxy-substituted donors have half-wave potential in the range 0.9–1.0 V versus SCE which characterizes them as good to fair electron donors. The dioxins are more soluble than the corresponding all-carbon acenes. We have also demonstrated that good quality cation radical salts can be synthesized from dibenzodioxins, especially those with ethylenedioxy-substitution. However, the longer derivatives do not show any promising properties in terms of the results achieved from cyclovoltammetry and electrocrystallization.

4. Experimental

4.1. General

All operations except where indicated were performed in ambient atmosphere, without any special care taken for the exclusion of air or moisture. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AM 400 and at 500 and 125 MHz, respectively, on a Bruker AM 500. Mass spectra were recorded on a Finnegan SSQ 7000 (electron impact). Elemental analyses were performed by Analytische Laboratorien GmbH, Germany. THF was freshly distilled from sodium benzophenone ketyl, and NMP and DMPU were dried over CaH_2. All other commercial reagents and solvents were used as received, without further purification. Melting points are uncorrected. Commercial compounds: **2**, **15**, **18**, **24**, **46**, **48**, **50** and **52**. Substances **4**,[25] **17**,[26] **23**,[27] **38** and **42**,[28] **59**[18] were prepared according to literature procedures. We have provided sufficient analytical data for all end-products to be unequivocally characterized, whereas some of the intermediates have in a few cases only been characterized by NMR.

4.1.1. 6,7-Diiodo-2,3-dihydrobenzo[1,4]dioxin 3. I_2 (17.74 g, 69.9 mmol) and H_5IO_6 (5.31 g, 23.3 mmol) were dissolved in a mixture of 100 mL HOAc, 10 mL H_2O and 5 mL conc. H_2SO_4. 1,4-benzodioxane (11.10 g, 81.5 mmol) was then added with stirring. The reaction flask was then sealed with a septum and heated to 50 °C overnight. After cooling to rt crystals were filtered off and dissolved in CH_2Cl_2. Addition of H_2O to the reaction mixture afforded more crystals. The aqueous phase was extracted with CH_2Cl_2 and the organic layers were combined, washed with H_2O, dried over $MgSO_4$ and the solvent was then evaporated yielding 27.78 g (82%) of sufficiently pure product **3**. Recrystallization from MeOH afforded 11.57 g (37%) analytically pure shiny crystals of **3**.

Mp=118.9–119.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.22 (s, 4H), 7.34 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ=64.1, 96.1, 127.3, 144.2. MS (EI) *m/e* (%) 387.9 (M^+, 100).

4.1.2. Diodoprehnitene 5. I_2 (35.87 g, 141.3 mmol) and H_5IO_6 (10.73 g, 47.1 mmol) were dissolved in 500 mL of a mixture of HOAc, H_2O and conc. H_2SO_4 in the proportions of 100/20/3 respectively. 1,2,3,4-Tetramethylbenzene (22.13 g, 164.9 mmol) was then added under stirring. The flask was then sealed and heated to 50–55 °C overnight. After cooling to rt the crystals formed were collected by filtration, washed with hexane, and dried to give 51.10 g of NMR-pure crystalline material. An additional 7.35 g of semicrystalline material could be isolated from the reaction mixture by extractive methods, which could be recrystallized from EtOH to give 1.90 g of pure product as white crystals. The combined yield of **5** was 83%.

Mp=184–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.28 (s, 6H), 2.69 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=18.7, 31.7, 114.8, 135.7, 139.8. GC-MS (EI) *m/e* (%) 386 (M^+, 100).

4.1.3. Diiodo-1,2,3,4-tetramethoxybenzene 6. I_2 (7.61 g, 30.0 mmol) and H_5IO_6 (2.28 g, 10.0 mmol) were dissolved in 100 mL of a mixture of HOAc, H_2O and conc. H_2SO_4 in the proportions of 100/20/3 respectively. 1,2,3,4-Tetramethoxybenzene[29] (6.94 g, 35.0 mmol) was then added under stirring. The flask was then sealed and heated to 50–55 °C overnight. After cooling to rt the reaction mixture was separated between H_2O and CH_2Cl_2 the organic phase was then washed with additional H_2O, $NaHCO_3$ solution, $Na_2S_2O_3$ solution and finally brine. After drying over $MgSO_4$ and evaporation under reduced pressure, 12.86 g of **6** as a heavy oil could be isolated. Crystallization occurred after a few weeks, mp=29–30 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ=3.80, (s, 6H), 3.95, (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=60.7, 61.2, 99.5, 147.3, 151.0. GC-MS (EI) *m/e* (%) 450 (M^+, 100).

4.1.4. 3,4-Diiodo-2,5-dimethylthiophene 7. I_2 (19.39 g, 76.4 mmol) and H_5IO_6 (5.81 g, 25.5 mmol) were dissolved in 250 mL of a mixture of HOAc, H_2O and conc. H_2SO_4 in the proportions of 100/20/3 respectively. 2,5-dimethylthiophene (10.00 g, 89.1 mmol) was then added. The reaction was heated to 30 °C and stirred overnight. The reaction mixture was transferred to a separatory funnel and H_2O was added. The H_2O phase was extracted 4×300 mL with CH_2Cl_2. The organic phase was then washed with 500 mL H_2O, 4×500 mL $NaHCO_3$ solution and 500 mL $Na_2S_2O_3$ solution. After drying over $MgSO_4$ and evaporation under reduced pressure could the mayor part of the product be achieved by hot filtration from 200 mL EtOH. An additional amount of product was obtained from the filtrate of the hot filtration through crystallization overnight. The total yield was 15.70 g (48%) of slightly brown crystals.

R_f (hexane/CH_2Cl_2; 1:1)=0.55. Mp=77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.50 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ=19.8, 93.4, 137.0. GC-MS (EI) *m/e* (%) 364 (M^+, 100).

4.1.5. 6,7-Dibromo-2,3-dihydrobenzo(1,4-dithiin) 13. 2,3-Dihyd-robenzo(1,4-dithiin)[30] (10.30 g, 61.2 mmol) was dissolved in 250 mL of CH_2Cl_2 and Br_2 (6.6 mL, 128.6 mmol) dissolved in 50 mL of CH_2Cl_2 was added

dropwise during 30 min. The mixture was allowed to stir for an additional 1 h, and then H_2O was added. The resulting mixture was transferred to a separatory funnel, the phases separated, and the organic phase was washed with an additional 200 mL of H_2O, 175 mL of $NaHCO_3$ solution, 200 mL of $Na_2S_2O_3$ solution, and finally with 200 mL of brine. The resulting solution was dried over $MgSO_4$ and concentrated under reduced pressure, to yield 18.92 g (95%) of pink crystals with satisfactory NMR-purity. Further purification can be achieved by recrystallization from EtOH.

Mp = 127–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.25 (s, 4H, CH_2), 7.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 28.7, 120.4, 132.1, 132.4. GC-MS (EI) *m/e* (%) 326 (M^+ + 2, 100).

4.1.6. 5,8-Dimethyl-6,7-dibromo-2,3-dihydrobenzo(1,4-dithiin) 14. Commercially available 2,5-dimethylcyclohexanone (5.00 g, 39.6 mmol, isomeric mixture) was dissolved in 50 mL CH_2Cl_2 together with 1,2-ethanedithiol (3.32 mL, 39.6 mmol). Borontrifluoride etherate (0.73 mL, 5.9 mmol) was then cautiously added and the resulting solution was left on stirring at ambient temperature for 1 h, at which time TLC showed consumption of all starting ketone. The reaction was stopped by the addition of H_2O, the resulting phases were separated in a separatory funnel. The organic phase was washed with $NaHCO_3$ solution and with an additional portion of H_2O, dried over $MgSO_4$ and subsequently concentrated under reduced pressure to give 6.62 g (83%) of the corresponding ethylenedithioketal (6,9-dimethyl-1,4-dithiaspiro[4,5]-decane) as an oily material. Despite the complicated ^{1}H NMR due to the mixture of isomers, ^{13}C NMR showed no additional signals other than two sets of nine signals that could be attributed to two isomers of the desired product.

^{13}C NMR: major isomer: 18.07, 21.96, 32.50, 34.30, 34.50, 38.74, 39.87, 42.78, 54.30; minor isomer: 17.52, 22.14, 27.57, 31.90, 38.15, 39.17, 41.48, 45.76, 74.47.

We therefore decided to use these products directly in the following reaction. Thus the ethylenedithioketal (3.00 g, 9.9 mmol) was dissolved in 70 mL of CH_2Cl_2 and Br_2 (11.84 g, 74.1 mmol), dissolved in 20 mL of CH_2Cl_2 was added during 30 min. After addition the resulting dark solution was left under stirring for 1 h, brought to a brief reflux, and quenched with H_2O after cooling. The resulting mixture was transferred to a separatory funnel, phases separated, and the organic phase washed with an additional portion of H_2O, then $NaHCO_3$ solution, $Na_2S_2O_3$ solution, and finally with brine. The resulting solution was dried over $MgSO_4$ and concentrated under reduced pressure, to yield 5.63 g of semicrystalline material. Recrystallization from EtOH yielded 5.00 g (95%) of slightly reddish crystals.

Mp = 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.58 (s, 6H), 3.24 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 22.8, 30.3, 124.7, 132.7, 135.5. GC-MS (EI) *m/e* (%) 354 (M^+ + 2, 100).

4.1.7. Dibromo-1,2,3,4-tetramethoxybenzene 16. 1,2,3,4-Tetra-methoxybenzene (5.71 g, 28.8 mmol) was dissolved in 50 mL of CH_2Cl_2 under stirring. Bromine (9.67 g, 60.5 mmol) in 50 mL CH_2Cl_2 was then added dropwise during 1 h. The resulting light brown mixture was transferred to a separatory funnel and washed with 200 mL of H_2O, 175 mL of $NaHCO_3$ solution, 200 mL of $Na_2S_2O_3$ solution, and finally with 200 mL of brine. The resulting solution was dried over $MgSO_4$ and concentrated under reduced pressure, to give **16** in quantitative yield as a heavy oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.85 (s, 6H), 3.93 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 61.0, 61.4, 115.1, 147.2, 148.5. GC-MS (EI) *m/e* (%) 356 (M^+ + 2, 100).

Synthesis of dioxins **8**-**12** and **19**-**22**, general procedure: NaH (42.0 mmol, 60 or 80% oil dispersion) was cautiously added to 2,3-dihydroxynaphthalene, (**2**), (3.20 g, 20.0 mmol), dissolved in DMPU (200 mL) under nitrogen. After hydrogen evolution had ceased, Cu(I)I (7.62 g, 40.0 mmol) was added together with the appropriate dihaloaromatic electrophile (20.0 mmol). The resulting dark solution was warmed to 150 °C during 21 h and the bulk of the solvent was then distilled under pump vacuum. The tarry residue was treated with 2 M HCl, the precipitate filtered and dissolved in CH_2Cl_2 with the aid of an ultrasonic bath. This solution was once again filtered, the filtrate washed with 2 M NaOH, dried and evaporated. The crude product thus obtained was treated with EtOH from which the product precipitated. The product was submitted to gradient chromatography (hexane/CH_2Cl_2) which usually afforded NMR-pure material. An analytically pure sample was obtained after recrystallization from toluene:EtOH or sublimation (1.5×10^{-2} mbar).

4.1.8. Dioxin 8. Chromatography gave 505 mg (8%) of white crystals.

Mp > 260 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.23 (s, 4H, CH_2), 6.51 (s, 2H, CH), 7.21 (s, 2H, CH), 7.32 (m, 2H, CH), 7.63 (m, 2H, CH). ^{13}C NMR (DMSO-d_6) δ = 64.14 (OCH_2), 104.82 (C–H), 111.96 (C–H), 125.43 (C–H), 126.79 (C–H), 130.42 q, 134.54 q, 139.18 q, 140.90 q. MS (EI) *m/e* (%) 292.1 (M^+, 100).

Anal. Calcd for $C_{18}H_{12}O_4$: C, 73.96; H, 4.15. Found: C, 73.94; H, 4.20. Anal. Calcd for 2:1 salt of $(\mathbf{8})_2AsF_6$: C, 55.90; H, 3.13; F, 14.74. Found: C, 55.75; H, 3.07; F, 14.97.

4.1.9. Dioxin 9. The crude product was sublimed at 215 °C, which gave 1.40 g (25%) of grey crystals.

R_f (toluene) = 0.79. Mp > 230 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (s, 4H, CH), 7.36 (m, 4H, CH), 7.69 (m, 4H, CH). MS (EI) *m/e* (%) 284 (M^+, 100).

4.1.10. Dioxin 10. Chromatography yielded 1.23 g (21%) of white crystals.

R_f (hexane/CH_2Cl_2; 1:1) = 0.83. Mp = 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.16 (s, 6H,CH_3), 2.24 (s, 6H, CH_3), 7.27 (s, 2H, CH), 7.31 (m, 2H, CH), 7.63 (m, 2H,

CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ=11.7, 15.7, 111.6, 121.1, 124.8, 126.6, 129.8, 130.7, 137.3, 142.4. MS (EI) *m/e* (%) 290 (M^+, 100). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.44; H, 6.34.

4.1.11. Dioxin 11. 106 mg (2%) of white crystals was achieved after chromatography.

R_f (CH_2Cl_2)=0.3. Mp=127–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.91 (s, 6H, CH_3), 3.97 (s, 6H, CH_3), 7.34 (m, 2H, CH), 7.36 (s, 2H, CH), 7.66 (m, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ=61.8, 61.9, 112.4, 125.4, 126.8, 130.9, 132.4, 137.7, 141.0, 142.6. MS (EI) *m/e* (%) 354 (M^+, 53). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.78; H, 5.13. Found: C, 67.47; H, 5.25.

4.1.12. Dioxin 12. Chromatography yielded 463 mg (9%) of off-white crystals. This compound can also be recrystallized from EtOH to give beige needles.

R_f (hexane/CH_2Cl_2; 1:1)=0.54. Mp=159–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.30 (6H, s), 7.32–7.35 (4H, m), 7.66 (2H, dd, J=6.3, 3.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=10.6, 109.3, 112.4, 125.1, 126.7, 130.3, 134.3, 140.9. MS (EI) *m/e* (%) 268 (M^+, 100). Anal. Calcd for $C_{16}H_{12}O_2S$: C, 71.62; H, 4.51. Found: C, 71.42; H, 4.50.

4.1.13. Dioxin 19. Chromatography yielded 2.21 g (34%) of white crystals.

R_f (hexane/CH_2Cl_2; 1:1)=0.43. Mp=233–234 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.24 (s, 4H, CH2), 6.82 (s, 2H, CH), 7.24 (s, 2H, CH), 7.33 (m, 2H, CH), 7.64 (m, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ=29.5, 112.2, 116.5, 125.3, 126.4, 126.8, 130.7, 139.5, 141.4. MS (EI) *m/e* (%) 324 (M^+, 100). Anal. Calcd for $C_{18}H_{12}O_2S_2$: C, 66.64; H, 3.74. Found: C, 66.45; H, 3.81.

4.1.14. Dioxin 20. Chromatography yielded 342 mg (8%) of white crystals.

Mp=195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.31 (s, 1H), 3.21 (s, 1H), 7.27 (s, 1H), 7.32 (dd, 2H, J=6.3, 3.3 Hz), 7.63 (dd, 2H, J=6.3, 3.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=12.0, 30.2, 111.9, 122.2, 125.1, 126.7, 127.0, 130.7, 137.5, 141.8. MS (EI) *m/e* (%) 352 (M^+, 100), 337 (10), 324 (20). Anal. Calcd for $C_{20}H_{16}O_2S_2$: C, 68.15; H, 4.58. Found: C, 67.96; H, 4.65.

4.1.15. Dioxin 21. Chromatography yielded 231 mg (4%) of off-white crystals.

R_f (hexane:CH_2Cl_2; 1:1)=0.51. Mp >240 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=5.92 (s, 2H, CH2), 6.52 (s, 2H, CH), 7.20 (s, 2H, CH), 7.32 (m, 2H, CH), 7.63 (m, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ=98.3, 101.5, 111.8, 126.7, 130.8, 135.6, 141.7, 143.0. MS (EI) *m/e* (%) 278 (M^+, 100). Anal. Calcd for $C_{17}H_{10}O_4$: C, 73.37; H, 3.63. Found: C, 73.60; H, 3.76. Anal. Calcd for (**21**)AsF_6: C, 43.70; H, 2.16. Found: C, 43.47; H, 2.06.

4.1.16. Dioxin 22. Chromatography yielded 2.54 g (43%) of white crystals.

R_f (hexane/CH_2Cl_2; 1:1)=0.53. Mp=156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.86 (s, 6H, CH_3), 6.56 (s, 2H, CH), 7.21 (s, 2H, CH), 7.33 (m, 2H, CH), 7.64 (m, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ=56.3, 100.9, 111.8, 125.1, 126.6, 130.7, 134.3, 141.7, 144.8. MS (EI) *m/e* (%) 294 (M^+, 100). Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.45; H, 4.80. Found: C, 73.43; H, 4.75.

4.1.17. 2,3-Dihydrobenzo[1,4]dioxin-6,7-diol 25. 1,4-Benzodioxane-6-carboxaldehyde (57.46 g, 0.35 mol) was dissolved in CH_2Cl_2 (1200 mL) and MCPBA (45.30 g, 0.525 mol, 50% in H_2O) was added to the solution, which was gently refluxed at 45 °C for 17 h and a yellow precipitate formed. The CH_2Cl_2 was evaporated and the residue was dissolved in EtOAc, washed with a saturated $NaHCO_3$ solution, followed by brine and then dried over $MgSO_4$. The solvent was evaporated yielding 55.3 g (88%) of formate as a red brown oil. This intermediate product was dissolved in MeOH and was hydrolyzed at rt for 45 min with a KOH solution (10% excess). The solution was neutralized with 2 M HCl and the aqueous phase was extracted with CH_2Cl_2, dried over $MgSO_4$ and evaporated to dryness yielding 39.7 g (85%) of 2,3-dihydrobenzo[1,4]dioxin-6-ol. 15 g of the crude product was submitted to chromatography on a silica gel column (hexane/EtOAc; 80:20), affording 10 g pure material as a brown oil and 4.5 g of material with some small impurities (overall yield of 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=4.21 (m, 4H), 6.32 (dd, 1H, J=8.5, 2.7 Hz), 6.38 (d, 1H, J=2.7 Hz), 6.72 (d, 1H, J=8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ=64.1, 64.6, 104.3, 108.3, 117.6, 137.6, 143.8, 150.0.

To a solution of KH_2PO_4 (7.08 g, 52.0 mmol) in 450 mL H_2O, cooled on an ice-bath, $NO(KSO_3)_2$ (Fremy's salt) (50.00 g, 186.3 mmol) was added in portions under vigorous stirring. 2,3-dihydrobenzo[1,4]dioxin-6-ol (14.18 g, 93.2 mmol) was dissolved in 20 mL MeOH and added dropwise to the mixture during 25 min and was then left stirring on the ice-bath for a further 1 h. The red precipitate that formed was filtered, washed with H_2O and dried in a desiccator, yielding 2,3-dihydrobenzo[1,4]dioxin-6,7-dione in 10.99 g (71%) yield as orange crystals.

Mp=223–226 °C (lit. 232 °C[31]). ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.43 (s, 4H), 5.88 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=64.7, 108.6, 157.7, 179.2. MS (EI) *m/e* (%) 168.2 (M^++2,20) 166.2 (M^+, 10), 138.2 (100).

The 2,3-dihydrobenzo[1,4]dioxin-6,7-dione was suspended in 200 mL H_2O and reduced by addition of $Na_2S_2O_4$. The suspension was transferred to a separatory funnel and extracted with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$ and the solvent was evaporated yielding beige crystals of **25**, 9.23 g (75%).

Mp=173.5–174.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ=4.07 (s, 4H), 6.24 (s, 2H) 8.46 (s, 2H, −OH). ^{13}C NMR (100MHz, DMSO-d_6) δ=63.9, 104.2, 135.2, 139.2. MS (EI) *m/e* (%) 168.2 (M^+, 100).

4.1.18. 6,7-Dibromo-2,3-dihydrobenzo[1,4]dioxin 26. Br_2 (25.83 g, 161.6 mmol) dissolved in 50 mL CH_2Cl_2 was

added dropwise to 1,4-benzodioxane (10.00 g, 73.5 mmol) in 50 mL CH_2Cl_2. The reaction mixture was stirred at rt overnight. The precipitate that formed was dissolved in an additional amount of CH_2Cl_2 and extracted with H_2O, a $Na_2S_2O_3$ solution and finally brine. The organic phase was dried over $MgSO_4$ and the solvent evaporated, yielding white crystals of **26**, 19.42 g (90%).

Mp = 139.1–139.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.23 (s, 4H), 7.12 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 64.2, 115.1, 121.6, 143.5. MS (EI) *m/e* (%) 296.0 (50), 294.0 (M^+, 100), 292.0 (50).

4.1.19. Dibromoprehnitene 31. 1,2,3,4-Tetramethylbenzene (prehnitene, 53.66 g, 0.4 mol) was dissolved in 300 mL of CH_2Cl_2. Br_2 (41 mL, 0.8 mol) dissolved in 100 mL of CH_2Cl_2 was added under stirring during 1 h. The reaction mixture was then left stirring for an additional 1 h. Subsequently, H_2O was added to quench the reaction. The phases were separated in a separatory funnel, and the organic layer washed with a $NaHCO_3$ solution, H_2O, and finally brine. After drying over $MgSO_4$ the solution was concentrated under reduced pressure to give 84.90 g (73%) of NMR-pure **31** as white crystals.

Mp = 204–205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.25 (s, 6H), 2.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.8, 22.7, 125.5, 135.4, 135.6. GC-MS (EI) *m/e* (%) 292 (M^+ + 2, 100).

4.1.20. Dihydroxyprehnitene 32. Sodium (4.72 g, 205.3 mmol) was added to 250 mL of dry MeOH. After completion of the reaction, anhydrous DMF (185 mL), Cu(I)I (6.50 g, 34.2 mmol), and dibromoprehnitene **31** (10.00 g, 34.2 mmol) was added. The temperature was raised to 120 °C and the reaction mixture was stirred under a reflux condenser during 14 h. The reaction mixture was then mixed with 250 mL 1 M HCl, and the resulting precipitate filtered off and washed with H_2O.

The resulting solids were dissolved in CH_2Cl_2, the resulting organic phase repeatedly washed with H_2O to remove remaining DMF, dried with $MgSO_4$ and concentrated under reduced pressure to give 6.02 g of crude dimethoxyprehnitene (1,2-dimethoxy-3,4,5,6-tetramethylbenzene) that could be used in the next reaction without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.16 (s, 6H), 2.19 (s, 6H), 3.79 (s, 3H). MS (EI) *m/e* (%) 194 (M^+, 94).

1,2-Dimethoxy-3,4,5,6-tetramethylbenzene (5.80 g, 29.9 mmol) was dissolved in 60 mL of conc. HBr and tetra-*n*-butylammonium bromide (120 mg) was added. The resulting mixture was brought to reflux. After 3 h, the reaction mixture was poured onto an ice–H_2O mixture, and the resulting precipitate filtered off. The achieved solids were subjected to gradient chromatography (hexane/CH_2Cl_2/MeOH) to give 1.52 g of pure 1,2-dihydroxy-3,4,5,6-tetramethylbenzene **32** as off-white crystals.

Mp = 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.14 (s, 6H), 2.17 (s, 6H), 5.00 (broad s, 2H). MS (EI) *m/e* (%) 166 (M^+, 100).

4.1.21. Dibromodiarylether 39. Diaryl ether **38** (8.95 g, 31.2 mmol) was dissolved in 100 mL CH_2Cl_2 in a 250 mL three-necked round bottom flask. Br_2 (3.36 g, 65.6 mmol) dissolved in CH_2Cl_2 was added dropwise. The reaction was stirred at ambient temperature for 3.5 h and was then washed with 100 mL H_2O, 2×100 mL $NaHCO_3$, 100 mL brine and finally 100 mL $Na_2S_2O_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure, to yield 12.90 g (94%) **39** as off-white crystals.

Mp = 151–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.22 (s, 8H, CH_2), 6.41 (s, 2H, CH), 7.11 (s, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 64.1, 64.4, 104.5, 108.4, 121.2, 140.4, 143.3, 147.6. MS (EI) *m/e* (%) 445.9 (M^+ + 4, 45), 443.8 (M^+ + 2, 100), 441.9 (M^+, 45).

4.1.22. Monoaldehyde 40. Dibromodiarylether **39** (10.00 g, 22.6 mmol) was dissolved in 150 mL THF and cooled to −70 °C under nitrogen. *n*-Butyllithium (9 mL, 2.5 M) was added dropwise and the reaction mixture was left stirring for 1 h. DMF (1.9 mL, freshly distilled) was then added. After 10 min the cooling bath was removed and the temperature allowed to rise to ambient. The reaction mixture was heated for 1 h. The solvent was then removed by evaporation and the crude product dissolved in CH_2Cl_2 and washed with 2 M HCl. Subsequent drying over $MgSO_4$ and removal of solvent, yielded 9.40 g (quant.) crude product, which was submitted to gradient chromatography (hexane/CH_2Cl_2/MeOH). The pure fractions were collected and 4.36 g (49%) of **40** as off-white crystals, was achieved after evaporation of solvent.

R_f (CH_2Cl_2) = 0.23. Mp = 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.25 (s, 8H, CH_2), 6.24 (s, 1H, CH), 6.60 (s, 1H, CH), 7.14 (s, 1H, CH), 7.43 (s, 1H, CH), 10.36 (s, 1H, CHO).

4.1.23. Bromophenol 41. Monoaldehyde **40** (4.36 g, 11.1 mmol) was dissolved in 90 mL CH_2Cl_2. MCPBA (3.58 g, 16.6 mmol, 80% in H_2O) was added. The mixture was refluxed overnight. The solvent was evaporated and the residue was dissolved in EtOAc, which was extracted with 2×125 mL $NaHCO_3$ and 100 mL brine. The organic phase was dried over $MgSO_4$, and concentrated under reduced pressure. 3.86 g (84%) formate was achieved and was immediately hydrolyzed.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.22 (s, 4H, CH_2), 4.23 (s, 4H, CH_2), 6.41 (s, 1H, CH), 6.52 (s, 1H, CH), 6.74 (s, 1H, CH), 7.09 (s, 1H, CH), 8.26 (s, 1H, OCHO).

The formate (3.86 g, 9.4 mmol) was suspended in MeOH, the material did not dissolve even during heating. The mixture was set under nitrogen atmosphere and KOH (0.58 g, 10.3 mmol) was added with subsequent darkening of the mixture. The hydrolysis was carried out in 1.5 h. The blend was neutralized with the addition of 2 M HCl and transferred to a separatory funnel. The H_2O phase was extracted with 4×100 mL CH_2Cl_2. The extracts were dried over $MgSO_4$ and rotary evaporated, affording **41** in

quantitative yield as brown crystals. The product was immediately used in the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ=1.65 (broad s, 1H, OH), 4.22 (s, 8H, CH_2), 6.35 (s, 1H, CH), 6.55 (s, 1H, CH), 6.57 (s, 1H, CH), 7.10 (s, 1H, CH).

4.1.24. Tri-dioxin 27. Bromophenol **41** (3.62 g, 9.5 mmol) was transferred to a 100 mL three-necked round bottom flask and 50 mL DMPU was added. NaH (0.42 g, 10.5 mmol, 60% oil dispersion) was added and then Cu(I)I (1.9 g, 10.0 mmol). The temperature was raised to 140 °C and the reaction was stirred for 65 h. The solvent was distilled off and the residue was succumbed to 2 M HCl. The precipitate that formed was filtered and extracted into CH_2Cl_2 (2 times) with sonification. The organic phase was extracted with 2 M NaOH and there after dried over $MgSO_4$. Subsequent evaporation of solvent yielded 3.06 g crude product, which was recrystallized from a mixture of EtOH and toluene to give 900 mg tri-dioxin (31%) The mother liquor was evaporated and then boiled with EtOH, yielding additional 300 mg of **27**. The recrystallized fraction was sublimed at 250 °C, to give an analytically pure sample as white crystals.

Mp >255 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.19 (s, 8H, CH_2), 6.38 (s, 4H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 64.3, 104.76, 135.7, 138.8. MS (EI) *m/e* (%) 300 (M^+, 100). Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 63.79; H, 4.08. Anal. Calcd for (**27**)$_2ClO_4$: C, 54.90; H, 3.46; Cl, 5.06. Found: C, 55.04; H, 3.57; Cl, 5.22. Anal. Calcd for (**27**)$_2AsF_6$: C, 48.68; H, 3.07; F, 14.44. Found: C, 48.68; H, 14.51. Anal. Calcd for (**27**)$_2PF_6$: C, 51.55; H, 3.25; F, 15.29. Found: C, 51.58; H, 3.26; F, 15.11.

4.1.25. Dibromo arylether 43. In a procedure similar to that used for preparing **39**, diarylether **42** (1.03 g, 4.0 mmol) was reacted with Br_2 (1.34 g, 8.4 mmol) to give a quantitative yield of **43** as off-white crystals.

Mp=119–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=5.98 (s, 4H, CH_2), 6.42 (s, 2H, CH), 7.04 (s, 2H, CH). MS (EI) *m/e* (%) 416 (M^+, 38), 256 (M^+-2Br, 100).

4.1.26. Monoaldehyde 44. In a procedure similar to that used for preparing **40**, **42** (7.5 g) was converted to 3.1 g of pure **44** (47%) as brownish crystals.

Mp=156–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.02 (s, 2H, CH_2), 6.03 (s, 2H, CH_2), 6.22 (s, 1H, CH), 6.61 (s, 1H, CH), 7.07 (s, 1H, CH), 7.32 (s, 1H, CH), 10.38 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ=98.11, 102.52, 102.84, 103.41, 105.69, 105.90, 112.70, 119.87, 144.00, 145.65, 146.68, 148.18, 154.04, 157.80, 187.54. MS (EI) *m/e* (%) 366 (M^++2), 364 (M^+, 16), 285 (M^+-Br, 100).

4.1.27. Bromophenol 45. In a procedure similar to that for preparing **41**, Monoaldehyde **44** (2.15 g) was reacted with MCPBA to give a quantitative yield (2.24 g) of formate.

^{1}H NMR (400 MHz, $CDCl_3$) δ=5.97 (s, 2H, CH_2), 5.98 (s, 2H, CH_2), 6.42 (s, 1H, CH), 6.52 (s, 1H, CH), 6.70 (s, 1H, CH), 7.01 (s, 1H, CH), 8.25 (s, 1H, OCHO).

The formate was subsequently hydrolyzed to give 1.70 g (86%) of brown crude phenol **45**, which was immediately used in the cyclization reaction.

^{1}H NMR (400 MHz, $CDCl_3$) δ=5.32 (bs, 1H, OH), 5.89 (s, 2H, CH_2), 5.98 (s, 2H, CH_2), 6.38 (s, 1H, CH), 6.52 (s, 1H, CH), 6.61 (s, 1H, CH), 7.03 (s, 1H, CH).

4.1.28. Bis(dioxolo)dibenzodioxin 34. In a procedure analogous to the one used for preparing **27**, **45** (1.8 g) could be transformed to 500 mg (36%) of pure **34** as white crystals.

Mp >210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=5.89 (4H, s), 6.40 (4H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ=98.1, 101.4, 136.0, 142.9. MS (EI) *m/e* (%) 272 (M^+, 100). Anal. Calcd for $C_{14}H_8O_6$: C, 61.77; H, 2.96. Found: C, 61.76; H, 3.09.

4.1.29. Dibromodibenzodioxin 47. 2,3-Dihydrobenzo[1,4]dioxin-6,7-diol **25** (5.23 g, 31.1 mmol) was dissolved in 400 mL of dry DMPU, hereafter sodium hydride (2.8 g 60% oil dispersion) was added in portions during 15 min. After evolution of hydrogen had ceased 1,2-dibromo-4,5-difluorobenzene **46** (8.46 g 31.1 mmol) was added in portions to the green solution. The flask was sealed and put under a slightly positive nitrogen pressure and heated to 150 °C overnight. The resulting mixture was concentrated under reduced pressure to yield a semisolid mass that was treated with 200 mL of EtOH. The resulting crystals could be collected by filtration, and was rinsed with MeOH, H_2O and then MeOH again. After drying, a quantitative (12.44 g) yield of **47** could be collected. An analytically pure sample could be achieved from sublimation at 230 °C (1.5×10^{-2} mbar), yielding light yellow crystals. Mp >200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 4.20 (s, 4H), 6.42 (s, 2H), 7.08 (s, 2H). **47** is too insoluble to give any ^{13}C NMR. MS (EI) *m/e* (%) 401.9 (50), 399.9 (M^+, 100), 397.9 (30). Anal. Calcd for $C_{14}H_8Br_2O_4$: C, 42.02; H, 2.02. Found: C, 41.86; H, 2.03.

4.1.30. Difluorodibenzodioxin 49. 2,3-Dihydrobenzo[1,4]-dioxin-6,7-diol **25** (53.4 mmol) was dissolved in 75 mL dry DMPU (nitrogen atmosphere). 1.1 equiv. of NaH (60% oil dispersion) were added. After 50 min 1,2,4,5-tetrafluorobenzene **48** (53.4 mmol) was added and the temperature was raised to 70 °C for 30 min, when an additional amount of 1.1 equiv. of NaH was added. The temperature was raised to 140 °C and the mixture was stirred for 8 h. Afterwards the solvent was removed by distillation and the residue was treated with 2 M HCl. The light brown precipitate that formed was filtered and recrystallized from EtOH and warm filtered, yielding 10.69 g (72%) beige crystals of product **49**. An analytically pure sample could be attained from sublimation at 230 °C (1.5×10^{-2} mbar), yielding light yellow crystals.

Mp >200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.20 (s, 4H), 6.41 (s, 2H), 6.68 (t, 2H, J=8.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ=64.1, 104.8, 105.8 (q), 134.0, 137.2, 139.4, 144.1. MS (EI) *m/e* (%) 278.1 (M^+, 100). Anal. Calcd for $C_{14}H_8F_2O_4$: C, 60.44; H, 2.90. Found: C, 60.26; H, 3.03.

4.1.31. Bromodibenzodioxin 51. To a solution of **25**

(1.88 g, 11.2 mmol) in 15 mL of dry DMPU, under argon atmosphere, 1.1 equiv. of NaH were added. After stirring the reaction mixture for 25 min, 3,4-difluorobromobenzene **50** (1.28 g, 11.2 mmol) was added and the mixture was stirred at 70 °C for another 20 min. An additional amount of 1.1 equiv. of NaH was then added and the temperature was raised to 140 °C and the mixture left for 4 h. After cooling to rt, the reaction mixture was poured onto H_2O. The precipitate was filtered, washed with H_2O and recrystallized from EtOH yielding 1.42 g (39%) beige crystals of **51**.

Mp = 181.1–181.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.20 (s, 4H), 6.40 (s, 1H), 6.41 (s, 1H), 6.96 (dd, 1H, J = 8.3, 2.3 Hz), 6.98 (d, 1H, J = 2.3 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 64.3 (2C), 104.9, 105.0, 114.9, 117.5, 119.4, 126.3, 135.3, 135.5, 139.1, 139.2, 141.2, 142.6. MS (EI) *m/e* (%) 322.1 (90), 320.1 (M^+, 100). Anal. Calcd for $C_{14}H_9BrO_4$: C, 52.36; H, 2.82. Found: C, 52.48; H, 2.90.

4.1.32. Tetra-dioxin 33. 2,3-Dihydrobenzo[1,4]dioxin-6,7-diol **25** (1.84 g, 10.94 mmol) and 1,2,4,5-tetrafluorobenzene **48** (0.83 g, 5.53 mmol, 0.5 equiv.) were dissolved in NMP (50 mL) under nitrogen. NaH (0.5 g, 12.5 mmol, 1.14 equiv., 60% oil dispersion) was added cautiously. After gas evolution ceased the solution was heated to 95 °C. After 40 min the flask was removed from the heating bath and another 0.6 g of NaH was added cautiously. After gas evolution ceased the solution was heated to 205 °C and left to react overnight. The solution was poured onto a 2 M HCl/ice slurry (400 mL), whereby a precipitate was formed. The precipitate was filtered, rinsed generously with H_2O and then EtOH to give 1.79 g (81%) of grey tetra-dioxin **33** that is essentially NMR-pure. The product could be recrystallized from DMF. An analytically pure material could also be obtained from sublimation at 220 °C (1.5×10^{-2} mbar). We did not succeed in achieving good ^{13}C NMR of this compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.39, (s, 2H), 6.37 (s, 1H), 4.20 (s, 4H). MS (EI) *m/e* (%) 406.1 (M^+, 100). Anal. Calcd for $C_{22}H_{14}O_8$: C, 65.03; H, 3.47. Found: C, 64.87; H, 3.58.

4.1.33. Benzo[1,3]dioxole-5,6-diol 53. Sesamol (benzo[1,3]-dioxole-5-ol) was treated according to the procedure for 2,3-dihydrobenzo[1,4]dioxin-6-ol, yielding benzo[1,3]-dioxole-5,6-dione as thin orange crystals (71%).

Mp 194–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.03 (s, 2H), 6.10 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 101.3, 104.1, 160.8, 177.3. MS (EI) *m/e* (%) 152.2 (M^+, 100).

The benzo[1,3]dioxole-5,6-dione was then reduced by $Na_2S_2O_4$, as described for the preparation of **25**, yielding 0.95 g (68%) light brown crystals of **53**.

Mp 158–160 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.78 (s, 2H), 6.40 (s, 2H) 8.47 (s, 2H, –OH). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 98.2, 100.0, 138.8, 139.0.MS (EI) *m/e* (%) 154.0 (M^+, 100).

4.1.34. Monomethoxylated dibenzodioxin 54. The difluorodibenzodioxin **49** (3.00 g, 10.8 mmol) was dissolved in 25 mL dry NMP (nitrogen atmosphere). Sodium methoxide (10.8 mmol, 1 equiv. 25% w/v in MeOH) was added and the temperature was raised to 90 °C. The dark brown reaction mixture was left on stirring overnight. After cooling to rt, the reaction mixture was poured on ice H_2O and a precipitate formed. Filtration by suction and washing with H_2O yielded 2.59 g (83%) beige crystals of **54**.

Mp > 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.82 (s, 3H), 4.20 (s, 4H), 6.40 (s, 2H), 6.50 (d, 1H, J = 7.9 Hz), 6.64 (d, 1H, J = 11.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 56.6, 64.1, 102.7, 104.8 (q), 133.6, 133.6, 134.5, 137.0, 139.2, 139.2, 143.1, 143.2, 145.9, 147.8. MS (EI) *m/e* (%) 290.2 (M^+, 100). Anal. Calcd for $C_{15}H_{11}FO_5$: C, 62.07; H, 3.82. Found: C, 61.89; H, 3.98.

4.1.35. Dimethoxydibenzodioxin 55. Compound **49** (7.3 mmol) was dissolved in dry 40 mL dry NMP (nitrogen atmosphere). NaOMe (29.2 mmol, 4 equiv. 25% w/v in MeOH) was added and the temperature was raised to 130 °C. The dark brown reaction mixture was left stirring overnight. After cooling to rt, the reaction mixture was poured onto 200 mL ice/H_2O. The light brown precipitate formed was filtered by suction and washed with H_2O and yielded 1.33 g (61%) beige crystals of **55** after drying.

Mp > 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.81 (s, 6H), 4.20 (s, 4H), 6.39 (s, 2H), 6.45 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 56.2, 64.3, 100.3, 104.7, 134.2, 135.6, 138.6, 144.2. MS (EI) *m/e* (%) 302.2 (M^+, 100). Anal. Calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.75; H, 4.84.

4.1.36. Fluorophenol 56. Compound **54** was dissolved in 40 mL dry 1,2-dichloroethane and the solution was purged with N_2. $BBr_3S(CH_3)_2$ (4 equiv.) was added and the mixture was refluxed overnight. When no starting material was left the mixture was cooled, H_2O and Et_2O were added and the layers were separated. The H_2O phase was extracted 2 times with Et_2O and the combined organic layers were extracted with brine and dried over $MgSO_4$. The solvent was evaporated in vacuum yielding 0.76 g (93%) of **56** as light brown crystals. An analytically pure sample could be obtained from sublimation at 210 °C (1.5×10^{-2} mbar) of 150 mg of material, yielding 120 mg light yellow crystals of pure **56**.

Mp > 200 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.18 (s, 4H), 6.50 (s, 1H), 6.52 (d, 1H, J = 8.3 Hz), 6.53 (s, 1H), 6.88 (d, 1H, J = 11.1 Hz). MS (EI) *m/e* (%) 276.2 (M^+, 100). Anal. Calcd for $C_{14}H_9FO_5$: C, 60.88; H, 3.28. Found: C, 61.08; H, 3.38.

4.1.37. Dihydroxydibenzodioxin 57. *Compound* **55** was demethylated according to the procedure for compound **56**, yielding 0.94 g (86%) grey crystals of **57**.

Mp > 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.20 (s, 4H), 6.39 (s, 2H), 6.43 (s, 2H). MS (EI) *m/e* (%) 274.2 (M^+, 100).

4.1.38. 2,3,6,7-Tetramethoxynaphthalene 60. Sodium (2.3 g) was added in portions to 700 mL of dry MeOH. After complete dissolution of the sodium, 100 mL of DMF, Cu(I)I (22.3 g) and 2,7-dibromo-3,6-dimethoxynaphthalene

(41.0 g, 118.4 mmol) **59** was added cautiously. The resulting reaction mixture was refluxed under nitrogen overnight. The reaction was quenched with 400 mL of 2 M HCl and diluted with 1.6 L of H_2O. The precipitate was filtered off and recrystallized to give 18.7 g (64%) of 2,3,6,7-tetramethoxy-naphthalene **60**.

Mp >200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.97 (s, 3H), 7.04 (s, 1H), MS (EI) *m/e* (%) 248 (M^+, 100).

4.1.39. 2,3,6,7-Tetrahydroxynaphthalene 61. 2,3,6,7-Tetrameth-oxynaphthalene (5.0 g, 20.1 mmol) and tetra-*n*-butyl-ammonium bromide (100 mg) was added to 50 mL of conc. HBr. The mixture was brought to reflux for 20 min, whereafter it was added to an ice/H_2O mixture, some Zinc dust was added and the mixture was filtered again. The filtrate is then evaporated under reduced pressure, the residue dried under vacuum, to give a quantitative yield of **61**, which was used immediately in the following reaction.

^{1}H NMR (400 MHz, DMSO-d_6) δ=6.80 (s, 1H), –OH protons could not be detected. ^{13}C NMR (100 MHz, DMSO-d_6) δ=108.4, 123.8, 144.4

4.1.40. 2,3,6,7-Bis(ethylenedioxy)naphthalene 36. The crude 2,3,6,7-tetrahydroxynaphthalene **61**, from the previous preparation was dissolved under nitrogen in dry DMSO (200 mL), where after K_2CO_3 (27.6 g, 0.2 mol) and 1-bromo-2-chloroethane (11.53 g, 80.4 mmol) was added. The resulting mixture was heated to 100 °C during 48 h. After cooling to rt the mixture was diluted with H_2O. The resulting precipitate was filtered off and purified by gradient chromatography (hexanes/EtOAc) to give 1.14 g (23%) of NMR-pure **36**.

Mp=231–233 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.30 (8H, s), 7.06 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ=64.6, 111.0, 125.5, 142.8. MS (EI) *m/e* (%) 244 (M^+, 100%). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.59; H, 5.14.

4.1.41. 2,3,6,7-Tetramethoxyanthracene 62. 2,3,6,7-Tetramethoxy-9,10-anthraquinone **63**[32] (4.5 g, 13.7 mmol), and tetra-*n*-butylammonium borohydride (17 g) were added to 200 mL CH_2Cl_2. The resulting suspension was cooled to 0 °C, and iodomethane (4.5 mL) was added slowly during 20 min. The reaction was allowed to reach ambient temperature overnight, to give an almost clear solution, with just a tint of yellow. Since TLC showed presence of starting material, the mixture was once again cooled to 0 °C, and additional tetra-*n*-butylammonium borohydride (10 g) and iodomethane (3 mL) were added. The mixture was once again allowed to reach rt overnight, where after 5 mL of H_2O was added to quench the reaction. The mixture was concentrated under reduced pressure, and the resulting semisolid mass was treated with 200 mL of EtOH. The resulting crystals were collected by filtration and rinsed thoroughly to give 3.7 g of crude material. Purification by sublimation (1.5×10^{-2} mbar) gave 410 mg **63** of good purity, together with 2.0 g of impure material. The impure material was purified by gradient chromatography (1,2-dichloroethane/MeOH) to give an additional 455 mg. Combined yield: 865 mg (21%).

Mp >200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.90 (12H, s), 7.27 (4H, s), 8.10 (2H, s). MS (EI) *m/e* (%) 298.2 (M^+, 100%).

4.1.42. 2,3,6,7-Tetrahydroxyanthracene 64. 2,3,6,7-Tetramethoxy-anthracene **62** (470 mg, 1.6 mmol) and tetra-*n*-butyl-ammonium bromide (6 mg) was added to 30 mL of conc. HBr. The mixture was brought to reflux overnight. Afterwards it was added to an ice/H_2O mixture and then brown precipitate was filtered off. The residue was dried in desiccator overnight, to give 387 mg of crude **64**, which was treated with boiling MeOH. The solvent was evaporated yielding 323 mg (85%) of almost pure **64**, which was used rapidly in the following reaction.

^{1}H NMR (400 MHz, DMSO-d_6) δ=3.89 (4H, bs), 7.05 (4H, s), 7.77 (2H, s). MS (EI) *m/e* (%) 242.3 (M^+, 100%).

4.1.43. 2,3,6,7-Bis(ethylenedioxy)anthracene 37. The crude 2,3,6,7-tetrahydroxyanthracene **64** (300 mg, 1.2 mmol) from the previous preparation was dissolved under nitrogen in dry DMSO (10 mL), where after K_2CO_3 (1.712 g, 12 mol) and 1-bromo-2-chloroethane (0.4 ml, 5.0 mmol) was added. The resulting mixture was heated to 100 °C during 48 h. After cooling to rt the mixture was diluted with H_2O. The resulting precipitate was filtered off and purified by column chromatography (CH_2Cl_2) to give 91 mg (25%) pure bright fluorescent yellow crystals of **36**.

Mp >200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.36 (8H, s), 7.29 (4H, s), 8.00 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ=64.5, 110.8, 122.1, 127.9, 143.9. MS (EI) *m/e* (%) 294.3 (M^+, 100%). Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.25; H, 4.87.

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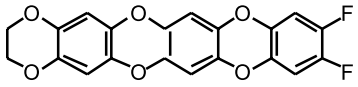

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32. Prepared according to lit.,[21] ^{1}H NMR (400 MHz, $CDCl_3$) $\delta =$ 4.07 (12H, s), 7.68 (4H, s).